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Iron-catalyzed regioselective cyclotrimerization of alkynes to benzenes

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Dedicated to Prof. V. Chandrasekhar on the occasion of his 60th birthday with our best wishes and great admiration for his enormous and inspiring contribution to organometallic chemistry.

Keywords:
Cyclotrimerization
Iron pincer
Alkyne
EPR
Catalysis

ABSTRACT

We report the synthesis and characterization of simple di(aminomethyl)pyridine ligated iron-pincer complexes, which catalyzed the regioselective [2+2+2] cyclotrimerization of terminal aryl and alkyl alkynes to provide the 1,2,4-trisubstituted benzene molecules. Interestingly, internal alkynes also exhibited similar cyclization and resulted in hexa-substituted benzene compounds. Increased steric bulk on pincer ligands diminished the selectivity for cycloaddition. Cyclotrimerization reactions proceeded at room temperature upon activation of catalyst by a Grignard reagent. EPR studies indicated thermally induced spin crossover effect in catalyst.

1. Introduction

Synthesis of highly functionalized aromatic compounds finds utmost importance in pharmaceutical as well as material synthesis. In this direction, Reppe introduced a powerful and elegant approach for the synthesis of benzene compounds with multiple substitutions via [2+2+2] cyclotrimerization of alkynes [1]. Using various transition metals, number of procedures have been reported for the synthesis of arene compounds [1c,2,3]. However, selective construction of benzene rings remains a challenging task because of the poor regioselectivity, which depends on catalyst and substrates, initial formation of metallacyclopentadiene from alkyne-dimerization and subsequent cycloaddition of third alkyne [4]. As a result, such selective trimerization of alkynes is realized using stoichiometric amounts of zirconium [5] and titanium complexes [1b,6]. Alternatively, the regioselectivity problem was addressed by introducing partially intermolecular reactions in which the use of tethered diynes provided the required geometric and entropic restrictions, and resulted in the selective formation of arenes [1a,6a,7].

Homogeneous iron-catalysts have arguably started to challenge the dominance of noble transition metals [8]. Iron-catalyzed [2+2+2] cyclotrimerization [9] of alkynes to selective formation of benzene motifs is a challenge. In literature, different combination of iron complexes, ligands and activators have been shown to exhibit higher catalytic efficiency with wide substrate scope for 1,2,4-trisubstituted benzene derivatives. In addition to that, activator free and low oxidation state (0, +1) iron complexes have also been used [10]. However, in an intermolecular reaction, simple iron salts or even iron-carbene complexes predominantly dimerize the reactive terminal alkynes to provide a mixture (E, Z and geminal) of products [11] or self-coupled products [12]. Iron-catalyzed intermolecular cyclotrimerization of terminal alkynes remains rare with poor regioselectivity [13]. Thus, development of a defined and efficient iron catalyst for regioselective construction of 1,2,4-trisubstituted benzene compounds would be of high interest.

Transition metal pincer complexes with planar backbone are efficient catalysts for numerous organic reactions. As the tridentate pincer ligands cover more than half of the metal coordination

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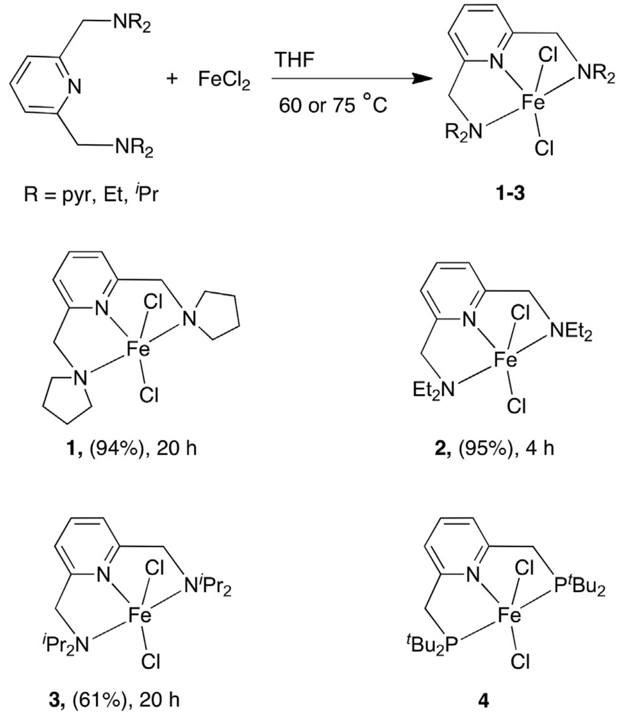
sphere, they offer better control over the metal coordination sites and enforce selectivity in catalytic processes. Using such iron-pincer complexes, number of atom-economical transformations [14] including the Z-selective dimerization of terminal alkynes [15] were reported recently. In this report, we disclose the syntheses and structure of new NNN iron-pincer complexes and their catalytic applications in intermolecular regioselective [2+2+2] cycloaddition of both terminal and internal alkynes.

2. Results and discussion

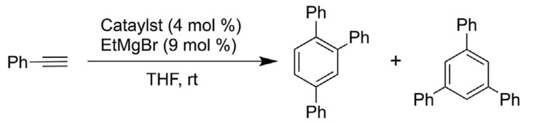
Attempted cyclotrimerization of phenylacetylene with $FeCl_2$ (4 mol%) and ethylmagnesium bromide (9 mol%) as an activating reagent resulted in good conversion; but only to result in mixture of compounds, in which the cyclotrimerization products were found in low yields (entry 1, Table 1). Thus, we envisaged utilizing easily accessible and stable iron-pincer complexes for the catalytic cyclotrimerization of alkynes. The reaction of 2,6-bis(pyrrolidin-1-ylmethyl)pyridine (NNN^{pyr}), *N*,*N*'-(pyridine-2,6-diylbis(methylene)) bis(*N*-ethylethanamine) (NNN^{Et}), *N*,*N*'-(pyridine-2,6-diylbis (methylene))bis(*N*-isopropylpropan-2-amine) (NNN^{iPr}), and 2,6-bis((di-*tert*-butylphosphino)methyl)pyridine (PNP^{tBu}) ligands with anhydrous $FeCl_2$ provided the paramagnetic iron(II) pincer complexes **1**–**4**, respectively in very good yields (Scheme 1). The single-crystal X-ray analyses of complexes $[(NNN^{pyr})FeCl_2]$ **1** and $[(NNN^{Et})FeCl_2]$ **2** revealed distorted square pyramidal geometry around the iron centers (Fig. 1)

Upon reaction of phenylacetylene and EtMgBr (9 mol%) with complex **1** (4 mol%) provided excellent conversion (97%), and 76% isolated yield of trisubstituted benzene products with 93:7 (**6a:7a**) selectivity for 1,2,4-triphenylbenzene and 1,3,5-triphenylbenzene (entry 2, Table 1). When similar experiment was carried out using only 4 mol% of EtMgBr (1 equiv. relative to catalyst), both conversion of alkyne and yield of the trimerization products decreased (entry 3, Table 1), indicating that two equivalents of activator (relative to catalyst) is essential for efficient catalysis. Notably, the sequence of addition of reagents (alkyne, catalyst, THF and finally activator EtMgBr) is important. When this addition sequence was altered and ethylmagnesium bromide was added before the addition of phenylacetylene, no desired product formation occurred (entry 4, Table 1). Use of iron-pincer $[(NNN^{Et})FeCl_2]$ complex **2** as a catalyst provided similar results as that of catalyst **1** (entry 5, Table 1). However, when $[(NNN^{iPr})FeCl_2]$ complex **3** was used as a catalyst (4 mol%) both conversion and yield of the corresponding benzene products were diminished (entry 6, Table 1). Further to test the role of stability and electronic influence of the catalyst in the cyclotrimerization reactions, the $[(PNP^{tBu})FeCl_2]$ complex **4** was prepared [16]. Upon using **4** as a catalyst (4 mol%), although 94% conversion of phenylacetylene was observed, the desired products formed only in 72% yield. Thus, iron-complex **1** was found to be a suitable catalyst for the selective [2+2+2] cycloaddition of terminal aryl alkynes to 1,2,4-trisubstituted benzenes. Further, using **1** as a catalyst cyclotrimerization of phenylacetylene in the presence of mercury (10 mol%) provided the products in 70% yield, indicating the involvement of soluble molecular catalyst in the reaction. These results confirm that by suitable modification of pincer ligands, both reactivity and selectivity in iron-catalyzed [2+2+2] cycloaddition of terminal aryl alkynes can be controlled.



Scheme 1. NNN- and PNP-iron complexes for alkyne trimerization.

Table 1
Iron-catalyzed cyclotrimerization of Phenylacetylene.[a]



5a **6a** **7a**

entry	catalyst	time (h)	conv. (%)[b]	yield (%)[c]	6a/7a[d]
1	$FeCl_2$	16	95	47	90/10
2	**1**	5	97	76	93/7
3[e]	**1**	16	85	54	93/7
4[f]	**1**	16	18	0	-
5	**2**	5	> 99	75	93/7
6	**3**	5	79	61	93/7
7	**4**	5	94	72	93/7

[a] Conditions: Phenylacetylene (0.5 mmol), catalyst (4 mol%), and THF (1 mL) were added in a scintillation vial and EtMgBr (9 mol%) was added at the end.
[b] Conversion determined by GC using toluene (0.5 mmol) as an internal standard.
[c] Yield of the products (**6a** and **7a**) after column chromatography.
[d] Ratio determined by GC.
[e] EtMgBr (4 mol%) was used.
[f] EtMgBr, catalyst and THF (1 mL) was added prior to phenylacetylene.

