
Supplementary Information

Convenient construction of tetraphenylethene (TPE) derivatives through Cu(II) mediated cascade dehydrogenation of EWG-activated diphenylmethane

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Table of content

1.	General information	2
2.	Experimental procedure.	3
	2.1. Synthesis of starting materials	4
	2.2. Reaction optimization	14
	2.3. Mechanism consideration	16
	The latent organocopper(II) species	17
	The influence of electronic characterization of substrate on the reaction	17
	The role of carboxylate anion	17
	2.4. Additional example for tandem dehydrogenative homocoupling	19
	2.5. Unsuccessful substrates	20
	2.6. Oxygen as terminal oxidant (adopt from reported procedure)	20
	2.7. Product characterization	21
	2.8. Gram synthesis	50
	2.9. Derivatization of nitro group	53
	2.10. X-ray crystallographic data	57
3.	Copy of NMR spectra	64
	3.1. References	165

1. General information

Copper pivalate ($\text{Cu}(\text{OPiv})_2$) was prepared according to the reported procedure^[1] without any modification. Hexamethylphosphoramide (HMPA), N,N-Dimethylacetamide (DMAc), N,N-dimethylformamides (DMF), N-Methylpyrrolidone (NMP), 1,3-Dimethyl-2-imidazolidinone (DMI), dimethylpropyleneurea (DMPU) and DMSO (Dimethyl sulfoxide) was distilled from CaH_2 under reduced pressure and stored over 3Å or 4Å molecular sieves in glovebox before use. Dioxane and xylene was distilled from Na. The solvent used to prepare starting material was purchased from commercial vendors and used without purification. Unless otherwise noted, all model reactions were performed under nitrogen with the exclusion of moisture using Schlenk techniques. Column chromatography or preparative thin layer chromatography (prep-TLC) was performed on silica gel 300-400 mesh, and visualization was accomplished with UV light. ^1H , ^{13}C , and ^{19}F NMR spectra of all compounds were recorded at 400, 101, and 377 MHz with CDCl_3 as the solvent, respectively. All coupling constants (J values) were reported in Hertz (Hz). Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references (CDCl_3 : $\delta \text{H} = 7.26 \text{ ppm}$, $\delta \text{C} = 77.00 \text{ ppm}$), the following abbreviations were used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublet; td, triplet doublet; and br, broad. HRMS data were recorded on instrument equipped with an ESI source. The absolute geometry of the *E* and *Z* isomer for TPE was confirmed by 2D NOESY spectrum^[2] or single crystal X-ray diffraction.

2. Experimental procedure.

The 1-benzyl-4-nitrobenzene^[3] (**s-1**, 1817-77-2), 4-benzylbenzotrile^[4] (**s-22**, 23450-31-9), 4,4'-methylene dibenzotrile^[5] (**s-23**, 10466-37-2), 1,1'-(methylenebis(4,1-phenylene))bis(ethan-1-one)^[6] (**s-24**, 790-82-9), di(pyridin-2-yl)methane^[7] (**s-26**, 1132-37-2) were known compound. The preparation of these compounds was adapted from the reported procedure without large modification.

bis(4-nitrophenyl)methane^[8] (**s-2**, 1817-74-9), 4-(4-nitrobenzyl)benzotrile^[9] (**s-3**, 850223-44-8), 4-(4-nitrobenzyl)benzaldehyde (**s-4**, 1874222-07-7), 1-(4-(4-nitrobenzyl)phenyl)ethan-1-one^[10] (**s-5**, 181935-82-0), 1-chloro-4-(4-nitrobenzyl)benzene^[11] (**s-8**, 30203-94-2), 1-bromo-4-(4-nitrobenzyl)benzene^[12] (**s-9**, 1351376-94-7), 1-fluoro-4-(4-nitrobenzyl)benzene^[13] (**s-10**, 38695-23-7), 1-(tert-butyl)-4-(4-nitrobenzyl)benzene^[14] (**s-13**, 2411959-64-1), 1-methoxy-4-(4-nitrobenzyl)benzene^[15] (**s-14**, 22865-59-4), methyl(4-(4-nitrobenzyl)phenyl)sulfane^[10] (**s-15**, 199916-54-6), 2-(4-nitrobenzyl)naphthalene^[16] (**s-16**, 3042-62-4), 4-(4-nitrobenzyl)-1,1'-biphenyl^[11] (**s-18**, 1316859-67-2), 4-benzylbenzaldehyde^[17] (**s-20**, 67468-65-9), 4,4'-methylene dibenzaldehyde^[18] (**s-21**, 67-37-8), bis(4-(methylsulfonyl)phenyl)methane^[19] (**s-25**, 22183-07-9), di(pyridin-4-yl)methane (**s-27**, 60776-05-8) were known compound, but synthesized from a new procedure. methyl 4-(4-nitrobenzyl)benzoate (**s-6**, 181935-85-3), N,N-dimethyl-4-(4-nitrobenzyl)benzamide (**s-7**), 1-nitro-4-(4-(trifluoromethyl)benzyl)benzene (**t-11**, 1304788-88-2), 1-nitro-4-(4-(trifluoromethoxy)benzyl)benzene (**s-12**), 3-(4-nitrobenzyl)-1,1'-biphenyl (**s-17**), bis(4'-nitro-[1,1'-biphenyl]-4-yl)methane (**s-19**), were unknown compound. The preparation and characterization of these compounds are provided below. bis(4-iodophenyl)methane that used to prepare the bis(4-(methylsulfonyl)phenyl)methane (**s-25**) and bis(4'-nitro-[1,1'-biphenyl]-4-yl)methane (**s-19**), was synthesized by a reported procedure^[20] without modification.

Table S1. Known compound synthesized by procedure described in literature without any modification.

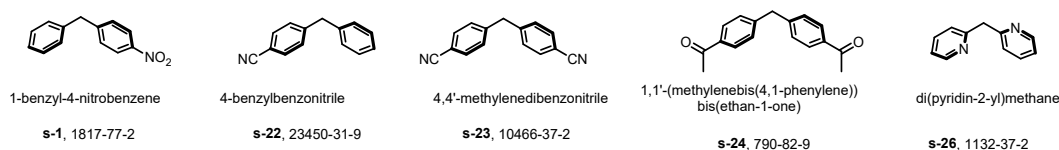
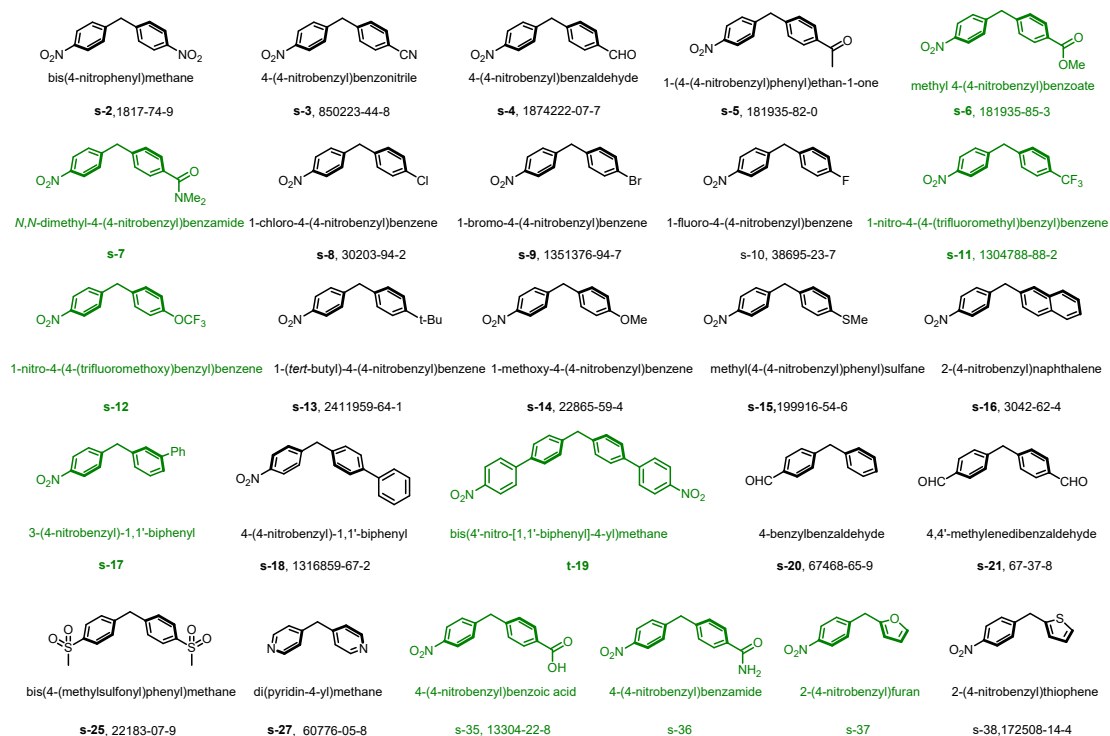


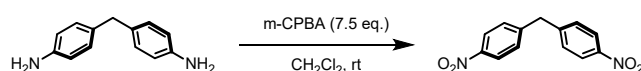
Table S2. Compounds prepared by new procedure.



Caution: dangerous! Caution should be taken when handling 4-Nitrobenzyl bromide and 4-nitrobenzyl chloride used to prepare diphenylmethane derivatives, which were sensitizing chemicals and may cause serious skin irritation when exposed to. Standard chemical safety protocols to minimize exposure and prevent accidental ingestion, inhalation, or dermal contact should be carefully taken.

2.1. Synthesis of starting materials

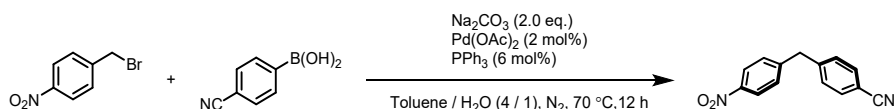
bis(4-nitrophenyl)methane (**s-2**, known compound, 1817-74-9)



A solution of 4,4'-methylenedianiline (3.97 g, 20 mmol, 1.0 eq.) was added to a stirred suspension of *m*-CPBA in dichloromethane (25.88 g suspended in 40 mL CH_2Cl_2 , 150 mmol, 7.5 eq.) dropwise with constant pressure dropping funnel, during which the solid gradually dissolved and the mixture turns to greenish and finally yellowish from colorless. After the addition was complete, the mixture was stirred at room temperature (approximately 30 °C) for additional 4 h, resulting in the colorless precipitate formation. The solid was removed by filtration, and two portions of dichloromethane (50 mL \times 2) were used to rinse the filter cake. The filtrate was transferred to a separatory funnel and diluted with petroleum ether (100 mL) followed by sequential wash with saturated aqueous Na_2CO_3 (50 mL \times 5) (after that, the organic layer became colorless), diluted hydrochloric acid (1 M, 50 mL \times 2), water (50 mL), and brine (50 mL), the resulting solution was filtered with a short pad of silica gel and concentrated by vacuum, and the crude material was further purified by silica gel chromatography, affording the title compound (4.23 g, 81% yield) as a colorless solid. **$^1\text{H NMR}$ (400 MHz, CDCl_3)** δ 8.17 (d, J = 7.8 Hz, 4H), 7.34 (d, J = 7.9 Hz, 4H), 4.19 (s, 2H). **$^{13}\text{C NMR}$ (101 MHz, CDCl_3)** δ 147.0, 146.8, 129.9, 124.1, 41.4.

Characterization data conforms with the literature.^[8]

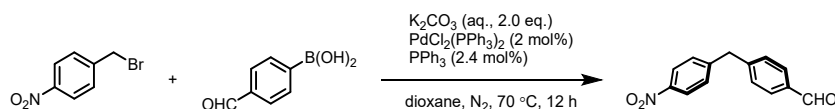
4-(4-nitrobenzyl)benzonitrile (s-3, known compound, 850223-44-8)



To a 250 mL Schlenk tube was added (4-cyanophenyl)boronic acid (955 mg, 6.5 mmol, 1.3 eq.), $\text{Pd}(\text{OAc})_2$ (22.5 mg, 2 mol%), PPh_3 (78.6 mg, 6 mol%), and a stirred bar. The mixture was evacuated and backfilled with N_2 for three cycles. Then, under N_2 flow, the Na_2CO_3 aqueous solution (1.06 g Na_2CO_3 dissolved in 5 mL water, 10.0 mmol, 2.0 eq.) and 1-(bromomethyl)-4-nitrobenzene (1.08 g, dissolved in 20 mL toluene, 5.0 mmol, 1.0 eq.) was sequentially added with Pasteur pipette. The tube was capped, and the mixture was stirred in an oil bath preheated at 70 °C for 12 h. The reaction mixture was cooled to room temperature and then filtered with a short pad of celite. The filter cake was washed with additional ethyl acetate. The filtrate was transferred to a separatory funnel, and the collected organic phase was washed with brine. After removing the solvent by vacuum, the remaining mixture was purified by silica gel chromatography, affording the 4-(4-nitrobenzyl)benzonitrile as a colorless solid. $R_f = 0.2$ (eluent = dichloromethane/petroleum ether = 1/2), $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.16 (d, $J = 8.6$ Hz, 2H), 7.60 (d, $J = 8.2$ Hz, 2H), 7.33 (d, $J = 8.4$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 4.14 (s, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.0, 144.7, 132.7, 129.8 (129.86), 129.8 (129.81), 124.0, 118.7, 110.9, 41.7.

Data conforms with the literature well.^[9]

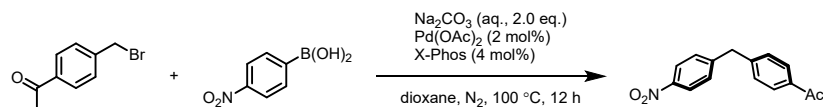
4-(4-nitrobenzyl)benzaldehyde (s-4, known compound, 1874222-07-7)



A 250 mL Schlenk tube was charged with 1-(bromomethyl)-4-nitrobenzene (1.08 g, 5.0 mmol, 1.0 eq.), (4-formylphenyl)boronic acid (890 mg, 5.9 mmol, 1.18 eq.), $\text{PdCl}_2(\text{PPh}_3)_2$ (70.2 mg, 2 mol%), PPh_3 (32 mg, 2.4 mol%), and a stirred bar. The mixture was evacuated and backfilled with N_2 for three cycles. Then, under N_2 flow, aqueous K_2CO_3 (1.38 g dissolved in 5 mL water, 10.0 mmol, 2.0 eq.) and dioxane (20 mL) were added with a Pasteur pipette. The tube was capped, and the resulting mixture was stirred in an oil bath preheated at 70 °C for 12 h. After cooling to room temperature, the mixture was filtered through a short pad of silica gel, which was washed with additional ethyl acetate. After concentration of the collected filtrate by vacuum, the remaining solid was brought into silica gel chromatography to give the 4-(4-nitrobenzyl)benzaldehyde as a yellowish solid. $R_f = 0.2$, eluent = dichloromethane/petroleum ether = 1/1. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.97 (s, 1H), 8.14 (d, $J = 8.4$ Hz, 2H), 7.83 (d, $J = 7.8$ Hz, 2H), 7.34 (d, $J = 8.1$ Hz, 4H), 4.16 (s, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 191.8, 147.4, 146.8, 146.3, 135.2, 130.3, 129.8, 129.7, 124.0, 41.8.

Characterization data conforms with the literature^[21] well.

1-(4-(4-nitrobenzyl)phenyl)ethan-1-one (s-5, known compound, 181935-82-0)

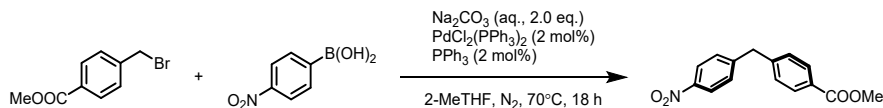


A 250 mL Schlenk tube was charged with 1-(4-(bromomethyl)phenyl)ethan-1-one (0.53 g, 2.5 mmol, 1.0 eq.), (4-nitrophenyl)boronic acid (0.50 g, 3.0 mmol, 1.2 eq.), $\text{Pd}(\text{OAc})_2$ (11.2 mg, 2 mol%), X-Phos (47.7 mg, 4 mol%), and a stirred bar. The mixture was evacuated and backfilled with N_2 for three cycles. Then, under N_2 flow, the Na_2CO_3 aqueous solution (0.53 g Na_2CO_3 dissolved in 2.5 mL water, 5.0 mmol, 2.0 eq.) and dioxane (10 mL) were sequentially added with Pasteur pipette. The tube was capped, and the mixture was stirred in an oil bath preheated at 100 °C for 12 h. After cooling to room temperature, needle crystalline was precipitated, and ethyl acetate (20 mL) was added to dissolve the crystal under ultrasound. The mixture was filtered through a short pad of celite, which was washed with additional ethyl acetate (50 mL). The filtrate was collected, and most of the dioxane and ethyl acetate was removed by vacuum. Additional ethyl acetate was added to resolve the mixture, and the resulting biphasic solution was transferred to a separatory funnel. The collected organic layer was washed with brine (10 mL), filtered with a short pad of silica gel, and concentrated under vacuum. The remaining solid was purified by silica gel chromatography, affording the title compound as

a yellowish solid (255 mg, 40% yield). $R_f = 0.5$ (eluent= dichloromethane). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.15 (d, $J = 8.3$ Hz, 2H), 7.91 (d, $J = 7.9$ Hz, 2H), 7.33 (d, $J = 8.3$ Hz, 2H), 7.26 (d, $J = 7.9$ Hz, 2H), 4.13 (s, 2H), 2.58 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 197.7, 147.8, 144.7, 135.9, 129.8, 129.3, 129.0, 124.0, 41.7, 26.7.

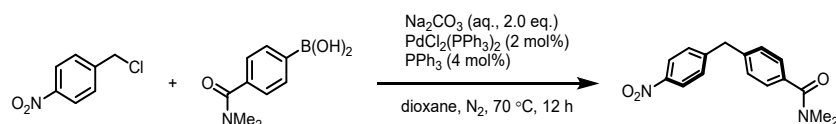
Characterization data conforms with literature well.^[10]

methyl 4-(4-nitrobenzyl)benzoate (s-6, new compound, 181935-85-3)



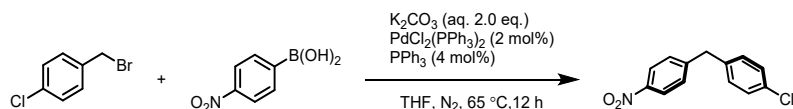
A 250 mL Schlenk tube was charged with methyl 4-(bromomethyl)benzoate (1.15 g, 5.0 mmol, 1.0 eq.), (4-nitrophenyl)boronic acid (1.00 g, 6.0 mmol, 1.2 eq.), $\text{PdCl}_2(\text{PPh}_3)_2$ (70.2 mg, 2 mol%), PPh_3 (26.2 mg, 2 mol%), and a stirred bar. The mixture was evacuated and backfilled with N_2 for three cycles. Then, under N_2 flow, the Na_2CO_3 aqueous solution (1.06 g Na_2CO_3 dissolved in 5 mL water, 10.0 mmol, 2.0 eq.) and 2-MeTHF (20 mL) was sequentially added with Pasteur pipette. The tube was capped and stirred in an oil bath preheated at 70 °C for 18 h. After cooling to room temperature, the mixture was filtered through a short pad of celite. The tube was washed with additional ethyl acetate (ca. 50 mL), which was used to rinse the short pad of celite. The filtrate was transferred to a 125 mL separatory funnel, the aqueous layer was removed, the organic layer was washed with brine (20 mL) and concentrated by vacuum. The remaining solid was dissolved in 20 mL dichloromethane and filtered through a short pad of silica gel, which was rinsed with additional dichloromethane. The solvent was removed by vacuum, and the remaining solid was brought into silica gel chromatography, giving the methyl 4-(4-nitrobenzyl)benzoate as a colorless solid (1.15 g, 84%), $R_f = 0.19$ (eluent = dichloromethane/petroleum ether = 1.0/1.5). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.14 (d, $J = 8.7$ Hz, 2H), 7.98 (d, $J = 8.3$ Hz, 2H), 7.32 (d, $J = 8.6$ Hz, 2H), 7.24 (d, $J = 8.3$ Hz, 2H), 4.12 (s, 2H), 3.90 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.8, 147.8, 146.7, 144.5, 130.2, 129.8, 129.0, 128.8, 123.9, 52.2, 41.7. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{15}\text{H}_{14}\text{NO}_4^+$ 272.0917, found 272.0919. Melting point :125 – 128 °C.

N,N-dimethyl-4-(4-nitrobenzyl)benzamide, (s-7, new compound)



A 250 mL Schlenk tube was charged with (4-(dimethylcarbamoyl)phenyl)boronic acid (2.32 g, 12.0 mmol, 1.2 eq.), $\text{PdCl}_2(\text{PPh}_3)_2$ (140.4 mg, 2 mol%), PPh_3 (105.0 mg, 4 mol%), and a stirred bar. The mixture was evacuated and backfilled with N_2 for three cycles. Then, under N_2 flow, the Na_2CO_3 aqueous solution (2.12 g dissolved in 10 mL water, 20 mmol, 2.0 eq.) and 1-(chloromethyl)-4-nitrobenzene (1.72 g, dissolved in 40 mL dioxane, 10.0 mmol, 1.0 eq.) was sequentially added with Pasteur pipette. The tube was capped, and the mixture was stirred in an oil bath preheated at 70 °C for 12 h. After cooling to room temperature, the mixture was filtered through a short pad of celite, which was washed with additional ethyl acetate. The filtrate was collected, and the volatile was removed by vacuum. The remaining solid was brought into silica gel chromatography to give the N,N-dimethyl-4-(4-nitrobenzyl)benzamide as a colorless solid. $R_f = 0.1$, eluent: ethyl acetate/dichloromethane = 1/100. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.12 (d, $J = 8.3$ Hz, 2H), 7.36 (d, $J = 7.9$ Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 7.18 (d, $J = 7.9$ Hz, 2H), 4.08 (s, 2H), 3.08 (s, 3H), 2.97 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 171.3, 148.2, 146.6, 140.7, 134.9, 129.7, 128.9, 127.7, 123.8, 41.5, 39.6, 35.4. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_3^+$ 285.1234, found 285.1225. Melting point :69 – 74 °C.

1-chloro-4-(4-nitrobenzyl)benzene (s-8, known compound, 30203-94-2)

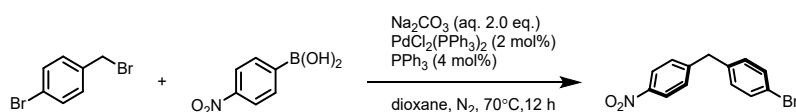


A 350 mL Schlenk tube was charged with 1-(bromomethyl)-4-chlorobenzene (3.08 g, 15.0 mmol, 1.0 eq.), (4-nitrophenyl)boronic acid (3.00 g, 18.0 mmol, 1.2 eq.), $\text{PdCl}_2(\text{PPh}_3)_2$ (210.6 mg, 2 mol%), PPh_3 (157.4 mg, 4 mol%), and a stirred bar. The mixture was evacuated and backfilled with N_2 for three cycles. Then, under N_2

flow, aqueous K_2CO_3 (4.15 g dissolved in 10 mL water, 30 mmol, 2.0 eq.) and THF (60 mL) were sequentially added with Pasteur pipette. The tube was capped, and the mixture was stirred in an oil bath preheated at 65 °C for 12 h. The reaction mixture was cooled to room temperature and transferred to a separatory funnel (additional ethyl acetate was used to rinse the tube), the organic layer was separated, and the aqueous layer was extracted with ethyl acetate (10 mL). The combined organic phase was concentrated under vacuum, during which few precipitate formed, additional dichloromethane was added, and the solid did not dissolve. The suspension was filtered to remove the solid, and the filtrate was concentrated under vacuum, the remaining solid was purified with silica gel chromatography to give the 1-chloro-4-(4-nitrobenzyl)benzene (3.53 g, 95%) as a colorless solid, eluent: dichloromethane/petroleum ether = 1/5. (R_f = 0.19, eluent: dichloromethane/petroleum ether = 1/6). 1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 7.10 (d, J = 8.3 Hz, 2H), 4.04 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 146.7, 137.7, 132.7, 130.3, 129.7, 129.0, 123.9, 41.0.

Characterization data conforms with the literature well.^[11]

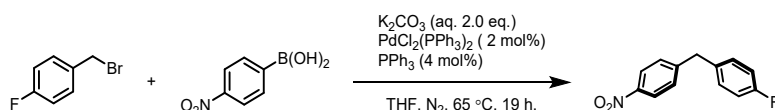
1-bromo-4-(4-nitrobenzyl)benzene (s-9, known compound, 1351376-94-7)



A 350 mL Schlenk tube was charged with 1-bromo-4-(bromomethyl)benzene (10.0 g, 40.0 mmol, 1.0 eq.), (4-nitrophenyl)boronic acid (7.34 g, 44.0 mmol, 1.1 eq.), $PdCl_2(PPh_3)_2$ (562.0 mg, 2 mol%), PPh_3 (420.0 mg, 4 mol%), and a stirred bar. The mixture was evacuated and backfilled with N_2 for three cycles. Then, under N_2 flow, Na_2CO_3 (8.48 g dissolved in 40 mL water, 80 mmol, 2.0 eq.) and dioxane (160 mL) were sequentially added with Pasteur pipette. The tube was capped and stirred in an oil bath preheated at 70 °C for 12 h. After cooling to room temperature, the mixture was filtered with celite. The tube was rinsed with additional ethyl acetate (50 mL \times 2) and filtered. The filtrate was concentrated under vacuum to oil, which was dissolved with ethyl acetate, transferred to a separatory funnel, and washed with brine (30 mL \times 4). The organic layer was filtered with a short pad of silica gel, and the solvent was removed by the vacuum. After silica gel chromatography, the 1-bromo-4-(4-nitrobenzyl)benzene (8.72 g, 74%) was obtained as a colorless solid. R_f = 0.2, eluent = dichloromethane/petroleum ether = 1/6. 1H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 7.05 (d, J = 8.3 Hz, 2H), 4.03 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 146.6, 138.2, 132.0, 130.7, 129.7, 123.9, 120.8, 41.1.

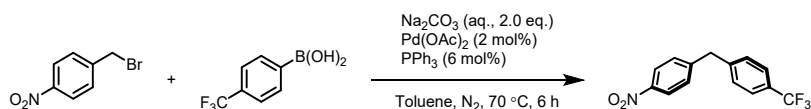
Characterization data conforms with the literature well.^[12]

1-fluoro-4-(4-nitrobenzyl)benzene (s-10, known compound, 38695-23-7)

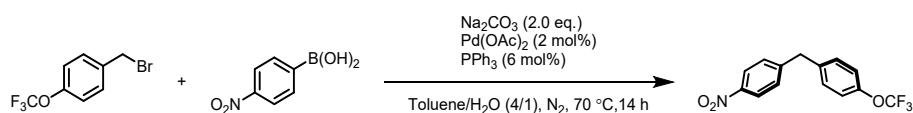


A 250 mL Schlenk tube was charged with 1-(bromomethyl)-4-fluorobenzene (1.27 g, 6.7 mmol, 1.0 eq.), (4-nitrophenyl)boronic acid (1.34 g, 8.0 mmol, 1.2 eq.), $PdCl_2(PPh_3)_2$ (94.1 mg, 2 mol%), PPh_3 (70.3 mg, 4 mol%), and a stirred bar. The mixture was evacuated and backfilled with N_2 for three cycles. Aqueous K_2CO_3 (1.85 g dissolved in 6 mL water, 13.4 mmol, 2.0 eq.) and THF (25 mL) were added, then the tube was capped and brought into an oil bath preheated at 65 °C and stirred for 19 h. After cooling to room temperature, the reaction mixture was transferred to a separatory funnel, and additional ethyl acetate (30 mL) was used to rinse the tube. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layer was filtered with a short pad of celite. The filtrate was concentrated by vacuum, and the residual was dissolved in 40 mL dichloromethane and filtered through a short pad of silica gel. After concentration of the filtrate, the crude material was further purified by silica gel chromatography to afford the 1-fluoro-4-(4-nitrobenzyl)benzene (1.30 g, 83%) as a colorless solid. R_f = 0.25, Eluent = dichloromethane/petroleum ether = 1/8. 1H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.14 (dd, J = 8.4, 5.4 Hz, 2H), 7.00 (t, J = 8.7 Hz, 2H), 4.05 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8 (d, J = 245.3 Hz), 148.7, 146.7, 135.0 (d, J = 3.4 Hz), 130.5 (d, J = 8.0 Hz), 129.6, 123.9, 115.7 (d, J = 21.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.04 – -116.13 (m).

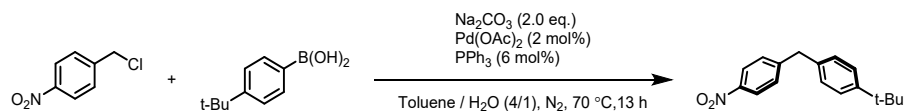
characterization data conform to literature well.^[13]

nitro-4-(4-(trifluoromethyl)benzyl)benzene (s-11, new compound, 1304788-88-2)

A 250 mL Schlenk tube was charged with (4-trifluoromethylphenyl)boronic acid (1.23 g, 6.5 mmol, 1.3 eq.), $\text{Pd}(\text{OAc})_2$ (22.5 mg, 2 mol%), PPh_3 (78.6 mg, 6 mol%), and a stirred bar. The mixture was evacuated and backfilled with N_2 for three cycles. Then, under N_2 flow, the Na_2CO_3 aqueous solution (1.06 g Na_2CO_3 dissolved in 5 mL water, 10 mmol, 2.0 eq.) and 1-(bromomethyl)-4-nitrobenzene (1.08 g, dissolved in 20 mL toluene, 5.0 mmol, 1.0 eq.) was sequentially added with Pasteur pipette. The tube was capped, and the mixture was stirred in an oil bath preheated at 70 °C for 6 h. The reaction mixture was cooled to room temperature and then filtered with a short pad of celite, which was washed with additional ethyl acetate. The aqueous layer was removed, and the organic phase was washed with brine. The volatile was removed by vacuum, and the remaining mixture was purified by silica gel chromatography, affording the 1-nitro-4-(4-(trifluoromethyl)benzyl)benzene as a colorless solid. $R_f = 0.17$, eluent: dichloromethane/petroleum ether = 1/8. **$^1\text{H NMR}$ (400 MHz, CDCl_3)** δ 8.15 (d, $J = 8.7$ Hz, 2H), 7.58 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.6$ Hz, 2H), 7.30 (d, $J = 8.1$ Hz, 2H), 4.15 (s, 2H). **$^{13}\text{C NMR}$ (101 MHz, CDCl_3)** δ 147.6, 146.7, 143.3, 129.7, 129.3, 129.1 (q, $J = 32.9$ Hz), 125.7 (q, $J = 3.8$ Hz), 124.1 (q, $J = 272.1$ Hz), 123.9, 41.4. **$^{19}\text{F NMR}$ (376 MHz, CDCl_3)** δ -62.51. **HRMS (ESI) m/z:** $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{14}\text{H}_{11}\text{NO}_2\text{F}_3$ 282.0736, found 282.0739. Melting point :59 – 62 °C.

1-nitro-4-(4-(trifluoromethoxy)benzyl)benzene (s-12, new compound)

A 250 mL Schlenk tube was charged with 1-(bromomethyl)-4-(trifluoromethoxy)benzene (1.28 g, 5.0 mmol, 1.0 eq.), (4-nitrophenyl)boronic acid (1.0 g, 6.0 mmol, 1.2 eq.), Na_2CO_3 (1.06 g, 10.0 mmol, 2.0 eq.), $\text{Pd}(\text{OAc})_2$ (22.5 mg, 2 mol%), PPh_3 (78.6 mg, 6 mol%), and a stirred bar. The mixture was evacuated and backfilled with N_2 for three cycles. Then, under N_2 flow, water (5 mL) and toluene (20 mL) were sequentially added with Pasteur pipette. The tube was capped, and the mixture was stirred in an oil bath preheated at 70 °C for 14 h. The reaction mixture was cooled to room temperature and then filtered with a short pad of celite, which was washed with additional ethyl acetate (ca. 80 mL). The aqueous layer was removed, and the organic phase was washed with brine (20 mL \times 2). The solvent was removed by vacuum, and the remaining mixture was purified by silica gel chromatography to afford the 1-nitro-4-(4-(trifluoromethoxy)benzyl)benzene (1.34 g, 90%) as a colorless solid. $R_f = 0.17$, eluent: dichloromethane/petroleum ether = 1/8. **$^1\text{H NMR}$ (400 MHz, CDCl_3)** δ 8.15 (d, $J = 8.6$ Hz, 2H), 7.33 (d, $J = 8.6$ Hz, 2H), 7.23 – 7.14 (m, 4H), 4.09 (s, 2H). **$^{13}\text{C NMR}$ (101 MHz, CDCl_3)** δ 148.2, 148.1 (q, $J = 1.7$ Hz), 146.7, 138.0, 130.3, 129.7, 123.9, 120.7 (d, $J = 257.0$ Hz), 41.0. **$^{19}\text{F NMR}$ (376 MHz, CDCl_3)** δ -57.96. **HRMS (ESI) m/z:** $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{14}\text{H}_{10}\text{NO}_3\text{F}_3\text{Na}$ 320.0505, found 320.0499. Melting point :30 – 34 °C.

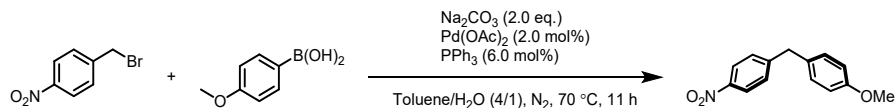
1-(tert-butyl)-4-(4-nitrobenzyl)benzene (s-13, known compound, 2411959-64-1)

A 250 mL Schlenk tube was charged with 1-(chloromethyl)-4-nitrobenzene (858 mg, 5.0 mmol, 1.0 eq.), (4-(tert-butyl)phenyl)boronic acid (1.07g, 6.0 mmol, 1.2 eq.), Na_2CO_3 (1.06 g, 10.0 mmol, 2.0 eq.), $\text{Pd}(\text{OAc})_2$ (22.0 mg, 2 mol%), PPh_3 (78.0 mg, 6 mol%), and a stirred bar. The mixture was evacuated and backfilled with N_2 for three cycles. Then, under N_2 flow, water (5 mL) and toluene (20 mL) were sequentially added with Pasteur pipette. The tube was capped, and the mixture was stirred in an oil bath preheated at 70 °C for 13 h. After cooling to room temperature, the reaction mixture was transferred to a separatory funnel, the tube was washed with additional ethyl acetate (20 mL) and brine (10 mL), and all rinse was transferred to the separatory funnel. The aqueous layer was removed, and the organic phase was washed with saturated brine (10 mL). The volatile was removed by vacuum, and the remaining mixture was purified by silica gel chromatography, affording the 1-(tert-butyl)-4-(4-nitrobenzyl)benzene (1.13 g, 83%) as a colorless solid. $R_f = 0.20$, eluent:

dichloromethane/petroleum ether = 1/8, **¹H NMR (400 MHz, CDCl₃)** δ 8.14 (d, *J* = 8.7 Hz, 2H), 7.38 – 7.30 (m, 4H), 7.10 (d, *J* = 8.2 Hz, 2H), 4.05 (s, 2H), 1.31 (s, 9H). **¹³C NMR (101 MHz, CDCl₃)** δ 149.8, 149.2, 146.6, 136.2, 129.8, 128.7, 125.8, 123.87, 41.3, 34.5, 31.4.

Characterization data conforms with the literature.^[14]

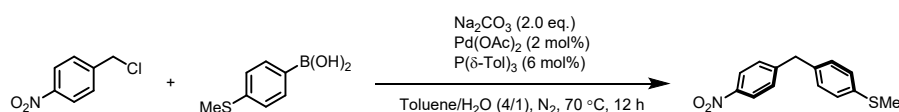
1-methoxy-4-(4-nitrobenzyl)benzene (s-14, known compound, 22865-59-4)



A 250 mL Schlenk tube was charged with 1-(bromomethyl)-4-nitrobenzene (2.16 g, 10.0 mmol, 1.0 eq.), (4-methoxyphenyl)boronic acid (1.82 g, 12.0 mmol, 1.2 eq.), Na₂CO₃ (2.12 g, 20.0 mmol, 2.0 eq.), Pd(OAc)₂ (44.0 mg, 2 mol%), PPh₃ (157.0 mg, 6 mol%), and a stirred bar. The mixture was evacuated and backfilled with N₂ for three cycles. Then, under N₂ flow, water (10 mL) and toluene (40 mL) were sequentially added with Pasteur pipette. The tube was capped, and the mixture was stirred in an oil bath preheated at 70°C for 11 h. After cooling to room temperature, the reaction mixture was transferred to a separatory funnel, and the tube was washed with additional ethyl acetate (10 mL) and water (10 mL) and all rinse was transferred to the separatory funnel. The aqueous layer was removed, and the organic phase was washed with brine (20 mL), filtered through a short plug of celite, and dried with anhydrous Na₂SO₄. The solvent was removed by vacuum, and the remaining mixture was purified by silica gel chromatography, affording the 1-methoxy-4-(4-nitrobenzyl)benzene (2.00 g, 82%) as a yellowish oil. *R_f* = 0.21, eluent: ethyl acetate/petroleum ether=1/60. **¹H NMR (400 MHz, CDCl₃)** δ 8.13 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.86 (d, *J* = 8.2 Hz, 2H), 4.02 (s, 2H), 3.80 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 158.5, 149.5, 146.5, 131.3, 130.0, 129.6, 123.8, 114.3, 55.4, 40.9.

Characterization data conforms with the literature.^[15]

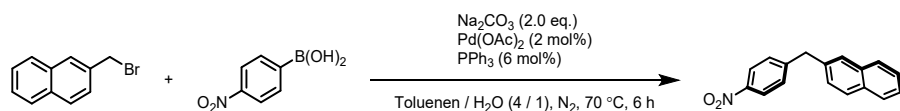
methyl(4-(4-nitrobenzyl)phenyl)sulfane (s-15, known compound, 199916-54-6)



A 250 mL Schlenk tube was charged with 1-(chloromethyl)-4-nitrobenzene (858 mg, 5.0 mmol, 1.0 eq.), (4-(methylthio)phenyl)boronic acid (1.00 g, 6.0 mmol, 1.2 eq.), Na₂CO₃ (1.06 g, 10.0 mmol, 2.0 eq.), Pd(OAc)₂ (22.0 mg, 2 mol%), P(δ-Tol)₃ (91.0 mg, 6 mol%), and a stirred bar. The mixture was evacuated and backfilled with N₂ for three cycles. Then, under N₂ flow, water (5 mL) and toluene (20 mL) were sequentially added with Pasteur pipette. The tube was capped, and the mixture was stirred in an oil bath preheated at 70°C for 12 h. After cooling to room temperature, the reaction mixture was transferred to a separatory funnel, and the tube was washed with additional ethyl acetate (20 mL) and water (10 mL). All rinse was transferred to the separatory funnel. The aqueous layer was removed, and the organic phase was washed with saturated brine (10 mL). The volatile was removed by vacuum, and the remaining mixture was purified by silica gel chromatography to afford the methyl(4-(4-nitrobenzyl)phenyl)sulfane as a colorless solid. (*R_f* = 0.25, eluent = dichloromethane/petroleum ether = 1/6). **¹H NMR (400 MHz, CDCl₃)** δ 8.12 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 8.7 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 4.03 (s, 2H), 2.46 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 148.8, 146.5, 136.8, 136.1, 129.6, 129.5, 127.1, 123.7, 41.1, 15.9.

Characterization data conforms with the literature well.^[10]

2-(4-nitrobenzyl)naphthalene (s-16, known compound, 3042-62-4)

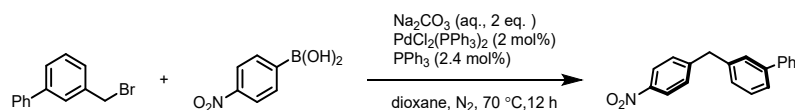


A 250 mL Schlenk tube was charged with 2-(bromomethyl)naphthalene (1.11 g, 5 mmol, 1.0 eq.), (4-nitrophenyl)boronic acid (1.00 g, 6.0 mmol, 1.2 eq.), Na₂CO₃ (1.06 g, 10.0 mmol, 2.0 eq.), Pd(OAc)₂ (22.0 mg, 2 mol%), PPh₃ (78.0 mg, 6 mol%), and a stirred bar. The mixture was evacuated and backfilled with N₂ for three cycles. Then, under N₂ flow, water (5 mL) and toluene (20 mL) were sequentially added with Pasteur pipette. The tube was capped, and the mixture was stirred in an oil bath preheated at 70 °C for 6 h. After

cooling to room temperature, the reaction mixture was transferred to a separatory funnel, and the tube was washed with additional ethyl acetate (20 mL) and water (20 mL). All rinse was transferred to the separatory funnel. The organic layer was collected, and the organic phase was washed with saturated brine (20 mL × 2). The organic layer was combined and filtered with a short plug of celite. The volatile was removed by vacuum, and the remaining mixture was purified by silica gel chromatography, affording the 2-(4-nitrobenzyl)naphthalene (1.2 g, 91% yield) as a yellowish solid. $R_f = 0.16$, Eluent: dichloromethane/petroleum ether = 1/5). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.15 (d, $J = 8.7$ Hz, 2H), 7.86 – 7.78 (m, 3H), 7.65 (s, 1H), 7.53 – 7.45 (m, 2H), 7.37 (d, $J = 8.5$ Hz, 2H), 7.29 (dd, $J = 8.4, 1.8$ Hz, 1H), 4.24 (s, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 148.8, 146.6, 136.7, 133.6, 132.3, 129.8, 128.6, 127.8, 127.6, 127.5, 127.3, 126.4, 125.9, 123.8, 41.9.

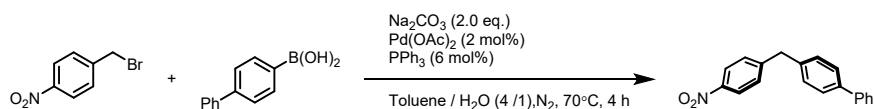
The characterization data conforms with the literature well.^[16]

3-(4-nitrobenzyl)-1,1'-biphenyl (s-17, new compound)



A 250 mL Schlenk tube was charged with 3-(bromomethyl)-1,1'-biphenyl (1.24 g, 5.0 mmol, 1.0 eq.), (4-nitrophenyl)boronic acid (1.00 g, 6.0 mmol, 1.2 eq.), $\text{PdCl}_2(\text{PPh}_3)_2$ (70.2 mg, 2 mol%), PPh_3 (32.0 mg, 2.4 mol%), and a stirred bar. The mixture was evacuated and backfilled with N_2 for three cycles. Then, under N_2 flow, Na_2CO_3 (1.06 g dissolved in 5 mL water, 10.0 mmol, 2.0 eq.) and dioxane (20 mL) were sequentially added with Pasteur pipette. The tube was capped, and the mixture was stirred in an oil bath preheated at 70 °C for 12 h. After cooling to room temperature, the mixture was filtered through a short pad of celite, which was washed with additional ethyl acetate (10 mL × 3). The filtrate was collected, and the volatile was removed by vacuum. The remaining oil was dissolved in 30 mL ethyl acetate and washed with brine (5 mL). After removing the solvent, the crude product was purified by silica gel chromatography, affording the 3-(4-nitrobenzyl)-1,1'-biphenyl (1.06 g, 73% yield) as a colorless solid. $R_f = 0.19$ (Eluent = dichloromethane/petroleum ether = 1/6). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.17 (d, $J = 8.3$ Hz, 2H), 7.59 (d, $J = 7.6$ Hz, 2H), 7.52 (d, $J = 7.7$ Hz, 1H), 7.50 – 7.34 (m, 7H), 7.18 (d, $J = 7.5$ Hz, 1H), 4.16 (s, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 148.8, 146.6, 141.9, 140.9, 139.7, 129.7, 129.3, 128.8, 127.9, 127.8, 127.5, 127.2, 125.7, 123.8, 41.8. **HRMS (ESI)** m/z : $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{19}\text{H}_{15}\text{NO}_2\text{Na}^+$ 312.0995, found 312.1000. Melting point :90 – 93 °C.

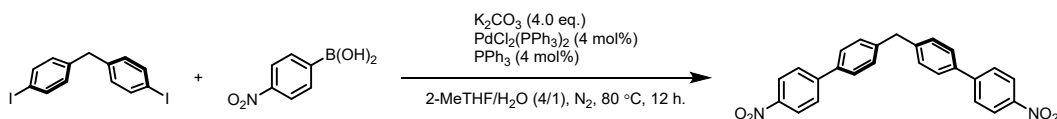
4-(4-nitrobenzyl)-1,1'-biphenyl (s-18, known compound, 1316859-67-2)



A 250 mL Schlenk tube was charged with 1-(bromomethyl)-4-nitrobenzene (2.16 g, 10.0 mmol, 1.0 eq.), [1,1'-biphenyl]-4-ylboronic acid (2.38 g, 12.0 mmol, 1.2 eq.), Na_2CO_3 (2.12 g, 20 mmol, 2.0 eq.), $\text{Pd}(\text{OAc})_2$ (44.0 mg, 2.0 mol%), PPh_3 (157.0 mg, 6.0 mol%), and a stirred bar. The mixture was evacuated and backfilled with N_2 for three cycles. Water (10 mL) and toluene (40 mL) were added. The tube was capped, brought into an oil bath preheated at 70 °C, and stirred for 4 h. After cooling to room temperature, the reaction mixture was transferred to a separatory funnel. The tube was washed with additional ethyl acetate (20 mL) and water (20 mL), and all rinse was transferred to the separatory funnel. The aqueous layer was removed, and the organic phase was washed with saturated aqueous Na_2CO_3 three times, dried with Na_2SO_4 , and filtered. The volatile was removed by vacuum, and the remaining mixture was purified by silica gel chromatography, affording the 4-(4-nitrobenzyl)-1,1'-biphenyl (2.10 g, 72% yield) as a colorless solid. $R_f = 0.32$, eluent: ethyl acetate/petroleum ether = 1/60. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.15 (d, $J = 8.2$ Hz, 2H), 7.61 – 7.51 (m, 4H), 7.46 – 7.40 (m, 2H), 7.40 – 7.29 (m, 3H), 7.27 – 7.20 (m, 2H), 4.11 (s, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 148.8, 146.6, 140.7, 139.8, 138.3, 129.8, 129.4, 128.9, 127.6, 127.4, 127.1, 123.9, 41.4.

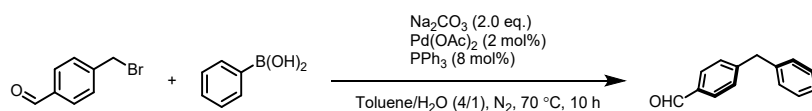
Characterization data conforms with the literature.^[11]

bis(4'-nitro-[1,1'-biphenyl]-4-yl)methane (s-19, new compound)



A 250 mL Schlenk tube was charged with bis(4-iodophenyl)methane (841 mg, 2.0 mmol, 1.0 eq.), (4-nitrophenyl)boronic acid (1.00 g, 6.0 mmol, 3.0 eq.), K_2CO_3 (1.11 g, 8.0 mmol, 4.0 eq.), $PdCl_2(PPh_3)_2$ (56.1 mg, 4 mol%), PPh_3 (20.9 mg, 4 mol%) and a stirring bar, pumped under high vacuum and backfilled with N₂ for three cycles, 2-MeTHF (20 mL) and water (4 mL) were added under N₂ flow. The tube was capped, and the reaction mixture was stirred in an oil bath preheated at 80 °C for 12 h. After cooling to room temperature, the mixture was transferred to a 125 mL separatory funnel (additional ethyl acetate (10 mL × 3) and water (10 mL) was used to rinse the tube). The top organic layer was retained, washed with brine (10 mL), filtered through a short pad of silica gel, and concentrated by vacuum. The residual was finally purified with silica gel chromatography, affording the title compound (641 mg, 78% yield) as a colorless crystalline. Eluent: dichloromethane/petroleum ether = 1.0/2.5, R_f = 0.16. **¹H NMR (400 MHz, CDCl₃)** δ 8.28 (d, J = 8.8 Hz, 4H), 7.72 (d, J = 8.8 Hz, 4H), 7.58 (d, J = 8.0 Hz, 4H), 7.36 (d, J = 8.0 Hz, 4H), 4.12 (s, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 147.3, 147.1, 141.7, 136.9, 129.8, 127.7, 127.6, 124.2, 41.4. **HRMS (ESI)** m/z : [M-H]⁻ calculated for C₂₅H₁₇N₂O₄ 409.1194, found 409.1187. Melting point :149 – 150 °C.

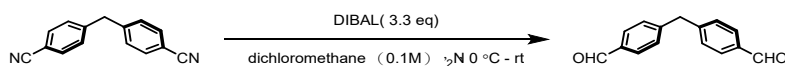
4-benzylbenzaldehyde (s-20, known compound, 67468-65-9)



A 250 mL Schlenk tube was charged with 4-(bromomethyl)benzaldehyde (995.0 mg, 5.0 mmol, 1.0 eq.), phenylboronic acid (793 mg, 6.5 mmol, 1.3 eq.), Na_2CO_3 (1.06 g, 10 mmol, 2.0 eq.), $Pd(OAc)_2$ (22.0 mg, 2.0 mol%), PPh_3 (105.0 mg, 8.0 mol%), and a stirred bar. The mixture was evacuated and backfilled with N₂ for three cycles, followed by water (5 mL) and toluene (20 mL) addition. The tube was capped, brought into an oil bath preheated at 70 °C, and stirred for 10 h. The reaction mixture was cooled to room temperature and then transferred to a separatory funnel. The tube was washed with additional toluene and water, and all rinse was transferred to the separatory funnel. The aqueous layer was removed, and the organic phase was washed with water (15 mL × 2) and filtered through a short pad of celite. The volatile was removed by vacuum, and the remaining mixture was purified by silica gel chromatography to afford the 4-benzylbenzaldehyde (882.0 mg, 89%) as a red-orange oil. R_f = 0.19, eluent: dichloromethane/petroleum ether = 3/1. **¹H NMR (400 MHz, CDCl₃)** δ 9.95 (s, 1H), 7.78 (d, J = 8.2 Hz, 2H), 7.36 – 7.26 (m, 4H), 7.23 (d, J = 8.3 Hz, 1H), 7.17 (d, J = 6.9 Hz, 2H), 4.04 (s, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 191.9, 148.4, 139.8, 134.7, 130.1, 129.6, 129.0, 128.7, 126.5, 42.1.

The characterization data conforms with the literature well.^[17]

4,4'-methylene dibenzaldehyde (s-21, known compound, 67-37-8)

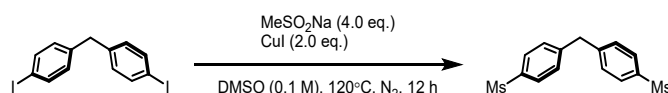


A 100 mL flask equipped with a rubber septum and glass stopper was charged with 4,4'-methylene dibenzonitrile (655.0 mg, 3.0 mmol, 1.0 eq.) and a stirred bar. The mixture was evacuated and backfilled with N₂ for three cycles. Then, dry dichloromethane (30 mL) was added with a syringe. The mixture was cooled with ice bath to approximately 0 °C, after which DIBAL (10 mL, 1M in hexane, 3.3 eq.) was slowly added with a syringe, during which the reaction mixture was maintained below 10 °C. After addition, the reaction mixture was stirred at room temperature for additional 12 h. The reaction mixture was quenched with hydrochloric acid (60 mL, 2M) and stirred for 2 h, and the reaction mixture was transferred to the separatory funnel. The organic layer was collected, the aqueous layer was extracted with dichloromethane (20 mL × 2), and the combined solution was passed with a short pad of silica gel and concentrated by rotary evaporator. The crude material was purified by silica gel chromatography, affording the 4,4'-methylene dibenzaldehyde (477.3 mg, 70%) as a colorless solid. R_f = 0.35. Eluent = dichloromethane. **¹H NMR (400 MHz, CDCl₃)** δ 9.98

(s, 2H), 7.83 (d, $J = 8.0$ Hz, 4H), 7.35 (d, $J = 7.8$ Hz, 4H), 4.14 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 191.9, 147.0, 135.0, 130.3, 129.7, 42.2.

Characterization data conforms with the literature well.^[18]

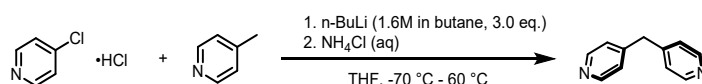
bis(4-(methylsulfonyl)phenyl)methane (s-25, known compound, 22183-07-9)



A 250 mL Schlenk tube was charged with bis(4-iodophenyl)methane (2.10 g, 5.0 mmol, 1.0 eq.), MeSO_2Na (2.04 g, 20.0 mmol, 4.0 eq.), CuI (1.90 g, 10.0 mmol, 2.0 eq.) and a stirred bar. The mixture was evacuated and backfilled with N_2 for three cycles. Then, under N_2 flow, DMSO (used as received without any purification, 50 mL) was added. The tube was capped, and the mixture was stirred at room temperature for 5 min and then brought to an oil bath preheated at 120 °C with stirring for 12 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (250 mL) and petroleum ether (25 mL), which was filtered with a short pad of silica gel (additional ethyl acetate was used to rinse the filter cake). The filtrate was transferred to a separatory funnel, the solution was washed with brine (50 mL \times 5), and the organic layer was collected and filtered with a short pad of silica gel again (rinse with ethyl acetate). The volatile was removed by vacuum, during which colorless crystal was precipitated, washed with petroleum ether, and dried under vacuum, affording the bis(4-(methylsulfonyl)phenyl)methane (1.39 g, 85%) as a colorless crystalline. ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, $J = 8.0$ Hz, 4H), 7.37 (d, $J = 8.1$ Hz, 4H), 4.15 (s, 2H), 3.04 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.9, 139.1, 129.9, 127.9, 44.6, 41.6.

The characterization data conforms with the literature well.^[19]

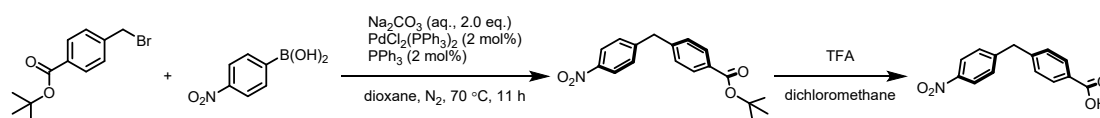
di(pyridin-4-yl)methane (s-27, known compound, 60776-05-8)



Under N_2 , 4-picoline (23.4 mL, 240 mmol, 3.0 eq.) was added to dry THF (140 mL) under ambient temperature, and the solution was cooled below -70 °C followed by addition of $n\text{-BuLi}$ (1.6 M in butane, 150 mL, 3.0 eq.) in 110 min while maintaining the internal temperature below -50 °C. The mixture was stirred for another 30 min, after which was warmed to -20 °C and 4-chloropyridine hydrochloride (12 g, 80 mmol, 1.0 eq.) was added. The resulting mixture was warmed to room temperature and refluxed under 50 – 60 °C for 45 min, and the reaction was monitored by TLC, which shows all the 4-chloropyridine was consumed. The mixture was cooled to room temperature and quenched with saturated aqueous ammonia chloride (500 mL). The volatile was removed by vacuum, and the remaining mixture was extracted with ethyl acetate (500 mL \times 3) and dried with anhydrous Na_2SO_4 . The solvent was removed by vacuum to give an oil, which was put on reduced distillation, giving di(4-pyridyl)methane as a colorless oil (8.02 g, 58% yield based on 4-chloropyridine hydrochloride). ^1H NMR (400 MHz, CDCl_3) δ 8.50 (d, $J = 4.6$ Hz, 4H), 7.07 (d, $J = 4.5$ Hz, 4H), 3.93 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.1, 147.7, 124.2, 40.5.

Characterization data conforms with the literature well.^[22]

4-(4-nitrobenzyl)benzoic acid (s-35, new compound, 13304-22-8)

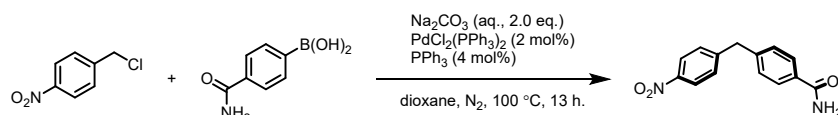


Step1: To a 250 mL Schlenk tube was added tert-butyl 4-(bromomethyl)benzoate (1.36 g, 5.0 mmol, 1.0 eq.), (4-nitrophenyl)boronic acid (1.00 g, 6.0 mmol, 1.2 eq.), $\text{PdCl}_2(\text{PPh}_3)_2$ (70.2 mg, 2 mol%), PPh_3 (32.0 mg, 2 mol%), and a stirred bar. The mixture was evacuated and backfilled with N_2 for three cycles. Then, under N_2 flow, the Na_2CO_3 solution (1.06 g Na_2CO_3 dissolved in 5 mL water, 10.0 mmol, 2.0 eq.) and dioxane (20 mL) was sequentially added with Pasteur pipette. The tube was capped, and the mixture was stirred in an oil bath preheated at 70 °C for 11 h. The reaction mixture was cooled to room temperature and then filtered with a short pad of celite. The filter cake was washed with additional ethyl acetate. The filtrate was transferred to a separatory funnel, and the collected organic phase was washed with brine. After removing the solvent by

vacuum, the remaining mixture was purified by silica gel chromatography, affording the tert-butyl 4-(4-nitrobenzyl)benzoate as a colorless solid. $R_f = 0.14$, (eluent = dichloromethane/petroleum ether = 1/2), $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.18 (d, $J = 8.4$ Hz, 2H), 7.99 (d, $J = 8.1$ Hz, 2H), 7.37 (d, $J = 8.4$ Hz, 2H), 7.27 (d, $J = 8.0$ Hz, 2H), 4.17 (s, 2H), 1.63 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.5, 148.0, 146.7, 143.9, 130.7, 130.0, 129.7, 128.9, 123.9, 81.1, 41.6, 28.2. **HRMS (ESI)** m/z : $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{18}\text{H}_{19}\text{NO}_4\text{Na}^+$ 336.1206, found 336.1204. Melting point: 38 – 40 °C.

Step 2: tert-butyl 4-(4-nitrobenzyl)benzoate (918 mg, 2.93 mmol, 1.0 eq.) was dissolved in dichloromethane (12 mL) and stirred at room temperature (ca. 10 °C), trifluoroacetic acid (4 mL) was slowly added, the resulting mixture was stirred for 40 min, thin-layer chromatography (TLC) analysis indicated the formation of the target product, and large amount of starting material remained. Subsequent stirring of the mixture at 30 °C in an oil bath for 4 hours led to the TLC confirmation that all reactants were fully converted. The solvent was then removed under reduced pressure using a rotary evaporator, resulting in the isolation of a colorless solid, which was further purified by slurry in dichloromethane, yielding the pure product (680 mg, 90% yield) as a colorless powder. $^1\text{H NMR}$ (400 MHz, DMSO) δ 12.87 (s, 1H), 8.16 (d, $J = 8.4$ Hz, 2H), 7.88 (d, $J = 7.9$ Hz, 2H), 7.52 (d, $J = 8.4$ Hz, 2H), 7.38 (d, $J = 8.0$ Hz, 2H), 4.17 (s, 2H). $^{13}\text{C NMR}$ (101 MHz, DMSO) δ 167.1, 148.7, 146.0, 145.0, 130.0, 129.7, 129.0, 129.0, 123.7, 40.4. **HRMS (ESI)** m/z : $[\text{M}-\text{H}]^-$ calculated for $\text{C}_{14}\text{H}_{10}\text{NO}_4^-$ 256.0615, found 256.0613. **Melting point:** 219 – 222 °C.

4-(4-nitrobenzyl)benzamide (s-36, new compound)



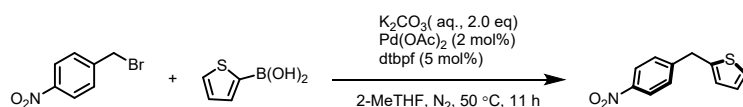
A 250 mL Schlenk tube was charged with (4-carbamoylphenyl)boronic acid (1.98 g, 12 mmol, 1.2 eq.), $\text{PdCl}_2(\text{PPh}_3)_2$ (140.4 mg, 2 mol%), PPh_3 (105.0 mg, 4 mol%), and a stirred bar. The mixture was evacuated and backfilled with N_2 for three cycles. Then, under N_2 flow, the Na_2CO_3 solution (2.12 g dissolved in 10 mL water, 20 mmol, 2.0 eq.) and 1-(chloromethyl)-4-nitrobenzene (1.72 g, dissolved in 40 mL dioxane, 10.0 mmol, 1.0 eq.) was sequentially added with Pasteur pipette. The tube was capped, and the mixture was stirred in an oil bath preheated at 100 °C for 3 h. After cooling to room temperature, the mixture was filtered through a short pad of celite, which was washed with additional ethyl acetate. The filtrate was collected, and the solvent was removed by vacuum. The remaining solid was brought into silica gel chromatography to give the 4-(4-nitrobenzyl)benzamide as a colorless solid. $R_f = 0.29$, (eluent = methanol/dichloromethane = 1/40). $^1\text{H NMR}$ (400 MHz, DMSO) δ 8.15 (d, $J = 8.6$ Hz, 2H), 7.92 (s, 1H), 7.82 (d, $J = 8.1$ Hz, 2H), 7.51 (d, $J = 8.6$ Hz, 2H), 7.34 (d, $J = 8.1$ Hz, 3H), 4.14 (s, 2H). $^{13}\text{C NMR}$ (101 MHz, DMSO) δ 167.6, 149.0, 146.0, 143.2, 132.5, 129.9, 128.7, 127.9, 123.6, 40.3. **HRMS (ESI)** m/z : $[\text{M}-\text{H}]^-$ calculated for $\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_3^-$ 255.0775, found 255.0777. Melting point: 111 – 115 °C.

2-(4-nitrobenzyl)furan (s-37, new compound)



A 250 mL Schlenk tube was charged with 1-(bromomethyl)-4-nitrobenzene (2.16 g, 10.0 mmol, 1.0 eq.), furan-2-ylboronic acid (1.45 g, 13 mmol, 1.3 eq.), $\text{Pd}(\text{OAc})_2$ (44.9 mg, 2 mol%), S-Phos (246.3 mg, 6 mol%), and a stirred bar. The mixture was evacuated and backfilled with N_2 for three cycles. Then, under N_2 flow, the Na_2CO_3 solution (2.12 g dissolved in 10 mL water, 20 mmol, 2.0 eq.) and 2-MeTHF (40 mL) was sequentially added with Pasteur pipette. The tube was capped, and the mixture was stirred in an oil bath preheated at 80 °C for 5 h. After cooling to room temperature, the mixture was transferred to a separatory funnel (the reaction tube was washed with few ethyl acetate), the collected organic layer was washed with brine (10 mL) and filtered through a short pad of celite, the filtrate was collected, and the solvent was removed by vacuum. The residue was brought into silica gel chromatography to give the 2-(4-nitrobenzyl)furan as a colorless oil, which slowly solidified upon storage at room temperature. $R_f = 0.35$, (eluent = ethyl acetate/petroleum ether = 1/100.), $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.19 – 8.12 (m, 2H), 7.42 – 7.32 (m, 3H), 6.36 – 6.29 (m, 1H), 6.11 – 6.06 (m, 1H), 4.08 (s, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 152.4, 145.9, 142.2, 129.5, 123.9, 110.5, 107.2, 34.3. **HRMS (ESI)** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{11}\text{H}_{10}\text{NO}_3^+$ 204.0655, found 204.0648. Melting point: 34 – 35 °C.

2-(4-nitrobenzyl)thiophene (s-38, known compound, 172508-14-4)

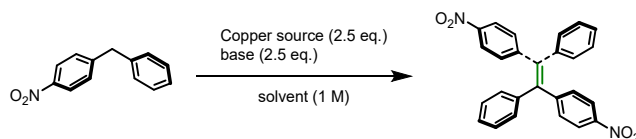


A 250 mL Schlenk tube was charged with 1-(bromomethyl)-4-nitrobenzene (2.16 g, 10.0 mmol, 1.0 eq.), thiophen-2-ylboronic acid (1.92 g, 15 mmol, 1.5 eq.), $Pd(OAc)_2$ (44.9 mg, 2 mol%), dtbpf (237.2 mg, 5 mol%), and a stirred bar. The mixture was evacuated and backfilled with N_2 for three cycles. Then, under N_2 flow, the K_2CO_3 aqueous solution (2.76 g dissolved in 10 mL water, 20 mmol, 2.0 eq.) and 2-MeTHF (50 mL) was sequentially added with Pasteur pipette. The tube was capped, and the mixture was stirred in an oil bath preheated at 50 °C for 11 h. After cooling to room temperature, the mixture was transferred to a separatory funnel (the reaction tube was washed with few ethyl acetate), the collected organic layer was washed with brine (10 mL) and filtered through a short pad of celite, the filtrate was collected, and the solvent was removed by vacuum. The residue was brought into silica gel chromatography to give the 2-(4-nitrobenzyl)thiophene as a colorless oil, this oil slowly solidified upon storage at room temperature. R_f = 0.33, (eluent = ethyl acetate/petroleum ether = 1/100.) 1H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.1 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.22 – 7.18 (m, 1H), 6.99 – 6.94 (m, 1H), 6.87 – 6.83 (m, 1H), 4.26 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.99, 141.56, 129.42, 127.18, 126.03, 124.79, 123.88, 35.78. HRMS (ESI) m/z : $[M+H]^+$ calculated for $C_{11}H_{10}NO_2S^+$ 220.0427, found 220.0418. Melting point: 23 – 26 °C.

Characterization data conforms with the literature well.^[23]

2.2. Reaction optimization

General procedure



In the glovebox, a 25 mL Schlenk tube was added 4-benzylnitrobenzene (64 mg, 0.30 mmol, 1.0 eq.), Copper source (0.75 mmol, 2.5 eq.), and base (0.75 mmol, 2.5 eq.). The tube was capped, and the solvent was added via a syringe under N_2 flow. The mixture was stirred in an oil bath preheated at 120 °C for 12 h. The mixture was cooled to room temperature, followed by addition of diluted aqueous hydrochloride (1 M, 10 mL) and ethyl acetate (10 mL). The mixture was transferred to a separatory funnel, and the tube was rinsed with another portion of ethyl acetate (40 mL). All rinse was transferred to the separatory funnel, the aqueous layer was removed, and the organic layer was sequentially washed with diluted aqueous hydrochloride (1 M, 10 mL \times 2), saturated aqueous $NaHCO_3$ (10 mL), and brine (10 mL). The volatile was removed under vacuum to afford the crude material, which was further purified by prep-TLC (dichloromethane/petroleum=1/1) to give a yellowish solid as the corresponding TPE as a mixture of the *E* and *Z* isomers. The yield refers to the total yield of two isomers.

Table S3. Effect of solvents.

entry	Solvent (5 mL)	Cu source	base	yield(%)
1	DMAc	$Cu(OAc)_2$	None	n.d. or trace
2	DMAc	$Cu(OAc)_2$	<i>t</i> -BuOK	71 (83) ^a
3	DMF	$Cu(OAc)_2$	<i>t</i> -BuOK	52
4	DMSO	$Cu(OAc)_2$	<i>t</i> -BuOK	64
5	HMPA	$Cu(OAc)_2$	<i>t</i> -BuOK	77
6	NMP	$Cu(OAc)_2$	<i>t</i> -BuOK	36
7	DMI	$Cu(OAc)_2$	<i>t</i> -BuOK	55
8	DMPU	$Cu(OAc)_2$	<i>t</i> -BuOK	66
9	Dioxane	$Cu(OAc)_2$	<i>t</i> -BuOK	n.d. or trace
10	xylene	$Cu(OAc)_2$	<i>t</i> -BuOK	n.d. or trace

Reaction condition : a. Cu(OPiv)₂ (2.5 eq.), t-BuOK (2.5 eq.), PivOK (2.5 eq.), N₂, 120 °C, 12 h.

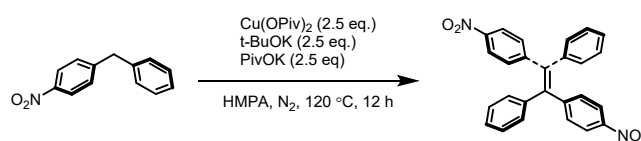
Table S4. Effect of the copper sources.

entry	copper salt	base	Solvent (3 mL)	yield(%)
1	Cu(OAc) ₂	<i>t</i> -BuOK	HMPA	78
2	Cu(TFA) ₂	<i>t</i> -BuOK	HMPA	27
3	Cu(OPiv) ₂	<i>t</i> -BuOK	HMPA	89
4	Cu(PhCOO) ₂	<i>t</i> -BuOK	HMPA	73
5	CuCl ₂	<i>t</i> -BuOK	HMPA	n.d. or trace
6	CuBr ₂	<i>t</i> -BuOK	HMPA	18
7	Cu(OTf) ₂	<i>t</i> -BuOK	HMPA	23
8	CuSO ₄	<i>t</i> -BuOK	HMPA	n.d. or trace
9	Cu ₃ (PO ₄) ₂	<i>t</i> -BuOK	HMPA	n.d. or trace
10	CuO	<i>t</i> -BuOK	HMPA	14

Table S5. Effect of base.

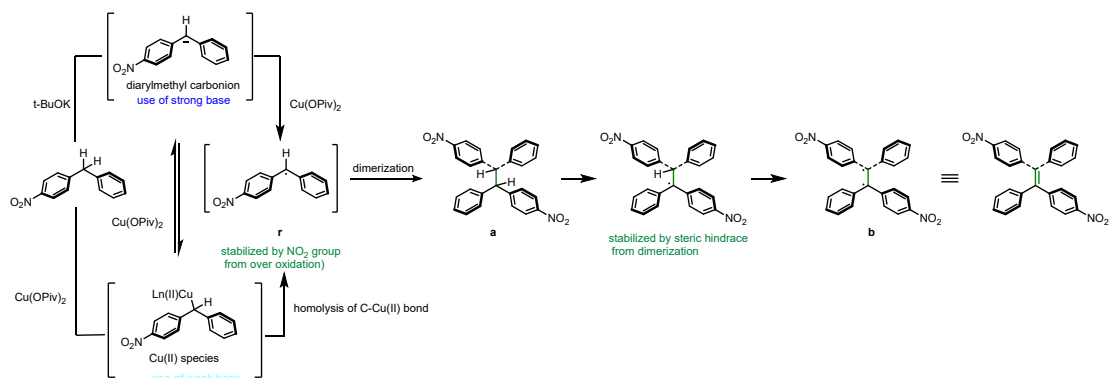
entry	copper source	bases	Solvent (3 mL)	yield(%)
1	Cu(OPiv) ₂	<i>t</i> -BuOK	HMPA	89
2	Cu(OPiv) ₂	<i>t</i> -BuONa	HMPA (5mL)	88
4	Cu(OPiv) ₂	<i>t</i> -BuOLi	HMPA	80
5	Cu(OPiv) ₂	K ₃ PO ₄	HMPA	67
6	Cu(OPiv) ₂	KOAc	HMPA	61
7	Cu(OPiv) ₂	KOPiv	HMPA	66
8	Cu(OPiv) ₂	CsF	HMPA	66
9	Cu(OPiv) ₂	K ₂ CO ₃	HMPA	72
10	Cu(OPiv) ₂	pyridine	HMPA	n.d. or trace
11	Cu(OPiv) ₂	Et ₃ N	HMPA	n.d. or trace
12	Cu(OPiv) ₂	DBU	HMPA	28

Table S6. Effect of temperature and catalytic loading on the reaction efficiency.



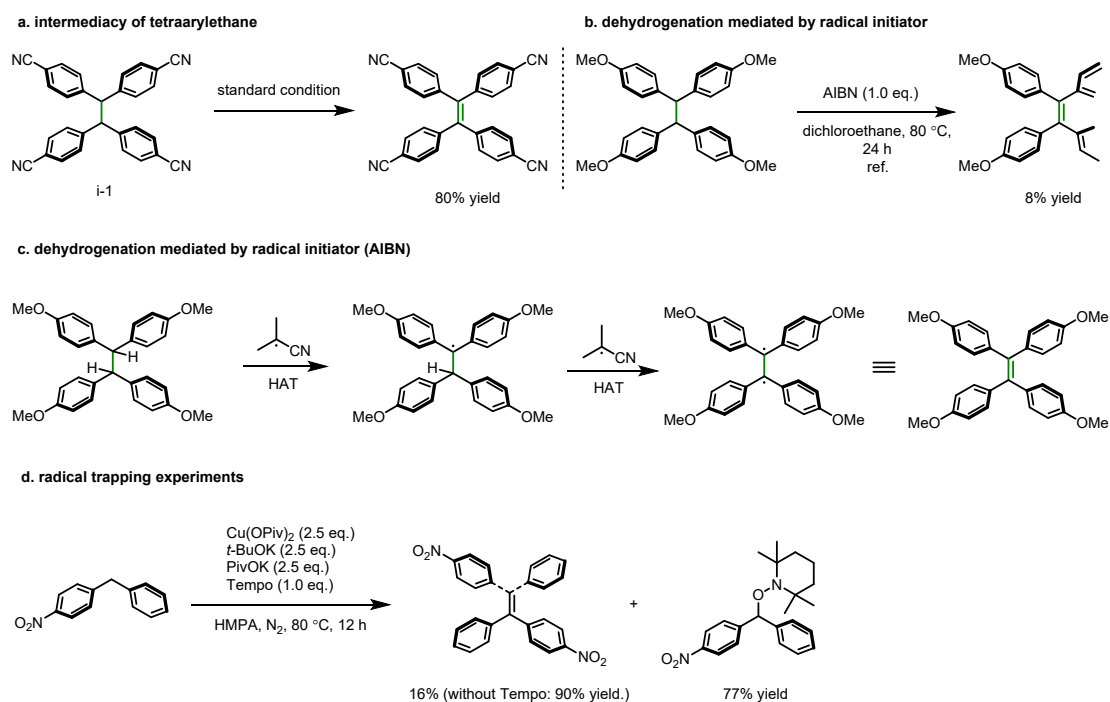
entry	Variation from standard condition	yield(%)
1	none	93%
2	100 °C instead of 120 °C	95%
4	80 °C instead of 120 °C	90%
5	60 °C instead of 120 °C	56%
6	10 mol% Cu(OPiv) ₂ used instead of 2.5 eq.	n.d. or trace

2.3. Mechanism consideration



Scheme S1. Plausible mechanism.

A proposed mechanism for the described reaction is shown in **Scheme S1**. Taking 1-benzyl-4-nitrobenzene (**s-1**) as demonstration, the reaction was started with facile deprotonation by *t*-BuOK to produce a resonance-stabilized carbanion (pK_a for 1-benzyl-4-nitrobenzene; 15.8 in DMSO, pK_a for *t*-BuOH; 32.2 in DMSO), followed by the single electron oxidation by $\text{Cu}(\text{OPiv})_2$ to produce a resonance-stabilized carbon radical, at which point two reaction pathways may proceed: **1**) radical-radical recombination to afford the tetraphenylethane (**a**) owing to insufficient steric inhibition by two benzene rings. **2**) Overoxidation by $\text{Cu}(\text{OPiv})_2$ to the resonance-stabilized carbocation (not shown), which was trapped by the nucleophiles such as pivalate anion or adventitious water (or OH^-) in the solvent to produce the corresponding additives. In our case, the incorporation of a strong electron-withdrawing group undoubtedly disfavors the overoxidation pathway by destabilizing the proposed carbocation intermediate, which was manifest in that higher half-wave oxidation potential have the diphenylmethyl radicals with strong electron-withdraw group adored in the para position of the phenyl ring,^[24] such that the dimerization pathway predominates to give the 1,2-bis(4-nitrophenyl)-1,2-diphenylethane (**a**), for which benzylic C-H has the similar polarity with the starting material (**s-1**), and is expected to be capable of undergoing two-step, successive C-H single electron oxidation process to give a diradical (**b**), which is isoelectronic with the alkene (**t-1**). When weak base was used in our procedure, the partially dehydrogenative product may isolated as the byproduct. For example, using K_3PO_4 as the base in the gram preparation of tetracyanophenylethene (**t-23**), the cyano-substituted tetraphenylethane (**i-1**) can be isolated as a side product, which can be transferred to the corresponding TPE in 80% yield (**Scheme S2-a**). An example of dehydrogenation of tetraphenylethane by AIBN giving tetraphenylethene (TPE) was documented (**Scheme S2-b**),^[25] which can be illuminated via the radical-mediated benzylic H abstraction. The most compelling evidence for free radical participation is derived from radical trapping experiments (Scheme S2-c): at 80 °C, **s-1** undergoes dehydrogenative homocoupling affording the TPE with 90% yield. Incorporation of the radical scavenger, Tempo, into the reaction led to a profound reaction suppression, diminishing the yield to 16%, with isolation of the radical adduct **a-r** with 77% yield.



Scheme S2. The clue as to intermediacy of tetraphenylethane derivatives.

The latent organocopper(II) species

Under base-free condition, benzyl-4-nitrobenzene (**s-1**) producing dimer (**a**) (16% yield), bis(4-nitrophenyl)methane (**s-2**) undergo dehydrogenation to give the corresponding TPE in 69% yield, 4-benzylpyridine, 2-benzylpyridine, and di(pyridin-2-yl)methane were reported to undergo partial dehydrogenation giving the corresponding tetraarylethane,^[26] implying that the activated diarylmethane may directly reacts with the copper(II) carboxylate to give an organocopper(II) species,^[27] subsequent homolysis of C(sp³)-Cu(II) bond to provide the radical (**r**) and Cu(I) species, with the concomitant formation of carboxylic acid, which was believed by us as the culprit for the reaction stall at the tetraphenylethane (**a**) formation stage by protonating the organic copper(II) species or driving the reaction backward.

The influence of electronic characterization of substrate on the reaction

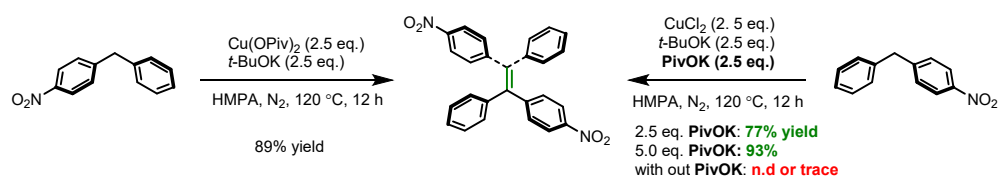
The electron-neutral diphenylmethane, which has weak acidified benzylic C-H bond with pK_a of 32.3 in DMSO, is an invalid substrate in our protocol, for which dehydrogenative coupling fails, and a large amount of starting material remains with few amounts of diphenylmethanone observed. In principle, it can be deprotonated reversibly by the *t*-BuOK (pK_a = 32.2 for *t*-BuOH in DMSO) to afford the diphenylmethyl carbanion, unlike its nitro-activated counterpart, the absence of electron-withdrawing group on para or ortho position make the overoxidation by Cu(II) carboxylate easily producing a resonance-stabilized diphenylmethyl carbocation, which was then captured by the water (or OH⁻) to give the diphenylmethanol and finally observed diphenylmethanone.^[28] This procedure was expected to be facilitated by the electron-donating group presented on the para position of the benzylic C-H bond, which was supported by the isolation of diphenylmethanone derivatives (**i-2** and **i-3**) as the main side product in the scale preparation of 1,2-bis(4-methoxyphenyl)-1,2-bis(4-nitrophenyl)ethene (**s-14**) and 1,2-bis(4-(methylthio)phenyl)-1,2-bis(4-nitrophenyl)ethene (**s-15**).^[29] In contrast to diphenylmethane, 9H-fluorene was dehydrogenated to [9,9]-bifluorenylidene (**t-28**) with moderate efficiency (45% yield). This can be tentatively explained by comparison with half-wave oxidation potential of the corresponding radical ($E_{1/2}^{ox}$ for Ph₂CH radical: 0.35 V versus SCE in MeCN, $E_{1/2}^{ox}$ for 9-fluorenyl radical: 0.76 V versus SCE in MeCN).^[30]

The role of carboxylate anion

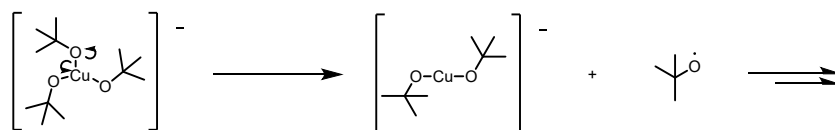
The paramount role the carboxylate anion plays in our dehydrogenation process was further demonstrated by the successful use of CuCl₂, *t*-BuOK, and PivOK combination for the dehydrogenation of **s-1** (Scheme S3-a), which is in strict contrast to the case in the absence of PivOK. We hypothesized that their disparate reactivity for different copper(II) sources can be related to their different reductive potential and, hence the

compatibility with the base. Lei and coworkers have elucidated a single electron transfer event between CuCl_2 and $t\text{-BuONa}$ in polar aprotic solvent (DMF, DMA, and NMP) (Scheme S3-b),^[31] which was believed by us as the culprit of the failure to use this type of copper(II) source alone in combination with $t\text{-BuOK}$ for the dehydrogenation of our substrates. Copper(II) salt with weak ligands like CuCl_2 , CuBr_2 , $\text{Cu}(\text{OTf})_2$, $\text{Cu}(\text{SO}_4)_2$ et al. are high oxidative species, the SET between $\text{Cu}(\text{II})$ source and the $t\text{-BuOK}$ may compete with the productive pathway, resulting a low yield. Incorporation of a bidentate ligand with good electron donation was expected to stabilize the high valent copper(II) species, and elevated selectivity of the $\text{Cu}(\text{II})$ oxidation can be achieved by using the copper(II) carboxylate. To test this hypothesis, we carried out a control experiment (Figure S1): under N_2 , mixing $\text{Cu}(\text{OPiv})_2$ (2.5 eq.), $t\text{-BuOK}$ (2.5 eq.), produce a blackish green solution (**solution A**). CuCl_2 (2.5 eq.) and $t\text{-BuOK}$ in HMPA result in a brown solution (**solution B**). After heating in N_2 at 120°C for 12 hours, it was found that the color of CuCl_2 faded to form yellowish transparent **solution b**, indicating a possible reaction between CuCl_2 and $t\text{-BuOK}$, while the $\text{Cu}(\text{OPiv})_2$ in HMPA (**solution A**) have no clear color change. The resulting **solution a** and **b** was added to the substrate (**s-1**) respectively (for **solution b**, additional 2.5 eq. PivOK was added to retain the reactivity, see **Scheme S3-a**) and heated for another 12 h in N_2 at 120°C (**step 2**). The corresponding TPE can still be obtained with 74% yield with **solution a**, while the **solution b** produces trace amount of product, indicating that $\text{Cu}(\text{OPiv})_2$ is much more stable than CuCl_2 toward $t\text{-BuOK}$, and CuCl_2 is consumed in **step 1** for **solution B** before engaging in the productive dehydrogenation process.

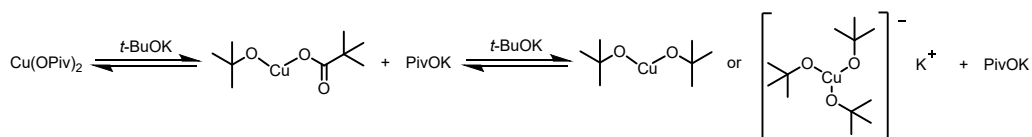
a. paramount influence of PivOK on reaction efficiency.



b. deactivated pathway of $\text{Cu}(\text{II})$ observed by Lei and coworker.



c. The proposed influence of additional PivOK on preventing of $\text{Cu}(\text{II})$ from degradation by $t\text{-BuOK}$.



Scheme S3. The role of PivOK play and decay of CuCl_2 in the presence of $t\text{-BuONa}$.

It is important to use additional 2.5 eq. PivOK for achieving good yield when less reactive substrate is used. For example, 4-benzylbenzonitrile produce the corresponding TPE in 70% yield under standard condition (2.5 eq. PivOK was used as additive). Otherwise, only 46% yield of TPE can be obtained. This can be explained by that the additional PivOK prevents the $\text{Cu}(\text{OPiv})_2$ from degradation by shifting the equilibrium backward, as shown above.

In general, our preliminary experiments coupled with Lei's work, suggest that the stability of $\text{Cu}(\text{OPiv})_2$ to $t\text{-BuOK}$ is one of the key factors for the success of our procedure, and addition of ligands to enhance the stability of $\text{Cu}(\text{II})$ toward reducing agents can play a vital role in the reaction.

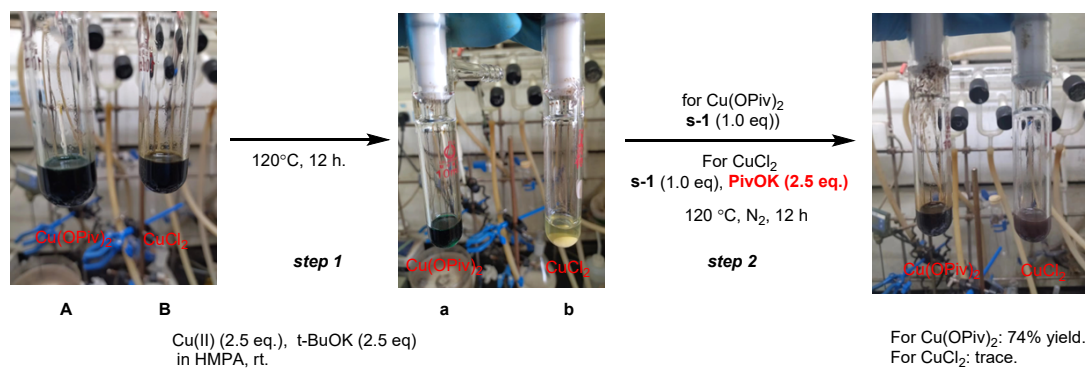


Figure S1. Comparison of stability of Cu(OPiv)₂ and CuCl₂ toward *t*-BuOK.

2.4. Additional example for tandem dehydrogenative homocoupling

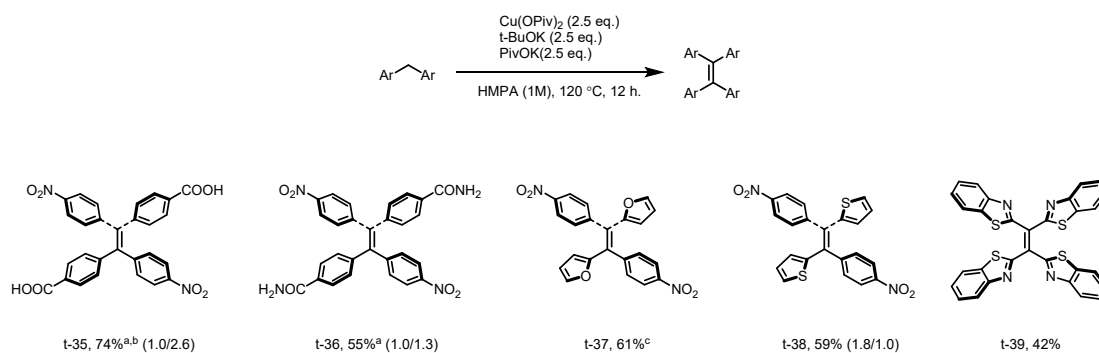
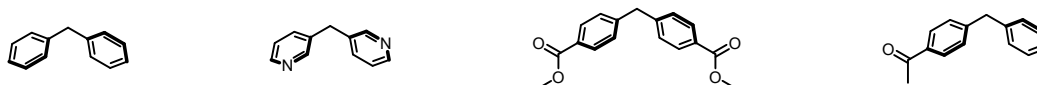


Table S7. Additional examples for benzylic C–H trifluoromethylation. All yields are isolated, see product characterizations section for full experimental details. a. Isolated as their methylation product. b. Isolated as the structurally undefined mixture of *E/Z* mixture, whose ratio was estimated by NMR. c. The *Z*-isomer spontaneously converts to the *E*-isomer during the purification and storage.

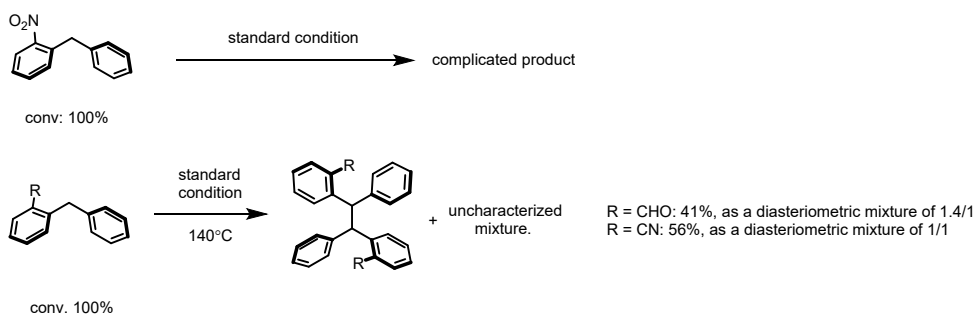
2.5. Unsuccessful substrates

a. Electron-neutral or Weak activated substrates



Note: Low conversion of starting materials or slow dehydrogenation observed, and side reaction compete.

b. Steric-demand substrate



Note: full conversion and partial dehydrogenation observed.

c. Sensitive functional group

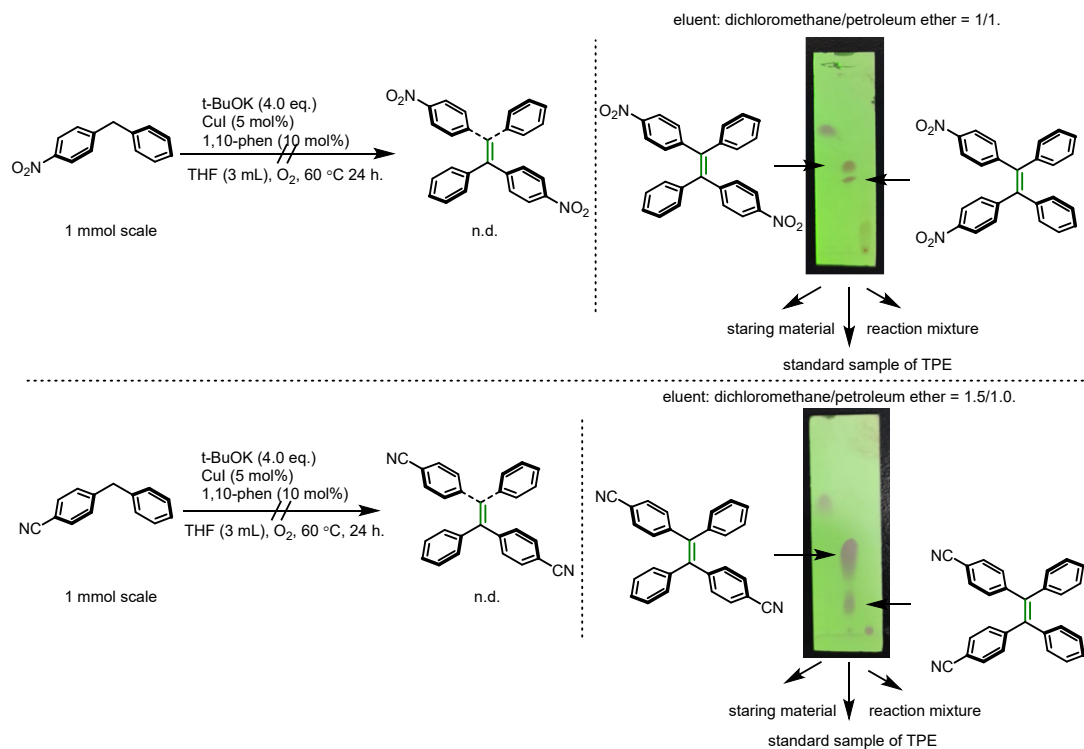


Note: complicated product observed.

Scheme S4. selected example of unsuccessful substrates.

2.6. Oxygen as terminal oxidant (adopt from reported procedure)

The previous documented method for tandem dehydrogenation of benzylpyridine is found to be unable to prepare the TPE derivatives, although full conversion of starting material, no detectable product was found as indicated by the TLC analysis).



Scheme S5. Attempt to prepare the TPE with O₂ as oxidant.

General procedure

Reactions were adopted from reported procedures, literature using water to quenching the reaction, whereas we used saturated ammonium chloride. A Schlenk tube charged with diarylmethane (1 mmol, 1.0 eq), CuI (9.5 mg, 5 mol%), 1,10-phenanthroline (18.0 mg, 10 mol%) and a stir bar was evacuated and backfilled with O₂ for three cycles. under O₂ flow, dry THF (3 mL) was added. The tube was capped and stirred in an oil bath preheated at 60 °C for 24 h. after cooling to room temperature, the mixture was quenched with saturated aqueous ammonium (20 mL) and extracted with ethyl acetate (10 mL×3). The organic layer was used to perform TLC analysis.

2.7. Product characterization

General procedure

In the glovebox, a 25 mL Schlenk tube was added diarylmethane (0.30 mmol, 1.0 eq.), Copper source (0.75 mmol, 2.5 eq.), and base (0.75 mmol, 2.5 eq). The tube was capped, and the solvent was added via a syringe under N₂ flow. The mixture was stirred in an oil bath preheated at 120 °C for 12 h. The mixture was cooled to room temperature, followed by addition of diluted aqueous hydrochloride (1M, 10 mL) and ethyl acetate (10 mL). The mixture was transferred to a separatory funnel, and the tube was rinsed with another portion of ethyl acetate (40 mL). All rinse was transferred to the separatory funnel, the aqueous layer was removed, and the organic layer was sequentially washed with diluted aqueous hydrochloride (1 M, 10 mL × 2), saturated aqueous NaHCO₃ (10 mL), and brine (10 mL). The organic layer was filtered through a short pad of silica gel with ethyl acetate as eluent. The solvent was removed under vacuum to afford the crude material, which was further purified by prep-TLC or silica gel chromatography to give the desired product.

Comment

In principle, the determination of the absolute configuration of unsymmetric TPE can be achieved based on 2D H-H NOESY (Figure S2),^[2] in which the absolute configuration was established by the fact that the phenyl ring in the same side of the double bond (ring **a** and **b**) have shorter space distance compared with ring **a** and

d, thus providing a basis for differentiating the two isomers by comparing the NOE of the H atom attached to, such that the correlation signal of H2 and H3 in *E* isomer can be detected (green line), the H2-H3' has a longer distance, and the NOE cannot be detected (blue line). In the *Z* isomer, only the H2-H3' correlation exist, so the NOE is invisible. In the previous report, the Overhauser effect (NOE) was reported to be observed only between the hydrogen atom (H2 and H3) in the trans isomer (*E*) of the unsymmetric TPE. on the contrary, no such a NOE was detected in the *Z* isomer.

However, in our research, the NOE was found in both *E* and *Z* isomers when magnifying the correlation signal, in such cases, qualitative comparison of the correlation signal seems to be inaccurate and may make the structural assignment arbitrary when unequally magnifying the signal to make one correlation invisible or visible. So, we use a method described previously,^[32] where the relative volume integration of the cross peak is taken as the indicator for the H-H distance, in our case, the distance of neighboring H1 and H2 in a phenyl ring was expected to be invariable in all cases, and their NOE volume integration was artificially normalized to 100 as the basis for comparison. By quantitative comparison of the volume integration related to the H1-H2 correlation, we attribute the larger correlation to the *E* isomer and the small correlation to the *Z* isomer, as see below for details.

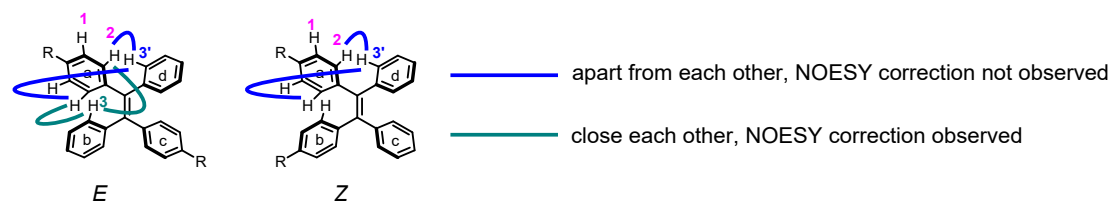
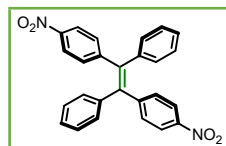


Figure S2. Differentiating *E/Z* isomer by NOESY.

1,2-bis(4-nitrophenyl)-1,2-diphenylethene (**t-1**)

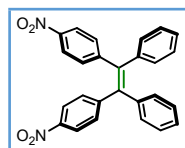
The reaction was conducted on 0.30 mmol scale according to the general procedure. Heating the mixture of 1-benzyl-4-nitrobenzene (64.0 mg, 0.30 mmol, 1.0 eq.), Cu(OPiv)₂ (199.0 mg, 0.75 mmol, 2.5 eq.), *t*-BuOK (84.0 mg, 0.75 mmol, 2.5 eq.), PivOK (105 mg, 0.75 mmol, 2.5 eq.) in HMPA (3 mL) under N₂ for 12 h. The title compound was purified by prep-TLC. Eluent = dichloromethane/petroleum ether = 1/1.

(*E*)-1,2-bis(4-nitrophenyl)-1,2-diphenylethene (**t-1-E**, new compound)



As a yellowish solid (40.8 mg, 64% yield). $R_f = 0.37$ (eluent = dichloromethane/hexane = 1/1), ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 8.6 Hz, 4H), 7.24 – 7.14 (m, 10H), 6.98 (d, *J* = 7.8 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 149.9, 146.4, 141.6, 141.5, 132.0, 131.2, 128.6, 128.1, 123.2. HRMS (ESI) *m/z*: [M+Na]⁺ calculated for C₂₆H₁₈N₂O₄Na⁺ 445.1159, found 445.1161. **Melting point:** 227 - 230°C.

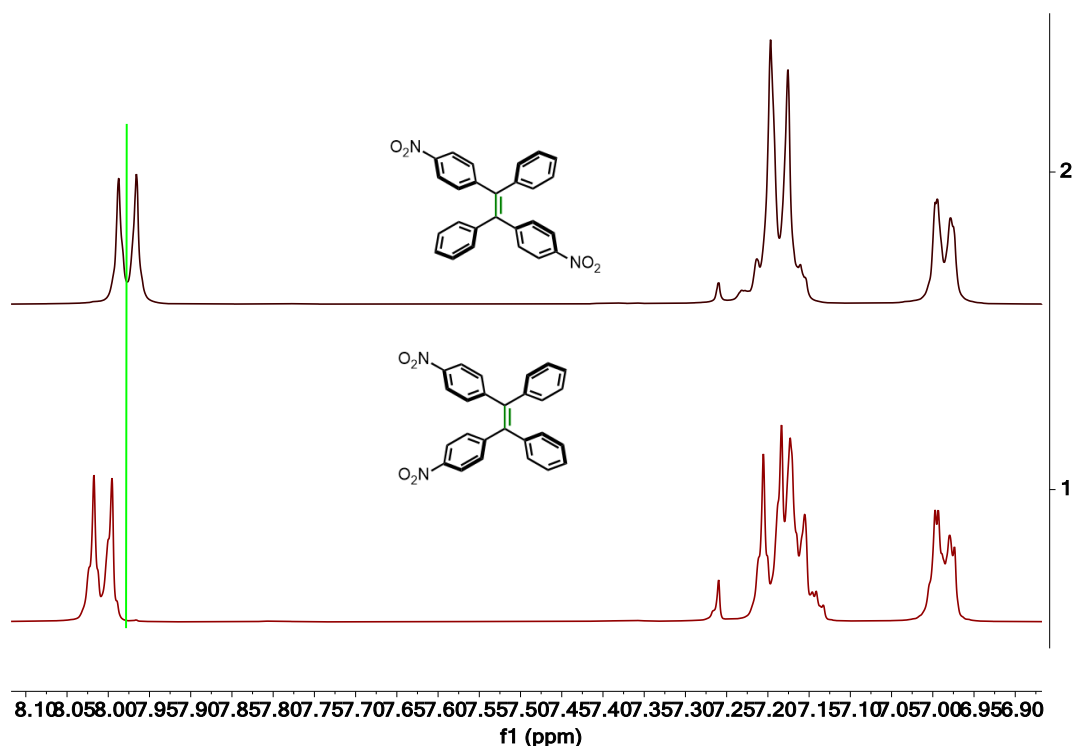
(*Z*)-1,2-bis(4-nitrophenyl)-1,2-diphenylethene (**t-1-Z**, known compound, 102687-88-7)



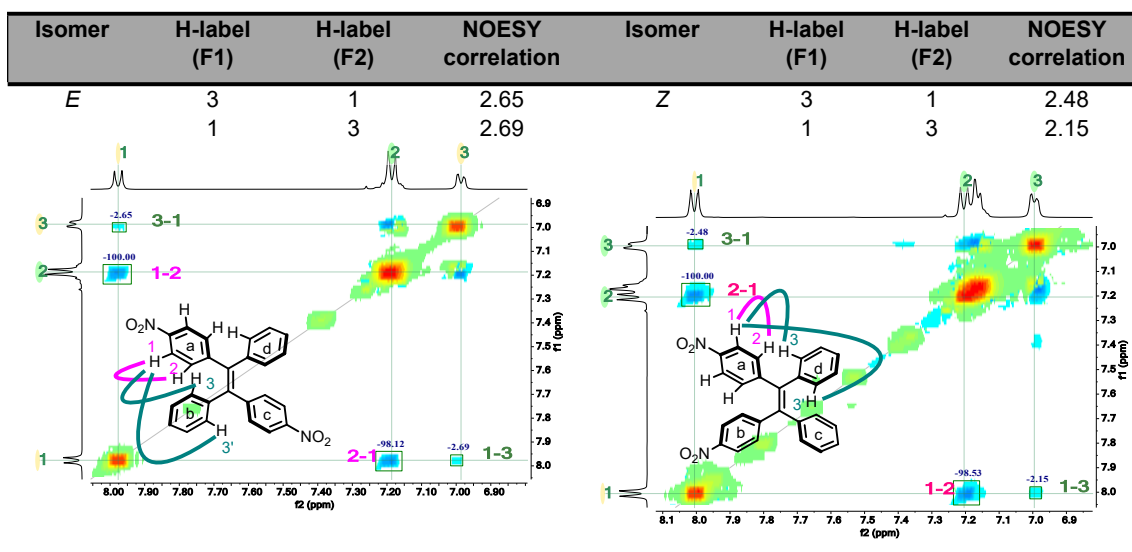
As a colorless solid (19.6 mg, 30% yield). $R_f = 0.27$ (eluent = dichloromethane/hexane = 1/1), ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 8.8 Hz, 4H), 7.23 – 7.12 (m, 10H), 7.02 – 6.96 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 149.8, 146.6, 141.7, 141.5, 132.1, 131.1, 128.3, 127.8, 123.5.

Its characterization data match the one found in the literature well.^[33]

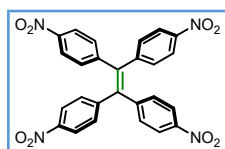
stacked 1H NMR spectra of two isomer.



2D H-H NOESY



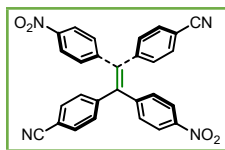
1,1,2,2-tetrakis(4-nitrophenyl)ethene (t-2, known compound, 47797-98-8)



According to the general procedure, heating the mixture of bis(4-nitrophenyl)methane (77.5 mg, 0.30 mmol, 1.0 eq.), Cu(OPiv)₂ (199.0 mg, 0.75 mmol, 2.5 eq.), *t*-BuOK (84 mg, 0.75 mmol, 2.5 eq.), PivOK (105 mg, 0.75 mmol, 2.5 eq.) in HMPA (3 mL) under N₂ for 12 h, after silica gel chromatography affording the 1,1,2,2-tetrakis(4-nitrophenyl)ethene (76.0 mg, 98% yield) as yellow-beige solid. *R*_f = 0.50 (eluent: dichloromethane/petroleum ether = 3/1). ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 8.1 Hz, 8H), 7.19 (d, *J* = 8.2 Hz, 8H). ¹³C NMR (101 MHz, CDCl₃) δ 147.4, 147.2, 141.6, 131.9, 124.0.

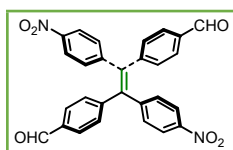
Characterization data conforms with those reported well.^[34]

4,4'-(1,2-bis(4-nitrophenyl)ethene-1,2-diyl)dibenzonitrile (t-3, as mixture of *E/Z* isomer, new compound)



According to the general procedure with a little modification (at 100 °C) by heating the 4-(4-nitrobenzyl)benzonitrile (71.4 mg, 0.30 mmol, 1.0 eq.), Cu(OPiv)₂ (199 mg, 0.75 mmol, 2.5 eq.) *t*-BuOK (84 mg, 0.75 mmol, 2.5 eq.), PivOK (105 mg, 0.75 mmol, 2.5 eq.) in HMPA (3 mL) under N₂ at 100°C for 12 h. Prep-TLC affording the 4,4'-(1,2-bis(4-nitrophenyl)ethene-1,2-diyl)dibenzonitrile was obtained as yellow-beige solid (57.0 mg, 80% yield). $R_f = 0.39$, eluent = dichloromethane/petroleum ether = 3/1. **¹H NMR (400 MHz, CDCl₃)** δ 8.05 – 7.99 (m, 4H), 7.51 – 7.45 (m, 4H), 7.20 – 7.14 (m, 4H), 7.14 – 7.08 (m, 4H). **¹³C NMR (101 MHz, CDCl₃)** δ 147.4 (147.48), 147.4 (147.46), 147.1, 145.4, 145.3, 141.5, 132.4, 132.3, 132.2, 131.9, 131.6, 123.8 (123.86), 123.8 (123.82), 118.1, 118.0, 112.1 (112.18), 112.1 (112.14). **HRMS (ESI)** *m/z*: [M+Na]⁺ calculated for C₂₈H₁₆N₄O₄Na⁺ 495.1064, found 495.1059.

4,4'-(1,2-diphenylethene-1,2-diyl)dibenzaldehyde (t-4, as mixture of *E/Z* isomer, new compound)

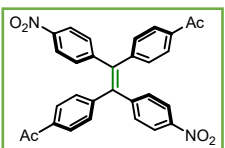


According to the general procedure, heating the 4-(4-nitrobenzyl)benzaldehyde (72.4 mg, 0.30 mmol, 1.0 eq.), Cu(OPiv)₂ (199 mg, 0.75 mmol, 2.5 eq.) *t*-BuOK (84 mg, 0.75 mmol, 2.5 eq.), PivOK (105 mg, 0.75 mmol, 2.5 eq.) in HMPA (3 mL) under N₂ for 12 h. Prep-TLC affording the 4,4'-(1,2-bis(4-nitrophenyl)ethene-1,2-diyl)dibenzaldehyde as a yellow solid. (50.5 mg, 70% yield). $R_f = 0.29$, eluent = dichloromethane/petroleum ether = 5/1. **¹H NMR (400 MHz, CDCl₃)** δ 9.96 – 9.89 (m, 2H), 8.06 – 7.97 (m, 4H), 7.73 – 7.65 (m, 4H), 7.23 – 7.14 (m, 8H). **¹³C NMR (101 MHz, CDCl₃)** δ 191.4, 191.3, 148.1, 148.0, 147.1 (147.17), 147.1 (147.11), 147.0 (147.09), 147.0 (147.05), 141.9, 135.7, 135.6, 132.0, 131.9, 131.7 (131.73), 131.7 (131.72), 129.8, 129.7, 123.8, 123.6. (1 overlapped peaks), **HRMS (ESI)** *m/z*: [M+H]⁺ calculated for C₂₈H₁₉N₂O₆⁺ 479.1238, found 479.1247.

