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Electrochemical Ni–H Catalysis for Selective Tail-to-Tail Reductive Dimerization of Terminal Alkynes to 2,3-Dibranched Butadienes

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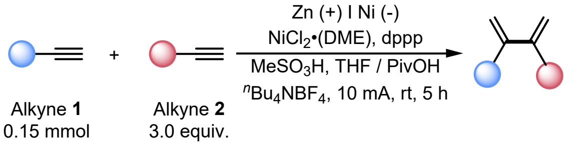
General information

All reactions were run under a nitrogen atmosphere on an undivided cell. All glassware was oven dried at 110 °C for hours and cooled down under vacuum. The instrument for electrolysis was dual display potentiostat (DJS-292B) (made in China). Cyclic voltammograms were obtained on a CHI 760E potentiostat. The anodic electrode was zinc plate (1.5 cm × 1.5 cm × 0.03 cm) and cathodic electrode was nickel sheet (1.5 cm × 1.5 cm × 0.05 cm). These electrodes were commercially available from Gaoss Union China. Unless otherwise noted, all the substrates were obtained from commercial suppliers and used without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 °C). All new compounds were characterized by ^{1}H NMR, ^{13}C NMR and **HRMS**. The known compounds were characterized by ^{1}H NMR, ^{13}C NMR. ^{1}H and ^{13}C NMR data were recorded with ADVANCE III 400 MHz with tetramethylsilane as an internal standard. High resolution mass spectra (**HRMS**) were measured with a Waters Micromass GCT instrument. All chemical shifts (δ) were reported in ppm and coupling constants (*J*) in Hz. All chemical shifts were reported relative to tetramethylsilane (0 ppm for ^{1}H), $CDCl_3$ (77.16 ppm for ^{13}C).

General procedure

The synthesis of **9** is representative: Phenylacetylene (**1**, 0.3 mmol, 1.0 equiv.), $^n Bu_4NBF_4$ (197.6 mg, 0.6 mmol, 2.0 equiv.), $NiCl_2 \cdot DME$ (0.06 mmol, 20 mol%), dppp (0.072 mmol, 24 mol%) were placed in an oven-dried undivided three-necked bottle (10 mL). The bottle was equipped with a stir bar, zinc plate (1.5 cm × 1.5 cm × 0.03 cm) as anode and nickel plate (1.5 cm × 1.5 cm × 0.05 cm) as cathode. The bottle was flushed with argon. Degased dry tetrahydrofuran (THF, 6 mL) and commercially pivalic acid (PivOH) (synthesis of **4-24**, 10.0 equiv.; synthesis of **25-42**, 30.0 equiv.) were added in order. Lastly, methanesulfonic acid (0.45 mmol, 1.5 equiv.) was injected. The reaction mixture was stirred for 30 min firstly and then electrolyzed at a constant current of 10 mA at room temperature for 5 h. After completion of the reaction, the product was identified by TLC. The solvent was removed under reduced pressure by an aspirator, then the pure product was obtained by flash column chromatography on silica gel.

General procedure for the synthesis of 43-52

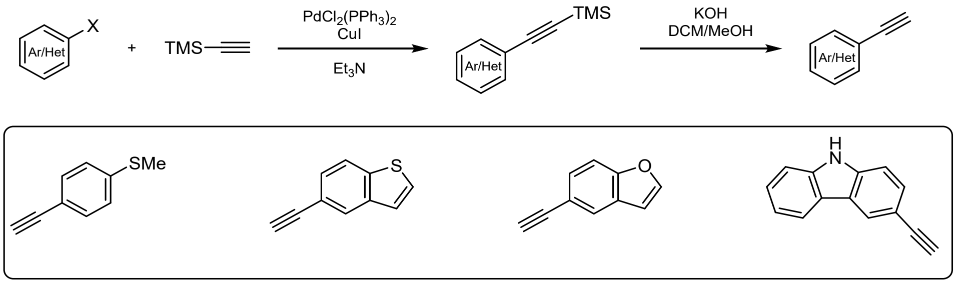


The synthesis of **43** is representative: 4-Ethynylanisole (0.15 mmol, 1.0 equiv.), ^{n}Bu$_4$NBF$_4$ (197.6 mg, 0.6 mmol), NiCl$_2$·DME (0.06 mmol), dppp (0.072 mmol) were placed in an oven-dried undivided three-necked bottle (10 mL). The bottle was equipped with a stir bar, zinc plate (1.5 cm × 1.5 cm × 0.03 cm) as anode and nickel plate (1.5 cm × 1.5 cm × 0.05 cm) as cathode. The bottle was flushed with argon. Degased dry tetrahydrofuran (THF, 6 mL), commercially pivalic acid (PivOH, 3.0 mmol) and phenylacetylene (0.45 mmol) were added in order. Lastly, methanesulfonic acid (0.45 mmol) was injected. The reaction mixture was stirred for 30 min firstly and then electrolyzed at a constant current of 10 mA at room temperature for 5 h. After completion of the reaction, the product was identified by TLC. The solvent was removed under reduced pressure by an aspirator, then the pure product was obtained by flash column chromatography on silica gel.

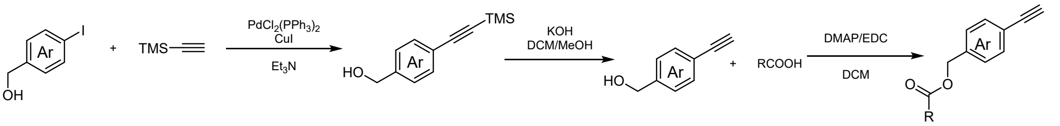
General procedure for the synthesis of 53-56

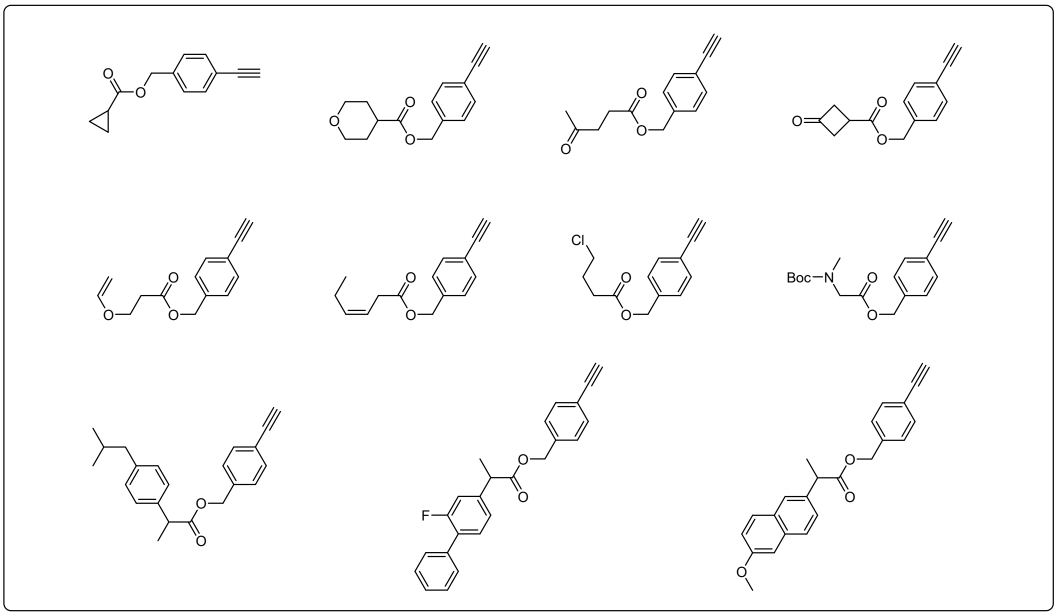
The synthesis of **53** is representative: 3-Ethynylthiophene (0.15 mmol, 1.0 equiv.), ^{n}Bu$_4$NBF$_4$ (197.6 mg, 0.6 mmol), NiCl$_2$·DME (0.06 mmol), dppp (0.072 mmol) were placed in an oven-dried undivided three-necked bottle (10 mL). The bottle was equipped with a stir bar, zinc plate (1.5 cm × 1.5 cm × 0.03 cm) as anode and nickel plate (1.5 cm × 1.5 cm × 0.05 cm) as cathode. The bottle was flushed with argon. Degased dry tetrahydrofuran (THF, 6 mL), commercially pivalic acid (PivOH, 1 mL) and alkyl alkynes (0.225 mmol) were added in order. Lastly, methanesulfonic acid (0.45 mmol) was injected. The reaction mixture was stirred for 30 min firstly and then electrolyzed at a constant current of 10 mA at room temperature for 5 h. After completion of the reaction, the product was identified by TLC. The solvent was removed under reduced pressure by an aspirator, then the pure product was obtained by flash column chromatography on silica gel.

Procedure for substrates synthesis



Method A[1-2]: The corresponding aryl iodide or aryl bromide (10 mmol, 1.0 equiv.), $PdCl_2(PPh_3)_2$ (140.4 mg, 2 mol%), CuI (76.2 mg, 4 mol%) and Et_3N (50 mL) were added to a 100 mL schlenk flask with a stir bar under an atmosphere of nitrogen. Then the ethynyltrimethylsilane (12 mmol, 1.2 equiv.) was added. If substrate is aryl iodide, then the mixture stirred at room temperature overnight. If substrate is aryl bromide, then the mixture was stirred at 80 °C overnight. Afterwards, 60 mL water was added and the reaction mixture was extracted with EtOAc (3 × 15 mL), washed with brine and dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether and ethyl acetate as the eluent. Then the obtained trimethyl(phenylethynyl)silane (8 mmol, 1.0 equiv.) were added to the solution of KOH (32 mmol, 4.0 equiv.) in DCM (15 mL) and MeOH (3 mL) at room temperature for 4 hours to go silyl deprotection. Finally, purify the crude product by silica gel column chromatography using petroleum ether.

