Supporting information

Cobalt-NHC Promoted Selective Functionalization of Alkynes *via* Auxiliary-Ligand Modulation

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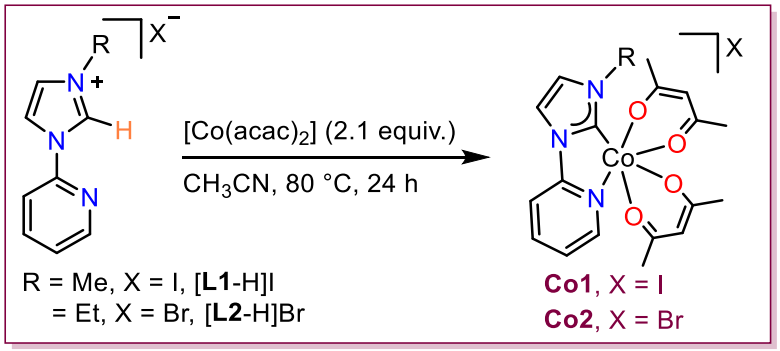
General experimental description:

All the reactions were performed under inert atmosphere unless stated otherwise. All non-deuterated solvents used for the synthesis were distilled by standard methods, whereas the deuterated solvents were used as received from the commercial sources. NMR spectra were recorded using the Bruker 400 and 500 MHz FT-NMR spectrometers at ambient temperature and all the $^{1}H/^{13}C\{^{1}H\}$ NMR spectra were referenced internally to the residual solvent signals. ^{11}B NMR spectra were referenced externally to $BF_3{\cdot}Et_2O$ in $CDCl_3$ (δ = 0 ppm), ^{19}F NMR spectra were referenced to α,α,α-trifluorotoluene (0.05% in $CDCl_3$; δ = -63.73 ppm). The ESI-MS spectra were measured with an Agilent 6545A Q-TOF Mass spectrometer. The chemicals such as the cobalt precursor, $[Co(Cp^*)COI_2]$[1a] and the salts [**L1-3**][1b-c] were synthesized according to literature procedures. The starting materials 4-ethynylbenzotrifluoride, 2-ethynyl anisole, methyl 4-ethynylbenzoate, 6-methoxy 1-ethynylnaphthalene, 1-ethynyl naphthalene, 9-ethynylphenanthrene, 1,4-diethynyl benzene and phenylacetylene-*D* were synthesized according to the literature procedures.[1d-f] All other chemicals were purchased from commercial sources and used as received.

General Procedure for the synthesis of complexes:



The azolium salts [**L1-2**-H]I/Br (100 mg, 1 equiv.) and the metal precursor $Co(acac)_2$ (2.1 equiv.) were taken in a Schlenk tube followed by the addition of acetonitrile in open-air. The reaction mixture was then stirred at 80 °C for 24 h. After that, the reaction mixture was dried in vacuo and the obtained residue was purified by column chromatography using DCM/methanol as eluent to get the corresponding complexes as air-stable reddish-brown solid.

Complex (Co1): The complex **Co1** was synthesized following the general procedure using 100 mg of [**L1-**H]I (Yield: 146 mg, 0.267 mmol, 77%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.88 (d, 1H), 8.42-8.40 (m, 1H), 8.38-8.35 (m, 1H), 8.26 (d, J = 6.2 Hz, 1H), 8.00 (d, J = 2.3 Hz, 1H), 7.62 (t, J = 7.23 Hz, 1H), 5.68 (s, 1H), 5.63 (s, 1H), 3.96 (s, 3H), 2.46 (s, 3H), 2.12 (s, 3H), 1.76 (s, 3H), 1.68 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) δ 190.4, 189.5, 189.4,

188.0, 161.3, 152.5, 150.3, 143.5, 128.7, 123.8, 119.2, 113.0, 98.3, 97.8, 35.8, 27.4, 26.1, 25.7, 25.6 ppm. MS (ESI, positive ions): *m/z* 416.1034 (calcd. for $[M\text{-}I]^+$: *m/z* 416.1017).

Complex (Co2): The complex **Co2** was synthesized following the general procedure using 100 mg of [**L2-**H]Br (Yield: 169 mg, 0.330 mmol, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.42 (s, 1H), 8.95 (d, J = 8.1 Hz, 1H), 8.22 (t, J = 7.7 Hz, 1H), 8.06 (d, J = 5.8 Hz, 1H), 7.67 (s, 1H), 7.37 (t, J = 6.6 Hz, 1H), 5.48 (s, 1H), 5.40 (s, 1H), 4.40-4.35 (m, 1H), 4.20-4.15 (m, 1H), 2.39 (s, 3H), 2.03 (s, 3H), 1.73 (s, 3H), 1.66 (s, 3H), 1.41 (t, J = 7.3 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 190.1, 190.0, 189.0, 160.5, 153.7, 149.4, 143.4, 126.4, 123.0, 121.8, 115.0, 98.5, 98.0, 45.0, 27.5, 26.5, 26.0, 25.8, 17.0 ppm. MS (ESI, positive ions): *m/z* 430.1186 (calcd. for $[M\text{-}Br]^+$: *m/z* 430.1173).

Synthesis of complex (Co3): The azolium salt [**L3**-H]Br (1 equiv.) and Ag_2O (0.6 equiv.) were taken in a Schenk tube, and after addition of acetonitrile, the reaction mixture was stirred in dark at ambient temperature. After 12 h of reaction time, metal precursor $Co(acac)_2$ (1 equiv.) was added and again stirred for 12 h at room temperature. The crude reaction mixture was first filtered through a small pad of celite, and the obtained filtrate was dried and purified *via* column chromatography using DCM/methanol as eluent to get the complex **Co3** as a reddish-pink solid (Yield: 161 mg, 0.307 mmol, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.59 (s, 1H), 8.99 (d, J = 8.28 Hz, 1H), 8.22-8.19 (m, 1H), 8.07 (d, J = 5.4 Hz, 1H), 7.52 (s, 1H), 7.35 (t, J = 6.23 Hz, 1H), 5.51 (s, 1H), 5.42 (s, 1H), 4.81-4.75 (m, 1H), 2.41 (s, 3H), 2.05 (s, 3H), 1.76 (s, 3H), 1.70 (s, 3H), 1.56 (d, J = 6.71 Hz, 3H), 1.45 (d, J = 6.71 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 190.2, 190.1, 189.1, 189.0, 159.4, 153.9, 149.4, 143.4, 122.9, 122.5, 121.6, 115.2, 98.6, 98.1, 51.1, 27.6, 26.6, 26.1, 25.9, 23.7, 23.5 ppm. MS (ESI, positive ions): *m/z* 444.1341 (calcd. for $[M\text{-}Br]^+$: *m/z* 444.1330).

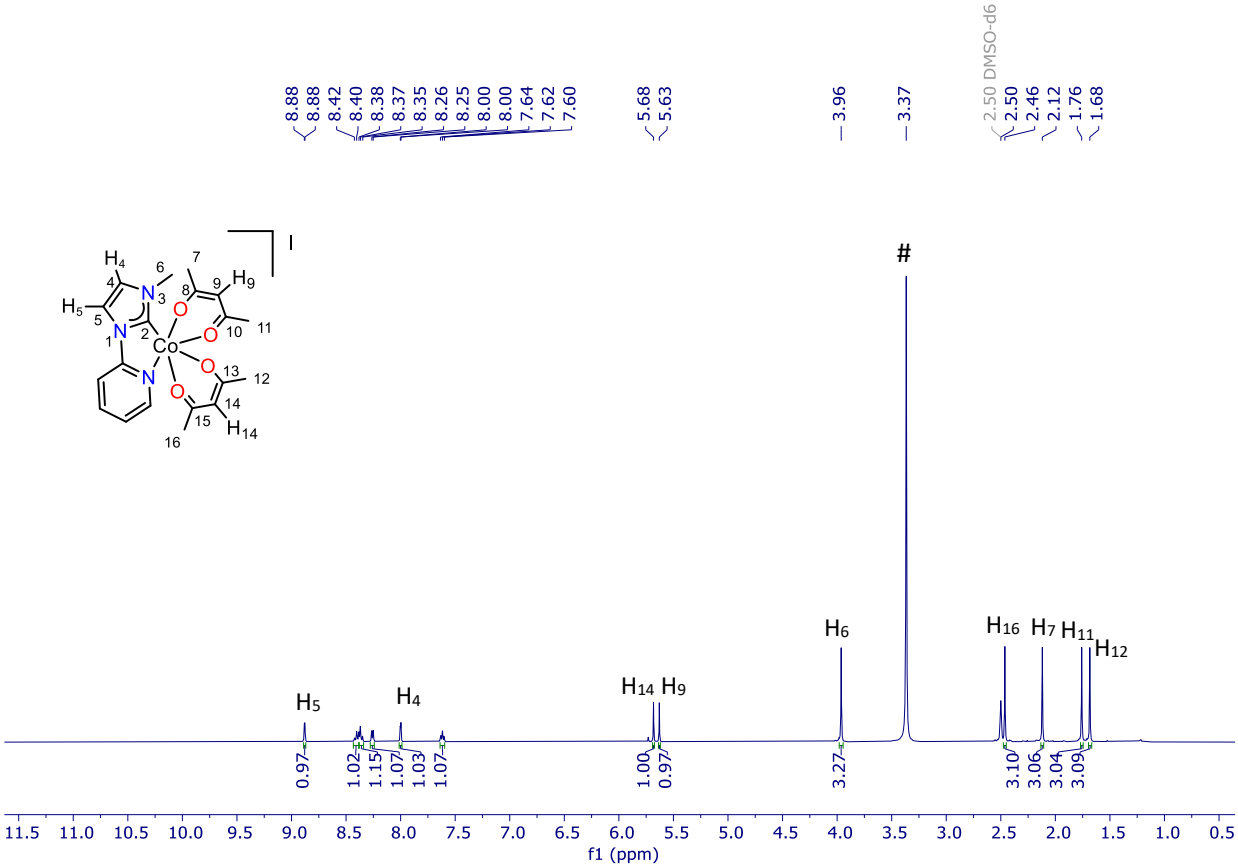


Figure S1. ^{1}H NMR spectrum of **Co1** in DMSO-d_6. # Indicate the solvent impurity of H_2O

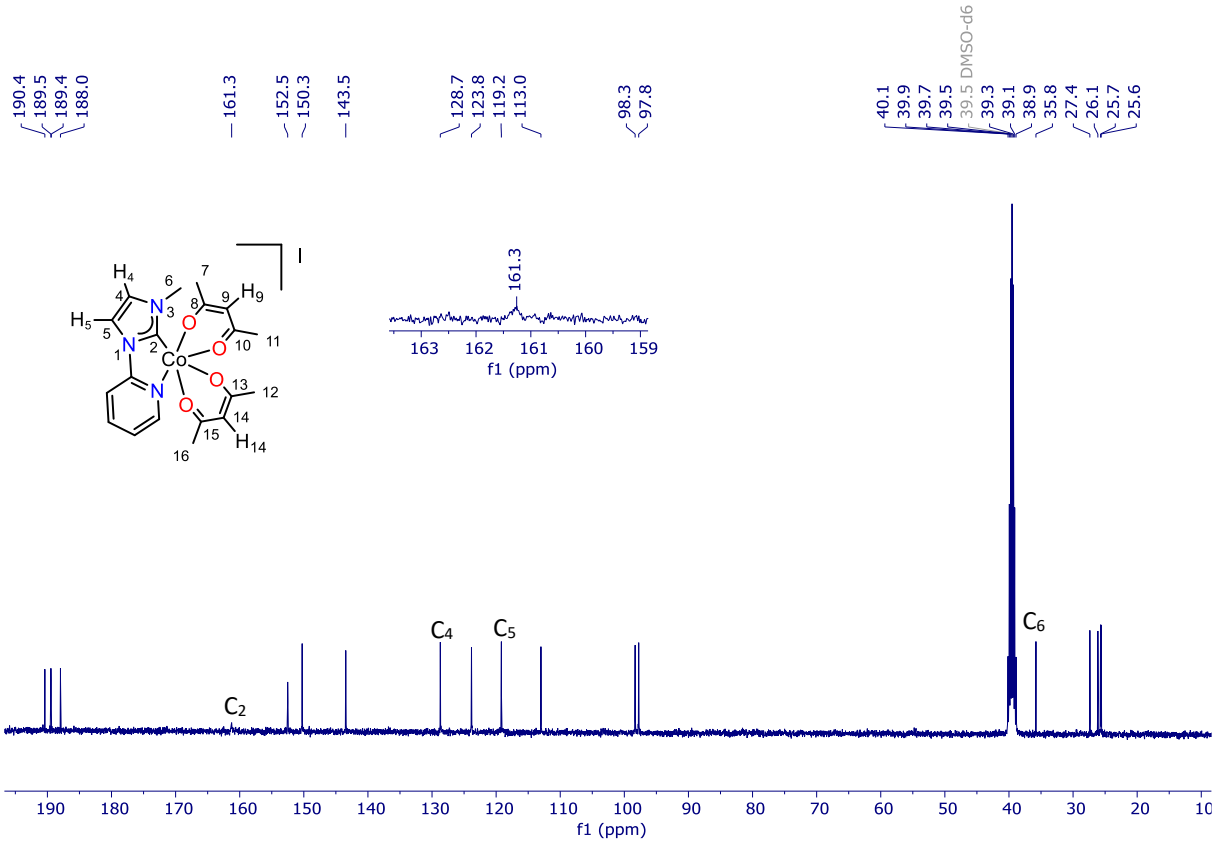


Figure S2. ^{13}C{^{1}H} NMR spectrum of **Co1** in DMSO-d_6

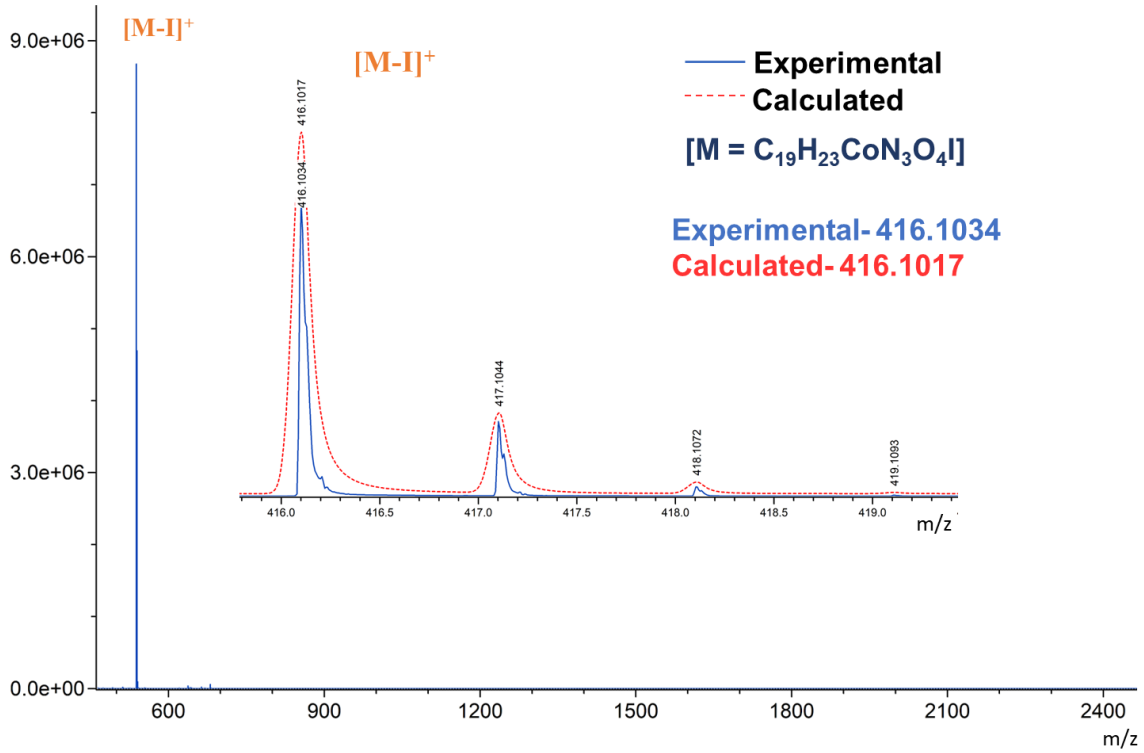


Figure S3. ESI-MS (positive ions) spectrum of the **Co1** complex

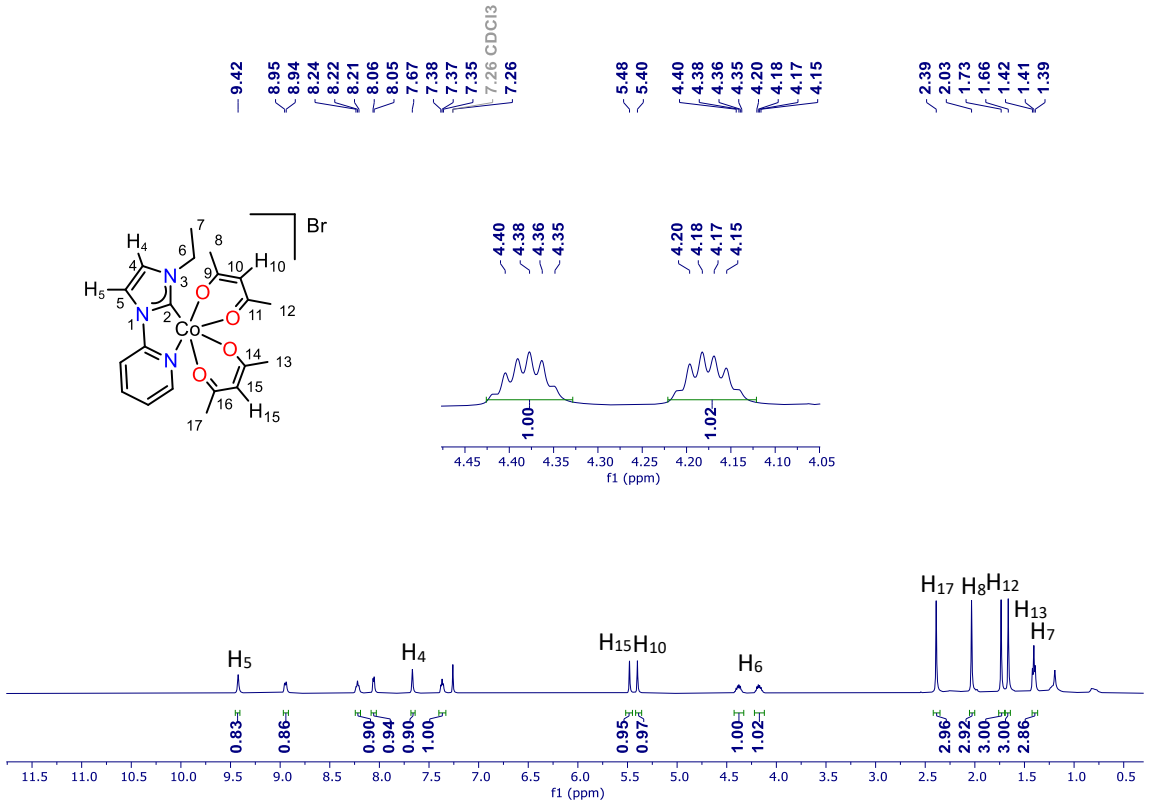


Figure S4. ^{1}H NMR spectrum of **Co2** in $CDCl_3$

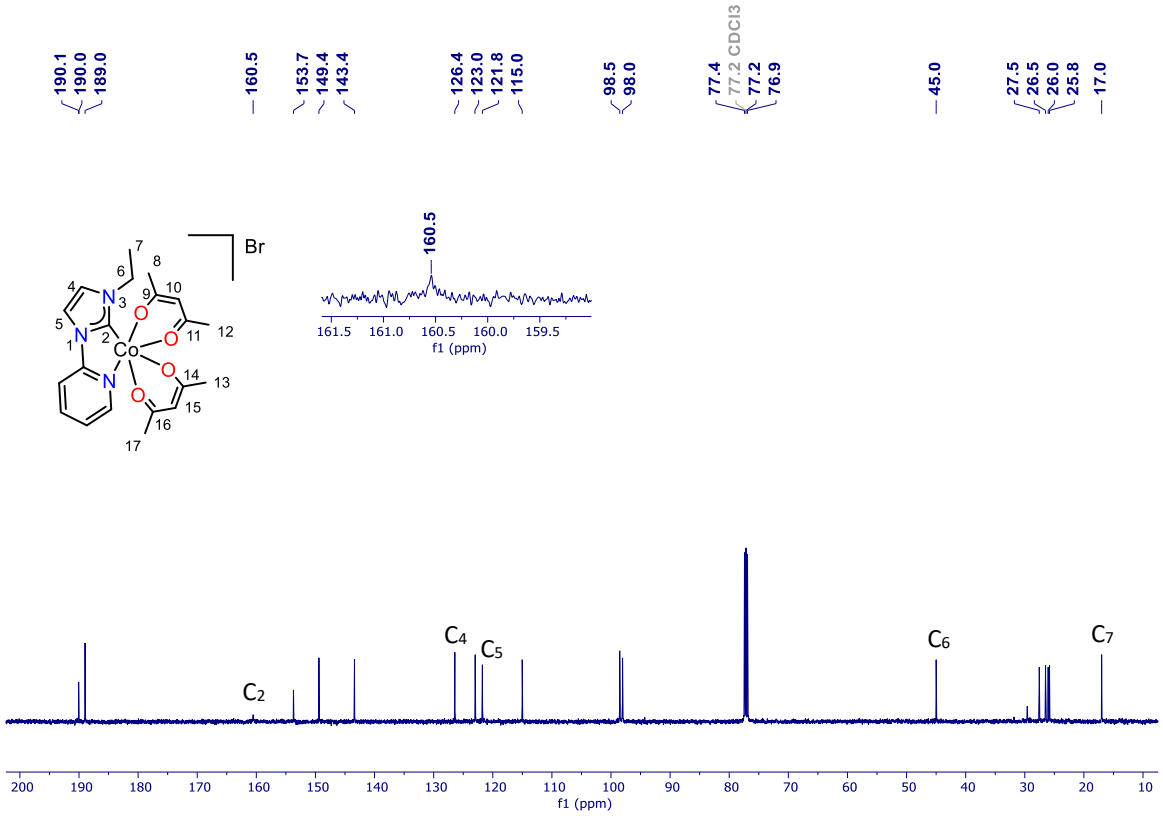


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of **Co2** in $CDCl_3$

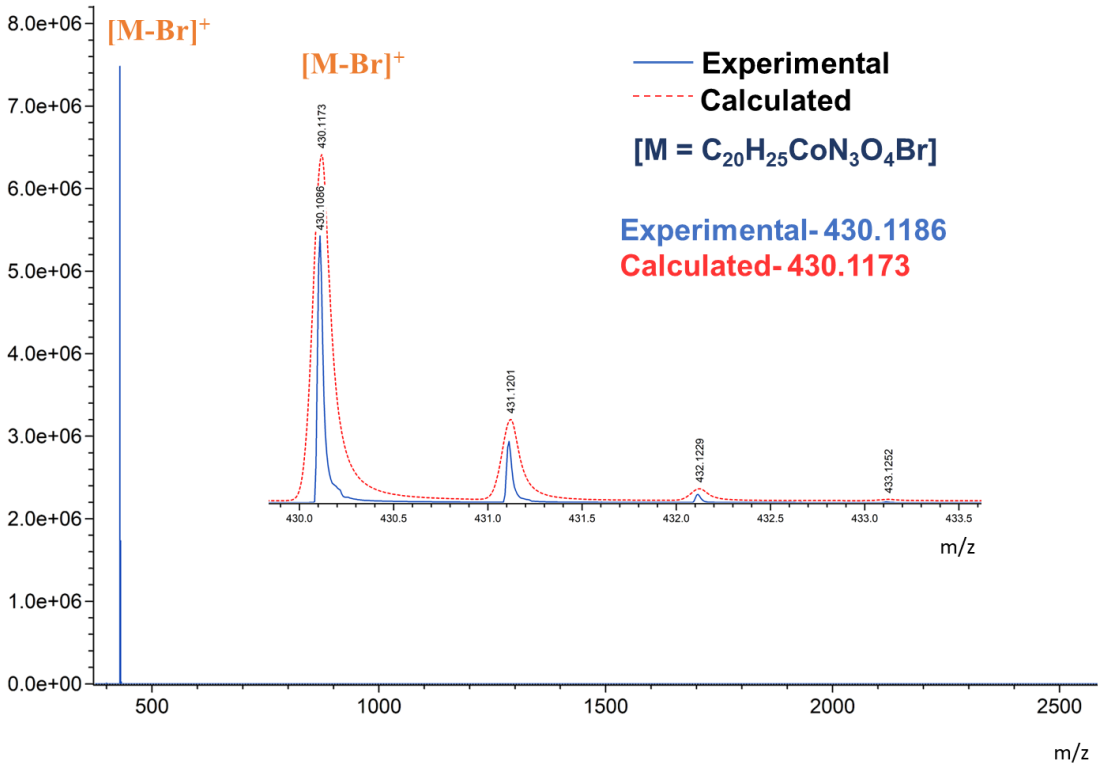


Figure S6. ESI-MS (positive ions) spectrum of the **Co2** complex

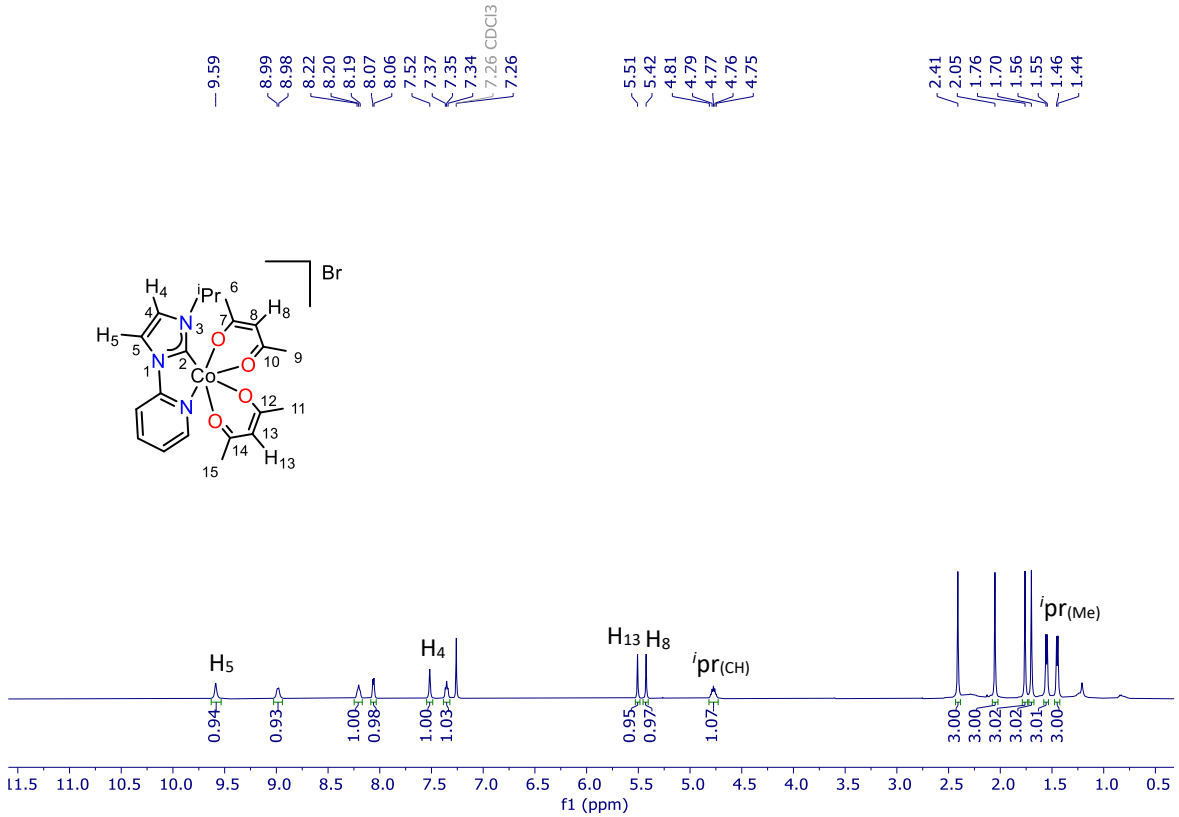


Figure S7. ^{1}H NMR spectrum of **Co3** in $CDCl_3$

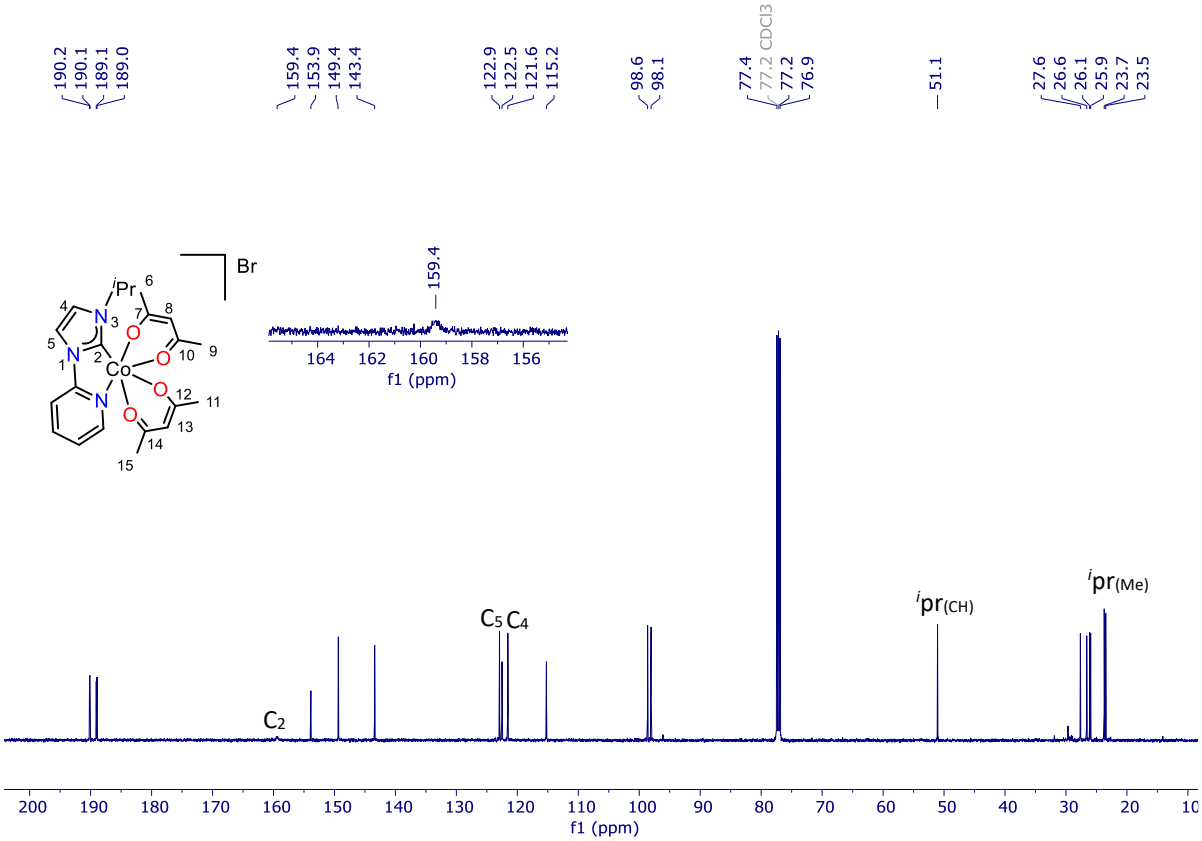


Figure S8. ^{13}C{^{1}H} NMR spectrum of **Co3** in $CDCl_3$

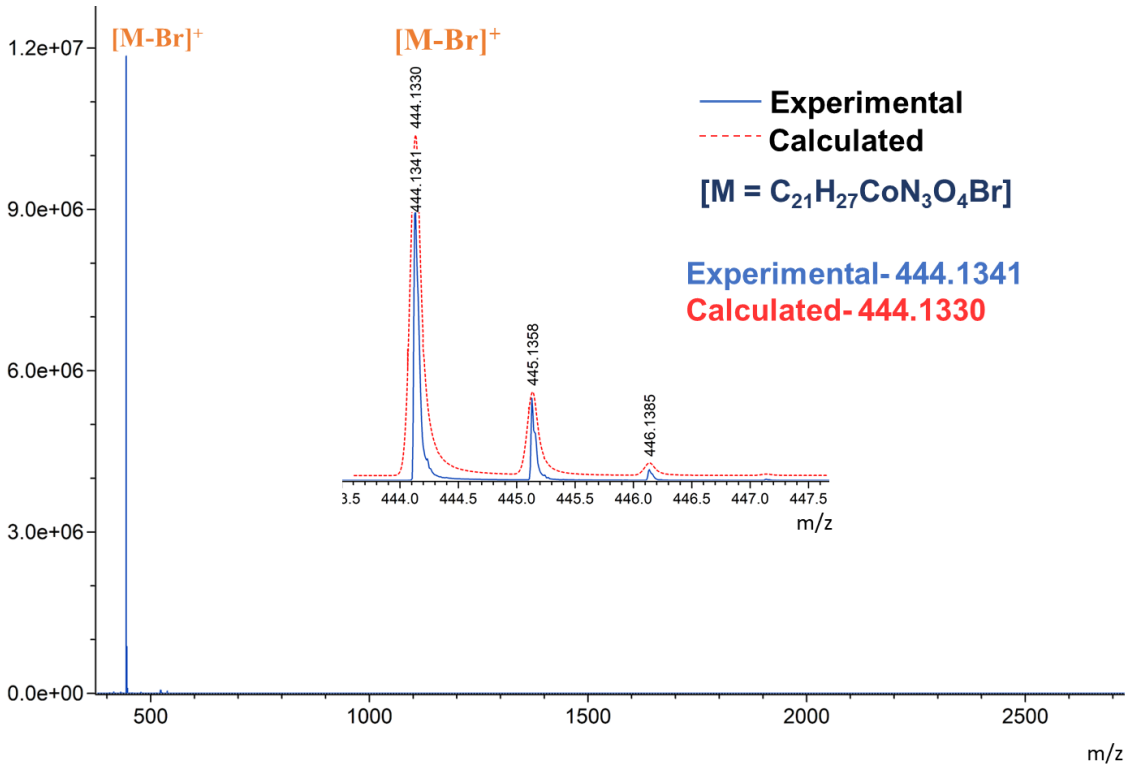
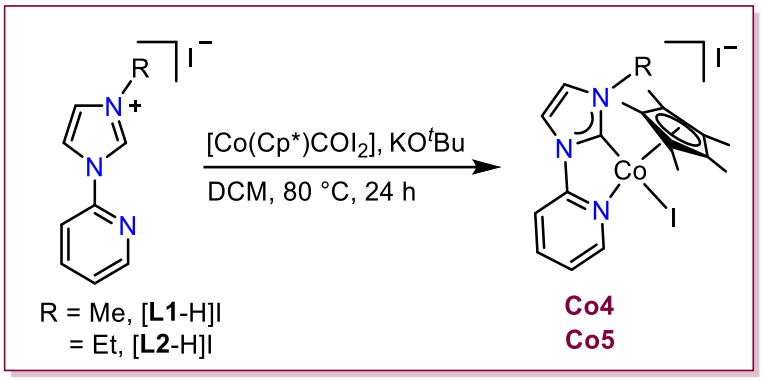


Figure S9. ESI-MS (positive ions) spectrum of the **Co3** complex

General Procedure for the synthesis of complexes Co4-Co5:



The metal precursor [Co(Cp*)(CO)I_2] (1.2 equiv.), ligands [**L1-2**-H]I (100 mg, 1 equiv.) and KO^{t}Bu (1.2 equiv.) were taken in a pressure tube followed by the addition of DCM. The closed pressure tube was then stirred at 80 °C for 24 h. After that, the reaction mixture was filtered through a small pad of celite and the filtrate was dried in vacuo. The obtained residue was purified by column chromatography using DCM/methanol as eluent to get the air-stable complex as reddish-brown solid.

Caution: The reaction temperature of 80 °C is above the boiling point of DCM. So, the reaction was conducted in a thick-walled pressure tube with a Teflon cap inside a fume hood with precaution.

Complex (Co4): The complex **Co4** was synthesized according to the general procedure using 100 mg of [**L1**-H]I (Yield: 169 mg, 0.278 mmol, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84 (d, J = 6.0 Hz, 1H), 8.68 (s, 1H), 8.46 (d, J = 8.4 Hz, 1H), 8.08 (t, J = 7.9 Hz, 1H), 7.65 (s, 1H), 7.49 (t, J = 6.6 Hz, 1H), 4.12 (s, 3H), 1.67 (s, 15H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 184.5, 153.9, 152.7, 142.1, 128.9, 123.6, 121.2, 114.3, 96.8, 39.9, 11.2 ppm. MS (ESI, positive ions): *m/z* 480.0316 (calcd. for $[M\text{-}I]^+$: *m/z* 480.0343).

Complex (Co5): The complex **Co5** was synthesized according to the general procedure using 100 mg of [**L2**-H]I (Yield: 171 mg, 0.275 mmol, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84-8.82 (m, 1H), 8.76 (d, J = 2.4 Hz, 1H), 8.46 (d, J = 8.2 Hz, 1H), 8.10-8.07 (m, 1H), 7.65 (d, J = 2.4 Hz, 1H), 7.48 (t, J = 6.0 Hz, 1H), 4.60-4.53 (m, 1H), 4.36-4.29 (m, 1H), 1.65 (s, 15H), 1.58 (t, J = 7.3 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 184.0, 154.2, 152.8, 142.1, 125.9, 123.5, 121.7, 114.2, 96.8, 47.3, 15.4, 11.1 ppm. MS (ESI, positive ions): *m/z* 494.0495 (calcd. for $[M\text{-}I]^+$: *m/z* 494.0502).

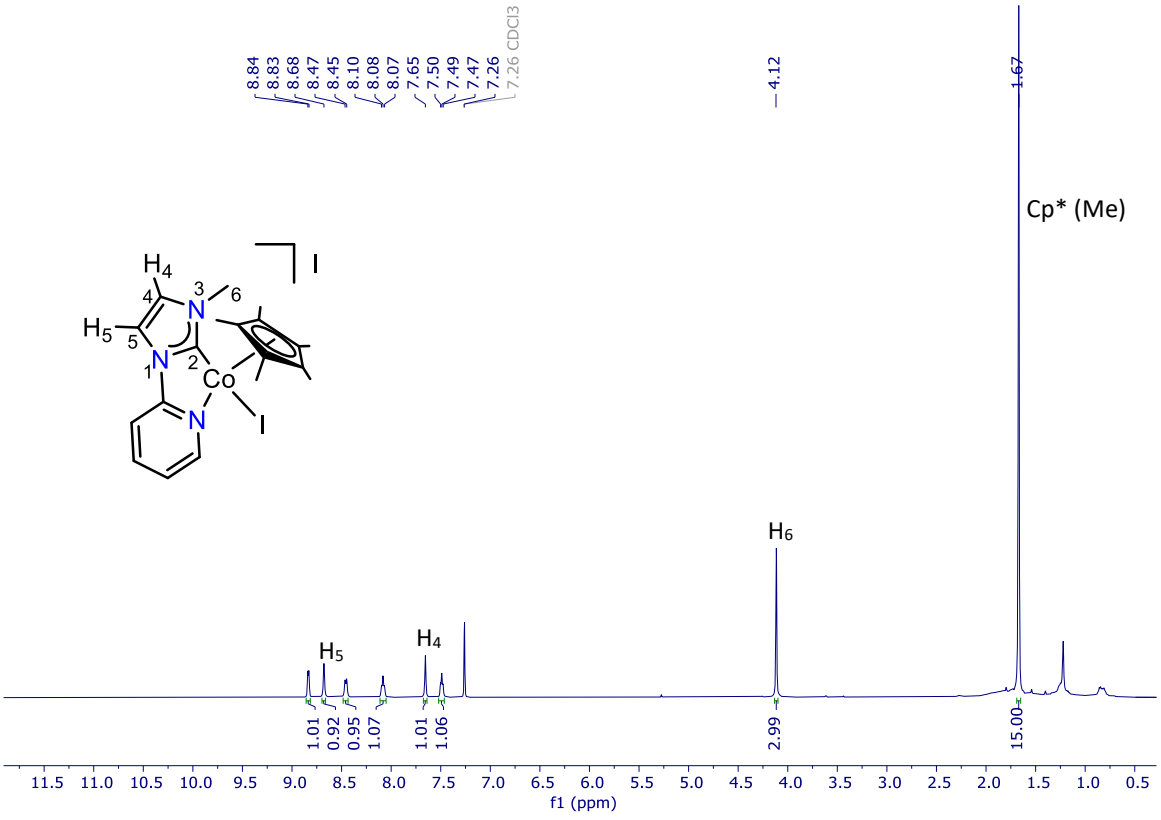


Figure S10. ^{1}H NMR spectrum of **Co4** in $CDCl_3$

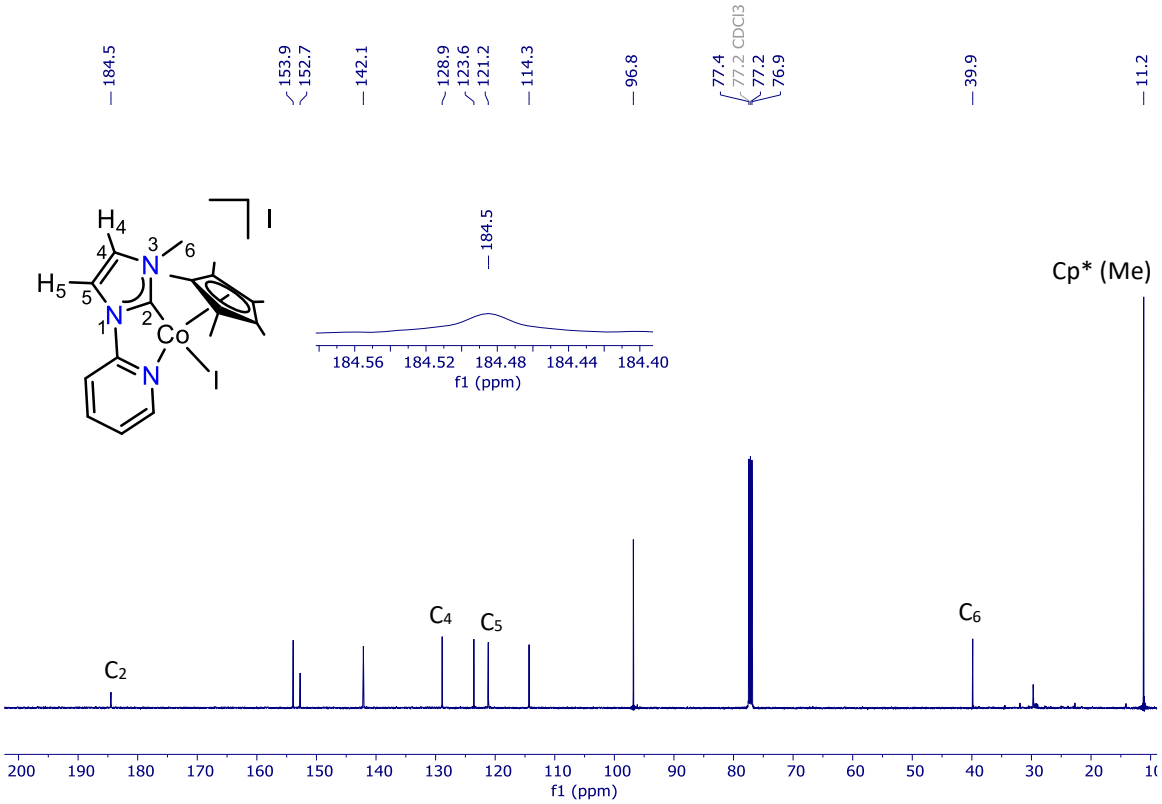


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **Co4** in $CDCl_3$

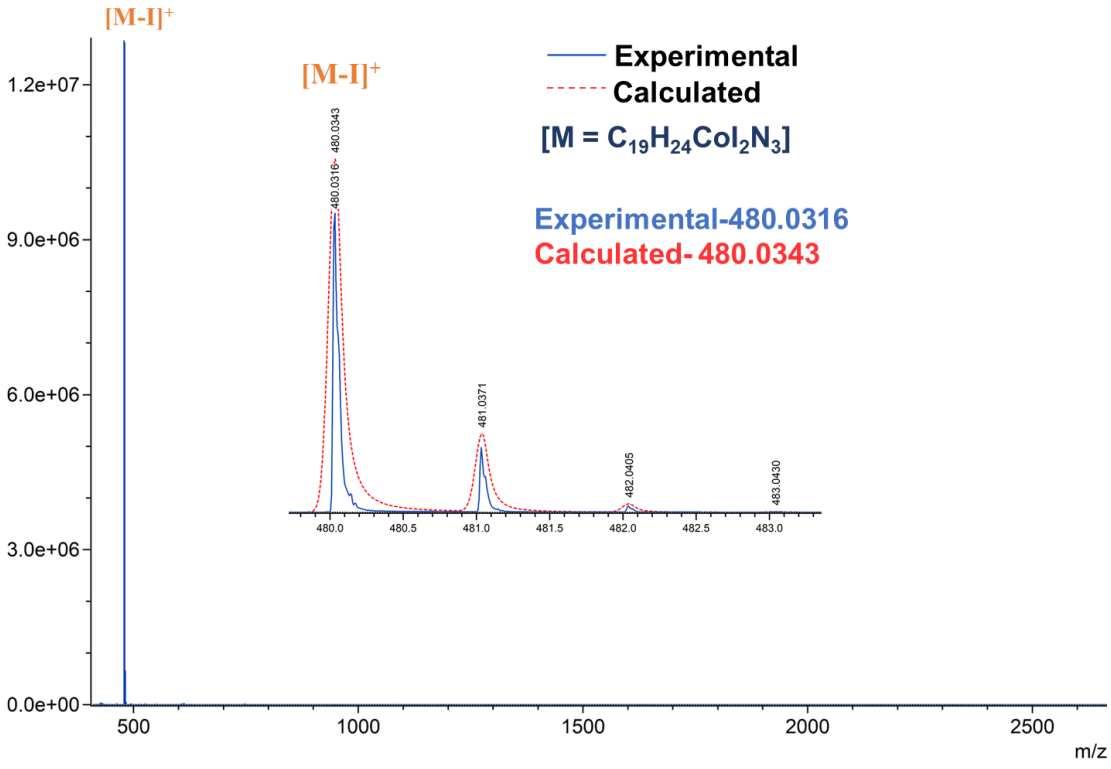


Figure S12. ESI-MS (positive ions) spectrum of the **Co4** complex

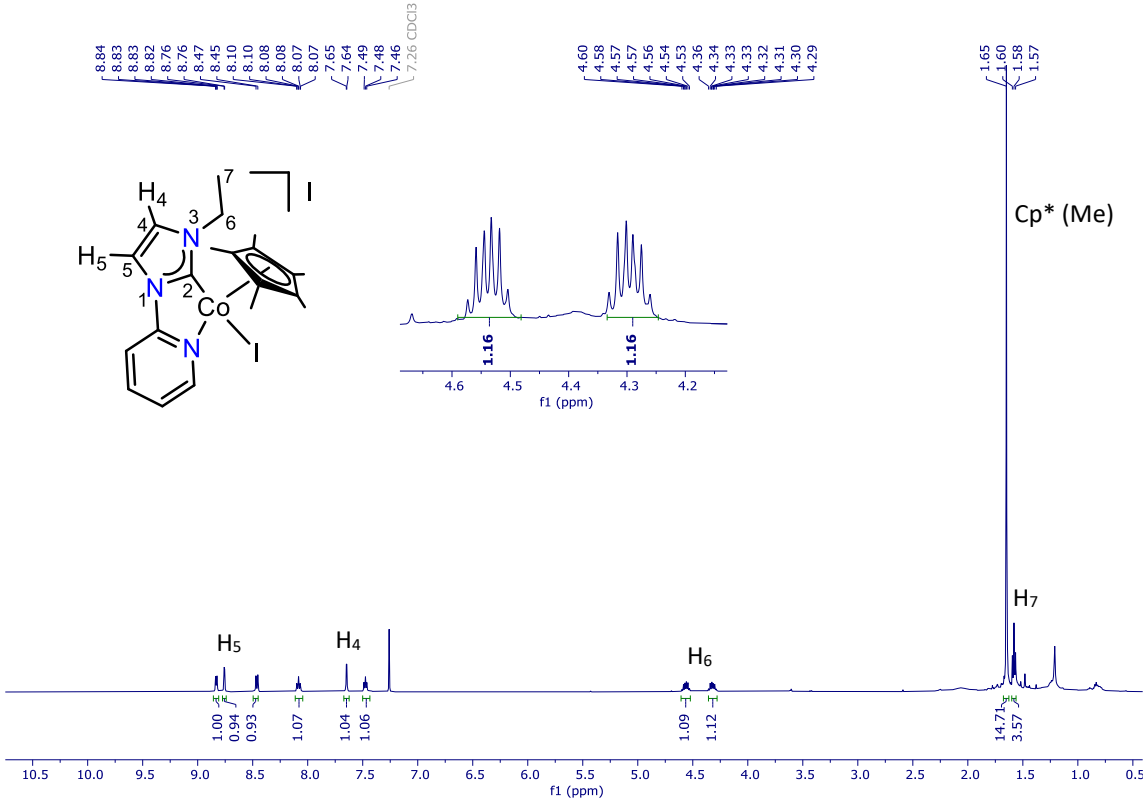


Figure S13. ^{1}H NMR spectrum of **Co5** in $CDCl_3$

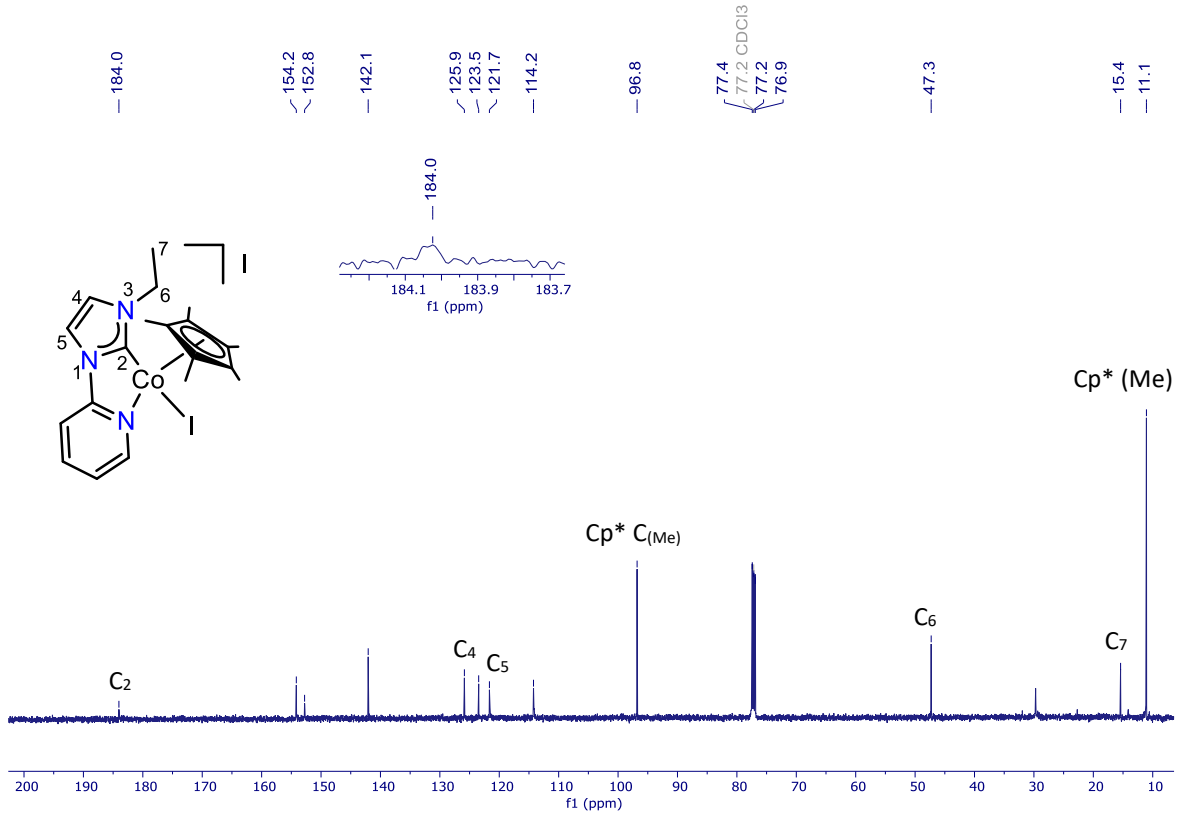


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of **Co5** in $CDCl_3$

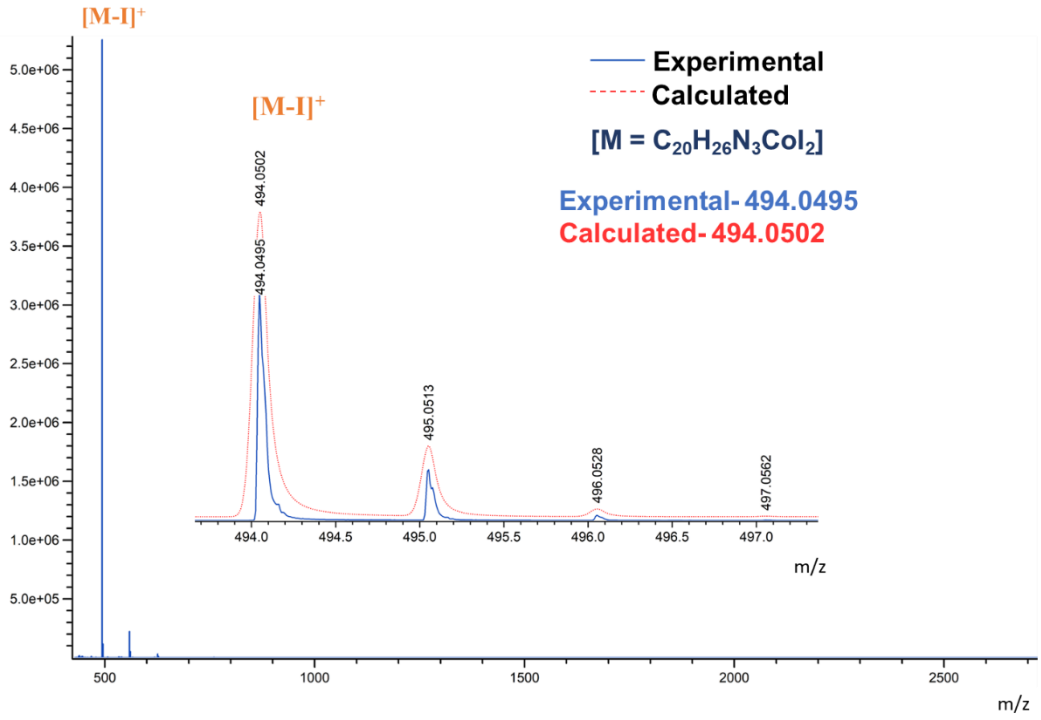


Figure S15. ESI-MS (positive ions) spectrum of the **Co5** complex

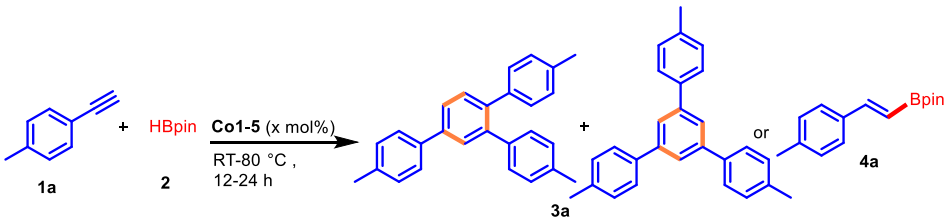
General procedure for cyclotrimerization of terminal alkynes:

A pressure tube was charged with catalyst **Co1** (0.010 mmol, 2 mol%), pinacolborane (0.15 mmol, 0.3 equiv.), alkyne (0.5 mmol), and toluene (0.5 mL, in case of solid substrates only). Then the reaction mixture was allowed to stir at room temperature. After completion of the reaction, pure products were isolated *via* column chromatography using ethyl acetate and hexane as eluents. The regioselectivity of the products was determined by ^{1}H NMR analysis.

