Assembly of unsymmetrical 1,3,5-triarylbenzenes via tandem reaction of β -arylethenesulfonyl fluorides and α -cyano- β -methyleneones

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A transition-metal-free tandem reaction of β -arylethenesulfonyl fluorides and α -cyano- β -methyleneones has been revealed. In the presence of cesium carbonate, 2-arylethenesulfonyl fluorides react with α -cyano- β -methyleneones through a tandem Diels-Alder cycloaddition/sulfur (VI) fluoride exchange/elimination process to afford cyclohexadiene, which further undergoes decyanolative aromatization in one-pot to produce 1,3,5-triarylbenzenes in moderate to good yields. In addition, direct oxidative aromatization of cyclohexadiene intermediate will construct 2,4,6-triarylbenzonitriles.

1,3,5-Triarylbenzenes are privileged structural motifs found in many advanced functional materials, pharmaceuticals and biologically active molecules.¹ In particular, owing to their unique photophysical and electrochemical properties, 1,3,5-triarylbenzenes have been widely used as key building blocks in the synthesis of organic light-emitting diodes,² electrode devices,³ electroluminescent materials,⁴ conducting polymers,⁵ resist materials⁶ and potential chemosensors.⁷ Therefore, considerable efforts have been exerted to develop efficient methods for the construction of these versatile frameworks. In the past decades, transition-metal catalyzed [2+2+2] cyclootrimerization of aryl alkynes,⁸ acid-catalyzed condensation of aryl ketones⁹ and transition-metal catalyzed Suzuki-Miyaura reaction¹⁰ of 1,3,5-trihalobenzenes had been well established, which provide powerful tools for the synthesis of symmetrical 1,3,5-triarylbenzenes. In sharp contrast, efficient methods for the synthesis of unsymmetrical hetero-1,3,5-triarylbenzenes have rarely been developed. Transition-metal catalyzed heterotrimerization of different aryl alkynes and acid-catalyzed hetero condensation of different arylketones are inefficient for the synthesis of hetero-1,3,5-triarylbenzenes due to very low chemo- and regioselectivity. Transition-metal catalyzed cross-coupling reactions provide an important strategy for the synthesis of these unsymmetrical compounds.¹¹ However, this method often suffers from multistep reactions, unavoidable heavy metal wastes and harsh reaction conditions. Recently, Ye and coworkers¹² reported one of the most efficient to date methods for the preparation of unsymmetrical 1,3,5-triarylbenzenes through an N-heterocyclic carbene catalyzed tandem reaction of bromoenals. Despite progress made in this research field, the development of new method for the synthesis of unsymmetrical 1,3,5-triarylbenzenes is still highly desirable.

The sulfur (VI) fluoride exchange (SuFEx) click chemistry that first developed by Sharpless¹³ has been proven to be a powerful technology for modular assembly functional molecules. Among

different SuFEx connective hubs, ethenesulfonyl fluoride (ESF) and β -arylethenesulfonyl fluorides¹⁴ have gained significant attention because of the dual-functional nature. e.g., Arylethenesulfonyl fluorides can serve as bis-electrophiles to undergo tandem Michael addition/SuFEx click reaction¹⁵ to give δ -sultones efficiently. In line with our continued interest in the synthesis of polycyclic aromatic hydrocarbons¹⁶ and SuFEx click chemistry,¹⁷ we envisioned that arylethenesulfonyl fluorides can react with α -cyano- β -methyleneones through cycloaddition-SuFEx click reaction to give β -sultone-fused cyclohexadiene **A**, the elimination of which would lead to the formation of 1,3,5-triarylbenzenes.

Scheme 1. Working hypothesis

As shown in Table 1, we first tested the reaction of α -cyano- β -methyleneone **1a** with 1.5 equivalents β -arylethenesulfonyl fluoride **2a** in acetonitrile in the presence of Cs_2CO_3 under an air atmosphere at room temperature. Indeed, the desired triarylbenzene **3a** was successfully formed in 20% yield (Table 1, entry 1). When K_2CO_3 , or NaOH was used as base instead of Cs_2CO_3 , only very low yield was obtained (Table 1, entries 2 and 3). Organic bases, such as DBU, DBN, triethylamine, DMAP and pyridine did not promote the reaction (Table 1, entries 4-8). The screening of reaction media showed that most examined solvents were inefficient for the reaction (Table 1, entries 9-17), and only ethyl acetate afforded better yield (Table 1, entry 17). Increasing the amount of Cs_2CO_3 to 3.0 equivalents, the desired **3a** was furnished in 45% yield (Table 1, entries 18 and 19). Raising reaction temperature to 78 °C, the desired product was obtained in a maximum 56% yield (Table 1, entry 20). However, further increasing Cs_2CO_3 to 5.0 equivalents or using 2.0 equivalents of **2a** cannot improve the product formation (Table 1, entries 21 and 22). A comparable yield was obtained when the reaction was conducted under a nitrogen atmosphere (Table 1, entry 23). Our further elaboration of the reaction conditions did not obtain a higher yield of **3a**.

Table 1. Optimization of Reaction Conditions ^a

Entry	Base	Solvent	T	Time/h	Yield(%) ^b
1	Cs_2CO_3 (1.0 eq)	CH_3CN	rt	48	20

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2	K ₂ CO ₃ (1.0 eq)	CH ₃ CN	rt	48	9
3	NaOH (1.0 eq)	CH ₃ CN	rt	48	8
4	DBU (1.0 eq)	CH ₃ CN	rt	48	NR
5	DBN (1.0 eq)	CH ₃ CN	rt	48	NR
6	Et ₃ N (1.0 eq)	CH ₃ CN	rt	48	NR
7	DMAP (1.0 eq)	CH ₃ CN	rt	48	NR
8	pyridine (1.0 eq)	CH ₃ CN	rt	48	NR
9	Cs ₂ CO ₃ (1.0 eq)	Et ₂ O	rt	48	trace
10	Cs ₂ CO ₃ (1.0 eq)	MTBE	rt	48	trace
11	Cs ₂ CO ₃ (1.0 eq)	THF	rt	48	12
12	Cs ₂ CO ₃ (1.0 eq)	1,4-dioxane	rt	48	trace
13	Cs ₂ CO ₃ (1.0 eq)	DCM	rt	48	11
14	Cs ₂ CO ₃ (1.0 eq)	DCE	rt	48	trace
15	Cs ₂ CO ₃ (1.0 eq)	DMF	rt	48	trace
16	Cs ₂ CO ₃ (1.0 eq)	DMSO	rt	48	trace
17	Cs ₂ CO ₃ (1.0 eq)	EtOAc	rt	12	36
18	Cs ₂ CO ₃ (2.0 eq)	EtOAc	rt	12	40
19	Cs ₂ CO ₃ (3.0 eq)	EtOAc	rt	12	45
20	Cs ₂ CO ₃ (3.0 eq)	EtOAc	78 °C	5	56
21	Cs ₂ CO ₃ (5.0 eq)	EtOAc	78 °C	5	45
22 ^c	Cs ₂ CO ₃ (3.0 eq)	EtOAc	78 °C	5	49
23 ^d	Cs ₂ CO ₃ (3.0 eq)	EtOAc	78 °C	5	55

^a Reaction conditions: **1a** (0.20 mmol), **2a** (0.30 mmol), solvent 2.0 mL, room temperature, under air. ^b Isolated yields. ^c Using 2.0 equiv **2a**. ^d Under a nitrogen atmosphere.