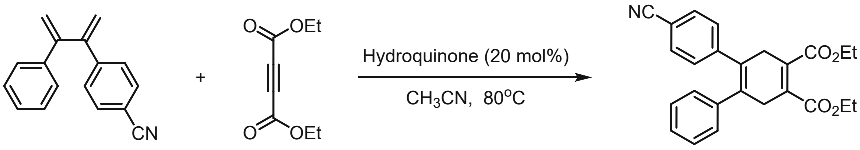




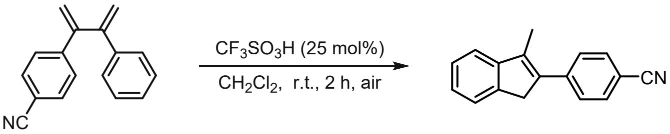
Method B[3]: The corresponding aryl iodide (10 mmol, 1 equiv.), $PdCl_2(PPh_3)_2$ (140.4 mg, 2 mol%), CuI (76.2 mg, 4 mol%) and Et_3N (50 mL) were added to a 100 mL schlenk flask with a stir bar under an atmosphere of nitrogen. Then the ethynyltrimethylsilane (12 mmol, 1.2 equiv.) was added and the reaction mixture stirred at room temperature overnight. Afterwards, 60 mL water was added and the reaction mixture was extracted with ethyl acetate (EtOAc) (3 × 15 mL), washed with brine and dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether and ethyl acetate as the eluent. Then the obtained trimethyl(phenylethynyl)silane were added to the solution of KOH (6.0 equiv.) in DCM (15 mL) and MeOH (15 mL) at room temperature for 4 hours to go silyl deprotection. Purify the crude product by silica gel column chromatography using petroleum ether. Then using EDC (1.5 equiv.), DMAP (1.2 equiv.), and corresponding alcohol (1 equiv.) and acid

(1.2 equiv.) in dry DCM (0.5 M), Purify the crude product by silica gel column chromatography using petroleum ether and ethyl acetate (PE : EA = 5:1).

Application and product derivatizations

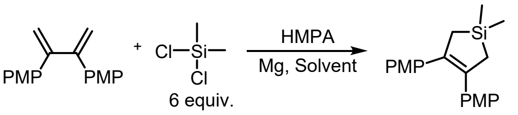


An oven-dried 25 mL schlenk tube equipped with a magnetic stir bar was charged with a mixture of **47** (0.2 mmol, 1.0 equiv.), hydroquinone (0.04 mmol, 20 mol%), and CH_3CN (1 mL). Then, diethyl but-2-ynedioate (0.6 mmol, 3.0 equiv.) was added to the mixture via syringe under a nitrogen atmosphere. After the reaction mixture was stirred at 80 °C for 24 h, the solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography using petroleum ether-ethyl acetate (10:1 v/v) as the eluent to afford the desired product **57**.

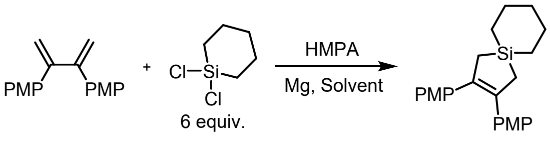


An oven-dried 25 mL schlenk tube equipped with a magnetic stir bar was charged with a mixture of **47** (0.5 mmol, 1.0 equiv.) and trifluoromethanesulfonic acid (CF_3SO_3H, 10 μL, 0.125 mmol, 25 mol%). Then DCM (5 mL) was added to the mixture via syringe under air .After the reaction mixture was stirred at rt for 2 h, the solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography using petroleum ether-ethyl acetate (50:1 v/v) as the eluent to afford the desired product **58**.

Hydrosilylation of **12** with dimethyldichlorosilane

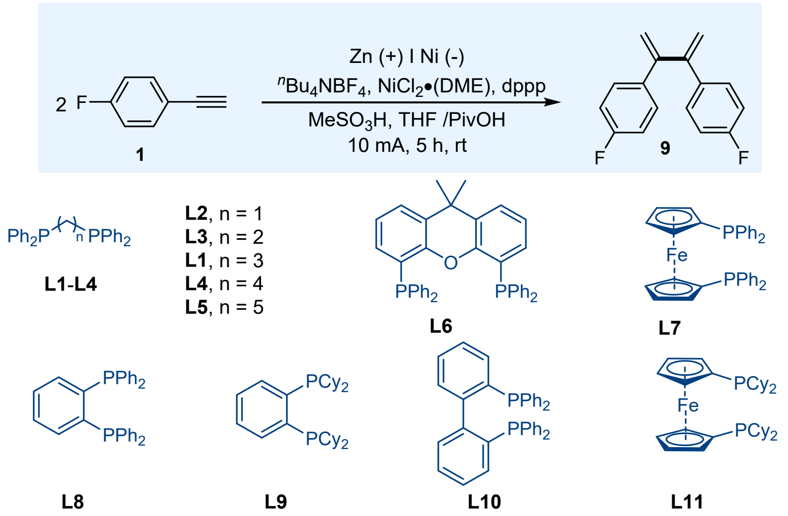


An oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with a mixture of 4,4'-(buta-1,3-diene-2,3-diyl)bis(methoxybenzene) **12** (0.2 mmol, 1.0 equiv.), magnesium powder (0.5 mmol, 2.5 equiv.), and hexamethylphosphoric triamide (HMPA, 1 mL). Then, 1,1-dimethyldichlorosilane (1.2 mmol, 6.0 equiv.) was added to the mixture via syringe under a nitrogen atmosphere. After the reaction mixture was stirred at 240 °C for 1 h, the solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography using petroleum ether-ethyl acetate (20:1 v/v) as the eluent to afford the desired product **59**.



An oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with a mixture of 4,4'-(buta-1,3-diene-2,3-diyl)bis(methoxybenzene) **12** (0.2 mmol, 1.0 equiv.), magnesium powder (0.5 mmol, 2.5 equiv.), and hexamethylphosphoric triamide (HMPA, 1 mL). Then, 1,1-dichlorosilinane (1.2 mmol, 6.0 equiv.) was added to the mixture via syringe under a nitrogen atmosphere. After the reaction mixture was stirred at 240 °C for 1 h, the solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography using petroleum ether-ethyl acetate (20:1 v/v) as the eluent to afford the desired product **60**.

Optimization of reaction parameters

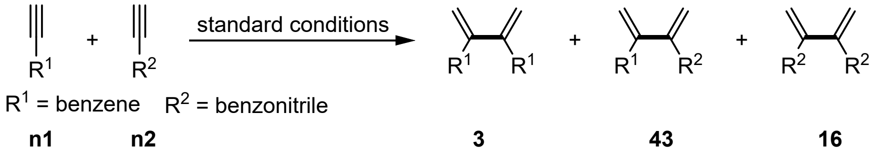


Entry	Deviation from standard condition[a]	Yield[%][b]
1	none	82[c]
2	Mg, Al plate instead of Ni plate	5, 12
3	Ni(COD)$_2$, NiBr$_2$, NiI$_2$ instead of NiCl$_2$· (DME)	23-41
4	no NiCl$_2$·(DME)	n.d.
5	**L2** instead of **L1**	n.d.
6	**L3** instead of **L1**	38
7	**L4** instead of **L1**	53
8	**L5** instead of **L1**	n.d.
9	**L6** instead of **L1**	n.d.
10	**L7** instead of **L1**	n.d.

11	**L8** instead of **L1**	38
12	**L9** instead of **L1**	38
13	**L10** instead of **L1**	n.d.
14	**L11** instead of **L1**	38
15	MeCN	trace
16	DMF	23
17	DMSO	n.d.
18	No $MeSO_3H$	42
19	No PivOH	54
20	under air atmosphere	trace
21	without current	n.d.
22[d]	Zn, Mg, Mn, Al as chemical reducing agent	trace - 9

Table S1: [a]Standard reaction conditions: zinc plate (1.5 cm × 1.5 cm × 0.03 cm) as the anode and the nickel plate (1.5 cm × 1.5 cm × 0.05 cm) as the cathode, constant current = 10 mA, **1** (0.3 mmol), $NiCl_2 \cdot (DME)$ (20 mol%), 1,3-bis(diphenylphosphaneyl)propane(dppp) (24 mol%), $^{n}Bu_4NBF_4$ (0.6 mmol), THF (6.0 mL), $MeSO_3H$ (1.5 equiv.), PivOH (10.0 equiv.), undivided cell, N_2, 28 °C, 5 h. [b]Yields were determined by ^{19}F NMR analysis with fluorobenzene as the internal standard. [c]Isolated yield. [d]Without current.