General procedure for the hydroboration of terminal alkynes:

A pressure tube was charged with catalyst **Co5** (0.010 mmol, 2 mol%), pinacolborane (0.65 mmol, 1.3 equiv.), alkyne (0.5 mmol), and toluene (0.5 mL, in case of solid substrates only). Then the reaction mixture was kept in a preheated oil bath at 80 °C. After completion of the reaction, pure products were isolated using column chromatography using ethyl acetate and hexane as eluents.

Table S1: Optimization of the reaction conditions[a]



Entry	Catalyst	HBpin (equiv.)	Temperature	Total yield (%) of 3a[b] (1,2,4 : 1,3,5)[f]	4a (%)[b]
1	**Co1**	**0.3**	**RT**	**78 (84/16)**	**12**
2	**Co2**	0.3	RT	76 (72/28)	13
3	**Co3**	0.3	RT	73 (61/39)	11
4	**Co4**	0.3	RT	15	26
5	**Co5**	0.3	RT	12	27
6	**Co1**	0.8	RT	77	19
7	**Co1**	1.3	RT	75	22
8	**Co5**	1.3	RT	18	53
9	**Co5**	1.3	60 °C	16	71
10	**Co5**	**1.3**	**80 °C**	**14**	**85**
11	**Co4**	**1.3**	**80 °C**	**12**	**84**
12	**Co1**	-	RT	-	-
13	-	0.3	RT	-	-
14	$Co(acac)_2$	0.3	RT	17	9
15	$Co(Cp^*)COI_2$	1.3	80 °C	10	14
16[c]	**Co1**	0.3	RT	-	-
17[d]	**Co1**	0.3	RT	61	Trace
18[c]	**Co5**	1.3	80 °C	-	-
19[e]	**Co1**	0.02	RT	21	-
20	**Co4**	-	RT	-	-
21	**Co5**	-	RT	-	-
22	**Co1**	1.3	80 °C	72	15
23	**Co1**	-	80 °C	-	-
24[g]	**Co1**	0.3	RT	29	-
25[h]	**Co1**	0.3	80 °C	3[i]	-

[a]**Reaction condition**: **1a** (0.5 mmol), **2** (0.15-0.65 mmol), **Co1-5** (2 mol%), RT - 80 °C, 12 h. [b]All are isolated yields. [c]Bis(pinacolato)diboron instead of HBpin, 0.5 mL toluene was used. [d]Toluene (0.5 mL). [e]**1a** (1 mmol). [f]Based on ^{1}H NMR. [g]$NaBHEt_3$ instead of HBpin. [h]Ph_2SiH_2 instead of HBpin. [i]GC conversion, using mesitylene as an internal standard

Procedure for the calculation of TON for cyclotrimerization reaction:

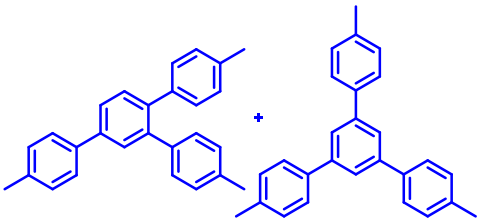
A pressure tube was charged with catalyst **Co1** (0.1 mol%), pinacolborane (0.6 mmol), and phenylacetylene (2 mmol). Then the reaction mixture was allowed to stir at room temperature for 12 h. After completion of the reaction, a small portion of the aliquot was analyzed by GC-MS. The obtained data based on GC-MS analysis (using mesitylene as an internal standard) shows 39% conversion which gives TON of 390 and TOF 32.5 h^{-1}.

Procedure for the calculation of TON for hydroboration reaction:

A pressure tube was charged with catalyst **Co5** (0.1 mol%), pinacolborane (2.6 mmol), and phenylacetylene (2 mmol). Then the reaction mixture was kept in a preheated oil bath at 80 °C for 12 h. After completion of the reaction, a small portion of the aliquot was analyzed by GC-

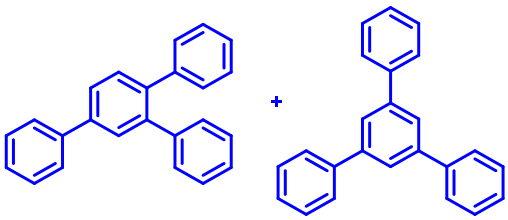
MS. The obtained data based on GC-MS analysis (using mesitylene as an internal standard) shows 47% conversion which gives TON of 470 and TOF 39.2 h^{-1}.

Analytical data for the cyclotrimerized products:



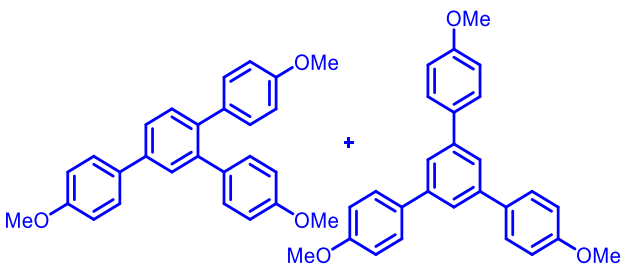
4,4''-dimethyl-4'-(*p*-tolyl)-1,1':2',1''-terphenyl (Compound 3a):[2] Compound **3a** was synthesized following the general procedure by reacting phenylacetylene (55 µL, 0.5 mmol) and pinacolborane (22 µL, 0.15 mmol) for 12 h at RT (white solid: 0.045 g, 0.13 mmol, 78%). Isomeric ratio of 1,2,4 to 1,3,5: 84:16

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 3H, for 1,3,5 isomer, 16%), 7.63-7.56 (m, 6H), 7.47 (d, J = 7.8 Hz, 1H), 7.12-7.03 (m, 10H), 2.42 (s, 9H, for 1,3,5 isomer,16%), 2.41 (s, 3H), 2.33 (s, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.3, 140.9, 140.2, 139.3, 138.9, 138.5, 138.5, 137.9, 137.4, 137.3, 136.3, 136.2, 131.2, 129.9, 129.8, 129.7, 129.4, 128.8, 128.8, 127.3, 127.1, 125.9, 124.7, 21.3 ppm.



4'-phenyl-1,1':2',1''-terphenyl (Compound 3b):[2] Yellow solid (0.041 g, 0.13 mmol, 80%). Isomeric ratio of 1,2,4 to 1,3,5: 92:8

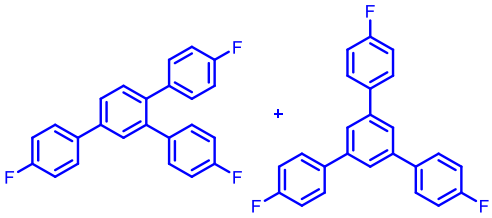
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 3H, for 1,3,5 isomer, 8%), 7.73-7.65 (m, 4H), 7.53 (d, J = 8.03, 1H), 7.49-7.46 (m, 2H), 7.42-7.36 (m, 2H), 7.26-7.19 (m, 10H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.5, 141.7, 141.3, 141.3, 141.2, 140.8, 140.5, 139.7, 131.2, 130.1, 130.0, 129.6, 129.0, 129.0, 128.1, 128.0, 127.7, 127.6, 127.5, 127.3, 126.7, 126.7, 126.3, 125.3 ppm.



4,4''-dimethoxy-4'-(4-methoxyphenyl)-1,1':2',1''-terphenyl (compound 3c):[2] White solid (0.049 g, 0.12 mmol, 75%).

Isomeric ratio of 1,2,4 to 1,3,5: 90:10

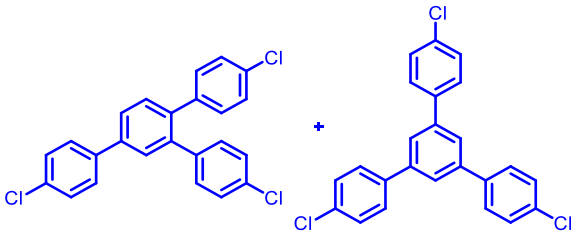
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 3H, for 1,3,5 isomer, 10%), 7.65-7.55 (m, 5H), 7.45 (d, J = 7.8 Hz, 1H), 7.14-7.10 (m, 4H), 7.03-6.99 (m, 3H), 6.81-6.78 (m, 4H), 3.88 (s, 9H, for 1,3,5 isomer, 10%), 3.87 (s, 3H), 3.80 (s, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.4, 159.3, 158.4, 158.4, 142.0, 140.5, 139.7, 138.6, 134.3, 134.0, 133.9, 133.3, 131.1, 131.1, 131.0, 129.0, 128.5, 128.2, 125.5, 124.0, 114.4, 113.5, 55.5, 55.3 ppm.



4,4''-difluoro-4'-(4-fluorophenyl)-1,1':2',1''-terphenyl (compound 3d):[2] Yellow solid (0.044 g, 0.12 mmol, 74%).

Isomeric ratio of 1,2,4 to 1,3,5: 90:10

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (s, 3H, for 1,3,5 isomer, 10%), 7.65 -7.57 (m, 5H), 7.46 (d, J = 7.9 Hz, 1H), 7.20-7.09 (m, 8H), 6.97-6.92 (m, 4H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.8, 163.0, 163.0, 161.8, 161.1, 161.0, 141.7, 140.2, 139.8, 138.7, 137.3, 136.9, 136.9, 136.6, 131.5, 131.5, 131.5, 131.4, 131.2, 129.3, 129.1, 129.0, 128.9, 128.8, 126.3, 125.0, 116.0, 115.8, 115.3, 115.3, 115.1, 115.1 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ -115.00, -115.17, -115.63, -115.76 ppm.

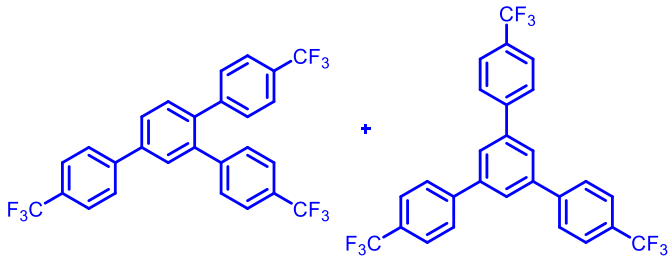


4,4''-dichloro-4'-(4-chlorophenyl)-1,1':2',1''-terphenyl (compound 3e):[2] White solid (0.048 g, 0.12 mmol, 71%).

Isomeric ratio of 1,2,4 to 1,3,5: 92:8

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 3H, for 1,3,5 isomer, 8%), 7.67-7.63 (m, 2H), 7.60-7.53 (m, 2H), 7.49 (d, J = 7.9 Hz, 1H), 7.44 -7.35 (m, 3H), 7.26-7.22 (m, 5H), 7.18-7.13 (m, 2H),

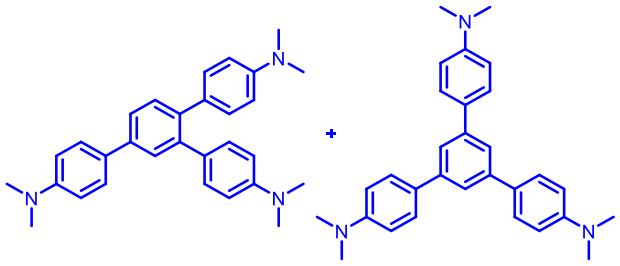
6.98 (t, J = 7.7 Hz, 2H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 142.8, 142.6, 142.4, 142.1, 141.5, 139.9, 139.8, 138.8, 135.0, 134.2, 134.2, 131.3, 130.3, 130.3, 129.8, 129.8, 129.4, 129.4, 129.4, 128.3, 128.3, 128.0, 127.9, 127.6, 127.4, 127.3, 127.2, 126.8, 125.7, 125.4 ppm.



4,4''-bis(trifluoromethyl)-4'-(4-(trifluoromethyl)phenyl)-1,1':2',1''-terphenyl (compound 3f):[2] Yellow solid (0.065 g, 0.13 mmol, 76%).

Isomeric ratio of 1,2,4 to 1,3,5: 92:8

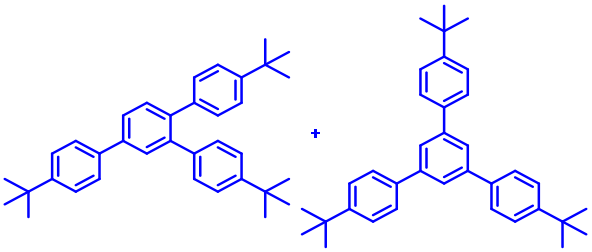
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H, for 1,3,5 isomer, 8%), 7.79-7.72 (m, 6H), 7.67 (d, J = 8 Hz, 1H), 7.57-7.52 (m, 5H), 7.32-7.28 (m, 4H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 144.5, 144.2, 143.7, 141.7, 140.1, 139.2, 131.6, 130.3, 130.2, 129.8, 127.8, 127.6, 127.3, 126.3, 126.1, 126.1, 125.4, 125.4, 125.4 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.48, -62.49, -62.50 ppm.



4'-(4-(dimethylamino)phenyl)-N^4,N^4,$N^{4''}$,$N^{4''}$-tetramethyl-[1,1':2',1''-terphenyl]-4,4''-diamine (compound 3g):[2] Yellow solid (0.053 g, 0.12 mmol, 73%).

Isomeric ratio of 1,2,4 to 1,3,5: 95:5

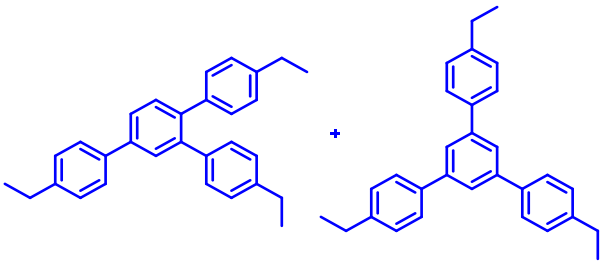
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 3H, for 1,3,5 isomer, 5%), 7.66-7.63 (m, 3H), 7.60-7.58 (m, 1H), 7.48 (d, J = 7.9 Hz, 1H), 7.21-7.16 (m, 4H), 6.89-6.87 (m, 2H), 6.73-6.70 (m, 4H), 3.05 (s, 18H, for 1,3,5 isomer, 5%), 3.04 (s, 6H), 2.99-2.98 (m, 12H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 150.2, 150.0, 149.2, 149.1, 142.1, 140.6, 139.6, 138.2, 131.0, 130.7, 130.6, 130.2, 130.0, 129.3, 128.6, 128.0, 127.7, 124.6, 122.7, 113.0, 112.3, 40.7, 40.7, 40.7 ppm. HRMS (ESI) m/z: $[M + H]^+$: Calcd for $C_{30}H_{34}N_3$ 436.2753; Found 436.2700.



4,4''-di-*tert*-butyl-4'-(4-(*tert*-butyl)phenyl)-1,1':2',1''-terphenyl (compound 3h):[3] Yellow solid (0.054 g, 0.11 mmol, 68%).

Isomeric ratio of 1,2,4 to 1,3,5: 93:7

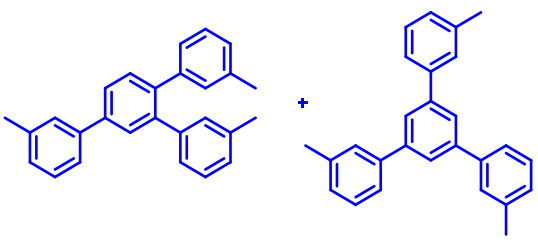
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 3H, for 1,3,5 isomer, 7%), 7.69 (s, 1H), 7.63 (d, J = 7.9 Hz, 3H), 7.54-7.49 (m, 3H), 7.27-7.24 (m, 5H), 7.15-7.12 (m, 4H), 1.41 (s, 27H, for 1,3,5 isomer, 7%), 1.40 (s, 9H), 1.33 (s, 18H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.4, 149.5, 149.4, 141.0, 140.0, 139.4, 138.8, 138.4, 138.0, 131.1, 129.7, 129.6, 129.4, 127.1, 126.9, 125.9, 124.8, 124.8, 34.7, 34.6, 31.5, 31.5 ppm.



4,4''-diethyl-4'-(4-ethylphenyl)-1,1':2',1''-terphenyl (compound 3i):[3] Yellow solid (0.048 g, 0.12 mmol, 74%).

Isomeric ratio of 1,2,4 to 1,3,5: 78:22

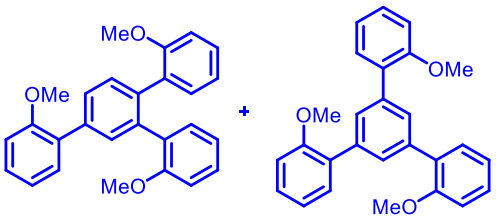
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 3H, for 1,3,5 isomer, 22%), 7.64-7.59 (m, 5H), 7.48 (d, J = 7.9 Hz, 1H), 7.33-7.28 (m, 4H), 7.14-7.05 (m, 7H), 2.75-2.68 (m, 4H), 2.66-2.61 (m, 4H), 1.32-1.26 (m, 6H), 1.25-1.22 (m, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.8, 143.6, 142.6, 142.5, 142.4, 141.0, 140.2, 139.4, 139.2, 138.9, 138.8, 138.3, 131.2, 130.0, 129.9, 129.5, 128.5, 127.5, 127.5, 127.4, 127.2, 125.9, 124.8, 28.7, 28.6, 15.7, 15.7, 15.5 ppm. HRMS (ESI) *m/z*: $[M + H]^+$: Calcd for $C_{30}H_{31}$ 391.2426; Found 391.2401.



3,3''-dimethyl-4'-(*m*-tolyl)-1,1':2',1''-terphenyl (compound 3j):[3] Brown liquid (0.040 g, 0.11 mmol, 69%).

Isomeric ratio of 1,2,4 to 1,3,5: 77:23

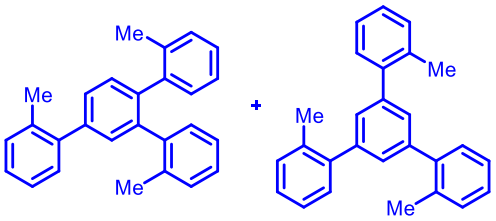
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 3H, 1,3,5 isomer, 23%), 7.67-7.63 (m, 2H), 7.53-7.49 (m, 5H), 7.41-7.35 (m, 2H), 7.23-7.19 (m, 3H), 7.11-7.02 (m, 8H), 6.95-6.93 (t, J = 7.9 Hz, 3H), 2.47 (s, 9H, 1,3,5 isomer, 23%), 2.45 (s, 3H), 2.30-2.29 (m, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.5, 141.7, 141.4, 141.3, 141.2, 140.8, 140.4, 139.7, 138.6, 138.5, 137.6, 137.5, 131.1, 130.7, 129.5, 128.9, 128.4, 128.3, 128.1, 127.8, 127.4, 127.3, 127.2, 127.2, 126.1, 125.3, 124.6, 124.4, 21.7, 21.5 ppm.



2,2''-dimethoxy-4'-(2-methoxyphenyl)-1,1':2',1''-terphenyl (compound 3k):[2] White solid (0.044 g, 0.11 mmol, 67%).

Isomeric ratio of 1,2,4 to 1,3,5: 66:34

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 3H, 1,3,5 isomer, 34%), 7.64 (s, 2H), 7.48 (d, J = 6.9 Hz, 3H), 7.37-7.32 (m, 2H), 7.20-7.02 (m, 8H), 6.88-6.73 (m, 4H), 3.86 (s, 6H), 3.53 (s, 2H), 3.50 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.7, 156.4, 137.8, 137.2, 131.9, 131.7, 131.6, 131.3, 131.2, 131.0, 131.0, 130.5, 130.3, 129.7, 128.6, 128.5, 128.4, 128.1, 120.9, 119.9, 111.2, 111.2, 110.3, 55.7, 55.6, 55.0, 55.0 ppm.

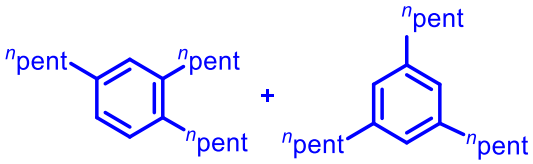


2,2''-dimethyl-4'-(*o*-tolyl)-1,1':2',1''-terphenyl (compound 3l):[3] Yellow liquid (0.038 g, 0.11 mmol, 65%).

Isomeric ratio of 1,2,4 to 1,3,5: 52:48

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 3H, 1,3,5 isomer, 52%), 7.62-7.56 (m, 7H), 7.47 (d, J = 7.8 Hz, 1H), 7.29 (d, J = 8.4 Hz, 4H), 7.12-7.03 (m, 9H), 2.42 (s, 4H), 2.41 (s, 3H), 2.33 (s, 4H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.5, 141.7, 141.4, 141.3, 141.2, 140.8, 140.4,

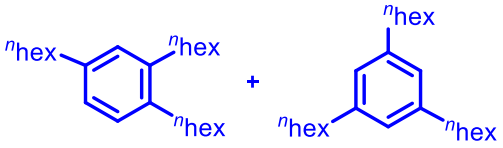
139.7, 138.6, 138.5, 137.6, 137.5, 131.1, 130.7, 130.7, 129.5, 128.9, 128.9, 128.4, 128.3, 128.3, 128.1, 127.8, 127.7, 127.4, 127.3, 127.2, 127.2, 126.1, 125.3, 124.6, 124.4, 21.7, 21.5 ppm.



1,2,4-tripentylbenzene (compound 3m):[2] Yellow oil (0.033 g, 0.11 mmol, 68%).

Isomeric ratio of 1,2,4 to 1,3,5: 90:10

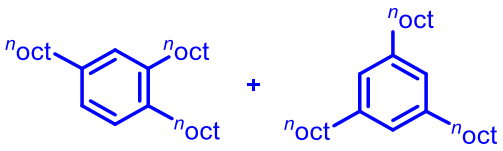
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, J = 7.7 Hz, 1H), 6.99-6.95 (m, 2H), 6.85 (s, 3H, 1,3,5 isomer, 10%), 2.64-2.57 (m, 8H), 1.67-1.56 (m, 8H), 1.50-1.36 (m, 10H), 1.01-0.95 (m, 12H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.8, 140.5, 140.3, 137.8, 129.4, 129.1, 126.0, 125.9, 35.9, 35.5, 33.9, 33.9, 33.7, 32.6, 32.2, 23.1, 23.0, 22.7, 22.6, 14.1 ppm.



1,2,4-trihexylbenzene (compound 3n):[2] Yellow oil (0.042 g, 0.13 mmol, 76%).

Isomeric ratio of 1,2,4 to 1,3,5: 92:8

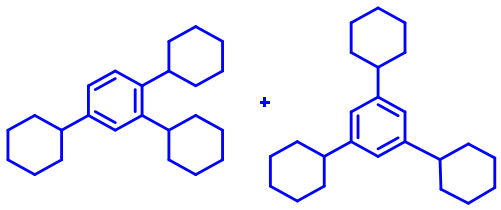
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, J = 7.6 Hz, 1H), 6.96-6.93 (m, 2H), 6.82 (s, 3H, 1,3,5 isomer, 8%), 2.61-2.54 (m, 7H), 1.64-1.52 (m, 12H), 1.46-1.34 (m, 12H), 0.98-0.92 (m, 14H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.8, 140.4, 140.3, 137.8, 129.4, 129.1, 126.0, 125.8, 35.8, 35.4, 33.9, 33.9, 33.8, 33.7, 32.6, 32.2, 23.1, 23.0, 22.7, 22.7, 14.2, 14.1 ppm.



1,2,4-trioctylbenzene (compound 3o):[2] Yellow oil (0.049 g, 0.12 mmol, 71%).

Isomeric ratio of 1,2,4 to 1,3,5: 89:11

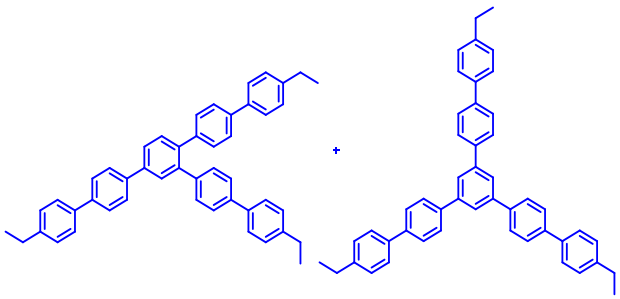
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09-7.06 (m, 1H), 6.99- 6.96 (m, 2H), 6.85 (s, 3H, 1,3,5 isomer, 11%), 2.63-2.56 (m, 7H), 1.66-1.57 (m, 7H), 1.45-1.31 (m, 31H), 0.94 (d, J = 5.1 Hz, 12H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.8, 140.5, 140.3, 137.8, 129.4, 129.1, 126.0, 125.9, 36.2, 35.8, 33.0, 32.6, 32.5, 32.1, 32.0, 31.7, 31.6, 31.6, 29.7, 29.3, 22.8, 14.2 ppm.



benzene-1,2,4-triyltricyclohexane (compound 3p):[2] Yellow oil (0.034 g, 0.10 mmol, 64%).

Isomeric ratio of 1,2,4 to 1,3,5: 90:10

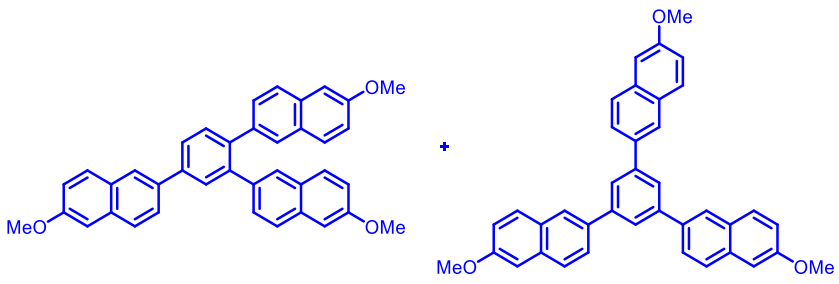
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, J = 8.0 Hz, 1H), 7.10 (d, J = 2.1 Hz, 1H), 7.04-7.01 (m, 1H), 6.92 (s, 3H, 1,3,5 isomer, 10%), 2.84-2.75 (m, 2H), 2.52-2.46 (m, 1H), 1.94-1.76 (m, 19H), 1.56-1.37 (m, 17H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.9, 145.2, 144.6, 142.2, 125.7, 124.6, 124.0, 123.0, 45.0, 44.5, 39.5, 39.2, 34.9, 34.9, 34.8, 34.7, 27.5, 27.2, 26.5, 26.4 ppm.



4,4''''-diethyl-4''-(4'-ethyl-[1,1'-biphenyl]-4-yl)-1,1':4',1'':2'',1''':4''',1''''-quinquephenyl (compound 3q): Yellow solid (0.077 g, 0.12 mmol, 75%).

Isomeric ratio of 1,2,4 to 1,3,5: 84:16

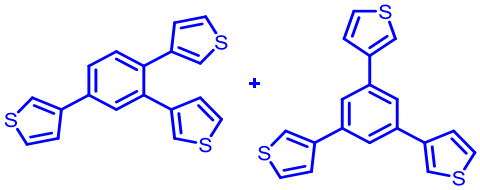
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 3H, 1,3,5 isomer, 16%), 7.81-7.77 (m, 4H), 7.74-7.69 (m, 4H), 7.62-7.58 (m, 4H), 7.55-7.48 (m, 7H), 7.33-7.27 (m, 9H), 2.76-2.66 (m, 7H), 1.33-1.26 (m, 11H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.7, 143.7, 143.5, 142.1, 140.8, 140.6, 140.4, 140.3, 140.1, 139.9, 139.9, 139.4, 139.3, 138.2, 131.4, 130.4, 130.4, 129.5, 128.5, 128.4, 127.8, 127.6, 127.5, 127.1, 127.1, 127.0, 126.7, 126.6, 126.2, 125.0, 28.7, 28.7, 15.7 ppm. HRMS (ESI) *m/z*: $[M + H]^+$: Calcd. for $C_{48}H_{43}$ 619.3365; Found 619.3343.



6,6',6''-(benzene-1,2,4-triyl)tris(2-methoxynaphthalene) (compound 3r): Yellow solid (0.066 g, 0.12 mmol, 72%).

Isomeric ratio of 1,2,4 to 1,3,5: 83:17

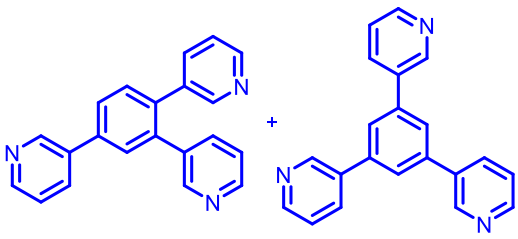
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.11 (s, 1H), 8.02 (s, 1H), 7.90 (d, J = 11.1 Hz, 2H), 7.85 (s, 4H), 7.80 (d, J = 6.0 Hz, 2H), 7.70-7.65 (m, 4H), 7.47 (t, J = 7.4 Hz, 2H), 7.21-7.16 (m, 5H), 7.12 (d, J = 8.9 Hz, 2H), 7.05 (s, 2H), 3.96-3.95 (m, 5H), 3.90 (s, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.0, 158.0, 157.8, 142.6, 141.2, 140.5, 139.5, 137.3, 136.9, 136.6, 135.9, 134.1, 134.1, 133.4, 133.4, 131.7, 130.0, 129.9, 129.7, 129.4, 129.1, 128.4, 128.3, 127.5, 126.4, 126.3, 126.2, 126.1, 125.8, 125.3, 119.4, 119.4, 118.9, 118.9, 105.8, 105.8, 55.5, 55.4 ppm. HRMS (ESI) *m/z*: $[M + H]^+$: Calcd. for $C_{39}H_{31}O_3$ 547.2273; Found 547.2254.



3,3',3''-(benzene-1,2,4-triyl)trithiophene (compound 3s):[2] White solid (0.042 g, 0.13 mmol, 77%).

Isomeric ratio of 1,2,4 to 1,3,5: 87:13

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (s, 1H, 1,3,5 isomer, 13%), 7.68 (d, J = 7.9 Hz, 1H), 7.61-7.58 (m, 1H), 7.55-7.40 (m, 6H), 7.23-7.18 (m, 2H), 7.14-7.13 (m, 1H), 7.09-7.08 (m, 1H), 6.85-6.81 (m, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.3, 142.2, 141.8, 141.8, 137.1, 135.9, 135.2, 134.3, 130.8, 129.1, 129.0, 128.4, 126.6, 126.5, 126.5, 126.4, 125.6, 125.0, 124.9, 123.8, 123.1, 123.0, 121.0, 120.7 ppm.



3,3',3''-(benzene-1,2,4-triyl)tripyridine (compound 3t): Brown solid (0.036 g, 0.12 mmol, 70%).

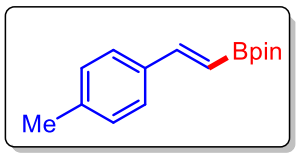
Isomeric ratio of 1,2,4 to 1,3,5: 90:10

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.66 (s, 2H), 8.51 (s, 4H), 8.00-7.95 (m, 1H), 7.80 (s, 3H, 1,3,5 isomer, 11%), 7.74 (d, J = 7.9 Hz, 1H), 7.66 (s, 1H), 7.58 (d, J = 7.9 Hz, 1H), 7.46-7.41 (m, 3H), 7.22-7.17 (m, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.6, 140.0,

139.7, 139.5, 139.3, 139.2, 138.8, 138.7, 134.1, 134.0, 133.2, 133.1, 131.3, 131.2, 131.2, 129.2, 129.2, 129.2, 128.7, 128.5, 128.5, 128.5, 126.5, 125.2 ppm. HRMS (ESI) *m/z*: $[M + Na]^+$: Calcd. for $C_{21}H_{15}N_3Na$ 332.1164; Found 332.1139.

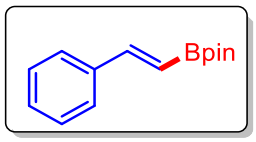
Analytical data for the hydroborated products:

(E)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (compound 4a):[4]



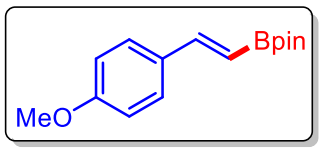
Compound 3a was synthesized following the general procedure by reacting phenylacetylene (55 µL, 0.5 mmol) and pinacolborane (94 µL, 0.65 mmol) for 12 h at 80 ºC pale-yellow liquid (0.104 g, 0.42 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.35 (m, 3H), 7.14 (d, J = 7.9 Hz, 2H), 6.12 (d, J = 18.5 Hz, 1H), 2.35 (s, 3H), 1.31 (s, 12H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.6, 139.1, 134.9, 129.4, 127.2, 83.4, 24.9, 21.5 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.31 ppm.

(E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (compound 4b):[4] Pale-yellow liquid (0.101 g, 0.44 mmol, 88%).

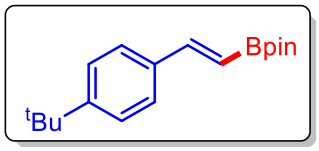


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 7.2 Hz, 2H), 7.41 (d, J = 18.5 Hz, 1H), 7.36-7.29 (m, 3H), 6.18 (d, J = 18.4 Hz, 1H), 1.32 (s, 12H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.6, 137.6, 129.0, 128.7, 127.2, 83.5, 24.9 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.35 ppm.

(E)-2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (compound 4c):[4] Pale-yellow liquid (0.108 g, 0.41 mmol, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.7 Hz, 2H), 7.35 (d, J = 18.4 Hz, 1H), 6.86 (d, J = 8.8 Hz, 2H), 6.01 (d, J = 18.4 Hz, 1H), 3.80 (s, 3H), 1.31 (s, 12H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.4, 149.2, 130.5, 128.6, 114.1, 83.3, 55.4, 24.9 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.37 ppm.

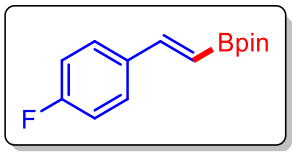


(E)-2-(4-(*tert*-butyl)styryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (compound 4d):[4]

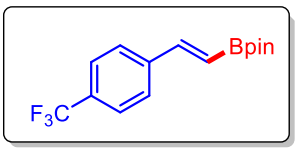


Pale-yellow liquid (0.123 g, 0.43 mmol, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.41 (m, 3H), 7.37-7.35 (m, 2H), 6.13 (d, J = 18.4 Hz, 1H), 1.32 (s, 21H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.3, 149.5, 134.9, 127.0, 125.6, 83.4, 31.4, 25.0 ppm.

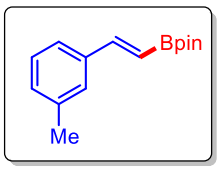
(E)-2-(4-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (compound 4e):[5] Pale-yellow liquid (0.100 g, 0.37 mmol, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.44 (m, 2H), 7.35 (d, J = 18.4 Hz, 1H), 7.02 (t, J = 8.6 Hz, 2H), 6.07 (d, J = 18.4 Hz, 1H), 1.31 (s, 12H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.5, 162.0, 148.3, 133.8, 128.9, 128.8, 115.8, 115.6, 83.5, 24.9 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.32 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ -112.37 ppm.



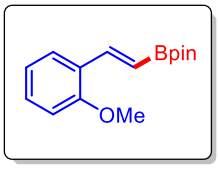
(E)-4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (compound 4f):[4] Pale-yellow liquid (0.115 g, 0.38 mmol, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (m, 4H), 7.40 (d, J = 18.5 Hz, 1H), 6.26 (d, J = 18.4 Hz, 1H), 1.32 (s, 12H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.8, 140.9, 130.7, 130.4, 127.6, 127.3, 125.7, 125.7, 125.7, 125.6, 83.8, 24.9 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.42 ppm.



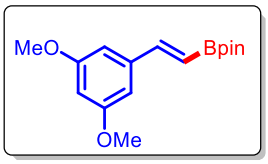
(E)-4,4,5,5-tetramethyl-2-(3-methylstyryl)-1,3,2-dioxaborolane (compound 4g):[5] Pale-yellow liquid (0.093, 0.38 mmol, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 18.4 Hz, 1H), 7.26-7.25 (m, 2H), 7.20-7.16 (m, 1H), 7.07 (d, J = 7.3 Hz, 1H), 6.11 (d, J = 18.4 Hz, 1H), 2.30 (s, 3H), 1.27 (s, 12H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.8, 138.2, 137.6, 129.8, 128.6, 127.9, 124.4, 83.4, 24.9, 21.5 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.26 ppm.



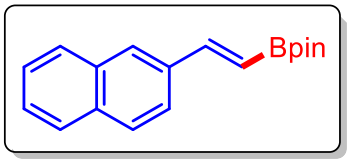
(E)-2-(2-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (compound 4h):[5] Pale-yellow liquid (0.096 g, 0.37 mmol, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 18.7 Hz, 1H), 7.54 (d, J= 6.8 Hz, 1H), 7.24 (t, J = 7.2 Hz, 1H), 6.91 (t, J = 7.5 Hz, 1H), 6.84 (d, J = 8.2 Hz, 1H), 6.18 (d, J = 18.6 Hz, 1H), 3.81 (s, 3H), 1.29 (s, 12H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.4, 144.2, 130.1, 127.1, 126.6, 120.6, 110.9, 83.3, 55.4, 24.9 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.45 ppm. HRMS (ESI): calcd. for $C_{15}H_{22}BO_3$ ($[M+H]^+$): 261.1665, found: 261.16641.



(E)-2-(3,5-dimethoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (compound 4i):[5] Pale-yellow liquid (0.117 g, 0.40 mmol, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, J = 18.4 Hz, 1H), 6.65 (d, J = 2.3 Hz, 2H), 6.41 (t, J = 2.2 Hz, 1H), 6.13 (d, J = 18.4 Hz, 1H), 3.78 (s, 6H), 1.30 (s, 12H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.0, 149.5, 139.6, 105.1, 101.4, 83.5, 55.4, 24.9 ppm.

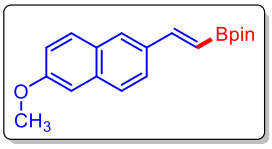


(E)-4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)vinyl)-1,3,2-dioxaborolane (compound 4j):[5]



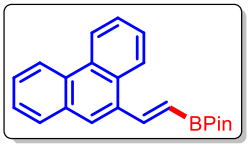
Pale-yellow liquid (0.119 g, 0.42 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.80 (m, 4H), 7.71 (d, J = 8.6 Hz, 1H), 7.59 (d, J = 18.4 Hz, 1H), 7.48-7.46 (m, 2H), 6.31 (d, J = 18.4 Hz, 1H), 1.35 (s, 12H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.7, 135.1, 133.9, 133.6, 128.5, 128.4, 128.1, 127.8, 126.5, 126.4, 123.5, 83.5, 25.0 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.69 ppm.

(E)-2-(2-(6-methoxynaphthalen-2-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (compound 4k):[5]



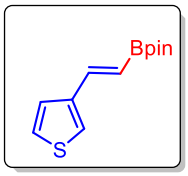
Pale-yellow liquid (0.129 g, 0.41 mmol, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.72 (d, J = 8.9 Hz, 1H), 7.68-7.65 (m, 2H), 7.54 (d, J = 18.4 Hz, 1H), 7.14-7.12 (m, 1H), 7.11 (d, J = 2.3 Hz, 1H), 6.22 (d, J = 18.4 Hz, 1H), 3.92 (s, 3H), 1.33 (s, 12H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.4, 149.8, 135.2, 133.1, 130.1, 129.0, 128.0, 127.2, 124.2, 119.2, 106.1, 83.5, 55.5, 25.0 ppm.

(E)-4,4,5,5-tetramethyl-2-(2-(phenanthren-9-yl)vinyl)-1,3,2-dioxaborolane (compound 4l):[5]



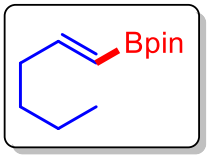
Pale-yellow liquid (0.124 g, 0.37 mmol, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, J = 8.0 Hz, 1H), 8.66 (d, J = 8.1 Hz, 1H), 8.30 (d, J = 8.0 Hz, 1H), 8.23 (d, J = 18.1 Hz, 1H), 7.97 (s, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.68-7.59 (m, 4H), 6.37 (d, J = 18.0 Hz, 1H), 1.38 (s, 12H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.3, 134.7, 131.8, 130.8, 130.5, 130.4, 129.2, 127.0, 126.9, 126.8, 126.7, 125.5, 124.8, 123.2, 122.6, 83.6, 25.0 ppm.

(E)-4,4,5,5-tetramethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-dioxaborolane (compound 4m):[5]



Pale-yellow liquid (0.092 g, 0.39 mmol, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 18.4 Hz, 1H), 7.31-7.28 (m, 2H), 7.27-7.25 (m, 1H), 5.94 (d, J = 18.3 Hz, 1H), 1.30 (s, 12H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.3, 141.4, 126.2, 125.2, 125.0, 83.4, 24.9 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.28 ppm.

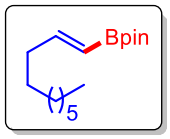
(E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (compound 4n):[5]



Pale-yellow liquid (0.072 g, 0.34 mmol, 69%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.66-6.60 (m, 1H), 5.42 (d, J = 18.0 Hz, 1H), 2.17-2.13 (m, 2H), 1.41-1.38 (m, 2H), 1.34-1.31 (m, 2H), 1.26 (s, 12H), 0.88 (t, J = 7.2 Hz, 3H) ppm.

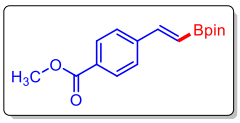
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 154.9, 83.1, 35.6, 30.5, 24.9, 22.4, 14.0 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 29.86 ppm.

(E)-2-(dec-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (compound 4o):[5] Pale-



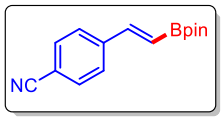
yellow liquid (0.084 g, 0.31 mmol, 63%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.67-6.59 (m, 1H), 5.42 (d, J = 18.0 Hz, 1H), 2.16-2.11 (m, 2H), 1.41-1.37 (m, 2H), 1.26 (s, 12H), 0.87-0.86 (m, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 155.0, 83.1, 36.0, 32.0, 29.6, 29.4, 28.4, 24.9, 22.8, 14.2 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 29.67 ppm.

Methyl (E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzoate (compound



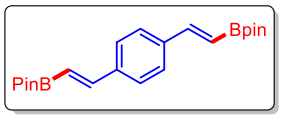
4p):[5] Pale-yellow liquid (0.104 g, 0.36 mmol, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 18.4 Hz, 1H), 6.27 (d, J = 18.4 Hz, 1H), 3.90 (s, 3H), 1.31 (s, 12H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 166.9, 148.3, 141.9, 130.3, 130.0, 127.0, 83.7, 52.2, 24.9 ppm.

(E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzonitrile (compound 4q):



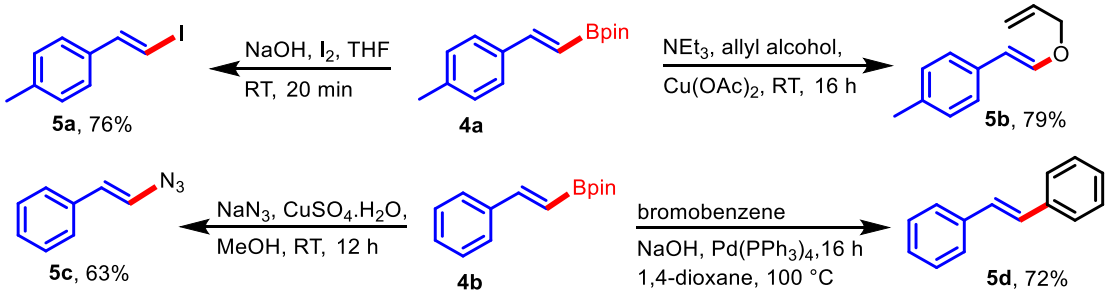
Pale-yellow liquid (0.090 g, 0.35 mmol, 71%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63-7.61 (m, 2H), 7.54 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 18.4 Hz, 1H), 6.27 (d, J = 18.4 Hz, 1H), 1.31 (s, 12H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 147.2, 141.9, 132.6, 127.6, 118.9, 112.2, 83.9, 24.9 ppm.

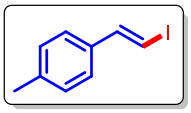
1,4-bis((E)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzene (compound

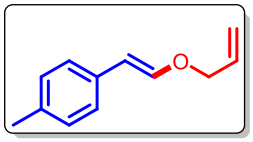


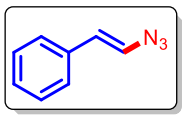
4r):[5] Pale-yellow liquid (0.141 g, 0.37 mmol, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.44 (m, 4H), 7.37 (d, J = 18.4 Hz, 2H), 6.18 (d, J = 18.4 Hz, 2H), 1.31 (s, 24H) ppm. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 149.0, 148.5, 138.1, 132.5, 127.5, 127.0, 83.5, 24.9 ppm.

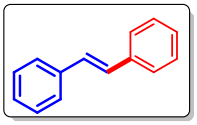
Scheme S1. Post-modification of hydroborated products



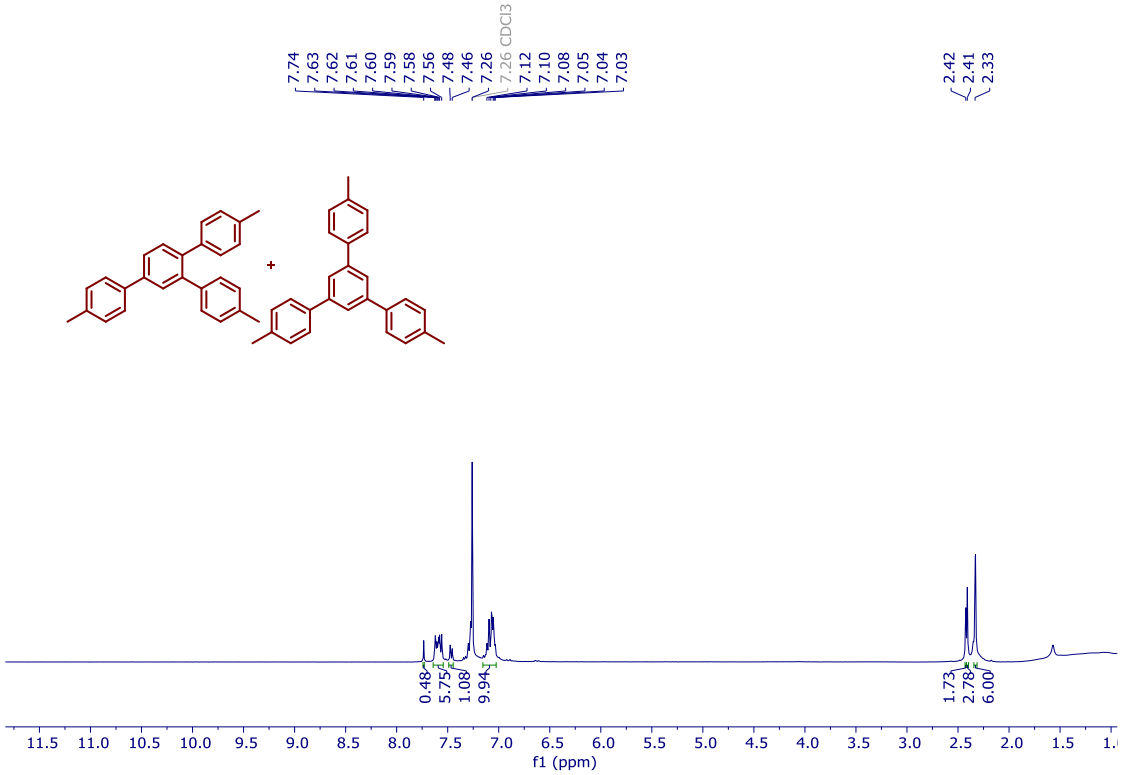
Compound **5a** was synthesized following the reported procedure.[5] Compound **4a** (0.122 g, 0.5  mmol) in THF (5 mL) solution was added to a 3.0 M solution of NaOH (60 mg, 1.5 mmol). After ~10 minutes, I_2 (0.25 g, 1.0 mmol) was added to the above reaction mixture and stirred for 30 minutes at room temperature. After completion of the reaction, the reaction mixture was diluted with dichloromethane and the organic phase was washed with a saturated solution of $Na_2S_2O_3$ then with brine. The organic phase was dried over $MgSO_4$ and concentrated under vacuum. The crude residue was purified by column chromatography to provide **5a** as a colourless liquid (93 mg, 0.38 mmol, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 14.9 Hz, 1H), 7.20-7.12 (m, 4H), 6.74 (d, J = 14.8 Hz, 1H), 2.32 (s, 3H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 145.0, 138.5, 135.2, 129.5, 126.1, 75.4, 21.4 ppm.

Compound **5b** was synthesized following the reported procedure.[5] A Schlenk tube was charged  with compound (**4a**, 0.122 g, 0.5 mmol), allyl alcohol (3 mL), triethylamine (0.20 g, 2.0 mmol), $Cu(OAc)_2$ (0.182 g, 1.0 mmol) and the reaction mixture was stirred for 16 h at room temperature. After completion of the reaction, the reaction mixture was diluted with dichloromethane and washed with water, brine, and dried over anhydrous $MgSO_4$. The volatiles from the organic phase were removed under reduced pressure. The crude residue was purified by column chromatography to get the compound **5b** as a yellow liquid (80 mg, 0.40 mmol, 79%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13-7.06 (m, 4H), 6.95 (d, J = 10.4 Hz, 1H), 6.02-5.96 (m, 1H), 5.88 (d, J = 13.0 Hz, 1H), 5.38 (d, J = 20.3 Hz, 1H), 5.28 (d, J = 9.2 Hz, 1H), 4.37 (d, J = 6.9 Hz, 2H), 2.31 (s, 3H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 147.0, 135.5, 133.5, 133.4, 129.4, 125.2, 118.0, 106.8, 70.9, 21.2 ppm.

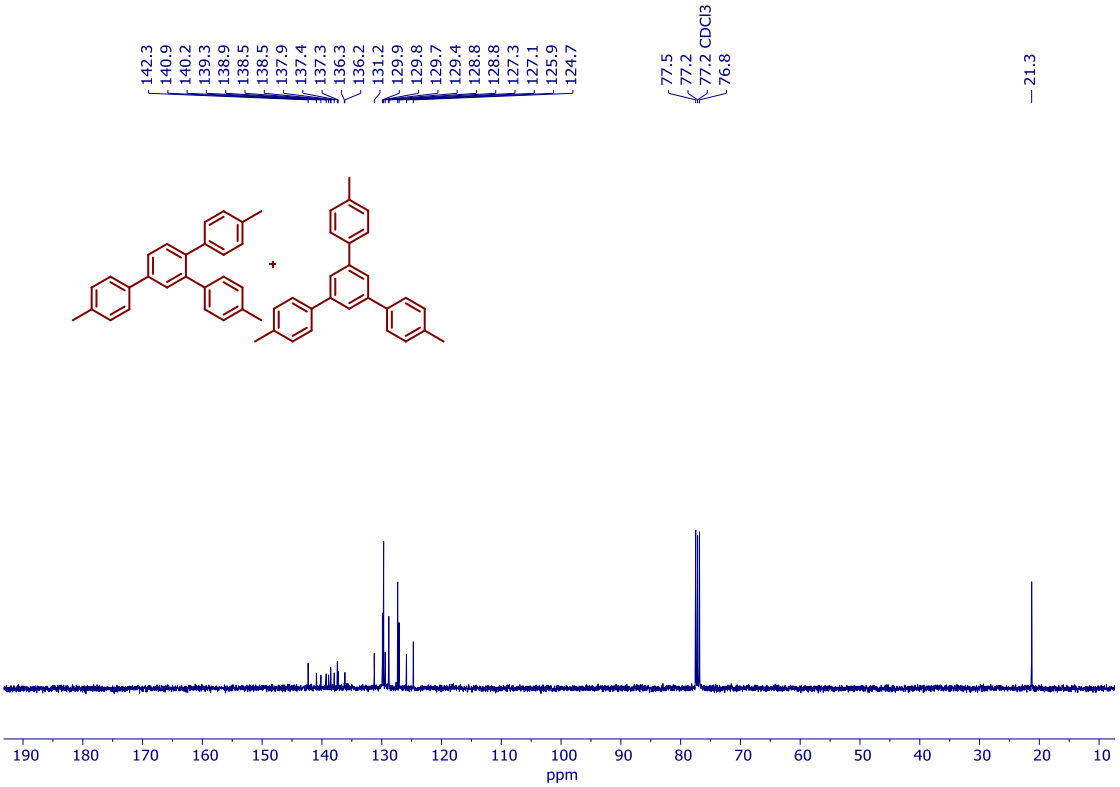
Compound **5c** was synthesized following the reported procedure.[5] In a round bottom flask,  sodium azide (81 mg, 1.25 mmol), $CuSO_4.5H_2O$ (0.125 g, 0.5 mmol), and **4b** (0.115 g, 0.5 mmol) were dissolved in MeOH (4 mL) and the reaction mixture was stirred for 4 h at room temperature. All volatile solvents were removed under reduced pressure and the crude residue was dissolved in dichloromethane, purified by column chromatography to get the compound **5c** as a colourless liquid (46 mg, 0.32 mmol, 63%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.27 (m, 4H), 7.23-7.21 (m, 1H), 6.61 (d, J = 13.8 Hz, 1H), 6.28 (d, J = 13.8 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 128.9, 127.5, 126.9, 126.0, 120.0 ppm.

Compound **5d** was synthesized following the reported procedure.[5] To a Schlenk tube,  $Pd(PPh_3)_4$ (29 mg, 5 mol%), bromobenzene (0.17 g, 0.8 mmol), NaOH (40 mg, 1.0 mmol), and **4b** (0.115 g, 0.5 mmol) were dissolved in 1,4-dioxane and the reaction mixture was stirred at 100 °C for 16 h. After the completion of reaction, the reaction mixture was concentrated under vacuum and the crude residue was dissolved in dichloromethane, purified by column chromatography to get the compound **5d** as a white solid (65 mg, 0.36 mmol, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (m, 4H), 7.43-7.34 (m, 6H), 7.19 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 137.4, 128.8, 127.7, 126.7 ppm.

