Supplementary Information (SI) for RSC Mechanochemistry.

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Mechanochemical McMurry reaction

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1. General Information

Unless specified otherwise, all the reactions have been performed under air in a 5 ml Stainless steel jar brought from Retsch. 10mm SS ball and Zr ball brought from Amazon India and Retsch. Reaction temperatures correspond to the temperature of the bath surrounding the vessel. Analytics: ^{1}H, ^{13}C and ^{19}F NMR spectra has been recorded on Bruker (^{1}H: 500 MHz, ^{13}C {^{1}H}: 126 MHz, ^{19}F {^{1}H}: 470 MHz) and JEOL (^{1}H: 400 MHz, ^{13}C {^{1}H}: 101 MHz, ^{19}F {^{1}H}: 376 MHz) at room temperature and were referenced to the resonances of the solvent used. Multiplicities have been indicated as: br (broad), s (singlet), d (doublet), t (triplet), dd (doublet of doublet), dt (doublet of triplet) or m (multiplet). Coupling constants (J) are reported in Hertz (Hz). For thin-layer chromatography (TLC) analysis, Merck pre-coated TLC plates (silica gel 60 F254 0.25 mm) were used, and visualization was accomplished by UV light (254 nm), I2, KMnO4, and cerium molybdate.

Chemicals: Commercially available chemicals were bought from Sigma–Aldrich, Alfa–Aesar, Avra Synthesis, BLD Pharma, and used without further purification.

2. Mechanochemical setup in the lab

Reaction setup 1

10 mm stainless steel ball

5 mL stainless steel ball

Reaction setup 2

10 mm Teflon ball

5 mL Teflon tube

Reaction setup: Teflon tube inside SS jar

Retsch MM400 mixer mill

3. General procedure for Solid-state mechanochemical McMurry reaction

Procedure for setup 1

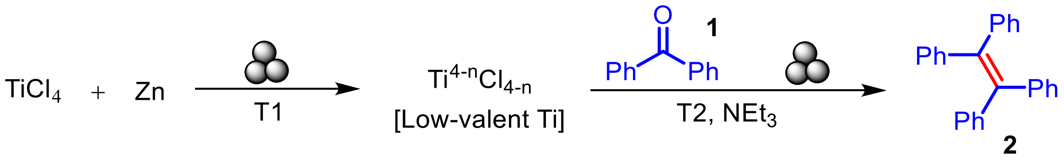
Zn powder (1.2 mmol) and $TiCl_4$ (0.6 mmol) were placed in a 5 mL stainless steel (ss, 316 grade) milling jar with two 10 mm ss balls. The jar was then closed in the open air and placed in the ball mill (Retsch MM 400). After grinding for 90 min at 30 Hz frequency, the jar was opened in air, and then Et_3N (0.7 mmol) and the carbonyl compound (0.1 mmol) were added. The jar was again closed in the open air and placed in the ball mill. After grinding for 120 min at 30 Hz, the jar was opened in air and neutralised with saturated $NaHCO_3$ solution (5 mL). The organics were extracted with CH_2Cl_2 (2 × 10 mL), filtered over celite, dried over Na_2SO_4, and evaporated in *vacuo*. Crude yields of the products were determined by GC-FID analysis using mesitylene as the internal standard. The product was then isolated via flash column chromatography (SiO_2).

Procedure for setup 2

Zn powder (1.2 mmol) and $TiCl_4$ (0.6 mmol) were placed in a 5 ml Teflon tube, and that was placed in a teflon capsule with two 10 mm Teflon balls. The jar was then closed in the open air and placed in the ball mill (Retsch MM 400). After grinding for 90 min at 30 Hz frequency, the jar was opened in air, and then Et_3N (0.7 mmol) and the carbonyl compound (0.1 mmol) were added. The jar was again closed in the open air and placed in the ball mill (Retsch MM 400). After grinding for 120 min at 30 Hz, the jar was opened in air and neutralised with saturated $NaHCO_3$ solution (5 ml). The organics were extracted with CH_2Cl_2 (2 × 10 mL), filtered over celite, dried over Na_2SO_4, and evaporated in *vacuo*. Crude yields of the products were determined by GC-FID analysis using mesitylene as the internal standard. The product was then isolated via flash column chromatography (SiO_2).

4. Detailed optimization of the reaction condition

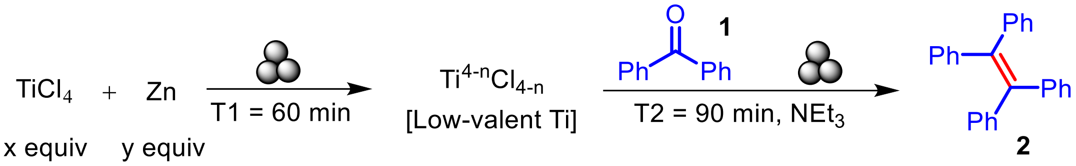
Table S1: Effect of time:[a]



Entry	T1 (min)	T2 (min)	Yield (%)[a]
1	30	90	trace
2	60	90	64
3	90	90	83
4	60	120	99

[a]Reaction condition: **1** (0.1 mmol), Zn (1.2 mmol, 68 mg), $TiCl_4$ (0.6 mmol, 65 µL), Et_3N (7 equiv.), 30 Hz, 5 mL SS jar, two 10 mm SS balls. Yields are determined *via* GC-FID analysis of crude reaction mixture using mesitylene as an internal standard.

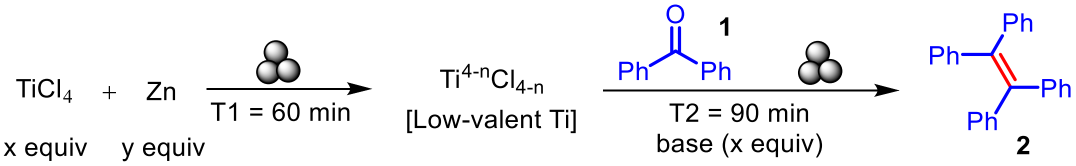
Table S2: Effect of equiv. of Zn and $TiCl_4$:[a]



Entry	$TiCl_4$ (x equiv.)	Zn (y equiv.)	Yield (%)[a]
1	4	6	15
2	4	8	42
3	4	10	45
4	6	6	34
5	6	10	47
6	6	12	64

[a]Reaction condition: **1** (0.1 mmol), Zn (x equiv.), $TiCl_4$ (y equiv.), Et_3N (0.7 equiv., 97 µL), 30 Hz, 5 mL SS jar, two 10 mm SS balls. Yields are determined *via* GC-FID analysis of crude reaction mixture using mesitylene as an internal standard.

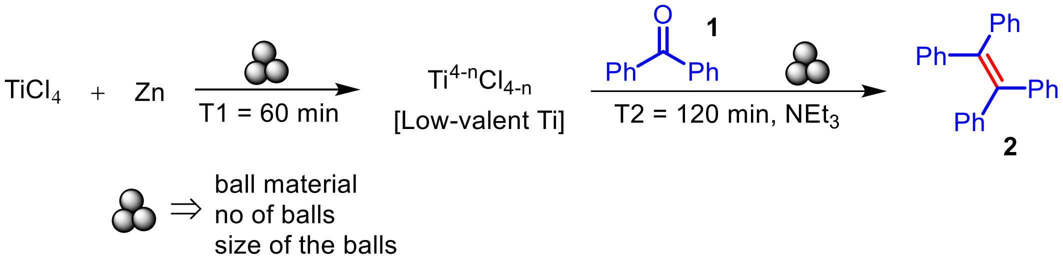
Table S3: Effect of Base:[a]



Entry	Base	x equiv.	Yield (%)[a]
1	Et_3N	7.0	64
2	pyridine	7.0	12
3	4-pyridinecarbonitrile	10	2
4	KOAc	6	40
5	K_2CO_3	10	13
6	$KHCO_3$	12	trace
7	Et_3N	4.5	40
8	Et_3N	3.0	15

[a]Reaction condition: **1** (0.1 mmol), Zn (1.2 mmol, 68 mg), $TiCl_4$ (0.6 mmol, 65 µL), Base (x equiv.), 30 Hz, 5 mL SS jar, two 10 mm SS balls. Yields are determined *via* GC-FID analysis of crude reaction mixture using mesitylene as an internal standard.

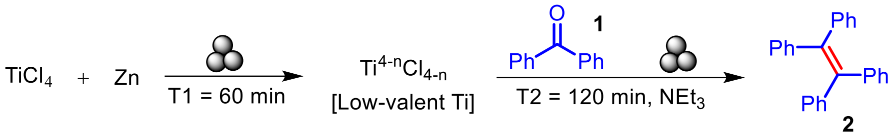
Table S4: Effect of milling parameters:[a]



Entry	Ball material	Size (x mm)	No of balls (X)	Yield (%)[a]
1	SS	10	2	99
2	SS	10	1	63
3	SS	5	4	60
4[b]	SS	10	2	75
5	Zr	10	2	94
6	Teflon	10	2	70
7[c]	Teflon	10	2	97

[a]Reaction condition: **1** (0.1 mmol), Zn (1.2 mmol, 68 mg), $TiCl_4$ (0.6 mmol, 65 µL), Et_3N (7 equiv.), 30 Hz, 5 mL SS or Teflon jar, two 10 mm SS or Zr or Teflon balls. Yields are determined *via* GC-FID analysis of crude reaction mixture using mesitylene as an internal standard. [b]20Hz frequency instead of 30Hz. [c]Teflon capsule is used in stainless steel jar.

5. Green metrics calculation for mechanochemical Mcmurry reaction



Entry	Molecular weight (au)	Scale of reaction (mmol)	Mass (g)
$TiCl_4$	189.679	0.6	0.1138
Zn	65.38	1.2	0.0784
1	182.217	0.1	0.0182
NEt_3	101.191	0.7	0.0708
2	332.446	0.0495	0.01645
$NaHCO_3$	84.007	-	0.115
H_2O	18.0153	5 mL	4.98
CH_2Cl_2	84.93	20 mL	26.6
Celite	-	-	5.0
Na_2SO_4	142.04	-	10.0
Silica gel	-	-	60.0
Ethyl acetate	86.178	1.5 mL	1.34
Hexane	88.11	148.5 mL	98.01

1) Atom economy

$$\text{Atom economy} = \frac{\text{Molecular mass of desired product}}{\text{Molecular mass of reactants}} \text{ X } 100\%$$

$$\text{Atom economy} = \frac{332.446}{182.217 + 182.217} \text{ X } 100\%$$

$$\text{Atom economy} = \frac{332.446}{364.434} \text{ X } 100\%$$

$$\text{Atom economy} = 91.22\%$$

2) Atom efficiency

$$\text{Atom efficiency} = (\%\text{ Yield of desired product X \% Atom economy})/\ 100\%$$

$$\text{Atom efficiency} = 99 \text{ X } 91.22\ /\ 100\%$$

$$\text{Atom efficiency} = 90.31\%$$

3) Carbon economy

$$\text{Carbon economy} = \frac{\text{Number of carbon atoms in desired product}}{\text{Number of carbon atoms in reactants}} \text{ X } 100\%$$

$$\text{Carbon economy} = \frac{26}{26} \text{ X } 100\%$$

$$\text{Carbon economy} = 100.00\%$$

4) Percentage yield

$$\text{Percentage yield} = \frac{\text{Actual mass of product}}{\text{Theoretical mass of product}} \text{ X } 100\%$$

$$\text{Percentage yield} = \frac{0.01645\text{ g}}{0.01662\text{ g}} \text{ X } 100\%$$

$$\text{Percentage yield} = 98.97\%$$

5) Reaction mass efficiency

$$\text{Reaction mass efficiency} = \frac{\text{Mass of isolated product}}{\text{Mass of all reactants}} \text{ X } 100\%$$

$$\text{Reaction mass efficiency} = \frac{0.0161\text{ g}}{0.0182 + 0.0182\text{ g}} \text{ X } 100\%$$

$$\text{Reaction mass efficiency} = \frac{0.0161\text{ g}}{0.0364} \text{ X } 100\%$$

$$\text{Reaction mass efficiency} = 44.23\%$$

6) Effective mass efficiency

$$\text{EME} = \frac{\text{Actual mass of desired product}}{\text{Mass of non-benign reagents}} \text{ X } 100\%$$

$$\text{EME} = \frac{0.01645}{} \text{ X } 100\%$$

$$\text{EME} = 1.645\%$$

7) Environmental factor

$$\text{E-factor} = \frac{\text{Amount of total waste}}{\text{Amount of product}}$$

$$\text{E-factor} = \frac{\begin{array}{c} 0.1138 + 0.0784 + 0.0182 + \\ 0.0182 + 0.0708 - 0.01645\text{ g} \end{array}}{0.01645\text{ g}}$$

$$\text{E-factor} = 17.20$$

8) The Eco Scale

Sr.no.	Parameter		Penalty points
1	Yield	(100 - 99%)/2	0.5
2	Price of reaction components (to obtain 0.1 mmol of end product)	Inexpensive (< $10)	0
3	Safety	Dangerous for environment	5
4	Technical setup	Common setup	0
5	Temperature/ Time	No heating, > 1 h	3
6	Workup and purification	Classical chromatography	10
			Total penalty points = 18.5

9) Process mass intensity (PMI)

$$\text{PMI} = \frac{\text{Total mass of process}}{\text{Mass of product}}$$

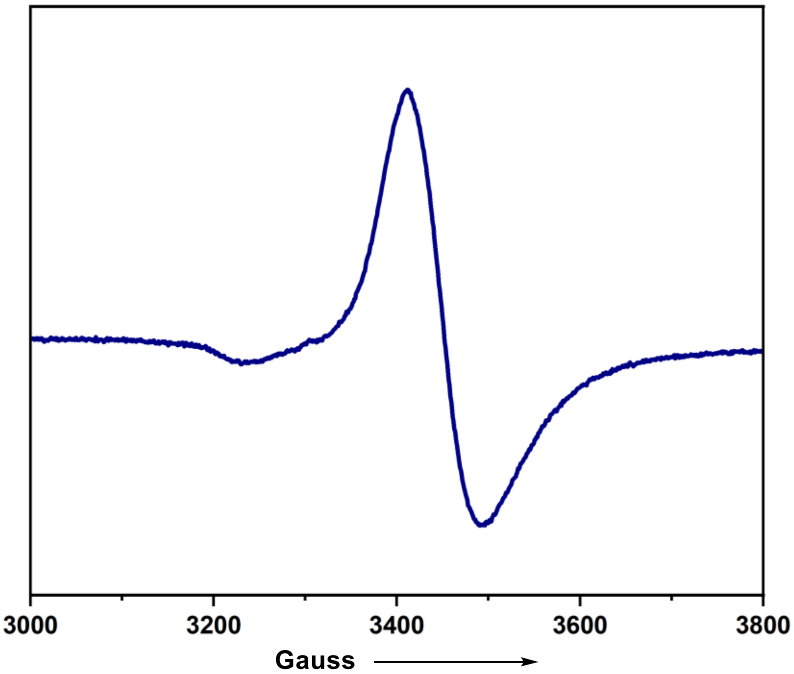
$$\text{PMI} = \frac{0.1138 + 0.0784 + 0.0182 + 0.0182 + 0.0708 \text{ g}}{0.01645 \text{ g}}$$

$$\text{PMI} = \frac{0.2994}{0.01645}$$

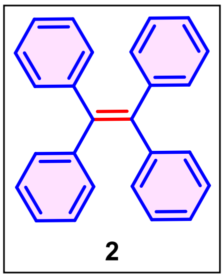
$$\text{PMI} = 18.20$$

6. EPR spectroscopic study

Zn powder (2.4 mmol) and $TiCl_4$ (1.2 mmol) were placed in a Teflon tube, and that was placed in a teflon capsule with two 10 mm Teflon balls. The jar was then closed in the open air and placed in the ball mill (Retsch MM 400). After grinding for 30 min at 30 Hz frequency, the jar was opened and the semi solid was instantly taken in a EPR tube and freeze it in liq N_2 and the EPR was measured in 85 K. The species obtained was characterized as Ti^{3+} intermediate by EPR spectroscopy. The spectrum obtained shows an isotopic species with S = 1/2 and g value 1.93.



7. Characterisation of product

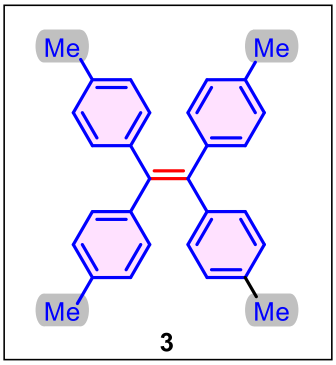


2

1,1,2,2-tetraphenylethene (2)[1] Prepared according to the general procedure as described above. It was purified by flash chromatography with hexane/ethyl acetate in 1% mixture (R_f = 0.4) to afford a white solid. Yield 16.0 mg (0.048 mmol, 97%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 8H), 7.62 – 7.57 (m, 4H), 7.51 – 7.46 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 141.1, 131.4, 127.7, 126.5.

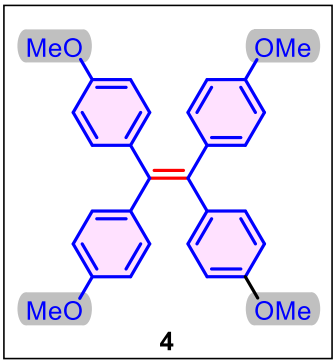


3

1,1,2,2-tetra-*p*-tolylethene (3)[2] Prepared according to the general procedure as described above. It was purified by flash chromatography with hexane/ethyl acetate in 1% mixture (R_f = 0.4) to afford a white solid. Yield 17.5 mg (0.045 mmol, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.2 Hz, 8H), 7.20 (dt, J = 7.9, 0.7 Hz, 8H), 2.36 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 139.9, 135.7, 131.3, 128.4, 21.3.

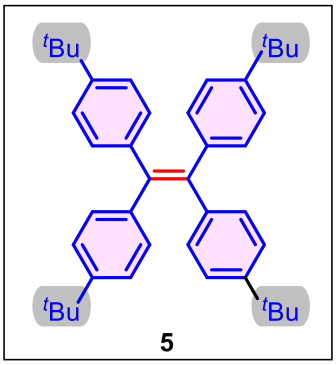


4

1,1,2,2-tetrakis(4-methoxyphenyl) ethene (4)[3] Prepared according to the general procedure as described above. It was purified by flash chromatography with hexane/ethyl acetate in 2% mixture ($R_f = 0.3$) to afford a white solid. Yield 21.4 mg (0.0475 mmol, 95%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 6.93 (d, $J = 8.8$ Hz, 8H), 6.64 (d, $J = 8.8$ Hz, 8H), 3.74 (s, 12H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 157.9, 138.5, 137.0, 132.6, 113.1, 55.2.

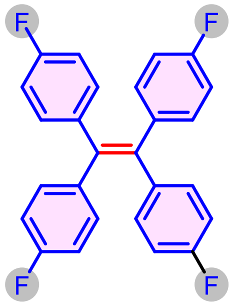


5

1,1,2,2-tetrakis(4-isopropylphenyl) ethene (5)[2] Prepared according to the general procedure as described above. It was purified by flash chromatography with hexane/ethyl acetate in 1% mixture ($R_f = 0.4$) to afford a brown solid. Yield 26.6 mg (0.048 mmol, 96%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.06 (d, $J = 8.5$ Hz, 1H), 6.92 (d, $J = 8.7$ Hz, 1H), 1.24 (s, 6H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 148.8, 141.0, 130.9, 124.1, 34.3, 31.2.

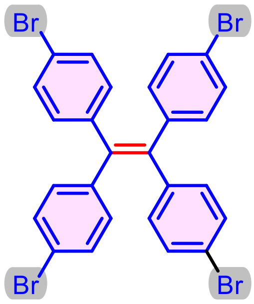


6

1,1,2,2-tetrakis(4-fluorophenyl) ethene (6)[4] Prepared according to the general procedure as described above. It was purified by flash chromatography with hexane/ethyl acetate in 1% mixture ($R_f = 0.5$) to afford a white solid. Yield 18.8 mg (0.0465 mmol, 93%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (dd, $J = 8.8, 5.5$ Hz, 8H), 6.82 (t, $J = 8.7$ Hz, 8H).

^{13}C NMR (126 MHz, $CDCl_3$) 162.9, 160.4, 139.2 (d, $J = 3.5$ Hz), 132.9 (d, $J = 7.9$ Hz), 115.0 (d, $J = 21.4$ Hz).

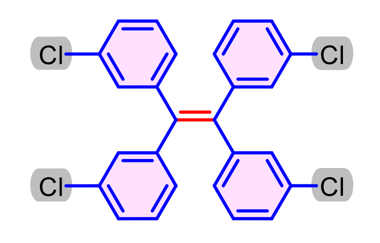


7

1,1,2,2-tetrakis(4-bromophenyl) ethene (7)[5] Prepared according to the general procedure as described above. It was purified by flash chromatography with hexane/ethyl acetate in 1% mixture ($R_f = 0.4$) to afford a white solid. Yield 30.8 mg (0.048 mmol, 96%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, $J = 8.7$ Hz, 8H), 6.84 (d, $J = 8.6$ Hz, 8H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 139.7, 132.8, 131.4, 121.4.

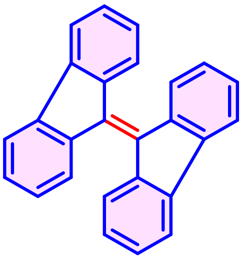


8

1,1,2,2-tetrakis(3-chlorophenyl)ethene (8)[6] Prepared according to the general procedure as described above. It was purified by flash chromatography with hexane/ethyl acetate in 1% mixture ($R_f = 0.4$) to afford a white solid. Yield 20.3 mg (0.0435 mmol, 87%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.16 (ddd, *J* = 8.0, 2.1, 1.1 Hz, 4H), 7.10 (t, *J* = 7.8 Hz, 4H), 7.00 (t, *J* = 1.9 Hz, 4H), 6.90 (dt, *J* = 7.6, 1.3 Hz, 4H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 143.8, 140.1, 134.0, 130.8, 129.3, 129.2, 127.5.

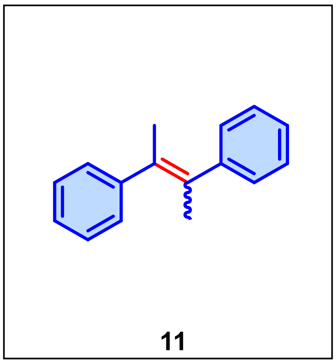


9

9,9'-bifluorenylidene (9)[7] Prepared according to the general procedure as described above. It was purified by flash chromatography with hexane/ethyl acetate in 1% mixture ($R_f = 0.3$) to afford a white solid. Yield 15.7 mg (0.048 mmol, 96%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.39 (dt, *J* = 7.8, 0.9 Hz, 4H), 7.71 (ddd, *J* = 7.6, 1.3, 0.7 Hz, 4H), 7.33 (td, *J* = 7.4, 0.9 Hz, 4H), 7.23 – 7.18 (m, 4H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 141.4, 141.1, 138.4, 129.3, 127.0, 126.8, 120.0.

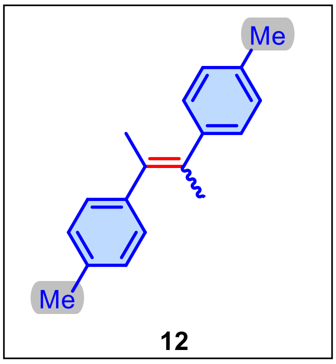


11

But-2-ene-2,3-diyldibenzene (11)[8] Prepared according to the general procedure as described above. It was purified by flash chromatography with hexane/ethyl acetate in 1% mixture (R_f = 0.4) to afford a white solid. Yield 10 mg (0.048 mmol, 96%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.30 – 7.27 (m, 2H), 7.10 – 7.04 (m, 4H), 7.04 – 6.99 (m, 2H), 6.98 – 6.93 (m, 4H), 2.17 (s, 6H), 1.88 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.2, 132.1, 129.2, 128.3, 128.2, 127.5, 127.5, 125.5, 29.7, 21.5.

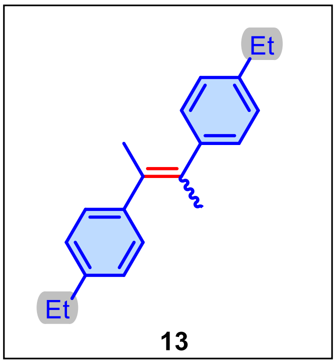


12

4,4'-(but-2-ene-2,3-diyl)bis(methylbenzene) (12)[9] Prepared according to the general procedure as described above. It was purified by flash chromatography with hexane/ethyl acetate in 1% mixture (R_f = 0.4) to afford a white solid. Yield 11.2 mg (0.0475 mmol, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.11 (m, 2H), 6.93 – 6.84 (m, 7H,), 2.38 (s, 1H), 2.24 (s, 6H), 2.14 (s, 6H), 1.88 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 141.6, 135.6, 134.8, 132.6, 132.2, 129.0, 128.8, 128.2, 128.1, 22.5, 21.6, 21.1, 21.0.