With the optimized reaction conditions in hand, the generality of the tandem reaction was next examined (Table 2). Both electron-donating substituents (Ar¹, Ar² = 4-MeOC₆H₄, 4-MeC₆H₄) and electron-withdrawing substituents (Ar¹, Ar² = 4-ClC₆H₄, 4-FC₆H₄) substituted β-arylenones worked well, producing the desired 1,3,5-triarylbenzenes in moderate to good yields (**3a–3h**). In addition, different positions and electronic properties of the substituents on the aryl rings of β-arylenones have no obvious influence on the reaction yield (**3i–3m**). The bulky naphthyl-derived enones participated in the tandem reaction to afford the corresponding products in good yields (**3n–3p**). On the other hand, both electron-withdrawing and electron-donating substituted arylenesulfonfyl fluorides smoothly underwent the reaction to furnish the corresponding triarylbenzenes (**3q–3t**). When ESF was employed for the reaction, diphenyl benzene **3u** was formed in 50% yield.

Table 2. Synthesis of 1,3,5-triarylbenzenes ^{a, b}

^a Reaction condition: **1** (0.30 mmol), **2** (0.45 mmol), Cs₂CO₃ (0.90 mmol), EtOAc (3.0 mL), 78 °C, then, DBU (0.60 mmol), rt. ^b Isolated yields based on **1**.

During the synthesis of 1,3,5-triarylbenzenes, we isolated 2,4,6-triarylbenzotrioles as side products, which are important subunits found in many natural products and biologically active compounds. We concluded that the reaction was conducted in an air atmosphere, and the oxidation of cyclohexadiene intermediate **IV** (Scheme 2) by oxygen may produce these compounds. To our delight, with the addition of 1.5 equivalents 3,3',5,5'-tetra-butylidiphenylquinone (DQ) as oxidant to the reaction mixture,

different substituted benzonitriles were formed in moderate yield (Table 3).

Table 3. Synthesis of triarylbenzonitriles ^{a, b}

^a Reaction condition: **1** (0.30 mmol), **2** (0.45 mmol), Cs_2CO_3 (0.90 mmol), DQ (0.60 mmol), EtOAc (3.0 mL), 78 °C. ^b Isolated yields based on **1**.

Based on the pioneering work of Ye,¹² Qin¹⁵ and our previous studies,¹⁶ a plausible mechanism was proposed and depicted in Scheme 2. In the presence of a base, α -cyano- β -methyleneone undergoes deprotonation to generate dienolate intermediate **I**, which subsequently undergoes Diels-Alder reaction with arylethanesulfonyl fluoride to produce species **II**, the intramolecular SuFEx click reaction of intermediate **II** results in the formation of β -sultone fused cyclohexene **III**. The release of SO_3 leads to the formation of cyclohexadiene **IV**. Finally, DBU-promoted elimination of HCN results in the formation of 1,3,5-triarylbenzene. Additionally, in the presence of oxidant DQ, **IV** will undergo oxidative aromatization to produce triaryl benzonitrile.

Scheme 2. Proposed Mechanism

In order to further shed light on the mechanism of the reaction, several control experiments were then conducted (Scheme 3). At the first stage of the reaction, we successfully isolated cyclohexadiene intermediate **3u'** in 55% yield (eq 1), and the structure of which was confirmed by single-crystal X-ray analysis.¹⁸ Under the promotion of 2.0 equivalents of DBU, **3u'** undergoes

decanolative aromatization to afford **3u** in 95% yield (eq 2). The oxidation of **3u'** gives benzonitrile **4f** in 88% yield (eq 2).

Scheme 3. Control Experiments

Conclusions

In conclusion, we have developed a novel protocol for the synthesis of unsymmetrical 1,3,5-triarylbenzenes. This protocol features the application of SuFEx click chemistry, transition-metal-free conditions and simple "one-pot" synthesis. Further studies on the applications of this method are currently underway in our laboratory.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- (a) T. R. Cook, Y.-R. Zheng and P. J. Stang, Metal–Organic Frameworks and Self-Assembled Supramolecular Coordination Complexes: Comparing and Contrasting the Design, Synthesis, and Functionality of Metal–Organic Materials, *Chem. Rev.*, 2013, **113**, 734–777; (b) F. F. Becker, C. Mukhopadhyay, L. Hackfeld, I. Banik and B. K. Banik, Polycyclic aromatic compounds as anticancer agents: synthesis and biological evaluation of dibenzofluorene derivatives, *Bioorg. Med. Chem.*, 2000, **8**, 2693–2699; (c) D. H. Williams and B. Bardsley, The Vancomycin Group of Antibiotics and the Fight against Resistant Bacteria, *Angew. Chem. Int. Ed. Engl.*, 1999, **38**, 1172–1193; (d) K. C. Nicolaou, C. N. Boddy, S. Brase and N. Winssinger, Chemistry, Biology, and Medicine of the Glycopeptide Antibiotics, *Angew. Chem. Int. Ed. Engl.*, 1999, **38**, 2096–2152.
- (a) S. Kotha, D. Kashinath and S. Kumar, Synthesis of liquid crystalline materials based on 1,3,5-triphenylbenzene and 2,4,6-triphenyl-1,3,5-s-triazine, *Tetrahedron Lett.*, 2008, **49**, 5419–5423; (b) J. Luo, Y. Zhou, Z.-Q. Niu, Q.-F. Zhou, Y. Ma and J. Pei, Three-Dimensional Architectures for Highly Stable Pure Blue Emission, *J. Am. Chem. Soc.*, 2007, **129**, 11314–11315; (c) I. A. Khotina, O. E. Shmakova, D. Y. Baranova, N. S. Burenkova, A. A. Gurskaja, P. M. Valetsky and L. M. Bronstein, Highly Branched Polyphenylenes with 1,3,5-Triphenylbenzene Fragments via Cyclocondensation of