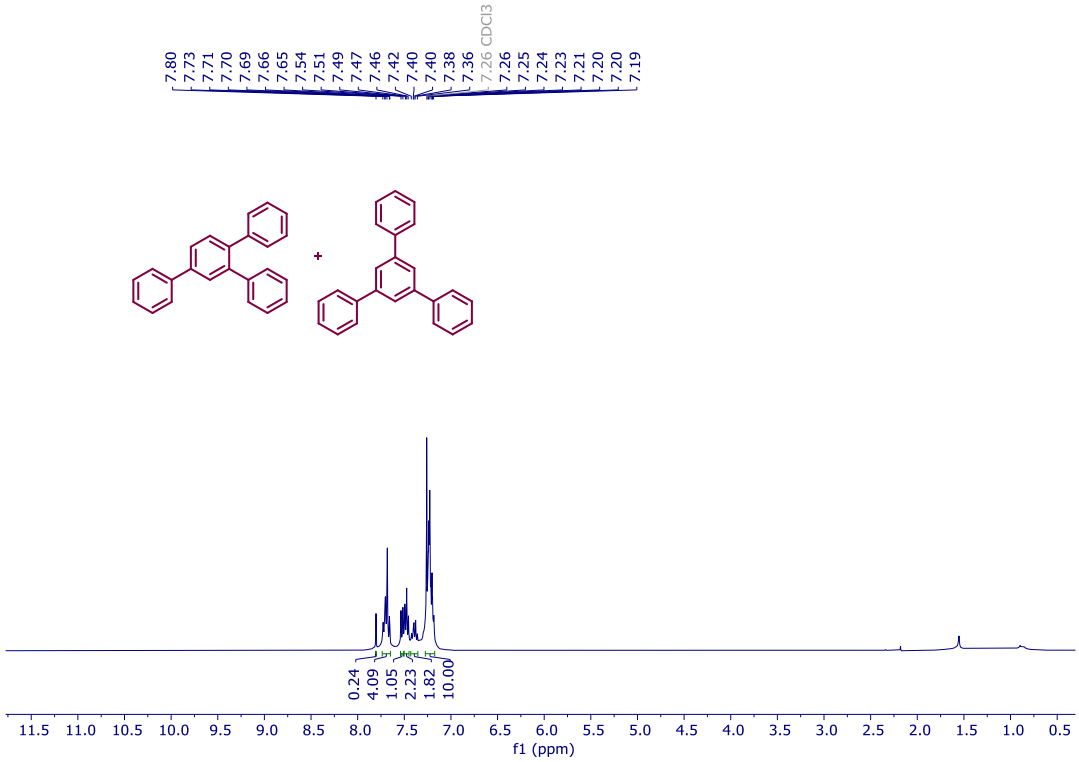
^{1}H and $^{13}C\{^1H\}$ spectra of the isolated compounds:



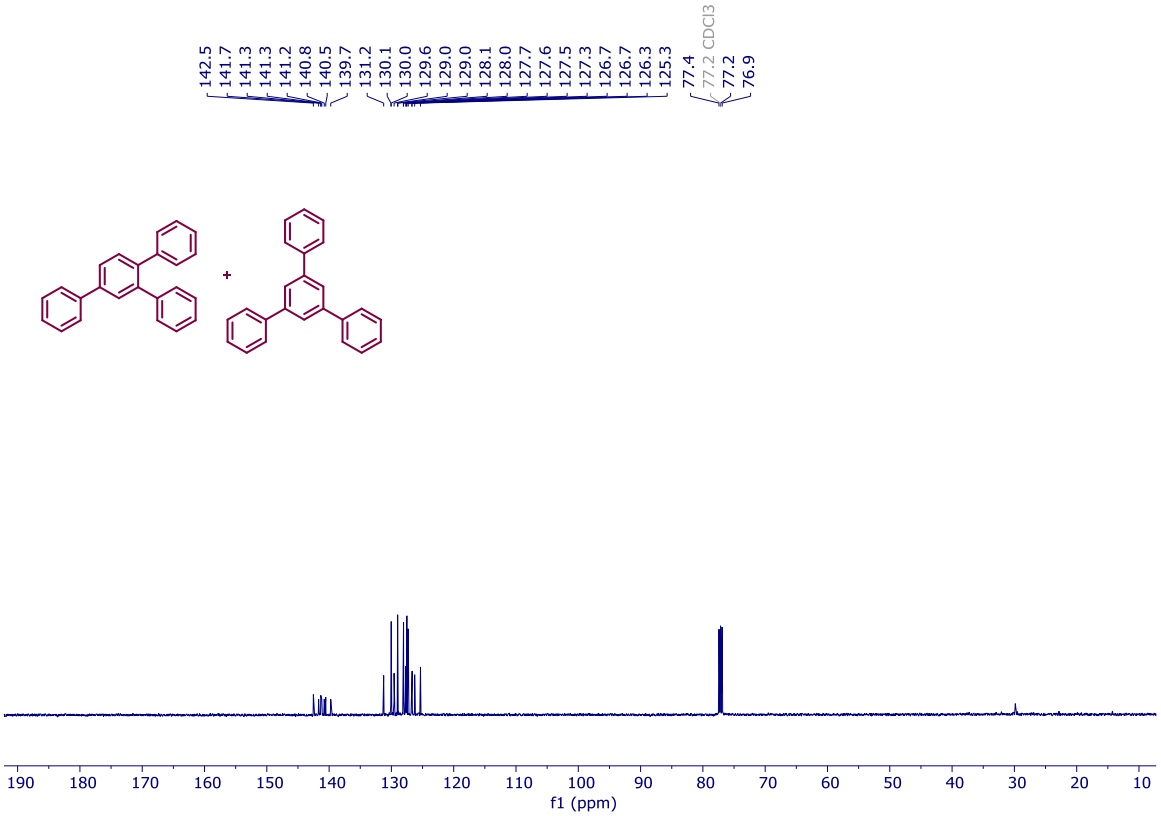
*^{1}H NMR of 4,4''-dimethyl-4'-(p-tolyl)-1,1':2',1''-terphenyl (Compound-**3a**) in $CDCl_3$*



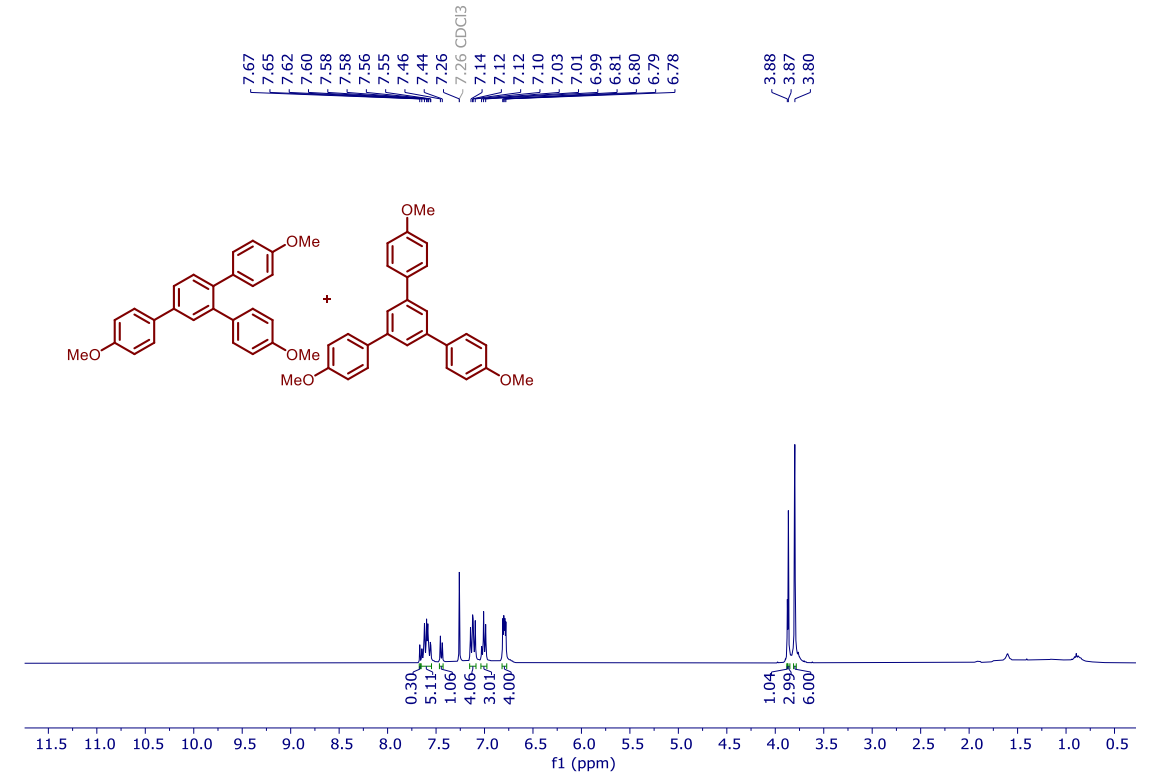
*$^{13}C\{^{1}H\}$ NMR of 4,4''-dimethyl-4'-(p-tolyl)-1,1':2',1''-terphenyl (Compound-**3a**) in $CDCl_3$*



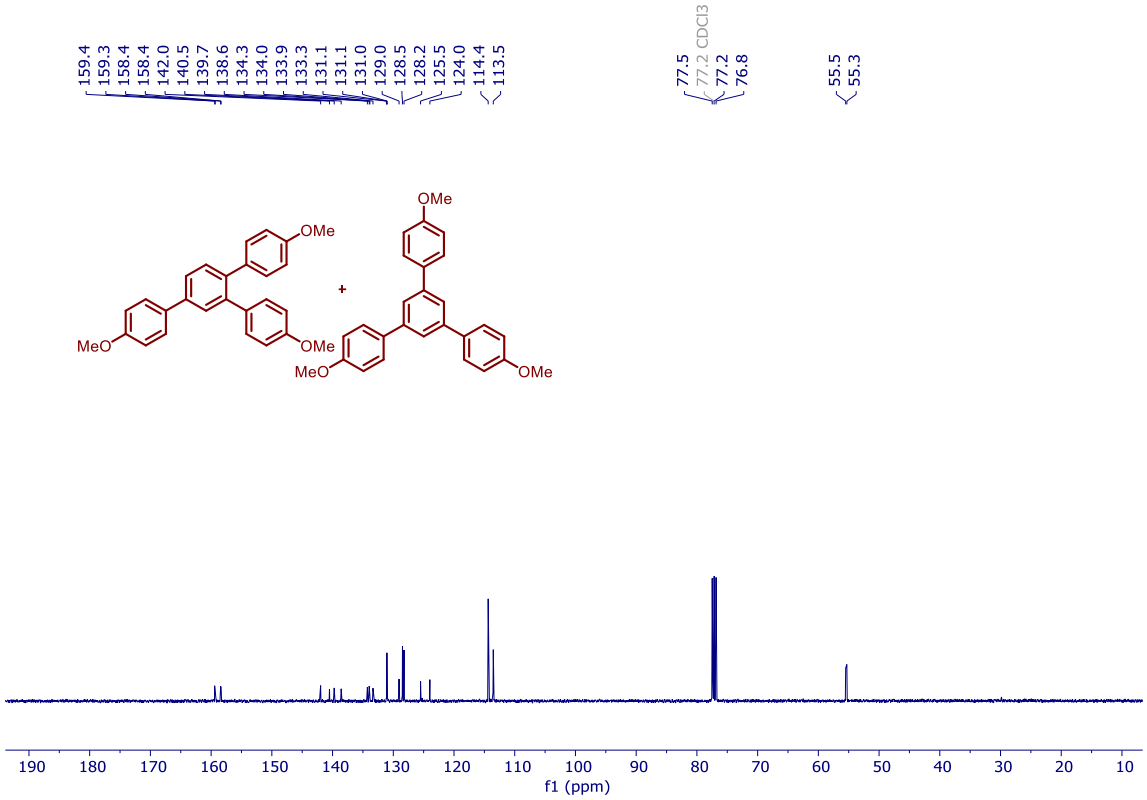
*^{1}H NMR of 4'-phenyl-1,1':2',1''-terphenyl (Compound-**3b**) in $CDCl_3$*



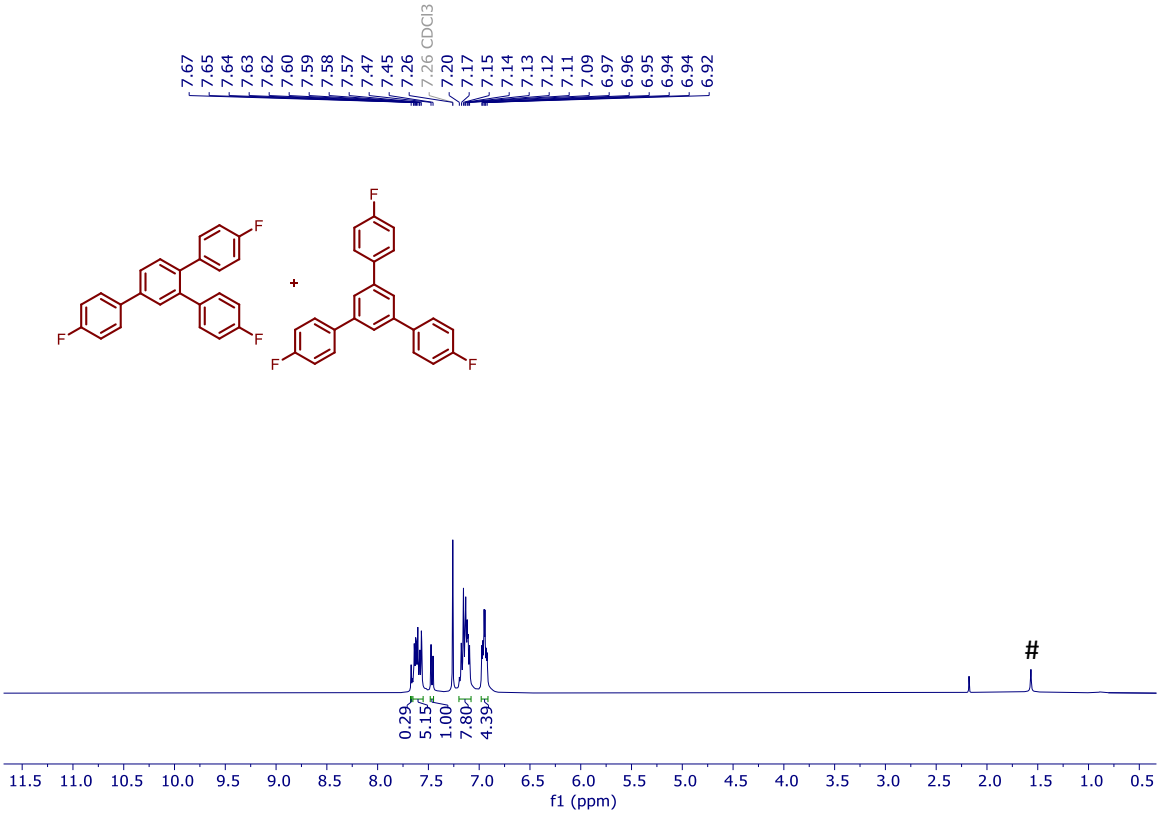
*$^{13}C\{^{1}H\}$ NMR of 4'-phenyl-1,1':2',1''-terphenyl (Compound-**3b**) in $CDCl_3$*



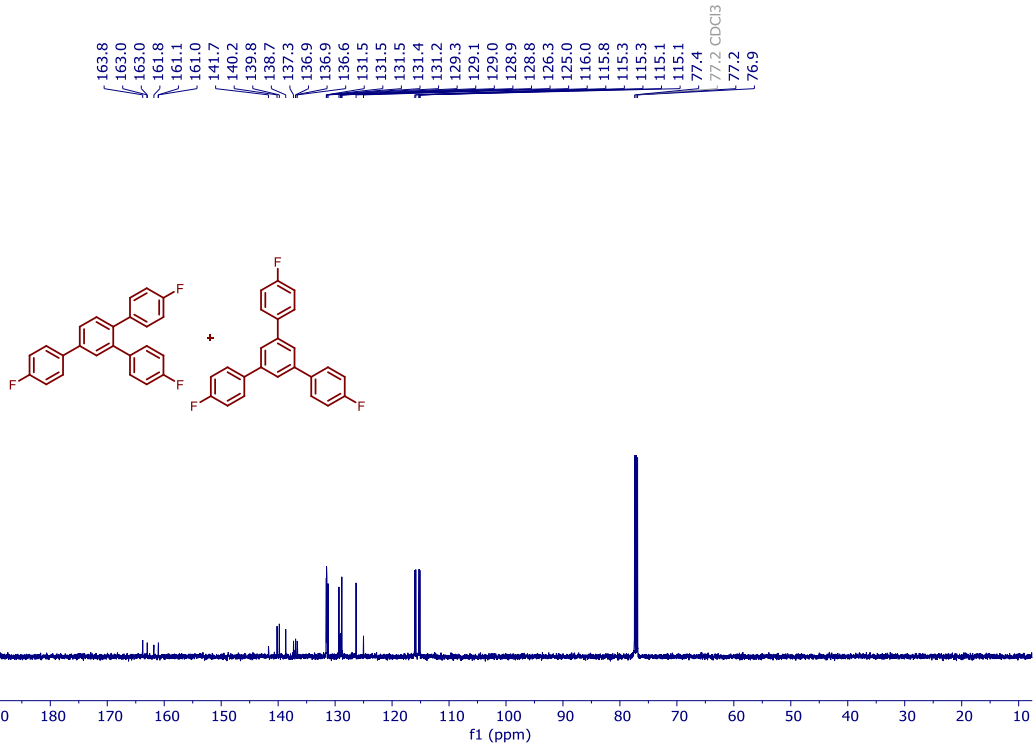
*^{1}H NMR of 4,4''-dimethoxy-4'-(4-methoxyphenyl)-1,1':2',1''-terphenyl (Compound-**3c**) in $CDCl_3$*



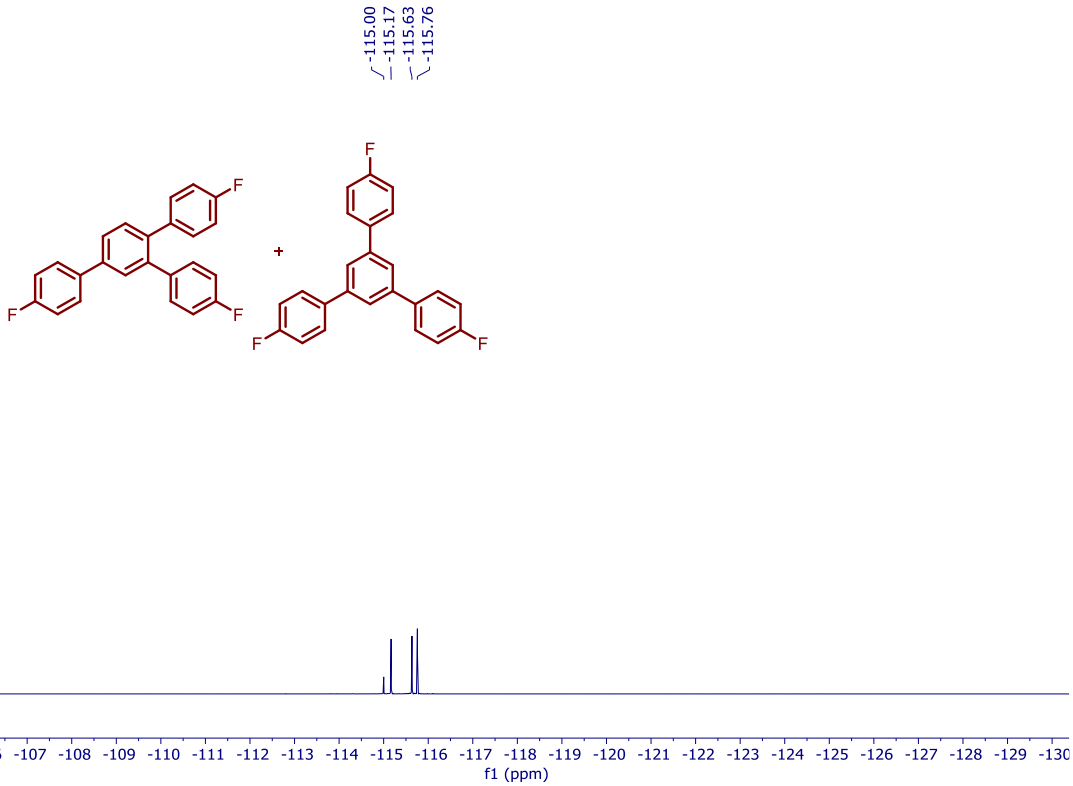
*$^{13}C\{^{1}H\}$ NMR of 4,4''-dimethoxy-4'-(4-methoxyphenyl)-1,1':2',1''-terphenyl (Compound-**3c**) in $CDCl_3$*



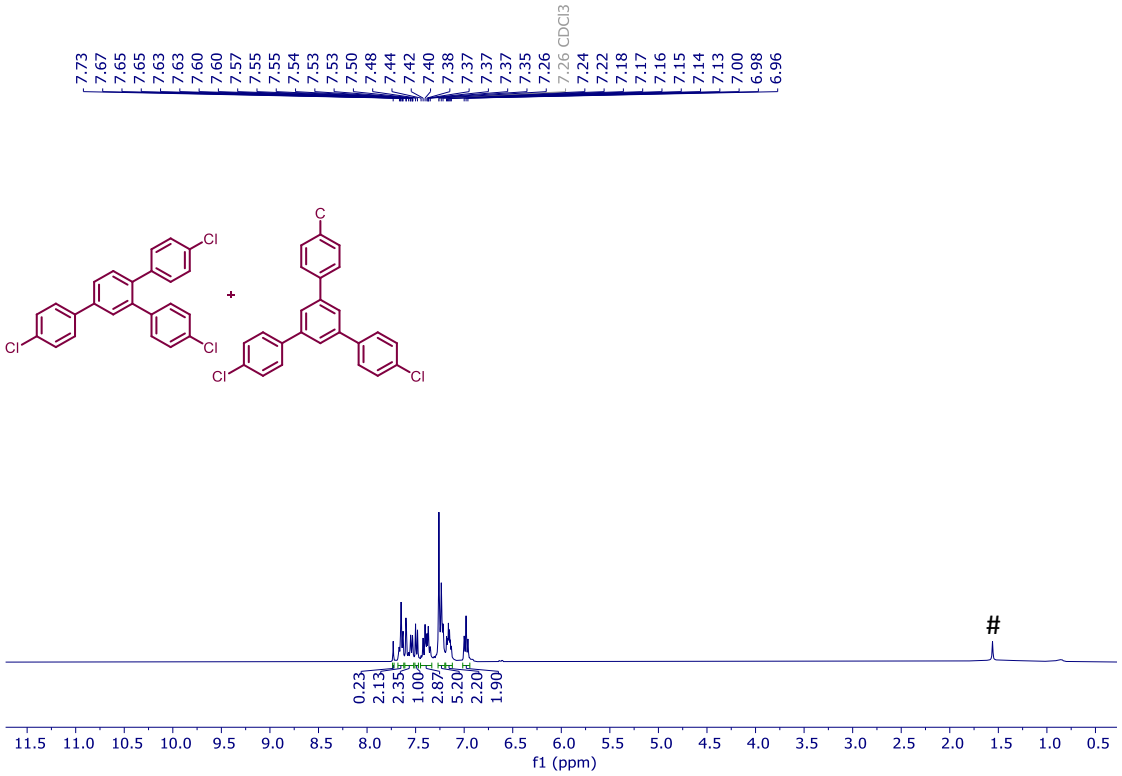
*^{1}H NMR of 4,4''-difluoro-4'-(4-fluorophenyl)-1,1':2',1''-terphenyl (Compound-**3d**) in $CDCl_3$. # indicates the solvent impurity of H_2O in $CDCl_3$*



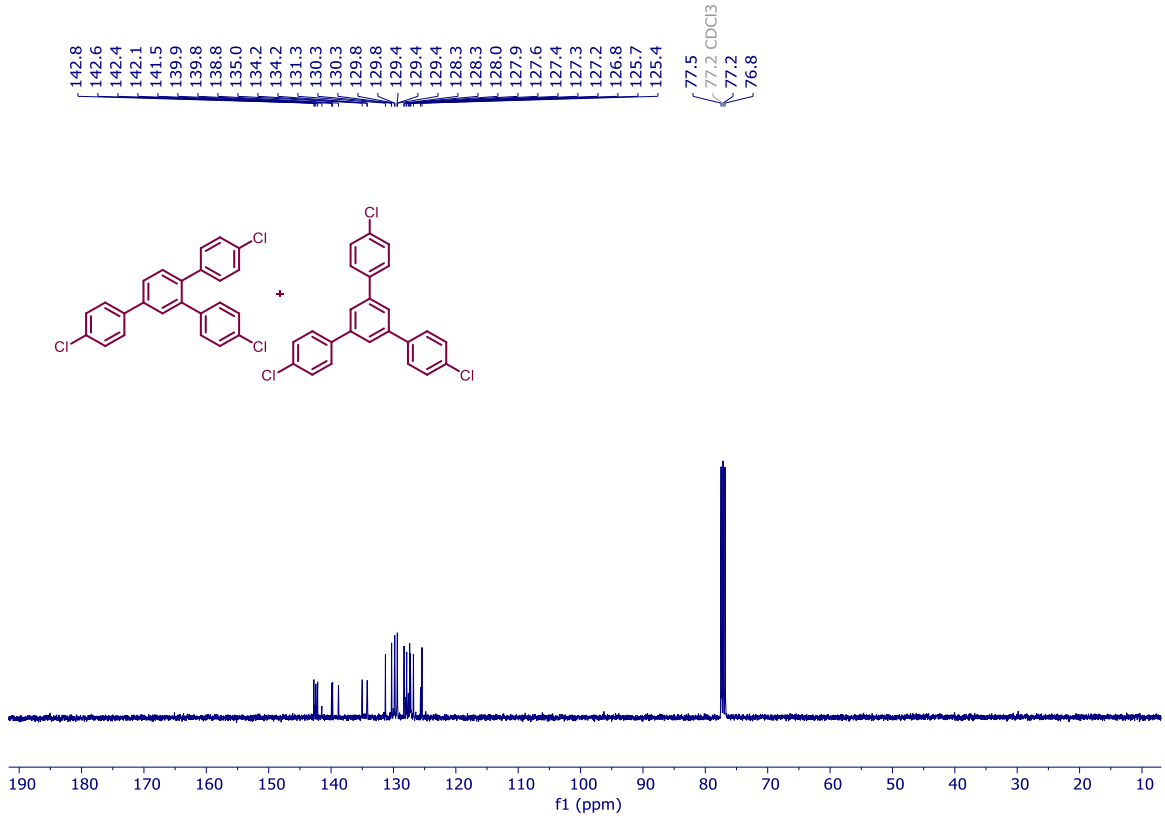
*$^{13}C\{^{1}H\}$ NMR of 4,4''-difluoro-4'-(4-fluorophenyl)-1,1':2',1''-terphenyl (Compound-**3d**) in $CDCl_3$*



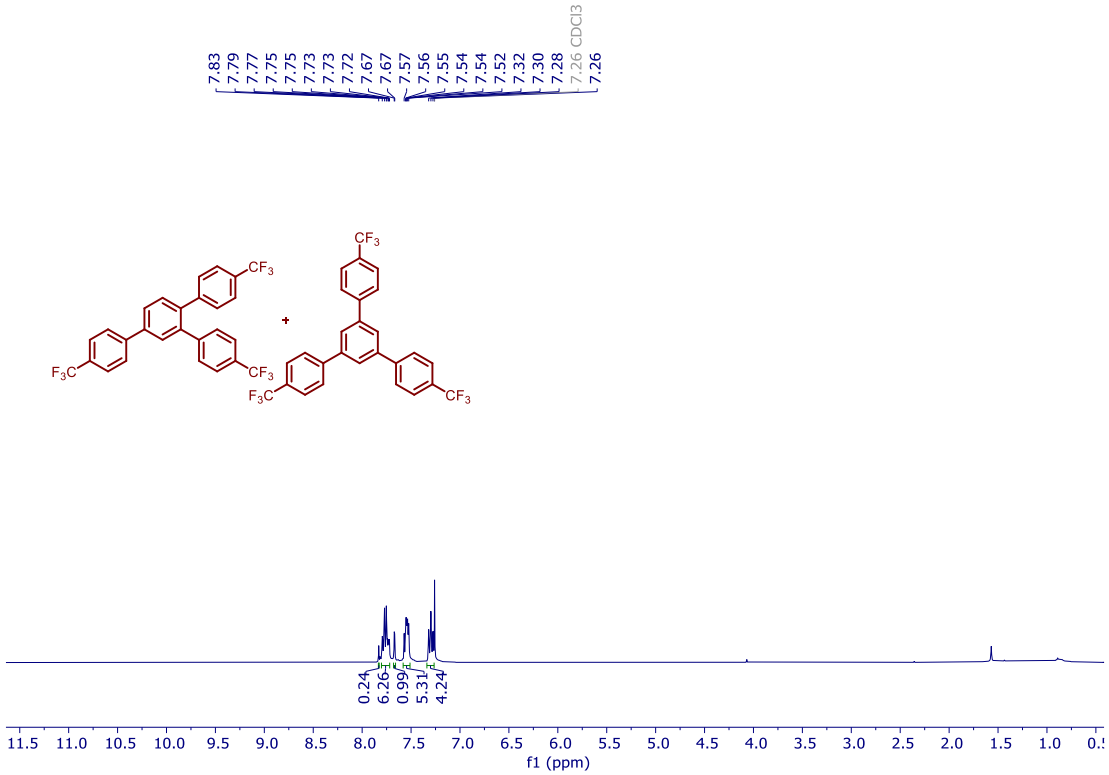
*^{19}F NMR of 4,4''-difluoro-4'-(4-fluorophenyl)-1,1':2',1''-terphenyl (Compound-**3d**) in $CDCl_3$*



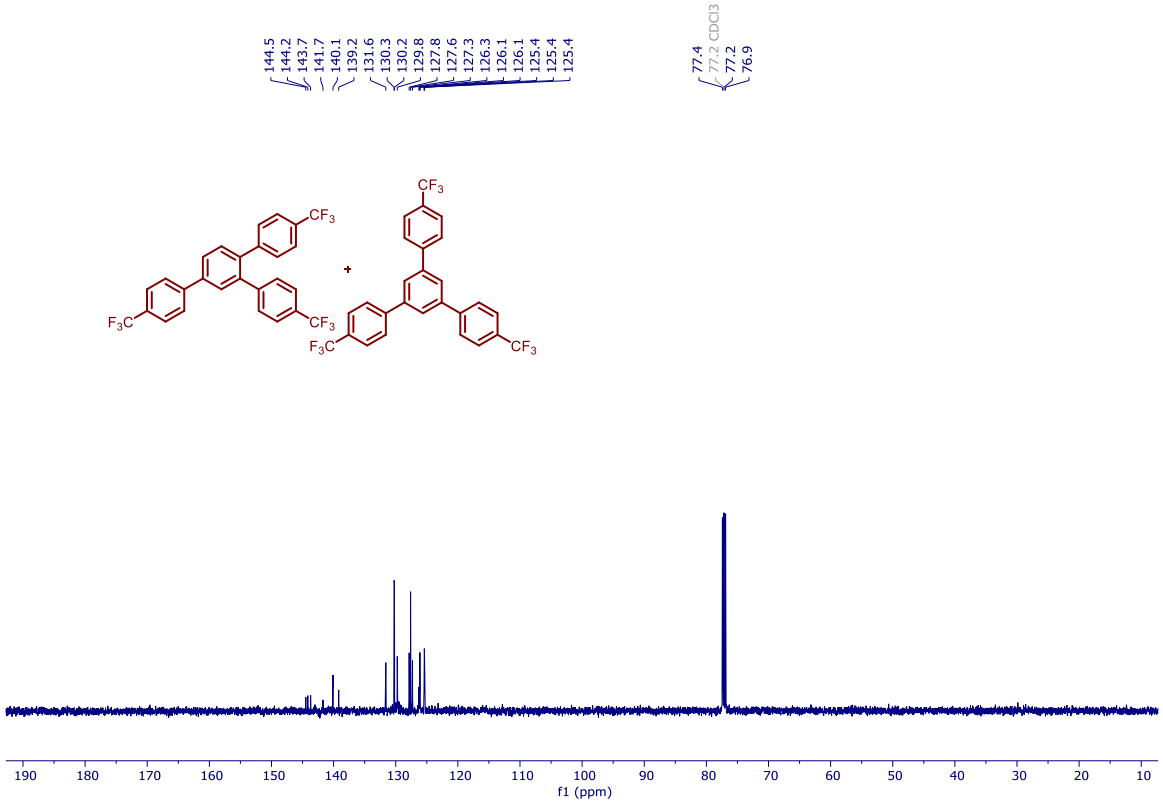
*[1]H NMR of 4,4''-dichloro-4'-(4-chlorophenyl)-1,1':2',1''-terphenyl (Compound-**3e**) in $CDCl_3$. # indicates the solvent impurity of H_2O in $CDCl_3$*



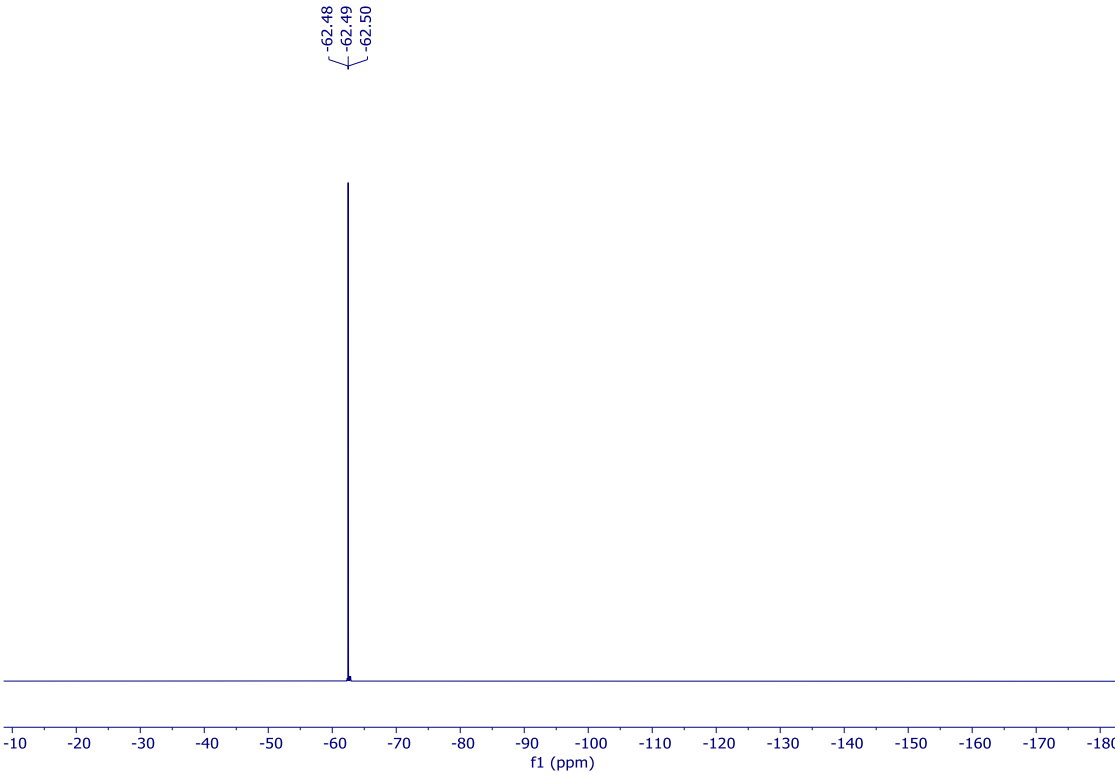
*[13]C{[1]H} NMR of 4,4''-dichloro-4'-(4-chlorophenyl)-1,1':2',1''-terphenyl (Compound-**3e**) in $CDCl_3$*



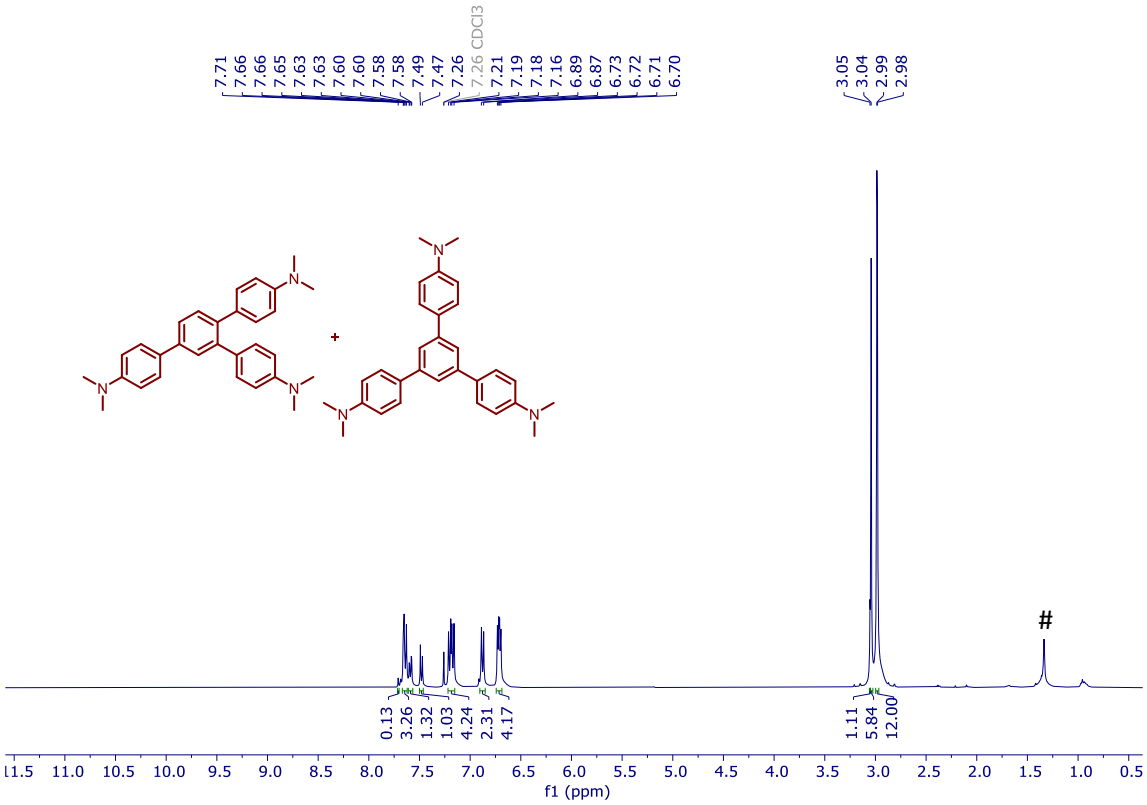
*^{1}H NMR of 4,4''-bis(trifluoromethyl)-4'-(4-(trifluoromethyl)phenyl)-1,1':2',1''-terphenyl (Compound-**3f**) in $CDCl_3$*



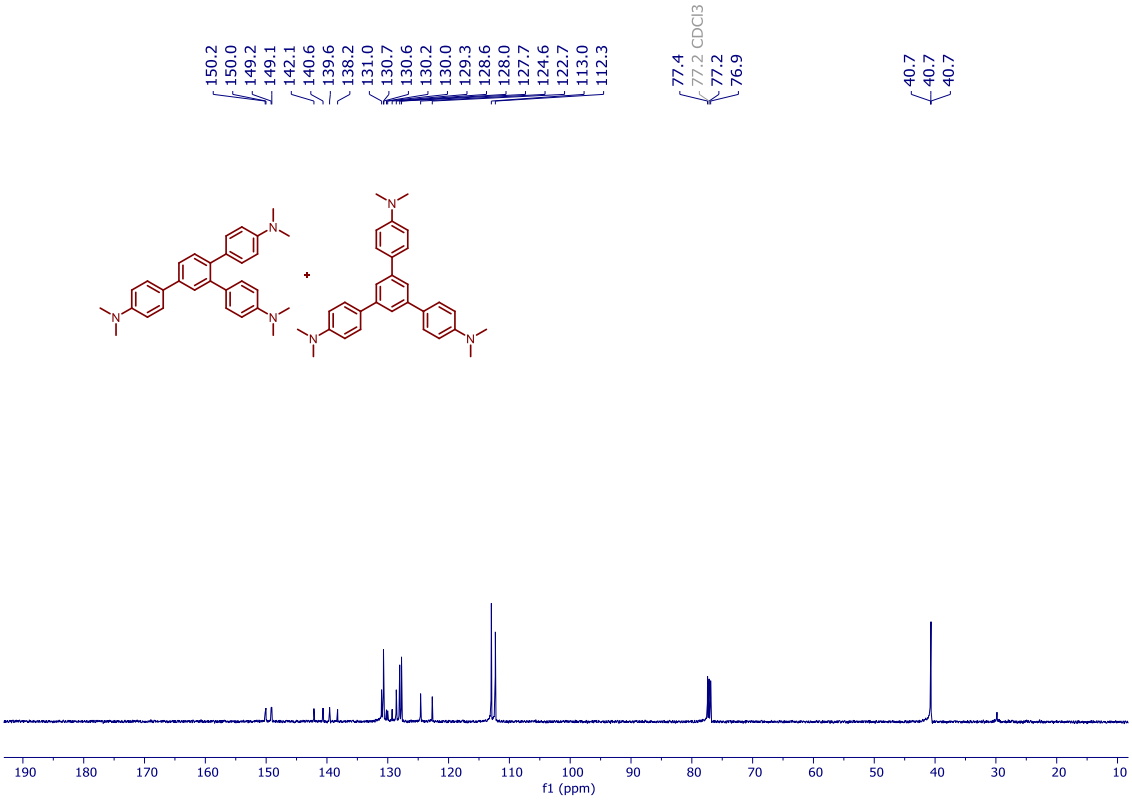
*$^{13}C\{^{1}H\}$ NMR of 4,4''-bis(trifluoromethyl)-4'-(4-(trifluoromethyl)phenyl)-1,1':2',1''-terphenyl (Compound-**3f**) in $CDCl_3$*



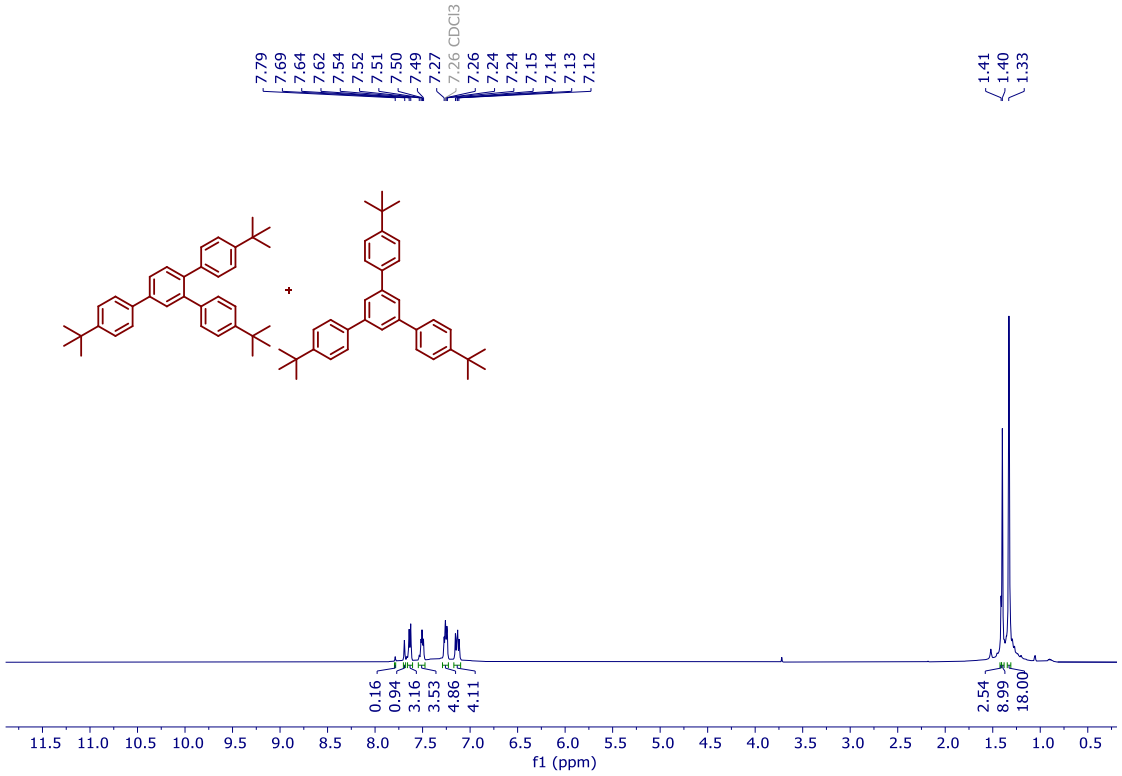
*^{19}F NMR of 4,4''-bis(trifluoromethyl)-4'-(4-(trifluoromethyl)phenyl)-1,1':2',1''-terphenyl (Compound-**3f**) in $CDCl_3$*



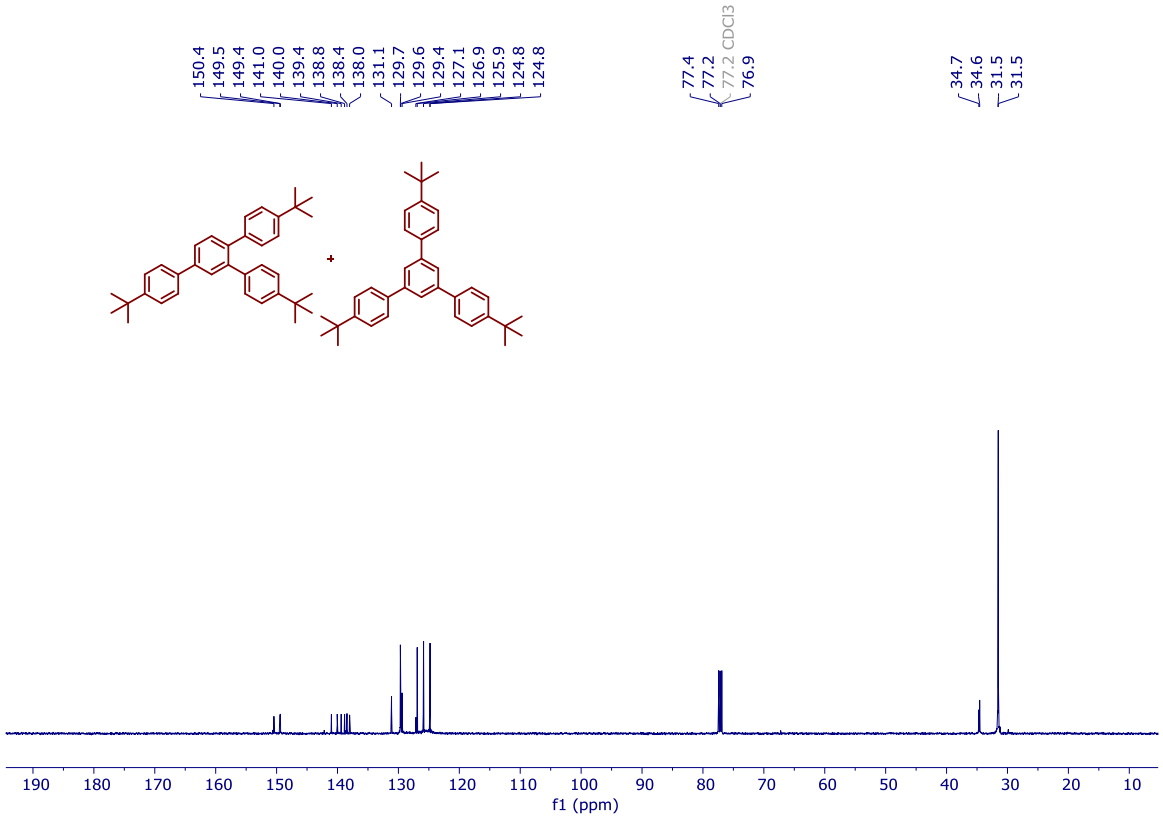
*^{1}H NMR of 4'-(4-(dimethylamino)phenyl)-$N^4,N^4,N^{4''},N^{4''}$-tetramethyl-[1,1':2',1''-terphenyl]-4,4''-diamine (Compound-**3g**) in $CDCl_3$. # indicates the solvent impurity of H_2O in $CDCl_3$*



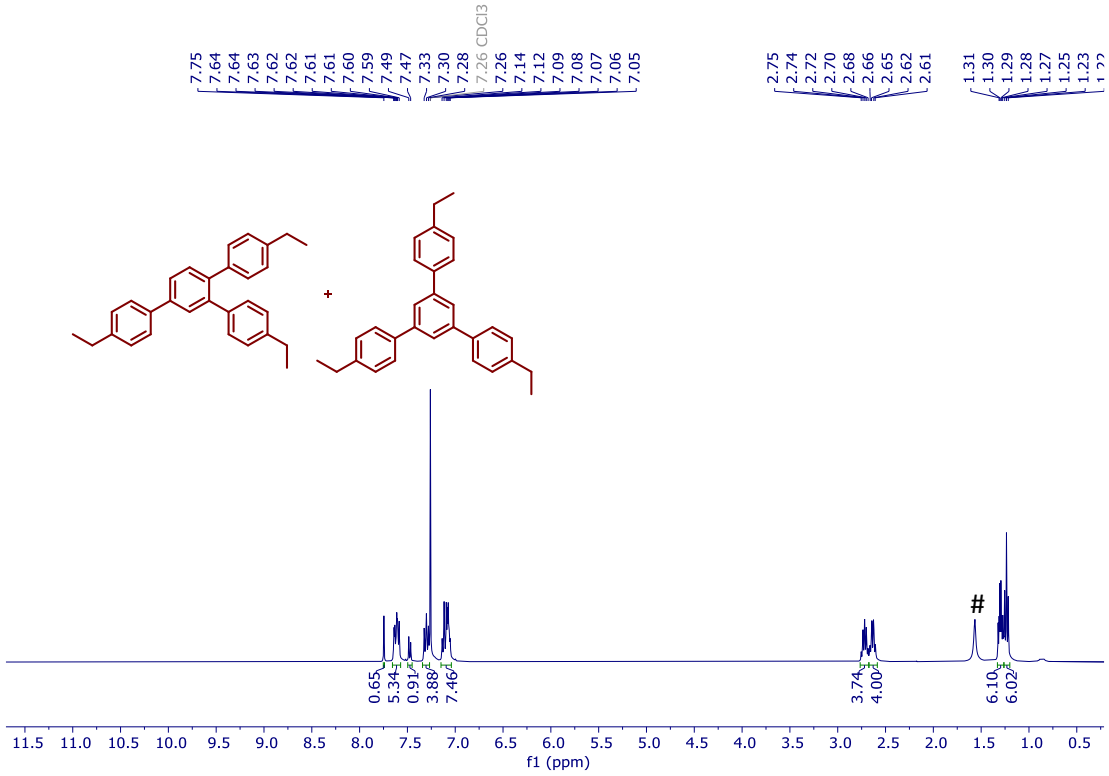
*$^{13}C\{^{1}H\}$ NMR of 4'-(4-(dimethylamino)phenyl)-N^4,N^4,$N^{4''}$,$N^{4''}$-tetramethyl-[1,1':2',1''-terphenyl]-4,4''-diamine (Compound-**3g**) in $CDCl_3$*



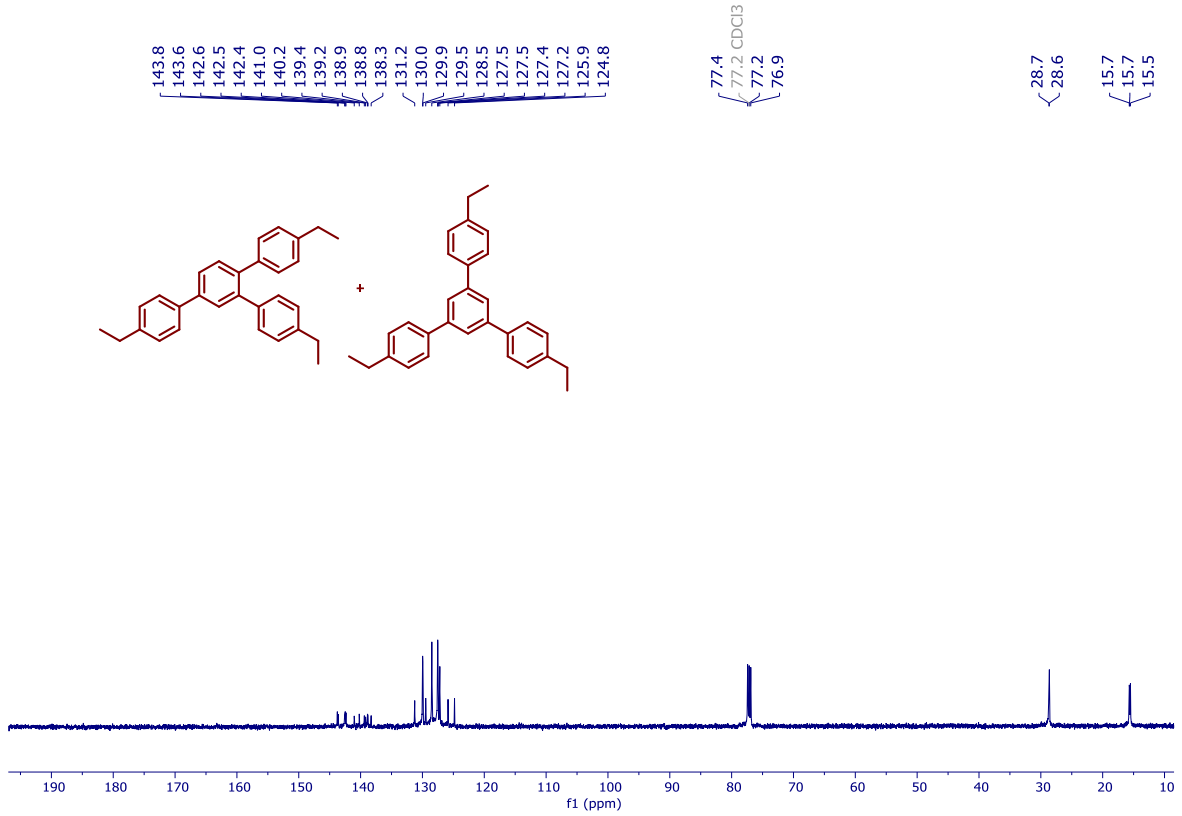
*^{1}H NMR of 4,4''-di-tert-butyl-4'-(4-(tert-butyl)phenyl)-1,1':2',1''-terphenyl (Compound-**3h**) in $CDCl_3$*



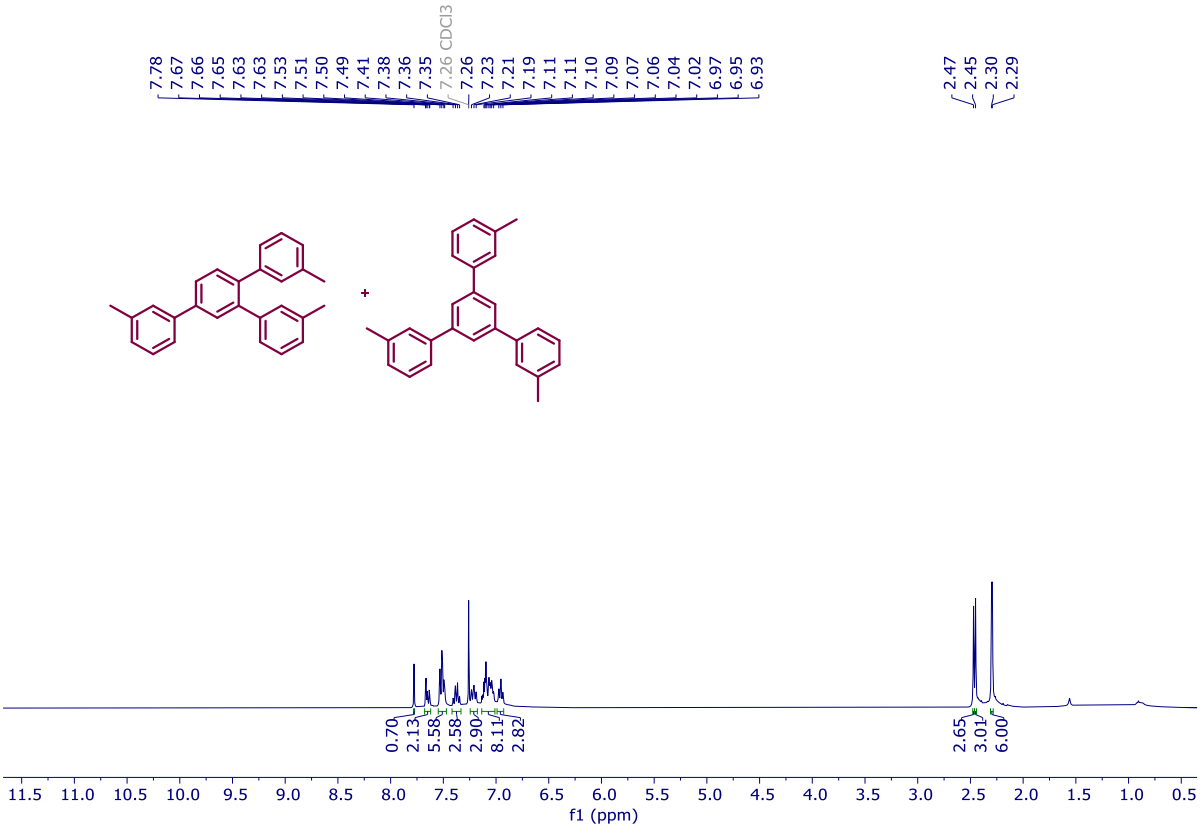
*$^{13}C\{^{1}H\}$ NMR of 4,4''-di-tert-butyl-4'-(4-(tert-butyl)phenyl)-1,1':2',1''-terphenyl (Compound-**3h**) in $CDCl_3$*



