SUPPORTING INFORMATION

Iron-Catalyzed Cross-Coupling of Thioesters and Organomanganese Reagents

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1. General Information

1.1 Chemicals

All reactions with organometallic species and catalyst were carried out under Ar or N_2 atmosphere with pre-dried glassware using common air-free techniques, unless noted otherwise. Dry THF was stored in a Schlenk-round bottom flask (RBF) under inert gas over microwave-activated 3 Å MS (20% w/v, at least 3 days storage). Before, it was distilled over Na/benzophenone. The non-degassed THF used in catalytic reactions was obtained by adding pre-distilled THF (stored over freshly crushed KOH for at least 2 days) through a filter into a container under inert gas with microwave-activated 3 Å MS (50% v/v, at least 10 days storage).

LiCl and magnesium turnings (p.A. grade) were supplied by the central chemical desk of the University of Tübingen. $MnCl_2$ was supplied by Acros Organics (99+%), stored in a screw-capped plastic bottle. Iron(III) acetyl acetonate used for the catalytic reaction was supplied by either Acros Organics (99+% for optimization reactions) or Sigma Aldrich (≥99.9% for substrate screening). Other chemicals were purchased from abcr, Acros, BLDChem, Carbolution Chemicals, Fluka, Fluorochem, Merck, Sigma-Aldrich or TCI.

Thiols were usually distilled prior to use, degassed and stored at -10 °C in Schlenk vessels under inert gas. Depending on the chemical vendor the stated purity of ethanethiol was incorrect. Hence, NMR analysis of the purchased thiol is highly recommended, especially for ethanethiol. The ethanthiol mainly used was supplied by Acros Organics. *CAUTION!* Ethanethiol possesses a high vapour pressure and connection to an inert gas line will lead to high contamination of the inert gas. Thus, this thiol should always be handled on a separate line. Thioesters were handled under air and stored at 0 °C.

Syntheses of thioesters **1a**, **1ab**, **1ac**, **1c**, **1f, 1n**, **1p**, **1l**, **1J** were reported in previous publications of our group.[1]

1.2 General Techniques

The catalytic reactions were mainly conducted using a Julabo FT902 Cryostate with an acetone bath. The cryostat was set to -15 °C achieving a cooling bath temperature range from -15 °C to -20 °C.

Solvents for chromatography were distilled prior to use. Column chromatography was carried out either manually or by a Puriflash system (Interchim XS420) using silica gel (0.04–0.063 mm) from Machery&Nagel unless noted otherwise. TLC analysis was carried out using aluminium-backed plates coated with SiO_2 60 F_{254} (0.2 mm thickness) and the compounds detected under UV light (254 nm) or after staining with a $KMnO_4$ or anisaldehyde TLC dip solution and gentle heating or by treating with iodine vapours.

Definition of "Gradient" used below: In separations using the Puriflash system, a gradient was developed around a suitable (target spot Rf ca. 0.40–0.20) binary eluent combination X:Y (where the latter is the strong solvent, X+Y=100) . The eluent programs are given for each respective compound.

Dry-column vacuum chromatography was performed following literature procedure.[2] SiO_2 employed for these separation was supplied by Merck (Silica Gel 60 0.015–0.040 mm) and samples were subjected to wet loading by injection into *n*-hexane or petroleum ether (60/90) layer during column flow.

1.3 Analytical Techniques

NMR spectra were recorded using a Bruker Avance 400, a Bruker Avance III HD 300 NanoBay or a Bruker Avance III HDX 600, ^{13}C-NMR and ^{31}P-NMR experiments were performed in proton-decoupled mode, which is not noted explicitly. Chemical shifts are reported in parts per million relative to the residual NMR solvent signals[3] (chloroform: ^{1}H δ = 7.26 ppm and ^{13}C δ = 77.16 ppm; dichloromethane: ^{1}H δ = 5.32 and ^{13}C δ = 53.84) and the *J*-coupling constants are given in Hertz with the usual designations for splitting patterns (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, hept = heptet, m = multiplet, br = broad).

HR-MS(ESI, APCI, EI) measurements were carried out by the mass spectrometry department of the Institute of Organic Chemistry, University of Tübingen. Measurements were carried out using maXis 4G from Bruker (ESI, APCI) or by a MAT95 from Finnegan (EI).

GC-LR-MS (EI) analysis was carried out by our standard GC/MS method. An Agilent 190915-433UI column (30 m $\times$ 250 µm $\times$ 0.25 µm) was used. Program: Heating from 50 °C to 280 °C within 15 minutes. Also, samples were measured by the MS-department of the University of Tübingen with an 8890 GC system and 5977B MSD. For these measurements, temperature program started by holding 3 min at 40 °C, then heating to 320 °C within 32 min and holding for 10 min at the same temperature. These measurements are marked with 'method B'.

GC-FID (flame ionization detection) analysis was carried out on an Agilent 7820A system using dry hydrogen as carrier gas. An Agilent 19091J-431 column (30 m $\times$ 320 µm $\times$ 0.25 µm) was used. Program 50-280M12: Heating from 50 °C to 280 °C within 12 minutes.

Melting point determination was achieved by using a MPM HV 3 machine with a visual detection (heating rate 1 °C/min). FT-IR spectra were recorded using a Cary 630 FTIR by applying the sample neat on a diamond ATR sampler.

2. General Procedures

General Procedure A (GP-A) – Synthesis of thioesters *via* Steglich esterification

The reaction was conducted following a modified literature procedure.[4] In a round bottom flask (RBF) equipped with a stirring bar carboxylic acid was dissolved in dichloromethane (DCM) and ethanethiol (2.2 mL, 30 mmol, 3 equiv.) was added. The solution was cooled to 0 °C and 4-dimethylaminopyridine (DMAP) was added (0.1 equiv.). Over a period of 2 min *N,N*'-dicyclohexylcarbodiimide (DCC) or *N,N*'-diisopropylcarbodiimide (DIC) (1.1 equiv.) were added in portions at the same temperature. The reaction was allowed to warm to room temperature and stirred overnight. Then, the suspension was filtered and the crude solution reduced *in vacuo*. Further work-up steps are given for each respective substrate.

General remark:

Even if purification was attempted by filtration through a silica plug as is mentioned in several literature procedures[5], residue signals in the ^{1}H and ^{13}C NMR-spectra can be observed, which might stem either from the dialkylurea or rearrangement product. These side products can also cause problems with column separations and even bulb-to-bulb distillation. In order to remove these impurities, extraction of most products was achieved by extraction of DCM solution with 3×6 M HCl, which made column separation obsolete in most cases.

General Procedure B (GP-B) – Synthesis of thioesters from acid chlorides

In a RBF equipped with a stirring bar ethanethiol (1.2 equiv.) was dissolved in DCM (0.5 M in respect to the acid chloride), put under an Ar-atmosphere and cooled to 0 °C. Then, triethylamine (1.0 equiv.) was added. The acid chloride (usually 10 mmol) was diluted in DCM (2 M or until homogeneous) and slowly added *via* syringe (over 5 min) to the vigorously stirred solution of thiol. After 30 min at 0 °C, the mixture was stirred at room temperature until no more starting material was observed (thin layer chromatography (TLC) control – usually after 1–1.5 h). Water was added to the reaction mixture and the solution was extracted with aq. 6 M HCl, sat. aq. $NaHCO_3$ and brine. The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated *in vacuo*.

General Procedure C (GP-C) – Synthesis of organomanganese halides

Synthesis of Grignard reagents:

In a Schlenk RBF equipped with a stirring bar and septum, magnesium turnings (1.3 equiv.) were dried using a propane torch under high vacuum. The flask was allowed to cool to room temperature under vacuum, then flushed with inert gas. A crumb of iodine was added and gently heated until vapours emerged. The inert gas tap was closed, and the turnings were stirred in iodine vapour for 5 min. After this, an ice bath was put under the flask and the turnings were stirred for another 5 min or until complete resublimation of iodine. Then, the inert gas tab was opened and anhydrous tetrahydrofuran (THF) was added at once (aimed concentration was 1.3 M in respect of aryl bromide). A few drops of organobromide (1.0 equiv.) were added until a visible change in color and emergence of reaction heat were observable. The mixture was cooled with a water-ice bath (ca. 10 °C) and the rest of the organobromide was added. After no strong heat generation was observable the bath was removed,

and the reaction was stirred overnight at room temperature. Quantification was achieved by Knochel iodometric titration.[6]

Synthesis of the soluble manganese precursor:

The ate complex was synthesized according to a modified literature procedure.[7] In a Schlenk-RBF equipped with stirring bar and septum, LiCl (3.56 g, 84 mmol, 2.1 equiv.) was dried with a propane torch under vacuum, allowed to cool and put under an Ar. Then, manganese dichloride tetrahydrate (7.92 g, 40 mmol, 1 equiv.) was added and the salts were dried under high vacuum for at least 4 h at 120 °C. Afterwards, the RBF was allowed to cool to room temperature and anhydrous degassed THF was added (40 mL). The suspension was stirred until a homogenous yellow solution was obtained (at least 24 h and up to 5 d).

Synthesis of the organomanganese halide:

The reaction was conducted according to a modified literature procedure.[8] In a Schlenk-RBF equipped with stirring bar and septum manganese ate complex (1.2 equiv.) was diluted with anhydrous THF (designated concentration was 0.25 M of the organomanganese halide). The reaction mixture was cooled in a cooling bath to at least -5 °C and Grignard reagent (1.0 equiv. based on titre) was slowly added. The mixture was stirred for 2 h at the same temperature, titrated (iodometric) and then used up the same day.

General remark:

Depending on the supplier and batch of the manganese chloride, reproducibility issues for the synthesis of ate complex occurred. This can lead to ethyl manganese reagents that decompose over various time frames (yields <10% after 1 h or even loss of concentration within hours). These problems were solved by using high purity manganese dichloride. We therefore concluded that the difference in batches is the presence of metal impurities that catalyse the decomposition of the reagent, as is known for dialkyl manganese compounds.[9]

From experience, the drying of LiCl can be achieved using a propane torch or heat gun, however, manganese dichloride should not be heated over 150 °C as observed by color changes (with propane torch to green/turquoise). This leads to very low transmetalation yields by the ate complex solution and irreproducible results in subsequent reactions. If, after adding THF to the dried salts, a clear yellow solution forms within 10 min after addition, the compounds were too wet and the ate complex should be discarded as no reasonable transmetalation is possible. After the appropriate time of stirring, the color of the ate complex solution varies from citrus yellow (optimal) to orange (showed reduced yields). Purchased $MnCl_2$•2 LiCl complex can not be recommended which – in our case – contained significant impurities. We also recommend the use of stirring bars cleaned in *aqua regia* as traces of inorganic salts can catalyze the decomposition of ethyl manganese reagent rapidly.

The decomposition of these temperature sensitive compounds is easily visible at room temperature, as black precipitate forms. However, the decomposition can take place at lower temperatures than room temperature, while the solution keeps its characteristic yellow/orange/red color (depending on oxygen content). Iodometric titration will not help quantify the concentration of these manganese

organyle solutions, since reduced manganese species/nanoparticles are also oxidized, when treated with iodine.

General Procedure D (GP-D) – Optimization of iron-catalyzed Fukuyama coupling of alkyl manganese reagents

In a flame-dried Schlenk-tube equipped with a stirring bar and septum iron(III) acetaly acetonate ($Fe(acac)_3$) (5.9 mg, 16.7 µmol, 5 mol%) was added and vacuum applied. After flushing with Ar, the precatalyst was dissolved in 1 mL of THF (dried over 50% v/v 3 Å preactivated molecular sieves for 1 week, not degassed) and cooled to -20 °C. Thioester **1a** (53.4 mg, 333 µmol) was added to the mixture. Then, organomanganese reagent prepared according to GP-C (1.2 mmol; 0.18–0.30 M in THF based on titre) was added and the mixture was stirred for 10 min. Before quenching, the internal standard *n*-pentadecane (100 µL) was added. The reaction was quenched using sat. aq. NH_4Cl solution (ca. 1 mL) and the organic layer was diluted with 3 mL of organic solvent (Et_2O or EtOAc). The organic layer was separated, filtered through a pad of anhydrous $MgSO_4$, basic Al_2O_3 and Celite in a pasteur pipette before diluting with DCM and analysis *via* gas chromatrography with flame ionization detection (GC-FID).

General Procedure E (GP-E) – Iron-catalyzed Fukuyama coupling of ethyl/hexyl manganese reagents

In a flame-dried Schlenk-tube equipped with a stirring bar and septum, $Fe(acac)_3$ (17.7 mg, 50 µmol, 5 mol%) was added and vacuum applied for 10 min. After flushing with Ar the catalyst was dissolved in 3 mL of THF (dried over 50% v/v 3 Å preactivated molecular sieves for 1 week, not degassed) and cooled to -20 °C. Thioester (1.0 mmol) was added to the mixture. Then, ethyl or hexyl manganese reagent prepared according to GP-C (1.2 mmol; 0.18–0.32 M in THF based on titre) was added and the mixture was stirred for 10 min. The reaction was quenched using sat. NH_4Cl solution (ca. 2 mL), the organic layer was diluted with 10 mL of organic solvent (Et_2O or EtOAc) and the aqueous layer extracted using 4×10 mL of respective solvent. The combined organic layers were dried over $MgSO_4$ and the solvent removed under reduced pressure.

General remark:

For the catalytic conversion of substrates, we recommend the use of anisaldehyde stain for TLC analysis in case of less functionalized substrates. Although most aliphatic thioesters can be observed by UV-detection with 254 nm (weak extinction), anisaldehyde staining is able to distinguish between starting material (yellow color – fades within 30 minutes) and product (blue color – fades after hours).

General Procedure F (GP-F) – Iron-catalyzed Fukuyama coupling of different alkyl manganese reagents

In a flame-dried Schlenk-tube equipped with a stirring bar and septum, $Fe(acac)_3$ (17.7 mg, 50 µmol, 5 mol%) was added and vacuum applied for 10 min. After flushing with Ar, the precatalyst was dissolved in 3 mL of THF (dried over 50% v/v 3 Å preactivated molecular sieves for 1 week, not degassed) and cooled to -20 °C. Thioester **1b** (194 mg, 1.00 mmol) was added to the mixture. Then, organomanganese reagent prepared according to GP-C (1.2 mmol; 0.20–0.28 M in THF based on titre) was added and the mixture stirred for 10 min. The reaction was quenched using sat. NH_4Cl solution (ca. 2 mL), the organic layer was diluted with 10 mL of organic solvent (Et_2O or EtOAc) and the aqueous

layer was extracted using 4 × 10 mL of respective solvent. The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure.

General Procedure G (GP-G) – Reaction progress of iron-catalyzed Fukuyama coupling of alkyl manganese reagents

In a flame-dried Schlenk-tube equipped with a stirring bar and septum $Fe(acac)_3$ (13.2 mg, 37.5 µmol, 5 mol%) was added and vacuum applied. After flushing with Ar, the precatalyst was dissolved in 2 mL of THF (dried over 50% v/v 3 Å preactivated molecular sieves for 1 week, not degassed) and cooled to -20 °C. Then, thioester (750 µmol) and *n*-pentadecane (100 µL) were added. Organomanganese reagent prepared according to GP-C (1.2 mmol; 0.18–0.33 M in THF based on titre) was added. Samples (~200 µL) were withdrawn from the reaction solution using separate syringes, which were inertized in a separate vessel. The samples were quenched by addition of sat. aq. NH_4Cl solution (ca. 1 mL) and the organic layer was diluted with 0.5 mL of organic solvent (EtOAc). The organic layer was filtered through a pad of $MgSO_4$, basic Al_2O_3 and Celite in a pasteur pipette before diluting with DCM and analysis *via* GC-FID.

General Procedure F (GP-G) – Reaction observation of catalyst decomposition

In a flame-dried Schlenk-tube equipped with a stirring bar and septum $Fe(acac)_3$ (5.9 mg, 16.7 µmol, 5 mol%) was added and vacuum applied. After flushing with Ar, the precatalyst was dissolved in 1 mL of THF (dried over 50% v/v 3 Å preactivated molecular sieves for 1 week, not degassed) and cooled to -20 °C. Organomanganese reagent prepared according to GP-C (1.2 mmol; 0.20–0.28 M in THF based on titre) was added and the mixture was stirred for a specific time (10 min, 30 min or 60 min). Then, thioester **1a** (53.4 mg, 333 µmol) was added and the mixture was stirred for 10 min at the same temperature. Before quenching, *n*-pentadecane (100 µL) was added. The reaction was quenched using sat. aq. NH_4Cl solution (ca. 1 mL) and the organic layer diluted with 1 mL of organic solvent (EtOAc). The organic layer was filtered through a pad of anhydrous $MgSO_4$, basic Al_2O_3 and Celite in a pasteur pipette before diluting with DCM and analysis *via* GC-FID.

3. General Procedures – Pictures

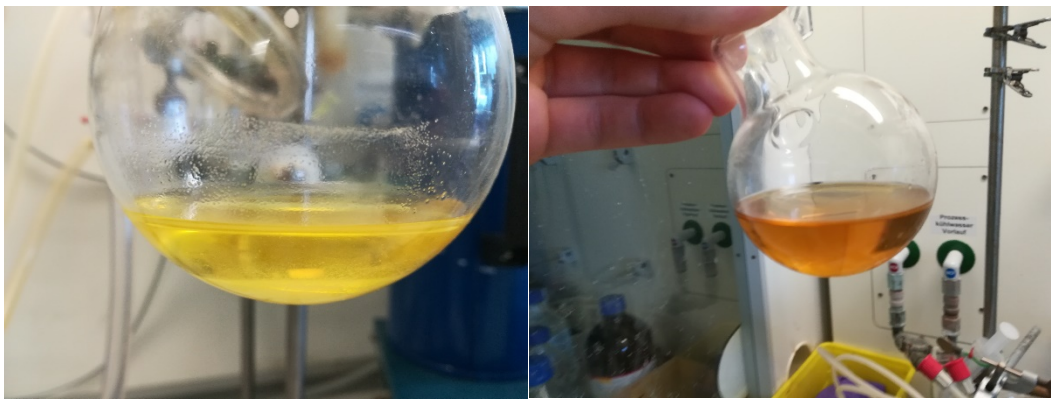


Figure S1. Left: $MnCl_2 \cdot 2LiCl$ furnishing high yields in transmetalation. Right: Ate complex with likely impurities of $MnCl_2$ leading to low yields in transmetalation.

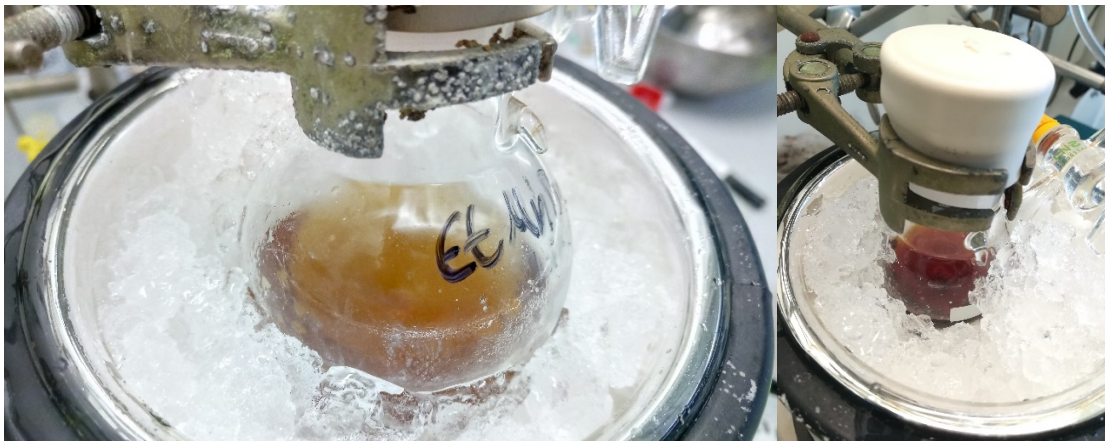


Figure S2. Ethyl manganese reagent color depending on purity and oxygen content from orange to orange-red.

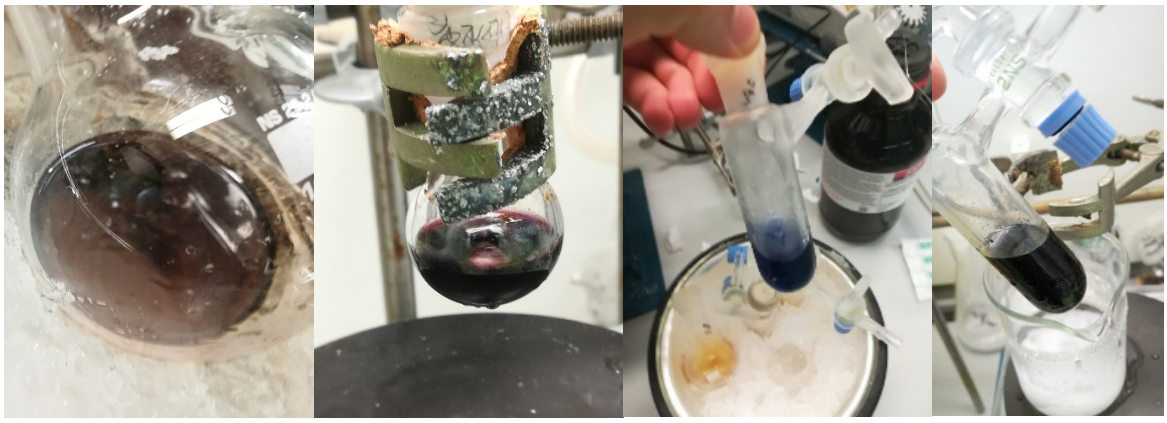
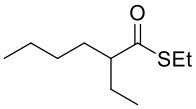


Figure S3. Oxygenated manganese reagent solutions from left to right: 2-Methylpropyl-, *iso*-propyl, *tert*-butyl and benzyl manganese halide (colors from left to right: brown-purple, wine red, ink blue, black-green).

4. Overview of low yielding substrates



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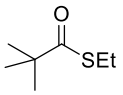

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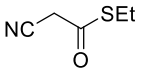

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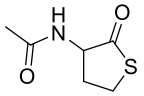

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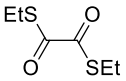

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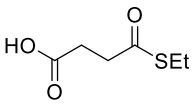

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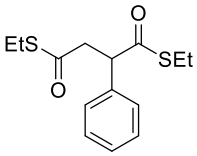
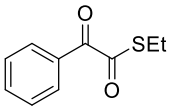
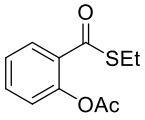


reaction poisoning



decarbonylation products



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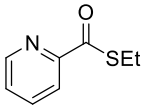

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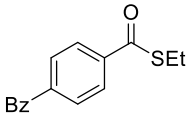

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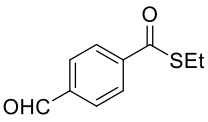
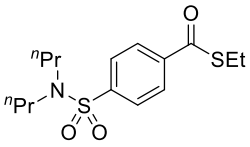
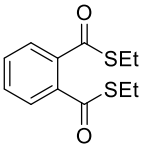


traces of product



low yield



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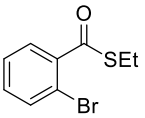
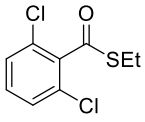
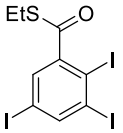


tandem coupling



tandem coupling



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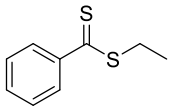

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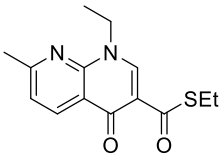
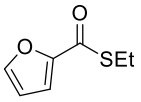


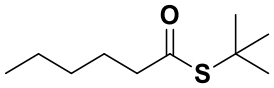
low yield



low yield

5. Synthesis and Analytical Data of Starting Materials

S-(*tert*-butyl) hexanethioate (**1ad**)



1ad

According to GP-A, the product **1ad** was synthesized using hexanoic acid (1.25 mL, 10.0 mmol, 1.0 equiv.), 2-methylpropane-2-thiol (2.2 mL, 30 mmol, 3 equiv.), DMAP (122 mg, 1.00 mmol, 0.1 equiv.) and DCC (2.27 g, 11.0 mmol, 1.1 equiv.). Purification was achieved by filtration through a short silica plug using Hex/EA (8:2) and washing the filtrate with 6 M HCl (2 × 20 mL), 10% aq. KOH (1 × 20 mL), sat. aq. $NaHCO_3$ (1 × 20 mL) and brine (1 × 20 mL). The product was yielded as a colorless oil (1.53 g, 8.12 mmol, 81%).

$C_{10}H_{20}OS$ (188.33 g/mol)

R_f: 0.23 (*n*Hex) [$KMnO_4$, UV]

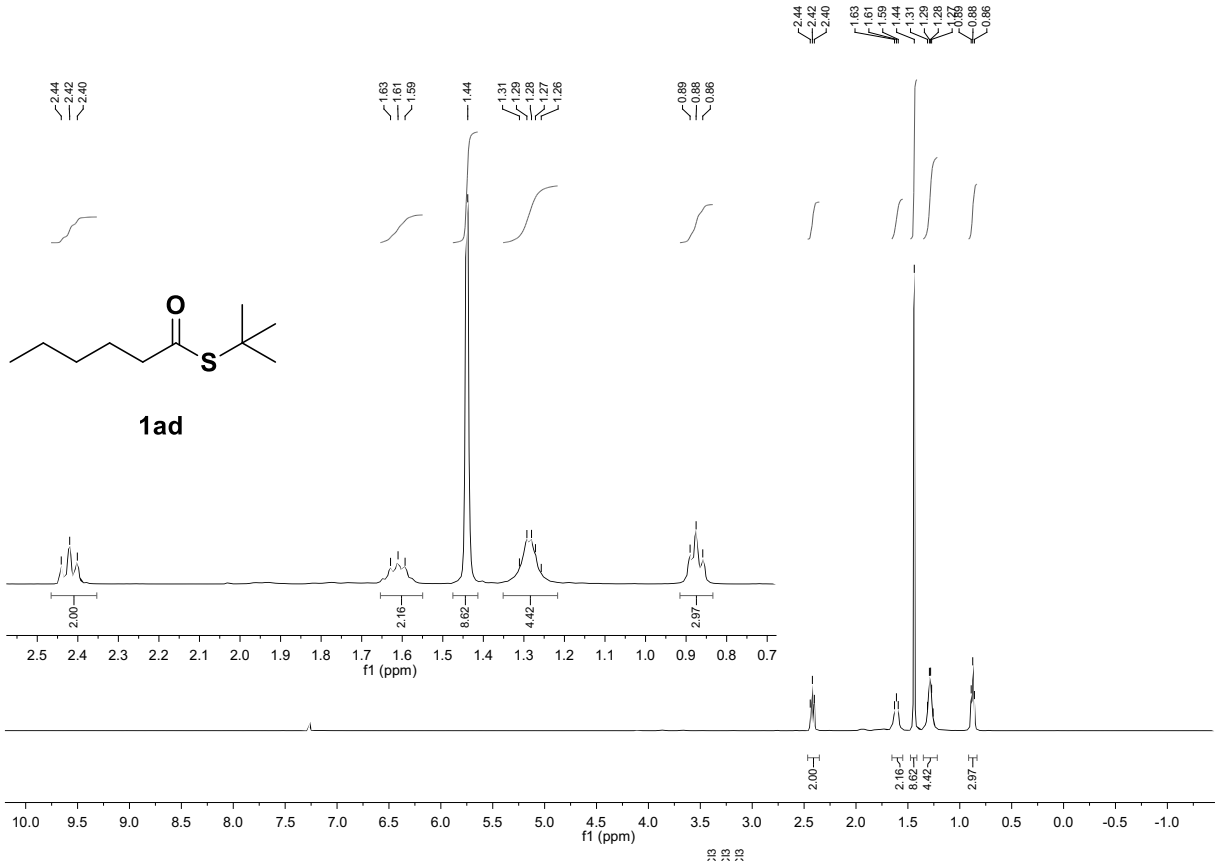
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.42 (t, *J* = 7.6 Hz, 2H), 1.65 – 1.55 (m, 2H), 1.49 – 1.39 (m, 9H, C(C*H*$_3$)$_3$), 1.31 –1.26 (m, 4H), 0.87 (t, *J* = 7.1, 3H, C*H*$_3$).

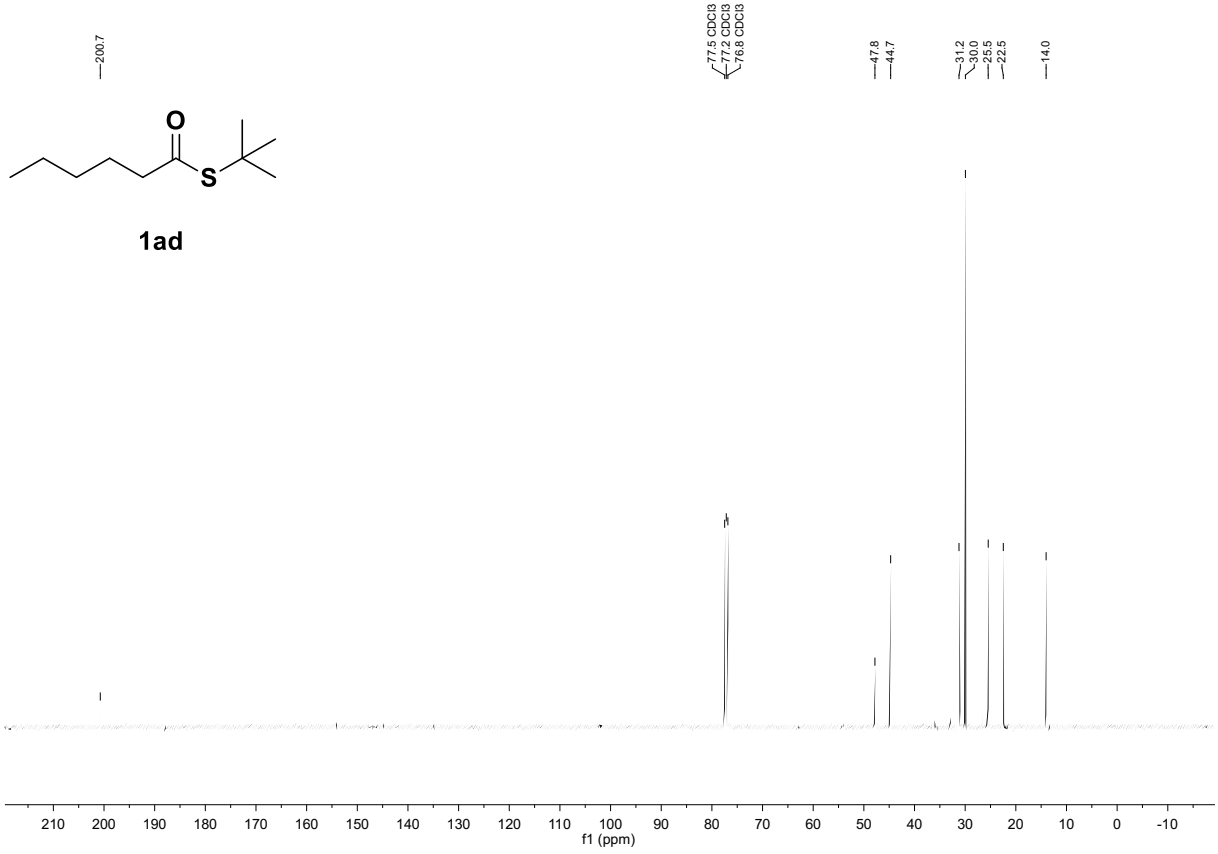
^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.8 (C*O*SEt), 47.8, 44.7, 31.2, 30.0, 25.5, 22.5, 14.0.

GC-MS (EI): t_r = 4.57 min, m/z(%) = 131 (22, [$M^{+\bullet}$-$C_4H_9^{\bullet}$]), 99 (89, [$M^{+\bullet}$-$SC_4H_9^{\bullet}$]), 71 (42, [$M^{+\bullet}$-$SC_4H_9^{\bullet}$-CO]), 57 (100, [$C_4H_9^{+\bullet}$]).

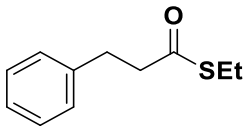
HR-MS (ESI): m/z calc. for $[M+Na]^+$ 188.122937, found 188.12047.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2991 (w, C-H_{aliph}), 2955 (m, C-H_{aliph}), 2924 (m), 2864 (w), 1683 (s, C=O), 1456 (m), 1418 (w), 1388 (w), 1362 (m), 1337 (w), 1300 (w), 1210 (w), 1164 (m), 1120 (m), 1071 (w), 1027 (m), 1004 (m), 956 (m), 919 (w), 736 (w), 699 (w).


2.44
2.42
2.40
1.63
1.61
1.59
1.44
1.31
1.29
1.28
1.27
1.26
0.89
0.88
0.86
O
S
1ad
2.00
2.16
8.62
4.42
2.97
f1 (ppm)


200.7
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
47.8
44.7
31.2
30.0
25.5
22.5
14.0
O
S
1ad
f1 (ppm)

S-ethyl 3-phenylpropanethioate (**1b**)



1b

According to GP-A, the product **1b** was synthesized using 3-phenylpropanoic acid (3.75 g, 25 mmol, 1.0 equiv.), ethanethiol (5.4 mL, 75 mmol, 3 equiv.), DMAP (305.4 mg, 2.5 mmol, 0.1 equiv.) and DCC (5.67 g, 27.5 mmol, 1.1 equiv.). Purification was achieved by filtration through a short silica plug using *n*-hexane (*n*Hex)/ethylacetate (EA) (8:2) and washing the filtrate with 6 M HCl (2 × 10 mL), sat. aq. $NaHCO_3$ (1 × 10 mL) and brine (1 × 10 mL). The product was yielded as a colorless oil (3.86 g, 19.87 mmol, 79%). The analytical data is in good accordance to reported literature.[1a]

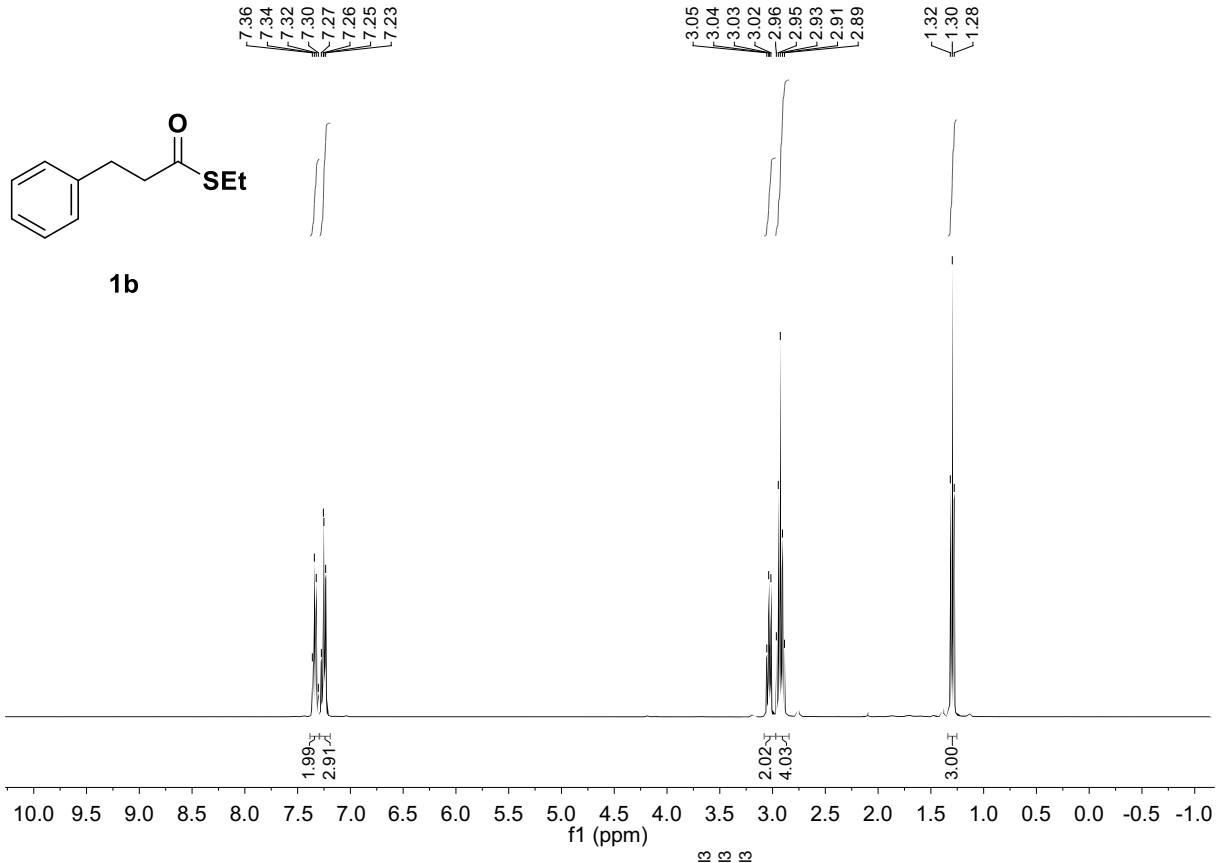
$C_{11}H_{14}OS$ (194.29 g/mol)

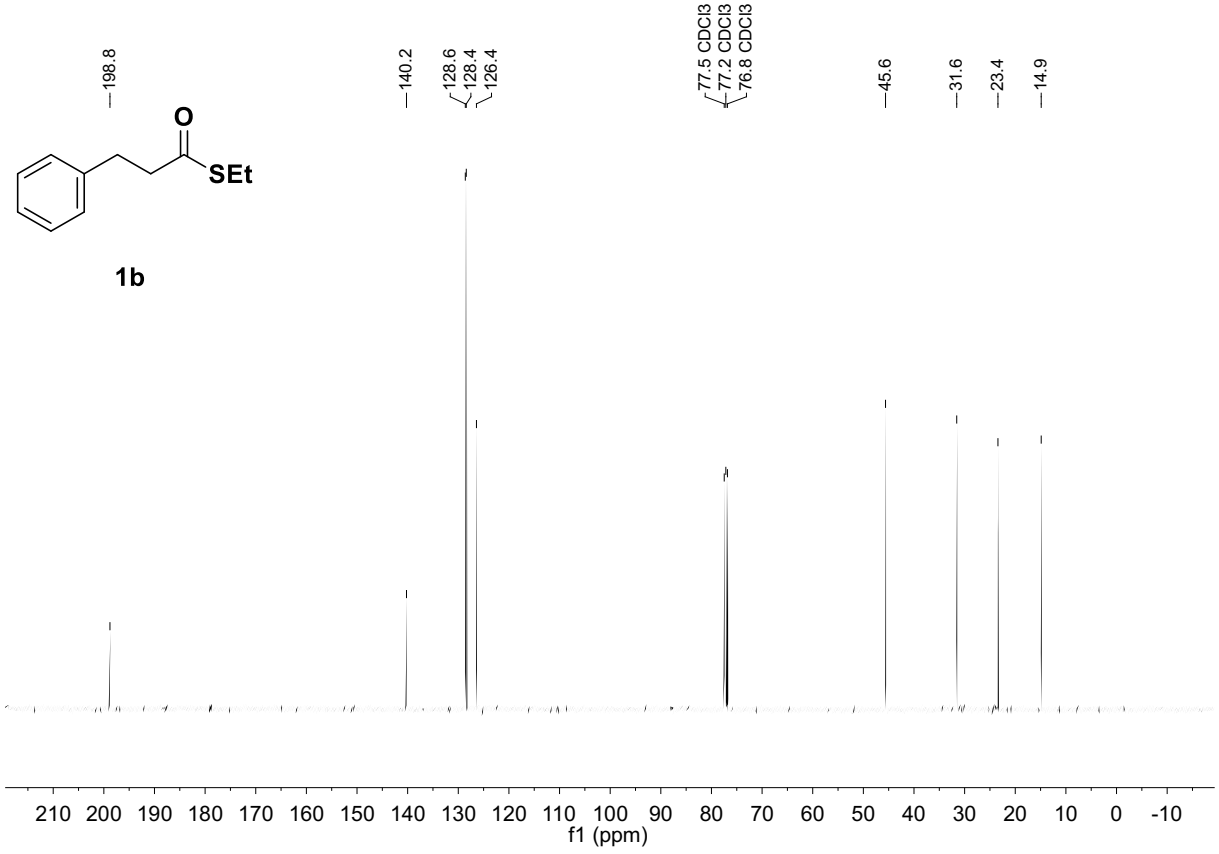
R_f: 0.30 (*n*Hex/Et_2O = 9:1) [anis (yellow), UV - weak]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 – 7.29 (m, 2H), 7.29 – 7.18 (m, 3H), 3.08 – 2.99 (m, 2H), 3.00 – 2.84 (m, 4H), 1.30 (t, *J* = 7.4 Hz, 3H).

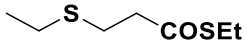
^{13}C NMR (101 MHz, $CDCl_3$): δ = 198.8 (*C*OSEt), 140.2 (C_{Ar}), 128.6 (C_{Ar}), 128.4 (C_{Ar}), 126.4 (C_{Ar}), 45.6, 31.6, 23.4, 14.9.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3062 (w, C-H_{arom}), 3025 (w, C-H_{arom}), 2965 (w, C-H_{arom}), 2928 (w, C-H_{arom}), 2868 (w, C-H_{arom}), 1683 (vs, C=O), 1601 (w), 1493 (w), 1448 (m), 1411 (w), 1373 (w), 1345 (w), 1262 (w), 1172 (w), 1045 (s), 967 (s), 878 (w), 840 (w), 740 (s), 695 (s).


7.36
7.34
7.32
7.30
7.27
7.26
7.25
7.23
3.05
3.04
3.03
3.02
2.96
2.95
2.93
2.91
2.89
1.32
1.30
1.28
O
SEt
1b
1.99
2.91
2.02
4.03
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


198.8
140.2
128.6
128.4
126.4
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
45.6
31.6
23.4
14.9
O
SEt
1b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

S-ethyl 3-(ethylthio)propanethioate (**1d**)



1d

(The product was unanticipatedly synthesized.) The product **1d** was synthesized from 3-chloropropanoic acid (1.09 g, 10.0 mmol), which was dissolved in acetone (20 mL). Then, 2-chloro-4,6-dimethoxy-1,3,5-triazine (2.11 g, 12.0 mmol, 1.2 equiv.) and triethylamine (4.2 mL, 30 mmol, 3 equiv.) were added. A precipitation of white solid was observed. The reaction stirred at room temperature for 1 h. After this, ethanethiol (815 µL, 11.0 mmol, 1.1 equiv.) was added and the reaction was stirred for 2 h at room temperature. Purification was achieved by evaporating the solvent under reduced pressure and diluting the crude product in EA (60 mL). The organic layer was washed with 6 M HCl (3 × 10 mL), sat. aq. $NaHCO_3$ (1 × 10 mL) and brine (1 × 10 mL) and dried with anhydrous Na_2SO_4. The product was obtained as a colorless oil with a distinct strong odor (551 mg, 3.09 mmol, 56% - in respect to thiol).

$C_7H_{14}OS_2$ (178.05 g/mol)

R_f: 0.08 (*n*Hex) [$KMnO_4$]

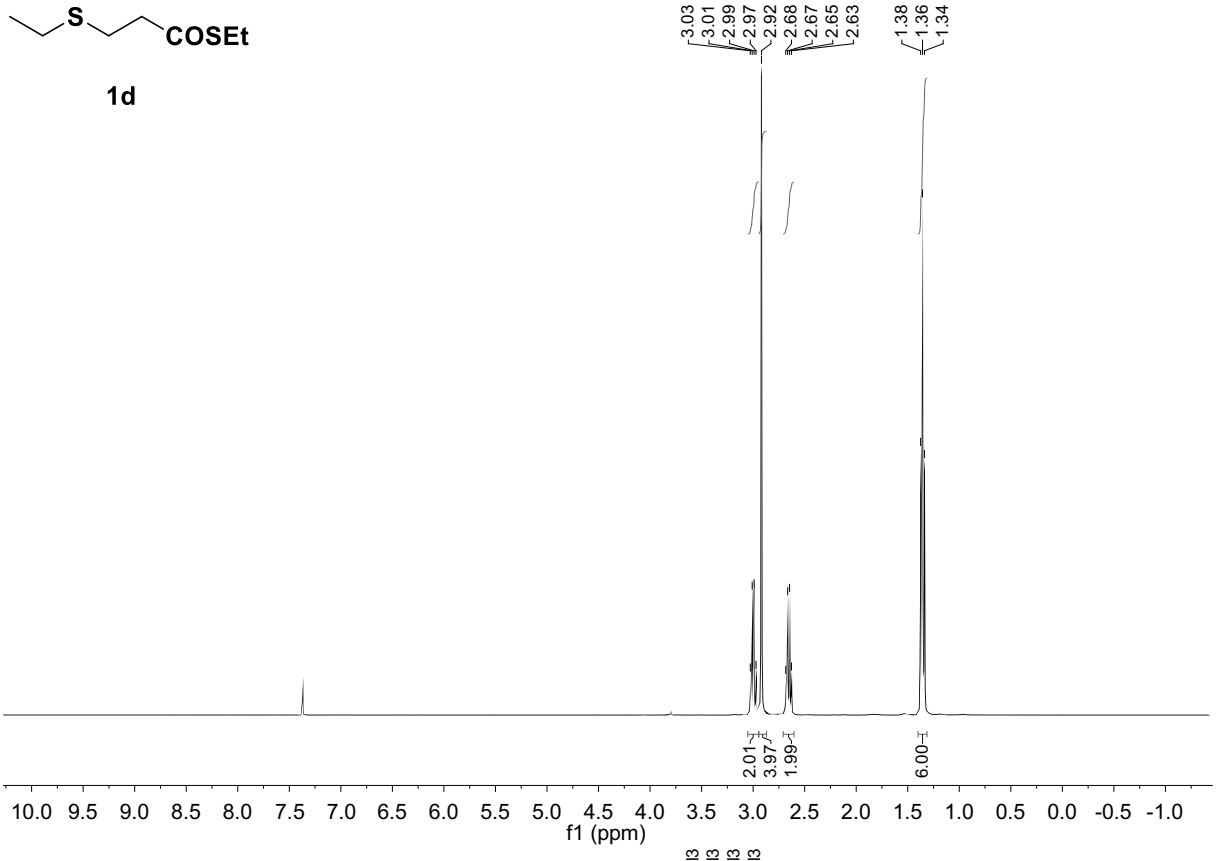
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.89 (q, *J* = 7.4 Hz, 2H), 2.81 (s, 4H), 2.55 (q, *J* = 7.4 Hz, 2H), 1.25 (t, *J* = 7.4 Hz, 6H).

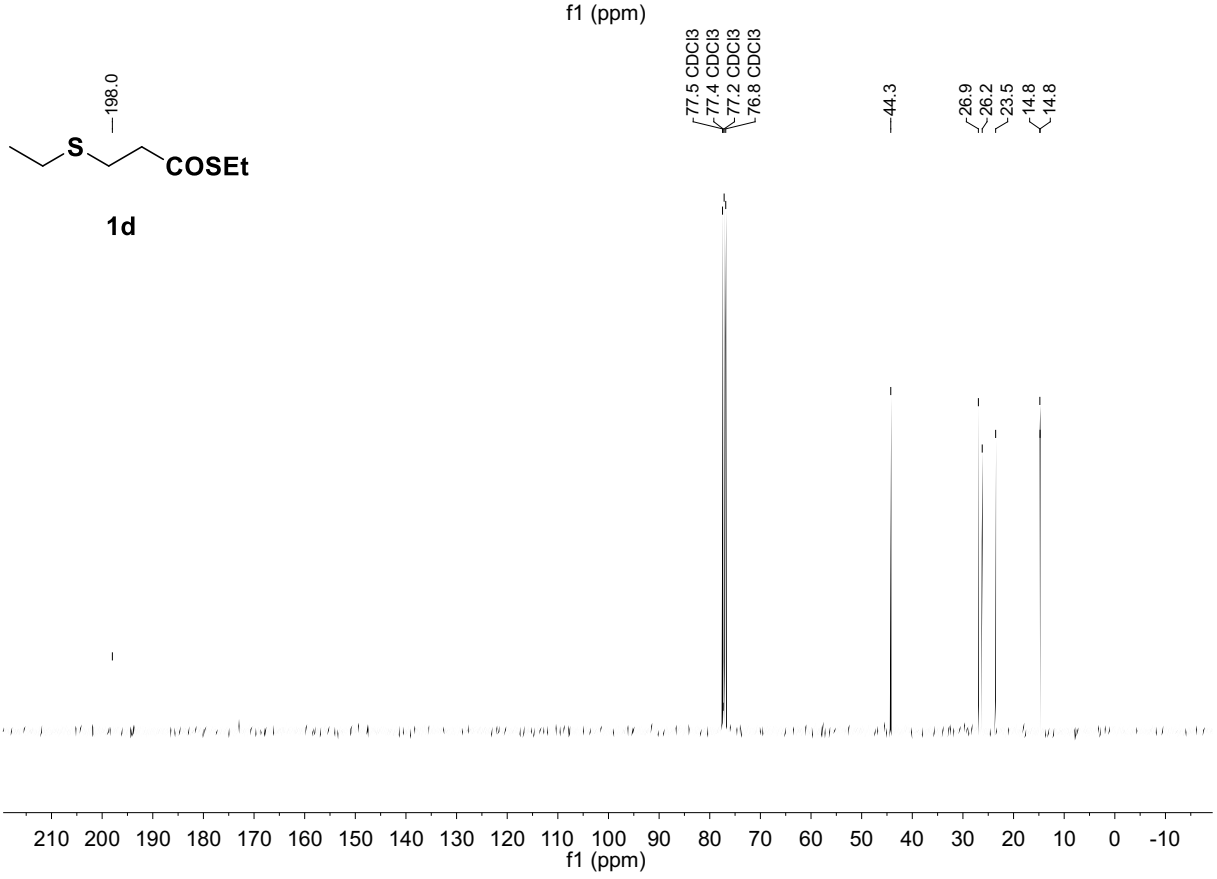
^{13}C NMR (101 MHz, $CDCl_3$): δ = 198.0 (*C*OSEt), 44.3, 26.9, 26.2, 23.5, 14.81, 14.76.

GC-MS (EI): t_r = 5.43 min, m/z(%) = 178 (17, $[M^{+\bullet}]$), 149 (15, $[M^{+\bullet}\text{-}C_2H_5^{\bullet}]$), 117 (20, $[M^{+\bullet}\text{-}SC_2H_5^{\bullet}]$), 89 (71, $[M^{+\bullet}\text{-}SC_2H_5^{\bullet}\text{-}CO]$), 75 (100, $[M^{+\bullet}\text{-}SC_2H_5^{\bullet}\text{-}CO\text{-}CH_2]$).

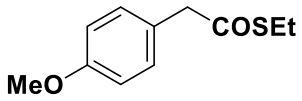
HR-MS (ESI): m/z calc. for $[M+Na]^+$ 201.03783, found 201.03810.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2965 (w, C-H_{aliph}), 2924 (w, C-H_{aliph}), 2872 (w, C-H_{aliph}), 1683 (vs, C=O), 1448 (m), 1415 (m), 1374 (w), 1329 (w), 1262 (m), 1225 (w), 1164 (w), 1037 (s), 957 (s), 870 (w), 759 (w), 699 (m).


S
COSEt
1d
3.03
3.01
2.99
2.97
2.92
2.68
2.67
2.65
2.63
1.38
1.36
1.34
2.01
3.97
1.99
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


198.0
77.5 CDCl3
77.4 CDCl3
77.2 CDCl3
76.8 CDCl3
44.3
26.9
26.2
23.5
14.8
14.8
S
COSEt
1d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

S-ethyl 2-(4-methoxyphenyl)ethanethioate (**1e**)



1e

According to GP-A, the product **1e** was synthesized using *para*-methoxy phenyl acetic acid (1.69 g, 10.0 mmol, 1.0 equiv.), ethanethiol (2.2 mL, 30 mmol, 3 equiv.), DMAP (122 mg, 1.00 mmol, 0.1 equiv.) and DCC (2.27 g, 11.0 mmol, 1.1 equiv.). Purification was achieved by filtration through a short silica plug using *n*Hex/EA (9:1) and washing the filtrate with 6 M HCl (2 × 20 mL), sat. $NaHCO_3$ (1 × 20 mL) and brine (1 × 20 mL). The product was obtained as a pale-yellow oil (1.71 g, 8.13 mmol, 81%).

$C_{11}H_{14}O_2S$ (210.29 g/mol)

R_f: 0.51 (*n*Hex/Et_2O = 9:1) [$KMnO_4$, UV]

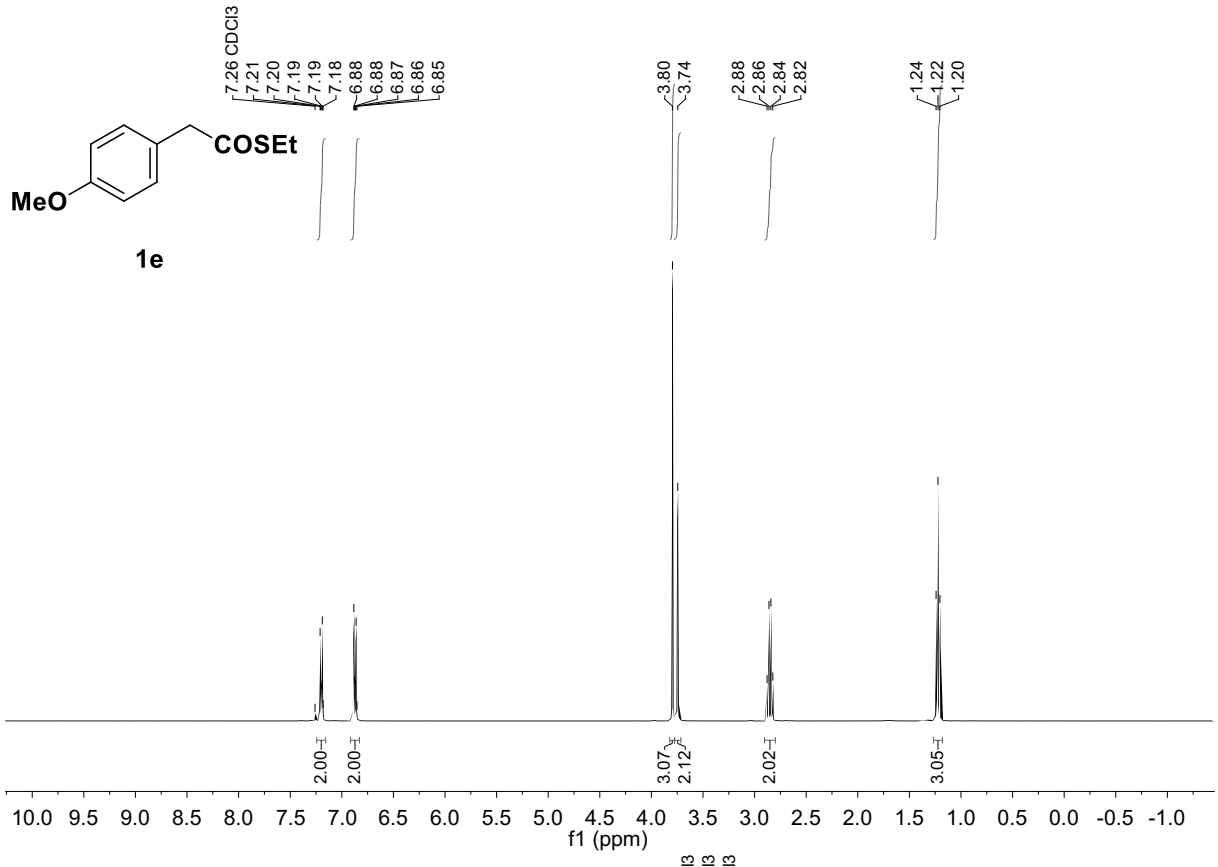
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 – 7.11 (m, 2H, Ar*H*), 6.94 – 6.79 (m, 2H, Ar*H*), 3.80 (s, 3H, OCH_3), 3.75 (s, 2H,PhCH_2), 2.85 (q, *J* = 7.4 Hz, 2H, COCH_2CH$_3$), 1.22 (t, *J* = 7.4 Hz, 3H, COCH$_2$CH_3).

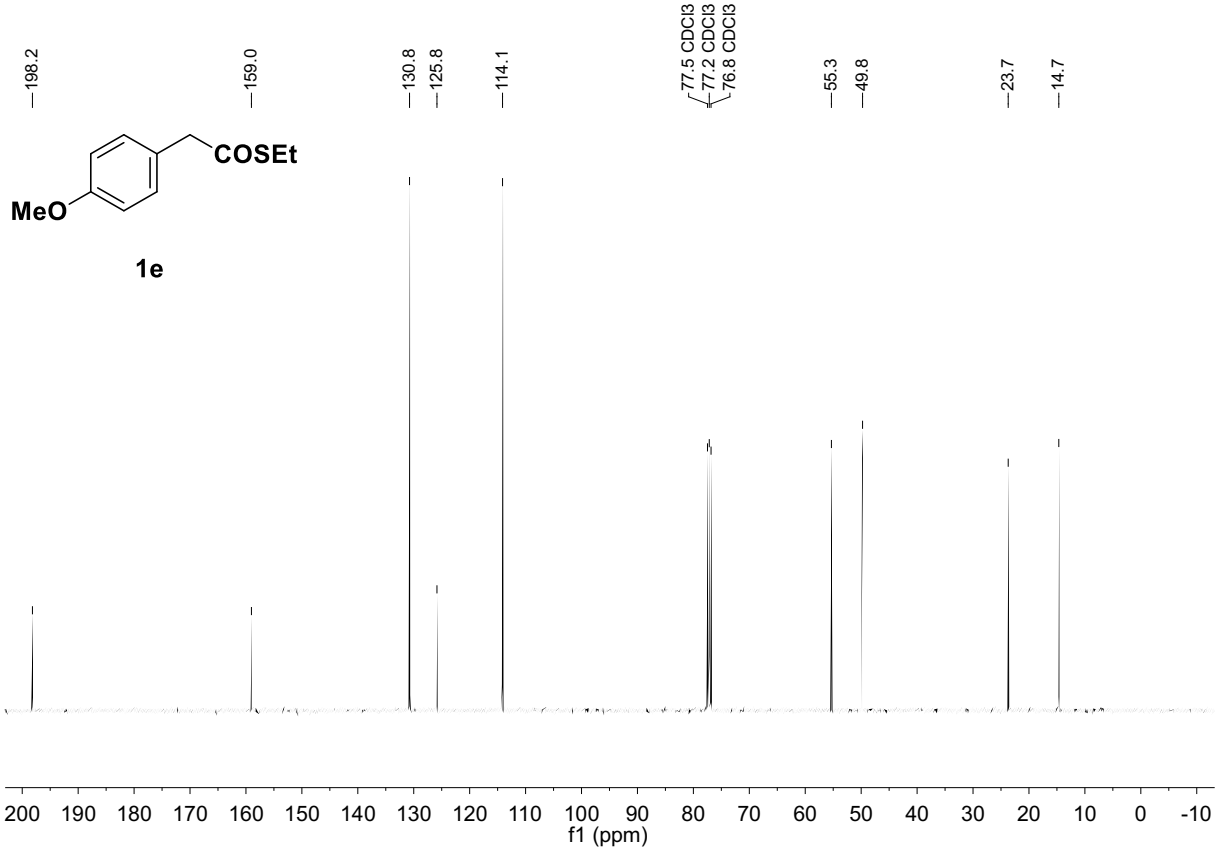
^{13}C NMR (101 MHz, $CDCl_3$): δ = 198.2 (*C*O), 159.0 (C_{Ar}), 130.8 (C_{Ar}), 125.9 (C_{Ar}), 114.1 (C_{Ar}), 55.3 (OCH_3), 49.8 (Ph*C*H$_2$), 23.7 (CO*C*H$_2$CH$_3$), 14.7 (CO*C*H$_2$CH$_3$).

GC-MS (EI): t_r = 5.53 min, m/z(%) = 210 (1, [$M^{+\bullet}$]), 121 (100, [$M^{+\bullet}$-$C_3H_5OS^{\bullet}$]).

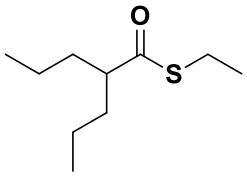
HR-MS (ESI): m/z calc. for $[M+Na]^+$ 233.06067, found 233.06103.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3062 (w, C-H_{arom}), 3032 (w, C-H_{arom}), 2962 (w, C-H_{aliph}), 2928 (w, C-H_{aliph}), 2834 (w, C-H_{aliph}), 1679 (s, C=O), 1608 (m), 1582 (w), 1508 (s), 1453 (m), 1418 (w), 1377 (w), 1299 (w), 1243 (vs, C-O), 1176 (s), 1109 (w), 1027 (s), 923 (w), 818 (m), 774 (s), 721 (w), 691 (m).


7.26 CDCl3
7.21
7.20
7.19
7.19
7.18
6.88
6.88
6.87
6.86
6.85
3.80
3.74
2.88
2.86
2.84
2.82
1.24
1.22
1.20
COSEt
MeO
1e
2.00
2.00
3.07
2.12
2.02
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


198.2
159.0
130.8
125.8
114.1
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
55.3
49.8
23.7
14.7
COSEt
MeO
1e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

S-ethyl 2-propylpentanethioate (**1g**)



1g

According to GP-A, the product **1g** was synthesized using valproic acid (1.60 mL, 10.0 mmol, 1.0 equiv.), ethanethiol (2.2 mL, 30 mmol, 3 equiv.), DMAP (122 mg, 1.00 mmol, 0.1 equiv.) and DCC (2.27 g, 11.0 mmol, 1.1 equiv.). Purification was achieved by filtration through a short silica plug (*n*Hex/EA = 9:1) and washing the solution with 6 M HCl (2 × 20 mL), 10% aq. KOH (1 × 20 mL), sat. $NaHCO_3$ (1 × 20 mL) and brine (1 × 20 mL). The organic layer was dried with anhydrous $MgSO_4$ and the solvent evaporated under reduced pressure to yield the target compound as a colorless oil (1.59 g, 8.44 mmol, 84%).

$C_{10}H_{20}OS$ (188.33 g/mol)

R_f: 0.65 (PE/EA = 97:3) [UV, anis - yellow]

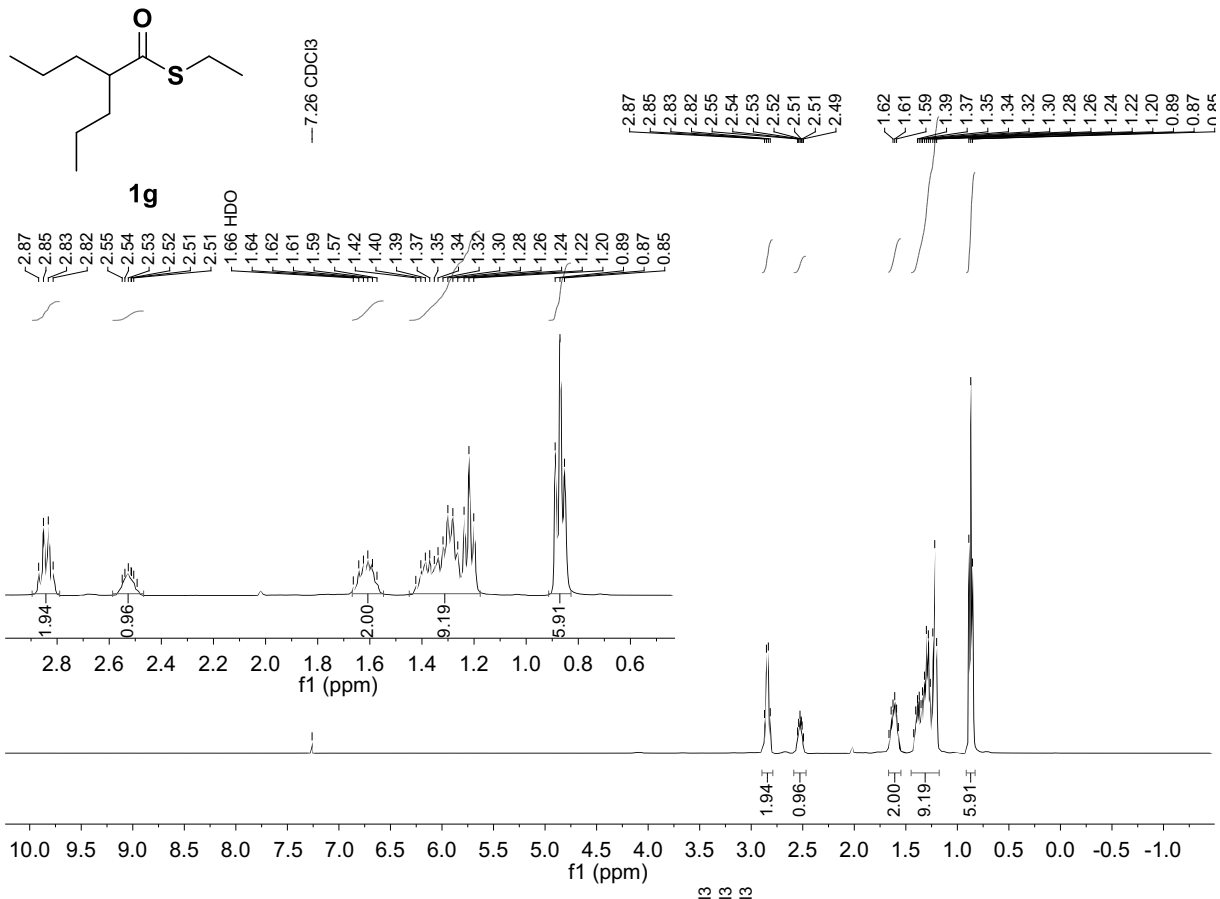
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.84 (qd, *J* = 7.4, 2.2 Hz, 2H), 2.60 – 2.44 (m, 1H), 1.72 – 1.54 (m, 2H), 1.45 – 1.09 (m, 9H), 0.91 – 0.82 (m, 6H).

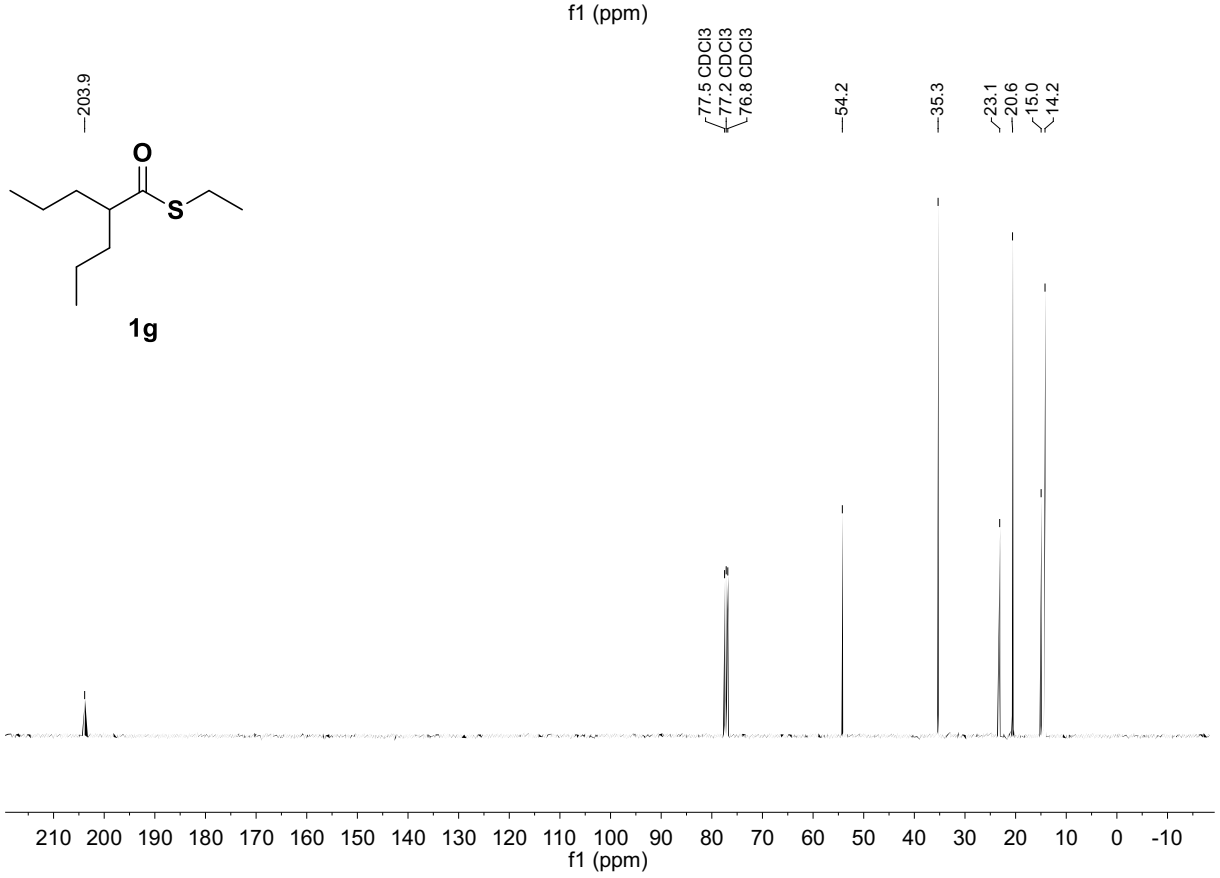
^{13}C NMR (75 MHz, $CDCl_3$): δ = 203.9 (*C*OSEt), 54.2, 35.3, 23.2, 20.6, 15.0, 14.2.

GC-MS (EI): t_r = 4.79 min, m/z(%) = 127 (9, $[M^{+\bullet}\text{-}C_2H_5S^{\bullet}]$), 99 (5, $[M^{+\bullet}\text{-}C_2H_5S^{\bullet}\text{-}CO]$), 57 (100).

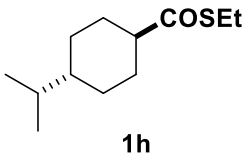
HR-MS (APCI): m/z calc. for $[M+H]^+$ 189.13076, found 189.13114.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2958 (m, C-H_{aliph}), 2928 (m, C-H_{aliph}), 2869 (m, C-H_{aliph}), 1683 (vs, C=O), 1456 (m), 1377 (w), 1265 (w), 1232 (w), 1151 (w), 1116 (w), 1053 (w), 997 (s), 941 (m), 900 (m), 870 (w), 766 (m), 710 (w), 688 (w).


O
S
1g
7.26 CDCl3
2.87
2.85
2.83
2.82
2.55
2.54
2.53
2.52
2.51
2.51
2.49
1.62
1.61
1.59
1.39
1.37
1.35
1.34
1.32
1.30
1.28
1.26
1.24
1.22
1.20
0.89
0.87
1.66 HDO
1.64
1.62
1.61
1.59
1.57
1.42
1.40
1.39
1.37
1.35
1.34
1.32
1.30
1.28
1.26
1.24
1.22
1.20
0.89
0.87
0.85
1.94
0.96
2.00
9.19
5.91
2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
f1 (ppm)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


203.9
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
54.2
35.3
23.1
20.6
15.0
14.2
O
S
1g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

S-ethyl *trans*-4-*iso*-propylcyclohexane-1-carbothioate (**1h**)



1h

According to GP-A, the product **1h** was synthesized using *trans*-4-*iso*-propylcyclohexane carboxylic acid (1.70 g, 10.0 mmol, 1.0 equiv.), ethanethiol (2.2 mL, 30 mmol, 3 equiv.), DMAP (122 mg, 1.00 mmol, 0.1 equiv.) and DCC (2.27 g, 11.0 mmol, 1.1 equiv.). Purification was achieved by filtration through a short silica plug (*n*Hex/EA = 8:2 v/v) and washing the filtrate with 6 M HCl (2 × 100 mL), sat. $NaHCO_3$ (1 × 100 mL) and brine (1 × 100 mL). The product was obtained as a colorless oil (1.47 g, 6.86 mmol, 69%).

$C_{12}H_{22}OS$ (214.37 g/mol)

R_f: 0.44 (*n*Hex/EA = 98:2) [anis – blue, UV]

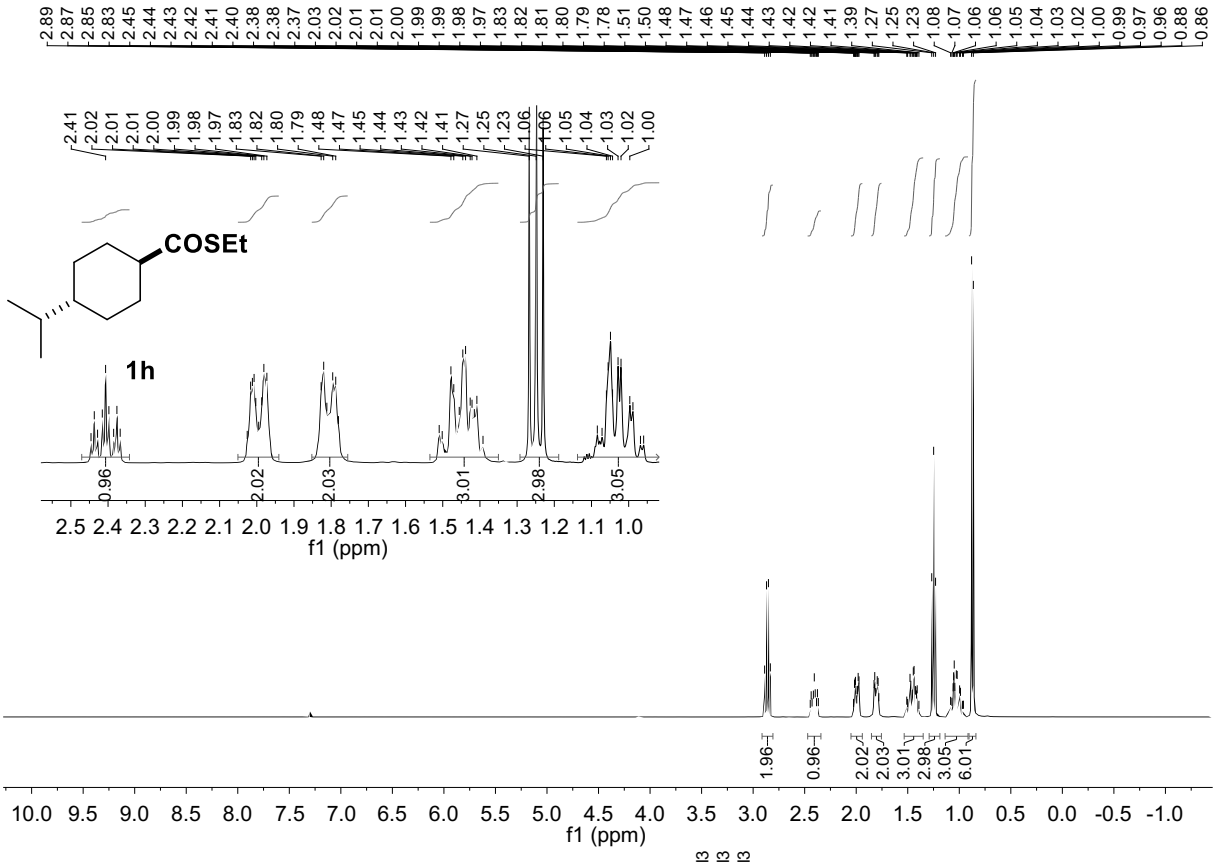
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.85 (q, *J* = 7.4 Hz, 2H, SC*H*$_2$CH$_3$), 2.40 (tt, *J* = 12.2, 3.5 Hz, 1H, C*H*COSEt), 2.04 – 1.93 (m, 2H), 1.83 – 1.75 (m, 1H), 1.53 – 1.35 (m, 3H), 1.24 (t, *J* = 7.4 Hz, 3H, SCH$_2$C*H*$_3$), 1.13 – 0.93 (m, 3H), 0.86 (d, *J* = 6.8 Hz, 6H, C*H*$_3$CHC*H*$_3$).

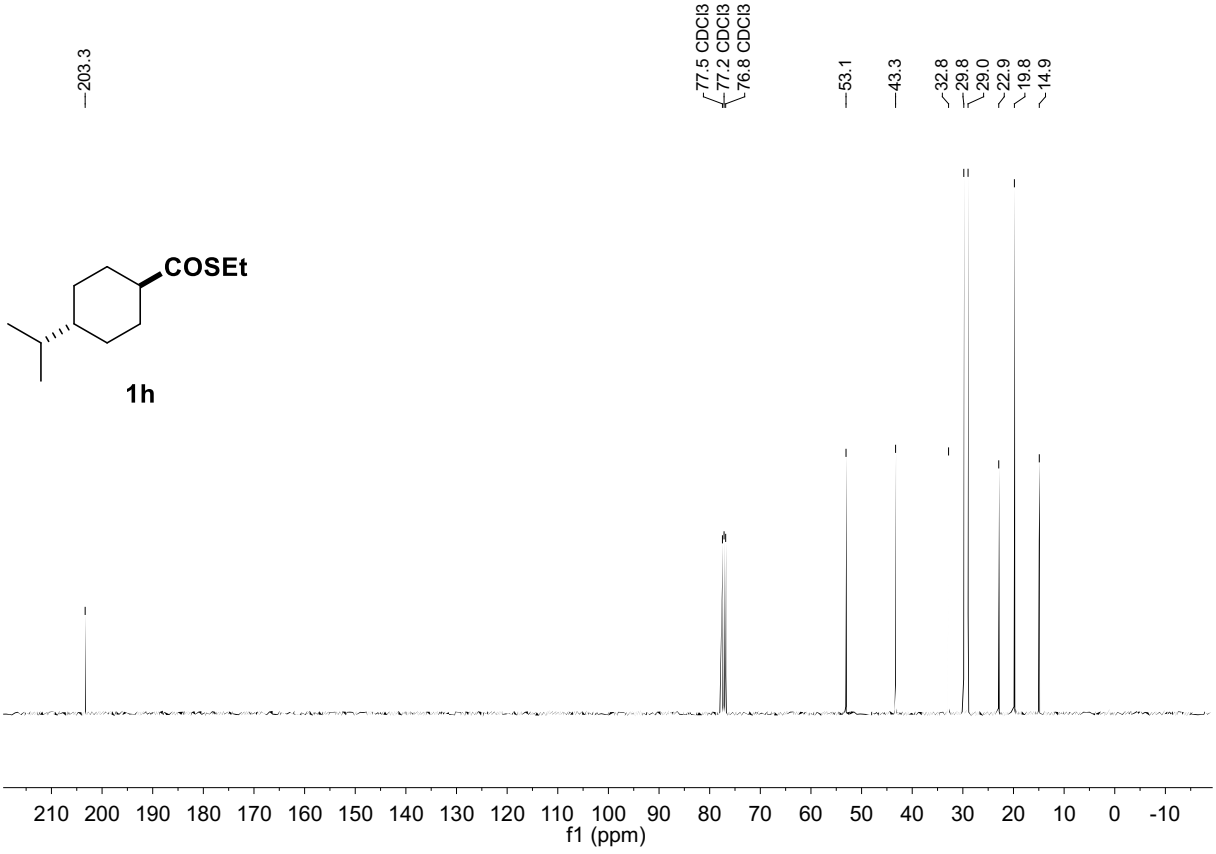
^{13}C NMR (101 MHz, $CDCl_3$): δ = 203.3 (*C*OSEt), 53.1, 43.3, 32.8, 29.8, 29.0, 22.9, 19.8, 14.9.

GC-MS (EI): t_r = 6. 86 min, m/z(%) = 153 (15, [$M^{+\bullet}$-$C_2H_5S^{\bullet}$-CO]), 81 (100).

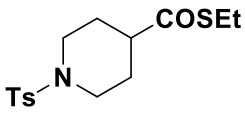
HR-MS (ESI): m/z calc. for $[M+Na]^+$ 237.12836, found 237.12858.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2928 (s, C-H_{aliph}), 2860 (m, C-H_{aliph}), 1683 (s, C=O), 1448 (m), 1415 (w), 1370 (w), 1311 (w), 1265 (w), 1232 (w), 1163 (w), 1146 (w), 1112 (w), 1053 (m), 980 (s), 934 (m), 897 (w), 878 (w), 874 (w), 837 (w), 807 (s), 759 (w), 706 (w).


COSEt
1h
f1 (ppm)


COSEt
1h
f1 (ppm)

S-ethyl 1-tosylpiperidine-4-carbothioate (**1i**)



1i

According to GP-A, the product **1i** was synthesized using 1-tosylpiperidine-4-carboxylic acid (2.83 g, 10.0 mmol, 1.0 equiv.), ethanethiol (2.2 mL, 30 mmol, 3 equiv.), DMAP (122 mg, 1.00 mmol, 0.1 equiv.) and DCC (2.27 g, 11.0 mmol, 1.1 equiv.). Purification was achieved by filtration through a short silica plug (Hex/EA = 9:1). The product was recrystallized from Et_2O to yield colorless crystals (2.31 g, 7.05 mmol, 71%). The data is in accordance with reported literature.[1a]

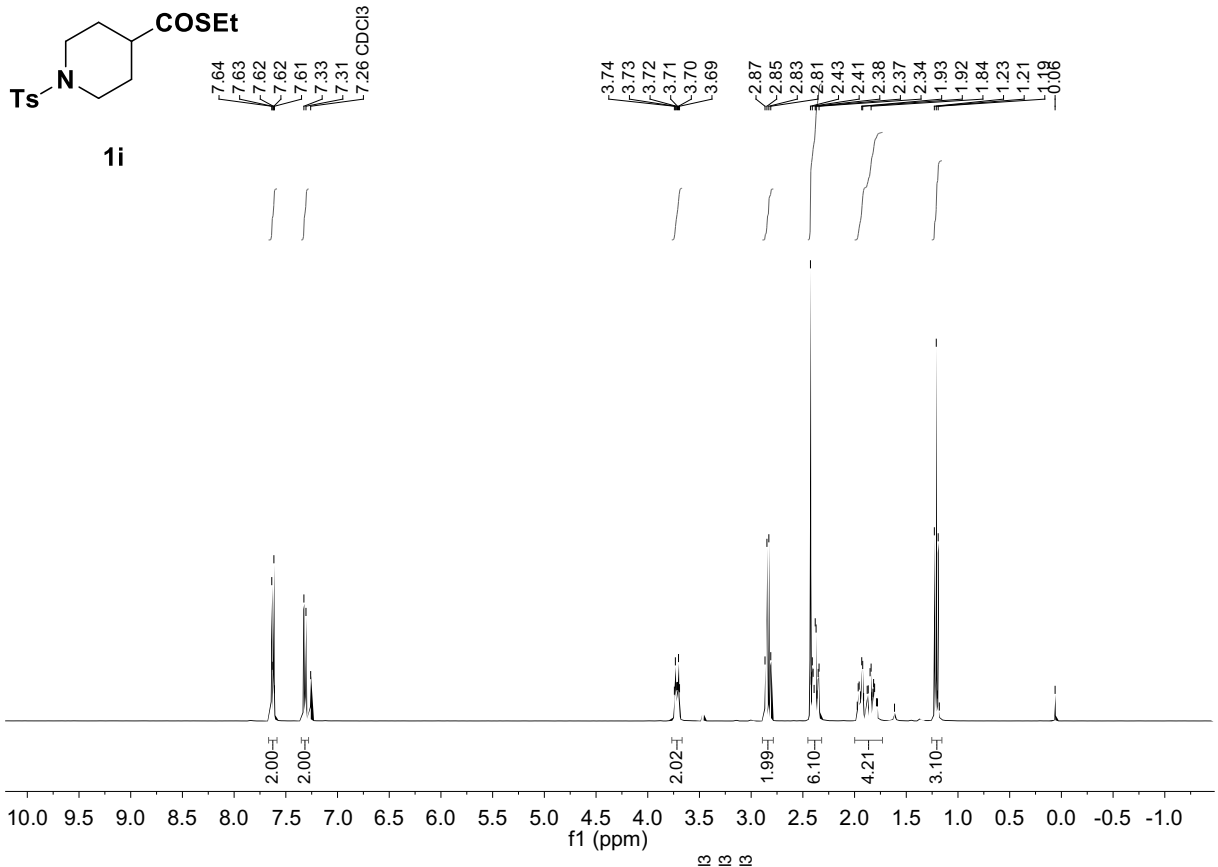
$C_{15}H_{21}NO_3S_2$ (327.46 g/mol)

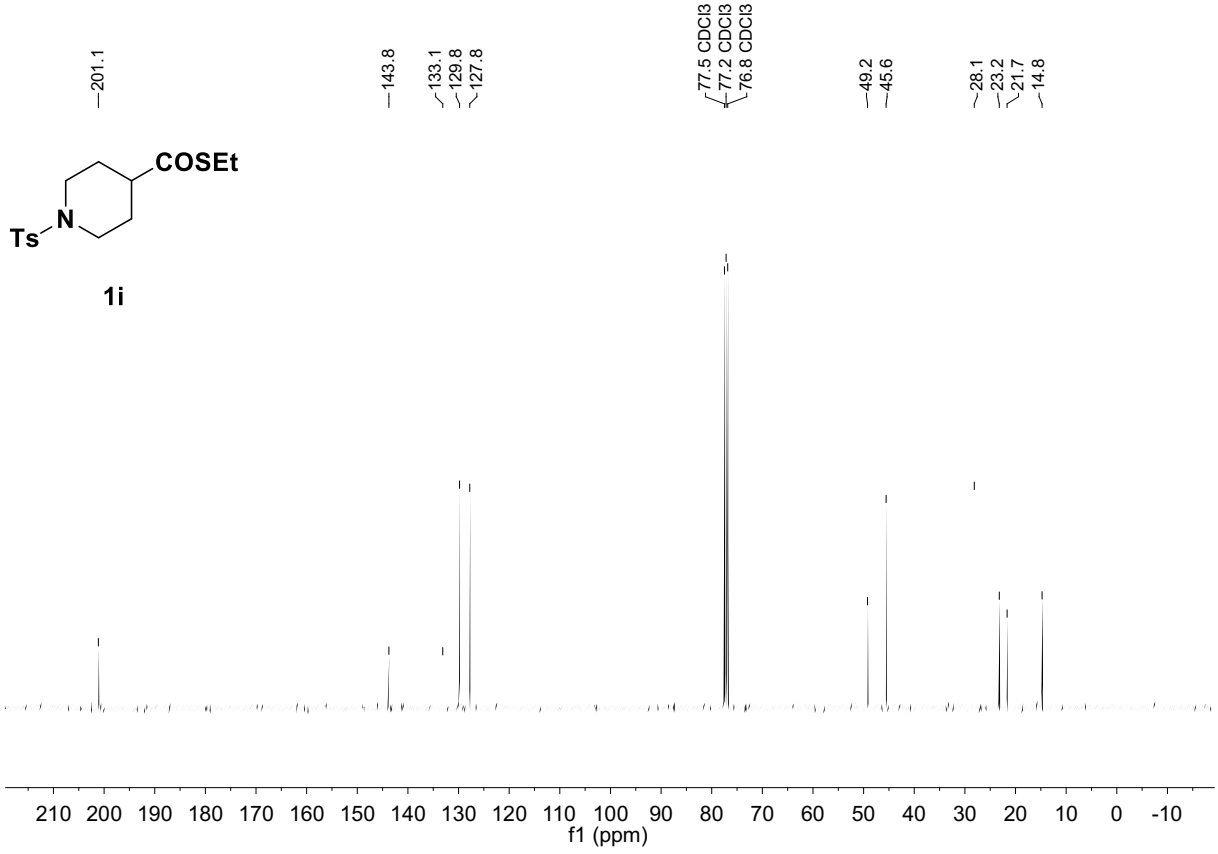
R_f: 0.14 (*n*Hex/EA = 9:1) [$KMnO_4$, UV]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 – 7.62 (m, 2H), 7.40 – 7.27 (m, 2H), 3.82 – 3.65 (m, 2H), 2.84 (q, *J* = 7.4 Hz, 2H), 2.43 (s, 3H), 2.42 – 2.33 (m, 3H), 1.99 – 1.91 (m, 2H), 1.88 – 1.77 (m, 2H), 1.21 (t, *J* = 7.4 Hz, 3H).

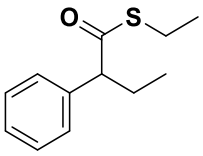
^{13}C NMR (101 MHz, $CDCl_3$): δ = 201.1 (*C*OSEt), 143.8 (C_{Ar}), 133.1 (C_{Ar}), 129.8 (C_{Ar}), 127.8 (C_{Ar}), 49.2, 45.6, 28.1, 23.2, 21.7, 14.8.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2937 (w, C-H_{aliph}), 2831 (w, C-H_{aliph}), 1683 (m, C=O), 1594 (w), 1493 (w), 1448 (w), 1377 (w), 1346 (w), 1329 (w), 1299 (w), 1254 (w), 1221 (w), 1155 (m), 1120 (w), 1094 (w), 1064 (w), 984 (w), 975 (w), 922 (m), 828 (w), 803 (m), 721 (m).


COSEt
N
Ts
1i
7.64
7.63
7.62
7.62
7.61
7.33
7.31
7.26 CDCl3
3.74
3.73
3.72
3.71
3.70
3.69
2.87
2.85
2.83
2.81
2.43
2.41
2.38
2.37
2.34
1.93
1.92
1.84
1.23
1.21
1.19
0.08
2.00
2.00
2.02
1.99
6.10
4.21
3.10
f1 (ppm)


201.1
143.8
133.1
129.8
127.8
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
49.2
45.6
28.1
23.2
21.7
14.8
COSEt
N
Ts
1i
f1 (ppm)

S-ethyl 2-phenylbutanethioate (**1j**)



1j

According to GP-A, the product **1j** was synthesized using 2-phenylbutyric acid (1.64 g, 10.0 mmol, 1.0 equiv.), ethanethiol (2.2 mL, 30 mmol, 3.0 equiv.), DMAP (122 mg, 1.00 mmol, 0.1 equiv.) and DCC (2.27 g, 11.0 mmol, 1.1 equiv.). Purification was achieved by filtration through a short silica plug using a solvent mixture (*n*Hex/EA = 30:1 v/v). The product was obtained as a colorless oil (1.93 g, 9.26 mmol, 93%).

$C_{12}H_{16}OS$ (208.32 g/mol)

R_f: 0.27 (*n*Hex/Et_2O = 30:1) [$KMnO_4$]

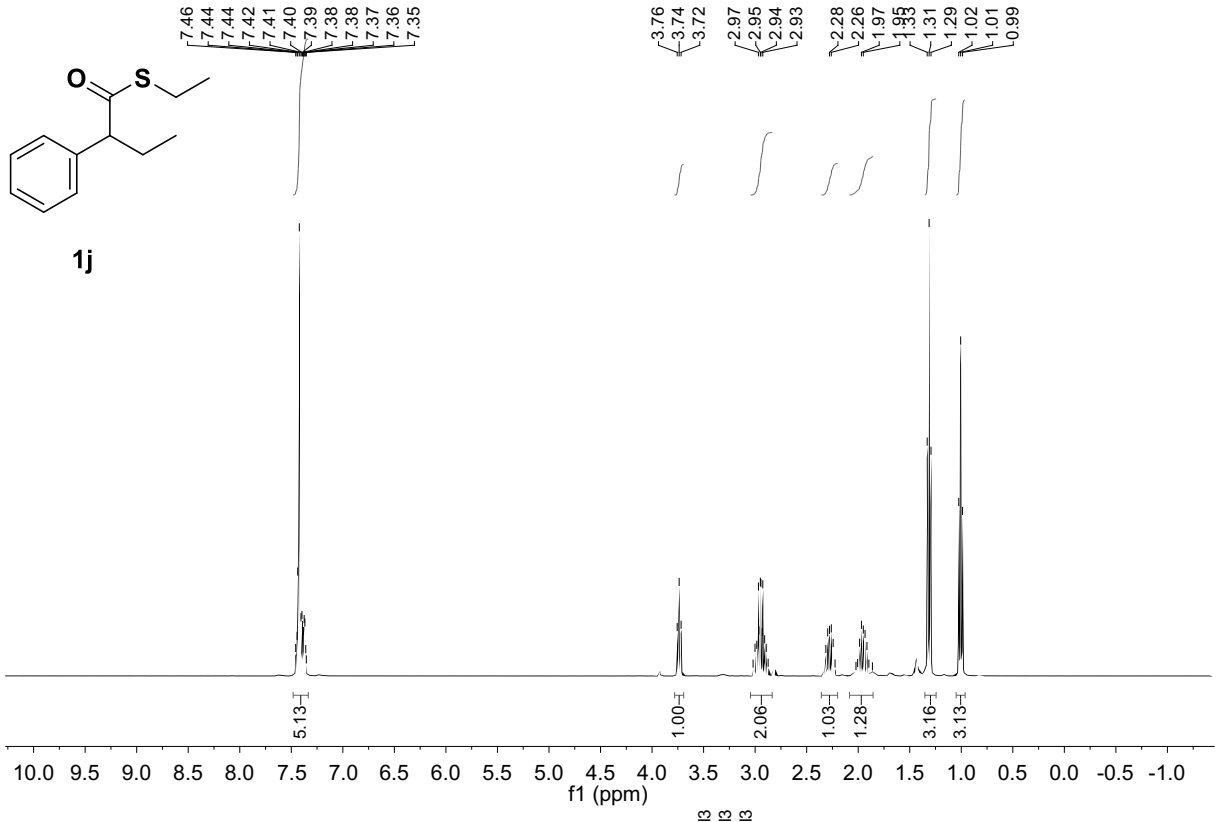
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 – 7.11 (m, 5H), 3.65 (t, *J* = 7.6 Hz, 1H), 2.98 – 2.79 (m, 2H), 2.19 (dt, *J* = 13.5, 7.3 Hz, 1H), 1.87 (dt, *J* = 13.6, 7.4 Hz, 1H), 1.23 (t, *J* = 7.4 Hz, 3H), 0.92 (t, *J* = 7.4 Hz, 3H).

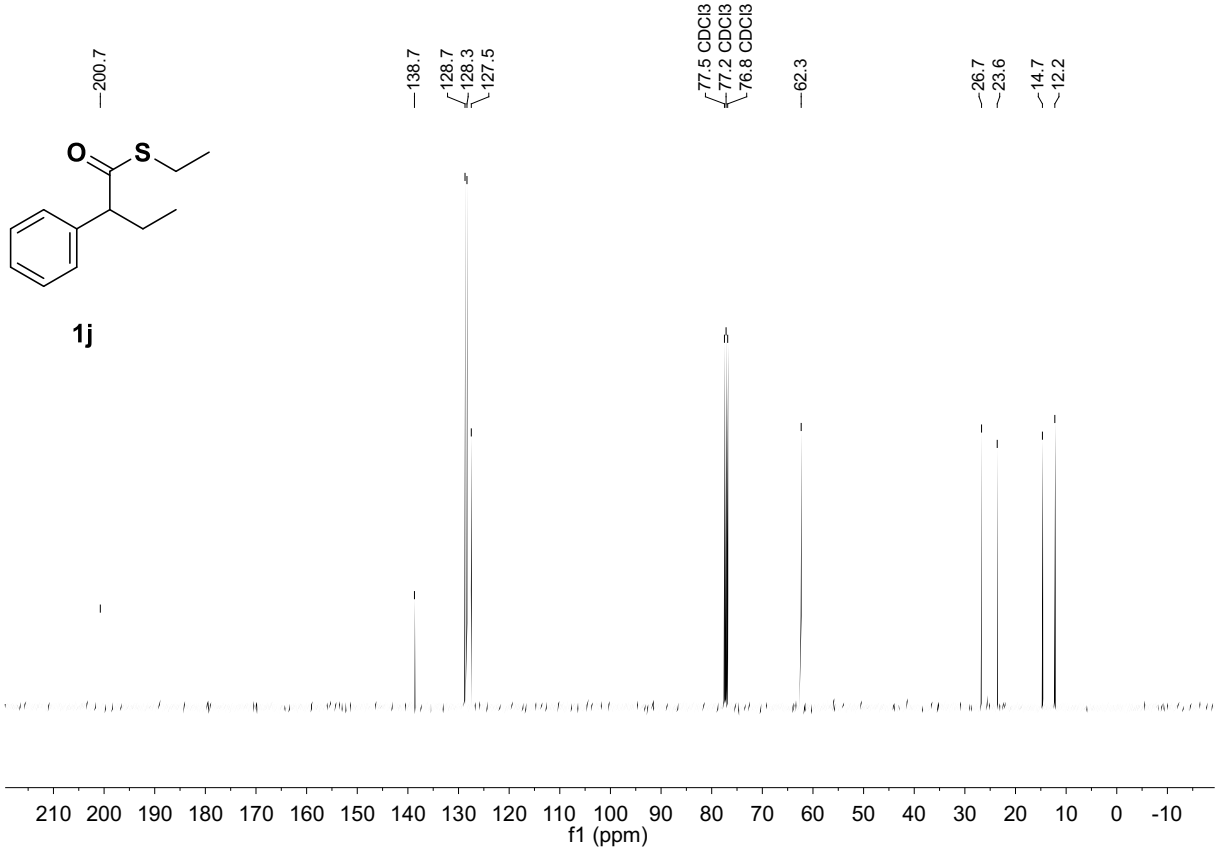
^{13}C NMR (101 MHz, $CDCl_3$): 200.7 (*C*OSEt), 138.7 (C_{Ar}), 128.7 (C_{Ar}), 128.3 (C_{Ar}), 127.5(C_{Ar}), 62.3, 26.7, 23.1, 14.7, 12.2.

GC-MS (EI): t_r = 6.54 min, m/z(%) = 208 (2, [$M^{+\bullet}$]), 147 (7, [$M^{+\bullet}$-$C_2H_5S^{\bullet}$]), 119, (37, [$M^{+\bullet}$-$C_2H_5S^{\bullet}$-CO]), 91 (100, [$Bn^{+\bullet}$]).

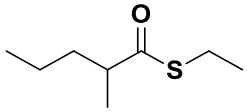
HR-MS (ESI): m/z calc. for $[M+Na]^+$ 231.08141, found 231.08181.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3062 (w, C-H_{arom}), 3028 (w, C-H_{arom}), 2965 (w, C-H_{aliph}), 2928 (w, C-H_{aliph}), 2872 (w, C-H_{aliph}), 2116 (w), 1682 (s, C=O), 1597 (w), 1493 (w), 1452 (m), 1415 (w), 1377 (w), 1340 (w), 1299 (w), 1261 (w), 1113 (w), 977 (s), 909 (w), 840 (w), 814 (m), 736 (m), 699 (s).


7.46
7.44
7.44
7.42
7.41
7.40
7.39
7.38
7.38
7.37
7.36
7.35
3.76
3.74
3.72
2.97
2.95
2.94
2.93
2.28
2.26
1.97
1.95
1.33
1.31
1.29
1.02
1.01
0.99
O
S
1j
5.13
1.00
2.06
1.03
1.28
3.16
3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


200.7
138.7
128.7
128.3
127.5
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
62.3
26.7
23.6
14.7
12.2
O
S
1j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

S-ethyl 2-methylpentanethioate (**1k**)



1k

According to GP-A, the product **1k** was synthesized using 2-methylvaleric acid (1.25 mL, 10.0 mmol, 1.0 equiv.), ethanethiol (2.2 mL, 30 mmol, 3.0 equiv.), DMAP (122 mg, 1.00 mmol, 0.1 equiv.) and DCC (2.27 g, 11.0 mmol, 1.1 equiv.). Purification was achieved by filtration through a short silica plug (*n*Hex/EA = 30:1 v/v) and washing the gained diluted solution with 6 M HCl (3 × 20 mL), sat. aq. $NaHCO_3$ (2 × 20 mL) and brine (1 × 20 mL). The product was obtained as a colorless oil (1.22 g, 7.61 mmol, 76%).

$C_8H_{16}OS$ (160.28 g/mol)

R_f: 0.57 (PE/EA = 97:3) [$KMnO_4$]

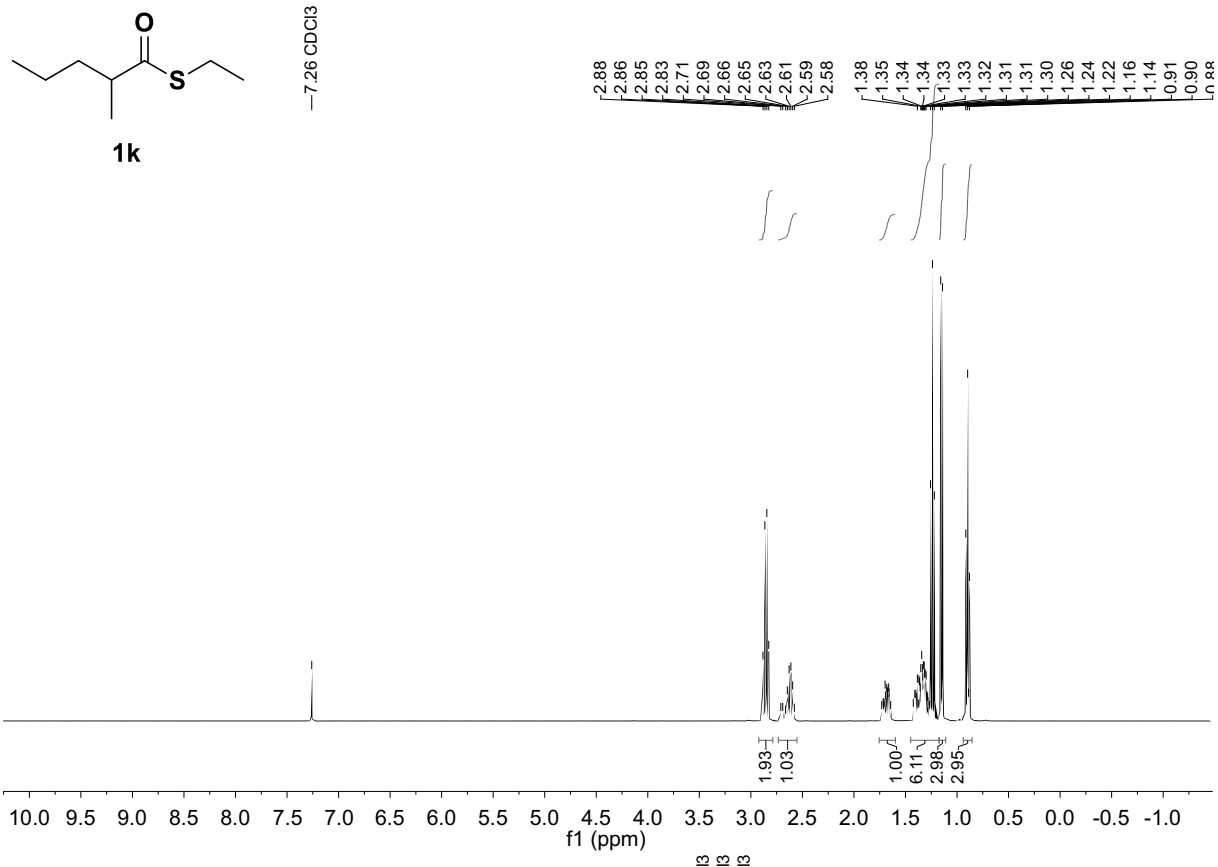
^{1}H NMR (400 MHz, $CDCl_3$): 2.85 (q, *J* = 7.3 Hz, 2H), 2.69 – 2.55 (m, 1H), 1.76 – 1.60 (m, 1H), 1.45 – 1.17 (m, 6H), 1.15 (d, *J* = 6.9 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 3H).

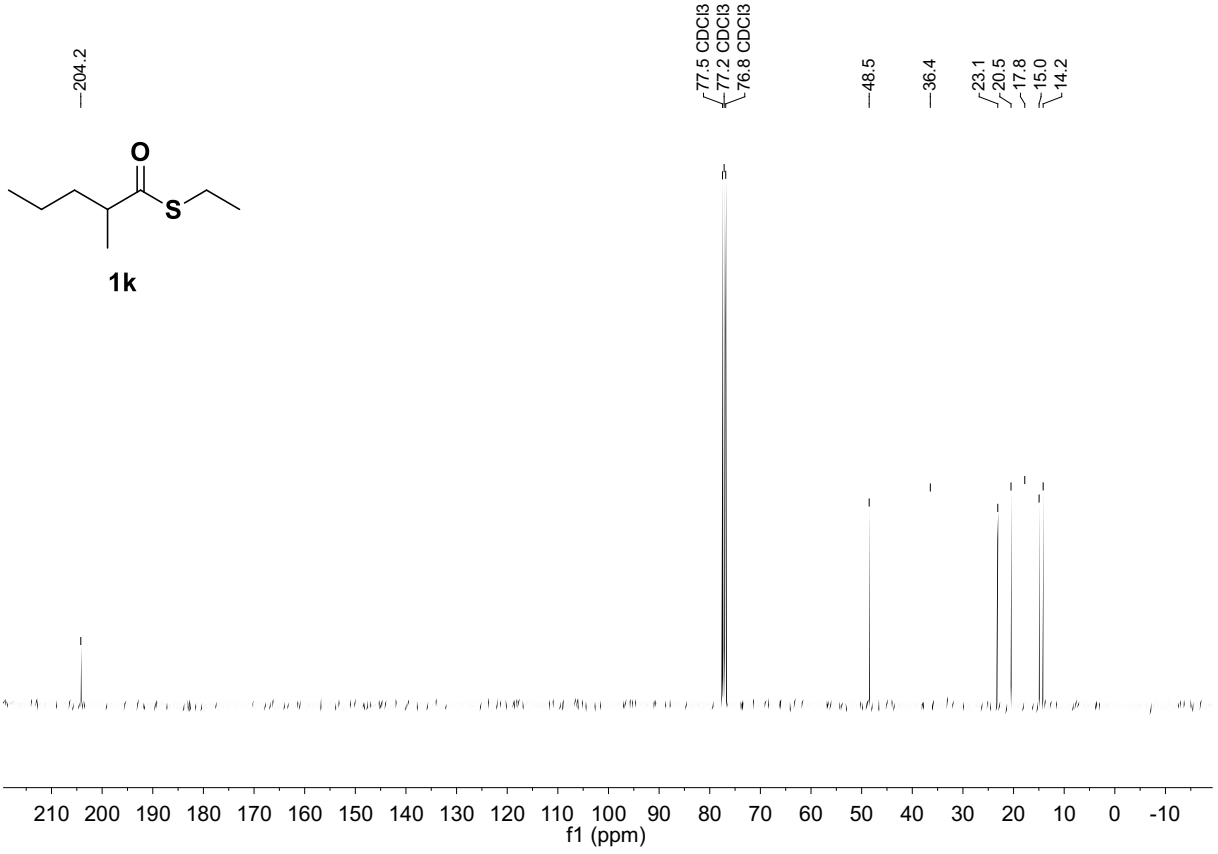
^{13}C NMR (101 MHz, $CDCl_3$): 204.2 (*C*OSEt), 48.5, 36.4, 23.1, 20.5, 17.8, 15.0, 14.2.

HR-MS (APCI): m/z calc. for $[M+H]^+$ 161.09946, found 161.09972.