- Acetylaromatic Compounds and NiO-Catalyzed Dehalogenation: Synthesis and Light Emission, *Macromolecules*, 2003, **36**, 8353-8360; (d) K. Suzuki, A. Seno, H. Tanabe and K. Ueno, New host materials for blue emitters, *Synth. Met.*, 2004, **143**, 89-96.
3. (a) M. J. Plater, M. McKay and T. Jackson, Synthesis of 1,3,5-tris[4-(diaryl amino)phenyl]benzene and 1,3,5-tris(diaryl amino)benzene derivatives, *J. Chem. Soc., Perkin Trans. 1*, 2000, **16**, 2695-2701; (b) L. Akcelrud, Electroluminescent polymers, *Prog. Polym. Sci.*, 2003, **28**, 875-962.
 4. J. Pang, E. J. P. Marcotte, C. Seward, R. S. Brown and S. Wang, A blue luminescent star-shaped ZnII complex that can detect benzene, *Angew. Chem. Int. Ed.*, 2001, **40**, 4042-4045.
 5. (a) L.-R. Tsai, C.-W. Li and Y. Chen, Synthesis, characterization, and optoelectronic properties of hyperbranched polyfluorenes containing pendant benzylether dendrons, *Journal of Polym. Sci. Part A: Polym. Chem.*, 2008, **46**, 5945-5958; (b) C. Gu, N. Huang, J. Gao, F. Xu, Y. Xu and D. Jiang, Controlled Synthesis of Conjugated Microporous Polymer Films: Versatile Platforms for Highly Sensitive and Label-Free Chemo- and Biosensing, *Angew. Chem. Int. Ed.*, 2014, **53**, 4850-4855.
 6. Y. Shirota, Photo- and electroactive amorphous molecular materials—molecular design, syntheses, reactions, properties, and applications, *J. Mater. Chem.*, 2005, **15**, 75-93.
 7. P. Vishnoi, M. G. Walawalkar, S. Sen, A. Datta, G. N. Patwari and R. Murugavel, Selective fluorescence sensing of polynitroaromatic explosives using triaminophenylbenzene scaffolds, *Phys. Chem. Chem. Phys.*, 2014, **16**, 10651-10658.
 8. (a) M. Amatore and C. Aubert, Recent Advances in Stereoselective [2+2+2] Cycloadditions, *Eur. J. Org. Chem.*, 2015, **2015**, 265-286; (b) A. Roglans, A. Pla-Quintana and M. Solà, Mechanistic Studies of Transition-Metal-Catalyzed [2+2+2] Cycloaddition Reactions, *Chem. Rev.*, 2021, **121**, 1894-1979; (c) D. L. J. Broere and E. Ruijter, Recent Advances in Transition-Metal-Catalyzed [2+2+2]-Cyclo(co)trimerization Reactions, *Synthesis*, 2012, **44**, 2639-2672; (d) K. Yang, P. Wang, Z.-Y. Sun, M. Guo, W. Zhao, X. Tang and G. Wang, Hydrogen-Bonding Controlled Nickel-Catalyzed Regioselective Cyclotrimerization of Terminal Alkynes, *Org. Lett.*, 2021, **23**, 3933-3938; (e) A. F. Orsino, M. Gutiérrez del Campo, M. Lutz and M.-E. Moret, Enhanced Catalytic Activity of Nickel Complexes of an Adaptive Diphosphine-Benzophenone Ligand in Alkyne Cyclotrimerization, *ACS Catal.*, 2019, **9**, 2458-2481; (f) C. B. Provis-Evans, S. Lau, V. Krewald and R. L. Webster, Regioselective Alkyne Cyclotrimerization with an In Situ-Generated [Fe(II)H(salen)]-Bpin Catalyst, *ACS Catal.*, 2020, **10**, 10157-10168; (g) M. Neumeier, U. Chakraborty, D. Schaarschmidt, V. de la Pena O'Shea, R. Perez-Ruiz and A. Jacobi von Wangelin, Combined Photoredox and Iron Catalysis for the Cyclotrimerization of Alkynes, *Angew. Chem. Int. Ed.*, 2020, **59**, 13473-13478; (h) K. V. Wagh and B. M. Bhanage, Amberlyst-15/[Bmim][PF₆] Catalyzed Synthesis of C3-Symmetric Triarylbenzenes via Cyclotrimerization of Alkynes, *ACS Sustainable Chem. Eng.*, 2016, **4**, 4232-4236; (i) A. Sen, T. Sato, A. Ohno, H. Baek, A. Muranaka and Y. M. A. Yamada, Polymer-Supported-Cobalt-Catalyzed Regioselective Cyclotrimerization of Aryl Alkynes, *JACS Au*, 2021, **1**, 2080-2087; (j) J. Nogami, Y. Tanaka, H. Sugiyama, H. Uekusa, A. Muranaka, M. Uchiyama and K. Tanaka, Enantioselective Synthesis of Planar Chiral Zigzag-Type Cyclophenylene Belts by Rhodium-Catalyzed Alkyne Cyclotrimerization, *J. Am. Chem. Soc.*, 2020, **142**, 9834-9842; (k) T. Sugahara, J.-D. Guo, T. Sasamori, S. Nagase and N. Tokitoh, Regioselective Cyclotrimerization of Terminal Alkynes Using a Digermyne, *Angew. Chem. Int. Ed.*, 2018, **57**, 3499-3503; (l) L. Shen, Y. Zhao, Q. Luo, Q.-S. Li, B. Liu, C. Redshaw, B. Wu and X.-J. Yang, Cyclotrimerization of alkynes catalyzed by a self-supported cyclic tri-nuclear nickel(0) complex with α -diimine ligands, *Dalton Trans.*, 2019, **48**, 4643-4649.
 9. (a) J.-X. Yang, X.-T. Tao, C. X. Yuan, Y. X. Yan, L. Wang, Z. Liu, Y. Ren and M.-H. Jiang, A Facile Synthesis and Properties of Multicarbazole Molecules Containing Multiple Vinylene Bridges, *J. Am. Chem. Soc.*, 2005, **127**, 3278-3279; (b) X.-Y. Cao, X.-H. Liu, X.-H. Zhou, Y. Zhang, Y. Jiang, Y. Cao, Y.-X. Cui and J. Pei, Giant Extended π -Conjugated Dendrimers Containing the 10,15-Dihydro-5H-diindeno[1,2-a;1',2'-c]fluorene Chromophore: Synthesis, NMR Behaviors, Optical Properties, and Electroluminescence, *J. Org. Chem.*, 2004, **69**, 6050-6058; (c) A. Kumar, M. Dixit, S. P. Singh, R. Raghunandan, P. R. Maulik and A. Goel, Reusable resin Amberlyst 15 catalyzed new convenient protocol for accessing arylated benzene scaffolds, *Tetrahedron Lett.*, 2009, **50**, 4335-4339; (d) R. Tayebjee and M. Jarrahi, H6P2W18O62/Nanoclinoptilolite as an efficient nanohybrid catalyst in the cyclotrimerization of aryl methyl ketones under solvent-free conditions, *RSC Adv.*, 2015, **5**, 21206-21214; (e) K. Deng, Q.-Y. Huai, Z.-L. Shen, H.-J. Li, C. Liu and Y.-C. Wu, Rearrangement of Dypnones to 1,3,5-Triarylbenzenes, *Org. Lett.*, 2015, **17**, 1473-1476; (f) Y. Zhao, J. Li, C. Li, K. Yin, D. Ye and X. Jia, PTSA-catalyzed green synthesis of 1,3,5-triarylbenzene under solvent-free conditions, *Green Chem.*, 2010, **12**, 1370-1372.
 10. (a) L. Liu, Y. Dong, B. Pang and J. Ma, [Bmim]PF₆-Promoted Ligandless Suzuki-Miyaura Coupling Reaction of Potassium Aryltrifluoroborates in Water, *J. Org. Chem.*, 2014, **79**, 7193-7198; (b) S. Paul and J. H. Clark, A highly active and reusable heterogeneous catalyst for the Suzuki reaction: synthesis of biaryls and polyaryls, *Green Chem.*, 2003, **5**, 635-638; (c) M. A. Pena, I. Pérez, J. P. Sestelo and L. A. Sarandeses, Multifold and sequential cross-coupling reactions with indium organometallics, *Chem. Commun.*, 2002, **19**, 2246-2247; (d) H. Noguchi, T. Shioda, C.-M. Chou and M. Suginome, Differentially Protected Benzenediboronic Acids: Divalent Cross-Coupling Modules for the Efficient Synthesis of Boron-Substituted Oligoarenes, *Org. Lett.*, 2008, **10**, 377-380; (e) P. A. Bonvallet, C. J. Breitzkreuz, Y. S. Kim, E. M. Todd, K. Traynor, C. G. Fry, M. D. Ediger and R. J. McMahon, Organic Glass-Forming Materials: 1,3,5-Tris(naphthyl)benzene Derivatives, *J. Org. Chem.*, 2007, **72**, 10051-10057; (f) V. Ramakrishna and N. Dastagiri Reddy, Synthesis of zwitterionic palladium complexes and their application as catalysts in cross-coupling reactions of aryl, heteroaryl and benzyl bromides with organoboron reagents in neat water, *Dalton Trans.*, 2017, **46**, 8598-8610.
 11. (a) D.-G. Yu, M. Yu, B.-T. Guan, B.-J. Li, Y. Zheng, Z.-H. Wu and Z.-J. Shi, Carbon-Carbon Formation via Ni-Catalyzed Suzuki-Miyaura Coupling through C-CN Bond Cleavage of Aryl Nitrile, *Org. Lett.*, 2009, **11**, 3374-3377; (b) F. Zhao, Y.-F. Zhang, J. Wen, D.-G. Yu, J.-B. Wei, Z. Xi and Z.-J. Shi, Programmed Selective sp² C-O Bond Activation toward Multiarylated Benzenes, *Org. Lett.*, 2013, **15**, 3230-3233.
 12. (a) C.-L. Zhang and S. Ye, N-Heterocyclic Carbene-Catalyzed Construction of 1,3,5-Trisubstituted Benzenes from Bromoenals and α -Cyano- β -methylenones, *Org. Lett.*, 2016, **18**, 6408-6411; (b) C.-L. Zhang, Z.-F. Zhang, Z.-H. Xia, Y.-F. Han and S. Ye, DBU-Mediated Construction of 1,3,5-Trisubstituted Benzenes via Annulation of α,β -Unsaturated Carboxylic Acids and α -Cyano- β -methylenones, *J. Org. Chem.*, 2018, **83**, 12507-12513; (c) T. Zhu, C. Mou, B. Li, M. Smetankova, B.-A. Song and Y.-R. Chi, N-Heterocyclic Carbene-Catalyzed δ -Carbon LUMO Activation of Unsaturated Aldehydes, *J. Am. Chem. Soc.*, 2015, **137**, 5658-5661; (d) C.-L. Zhang, Z.-H. Gao,

