Synthesis and styrene copolymerization of bromo, chloro, and fluoro ring-substituted 2-methoxyethyl phenylcyanoacrylates

Fernanda Aviles, Grace D. Lee, Mae I. Z. Madrid, Jullisa J. Maya, Andrew S. Nuelle, Nancy Padilla, Gia K. Pappas, Rechal K. Patel, Emily Schroeder, Farheen Shethwala, Jordan Villa, Misael Villegas, Sara M. Rocus, William S. Schjerven, and Gregory B. Kharas

DePaul University, Chemistry and Biochemistry Department, 1110 West Belden Avenue, Chicago, IL 60614-3214

Abstract

Novel halogen ring-substituted 2-methoxyethyl phenylcyanoacrylates, RPhCH=C(CN)$CO_2CH_2CH_2OCH_3$ (where R is 2-bromo, 3-bromo, 4-bromo, 2-chloro, 3-chloro, 4-chloro, 2-fluoro, 3-fluoro, 4-fluoro, 2-trifluoromethyl, 3-trifluoromethyl, 4-trifluoromethyl) were prepared and copolymerized with styrene. The acrylates were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-substituted benzaldehydes and 2-methoxyethyl cyanoacetate, and characterized by CHN analysis, IR, ^{1}H and ^{13}C NMR. All the acrylates were copolymerized with styrene in solution with radical

initiation (ABCN) at 70°C. The compositions of the copolymers were calculated from nitrogen analysis.

*Contact: gkharas@depaul.edu

1. Introduction

Fluoro ring-substituted ethyl phenylcyanoacrylates (EPCA) were reported in synthesis and characterization of a crown-shaped 36-molybdate cluster related to catalysis of Knoevenagel condensation [1]; in preparation of bicyclic pyridine derivatives as fatty acid binding protein inhibitors [2]; in use of amine-functional polysiloxanes as efficient polymeric organocatalyst for amino catalysis in multicomponent Gewald reaction, α-allylic alkylation of aldehydes, and Knoevenagel condensation [3]; in synthesis and application of polystyrene-supported NADH model [4]; in preparation of heterocyclic compounds as xanthine oxidase inhibitors [5]; in total synthesis and study of analgesic activity of 6-fluoroindan-1-carboxylic acid [6]; in design, synthesis and application of polysiloxane-supported NADH model [7]; in investigation into the oxidation mechanism of Hantzsch 1,4-dihydropyridines by ethyl α-cyanocinnamates and benzylidenemalononitriles [8]; in stereoselective synthesis of trans-4, 5-substituted 1,4,5,6-tetrahydropyridine-2-(olates)thiolates [9]; in studies stereochemistry of interaction of pyridinium ylides with α,β-unsaturated nitriles [10]; in synthesis of condensed 2-amino-4H-pyrans and characterization molecular structure of 2-amino-7,7-dimethyl-4-(3-fluorophenyl)-5-oxo-3-(ethoxycarbonyl)-5,6,7,8-tetrahydro-4H-benzo[b]pyran [11]; in studies of neuroleptic activity and dopamine-uptake inhibition in 1-piperazino-3-

phenylindans [12]; in preparation, studies of properties, and reactions of conjugated heteroenoid compounds and related compounds [13]; in studies of polarographic half-wave potentials and ultraviolet absorption spectra of conjugated heteroenoid compounds [14], and their equilibrium reactions with butanol [15]. 4-(Trifluoromethyl) ring-substituted EPCA was involved in C(sp3)-H functionalizations of light hydrocarbons using decatungstate photocatalysis in flow [16]; in conjugate hydrocyanation of α-cyanoacrylates using potassium hexacyanoferrate(II) as cyanating reagent [17]; in catalysis with a core-shell-satellite structured Fe_3O_4S-NH_2 nanocomposite of multistep cascade reaction sequences [18], and in construction of heterocycles via 1,4-dipolar cycloaddition of quinoline-DMAD zwitterion with various dipolarophiles [19].