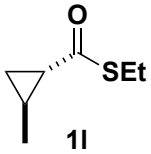
GC-MS (EI): t_r = 3.53 min, m/z(%) = 131 (12, $[M^{+\bullet}]$), 99 (32, $[M^{+\bullet}\text{-}C_2H_5S^{\bullet}]$), 71, (100, $[M^{+\bullet}\text{-}C_2H_5S^{\bullet}\text{-}CO]$).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2962 (m, C-H_{aliph}), 2928 (m, C-H_{aliph}), 2872 (w, C-H_{aliph}), 1684 (vs, C=O), 1455 (m), 1418 (w), 1377 (w), 1344 (w), 1265 (w), 1232 (w), 1161 (w), 1103 (w), 1098 (w), 1031 (w), 997 (w), 960 (vs), 908 (m), 870 (w), 755 (w), 695 (w).


O
S
1k
7.26 CDCl3
2.88
2.86
2.85
2.83
2.71
2.69
2.66
2.65
2.63
2.61
2.59
2.58
1.38
1.35
1.34
1.34
1.33
1.33
1.32
1.31
1.31
1.30
1.26
1.24
1.22
1.16
1.14
0.91
0.90
1.93
1.03
1.00
6.11
2.98
2.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


204.2
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
48.5
36.4
23.1
20.5
17.8
15.0
14.2
O
S
1k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

S-ethyl *trans*-2-methylcyclopropane-1-carbothioate (**1l**)



1l

According to GP-A, the product **1l** was synthesized using 2-methylcyclopropane-1-carboxylic acid (0.97 mL, 10.0 mmol, 1.0 equiv.), ethanethiol (2.2 mL, 30 mmol, 3.0 equiv.), DMAP (122 mg, 1.00 mmol, 0.1 equiv.) and DCC (2.27 g, 11.0 mmol, 1.1 equiv.). Purification was achieved by dry column vacuum chromatography (*n*Hex). The product was obtained as a colorless oil (751.4 mg, 5.21 mmol, 52%). The analytical data is in good accordance to previously published literature.[10]

$C_7H_{12}OS$ (144.23 g/mol)

trans/cis= 10:1

R_f: 0.26 (*n*Hex) [UV, anis - yellow]

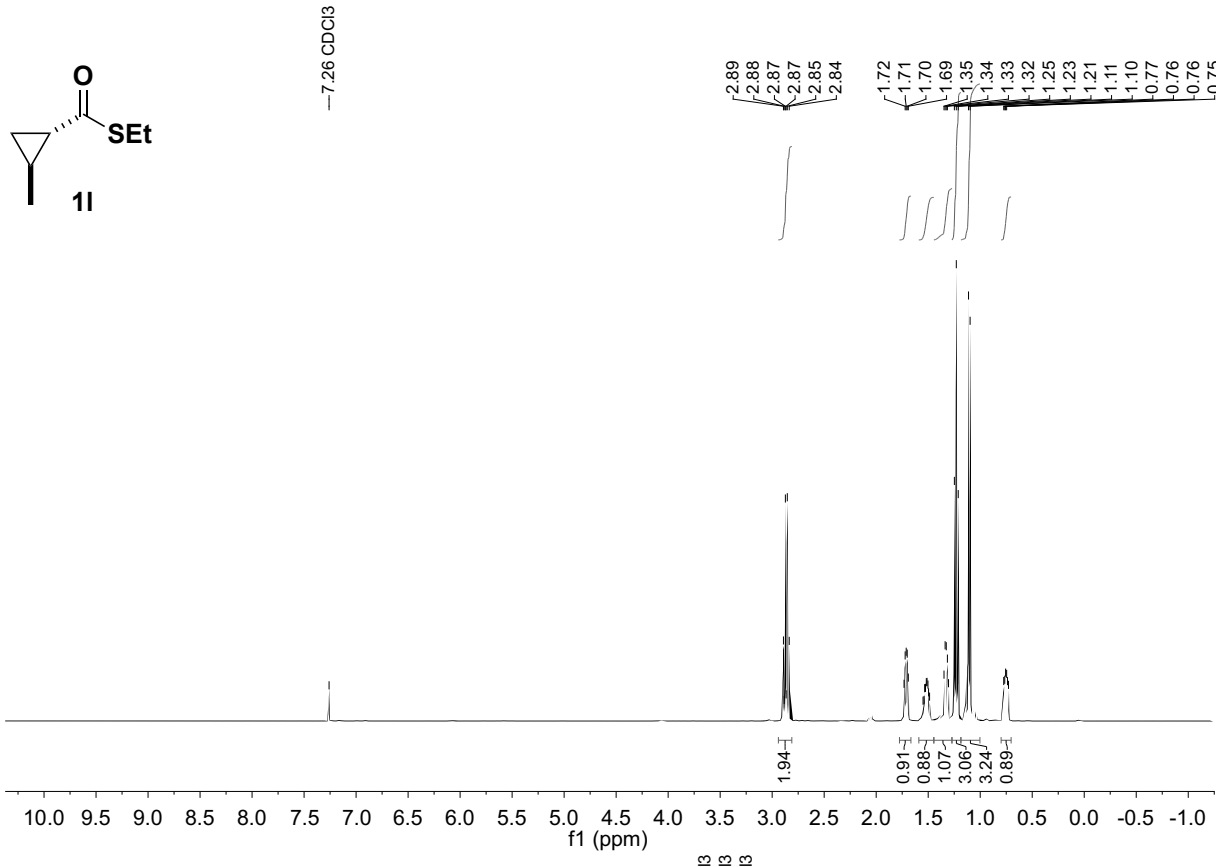
^{1}H NMR (400 MHz, $CDCl_3$, mixture): 2.86 (q, *J* = 7.4 Hz, 2H, SC*H*$_2$), 1.71 (dt, *J* = 8.3, 4.3 Hz, 1H), 1.57 – 1.45 (m, 1H), 1.43 – 1.26 (m, 1H), 1.23 (t, *J* = 7.4 Hz, 3H, SCH_2CH_3), 1.10 (d, *J* = 6.1 Hz, 3H, $CHCH_3$), 0.77 – 0.73 (m, 1H).

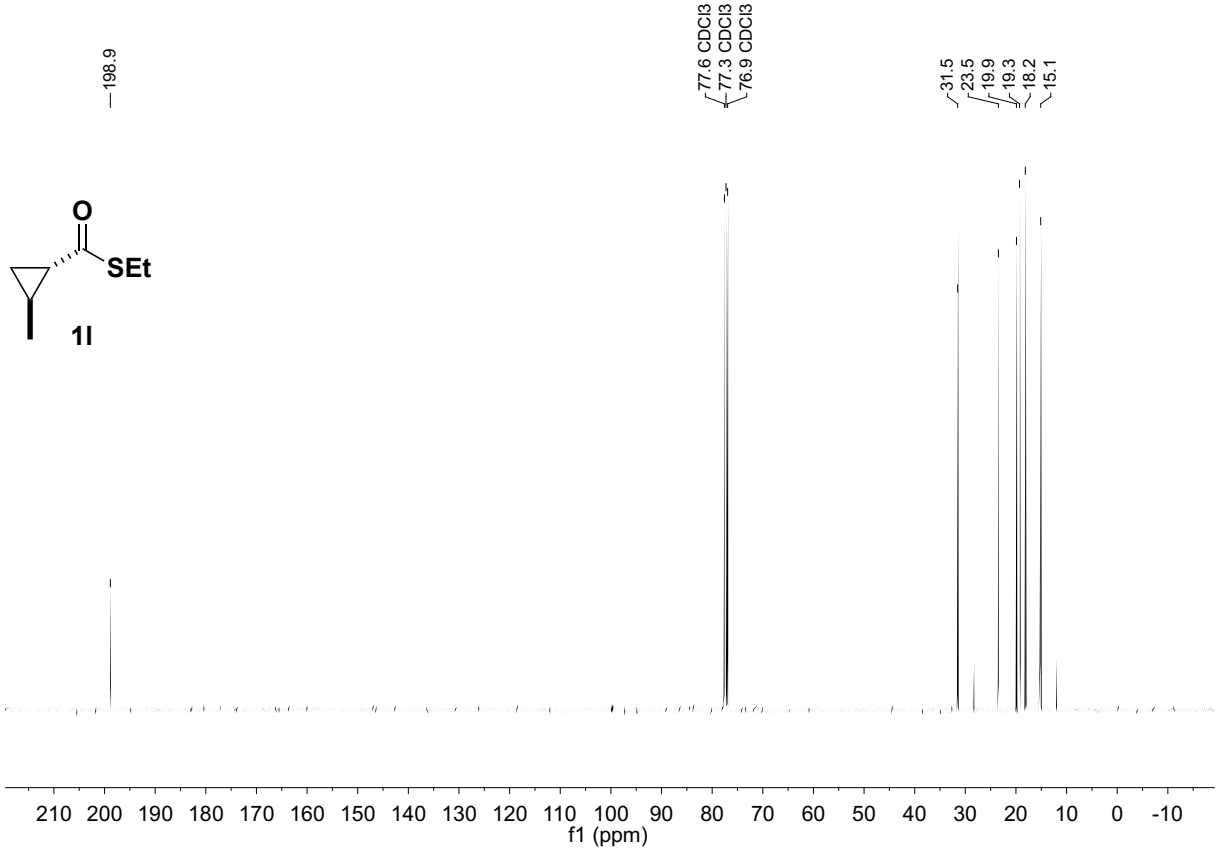
^{13}C NMR (101 MHz, $CDCl_3$, mixture): 198.9 (*C*OSEt), 31.5, 23.5, 19.9, 19.3, 18.2, 15.1.

HR-MS (EI): m/z calc. for $[M]^+$ 144.060337, found 144.05855.

GC-MS (EI, method B): t_r = 11.03 min, m/z(%) = 144 (10, $[M^{+\bullet}]$), 83 (100, $[M^{+\bullet}\text{-}C_2H_5S^{\bullet}]$).

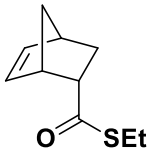
IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2961 (w, C-H_{aliph}), 2928 (w, C-H_{aliph}), 2872 (w, C-H_{aliph}), 1675 (vs, C=O), 1445 (m), 1399 (m), 1374 (m), 1314 (w), 1265 (w), 1180 (w), 1060 (s), 1027 (s), 952 (s), 903 (s), 843 (w), 777 (w), 743 (s), 662 (w).


O
SEt
1l
7.26 CDCl3
2.89
2.88
2.87
2.87
2.85
2.84
1.72
1.71
1.70
1.69
1.35
1.34
1.33
1.32
1.25
1.23
1.21
1.11
1.10
0.77
0.76
1.94
0.91
0.88
1.07
3.06
3.24
0.89
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

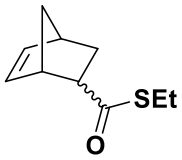

O
SEt
1l
198.9
77.6 CDCl3
77.3 CDCl3
76.9 CDCl3
31.5
23.5
19.9
19.3
18.2
15.1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

S-ethyl (1*S**,2*S**,4*S**)-bicyclo[2.2.1]hept-5-ene-2-carbothioate (**1m**)

and a mixture with diastereomer (**1m+1m'**)



1m



1m+1m'

According to GP-A, the both products were synthesized using bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (1.38 g, 10.0 mmol, 1.0 equiv.), ethanethiol (2.2 mL, 30 mmol, 3.0 equiv.), DMAP (122 mg, 1.00 mmol, 0.1 equiv.) and DCC (2.27 g, 11.0 mmol, 1.1 equiv.). Purification was achieved by flash column chromatography (23 g SiO_2, isocratic *n*Hex/EA = 98:2 v/v, 15 CV). The separation yielded pure *exo*-product as well as a mixture of *endo*- and *exo*-product. The products were obtained as a colorless oil (sum of products: 837.1 mg, 4.59 mmol, 46%).

$C_{10}H_{14}OS$ (182.28 g/mol)

R_f: 0.20 (PE/EA = 98:2) [$KMnO_4$, anis, UV]

1m: ^{1}H NMR (400 MHz, $CDCl_3$): 6.20 (dd, *J* = 5.7, 3.1 Hz, 1H), 5.93 (dd, *J* = 5.7, 2.8 Hz, 1H), 3.27 (tq, *J* = 3.1, 1.5 Hz, 1H), 3.18 (dt, *J* = 9.0, 3.9 Hz, 1H), 2.95 – 2.74 (m, 3H), 1.86 (ddd, *J* = 11.8, 9.1, 3.7 Hz, 1H), 1.59 – 1.39 (m, 2H), 1.35 – 1.17 (m, 4H).

1m: ^{13}C NMR (101 MHz, $CDCl_3$): 201.0 (*C*OSEt), 137.9 (C_{alkene}), 132.0 (C_{alkene}), 53.0, 49.7, 47.3, 42.9, 29.5, 23.3, 15.0.

d.r. (**1m** + **1m'**) = 5 (*endo*) : 3 (*exo*)

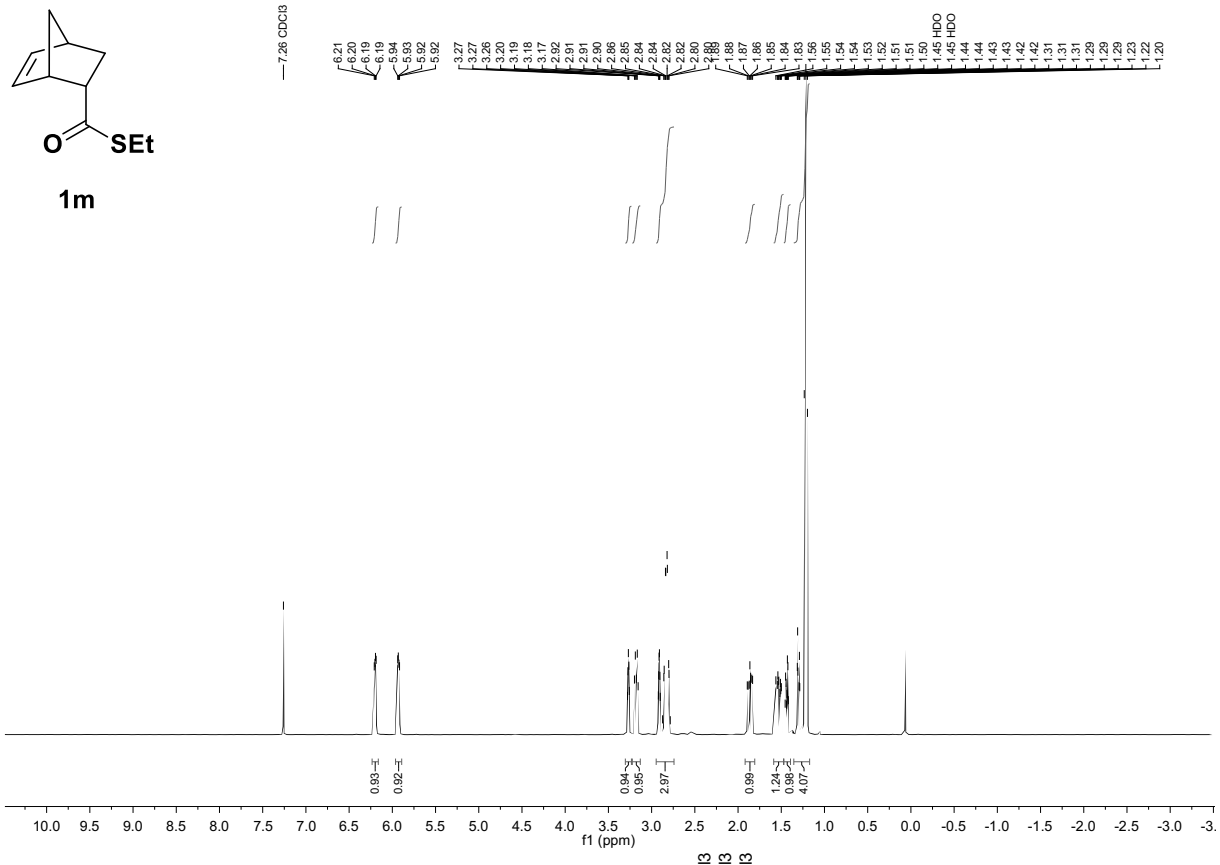
1m + 1m': ^{1}H NMR (400 MHz, $CDCl_3$): 6.23 – 6.07 (m), 5.92 (dd, *J* = 5.7, 2.8 Hz), 3.26 (tq, *J* = 3.3, 1.6 Hz), 3.17 (dt, *J* = 9.0, 3.9 Hz), 3.04 (ddt, *J* = 3.3, 2.3, 1.2 Hz), 2.96 – 2.75 (m), 2.45 (ddd, *J* = 8.2, 4.5, 1.9 Hz), 1.98 – 1.80 (m), 1.62 – 1.17 (m).

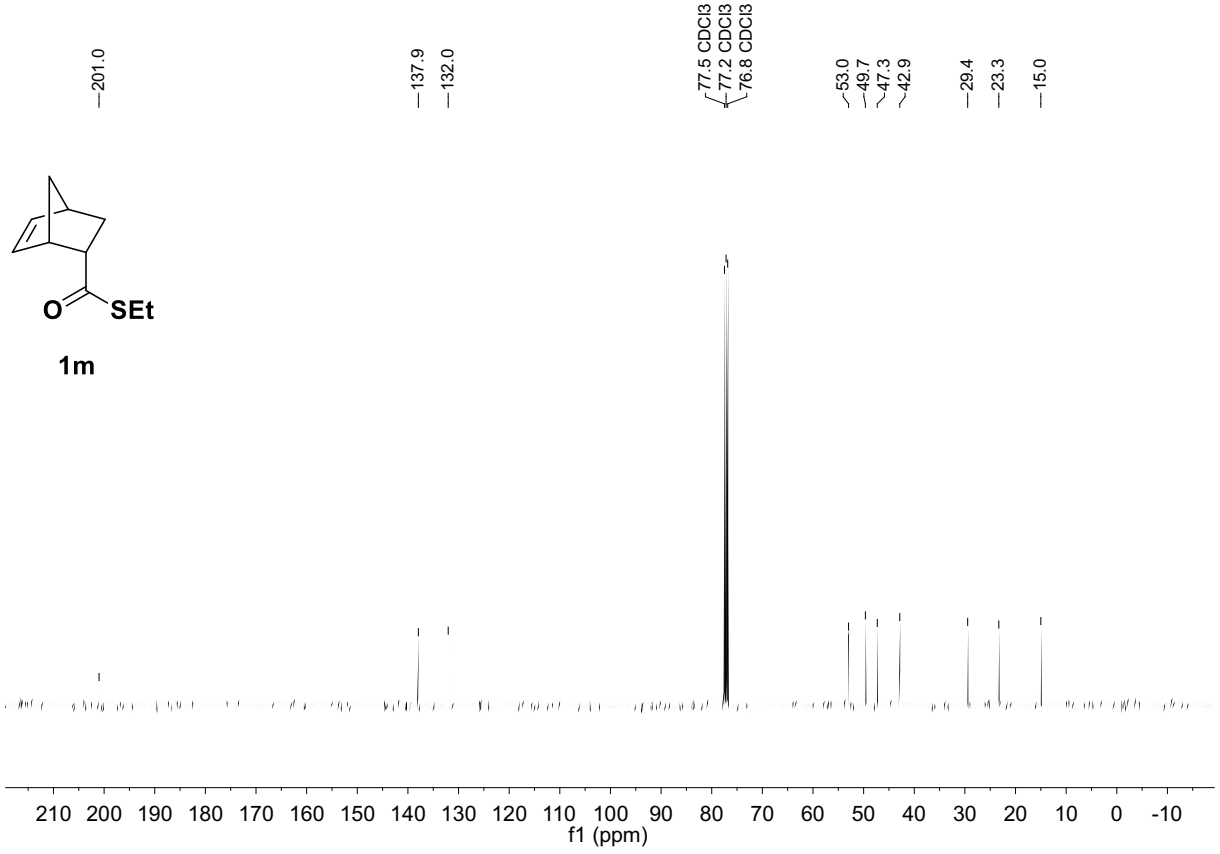
1m + 1m': ^{13}C NMR (101 MHz, $CDCl_3$): 202.6 (*C*OSEt), 201.0 (*C*OSEt), 138.6 (C_{alkene}), 137.9 (C_{alkene}), 135.8 (C_{alkene}), 132.0 (C_{alkene}), 53.0, 52.6, 49.6, 47.9, 47.3, 46.4, 42.9, 41.9, 30.8, 29.4, 23.5, 23.3, 15.00, 14.98.

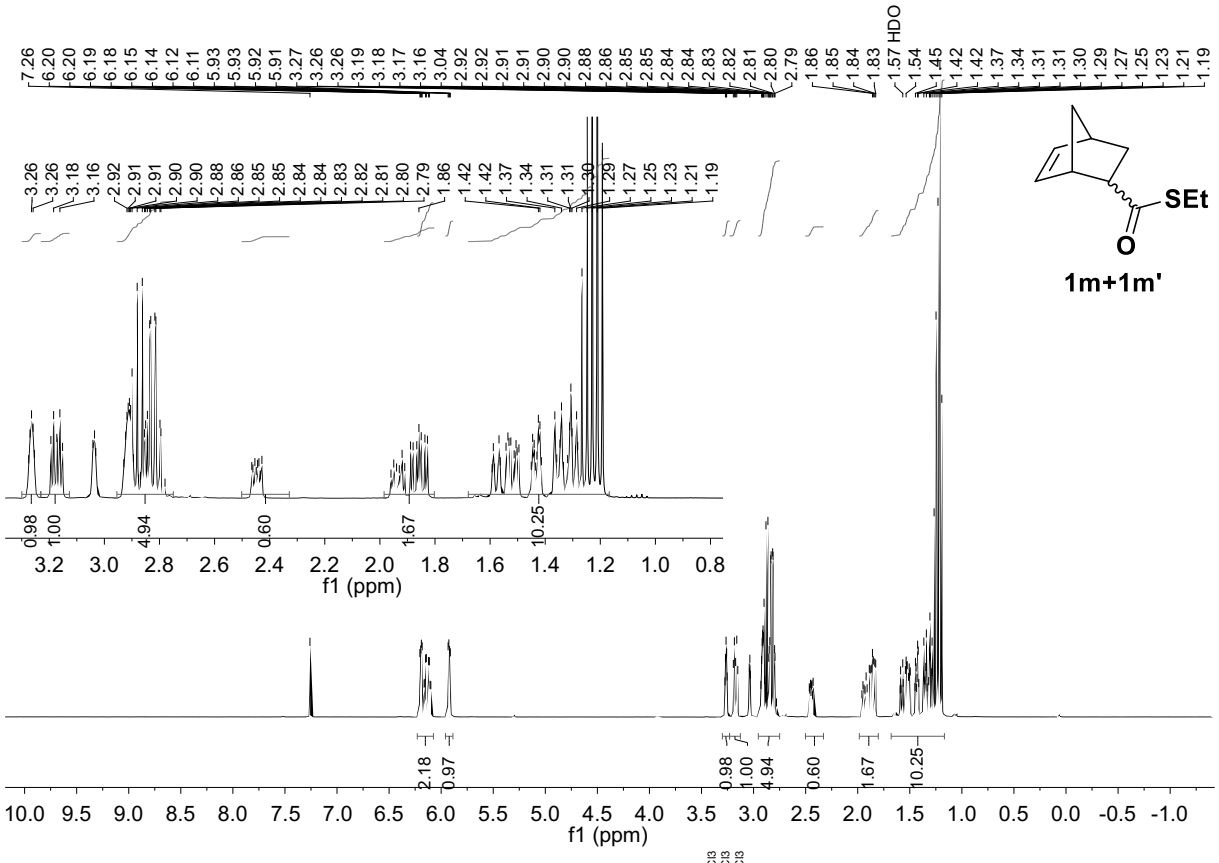
HR-MS (ESI): m/z calc. for $[M+Na]^+$ 205.06576, found 205.06614.

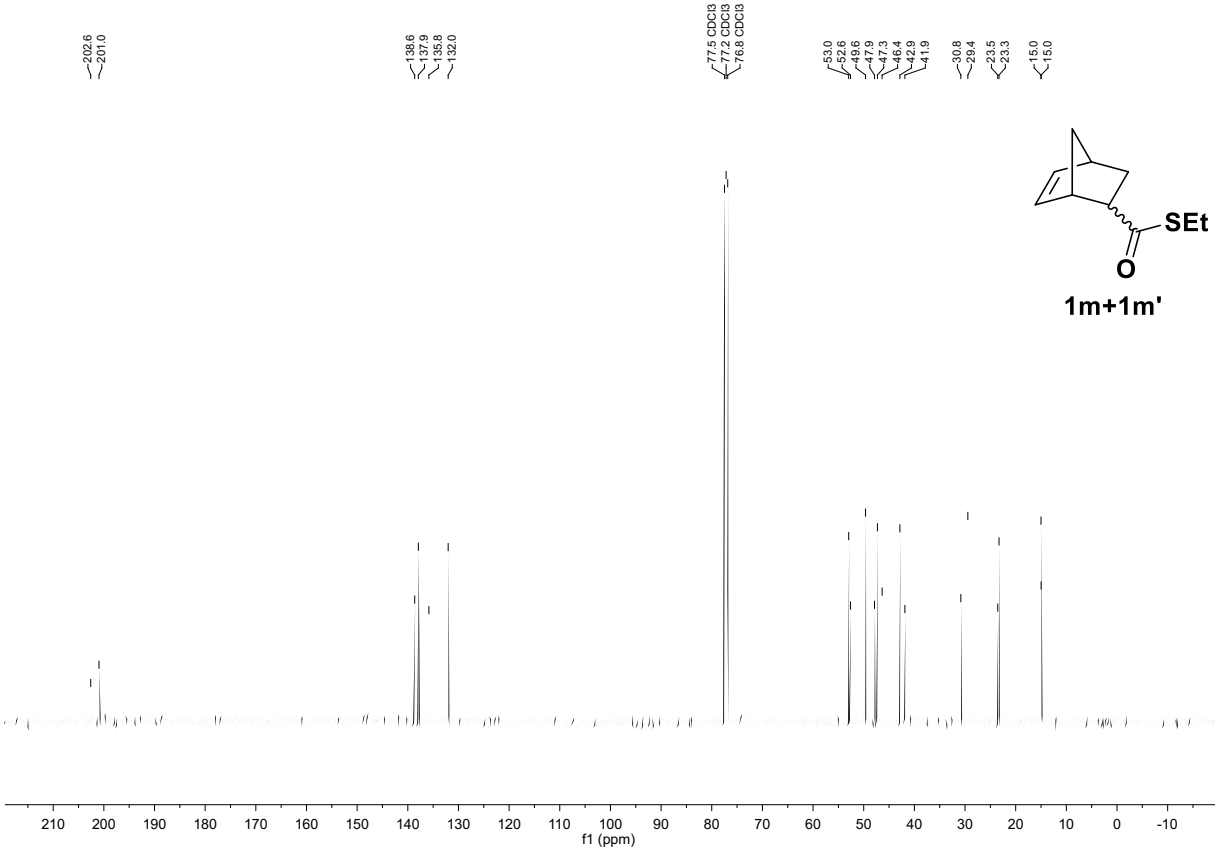
GC-MS (EI): t_r = 5.48 min, m/z(%) = 182 (12, $[M^{+\bullet}-SC_2H_5^{\bullet}]$), 121 (37, $[M^{+\bullet}-SC_2H_5^{\bullet}]$), 55 (100).

IR (**1m**, ATR, $\tilde{\nu}$ [cm^{-1}]): 3062 (w, C-H_{arom}), 2969 (m, C-H_{aliph}), 2935 (w, C-H_{aliph}), 2869 (w, C-H_{aliph}), 1683 (s, C=O), 1448 (w), 1415 (w), 1374 (w), 1333 (w), 1262 (m), 1224 (w), 1176 (w), 1131 (w), 1126 (w), 1065 (s), 1030 (m), 1000 (s), 966 (w), 920 (m), 844 (s), 807 (m), 777 (m), 747 (m), 706 (vs).

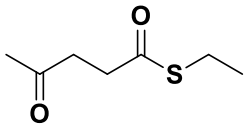

O
SEt
1m
7.26 CDCl3
f1 (ppm)


O
SEt
1m
201.0
137.9
132.0
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
53.0
49.7
47.3
42.9
29.4
23.3
15.0
f1 (ppm)


SEt
O
1m+1m'
f1 (ppm)


SEt
O
1m+1m'
f1 (ppm)

S-ethyl 4-oxopentanethioate (**1o**)



1o

According to GP-A, the product **1o** was synthesized using levulinic acid (2.1 mL, 20 mmol, 1 equiv.), ethanethiol (5.9 mL, 80 mmol, 4 equiv.), DMAP (244 mg, 2.00 mmol, 0.1 equiv.) and DCC (4.54 g, 22.0 mmol, 1.1 equiv.). Purification was achieved by manual column chromatography (*n*Hex/Et_2O = 7:3). The product was obtained as a colorless oil with a sweet smell (1.23 g, 7.68 mmol, 38%).

$C_7H_{12}O_2S$ (160.23 g/mol)

R_f: 0.26 (*n*Hex/Et_2O = 7:3) [$KMnO_4$]

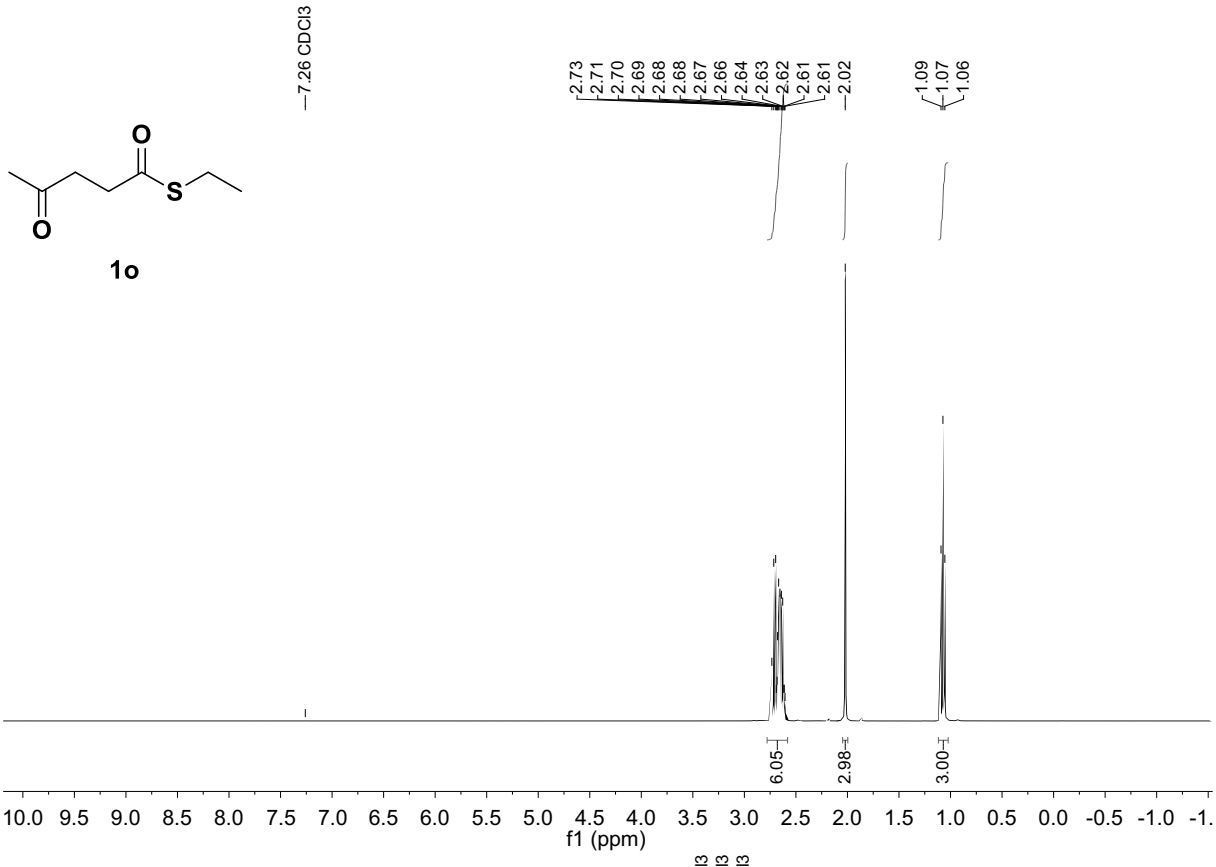
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.73–2.63 (m, 6H), 2.02 (s, 3H, COCH_3), 1.07 (t, *J* = 7.4 Hz, 3H, $COSCH_2CH_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 205.8 ($C_{ketone}O$), 198.0 ($C_{thioester}O$), 37.7 37.2, 29.5, 23.0, 14.5.

GC-MS (EI): t_r = 4.67 min, m/z(%) = 99 (100, [$M^{+\bullet}$-$C_2H_5S^{\bullet}$]).

HR-MS (ESI): m/z calc. for $[M+Na]^+$ 183.04502, found 183.04536.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2969 (w, C-H_{aliph}), 2928 (w, C-H_{aliph}), 2876 (w, C-H_{aliph}), 1716 (s, C=O_{ketone}), 1682 (vs, C=$O_{thioester}$), 1448 (w), 1407 (m), 1361 (m), 1292 (w), 1262 (w), 1224 (w), 1191 (w), 1161 (m), 1071 (m), 989 (s), 953 (s), 855 (w), 740 (w), 703 (w).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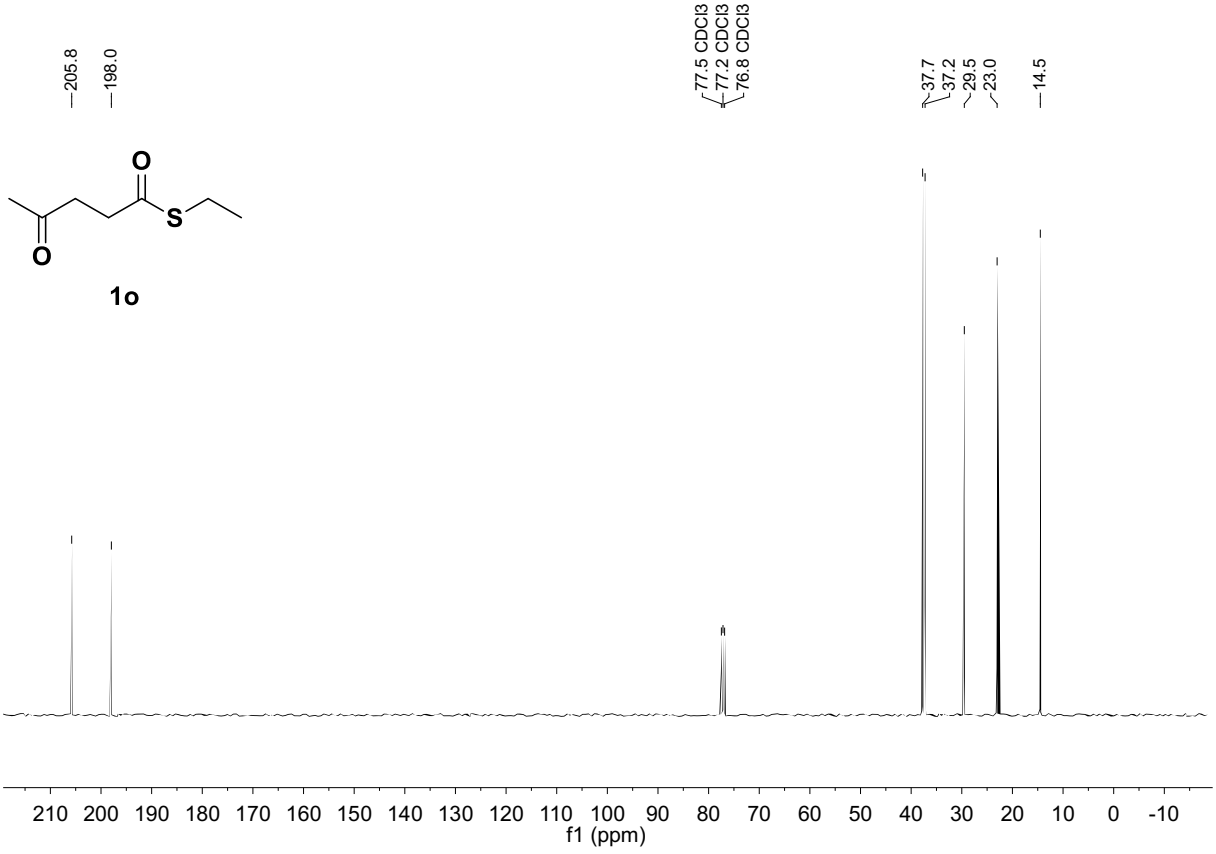
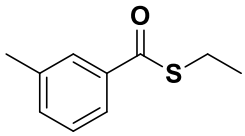
2.73
2.71
2.70
2.69
2.68
2.68
2.67
2.66
2.64
2.63
2.62
2.61
2.61
2.02
1.09
1.07
1.06
O
S
O
1o
6.05
2.98
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.
f1 (ppm)


205.8
198.0
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
37.7
37.2
29.5
23.0
14.5
O
S
O
1o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

S-ethyl 3-methylbenzothioate (**1q**)



1q

According to GP-B, the product **1q** was synthesized using 3-methyl benzoyl chloride (1.32 g, 10.0 mmol, 1.0 equiv.), ethanethiol (793 µL, 11.0 mmol, 1.1 equiv.) and triethylamine (1.4 mL, 10 mmol, 1 equiv.). Purification was achieved by filtration through a short silica plug (*n*Hex/EA = 98:2 v/v) and washing the filtrate with 6 M HCl (2 × 30 mL) and brine (1 × 30 mL). The product was obtained as a colorless oil (1.49 g, 8.27 mmol, 83%).

$C_{10}H_{12}OS$ (180.27 g/mol)

R_f: 0.41 (PE/EA = 98:2) [$KMnO_4$]

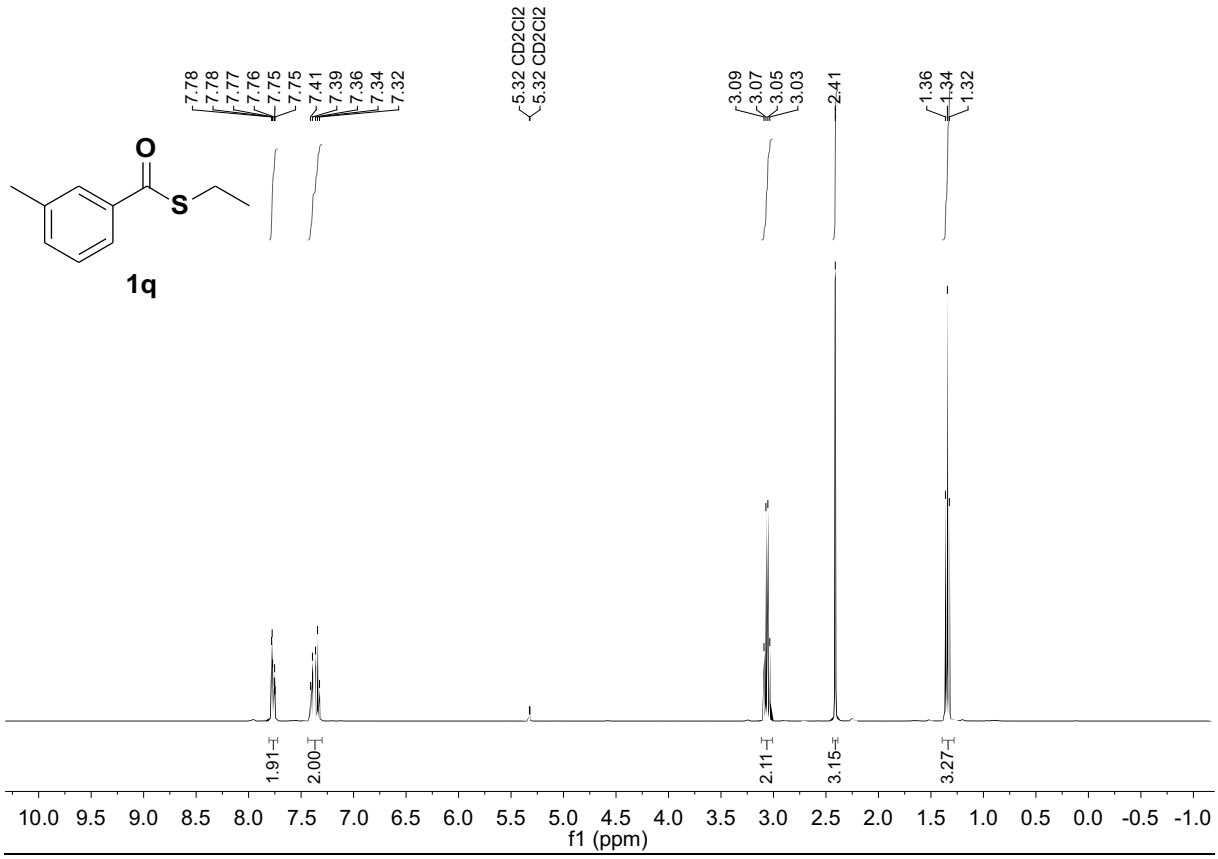
^{1}H NMR (400 MHz, CD_2Cl_2) : δ = 7.81 – 7.72 (m, 2H, Ar*H*), 7.44 – 7.30 (m, 2H, Ar*H*), 3.06 (q, *J* = 7.4 Hz, 2H, SCH_2CH_3), 2.41 (s, CH_3), 1.34 (t, *J* = 7.4 Hz, 3H, SCH_2CH_3).

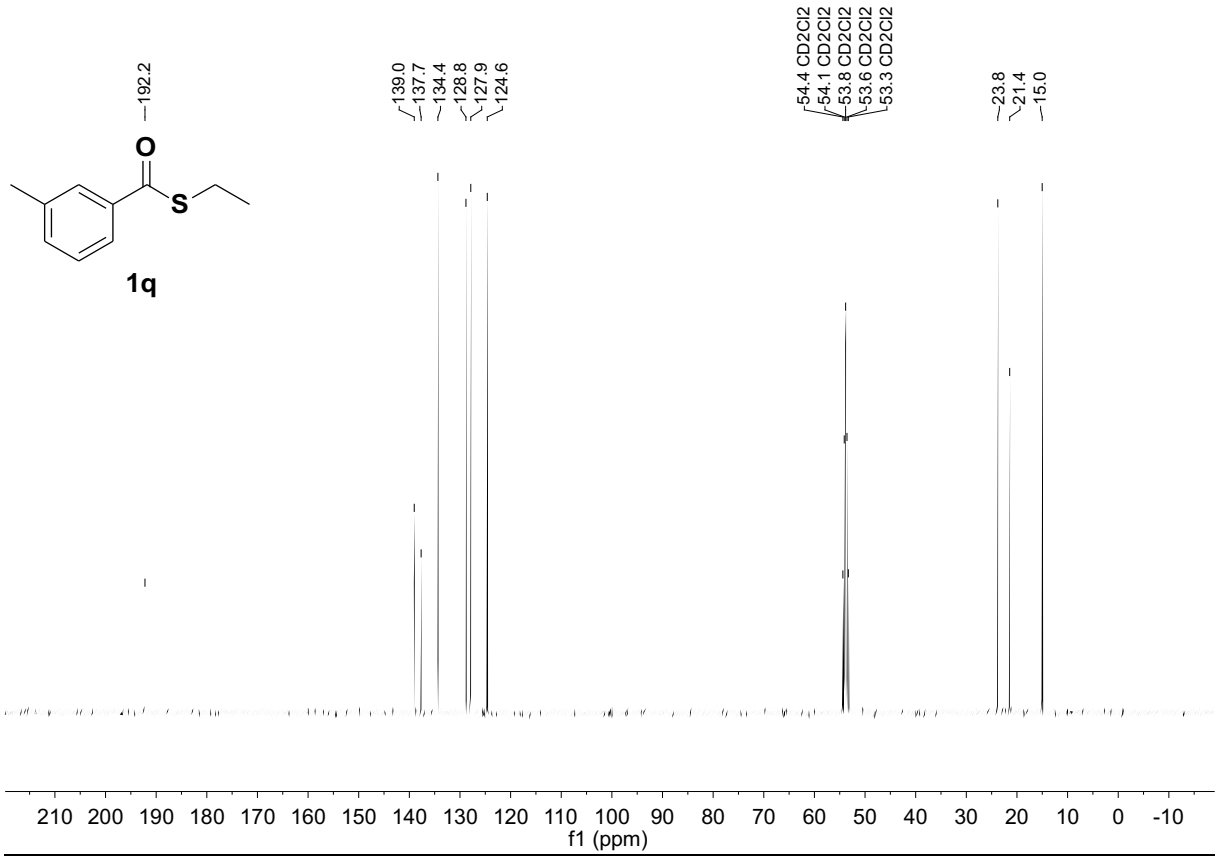
^{13}C NMR (101 MHz, CD_2Cl_2): δ = 192.2 (*C*OSEt), 139.0 (C_{Ar}), 137.7 (C_{Ar}), 134.4 (C_{Ar}), 128.8 (C_{Ar}), 127.9 (C_{Ar}), 124.6 (C_{Ar}), 23.8, 21.4, 15.0.

HR-MS (APCI): m/z calc. for $[M+Na]^+$ 181.06816, found 181.06865.

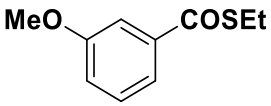
GC-MS (EI): t_r = 6.23 min, m/z(%) = 180 (8, $[M^{+\bullet}]$), 119 (100, $[M^{+\bullet}-C_2H_5S^{\bullet}]$), 91 (58, $[M^{+\bullet}-C_2H_5S^{\bullet}-CO]$).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3043 (w, C-H_{arom}), 2965 (w, C-H_{aliph}), 2925 (w, C-H_{aliph}), 2868 (w, C-H_{aliph}), 1657 (vs, C=O), 1591 (m), 1478 (w), 1448 (m), 1418 (w), 1377 (w), 1243 (s), 1151 (s), 1094 (w), 1049 (w), 1008 (w), 945 (s), 889 (w), 833 (s), 792 (vs), 691 (s).


7.78
7.78
7.77
7.76
7.75
7.75
7.41
7.39
7.36
7.34
7.32
5.32 CD2Cl2
5.32 CD2Cl2
3.09
3.07
3.05
3.03
2.41
1.36
1.34
1.32
O
S
1q
1.91
2.00
2.11
3.15
3.27
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


192.2
139.0
137.7
134.4
128.8
127.9
124.6
54.4 CD2Cl2
54.1 CD2Cl2
53.8 CD2Cl2
53.6 CD2Cl2
53.3 CD2Cl2
23.8
21.4
15.0
O
S
1q
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

S-ethyl 3-methoxybenzothioate (**1r**)



1r

According to GP-A, the product **1r** was synthesized using 3-methoxybenzoic acid (1.52 g, 10.0 mmol, 1.0 equiv.), ethanethiol (2.2 mL, 30 mmol, 3 equiv.), DMAP (122 mg, 1.00 mmol, 0.1 equiv.) and DCC (2.27 g, 11.0 mmol, 1.1 equiv.). Purification was achieved by filtration through a short silica plug using Hexane/EA (9:1 v/v) and washing the filtrate with 6 M HCl (2 × 20 mL), sat. $NaHCO_3$ (1 × 20 mL) and brine (1 × 20 mL). The product was obtained as a colorless oil (1.61 g, 8.21 mmol, 82%).

$C_{10}H_{12}O_2S$ (196.26 g/mol)

R_f: 0.58 (*n*Hex/EA = 9:1) [UV]

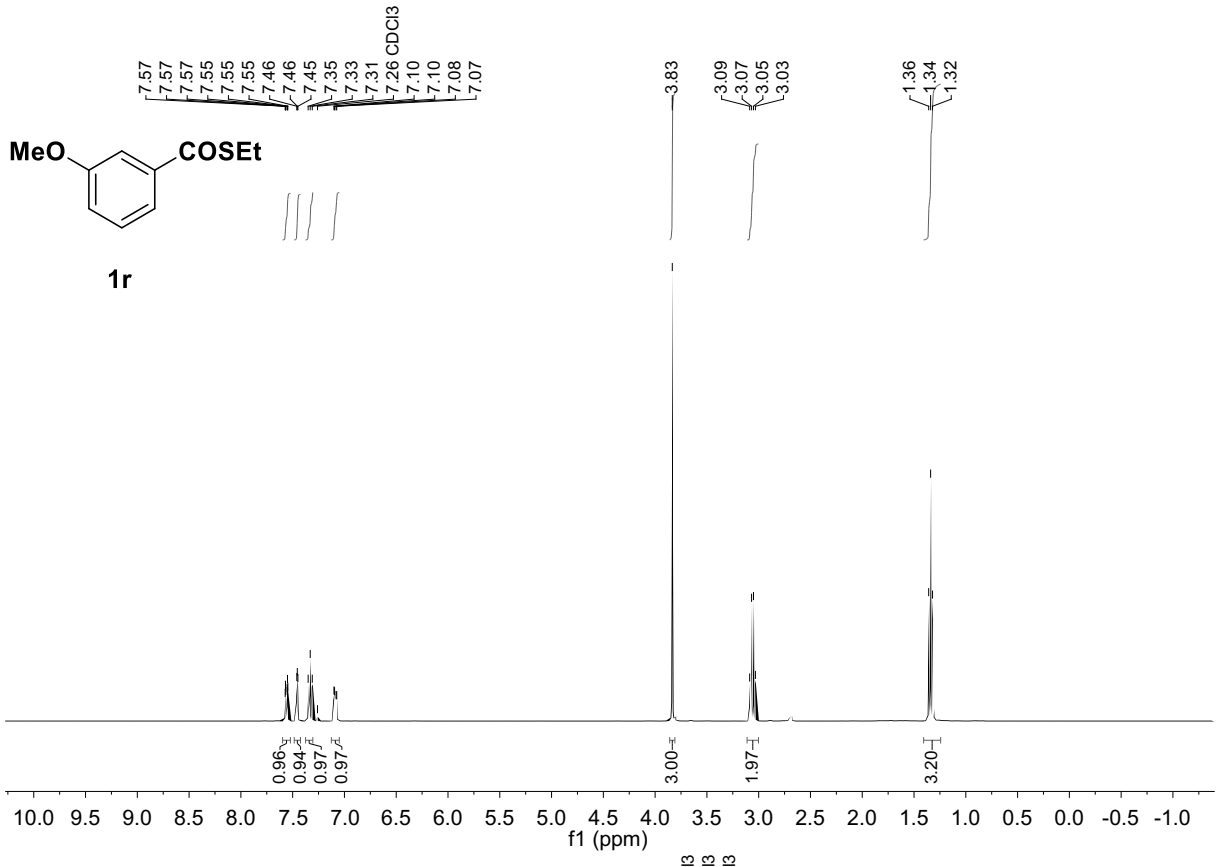
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (ddd, *J* = 7.7, 1.6, 1.0 Hz, 1H), 7.45 (dd, *J* = 2.6, 1.6 Hz, 1H), 7.33 (t, *J* = 8.1 Hz, 1H), 7.09 (ddd, *J* = 8.1, 2.6, 1.0 Hz, 1H), 3.83 (s, 3H), 3.06 (q, *J* = 7.4 Hz, 2H), 1.34 (t, *J* = 7.4 Hz, 3H).

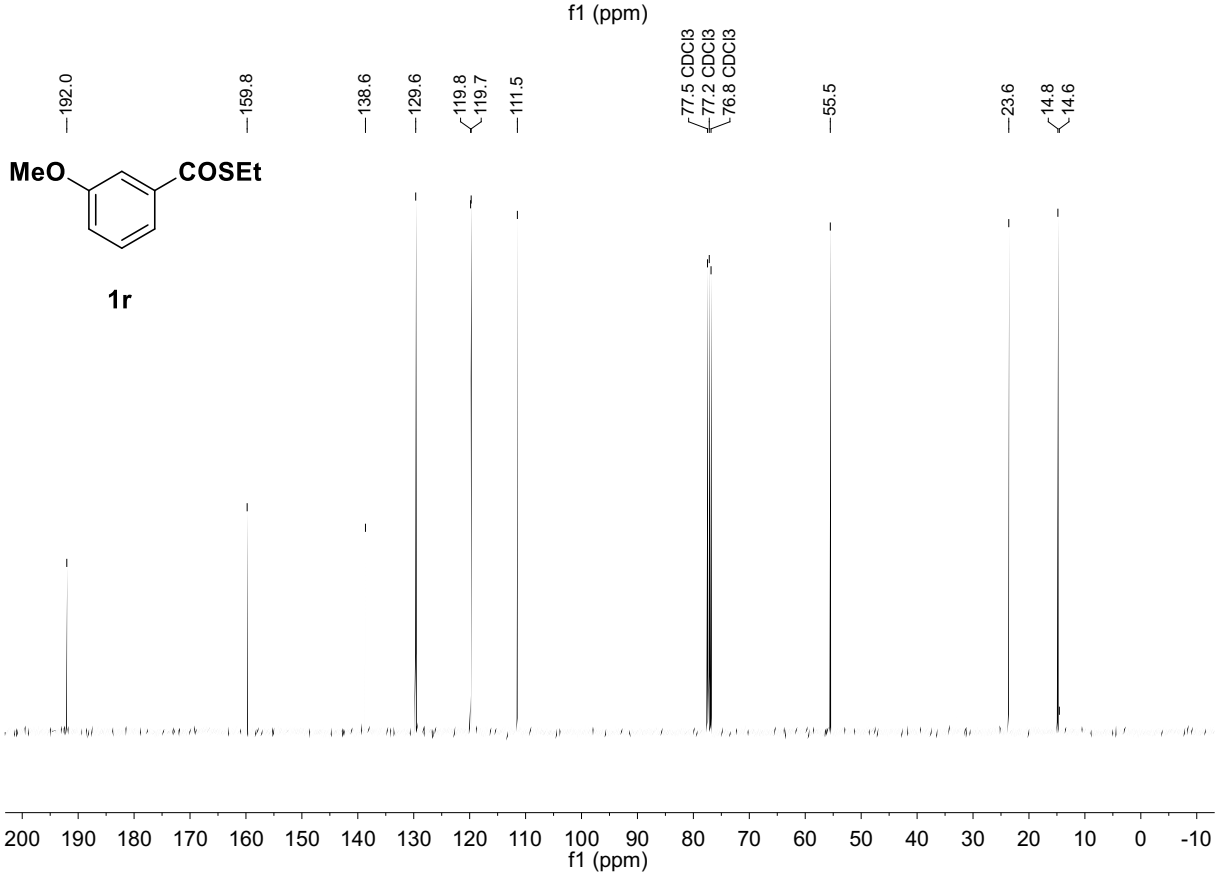
^{13}C NMR (101 MHz, $CDCl_3$): δ = 192.0 (*C*OEt), 159.8 (C_{Ar}), 138.6 (C_{Ar}), 129.7 (C_{Ar}), 119.8(C_{Ar}), 119.3 (C_{Ar}), 111.5 (C_{Ar}), 55.5 (O*C*H$_3$), 23.6, 14.8.

GC-MS (EI, method B): t_r = 18.69 min, m/z(%) = 196 (17, [$M^{+\bullet}$]), 135 (100, [$M^{+\bullet}$-$C_2H_5S^\bullet$]), 107 (100, [$M^{+\bullet}$-$C_2H_5S^\bullet$-CO]).

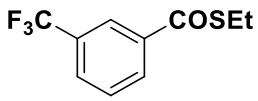
HR-MS (ESI): m/z calc. for $[M+Na]^+$ 219.04502, found 219.04545.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3070 (w, C-H_{arom}), 2969 (w, C-H_{aliph}), 2932 (w, C-H_{aliph}), 2875 (w, C-H_{aliph}), 2835 (w, C-H_{aliph}), 1735 (m), 1660 (s, C=O), 1588 (m), 1481 (m), 1455 (m), 1429 (m), 1370 (w), 1318 (w), 1288 (w), 1249 (vs, C-O-C), 1191 (m), 1158 (s), 1090 (w), 1042 (s), 967 (m), 941 (s), 874 (w), 833 (m), 789 (vs), 695 (s).


7.57
7.57
7.57
7.55
7.55
7.55
7.46
7.46
7.45
7.35
7.33
7.31
7.26 CDCl3
7.10
7.10
7.08
7.07
3.83
3.09
3.07
3.05
3.03
1.36
1.34
1.32
MeO
COSEt
1r
0.96
0.94
0.97
0.97
3.00
1.97
3.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


192.0
159.8
138.6
129.6
119.8
119.7
111.5
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
55.5
23.6
14.8
14.6
MeO
COSEt
1r
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

S-ethyl 3-(trifluoromethyl)benzothioate (**1s**)



1s

According to GP-B, the product **1s** was synthesized using 3-(trifluoromethyl)benzoyl chloride (1.48 mL, 10.0 mmol, 1.0 equiv.), ethanethiol (793 µL, 11.0 mmol, 1.1 equiv.) and triethylamine (1.4 mL, 10 mmol, 1 equiv.). Purification was achieved by bulb-to-bulb distillation (4 mbar, 180 °C). The product was obtained as a yellow oil (1.74 g, 7.43 mmol, 74%).

$C_{10}H_9F_3OS$ (234.24 g/mol)

R_f: 0.30 (*n*Hex) [UV, anis]

1H NMR (300 MHz, CDCl3): δ = 8.24 – 8.16 (m, 1H), 8.15 – 8.09 (m, 1H), 7.84 – 7.77 (m, 1H), 7.62 – 7.55 (m, 1H), 3.11 (q, J = 7.4 Hz, 2H, C*H*$_2$CH$_3$), 1.36 (t, J = 7.4 Hz, 3H, CH$_2$C*H*$_3$).

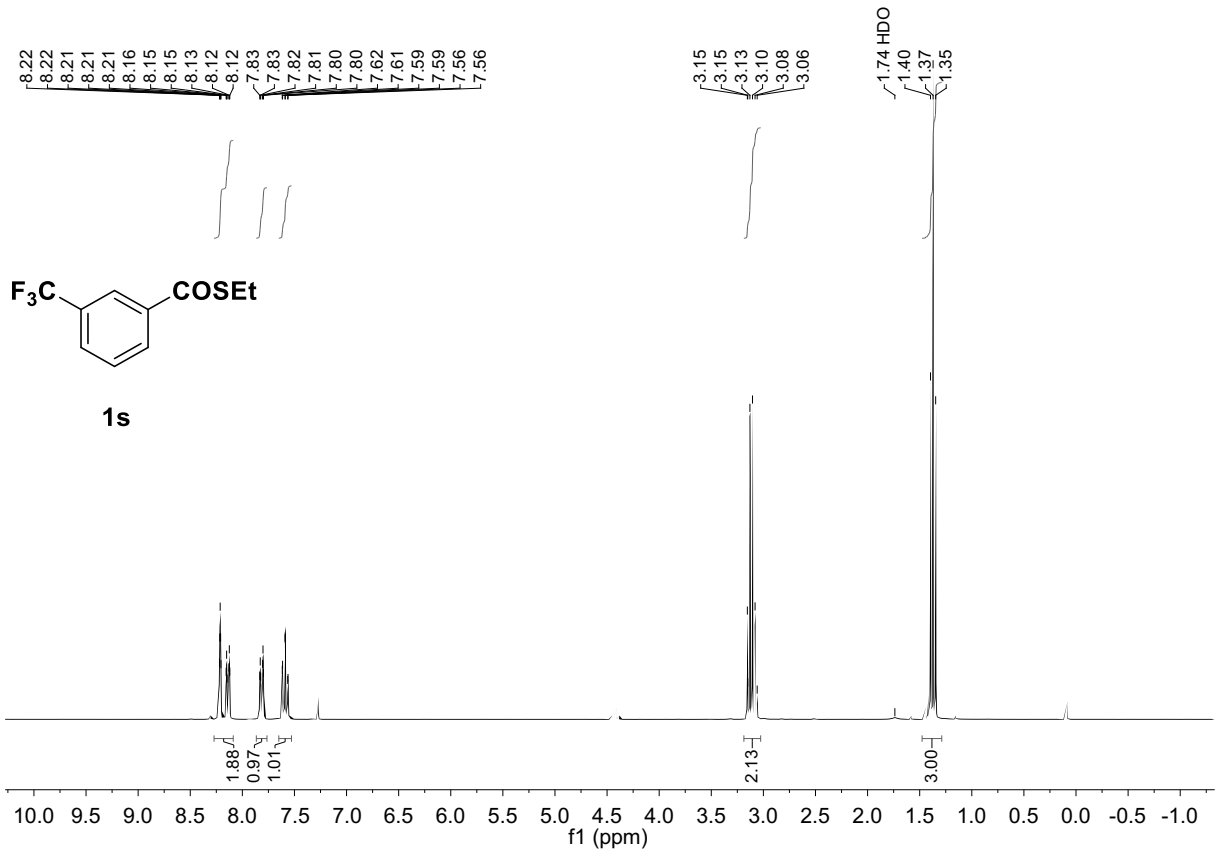
^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.0 (*C*OSEt), 137.9, 131.4 (q, J^2_{C-F} = 33.0 Hz, *C*-CF$_3$), 130.5, 129.7 (q, J^3_{C-F} = 3.7 Hz), 125.5 (q, J^1_{C-F} = 271.5 Hz, *C*F$_3$), 124.15 (q, J^3_{C-F} = 3.9 Hz), 23.86 (*C*H$_2$CH$_3$), 14.74 (CH$_2$*C*H$_3$).

^{19}F-NMR (377 MHz, $CDCl_3$): δ = –62.9 (s).

GC-MS (EI, method B): t_r = 15.07 min, m/z(%) = 234 (9, [M$^{+\bullet}$]), 173 (100, [M$^{+\bullet}$-C$_2$H$_5$S$^\bullet$]), 145 (45, [M$^{+\bullet}$-C$_2$H$_5$S$^\bullet$-CO]).

HR-MS (APCI): m/z calc. for [M+H]$^+$ 235.03990, found 235.04022.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3040 (w, C-H$_{arom}$), 2995 (w, C-H$_{aliph}$), 2951 (w, C-H$_{aliph}$), 2891 (w, C-H$_{aliph}$), 2813 (w, C-H$_{aliph}$), 1560 (s, C=O), 1452 (s, C-CF$_3$), 1344 (s), 1198(s, CF$_3$), 1109 (s, CF$_3$), 934(m), 807 (s).


8.22
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8.15
8.13
8.12
8.12
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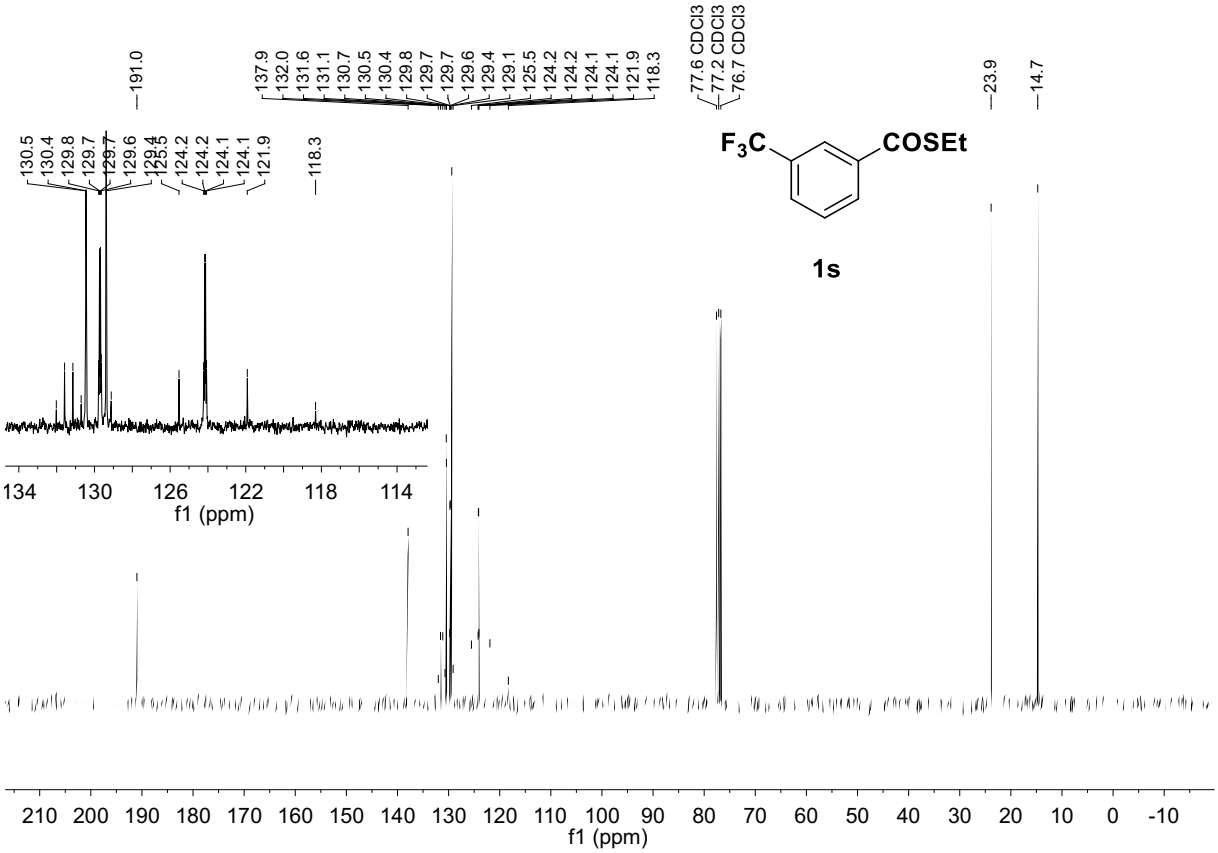
7.82
7.81
7.80
7.80
7.62
7.61
7.59
7.59
7.56
7.56
3.15
3.15
3.13
3.10
3.08
3.06
1.74 HDO
1.40
1.37
1.35
F3C
COSEt
1s
1.88
0.97
1.01
2.13
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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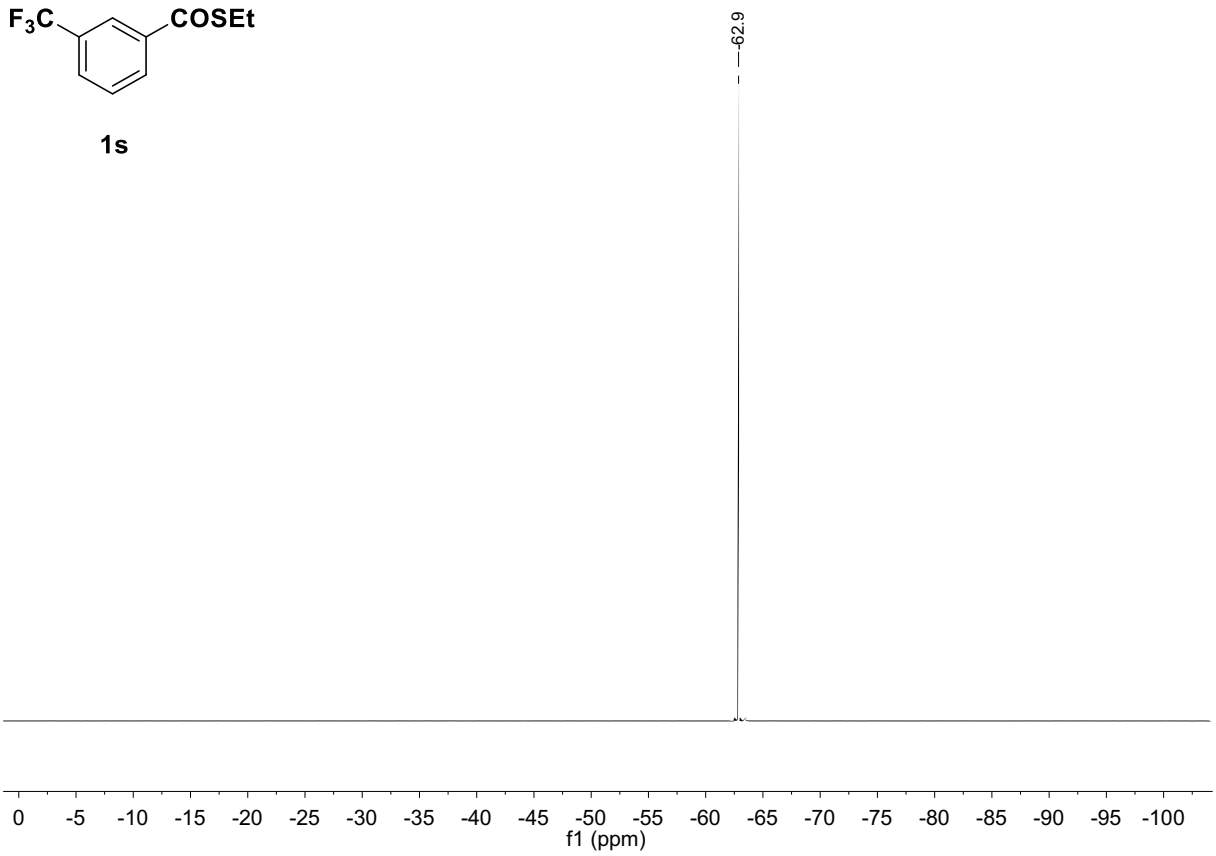
130.7
130.5
130.4
129.8
129.7
129.7
129.6
129.4
129.1
125.5
124.2
124.2
124.1
124.1
121.9
118.3
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
23.9
14.7
F3C
COSEt
1s
134 130 126 122 118 114
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


F3C
COSEt
1s
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0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
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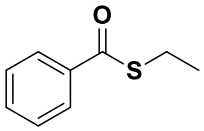
-90
-95
-100
f1 (ppm)

S-ethyl benzothioate (**1t**)



1t

According to GP-B, the product **1t** was synthesized using benzoyl chloride (2.2 mL, 20 mmol), ethanethiol (1.8 mL, 24 mmol, 1.2 equiv.) and triethylamine (2.8 mL, 20 mmol, 1 equiv.). Purification was achieved by bulb-to-bulb distillation (4 mbar, 160 °C). The product was obtained as a light yellow oil (2.90 g, 17.4 mmol, 87%). The NMR spectra are in accordance to previous literature values.[11]

$C_9H_{10}OS$ (166.24 g/mol)

R_f: 0.44 (*n*Hex/EA = 30:1) [UV]

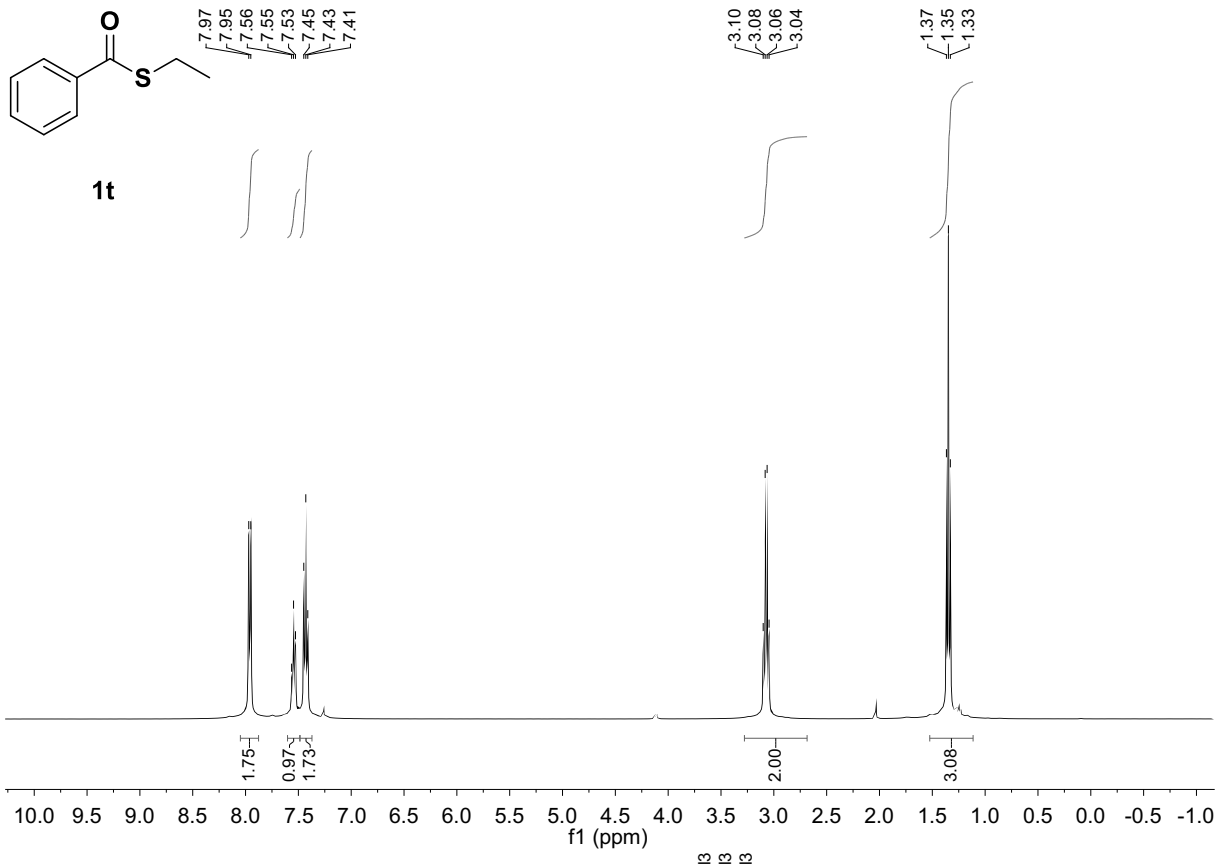
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 – 7.88 (m, 2H, Ar*H*), 7.59 – 7.49 (m, 1H, Ar*H*), 7.46 – 7.36 (t, *J* = 7.7 Hz, 2H , Ar*H*), 3.07 (q, *J* = 7.4 Hz, 2H, SC*H*$_2$CH$_3$), 1.35 (t, *J* = 7.4 Hz, 3H, SCH$_2$C*H*$_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 192.1 (*C*OSEt), 137.3 (C_{Ar}), 133.3 (C_{Ar}), 128.6 (C_{Ar}), 127.2 (C_{Ar}), 23.5 (S*C*H$_2$CH$_3$), 14.9 (SCH$_2$*C*H$_3$).

GC-MS (EI): t_r = 5.61 min, m/z(%) = 166 (12, [$M^{+\bullet}$]), 105 (100, [$M^{+\bullet}$-$C_2H_5S^{\bullet}$]), 77 (35, [$M^{+\bullet}$-$C_2H_5S^{\bullet}$-CO]).

HR-MS (APCI): m/z calc. for $[M+H]^+$ 167.05251, found 167.05286.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3059 (w, C-H$_{arom}$), 3032 (w, C-H$_{arom}$), 2969 (w, C-H$_{aliph}$), 2928 (w, C-H$_{aliph}$), 2872 (w, C-H$_{aliph}$), 1657 (vs, C=O), 1584 (m), 1485 (w), 1448 (m), 1414 (w), 1374 (w), 1310 (w), 1266 (w), 1239 (w), 1202 (vs), 1172 (s), 1101 (w), 1069 (w), 1027 (w), 997 (w), 971 (w), 904 (vs), 770 (s), 684 (vs).


7.97
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7.55
7.53
7.45
7.43
7.41
3.10
3.08
3.06
3.04
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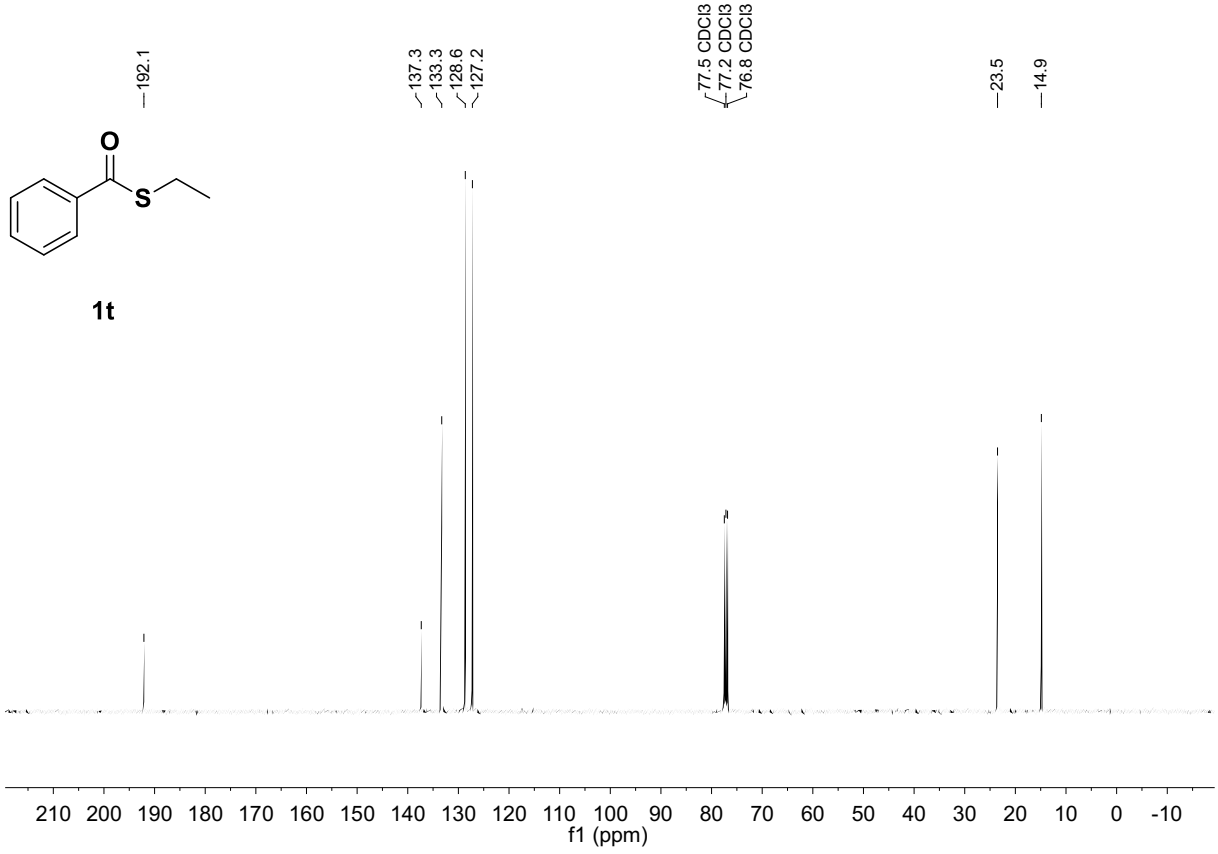
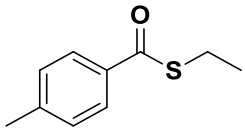
1.35
1.33
1t
1.75
0.97
1.73
2.00
3.08
f1 (ppm)


192.1
137.3
133.3
128.6
127.2
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
23.5
14.9
1t
f1 (ppm)

S-ethyl 4-methylbenzothioate (**1u**)



1u

According to GP-B, the product **1s** was synthesized using 4-methylbenzoyl chloride (1.3 mL, 10.0 mmol, 1.0 equiv.), ethanethiol (793 µL, 11.0 mmol, 1.1 equiv.) and triethylamine (1.4 mL, 10 mmol, 1 equiv.). The product was purified by DCVC (PE/EA = 98:2 v/v). The product was obtained as a colorless oil (1.44 g, 7.99 mmol, 80%). The analytical data is in good accordance to reported literature.[12]

$C_{10}H_{12}OS$ (180.27 g/mol)

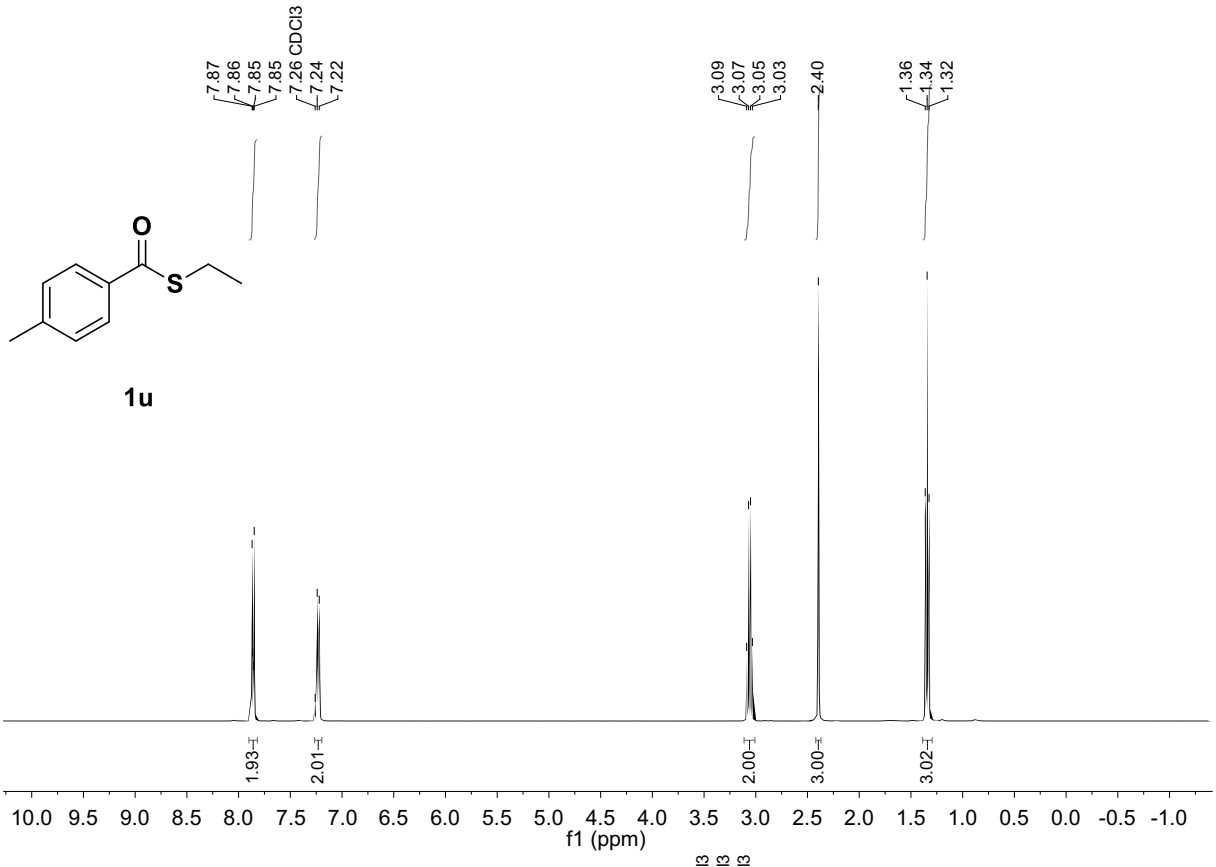
R_f: 0.41 (PE/EA = 98:2 v/v) [$KMnO_4$, anis]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 – 7.82 (m, 2H, Ar*H*), 7.23 (d, *J* = 8.0 Hz, 2H, Ar*H*), 3.06 (q, *J* = 7.4 Hz, 2H, CH_2CH$_3$), 2.40 (s, 3H, ArCH_3), 1.34 (t, *J* = 7.4 Hz, 3H, CH$_2$CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 191.8 (*C*OSEt), 144.1 (C_{Ar}), 134.8 (C_{Ar}), 129.3 (C_{Ar}), 127.3 (C_{Ar}), 23.4, 21.8, 15.0.

GC-MS (EI, method B): t_r = 17.22 min, m/z(%) = 180 (6, [$M^{+\bullet}$]), 119 (100, [$M^{+\bullet}$-$C_2H_5S^{\bullet}$]), 91 (35, [$M^{+\bullet}$-$C_2H_5S^{\bullet}$-CO]).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3029 (w, C-H_{arom}), 2965 (w, C-H_{aliph}), 2924 (w, C-H_{aliph}), 2869 (w, C-H_{aliph}), 2820 (w, C-H_{aliph}), 1702 (w), 1654 (vs, C=O), 1604 (s), 1571 (w), 1504 (w), 1448 (m), 1410 (w), 1374 (w), 1303 (w), 1265 (w), 1243 (w), 1207 (vs), 1172 (s), 1113 (w), 1047 (w), 971 (w), 945 (w), 907 (vs), 818 (s), 785 (m), 717 (m).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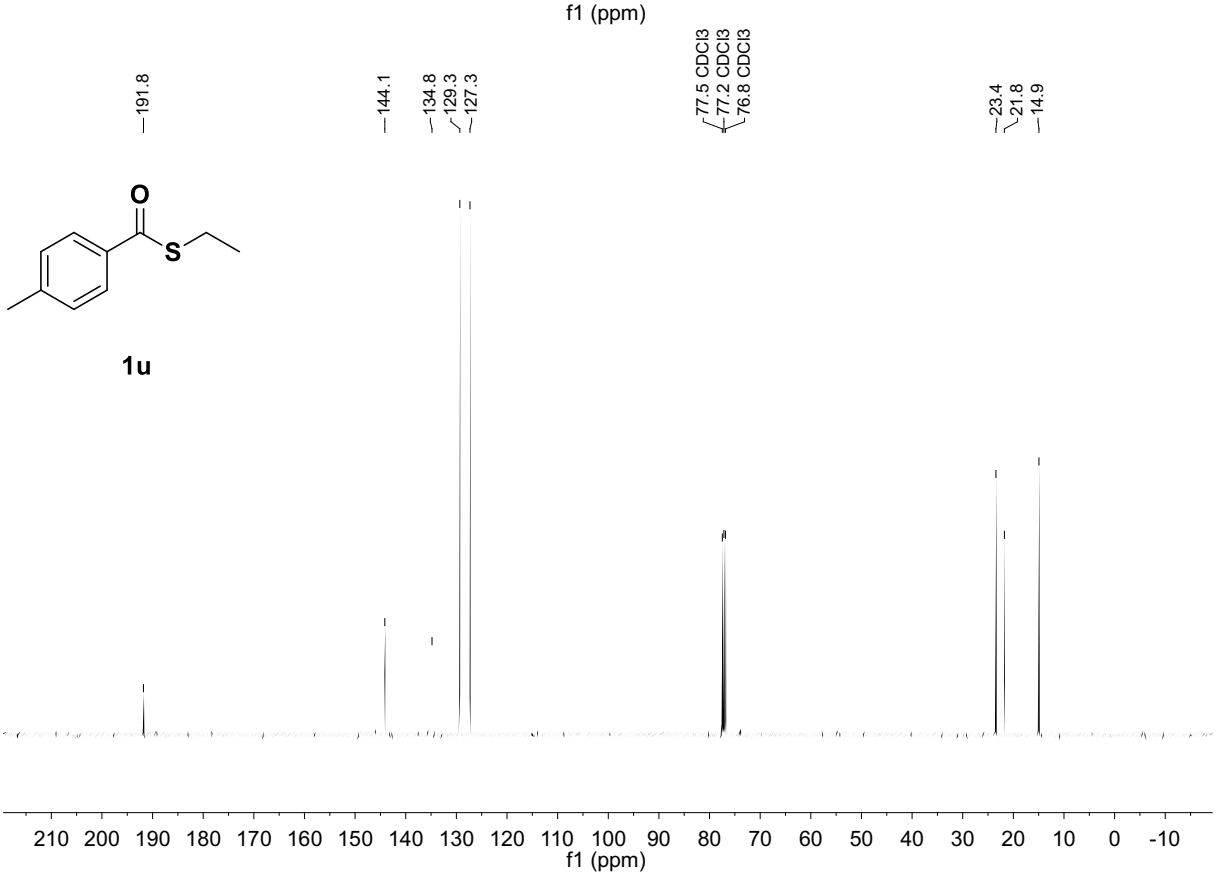
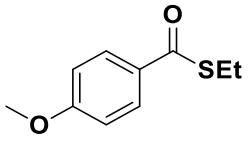
7.86
7.85
7.85
7.26 CDCl3
7.24
7.22
3.09
3.07
3.05
3.03
2.40
1.36
1.34
1.32
O
S
1u
1.93
2.01
2.00
3.00
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


191.8
144.1
134.8
129.3
127.3
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
23.4
21.8
14.9
O
S
1u
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

S-ethyl 4-methoxybenzothioate (**1v**)



1v

According to GP-B, the product **1s** was synthesized using 4-methylbenzoyl chloride (1.4 mL, 10.0 mmol, 1.0 equiv.), ethanethiol (793 µL, 11.0 mmol, 1.1 equiv.) and triethylamine (1.4 mL, 10 mmol, 1 equiv.). The product was purified by DCVC (PE:EA = 98:2 v/v). The product was obtained as a colorless oil (1.44 g, 8.00 mmol, 80%). The analytical data is in good accordance to previously published literature.[13]

$C_{10}H_{12}O_2S$ (196.26 g/mol)

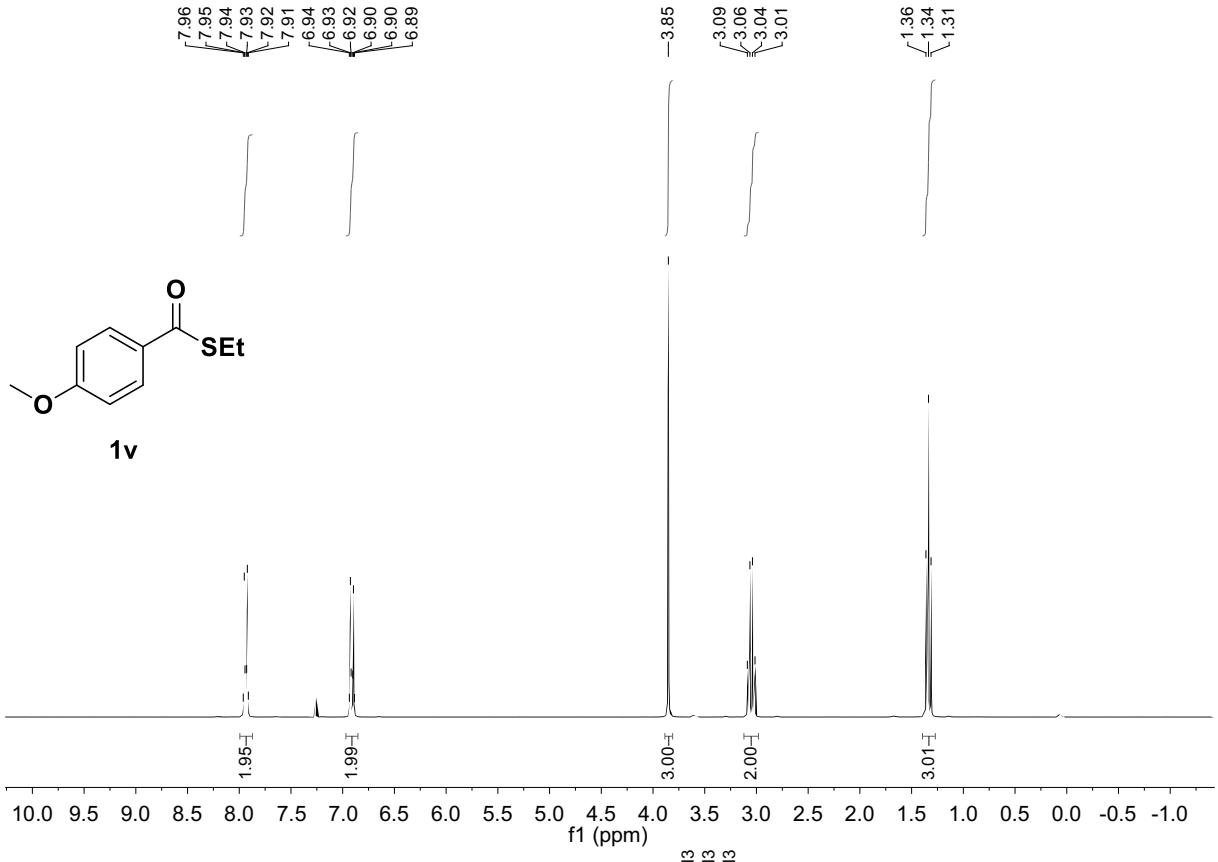
R_f: 0.24 (PE/EA = 98:2) [UV, $KMnO_4$]

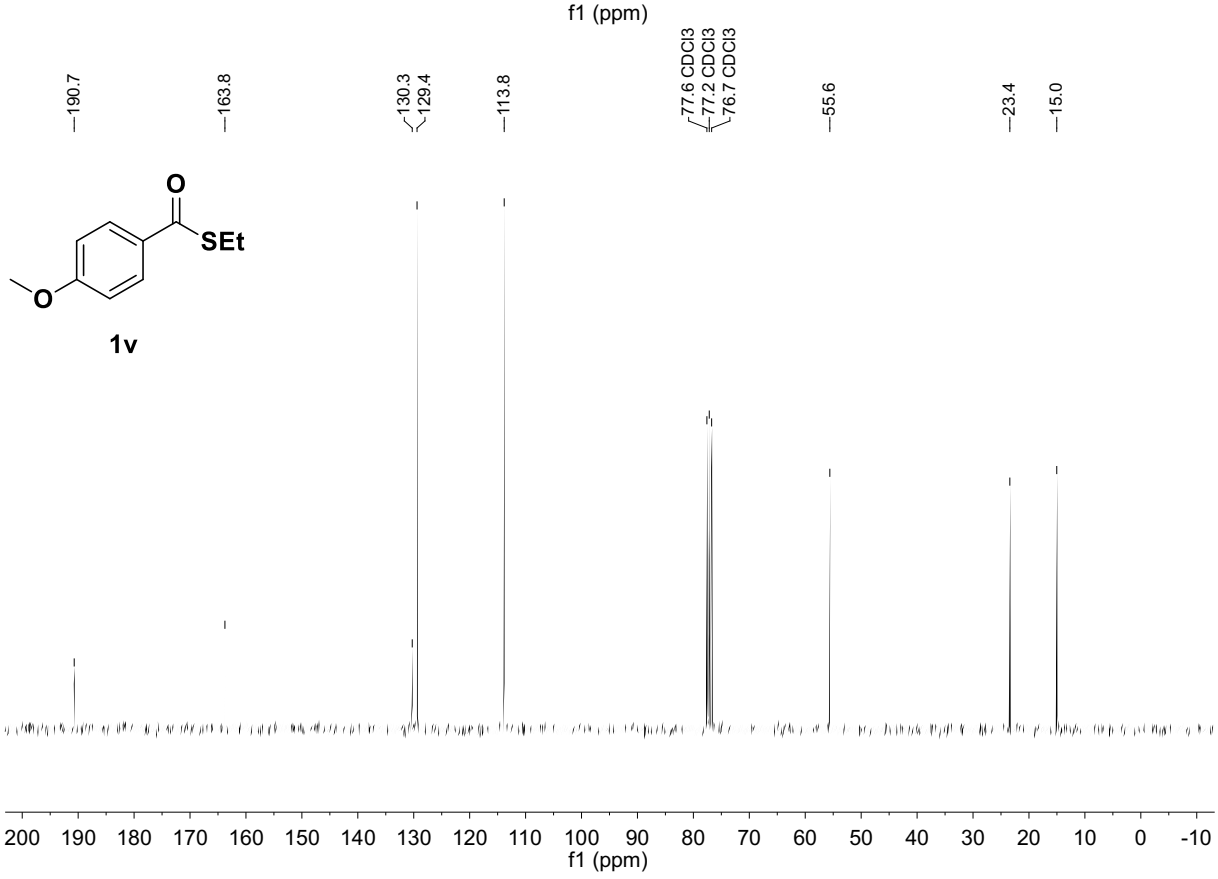
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.99 – 7.88 (m, 2H, Ar*H*), 6.97 – 6.85 (m, 2H, Ar*H*), 3.85 (s, *J* = 0.6 Hz, 3H, O-C*H*$_3$), 3.05 (q, *J* = 7.4 Hz, 2H, C*H*$_2$CH$_3$), 1.34 (t, *J* = 7.4 Hz, 3H, CH$_2$C*H*$_3$).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.7 (*C*OSEt), 163.8 (C_{Ar}), 130.3 (C_{Ar}), 129.4 (C_{Ar}), 113.8 (C_{Ar}), 55.6 (O-*C*H$_3$), 23.4 (*C*H$_2$CH$_3$), 15.0 (CH$_2$*C*H$_3$).

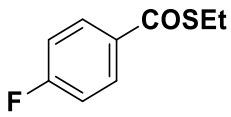
GC-MS (EI, method B): t_r = 19.30 min, m/z(%) = 196 (7, [$M^{+\bullet}$]), 135 (100, [$M^{+\bullet}$-$C_2H_5S^{\bullet}$]), 107 (10, [$M^{+\bullet}$-$C_2H_5S^{\bullet}$-CO]).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2965 (w, C-H_{aliph}), 2928 (w, C-H_{aliph}), 2872 (w, C-H_{aliph}), 2838 (w, C-H_{aliph}), 1650 (s, C=O), 1597 (vs), 1504 (s), 1452 (m), 1415 (w), 1307 (m), 1255 (s), 1213 (vs, C_{arom}-O_{ether}), 1161 (vs C_{aliph}-O_{ether}), 1113 (m), 1057 (w), 1027 (s), 971 (w), 948 (w), 907 (vs), 833 (vs), 792 (m), 732 (w).


7.96
7.95
7.94
7.93
7.92
7.91
6.94
6.93
6.92
6.90
6.90
6.89
3.85
3.09
3.06
3.04
3.01
1.36
1.34
1.31
O
SEt
O
1v
1.95
1.99
3.00
2.00
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


190.7
163.8
130.3
129.4
113.8
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
55.6
23.4
15.0
O
SEt
O
1v
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

S-ethyl 4-fluorobenzothioate (**1w**)



1w

According to GP-A, the product **1w** was synthesized using *para*-fluorobenzoic acid (1.40 g, 10.0 mmol, 1.0 equiv.), ethanethiol (2.2 mL, 30 mmol, 3 equiv.), DMAP (122 mg, 1.00 mmol, 0.1 equiv.) and DCC (2.27 g, 11.0 mmol, 1.1 equiv.). Purification was achieved by filtration through a short silica plug using DCM and washing the filtrate with 6 M HCl (2 × 20 mL), sat. $NaHCO_3$ (1 × 20 mL) and brine (1 × 20 mL). The product was obtained as a colorless oil (1.41 g, 7.65 mmol, 77%). The spectral data is in accordance to reported literature.[13]

C_9H_9FOS (184.23 g/mol)

R_f: 0.49 (*n*Hex/EA = 30:1) [$KMnO_4$]

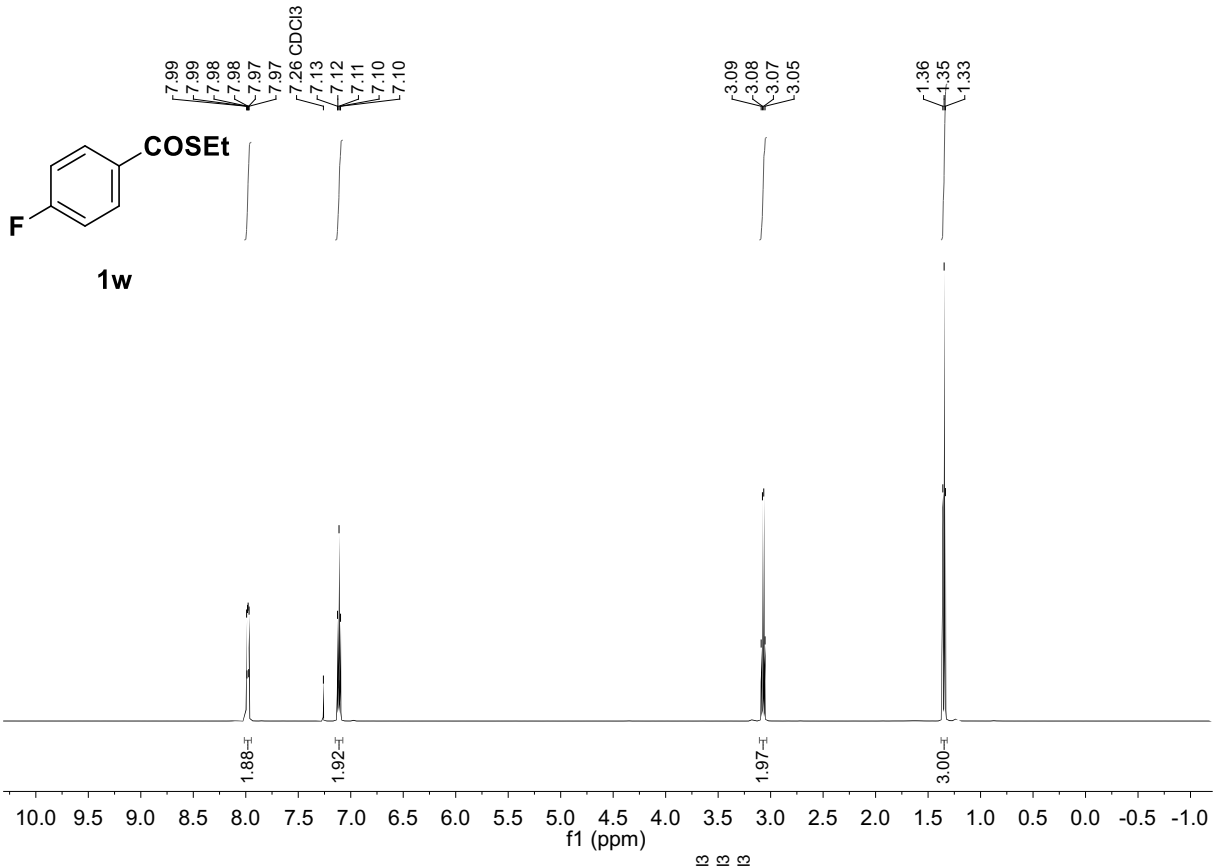
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.01 – 7.95 (m, 2H), 7.15 – 7.08 (m, 2H), 3.07 (q, *J* = 7.4 Hz, 2H), 1.35 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 166.0 (d, J^1_{C-F} = 254.6 Hz), 133.7 (d, J^4_{C-F} = 3.1 Hz), 129.8 (d, J^3_{C-F} = 9.3 Hz), 115.8 (d, J^2_{C-F} = 22.1 Hz), 23.7 (S*C*H$_2$), 14.9 (SCH$_2$*C*H$_3$).

^{19}F NMR (565 MHz, $CDCl_3$): δ = -105.1 (m).

GC-MS (EI, method B): t_r = 15.21 min, m/z(%) = 184 (9, [$M^{+\bullet}$]), 123 (100, [$M^{+\bullet}$-$C_2H_5S^\bullet$]), 95 (32, [$M^{+\bullet}$-$C_2H_5S^\bullet$-CO]).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2973 (w, C-H_{aliph}), 2935 (w, C-H_{aliph}), 2875 (w, C-H_{aliph}), 1653 (s, C=O), 1594 (s), 1541 (w), 1500 (s), 1448 (w), 1407 (w), 1295 (w), 1228 (vs), 1202 (vs), 1150 (s), 1098 (w), 1057 (w), 1008 (w), 967 (w), 945 (w), 915 (vs), 840 (vs), 811 (s), 729 (w).


7.99
7.99
7.98
7.98
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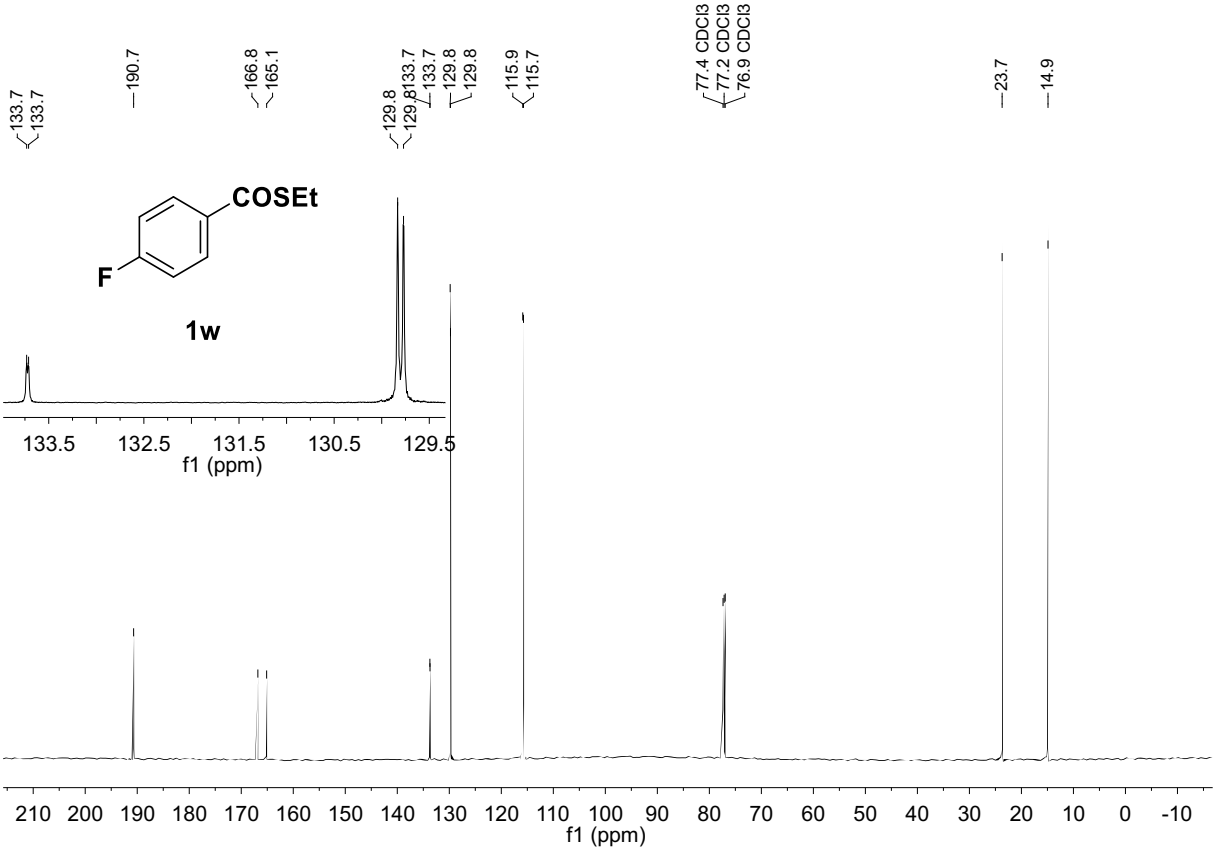
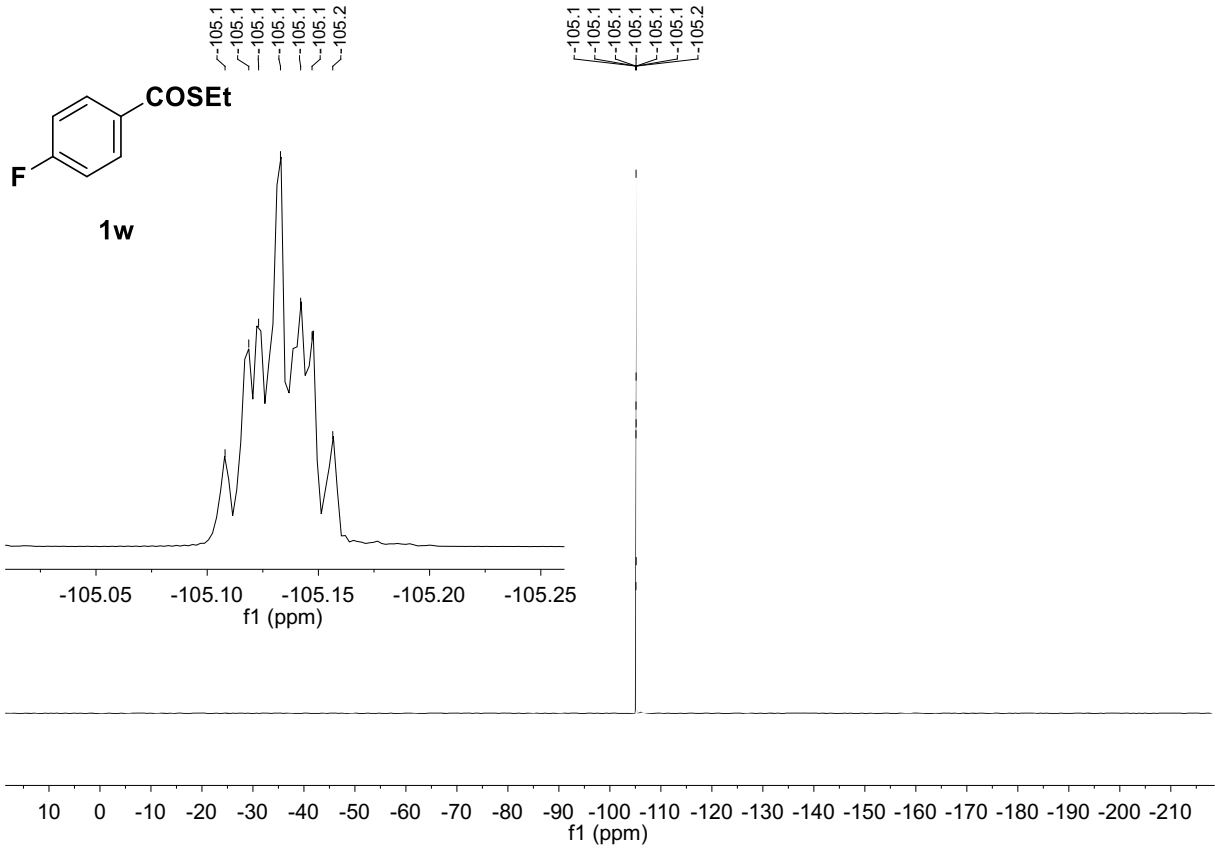
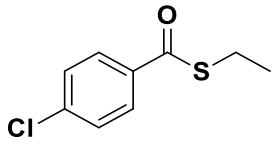
7.97
7.26 CDCl3
7.13
7.12
7.11
7.10
7.10
3.09
3.08
3.07
3.05
1.36
1.35
1.33
COSEt
F
1w
1.88
1.92
1.97
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


133.7
133.7
190.7
166.8
165.1
129.8
129.8
133.7
133.7
129.8
129.8
115.9
115.7
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
23.7
14.9
COSEt
F
1w
133.5 132.5 131.5 130.5 129.5
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-105.1
-105.1
-105.1
-105.1
-105.1
-105.1
-105.2
COSEt
F
1w
-105.05
-105.10
-105.15
-105.20
-105.25
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

S-ethyl 4-chlorobenzothioate (**1x**)



1x

According to GP-A, the product **1x** was synthesized using 4-chlorobenzoic acid (1.57 g, 10.0 mmol, 1.0 equiv.), ethanethiol (2.2 mL, 30 mmol, 3 equiv.), DMAP (122 mg, 1.00 mmol, 0.1 equiv.) and DIC (1.7 mL, 11 mmol, 1.1 equiv.). Purification by DCVC (*n*Hex/EA = 30:1 v/v) and yielded the product as a colorless oil (1.18 g, 5.88 mmol, 59%).