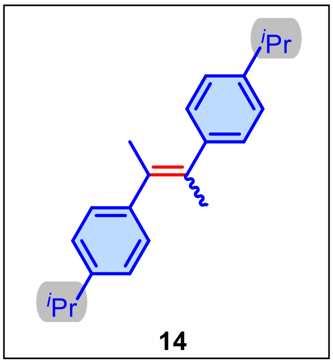


13

4,4'-(but-2-ene-2,3-diyl) bis(ethylbenzene) (13)[10] Prepared according to the general procedure as described above. It was purified by flash chromatography with hexane/ethyl acetate in 1% mixture ($R_f = 0.4$) to afford a white solid. Yield 12.5 mg (0.0475 mmol, 95%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.20 (s, 2H), 6.94 – 6.85 (m, 8H), 2.67 (q, $J = 7.6$ Hz, 1H), 2.54 (q, $J = 7.6$ Hz, 4H), 2.15 (s, 6H), 1.89 (s, 2H), 1.27 (t, 1H), 1.16 (t, $J = 7.6$ Hz, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 142.0, 141.2, 132.3, 129.1, 128.3, 127.6, 127.0, 28.6, 28.4, 22.6, 21.6, 15.5, 15.4.

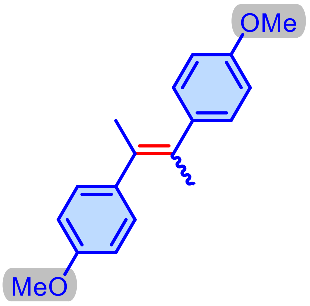


14

1,1,2,2-tetrakis(4-isopropylphenyl) ethene (14)[11] Prepared according to the general procedure as described above. It was purified by flash chromatography with hexane/ethyl acetate in 1% mixture ($R_f = 0.4$) to afford a white solid. Yield 13.7 mg (0.047 mmol, 94%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.24 – 7.18 (m, 4H), 6.97 – 6.83 (m, 8H), 2.93 (p, $J = 6.9$ Hz, 1H), 2.78 (h, $J = 7.0$ Hz, 2H), 2.15 (d, $J = 1.7$ Hz, 6H), 1.90 (d, $J = 1.8$ Hz, 3H), 1.32 – 1.23 (m, 8H), 1.17 (dd, $J = 6.8, 1.7$ Hz, 12H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 146.7, 145.9, 142.1, 142.0, 132.7, 132.4, 129.1, 128.3, 126.1, 125.5, 33.8, 33.6, 29.8, 24.1, 24.0, 22.6, 21.6.

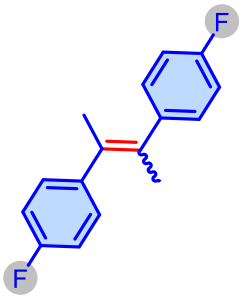


15

4,4'-(but-2-ene-2,3-diyl)bis(methoxybenzene) (15)[9] Prepared according to the general procedure as described above. It was purified by flash chromatography with hexane/ethyl acetate in 1% mixture ($R_f = 0.4$) to afford a white solid. Yield 12.6 mg (0.047 mmol, 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, $J = 8.6$ Hz, 1H), 6.91 (d, $J = 10.3$ Hz, 1H), 6.89 (d, $J = 8.7$ Hz, 5H), 6.65 (d, $J = 8.7$ Hz, 4H), 3.84 (s, 2H), 3.73 (s, 9H), 2.14 (s, 9H), 1.88 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 157.3, 137.3, 137.0, 132.3, 131.7, 130.3, 129.4, 113.5, 113.0, 55.3, 55.1, 22.6, 21.6.

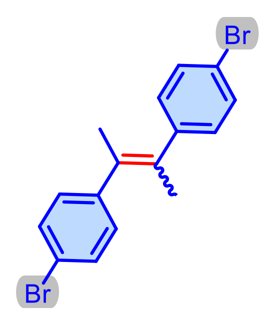


16

4,4'-(but-2-ene-2,3-diyl)bis(fluorobenzene) (16)[12] Prepared according to the general procedure as described above. It was purified by flash chromatography with hexane/ethyl acetate in 1% mixture ($R_f = 0.4$) to afford a white solid. Yield 11.5 mg (0.047 mmol, 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.19 (m, 1H), 7.08 – 7.03 (m, 1H), 6.91 – 6.86 (m, 4H), 6.80 – 6.75 (m, 4H), 2.17 (s, 1H), 2.13 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.85, 159.90, 140.30 (d, $J = 3.3$ Hz), 132.25, 130.57 (d, $J = 7.7$ Hz), 129.73 (d, $J = 7.7$ Hz), 115.04 (d, $J = 21.1$ Hz), 114.52 (d, $J = 21.1$ Hz).

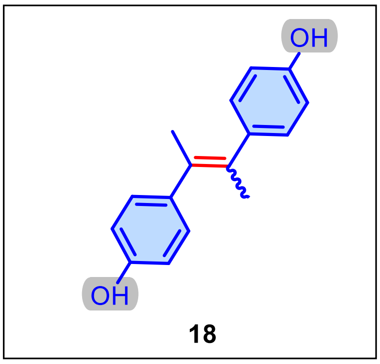


17

4,4'-(but-2-ene-2,3-diyl)bis(bromobenzene) (17)[13] Prepared according to the general procedure as described above. It was purified by flash chromatography with hexane/ethyl acetate in 1% mixture ($R_f = 0.4$) to afford a white solid. Yield 17.4 mg (0.048 mmol, 96%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.52 – 7.47 (d, 1H), 7.25 – 7.19 (d, 4H), 7.12 (d, $J = 8.4$ Hz, 1H), 6.84 – 6.78 (d, 4H), 2.12 (s, 6H), 1.84 (s, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 143.5, 143.2, 132.6, 132.5, 131.4, 130.9, 130.8, 130.0, 120.3, 119.7, 22.4, 21.4.

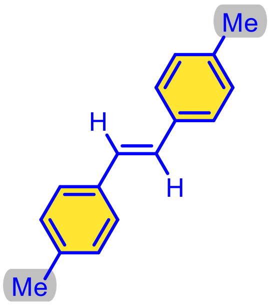


18

Hex-3-ene-3,4-diyldibenzene (18)[14] Prepared according to the general procedure as described above. It was purified by flash chromatography with hexane/ethyl acetate in 1% mixture ($R_f = 0.4$) to afford a white solid. Yield 9.1 mg (0.038 mmol, 76%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.13 (d, $J = 8.6$ Hz, 4H), 7.06 (d, $J = 8.4$ Hz, 1H), 6.83 (d, $J = 8.6$ Hz, 4H), 6.74 (d, $J = 8.6$ Hz, 1), 6.56 (d, $J = 8.6$ Hz, 2H), 2.11 (s, 3H), 1.86 (s, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 153.2, 137.4, 137.1, 130.4, 129.6, 114.9, 114.5.

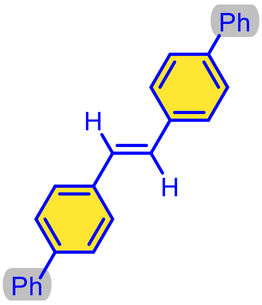


20

(*E*)-1,2-di-*p*-tolylethene (20)[15] Prepared according to the general procedure as described above. It was purified by flash chromatography with hexane/ethyl acetate in 1% mixture (R_f = 0.4) to afford a white solid. Yield 9.36 mg (0.045 mmol, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 4H), 7.20 – 7.14 (m, 4H), 7.05 (s, 2H), 2.36 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 134.7, 129.3, 127.6, 126.3, 21.2.

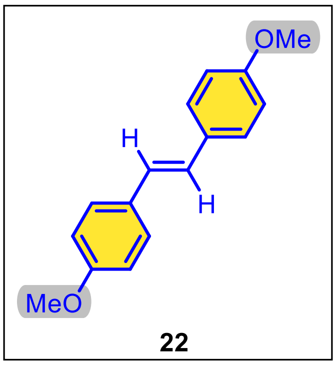


21

(*E*)-1,2-di([1,1'-biphenyl]-4-yl) ethene (21)[16] Prepared according to the general procedure as described above. It was purified by flash chromatography with hexane/ethyl acetate in 1% mixture (R_f = 0.4) to afford a white solid. Yield 11.6 mg (0.035 mmol, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 5H), 7.51 – 7.49 (m, 3H), 7.46 – 7.42 (m, 3H), 7.40 (td, *J* = 6.5, 1.7 Hz, 5H), 7.36 – 7.31 (m, 2H), 6.65 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 139.9, 136.4, 130.1, 129.5, 128.9, 127.4, 127.0, 126.9.

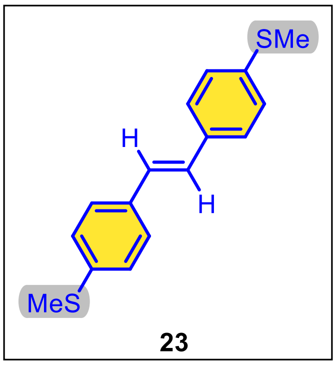


22

(*E*)-1,2-bis(4-methoxyphenyl) ethene (22)[17] Prepared according to the general procedure as described above. It was purified by flash chromatography with hexane/ethyl acetate in 2% mixture (R_f = 0.3) to afford a white solid. Yield 10.4 mg (0.0435 mmol, 87%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.45 – 7.41 (d, 4H), 6.93 (s, 2H), 6.91 – 6.87 (d, 4H), 3.83 (s, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 159.0, 130.5, 127.4, 126.2, 114.1, 55.3.

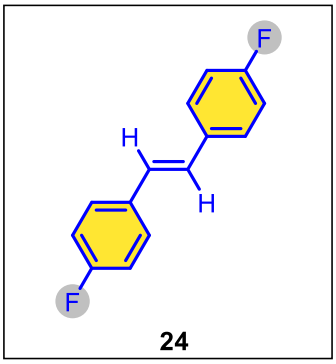


23

(*E*)-1,2-bis(4-(methylthio) phenyl) ethene (23)[17] Prepared according to the general procedure as described above. It was purified by flash chromatography with hexane/ethyl acetate in 1% mixture (R_f = 0.4) to afford a yellow lequid. Yield 11.5 mg (0.0425 mmol, 85%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.44 – 7.40 (m, 4H), 7.26 – 7.22 (m, 4H), 7.01 (s, 2H), 2.50 (s, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 137.7, 134.3, 127.4, 126.8, 126.7, 15.8.

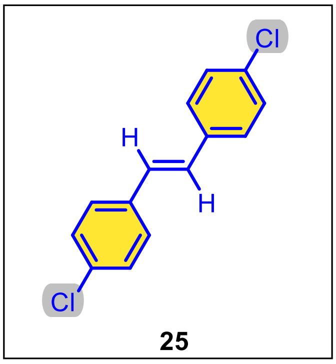


24

(*E*)-1,2-bis(4-fluorophenyl) ethene (24)[18] Prepared according to the general procedure as described above. It was purified by flash chromatography with hexane/ethyl acetate in 1% mixture ($R_f = 0.4$) to afford a brown solid. Yield 10 mg (0.046 mmol, 92%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.50 – 7.43 (m, 4H), 7.09 – 7.01 (m, 4H), 6.98 (s, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 162.36 (d, $J = 247.3$ Hz), 133.37 (d, $J = 3.3$ Hz), 127.92 (d, $J = 8.2$ Hz), 127.30, 115.67 (d, $J = 21.6$ Hz).

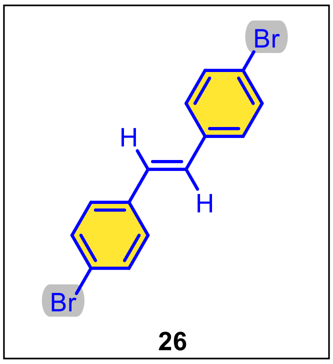


25

(*E*)-1,2-bis(4-chlorophenyl) ethene (25)[19] Prepared according to the general procedure as described above. It was purified by flash chromatography with hexane/ethyl acetate in 1% mixture ($R_f = 0.4$) to afford a white solid. Yield 11.16 mg (0.045 mmol, 90%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.46 – 7.40 (d, 4H), 7.36 – 7.30 (d, 4H), 7.02 (s, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 135.5, 133.4, 128.9, 127.9, 127.7.

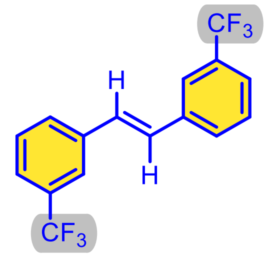


26

(*E*)-1,2-bis(4-bromophenyl) ethene (26)[20] Prepared according to the general procedure as described above. It was purified by flash chromatography with hexane/ethyl acetate in 1% mixture ($R_f = 0.4$) to afford a white solid. Yield 15.5 mg (0.0465 mmol, 93%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 4H), 7.39 – 7.33 (m, 4H), 7.02 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.9, 131.8, 128.1, 128.0, 121.6.



27

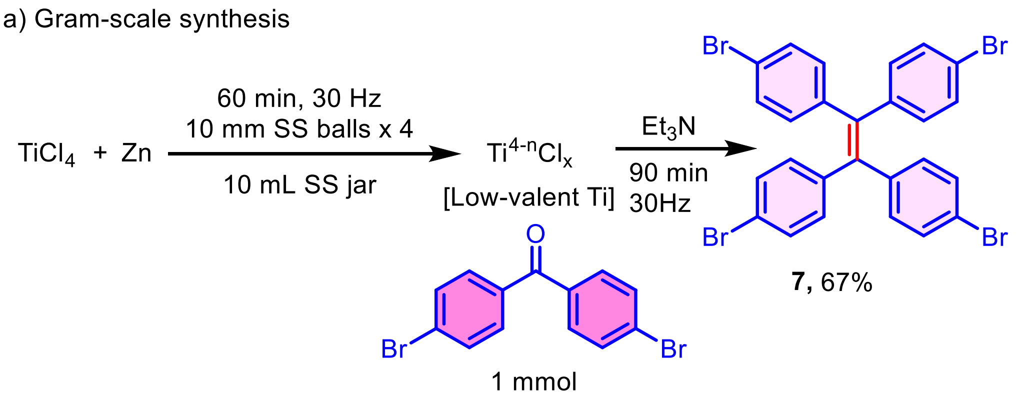
(*E*)-1,2-bis(3-(trifluoromethyl) phenyl) ethene (27)[21] Prepared according to the general procedure as described above. It was purified by flash chromatography with hexane/ethyl acetate in 1% mixture ($R_f = 0.4$) to afford a white solid. Yield 14.3 mg (0.0455 mmol, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 2.0 Hz, 2H), 7.72 – 7.67 (m, 2H), 7.58 – 7.46 (m, 4H), 7.19 (s, 2H).

^{13}C[^{1}H][^{19}F] NMR (101 MHz, $CDCl_3$) δ 137.6, 131.4, 129.9, 129.4, 129.1, 124.7, 124.1, 123.4.

8. Synthetic application

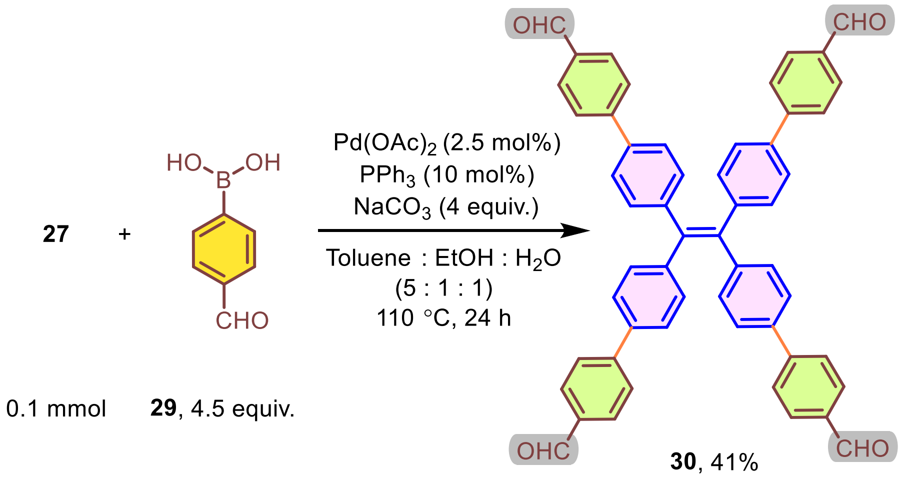
8.1. Gram-scale synthesis



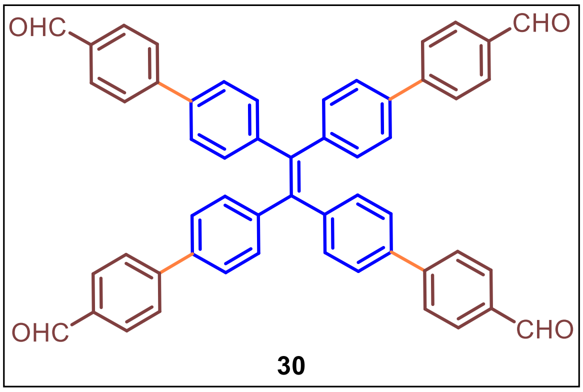
Procedure for setup

Zn powder (12 equiv., 12 mmol, 780 mg) and $TiCl_4$ (6 equiv., 6 mmol, 655 µL) were placed in a 10 mL stainless steel (ss, 316 grade) milling jar with four 10 mm ss balls. The jar was then closed in the open air and placed in the ball mill (Retsch MM 400). After grinding for 90 min at 30 Hz frequency, the jar was opened in air, and then Et_3N (7 equiv., 7 mmol, 973 µL) and the carbonyl compound (1 mmol, 337 mg) were added. The jar was again closed in the open air and placed in the ball mill (Retsch MM 400). After grinding for 120 min at 30 Hz, the jar was opened in air and neutralised with saturated $NaHCO_3$ solution (5 ml). The organics were extracted with CH_2Cl_2 (2 × 10 mL), filtered over celite, dried over Na_2SO_4, and evaporated in *vacuo*. Crude yields of the products were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as the internal standard. The product was then isolated as a white solid via flash column chromatography (SiO_2) with a yield of 67% (215 mg, 0.335 mmol).

8.2. Synthesis of building block for COF



Tetraaryl alkene (0.1 mmol, 1 equiv., 64.3 mg), boronic acid **30** (0.45 mmol, 4.5 equiv., 67 mg), Pd(OAc)$_2$ (2.5 mol%, 1 mg), PPh$_3$ (10 mol%, 2.6 mg), Na$_2$CO$_3$ (0.4 mmol, 42 mg) taken in a 15 mL reaction tube, then degassed solvent mixture (toluene:EtOH:H$_2$O, 5:1:1, 700 µL) was added in the reaction tube. Then the reaction was stirred at 110 ˚C for 24 h. Then the reaction is quenched with 1N NaOH, the organic layer is separated with EtOAc, and concentrated under vacuum. Then the crude product was isolated with column chromatography (30% EtOAc in hexane) as a yellow solid. Isolated yield was 41% (15.3 mg, 0.0205 mmol).



30

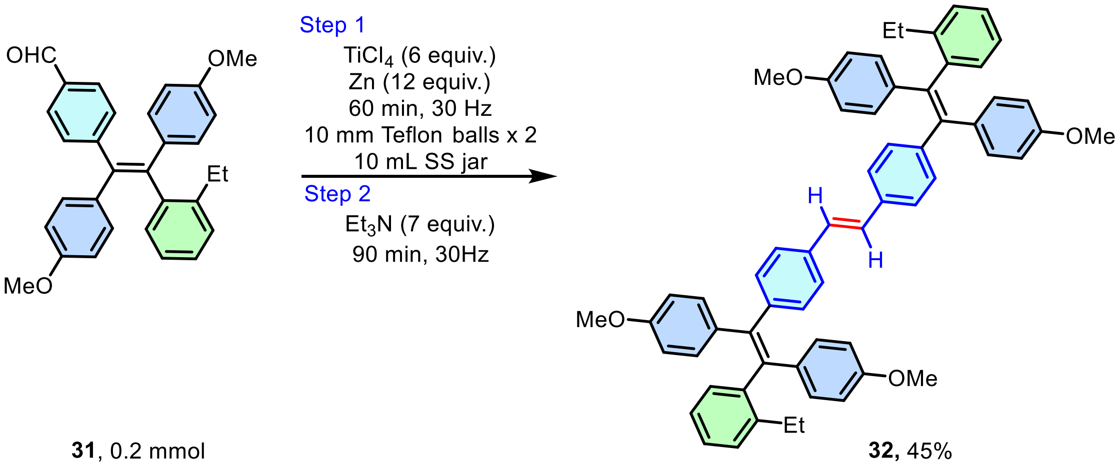
4',4''',4''''',4'''''''-(ethene-1,1,2,2-tetrayl)tetrakis(([1,1'-biphenyl]-4-carbaldehyde)) (30)

^{1}H NMR (400 MHz, CDCl$_3$) δ 10.03 (s, 4H), 7.91 (d, J = 8.6 Hz, 8H), 7.73 (d, J = 8.2 Hz, 8H), 7.47 (d, J = 8.7 Hz, 8H), 7.22 (d, J = 8.6 Hz, 8H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 191.9, 146.5, 143.7, 140.8, 138.0, 135.3, 132.2, 130.4, 127.5, 126.9.

HRMS calc for $C_{54}H_{37}O_4$ $[M + H]^+$ 749.2686, found 749.2688.

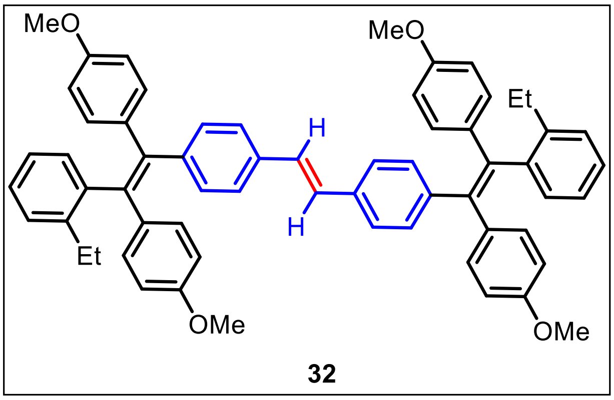
8.3. Synthesis of polyaromatic alkene



31, 0.2 mmol

32, 45%

Zn powder (6 equiv.) and $TiCl_4$ (12 equiv.) were placed in a 10 ml Teflon tube, and that was placed in a stainless steel capsule (ss, 316 grade) with two 10 mm Teflon balls. The jar was then closed in the open air and placed in the ball mill (Retsch MM 400). After grinding for 90 min at 30 Hz frequency, the jar was opened in air, and then Et_3N (7 equiv.) and the tetrasubstituted olefin compound **31** (0.1 mmol) were added. The jar was again closed in the open air and placed in the ball mill (Retsch MM 400). After grinding for 120 min at 30 Hz, the jar was opened in air and neutralised with saturated $NaHCO_3$ solution (5 mL). The organics were extracted with CH_2Cl_2 (2 × 10 mL), filtered over celite, dried over Na_2SO_4, and evaporated in *vacuo*. The product was then isolated via flash column chromatography (SiO_2), with 10% Ethyl acetate in hexane as an eluent. Compound **32** was isolated in 45% yield (19 mg) as a yellow solid.



32

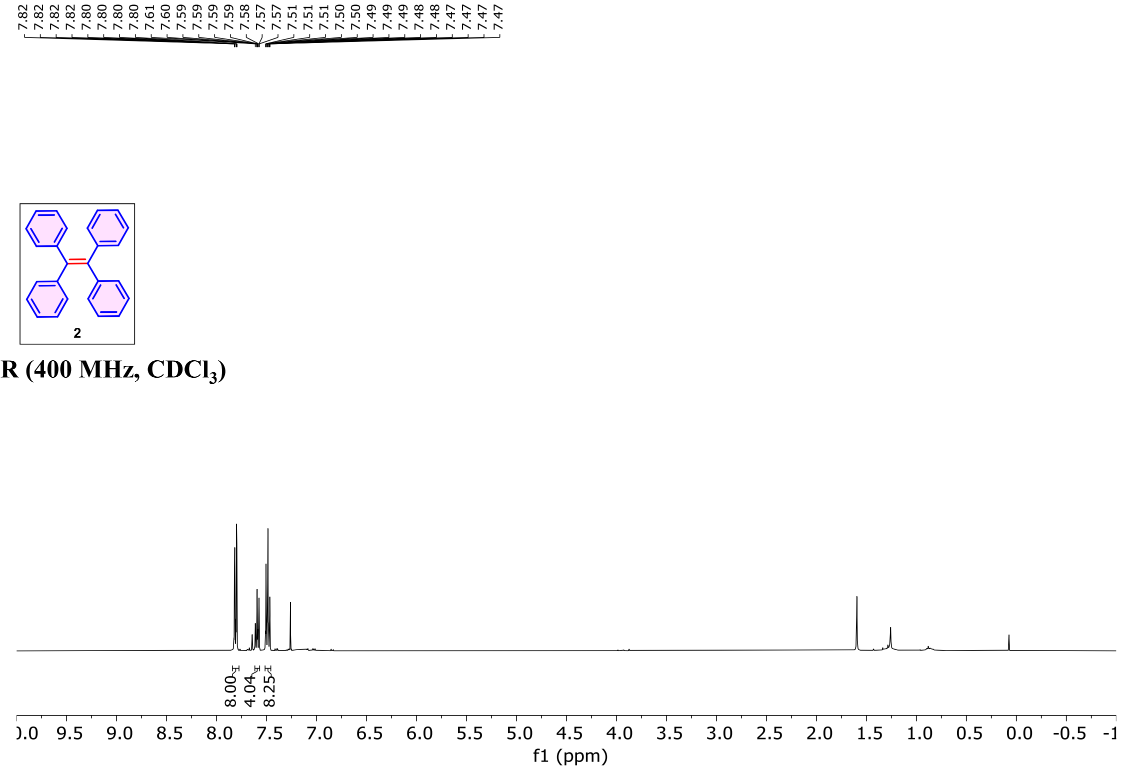
(*E*)-1,2-bis(4-((Z)-2-(2-ethylphenyl)-1,2-bis(4-methoxyphenyl)vinyl)phenyl)ethene (32)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.3 Hz, 3H), 7.10 (s, 4H), 7.07 – 6.96 (m, 10H), 6.87 (dd, *J* = 8.5, 5.7 Hz, 8H), 6.62 – 6.53 (m, 8H), 3.78 – 3.66 (m, 12H), 2.55 (dt, *J* = 15.0, 7.5 Hz, 2H), 2.49 – 2.31 (m, 2H), 0.94 (dd, *J* = 7.8, 7.3 Hz, 6H).