In this work we have prepared halogen ring-substituted 2-methoxyethyl phenylcyanoacrylates, RPhCH=C(CN)$CO_2CH_2CH_2OCH_3$, where R is 2-bromo, 3-bromo, 4-bromo, 2-chloro, 3-chloro, 4-chloro, 2-fluoro, 3-fluoro, 4-fluoro, 2-trifluoromethyl, 3-trifluoromethyl, 4-trifluoromethyl, and explored the feasibility of their copolymerization with styrene. To the best of our knowledge there have been no reports on either synthesis of these compounds, nor their copolymerization with styrene [20].

2. Experimental

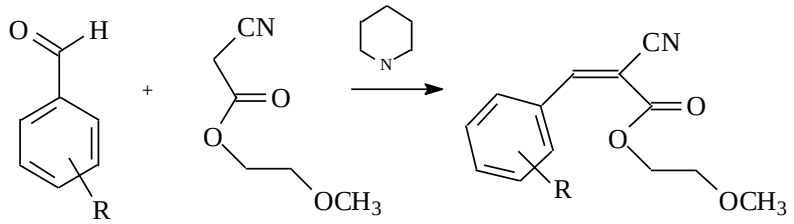
2-Bromo, 3-bromo, 4-bromo, 2-chloro, 3-chloro, 4-chloro, 2-fluoro, 3-fluoro, 4-fluoro, 2-trifluoromethyl, 3-trifluoromethyl, 4-trifluoromethyl-substituted benzaldehydes, 2-methoxyethyl cyanoacetate (≥98.0%), piperidine (99%), styrene (≥99%), 1,1'-

azobis(cyclohexanecarbonitrile) (98%), (ABCN), and toluene (98%) supplied from Sigma-Aldrich Co., were used as received. Instrumentation is reported in [21].

3. Results and discussion

3.1. Synthesis and characterization of 2-methoxyethyl phenylcyanoacrylates

All MEPA compounds were synthesized by Knoevenagel condensation [22] of appropriate benzaldehydes with 2-methoxyethyl cyanoacetate, catalyzed by base, piperidine (Scheme 1).



Scheme 1. Synthesis of 2-methoxyethyl phenylcyanoacrylates, where R is 2-bromo, 3-bromo, 4-bromo, 2-chloro, 3-chloro, 4-chloro, 2-fluoro, 3-fluoro, 4-fluoro, 2-trifluoromethyl, 3-trifluoromethyl, 4-trifluoromethyl.

The preparation procedure was essentially the same for all the MEPA compounds. In a typical synthesis, equimolar amounts of 2-methoxyethyl cyanoacetate and an appropriate benzaldehyde were mixed in equimolar ratio in a 20 mL vial. A few drops of piperidine were added with stirring. The product of the reaction was isolated by filtration and purified by crystallization from 2-propanol. The condensation reaction proceeded smoothly, yielding products, which were purified by conventional techniques. The compounds were characterized by IR, ^{1}H and ^{13}C NMR spectroscopies. No stereochemical analysis of the

novel alkoxy ring-substituted MEPA was performed since no stereoisomers (*E* or/and *Z*) of known configuration were available.

3.1.1. *2-Methoxyethyl 2-bromophenylcyanoacrylate*

Yield: 82%; mp 56°C; ^{1}H NMR: δ8.3 (s, 1H, CH=), 8.2-7.4 (m, 4H, Ph), 4.5 (t, 2H, $OCOCH_2$), 3.7 (t, 2H, OCH_2), 3.4 (s, 3H, OCH_3); ^{13}C NMR: δ 163 (C=O), 154 (HC=), 136, 132, 129, 128, 127, 115 (Ph), 116 (CN), 106 (C=), 74 (OCH_2), 64 ($OCOCH_2$), 59 (OCH_3); IR: (cm^{-1}) 2992 (m, C-H), 2228 (m, CN), 1734 (s, C=O), 1585 (s, C=C), 1263 (s, C-O-CH_3), 708 (s, C-H out of plane). Anal. calcd. for $C_{13}H_{12}BrNO_3$: C, 50.34; H, 3.90; N, 4.52; Found: C, 48.14; H, 3.86; N, 4.54.