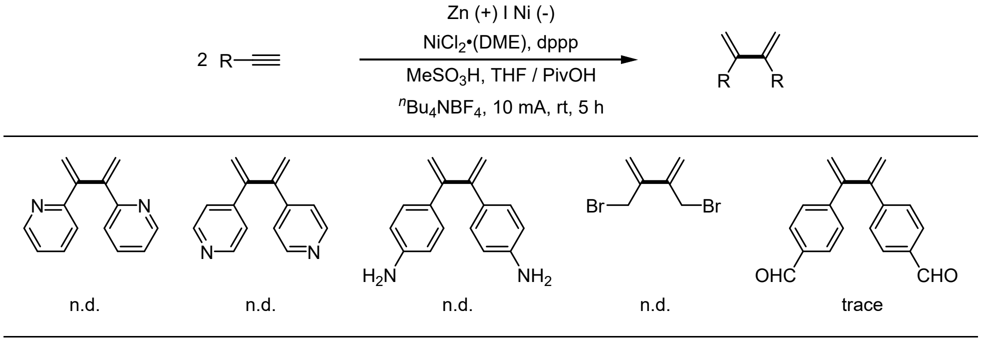
Reductive cross-dimerization



Entry	**n1** / mmol	**n2** / mmol	Yield of **43**[a]	Yield of **3**[a]	Yield of **16**[a]
1	0.15	0.15	11%	21%	n.d.
2	0.15	0.225	20%	19%	n.d.
3	0.15	0.3	25%	12%	n.d.
4	0.15	0.45	40%	13%	n.d.
5	0.15	0.75	37%	9%	n.d.

Table S2: Standard reaction conditions: zinc plate (1.5 cm × 1.5 cm × 0.03 cm) as the anode and the nickel plate (1.5 cm × 1.5 cm × 0.05 cm) as the cathode, constant current = 10 mA, terminal acetylene (**n1** and **n2**), $NiCl_2$·(DME) (20 mol%), 1,3-bis(diphenylphosphaneyl)propane(dppp) (24 mol%), $^{n}Bu_4NBF_4$ (0.6 mmol), THF (6.0 mL), $MeSO_3H$ (1.5 equiv.), PivOH (10.0 equiv.), undivided cell, N_2, 28 °C, 5 h. [a]Yields were determined by ^1H NMR analysis with 1,3,5-trimethoxybenzene as the internal standard.

Unsuccessful substrates



Scheme S1: Standard reaction conditions: zinc plate (1.5 cm × 1.5 cm × 0.03 cm) as the anode and the nickel plate (1.5 cm × 1.5 cm × 0.05 cm) as the cathode, constant current = 10 mA, **1** (0.3 mmol), $NiCl_2$·(DME) (20 mol%), 1,3-bis(diphenylphosphaneyl)propane(dppp) (24 mol%), $^{n}Bu_4NBF_4$ (0.6 mmol), THF (6.0 mL), $MeSO_3H$ (1.5 equiv.), PivOH (10.0 equiv.), undivided cell, N_2, 28 °C, 5 h.

CV and SWV tests

Cyclic voltammetry tests were performed in a three-electrode cell connected to a schlenk line under nitrogen at room temperature. The working electrode was a platinum plate electrode, the counter electrode was a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. Anhydrous degassed THF (6 mL) containing 0.6 mmol $^{n}Bu_4NBF_4$ were poured into the electrochemical cell in all experiments. Unless otherwise stated, the concentration of all substances to be measured is 0.01 M. The scan rate was 0.1 V/s.

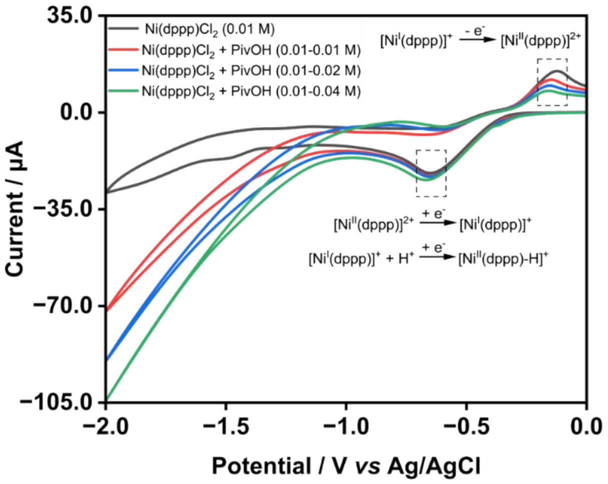


Figure S1: Effect of adding different concentrations of PivOH on CV curve of $Ni(dppp)Cl_2$

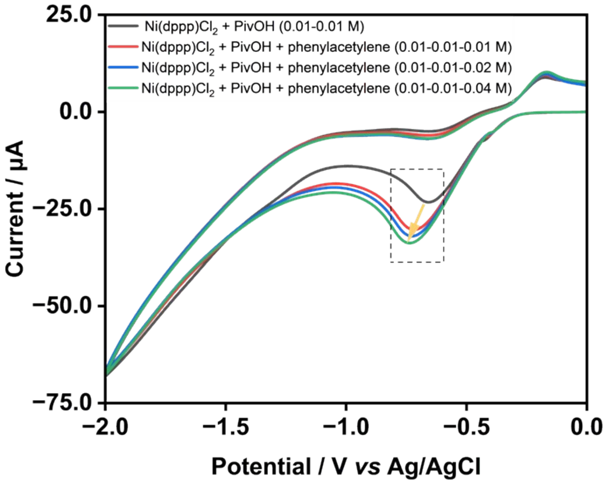


Figure S2: The effect of adding PivOH and phenylacetylene on the CV curve of $Ni(dppp)Cl_2$

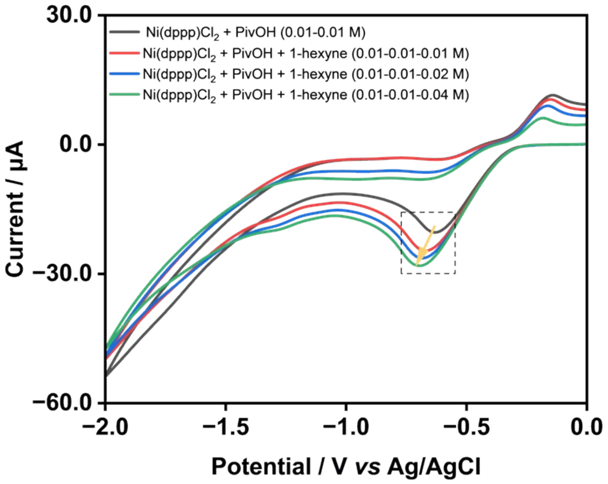


Figure S3: The effect of adding PivOH and 1-hexyne on the CV curve of $Ni(dppp)Cl_2$

Square-wave voltammetry tests were performed in a three-electrode cell connected to a schlenk line under nitrogen at room temperature. The working electrode was a platinum plate electrode, the counter electrode was a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. Anhydrous degassed THF (6 mL) containing 0.6 mmol ${}^{n}Bu_4NBF_4$ were poured into the electrochemical cell in all experiments. Unless otherwise stated, the concentration of all substances to be measured is 0.01 M. SWV test parameters were voltage increment 0.02V, amplitude 0.05V and frequency 50 Hz respectively.

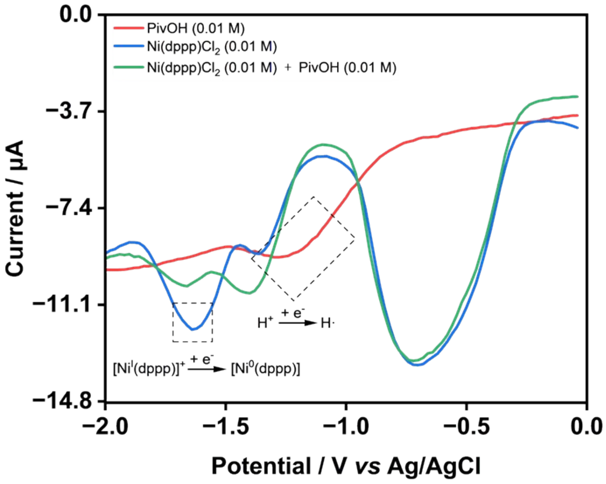


Figure S4: The SWV curve of $Ni(dppp)Cl_2$, PivOH and $Ni(dppp)Cl_2$ with PivOH

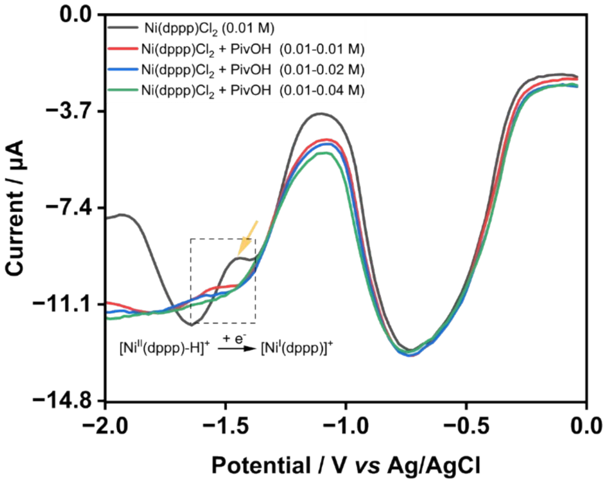


Figure S5: Effect of adding different concentrations of PivOH on SWV curve of $Ni(dppp)Cl_2$

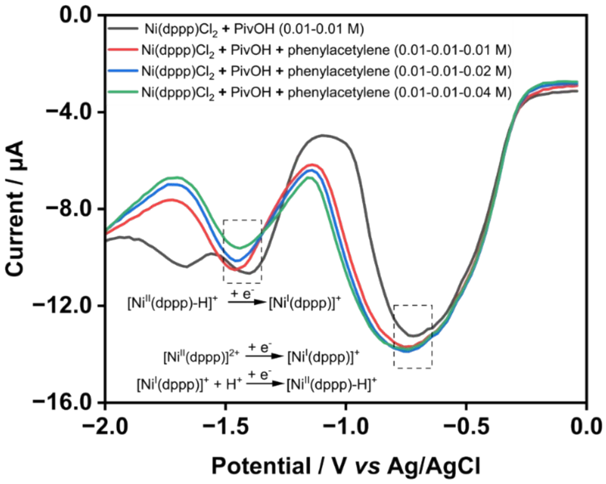


Figure S6: The effect of adding PivOH and phenylacetylene on the SWV curve of Ni(dppp)Cl$_2$