1,1'-((1,2-bis(4-nitrophenyl)ethene-1,2-diyl)bis(4,1-phenylene))bis(ethan-1-one)

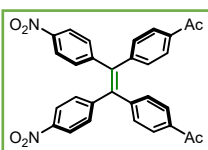
The reaction was conducted on 0.30 mmol scale according to the general procedure, Heating the mixture of 1-(4-(4-nitrobenzyl)phenyl)ethan-1-one (76.6 mg, 0.30 mmol, 1.0 eq.), Cu(OPiv)₂ (199.0 mg, 0.75 mmol, 2.5 eq.), *t*-BuOK (67.3 mg, 0.60 mmol, 2.0 eq.), PivOK (84.0 mg, 0.60 mmol, 2.0 eq.) in HMPA (3 mL) under N₂ for 12 h. the title compound was purified by the prep-TLC, eluent = ethyl acetate/dichloromethane = 1/60.

(*E*)-1,1'-((1,2-bis(4-nitrophenyl)ethene-1,2-diyl)bis(4,1-phenylene))bis(ethan-1-one) (t-5-*E*, new compound)



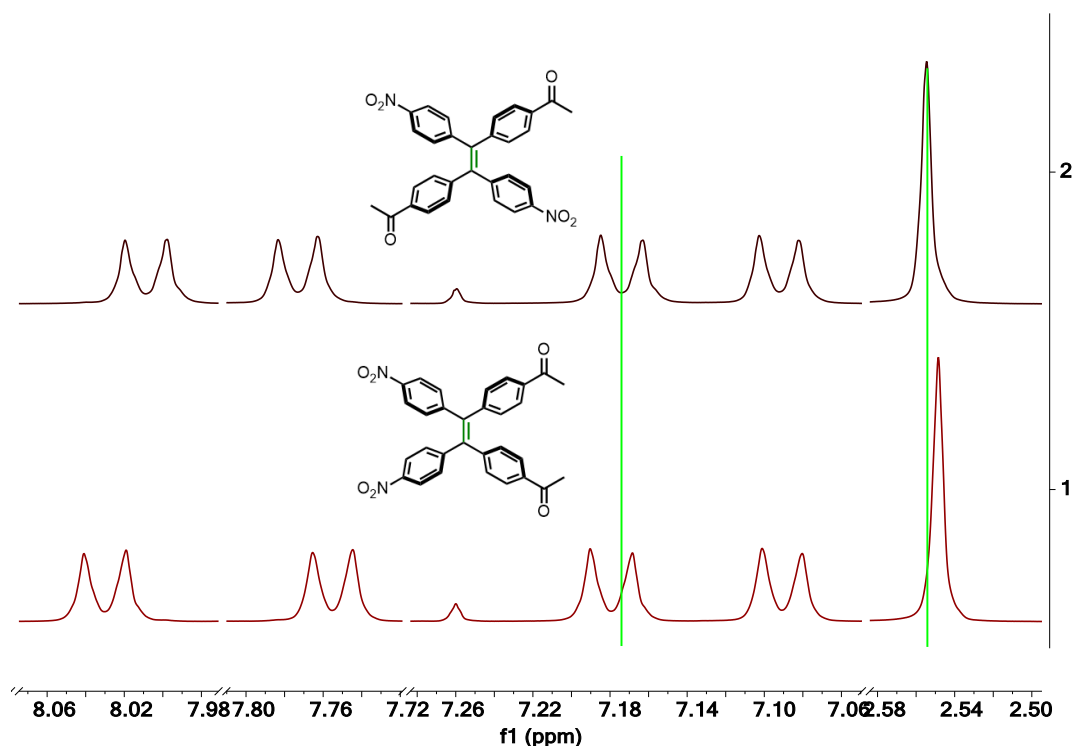
As a yellowish solid (28.8 mg, 37% yield), $R_f = 0.63$, eluent: ethyl acetate/dichloromethane = 1/60. **¹H NMR (400 MHz, CDCl₃)** δ 8.01 (d, *J* = 8.7 Hz, 4H), 7.77 (d, *J* = 8.2 Hz, 4H), 7.17 (d, *J* = 8.6 Hz, 4H), 7.09 (d, *J* = 8.2 Hz, 4H), 2.56 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 197.2, 148.4, 147.0, 145.8, 141.7, 136.5, 132.0, 131.3, 128.6, 123.6, 26.7. **HRMS (ESI)** *m/z*: [M+Na]⁺ calculated for C₃₀H₂₂N₂O₆Na⁺ 529.1370, found 529.1364. **Melting point:** 170 - 171 °C.

(*Z*)-1,1'-((1,2-bis(4-nitrophenyl)ethene-1,2-diyl)bis(4,1-phenylene))bis(ethan-1-one) (t-5-*Z*, new compound)

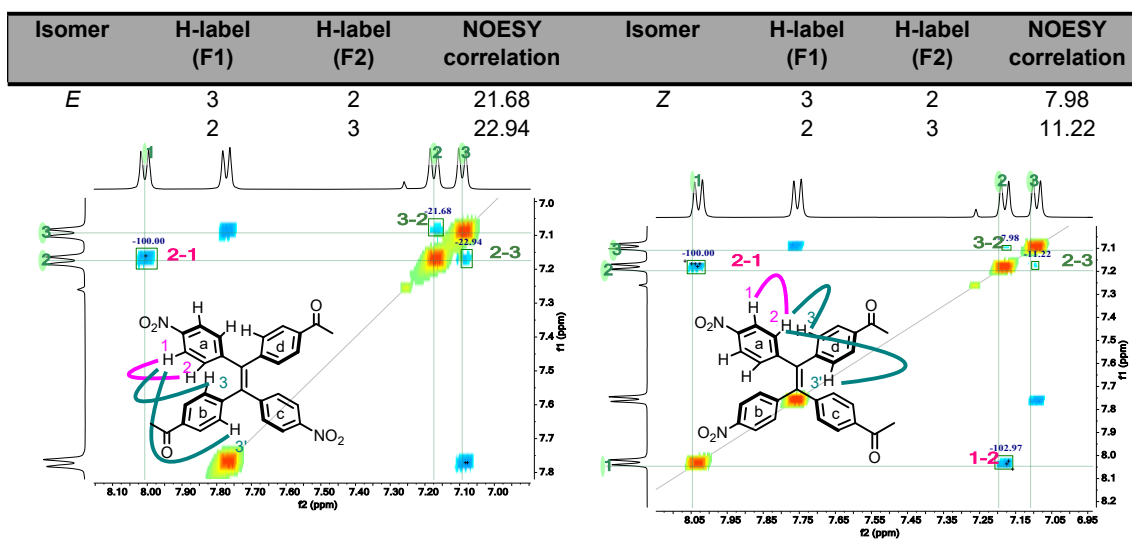


As a yellowish foamy solid (25.5 mg, 33% yield), $R_f = 0.40$ (eluent = ethyl acetate/dichloromethane = 1/60). **¹H NMR (400 MHz, CDCl₃)** δ 8.03 (d, *J* = 8.7 Hz, 4H), 7.76 (d, *J* = 8.1 Hz, 4H), 7.18 (d, *J* = 8.7 Hz, 4H), 7.09 (d, *J* = 8.1 Hz, 4H), 2.55 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 197.4, 148.4, 147.1, 145.9, 141.7, 136.4, 132.0, 131.3, 128.5, 123.8, 26.7. **HRMS (ESI)** *m/z*: [M+Na]⁺ calculated for C₃₀H₂₂N₂O₆Na⁺ 529.1370, found 529.1378. **Melting point:** 102 -103 °C.

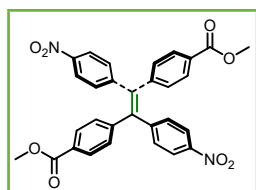
Stacked 1H NMR spectra differential of the *E* and *Z* isomer.



comparison of 2D H-H NOESY the *E* and *Z* isomer



Dimethyl 4,4'-(1,2-bis(4-nitrophenyl)ethene-1,2-diyl)-dibenzoate (*t*-6, as mixture of *E/Z* isomer, new compound)

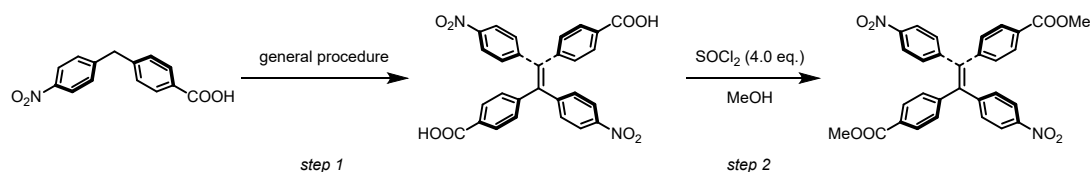


The reaction was conducted on 0.30 mmol scale according with a slight modification (80 °C). Heating the mixture of methyl 4-(4-nitrobenzyl)benzoate (81.4 mg, 0.30 mmol, 1.0 eq.), Cu(OPiv)₂ (199.0 mg, 0.75 mmol, 2.5 eq.), *t*-BuOK (84 mg, 0.75 mmol, 2.5 eq), PivOK (105.0 mg, 0.75 mmol, 2.5 eq.) in HMPA (3 mL) under N₂ for 12 h. The title compound was purified by the prep-TLC as a yellow solid (68.8 mg, 85% yield as the mixture of *E/Z* isomer), *R*_f = 0.52, 0.45. (the two spots were too close to one another, making their separation by preparative thin-

layer chromatography (prep-TLC) challenging), eluent = ethyl acetate/petroleum ether = 1/6, ¹H NMR (400 MHz, CDCl₃) δ 8.08 – 7.95 (m, 4H), 7.91 – 7.77 (m, 4H), 7.23 – 7.12 (m, 4H), 7.11 – 7.00 (m, 4H), 3.93 – 3.84

(m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 166.3, 166.2, 148.3 (148.38), 148.3 (148.34), 146.9, 146.8, 145.7, 145.6, 141.6 (141.67), 141.6 (141.65), 141.6, 131.9, 131.8, 131.0, 130.9, 129.7, 129.6, 123.6, 123.4, 52.2 (52.28), 52.2 (52.24). HRMS (ESI) m/z: [M+Na]⁺ calculated for C₃₀H₂₂N₂O₈Na⁺ 561.1269, found 561.1268.

Method 2



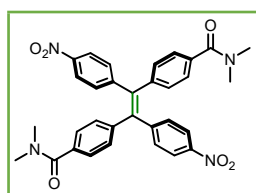
step 1: The reaction was conducted on 0.30 mmol scale according to general procedure without large modification. Heating the mixture of 4-(4-nitrobenzyl)benzoic acid (77.2 mg, 0.30 mmol, 1.0 eq.), Cu(OPiv)₂ (199.0 mg, 0.75 mmol, 2.5 eq.), *t*-BuOK (84 mg, 0.75 mmol, 2.5 eq.), PivOK (105.0 mg, 0.75 mmol, 2.5 eq.) in HMPA (3 mL) under N₂ for 12 h. After workup (the step involving washing with saturated NaHCO₃ solution was replaced by washing with saturated brine), the crude product was treated under high vacuum at 120 °C for 6 h to remove the residual pivalic acid.

Step 2: the crude product obtained in step 1 was then dispersed in 6 mL methanol and stirred. thionyl chloride (87 μL, 1.2 mmol, 4.0 eq.) was added to the mixture at ambient temperature. Subsequently, the mixture was refluxed for 6 h in an oil bath preheated at 70 °C. After cooling to room temperature, methanol was removed from the reaction mixture by rotary evaporator. The remaining solid was dissolved in 25 mL ethyl acetate and placed into a separatory funnel. After washing the organic phase with saturated NaHCO₃ (aq., 5 mL) and brine (5 mL), it was filtered through a brief silica gel column. The solvent was then removed via rotary evaporation, and the crude product was purified by prep-TLC, producing the title compound as a colorless solid (60.0 mg, 74% yield) as the mixture of *E/Z* isomer (1.0/2.6, absolute configuration was not assigned).

4,4'-(1,2-bis(4-nitrophenyl)ethene-1,2-diyl)bis(*N,N*-dimethylbenzamide)

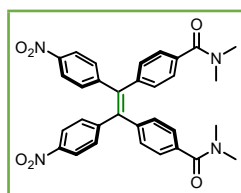
The reaction was conducted on 0.30 mmol scale according to the general procedure with a bit of modification. Heating the mixture of *N,N*-dimethyl-4-(4-nitrobenzyl)benzamide (85.3 mg, 0.30 mmol, 1.0 eq.), Cu(OPiv)₂ (199.0 mg, 0.75 mmol, 2.5 eq.), *t*-BuOK (67.3 mg, 0.60 mmol, 2.0 eq.), PivOK (84.0 mg, 0.60 mmol, 2.0 eq.) in HMPA (3 mL) at 100 °C for 12 h. After cooling to room temperature, the mixture was diluted with ethyl acetate (10 mL) and diluted hydrochloric acid (aq. 10 mL, 0.25 M), the mixture was transferred to a separatory funnel, the tube was washed with additional ethyl acetate (40 mL), and combined to the separatory funnel, the aqueous layer was removed, and the organic layer was sequentially washed with hydrochloric acid (aq., 10 mL × 2, 0.25 M), saturated NaHCO₃ (10 mL) and brine (10 mL). The volatile was removed under vacuum. The remaining mixture was further purified by the prep-TLC to afford the title compound (eluent = THF/dichloromethane = 1/10, prep-TLC).

(*E*)-4,4'-(1,2-bis(4-nitrophenyl)ethene-1,2-diyl)bis(*N,N*-dimethylbenzamide) (t-7-*E*, new compound)



As a colorless solid (31.6 mg, 37% yield), *R*_f = 0.39 (eluent = tetrahydrofuran/dichloromethane = 1/15), ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 8.8 Hz, 4H), 7.26 (d, *J* = 8.3 Hz, 4H), 7.20 (d, *J* = 8.7 Hz, 4H), 7.03 (d, *J* = 8.2 Hz, 4H), 3.08 (s, 6H), 2.94 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 170.7, 149.0, 146.8, 142.5, 141.4, 136.0, 132.1, 131.1, 127.5, 123.4, 39.6, 35.5. HRMS (ESI) m/z: [M+Na]⁺ calculated for C₃₂H₂₈N₄O₆Na⁺ 587.1901, found 587.1905. Melting point: 302 - 305 °C.

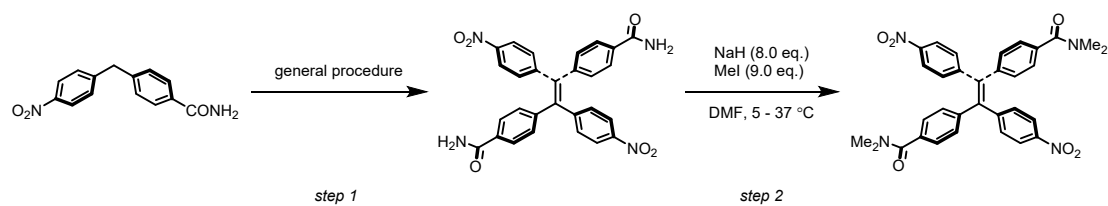
(*Z*)-4,4'-(1,2-bis(4-nitrophenyl)ethene-1,2-diyl)bis(*N,N*-dimethylbenzamide) (t-7-*Z*, new compound)



As a yellowish solid (35.8 mg, 42% yield), *R*_f = 0.07, (eluent = tetrahydrofuran/dichloromethane = 1/15), ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 8.5 Hz, 4H), 7.22 (d, *J* = 8.0 Hz, 4H), 7.18 (d, *J* = 8.5 Hz, 4H), 7.02 (d, *J* = 8.0 Hz, 4H), 3.06 (s, 6H), 2.92 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 170.8, 148.9, 146.9, 142.6, 141.4, 135.8, 132.1, 131.1, 127.3, 123.6, 39.6, 35.4. HRMS (ESI) m/z: [M+Na]⁺ calculated for C₃₂H₂₈N₄O₆Na⁺ 587.1901, found 587.1905. Melting point:

218 - 222 °C.

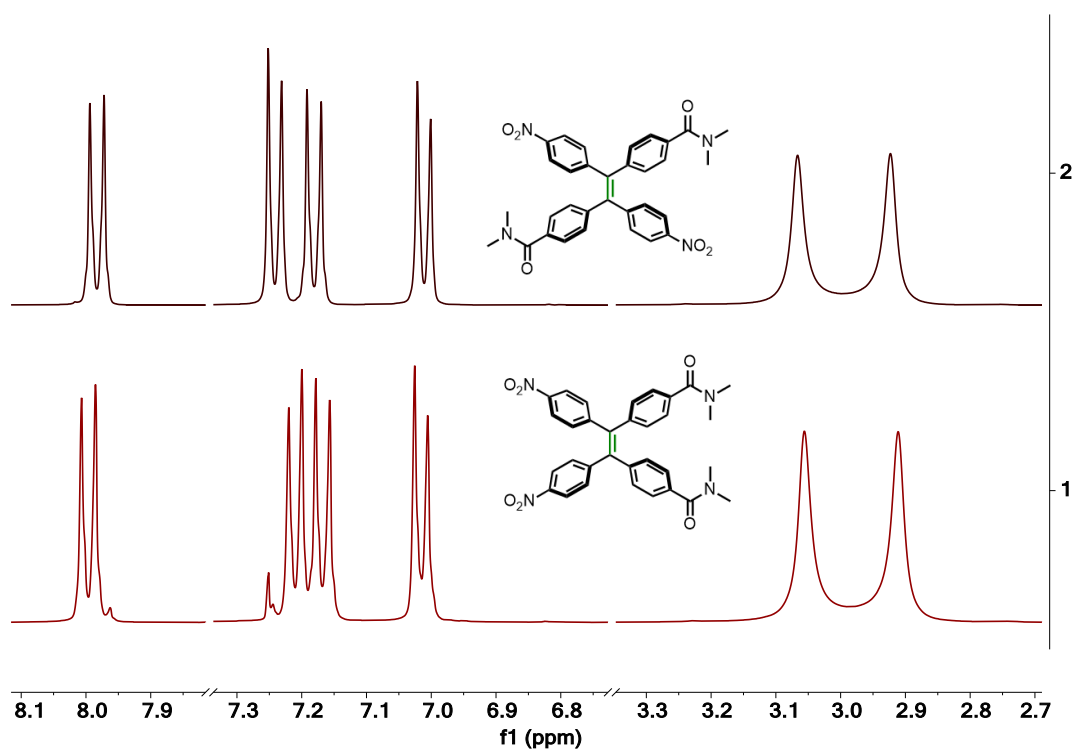
Method 2



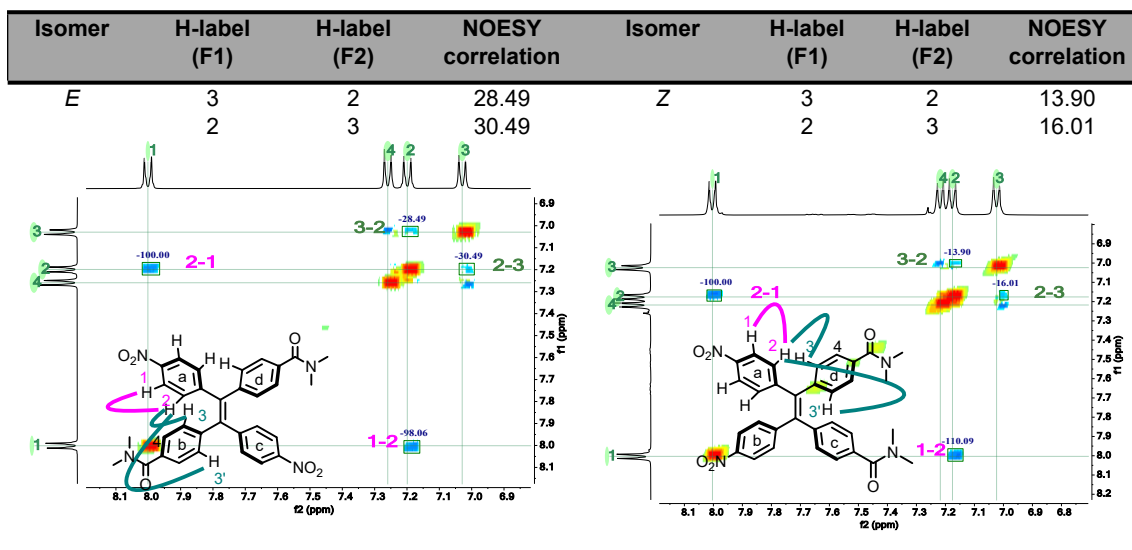
step 1: The reaction was conducted on 0.30 mmol scale according to general procedure, Heating the mixture of 4-(4-nitrobenzyl)benzamide (76.9 mg, 0.30 mmol, 1.0 eq.), Cu(OPiv)₂ (199.0 mg, 0.75 mmol, 2.5 eq.), t-BuOK (84.0 mg, 0.75 mmol, 2.5 eq.), PivOK (105.0 mg, 0.75 mmol, 2.5 eq.) in HMPA (3 mL) under N₂ for 12 h. After workup, the crude product was treated under high vacuum at 120°C for 1 h to remove the residual pivalic acetic acid.

Step 2: The crude product obtained in *step 1* was then dissolved in 6 mL dry DMF. Under stirring, NaH (60% w/w, dispersed in mineral oil, 96.0 mg, 2.4 mmol, 8.0 eq.) was added to the mixture at ambient temperature (ca. 5°C). the mixture was stirred at room temperature for 2 min followed by addition of MeI (149 μl, 2.4 mmol, 8.0 eq.). The reaction mixture was stirred at room temperature for another 30 min and quenched with brine (15 mL) and ethyl acetate (60 mL) and transferred to a separatory funnel. The collected organic layer was washed with brine (10 mL × 5) and filtered through a short pad of silica gel. The solvent was removed by vacuum, the residue was brought into prep-TLC to afford the *t*-7-*E* (20.4 mg, 24% yield) and *t*-7-*Z* (26.5 mg, 31% yield).

Stacked 1H NMR spectra differential of the *E* and *Z* isomer.



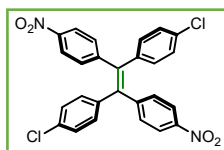
comparison of 2D H-H NOESY the *E* and *Z* isomer



1,2-bis(4-nitrophenyl)-1,2-bis(4-chlorophenyl)ethene

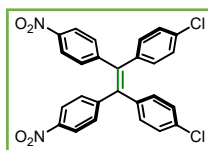
The reaction was conducted on 0.30 mmol scale with minor modification, heating the mixture of 1-chloro-4-(4-nitrobenzyl)benzene (74.3 mg, 0.30 mmol, 1.0 eq.), Cu(OPiv)₂ (199 mg, 0.75 mmol, 2.5 eq.), t-BuOK (84.0 mg, 0.75 mmol, 2.5 eq.), PivOK (105.0 mg, 0.75 mmol, 2.5 eq.) in HMPA (3 mL) under N₂ for 12 h. The title compound was purified by the prep-TLC, eluent = dichloromethane/petroleum ether = 1/1.

(*E*)-1,2-bis(4-nitrophenyl)-1,2-bis(4-chlorophenyl)ethene (t-8-*E*, new compound)



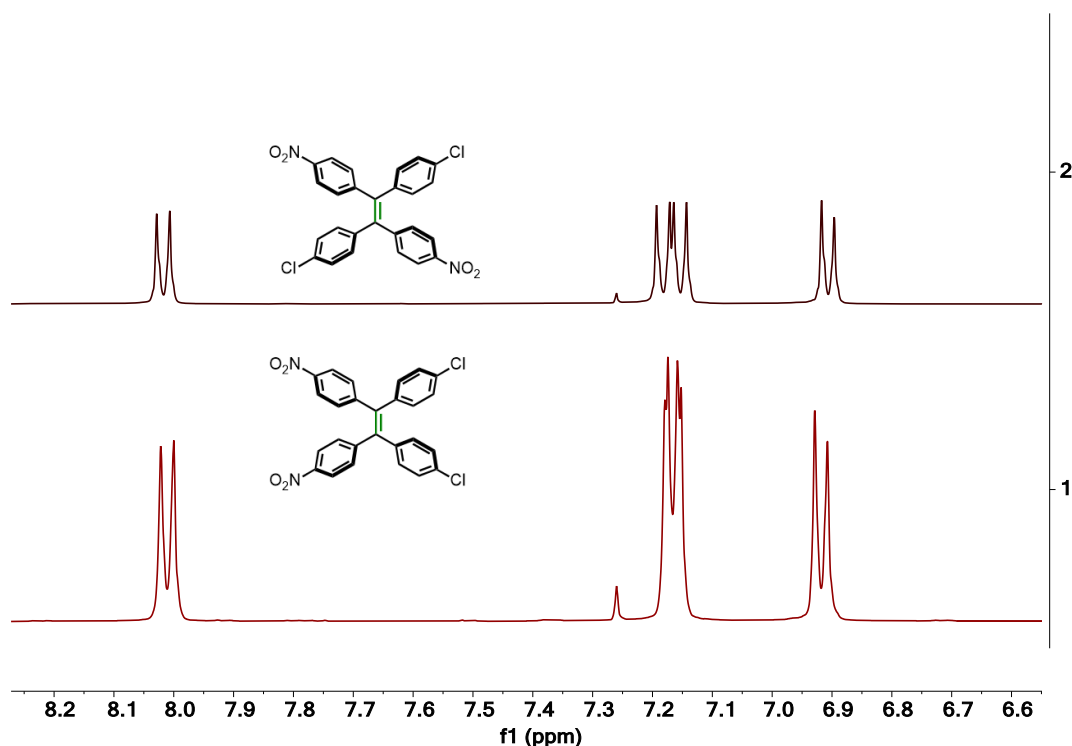
As a bright yellowish solid (40.8 mg, 55% yield), $R_f = 0.47$, eluent = dichloromethane/petroleum ether = 1/1. ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, $J = 8.7$ Hz, 4H), 7.18 (d, $J = 8.7$ Hz, 4H), 7.15 (d, $J = 8.5$ Hz, 4H), 6.91 (d, $J = 8.4$ Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 149.03, 146.80, 140.84, 139.71, 134.36, 132.44, 132.05, 129.04, 123.62. ¹H NMR (400 MHz, CD₂Cl₂) δ 8.00 (d, $J = 8.8$ Hz, 4H), 7.19 (d, $J = 8.8$ Hz, 4H), 7.15 (d, $J = 8.5$ Hz, 4H), 6.92 (d, $J = 8.5$ Hz, 4H). ¹³C NMR (101 MHz, CD₂Cl₂) δ 149.3, 147.0, 141.1, 140.1, 134.2, 132.8, 132.3, 129.0, 123.7. HRMS (ESI) m/z : [M+Na]⁺ calculated for C₂₆H₁₆N₂O₄Cl₂Na⁺ 513.0380, found 513.0372. Melting point: 221 – 222 °C.

(*Z*)-1,2-bis(4-nitrophenyl)-1,2-bis(4-chlorophenyl)ethene (t-8-*Z*, new compound)

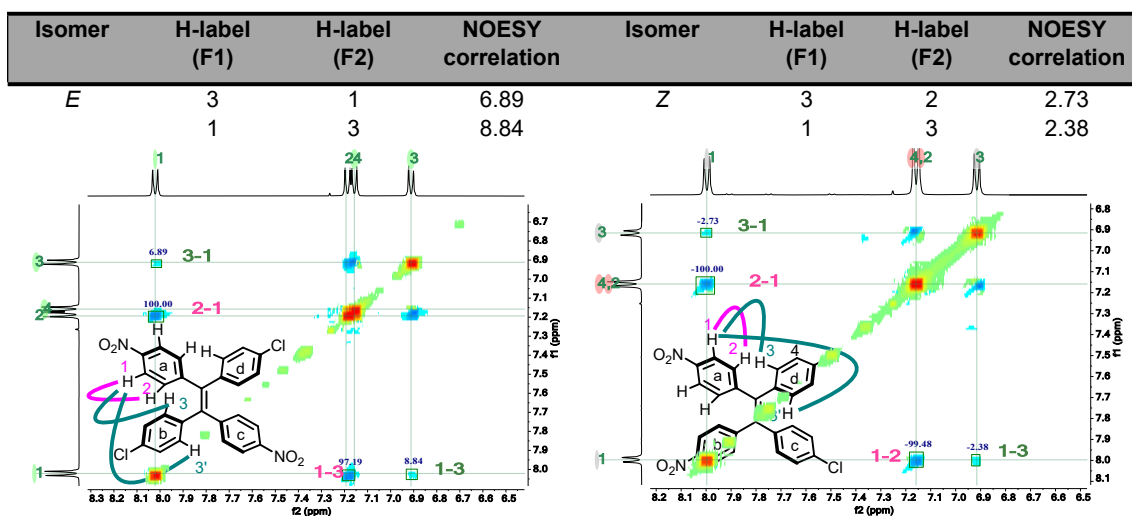


As a bright yellowish solid (31.2 mg, 42% yield). $R_f = 0.35$, eluent = dichloromethane/petroleum ether = 1/1. ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, $J = 8.8$ Hz, 4H), 7.23 – 7.13 (m, 8H), 6.96 – 6.87 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 148.9, 146.9, 140.8, 139.8, 134.1, 132.4, 132.0, 128.9, 123.7. HRMS (ESI) m/z : [M+H]⁺ calculated for C₂₈H₁₇N₂O₄⁺ 491.0560, found 491.0558. Melting point: 126 – 127 °C.

Stacked ¹H NMR spectra of the *E* and *Z* isomer.



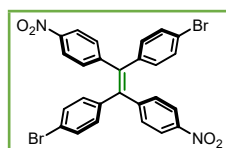
NOESY



1,2-bis(4-nitrophenyl)-1,2-bis(4-bromophenyl)ethene

The reaction was conducted on 0.30 mmol scale according to the general procedure, heating the mixture of 1-bromo-4-(4-nitrobenzyl)benzene (87.6 mg, 0.30 mmol, 1.0 eq.), Cu(OPiv)₂ (199 mg, 0.75 mmol, 2.5 eq.), *t*-BuOK (84 mg, 0.75 mmol, 2.5 eq.), PivOK (105.0 mg, 0.75 mmol, 2.5 eq.) in HMPA (3 mL) under N₂ for 12 h. the title compound was purified by the prep-TLC, eluent = dichloromethane/petroleum ether = 1/1. **Melting point:**

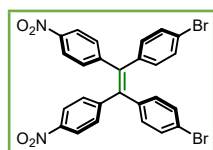
(*E*)-1,2-bis(4-nitrophenyl)-1,2-bis(4-bromophenyl)ethene (*t*-9-*E*, new compound)



As a yellowish colorless solid (45.5 mg, 52% yield). *R*_f = 0.46, eluent = dichloromethane/petroleum ether = 1/1. ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 8.2 Hz, 4H), 7.31 (d, *J* = 8.1 Hz, 4H), 7.18 (d, *J* = 8.4 Hz, 4H), 6.84 (d, *J* = 8.2 Hz, 4H).

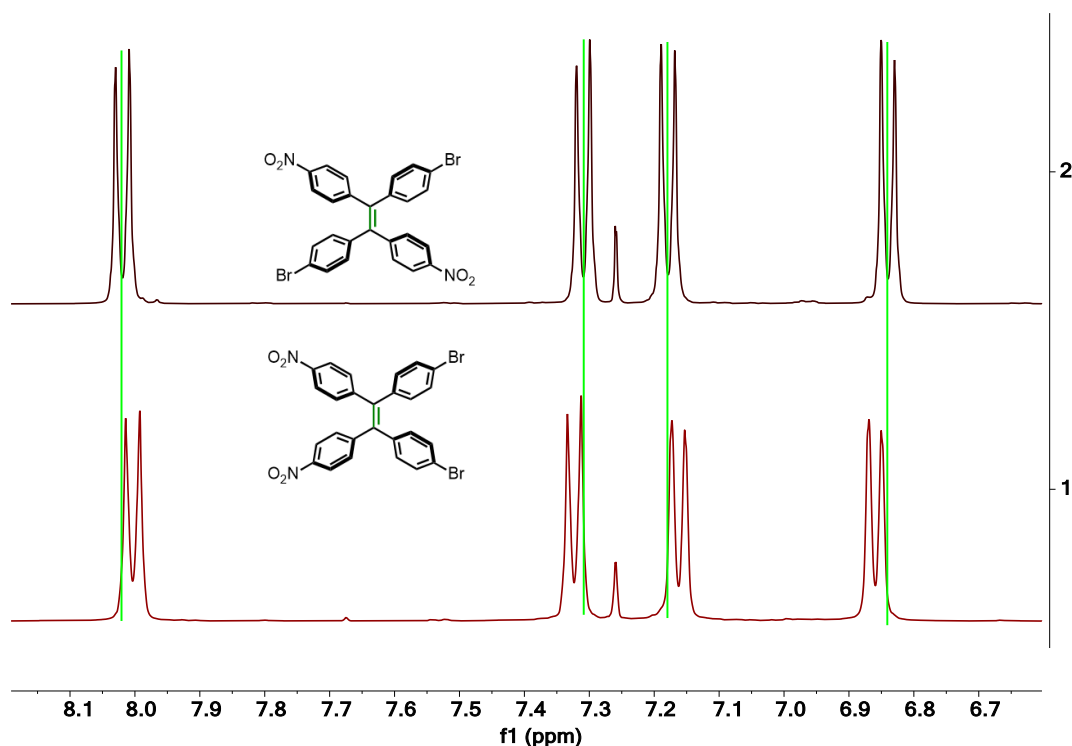
^{13}C NMR (101 MHz, CDCl_3) δ 148.9, 146.8, 140.8, 140.2, 132.6, 132.0, 131.9, 123.6, 122.6. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{28}\text{H}_{16}\text{N}_2\text{O}_4^{79}\text{Br}_2\text{Na}^+$ 600.9369, found 600.9372. Melting point: 233 - 236 °C.

(Z)-1,2-bis(4-nitrophenyl)-1,2-bis(4-bromophenyl)ethene (t-9-Z, new compound)

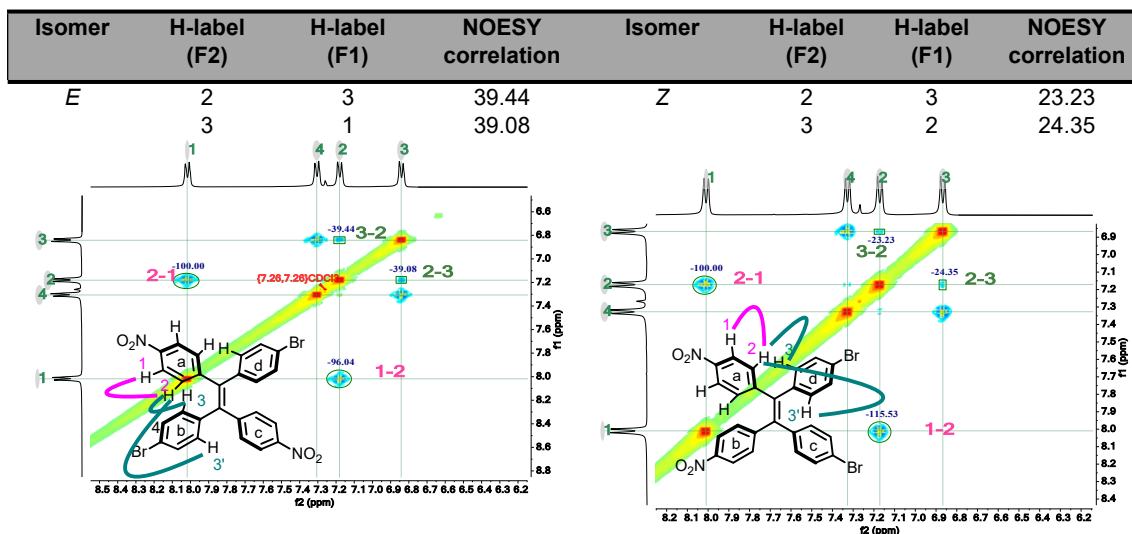


As a yellowish solid (34.8 mg, 39% yield). R_f = 0.34, eluent = dichloromethane/petroleum ether = 1/1). ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, J = 8.7 Hz, 4H), 7.32 (d, J = 8.5 Hz, 4H), 7.16 (d, J = 7.9 Hz, 4H), 6.86 (d, J = 7.5 Hz, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.8, 146.9, 140.8, 140.2, 132.6, 132.0, 131.8, 123.71, 122.4. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{26}\text{H}_{16}\text{N}_2\text{O}_4^{79}\text{Br}_2\text{Na}^+$ 600.9369, found 600.9373. Melting point: 166 - 167 °C.

Stacked ^1H NMR spectra of the *E* and *Z* isomer.



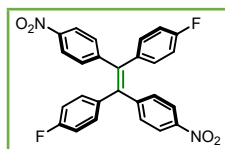
NOESY



1,2-bis(4-fluorophenyl)-1,2-bis(4-nitrophenyl)ethene

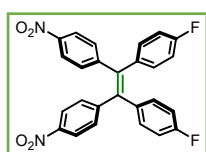
The reaction was conducted on 0.30 mmol scale according to the general procedure, heating the mixture of 1-fluoro-4-(4-nitrobenzyl)benzene (69.4 mg, 0.30 mmol, 1.0 eq.), Cu(OPiv)₂ (199 mg, 0.75 mmol, 2.5 eq.), *t*-BuOK (84 mg, 0.75 mmol, 2.5 eq.), PivOK (105.0 mg, 0.75 mmol, 2.5 eq.) in HMPA (3 mL) under N₂ for 12 h. the title compound was purified by the prep-TLC, eluent = dichloromethane/petroleum ether = 1.5/1.0.

(*E*)-1,2-bis(4-fluorophenyl)-1,2-bis(4-nitrophenyl)ethene (t-10-*E*, new compound)



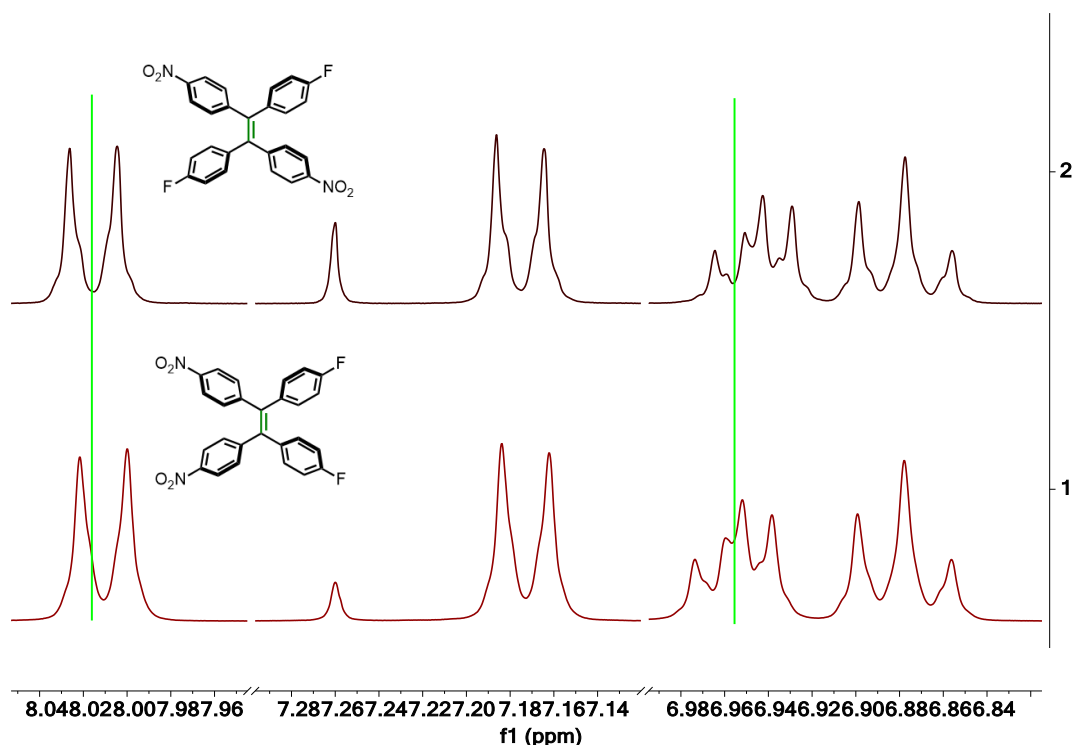
As a yellow foamy solid (37.9 mg, 55% yield). $R_f = 0.4$ (eluent = dichloromethane/petroleum ether = 1/1), ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 8.7 Hz, 4H), 7.17 (d, *J* = 8.8 Hz, 4H), 6.95 (dd, *J* = 8.7, 5.5 Hz, 4H), 6.88 (t, *J* = 8.6 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 163.5, 161.0, 149.4, 146.7, 140.7, 137.3 (137.38), 137.3 (137.35), 132.9 (132.99), 132.9 (132.90), 132.0, 123.5, 116.0, 115.7. ¹⁹F NMR (376 MHz, CDCl₃) δ -112.18 – -112.29 (m). HRMS (ESI) *m/z*: [M+Na]⁺ calculated for C₂₆H₁₆N₂O₄F₄Na⁺ 481.0970, found 481.0965. Melting point: 220 – 222 °C.

(*Z*)-1,2-bis(4-fluorophenyl)-1,2-bis(4-nitrophenyl)ethene (t-10-*Z*, new compound)

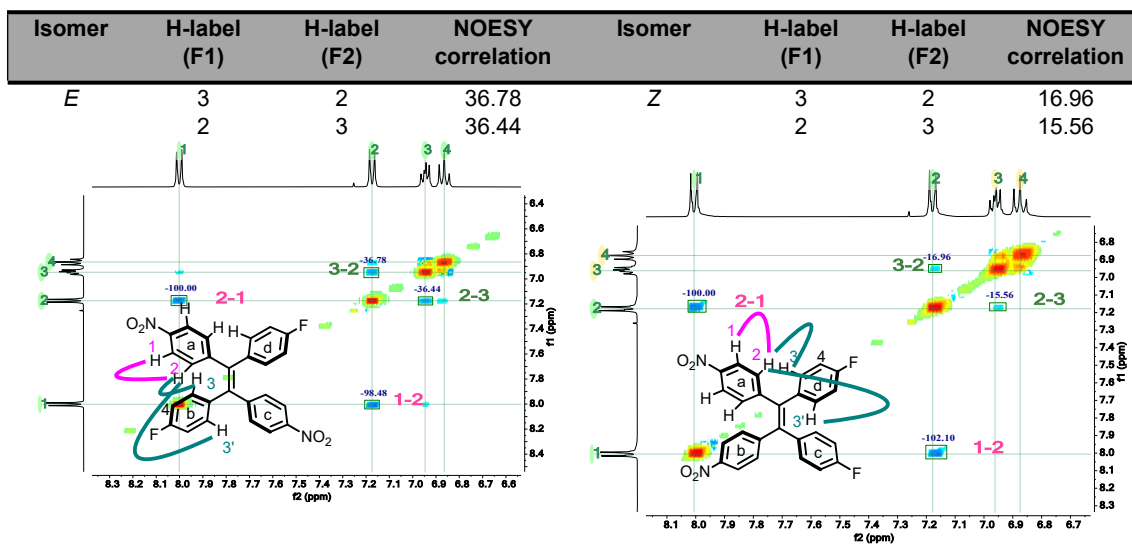


As a yellow solid (28.9 mg, 42% yield). $R_f = 0.3$, (eluent = dichloromethane/petroleum ether = 1/1) ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 8.8 Hz, 4H), 7.17 (d, *J* = 8.7 Hz, 4H), 6.96 (dd, *J* = 8.6, 5.5 Hz, 4H), 6.88 (t, *J* = 8.6 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 163.4, 160.9, 149.3, 146.8, 140.6, 137.5 (137.55), 137.5 (137.52), 132.9, 132.8, 132.0, 123.6, 115.7, 115.5. ¹⁹F NMR (376 MHz, CDCl₃) δ -112.59 – -112.69 (m). HRMS (ESI) *m/z*: [M+Na]⁺ calculated for C₂₆H₁₆N₂O₄F₄Na⁺ 481.0970, found 481.0967. Melting point: 239 – 242 °C.

Stacked ¹H NMR spectra of the *E* and *Z* isomer.



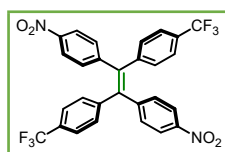
NOESY



1,2-bis(4-nitrophenyl)-1,2-bis(4-(trifluoromethyl)phenyl)ethene

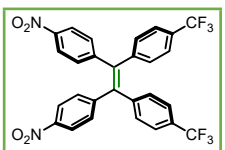
The reaction was conducted on 0.30 mmol scale according to the general procedure, heating the mixture of 1-nitro-4-(4-(trifluoromethyl)benzyl)benzene (84.4 mg, 0.30 mmol, 1.0 eq.), Cu(OPiv)₂ (199 mg, 0.75 mmol, 2.5 eq.), *t*-BuOK (84.0 mg, 0.75 mmol, 2.5 eq.), PivOK (105.0 mg, 0.75 mmol, 2.5 eq.) in HMPA (3 mL) under N₂ for 12 h. the title compound was purified by the prep-TLC, eluent = dichloromethane/petroleum ether = 1/1.

(*E*)-1,2-bis(4-nitrophenyl)-1,2-bis(4-(trifluoromethyl)phenyl)ethene (**t-11-E**, new compound)



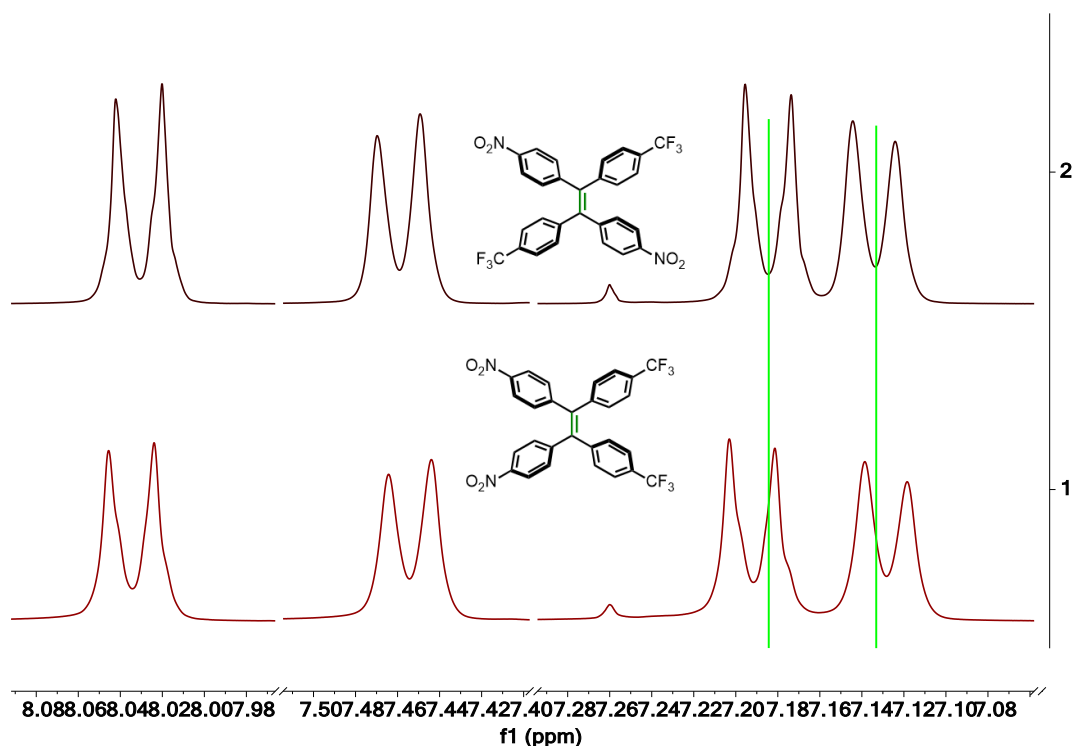
As a yellowish solid (38.5 mg, 45% yield). $R_f = 0.47$, eluent = dichloromethane/petroleum ether = 1 / 1. ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, $J = 8.8$ Hz, 4H), 7.46 (d, $J = 8.0$ Hz, 4H), 7.18 (d, $J = 8.8$ Hz, 4H), 7.13 (d, $J = 8.1$ Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 148.2, 147.0, 144.7, 141.4, 132.0, 131.4, 130.3 (q, $J = 32.7$ Hz), 125.7 (q, $J = 3.8$ Hz), 123.7 (132.79) (q, $J = 272.3$ Hz), 123.7 (132.72). ¹⁹F NMR (376 MHz, CDCl₃) δ -62.77. HRMS (ESI) m/z : [M+Na]⁺ calculated for C₂₈H₁₆N₂O₄F₆Na⁺ 581.0907, found 581.0902. **Melting point:** 192 -193 °C.

(*Z*)-1,2-bis(4-nitrophenyl)-1,2-bis(4-(trifluoromethyl)phenyl)ethene (**t-11-Z**, new compound)



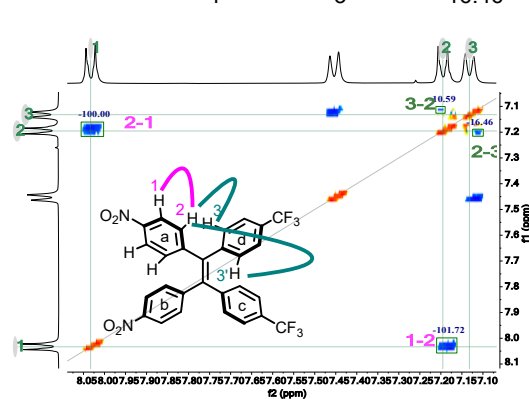
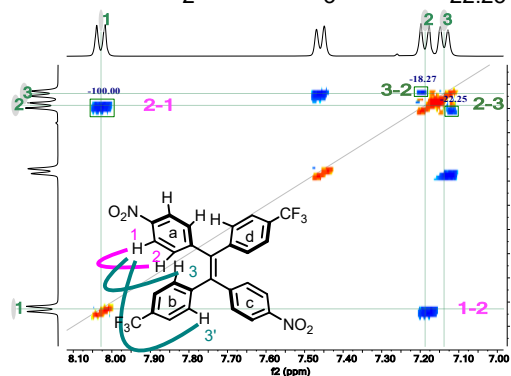
As a yellowish solid (40.0 mg, 47% yield). $R_f = 0.32$, eluent = dichloromethane/petroleum ether = 1 / 1. ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, $J = 8.8$ Hz, 4H), 7.45 (d, $J = 8.1$ Hz, 4H), 7.19 (d, $J = 8.6$ Hz, 4H), 7.13 (d, $J = 8.0$ Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 148.3, 147.1, 144.6, 141.4, 132.0, 131.4, 130.2 (q, $J = 32.7$ Hz), 125.6 (q, $J = 3.8$ Hz), 123.8 (132.84) (d, $J = 272.3$ Hz), 123.8 (132.82). ¹⁹F NMR (376 MHz, CDCl₃) δ -62.77. HRMS (ESI) m/z : [M+Na]⁺ calculated for C₂₈H₁₆N₂O₄F₆Na⁺ 581.0907, found 581.0902. **Melting point:** 218 -221 °C.

Stacked 1H NMR spectra of the *E* and *Z* isomer.



NOESY

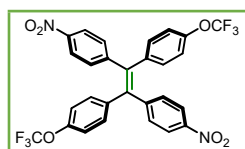
Isomer	H-label (F1)	H-label (F2)	NOESY correlation	Isomer	H-label (F1)	H-label (F2)	NOESY correlation
<i>E</i>	3	2	18.27	<i>Z</i>	3	2	10.59
	2	3	22.25		1	3	16.46



1,2-bis(4-nitrophenyl)-1,2-bis(4-(trifluoromethoxy)phenyl)ethene

The reaction was conducted on 0.30 mmol scale according to the general procedure, heating the mixture of 1-nitro-4-(4-(trifluoromethoxy)benzyl)benzene (89.2 mg, 0.30 mmol, 1.0 eq.), Cu(OPiv)₂ (199 mg, 0.75 mmol, 2.5 eq.), *t*-BuOK (84.0 mg, 0.75 mmol, 2.5 eq.), PivOK (105.0 mg, 0.75 mmol, 2.5 eq.) in HMPA (3 mL) under N₂ for 12 h. the title compound was purified by the PreTLC, eluent = dichloromethane/petroleum ether = 1 / 1.

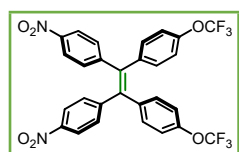
(*E*)-1,2-bis(4-nitrophenyl)-1,2-bis(4-(trifluoromethoxy)phenyl)ethene (*t*-12-*E*, new compound)



As a yellow solid (45.7 mg, 51% yield). R_f = 0.62, eluent = dichloromethane/petroleum ether = 1/1. ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, J = 8.8 Hz, 4H), 7.19 (d, J = 8.7 Hz, 4H), 7.07 – 6.98 (m, 8H). ¹³C NMR (101 MHz, CDCl₃) δ 148.9 (q, J = 1.8 Hz), 148.8, 146.9, 140.8, 139.7, 132.6, 132.0, 123.6,

121.7 (q, $J = 258.4$ Hz), 120.9. ^{19}F NMR (376 MHz, CDCl_3) δ -57.84. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{28}\text{H}_{16}\text{N}_2\text{O}_6\text{F}_6\text{Na}^+$ 613.0805, found 613.0808. Melting point: 129 – 130 °C.

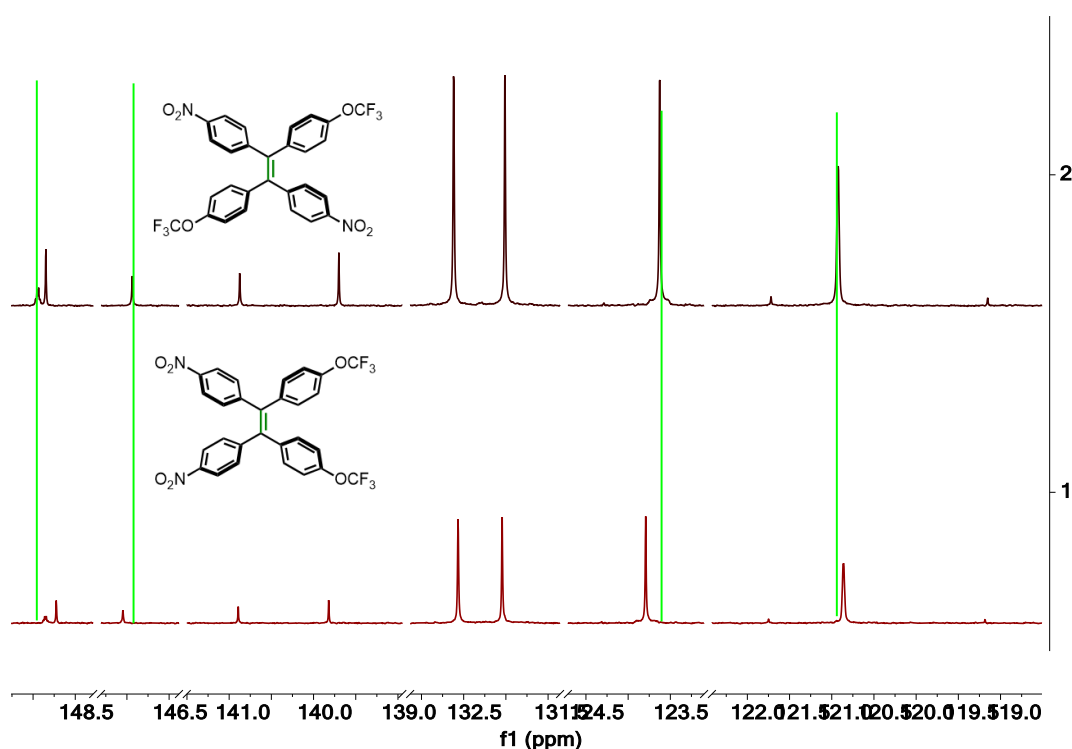
(Z)-1,2-bis(4-nitrophenyl)-1,2-bis(4-(trifluoromethoxy)phenyl)ethene (t-12-Z, new compound)



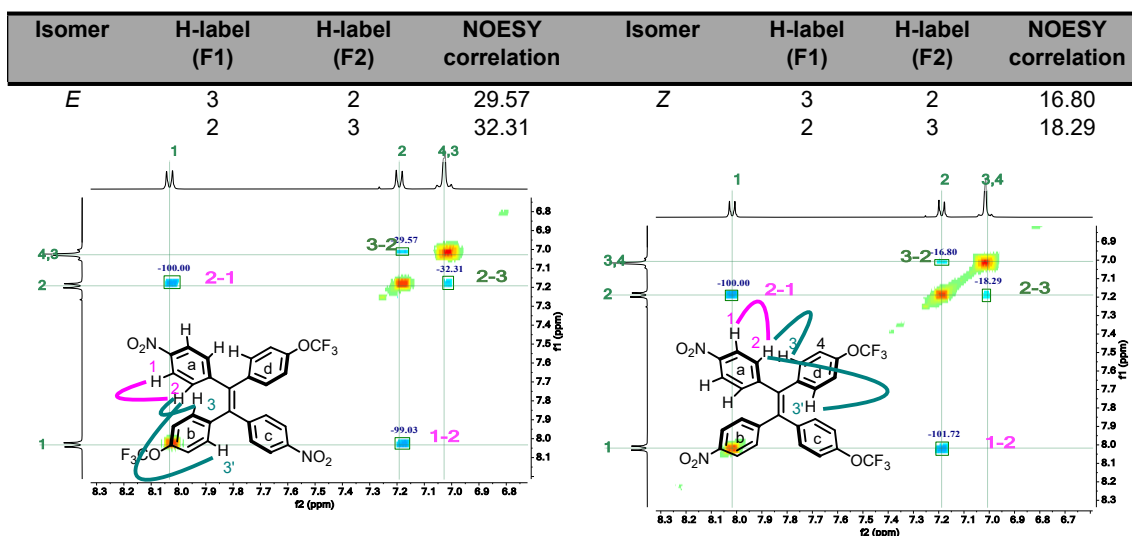
As a yellow solid (38.4 mg, 43% yield). $R_f = 0.45$, eluent = dichloromethane/petroleum ether = 1/1. ^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, $J = 8.8$ Hz, 4H), 7.19 (d, $J = 8.8$ Hz, 4H), 7.06 – 6.98 (m, 8H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.8 (q, $J = 1.8$ Hz), 148.7, 147.0, 139.8, 132.5, 132.0, 123.7, 120.8, 120.4 (d, $J = 258.1$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -57.91. HRMS (ESI) m/z :

$[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{28}\text{H}_{16}\text{N}_2\text{O}_6\text{F}_6\text{Na}^+$ 613.0805, found 613.0804. Melting point: 118 - 120 °C.

Stacked ^{13}C NMR spectra of the *E* and *Z* isomer.



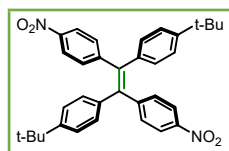
NOESY



1,2-bis(4-(tert-butyl)phenyl)-1,2-bis(4-nitrophenyl)ethene

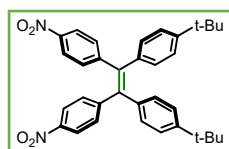
The reaction was conducted on 0.30 mmol scale according to the general procedure, heating the mixture of 1-(tert-butyl)-4-(4-nitrobenzyl)benzene (80.8 mg, 0.30 mmol, 1.0 eq.), Cu(OPiv)₂ (199 mg, 0.75 mmol, 2.5 eq.), *t*-BuOK (84.0 mg, 0.75 mmol, 2.5 eq.), PivOK (105.0 mg, 0.75 mmol, 2.5 eq.) in HMPA (3.0 mL) under N₂ for 12 h. the title compound was purified by the prep-TLC, eluent = dichloromethane/petroleum ether = 1 / 1.

(*E*)-1,2-bis(4-(tert-butyl)phenyl)-1,2-bis(4-nitrophenyl)ethene (t-13-*E*, new compound)



As a yellow solid (49.3 mg, 61% yield). $R_f = 0.7$, ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, $J = 8.8$ Hz, 4H), 7.18 (d, $J = 8.8$ Hz, 4H), 7.15 (d, $J = 8.4$ Hz, 4H), 6.86 (d, $J = 8.4$ Hz, 4H), 1.26 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 151.2, 150.5, 146.3, 141.1, 138.6, 132.1, 130.9, 125.4, 123.1, 34.7, 31.3. HRMS (ESI) m/z : [M+Na]⁺ calculated for C₃₄H₃₄N₂O₄Na⁺ 557.2411, found 557.2416. Melting point: 225 – 226 °C.

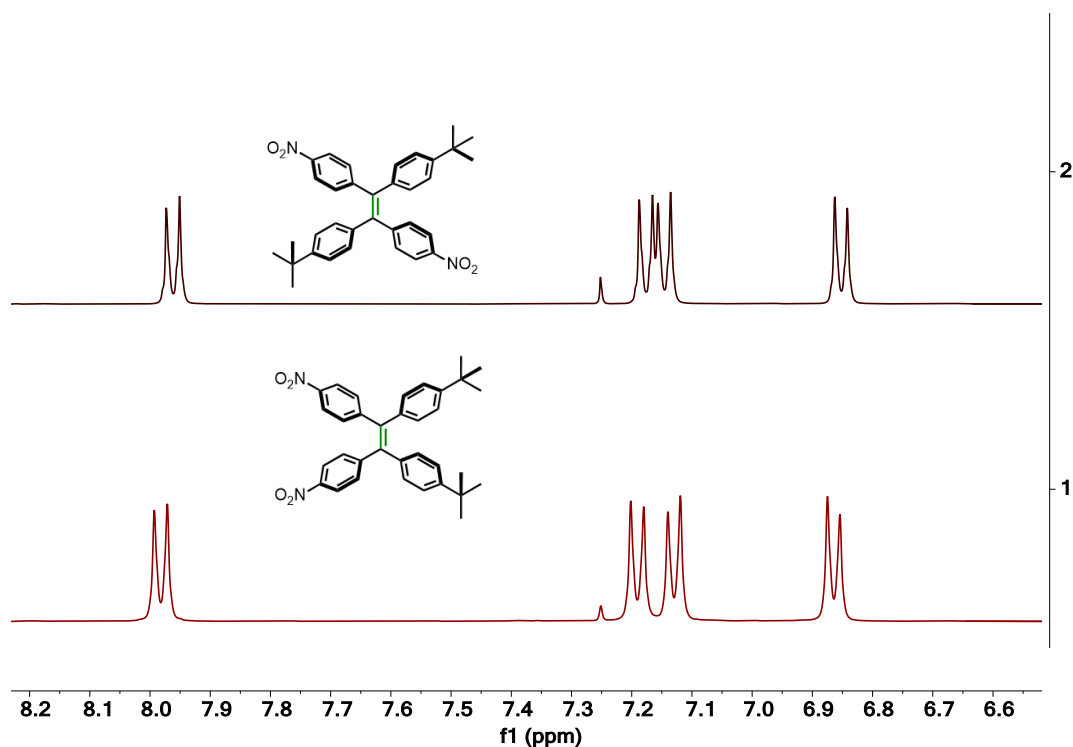
(*Z*)-1,2-bis(4-(tert-butyl)phenyl)-1,2-bis(4-nitrophenyl)ethene (t-13-*Z*, new compound)



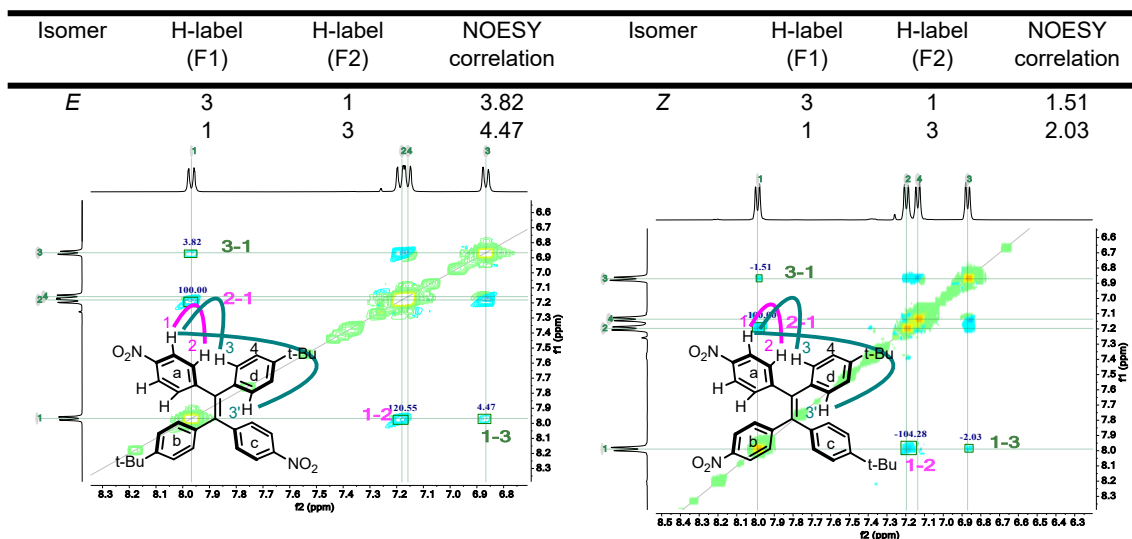
As a yellow solid (29.0 mg, 36% yield), $R_f = 0.53$, ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, $J = 8.5$ Hz, 4H), 7.20 (d, $J = 8.5$ Hz, 4H), 7.14 (d, $J = 8.2$ Hz, 4H), 6.87 (d, $J = 8.3$ Hz, 4H), 1.26 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 150.8, 150.2, 146.5, 141.1, 138.8, 132.2, 130.8, 125.0, 123.4, 34.6, 31.3. HRMS (ESI) m/z : [M+Na]⁺ calculated for C₃₄H₃₄N₂O₄Na⁺ 557.2411, found 557.2417. Melting point: 218 - 220 °C.

°C.

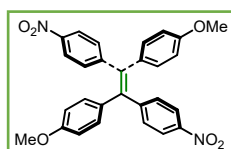
Stacked 1H NMR spectra of the *E* and *Z* isomer.



NOESY

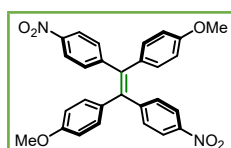


1,2-bis(4-methoxyphenyl)-1,2-bis(4-nitrophenyl)ethene (t-14, as mixture of *E/Z* isomer, new compound)



The reaction was conducted on 0.15 mmol scale according to the general procedure, heating the mixture of 1-methoxy-4-(4-nitrobenzyl)benzene (36.5 mg, 0.15 mmol, 1.0 eq.), Cu(OPiv)₂ (99.0 mg, 0.37 mmol, 2.5 eq.), *t*-BuOK (43.0 mg, 0.37 mmol, 2.5 eq.), PivOK (52.0 mg, 0.37 mmol, 2.5 eq.) in HMPA (1.5 mL) under N₂ for 12 h. the title compound was purified by the prep-TLC, (eluent = dichloromethane/petroleum ether = 1/1), affording the title compound as the inseparable mixture of *E* and *Z* isomer (34.7 mg, 95% yield), During our gram preparation, the pure *E* isomer was successfully isolated as a yellow crystalline and characterized by NMR and single crystallography independently, but the isolation of pure *Z* isomer failed. **¹H NMR (400 MHz, CDCl₃)** δ 7.98 (dd, *J* = 8.9, 2.6 Hz, 2H), 7.23 – 7.14 (m, 2H), 6.93 – 6.84 (m, 2H), 6.73 – 6.65 (m, 2H), 3.78 – 3.74 (m, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 159.2, 159.0, 150.6, 150.4, 146.5, 146.3, 140.4, 140.2, 134.4, 134.0, 132.6, 132.5, 132.2, 132.1, 123.4, 123.2, 113.9, 113.7, 55.3.

(*E*)-1,2-bis(4-methoxyphenyl)-1,2-bis(4-nitrophenyl)ethene (t-14-*E*, new compound)

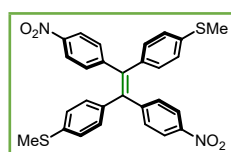


As a yellow crystalline, **¹H NMR (400 MHz, CDCl₃)** δ 7.98 (d, *J* = 8.8 Hz, 4H), 7.20 (d, *J* = 8.8 Hz, 4H), 6.87 (d, *J* = 8.8 Hz, 4H), 6.68 (d, *J* = 8.8 Hz, 4H), 3.76 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 159.2, 150.6, 146.3, 140.4, 134.0, 132.6, 132.1, 123.2, 113.9, 55.3. **HRMS (ESI) m/z:** [M+Na]⁺ calculated for C₂₈H₂₂N₂O₆Na⁺ 505.1370, found 505.1371. **Melting point:** 215 - 217°C.

1,2-bis(4-nitrophenyl)-1,2-bis(4-methylthiophenyl)ethene

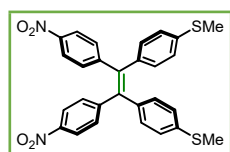
The reaction was conducted on 0.30 mmol scale according to the general procedure. Heating the mixture of methyl(4-(4-nitrobenzyl)phenyl)sulfane (77.8 mg, 0.30 mmol, 1.0 eq.), Cu(OPiv)₂ (199.0 mg, 0.75 mmol, 2.5 eq.), *t*-BuOK (84.0 mg, 0.75 mmol, 2.5 eq.), PivOK (105.0 mg, 0.75 mmol, 2.5 eq.) in HMPA (3 mL) under N₂ for 12 h. the title compound was eventually purified by the prep-TLC, eluent = dichloromethane/petroleum ether = 1.5/1.0.

(*E*)-1,2-bis(4-nitrophenyl)-1,2-bis(4-methylthiophenyl)ethene (t-15-*E*, new compound)



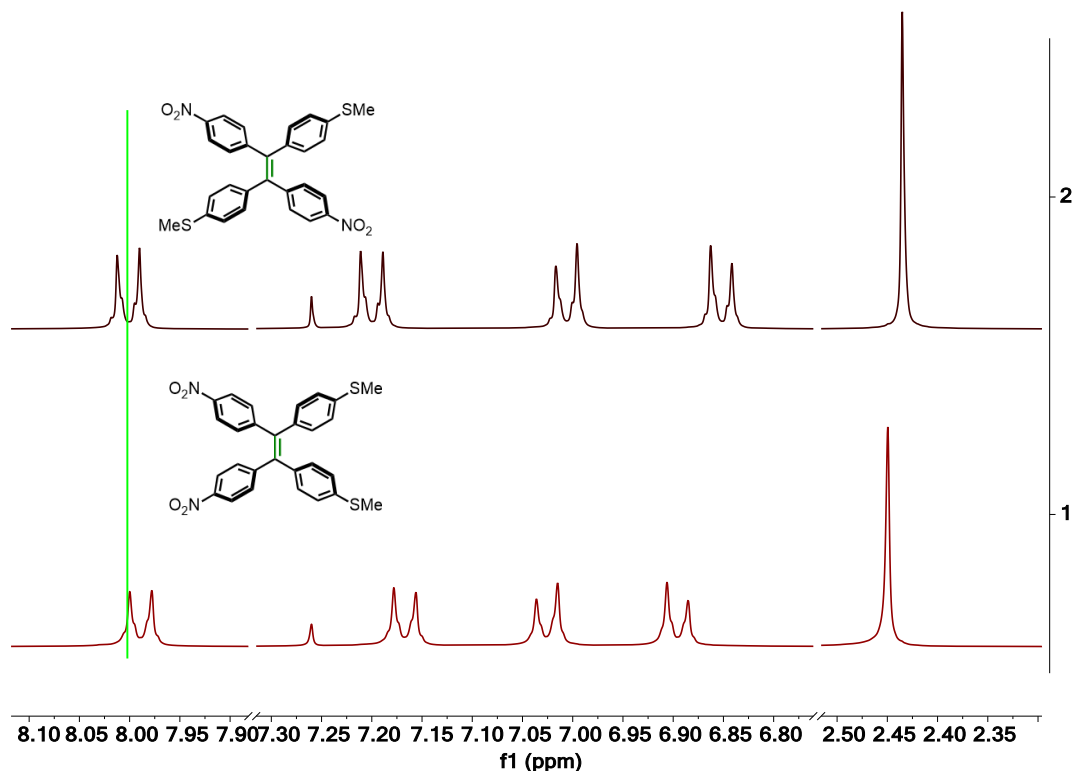
The title compound was isolated as a yellow powder (47.1 mg, 61% yield). **R_f** = 0.38 eluent = dichloromethane/petroleum ether = 1/1). **¹H NMR (400 MHz, CDCl₃)** δ 8.00 (d, *J* = 8.8 Hz, 4H), 7.20 (d, *J* = 8.8 Hz, 4H), 7.01 (d, *J* = 8.5 Hz, 4H), 6.85 (d, *J* = 8.5 Hz, 4H), 2.44 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 149.9, 146.5, 140.8, 139.2, 137.9, 132.1, 131.6, 125.8, 123.4, 15.2. **HRMS (ESI) m/z:** [M+Na]⁺ calculated for C₂₈H₂₂N₂O₄S₂Na⁺ 537.0913, found 537.0903. **HRMS (ESI) m/z:** [M+Na]⁺ calculated for C₂₈H₂₂N₂O₄S₂Na⁺ 537.0913, found 537.0912. **Melting point:** 185 - 187 °C.

(Z)-1,2-bis(4-nitrophenyl)-1,2-bis(4-methylthiophenyl)ethene (t-15-Z, new compound)



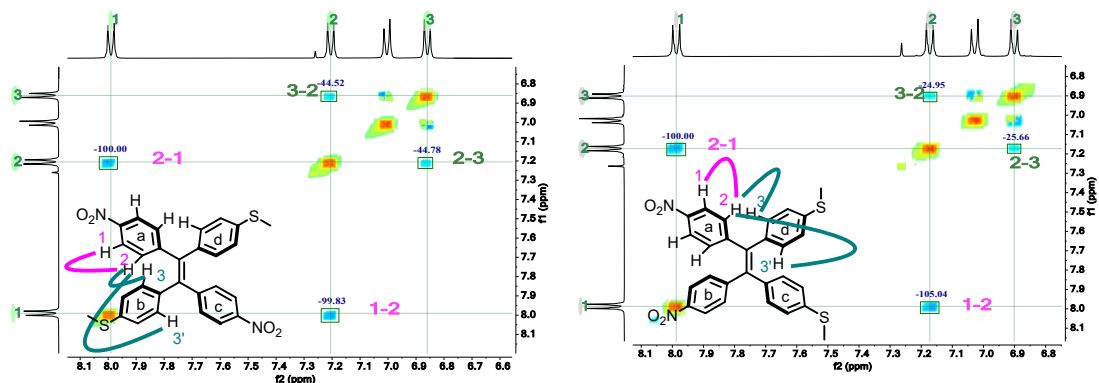
The title compound was isolated as a yellow foamy solid (28.2 mg, 36% yield), $R_f = 0.33$, eluent = dichloromethane/petroleum ether = 1/1). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.99 (d, $J = 8.8$ Hz, 4H), 7.17 (d, $J = 8.8$ Hz, 4H), 7.03 (d, $J = 8.5$ Hz, 4H), 6.90 (d, $J = 8.5$ Hz, 4H), 2.45 (s, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 149.8, 146.7, 140.7, 138.8, 138.1, 132.2, 131.5, 125.7, 123.5, 15.2. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}_4\text{S}_2\text{Na}^+$ 537.0913, found 537.0907. Melting point: 218 - 221 °C.

Stacked $^1\text{H NMR}$ spectra of the *E* and *Z* isomer.



NOESY

Isomer	H-label (F1)	H-label (F2)	NOESY correlation	Isomer	H-label (F1)	H-label (F2)	NOESY correlation
<i>E</i>	3	2	44.52	<i>Z</i>	3	2	24.95
	2	3	44.78		2	3	25.66

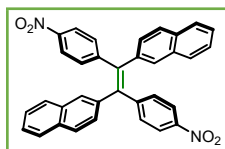


1,2-di(naphthalen-2-yl)-1,2-bis(4-nitrophenyl)ethene

The reaction was conducted on 0.30 mmol scale according to the general procedure, heating the mixture of 2-(4-nitrobenzyl)naphthalene (79.0 mg, 0.30 mmol, 1.0 eq.), $\text{Cu}(\text{O}i\text{Pr})_2$ (199 mg, 0.75 mmol, 2.5 eq.), *t*-BuOK

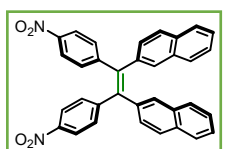
(84.0 mg, 0.75 mmol, 2.5 eq.), PivOK (105.0 mg, 0.75 mmol, 2.5 eq.) in HMPA (3 mL) under N₂ for 12 h. the title compound was purified by the prep-TLC, eluent = dichloromethane/petroleum ether = 1 / 1.

(E)-1,2-di(naphthalen-2-yl)-1,2-bis(4-nitrophenyl)ethene (t-16-E, new compound)



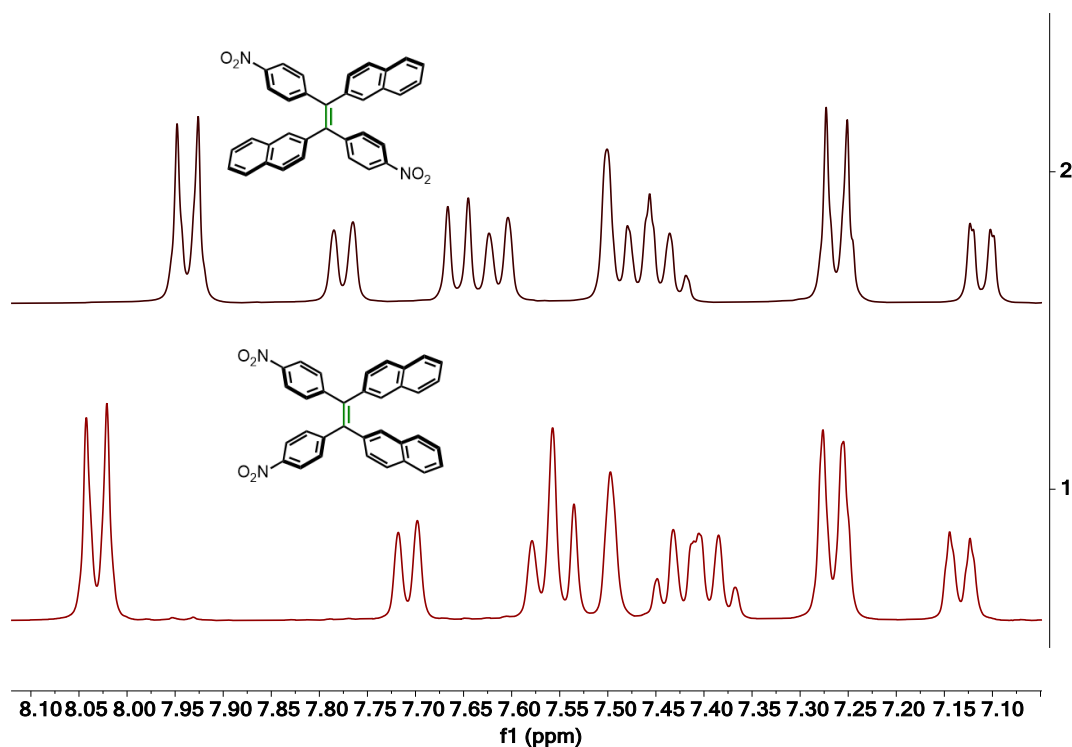
As a yellowish powder (50.2 mg 64% yield). R_f = 0.52 (eluent = dichloromethane/petroleum ether = 1 / 1, analysis TLC plate), **¹H NMR (400 MHz, CDCl₃)** δ 7.94 (d, J = 8.7 Hz, 4H), 7.78 (d, J = 7.9 Hz, 2H), 7.66 (d, J = 8.5 Hz, 2H), 7.61 (d, J = 7.8 Hz, 2H), 7.52 – 7.40 (m, 6H), 7.26 (d, J = 8.7 Hz, 4H), 7.11 (d, J = 8.5 Hz, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 149.9, 146.5, 141.9, 139.1, 133.1, 132.6, 132.3, 130.9, 128.6, 128.3, 128.1, 127.8, 126.9, 126.7, 123.4. **HRMS (ESI)** m/z : [M+Na]⁺ calculated for C₃₄H₂₂N₂O₄Na⁺ 545.1472, found 525.1472. **Melting point:** 244 - 245 °C.

(Z)-1,2-di(naphthalen-2-yl)-1,2-bis(4-nitrophenyl)ethene (t-16-Z, new compound)

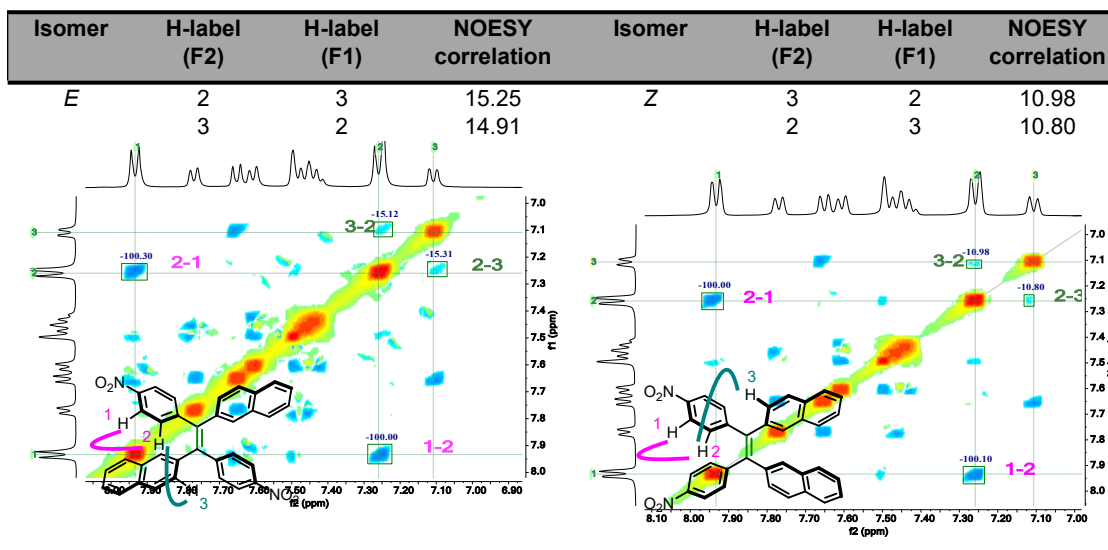


As a yellow foamy solid (27.0 mg, 34% yield). R_f = 0.42, eluent = dichloromethane/petroleum ether = 1 / 1. **¹H NMR (400 MHz, CDCl₃)** δ 8.03 (d, J = 8.5 Hz, 4H), 7.71 (d, J = 8.0 Hz, 2H), 7.59 – 7.52 (m, 4H), 7.50 (s, 2H), 7.47 – 7.34 (m, 4H), 7.27 (d, J = 8.4 Hz, 4H), 7.13 (d, J = 8.5 Hz, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 150.1, 146.7, 141.7, 139.2, 133.1, 132.6, 132.3, 130.9, 128.7, 128.2, 127.9, 127.7, 126.7, 126.4, 123.6. **HRMS (ESI)** m/z : [M+Na]⁺ calculated for C₃₄H₂₂N₂O₄Na⁺ 545.1472, found 545.1474. **Melting point:** 156 - 157 °C.

Stacked 1H NMR spectra.



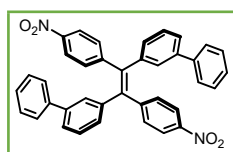
NOESY



1,2-di([1,1'-biphenyl]-3-yl)-1,2-bis(4-nitrophenyl)ethene

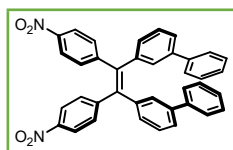
The reaction was conducted on 0.30 mmol scale according to the general procedure, heating the mixture of 3-(4-nitrobenzyl)-1,1'-biphenyl (86.8 mg, 0.30 mmol, 1.0 eq.), Cu(OPiv)₂ (199 mg, 0.75 mmol, 2.5 eq.), *t*-BuOK (84.0 mg, 0.75 mmol, 2.5 eq.), PivOK (105.0 mg, 0.75 mmol, 2.5 eq.) in HMPA (3 mL) under N₂ for 12 h. the title compound was purified by the prep-TLC, eluent = dichloromethane/petroleum ether = 1.5 / 1.0.

(*E*)-1,2-di([1,1'-biphenyl]-3-yl)-1,2-bis(4-nitrophenyl)ethene (t-17-*E*, new compound)



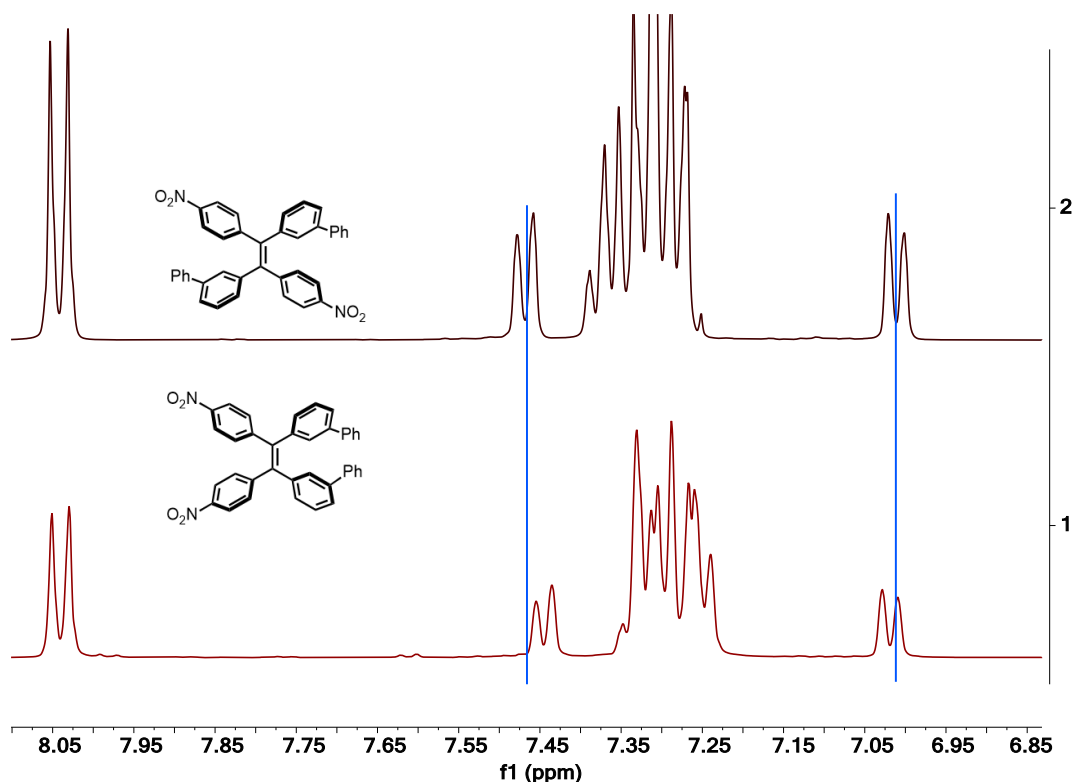
As a yellow solid (50.0 mg, 58% yield). R_f = 0.60, eluent = dichloromethane/petroleum ether = 1/1. ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 8.8 Hz, 4H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.27 (m, 18H), 7.02 (d, *J* = 8.0 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 149.8, 146.6, 141.8 (141.89), 141.8 (141.82), 141.6, 140.3, 132.1, 130.0 (130.07), 130.0 (130.06), 129.1, 128.9, 127.7, 127.0, 126.9, 123.3. HRMS (ESI) *m/z*: [M+Na]⁺ calculated for C₃₈H₂₆N₂O₄Na⁺ 597.1785, found 597.1783. Melting point: 199 - 200 °C

(*Z*)-1,2-di([1,1'-biphenyl]-3-yl)-1,2-bis(4-nitrophenyl)ethene (t-17-*Z*, new compound)

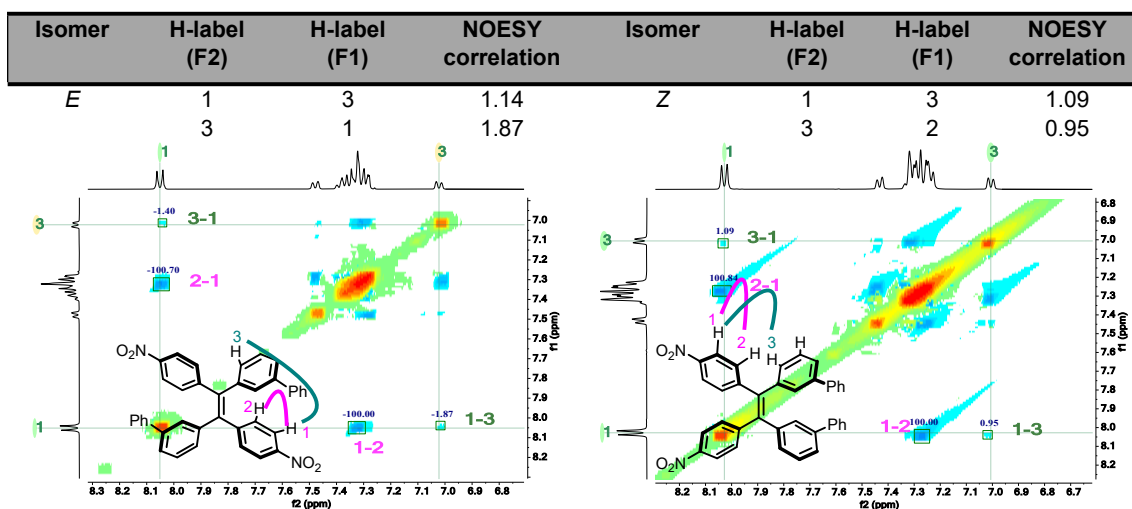


As a yellow solid (33.6 mg, 38% yield). R_f = 0.46, eluent = dichloromethane/petroleum ether = 1/1. ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J* = 8.4 Hz, 4H), 7.43 (d, *J* = 7.7 Hz, 2H), 7.35 – 7.20 (m, 19H, overlap with chloroform signal), 7.01 (d, *J* = 7.7 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 149.4, 146.8, 142.2, 141.8, 141.5, 140.6, 132.1, 130.4, 129.9, 128.9, 128.8, 127.6, 127.1, 126.7, 123.6. HRMS (ESI) *m/z*: [M+Na]⁺ calculated for C₃₈H₂₆N₂O₄Na⁺ 597.1785, found 597.1781. Melting point: 111-113 °C.

Stacked 1H NMR spectra.



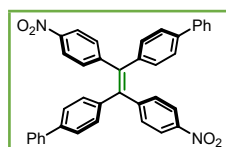
NOESY



1,2-bis(4-nitrophenyl)-1,2-bisphenylethane

The reaction was conducted on 0.30 mmol scale according to the general procedure, heating the mixture of 4-(4-nitrobenzyl)-1,1'-biphenyl (86.8 mg, 0.30 mmol, 1.0 eq.), Cu(OPiv)₂ (199 mg, 0.75 mmol, 2.5 eq.), *t*-BuOK (84.0 mg, 0.75 mmol, 2.5 eq.), PivOK (105.0 mg, 0.75 mmol, 2.5 eq.) in HMPA (3 mL) under N₂ for 12 h. the title compound was purified by the prep-TLC, eluent = dichloromethane/petroleum ether = 1.5/1.0.

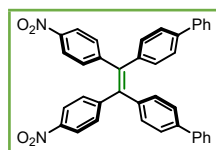
(*E*)-1,2-bis(4-nitrophenyl)-1,2-bisphenylethane (*t*-18-*E*, new compound)



As a yellow solid (53.0 mg, 61% yield), $R_f = 0.57$, eluent = dichloromethane/petroleum ether = 1.5/1.0. ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, $J = 8.6$ Hz, 4H), 7.56 (d, $J = 7.5$ Hz, 4H), 7.47 – 7.40 (m, 8H), 7.35 (t, $J = 7.2$ Hz, 2H), 7.29 (d, $J = 8.6$ Hz, 4H), 7.06 (d, $J = 8.1$ Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ

150.0, 146.6, 141.3, 140.7, 140.5, 140.0, 132.2, 131.7, 129.0, 127.8, 127.1, 127.0, 123.4. **HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{38}H_{26}N_2O_4Na^+$ 597.1785, found 597.1789. **Melting point:** 265 – 269 °C.

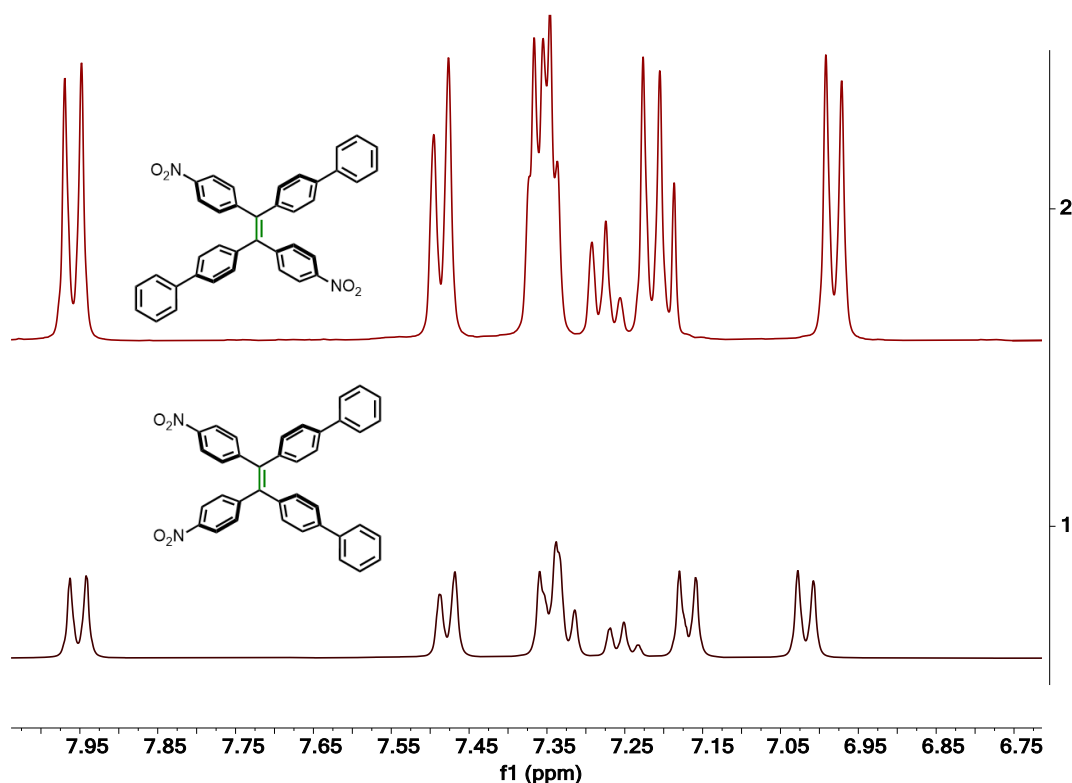
(E)-1,2-bis(4-nitrophenyl)-1,2-bisphenylethene (t-18-Z, new compound)



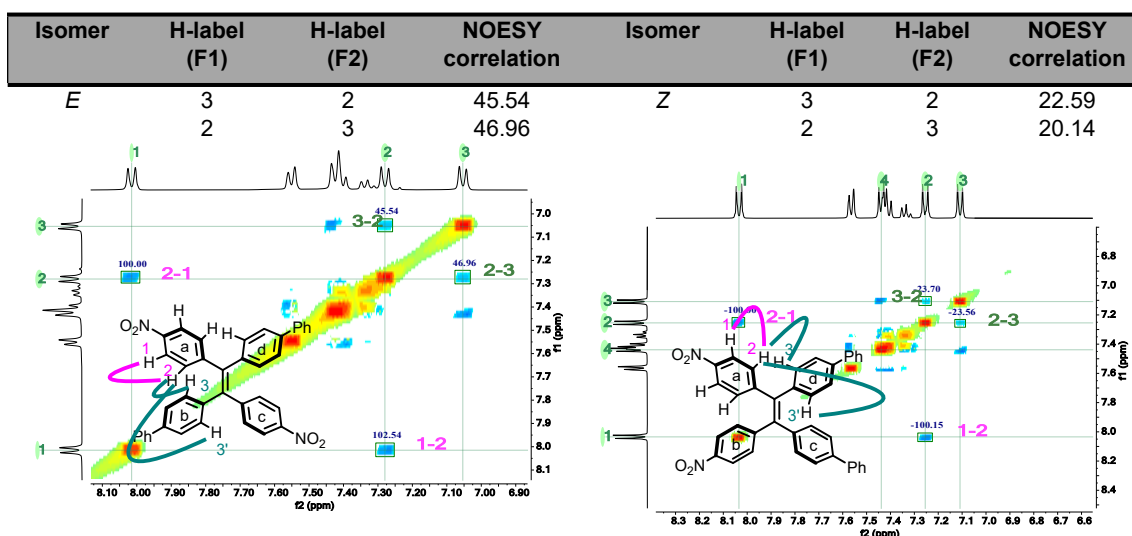
As a yellow solid (31.9 mg, 37% yield), $R_f = 0.35$, eluent = dichloromethane/petroleum ether = 1.5/1.0. 1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, $J = 8.4$ Hz, 4H), 7.48 (d, $J = 7.7$ Hz, 4H), 7.38 – 7.30 (m, 8H), 7.25 (t, $J = 7.1$ Hz, 2H), 7.17 (d, $J = 8.3$ Hz, 4H), 7.02 (d, $J = 7.9$ Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 146.7, 141.1, 140.7, 140.4, 140.1, 132.2, 131.7, 128.9, 127.7, 127.0, 126.9, 123.5.

HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{38}H_{26}N_2O_4Na^+$ 597.1785, found 597.1784. **Melting point:** 120 – 125 °C.

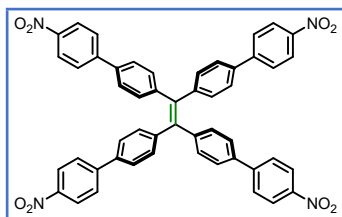
Stacked 1H NMR spectra.



NOESY



1,1,2-tetrakis(4'-nitro-[1,1'-biphenyl]-4-yl)ethene (t-19, known compound, 2177279-46-6)



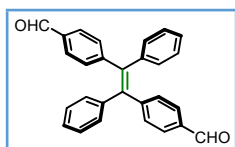
The reaction was conducted on 0.30 mmol scale according to the general procedure but at 140°C. Under N₂, stirring the mixture of bis(4'-nitro-[1,1'-biphenyl]-4-yl)methane (123.1 mg, 0.30 mmol, 1.0 eq.), Cu(OPiv)₂ (199 mg, 0.75 mmol, 2.5 eq.), *t*-BuOK (84.0 mg, 0.75 mmol, 2.5 eq.), PivOK (105.0 mg, 0.75 mmol, 2.5 eq.) in HMPA (3 mL) at 140 °C for 12 h. the title compound was purified by the prep-TLC affording the title compound (102.7 mg, 83% yield) as yellow powder. eluent = dichloromethane/petroleum ether = 3.0 /1.0. **¹H NMR (400 MHz, CDCl₃)** δ 8.27 (d, *J* = 8.8 Hz, 8H), 7.71 (d, *J* = 8.9 Hz, 8H), 7.47 (d, *J* = 8.4 Hz, 8H), 7.24 (d, *J* = 8.4 Hz, 8H). **¹³C NMR (101 MHz, CDCl₃)** δ 147.2, 146.8, 143.9, 140.9, 137.3, 132.3, 127.6, 127.1, 124.2.

The characterization data conforms with the literature well.^[35]

4,4'-(1,2-diphenylethene-1,2-diyl)dibenzaldehyde

The reaction was conducted on 0.30 mmol scale according to the general procedure, heating the mixture of 4-benzylbenzaldehyde (65.4 mg, 0.33 mmol, 1.0 eq.), Cu(OPiv)₂ (219 mg, 0.82 mmol, 2.5 eq.), *t*-ArmyLOK (104.0 mg, 0.82 mmol, 2.5 eq.), PivOK (116.0 mg, 0.82 mmol, 2.5 eq.) in HMPA (3 mL) under N₂ for 12 h. the title compound was purified by the prep-TLC, eluent = dichloromethane/petroleum ether = 3/1.

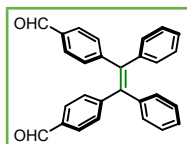
(*E*)-4,4'-(1,2-diphenylethene-1,2-diyl)dibenzaldehyde (t-20-*E*, known compound, 2181790-84-9)



As a colorless solid (25.3 mg, 43% yield), *R*_f = 0.32, eluent = dichloromethane/petroleum ether = 3/1. **¹H NMR (400 MHz, CDCl₃)** δ 9.91 (s, 2H), 7.63 (d, *J* = 8.2 Hz, 4H), 7.20 (d, *J* = 8.1 Hz, 4H), 7.18 – 7.10 (m, 6H), 7.04 – 6.97 (m, 4H). **¹³C NMR (101 MHz, CDCl₃)** δ 191.9, 149.8, 142.2, 141.8, 134.7, 131.9, 131.3, 129.3, 128.3, 127.5.

The characterization data conforms with the literature well.^[36]

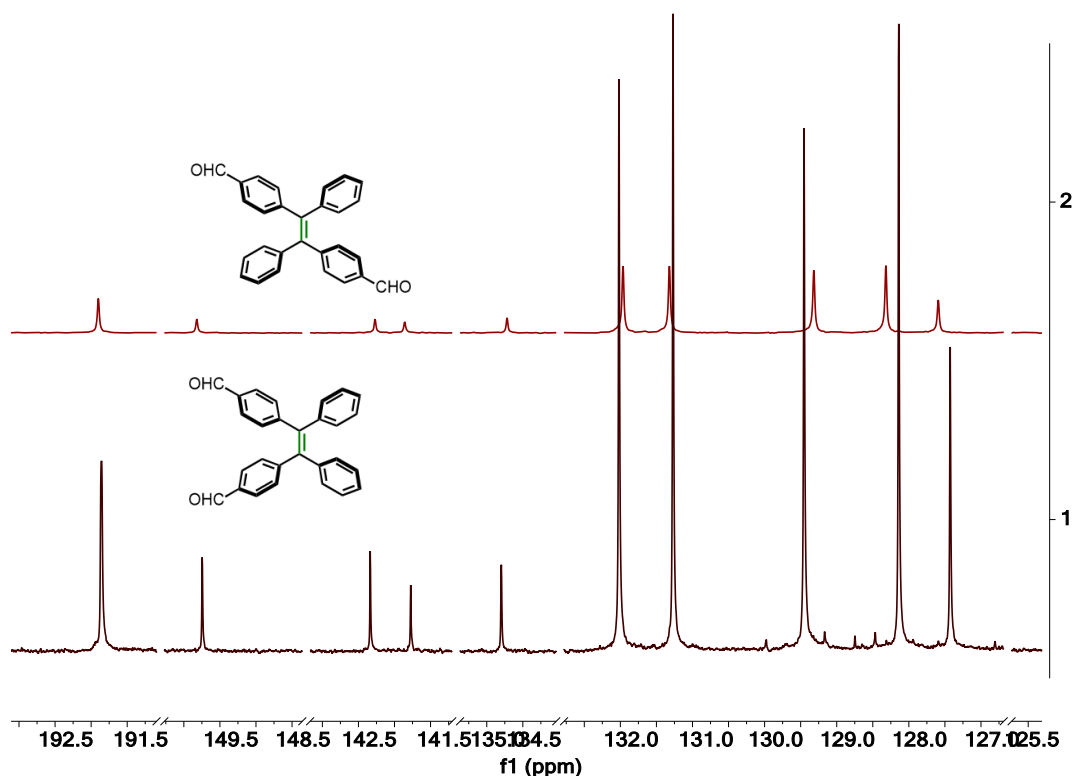
(*Z*)-4,4'-(1,2-diphenylethene-1,2-diyl)dibenzaldehyde (t-20-*Z*, new compound, 1421321-70-1)



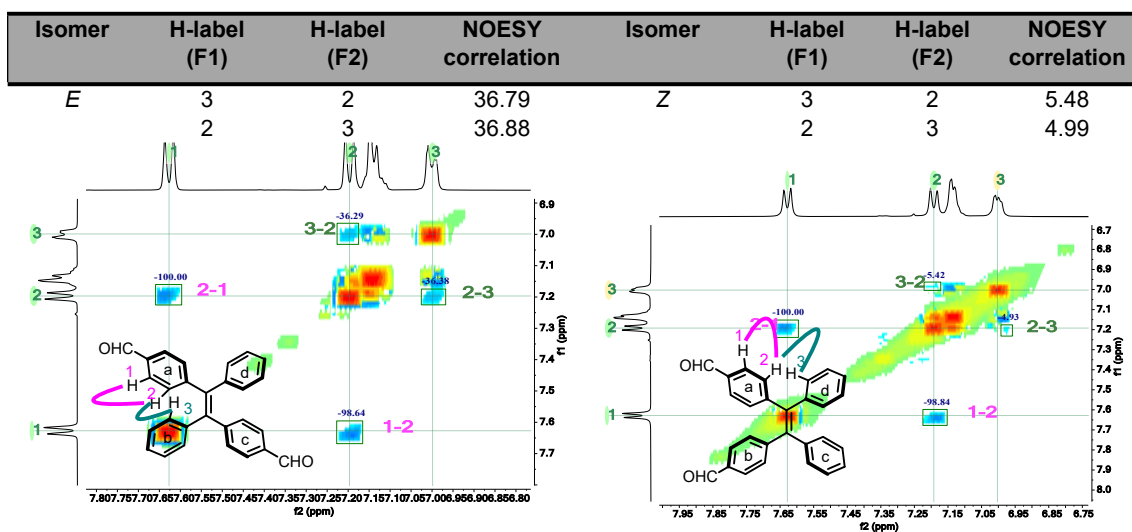
As a colorless solid (16.1 mg, 27% yield), *R*_f = 0.16, eluent = dichloromethane/petroleum ether = 3/1, **¹H NMR (400 MHz, CDCl₃)** δ 9.91 (s, 2H), 7.64 (d, *J* = 7.8 Hz, 4H), 7.20 (d, *J* = 7.9 Hz, 4H), 7.17 – 7.09 (m, 6H), 7.05 – 6.97 (m, 4H). **¹³C NMR (101 MHz, CDCl₃)** δ 191.8, 149.7, 142.3, 141.7, 134.8, 132.0, 131.2, 129.4, 128.1, 127.4. **HRMS (ESI) *m/z***: [M+H]⁺ calculated for C₂₈H₂₀O₂⁺ 389.1536, found 389.1531.

Melting point: 160 - 163°C.

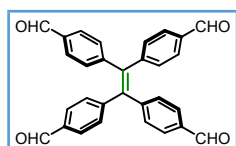
Stacked ¹H NMR spectra of the *E* and *Z* isomer.



NOESY



4,4',4''-(ethene-1,1,2,2-tetrayl)tetrabenzaldehyde (t-21, known compound, 2170451-48-4)



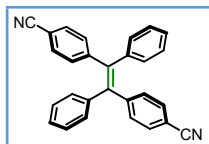
The reaction was conducted on 0.30 mmol scale according to the general procedure, heating the mixture of 4,4'-methylenedibenzaldehyde (67.3 mg, 0.30 mmol, 1.0 eq.), Cu(OPiv)₂ (199 mg, 0.75 mmol, 2.5 eq.), *t*-BuOK (84.0 mg, 0.75 mmol, 2.5 eq.), PivOK (105.0 mg, 0.75 mmol, 2.5 eq.) in HMPA (3 mL) under N₂ for 12 h. the title compound was purified by the prep-TLC, as a yellowish powder (45.0 mg, 67%), *R*_f = 0.2, eluent = ethyl acetate/dichloromethane = 1.0 /100.0. ¹H NMR (400 MHz, CDCl₃) δ 9.96 – 9.90 (m, 4H), 7.67 (d, *J* = 8.3 Hz, 8H), 7.18 (d, *J* = 8.1 Hz, 8H). ¹³C NMR (101 MHz, CDCl₃) δ 191.6, 148.0, 142.2, 135.3, 131.8, 129.7.