3.1.2. *2-Methoxyethyl 3-bromophenylcyanoacrylate*

Yield: 95%; mp 56.2°C; ^{1}H NMR: δ8.2 (s, 1H, CH=), 8.1-7.3 (m, 4H, Ph), 4.5 (t, 2H, $OCOCH_2$), 3.7 (t, 2H, OCH_2), 3.4 (s, 3H, OCH_3); ^{13}C NMR: δ162 (C=O), 153 (HC=), 132, 131, 130 (Ph), 116 (CN), 100 (C=), 64 ($OCOCH_2$), 59 (OCH_3); IR: (cm^{-1}) 2982 (m, C-H), 2224 (m, CN), 1747 (s, C=O), 1609 (s, C=C), 1257 (s, C-O-CH_3), 781, 677 (s, C-H out of plane). Anal. calcd. for $C_{13}H_{12}BrNO_3$: C, 50.34; H, 3.90; N, 4.52; Found: C, 48.03; H, 3.63; N, 4.57.

3.1.3. *2-Methoxyethyl 4-bromophenylcyanoacrylate*

Yield 73%; mp 42.4°C; ^{1}H NMR δ8.2 (s, 1H, CH=), 7.9-6.9 (m, 4H, Ph), 4.8 (t, 2H, $OCOCH_2$), 3.7 (t, 2H, OCH_2), 3.4 (s, 3H, OCH_3); ^{13}C NMR: δ 162 (C=O), 154 (HC=), 132, 131, 130 (Ph), 115 (CN), 103 (C=), 70 (OCH_2), 66 ($OCOCH_2$), 59 (OCH_3); IR: (cm^{-}

^{1}) 2928 (m, C-H), 2220 (m, CN), 1732 (s, C=O), 1603 (s, C=C), 1257 (s, C-O-CH_3), 791 (s, C-H out of plane). Anal. calcd. for $C_{13}H_{12}BrNO_3$: C, 50.34; H, 3.90; N, 4.52; Found: C, 48.09; H, 3.77; N, 4.19.

3.1.4. ***2-Methoxyethyl 2-chlorophenylcyanoacrylate***

Yield 82%; ^{1}H NMR δ8.2 (s, 1H, CH=), 7.9-7.3 (m, 4H, Ph), 4.3 (t, 2H, $OCOCH_2$), 3.7 (t, 2H, OCH_2), 3.4 (s, 3H, CH_3O); ^{13}C NMR δ 164 (C=O), 155 (HC=), 134, 133, 130, 129 (Ph), 115 (CN), 106 (C=), 70 (OCH_2), 66 ($OCOCH_2$), 59 (OCH_3); IR (cm^{-1}): 2884 (m, C-H), 2226 (m, CN), 1732 (s, C=O), 1609 (s, C=C), 1203 (s, C-O-CH_3), 862, 750 (s, C-H out of plane). Anal. Calcd. for $C_{13}H_{12}ClNO_3$: C, 58.77; H, 4.55; N, 5.27; Found: C, 54.77; H, 4.64; N, 5.17.

3.1.5. ***2-Methoxyethyl 3-chlorophenyl)phenylcyanoacrylate***

Yield 72%; mp 58.1°C; ^{1}H NMR δ8.2 (s, 1H, CH=), 7.9-7.3 (m, 4H, Ph), 4.8 (t, 2H, $OCOCH_2$), 3.7 (t, 2H, OCH_2), 3.4 (s, 3H, CH_3O); ^{13}C NMR δ 162 (C=O), 153 (HC=), 137, 135, 134, 130, 129 (Ph), 115 (CN), 105 (C=), 70 (OCH_2), 66 ($OCOCH_2$), 59 (OCH_3); IR (cm^{-1}): 2945 (m, C-H), 2226 (m, CN), 1717 (s, C=O), 1609 (s, C=C), 1271 (s, C-O-CH_3), 851, 787 (s, C-H out of plane). Anal. Calcd. for $C_{13}H_{12}ClNO_3$: C, 58.77; H, 4.55; N, 5.27; Found: C, 55.63; H, 4.51; N, 5.40.