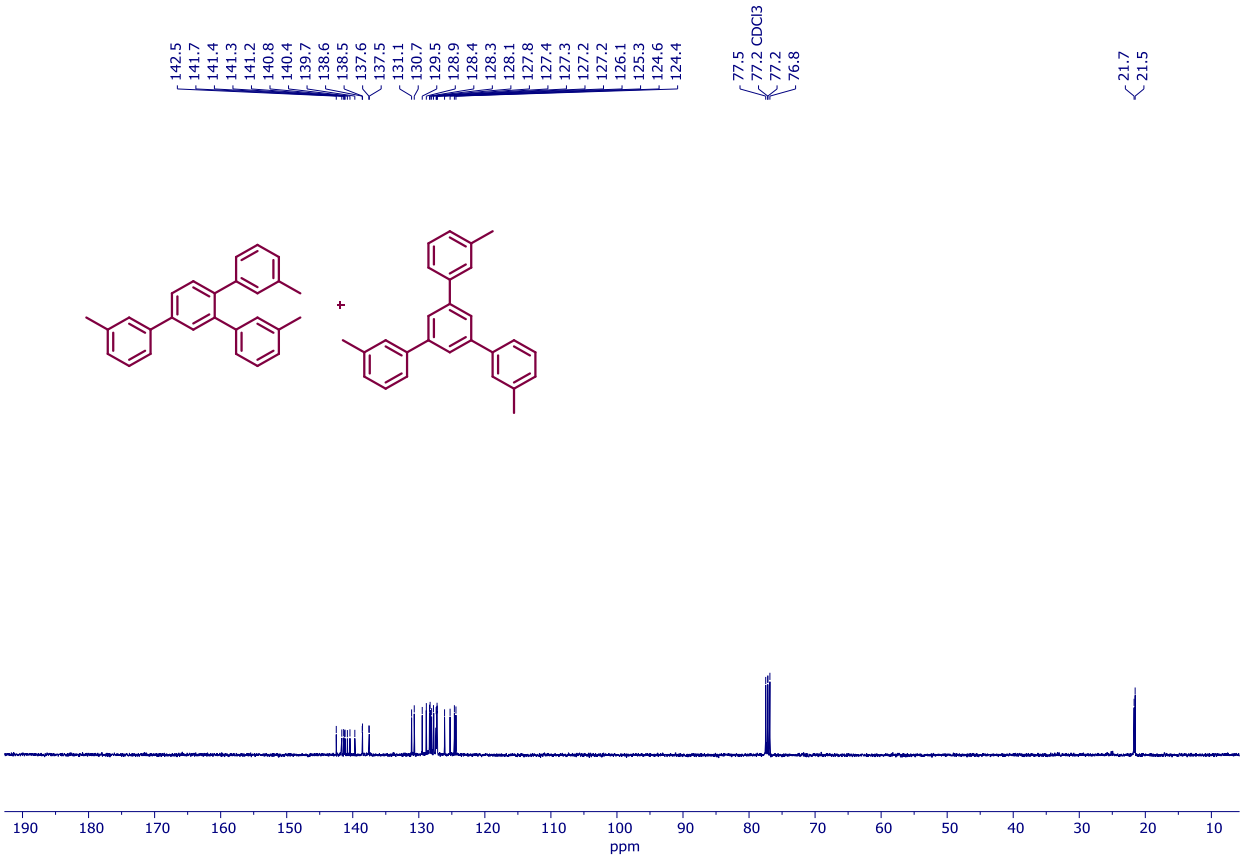
*^{1}H NMR of 4,4''-diethyl-4'-(4-ethylphenyl)-1,1':2',1''-terphenyl (Compound **3i**) in $CDCl_3$. # indicates the solvent impurity of H_2O in $CDCl_3$*



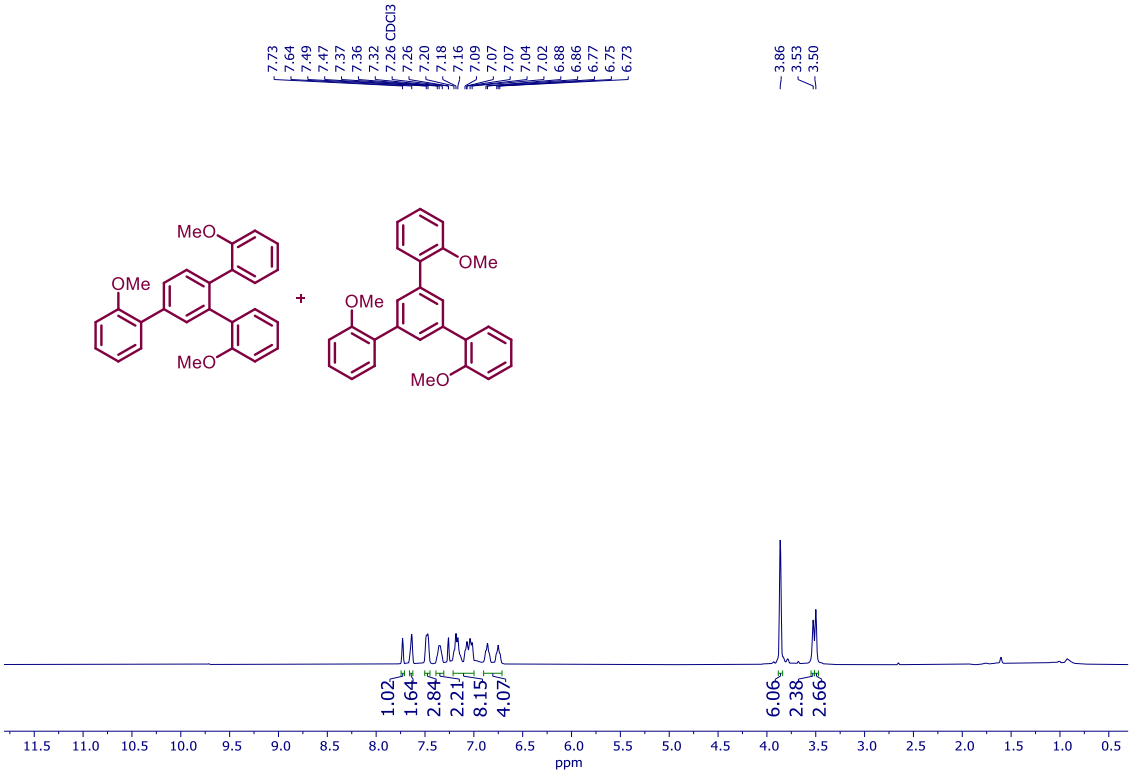
*$^{13}C\{^{1}H\}$ NMR of 4,4''-diethyl-4'-(4-ethylphenyl)-1,1':2',1''-terphenyl (Compound **3i**) in $CDCl_3$*



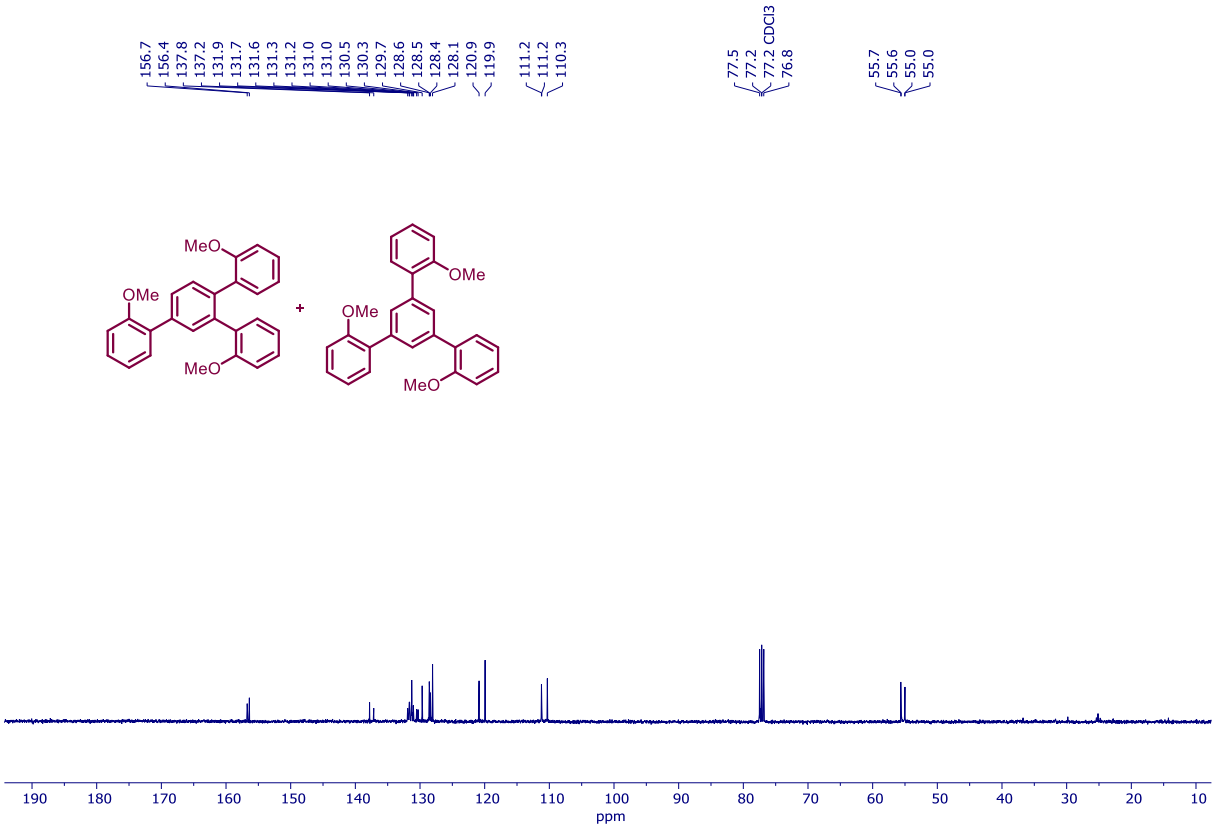
*^{1}H NMR of 3,3''-dimethyl-4'-(m-tolyl)-1,1':2',1''-terphenyl (Compound-**3j**) in $CDCl_3$*



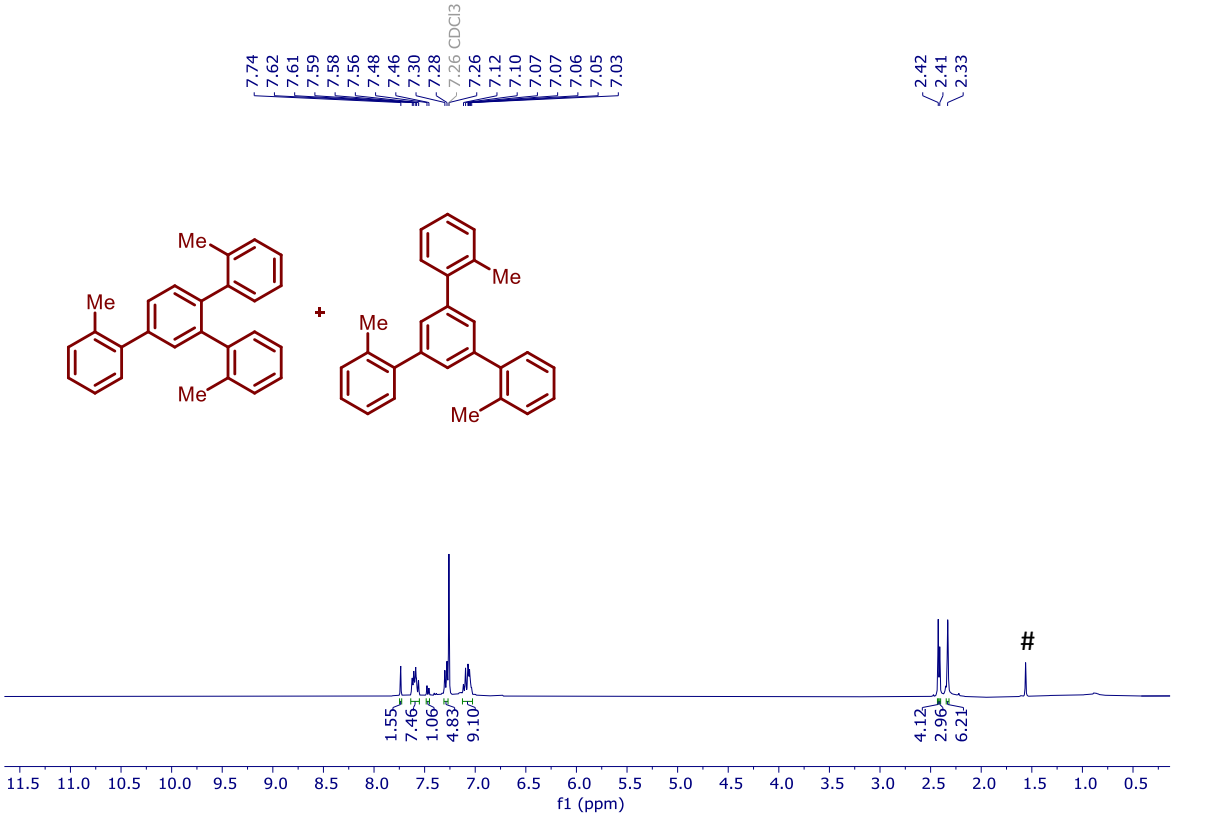
*$^{13}C\{^{1}H\}$ NMR of 3,3''-dimethyl-4'-(m-tolyl)-1,1':2',1''-terphenyl (Compound-**3j**) in $CDCl_3$*



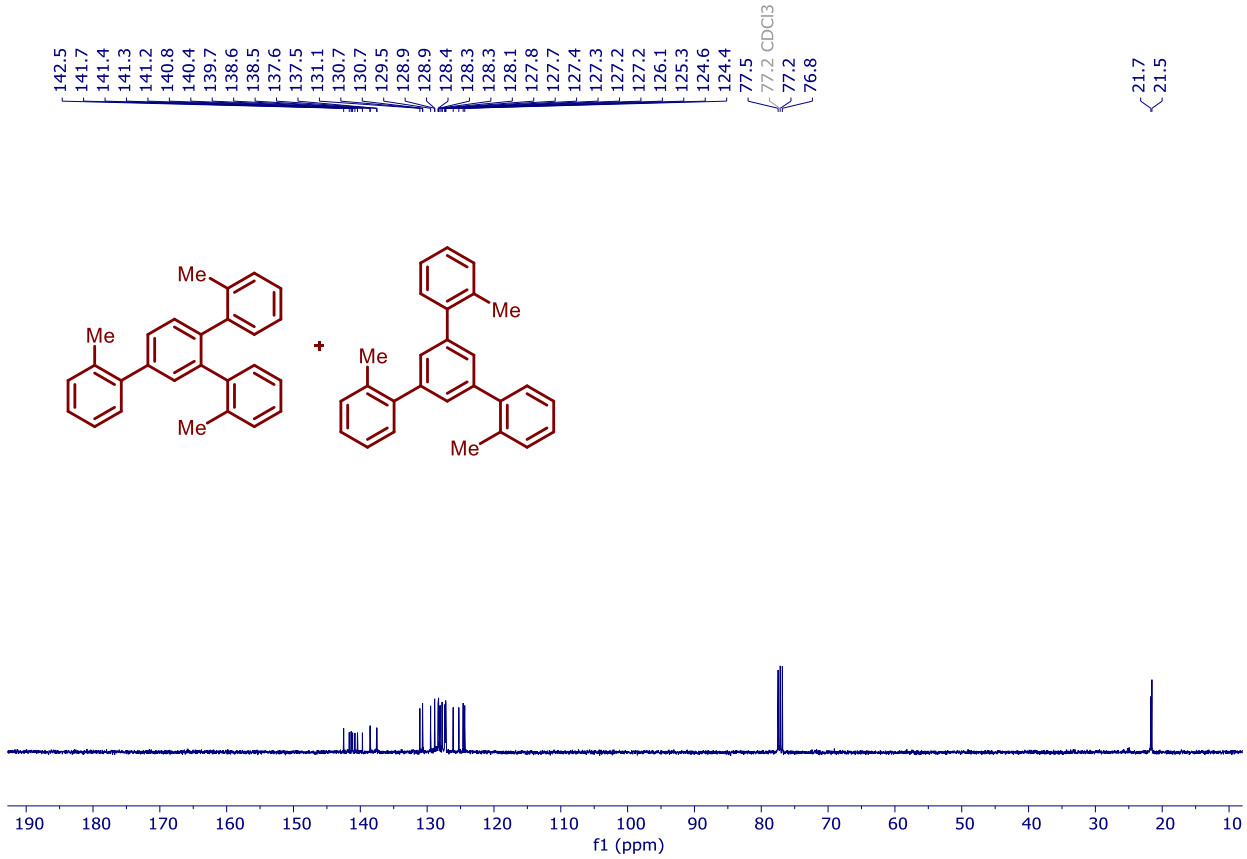
*^{1}H NMR of 2,2''-dimethoxy-4'-(2-methoxyphenyl)-1,1':2',1''-terphenyl (Compound **3k**) in $CDCl_3$*



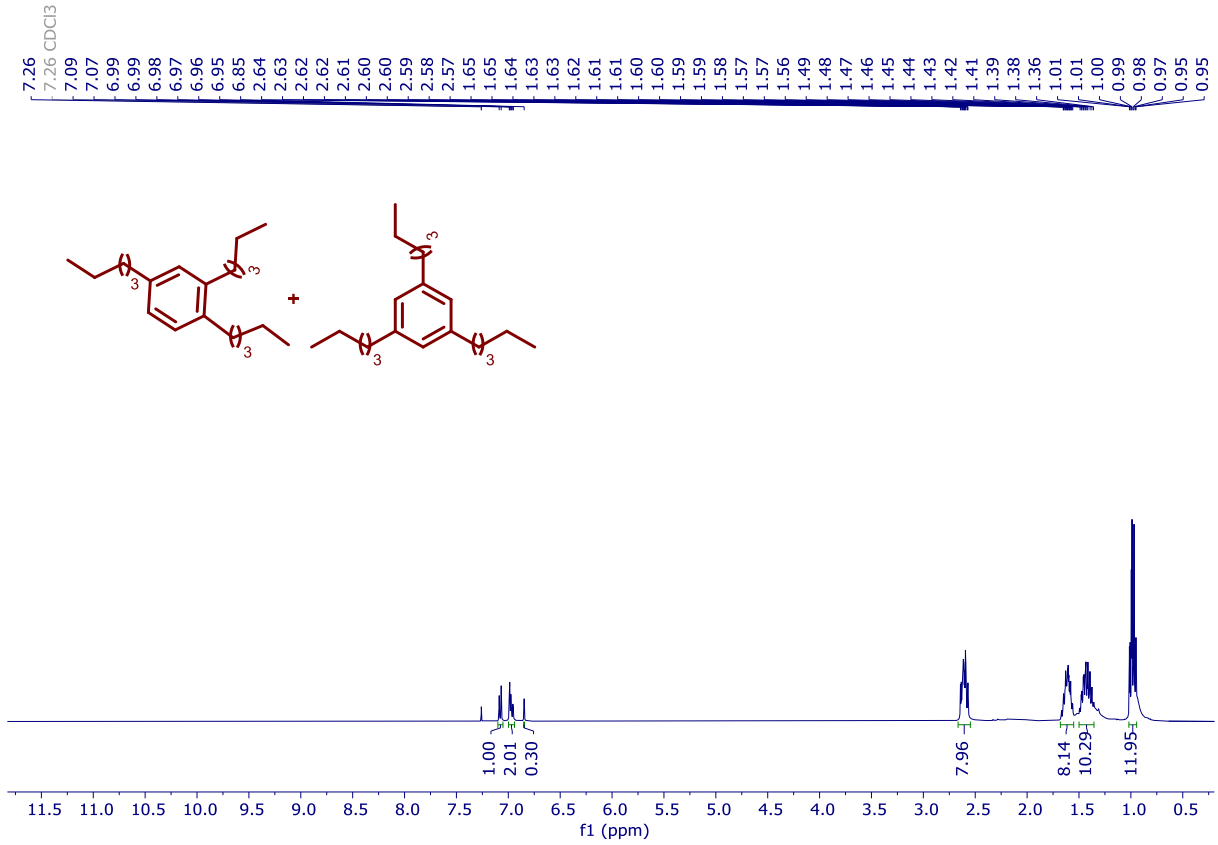
*$^{13}C\{^{1}H\}$ NMR of 2,2''-dimethoxy-4'-(2-methoxyphenyl)-1,1':2',1''-terphenyl (Compound **3k**) in $CDCl_3$*



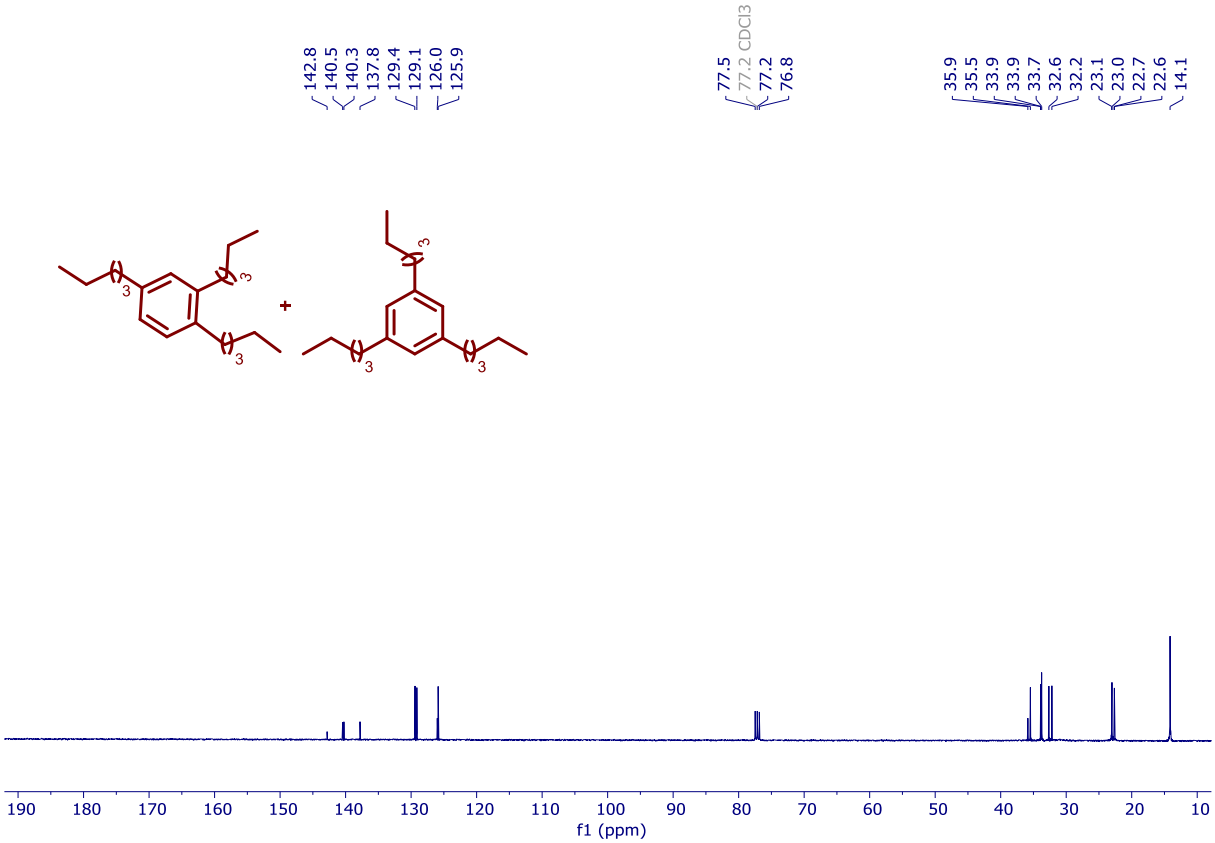
*^{1}H NMR of 2,2''-dimethyl-4'-(o-tolyl)-1,1':2',1''-terphenyl (Compound **3l**) in $CDCl_3$. # indicates the solvent impurity of H_2O in $CDCl_3$.*



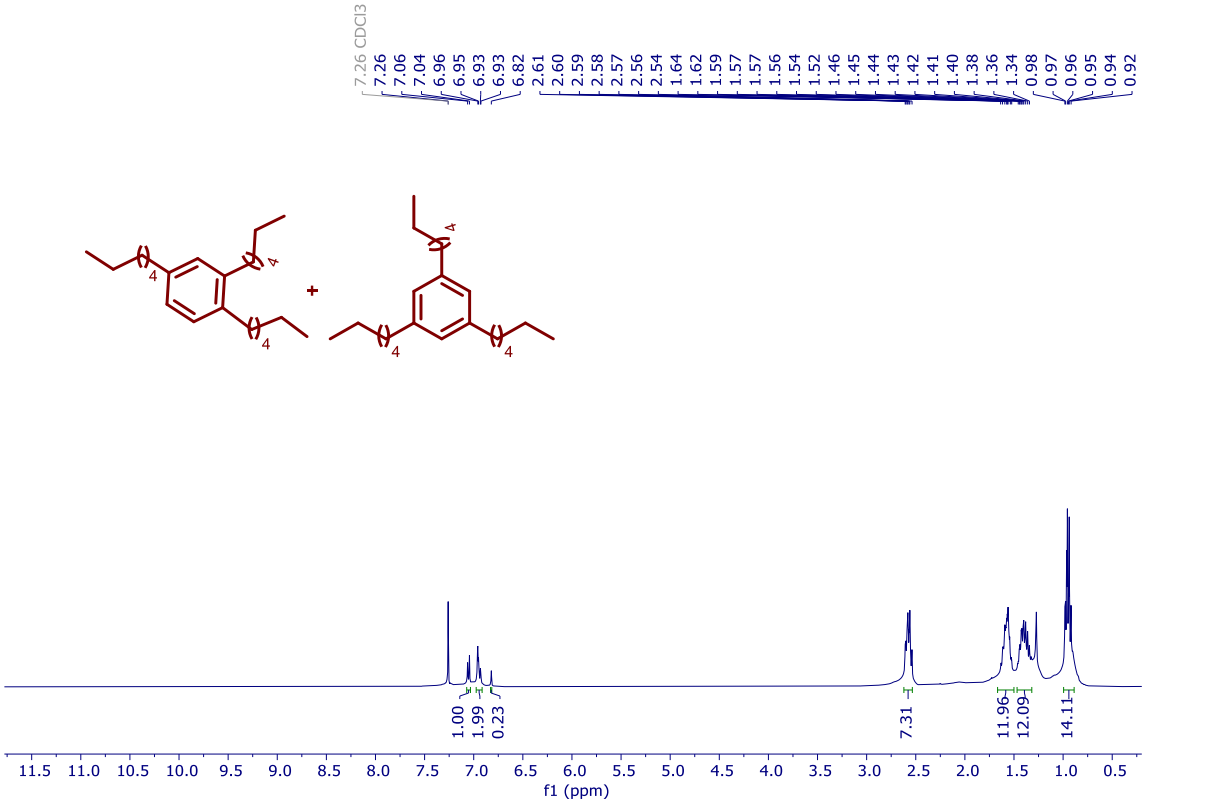
*$^{13}C\{^{1}H\}$ NMR of 2,2''-dimethyl-4'-(o-tolyl)-1,1':2',1''-terphenyl (Compound **3l**) in $CDCl_3$*



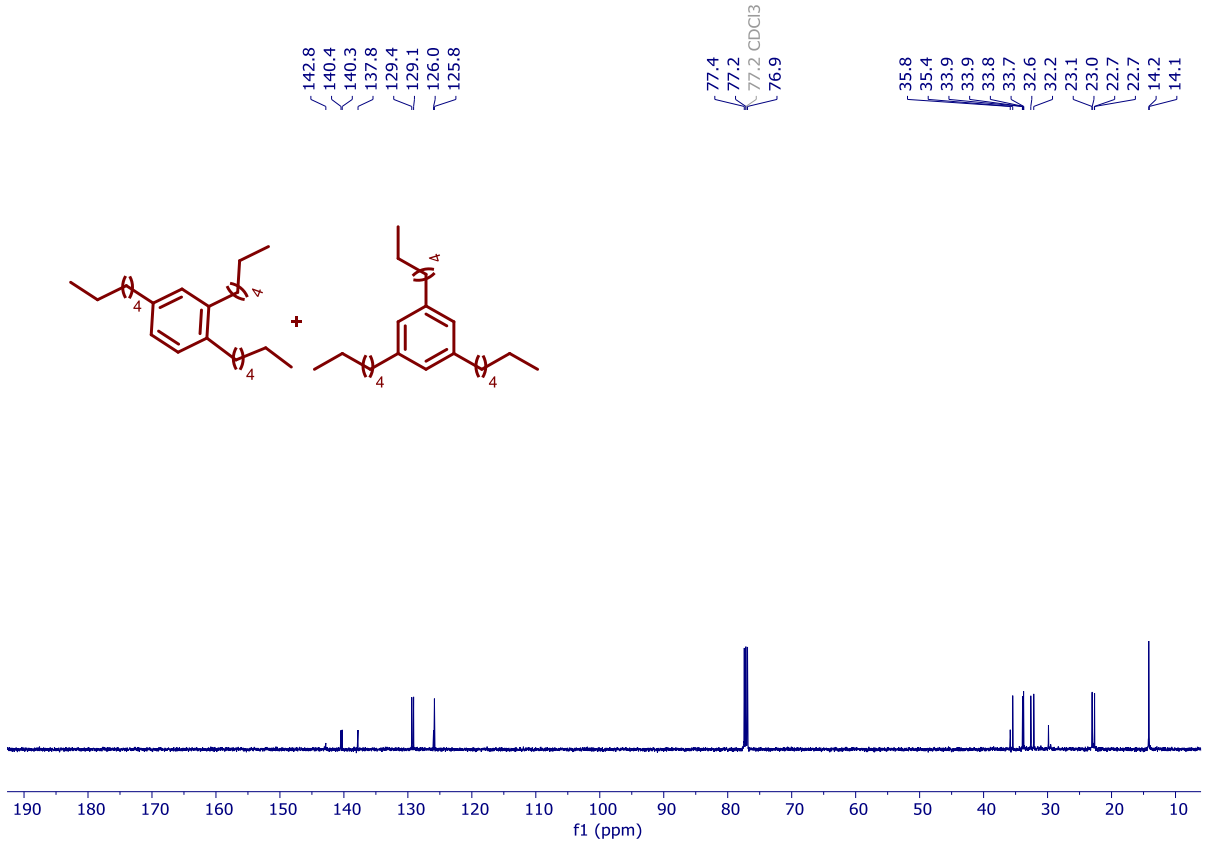
*^{1}H NMR spectrum of 1,2,4-tripentylbenzene (Compound **3m**) in $CDCl_3$*



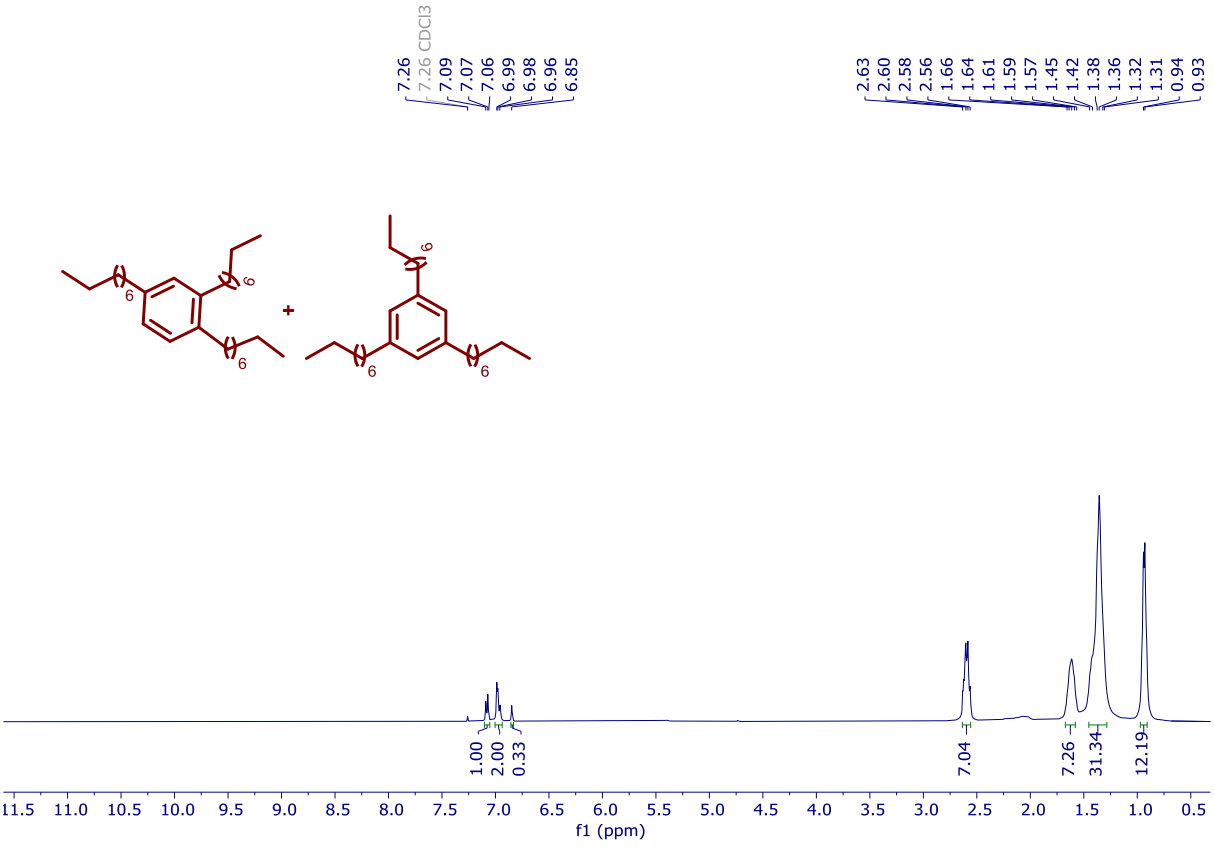
*$^{13}C\{^{1}H\}$ NMR spectrum of 1,2,4-tripentylbenzene (Compound **3m**) in $CDCl_3$*



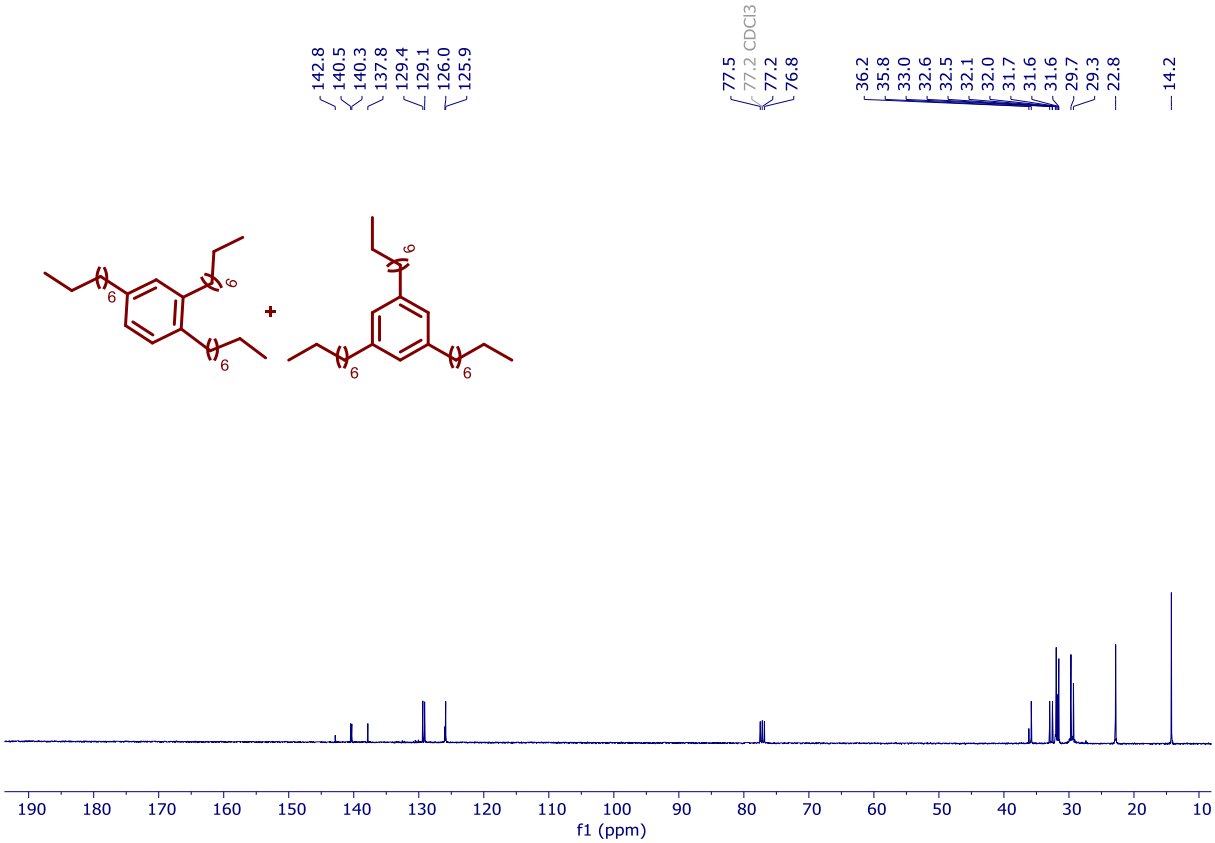
*^{1}H NMR spectrum of 1,2,4-trihexylbenzene (Compound **3n**) in $CDCl_3$*



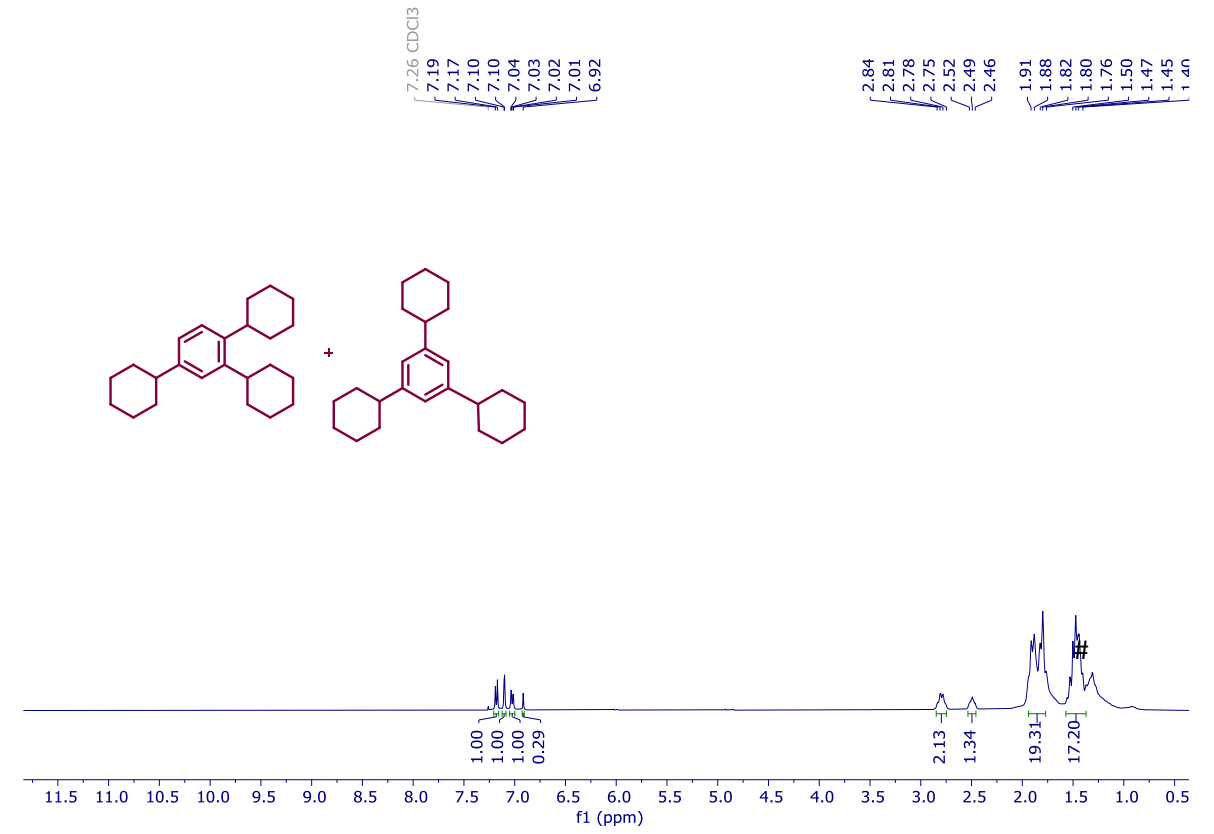
*$^{13}C\{^{1}H\}$ NMR spectrum of 1,2,4-trihexylbenzene (Compound **3n**) in $CDCl_3$*



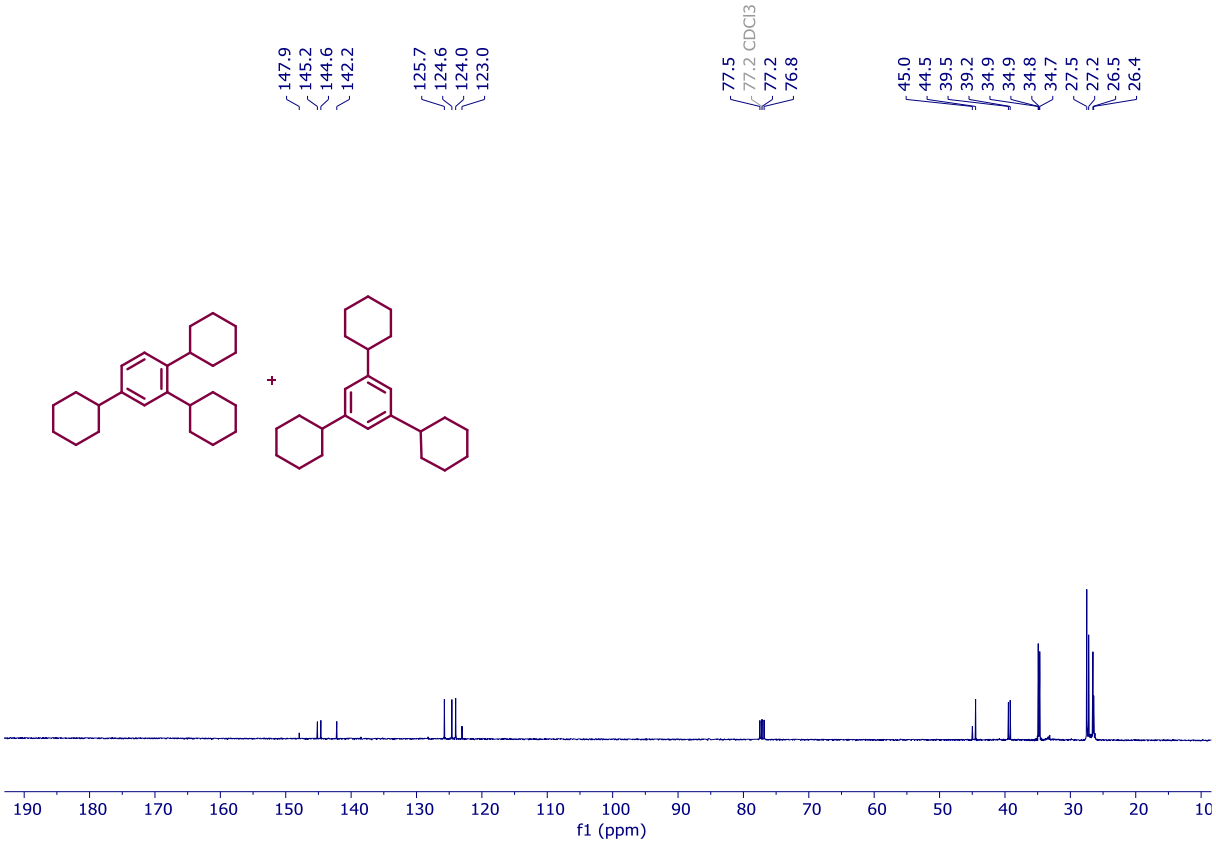
*^{1}H NMR spectrum of 1,2,4-trioctylbenzene (Compound **3o**) in $CDCl_3$*



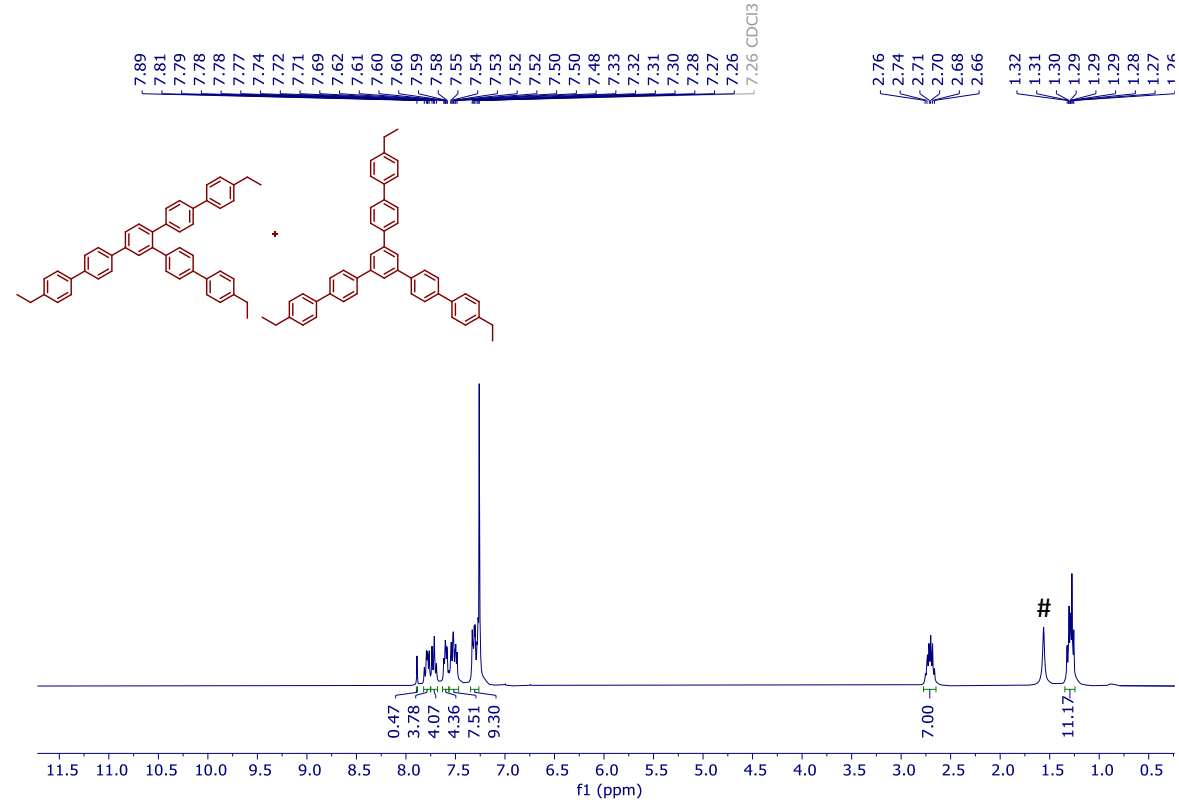
*$^{13}C\{^{1}H\}$ NMR spectrum of 1,2,4-trioctylbenzene (Compound **3o**) in $CDCl_3$*



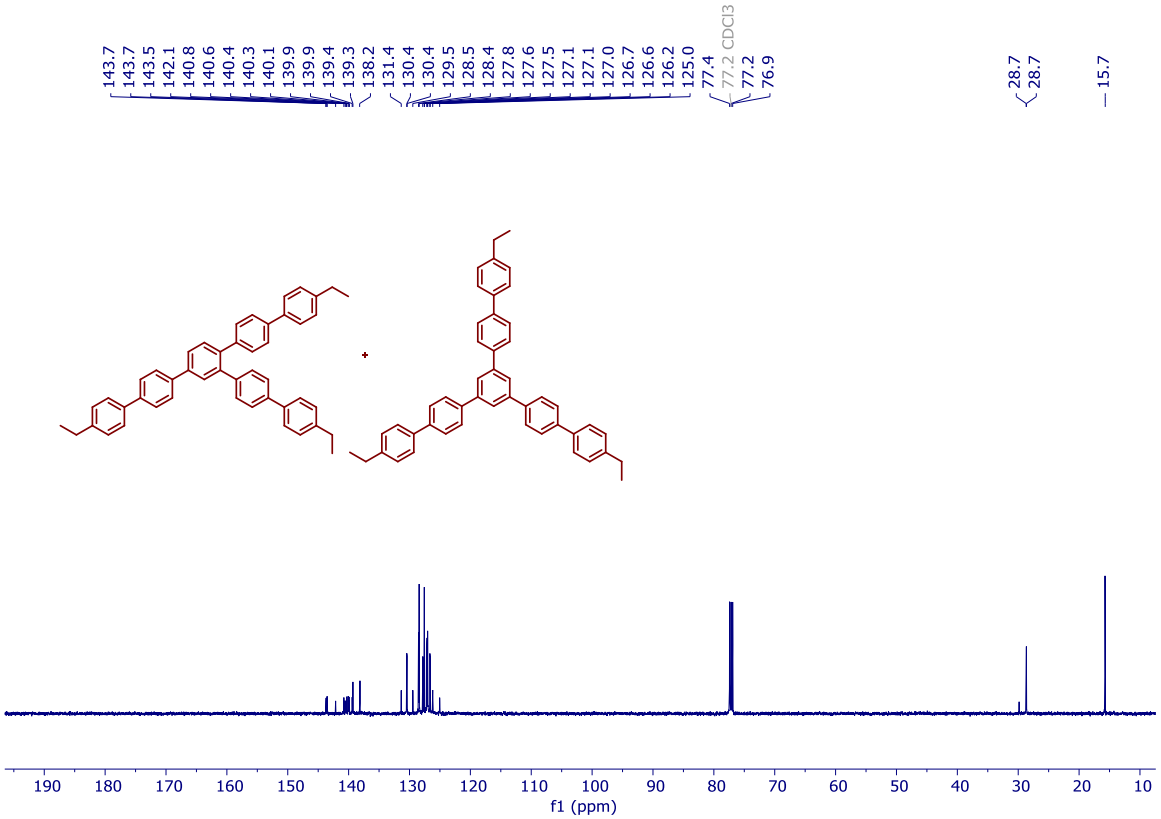
*^{1}H NMR spectrum of benzene-1,2,4-triyltricyclohexane (Compound **3p**) in $CDCl_3$. # corresponds to grease*



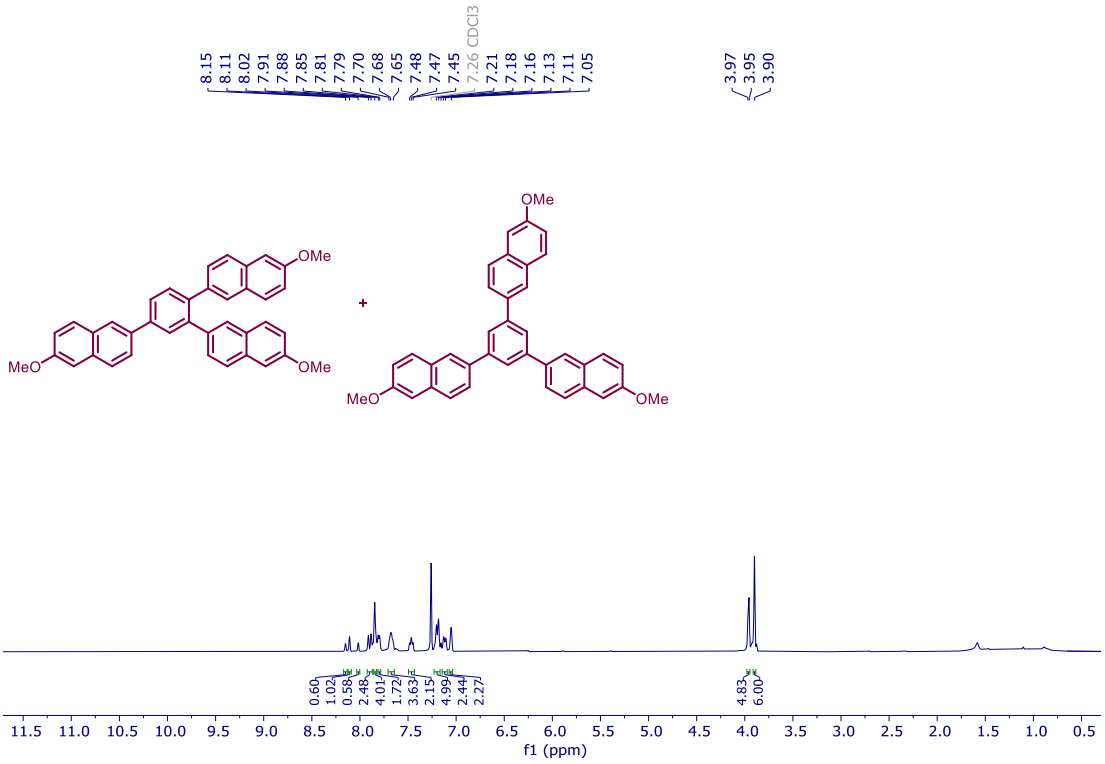
*$^{13}C\{^{1}H\}$ NMR spectrum of benzene-1,2,4-triyltricyclohexane (Compound **3p**) in $CDCl_3$*



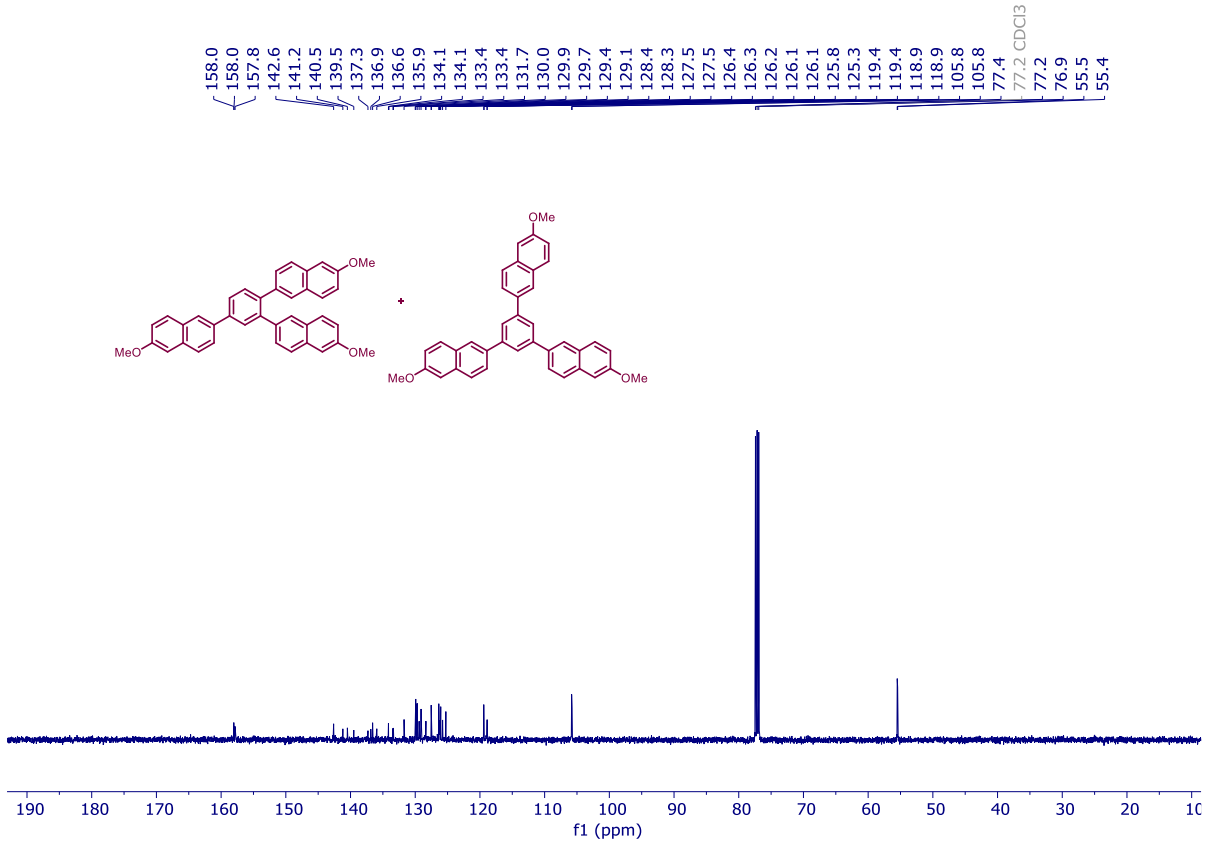
*^{1}H NMR of 4,4""-diethyl-4"-(4'-ethyl-[1,1'-biphenyl]-4-yl)-1,1':4',1":2",1"':4"',1""-quinquephenyl (Compound **3q**) in $CDCl_3$. # indicates the solvent impurity of H_2O in $CDCl_3$*