C_9H_9ClOS (200.68 g/mol)

R_f: 0.38 (*n*Hex/EA = 99:1) [UV]

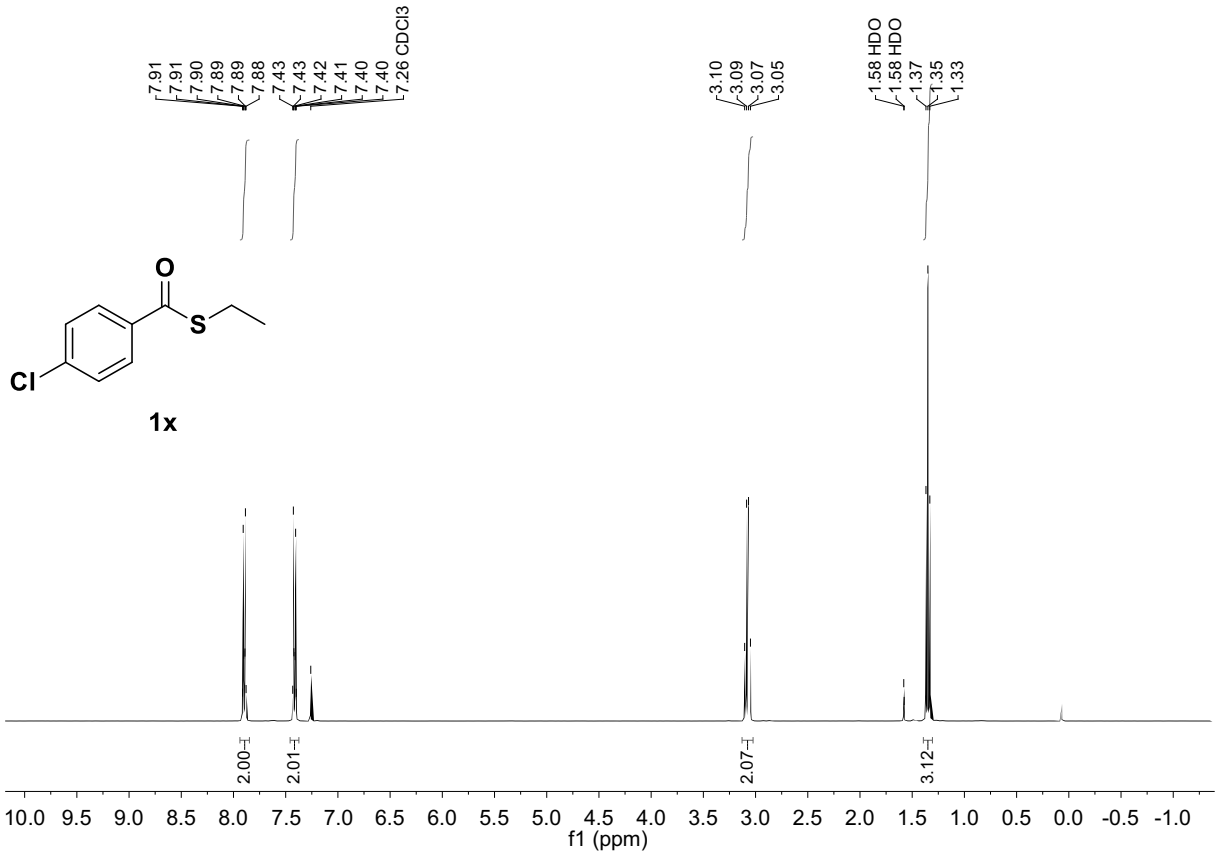
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91−7.88 (m, 2H, Ar*H*), 7.43−7.40 (m, 2H, Ar*H*), 3.08 (q, *J* = 7.4 Hz, 2H, CH_2CH_3), 1.35 (t, J = 7.4 Hz, 3H, CH_2CH_3).

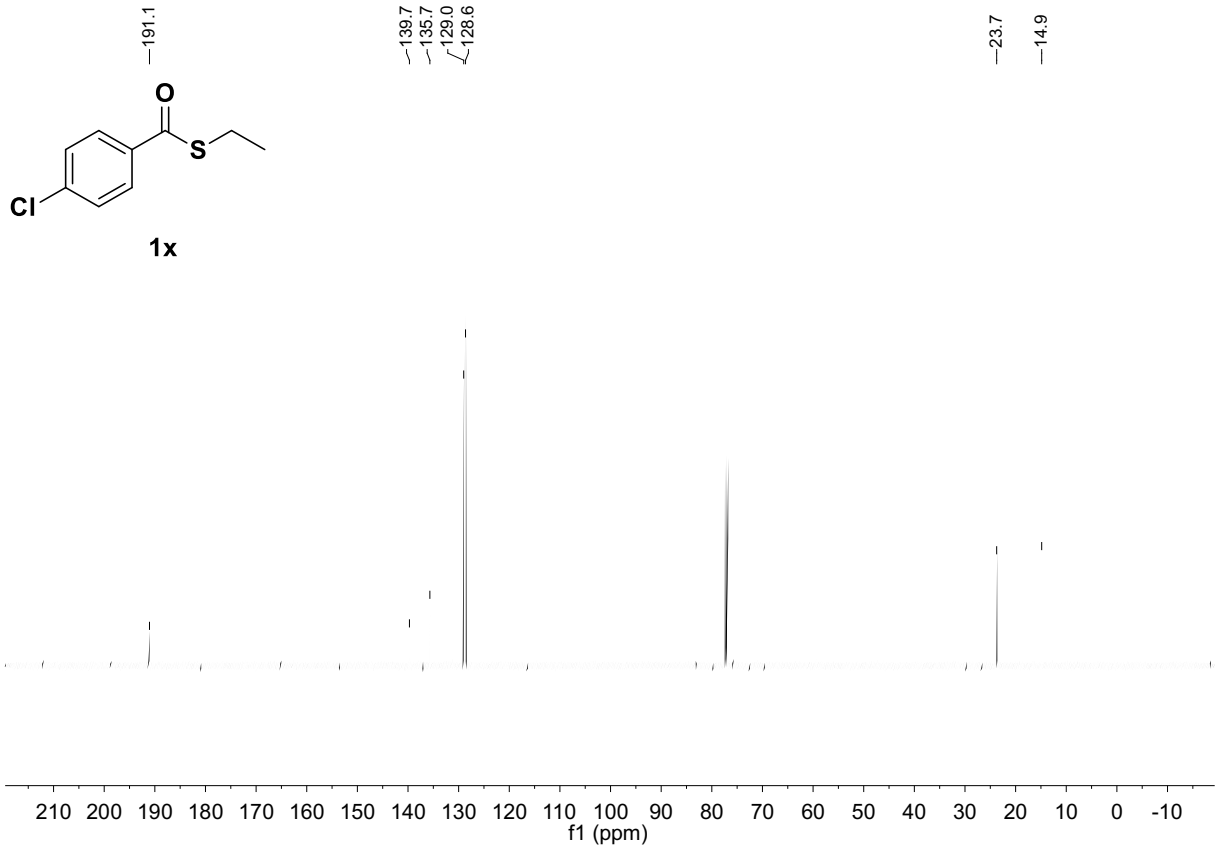
^{13}C NMR (101 MHz, $CDCl_3$): δ = 191.1 (*C*O), 139.7 (C_{Ar}), 135.7 (C_{Ar}), 129.0 (C_{Ar}), 128.6 (C_{Ar}), 23.7 (SCH_2CH_3), 14.8 (SCH_2CH_3).

GC-MS (EI,): t_r = 6.66 min, m/z(%) = 202 (2, $[M^{+\bullet}]$), 200 (5, $[M^{+\bullet}]$), 141 (32, $[M^{+\bullet}\text{-}C_2H_5S^{\bullet}]$), 139 (100, $[M^{+\bullet}\text{-}C_2H_5S^{\bullet}]$), 113 (9, $[M^{+\bullet}\text{-}C_2H_5S^{\bullet}\text{-CO}]$), 111 (27, $[M^{+\bullet}\text{-}C_2H_5S^{\bullet}\text{-CO}]$).

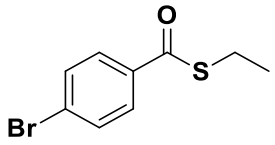
HR-MS (EI): m/z calc. for $[M]^+$ 200.005714, found 200.00387.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3088 (w, C-H_{arom}), 3062 (w, C-H_{arom}), 2969 (w, C-H_{aliph}), 2928 (w, C-H_{aliph}), 2872 (w, C-H_{aliph}), 1658 (vs, C=O), 1583 (s), 1482 (m), 1448 (w), 1396 (m), 1270 (w), 1202 (vs), 1169 (s), 1090 (s), 1012 (w), 971 (w), 908 (vs), 830 (vs), 726 (m).


7.91
7.91
7.90
7.89
7.89
7.88
7.43
7.43
7.42
7.41
7.40
7.40
7.26 CDCl3
3.10
3.09
3.07
3.05
1.58 HDO
1.58 HDO
1.37
1.35
1.33
O
S
Cl
1x
2.00
2.01
2.07
3.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


191.1
139.7
135.7
129.0
128.6
23.7
14.9
O
S
Cl
1x
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

S-ethyl 4-bromobenzothioate (**1y**)



1y

According to GP-A, the product **1y** was synthesized using 4-bromobenzoic acid (2.01 g, 10.0 mmol, 1.0 equiv.), ethanethiol (2.2 mL, 30 mmol, 3 equiv.), DMAP (122.2 mg, 1.0 mmol, 0.1 equiv.) and DIC (1.7 mL, 11 mmol, 1.1 equiv.). Purification by filtration through a silica plug (*n*Hex/EA = 99:1) and subsequent distillation of side product (4 mbar, 155 °C) yielded the product as a colorless oil (1.87 g, 7.63 mmol, 76%, 95% purity). The analytical data is in good accordance to reported literature.[5]

C_9H_9BrOS (245.13 g/mol)

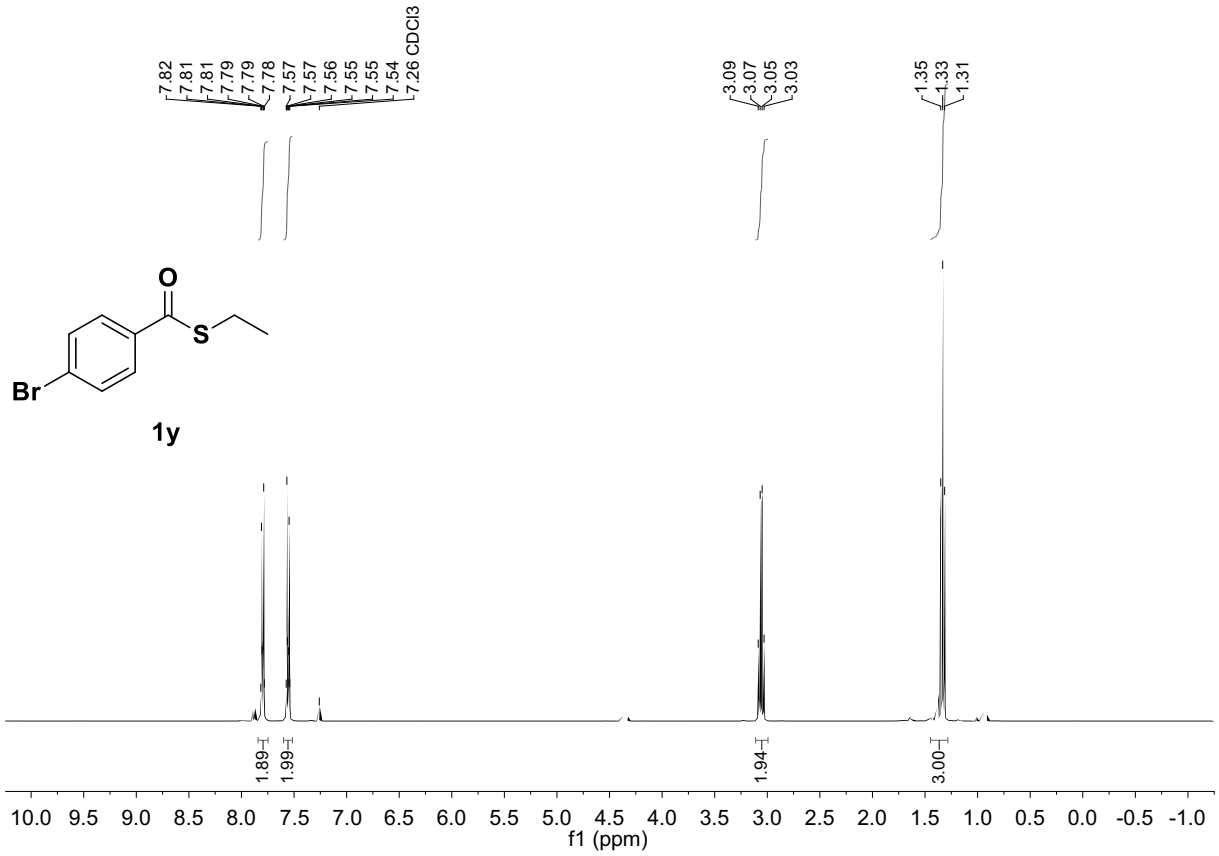
R_f: 0.32 (*n*Hex/EA = 99:1) [UV]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82−7.78 (m, 2H, Ar*H*), 7.57−7.54 (m, 2H, Ar*H*), 3.06 (q, *J* = 7.4 Hz, 2H, C*H*$_2$CH$_3$), 1.33 (t, J = 7.4 Hz, 3H, CH$_2$C*H*$_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 191.3 (*C*O), 136.1 (C_{Ar}), 132.0 (C_{Ar}), 128.8 (C_{Ar}), 128.4 (C_{Ar}), 23.7 (S*C*H$_2$CH$_3$), 14.8 (SCH$_2$*C*H$_3$).

GC-MS (EI): t_r = 7.26 min, m/z(%) = 246 (6, [$M^{+\bullet}$]), 244 (6, [$M^{+\bullet}$]), 185 (100, [$M^{+\bullet}$-$SC_2H_5^{\bullet}$]), 183 (100, [$M^{+\bullet}$-$SC_2H_5^{\bullet}$]), 157 (28, [$M^{+\bullet}$-$SC_2H_5^{\bullet}$-CO]), 155 (28, [$M^{+\bullet}$-$SC_2H_5^{\bullet}$-CO]).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3084 (w, C-H$_{arom}$), 3058 (w, C-H$_{arom}$), 2965 (w, C-H$_{aliph}$), 2928 (w, C-H$_{aliph}$), 2868 (w, C-H$_{aliph}$), 1720 (w), 1657 (vs, C=O), 1579 (s), 1478 (m), 1451 (w), 1392 (m), 1269 (m), 1202 (vs), 1169 (s), 1102 (w), 1064 (s), 1008 (m), 967 (w), 945 (w), 941 (w), 905 (vs), 826 (vs), 755 (w), 714 (s), 677 (w).


7.82
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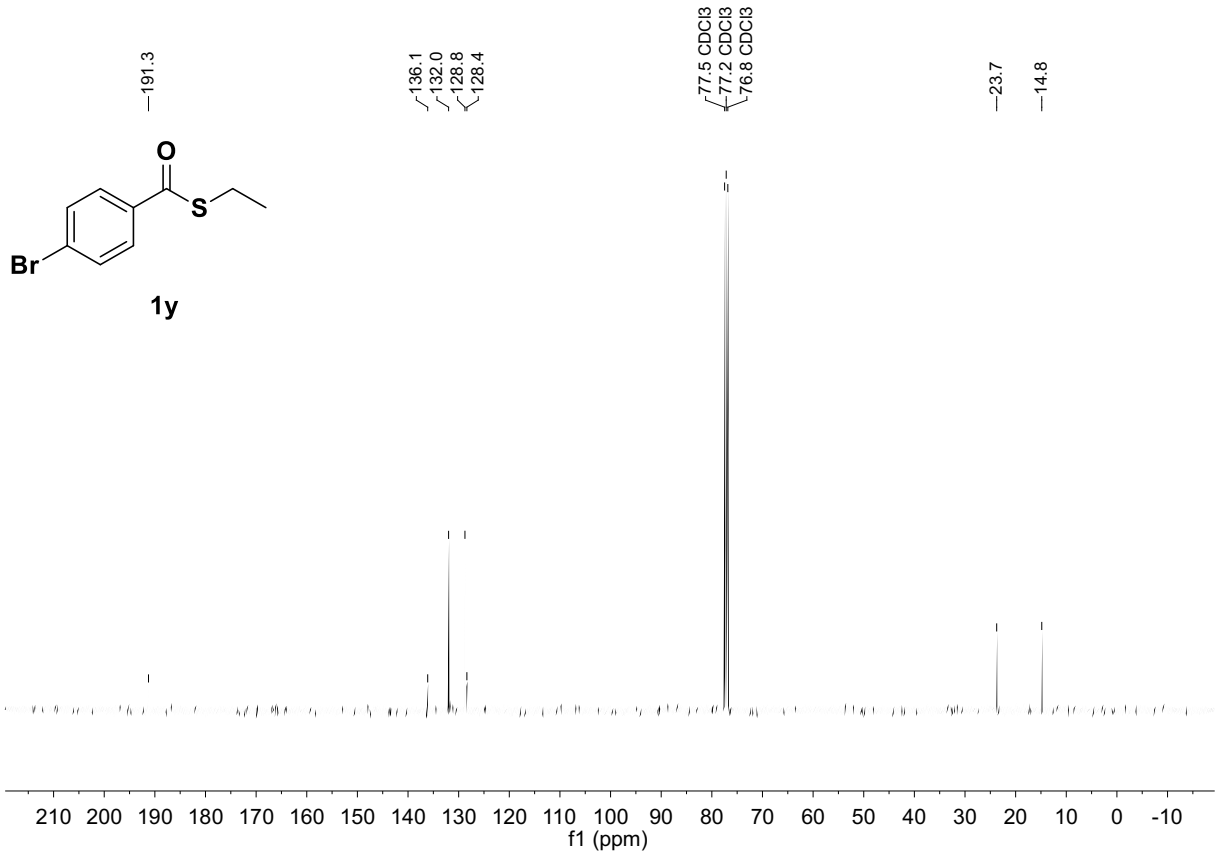
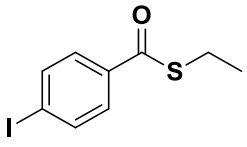
7.79
7.79
7.78
7.57
7.57
7.56
7.55
7.55
7.54
7.26 CDCl3
3.09
3.07
3.05
3.03
1.35
1.33
1.31
O
S
Br
1y
1.89
1.99
1.94
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


191.3
136.1
132.0
128.8
128.4
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
23.7
14.8
O
S
Br
1y
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

S-ethyl 4-iodobenzothioate (**1z**)



1z

According to GP-A, the product **1z** was synthesized using 4-iodobenzoic acid (2.48 g, 10.0 mmol, 1.0 equiv.), ethanethiol (2.2 mL, 30 mmol, 3 equiv.), DMAP (122 mg, 1.00 mmol, 0.1 equiv.) and DIC (1.7 mL, 11 mmol, 1.1 equiv.). Purification by filtration through a silica plug (*n*Hex/EA = 99:1 v/v) yielded the product as an orange oil (2.31 g, 7.91 mmol, 79%, 95% purity). The spectral data matches reported literature examples.[5]

C_9H_9IOS (292.12 g/mol)

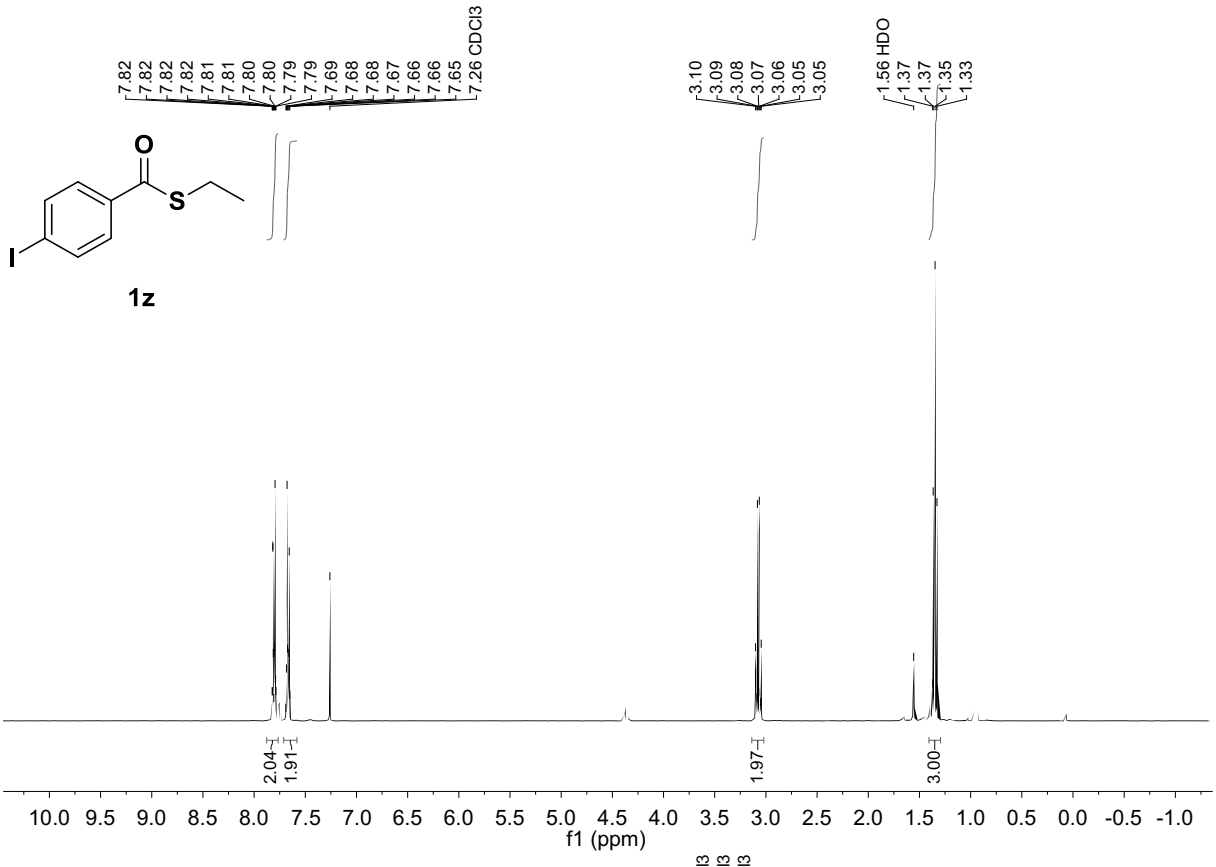
R_f: 0.31 (*n*Hex/EA = 99:1) [UV]

Melting point: 58.9–60.0 °C (EA)

^{1}H NMR (400 MHz, $CDCl_3$): δ =7.92 – 7.73 (m, 2H, Ar*H*), 7.71 – 7.55 (m, 2H, Ar*H*), 3.07 (q, *J* = 7.4 Hz, 2H, CH_2CH_3), 1.35 (t, *J* = 7.4 Hz, 3H, CH_2CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 191.6 (*C*O), 138.0 (C_{Ar}), 136.7 (C_{Ar}), 128.7 (C_{Ar}), 101.1 (C_{Ar}I), 23.7 (CH_2CH_3), 14.8 (CH_2CH_3).

GC-MS (EI): t_r = 8.01 min, m/z(%) = 293 (1, [$M^{+\bullet}$]), 292 (12, [$M^{+\bullet}$]), 232 (9, [$M^{+\bullet}$]), 231 (100, [$M^{+\bullet}$]), 204 (3, [$M^{+\bullet}$]), 203 (24, [$M^{+\bullet}$]).


7.82
7.82
7.82
7.82
7.81
7.81
7.80
7.80
7.79
7.79
7.69
7.68
7.68
7.67
7.66
7.66
7.65
7.26 CDCl3
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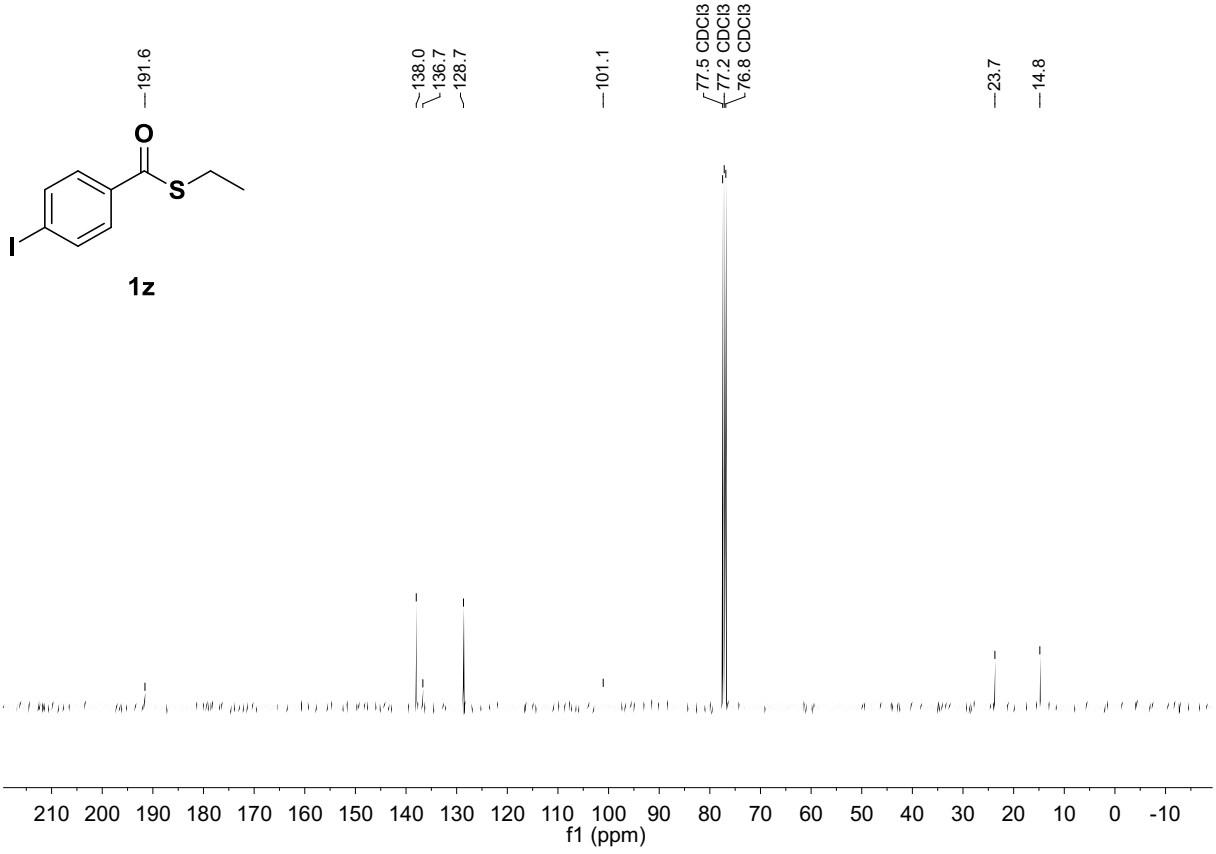
3.09
3.08
3.07
3.06
3.05
3.05
1.56 HDO
1.37
1.37
1.35
1.33
O
S
I
1z
2.04
1.91
1.97
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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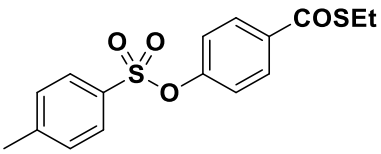
138.0
136.7
128.7
101.1
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
23.7
14.8
O
S
I
1z
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

S-ethyl 4-(tosyloxy)benzothioate (**1A**)



1A

According to GP-A, the product **1A** was synthesized using 4-(tosyloxy)benzoic acid (1.17 g, 4 mmol, 1.0 equiv.), ethanethiol (890 µL, 30.0 mmol, 3 equiv.), DMAP (48.9 mg, 400 µmol, 0.1 equiv.) and DCC (909 mg, 4.40 mmol, 1.1 equiv.). Purification was achieved by filtration through a short silica plug using *n*Hex/EA (8:2 v/v) and washing the filtrate with 6 M HCl (2 × 100 mL), aq. KOH (1 × 100 mL, 10% w/v), sat. $NaHCO_3$ (1 × 100 mL) and brine (1 × 100 mL). The product was obtained as a colorless solid (868 mg, 2.71 mmol, 68%). The spectral data is in good accordance to previously reported literature examples.[13]

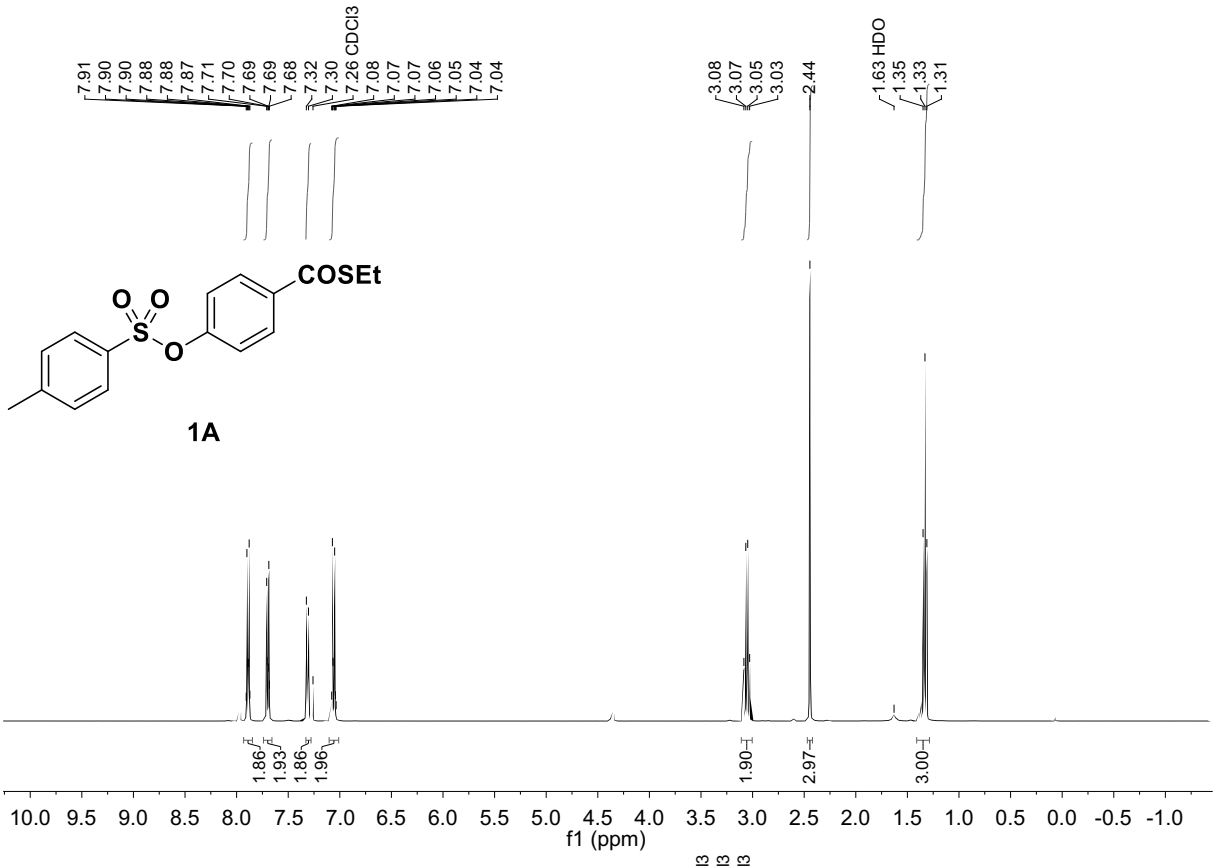
$C_{16}H_{16}O_3S_2$ (320.05 g/mol)

R_f: 0.58 (*n*Hex/EA = 8:2 v/v) [UV]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 – 7.85 (m, 2H), 7.74 – 7.66 (m, 2H), 7.35 – 7.27 (m, 2H), 7.10 – 7.01 (m, 2H), 3.06 (q, *J* = 7.4 Hz, 2H, C*H*$_2$CH$_3$), 2.44 (s, 3H, Ar-C*H*$_3$), 1.33 (t, *J* = 7.4 Hz, 3H, CH$_2$C*H*$_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 190.9 (*C*OSEt), 153.2 (C_{Ar}), 145.9 (C_{Ar}), 135.9 (C_{Ar}), 132.1 (C_{Ar}), 130.0 (C_{Ar}), 128.9 (C_{Ar}), 128.6 (C_{Ar}), 122.6 (C_{Ar}), 23.8, 21.9, 14.8.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2962 (w, C-H$_{aliph}$), 2928 (w, C-H$_{aliph}$), 2872 (w, C-H$_{aliph}$), 1653 (m, C=O), 1590 (w), 1493 (w), 1451 (w), 1407 (w), 1374 (m), 1295 (w), 1273 (w), 1202 (s), 1150 (s), 1090 (m), 1012 (w), 964 (w), 912 (m), 858 (s), 807 (m), 751 (s), 717 (s), 673 (s).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7.90
7.90
7.88
7.88
7.87
7.71
7.70
7.69
7.69
7.68
7.32
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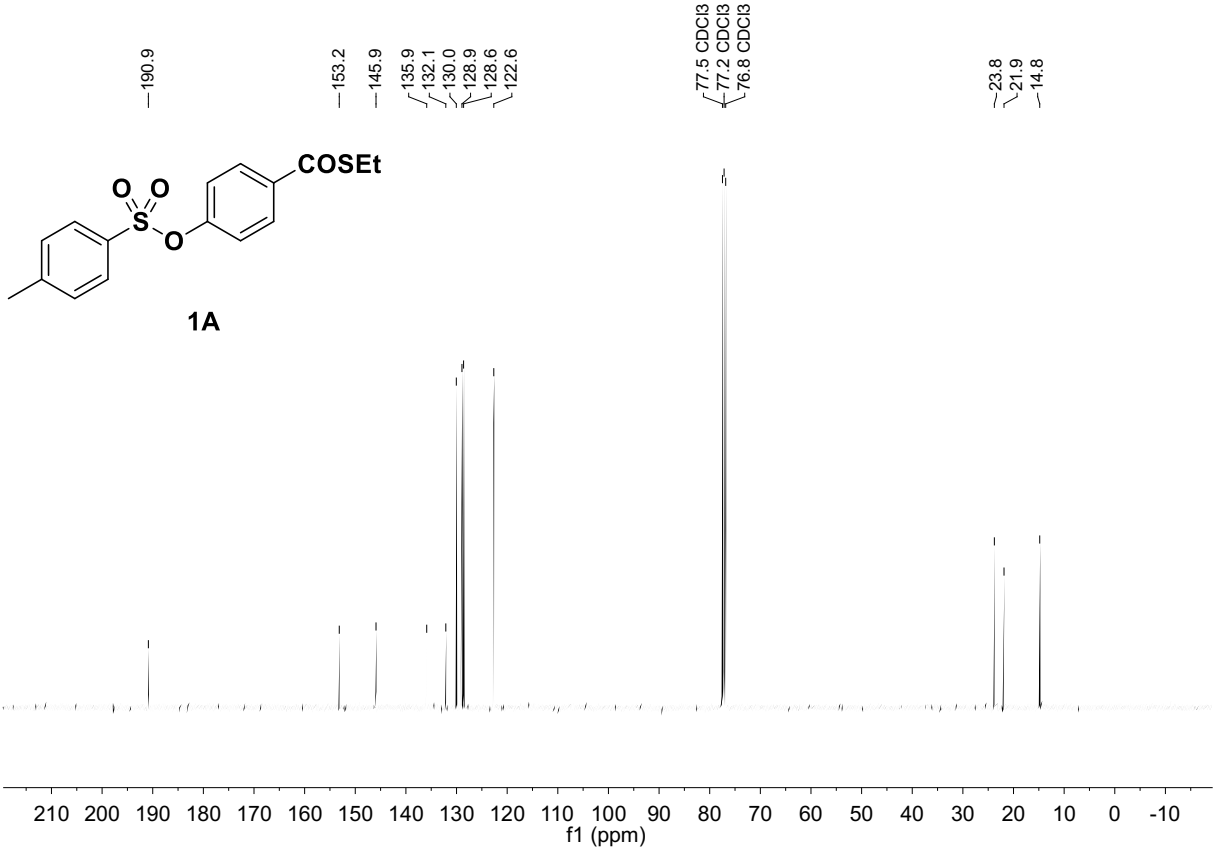
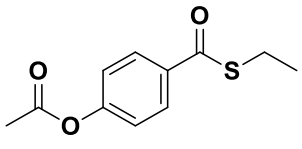
7.26 CDCl3
7.08
7.07
7.07
7.06
7.05
7.04
7.04
3.08
3.07
3.05
3.03
2.44
1.63 HDO
1.35
1.33
1.31
COSEt
1A
1.86
1.93
1.86
1.96
1.90
2.97
3.00
f1 (ppm)


190.9
153.2
145.9
135.9
132.1
130.0
128.9
128.6
122.6
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
23.8
21.9
14.8
COSEt
1A
f1 (ppm)

4-((ethylthio)carbonyl)phenyl acetate (**1B**)



1B

According to GP-A, the product **1B** was synthesized using 4-acetoxybenzoic acid (3.60 g, 20.0 mmol, 1.0 equiv.), ethanethiol (7.2 mL, 100 mmol, 5 equiv.), DMAP (244 mg, 2.00 mmol, 0.1 equiv.) and DCC (4.54 g, 22.0 mmol, 1.1 equiv.). Purification was achieved by DCVC (*n*Hex/EA = 9:1 v/v). The product was obtained as a slightly yellow-colored oil (1.21 g, 5.40 mmol, 54%).

$C_{11}H_{12}O_3S$ (224.27 g/mol)

R_f: 0.06 (*n*Hex/EA = 9:1) [$KMnO_4$, UV]

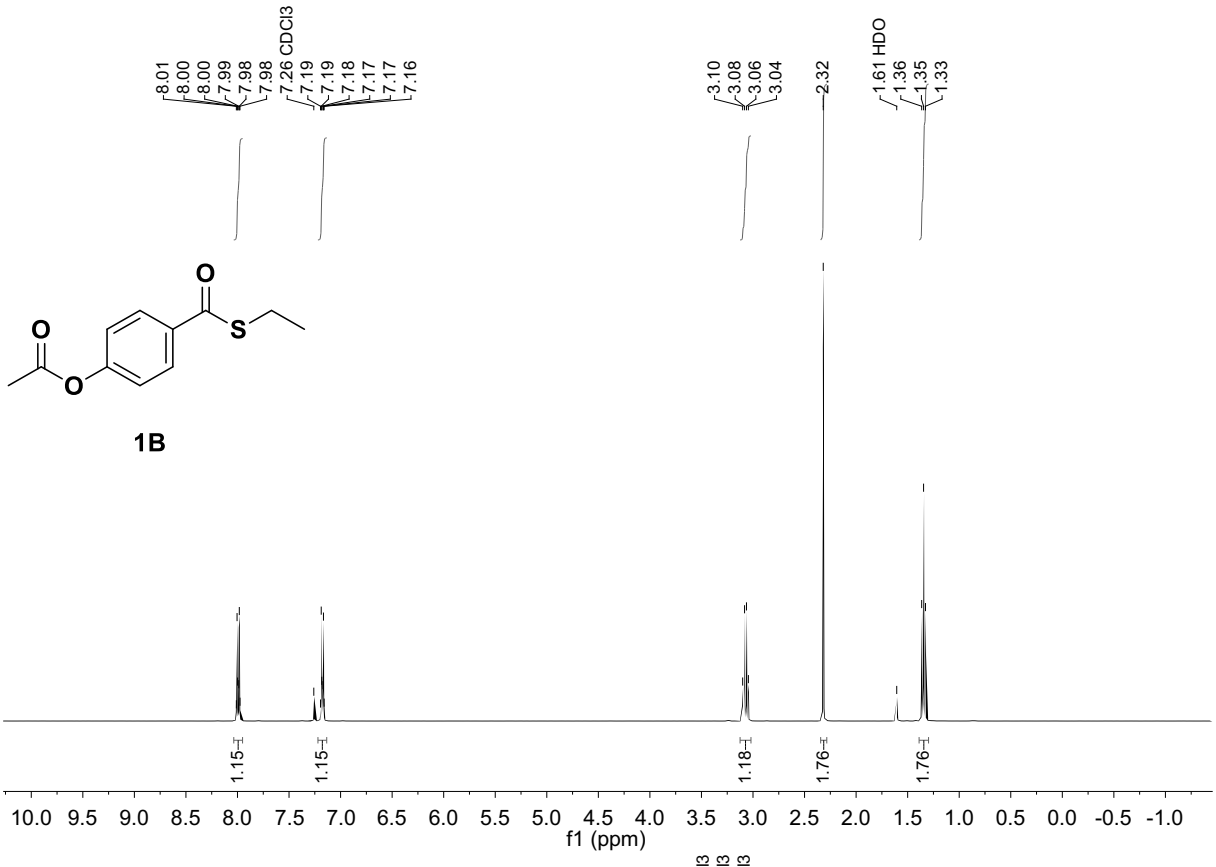
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 – 7.95 (m, 2H, Ar*H*), 7.22 – 7.13 (m, 2H, Ar*H*), 3.07 (q, *J* = 7.4 Hz, 2H, CH_2CH_3), 2.32 (s, 3H, CH_3CO_2), 1.35 (t, *J* = 7.4 Hz, 3H, CH_2CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 191.0 (*C*OSEt), 168.9 (CO_2Ar), 154.6 (C_{Ar}), 134.9 (C_{Ar}), 128.8 (C_{Ar}), 121.9 (C_{Ar}), 23.7, 21.3, 14.9.

GC-MS (EI, method B): t_r = 20.41 min, m/z(%) = 224 (3, [$M^{+\bullet}$]), 163 (58, [$M^{+\bullet}$-$C_2H_5S^{\bullet}$]), 122 (9), 121 (100).

HR-MS (ESI): m/z calc. for $[M+Na]^+$ 247.03994, found 247.04014.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3062 (w, C-H_{arom}), 2969 (w, C-H_{aliph}), 2928 (w, C-H_{aliph}), 2872 (w, C-H_{aliph}), 1754 (m, C=O_{ester}), 1650 (m, C=$O_{thioester}$), 1589 (w), 1493 (w), 1448 (w), 1433 (w), 1407 (w), 1369 (w), 1295 (w), 1179 (s), 1150 (m), 1101 (m), 1049 (w), 1005 (m), 969 (w), 907 (s), 848 (s), 803 (m), 759 (w), 732 (m), 681 (m).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8.00
7.99
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7.98
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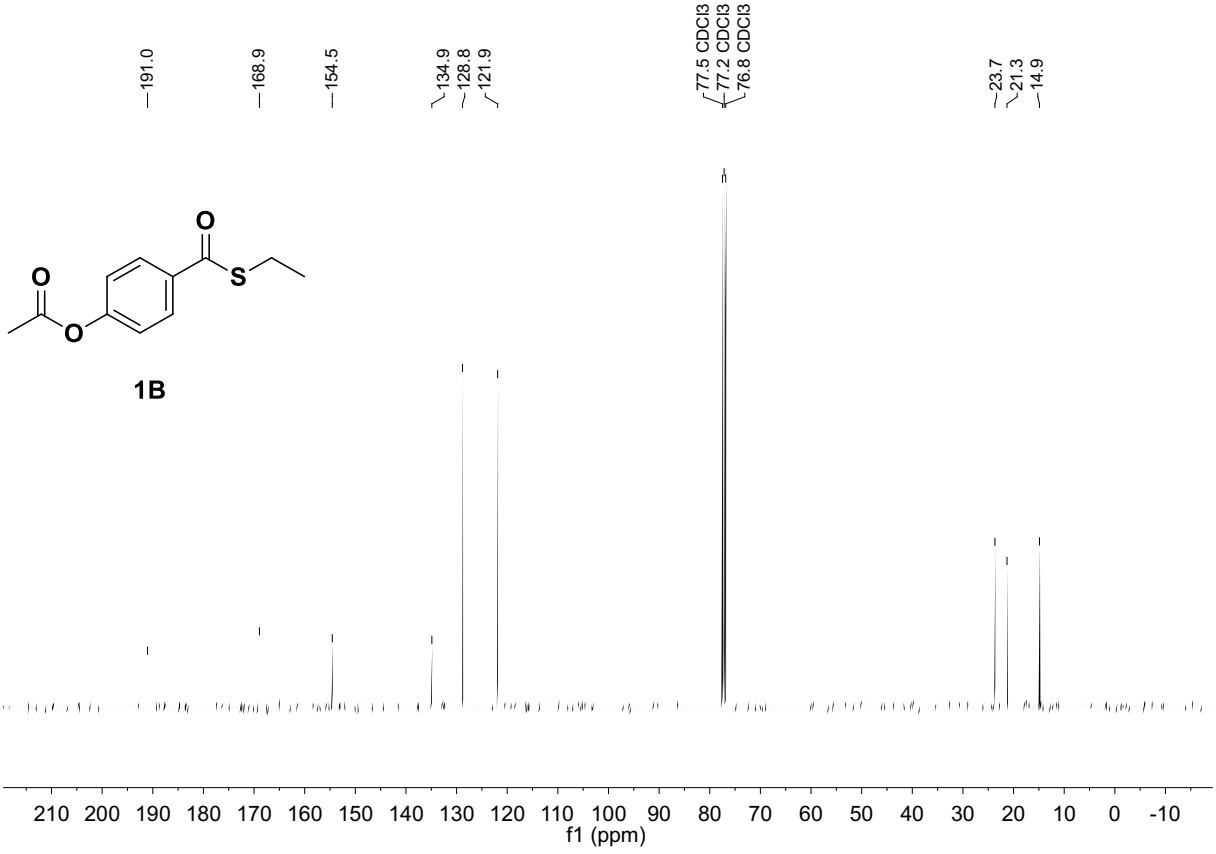
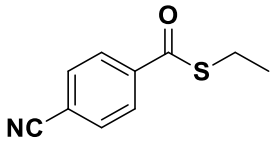
7.19
7.18
7.17
7.17
7.16
3.10
3.08
3.06
3.04
2.32
1.61 HDO
1.36
1.35
1.33
O
O
S
O
O
1B
1.15
1.15
1.18
1.76
1.76
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


191.0
168.9
154.5
134.9
128.8
121.9
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
23.7
21.3
14.9
O
O
S
O
O
1B
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

S-ethyl 4-cyanobenzothioate (**1C**)



1C

According to GP-A, the product **1C** was synthesized using 4-cyanobenzoic acid (1.91 g, 10.0 mmol, 1.0 equiv.), ethanethiol (2.2 mL, 30 mmol, 3 equiv.), DMAP (122 mg, 1.00 mmol, 0.1 equiv.) and DCC (2.27 g, 11.0 mmol, 1.1 equiv.). Purification was achieved by filtration through a short silica plug using Hex/EA (9:1) and washing the filtrate with 6 M HCl (2 × 20 mL), 10% aq. KOH (1 × 20 mL), sat. $NaHCO_3$ (1 × 20 mL) and brine (1 × 20 mL). The product was yielded as colorless solid (1.45 g, 7.58 mmol, 76%). The data is in accordance with reported literature.[13]

$C_{10}H_9NOS$ (191.25 g/mol)

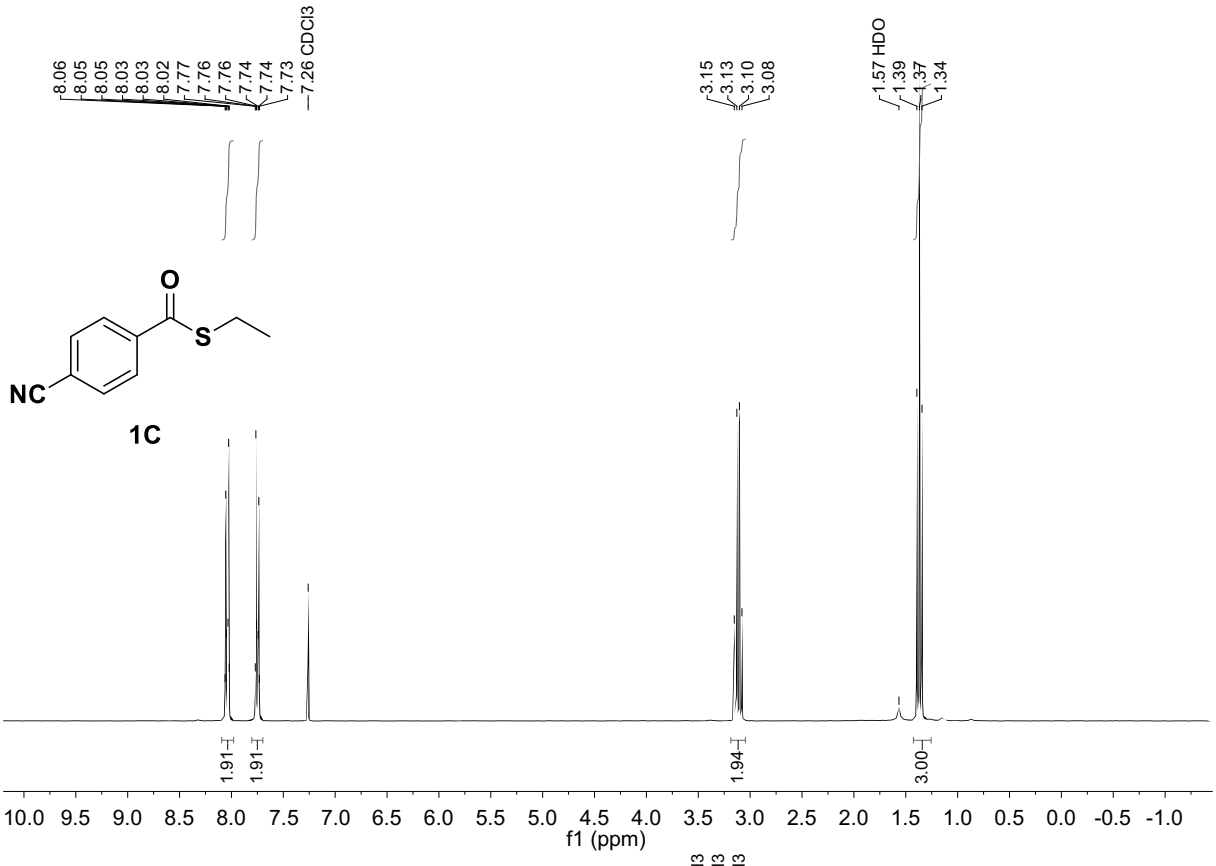
R_f: 0.30 (*n*Hex/Et_2O = 9:1) [$KMnO_4$]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 – 7.95 (m, 2H, Ar*H*), 7.79 – 7.71 (m, 2H, Ar*H*), 3.12 (q, *J* = 7.4 Hz, 2H, S$CH_2$$CH_3$), 1.37 (t, *J* = 7.4 Hz, 3H, SCH_2CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.9 (*C*O), 140.4 (C_{Ar}), 132.6 (C_{Ar}), 127.8 (C_{Ar}), 118.0 (*C*N), 116.6 (C_{Ar}), 24.1 (S$CH_2$$CH_3$), 14.7 ($SCH_2CH_3$).

GC-MS (EI): t_r = 7.29 min, m/z(%) = 191 (6, [$M^{+\bullet}$]), 130 (100, [$M^{+\bullet}$-$C_2H_5S^\bullet$]), 102 (28, [$M^{+\bullet}$ -$C_2H_5S^\bullet$-CO]).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3085 (w, C-H_{arom}), 2968 (w, C-H_{aliph}), 2928 (w, C-H_{aliph}), 2872 (w, C-H_{aliph}), 2220 (w, C≡N), 1646 (s, C=O), 1560 (w), 1500 (w), 1452 (w), 1403 (m), 1377 (w), 1278 (w), 1198 (s), 1161 (m), 1113 (w), 1057 (w), 1016 (w), 964 (w), 914 (s), 833 (s), 829 (s), 763 (s), 733 (m).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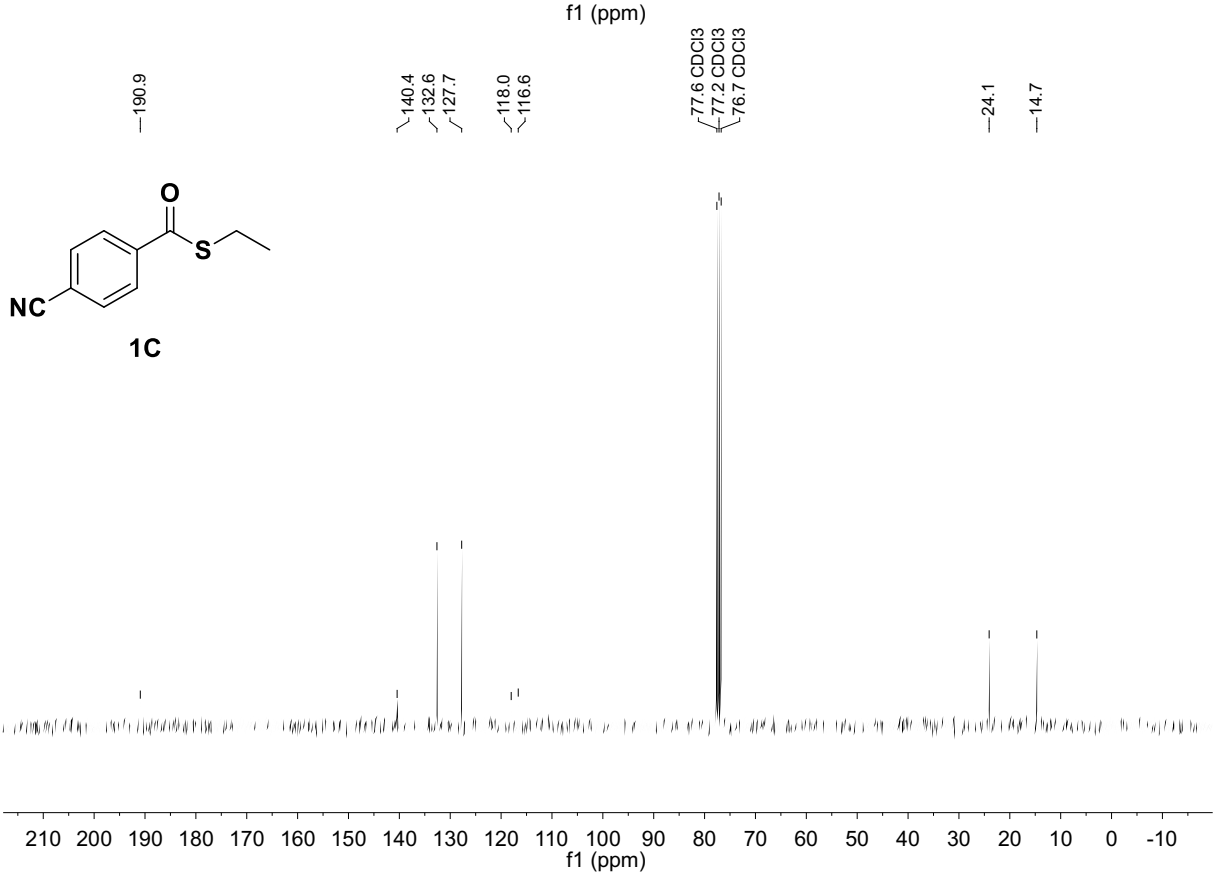
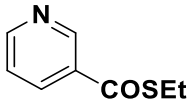
8.05
8.03
8.03
8.02
7.77
7.76
7.76
7.74
7.74
7.73
7.26 CDCl3
3.15
3.13
3.10
3.08
1.57 HDO
1.39
1.37
1.34
O
S
NC
1C
1.91
1.91
1.94
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


190.9
140.4
132.6
127.7
118.0
116.6
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
24.1
14.7
O
S
NC
1C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

S-ethyl pyridine-3-carbothioate (**1E**)



1E

According to GP-A, the product **1E** was synthesized using nicotinic acid (1.23 g, 10.0 mmol, 1.0 equiv.), ethanethiol (2.2 mL, 30 mmol, 3 equiv.), DMAP (122 mg, 1.00 mmol, 0.1 equiv.) and DCC (2.27 g, 11.0 mmol, 1.1 equiv.). Purification was achieved by filtration through a short silica plug (*n*Hex/EA 9:1 v/v) and washing the filtrate with 6 M HCl (2 × 20 mL). The aqueous layer was neutralized with aq. KOH solution (10% w/v) and extracted with EA (4 × 25 mL). Then, the organic layer was washed with brine (1 × 20 mL) and furnished **1E** as a slightly yellow-colored oil (436 mg, 2.76 mmol, 28%). The analytical data is in accordance with reported literature.[5]

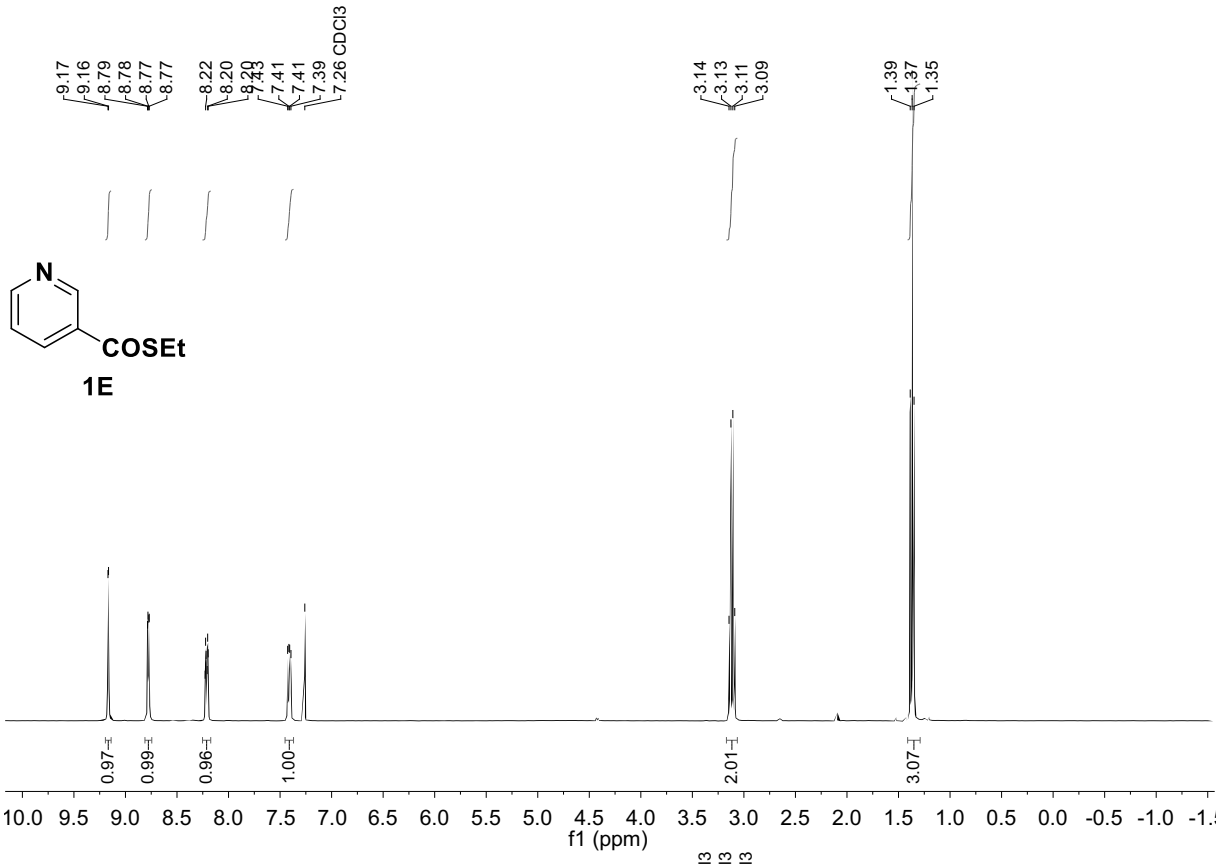
C_8H_9NOS (167.23 g/mol)

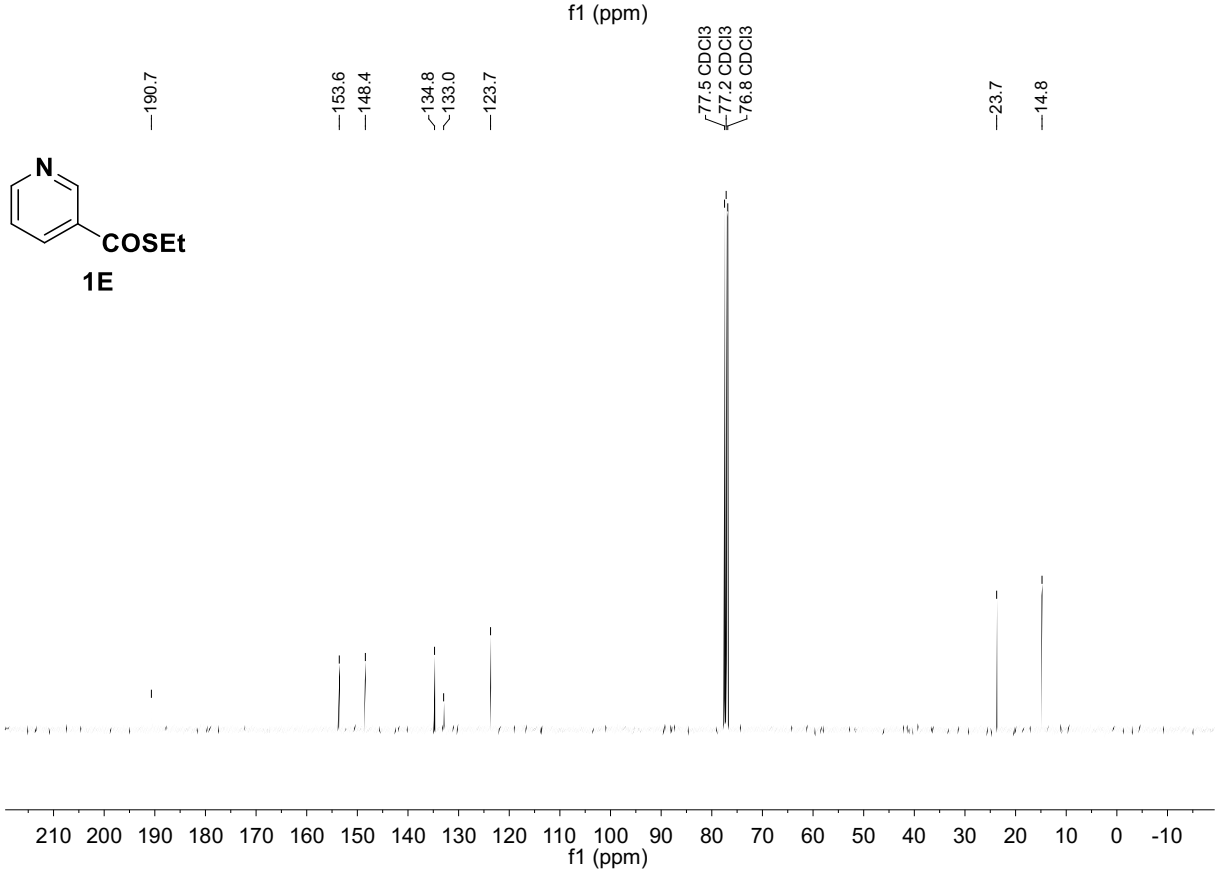
R_f: 0.35 (*n*Hex/EA = 9:1) [$KMnO_4$, UV]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.17 (d, *J* = 2.2 Hz, 1H, Ar*H*), 8.78 (dd, *J* = 4.8, 1.7 Hz, 1H, Ar*H*), 8.25 – 8.17 (m, 1H, Ar*H*), 7.41 (ddt, *J* = 7.1, 4.9, 1.1 Hz, 1H, Ar*H*), 3.12 (q, *J* = 7.4 Hz, 2H), 1.37 (t, *J* = 7.4 Hz, 3H).

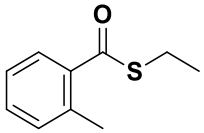
^{13}C NMR (101 MHz, $CDCl_3$): δ = 190.7 (*C*OSEt), 153.6 (C_{Ar}), 148.4 (C_{Ar}), 134.8(C_{Ar}), 133.0 (C_{Ar}), 123.7 (C_{Ar}), 23.7, 14.8.

GC-MS (EI): t_r = 5.86 min, m/z(%) = 167 (10, [$M^{+\bullet}$]), 106 (100, [$M^{+\bullet}$-$C_2H_5S^{\bullet}$]), 78 (66, [$M^{+\bullet}$-$C_2H_5S^{\bullet}$-CO]).


9.17
9.16
8.79
8.78
8.77
8.77
8.22
8.20
8.20
7.43
7.41
7.41
7.39
7.26 CDCl3
3.14
3.13
3.11
3.09
1.39
1.37
1.35
N
COSEt
1E
0.97
0.99
0.96
1.00
2.01
3.07
f1 (ppm)


190.7
153.6
148.4
134.8
133.0
123.7
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
23.7
14.8
N
COSEt
1E
f1 (ppm)

S-ethyl 2-methylbenzothioate (**1F**)



1F

According to GP-A, the product **1F** was synthesized using 2-methylbenzoic acid (1.36 g, 10.0 mmol, 1.0 equiv.), ethanethiol (2.2 mL, 45 mmol, 3 equiv.), DMAP (122 mg, 1.00 mmol, 0.1 equiv.) and DCC (2.27 g, 11.0 mmol, 1.1 equiv.). Purification was achieved by filtration through a short silica plug using DCM and washing the obtained solution with 6 M HCl (1 × 20 mL), 1 M HCl (1 × 20 mL), sat. $NaHCO_3$ (1 × 20 mL) and brine (1 × 20 mL). The product was obtained as a colorless oil (860 mg, 4.77 mmol, 48%). The analytical data is in good accordance to reported literature.[5]

$C_{10}H_{12}OS$ (180.27 g/mol)

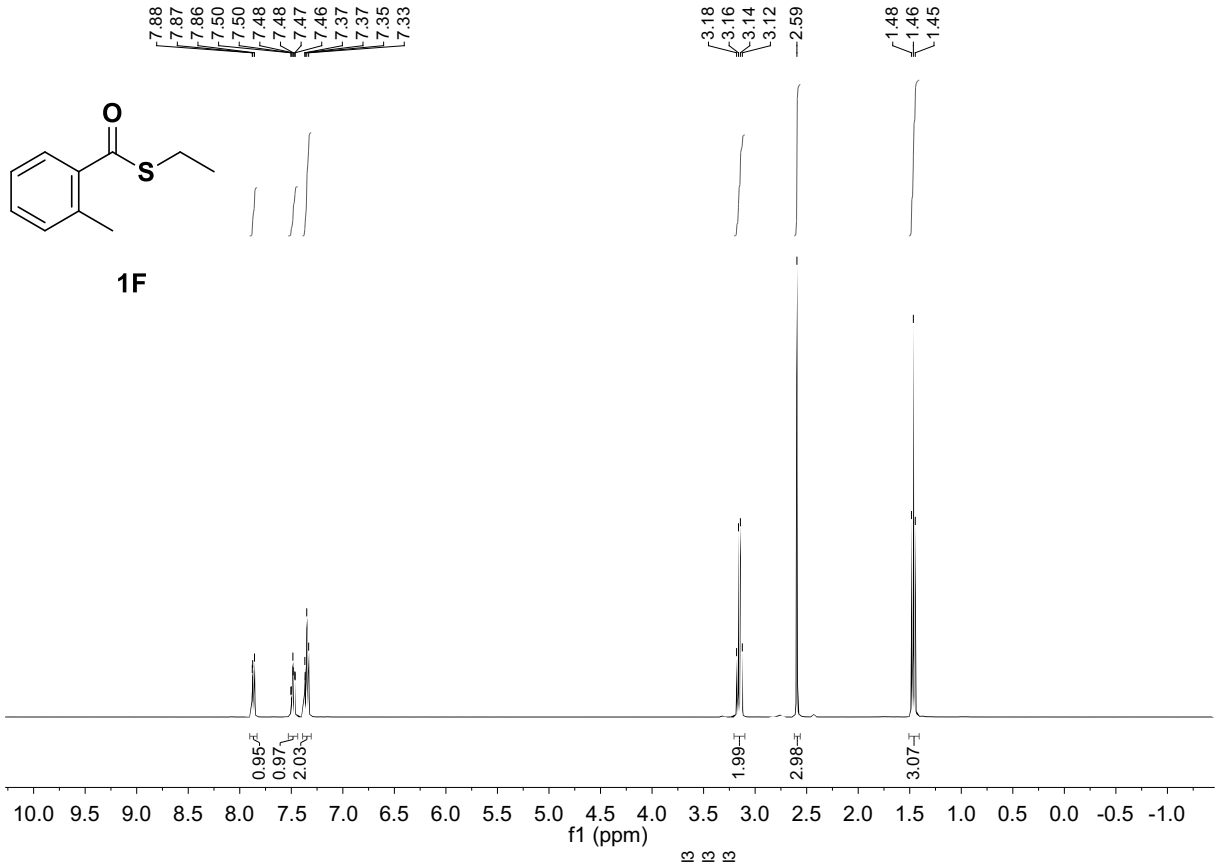
R_f: 0.46 (*n*Hex/EA = 9:1 v/v) [$KMnO_4$, anis, UV]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.47 (td, *J* = 7.5, 1.4 Hz, 1H), 7.38 – 7.30 (m, 2H), 3.14 (q, *J* = 7.4 Hz, 2H, SC*H*$_2$CH$_3$), 2.59 (s, 3H, PhC*H*$_3$), 1.46 (t, *J* = 7.4 Hz, 3H, SCH$_2$C*H*$_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 194.7 (*C*OSEt), 137.9 (*C*$_{Ar}$), 136.8 (*C*$_{Ar}$), 131.6 (*C*$_{Ar}$), 131.6 (*C*$_{Ar}$), 128.5 (*C*$_{Ar}$), 125.8 (*C*$_{Ar}$), 24.1 (S*C*H$_2$CH$_3$), 20.7 (Ph*C*H$_3$), 14.9 (SCH$_2$*C*H$_3$).

GC-MS (EI): t_r = 5.95 min, m/z(%) = 119 (100, [$M^{+\bullet}$-$C_2H_5S^{\bullet}$]), 91 (27, [$M^{+\bullet}$-$C_2H_5S^{\bullet}$-CO]).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3062 (w, C-H$_{arom}$), 3018 (w, C-H$_{arom}$), 2968 (w, C-H$_{aliph}$), 2928 (w, C-H$_{aliph}$), 2872 (w, C-H$_{aliph}$), 1660 (vs, C=O), 1601 (w), 1597 (w), 1568 (w), 1481 (w), 1452 (m), 1377 (w), 1288 (w), 1284 (w), 1265 (w), 1191 (s), 1123 (w), 1047 (w), 971 (w), 945 (w), 900 (vs), 762 (s), 721 (s), 680 (s).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7.37
7.37
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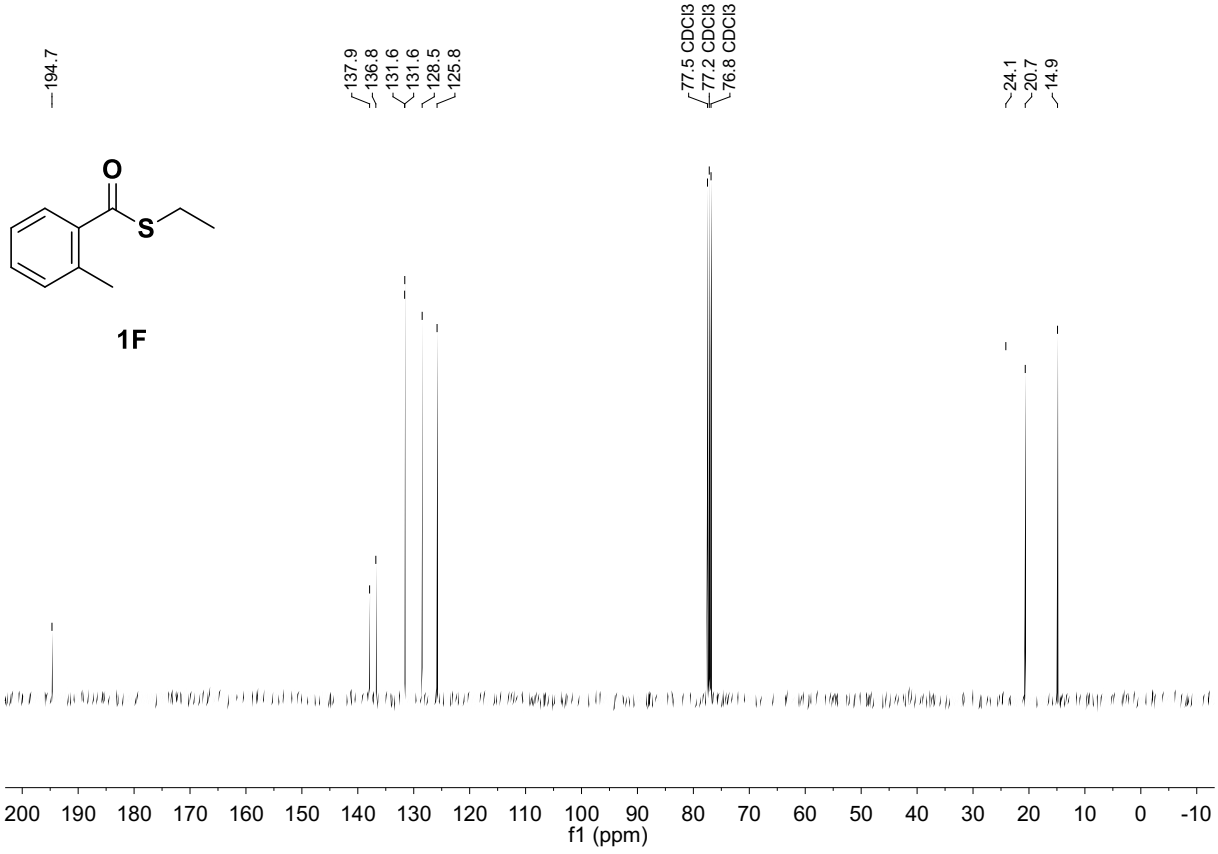
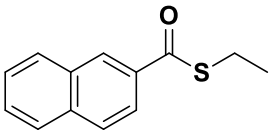
7.33
3.18
3.16
3.14
3.12
2.59
1.48
1.46
1.45
O
S
1F
0.95
0.97
2.03
1.99
2.98
3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


194.7
137.9
136.8
131.6
131.6
128.5
125.8
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
24.1
20.7
14.9
O
S
1F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

S-ethyl naphthalene-2-carbothioate (**1G**)



1G

Naphthoic acid (1.72 g, 10 mmol) was dissolved in DCM (50 mL) and 2-chloro-4,6-dimethoxy-1,3,5-triazine (2.11 g, 12.0 mmol, 1.2 equiv.) as well as triethylamine (4.0 mL, 30 mmol, 3.0 equiv.) was added. The reaction mixture was stirred at room temperature for 2 h. Then, ethanethiol (0.94 mL, 13 mmol, 1.3 equiv.) was added and the reaction stirred for 1 h. Afterwards, the crude reaction mixture was extracted with 6 M HCl (2 × 20 mL), sat. $NaHCO_3$ (1 × 20 mL) and brine (1 × 20 mL) and dried over anhydrous Mg_2SO_4. The product was yielded as a colorless solid (1.04 g, 4.81 mmol, 48%, 95% purity). The spectral data is in good accordance with reported literature.[13]

$C_{13}H_{12}OS$ (216.30 g/mol)

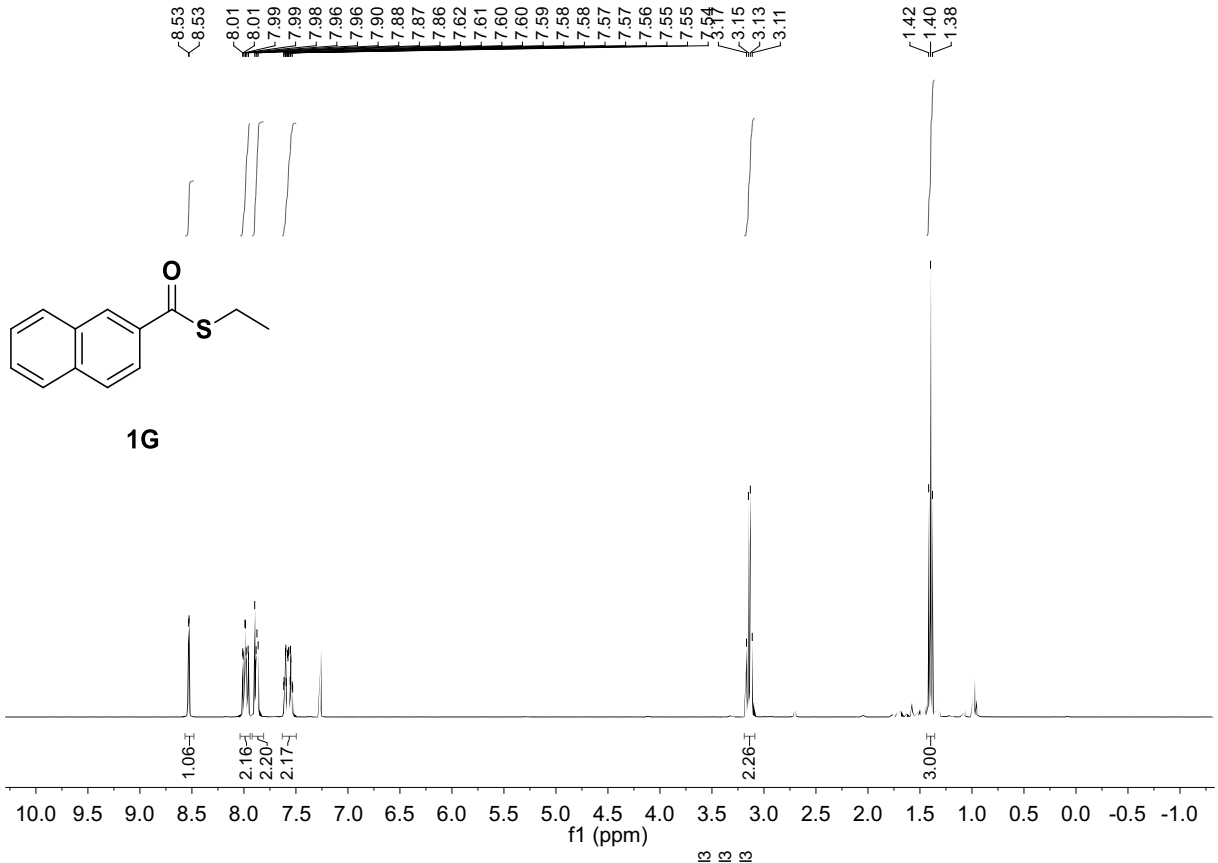
R_f: 0.45 (PE/EA = 97:3) [$KMnO_4$, anis, UV]

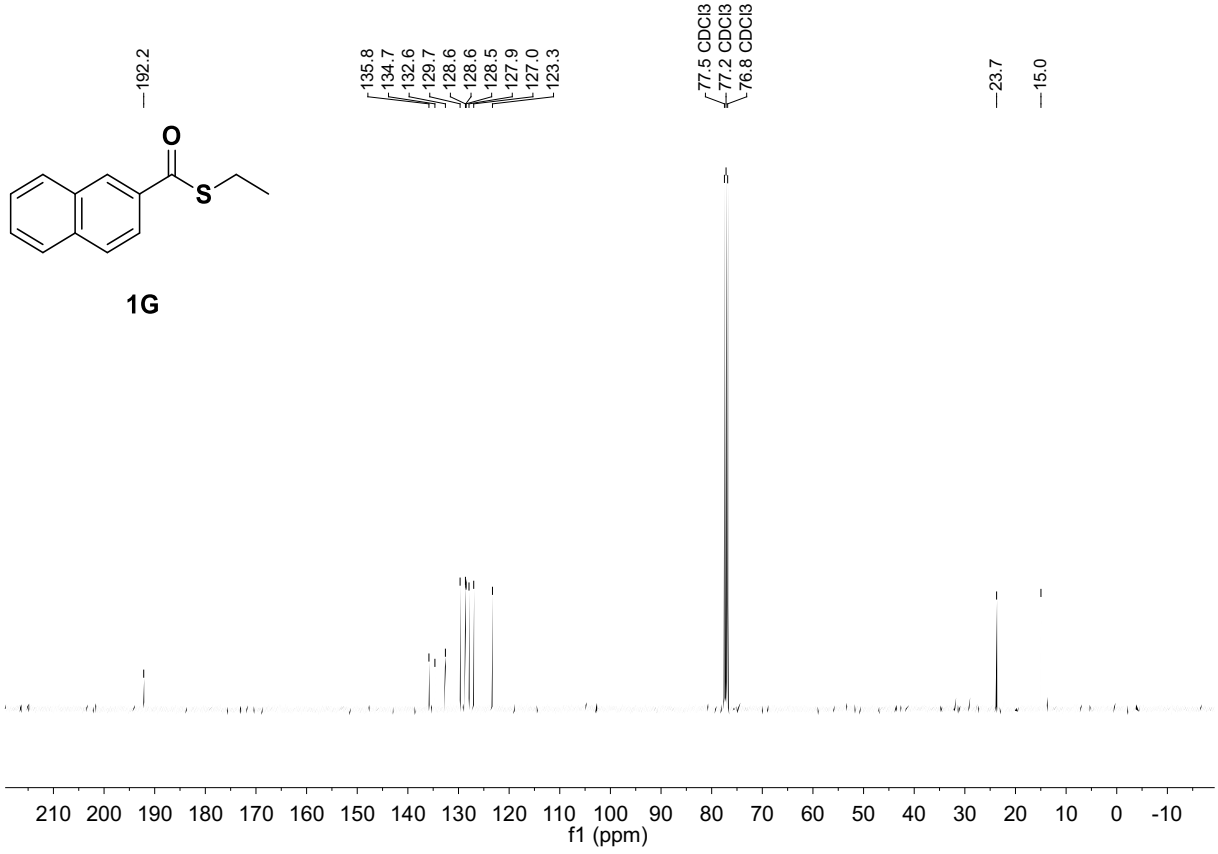
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 – 8.50 (m, 1H, Ar*H*), 8.04 – 7.93 (m, 2H, Ar*H*), 7.92 – 7.84 (m, 2H, Ar*H*), 7.64 – 7.51 (m, 2H, Ar*H*), 3.14 (q, *J* = 7.4 Hz, 2H, SC*H*$_2$), 1.40 (t, *J* = 7.4 Hz, 3H, SCH$_2$C*H*$_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 192.2 (*C*OSEt), 135.8 (C_{Ar}), 134.7 (C_{Ar}), 132.6 (C_{Ar}), 129.7 (C_{Ar}), 128.63 (C_{Ar}), 128.56 (C_{Ar}), 128.5 (C_{Ar}), 127.9 (C_{Ar}), 127.0 (C_{Ar}), 123.3 (C_{Ar}), 23.7 (S*C*H$_2$CH$_3$), 15.0 (SCH$_2$*C*H$_3$).

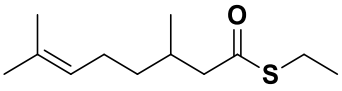
GC-MS (EI): t_r = 8.96 min, m/z(%) = 216 (9, [$M^{+\bullet}$]), 155 (100, [$M^{+\bullet}$-$C_2H_5S^{\bullet}$]), 127 (69, [$M^{+\bullet}$-$C_2H_5S^{\bullet}$-CO]).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3055 (w, C-H$_{arom}$), 2961 (w, C-H$_{aliph}$), 2924 (w, C-H$_{aliph}$), 2868 (w, C-H$_{aliph}$), 2820 (w, C-H$_{aliph}$), 1642 (s, C=O), 1571 (w), 1452 (w), 829 (w).


8.53
8.53
8.01
8.01
7.99
7.99
7.98
7.96
7.96
7.90
7.88
7.87
7.86
7.62
7.61
7.60
7.60
7.59
7.58
7.58
7.57
7.57
7.56
7.55
7.55
7.54
3.17
3.15
3.13
3.11
1.42
1.40
1.38
O
S
1G
1.06
2.16
2.20
2.17
2.26
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


192.2
135.8
134.7
132.6
129.7
128.6
128.6
128.5
127.9
127.0
123.3
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
23.7
15.0
O
S
1G
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

S-ethyl 3,7-dimethyloct-6-enethioate (**1H**)



1H

According to GP-A, the product **1H** was synthesized using citronellic acid (1.84 mL, 10.0 mmol, 1.0 equiv.), ethanethiol (2.16 mL, 30.0 mmol, 3 equiv.), DMAP (122 mg, 1.00 mmol, 0.1 equiv.) and DCC (2.27 g, 11.0 mmol, 1.1 equiv.). Purification was achieved by filtration through a short silica plug using DCM and washing the filtrate with 6 M HCl (2 × 20 mL), sat. $NaHCO_3$ (1 × 20 mL) and brine (1 × 20 mL). A second filtration through a silica plug was necessary to remove trace impurities. The product was obtained as a colorless oil (1.56 g, 7.28 mmol, 73%). The spectral data is in good accordance to previously reported literature.[14]

$C_{12}H_{22}OS$ (214.37 g/mol)

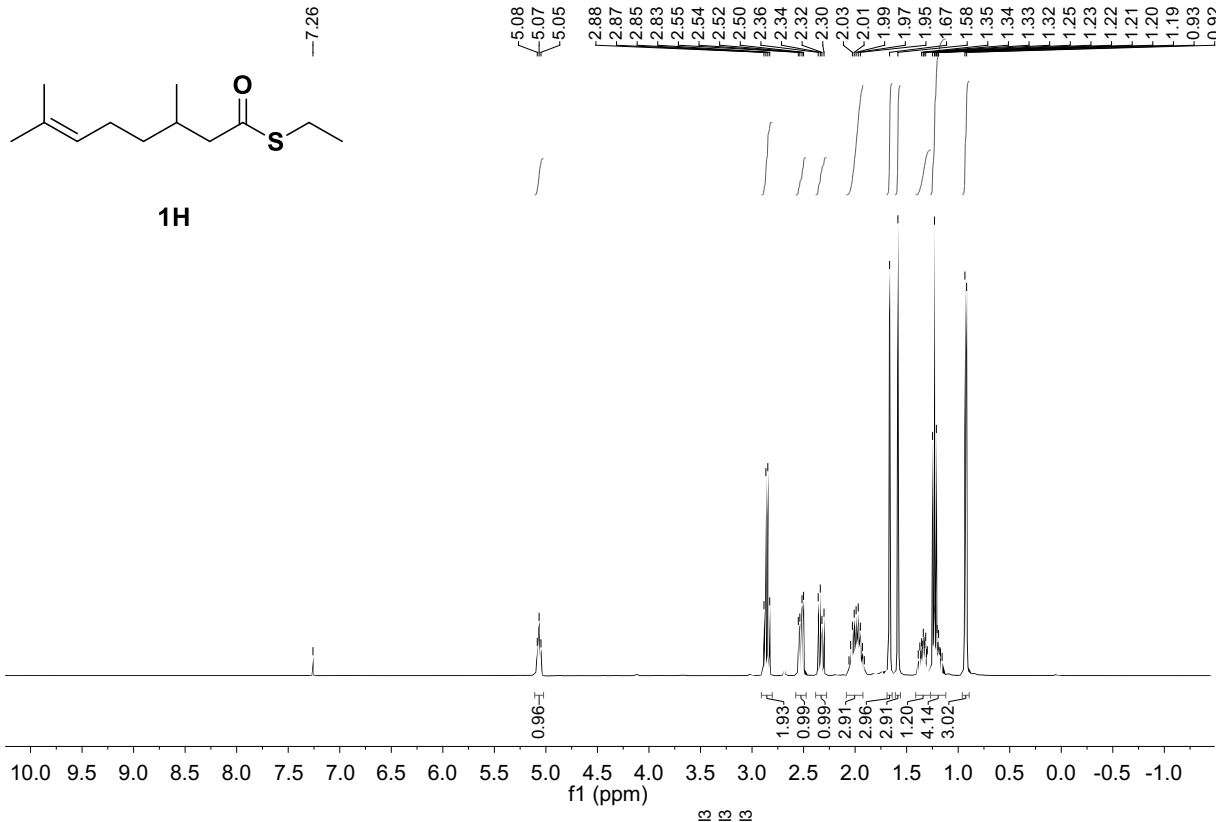
R_f: 0.26 (*n*Hex) [anis]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.11 – 5.02 (m, 1H, $CH_2CHC(CH_3)_2$), 2.86 (q, *J* = 7.4 Hz, 2H, $COSCH_2CH_3$), 2.53 (dd, *J* = 14.4, 5.9 Hz, 1H), 2.33 (dd, *J* = 14.4, 8.2 Hz, 1H), 2.10 – 1.89 (m, 3H), 1.66 (d, *J* = 1.7 Hz, 3H), 1.58 (d, *J* = 1.5 Hz, 3H), 1.41 – 1.12 (m, 5H), 0.93 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 199.3 (*C*OSEt), 131.7 ($CH_2CHC(CH_3)_2$), 124.3 ($CH_2CHC(CH_3)_2$), 51.4, 36.8, 30.9, 25.8, 25.5, 23.4, 19.5, 17.8, 14.9.

GC-MS (EI): t_r = 6.30 min, m/z(%) = 152 (19, $[M^{+\bullet}\text{-}C_2H_5S^{\bullet}]$), 69 (100, $[C_5H_9^{+\bullet}]$).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2962 (m, C-H_{aliph}), 2922 (m, C-H_{aliph}), 2872 (w, C-H_{aliph}), 2863 (w, C-H_{aliph}), 1687 (s, C=O), 1451 (m), 1377 (w), 1348 (w), 1265 (w), 1236 (w), 1209 (w), 1169 (w), 1107 (w), 1046 (w), 1004 (s), 938 (w), 889 (w), 826 (w), 753 (m), 688 (w).


7.26
5.08
5.07
5.05
2.88
2.87
2.85
2.83
2.55
2.54
2.52
2.50
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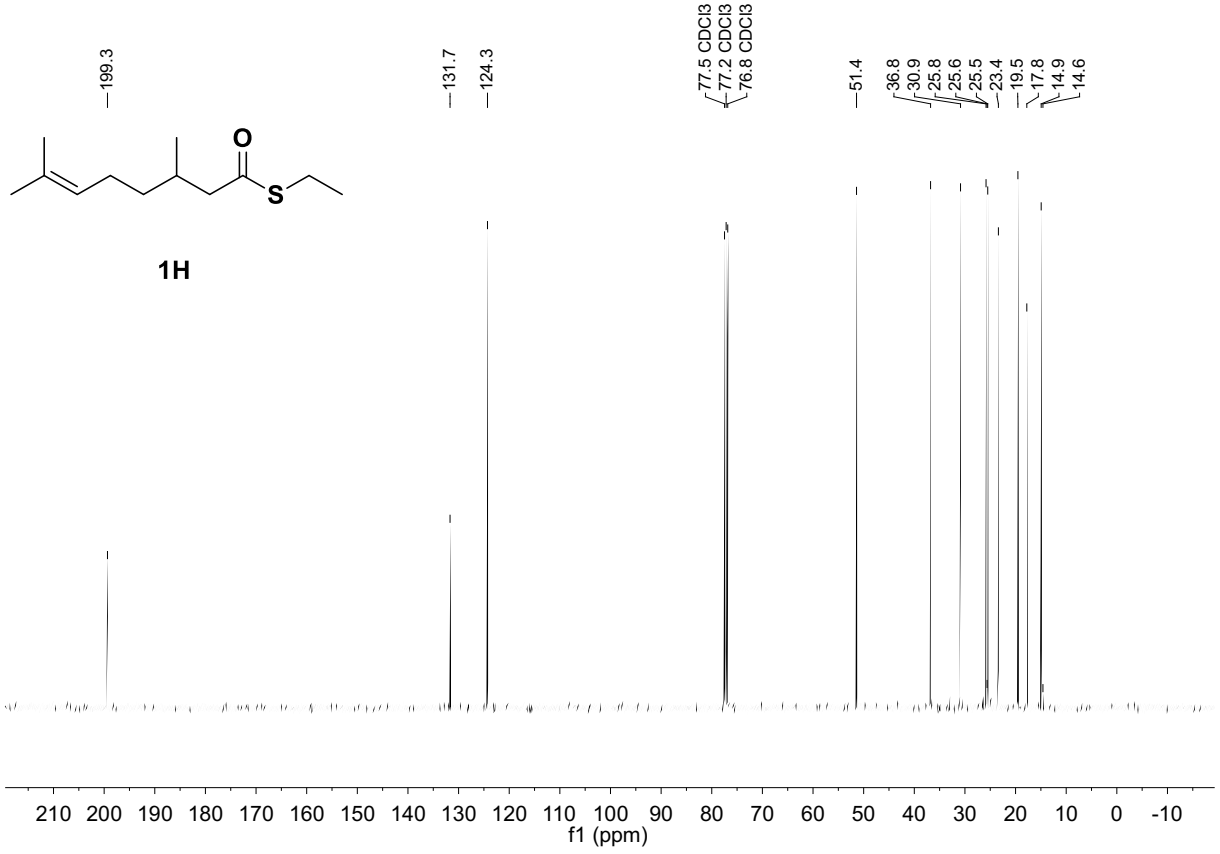
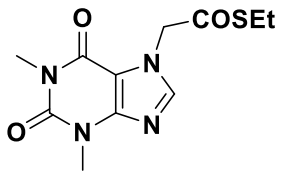
2.34
2.32
2.30
2.03
2.01
1.99
1.97
1.95
1.67
1.58
1.35
1.34
1.33
1.32
1.25
1.23
1.22
1.21
1.20
1.19
0.93
O
S
1H
0.96
1.93
0.99
0.99
2.91
2.96
2.91
1.20
4.14
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


199.3
131.7
124.3
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
51.4
36.8
30.9
25.8
25.6
25.5
23.4
19.5
17.8
14.9
14.6
O
S
1H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

S-ethyl 2-(1,3-dimethyl-2,6-dioxo-1,2,3,6-tetrahydro-7*H*-purin-7-yl)ethanethioate (**1K**)



1K

The compound **1K** was synthesized using theophylline-7-acetic acid (2.82 g, 10.0 mmol, 1.0 equiv.) and oxalyl chloride (1.0 mL, 12 mmol, 1.2 equiv.) in DCM (80 mL). After the addition of a drop of dry DMF, the reaction was stirred for 30 min at room temperature. The solvent was evaporated and residual oxalyl chloride was distilled off *in vacuo*. The crude acid chloride was suspended in DCM (40 mL) and solution of ethanethiol (790 µL, 11.0 mmol, 3 equiv.) and triethylamine (1.5 mL, 11 mmol, 1.1 equiv.) in DCM (40 mL) were added dropwise at 0 °C. The reaction stirred at room temperature for 16 h. The reaction was quenched with demineralized water (ca. 10 mL) after which a white solid precipitated. Addition of sat. aq. Na_2CO_3 sol. (ca. 20 mL) led to a clear biphasic solution. The product was recrystallized in a mixture (*n*Hex/DCM = 1:1 v/v) as a white solid (635 mg, 2.25 mmol, 23%).

$C_{11}H_{14}N_4O_3S$ (282.32 g/mol)

R_f: 0.13 (*n*Hex/EA = 1:1) [$KMnO_4$]

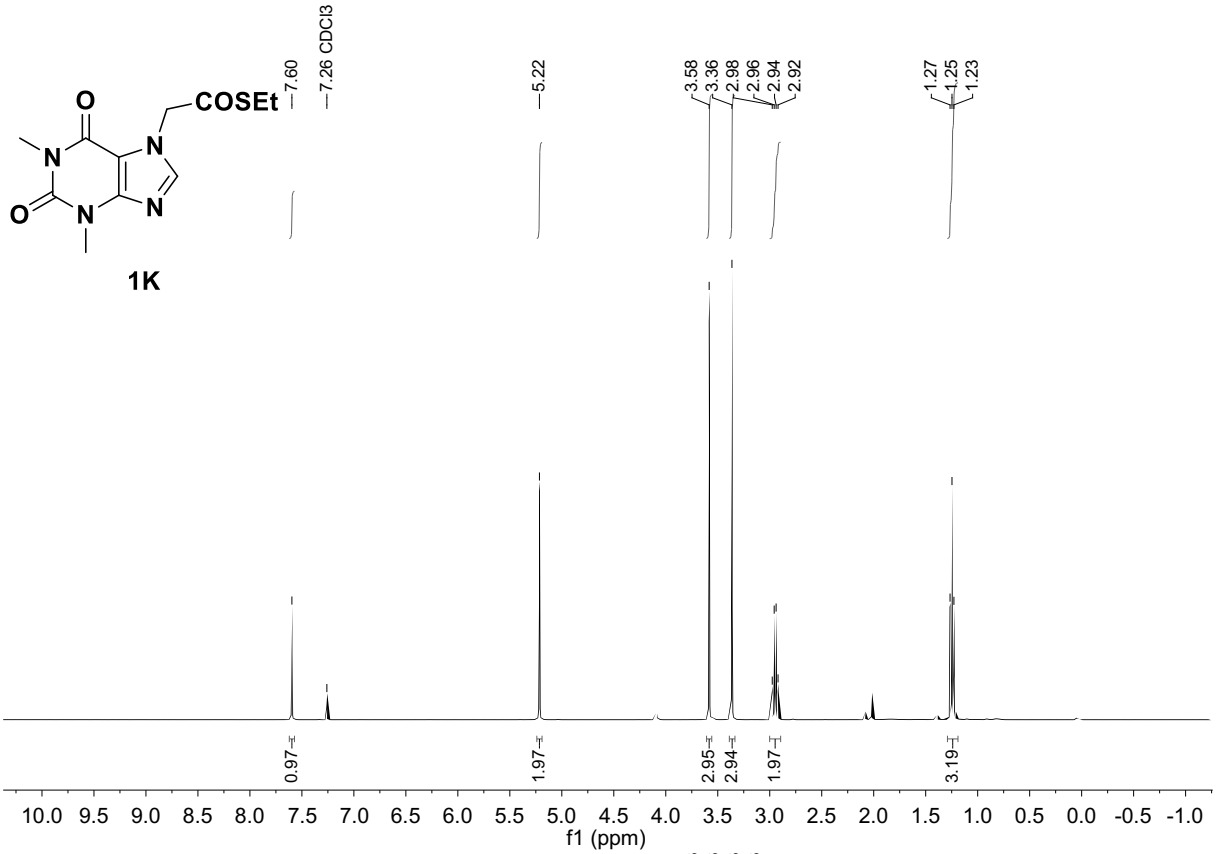
Melting point: 101.2-101.9 °C (DCM).

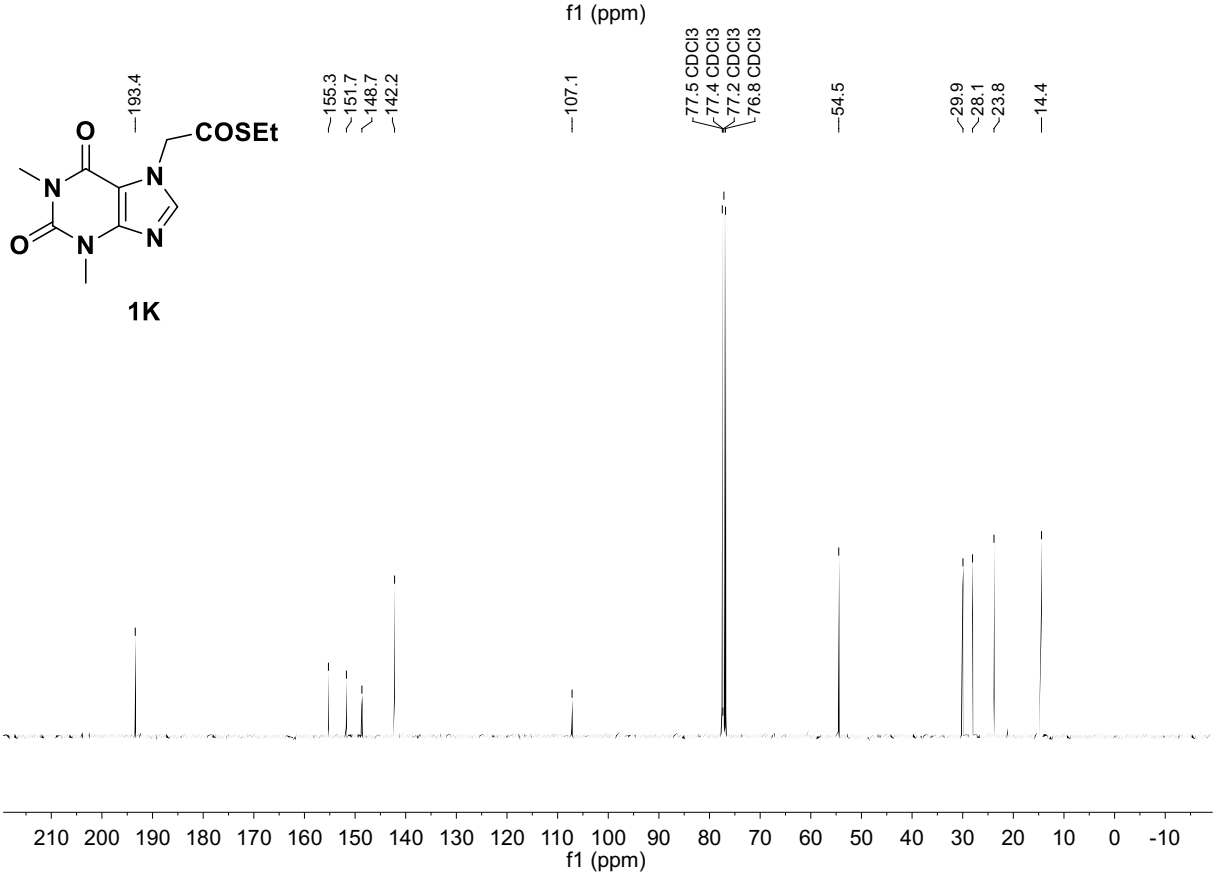
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (s, 1H, NC*H*N), 5.22 (s, 2H, NCH_2COSEt), 3.58 (s, 3H, CH_3), 3.36 (s, 3H, CH_3), 2.95 (q, *J* = 7.4 Hz, 2H, SCH_2CH$_3$), 1.25 (t, *J* = 7.4 Hz, 3H, SCH$_2$CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.4 (*C*OSEt), 155.3, 151.7, 148.7, 142.2, 107.2, 54.5, 29.9, 28.1, 23.8, 14.4.

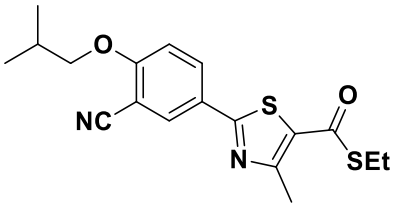
HR-MS (ESI): m/z calc. for $[M+Na]^+$305.06788, found 305.06787.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3099 (w, C-H$_{arom}$), 2982 (w, C-H$_{aliph}$), 2940 (w, C-H$_{aliph}$), 2880 (w, C-H$_{aliph}$), 1653 (s, C=O$_{thioester}$), 1604 (m), 1542 (m), 1448 (m), 1400 (m), 1370 (m), 1337 (w), 1281 (w), 1228 (m), 1184 (m), 1053 (w), 1023 (m), 968 (m), 885 (w), 822 (w), 799 (w), 740 (s).