3.1.6. ***2-Methoxyethyl 4-chlorophenoxy)phenylcyanoacrylate***

Yield 87%; mp 86.9°C; ^{1}H NMR δ8.2 (s, 1H, CH=), 8.1-7.3 (m, 4H, Ph), 4.8 (t, 2H, $OCOCH_2$), 3.7 (t, 2H, OCH_2), 3.4 (s, 3H, CH_3O); ^{13}C NMR δ162 (C=O), 154 (HC=), 140, 132, 131, 130, 129 (Ph), 115 (CN), 103 (C=), 70 (OCH_2), 66 ($OCOCH_2$), 59

(OCH_3); IR (cm^{-1}): 2899 (m, C-H), 2222 (m, CN), 1724 (s, C=O), 1612 (s, C=C), 1290 (s, C-O-CH_3), 829, 760 (s, C-H out of plane). Anal. Calcd. for $C_{13}H_{12}ClNO_3$: C, 58.77; H, 4.55; N, 5.27; Found: C, 56.06; H, 4.63; N, 5.60.

3.1.7. ***2-Methoxyethyl 2-fluorophenylcyanoacrylate***

Yield 84; ^{1}H NMR δ 8.6 (s, 1H, CH=), 8.4-7.0 (m, 4H, Ph), 4.5 (t, 2H, $OCOCH_2$), 3.7 (t, 2H, OCH_2), 3.4 (s, 3H, CH_3O); ^{13}C NMR δ 163 (C=O), 154 (HC=), 146, 135, 129, 125, 120 (Ph), 117 (CN), 105 (C=), 70 (OCH_2), 65 ($OCOCH_2$), 59 (OCH_3); IR (cm^{-1}): 2934 (m, C-H), 2228 (m, CN), 1742 (s, C=O), 1610 (s, C=C), 1236 (s, C-O-CH_3), 804 (s, C-H out of plane). Anal. Calcd. for $C_{13}H_{12}FNO_3$: C, 62.65; H, 4.85; N, 5.62; Found: C, 63.42; H, 4.61; N, 5.49.

3.1.8. ***2-Methoxyethyl 3-fluorophenylcyanoacrylates***

Yield 78%; ^{1}H NMR δ 8.2 (s, 1H, CH=), 7.8-7.0 (m, 4H, Ph), 4.5 (t, 2H, $OCOCH_2$), 3.7 (t, 2H, OCH_2), 3.4 (s, 3H, CH_3O); ^{13}C NMR δ 163 (C=O), 153 (HC=), 133, 132, 127, 122, 120, 117 (Ph), 116 (CN), 104 (C=), 70 (OCH_2), 65 ($OCOCH_2$), 59 (OCH_3); IR (cm^{-1}): 2935 (m, C-H), 2224 (m, CN), 1734 (s, C=O), 1614 (s, C=C), 1227 (s, C-O-CH_3), 872, 762 (s, C-H out of plane). Anal. Calcd. for $C_{13}H_{12}FNO_3$: C, 62.65; H, 4.85; N, 5.62; Found: C, 58.15; H, 4.75; N, 5.55.

3.1.9. ***2-Methoxyethyl 4-fluorophenylcyanoacrylate***

Yield 77%; ^{1}H NMR δ 8.2 (s, 1H, CH=), 8.1-7.1 (m, 4H, Ph), 4.5 (t, 2H, $OCOCH_2$), 3.7 (t, 2H, OCH_2), 3.5 (s, 3H, CH_3O); ^{13}C NMR δ 164 (C=O), 154 (HC=), 133, 129, 116 (Ph), 115 (CN), 102 (C=), 70 (OCH_2), 65 ($OCOCH_2$), 62 (OCH_3); IR (cm^{-1}): 2966 (m,

C-H), 2224 (m, CN), 1720 (s, C=O), 1597 (s, C=C), 1240 (s, C-O-CH_3), 841 (s, C-H out of plane). Anal. Calcd. for $C_{13}H_{12}FNO_3$: C, 62.65; H, 4.85; N, 5.62; Found: C, 60.33; H, 4.96; N, 5.85.