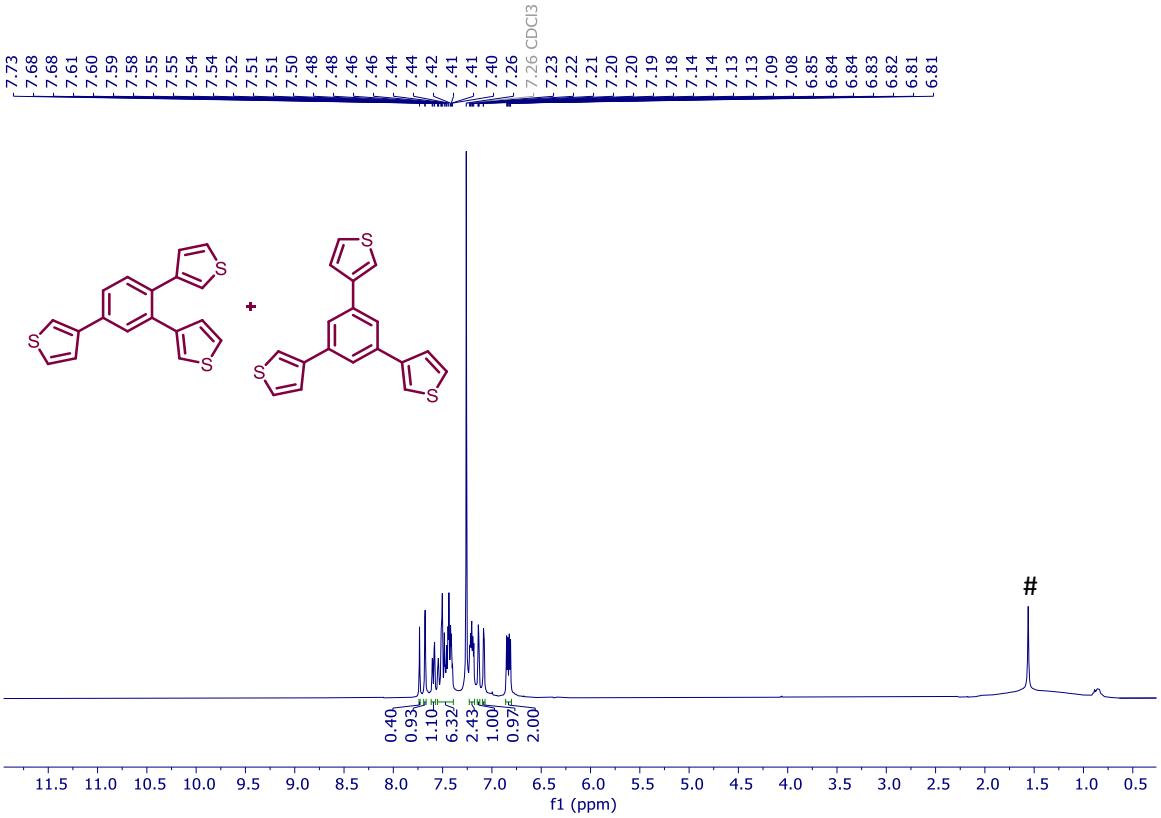
*$^{13}C\{^{1}H\}$ NMR of 4,4''''-diethyl-4''-(4'-ethyl-[1,1'-biphenyl]-4-yl)-1,1':4',1'':2'',1''':4''',1''''-quinquephenyl (Compound **3q**) in $CDCl_3$*



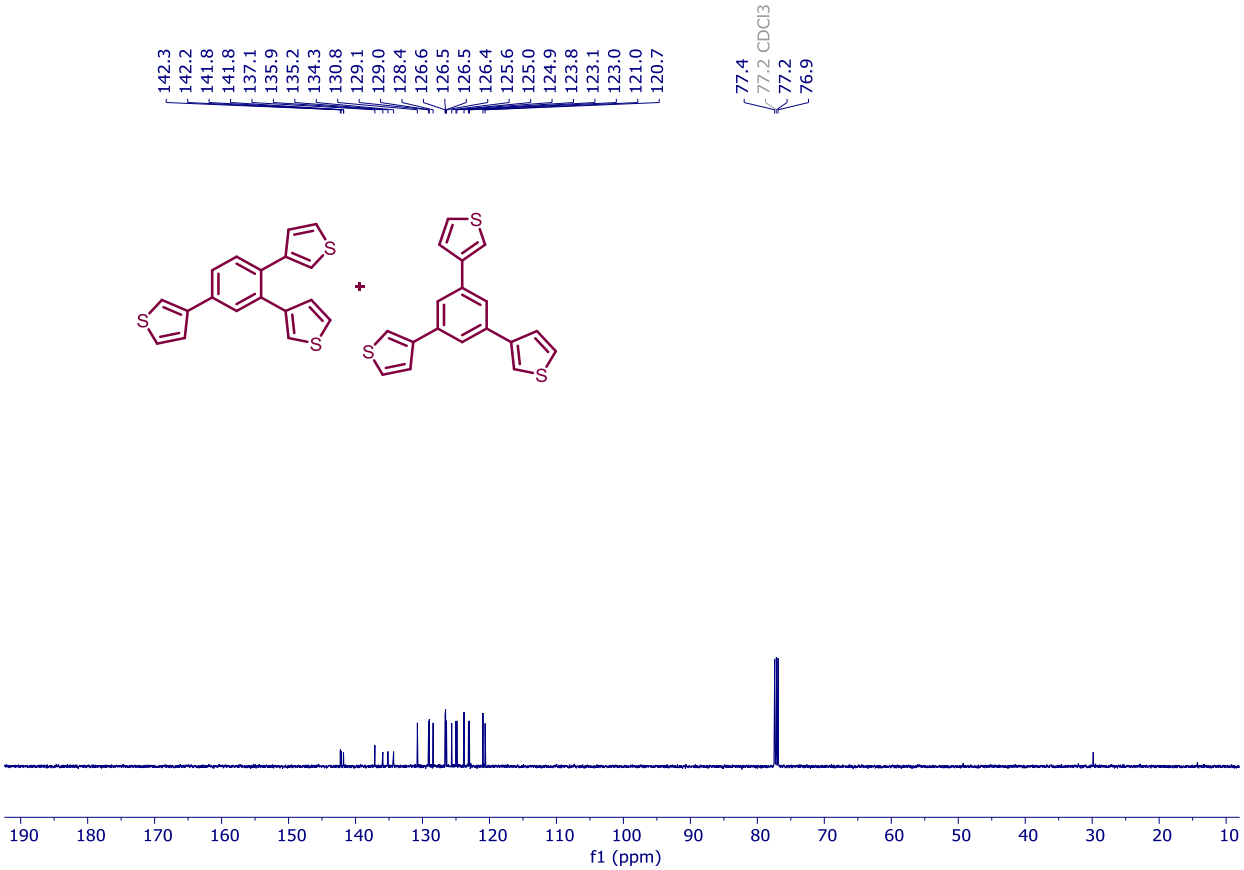
*^{1}H NMR of 6,6',6''-(benzene-1,2,4-triyl)tris(2-methoxynaphthalene) (Compound **3r**) in $CDCl_3$*



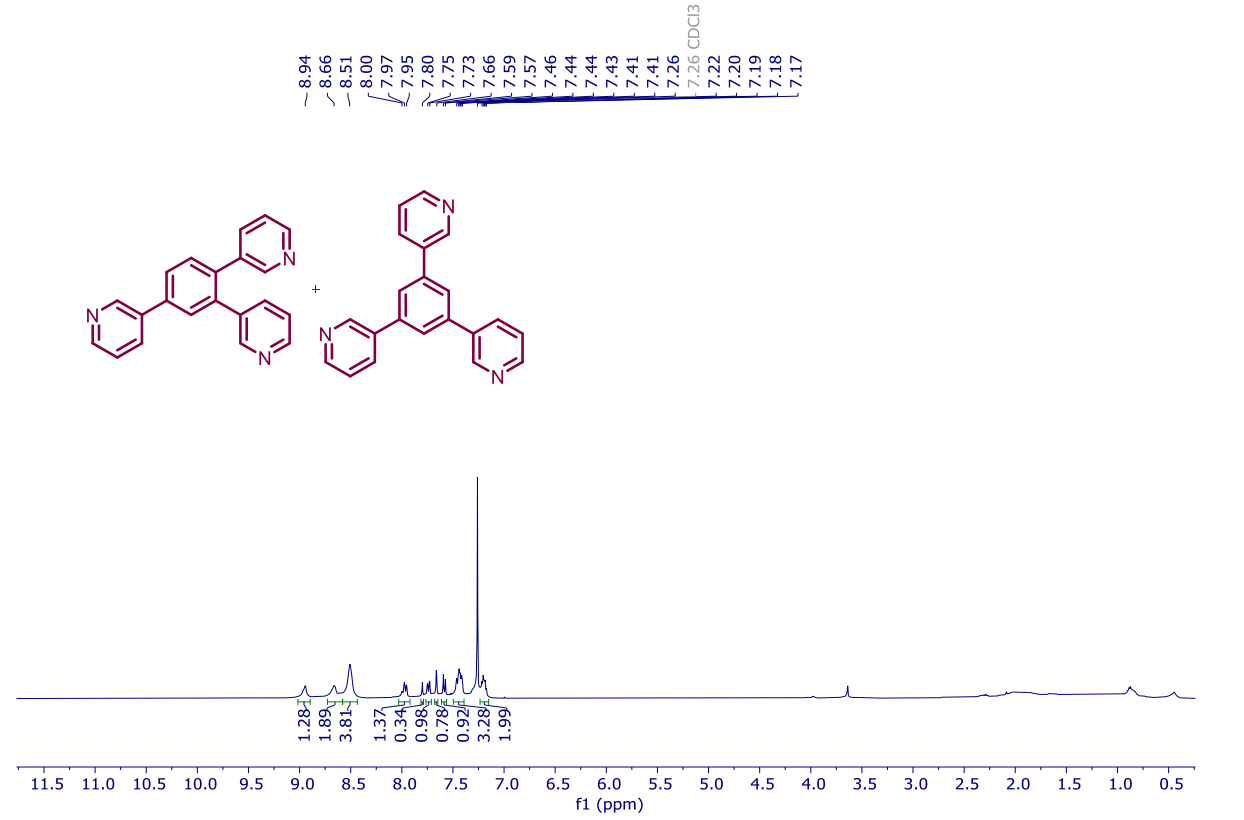
*$^{13}C\{^{1}H\}$ NMR of 6,6'-(2-(7-methoxynaphthalen-2-yl)-1,4-phenylene)bis(2-methoxynaphthalene) (Compound **3r**) in $CDCl_3$*



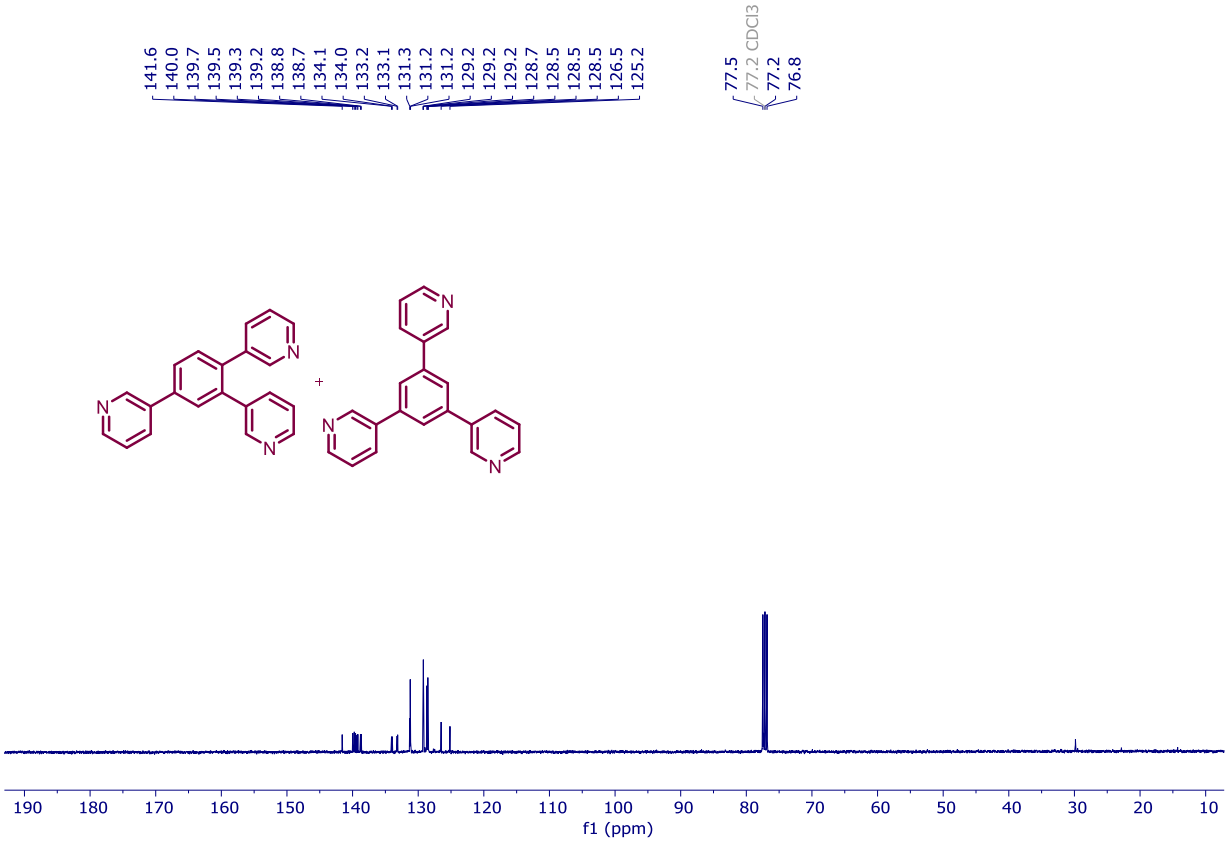
*^{1}H NMR of 3,3',3''-(benzene-1,2,4-triyl)trithiophene (Compound **3s**) in $CDCl_3$. # indicates the solvent impurity of H_2O in $CDCl_3$*



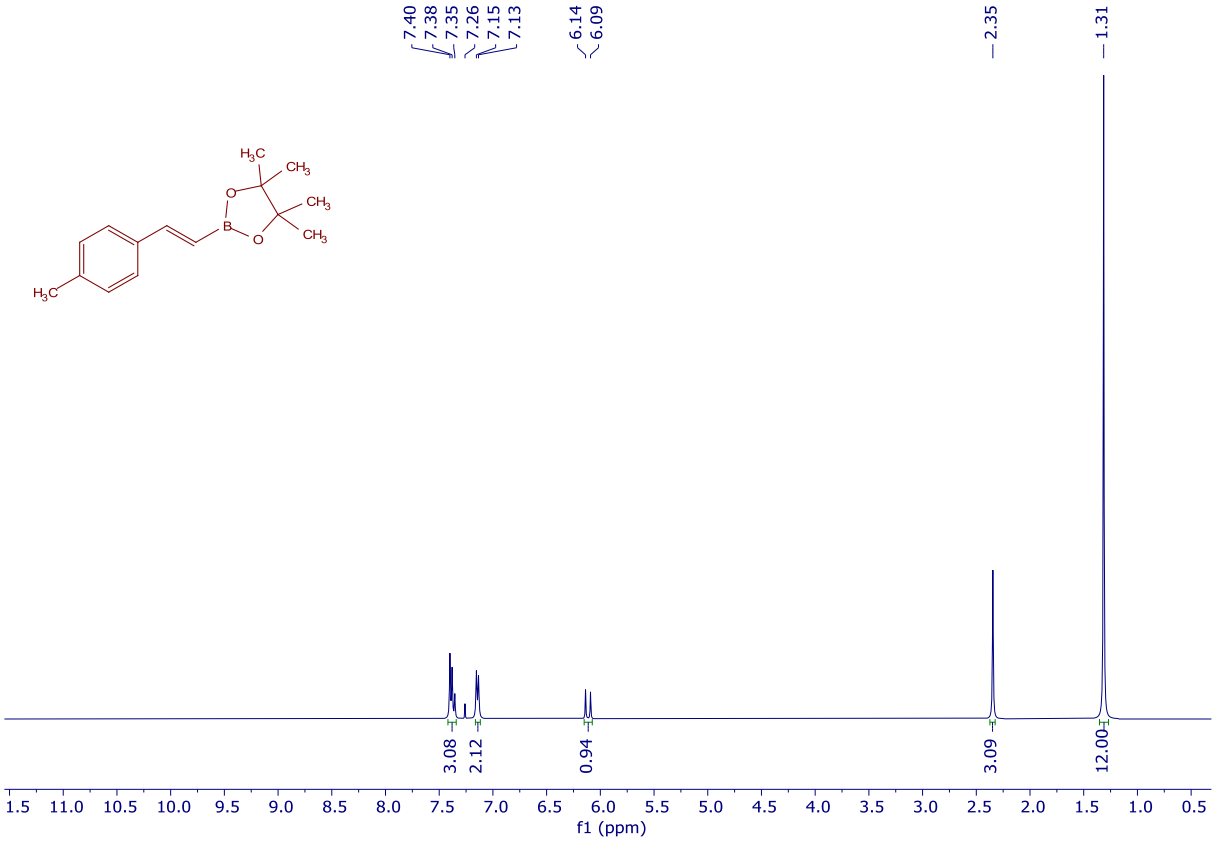
*$^{13}C\{^{1}H\}$ NMR of 3,3',3''-(benzene-1,2,4-triyl)trithiophene (Compound **3s**) in $CDCl_3$*



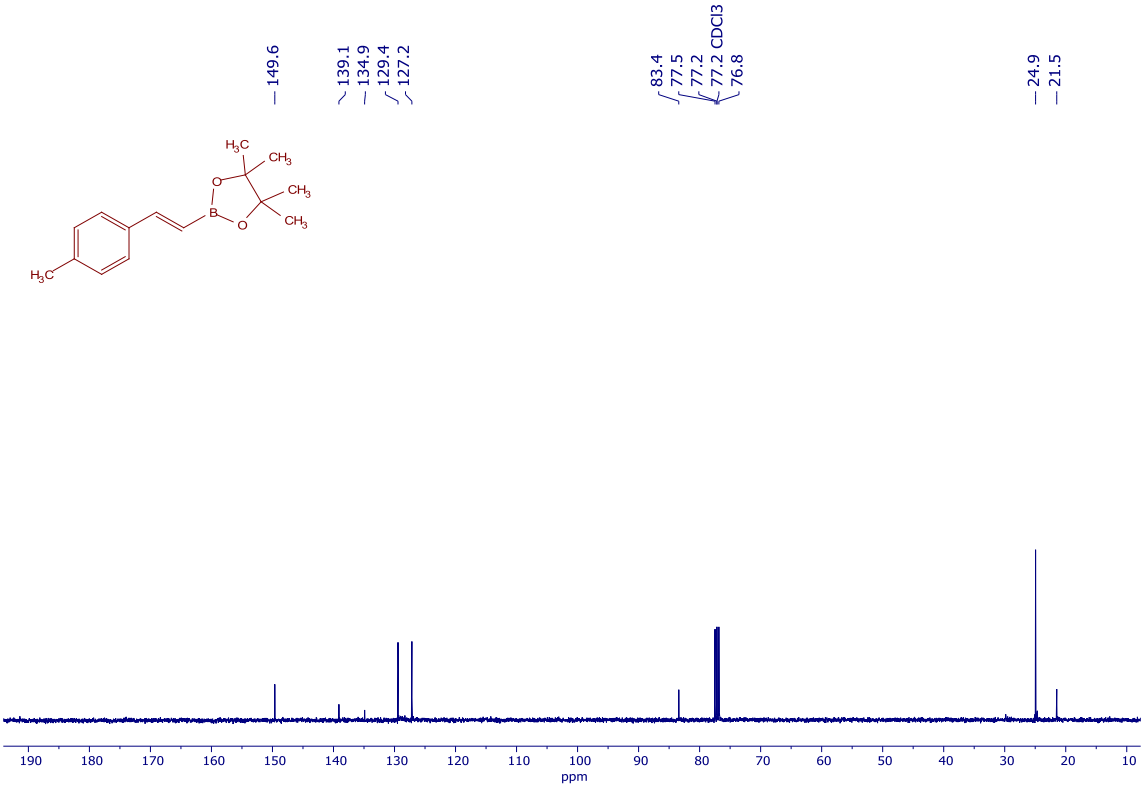
*^{1}H NMR of 3,3',3''-(benzene-1,2,4-triyl)tripyridine (Compound **3t**) in $CDCl_3$*



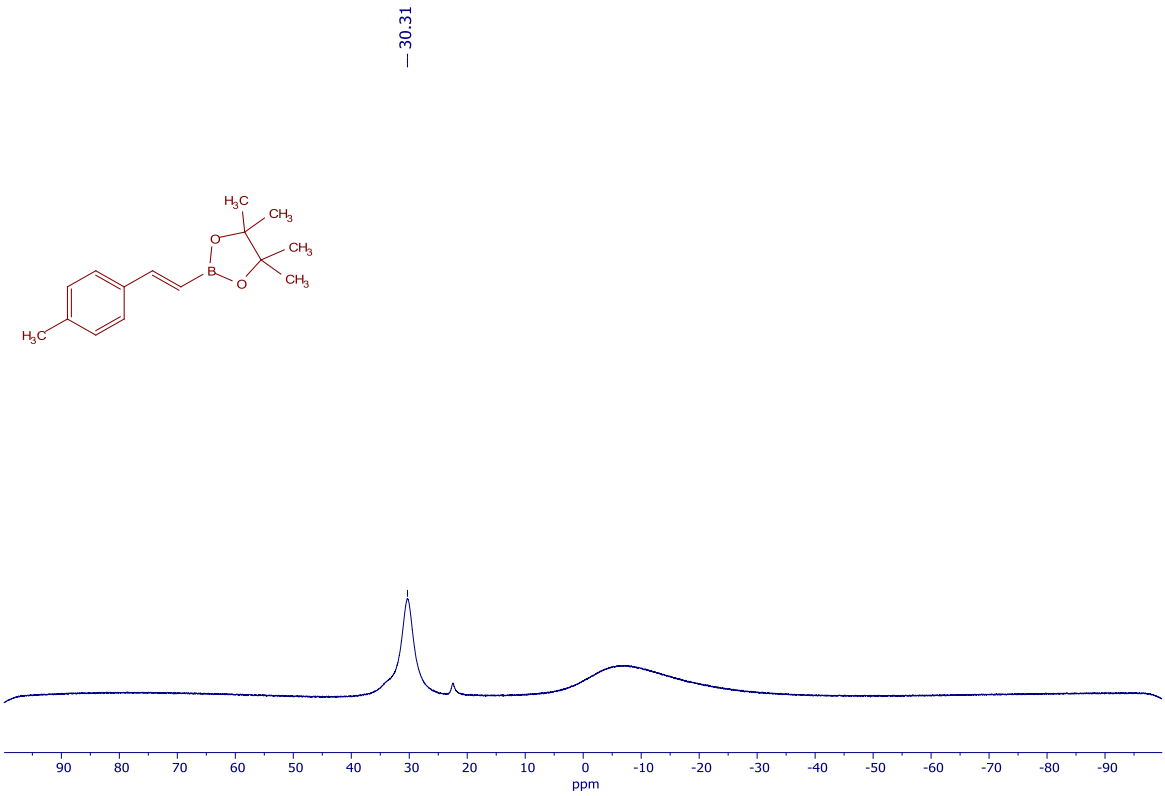
*$^{13}C\{^{1}H\}$ NMR of 3,3',3''-(benzene-1,2,4-triyl)tripyridine (Compound **3t**) in $CDCl_3$*



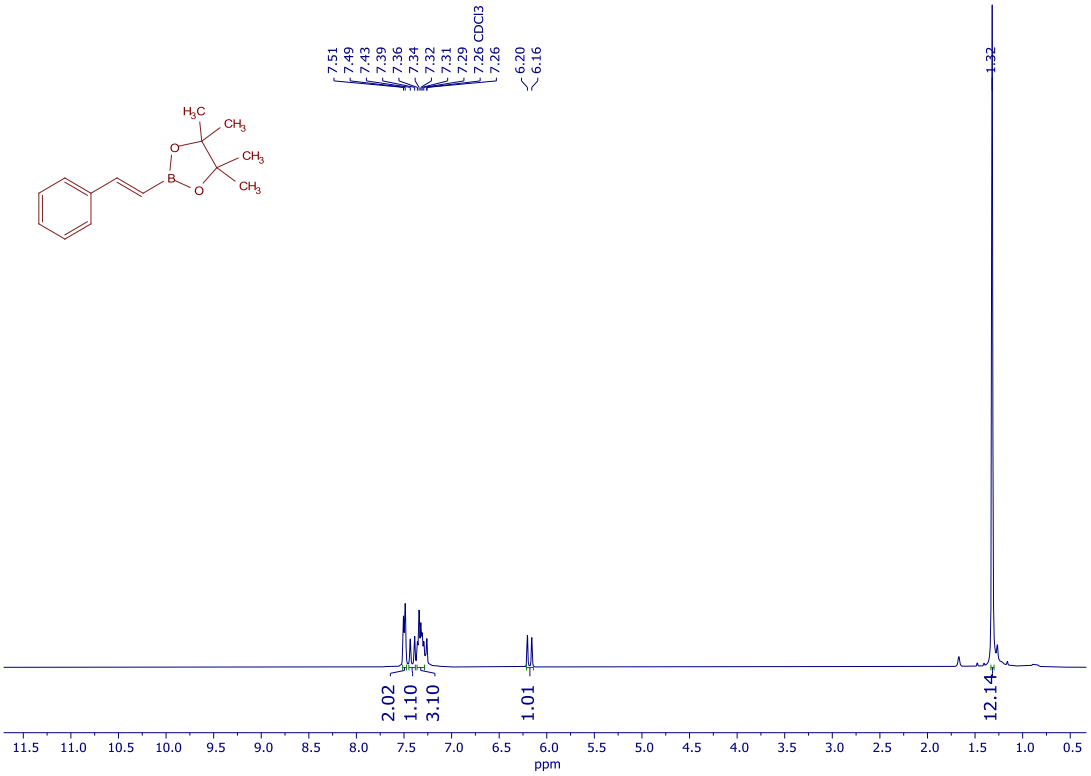
*^{1}H NMR of (E)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (Compound **4a**) in $CDCl_3$*



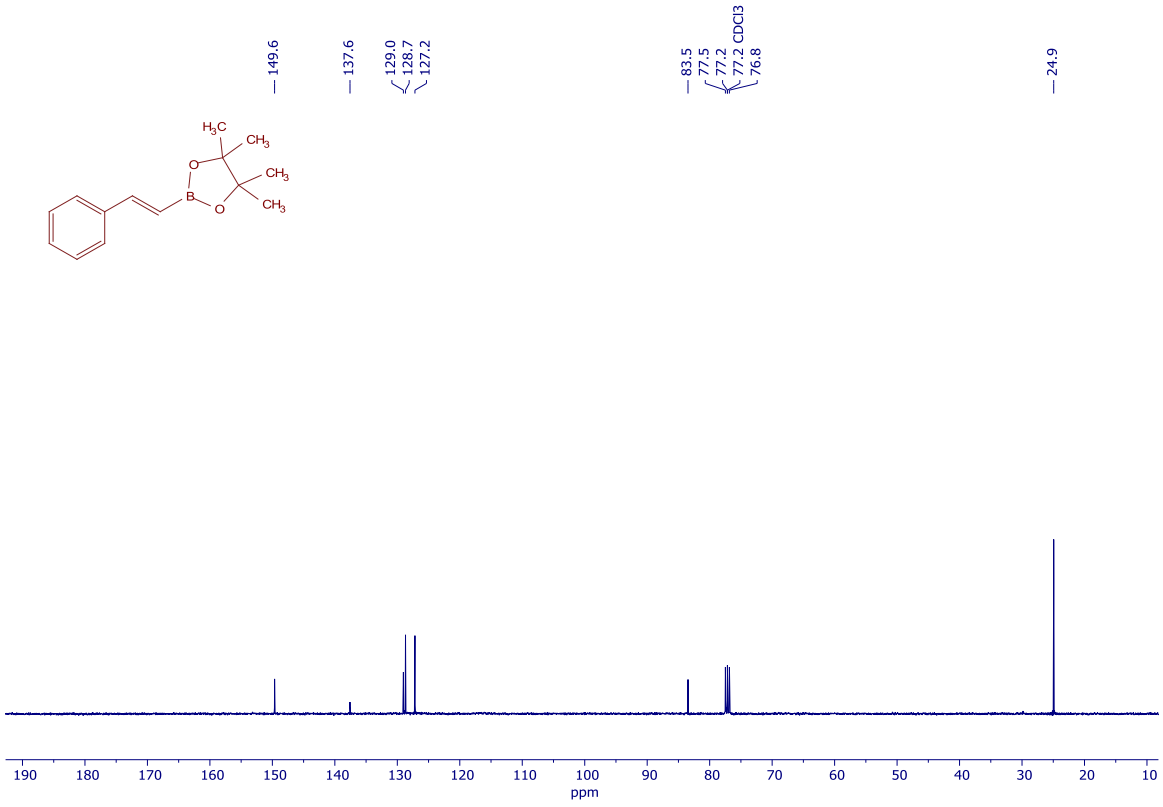
*$^{13}C\{^{1}H\}$ NMR of (E)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (Compound **4a**) in $CDCl_3$*



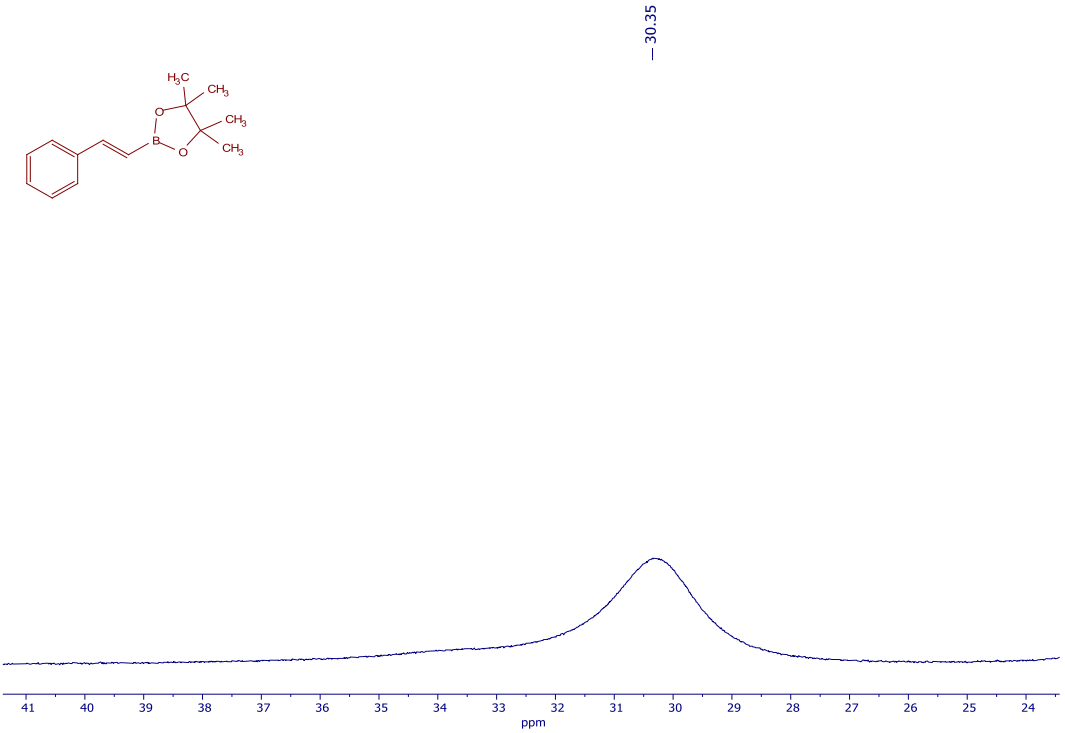
*^{11}B NMR of (E)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (Compound **4a**) in $CDCl_3$*



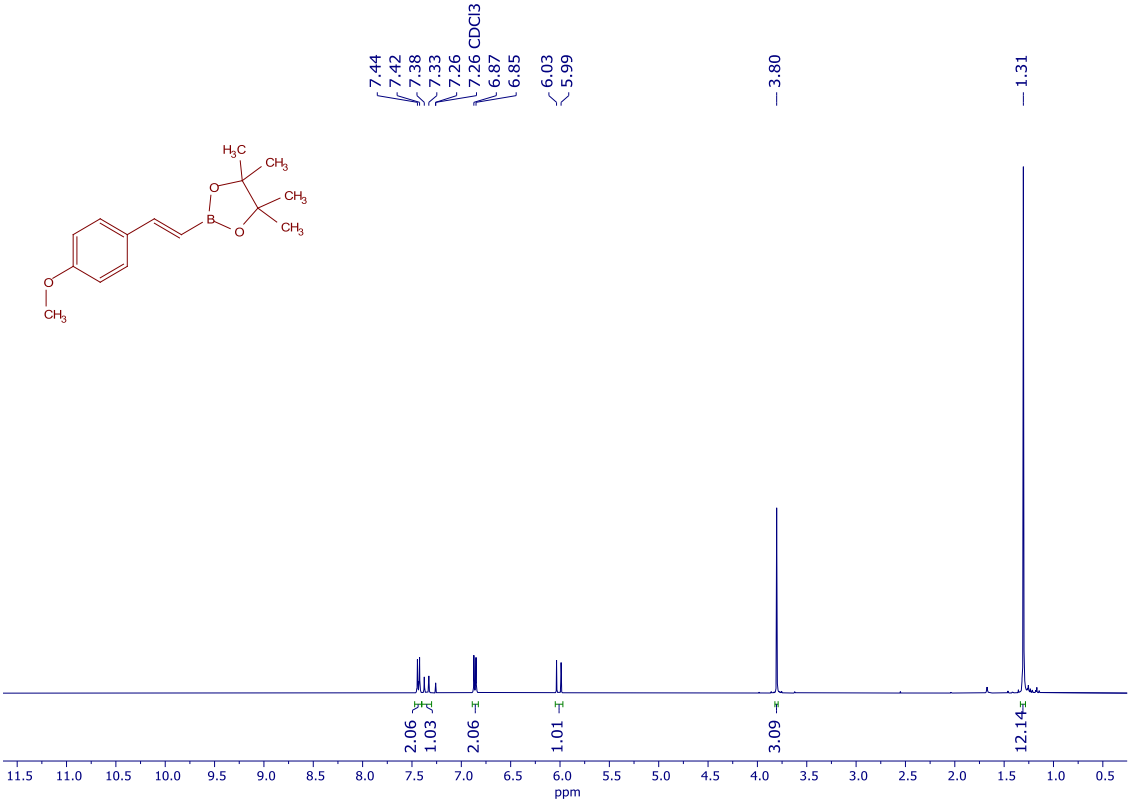
*[1]H NMR of (E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (Compound **4b**) in $CDCl_3$*



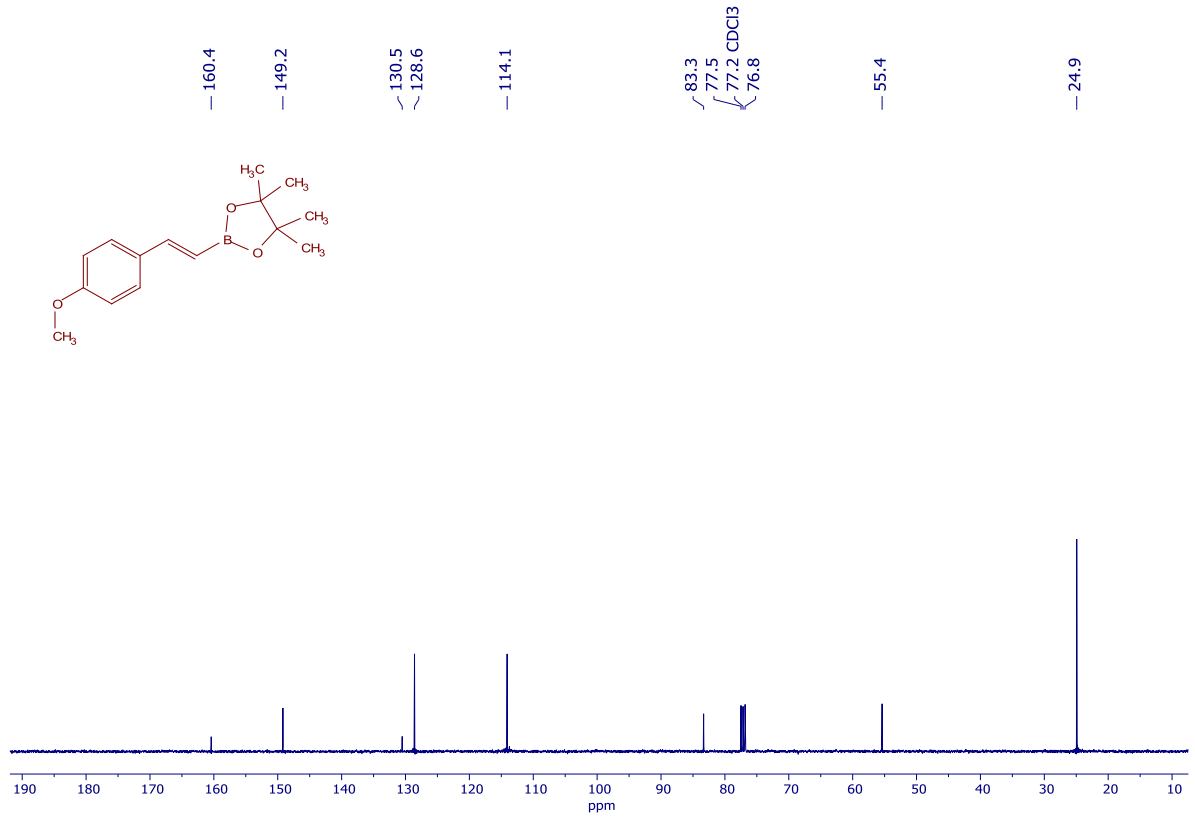
*[13]C{[1]H} NMR of (E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (Compound **4b**) in $CDCl_3$*



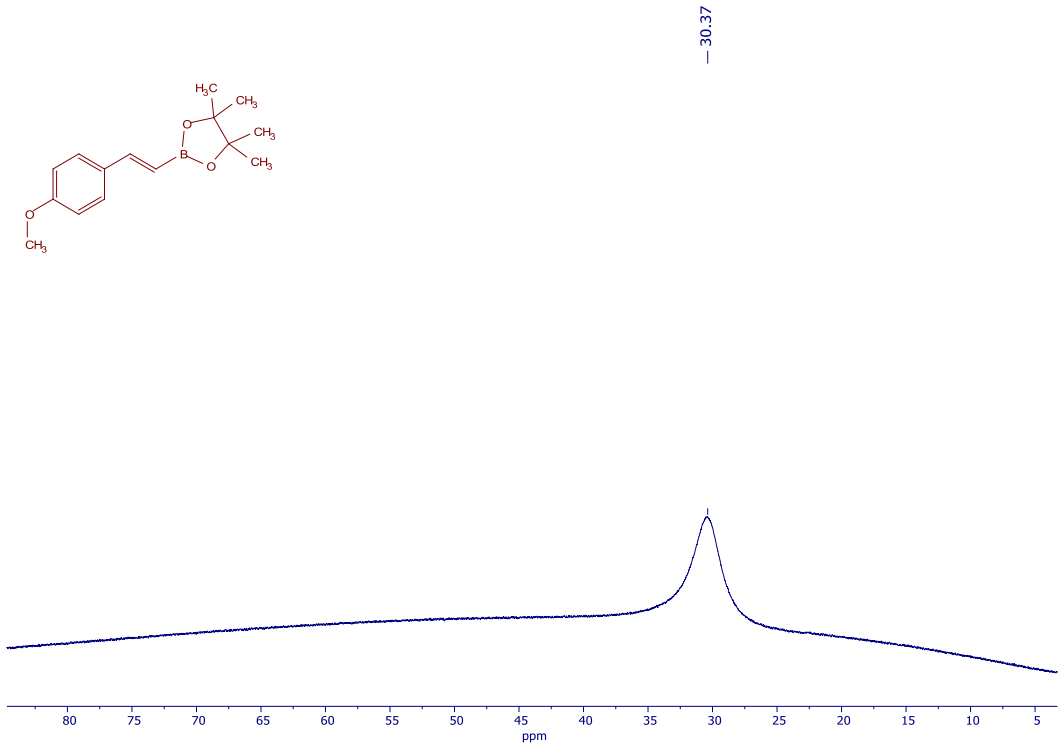
*[11]B NMR of (E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (Compound **4b**) in $CDCl_3$*



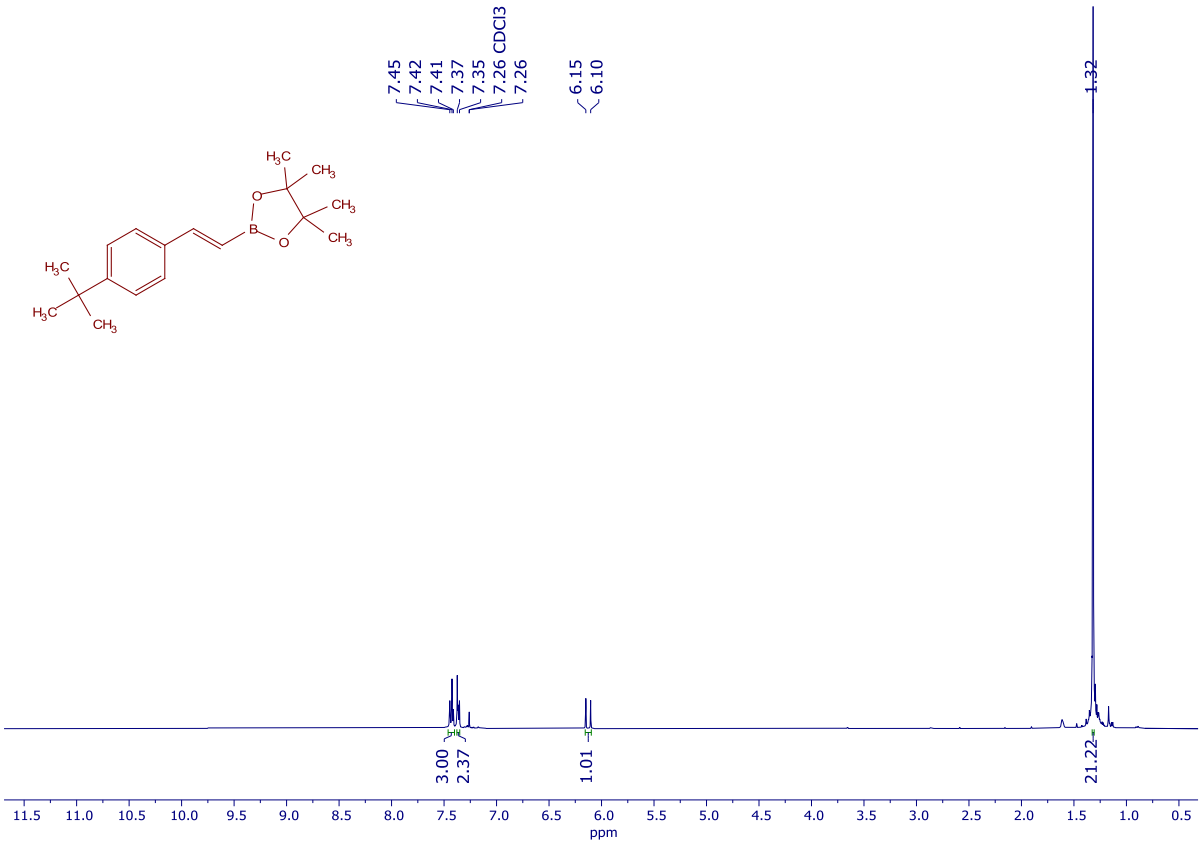
*[1]H NMR (E)-2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound **4c**) in $CDCl_3$*



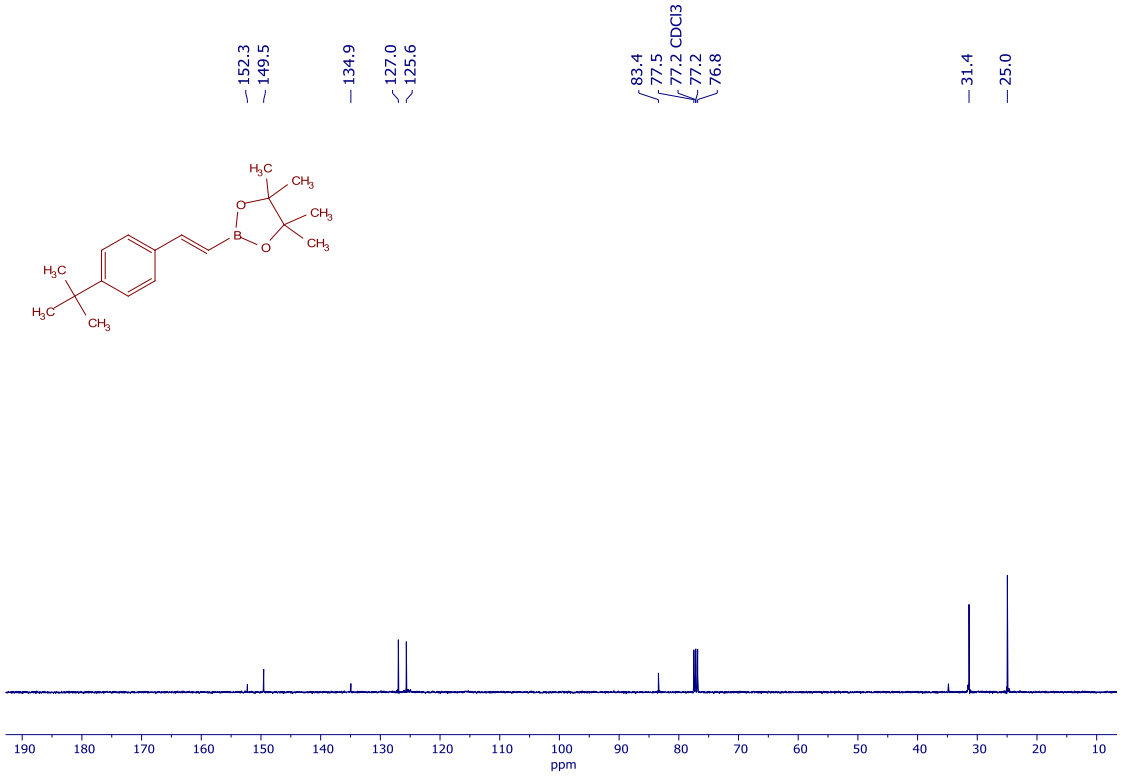
*$^{13}C\{^{1}H\}$ NMR of (E)-2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound **4c**) in $CDCl_3$*



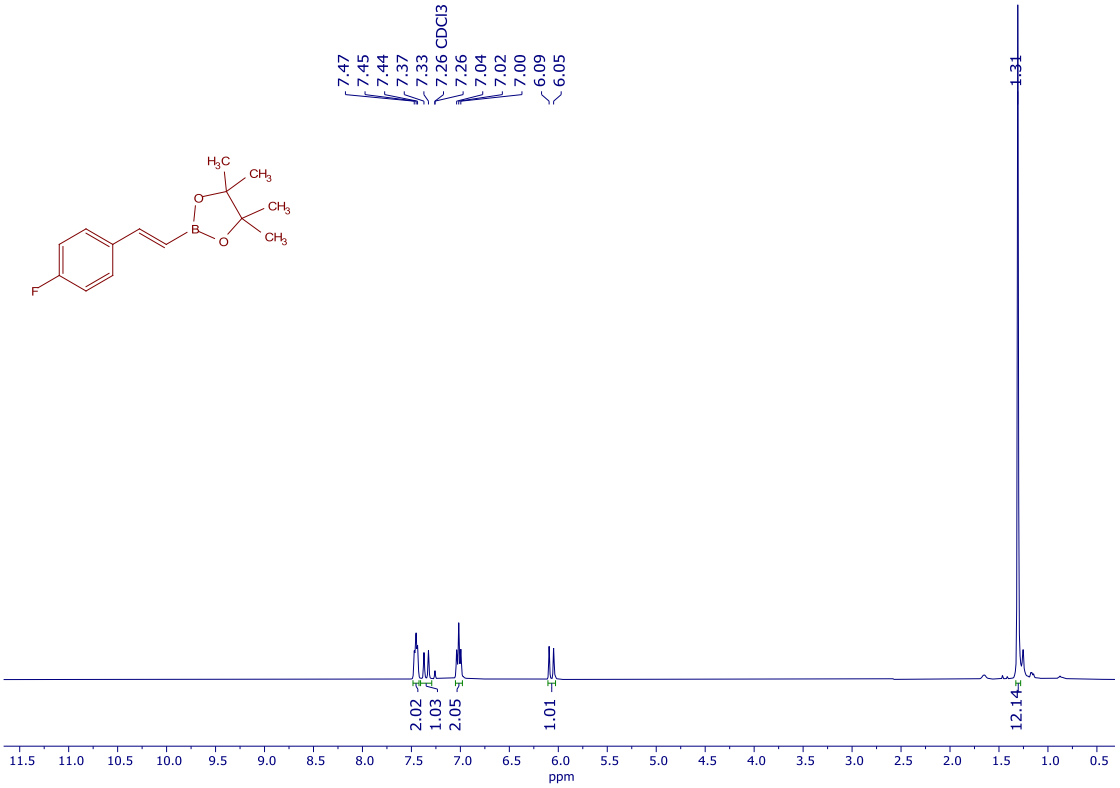
*^{11}B NMR of (E)-2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound **4c**) in $CDCl_3$*



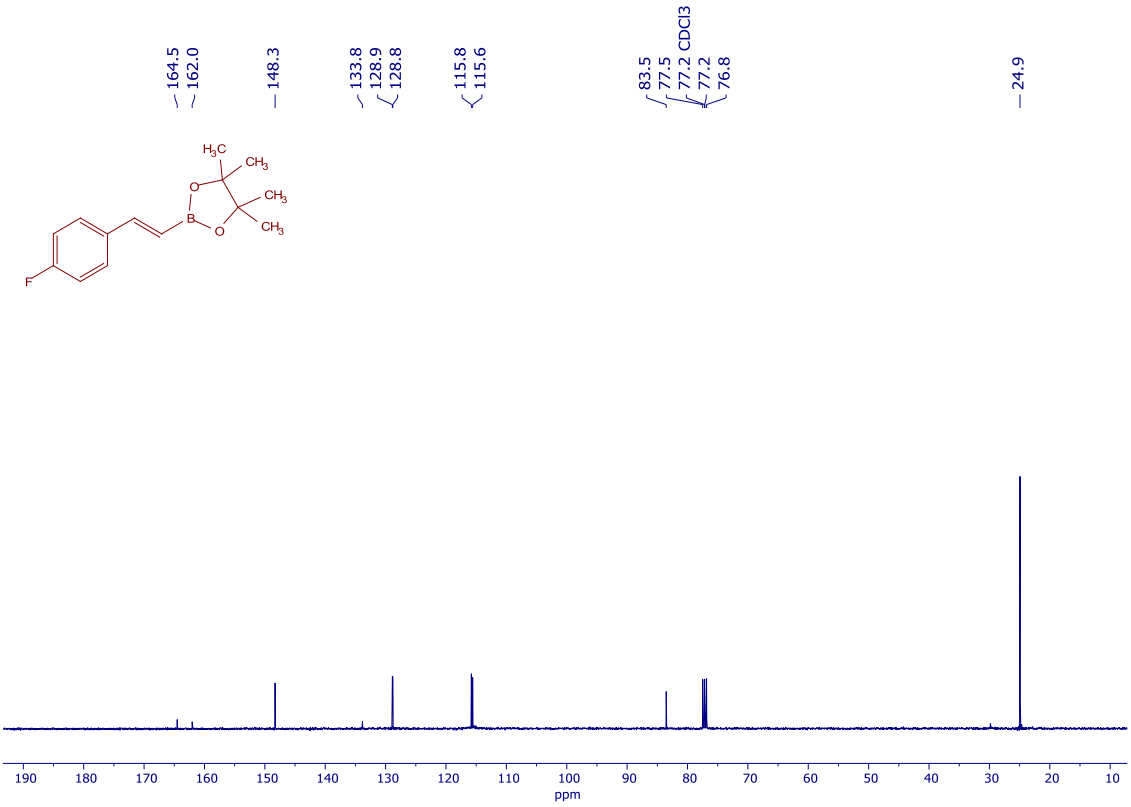
*^{1}H NMR of (E)-2-(4-(tert-butyl)styryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound **4d**) in $CDCl_3$*



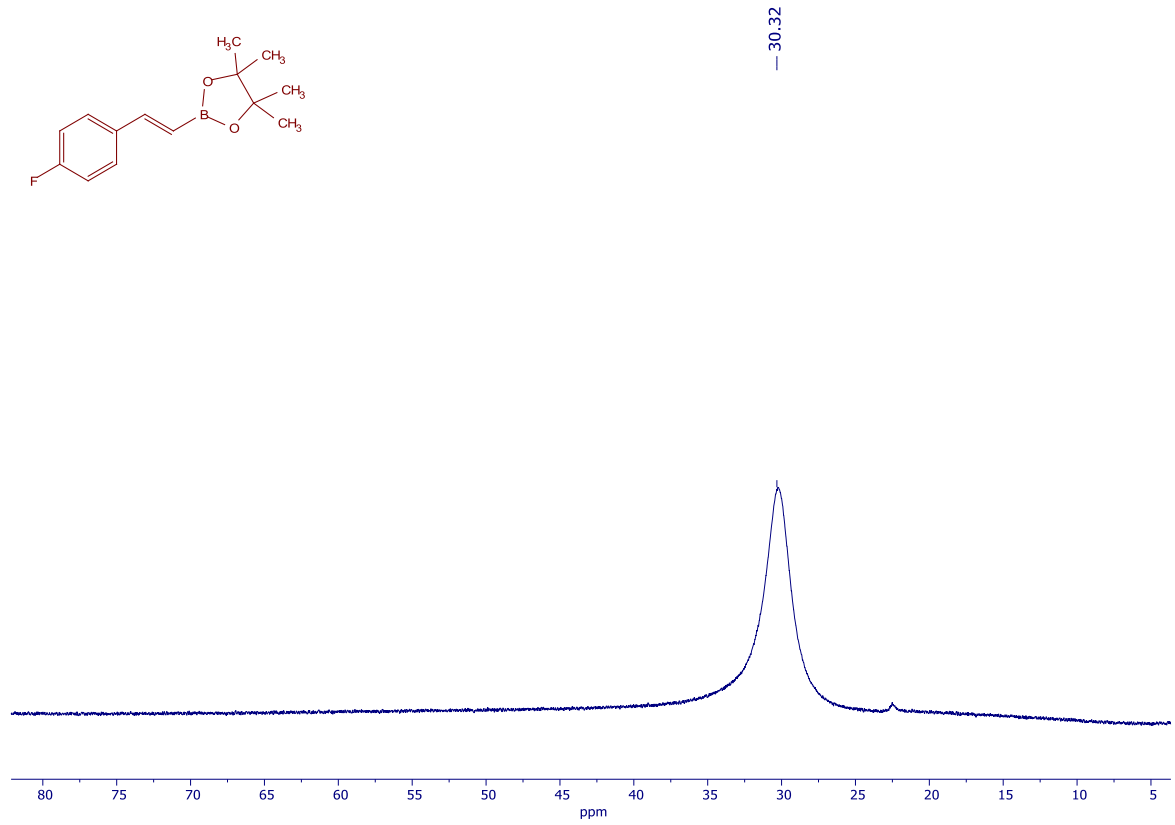
*$^{13}C\{^{1}H\}$ NMR of (E)-2-(4-(tert-butyl)styryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound **4d**) in $CDCl_3$*