Next, we studied the cyclotrimerization of various substituted aryl terminal alkynes catalyzed by complex **1** and the results are summarized in Table 2. Arylacetylenes containing electron-donating substituents such as methyl, methoxy afforded the corresponding 1,2,4-trisubstituted benzenes in moderate yields with very high regioselectivity (entries 2–6, Table 2). While phenylacetylenes containing methyl substituents underwent complete conversion in 3–5 h, the methoxy substituted phenylacetylenes required longer reaction time (14–16 h, entries 4,5, Table 2). Arylacetylenes containing electron-withdrawing groups such as 4-fluro, 2-trifluromethyl and 3,5-di(trifluormethyl) substituents provided cyclotrimerization products with the corresponding 1,2,4-trisubstituted benzenes in 58%, 51% and 67% yields, respectively at room temperature (entries 7–9, Table 2).

Remarkably, this iron-pincer catalyzed [2+2+2] cyclotrimerization is also applicable to aliphatic alkynes. An assortment of linear, branched alkyl as well as aryl-alkyl substituted acetylenes underwent efficient cyclotrimerization to provide the corresponding products in moderate yields (entries 1–8, Table 3). Notably,

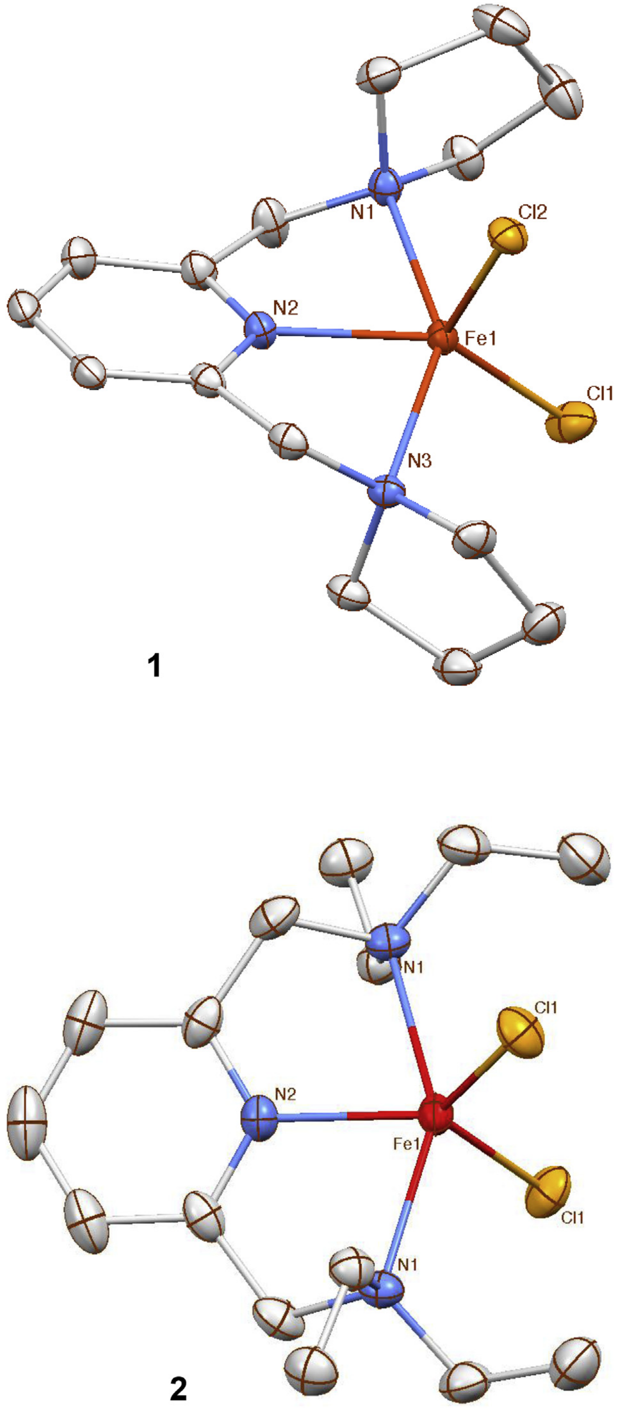
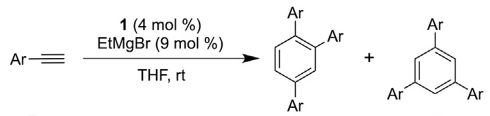
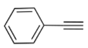
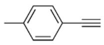
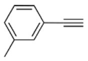
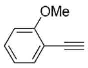
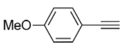
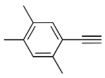
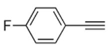
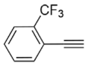
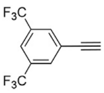


Fig. 1. Single-crystal X-ray structures of NNN-iron pincer complexes 1 and 2 (ellipsoids are drawn at 30% probability).

Table 2
Iron-catalyzed cyclotrimerization of aryl terminal alkynes.[a]



5 6 7

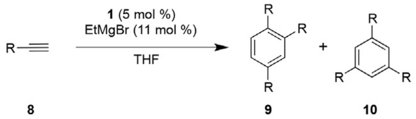
entry	substrate 5		time (h)	conv. (%)[b]	yield (%)[c]	ratio: 6/7[d]
1		**a**	5	97	76	93/7
2		**b**	3	91	62	93/7
3		**c**	5	95	64	92/8
4	 OMe	**d**	14	99	76	92/8
5	 MeO	**e**	16	98	67	92/8
6		**f**	5	>99	64	92/8
7	 F	**g**	16	99	58	94/6
8	 CF_3	**h**	5	92	51	92/8
9	 F_3C F_3C	**i**	14	96	67	97/3

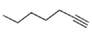
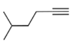
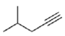
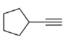
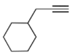
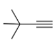
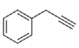
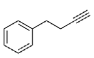
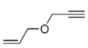
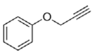
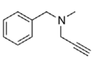
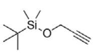
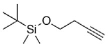
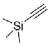
[a] Conditions: Arylacetylene (0.5 mmol), catalyst **1** (4 mol%), and THF (1 mL) were added in a scintillation vial and EtMgBr (9 mol%) was added at the end.
[b] Conversion determined by GC using toluene (0.5 mmol) as an internal standard.
[c] Yield of the products (**6** and **7**) after isolation from column chromatography.
[d] Ratio determined by GC.

wide range of functional groups such as alkenes, allyl, aryl and silyl ethers (*tert*-butyldimethylsilyl, TBDMS), and amines were well tolerated under these experimental conditions; however, these functionalized acetylenes required heating of the reaction mixture at 70 °C to obtain the moderate to quantitative conversions (entries 9–13, Table 3). Further, we have also tested catalyst **1**–**4** for the cyclotrimerization reactions with aliphatic 4-(*tert*-butyldimethylsilyloxy)-1-butyne at 70 °C, where complex **1** provided best yield (76%, entry 13, Table 3) compared to other catalysts **2**–**4** (68%, 56% and 60% yields, respectively) for the cyclotrimerized products (**9m:10m**). Unfortunately, all aliphatic alkynes used in Table 3 provided poor regioselectivity, and 1,3,5-trisubstituted benzenes were also formed in considerable amount together with the major isomer of 1,2,4-trisubstituted benzenes. Out of all the terminal alkynes tested only prop-2-yn-1-ylbenzene and but-3-yn-1-ylbenzene showed reversal of regioselectivity; 1,3,5-trisubstituted benzenes were found to be the major regioisomers with these two terminal alkynes (entries 7 and 8, Table 3). When trimethylsilyl acetylene was employed for cyclotrimerization, efficient reaction occurred at room temperature and the trisubstituted benzenes were obtained in 80% yield with moderate regioselectivity (entry 14, Table 3). Polymeric or complex mixture of side products were observed in all reactions in minor amount. However, electron deficient acetylene carboxylates such as methyl and ethyl propiolate failed to provide desired benzene products.

Further, cyclotrimerization of internal alkynes like 1-phenyl-1-propyne, 1-phenyl-1-butyne and 1-phenyl-1-hexyne was performed using catalyst **1**, which provided single regioisomer **12a, 12b** and **12c** in 55%, 42% and 45% yields, respectively (See Scheme 2). Representative single-crystal structure of **6g** and **12a** further confirmed cyclotrimerization of terminal and internal alkynes (Fig. 2). Although, remarkable regioselectivity was observed with arylalkyl internal alkynes, use of dialkyl and

Table 3
Iron-catalyzed cyclotrimerization of aliphatic terminal alkynes.[a]



entry	substrate 8		time (h)	temp. (°C)	conv. (%)[b]	yield (%)[c]	ratio: 9/10[d]
1		**a**	9	rt	93	57	54/46
2		**b**	13	rt	>99	63	55/45
3		**c**	13	rt	>99	68	63/37
4		**d**	9	rt	86	51	50/50
5		**e**	13	rt	>99	66	56/44
6		**f**	5	rt	n.c	70	69/31
7		**g**	22	rt	>99	42	42/58
8		**h**	13	rt	99	53	45/55
9		**i**	15	70	>99	61	59/41
10		**j**	24	70	>99	36	50/50
11		**k**	22	70	73	50	59/41
12		**l**	9	70	96	72	72/28
13[e]		**m**	18	70	99	76	60/40
14		**n**	3	rt	n.c	80	68/32

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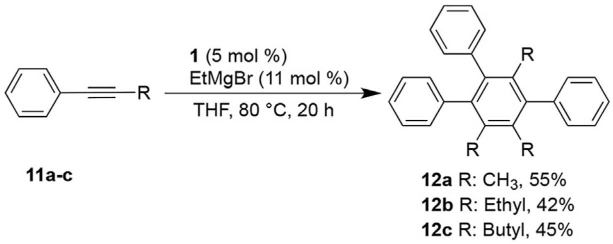
[a] Conditions: terminal alkyne (0.5 mmol), catalyst **1** (5 mol%), and THF (1 mL) were taken in a scintillation vial. EtMgBr (11 mol%) was added and reaction was carried out at room temperature.

[b] Conversion was determined by GC using toluene (0.5 mmol) as an internal standard.