3.1.10. ***2-Methoxyethyl 2-trifluoromethylphenylcyanoacrylates***

Yield 91%; ^{1}H NMR δ 8.1 (s, 1H, CH=), 7.9-7.6 (m, 4H, Ph), 4.3 (t, 2H, $OCOCH_2$), 3.6 (t, 2H, OCH_2), 3.4 (s, 3H, CH_3O); ^{13}C NMR δ 164 (C=O), 152 (HC=), 133, 132, 131, 126 (Ph), 114 (CN), 125 (CF_3), 120 (C=), 70 (OCH_2), 64 ($OCOCH_2$), 59 (OCH_3); IR (cm^{-1}): 2935 (m, C-H), 2231 (m, CN), 1749 (s, C=O), 1601 (s, C=C), 1296 (s, C-O-CH_3), 819, 771 (s, C-H out of plane). Anal. Calcd. for $C_{14}H_{12}F_3NO_3$: C, 56.19; H, 4.04; N, 4.68; Found: C, 52.98; H, 4.42; N, 4.44.

3.1.11. ***2-Methoxyethyl 3-trifluoromethylphenylcyanoacrylates***

Yield 81%; ^{1}H NMR δ 8.3 (s, 1H, CH=), 8.2-7.5 (m, 4H, Ph), 4.5 (t, 2H, $OCOCH_2$), 3.7 (t, 2H, OCH_2), 3.4 (s, 3H, CH_3O); ^{13}C NMR δ 163 (C=O), 153 (HC=), 137, 133, 132, 124 (Ph), 125 (CF_3), 116 (CN), 105 (C=), 69 (OCH_2), 64 ($OCOCH_2$), 59 (OCH_3); IR (cm^{-1}): 2914 (m, C-H), 2235 (m, CN), 1718 (s, C=O), 1609 (s, C=C), 1227 (s, C-O-CH_3), 866, 806, 762 (s, C-H out of plane). Anal. Calcd. for $C_{14}H_{12}F_3NO_3$: C, 56.19; H, 4.04; N, 4.68; Found: C, 52.98; H, 4.42; N, 4.44.

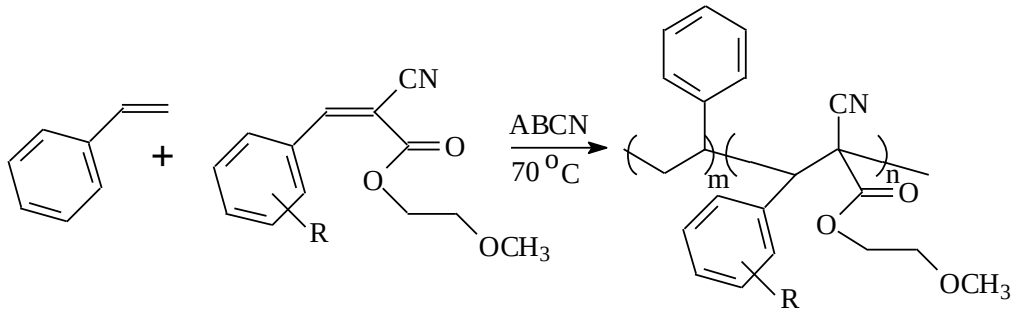
3.1.12. ***2-Methoxyethyl 4-trifluoromethylphenylcyanoacrylates***