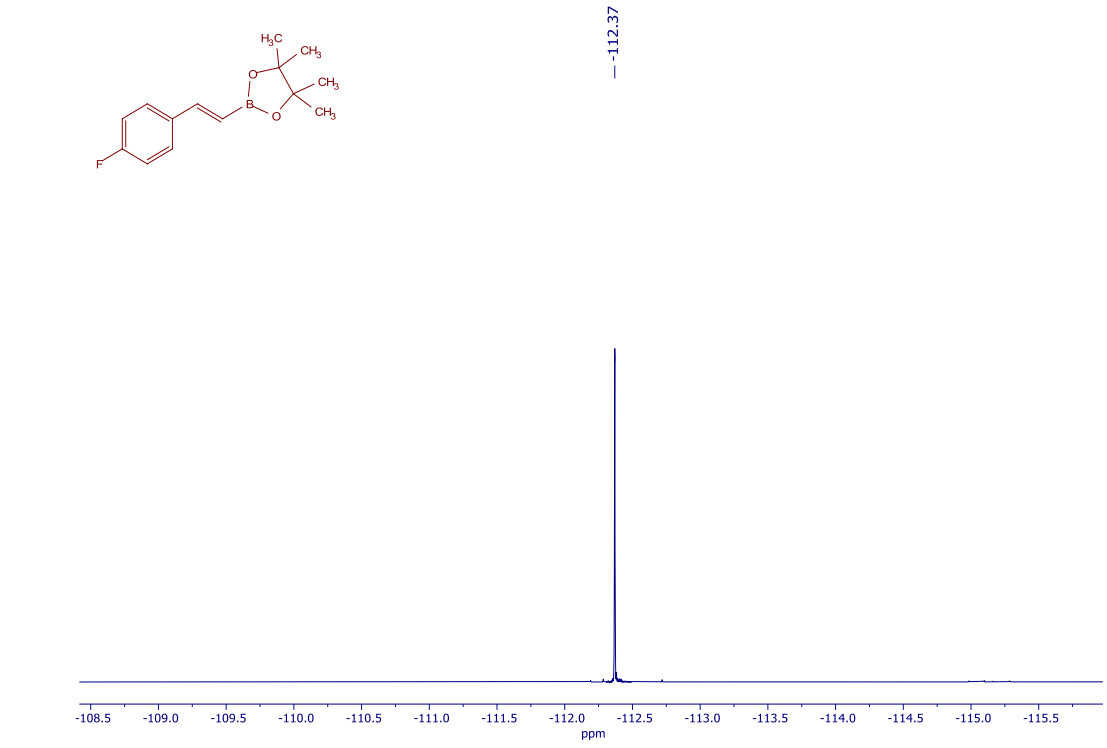
*[1]H NMR of (E)-2-(4-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound **4e**) in $CDCl_3$*



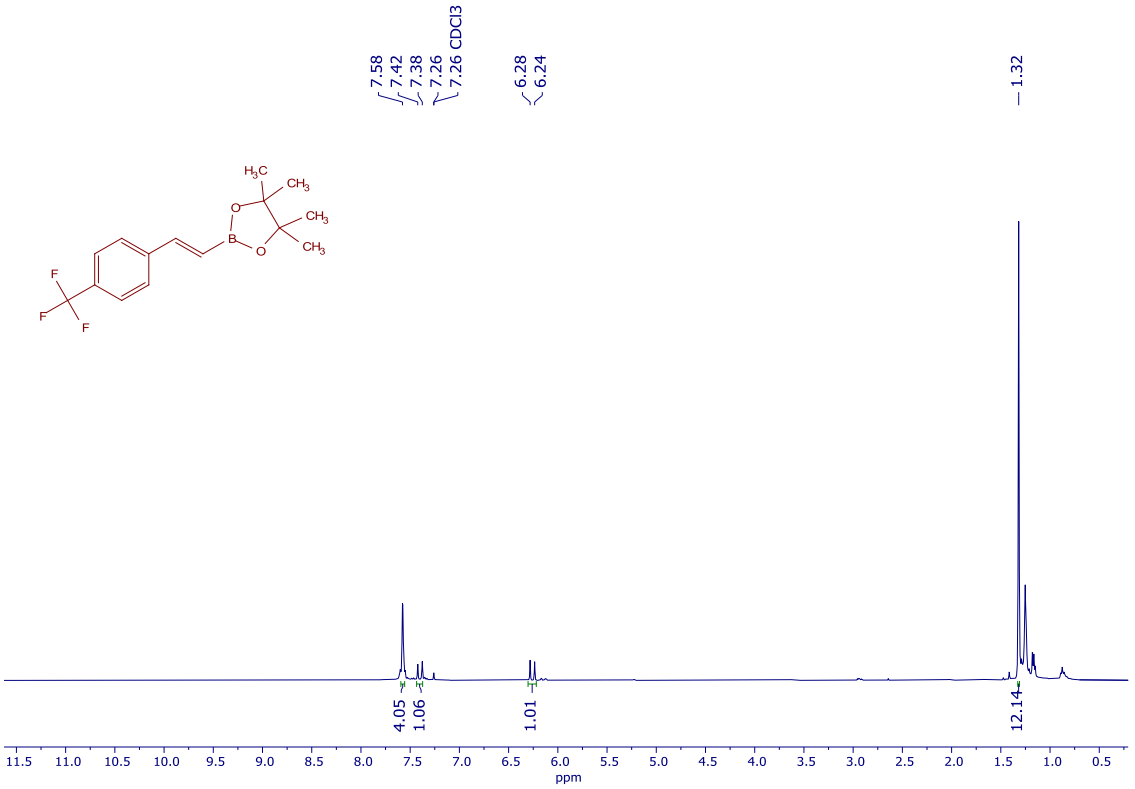
*[13]C{[1]H} NMR of ((E)-2-(4-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound **4e**) in $CDCl_3$*



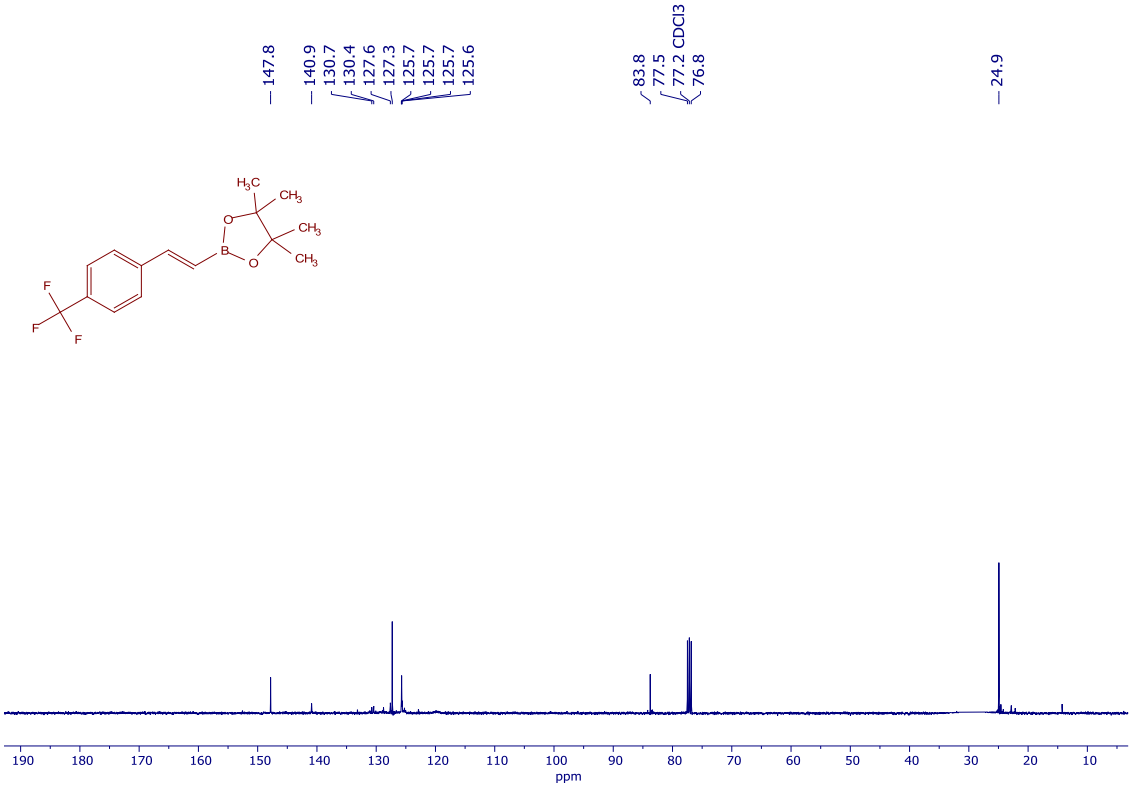
*^{11}B NMR of (E)-2-(4-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound **4e**) in $CDCl_3$*



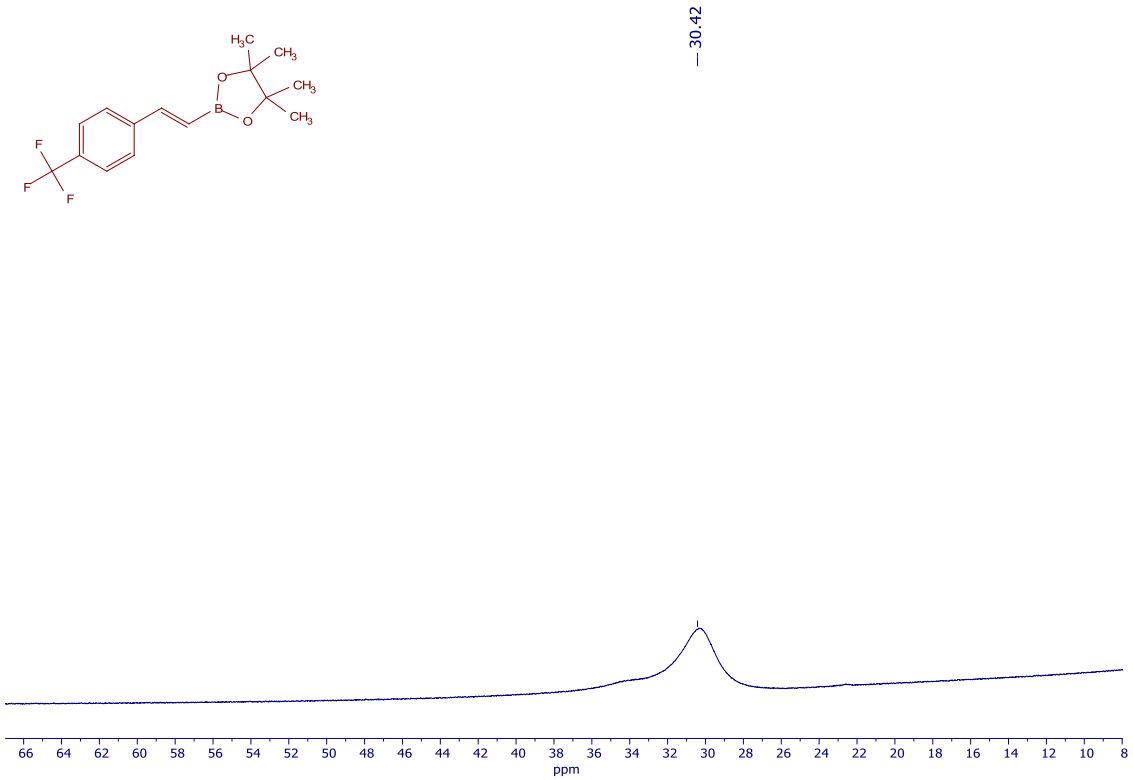
*^{19}F NMR of (E)-2-(4-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound **4e**) in $CDCl_3$*



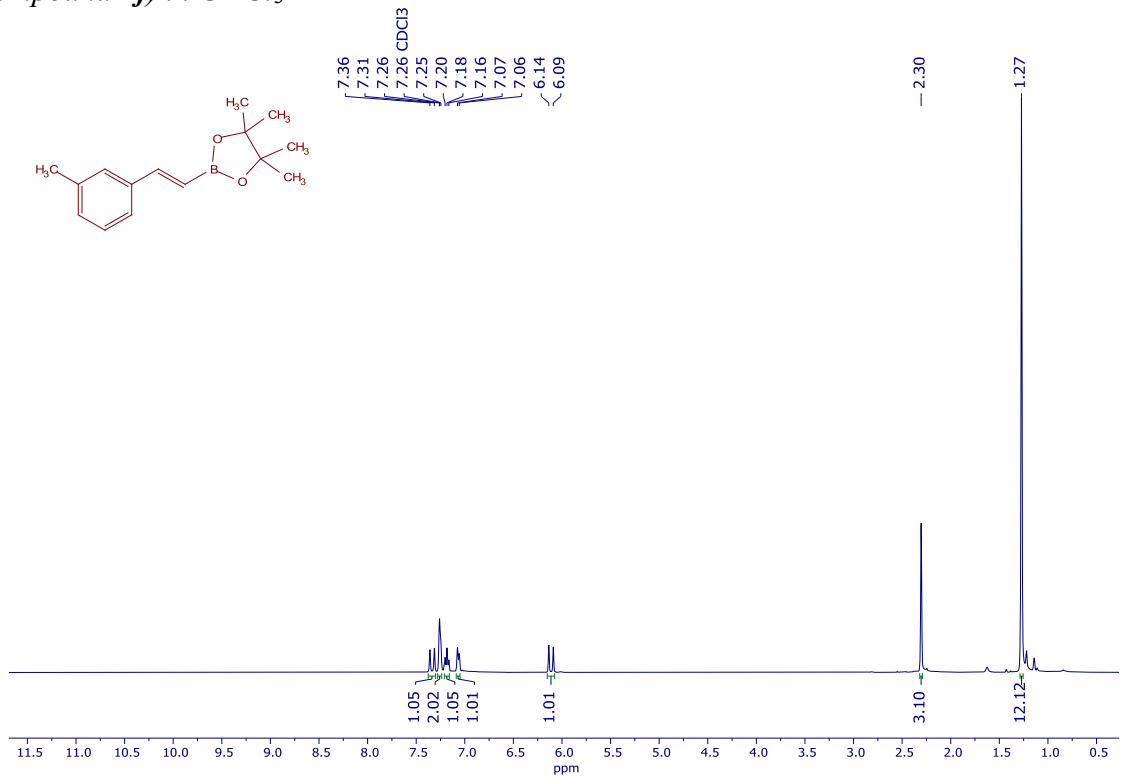
*^{1}H NMR of (E)-4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (Compound **4f**) in $CDCl_3$*



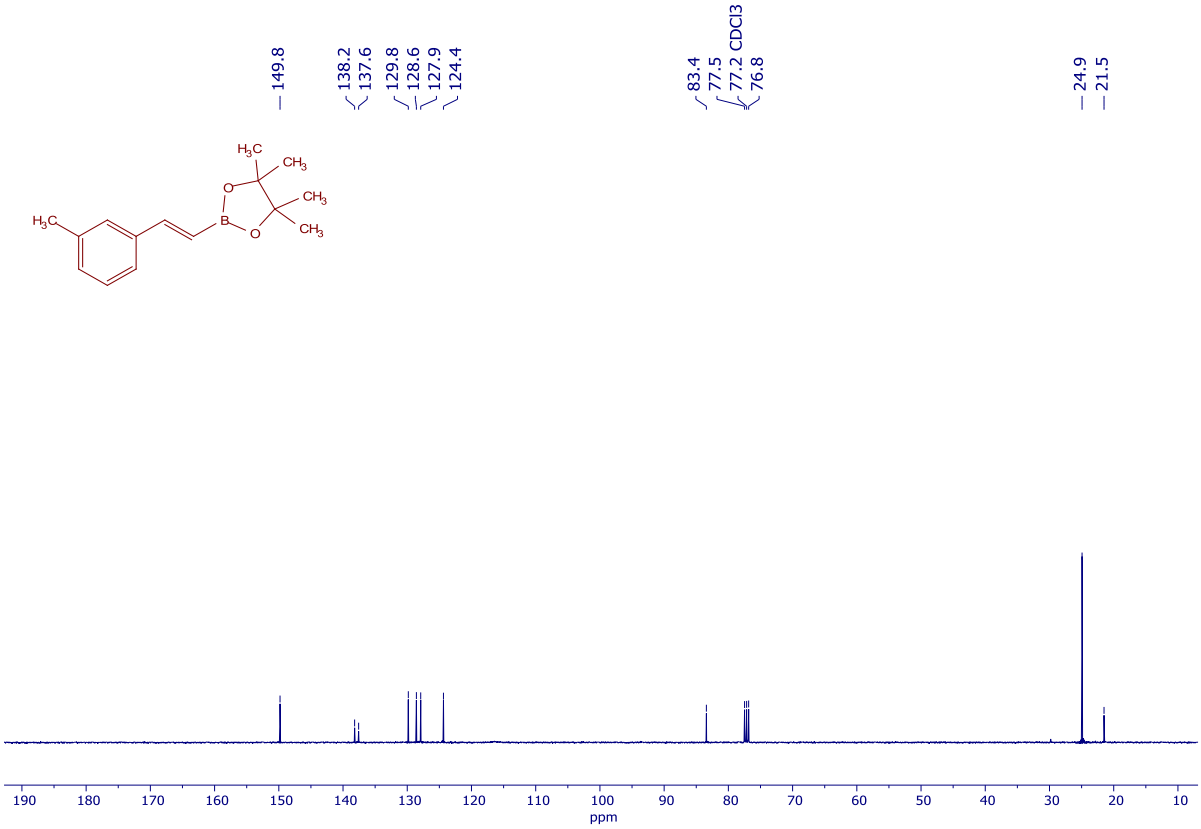
*$^{13}C\{^{1}H\}$ NMR of (E)-4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (Compound **4f**) in $CDCl_3$*



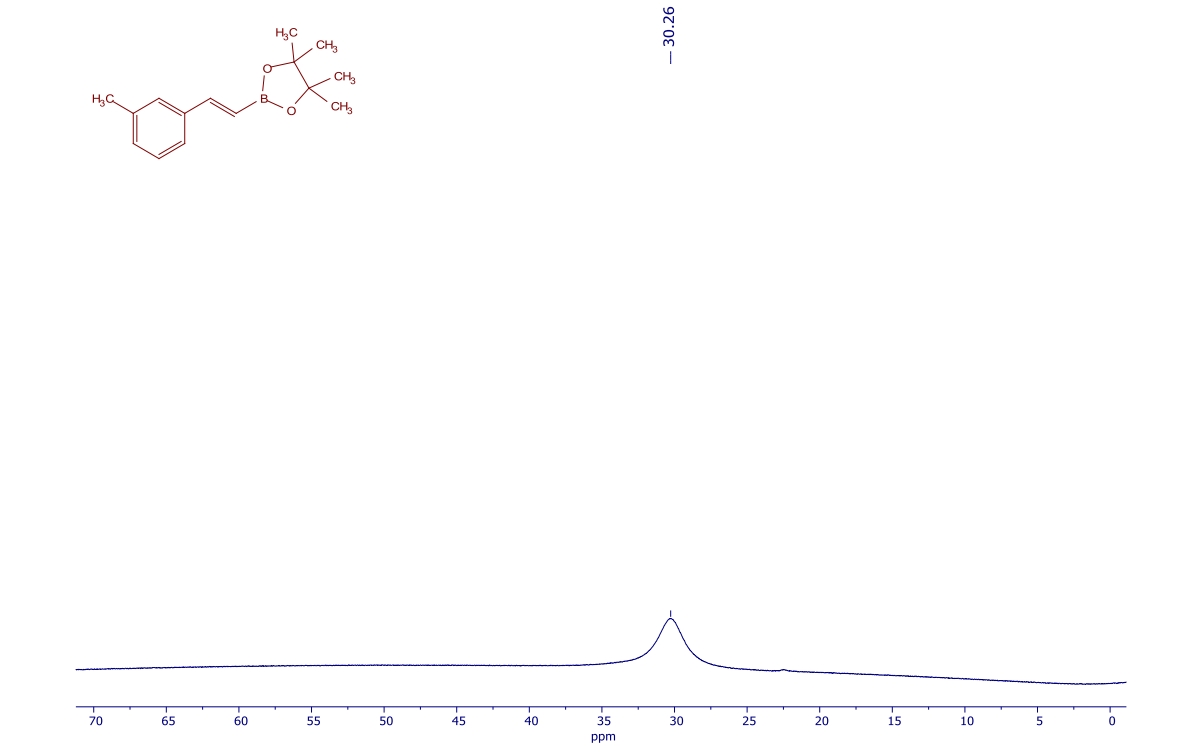
*^{11}B NMR of (E)-4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (Compound **4f**) in $CDCl_3$*



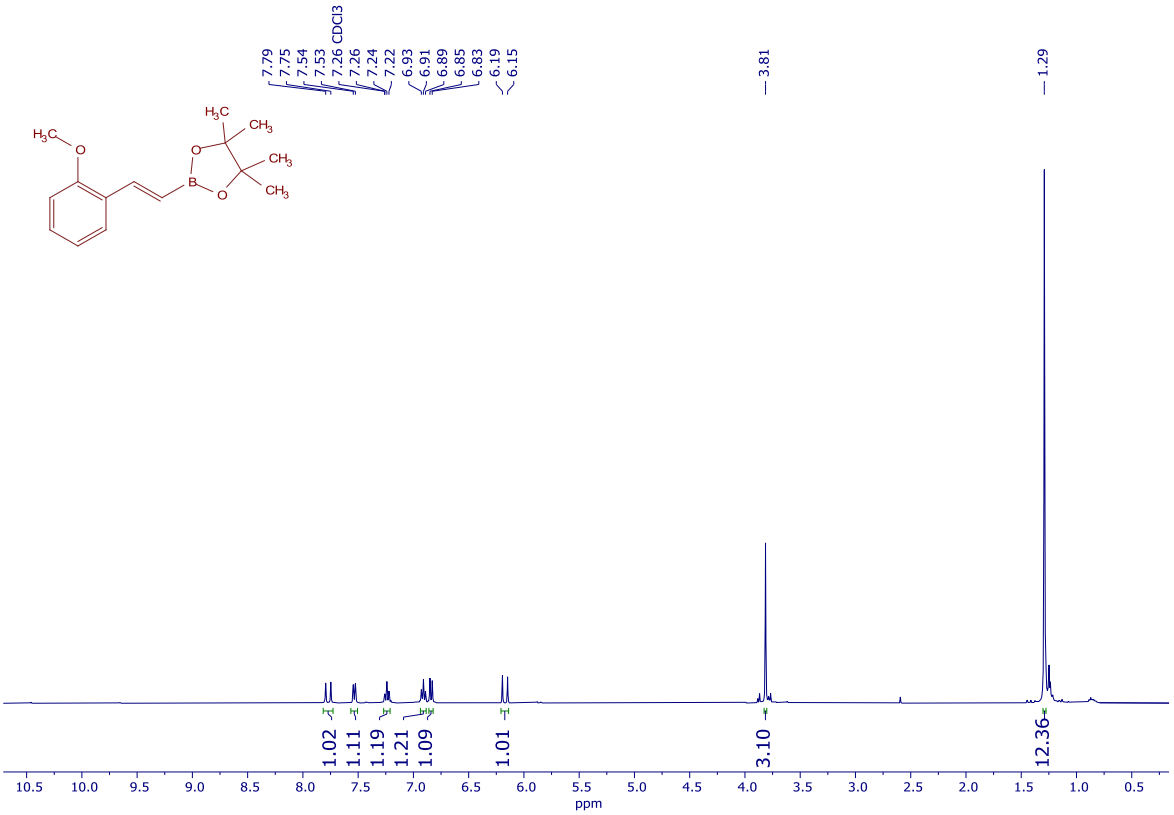
*^{1}H NMR of (E)-4,4,5,5-tetramethyl-2-(3-methylstyryl)-1,3,2-dioxaborolane (Compound **4g**) in $CDCl_3$*



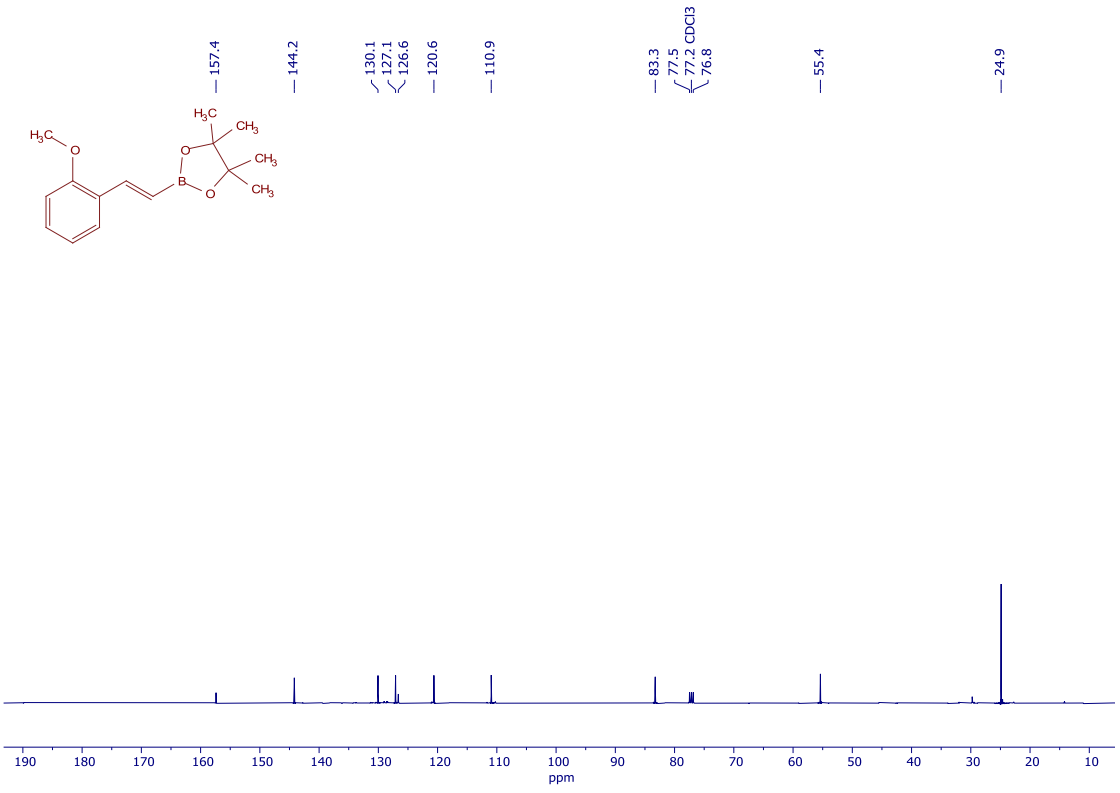
*$^{13}C\{^{1}H\}$ NMR of (E)-4,4,5,5-tetramethyl-2-(3-methylstyryl)-1,3,2-dioxaborolane (Compound **4g**) in $CDCl_3$*



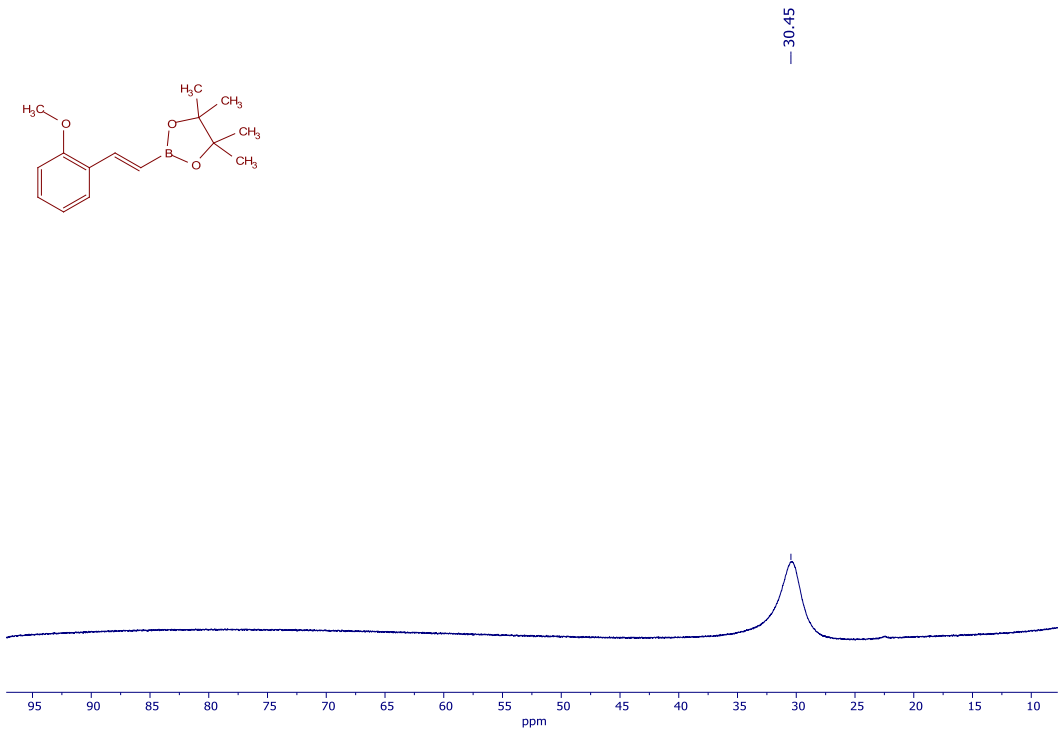
*^{11}B NMR of ((E)-4,4,5,5-tetramethyl-2-(3-methylstyryl)-1,3,2-dioxaborolane (Compound **4g**) in $CDCl_3$*



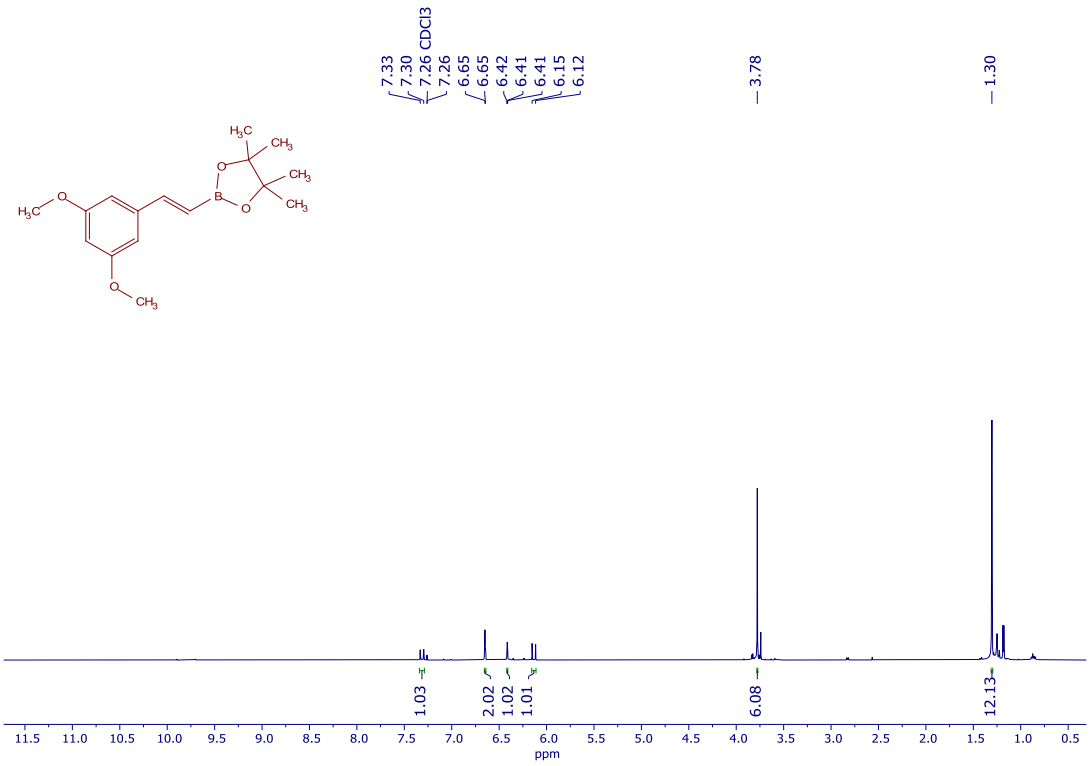
*^{1}H NMR of (E)-2-(2-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound **4h**) in $CDCl_3$*



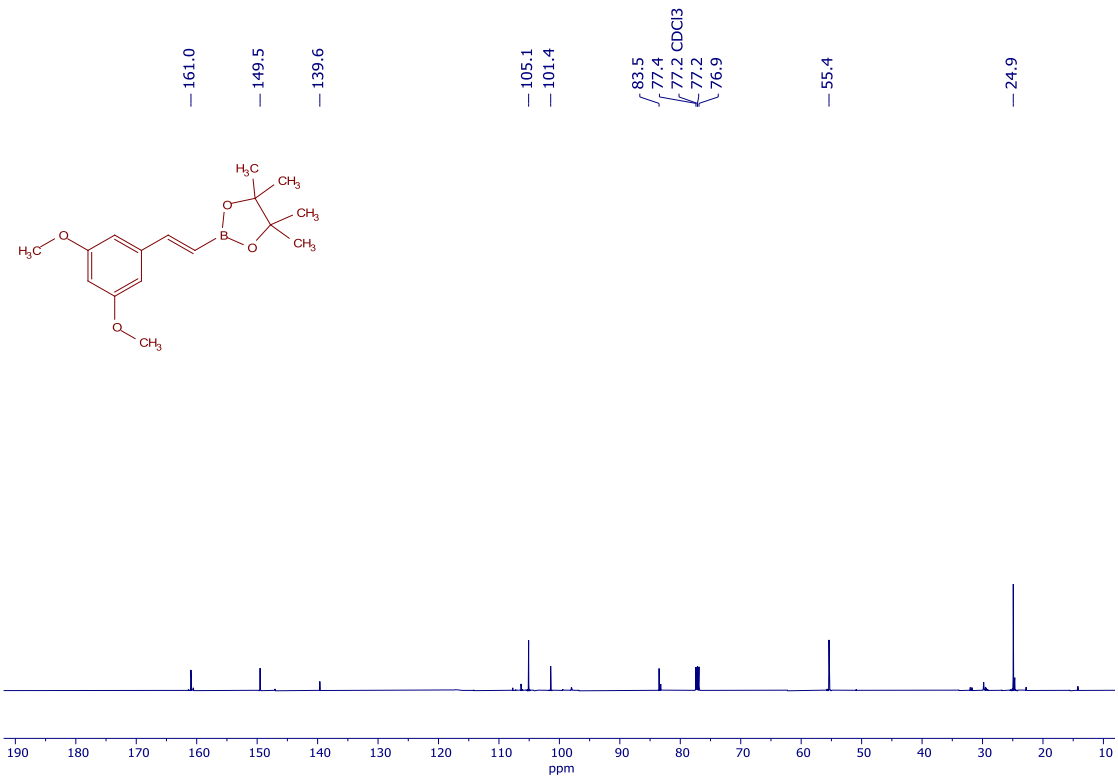
*$^{13}C\{^{1}H\}$ NMR of (E)-2-(2-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound **4h**) in $CDCl_3$*



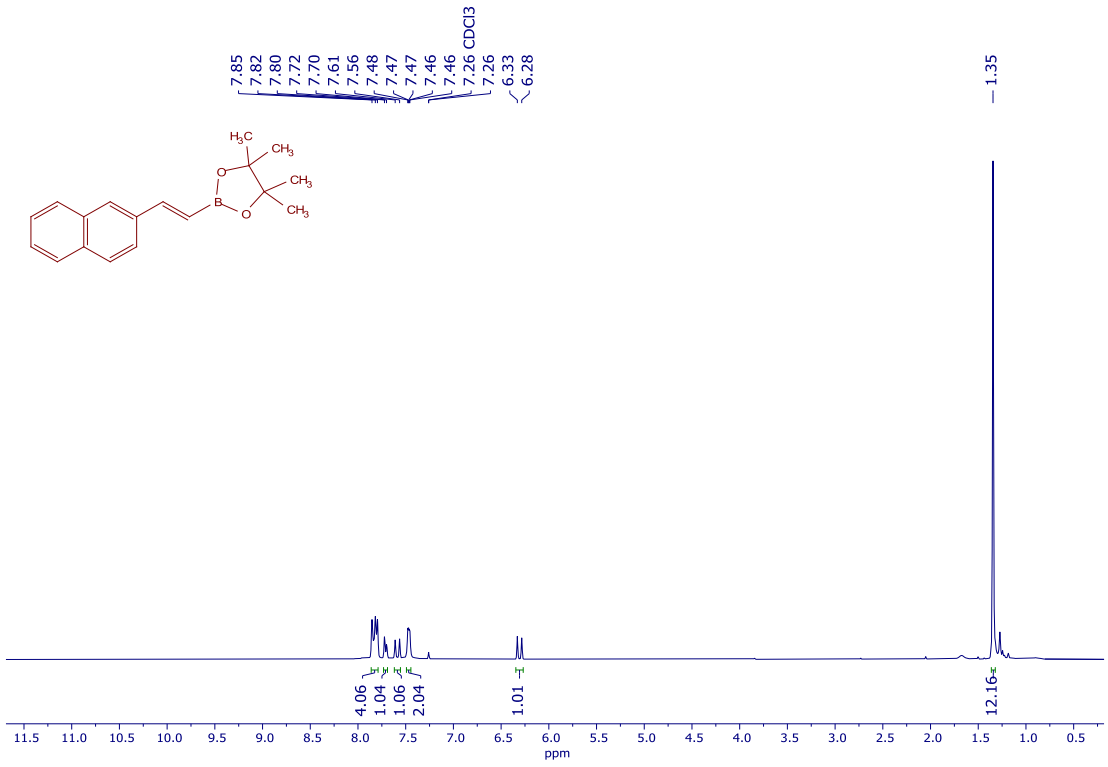
*[11]B NMR of (E)-2-(2-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound **4h**) in $CDCl_3$*



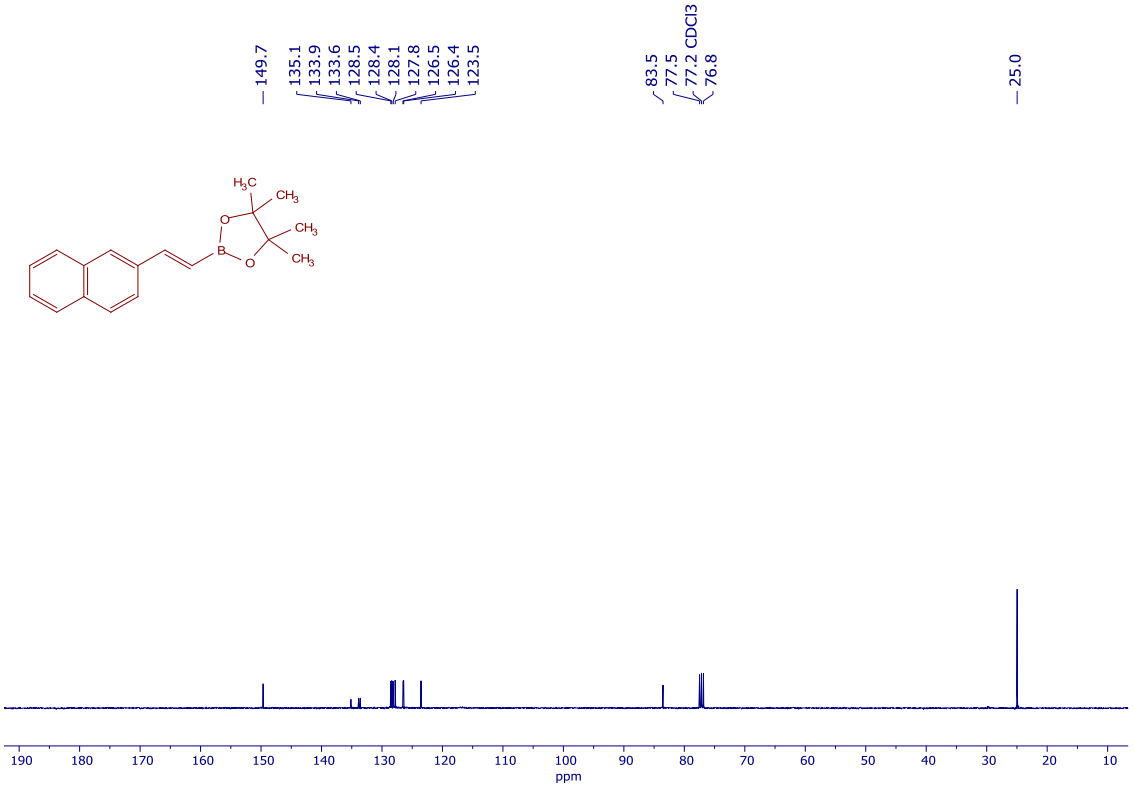
*[1]H NMR of (E)-2-(3,5-dimethoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound **4i**) in $CDCl_3$*



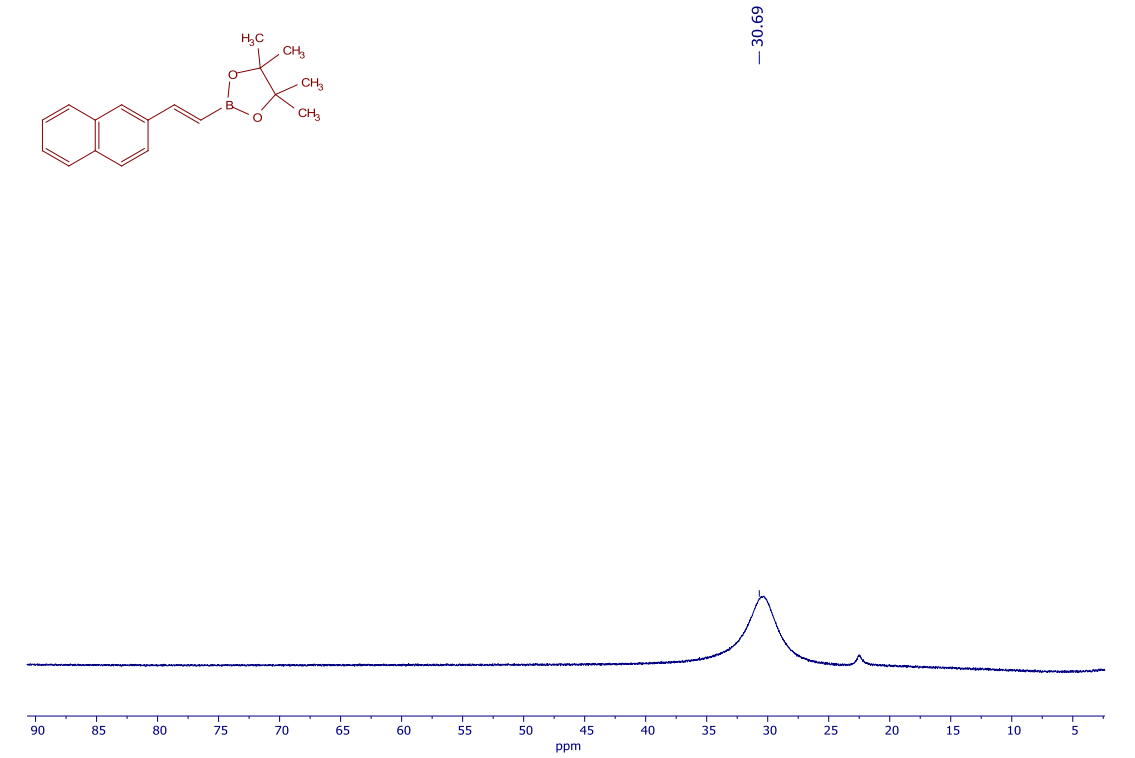
*$^{13}C\{^{1}H\}$ NMR of (E)-2-(3,5-dimethoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound **4i**) in $CDCl_3$*



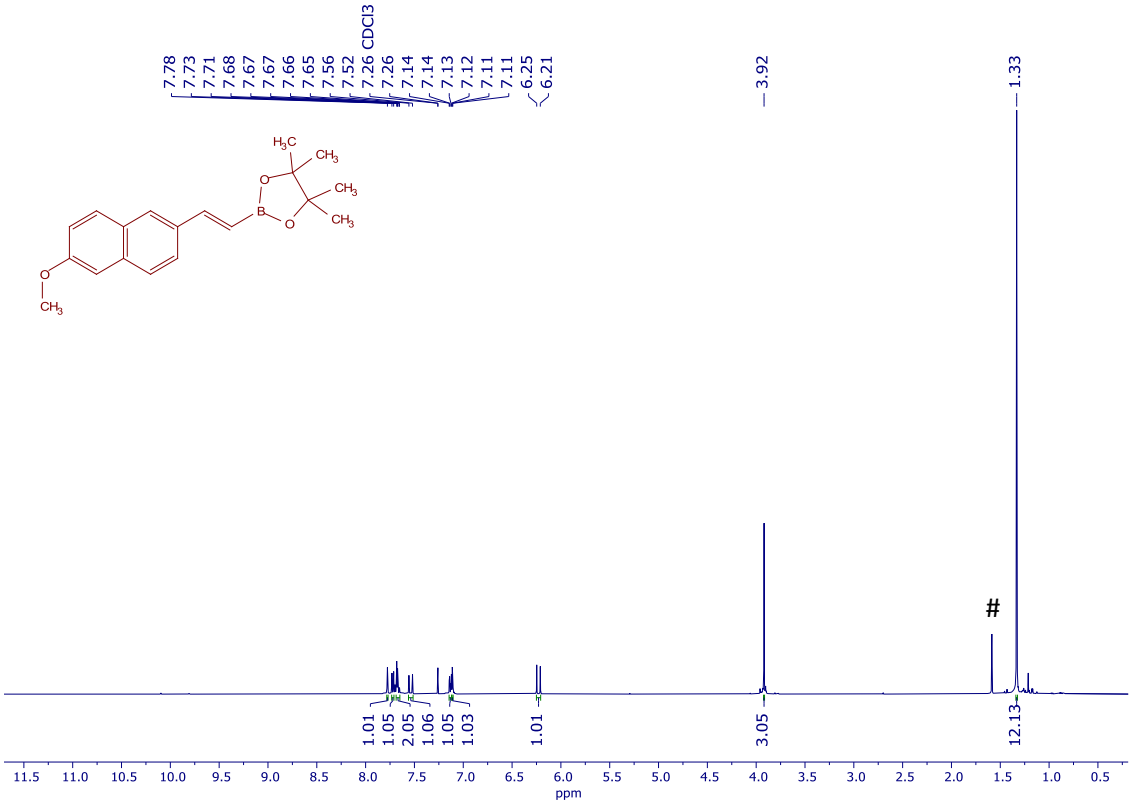
*^{1}H NMR of (E)-4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)vinyl)-1,3,2-dioxaborolane (Compound **4j**) in $CDCl_3$*



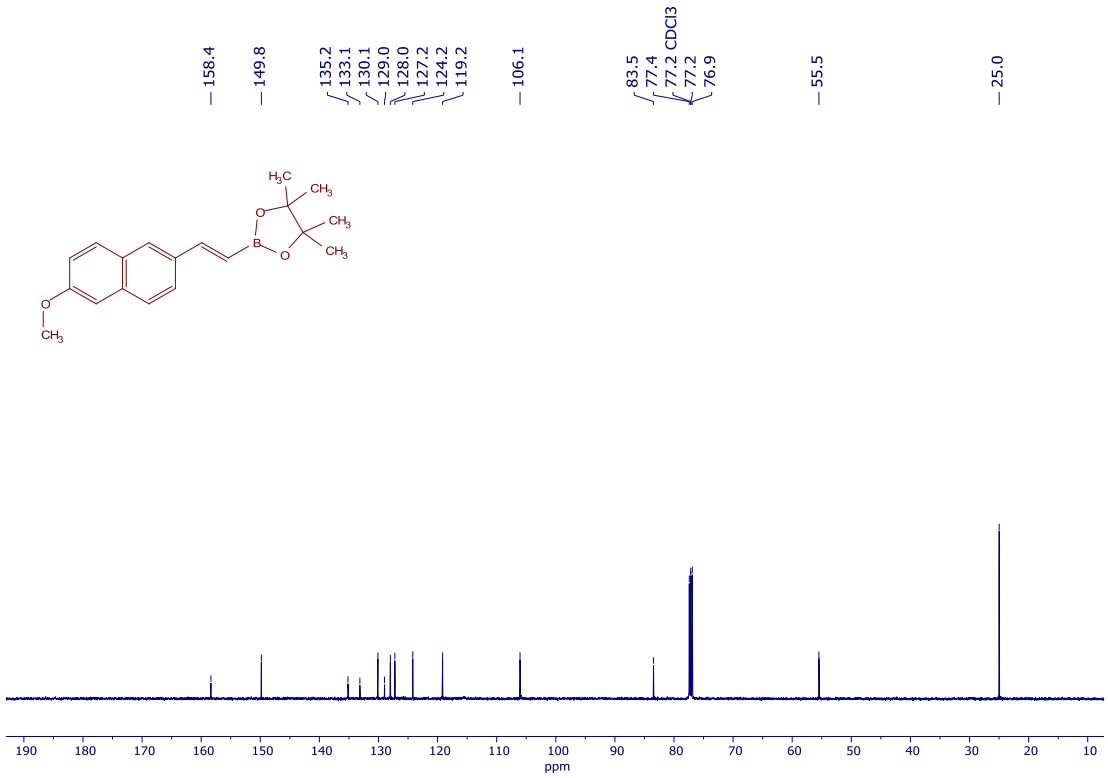
*$^{13}C\{^{1}H\}$ NMR of (E)-4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)vinyl)-1,3,2-dioxaborolane (Compound **4j**) in $CDCl_3$*



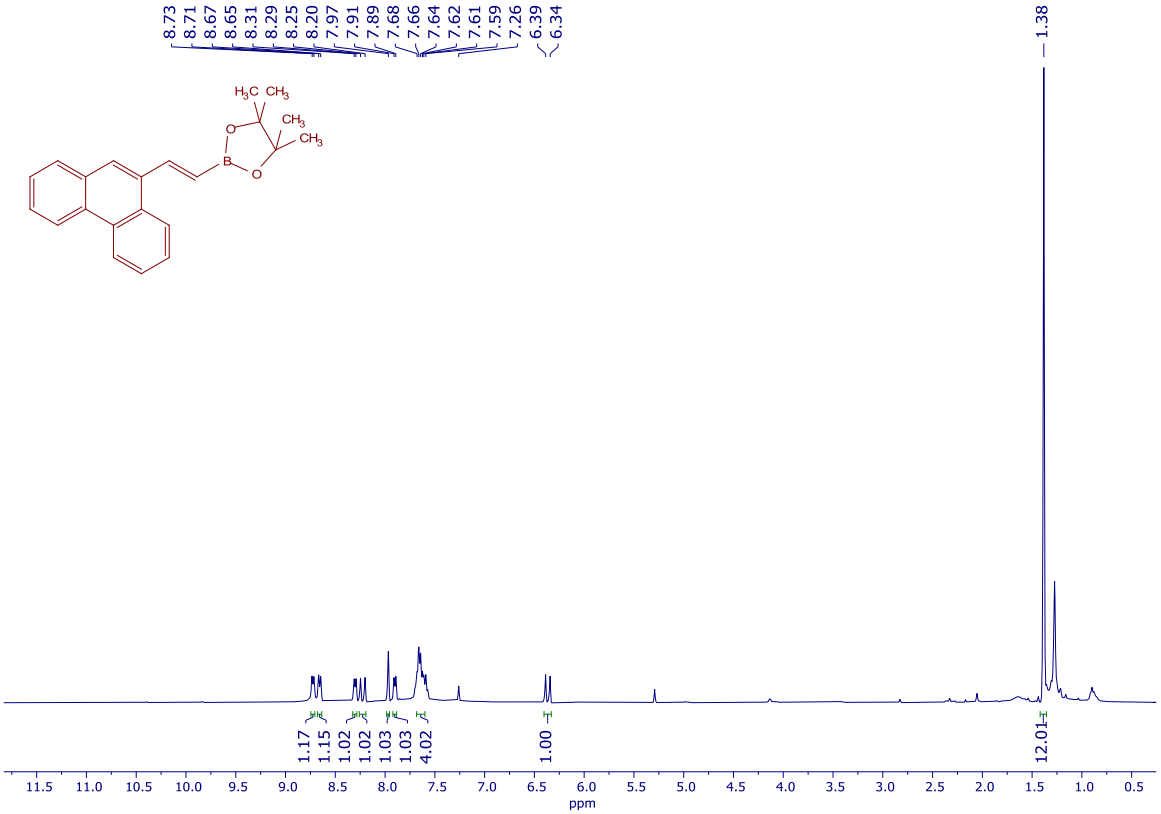
*^{11}B NMR of (E)-4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)vinyl)-1,3,2-dioxaborolane (Compound **4j**) in $CDCl_3$*



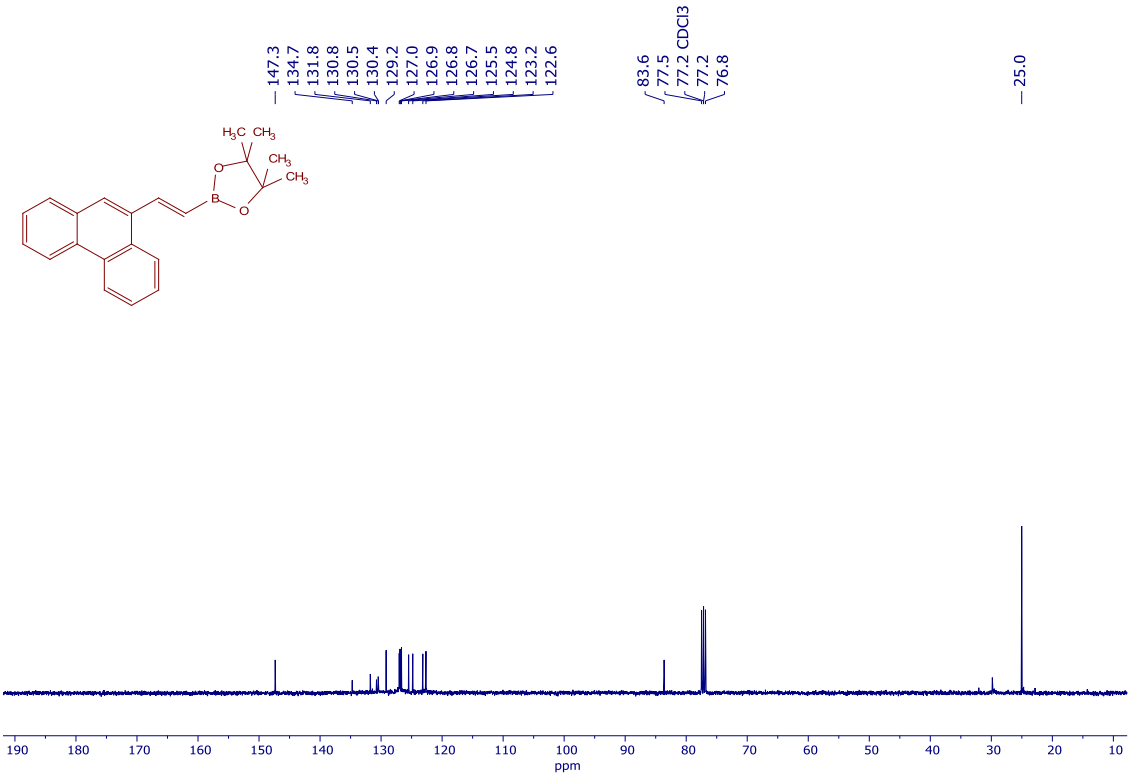
*^{1}H NMR of (E)-4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)vinyl)-1,3,2-dioxaborolane (Compound **4k**) in $CDCl_3$. # indicates the solvent impurity of H_2O in $CDCl_3$*