Characterization data conforms with those reported well.^[37]

4,4'-(1,2-diphenylethene-1,2-diyl)dibenzonitrile

The reaction was conducted on 0.30 mmol scale with a modified procedure. Heating the mixture of 4-benzylbenzonitrile (58.0 mg, 0.30 mmol, 1.0 eq.), Cu(OPiv)₂ (199 mg, 0.75 mmol, 2.5 eq.), *t*-BuOK (84.0 mg, 0.75 mmol, 2.5 eq.), PivOK (105.0 mg, 0.75 mmol, 2.5 eq.) in HMPA (3 mL) at 160°C for 12 h. the title compound was purified by the prep-TLC, eluent = dichloromethane/petroleum ether = 1.5 /1.0.

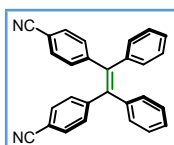
(*E*)-4,4'-(1,2-diphenylethene-1,2-diyl)dibenzonitrile (t-22-*E*, known compound, 2244891-05-0)



The title compound was isolated as a colorless solid (24.0 mg, 41% yield), $R_f = 0.28$ (eluent = dichloromethane/petroleum ether = 1.5/1.0). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.39 (d, $J = 8.5$ Hz, 4H), 7.20 – 7.09 (m, 10H), 6.99 – 6.93 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.9, 141.6, 141.5, 131.8, 131.7, 131.2, 128.4, 127.8, 118.8, 110.5.

Characterization data matched those previously reported.^[38]

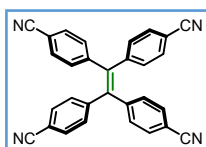
(*Z*)-4,4'-(1,2-diphenylethene-1,2-diyl)dibenzonitrile (t-22-*Z*, known compound, 78024-99-4)



The title compound was isolated as a colorless solid (16.3 mg, 28% yield), $R_f = 0.19$, (eluent = dichloromethane/petroleum ether = 1.5/1.0), $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.43 (d, $J = 8.4$ Hz, 4H), 7.17 – 7.08 (m, 10H), 6.99 – 6.94 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.8, 141.8, 141.4, 132.0, 131.9, 131.1, 128.2, 127.6, 118.7, 110.8.

Characterization data matched those previously reported.^[38]

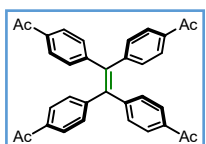
1,1,2,2-tetrakis(4-cyanophenyl)ethene (t-23, known compound, 78024-99-4)



The reaction was conducted on 0.30 mmol scale according to the general procedure, heating the mixture of 4,4'-methylenedibenzonitrile (65.5 mg, 0.30 mmol, 1.0 eq.), Cu(OPiv)₂ (199 mg, 0.75 mmol, 2.5 eq.), *t*-BuOK (67.3 mg, 0.60 mmol, 2.0 eq.), PivOK (84.0 mg, 0.60 mmol, 2.0 eq.) in HMPA (3 mL) under N₂ for 12 h. the title compound was purified by the prep-TLC, (eluent = ethyl acetate/dichloromethane = 1/150, $R_f = 0.39$) as a colorless solid (57.8 mg, 89% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.48 (d, $J = 8.2$ Hz, 8H), 7.07 (d, $J = 8.2$ Hz, 8H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 145.6, 141.6, 132.4, 131.7, 118.1, 112.1.

Characterization data conforms with those reported well.^[39]

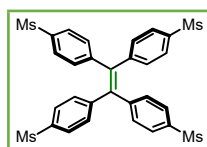
Tetrakis(4-acetylphenyl)ethylene (t-24, known compound, 4780-53-4)



The reaction was conducted on 0.30 mmol scale according to the general procedure, heating the mixture of 1,1'-(methylenebis(4,1-phenylene))bis(ethan-1-one) (75.7 mg, 0.30 mmol, 1.0 eq.), Cu(OPiv)₂ (279 mg, 1.05 mmol, 3.5 eq.), *t*-BuOK (117.8 mg, 1.05 mmol, 3.5 eq.), PivOK (147.2.0 mg, 1.05 mmol, 3.5 eq.) in HMPA (3 mL) under N₂ for 12 h. the title compound was purified by the prep-TLC as a colorless solid (25.4 mg, 33% yield). $R_f = 0.40$, eluent = ethyl acetate/dichloromethane = 1/15, $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.72 (d, $J = 8.4$ Hz, 8H), 7.08 (d, $J = 8.1$ Hz, 8H), 2.53 (s, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 197.6, 147.0, 141.7, 135.9, 131.4, 128.2, 26.6.

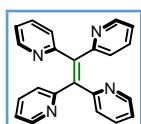
Characterization data conforms with those reported well.^[40]

1,1,2,2-tetrakis(4-(methylsulfonyl)phenyl)ethene (t-25, new compound)



According to the general procedure on 0.30 mmol scale, stirring mixture of bis(4-(methylsulfonyl)phenyl)methane (97.3 mg, 0.3 mmol, 1.0 eq.), Cu(OPiv)₂ (199 mg, 0.75 mmol, 2.5 eq.), *t*-amyLOK (95.0 mg, 0.75 mmol, 2.5 eq.) in HMPA (3 mL) under N₂ for 12 h, affording the title compound (47.4 mg, 49% yield) as a colorless solid after prep-TLC. $R_f = 0.4$ (eluent = methanol /dichloromethane = 1/ 25). $^1\text{H NMR}$ (400 MHz, CD_2Cl_2) δ 7.74 (d, $J = 8.1$ Hz, 8H), 7.23 (d, $J = 8.0$ Hz, 8H), 3.02 (s, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.1, 141.8, 140.4, 132.3, 127.8, 44.6. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{30}\text{H}_{28}\text{N}_4\text{O}_4\text{Na}^+$ 667.0559, found 667.0550. Melting point: >320°C.

Tetrakis(2-pyridyl)ethylene (t-26, known compound, 627533-39-5)

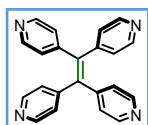


The reaction was conducted on 0.30 mmol scale with a little modification of the general procedure. Heating the mixture of di(pyridin-2-yl)methane (52.1 mg, 0.306 mmol, 1.0 eq.), Cu(OPiv)₂ (203.3 mg, 0.765 mmol, 2.5 eq.), *t*-BuOK (85.8 mg, 0.765 mmol, 2.5 eq.), PivOK (107.3 mg, 0.765 mmol, 2.5 eq.) in HMPA (3 mL) under N₂ for 12 h. After cooling to room

temperature, the reaction mixture was transferred to a 25 mL round bottom flask, and the HMPA was removed on high vacuum, after which ethyl acetate (50 ml), aqueous ammonium (5 mL) and brine (5 mL) was added to dissolve the crude and transferred to a separatory funnel, the blue aqueous layer was removed, the organic layer was sequentially washed with a mixture of ammonium and brine (v/v = 1/1, 10 mL, × 2) and brine (10 mL × 2), the volatile was removed on rotary evaporation, the remaining oil was dried on high vacuum to remove the few HMPA, the remaining solid was further purified by prep-TLC to afford the title compound as a colorless solid (45.9 mg, 89% yield). eluent = methanol/dichloromethane = 1/20, R_f = 0.39), $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.52 – 8.46 (m, 4H), 7.40 (td, J = 7.7, 1.8 Hz, 4H), 7.10 – 7.06 (m, 4H), 7.06 – 7.01 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 160.0, 149.4, 144.2, 135.9, 126.5, 121.9.

Characterization data conforms with those reported well.^[41]

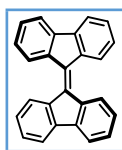
Tetrakis(4-pyridyl)ethylene (t-27, known compound, 2040295-11-0)



The reaction was conducted on 0.30 mmol scale with a little modification of the general procedure, heating the mixture of di(pyridin-4-yl)methane (50.9 mg, 0.30 mmol, 1.0 eq.), $\text{Cu}(\text{OPiv})_2$ (199.0 mg, 0.75 mmol, 2.5 eq.), $t\text{-BuOK}$ (84.0 mg, 0.75 mmol, 2.5 eq.), PivOK (105.0 mg, 0.75 mmol, 2.5 eq.) in HMPA (3 mL) under N_2 for 12 h. After cooling to the room temperature, the reaction mixture was transferred to a 25 mL round bottom flask, the HMPA was removed on high vacuum, after which ethyl acetate (50 mL), aqueous ammonium (5 mL) and brine (5 mL) was added to dissolve the crude and transferred to a separatory funnel, the blue aqueous layer was removed, the organic layer was sequentially washed with mixture of ammonium and brine (5 mL/5 mL, × 2) and brine (10 mL × 2), the volatile was removed on rotary evaporation, the remaining oil was dried on high vacuum to remove the few HMPA, the remaining solid was further purified by prep-TLC to afford the title compound as a colorless solid (40.0 mg, 79% yield). eluent = methanol/dichloromethane = 1/10, R_f = 0.30). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.45 (d, J = 6.1 Hz, 8H), 6.89 (d, J = 6.1 Hz, 8H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 150.2, 148.2, 140.2, 125.2.

Characterization data conforms with the literature well.^[42]

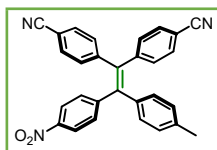
9,9'-bifluorenylidene (t-28, known compound, 746-47-4)



The reaction was conducted on 0.3 mmol scale with a little modification of the general procedure. Heating the mixture of 9H-fluorene (49.9 mg, 0.30 mmol, 1.0 eq.), $\text{Cu}(\text{OAc})_2$ (136 mg, 0.75 mmol, 2.5 eq.), K_3PO_4 (159 mg, 0.75 mmol, 2.5 eq.) and in DMAc (3 mL) at 120 °C for 12 h. after purification by silica gel chromatography, the title compound was obtained as orange solid (22.5 mg, 45% yield). R_f = 0.20, eluent = petroleum ether. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.39 (d, J = 7.9 Hz, 4H), 7.71 (d, J = 7.5 Hz, 4H), 7.33 (t, J = 7.4 Hz, 4H), 7.21 (t, J = 7.6 Hz, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 141.4, 141.1, 138.3, 129.2, 127.0, 126.8, 120.0.

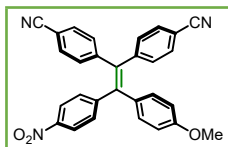
Characterization data conforms with the literature well.^[43]

4,4'-(2-(4-nitrophenyl)-2-(p-tolyl)ethene-1,1-diyl)dibenzonitrile (t-29, new compound)



Conducted on 0.15 mmol scale. Heating the mixture of 4,4'-methylene dibenzonitrile (32.7 mg, 0.15 mmol, 1.0 eq.), 1-methyl-4-(4-nitrobenzyl)benzene (68.2 mg, 0.30 mmol, 2.0 eq.), $\text{Cu}(\text{OPiv})_2$ (253 mg, 0.95 mmol, 6.3 eq.), $t\text{-BuOK}$ (107mg, 0.95 mmol, 6.3 mmol), PivOK (133 mg, 0.95 mmol, 6.3 eq.) in 3 mL HMPA at 120°C for 12h. After workup by general procedure, the remaining solid was further purified with silica gel chromatography to afford the title compound as a colorless solid. (38.8 mg, 58% yield based on 4,4'-methylene dibenzonitrile), R_f = 0.48, eluent: dichloromethane/petroleum ether = 4.0/1.0. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.00 (d, J = 8.7 Hz, 2H), 7.48 – 7.40 (m, 4H), 7.17 (d, J = 8.4 Hz, 2H), 7.13 – 7.06 (m, 4H), 6.98 (d, J = 7.8 Hz, 2H), 6.82 (d, J = 7.7 Hz, 2H), 2.29 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 149.1, 146.8 (146.86), 146.8 (146.84), 146.6, 143.4, 139.3, 138.5, 137.8, 132.2, 132.0, 131.9, 131.8, 130.9, 129.3, 123.4, 118.6, 118.3, 111.4, 111.1, 21.3. **HRMS (ESI)** m/z: $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{29}\text{H}_{19}\text{N}_3\text{O}_2\text{Na}^+$ 464.1370, found 464.1374. **Melting point:** 140 - 142 °C.

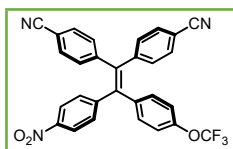
4,4'-(2-(4-methoxyphenyl)-2-(4-nitrophenyl)ethene-1,1-diyl)dibenzonitrile (t-30, new compound)



Conducted on 0.15 mmol scale. Heating the mixture of 4,4'-methylene dibenzonitrile (32.7 mg, 0.15 mmol, 1.0 eq.), 1-methoxy-4-(4-nitrobenzyl)benzene (73.0 mg, 0.30 mmol, 2.0 eq.), $\text{Cu}(\text{OPiv})_2$ (253 mg, 0.95 mmol, 6.3 eq.), $t\text{-BuOK}$ (107mg, 0.95 mmol, 6.3 mmol), PivOK (133 mg, 0.95 mmol, 6.3 eq.) in 3 mL HMPA at 120 °C for 12 h. After workup by general procedure, the remaining

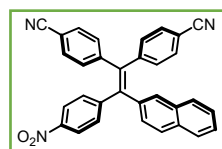
crude was further purified with silica gel chromatography to afford the title compound (24.7 mg, 36% yield based on 4,4'-methylenedibenzonitrile) as a yellow foamy solid, $R_f = 0.36$, eluent: dichloromethane/petroleum ether = 3/1. **¹H NMR (400 MHz, CDCl₃)** δ 8.00 (d, $J = 8.2$ Hz, 2H), 7.49 – 7.41 (m, 4H), 7.17 (d, $J = 8.3$ Hz, 2H), 7.13 – 7.06 (m, 4H), 6.85 (d, $J = 8.3$ Hz, 2H), 6.69 (d, $J = 8.4$ Hz, 2H), 3.77 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 159.6, 149.2, 147.0, 146.9, 146.7, 143.1, 138.8, 133.0, 132.5, 132.2, 132.1 (132.13), 132.1 (132.10), 131.9, 131.8, 123.5, 118.6, 118.3, 114.0, 111.4, 111.1, 55.3. **HRMS (ESI)** m/z : [M+Na]⁺ calculated for C₂₉H₁₉N₃O₃Na⁺ 480.1319, found 480.1318. **Melting point:** 122 - 123 °C.

4,4'-(2-(4-nitrophenyl)-2-(4-(trifluoromethoxy)phenyl)ethene-1,1-diyl)dibenzonitrile (t-31, new compound)



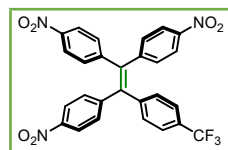
Conducted on 0.15 mmol scale, stirring the mixture of 4,4'-methylenedibenzonitrile (32.7 mg, 0.15 mmol, 1.0 eq.), 1-nitro-4-(4-(trifluoromethoxy)benzyl)benzene (89.2 mg, 0.30 mmol, 2.0 eq.), Cu(OPiv)₂ (253 mg, 0.95 mmol, 6.3 eq.), *t*-BuOK (107mg, 0.95 mmol, 6.3 mmol), PivOK (133 mg, 0.95 mmol, 6.3 eq.) in 3 mL HMPA at 120 °C for 12 h. After workup by general procedure, the remaining crude was further purified with prep-TLC to afford the title compound as a yellowish solid (29.0 mg, 37% yield based on 4,4'-methylenedibenzonitrile), $R_f = 0.4$, (eluent = dichloromethane/hexane = 3/1). **¹H NMR (400 MHz, CDCl₃)** δ 8.03 (d, $J = 8.8$ Hz, 2H), 7.47 (d, $J = 8.3$ Hz, 4H), 7.17 (d, $J = 8.9$ Hz, 2H), 7.10 (d, $J = 8.5$ Hz, 4H), 7.01 (q, $J = 8.9$ Hz, 4H). **¹³C NMR (101 MHz, CDCl₃)** δ 149.0 (q, $J = 1.8$ Hz), 148.3, 147.1, 146.1, 146.0, 141.7, 140.7, 139.2, 132.5, 132.3, 132.2, 131.9, 131.8, 131.7, 123.7, 120.8, 120.3 (q, $J = 258.3$ Hz), 118.3, 118.2, 111.9, 111.7. **¹⁹F NMR (376 MHz, CDCl₃)** δ -57.82. **HRMS (ESI)** m/z : [M+Na]⁺ calculated for C₂₉H₁₆N₃O₃F₃Na⁺ 534.1035, found 534.1039. **Melting point:** 96 - 98 °C.

4,4'-(2-(naphthalen-2-yl)-2-(4-nitrophenyl)ethene-1,1-diyl)dibenzonitrile (t-32, new compound)



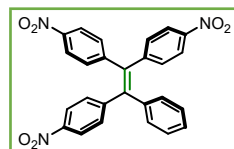
Conducted on 0.15 mmol scale, heating the mixture of 4,4'-methylenedibenzonitrile (32.7 mg, 0.15 mmol, 1.0 eq.), 2-(4-nitrobenzyl)naphthalene (79.0 mg, 0.30 mmol, 2.0 eq.), Cu(OPiv)₂ (253 mg, 0.95 mmol, 6.3 eq.) *t*-BuOK (107mg, 0.95 mmol, 6.3 mmol), PivOK (133 mg, 0.95 mmol, 6.3 eq.) in 3 mL HMPA at 120 °C for 12 h. After workup by general procedure, the remaining crude was further purified with silica gel chromatography to afford the title compound as a brown solid. (34.6 mg, 48% yield based on 4,4'-methylenedibenzonitrile), $R_f = 0.4$, eluent = dichloromethane/petroleum ether = 2/1). **¹H NMR (400 MHz, CDCl₃)** δ 8.03 (d, $J = 8.7$ Hz, 2H), 7.78 (d, $J = 8.0$ Hz, 1H), 7.65 (d, $J = 8.5$ Hz, 1H), 7.60 (d, $J = 7.9$ Hz, 1H), 7.54 – 7.37 (m, 7H), 7.22 (d, $J = 8.7$ Hz, 2H), 7.18 – 7.12 (m, 4H), 7.04 (dd, $J = 8.5, 1.8$ Hz, 1H). **¹³C NMR (101 MHz, CDCl₃)** δ 148.9, 146.9, 146.5 (146.55), 146.5 (146.50), 143.2, 140.1, 138.2, 133.0, 132.7, 132.3, 132.1, 131.9, 131.8, 130.8, 128.3, 128.1 (128.15), 128.1 (128.12), 127.7, 127.1, 126.8, 123.5, 118.4, 118.3, 111.6, 111.3. **HRMS (ESI)** m/z : [M+Na]⁺ calculated for C₃₂H₁₉N₃O₂Na⁺ 500.1369, found 500.1367. **Melting point:** 192 – 197 °C.

4,4',4''-(2-(4-(trifluoromethyl)phenyl)ethene-1,1,2-triyl)tris(nitrobenzene) (t-33, new compound)



Conducted on 0.15 mmol scale, stirring the mixture of 1-nitro-4-(4-(trifluoromethyl)benzyl)benzene (42.2 mg, 0.15 mmol, 1.0 eq.), bis(4-nitrophenyl)methane (77.4 mg, 0.30 mmol, 2.0 eq.), Cu(OPiv)₂ (253 mg, 0.95 mmol, 6.3 eq.), *t*-BuOK (107mg, 0.95 mmol, 6.3 eq.), PivOK (133 mg, 0.95 mmol, 6.3 eq.) in 3 mL HMPA at 120 °C for 12 h. After workup by general procedure, the remaining crude was further purified with prep-TLC to afford the title compound (18.0 mg, 22% yield based on 1-nitro-4-(4-(trifluoromethyl)benzyl)benzene) as a yellow solid. $R_f = 0.38$, eluent: dichloromethane/petroleum ether = 1.5/1.0. **¹H NMR (400 MHz, CDCl₃)** δ 8.07 – 8.00 (m, 6H), 7.46 (d, $J = 8.1$ Hz, 2H), 7.23 – 7.17 (m, 6H), 7.14 (d, $J = 8.0$ Hz, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 147.7, 147.6 (147.67), 147.6 (147.64), 147.1, 147.0, 144.2 (144.24), 144.2 (144.23), 142.4, 140.5, 131.9 (131.91), 131.9 (131.92), 131.3, 130.4 (d, $J = 32.6$ Hz), 125.7 (q, $J = 3.7$ Hz), 123.8, 123.7, 123.6 (q, $J = 272.5$ Hz). **¹⁹F NMR (376 MHz, CDCl₃)** δ -62.79. **HRMS (ESI)** m/z : [M]⁺ calculated for C₂₇H₁₇F₃N₃O₆⁺ 536.1064, found 536.1060. **Melting point:** 109 - 112 °C.

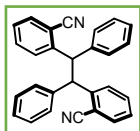
4,4',4''-(2-phenylethene-1,1,2-triyl)tris(nitrobenzene) (t-34, new compound)



Conducted on 0.15 mmol scale, stirring the mixture of 1-benzyl-4-nitrobenzene (32.0 mg, 0.15 mmol, 1.0 eq.), bis(4-nitrophenyl)methane (77.4 mg, 0.30 mmol, 2.0 eq.), Cu(OPiv)₂ (253 mg, 0.95 mmol, 6.3 eq.), *t*-BuOK (107mg, 0.95 mmol, 6.3 eq.), PivOK (133 mg, 0.95 mmol, 6.3 eq.) in 3 mL HMPA at 120 °C for 12 h. After workup by general procedure, the remaining crude was further purified with prep-TLC to

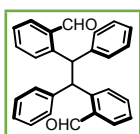
afford the title compound (16.4 mg, 23% yield based on 1-benzyl-4-nitrobenzene) as a yellow solid. $R_f = 0.29$, Eluent = dichloromethane/petroleum ether = 1.5/1.0. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.07 – 7.98 (m, 6H), 7.25 – 7.15 (m, 9H), 7.01 – 6.96 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 148.6, 148.5, 148.3, 147.0, 146.8, 144.2, 140.7, 139.1, 132.0 (132.09), 132.0 (132.03), 131.0, 128.8, 128.7, 123.9, 123.6, 123.6. **HRMS (ESI)** m/z: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{26}\text{H}_{18}\text{N}_3\text{O}_6^+$ 468.1190, found 468.1195. **Melting point:** 79 – 81 °C.

2,2'-(1,2-diphenylethane-1,2-diyl)dibenzonitrile (i-4, new compound)



According to the general procedure on 0.30 mmol scale, heating the mixture of 2-benzylbenzonitrile (60 mg, 0.31 mmol, 1.0 eq.), $\text{Cu}(\text{OPiv})_2$ (206 mg, 0.77 mmol, 2.5 eq.), *t*-BuOK (87.0 mg, 0.77 mmol, 2.5 eq.), PivOK (109 mg, 0.77 mmol, 2.5 eq.) to afford the title compound as a colorless solid. (32.6 mg, 56% yield), The product was characterized as a mixture of diastereomers (1:1). $R_f = 0.57$ (eluent = dichloromethane/petroleum ether = 1.5/1.0), $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.76 – 7.67 (m, 2H), 7.53 – 7.31 (m, 8H), 7.23 – 7.01 (m, 8H), 5.45 (s, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 146.4 (146.48), 146.4 (146.42), 140.3 (140.36), 140.3 (140.32), 133.4, 133.2, 132.9, 132.8, 128.9, 128.8, 128.4, 128.3, 128.0 (128.09), 128.0 (128.00), 127.1 (127.19), 127.1 (127.13), 127.0 (127.07), 127.0 (127.00), 118.4 (118.48), 118.4 (118.47), 112.8, 112.6, 53.2 (53.29), 53.2 (53.25). **HRMS (ESI)** m/z: $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{28}\text{H}_{20}\text{N}_2\text{Na}^+$ 407.1519, found 407.1523.

2,2'-(1,2-diphenylethane-1,2-diyl)dibenzaldehyde (i-5, new compound)

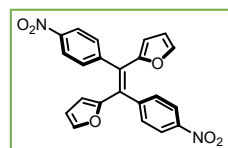


According to the general procedure on 0.30 mmol scale, heating the mixture of 2-benzylbenzaldehyde (60.8 mg, 0.31 mmol, 1.0 eq.), $\text{Cu}(\text{OPiv})_2$ (206 mg, 0.77 mmol, 2.5 eq.), *t*-BuOK (70 mg, 0.62 mmol, 2.0 eq.), PivOK (87 mg, 0.62 mmol, 2.0 eq.) to afford the title compound (24.4 mg, 41% yield) as a colorless solid. $R_f = 0.35$, eluent = dichloromethane/petroleum ether = 1/1. The product was characterized as a mixture of diastereomers (1.0:1.4). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.13 (s, 1H), 10.06 (s, 1H), 7.75 (d, $J = 7.9$ Hz, 2H), 7.65 (d, $J = 7.9$ Hz, 1H), 7.52 (d, $J = 7.8$ Hz, 3H), 7.44 (d, $J = 7.3$ Hz, 1H), 7.35 (t, $J = 7.6$ Hz, 1H), 7.28 – 7.15 (m, 8H), 7.03 (ddt, $J = 28.2, 17.1, 7.4$ Hz, 8H), 6.50 (d, $J = 15.7$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 193.8 (193.87), 193.8 (193.86), 145.7, 145.6, 142.3, 134.7, 134.6, 133.8 (133.88), 133.8 (133.80), 133.5, 133.3, 129.5, 129.2, 129.0, 128.9, 128.3, 128.2, 126.5 (126.58), 126.5 (126.56), 126.3 (126.35), 126.3 (126.32), 47.8, 47.5. **HRMS (ESI)** m/z: $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{28}\text{H}_{22}\text{O}_2\text{Na}^+$ 413.1512, found 413.1518.

1,2-di(furan-2-yl)-1,2-bis(4-nitrophenyl)ethene

The reaction was conducted on 0.30 mmol scale according to the general procedure. Heating the mixture of 2-(4-nitrobenzyl)furan (61.0 mg, 0.30 mmol, 1.0 eq.), $\text{Cu}(\text{OPiv})_2$ (199 mg, 0.75 mmol, 2.5 eq.), *t*-BuOK (84.0 mg, 0.75 mmol, 2.5 eq.), PivOK (105.0 mg, 0.75 mmol, 2.5 eq.) in HMPA (3 mL) at 120 °C for 12 h. Prep-TLC ($R_f = 0.56$, eluent = dichloromethane/petroleum ether = 1.5/1.0) provide the (*E*)-1,2-di(furan-2-yl)-1,2-bis(4-nitrophenyl)ethene (t-37-*E*) and the crude (*Z*)-1,2-di(furan-2-yl)-1,2-bis(4-nitrophenyl)ethene (t-37-*Z*), which was further purified by the prep-TLC (eluent = ethyl acetate/petroleum ether = 1/3).

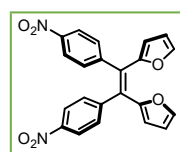
(*E*)-1,2-di(furan-2-yl)-1,2-bis(4-nitrophenyl)ethene (t-37-*E*, new compound)



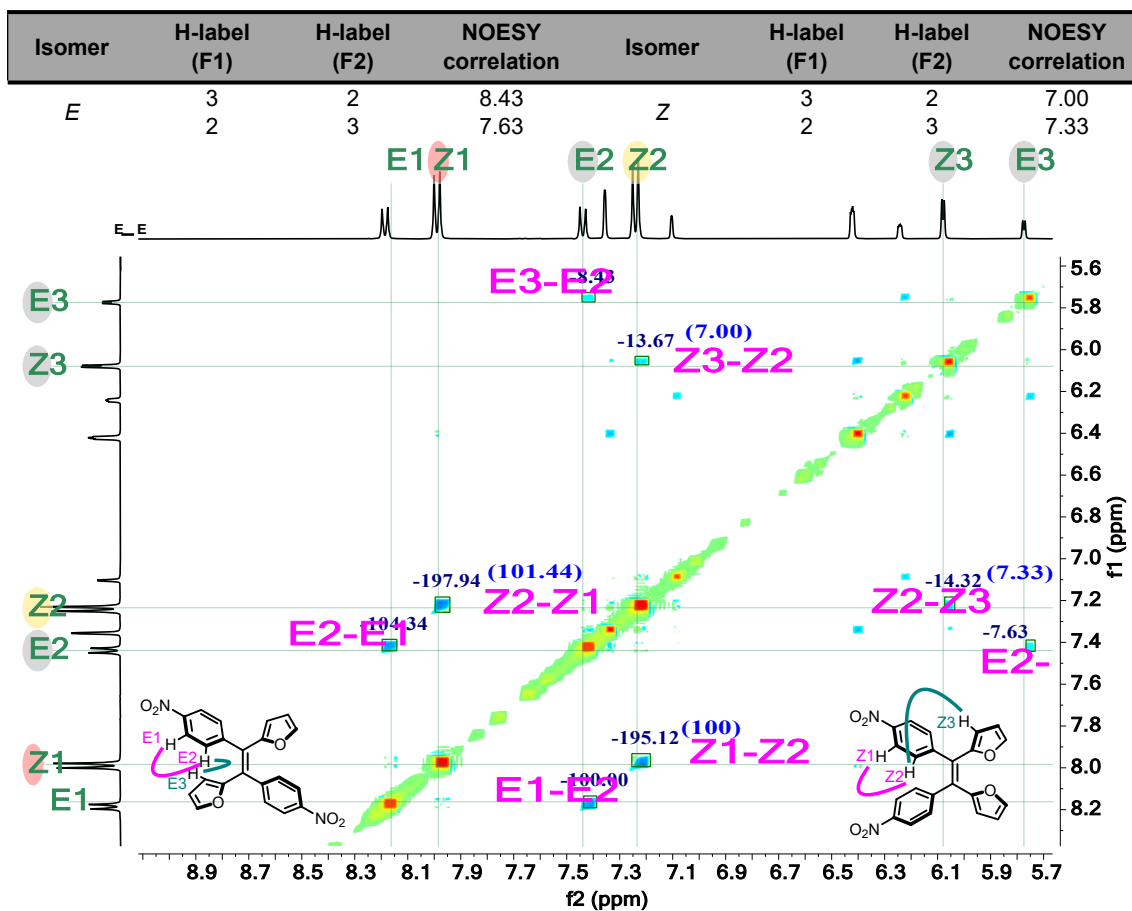
The title compound was isolated as an orange solid (30.9 mg, 51% yield), $R_f = 0.56$ (eluent = dichloromethane/petroleum ether = 1.5/1.0). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.21 (d, $J = 8.4$ Hz, 4H), 7.47 (d, $J = 8.4$ Hz, 4H), 7.13 (s, 2H), 6.30 – 6.24 (m, 2H), 5.81 (d, $J = 3.4$ Hz, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.1, 147.4, 147.2, 143.2, 131.3, 128.3, 123.5, 114.2, 111.7. **HRMS (ESI)** m/z: $[\text{M}-\text{H}]^-$ calculated for $\text{C}_{22}\text{H}_{13}\text{N}_2\text{O}_6^-$ 401.0779, found 401.0782. Melting point: 221 – 222 °C.

(*Z*)-1,2-di(furan-2-yl)-1,2-bis(4-nitrophenyl)ethene (t-37-*Z*, new compound)

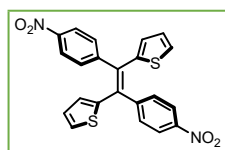
We discovered that the *Z*-isomer spontaneously converts to the *E*-isomer during the purification process and storage, thus, we were unable to obtain a pure compound.



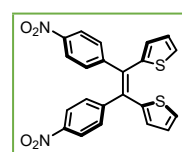
The title compound was isolated as an orange solid (6.4 mg, 10% yield, Contains a small amount of the *E*-isomer.), $R_f = 0.61$ (eluent = dichloromethane/petroleum ether = 1.5/1.0). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.02 (d, $J = 8.7$ Hz, 4H), 7.39 (d, $J = 0.9$ Hz, 2H), 7.27 (d, $J = 8.6$ Hz, 4H), 6.47 – 6.43 (m, 2H), 6.11 (d, $J = 3.3$ Hz, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.6, 147.1, 146.5, 143.2, 132.2, 129.9, 123.5, 113.4, 111.8. **HRMS (ESI)** m/z: $[\text{M}-\text{H}]^-$ calculated for $\text{C}_{22}\text{H}_{13}\text{N}_2\text{O}_6^-$ 401.0779, found 401.0782.

NOESY (stack)

1,2-bis(4-nitrophenyl)-1,2-di(thiophen-2-yl)ethene

The reaction was conducted on 0.30 mmol scale according to the general procedure. Heating the mixture of 2-(4-nitrobenzyl)thiophene (65.8 mg, 0.30 mmol, 1.0 eq.), Cu(OPiv)₂ (199 mg, 0.75 mmol, 2.5 eq.), *t*-BuOK (84.0 mg, 0.75 mmol, 2.5 eq.), PivOK (105.0 mg, 0.75 mmol, 2.5 eq.) in HMPA (3 mL) at 120°C for 12 h. Prep-TLC provide the (*E*)-1,2-bis(4-nitrophenyl)-1,2-di(thiophen-2-yl)ethene (*t*-38-*E*) and the crude (*Z*)-1,2-bis(4-nitrophenyl)-1,2-di(thiophen-2-yl)ethene (*t*-38-*Z*), which was further purified by the prep-TLC (eluent = ethyl acetate/petroleum ether = 1/3).

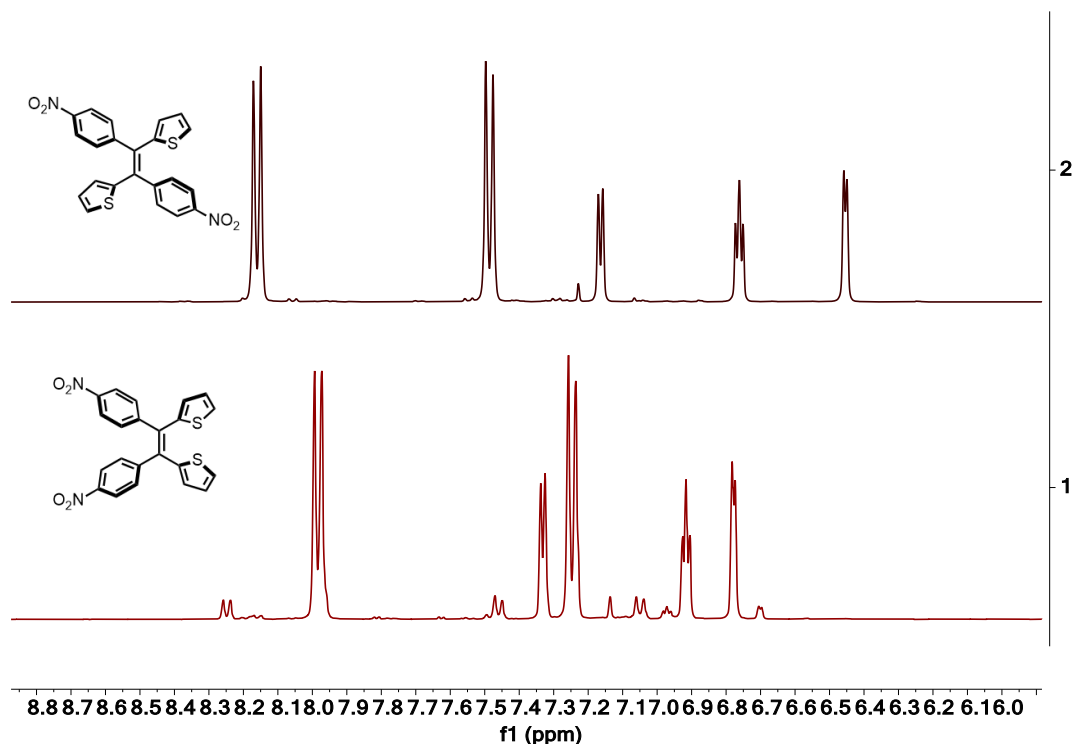
(*E*)-1,2-bis(4-nitrophenyl)-1,2-di(thiophen-2-yl)ethene (*t*-38-*E*, new compound)


The title compound was isolated as an orange solid (25.1 mg, 38% yield), *R*_f = 0.57 (eluent = ethyl acetate/petroleum ether = 1/10). ¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, *J* = 8.3 Hz, 4H), 7.52 (d, *J* = 8.4 Hz, 4H), 7.20 (d, *J* = 5.1 Hz, 2H), 6.79 (dd, *J* = 5.0, 3.7 Hz, 2H), 6.49 (d, *J* = 3.6 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 149.02, 147.59, 143.41, 133.50, 131.98, 130.77, 128.17, 126.90, 123.98. HRMS (ESI) *m/z*: [M-H]⁻ calculated for C₂₂H₁₃N₂O₄S₂⁻ 433.0322, found 433.0328. Melting point: 203 - 204 °C.

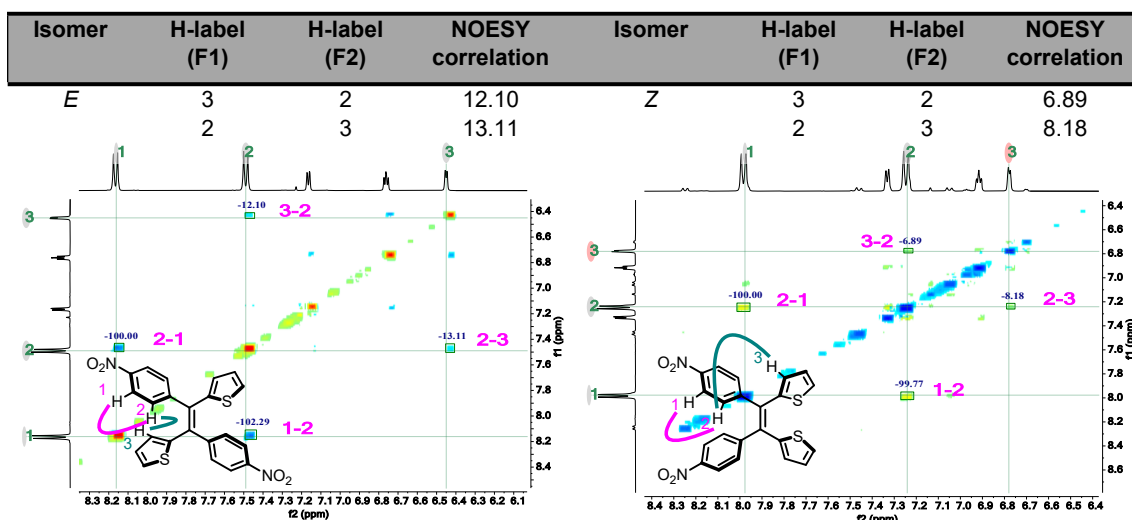
(*Z*)-1,2-bis(4-nitrophenyl)-1,2-di(thiophen-2-yl)ethene (*t*-38-*Z*, new compound)


The title compound was isolated as an orange solid (13.9 mg, 21% yield, contains a small amount of an unknown impurity that cannot be removed by Pre-TLC), *R*_f = 0.5 (eluent = ethyl acetate/petroleum ether = 1/10). ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 8.3 Hz, 4H), 7.37 (d, *J* = 5.1 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 4H), 6.97 - 6.93 (m, 2H), 6.83 - 6.80 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 148.72, 146.96, 143.49, 134.89, 131.84, 130.65, 128.57, 127.18, 123.53. HRMS (ESI) *m/z*: [M-H]⁻ calculated for C₂₂H₁₃N₂O₄S₂⁻ 433.0322, found 433.0328. Melting point: 60 - 61 °C.

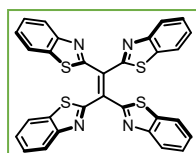
Stacked ¹H NMR spectra of the *E* and *Z* isomer.



NOESY



1,1,2,2-tetrakis(benzo[d]thiazol-2-yl)ethene (**t-39**, new compound)

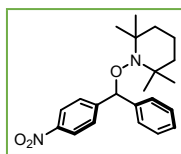


The reaction was conducted on 0.30 mmol scale with a modified procedure. Heating the mixture of bis(benzo[d]thiazol-2-yl)methane (84.7 mg, 0.30 mmol, 1.0 eq.), Cu(OPiv)₂ (199.0 mg, 0.75 mmol, 2.5 eq.), *t*-BuOK (84.0 mg, 0.75 mmol, 2.5 eq.), PivOK (105.0 mg, 0.75 mmol, 2.5 eq.) in HMPA (3 mL) at 120°C for 12 h. The mixture was diluted with ethyl acetate (50 mL), ammonium (aq. 25%, 15 mL), and brine (5 mL) and filtered through a short pad of Celite (50 mL ethyl acetate was used to rinse the filter cake), the mixture was transferred to a separatory funnel, the collected organic layer was washed with mixture of ammonium (aq. 25%, 15 mL) and brine (5 mL), and additional brine (20 mL × 5). The organic layer was filtered through a short pad of silica gel, the solvent was removed on vacuum, Pre-TLC afford the title compound as a yellow solid (36.1 mg, 42% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.1 Hz, 4H), 7.82 (d, *J* = 8.0 Hz, 4H), 7.47 (t, *J* = 7.7 Hz, 4H), 7.40 (t,

$J = 7.6$ Hz, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 163.7, 153.1, 137.0, 135.8, 126.5, 126.3, 124.5, 121.7. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{30}\text{H}_{17}\text{N}_4\text{O}_4^+$ 561.0331, found 561.0315. Melting point: 285 - 288 °C

2,2,5,5-tetramethyl-1-((4-nitrophenyl)(phenyl)methoxy)pyrrolidine (i-6, new compound)



The reaction was conducted on 0.30 mmol scale with a modified procedure. Heating the mixture of 1-benzyl-4-nitrobenzene (64.0 mg, 0.30 mmol, 1.0 eq.), $\text{Cu}(\text{OPiv})_2$ (199.0 mg, 0.75 mmol, 2.5 eq.), $t\text{-BuOK}$ (84.0 mg, 0.75 mmol, 2.5 eq.), PivOK (105.0 mg, 0.75 mmol, 2.5 eq.) and Tempo (46.9 mg, 0.3 mmol, 1.0 eq.) in HMPA (3 mL) at 80°C for 12 h. After workup (general procedure), prep-TLC (dichloromethane/petroleum ether = 1/1) afford the mixture of t-1-E and title compound, which was further purified by prep-TLC ($R_f = 0.65$, ethyl acetate/ petroleum ether = 1/25), giving the pure title compound (86.1 mg, 77% yield) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, $J = 8.2$ Hz, 2H), 7.54s (d, $J = 8.3$ Hz, 2H), 7.34 (d, $J = 7.6$ Hz, 2H), 7.28 (t, $J = 7.5$ Hz, 2H), 7.19 (t, $J = 7.3$ Hz, 1H), 5.75 (s, 1H), 1.61 – 1.25 (m, 6H), 1.16 (d, $J = 6.1$ Hz, 6H), 0.72 (d, $J = 10.2$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.82, 146.38, 142.95, 128.31, 127.08, 126.94, 126.43, 123.46, 89.85, 40.08, 33.69, 20.20, 16.79. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{22}\text{H}_{29}\text{N}_2\text{O}_3^+$ 369.2173, found 369.2167.

2.8. Gram synthesis

Reaction setup (take the preparation of 1,2-bis(4-methoxyphenyl)-1,2-bis(4-nitrophenyl)ethene as the demonstration)

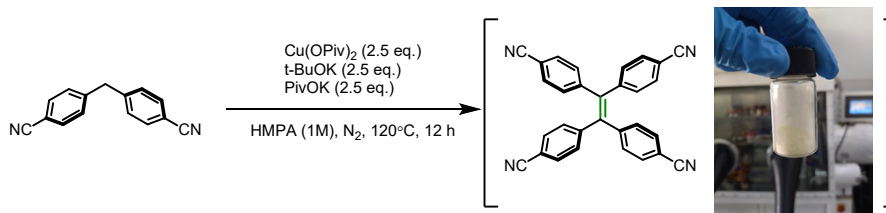
1. stirring and heating



2. addition of HCl (aq.)



4,4',4'',4'''-(ethene-1,1,2,2-tetrayl)tetrabenzonitrile

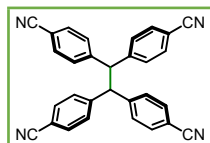


In a glove box, a flame-dried, 350 mL Schlenk tube charged with 4,4'-methylene-dibenzonitrile (1.25 g, 5.73 mmol, 1.0 eq.), copper pivalate (3.81 g, 14.33 mmol, 2.5 eq.), and a Teflon-coated stir bar was added $t\text{-BuOK}$ (1.61 g, 14.33 mmol, 2.5 eq.), and PivOK (2.01 g, 14.33 mmol, 2.5 eq.), and HMPA (57 mL), after which the tube was placed out of the glove box and brought into stir in an oil bath preheated at 120 °C for 12 hours. After cooling to room temperature, diluted hydrochloride acid (1M, 190 mL) was added, producing a large amount of precipitate. The mixture was filtered, and the cake was dissolved in ethyl acetate (150 mL) and transferred to a separatory funnel. The top organic layer was retained and washed with saturated aqueous solution of NaHCO_3 (30 mL) and brine (30 mL). After filtration through a short plug of silica gel, the filtrate was concentrated by vacuum. The remaining brownish solid was further purified by silica gel chromatography, providing the title compound as a pale solid (0.95 g, 76% yield), eluent = dichloromethane.

Note:

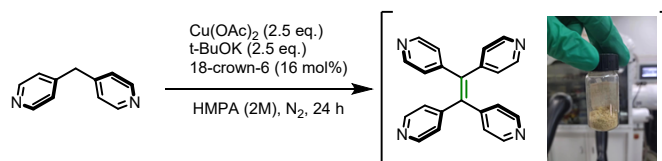
If the dehydrogenation (1.5 g scale) was conducted with $\text{Cu}(\text{OAc})_2$ (3.0 eq.), K_3PO_4 (3.0 eq.), and 18-crown-6 (20 mol%) in DMAc (1M), the title compound was produced with 64% yield, with 19% yield of 4,4',4'',4'''-(ethane-1,1,2,2-tetrayl)tetrabenzonitrile being isolated as a side product.

4,4',4'',4'''-(ethane-1,1,2,2-tetrayl)tetrabenzonitrile (i-1, new compound)



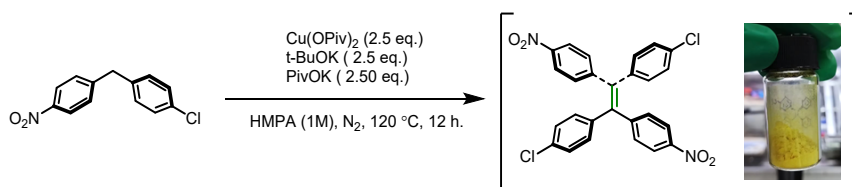
The side product (288 mg, 19% yield) was isolated as a colorless solid, $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.49 (d, J = 8.0 Hz, 8H), 7.21 (d, J = 8.1 Hz, 9H), 4.84 (s, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 145.7, 132.9, 129.0, 118.1, 111.6, 55.7. R_f = 0.22, eluent = ethyl acetate/dichloromethane = 1/100, HRMS (ESI) m/z : $[\text{M}-\text{H}]^-$ calculated for $\text{C}_{30}\text{H}_{17}\text{N}_4$ 433.1459, found 433.1465. Melting point: $>320^\circ\text{C}$.

1,1,2,2-tetra(pyridin-4-yl)ethene



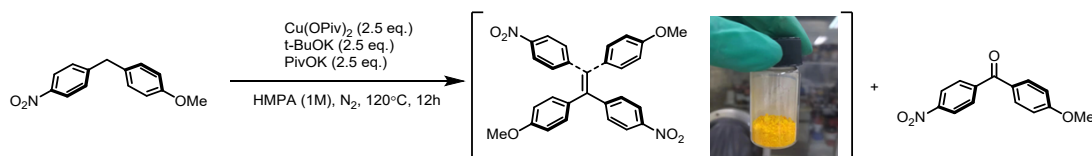
A flame-dried flask charged with di(pyridin-4-yl)methane (5.10 g, 30 mmol, 1.0 eq.), $\text{Cu}(\text{OAc})_2$ (13.6 g, 75 mmol, 2.5 eq.), $t\text{-BuOK}$ (8.4 g, 75 mmol, 2.5 eq.), and 18-crown-6 (1.3 g, 4.9 mmol, 16 mol%) and a stirred bar was evacuated and backfilled with N_2 . Under N_2 flow protection, dry HMPA (150 mL) was added with one portion. The mixture was stirred under 120°C for 24 h under N_2 balloon protection. After cooling to room temperature, the flask was connected to high vacuum to remove the solvent with heating. A mixture of dichloromethane and ammonium (aq. 25%) was used to dissolve the remaining solid. The biphasic solution was transferred to a separatory funnel. The deep blue aqueous layer was removed, and the organic layer was washed with water twice. After drying with Na_2SO_4 , the solution was filtered and concentrated under vacuum. The crude material was further purified with silica gel chromatography to afford the title compound (3.7g, 73% yield) as a brownish solid (with a trace of impurity with blue fluorescence under UV lamp).

1,2-bis(4-chlorophenyl)-1,2-bis(4-nitrophenyl)ethene



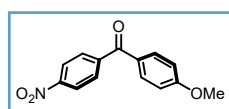
In glove box, a flame-dried, 350 mL Schlenk tube charged with 1-chloro-4-(4-nitrobenzyl)benzene (1.50 g, 6.0 mmol, 1.0 eq.), copper pivalate (3.99 g, 15.0 mmol, 2.5 eq.) and a Teflon-coated stir bar was added potassium tert-butoxide (1.68 g, 15.0 mmol, 2.5 eq.), potassium pivalate (2.10 g, 15.0 mmol, 2.5 eq.), and hexamethylphosphoramide (60 mL), after which the tube was placed out of the glove box and brought into stir on an oil bath preheated at 120°C for 12 hours. After cooling to room temperature, diluted hydrochloride acid (1M, 200 mL) was added, during which a large amount of precipitate was produced. The mixture was filtered, and additional diluted hydrochloride acid (1 M, ca. 200 mL) was used to rinse the tube. The solid was collected and dried under air and vacuum. Further purification by silica gel chromatography provided the title compound as a yellow solid (1.41 g, 95% yield, as a mixture of *E* and *Z* isomer), eluent = dichloromethane/petroleum ether = 1/2.

1,2-bis(4-methoxyphenyl)-1,2-bis(4-nitrophenyl)ethene



In glove box, a flame-dried, 350 mL Schlenk tube was charged with 1-methoxy-4-(4-nitrobenzyl)benzene (1.46 g, 6 mmol, 1.0 eq.), copper pivalate (3.99 g, 15.0 mmol, 2.5 eq.), *t*-BuOK (1.68 g, 15 mmol, 2.5 eq.), PivOK (2.10 g, 15.0 mmol, 2.5 eq.) and a Teflon-coated stirred bar. After the addition of HMPA (60 mL), The tube was capped, and the reaction mixture was stirred in an oil bath preheated at 120 °C for 12 h. After cooling to room temperature, diluted hydrochloric acid (200 mL, 1M) was added in one portion. At this point, yellow precipitate was formed. The precipitate was collected by filtration, the filtrate was extracted with ethyl acetate (40 mL×2), the aqueous layer was removed, and the organic layer was combined and washed with diluted hydrochloric acid (1 M, 20 mL × 3). The precipitate was dissolved in the organic layer, which was then sequentially washed with saturated aqueous NaHCO₃ (20 mL) and brine (20 mL) and filtered with a short pad of silica gel after removing the volatile by rotary evaporation. The residual was brought into silica gel chromatography to afford the title compound (1.37 g, contaminated by pivalate acid), the crude material was dissolved in ethyl acetate (100 mL) and washed with saturated NaHCO₃ (20 mL × 2) and brine (20 mL) to remove residual pivalate acid. The volatile was removed on vacuum to afford yellow solid as the *E* and *Z* mixture of the 1,2-bis(4-methoxyphenyl)-1,2-bis(4-nitrophenyl)ethene (1.24 g, 85% yield). During the purification of the title compound by silica gel chromatography, a few amounts of (4-methoxyphenyl)(4-nitrophenyl)methanone was isolated and characterized by ¹H and ¹³C NMR spectroscopy.

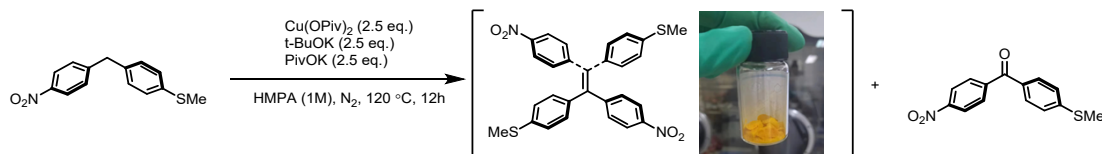
(4-methoxyphenyl)(4-nitrophenyl)methanone (i-2, known compound, 1151-94-6)



¹H NMR (400 MHz, CDCl₃) δ 8.33 (d, *J* = 8.7 Hz, 2H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 8.9 Hz, 2H), 6.99 (d, *J* = 9.0 Hz, 2H), 3.91 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 193.6, 164.1, 143.9, 132.8, 130.4, 129.0, 123.6, 114.1, 55.7.

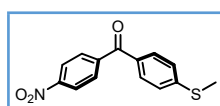
Characteristic data match the literature well.^[44]

1,2-bis(4-(methylthio)phenyl)-1,2-bis(4-nitrophenyl)ethene



In glove box, a flame-dried, 350 mL Schlenk tube was charged with methyl(4-(4-nitrobenzyl)phenyl)sulfane (1.46 g, 5.6 mmol, 1.0 eq.), copper pivalate (3.72 g, 14.0 mmol, 2.5 eq.), *t*-BuOK (1.57 g, 14 mmol, 2.5 eq.), PivOK (1.96 g, 14.0 mmol, 2.5 eq.) and a Teflon-coated stirred bar. After the addition of HMPA (56 mL), the tube was capped, and the reaction mixture was stirred in an oil bath preheated at 120 °C for 12 h. After cooling to room temperature, diluted hydrochloric acid (186 mL, 1M) was added in one portion. At this point, yellow precipitate was formed. The precipitate was collected by filtration (a small amount of water was used to rinse the tube). The precipitate was dissolved in ethyl acetate (100 mL), which was then sequentially washed with saturated aqueous NaHCO₃ (20 mL) and brine (20 mL) and filtered with a short pad of silica gel. After removing the volatile by rotary evaporation. 1.34 g (92% yield) 1,2-bis(4-(methylthio)phenyl)-1,2-bis(4-nitrophenyl)ethene was obtained as the mixture of *E* and *Z* isomer after silica gel chromatography (eluent = dichloromethane/petroleum ether = 1/1). During the purification of the title compound by silica gel chromatography, a trace amount of (4-(methylthio)phenyl)(4-nitrophenyl)methanone was isolated and characterized by ¹H and ¹³C NMR spectroscopy.

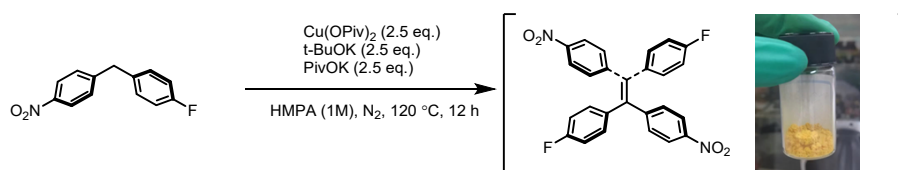
(4-(methylthio)phenyl)(4-nitrophenyl)methanone (i-3, known compound, 127615-48-9)



¹H NMR (400 MHz, CDCl₃) δ 8.33 (d, *J* = 8.7 Hz, 2H), 7.89 (d, *J* = 8.6 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 2.55 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 193.9, 149.7, 147.1, 143.3, 132.3, 130.7, 130.5, 125.0, 123.6, 14.8.

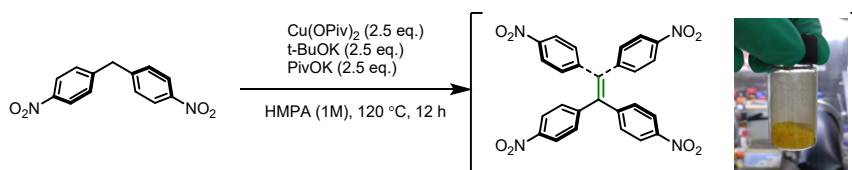
The characteristic data conforms with the literature well.^[45]

1,2-bis(4-fluorophenyl)-1,2-bis(4-nitrophenyl)ethene



In glove box, a flame-dried, 350 mL Schlenk tube was charged with 1-fluoro-4-(4-nitrobenzyl)benzene (1.27 g, 5.5 mmol, 1.0 eq.), copper pivalate (3.65 g, 13.7 mmol, 2.5 eq.), *t*-BuOK (1.54 g, 13.7 mmol, 2.5 eq.), PivOK (1.92 g, 13.7 mmol, 2.5 eq.) and a Teflon-coated stirred bar. After the addition of HMPA (55 mL), the tube was capped, and the reaction mixture was stirred in an oil bath preheated at 120 °C for 12 h. After cooling to room temperature, the addition of diluted hydrochloric acid (183 mL, 1M) to the reaction mixture produced a suspension from which the crude product was successfully isolated by filtration as a yellow solid. (few amount of water was used to rinse the tube), the filtrate was extracted with ethyl acetate (40 mL × 2), the aqueous layer was removed, and the organic layer was combined and washed with diluted hydrochloric acid (1M, 20 mL × 3). The precipitate was dissolved in the organic layer (during the transfer of solid, additional ethyl acetate was used to rinse the funnel), which was then sequentially washed with saturated aqueous NaHCO₃ (20 mL) and brine (20 mL) and filtered with a short pad of silica gel, after removing the volatile by rotary evaporation. 1.15 g (90% yield) 1,2-bis(4-fluorophenyl)-1,2-bis(4-nitrophenyl)ethene was obtained as the mixture of *E* and *Z* isomer after silica gel chromatography (eluent = dichloromethane/petroleum ether = 1/1).

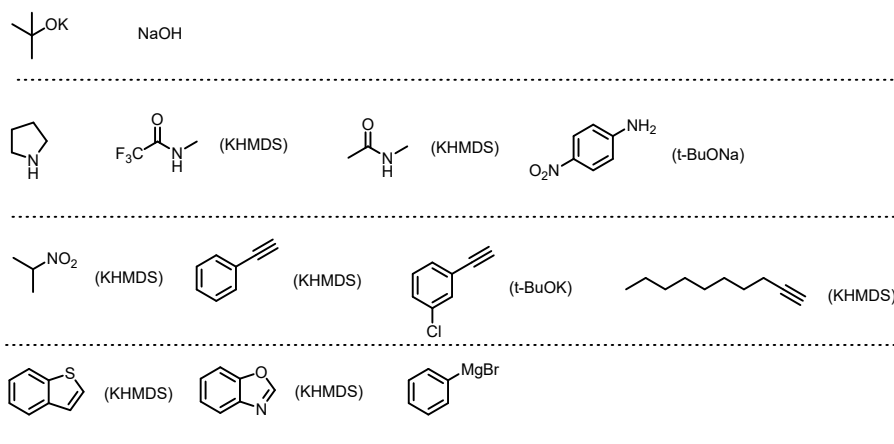
1,1,2,2-tetrakis(4-nitrophenyl)ethene



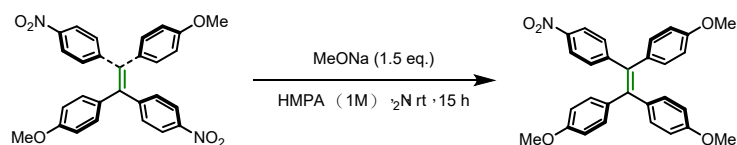
In the glove box, a flame-dried, 350 mL Schlenk tube charged with bis(4-nitrophenyl)methane (2.00 g, 7.75 mmol, 1.0 eq.), copper pivalate (5.15 g, 19.4 mmol, 2.50 eq.) and a Teflon-coated stir bar was added *t*-BuOK (2.17 g, 19.4 mmol, 2.5 eq.), potassium pivalate (2.72 g, 19.4 mmol, 2.5 eq.), and HMPA (77 mL), after which the tube was placed out of the glove box and brought into stir on an oil bath preheated at 120 °C for 12 hours. After cooling to room temperature, diluted hydrochloride acid (1M, 230 mL) was added, during which a large amount of precipitate was produced. The mixture was filtered, and the solid was collected and dissolved in ethyl acetate (170 mL), which was transferred to a 500 mL separatory funnel. The organic layer was washed with brine (20 mL × 2) and passed through a short pad of silica gel. After removing the solvent by the rotator evaporator, further silica gel chromatographic purification provides the title compound as a yellow crystalline (1.94 g, 97% yield), eluent = dichloromethane/petroleum ether = 2/1.

2.9. Derivatization of nitro group

For aromatic nucleophilic substitution of nitro group in TPE, preliminary attempt to use following nucleophile or nucleophile/base combination failed.

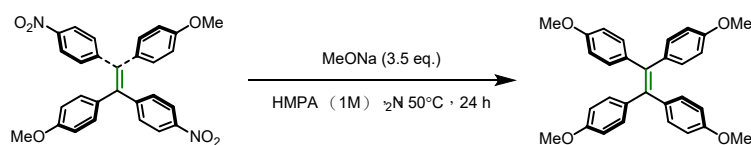


4,4',4''-(2-(4-nitrophenyl)ethene-1,1,2-triyl)tris(methoxybenzene) (d-1, new compound)



A 10 mL Schlenk tube was charged with 1,2-bis(4-methoxyphenyl)-1,2-bis(4-nitrophenyl)ethene (48.2 mg, 0.10 mmol, 1.0 eq., the mixture of *E/Z* isomer), sodium methoxide (8.1 mg, 0.15 mmol, 1.5 eq.) and a stir bar. The mixture was evacuated and backfilled with N_2 for 3 cycles, under N_2 flow, dry HMPA (1 mL) was added with syringe. The tube was capped, and the mixture was stirred at room temperature (ca. 25 °C) for 15 h. The mixture was partitioned with hydrochloric acid (5 mL, 1M) and ethyl acetate (25 mL) and transferred to a 125 mL separatory funnel. The aqueous layer was removed, and the organic layer was successively washed with hydrochloric acid (5 mL \times 2, 1M) and brine (5 mL \times 2) filtered through a short pad of silica gel. The solution was concentrated on vacuum, and the resulting residue was brought into silica gel chromatography to afford the title compound (33.0 mg, 70% yield) as a yellow solid. $R_f = 0.23$, Eluent = ethyl acetate/petroleum ether = 1/25. 1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, $J = 8.6$ Hz, 2H), 7.16 (d, $J = 8.6$ Hz, 2H), 6.98 – 6.86 (m, 6H), 6.71 – 6.62 (m, 6H), 3.77 – 3.74 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 158.6, 158.4, 152.2, 145.7, 142.5, 136.8, 135.7, 135.6, 135.5, 132.8, 132.7, 132.6, 132.2, 123.1, 113.6, 113.5, 113.3, 55.2. HRMS (ESI) m/z : $[M+Na]^+$ calculated for $C_{28}H_{25}NO_5Na^+$ 490.1625, found 490.1624. Melting point: 138 °C - 139 °C.

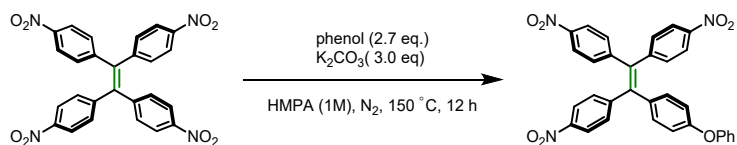
1,1,2,2-tetrakis(4-methoxyphenyl)ethene (d-2, known compound, 361345-02-0)



A 10 mL Schlenk tube was charged with 1,2-bis(4-methoxyphenyl)-1,2-bis(4-nitrophenyl)ethene (48.2 mg, 0.10 mmol, 1.0 eq., mixture of *E/Z* isomer), sodium methoxide (19.0 mg, 0.35 mmol, 3.5 eq.) and a stir bar. The mixture was evacuated and backfilled with N_2 for 3 cycles, under N_2 flow, dry HMPA (1 mL) was added with syringe. The tube was capped, and the mixture was stirred on an oil bath preheated on 50 °C for 24 h. The mixture was transferred to a 125 mL separatory funnel, and 25 mL ethyl acetate was used to rinse the tube. The organic layer was washed successively with diluted hydrochloric acid (5 mL \times 3, 1M) and brine (5 mL) and filtered through a short pad of silica gel, the solution was concentrated on vacuum, and the resulting residue was brought into silica gel chromatography to afford the title compound (41.2 mg, 90% yield) as a yellowish solid. Eluent = dichloromethane/petroleum ether = 1.0/1.0. $R_f = 0.24$. 1H NMR (400 MHz, $CDCl_3$) δ 6.94 (d, $J = 8.2$ Hz, 8H), 6.65 (d, $J = 8.2$ Hz, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 138.5, 137.0, 132.6, 113.1, 55.2.

Characterization data conforms with the literature^[46].

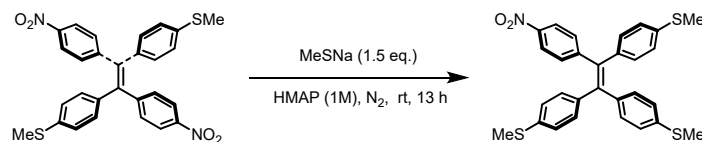
4,4',4''-(2-(4-phenoxyphenyl)ethene-1,1,2-triyl)tris(nitrobenzene) (d-7, new compound)



A 10 mL Schlenk tube was charged with 1,1,2,2-tetrakis(4-nitrophenyl)ethane (51.2 mg, 0.10 mmol, 1.0 eq.), phenol (24 μ L, ca. 26.0 mg, 2.7 eq.), K_2CO_3 (41.5 mg, 0.3 mmol, 3.0 eq.) and a stir bar was added. The mixture was evacuated and backfilled with N_2 for 3 cycles, under N_2 flow, dry HMPA (1 mL) was added with syringe. The tube was capped, and the mixture was stirred on an oil bath preheated on 150 °C for 12 h. The mixture was transferred to a 125 mL separatory funnel, and 25 mL ethyl acetate was used to rinse the tube. The organic layer was washed successively with diluted hydrochloric acid (5 mL \times 3, 1M) and brine (5 mL) and filtered through a short pad of silica gel. The solution was concentrated on vacuum, and the resulting residue was brought into prep-TLC to afford the title compound (29.0 mg, 47% yield) as a yellowish foamy solid. Eluent = dichloromethane/petroleum ether = 1.5/1.0. $R_f = 0.36$. 1H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.00 (m, 6H), 7.40 – 7.32 (m, 2H), 7.25 – 7.10 (m, 7H), 7.00 (d, $J = 7.8$ Hz, 2H), 6.91 (d, $J = 8.3$ Hz, 2H), 6.79 (d, $J =$

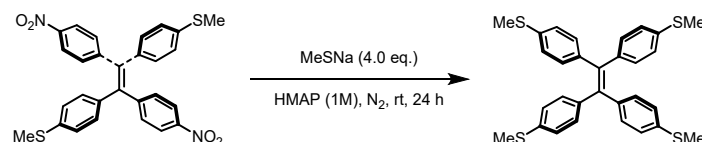
8.4 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 158.1, 155.9, 148.7 (149.77), 148.7 (148.71), 148.4, 147.1, 147.0, 146.9, 143.7, 138.7, 134.9, 132.6, 132.1, 132.0, 130.0, 124.3, 123.9, 123.7 (123.76), 123.7 (123.72), 119.8, 118.1. HRMS (ESI) m/z: [M]⁻ calculated for C₃₂H₂₁N₃O₇⁻ 559.1385, found 559.1377. Melting point: 105 °C – 109 °C.

((2-(4-nitrophenyl)ethene-1,1,2-triyl)tris(benzene-4,1-diyl))tris(methylsulfane) (d-3, new compound)



A 10 mL Schlenk tube was charged with 1,2-bis(4-(methylthio)phenyl)-1,2-bis(4-nitrophenyl)ethene (51.5 mg, 0.10 mmol, 1.0 eq., mixture of *E/Z* isomer), sodium methanethiolate (10.5 mg, 0.15 mmol, 1.5 eq.) and a stir bar was added. The tube was evacuated and backfilled with N₂ for 3 cycles, under N₂ flow, dry HMPA (1 mL) was added with syringe. The tube was capped, and the mixture was stirred at room temperature (ca. 20 °C) for 13 h. 25 mL ethyl acetate and diluted hydrochloric acid (1M, 5 mL) was used to rinse the tube. The mixture was transferred to a 125 mL separatory funnel, the aqueous layer was removed, and the organic layer was washed successively with additional diluted hydrochloric acid (5 mL × 2, 1M), brine (5 mL × 2) and filtrate through a short pad of silica gel, the solution was concentrated on vacuum, and the resulting residue was brought into silica gel chromatography to afford the title compound (36.7 mg, 71% yield) as a colorless solid. Eluent = dichloromethane/petroleum ether = 1.0/1.0. R_f = 0.45. ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.6 Hz, 2H), 7.17 (d, *J* = 8.6 Hz, 2H), 7.04 – 6.96 (m, 6H), 6.95 – 6.86 (m, 6H), 2.46 – 2.40 (m, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 151.1, 146.0, 142.6, 139.3, 139.2 (139.26), 139.2 (139.23), 138.2, 137.8 (137.88), 137.8 (137.83), 137.7, 132.2, 131.8, 131.7 (131.79), 131.7 (131.73), 125.7, 125.6, 125.5, 123.2, 15.3 (15.38), 15.3 (15.36), 15.3 (15.34). HRMS (ESI) m/z: [M+Na]⁺ calculated for C₂₉H₂₅NO₂S₃Na⁺ 538.0940, found 538.0945. Melting point: 186 °C – 190 °C.

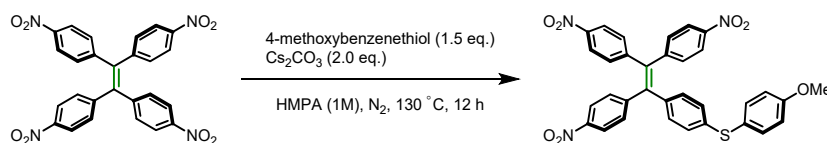
1,1,2,2-tetrakis(4-(methylthio)phenyl)ethene (d-4, known compound, 361345-02-0)



A 10 mL Schlenk tube was charged with 1,2-bis(4-(methylthio)phenyl)-1,2-bis(4-nitrophenyl)ethene (51.5 mg, 0.10 mmol, 1.0 eq., mixture of *E/Z* isomer), sodium methanethiolate (28.0 mg, 0.35 mmol, 3.5 eq.) and a stir bar. The mixture was evacuated and backfilled with N₂ for 3 cycles, under N₂ flow, dry HMPA (1 mL) was added with syringe. The tube was capped, and the mixture was stirred at room temperature (ca. 20 °C) for 24 h. the mixture was transferred to a 125 mL separatory funnel, and 25 mL ethyl acetate was used to rinse the tube. The organic layer was washed successively with diluted hydrochloric acid (5 mL×3, 1M) and brine (5 mL) and filtered through a short pad of silica gel. The solution was concentrated on vacuum, and the resulting residue was brought silica gel chromatography, affording the title compound (26.6 mg, 51% yield) as a colorless solid. Eluent = dichloromethane/petroleum ether = 1/2. R_f = 0.19. ¹H NMR (400 MHz, CDCl₃) δ 6.98 (d, *J* = 8.1 Hz, 4H), 6.92 (d, *J* = 8.3 Hz, 4H), 2.43 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 140.4, 139.5, 136.7, 131.9, 125.6, 15.5.

Characterization data conforms with the literature well.^[39]

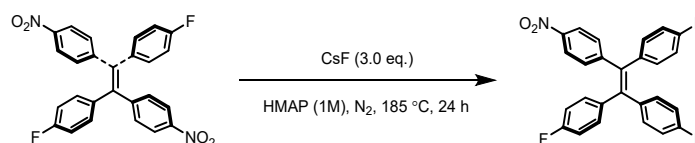
(4-methoxyphenyl)(4-(1,2,2-tris(4-nitrophenyl)vinyl)phenyl)sulfane (d-8, new compound)



A 10 mL Schlenk tube was charged with 1,1,2,2-tetrakis(4-nitrophenyl)ethene (51.2 mg, 0.1 mmol, 1.0 eq. as mixture of *E/Z* isomer), Cs₂CO₃ (65.0 mg, 0.2 mmol, 2.0 eq.) and a stir bar, the tube was evacuated and backfilled with N₂ for 3 cycles, under N₂ flow, 4-methoxybenzenethiol (19 μL, 0.15 mmol, 1.5 eq.) and dry

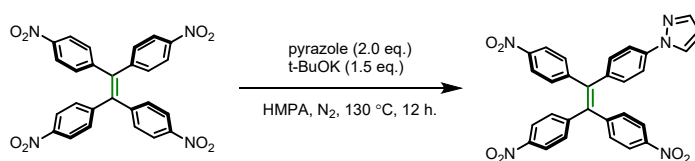
HMPA (1 mL) was added with syringe, the tube was capped, and the mixture was heated on an oil bath preheated on 130 °C for 12 h. The reaction mixture was cooled to room temperature and transferred to a 125 mL separatory funnel, and 25 mL ethyl acetate was used to rinse the tube. The organic layer was washed successively with diluted hydrochloric acid (5 mL × 3, 1M) and brine (5 mL × 2) and filtered through a short pad of silica gel. The solution was concentrated on vacuum, and the resulting residue was brought into prep-TLC to afford the title compound (37.0 mg, 61% yield) as a colorless solid. Eluent = dichloromethane/petroleum ether = 3.0/1.0. $R_f = 0.23$. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.05 – 7.98 (m, 6H), 7.40 (d, $J = 8.6$ Hz, 2H), 7.22 – 7.12 (m, 6H), 6.93 – 6.85 (m, 4H), 6.79 (d, $J = 8.4$ Hz, 2H), 3.82 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 160.5, 148.5, 148.3, 147.0 (147.08), 147.0 (147.00), 146.8, 143.6, 141.0, 138.8, 137.4, 136.4, 132.0 (132.09), 132.0 (132.07), 132.0 (132.02), 131.5, 126.7, 123.8, 123.7, 123.6, 122.0, 115.3, 55.5. **HRMS (ESI)** m/z : $[\text{M}]^-$ calculated for $\text{C}_{33}\text{H}_{23}\text{N}_3\text{O}_7\text{S}^-$ 605.1262, found 605.1251. **Melting point**: 210 – 213 °C.

4,4',4''-(2-(4-nitrophenyl)ethene-1,1,2-triyl)tris(fluorobenzene) (d-5, new compound)



A 10 mL Schlenk tube was charged with 1,2-bis(4-fluorophenyl)-1,2-bis(4-nitrophenyl)ethene (45.8 mg, 0.1 mmol, 1.0 eq. mixture of *E/Z* isomer), CsF (45.6 mg, 0.30 mmol, 3.0 eq.) and a stir bar. The tube was evacuated and backfilled with N_2 for 3 cycles, under N_2 flow, dry HMPA (1 mL) was added with syringe, the tube was capped, and the mixture was heated on an oil bath preheated on 185 °C for 24 h. The reaction mixture was cooled to room temperature and transferred to a 125 mL separatory funnel, and 25 mL ethyl acetate was used to rinse the tube. The organic layer was washed successively with diluted hydrochloric acid (5 mL × 3, 1M) and brine (5 mL × 2) and filtered through a short pad of silica gel. The solution was concentrated on vacuum, and the resulting residue was brought into silica gel chromatography to afford the title compound (21.3 mg, 49% yield) as a colorless solid. Eluent = dichloromethane/petroleum ether = 1.0/1.0. $R_f = 0.23$. eluent = ethyl acetate/petroleum ether = 1/5. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.99 (d, $J = 8.3$ Hz, 2H), 7.15 (d, $J = 8.3$ Hz, 2H), 7.00 – 6.91 (m, 6H), 6.89 – 6.80 (m, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 163.3, 163.2, 163.1, 160.8, 160.7, 160.6, 150.4, 146.3, 141.9, 138.4 (138.46), 138.4 (138.43), 138.3 (138.36), 138.3 (138.33), 138.3 (138.32), 138.2 (138.28), 138.2 (138.23), 133.0, 132.9 (132.98), 132.9 (132.95), 132.9 (132.90), 132.0, 123.4, 115.6 (115.63), 115.6 (115.60), 115.4, 115.3, 115.1. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -113.29 (hept, $J = 4.6$ Hz), -113.65 (hept, $J = 4.9$ Hz), -113.72 (hept, $J = 5.2$ Hz). **HRMS (ESI)** m/z : $[\text{M}+\text{K}]^+$ calculated for $\text{C}_{26}\text{H}_{16}\text{NO}_2\text{FK}^+$ 470.0765, found 470.0756. **Melting point**: 184 - 185 °C.

1-(4-(1,2,2-tris(4-nitrophenyl)vinyl)phenyl)-1H-pyrazole (d-6, new compound)



A 10 mL Schlenk tube was charged with 1,1,2,2-tetrakis(4-nitrophenyl)ethene (51.2 mg, 0.1 mmol, 1.0 eq.), pyrazole (13.6 mg, 0.20 mmol, 2.0 eq.), *t*-BuOK (16.8 mg, 0.15 mmol, 1.5 eq.) and a stir bar. The tube was evacuated and backfilled with N_2 for 3 cycles, under N_2 flow, dry HMPA (1 mL) was added with syringe, the tube was capped, and the mixture was heated on an oil bath preheated on 130 °C for 12 h. The reaction mixture was cooled to room temperature and transferred to a 125 mL separatory funnel, and 25 mL ethyl acetate was used to rinse the tube. The organic layer was washed successively with diluted hydrochloric acid (5 mL × 3, 1M) and brine (5 mL × 2) and filtered through a short pad of silica gel. The solution was concentrated on vacuum, and the resulting residue was brought into silica gel chromatography to afford the title compound (32.4 mg, 60% yield) as a colorless solid. Eluent = dichloromethane/petroleum ether = 1.0/1.0. $R_f = 0.45$, eluent = ethyl acetate/dichloromethane = 1/150. $^1\text{H NMR}$ (400 MHz, DMSO) δ 8.47 (d, $J = 2.6$ Hz, 1H), 8.13 – 8.06 (m, 6H), 7.75 – 7.70 (m, 3H), 7.38 – 7.30 (m, 6H), 7.17 – 7.12 (m, 2H), 6.53 (t, $J = 2.0$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, DMSO) δ 149.0, 148.9, 148.7, 146.8 (146.89), 146.8 (146.81), 146.7, 142.7, 141.7, 139.5, 139.4, 138.8, 132.6, 132.5, 132.4, 128.2, 124.0, 123.9 (123.97), 123.9 (123.95), 118.4, 108.6. **HRMS (ESI)** m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{29}\text{H}_{20}\text{N}_5\text{O}_6^+$ 534.1408, found 534.1405. **Melting point**: 264- 265 °C.

2.10. X-ray crystallographic data

(E)-1,2-bis(4-nitrophenyl)-1,2-diphenylethene (t-1-E)

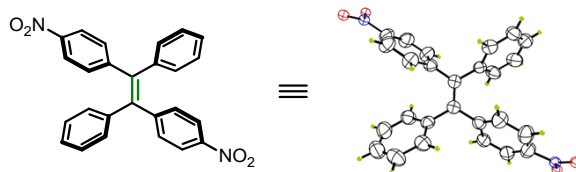


Table S6. Crystal data and structure refinement for **t-1-E**.

Identification code	t-1-E
Empirical formula	C ₂₆ H ₁₈ N ₂ O ₄
Formula weight	422.42
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	20.3504(18)
b/Å	10.4953(9)
c/Å	20.6433(15)
α/°	90
β/°	90.595(7)
γ/°	90
Volume/Å ³	4408.8(6)
Z	8
ρ _{calc} /g/cm ³	1.273
μ/mm ⁻¹	0.087
F(000)	1760.0
Crystal size/mm ³	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.946 to 59.988
Index ranges	-26 ≤ h ≤ 27, -14 ≤ k ≤ 14, -27 ≤ l ≤ 28
Reflections collected	22454
Independent reflections	11189 [R _{int} = 0.0484, R _{sigma} = 0.0923]
Data/restraints/parameters	11189/0/577
Goodness-of-fit on F ²	0.967
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0723, wR ₂ = 0.1839
Final R indexes [all data]	R ₁ = 0.1686, wR ₂ = 0.2350
Largest diff. peak/hole/e Å ⁻³	0.39/-0.30

(E)-1,2-bis(4-nitrophenyl)-1,2-bis-4-fluorophenylethene (t-10-E)

The crystal was obtained by diffusion of hexane into the chloroform solution of the title compound in an NMR tube.

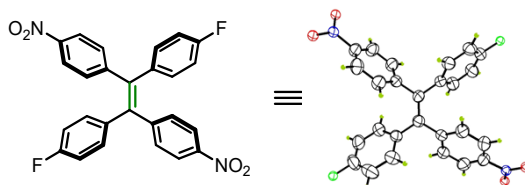


Table S7. Crystal data and structure refinement for **t-10-E**.

Identification code	t-10-E
Empirical formula	C ₂₆ H ₁₆ F ₂ N ₂ O ₄
Formula weight	458.41
Temperature/K	296.15
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	20.411(2)
b/Å	10.2727(10)
c/Å	21.090(2)
α/°	90
β/°	90.997(2)
γ/°	90
Volume/Å ³	4421.4(8)
Z	8
ρ _{calc} /g/cm ³	1.377
μ/mm ⁻¹	0.105
F(000)	1888.0
Crystal size/mm ³	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.828 to 55.396
Index ranges	-26 ≤ h ≤ 26, -12 ≤ k ≤ 13, -20 ≤ l ≤ 27
Reflections collected	26062
Independent reflections	10067 [R _{int} = 0.0799, R _{sigma} = 0.1150]
Data/restraints/parameters	10067/22/623
Goodness-of-fit on F ²	1.011
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0849, wR ₂ = 0.1440
Final R indexes [all data]	R ₁ = 0.2127, wR ₂ = 0.1847
Largest diff. peak/hole/e Å ⁻³	0.30/-0.26

(Z)-1,2-bis(4-nitrophenyl)-1,2-bis-4-fluorophenylethene (t-10-Z)

The crystal was obtained by diffusion of hexane into the chloroform solution of the title compound in an NMR tube.

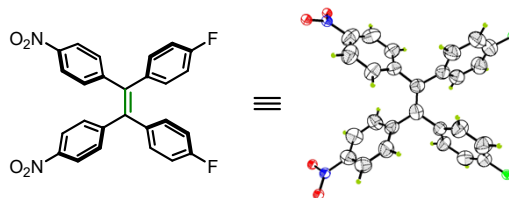


Table S8. Crystal data and structure refinement for **t-10-Z**.

Identification code	t-10-Z
Empirical formula	C ₂₆ H ₁₆ F ₂ N ₂ O ₄
Formula weight	458.41
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	9.9508(13)
b/Å	14.825(2)
c/Å	15.415(2)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	2274.0(5)
Z	4
ρ _{calc} /cm ³	1.339
μ/mm ⁻¹	0.102
F(000)	944.0
Crystal size/mm ³	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.812 to 59.146
Index ranges	-11 ≤ h ≤ 13, -16 ≤ k ≤ 19, -17 ≤ l ≤ 19
Reflections collected	14550
Independent reflections	5522 [R _{int} = 0.0976, R _{sigma} = 0.1603]
Data/restraints/parameters	5522/0/308
Goodness-of-fit on F ²	1.000
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0653, wR ₂ = 0.1503
Final R indexes [all data]	R ₁ = 0.1968, wR ₂ = 0.2060
Largest diff. peak/hole / e Å ⁻³	0.27/-0.18
Flack parameter	-0.1(10)

(E)-1,2-bis(4-(tert-butyl)phenyl)-1,2-bis(4-nitrophenyl)ethene (t-13-E)

The crystal was obtained by diffusion of hexane into the chloroform solution of the title compound in an NMR tube.

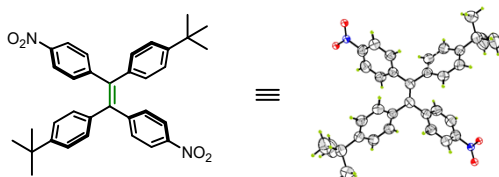


Table S9. Crystal data and structure refinement for **t-13-E**.

Identification code	t-13-E.
Empirical formula	C ₃₄ H ₃₄ N ₂ O ₄
Formula weight	534.63
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Pccn
a/Å	16.5741(17)
b/Å	17.7593(18)
c/Å	10.1074(9)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	2975.1(5)
Z	4
ρ _{calc} /cm ³	1.194
μ/mm ⁻¹	0.078
F(000)	1136.0
Crystal size/mm ³	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.588 to 62.342
Index ranges	-23 ≤ h ≤ 19, -19 ≤ k ≤ 25, -12 ≤ l ≤ 13
Reflections collected	15522
Independent reflections	3898 [R _{int} = 0.0721, R _{sigma} = 0.0715]
Data/restraints/parameters	3898/87/215
Goodness-of-fit on F ²	1.046
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0610, wR ₂ = 0.1393
Final R indexes [all data]	R ₁ = 0.1782, wR ₂ = 0.1940
Largest diff. peak/hole / e Å ⁻³	0.15/-0.21

(E)-1,2-bis(4-methoxyphenyl)-1,2-bis(4-nitrophenyl)ethene (t-14-E)

The crystal was obtained by slow evaporation of the title compound in ethyl acetate/petroleum ether.

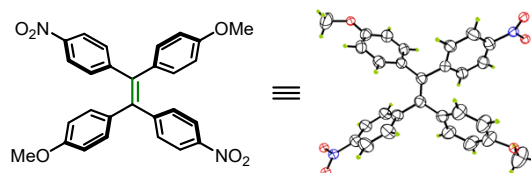


Table S10. Crystal data and structure refinement for t-14-E

Identification code	t-14-E
Empirical formula	C ₂₈ H ₂₂ N ₂ O ₆
Formula weight	482.47
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P21/c
a/Å	11.7545(6)
b/Å	9.3869(6)
c/Å	22.4744(11)
α/°	90
β/°	97.626(4)
γ/°	90
Volume/Å ³	2457.9(2)
Z	4
ρ _{calc} /cm ³	1.304
μ/mm ⁻¹	0.093
F(000)	1008.0
Crystal size/mm ³	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.708 to 61.602
Index ranges	-15 ≤ h ≤ 15, -12 ≤ k ≤ 8, -29 ≤ l ≤ 30
Reflections collected	17441
Independent reflections	6136 [R _{int} = 0.0237, R _{sigma} = 0.0299]
Data/restraints/parameters	6136/6/337
Goodness-of-fit on F ²	1.063
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0452, wR ₂ = 0.1178
Final R indexes [all data]	R ₁ = 0.0687, wR ₂ = 0.1299
Largest diff. peak/hole/e Å ⁻³	0.18/-0.19

(E)-1,2-di([1,1'-biphenyl]-4-yl)-1,2-bis(4-nitrophenyl)ethene (t-18-E)

The crystal was obtained by slow evaporation d-chloroform solution of the title compound in an NMR tube.

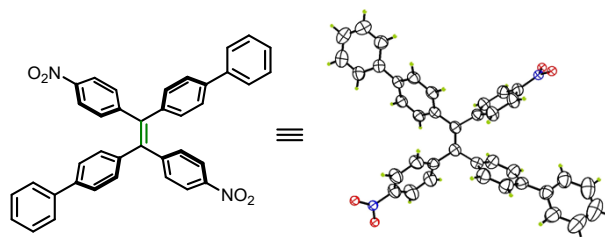


Table S11. Crystal data and structure refinement for **t-18-E**

Identification code	t-18-E
Empirical formula	C ₃₉ H ₂₇ Cl ₃ N ₂ O ₄
Formula weight	693.97
Temperature/K	293.15
Crystal system	triclinic
Space group	P-1
a/Å	9.8501(3)
b/Å	17.0296(6)
c/Å	21.4505(7)
α/°	86.140(3)
β/°	82.858(3)
γ/°	76.587(3)
Volume/Å ³	3470.1(2)
Z	4
ρ _{calc} /cm ³	1.328
μ/mm ⁻¹	0.308
F(000)	1432.0
Crystal size/mm ³	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.83 to 62.204
Index ranges	-13 ≤ h ≤ 13, -23 ≤ k ≤ 23, -4 ≤ l ≤ 30
Reflections collected	17476
Independent reflections	17476 [R _{int} = ?, R _{sigma} = 0.0611]
Data/restraints/parameters	17476/120/903
Goodness-of-fit on F ²	0.994
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0677, wR ₂ = 0.1936
Final R indexes [all data]	R ₁ = 0.1408, wR ₂ = 0.2285
Largest diff. peak/hole/e Å ⁻³	0.49/-0.54

(Z)-1,2-di([1,1'-biphenyl]-4-yl)-1,2-bis(4-nitrophenyl)ethene (t-18-Z)

The crystal was obtained by slow evaporation d-chloroform solution of the title compound in an NMR tube.

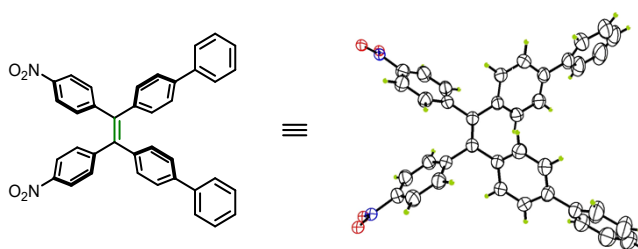
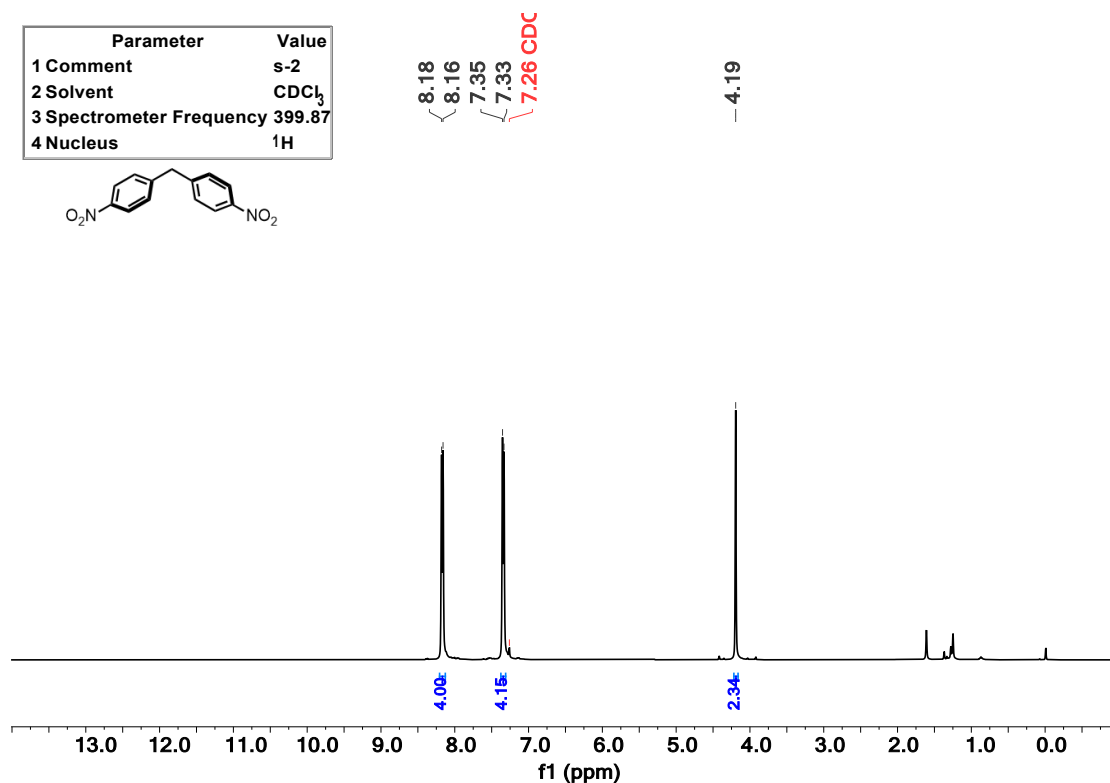
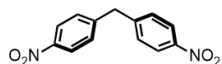


Table S12. Crystal data and structure refinement for **t-18-Z**

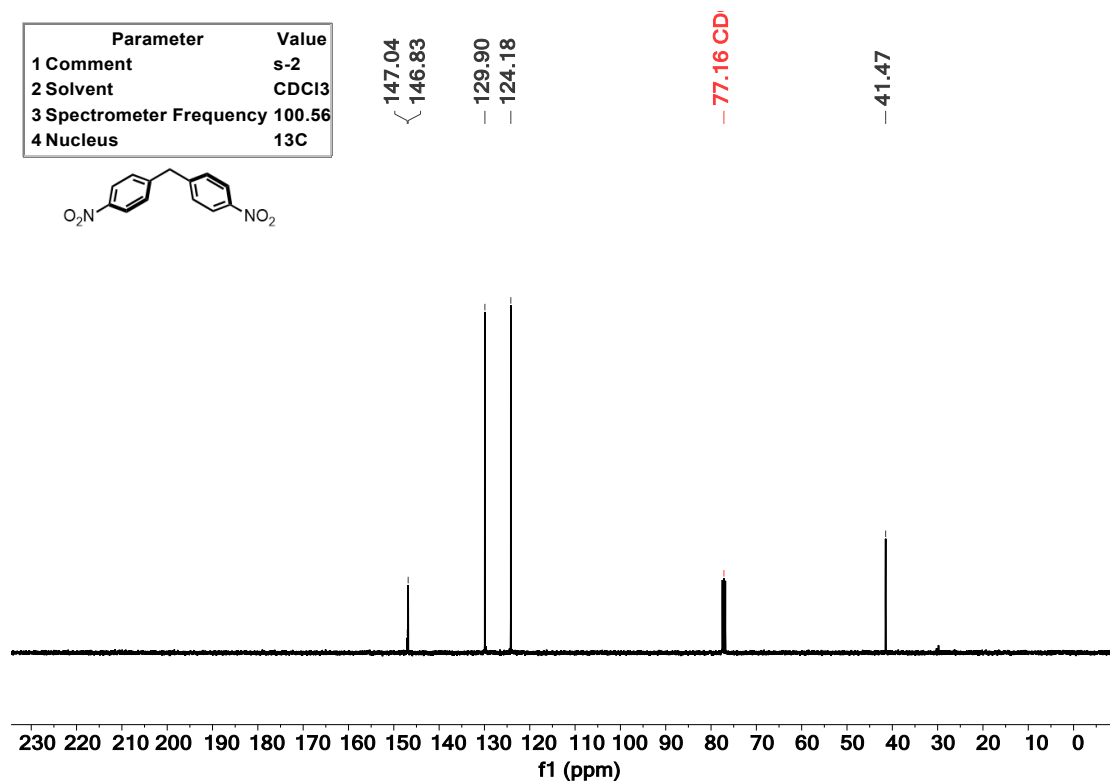
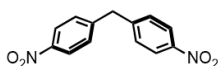
Identification code	T-18-Z
Empirical formula	C ₃₉ H ₂₈ Cl ₃ N ₂ O ₄
Formula weight	694.98
Temperature/K	293(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	22.6110(16)
b/Å	15.7246(9)
c/Å	10.9215(8)
α/°	90
β/°	118.760(7)
γ/°	90
Volume/Å ³	3404.1(4)
Z	4
ρ _{calc} /cm ³	1.356
μ/mm ⁻¹	0.314
F(000)	1436.0
Crystal size/mm ³	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.11 to 62.324
Index ranges	-28 ≤ h ≤ 31, -22 ≤ k ≤ 20, -15 ≤ l ≤ 12
Reflections collected	10179
Independent reflections	3908 [R _{int} = 0.0237, R _{sigma} = 0.0324]
Data/restraints/parameters	3908/114/273
Goodness-of-fit on F ²	1.061
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0590, wR ₂ = 0.1658
Final R indexes [all data]	R ₁ = 0.0875, wR ₂ = 0.1845
Largest diff. peak/hole/e Å ⁻³	0.28/-0.28

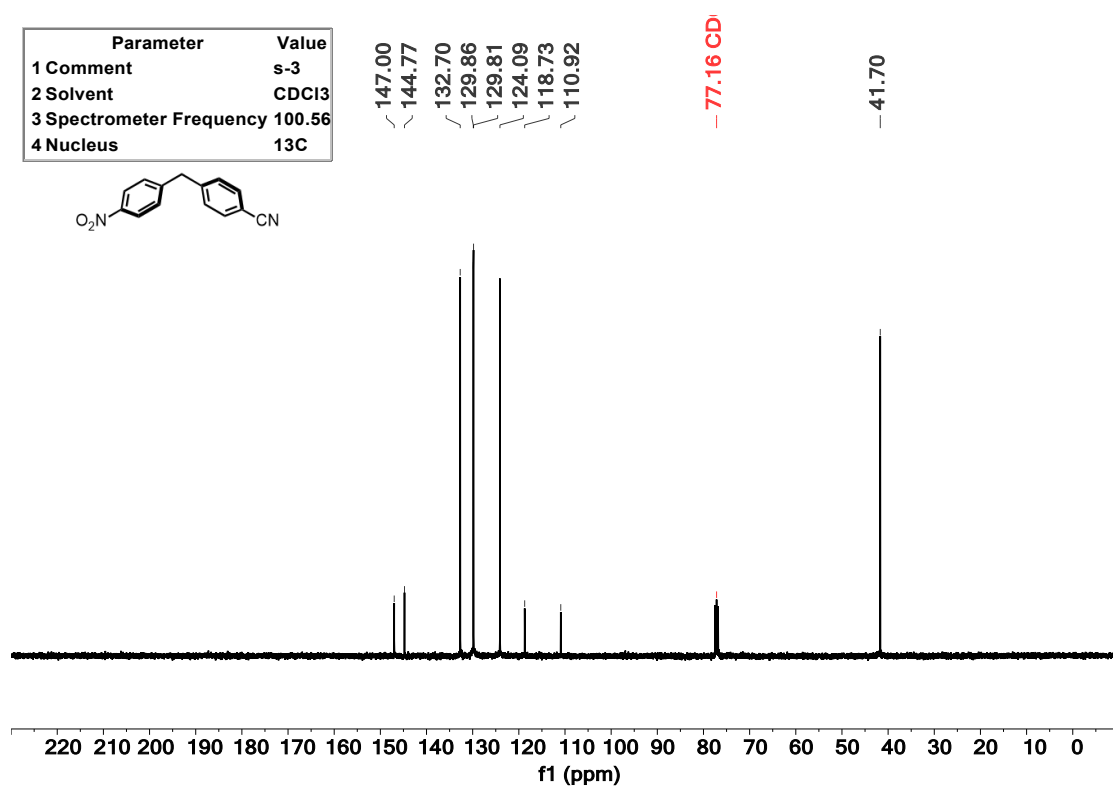
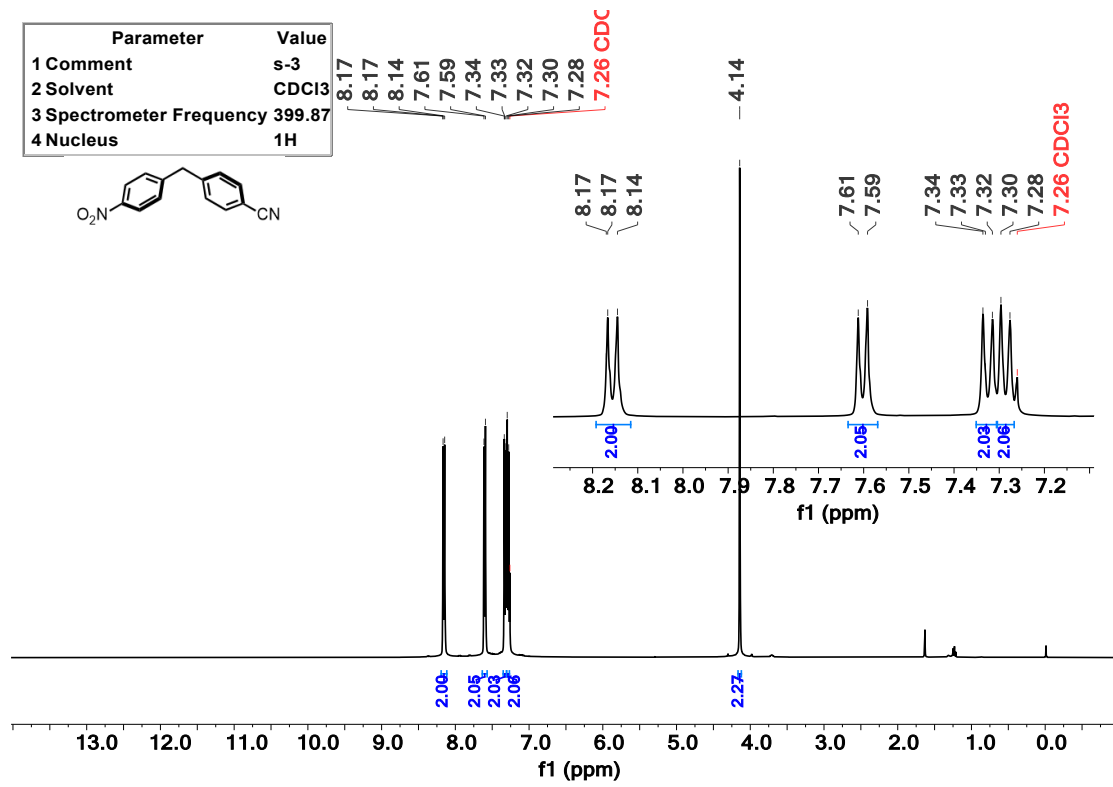
3. Copy of NMR spectra

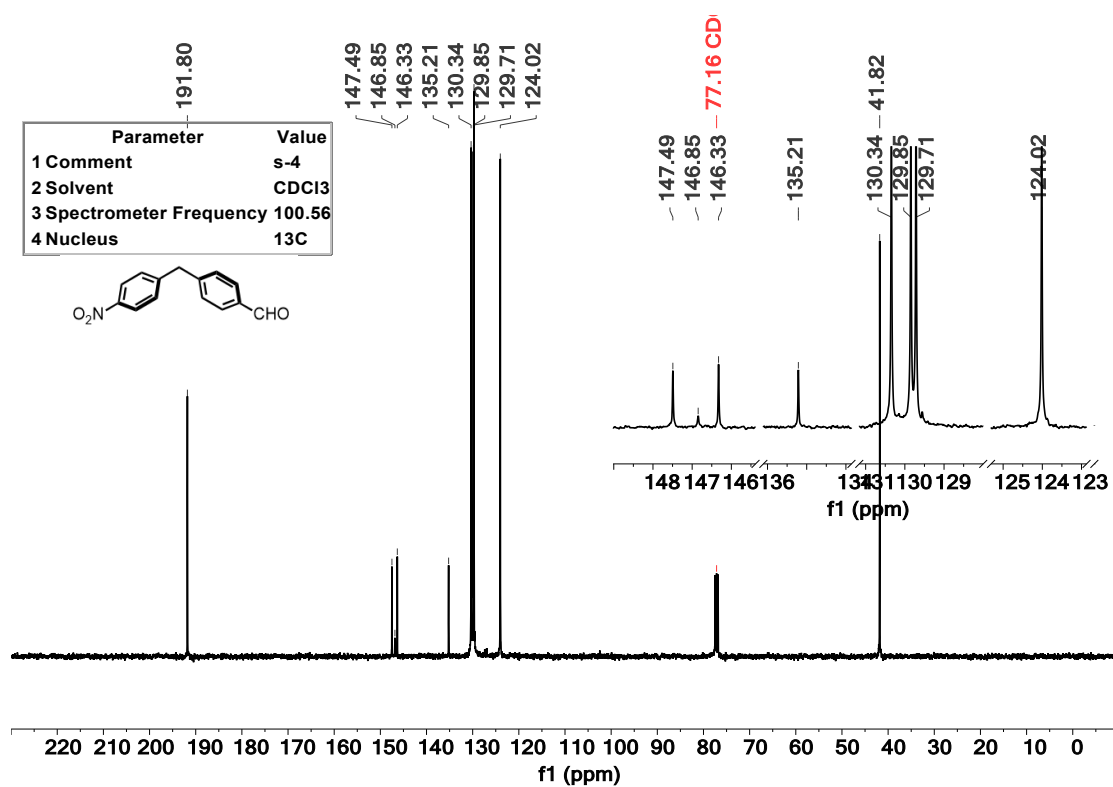
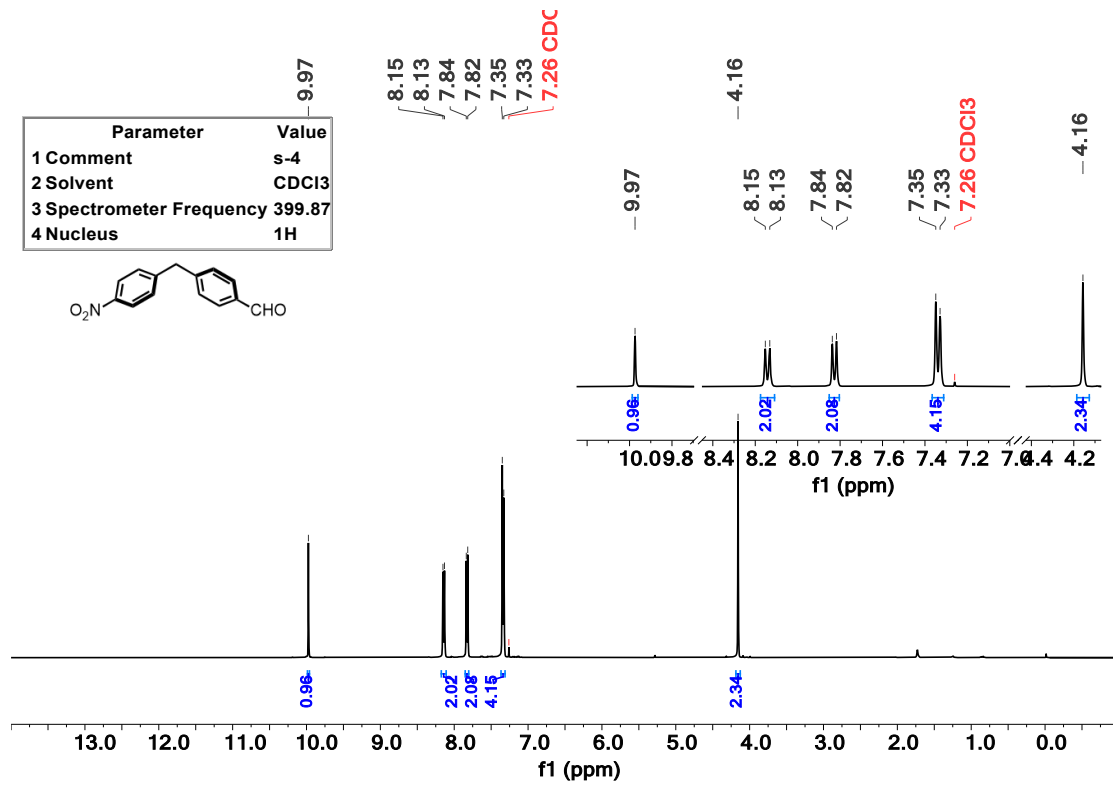
Parameter	Value
1 Comment	s-2
2 Solvent	CDCl ₃
3 Spectrometer Frequency	399.87
4 Nucleus	¹ H