[c] Yield of the products (**9** and **10**) after isolation from column chromatography.

[d] Ratio determined by GC (for entries 1–8) and from ^{1}H NMR (for entries 9–14) after isolation.

[e] Reactions were also carried out with catalyst **2** (68%), catalyst **3** (56%), catalyst **4** (60%). n.c: not calculated.



Scheme 2. Iron-catalyzed regioselective cyclotrimerization reaction of internal alkynes.

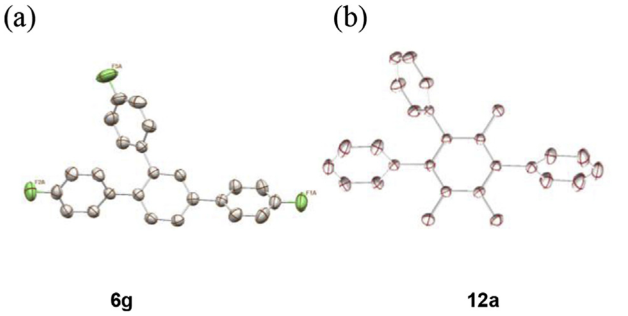


Fig. 2. Single-crystal X-ray structure of cyclotrimerized products (a) **6g** and (b) **12a.** Ellipsoids are drawn at 30% probability.

diaryl internal alkynes (4-octyne and diphenylacetylene, respectively) failed to provide cyclotrimerization reactions under this catalysis.

When the rate of cyclotrimerization of phenylacetylene catalyzed by iron-pincer complex **1** was monitored using GC, 93% conversion occurred in 5 h indicating the rapid reaction of alkynes (Fig. 3).

Upon reaction of complex **1** (0.05 mmol) with two equivalents of

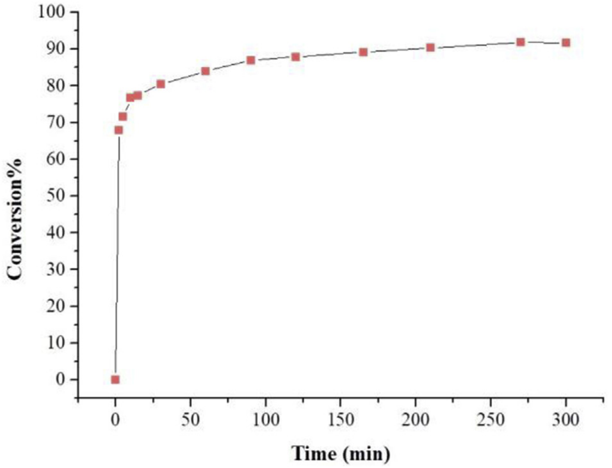


Fig. 3. Conversion of phenylacetylene in catalytic reaction with **1** and EtMgBr. Monitoring of the reaction progress using GC analysis.

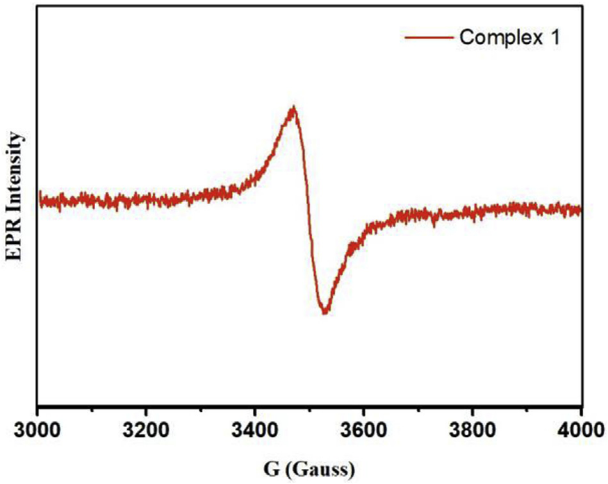
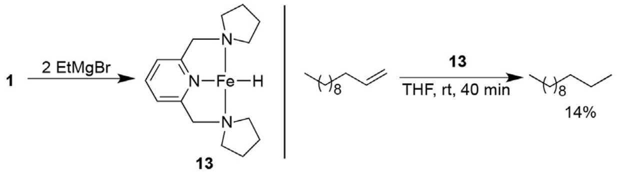


Fig. 4. X-band EPR of NNN-Fe catalyst **1** recorded at 298 K.

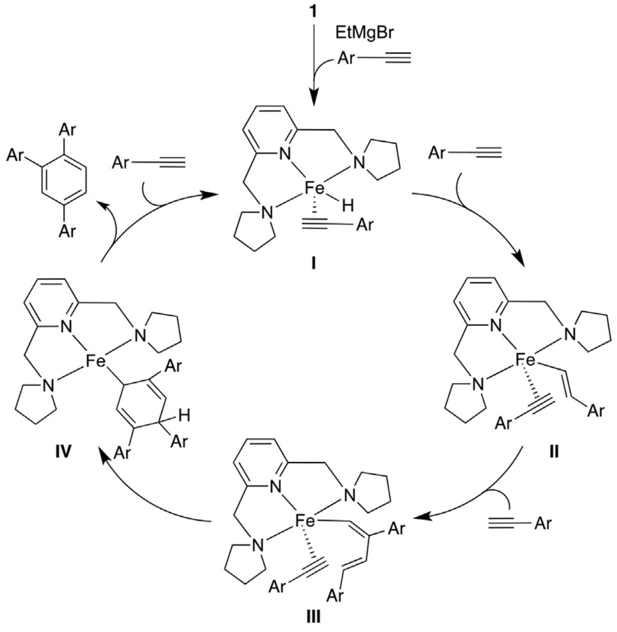
ethylmagnesium bromide (0.1 mmol) and stoichiometric amount of dodecene (0.05 mmol) in a closed vial under nitrogen atmosphere, immediate color change from yellow to brown was observed; however, after 10 min the reaction mixture turned turbid indicating the decomposition of active species. GC analysis of the reaction mixture after 40 min (using toluene as an internal standard) confirmed 14% formation of dodecane (Scheme 3), indicating the possible formation of an iron-hydride intermediate **13** [13b].

Electron paramagnetic resonance (EPR) measurements were carried out at 298 K in THF to investigate the spin state of complex **1**. Complex **1** shows a single EPR signal at room temperature, which is attributable to an S = 2 system (high spin-d^6-Fe^{II}, Fig. 4). The g value (g = 2.01) of **1** is largely deviated from that (2.0023) of free electron. The width between extreme slopes (60 G) of this EPR signal is much broader than that of conventional organic radicals, and therefore, no hyperfine structure is observed. However, EPR analysis of complex **1** at 100 K revealed the disappearance of signal, observed at 298 K (low spin-d^6-Fe^{II}). This clearly indicates thermally induced spin crossover effect. Moreover, complex **1** has a solid-state magnetic moment of 5.2 μ_B at 298 K, indicating four unpaired electrons at the iron center. The measured magnetic moment is larger than spin-only value for an S = 2 spin state (4.89 μ_B), but still within the range of the reported high spin distorted square-pyramidal iron(II) compounds [16].

Although more studies are required, on the basis of experimental observations, a catalytic cycle for cyclotrimerization of alkynes involving Fe(I) intermediacy was proposed [17] as depicted in Scheme 4. Reaction of catalyst **1** with Grignard reagent and alkyne generates the Fe(I)-monohydride intermediate **I**. Upon insertion of coordinated alkyne into Fe–H bond and further preliminary interaction of another alkyne motif leads to the formation of **II**. Coordinated alkene and alkyne functionalities over the metal center further react to create a dienyl ligand and further coordination of third alkyne motif results in formation of intermediate **III**. Subsequent [4 + 2] cycloaddition between the metal coordinated dienyl ligand and alkyne leads to formation of cyclic hexadienyl coordinated intermediate **IV**. A Hydride elimination from coordinated unsaturated carbocycle liberates regioselective 1,2,4-triaryl benzene molecule and further reaction with alkyne can regenerate the intermediate **I** to complete one loop of the catalytic cycle. When aliphatic alkynes were employed in the catalysis, perhaps the steric incompatibilities led to the formation of another regioisomer-1,3,5-trialkyl benzene in a considerable percentage. The intermolecular cycloaddition pathway of iron-coordinated dienyl ligand with alkynes may also be operative.



Scheme 3. Stoichiometric reaction of iron complex 1 with Grignard reagent and alkene.



Scheme 4. Proposed catalytic cycle for Fe-catalyzed [2+2+2] cycloaddition ceaction

3. Conclusion

In summary, we have described regioselective cyclotrimerization of aryl terminal alkynes and internal alkynes using simple and easily accessible NNN iron-pincer catalysts to provide the corresponding 1,2,4-trisubstituted and hexa-substituted benzene molecules. While arylalkynes provided up to 97% regioselective 1,2,4-trisubstituted isomers, aliphatic alkynes displayed poor regioselectivity perhaps due to the steric incompatibility on the metal coordination sphere. Notably, the arylalkyl internal alkynes provided hexasubstituted benzene compounds as single regioisomers. Mechanistic studies indicate the involvement of molecular catalyst and the reaction proceeds upon activation of iron dichloride to iron(I)-hydride intermediate by a Grignard reagent. Catalytic [2+2+2] cycloaddition is suggested to occur upon coordination of alkynes with Fe(I) intermediates in a stepwise reaction pathway.