COSEt
1K
7.60
7.26 CDCl3
5.22
3.58
3.36
2.98
2.96
2.94
2.92
1.27
1.25
1.23
0.97
1.97
2.95
2.94
1.97
3.19
f1 (ppm)


COSEt
1K
193.4
155.3
151.7
148.7
142.2
107.1
77.5 CDCl3
77.4 CDCl3
77.2 CDCl3
76.8 CDCl3
54.5
29.9
28.1
23.8
14.4
f1 (ppm)

S-ethyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carbothioate (**1L**)



1L

According to GP-A, the product **1L** was synthesized using febuxostat (2.21 g, 7.0 mmol, 1.0 equiv.), ethanethiol (1.6 mL, 21 mmol, 3 equiv.), DMAP (85.5 mg, 700 µmol, 0.1 equiv.) and DIC (1.21 mL, 7.7 mmol, 1.1 equiv.). Purification was achieved by filtration through a silica pad (PE/Et_2O = 1:1) and recrystallization in pure Et_2O. The product was yielded as slightly yellow crystals (685 mg, 1.90 mmol, 27%). The analytical data is in good accordance to literature examples.[13]

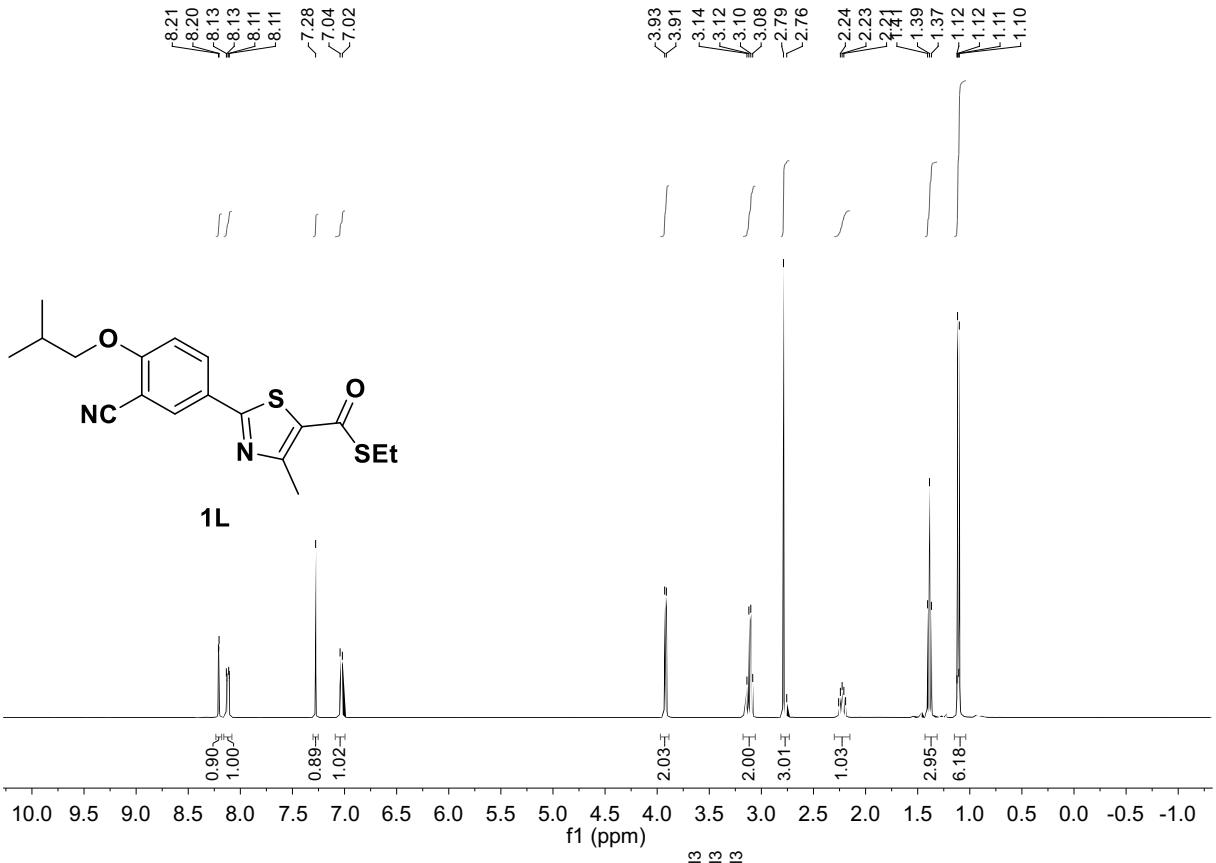
$C_{18}H_{20}N_2O_2S_2$ (360.49 g/mol)

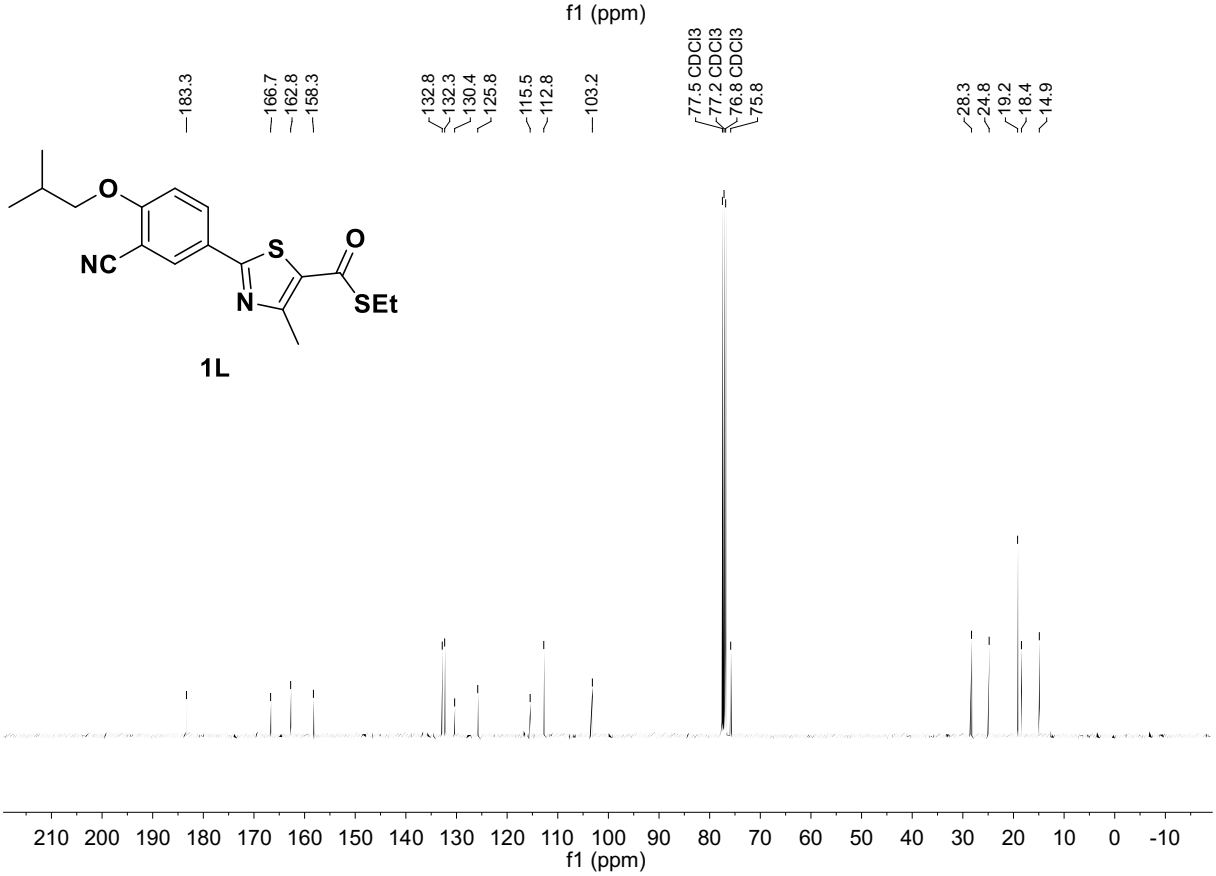
R_f: 0.32 (*n*Hex/Et_2O = 8:2) [UV]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 2.3 Hz, 1H), 8.10 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.01 (d, *J* = 8.9 Hz, 1H), 3.90 (d, *J* = 6.5 Hz, 2H), 3.09 (q, *J* = 7.4 Hz, 2H), 2.77 (s, 3H), 2.28 – 2.13 (m, 1H), 1.37 (t, *J* = 7.4 Hz, 3H), 1.09 (d, *J* = 6.7 Hz, 6H).

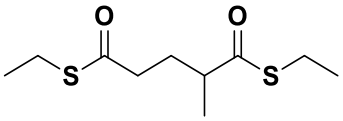
^{13}C NMR (101 MHz, $CDCl_3$): δ = 183.3 (*C*OSEt), 166.7, 162.8, 158.3, 132.8, 132.3, 130.4, 125.8, 115.5, 112.8, 103.2, 75.8, 28.3, 24.8, 19.2, 18.4, 14.9.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3084 (w, C-H_{arom}), 2965 (w, C-H_{aliph}), 2928 (w, C-H_{aliph}), 2869 (w, C-H_{aliph}), 2227 (w, C≡N),1642 (m), 1597 (w), 1500 (m), 1467 (w), 1426 (m), 1366 (m), 1288 (s), 1262 (m), 1191 (s), 1124 (m), 1028 (w), 989 (s), 956 (m), 911 (w), 870 (s), 826 (s), 766 (m), 718 (m), 673 (m).


8.21
8.20
8.13
8.13
8.11
8.11
7.28
7.04
7.02
3.93
3.91
3.14
3.12
3.10
3.08
2.79
2.76
2.24
2.23
2.21
1.41
1.39
1.37
1.12
1.12
1.11
1.10
O
NC
S
N
O
SEt
1L
0.90
1.00
0.89
1.02
2.03
2.00
3.01
1.03
2.95
6.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


183.3
166.7
162.8
158.3
132.8
132.3
130.4
125.8
115.5
112.8
103.2
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
75.8
28.3
24.8
19.2
18.4
14.9
O
NC
S
N
O
SEt
1L
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

S,S-diethyl 2-methylpentanebis(thioate) (**4**)



4

According to GP-A, the product **4** was synthesized using 2-methyl glutaric acid (1.46 g, 10.0 mmol, 1.0 equiv.), ethanethiol (3.6 mL, 50.0 mmol, 5.0 equiv.), DMAP (244.34 mg, 2 mmol, 0.1 equiv.) and DCC (4.54 g, 22 mmol, 2.2 equiv.). Purification achieved by filtration through a silica pad (PE/EA = 9:1 v/v). The combined organic layers were extracted solution with 6 M HCl (2 × 30 mL), aq. KOH sol. (2 × 30 mL, 10% w/v), sat. $NaHCO_3$ (1 × 20 mL) and brine (1 × 20 mL). The product was yielded as a colorless oil (2.00 g, 8.56 mmol, 86%). The analytical data is in good accordance to literature examples.[13]

$C_{10}H_{18}O_2S_2$ (234.37 g/mol)

R_f: 0.67 (*n*Hex/EA = 9:1) [$KMnO_4$, anis – yellow, UV - weak]

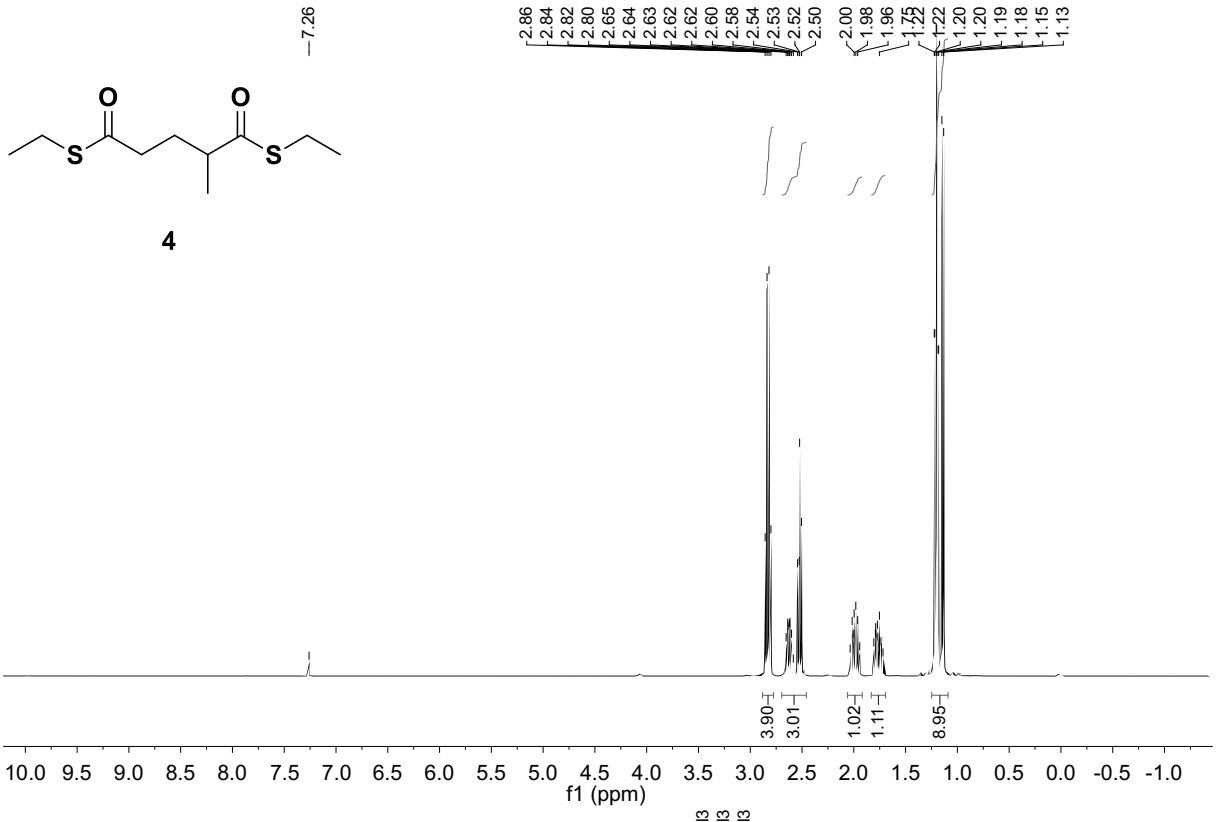
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.83 (qd, *J* = 7.4, 0.7 Hz, 4H), 2.70 – 2.46 (m, 3H), 2.06 – 1.91 (m, 1H), 1.83 – 1.71 (m, 1H), 1.25 – 1.10 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 203.0 (*C*OSEt), 198.8 (*C*OSEt), 47.5, 41.4, 29.3, 23.4, 23.2, 17.8, 14.8.

HR-MS (ESI): m/z calc. for $[M+Na]^+$ 257.06404, found 257.06442.

GC-MS (EI, method B): t_r = 19.14 min, m/z(%) = 173 (100, $[M^{+\bullet}- C_2H_5S^\bullet]$), 145 (39, $[M^{+\bullet}-C_2H_5S^\bullet-CO]$), 89 (56, $[C_3H_5OS^\bullet]$).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2969 (w, C-H_{aliph}), 2931 (w, C-H_{aliph}), 2872 (w, C-H_{aliph}), 1679 (vs, C=O), 1452 (m), 1414 (w), 1374 (w), 1314 (w), 1262 (w), 1191 (w), 1127 (w), 1049 (m), 1020 (m), 957 (vs), 892 (m), 814 (w), 741 (m), 691 (w).


7.26
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2.64
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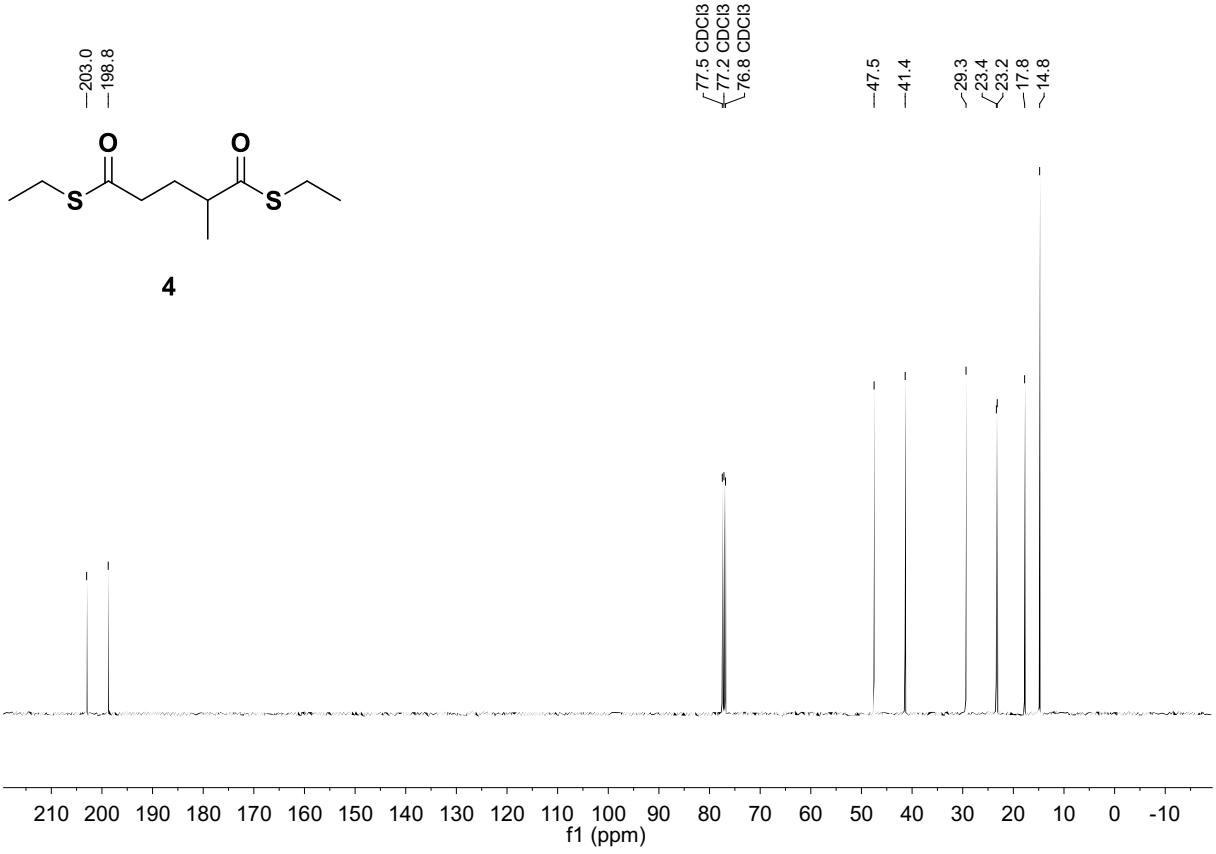
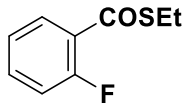
2.62
2.62
2.60
2.58
2.54
2.53
2.52
2.50
2.00
1.98
1.96
1.22
1.20
1.20
1.19
1.18
1.15
1.13
O
O
S
S
4
3.90
3.01
1.02
1.11
8.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


203.0
198.8
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
47.5
41.4
29.3
23.4
23.2
17.8
14.8
O
O
S
S
4
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

S-ethyl 2-fluorobenzothioate (**8**)



8

According to GP-A, the product **8** was synthesized using 2-fluorobenzoic acid (700.6 mg, 5.00 mmol, 1.0 equiv.), ethanethiol (1.1 mL, 15.0 mmol, 3 equiv.), DMAP (61.1 mg, 500 µmol, 0.1 equiv.) and DCC (1.13 g, 5.50 mmol, 1.1 equiv.). Purification was achieved by filtration through a short silica plug using DCM and washing the filtrate with 6 M HCl (2 × 20 mL), sat. $NaHCO_3$ (1 × 20 mL) and brine (1 × 20 mL). The product was obtained as a colorless oil (812 mg, 4.40 mmol, 88%).

C_9H_9FOS (184.23 g/mol)

R_f: 0.44 (*n*Hex/EA = 30:1) [UV]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (td, *J* = 7.5, 1.8 Hz, 1H), 7.49 (dddd, *J* = 8.2, 7.3, 5.0, 1.8 Hz, 1H), 7.20 (td, *J* = 7.6, 1.1 Hz, 1H), 7.13 (ddd, *J* = 10.8, 8.3, 1.1 Hz, 1H), 3.07 (q, *J* = 7.4 Hz, 2H), 1.35 (t, *J* = 7.4 Hz, 3H).

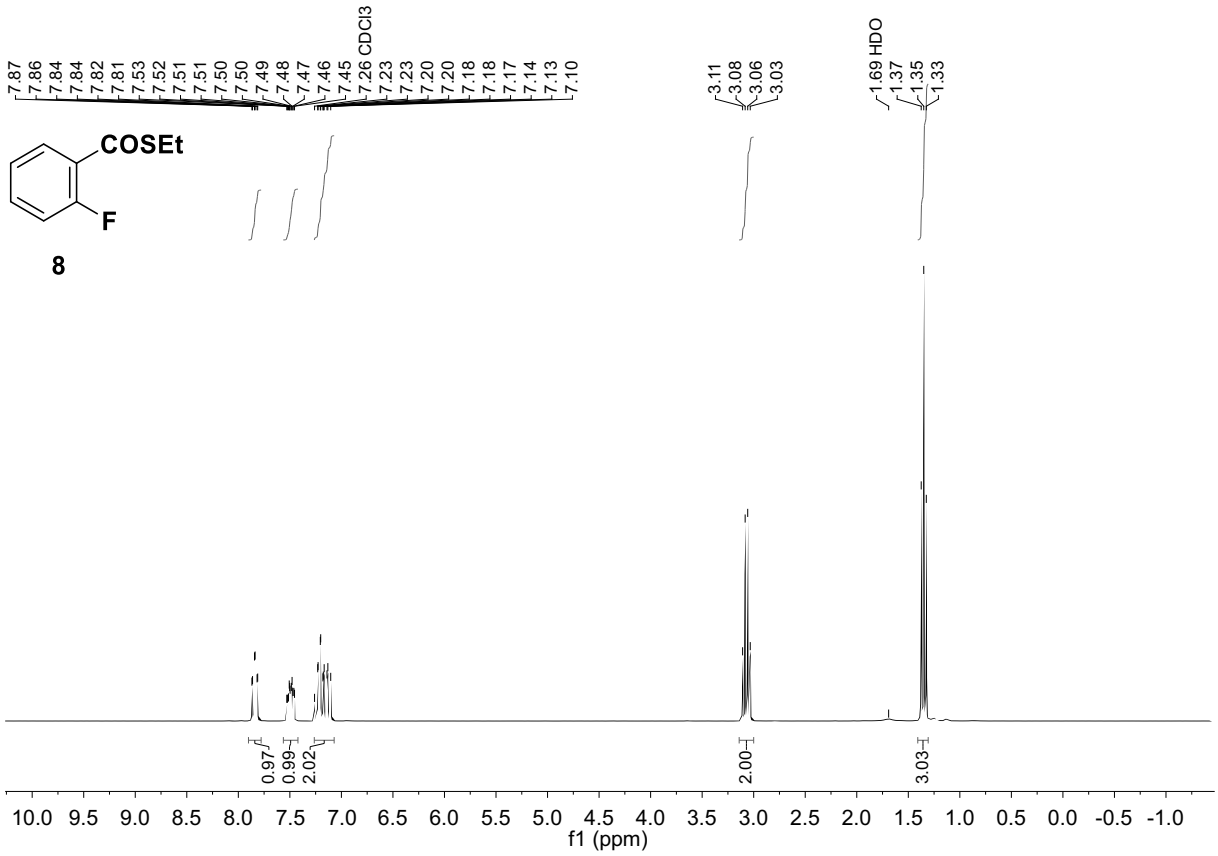
^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.1 (d, J^3_{C-F} = 4.5 Hz), 160.4 (d, J^1_{C-F} = 257.6 Hz), 134.2 (d, J^3_{C-F} = 8.9 Hz), 129.8 (d, J^4_{C-F} = 1.7 Hz), 125.9 (d, J^2_{C-F} = 11.4 Hz), 124.3 (d, J^3_{C-F} = 3.7 Hz), 117.0 (d, J^2_{C-F} = 22.3 Hz), 23.9 (CH_2CH_3), 14.6(CH_2CH_3)

^{19}F NMR (376 MHz, $CDCl_3$): δ = -111.1 (s).

GC-MS (EI): t_r = 5.65 min, m/z = 184 (6, $[M^{+\bullet}]$), 123 (100, $[M^{+\bullet}\text{-}C_2H_5S^{\bullet}]$), 95 (26, $[M^{+\bullet}\text{-}C_2H_5S^{\bullet}\text{-}CO]$).

HR-MS (ESI): m/z calc. for $[M+Na]^+$ 207.02503, found 207.02529.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3074 (w, C-H_{arom}), 3040 (w, C-H_{arom}), 2972 (w, C-H_{aliph}), 2931 (w, C-H_{aliph}), 2872 (w, C-H_{aliph}), 1668 (s, C=O), 1645 (s), 1605 (s), 1579 (w), 1481 (s), 1448 (s), 1414 (w), 1377 (w), 1266 (s), 1225 (m), 1195 (s), 1153 (m), 1105 (m), 971 (w), 912 (vs), 807 (m), 759 (vs).


7.87
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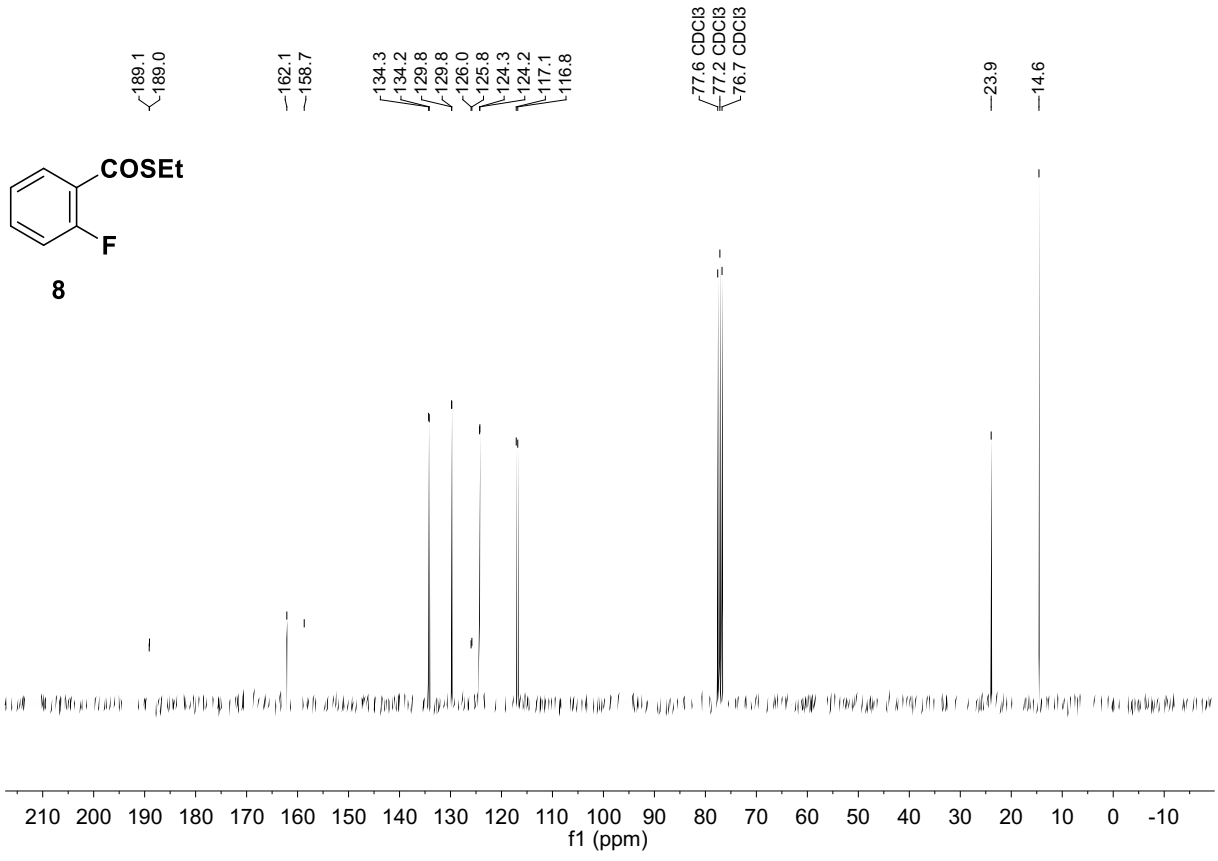
7.84
7.84
7.82
7.81
7.53
7.52
7.51
7.51
7.50
7.50
7.49
7.48
7.47
7.46
7.45
7.26 CDCl3
7.23
7.20
7.20
7.18
7.18
7.17
7.14
7.13
7.10
3.11
3.08
3.06
3.03
1.69 HDO
1.37
1.35
1.33
COSEt
F
8
0.97
0.99
2.02
2.00
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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189.0
162.1
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134.3
134.2
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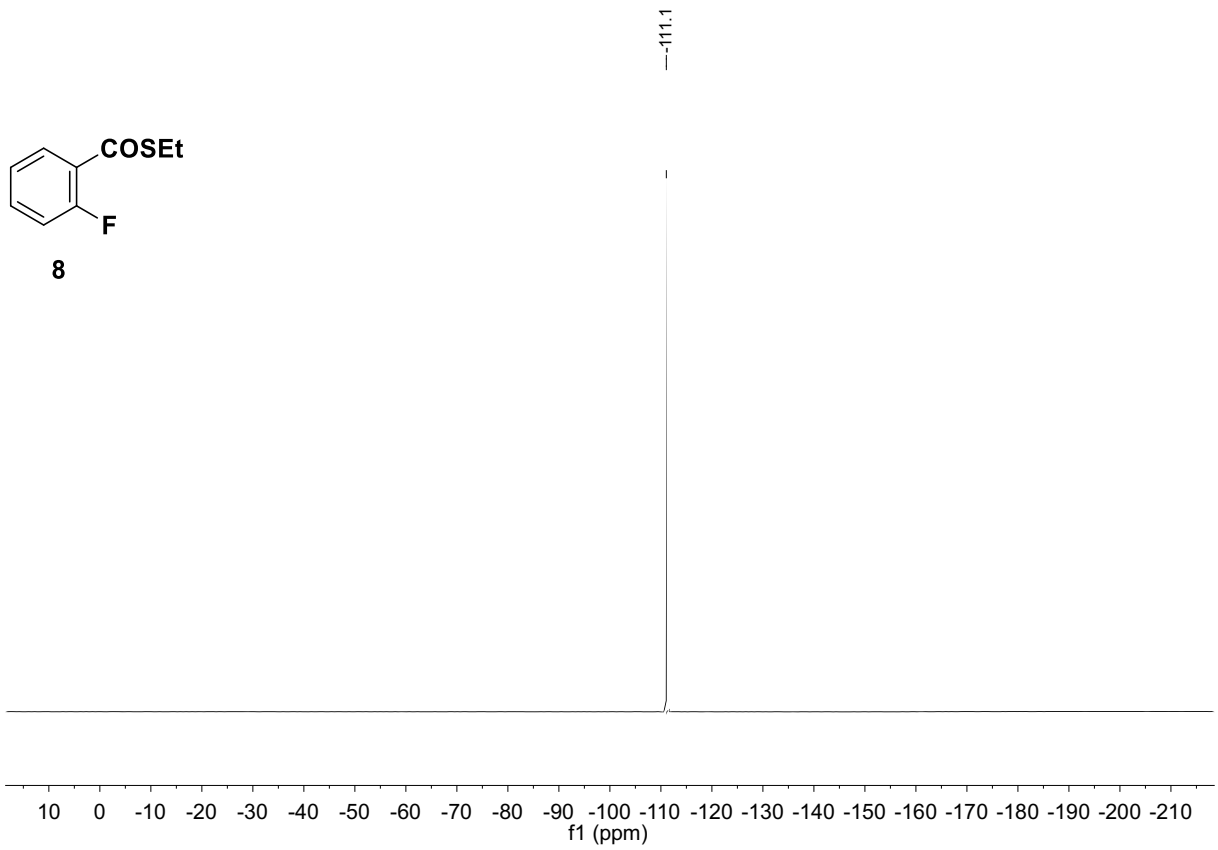
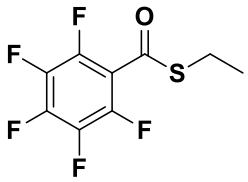
117.1
116.8
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
23.9
14.6
COSEt
F
8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-111.1
COSEt
F
8
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

S-ethyl 2,3,4,5,6-pentafluorobenzothioate (**10**)



10

The compound **10** was synthesized after a modified GP-B. Ethanethiol (792 µL, 11.0 mmol, 1.1 equiv.) and triethylamine (1.39 mL, 10.0 mmol, 1.0 equiv.) were dissolved in 50 mL *n*-hexane. After cooling the mixture to 0 °C, 2,3,4,5,6-pentafluorobenzoyl chloride (1.44 mL, 10.0 mmol) was added slowly over 5 min to the reaction mixture. The reaction was allowed to warm to room temperature and stirred for 12 h. The reaction mixture was quenched with the addition of 10 mL demineralized water. The organic layer was extracted sat. $NaHCO_3$ solution (2 × 30 mL) and brine (1 × 30 mL). The organic layer was dried using $MgSO_4$. The product was obtained as a colorless oil (1.92 g, 7.49 mmol, 75%).

$C_9H_{15}F_5OS$ (256.19 g/mol)

R_f: 0.36 (*n*Hex) [$KMnO_4$, UV]

^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.14 (q, *J* = 7.4 Hz, 2H, COC*H*$_2$CH$_3$), 1.39 (td, *J* = 7.4, 0.9 Hz, 3H, COCH$_2$C*H*$_3$).

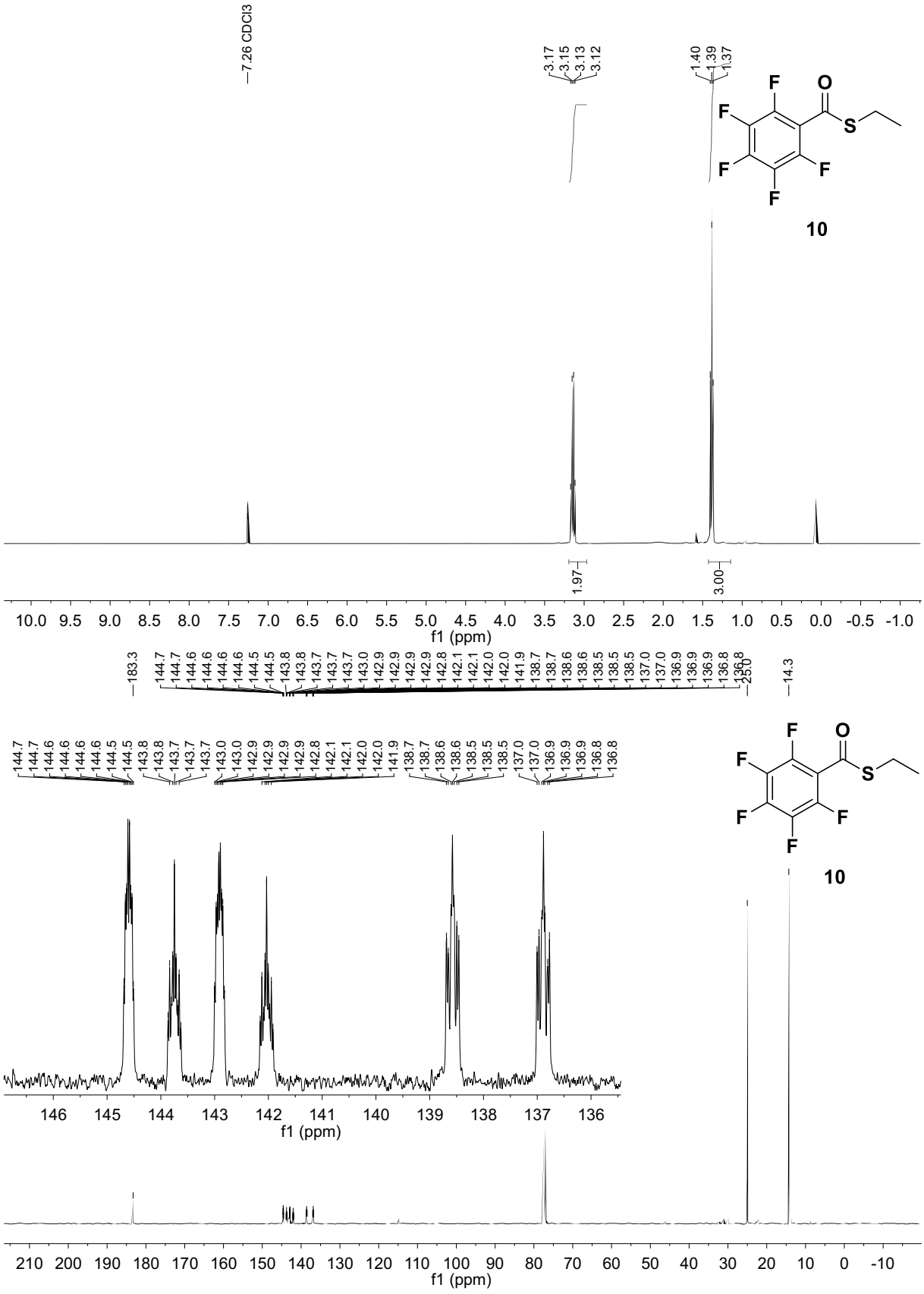
^{13}C NMR (151 MHz, $CDCl_3$): δ = 183.3 (*C*OSEt), 143.8 (dddd, *J* = 255.1, 15.6, 7.5, 4.4 Hz, C_{Ar}F), 142.9 (dtt, *J* = 258.8, 13.2, 4.4 Hz), 137.7 (dddd, *J* = 254.4, 16.7, 13.2, 5.1 Hz), 25.0 (S*C*H$_2$CH$_3$), 14.3 (SCH$_2$H$_3$).

^{19}F NMR (376 MHz, $CDCl_3$): δ = -139.7 – -142.1 (m), -149.70 (tt, *J* = 20.8, 3.3 Hz), -159.8 – -160.0 (m).

HR-MS (APCI): m/z calc. for $[M+H]^+$ 257.00540, found 257.00565.

GC-MS (EI): t_r = 5.37 min, m/z = 256 (53, $[M^{+\bullet}]$), 195 (100, $[M^{+\bullet}\text{-}C_2H_5S^{\bullet}]$), 167 (32, $[M^{+\bullet}\text{-}C_2H_5S^{\bullet}\text{-CO}]$).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2976 (w, C-H$_{aliph}$), 2936 (w, C-H$_{aliph}$), 2879 (w, C-H$_{aliph}$), 1668 (s, C=O), 1492 (vs), 1414 (m), 1377 (w), 1314 (s), 1265 (w), 1131 (vs), 1053 (w), 979 (vs), 811 (vs), 770 (s), 725 (s).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3.13
3.12
1.40
1.39
1.37
F
O
F
S
F
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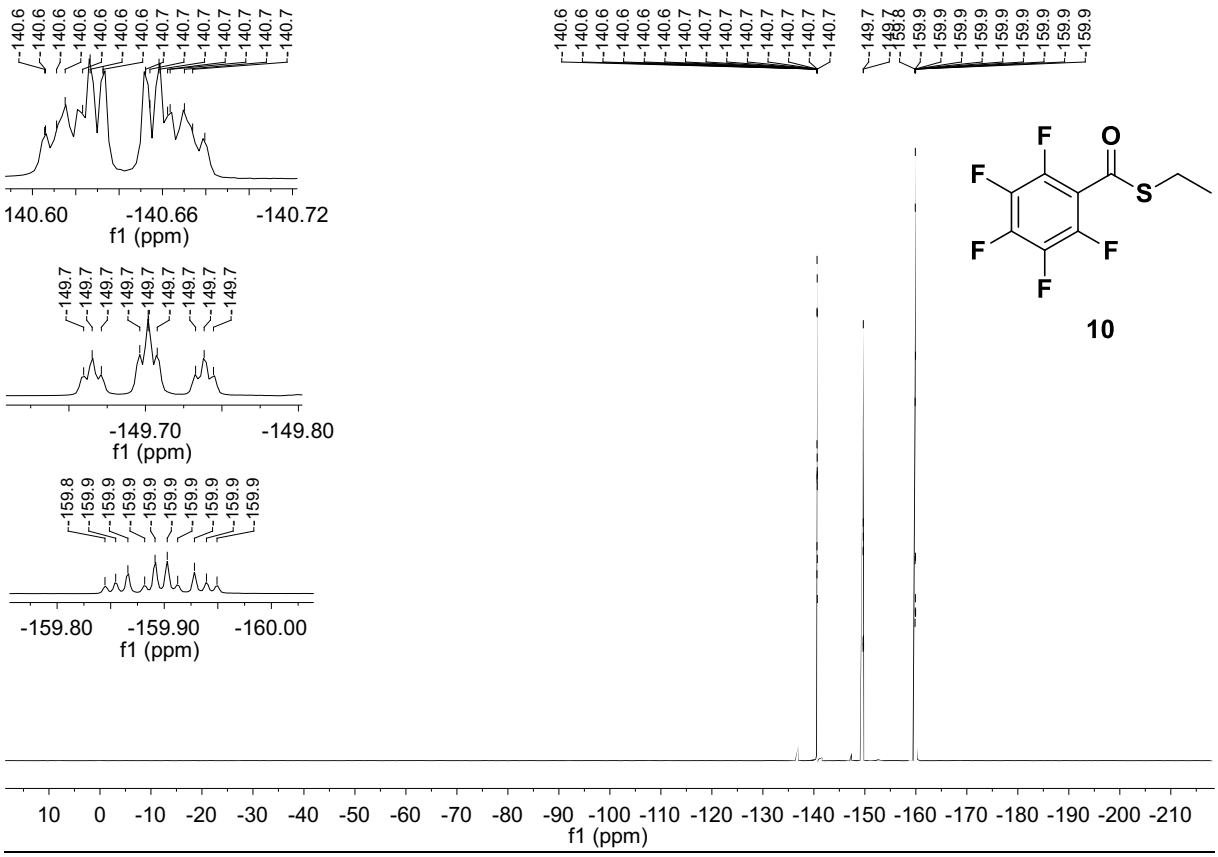
10
1.97
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
183.3
144.7
144.6
144.5
143.8
143.7
143.0
142.9
142.8
142.1
142.0
141.9
138.7
138.6
138.5
137.0
136.9
136.8
CDCl3
14.3
146 145 144 143 142 141 140 139 138 137 136
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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-140.66
-140.72
f1 (ppm)
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-149.80
-159.8
-159.9
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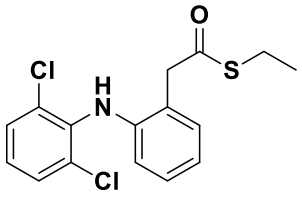
-159.9
F
O
S
10
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

S-ethyl 2-(2-((2,6-dichlorophenyl)amino)phenyl)ethanethioate (**12**)



12

According to GP-A, the product **12** was synthesized using diclofenac (2.96 g, 10.0 mmol, 1.0 equiv.), ethanethiol (2.2 mL, 30 mmol, 3 equiv.), DMAP (122 mg, 1.00 mmol, 0.1 equiv.) and DCC (2.27 g, 11.0 mmol, 1.1 equiv.). Purification was achieved by fritting through a silica plug (nHex/EA = 1:1 v/v + few drops NEt_3). Afterwards, the solvents were evaporated. Then, the crude solid was redissolved in EA (ca. 20 mL) and extracted with 6 M aq. HCl (2 × 20 mL). The organic layer was reduced *in vacuo* and *n*Hex added. The hydrochloride salt crystallized at –20 °C. The solids were separated from the solvent, washed with *n*Hex and afterwards redissolved in EA (ca. 40 mL). After this, the solution was extracted with aq. KOH solution (10% w/v) and solvents evaporated. The product was yielded as a lightly brown solid (599 mg, 1.76 mmol, 18%).

$C_{16}H_{15}Cl_2NOS$ (340.26 g/mol)

R_f: 0.20 (*n*Hex/Et_2O = 8:2) [UV]

Melting point: 77.0 –77.7 °C (EA).

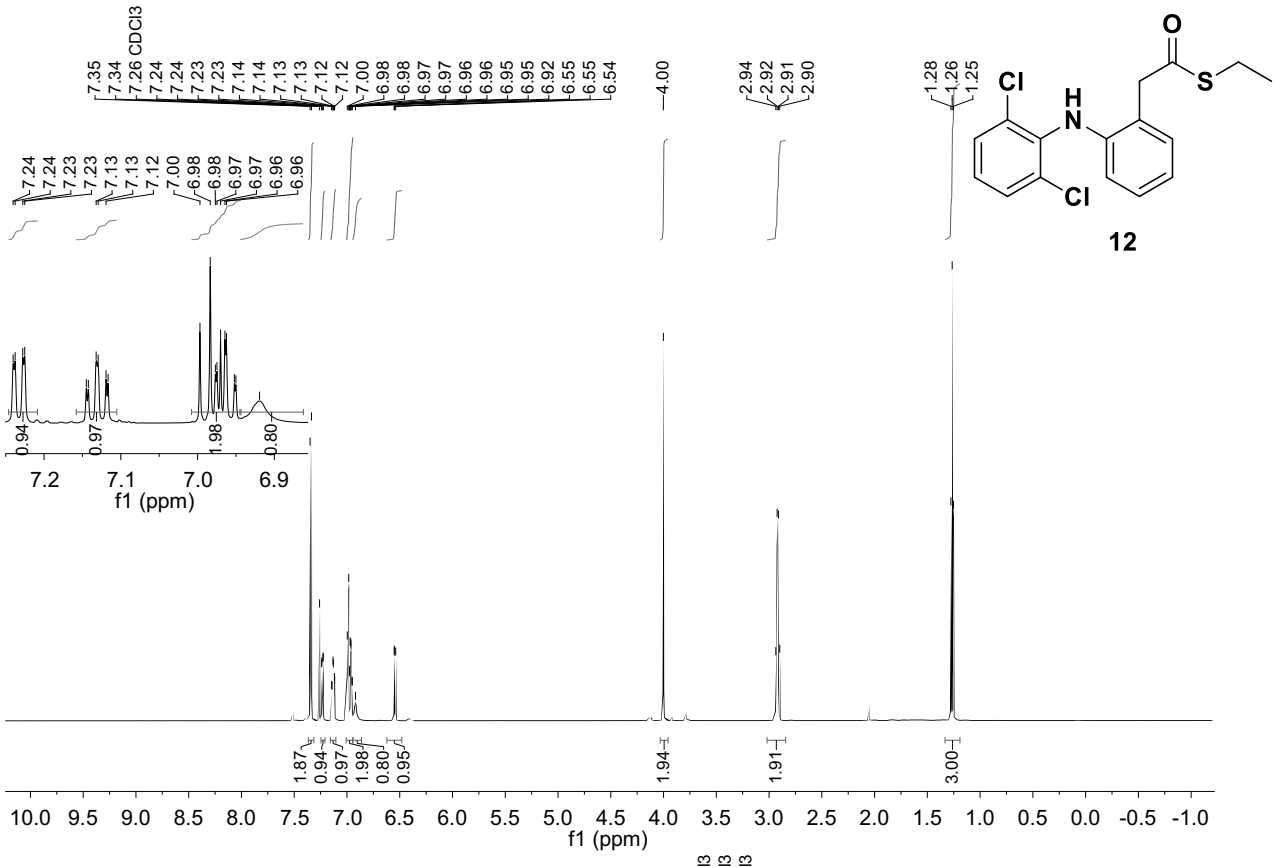
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.23 (dd, *J* = 7.5, 1.5 Hz, 1H, Ar*H*), 7.13 (td, *J* = 7.8, 1.6 Hz, 1H, Ar*H*), 7.02 – 6.94 (m, 2H, Ar*H*), 6.92 (br s, *J* = 5.1 Hz, 1H, N*H*), 6.54 (dd, *J* = 8.0, 1.1 Hz, 1H, Ar*H*), 4.00 (s, 2H, ArCH_2), 2.92 (q, *J* = 7.4 Hz, 2H, CH_2CH_3), 1.26 (t, *J* = 7.4 Hz, 3H, CH_2CH_3).

^{13}C NMR (151 MHz, $CDCl_3$): 199.0 (*C*OSEt), 142.9 (C_{Ar}), 137.9 (C_{Ar}), 131.1 (C_{Ar}), 129.7 (C_{Ar}), 129.0 (C_{Ar}), 128.3 (C_{Ar}), 124.6 (C_{Ar}), 124.2 (C_{Ar}), 122.1 (C_{Ar}), 118.3 (C_{Ar}), 47.8, 24.0, 14.7.

HR-MS (ESI): m/z calc. for $[M+Na]^+$ 362.01436, found 362.01450.

GC-MS (EI): t_r = 11.36 min, m/z(%) = 339 (6, $[M^{+\bullet}]$), 278 (53, $[M^{+\bullet}\text{-}SC_2H_5^{\bullet}]$), 214 (100).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3290 (w, br, N-H), 2924 (w, C-H_{aliph}), 1735 (w), 1661 (m, C=O), 1575 (w), 1500 (m), 1448 (m), 1410 (w), 1292 (w), 1243 (w), 1195 (w), 1169 (w), 1095 (w), 1042 (w), 1012 (m), 971 (w), 915 (w), 870 (w), 837 (w), 769 (m), 743 (s), 703 (m), 672 (m).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7.14
7.13
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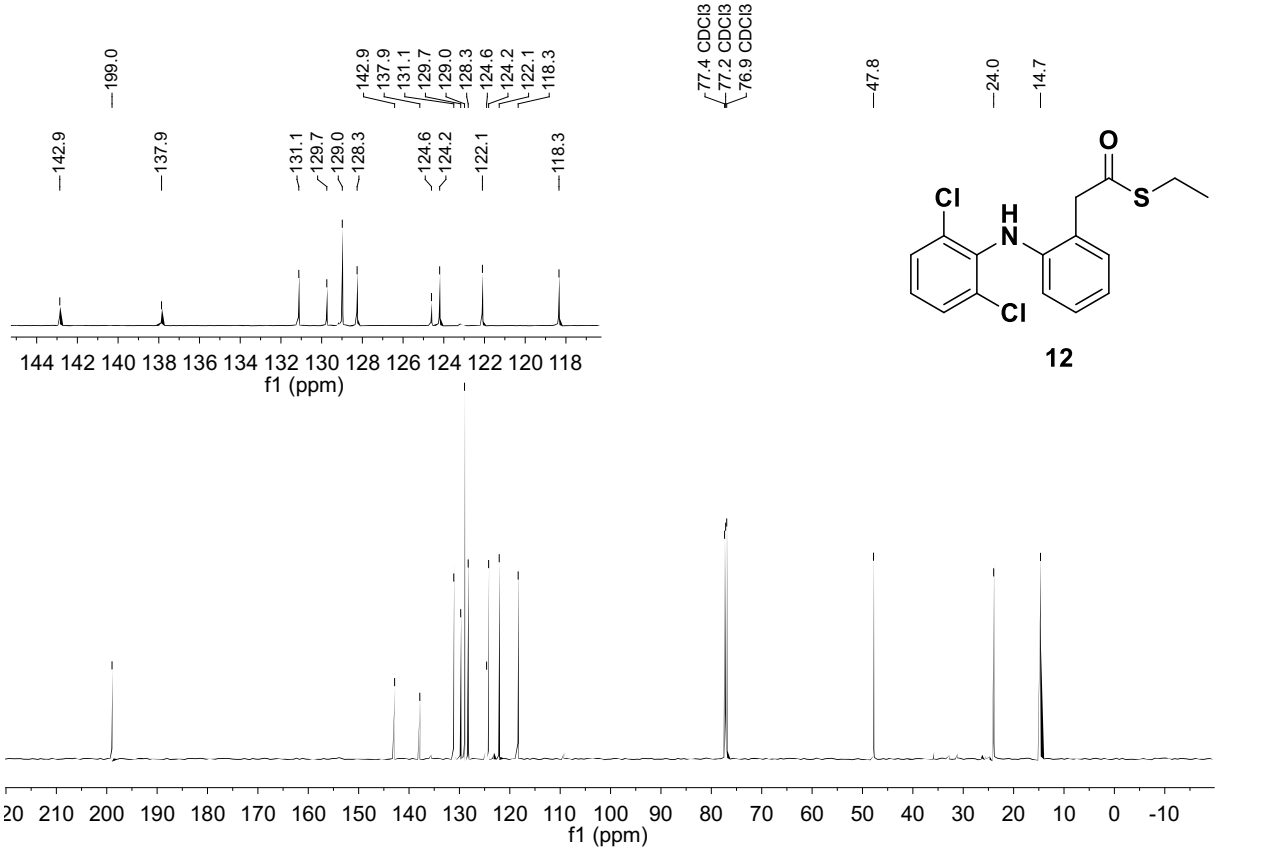
6.95
6.95
6.92
6.55
6.55
6.54
4.00
2.94
2.92
2.91
2.90
1.28
1.26
1.25
0.94
0.97
1.98
0.80
7.2
7.1
7.0
6.9
f1 (ppm)
1.87
0.94
0.97
1.98
0.80
0.95
1.94
1.91
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
Cl
H
N
Cl
O
S
12


199.0
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137.9
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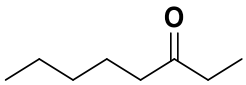
129.0
128.3
124.6
124.2
122.1
118.3
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
47.8
24.0
14.7
144 142 140 138 136 134 132 130 128 126 124 122 120 118
f1 (ppm)
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
Cl
H
N
Cl
O
S
12

6. Analytical Data of Products

octan-3-one (**3aa**)



3aa

According to GP-E, the product **3aa** was synthesized using ethyl manganese bromide lithium chloride complex (0.25 M, 4.80 mL, 1.20 mmol, 1.2 equiv.) and *S*-ethyl hexanethioate ester **1aa** (160 mg, 1.00 mmol). Purification was achieved by column chromatography (*n*Hex/Et_2O = 30:1 v/v). The product was obtained as a colorless oil with a pleasant flowery smell (100 mg, 780 µmol, 78%). The analytical data is in good accordance to reported literature.[15]

$C_8H_{16}O$ (128.22 g/mol)

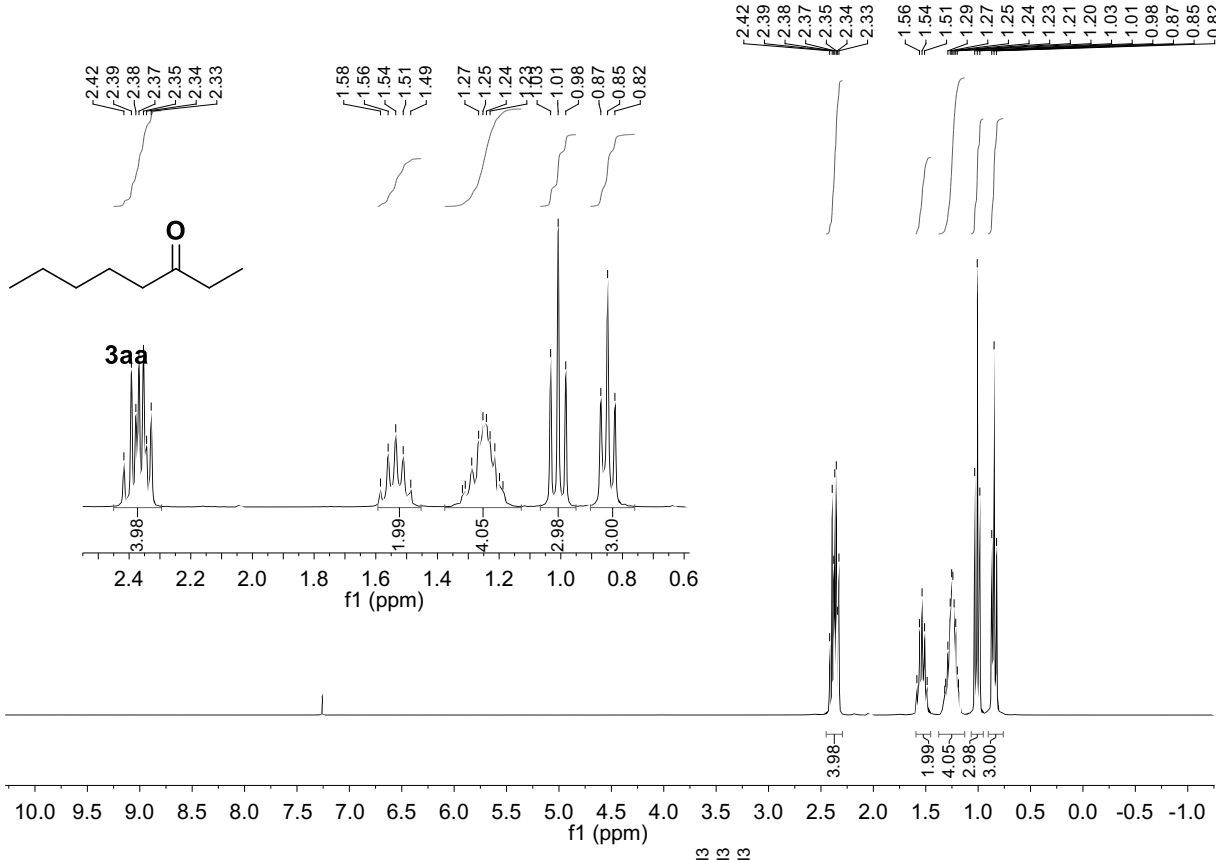
R_f: 0.47 (*n*Hex/Et_2O = 30:1) [anis - blue]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.44 – 2.27 (m, 4H), 1.54 (p, *J* = 7.4 Hz, 2H), 1.33 – 1.13 (m, 4H), 1.01 (t, *J* = 7.3 Hz, 3H), 0.85 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 212.0 (*C*O), 42.5, 35.9, 31.5, 23.7, 22.5, 14.0, 7.9.

GC-MS (EI): t_r = 2.80 min, m/z(%) = 128 (3, [$M^{+\bullet}$]), 99 (40, [$M^{+\bullet}$-$C_2H_5^{\bullet}$]), 57 (100).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2973 (w, C-H_{aliph}), 2939 (w, C-H_{aliph}), 2909 (w, C-H_{aliph}), 2835 (w, C-H_{aliph}), 1683 (s, C=O), 1586 (s), 1482 (m), 1456 (m), 1429 (m), 1344 (m), 1322 (m), 1284 (m), 1251 (s), 1198 (s), 1169 (s), 1083 (w), 1042 (s), 967 (m), 874 (w), 837 (m), 777 (s), 728 (w), 684 (s).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1.58
1.56
1.54
1.51
1.49
1.27
1.25
1.24
1.23
1.03
1.01
0.98
0.87
0.85
0.82
1.56
1.54
1.51
1.29
1.27
1.25
1.24
1.23
1.21
1.20
1.03
1.01
0.98
0.87
0.85
O
3aa
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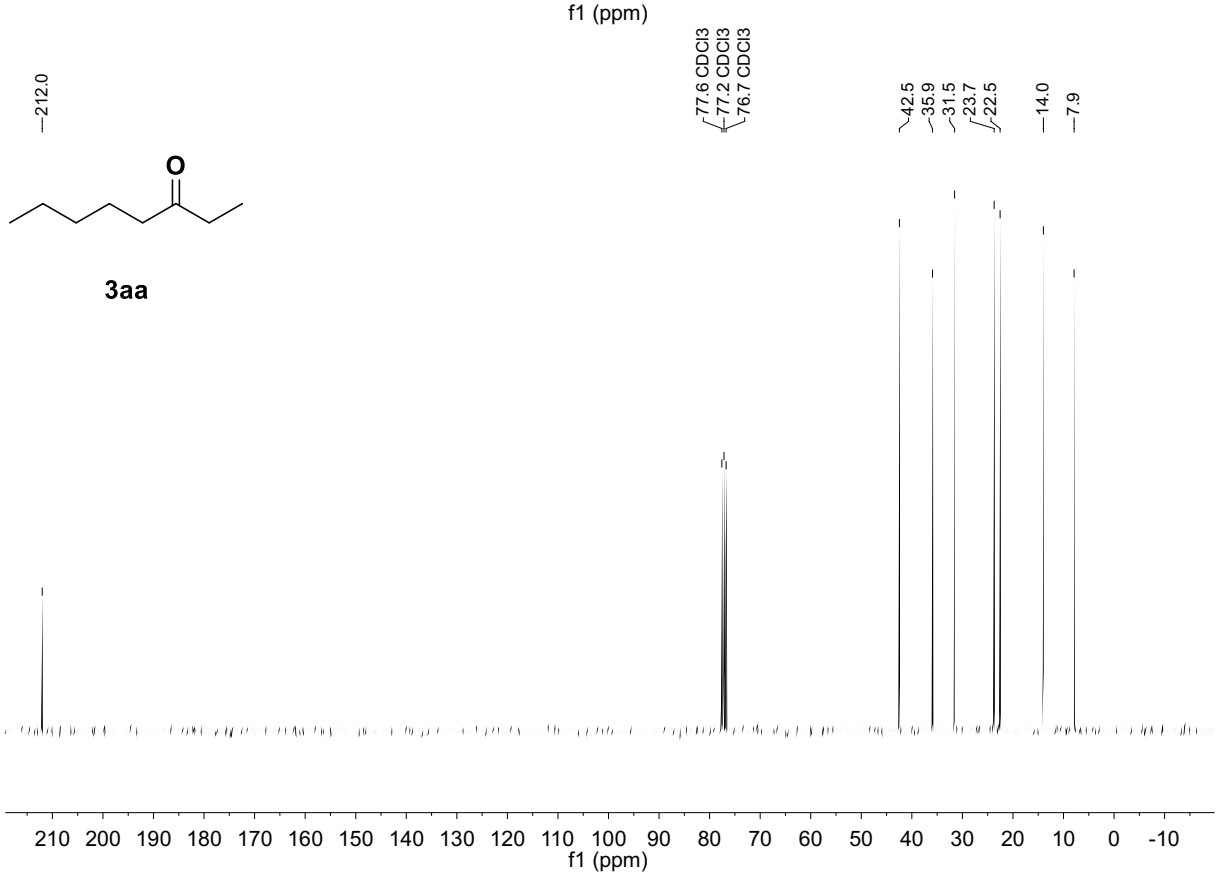
1.99
4.05
2.98
3.00
f1 (ppm)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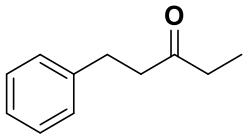
77.2 CDCl3
76.7 CDCl3
42.5
35.9
31.5
23.7
22.5
14.0
7.9
O
3aa
f1 (ppm)

1-phenylpentan-3-one (**3ba**)



3ba

According to GP-E, the product **3ba** was synthesized using ethylmanganese bromide lithium chloride complex (0.28 M, 4.3 mL, 1.2 mmol, 1.2 equiv.) and *S*-ethyl 3-phenylpropanethioate **1b** (194 mg, 1.00 mmol). Purification was achieved by column chromatography (*n*Hex/Et_2O = 9:1 v/v). The product was obtained as a colorless oil (154 mg, 950 µmol, 95%). The analytical data is in good accordance with the reported literature.[16]

Upscale Experiment:

The reaction was set up with the following changes: *S*-ethyl 3-phenylpropanethioate **1b** (1.00 g, 5.15 mmol), iron(III) acetyl acetonate (90.9 mg, 257 µmol, 0.05 equiv.) were dissolved in THF (15 mL not degassed) and cooled to -20 °C. Then, ethylmanganese bromide lithium chloride complex (0.22 M, 28 mL, 6.2 mmol, 1.2 equiv.) was added in 3 portions and the reaction stirred for 10 min at the same temperature. The reaction was quenched with aq. sat. NH_4Cl solution (30 mL). The solution was diluted with ethyl acetate (20 mL) and the aq. layer extracted with the same solvent (3 × 30 mL). Purification was achieved by manual column chromatography (*n*Hex/EA = 98:2 v/v) to yield a colorless oil (742 mg, 4.57 mmol, 89%).

$C_{11}H_{14}O$ (162.23 g/mol)

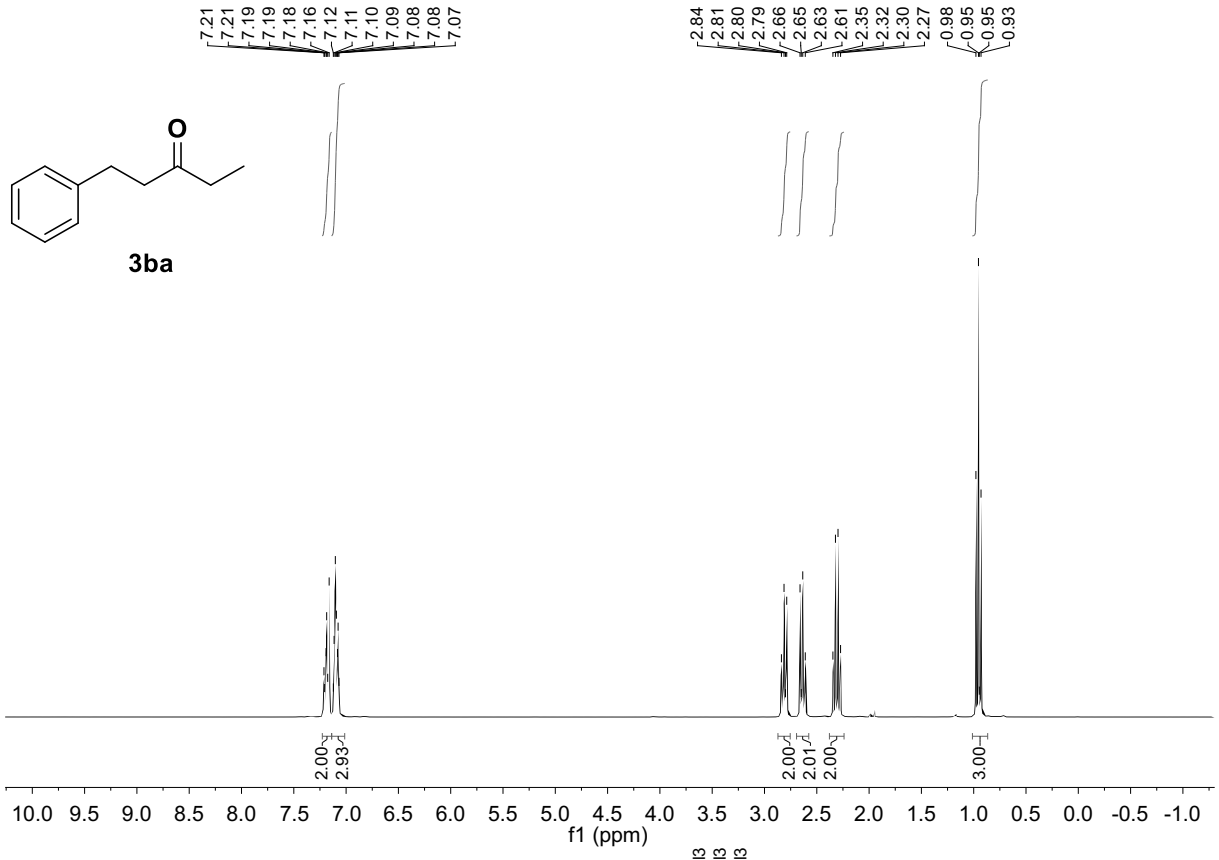
R_f: 0.30 (*n*Hex/Et_2O = 9:1) [$KMnO_4$]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22–7.16 (m, 2H), 7.13– 7.07 (m, 3H), 2.84 – 2.79 (m, 2H), 2.67– 2.63 (m, 2H), 2.31 (q, *J* = 7.3 Hz, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 210.6 (*C*O), 141.2 (C_{Ar}), 128.5 (C_{Ar}), 128.4 (C_{Ar}), 126.1 (C_{Ar}), 43.9, 36.2, 29.9, 7.8 (CH_2CH_3).

GC-MS (EI): t_r = 5.37 min, m/z(%) = 162 (49, [$M^{+\bullet}$]), 133 (39,[$M^{+\bullet}$-$C_2H_5^\bullet$]), 105 (95, [$M^{+\bullet}$-$C_2H_5^\bullet$-CO]), 91 (100, $Bn^{+\bullet}$), 77, 57.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3062 (w, C-H_{arom}), 3025 (w, C-H_{arom}), 2973 (w, C-H_{aliph}), 2935 (w, C-H_{aliph}), 2905 (w, C-H_{aliph}), 1709 (s, C=O), 1601 (w), 1493 (w), 1452 (m), 1411 (m), 1367 (m), 1265 (w), 1163 (w), 1112 (m), 1079 (w), 1053 (w), 1031 (w), 974 (w), 948 (w), 788 (w), 744 (s), 699 (s).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7.08
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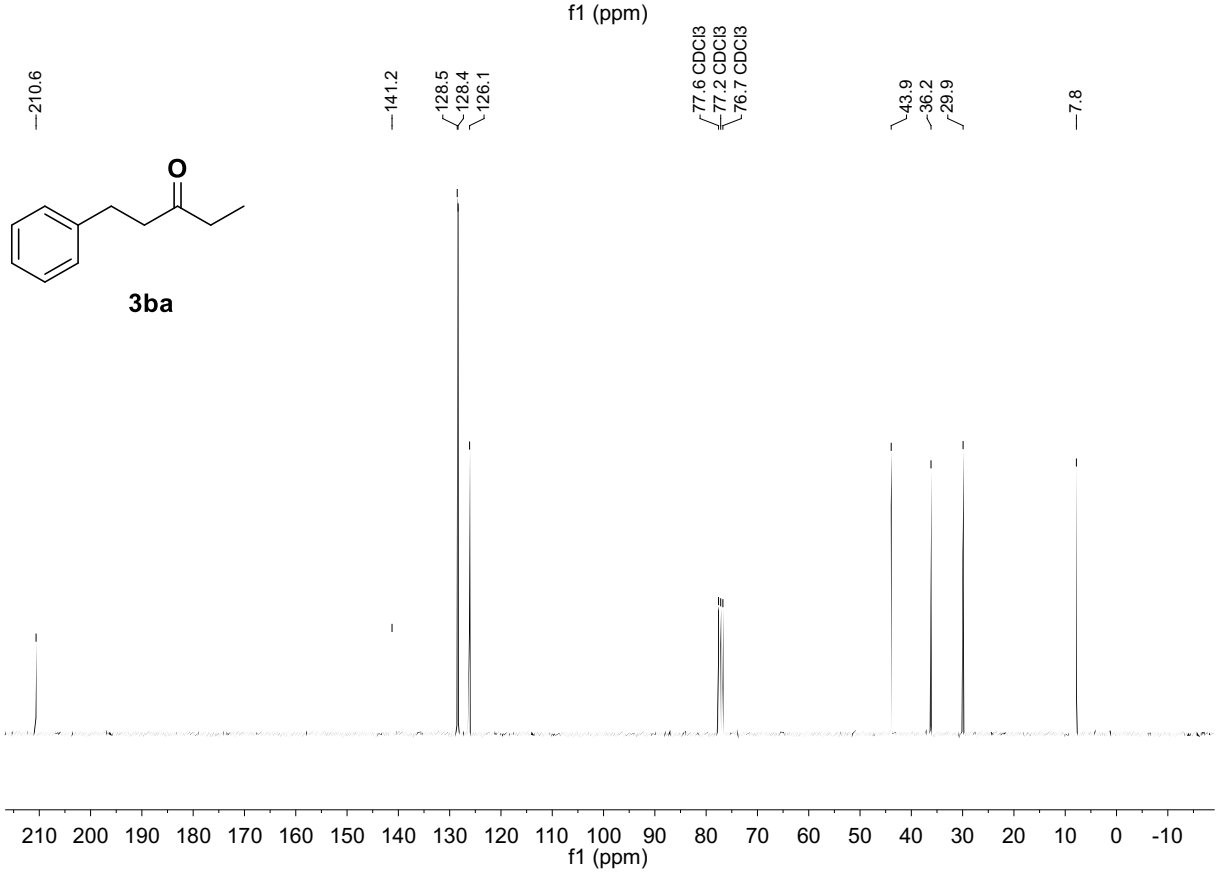
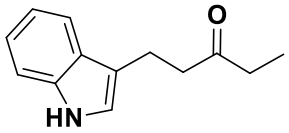
2.81
2.80
2.79
2.66
2.65
2.63
2.61
2.35
2.32
2.30
2.27
0.98
0.95
0.95
0.93
O
3ba
2.00
2.93
2.00
2.01
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


210.6
141.2
128.5
128.4
126.1
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
43.9
36.2
29.9
7.8
O
3ba
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1-(*1H*-indol-3-yl)pentan-3-one (**3ca**)



3ca

According to GP-E, the product **3ca** was synthesized using ethyl manganese bromide lithium chloride complex (0.20 M, 11 mL, 2.2 mmol, 2.2 equiv.) and *S*-ethyl 3-(1H-indol-2-yl)propanethioate **1c** (233 mg, 1.00 mmol). Purification was achieved by flash column chromatography (14 g SiO_2, 1 CV 9:1 = *n*Hex/EA, then gradient over 10 CV to 6:4 = *n*Hex/EA, then holding for 3 CV). The product was obtained as a colorless crystalline solid (163 mg, 810 µmol, 81%). The analytical data is in good accordance with the reported literature.[17]

$C_{13}H_{15}NO$ (201.27 g/mol)

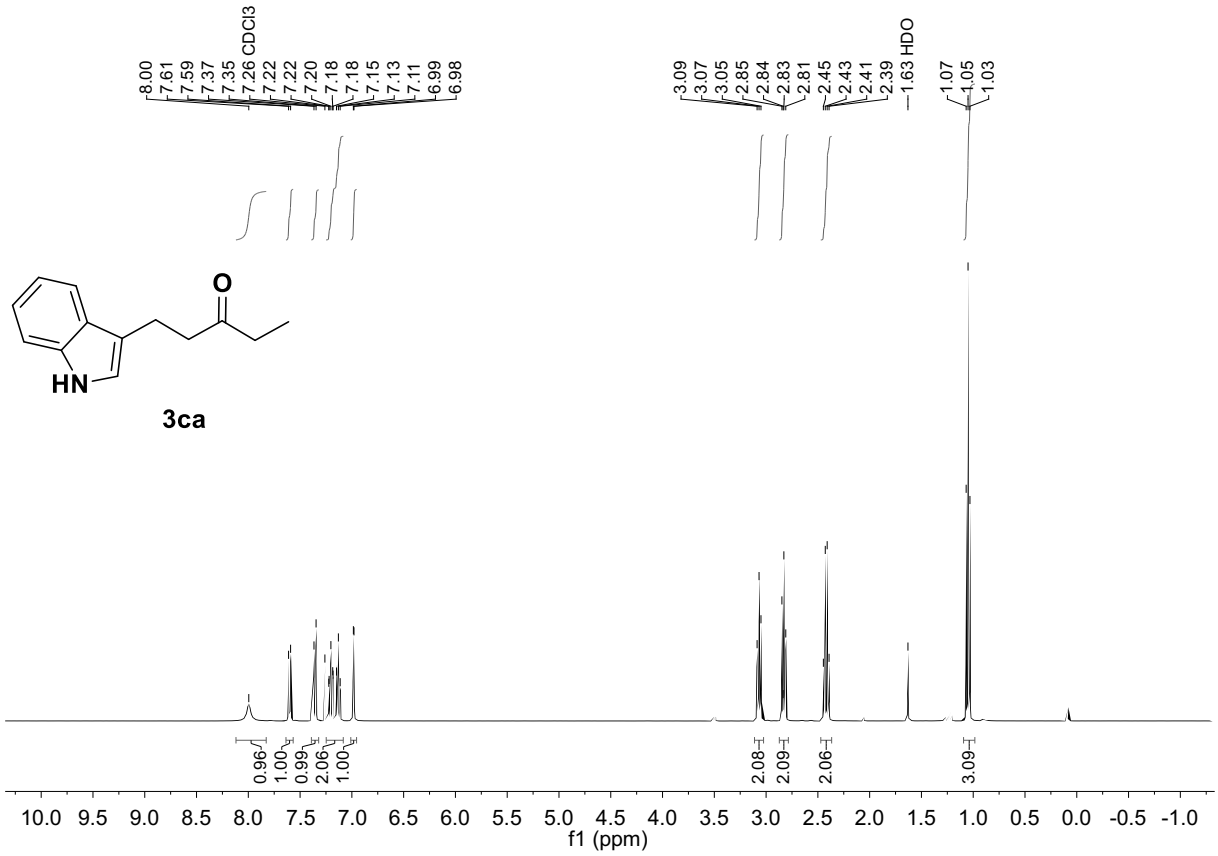
R_f: 0.32 (*n*Hex/Et_2O = 8:2) [$KMnO_4$]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (br s, N*H*, 1H), 7.65 – 7.57 (m, 1H), 7.36 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.20 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.13 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.02 – 6.94 (m, 1H), 3.07 (t, *J* = 7.3 Hz, 2H), 2.83 (t, *J* = 7.3 Hz, 2H), 2.42 (q, *J* = 7.3 Hz, $COCH_2CH_3$,2H), 1.05 (t, *J* = 7.3 Hz, $COCH_2CH_3$,3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 211.6 (*C*O), 136.4, 127.3, 122.1, 121.6, 119.4, 118.8, 115.5, 111.3, 42.9, 36.2, 19.6, 7.9.

GC-MS (EI): t_r = 9.07 min, m/z(%) = 201 (30, [$M^{+\bullet}$]), 144 (39, [$M^{+\bullet}$-$C_3H_5O^{\bullet}$]), 130 (100, [$M^{+\bullet}$-$C_5H_9O^{\bullet}$]).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3315 (w, br, N-H), 2972 (w, C-H_{aliph}), 2931 (w, C-H_{aliph}), 2894 (w, C-H_{aliph}), 2885 (w, C-H_{aliph}), 2846 (w, C-H_{aliph}), 1698 (m, C=O), 1616 (w), 1558 (w), 1443 (w), 1407 (w), 1377 (m), 1332 (m), 1265 (w), 1217 (m), 1105 (m), 1042 (m), 1005 (w), 974 (w), 919 (w), 855 (w), 807 (w), 777 (w), 729 (s).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7.26 CDCl3
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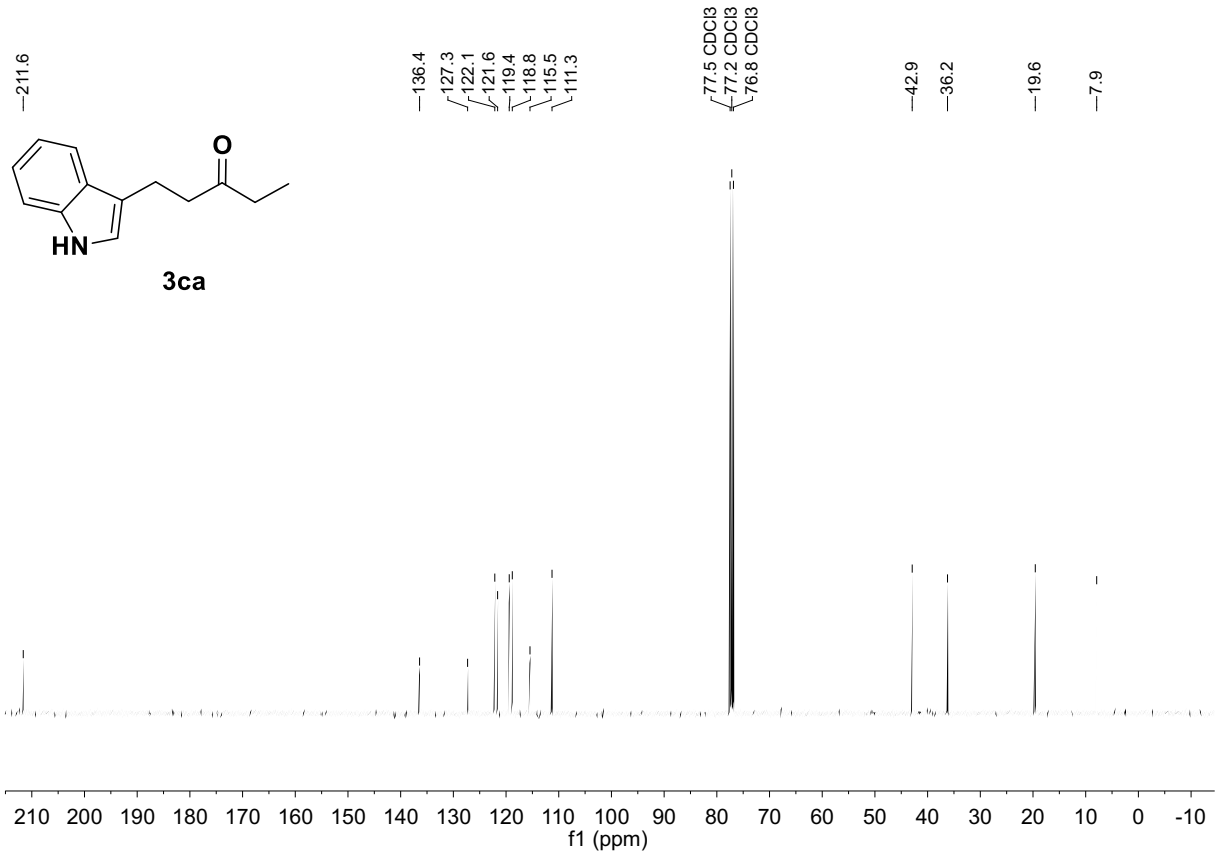
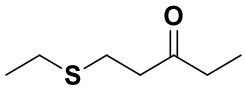
7.22
7.20
7.18
7.18
7.15
7.13
7.11
6.99
6.98
3.09
3.07
3.05
2.85
2.84
2.83
2.81
2.45
2.43
2.41
2.39
1.63 HDO
1.07
1.05
1.03
O
HN
3ca
0.96
1.00
0.99
2.06
1.00
2.08
2.09
2.06
3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


211.6
136.4
127.3
122.1
121.6
119.4
118.8
115.5
111.3
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
42.9
36.2
19.6
7.9
O
HN
3ca
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1-*S*-(ethylthio)pentan-3-one (**3da**)



3da

According to GP-E, the product **3da** was synthesized using ethylmanganese bromide lithium chloride complex (0.25 M, 4.7 mL, 1.2 mmol, 1.2 equiv.) and 3-*S*-(ethylthio)-propylcarboxylic acid *S*-ethyl thioester **1d** (178 mg, 1.00 mmol). Purification was achieved by filtering the crude product through a pad of silica (*n*Hex/Et_2O = 95:5 v/v). The product was obtained as a yellow oil with an unpleasant smell (128.2 mg, 877 µmol, 88%).

$C_7H_{14}OS$ (146.25 g/mol)

R_f: 0.24 (PE/EA = 97:3) [anis]

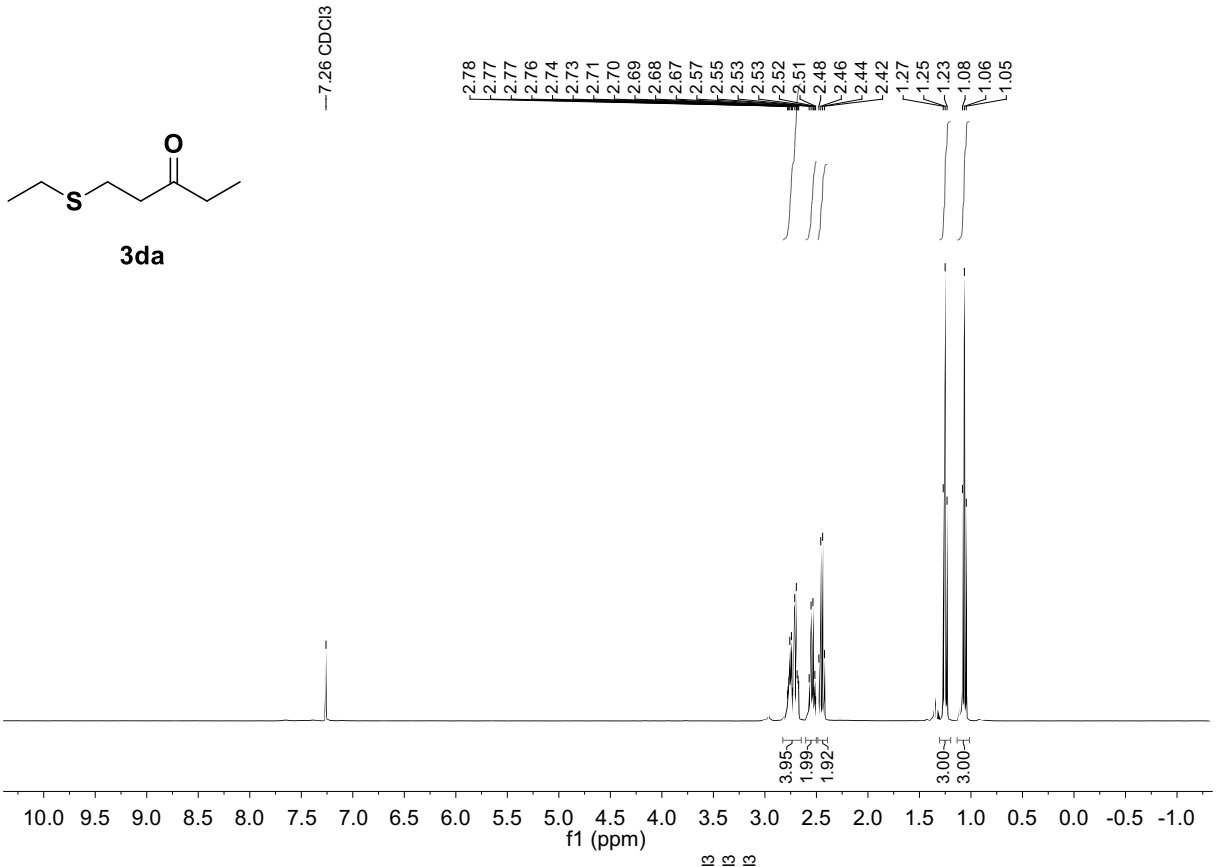
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.83 – 2.65 (m, 4H), 2.54 (q, *J* = 7.4 Hz, 2H), 2.45 (q, *J* = 7.3 Hz, 2H), 1.25 (t, *J* = 7.4 Hz, 3H), 1.06 (t, *J* = 7.3 Hz, 3H).

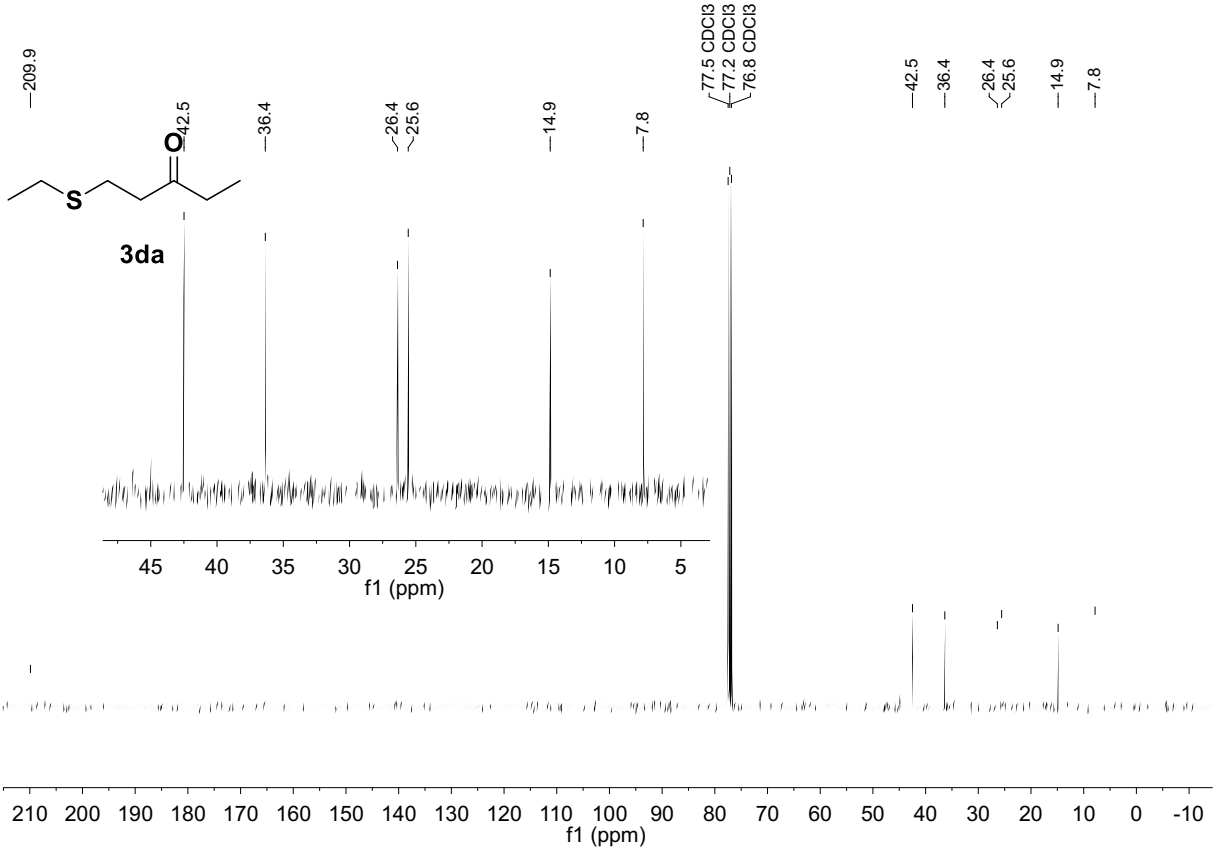
^{13}C NMR (101 MHz, $CDCl_3$): δ = 209.9 (*C*O), 42.5, 36.4, 26.4, 25.6, 14.9, 7.8.

GC-MS (EI): t_r = 4.11 min, m/z (%) = 146 (39, [$M^{+\bullet}$]), 117 (15, [$M^{+\bullet}$-$C_2H_5^{\bullet}$]), 89 (47,[$M^{+\bullet}$-$C_2H_5^{\bullet}$-CO]), 57 (100, [$C_3H_5O^{+\bullet}$]).

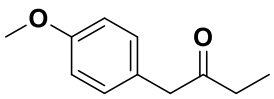
HR-MS (ESI): m/z calc. for $[M+Na]^+$ 151.07295, found 151.07319.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2969 (m, C-H_{aliph}), 2928 (m, C-H_{aliph}), 1710 (s, C=O), 1452 (m), 1414 (m), 1355 (m), 1262 (m), 1191 (w), 1165 (w), 1109 (m), 1059 (w), 971 (w), 945 (w), 882 (w), 785 (w), 740 (w).


7.26 CDCl3
2.78
2.77
2.77
2.76
2.74
2.73
2.71
2.70
2.69
2.68
2.67
2.57
2.55
2.53
2.53
2.52
2.51
2.48
2.46
2.44
2.42
1.27
1.25
1.23
1.08
1.06
1.05
O
S
3da
3.95
1.99
1.92
3.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


209.9
42.5
36.4
26.4
25.6
14.9
7.8
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
O
S
3da
45 40 35 30 25 20 15 10 5
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1-(4-*para*-anisyl)butan-2-one (**3ea**)



3ea

According to GP-E, the product **3ea** was synthesized using ethylmanganese bromide lithium chloride complex (7.1 mL, 1.2 mmol, 0.17 M, 1.2 equiv.) and *S*-ethyl 2-(4-methoxyphenyl)ethanethioate **1e** (210 mg, 1.00 mmol). Purification was achieved by manual column chromatography (*n*Hex/EA = 30:1 v/v). The product was obtained as a brown oil (135 mg, 757 µmol, 76%). The analytical data is in good accordance to reported literature.[18]

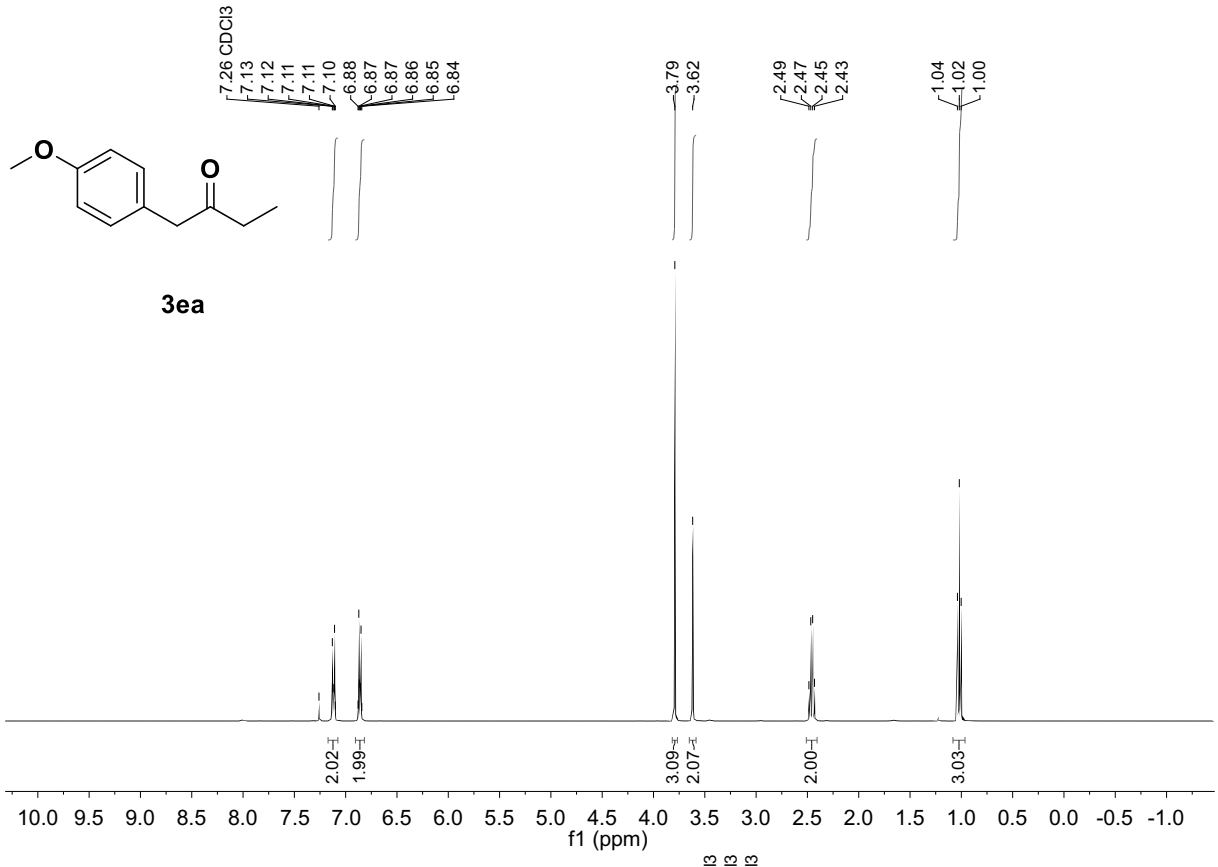
$C_{11}H_{14}O_2$ (178.23 g/mol)

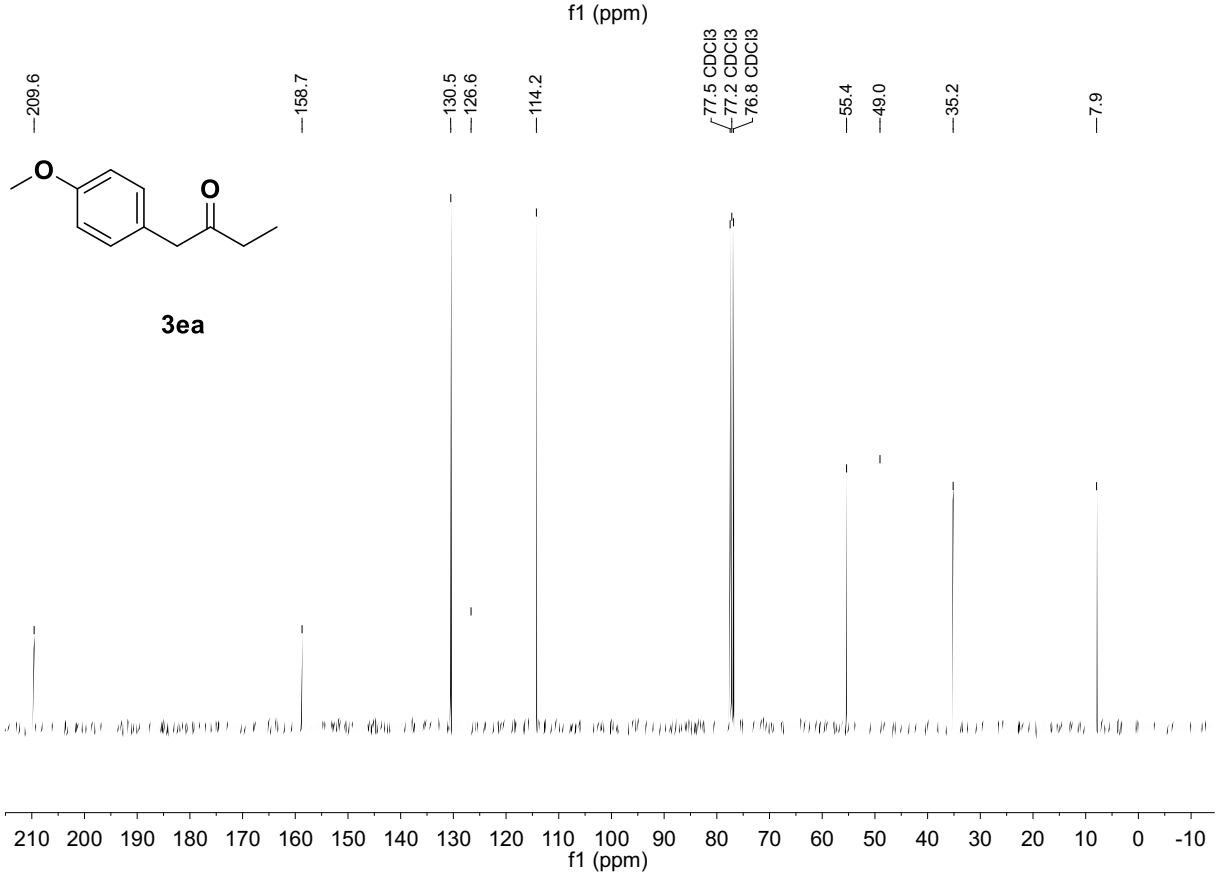
R_f: 0.25 (*n*Hex/EA = 30:1 v/v) [anis]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 – 7.08 (m, 2H, Ar*H*), 6.90 – 6.82 (m, 2H, Ar*H*), 3.79 (s, 3H, OCH_3), 3.62 (s, 2H, PhCH_2), 2.46 (q, *J* = 7.3 Hz, 2H, COCH_2CH$_3$), 1.02 (t, *J* = 7.3 Hz, 3H, COCH_2CH$_3$).

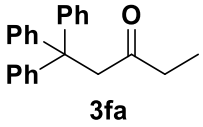
^{13}C NMR (101 MHz, $CDCl_3$): δ = 209.6 (*C*O), 158.7 (C_{Ar}), 130.5 (C_{Ar}), 126.6 (C_{Ar}), 114.2 (C_{Ar}), 55.4, 49.0, 35.2 (CH_2CH_3), 7.9 (CH_2CH_3).

GC-MS (EI): t_r = 6.31 min, m/z(%) = 178 (12, [$M^{+\bullet}$]), 121 (100, [$M^{+\bullet}$-$C_3H_5^{\bullet}$]).


7.26 CDCl3
7.13
7.12
7.11
7.11
7.10
6.88
6.87
6.87
6.86
6.85
6.84
3.79
3.62
2.49
2.47
2.45
2.43
1.04
1.02
1.00
O
O
3ea
2.02
1.99
3.09
2.07
2.00
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


209.6
158.7
130.5
126.6
114.2
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
55.4
49.0
35.2
7.9
O
O
3ea
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1,1,1-triphenylpentan-3-one (**3fa**)



3fa

According to GP-E, the product **3fa** was synthesized using ethylmanganese bromide lithium chloride complex (4.4 mL, 1.2 mmol, 0.27 M, 1.2 equiv.) and *S*-ethyl 3,3,3-triphenylpropanethioate **1f** (210 mg, 1.00 mmol). Purification was achieved by flash column chromatography (23 g SiO_2, 8 CV pure PE to PE/EA = 92:8). The product was obtained as colorless solid (206 mg, 655 µmol, 66%).

$C_{23}H_{22}O$ (314.43 g/mol)

R_f: 0.22 (PE/EA = 30:1) [UV]

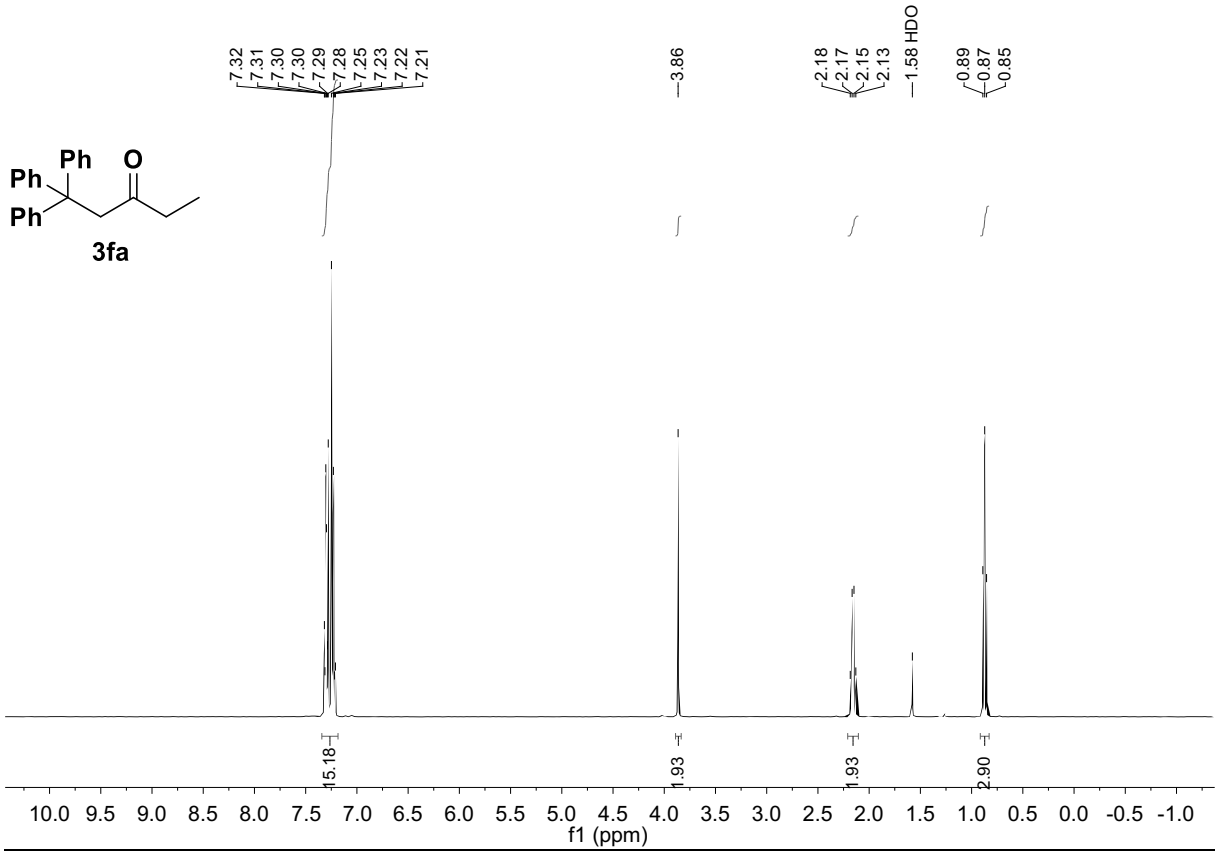
Melting point: 89.7–90.1 °C (EA).

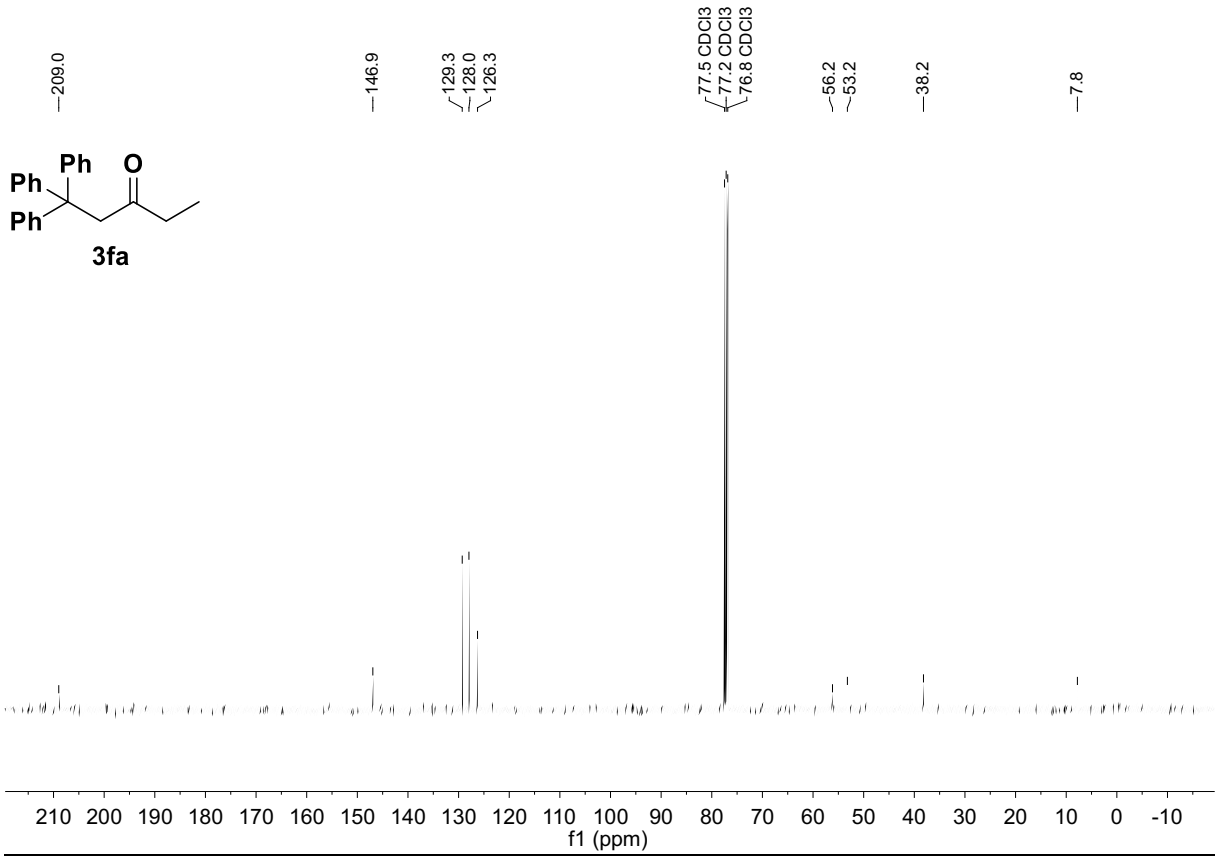
GC-MS (EI): t_r = 11.18 min, m/z(%) = 243 (100, $[M^{+\bullet}]$), 165 (76, $[M^{+\bullet}\text{-}C_6H_6^{\bullet}]$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 – 7.18 (m, 15H, Ar*H*), 3.86 (s, 2H, $Ph_3C\text{-}CH_2$), 2.16 (q, *J* = 7.2 Hz, 2H, $COCH_2$), 0.87 (t, *J* = 7.2 Hz, 3H, $COCH_2CH_3$).