Procedure for the kinetic electricity on/off experiments of the model reaction

Under N$_2$, to an oven-dried undivided three-necked bottle (10 mL) equipped with a magnetic stir bar were added parafluoroacetylene (0.05 M), ^{n}Bu$_4$NBF$_4$ (0.1 M), NiCl$_2$·DME (0.06 mmol), fluorobenzene as internal standard. zinc plate (15 mm × 15 mm × 0.3 mm) as anode and nickel plate (15 mm × 15 mm × 0.5 mm) as cathode. The bottle was flushed with argon. Degased dry tetrahydrofuran (THF, 6 mL) and commercially pivalic acid (PivOH, 10.0 equiv.) were added in order. Lastly, methanesulfonic acid (0.45 mmol, 1.5 equiv.) was injected. The reaction mixture was stirred for 30 min firstly and then electrolyzed at a constant current of 10 mA at room temperature. After that, the electricity was switched off and the mixture was stirred for the designed time interval without electricity before another aliquot was taken. During the reaction, the reaction was monitored by ^{19}F NMR to determine the yield of the product with fluorobenzene as the internal standard.

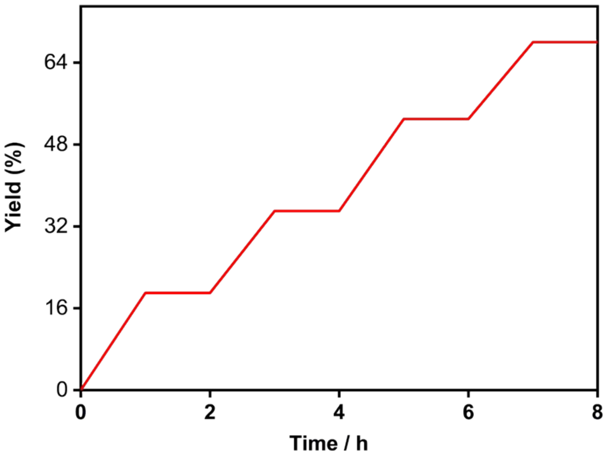
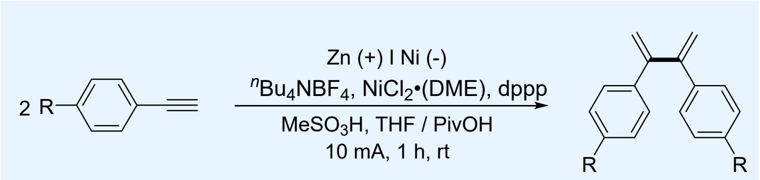


Fig S7. Electricity On-Off Experiment.

Hammett plot analysis.



R = OMe, Me, H, Cl, F

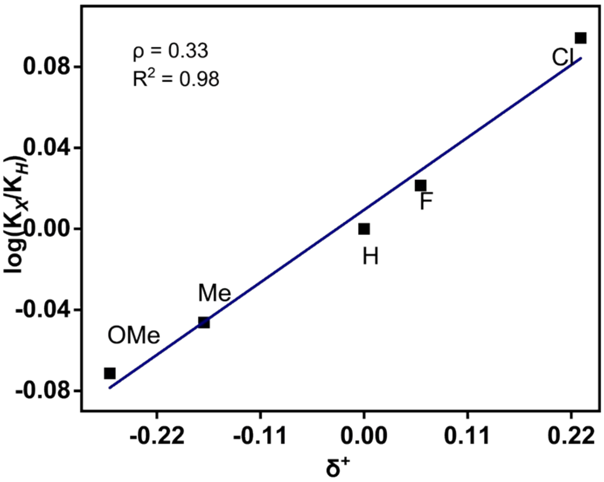
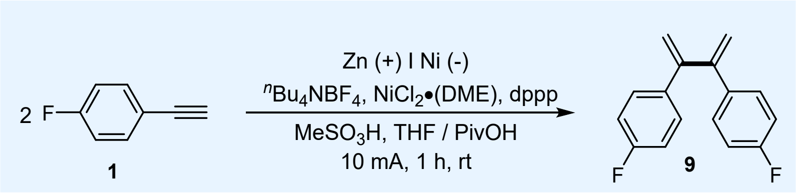


Fig S8. Hammett Plot determination.

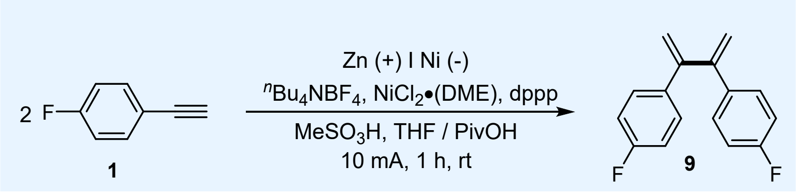
Hammett parameter data were collected from the following sources[4]. The corresponding substituted phenylacetylene (0.3 mmol, 1.0 equiv.), ^{n}Bu$_4$NBF$_4$ (0.6 mmol, 2.0 equiv.), NiCl$_2$·DME (0.06 mmol, 20 mol%) were placed in an oven-dried undivided three-necked bottle (10 mL). The bottle was equipped with a stir bar, zinc plate (15 mm × 15 mm × 0.3 mm) as anode and nickel plate (15 mm × 15 mm × 0.5 mm) as cathode. The bottle was flushed with argon. Degased dry tetrahydrofuran (THF, 6 mL) and commercially pivalic acid (PivOH, 10.0 equiv.) were added in order. Lastly, methanesulfonic acid (0.45 mmol, 1.5 equiv.) was injected. The reaction mixture was stirred for 30 min firstly and then electrolyzed at a constant current of 10 mA at room temperature for 1 h. During the reaction, the reaction was monitored by ^{19}F NMR to determine the yield of the product with fluorobenzene as the internal standard.

Reaction order analysis.



Dependence of the reaction rate on concentration of 1.

Under N_2, to an oven-dried undivided three-necked bottle (10 mL equipped with a magnetic stir bar were added parafluoroacetylene (0.0375 M, 0.045 M, 0.05 M, 0.0625 M, 0.075 M), ^{n}Bu$_4$NBF$_4$ (2.0 equiv.), NiCl$_2$·(DME) (20 mol%), fluorobenzene as internal standard. zinc plate (15 mm × 15 mm × 0.3 mm) as anode and nickel plate (15 mm × 15 mm × 0.5 mm) as cathode. The bottle was flushed with argon. Degased dry tetrahydrofuran (THF, 6 mL) and commercially pivalic acid (PivOH, 10.0 equiv.) were added in order. Lastly, methanesulfonic acid (0.45 mmol, 1.5 equiv.) was injected. The reaction mixture was stirred for 30 min firstly and then electrolyzed at a constant current of 10 mA at room temperature for 1 h. During the reaction, the reaction was monitored by ^{19}F NMR to determine the yield of the product.



Entry	Concentration of **1** / mol/L	Concentration of **9** / mol/L[a]	Yield[%][a]
1	0.0375	0.0133	53
2	0.045	0.0134	53
3	0.05	0.0135	54
4	0.0625	0.0133	53
5	0.075	0.0134	53

Table S3: [a]The concentration and yields of **9** were determined by ^{19}F NMR analysis with fluorobenzene as the internal standard.

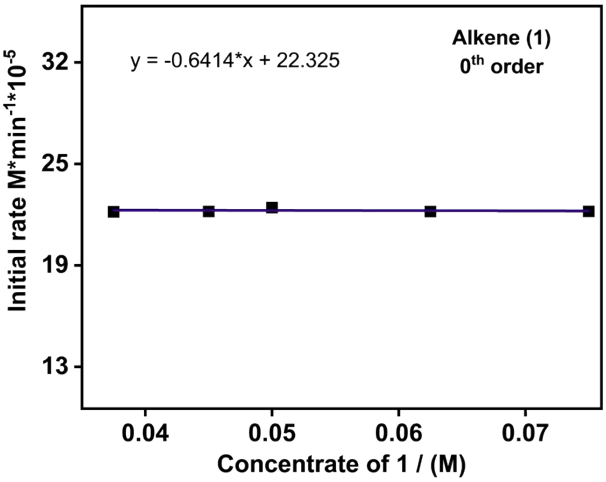
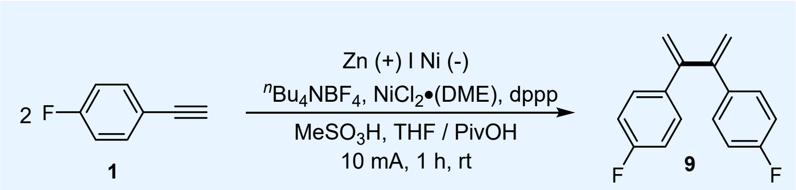


Fig S9. Reaction rate on concentration of **1**.

Dependence of the reaction rate on concentration of CAT.