- Z.-Q. Liang and S. Ye, N-Heterocyclic Carbene-Catalyzed Synthesis of Multi-Substituted Benzenes from Enals and α -Cyano- β -methylenones, *Adv. Synth. Catal.*, 2016, **358**, 2862-2866. (e) J. Wu, C. Mou, and Y.-R. Chi, Construction of Multi-Substituted Benzenes via NHC-Catalyzed Reactions of Carboxylic Esters, *Chin. J. Chem.* 2018, **36**, 333-337. (f) T. Zhu, P. Zheng, C. Mou, S. Yang, B.-A. Song, Y. R. Chi, Benzene construction via organocatalytic formal [3+3] cycloaddition reaction, *Nat. Commun.* 2014, **5**, 5027.
13. (a) J. Dong, L. Krasnova, M. G. Finn and K. B. Sharpless, Sulfur(VI) Fluoride Exchange (SuFEx): Another Good Reaction for Click Chemistry, *Angew. Chem. Int. Ed.*, 2014, **53**, 9430-9448; (b) A. S. Barrow, C. J. Smedley, Q. Zheng, S. Li, J. Dong and J. E. Moses, The growing applications of SuFEx click chemistry, *Chem. Soc. Rev.*, 2019, **48**, 4731-4758; (c) C. Lee, A. J. Cook, J. E. Elisabeth, N. C. Friede, G. M. Sammis and N. D. Ball, The Emerging Applications of Sulfur(VI) Fluorides in Catalysis, *ACS Catal.*, 2021, **11**, 6578-6589.
14. Y.-P. Meng, S.-M. Wang, W.-Y. Fang, Z.-Z. Xie, J. Leng, H. Alsulami and H.-L. Qin, Ethenesulfonyl Fluoride (ESF) and Its Derivatives in SuFEx Click Chemistry and More, *Synthesis*, 2020, **52**, 673-687.
15. (a) G.-F. Zha, G. A. L. Bare, J. Leng, Z.-P. Shang, Z. Luo and H.-L. Qin, Gram-Scale Synthesis of β -(Hetero)arylethenesulfonyl Fluorides via a Pd(OAc)₂ Catalyzed Oxidative Heck Process with DDQ or AgNO₃ as an Oxidant, *Adv. Synth. Catal.*, 2017, **359**, 3237-3242; (b) X. Chen, G.-F. Zha, G. A. L. Bare, J. Leng, S.-M. Wang and H.-L. Qin, Synthesis of a Class of Fused δ -Sultone Heterocycles via DBU-Catalyzed Direct Annulative SuFEx Click of Ethenesulfonyl Fluorides and Pyrazolones or 1,3-Dicarbonyl Compounds, *Adv. Synth. Catal.*, 2017, **359**, 3254-3260; (c) X. Chen, G.-F. Zha, W.-Y. Fang, K. P. Rakesh and H.-L. Qin, A portal to a class of novel sultone-functionalized pyridines via an annulative SuFEx process employing earth abundant nickel catalysts, *Chem. Commun.*, 2018, **54**, 9011-9014.
16. (a) W. Wang, H. Wan, G.-F. Du, B. Dai and L. He, Synthesis of Benzo[b]fluoranthenes and Spiroacridines from Fluorene-Derived Alkenes and N-Arylimines via a Tandem Reaction with Benzyne, *Org. Lett.*, 2019, **21**, 3496-3500; (b) Q. Wang, Y. An, G.-F. Du, Z.-H. Cai, B. Dai and L. He, Direct Assembly of Polysubstituted Naphthalenes via a Tandem Reaction of Benzyne and α -Cyano- β -methylenones, *J. Org. Chem.*, 2020, **85**, 14210-14218; (c) Y. An, F. Zhang, Z.-H. Cai, G.-F. Du, Direct Assembly of Polysubstituted Benzenes via Base-Catalyzed Benzannulation Reaction of α -Cyano- β -methylalkenyl-(hetero)aryl Ketones, *Chin. J. Org. Chem.* 2021, **41**, 3625-3632; (d) Y. An, F. Zhang, G.-F. Du, Z.-H. Cai and L. He, Construction of 6H-benzo[c]thiochromenes via a tandem reaction of arynes with thionoesters, *Org. Chem. Front.*, 2021, **8**, 6979-6984.
17. M.-Z. Lin, J.-Y. Luo, Y. Xie, G.-F. Du, Z.-H. Cai, B. Dai and L. He, Organocatalytic Silicon-Free SuFEx reactions for modular synthesis of sulfonate esters and sulfonamides, *ChemRxiv*, 2021, doi: 10.26434/chemrxiv-2021-kw8xx.
18. CCDC 2118497 (**3u'**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary Information

Assembly of unsymmetrical 1,3,5-triarylbenzenes via tandem reaction of β -arylethenesulfonyl fluorides and α -cyano- β -methylenones

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1. General information.

Unless otherwise indicated, all reactions were conducted under air atmosphere in oven-dried glassware with magnetic stirring bar. All other chemicals were obtained from commercial supplies and used as received without any further purification. Column chromatograph was performed with silica gel (200~300 mesh) and analytical TLC on silica gel 60-F₂₅₄. ¹H, ¹³C, ¹⁹F NMR spectras were recorded on a Bruker AVANCE III spectrometer (400 MHz, 100 MHz and 376 MHz, respectively), Chemical shifts are reported parts per million (ppm) referenced to CDCl₃ (δ 7.26 ppm), tetramethylsilane (TMS, δ 0.00 ppm) for ¹H, ¹³C and ¹⁹F NMR. Melting points of the products were measured on a micro melting point apparatus (SGW X-4) and uncorrected. High-resolution mass spectra (HRMS) were obtained on a Q Exactive mass spectrometry and a LTQ Orbitrap XL mass spectrometry equipped with an EI or ESI source from Thermo Scientific. X-Ray diffraction study for product **3u'** was carried out on Bruker D8 VENTURE photon II diffractometer with I μ s 3.0 microfocus X-ray source using APEX III program.