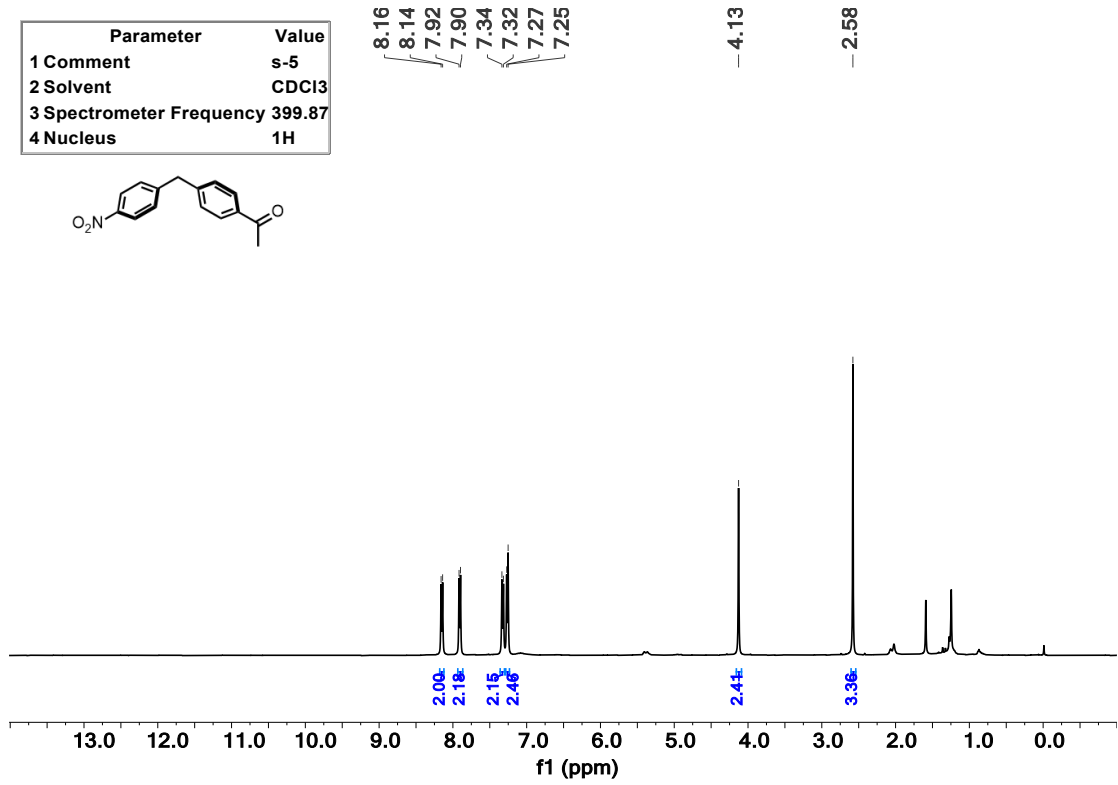
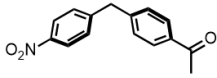
Parameter	Value
1 Comment	s-2
2 Solvent	CDCl ₃
3 Spectrometer Frequency	100.56
4 Nucleus	¹³ C



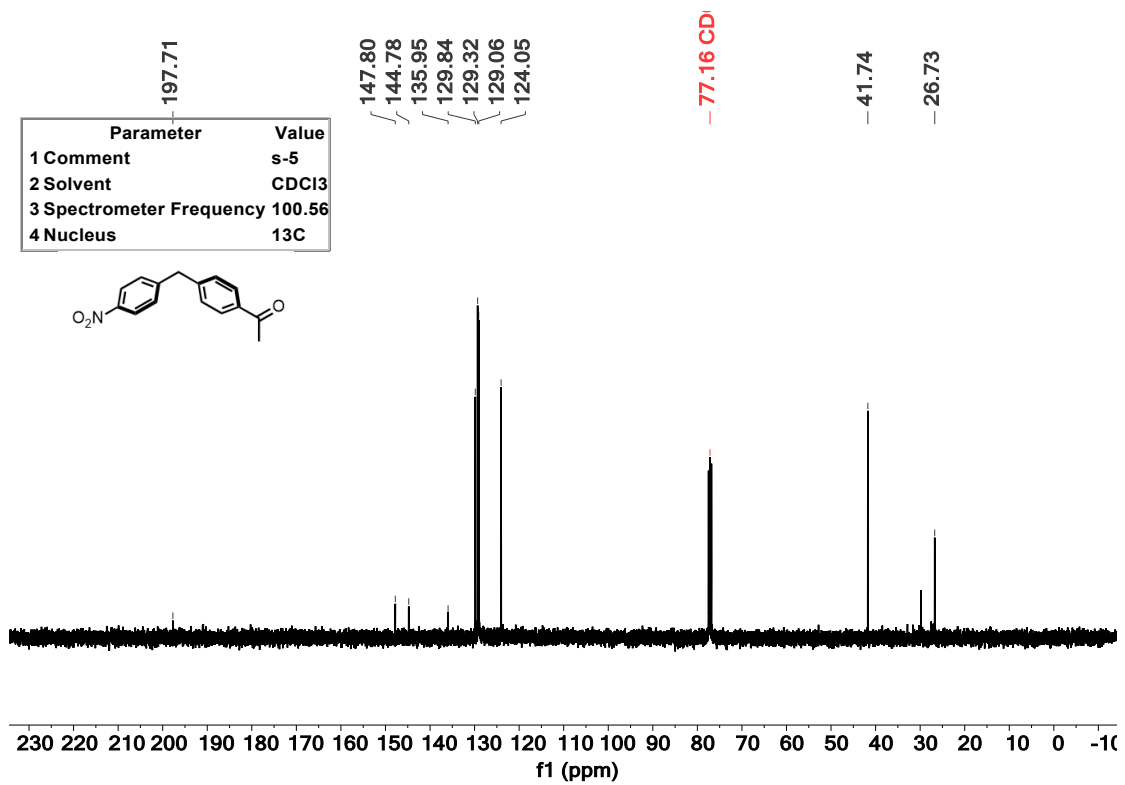
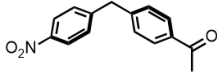




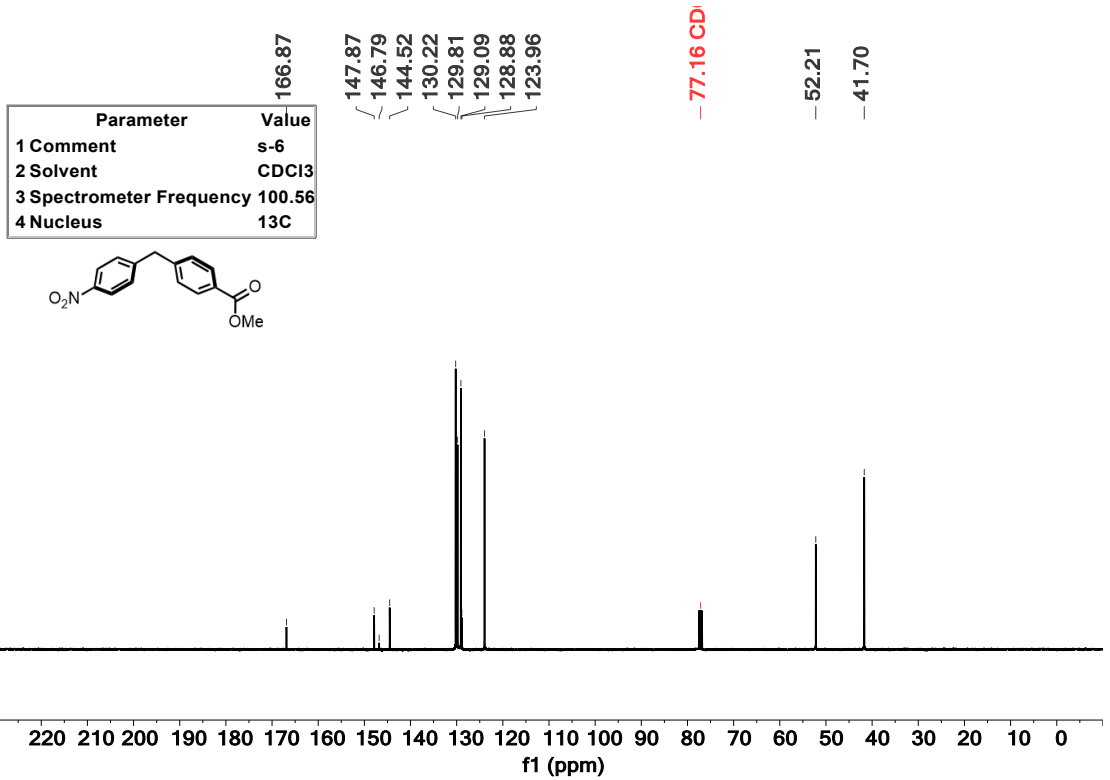
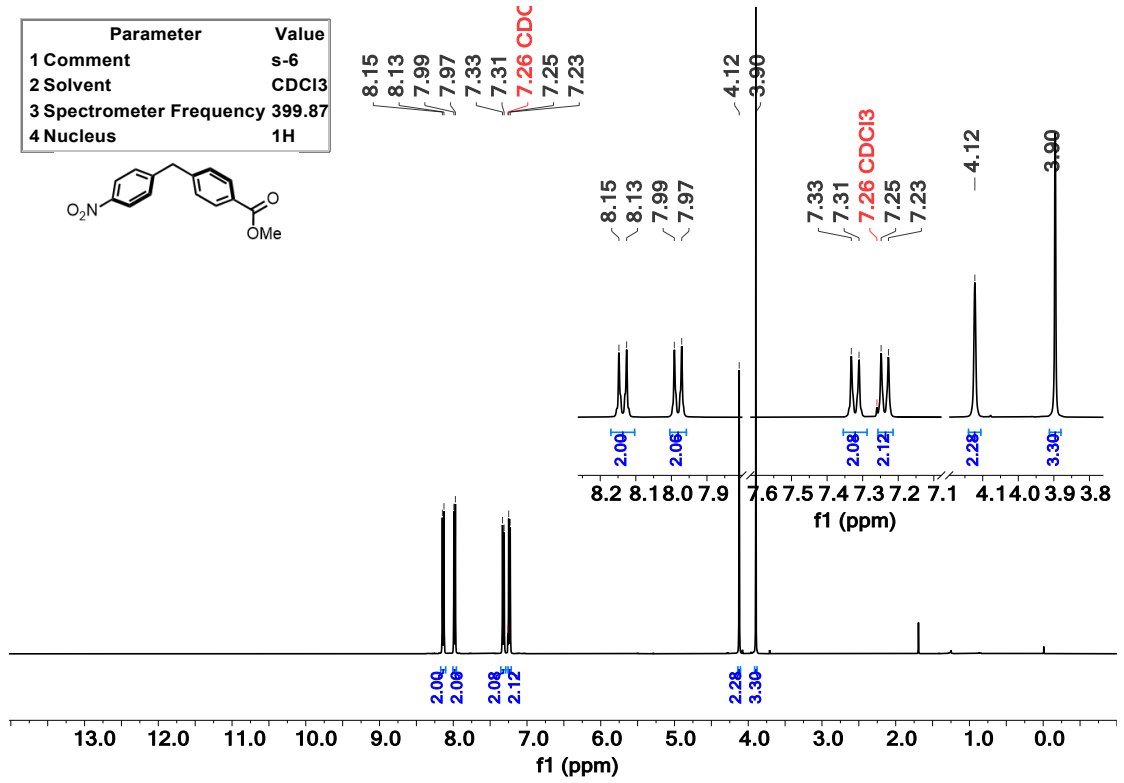
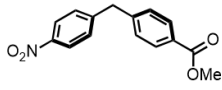
Parameter	Value
1 Comment	s-5
2 Solvent	CDCl3
3 Spectrometer Frequency	399.87
4 Nucleus	1H



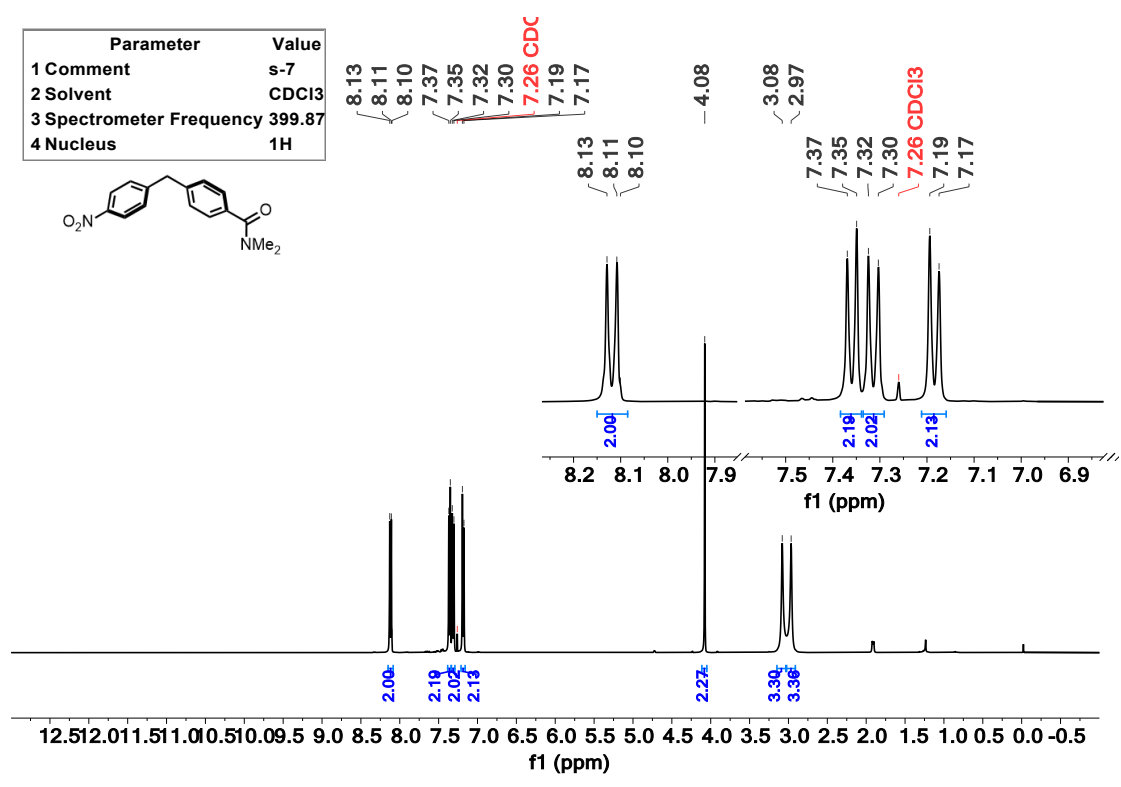
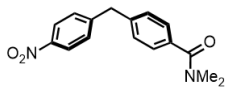
Parameter	Value
1 Comment	s-5
2 Solvent	CDCl3
3 Spectrometer Frequency	100.56
4 Nucleus	13C



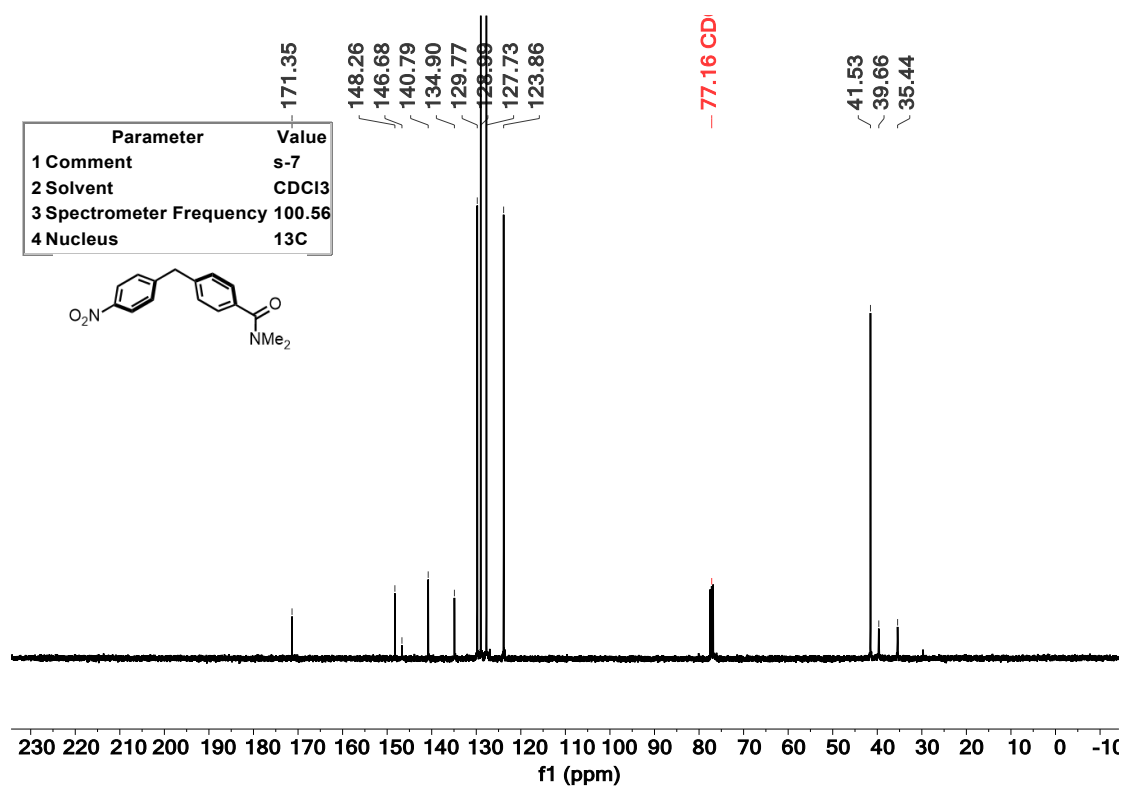
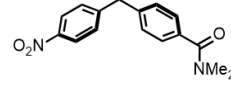
Parameter	Value
1 Comment	s-6
2 Solvent	CDCl3
3 Spectrometer Frequency	399.87
4 Nucleus	1H



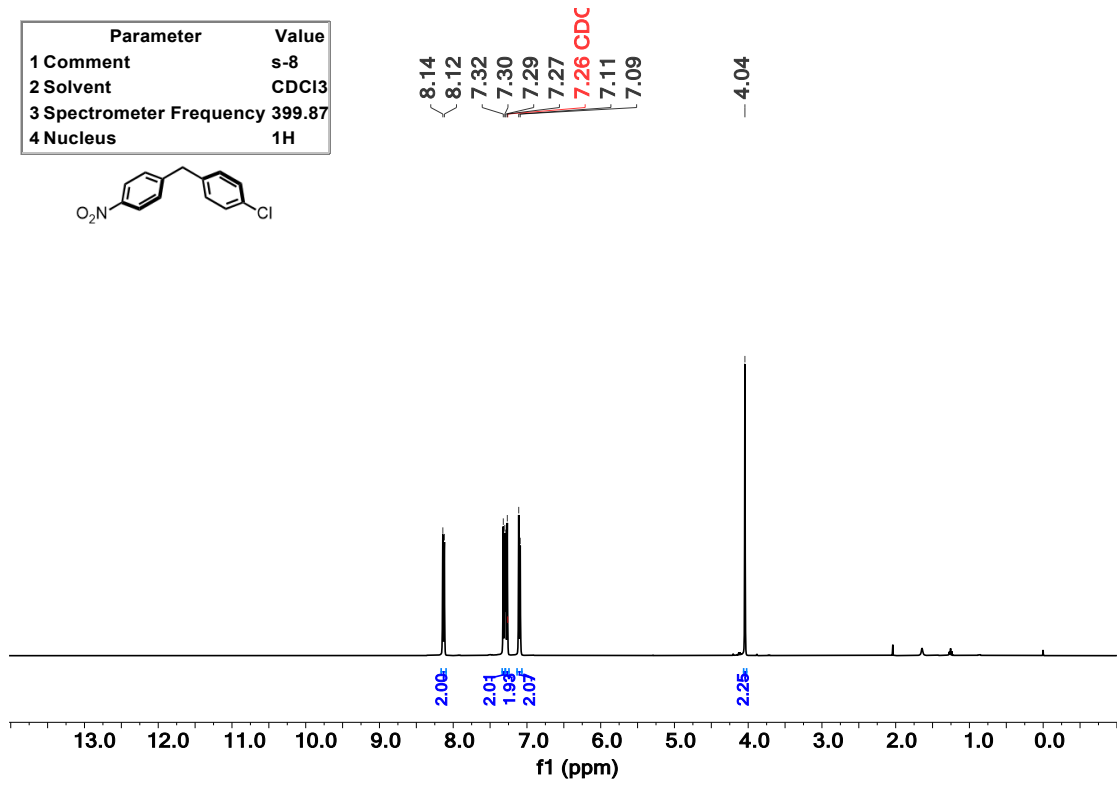
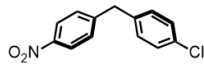
Parameter	Value
1 Comment	s-7
2 Solvent	CDCl ₃
3 Spectrometer Frequency	399.87
4 Nucleus	¹ H



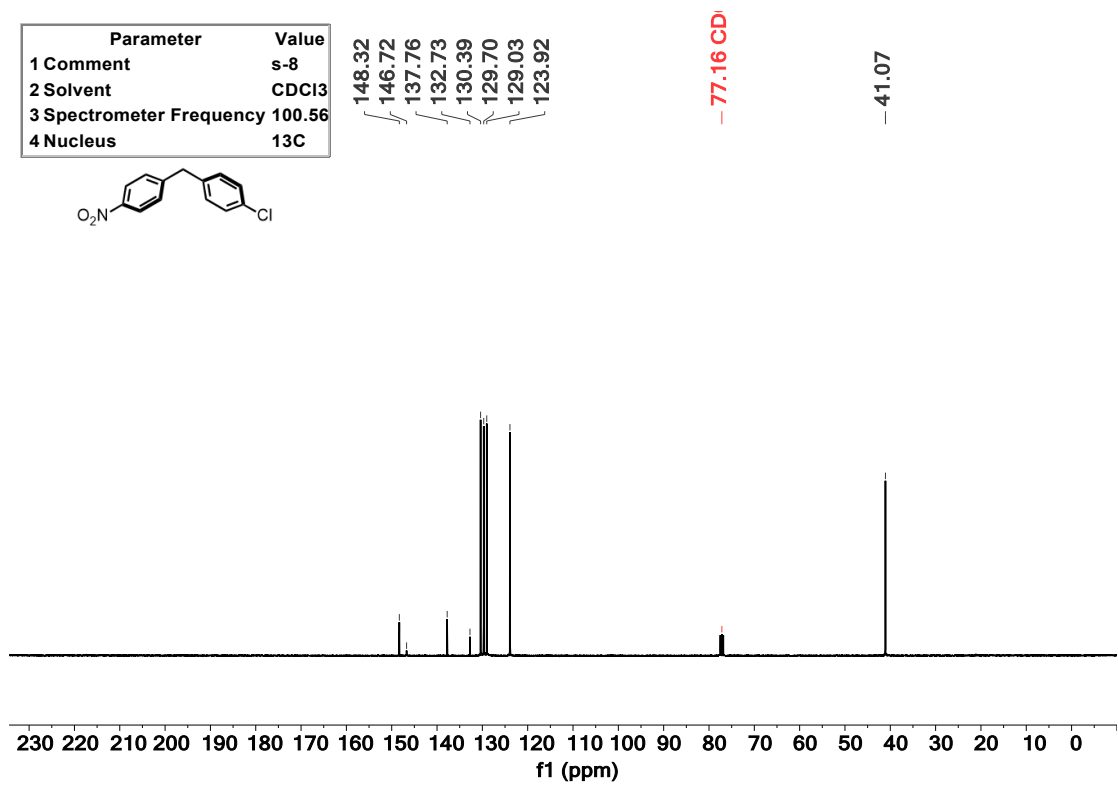
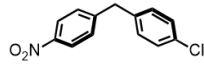
Parameter	Value
1 Comment	s-7
2 Solvent	CDCl ₃
3 Spectrometer Frequency	100.56
4 Nucleus	¹³ C



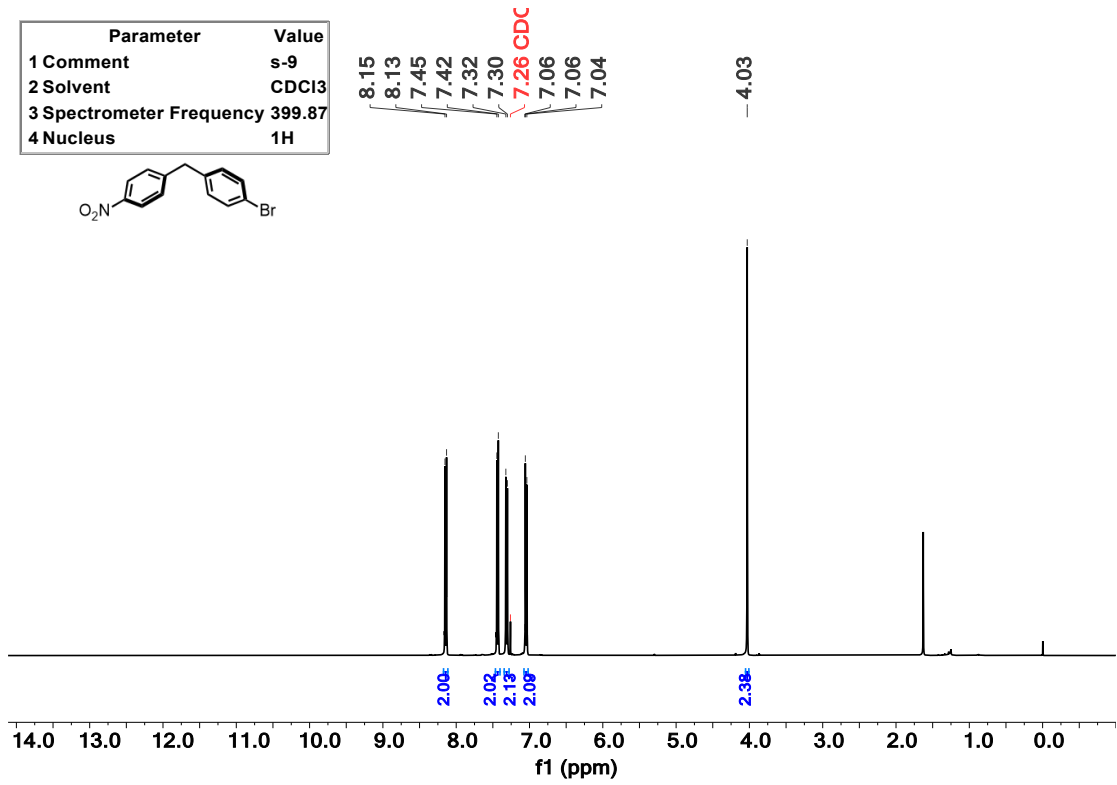
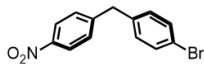
Parameter	Value
1 Comment	s-8
2 Solvent	CDCl3
3 Spectrometer Frequency	399.87
4 Nucleus	1H



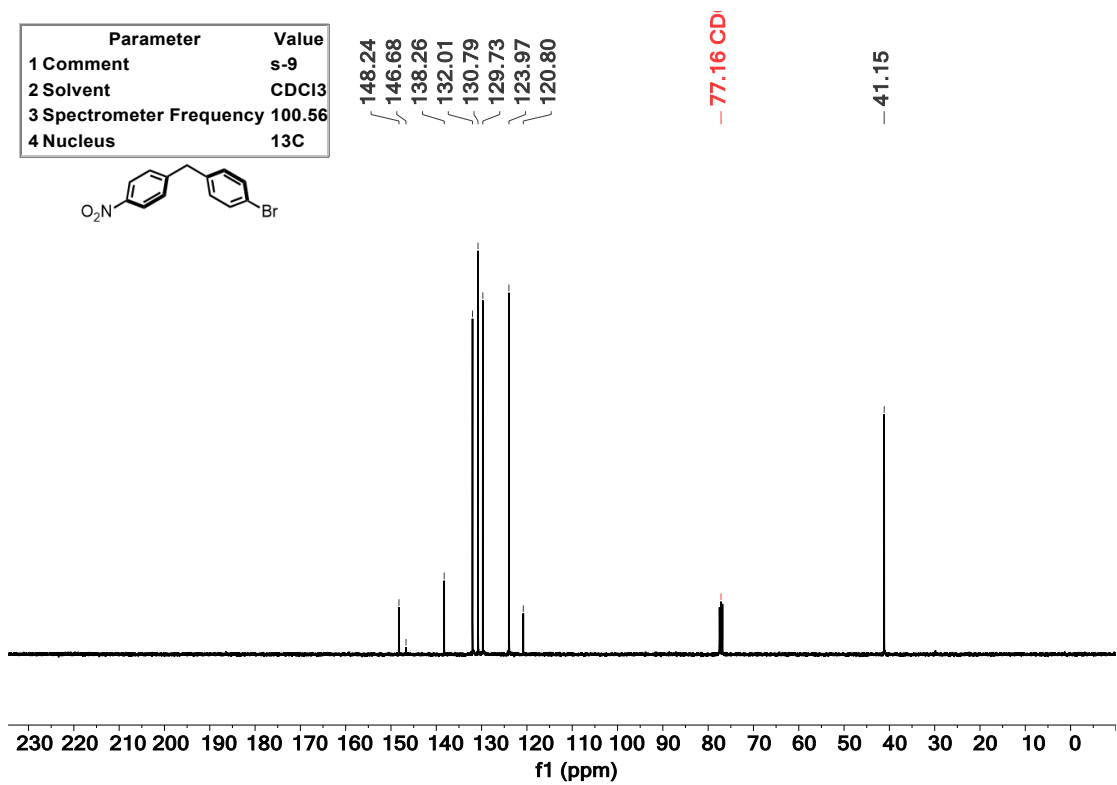
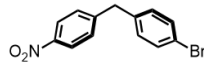
Parameter	Value
1 Comment	s-8
2 Solvent	CDCl3
3 Spectrometer Frequency	100.56
4 Nucleus	13C



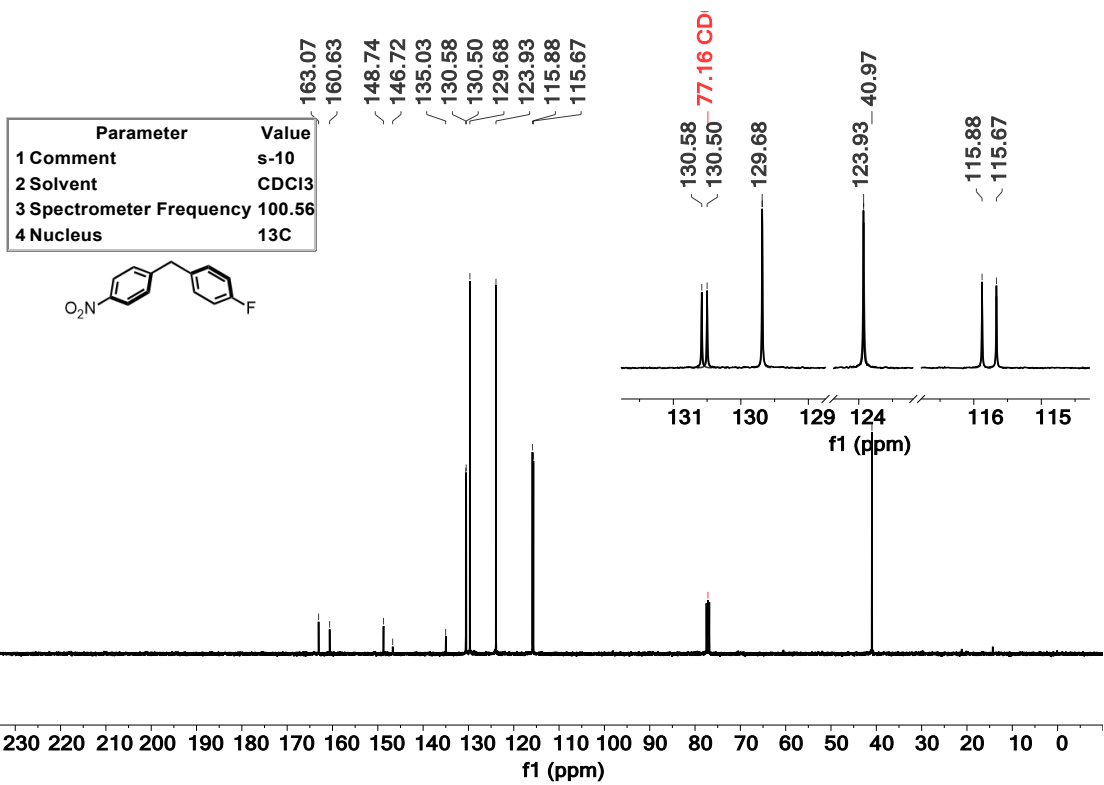
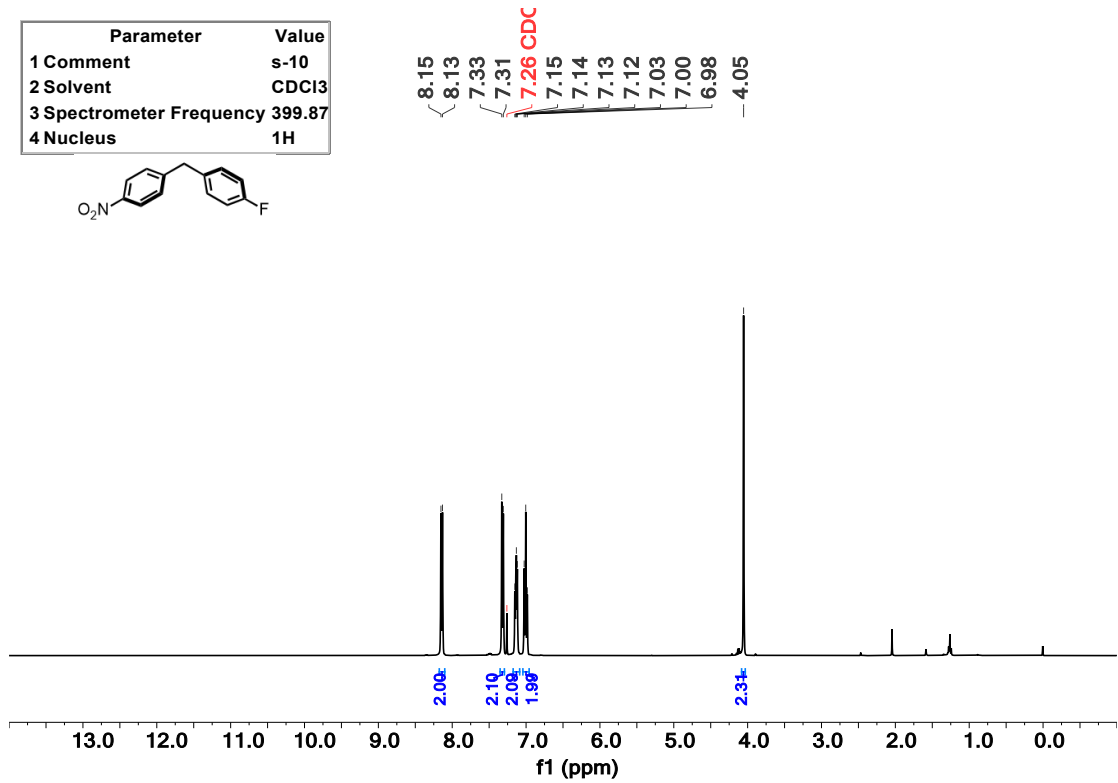
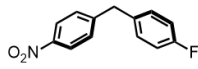
Parameter	Value
1 Comment	s-9
2 Solvent	CDCl3
3 Spectrometer Frequency	399.87
4 Nucleus	1H



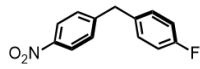
Parameter	Value
1 Comment	s-9
2 Solvent	CDCl3
3 Spectrometer Frequency	100.56
4 Nucleus	13C



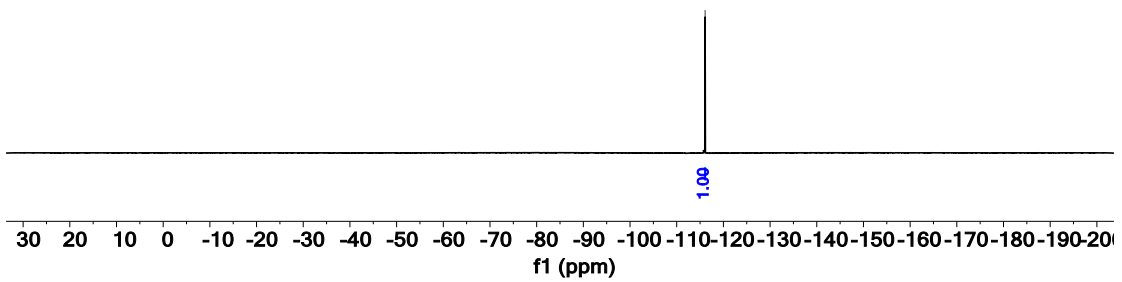
Parameter	Value
1 Comment	s-10
2 Solvent	CDCl3
3 Spectrometer Frequency	399.87
4 Nucleus	1H



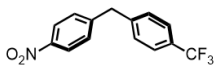
Parameter	Value
1 Comment	s-10
2 Solvent	CDCl3
3 Spectrometer Frequency	376.22
4 Nucleus	19F



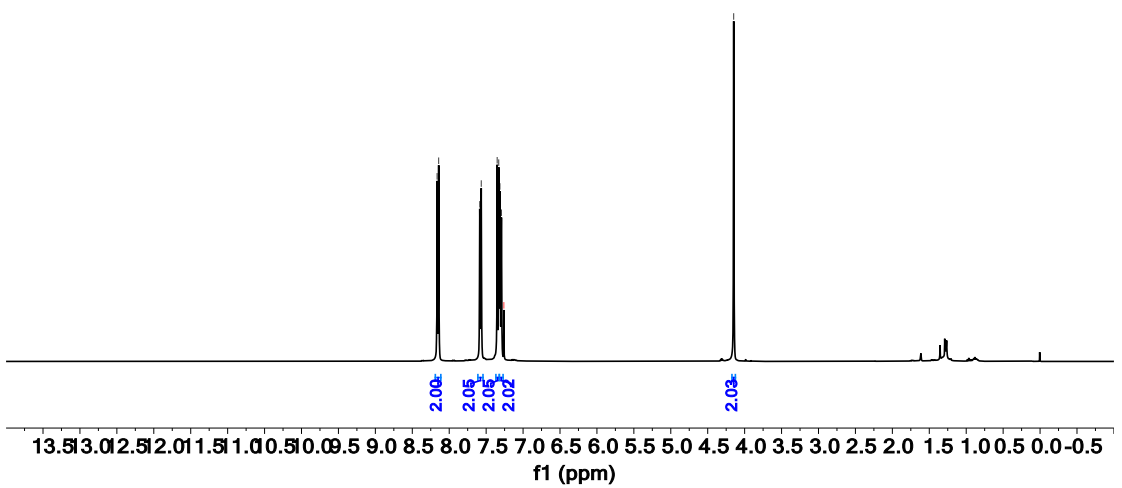
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-116.0
-116.1
-116.1

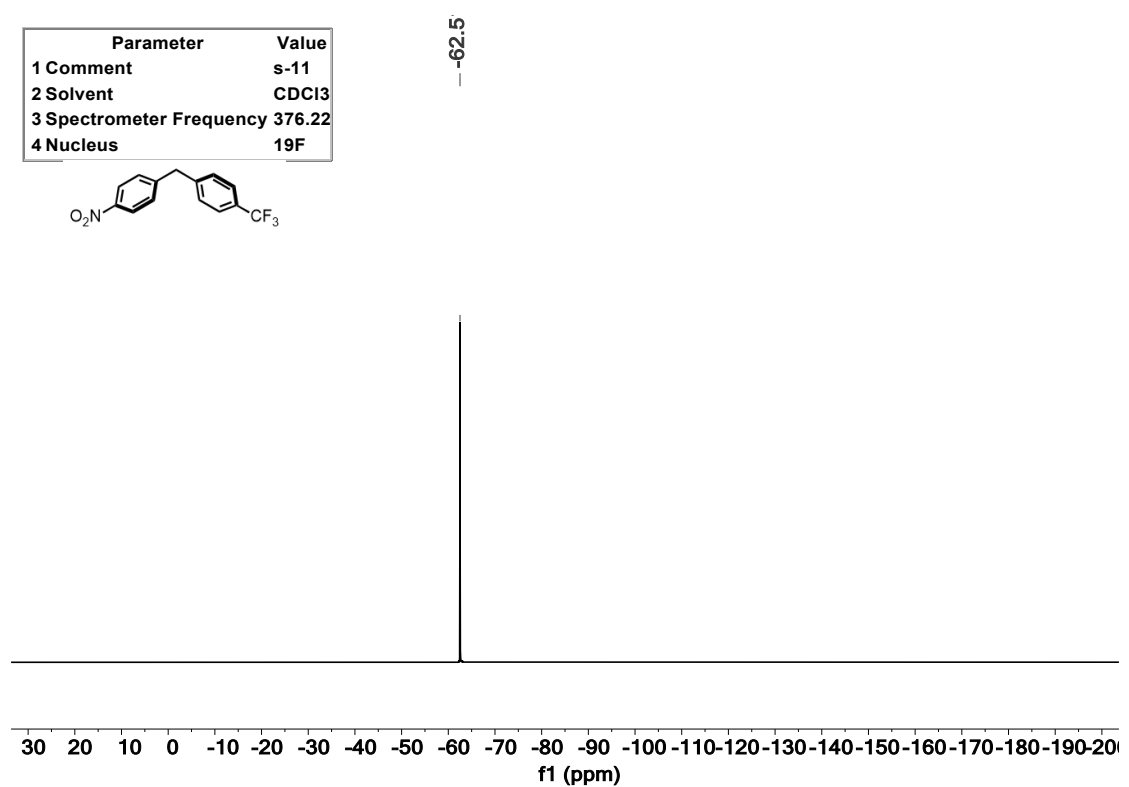
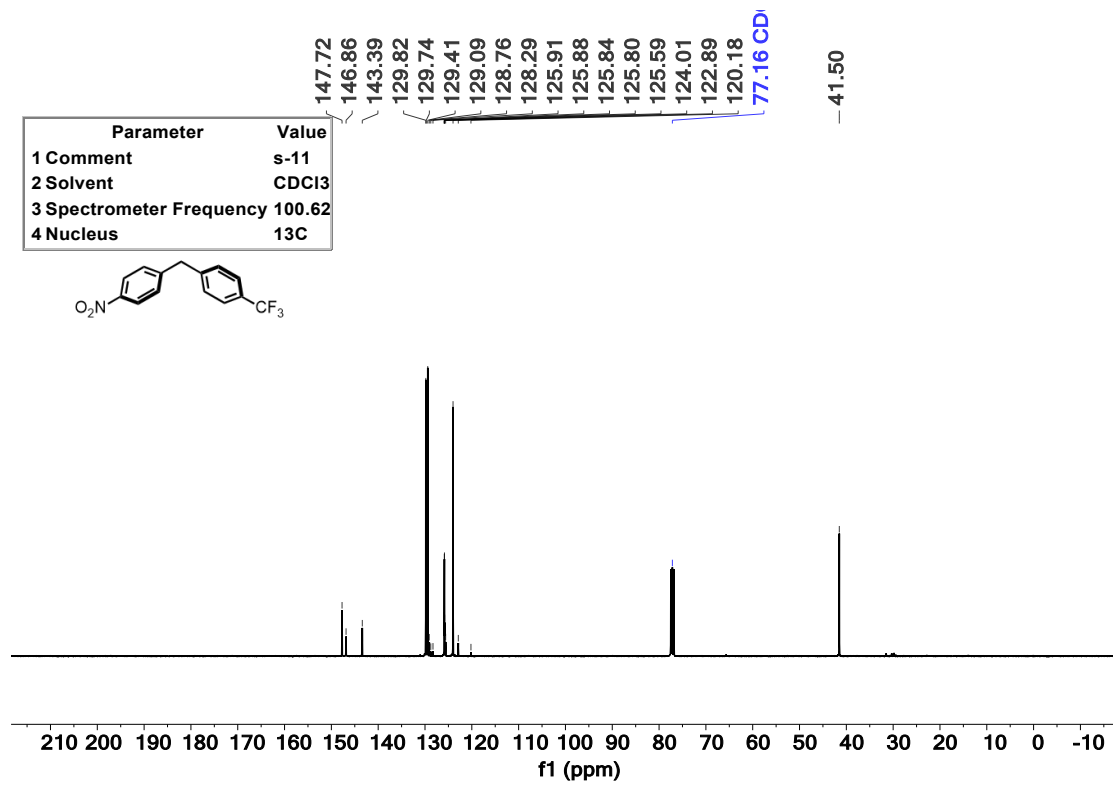


Parameter	Value
1 Comment	s-11
2 Solvent	CDCl3
3 Spectrometer Frequency	400.13
4 Nucleus	1H

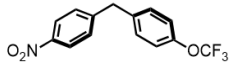


8.16
8.14
7.59
7.57
7.35
7.33
7.31
7.29
7.26 CDC
-4.15

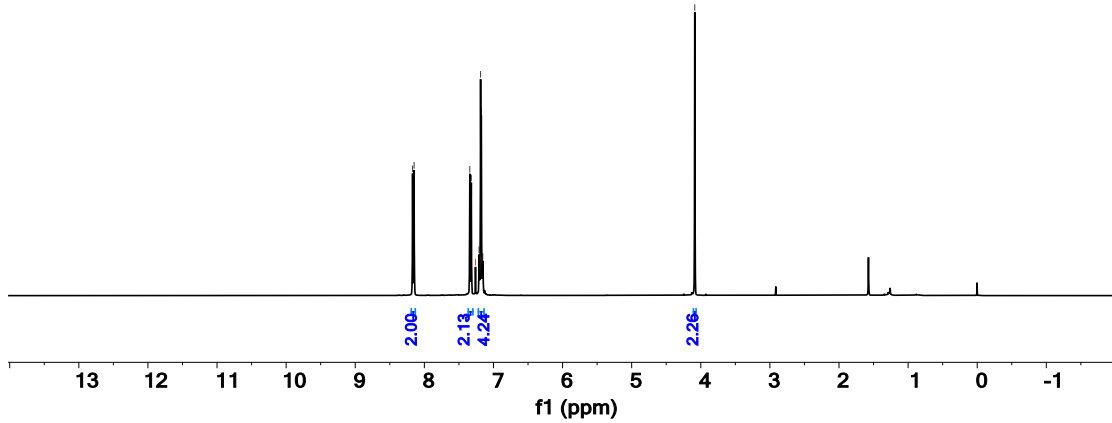




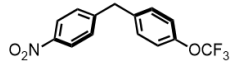
Parameter	Value
1 Comment	s-12
2 Solvent	CDCl3
3 Spectrometer Frequency	399.87
4 Nucleus	1H



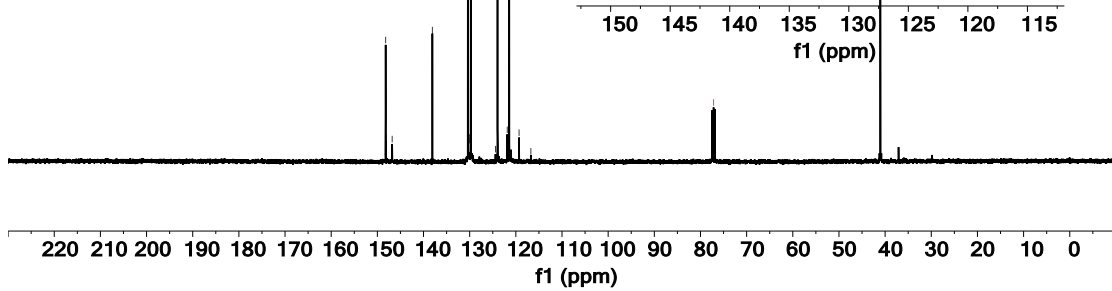
8.17
8.15
7.34
7.32
7.26 CDC
7.21
7.20
7.19
7.18
7.15
7.15
- 4.09



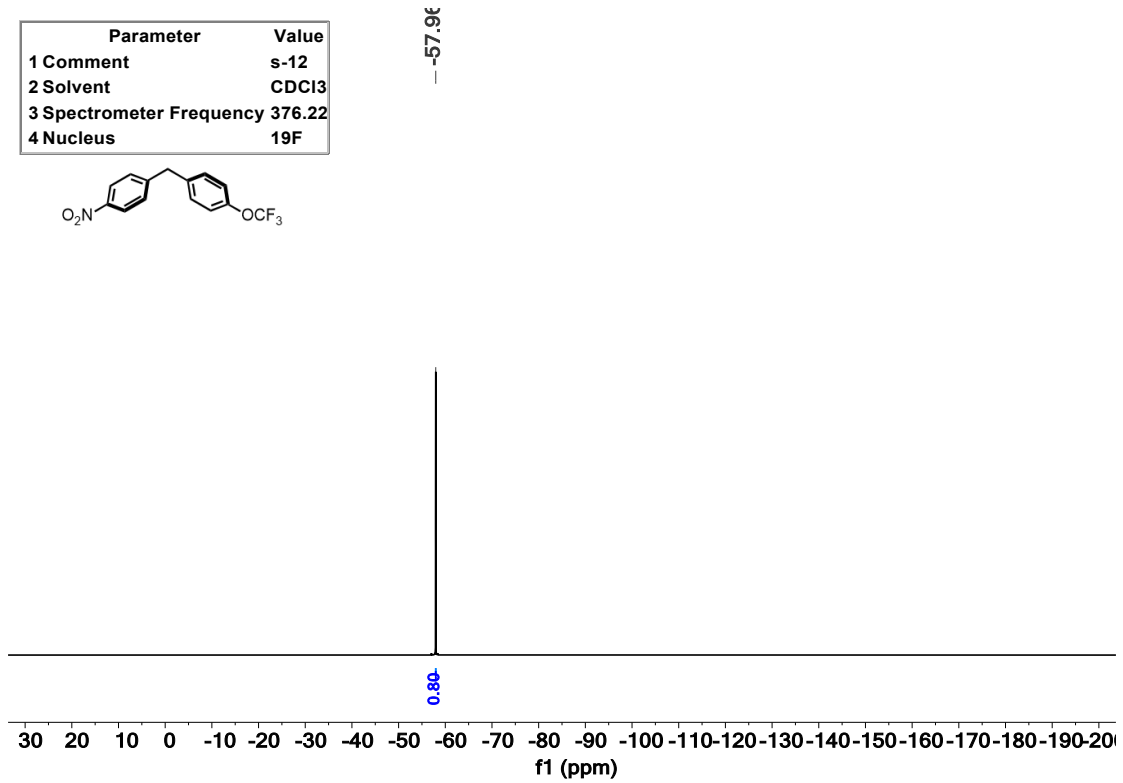
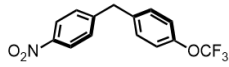
Parameter	Value
1 Comment	s-12
2 Solvent	CDCl3
3 Spectrometer Frequency	100.56
4 Nucleus	13C



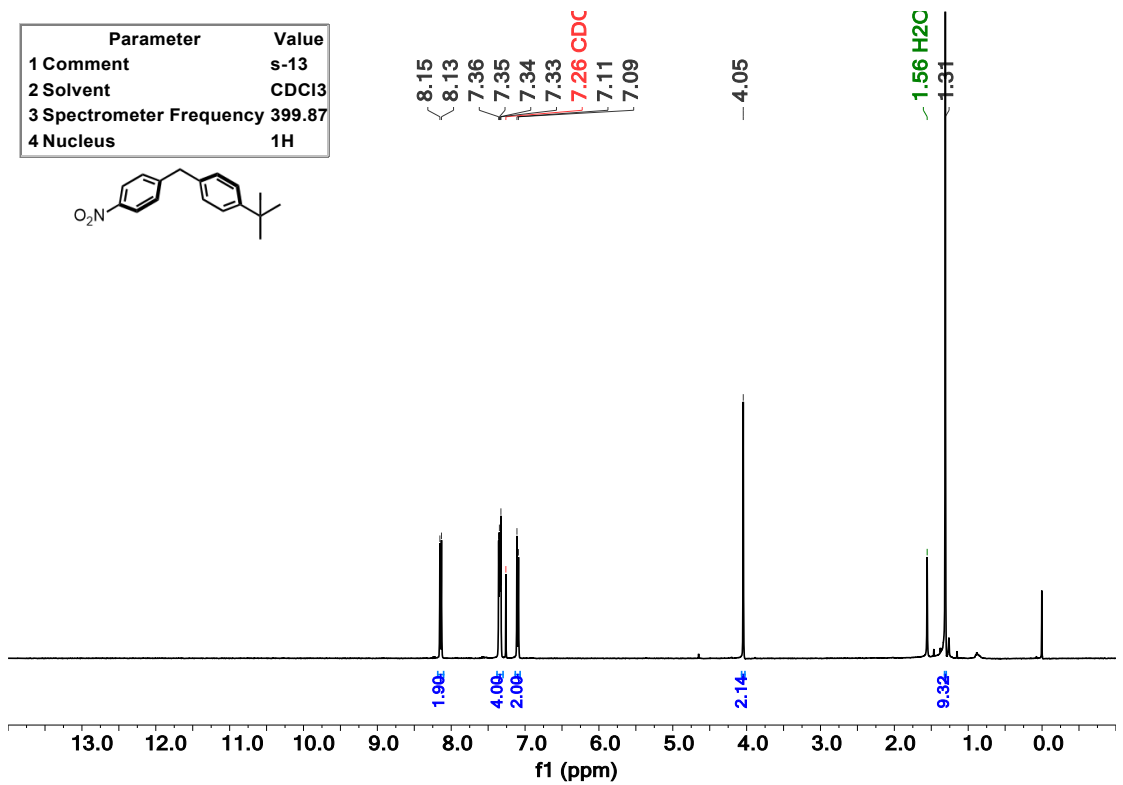
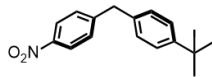
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148.14
148.12
146.79
138.08
130.37
129.76
124.41
123.96
121.86
121.43
119.30
116.75
- 77.16 CD
148.21
148.17
148.16
148.14
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138.08
130.37
129.76
124.41
123.96
121.86
121.43
119.30
116.75

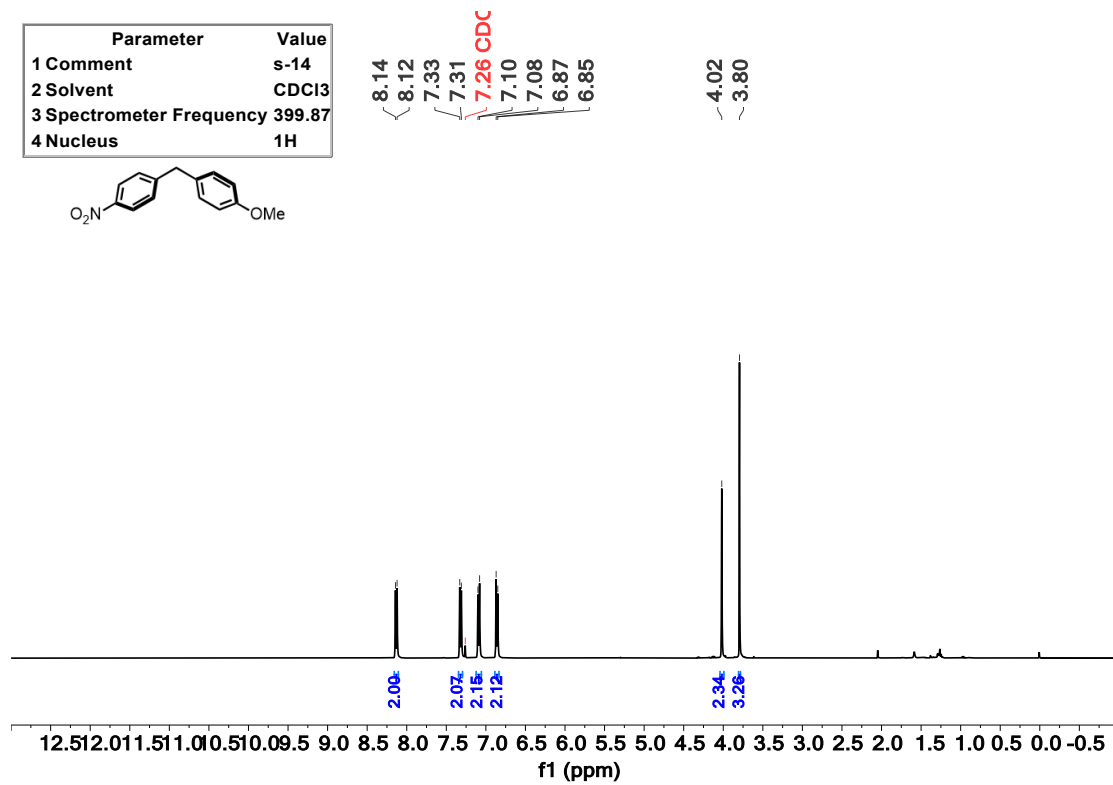
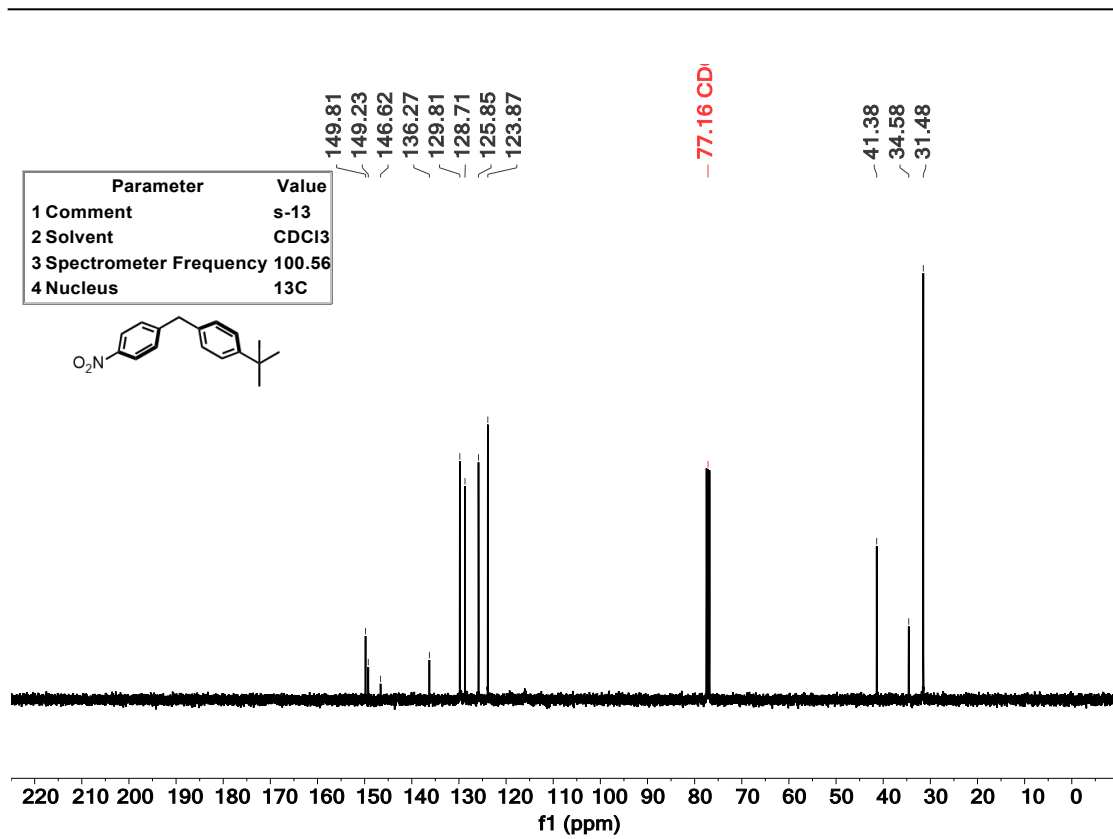


Parameter	Value
1 Comment	s-12
2 Solvent	CDCl3
3 Spectrometer Frequency	376.22
4 Nucleus	19F

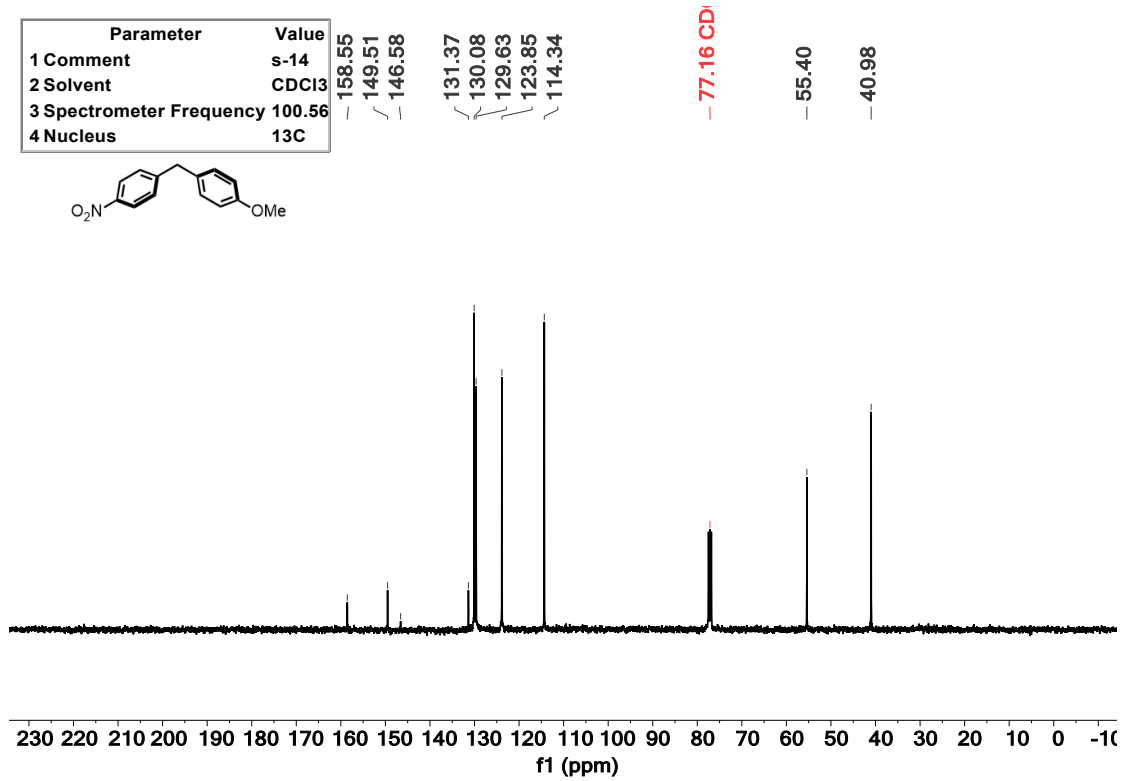
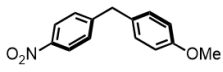


Parameter	Value
1 Comment	s-13
2 Solvent	CDCl3
3 Spectrometer Frequency	399.87
4 Nucleus	1H

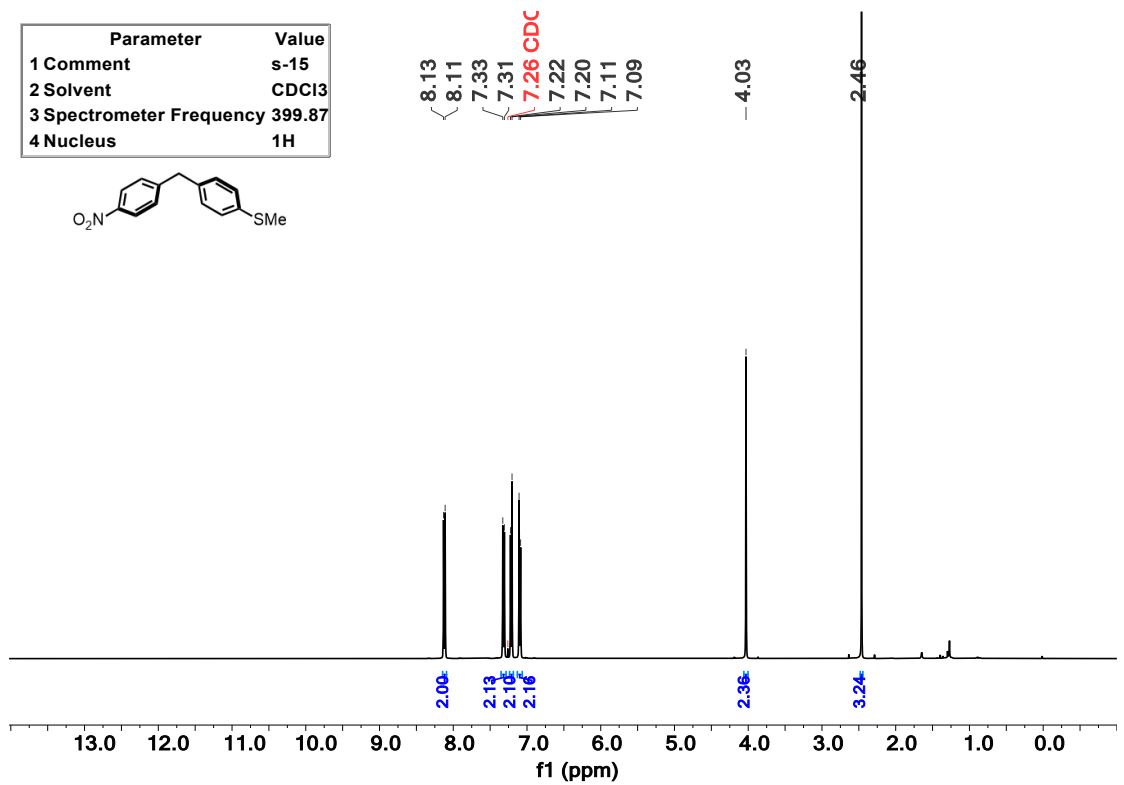
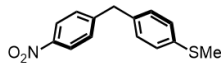




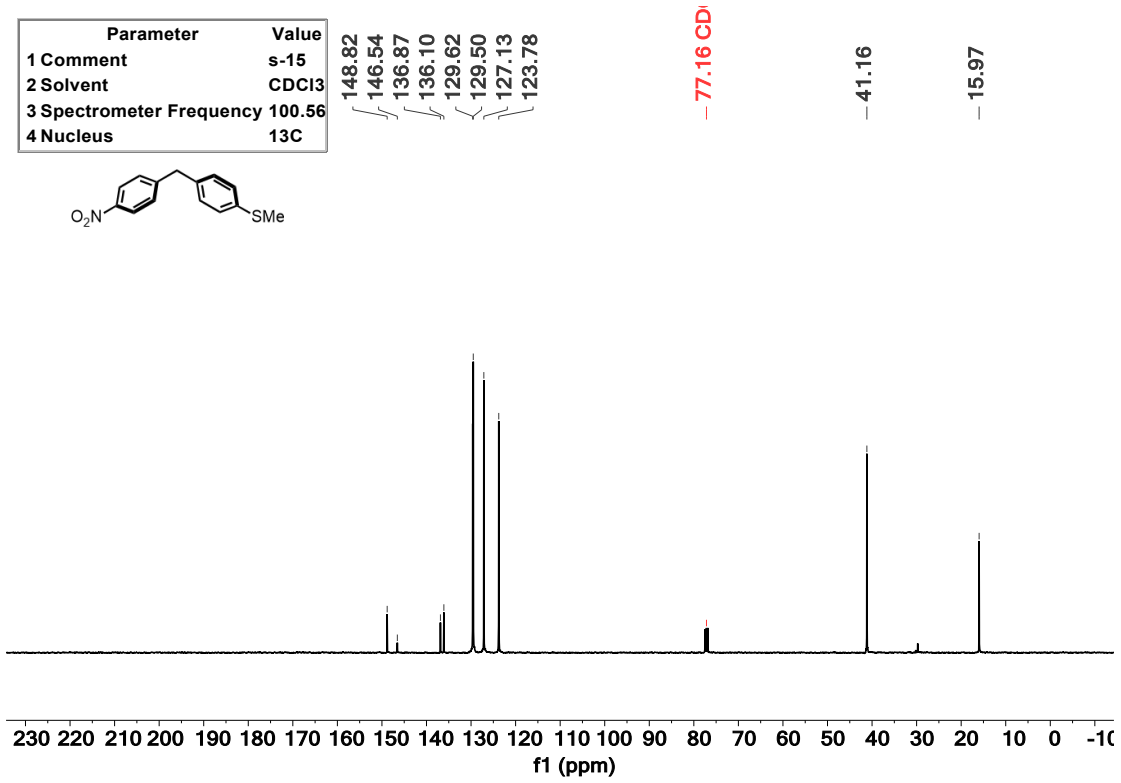
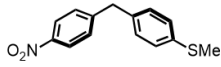
Parameter	Value
1 Comment	s-14
2 Solvent	CDCl ₃
3 Spectrometer Frequency	100.56
4 Nucleus	¹³ C



Parameter	Value
1 Comment	s-15
2 Solvent	CDCl ₃
3 Spectrometer Frequency	399.87
4 Nucleus	¹ H

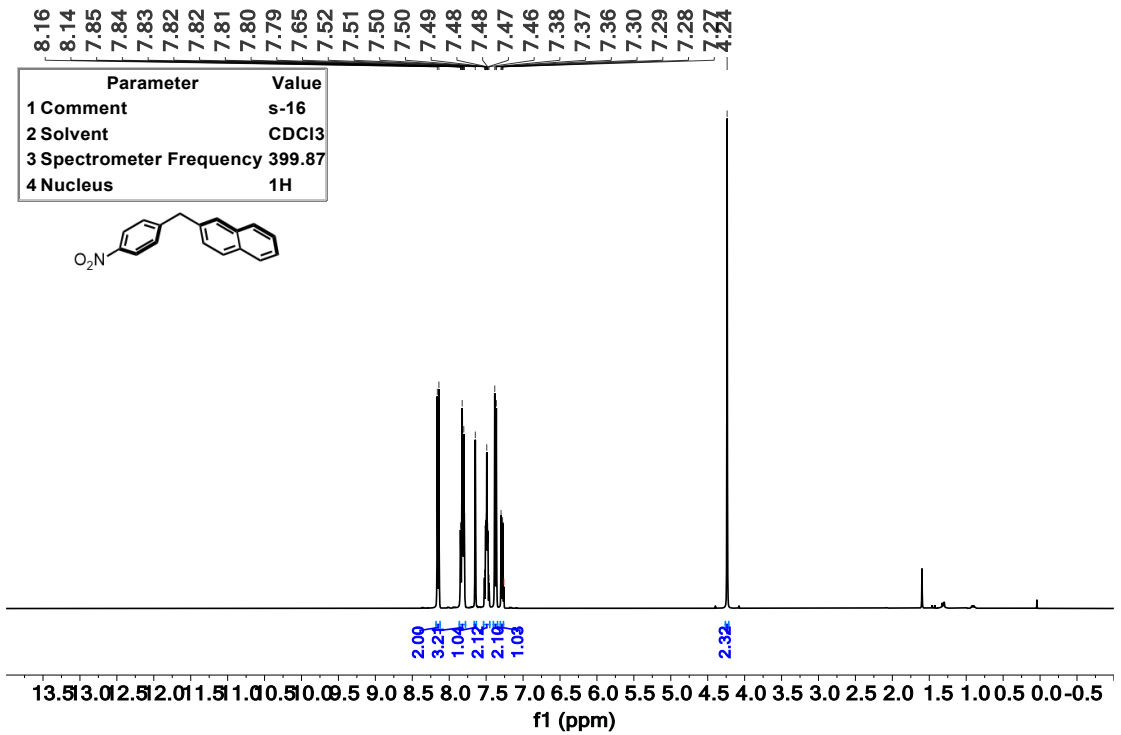
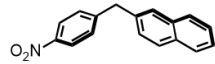


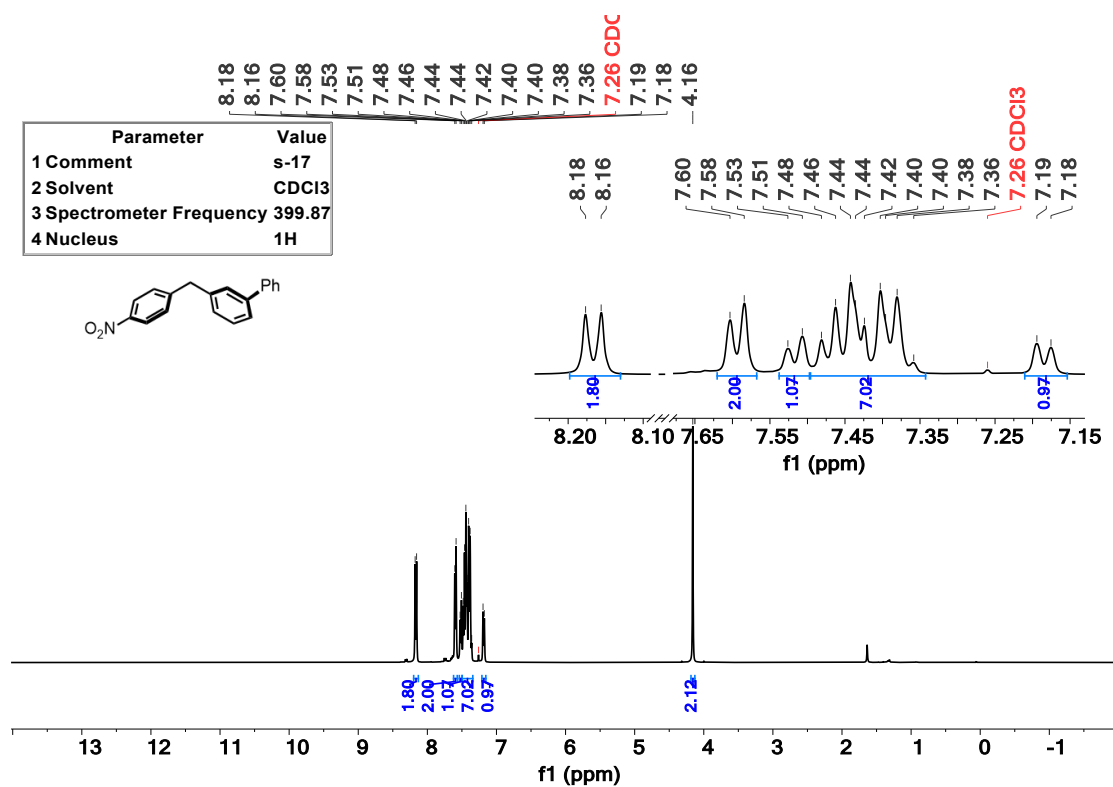
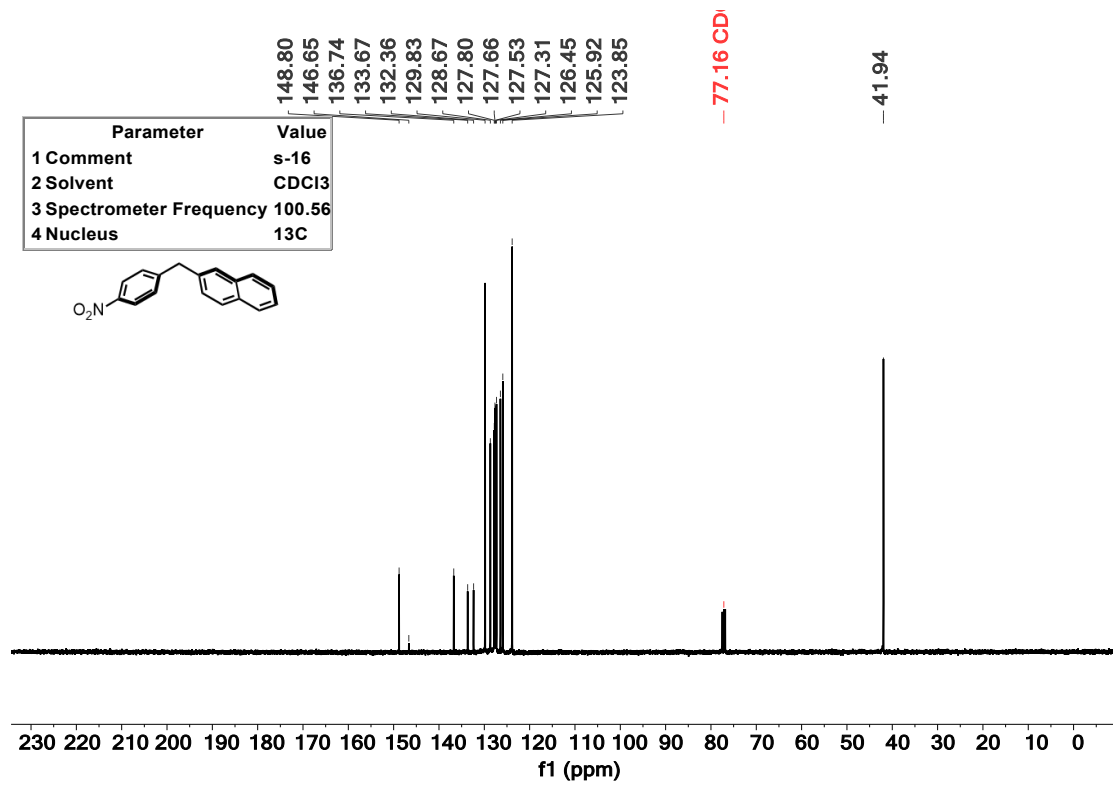
Parameter	Value
1 Comment	s-15
2 Solvent	CDCl3
3 Spectrometer Frequency	100.56
4 Nucleus	13C

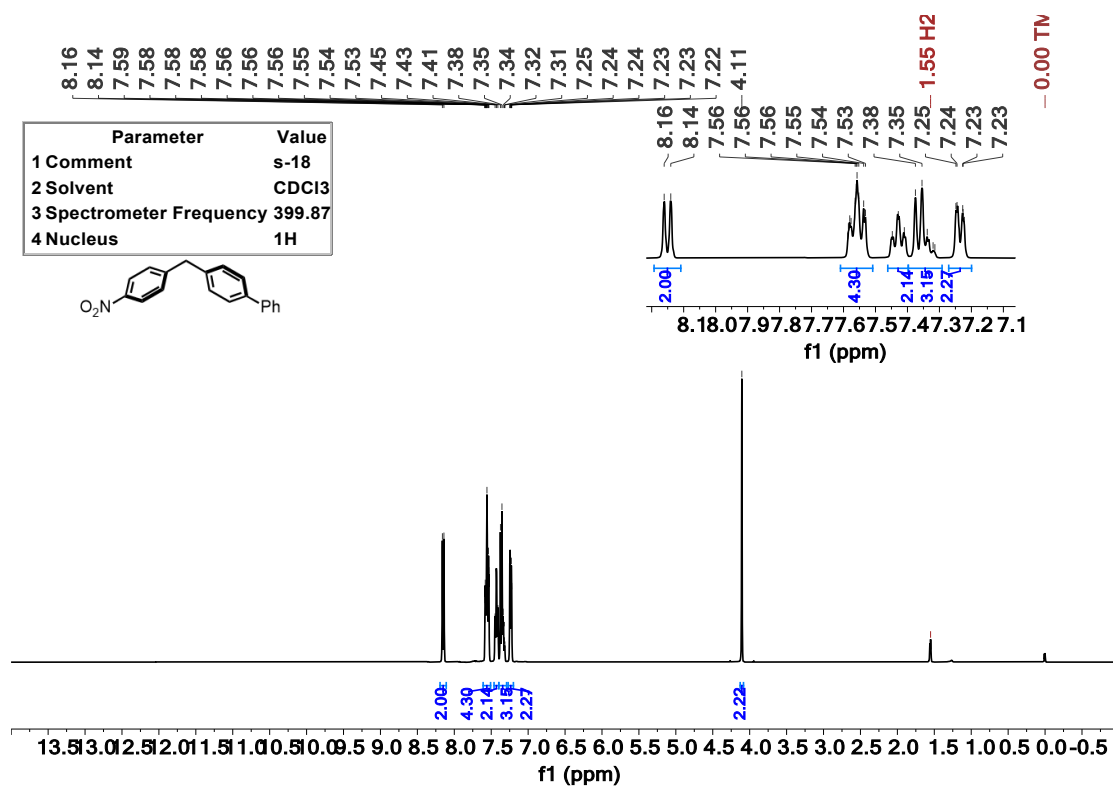
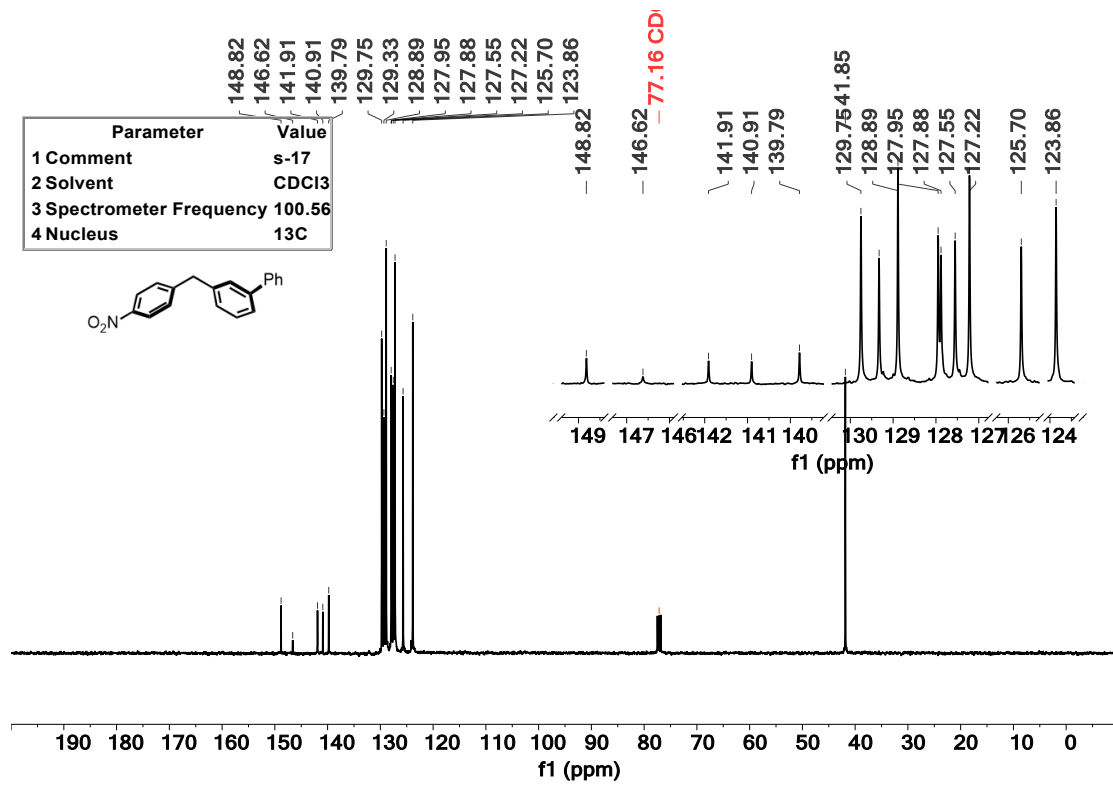


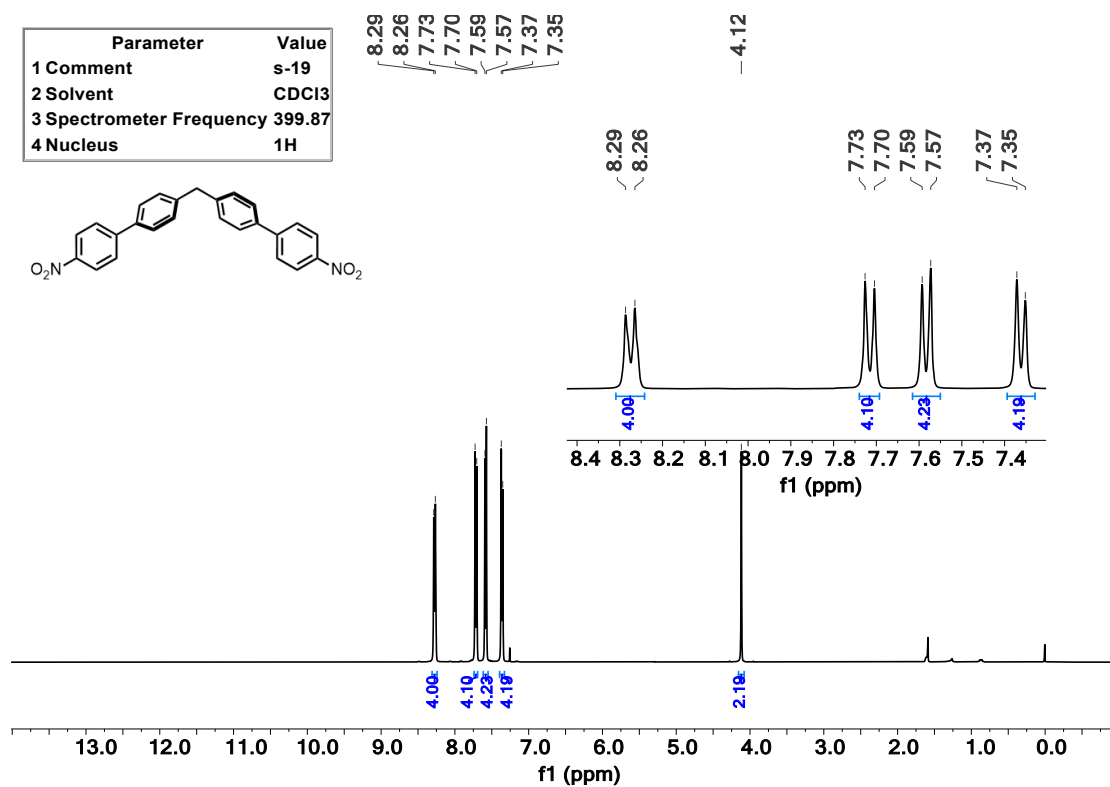
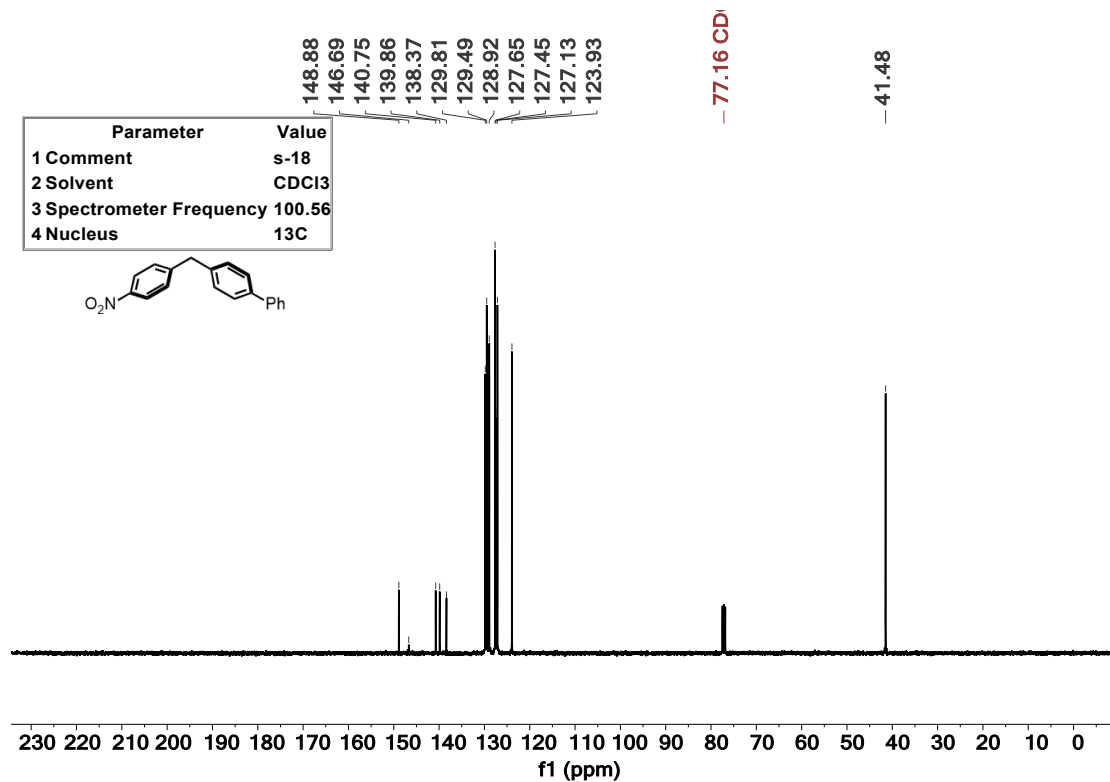
8.16
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7.84
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7.82
7.82
7.81
7.80
7.79
7.65
7.52
7.51
7.50
7.50
7.49
7.48
7.48
7.47
7.46
7.38
7.37
7.36
7.30
7.29
7.28
7.27
4.27

Parameter	Value
1 Comment	s-16
2 Solvent	CDCl3
3 Spectrometer Frequency	399.87
4 Nucleus	1H

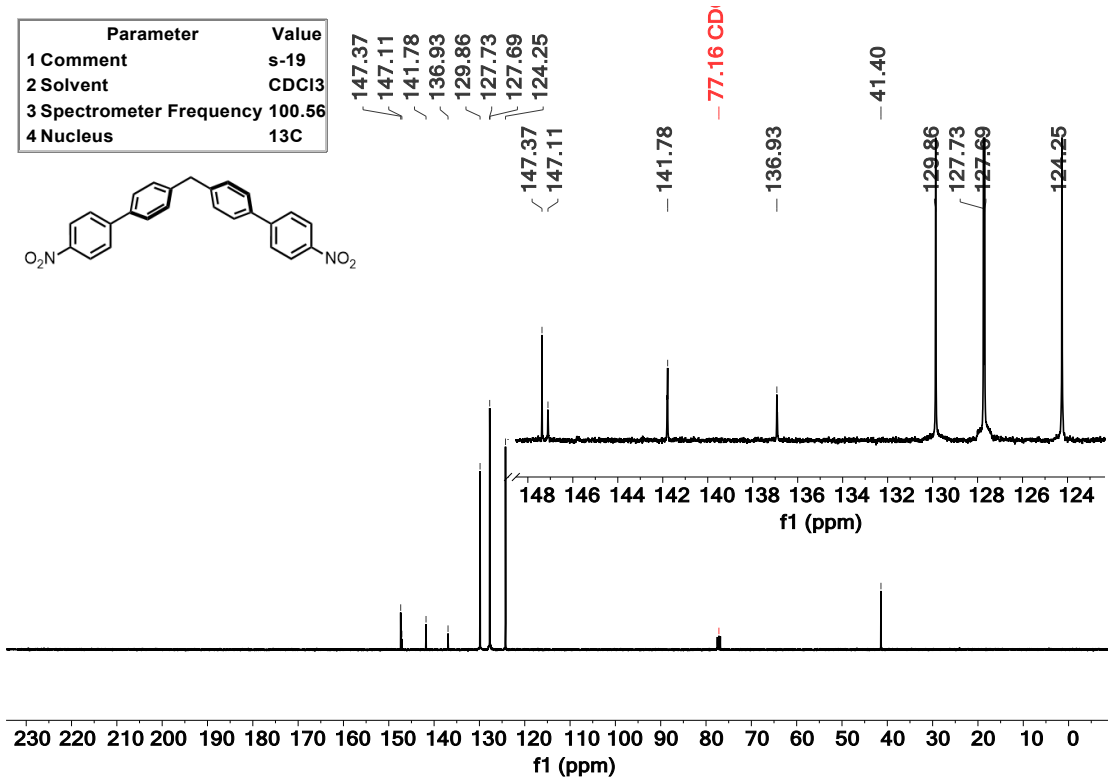
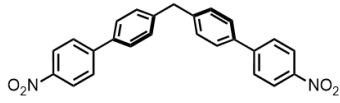




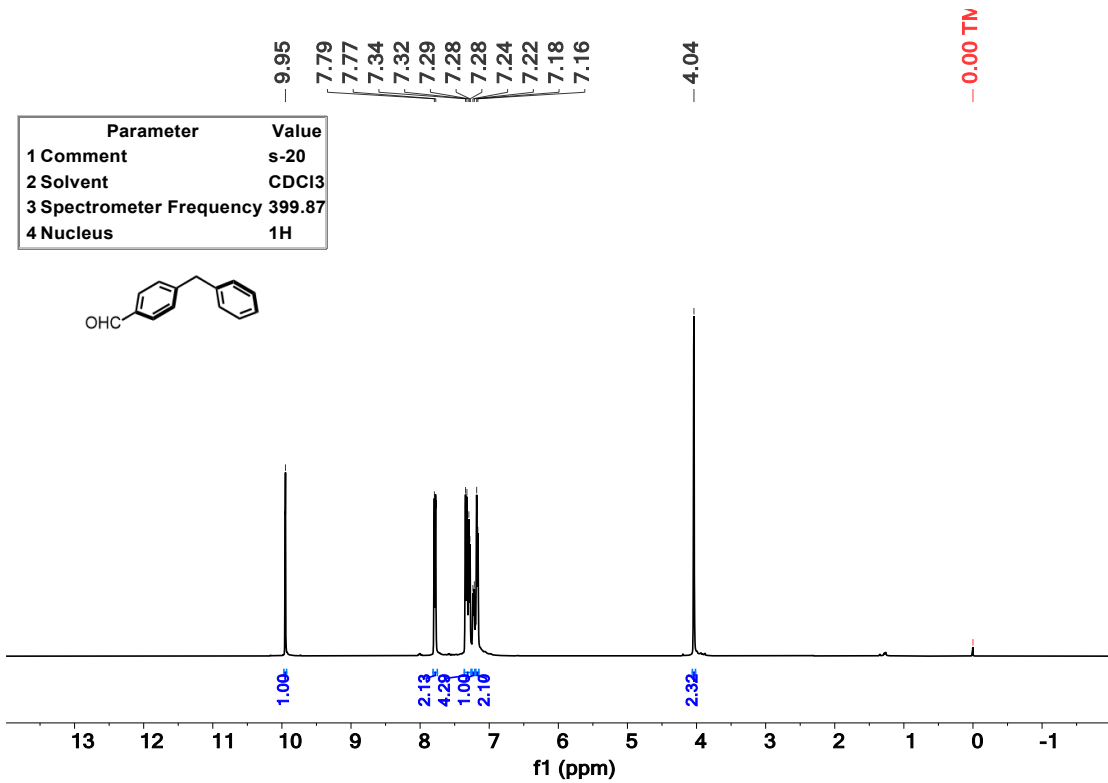
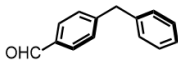


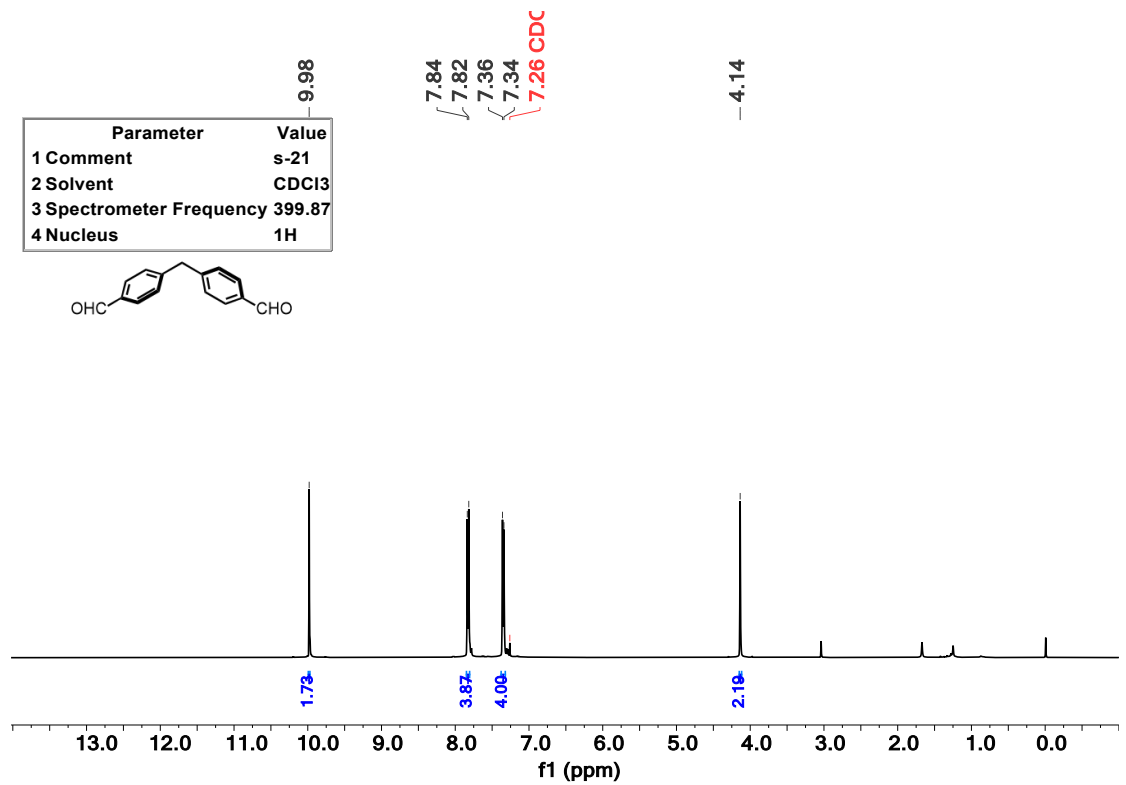
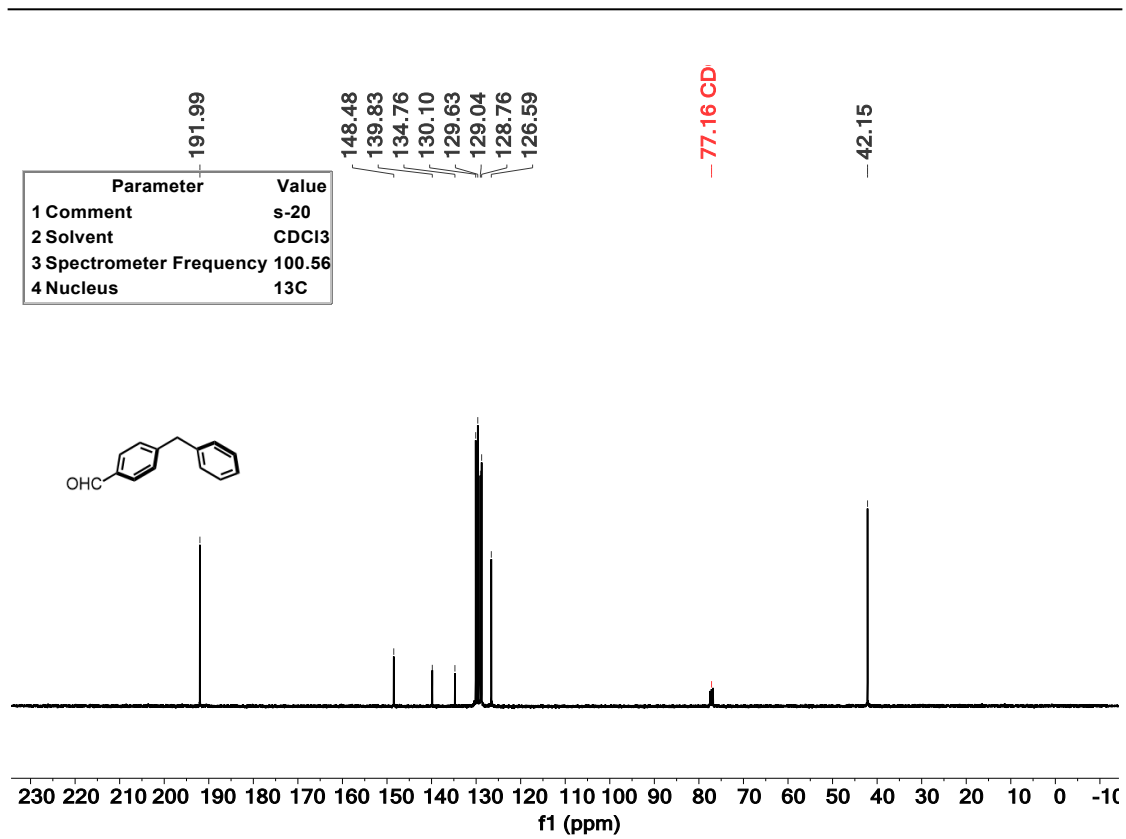


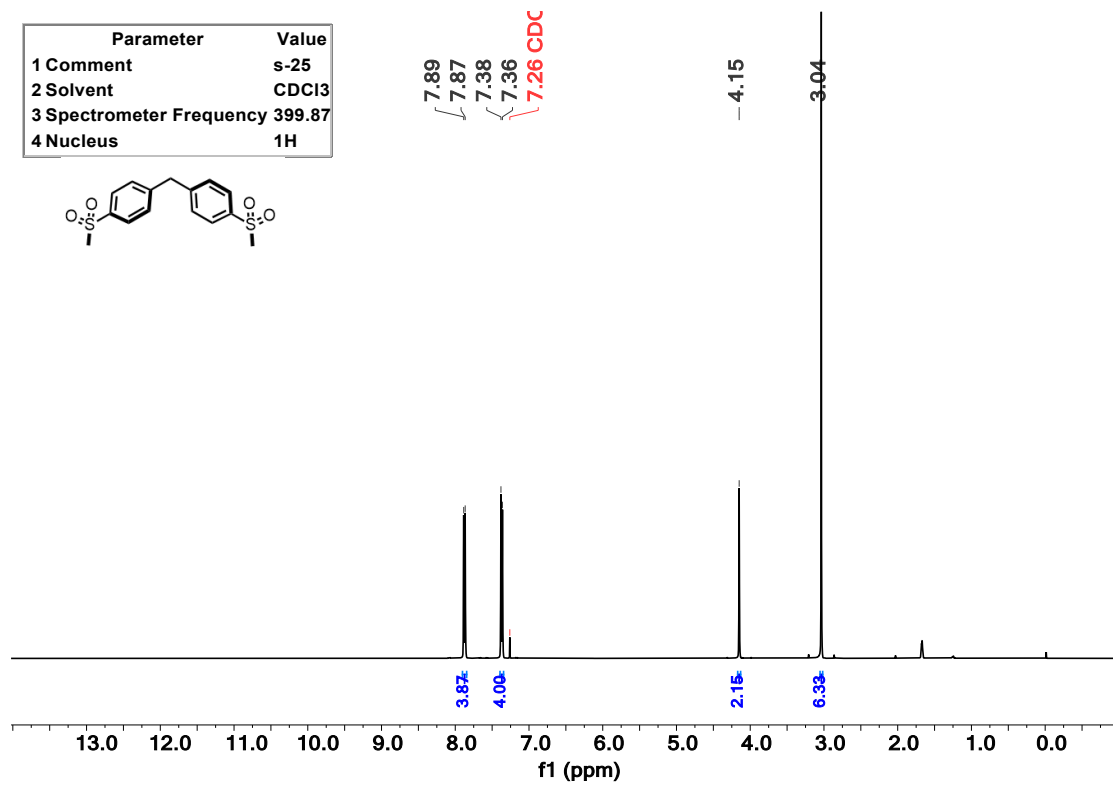
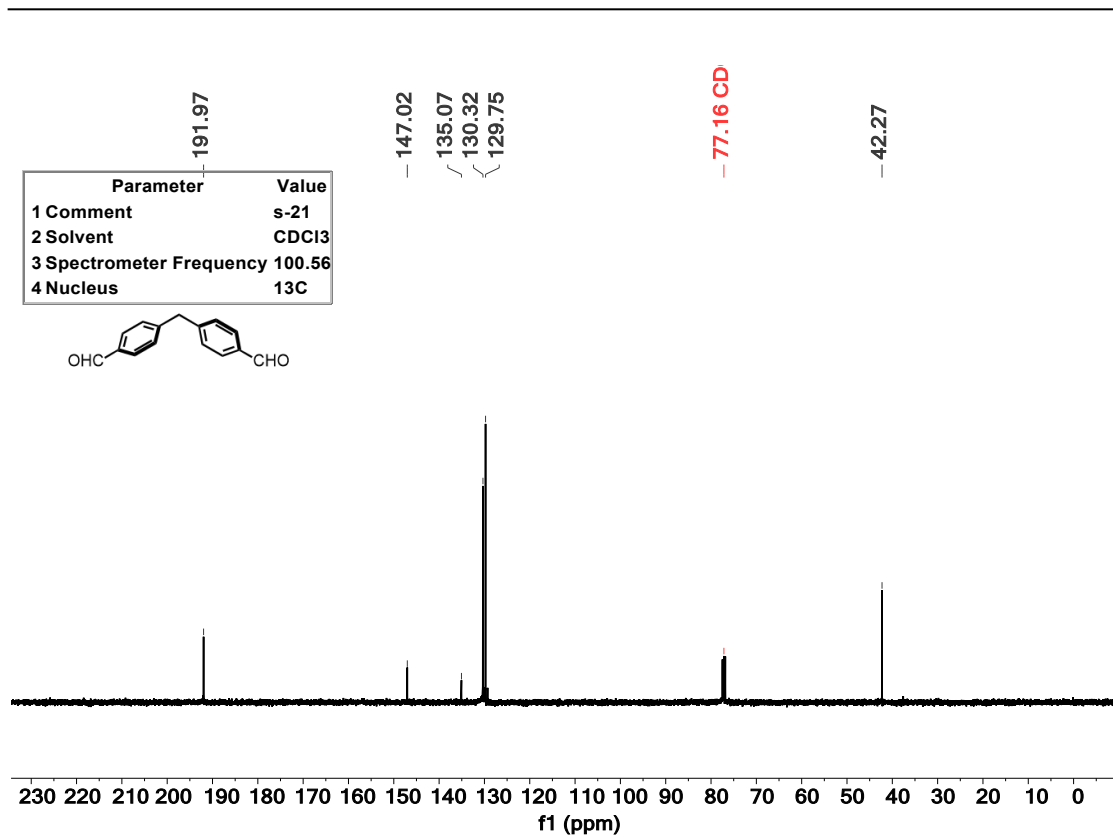
Parameter	Value
1 Comment	s-19
2 Solvent	CDCl3
3 Spectrometer Frequency	100.56
4 Nucleus	13C