Under N_2, to an oven-dried undivided three-necked bottle (10 mL equipped with a magnetic stir bar were added parafluoroacetylene (0.05 M), ^{n}Bu$_4$NBF$_4$ (0.6 mmol), NiCl$_2$·DME (from 0.005 M to 0.030 M), dppp (from 0.006 M to 0.036 M), fluorobenzene as internal standard. zinc plate (15 mm × 15 mm × 0.3 mm) as anode and nickel plate (15 mm × 15 mm × 0.5 mm) as cathode. The bottle was flushed with argon. Dry THF (6 mL) and commercially PivOH (10.0 equiv.) were added in order. Lastly, methanesulfonic acid (0.45 mmol, 1.5 equiv.) was injected. The reaction mixture was stirred for 30 min firstly and then electrolyzed at a constant current of 10 mA at room temperature for 1 h. During the reaction, the reaction was monitored by ^{19}F NMR to determine the yield of the product.



Entry	Concentration of **CAT** / mol/L	Concentration of **9** / mol/L[a]	Yield[%][a]
1	0.005	0.0027	11
2	0.01	0.0067	26
3	0.015	0.01	39
4	0.02	0.0135	54
5	0.03	0.0177	71

Table S4: [a]The concentration and yields of **9** were determined by ^{19}F NMR analysis with fluorobenzene as the internal standard.

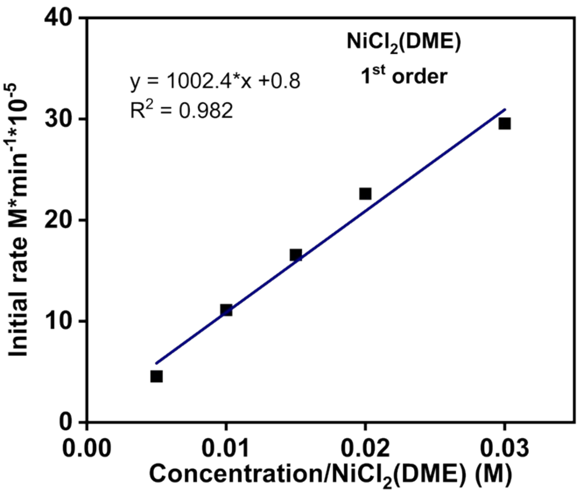
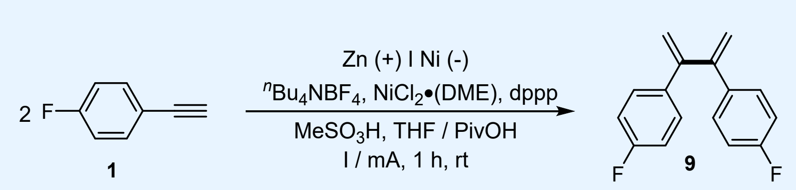


Fig S10. Reaction rate on concentration of CAT.

Dependence of the reaction rate on current.

Under N_2, to an oven-dried undivided three-necked bottle (10 mL equipped with a magnetic stir bar were added parafluoroacetylene (0.05 M), $^n Bu_4NBF_4$ (0.6 mmol), $NiCl_2 \cdot DME$ (0.01M), dppp (from 0.012 M), fluorobenzene as internal standard. zinc plate (15 mm × 15 mm × 0.3 mm) as anode and nickel plate (15 mm × 15 mm × 0.5 mm) as cathode. The bottle was flushed with argon. Dry THF (6 mL) and commercially PivOH (1 mL) were added in order. Lastly, methanesulfonic acid (0.45 mmol, 1.5 equiv.) was injected. The reaction mixture was stirred for 30 min firstly and then electrolyzed at a constant current (from 2 mA to 8 mA) at room temperature for 1 h. During the reaction, the reaction was monitored by ^{19}F NMR to determine the yield of the product.



Entry	Current / mA	Concentration of **9** / mol/L[a]	Yield[%][a]
1	2	0.0027	11
2	4	0.0039	16
3	5	0.0049	20
4	6	0.0071	28
5	8	0.009	36

Table S5: [a]The concentration and yields of **9** were determined by ^{19}F NMR analysis with fluorobenzene as the internal standard.

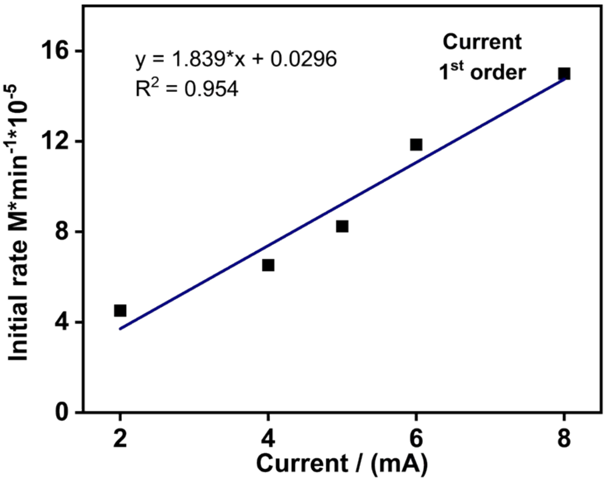
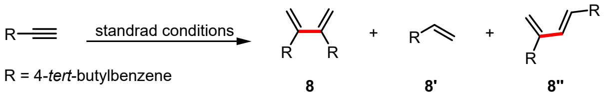


Fig S11. Reaction rate on concentration of current.

Kinetic Study



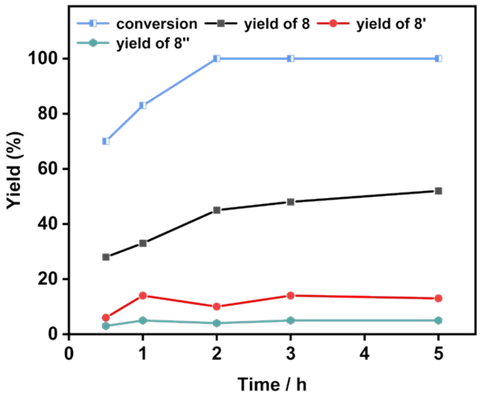
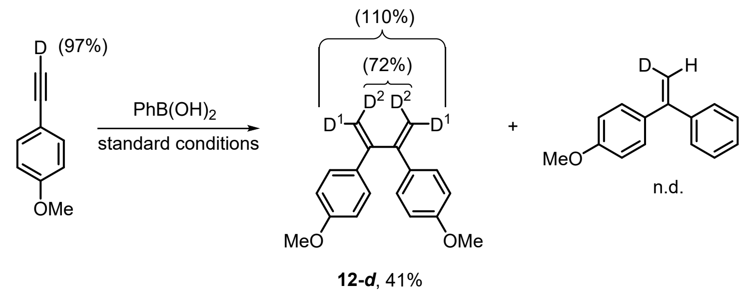


Figure 12. Kinetic study. The yields of products were determined by 1H-NMR analysis using 1,3,5-trimethoxybenzene as the internal standard.

4-*Tert*-butylphenylacetylene (0.3 mmol, 1.0 equiv.), ^{n}Bu$_4$NBF$_4$ (197.6 mg, 0.6 mmol, 2.0 equiv.), NiCl$_2$·DME (0.06 mmol, 20 mol%) were placed in an oven-dried undivided three-necked bottle (10 mL). The bottle was equipped with a stir bar, zinc plate (1.5 cm × 1.5 cm × 0.03 cm) as anode and nickel plate (1.5 cm × 1.5 cm × 0.05 cm) as cathode. The bottle was flushed with argon. Degased dry tetrahydrofuran (THF, 6 mL) and commercially PivOH (10.0 equiv.) were added in order. Lastly, methanesulfonic acid (0.45 mmol, 1.5 equiv.) was injected. The reaction mixture was stirred for 30 min firstly and then electrolyzed at a constant current of 10 mA at room temperature for 5 h. After completion of the reaction, the product was identified by TLC. The yields of products were determined by ^{1}H-NMR analysis using 1,3,5-trimethoxybenzene as the internal standard during 30 min, 1 h, 2 h, 3h, and 5 h after initiation.

Contral experiment.



4-Ethynylanisole-*d* (0.3 mmol, 1.0 equiv.), ^{n}Bu$_4$NBF$_4$ (197.6 mg, 0.6 mmol, 2.0 equiv.), NiCl$_2$·DME (0.06 mmol, 20 mol%), dppp (0.072 mmol, 24 mol%), and phenylboronic acid (0.3 mmol, 1.0 equiv.) were placed in an oven-dried undivided three-necked bottle (10 mL). The bottle was equipped with a stir bar, zinc plate (1.5 cm × 1.5 cm × 0.03 cm) as anode and nickel plate (1.5 cm × 1.5 cm × 0.05 cm) as cathode. The bottle was flushed with argon. Degased dry tetrahydrofuran (THF, 6 mL) and PivOH (10.0 equiv.) were added in order. Lastly, methanesulfonic acid (0.45 mmol, 1.5 equiv.) was injected. The reaction mixture was stirred for 30 min firstly and then electrolyzed at a constant current of 10 mA at room temperature for 5 h. After completion of the reaction, the product was identified by TLC. The solvent was removed under reduced pressure by an aspirator, then the pure product was obtained by flash column chromatography on silica gel.