2. General procedure for the synthesis of 1,3,5-triarylbenzenes

A 25 mL Schlenk tube equipped with a stir bar was charged with β -arylenone **1** (0.30 mmol), 2-arylethenesulfonyl fluoride **2** (0.45 mmol), and Cs₂CO₃ (0.90 mmol), ethyl acetate (3 mL) was added in turn to the Schlenk tube. The reaction mixture was stirred at 78 °C for 2 h until complete consumption of the starting

material (monitored by TLC). Then DBU was added to the reaction mixture and stirred for 2 h at room temperature. When the reaction was finished, the reaction mixture was diluted by dichloromethane, and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (silica gel, PE/EtOAc (v : v) = 300:1) to afford the desired product **3**.

3. General procedure for the synthesis of 1,3,5-triarylbenzonitriles

A 25 mL Schlenk tube equipped with a stir bar was charged with β -arylenones **1** (0.30 mmol), 2-arylethanesulfonyl fluorides **2** (0.45 mmol), DQ (0.60 mmol) and Cs_2CO_3 (0.90 mmol), ethyl acetate (3 mL) was added in turn to the Schlenk tube. The reaction mixture was stirred at 78 °C for 5 h until complete consumption of the starting material (monitored by TLC). When the reaction was finished, the reaction mixture was diluted by dichloromethane, and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (silica gel, PE/EtOAc (v : v) = 20:1) to afford the desired product **4**.

4. General procedure for control experiments.

A 25 mL Schlenk tube equipped with a stir bar was charged with enone **1a** (0.30 mmol), and Cs_2CO_3 (0.90 mmol), ethyl acetate (3 mL) and vinyl sulfonyl

fluoride **2u** (0.45 mmol) were added in turn to the Schlenk tube. The reaction mixture was stirred at 78 °C for 12 h until complete consumption of the starting material (monitored by TLC). When the reaction was finished, the reaction mixture was diluted by dichloromethane, and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (silica gel, PE/EtOAc (v : v) = 20:1) to afford the desired product **3u'** (55%, 42.4 mg).

A 25 mL Schlenk tube equipped with a stir bar was charged with **3u'** (31.0 mg, 0.12 mmol), ethyl acetate (1 mL) and DBU (37.0 mg, 0.24 mmol) was added in turn to the Schlenk tube. When the reaction was finished, the reaction mixture was diluted by dichloromethane, and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (silica gel, PE/EtOAc (v : v) = 300:1) to afford the desired product **3u**.

A 25 mL Schlenk tube equipped with a stir bar was charged with **3u'** (31.0 mg, 0.12 mmol) and DQ (98.0 mg, 0.24 mmol), ethyl acetate (1 mL) was added in turn to the Schlenk tube. When the reaction was finished, the reaction mixture was diluted by dichloromethane, and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (silica gel, PE/EtOAc (v : v) = 20:1) to afford the desired product **4f**.

5. Single-crystal X-ray structure analysis

Figure S1. Crystal structure of **3u'**

data-**3u'**

Table S1. Crystal data and structure refinement for **3u'**

Identification code	3u'	
Empirical formula	C ₁₉ H ₁₄ N	
Formula weight	256.31	
Temperature	173.0 K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	Pmn2 ₁	
Unit cell dimensions	a = 14.1719(5) Å	a = 90°.
	b = 8.9226(3) Å	b = 90°.
	c = 5.6638(2) Å	g = 90°.
Volume	716.19(4) Å ³	
Z	2	
Density (calculated)	1.189 Mg/m ³	
Absorption coefficient	0.528 mm ⁻¹	
F(000)	270	
Crystal size	0.16 x 0.13 x 0.12 mm ³	
Theta range for data collection	4.956 to 72.166°.	
Index ranges	-17<=h<=14, -11<=k<=11, -6<=l<=6	
Reflections collected	8521	
Independent reflections	1417 [R(int) = 0.0456]	
Completeness to theta = 67.679°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7536 and 0.6855	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1417 / 67 / 114	
Goodness-of-fit on F ²	1.083	
Final R indices [I>2sigma(I)]	R1 = 0.0337, wR2 = 0.0925	
R indices (all data)	R1 = 0.0353, wR2 = 0.0936	
Absolute structure parameter	0.5	
Extinction coefficient	0.008(3)	
Largest diff. peak and hole	0.158 and -0.137 e.Å ⁻³	

The CCDC number of product **3u'** is 2118497.

6. Characterization data of products

5'-phenyl-1,1':3',1''-terphenyl (known compound) ¹ White solid, 51.4 mg, 56% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.79 (s, 3H), 7.73 – 7.66 (m, 6H), 7.52 – 7.44 (m, 6H), 7.43 – 7.34 (m, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 142.5, 141.3, 129.0, 127.7, 127.5, 125.3.

4-methoxy-5'-phenyl-1,1':3',1''-terphenyl (known compound) ¹ White solid, 47.4 mg, 47% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.74 (s, 3H), 7.72 – 7.67 (m, 4H), 7.66 – 7.61 (m, 2H), 7.51 – 7.44 (m, 4H), 7.42 – 7.35 (m, 2H), 7.04 – 6.98 (m, 2H), 3.87 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 159.5, 142.5, 142.1, 141.4, 133.8, 129.0, 128.5, 127.6, 127.5, 124.9, 124.8, 114.4, 55.5.

4-chloro-4''-methoxy-5'-phenyl-1,1':3',1''-terphenyl (known compound) ¹ White solid, 46.7 mg, 42% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.75 (s, 1H), 7.71 – 7.65 (m, 4H), 7.62 (d, *J* = 8.4 Hz, 4H), 7.52 – 7.38 (m, 5H), 7.04 – 6.98 (m, 2H), 3.87 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 159.6, 142.6, 142.2, 141.2, 139.8, 133.8, 133.6, 129.1, 129.0, 128.7, 128.5, 127.8, 127.5, 125.2, 124.7, 124.5, 114.5, 55.5.

4-methyl-5'-phenyl-1,1':3',1''-terphenyl (known compound) ¹ White solid, 48.1 mg, 50% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.74 (m, 3H), 7.72 – 7.66 (m, 4H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.44 (m, 4H), 7.41 – 7.35 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 142.5, 142.4, 141.4, 138.4, 137.5, 129.7, 129.0, 127.7, 127.5, 127.3, 125.1, 125.0, 21.3.

4-chloro-4''-methyl-5'-phenyl-1,1':3',1''-terphenyl White solid, 65.9 mg, 62% yield. m.p. 160.3-161.0 °C; IR (cm⁻¹): 3030, 2922, 2854, 1595, 1549, 1492, 1091, 813, 761, 698; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.78 (s, 1H), 7.74 – 7.65 (m, 4H), 7.65 – 7.55 (m, 4H), 7.51 – 7.37 (m, 5H), 7.29 (d, *J* = 7.6 Hz, 2H), 2.42 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 142.6, 142.5, 141.2, 139.8, 138.2, 137.6, 133.8, 129.7, 129.1, 129.0, 128.7, 127.8, 127.5, 127.3, 125.4, 124.9, 124.8, 21.3; HRMS (EI) *m/z* calcd for C₂₅H₁₉Cl [M]⁺ 354.1175, found 354.1168.