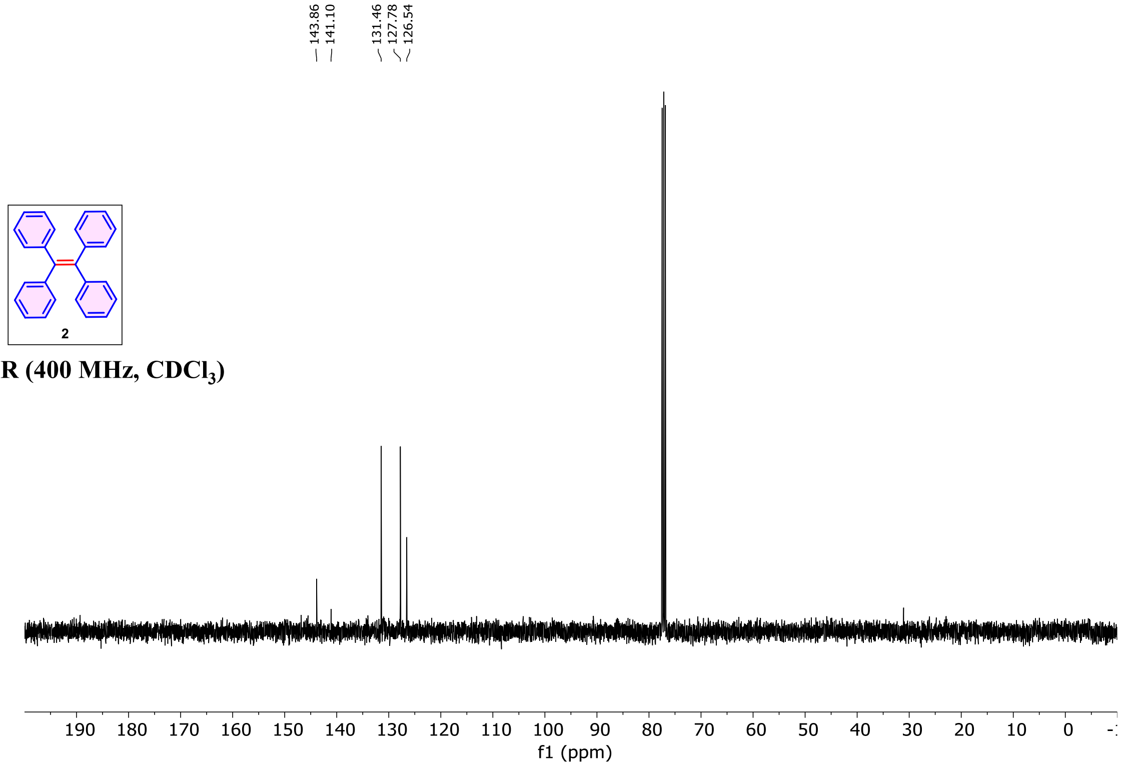
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 143.4, 139.5, 136.1, 132.7, 131.9, 131.9, 131.0, 128.3, 128.1, 126.9, 125.9, 125.9, 125.4, 125.3, 113.3, 113.0, 112.7, 55.1, 55.0, 25.9, 14.36.

HRMS calc for $C_{62}H_{57}O_4$ $[M + H]^+$ 865.4251, found 865.4237.

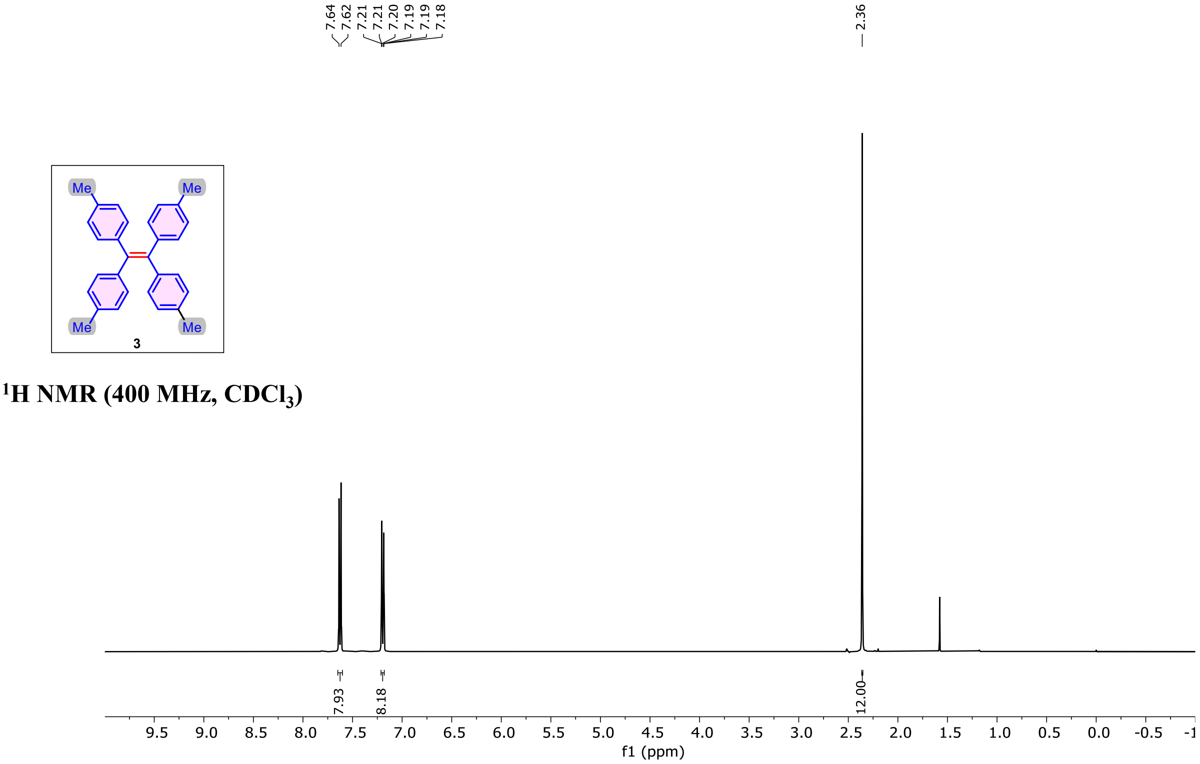
9. Copies of NMR spectra



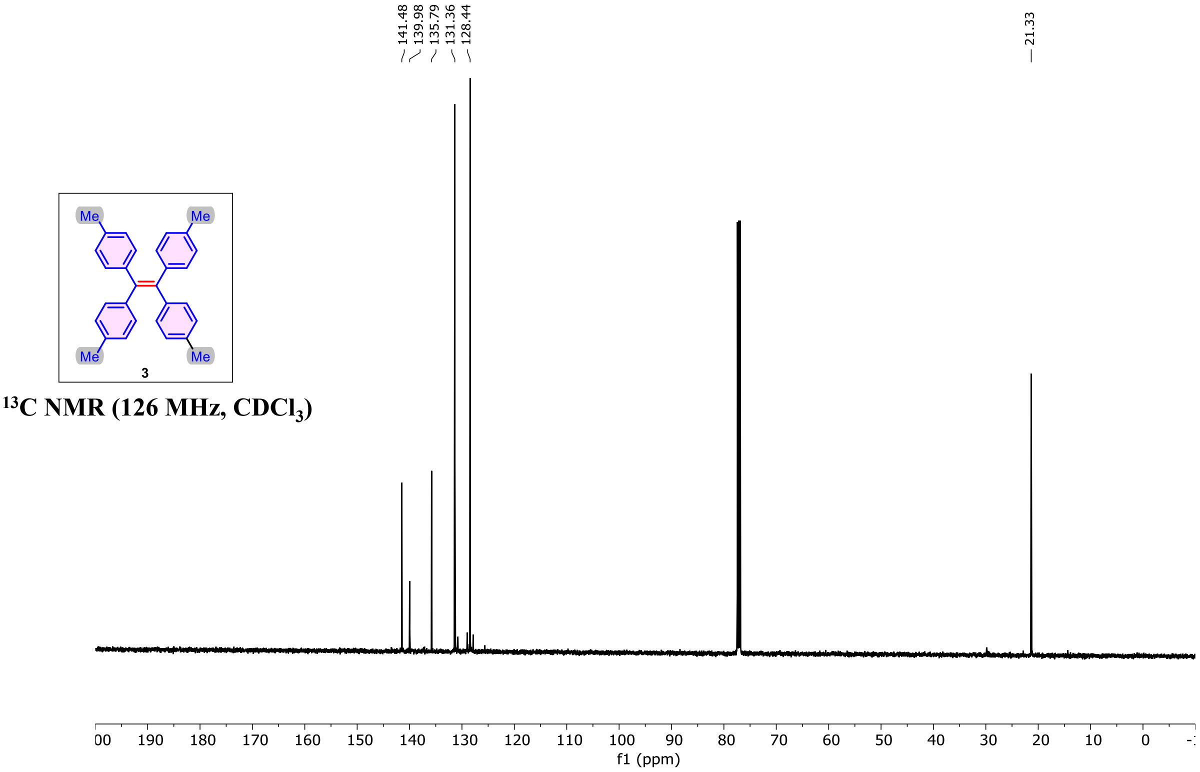
^{1}H NMR (400 MHz, CDCl$_3$)



^{1}H NMR (400 MHz, CDCl$_3$)



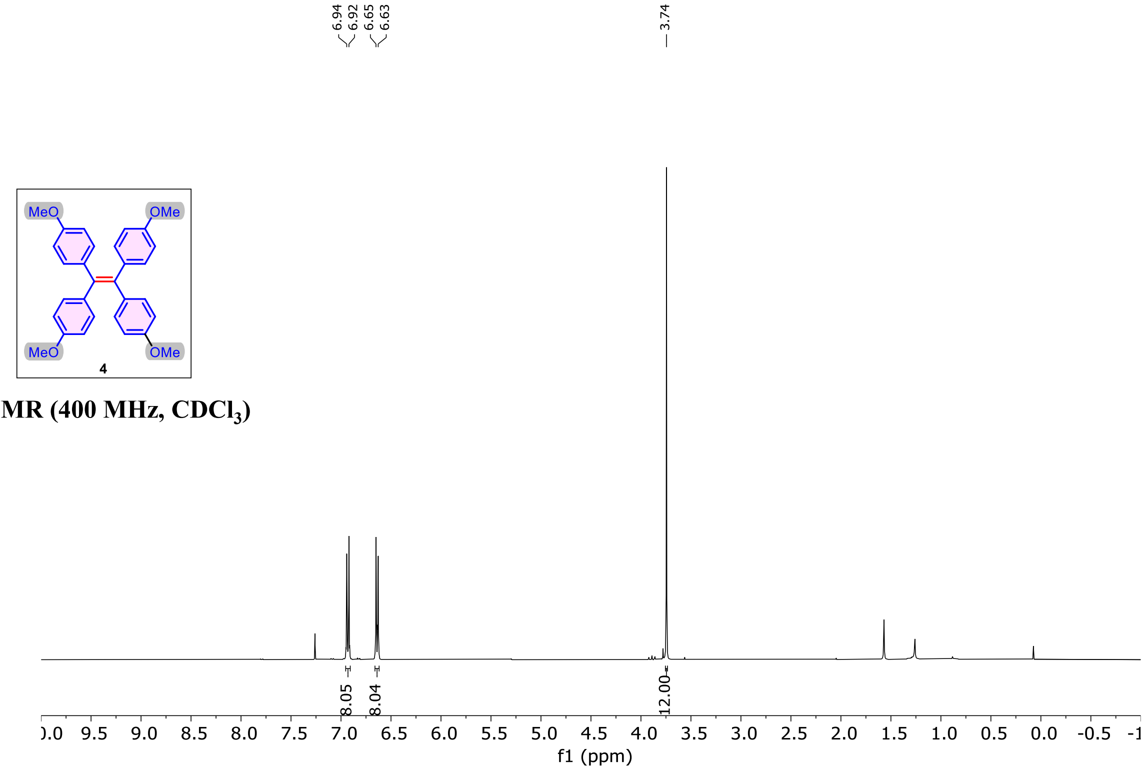
^{1}H NMR (400 MHz, CDCl$_3$)



^{13}C NMR (126 MHz, CDCl$_3$)

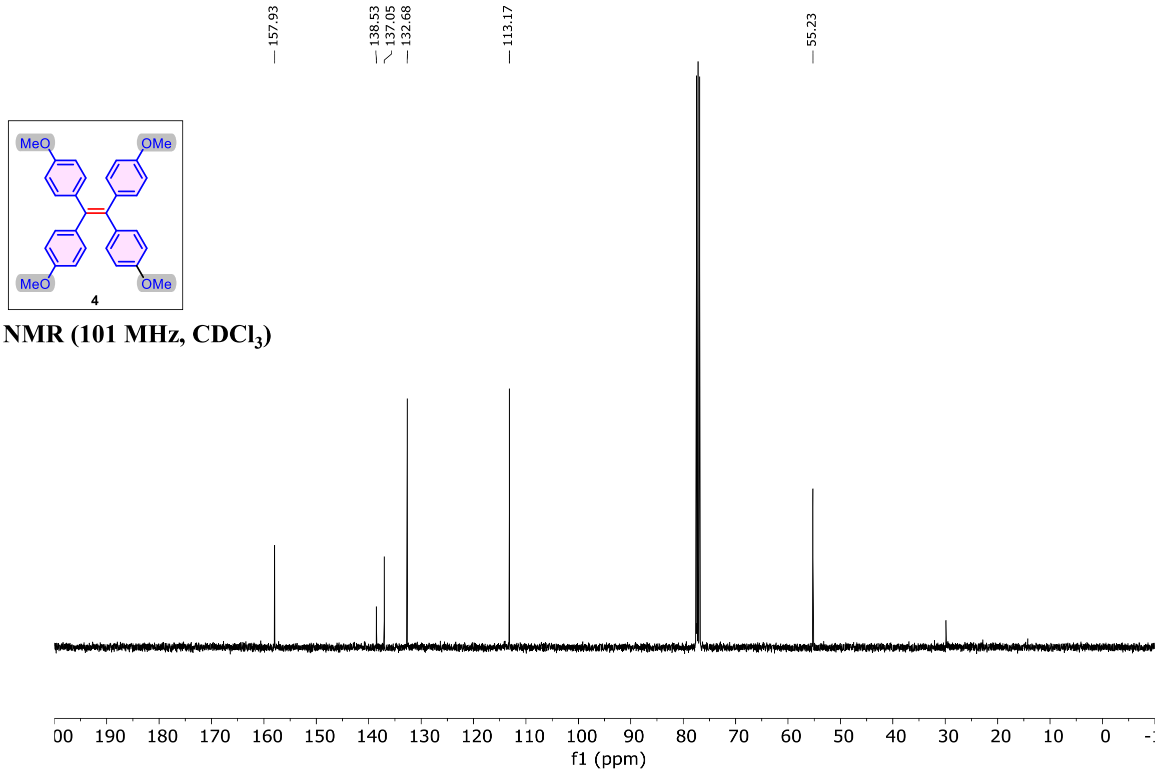
4

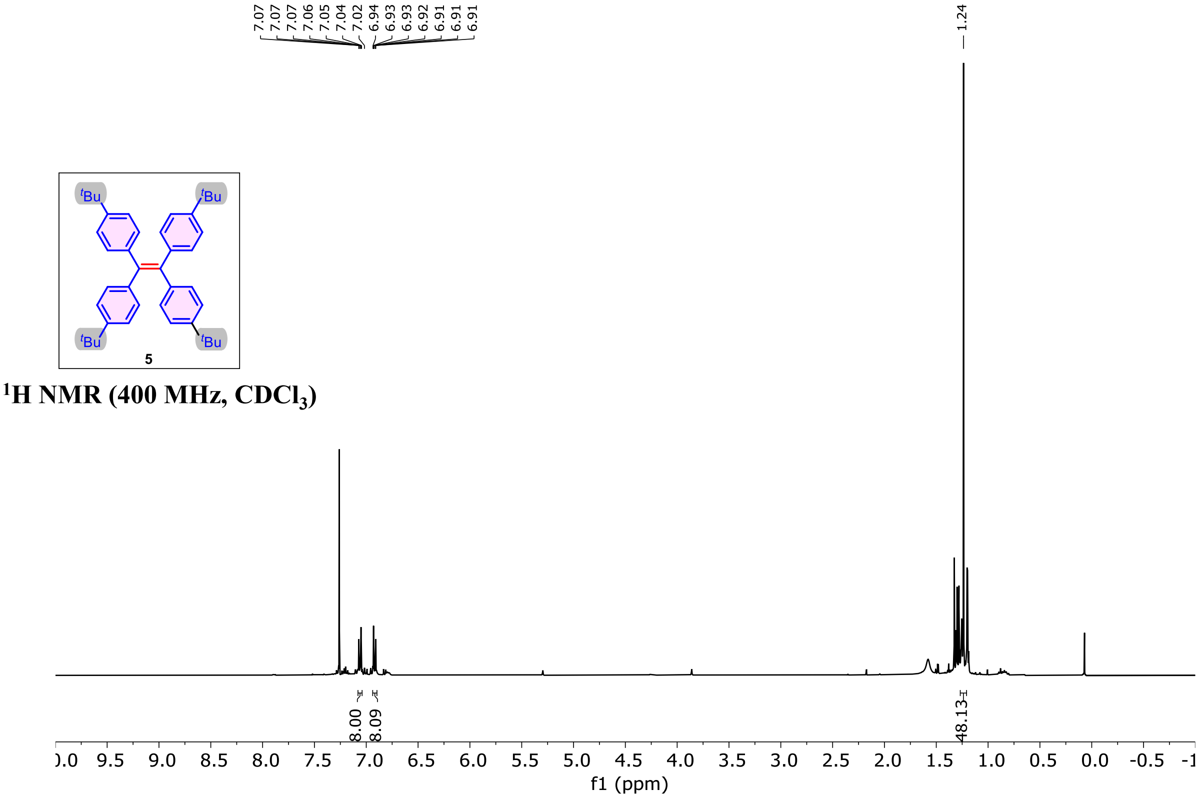
^{1}H NMR (400 MHz, $CDCl_3$)



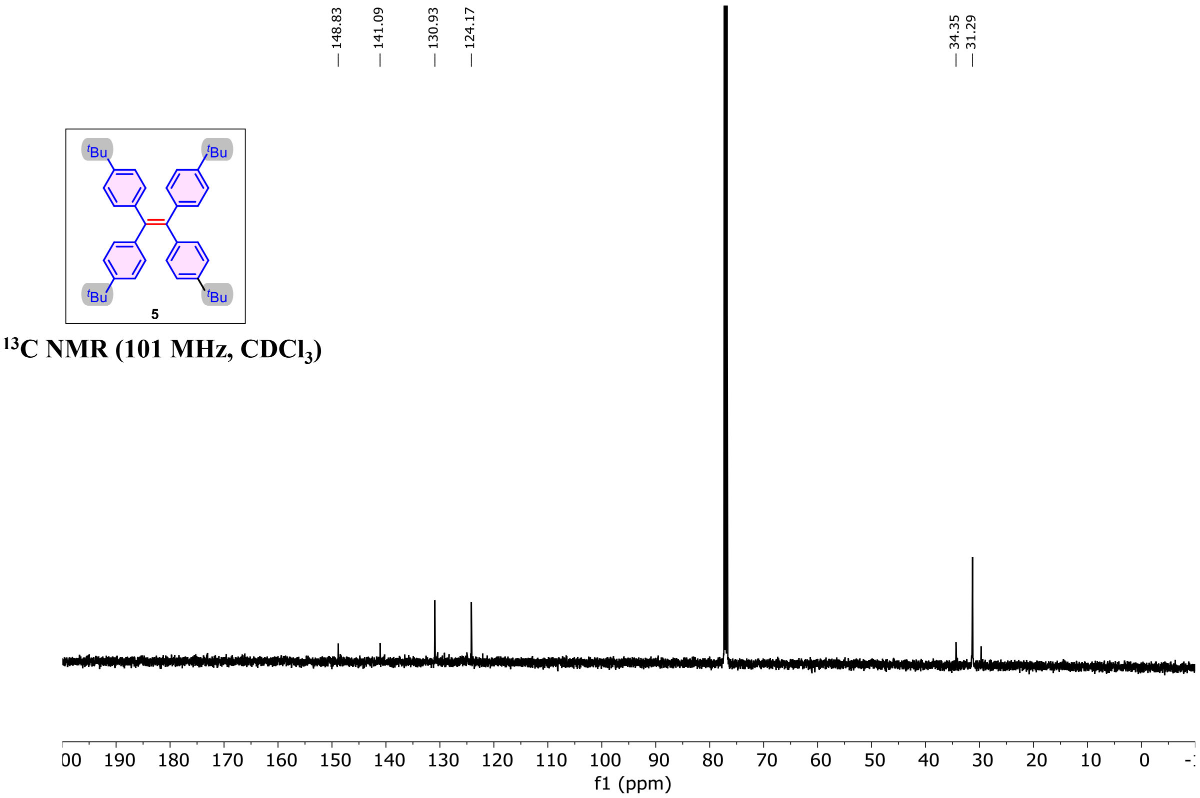
4

^{13}C NMR (101 MHz, $CDCl_3$)

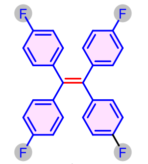




^{1}H NMR (400 MHz, CDCl$_3$)

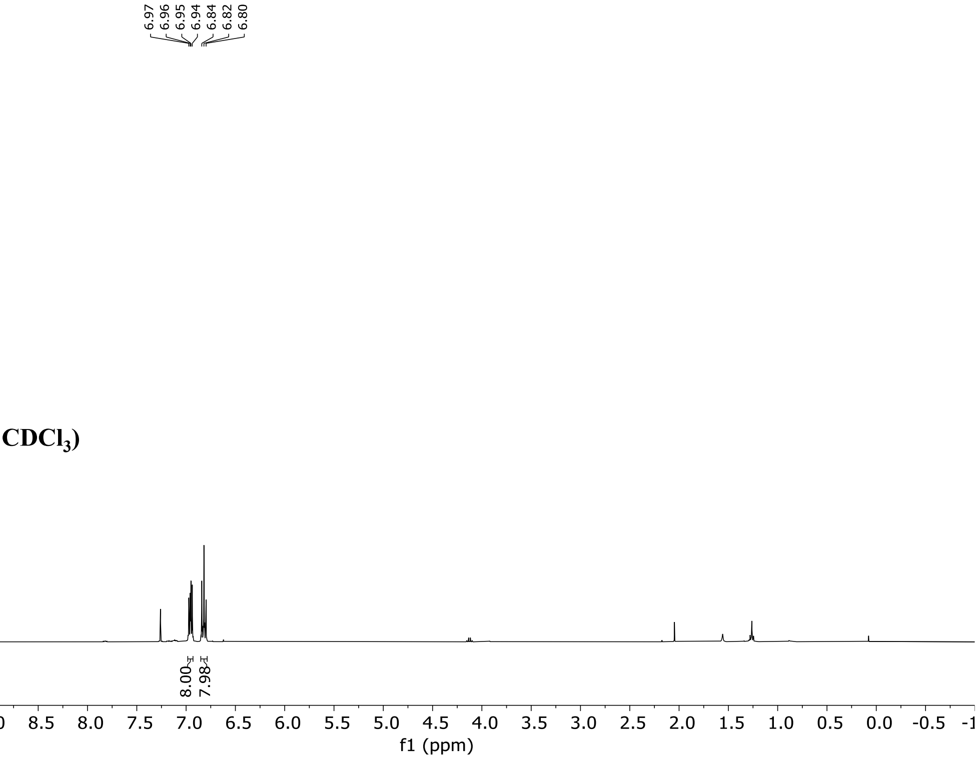


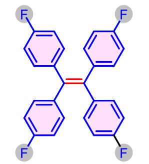
^{13}C NMR (101 MHz, CDCl$_3$)