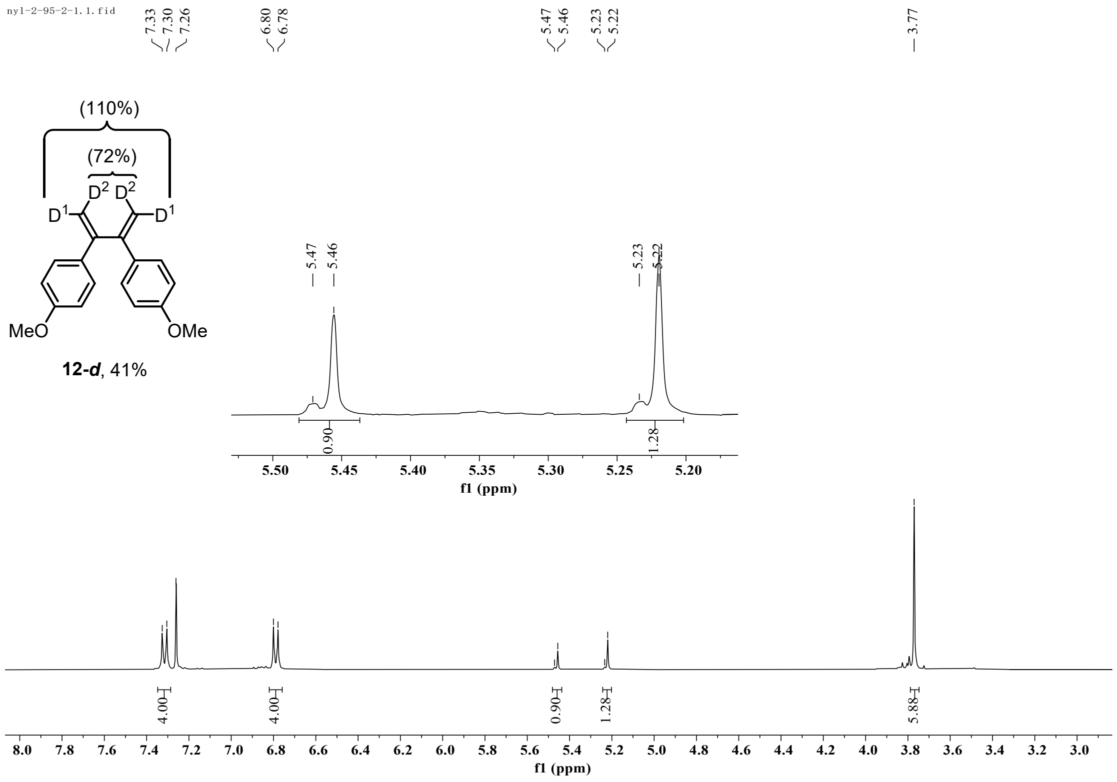
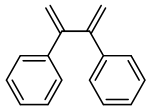
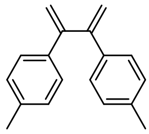


Figure S13. ^{1}H NMR spectrum of **12-*d*** (CDCl$_3$, 400 MHz).

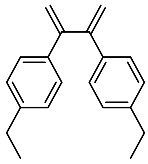
Procedure and analytical data of compounds.



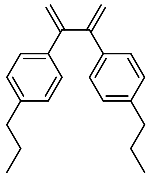
Buta-1,3-diene-2,3-diyldibenzene (**3**)[5]. White solid was obtained in 69% isolated yield, 21.4 mg, Rf = 0.4 (PE). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.39 (dd, *J* = 8.1, 1.7 Hz, 4H), 7.29 – 7.19 (m, 6H), 5.54 (t, *J* = 1.3 Hz, 2H), 5.31 (t, *J* = 1.4 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.9, 140.3, 128.3, 127.6, 116.5.



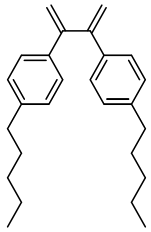
4,4'-(Buta-1,3-diene-2,3-diyl)bis(methylbenzene) (**4**)[5]. White solid was obtained in 55% NMR yield, Rf = 0.4 (PE). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 8.2 Hz, 4H), 7.06 (d, *J* = 7.9 Hz, 4H), 5.51 (d, *J* = 1.8 Hz, 2H), 5.26 (d, *J* = 1.8 Hz, 2H), 2.29 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.9, 137.4, 137.3, 129.0, 127.4, 115.5, 21.3.



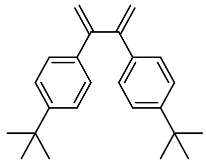
4,4'-(Buta-1,3-diene-2,3-diyl)bis(ethylbenzene) (**5**). Colorless oil was obtained in 54% NMR yield, Rf = 0.4 (PE). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 8.2 Hz, 4H), 7.10 (d, *J* = 8.3 Hz, 4H), 5.52 (d, *J* = 1.8 Hz, 2H), 5.25 (d, *J* = 1.7 Hz, 2H), 2.60 (q, *J* = 7.6 Hz, 4H), 1.20 (t, *J* = 7.6 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.8, 143.7, 137.7, 127.8, 127.4, 115.6, 28.6, 15.6.



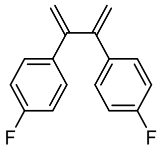
4,4'-(Buta-1,3-diene-2,3-diyl)bis(propylbenzene) (**6**)[6]. Colorless oil was obtained in 50% ^{1}H-NMR yield, Rf = 0.4 (PE). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 8.2 Hz, 4H), 7.07 (d, *J* = 8.2 Hz, 4H), 5.53 (d, *J* = 1.7 Hz, 2H), 5.25 (d, *J* = 1.8 Hz, 2H), 2.53 (dd, *J* = 8.6, 6.7 Hz, 4H), 1.66 – 1.56 (m, 4H), 0.92 (t, *J* = 7.3 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.9, 142.2, 137.7, 128.4, 127.4, 115.5, 37.9, 24.6, 14.0.



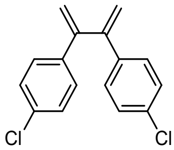
4,4'-(Buta-1,3-diene-2,3-diyl)bis(pentylbenzene) (7)[7]**.** Colorless oil was obtained in 43% ^{1}H-NMR yield, Rf = 0.4 (PE). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 8.2 Hz, 4H), 7.07 (d, *J* = 8.2 Hz, 4H), 5.52 (d, *J* = 1.8 Hz, 2H), 5.25 (d, *J* = 1.7 Hz, 2H), 2.54 (dd, *J* = 8.8, 6.8 Hz, 4H), 1.64 – 1.50 (m, 4H), 1.40 – 1.23 (m, 8H), 0.91 – 0.80 (m, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.7, 142.3, 137.5, 128.2, 127.2, 115.3, 35.6, 31.5, 31.0, 22.5, 14.0.



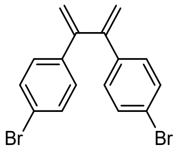
4,4'-(Buta-1,3-diene-2,3-diyl)bis(tert-butylbenzene) (8)[5]**.** Colorless oil was obtained in 52% ^{1}H-NMR yield, Rf = 0.4 (PE). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.39 – 7.33 (m, 4H), 7.32 – 7.27 (m, 4H), 5.55 (d, *J* = 1.7 Hz, 2H), 5.23 (d, *J* = 1.7 Hz, 2H), 1.29 (s, 18H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.4, 149.4, 137.3, 126.9, 125.1, 115.5, 34.5, 31.3.



4,4'-(Buta-1,3-diene-2,3-diyl)bis(fluorobenzene) (9)[5]. White solid was obtained in 72% ^{19}F-NMR yield, Rf = 0.7 (PE:EA = 5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.37 – 7.28 (m, 4H), 6.99 – 6.91 (m, 4H), 5.49 (d, *J* = 1.5 Hz, 2H), 5.30 (d, *J* = 1.5 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 162.5 (d, J_{C-F} = 247.5 Hz), 148.8, 136.1 (d, J_{C-F} = 3.0 Hz), 129.2 (d, J_{C-F} = 8.1 Hz),116.5, 115.2 (d, J_{C-F} = 22.2 Hz). **^{19}F NMR** (377 MHz, Chloroform-d) δ -114.67.

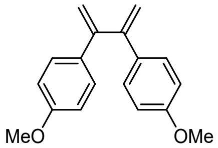


4,4'-(Buta-1,3-diene-2,3-diyl)bis(chlorobenzene) (**10**)[5]. Yellow solid was obtained in 52% isolated yield, 21.5 mg, Rf = 0.6 (PE:EA = 5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.30 – 7.26 (m, 4H), 7.25 – 7.19 (m, 4H), 5.53 (d, *J* = 1.5 Hz, 2H), 5.33 (d, *J* = 1.4 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 148.5, 138.4, 133.7, 128.9, 128.6,117.1.

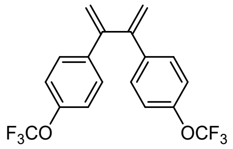


4,4'-(Buta-1,3-diene-2,3-diyl)bis(bromobenzene) (**11**)[5]. Yellow solid was obtained in 55%

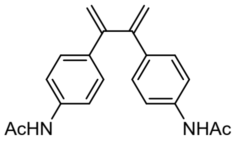
isolated yield, 30.3 mg, Rf = 0.6 (PE:EA = 5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.42 – 7.35 (m, 4H), 7.24 – 7.19 (m, 4H), 5.54 (d, *J* = 1.4 Hz, 2H), 5.34 (d, *J* = 1.4 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 148.5, 138.8, 131.6, 129.2, 121.9,117.2.



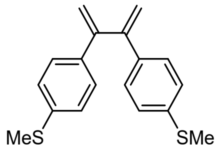
4,4'-(Buta-1,3-diene-2,3-diyl)bis(methoxybenzene) (12)^5. White solid was obtained in 69% isolated yield, 27.5 mg, Rf = 0.4 (PE:EA=5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 8.8 Hz, 4H), 6.79 (d, *J* = 8.8 Hz, 4H), 5.47 (d, *J* = 1.8 Hz, 2H), 5.24 (d, *J* = 1.7 Hz, 2H), 3.76 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.0, 149.3, 132.6, 128.5, 127.6, 125.9, 114.3, 113.5, 55.2.