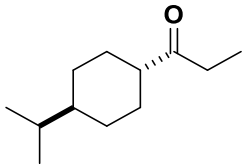
^{13}C NMR (101 MHz, $CDCl_3$): δ = 209.0 (*C*OEt), 146.9 ($C_{Ar,}$), 129.3 ($C_{Ar,}$), 128.0 (C_{Ar}), 126.3 ($C_{Ar,}$), 56.2, 53.2, 38.2 (CH_2CH_3), 7.8 (CH_3).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3058 (w, C-H_{arom}), 3021 (w, C-H_{arom}), 2928 (w, C-H_{aliph}), 2854 (w, C-H_{aliph}), 1694 (m, C=O), 1664 (w), 1593 (w), 1519 (w), 1489 (m), 1441 (m), 1404 (w), 1377 (w), 1333 (w), 1258 (w), 1220 (w), 1187 (w), 1161 (w), 1113 (w), 1083 (w), 1027 (m), 953 (m), 818 (w), 781 (w), 777 (w), 751 (m), 695 (s).


7.32
7.31
7.30
7.30
7.29
7.28
7.25
7.23
7.22
7.21
3.86
2.18
2.17
2.15
2.13
1.58 HDO
0.89
0.87
0.85
Ph
Ph
Ph
O
3fa
15.18
1.93
1.93
2.90
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


209.0
146.9
129.3
128.0
126.3
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
56.2
53.2
38.2
7.8
Ph
Ph
Ph
O
3fa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1-(*trans*-4-*iso*propylcyclohexyl)propan-1-one (**3ha**)



3ha

According to GP-E, the product **3ha** was synthesized using ethylmanganese bromide lithium chloride complex (5.5 mL, 1.2 mmol, 0.22 M, 1.2 equiv.) and *S*-ethyl *trans*-4-*iso*-propylcyclohexane-1-carbothioate **1h** (214 mg, 1.00 mmol). The reaction was stirred for 15 min at -20 °C. Purification was achieved by manual column chromatography (*n*Hex/EA = 98:2). The product was obtained as a colorless oil (130 mg, 713 µmol, 71%).

$C_{12}H_{22}O$ (182.31 g/mol)

R_f: 0.44 (*n*Hex/EA = 98:2) [anis]

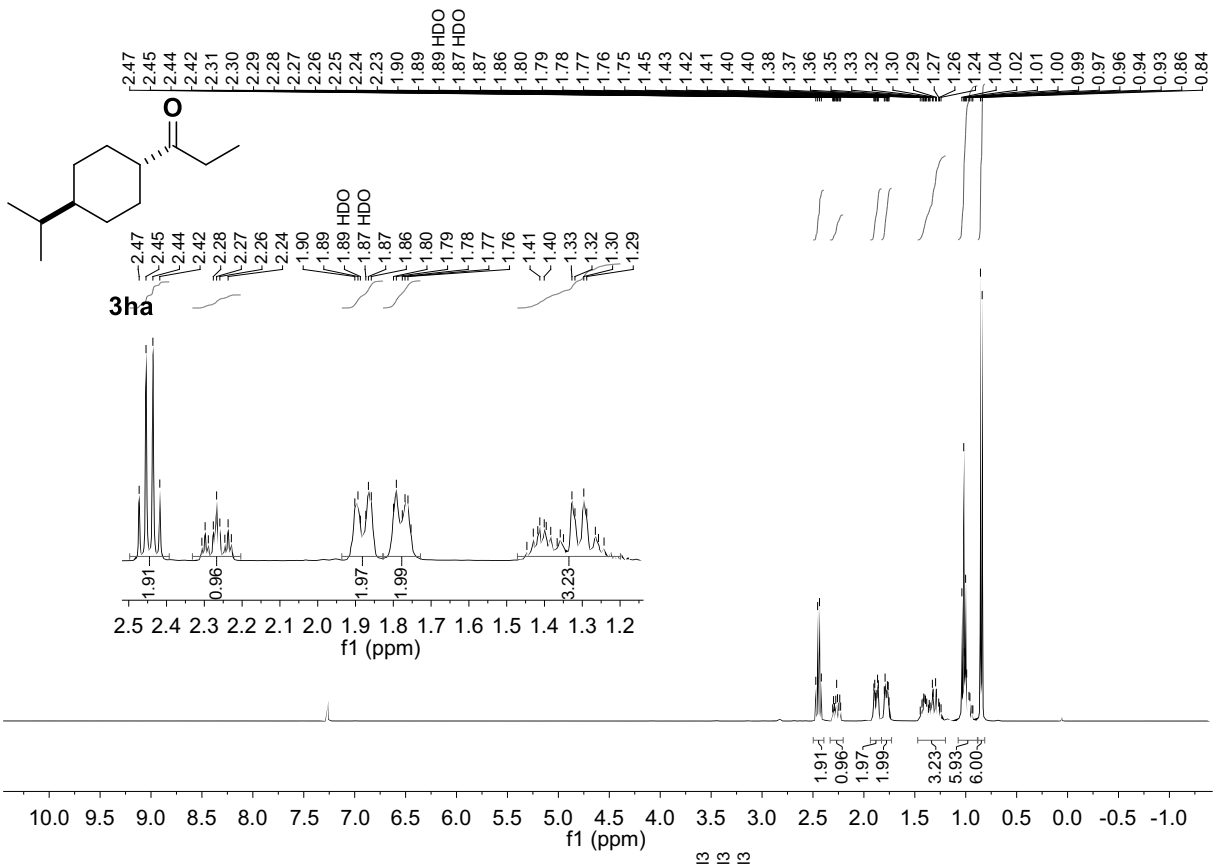
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.45 (q, *J* = 7.3 Hz, 2H, COCH_2), 2.27 (tt, *J* = 12.2, 3.4 Hz, 1H), 1.94 – 1.73 (m, 4H), 1.48 – 1.20 (m, 3H), 1.07 – 0.91 (m, 6H), 0.85 (d, *J* = 6.8 Hz, 6H,CH_3CHCH_3).

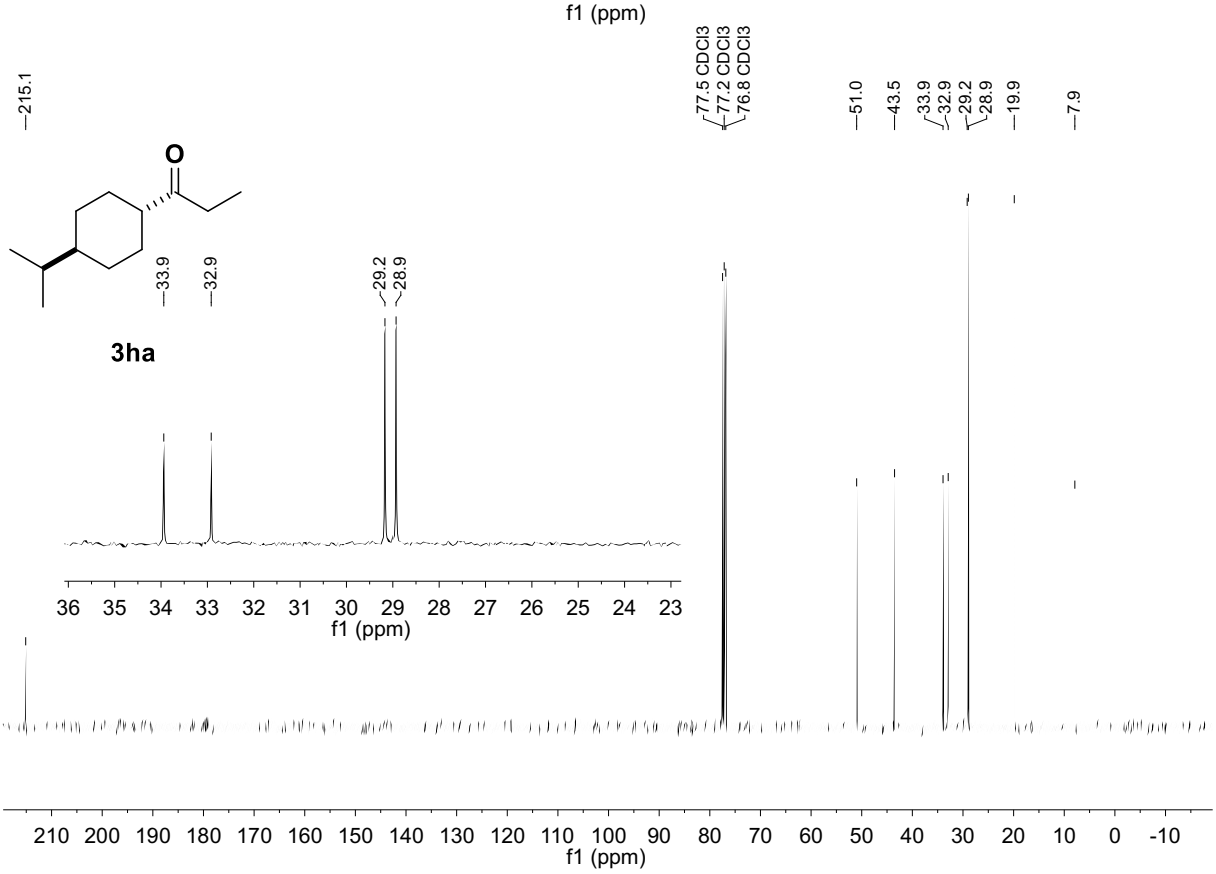
^{13}C NMR (101 MHz, $CDCl_3$): δ = 215.1 (*C*O), 51.0, 43.5, 33.9, 32.9, 29.2, 28.9, 19.9, 7.9.

GC-MS (EI,): t_r = 6.66 min, m/z(%) = 182 (13, [$M^{+\bullet}$]), 164 (17), 153 (16, [$M^{+\bullet}$-$C_2H_5^{\bullet}$]), 125 (49, [$M^{+\bullet}$-$C_2H_5^{\bullet}$-CO]), 110 (21, [$M^{+\bullet}$-$C_2H_5^{\bullet}$-CO-$CH_3^{\bullet}$]), 83 (46, [$C_6H_{11}^{+\bullet}$]), 69 (100, [$C_5H_9^{+\bullet}$]).

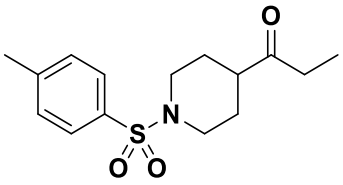
HR-MS (ESI): m/z calc. for $[M+Na]^+$ 205.15629 , found 205.15666.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2928 (s, C-H_{aliph}), 2857 (m, C-H_{aliph}), 1706 (s, C=O), 1452 (m), 1411 (w), 1373 (m), 1340 (w), 1229 (w), 1173 (w), 1143 (w), 1116 (w), 1076 (w), 1054 (w), 1012 (w), 982 (w), 941 (w), 897 (w), 852 (w), 796 (w).


3ha
f1 (ppm)


3ha
f1 (ppm)

1-(1-tosylpiperidin-4-yl)propan-1-one (**3ia**)



3ia

According to GP-E, the product **3ia** was synthesized using ethylmanganese bromide lithium chloride complex (5.7 mL, 1.2 mmol, 0.21 M, 1.2 equiv.) and *S*-ethyl 1-tosylpiperidine-4-carbothioate **1i** (327 mg, 1.00 mmol). Purification was achieved by manual column chromatography (*n*Hex/EA = 8:2 v/v). The product was obtained as a colorless solid (283 mg, 958 µmol, 96%).

$C_{16}H_{21}NO_3S$ (295.40 g/mol)

R_f: 0.38 (*n*Hex/EA = 8:2 v/v) [UV, anis]

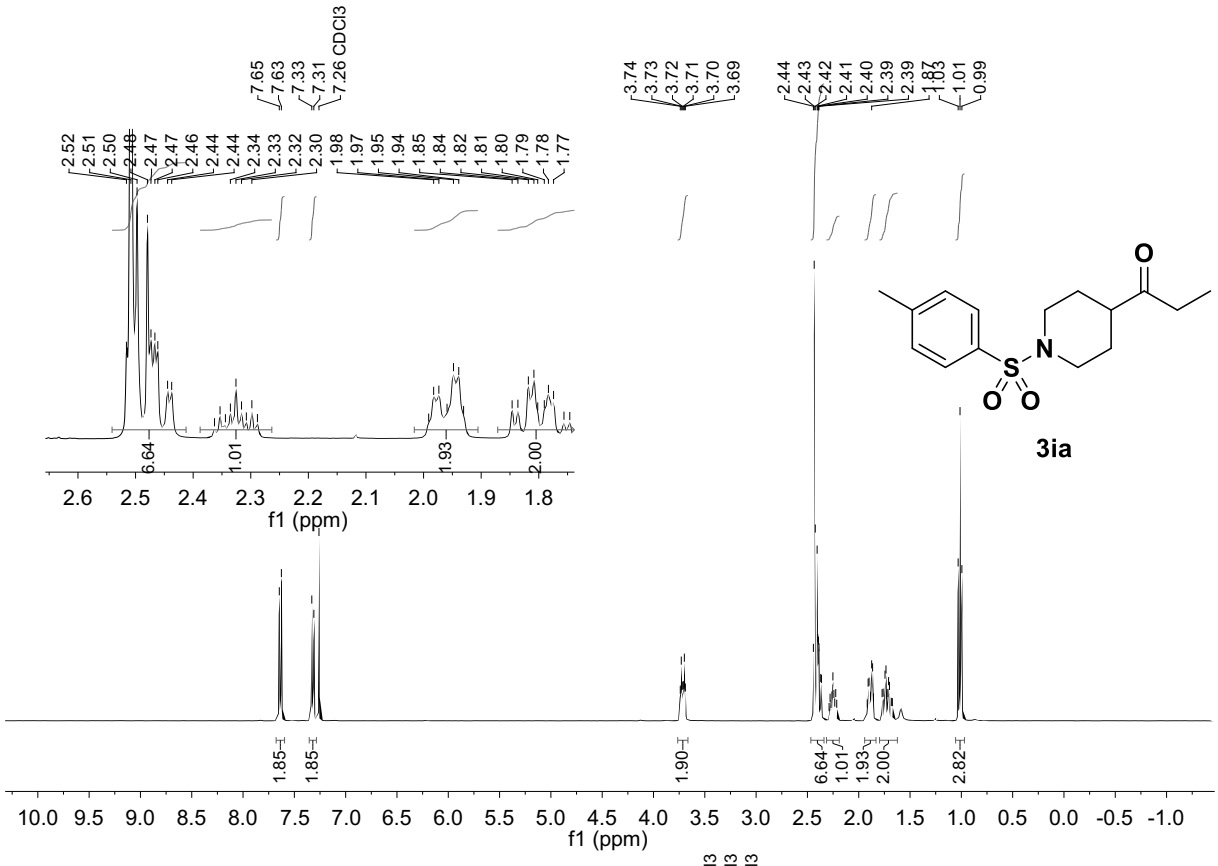
Melting point: 107.9–108.5 °C (EA).

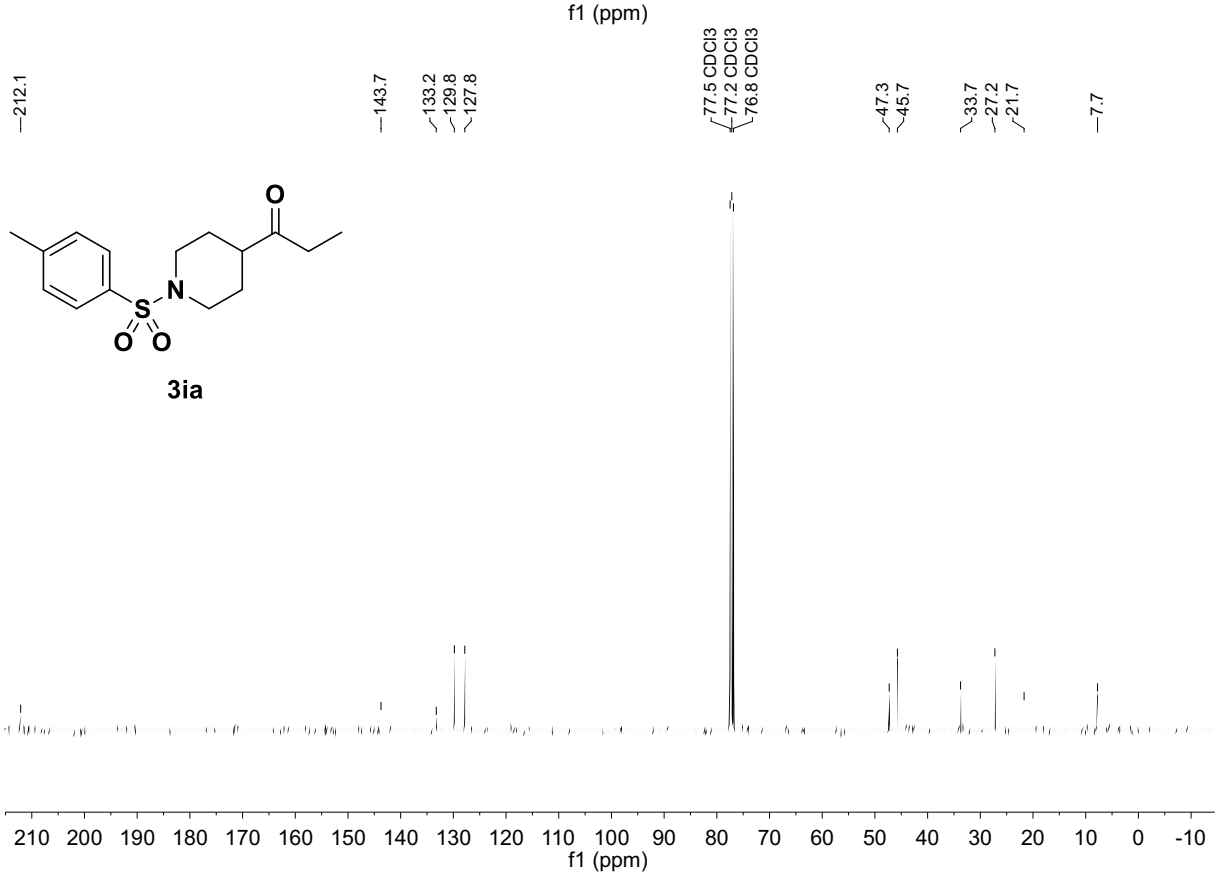
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 – 7.60 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 3.77 – 3.66 (m, 2H), 2.47 – 2.34 (m, 7H), 2.31 – 2.19 (m, 1H), 1.94 – 1.83 (m, 2H), 1.80 – 1.65 (m, 2H), 1.01 (t, *J* = 7.2 Hz, 3H, $COCH_2CH_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 212.1 (*C*O), 143.7 (C_{Ar}), 133.2 (C_{Ar}), 129.8 (C_{Ar}), 127.83 (C_{Ar}), 47.3, 45.7, 33.7, 27.2, 21.7, 7.8 (CH_3).

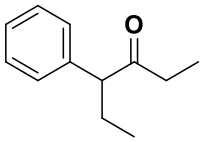
HR-MS (ESI): m/z calc. for $[M+Na]^+$ 318.11344 , found 318.11371.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2972 (w, C-H_{aliph}), 2920 (w, C-H_{aliph}), 2846 (w, C-H_{aliph}), 1702 (m, C=O), 1661 (w), 1593 (w), 1445 (w), 1410 (w), 1377 (w), 1322 (m), 1284 (m), 1243 (m), 1157 (s), 1127 (m), 1094 (m), 1053 (m), 1020 (w), 979 (w), 926 (m), 866 (w), 833 (w), 807 (w), 759 (w), 722 (m), 699 (m).


7.65
7.63
7.33
7.31
7.26 CDCl3
3.74
3.73
3.72
3.71
3.70
3.69
2.44
2.43
2.42
2.41
2.40
2.39
2.39
1.87
1.83
1.01
0.99
2.52
2.51
2.50
2.49
2.47
2.47
2.46
2.44
2.44
2.34
2.33
2.32
2.30
1.98
1.97
1.95
1.94
1.85
1.84
1.82
1.81
1.80
1.79
1.78
1.77
6.64
1.01
1.93
2.00
2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8
f1 (ppm)
O
N
S
O O
3ia
1.85
1.85
1.90
6.64
1.01
1.93
2.00
2.82
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


212.1
143.7
133.2
129.8
127.8
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
47.3
45.7
33.7
27.2
21.7
7.7
O
N
S
O O
3ia
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

4-phenylhexan-3-one (**3ja**)



3ja

According to GP-E, the product **3ja** was synthesized using ethylmanganese bromide lithium chloride complex (6.0 mL, 1.2 mmol, 0.2 M, 1.2 equiv.) and *S*-ethyl 2-phenylbutanethioate **1j** (208.32 mg, 1.00 mmol). Purification was achieved by manual column chromatography (*n*Hex/EA=98:2 v/v). The product was obtained as a colorless oil (62.2 mg, 353 µmol, 35%). The analytical data is in good accordance to reported literature.[19]

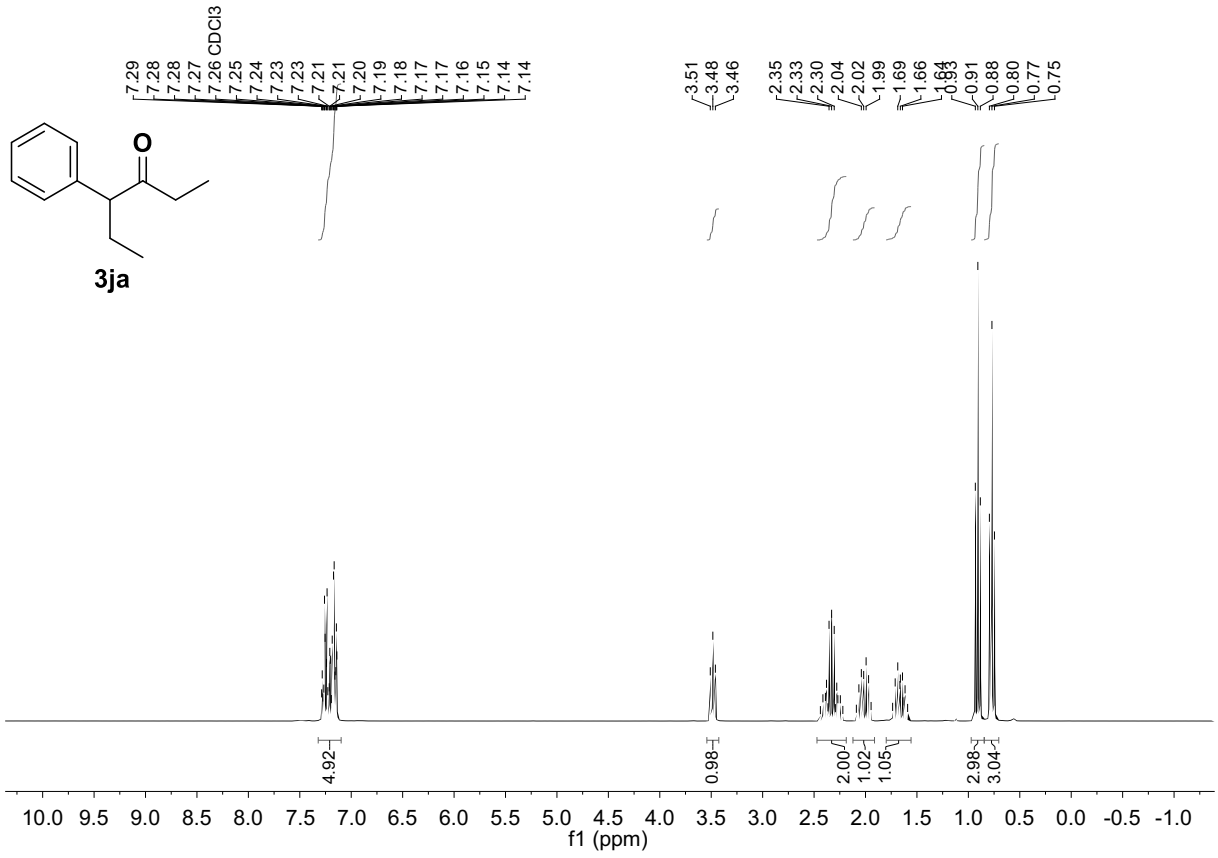
$C_{12}H_{16}O$ (176.26 g/mol)

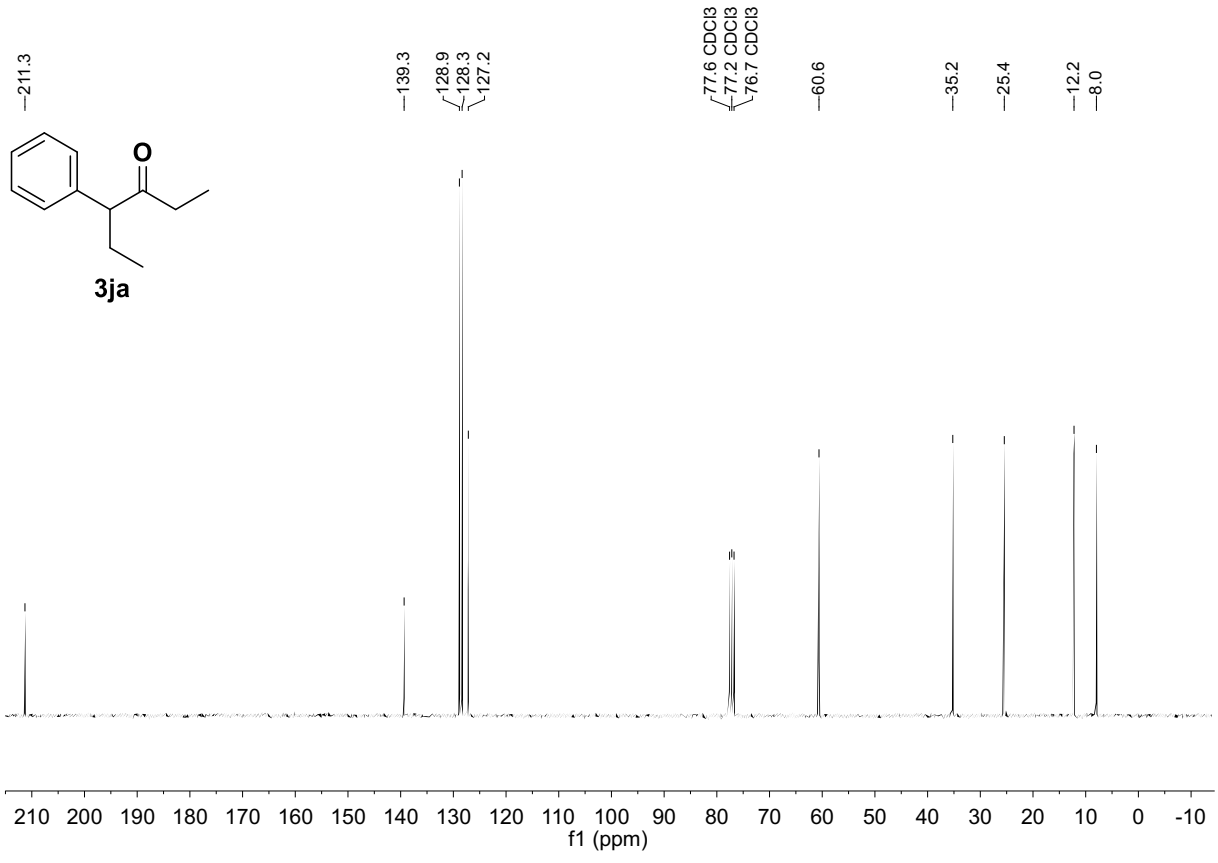
R_f: 0.67 (*n*Hex/EA = 30:1) [$KMnO_4$]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 – 7.10 (m, 5H), 3.48 (t, J = 7.4 Hz, 1H, PhC*H*), 2.47 – 2.19 (m, 2H), 2.12 – 1.91 (m, 1H), 1.80 – 1.56 (m, 1H), 0.91 (t, J = 7.3 Hz, 3H), 0.77 (t, J = 7.4 Hz, 3H).

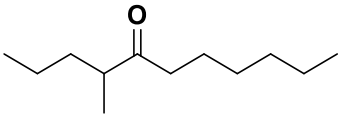
^{13}C NMR (75 MHz, $CDCl_3$): δ = 211.3 8 (*C*O), 139.3 (C_{Ar}), 128.9 (C_{Ar}), 128.3 (C_{Ar}), 127.2 (C_{Ar}), 60.6 (Ph*C*H), 35.2, 25.4, 12.2, 8.0 (*C*H_3).

GC-MS (EI): t_r = 5.22 min, m/z(%) = 176 (6, [$M^{+\bullet}$]), 119 (31, [$M^{+\bullet}$-$C_3H_5O^{\bullet}$]), 91 (100, [$Bz^{+\bullet}$]).


7.29
7.28
7.28
7.27
7.26 CDCl3
7.25
7.24
7.23
7.23
7.21
7.21
7.20
7.19
7.18
7.17
7.17
7.16
7.15
7.14
7.14
3.51
3.48
3.46
2.35
2.33
2.30
2.04
2.02
1.99
1.69
1.66
0.91
0.88
0.80
0.77
0.75
O
3ja
4.92
0.98
2.00
1.02
1.05
2.98
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


211.3
139.3
128.9
128.3
127.2
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
60.6
35.2
25.4
12.2
8.0
O
3ja
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

4-methylundecan-5-one (**3kb**)



3kb

According to GP-E, the product **3kb** was synthesized using hexylmanganese bromide lithium chloride complex (4.1 mL, 1.2 mmol, 0.29 M, 1.2 equiv.) and *S*-ethyl 2-methylpentanethioate **1k** (160 mg, 1.00 mmol). Purification was achieved by manual column chromatography (15-60 µm SiO_2 - Merck, *n*Hex/EA = 99:1 v/v). The product was obtained as a colorless oil (90.5 mg, 491 µmol, 49%).

$C_{12}H_{24}O$ (184.32 g/mol)

R_f: 0.34 (*n*Hex/EA =99:1 v/v) [anis]

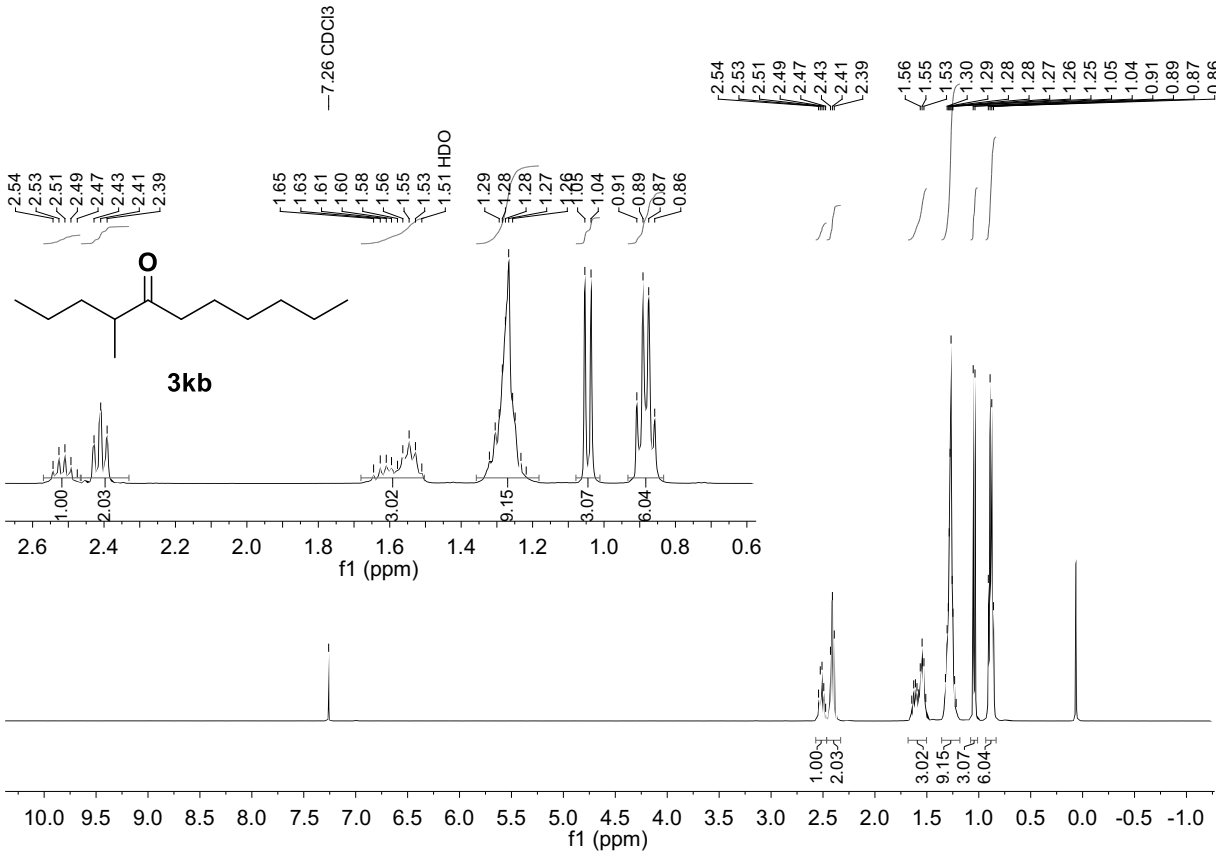
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.57 – 2.45 (m, 1H), 2.44 – 2.35 (m, 2H), 1.69 – 1.48 (m, 3H), 1.36 – 1.19 (m, 9H), 1.04 (d, *J* = 6.9 Hz, 3H, COCHC*H*$_3$), 0.93 – 0.83 (m, 6H).

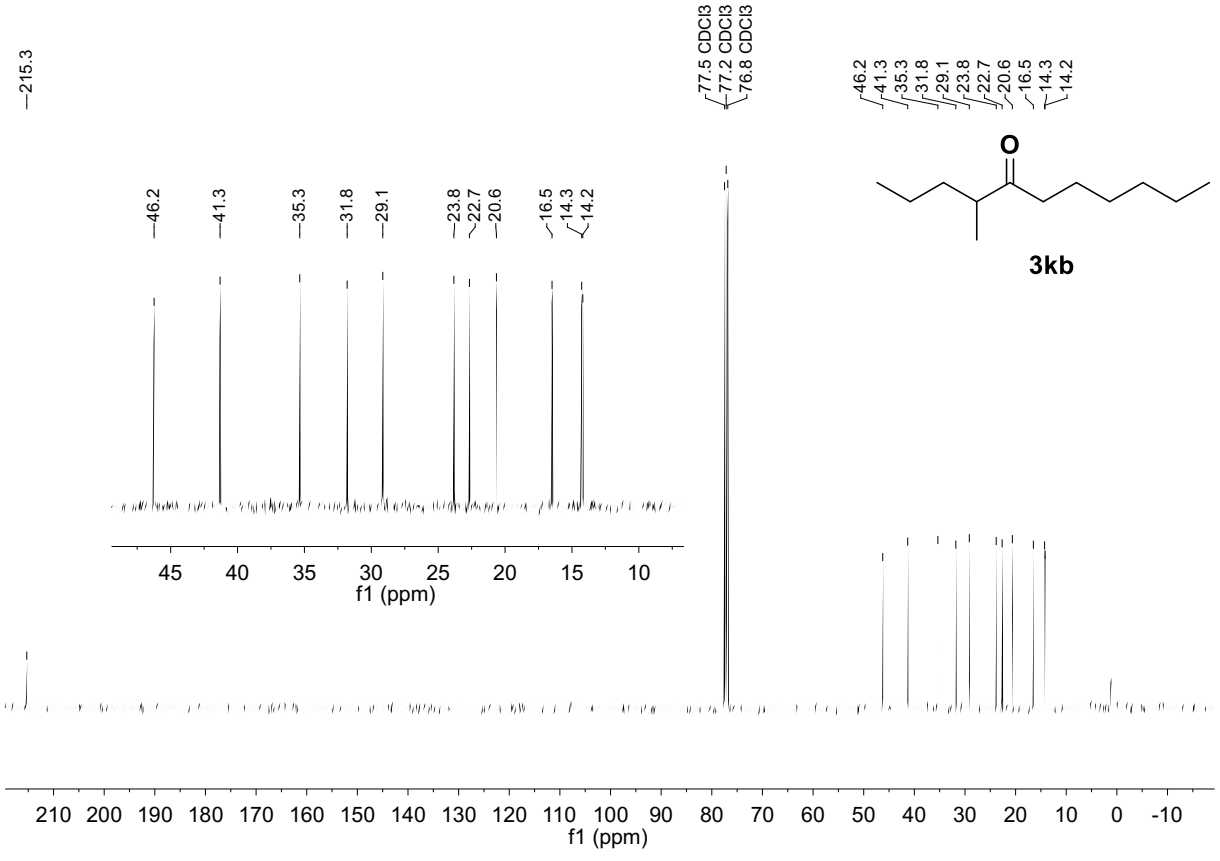
^{13}C NMR (101 MHz, $CDCl_3$): δ = 215.3 (*C*O), 46.2, 41.3, 35.3, 31.8, 29.1, 23.8, 22.7, 20.6, 16.5, 14.3, 14.2.

GC-MS (EI): t_r = 3.53 min, m/z(%) = 131 (17, [$M^{+\bullet}$-$C_5H_{11}^{\bullet}$]), 99 (38, [$M^{+\bullet}$-$C_6H_{13}^{\bullet}$]), 71 (100, [$M^{+\bullet}$-$C_6H_{13}^{\bullet}$-CO]), 55.

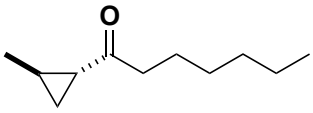
HR-MS (EI, 45 eV): m/z calc. for $[M]^+$ 184.182166, found 184.18068.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2957 (m, C-H_{aliph}), 2927 (s, C-H_{aliph}), 2863 (m, C-H_{aliph}), 1709 (s, C=O), 1459 (m), 1407 (w), 1373 (w), 1306 (w), 1261 (w), 1232 (w), 1191 (w), 1165 (w), 1101 (w), 1057 (w), 1016 (w), 870 (w), 803 (w), 731 (w).


7.26 CDCl3
1.51 HDO
3kb
1.00
2.03
3.02
9.15
3.07
6.04
f1 (ppm)


215.3
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
46.2
41.3
35.3
31.8
29.1
23.8
22.7
20.6
16.5
14.3
14.2
3kb
f1 (ppm)

trans-1-(2-methylcyclopropyl)heptan-1-one (**3lb**)



3lb

According to GP-E, the product **3lb** was synthesized using hexylmanganese bromide lithium chloride complex (4.1 mL, 1.2 mmol, 0.29 M, 1.2 equiv.) and *S*-ethyl 2-methylcyclopropane-1-carbothioate **1l** (144.2 mg, 1.00 mmol). Purification was achieved by manual column chromatography (*n*Hex/Et_2O = 99:1 to 7:3 v/v). The product was obtained as a colorless oil (96.2 mg, 572 µmol, 57%).

$C_{12}H_{20}O$ (168.28 g/mol)

R_f: 0.08 (*n*Hex/EA = 99:1 v/v) [anis - yellow]

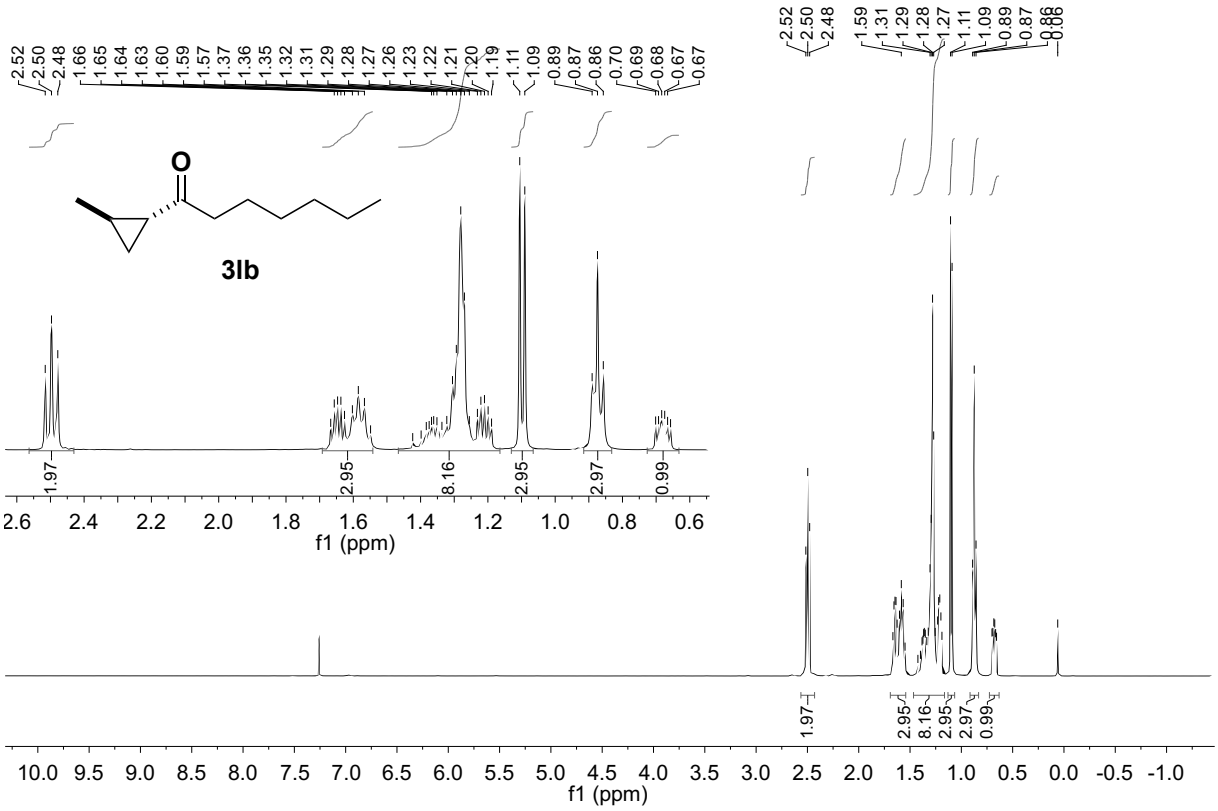
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.50 (t, *J* = 7.5 Hz, 2H), 1.69 – 1.54 (m, 3H), 1.47 – 1.14 (m, 8H), 1.10 (d, J = 6.0 Hz, 3H), 0.92 – 0.83 (m, 3H), 0.68 (ddd, *J* = 7.7, 6.3, 3.5 Hz, 1H).

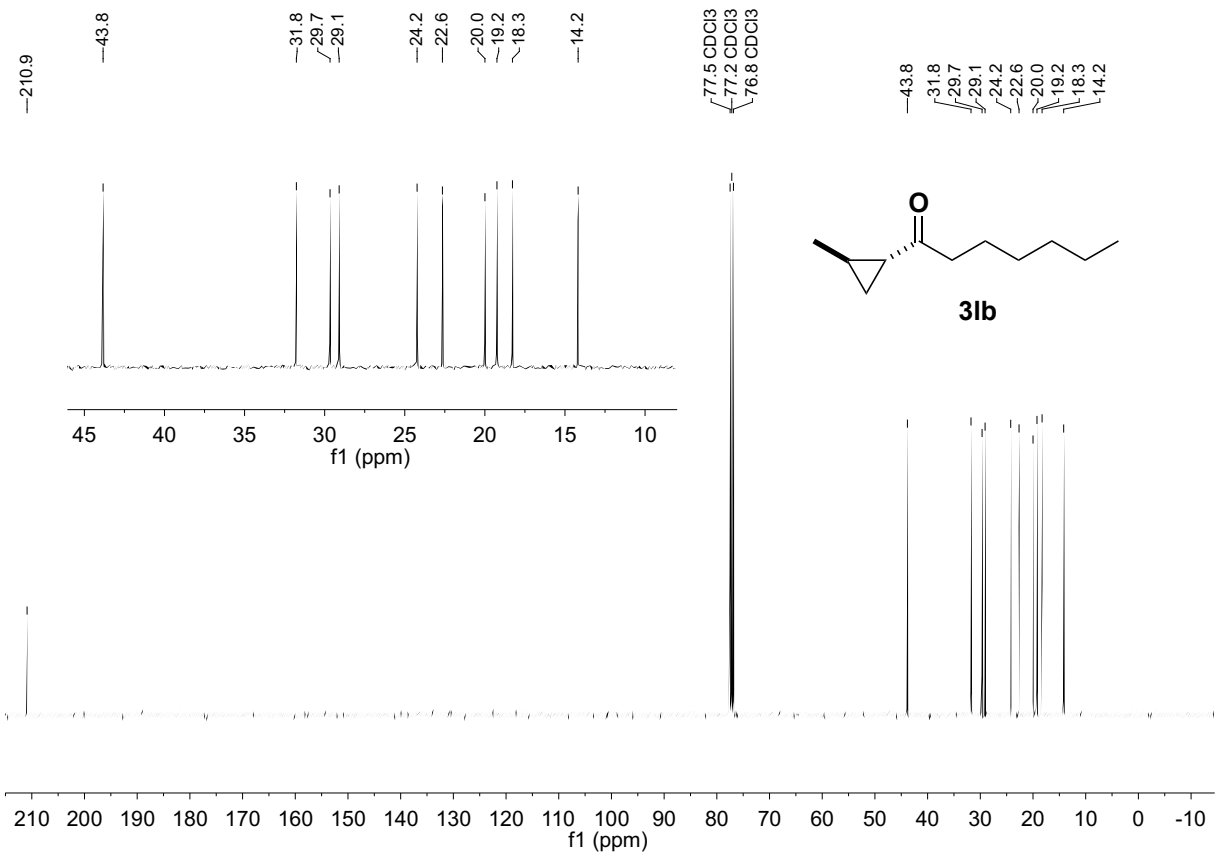
^{13}C NMR (101 MHz, $CDCl_3$): δ = 210.9 (*C*O), 43.8, 31.8, 29.7, 29.1, 24.2, 22.7, 20.0, 19.3, 18.3, 14.2.

GC-MS (EI): t_r = 4.78 min, m/z(%) = 168 (1, [$M^{+\bullet}$]), 98 (53, [$M^{+\bullet}$-C_5H_{10}]), 83 (100, [$M^{+\bullet}$-C_5H_{10}-$CH_3^{\bullet}$]), 55.

HR-MS (EI, 45 eV): m/z calc. for $[M]^+$ 168.15123, found 168.150866.

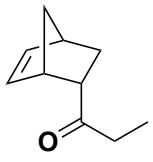
IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2954 (m, C-H_{aliph}), 2927 (m, C-H_{aliph}), 2861 (m, C-H_{aliph}), 1694 (s, C=O), 1456 (m), 1403 (m), 1377 (m), 1355 (w), 1351 (w), 1325 (w), 1262 (w), 1202 (w), 1161 (w), 1131 (w), 1082 (s), 1034 (m), 960 (w), 938 (w), 855 (m), 807 (w), 762 (w), 725 (w).


3Ib
f1 (ppm)

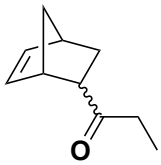

3Ib
f1 (ppm)

1-((1*S**,2*S**,4*S**)-bicyclo[2.2.1]hept-5-en-2-yl)propan-1-one (**3ma**)

and a mixture with diastereomer (**3ma+ma'**)



3ma



3ma + 3ma'

According to GP-E, the products **3ma** as well as **3ma + 3ma'** were synthesized using ethylmanganese bromide lithium chloride complex (7.1 mL, 1.2 mmol, 0.17 M, 1.2 equiv.) and *S*-ethyl (1*S*,2*R*,4*S*)-bicyclo[2.2.1]hept-5-ene-2-carbothioate **1ma** or the mixture **1ma + 1ma'** (144 mg, 1.00 mmol). Both purifications were achieved by manual column chromatography (*n*Hex/EA = 9:1 v/v). Additional purification was necessary which in both cases was achieved by bulb-to-bulb distillation (165 °C, 200 mbar). **3ma** was obtained as a colorless oil (113 mg, 752 µmol, 75%) and mixture **3ma + 3ma'** also as colorless oil (106 mg, 706 µmol, 71%, d.r. = 5(**3m**):3(**3m'**)).

$C_{10}H_{14}O$ (150.22 g/mol)

R_f: 0.30 (PE/EA = 98:2 v/v) [anis - yellow]

3ma: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.15 (dd, *J* = 5.7, 3.1 Hz, 1H, $C_{alkene}H$), 5.83 (dd, *J* = 5.7, 2.8 Hz, 1H, $C_{alkene}H$), 3.25 – 3.20 (m, 1H), 3.01 (dt, *J* = 9.1, 4.0 Hz, 1H), 2.92 – 2.87 (m, 1H), 2.44 (qd, *J* = 7.3, 3.3 Hz, 1H), 1.75 (ddd, *J* = 11.8, 9.1, 3.7 Hz, 1H), 1.54 – 1.40 (m, 2H), 1.32 (dt, *J* = 8.2, 1.6 Hz, 1H), 1.02 (t, *J* = 7.4 Hz, 3H).

3ma: ^{13}C NMR (101 MHz, $CDCl_3$): δ = 211.8 (*C*OEt), 137.9 (C_{alkene}), 131.5 (C_{alkene}), 51.4, 50.1, 46.1, 42.8, 35.0, 27.6, 8.1.

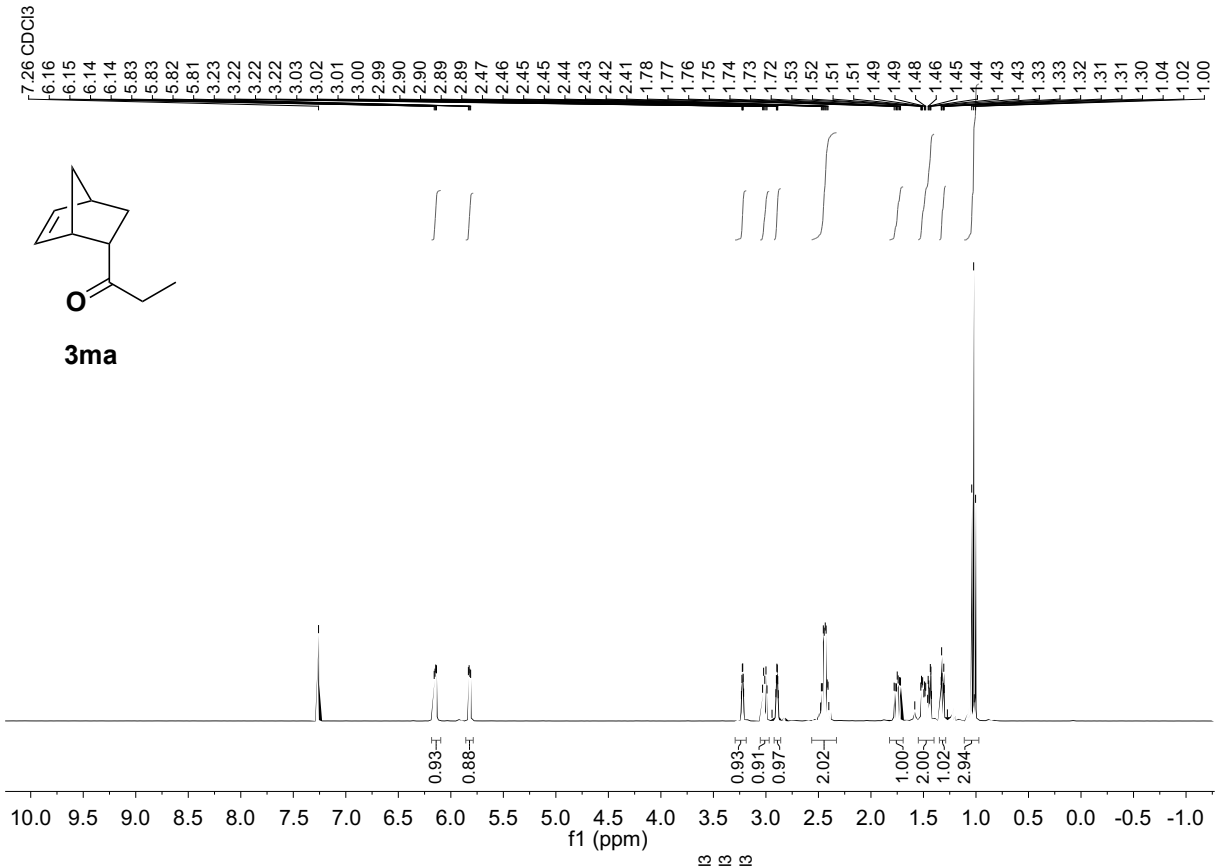
3ma + 3ma': ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.17 – 6.07 (m), 5.81 (dd, *J* = 5.8, 2.7 Hz, 1H), 3.21 (s), 3.05 – 2.85 (m), 2.63 – 2.32 (m), 1.85 (dt, *J* = 11.5, 4.1 Hz, 1H), 1.73 (ddd, *J* = 12.3, 8.9, 3.7 Hz, 1H), 1.51 – 1.17 (m), 1.10 – 0.96 (m).

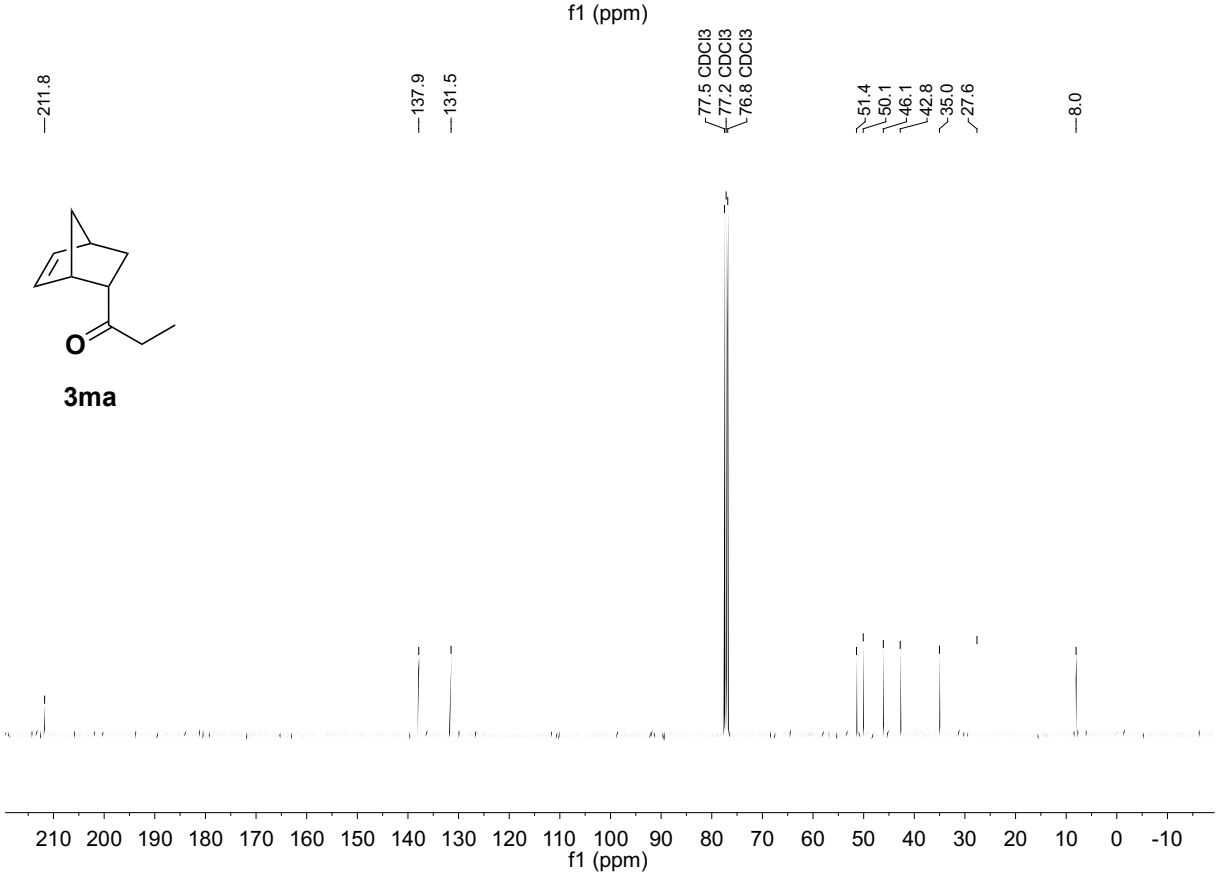
3ma + 3ma': ^{13}C NMR (101 MHz, $CDCl_3$): δ = 213.6 (*C*OEt), 211.7 (*C*OEt), 138.3 (C_{alkene}), 137.8 (C_{alkene}), 136.0 (C_{alkene}), 131.4 (C_{alkene}), 51.4, 50.5, 50.0, 46.08, 46.0, 45.8, 42.7, 41.8, 35.9, 35.0, 29.4, 27.6, 8.2, 8.0.

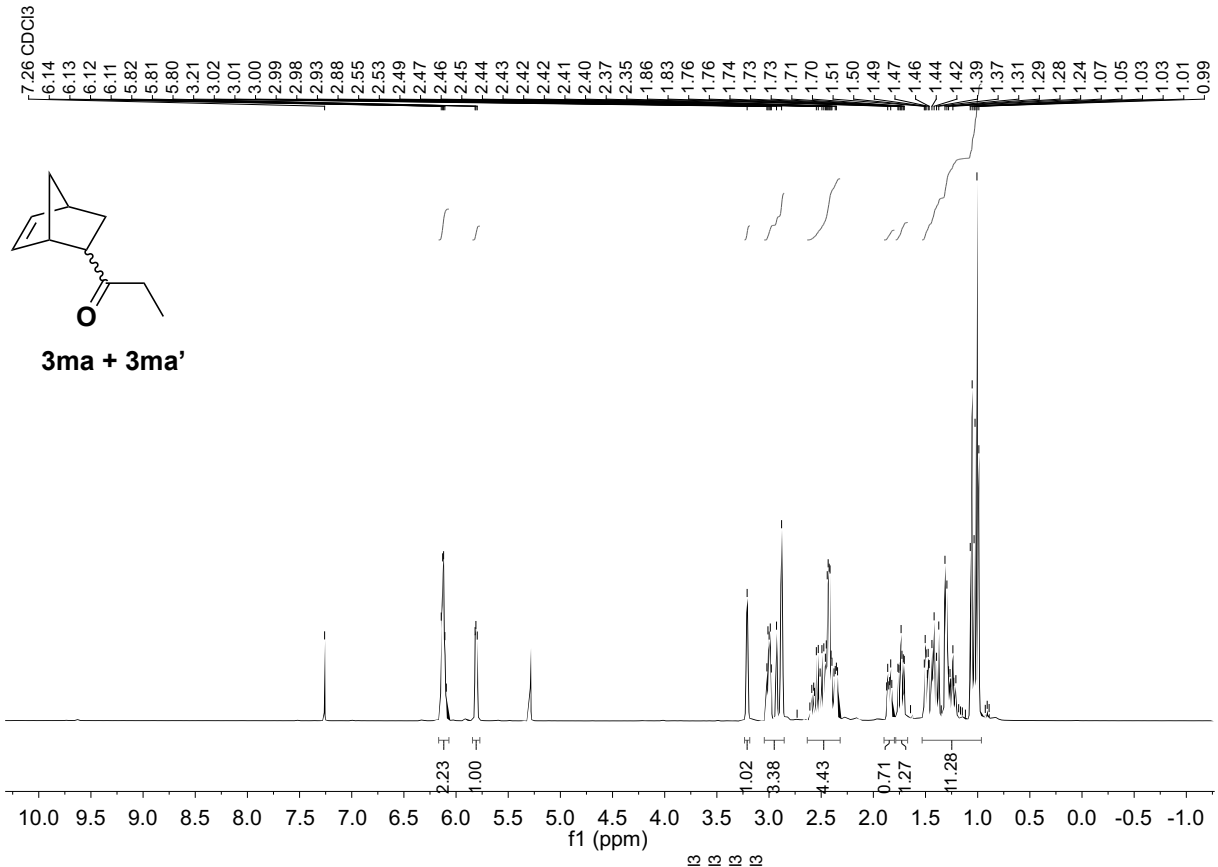
HR-MS (ESI): m/z calc. for $[M+Na]^+$ 173.09369, found 173.09396.

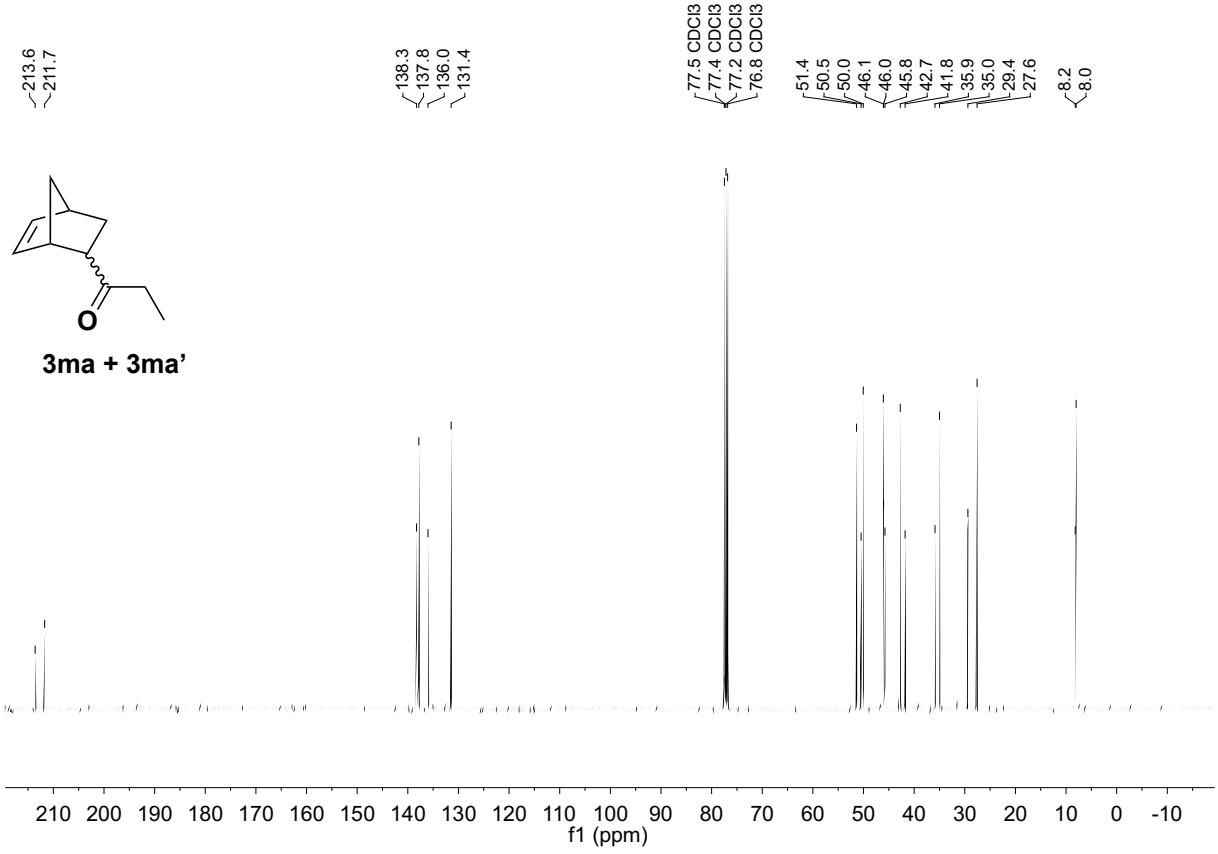
GC-MS (EI, , mixture): t_r = 4.04 min, m/z(%) = 150 (10, $[M^{+\bullet}]$), 66 (100, $[C_5H_6^{+\bullet}]$); t_r = 4.20 min, m/z(%) = 150 (12, $[M^{+\bullet}]$), 66 (100, $[C_5H_6^{+\bullet}]$).

IR (**3m**, ATR, $\tilde{\nu}$ [cm^{-1}]): 3136 (w, C-H_{arom}), 3062 (w, C-H_{arom}), 2969 (m, C-H_{aliph}), 2935 (w, C-H_{aliph}), 2869 (w, C-H_{aliph}), 1683 (s, C=O), 1448 (w), 1415 (w), 1374 (w), 1333 (w), 1262 (m), 1224 (w), 1176 (w), 1131 (w), 1126 (w), 1065 (s), 1030 (m), 1000 (s), 966 (w), 920 (m), 844 (s), 807 (m), 777 (m), 747 (m), 706 (vs).

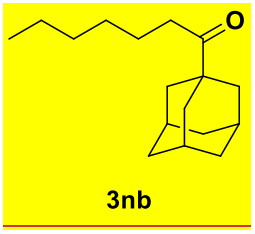

7.26 CDCl3
6.16 6.15 6.14 6.14 5.83 5.83 5.82 5.81 3.23 3.22 3.22 3.22 3.03 3.02 3.01 3.00 2.99 2.90 2.90 2.89 2.89 2.47 2.46 2.45 2.45 2.44 2.43 2.42 2.41 1.78 1.77 1.76 1.75 1.74 1.73 1.72 1.53 1.52 1.51 1.51 1.49 1.49 1.48 1.46 1.45 1.44 1.43 1.43 1.33 1.33 1.32 1.31 1.31 1.30 1.04 1.02 1.00
O
3ma
0.93 0.88 0.93 0.91 0.97 2.02 1.00 2.00 1.02 2.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


211.8
137.9
131.5
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
51.4
50.1
46.1
42.8
35.0
27.6
8.0
O
3ma
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.26 CDCl3
6.14
6.13
6.12
6.11
5.82
5.81
5.80
3.21
3.02
3.01
3.00
2.99
2.98
2.93
2.88
2.55
2.53
2.49
2.47
2.46
2.45
2.44
2.43
2.42
2.42
2.41
2.40
2.37
2.35
1.86
1.83
1.76
1.76
1.74
1.73
1.73
1.71
1.70
1.51
1.50
1.49
1.47
1.46
1.44
1.42
1.39
1.37
1.31
1.29
1.28
1.24
1.07
1.05
1.03
1.01
0.99
O
3ma + 3ma’
2.23
1.00
1.02
3.38
4.43
0.71
1.27
11.28
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


213.6
211.7
138.3
137.8
136.0
131.4
77.5 CDCl3
77.4 CDCl3
77.2 CDCl3
76.8 CDCl3
51.4
50.5
50.0
46.1
46.0
45.8
42.7
41.8
35.9
35.0
29.4
27.6
8.2
8.0
O
3ma + 3ma’
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1-(adamantan-1-yl)heptan-1-one (**3nb**)



According to GP-E, the product **3nb** was synthesized using hexyl manganese bromide lithium chloride complex (4.4 mL, 0.27 M, 1.2 mmol, 1.2 equiv.) and *S*-ethyl adamantane-1-carbothioate **1n** (224 mg, 1 mmol). The yield was calculated by determination of the relative composition R of the ethylthioate and ethyl ketone group in the ^{1}H NMR spectrum (298 µmol, 30%).

The sample concentration was determined by the formula:

$$R = \frac{n_p}{n_{SM}} = \frac{I_P}{N_p} / \frac{I_{SM}}{N_{SM}} = \frac{0.495}{1.00} = 0.5$$

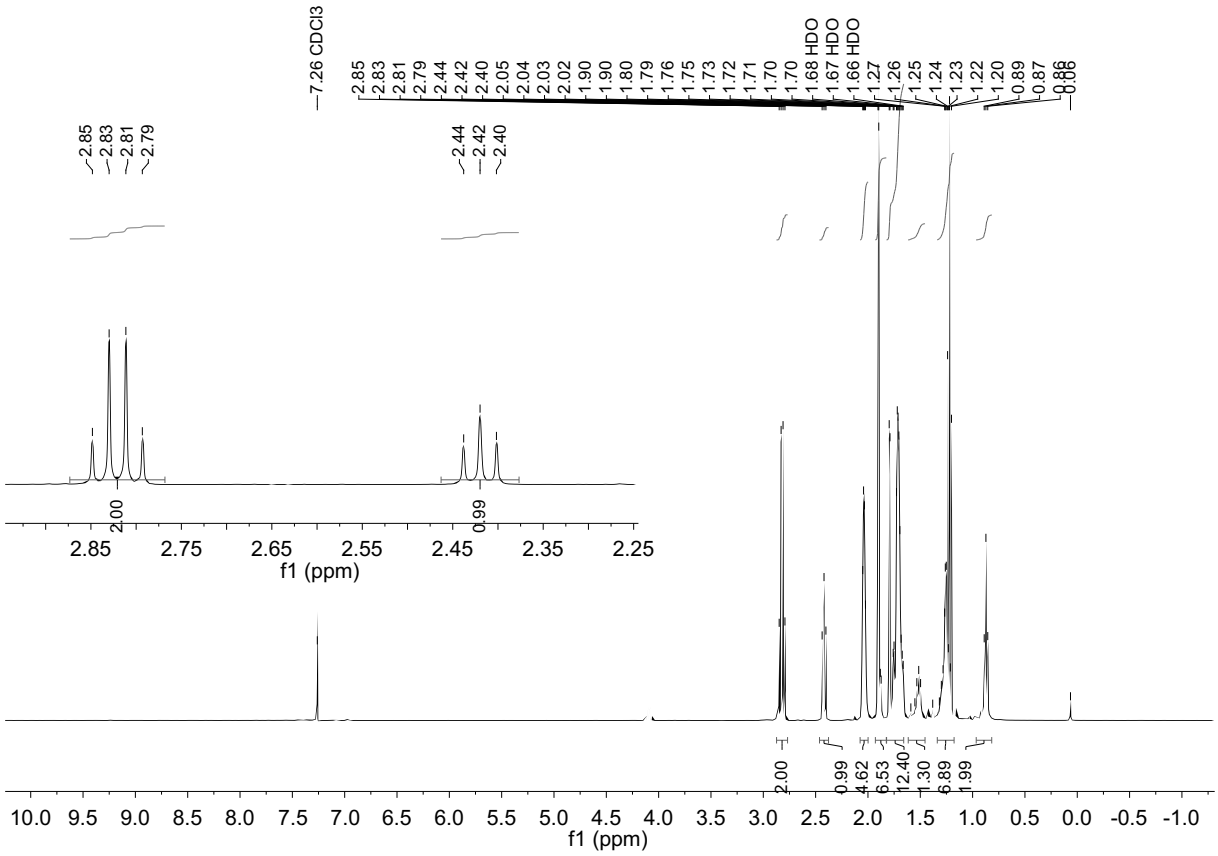
$$m_{total} = M_P * n_P + M_{SM} * \frac{n_P}{R}$$

$$n_P = \frac{m_{total}}{\left(\frac{M_{SM}}{R}\right) + M_P} = \frac{191\ mg}{\left(\frac{224.36\frac{g}{mol}}{0.49}\right) + 192.3\ \frac{g}{mol}} = 298\ \mu mol$$

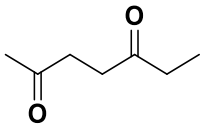
R: relative composition
I_p: Integral of product
I_{SM}: Integral starting material
n_P: amount of product
n_{SM}: amount of starting material
N_P: nuclei count of product
N_{SM}: nuclei count of starting material
M_P: molecular mass of the product
M_{SM}: molecular mass of the starting material

$C_{13}H_{20}O$ (192.30 g/mol)

R_f: 0.35 (*n*Hex/ACN = 99:1 v/v) [anis]


7.26 CDCl3
2.85
2.83
2.81
2.79
2.44
2.42
2.40
2.05
2.04
2.03
2.02
1.90
1.80
1.79
1.76
1.75
1.73
1.72
1.71
1.70
1.68 HDO
1.67 HDO
1.66 HDO
1.27
1.26
1.25
1.24
1.23
1.22
1.20
0.89
0.87
2.00
0.99
f1 (ppm)
2.00
0.99
4.62
6.53
12.40
1.30
6.89
1.99
f1 (ppm)

2,5-heptadion (**3oa**)



3oa

According to GP-E, the product **3oa** was synthesized using ethyl manganese bromide lithium chloride complex (0.25 M, 4.8 mL, 1.2 mmol, 1.2 equiv.) and *S*-ethyl 4-oxopentanethioate **1o** (160 mg, 1.00 mmol). Purification was achieved by column chromatography (*n*Hex/Et_2O = 1:1 v/v). The product was obtained as a yellow oil (94.7 mg, 739 µmol, 74%). The spectral data is in good accordance to previous literature.[20]

$C_7H_{12}O_2$ (128.17 g/mol)

R_f: 0.32 (*n*Hex/Et_2O = 1:1 v/v) [$KMnO_4$]

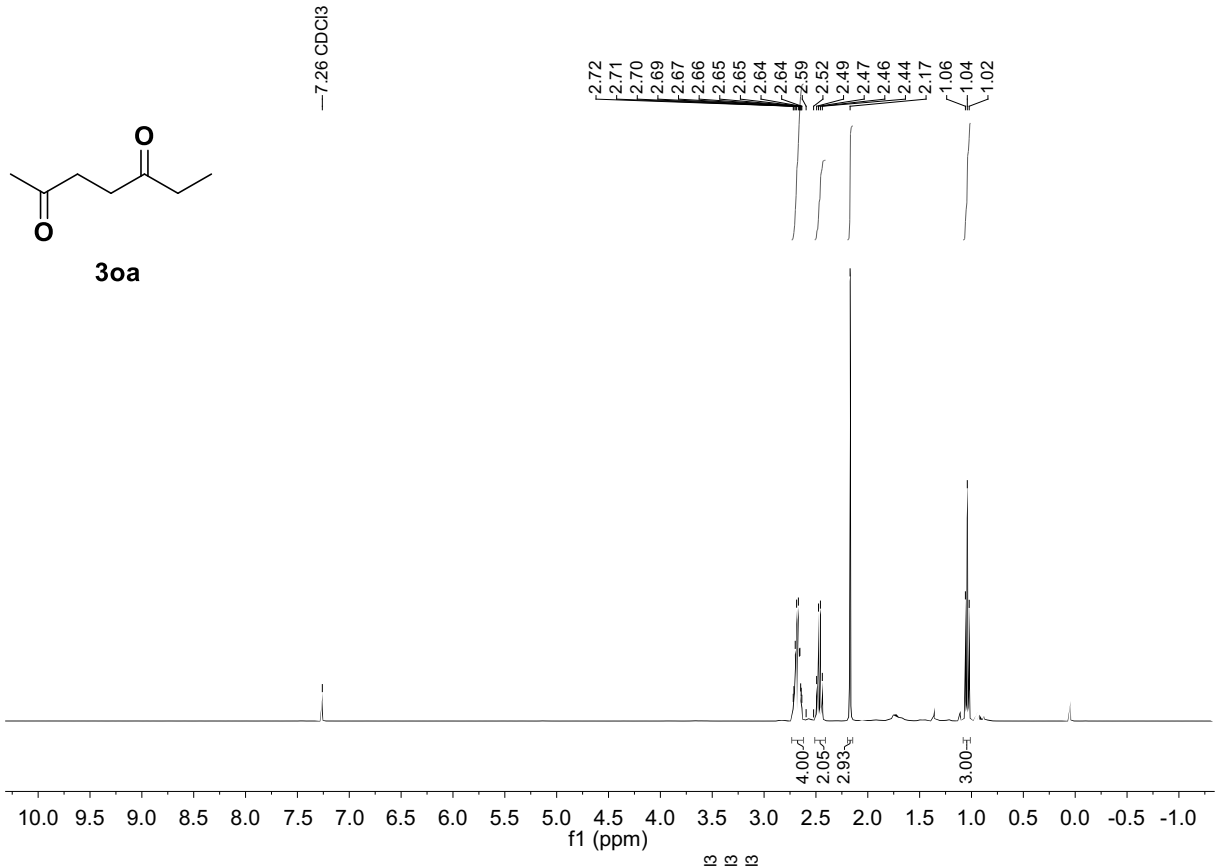
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.76 – 2.62 (m, 4H), 2.47 (q, *J* = 7.3 Hz, $COCH_2CH_3$, 2H), 2.17 (s, $COCH_3$, 3H), 1.04 (t, *J* = 7.3, $COCH_2CH_3$, 3H).

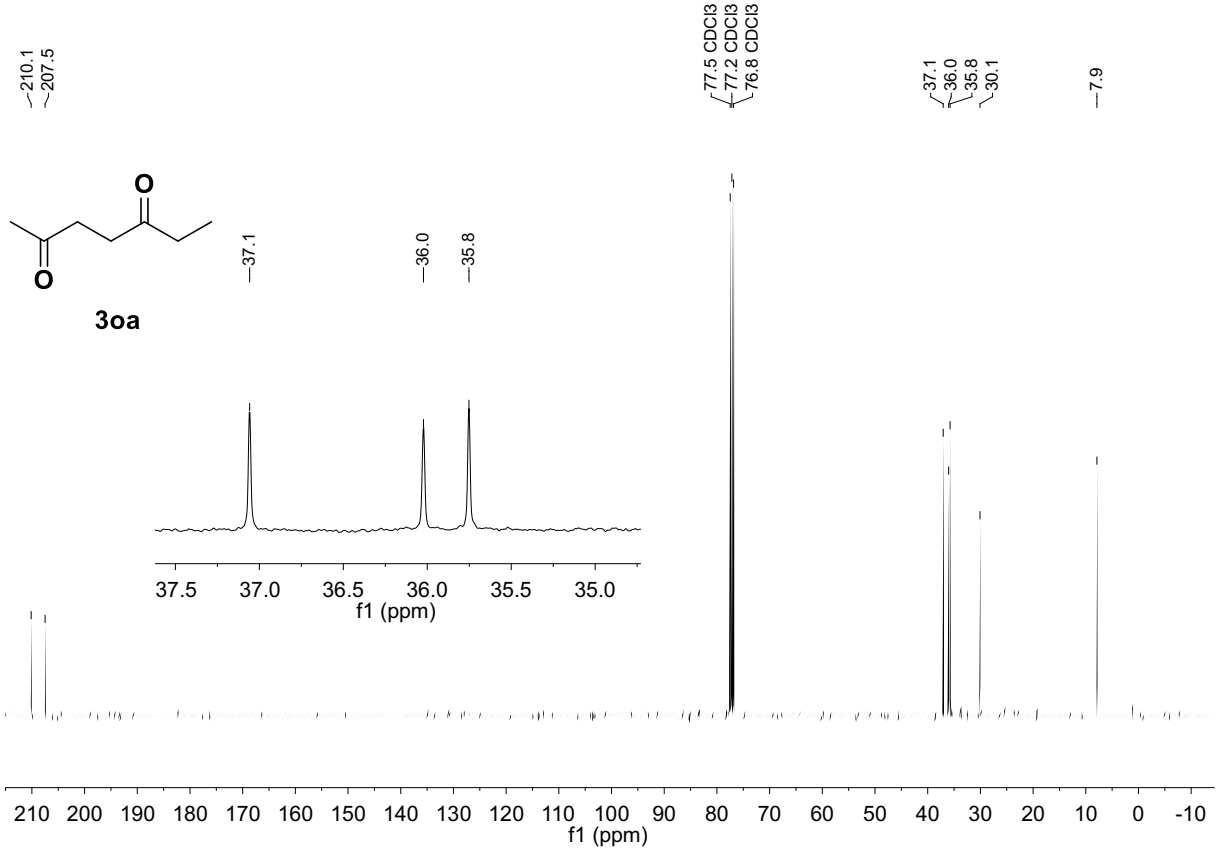
^{13}C NMR (101 MHz, $CDCl_3$): δ = 210.1 (*C*O), 207.5 (*C*O), 37.1, 36.0, 35.8, 30.1, 7.9.

GC-MS (EI): t_r = 3.07 min, m/z(%) = 99 (100, $[M^{+\bullet}\text{-}C_2H_5^{\bullet}]$).

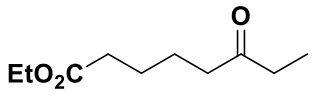
HR-MS (ESI): m/z calc. for $[M+Na]^+$ 151.07295, found 151.07319.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2976 (w, C-H_{aliph}), 2939 (w, C-H_{aliph}), 2879 (w, C-H_{aliph}), 1713 (s, C=O), 1455 (w), 1415 (w), 1370 (m), 1246 (m), 1176 (s), 1112 (m), 1028 (m), 971 (w), 859 (w), 796 (w), 766 (w).


7.26 CDCl3
2.72
2.71
2.70
2.69
2.67
2.66
2.65
2.65
2.64
2.64
2.59
2.52
2.49
2.47
2.46
2.44
2.17
1.06
1.04
1.02
O
O
3oa
4.00
2.05
2.93
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


210.1
207.5
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
37.1
36.0
35.8
30.1
7.9
O
O
3oa
37.1
36.0
35.8
37.5 37.0 36.5 36.0 35.5 35.0
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

ethyl 6-oxooctanoate (**3pa**)



3pa

According to GP-E, the product **3pa** was synthesized using ethylmanganese bromide lithium chloride complex (4.3 mL, 1.2 mmol, 0.28 M, 1.2 equiv.) and ethyl 6-(ethylthio)-6-oxohexanoate (218 mg, 1.00 mmol). Purification was achieved by manual column chromatography (*n*Hex/Et_2O = 7:3 v/v). The product was obtained as a colorless oil (150 mg, 805 µmol, 81%).

$C_{10}H_{18}O_3$ (186.25 g/mol)

R_f: 0.31 (*n*Hex/Et_2O = 7:3) [$KMnO_4$]

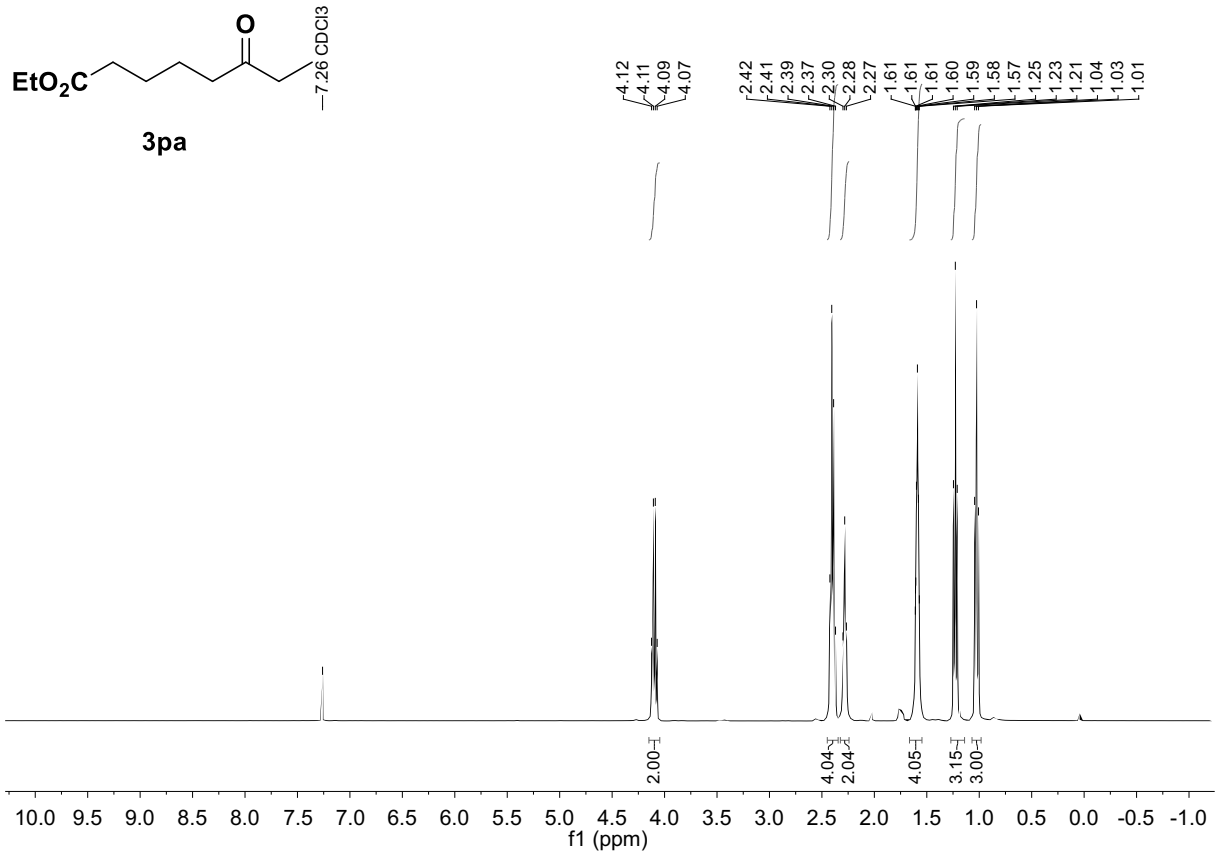
^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.10 (q, *J* = 7.2, 1.1 Hz, 2H), 2.42 – 2.37 (m, 4H), 2.32 – 2.23 (m, 2H), 1.65 – 1.52 (m, 4H), 1.23 (t, *J* = 7.2, 1.1 Hz, 3H), 1.03 (t, *J* = 7.4, 1.1 Hz, 3H).

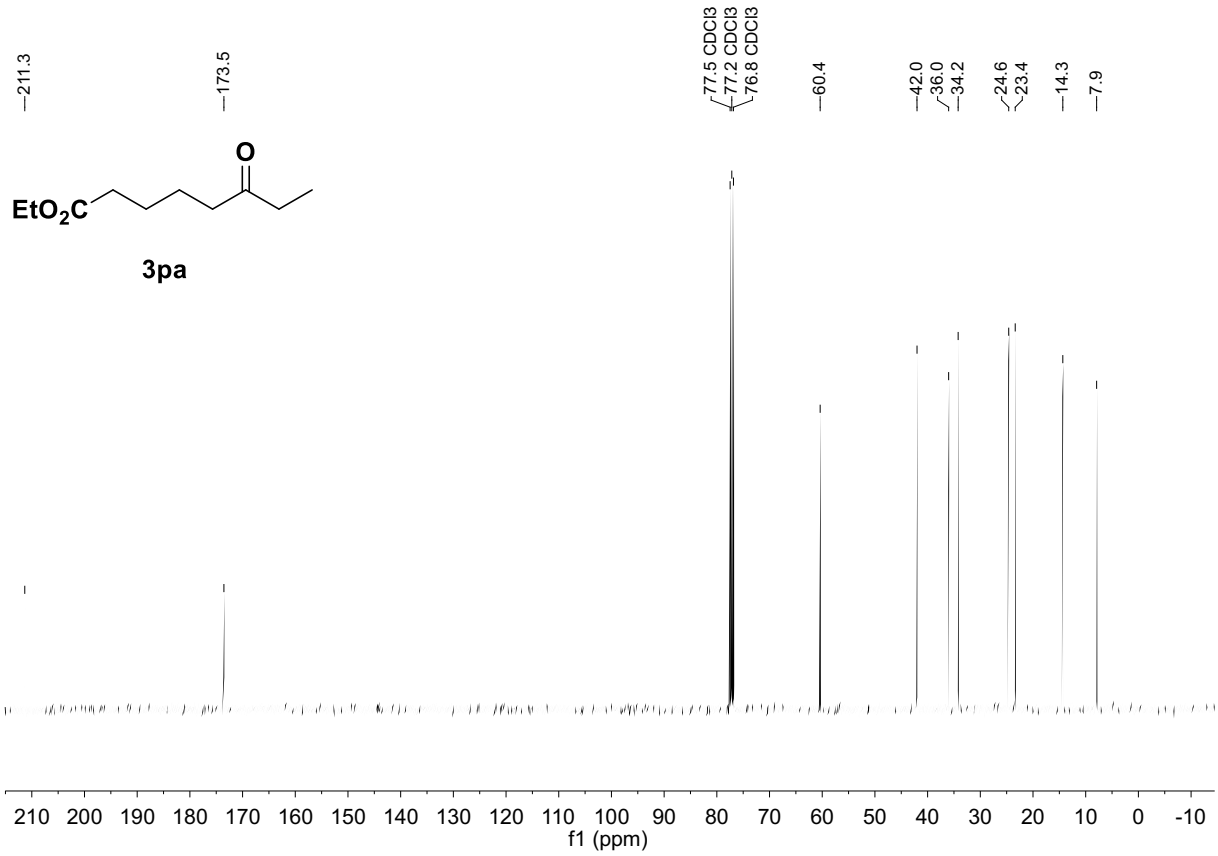
^{13}C NMR (101 MHz, $CDCl_3$): δ = 211.3 (*C*OEt), 173.5 (*C*O_2Et), 60.4, 42.0, 36.0, 34.2, 24.6, 23.4, 14.3, 7.9 ($COCH_2CH_3$).

GC-MS (EI): t_r = 5.59 min, m/z(%) = 157 (10, [$M^{+\bullet}$-$C_2H_5^{\bullet}$]), 115 (21, [$M^{+\bullet}$-$C_4H_7O^{\bullet}$]), 110 (69), 101 (23, [$M^{+\bullet}$-$C_5H_9O^{\bullet}$]), 57 (100, [$H_5C_2O^{+\bullet}$ or $H_9C_4^{+\bullet}$]).

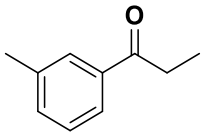
HR-MS (ESI): m/z calc. for $[M+Na]^+$ 209.11482, found 209.11522.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2976 (w, C-H_{aliph}), 2939 (w, C-H_{aliph}), 2879 (w, C-H_{aliph}), 1730 (s, C=O_{ester}), 1712 (s, C=O_{ketone}), 1455 (w), 1414 (w), 1370 (m), 1243 (m), 1176 (s), 1113 (m), 1028 (m).


O
EtO2C
7.26 CDCl3
3pa
4.12
4.11
4.09
4.07
2.42
2.41
2.39
2.37
2.30
2.28
2.27
1.61
1.61
1.61
1.60
1.59
1.58
1.57
1.25
1.23
1.21
1.04
1.03
1.01
2.00
4.04
2.04
4.05
3.15
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


211.3
173.5
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
60.4
42.0
36.0
34.2
24.6
23.4
14.3
7.9
O
EtO2C
3pa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1-(*m*-tolyl)propan-1-one (**3qa**)



3qa

According to GP-E, the product **3qa** was synthesized using ethylmanganese bromide lithium chloride complex (4.8 mL, 1.2 mmol, 0.25 M, 1.2 equiv.) and *S*-ethyl 3-methylbenzothioate **1q** (180 mg, 1.00 mmol). Purification was achieved by manual column chromatography (*n*Hex/Et_2O = 98:2 v/v). The product was obtained as a colorless oil (124.5 mg, 840 µmol, 84%). The analytical data is in accordance to previous literature examples.[21]

$C_{10}H_{12}O$ (148.21 g/mol)

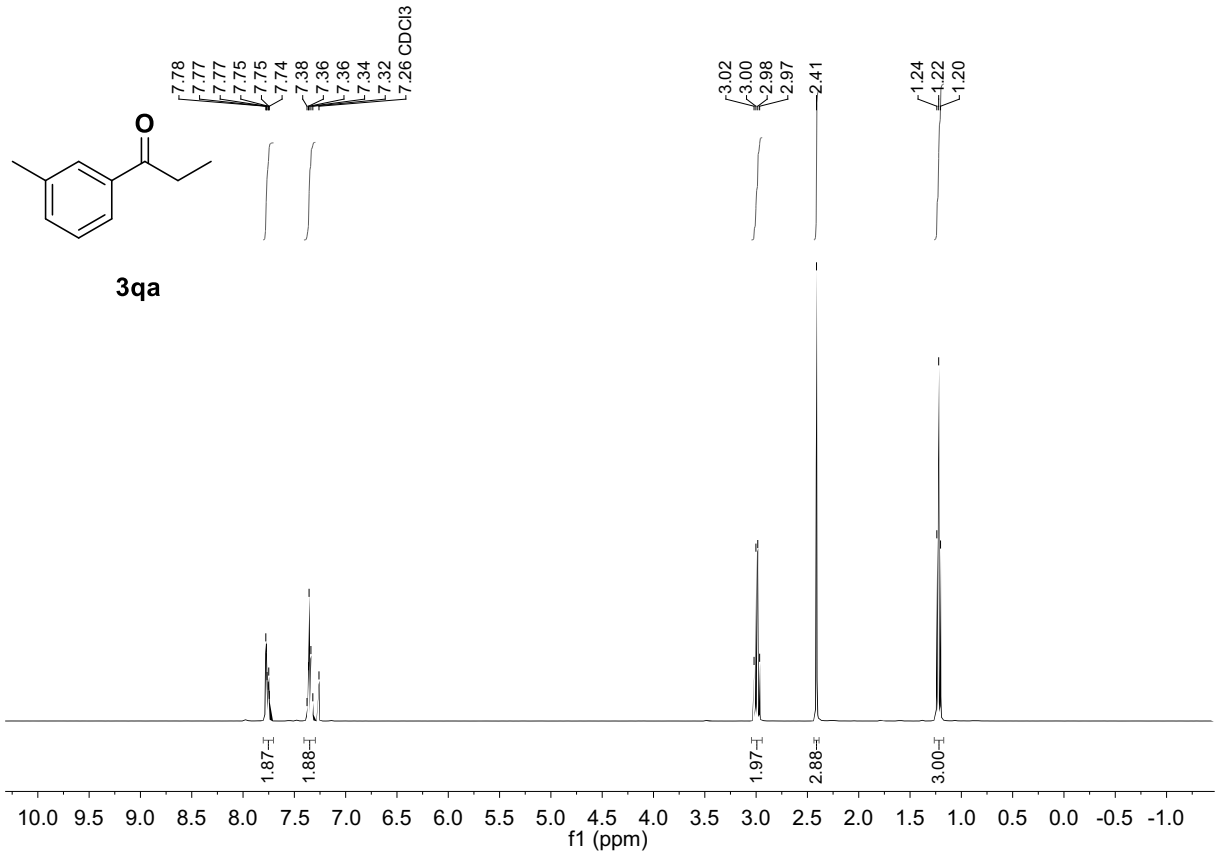
R_f: 0.15 (*n*Hex/Et_2O = 98:2 v/v)[anis]

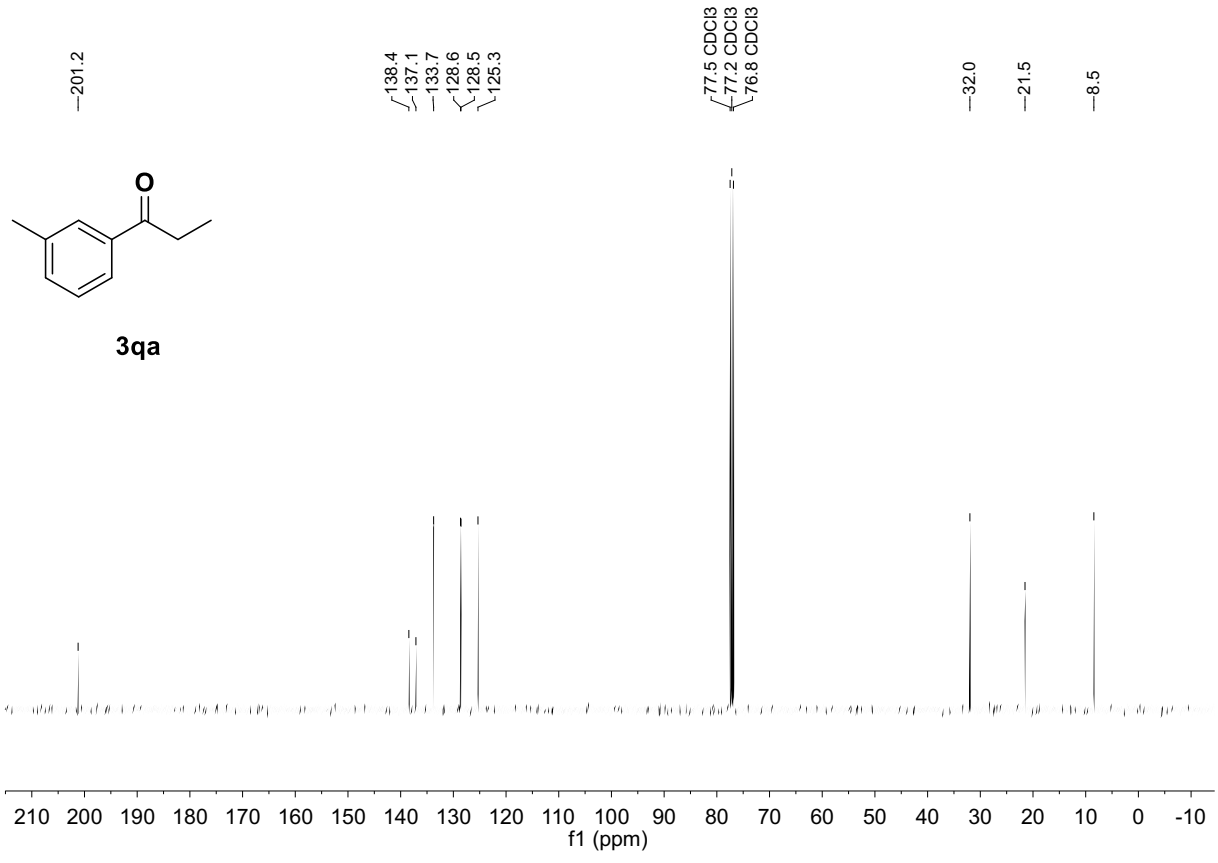
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 – 7.72 (m, 2H, Ar*H*), 7.41 – 7.29 (m, 2H, Ar*H*), 2.99 (q, *J* = 7.3 Hz, 2H, COCH_2CH$_3$), 2.41 (s, 3H, CH_3Ph), 1.22 (t, *J* = 7.3 Hz, 3H, COCH$_2$CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 201.2 (*C*O), 138.5 (C_{Ar}), 137.1 (C_{Ar}), 133.7 (C_{Ar}), 128.6 (C_{Ar}), 128.5 (C_{Ar}), 125.3 (C_{Ar}), 32.0 (Ph*C*H$_3$), 21.5 (*C*H$_2$CH$_3$), 8.5 (CH$_2$*C*H$_3$).

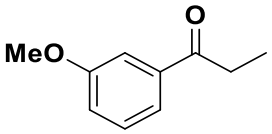
GC-MS (EI): t_r = 4.82 min, m/z(%) = 148 (14, [$M^{+\bullet}$]), 119 (100, [$M^{+\bullet}$-$C_2H_5^\bullet$]), 91 (55, [$M^{+\bullet}$-$C_2H_5^\bullet$-CO]).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3032 (w, C-H$_{arom}$), 2976 (w, C-H$_{aliph}$), 2935 (w, C-H$_{aliph}$), 2879 (w, C-H$_{aliph}$), 1683 (s, C=O), 1586 (w), 1455 (m), 1418 (w), 1348 (m), 1314 (w), 1280 (w), 1247 (s), 1165 (s), 1083 (w), 1034 (w), 1009 (w), 964 (m), 915 (w), 863 (w), 859 (w), 837 (w), 773 (s), 729 (m), 688 (s).


7.78
7.77
7.77
7.75
7.75
7.74
7.38
7.36
7.36
7.34
7.32
7.26 CDCl3
3.02
3.00
2.98
2.97
2.41
1.24
1.22
1.20
O
3qa
1.87
1.88
1.97
2.88
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


201.2
138.4
137.1
133.7
128.6
128.5
125.3
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
32.0
21.5
8.5
O
3qa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1-(3-methoxyphenyl)propan-1-one (**3ra**)



3ra

According to GP-E, the product **3ra** was synthesized using ethylmanganese bromide lithium chloride complex (6.3 mL, 1.2 mmol, 0.19 M, 1.2 equiv.) and *S*-ethyl 3-methoxybenzothioate **1r** (196.3 mg, 1.00 mmol). Extraction of the compound was achieved by utilizing Et_2O as solvent. Purification was achieved by column chromatography (*n*Hex/Et_2O = 98:2 v/v). The product was obtained as a colorless oil (60.5 mg, 368 µmol, 37%). The analytical data matches previous reports.[22]

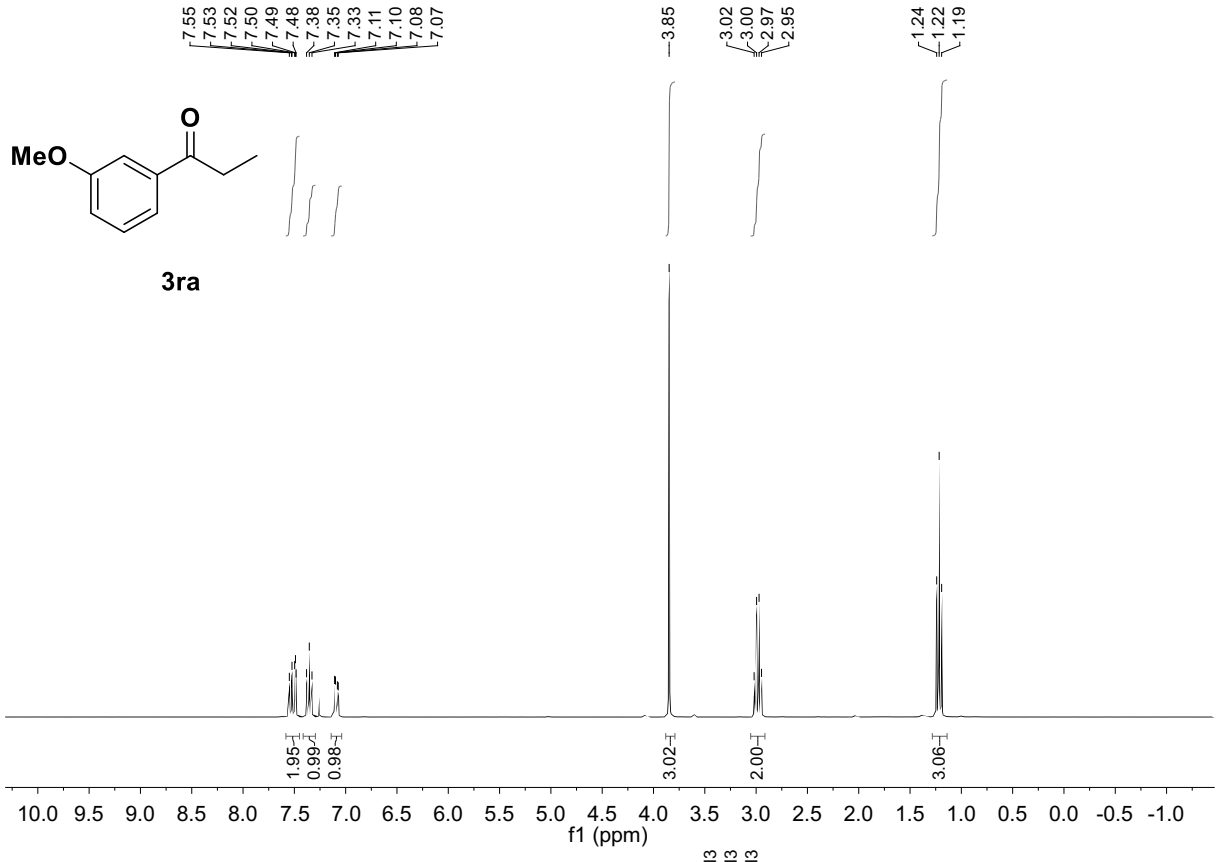
$C_{10}H_{12}O_2$ (164.20 g/mol)

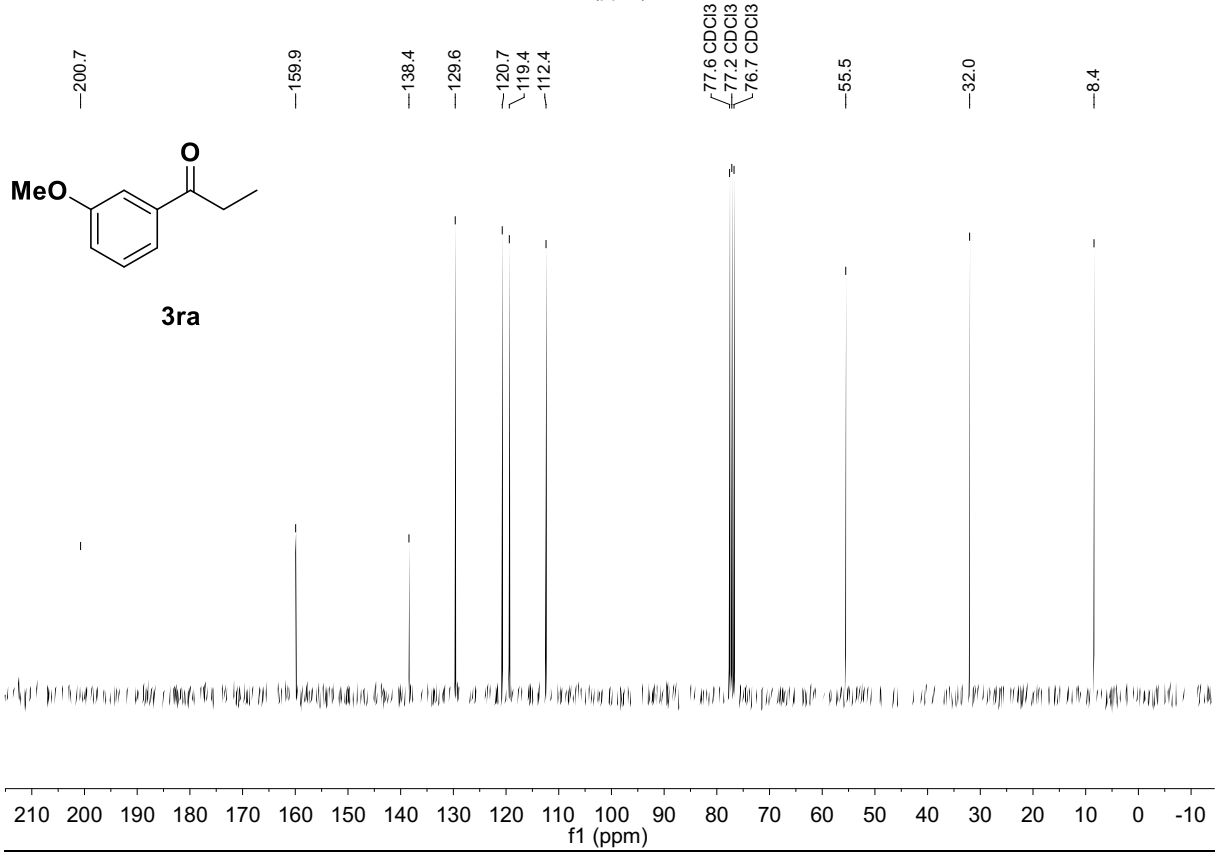
R_f: 0.11 (*n*Hex/Et_2O = 98:2) [anis]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 – 7.45 (m, 2H, Ar*H*), 7.35 (t, *J* = 7.9 Hz, 1H, Ar*H*), 7.09 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H, Ar*H*), 3.85 (s, 3H, OCH_3), 2.98 (q, *J* = 7.2 Hz, 2H, COCH_2CH$_3$), 1.22 (t, *J* = 7.2 Hz, 3H, COCH$_2$CH_3).

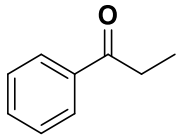
^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.7 (CO), 159.9 (C_{Ar}), 138.4 (C_{Ar}), 129.6 (C_{Ar}), 120.7 (C_{Ar}), 119.4 (C_{Ar}), 112.4 (C_{Ar}), 55.5(OCH$_3$), 32.0 (*C*H$_2$CH$_3$), 8.4 (CH$_2$*C*H$_3$).

GC-MS (EI): t_r = 5.73 min, m/z(%) = 164 (31, [$M^{+\bullet}$]), 135 (100, [$M^{+\bullet}$-$C_2H_5^{\bullet}$]), 107 (30, [$M^{+\bullet}$-$C_2H_5^{\bullet}$-CO]).