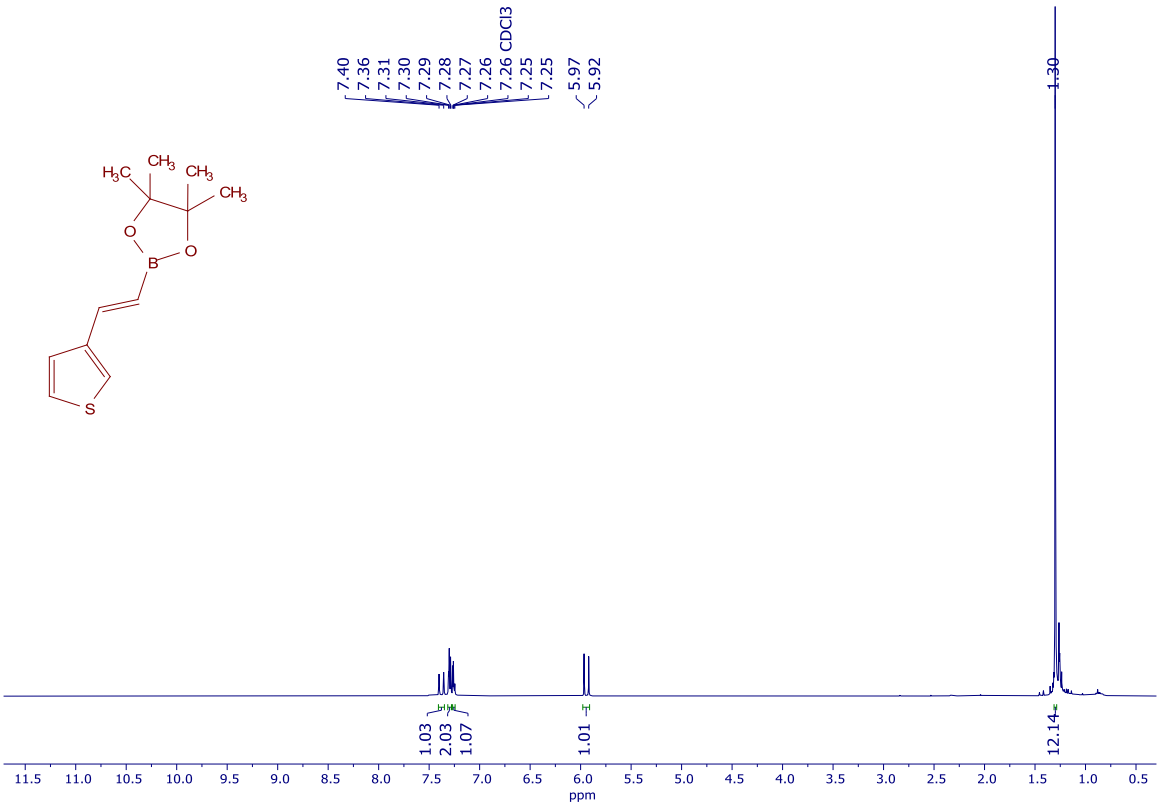
*$^{13}C\{^{1}H\}$ NMR of (E)-4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)vinyl)-1,3,2-dioxaborolane (Compound **4k**) in $CDCl_3$*



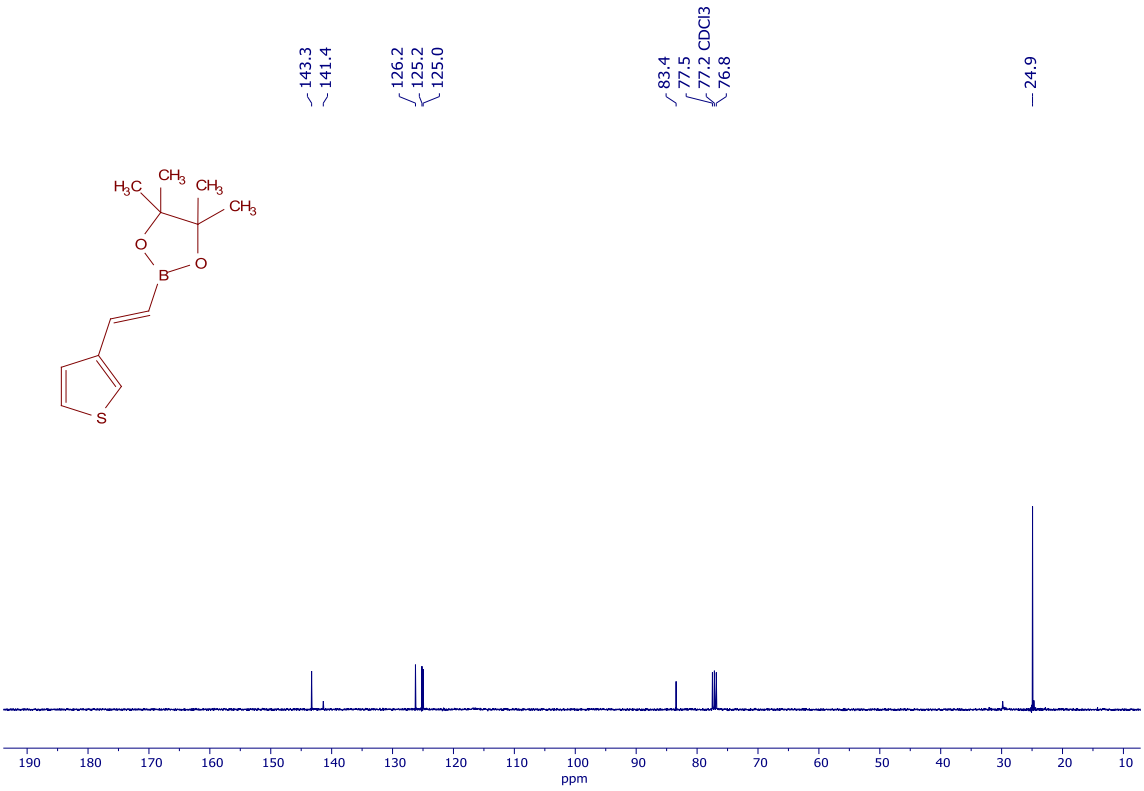
*[1]H NMR of (E)-4,4,5,5-tetramethyl-2-(2-(phenanthren-9-yl)vinyl)-1,3,2-dioxaborolane (Compound **4l**) in $CDCl_3$*



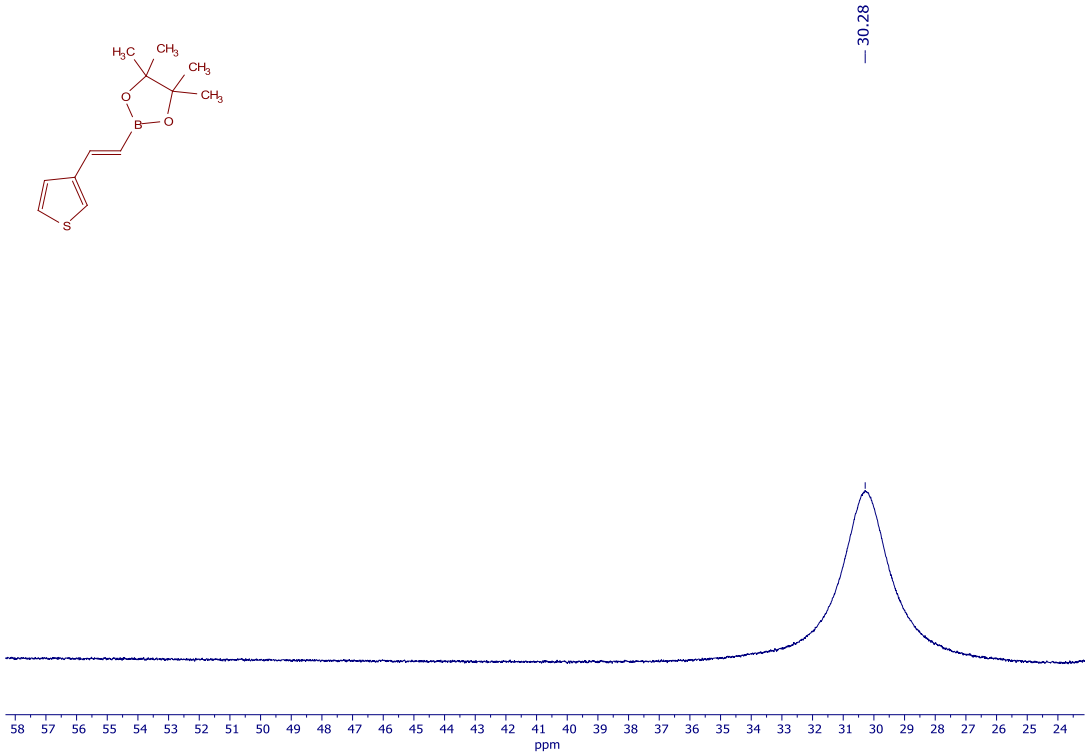
*[13]C{[1]H} NMR of (E)-4,4,5,5-tetramethyl-2-(2-(phenanthren-9-yl)vinyl)-1,3,2-dioxaborolane (Compound **4l**) in $CDCl_3$*



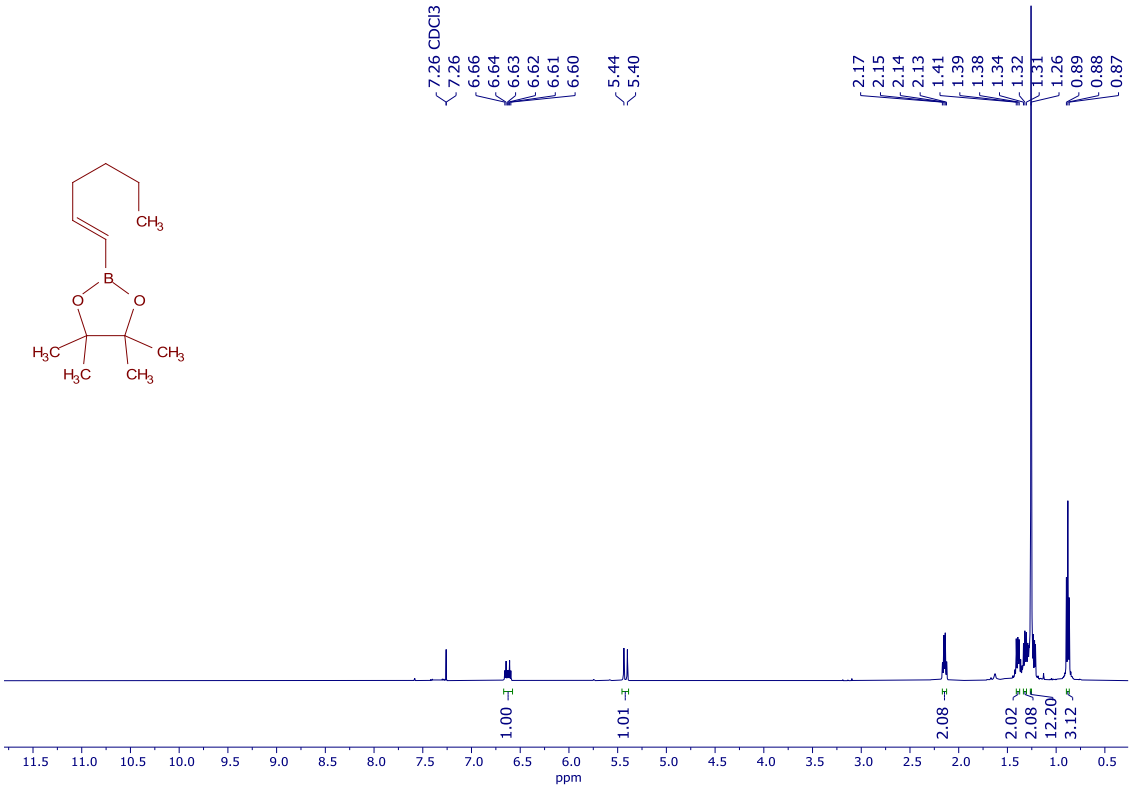
*^{1}H NMR (E)-4,4,5,5-tetramethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-dioxaborolane (Compound **4m**) in $CDCl_3$*



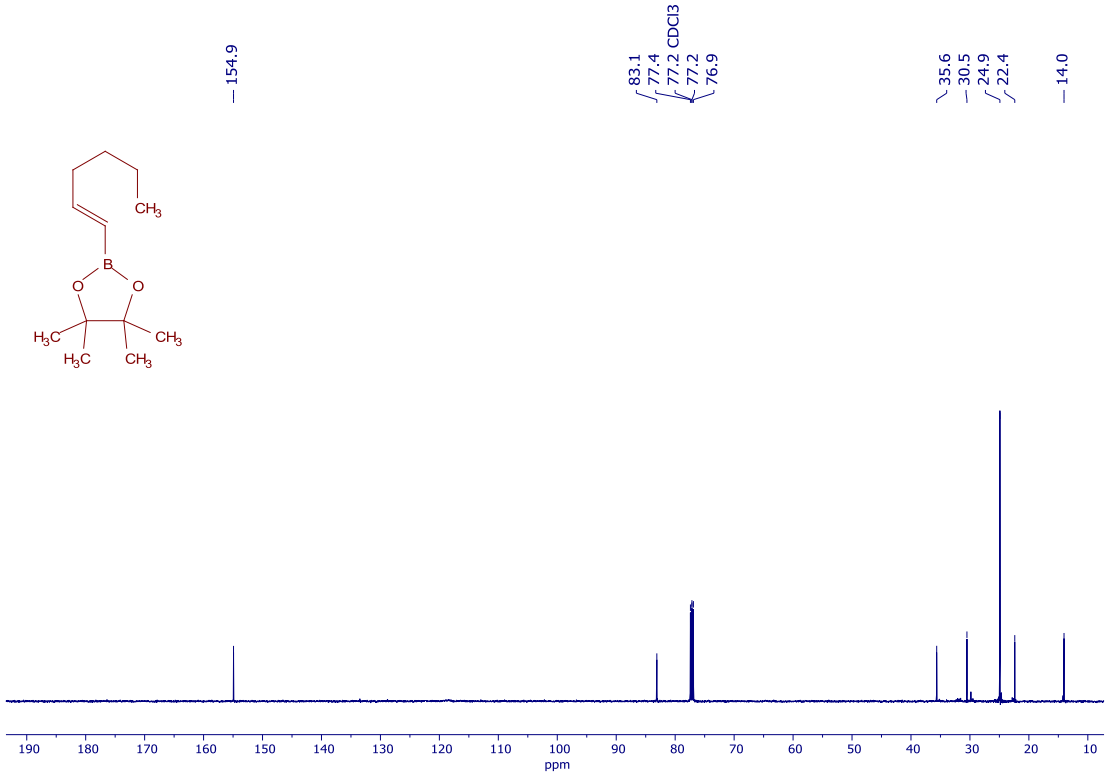
*$^{13}C\{^{1}H\}$ NMR of (E)-4,4,5,5-tetramethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-dioxaborolane (Compound **4m**) in $CDCl_3$*



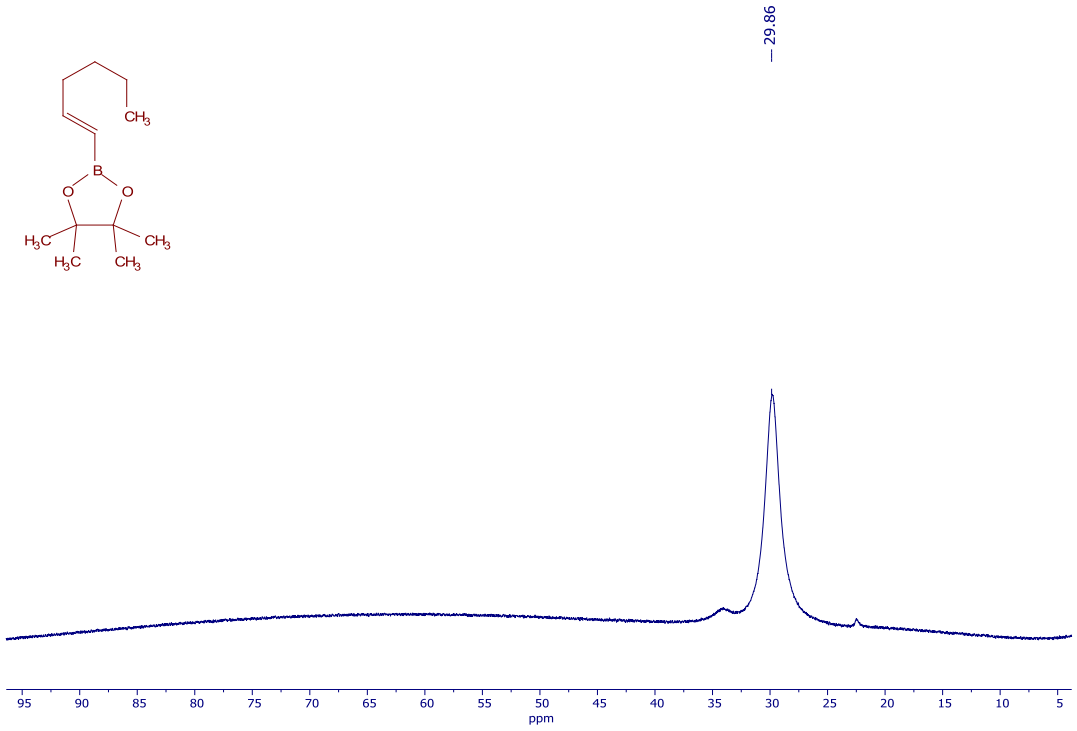
*^{11}B NMR of (E)-4,4,5,5-tetramethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-dioxaborolane (Compound **4m**) in $CDCl_3$*



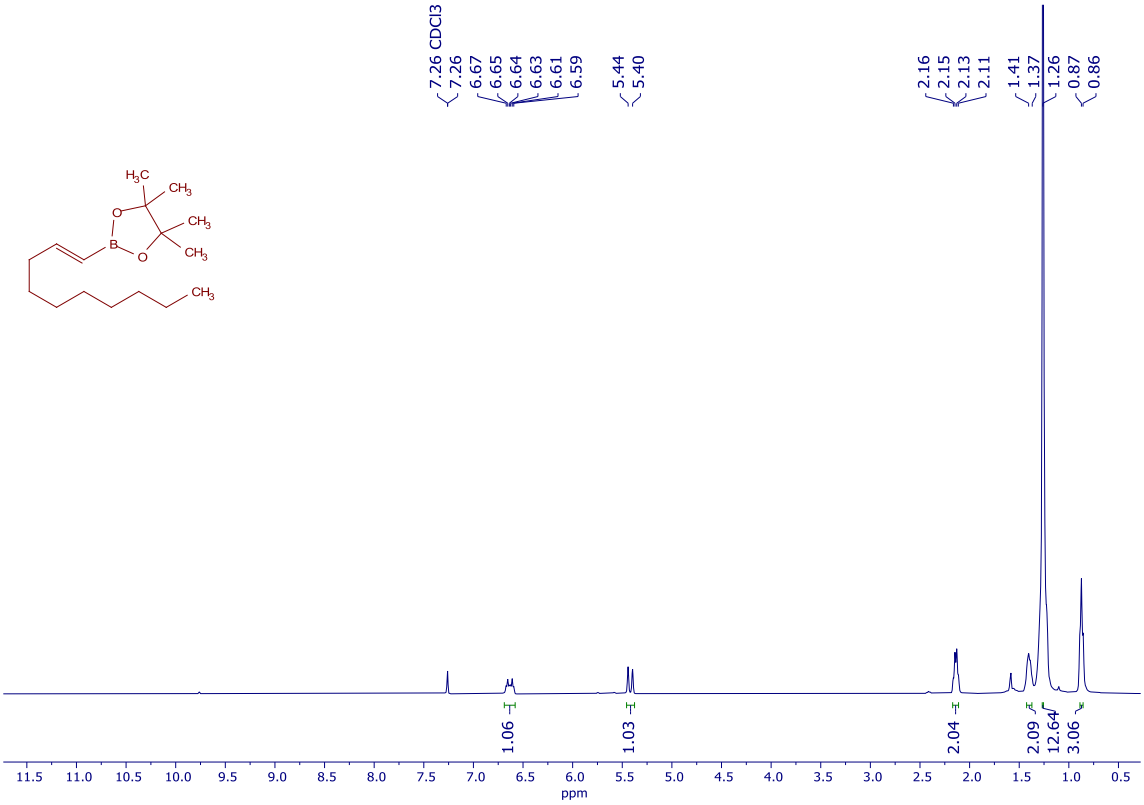
*^{1}H NMR of (E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound **4n**) in $CDCl_3$*



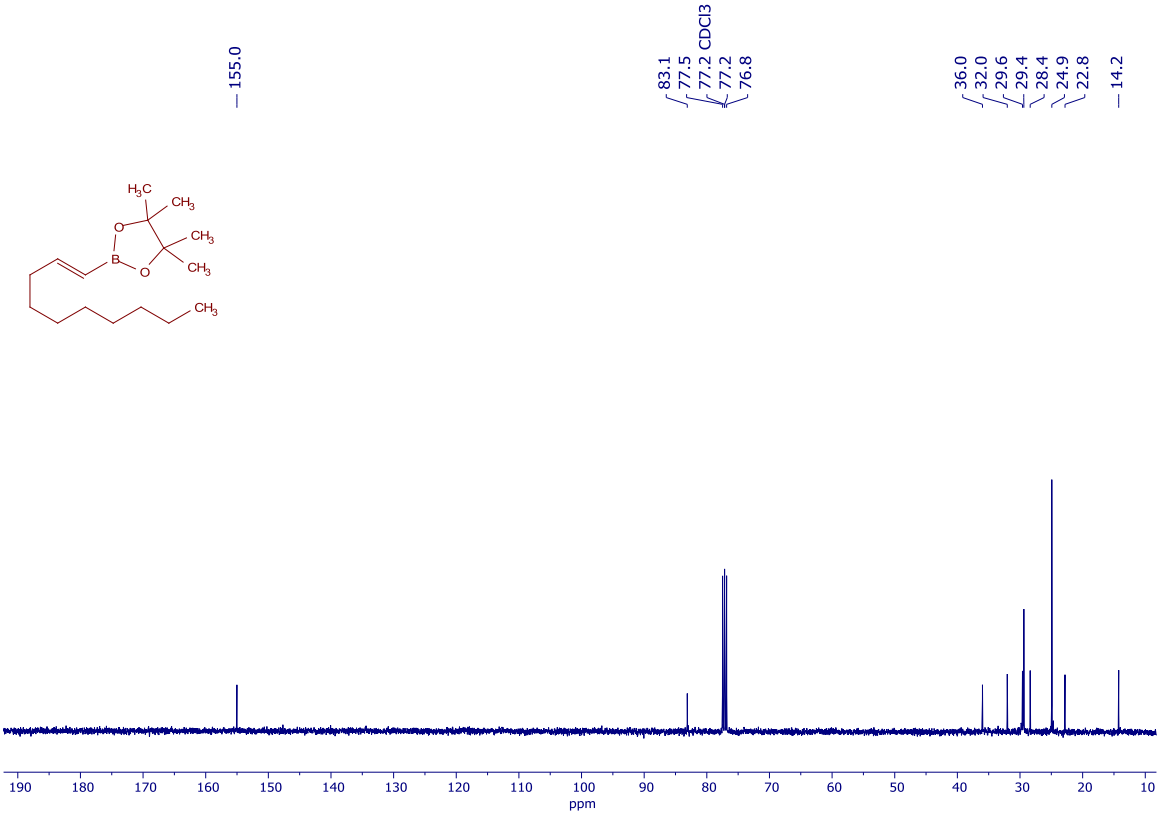
*$^{13}C\{^{1}H\}$ NMR of (E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound **4n**) in $CDCl_3$*



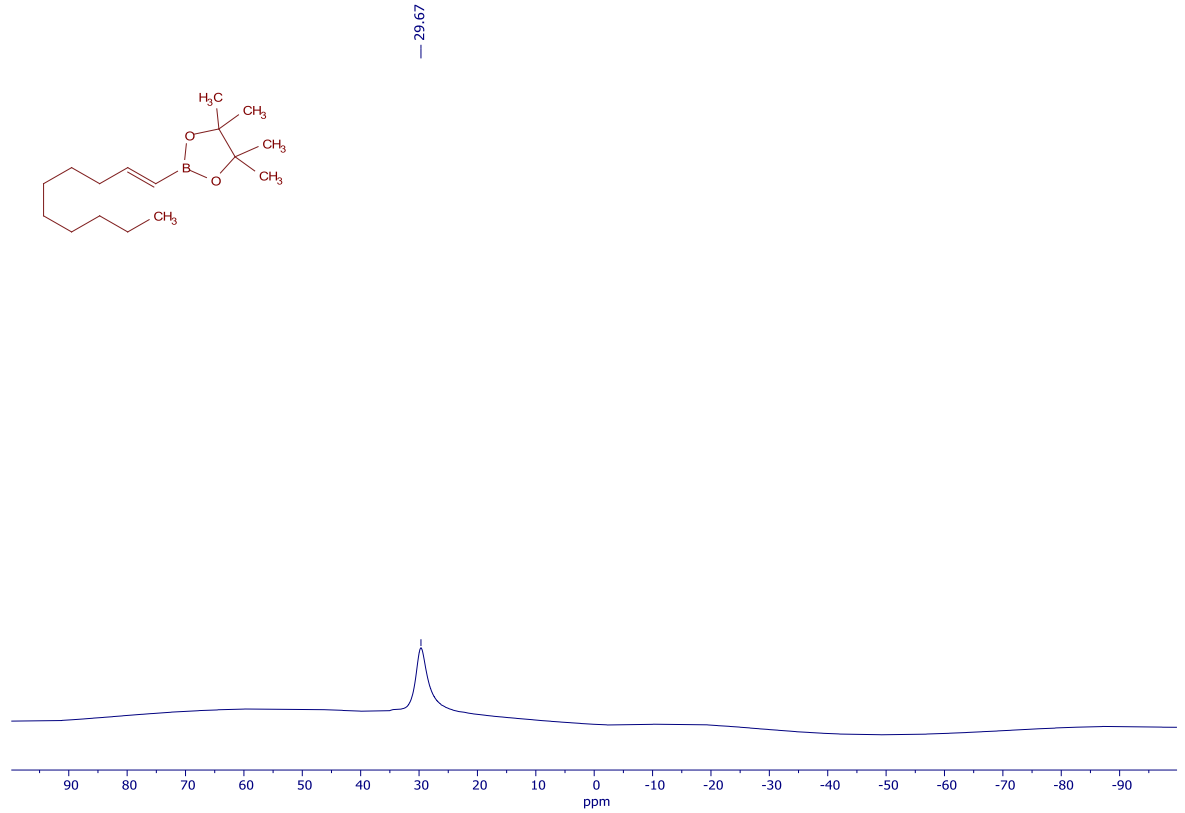
*^{11}B NMR of (E)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound **4n**) in $CDCl_3$*



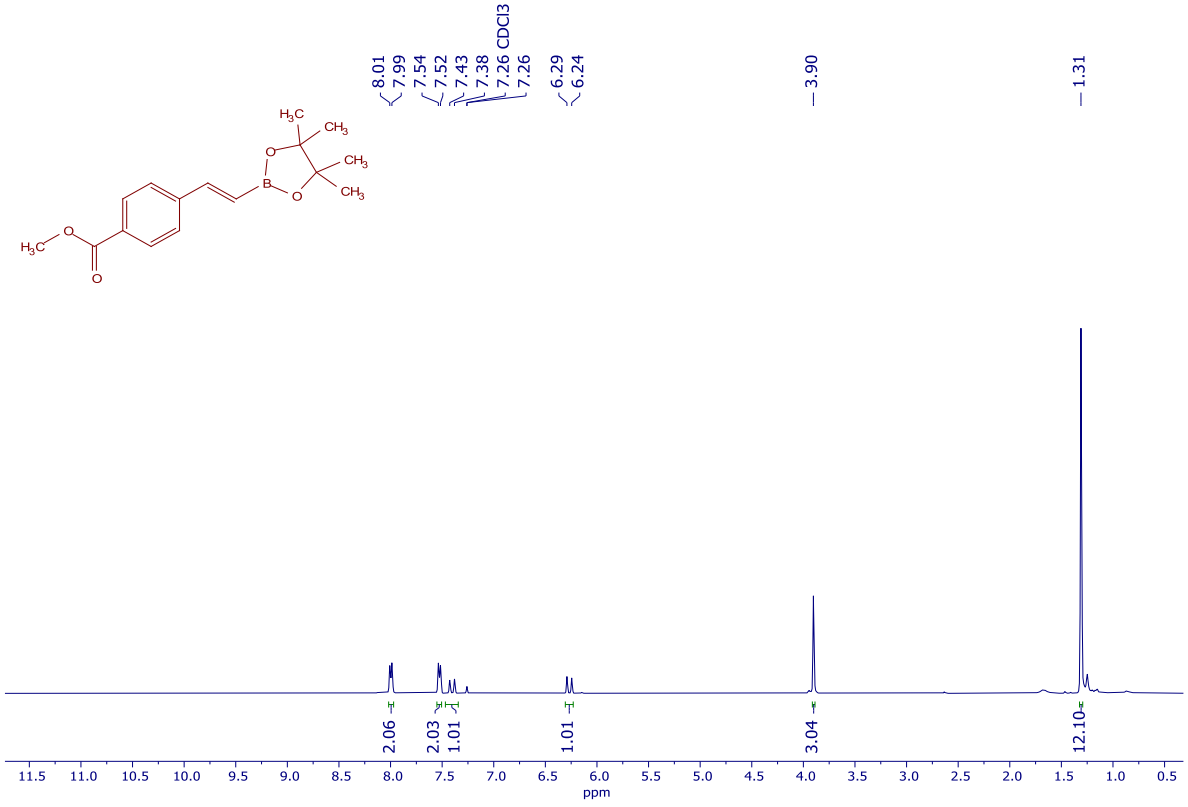
*^{1}H NMR of (E)-2-(dec-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound **4o**) in $CDCl_3$*



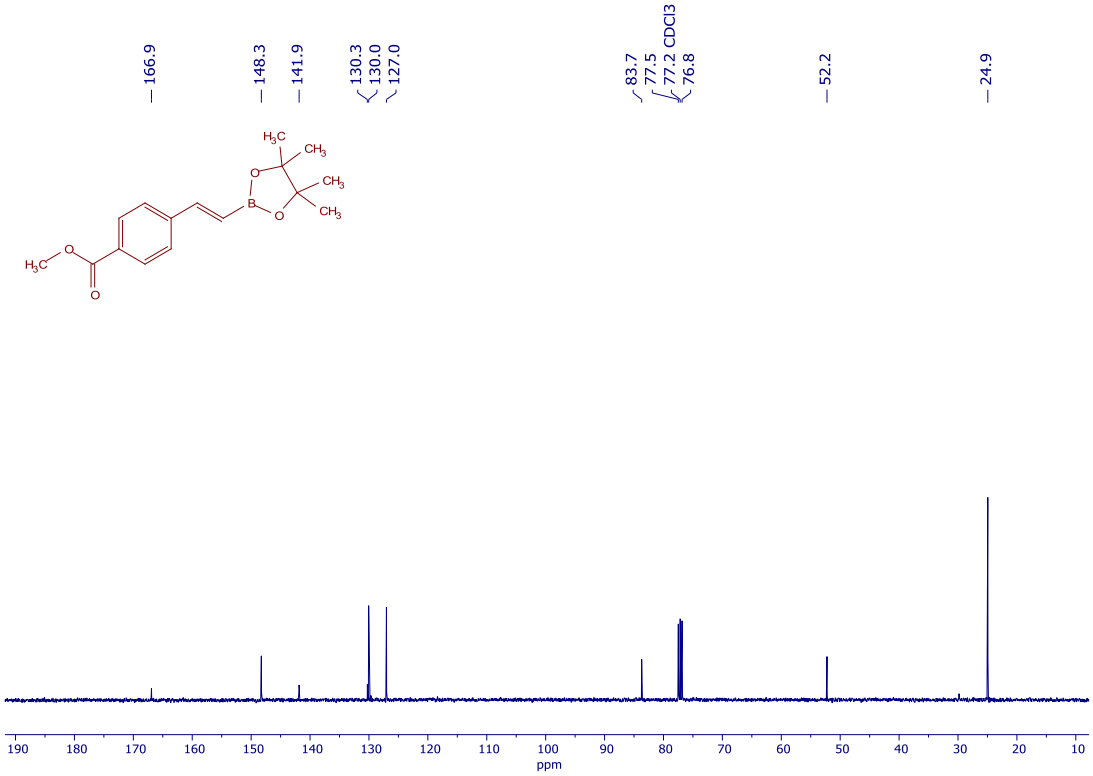
*$^{13}C\{^{1}H\}$ NMR of (E)-2-(dec-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound **4o**) in $CDCl_3$*



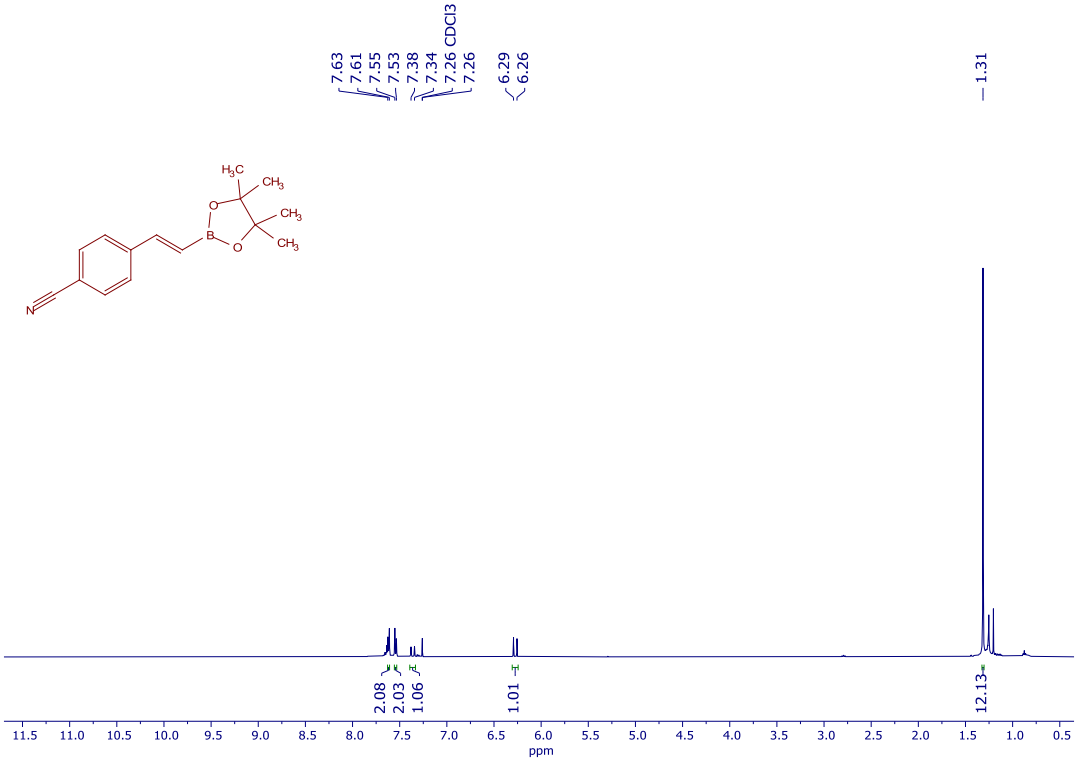
*^{11}B NMR of (E)-2-(dec-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound **4o**) in $CDCl_3$*



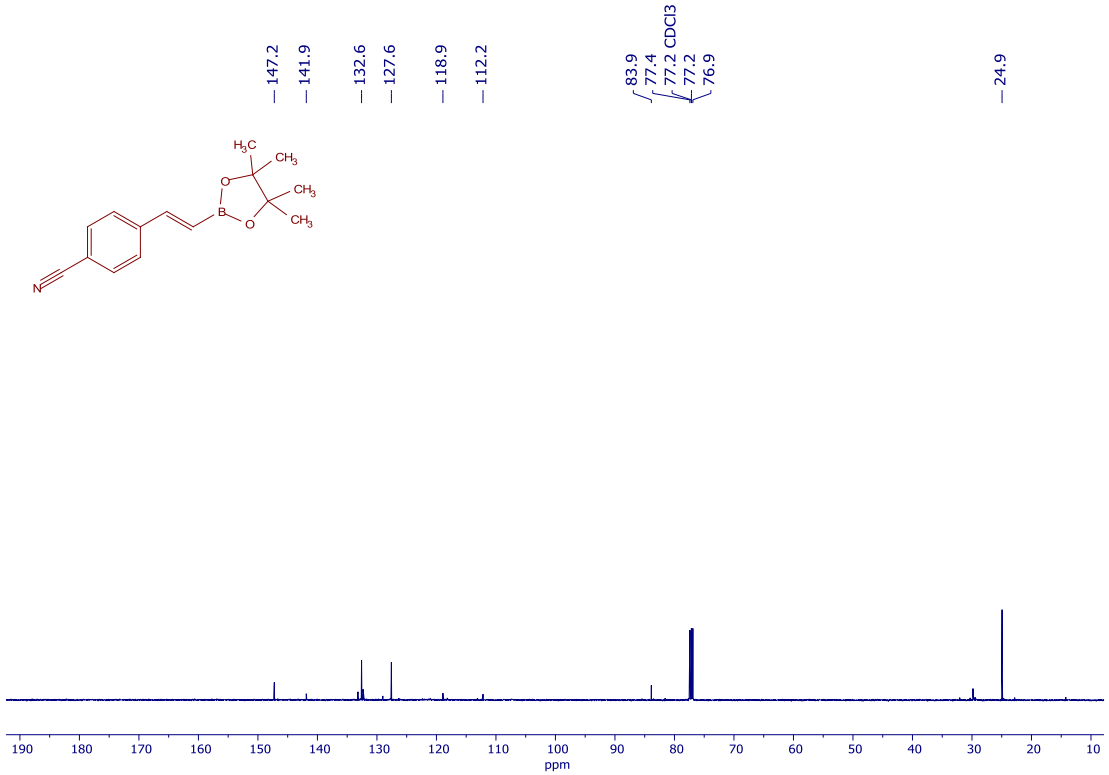
*^{1}H NMR of methyl (E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzoate (Compound **4p**) in $CDCl_3$*



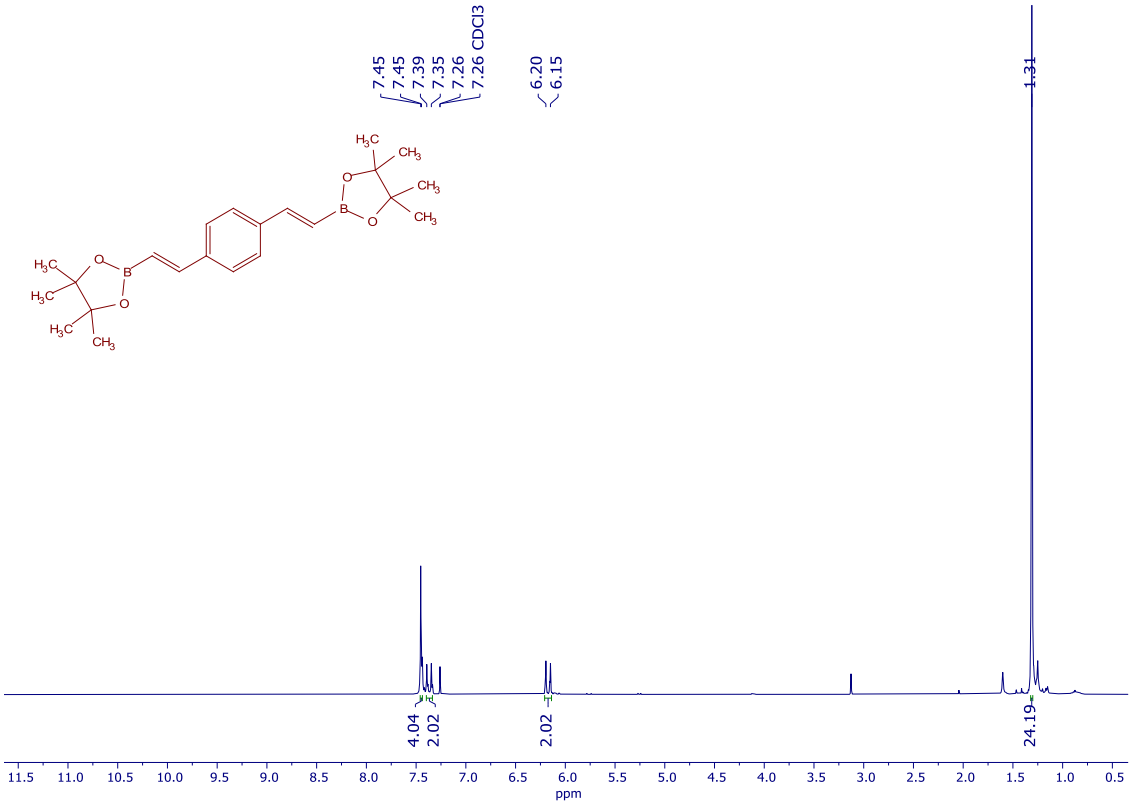
*$^{13}C\{^{1}H\}$ NMR of methyl (E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzoate (Compound **4p**) in $CDCl_3$*



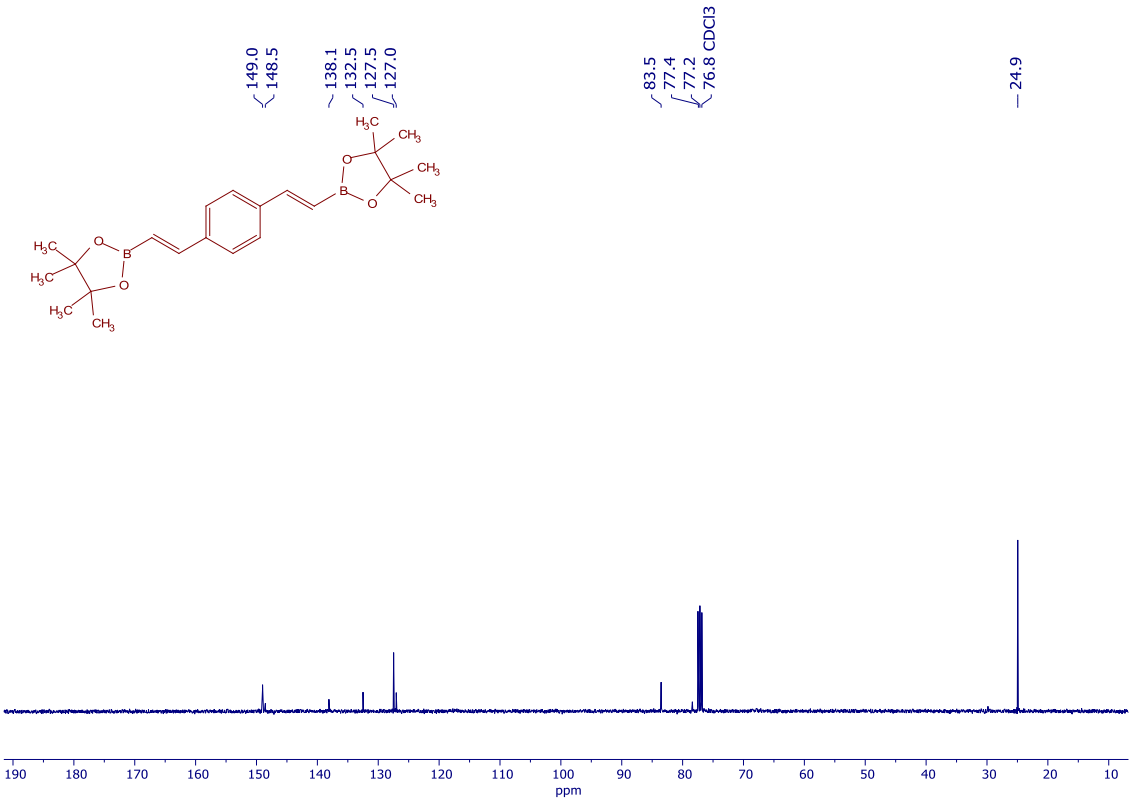
*^{1}H NMR of (E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzonitrile (Compound **4q**) in $CDCl_3$*



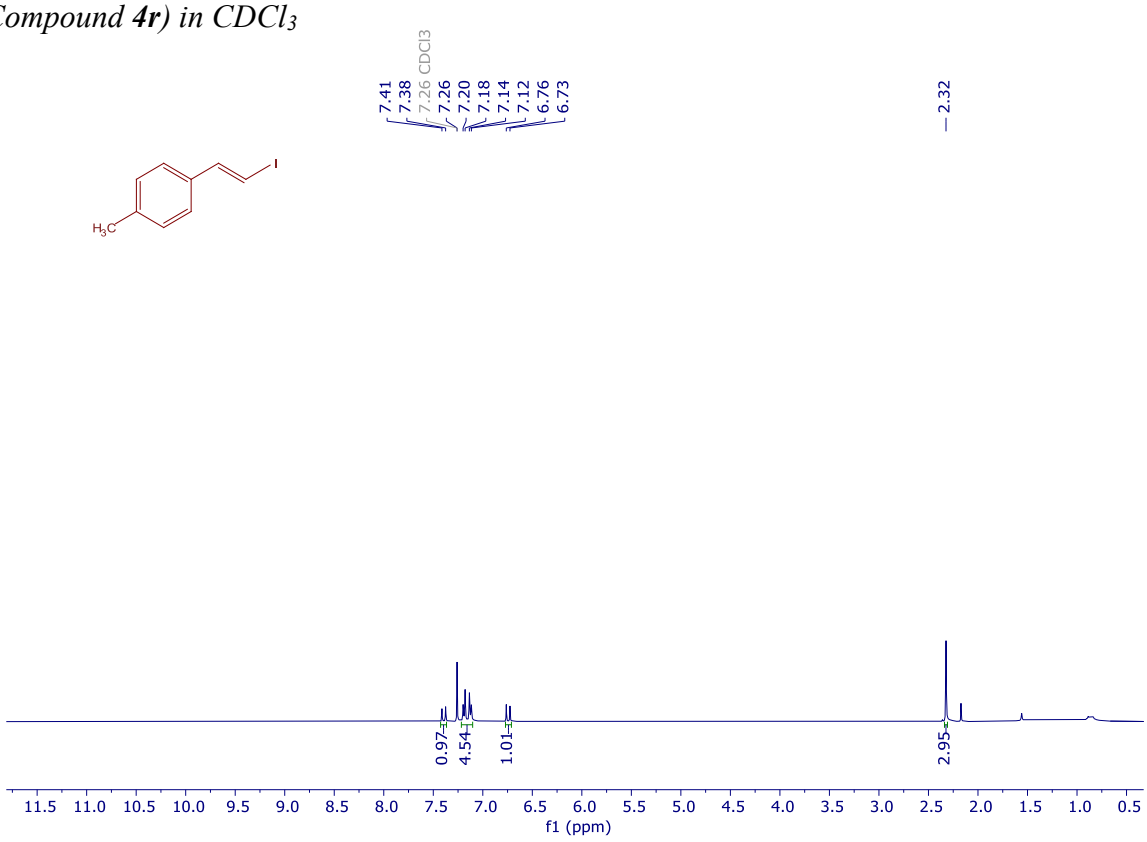
$^{13}C\{^{1}H\}$ NMR of ***(E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzonitrile (Compound 4q)*** *in $CDCl_3$*



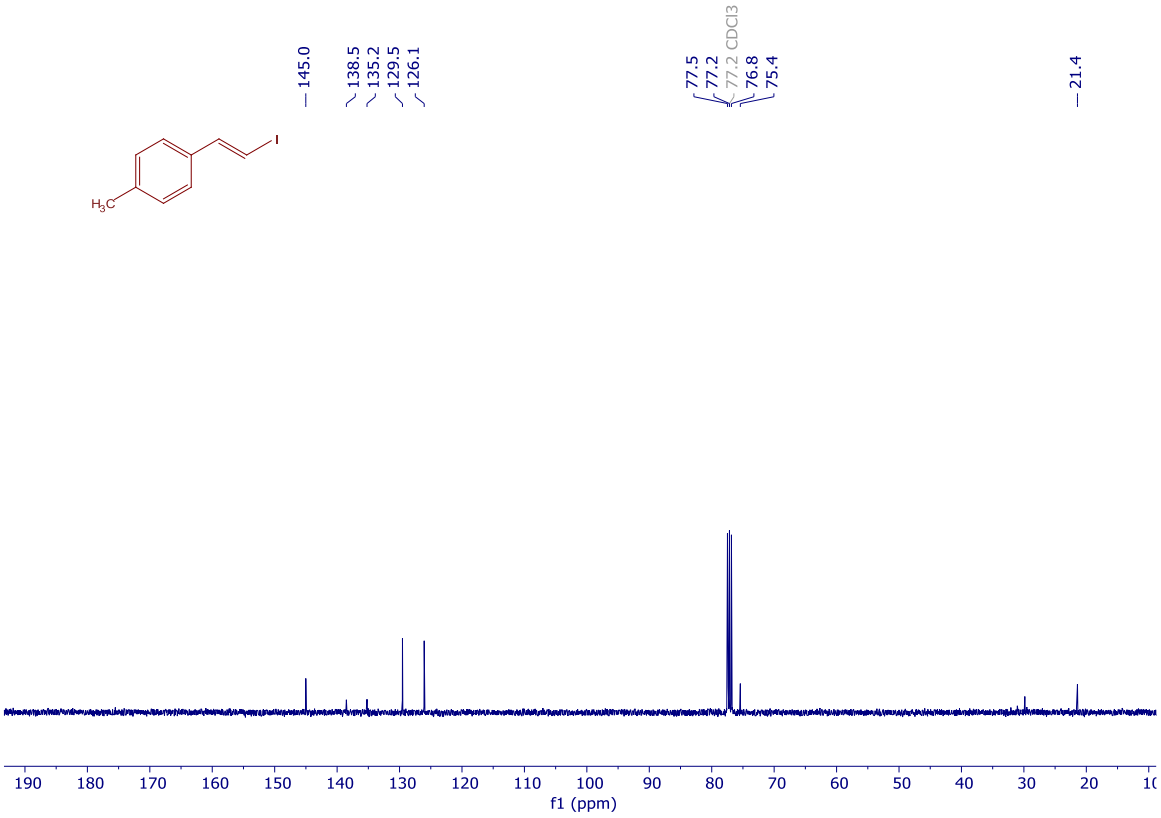
^{1}H NMR of 1,4-bis((E)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzene (Compound ***4r****) in $CDCl_3$*



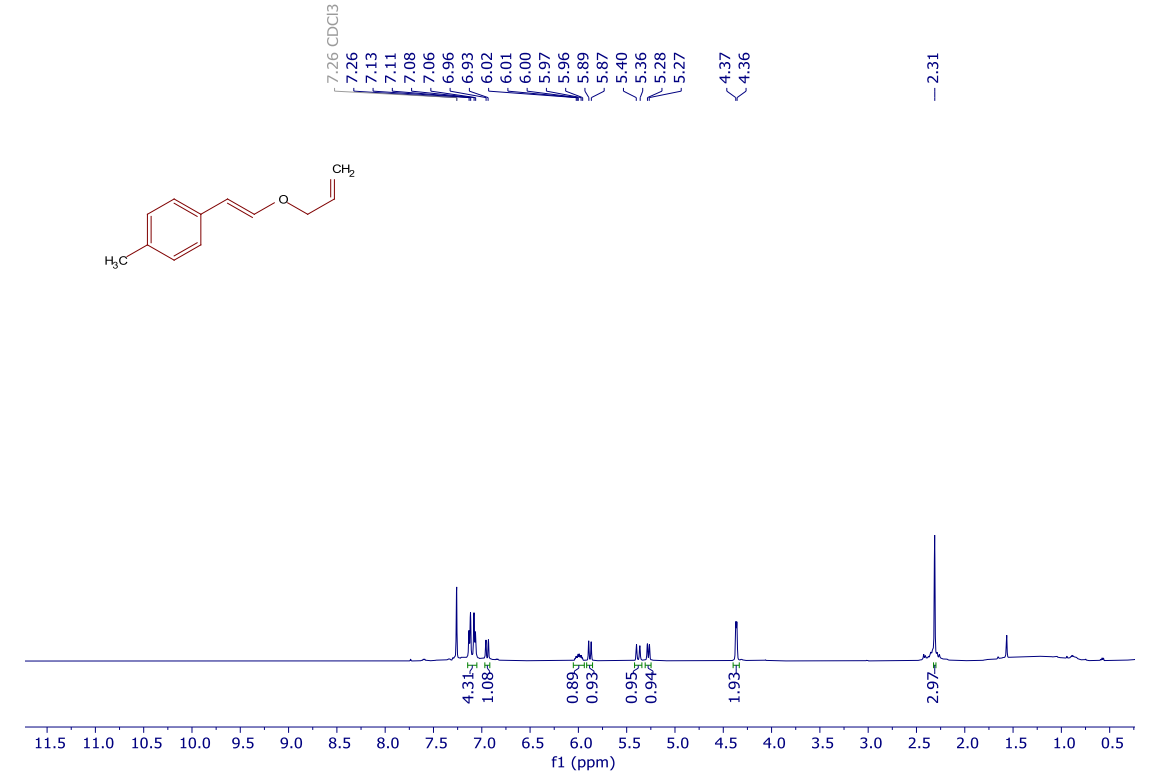
*$^{13}C\{^{1}H\}$ NMR of (1,4-bis((E)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzene (Compound **4r**) in $CDCl_3$*



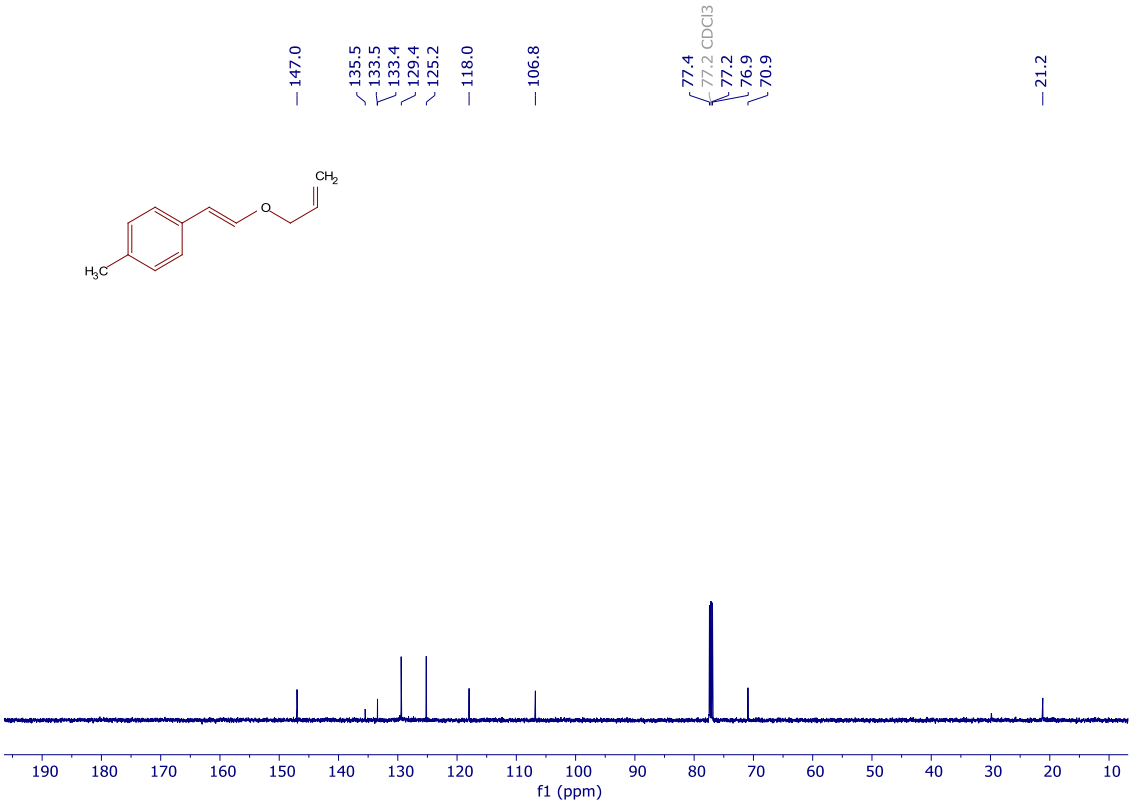
*^{1}H NMR of (E)-1-(2-iodovinyl)-4-methylbenzene (Compound **5a**) in $CDCl_3$*