6

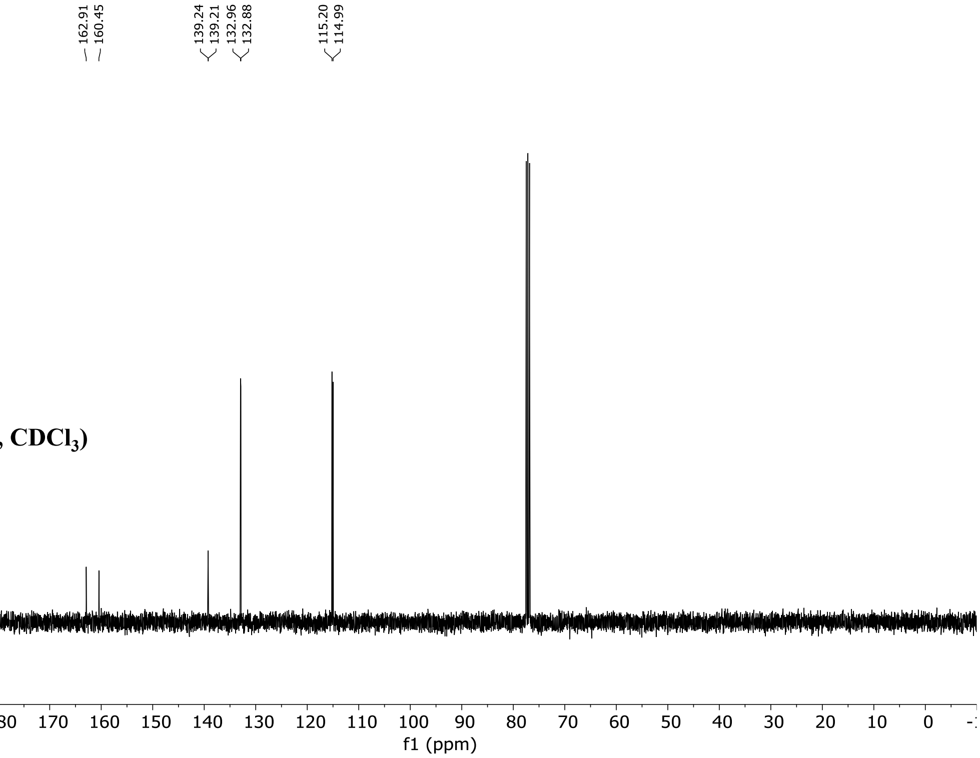
^{1}H NMR (400 MHz, CDCl$_3$)

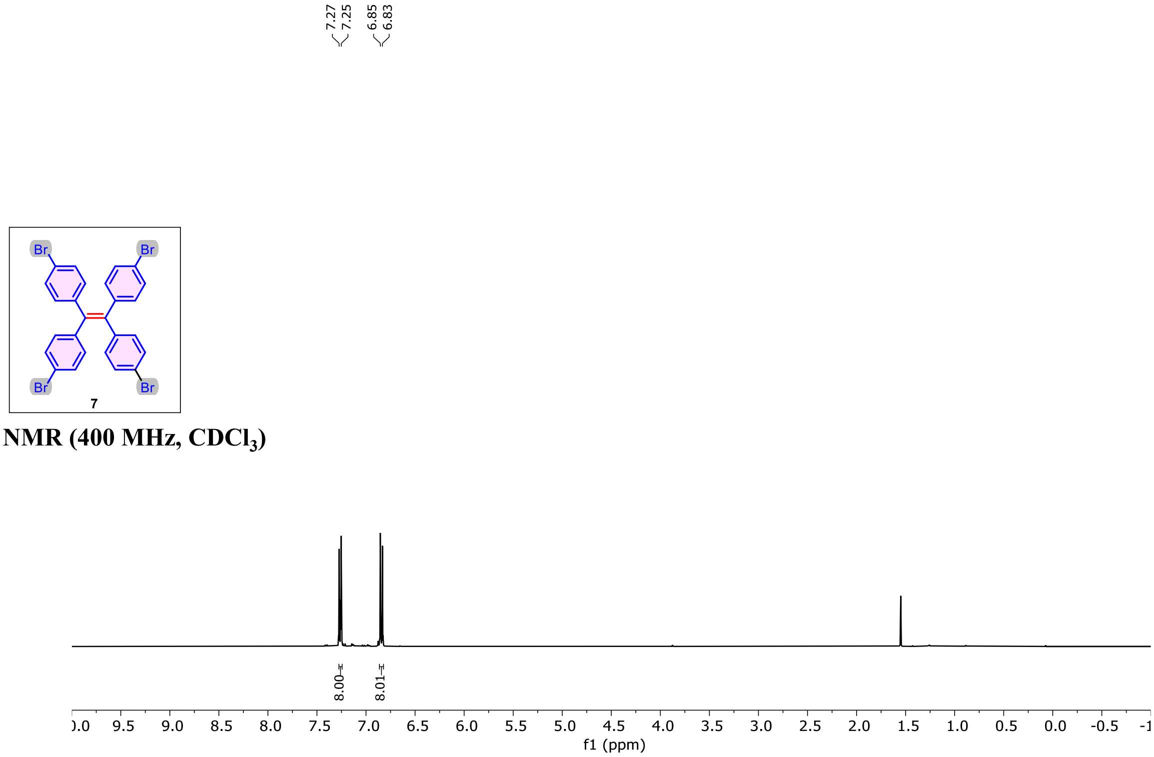




6

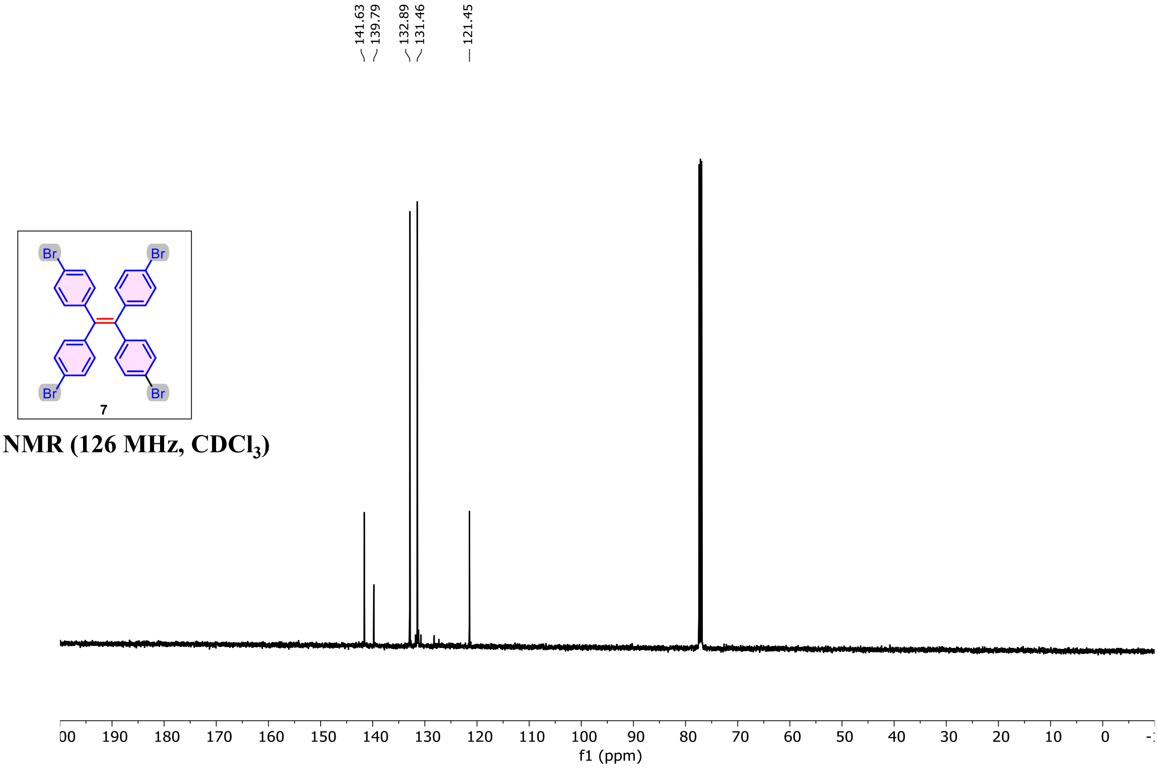
^{13}C NMR (101 MHz, CDCl$_3$)





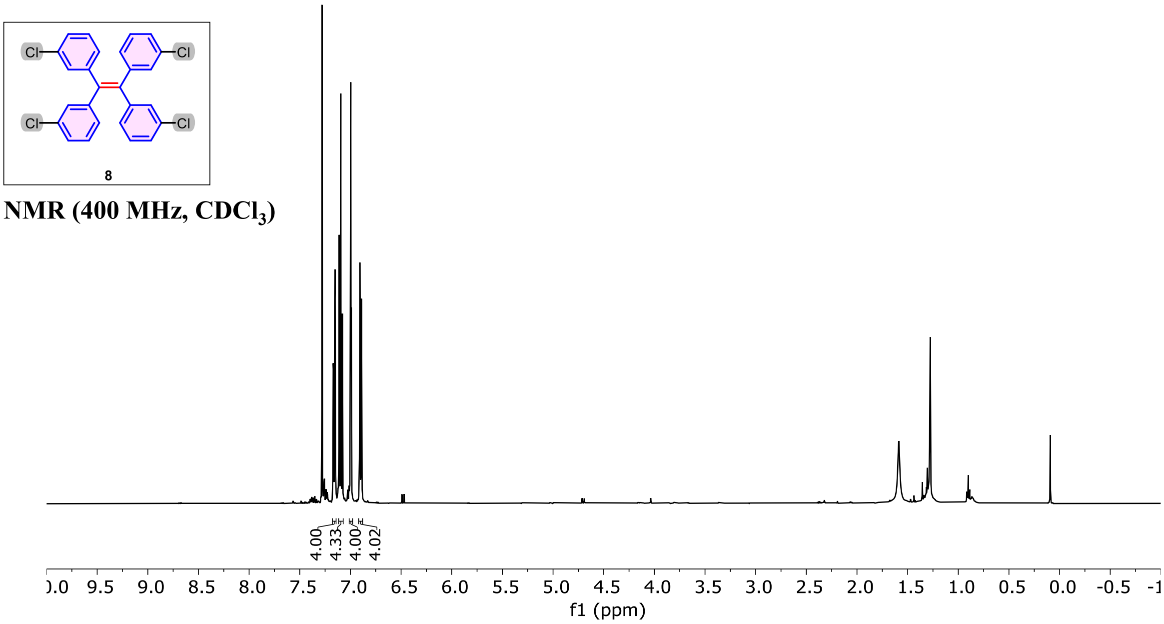
7

^{1}H NMR (400 MHz, CDCl$_3$)



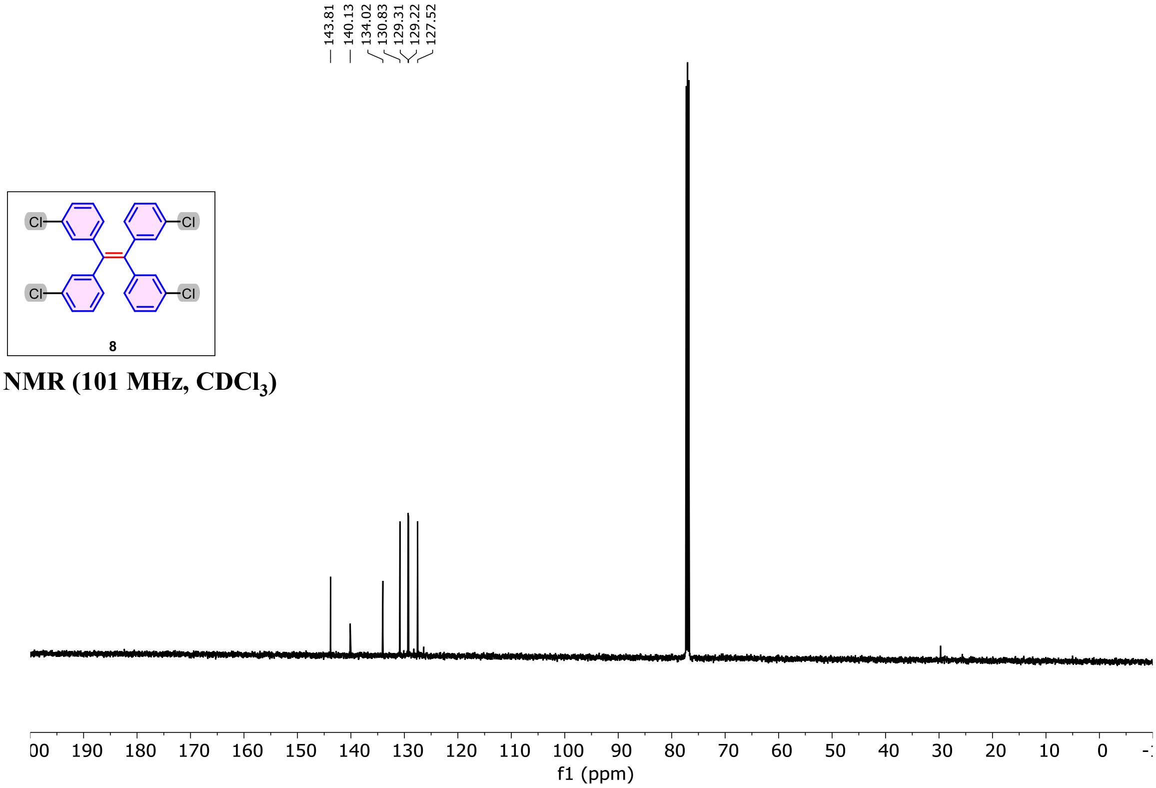
7

^{13}C NMR (126 MHz, CDCl$_3$)



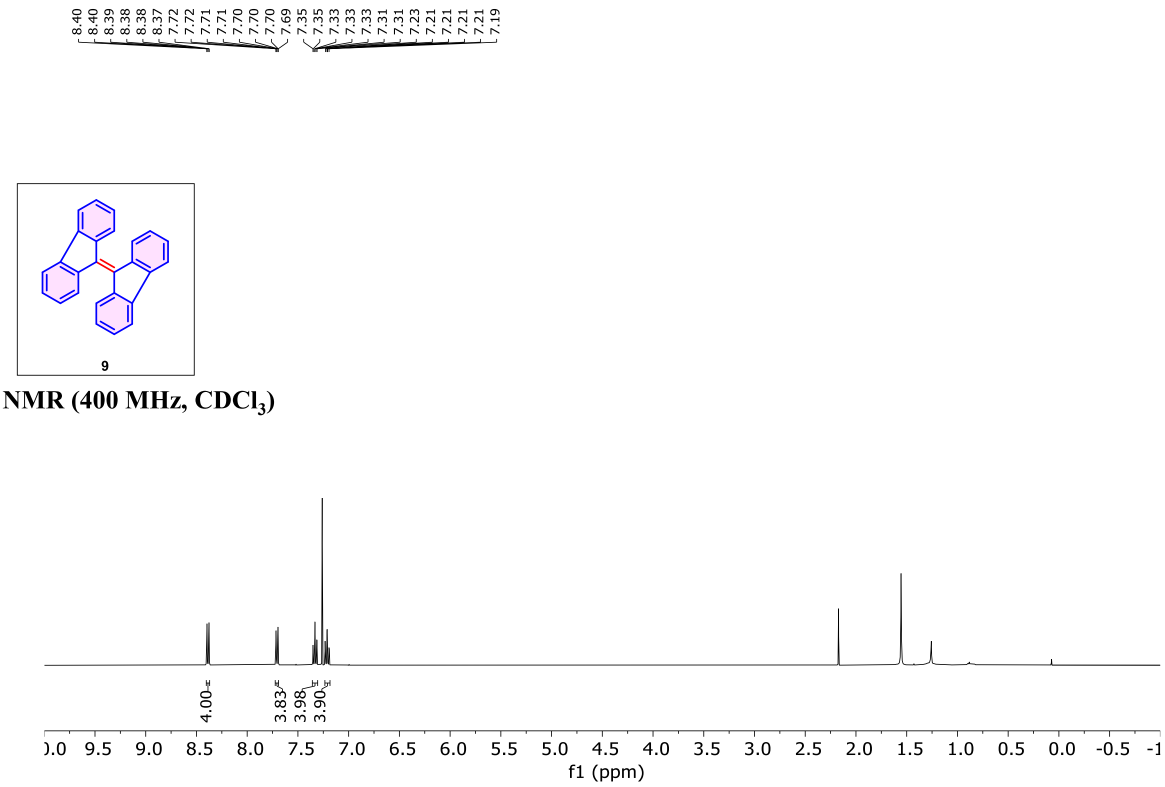
8

^{1}H NMR (400 MHz, CDCl$_3$)

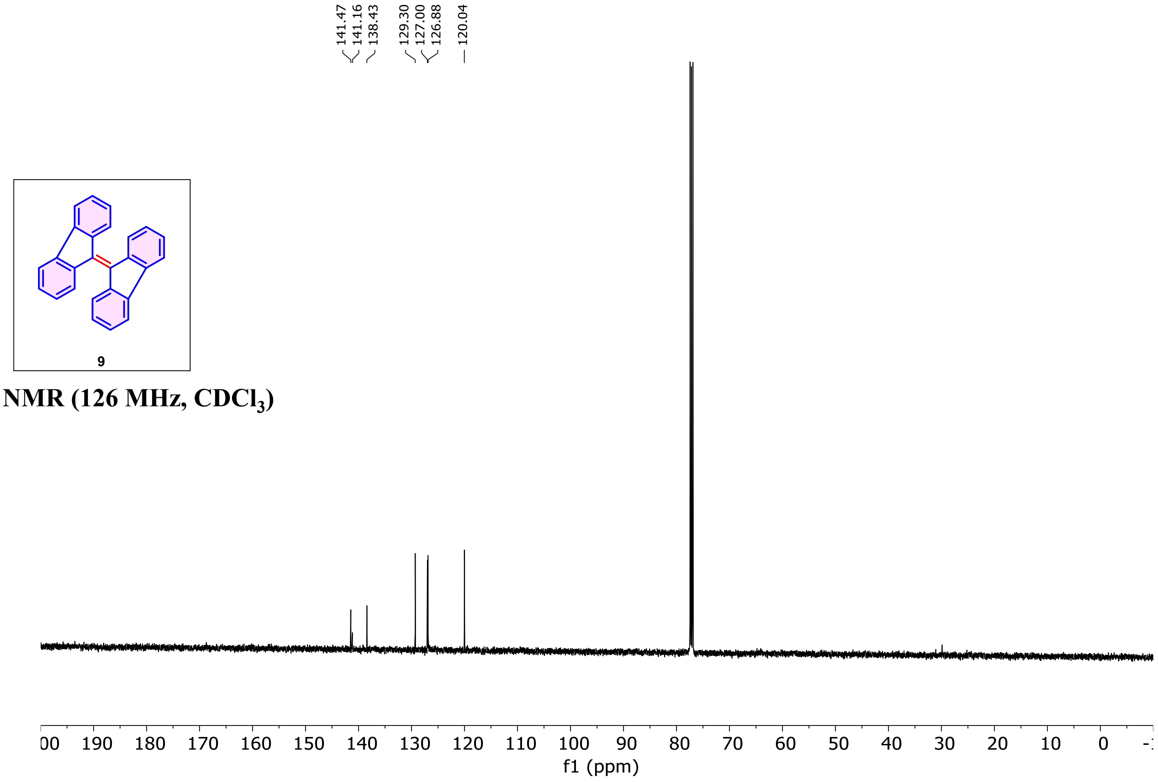


8

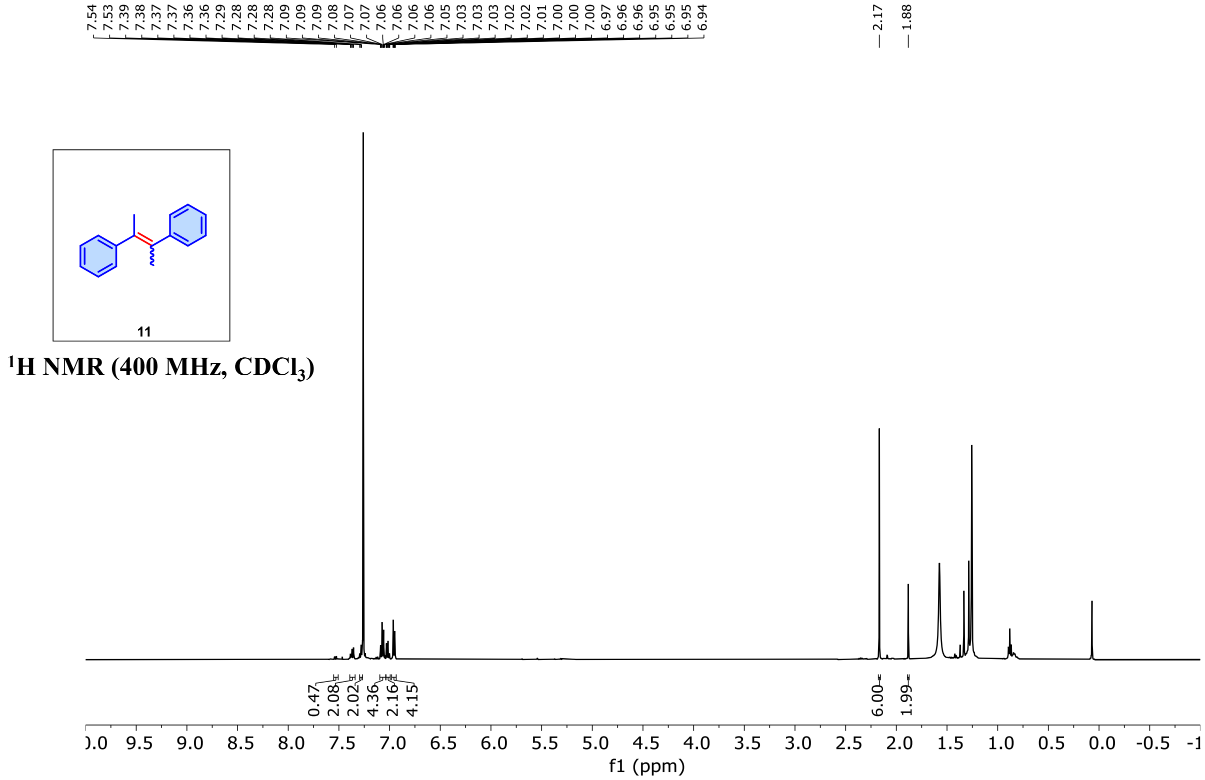
^{13}C NMR (101 MHz, CDCl$_3$)



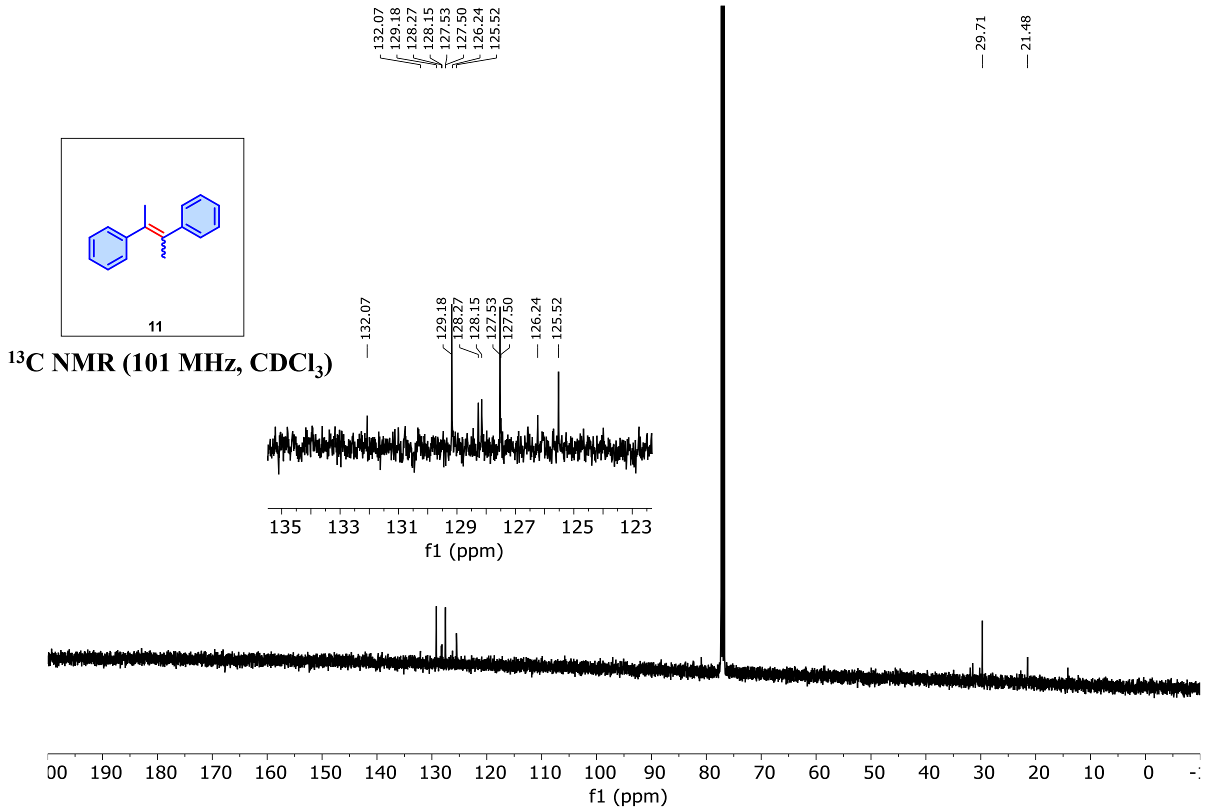
^{1}H NMR (400 MHz, CDCl$_3$)