4-fluoro-4''-methyl-5'-phenyl-1,1':3',1''-terphenyl White solid, 49.7 mg, 49% yield. m.p. 127.3-128.4 °C; IR (cm⁻¹): 3049, 2954, 2854, 1603, 1511, 1230, 1158, 913, 743, 692; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.76 (s, 1H), 7.72 – 7.63 (m, 6H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.50 – 7.45 (m, 2H), 7.42 – 7.36 (m, 1H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.22 – 7.09 (m, 2H), 2.42 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 162.7 (d, *J* = 249.0 Hz), 142.6, 142.5, 141.5, 141.3, 138.3, 137.6, 129.7, 129.09, 129.00, 127.7, 127.5, 127.3, 125.1, 125.0, 115.9 (d, *J* = 22.0 Hz), 21.3; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -112.9; HRMS (EI) *m/z* calcd for C₂₅H₁₉F [M]⁺ 338.1471, found 338.1462.

4-fluoro-5'-phenyl-1,1':3,1''-terphenyl (known compound) ¹ White solid, 48.6 mg, 50% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.74 (m, 1H), 7.74 – 7.70 (m, 2H), 7.70 – 7.66 (m, 4H), 7.66 – 7.59 (m, 2H), 7.51 – 7.42 (m, 4H), 7.42 – 7.34 (m, 2H), 7.20 – 7.09 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 162.8 (d, J = 245.0 Hz), 142.6, 141.5, 141.2, 137.4 (d, J = 3.0 Hz), 129.1, 129.0, 127.8, 127.5, 125.3, 125.2, 115.9 (d, J = 21.0 Hz); ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -115.3.

4,4''-dichloro-5'-(p-tolyl)-1,1':3,1''-terphenyl White solid, 53.7 mg, 46% yield. m.p. 239.5-240.2 °C; IR (cm⁻¹): 3535, 2392, 2280, 1598, 1513, 1492, 1441, 1092, 1012, 811; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.67 (m, 2H), 7.64 (s, 1H), 7.62 – 7.52 (m, 6H), 7.43 (d, J = 8.2 Hz, 4H), 7.28 (d, J = 8.0 Hz, 2H), 2.41 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 142.8, 141.4, 139.6, 138.0, 137.8, 133.9, 129.8, 129.2, 128.7, 127.3, 125.2, 124.6, 21.3; HRMS (EI) m/z calcd for C₂₅H₁₈Cl₂ [M]⁺ 388.0786, found 388.0779.

3-fluoro-4''-methyl-5'-phenyl-1,1':3,1''-terphenyl White solid, 50.7 mg, 50% yield. m.p. 135.0-136.4 °C; IR (cm⁻¹): 3056, 3035, 2923, 2851, 2367, 1584, 1514, 1179, 756, 697; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.77 (m, 1H), 7.76 – 7.71 (m, 2H), 7.71 – 7.64 (m, 2H), 7.63 – 7.55 (m, 2H), 7.52 – 7.45 (m, 3H), 7.44 – 7.35 (m, 3H), 7.29 (d, J = 8.0 Hz, 2H), 7.13 – 7.01 (m, 1H), 2.42 (s, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 163.4 (d, J = 244.0 Hz), 143.6 (d, J = 8.0 Hz), 142.6,

142.5, 141.1, 138.1, 137.7, 130.4 (d, $J = 8.0$ Hz), 129.8, 129.0, 127.8, 127.5, 127.3, 125.7, 125.0, 124.9, 123.1 (d, $J = 2.0$ Hz), 114.44 (d, $J = 21.0$ Hz), 114.38 (d, $J = 22.0$ Hz), 21.3; ^{19}F NMR (376 MHz, Chloroform- d) δ -113.0; HRMS (EI) m/z calcd for $\text{C}_{25}\text{H}_{19}\text{F}$ $[\text{M}]^+$ 338.1471, found 338.1462.

3-methyl-5'-phenyl-1,1':3',1''-terphenyl (known compound) ² White solid, 49.0 mg, 51% yield; ^1H NMR (400 MHz, Chloroform- d) δ 7.79 – 7.74 (m, 3H), 7.72 – 7.66 (m, 4H), 7.52 – 7.43 (m, 6H), 7.41 – 7.32 (m, 3H), 7.21 – 7.17 (m, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, Chloroform- d) δ 142.6, 142.4, 141.3, 141.2, 138.6, 129.0, 128.9, 128.4, 128.3, 127.7, 127.5, 125.3, 125.2, 124.6, 21.7.

4'-chloro-3-methyl-5'-phenyl-1,1':3',1''-terphenyl White solid, 55.3 mg, 52% yield. m.p. 156.0-157.1 $^{\circ}\text{C}$; IR (cm^{-1}): 3034, 2924, 2854, 1596, 1494, 1092, 878, 826, 760, 699; ^1H NMR (400 MHz, Chloroform- d) δ 7.72 – 7.68 (m, 1H), 7.64 (s, 2H), 7.60 (d, $J = 8.0$ Hz, 2H), 7.54 (d, $J = 8.4$ Hz, 2H), 7.43 – 7.36 (m, 5H), 7.36 – 7.26 (m, 3H), 7.15 – 7.10 (m, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, Chloroform- d) δ 142.8, 142.6, 141.2, 141.1, 139.8, 138.6, 133.8, 129.1, 129.0, 128.9, 128.7, 128.5, 128.3, 127.8, 127.5, 125.6, 125.1, 125.0, 124.6, 21.7; HRMS (EI) m/z calcd for $\text{C}_{25}\text{H}_{19}\text{Cl}$ $[\text{M}]^+$ 354.1175, found 354.1168.

3-fluoro-3''-methyl-5'-phenyl-1,1':3',1''-terphenyl White solid, 51.7 mg, 51% yield. m.p. 138.5-139.1 $^{\circ}\text{C}$; IR (cm^{-1}): 3056, 2922, 1610, 1582, 1408, 1265, 1178, 866, 752, 696; ^1H NMR (400 MHz, Chloroform- d) δ 7.80 (s, 1H), 7.75 (s, 2H), 7.70 (d, $J = 7.2$ Hz, 1H), 7.52 – 7.46 (m, 5H), 7.45 – 7.35 (m, 4H), 7.22 (d, $J = 7.6$ Hz,

1H), 7.08 (t, $J = 7.6$ Hz, 1H), 2.45 (s, 1H); ^{13}C NMR (100 MHz, Chloroform- d) δ 163.4 (d, $J = 244.0$ Hz), 143.6, 142.8, 142.6, 141.2, 141.1 (d, $J = 7.0$ Hz), 138.7, 130.5 (d, $J = 8.0$ Hz), 129.0, 128.9, 128.6, 128.3, 127.8, 127.5, 125.9, 125.2, 125.1, 124.6, 123.1 (d, $J = 3.0$ Hz), 114.5 (d, $J = 21.0$ Hz), 114.4 (d, $J = 23.0$ Hz), 21.7; ^{19}F NMR (376 MHz, Chloroform- d) δ -113.0; HRMS (EI) m/z calcd for $\text{C}_{25}\text{H}_{19}\text{F}$ $[\text{M}]^+$ 338.1471, found 338.1462.