4. Experimental section

4.1. General experimental

All catalytic reactions were performed under nitrogen atmosphere in an MBraun Glove-box. Chemicals were purchased from Acros, Sigma-Aldrich, Alfa-aesar and used without further purification. Dry solvents were prepared according to standard procedures. ^{1}H, ^{13}C, ^{29}Si, and ^{19}F NMR spectra were recorded using 400, 100.6, 79.5 and 376.5 MHz magnetic fields, respectively. ^{1}H and ^{13}C {^{1}H} NMR chemical shifts were reported in ppm downfield from tetramethylsilane. Multiplicity is abbreviated as s, singlet; d, doublet; dd, doublet of doublet; t, triplet; q, quartet; dq, doublet of quartet; m, multiplet; br, broad. Mass spectra were recorded on a micro TOF-Q II spectrometer. Magnetic susceptibility was recorded on magnetic susceptibility balance. GC-FID measurements were performed with Shimadzu series instrument. The GC-FID instrument equipped with a capillary column coated with nonpolar stationary phase rtX was used for molecular weight determination and identification, which allowed the separation of hydrocarbons according to their boiling point differences.

4.2. Synthesis of 2,6-bis(bromomethyl)pyridine [18]

To a 100 mL one neck round-bottomed flask equipped with a stirrer bar, guard tube and reflux condenser, pyridine-2,6-diyldimethanol (1 g, 7.05 mmol) and 60% HBr (7 mL) were added slowly. The reaction was heated at 125 °C for 7 h then cooled to room temperature. The resulting residue was dissolved in H_2O (25 mL) to give yellow solution. To this solution saturated $NaHCO_3$ was added to reach pH 8. The resulting aqueous solution was extracted with CH_2Cl_2 (4 × 25 mL), and the combined organic layers were dried over anhydrous sodium sulfate and filtered. The volatiles were evaporated under reduced pressure and the resulting residue was purified by flash column chromatography (10% ethyl acetate/hexane) to yield 2,6-bis(bromomethyl)pyridine (1.6 g, 84%) as white solid. ^{1}H NMR($CDCl_3$): δ 7.70 (t, $J = 8$ Hz, 1H), 7.37 (d, $J = 8$ Hz, 2H), 4.54 (s, 4H). ^{13}C{^{1}H}NMR ($CDCl_3$): δ 156.9, 138.3, 123.0, 33.6. HRMS (EI) m/z Calcd for $C_7H_8Br_2N$: $[M + H]^+$ 263.9018, found 263.9031.

4.3. Synthesis of 2,6, bis(pyrrolidine-1-ylmethyl)pyridine [19] (L1)

To a 50 mL two neck round-bottomed flask equipped with a stirrer bar, 2,6-bis(bromomethyl)pyridine (1 g, 3.8 mmol) was dissolved in dry acetonitrile (20 mL) under an argon atmosphere. The solution was cooled to 0 °C prior to the dropwise addition of pyrrolidine (1.09 g, 15.2 mmol) over a period of 5 min. The reaction was allowed to warm to room temperature (25 °C) and was stirred vigorously for a period of 24 h. The volatiles were removed under reduced pressure to give a pale yellow residue, which was diluted with 75 mL CH_2Cl_2 and neutralized with 1 M NaOH (1 × 30 mL) and washed with brine (1 × 30 mL). The organic layer was then dried over sodium sulfate, filtered, and concentrated under reduced pressure. The resulting reaction mixture was purified by alumina column chromatography (4% ethyl acetate/hexane) to yield 2,6-bis(pyrrolidine-1-ylmethyl)pyridine (0.69 g, 74%) as pale yellow oil. ^{1}H NMR ($CDCl_3$): δ7.56 (t, $J = 8$ Hz, 1H), 7.24 (d, $J = 8$ Hz, 2H), 3.74 (s, 4H), 2.53–2.56 (m, 8H), 1.74–1.77 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 158.9, 136.7, 120.9, 62.4, 54.4, 23.6. HRMS (EI) m/z Calcd for $C_{15}H_{24}N_3$: $[M + H]^+$ 246.1965, found 246.1957.

4.4. Synthesis of N,N'-(pyridine-2,6-diylbis(methylene))bis(N-ethylethanamine) [20] (L2)

To a 50 mL two neck round-bottomed flask equipped with a stirrer bar, 2,6-bis(bromomethyl)pyridine (0.5 g, 1.90 mmol), K_2CO_3(1.05 g, 7.6 mmol) was dissolved in dry acetonitrile (10 mL) under an argon atmosphere. The solution was cooled to 0 °C prior to the dropwise addition of diethylamine (0.55 g, 7.6 mmol) over a period of 5 min. The reaction was allowed to warm to room temperature (25 °C) and was stirred vigorously for a period of 24 h. The reaction mixture was concentrated under reduced pressure to give a pale yellow residue, which was diluted with 60 mL CH_2Cl_2 and neutralized with 1 M NaOH (1 × 30 mL) and washed with brine (1 × 20 mL). The organic layer was then dried over sodium sulfate, filtered and concentrated under reduced pressure. The resulting residue was purified by alumina column chromatography (4% ethyl acetate/hexane) to yield *N,N'*-(pyridine-2,6-diylbis(methylene)) bis(N-ethylethanamine)(0.38 g, 80%) as pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.55 (t, $J = 8$ Hz, 1H), 7.29 (d, $J = 8$ Hz, 2H), 3.67 (s, 4H), 2.53 (q, $J = 8$ Hz, 8H), 1.01 (t, $J = 4$ Hz, 12H). ^{13}C{^{1}H}NMR ($CDCl_3$): δ 159.8, 136.5, 120.6, 59.7, 47.3, 11.9. HRMS (EI) m/z Calcd for $C_{15}H_{28}N_3$: $[M + H]^+$ 250.2278, found 250.2279.

4.5. Synthesis of N,N'-(pyridine-2,6-diylbis(methylene))bis(N-isopropylpropan-2-amine) [20] (L3)

To a 50 mL two neck round-bottomed flask equipped with a stirrer bar, 2,6-bis(bromomethyl)pyridine (0.5 g, 1.90 mmol), K_2CO_3 (1.05 g, 7.6 mmol) was dissolved in dry acetonitrile (10 mL) under an argon atmosphere. The solution was cooled to 0 °C prior to the dropwise addition of diisopropylamine (0.77 g, 7.6 mmol) over a period of 5 min. The reaction was allowed to warm to room temperature (25 °C) and was stirred vigorously for a period of 24 h. The volatiles were removed under reduced pressure to give a pale yellow residue, which was diluted with 60 mL CH_2Cl_2 and neutralized with 1 M NaOH (1 × 30 mL) and washed with brine (1 × 20 mL). The organic layer was then dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The resulting residue was purified by alumina column chromatography (4% ethyl acetate/hexane) to yield *N,N'*-(pyridine-2,6-diylbis(methylene))bis(*N*-isopropylpropan-2-amine) (0.42 g, 72%) as pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.57 (t, $J = 8$ Hz, 1H), 7.44 (d, $J = 8$ Hz, 2H), 3.76 (s, 4H), 3.00–3.09 (m, 4H), 1.02 (d, $J = 8$ Hz, 24H). ^{13}C NMR ($CDCl_3$): δ 161.8, 135.5, 118.2, 50.6, 47.9, 19.9. HRMS (EI) m/z Calcd for $C_{19}H_{36}N_3$: $[M + H]^+$ 306.2904, found 306.2909.

4.6. Synthesis and Characterization of Complexes **1**–**4**

4.6.1. $(NNN^{pyr})FeCl_2$ (**1**)

To the suspension of $FeCl_2$ (127 mg, 1 mmol) in THF (15 mL) pyrrolidine-NNN ligand (245 mg, 1 mmol) was added. The reaction mixture was heated to 75 °C and vigorously stirred for a period of 20 h. The yellow solution was cooled to room temperature and filtered through 0.2 µm PTFE syringe filter. The filtrate was concentrated to 2 mL under vacuum. Hexane (15 mL) was added slowly to precipitate a bright yellow solid, which was isolated by filtration, washed with hexane (3 × 1 mL) and dried under vacuum yielding 352 mg (94% yield). The resulting complex is paramagnetic. Crystals suitable of X-ray quality were obtained by slow diffusion of hexane into a solution of **1** in CH_2Cl_2. IR (KBr): 3413, 2963, 2918, 2847, 1609, 1579, 1473, 1456, 1438, 1381, 1349, 1334, 1262, 1225, 1108, 1083, 1024, 863, 796, 757 cm^{-1}. HRMS (EI) *m*/*z* Calcd for $C_{15}H_{24}Cl_2FeN_3$: $[M + H]^+$ 372.0694, found 372.0664.

4.6.2. *(NNN^{Et})$FeCl_2$ (**2**)*

To the pale yellow suspension of $FeCl_2$ (127 mg, 1 mmol) in THF (15 mL) NNN^{Et} ligand (249 mg, 1 mmol) was added. The reaction mixture was heated to 75 °C and vigorously stirred for a period of 4 h. The yellow solution was cooled to room temperature and filtered through 0.2 mm PTFE syringe filter. The filtrate was concentrated to 2 mL under vacuum. Hexane (15 mL) was added slowly to precipitate a bright yellow solid, which was isolated by filtration, washed with hexane (3 × 1 mL) and dried under vacuum yielding 357 mg (95% yield). The resulting complex is paramagnetic. Crystals suitable of X-ray quality were obtained by slow diffusion of Hexane into a solution of **2** in CH_2Cl_2. IR (KBr): 3408, 2983, 2855, 1605, 1579, 1464, 1402, 1380, 1360, 1262, 1168, 1150, 1133, 1035, 1025, 800, 762, 734.1 cm^{-1}. MS (EI) *m*/*z* Calcd for $C_{15}H_{28}Cl_2FeN_3$: $[M + H]^+$ 376.1, found 376.1.