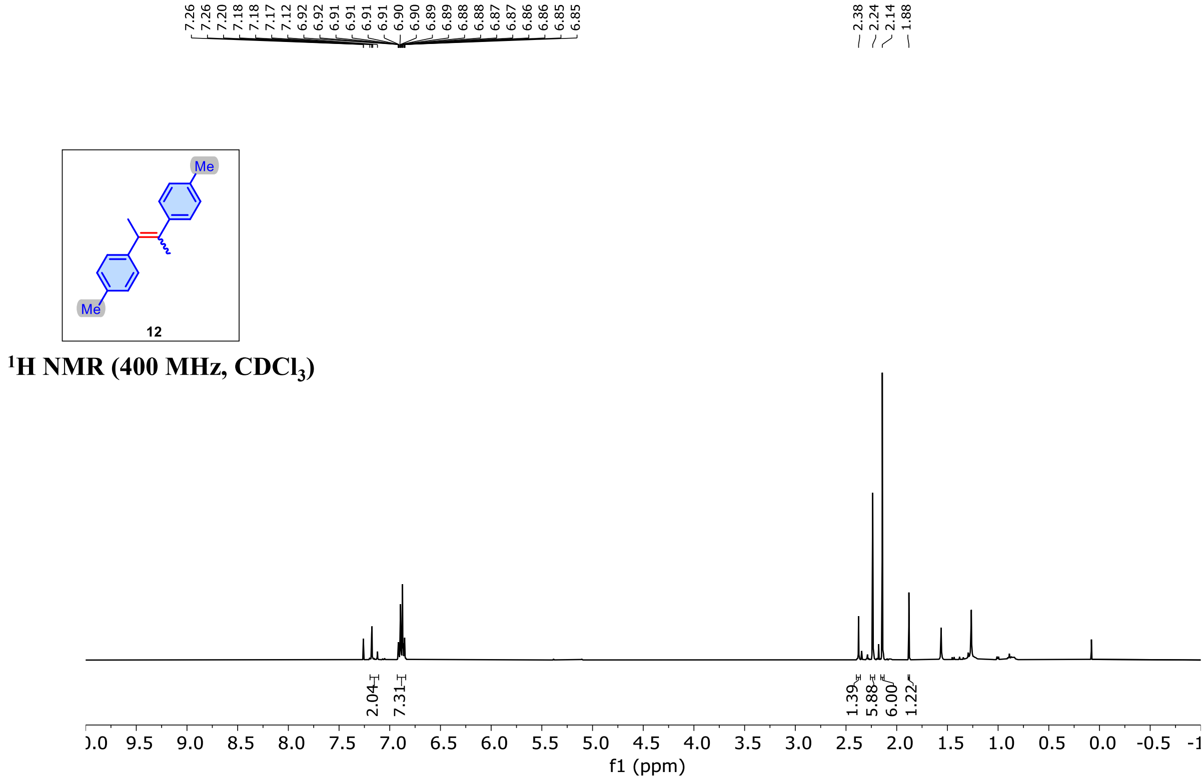
^{13}C NMR (126 MHz, CDCl$_3$)



^{1}H NMR (400 MHz, CDCl$_3$)



^{13}C NMR (101 MHz, CDCl$_3$)



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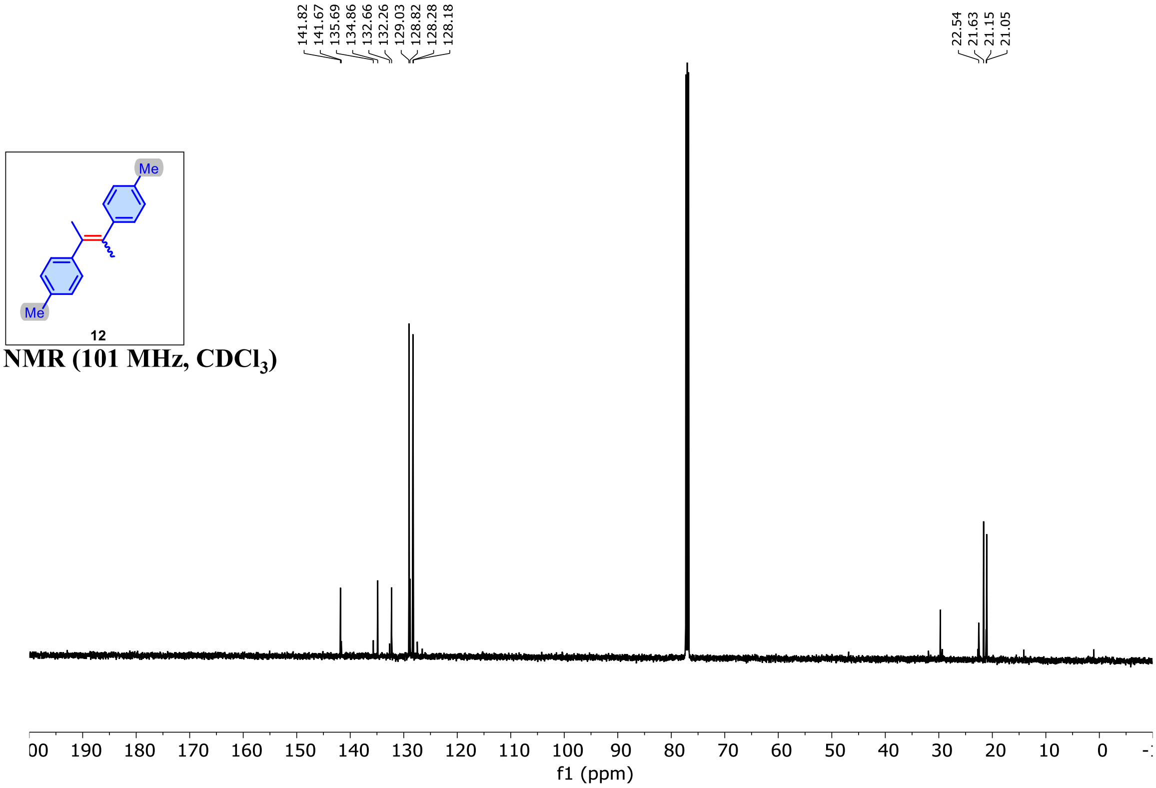

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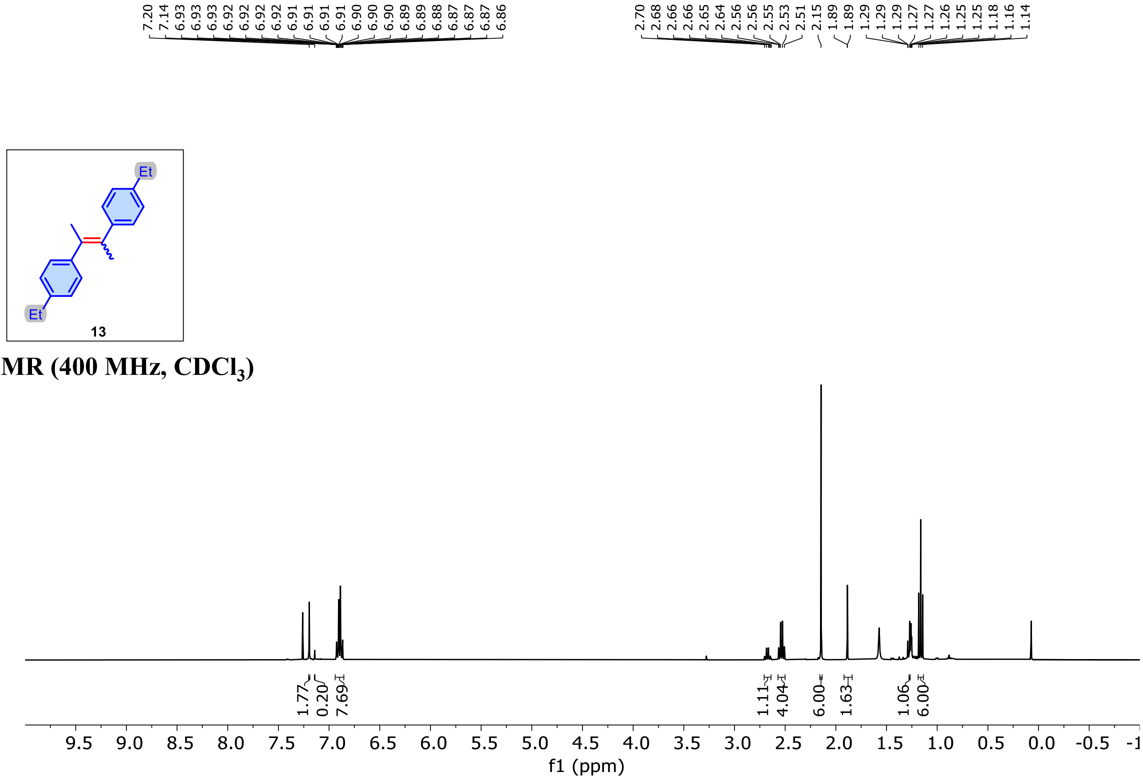

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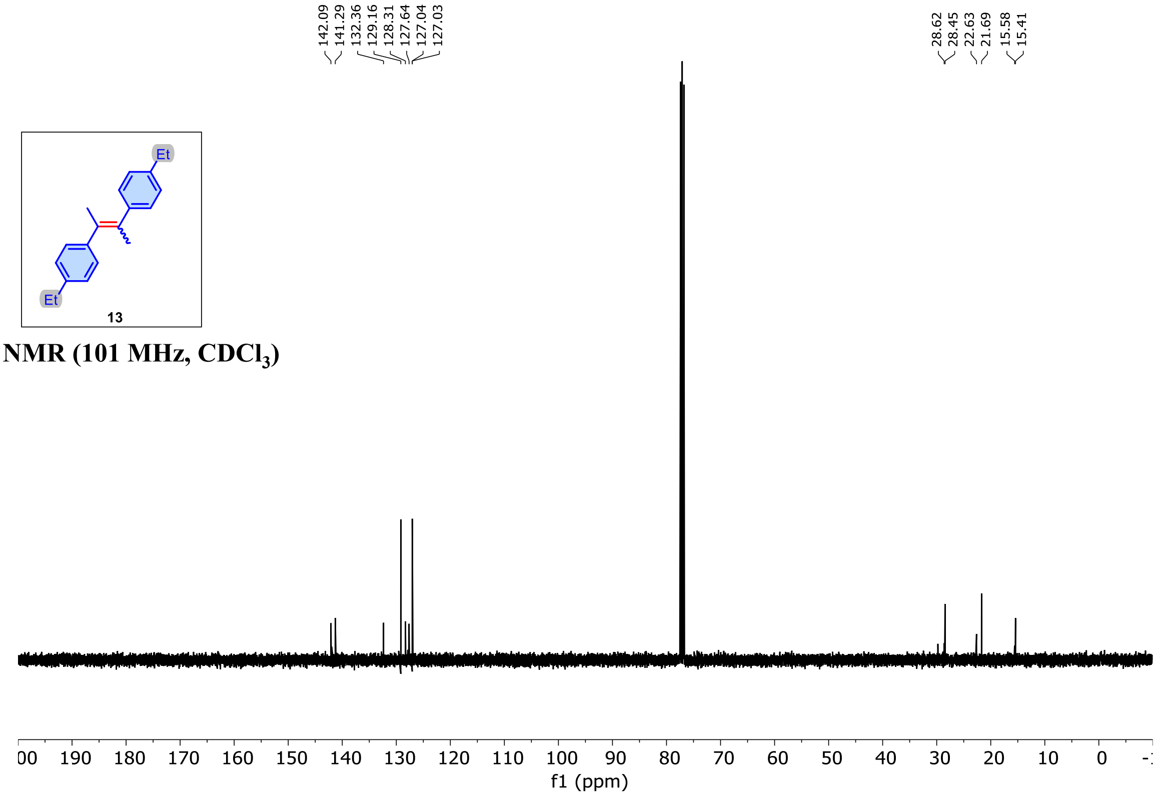

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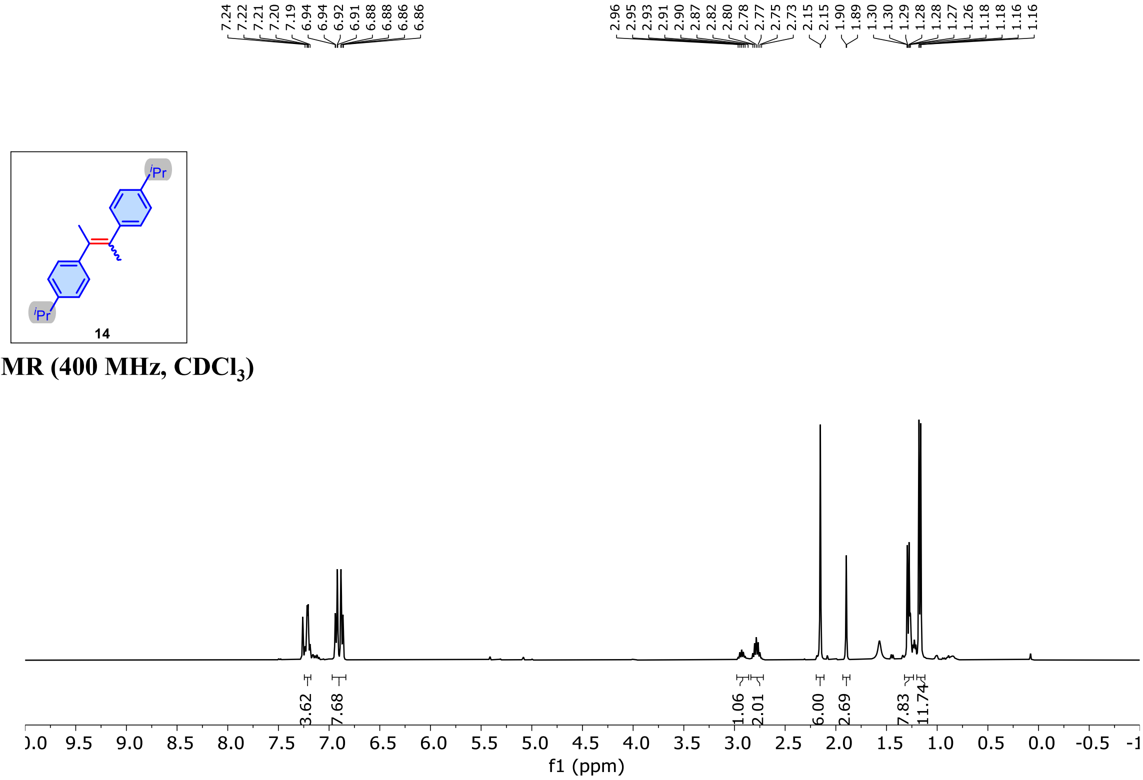

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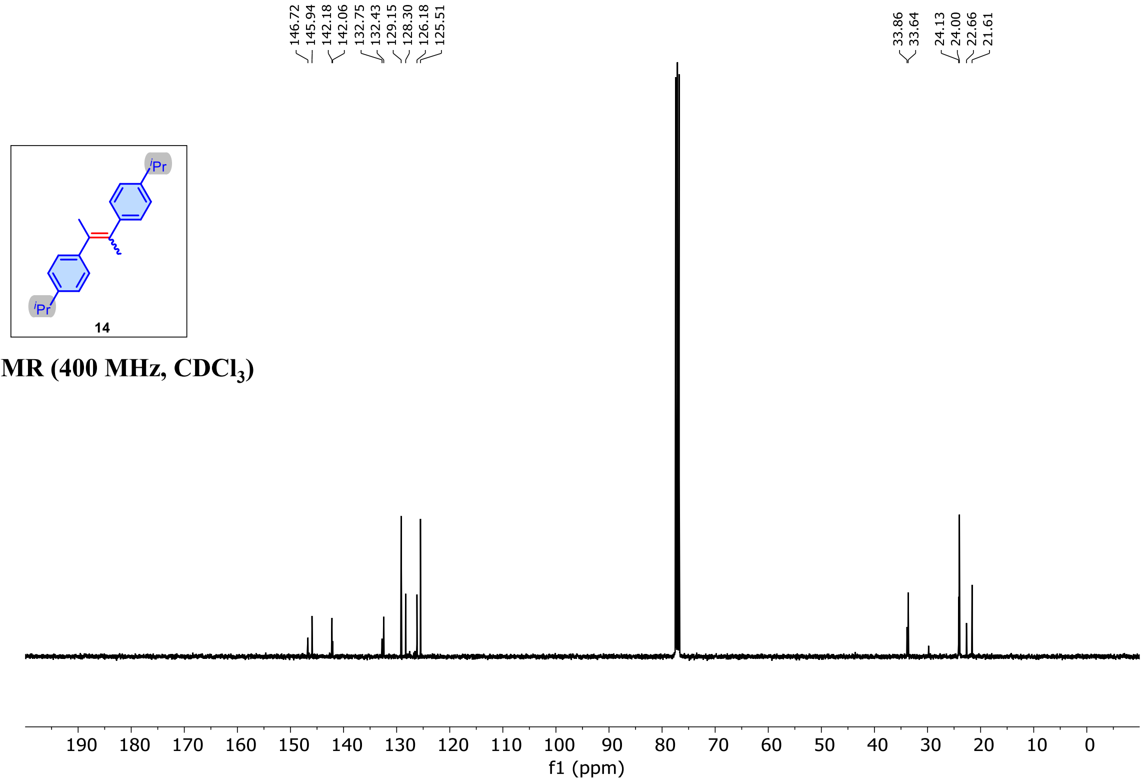

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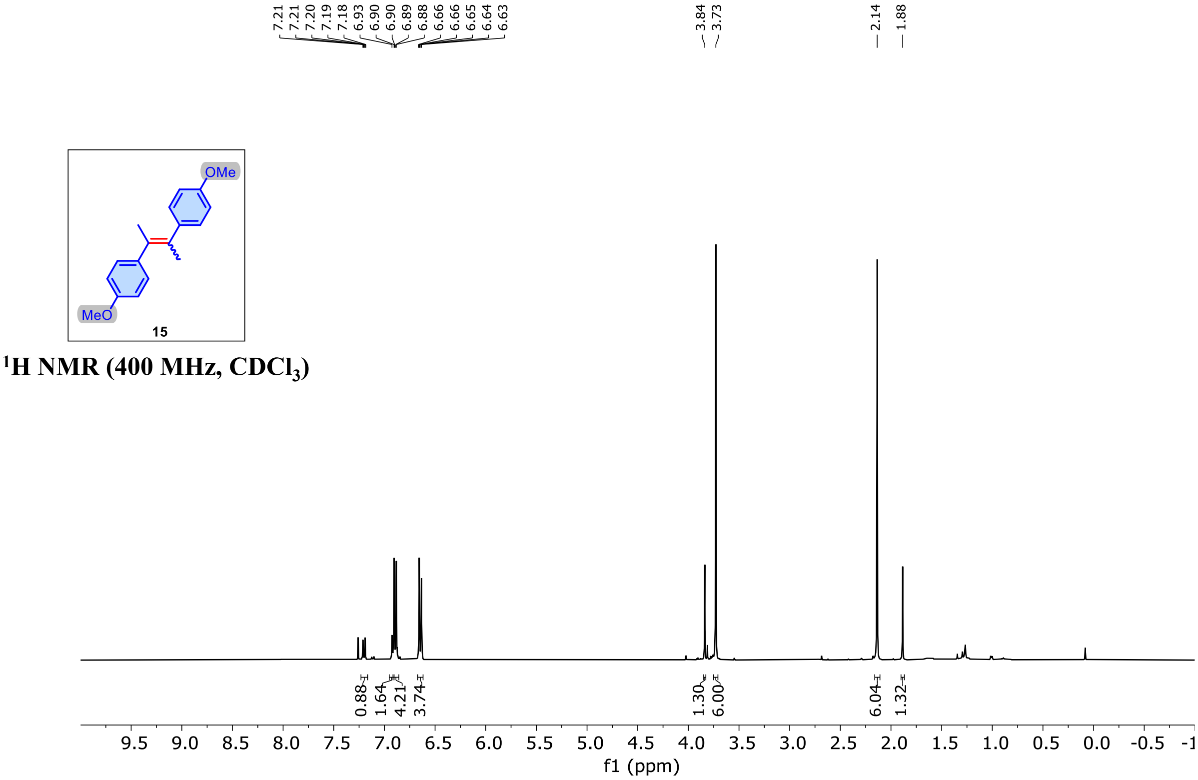

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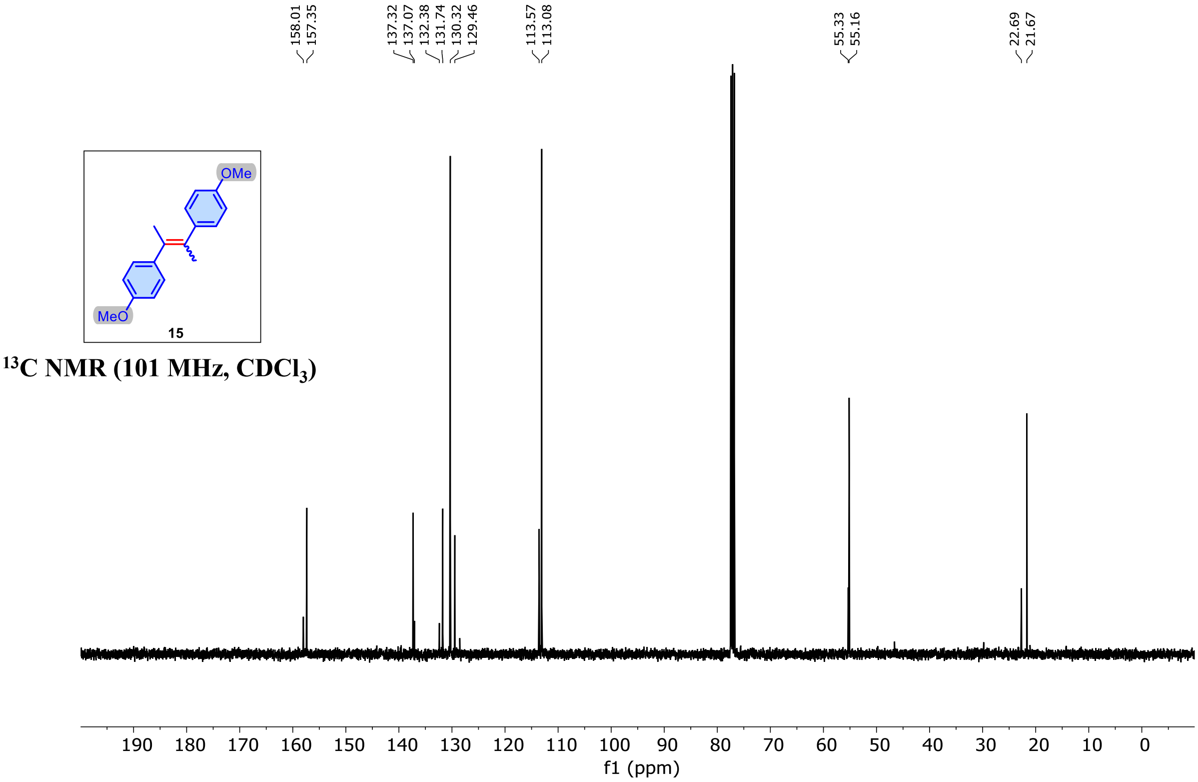

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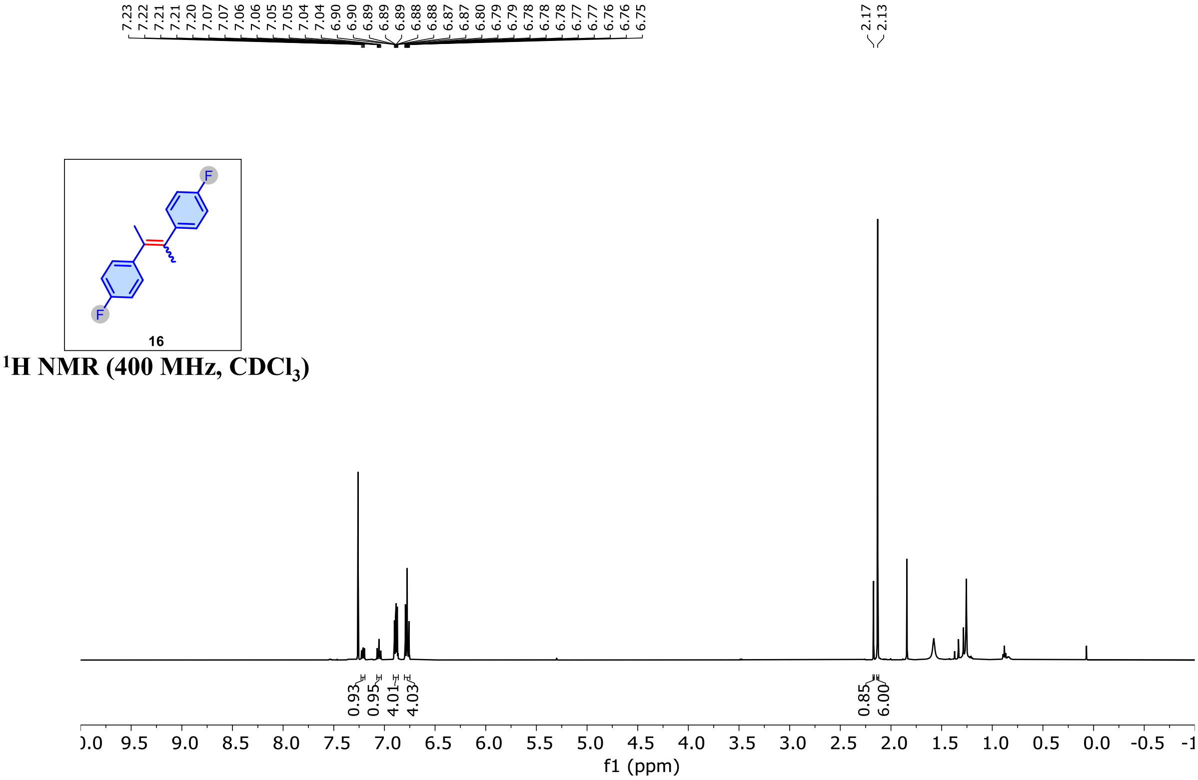