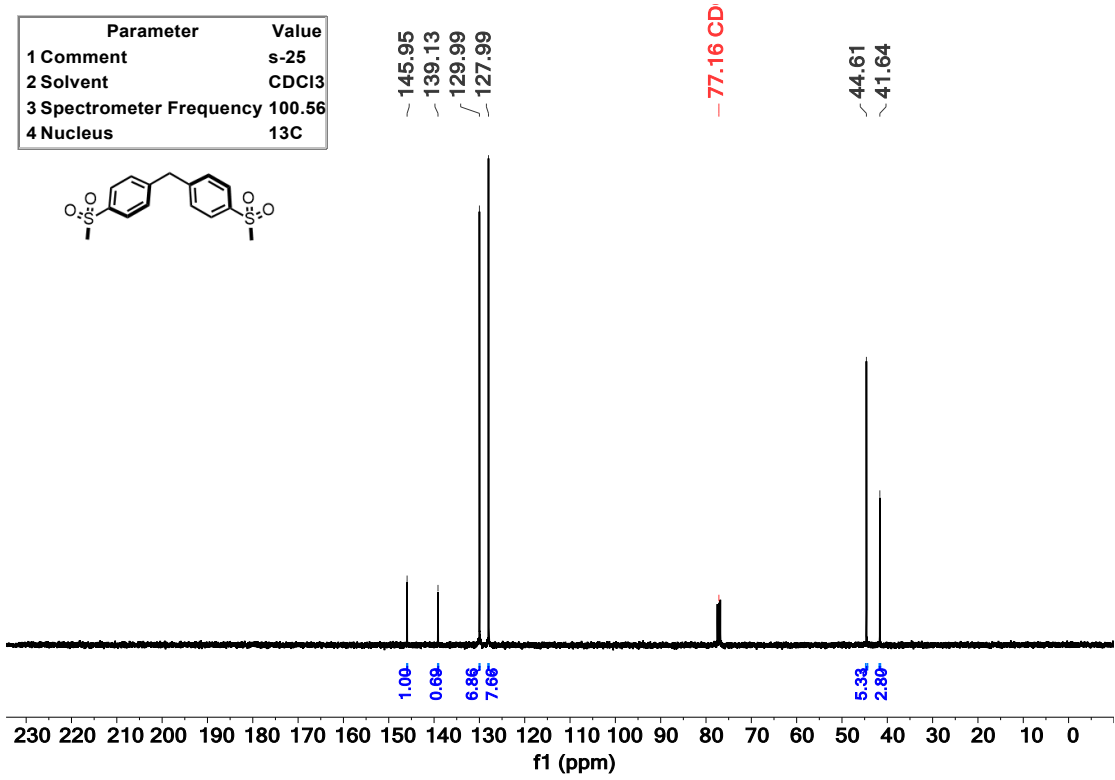
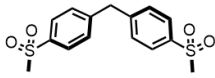
Parameter	Value
1 Comment	s-20
2 Solvent	CDCl3
3 Spectrometer Frequency	399.87
4 Nucleus	1H



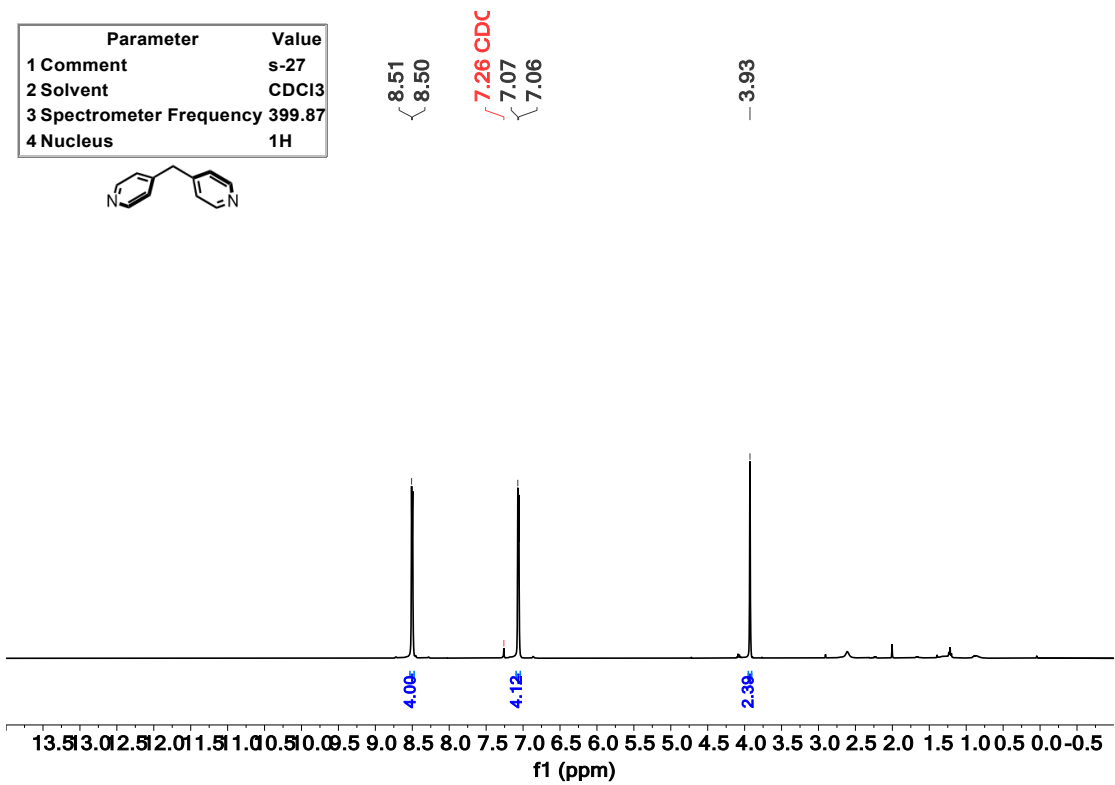
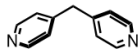




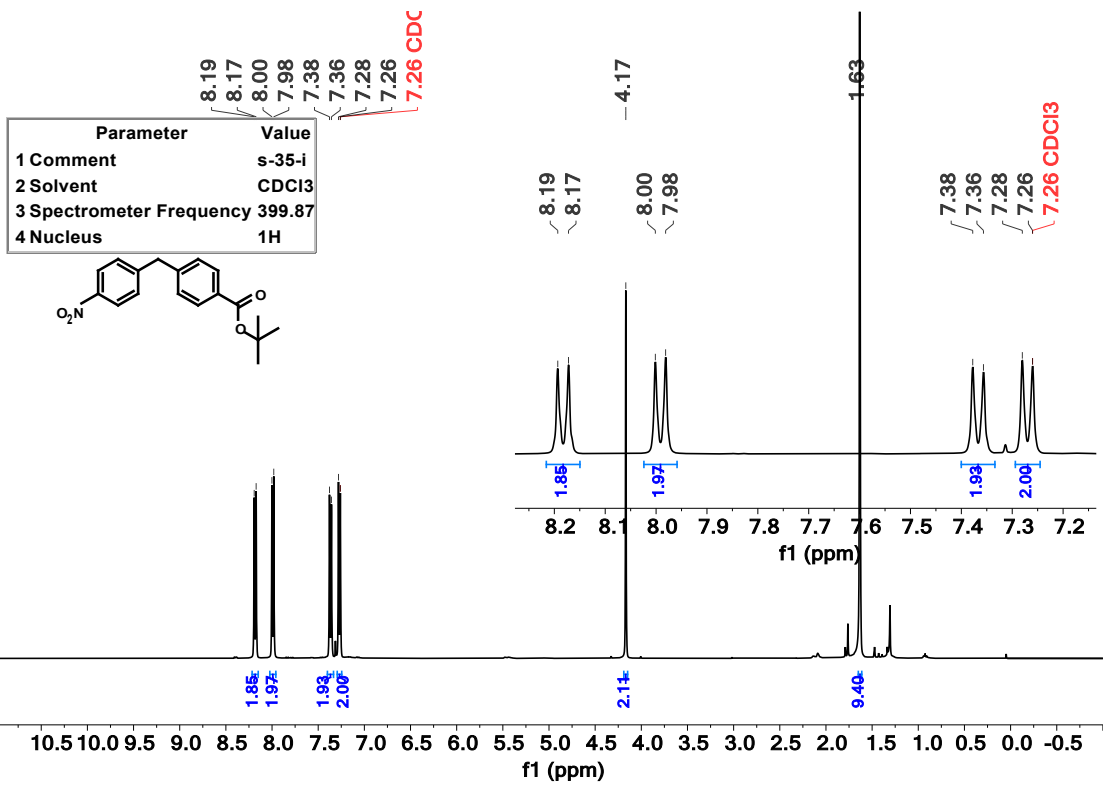
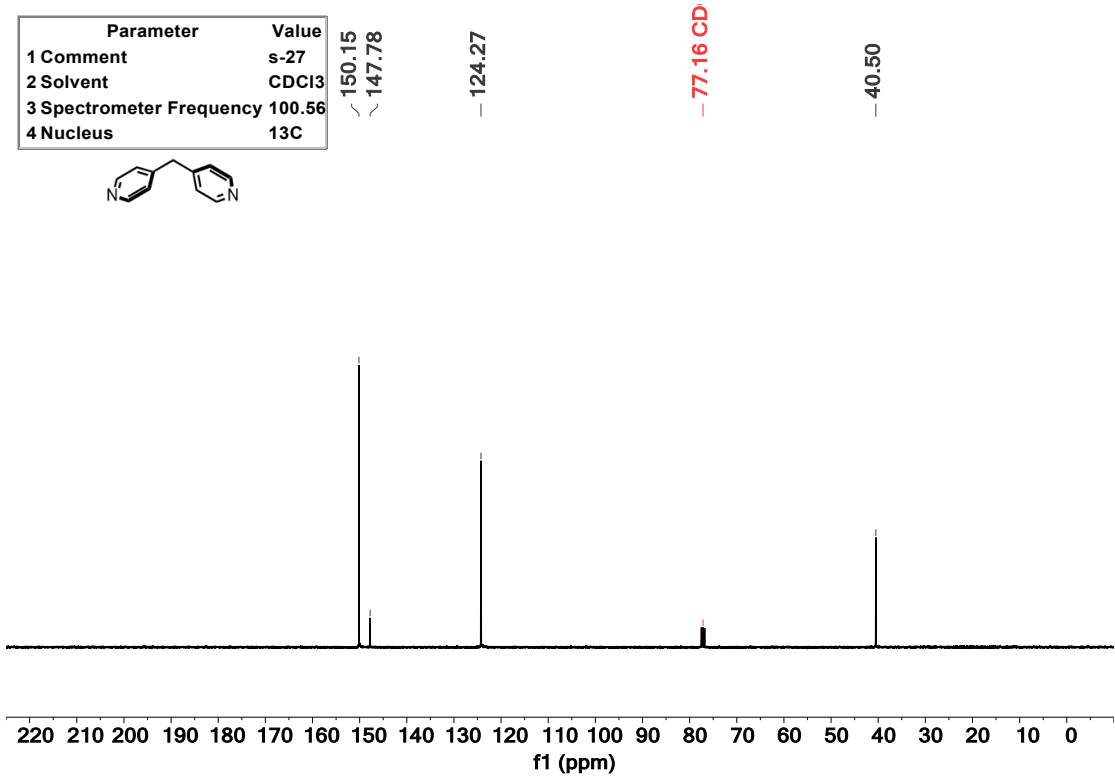
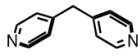
Parameter	Value
1 Comment	s-25
2 Solvent	CDCI3
3 Spectrometer Frequency	100.56
4 Nucleus	13C

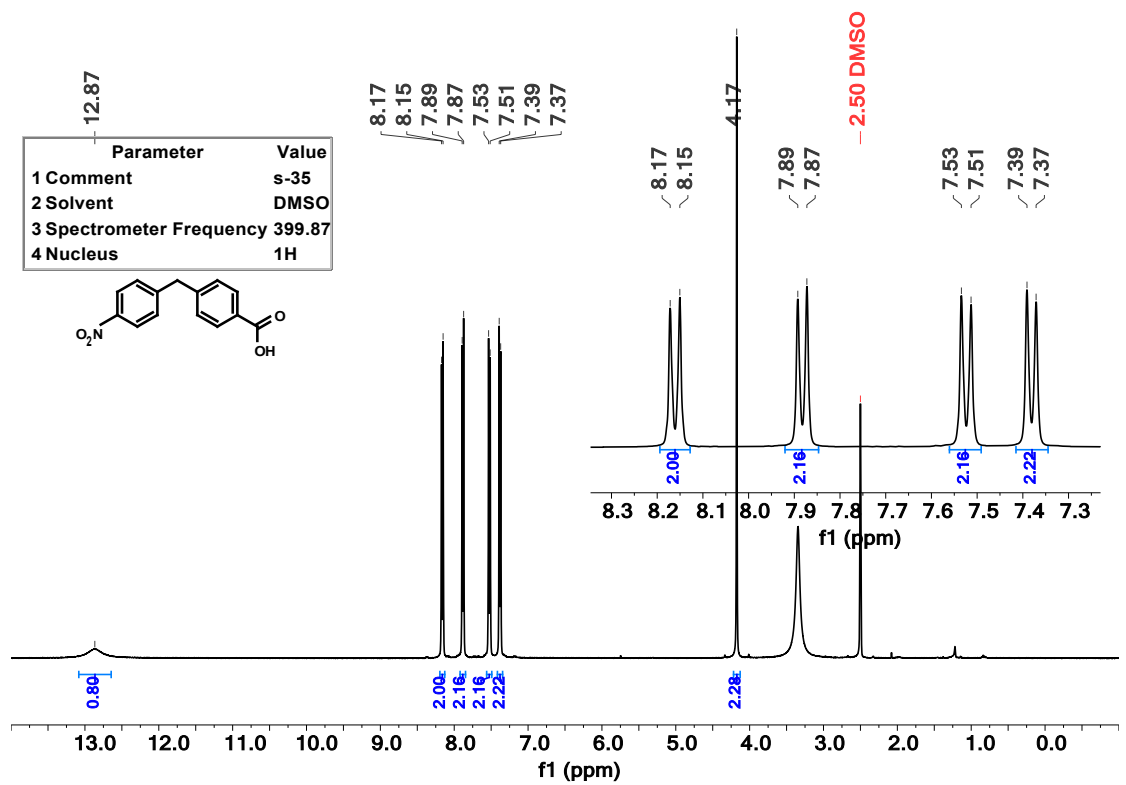
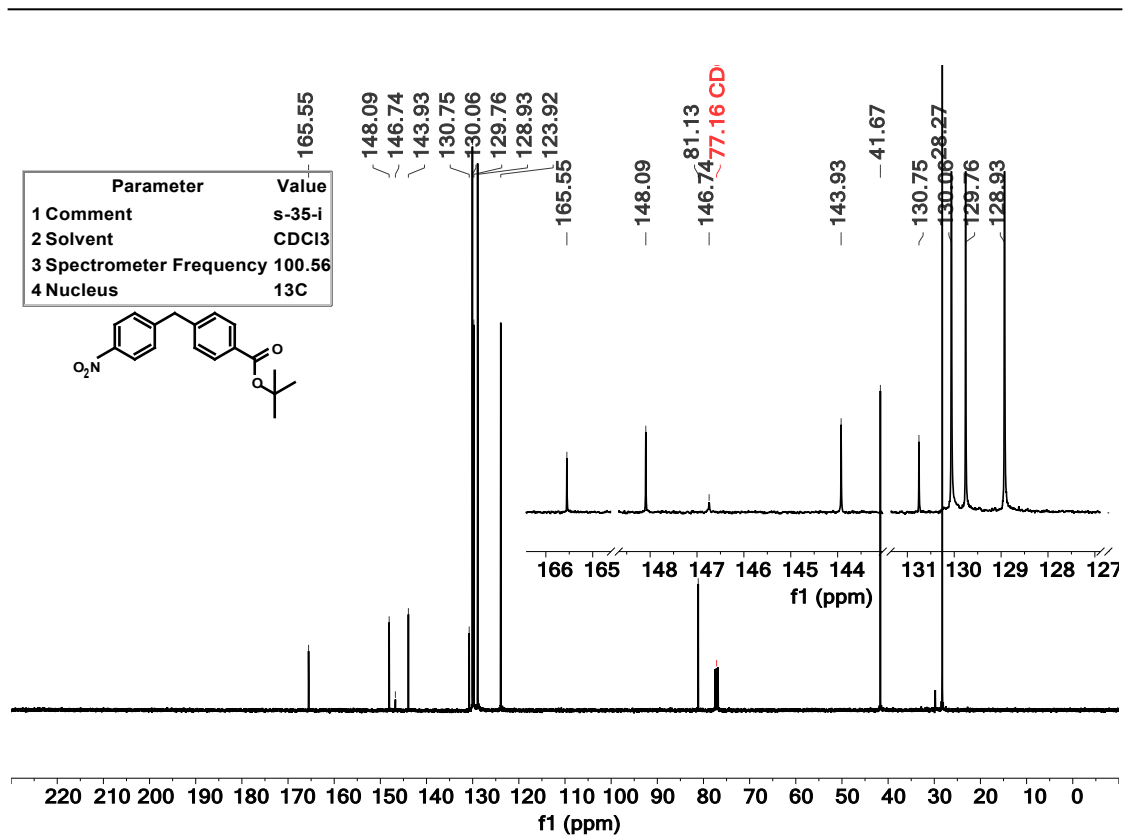


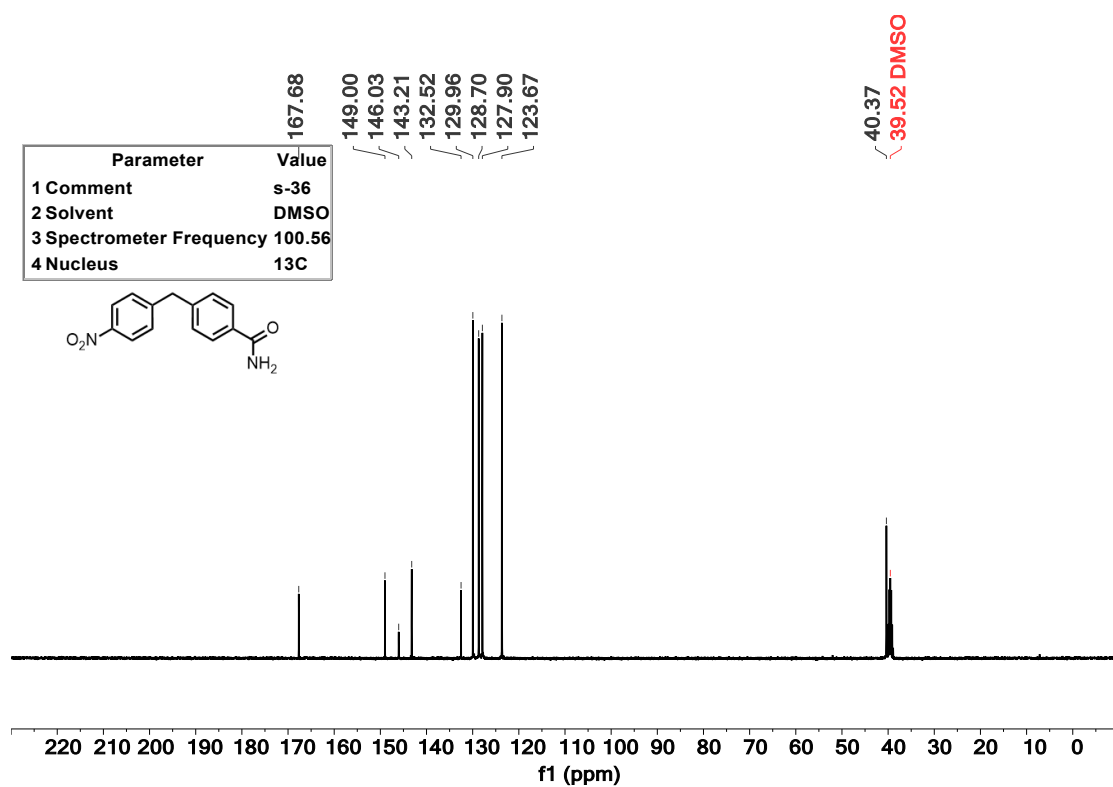
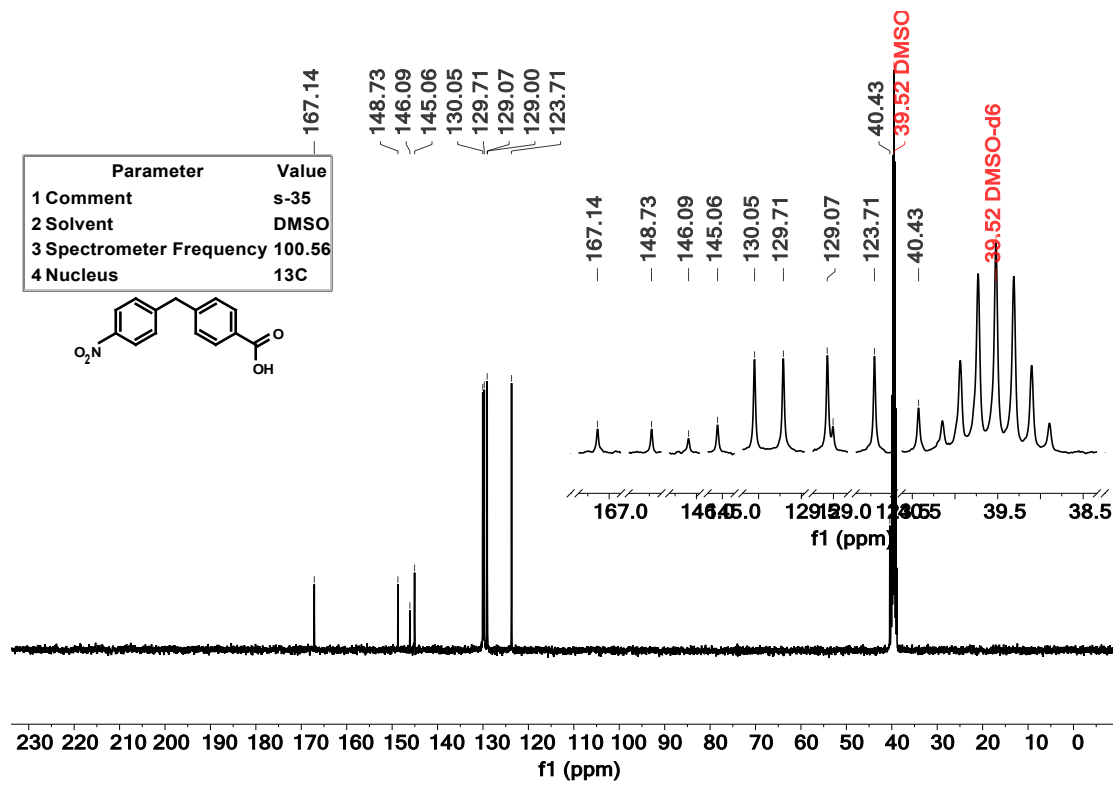
Parameter	Value
1 Comment	s-27
2 Solvent	CDCI3
3 Spectrometer Frequency	399.87
4 Nucleus	1H



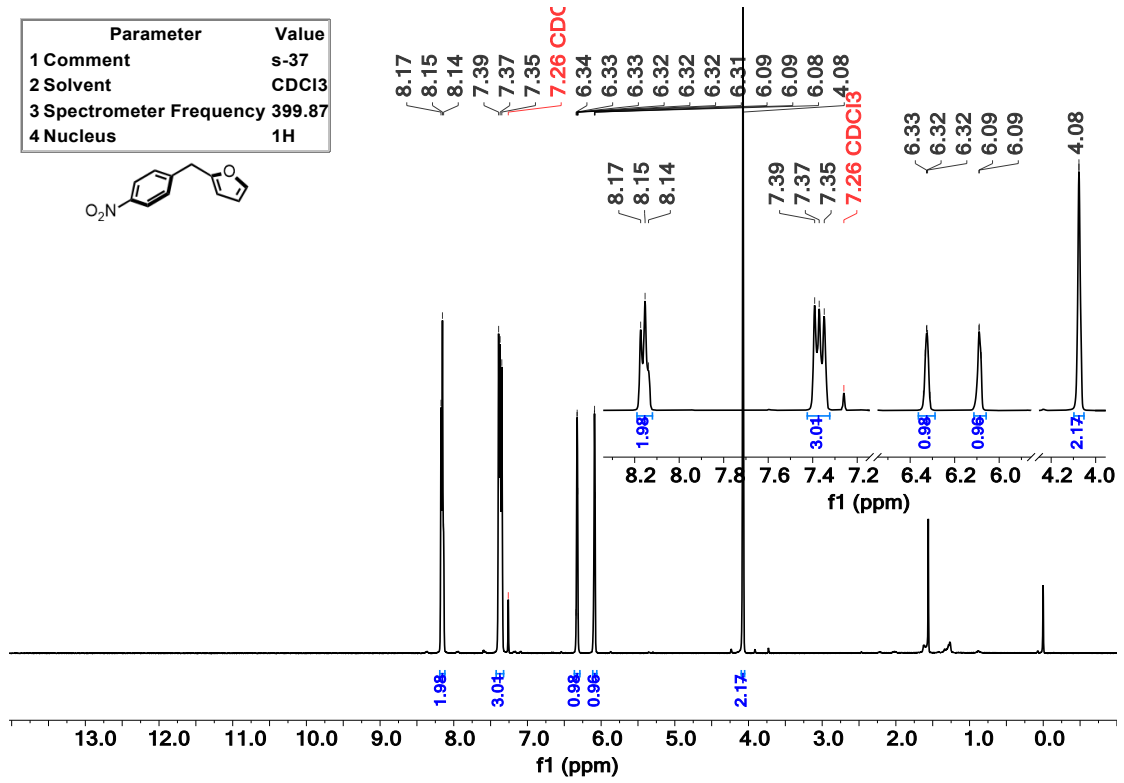
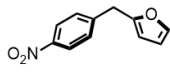
Parameter	Value
1 Comment	s-27
2 Solvent	CDCl ₃
3 Spectrometer Frequency	100.56
4 Nucleus	¹³ C



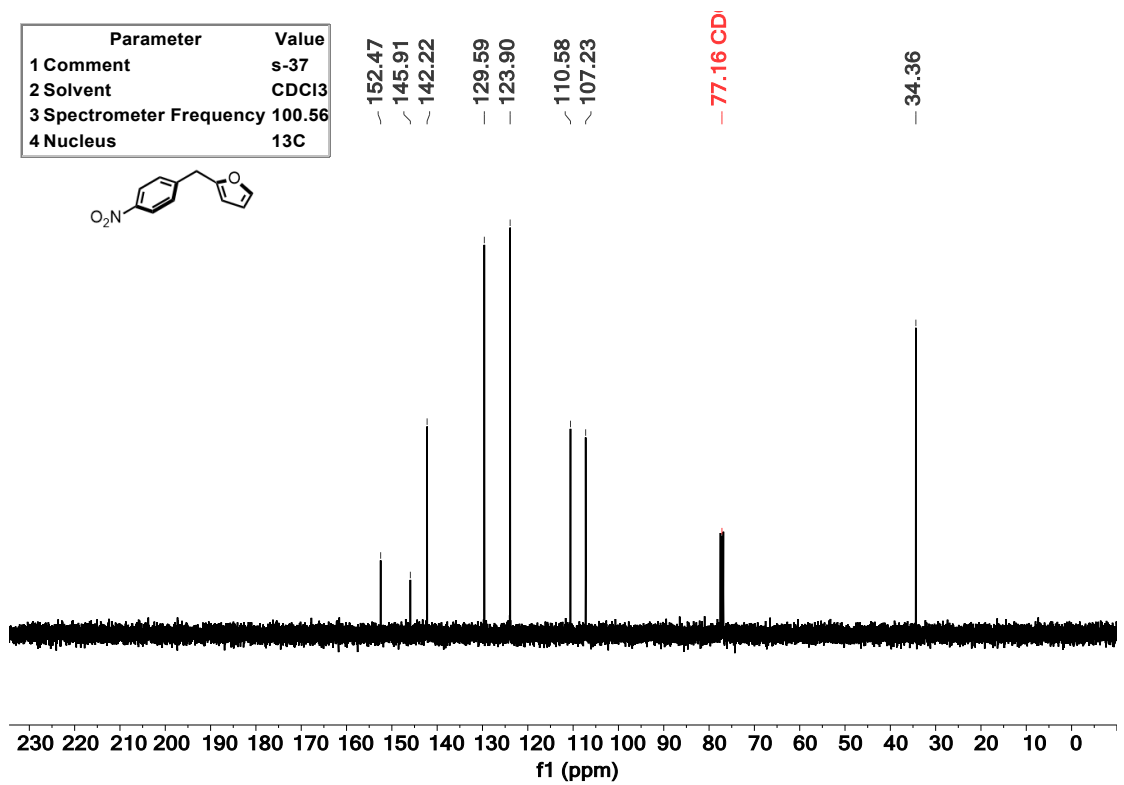
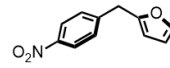


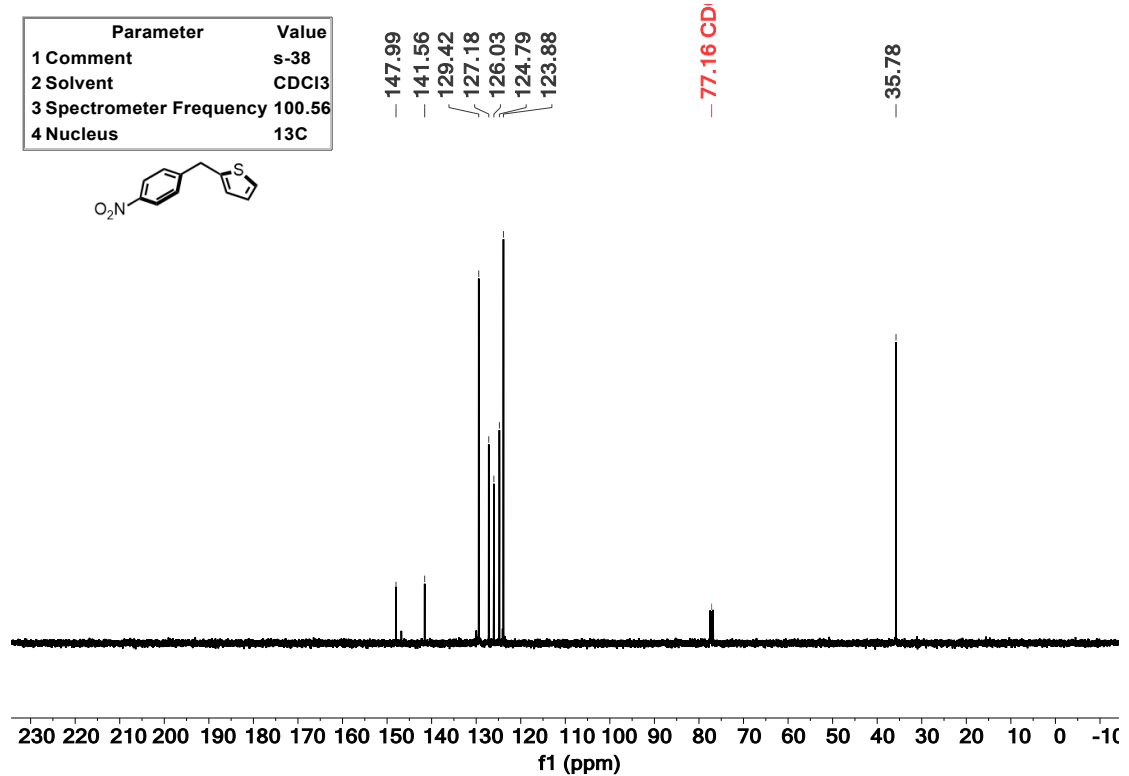
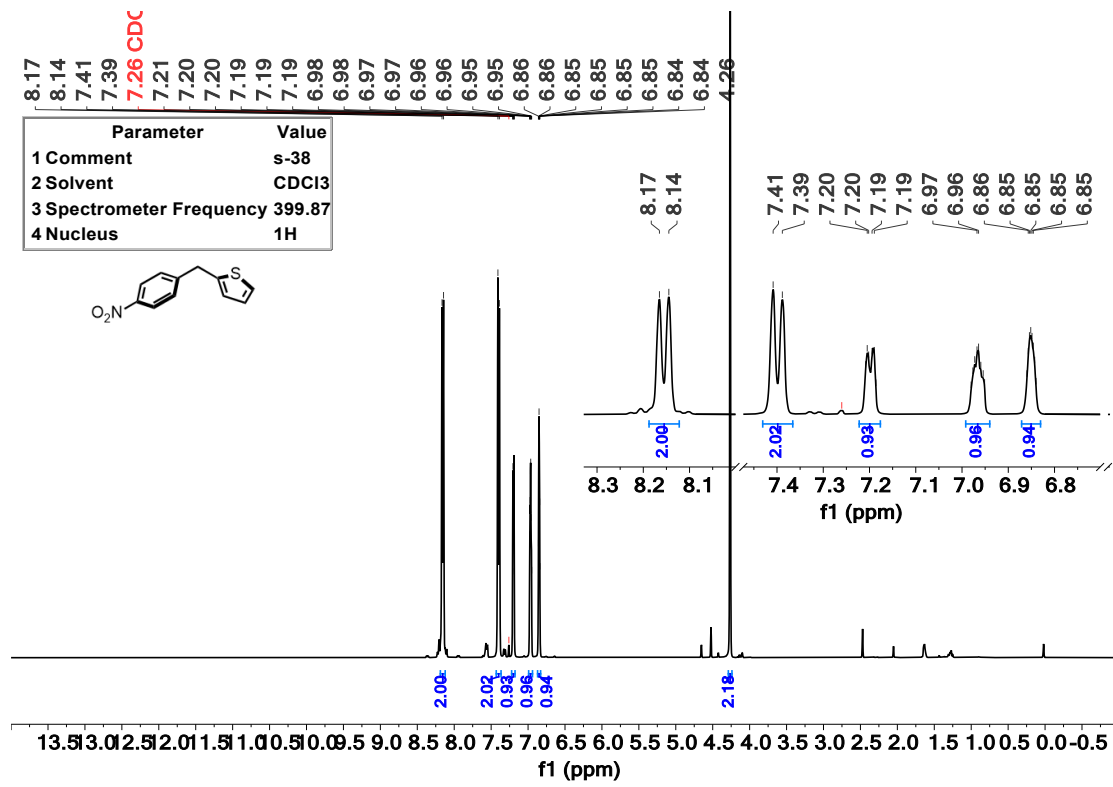


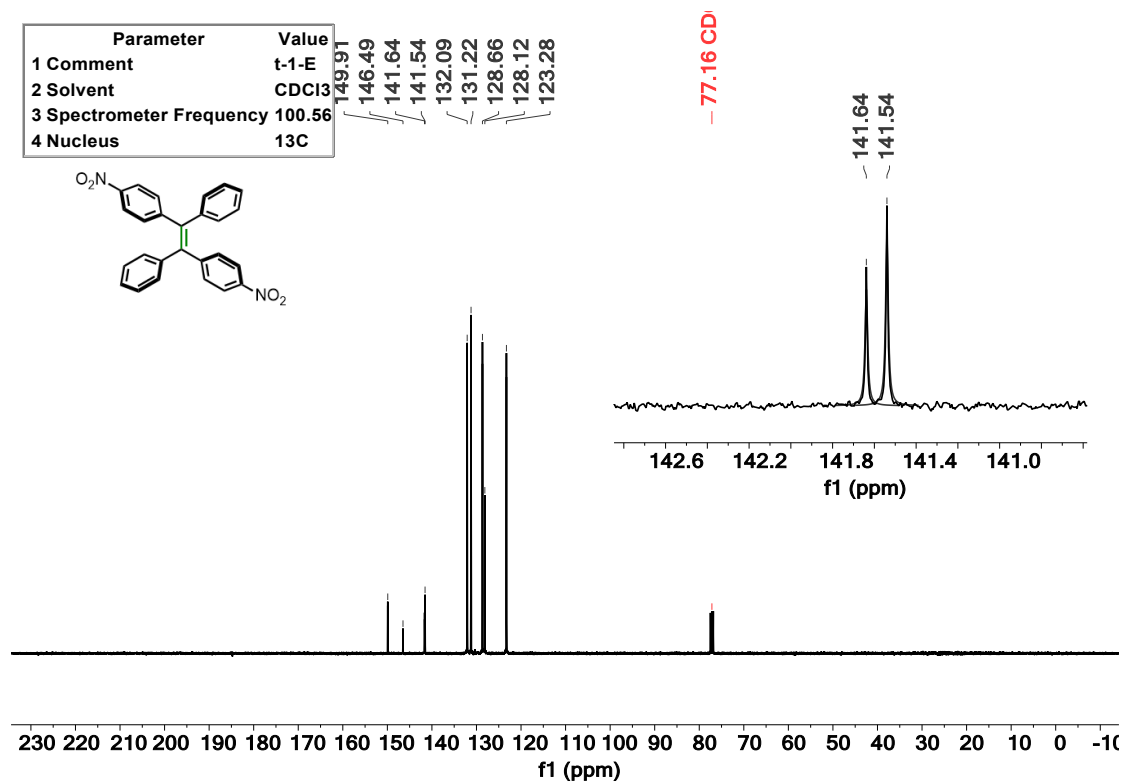
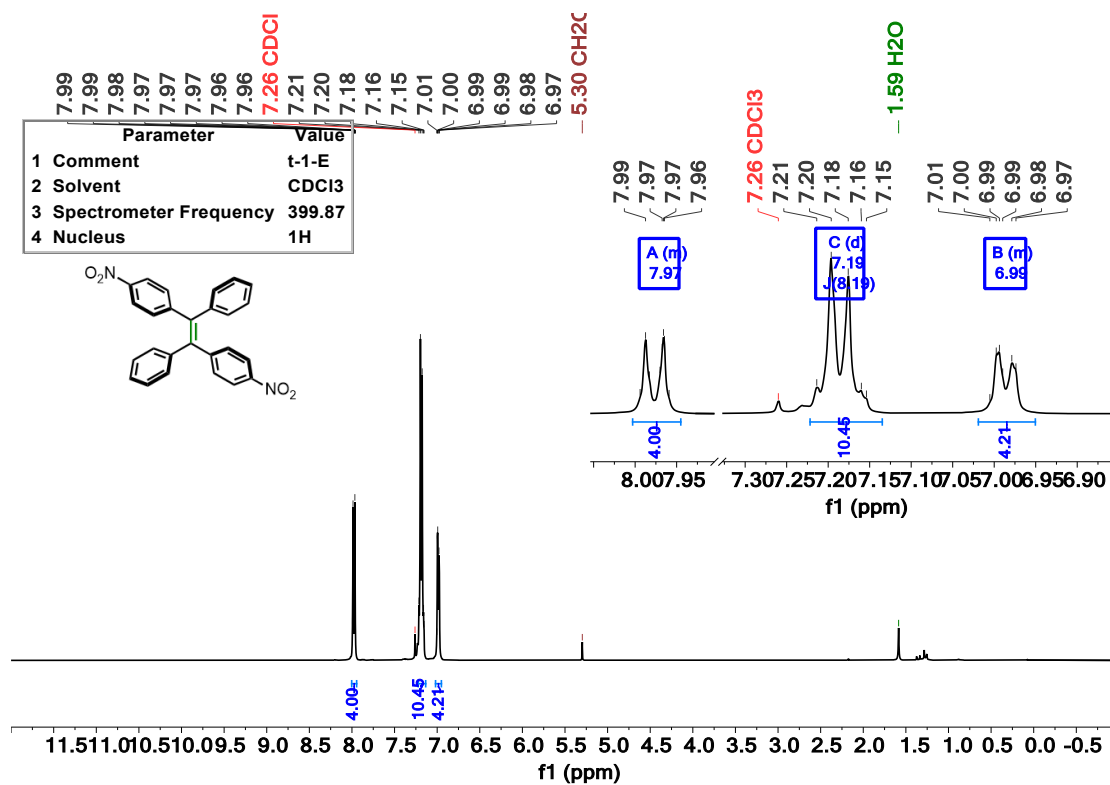
Parameter	Value
1 Comment	s-37
2 Solvent	CDCl3
3 Spectrometer Frequency	399.87
4 Nucleus	1H

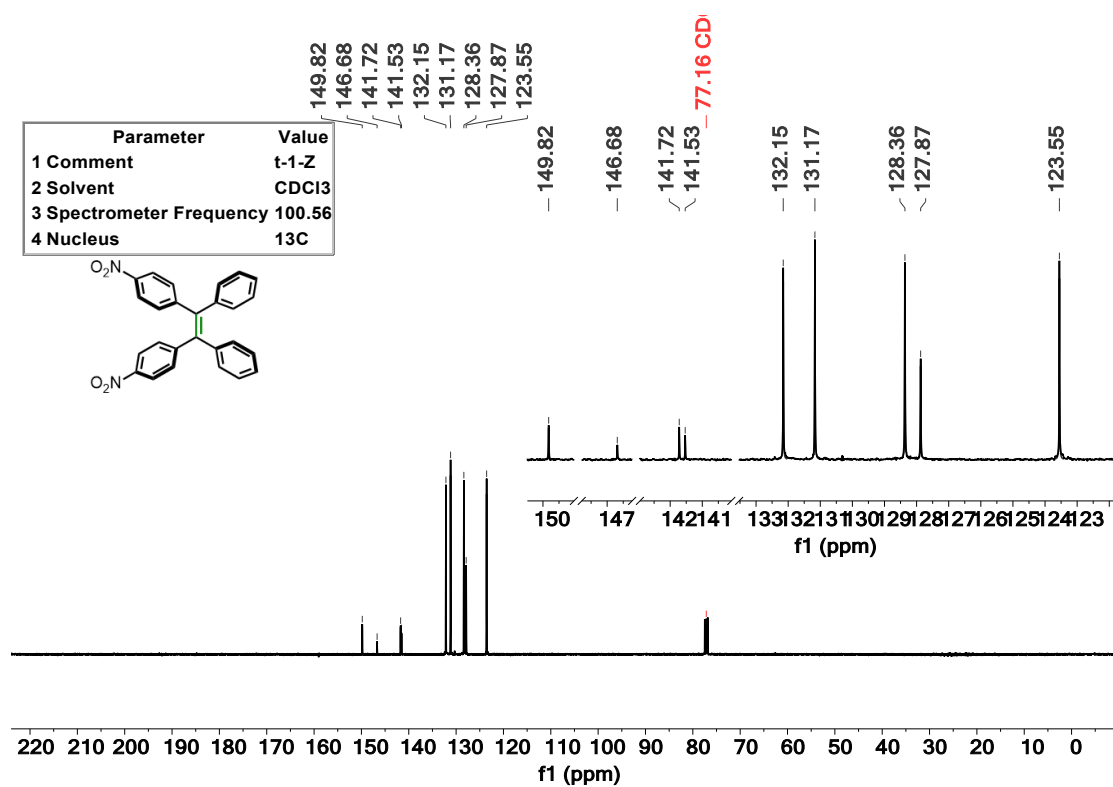
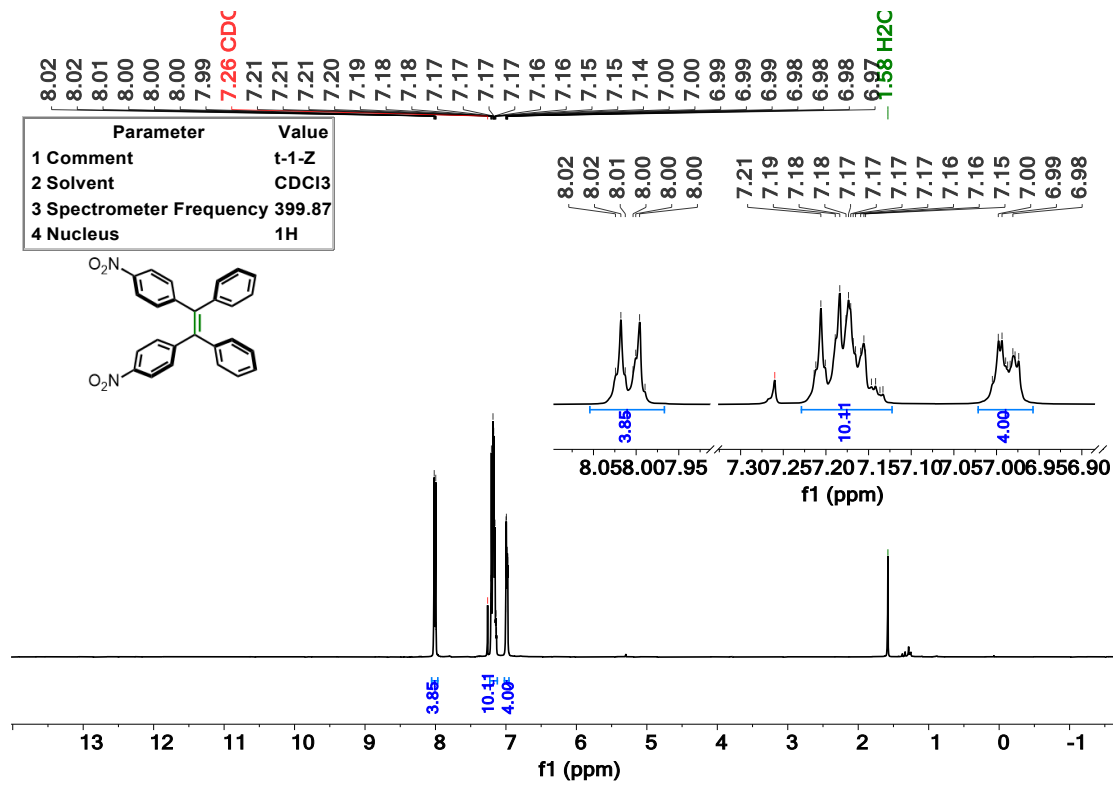


Parameter	Value
1 Comment	s-37
2 Solvent	CDCl3
3 Spectrometer Frequency	100.56
4 Nucleus	13C

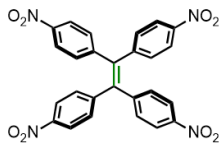




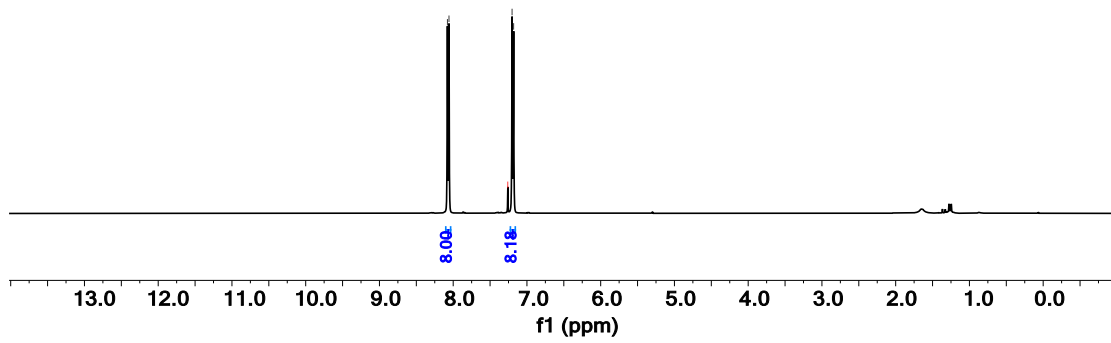




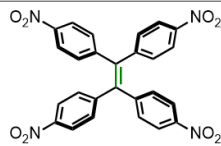
Parameter	Value
1 Comment	t-2
2 Solvent	CDCl3
3 Spectrometer Frequency	399.87
4 Nucleus	1H



8.08
8.06
7.26 CDC
7.20
7.18

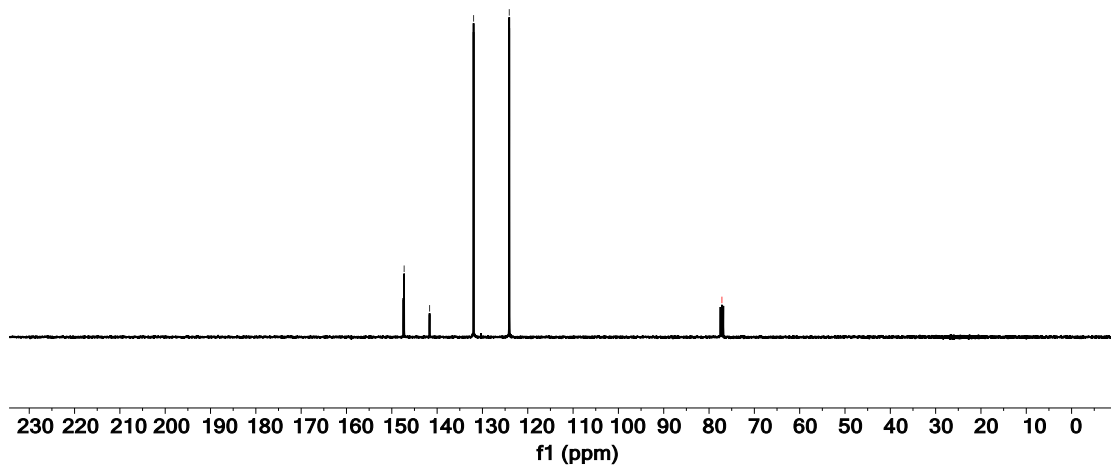


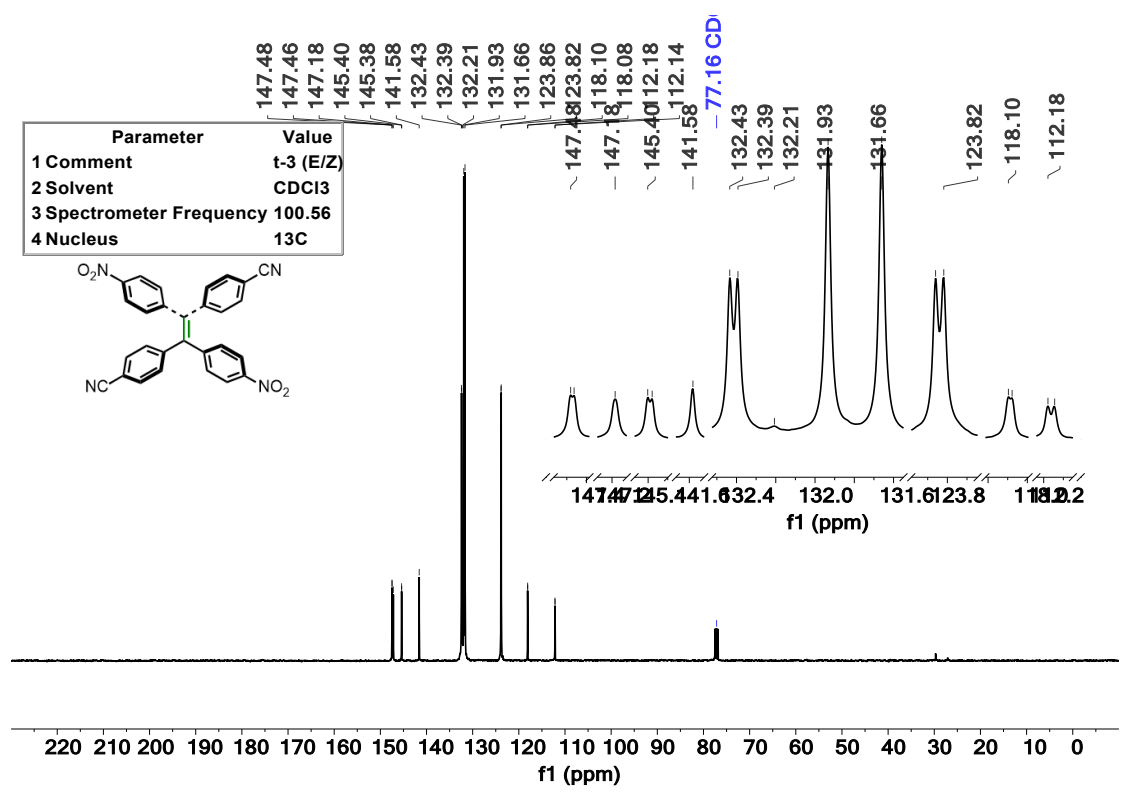
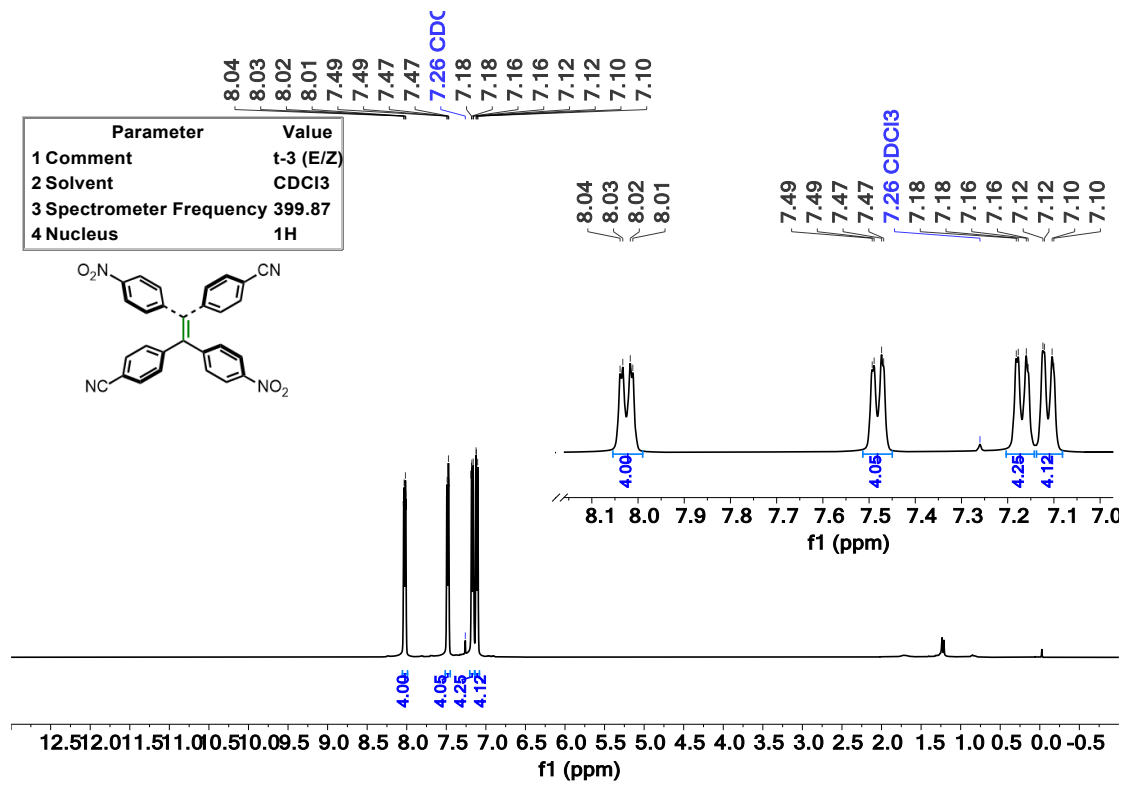
Parameter	Value
1 Comment	t-2
2 Solvent	CDCl3
3 Spectrometer Frequency	100.56
4 Nucleus	13C

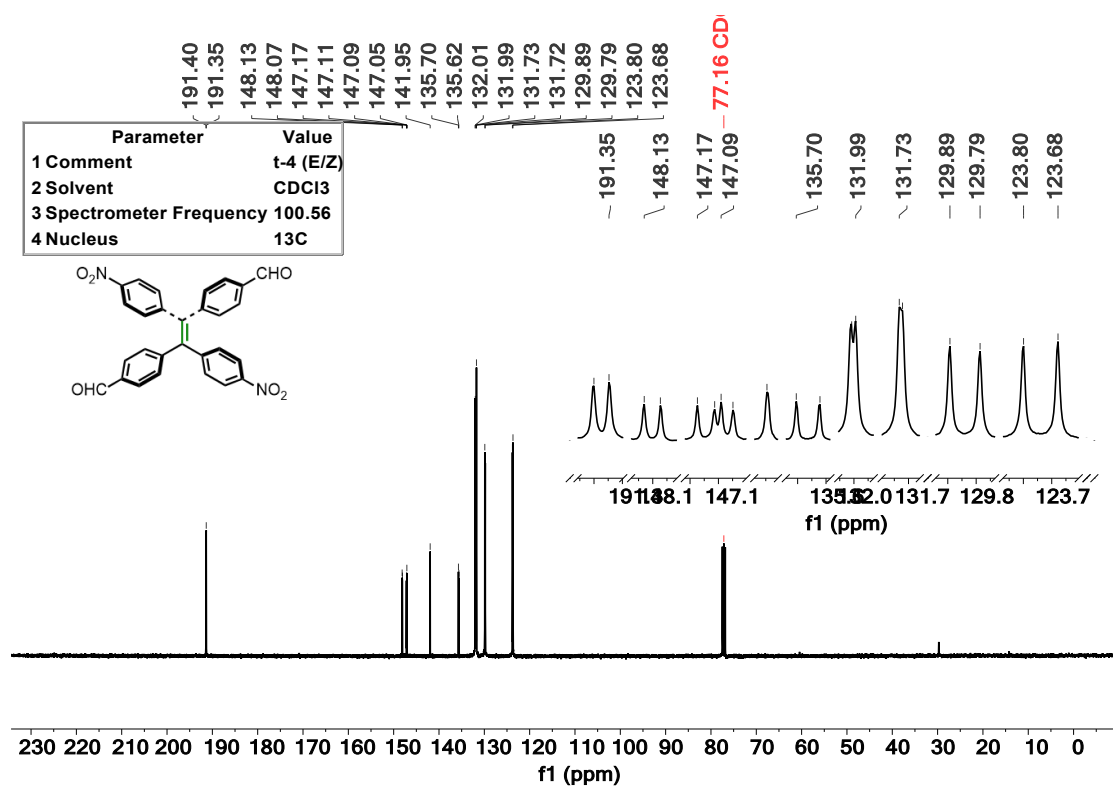
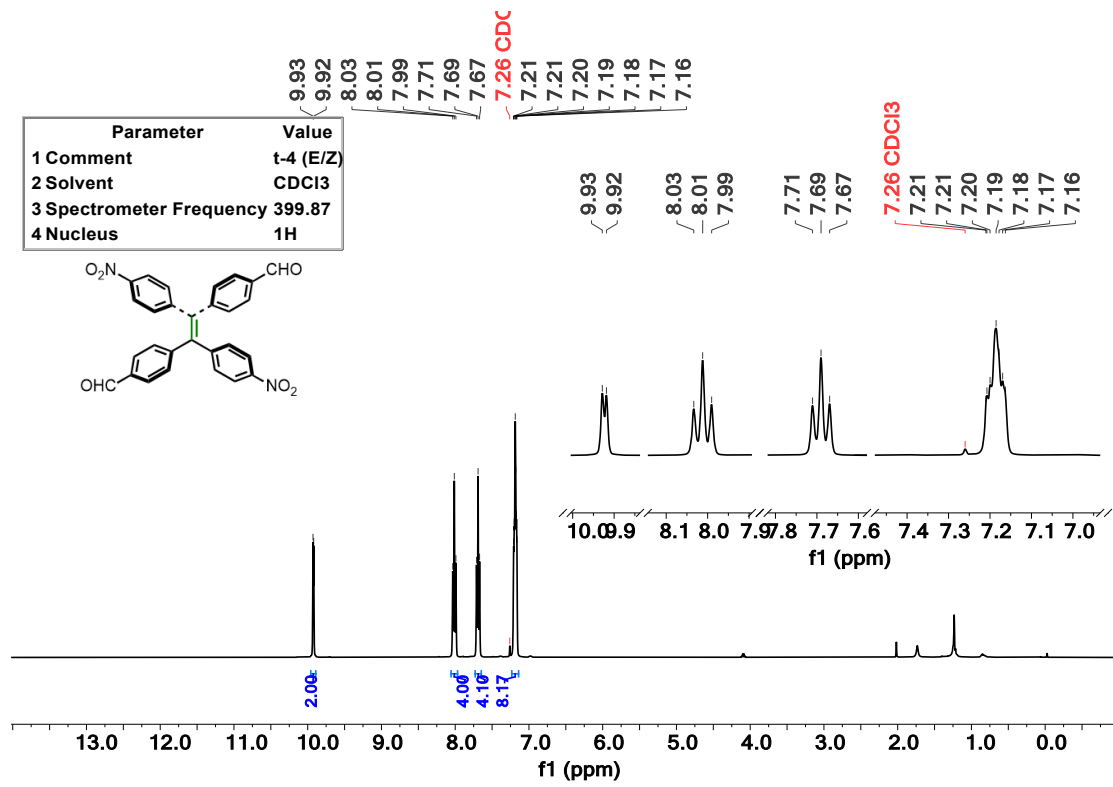


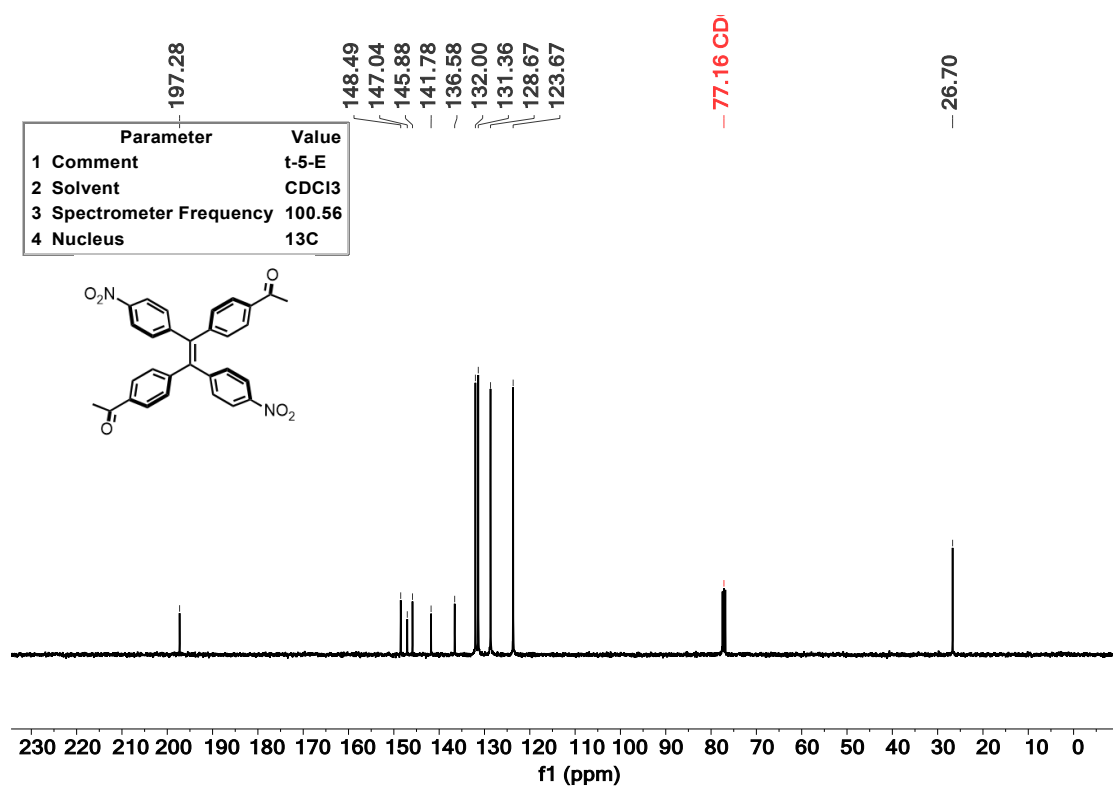
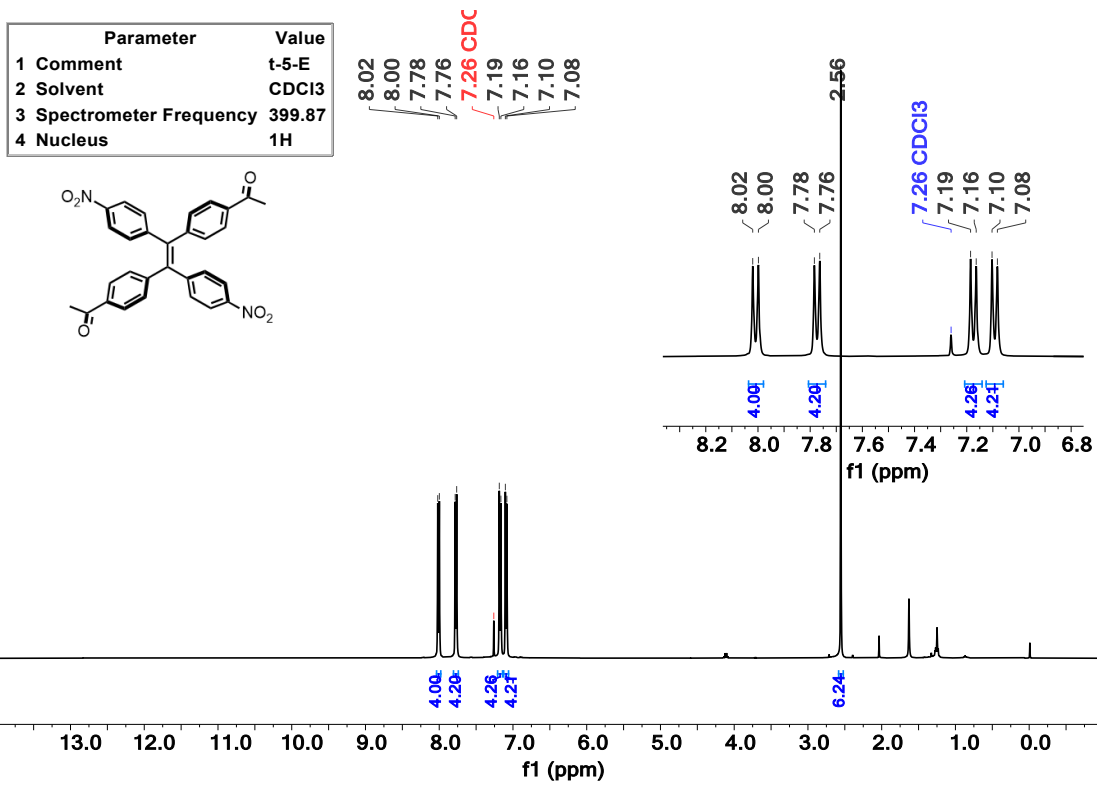
147.42
147.28
141.66
131.96
124.08

-77.16 CD

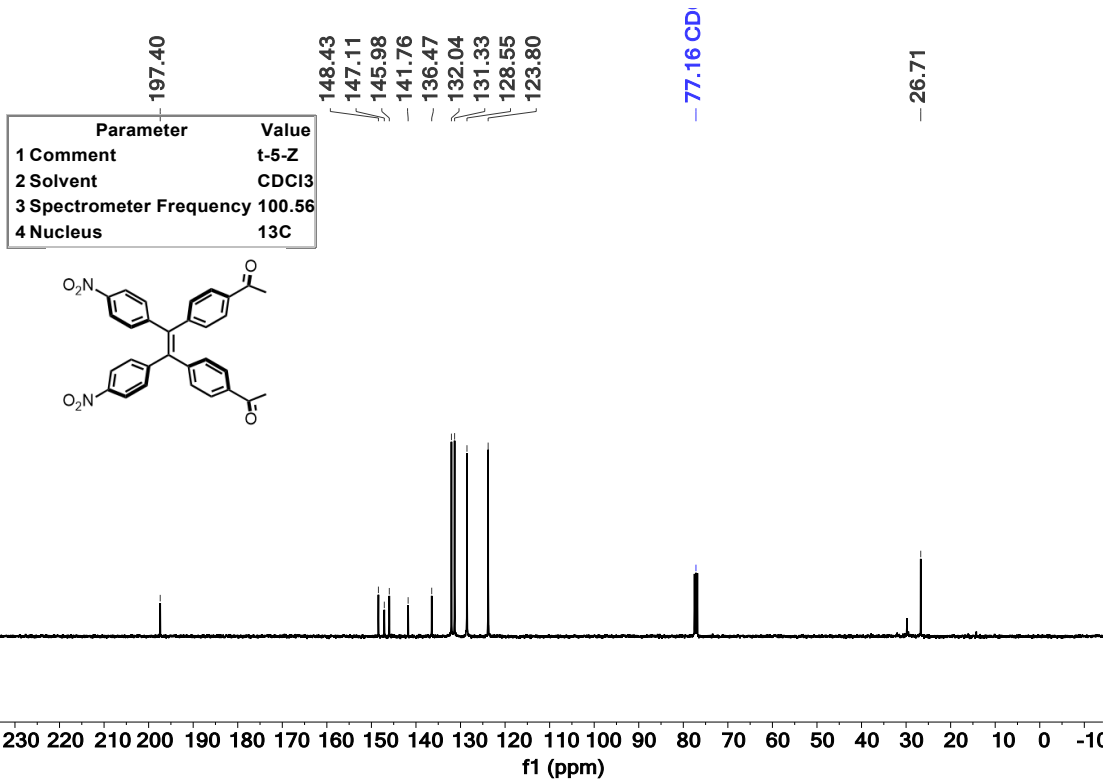
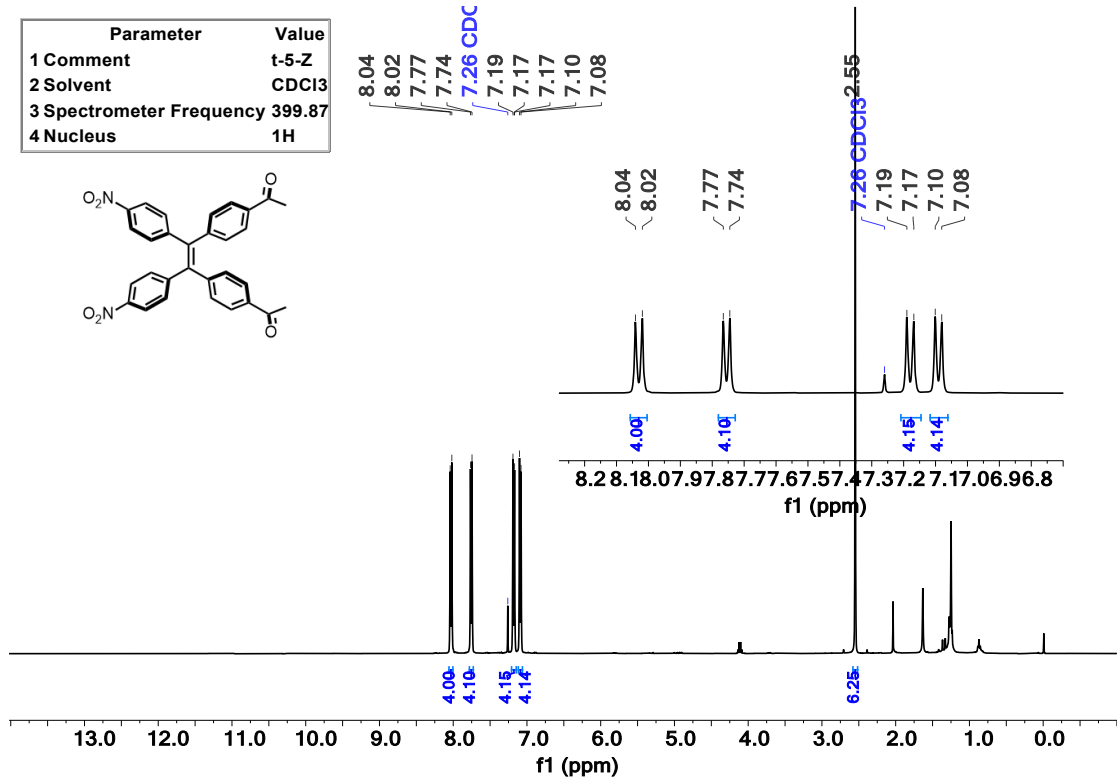
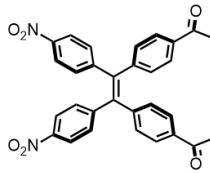


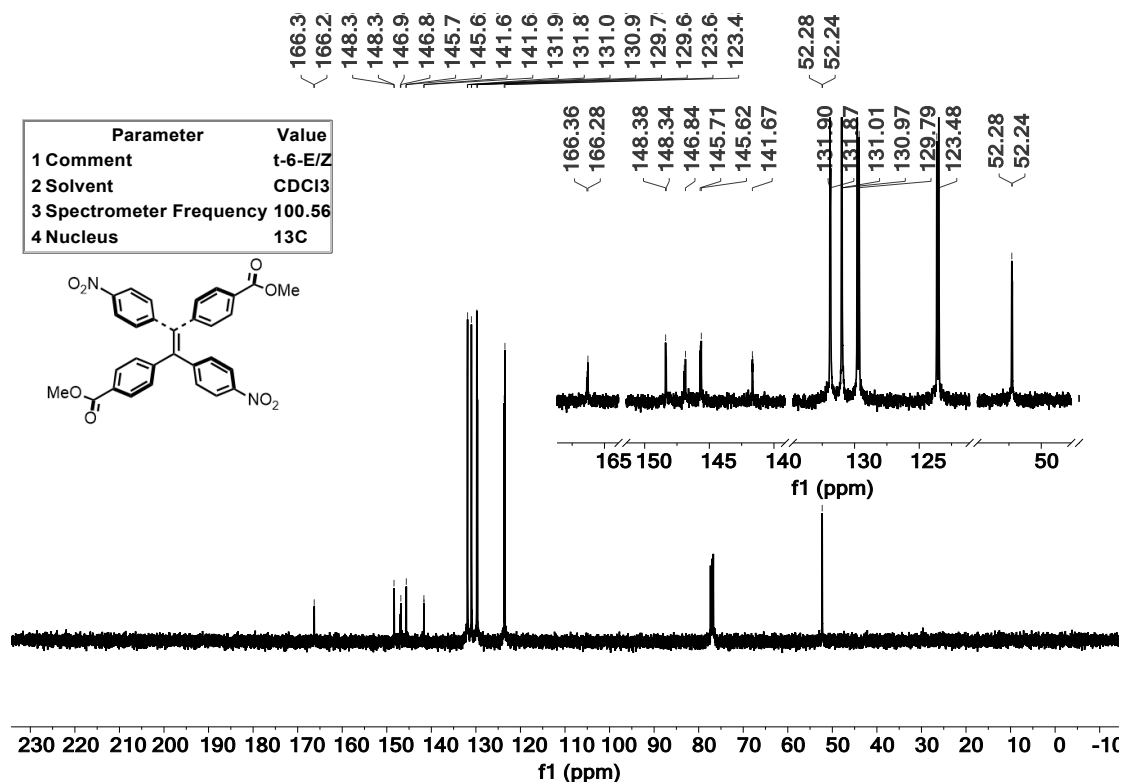
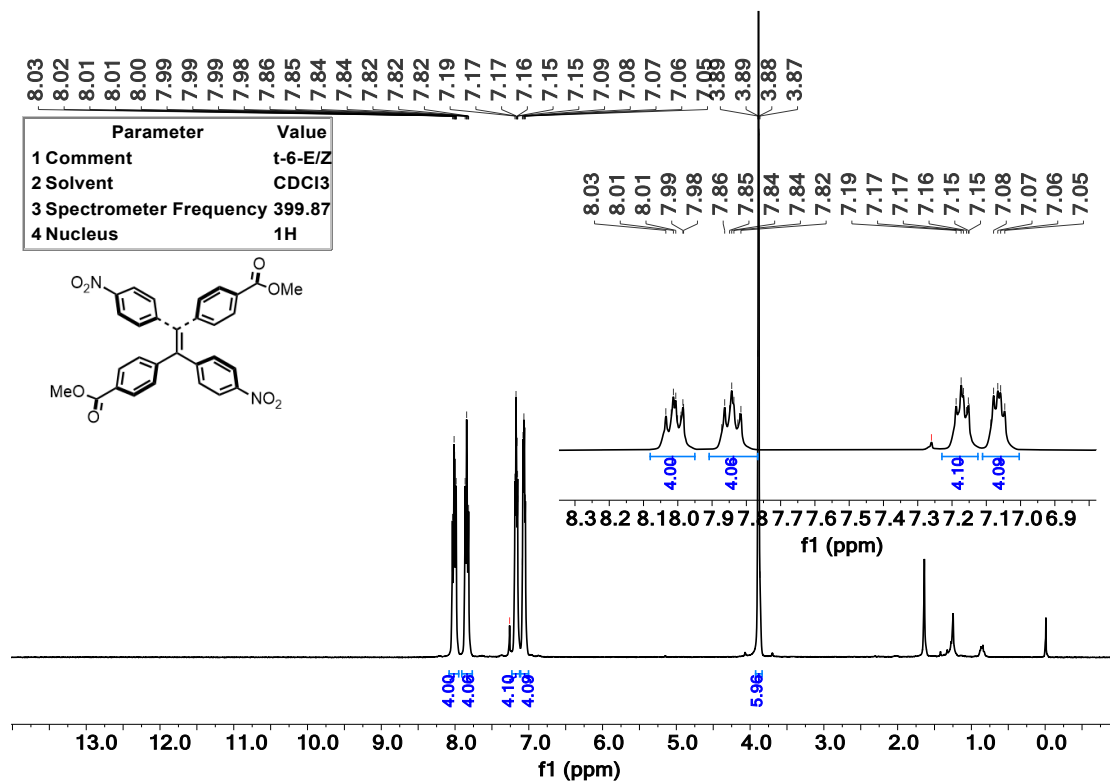




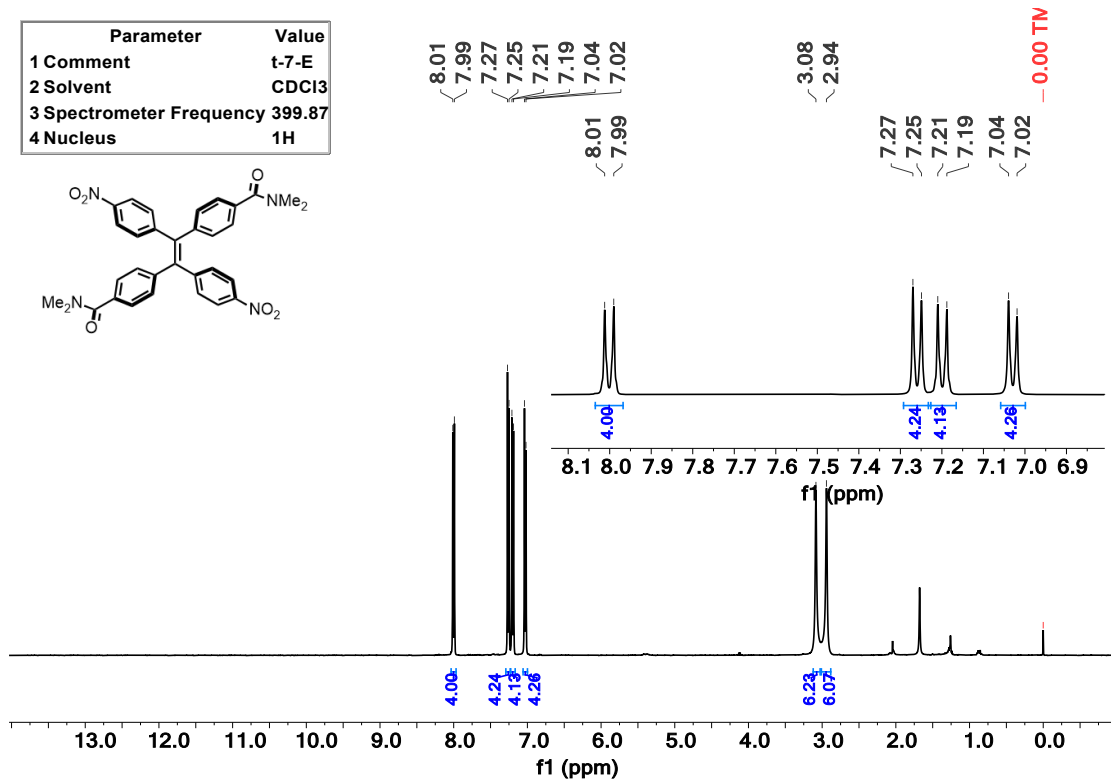
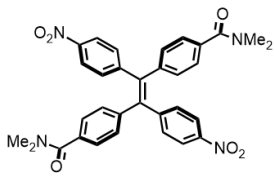


Parameter	Value
1 Comment	t-5-Z
2 Solvent	CDCl3
3 Spectrometer Frequency	399.87
4 Nucleus	1H

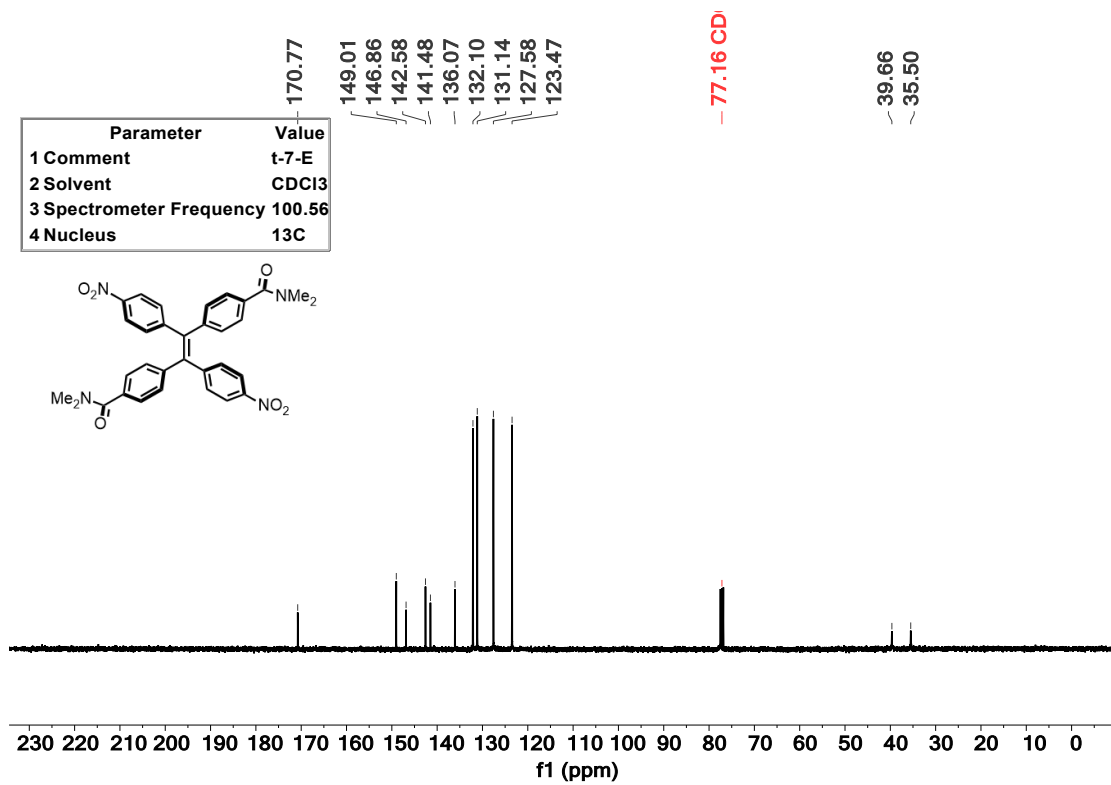
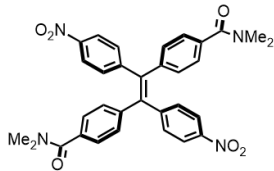


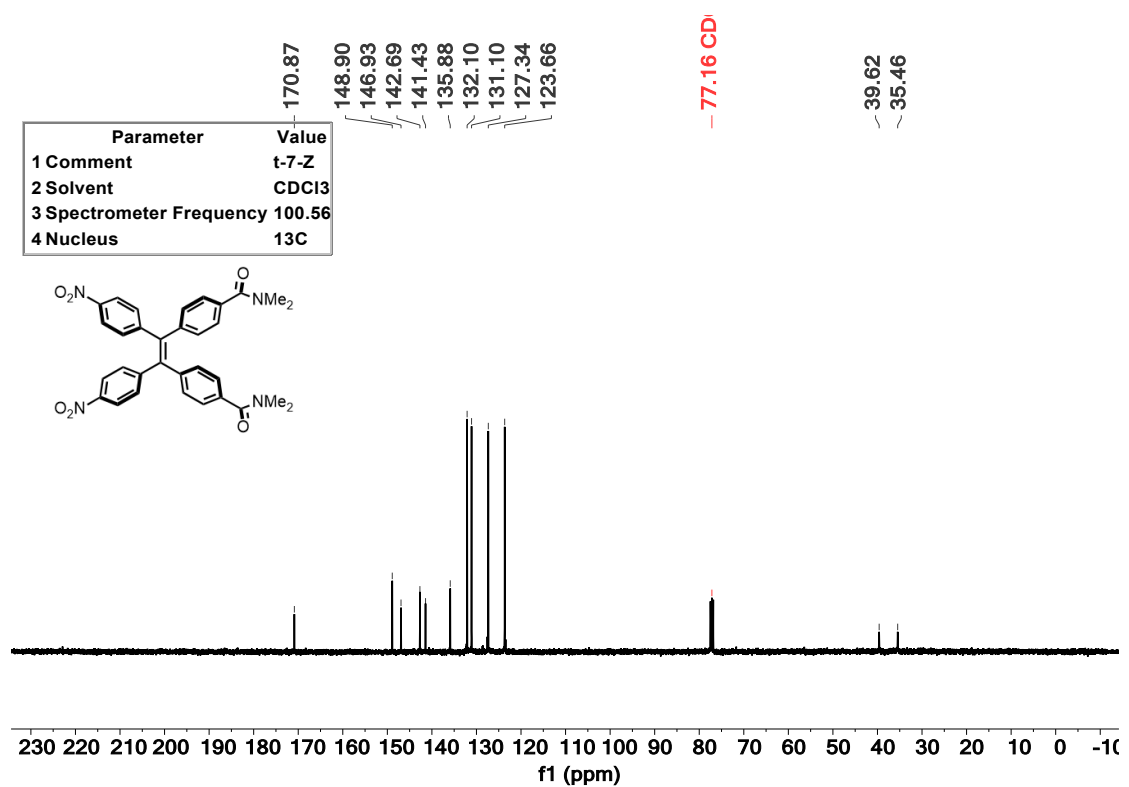
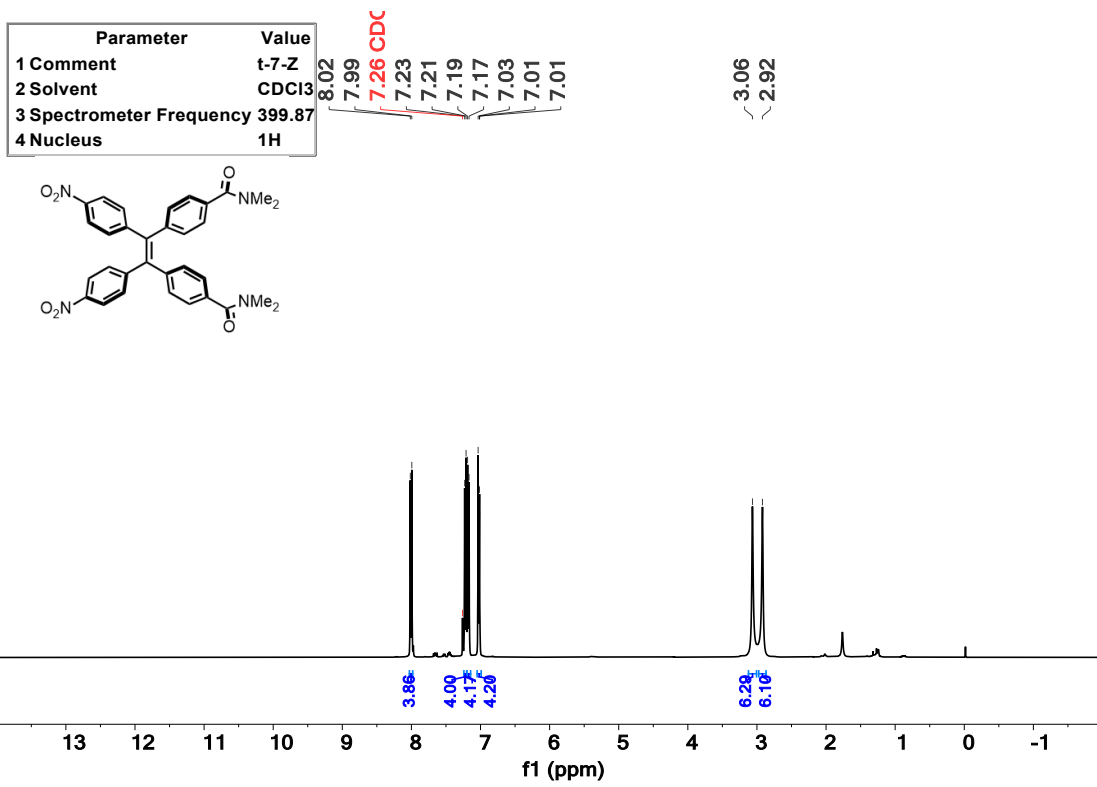


Parameter	Value
1 Comment	t-7-E
2 Solvent	CDCl3
3 Spectrometer Frequency	399.87
4 Nucleus	1H

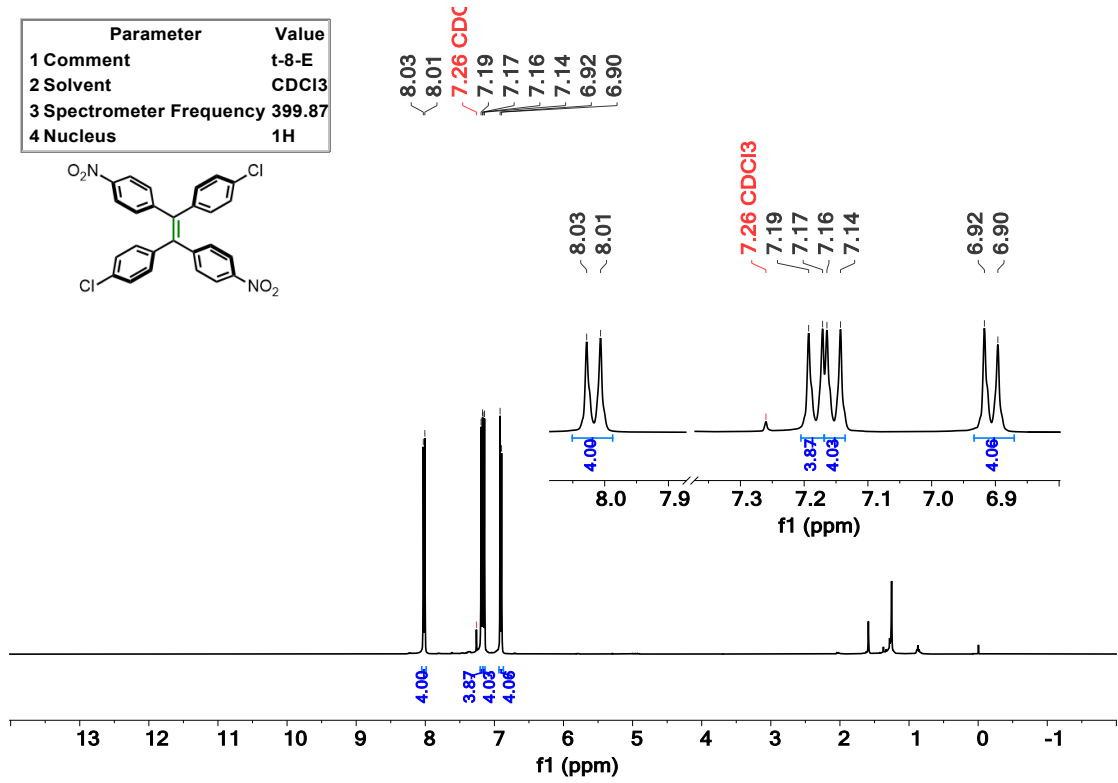
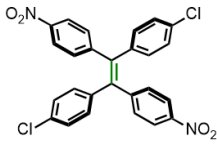


Parameter	Value
1 Comment	t-7-E
2 Solvent	CDCl3
3 Spectrometer Frequency	100.56
4 Nucleus	13C

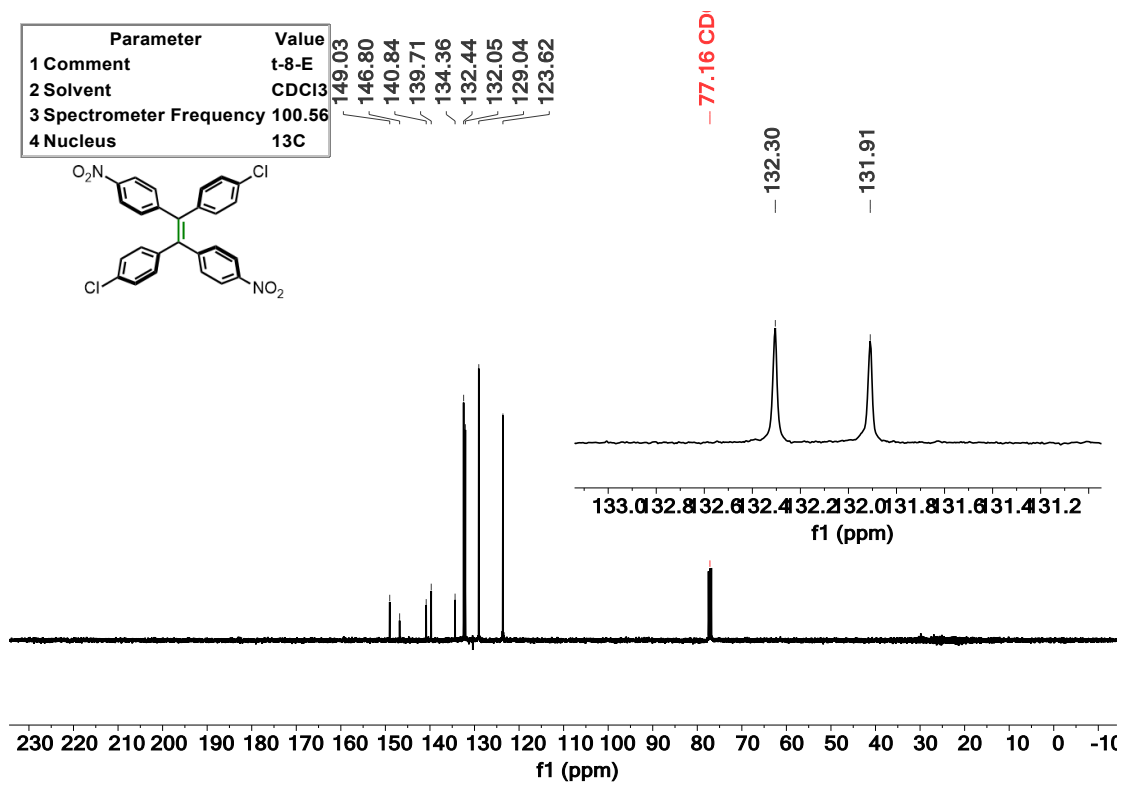
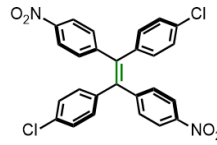




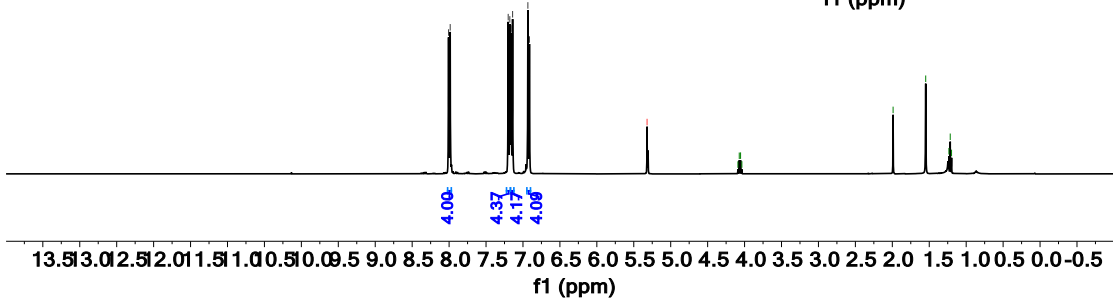
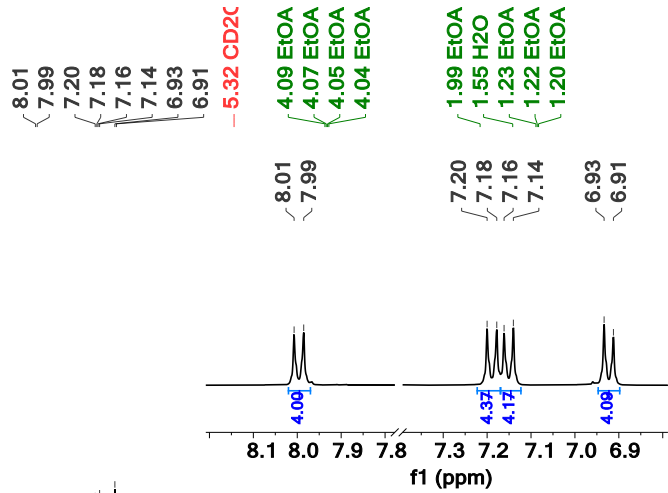
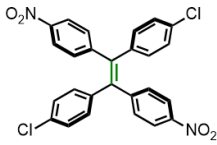
Parameter	Value
1 Comment	t-8-E
2 Solvent	CDCl ₃
3 Spectrometer Frequency	399.87
4 Nucleus	¹ H



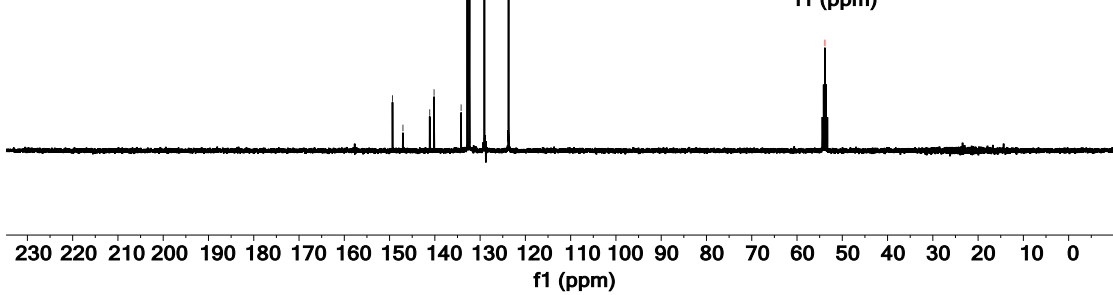
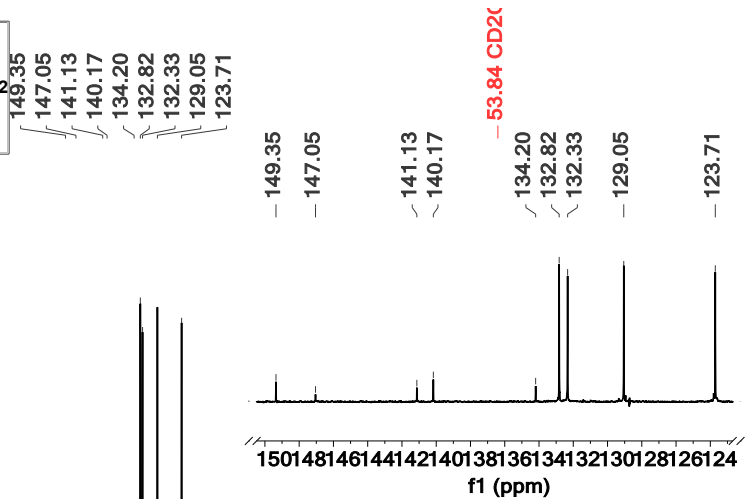
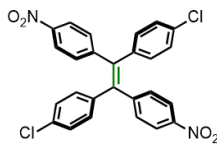
Parameter	Value
1 Comment	t-8-E
2 Solvent	CDCl ₃
3 Spectrometer Frequency	100.56
4 Nucleus	¹³ C



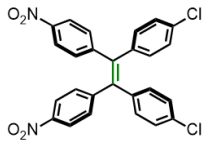
Parameter	Value
1 Comment	t-8-E
2 Solvent	CD2Cl2
3 Spectrometer Frequency	399.87
4 Nucleus	1H



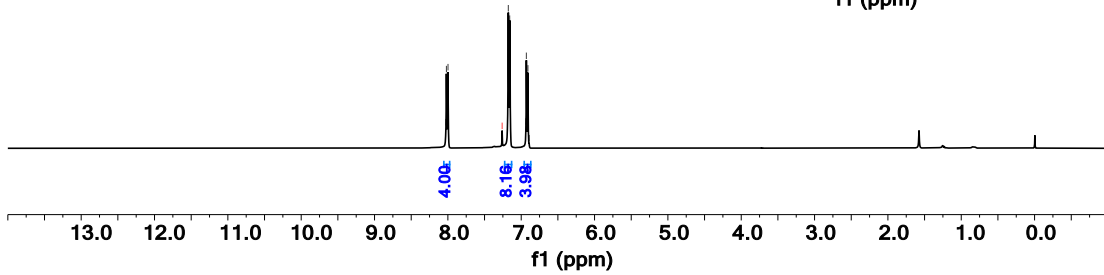
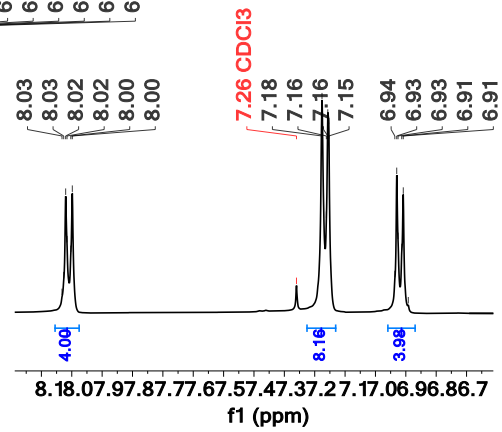
Parameter	Value
1 Comment	t-8-E
2 Solvent	CD2Cl2
3 Spectrometer Frequency	100.56
4 Nucleus	13C



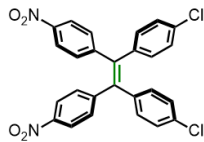
Parameter	Value
1 Comment	t-8-Z
2 Solvent	CDCl ₃
3 Spectrometer Frequency	400.13
4 Nucleus	¹ H



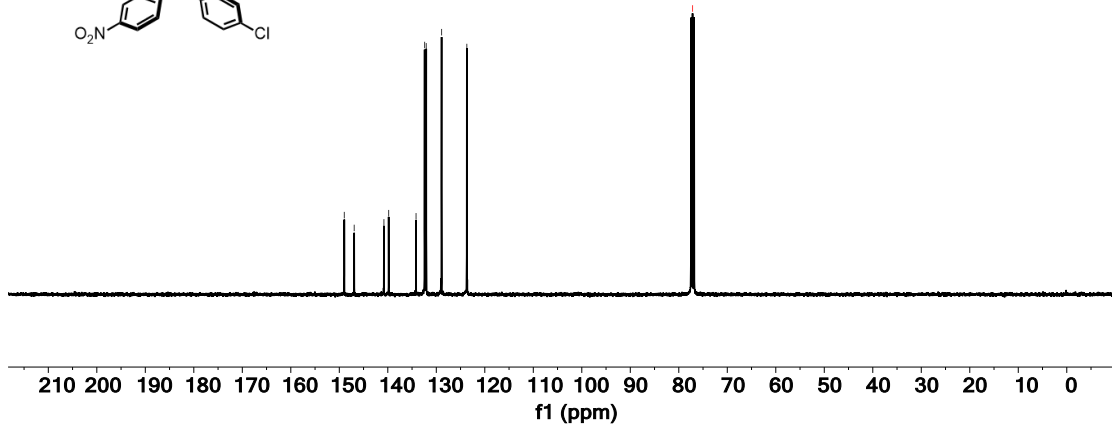
8.03
8.03
8.02
8.02
8.00
8.00
7.26 CDC
7.18
7.16
7.16
7.15
6.94
6.93
6.93
6.91
6.91
6.89



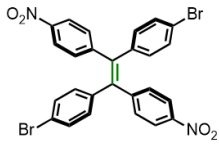
Parameter	Value
1 Comment	t-8-Z
2 Solvent	CDCl ₃
3 Spectrometer Frequency	100.62
4 Nucleus	¹³ C



148.97
146.93
140.80
139.82
134.17
132.41
132.07
128.91
123.71
-77.16 CD13



Parameter	Value
1 Comment	t-9-E
2 Solvent	CDCl3
3 Spectrometer Frequency	399.87
4 Nucleus	1H

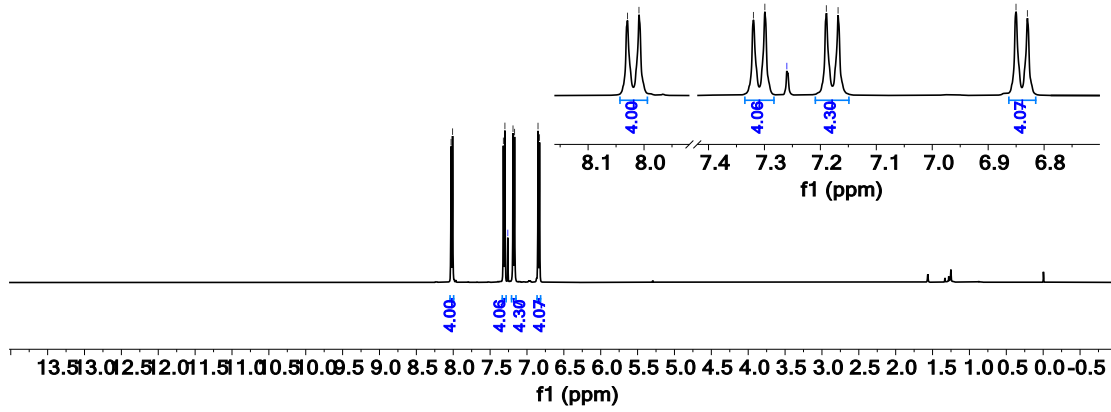


8.03
8.01
7.32
7.30
7.26 CDC
7.19
7.17
6.85
6.83

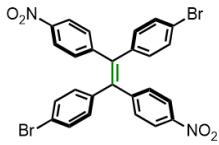
8.03
8.01

7.32
7.30
7.26 CDC13
7.19
7.17

6.85
6.83

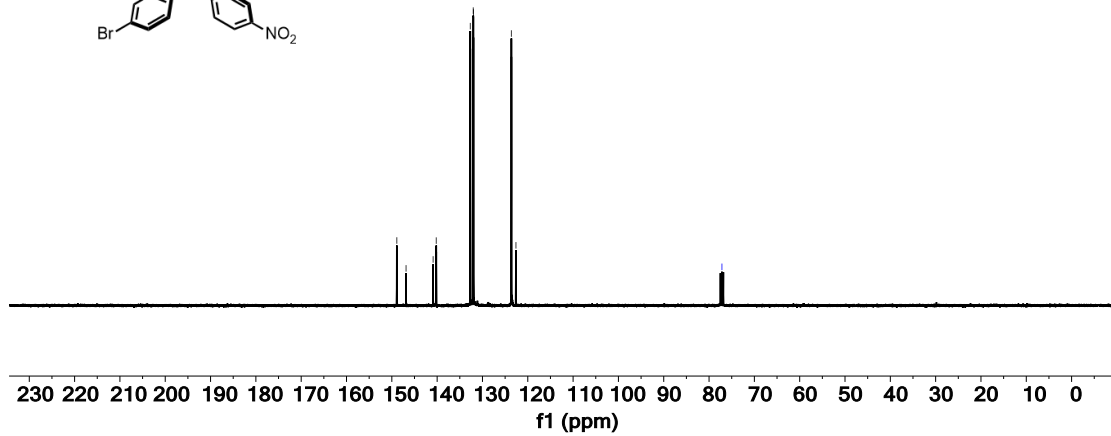


Parameter	Value
1 Comment	t-9-E
2 Solvent	CDCl3
3 Spectrometer Frequency	100.56
4 Nucleus	13C

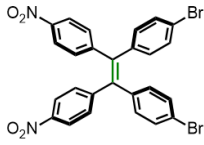


148.90
146.86
140.89
140.20
132.68
132.03
131.99
123.62
122.61

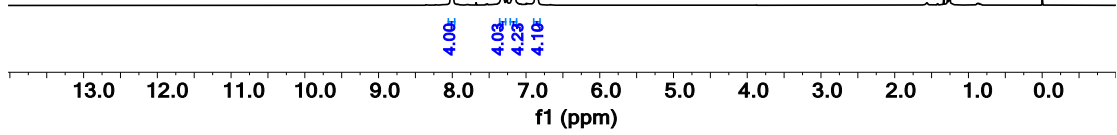
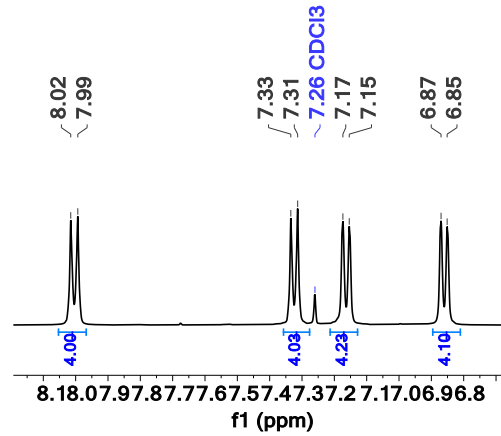
-77.16 CD