3,5-difluoro-5'-phenyl-1,1':3',1''-terphenyl (known compound) ³ White solid, 45.1 mg, 44% yield; ^1H NMR (400 MHz, Chloroform- d) δ 7.82 (s, 1H), 7.75 – 7.70 (m, 2H), 7.70 – 7.65 (m, 4H), 7.49 (t, $J = 7.6$ Hz, 4H), 7.44 – 7.36 (m, 2H), 7.24 – 7.16 (m, 2H), 6.90 – 6.74 (m, 1H); ^{13}C NMR (100 MHz, Chloroform- d) δ 163.5 (dd, $J = 246.0$ Hz), 144.6 (t, $J = 9.0$ Hz), 142.8, 140.8, 140.2, 129.1, 127.9, 127.5, 126.4, 125.0, 110.3 (dd, $J = 18.0$ Hz), 102.9 (t, $J = 25.0$ Hz); ^{19}F NMR (376 MHz, Chloroform- d) δ -109.5.

2-([1,1':3',1''-terphenyl]-5'-yl)naphthalene (known compound) ⁴ White solid, 67.3 mg, 63% yield; ^1H NMR (400 MHz, Chloroform- d) δ 8.14 (s, 1H), 7.96 – 7.89 (m, 4H), 7.89 – 7.79 (m, 3H), 7.75 – 7.68 (m, 4H), 7.54 – 7.45 (m, 6H), 7.43 – 7.34 (m, 2H); ^{13}C NMR (100 MHz, Chloroform- d) δ 142.6, 142.4, 141.3, 138.6, 133.8, 132.9, 129.0, 128.7, 128.4, 127.8, 127.7, 127.5, 126.5, 126.2, 125.8, 125.6, 125.4.

2-(4-chloro-[1,1':3',1''-terphenyl]-5'-yl)naphthalene White solid, 56.2 mg, 48% yield. m.p. 188.2-189.0 °C; IR (cm⁻¹): 3053, 2956, 2853, 1594, 1492, 1092, 885, 816, 760, 701; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.99 – 7.91 (m, 3H), 7.91 – 7.81 (m, 3H), 7.77 (s, 1H), 7.74 – 7.68 (m, 2H), 7.68 – 7.62 (m, 2H), 7.57 – 7.50 (m, 3H), 7.50 – 7.43 (m, 3H), 7.43 – 7.38 (m, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 142.8, 142.6, 141.4, 141.1, 139.7, 138.4, 133.9, 133.8, 132.9, 129.2, 129.1, 128.8, 128.4, 127.8, 127.5, 126.6, 126.3, 126.2, 125.9, 125.7, 125.3, 125.2; HRMS (EI) *m/z* calcd for C₂₈H₁₉Cl [M]⁺ 390.1175, found 390.1170.

2-(4-fluoro-[1,1':3',1''-terphenyl]-5'-yl)naphthalene White solid, 50.5 mg, 45% yield. m.p. 193.4-194.2 °C; IR (cm⁻¹): 3057, 2926, 2392, 1600, 1518, 1446, 1229, 1159, 834, 753; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.97 – 7.86 (m, 4H), 7.86 – 7.79 (m, 2H), 7.79 – 7.63 (m, 5H), 7.56 – 7.44 (m, 4H), 7.44 – 7.35 (m, 1H), 7.21 – 7.12 (m, 2H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 162.8 (d, *J* = 245.0 Hz), 142.7, 142.5, 141.6, 141.2, 138.5, 137.4 (d, *J* = 3.0 Hz), 133.8, 132.9, 129.1, 129.0, 128.7, 128.4, 127.84, 127.81, 127.5, 126.6, 126.3, 126.2, 125.8, 125.6, 125.4, 125.3, 115.9 (d, *J* = 21.0 Hz); ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -115.2; HRMS (EI) *m/z* calcd for C₂₈H₁₉F [M]⁺ 374.1471, found 374.1463.

4-chloro-5'-phenyl-1,1':3',1''-terphenyl (known compound) ¹ White solid, 58.2 mg, 57% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.77 (m, 1H), 7.73 (d, *J* = 1.6 Hz, 2H), 7.71 – 7.66 (m, 4H), 7.65 – 7.59 (m, 2H), 7.53 – 7.47 (m, 3H),

7.47 – 7.42 (m, 3H), 7.42 – 7.35 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.7, 141.2, 141.1, 139.7, 133.8, 129.2, 129.0, 128.7, 127.8, 127.5, 125.6, 125.1.

4-bromo-5'-phenyl-1,1':3',1''-terphenyl (known compound) ⁴ White solid, 46.2 mg, 40% yield; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.77 (m, 1H), 7.73 (d, J = 1.6 Hz, 2H), 7.71 – 7.64 (m, 4H), 7.63 – 7.53 (m, 4H), 7.52 – 7.44 (m, 4H), 7.43 – 7.34 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.7, 141.3, 141.1, 140.2, 132.1, 129.1, 129.0, 127.8, 127.5, 125.7, 125.0, 122.0.

3-fluoro-5'-phenyl-1,1':3',1''-terphenyl (known compound) ⁴ White solid, 55.4 mg, 57% yield; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.78 (m, 1H), 7.78 – 7.73 (m, 2H), 7.72 – 7.66 (m, 4H), 7.52 – 7.46 (m, 5H), 7.45 – 7.36 (m, 4H), 7.15 – 7.02 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.4 (d, J = 244.0 Hz), 143.6 (d, J = 8.0 Hz), 142.7, 141.1, 130.5 (d, J = 9.0 Hz), 129.0, 127.8, 127.5, 125.9, 125.2, 123.1 (d, J = 2.0 Hz), 114.5 (d, J = 21.0 Hz), 114.4 (d, J = 22.0 Hz); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -112.9.

5'-phenyl-3-(trifluoromethyl)-1,1':3',1''-terphenyl White solid, 44.9 mg, 40% yield. m.p. 199.3-200.6 °C; IR (cm⁻¹): 3035, 2924, 2853, 2377, 1596, 1497, 1321, 1126, 756, 698; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.84 – 7.80 (m, 1H), 7.77 (d, J = 1.6 Hz, 2H), 7.72 – 7.67 (m, 4H), 7.67 – 7.56 (m, 2H), 7.52 – 7.46 (m, 4H), 7.44 – 7.36 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.8, 142.1, 141.1, 141.0, 131.4 (q, J = 32.0 Hz), 130.8, 129.5,

129.1, 127.9, 127.5, 126.1, 125.3, 124.3 (d, $J = 271.0$ Hz), 124.5 – 124.2 (m), 122.8; ^{19}F NMR (376 MHz, Chloroform- d) δ -62.5; HRMS (EI) m/z calcd for $\text{C}_{25}\text{H}_{17}\text{F}_3$ $[\text{M}]^+$ 374.1282, found 374.1273.

1,1':3,1''-terphenyl (known compound) ⁵ White solid, 34.5 mg, 50% yield; ^1H NMR (400 MHz, Chloroform- d) δ 7.81 (s, 1H), 7.66 (s, 2H), 7.64 (s, 2H), 7.60 – 7.55 (m, 2H), 7.54 – 7.50 (m, 1H), 7.49 – 7.43 (m, 4H), 7.40 – 7.34 (m, 2H); ^{13}C NMR (100 MHz, Chloroform- d) δ 141.9, 141.3, 129.3, 128.9, 127.6, 127.4, 126.3, 126.2.

4',5'-dihydro-[1,1':3,1''-terphenyl]-2'-carbonitrile White solid, 42.4 mg, 55% yield. m.p. 74.5-75.3 °C; IR (cm^{-1}): 3057, 2919, 2850, 2397, 1598, 1552, 1492, 1443, 761, 698; ^1H NMR (400 MHz, Chloroform- d) δ 7.61 – 7.56 (m, 2H), 7.48 – 7.41 (m, 3H), 7.43 – 7.33 (m, 5H), 6.12 (t, $J = 4.8$ Hz, 1H), 2.81 – 2.73 (m, 2H), 2.52 – 2.44 (m, 2H); ^{13}C NMR (100 MHz, Chloroform- d) δ 155.8, 139.1, 138.5, 136.0, 129.6, 128.7, 128.4, 128.1, 127.92, 127.90, 126.0, 118.0, 108.8, 29.7, 22.5; HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{15}\text{NNa}^+$ $[\text{M}+\text{Na}]^+$ 280.1097, found 280.1097.