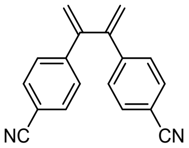
4,4'-(Buta-1,3-diene-2,3-diyl)bis((trifluoromethoxy)benzene) (13)^6. Colorless oil was obtained in 52% isolated yield, 29.1 mg, Rf = 0.4 (PE:EA=5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.8 Hz, 4H), 7.12 (d, *J* = 8.3 Hz, 4H), 5.55 (d, *J* = 1.4 Hz, 2H), 5.34 (d, *J* = 1.4 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 148.7 (q, $J_{C\text{-}F}$= 2.0 Hz), 148.2, 138.5, 128.8, 127.0, 127.0, 120.4 (q, $J_{C\text{-}F}$= 258.6 Hz), 117.5. **^{19}F NMR** (377 MHz, Chloroform-*d*) δ -57.82.



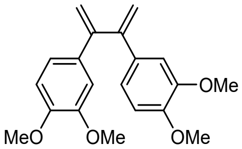
***N,N'*-(buta-1,3-diene-2,3-diylbis(4,1-phenylene))diacetamide (14).** Colorless oil was obtained in 42% ^{1}H-NMR yield, Rf = 0.4 (DCM : MeOH = 100:1). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.92 (s, 2H), 7.46 (d, *J* = 8.4 Hz, 4H), 7.26 (d, *J* = 8.7 Hz, 4H), 5.57 (d, *J* = 1.8 Hz, 2H), 5.23 (d, *J* = 1.7 Hz, 2H), 2.00 (s, 7H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 168.2, 148.7, 138.8, 133.7, 127.2, 118.7, 114.5, 24.0. **HRMS** (ESI) m/z calcd for $C_{20}H_{21}N_2O_2$ $(M+H)^+$: 321.1598, found : 321.1591.



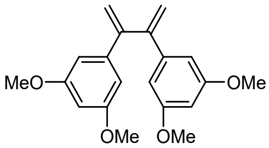
(Buta-1,3-diene-2,3-diylbis(4,1-phenylene))bis(methylsulfane) (15). Yellow oil was obtained in 55% isolated yield, 24.5 mg, Rf = 0.4 (PE:EA=5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 4H), 7.16 – 7.11 (m, 4H), 5.54 (d, *J* = 1.6 Hz, 2H), 5.30 (d, *J* = 1.6 Hz, 2H), 2.45 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.2, 137.9, 136.9, 127.9, 126.3, 115.8, 15.8. **HRMS** (ESI) m/z calcd for $C_{18}H_{19}S_2$ $(M+H)^+$: 299.0923, found : 299.0922.



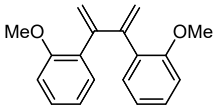
4,4'-(Buta-1,3-diene-2,3-diyl)dibenzonitrile (16)[5]. White solid was obtained in 8% ^{1}H-NMR yield, Rf = 0.4 (PE:EA=5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.1 Hz, 4H), 7.44 (d, *J* = 8.0 Hz, 4H), 5.68 (s, 2H), 5.48 (s, 2H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 147.6, 144.0, 132.4, 128.1, 119.8, 118.7, 111.8.



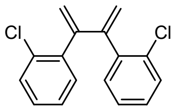
4,4'-(Buta-1,3-diene-2,3-diyl)bis(1,2-dimethoxybenzene) (17). White solid was obtained in 43% isolated yield, 21.0 mg, Rf = 0.3 (PE:EA=5:1). m.p. 108-110 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.96 - 6.92 (m, 4H), 6.76 (d, *J* = 8.3 Hz, 2H), 5.50 (s, 2H), 5.28 (s, 2H), 3.85 (s, 6H), 3.82 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.5, 148.5, 148.4, 133.0, 120.0, 114.7, 110.7, 110.5, 55.8, 55.7. **HRMS** (ESI) m/z calcd for $C_{20}H_{23}O_4$ $(M+H)^+$: 327.1591, found : 327.1591.



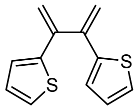
5,5'-(Buta-1,3-diene-2,3-diyl)bis(1,3-dimethoxybenzene) (18). Colorless oil was obtained in 43% isolated yield, 20.7 mg, Rf = 0.3 (PE:EA=5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.55 (d, *J* = 2.3 Hz, 4H), 6.35 (t, *J* = 2.3 Hz, 2H), 5.53 (d, *J* = 1.7 Hz, 2H), 5.32 (d, *J* = 1.6 Hz, 2H), 3.75 (s, 12H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.4, 149.5, 142.3, 116.7, 105.7, 99.5, 55.3. **HRMS** (ESI) m/z calcd for $C_{20}H_{23}O_4$ $(M+H)^+$: 327.1591, found : 327.1590.



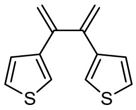
2,2'-(Buta-1,3-diene-2,3-diyl)bis(methoxybenzene) (19)[5]. White solid was obtained in 50% ^{1}H-NMR yield, Rf = 0.4 (PE:EA=3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.23 – 7.14 (m, 4H), 6.86 (t, *J* = 7.4 Hz, 2H), 6.80 (d, *J* = 8.1 Hz, 2H), 5.05 (d, *J* = 1.2 Hz, 2H), 5.00 (d, *J* = 1.3 Hz, 2H), 3.72 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.1, 147.3, 131.3, 131.0, 128.6, 120.4, 117.2, 111.1, 55.9.



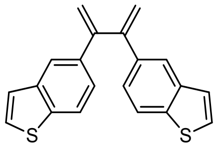
2,2'-(Buta-1,3-diene-2,3-diyl)bis(chlorobenzene) (20)[5]. Colorless oil was obtained in 34% ^{1}H-NMR yield, R_f = 0.6 (PE). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.46 – 7.41 (m, 2H), 7.39 – 7.35 (m, 2H), 7.30 – 7.26 (m, 4H), 5.16 (d, *J* = 1.0 Hz, 2H), 4.98 (s, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.4, 139.8, 133.5, 131.6, 129.6, 128.8, 126.7, 119.6.



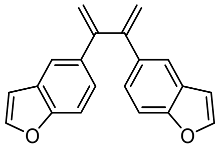
2,2'-(Buta-1,3-diene-2,3-diyl)dithiophene (21). Colorless oil was obtained in 25% isolated yield, 8.2 mg, Rf = 0.8 (PE:EA=20:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.16 (dd, *J* = 5.0, 1.2 Hz, 2H), 6.95 (dd, *J* = 3.6, 1.3 Hz, 2H), 6.90 (dd, *J* = 5.1, 3.6 Hz, 2H), 5.62 (d, *J* = 1.0 Hz, 2H), 5.25 (d, *J* = 1.0 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 143.6, 142.5, 127.4, 126.0, 124.9, 114.2. **HRMS** (ESI) m/z calcd for $C_{12}H_{11}S_2$ $(M+H)^+$: 219.0296, found : 219.0292.



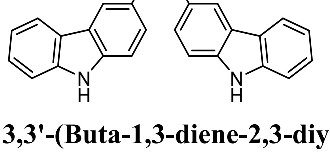
3,3'-(Buta-1,3-diene-2,3-diyl)dithiophene (22). Colorless oil was obtained in 56% isolated yield, 18.3 mg, Rf = 0.6 (PE:EA=20:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.23 (dd, *J* = 5.0, 2.9 Hz, 2H), 7.20 (dd, *J* = 5.1, 1.4 Hz, 2H), 7.12 (dd, *J* = 2.9, 1.4 Hz, 2H), 5.57 (d, *J* = 1.6 Hz, 2H), 5.26 (d, *J* = 1.6 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.5, 141.5, 126.4, 125.6, 122.9, 114.3. **HRMS** (ESI) m/z calcd for $C_{12}H_{11}S_2$ $(M+H)^+$: 219.0296, found : 219.0293.



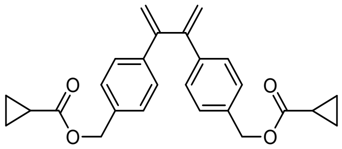
5,5'-(Buta-1,3-diene-2,3-diyl)bis(benzo[*b*]thiophene) (23). Colorless oil was obtained in 43% isolated yield, 20.5 mg, Rf = 0.5 (PE:EA=5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 1.8 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.45 (dd, *J* = 8.4, 1.7 Hz, 2H), 7.39 (d, *J* = 5.4 Hz, 2H), 7.27 (d, *J* = 5.2 Hz, 2H), 5.64 (d, *J* = 1.7 Hz, 2H), 5.40 (d, *J* = 1.7 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.9, 139.7, 138.9, 136.5, 126.7, 124.0, 124.0, 122.5, 122.1, 116.5. **HRMS** (ESI) m/z calcd for $C_{20}H_{18}NS_2$ $(M+NH_4)^+$: 336.0876, found: 336.0879.