7.55
7.53
7.52
7.50
7.49
7.48
7.38
7.35
7.33
7.11
7.10
7.08
7.07
3.85
3.02
3.00
2.97
2.95
1.24
1.22
1.19
MeO
O
3ra
1.95
0.99
0.98
3.02
2.00
3.06
f1 (ppm)


200.7
159.9
138.4
129.6
120.7
119.4
112.4
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
55.5
32.0
8.4
MeO
O
3ra
f1 (ppm)

propiophenone (**3ta**)



3ta

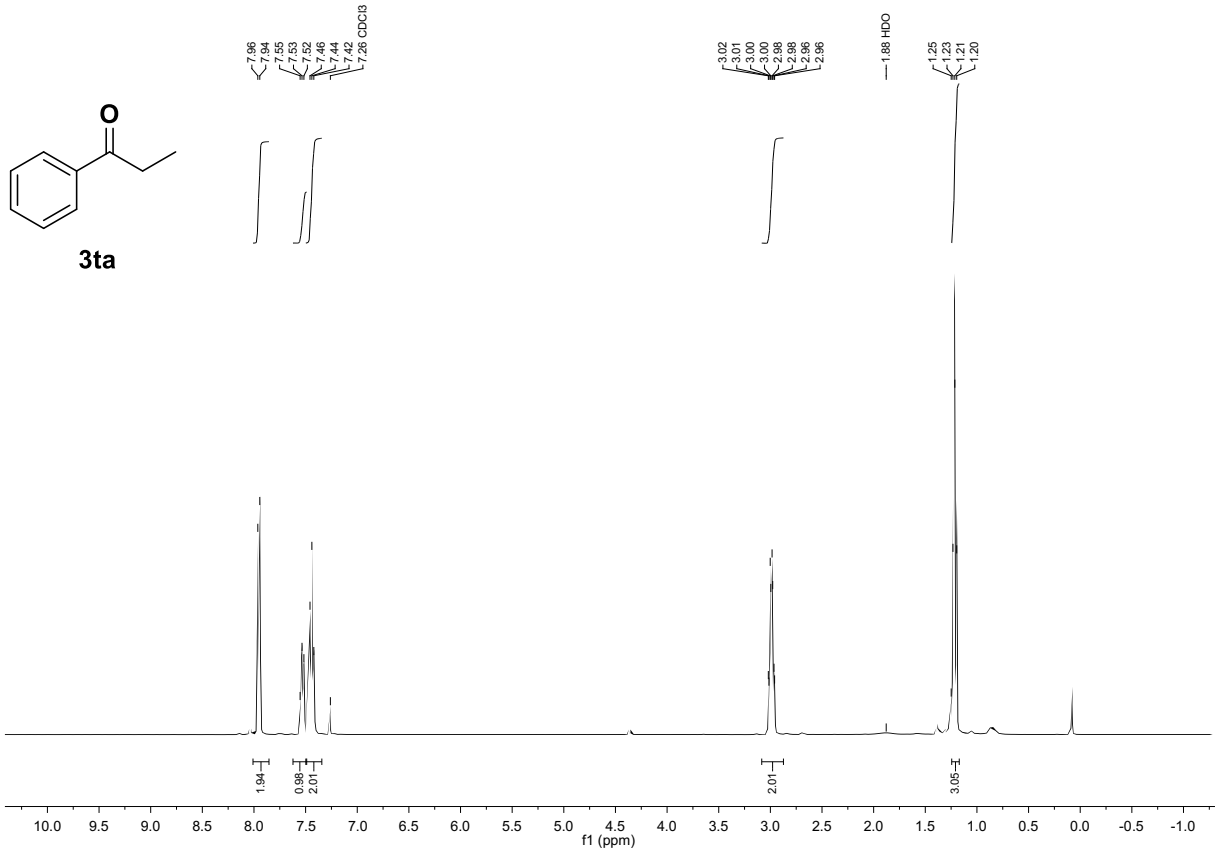
According to GP-E, the product **3ta** was synthesized using ethyl manganese bromide lithium chloride complex (4.14 mL, 1.2 mmol, 0.29 M, 1.2 equiv.) and *S*-ethyl benzothioate **1t** (166.3 mg, 1.00 mmol). Purification was achieved by column chromatography (*n*Hex/Et_2O = 95:5). The product was obtained as a yellow oil with a characteristic smell (128.0 mg, 954 µmol, 95%). The spectral data matches the data given by the chemical vendors (e.g. Sigma Aldrich).

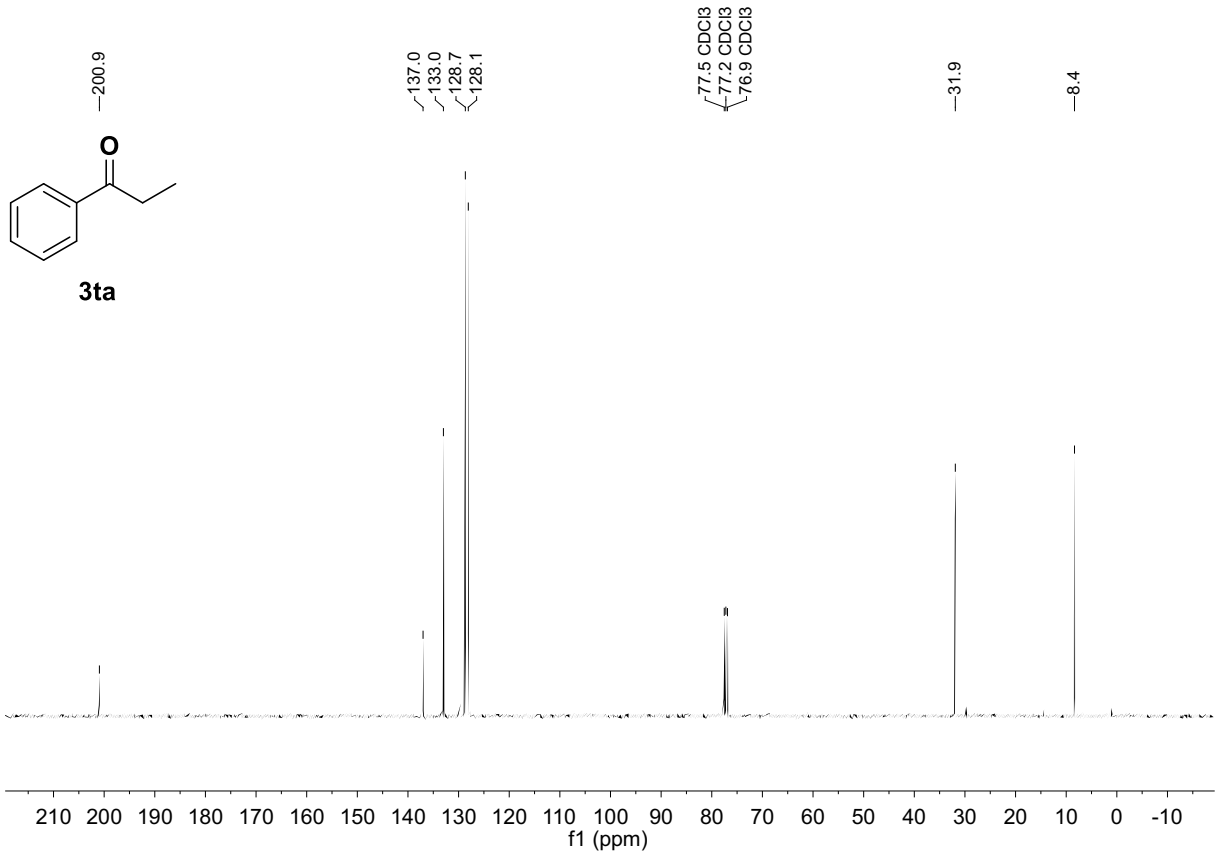
$C_9H_{10}O$ (134.18 g/mol)

R_f: 0.38 (*n*Hex/Et_2O = 95:5) [$KMnO_4$]

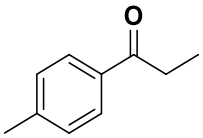
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (dt, *J* = 8.7, 1.6 Hz, Ar*H*, 2H), 7.58 – 7.49 (m, Ar*H*, 1H), 7.45 – 7.37 (m, Ar*H*, 2H), 2.99 (q, *J* = 7.2, $COCH_2CH_3$, 2H), 1.21 (t, *J* = 7.3, $COCH_2CH_3$, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.9 (*C*O), 137.0 (C_{Ar}), 132.9 (C_{Ar}), 128.6 (C_{Ar}), 128.0 (C_{Ar}), 31.9 ($COCH_2CH_3$), 8.3($COCH_2CH_3$).


7.96
7.94
7.55
7.53
7.52
7.46
7.44
7.42
7.26 CDCl3
3.02
3.01
3.00
3.00
2.98
2.98
2.96
2.96
1.88 HDO
1.25
1.23
1.21
1.20
O
3ta
1.94
0.98
2.01
2.01
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


200.9
137.0
133.0
128.7
128.1
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
31.9
8.4
O
3ta
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1-(*p*-tolyl)propan-1-one (**3ua**)



3ua

According to GP-E, the product **3ua** was synthesized using ethylmanganese bromide lithium chloride complex (4.4 mL, 1.2 mmol, 0.27 M, 1.2 equiv.) and *S*-ethyl 4-methylbenzothioate **1u** (148.2 mg, 1.00 mmol). Purification was achieved by manual column chromatography (*n*Hex/Et_2O = 98:2 v/v). The product was obtained as a colorless oil with a distinct smell (113.5 mg, 766 µmol, 77%). The spectral data matches previous literature examples.[23]

$C_{10}H_{12}O$ (148.21 g/mol)

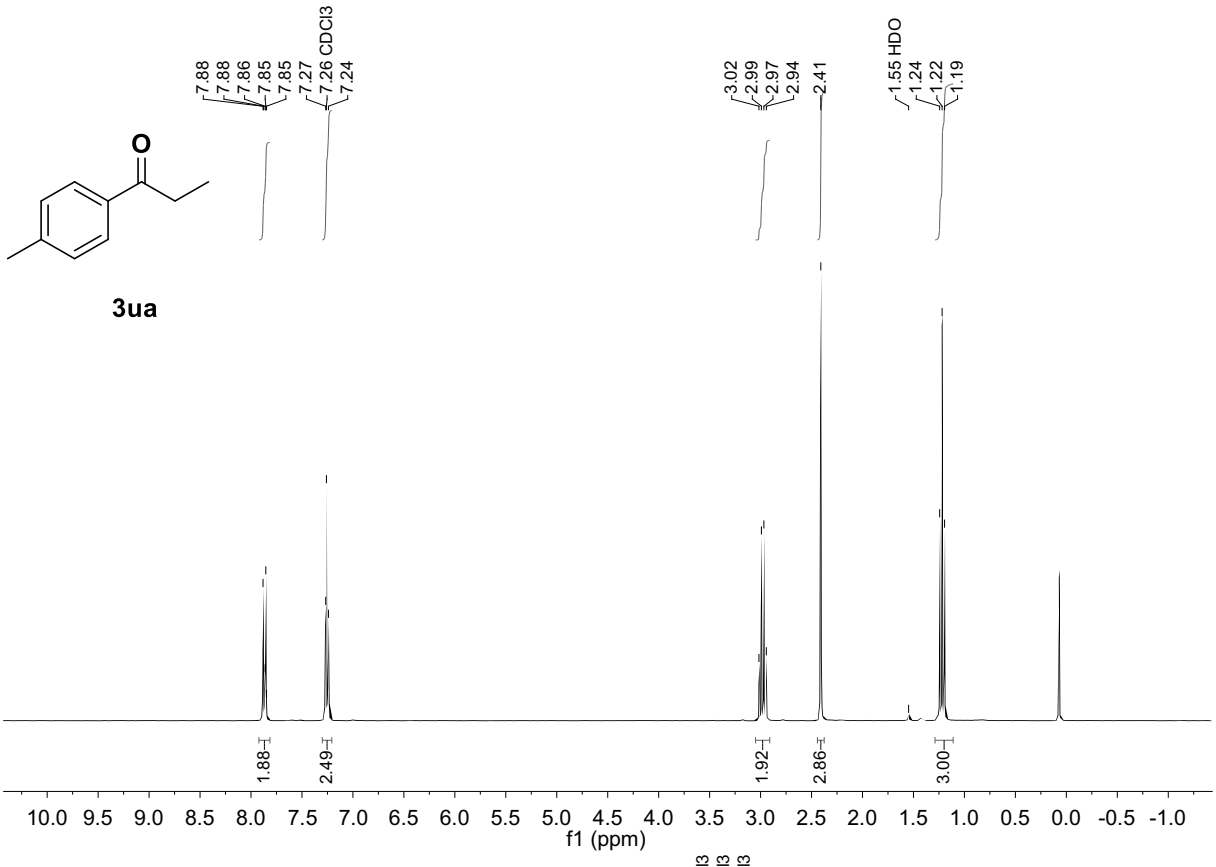
R_f: 0.17 (*n*Hex/Et_2O = 98:2 v/v) [anis]

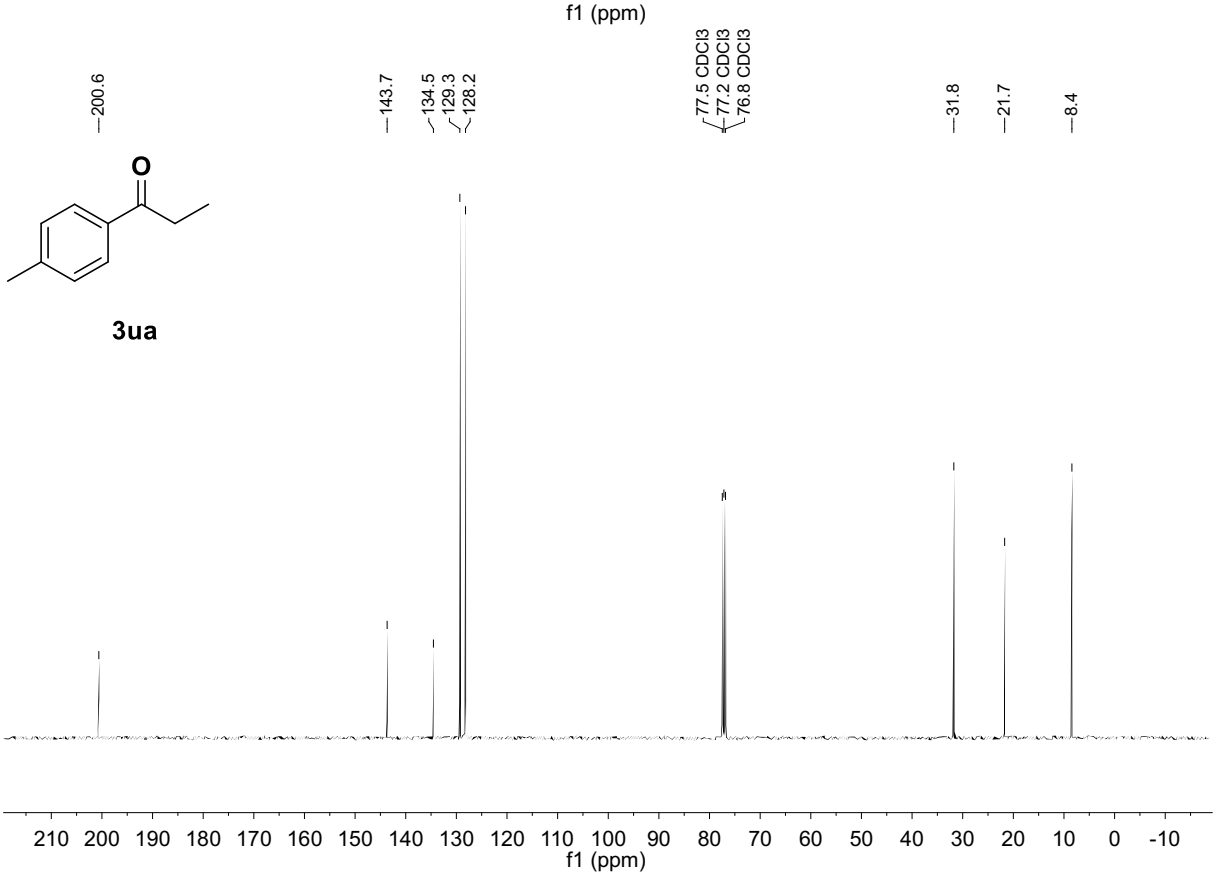
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92 – 7.81 (m, 2H, Ar*H*), 7.31 – 7.20 (m, 2H, Ar*H*), 2.98 (q, *J* = 7.3 Hz, 2H, CH_2), 2.41 (s, 3H, ArCH_3), 1.22 (t, *J* = 7.3 Hz, 3H, CH_2CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.6 (*C*OEt), 143.7 (C_{Ar}), 134.5 (C_{Ar}), 129.3 (C_{Ar}), 128.2 (C_{Ar}), 31.8 (CH_2CH_3), 21.8 (ArCH_3), 8.5 (CH_2CH_3).

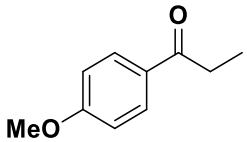
GC-MS (EI): t_r = 4.91 min, m/z(%) = 148 (11, [$M^{+\bullet}$]), 119 (100, [$M^{+\bullet}$-$C_2H_5^{\bullet}$]), 91 (50, [$M^{+\bullet}$-$C_2H_5^{\bullet}$-CO]).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3032 (w, C-H_{arom}), 2976 (w, C-H_{aliph}), 2935 (w, C-H_{aliph}), 2879 (w, C-H_{aliph}), 1679 (vs, C=O), 1605 (s), 1571 (w), 1452 (m), 1407 (m), 1351 (m), 1318 (w), 1280 (w), 1219 (s), 1180 (s), 1116 (w), 1083 (w), 1015 (m), 948 (s), 833 (w), 785 (s), 736 (w).


7.88
7.88
7.86
7.85
7.85
7.27
7.26 CDCl3
7.24
3.02
2.99
2.97
2.94
2.41
1.55 HDO
1.24
1.22
1.19
O
3ua
1.88
2.49
1.92
2.86
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


200.6
143.7
134.5
129.3
128.2
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
31.8
21.7
8.4
O
3ua
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1-(4-methoxyphenyl)propan-1-one (**3va**)



3va

According to GP-E, the product **3va** was synthesized using ethylmanganese bromide lithium chloride complex (4.4 mL, 1.2 mmol, 0.27 M, 1.2 equiv.) and *S*-ethyl 4-methoxybenzothioate **1v** (196 mg, 1.00 mmol). Purification was achieved by manual column chromatography (PE/EA = 97:3 v/v). The product was obtained as a yellow oil (146.5 mg, 892 µmol, 89%). The analytical data is in good accordance to reported literature.[21]

$C_{10}H_{12}O_2$(164.20 g/mol)

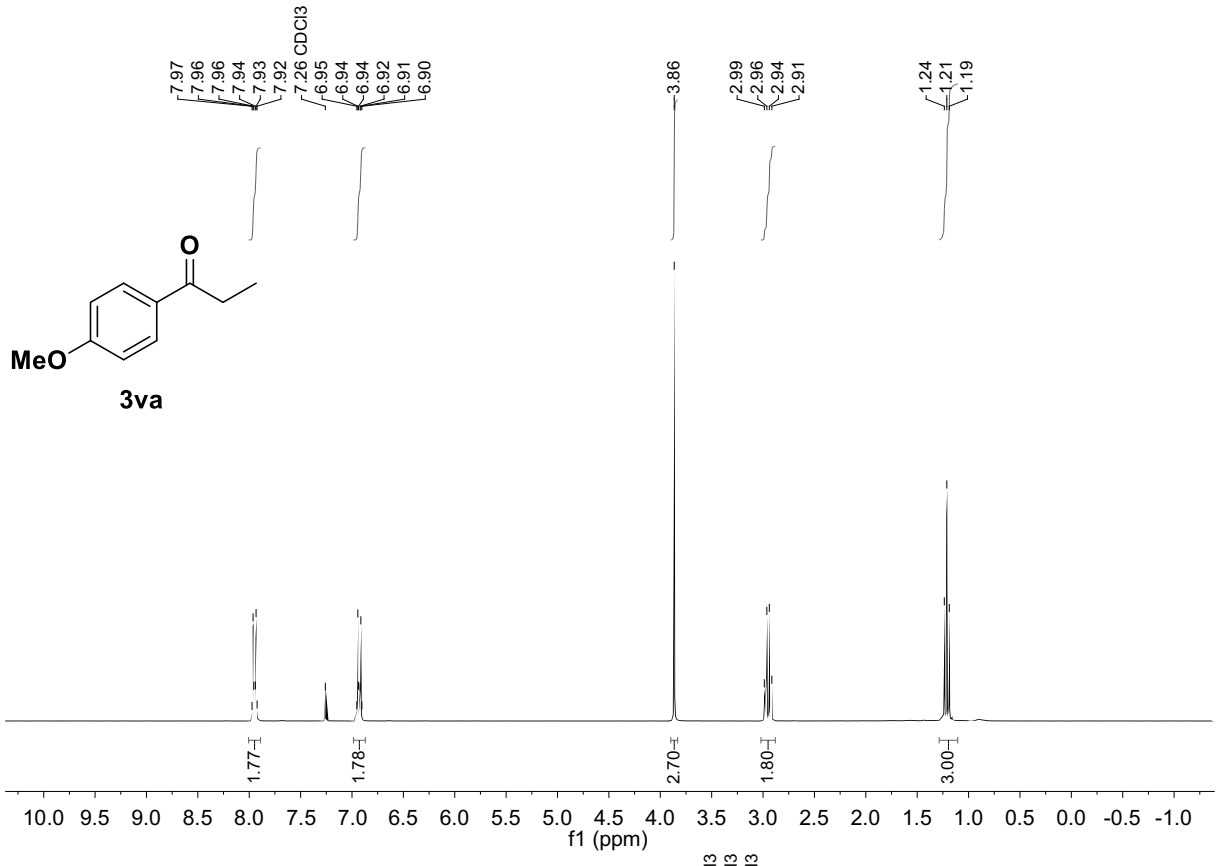
R_f: 0.13 (*n*Hex/Et_2O = 30:1) [anis]

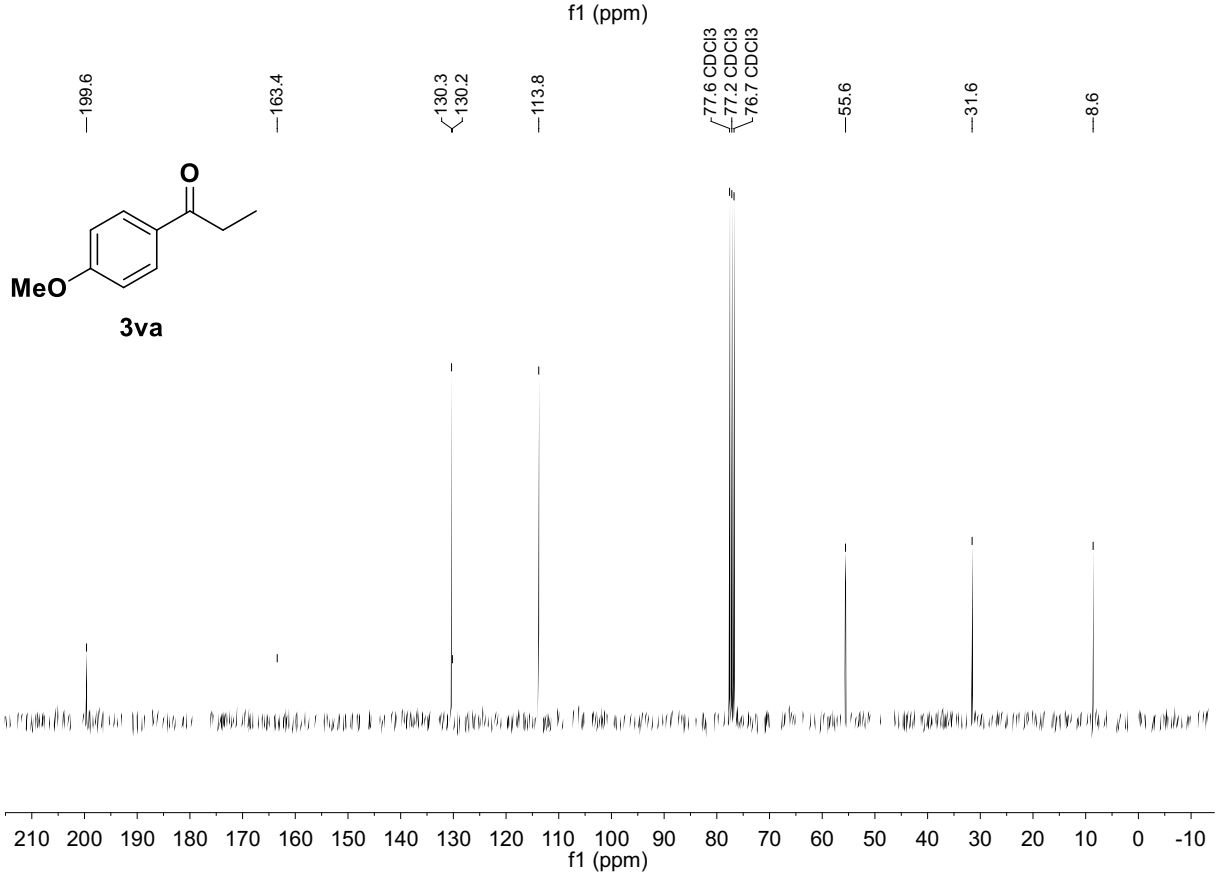
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 – 7.89 (m, 2H, Ar*H*), 6.99 – 6.87 (m, 2H, Ar*H*), 3.86 (s, 3H, OCH_3), 2.95 (q, *J* = 7.3 Hz, 2H,COC$H_2$$CH_3$), 1.21 (t, *J* = 7.3 Hz, 3H,$COCH_2$CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.6 (*C*O), 163.4 (C_{Ar}), 130.4 (C_{Ar}), 130.2 (C_{Ar}), 113.8 (C_{Ar}), 55.6 (OCH_3), 31.6 (CH_2CH_3), 8.6 (CH_2CH_3).

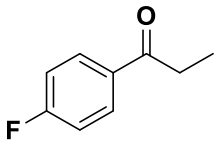
GC-MS (EI): t_r = 6.04 min, m/z(%) = 164 (16, [$M^{+\bullet}$]), 135 (100, [$M^{+\bullet}$-$C_2H_5^{\bullet}$]), 107(13, [$M^{+\bullet}$-$C_2H_5^{\bullet}$-CO]).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2972 (w, C-H_{aliph}), 2935 (w, C-H_{aliph}), 2909 (w, C-H_{aliph}), 2839 (w, C-H_{aliph}), 1675 (s, C=O), 1597 (s), 1508 (m), 1456 (m), 1415 (m), 1351 (m), 1310 (m), 1254 (s), 1224 (vs, C-O-C_{asymm}), 1168 (vs), 1109 (m), 1021 (s, C-O-C_{asymm}), 948 (s), 841 (s), 796 (s), 733 (w).


7.97
7.96
7.96
7.94
7.93
7.92
7.26 CDCl3
6.95
6.94
6.94
6.92
6.91
6.90
3.86
2.99
2.96
2.94
2.91
1.24
1.21
1.19
O
MeO
3va
1.77
1.78
2.70
1.80
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


199.6
163.4
130.3
130.2
113.8
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
55.6
31.6
8.6
O
MeO
3va
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1-(4-fluorophenyl)propan-1-one (**3wa**)



3wa

According to GP-E, the product **3wa** was synthesized using ethylmanganese bromide lithium chloride complex (0.21 M, 5.7 mL, 1.2 mmol, 1.2 equiv.) and *S*-ethyl 4-fluorobenzothioate **1w** (184 mg, 1.00 mmol). Purification was achieved by column chromatography (*n*Hex/Et_2O= 98:2 v/v). Due to compound volatility, evaporation of solvent was fully achieved by bulb-to-bulb-distillation (90 °C, 500 mbar). The product was obtained as a colorless oil (126 mg, 829 µmol, 83%). The analytical data is in good accordance previous literature examples.[24]

C_9H_9FO (152.17 g/mol)

R_f: 0.33 (*n*Hex/Et_2O= 98:2 v/v) [anis]

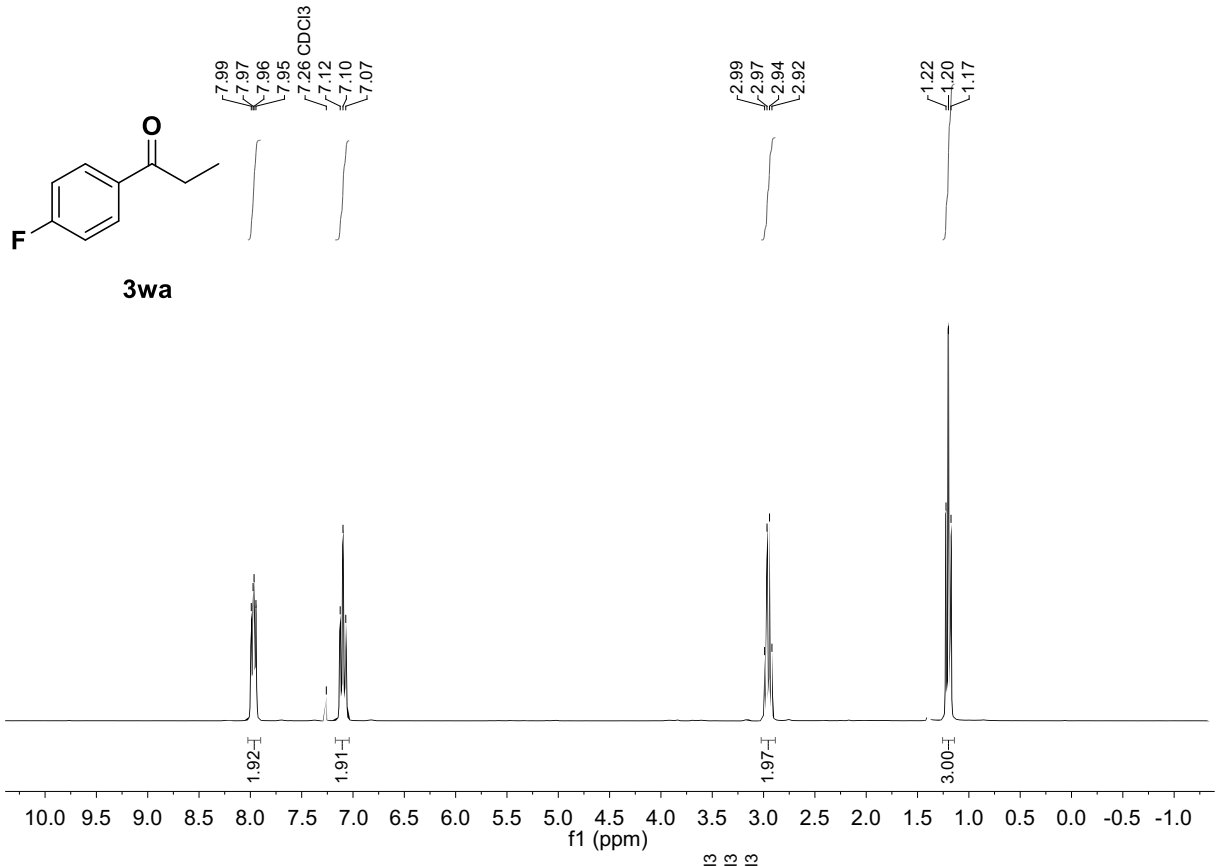
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.97 (ddd, *J* = 8.9, 5.4, 1.4 Hz, 2H), 7.17 – 7.02 (m, 2H), 2.95 (q, *J* = 7.3, 2H, COC$H_2$$CH_3$), 1.20 (t, *J* = 7.3, 3H, $COCH_2CH_3$).

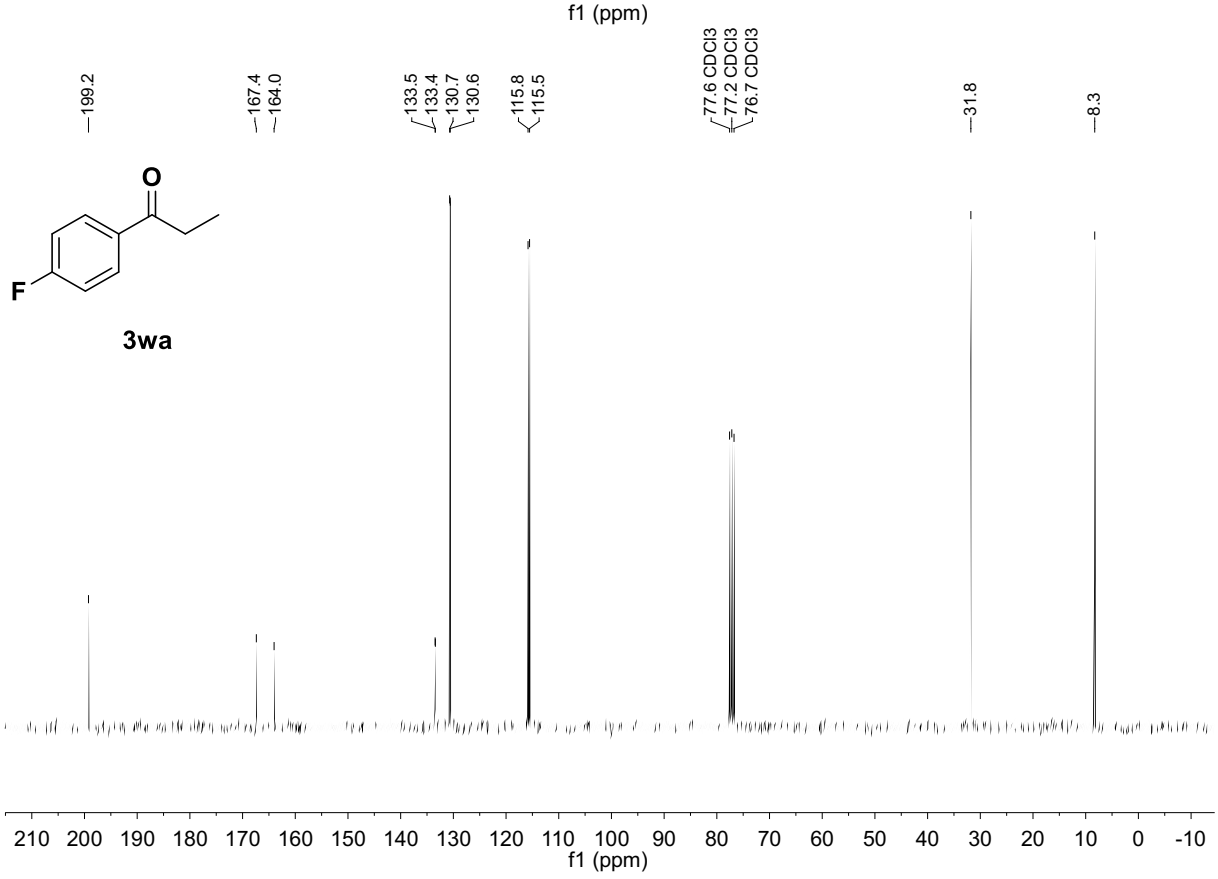
^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.7 (d, J^1_{C-F} = 254.2 Hz), 133.4 (d, J^4_{C-F} = 3.1 Hz), 130.7 (d, J^3_{C-F} = 9.2 Hz), 115.7 (d, J^2_{C-F} = 21.8 Hz), 31.8 (CH_2CH_3), 8.3 (CH_2CH_3).

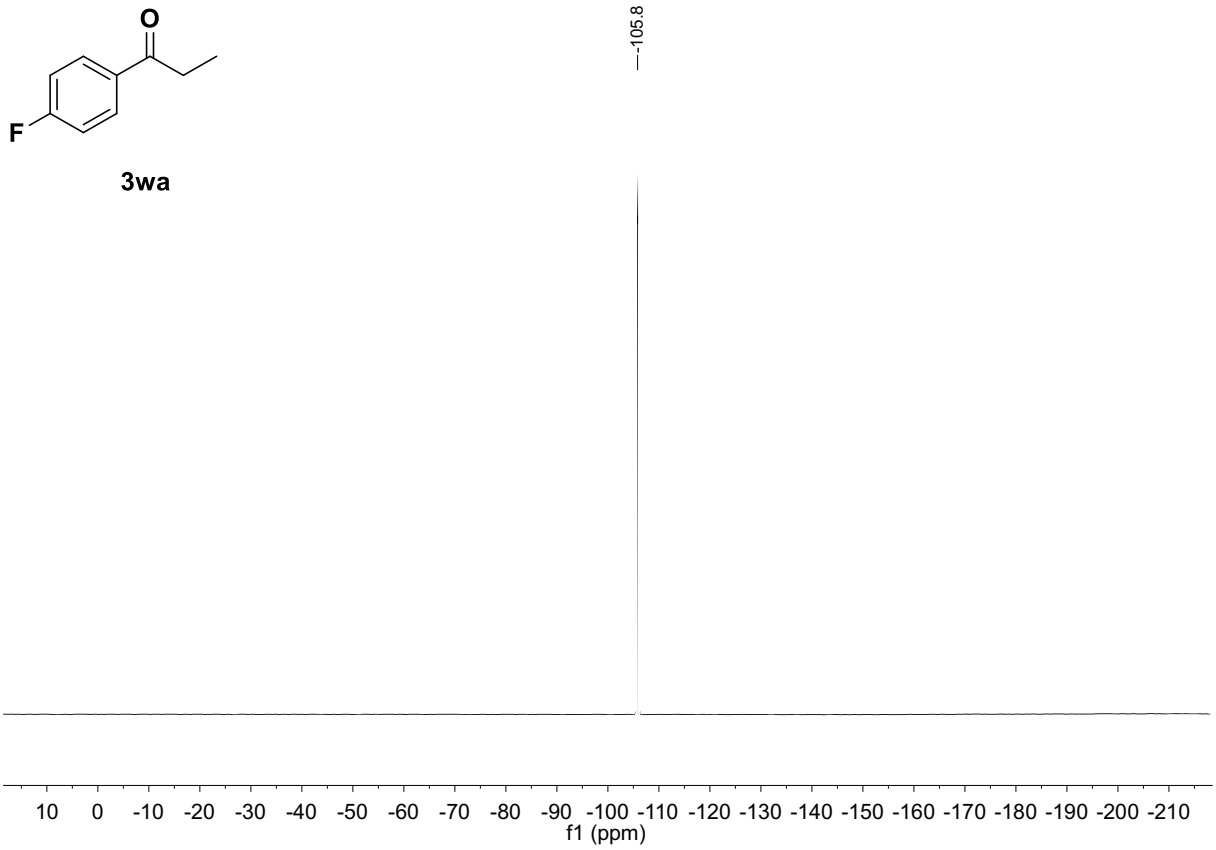
^{19}F NMR (282 MHz, $CDCl_3$): δ = -105.8 (s).

GC-MS (EI): t_r = 4.00 min, m/z(%) = 152(14, [$M^{+\bullet}$]), 123 (100, [$M^{+\bullet}$-$C_2H_5^\bullet$]), 95 (3, [$M^{+\bullet}$-$C_2H_5^\bullet$-CO]).

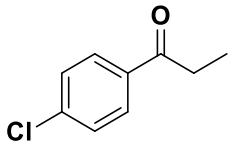
IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3065 (w, C-H_{arom}), 3025 (w, C-H_{arom}), 2969 (w, C-H_{aliph}), 2935 (w, C-H_{aliph}), 2905 (w, C-H_{aliph}), 2876 (w, C-H_{aliph}), 1709 (s), 1687 (s, C=O), 1597 (m), 1500 (m), 1455 (m), 1410 (w), 1374 (w), 1348 (m), 1305 (w), 1273 (w), 1221 (s), 1154 (m), 1131 (w), 1101 (w), 1016 (w), 986 (w), 952 (w), 904 (w), 848 (m), 800 (m), 751 (m), 699 (s).


7.99
7.97
7.96
7.95
7.26 CDCl3
7.12
7.10
7.07
2.99
2.97
2.94
2.92
1.22
1.20
1.17
O
F
3wa
1.92
1.91
1.97
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


199.2
167.4
164.0
133.5
133.4
130.7
130.6
115.8
115.5
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
31.8
8.3
O
F
3wa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
F
3wa
-105.8
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

1-(4-chlorophenyl)propan-1-one (**3xa**)



3xa

According to GP-E, the product **1x** was synthesized using ethyl manganese bromide lithium chloride complex (4.6 mL, 1.2 mmol, 0.26 M, 1.2 equiv.) and *S*-ethyl 4-chlorobenzothioate **1x** (234 mg, 1.00 mmol). Purification was achieved by manual column chromatography (*n*Hex/EA = 99:1 v/v) The product was obtained as a colorless solid (128.0 mg, 759 µmol, 76%). The analytical data matches previously reported literature.[25]

C_9H_9ClO (168.62 g/mol)

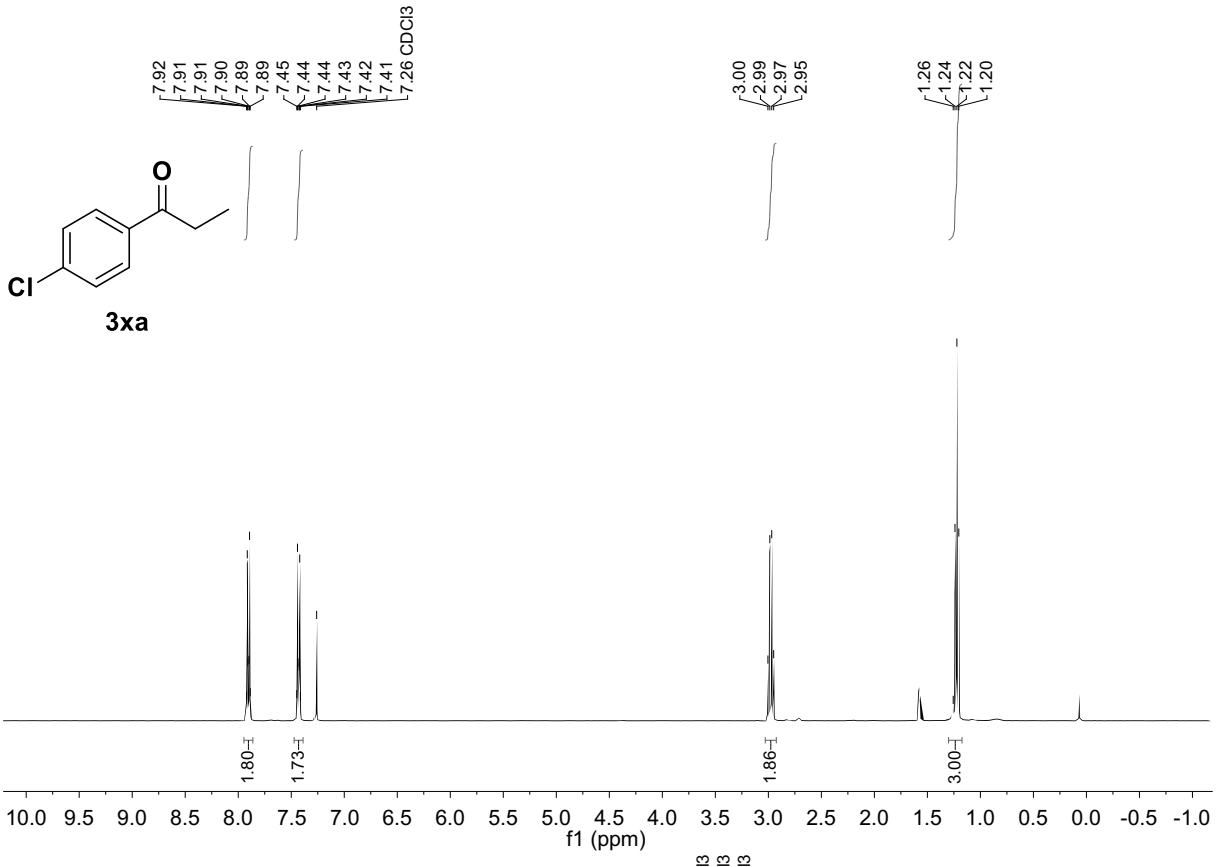
R_f: 0.18 (*n*Hex/EA = 99:1 v/v) [anis]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 – 7.86 (m, 2H, Ar*H*), 7.47 – 7.39 (m, 2H, Ar*H*), 2.98 (q, *J* = 7.2 Hz, 2H, CH_2CH$_3$), 1.22 (t, *J* = 7.2 Hz, 3H, CH$_2$CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 199.7 (*C*O), 139.4 (C_{Ar}), 135.3 (C_{Ar}), 129.5 (C_{Ar}), 129.0 (C_{Ar}), 31.4 (*C*H$_2$CH$_3$), 8.3 (CH$_2$*C*H$_3$).

GC-MS (EI): t_r = 5.35 min, m/z = 170 (3, [$M^{+\bullet}$]), 168 (10, [$M^{+\bullet}$]), 141 (31, [$M^{+\bullet}$-$C_2H_5^{\bullet}$]), 139 (100, [$M^{+\bullet}$-$C_2H_5^{\bullet}$]).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3065 (w, C-H$_{arom}$), 2977 (w, C-H$_{aliph}$), 2936 (w, C-H$_{aliph}$), 2905 (w, C-H$_{aliph}$), 2879 (w, C-H$_{aliph}$), 1683 (vs, C=O), 1616 (w), 1586 (s), 1482 (w), 1455 (w), 1400 (m), 1348 (m), 1314 (w), 1277 (w), 1213 (s), 1176 (w), 1090 (s), 1008 (s), 948 (s), 841 (m), 792 (s), 762 (m).


7.92
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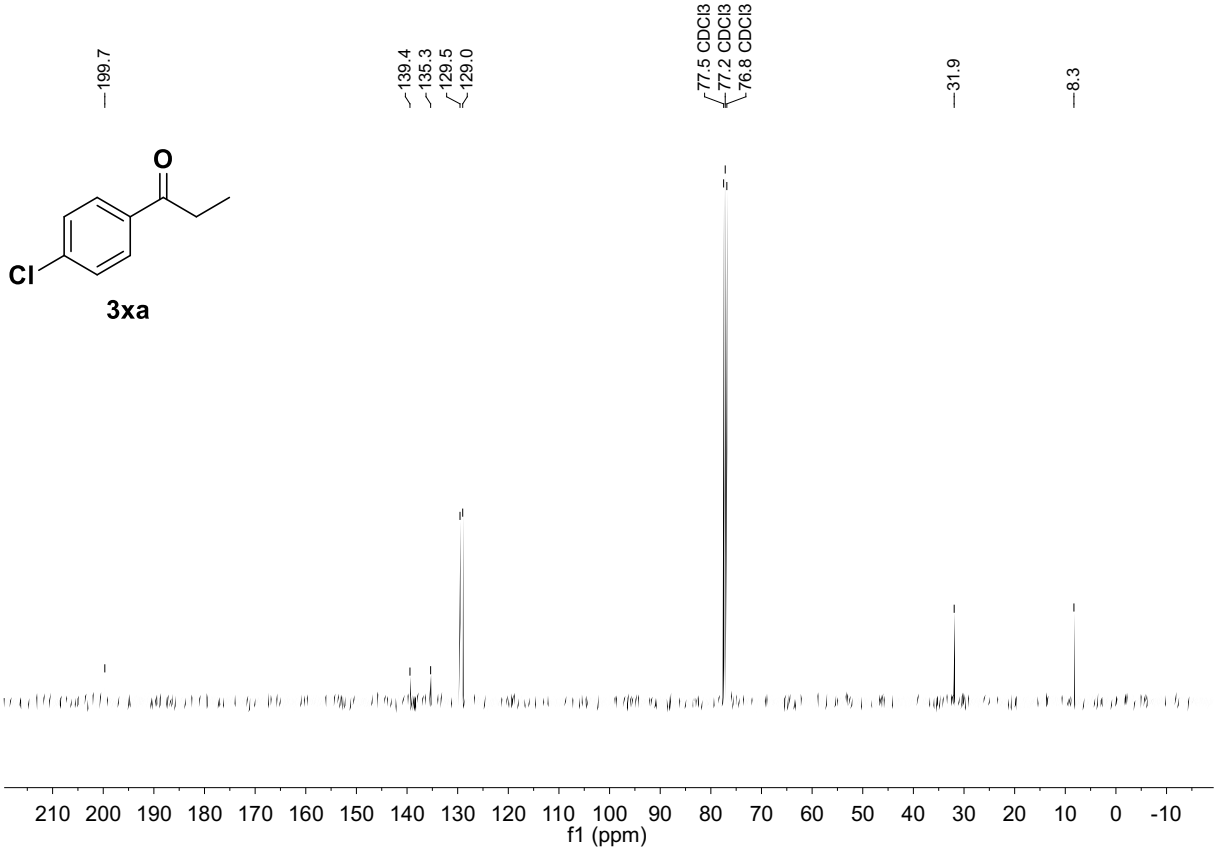
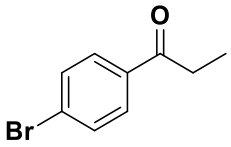
7.90
7.89
7.89
7.45
7.44
7.44
7.43
7.42
7.41
7.26 CDCl3
3.00
2.99
2.97
2.95
1.26
1.24
1.22
1.20
O
Cl
3xa
1.80
1.73
1.86
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


199.7
139.4
135.3
129.5
129.0
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
31.9
8.3
O
Cl
3xa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1-(4-bromophenyl)propan-1-one (**3ya**)



3ya

According to GP-E, the product **3ya** was synthesized using ethyl manganese bromide lithium chloride complex (4.6 mL, 1.2 mmol, 0.27 M, 1.2 equiv.) and *S*-ethyl 4-bromobenzothioate **1y** (245 mg, 1.00 mmol). Purification was achieved by manual column chromatography (*n*Hex/Et_2O = 99:1 v/v) The product was obtained as a colorless solid (131 mg, 614 µmol, 61%). The spectral data is in good accordance to previous literature.[26]

C_9H_9BrO (213.07 g/mol)

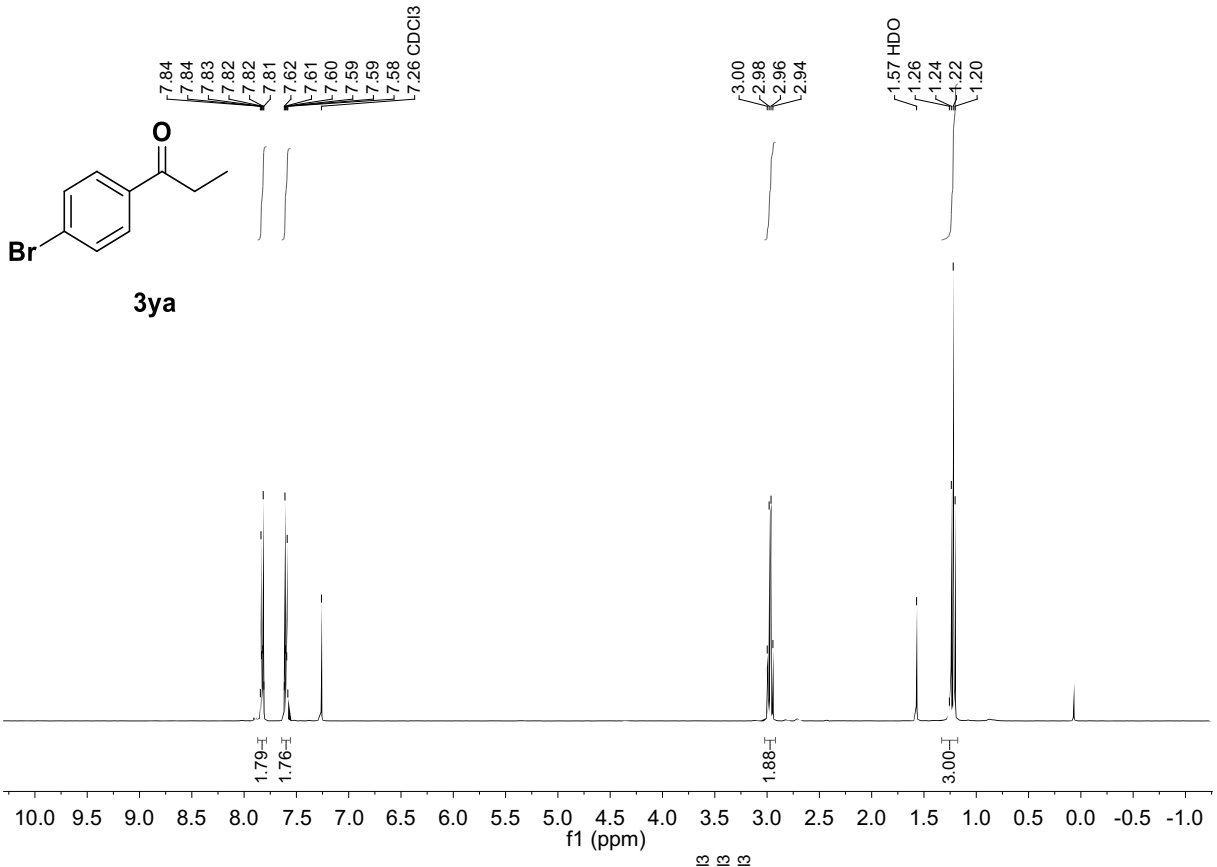
R_f: 0.19 (*n*Hex/EA = 99:1 v/v) [anis]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 – 7.79 (m, 2H), 7.64 – 7.56 (m, 2H), 2.97 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 199.9 (*C*O), 135.7 (C_{Ar}), 132.0 (C_{Ar}), 129.7 (C_{Ar}), 128.1 (C_{Ar}), 31.9 (CH_2CH_3), 8.3 (CH_2CH_3).

GC-MS (EI): t_r = 5.98 min, m/z(%) = 214 (11, $[M^{+\bullet}]$), 212 (13, $[M^{+\bullet}]$), 185 (95, $[M^{+\bullet}\text{-}C_2H_5^{\bullet}]$), 183 (100, $[M^{+\bullet}\text{-}C_2H_5^{\bullet}]$), 157 (23, $[M^{+\bullet}\text{-}C_2H_5^{\bullet}\text{-CO}]$), 155 (25, $[M^{+\bullet}\text{-}C_2H_5^{\bullet}\text{-CO}]$).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2969 (w, C-H_{aliph}), 2928 (w, C-H_{aliph}), 2872 (w, C-H_{aliph}), 1680 (s, C=O), 1579 (m), 1482 (w), 1452 (w), 1392 (m), 1351 (m), 1292 (w), 1265 (w), 1210 (s), 1172 (m), 1105 (w), 1064 (m), 1004 (m), 949 (s), 837 (m), 814 (w), 784 (s), 759 (m), 673 (w).


7.84
7.84
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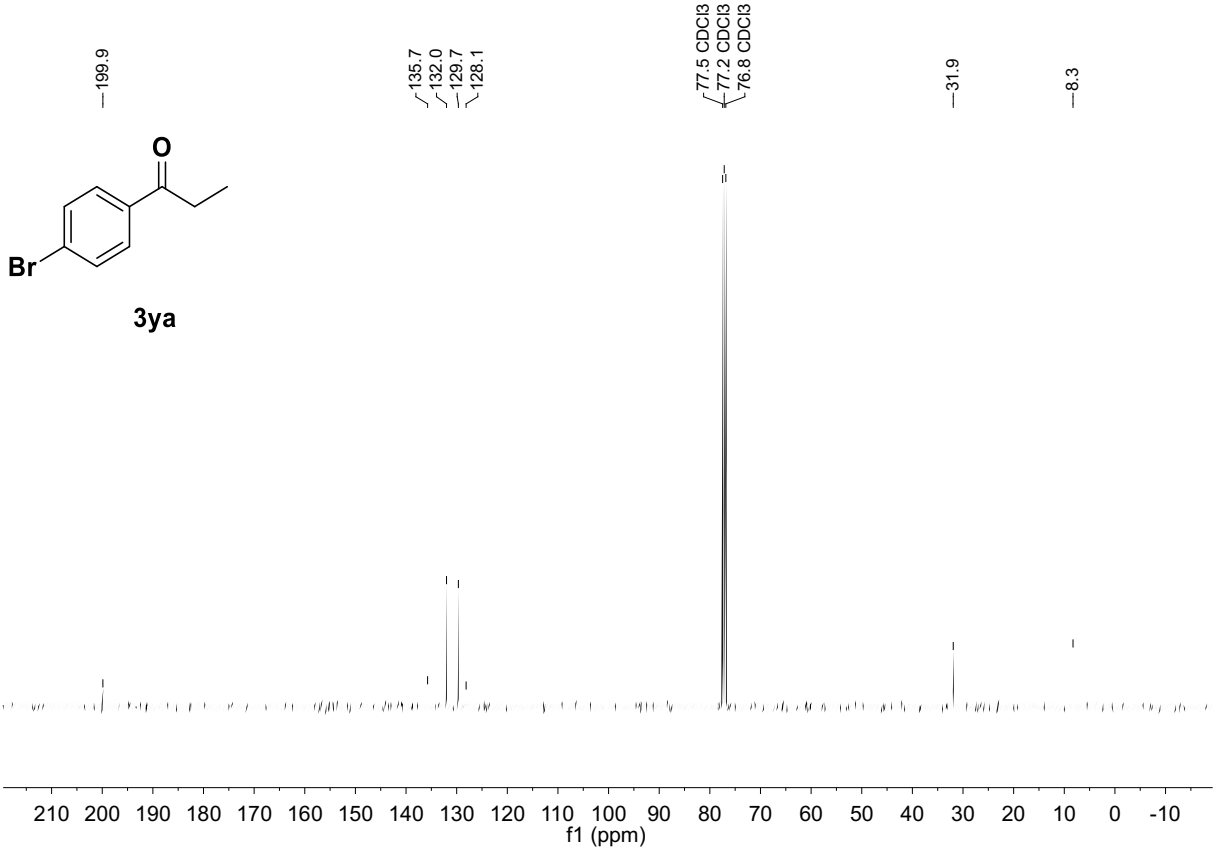
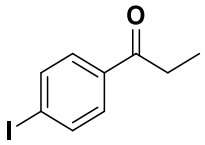
7.82
7.82
7.81
7.62
7.61
7.60
7.59
7.59
7.58
7.26 CDCl3
3.00
2.98
2.96
2.94
1.57 HDO
1.26
1.24
1.22
1.20
O
Br
3ya
1.79
1.76
1.88
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


199.9
135.7
132.0
129.7
128.1
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
31.9
8.3
O
Br
3ya
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1-(4-iodophenyl)propan-1-one (**3za**)



3za

According to GP-E, the product **3za** was synthesized using ethyl manganese bromide lithium chloride complex (4.6 mL, 1.2 mmol, 0.27 M, 1.2 equiv.) and *S*-ethyl 4-iodobenzothioate **1z** (292 mg, 1.00 mmol). Purification was achieved by manual column chromatography (*n*Hex/Et_2O = 99:1 v/v). The product was obtained as a slightly orange solid (169 mg, 651 µmol, 65%).

C_9H_9IO (260.07 g/mol)

R_f: 0.24 (*n*Hex/Et_2O = 99:1 v/v) [anis]

Melting point: 58.9–60.0 (EA).

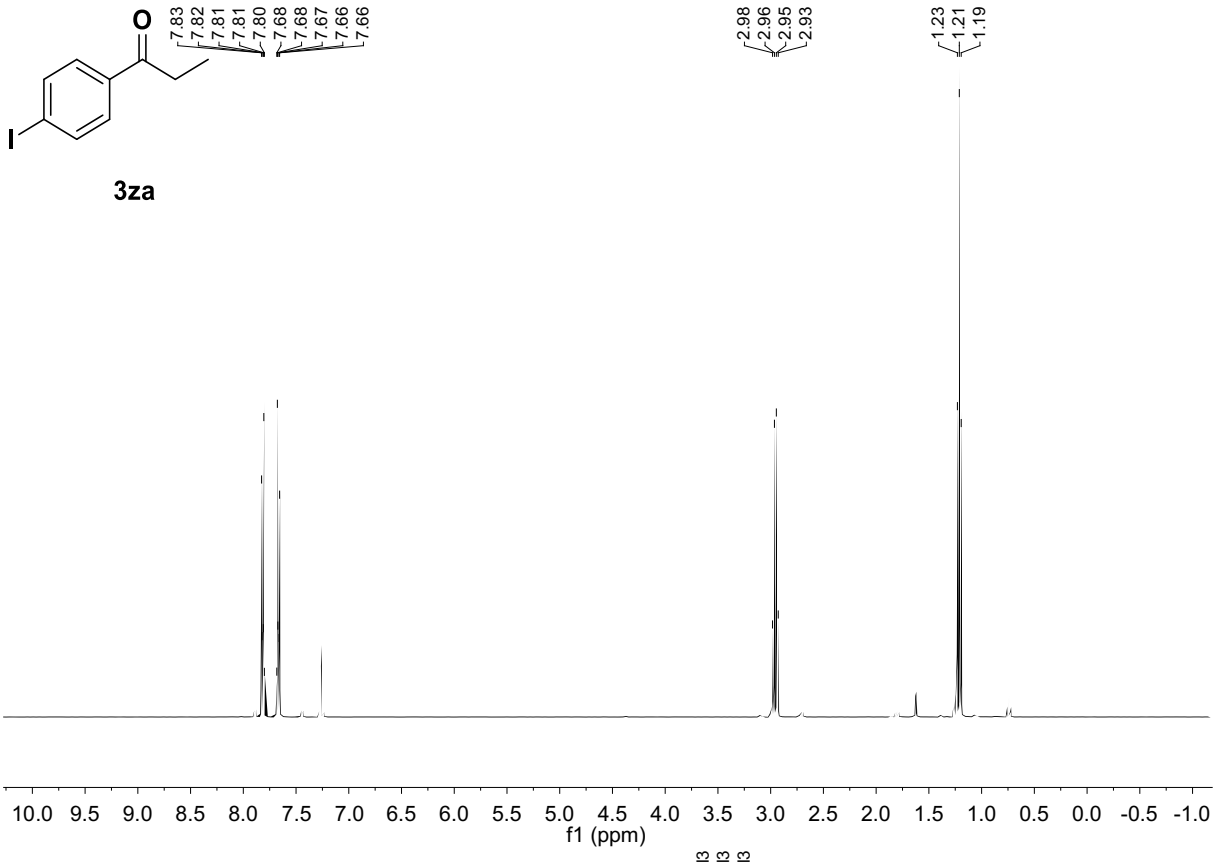
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 – 7.72 (m, 2H), 7.72 – 7.49 (m, 2H), 2.96 (q, *J* = 7.2 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H).

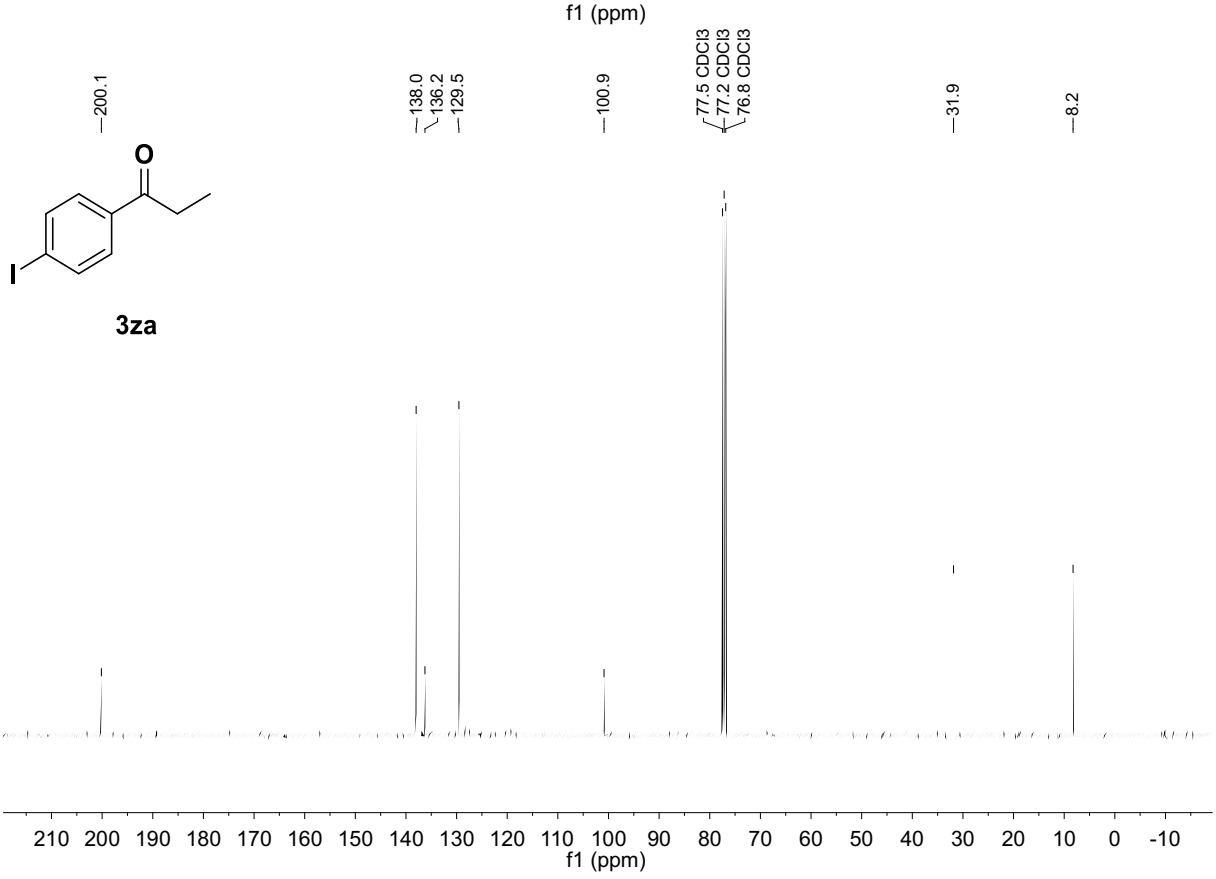
^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.2 (*C*OSEt), 138.0 (C_{Ar}), 136.3 (C_{Ar}), 129.5 (C_{Ar}), 100.9 (C_{Ar}), 31.9 (CH_2CH_3), 8.3 (CH_2CH_3).

GC-MS (EI): t_r = 6.74 min, m/z(%) = 260 (23, [$M^{+\bullet}$]), 231 (100, [$M^{+\bullet}$-$C_2H_5S^{\bullet}$]), 203 (19, [$M^{+\bullet}$-$C_2H_5S^{\bullet}$-CO]).

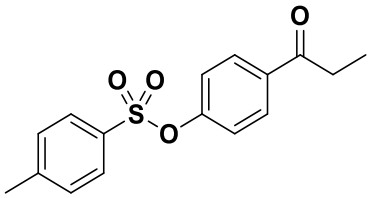
HR-MS (ESI): m/z calc. for $[M+Na]^+$ 282.95903, found 282.95900.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2969 (w, C-H_{aliph}), 2931 (w, C-H_{aliph}), 2898 (w, C-H_{aliph}), 2868 (w, C-H_{aliph}), 1676 (s, C=O), 1571 (m), 1478 (w), 1449 (w), 1385 (m), 1344 (m), 1269 (w), 1210 (m), 1176 (m), 1105 (w), 1083 (w), 1053 (w), 1027 (w), 997 (m), 945 (s), 840 (m), 784 (s), 751 (m), 666 (w).


O
I
7.83
7.82
7.81
7.81
7.80
7.68
7.68
7.67
7.66
7.66
2.98
2.96
2.95
2.93
1.23
1.21
1.19
3za
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


200.1
138.0
136.2
129.5
100.9
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
31.9
8.2
O
I
3za
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

4-propionylphenyl 4-methylbenzenesulfonate (**3Aa**)



3Aa

According to GP-E, the product **3Aa** was synthesized using ethylmanganese bromide lithium chloride complex (6.0 mL, 1.2 mmol, 0.2 M, 1.2 equiv.) and *S*-ethyl 4-(tosyloxy)benzothioate **1A** (336 mg, 1.00 mmol). Purification was achieved by manual column chromatography (*n*Hex/EA = 9:1 v/v) The product was obtained as a colorless soild (258 mg, 848 µmol, 85%).

$C_{16}H_{16}O_4S$ (304.36 g/mol)

R_f: 0.23 (*n*Hex/EA = 9:1 v/v) [UV]

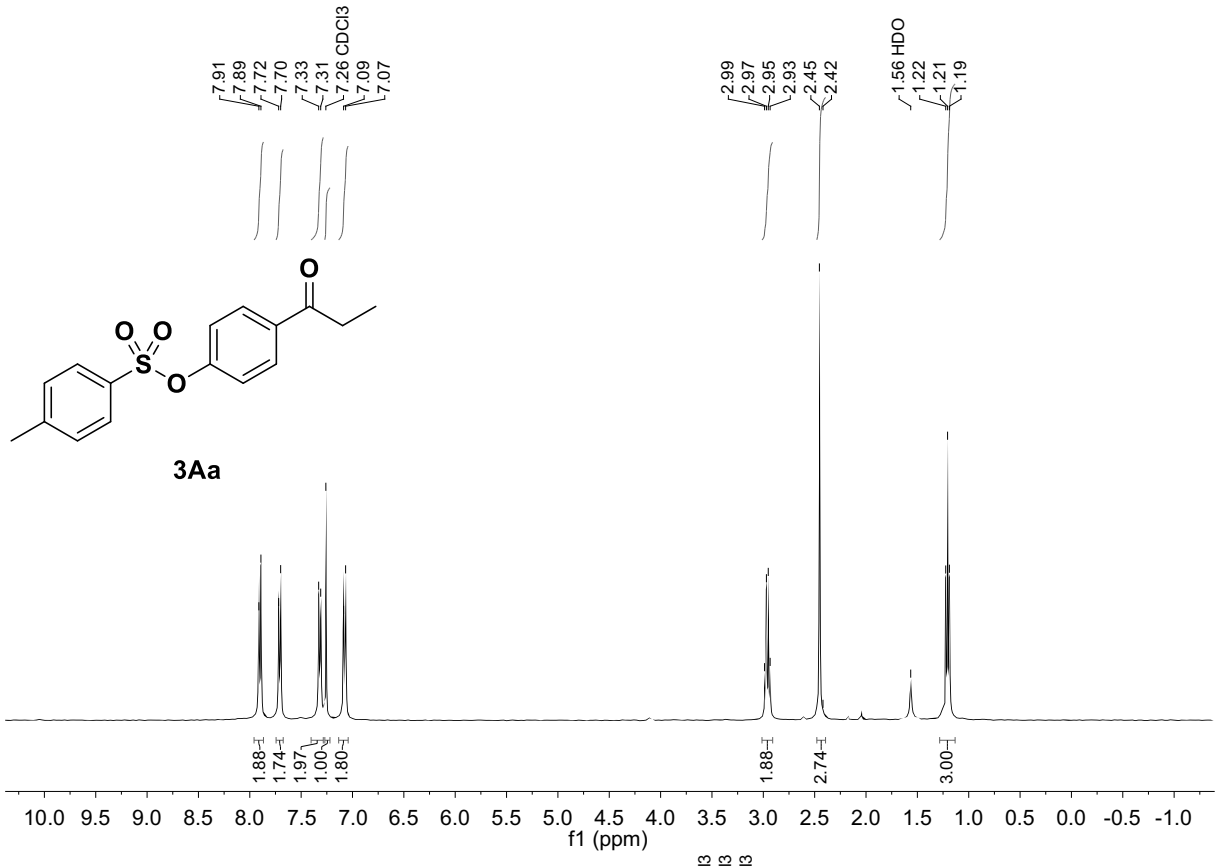
Melting point: 76.8–77.2 °C (EA).

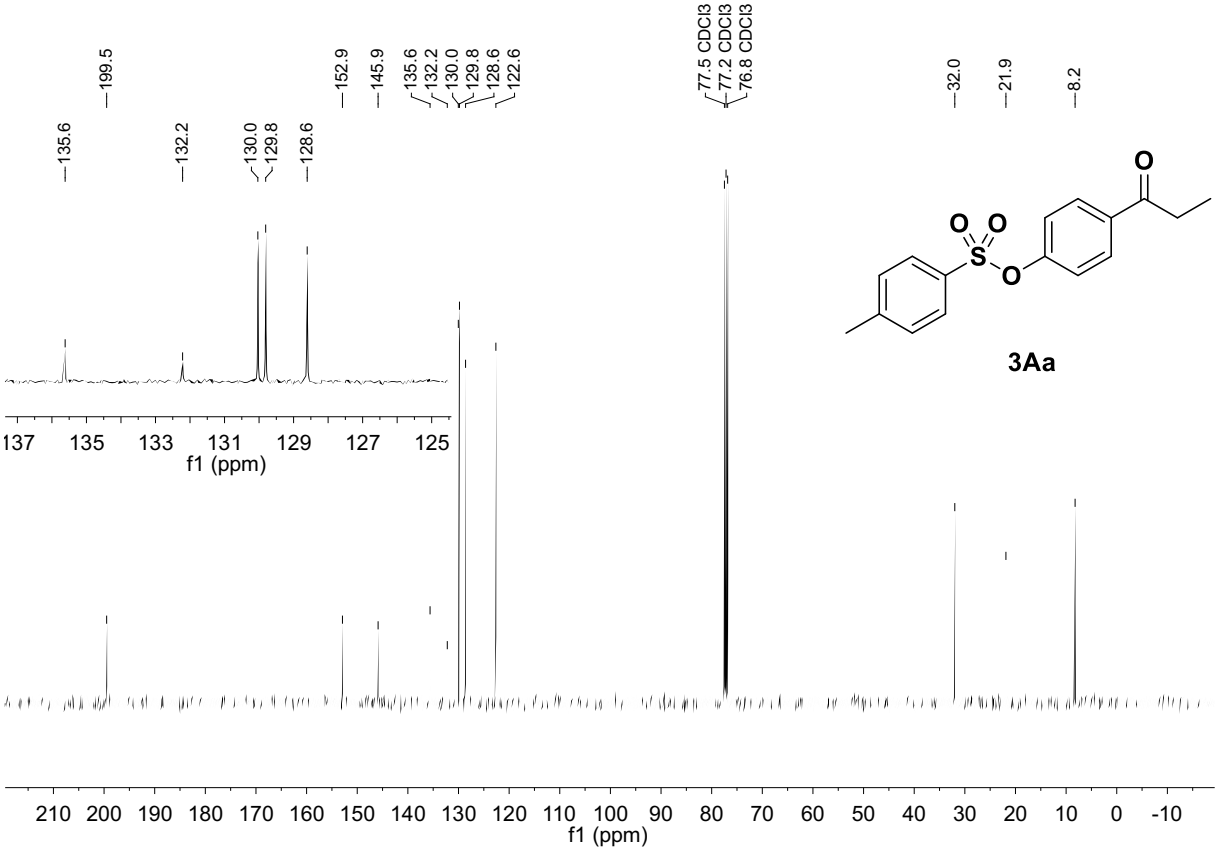
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 – 7.86 (m, 2H, Ar*H*), 7.75 – 7.67 (m, 2H, Ar*H*), 7.35 – 7.28 (m, 2H, Ar*H*), 7.12 – 7.04 (m, 2H, Ar*H*), 2.96 (q, *J* = 7.1 Hz, 2H, $COCH_2CH_3$), 2.45 (s, 3H, $ArCH_3$), 1.21 (t, *J* = 7.1 Hz, 3H, $COCH_2CH_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 199.5 (*C*O), 152.9 (C_{Ar}), 145.9 (C_{Ar}), 135.6 (C_{Ar}), 132.2 (C_{Ar}), 130.0 (C_{Ar}), 129.8 (C_{Ar}), 128.6 (C_{Ar}), 122.6 (C_{Ar}), 32.0, 21.9, 8.2.

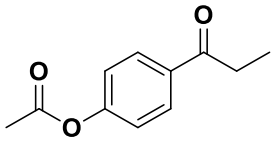
HR-MS (ESI): m/z calc. for $[M+Na]^+$ 327.06615, found 327.06592.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2972 (w, C-H_{aliph}), 2932 (w, C-H_{aliph}), 2880 (w, C-H_{aliph}), 1713 (s), 1679 (vs, C=O), 1452 (m), 1414 (w), 1373 (m, S=O), 1262 (w), 1191 (w), 1112 (w), 1049 (w), 1023 (w), 956 (s), 897 (w), 822 (w), 733 (w), 695 (w).


7.91
7.89
7.72
7.70
7.33
7.31
7.26 CDCl3
7.09
7.07
2.99
2.97
2.95
2.93
2.45
2.42
1.56 HDO
1.22
1.21
1.19
3Aa
1.88
1.74
1.97
1.00
1.80
1.88
2.74
3.00
f1 (ppm)


199.5
152.9
145.9
135.6
132.2
130.0
129.8
128.6
122.6
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
32.0
21.9
8.2
135.6
132.2
130.0
129.8
128.6
3Aa
f1 (ppm)

4-propionylphenyl acetate (**3Ba**)



3Ba

According to GP-E, the product **3Ba** was synthesized using ethylmanganese bromide lithium chloride complex (5.2 mL, 1.2 mmol, 0.23 M, 1.2 equiv.) and 4-((ethylthio)carbonyl)phenyl acetate **1B** (224 mg, 1.00 mmol). Purification was achieved by column chromatography (*n*Hex/EA = 9:1 v/v). The product was obtained as a colorless solid (150 mg, 781 µmol, 78%).

$C_{11}H_{12}O_3$ (192.13 g/mol)

R_f: 0.57 (*n*Hex/EA = 9:1 v/v) [anis]

Melting point: 56.9–57.7 °C (EA).

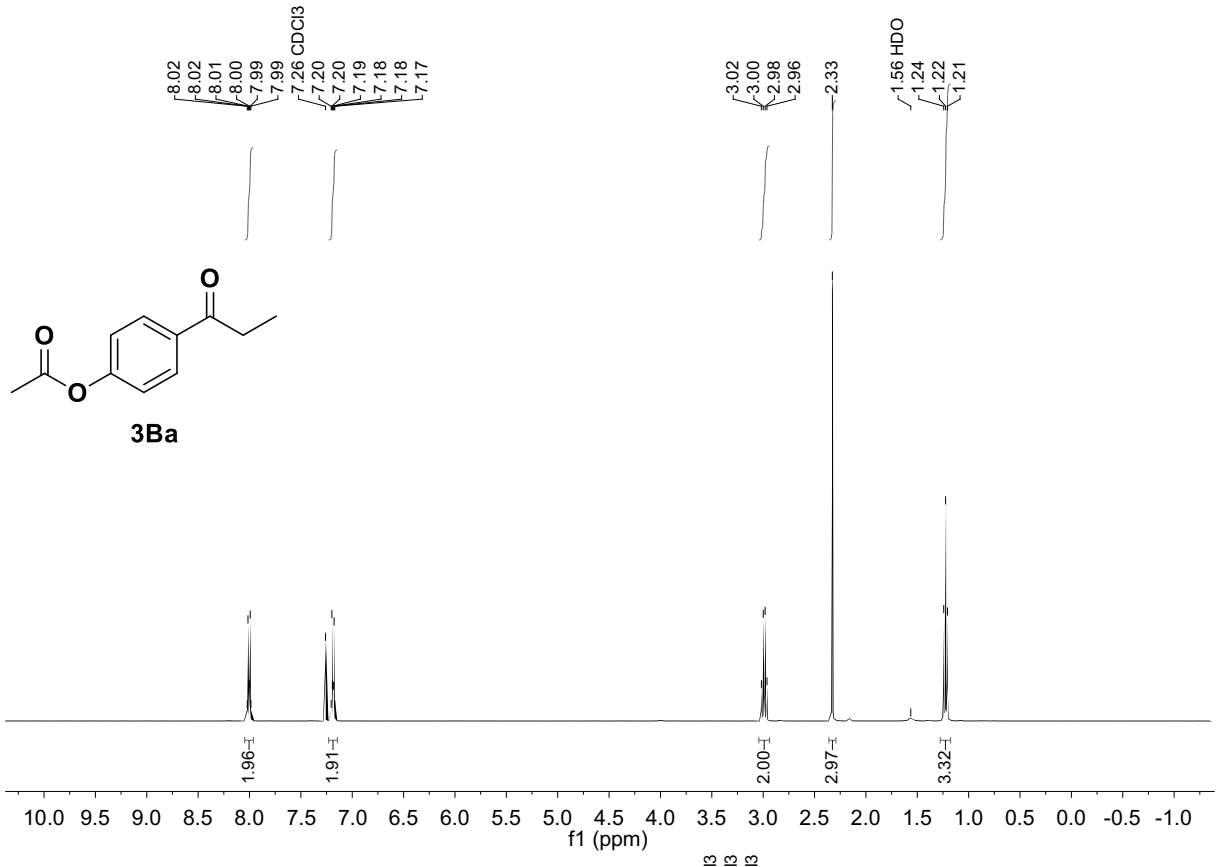
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 – 7.99 (m, 2H, Ar*H*, 7.26 – 7.17 (m, 2H, Ar*H*), 2.99 (q, *J* = 7.2 Hz, 2H, $COCH_2CH_3$), 2.33 (s, 3H,CH_3CO_2Ph), 1.22 (t, *J* = 7.2 Hz, 3H, $COCH_2CH_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 199.7 ($COCH_2CH_3$), 169.1 (*C*(O)OPh), 154.3 (C_{Ar}), 134.7 (C_{Ar}), 129.7 (C_{Ar}), 121.9 (C_{Ar}), 31.9 ($COCH_2CH_3$), 21.3 ($CH_3C(O)OPh$), 8.4 ($COCH_2CH_3$).

GC-MS (EI): t_r = 6.70 min, m/z(%) = 192 (7, [$M^{+\bullet}$]) , 163 (9, [$M^{+\bullet}$-$C_2H_5^{\bullet}$]), 150 (7), 134 (16), 121 (100).

HR-MS (ESI): m/z calc. for $[M+Na]^+$ 215.06786, found 215.06803.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3047 (w, C-H_{arom}), 2976 (w, C-H_{aliph}), 2935 (w, C-H_{aliph}), 1750 (s, C=O_{ketone}), 1676 (s, C=O_{ester}), 1593 (m), 1504 (w), 1459 (w), 1407 (m), 1366 (m), 1296 (w), 1198 (s), 1157 (s), 1105 (m), 1083 (w), 1079 (w), 1046 (w), 1009 (m), 953 (m), 912 (s), 863 (m), 859 (m), 818 (m), 788 (s), 744 (w), 714 (w), 661 (w).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8.00
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7.99
7.26 CDCl3
7.20
7.20
7.19
7.18
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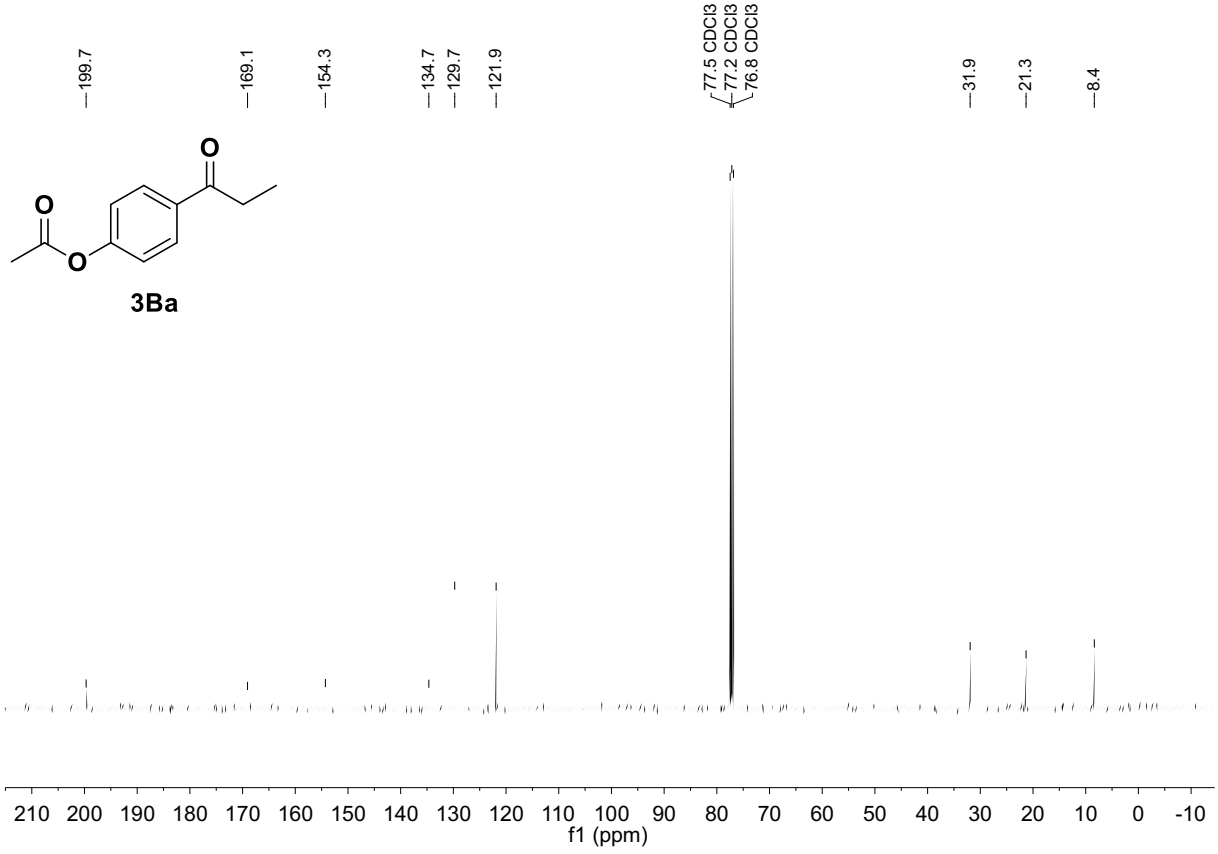
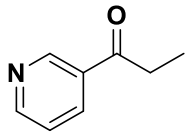
7.17
3.02
3.00
2.98
2.96
2.33
1.56 HDO
1.24
1.22
1.21
O
O
O
3Ba
1.96
1.91
2.00
2.97
3.32
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


199.7
169.1
154.3
134.7
129.7
121.9
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
31.9
21.3
8.4
O
O
O
3Ba
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1-(pyridin-3-yl)propan-1-one (**3Ea**)



3Ea

According to GP-E, the product **3Ea** was synthesized using ethylmanganese bromide lithium chloride complex (5.2 mL, 1.2 mmol, 0.23 M, 1.2 equiv.) and nicotinic acid *S*-ethyl thioester **1E** (167 mg, 1.00 mmol). Quenching of the reaction was performed with brine (5 mL). Purification was achieved by manual column chromatography (PE/EA = 8:2 v/v). The product was obtained as a yellow oil (70.1 mg, 519 µmol, 52%).

C_8H_9NO (135.17 g/mol)

R_f: 0.37 (PE/EA = 8:2 v/v) [UV, anis]

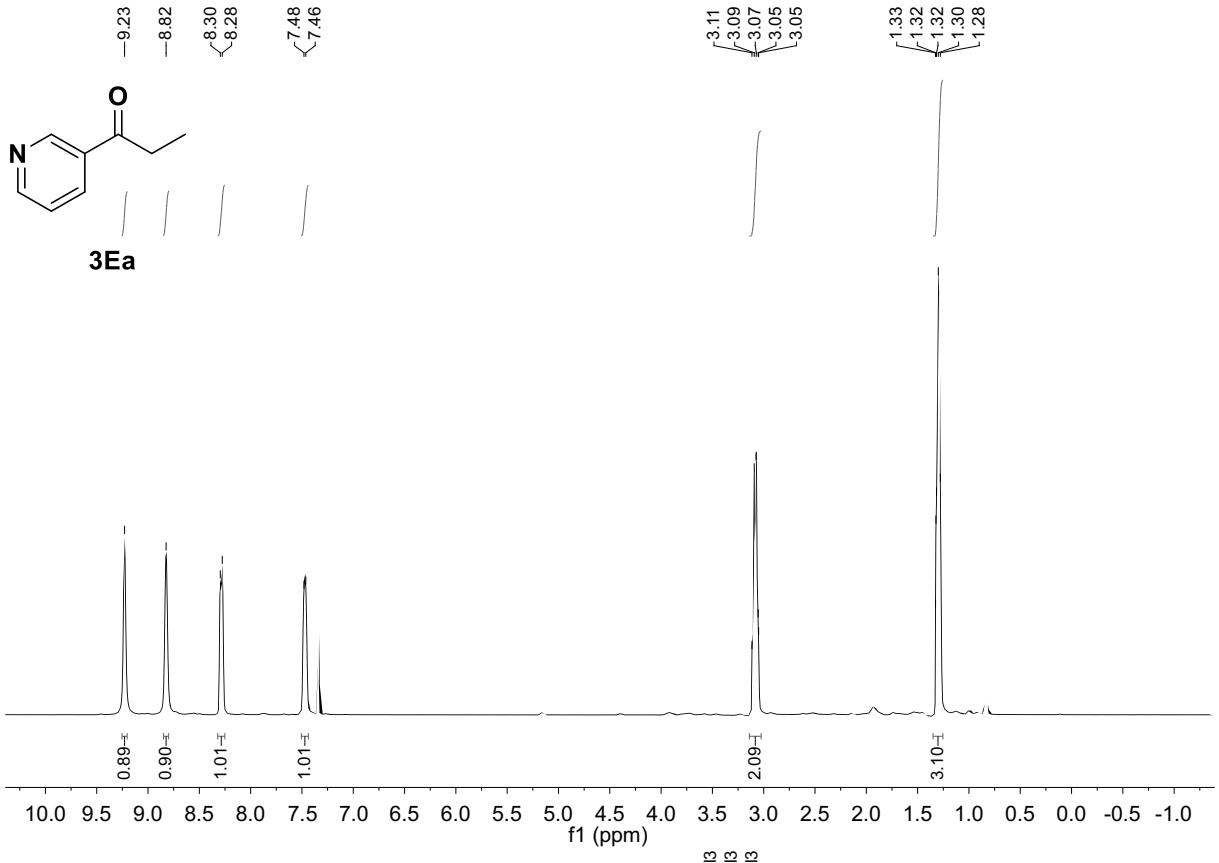
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.16 (s, 1H, Ar*H*), 8.75 (d, *J* = 5.2 Hz, 1H, Ar*H*), 8.21 (dd, *J* = 8.1, 3.5 Hz, 1H, Ar*H*), 7.40 (dt, *J* = 8.0, 3.4 Hz, 1H, Ar*H*), 3.07 – 2.95 (m, 2H, C*H*$_2$CH$_3$), 1.27 – 1.17 (m, 3H, CH$_2$C*H*$_3$).

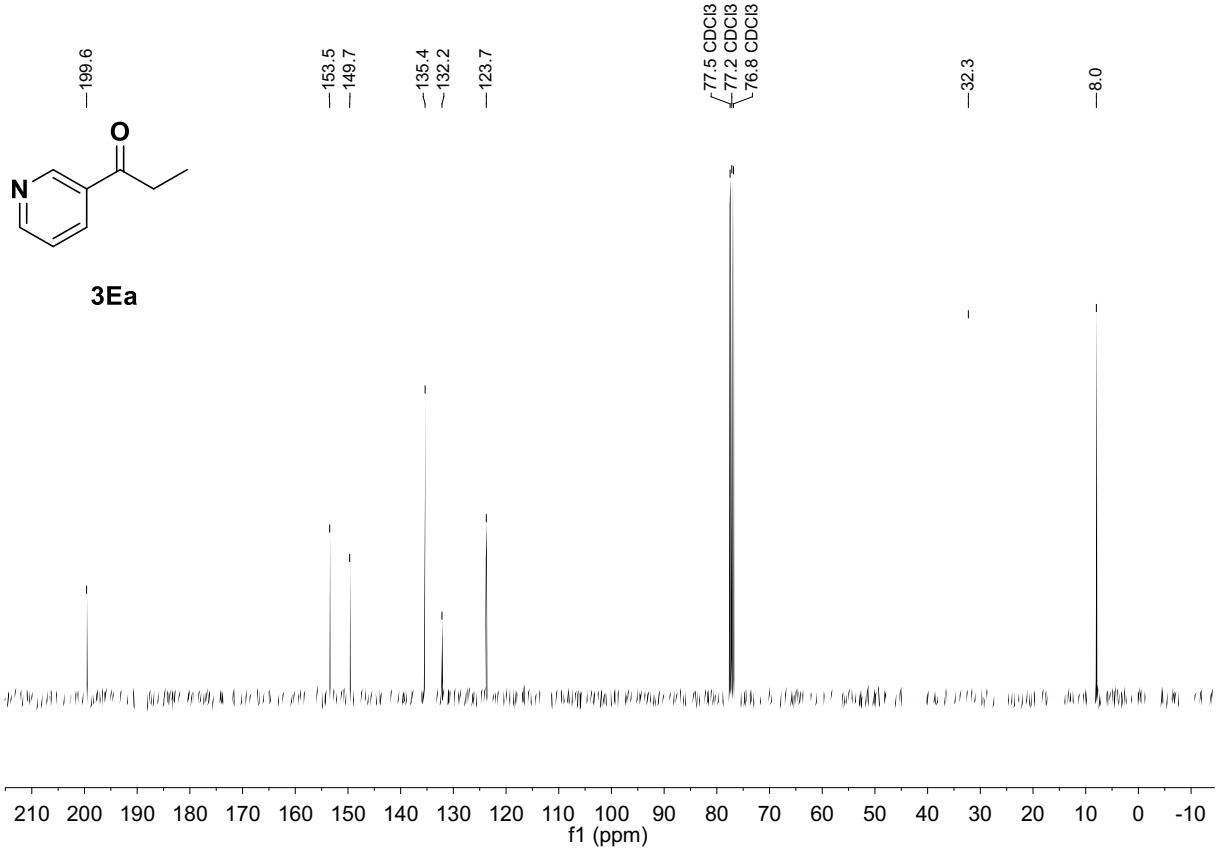
^{13}C NMR (101 MHz, $CDCl_3$): δ = 199.6 (*C*O), 153.5 (C_{Ar}), 149.7 (C_{Ar}), 135.4 (C_{Ar}), 132.2 (C_{Ar}), 123.8 (C_{Ar}), 32.3 (*C*H$_2$CH$_3$), 8.0 (CH$_2$*C*H$_3$).

GC-MS (EI): t_r = 13.22 min, m/z(%) = 135 (31, [$M^{+\bullet}$]), 106 (100, [$M^{+\bullet}$-$C_2H_5^{\bullet}$]), 78 (51, [$M^{+\bullet}$-$C_2H_5^{\bullet}$-CO]).

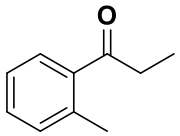
HR-MS (ESI): m/z calc. for $[M+H]^+$ 136.07569, found 136.07570.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3043 (w, C-H$_{arom}$), 2977 (w, C-H$_{aliph}$), 2939 (w, C-H$_{aliph}$), 2905 (w, C-H$_{aliph}$), 1687 (vs, C=O), 1582 (s), 1456 (w), 1415 (m), 1355 (m), 1280 (w), 1225 (s), 1191 (w), 1116 (w), 1086 (w), 1016 (m), 945 (s), 826 (w), 785 (s), 702 (s), 669 (w).


9.23
8.82
8.30
8.28
7.48
7.46
3.11
3.09
3.07
3.05
3.05
1.33
1.32
1.32
1.30
1.28
O
N
3Ea
0.89
0.90
1.01
1.01
2.09
3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


199.6
153.5
149.7
135.4
132.2
123.7
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
32.3
8.0
O
N
3Ea
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1-(*o*-tolyl)propan-1-one (**3Fa**)



3Fa

According to GP-E, the product **3Fa** was synthesized using ethyl manganese bromide lithium chloride complex (0.25 M, 4.7 mL, 1.2 mmol, 1.2 equiv.) and *S*-ethyl 2-methylbenzothioate **1F** (180 mg, 1.00 mmol). Purification was achieved by manual column chromatography (*n*Hex/EA = 30:1). The product was obtained as a yellow oil (91.1 mg, 615 µmol, 62%). The analytical data is in good accordance with the reported literature.[27]

$C_{10}H_{12}O$ (148.21 g/mol)

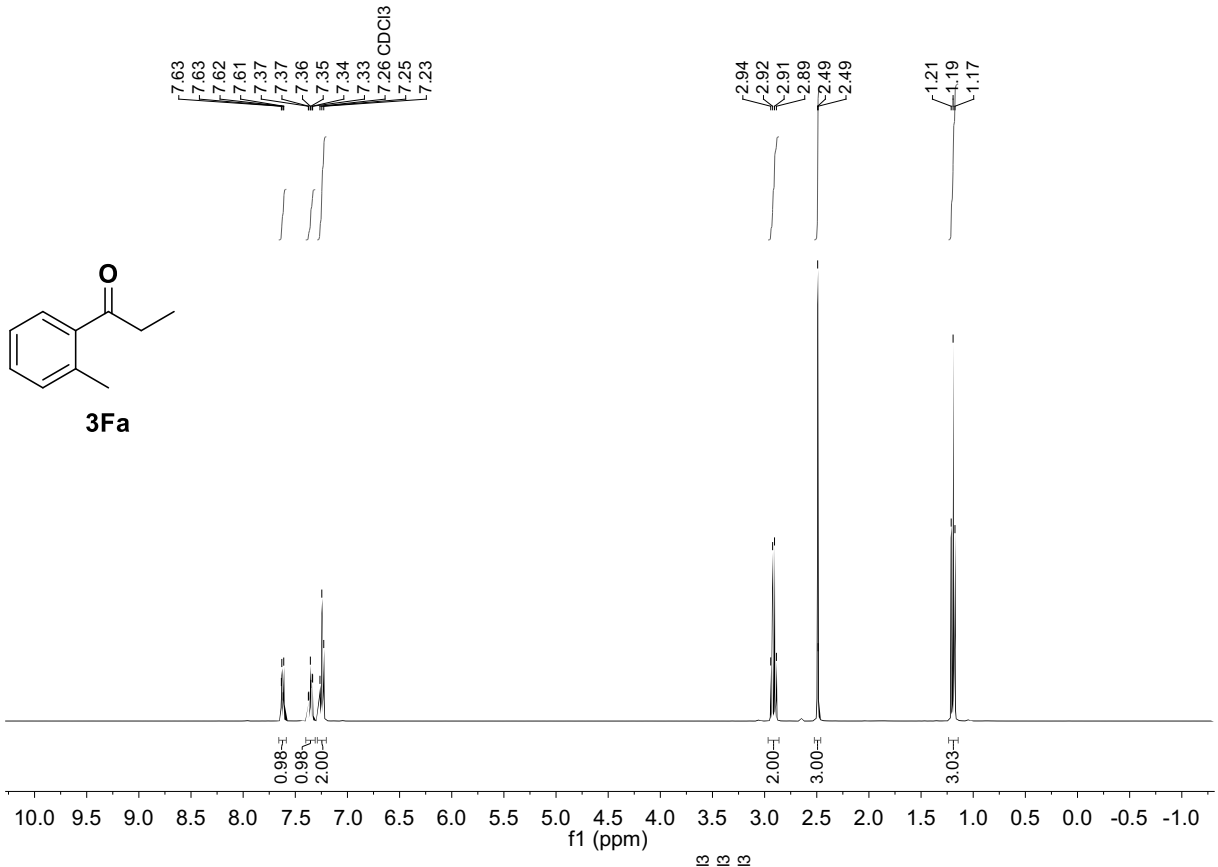
R_f: 0.21 (*n*Hex) [anis]

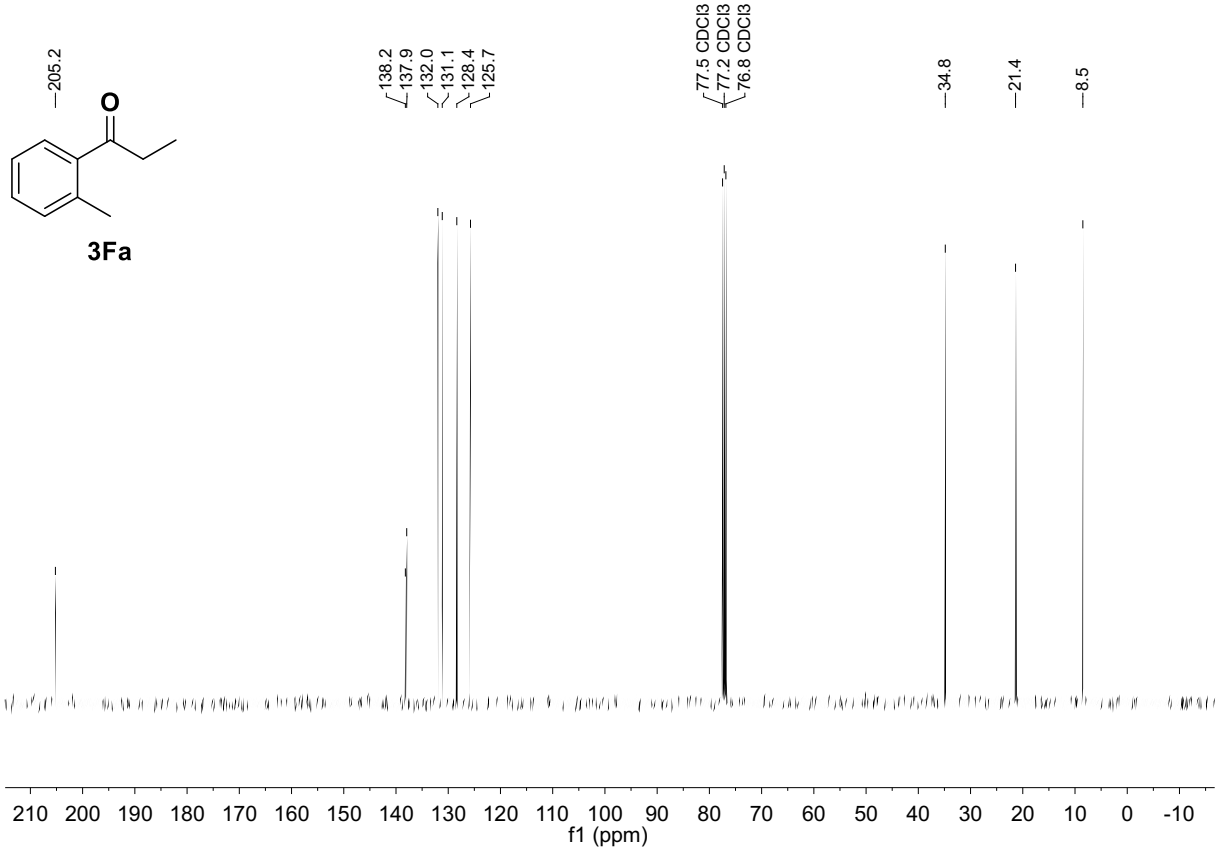
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 – 7.58 (m, 1H, Ar*H*), 7.40 – 7.31 (m, 1H, Ar*H*), 7.29 – 7.20 (m, 2H, Ar*H*), 2.91 (q, *J* = 7.3 Hz, 2H, CH_2CH$_3$), 2.49 (s, 3H, ArCH_3), 1.19 (t, *J* = 7.3 Hz, 3H, CH$_2$CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 205.2 (*C*O), 138.2 (C_{Ar}), 138.0 (C_{Ar}), 132.0 (C_{Ar}), 131.1 (C_{Ar}), 128.4 (C_{Ar}), 125.7 (C_{Ar}), 34.8, 21.4, 8.5.

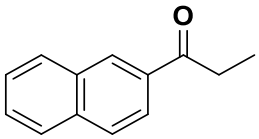
GC-MS (EI): t_r = 4.57 min, m/z(%) = 148 (12, [$M^{+\bullet}$]), 119 (100, [$M^{+\bullet}$-$C_2H_5^{\bullet}$]), 91 (55, [$M^{+\bullet}$-$C_2H_5^{\bullet}$-CO]).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3062 (w, C-H$_{arom}$), 3021 (w C-H$_{arom}$), 2973 (w, C-H$_{aliph}$), 2932 (w, C-H$_{aliph}$), 2879 (w, C-H$_{aliph}$), 1683 (s, C=O), 1597 (w), 1568 (w), 1482 (w), 1452 (m), 1415 (w), 1377 (w), 1343 (m), 1288 (w), 1213 (s), 1131 (w), 1076 (w), 1038 (w), 1009 (w), 944 (s), 796 (w), 747 (s).