5'-phenyl-[1,1':3,1''-terphenyl]-2'-carbonitrile (known compound) ⁶ White solid, 49.7 mg, 50% yield; ^1H NMR (400 MHz, Chloroform- d) δ 7.72 – 7.67 (m, 3H), 7.67 – 7.60 (m, 5H), 7.56 – 7.52 (m, 1H), 7.52 – 7.48 (m, 5H), 7.48 – 7.45 (m, 2H), 7.45 – 7.40 (m, 1H); ^{13}C NMR (100 MHz, Chloroform- d) δ 147.5, 145.3, 139.2, 138.9, 129.3, 129.2, 128.9, 128.8, 127.7, 127.5, 118.2, 109.2.

5'-(4-chlorophenyl)-[1,1':3',1''-terphenyl]-2'-carbonitrile (known compound) ⁷
 White solid, 62.5 mg, 57% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.64 (s, 4H), 7.63 – 7.60 (m, 3H), 7.60 – 7.57 (m, 1H), 7.55 – 7.50 (m, 3H), 7.50 – 7.48 (m, 2H), 7.48 – 7.42 (m, 3H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 147.7, 144.0, 138.7, 137.6, 135.2, 129.5, 129.2, 129.0, 128.9, 128.7, 127.4, 118.0, 109.5.

5'-(3-fluorophenyl)-[1,1':3',1''-terphenyl]-2'-carbonitrile (known compound) ⁸
 White solid, 52.4 mg, 50% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.60 (m, 6H), 7.56 – 7.47 (m, 6H), 7.47 – 7.42 (m, 2H), 7.37 (d, *J* = 9.2 Hz, 1H), 7.18 – 7.07 (m, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 163.4 (d, *J* = 246.0 Hz), 147.7, 143.9, 141.4 (d, *J* = 8.0 Hz), 138.6, 130.8 (d, *J* = 8.0 Hz), 129.2, 129.0, 128.9, 127.6, 123.2 (d, *J* = 3.0 Hz), 118.0, 115.8 (d, *J* = 21.0 Hz), 114.5 (d, *J* = 22.0 Hz), 109.8.; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -112.1.

5'-(naphthalen-2-yl)-[1,1':3',1''-terphenyl]-4'-carbonitrile (known compound) ⁶
 White solid, 56.1 mg, 49% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.12 (s, 1H), 7.99 (d, *J* = 8.8 Hz, 1H), 7.96 – 7.88 (m, 2H), 7.81 – 7.74 (m, 2H), 7.73 – 7.63 (m, 5H), 7.58 – 7.51 (m, 4H), 7.51 – 7.39 (m, 4H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 147.6, 145.3, 139.2, 133.3, 129.3, 129.2, 128.9, 128.8, 128.7, 128.6, 127.9, 127.7, 127.5, 126.9, 118.3, 109.4.

3-fluoro-5'-(naphthalen-2-yl)-[1,1':3',1''-terphenyl]-4'-carbonitrile White solid, 57.5 mg, 48% yield. m.p. 255.2-256.7 °C; IR (cm⁻¹): 3058, 2852, 1592, 1493, 1266, 1157, 1125, 853, 748, 699; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.11 (s, 1H), 7.99 (d, *J* = 8.8 Hz, 1H), 7.96 – 7.88 (m, 2H), 7.79 – 7.72 (m, 2H), 7.71 – 7.61 (m, 3H), 7.59 – 7.51 (m, 4H), 7.51 – 7.43 (m, 3H), 7.43 – 7.36 (m, 1H), 7.19 – 7.07 (m, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 163.4 (d, *J* = 245.0 Hz), 147.8, 147.7, 143.9, 141.4 (d, *J* = 7.0 Hz), 138.6, 136.0, 133.34, 133.30, 130.9 (d, *J* = 8.0 Hz), 129.2, 129.0, 128.9, 128.7, 128.6, 128.5, 127.9, 127.8, 127.7, 127.0, 126.8, 126.7, 123.2 (d, *J* = 3.03 Hz), 118.1, 115.8 (d, *J* = 21.0 Hz), 114.5 (d, *J* = 23.0 Hz), 110.0; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -112.0; HRMS (ESI) *m/z* calcd for C₂₉H₁₈FNNa⁺ [M+Na]⁺ 422.1315, found 422.1314.

[1,1':3',1''-terphenyl]-2'-carbonitrile (known compound) ⁶ White solid, 34.4 mg, 45% yield; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.64 (m, 1H), 7.62 – 7.55 (m, 4H), 7.54 – 7.51 (m, 1H), 7.51 – 7.49 (m, 2H), 7.49 – 7.4511 (m, 4H), 7.45 – 7.42 (m, 1H); ¹³C NMR (100 MHz, Chloroform-*d*) δ 147.1, 138.8, 132.4, 129.2, 129.0, 128.8, 128.7.

References.

1. C.-L. Zhang, S. Ye, N-Heterocyclic Carbene-Catalyzed Construction of 1,3,5-Trisubstituted Benzenes from Bromoenals and α -Cyano- β -methylenones, *Org. Lett.*, 2016, **18**, 6408 - 6411.
2. C.-L. Zhang, Z.-F. Zhang, Z.-H. Xia, Y.-F. Han, S. Ye, DBU-Mediated Construction of 1,3,5-Trisubstituted Benzenes via Annulation of α,β -Unsaturated Carboxylic Acids and α -Cyano- β -methylenones, *J. Org. Chem.*, 2018, **83**, 12507 - 12513.
3. J.-Y. Pan, R.-F. He, J.-H. Tan, Y.-N. Li, *PCT Int. Appl.* 2018095391, 31 May 2018.

4. F.-Y. Wang, J.-H. Shen, G.-L. Cheng, X.-L. Cui, Practical access to 1,3,5-triarylbenzenes from chalcones and DMSO, *RSC Advances.*, 2015, **5**, 73180 - 73183.
5. L.-F. Liu, Y.-H. Zhang, B.-W. Xin, Synthesis of Biaryls and Polyaryls by Ligand-Free Suzuki Reaction in Aqueous Phase, *J. Org. Chem.*, 2006, **71**, 3994 - 3997.
6. Q.-F. Jia, J. Wang, Synthesis of Biaryls and Polyaryls by Ligand-Free Suzuki Reaction in Aqueous Phase, *Org. Lett.*, 2016, **18**, 2212 - 2215.
7. C.-L. Zhang, Z.-H. Gao, Z.-Q. Liang, S. Ye, N-Heterocyclic Carbene-Catalyzed Synthesis of Multi- Substituted Benzenes from Enals and α -Cyano- β -methylenones, *Adv. Synth. Catal.*, 2016, **358**, 2862 - 2866.
8. M. K. R. Singam, A. Nagireddy and S. R. Maddi, Base-mediated benzannulation of α -cyanocrotonates with ynones: facile synthesis of benzonitriles and fluorenes, *Green Chem.*, 2020, **22**, 2370 - 2374.

7. Copies of NMR spectra

3a

3b

3c

3d

3e

3f

3h

3i

3l

3m

3q

3r

3s

3u

3u'

4a

4b

4c

4f