Yield 74%; mp 78.6°C; ^{1}H NMR δ 8.3 (s, 1H, CH=), 8.2-7.7 (m, 4H, Ph), 4.5 (t, 2H, $OCOCH_2$), 3.7 (t, 2H, OCH_2), 3.5 (s, 3H, CH_3O); ^{13}C NMR δ 162 (C=O), 153 (HC=), 134, 133, 131 (Ph), 126 (CF_3), 115 (CN), 106 (C=), 70 (OCH_2), 66 ($OCOCH_2$), 59

(OCH_3); IR (cm^{-1}): 2955 (m, C-H), 2228 (m, CN), 1726 (s, C=O), 1616 (s, C=C), 1121 (s, C-O-CH_3), 849, 764, 608 (s, C-H out of plane). Anal. Calcd. for $C_{14}H_{12}F_3NO_3$: C, 56.19; H, 4.04; N, 4.68; Found: C, 51.29; H, 3.86; N, 4.84.

3.2. *Synthesis and characterization of styrene – MEPA copolymers*

Copolymers of the ST and the MEPA compounds, P(ST-co-MEPA) were prepared in 25-mL glass screw cap vials at ST/MEPA = 3 (mol) the monomer feed using 0.12 mol/L of ABCN at an overall monomer concentration 2.44 mol/L in 10 mL of toluene. The copolymerization was conducted at 70ºC. After a predetermined time, the mixture was cooled to room temperature, and precipitated dropwise in methanol. The composition of the copolymers was determined based on the nitrogen content (cyano group in MEPA monomers). The novel synthesized MEPA compounds copolymerized readily with ST under free-radical conditions (Scheme 2) forming white flaky precipitates when their solutions were poured into methanol. The conversion of the copolymers was kept between 10 and 20% to minimize compositional drift (Table 1).



Scheme 2. Copolymerization of ST and halogen ring-substituted 2-methoxyethyl phenylcyanoacrylates, RPhCH = $C(CN)CO_2CH_2CH_2OCH_3$, where R is 2-bromo, 3-bromo,

4-bromo, 2-chloro, 3-chloro, 4-chloro, 2-fluoro, 3-fluoro, 4-fluoro, 2-trifluoromethyl, 3-trifluoromethyl, 4-trifluoromethyl.

Table 1. Copolymerization of Styrene and 2-Methoxyethyl phenylcyanoacrylates.

R	Yield[a] (wt%)	N (wt%)	ST in copol. (mol%)	MEPA in copol. (mol%)
2-Bromo	11.2	2.32	73.8	26.2
3-Bromo	14.3	2.51	70.4	29.6
4-Bromo	12.3	2.36	73.1	26.9
2-Chloro	16.7	2.56	73.0	27.0
3-Chloro	15.2	2.64	71.8	28.2
4-Chloro	12.3	2.55	73.2	26.8
2-Fluoro	14.4	2.63	73.1	26.9
3-Fluoro	12.9	2.64	73.0	27.0
4-Fluoro	14.5	2.58	73.8	26.2
2-Trifluoromethyl	12.6	1.75	82.8	17.2
3-Trifluoromethyl	13.5	2.12	77.7	22.3
4-Trifluoromethyl	14.4	2.25	75.7	24.3

Nitrogen elemental analysis showed that between 17.2 and 29.6 mol% of MEPA is present in the copolymers prepared at ST/MEPA = 3 (mol), which is indicative of relatively high reactivity of the MEPA monomers towards ST radical which is typical of halogen ring-substituted phenylcyanoacrylates. Since MEPA monomers do not homopolymerize, the most likely structure of the copolymers would be isolated MEPA monomer units alternating with short ST sequences (Scheme 2).

The copolymers prepared in the present work are all soluble in ethyl acetate, THF, DMF and $CHCl_3$ and insoluble in methanol, ethyl ether, and petroleum ether.

4 Conclusions

Novel halogen ring-substituted 2-methoxyethyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2CH_2CH_2OCH_3$ (where R is 2-bromo, 3-bromo, 4-bromo, 2-chloro, 3-chloro, 4-chloro, 2-fluoro, 3-fluoro, 4-fluoro, 2-trifluoromethyl, 3-trifluoromethyl, 4-trifluoromethyl) were prepared and copolymerized with styrene.