4.6.3. *(NNN^{iPr})$FeCl_2$ (**3**)*

To the suspension of $FeCl_2$ (16.4 mg, 0.13 mmol) in THF (4 mL) NNN ^{iPr} ligand (40 mg, 0.13 mmol) was added. The reaction mixture was heated to 60 °C and vigorously stirred for a period of 20 h. The yellow solution was cooled to room temperature and filtered through 0.2 μm PTFE syringe filter. The filtrate was concentrated to 1 mL under vacuum. Hexane (4 mL) was added slowly to precipitate off-white solid, which was isolated by filtration, washed with hexane (2 × 1 mL) and dried under vacuum. The title compound was isolated as off-white solid (34 mg, 61%). The resulting complex is paramagnetic. Attempts made to crystallize the complex remain unsuccessful. IR (KBr): 3418, 2980, 1627, 1455, 1397, 1308, 1282, 1173, 1190, 1093, 983, 814 cm^{-1}. ESI *m*/*z* Calcd for $C_{19}H_{36}Cl_2FeN_3$: $[M + H]^+$ 432.1633, found 432.1568.

Complex **4** was prepared by following reported literature procedure [16].

4.7. *X-ray analyses and crystal data of **1**, **2***

Crystals suited for single crystal x-ray diffraction measurements were mounted on a glass fiber. Geometry and intensity data were collected with a Bruker SMART D8 goniometer equipped with an APEXCCD detector and with an Incoatecmicrosource (Mo-Kα radiation, λ = 0.71073 Å, multilayer optics). Temperature was controlled using an Oxford Cryostream 700 instrument. Intensities were integrated with SAINT+ [21]and corrected for absorption with SADABS [22]. The structures were solved by direct methods and refined on $F^2$with SHELXL-97 [23,24].

4.8. *Crystal data of complexes*

4.8.1. *(NNN^{pyr})$FeCl_2$(**1**)*

$C_{15}H_{23}Cl_2Fe\,N_3$, yellow block, crystal dimensions: 0.28 × 0.26 x 0.21 mm^{-1}, $M = 372.11$, Orthorhombic with space group Pbca, $a = 12.9858(8)$Å, $b = 12.0845(8)$Å, $c = 21.5276(14)$Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 3378.3(4)$ $Å^3$, $Z = 8$, $F(000) = 1552.0$, μ-(MoK_α) = 1.206 mm^{-1}, 2θmax = 59.318, $\rho_{calcd} = 1.463$ Mg/m^3, T = 100(2)K, min/max transmission factors = 0.5363/0.7459, 54540 Reflections collected, 4758 unique (*R*1 = 0.0269), *WR2* = 0.0627(all data). Residual electron density max/min = 0.34/-0.39e.$Å^{-3}$.The structure has been deposited at the CCDC data center and can be retrieved using the deposit number 1823256.

4.8.2. *(NNN^{Et})$FeCl_2$ (**2**)*

$C_{15}H_{23}Cl_2FeN_3$, yellow block, crystal dimensions: 0.18 × 0.14 x 0.12 mm^{-1}, $M = 376.14$, monoclinic with space group P2/n, $a = 13.8250(14)$ Å, $b = 9.3017(10)$ Å, $c = 14.8050(15)$ Å, $\alpha = 90°$, $\beta = 97.27(7)°$, $\gamma = 90°$, $V = 1886.6(3)$ $Å^3$, $Z = 4$, $F(000) = 792.0$, μ-(MoK_α) = 1.080 mm^{-1}, 2θmax = 54.342, $\rho_{calcd} = 1.324$ Mg/m^3, T = 100(2)K, min/max transmission factors = 0.5356/0.7455, 15059 Reflections collected, 4150 unique (*R1* = 0.0398), *WR2* = 0.0929(all data). Residual electron density max/min = 0.28/-0.51e.$Å^{-3}$.The structure has been deposited at the CCDC data center and can be retrieved using the deposit number 1823257.

4.9. *General procedure for catalytic cyclotrimerization of alkynes*

To a stirred solution of catalyst **1** in THF (1 mL), alkyne (0.5 mmol) and then EtMgBr (11 mol%, 1 M in THF) was charged in PTFE screw-capped reaction vial equipped with a stirrer bar inside the glovebox. Then, the reaction mixture was brought outside and stirred at room temperature. Progress of the reaction was monitored by GC, which indicated the completion of the reaction in specified time. The reaction mixture was quenched by exposing it to the open atmosphere. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography to provide cyclotrimerized product.

4.9.1. *Kinetic studies on cylotrimerization of phenylacetylene catalyzed by **1***

The conversion of phenylacetylene versus time was monitored by GC. Within 2 min 70% conversion was observed by GC, for remaining 23% it has taken ~5 h (Fig. 3). Thus, these NNN iron pincer catalyst species were found to be highly active precursor catalysts for the phenylacetylene cyclotrimerization with an initial TOF of 1.05 s−1 (measured at 15 min).

4.9.2. *4′-Phenyl-1,1′:2′,1″-terphenyl and 5′-phenyl-1,1′:3′,1″-terphenyl (**6a** and **7a**)*

6a:7a = 93:7; determined by GC analysis, this product was isolated by flash column chromatography on silica gel (Hexane). Yield 39 mg (76%), White solid; IR (DCM): 3057 (w), 3025 (w), 1472, 1441, 1264, 1241, 1074, 1028, 836, 754, 739, 694, 629 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.81 (s), 7.67–7.71 (m, 4H), 7.54 (d, 8 Hz, 1H), 7.46–7.50 (m, 2H), 7.37–7.41 (m, 1H), 7.21–7.26 (m, 10H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 141.6, 141.3, 141.1, 140.7, 140.5, 139.7, 131.2, 130.1, 130.0, 129.6, 129.0, 128.1, 128.0, 127.6, 127.3, 126.7, 126.7, 126.3. HRMS (EI) *m*/*z* Calcd for $C_{24}H_{19}$: $[M + H]^+$ 307.1481, found 307.1470.

4.9.3. *4,4″-Dimethyl-4′-(p-tolyl)-1,1′:2′,1″-terphenyl and 4,4″-dimethyl-5′-(p-tolyl)-1,1′:3′,1″-terphenyl (**6b** and **7b**)*

6b:7b = 92:8; determined by GC analysis, this product was isolated by flash column chromatography on silica gel (hexane). Yield 36 mg (62%), White solid; IR (DCM): 3022 (w), 2919 (w), 2860 (w), 1512, 1479, 1451, 1239, 1110, 1019, 1006, 841, 805, 759, 737 cm^{-1}. ^1H NMR ($CDCl_3$): δ7.78 (s), 7.60–7.67 (m), 7.49–7.51 (m), 7.26–7.33 (m), 7.07–7.16 (m), 2.46 (s, 3H), 2.44 (s, 3H), 2.36 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.3, 141.5, 140.9, 140.2, 139.3, 138.9, 138.55, 138.50, 137.9, 137.4, 137.3, 136.2, 136.1, 134.3, 131.2, 129.9, 129.8, 129.7, 129.4, 128.82, 128.79, 127.3, 127.1, 125.8, 124.7, 29.8, 21.3. HRMS (EI) *m*/*z* Calcd for $C_{27}H_{25}$: $[M + H]^+$ 349.1951, found 349.1957.

4.9.4. *3,3″-Dimethyl-4′-(m-tolyl)-1,1′:2′,1″-terphenyl and 3,3″-dimethyl-5′-(m-tolyl)-1,1′:3′,1″-terphenyl (**6c** and **7c**)*

6c:7c = 93:7; determined by GC analysis, this product was isolated by flash column chromatography on silica gel (hexane). Yield 37 mg (64%), white solid; IR (DCM): 3049 (w), 2923 (w), 2853 (w), 1583, 1551, 1264, 1243, 1045, 834, 782, 733, 701, 637 cm-1 ^{1}H NMR ($CDCl_3$): δ7.67 (s), 7.52–7.56 (m), 7.38–7.42 (m), 7.23–7.27 (m), 7.07–7.12 (m), 6.82–6.86 (m), 2.36 (s, 3H), 2.34 (s, 3H), 2.19 (s, 3H), 2.18 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 142.5, 141.7, 141.4, 141.3, 141.2, 140.8, 140.4, 139.7, 138.55, 138.51, 137.55, 137.49, 131.1, 130.70, 130.68, 129.5, 128.9, 128.3, 128.1, 127.78, 127.76, 127.4, 127.3, 127.24, 127.20, 126.1, 124.6, 124.4, 29.9, 21.7, 21.5. HRMS (EI) *m/z* Calcd for $C_{27}H_{25}$: $[M + H]^+$ 349.1951, found 349.1980.

*4.9.5. 2,2″-Dimethoxy-4′-(2-methoxyphenyl)-1,1′:2′,1″-terphenyl and 2,2″-dimethoxy-4′-(2-methoxyphenyl)-1,1′:2′,1″-terphenyl (**6d** and **7d**)*

6d:7d = 92:8; determined by GC analysis, this product was isolated by flash column chromatography on silica gel (EtOAc/hexane − 1/30). Yield 50 mg (76%), yellow gel; IR (DCM): 2998 (w), 2923 (w), 2836 (w), 1528, 1515, 1478, 1462, 1287, 1243, 1173, 1115, 1031, 819, 798, 637 cm^{-1}.^{1}H NMR ($CDCl_3$): δ7.73 (s), 7.63–7.65 (m), 7.47–7.49 (m), 7.33–7.37 (m), 7.18–7.20 (m), 7.08–7.16 (m), 7.02–7.07 (m), 6.85 (t, 8 Hz), 6.75 (t, 8 Hz), 3.87 (s, 3H), 3. 86 (s, 3H), 3.53 (s, 3H), 3.50 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 156.7, 156.4, 137.2, 131.7, 131.6, 131.3, 131.2, 130.6, 128.5, 128.4, 128.1, 120.9, 119.9, 111.2, 110.34, 110.33, 55.7, 55.6, 55.05, 55.03. HRMS (EI) *m/z* Calcd for $C_{27}H_{25}O_3$: $[M + H]^+$ 397.1798, found 397.1775.