7.63
7.63
7.62
7.61
7.37
7.37
7.36
7.35
7.34
7.33
7.26 CDCl3
7.25
7.23
2.94
2.92
2.91
2.89
2.49
2.49
1.21
1.19
1.17
O
3Fa
0.98
0.98
2.00
2.00
3.00
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


205.2
O
3Fa
138.2
137.9
132.0
131.1
128.4
125.7
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
34.8
21.4
8.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1-(naphthalen-2-yl)propan-1-one (**3Ga**)



3Ga

According to GP-E, the product **3Ga** was synthesized using ethyl manganese bromide lithium chloride complex (4.5 mL, 0.27 M, 1.2 mmol, 1.2 equiv.) and *S*-ethyl naphthalene-2-carbothioate **1G** (216 mg, 1.00 mmol). Purification was achieved by manual column chromatography (*n*Hex/EA = 99:1). The product was obtained as a colorless solid (150 mg, 814 µmol, 81%). The analytical data is in good accordance with the reported literature.[28]

$C_{13}H_{12}O$ (184.21 g/mol)

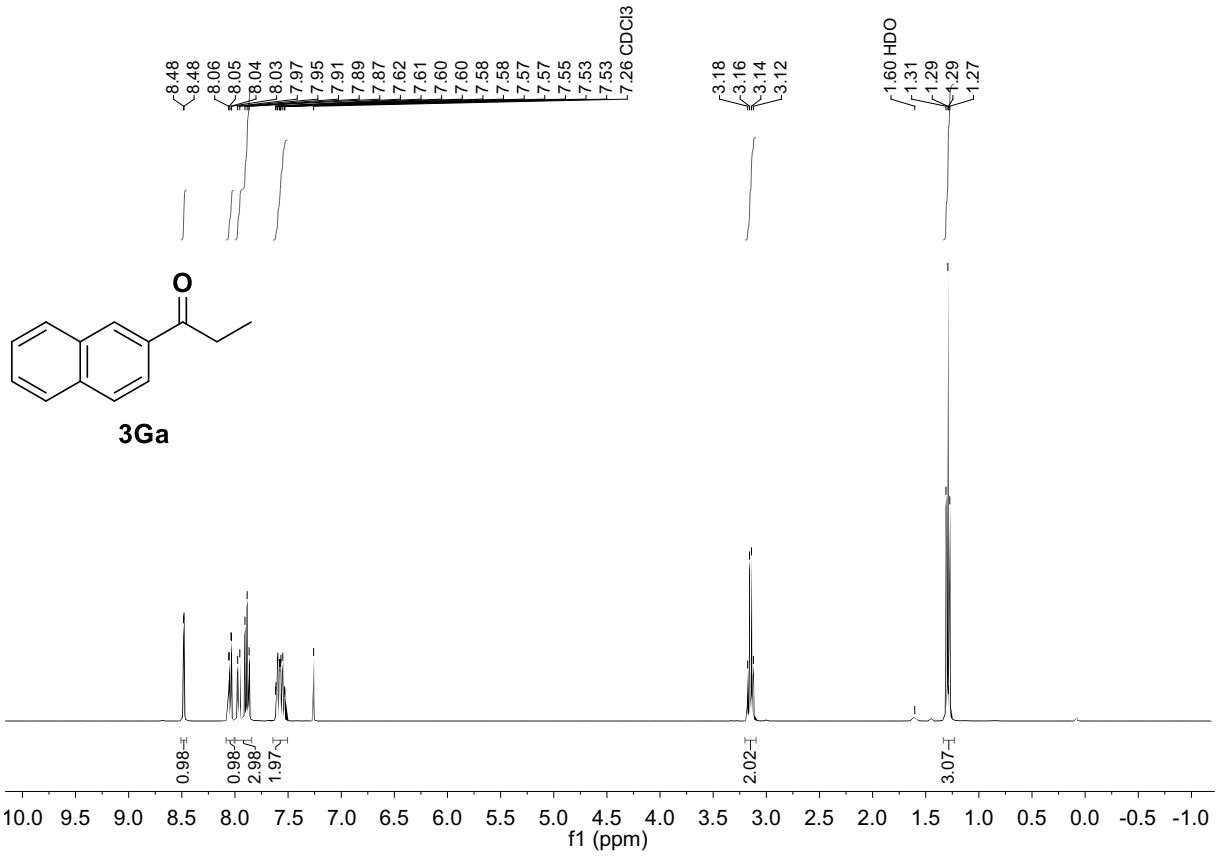
R_f: 0.17 (*n*Hex/EA = 99:1) [UV]

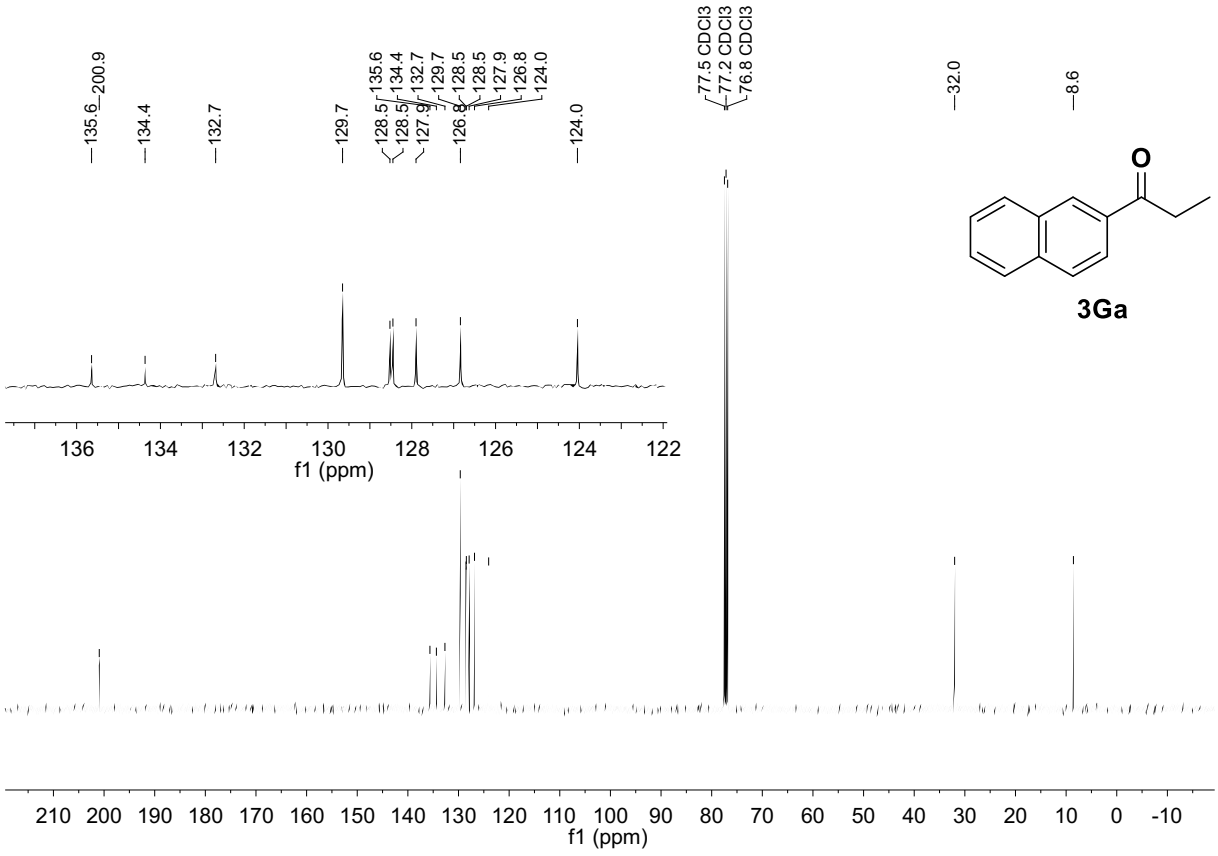
Melting point: 58.9–60.1 °C (EA).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 – 8.46 (m, 1H, Ar*H*), 8.05 (dd, *J* = 8.6, 1.7 Hz, 1H, Ar*H*), 8.00 – 7.84 (m, 3H, Ar*H*), 7.58 (dddd, *J* = 18.7, 8.1, 6.9, 1.4 Hz, 2H, Ar*H*), 3.15 (q, *J* = 7.3 Hz, 2H, CH_2CH_3), 1.29 (t, *J* = 7.3 Hz, 3H, CH_2CH_3).

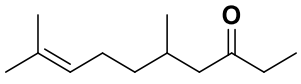
^{13}C NMR (101 MHz, CDCl3): δ= 200.9 (*C*OEt), 135.6 (C_{Ar}), 134.4 (C_{Ar}), 132.7 (C_{Ar}), 129.7 (C_{Ar}), 128.5 (C_{Ar}), 128.5 (C_{Ar}), 127.9 (C_{Ar}), 126.8 (C_{Ar}), 124.0 (C_{Ar}), 32.02 ($COCH_2$), 8.6 ($COCH_2CH_3$).

GC-MS (EI, method B): t_r = 19.91 min, m/z(%) = 184 (34, [$M^{+\bullet}$]), 155 (100, [$M^{+\bullet}$-$C_2H_5^{\bullet}$]), 127 (61, [$M^{+\bullet}$-$C_2H_5^{\bullet}$-CO]).


8.48
8.48
8.06
8.05
8.04
8.03
7.97
7.95
7.91
7.89
7.87
7.62
7.61
7.60
7.60
7.58
7.58
7.57
7.57
7.55
7.53
7.53
7.26 CDCl3
3.18
3.16
3.14
3.12
1.60 HDO
1.31
1.29
1.29
1.27
O
3Ga
0.98
0.98
2.98
1.97
2.02
3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


135.6
200.9
134.4
132.7
129.7
128.5
135.6
128.5
134.4
127.9
132.7
129.7
126.8
128.5
128.5
127.9
126.8
124.0
124.0
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
32.0
8.6
O
3Ga
136 134 132 130 128 126 124 122
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

5,9-dimethyldec-8-en-3-one (**3Ha**)



3Ha

According to GP-E, the product **3Ha** was synthesized using ethylmanganese bromide lithium chloride complex (4.6 mL, 1.2 mmol, 0.26 M, 1.2 equiv.) and citronellic acid *S*-ethylthioester **1H** (214 mg, 1.00 mmol). Purification was achieved by column chromatography (*n*Hex/Et_2O= 98:2 v/v to pure Et_2O) The product was obtained as a colorless oil with a pleasant smell (165 mg, 906 µmol, 91%). The analytical data is in accordance to reported literature.[21]

$C_{12}H_{22}O$ (182.17 g/mol)

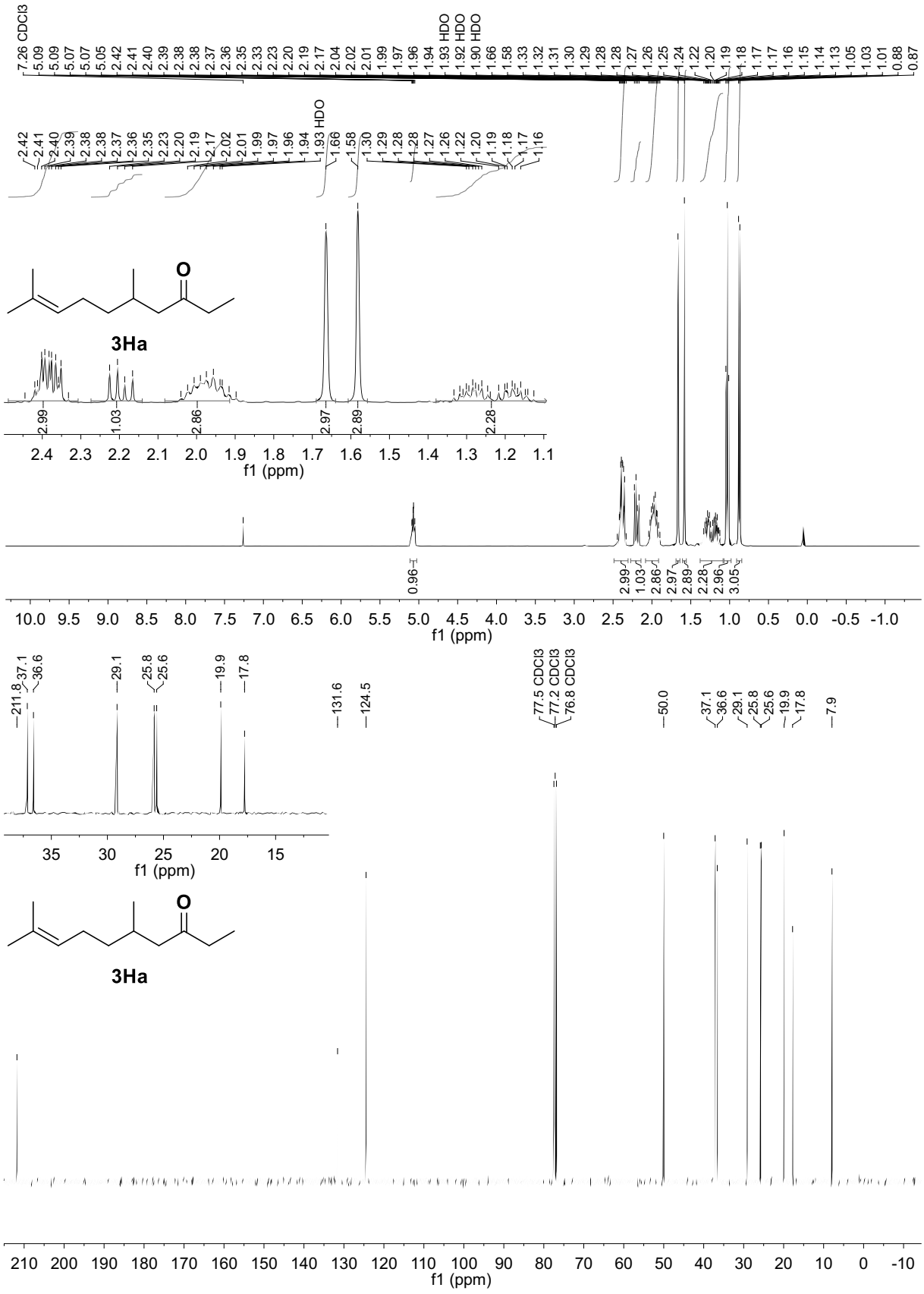
R_f: 0.24 (*n*Hex/Et_2O = 98:2 v/v) [anis - blue]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.12 – 5.02 (m, 1H, $C_{alkene}H$), 2.45 – 2.31 (m, 3H), 2.20 (dd, *J* = 15.7, 8.2 Hz, 1H), 2.08 – 1.87 (m, 3H), 1.66 (s, 3H), 1.58 (s, 3H), 1.38 – 1.10 (m, 2H), 1.03 (t, *J* = 7.3 Hz, 3H), 0.88 (d, *J* = 6.6 Hz, 3H).

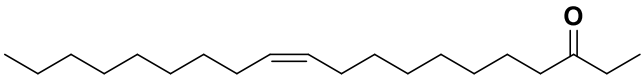
^{13}C NMR (101 MHz, $CDCl_3$): δ = 211.8 (*C*OEt), 131.6 (C_{alkene}), 124.5 (C_{alkene}), 50.0, 37.1, 36.6, 29.1, 25.8, 25.6, 19.9, 17.8, 7.9.

GC-MS (EI): t_r = 5.13 min, m/z(%) = 182 (7, [$M^{+\bullet}$]), 110 (45, [$C_8H_{14}^{+\bullet}$]), 57 (100, [$C_3H_5O^{+\bullet}$]).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2965 (m, C-H_{aliph}), 2920 (m, C-H_{aliph}), 2880 (w, C-H_{aliph}), 1709 (s, C=O), 1455 (m), 1411 (w), 1371 (m), 1280 (w), 1228 (w), 1146 (w), 1112 (m), 1027 (w), 975 (w), 941 (w), 890 (w), 822 (w).


7.26 CDCl3
1.93 HDO
1.92 HDO
1.90 HDO
O
3Ha
f1 (ppm)
211.8
37.1
36.6
29.1
25.8
25.6
19.9
17.8
131.6
124.5
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
50.0
7.9
O
3Ha
f1 (ppm)

(*Z*)-icos-11-en-3-one (**3Ia**)



3Ia

According to GP-E, the product **3Ha** was synthesized using ethylmanganese bromide lithium chloride complex (4.6 mL, 1.2 mmol, 0.26 M, 1.2 equiv.) and *S*-ethyl (*Z*)-octadec-9-enethioate **1I** (214 mg, 1.00 mmol). Purification was achieved by column chromatography (*n*Hex/Et_2O= 98:2 v/v to pure Et_2O) The product was obtained as a colorless oil (165 mg, 560 µmol, 56%).

$C_{20}H_{38}O$ (294.52 g/mol)

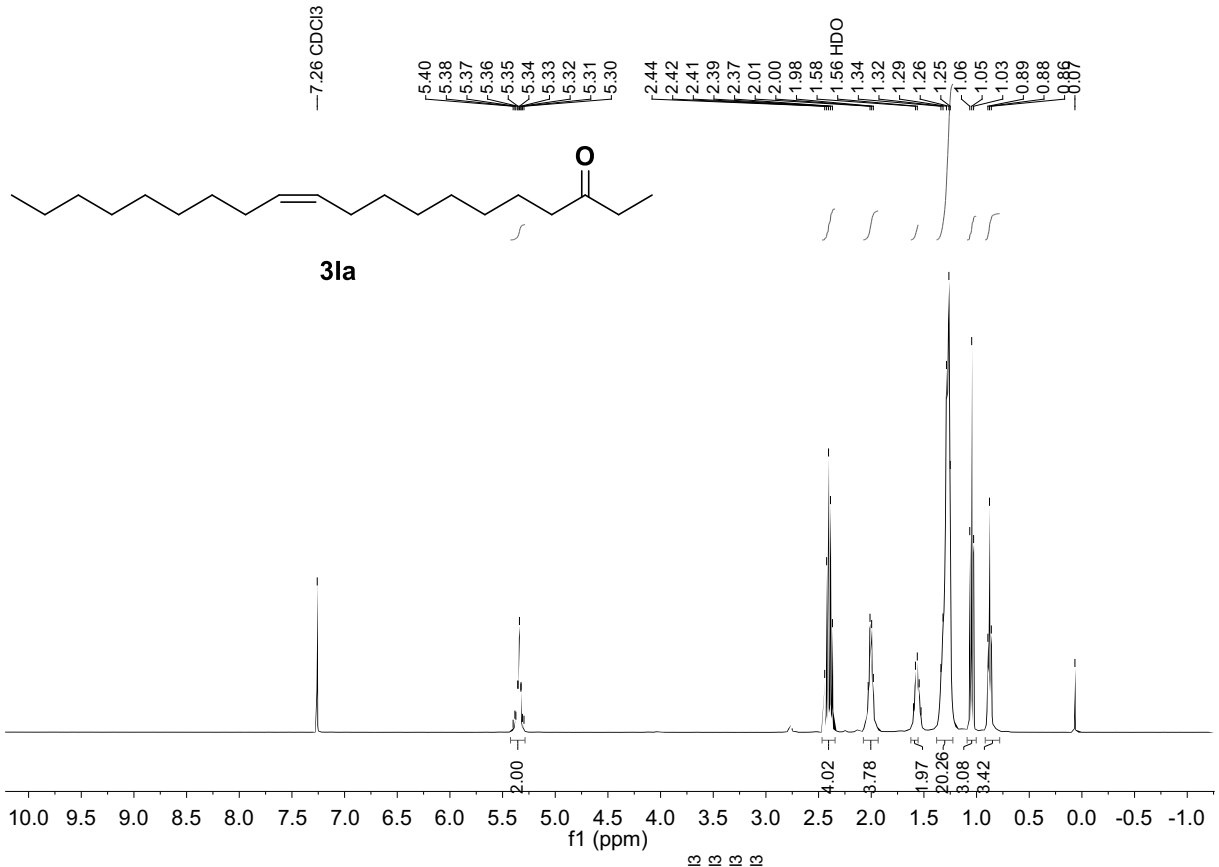
R_f: 0.38 (*n*Hex/EA = 9:1) [anis]

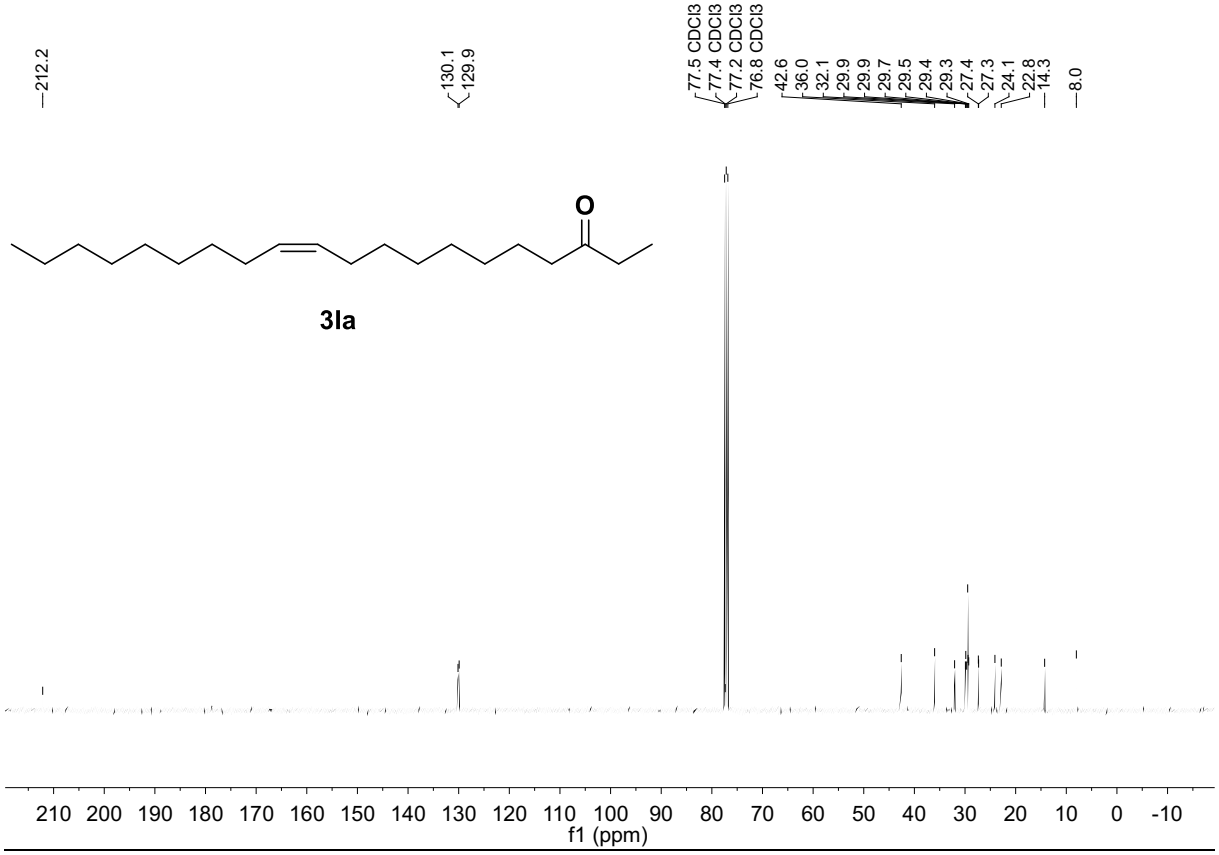
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.43 – 5.28 (m, 2H, CH_{alkene}), 2.47 – 2.34 (m, 4H), 2.08 – 1.92 (m, 4H), 1.62 – 1.54 (m, 2H), 1.38 – 1.22 (m, 20H), 1.05 (t, *J* = 7.3 Hz, 3H), 0.93 – 0.82 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 212.2 (*C*O), 130.1 (C_{alkene}), 129.9 (C_{alkene}), 42.6, 36.0, 32.1, 29.9, 29.9, 29.7, 29.5, 29.4, 29.1, 27.4, 27.3, 24.1, 22.8, 14.3, 8.0.

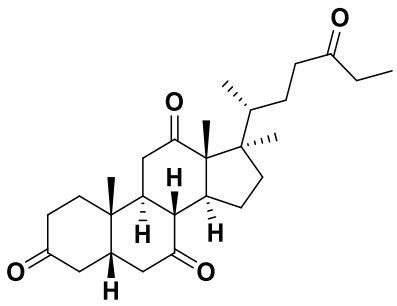
HR-MS (EI): m/z calc. for $[M]^+$ 294.291717, found 294.28958.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3002 (w, C-H_{alkene}), 2921 (s, C-H_{aliph}), 2853 (m, C-H_{aliph}), 1716 (m, C=O), 1459 (m), 1411 (w), 1370 (w), 1314 (w), 1273 (w), 1251 (w), 1169 (w), 1109 (w), 1030 (w), 967 (w), 721 (w).


7.26 CDCl3
5.40
5.38
5.37
5.36
5.35
5.34
5.33
5.32
5.31
5.30
2.44
2.42
2.41
2.39
2.37
2.01
2.00
1.98
1.58
1.56 HDO
1.34
1.32
1.29
1.26
1.25
1.06
1.05
1.03
0.89
0.88
O
3la
2.00
4.02
3.78
1.97
20.26
3.08
3.42
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


212.2
130.1
129.9
77.5 CDCl3
77.4 CDCl3
77.2 CDCl3
76.8 CDCl3
42.6
36.0
32.1
29.9
29.9
29.7
29.5
29.4
29.3
27.4
27.3
24.1
22.8
14.3
8.0
O
3la
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

(5*S*,8*R*,9*S*,10*S*,13*S*,14*S*,17*R*)-10,13,17-trimethyl-17-((*R*)-5-oxoheptan-2-yl)dodecahydro-3*H*-cyclopenta[a]phenanthrene-3,7,12(2*H*,4*H*)-trione (**3Ja**)



3Ja

According to GP-E, the product **3Ja** was synthesized using ethyl manganese bromide lithium chloride complex (7.1 mL, 0.17 M, 1.2 mmol, 1.2 equiv.) and dehydrocholic acid *S*-ethyl thioester **1J** (223 mg, 500 µmol). Purification was achieved by flash column chromatography (*n*Hex/EA = 9:1 to 40:60 and hold for 2 CV). The product was obtained as a colorless solid (120 mg, 290 µmol, 58%).

$C_{26}H_{38}O_4$ (414.59 g/mol)

R_f: 0.33 (*n*Hex/EA = 1:1) [anis]

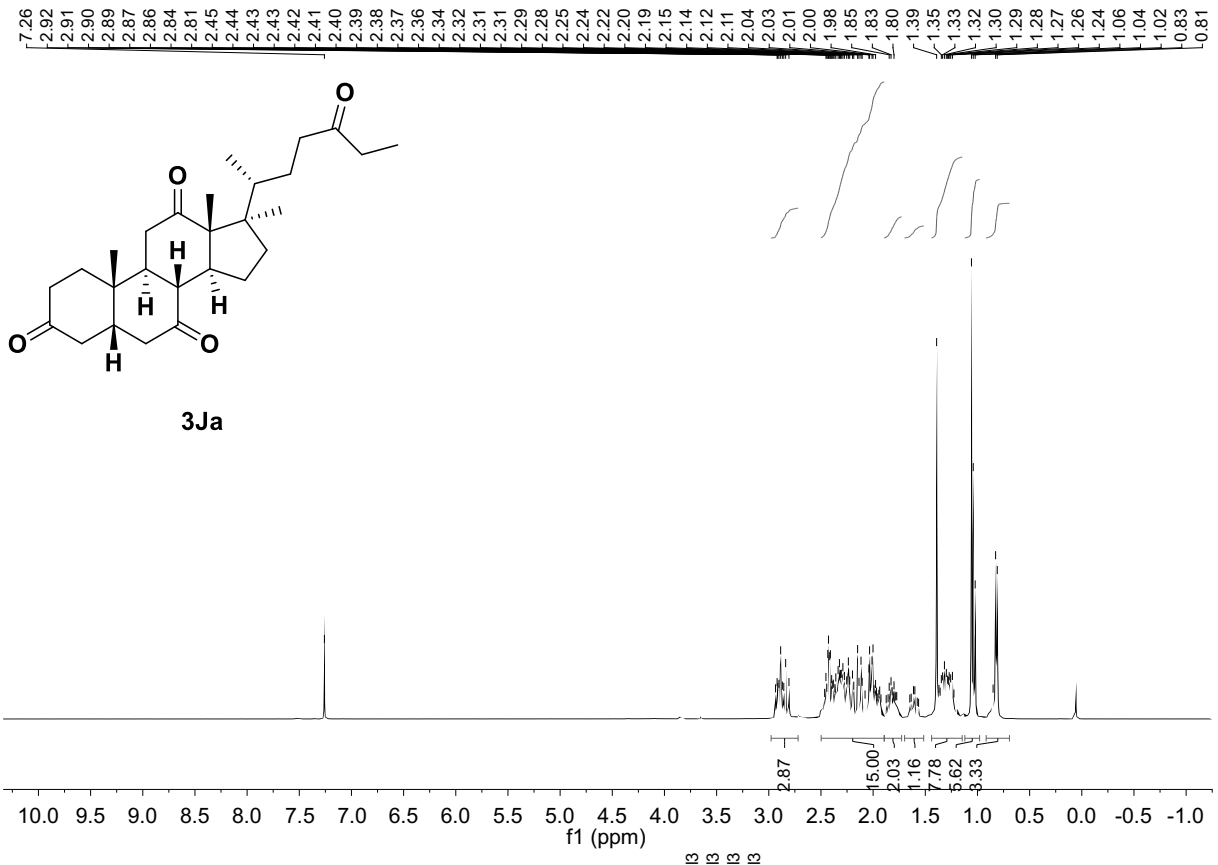
Melting point: 215 (decomp.).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.02 – 2.74 (m, 4H), 2.56 – 1.91 (m, 15H), 1.90 – 1.71 (m, 2H), 1.67 – 1.55 (m, 1H), 1.43 – 1.17 (m, 8H), 1.08 – 0.99 (m, 6H), 0.88 – 0.78 (m, 3H).

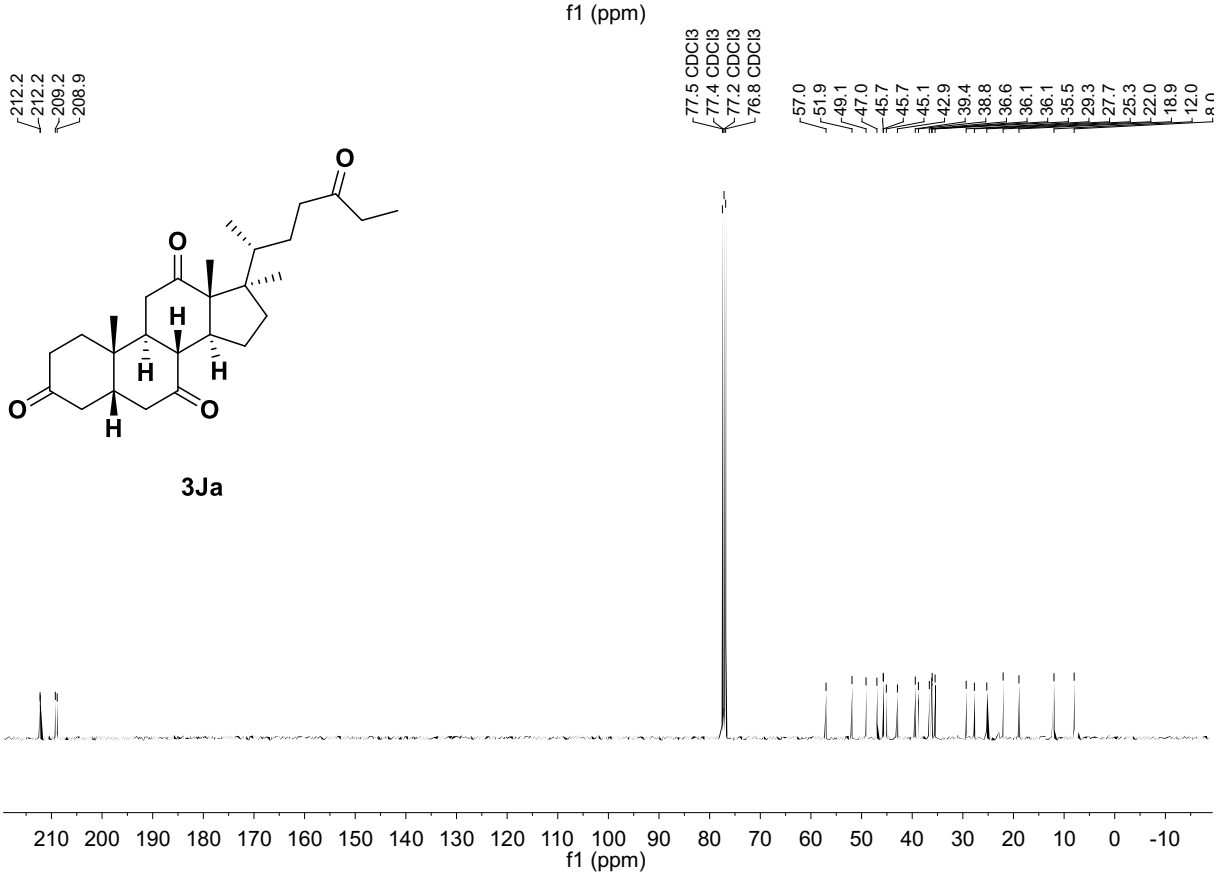
^{13}C NMR (101 MHz, $CDCl_3$): δ = 212.2 (*C*O), 212.2 2 (*C*O), 209.2 2 (*C*O), 208.9 2 (*C*O), 57.0, 51.9, 49.1, 47.0, 45.7, 45.7, 45.1, 42.9 39.4, 38.8, 36.6, 36.1, 36.1, 35.5, 35.4, 29.3, 27.7, 25.3, 22.0, 18.9, 12.0, 8.0.

HR-MS (ESI): m/z calc. for $[M+Na]^+$ 437.26623, found 437.26600.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2965 (w, C-H_{aliph}), 2913 (w, C-H_{aliph}), 2868 (w, C-H_{aliph}), 1705 (s, C=O), 1454 (w), 1432 (w), 1381 (w), 1343 (w), 1295 (w), 1273 (w), 1240 (w), 1184 (w), 1124 (w), 1120 (w), 1105 (w), 1072 (w), 1027 (w), 1004 (w), 952 (w), 930 (w), 896 (w), 870 (w), 833 (w), 803 (w), 777 (w), 725 (w), 684 (w).

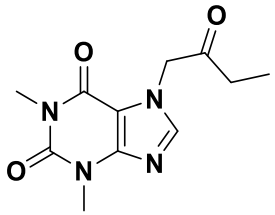

7.26 2.92 2.91 2.90 2.89 2.87 2.86 2.84 2.81 2.45 2.44 2.43 2.43 2.42 2.41 2.40 2.39 2.38 2.37 2.36 2.34 2.32 2.31 2.31 2.29 2.28 2.25 2.24 2.22 2.20 2.19 2.15 2.14 2.12 2.11 2.04 2.03 2.01 2.00 1.98 1.85 1.83 1.80 1.39 1.35 1.33 1.32 1.30 1.29 1.28 1.27 1.26 1.24 1.06 1.04 1.02 0.83 0.81
O
O
H
H
H
O
O
H
2.87 15.00 2.03 1.16 7.78 5.62 3.33
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

3Ja


212.2 212.2 209.2 208.9
77.5 CDCl3 77.4 CDCl3 77.2 CDCl3 76.8 CDCl3
57.0 51.9 49.1 47.0 45.7 45.7 45.1 42.9 39.4 38.8 36.6 36.1 36.1 35.5 29.3 27.7 25.3 22.0 18.9 12.0
O
O
H
H
H
O
O
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3Ja

1,3-dimethyl-7-(2-oxobutyl)-3,7-dihydro-1*H*-purine-2,6-dione (**3Ka**)



3Ka

According to GP-E, the product **3Ka** was synthesized using ethylmanganese bromide lithium chloride complex (4.6 mL, 1.2 mmol, 0.26 M, 1.2 equiv.) and *S*-ethyl 2-(1,3-dimethyl-2,6-dioxo-1,2,3,6-tetrahydro-7*H*-purin-7-yl)ethanethioate **1K** (282 mg, 1.00 mmol). The reaction stirred for 15 min at -20 °C. Purification was achieved by filtering the crude product through a pad of silica (solvent: DCM/MeOH = 40:1 v/v). Then, the product was further purified by recrystallization (*n*Hex/EtOH = 5:3 v/v) and obtained as a colorless solid (188 mg, 751 µmol, 75 %).

$C_{11}H_{14}N_4O_3$ (250.26 g/mol)

R_f: 0.18 (DCM:MeOH = 20:1) [UV, anis]

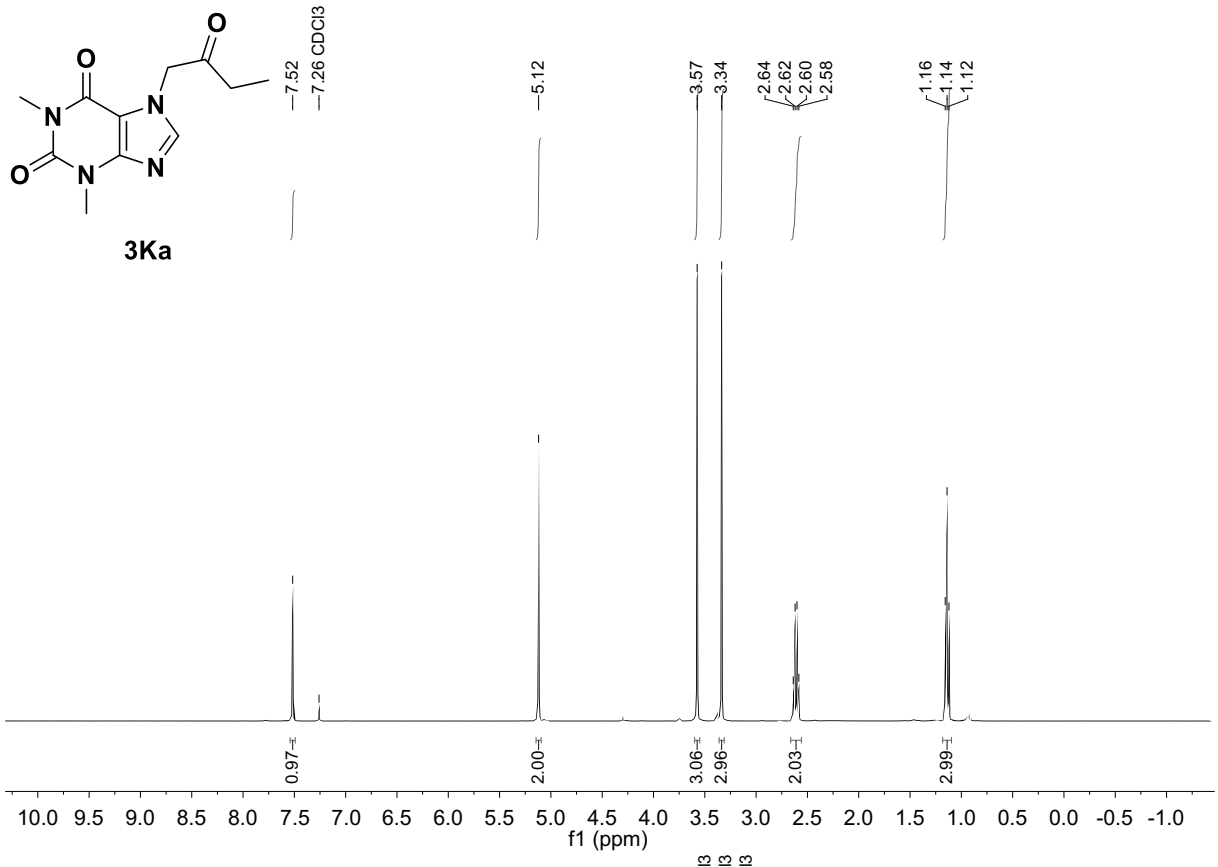
Melting point: 148.2–149.2 °C (EtOH).

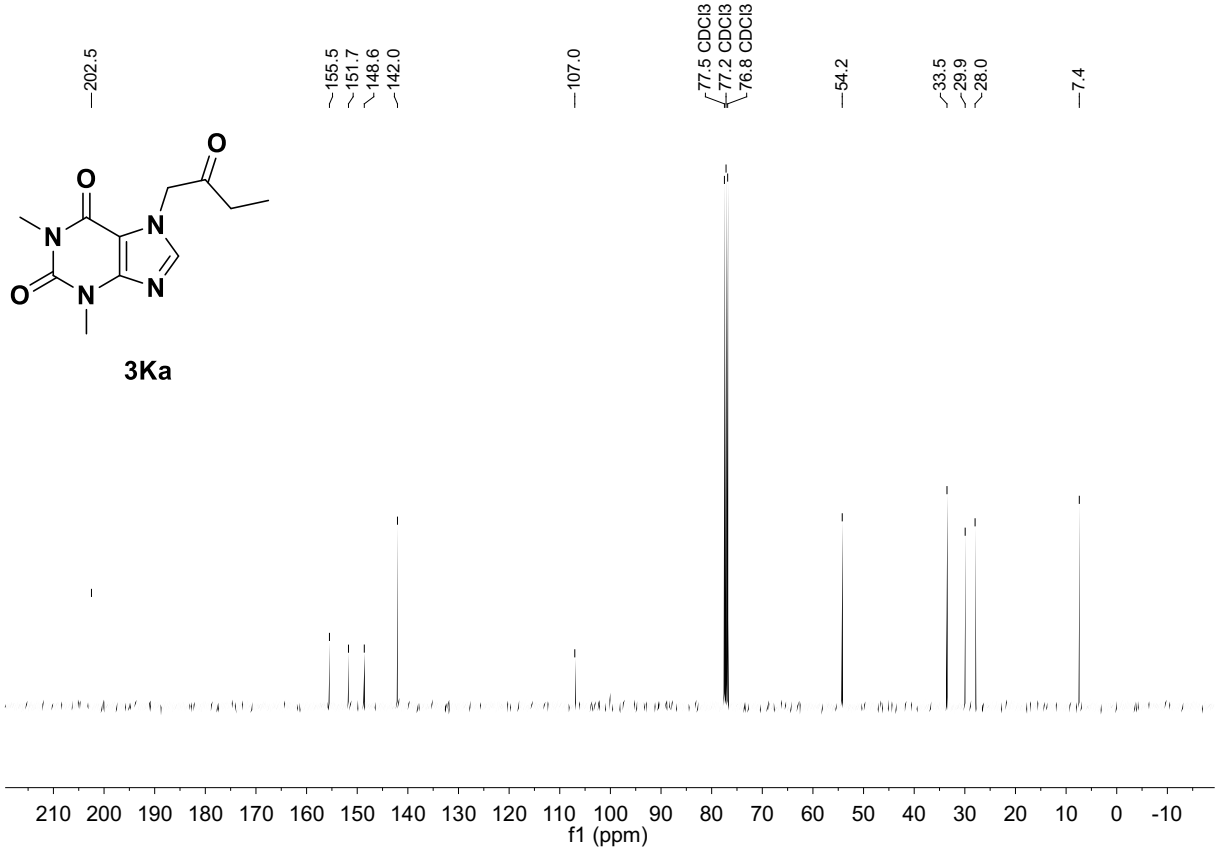
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (s, 1H, NC*H*), 5.12 (s, 2H, NCH_2CO), 3.57 (s, 3H, NCH_3), 3.34 (s, 3H, NCH_3), 2.61 (q, *J* = 7.4 Hz, 2H, COCH_2CH$_3$), 1.14 (t, *J* = 7.4 Hz, 3H, COCH$_2$CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 202.5 (*C*O), 155.5 (N*C*O), 151.7 (N*C*O), 148.6, 142.1, 107.0, 54.2 (N*C*H$_2$CO), 33.5 (*C*H$_2$CH$_3$), 29.9 (N*C*H$_3$), 28.0 (N*C*H$_3$), 7.4 (CH$_2$*C*H$_3$).

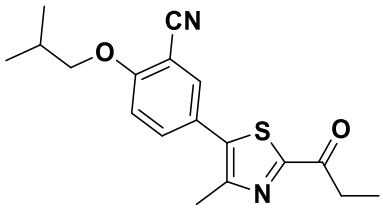
HR-MS (ESI): m/z calc. for $[M+Na]^+$ 273.09581, found 273.09588.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3125 (w, C-H$_{heterocyclic}$), 2965 (w, C-H$_{aliph}$), 2939 (w, C-H$_{aliph}$), 2887 (w, C-H$_{aliph}$), 1731 (w), 1693 (m, C=O$_{ketone}$), 1649 (s, C=O$_{amide}$), 1542 (m, C=O$_{amide}$), 1455 (m), 1429 (m), 1400 (m), 1370 (m), 1336 (w), 1292 (w), 1237 (m), 1187 (m), 1116 (m), 1072 (w), 1027 (m), 978 (w), 930 (w), 904 (w), 856 (w), 810 (w), 766 (m), 740 (m), 673 (w).


3Ka
7.52
7.26 CDCl3
5.12
3.57
3.34
2.64
2.62
2.60
2.58
1.16
1.14
1.12
0.97
2.00
3.06
2.96
2.03
2.99
f1 (ppm)


3Ka
202.5
155.5
151.7
148.6
142.0
107.0
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
54.2
33.5
29.9
28.0
7.4
f1 (ppm)

1-(2-(3-cyano-4-*iso*butoxyphenyl)-4-methylthiazyl)propanone (**3La**)



3La

According to GP-E, the product **3La** was synthesized using ethylmanganese bromide lithium chloride complex (2.5 mL, 1.2 mmol, 0.24 M, 1.2 equiv.) and *S*-ethyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carbothioate **1La** (180 mg, 0.500 mmol). Purification was achieved by flash liquid chromatography (23 SiO_2, gradient *n*Hex/EA from 95:5 to 85:15 over 15 CV, then gradient to 50:50 over 1 CV, hold for 5 CV). The product was obtained as a slightly yellow solid (65.1 mg, 198 µmol, 40%).

$C_{18}H_{20}N_2O_2S$ (328.43 g/mol)

R_f: 0.40 (*n*Hex/EA = 9:1 v/v) [anis, UV]

Melting point: 157.8–158.3 °C (EA).

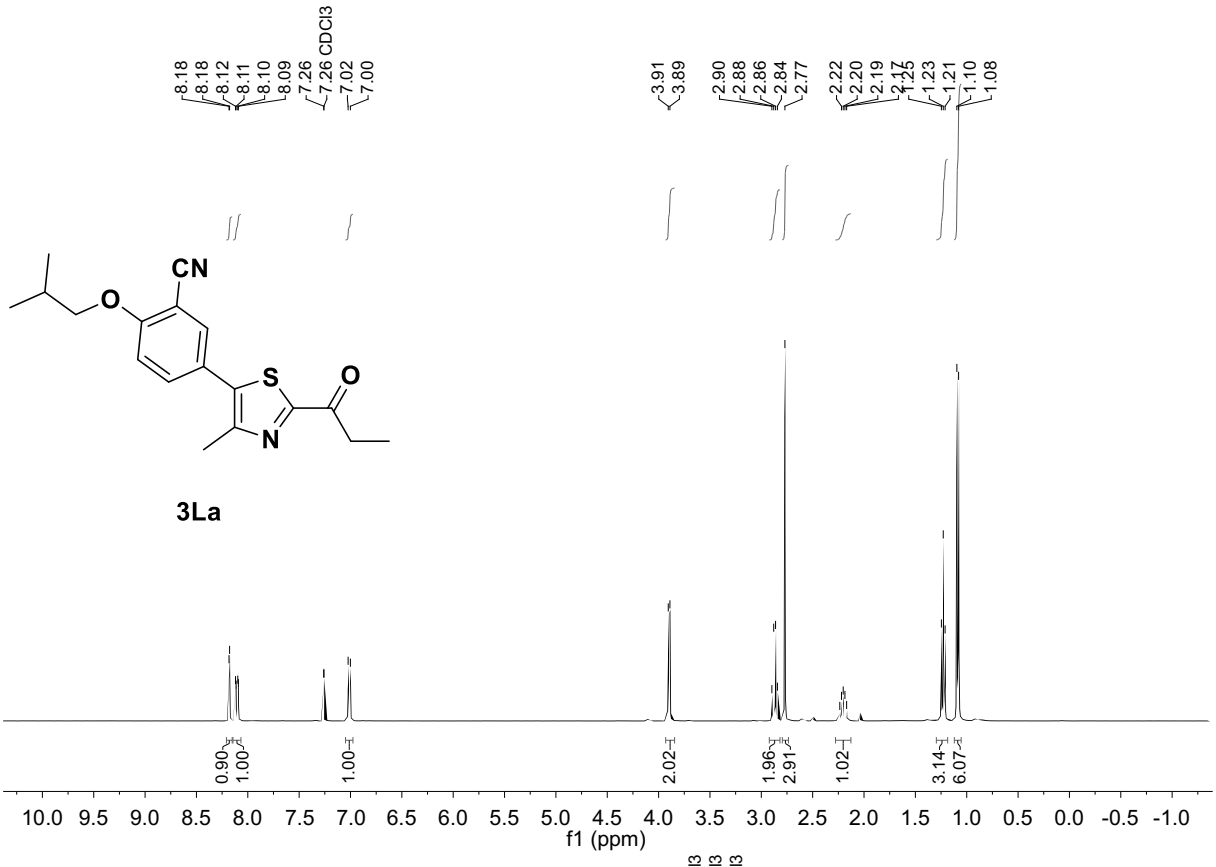
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 2.3 Hz, 1H), 8.11 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.01 (d, *J* = 8.9 Hz, 1H), 3.90 (d, *J* = 6.5 Hz, 2H), 2.87 (q, *J* = 7.2 Hz, 2H), 2.77 (s, 3H), 2.28 – 2.13 (m, 1H, C*H*(CH_3)$_2$), 1.23 (*t*, J = 7.2 Hz, 3H), 1.09 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.6 (*C*OEt), 166.3, 162.7, 159.6, 132.8, 132.3, 130.7, 126.0, 115.5, 112.8, 103.1, 75.8, 36.5, 28.3, 19.2, 18.6, 8.3.

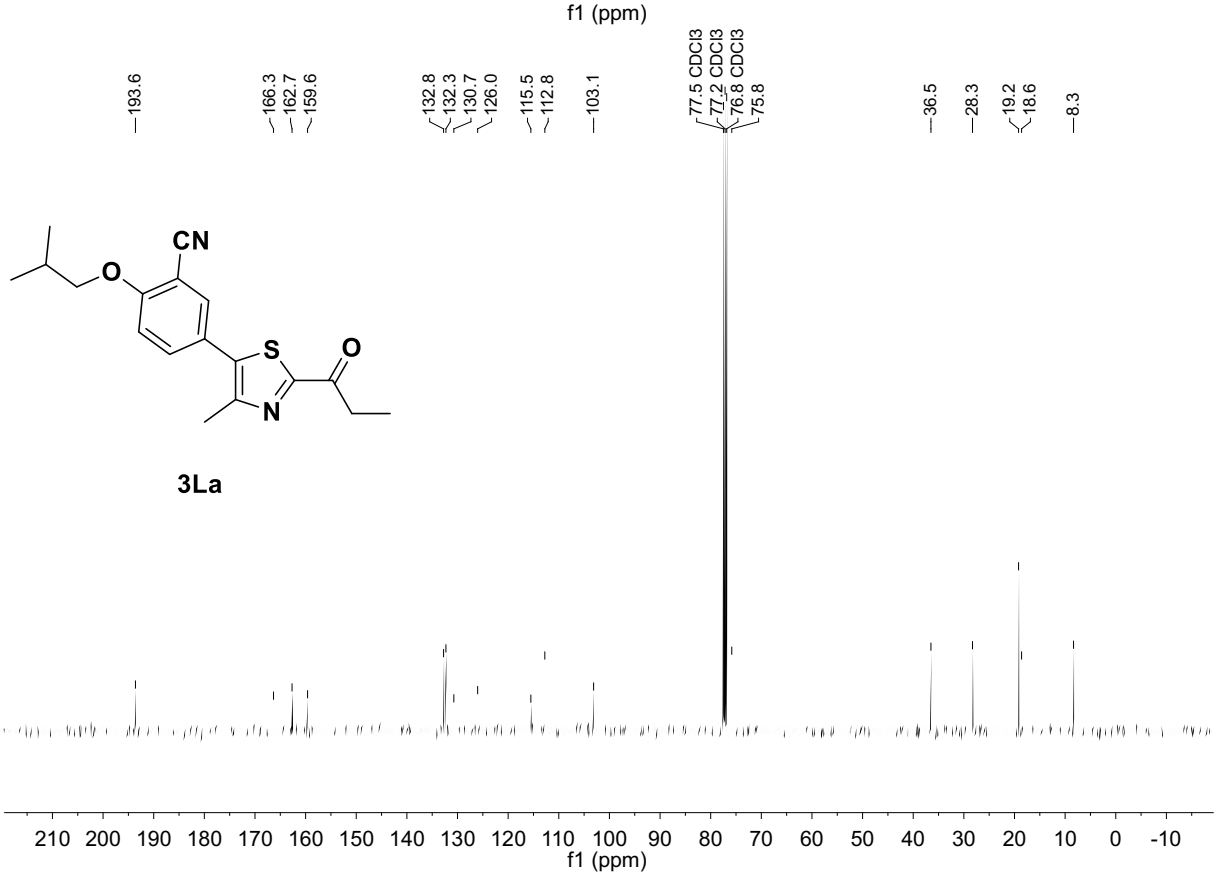
GC-MS (EI): t_r = 12.60 min, m/z(%) = 328 (12, [$M^{+\bullet}$]) , 272 (27), 243 (100), 215(10).

HR-MS (ESI): m/z calc. for $[M+Na]^+$ 351.11377, found 351.11376.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2973 (w, C-H_{aliph}), 2935 (w, C-H_{aliph}), 2909 (w, C-H_{aliph}), 2872 (w, C-H_{aliph}), 2225 (w, C≡N), 1645 (m, C=O), 1597 (w), 1504 (w), 1463 (w), 1422 (m), 1381 (w), 1377 (w), 1355 (w), 1288 (m), 1217 (m), 1168 (m), 1124 (m), 1064 (w), 1042 (w), 1038 (w), 1005 (m), 963 (m), 911 (w), 878 (w), 818 (m), 762 (w), 724 (w), 664 (w).

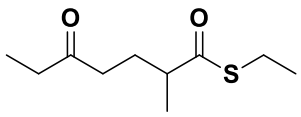

8.18
8.18
8.12
8.11
8.10
8.09
7.26
7.26 CDCl3
7.02
7.00
3.91
3.89
2.90
2.88
2.86
2.84
2.77
2.22
2.20
2.19
2.17
2.15
1.23
1.21
1.10
1.08
CN
O
S
O
N
0.90
1.00
1.00
2.02
1.96
2.91
1.02
3.14
6.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

3La


193.6
166.3
162.7
159.6
132.8
132.3
130.7
126.0
115.5
112.8
103.1
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
75.8
36.5
28.3
19.2
18.6
8.3
CN
O
S
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3La

S-ethyl 2-methyl-5-oxoheptanethioate (**5**)



5

According to GP-E, the product **5** was synthesized using ethyl manganese bromide lithium chloride complex (4.6 mL, 1.2 mmol, 0.26 M, 1.2 equiv.) and *S,S*-diethyl 2-methylpentanebis(thioate) **5** (234 mg, 1.00 mmol). Purification was achieved by column chromatography (*n*Hex/EA = 97:3 v/v) The product was obtained as a colorless oil (126 mg, 623 µmol, 62%).

$C_{10}H_{18}O_2S$ (202.31 g/mol)

R_f: 0.39 (*n*Hex/EA = 97:3 v/v) [anis]

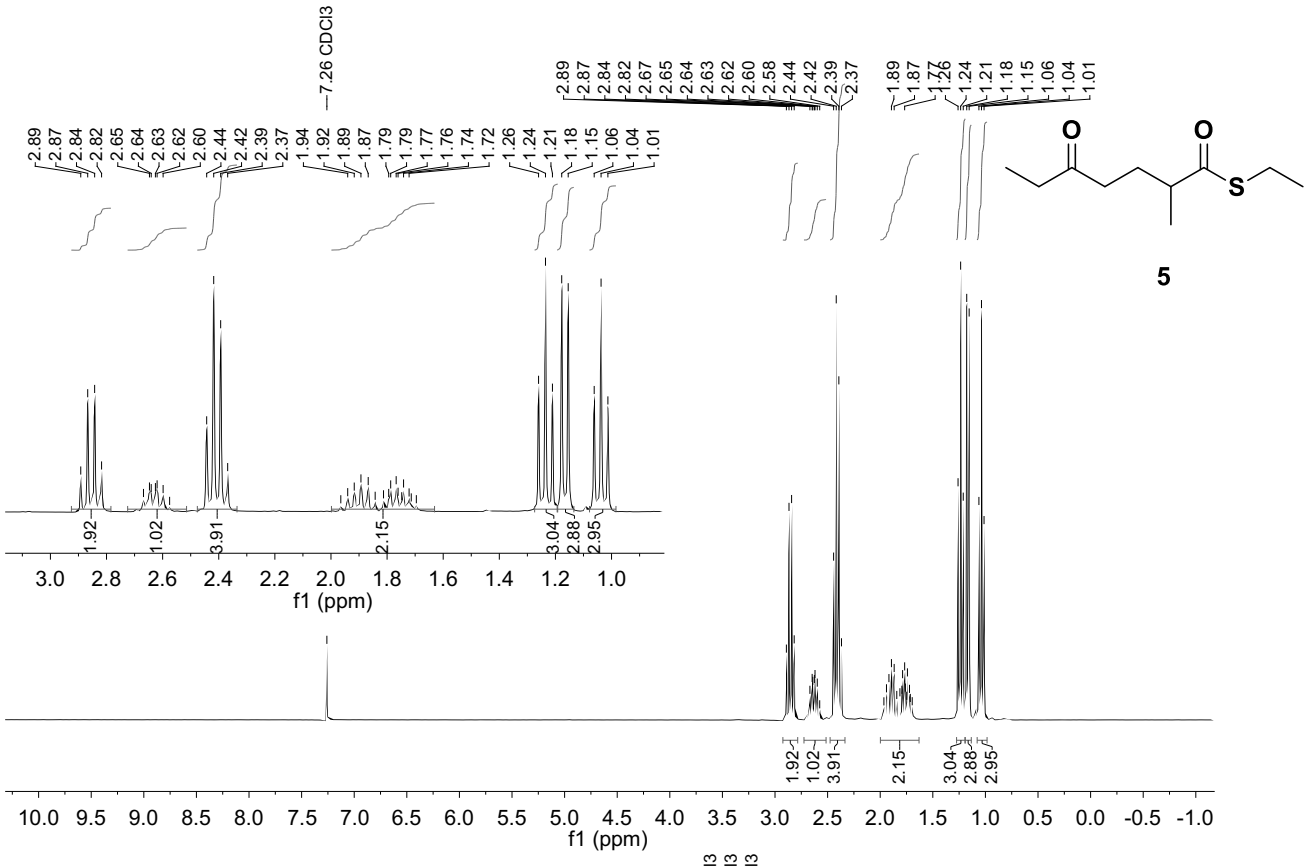
^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.85 (q, *J* = 7.4 Hz, 2H), 2.72 – 2.51 (m, 1H), 2.48 – 2.33 (m, 4H), 2.03 – 1.63 (m, 2H), 1.24 (t, *J* = 7.4 Hz, 3H), 1.17 (d, *J* = 6.9 Hz, 3H), 1.04 (t, *J* = 7.3 Hz, 3H).

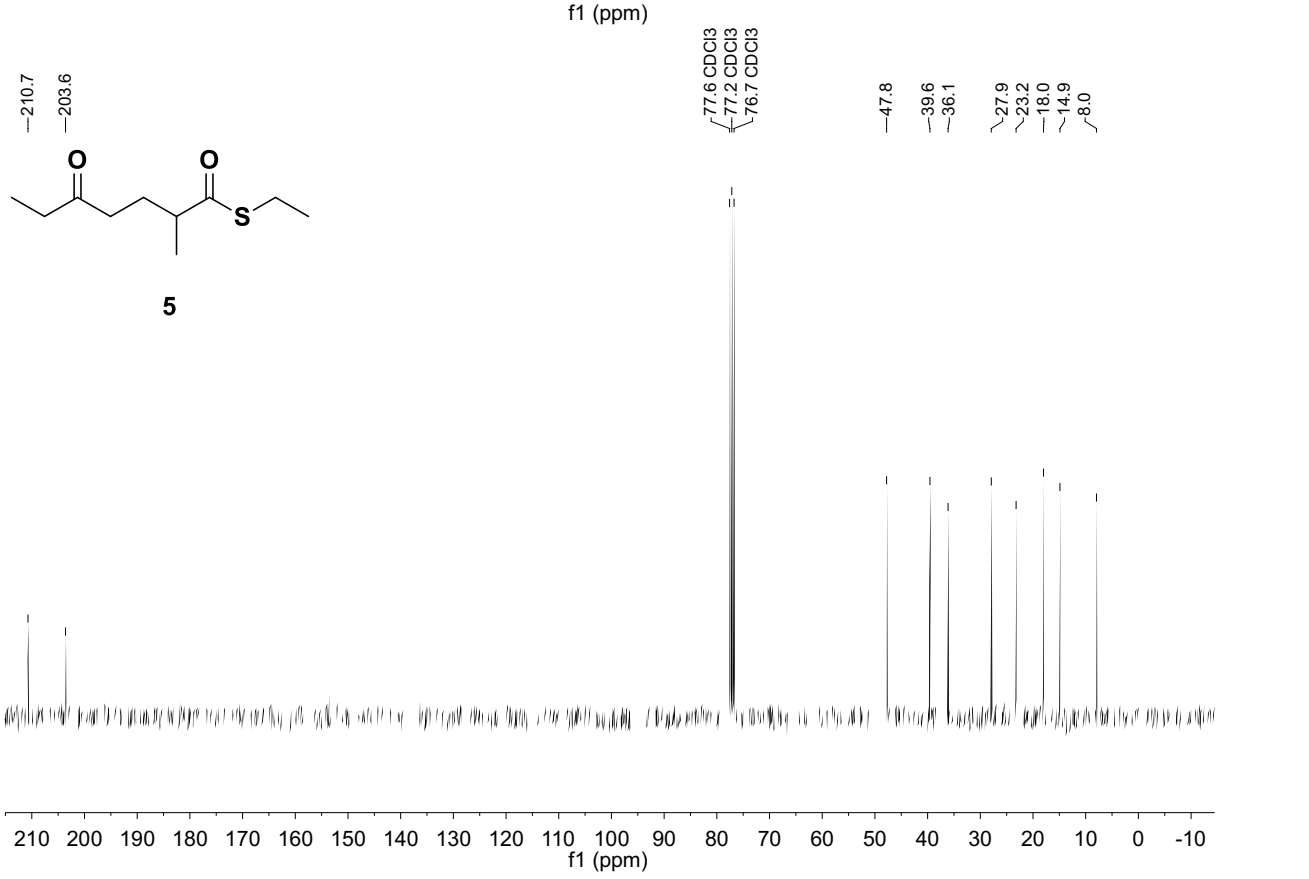
^{13}C NMR (75 MHz, $CDCl_3$): δ = 210.7 (Et*C*OCH_2), 203.60 (*C*OSEt), 47.8, 39.6, 36.1, 27.9, 23.2, 18.0, 14.9, 8.0.

GC-MS (EI): t_r = 6.09 min, m/z(%) = 141 (20, [$M^{+\bullet}$-$C_2H_5S^\bullet$]), 57 (100, [$M^{+\bullet}$-$C_7H_{13}OS^\bullet$]).

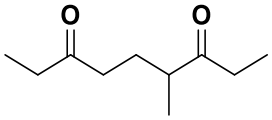
HR-MS (ESI): m/z calc. for $[M+Na]^+$ 225.09197, found 225.09236.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2972 (w, C-H_{aliph}), 2932 (w, C-H_{aliph}), 2879 (w, C-H_{aliph}), 1713 (s, C=O_{ketone}), 1679 (s, C=$O_{thioester}$), 1452 (m), 1414 (w), 1370 (m), 1262 (w), 1194 (w), 1112 (w), 1049 (w), 1019 (w), 956 (s), 897 (w), 822 (w), 736 (w), 695 (w).


7.26 CDCl3
2.89 2.87 2.84 2.82 2.65 2.64 2.63 2.62 2.60 2.44 2.42 2.39 2.37 1.94 1.92 1.89 1.87 1.79 1.79 1.77 1.76 1.74 1.72 1.26 1.24 1.21 1.18 1.15 1.06 1.04 1.01
1.92 1.02 3.91 2.15 3.04 2.88 2.95
f1 (ppm)
O
O
S
5


210.7
203.6
77.6 CDCl3
77.2 CDCl3
76.7 CDCl3
47.8
39.6
36.1
27.9
23.2
18.0
14.9
8.0
f1 (ppm)
O
O
S
5

4-methylnona-3,6-dione (**6**)



6

According to GP-E, the product **6** was synthesized using ethyl manganese bromide lithium chloride complex (4.80 mL, 0.20 M, 2.2 mmol, 1.2 equiv.) and *S,S*-diethyl 2-methylpentanebis(thioate) **4** (234 mg, 1.00 mmol). Purification was achieved by manual column chromatography (*n*Hex/EA = 9:1). The product was obtained as a colorless oil (135 mg, 793 µmol, 79%).

$C_{10}H_{18}O_2$ (170.25 g/mol)

R_f: 0.08 (*n*Hex/EA = 9:1) [anis]

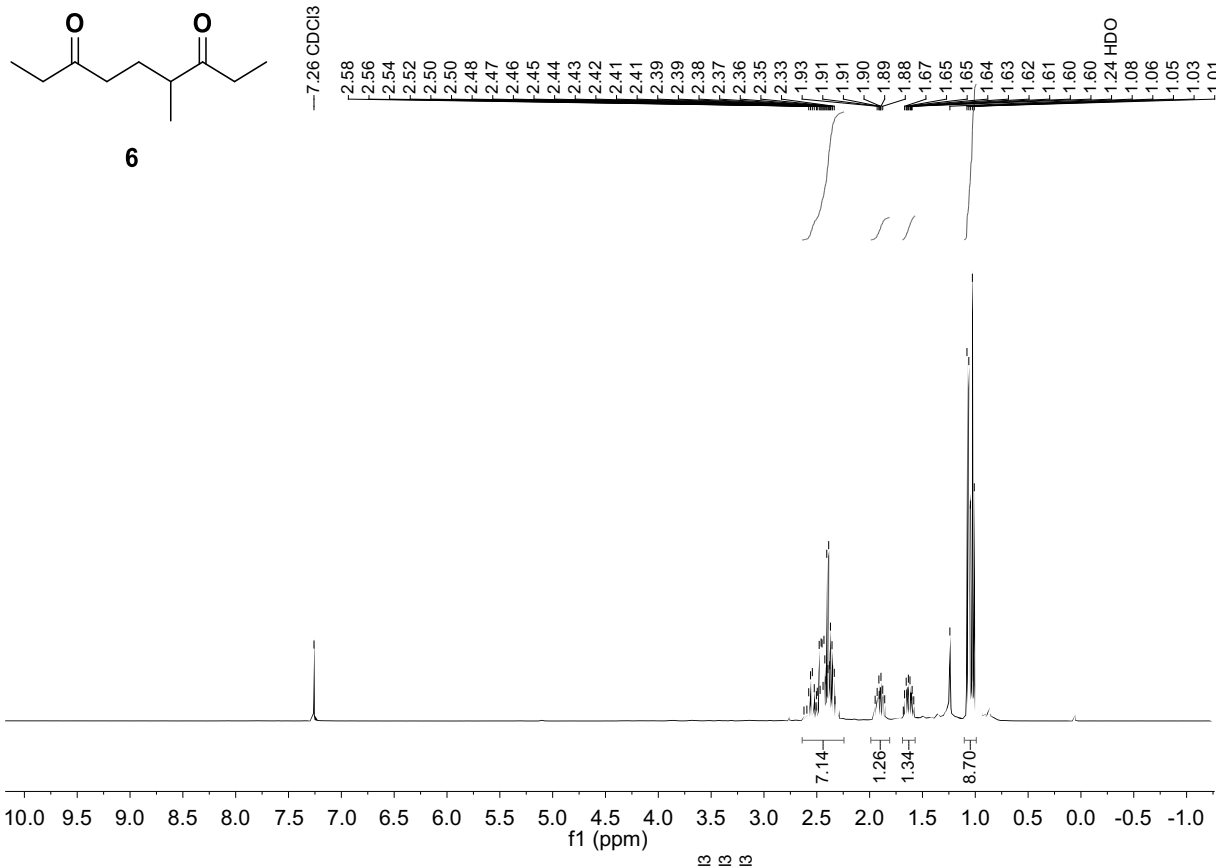
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.58 – 2.26 (m, 7H), 1.97 – 1.83 (m, 1H), 1.72 – 1.56 (m, 1H), 1.11 – 0.93 (m, 9H).

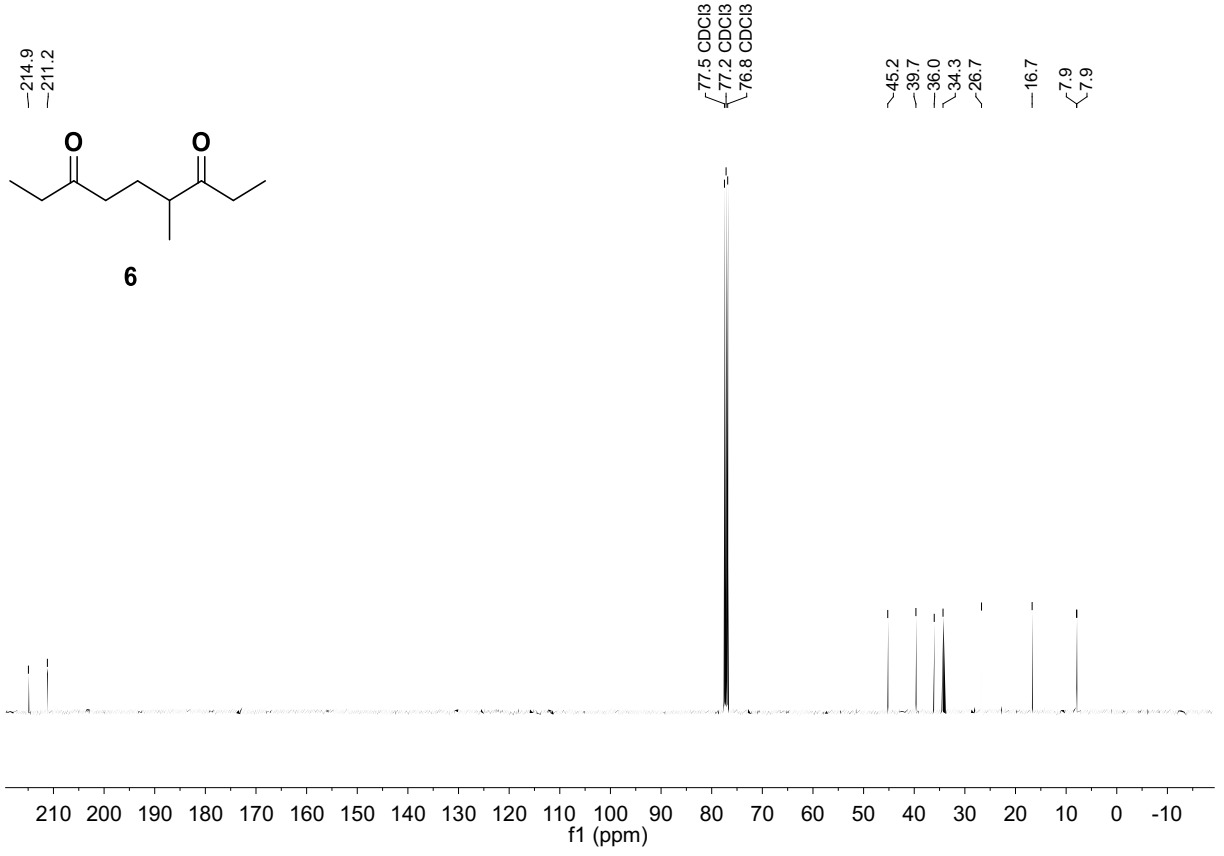
^{13}C NMR (101 MHz, $CDCl_3$): δ = 214.9 (*C*O), 211.2 (*C*O), 45.23, 39.7, 36.0, 34.3, 26.7, 16.7, 7.94, 7.90.

GC-MS (EI, method B): t_r = 14.20 min, m/z(%) = 170 (10, $[M^{+\bullet}]$), 141 (11, $[M^{+\bullet}\text{-}C_2H_5^{\bullet}]$), 141 (11, $[M^{+\bullet}\text{-}C_2H_5^{\bullet}\text{-}C_2H_4]$), 57 (100, $[C_3H_5O^{+\bullet}]$).

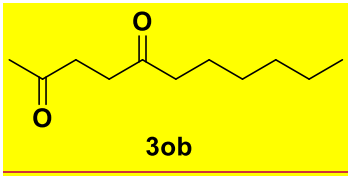
HR-MS (ESI): m/z calc. for $[M+Na]^+$ 193.11990 , found 193.12016.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2972 (m, C-H_{aliph}), 2932 (m, C-H_{aliph}), 2885 (w, C-H_{aliph}), 1709 (vs, C=O), 1456 (m), 1411 (w), 1370 (m), 1254 (w), 1191 (w), 1106 (m), 1030 (w), 971 (w).


O
O
6
7.26 CDCl3
2.58
2.56
2.54
2.52
2.50
2.50
2.48
2.47
2.46
2.45
2.44
2.43
2.42
2.41
2.41
2.39
2.39
2.38
2.37
2.36
2.35
2.33
1.93
1.91
1.91
1.90
1.89
1.88
1.67
1.65
1.65
1.64
1.63
1.62
1.61
1.60
1.60
1.24 HDO
1.08
1.06
1.05
1.03
7.14
1.26
1.34
8.70
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


214.9
211.2
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
45.2
39.7
36.0
34.3
26.7
16.7
7.9
7.9
O
O
6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2,5-undecadion (**3ob**)



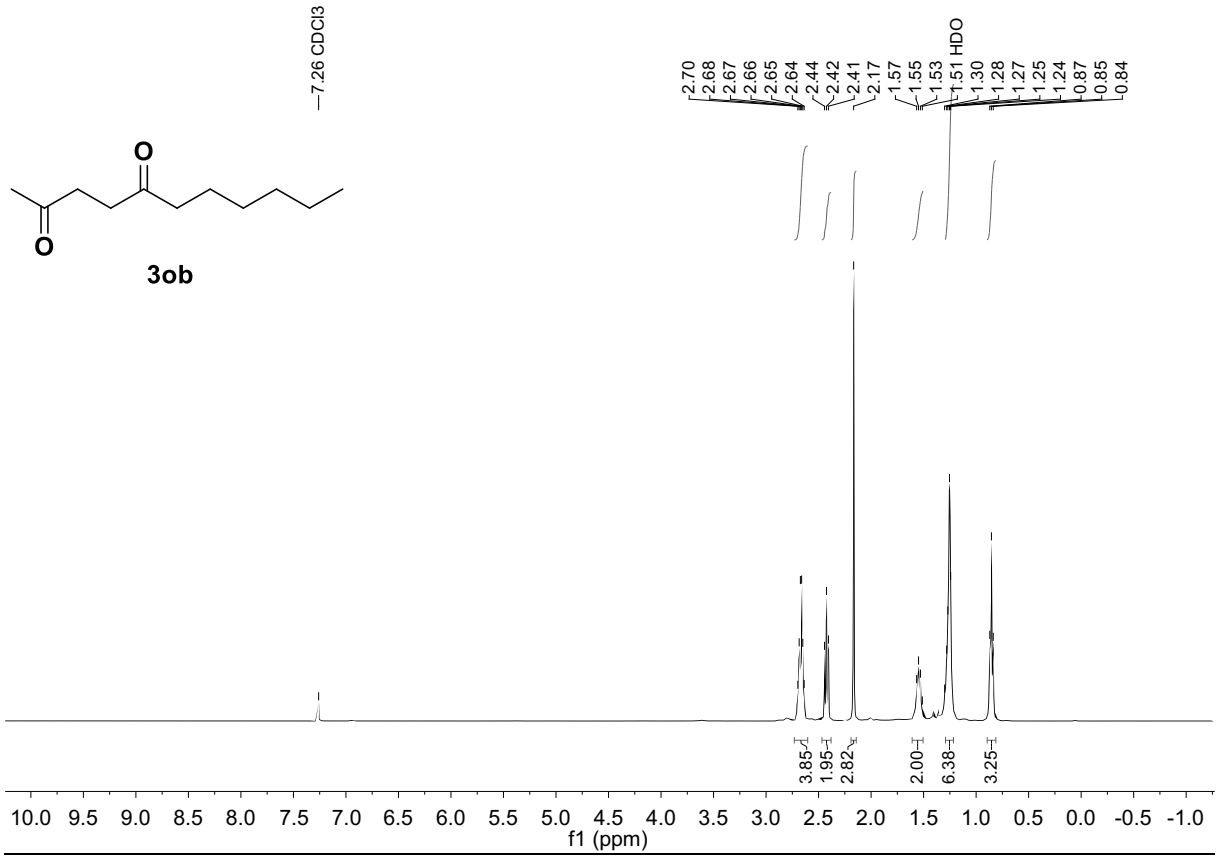
According to GP-E, the product **3ob** was synthesized using hexyl manganese bromide lithium chloride complex (0.25 M, 4.8 mL, 1.2 mmol, 1.2 equiv.) and *S*-ethyl 4-oxopentanethioate **1o** (160 mg, 1.00 mmol). Purification was achieved by bulb-to-bulb distillation (155 °C, 5 mbar). The product was obtained as a colorless oil which solidified after exposure to sonification (164 mg, 890 µmol, 89%). The spectral data is in good accordance to previous literature.[29]

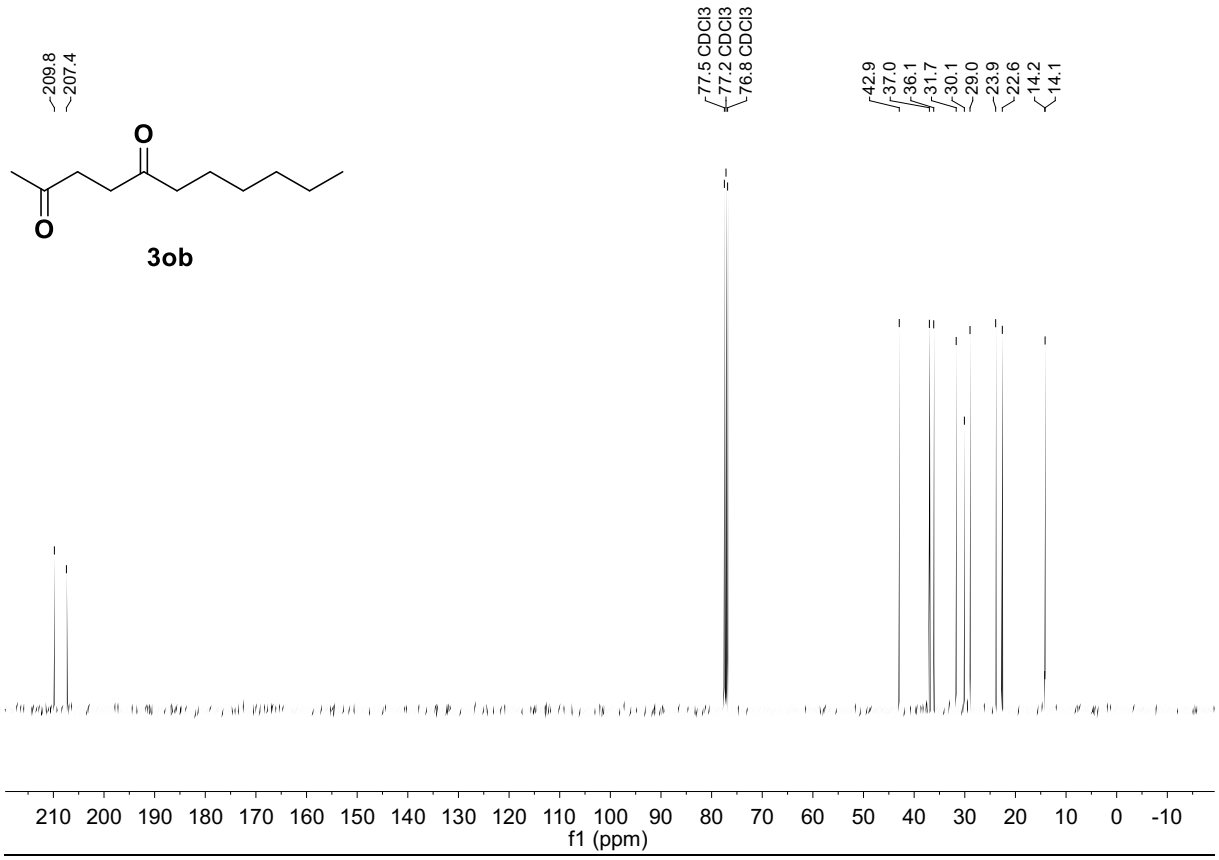
$C_{11}H_{20}O_2$ (184.28 g/mol)

R_f: 0.27 (*n*Hex/EA = 9:1 v/v) [anis]

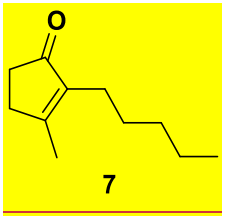
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.70 – 2.64 (m, 4H), 2.42 (t, *J* = 7.4 Hz, 2H), 2.17 (s, 3H), 1.61 – 1.51 (m, 2H), 1.30 – 1.18 (m, 6H), 0.85 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 209.8 (*C*O), 207.4 (*C*O), 42.4, 37.0, 36.1, 31.7, 30.1, 29.0, 23.9, 22.6, 14.2, 14.1.


7.26 CDCl3
2.70
2.68
2.67
2.66
2.65
2.64
2.44
2.42
2.41
2.17
1.57
1.55
1.53
1.51 HDO
1.30
1.28
1.27
1.25
1.24
0.87
0.85
0.84
O
O
3ob
3.85
1.95
2.82
2.00
6.38
3.25
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


209.8
207.4
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
42.9
37.0
36.1
31.7
30.1
29.0
23.9
22.6
14.2
14.1
O
O
3ob
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

dihydrojasmone (**7**)



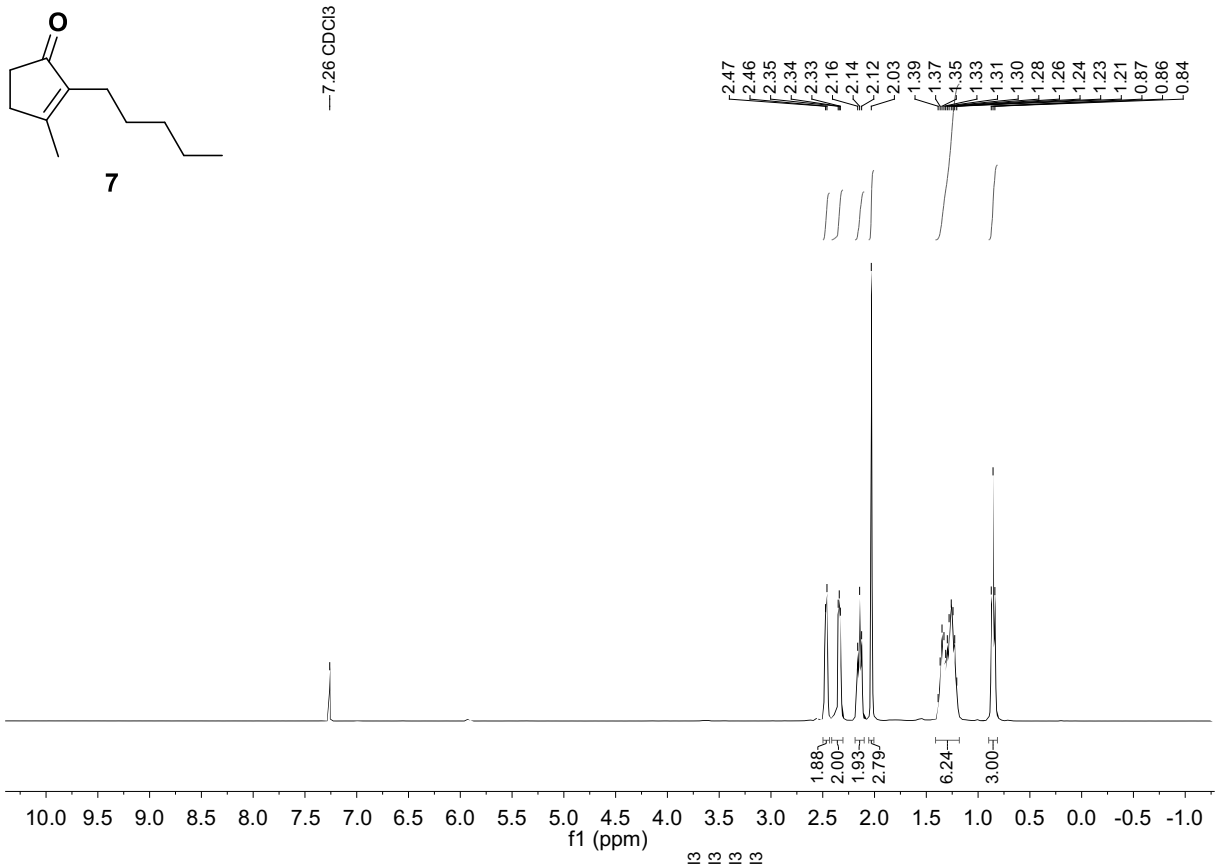
The compound **3ob** (151 mg, 819 µmol) was dissolved in ethanol (10 mL) and an aq. NaOH solution (2 mL, 10% w/v) was added. The reaction stirred under reflux for 3 h. Afterwards, the reaction was allowed to cool, the crude solution diluted with brine (5 mL) and was extracted with EA (4 × 10 mL). The combined organic layeres were dried over anhydrous $MgSO_4$ and solvent reduced *in vacuo*. The compound was yielded by bulb-to-bulb distillation (120 °C, 10 mbar) as a colorless oil with a distinct smell of jasmine flowers (70 mg, 421 µmol, 51%). The spectral data is in good accordance to previous literature.[30]

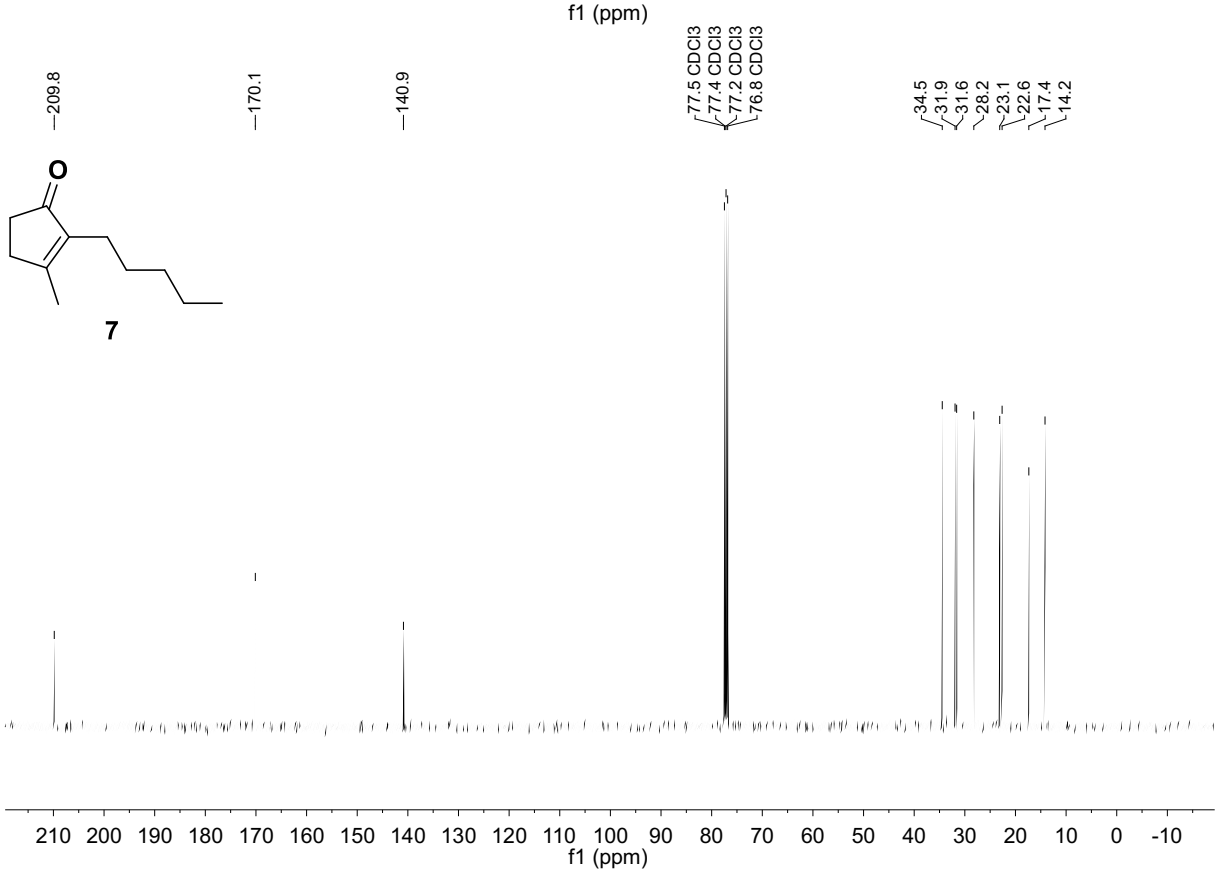
$C_{11}H_{18}O$ (166.26 g/mol)

R_f: 0.16 (PE/EA = 97:3 v/v) [anis]

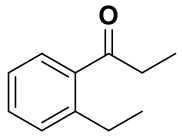
^{1}H NMR (400 MHz, $CDCl_3$): δ = δ 2.51 – 2.43 (m, 2H), 2.42 – 2.30 (m, 2H), 2.14 (t, *J* = 7.6 Hz, 2H), 2.03 (s, 3H, CC*H*$_3$), 1.41 – 1.16 (m, 6H), 0.86 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 209.8 (*C*O), 170.1 (C_{alkene}), 140.9 (C_{alkene}), 34.5, 31.9, 31.6, 28.2, 23.1, 22.6, 17.4, 14.2.


O
7
7.26 CDCl3
2.47
2.46
2.35
2.34
2.33
2.16
2.14
2.12
2.03
1.39
1.37
1.35
1.33
1.31
1.30
1.28
1.26
1.24
1.23
1.21
0.87
0.86
0.84
1.88
2.00
1.93
2.79
6.24
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


209.8
170.1
140.9
77.5 CDCl3
77.4 CDCl3
77.2 CDCl3
76.8 CDCl3
34.5
31.9
31.6
28.2
23.1
22.6
17.4
14.2
O
7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1-(2-ethylphenyl)propan-1-one (**9**)



9

According to GP-E, product **9** was synthesized using ethyl manganese bromide lithium chloride complex (0.20 M, 11.0 mL, 2.2 mmol, 2.2 equiv.) and *S*-ethyl 2-fluorobenzothioate **8** (184 mg, 1.00 mmol). Purification was achieved by column chromatography (*n*Hex/Et_2O = 98:2). The product was obtained as a colorless oil (110 mg, 678 µmol, 68%).

$C_{11}H_{14}O$ (162.23 g/mol)

R_f: 0.32 (*n*Hex/EA = 30:1 v/v) [anis]

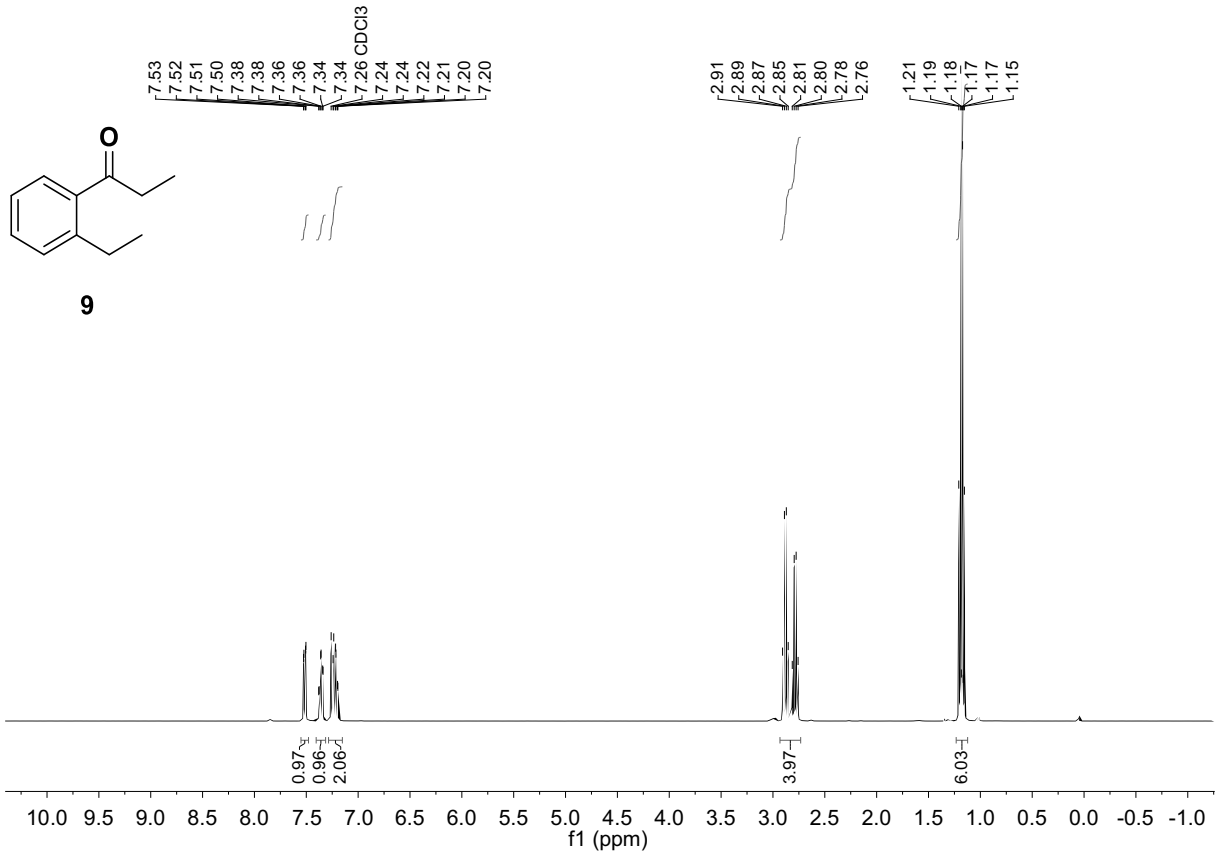
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (dd, *J* = 7.7, 1.3 Hz, 1H, Ar*H*), 7.40 – 7.31 (m, 1H, Ar*H*), 7.29 – 7.17 (m, 2H, Ar*H*), 2.93 – 2.73 (m, 4H), 1.23 – 1.12 (m, 6H).

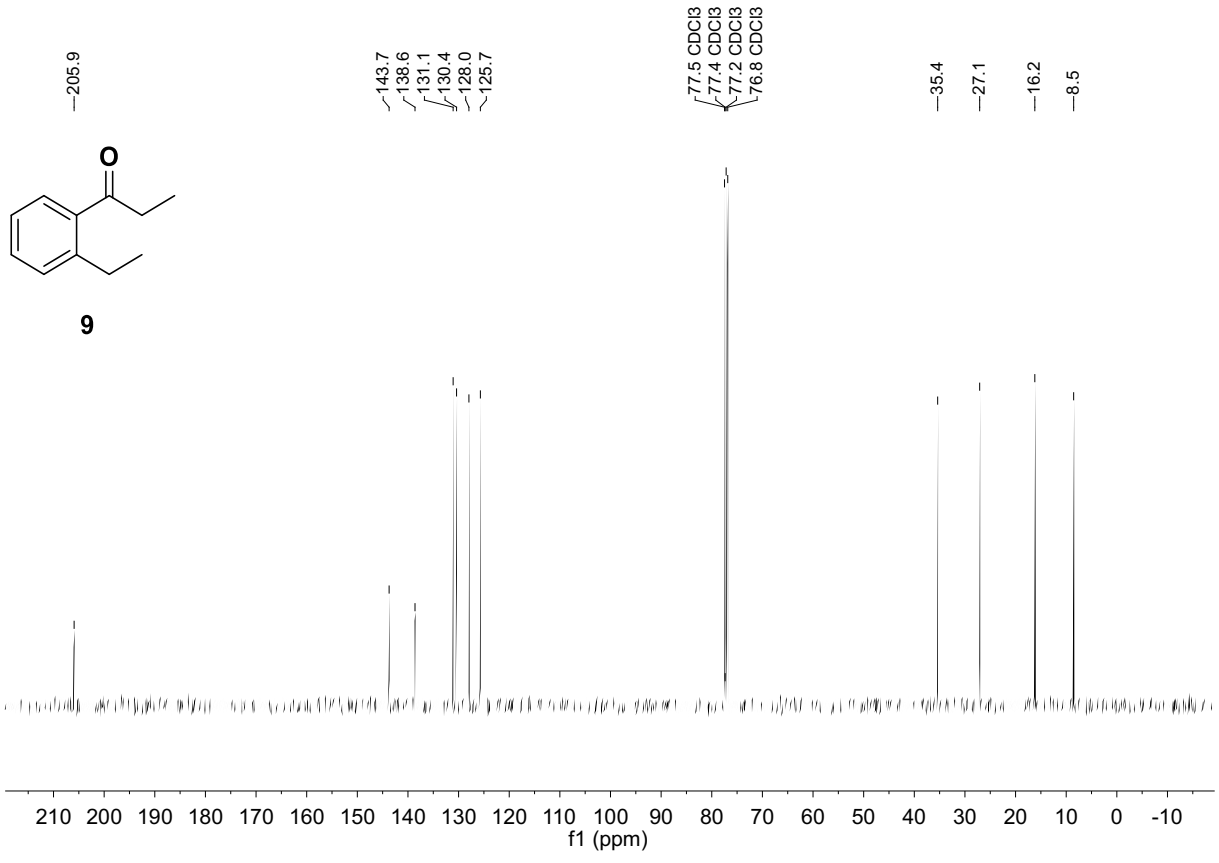
^{13}C NMR (101 MHz, $CDCl_3$): δ = 205.9 (*C*OEt), 143.7 (C_{Ar}), 138.6 (C_{Ar}), 131.1 (C_{Ar}), 130.4 (C_{Ar}), 128.0 (C_{Ar}), 125.7 (C_{Ar}), 35.4, 27.1, 16.2, 8.5.

GC-MS (EI): t_r = 14.43 min, m/z(%) = 162 (19, [$M^{+\bullet}$]), 133 (100, [$M^{+\bullet}$-$C_2H_5^{\bullet}$]), 105 (100, [$M^{+\bullet}$-$C_2H_5^{\bullet}$-CO]).

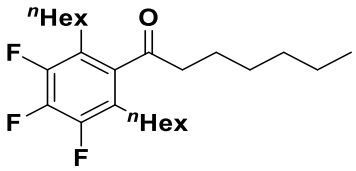
HR-MS (ESI): m/z calc. for $[M+Na]^+$ 185.09369, found 185.09362.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3066 (w, C-H_{arom}), 2973 (w, C-H_{aliph}), 2935 (w, C-H_{aliph}), 2876 (w, C-H_{aliph}), 1686 (vs, C=O), 1608 (m), 1575 (w), 1478 (m), 1451 (s), 1411 (w), 1348 (m), 1310 (w), 1269 (m), 1206 (s), 1150 (w), 1109 (w), 1070 (w), 1012 (w), 948 (s), 826 (w), 755 (vs).


7.53
7.52
7.51
7.50
7.38
7.38
7.36
7.36
7.34
7.34
7.26 CDCl3
7.24
7.24
7.22
7.21
7.20
7.20
2.91
2.89
2.87
2.85
2.81
2.80
2.78
2.76
1.21
1.19
1.18
1.17
1.17
1.15
O
9
0.97
0.96
2.06
3.97
6.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


205.9
143.7
138.6
131.1
130.4
128.0
125.7
77.5 CDCl3
77.4 CDCl3
77.2 CDCl3
76.8 CDCl3
35.4
27.1
16.2
8.5
O
9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1-(3,4,5-trifluoro-2,6-dihexylphenyl)heptan-1-one (**11**)



11

According to GP-E, the product **11** was synthesized using *n*-hexyl manganese chloride lithium chloride complex (5.9 mL, 0.27 M, 3.2 mmol, 3.2 equiv.) and *S*-ethyl 2,3,4,5,6-pentafluorobenzothioate **10** (128 mg, 500 µmol). Purification was achieved by flash column chromatography (23 g - 15 µm spherical SiO_2, pure *n*Hex, 2 CV). The product was obtained as a colorless oil (108 mg, 262 µmol, 52%).

$C_{25}H_{39}F_3O$ (412.58 g/mol)

R_f: 0.15 (*n*Hex) [UV]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.66 (t, *J* = 7.3 Hz, 2H, COCH_2), 2.45 – 2.36 (m, 4H), 1.76 – 1.64 (m, 2H), 1.54 – 1.44 (m, 4H), 1.43 – 1.19 (m, 18H), 0.94 – 0.84 (m, 9H, 3 × CH_3).

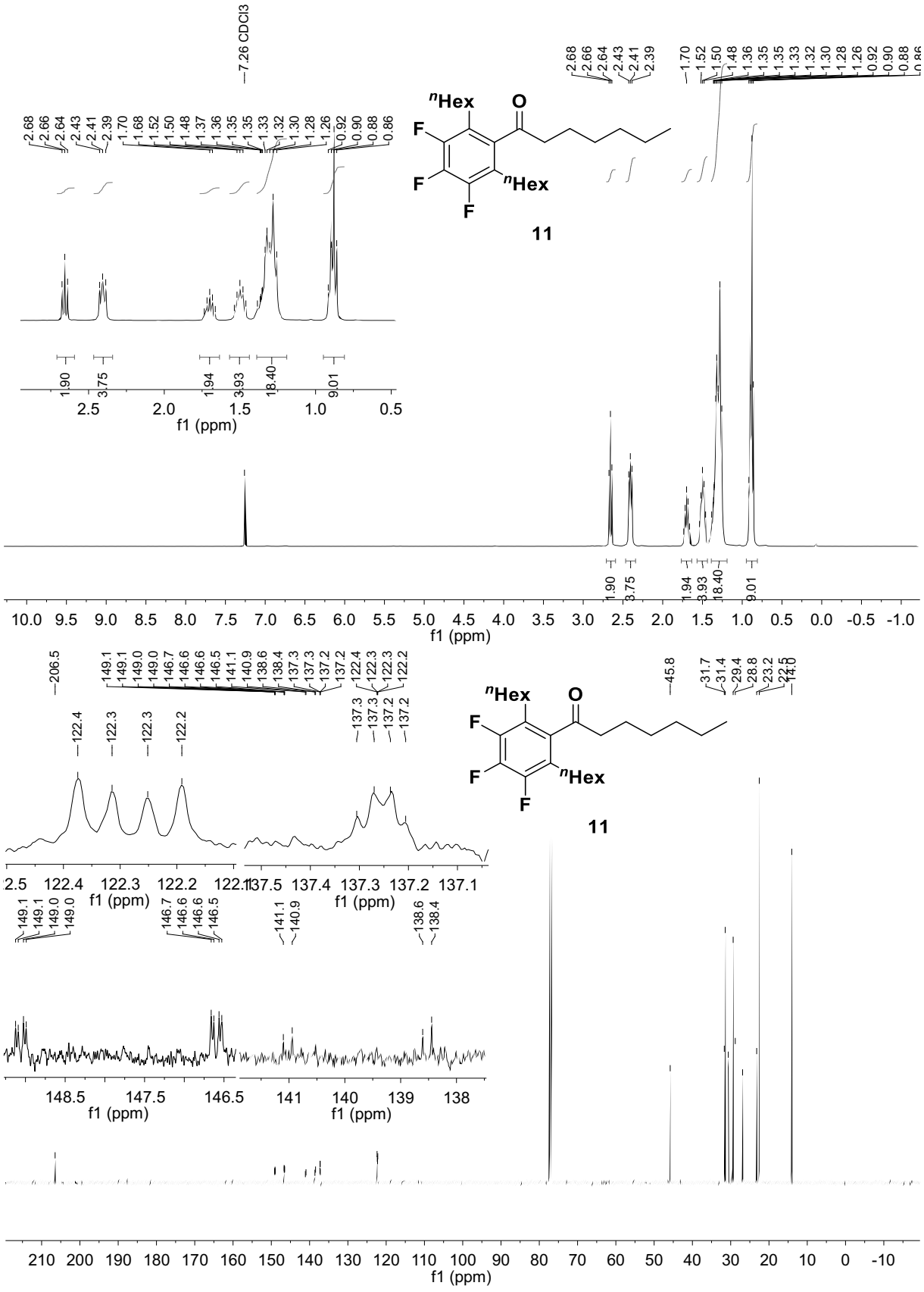
^{13}C NMR (101 MHz, $CDCl_3$): δ = 206.5 ,147.8 (ddd, *J* = 247.8, 10.0, 3.4 Hz), 139.8 (dd, *J* = 251.3, 16.1 Hz), 137.3 (dd, *J* = 3.4 Hz), 122.3 (dd, *J* = 12.4, 6.1 Hz), 45.8, 31.7, 31.4, 30.6, 29.4, 28.8, 26.9, 23.2, 22.5, 14.0.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -140.61 (d, J^3_{F-F} = 20.7 Hz), -160.24 (t, J^3_{F-F} = 20.7 Hz).

HR-MS (EI): m/z calc. for $[M]^+$ 412.294751, found 412.29544.

GC-MS (EI): t_r = 10.69 min, m/z(%) = 327 (100, $[M^{+\bullet}\text{-}C_6H_{13}^{\bullet}]$).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2954 (m, C-H_{aliph}), 2924 (s, C-H_{aliph}), 2858 (m, C-H_{aliph}), 1705 (m, C=O), 1616 (w), 1489 (m), 1456 (s), 1404 (w), 1359 (m), 1180 (w), 1124 (m), 1090 (m), 1045 (w), 1001 (w), 971 (w), 926 (w), 889 (w), 848 (w), 822 (w), 759 (w), 725 (w), 684 (w), 665 (w).


7.26 CDCl3
nHex
O
F
F
F
nHex
11
f1 (ppm)
206.5
149.1
149.0
146.7
146.6
146.5
141.1
140.9
138.6
138.4
137.3
137.2
122.4
122.3
122.2
45.8
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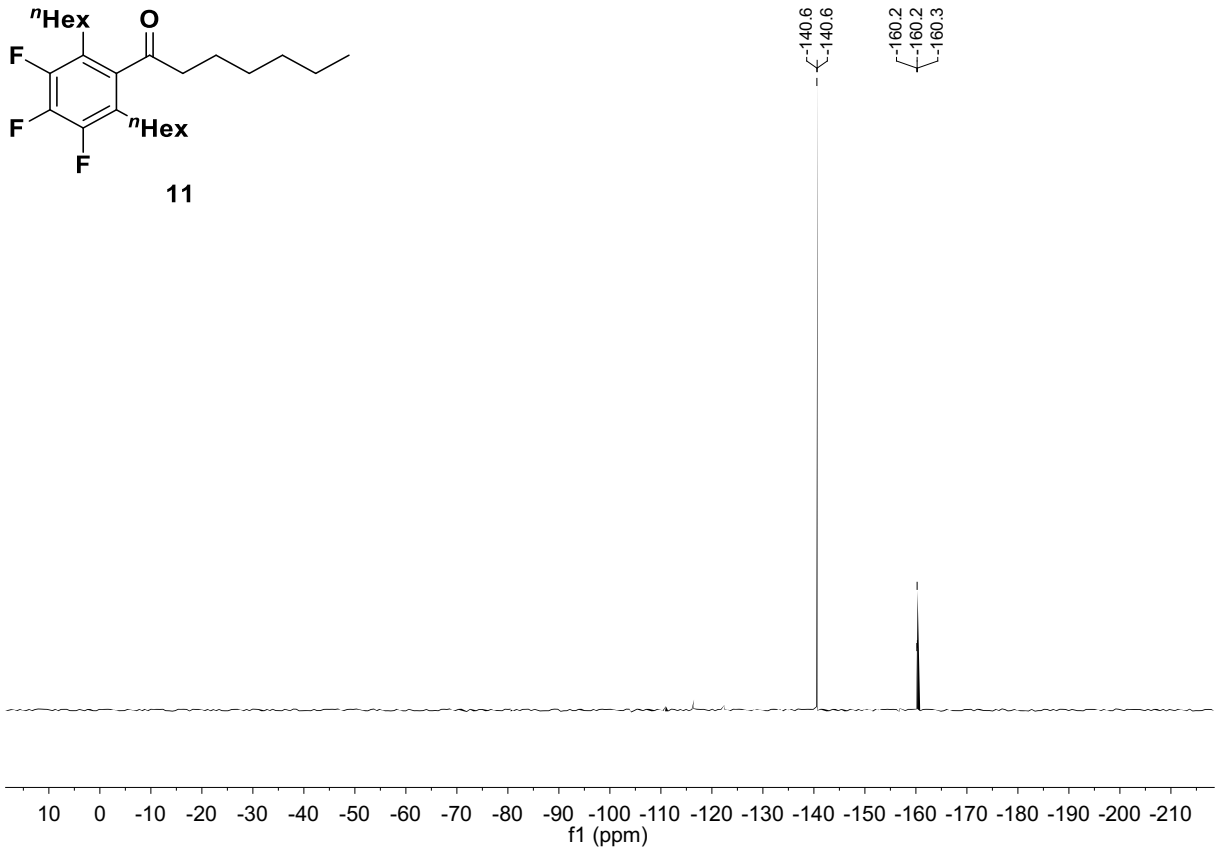
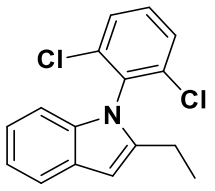
31.4
29.4
28.8
23.2
22.5
14.0


nHex
O
F
F
F
nHex
11
-140.6
-140.6
-160.2
-160.2
-160.3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

1-(2,6-dichlorophenyl)-2-ethyl-1H-indole (**13**)



13

According to GP-E, the product **13** was synthesized using ethyl manganese bromide lithium chloride complex (0.25 M, 4.80 mL, 1.2 mmol, 1.2 equiv.) and *S*-ethyl 2-(2-((2,6-dichlorophenyl)amino)phenyl)ethanethioate **12** (170 mg, 500 µmol). Purification was achieved by column chromatography (*n*Hex/EA = 9:1 v/v). The product was obtained as a brown oil (87.9 mg, 303 µmol, 61%).