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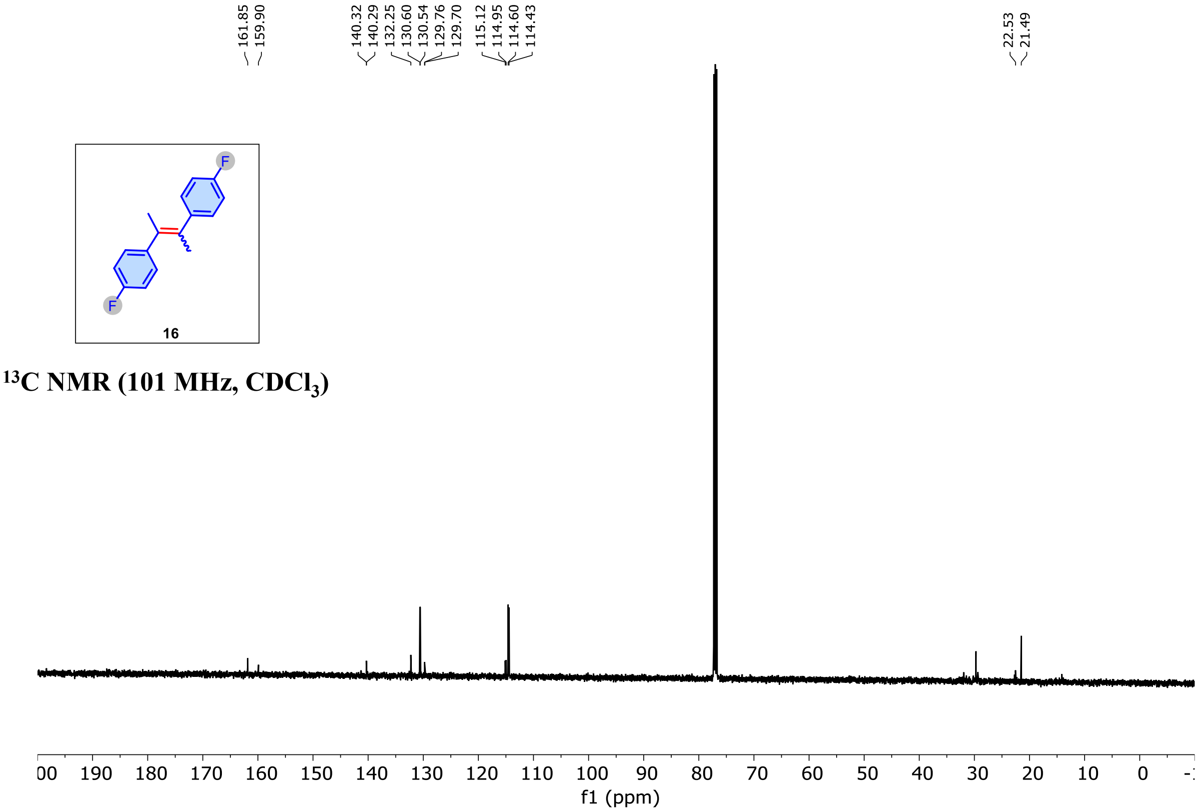

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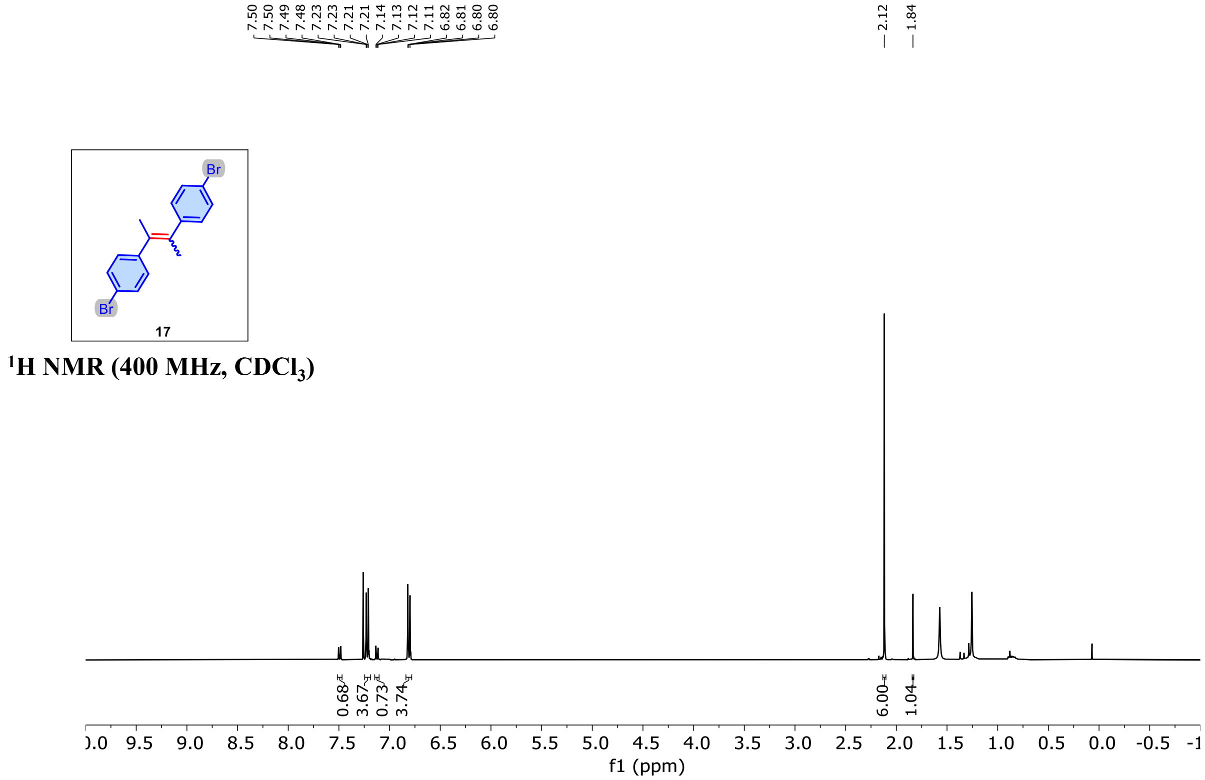

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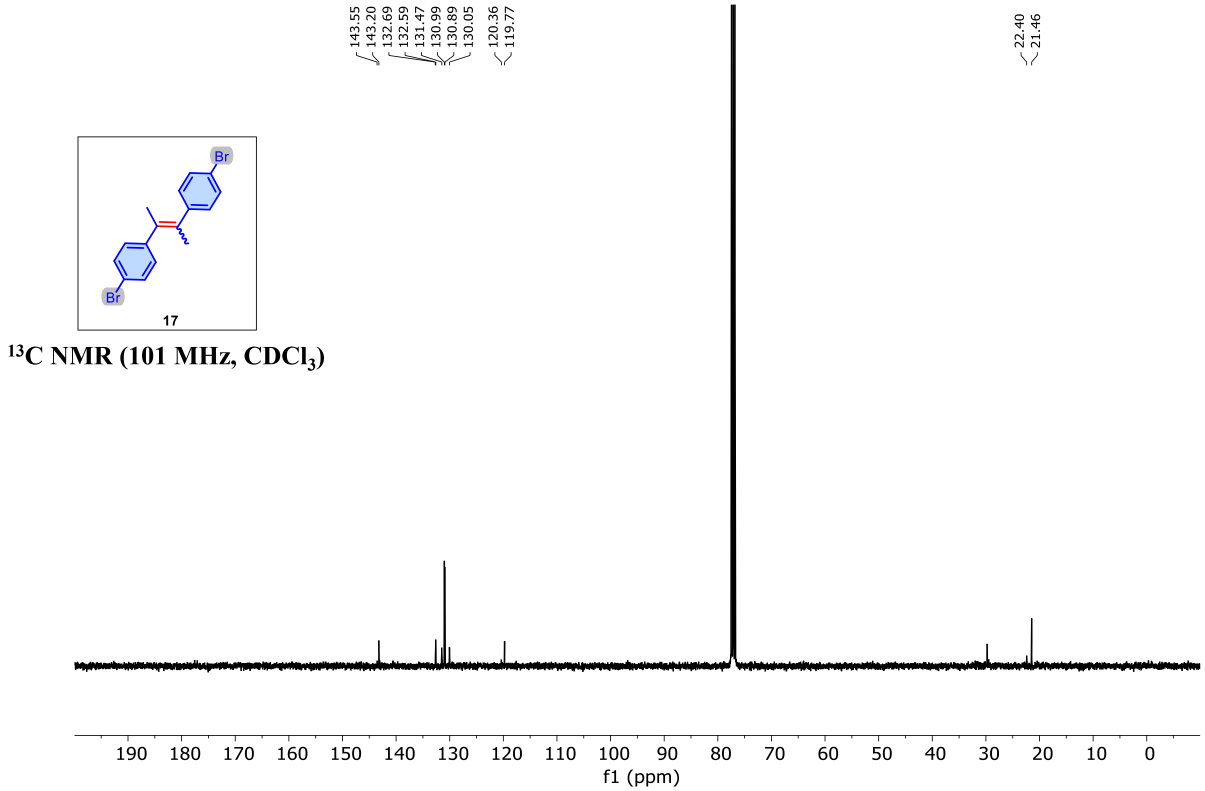

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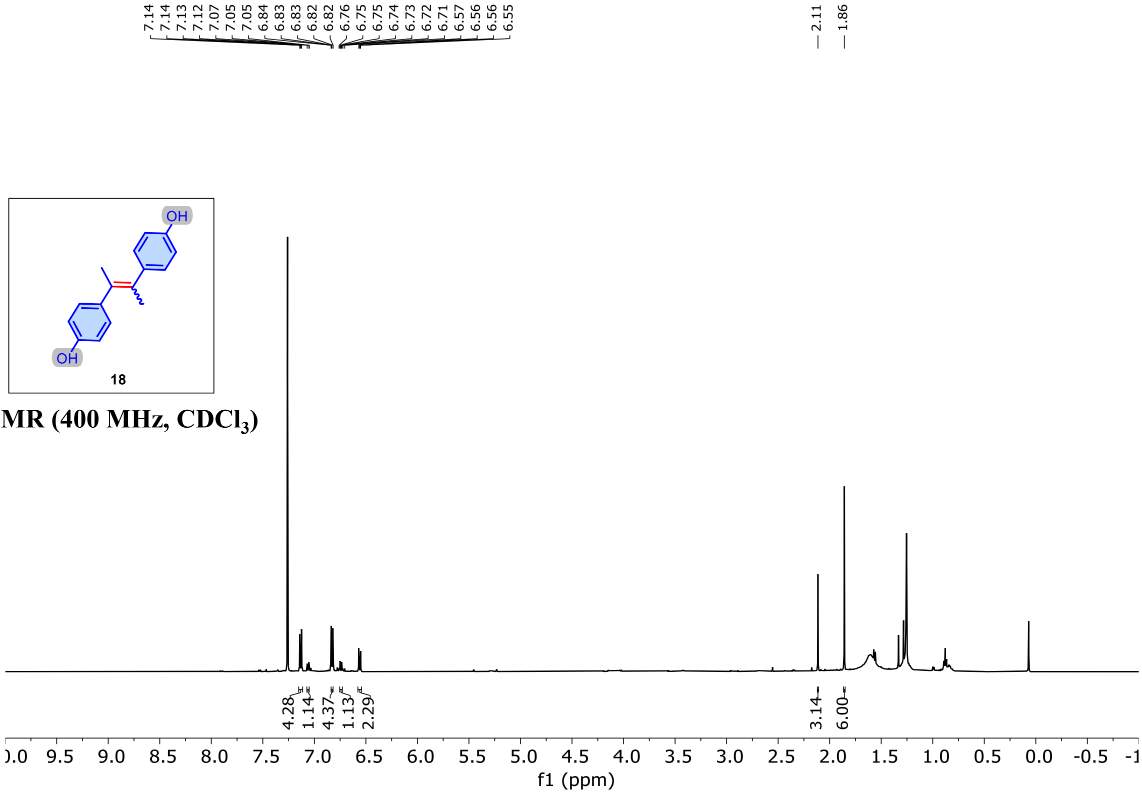

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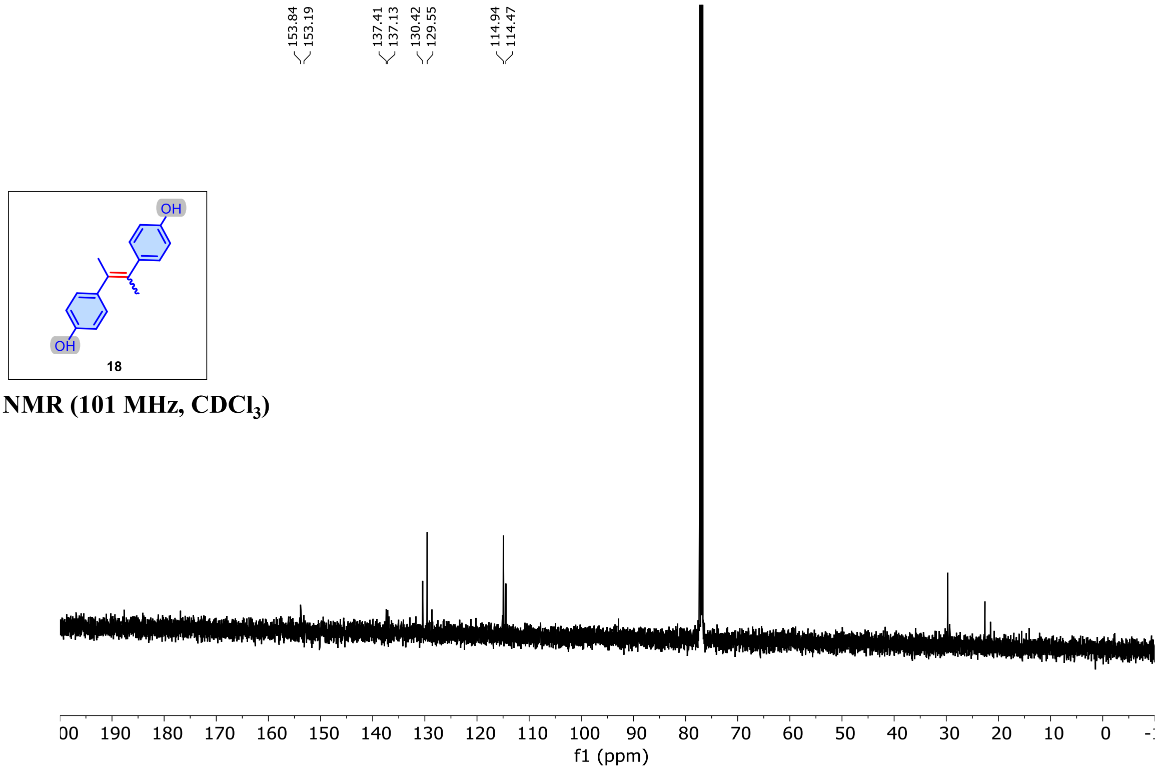

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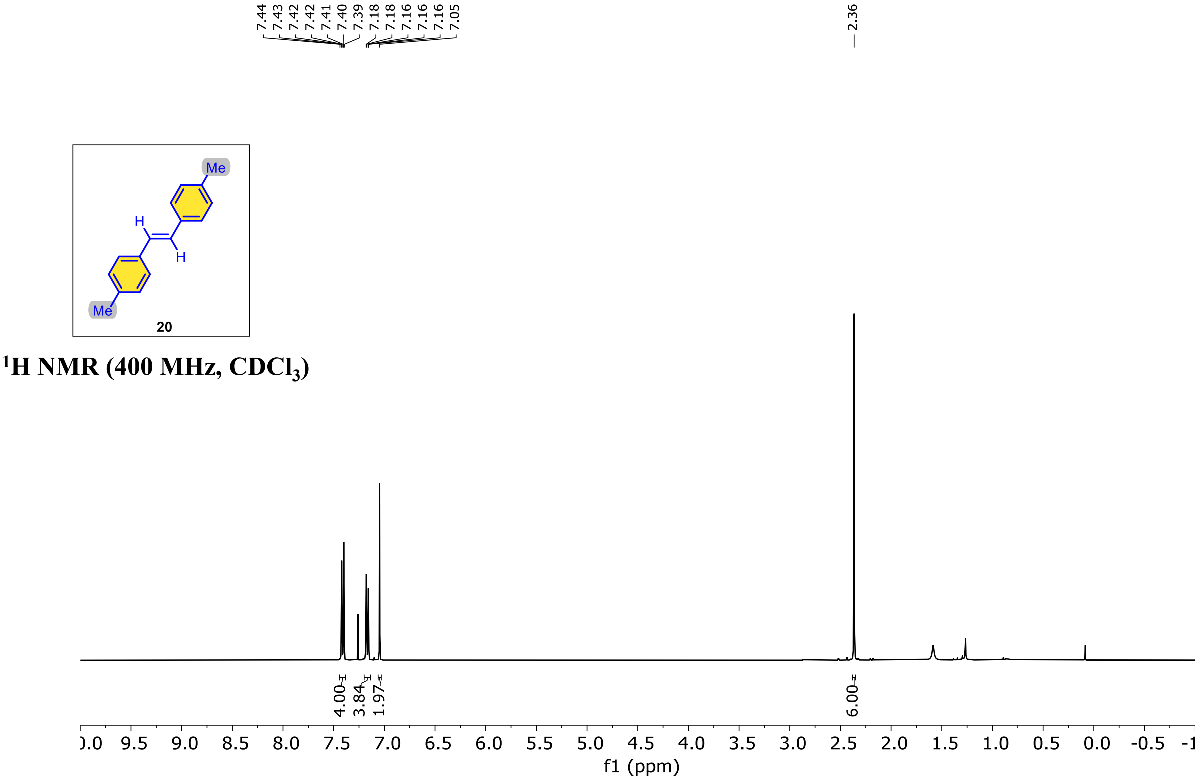

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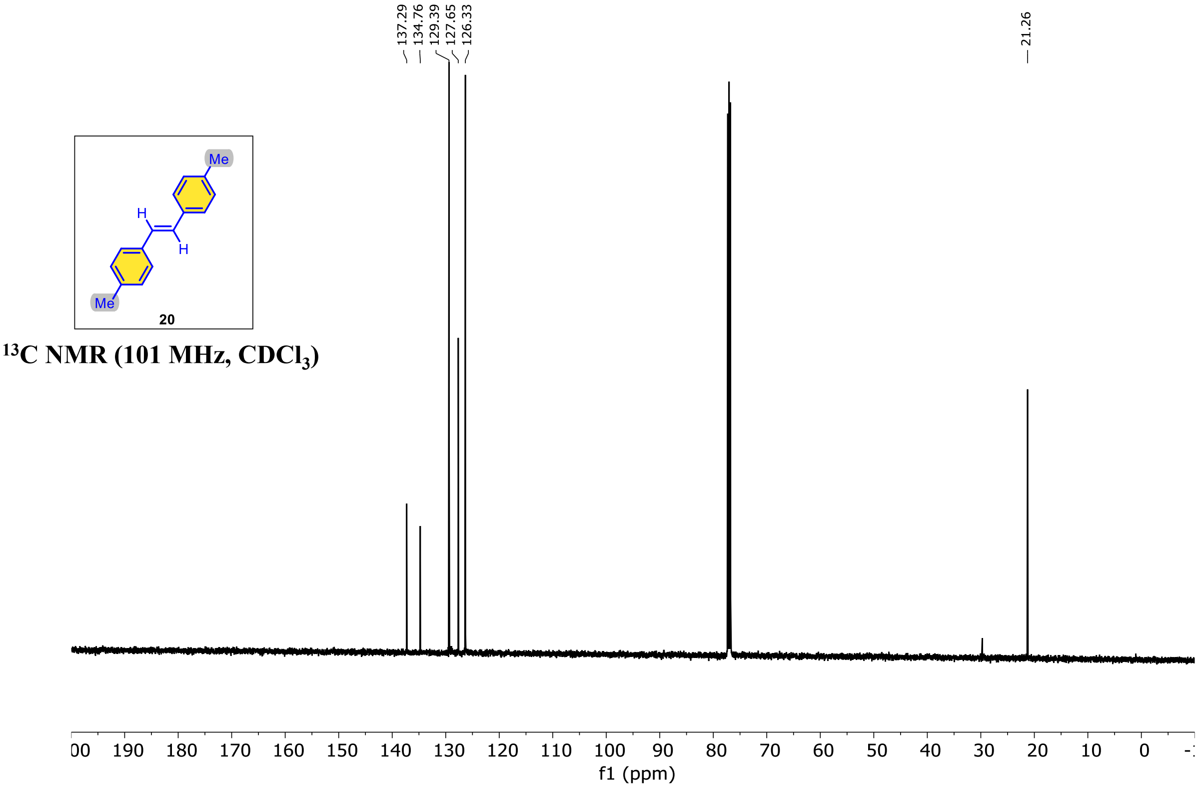

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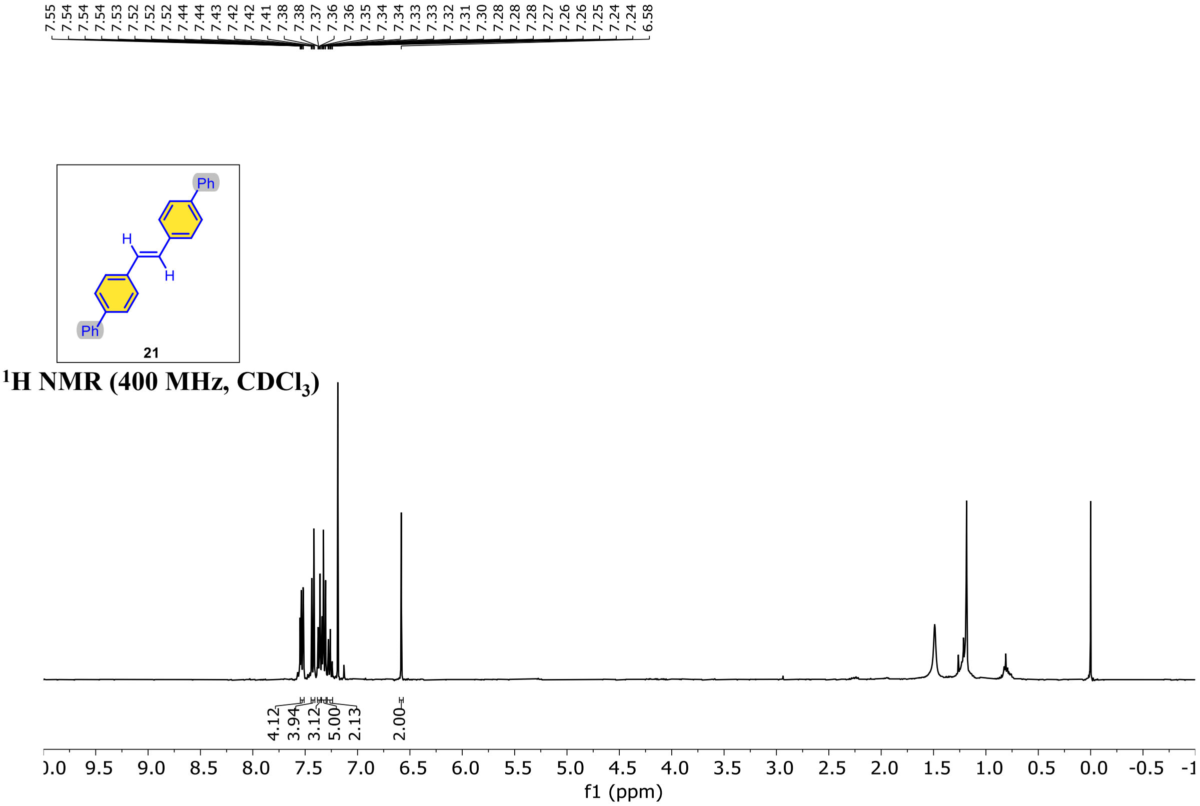
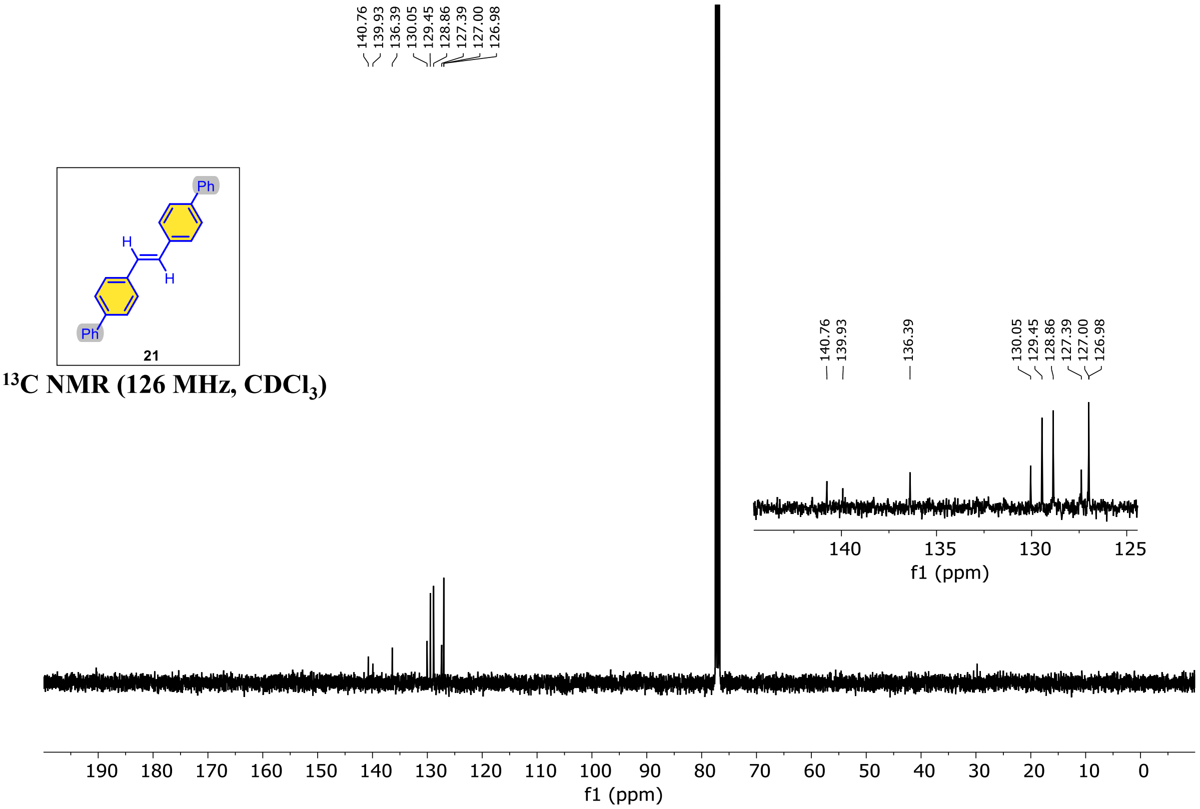