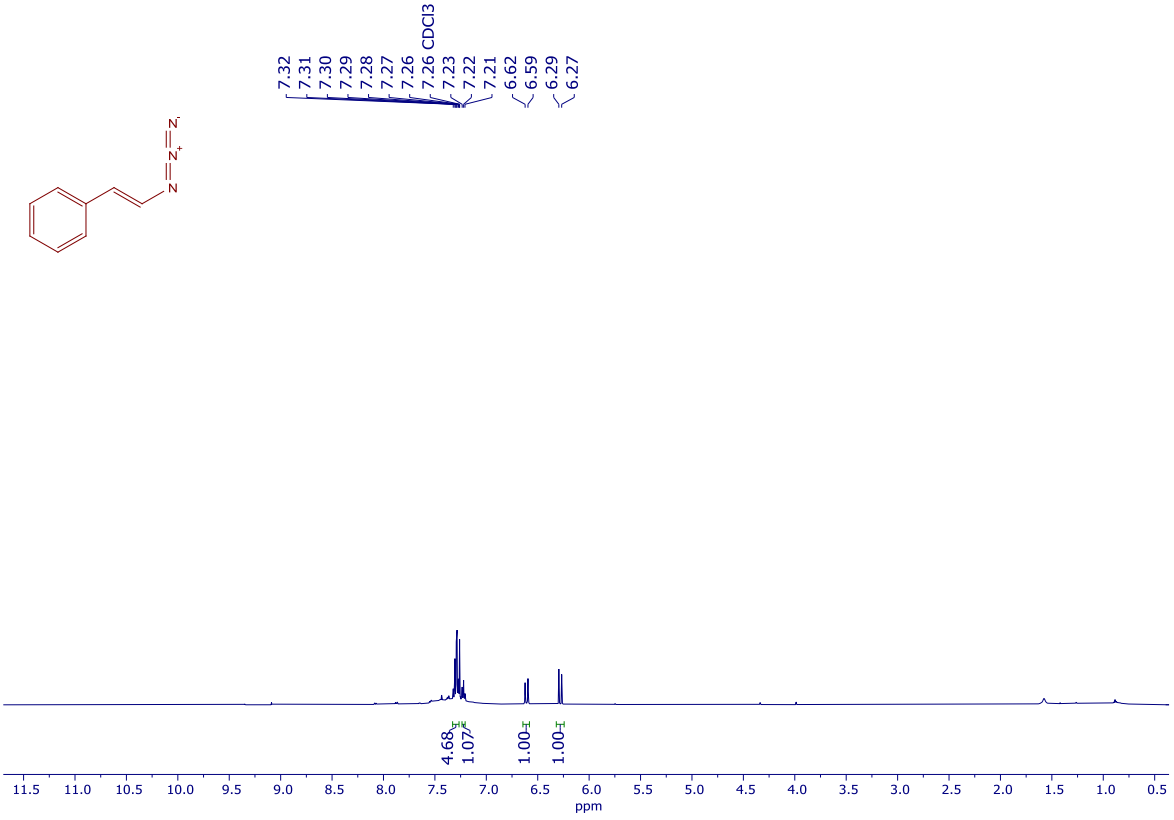
*$^{13}C\{^{1}H\}$ NMR of (E)-1-(2-iodovinyl)-4-methylbenzene (Compound **5a**) in $CDCl_3$*



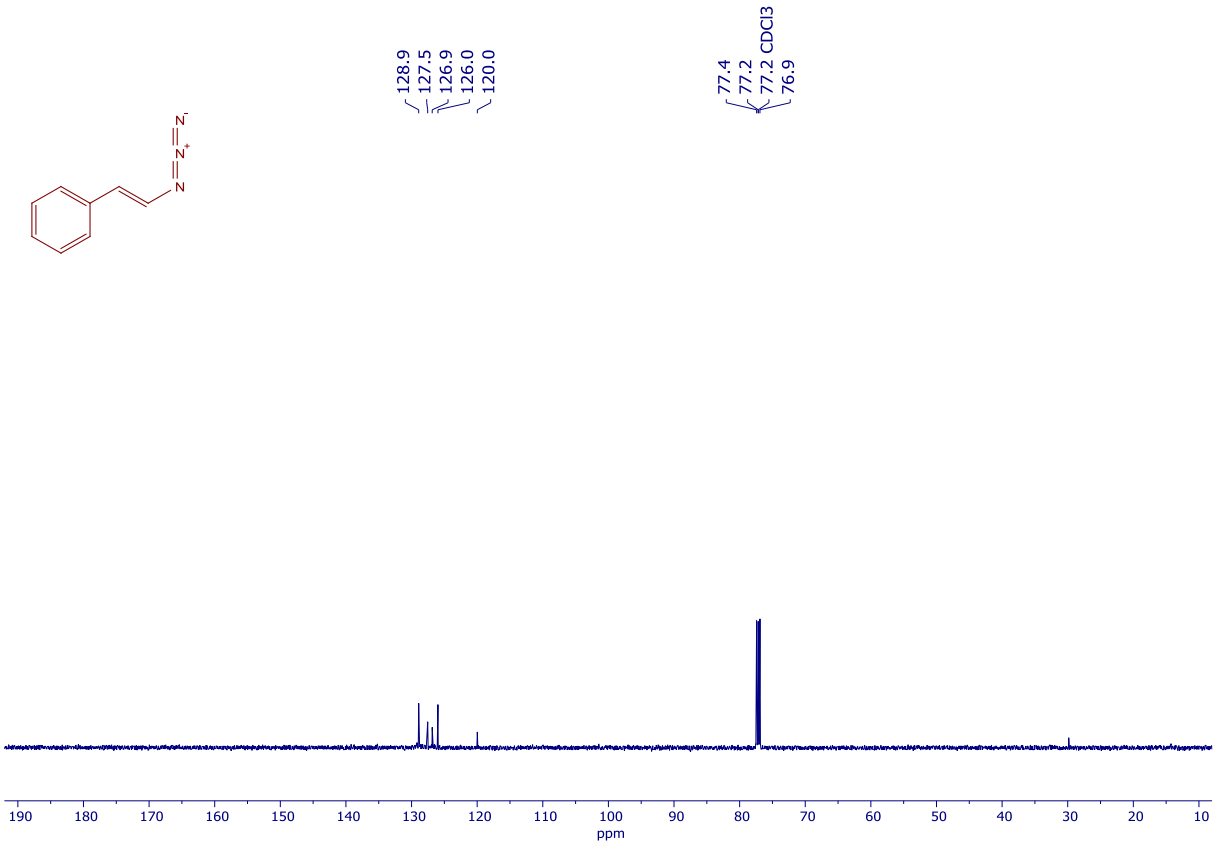
*^{1}H NMR of (E)-1-methyl-4-(2-(pent-4-en-1-yloxy)vinyl)benzene) (Compound **5b**) in $CDCl_3$*



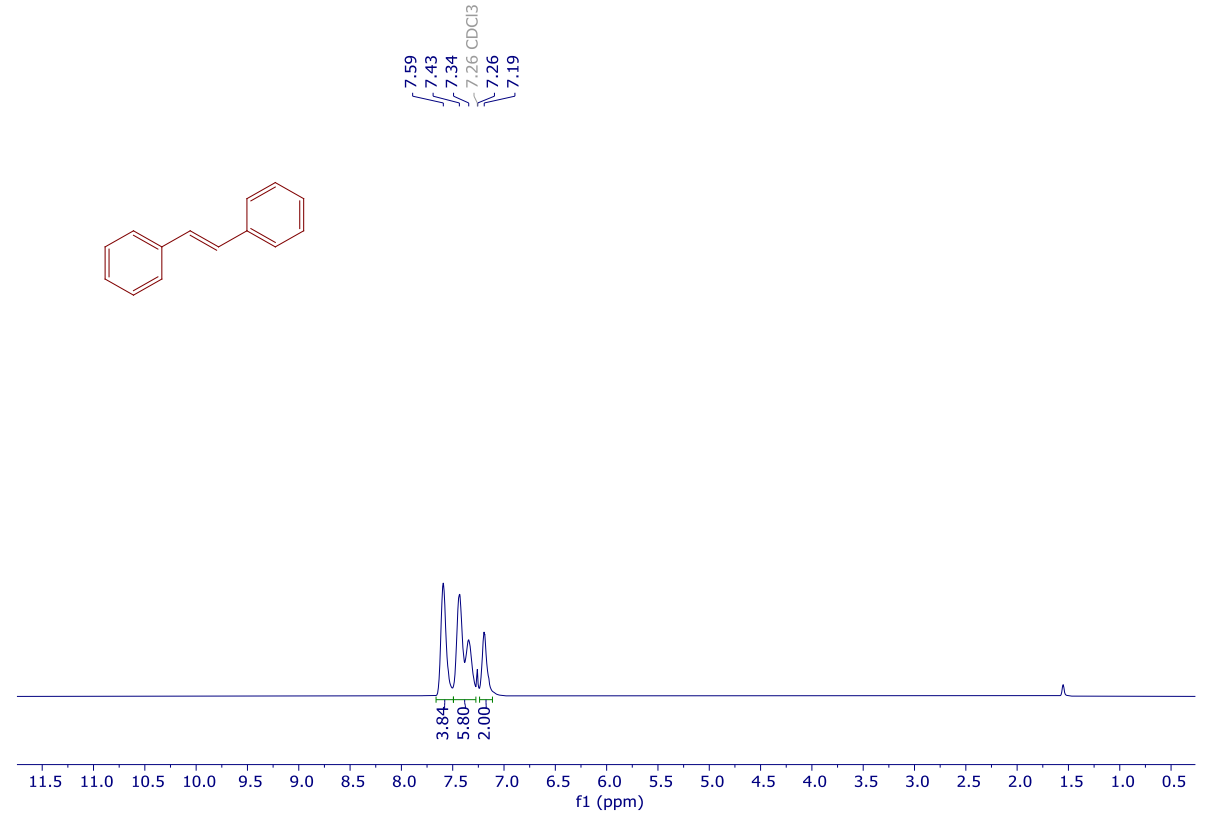
*$^{13}C\{^{1}H\}$ NMR of (E)-1-methyl-4-(2-(pent-4-en-1-yloxy)vinyl)benzene) (Compound **5b**) in $CDCl_3$*



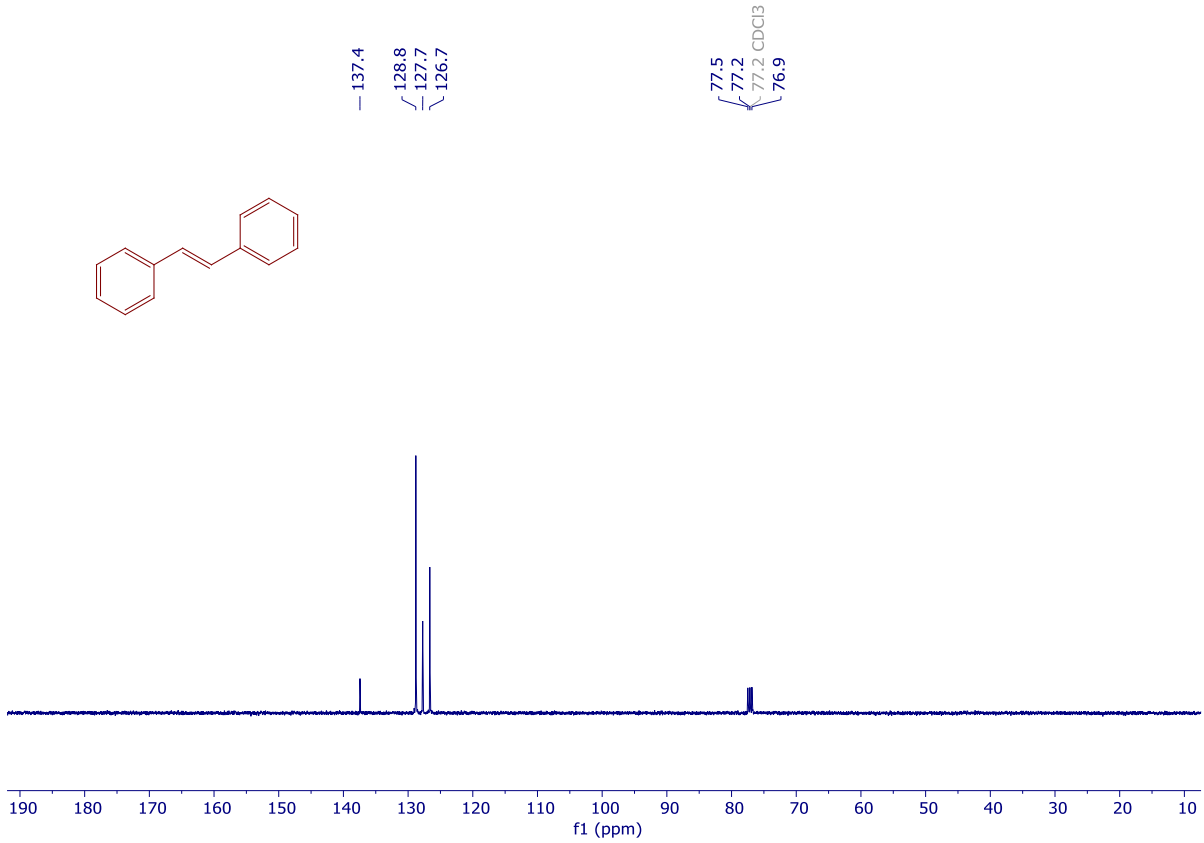
*^{1}H NMR of (E)-(2-azidovinyl)benzene (Compound **5c**) in $CDCl_3$*



*$^{13}C\{^{1}H\}$ NMR of (E)-(2-azidovinyl)benzene (Compound **5c**) in $CDCl_3$*



*^{1}H NMR of (E)-1,2-diphenylethene (Compound **5d**) in $CDCl_3$*



*$^{13}C\{^{1}H\}$ NMR of (E)-1,2-diphenylethene (Compound **5d**) in $CDCl_3$*

Control experiments

1. For cyclotrimerization reaction:

Metal hydride trapping experiment: A pressure tube was charged with catalyst **Co1** (0.010 mmol, 2 mol%), pinacolborane (0.15 mmol, 0.3 equiv.), phenylacetylene (0.5 mmol) and trityl PF_6 (0.5 mmol, 1 equiv.). Then the reaction mixture was allowed to stir at room temperature for 12 h. After completion of the reaction, formation of only trace amount of the product **3b** was observed.

Radical scavenger experiment: A pressure tube was charged with catalyst **Co1** (0.010 mmol, 2 mol%), pinacolborane (0.15 mmol, 0.3 equiv.), phenylacetylene (0.5 mmol, 1 equiv.) and TEMPO/BHT (0.5 mmol, 1 equiv.). Then the reaction mixture was allowed to stir at room temperature for 12 h. After completion of the reaction, the product **3b** (yield: 64-66%) was isolated by column chromatography.

Mercury dropping experiment: A pressure tube was charged with catalyst **Co1** (0.010 mmol, 2 mol%), pinacolborane (0.15 mmol, 0.3 equiv.), phenylacetylene (0.5 mmol, 1 equiv.) and

mercury (1 mmol, 2 equiv.). Then the reaction mixture was allowed to stir at room temperature for 12 h. After completion of the reaction, the product **3b** (0.037 g, 0.012 mmol, 73%) was isolated by column chromatography over silica gel using hexane as eluent.

2. For hydroboration reaction:

Metal hydride trapping experiment: A pressure tube was charged with catalyst **Co5** (0.010 mmol, 2 mol%), pinacolborane (0.65 mmol, 1.3 equiv.), alkyne (0.5 mmol, 1 equiv.) and trityl PF_6 (0.5 mmol, 1 equiv.). Then the reaction mixture was kept in a preheated oil bath at 80 °C for 12 h. After completion of the reaction, formation of only trace amount of the product **4b** was observed.

Radical scavenger experiment: A pressure tube was charged with catalyst **Co5** (0.010 mmol, 2 mol%), pinacolborane (0.65 mmol, 1.3 equiv.), alkyne (0.5 mmol, 1 equiv.) and TEMPO/BHT (0.5 mmol, 1 equiv.). Then the reaction mixture was kept in a preheated oil bath at 80 °C for 12 h. After completion of the reaction, the pure product **4b** (yield: 79-83%) was isolated by column chromatography.

Mercury dropping experiment: A pressure tube was charged with catalyst **Co5** (0.010 mmol, 2 mol%), pinacolborane (0.65 mmol, 1.3 equiv.), alkyne (0.5 mmol, 1 equiv.) and mercury (1 mmol, 2 equiv.). Then the reaction mixture was kept in a preheated oil bath at 80 °C for 12 h. After completion of the reaction, the pure product **4b** (0.041 g, 0.13 mmol, 81%,) was isolated by column chromatography.

3. Deuterium labelling experiment:

(i) Procedure for cyclotrimerization of phenylacetylene-D_1: A pressure tube was charged with catalyst **Co1** (0.010 mmol, 2 mol%), pinacolborane (0.15 mmol, 0.3 equiv.), phenylacetylene-D_1 (0.5 mmol, 1 equiv.). Then the reaction mixture was allowed to stir at room temperature for 12 h. After completion of the reaction, the product **3b-D_1** was isolated by column chromatography over silica gel using hexane as an eluent. The ^{1}H NMR analysis of the product **3b-D_1** revealed the 87% D incorporation in the product.

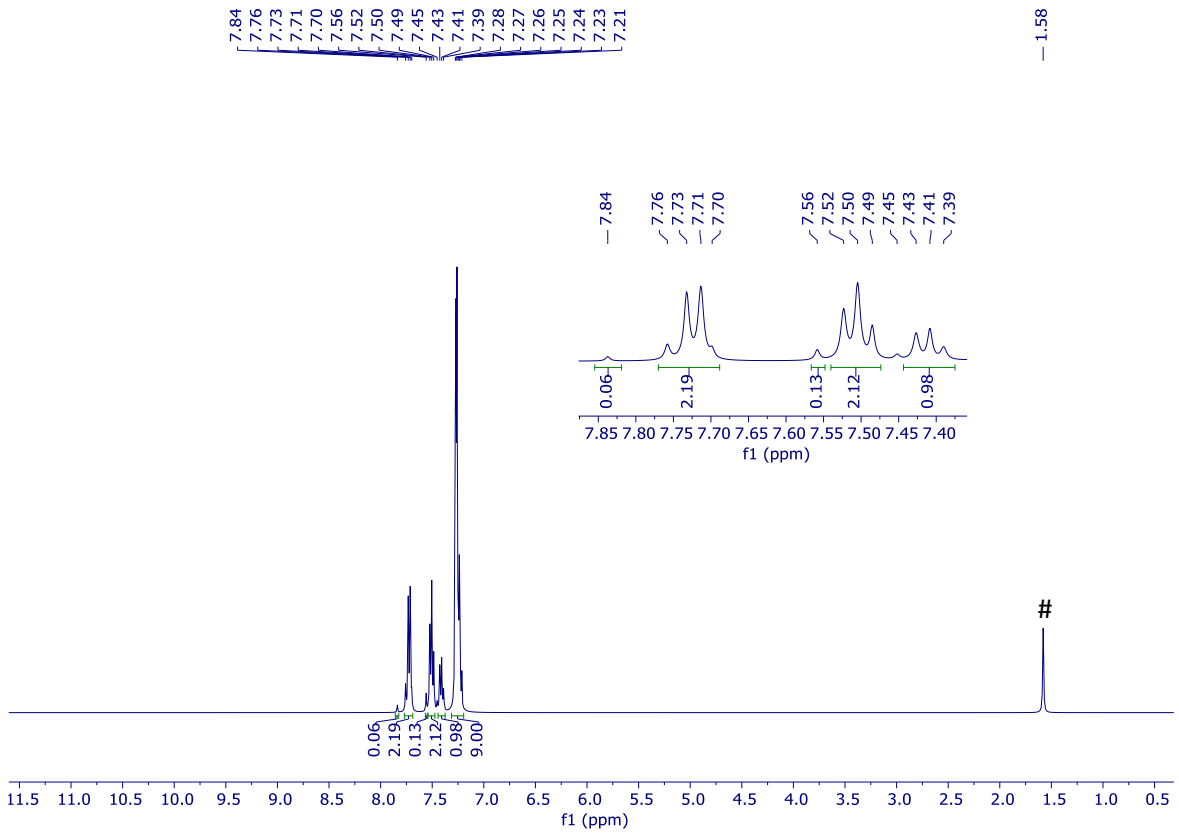


Figure S16. *^{1}H NMR of deuterium labelling experiment for cyclotrimerization reaction. # indicates the solvent impurity of H_2O in $CDCl_3$*

(ii) Procedure for hydroboration of phenylacetylene-D_1:

A pressure tube was charged with catalyst **Co5** (0.010 mmol, 2 mol%), pinacolborane (0.65 mmol, 1.3 equiv.), phenylacetylene-D_1 (0.5 mmol, 1 equiv.). Then the reaction mixture was kept in a preheated oil bath at 80 °C. After completion of the reaction, the compound, (*E*)-4,4,5,5-tetramethyl-2-(2-phenylvinyl-1-*D*)-1,3,2-dioxaborolane, was isolated as a pale-yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.2 Hz, 2H), 7.43-7.39 (m, 1H), 7.35-7.29 (m, 3H), 1.32 (s, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 149.6, 137.6, 129.0, 128.7, 127.2, 83.5, 25.2 ppm.

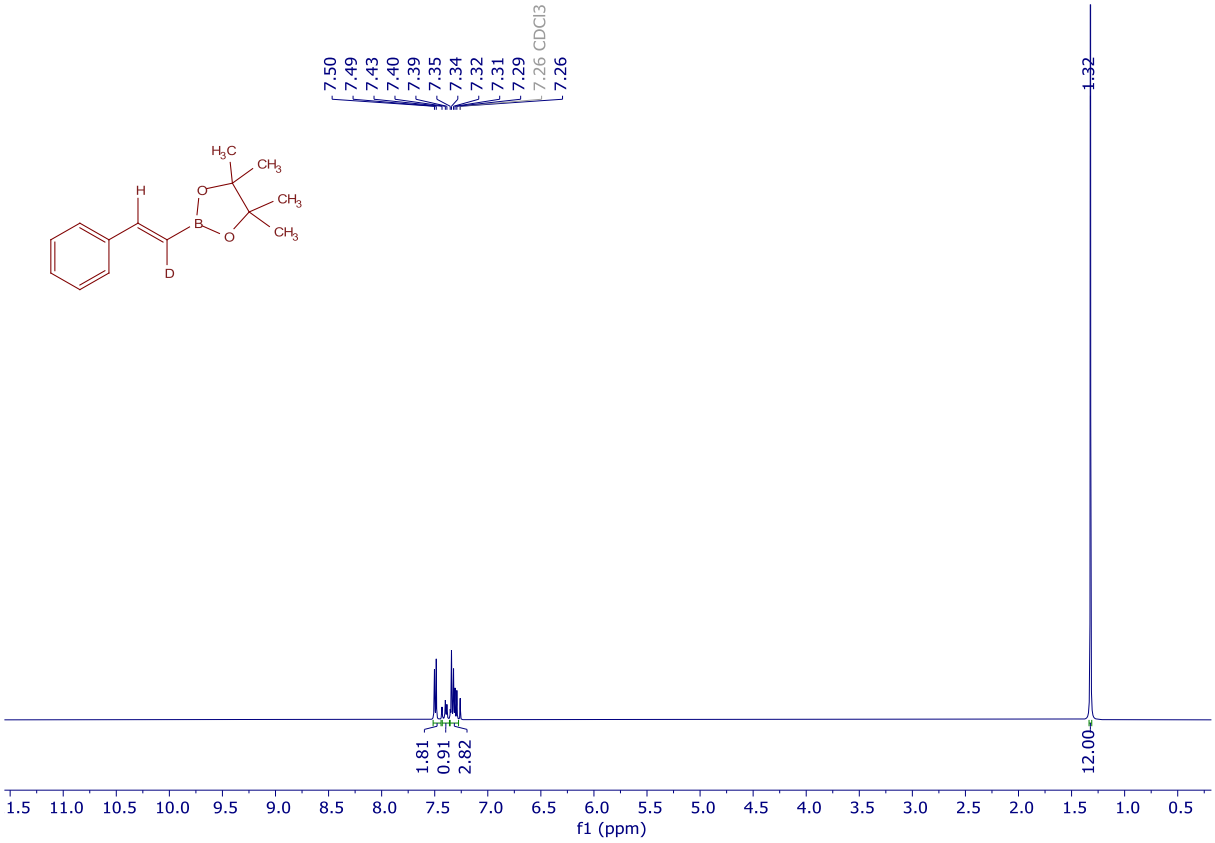


Figure S17. *^{1}H NMR of (E)-4,4,5,5-tetramethyl-2-(2-phenylvinyl-1-D)-1,3,2-dioxaborolane*

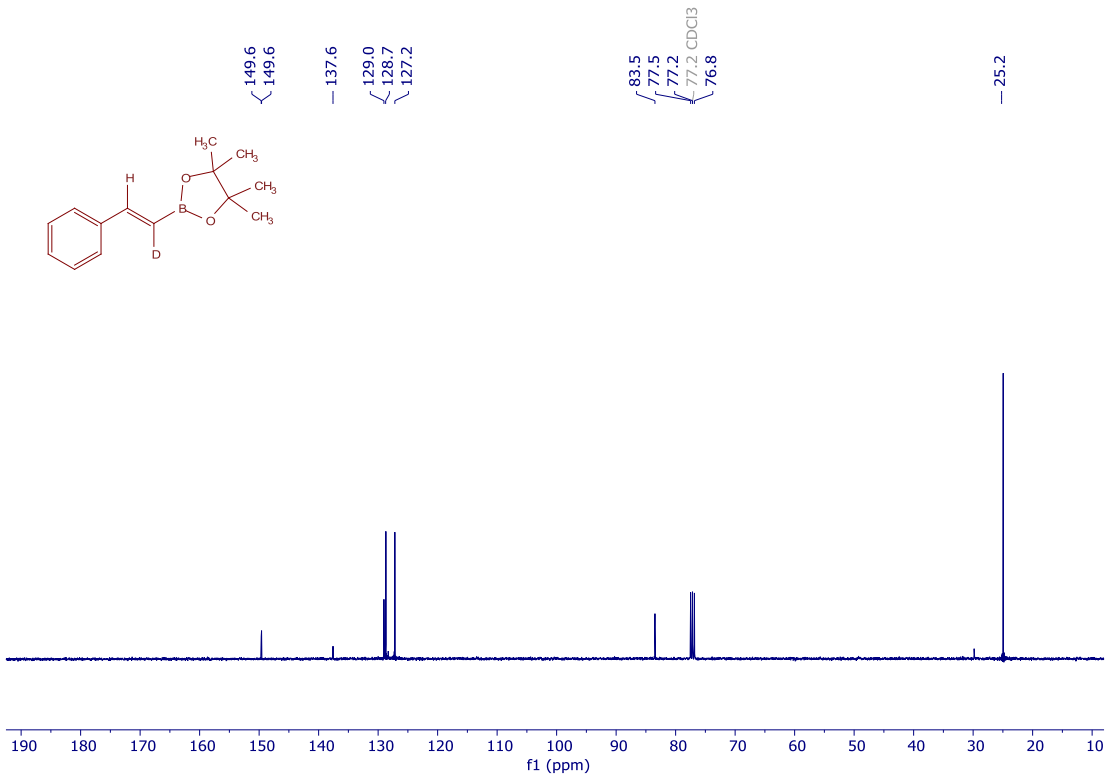
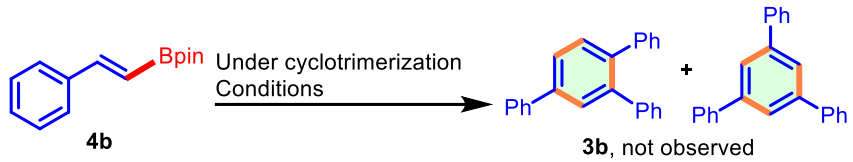


Figure S18. *$^{13}C\{^{1}H\}$ NMR of (E)-4,4,5,5-tetramethyl-2-(2-phenylvinyl-1-D)-1,3,2-dioxaborolane*

Scheme S2. Detection of intermediate



A pressure tube was charged with catalyst **Co1** (0.010 mmol, 2 mol%), pinacolborane (0.15 mmol, 0.3 equiv.) and **4b** (0.5 mmol). Then the reaction mixture was allowed to stir at room temperature for 12 h. After completion of the reaction, formation of the cyclotrimerized compound **3b** was not observed from TLC as well as GC-MS analysis.

4. *In situ* NMR monitoring experiment

(i) Procedure for detection of cobalt-hydride and possible intermediates (cyclotrimerization reaction)

Complex **Co1/Co2** (16/15 mg, 0.03 mmol) and pinacolborane (72 µL) were added in to a Young NMR tube. Subsequently, CD_3CN (0.5 mL) was added and the tube was closed with a PTFE stopper and allowed to stir at room temperature for 3 h. The mixture was then monitored using NMR and mass analysis (Figure S19-22). After adding phenylacetylene (110 µL, 0.045 mmol) into the same Young NMR tube, the reaction mixture was stirred at room temperature for 2 h and the outcome was monitored by GC-MS analysis.

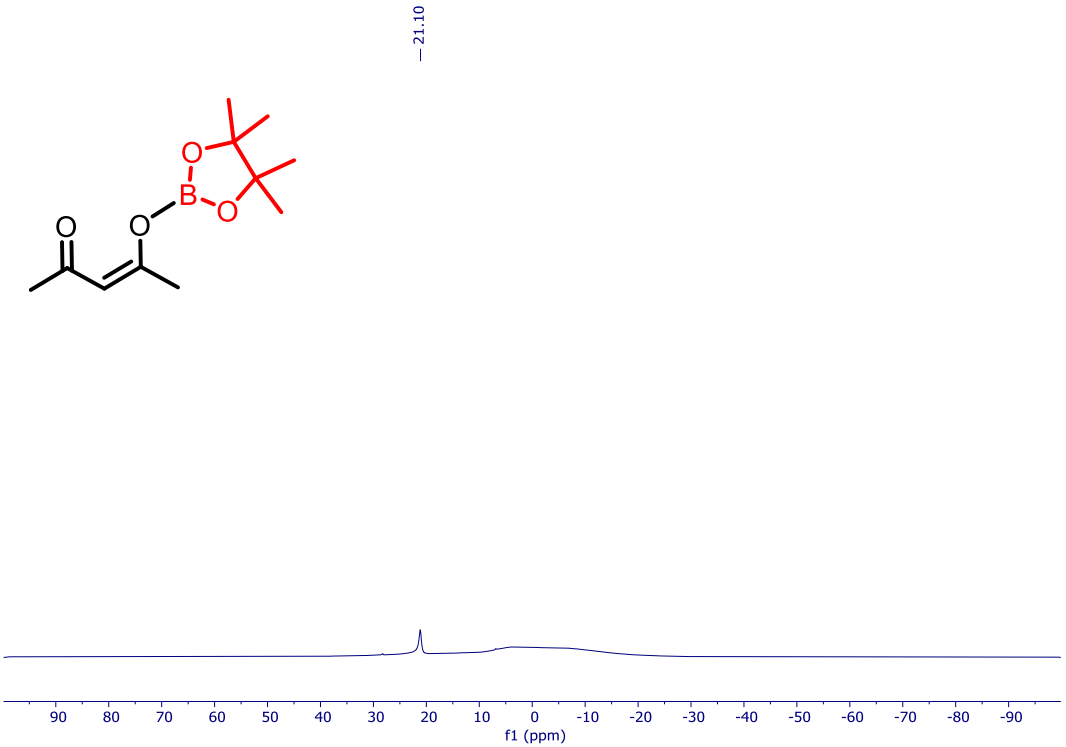


Figure S19. *^{11}B NMR spectrum of the reaction mixture between complex **Co1** and HBpin in CD_3CN (*) showing the formation of (acacBpin)*

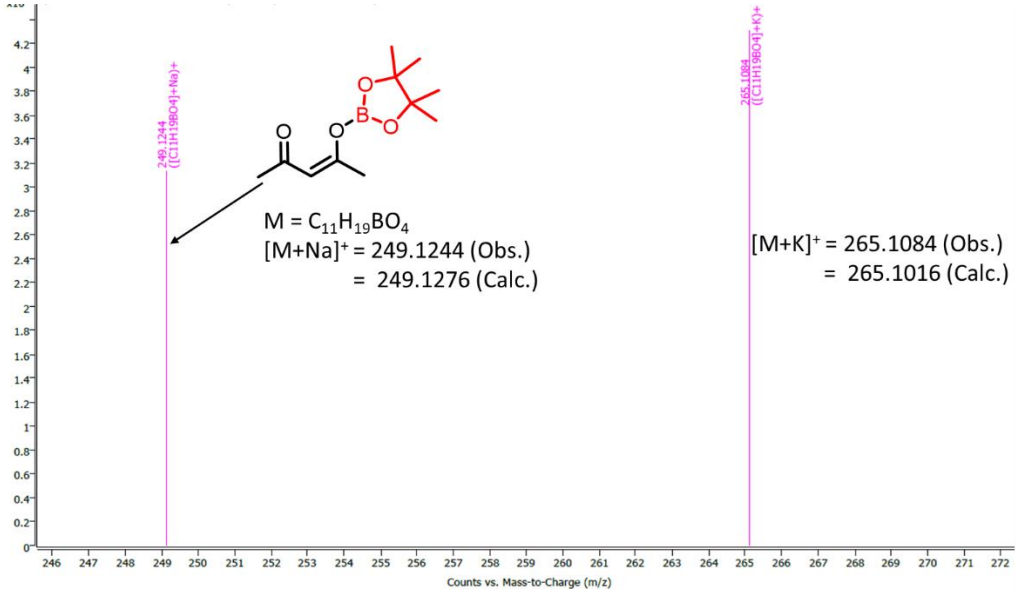


Figure S20. *Portion of ESI mass spectrum of the reaction mixture of a reaction between complex **Co1** and HBpin. M corresponds to molecular ion.*

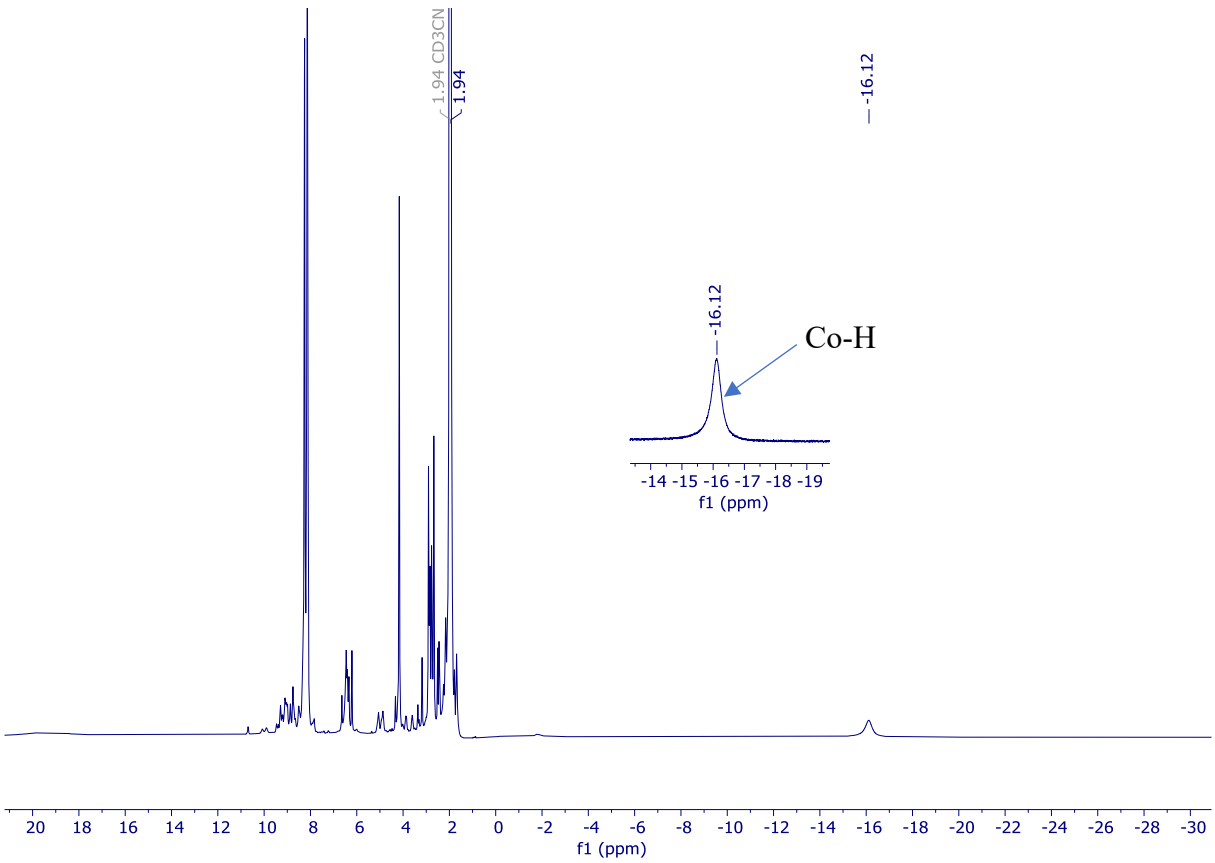


Figure S21. *^{1}H NMR spectrum of the reaction mixture of a reaction between complex **Co2** and HBpin in CD_3CN (*) showing the formation of a Co-H species*

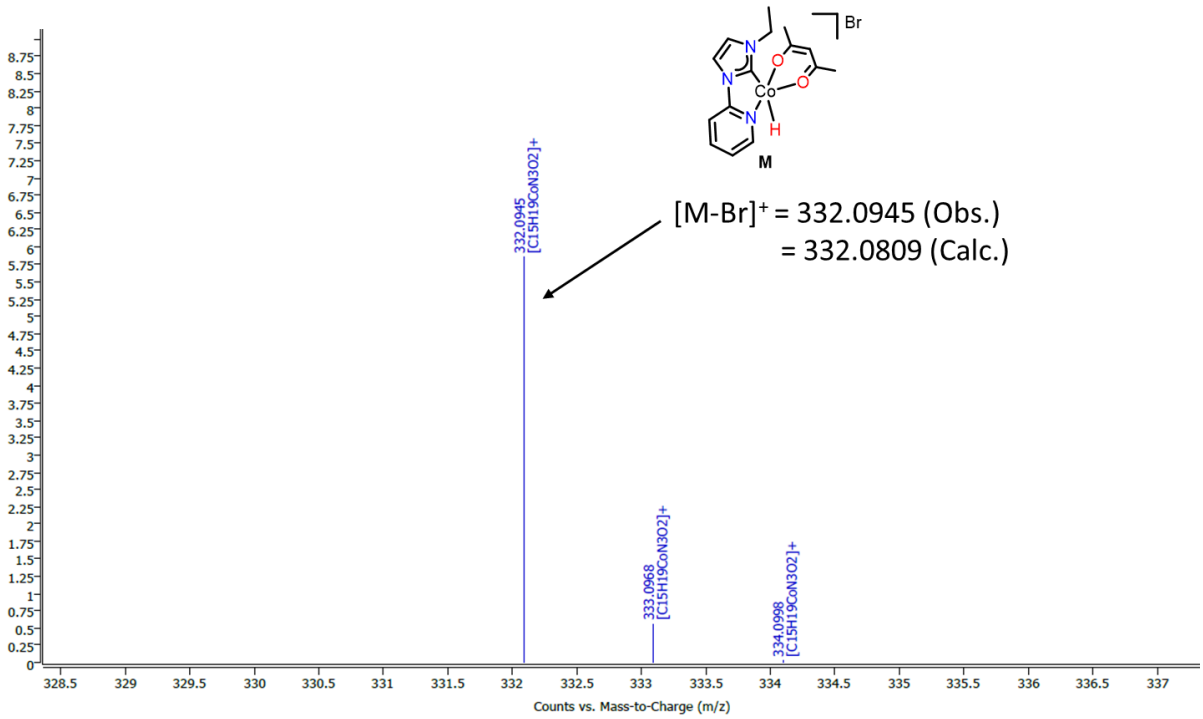


Figure S22. *Portion of ESI mass spectrum of the reaction mixture of a reaction between complex **Co2** and HBpin, showing the formation of anticipated cobalt-hydride species. M corresponds to molecular ion.*

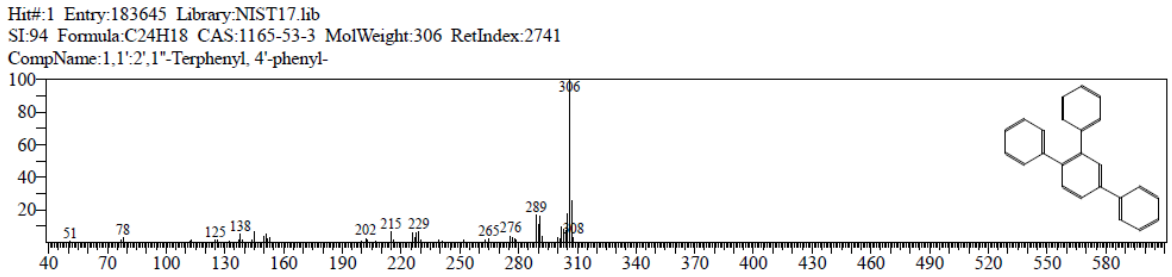


Figure S23. *GC-MS profile of the same reaction mixture, after the addition of phenylacetylene indicating the formation of the cyclotrimerized product (**3b**)*

ii) Procedure for the detection of cobalt-hydride and possible intermediates (hydroboration reaction)

Complex **Co5** (12 mg, 0.02 mmol) and pinacolborane (188 µL, 1.3 mmol) were added into a Young NMR tube. Subsequently, CD_3CN (0.5 mL) was added and the tube was closed with a PTFE stopper and allowed to stir at 80 °C for 1 h. The mixture was monitored using NMR analysis (Figure S24). Further, subsequent addition of phenylacetylene (109 µL, 1 mmol) into the same Young NMR tube, the reaction mixture was stirred at 80 °C for 4 h and the progress was monitored by NMR spectroscopy (Figure S25).

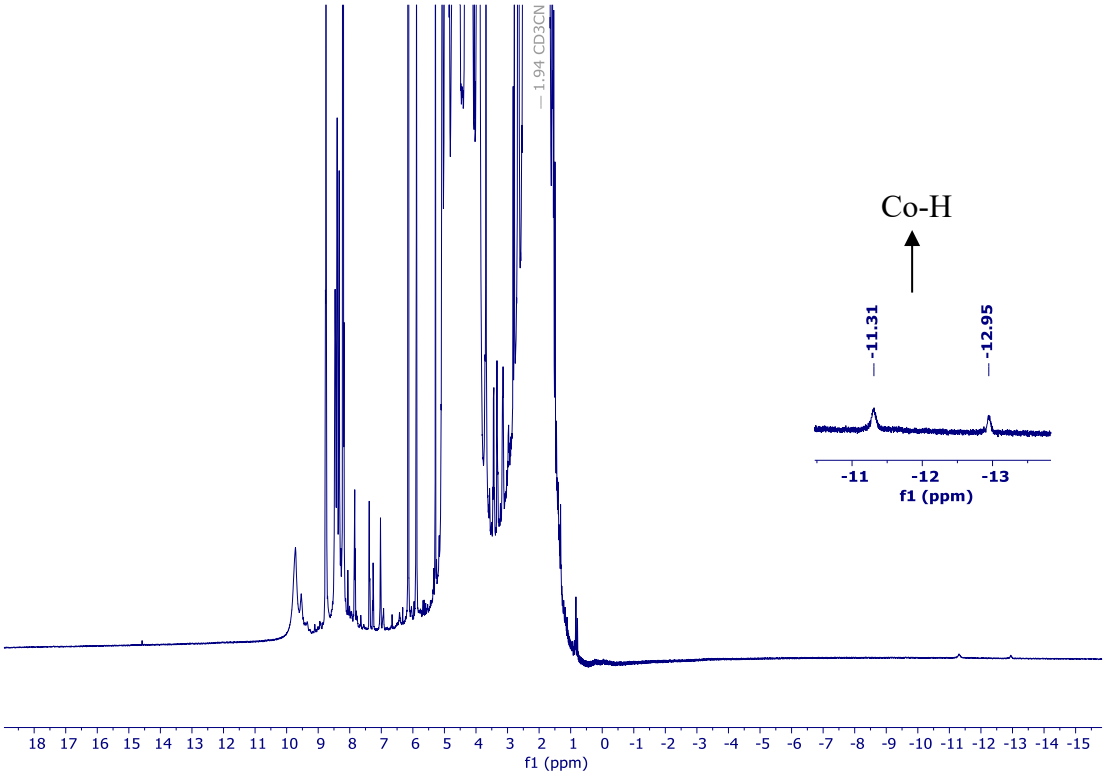


Figure S24. *^{1}H NMR spectrum of the reaction mixture of a reaction between complex **Co5** and HBpin in CD_3CN (*) showing the formation of a Co-H species*

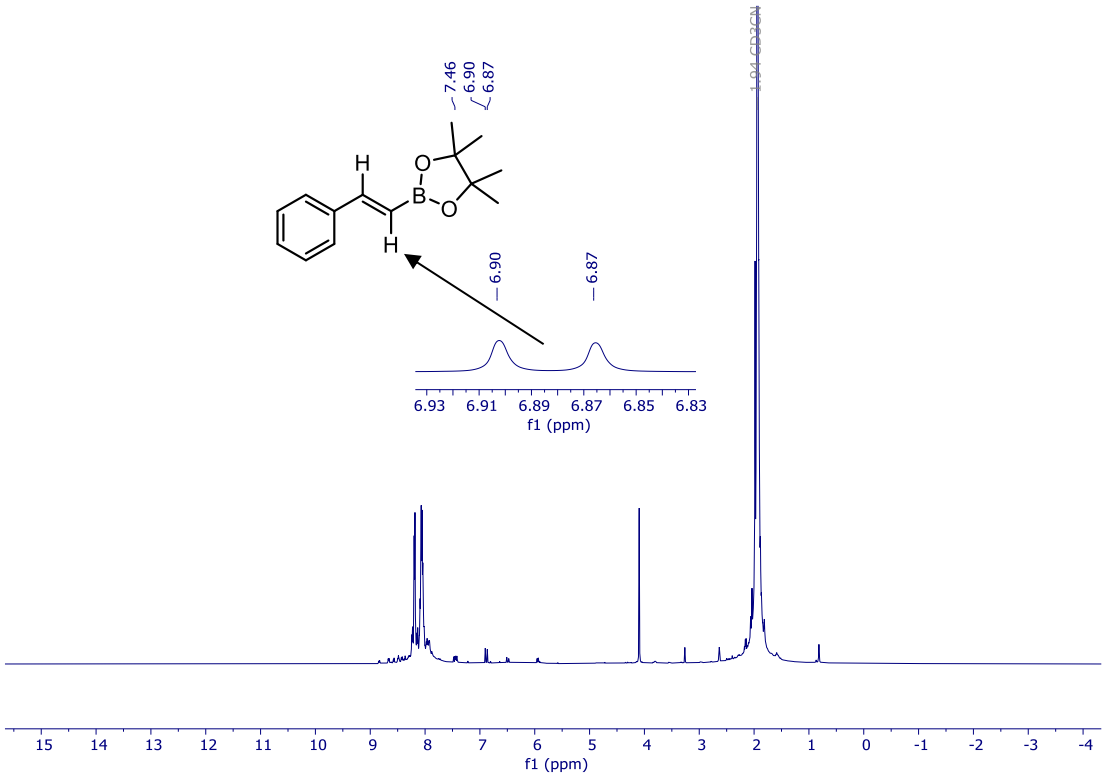


Figure S25. *^{1}H NMR spectrum of the same reaction mixture in CD_3CN (*) after the addition of 1 equiv. phenylacetylene indicating the formation of the hydroborated product (**4b**)*

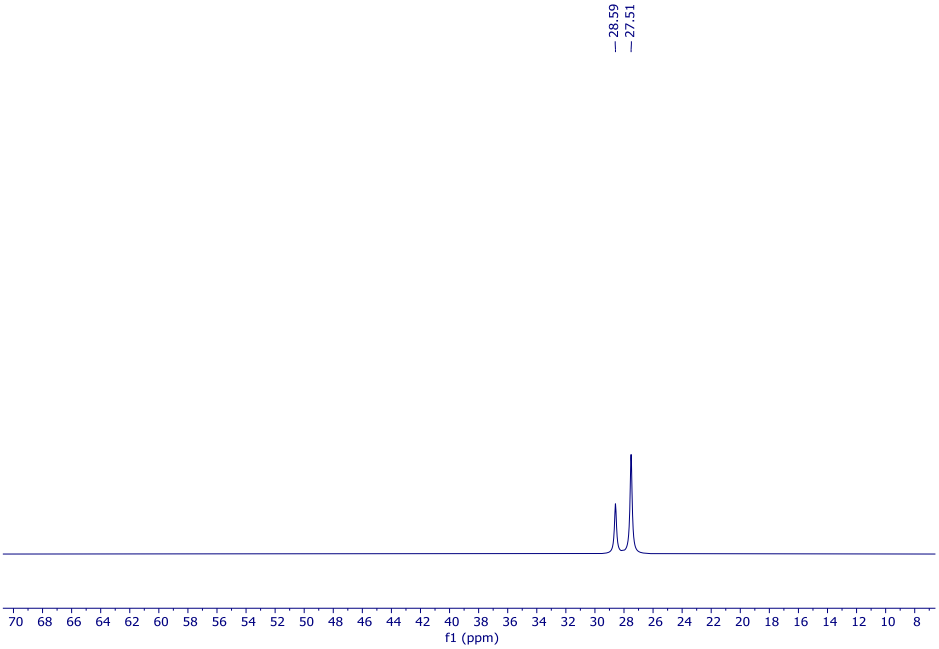
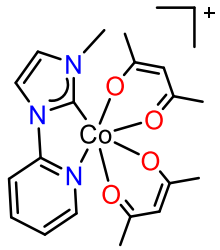


Figure S26. *^{11}B NMR spectrum of the reaction mixture between complex **Co5** and HBpin in CD_3CN (*)*

Computational details of the complexes Co1-3, Co5

All the calculations were performed using the Gaussian 16, Revision B.01 program.[6] All structures were optimized with B3LYP[7] functional. Co was treated with LANL2DZ (Loss Alamos National Laboratory 2 Double-Zeta) basis set, while the other atoms were treated using 6-31G**.[8]

Cartesian Coordinates of all the optimized geometries:



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6	3.915945859	-1.857433491	-0.269323930
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1	4.398265304	-1.021661485	-0.785829644
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6	0.898342554	1.612060901	-2.233885249
6	1.818168671	2.360972864	-1.487748810
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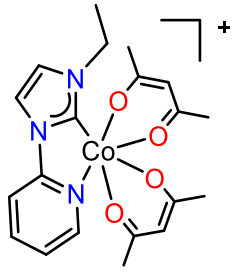

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6	-2.594641482	-2.652971928	-0.744936953
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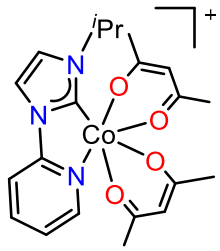

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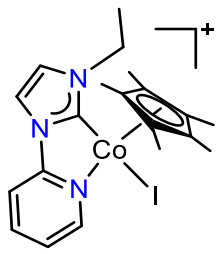

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1	3.490750871	3.718863551	-0.030328641
1	3.053190772	2.474804622	1.165134106
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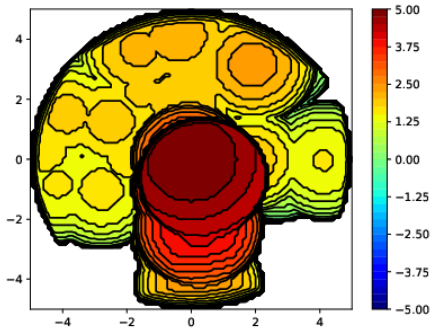
6	-0.437476378	3.432613177	-1.119864056
1	-1.163396420	4.220594736	-1.231751261

Analysis of steric properties

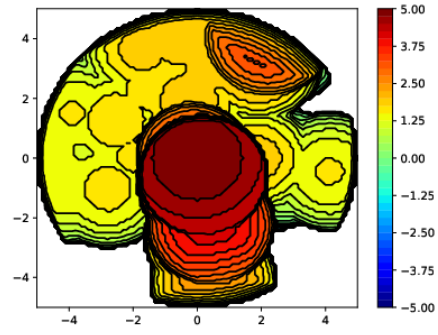
The %V_{bur} for the complexes **Co1-3** and **Co5** was calculated using the SambVca 2.0 tool.[9a] The bond radii were scaled by 1.17 and the sphere radius of 5 Å was chosen. A mesh spacing of 0.10 Å for the numerical integration was applied. Hydrogen atoms were neglected during the calculations. The steric map[9b] obtained for each case is given along with the %V_{bur} values.

a) Complex [(Co1-X]$^{2+}$, X = acac, (r = 5.0 Å)



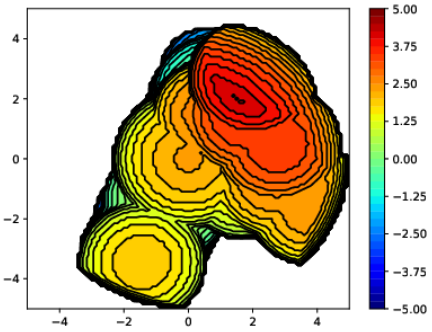
%V Free		**%V Buried**		% V Tot/V Ex	
52.9		**47.1**		99.9	
Quadrant	V f	V b	V t	%V f	%V b
SW	68.9	61.9	130.8	52.8	40.5
NW	60.6	70.2	130.8	46.2	45.9
NE	72.7	58.1	130.8	53.1	42.1
SE	70.3	60.5	130.8	59.5	59.9

b) Complex [(Co2-X]$^{2+}$, X = acac, (r = 5.0 Å)



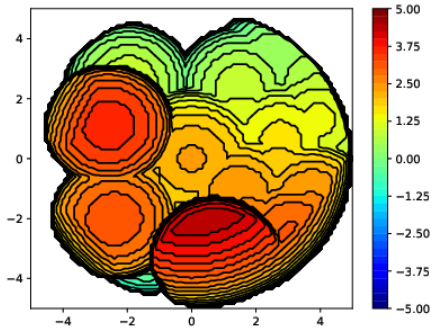
%V Free		**%V Buried**		% V Tot/V Ex	
50.5		**49.5**		99.9	
Quadrant	V f	V b	V t	%V f	%V b
SW	49.8	81.0	130.8	50.6	48.0
NW	40.2	90.6	130.8	48.1	46.1
NE	42.3	88.5	130.8	51.8	52.6
SE	39.5	91.3	130.8	51.5	51.3

c) Complex [(Co3-X]$^{2+}$, X = acac, (r = 5.0 Å)



%V Free		**%V Buried**		% V Tot/V Ex	
48.7		**51.3**		99.9	
Quadrant	V f	V b	V t	%V f	%V b
SW	50.1	80.7	130.8	44.1	50.1
NW	41.0	89.8	130.8	47.9	49.6
NE	44.3	86.5	130.8	49.3	52.6
SE	39.2	91.6	130.8	53.5	52.9

d) Complex [(Co5-X]$^{2+}$, X = I, (r = 5.0 Å)



%V Free		**%V Buried**		% V Tot/V Ex	
39.5		**60.5**		99.9	
Quadrant	V f	V b	V t	%V f	%V b
SW	40.2	90.6	130.8	30.7	69.3
NW	47.4	83.5	130.8	36.2	63.8
NE	63.7	67.1	130.8	48.7	51.3
SE	55.2	75.6	130.8	42.2	57.8

Single-Crystal X-ray Crystallography

Single crystal X-ray diffraction data were collected on a Bruker AXS Kappa Apex II equipped with a CCD detector (for **Co2**). The compound was measured using MoKα radiation (λ = 0.71073 Å).[10a] Crystals were selected using a polarizing optical microscope and then mounted in a crystal mounting loop using Paraton oil. The mounted crystal was then placed on a goniometer head and the crystal was centered with the help of a video microscope. The APEX2 and APEX2/SAINT programs were used for the data collection and unit cell refinement, respectively. Processing of the raw frame data was performed using SAINT/XPREP.[10b,c] The structure was solved by SHELXT-2014/5 and refined by full-matrix least squares techniques on F^2 using SHELXL-2019/2 computer program incorporated in WinGX program. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. The graphical representations were performed using the program Mercury.[10d] The crystal data (CCDC No. 2357116) and refinement details are summarized in Table S2.

Table S2. Crystallographic data for the complex **Co2**

Compound	**Co2**
CCDC No	2357116
Empirical formula	$C_{20}H_{25}BrCoN_3O_4 \cdot H_2O$
Formula weight	528.28
Crystal system	Monoclinic
Space group	*P* 2(1)/c
a (Å)	9.5864 (18)
b (Å)	13.892 (2)
c (Å)	17.545 (4)
α (°)	90
β (°)	100.802 (9)
γ (°)	90
V ($Å^3$)	2295.1 (7)
Z	4
D calc (Mg/m^3)	1.529
F (000)	1080
μ (mm^{-1})	2.523
θ Range (°)	1.883 to 24.811
Crystal size (mm)	0.180 x 0.150 x 0.120
No. of total reflns collected	17678
No. of unique reflns [$I > 2\sigma(I)$]	3952
Data/restraints/ parameters	3952/ 16 /284
Goodness-of-fit on F^2	1.046
Final R indices [$I > 2\sigma(I)$]	0.0558, 0.1491
R indices (all data)	0.0972, 0.1723

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