*4.9.6. 4,4″-Dimethoxy-4′-(4-methoxyphenyl)-1,1′:2′,1″-terphenyl and 4,4″-dimethoxy-5′-(4-methoxyphenyl)-1,1′:3′,1″-terphenyl (**6e** and **7e**)*

6e:7e = 92:8; determined by GC analysis, this product was isolated by flash column chromatography on silica gel (EtOAc/hexane − 1/30). Yield 44 mg (67%), yellow gel; IR (DCM): 2998 (w), 2929 (w), 2834 (w), 1606, 1522, 1509, 1478, 1462, 1286, 1236, 1173, 1108, 1031, 819, 799, 734, 641 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ7.57–7.69 (m), 7.46 (d, 8H), 7.11–7.16 (m), 7.00–7.04 (m), 6.79–6.83 (m), 3.88 (s, 3H), 3.87 (s, 3H), 3.81 (s, 3H), 3.81 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 159.3, 158.5, 158.4, 140.5, 139.7, 134.3, 133.9, 133.3, 131.1, 131.05, 131.01, 129.0, 128.2, 125.5, 114.4, 113.6, 113.5, 55.49, 55.47, 55.30, 55.29. HRMS (EI) *m/z* Calcd for $C_{27}H_{25}O_3$: $[M + H]^+$ 397.1798, found 397.1768.

*4.9.7. 2,2″,4,4″,5,5″-Hexamethyl-4′-(2,4,5-trimethylphenyl)-1,1′:2′,1″-terphenyl and 2,2″,4,4″,5,5″-hexamethyl-5′-(2,4,5-trimethylphenyl)-1,1′:3′,1″-terphenyl (**6f** and **7f**)*

6f:7f = 92:8; determined by GC analysis, this product was isolated by flash column chromatography on silica gel (hexane). Yield 46 mg (64%), yellow solid; IR (DCM): 2966 (w), 2918 (w), 2861 (w), 1479, 1451, 878, 842, 738, 705 cm^{-1}.^{1}H NMR ($CDCl_3$): δ7.14–7.21 (m), 7.04 (s), 6.97 (s), 6.74–6.75 (m), 2.23 (s, 4H), 2.18–2.19 (m, 7H), 2.08 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 1.94 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 141.4, 140.1, 139.2, 135.5, 134.7, 133.9, 132.9, 132.8, 132.7, 132.6, 131.9, 131.7, 131.4, 131.1, 130.5, 128.6, 127.5, 20.2, 19.4, 19.3, 19.2, 19.1. HRMS (EI) *m/z* Calcd for $C_{33}H_{37}$: $[M + H]^+$ 433.2890, found 433.2904.

*4.9.8. 4,4″-Difluoro-4′-(4-fluorophenyl)-1,1′:2′,1″-terphenyl and 4,4″-difluoro-5′-(4-fluorophenyl)-1,1′:3′,1″-terphenyl (**6g** and **7g**)*

6g:7g = 94:6; determined by GC analysis, this product was isolated by flash column chromatography on silica gel (hexane). Yield 35 mg (58%), white solid; IR (DCM): 3046 (w), 1603, 1522, 1509, 1480, 1222, 1158, 835, 820, 739 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.68 (s), 7.58–7.65 (m), 7.47 (d, J = 8 Hz, 1H), 7.11–7.19 (m), 6.93–6.98 (m). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 164.0, 163.25, 163.21, 161.5, 160.80, 160.76, 141.7, 139.8, 131.55, 131.51, 131.47, 131.4, 131.2, 129.3, 128.85, 128.77, 126.3, 116.0, 115.8, 115.31, 115.27, 115.09, 115.06. ^{19}F NMR ($CDCl_3$): δ −115.5, −115.4, −115.0, −114.8. (ESI-MS) *m/z* Calcd for $C_{24}H_{16}F_3$: $[M + H]^+$ 361.1, found 361.1.

*4.9.9. 2,2″-Bis(trifluoromethyl)-4′-(2-(trifluoromethyl)phenyl)-1,1′:2′,1″-terphenyl and 2,2″-bis(trifluoromethyl)-5′-(2-(trifluoromethyl)phenyl)-1,1′:3′,1″-terphenyl (**6h** and **7h**)*

6h:7h = 92:8; determined by GC analysis, This product was isolated by flash column chromatography on silica gel (hexane). Yield 44 mg (51%), white solid; IR (DCM): 3067 (w), 1473, 1309, 1264, 1163, 1102, 1007, 765, 755, 656, 632 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.67 (d, J = 8 Hz, 2H), 7.54–7.59 (m), 7.47–7.50 (m), 7.29–7.41 (m), 7.18–7.25 (m), 7.01–7.16 (m), 6.99 (t, J = 6 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 140.7, 139.3, 139.0, 137.5, 137.3, 132.2, 132.0, 131.4, 131.1, 130.7, 129.64, 129.62, 129.3, 129.0, 128.7, 127.9, 127.7, 127.3, 126.3, 126.25, 126.20, 125.9, 125.8, 125.6, 123.2, 123.1, 122.9. ^{19}F NMR ($CDCl_3$): δ −57.92, −57.91, −57.19, −57.18, −57.13. HRMS (EI) *m/z* Calcd for $C_{27}H_{16}F_9$: $[M + H]^+$ 511.1103, found 511.1116.

*4.9.10. 4′-(3,5-Bis(trifluoromethyl)phenyl)-3,3″,5,5″-tetrakis(trifluoromethyl)-1,1′:2′,1″-terphenyl and 5′-(3,5-bis(trifluoromethyl)phenyl)-3,3″,5,5″-tetrakis(trifluoromethyl)-1,1′:3′,1″-terphenyl (**6i** and **7i**)*

6i:7i = 97:3; determined by GC analysis, this product was isolated by flash column chromatography on silica gel (hexane). Yield 80 mg (67%), white solid; IR (DCM): 1371, 1273, 1171, 1126, 1079, 893, 833, 740, 706 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 8.10 (s, 2H), 7.96 (s, 1H), 7.82–7.86 (m, 2H), 7.80 (s, 1H), 7.76 (d, J = 2 Hz), 7.70–7.72 (m, 1H), 7.60 (s, 2H), 7.57 (s, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 141.8, 141.7, 141.6, 141.4, 141.3, 139.7, 139.6, 139.2, 139.0, 138.5, 138.3, 132.2, 131.3, 131.2, 129.8, 129.1, 129.0, 128.23, 128.16, 127.3, 126.9, 124.6, 124.2, 121.8, 121.5, 121.2, 118.8. ^{19}F NMR ($CDCl_3$): δ −64.34, −64.30, −63.8.

*4.9.11. 1,2,4-Tripentylbenzene and1,3,5-tripentylbenzene (**9a** and **10a**)*

9a:10a = 60:40; determined by ^{1}H NMR, this product was isolated by flash column chromatography on silica gel (hexane). Yield 28 mg (57%), yellow oil; IR (DCM): 2954, 2925, 2859, 1497, 1459, 1375, 829, 729 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.05 (d, J = 8 Hz, 1H), 6.93–6.95 (m, 2H), 6.82 (s, 3H), 2.53–2.59 (m), 1.57–1.62 (m), 1.33–1.37 (m), 0.88–0.93 (m). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 142.9, 140.5, 140.3, 137.8, 129.4, 129.1, 126.0, 125.8, 36.1, 35.7, 32.9, 32.4, 32.20, 32.19, 31.83, 31.81, 31.45, 31.43, 31.2, 22.75, 22.72, 14.2. HRMS (EI) *m/z* Calcd for $C_{21}H_{35}$: $[M - H]^+$ 287.2733, found 287.2728.

*4.9.12. 1,2,4-Triisopentylbenzene and 1,3,5-triisopentylbenzene (**9b** and **10b**)*

9b:10b = 60:40; determined by GC analysis, this product was isolated by flash column chromatography on silica gel (hexane). Yield 48 mg (63%), yellow oil; IR (DCM): 2954, 2929, 2869, 1466, 1383, 1367, 736, 704 cm-1 ^{1}H NMR ($CDCl_3$): δ 7.04 (d, J = 8 Hz, 1H), 6.93–6.95 (m, 2H), 6.82 (s, 3H), 2.53–2.57 (m), 1.46–1.56 (m), 0.93–0.98 (m). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 143.1, 140.7, 140.5, 137.9, 129.3, 129.2, 125.8, 41.12, 41.08, 34.0, 33.5, 30.8, 30.3, 28.6, 28.5, 28.0, 22.8, 22.7. (ESI-MS) *m/z* Calcd for $C_{21}H_{37}$: $[M + H]^+$ 289.2, found 289.2.

*4.9.13. 1,2,4-Triisobutylbenzene and 1,3,5-triisobutylbenzene (**9c** and **10c**)*

9c:10c = 63:37; determined by GC analysis, this product was isolated by flash column chromatography on silica gel (hexane). Yield 28 mg (68%), yellow oil; IR (DCM): 2954, 2927, 2869, 1735, 1464, 1383, 1367, 1264, 1243, 737, 721 cm-1 ^{1}H NMR ($CDCl_3$): δ 7.01 (d, J = 8 Hz, 1H), 6.88–6.91 (m, 2H), 6.75 (s, 3H), 2.46 (dd, J_1 = 7 Hz, J_2 = 2 Hz), 2.42 (d, J = 7 Hz), 1.81–1.86 (m, J = 7 Hz), 0.93 (d, J = 7 Hz), 0.90 (d, J = 7 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 141.1, 139.4, 138.7, 137.0, 131.0, 129.8, 127.5, 126.4, 45.6, 45.3, 42.2, 41.7, 30.50, 30.46, 30.0, 22.8, 22.6. HRMS (EI) *m/z* Calcd for $C_{18}H_{29}$: [M - H]$^+$ 245.2264, found 245.2232.