^{1}H NMR (400 MHz, $CDCl_3$)



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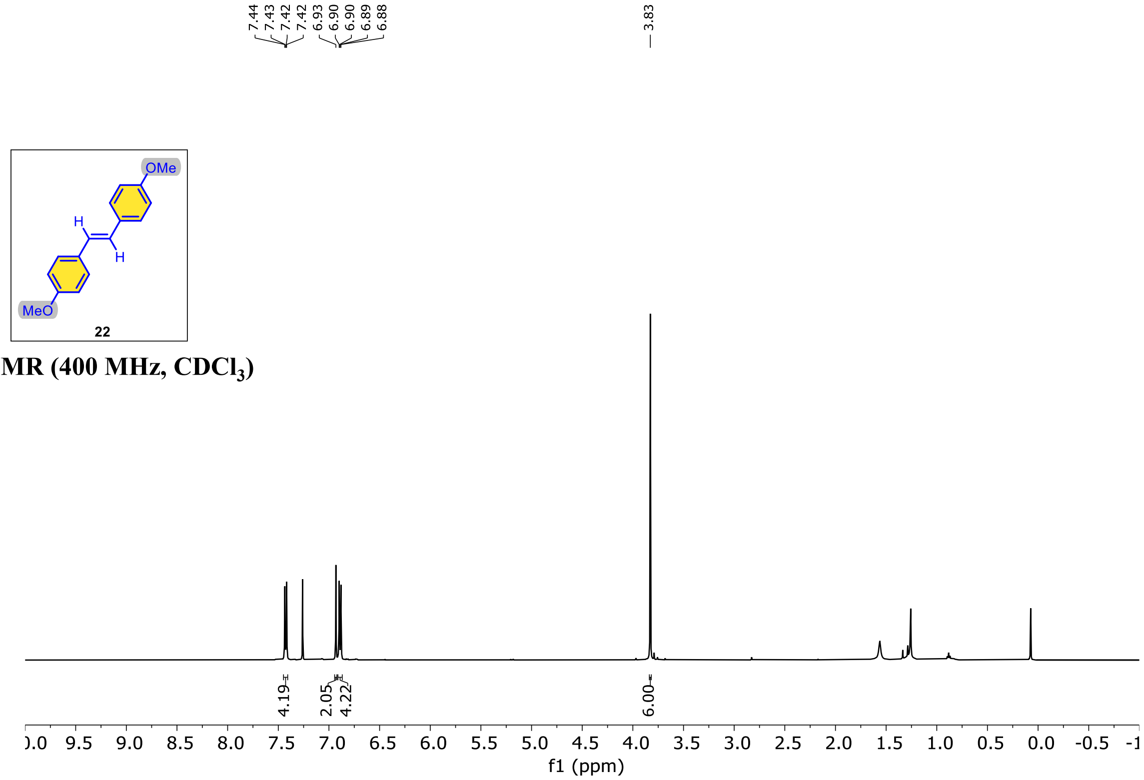
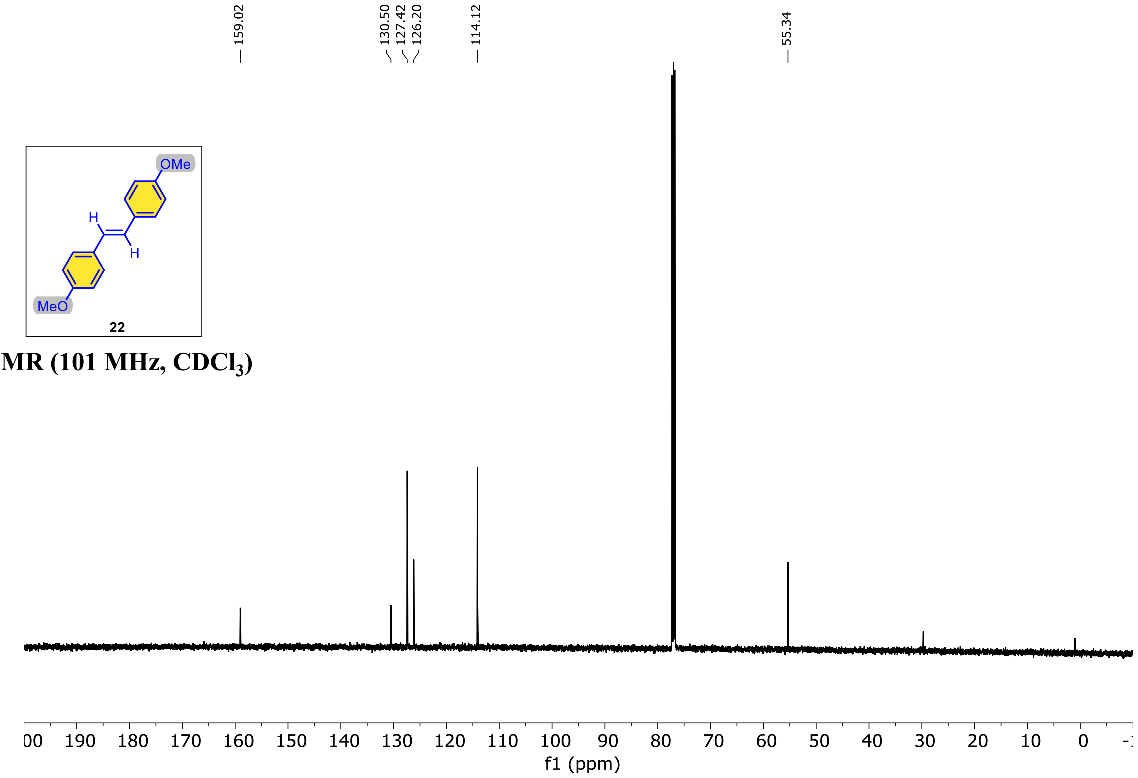
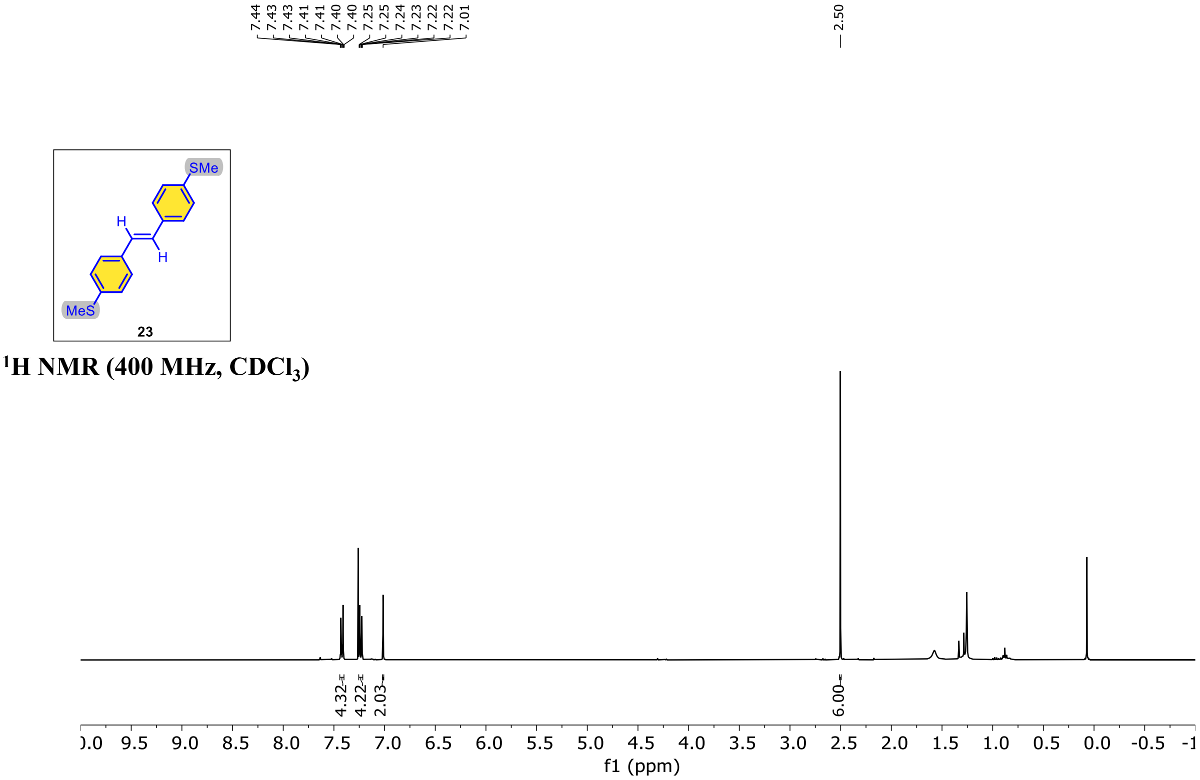


^{1}H NMR (400 MHz, CDCl$_3$)



^{13}C NMR (101 MHz, CDCl$_3$)



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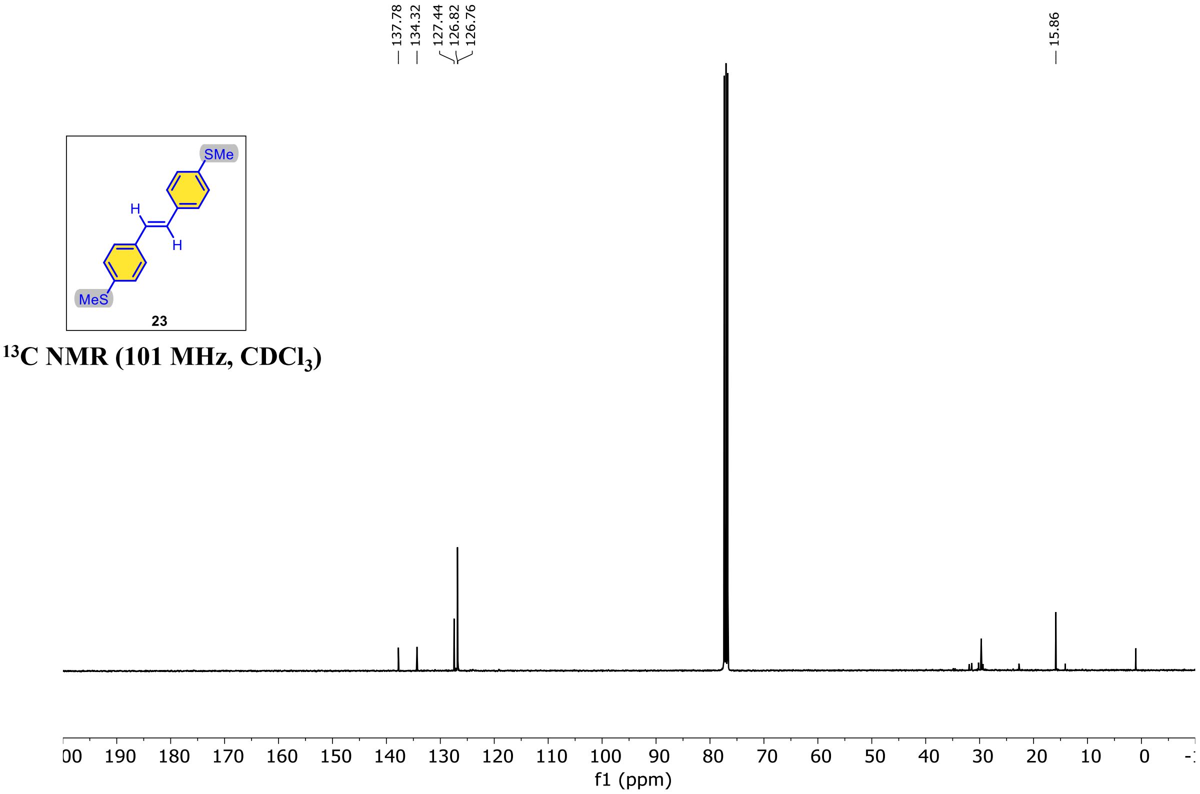

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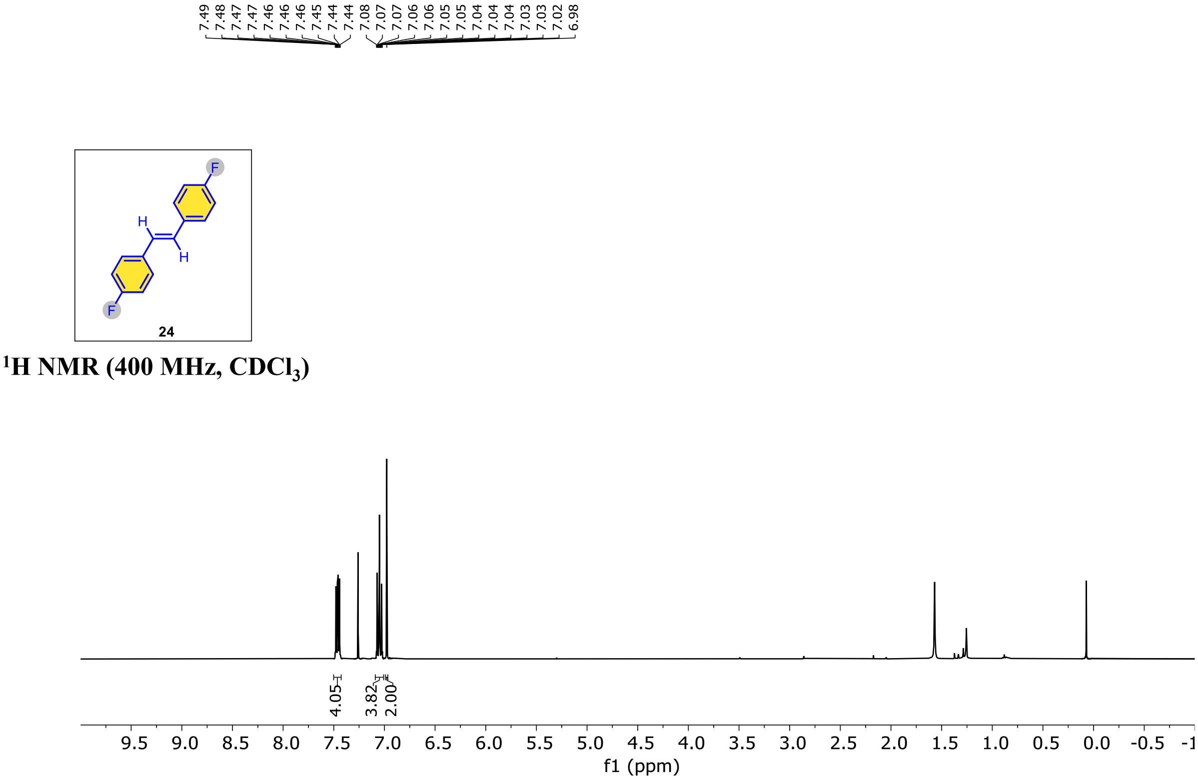

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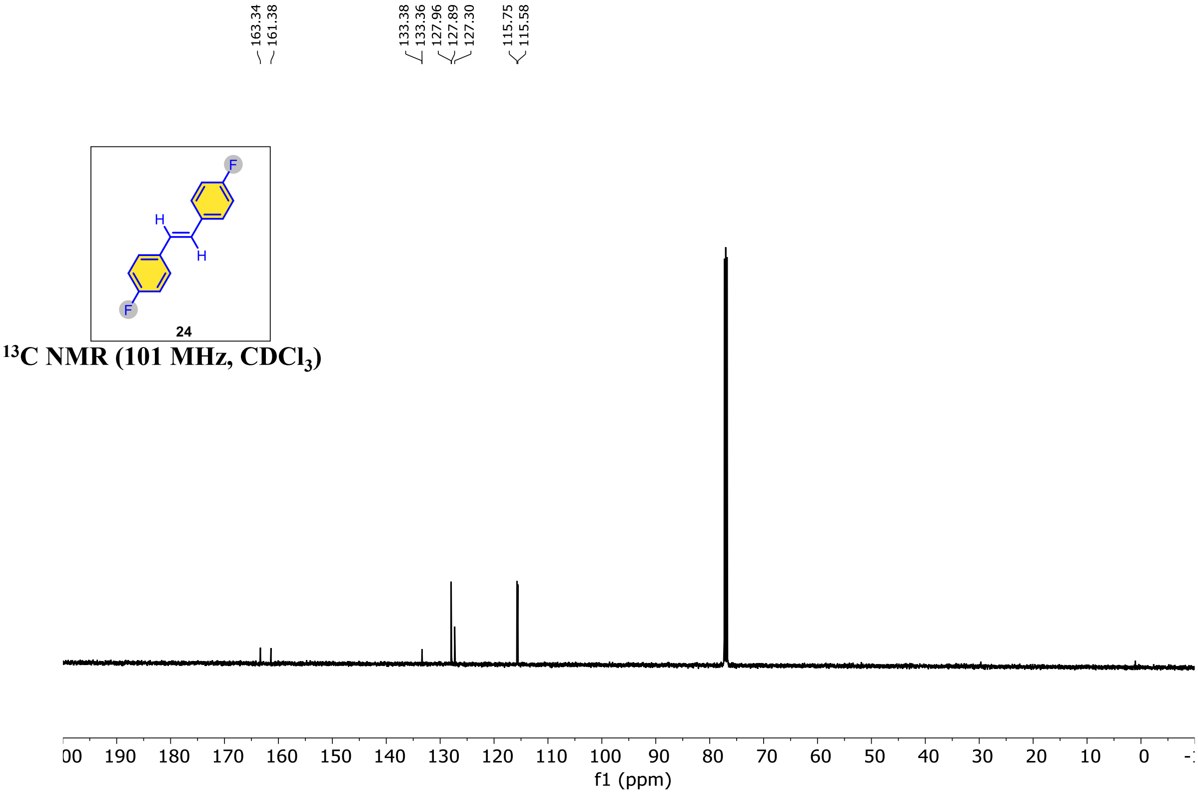

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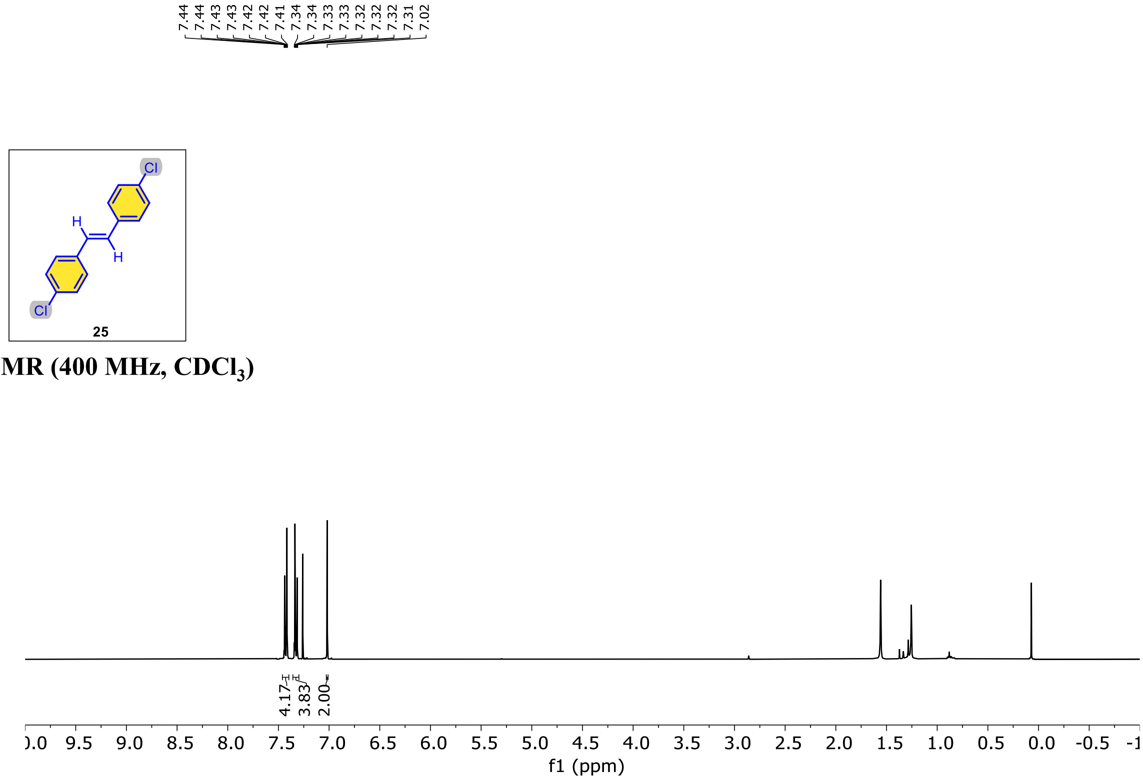

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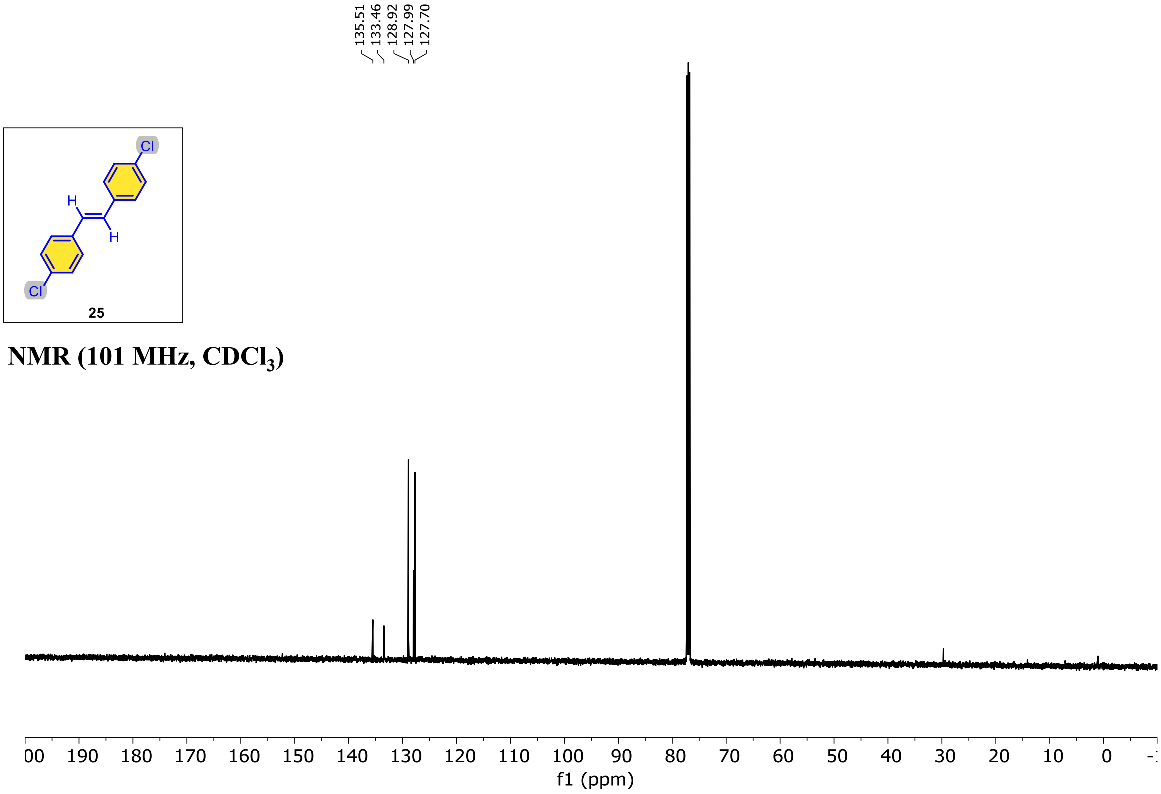