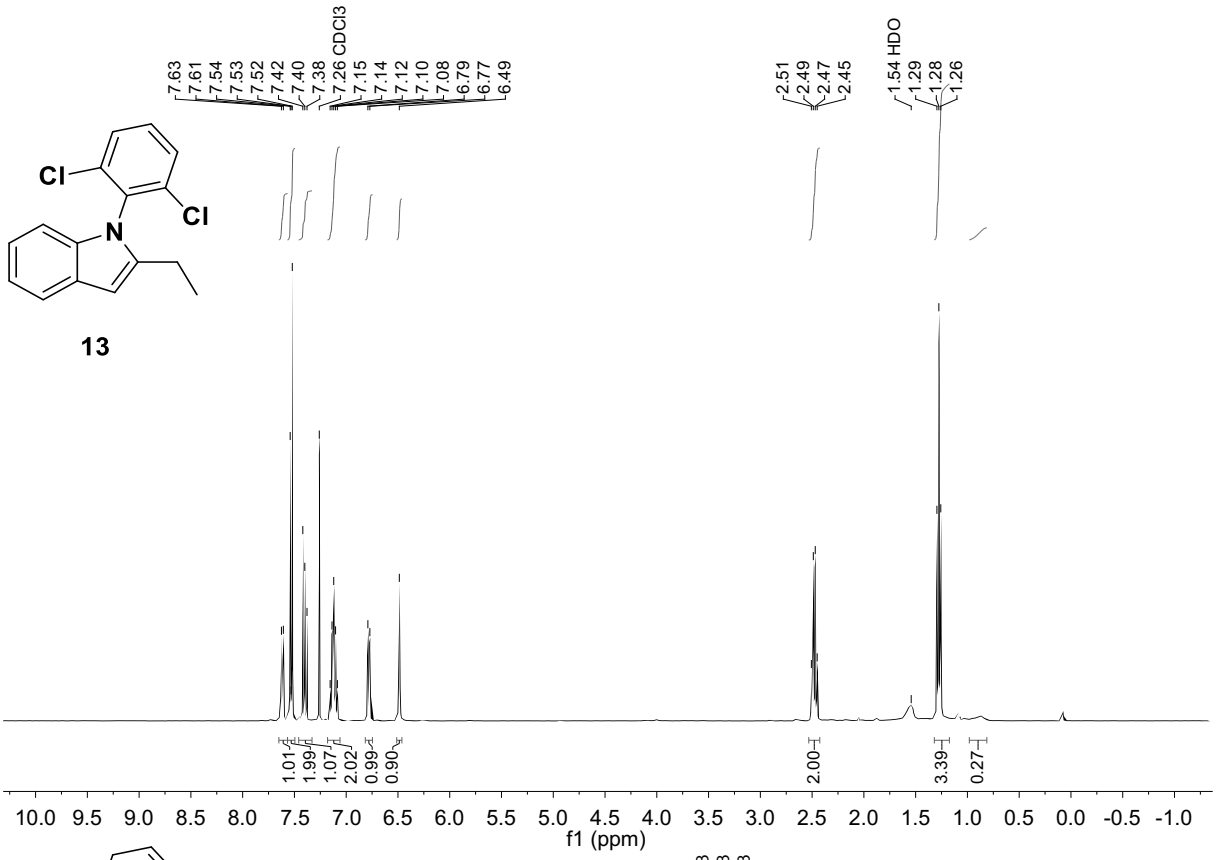
$C_{16}H_{13}Cl_2N$ (290.19 g/mol)

R_f: 0.67 (*n*Hex/EA = 9:1) [UV]

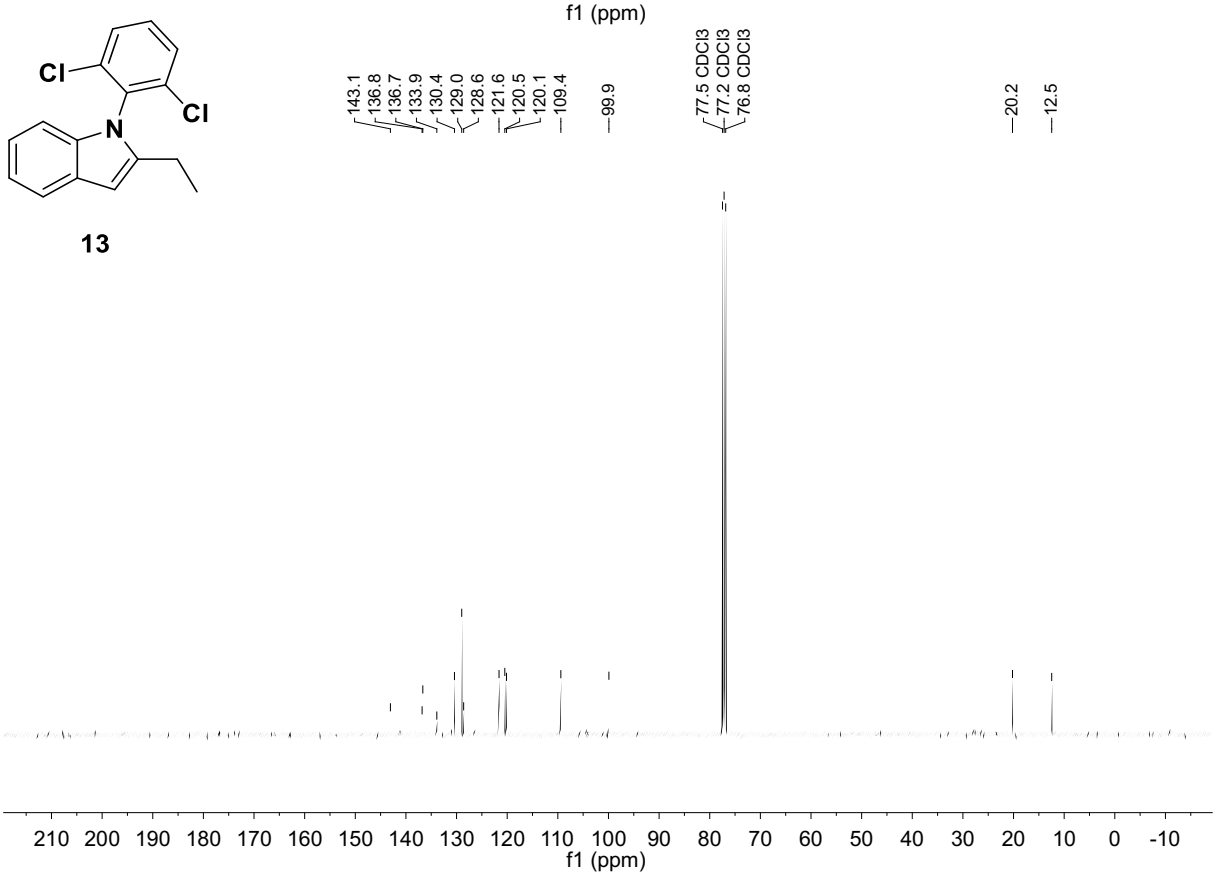
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 – 7.56 (m, 1H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.40 (dd, *J* = 8.7, 7.5 Hz, 1H), 7.18 – 7.03 (m, 2H), 6.78 (d, *J* = 7.4 Hz, 1H), 6.49 (d, *J* = 1.8 Hz, 1H), 2.48 (q, *J* = 7.5 Hz, 2H, CH_2CH_3), 1.28 (t, *J* = 7.5 Hz, 3H, CH_2CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.1, 136.8, 136.7, 133.9, 130.4, 129.0, 128.6, 121.6, 120.5, 120.1, 109.4, 99.9, 20.2, 12.5.

HR-MS (ESI): m/z calc. for $[M+Na]^+$ 312.03173, found 312.03181.

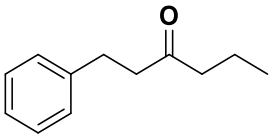

7.63
7.61
7.54
7.53
7.52
7.42
7.40
7.38
7.26 CDCl3
7.15
7.14
7.12
7.10
7.08
6.79
6.77
6.49
2.51
2.49
2.47
2.45
1.54 HDO
1.29
1.28
1.26
Cl
Cl
N
1.01
1.99
1.07
2.02
0.99
0.90
2.00
3.39
0.27
f1 (ppm)

13


143.1
136.8
136.7
133.9
130.4
129.0
128.6
121.6
120.5
120.1
109.4
99.9
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
20.2
12.5
Cl
Cl
N
f1 (ppm)

13

1-phenyl-hexan-3-one (**3bc**)



3bc

According to GP-F, the product **3bc** was synthesized using propyl manganese bromide lithium chloride complex (0.21 M, 5.7 mL, 1.2 mmol, 1.2 equiv.) and *S*-ethyl 3-phenylpropanethioate **1b** (194 mg, 1.00 mmol). Purification was achieved by column chromatography (*n*Hex/EA = 30:1 v/v). The product was obtained as a colorless oil with a sweet pleasant smell (149.5 mg, 848 µmol, 85%). The data is in good accordance to reported literature.[16]

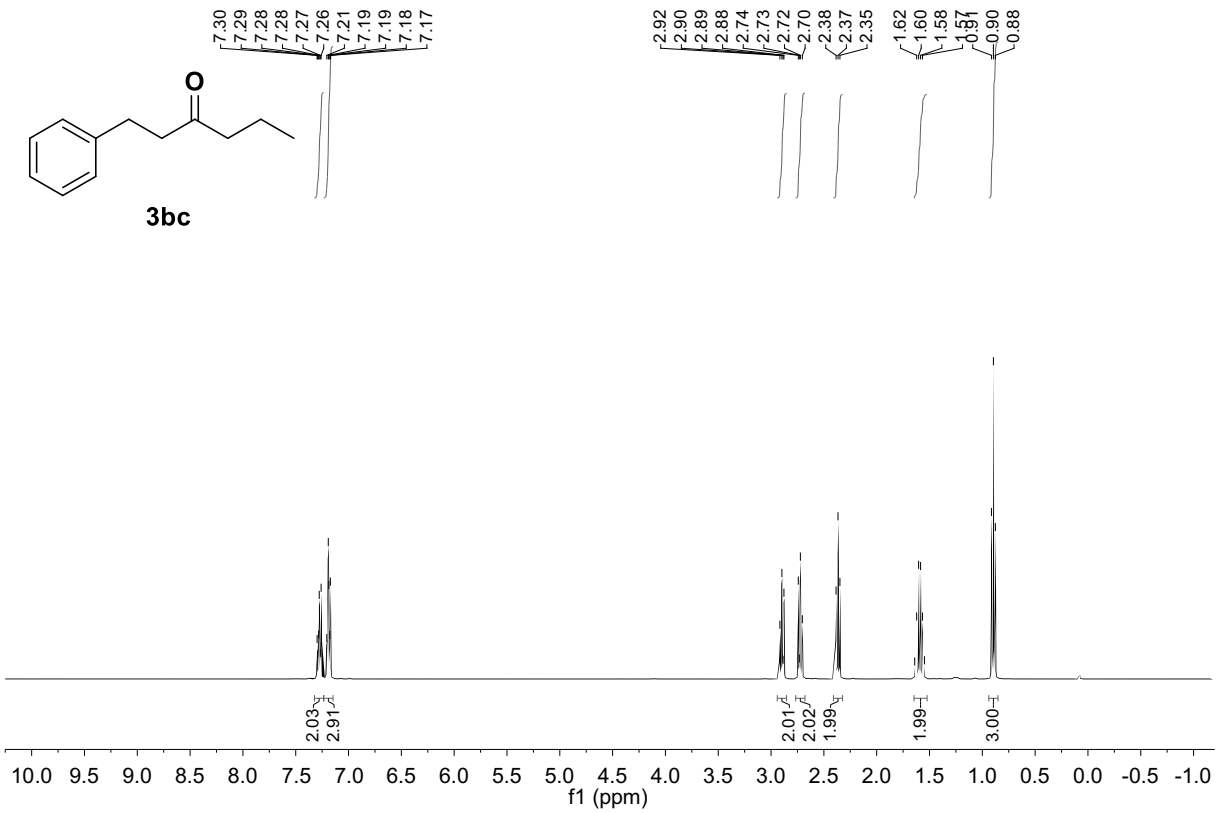
$C_{12}H_{16}O$ (176.26 g/mol)

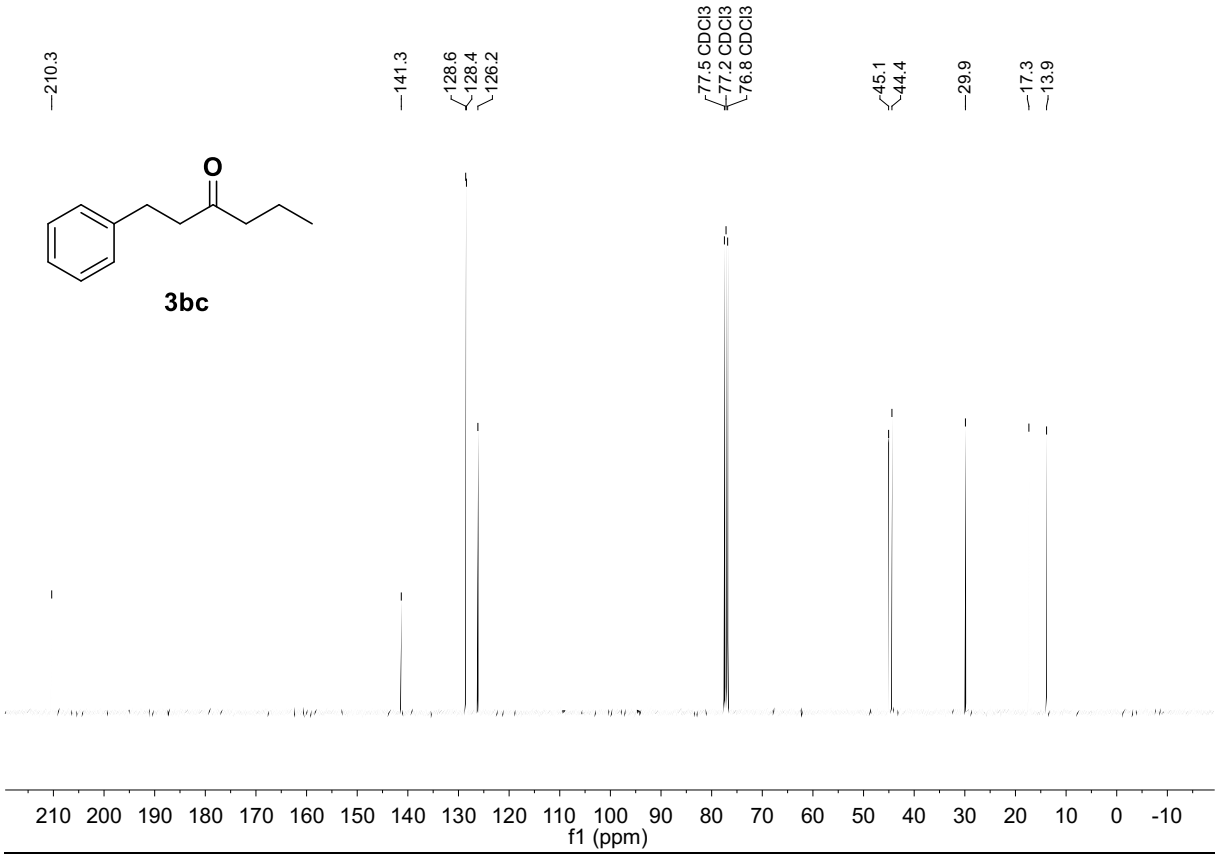
R_f: 0.24 (*n*Hex/EA = 30:1) [$KMnO_4$]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 – 7.25 (m, 2H, Ar*H*), 7.21 – 7.17 (m, 3H, Ar*H*), 2.90 (t, *J* = 7.7 Hz, 2H, $COCH_2CH_2Ph$), 2.72 (t, *J* = 7.7 Hz, 2H, $COCH_2CH_2Ph$), 2.37 (t, *J* = 7.3 Hz, 2H, $COCH_2CH_2CH_3$), 1.59 (h, *J* = 7.4 Hz, 2H, CH_2CH_3), 0.90 (t, *J* = 7.4 Hz, 3H, CH_2CH_3).

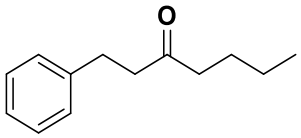
^{13}C NMR (101 MHz, $CDCl_3$): δ = 210.3 (*C*O), 141.3 (C_{Ar}), 128.6 (C_{Ar}), 128.4 (C_{Ar}), 126.2 (C_{Ar}), 45.1, 44.4, 29.9, 17.35, 13.9 (CH_3).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3062 (w, C-H_{arom}), 3025 (w, C-H_{arom}), 2958 (m, C-H_{aliph}), 2932 (w, C-H_{aliph}), 2875 (w, C-H_{aliph}), 1709 (s, C=O), 1601 (w), 1493 (w), 1452 (m), 1407 (w), 1369 (m), 1288 (w), 1275 (w), 1161 (w), 1124 (w), 1063 (w), 1031 (w), 1001 (w), 900 (w), 747 (s), 699 (s).


7.30
7.29
7.28
7.28
7.27
7.26
7.21
7.19
7.19
7.18
7.17
2.92
2.90
2.89
2.88
2.74
2.73
2.72
2.70
2.38
2.37
2.35
1.62
1.60
1.58
1.57
0.91
0.90
0.88
O
3bc
2.03
2.91
2.01
2.02
1.99
1.99
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


210.3
141.3
128.6
128.4
126.2
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
45.1
44.4
29.9
17.3
13.9
O
3bc
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1-phenylheptan-3-one (**3bd**)



3bd

The organomanganese reagent was synthesized by diluting $MnCl_2$·LiCl solution (3.6 mL, 1M in THF, 1.2 equiv.) with THF (7 mL) and slowly adding *n*butyllithium solution (1.2 mL, 3.0 mmol, 2.5 M in hexanes) at -79°C.[1] The solution was stirred for 1.5 h while warming up to -20 °C. Similar to GP-F, the product **3bd** was synthesized using the prepared *n*butylmanganese chloride lithium chloride complex (6 mL, 1.2 mmol, 0.2 M, 2 equiv.) and *S*-ethyl 3-phenylpropanethioate **1b** (194 mg, 1.00 mmol). Purification was achieved by column chromatography (*n*Hex/Et_2O = 99:1 v/v). The product was obtained as a colorless oil with a sweet smell (175 mg, 920 µmol, 92%). Analytical data is in good accordance to reported literature.[31]

$C_{13}H_{18}O$ (190.26 g/mol)

R_f: 0.26 (*n*Hex/Et_2O = 99:1 v/v) [UV]

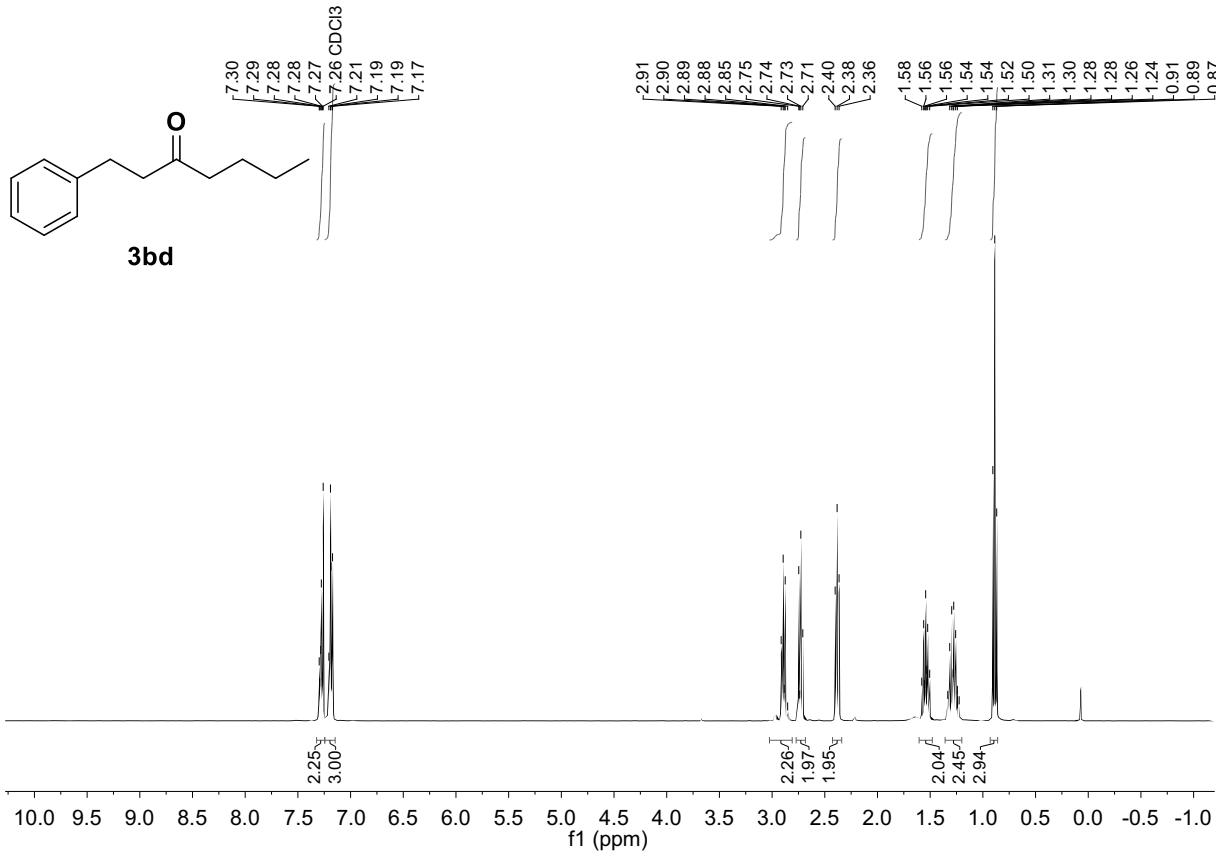
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.27 (m, 2H, ArH), 7.20–7.17 (m, 3H, ArH), 2.90 (t, *J* = 7.4 Hz, 2H), 2.73 (t, *J* = 7.4 Hz, 2H), 2.38 (t, *J* = 7.4 Hz, 2H), 1.62 – 1.47 (m, 2H), 1.35 – 1.20 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H).

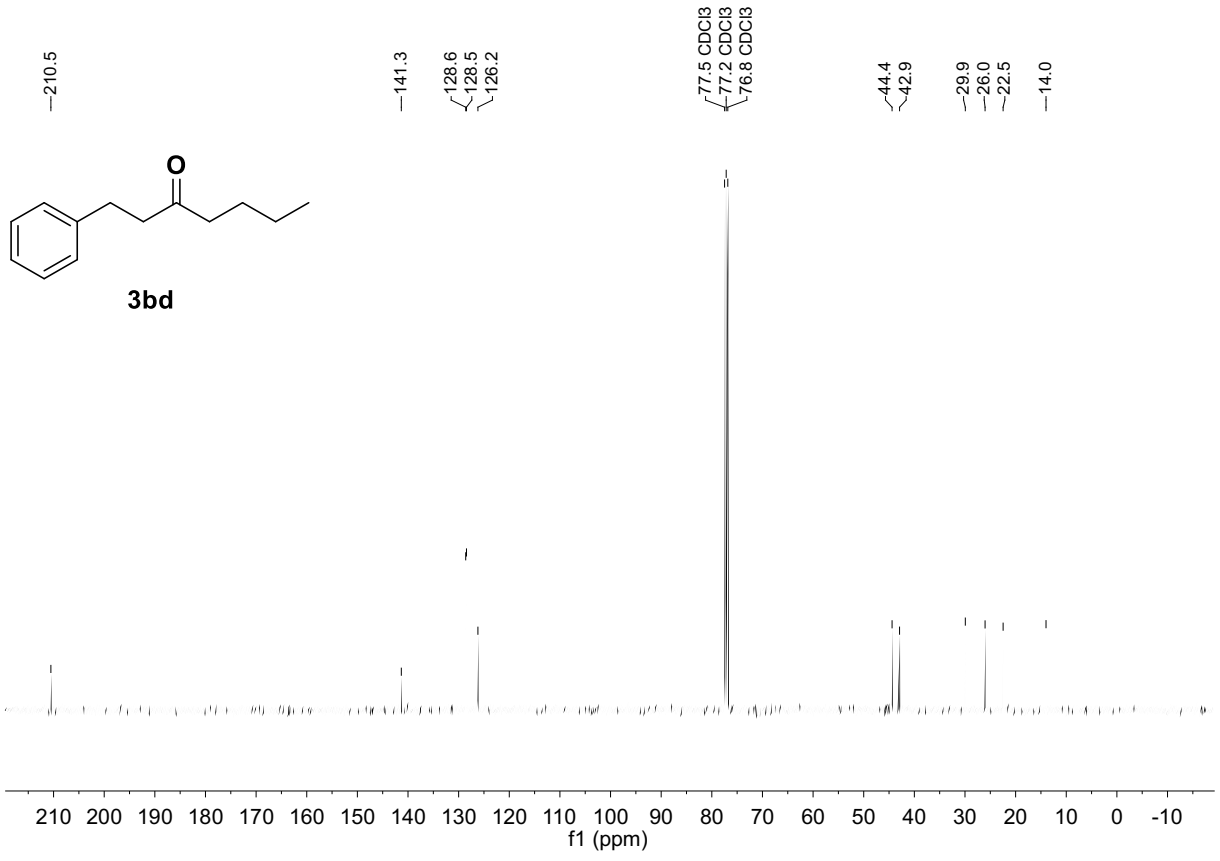
^{13}C NMR (101 MHz, $CDCl_3$): δ = 210.5 (*C*O), 141.3, 128.6, 128.4, 126.2, 44.4, 42.9, 29.9, 26.0, 22.5, 14.0 (*C*H_3).

GC-MS (EI): t_r = 6.59 min, m/z = 190 (9, [$M^{+\bullet}$]), 148 (16, [$M^{+\bullet}$-C_3H_6]), 105 (74, [$M^{+\bullet}$-C_3H_6 -CO]), 91 (100, [$Bn^{+\bullet}$]).

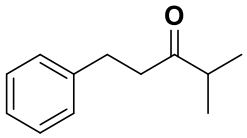
IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3062 (w, C-H_{arom}), 3025 (w, C-H_{arom}), 2954 (m, C-H_{aliph}), 2928 (m, C-H_{aliph}), 2868 (w, C-H_{aliph}), 1709 (s, C=O), 1601 (w), 1493 (w), 1452 (m), 1407 (w), 1369 (m), 1262 (w), 1202 (w), 1161 (w), 1124 (w), 1063 (w), 1031 (w), 971 (w), 911 (w), 744 (s), 699 (s).

[1] The concentration of this reagent could not be determined as the color change for iodometric titration was observed to be much slower in absence of Mg-cations. The hydrolysis of the reagent therefore prohibits accurate determination of the concentration


7.30
7.29
7.28
7.28
7.27
7.26 CDCl3
7.21
7.19
7.19
7.17
2.91
2.90
2.89
2.88
2.85
2.75
2.74
2.73
2.71
2.40
2.38
2.36
1.58
1.56
1.56
1.54
1.54
1.52
1.50
1.31
1.30
1.28
1.28
1.26
1.24
0.91
0.89
O
3bd
2.25
3.00
2.26
1.97
1.95
2.04
2.45
2.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


210.5
141.3
128.6
128.5
126.2
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
44.4
42.9
29.9
26.0
22.5
14.0
O
3bd
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

4-methyl-1-phenylpentan-3-one (**3be**)



3be

According to GP-F, the product **3be** was synthesized using *iso*-propyl manganese bromide lithium chloride complex (4.1 mL, 0.29 M, 1.2 mmol, 1.2 equiv.) and *S*-ethyl 3-phenylpropanethioate **1b** (194 mg, 1.00 mmol). Purification was achieved by column chromatography (*n*Hex/EA = 95:5 v/v). The product was obtained as a colorless oil with a sweet smell (158 mg, 896 µmol, 90%). The analytical data is in good accordance with the reported literature.[21]

$C_{12}H_{16}O$ (176.26 g/mol)

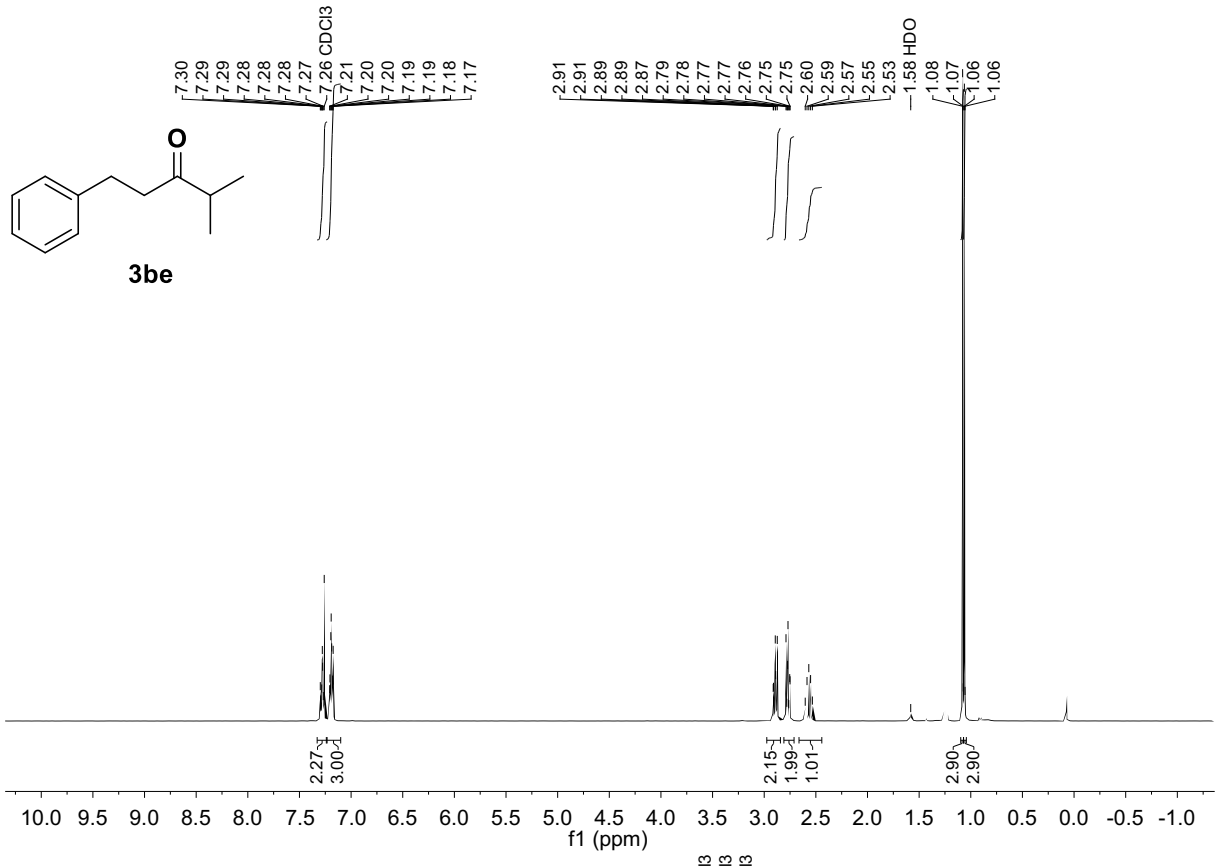
R_f: 0.33 (*n*Hex/Et_2O = 95:5 v/v) [UV]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.26 (m, 2H, Ar*H*), 7.20–7.17 (m, 3H, Ar*H*), 2.89 (t, *J* = 7.8, 2H), 2.79–2.75 (m, 2H), 2.62–2.52 (hept, *J* = 6.9 Hz, 1H), 1.08–1.06 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 213.9 (*C*O), 141.5 (C_{Ar}), 128.6 (C_{Ar}), 128.5 (C_{Ar}), 126.2 (C_{Ar}), 42.1, 41.2, 30.0, 18.3 (CH_3).

GC-MS (EI): t_r = 5.67 min, m/z(%) = 176 (19, $[M^{+\bullet}]$), 133 (40, $[M^{+\bullet}\text{-}C_3H_7^{\bullet}]$), 105 (100, $[M^{+\bullet}\text{-}C_3H_7^{\bullet}\text{-CO}]$), 91 (97, $[Bn^{+\bullet}]$).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3062 (w, C-H_{arom}), 3025 (w, C-H_{arom}), 2966 (m, C-H_{aliph}), 2928 (w, C-H_{aliph}), 2875 (w, C-H_{aliph}), 1709 (s, C=O), 1601 (w), 1493 (w), 1456 (m), 1407 (w), 1362 (w), 1284 (w), 1262 (w), 1183 (w), 1066 (m), 1031 (w), 997 (w), 964 (w), 926 (w), 747 (s), 699 (s).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2.60
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2.55
2.53
1.58 HDO
1.08
1.07
1.06
1.06
O
3be
2.27
3.00
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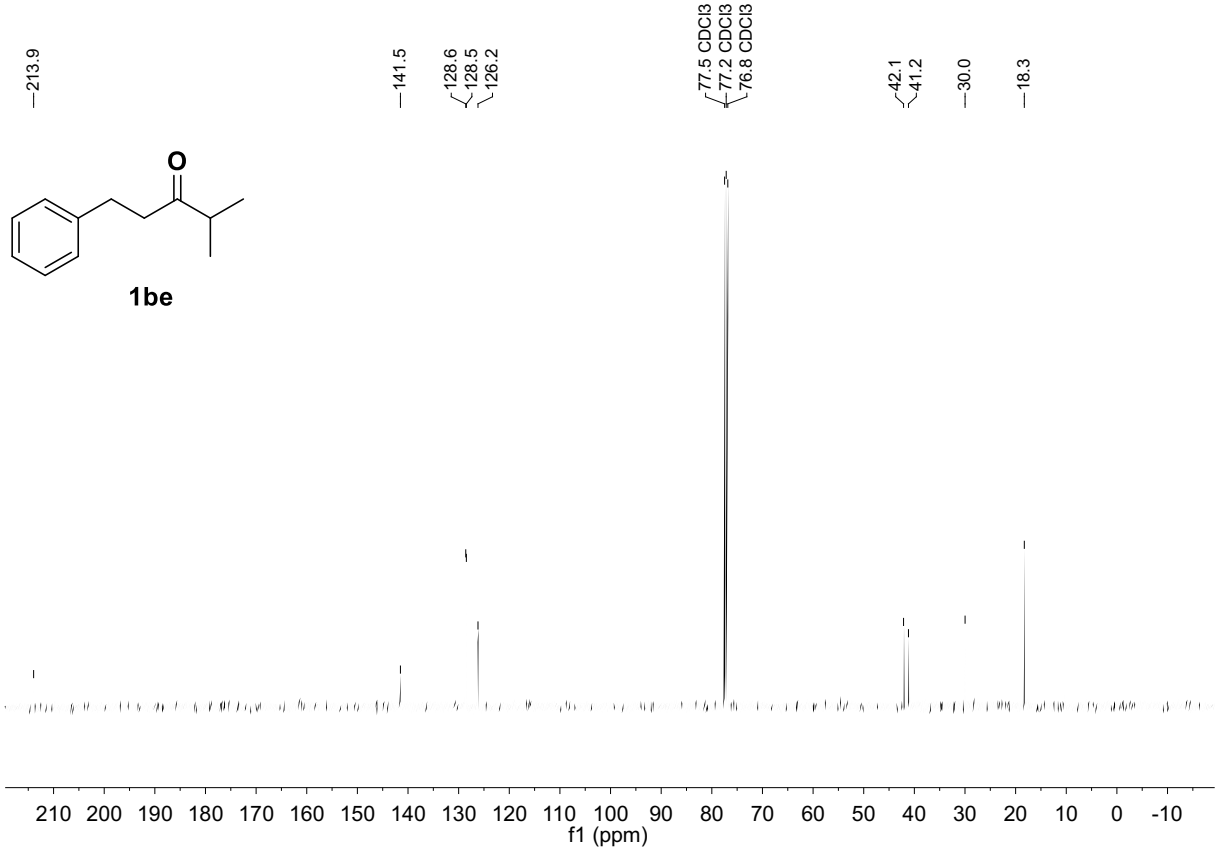
1.99
1.01
2.90
2.90
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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128.5
126.2
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76.8 CDCl3
42.1
41.2
30.0
18.3
O
1be
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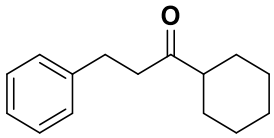
f1 (ppm)

1-cyclohexyl-3-phenylpropan-1-one (**3bf**)



3bf

According to GP-F, the product **3bf** was synthesized using cyclohexylmanganese bromide lithium chloride complex (3.8 mL, 0.32 M, 1.2 mmol, 1.2 equiv.) and *S*-ethyl 3-phenylpropanethioate **1b** (194 mg, 1.00 mmol). Purification was achieved by column chromatography (PE/EA = 30:1 v/v). The product was obtained as a colorless oil (188 mg, 896 µmol, 87%). The analytical data is in good accordance with the reported literature.[32]

$C_{15}H_{20}O$ (216.32 g/mol)

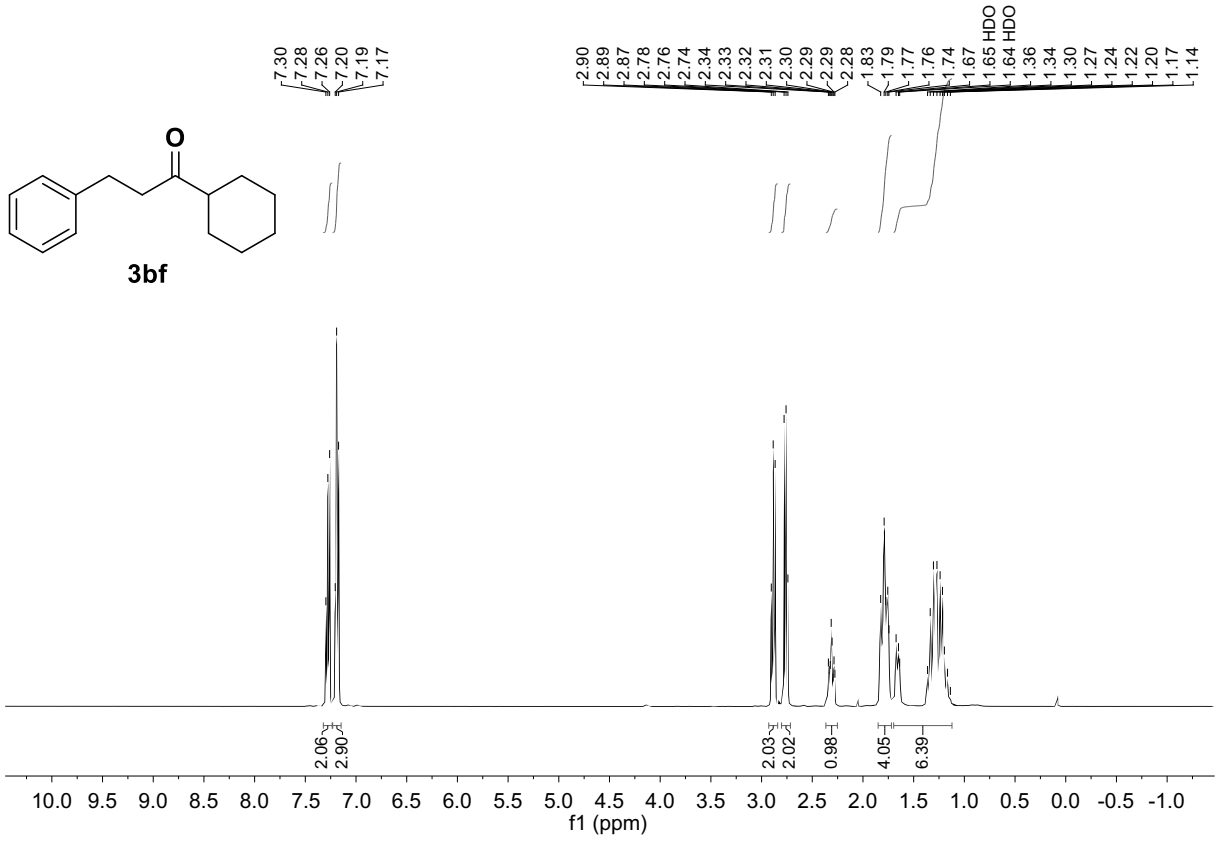
R_f: 0.14 (PE/EA = 30:1 v/v) [UV]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 – 7.24 (m, 2H, Ar*H*), 7.23 – 7.14 (m, 3H, Ar*H*), 2.89 (t, *J* = 7.8 Hz, 2H, $COCH_2CH_2Ph$), 2.76 (t, *J* = 7.8 Hz, 2H, $COCH_2CH_2Ph$), 2.31 (tt, *J* = 11.1, 3.4 Hz, 1H, COC*H*), 1.83 – 1.74 (m, 4H, Cy*H*), 1.67 – 1.14 (m, 6H, Cy*H*).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 213.3 (CO), 141.6 (C_{Ar}), 128.7 (C_{Ar}), 128.5 (C_{Ar}), 126.1 (C_{Ar}), 51.1, 42.4, 29.9, 28.5, 25.6, 25.8.

GC-MS (EI): t_r = 8.09, m/z(%) = 216 (27, [$M^{+\bullet}$]), 133 (41, [$M^{+\bullet}$-$C_6H_{11}^{\bullet}$]), 111 (23, [$M^{+\bullet}$-$C_8H_9^{\bullet}$]), 105 (74, [$M^{+\bullet}$-$C_6H_{11}^{\bullet}$-CO]), 91 (100, [$Bz^{+\bullet}$]), 83 (100, [$Cy^{+\bullet}$]).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3059 (w, C-H_{arom}), 3025 (w, C-H_{arom}), 2924 (s, C-H_{aliph}), 2853 (m, , C-H_{aliph}), 1705 (s, C=O), 1601 (w), 1493 (w), 1448 (m), 1407 (w), 1370 (w), 1319 (w), 1314 (w), 1297 (w), 1262 (w), 1187 (w), 1142 (w), 1083 (w), 1027 (w), 989 (m), 889 (w), 744 (m), 699 (s).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1.76
1.74
1.67
1.65 HDO
1.64 HDO
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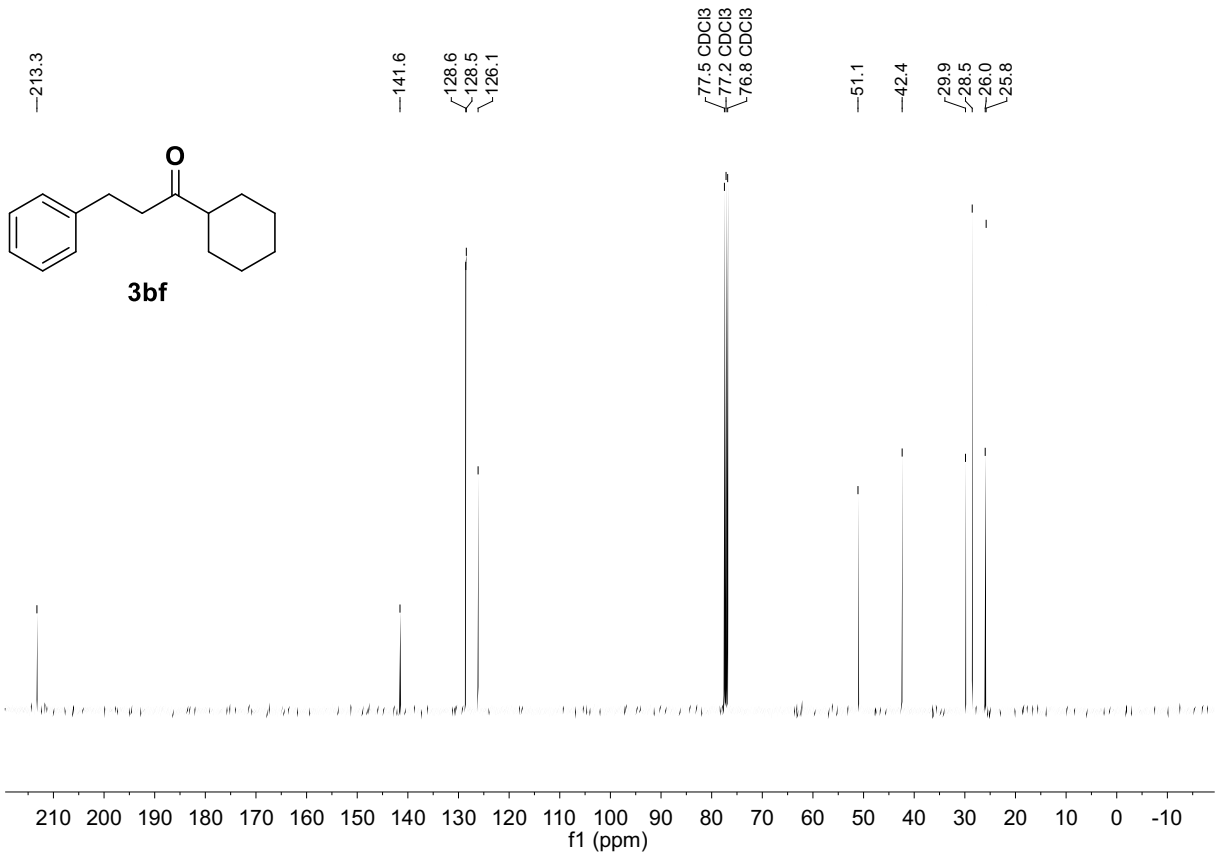
1.34
1.30
1.27
1.24
1.22
1.20
1.17
1.14
O
3bf
2.06
2.90
2.03
2.02
0.98
4.05
6.39
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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128.5
126.1
77.5 CDCl3
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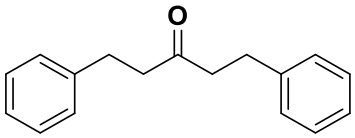
51.1
42.4
29.9
28.5
26.0
25.8
O
3bf
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1,5-diphenylpentan-3-one (**3bg**)



3bg

According to GP-F, the product **3bg** was synthesized using 2-phenylethylmanganese bromide lithium chloride complex (5.7 mL, 0.21 M, 1.2 mmol, 1.2 equiv.) and *S*-ethyl 3-phenylpropanethioate **1b** (194 mg, 1.00 mmol). Purification was achieved by flash column chromatography (23 g SiO_2, gradient from pure *n*Hex to *n*Hex:Et_2O 90:10 v/v over 14 CV and hold for 3 CV). The product was obtained as a colorless oil with a sweet smell (148 mg, 621 µmol, 62%). The analytical data is in good accordance with the reported literature.[33]

$C_{17}H_{18}O$ (238.33 g/mol)

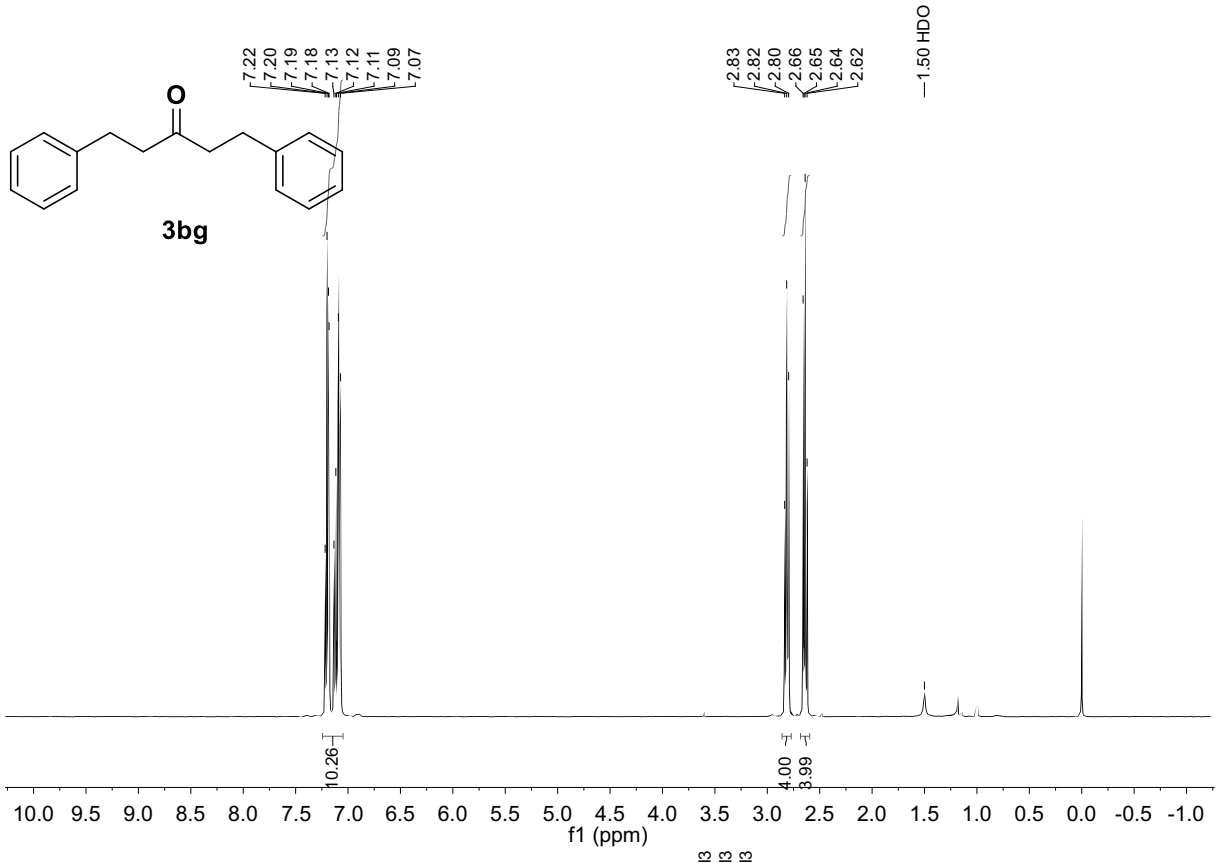
R_f: 0.47 (*n*Hex/Et_2O = 9:1 v/v) [UV]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26– 7.04 (m, 10H), 2.82 (t, *J* = 7.6 Hz, 1H), 2.64 (t, *J* = 7.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 209.3 (*C*O), 141.1 (C_{Ar}), 128.6 (C_{Ar}), 128.5 (C_{Ar}), 126.3 (C_{Ar}), 44.7 (Ph*C*H_2), 29.9 (PhCH_2*C*H_2).

GC-MS (EI): t_r = 9.33 min, m/z(%) = 238 (9, [$M^{+\bullet}$]), 133 (24, [$M^{+\bullet}$-$C_8H_9^{\bullet}$]), 105 (55, [$C_8H_9^{+\bullet}$]), 91 (100, [$Bn^{+\bullet}$]).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3058 (w, C-H_{arom}), 3025 (w, C-H_{arom}), 2924 (w, C-H_{aliph}), 2861 (w, C-H_{aliph}), 2801 (w, C-H_{aliph}), 1709 (s, C=O), 1601 (w), 1493 (m), 1448 (m), 1407 (m), 1366 (m), 1284 (w), 1183 (w), 1090 (m), 1027 (w), 978 (w), 911 (w), 744 (s), 695 (vs).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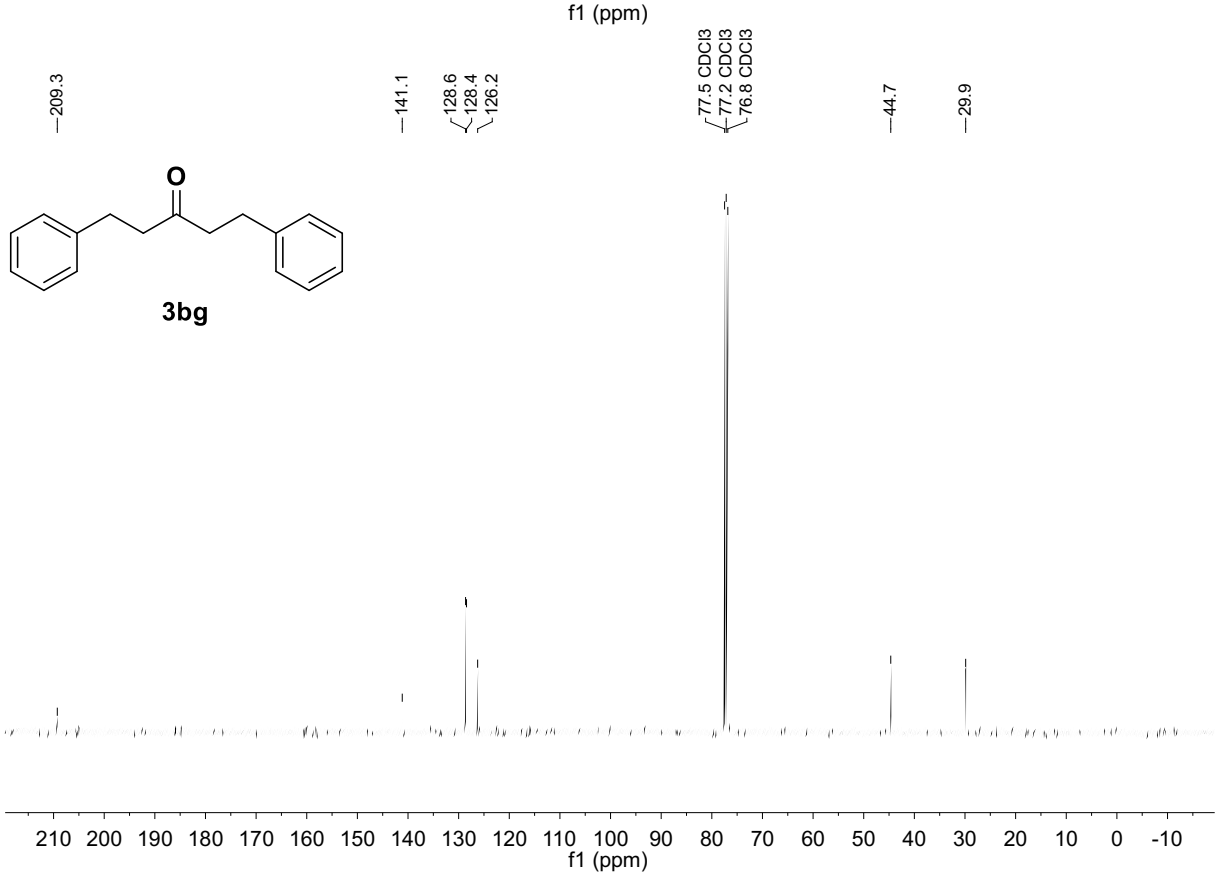
2.83
2.82
2.80
2.66
2.65
2.64
2.62
1.50 HDO
O
3bg
10.26
4.00
3.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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77.2 CDCl3
76.8 CDCl3
44.7
29.9
O
3bg
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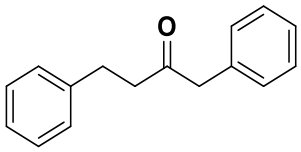
f1 (ppm)

1,4-diphenylbutan-2-one (**3bh**)



3bh

According to GP-F, the product **3bh** was synthesized using benzyl manganese bromide lithium chloride complex (4.4 mL, 0.27 M, 1.2 mmol, 1.2 equiv.) and *S*-ethyl 3-phenylpropanethioate **1b** (194 mg, 1.00 mmol). Purification was achieved by column chromatography (*n*Hex/Et_2O = 95:5 v/v). The product was obtained as a colorless oil with a sweet smell (49.0 mg, 218 µmol, 22%). The analytical data is in good accordance with the reported literature.[34]

$C_{16}H_{16}O$ (224.30 g/mol)

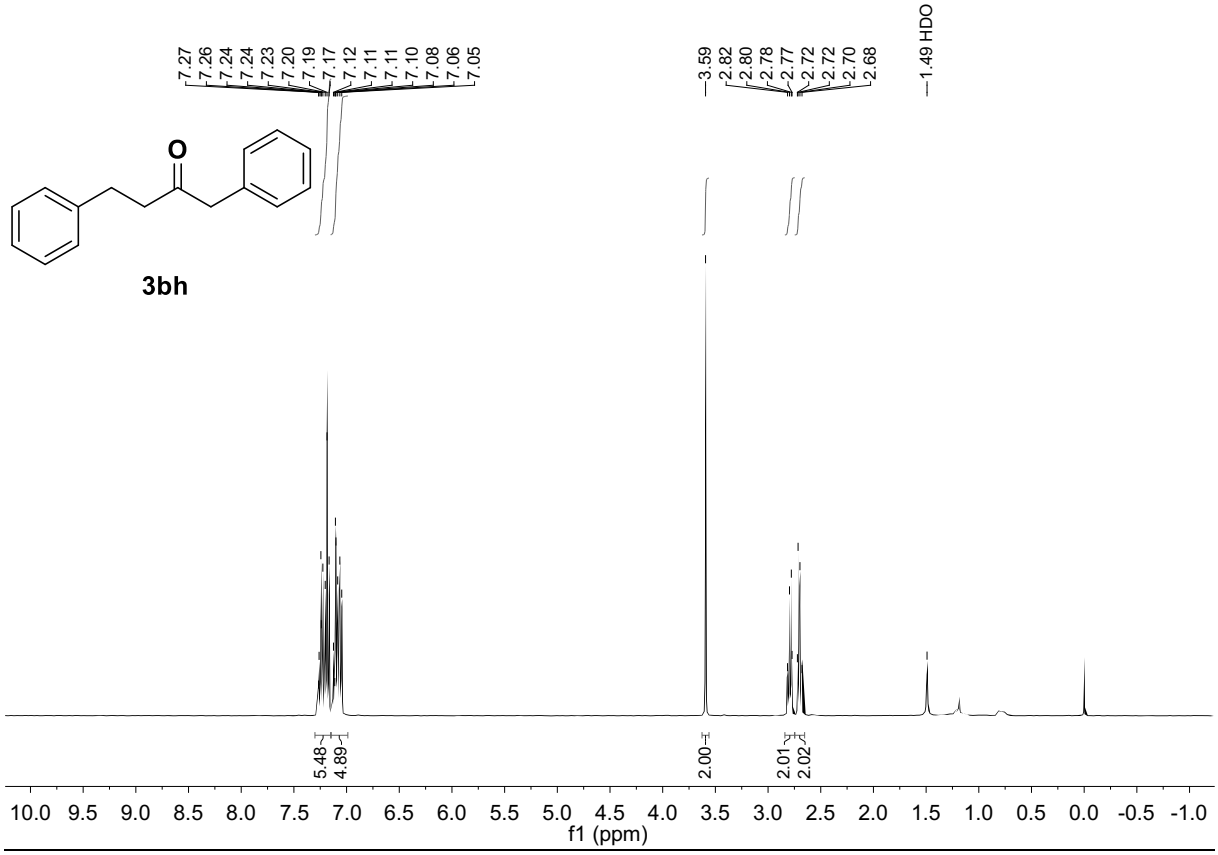
R_f: 0.21 (*n*Hex/Et_2O = 98:2 v/v) [UV]

^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 7.34 – 7.14 (m, 5H, Ar*H*), 7.14 – 7.00 (m, 5H, Ar*H*), 3.59 (s, 2H, PhCH_2CO), 2.84 – 2.75 (m, 2H), 2.75 – 2.65 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 207.6 (*C*O), 141.1 (C_{Ar}), 134.2 (C_{Ar}), 129.5 (C_{Ar}), 128.9 (C_{Ar}), 128.6 (C_{Ar}), 128.5 (C_{Ar}), 127.2 (C_{Ar}), 126.2 (C_{Ar}), 50.5, 43.6, 29.9.

GC-MS (EI): t_r = 8.67 min, m/z(%) = 224 (1, [$M^{+\bullet}$]), 133 (12, [$M^{+\bullet}$-$Bn^{\bullet}$]), 105 (22, [$M^{+\bullet}$-$Bn^{\bullet}$-CO]), 91 (100, [$Bn^{+\bullet}$]).

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3062 (w, C-H_{arom}), 3028 (w, C-H_{arom}), 2924 (w, C-H_{aliph}), 1701 (s, C=O), 1601 (w), 1493 (w), 1448 (w), 1411 (m), 1359 (w), 1280 (m), 1217 (m), 1153 (m), 1072 (w), 1027 (w), 997 (w), 934 (w), 914 (w), 833 (w), 781 (w), 744 (m), 695 (s).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7.05
3.59
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2.80
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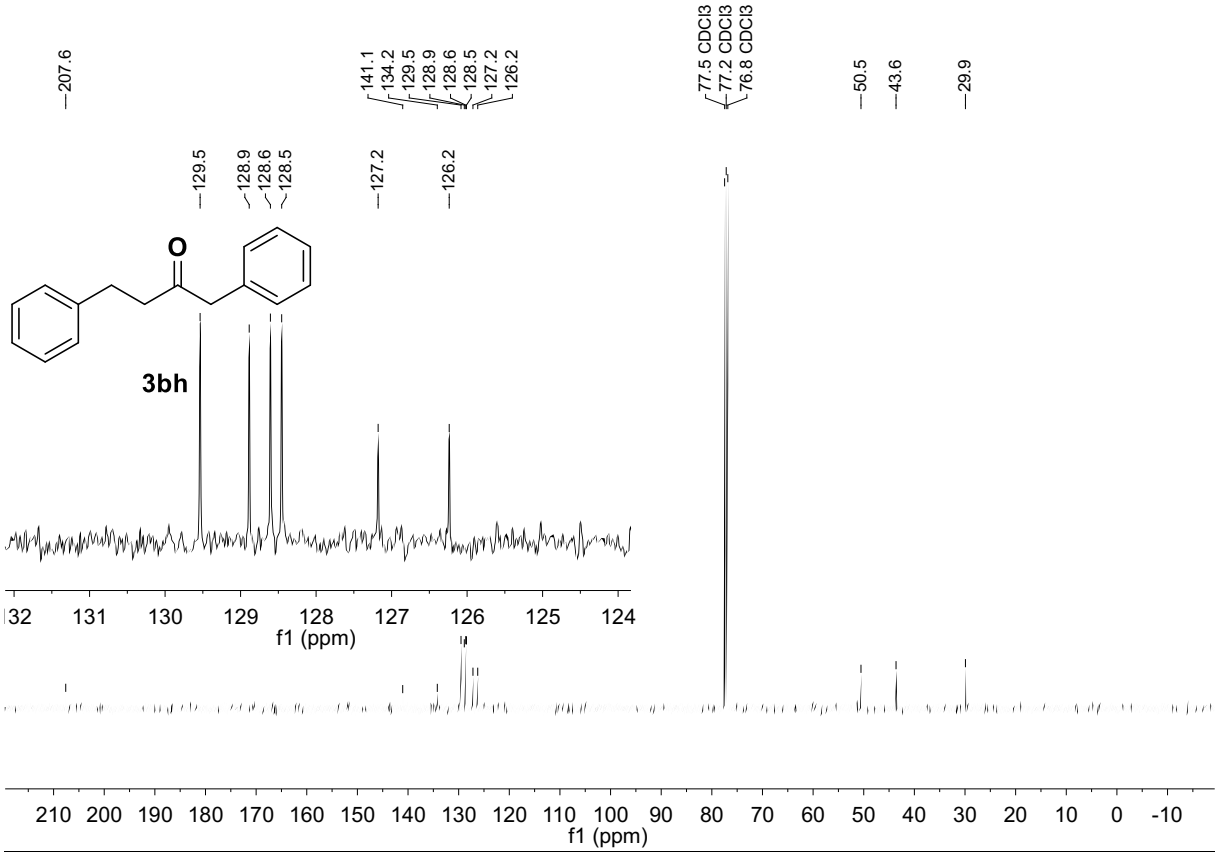
2.77
2.72
2.72
2.70
2.68
1.49 HDO
O
3bh
5.48
4.89
2.00
2.01
2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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128.6
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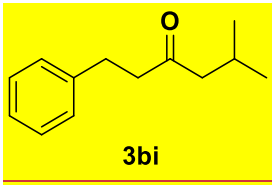
127.2
126.2
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
50.5
43.6
29.9
129.5
128.9
128.6
128.5
127.2
126.2
O
3bh
32 131 130 129 128 127 126 125 124
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

5-methyl-1-phenylhexan-3-one (**3bi**)



3bi

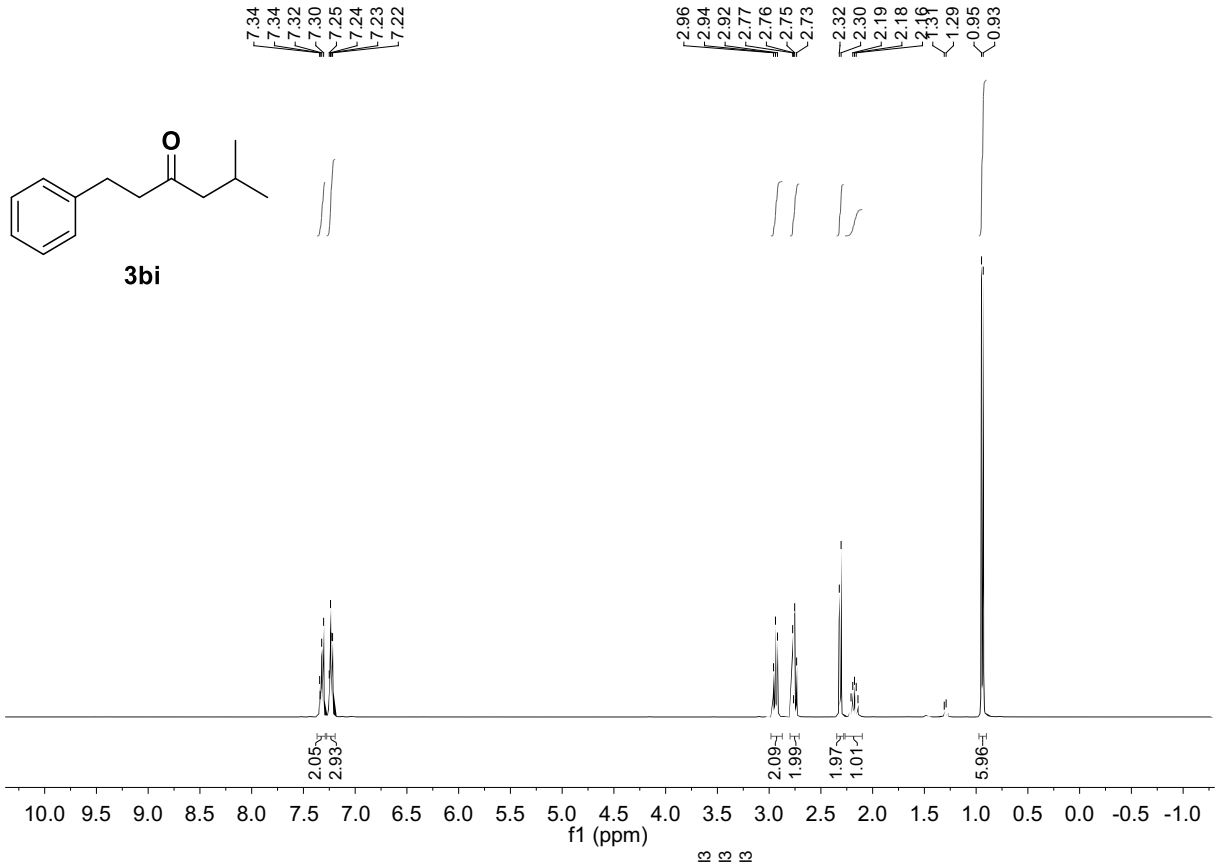
According to GP-F with minor deviations, the product **3bi** was synthesized using *iso*butyl manganese bromide lithium chloride complex (4.4 mL, 0.27 M, 1.2 mmol, 1.2 equiv.) and *S*-ethyl 3-phenylpropanethioate **1b** (194.3 mg, 1 mmol). Purification was achieved by flash column chromatography (23 g SiO_2, 15 µm spherical, *n*Hex/ACN = 99:1 v/v). The product was obtained as a colorless oil with a fruitful smell (99.3 mg, 522 µmol, 52%). The analytical data is in good accordance to reported literature.[35]

$C_{13}H_{18}O$ (190.29 g/mol)

R_f: 0.14 (*n*Hex/ACN = 50:1 v/v) [anis - blue]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 – 7.28 (m, 2H, Ar*H*), 7.28 – 7.19 (m, 3H), 2.94 (t, *J* = 7.6 Hz, 2H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.31 (d, *J* = 6.9 Hz, 2H, $COCH_2C(CH_3)_2$), 2.24 – 2.10 (m, 1H), 0.94 (d, *J* = 6.6 Hz, 6H, $CH(CH_3)_2$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 210.1 (*C*OEt), 141.3 (C_{Ar}), 128.6 (C_{Ar}), 128.5(C_{Ar}), 126.2(C_{Ar}), 52.2, 44.9, 29.8, 24.7, 22.7.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2.30
2.19
2.18
2.16
1.31
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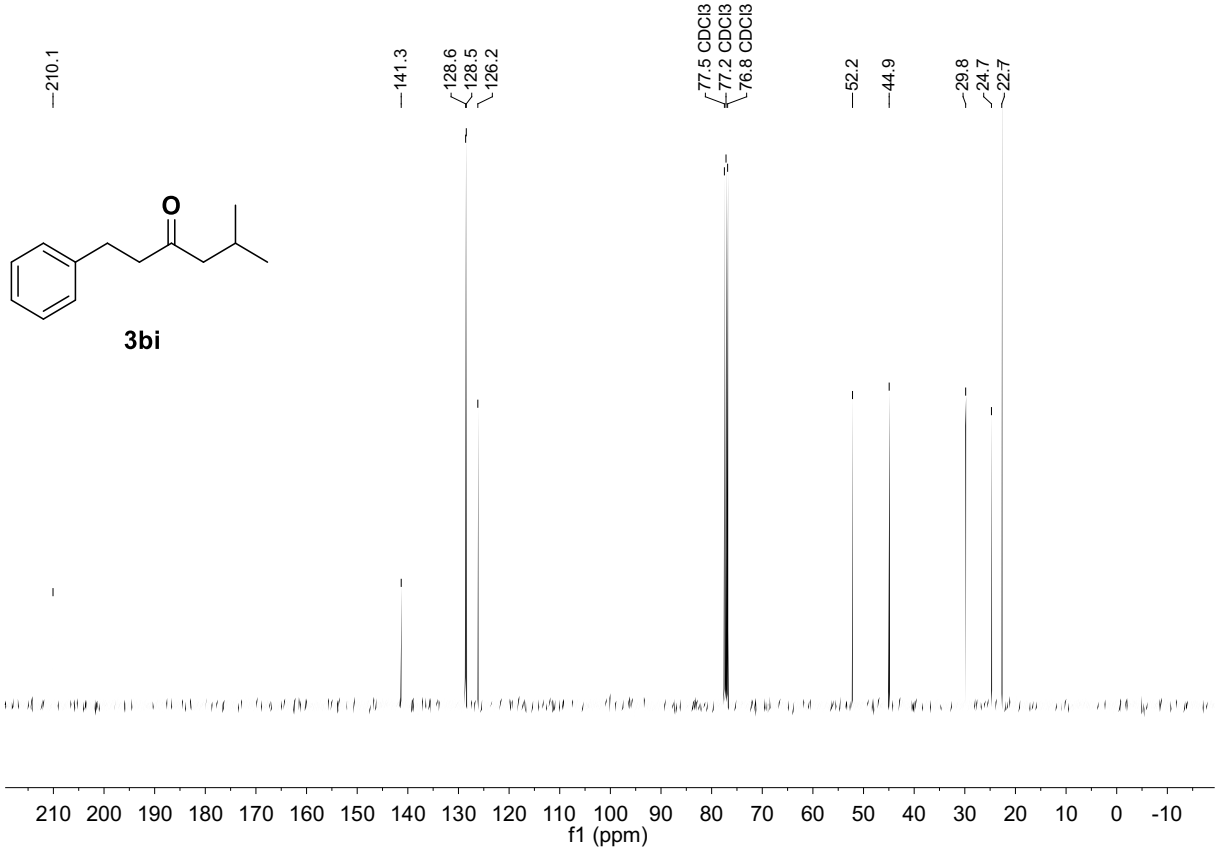
0.93
O
3bi
2.05
2.93
2.09
1.99
1.97
1.01
5.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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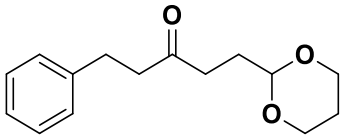
141.3
128.6
128.5
126.2
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
52.2
44.9
29.8
24.7
22.7
O
3bi
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1-(1,3-dioxan-2-yl)-5-phenylpentan-3-one (**3bj**)



3bj

According to GP-F, the product **3bj** was synthesized using (1,3-dioxan-2-ylethyl) manganese bromide lithium chloride complex (0.21 M, 5.7 mL, 1.2 mmol, 1.2 equiv.) and *S*-ethyl 3-phenylpropanethioate **1b** (194 mg, 1.00 mmol). Quenching the reaction was achieved by using brine solution (ca. 2 mL). Purification was achieved by column chromatography (*n*Hex/Et_2O = 1:1 v/v). The product was obtained as a colorless oil with a sweet smell (121 mg, 487 µmol, 49%).

$C_{15}H_{20}O_3$ (248.32 g/mol)

R_f: 0.45 (*n*Hex/Et = 30:1 v/v) [$KMnO_4$]

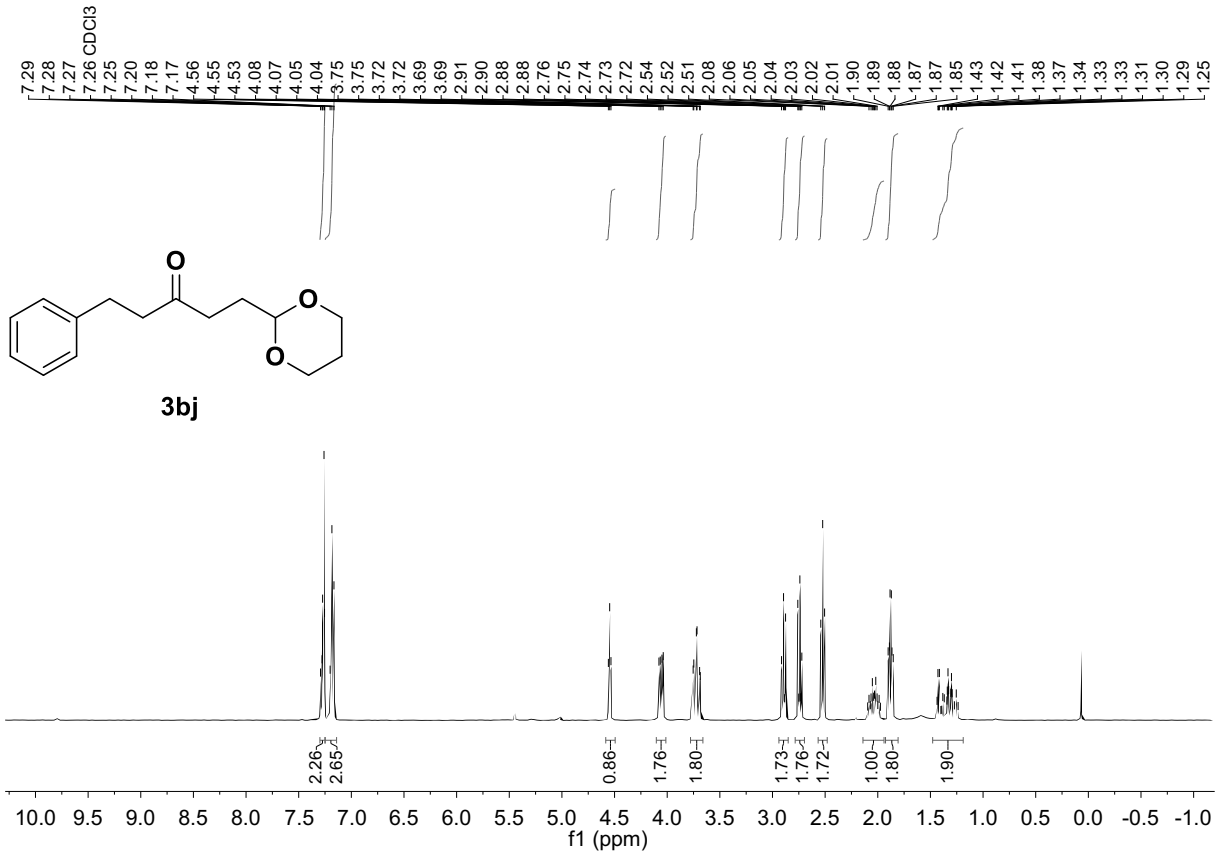
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.26 (m, 2H, Ar*H*), 7.20–7.17 (m, 3H, Ar*H*), 4.55 (t, *J* = 4.9 Hz, 1H), 4.06 (dt, *J* = 11.8 Hz, 5.0 Hz, 2H), 3.72 (dt, *J* = 12.2 Hz, 2.5 Hz, 2H), 2.91–2.88 (m, 2H), 2.76–2.72 (m, 2H), 2.52 (t, *J* = 7.2 Hz, 2H), 1.88 (dt, *J* = 7.2 Hz, 4.9 Hz, 2H), 1.43–1.24 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 209.6 (*C*O), 141.3 (C_{Ar}), 128.6 (C_{Ar}), 128.5 (C_{Ar}), 126.2 (C_{Ar}), 101 (O*C*HO), 67.0(*C*H_2OCHO, 2C), 44.4, 37.0, 29.9, 29.1, 25.9 (CH_2CH_3).

GC-MS (EI): t_r = 9.29 min, m/z(%) = 247 (3, [$M^{+\bullet}$]), 191 (6, [$M^{+\bullet}$-C_3H_5O]), 172 (42), 100 (100).

HR-MS (ESI): m/z calc. for $[M+Na]^+$ 271.13047, found 271.13055.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3059 (w, C-H_{arom}), 3025 (w, C-H_{arom}), 2958 (w, C-H_{aliph}), 2932 (w, C-H_{aliph}), 2850 (w, C-H_{aliph}), 1709 (s, C=O), 1601 (w), 1493 (w), 1448 (w), 1407 (w), 1370 (m), 1281 (w), 1240 (w), 1209 (w), 1176 (w), 1139 (s, C-O-$C_{asymm-stretch}$), 1092 (m), 1042 (m), 1004 (m), 923 (w), 889 (w), 848 (w), 747 (m), 699 (s).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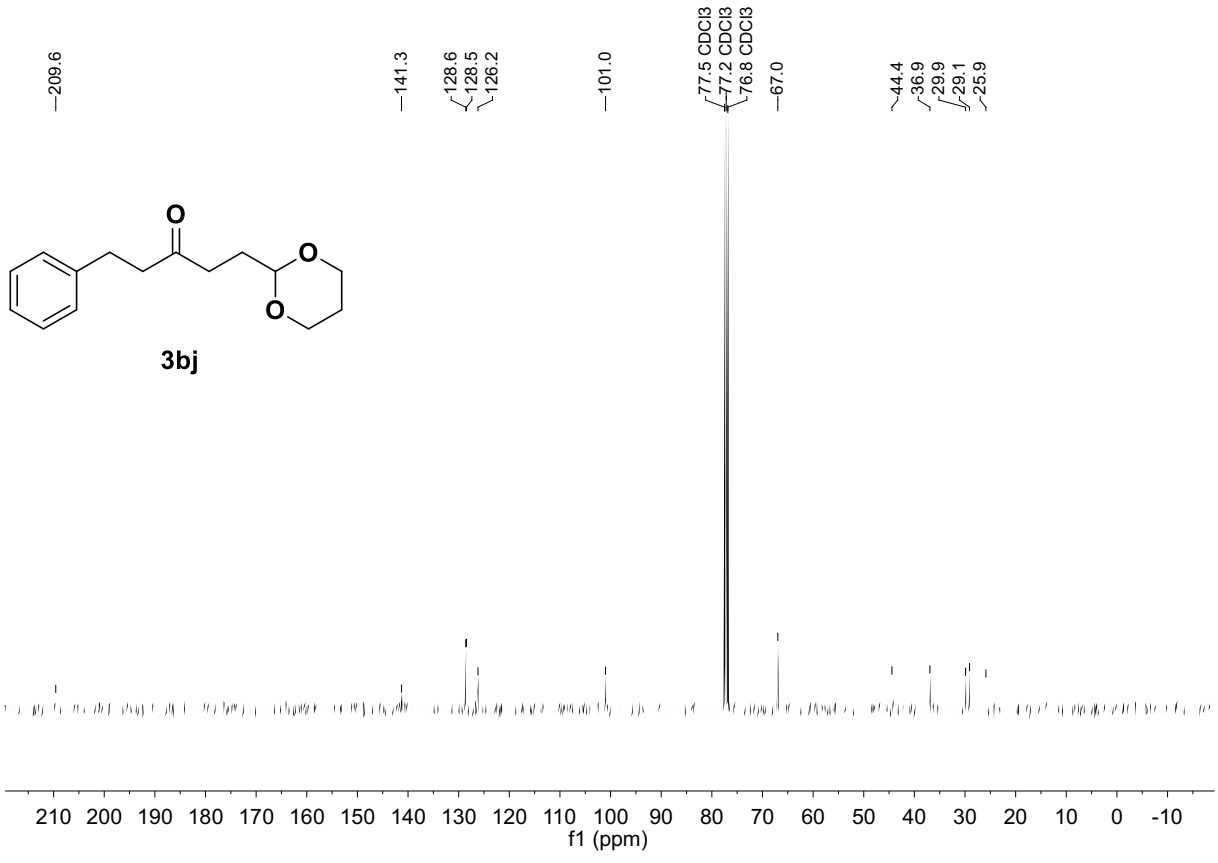
3.72
3.69
3.69
2.91
2.90
2.88
2.88
2.76
2.75
2.74
2.73
2.72
2.54
2.52
2.51
2.08
2.06
2.05
2.04
2.03
2.02
2.01
1.90
1.89
1.88
1.87
1.87
1.85
1.43
1.42
1.41
1.38
1.37
1.34
1.33
1.33
1.31
1.30
1.29
1.25
O
O
O
3bj
2.26
2.65
0.86
1.76
1.80
1.73
1.76
1.72
1.00
1.80
1.90
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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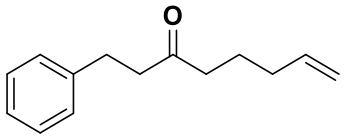
141.3
128.6
128.5
126.2
101.0
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
67.0
44.4
36.9
29.9
29.1
25.9
O
O
O
3bj
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1-phenyloct-7-en-3-one (**3bk**)



3bk

According to GP-F, the product **3bk** was synthesized using pent-4-enylemanganese bromide lithium chloride complex (4.0 mL, 0.3 M, 1.2 mmol, 1.2 equiv.) and *S*-ethyl 3-phenylpropanethioate **1b** (194 mg, 1.00 mmol). Purification was achieved by column chromatography (PE/EA = 30:1 v/v). The product was obtained as a colorless oil (161 mg, 796 µmol, 80%). The analytical data is in good accordance with the reported literature.[36]

$C_{14}H_{18}O$ (202.30 g/mol)

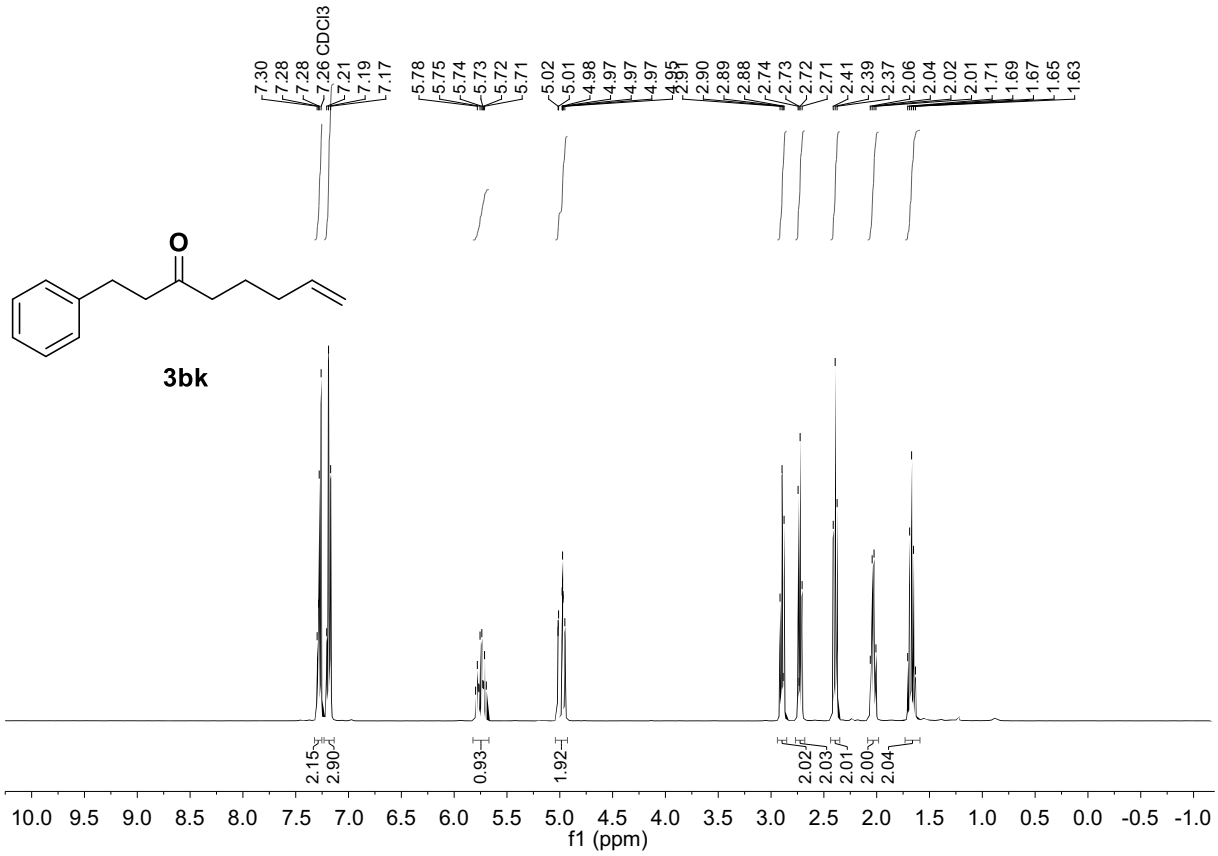
R_f: 0.29 (PE/EA = 30:1 v/v)[anis,$KMnO_4$,UV]

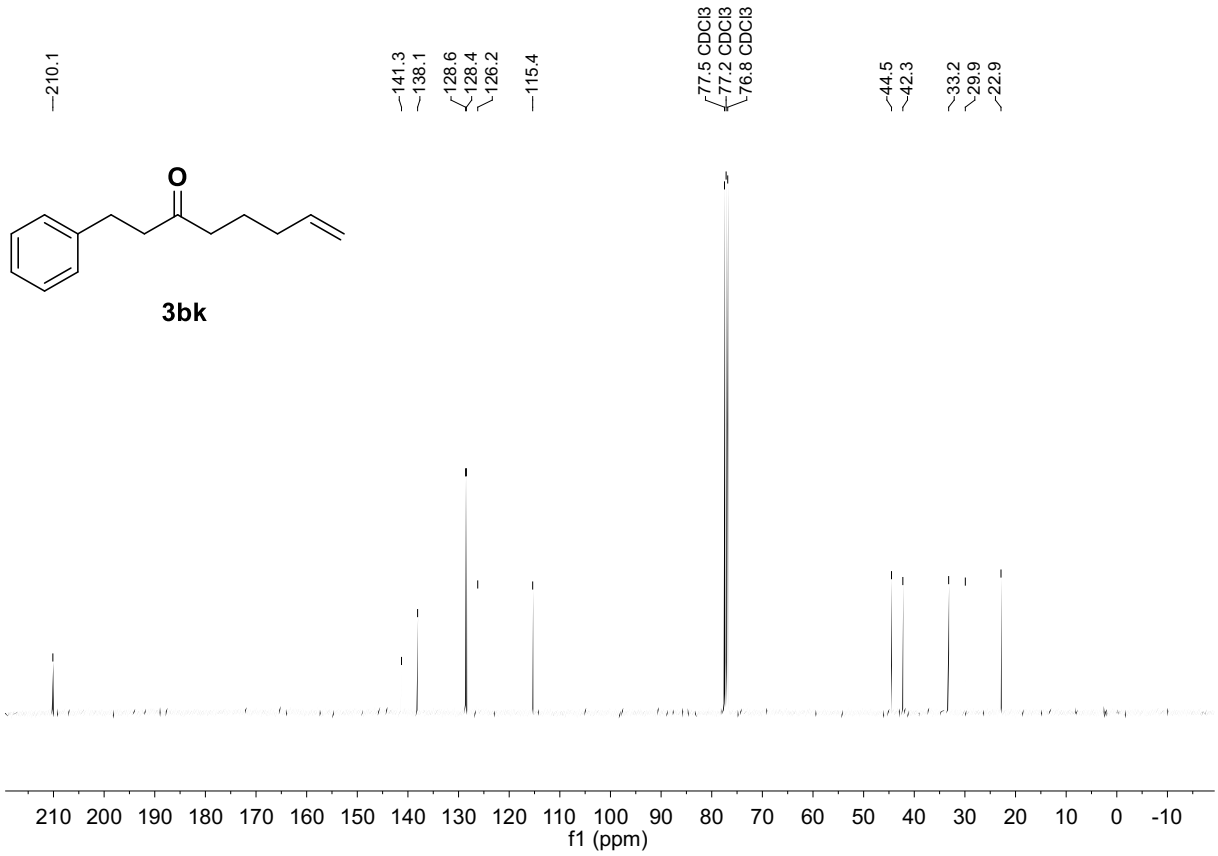
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 – 7.28 (m, 2H, C*H*$_{arom}$), 7.26 – 7.19 (m, 3H, C*H*$_{arom}$), 5.79 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H, C$_{alkene}$*H*CH$_2$), 5.15 – 4.81 (m, 2H, CHC$_{alkene}$*H*$_2$), 2.94 (t, *J* = 7.6 Hz, 2H, PhC*H*$_2$CH$_2$), 2.77 (t, *J* = 7.6, 2H, PhCH$_2$C*H*$_2$), 2.44 (t, *J* = 7.4 Hz, 2H), 2.13 – 1.99 (m, 2H), 1.71 (p, *J* = 7.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 210.1 (*C*O), 141.3 (*C*$_{Ar}$), 138.1 (*C*$_{alkene}$HCH$_2$), 128.6 (*C*$_{Ar}$), 128.5 (*C*$_{Ar}$), 126.2 (*C*$_{Ar}$), 115.4 (CH*C*$_{alkene}$H$_2$), 44.5, 42.3, 33.2, 29.9, 22.9.

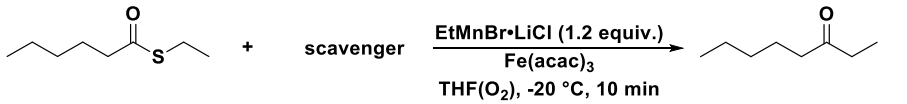
GC-MS (EI): t_r = 7.05 min, m/z(%) = 202 (5, [$M^{+\bullet}$]), 133 (28, [$M^{+\bullet}$-$C_5H_9^{\bullet}$]), 105 (58, [$M^{+\bullet}$-$C_5H_9^{\bullet}$-CO]), 91(100, [$Bz^{+\bullet}$]).

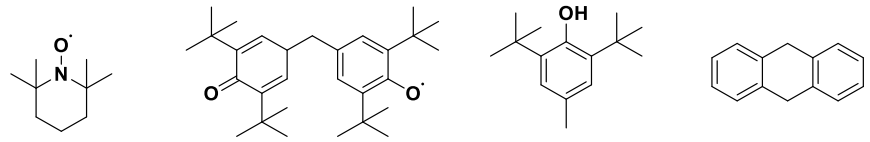
IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 3068 (w, C-H$_{arom}$), 3025 (w, C-H$_{arom}$), 2931 (w, C-H$_{aliph}$), 2865 (w, C-H$_{aliph}$), 1709 (s, C=O), 1638 (w), 1601 (w), 1493 (w), 1448 (m), 1408 (w), 1366 (m), 1300 (w), 1209 (w), 1187 (w), 1153 (w), 1083 (w), 1027 (w), 994 (m), 911 (s), 744 (m), 699 (s).


7.30
7.28
7.28
7.26 CDCl3
7.21
7.19
7.17
5.78
5.75
5.74
5.73
5.72
5.71
5.02
5.01
4.98
4.97
4.97
4.95
2.91
2.90
2.89
2.88
2.74
2.73
2.72
2.71
2.41
2.39
2.37
2.06
2.04
2.02
2.01
1.71
1.69
1.67
1.65
1.63
O
3bk
2.15
2.90
0.93
1.92
2.02
2.03
2.01
2.00
2.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


210.1
141.3
138.1
128.6
128.4
126.2
115.4
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
44.5
42.3
33.2
29.9
22.9
O
3bk
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

7. Radical Scavenger Experiments





TEMPO | Galvinoxyl | BH2T | DHA

	Product Yield Octan-3-one (Conversion):			
20 mol%:	80%(93)	75%(81)	94%(quant)	95%(quant)
2 equiv.:	0%(17)	0%(0)	21%(21)	94%(quant)

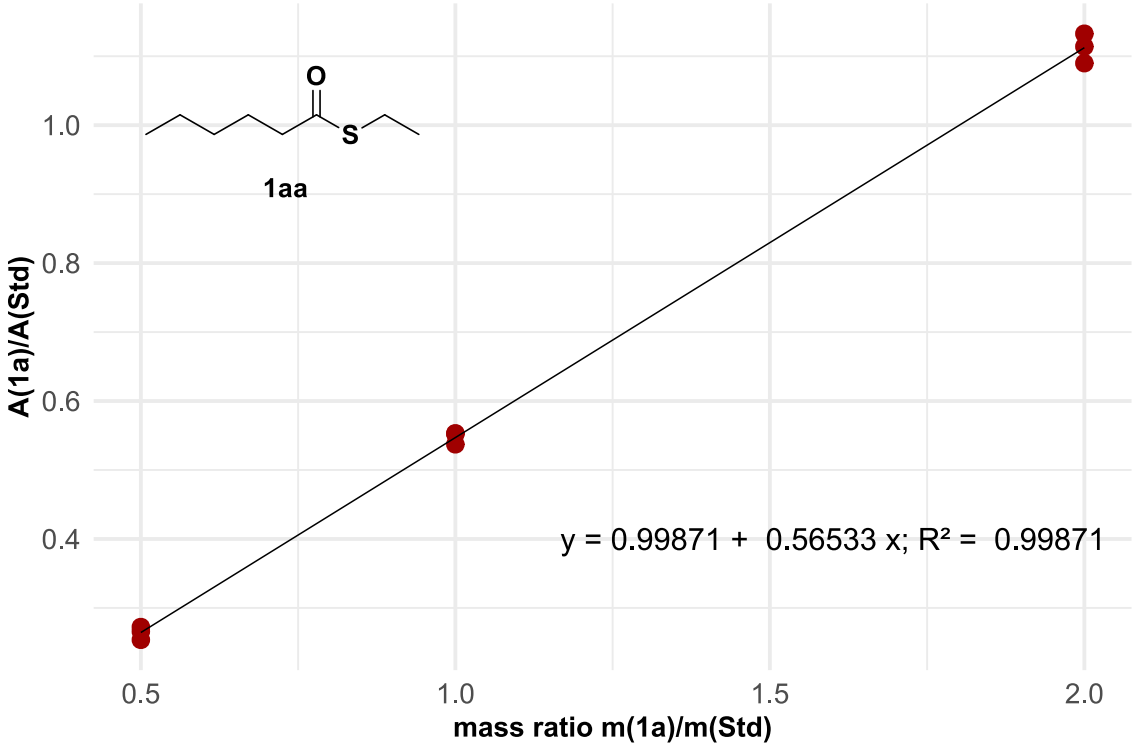
8. GC-calibrations

The quantification of GC-yields was achieved by adding a standard compound (*n*-pentadecane) to reaction mixtures before quenching (usually 100 µL) and applying the general formula:

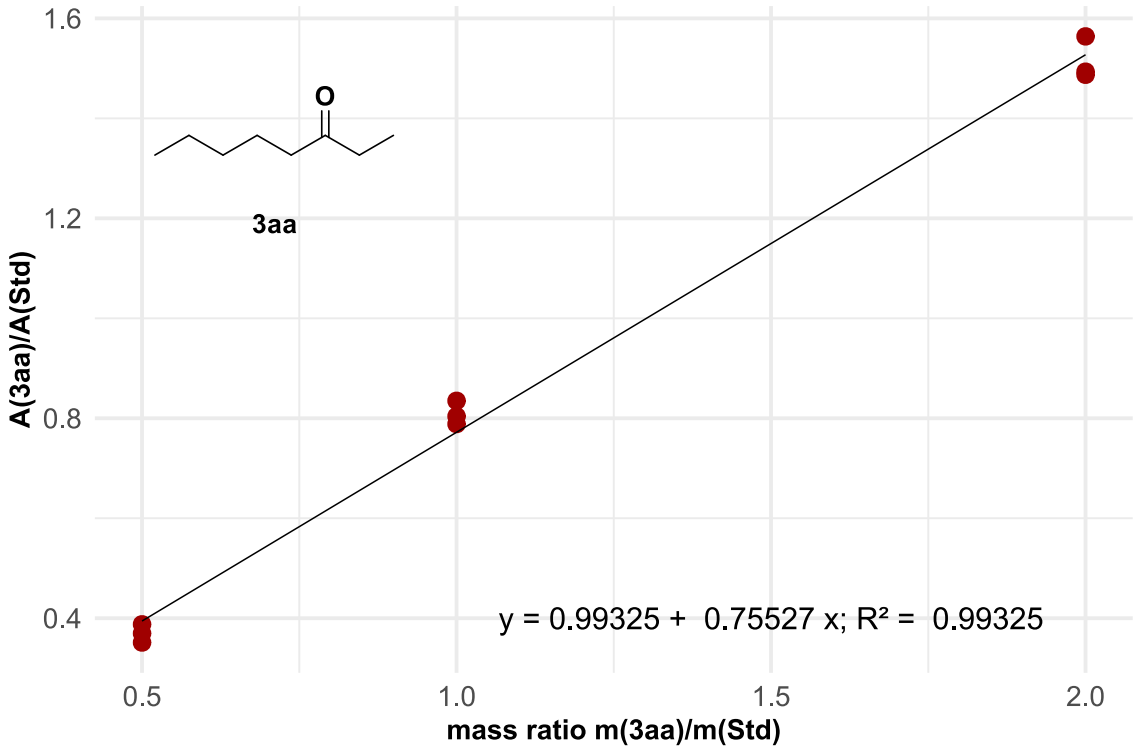
$$\frac{A(compound)}{A(standard)} = R \cdot \frac{m(compound)}{m(standard)}$$

R: Response factor of compound
A: Peak area determined by GC-FID
m: mass of compound

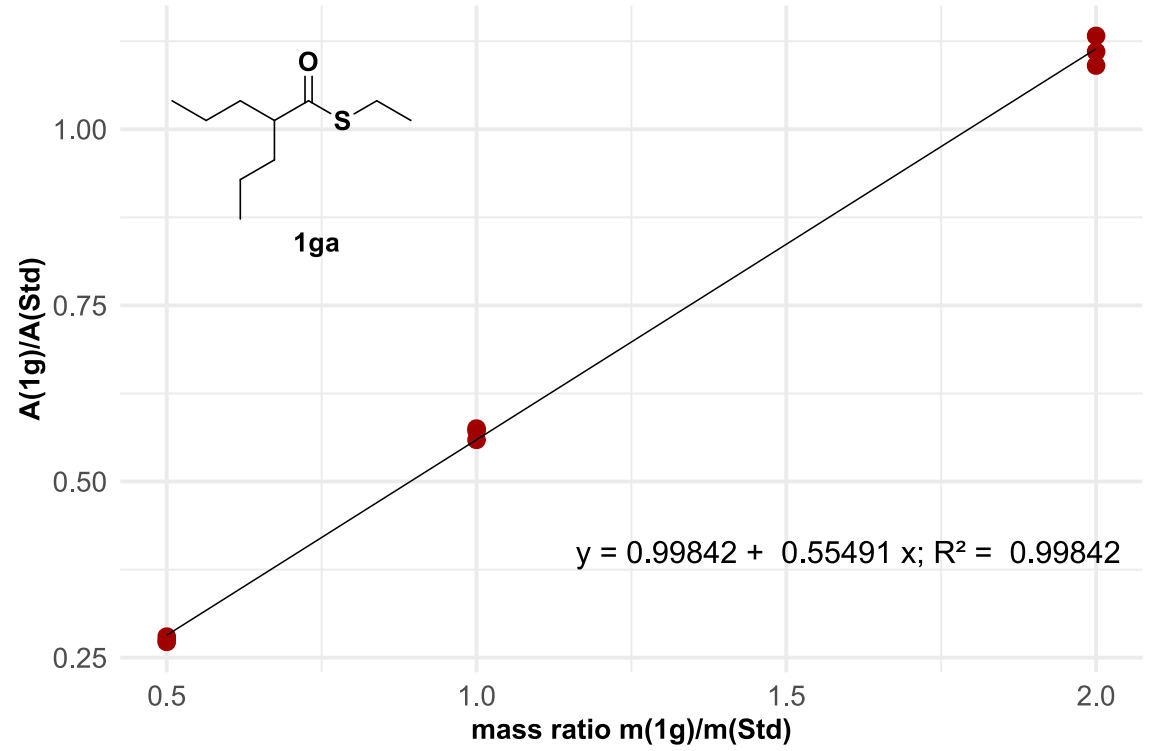
The R values were determined by GC calibrations of respective compounds with pentadecane in ethyl acetate and measuring different mass ratios.



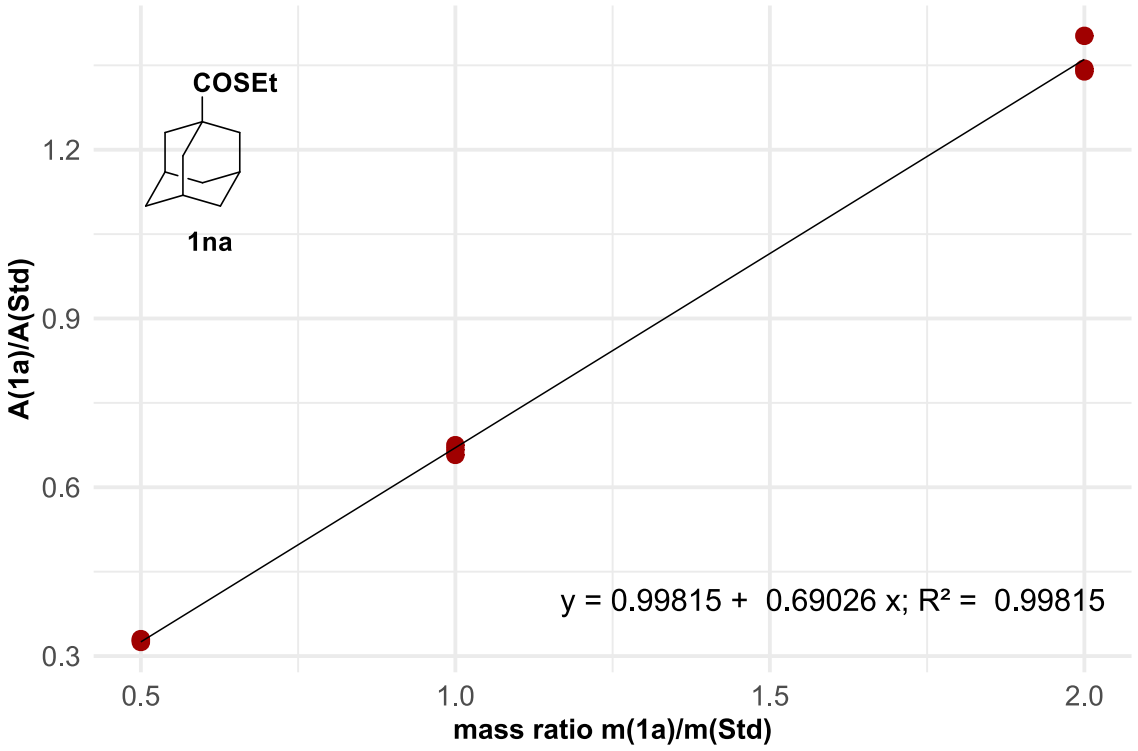
Mass ratio $\left[\frac{mg\ (Thioester)}{mg\ (Std)}\right]$	A (Thioester)	A (Std)	Area ratio $\left[\frac{A(Thioester)}{A\ (Std)}\right]$
2	1280.46	1174.91	1.08983
2	1179.71	1041.56	1.13263
2	1326.13	1190.43	1.11399
1	1354.55	2452.88	0.55222
1	1267.9	2360.24	0.53719
1	1396.66	2524.61	0.55322
0.5	742.16	2725.46	0.27231
0.5	572.54	2256.31	0.25375
0.5	646.49	2431.59	0.26587



Mass ratio $\left[\frac{mg\ (Ketone)}{mg\ (Std)}\right]$	A (Ketone)	A (Std)	Area ratio $\left[\frac{A(Ketone)}{A\ (Std)}\right]$
2	2106.35	1416.28	1.48724
2	2083.63	1332.24	1.56401
2	2094.51	1402.53	1.4933
1	2114.74	2532.78	0.83495
1	2135.04	2707.7	0.78851
1	2203.07	2740.25	0.80397
0.5	1033.79	2942.11	0.35138
0.5	1007.78	2726.59	0.36961
0.5	1044.16	2692.83	0.38776



Mass ratio $\left[\frac{mg\ (Thioester)}{mg\ (Std)}\right]$	A (Thioester)	A (Std)	Area ratio $\left[\frac{A(Thioester)}{A\ (Std)}\right]$
2	1179.71	1041.56	1.13263
2	1434.49	1292.1	1.11019
2	1419.66	1301.99	1.09037
1	1503.81	2614.12	0.57526
1	1499.16	2681.25	0.55913
1	1524.91	2666.18	0.57194
0.5	733.15	2618.6	0.27998
0.5	757.29	2760.1	0.27437
0.5	742.16	2725.46	0.27231



Mass ratio $\left[\frac{mg\ (Thioester)}{mg\ (Std)}\right]$	A (Thioester)	A (Std)	Area ratio $\left[\frac{A(Thioester)}{A\ (Std)}\right]$
2	1559.7	1112.16	1.40242
2	1630.03	1217.2	1.33916
2	1647.46	1225.74	1.34405
1	1581.74	2405.4	0.65758
1	1425.64	2112.69	0.67480
1	1560.57	2340.45	0.66678
0.5	809.28	2489.78	0.32504
0.5	652.96	1989.37	0.32822
0.5	736.88	2232.3	0.33010

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