*4.9.14. 1,2,4-Tricyclopentylbenzene and 1,3,5-tricyclopentylbenzene (**9d** and **10d**)*

9d:10d = 50:50; determined by ^{1}H NMR, this product was isolated by flash column chromatography on silica gel (hexane). Yield 24 mg (51%), yellow oil; IR (DCM): 2947, 2866, 1496, 1451, 1301, 1184, 1046, 886, 868, 712 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.20 (d, J = 8 Hz, 1H), 7.15 (d, 2 Hz, 1H), 7.05 (dd, J_1 = 8 Hz, J_2 = 2 Hz), 6.96 (s, 3H), 3.25–3.36 (m), 2.96 (pent, J = 8 Hz), 2.03–2.08 (m), 1.80–1.82 (m), 1.61–1.70 (m). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 146.3, 143.8, 143.6, 141.4, 125.7, 124.7, 124.5, 123.6, 46.3, 46.0, 41.3, 41.0, 35.12, 35.09, 34.84, 34.77, 25.69. HRMS (EI) *m/z* Calcd for $C_{21}H_{29}$: [M - H]$^+$ 281.2264, found 281.2243.

*4.9.15. (Benzene-1,2,4-triyltris(methylene))tricyclohexane and 1,3,5-tris(cyclohexylmethyl)benzene (**9e** and **10e**)*

9e:10e = 56:44; determined by GC analysis, this product was isolated by flash column chromatography on silica gel (hexane). Yield 40 mg (66%), yellow gel; IR (DCM): 2918, 2848, 1447, 1372, 1262, 1239, 1046, 737 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 6.99 (d, J = 8 Hz, 1H), 6.86–6.88 (m, 2H), 6.73 (s, 3H), 2.41–2.45 (m), 1.48–1.69 (m), 1.16–1.18 (m), 0.89–0.98 (m). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 140.7, 139.0, 138.2, 136.6, 131.2, 129.9, 127.6, 126.2, 44.3, 43.9, 40.9, 40.5, 40.0, 39.9, 39.6, 33.7, 33.4, 26.8, 26.6, 26.5. ESI-MS *m/z* Calcd for $C_{27}H_{41}$ [M - H]$^+$: 365.3 found 365.3.

*4.9.16. 1,2,4-Tri-tert-butylbenzene and 1,3,5-tri-tert-butylbenzene (**9f** and **10f**)*

9f:10f = 69:31; determined by GC analysis, this product was isolated by flash column chromatography on silica gel (hexane). Yield 29 mg (70%), yellow oil; IR (DCM): 2956, 2868, 1470, 1391, 1362, 1259, 1201, 893, 737 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.62 (d, J = 8 Hz, 1H), 7.50 (d, J = 8 Hz, 1H), 7.25 (s, 3H), 7.12 (dd, J_1 = 8 Hz, J_2 = 2 Hz), 1.56 (s), 1.54 (s), 1.33 (s), 1.31 (s). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 150.1, 147.5, 145.7, 129.3, 126.9, 122.4, 121.7, 119.6, 37.4, 35.1, 35.01, 34.97, 32.7, 32.3, 31.7, 31.5. ESI-MS *m/z* Calcd for $C_{18}H_{31}$: [M + H]$^+$ 247.2, found 247.2.

*4.9.17. (Benzene-1,2,4-triyltris(methylene))tribenzene and 1,3,5-tribenzylbenzene (**9g** and **10g**)*

9g:10g = 58:42; determined by GC analysis, this product was isolated by flash column chromatography on silica gel (hexane). Yield 34 mg (53%), yellow oil; IR (DCM): 3058, 3025, 2918, 1599, 1493, 1449, 1073, 1029, 726, 699 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.23–7.30 (m), 7.14–7.20 (m), 7.06 (d, J = 8 Hz), 6.88 (s, 3H), 3.93 (d, J = 8 Hz), 3.90 (s). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 141.4, 141.35, 141.29, 140.74, 140.68, 139.4, 139.0, 137.0, 131.5, 130.8, 129.02, 128.98, 128.9, 128.8, 128.54, 128.51, 128.49, 127.6, 127.3, 126.1, 126.1, 126.0, 41.9, 41.6, 39.2, 38.7. HRMS (EI) *m/z* Calcd for $C_{27}H_{25}$: [M + H]$^+$ 349.1951, found 349.1936.

*4.9.18. (Benzene-1,2,4-triyltris(ethane-2,1-diyl))tribenzene and 1,3,5-triphenethylbenzene (**9h** and **10h**)*

9h:10h = 45:55; determined by GC analysis, this product was isolated by flash column chromatography on silica gel (hexane). Yield 34 mg (53%), yellow oil; IR (DCM): 3025, 2927, 2857, 1602, 1495, 1452, 1074, 1029, 746, 699 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.35–7.36 (m), 7.26–7.27 (m), 7.03–7.08 (m), 6.90 (s, 1H), 2.94 (s). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 142.1, 141.9, 139.7, 139.5, 137.1, 129.7, 129.4, 128.6, 128.5, 128.4, 126.5, 126.4, 126.1, 126.0, 38.22, 38.17, 38.09, 37.9, 37.7, 35.0, 34.6. HRMS (EI) *m/z* Calcd for $C_{30}H_{31}$: [M + H]$^+$ 391.2420, found 391.2401.

*4.9.19. 1,2,4-Tris((allyloxy)methyl)benzene and 1,3,5-tris((allyloxy)methyl)benzene (**9i** and **10i**)*

9i:10i = 60:40; determined by GC analysis, this product was isolated by flash column chromatography on silica gel (hexane). Yield 37 mg (64%), colorless oil; IR (DCM): 2919, 2857, 1720, 1697, 1354, 1157, 1068, 990, 925, 835 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.34–7.36 (m, 3H), 7.24 (s, 3H), 5.89–5.96 (m), 5.26–5.30 (m), 5.17–5.19 (m), 4.56–4.57 (m), 4.50 (s), 3.99–4.02 (m). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 138.8, 138.0, 136.7, 135.9, 134.84, 134.81, 129.0, 128.3, 127.1, 126.4, 117.32, 117.29, 117.2, 72.0, 71.9, 71.44, 71.37, 71.3, 71.2, 69.8, 69.6. HRMS (EI) *m/z* Calcd for $C_{18}H_{23}O_3$: [M − H]$^+$ 287.1647, found 287.1645.

*4.9.20. ((Benzene-1,2,4-triyltris(methylene))tris(oxy))tribenzene and 1,3,5-tris(phenoxymethyl)benzene (**9j** and **10j**)*

9j:10j = 60:40; determined by ^{1}H NMR, this product was isolated by flash column chromatography on silica gel (hexane). Yield 24 mg (36%), yellow oil; IR (DCM): 3068, 2923, 1594, 1493, 1234, 1172, 1076, 1036, 743, 696 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.63 (s, 1H), 7.56 (d, J = 8 Hz, 1H), 7.50 (s), 7.46 (d, J = 8 Hz, 1H), 7.28–7.33 (m), 6.97–7.01 (m), 5.19 (s), 5.11 (s), 5.10 (s). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 158.8, 158.7, 138.1, 137.5, 135.0, 129.67, 129.65, 129.64, 129.3, 128.1, 127.5, 126.1, 121.30, 121.27, 121.20, 121.16, 115.0, 114.99, 114.97, 114.96, 69.8, 69.6, 68.0, 67.8. HRMS (EI) *m/z* Calcd for $C_{27}H_{24}NaO_3$: [M + Na]$^+$ 419.1618, found 419.1608.

*4.9.21. N,N′,N″-(Benzene-1,2,4-triyltris(methylene))tris(N-methyl-1-phenylmethanamine) and N,N′,N″-(benzene-1,3,5-triyltris(methylene))tris(N-methyl-1-phenylmethanamine) (**9k** and **10k**)*

9k:10k = 59:41; determined by GC analysis, this product was isolated by flash column chromatography on silica gel (hexane). Yield 40 mg (50%), yellow oil; IR (DCM): 3059, 3028, 2931, 2783, 1493, 1452, 1363, 1129, 1026, 738, 700 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.22–7.42 (m), 3.64 (d, J = 8 Hz), 3.53 (m), 3.49 (s), 2.18–2.20 (m), 2.12 (s), 2.11 (s). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 139.7, 139.4, 139.1, 138.1, 137.6, 137.0, 131.0, 130.3, 129.2, 129.13, 129.10, 128.5, 128.33, 128.28, 127.5, 127.03, 127.00, 126.98, 62.49, 62.46, 62.0, 61.93, 61.86, 61.8, 59.5, 59.2, 42.40, 42.37, 42.3. HRMS (EI) *m/z* Calcd for $C_{33}H_{40}N_3$: [M + H]$^+$ 478.3217, found 478.3208.

*4.9.22. ((Benzene-1,2,4-triyltris(methylene))tris(oxy))tris(tert-butyldimethylsilane) and 1,3,5-tris(((tert-butyldimethylsilyl)oxy)methyl)benzene (**9l** and **10l**)*

9l:10l = 69:31; determined by GC analysis, this product was isolated by flash column chromatography on silica gel (hexane). Yield 61 mg (72%), Yellow oil; IR (DCM): 3068, 2923, 1594, 1493, 1234, 1172, 1076, 1036, 743, 696 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.40 (s), 7.36 (d, J = 8 Hz, 1H), 7.20 (d, J = 8 Hz, 1H), 7.16 (s, 3H), 4.76 (s), 4.73 (s), 0.94 (s), 0.93 (s), 0.10 (s), 0.09 (s). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 141.5, 126.7, 124.7, 124.6, 122.5, 65.2, 63.0, 29.8, 26.15, 26.13, 26.09, 18.6, −5.08, −5.15. (ESI-MS) *m/z* Calcd for $C_{27}H_{54}NaO_3Si_3$: [M + Na]$^+$ 533.3, found 533.3.