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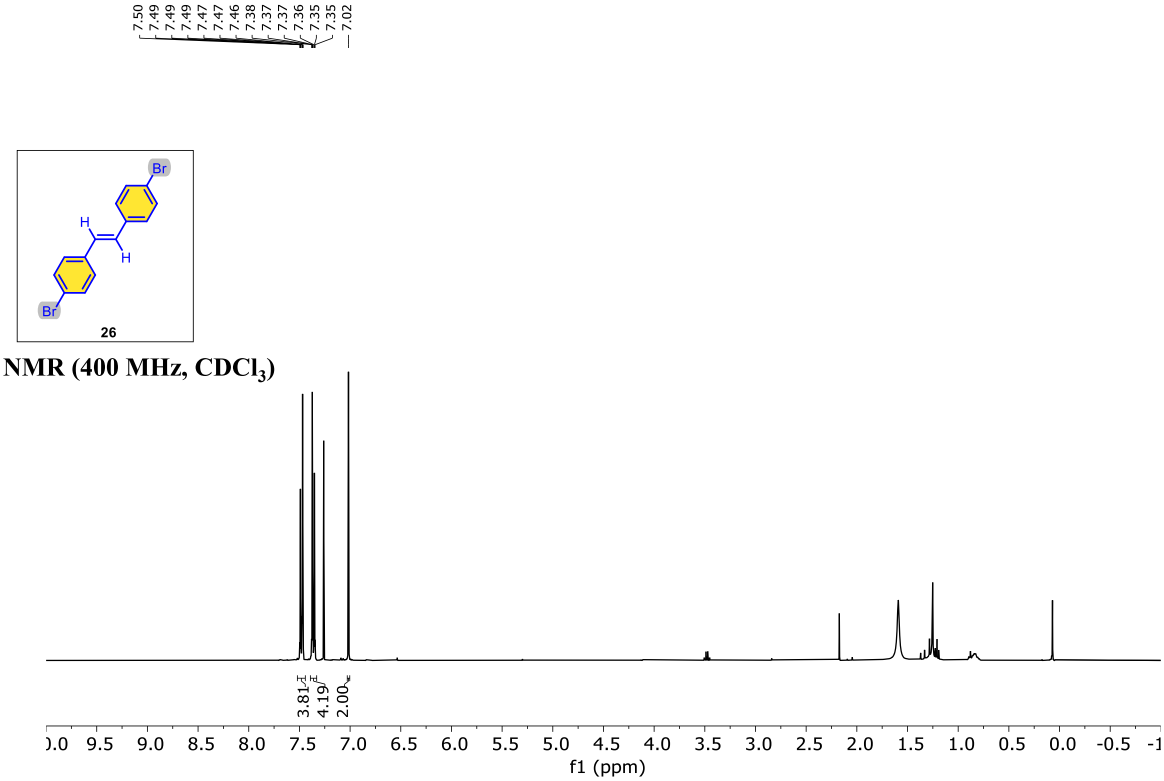

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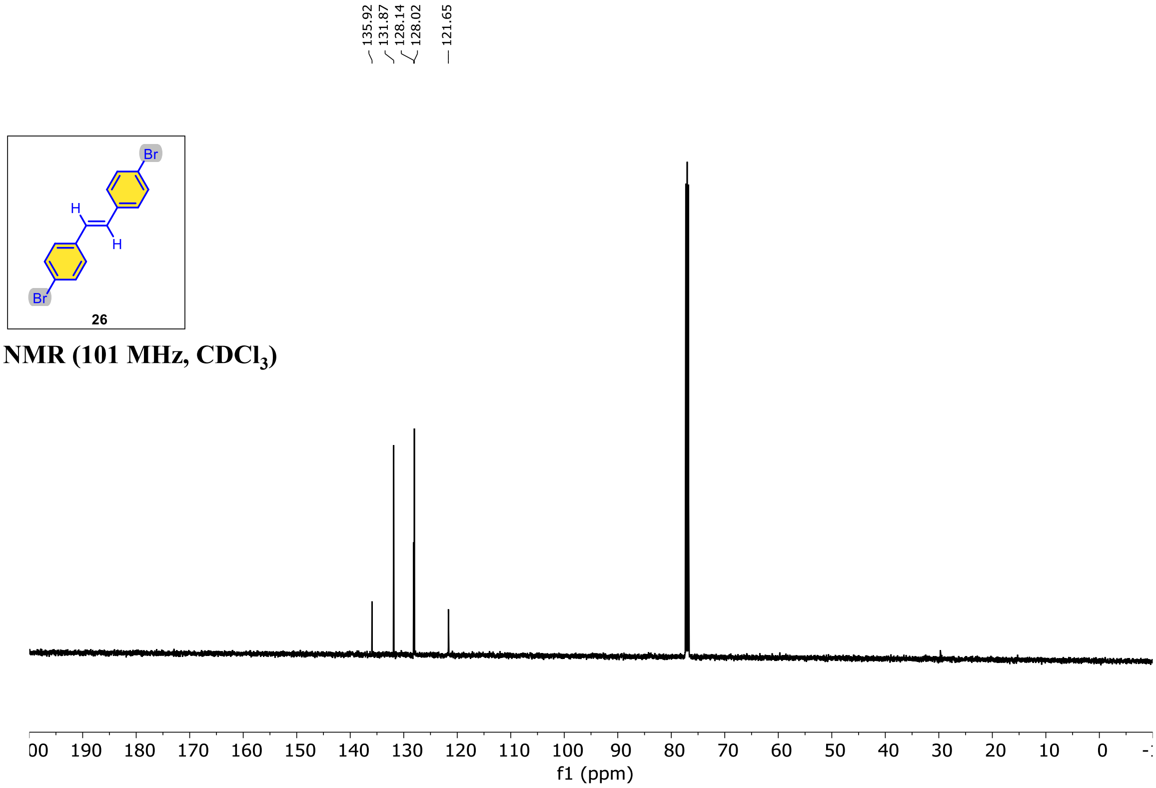
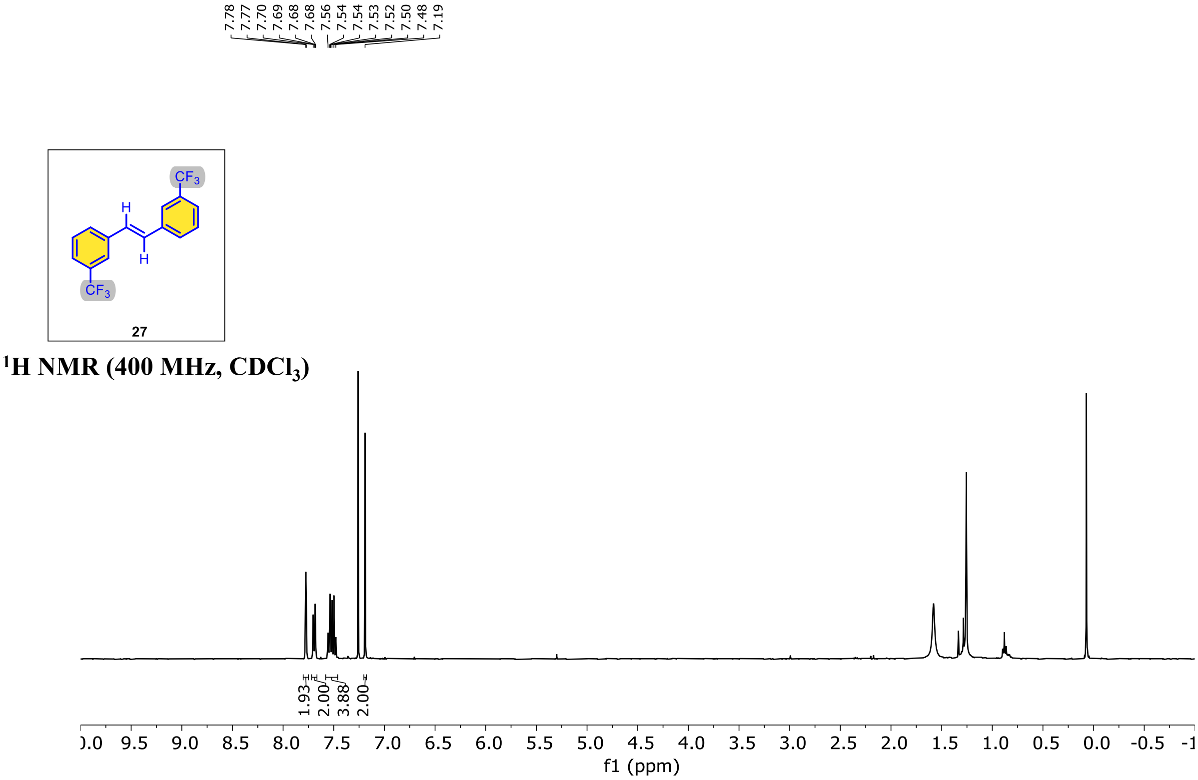
^{1}H NMR (400 MHz, CDCl$_3$)



26

^{13}C NMR (101 MHz, CDCl$_3$)



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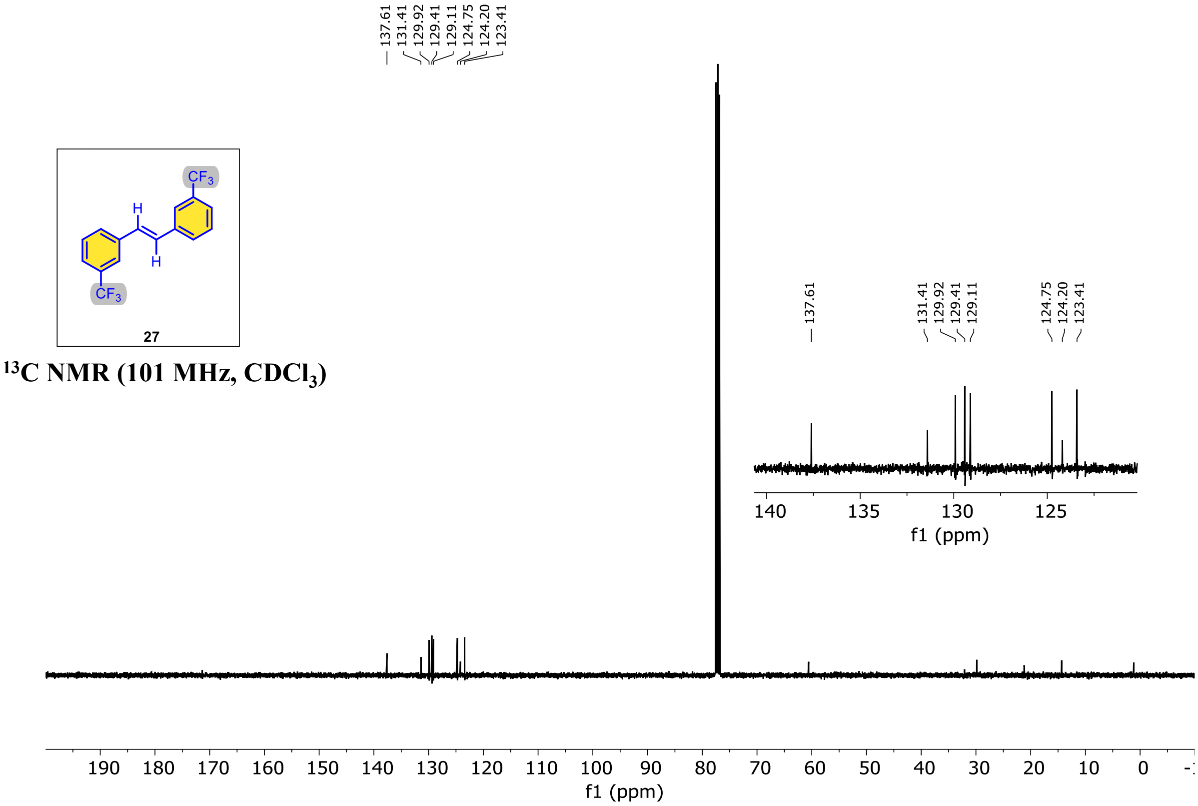

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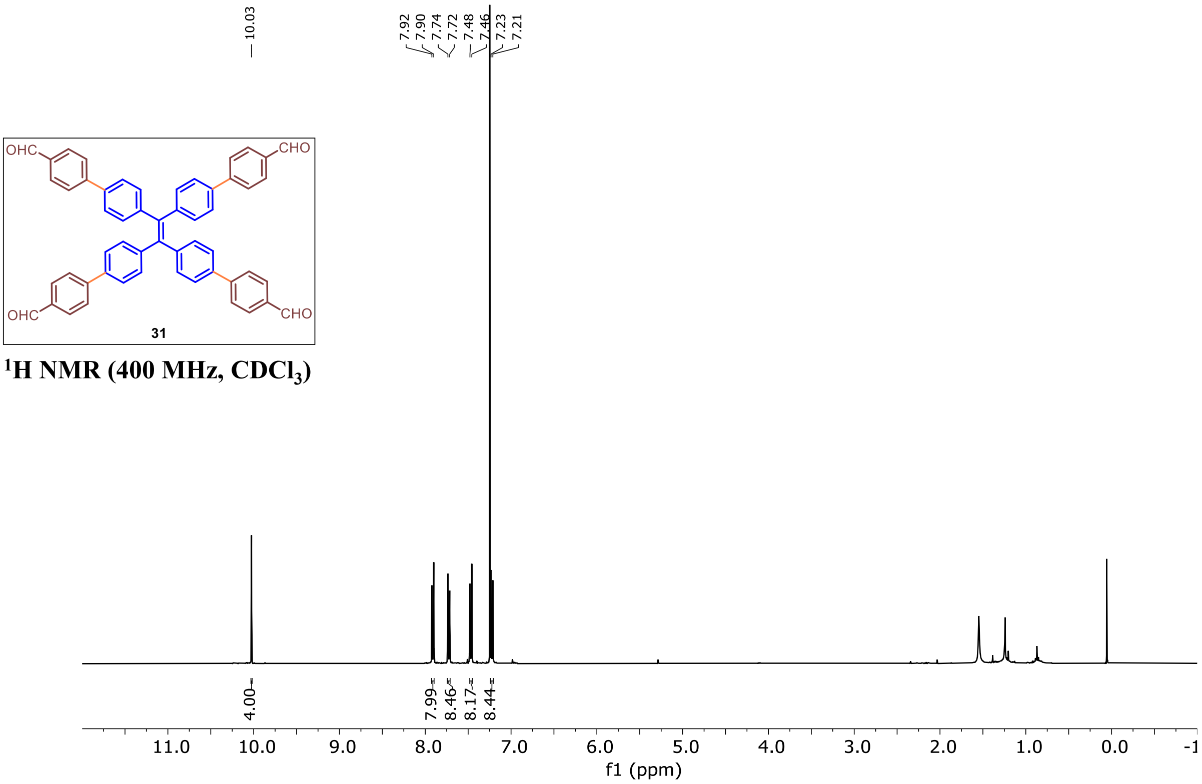
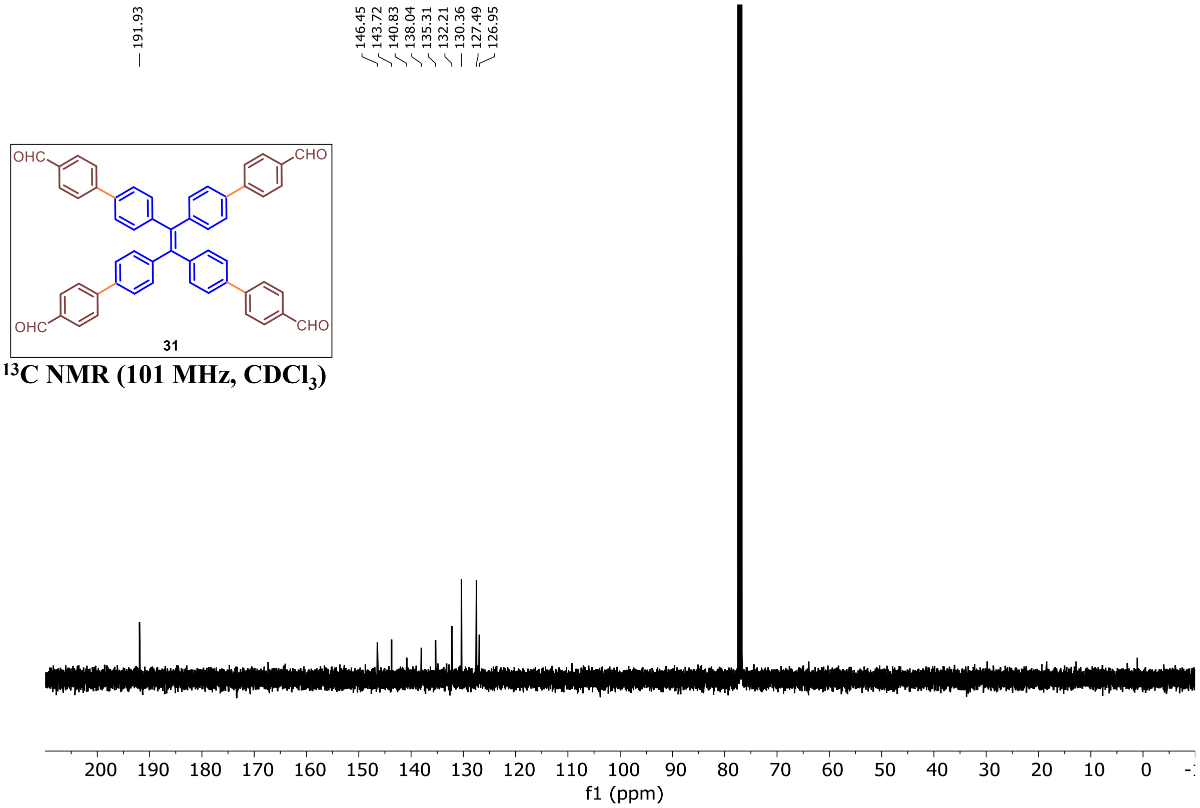


31

^{1}H NMR (400 MHz, CDCl$_3$)



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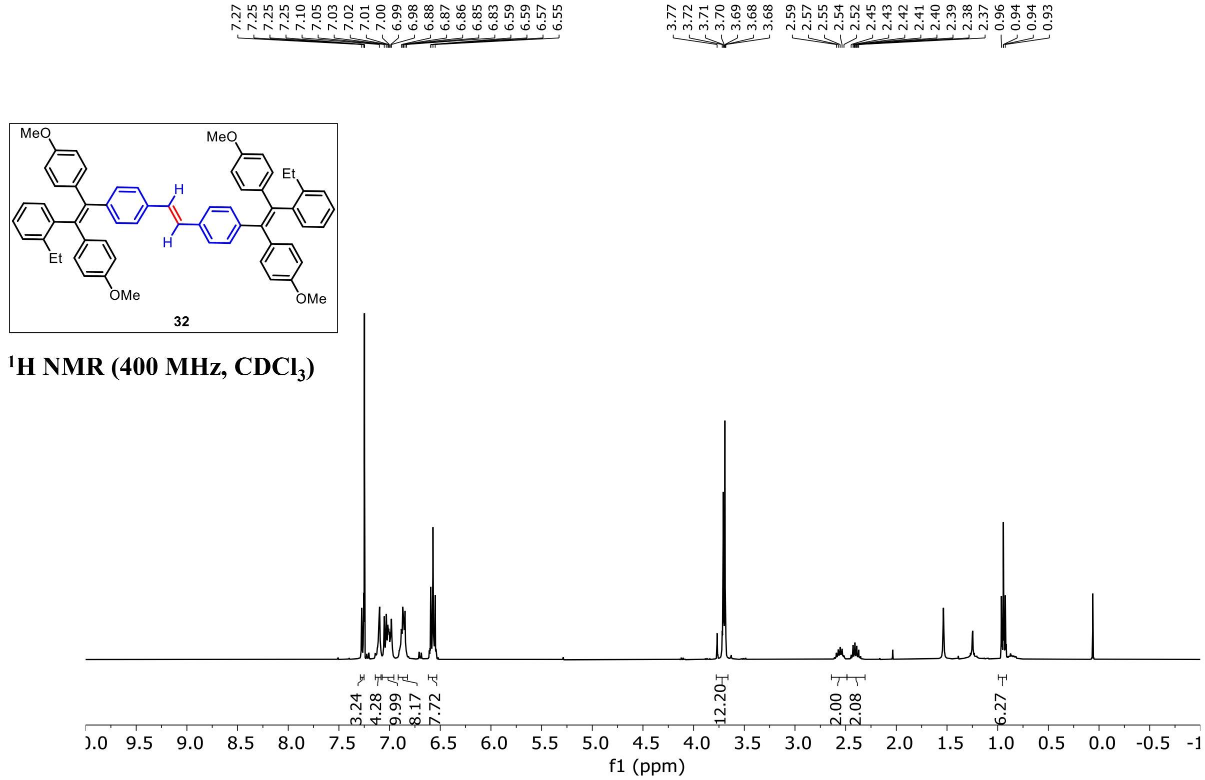
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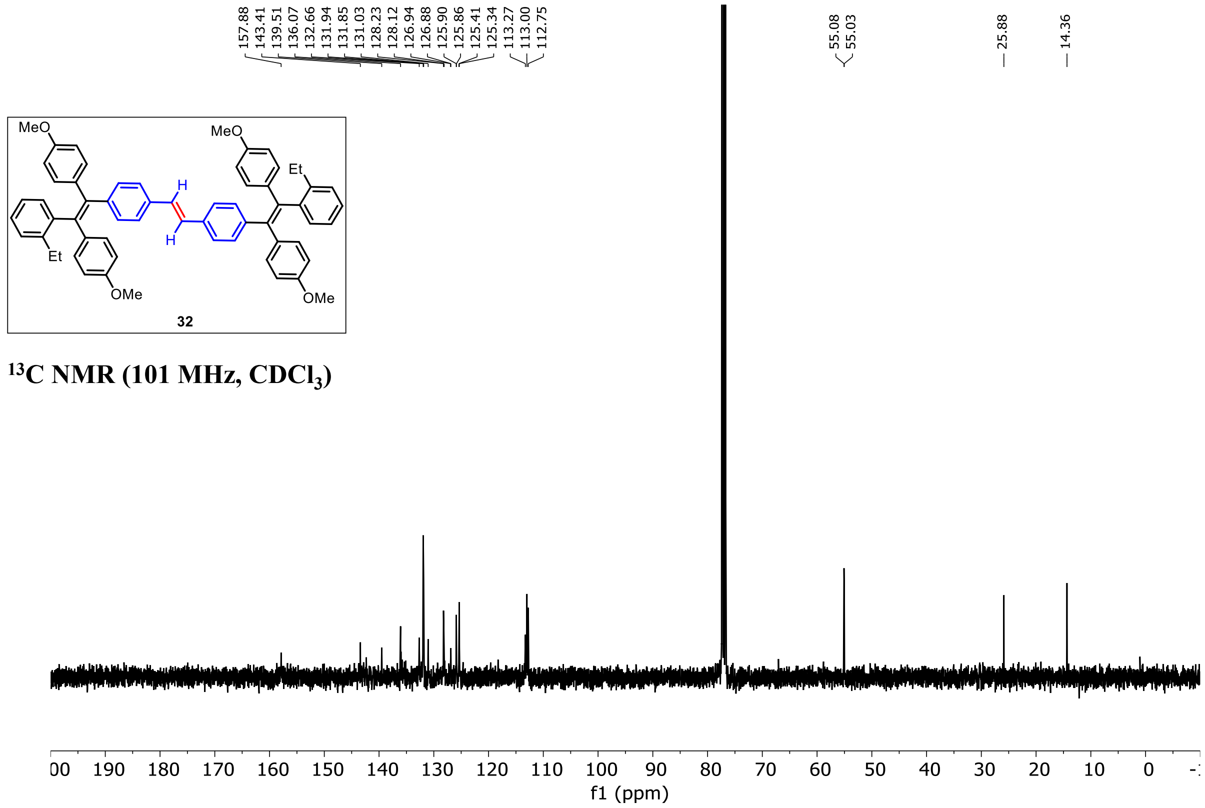
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^{13}C NMR (101 MHz, CDCl$_3$)

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