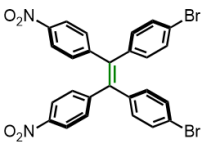
Parameter	Value
1 Comment	t-9-Z
2 Solvent	CDC13
3 Spectrometer Frequency	399.87
4 Nucleus	1H



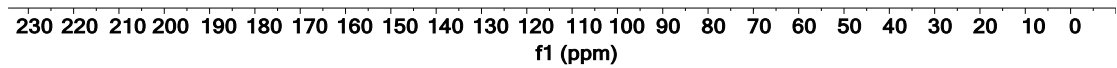
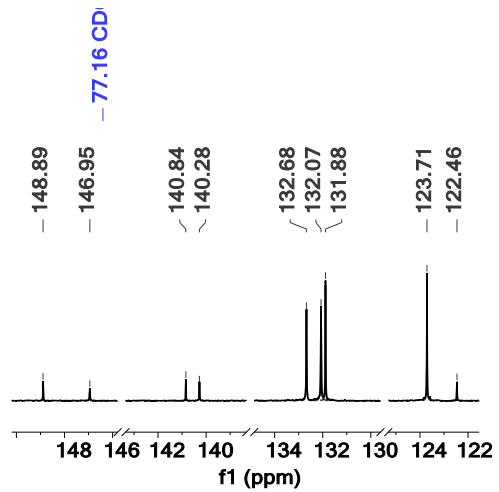
8.02
7.99
7.33
7.31
7.26 CDC
7.17
7.15
6.87
6.85



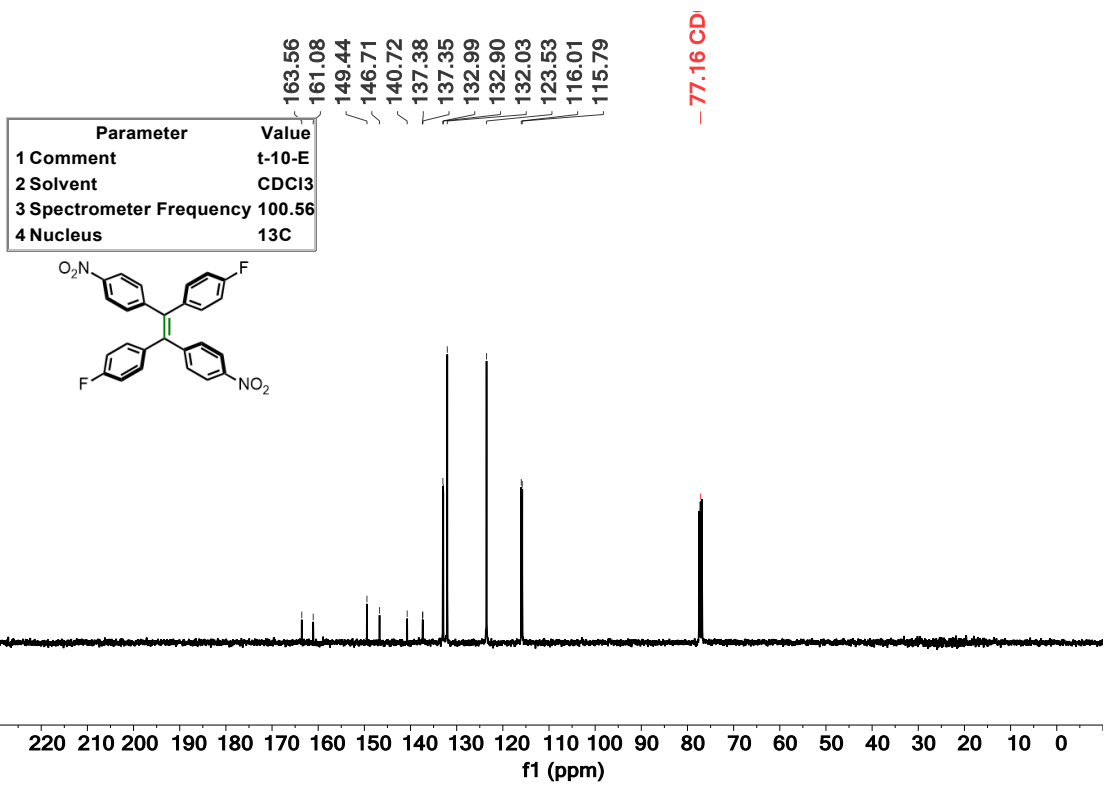
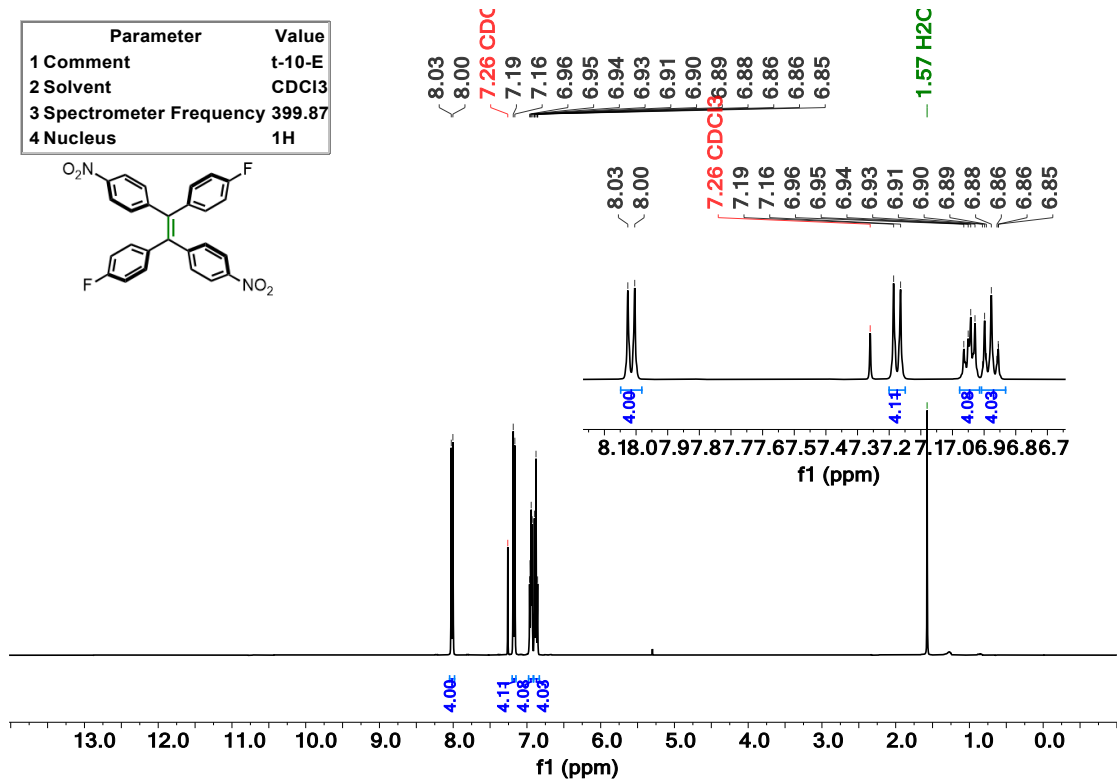
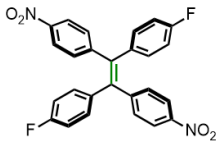
Parameter	Value
1 Comment	t-9-Z
2 Solvent	CDC13
3 Spectrometer Frequency	100.56
4 Nucleus	13C



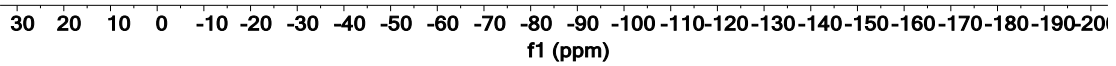
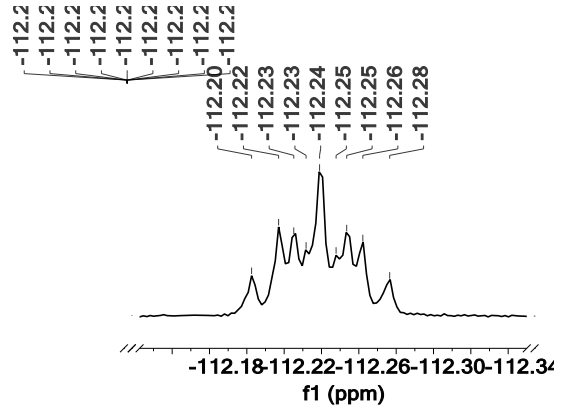
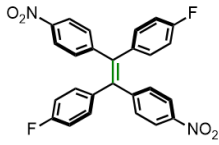
148.89
146.95
140.84
140.28
132.68
132.07
131.88
123.71
122.46



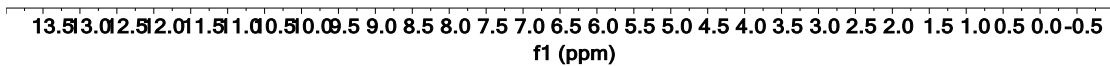
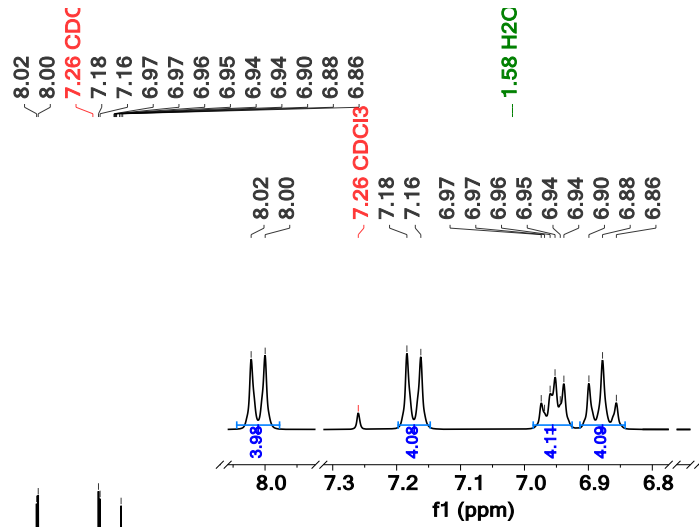
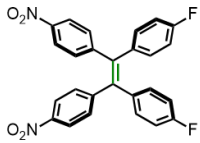
Parameter	Value
1 Comment	t-10-E
2 Solvent	CDCl3
3 Spectrometer Frequency	399.87
4 Nucleus	1H

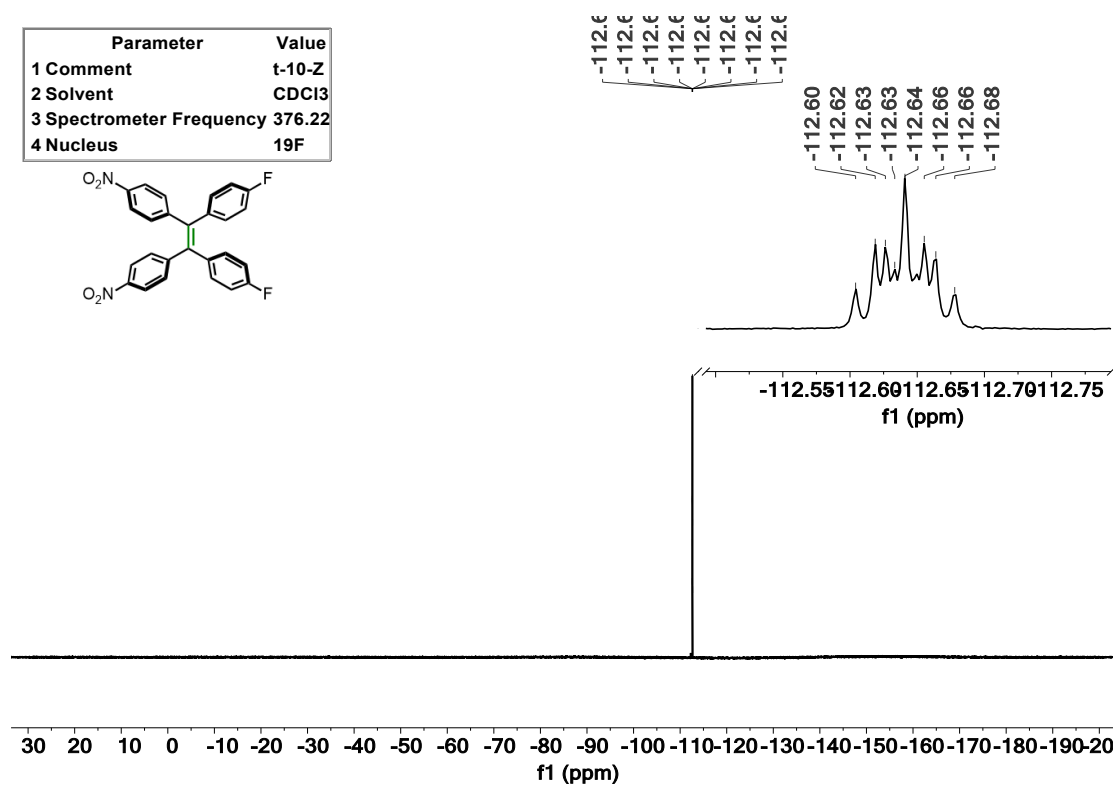
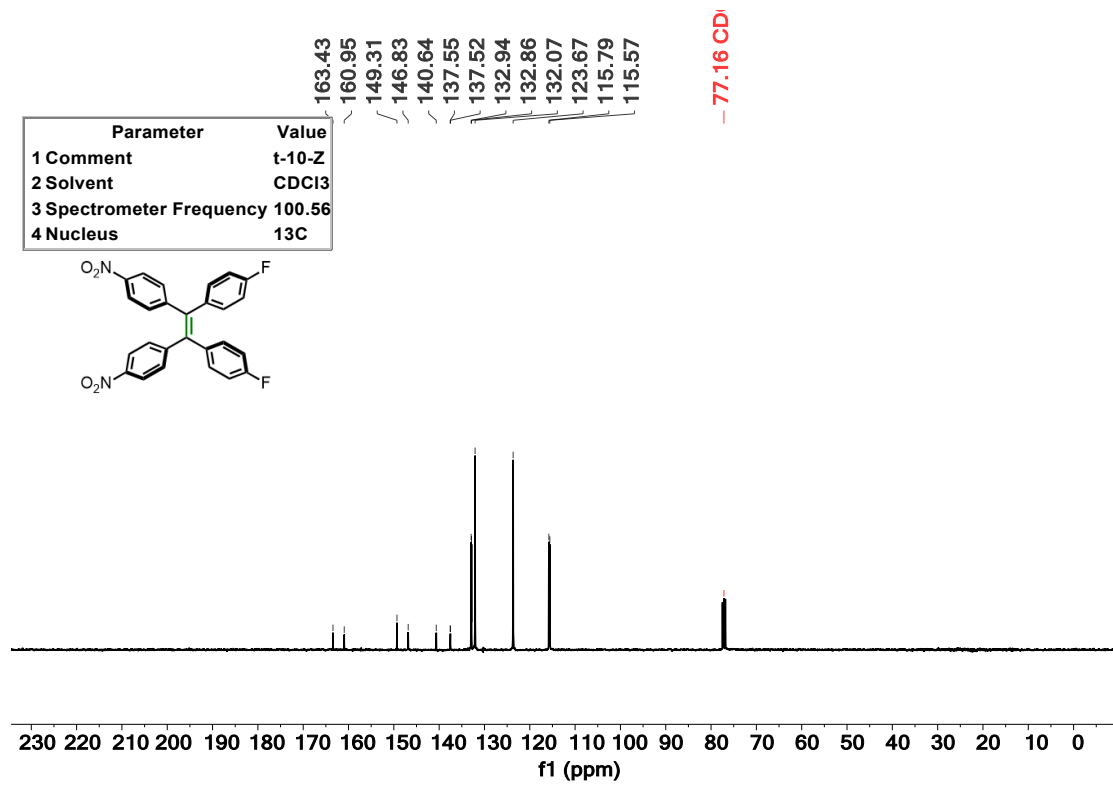


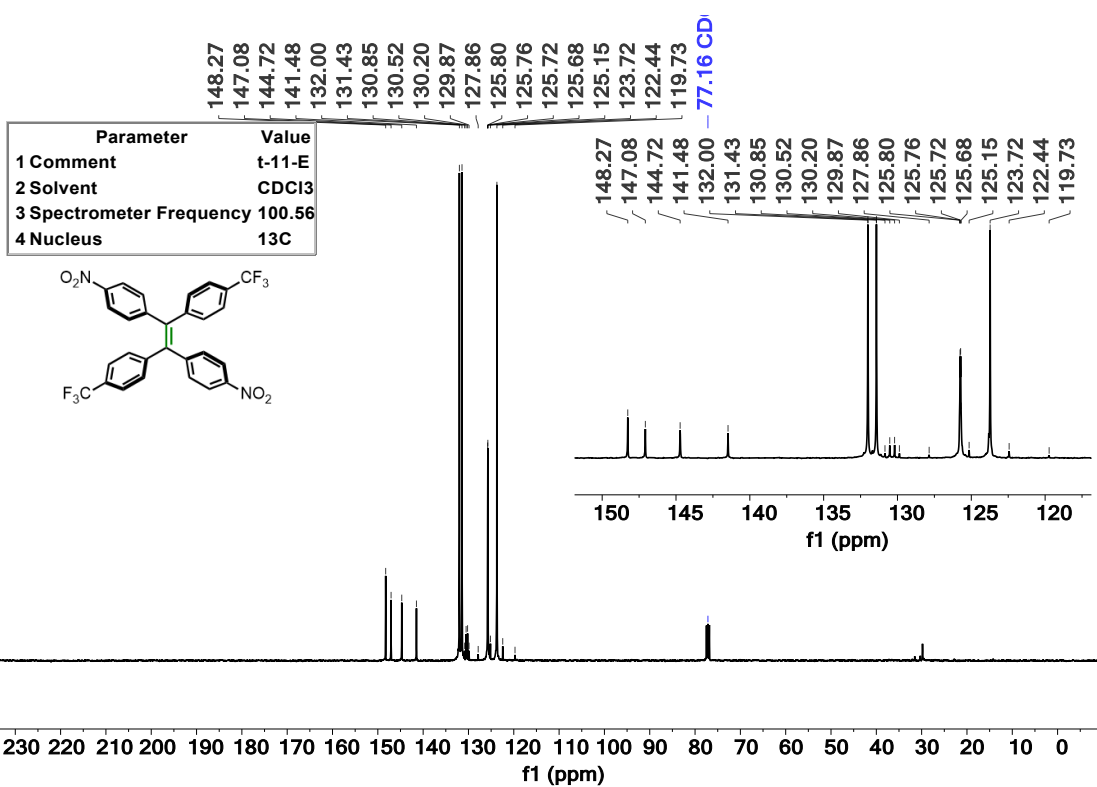
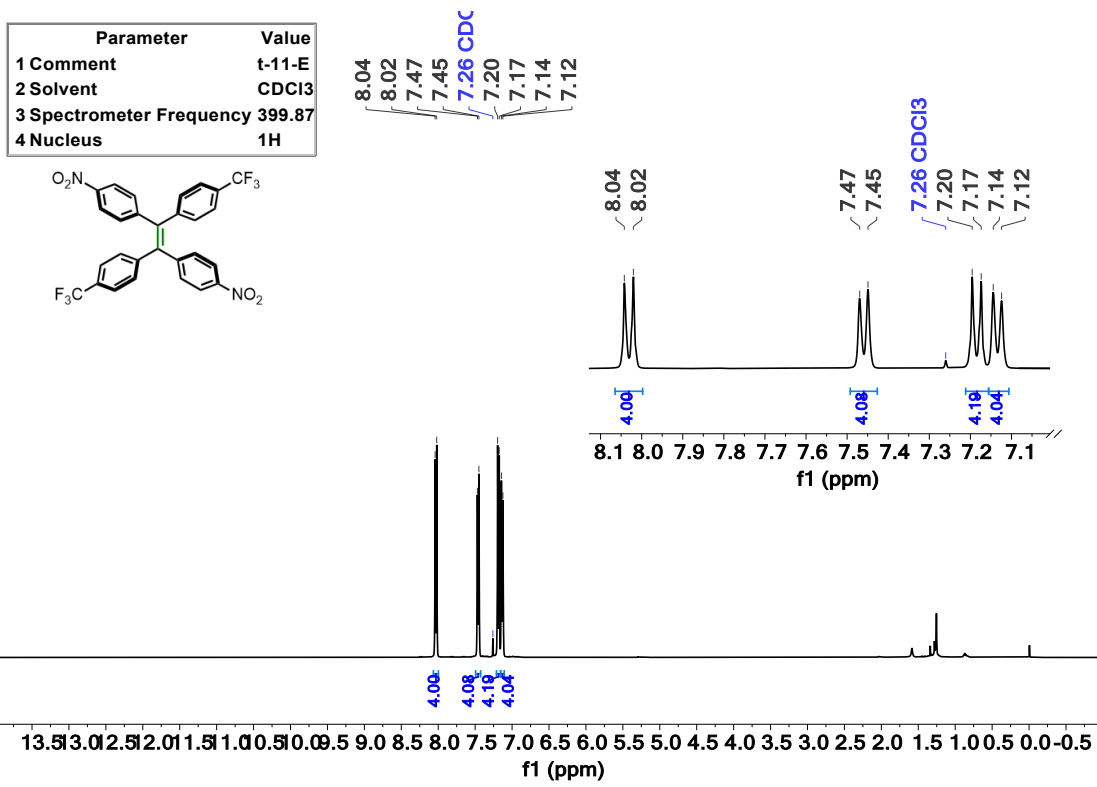
Parameter	Value
1 Comment	t-10-E
2 Solvent	CDCI3
3 Spectrometer Frequency	376.22
4 Nucleus	19F



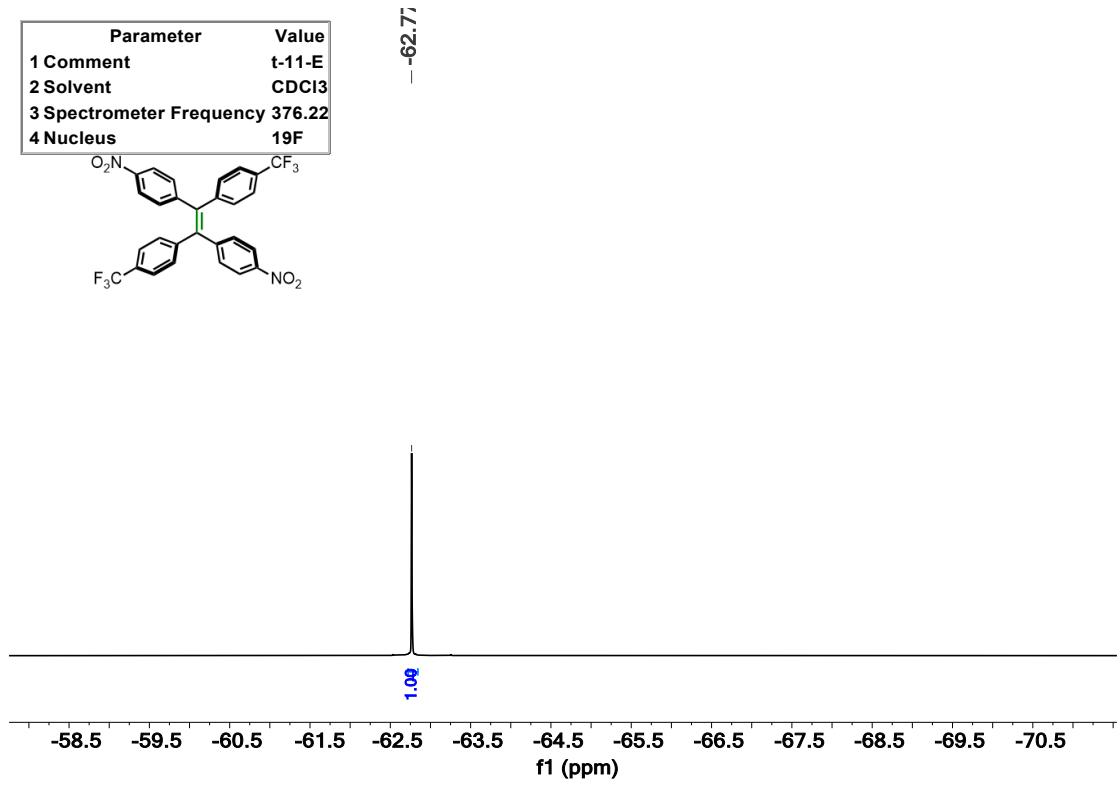
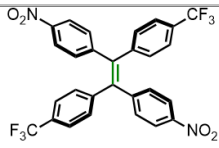
Parameter	Value
1 Comment	t-10-Z
2 Solvent	CDCI3
3 Spectrometer Frequency	399.87
4 Nucleus	1H



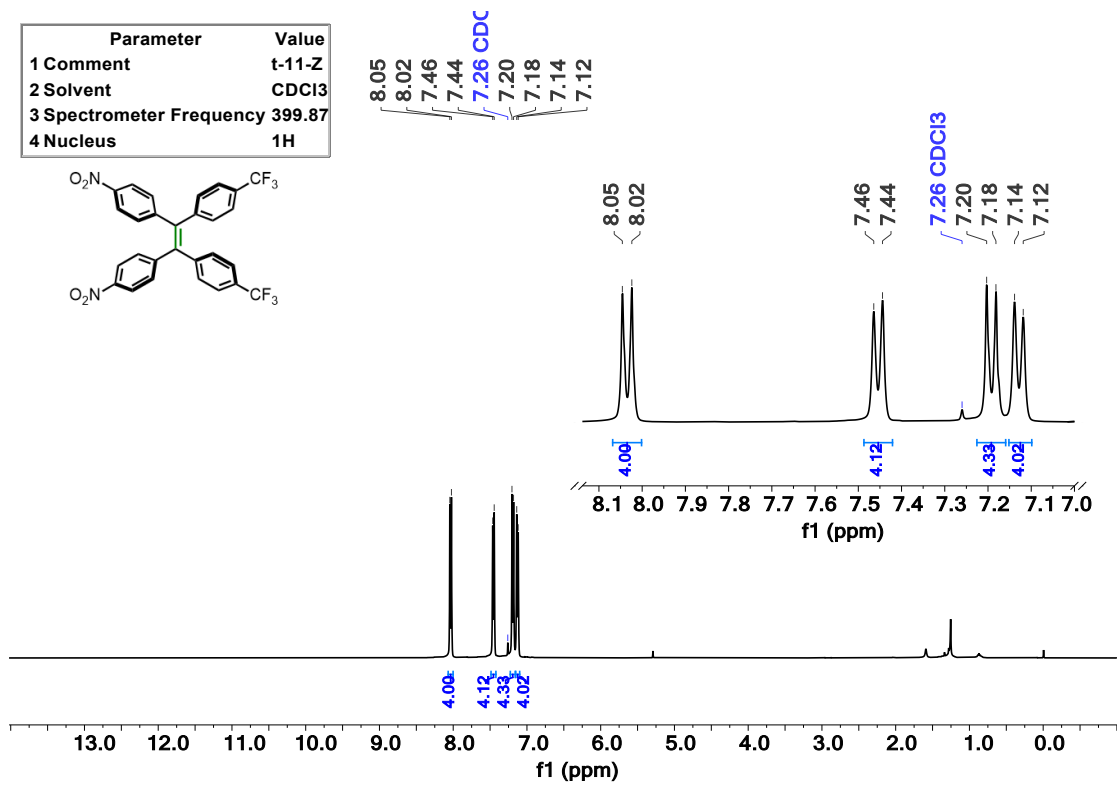
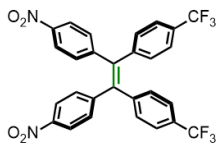


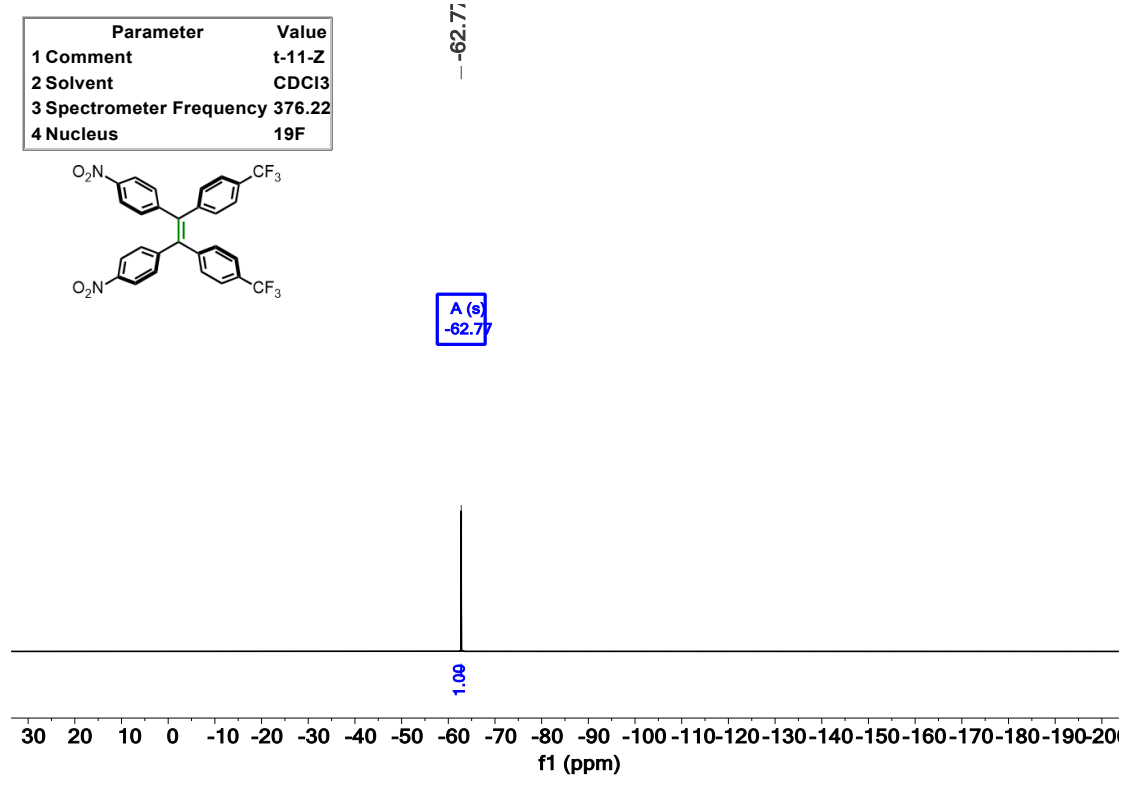
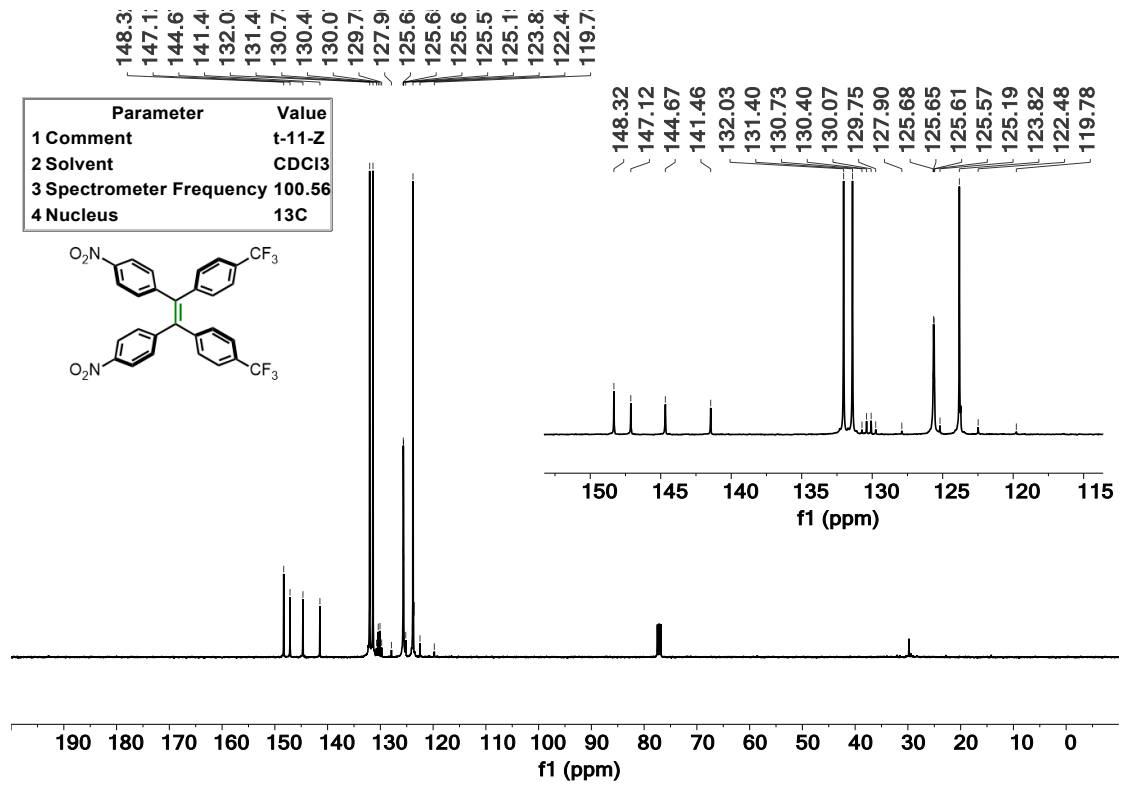


Parameter	Value
1 Comment	t-11-E
2 Solvent	CDCl3
3 Spectrometer Frequency	376.22
4 Nucleus	19F

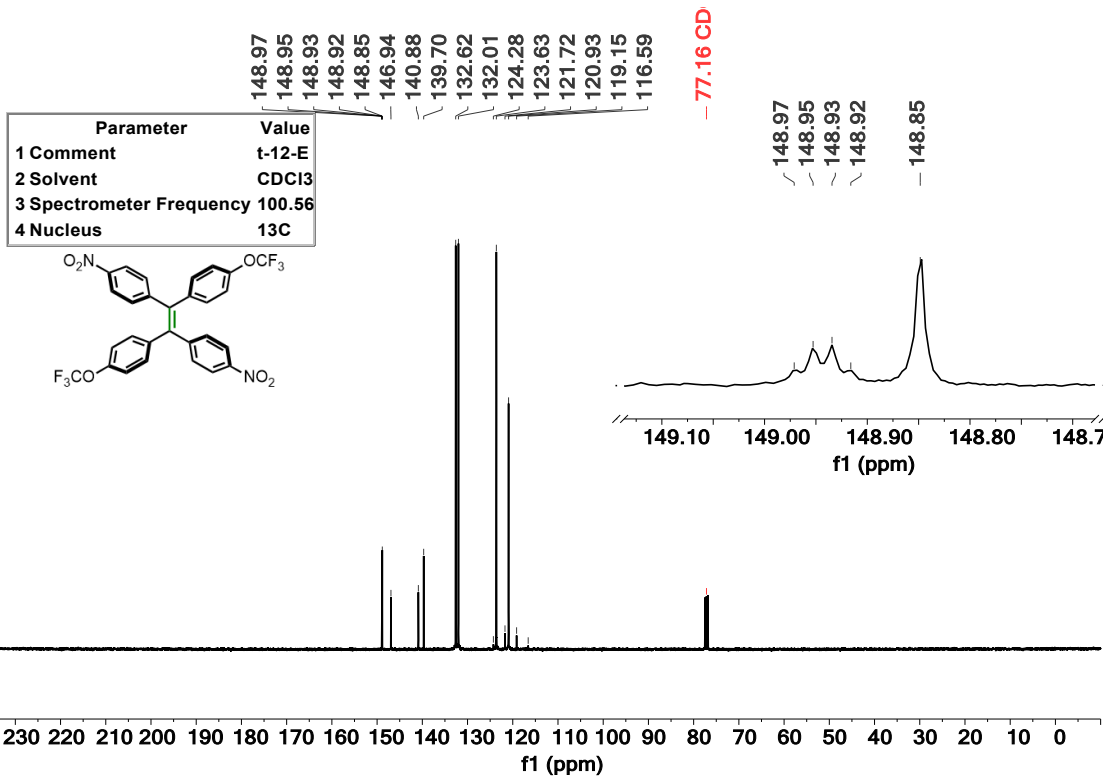
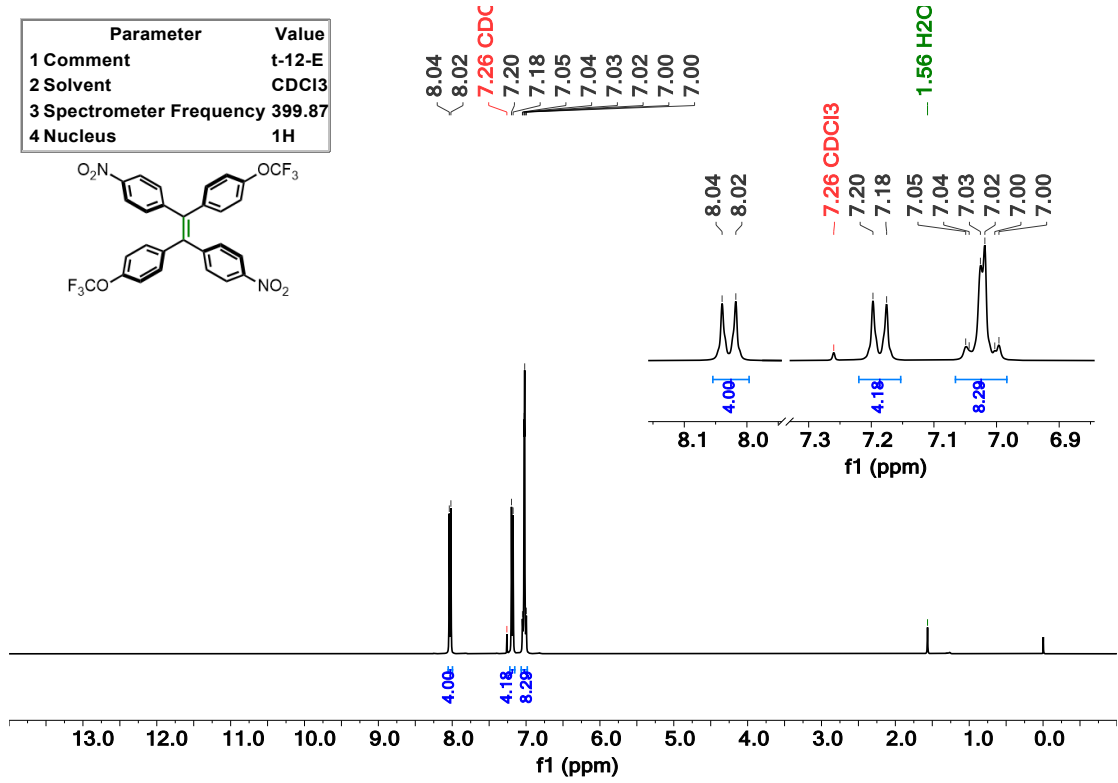
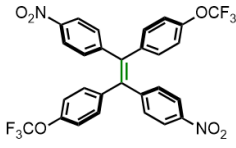


Parameter	Value
1 Comment	t-11-Z
2 Solvent	CDCl3
3 Spectrometer Frequency	399.87
4 Nucleus	1H

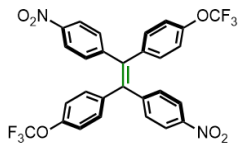




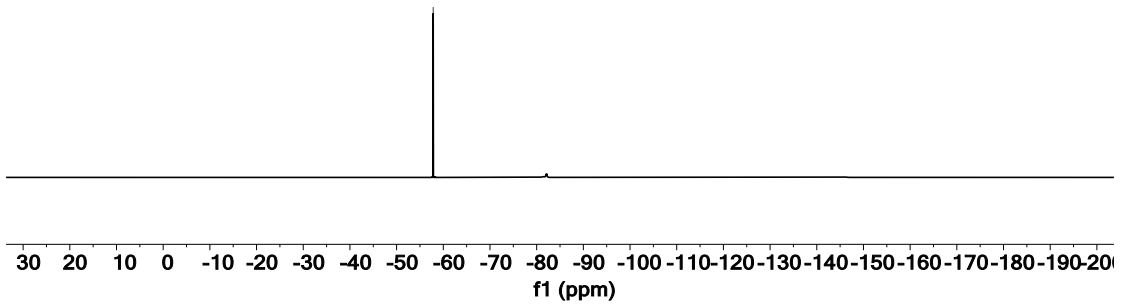
Parameter	Value
1 Comment	t-12-E
2 Solvent	CDCl3
3 Spectrometer Frequency	399.87
4 Nucleus	1H



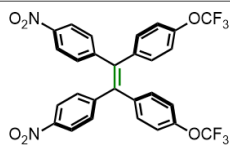
Parameter	Value
1 Comment	t-12-E
2 Solvent	CDCl3
3 Spectrometer Frequency	376.22
4 Nucleus	19F



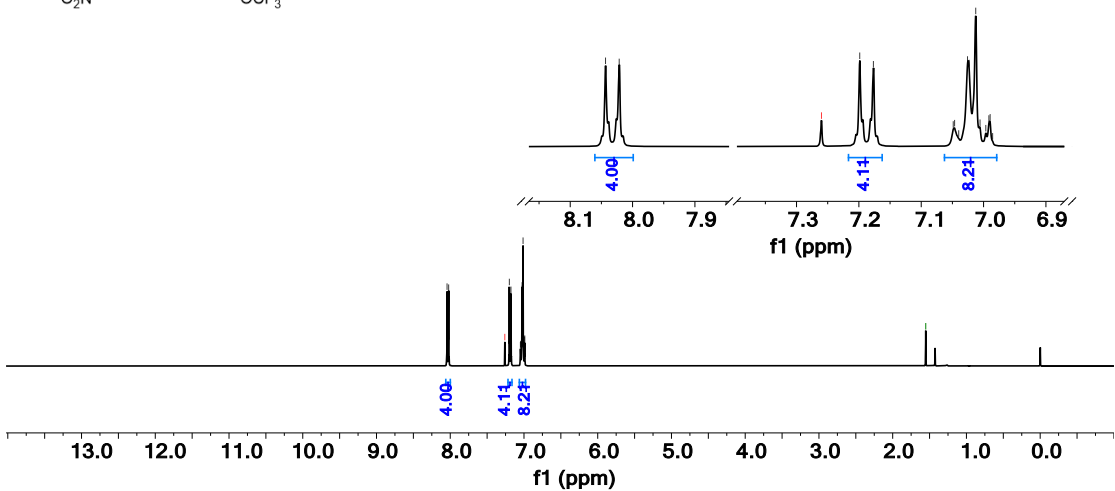
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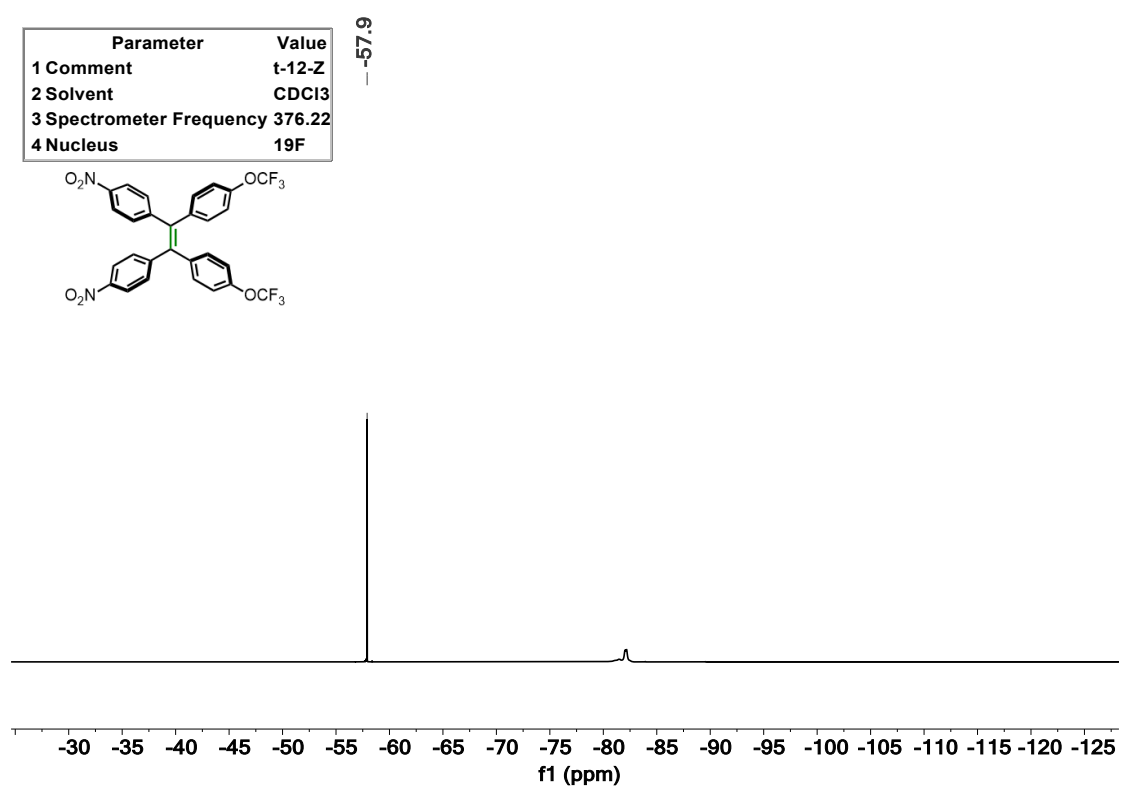
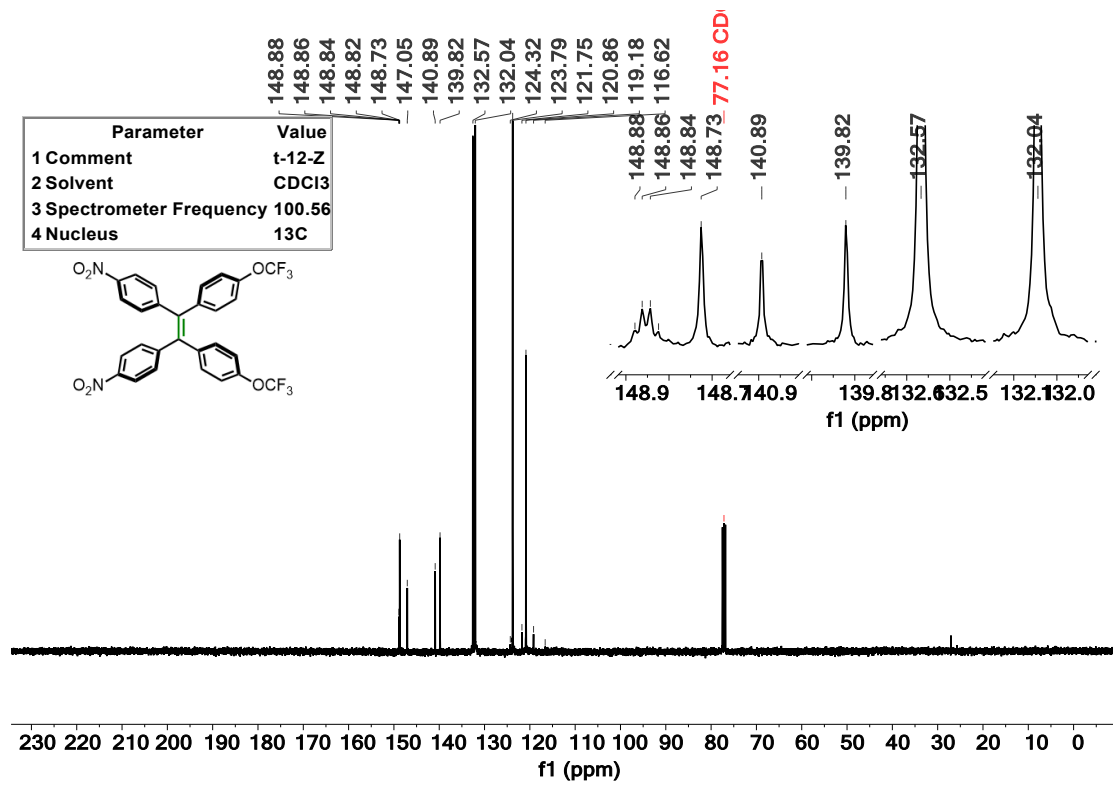


Parameter	Value
1 Comment	t-12-Z
2 Solvent	CDCl3
3 Spectrometer Frequency	399.87
4 Nucleus	1H

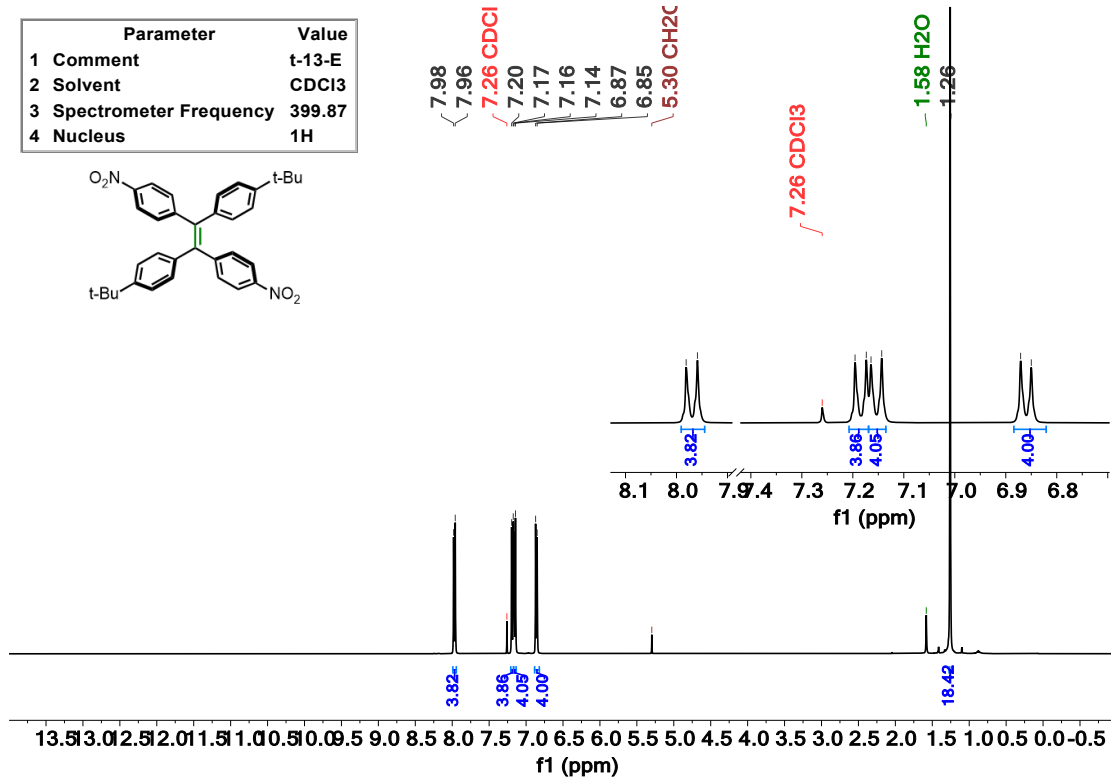
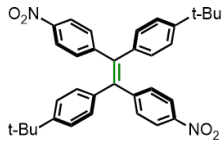


8.04
8.02
7.26 CDC
7.20
7.18
7.05
7.05
7.04
7.03
7.02
7.01
7.01
7.00
7.26 CDC
7.20
7.18
7.05
7.05
7.03
7.02
7.01
7.01
7.00
6.99
6.99
1.55 H2C

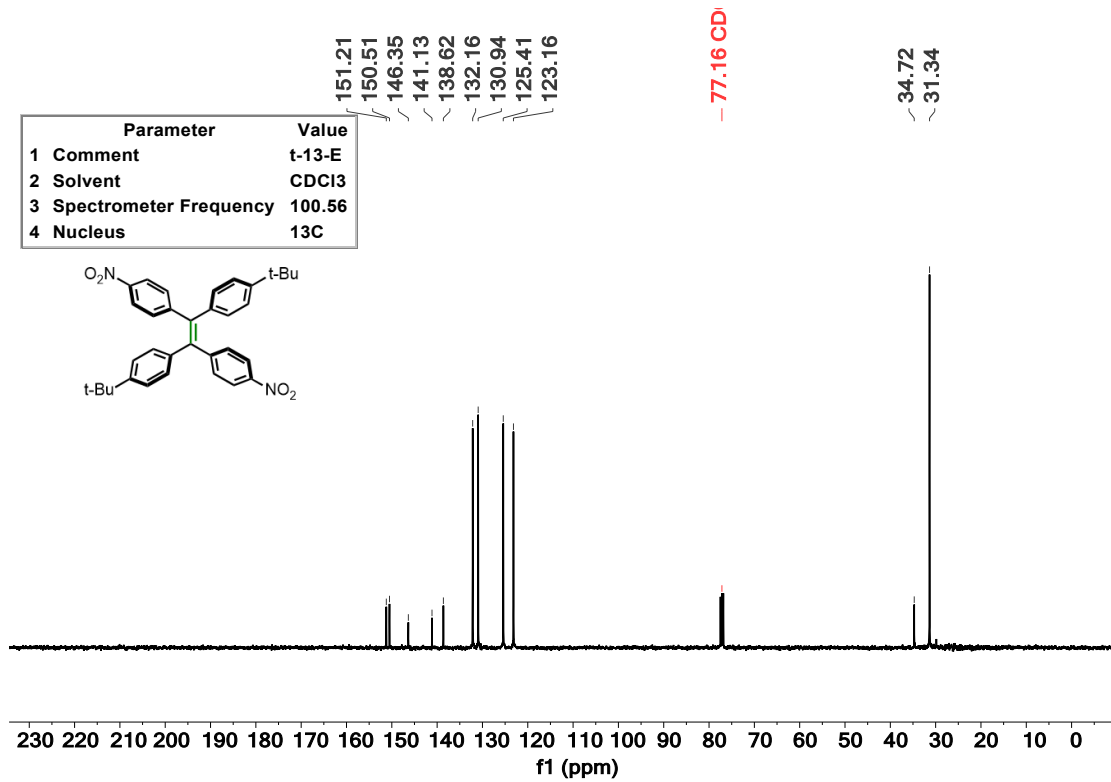
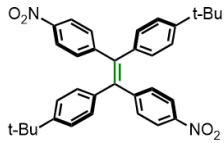




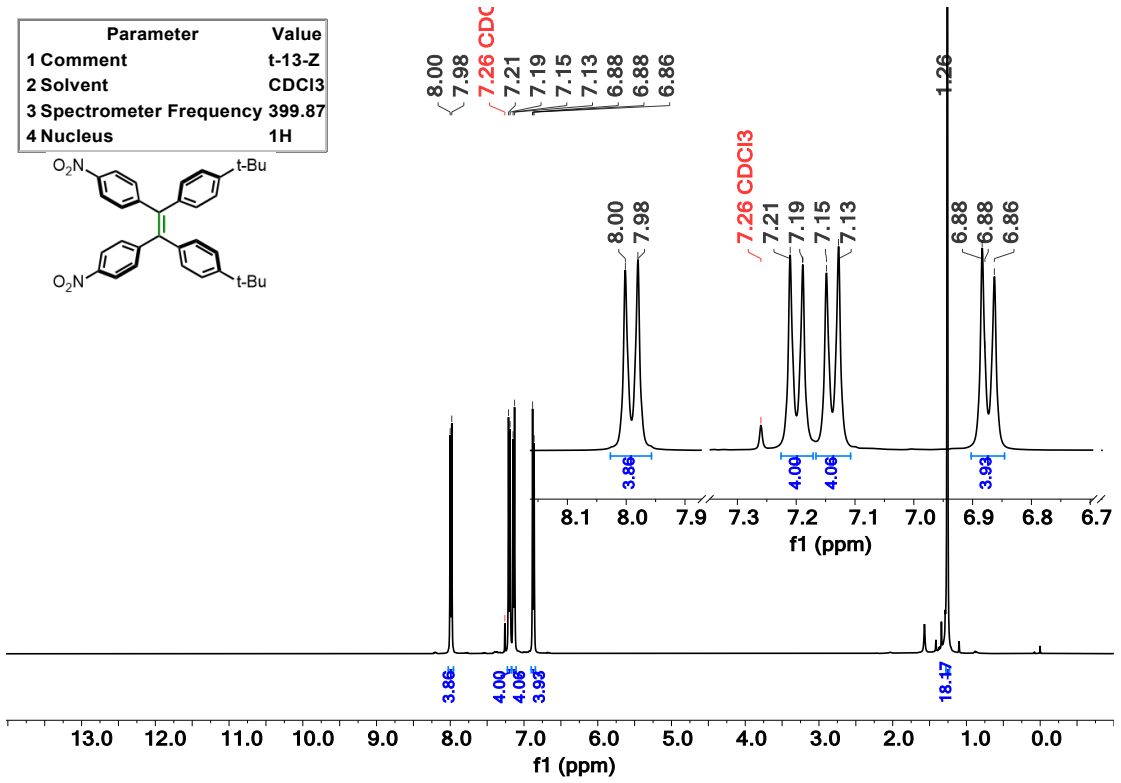
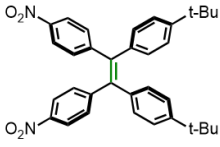
Parameter	Value
1 Comment	t-13-E
2 Solvent	CDCl3
3 Spectrometer Frequency	399.87
4 Nucleus	1H



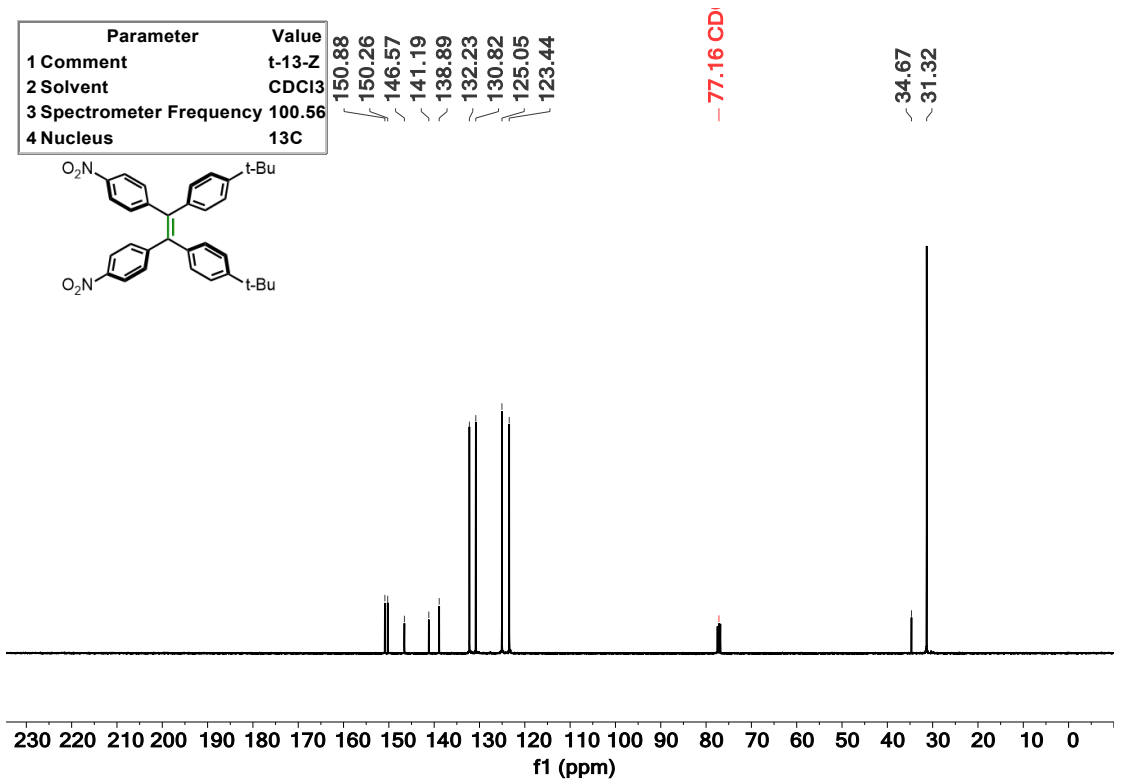
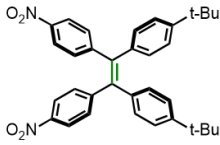
Parameter	Value
1 Comment	t-13-E
2 Solvent	CDCl3
3 Spectrometer Frequency	100.56
4 Nucleus	13C

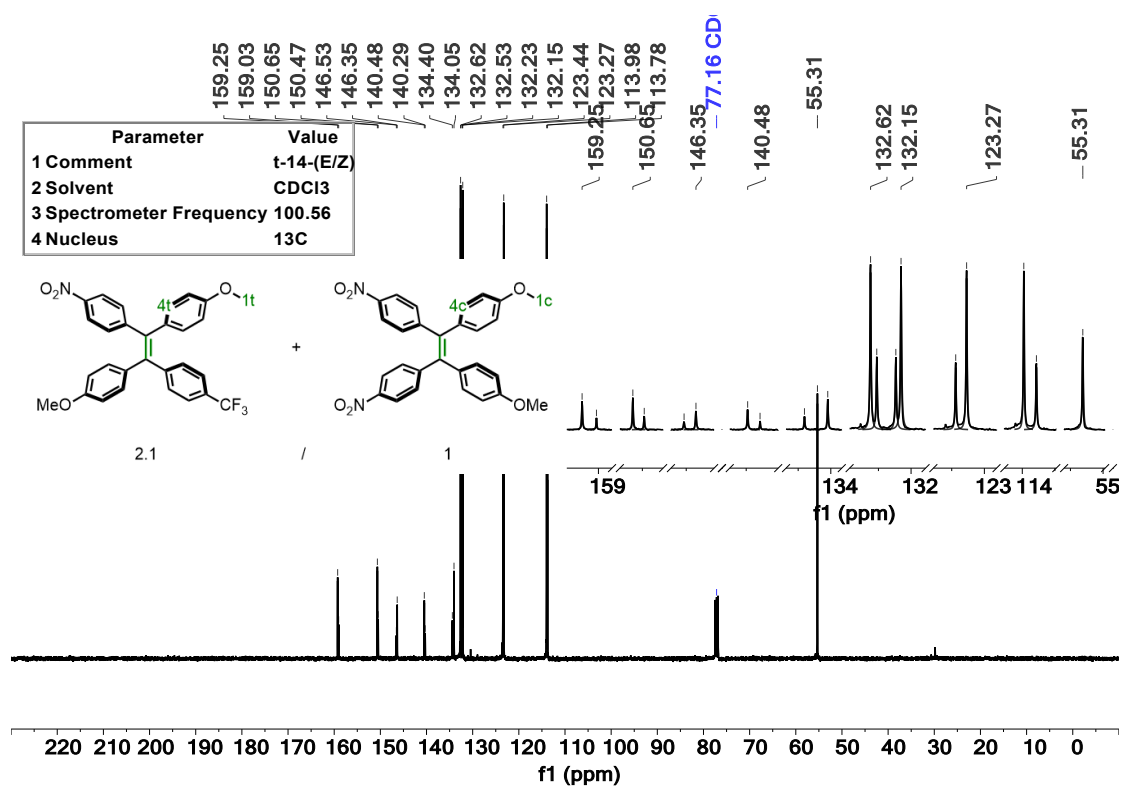
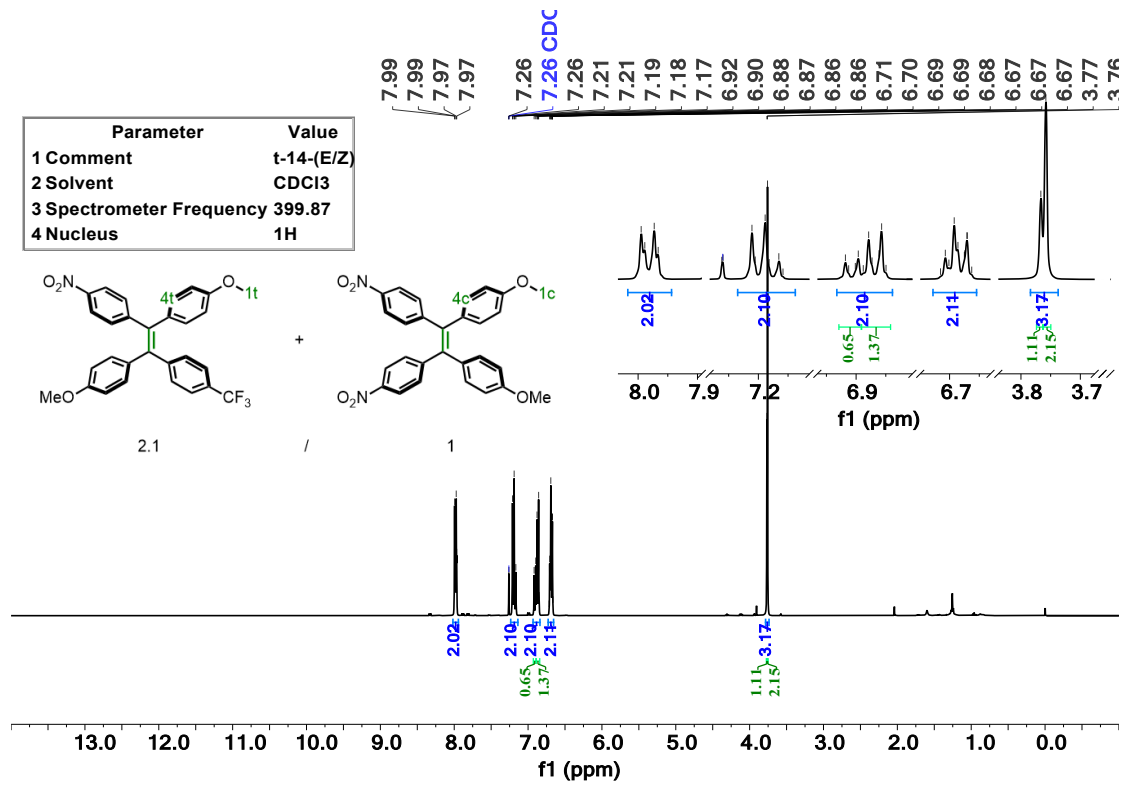


Parameter	Value
1 Comment	t-13-Z
2 Solvent	CDCl3
3 Spectrometer Frequency	399.87
4 Nucleus	1H

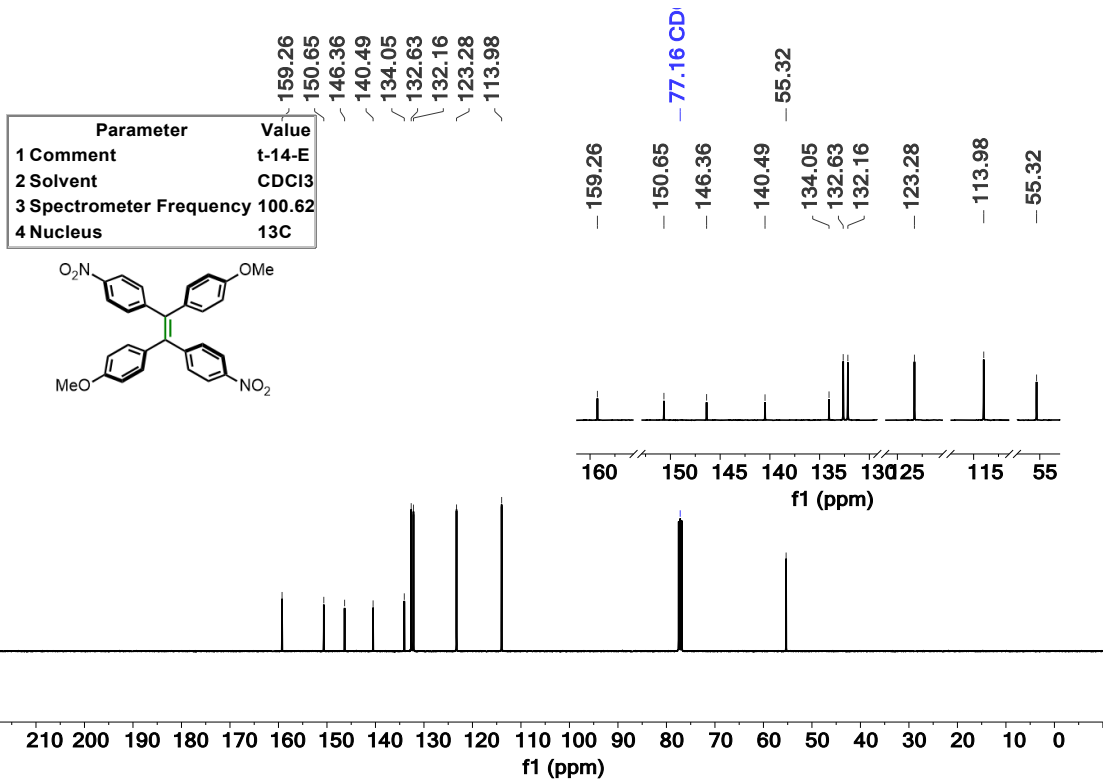
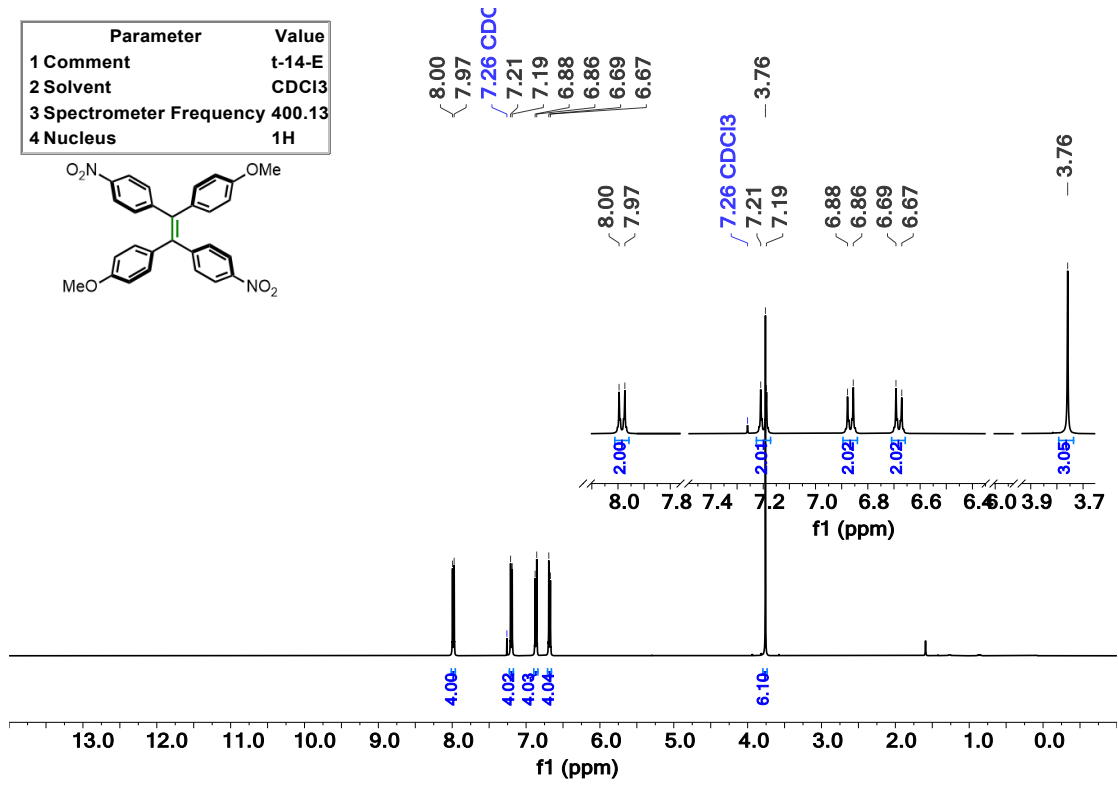
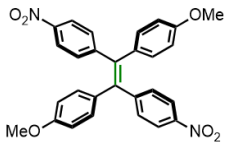


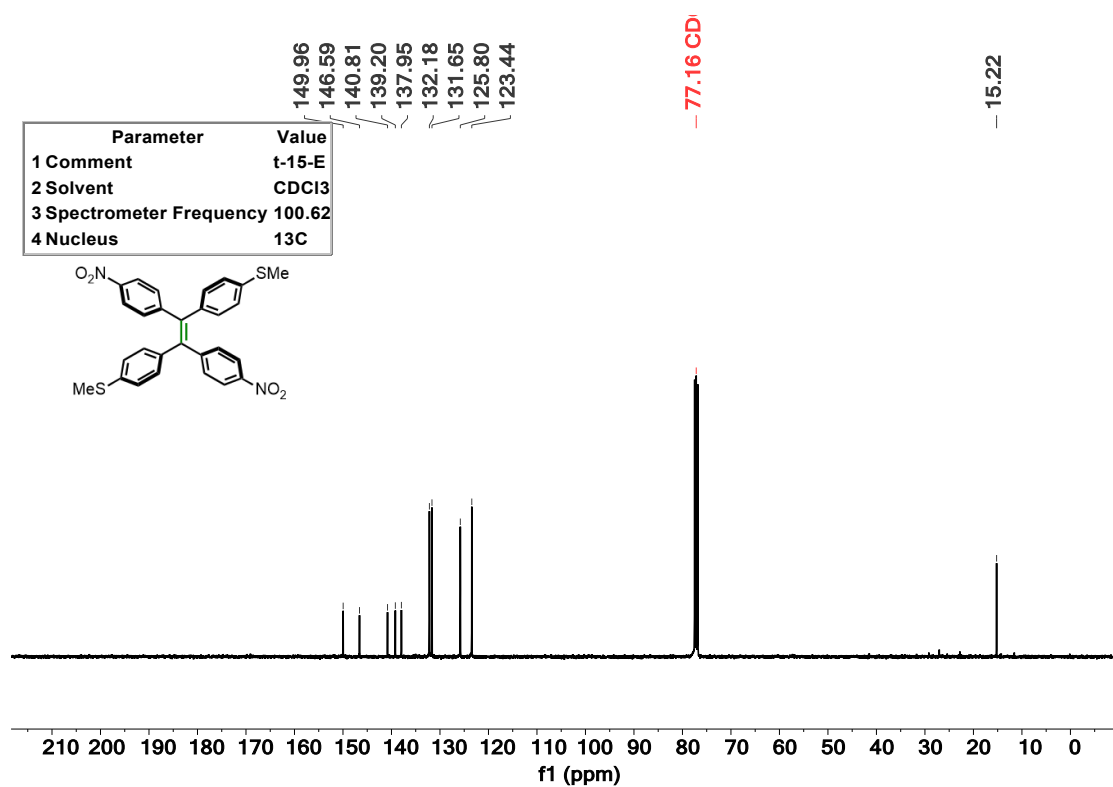
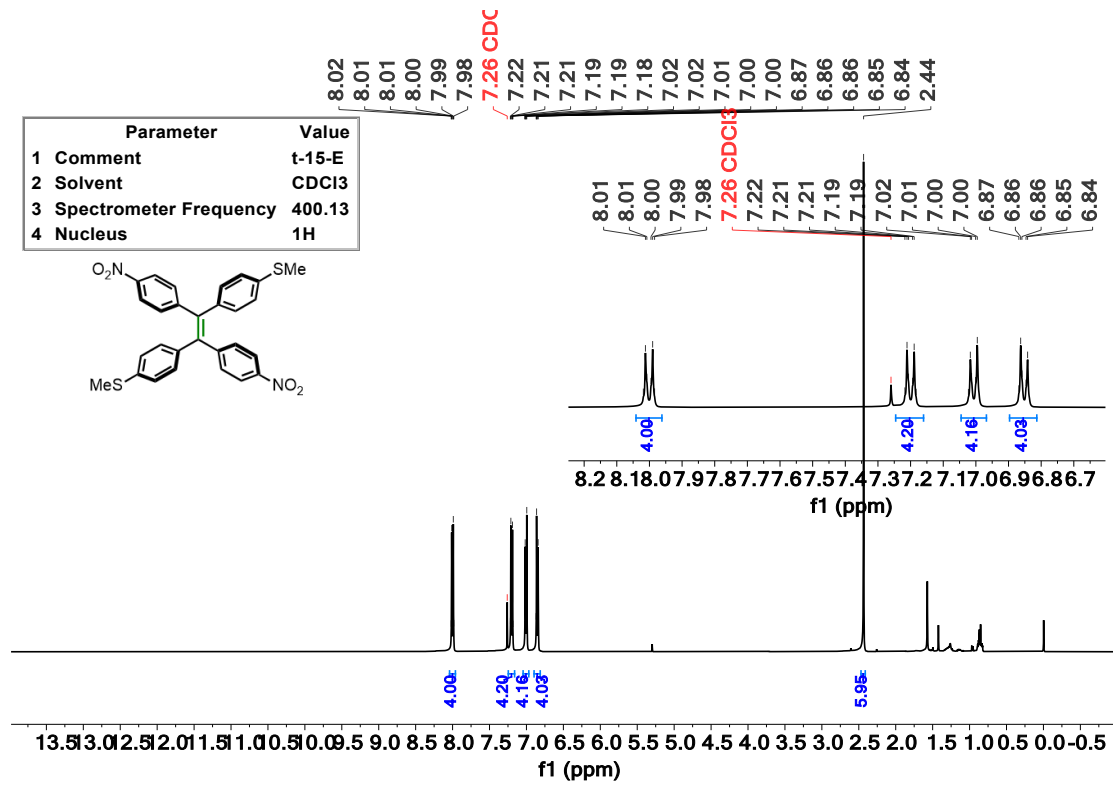
Parameter	Value
1 Comment	t-13-Z
2 Solvent	CDCl3
3 Spectrometer Frequency	100.56
4 Nucleus	13C

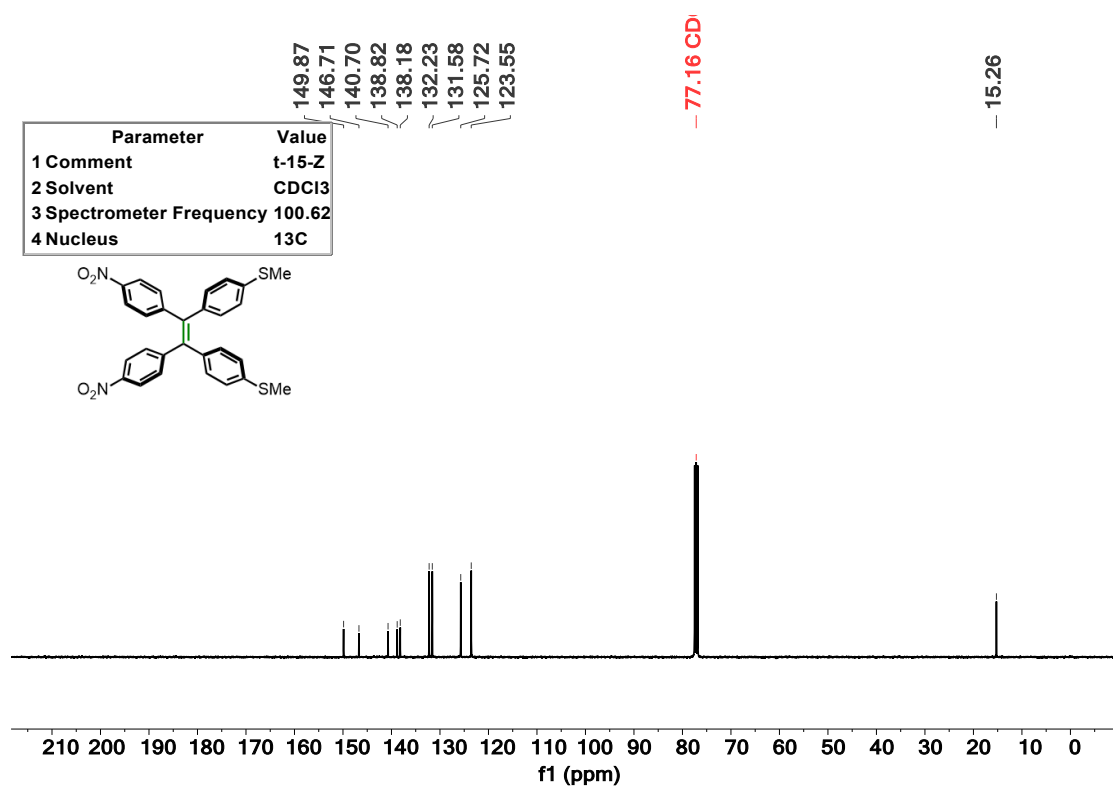
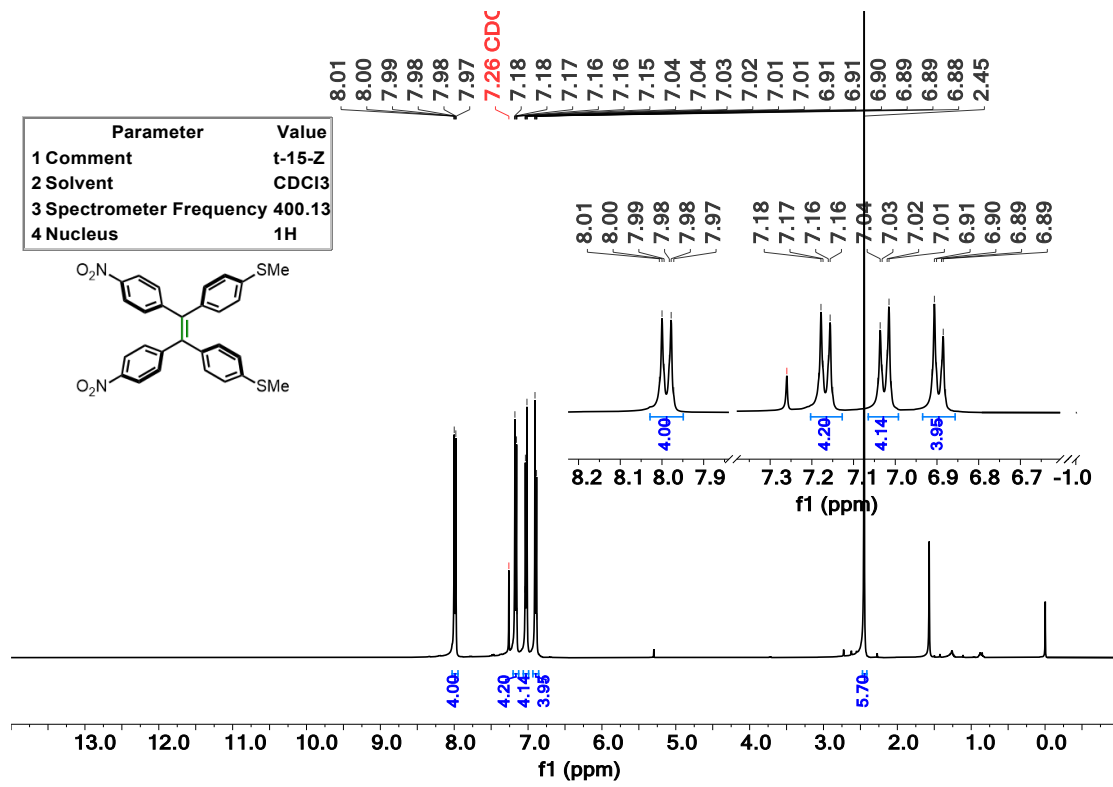


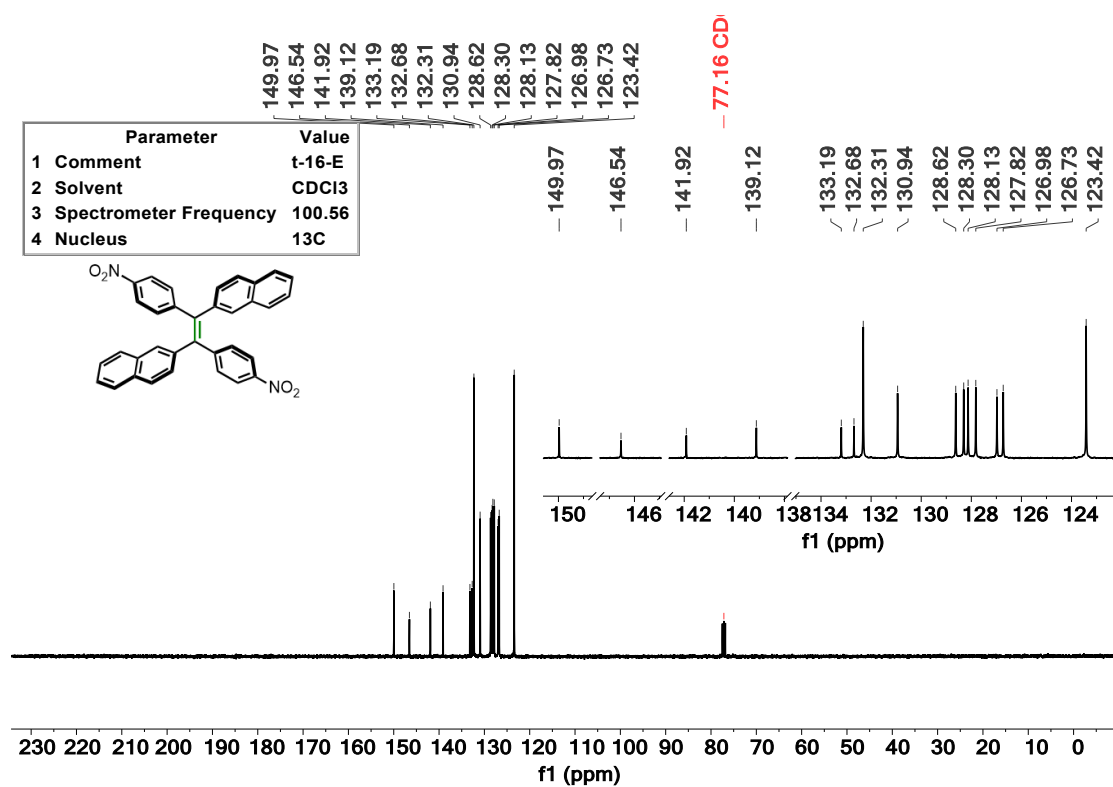
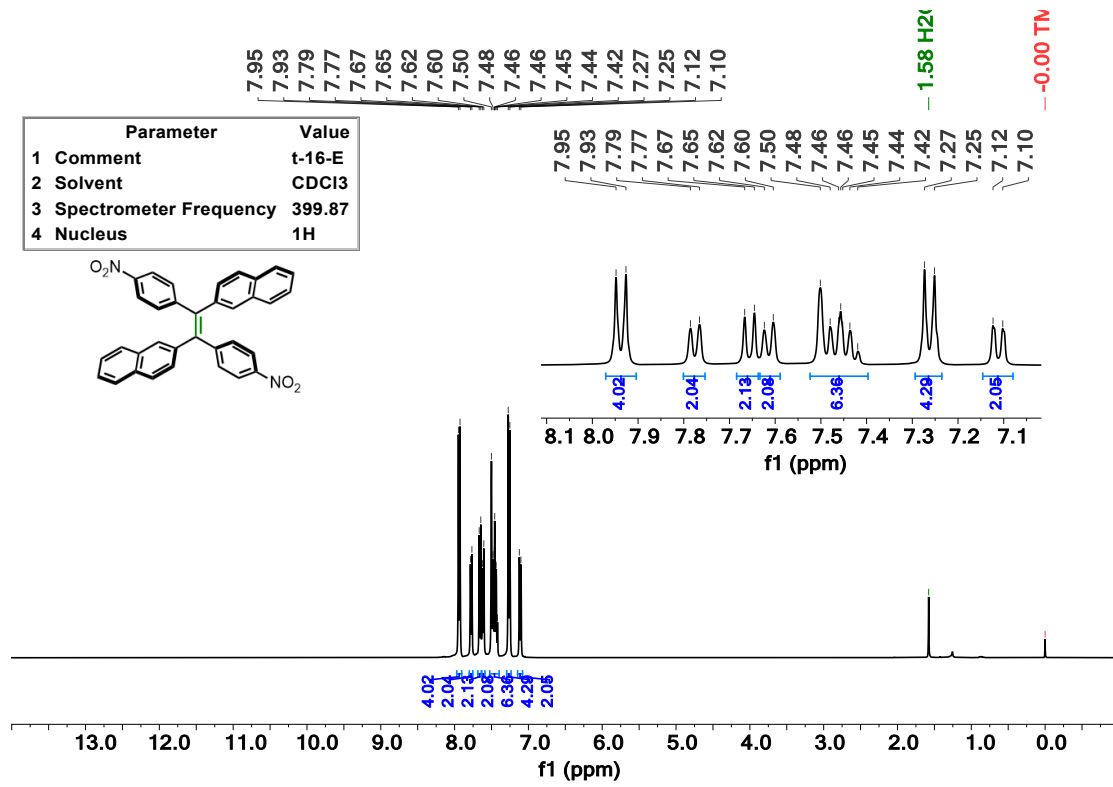


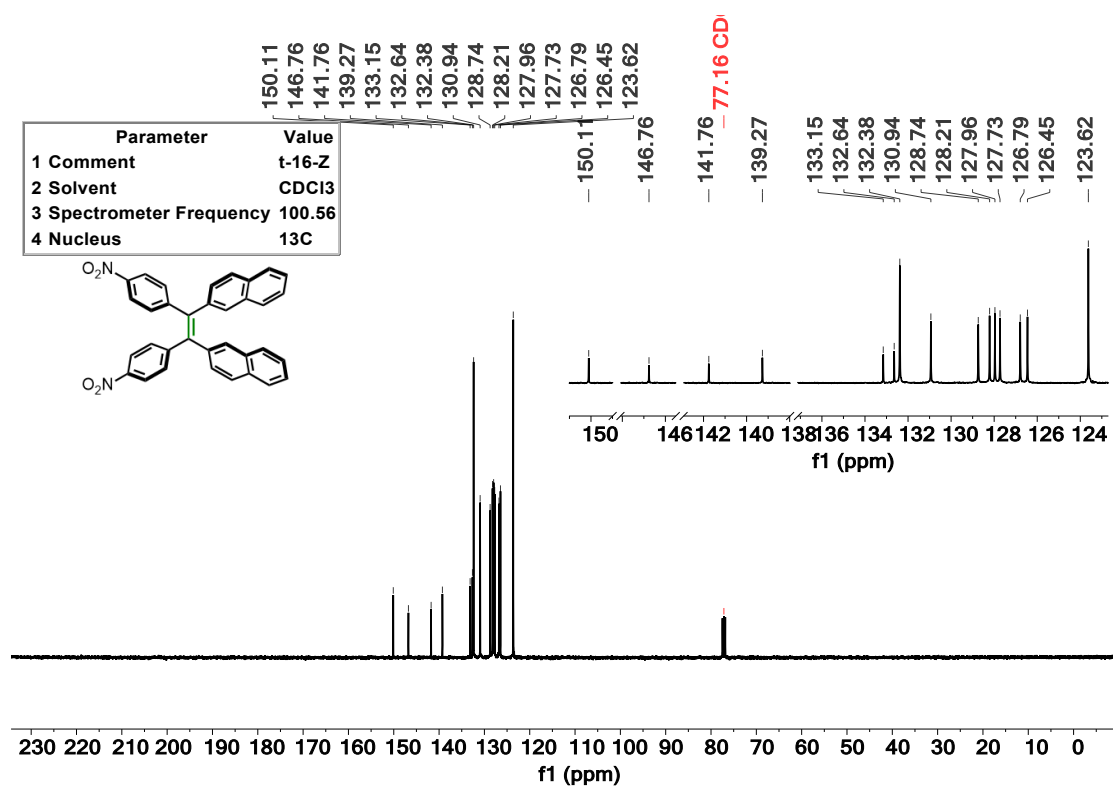
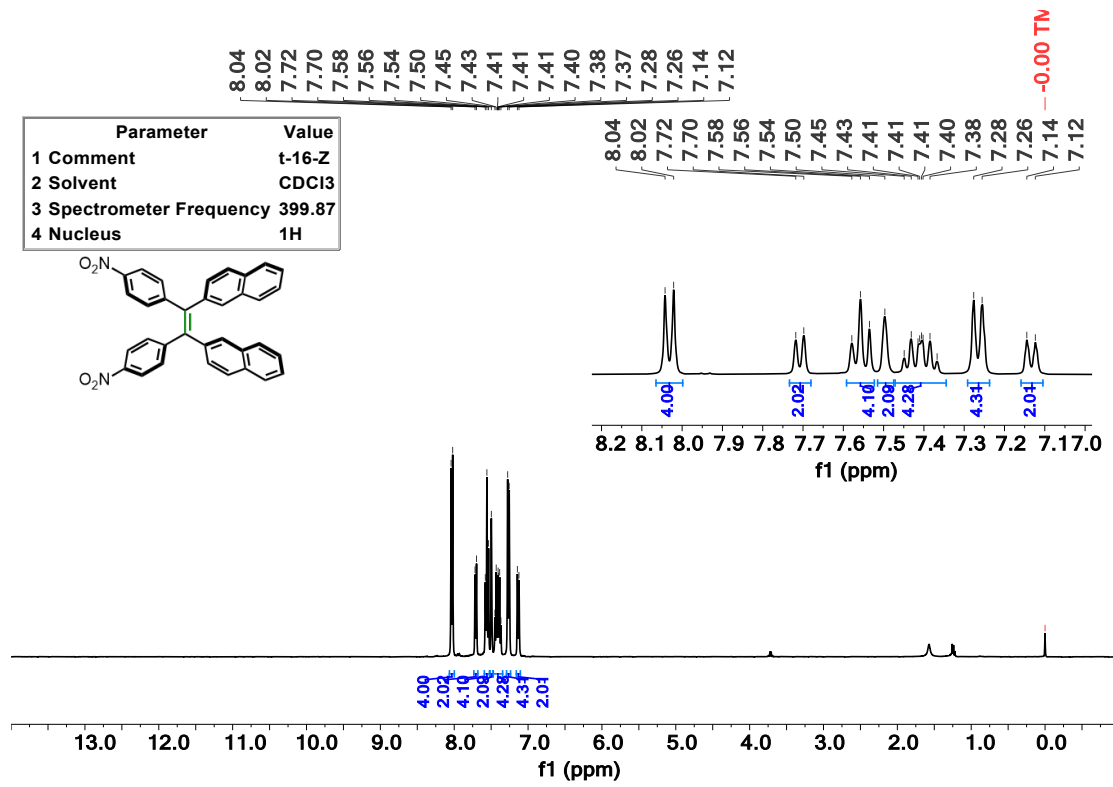
Parameter	Value
1 Comment	t-14-E
2 Solvent	CDCl3
3 Spectrometer Frequency	400.13
4 Nucleus	1H

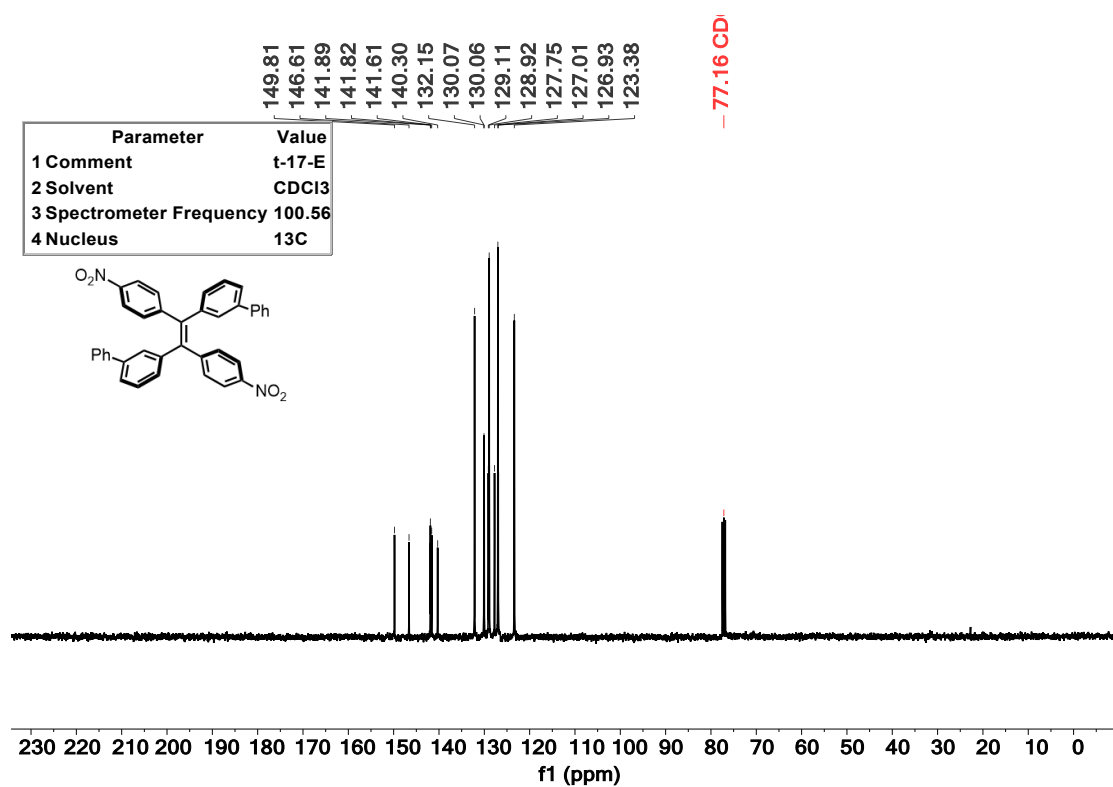
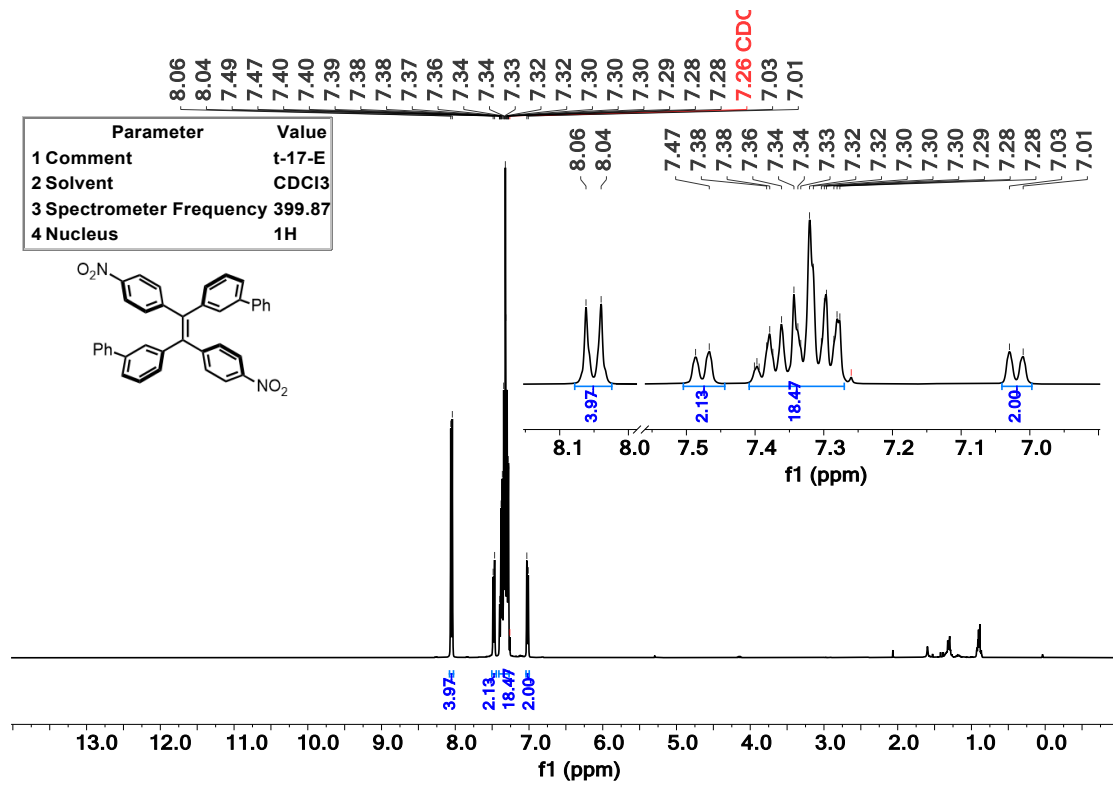


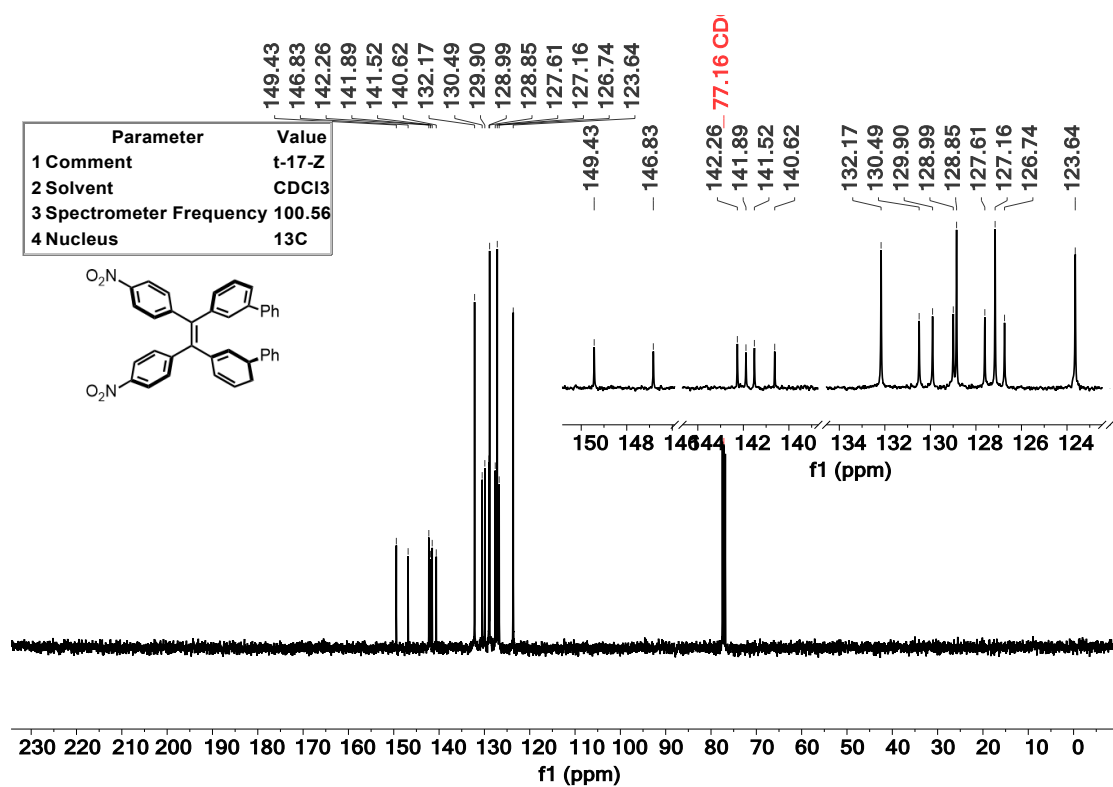
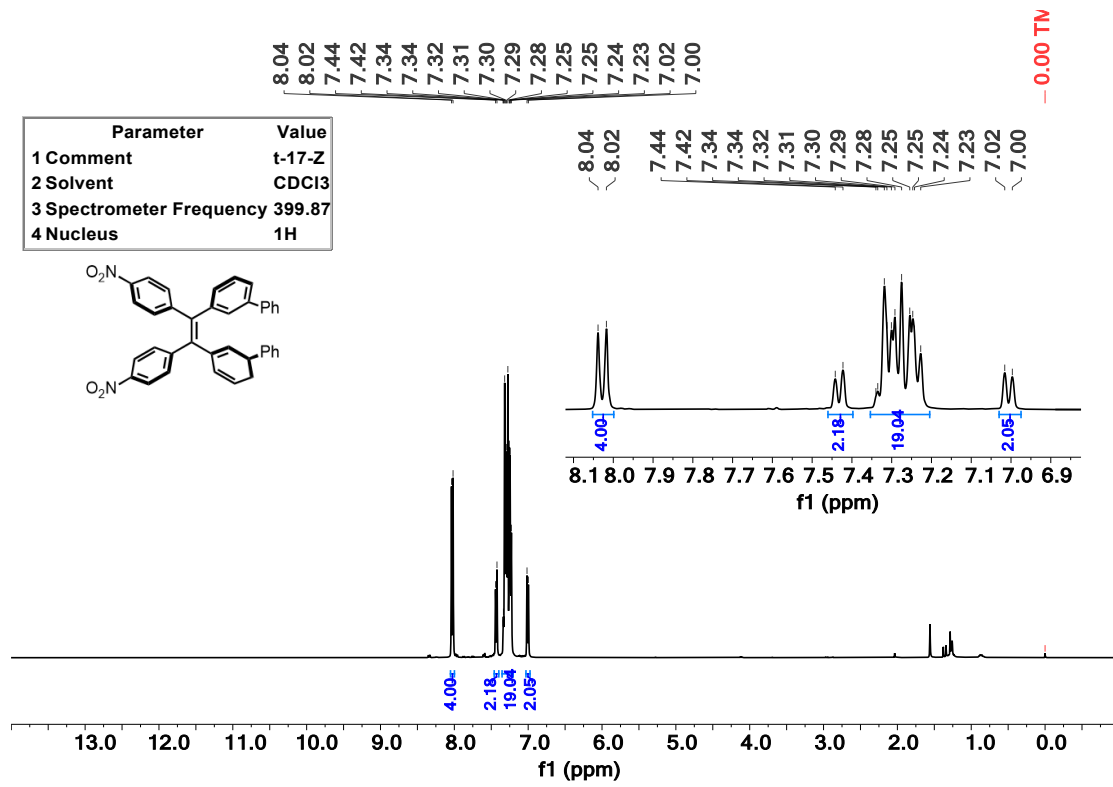