Acknowledgments

The authors are grateful to acknowledge that the project was partly supported by Chicago Society of Coating Technology (CSCT).

References

1. Synthesis and Characterization of a Crown-Shaped 36-Molybdate Cluster and Application in Catalyzing Knoevenagel Condensation. Xu, Qiaofei; Xu, Baijie; Kong, Hui; He, Peipei; Wang, Jiawei; Kannan, Thirumurthy; Ma, Pengtao; Wang, Jingping; Niu, Jingyang. Inorganic Chemistry (2020), 59(15), 10665-10672.

2. New bicyclic pyridine derivatives as fatty acid binding protein inhibitors and their preparation. Buettelmann, Bernd; Conte, Aurelia; Kuehne, Holger; Kuhn, Bernd; Neidhart, Werner; Obst Sander, Ulrike; Richter, Hans. PCT Int. Appl. (2014), WO 2014029723 A1 20140227.

3. Amine-functional polysiloxanes (AFPs) as efficient polymeric organocatalyst for amino catalysis: efficient multicomponent Gewald reaction, α-allylic alkylation of aldehydes, and

Knoevenagel condensation. Zheng, Zhan-Jiang; Liu, Lu-Xin; Gao, Guang; Dong, Hong; Jiang, Jian-Xiong; Lai, Guo-Qiao; Xu, Li-Wen. RSC Advances (2012), 2(7), 2895-2901.

4. Synthesis and application of polystyrene-supported NADH model. Zhang, Baolian; Zhu, Xiaoqing; Cheng, Jinpei. Huaxue Yanjiu Yu Yingyong (2009), 21(2), 159-163. Language: Chinese, Database: CAPLUS.

5. Preparation of heterocyclic compounds as xanthine oxidase inhibitors. Shimizu, Kazuo; Takigawa, Yasushi; Fujikura, Hideki; Iizuka, Masato; Hiratochi, Masahiro; Kikuchi, Norihiko. PCT Int. Appl. (2008), WO 2008126899 A1 20081023. Language: Japanese, Database: CAPLUS.

6. Total synthesis and analgesic activity of 6-fluoroindan-1-carboxylic acid. Das, Sharmistha; Yasmin, Hasina; Mehedi Masud, M.; Roy, Suvas C.; Nahar, Lutfun; Mukhlesur Rahman, M.; Gibbons, Simon; Bachar, Sitesh C.; Sarker, Satyajit D. Tetrahedron (2008), 64(37), 8642-8645.

7. Design, synthesis and application of polysiloxane-supported NADH model. Zhang, Bao-Lian; Zhu, Xiao-Qing; Al, Teng; Lu, Jin-Yong; Wang, Peng George; Cheng, Jin-Pei. Gaodeng Xuexiao Huaxue Xuebao (2003), 24(10), 1825-1829. Language: Chinese, Database: CAPLUS.

8. A detailed investigation into the oxidation mechanism of Hantzsch 1,4-dihydropyridines by ethyl α-cyanocinnamates and benzylidenemalononitriles. Zhu, Xiao-Qing; Zou, Hong-Ling; Yuan, Ping-Wei; Liu, Yang; Cao, Lei; Cheng, Jin-Pei. Perkin 2 (2000), (9), 1857-1861.

9. Stereoselective synthesis of trans-4,5-substituted 1,4,5,6-tetrahydropyridine-2-(olates) thiolates. Shestopalov, A. M.; Litvinov, V. P.; Rodinovskaya, L. A.; Sharanin, Yu. A. Synthesis (1991), (5), 402-4.

10. Stereochemistry of interaction of pyridinium ylides with α,β-unsaturated nitriles. Shestopalov, A. M.; Sharanin, Yu. A.; Litvinov, V. P. Khimiya Geterotsiklicheskikh Soedinenii (1990), (3), 363-9. Language: Russian, Database: CAPLUS.