*4.9.23. ((Benzene-1,2,4-triyltris(ethane-2,1-diyl))tris(oxy))tris(tert-butyldimethylsilane) and 1,3,5-tris(2-((tert-butyldimethylsilyl)oxy)ethyl)benzene (**9m** and **10m**)*

9 m:10 m = 60:40; determined by GC analysis, this product was isolated by flash column chromatography on silica gel (hexane). Yield 37 mg (64%), yellow oil; IR (DCM): 2931, 2891, 2858, 1466, 1385, 1253, 1092, 834, 775, 731, cm^{-1}.^{1}H NMR (CDCl$_3$): δ 7.07 (d, J = 8 Hz, 1H), 6.97–7.00 (m, 2H), 6.88 (s), 3.75–3.80 (m), 2.85 (t, J = 8 Hz), 2.77 (t, J = 8 Hz), 0.88 (s), 0–0.01 (m). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 139.0, 137.1, 135.0, 131.1, 130.2, 128.0, 127.2, 64.8, 64.5, 64.4, 39.7, 39.4, 36.5, 36.2, 26.1, 18.5, −5.2. HRMS (EI) *m/z* Calcd for

$C_{30}H_{61}O_3Si_3$: [M + H]$^+$ 553.3923, found 553.3940.

4.9.24. *(Benzene-1,2,4-triyltris(trimethylsilane) and 1,3,5-tris(trimethylsilyl)benzene (**9n** and **10n**)*

9n:10n = 60:40; determined by GC analysis, this product was isolated by flash column chromatography on silica gel (hexane). Yield 40 mg (80%), yellow oil; IR (DCM): 2955 (w), 2899 (w), 1250, 1147, 836, 750, 691 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.85 (s, 3H), 7.66–7.70 (m, 1H), 7.50–7.52 (m, 1H), 0.38 (d, J = 4 Hz), 0.28 (s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 146.7, 145.0, 140.1, 139.5, 134.5, 132.9, 2.1, 2.0, −1.1. (ESI-MS) m/z Calcd for $C_{15}H_{31}Si_3$: [M + H]$^+$ 295.1, found 295.1.

4.9.25. *3′,4′,6′-Trimethyl-5′-phenyl-1,1′:2′,1″-terphenyl [25] (**12a**)*

This product was isolated by flash column chromatography on silica gel (hexane). Yield 32 mg (55%), white solid; IR (DCM): 3021 (w), 2963 (w), 2930 (w), 2874 (w), 1444, 1373, 1076, 1049, 1047, 734, 698 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.47–7.50 (m, 2H), 7.37–7.41 (m, 1H), 7.28–7.31 (m, 2H), 7.00–7.18 (m, 10H), 2.09 (overlapped singlet, 2 × 3H), 1.76 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 142.6, 141.8, 141.7, 141.6, 140.8, 139.4, 134.1, 132.0, 131.4, 130.4, 129.5, 128.6, 127.5, 127.4, 126.6, 125.9, 125.8, 19.6, 18.4, 18.2. (ESI-MS) m/z Calcd for $C_{27}H_{25}$: [M +H]$^+$ 349.1, found 349.1.

4.9.26. *3′,4′,6′-Triethyl-5′-phenyl-1,1′:2′,1″-terphenyl [26] (**12b**)*

This product was isolated by flash column chromatography on silica gel (hexane). Yield 27 mg (42%), white solid; IR (DCM): 3022 (w), 2968 (w), 2931 (w), 2872 (w), 1440, 1371, 1071, 1047, 1042, 735, 697 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.42–7.46 (m, 2H), 7.35–7.39 (m, 3H), 7.02–7.14 (m, 10H), 2.44–2.53 (m, 4H), 2.10–2.18 (m, 2H), 0.96–1.04 (m, 6H), 0.65 (t, J = 8 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 141.7, 141.6, 141.5, 141.4, 141.3, 139.5, 139.4, 137.8, 137.4, 130.7, 130.6, 130.2, 127.9, 127.10, 127.07, 126.6, 125.75, 125.69, 24.7, 23.7, 23.6, 15.8, 15.4. HRMS (EI) m/z Calcd for $C_{30}H_{31}$: [M +H]$^+$ 391.2420, found 391.2401.

4.9.27. *3′,4′,6′-Tributyl-5′-phenyl-1,1′:2′,1″-terphenyl [26] (**12c**)*

This product was isolated by flash column chromatography on silica gel (hexane). Yield 36 mg (45%), white solid; IR (DCM): 3021 (w), 2955 (w), 2926 (w), 2870 (w), 1459, 1378, 1071, 1026, 1042, 749, 699 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.40–7.44 (m, 2H), 7.32–7.36 (m, 3H), 7.01–7.13 (m, 10H), 2.37–2.44 (m, 4H), 2.04–2.08 (m, 2H), 1.36–1.45 (m, 4H), 1.05–1.17 (m, 6H), 0.68–0.75 (m, 8H), 0.38 (t, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 141.73, 141.67, 141.42, 141.36, 139.4, 138.5, 136.7, 136.4, 130.8, 130.6, 130.2, 127.8, 127.04, 127.00, 126.5, 125.7, 125.6, 33.6, 33.0, 31.2, 30.6, 30.4, 23.3, 22.8, 13.7, 13.6, 13.2. HRMS (EI) m/z Calcd for $C_{36}H_{43}$: [M + H]$^+$ 475.3359, found 475.3321.

4.9.28. *Determination of the Molecular Structures of 4,4″-difluoro-4′-(4-fluorophenyl)-1,1′:2′,1″-terphenyl (**6g**), 4′-(3,5-bis(trifluoromethyl)phenyl)-3,3″,5,5″-tetrakis(trifluoromethyl)-1,1′:2′,1″-terphenyl (**6i**) and 3′,4′,6′-trimethyl-5′-phenyl-1,1′:2′,1″-terphenyl (**12a**) in the Solid State by Single Crystal X-ray Diffraction*

Single crystals of complexes **6g, 6i** and **12a** suitable for X-ray analysis was obtained from solutions of hexane-dichloromethane and hot hexane, respectively. Crystals suited for single crystal x-ray diffraction measurements were mounted on a glass fiber. Geometry and intensity data were collected with a Bruker SMART D8 goniometer equipped with an APEX CCD detector and with an Incoatecmicrosource (Mo-Kα radiation, λ = 0.71073 Å, multilayeroptics). Temperature was controlled using an Oxford Cryostream 700 instrument. Intensities were integrated with SAINT+ [21]and corrected for absorption with SADABS [22]. The structures were solved by direct methods and refined on $F^2$with SHELXL-97 [23,24].

4.10. *Crystal data of 6g, 6i and 12a*

4.10.1. *4,4″-Difluoro-4′-(4-fluorophenyl)-1,1′:2′,1″-terphenyl (**6g**)*

$C_{24}H_{15}F_3$, colorless block, crystal dimensions: 0.18 × 0.15 × 0.12 mm^3, M = 360.36, Monoclinic with space group P2$_1$/c, a = 12.3035(8)Å, b = 9.5708(7)Å, c = 30.749(2)Å, α = 90°, β = 96.009°, γ = 90°,V = 3600.9(4) Å^3, Z = 8,F(000) = 1488.0, μ-(MoK$_\alpha$) = 0.098 mm^{-1}, 2θmax = 57.346, ρ_{calcd} = 1.329 Mg/m^3, T = 296(2)K, min/max transmission factors = 0.6390/0.7458, 31818 Reflections collected, 9254 unique ($R1$ = 0.0554), $WR2$ = 0.1260 (all data). Residual electron density max/min = 0.16/-0.25e.Å^{-3}.The structure has been deposited at the CCDC data center and can be retrieved using the deposit number 1823258.

4.10.2. *4′-(3,5-bis(trifluoromethyl)phenyl)-3,3″,5,5″-tetrakis(trifluoromethyl)-1,1′:2′,1″-terphenyl (**6i**)*

$C_{30}H_{12}F_{18}$, colorless block, crystal dimensions: 0.14 × 0.13 × 0.11 mm^3, M = 714.40, Monoclinic with space group P21/c, a = 11.2394(5)Å, b = 16.1180(6)Å, c = 15.2720(5)Å, β = 91.835(2)°, V = 2765.21(18)Å^3, Z = 4, T = 296.15 K, μ(MoKα) = 0.185 mm-1, min/max transmission factors = 0.6108/0.7456, ρ_{calcd} = 1.716 g/cm3, 40456 Reflections collected, 6367 unique ($R1$ = 0.0709), 2θmax = 55.282°, $WR2$ = 0.2108 (all data). Residual electron density max/min = 1.28–1.07e.Å^{-3}. The structure has been deposited at the CCDC data center and can be retrieved using the deposit number 1858249.

4.10.3. *3′,4′,6′-Trimethyl-5′-phenyl-1,1′:2′,1″-terphenyl (**12a**)*

$C_{27}H_{24}$, colorless block, crystal dimensions: 0.19 × 0.17 × 0.12 mm^3, M = 348.46, Monoclinic with space group P1 21/c 1, a = 11.5979(8)Å, b = 11.2436(7)Å, c = 15.6132(10)Å, α = 90°, β = 99.630(4)°, γ = 90°, V = 2007.3(2) Å^3, Z = 4, F(000) = 744, μ-(MoK$_\alpha$) = 0.065 mm^{-1}, 2θmax = 56.772, ρ_{calcd} = 1.153 Mg/m^3, T = 298(2)K, min/max transmission factors = 0.5722/0.7457, 17427 Reflections collected, 5006 unique ($R1$ = 0.0522), $WR2$ = 0.1501 (all data). Residual electron density max/min = 0.199/−0.169e.Å^{-3}. The structure has been deposited at the CCDC data center and can be retrieved using the deposit number 1823259.

5. EPR studies

5.1. *EPR measurement parameters.*

Frequency = 9.45 GHz, modulation amplitude = 4 G, receiver gain = 2 × 10^2, modulation frequency = 100 KHz, conversion time = 20 msec, sweep width = 1000 G, center field = 3400 G, Power = 5.35 e $^{-1}$ mW.

Notes

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2018.12.007.

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