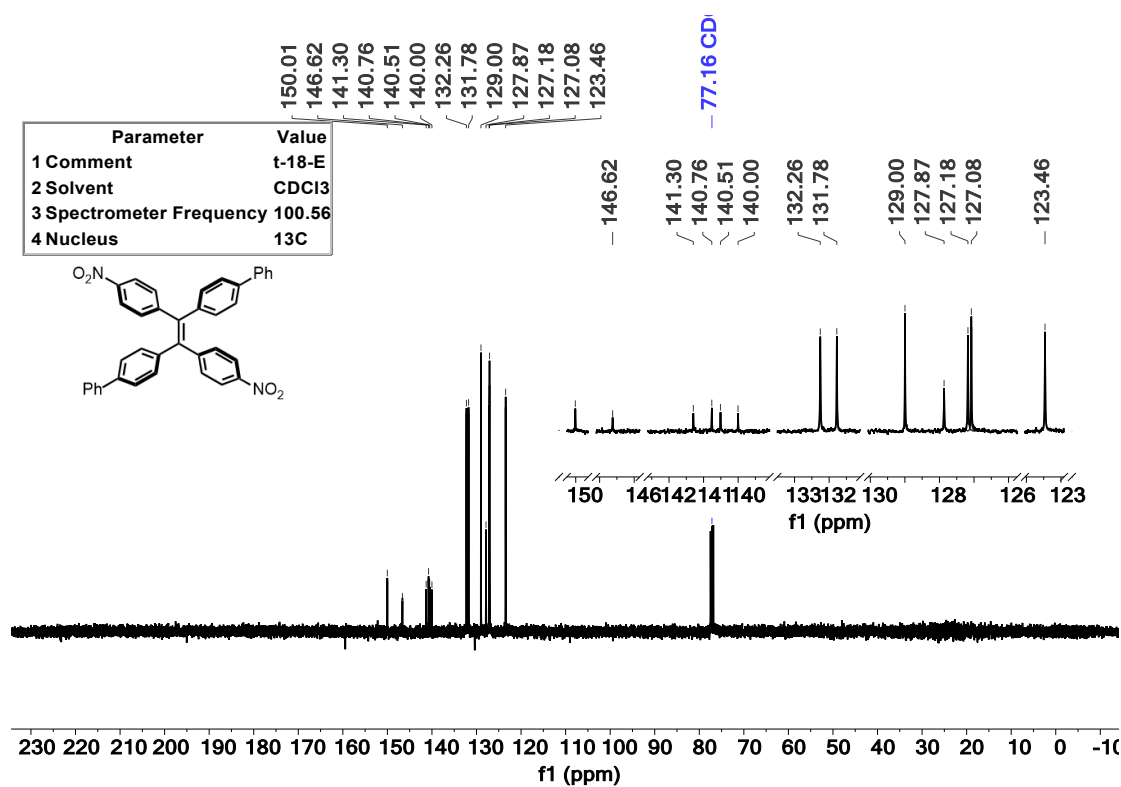
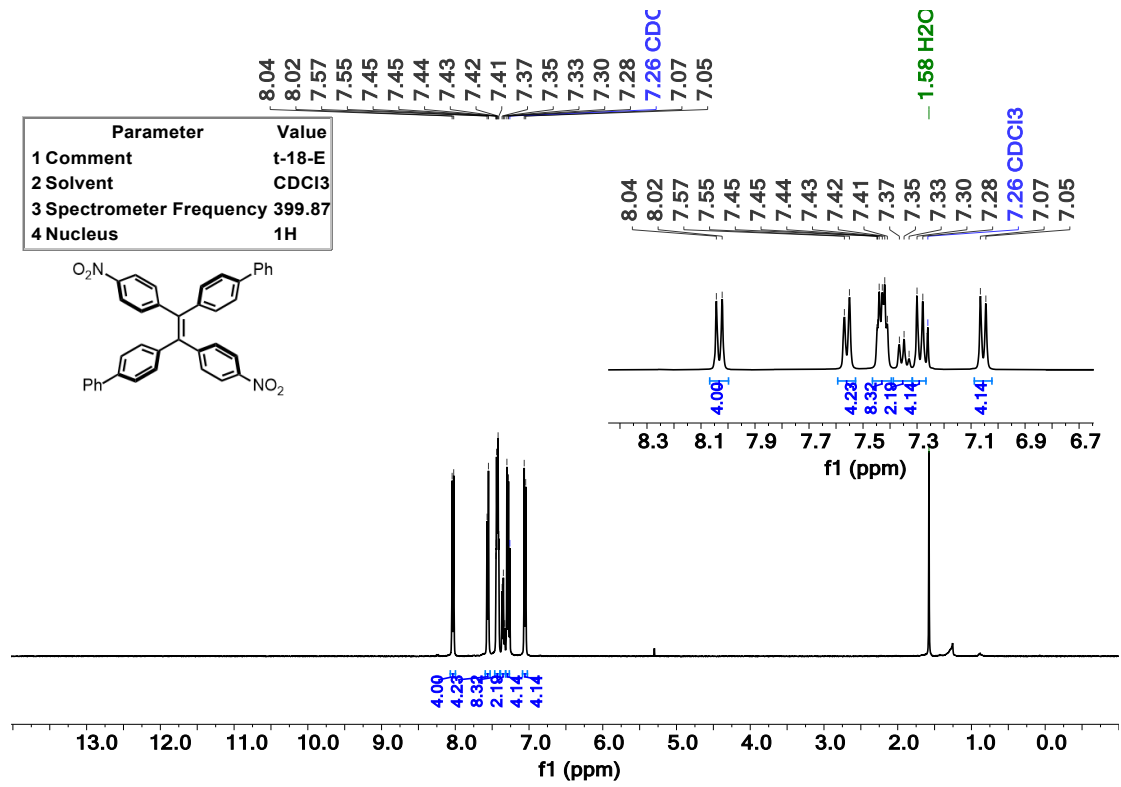


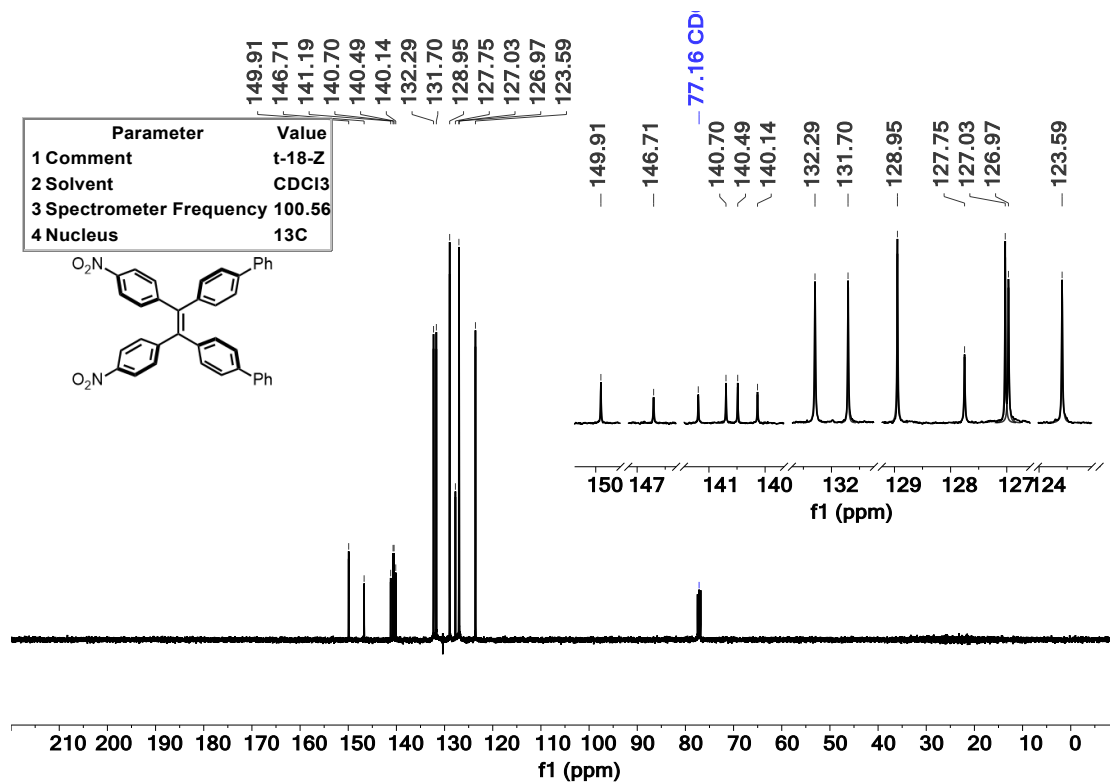
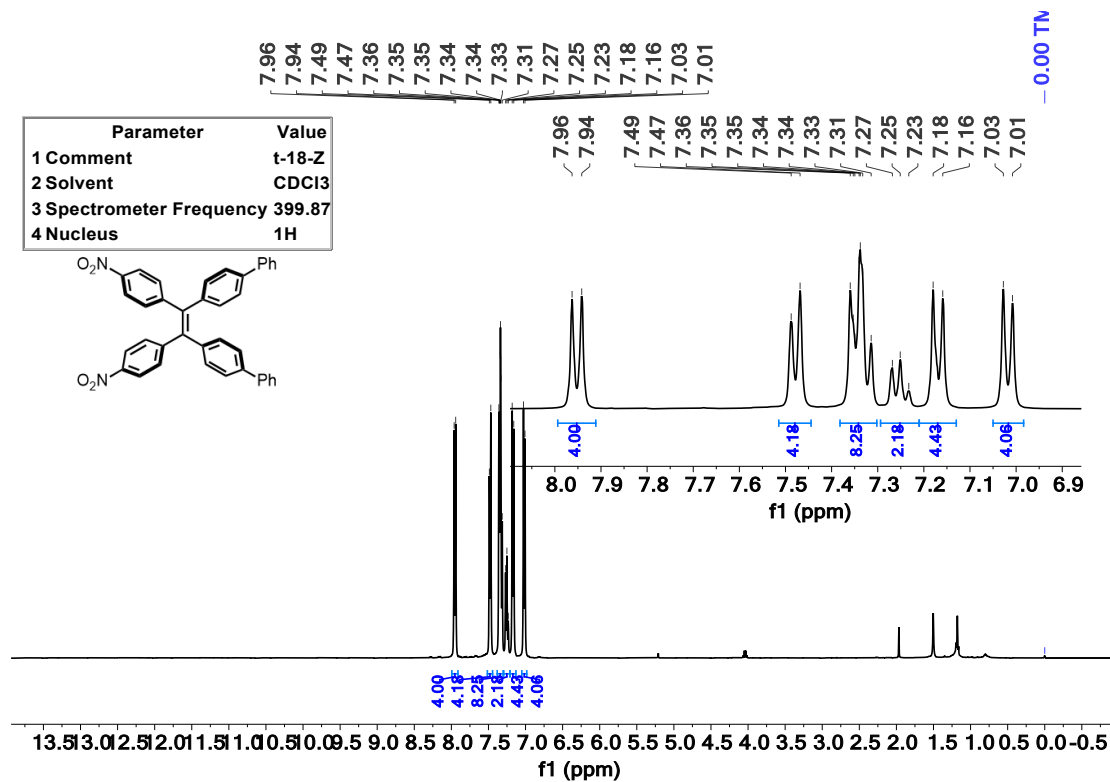


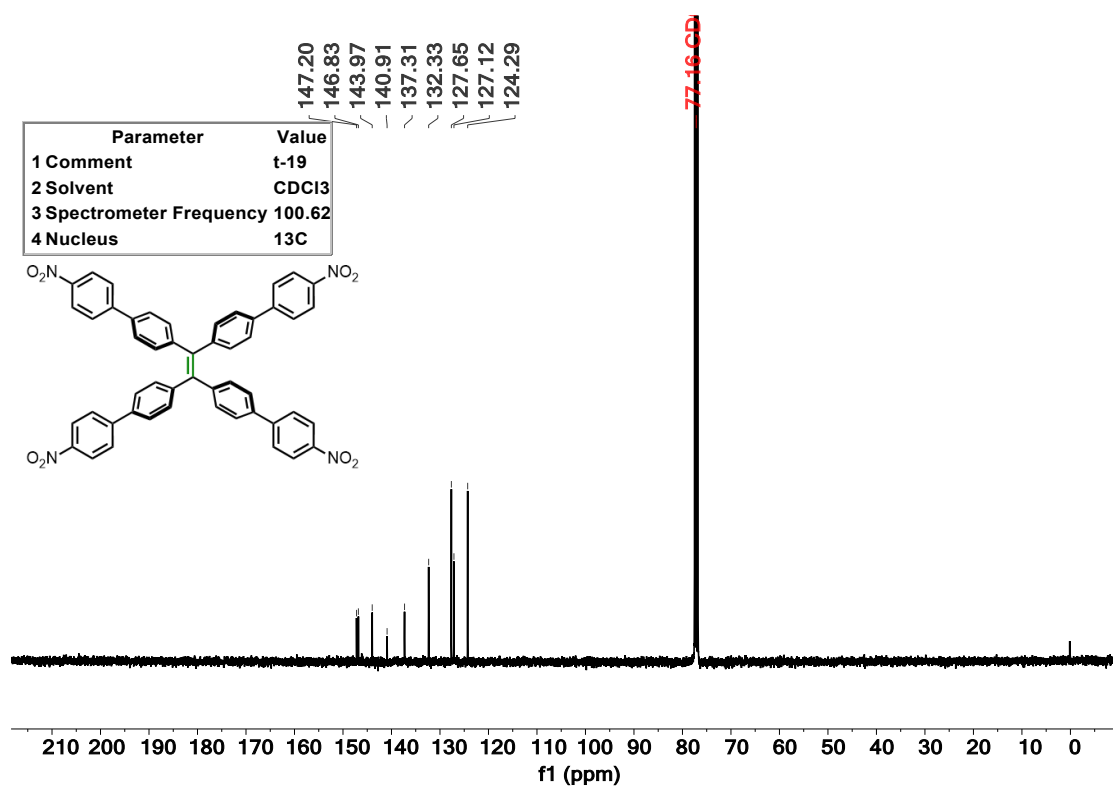
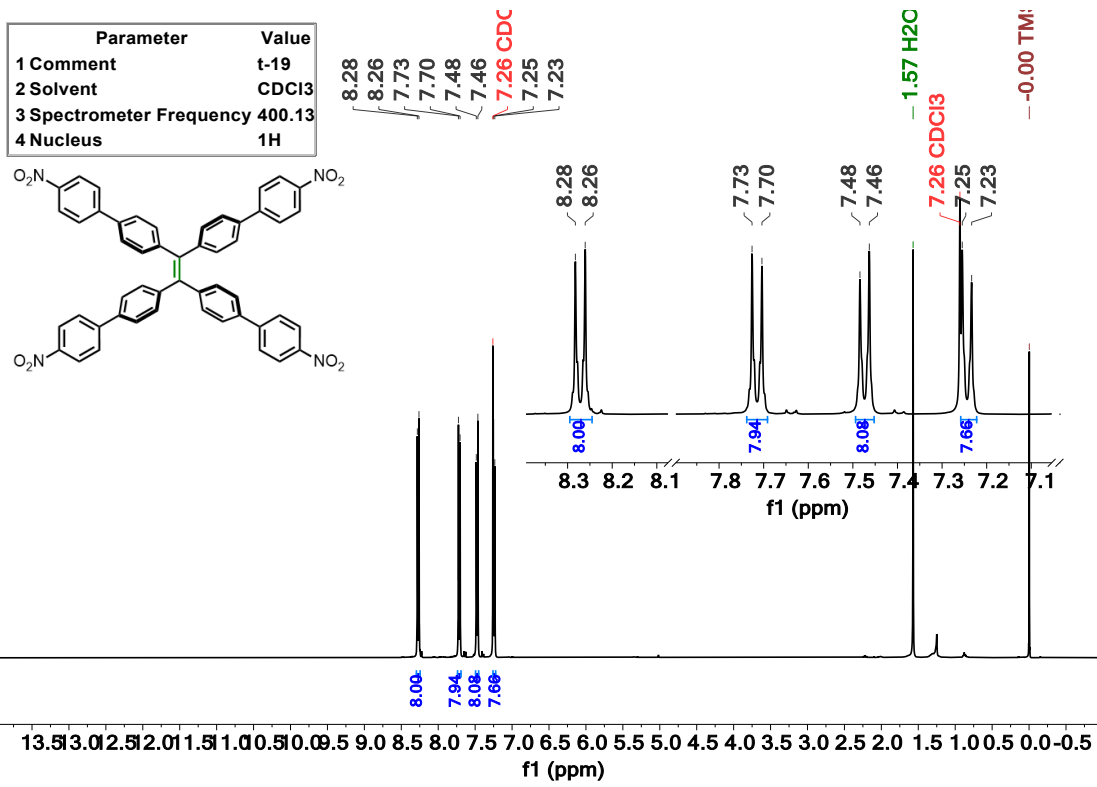


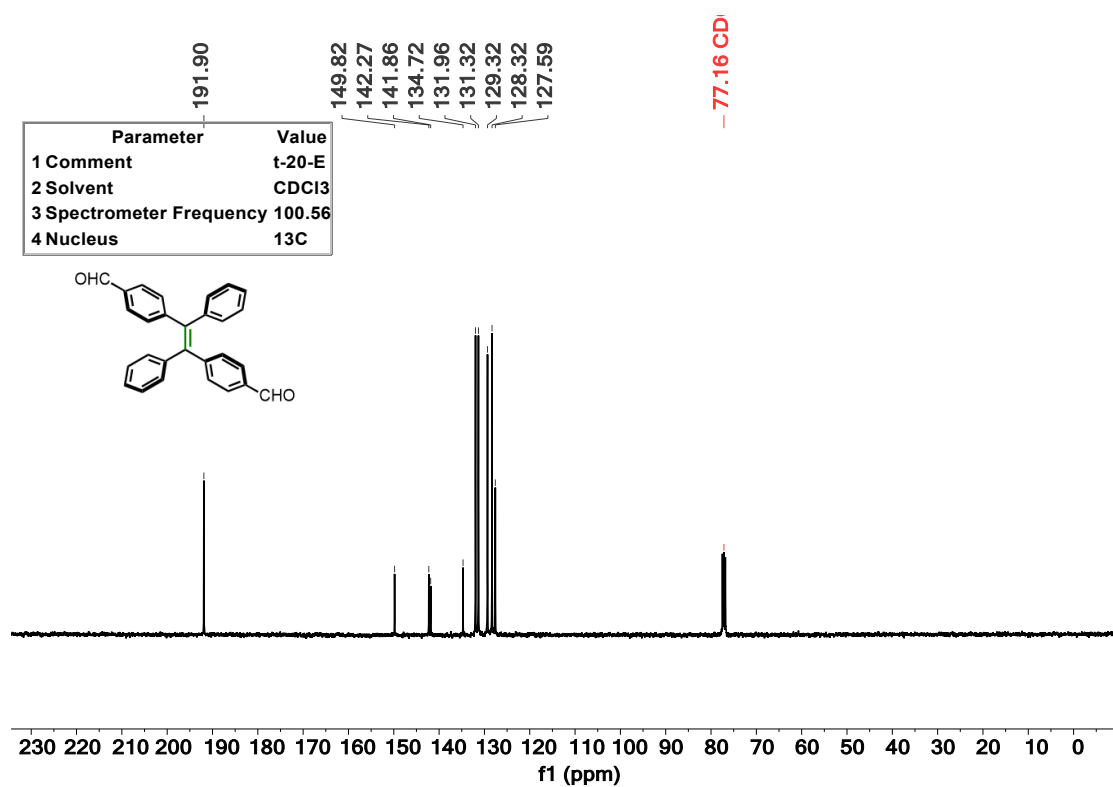
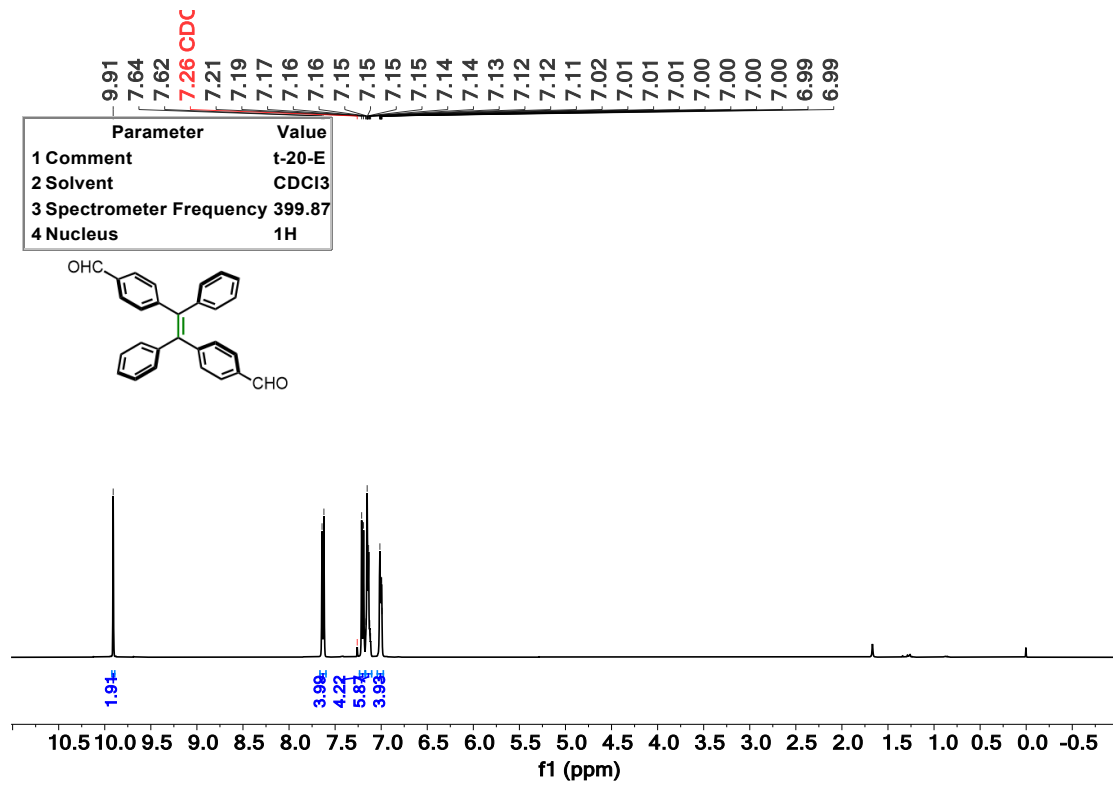


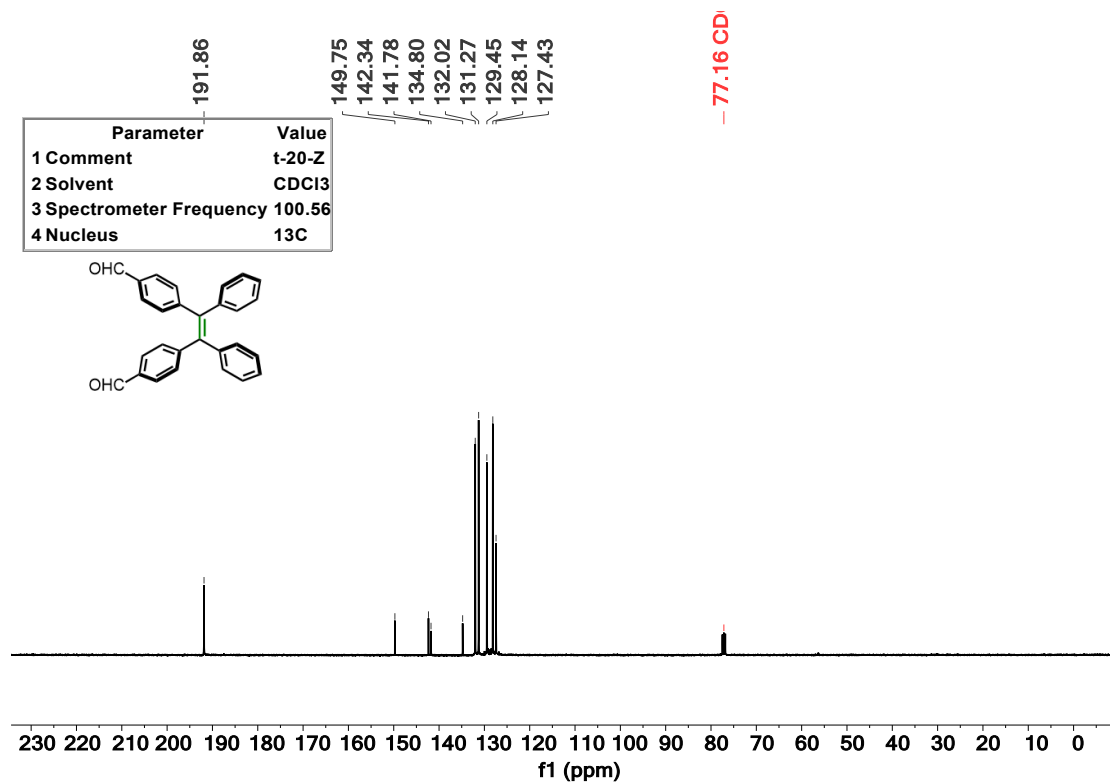
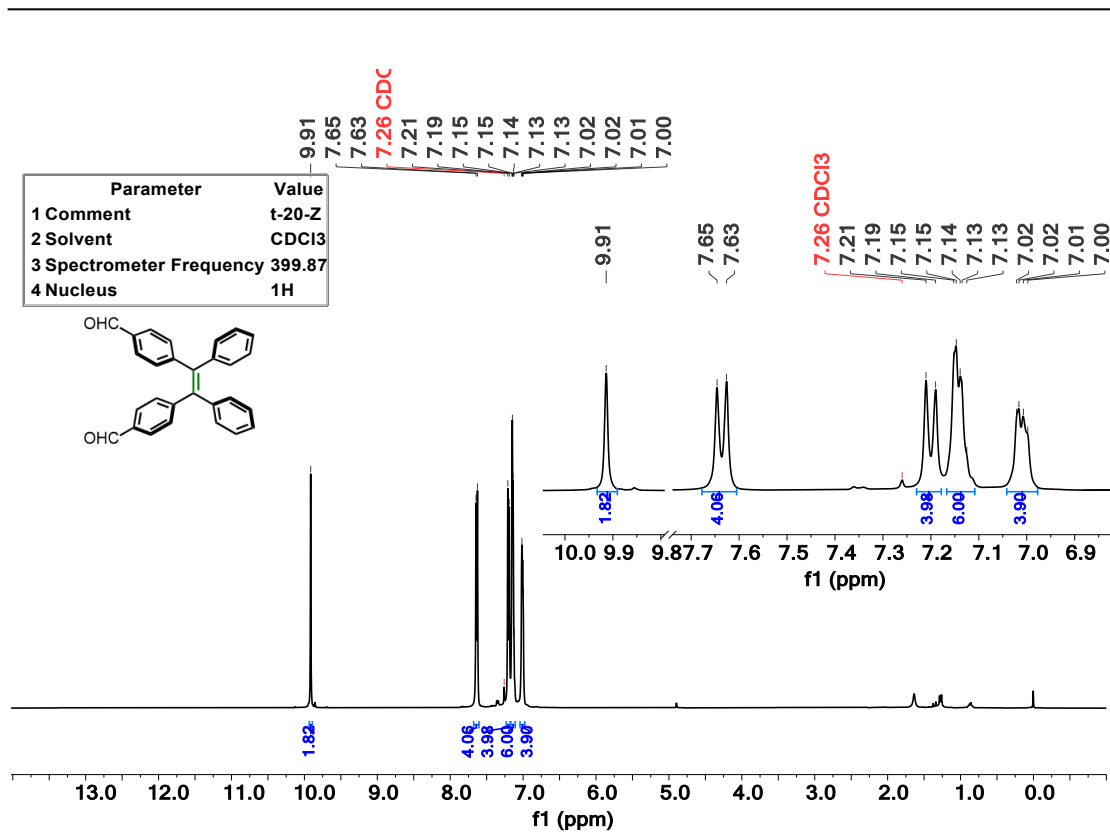


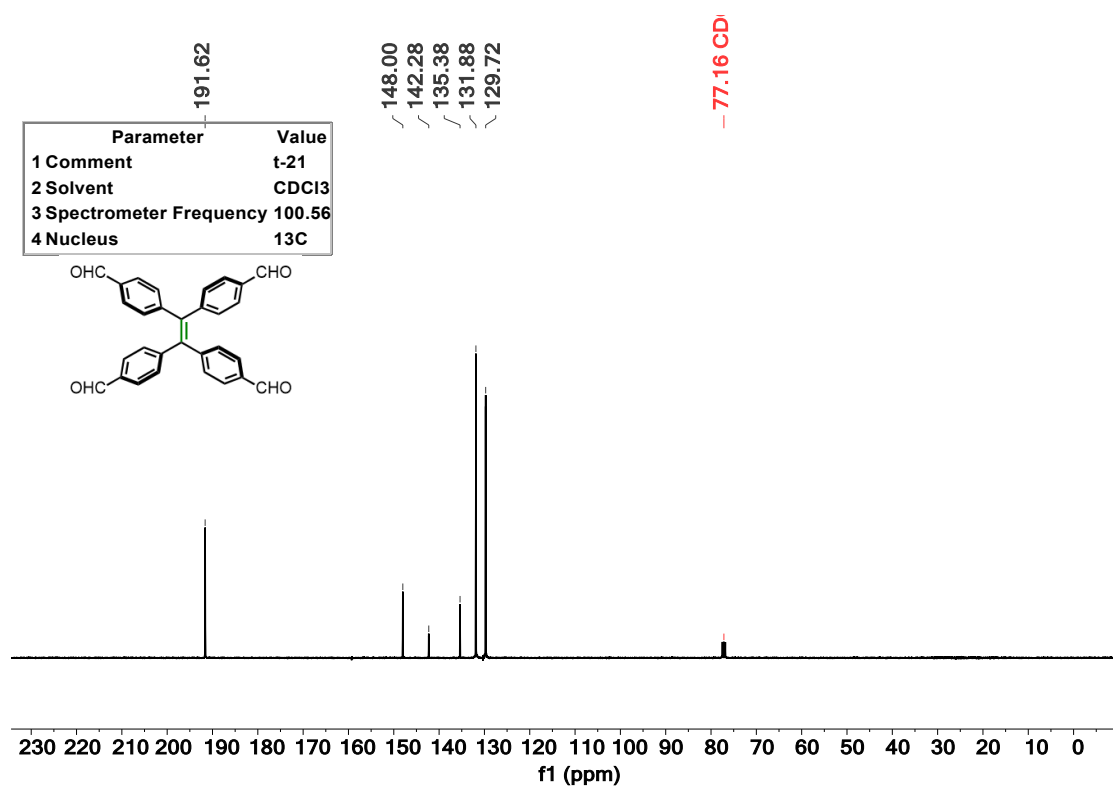
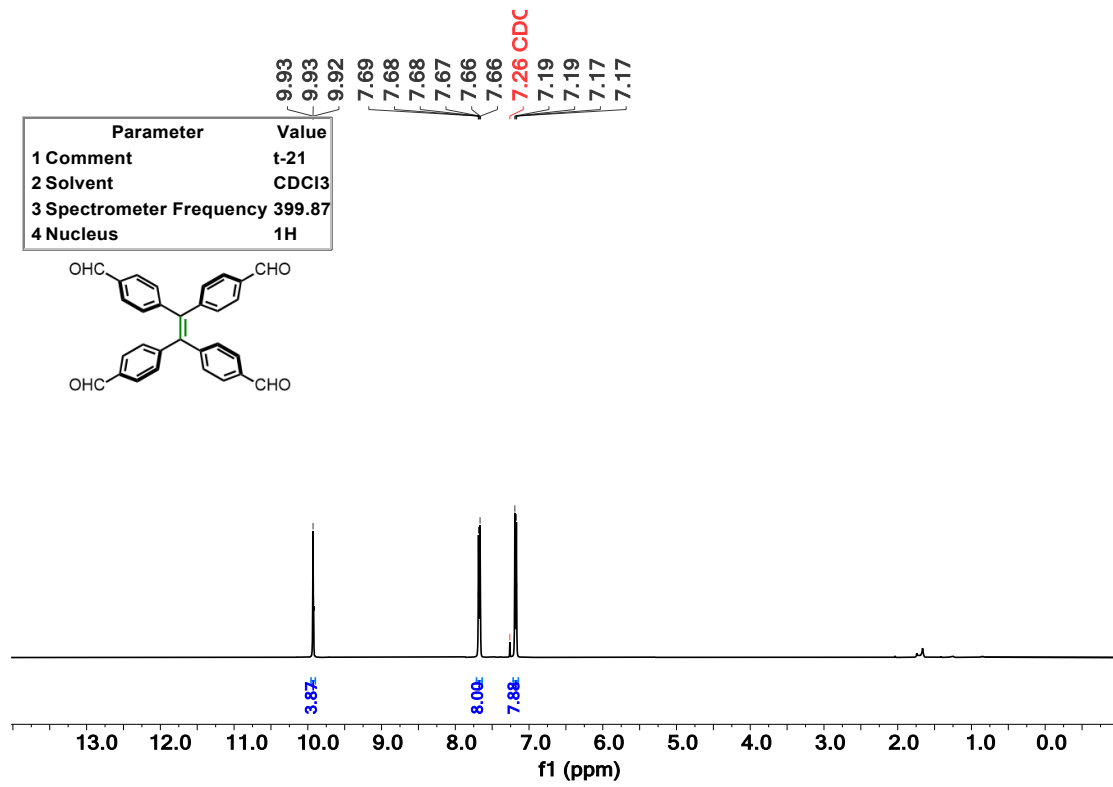


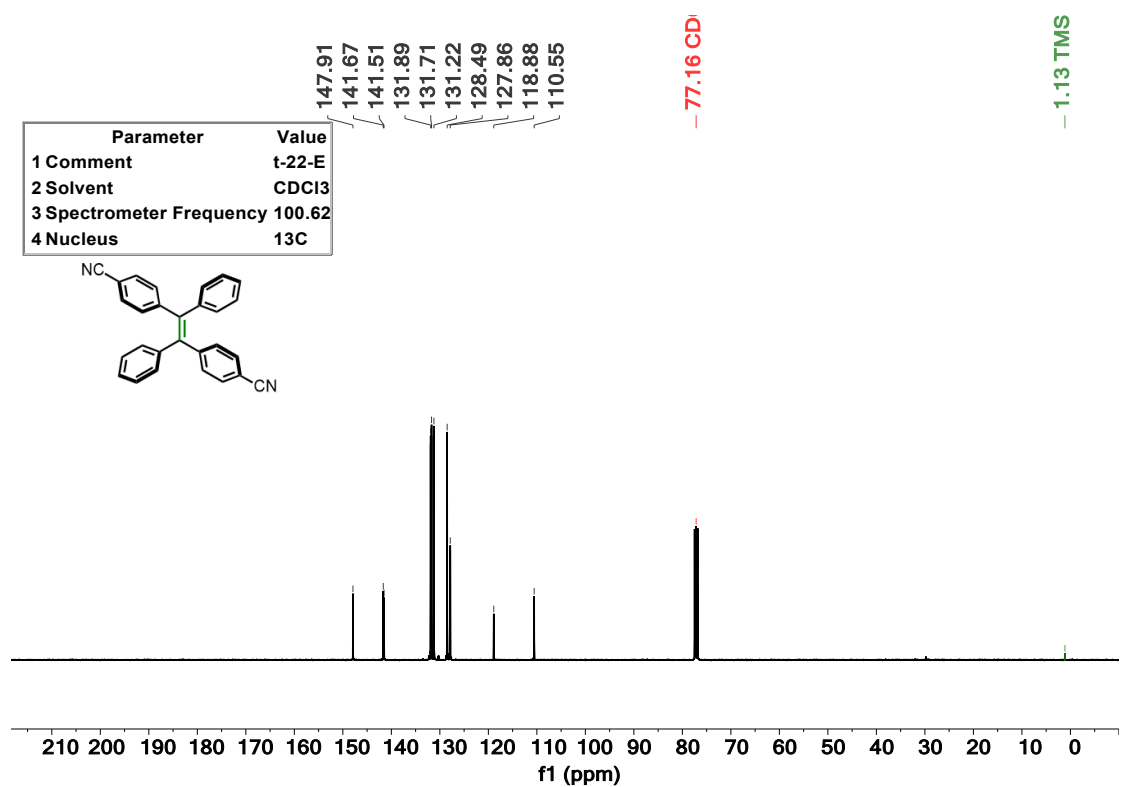
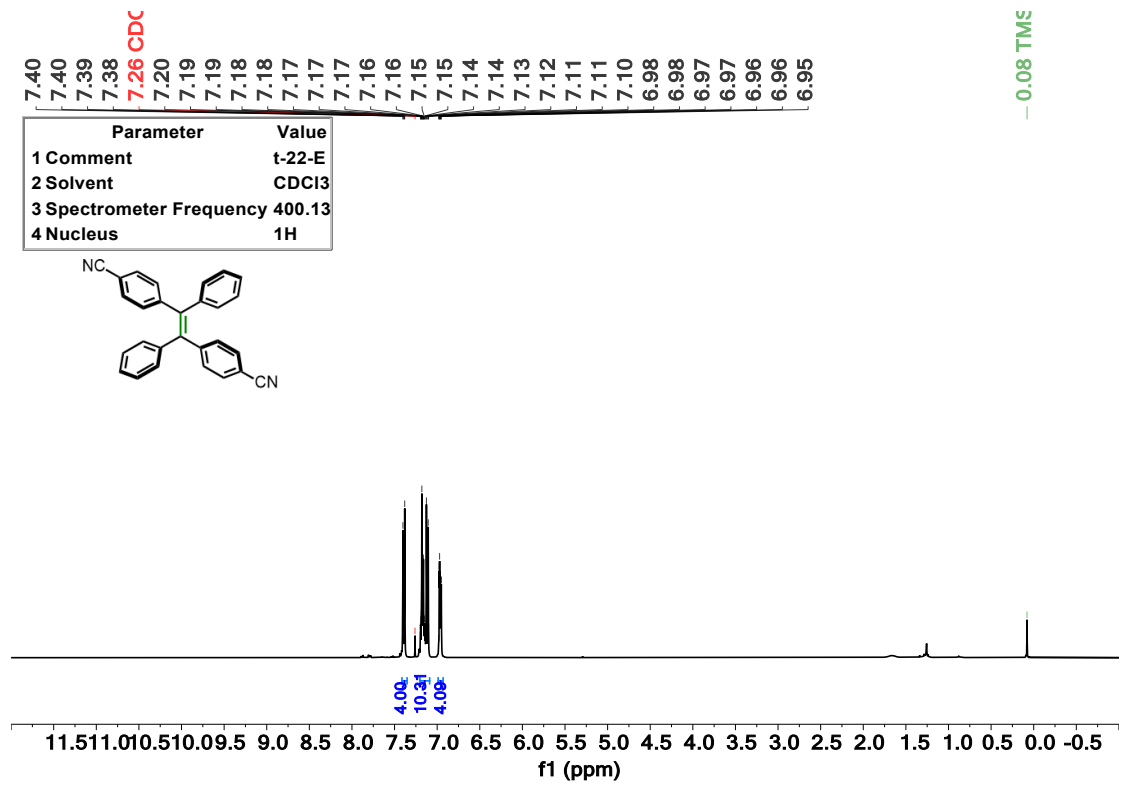


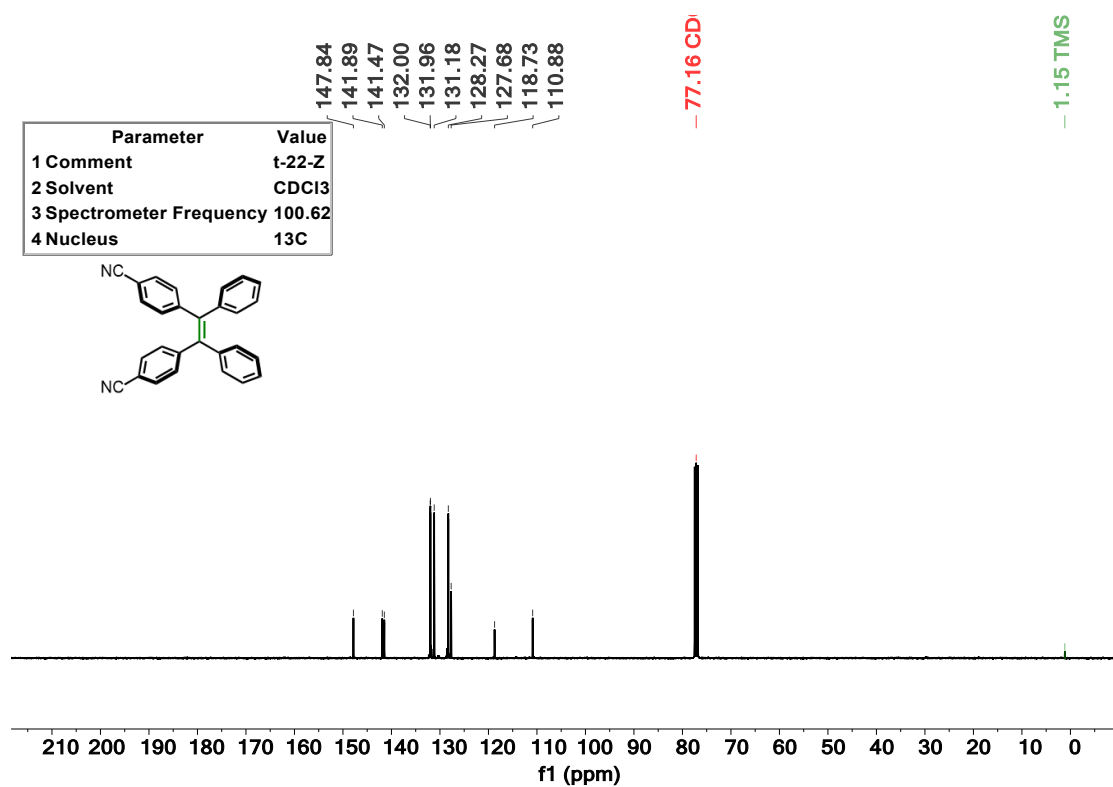
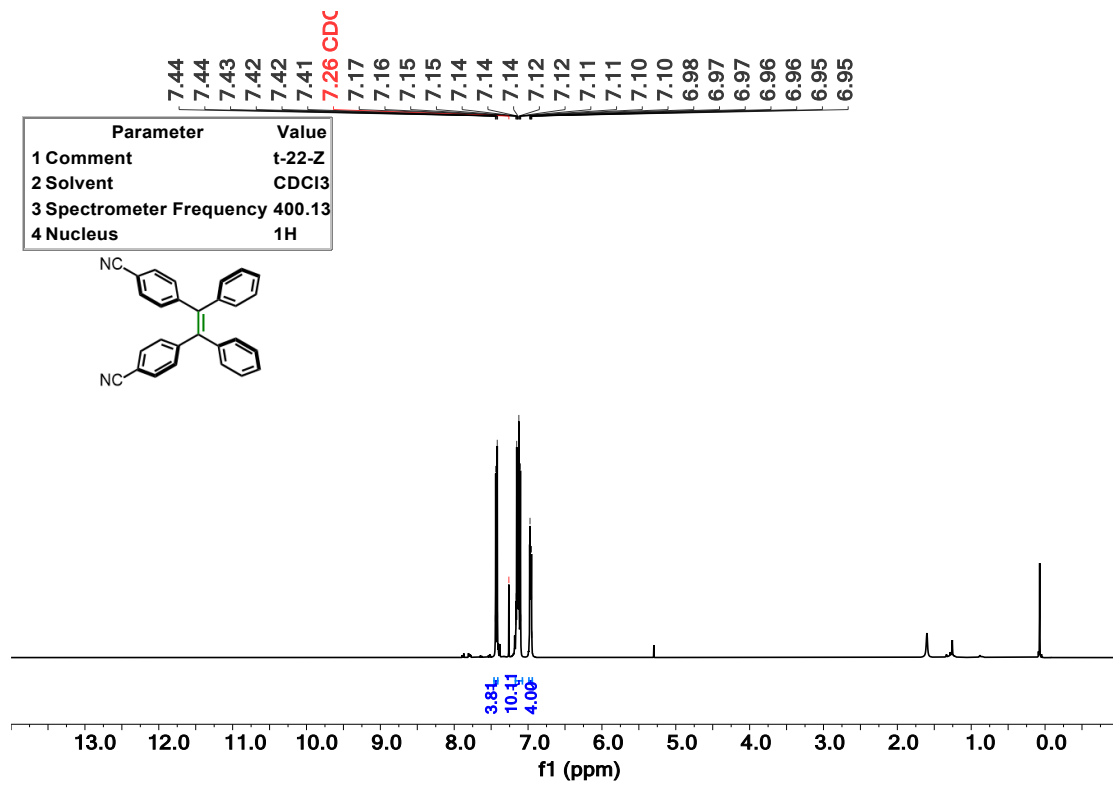


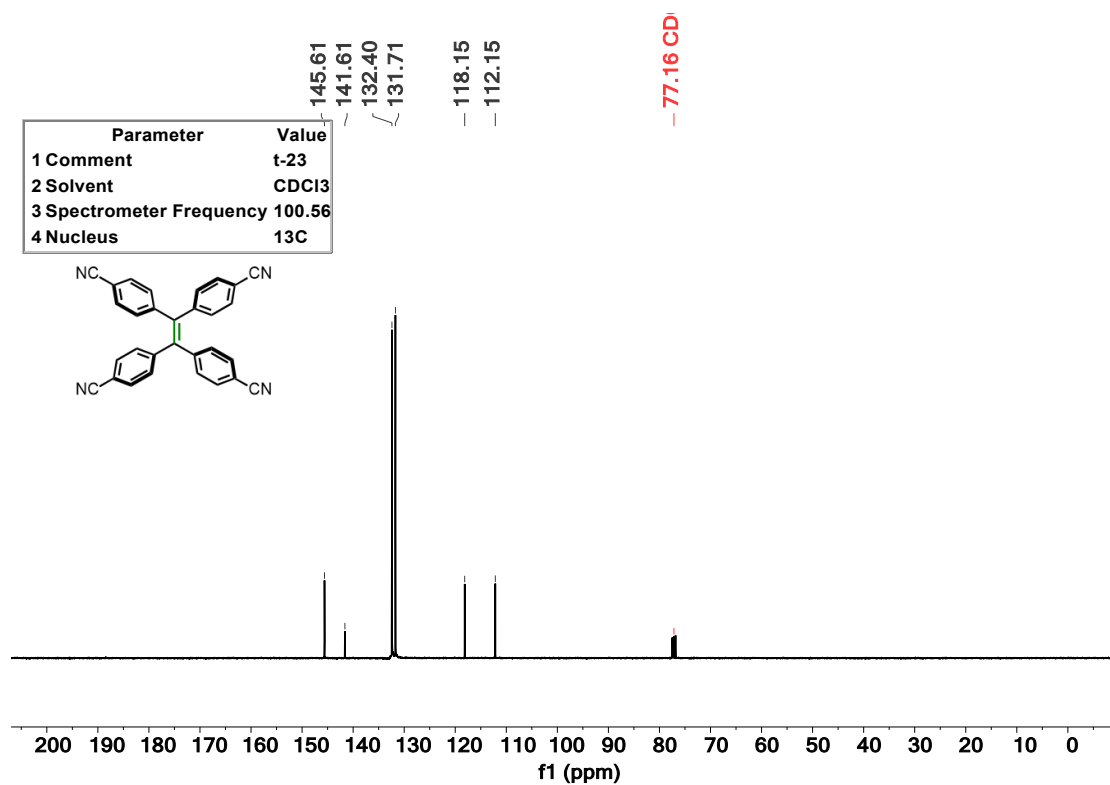
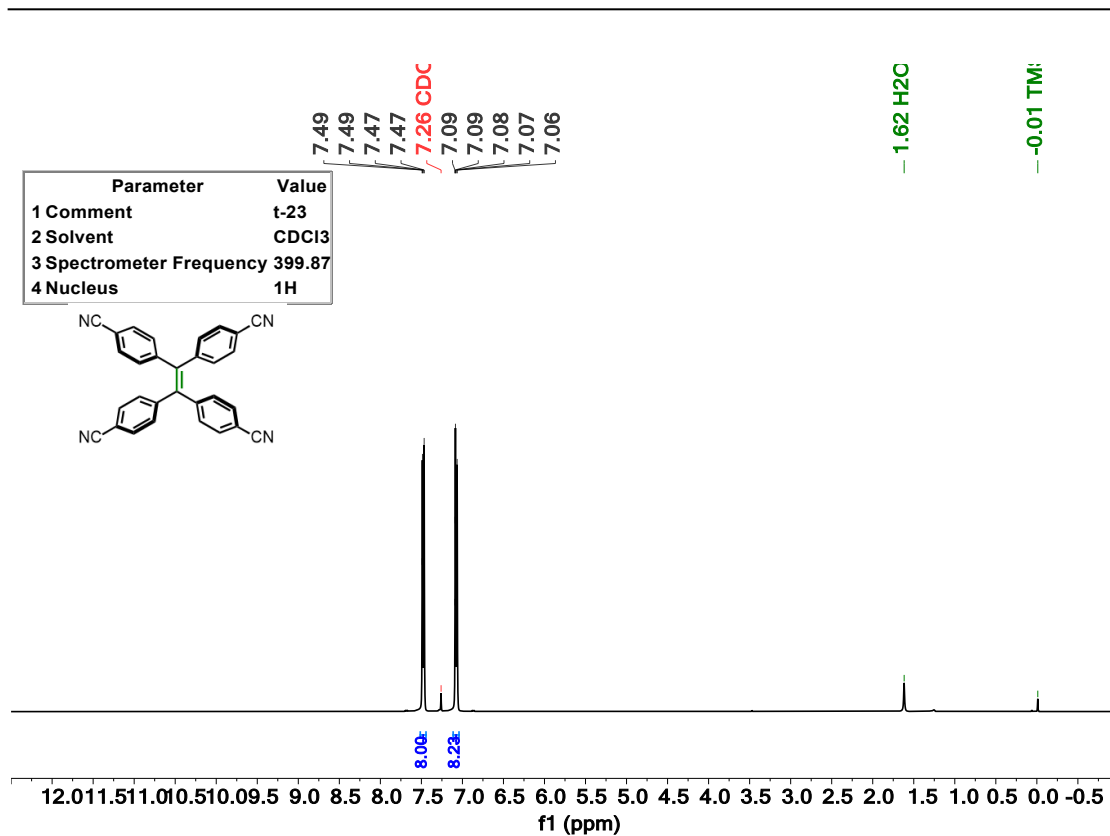


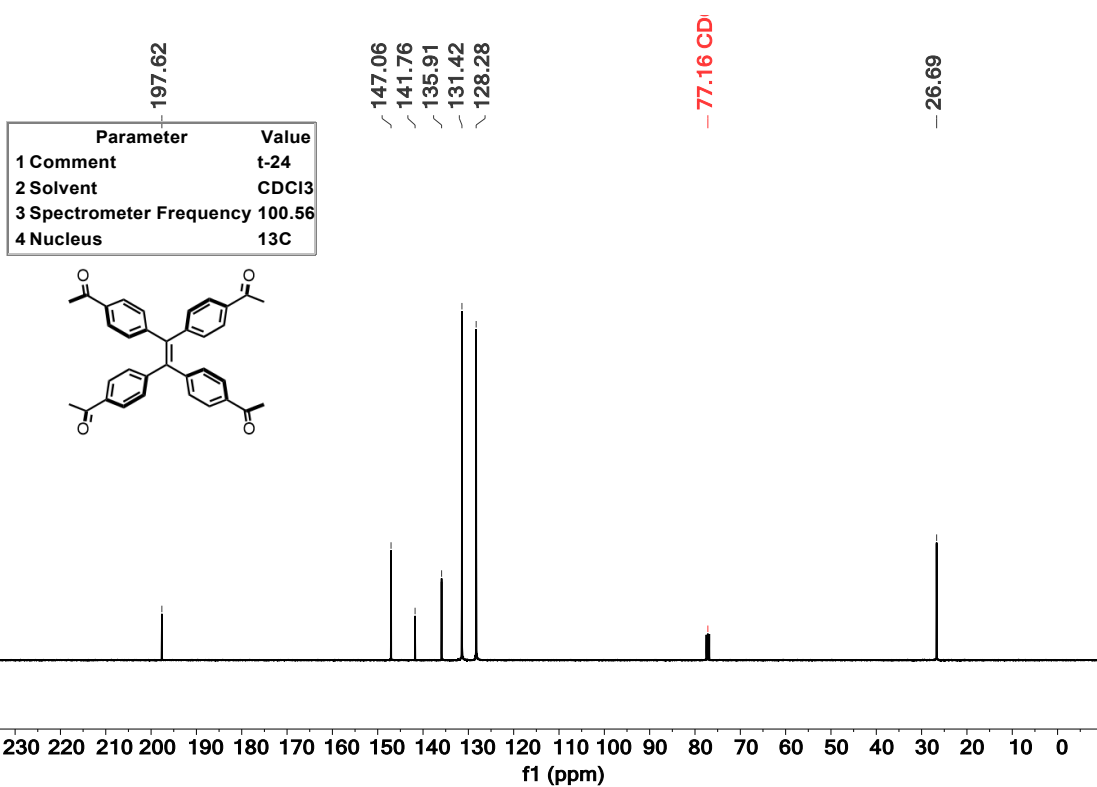
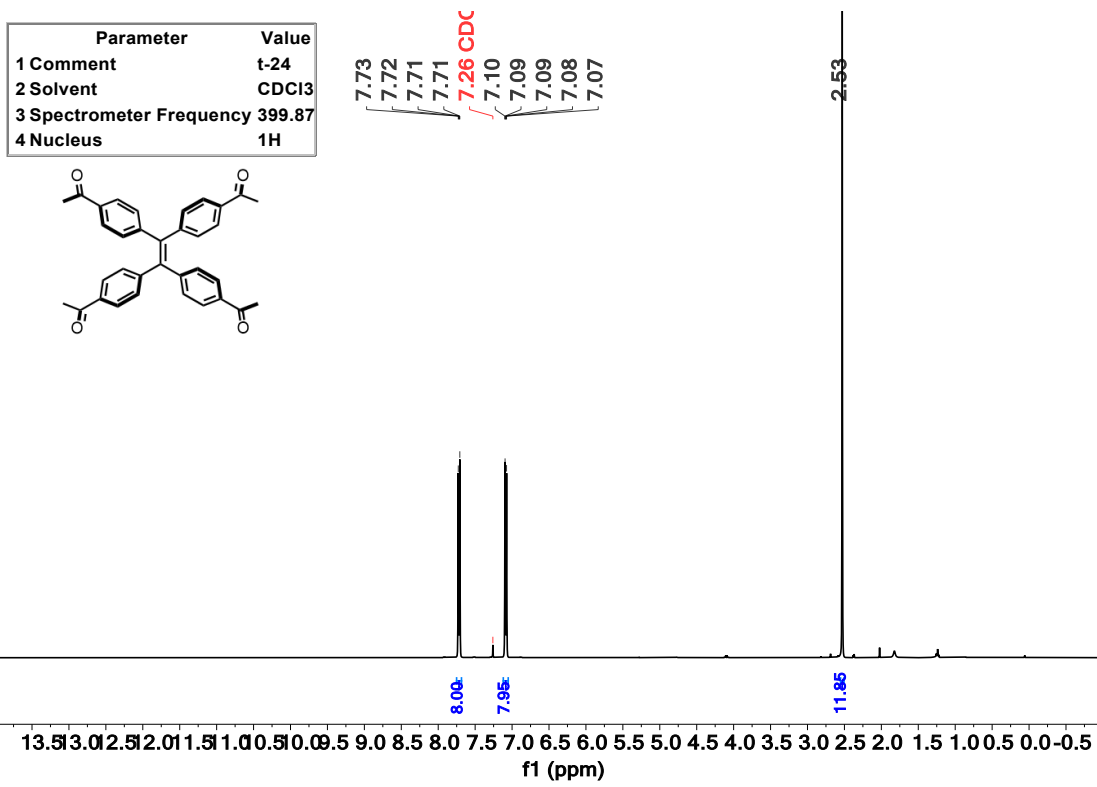




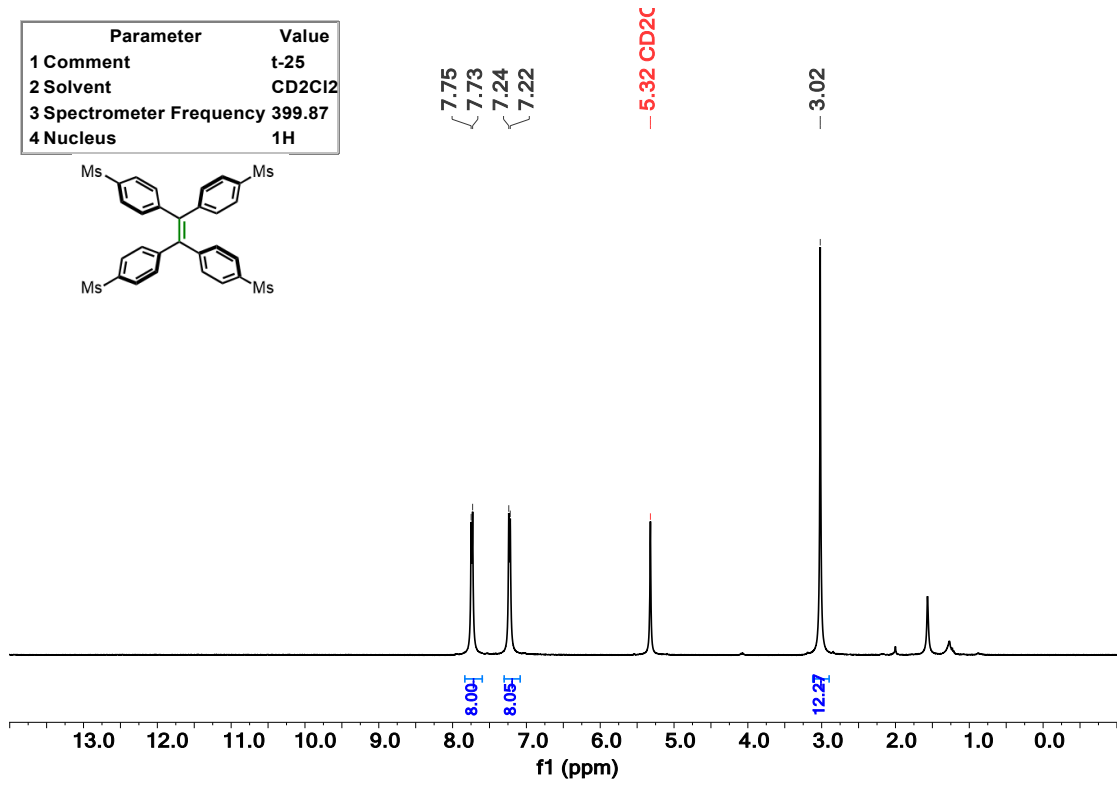
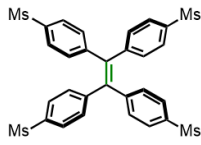




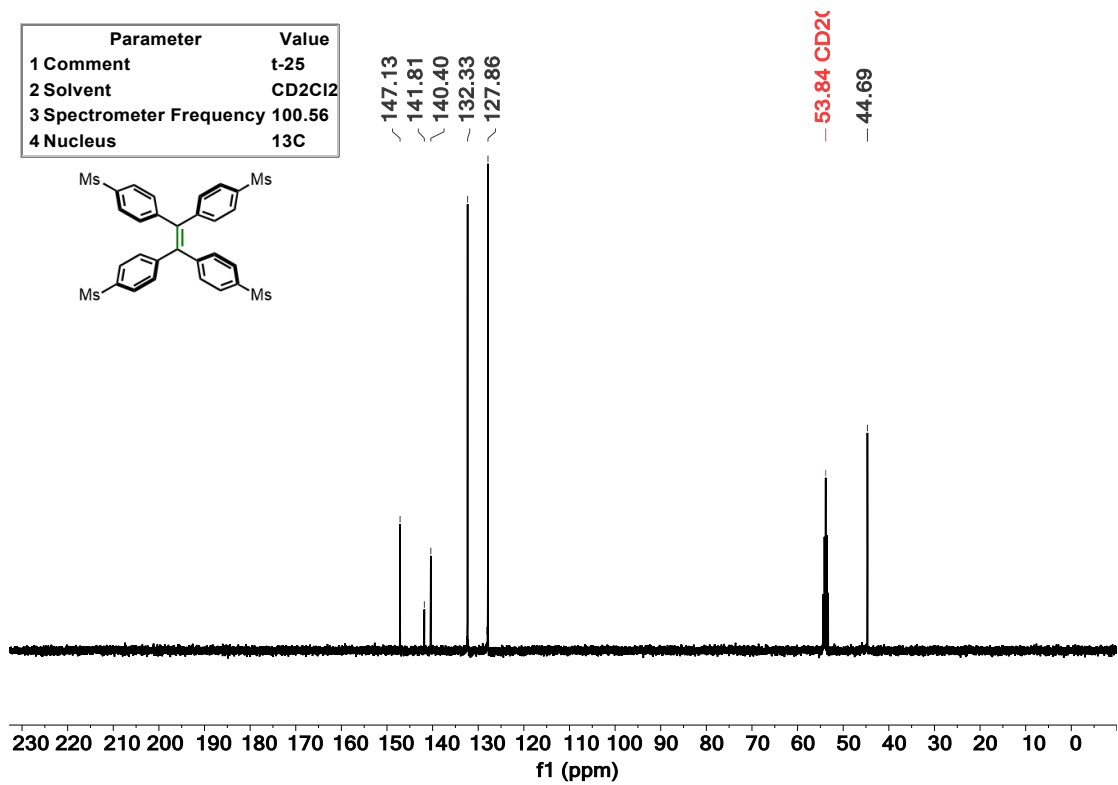
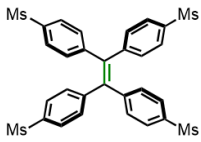


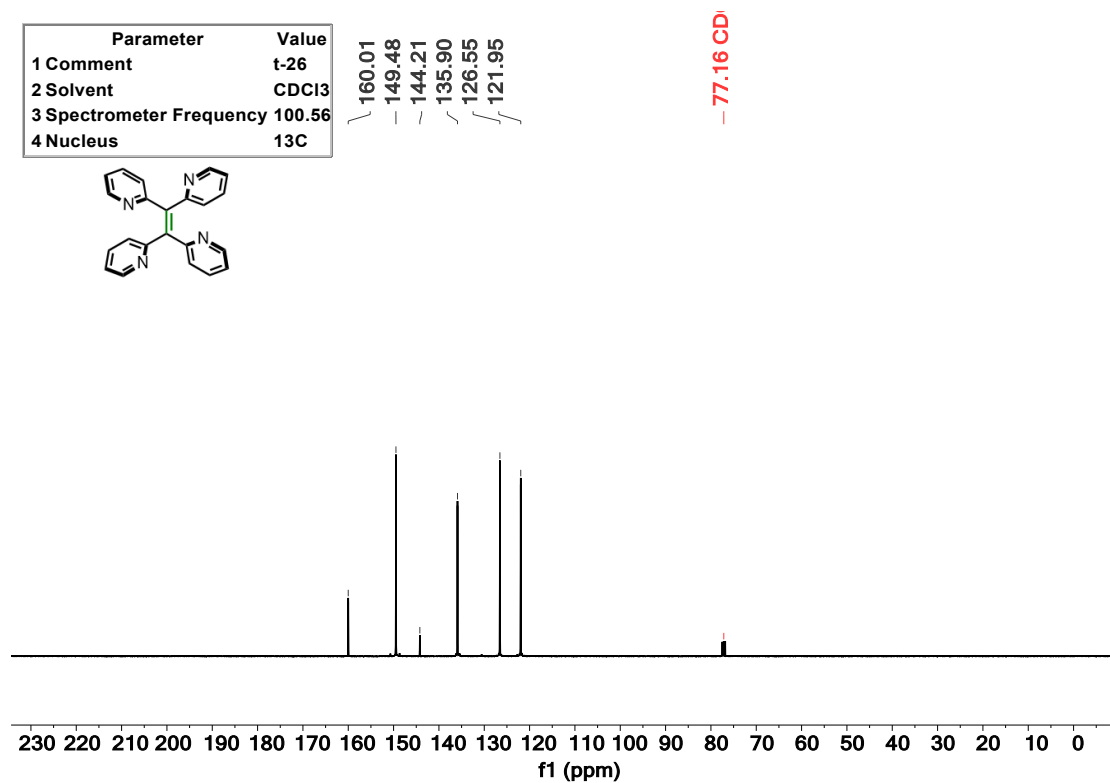
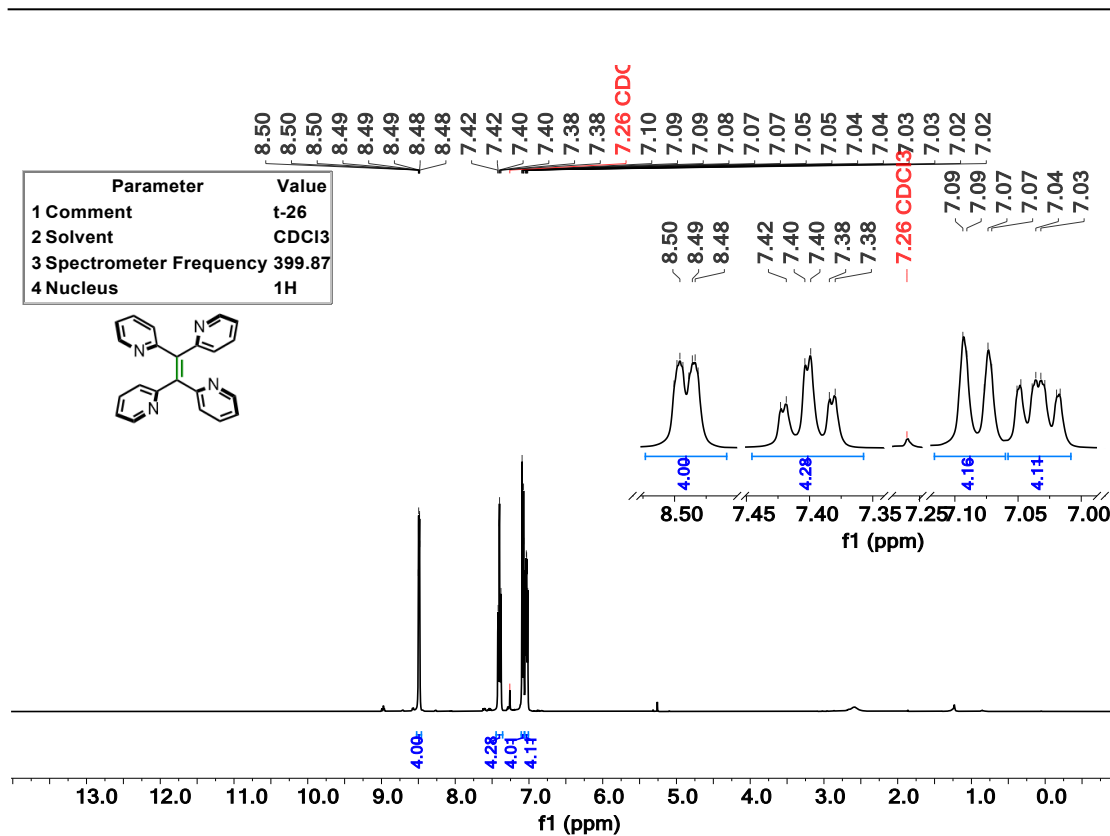


Parameter	Value
1 Comment	t-25
2 Solvent	CD2Cl2
3 Spectrometer Frequency	399.87
4 Nucleus	1H

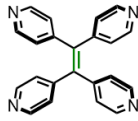


Parameter	Value
1 Comment	t-25
2 Solvent	CD2Cl2
3 Spectrometer Frequency	100.56
4 Nucleus	13C

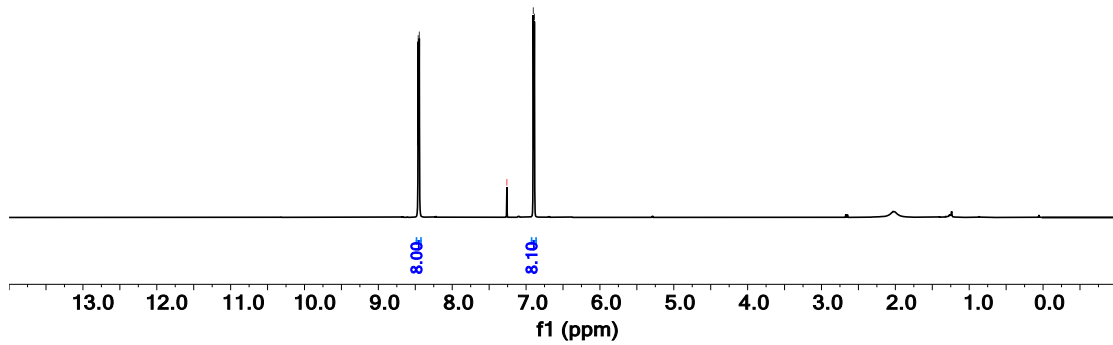




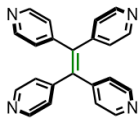
Parameter	Value
1 Comment	t-27
2 Solvent	CDCl ₃
3 Spectrometer Frequency	399.87
4 Nucleus	¹ H



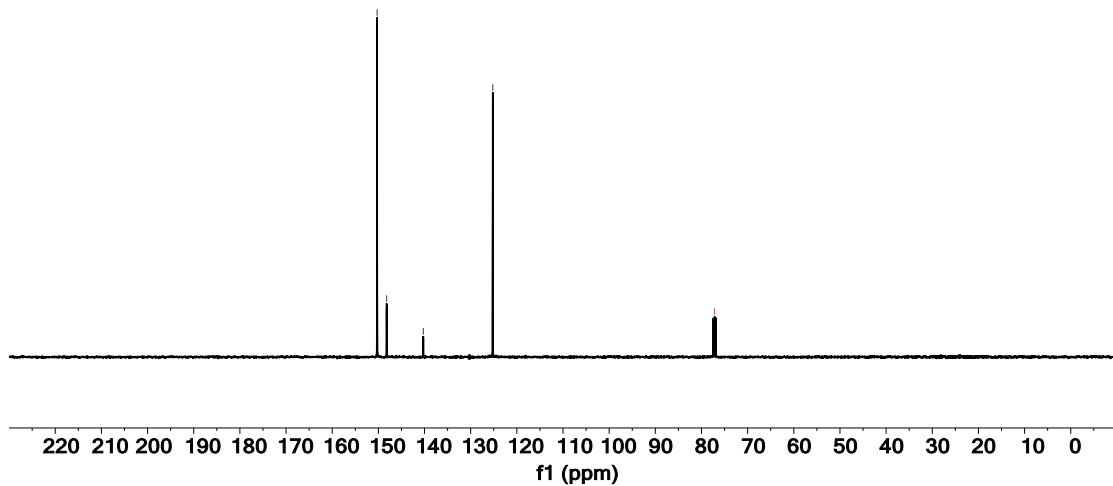
8.46
8.46
8.45
8.45
7.26 CDC
6.90
6.89
6.89



Parameter	Value
1 Comment	t-27
2 Solvent	CDCl ₃
3 Spectrometer Frequency	100.56
4 Nucleus	¹³ C

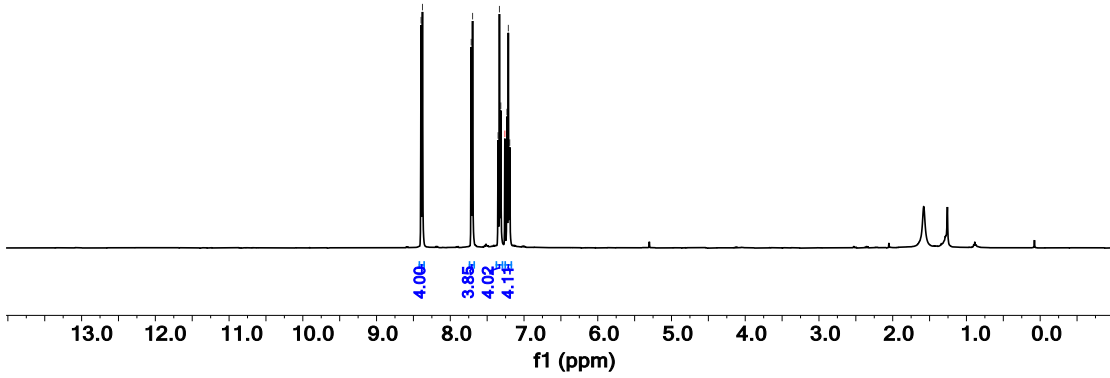
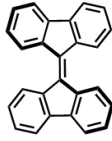


150.27
148.20
140.26
125.21
77.16 CD



Parameter	Value
1 Comment	t-28
2 Solvent	CDCl ₃
3 Spectrometer Frequency	399.87
4 Nucleus	¹ H

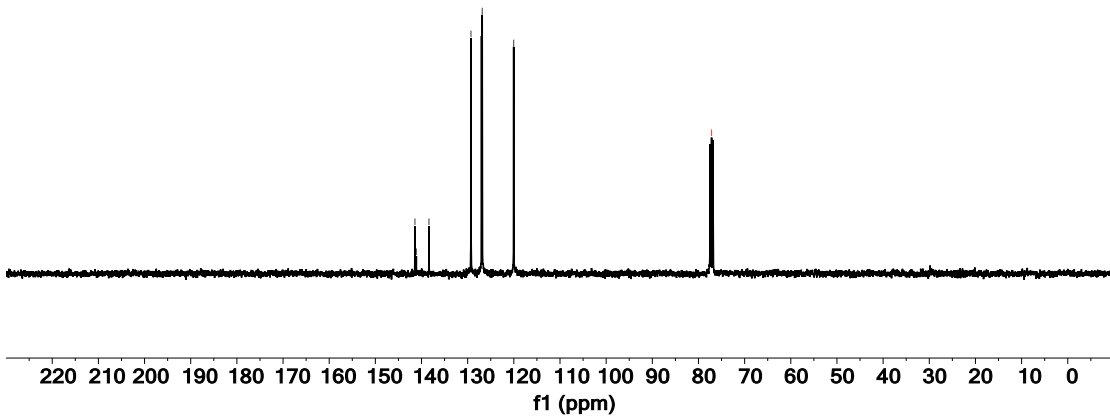
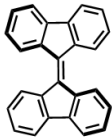
8.40
8.38
7.72
7.70
7.35
7.33
7.31
7.26 CDC
7.23
7.21
7.19

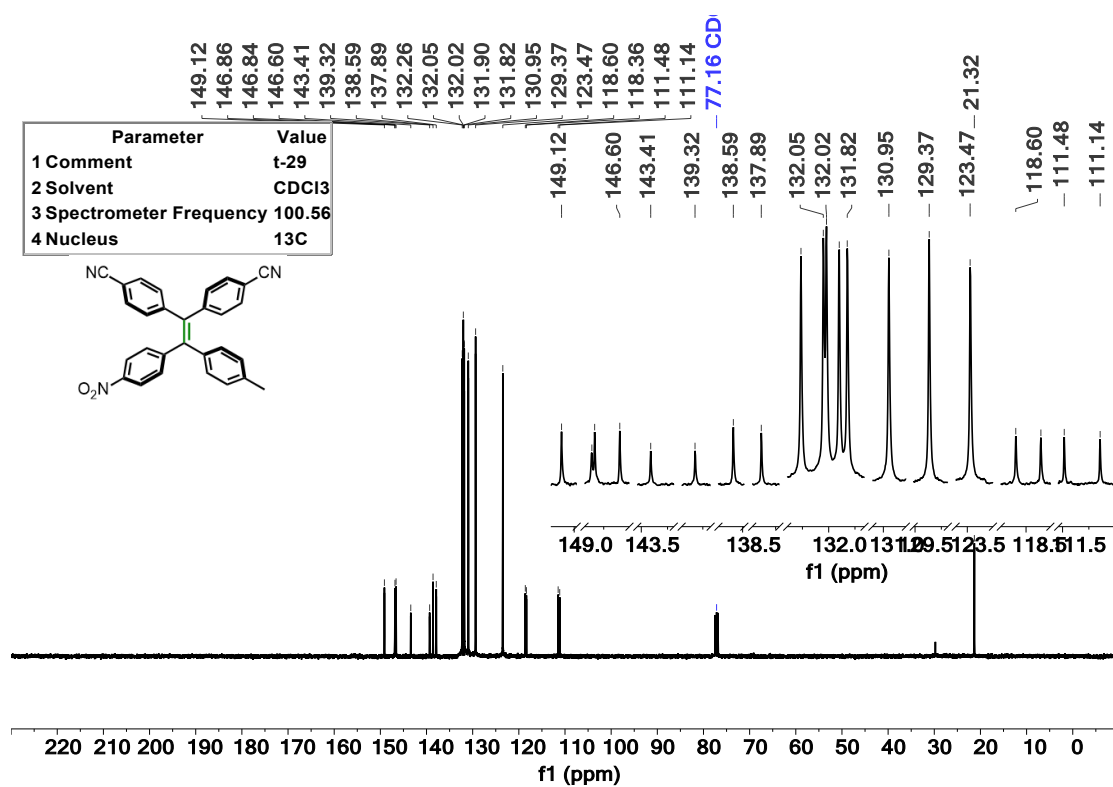
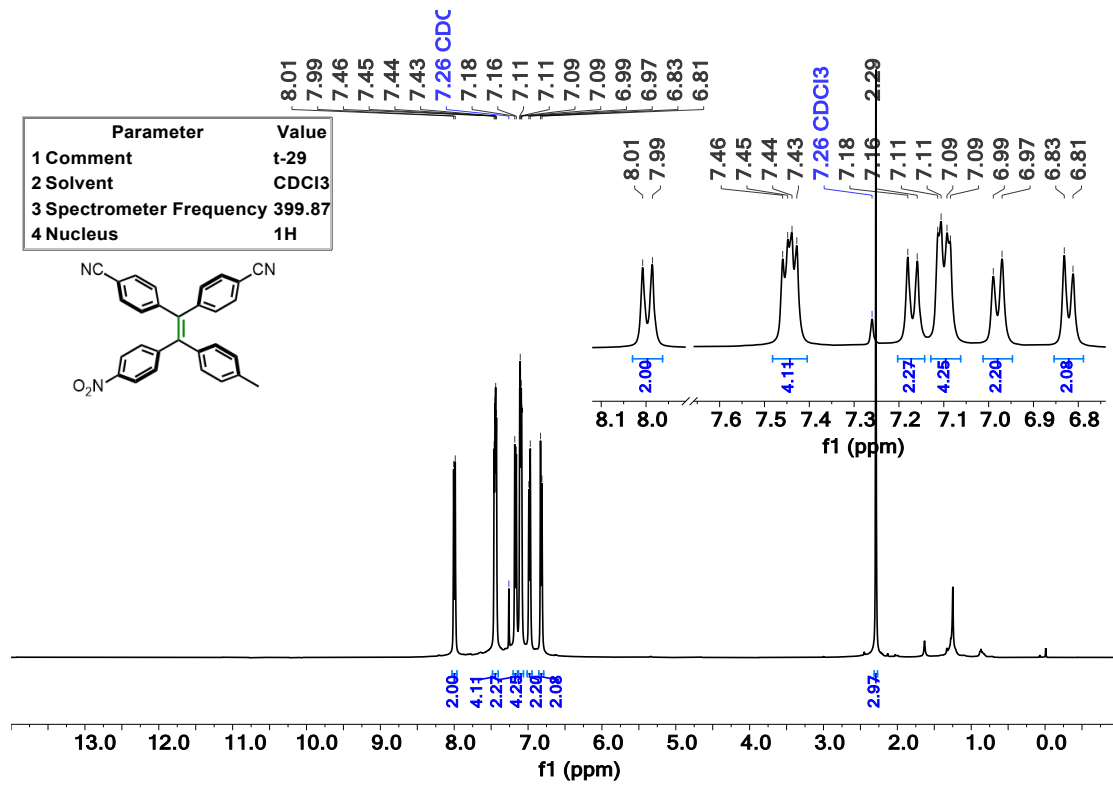


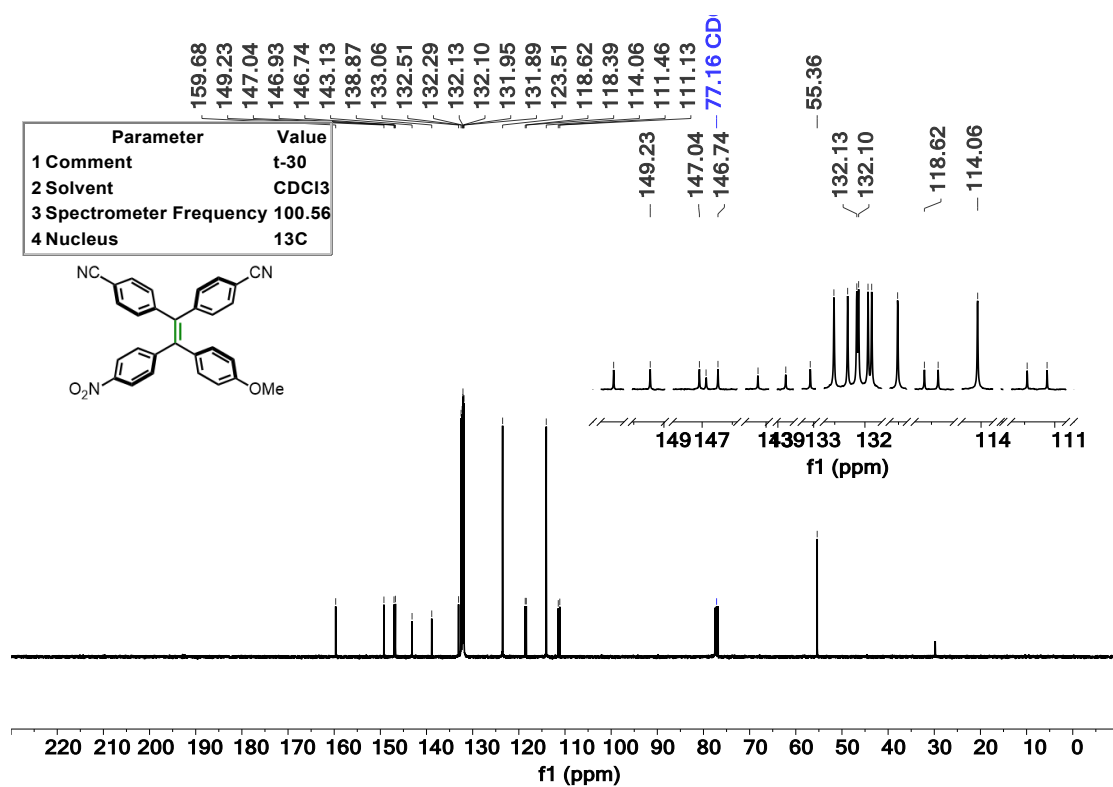
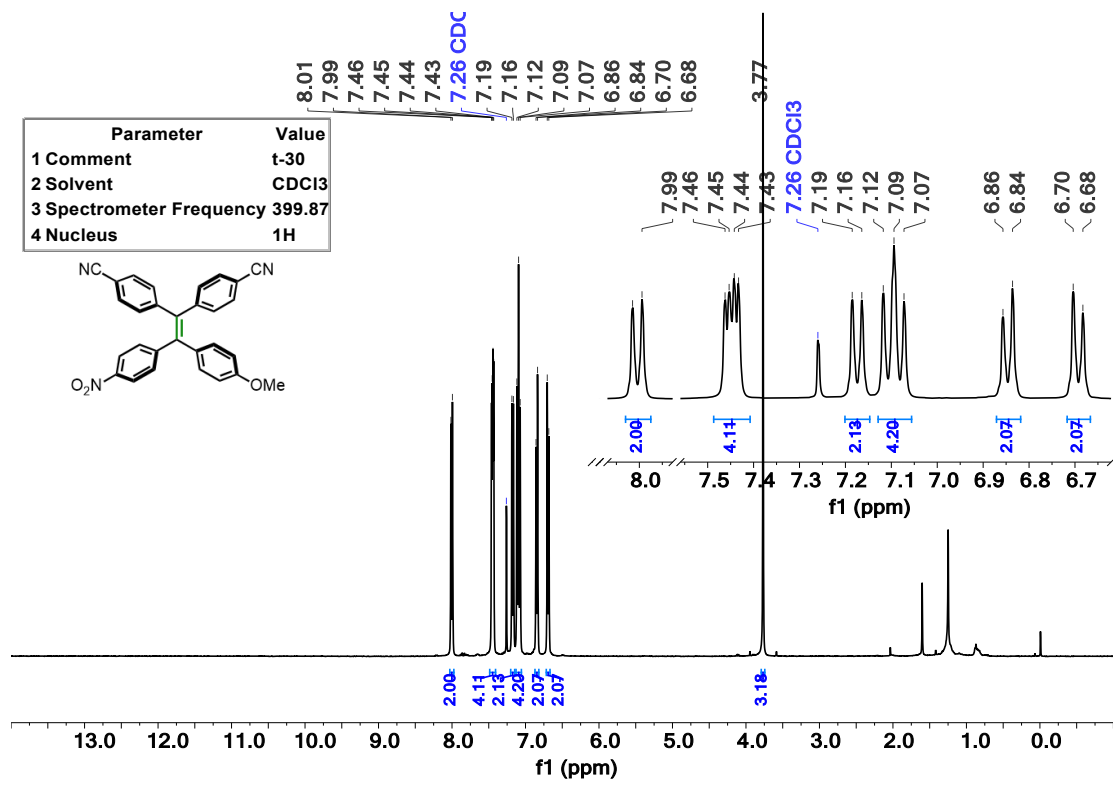
Parameter	Value
1 Comment	t-28
2 Solvent	CDCl ₃
3 Spectrometer Frequency	100.56
4 Nucleus	¹³ C

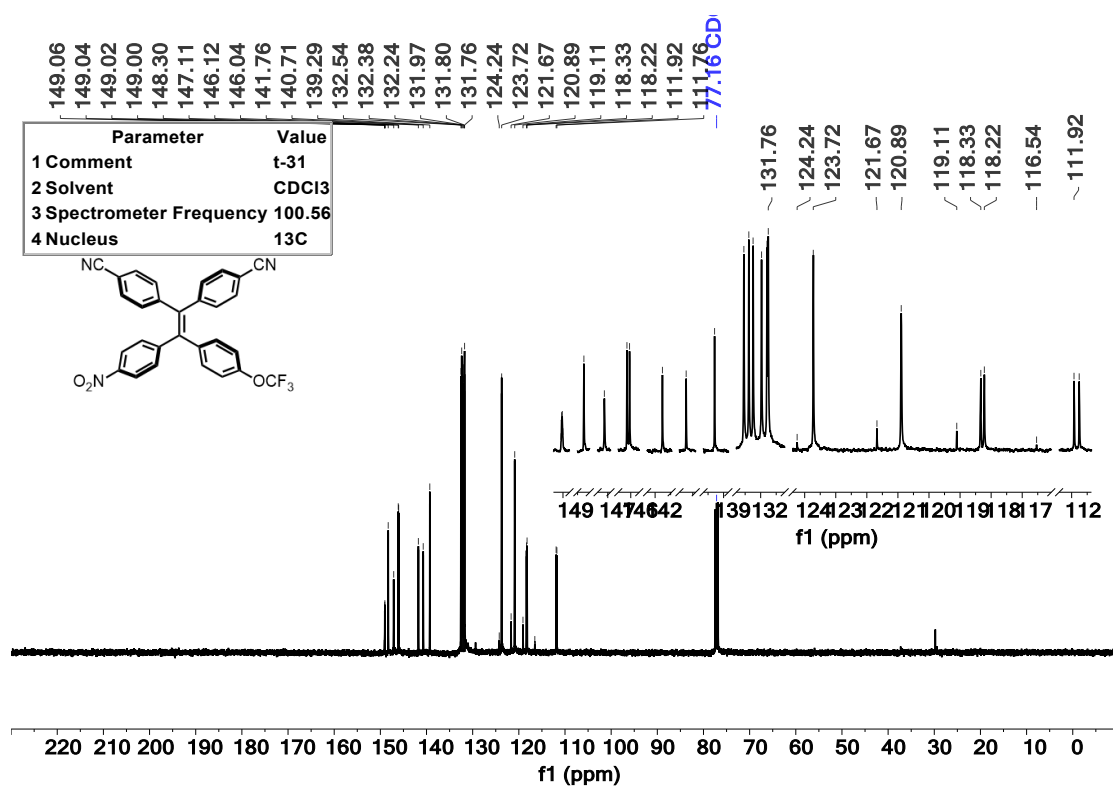
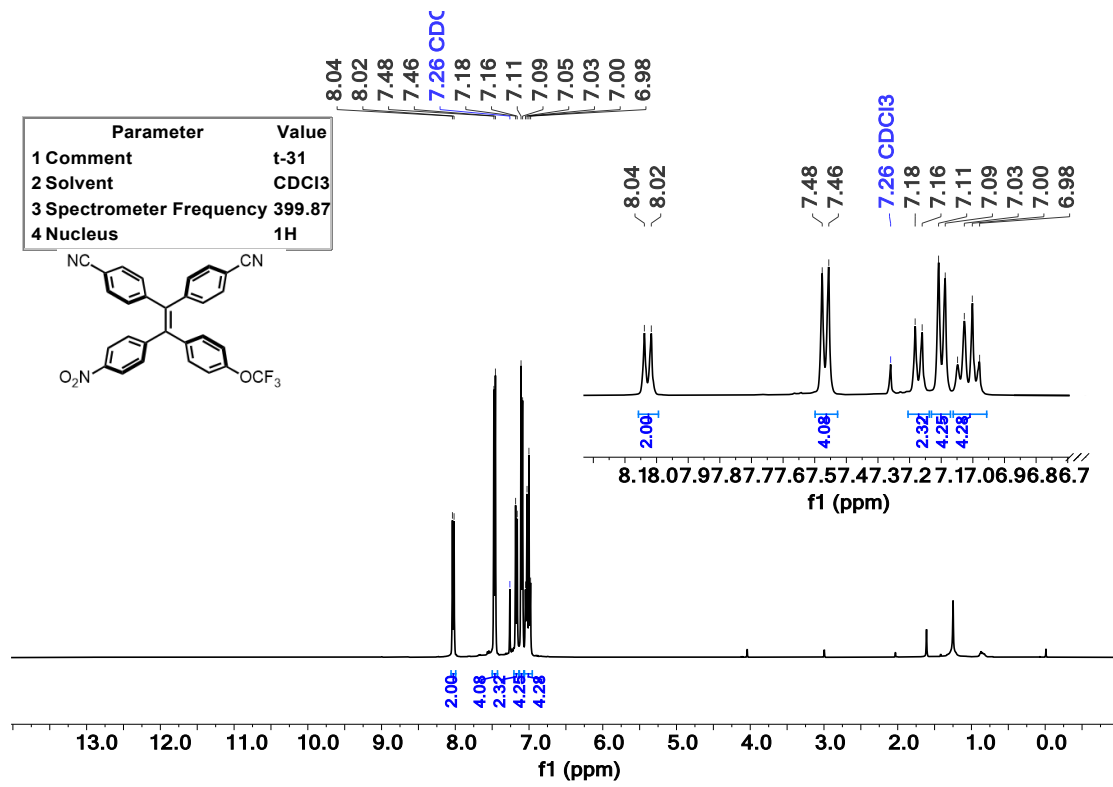
141.42
141.13
138.39
129.29
127.00
126.85
120.03

-77.16 CD₃

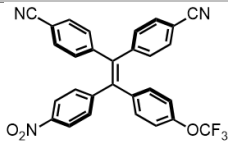








Parameter	Value
1 Comment	t-31
2 Solvent	CDCl3
3 Spectrometer Frequency	376.22
4 Nucleus	19F

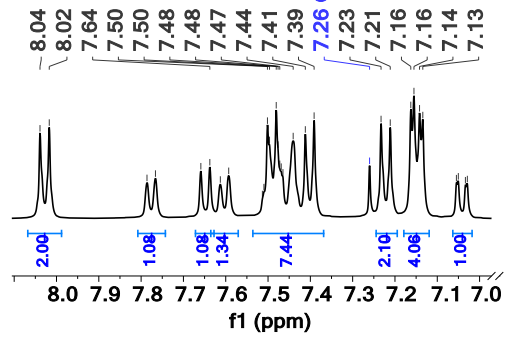
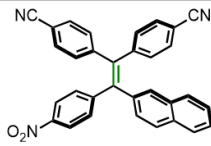


--57.82

30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

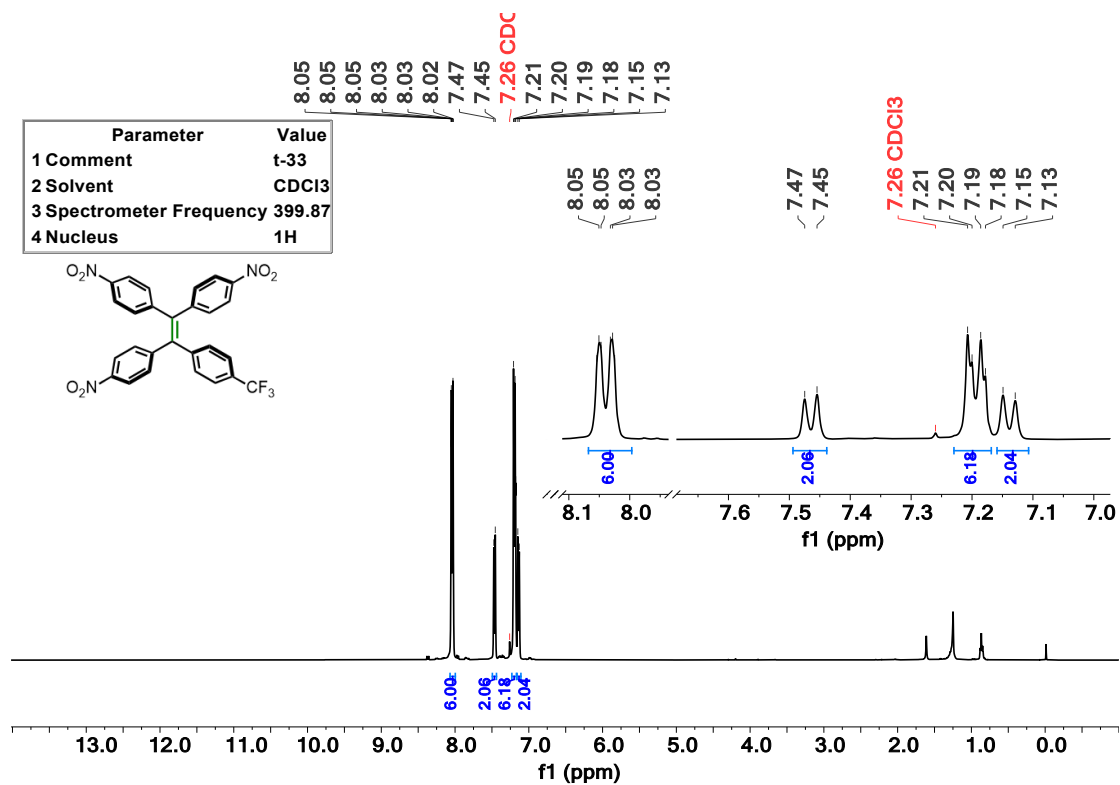
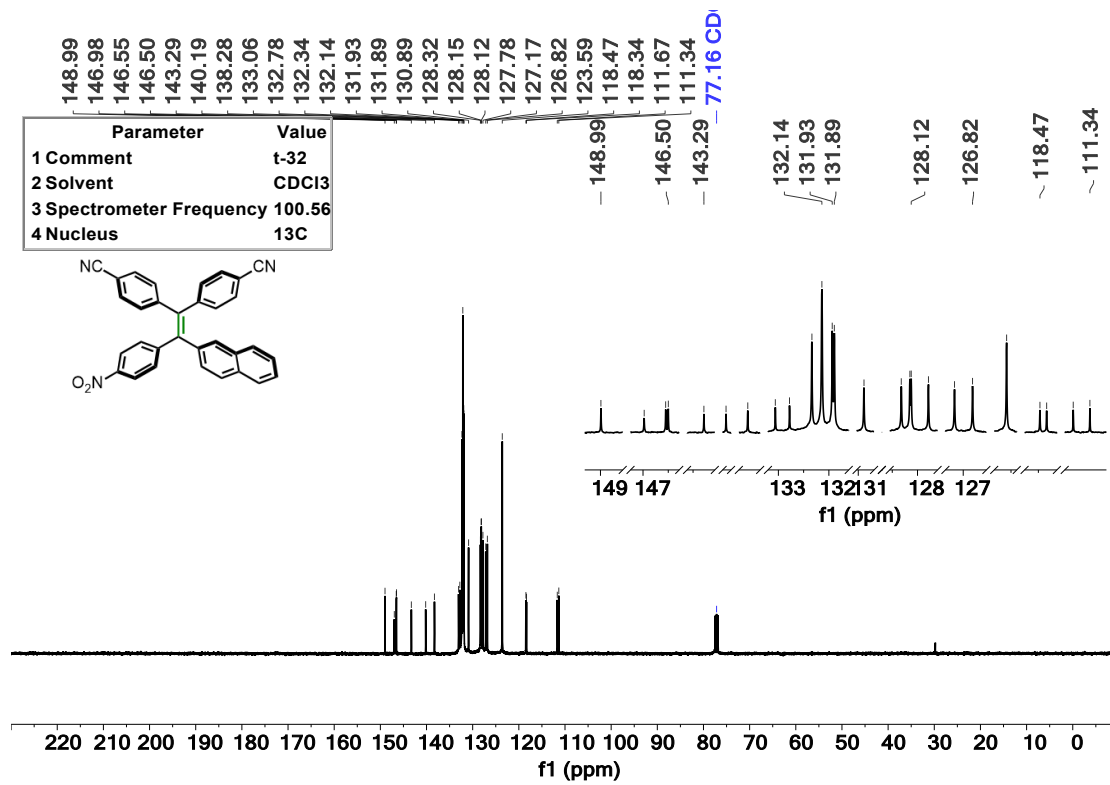
8.04
8.02
7.79
7.77
7.66
7.64
7.61
7.59
7.51
7.51
7.50
7.50
7.48
7.48
7.47
7.47
7.46
7.44
7.41
7.39
7.26 CDC
7.23
7.21
7.16
7.16
7.14
7.13
7.05
7.05
7.03
7.03
7.26 CDC13
1.26

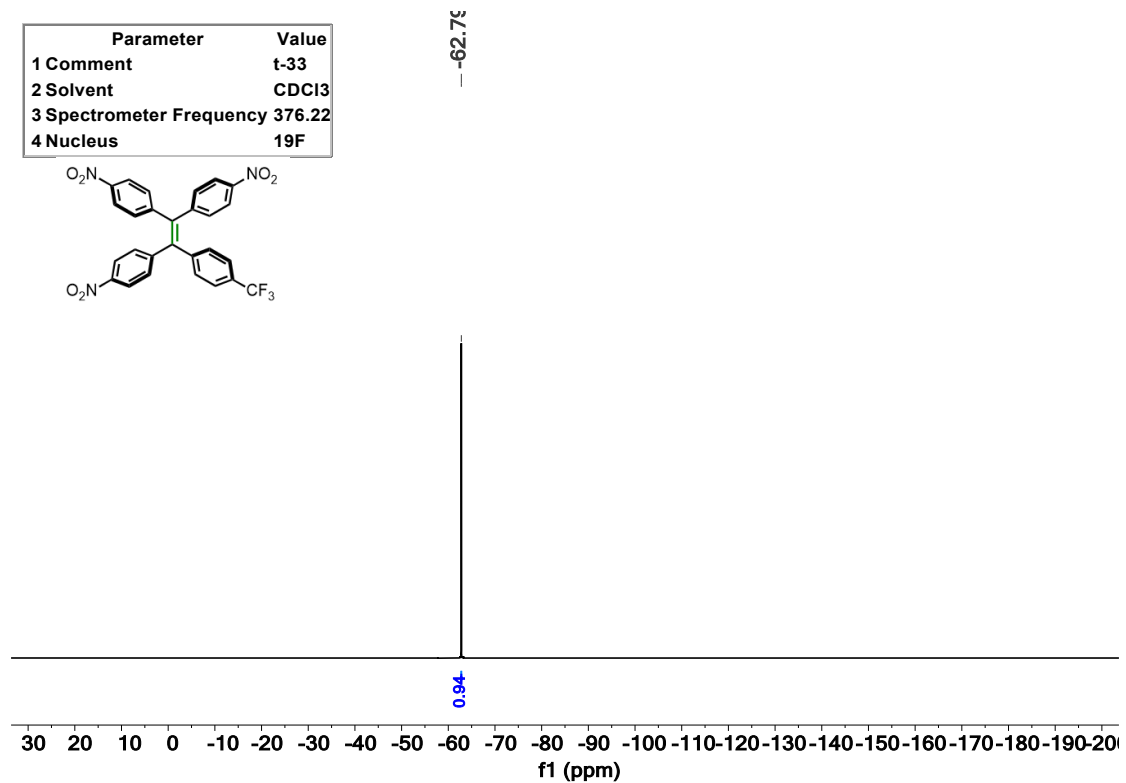
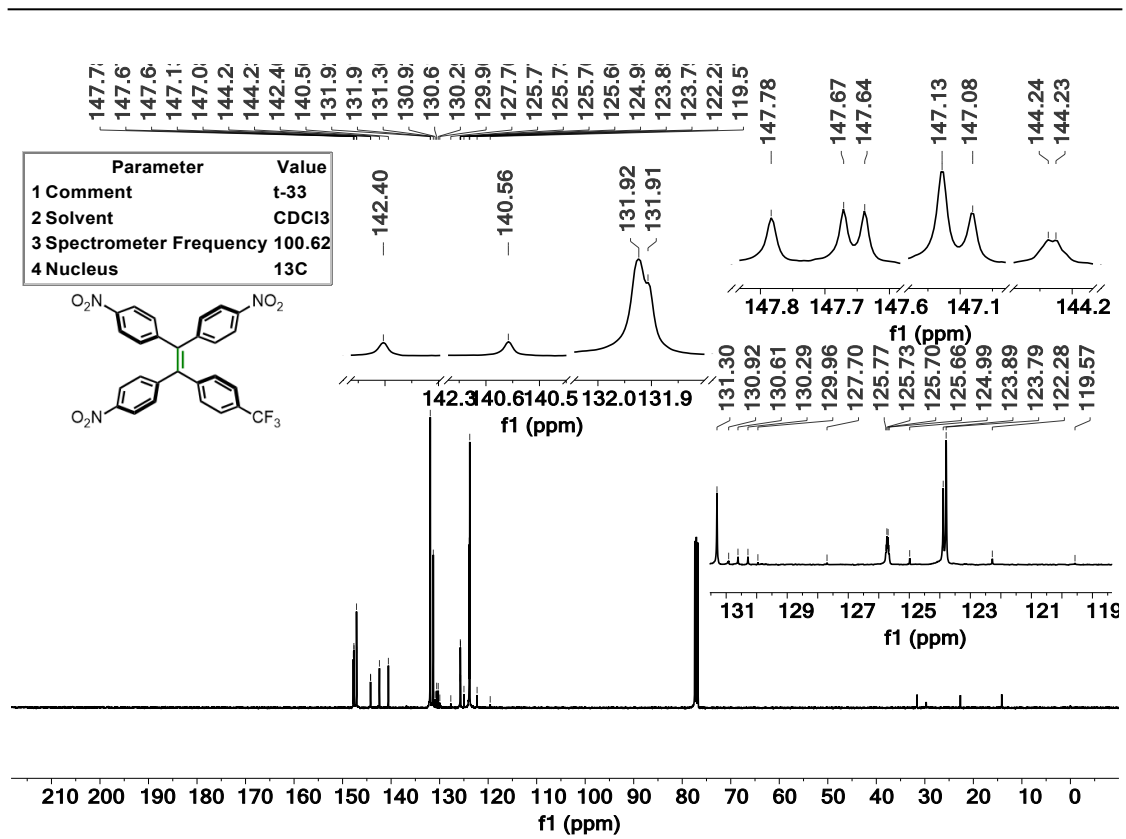
Parameter	Value
1 Comment	t-32
2 Solvent	CDCl3
3 Spectrometer Frequency	399.87
4 Nucleus	1H

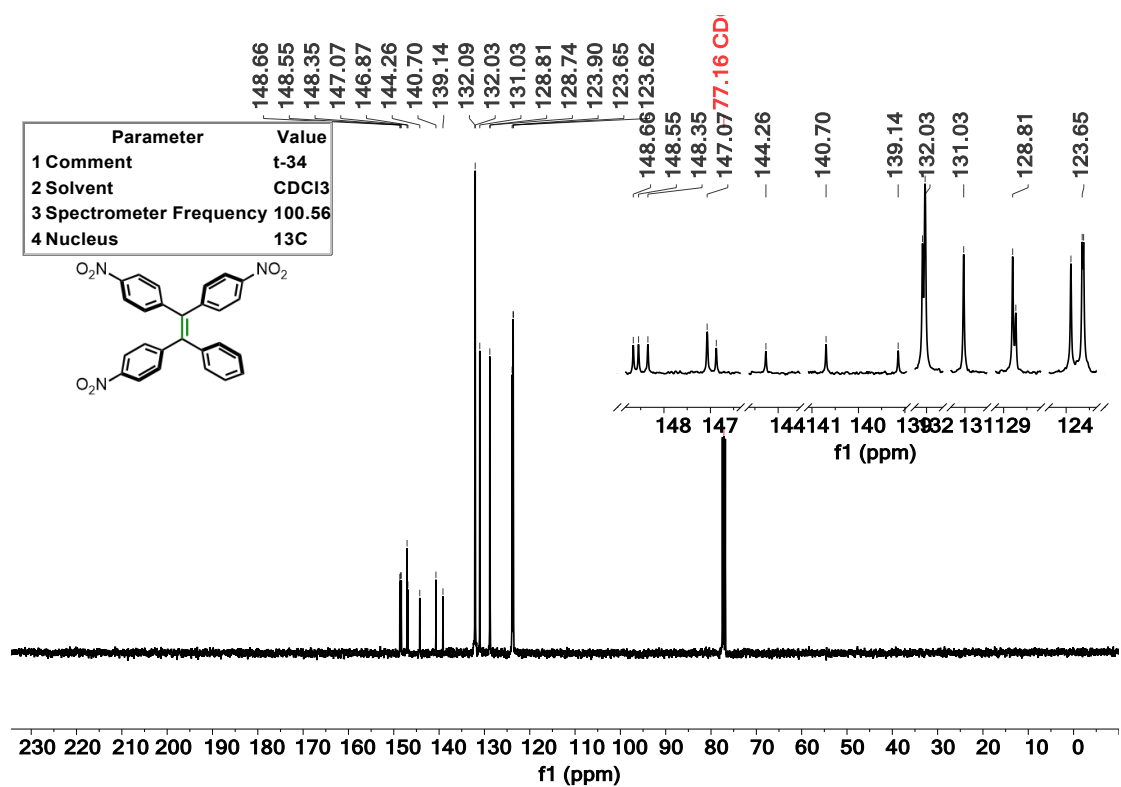
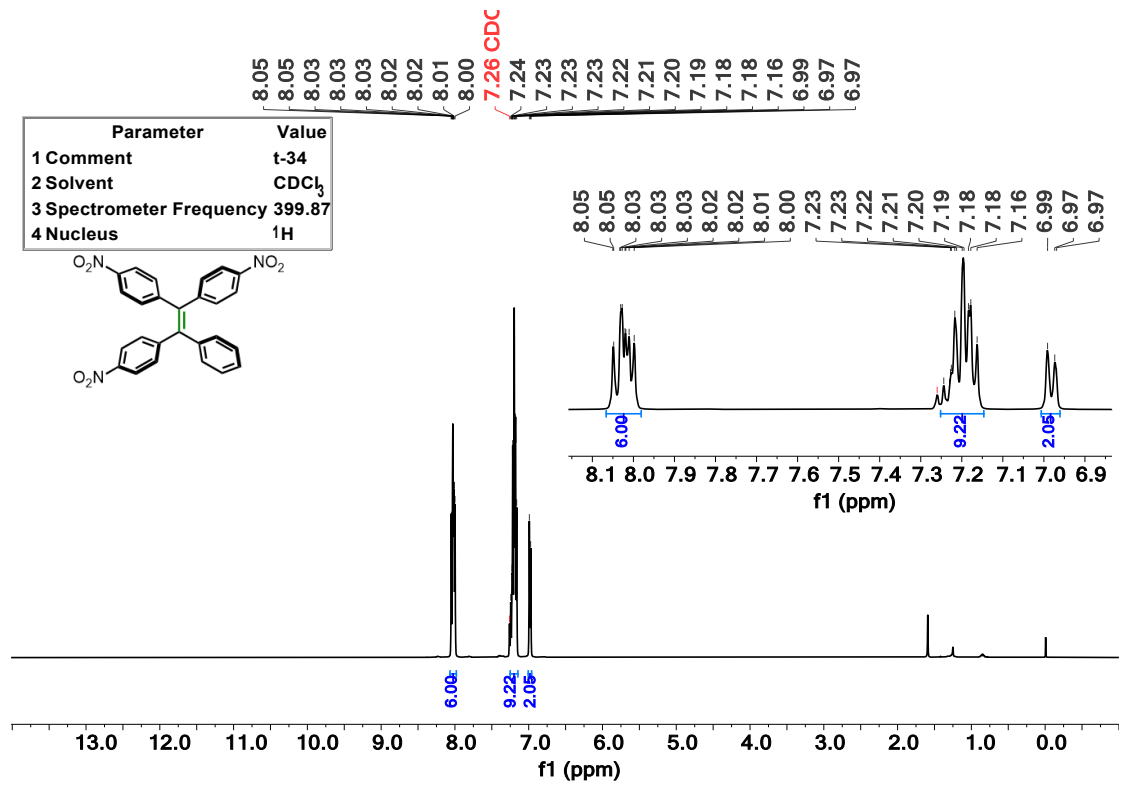