11. Cyclization reactions of nitriles. XX. Synthesis of condensed 2-amino-4H-pyrans and molecular structure of 2-amino-7,7-dimethyl-4-(3-fluorophenyl)-5-oxo-3-(ethoxycarbonyl)-5,6,7,8-tetrahydro-4H-benzo[b]pyran. Sharanina, L. G.; Nesterov, V. N.; Klokol, G. V.; Rodinovskaya, L. A.; Shklover, V. E.; Sharanin, Yu. A.; Struchkov, Yu. T.; Promonenkov, V. K. Zhurnal Organicheskoi Khimii (1986), 22(6), 1315-22. Language: Russian, Database: CAPLUS.

12. Neuroleptic activity and dopamine-uptake inhibition in 1-piperazino-3-phenylindans. Boegesoe, Klaus P. Journal of Medicinal Chemistry (1983), 26(7), 935-47.

13. Preparation, properties, and reactions of some conjugated heteroenoid compounds and related compounds. Holmes, H. L. Edited by Holmes, H. L. Struct.-Act. Relat. Some Conjugated Heteroenoid Compd., Catechol Monoethers Morphine Alkaloids (1975), 2, 625-725.

14. Polarographic half-wave potentials and ultraviolet absorption spectra of some conjugated heteroenoid compounds. Holmes, Henry L.; Currie, D. J. Canadian Journal of Chemistry (1969), 47(21), 4076-83.

15. Equilibrium reactions of butanethiol with some conjugated heteroenoid compounds. Pritchard, R. B.; Lough, C. E.; Currie, D. J.; Holmes, Henry L. Canadian Journal of Chemistry (1968), 46(5), 775-81.

16. C(sp3)-H functionalizations of light hydrocarbons using decatungstate photocatalysis in flow. Laudadio, Gabriele; Deng, Yuchao; van der Wal, Klaas; Ravelli, Davide; Nuno, Manuel; Fagnoni, Maurizio; Guthrie, Duncan; Sun, Yuhan; Noel, Timothy. Science (Washington, DC, United States) (2020), 369(6499), 92-96.

17. Eco-friendly conjugate hydrocyanation of α-cyanoacrylates using potassium hexacyanoferrate(II) as cyanating reagent. Zhang, Yu-Peng; Hu, Xiao-Chun; Li, Zheng From Chemical Papers (2015), 69(4), 596-603.

18. A core-shell-satellite structured Fe3O4S-NH2 d nanocomposite: a magnetically recyclable multifunctional catalyst for one-pot multistep cascade reaction sequences. Li, Ping; Yu, Yu; Liu, Hua; Cao, Chang-Yan; Song, Wei-Guo. Nanoscale (2014), 6(1), 442-448.

19. Construction of heterocycles via 1,4-dipolar cycloaddition of quinoline-DMAD zwitterion with various dipolarophiles. Nair, Vijay; Devipriya, S.; Suresh, Eringathodi. Tetrahedron (2008), 64(16), 3567-3577.

20. SciFinder; Structure Search. Chemical Abstracts Service: Columbus, OH; March 28, 2022. https://scifinder.cas.org

21. Synthesis and styrene copolymerization of novel trisubstituted ethylenes: 1. Alkyl ring-substituted 2-methoxyethyl phenylcyanoacrylates Maddy E. Ablan, Samer A. Abuelroos, Ryan C. Arthur, Sonya Balaji, Kimberly L. Burns, Ivana A. Chychula, Kayla

L. Corcoran, Yangfei Deng, Yelena Gritsaeva, Ana K. Hernandez, Sara M. Rocus, William S. Schjerven, and Gregory B. Kharas. ChemRxiv Version 1, Nov 22, 2020. https://doi.org/10.26434/chemrxiv.13262660.v1

22. Smith, M. B.; March, J. Addition to Carbon-Hetero Multiple Bonds, In March's Advanced Organic Chemistry, J. Wiley & Sons: New York, Ch.16, 1225, 2001.