2.00
1.08
1.08
1.34
7.44
2.10
4.06
1.00

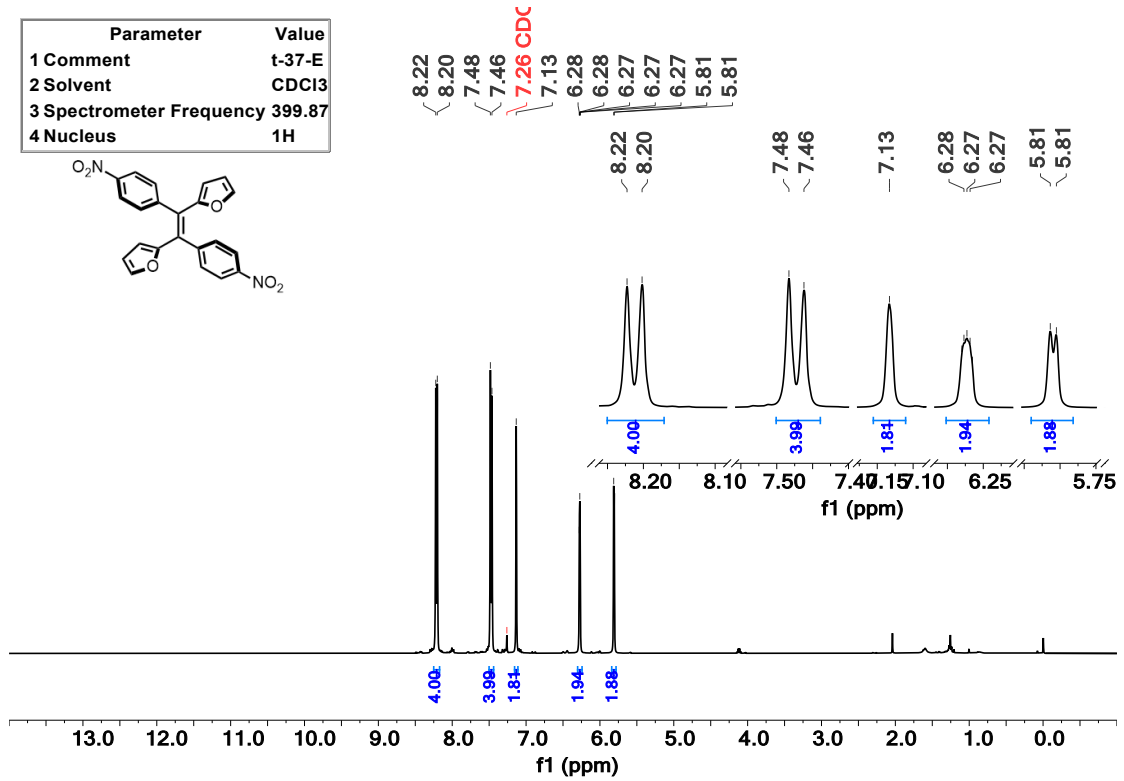
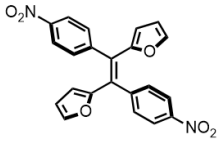
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)



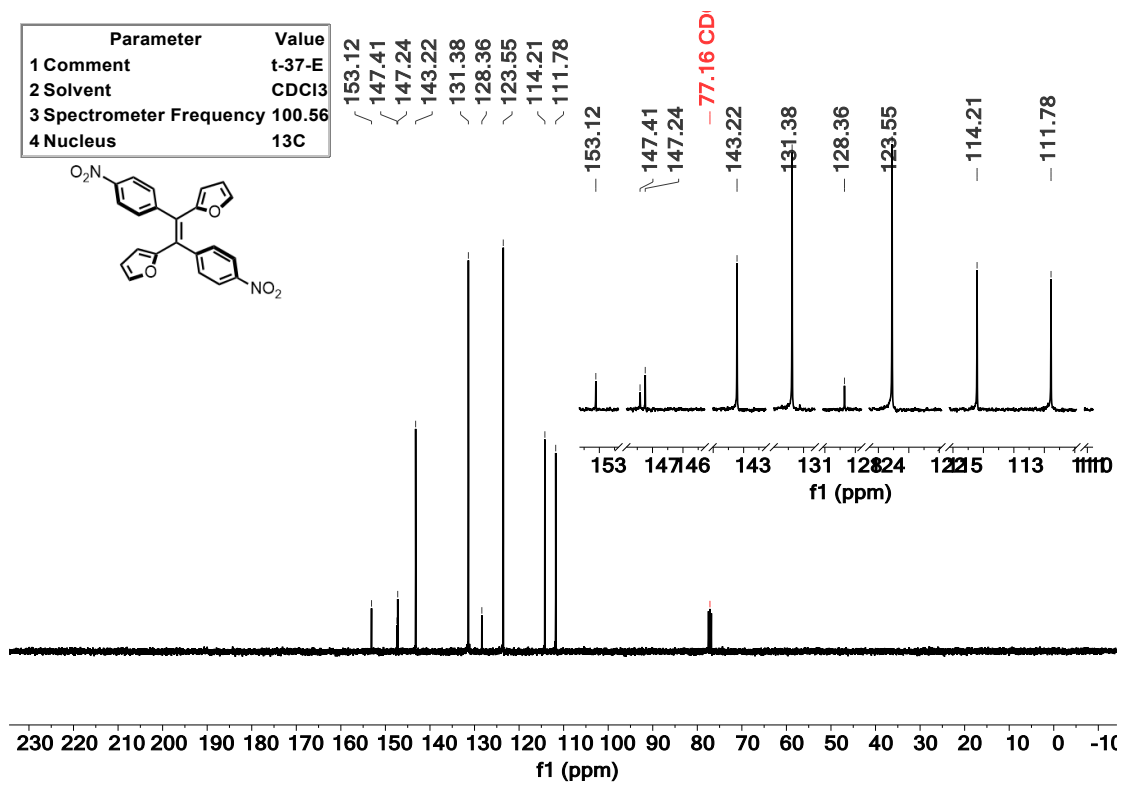
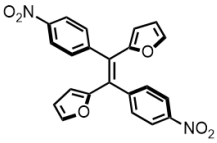


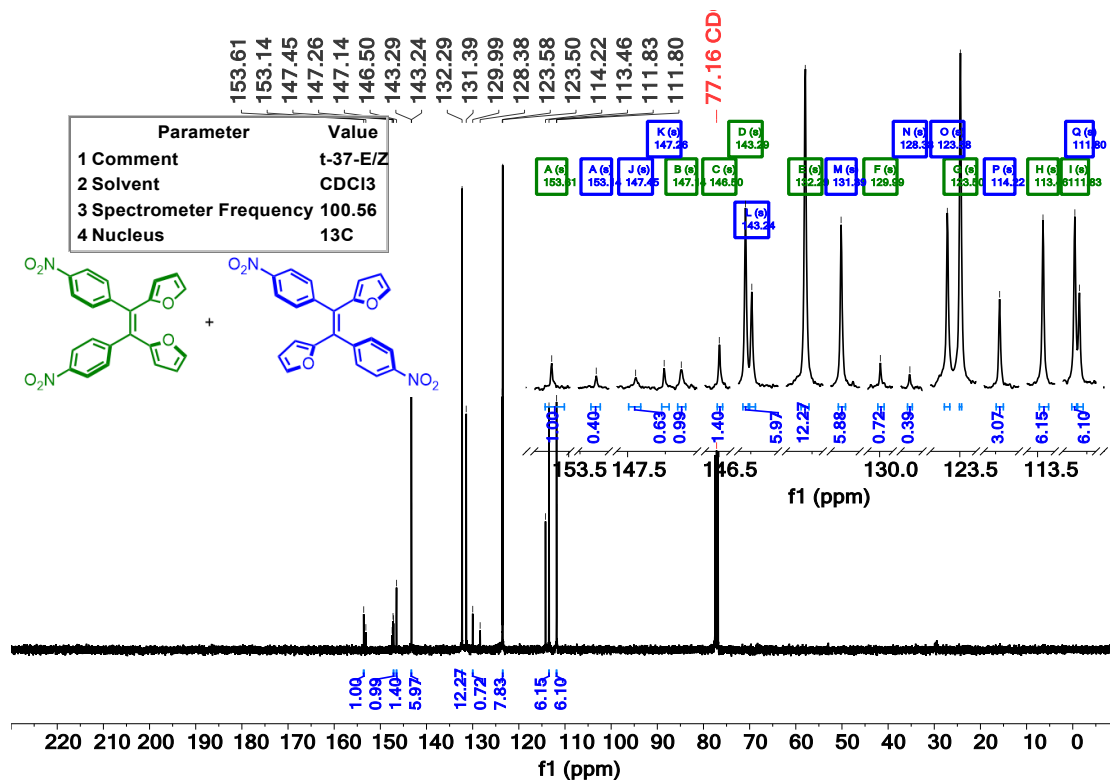
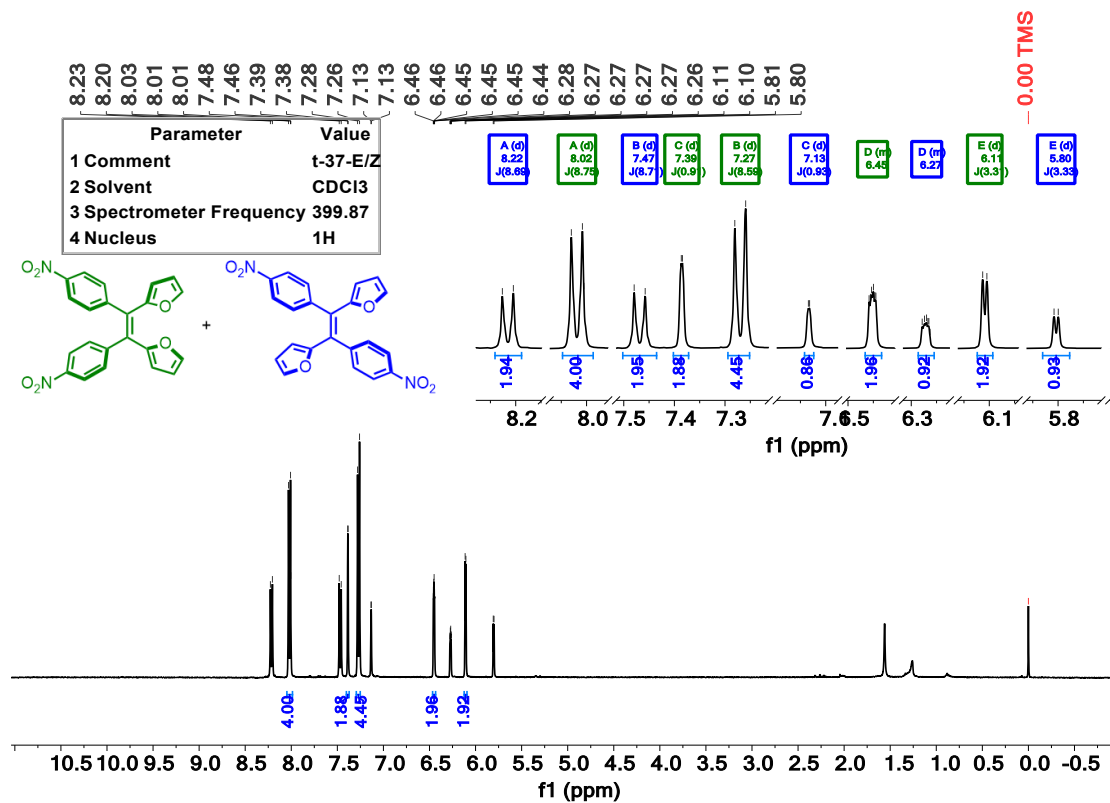


Parameter	Value
1 Comment	t-37-E
2 Solvent	CDCl3
3 Spectrometer Frequency	399.87
4 Nucleus	1H

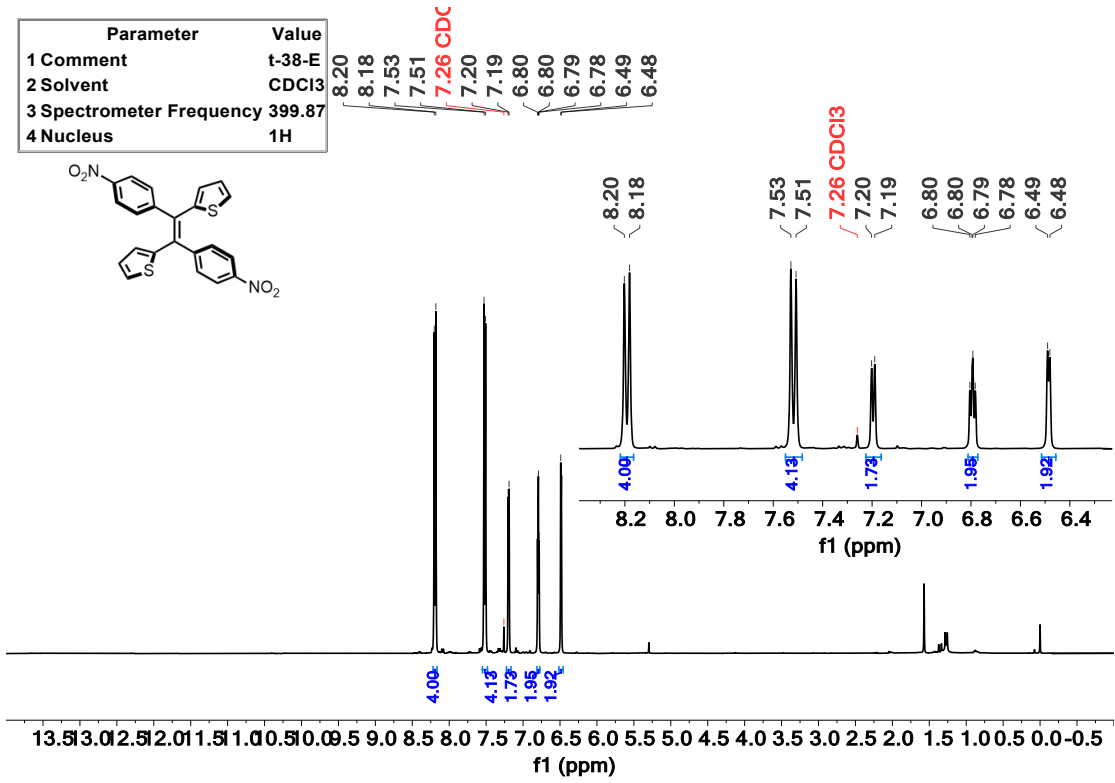
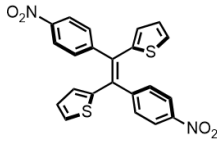


Parameter	Value
1 Comment	t-37-E
2 Solvent	CDCl3
3 Spectrometer Frequency	100.56
4 Nucleus	13C

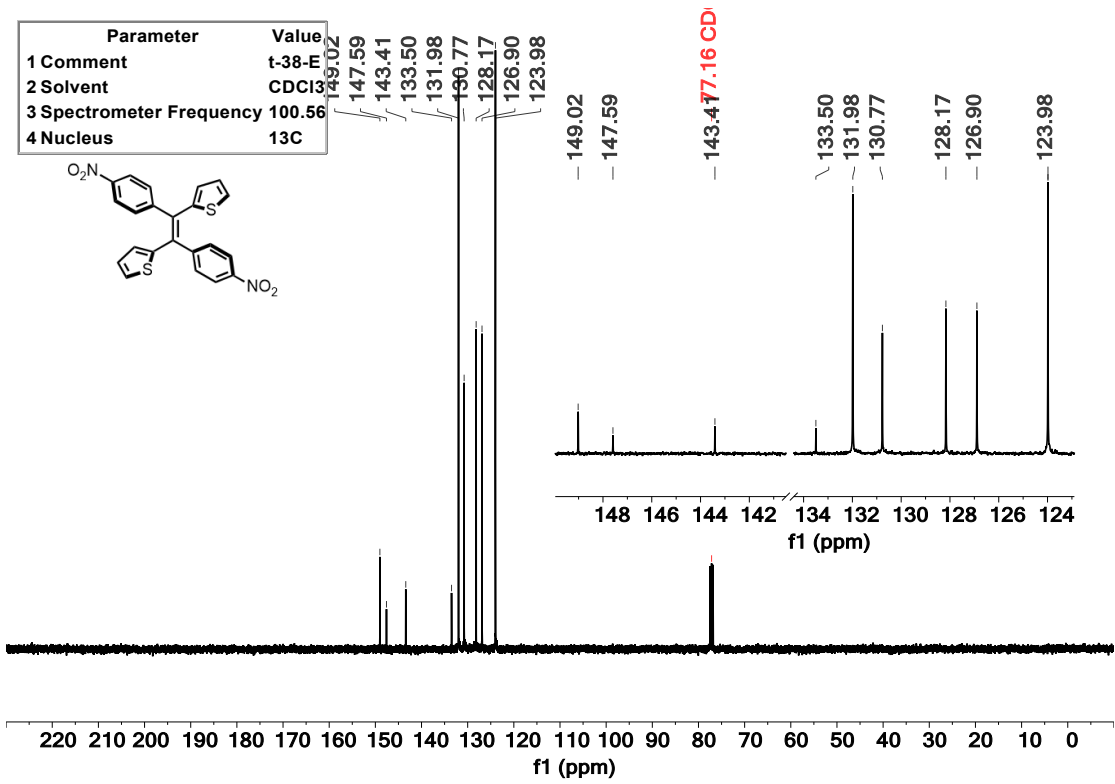
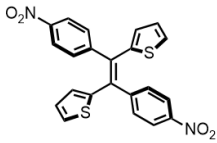


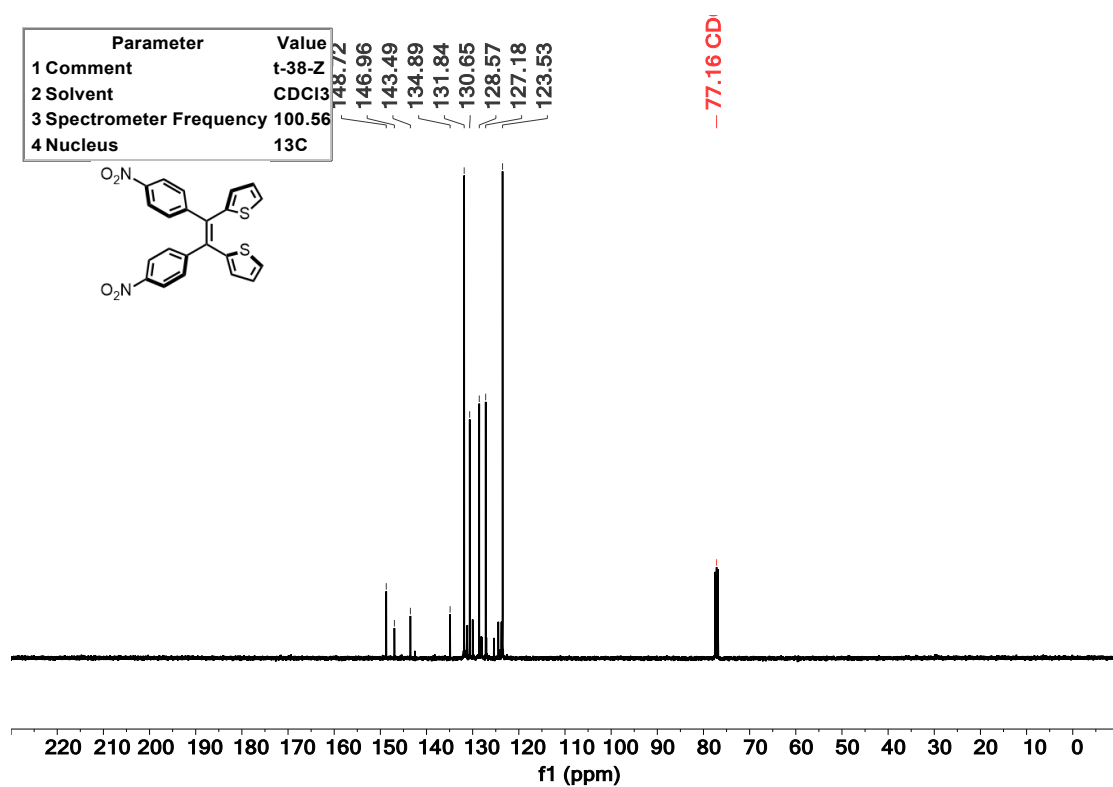
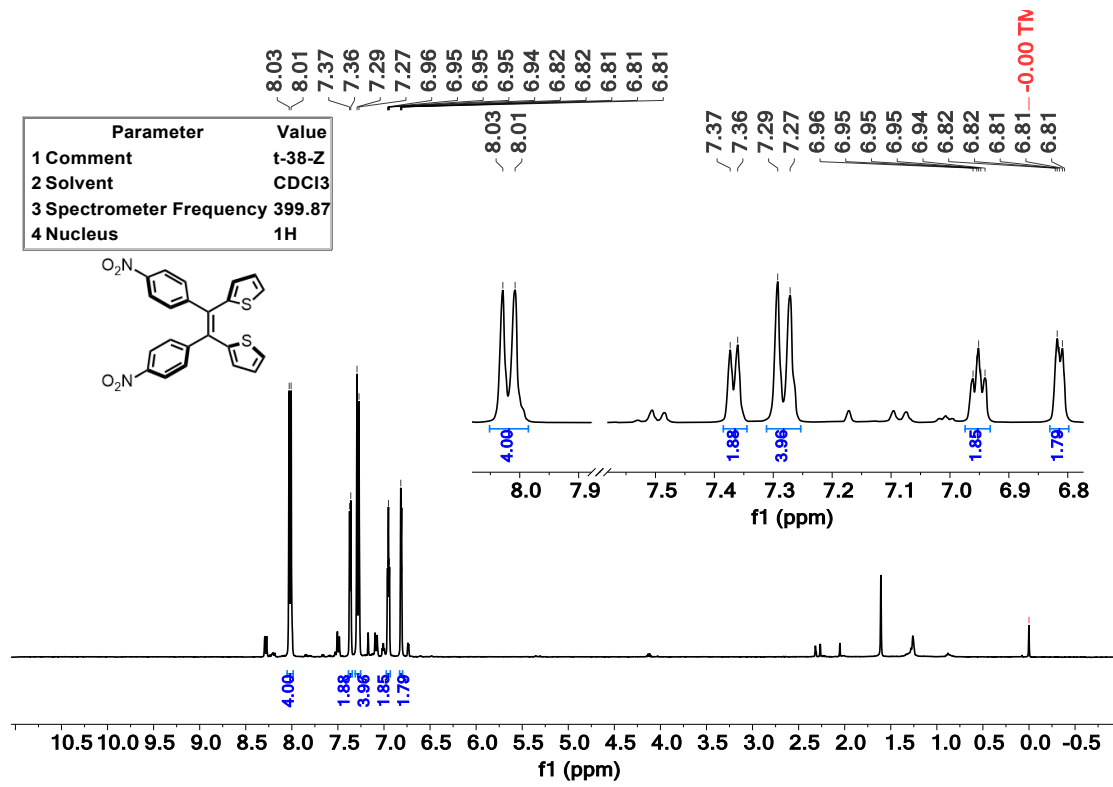


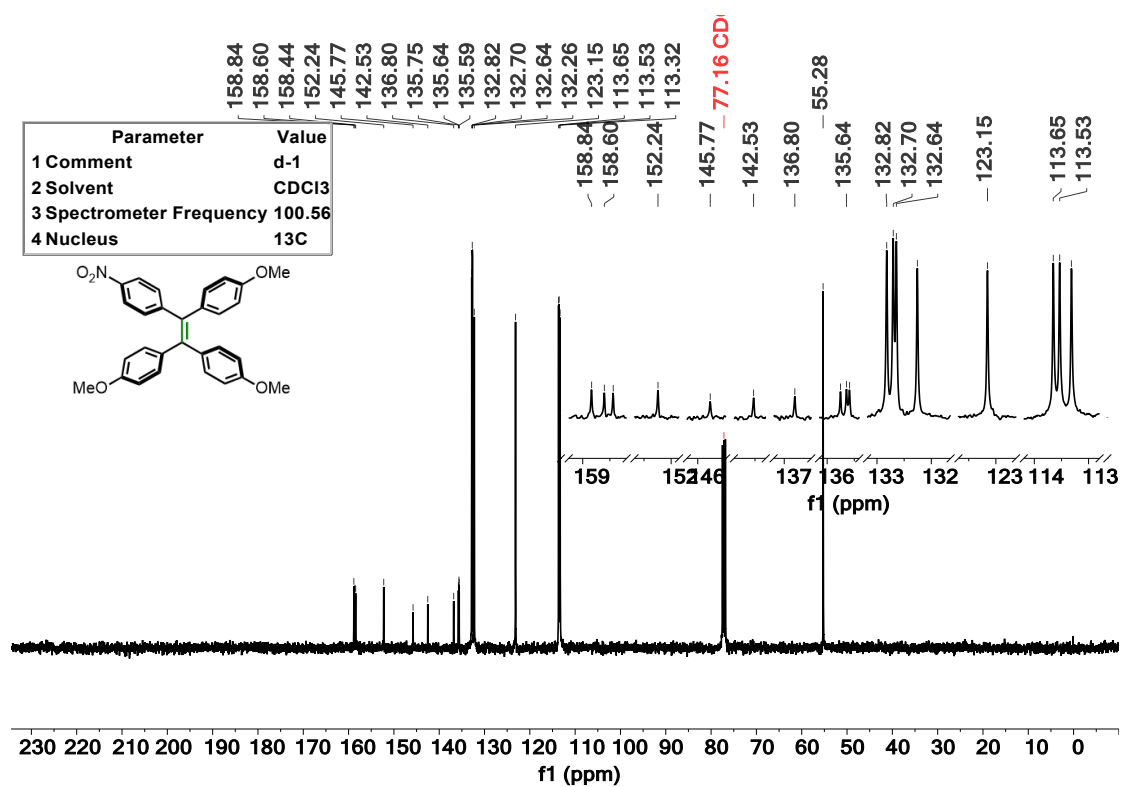
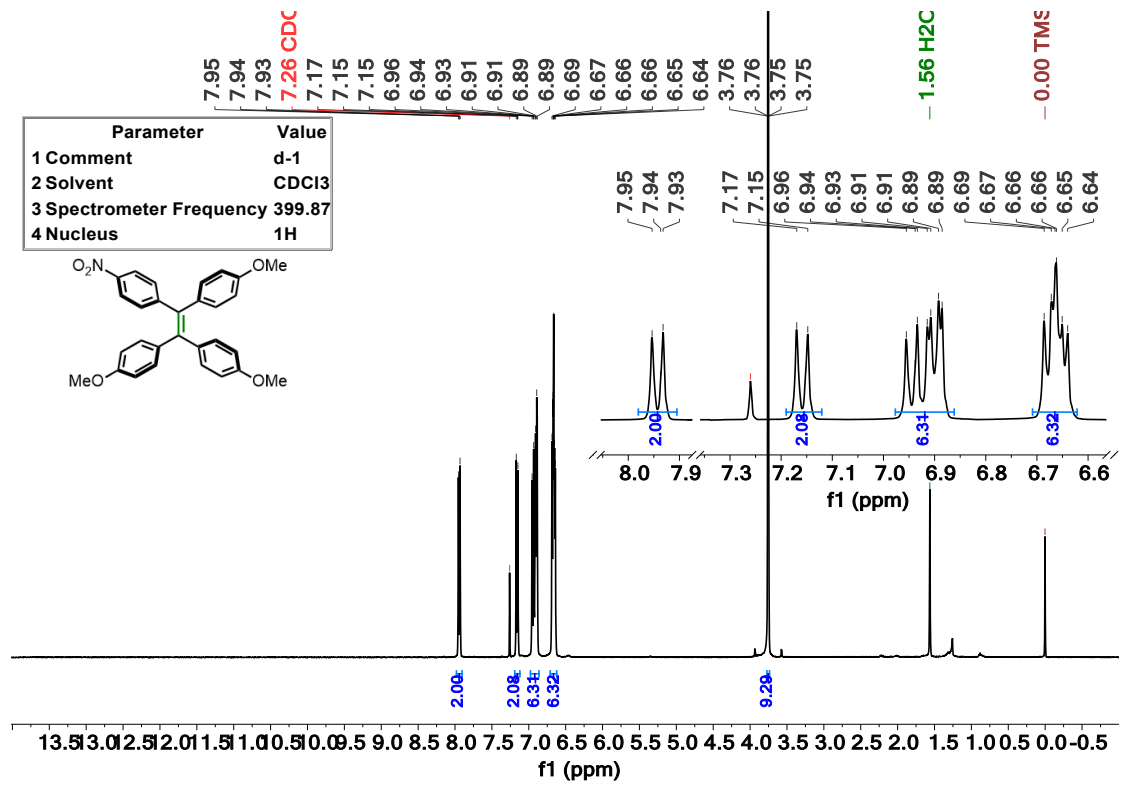
Parameter	Value
1 Comment	t-38-E
2 Solvent	CDCl ₃
3 Spectrometer Frequency	399.87
4 Nucleus	¹ H



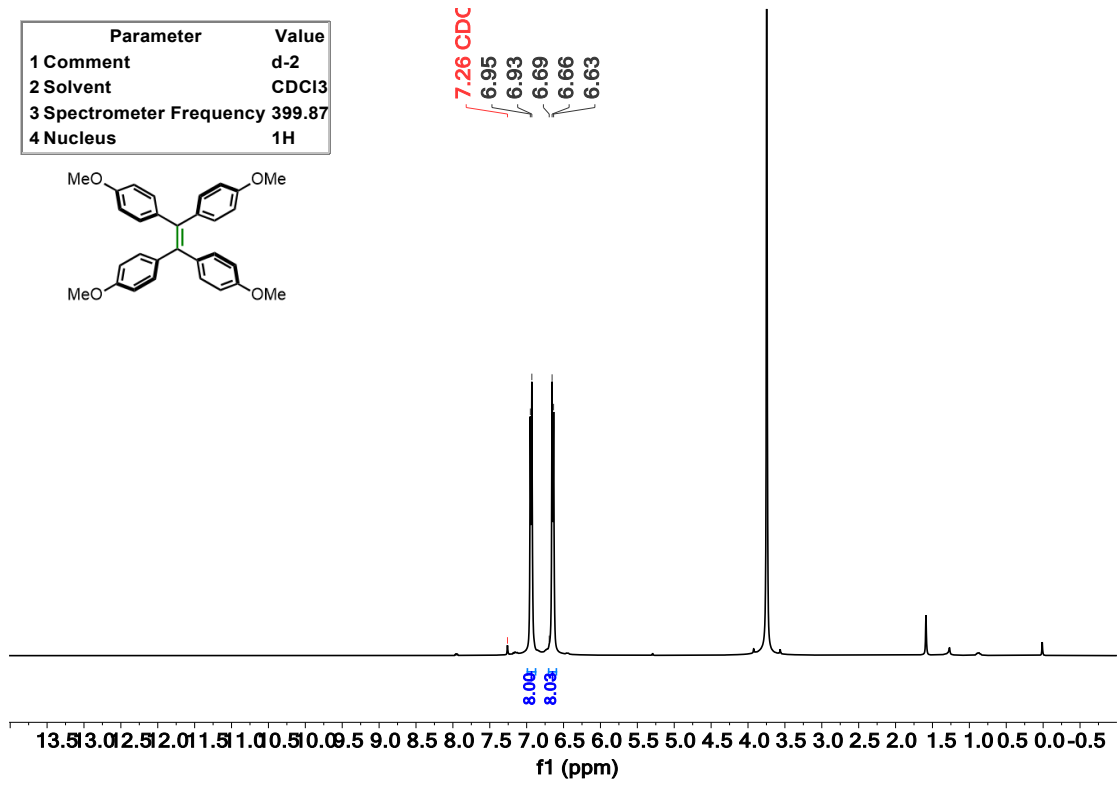
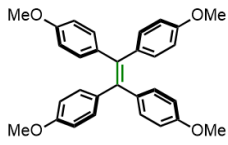
Parameter	Value
1 Comment	t-38-E
2 Solvent	CDCl ₃
3 Spectrometer Frequency	100.56
4 Nucleus	¹³ C



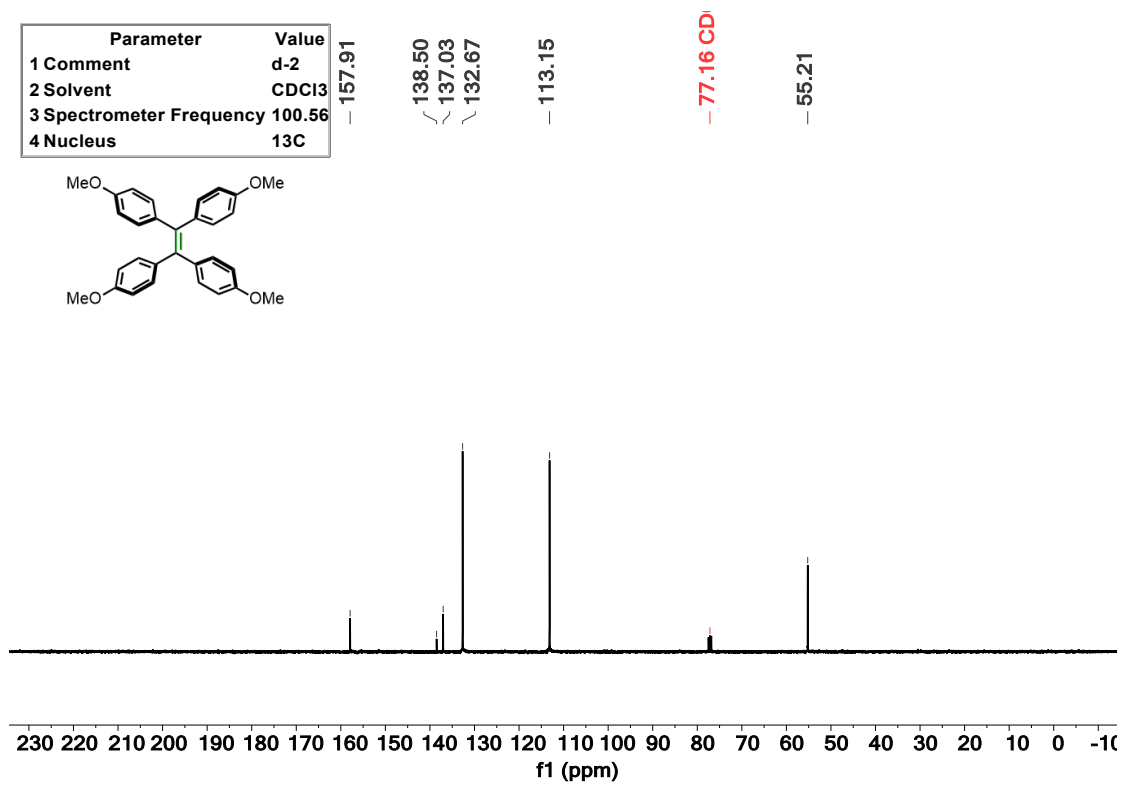
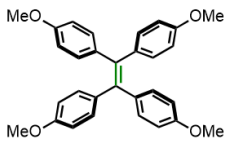


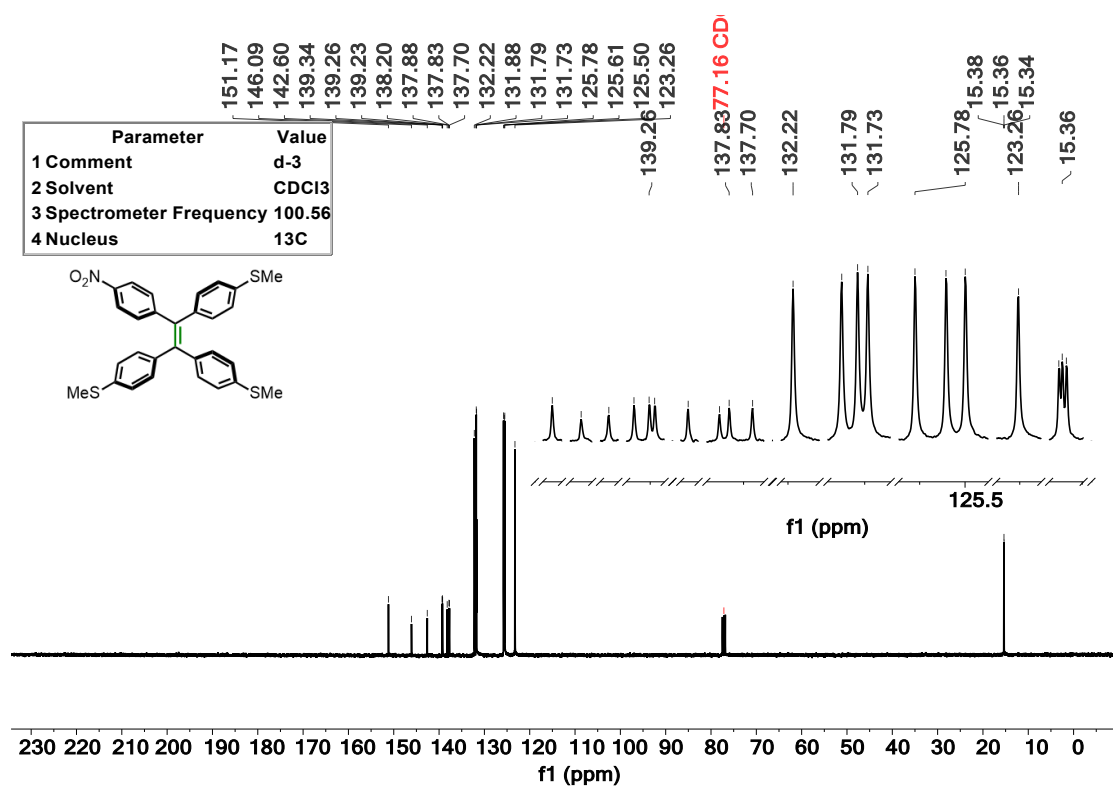
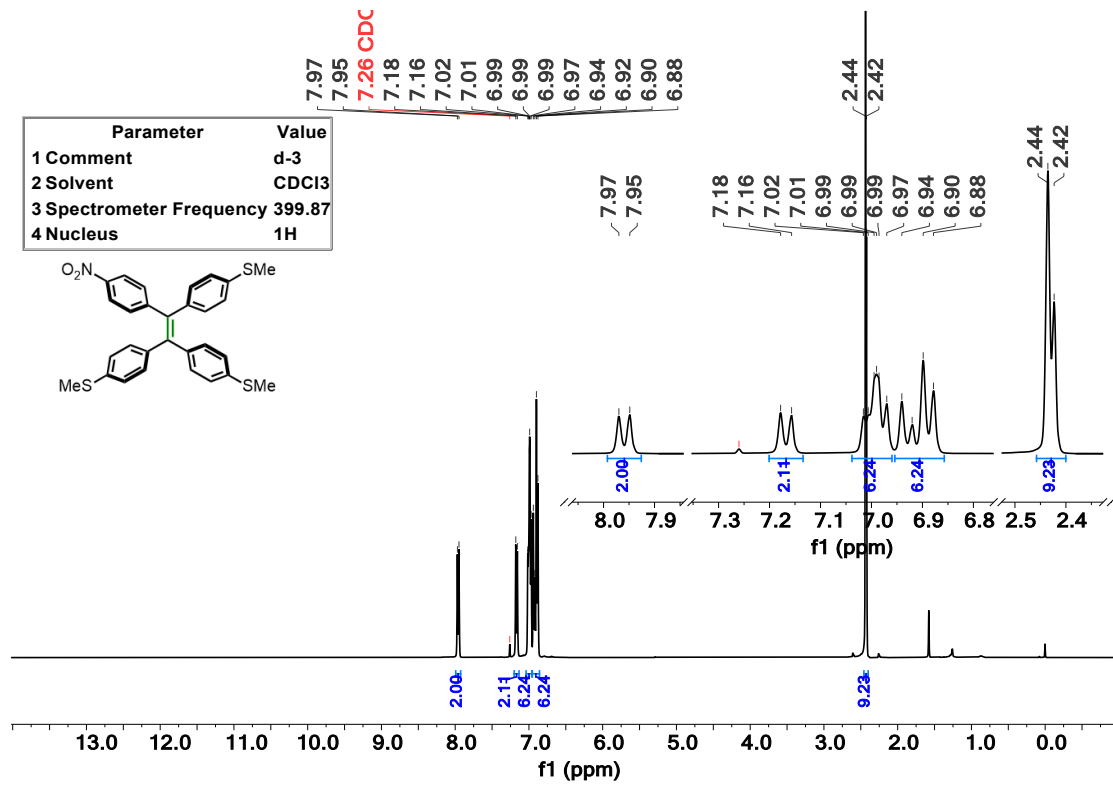


Parameter	Value
1 Comment	d-2
2 Solvent	CDCl ₃
3 Spectrometer Frequency	399.87
4 Nucleus	¹ H

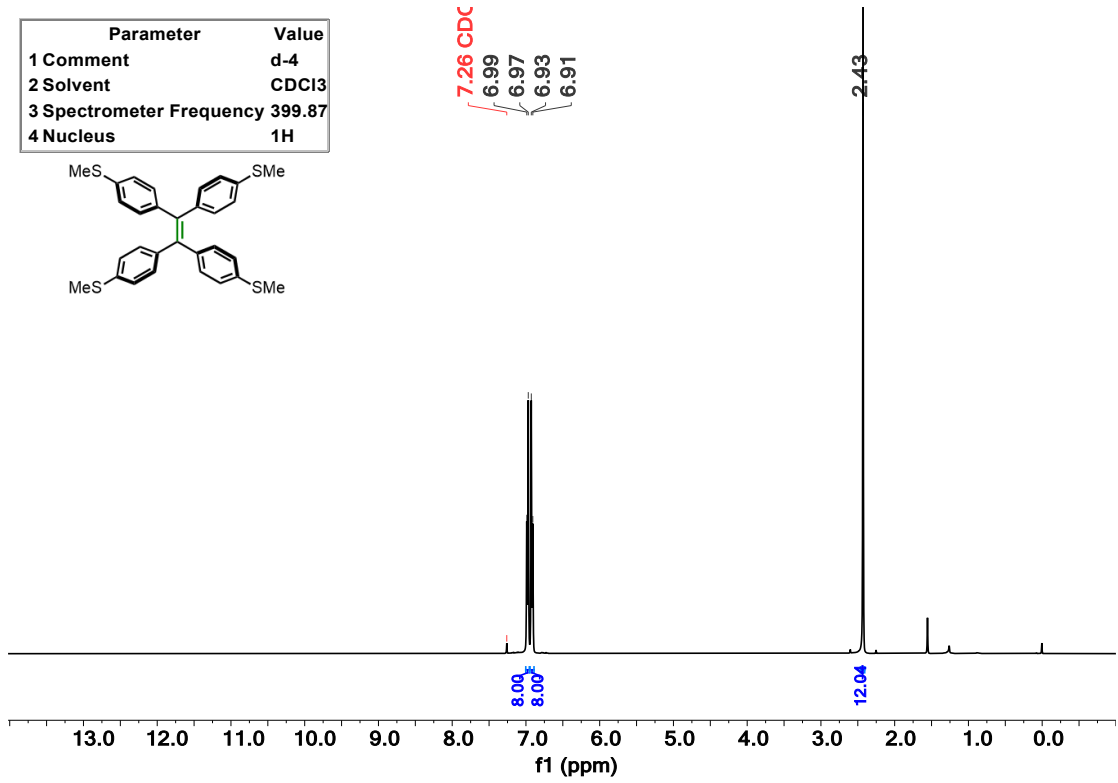
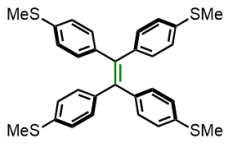


Parameter	Value
1 Comment	d-2
2 Solvent	CDCl ₃
3 Spectrometer Frequency	100.56
4 Nucleus	¹³ C

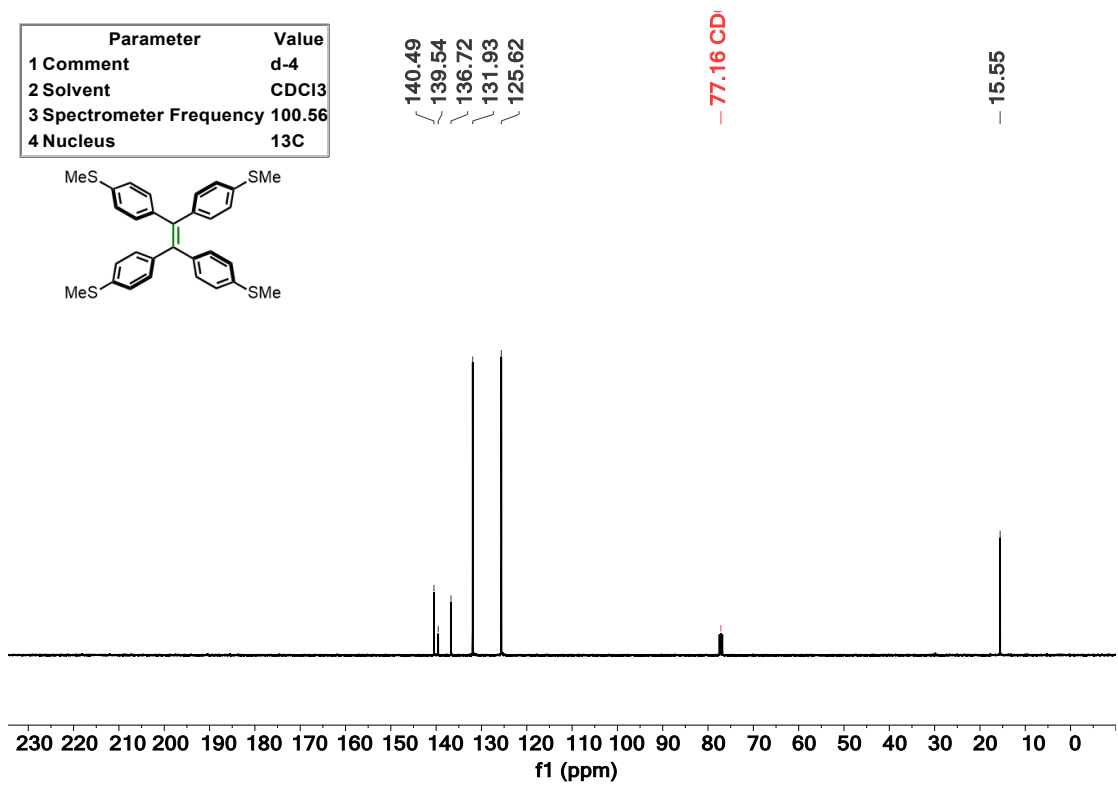
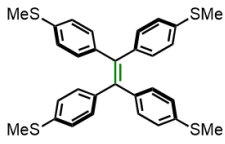




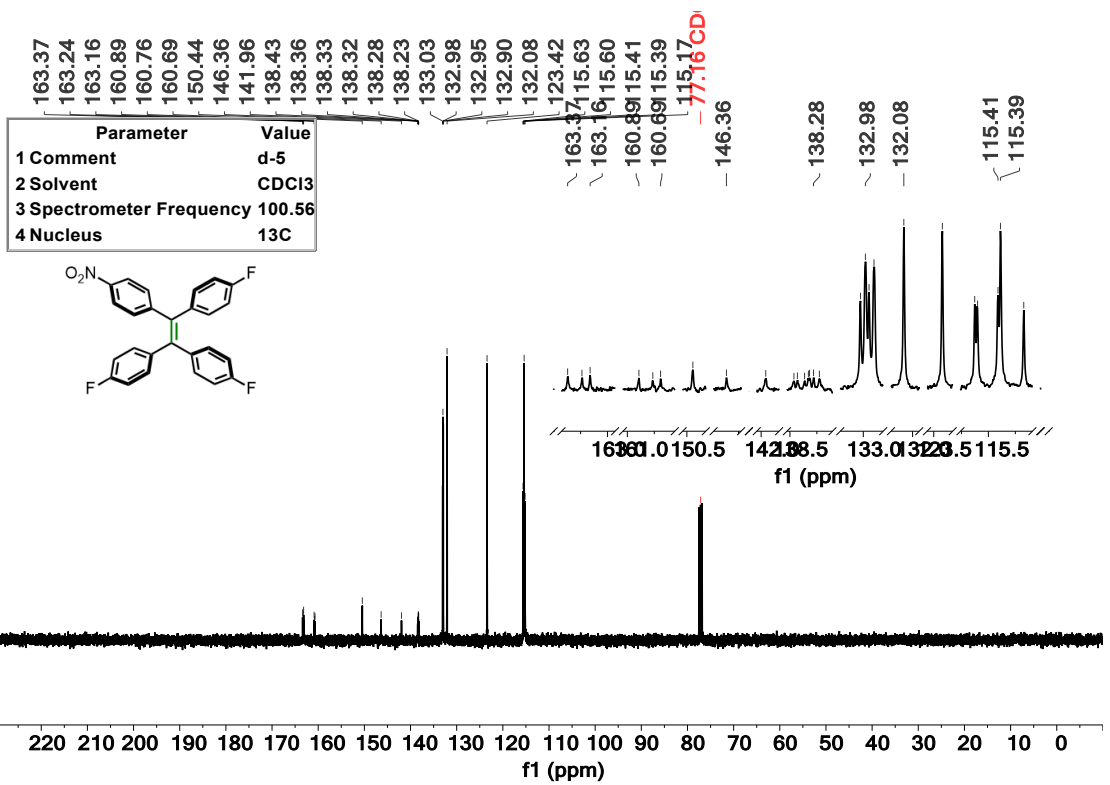
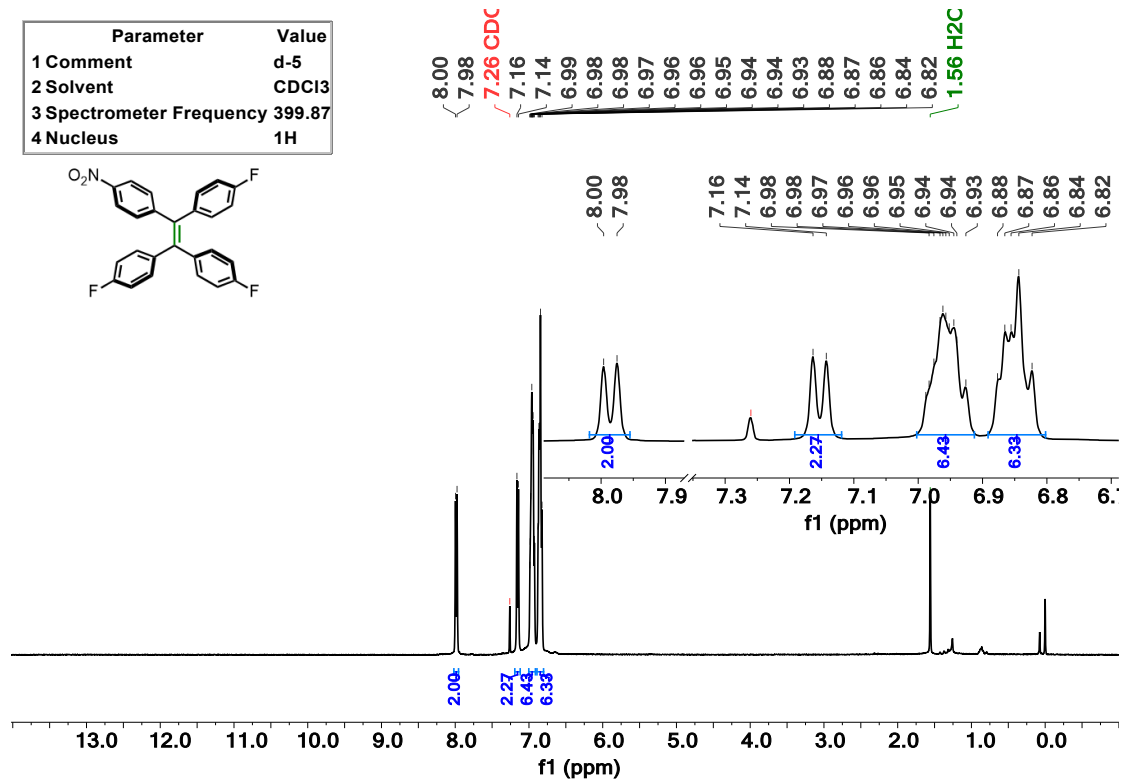
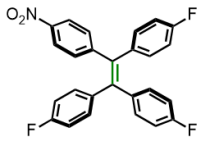
Parameter	Value
1 Comment	d-4
2 Solvent	CDCl3
3 Spectrometer Frequency	399.87
4 Nucleus	1H

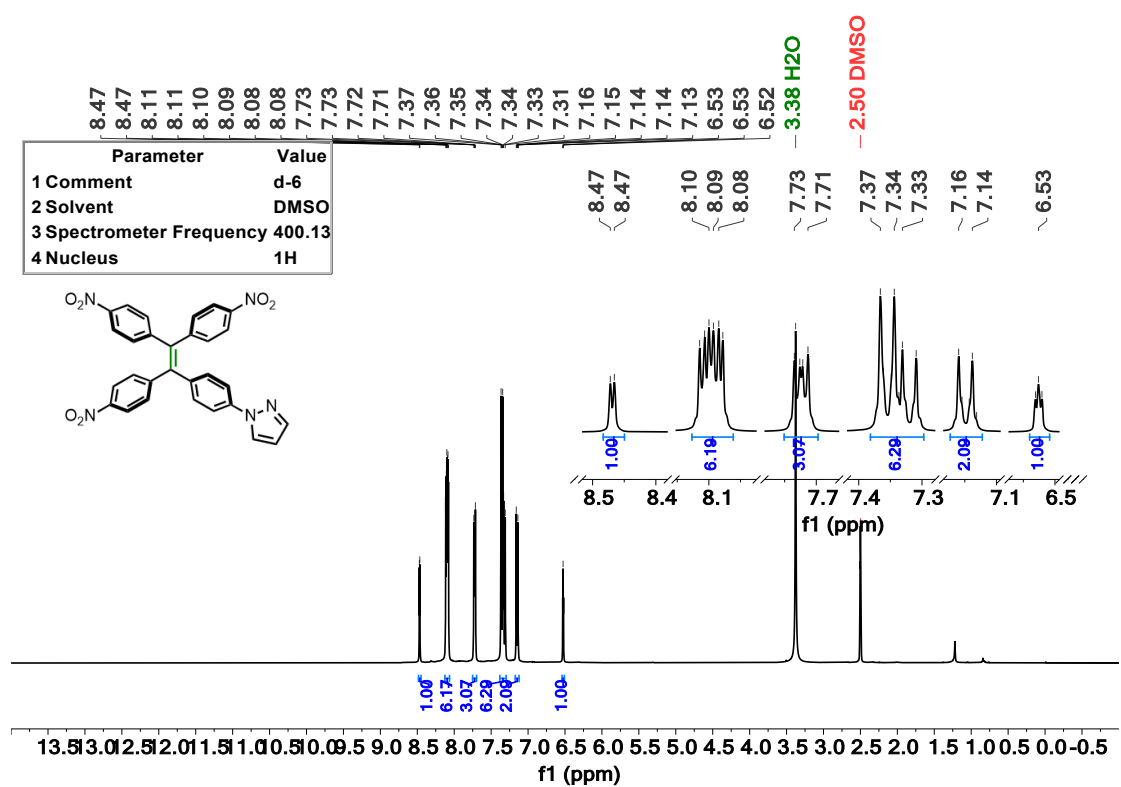
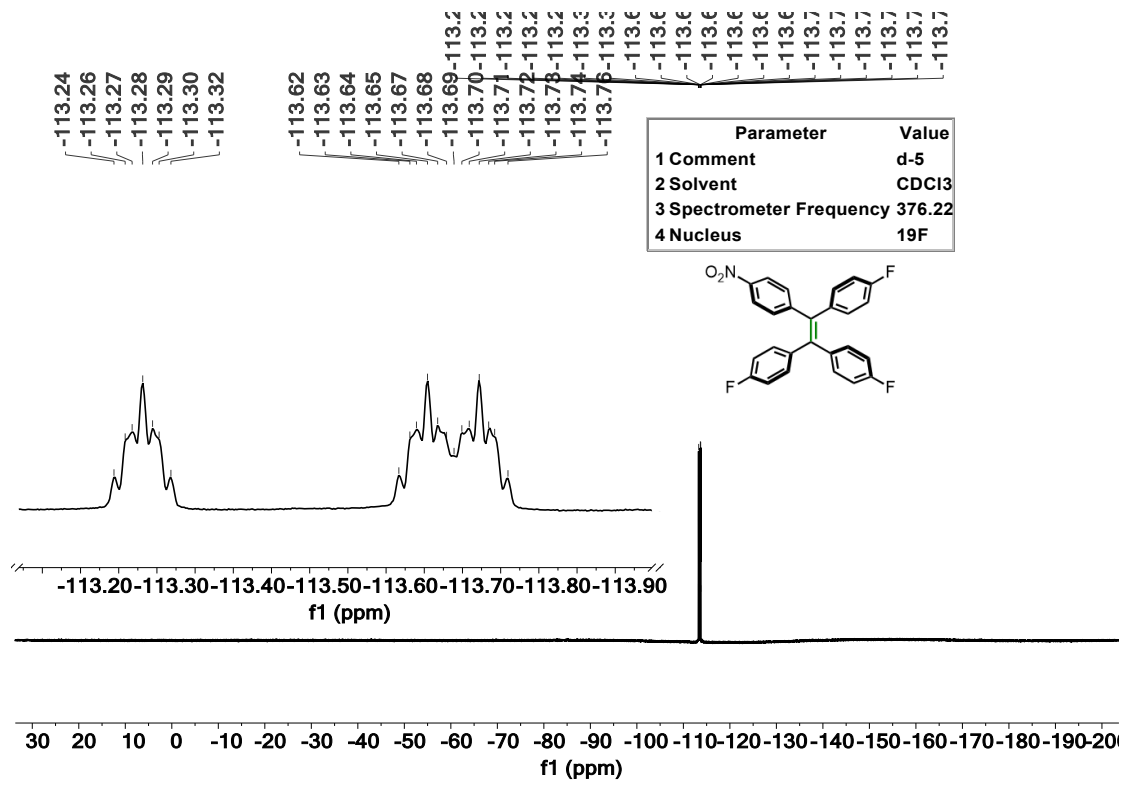


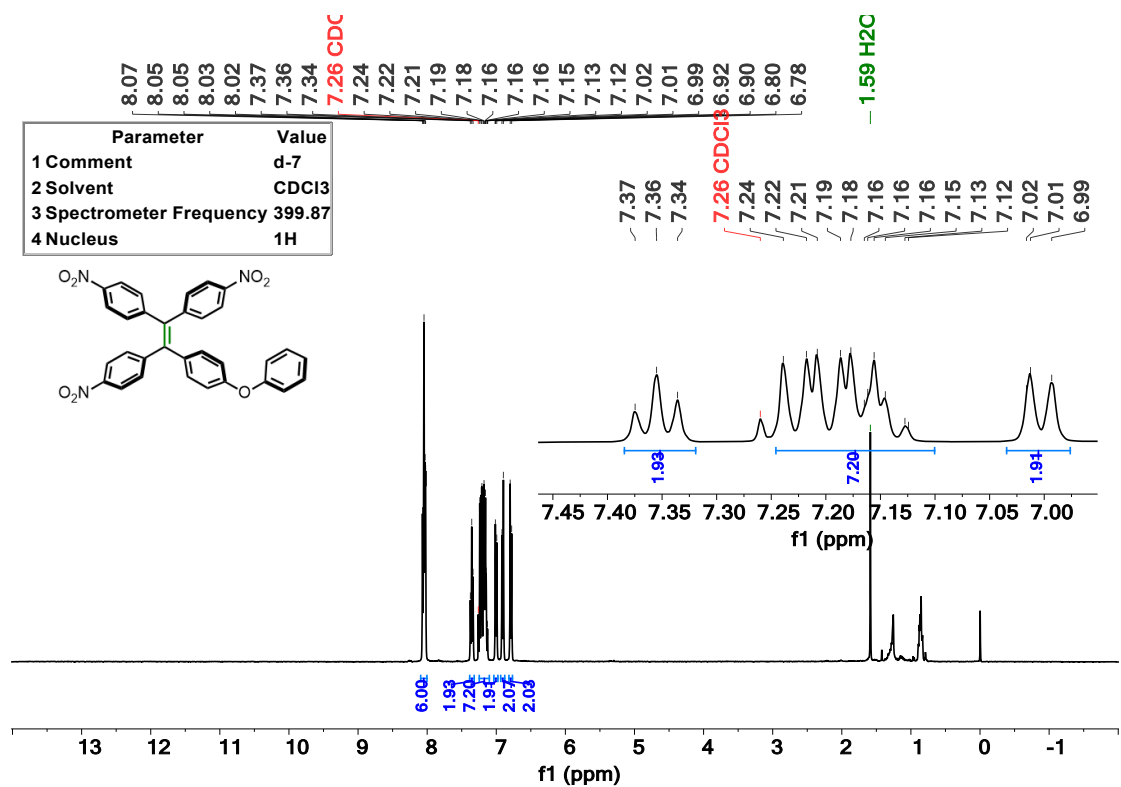
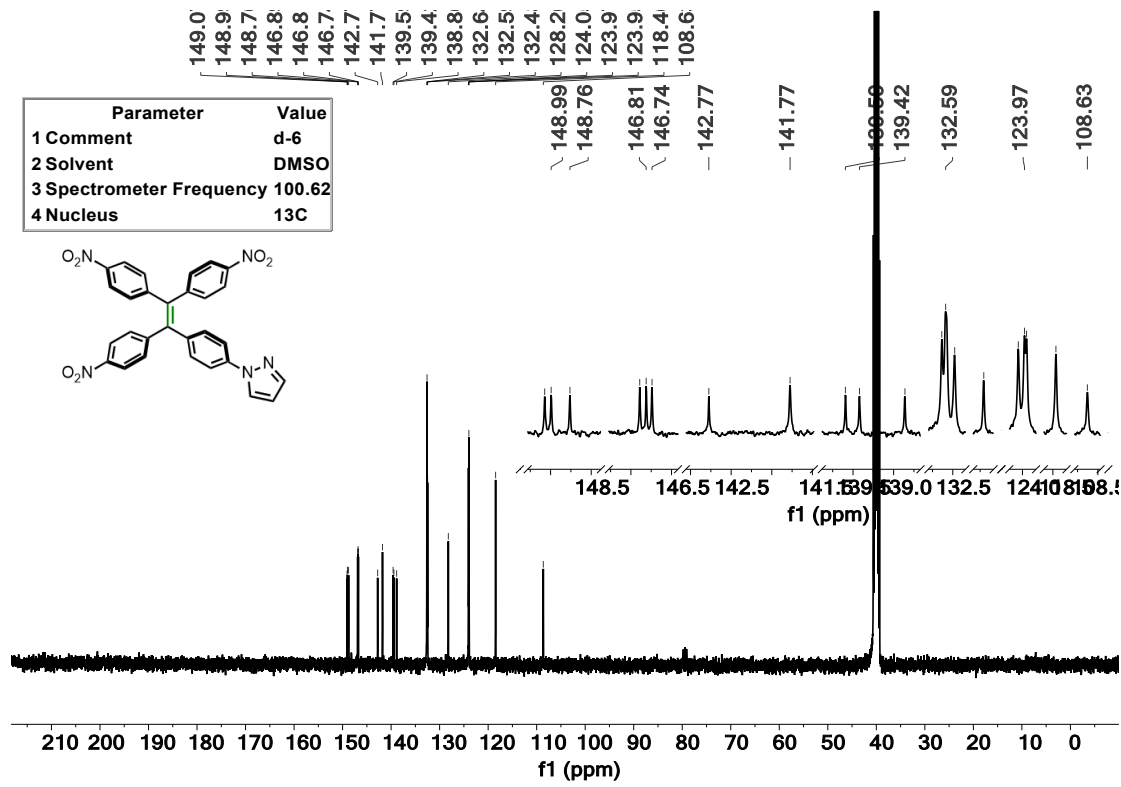
Parameter	Value
1 Comment	d-4
2 Solvent	CDCl3
3 Spectrometer Frequency	100.56
4 Nucleus	13C

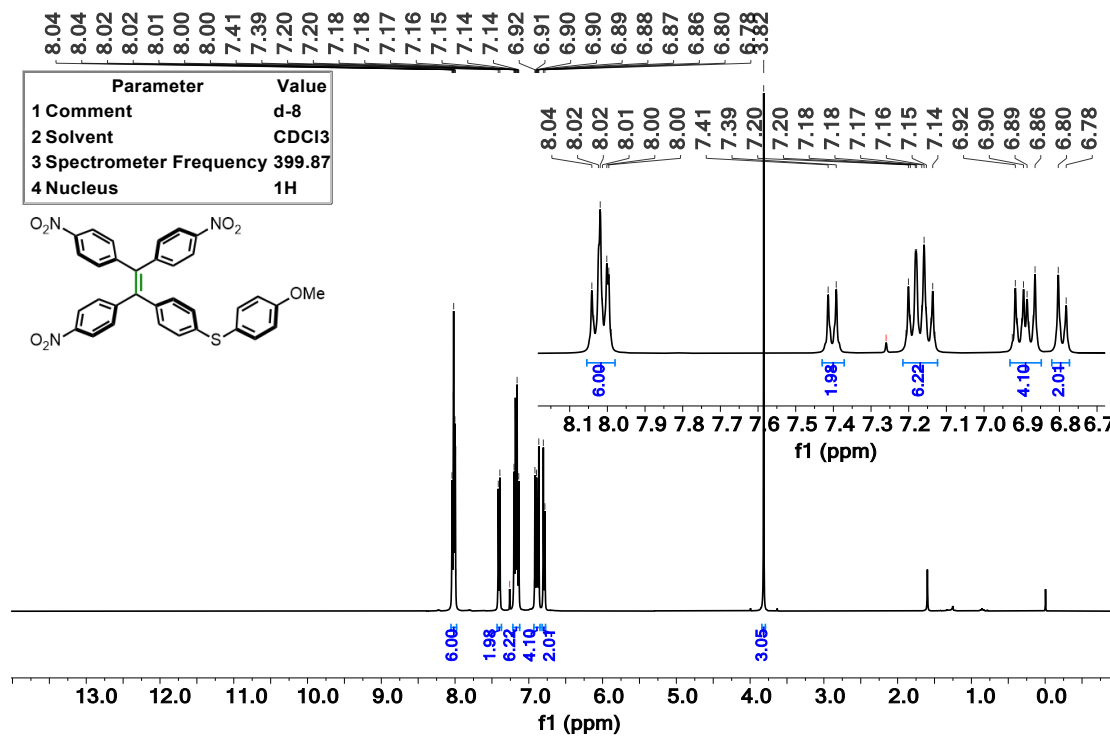
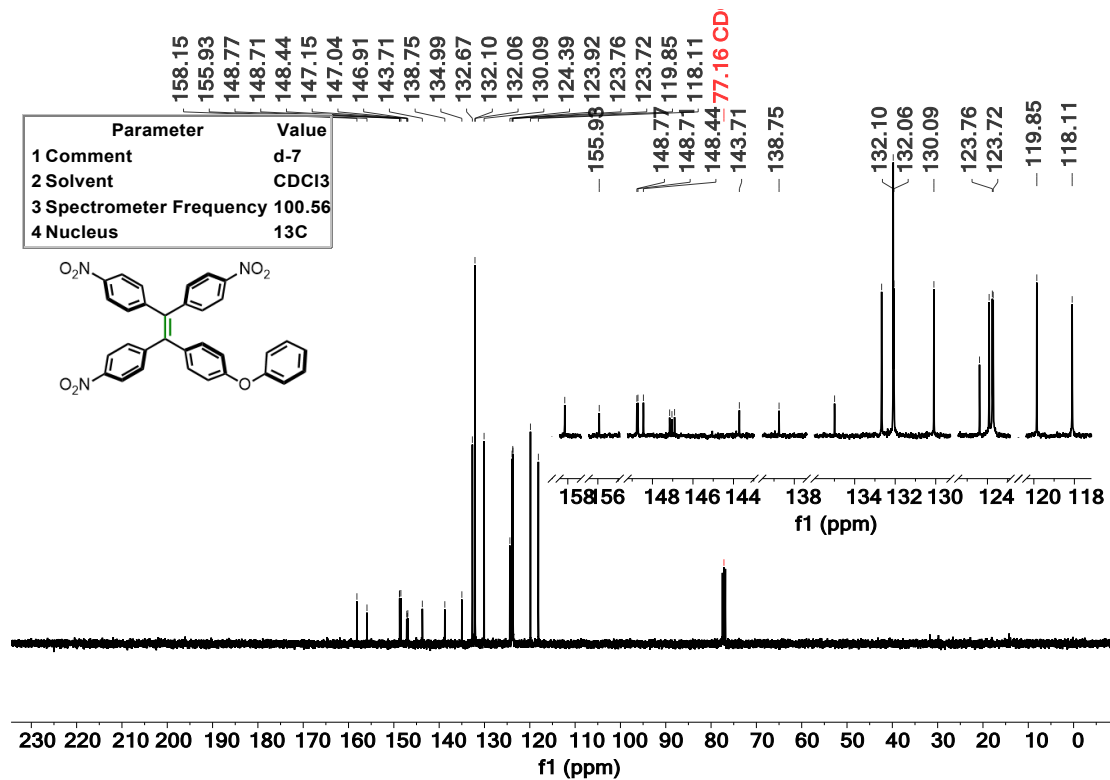


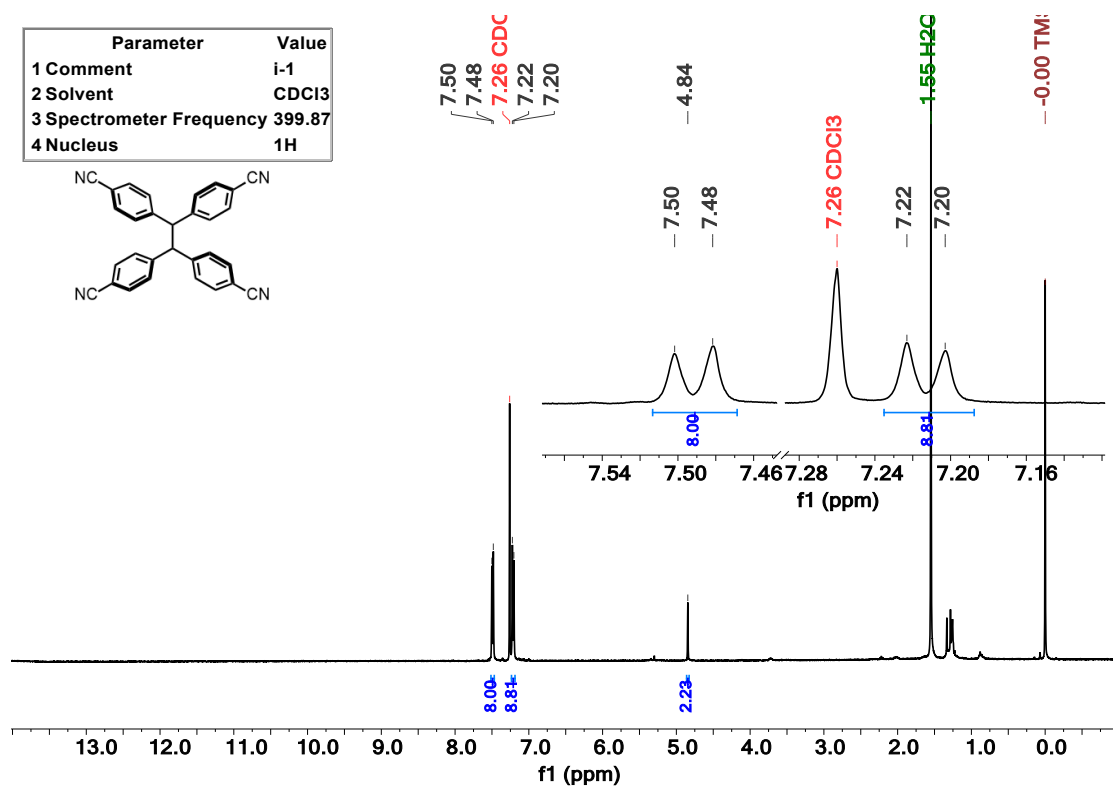
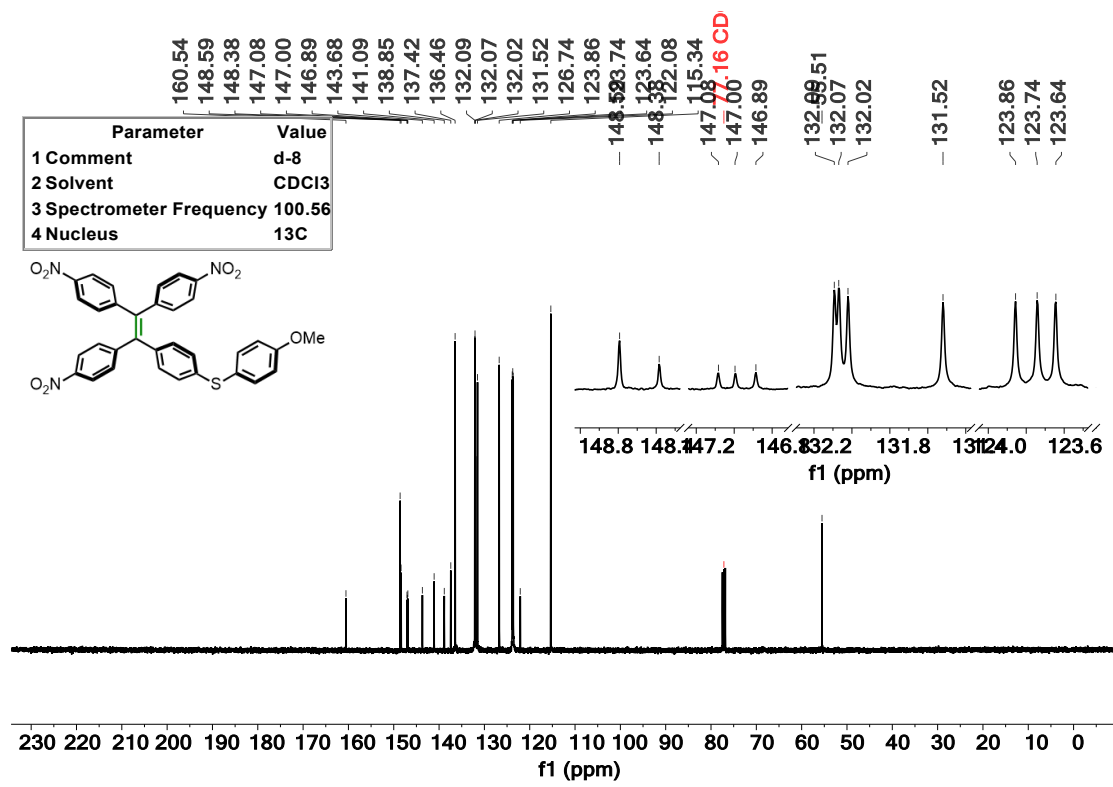
Parameter	Value
1 Comment	d-5
2 Solvent	CDCl3
3 Spectrometer Frequency	399.87
4 Nucleus	1H



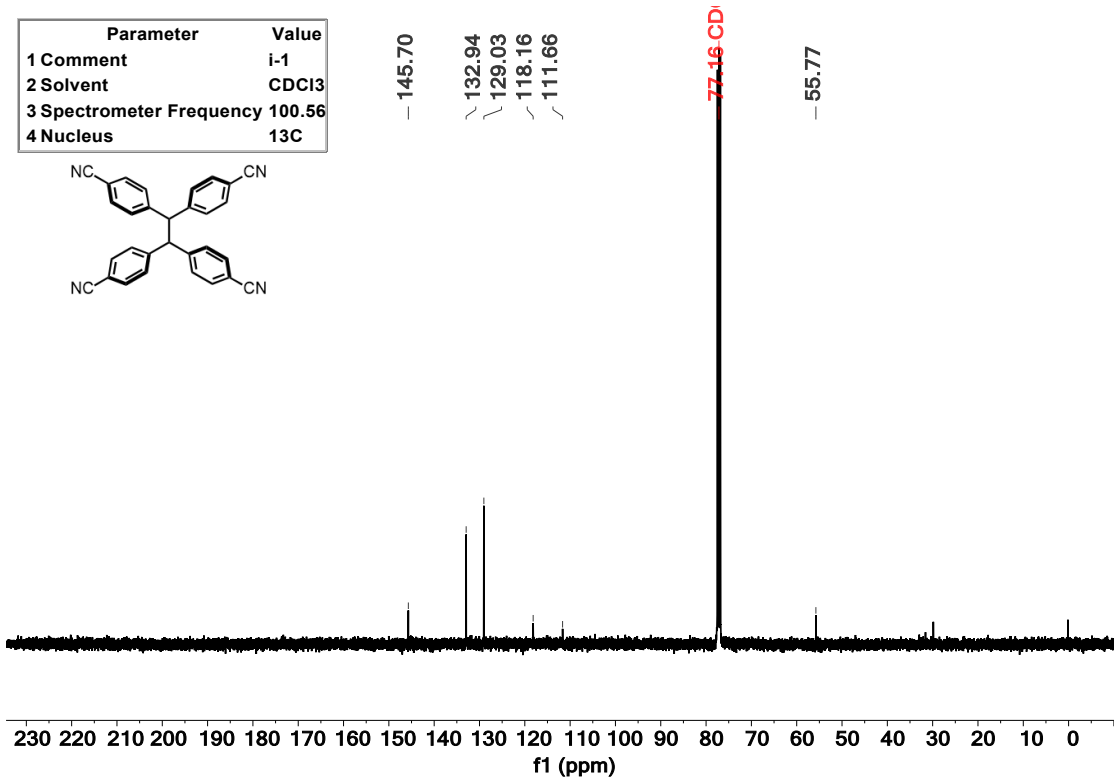
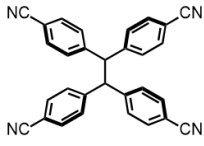




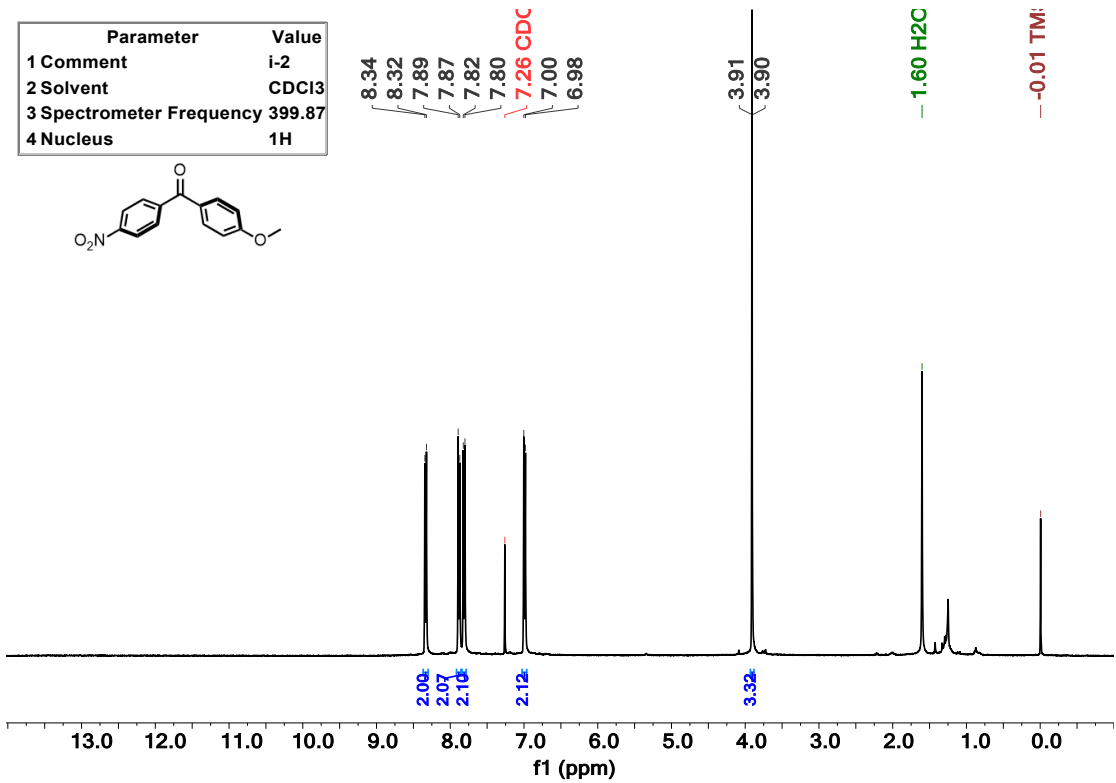
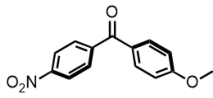


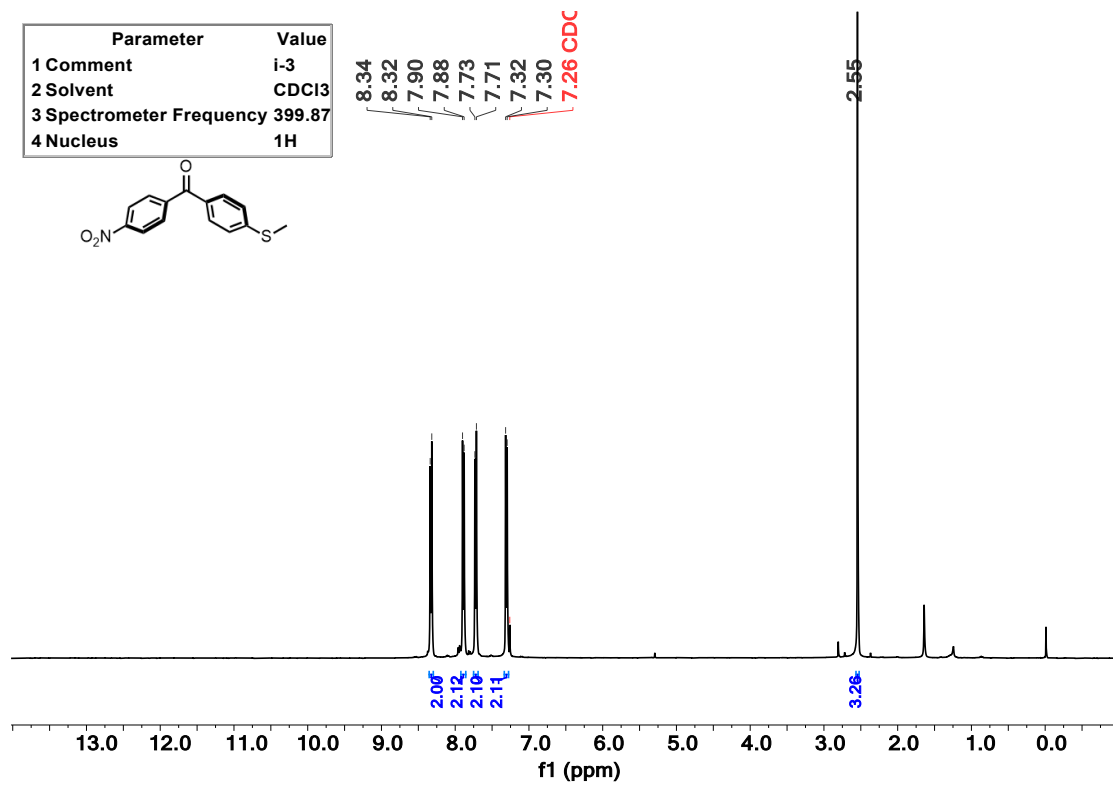
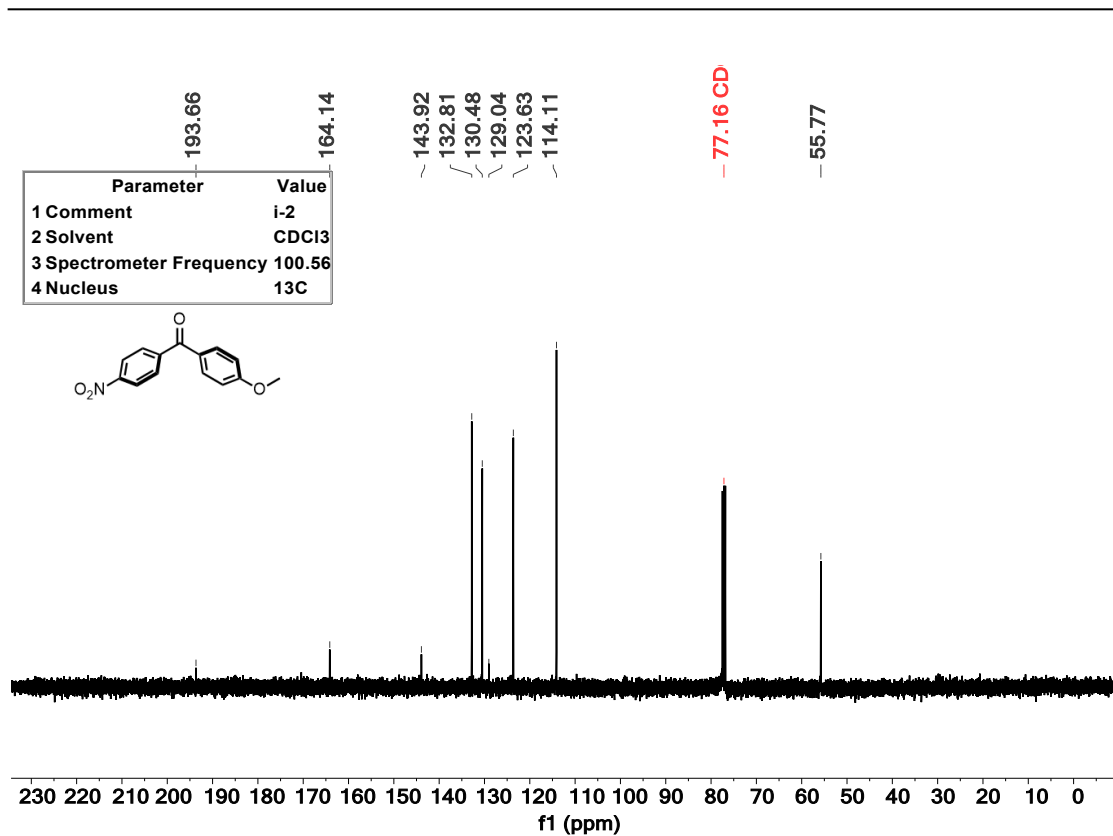


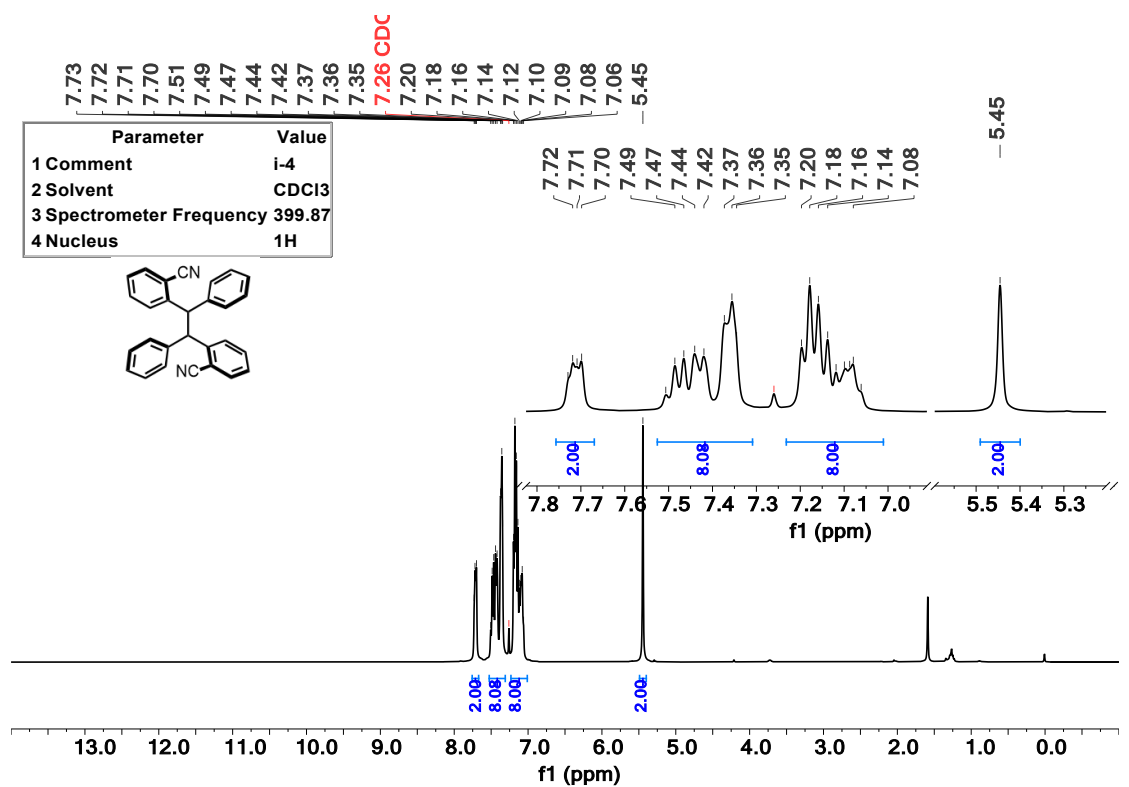
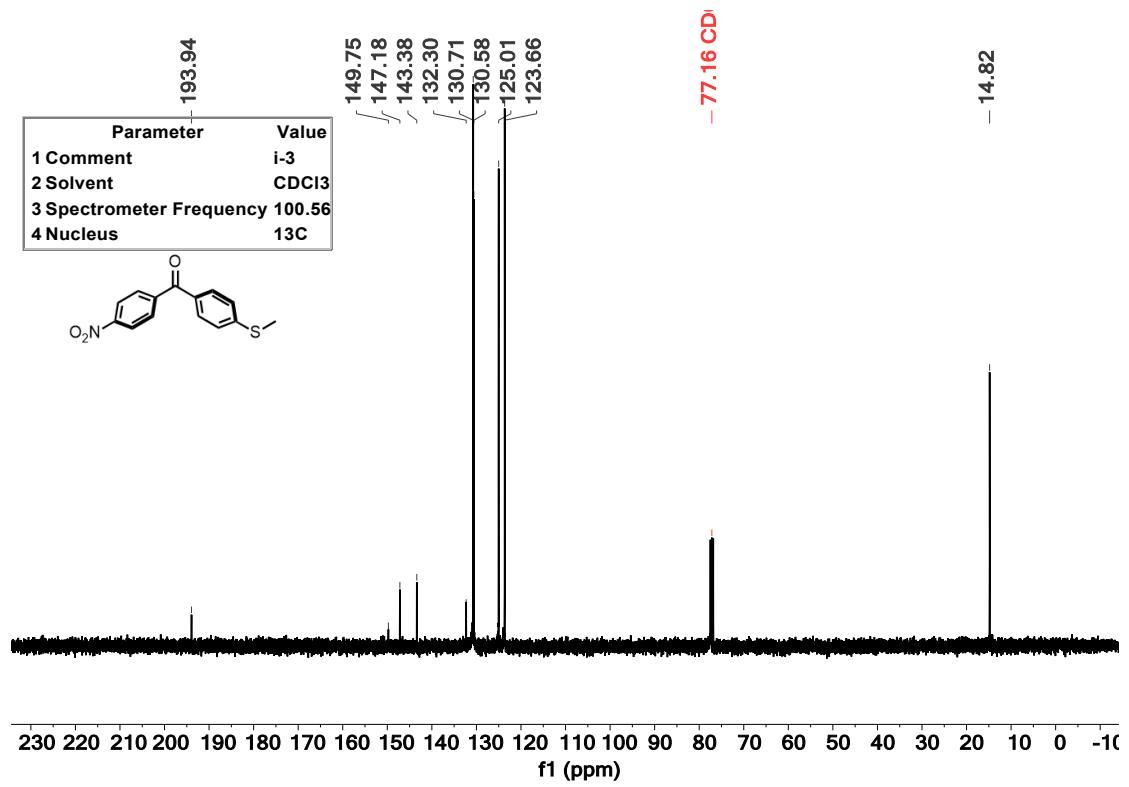
Parameter	Value
1 Comment	i-1
2 Solvent	CDCl3
3 Spectrometer Frequency	100.56
4 Nucleus	13C

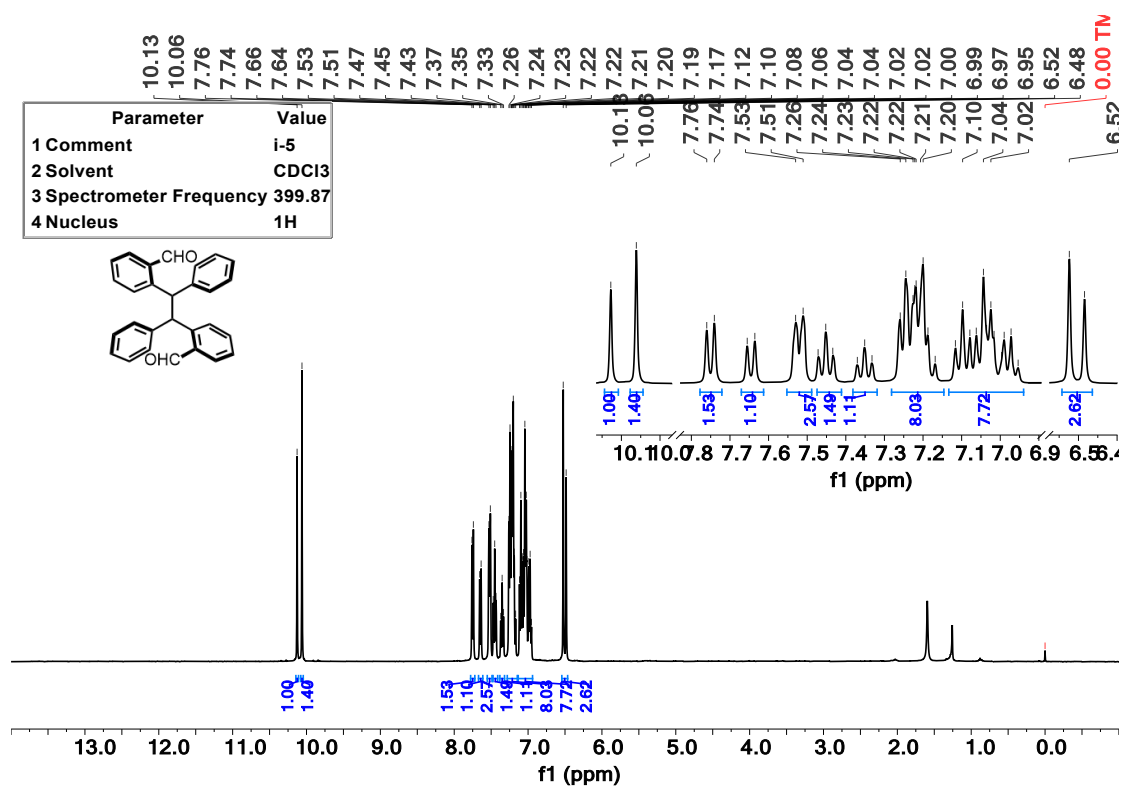
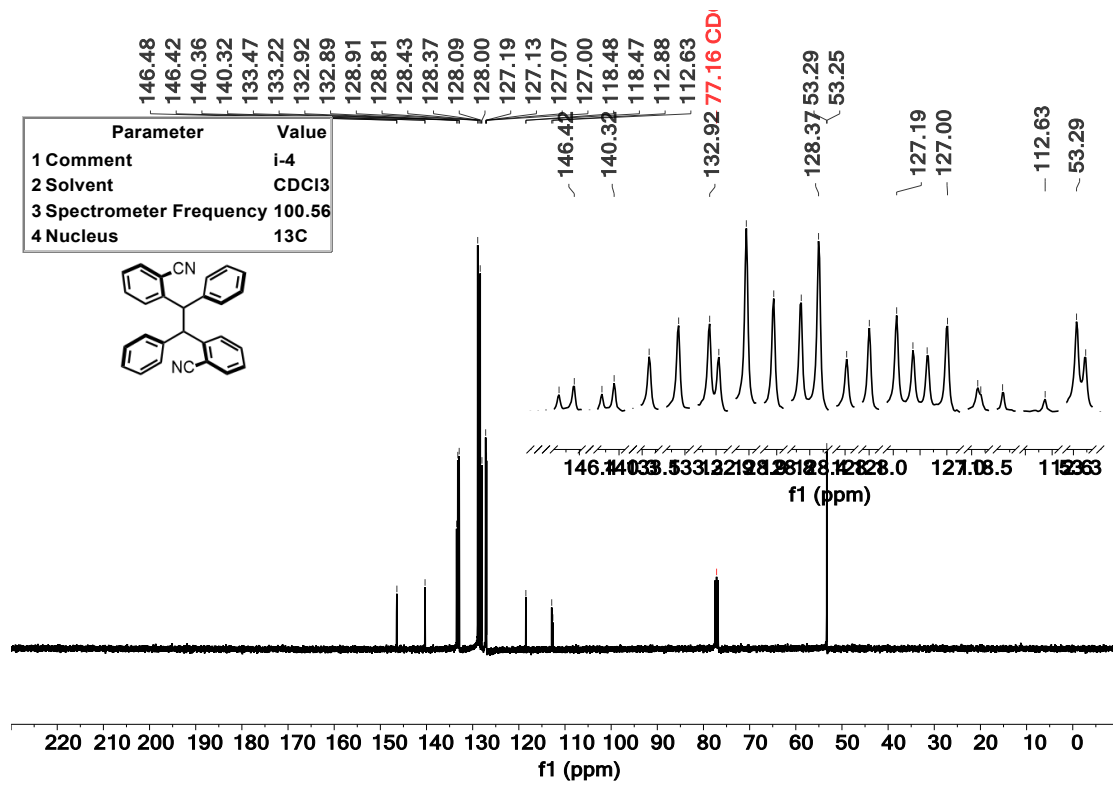


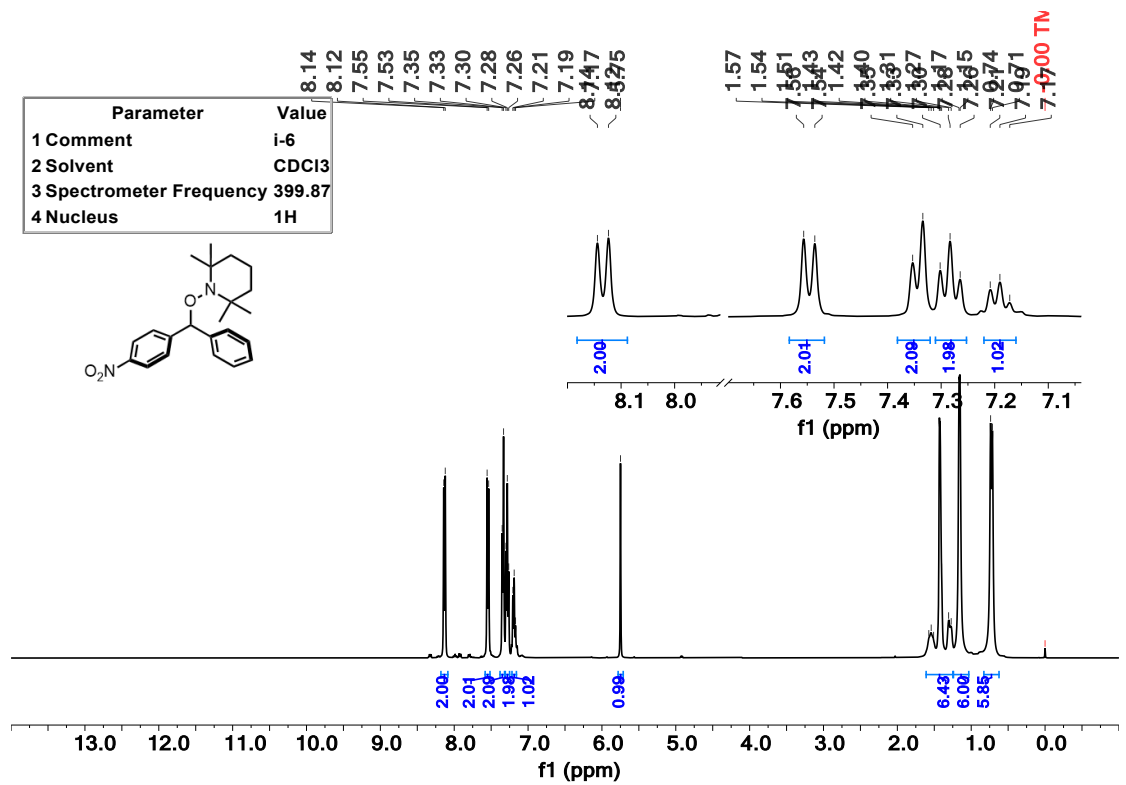
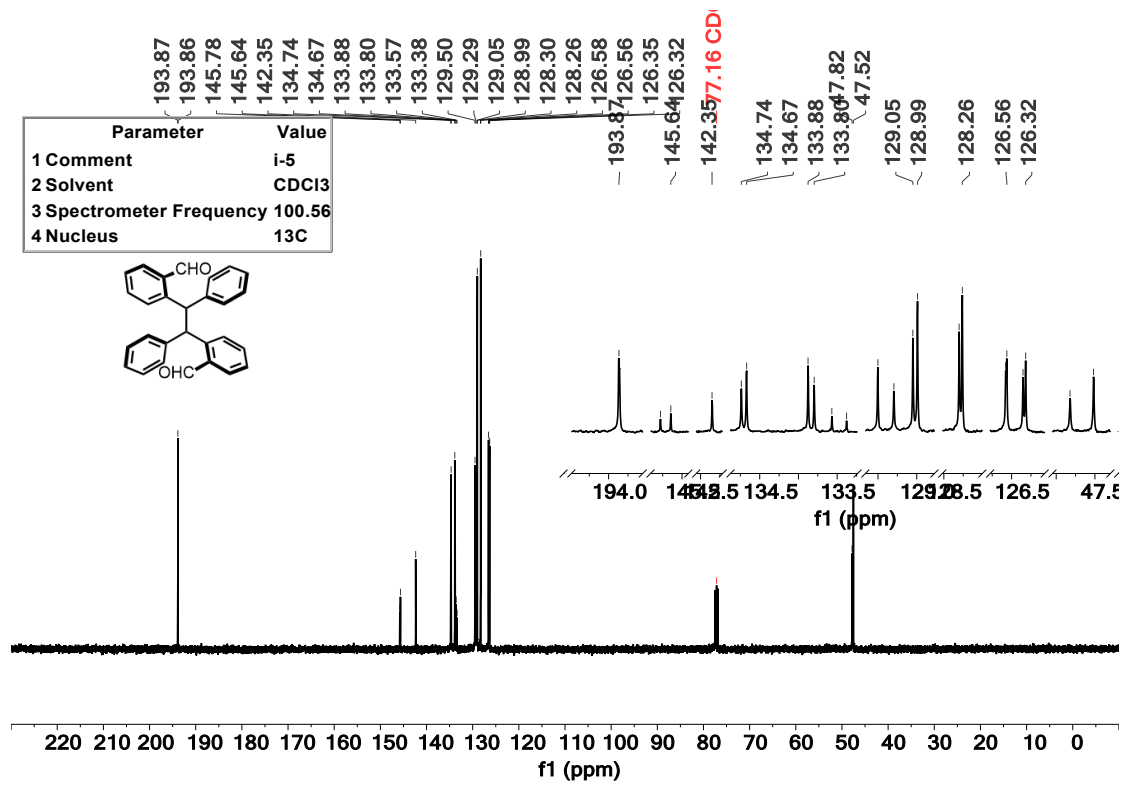
Parameter	Value
1 Comment	i-2
2 Solvent	CDCl3
3 Spectrometer Frequency	399.87
4 Nucleus	1H



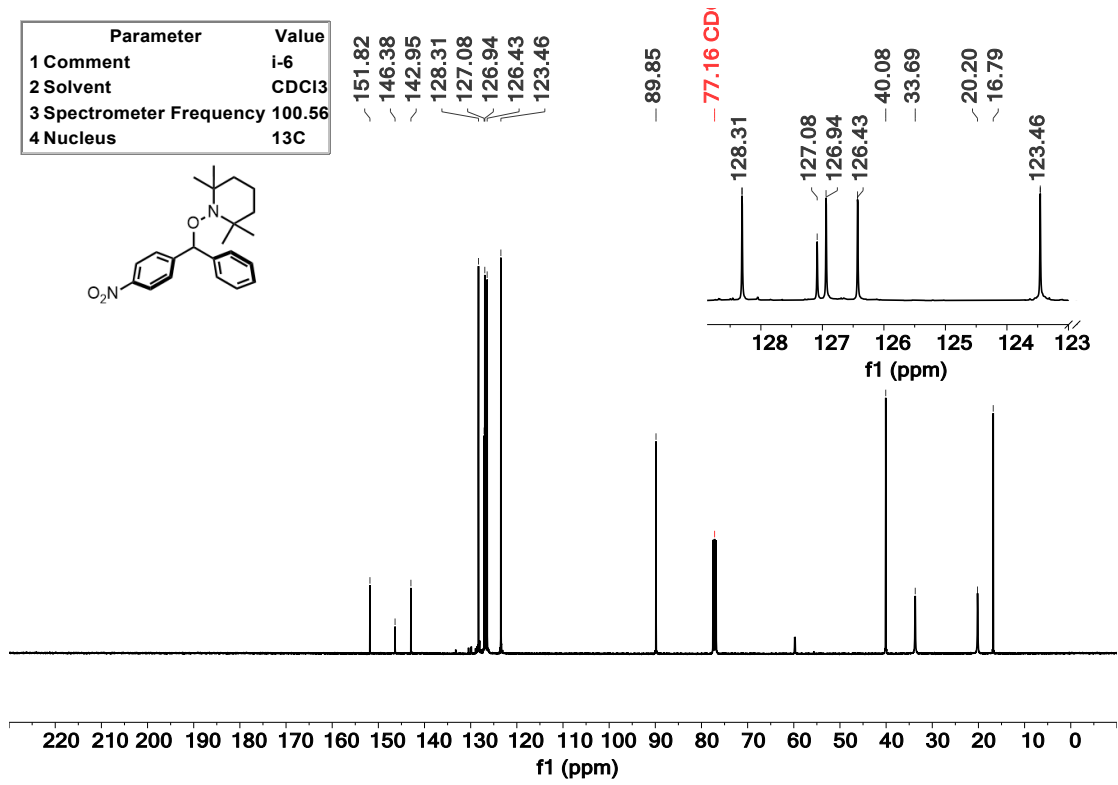
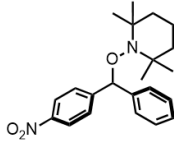








Parameter	Value
1 Comment	i-6
2 Solvent	CDCl3
3 Spectrometer Frequency	100.56
4 Nucleus	13C



3.1. References

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