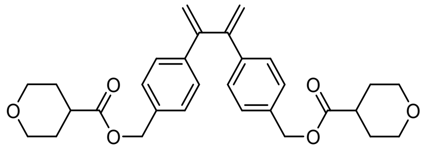
5,5'-(Buta-1,3-diene-2,3-diyl)bis(benzofuran) (24). Colorless oil was obtained in 75% isolated yield, 32.2 mg, Rf = 0.5 (PE:EA=5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.63 (s, 2H), 7.56 (d, *J* = 2.2 Hz, 2H), 7.38 (d, *J* = 1.2 Hz, 4H), 6.69 (d, *J* = 2.2 Hz, 2H), 5.55 (d, *J* = 1.7 Hz, 2H), 5.34 (d, *J* = 1.7 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 154.5, 150.3, 145.3, 135.3, 127.3, 124.2, 120.2, 115.9, 110.9, 106.7. **HRMS** (ESI) m/z calcd for $C_{20}H_{18}NO_2$ $(M+NH_4)^+$: 304.1333, found: 304.1336.



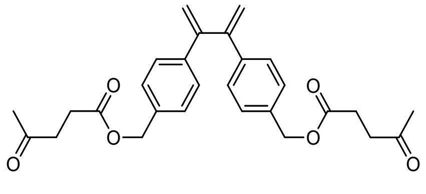
3,3'-(Buta-1,3-diene-2,3-diyl)bis(9*H*-carbazole) (25). Colorless oil was obtained in 75% isolated yield, 25.1 mg, Rf = 0.3 (PE:EA=3:1). ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 1.7 Hz, 2H), 8.16 – 8.09 (m, 2H), 7.85 – 7.78 (m, 2H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.56 (dd, *J* = 8.3, 1.8 Hz, 2H), 7.43 (dd, *J* = 6.0, 3.2 Hz, 4H), 5.73 (d, *J* = 1.5 Hz, 2H), 5.49 (d, *J* = 1.5 Hz, 2H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 149.8, 139.7, 138.7, 136.7, 135.6, 135.4, 126.7, 126.5, 124.3, 122.8, 122.5, 121.6, 120.5, 116.9. **HRMS** (ESI) m/z calcd for $C_{28}H_{21}N_2^+$ $(M+H)^+$: 385.1700, found: 385.1701.



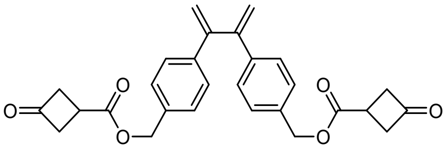
(Buta-1,3-diene-2,3-diylbis(4,1-phenylene))bis(methylene) dicyclopropanecarboxylate (26). Colorless oil was obtained in 47% isolated yield, 28.4 mg, Rf = 0.3 (PE:EA=5:1). ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.0 Hz, 4H), 7.29 – 7.22 (m, 4H), 5.56 (d, *J* = 1.6 Hz, 2H), 5.32 (d, *J* = 1.6 Hz, 2H), 5.07 (s, 4H), 1.64 (dq, *J* = 8.0, 4.6, 4.1 Hz, 2H), 1.01 (dt, *J* = 6.7, 3.5 Hz, 4H), 0.86 (tt, *J* = 7.0, 3.2 Hz, 4H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 174.8, 149.2, 139.9, 135.4, 128.1, 127.6, 116.7, 65.9, 12.9, 8.6. **HRMS** (ESI) m/z calcd for $C_{26}H_{30}O_4N$ $(M+NH_4)^+$: 420.2170, found: 420.2159.



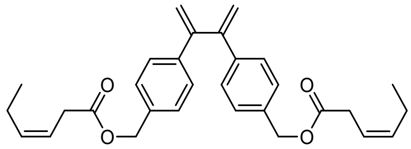
(Buta-1,3-diene-2,3-diylbis(4,1-phenylene))bis(methylene) bis(tetrahydro-2*H*-pyran-4-carboxylate) (27). Colorless oil was obtained in 45% isolated yield, 33.1 mg, Rf = 0.3 (PE:EA=5:1). ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.2 Hz, 5H), 7.24 (d, *J* = 8.2 Hz, 4H), 5.56 (d, *J* = 1.6 Hz, 2H), 5.32 (d, *J* = 1.5 Hz, 2H), 5.09 (s, 4H), 3.95 (dt, *J* = 11.6, 3.6 Hz, 4H), 3.45 – 3.37 (m, 4H), 2.63 – 2.52 (m, 2H), 1.88 – 1.79 (m, 8H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 174.2, 149.0, 139.9, 135.2, 127.9, 127.6, 116.8, 67.0, 65.9, 40.1, 28.6. **HRMS** (ESI) m/z calcd for $C_{30}H_{35}O_6$ $(M+H)^+$: 491.2428, found: 491.2429.



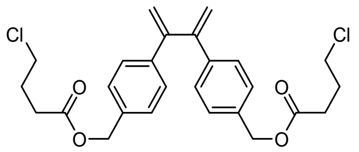
(Buta-1,3-diene-2,3-diylbis(4,1-phenylene))bis(methylene) bis(4-oxopentanoate) (28). Colorless oil was obtained in 40% isolated yield, 27.9 mg, Rf = 0.6 (PE:EA=1:1). ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 8.2 Hz, 4H), 7.24 (d, *J* = 8.2 Hz, 4H), 5.55 (d, *J* = 1.6 Hz, 2H), 5.32 (d, *J* = 1.6 Hz, 2H), 5.07 (s, 4H), 2.76 (t, *J* = 6.5 Hz, 4H), 2.61 (t, *J* = 6.3 Hz, 4H), 2.17 (s, 6H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 206.6, 172.6, 149.2, 134.0, 135.1, 128.1, 127.6, 116.8, 66.2, 37.9, 29.9, 28.0. **HRMS** (ESI) m/z calcd for $C_{28}H_{34}NO_6(M+NH_4)^+$: 480.2380, found: 480.2383.



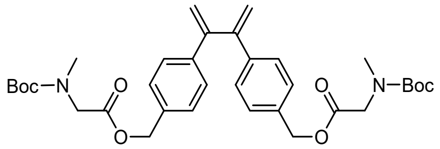
(Buta-1,3-diene-2,3-diylbis(4,1-phenylene))bis(methylene) bis(3-oxocyclobutane-1-carboxylate) (29). Colorless oil was obtained in 45% isolated yield, 31.1 mg, Rf = 0.3 (PE:EA=5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.3 Hz, 4H), 7.26 (d, *J* = 8.3 Hz, 4H), 5.58 (d, *J* = 1.5 Hz, 2H), 5.34 (d, *J* = 1.5 Hz, 2H), 5.14 (s, 4H), 3.49 – 3.36 (m, 4H), 3.34 – 3.20 (m, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 203.5, 173.8, 148.9, 140.2, 134.7, 128.2, 127.6, 117.0, 66.7, 51.6, 27.4. **HRMS** (ESI) m/z calcd for $C_{28}H_{30}NO_6(M+NH_4)^+$: 476.2067, found: 476.2066.



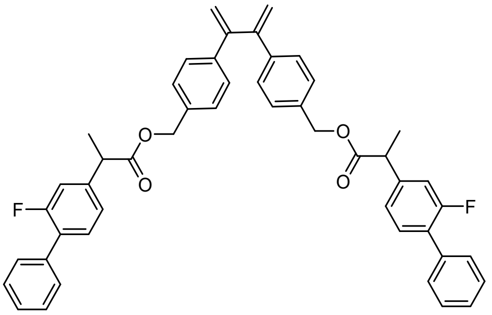
4-(3-(4-((((*E*)-pent-2-en-1-yl)oxy)methyl)phenyl)buta-1,3-dien-2-yl)benzyl (*Z*)-hex-3-enoate (30). Colorless oil was obtained in 52% isolated yield, 35.8 mg, Rf = 0.4 (PE:EA=5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.2 Hz, 4H), 7.28 – 7.21 (m, 4H), 5.65 – 5.46 (m, 6H), 5.32 (d, *J* = 1.6 Hz, 2H), 5.07 (s, 4H), 3.06 (dd, *J* = 6.6, 1.1 Hz, 4H), 2.08 – 1.99 (m 4H), 0.98 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 172.0, 149.1, 139.9, 136.5, 135.2, 128.1, 127.5, 120.3, 116.7, 66.0, 38.0, 25.5, 13.41. **HRMS** (ESI) m/z calcd for $C_{30}H_{38}NO_4(M+NH_4)^+$: 476.2795, found: 476.2790.



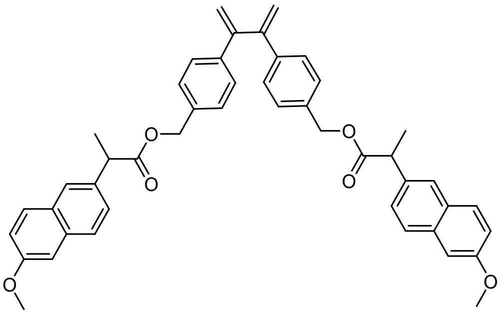
(Buta-1,3-diene-2,3-diylbis(4,1-phenylene))bis(methylene) bis(4-chlorobutanoate) (31). Colorless oil was obtained in 60% isolated yield, 42.8 mg, Rf = 0.8 (PE:EA=1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.3 Hz, 4H), 7.29 – 7.23 (m, 4H), 5.56 (d, *J* = 1.5 Hz, 2H), 5.33 (d, *J* = 1.6 Hz, 2H), 5.08 (s, 4H), 3.58 (t, *J* = 6.3 Hz, 4H), 2.54 (t, *J* = 7.2 Hz, 4H), 2.10 (tt, *J* = 7.1, 6.3 Hz, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 172. 5, 149.0, 140.0, 135.0, 128.1, 127.6, 116.8, 66.1, 44.0, 31.2, 27.6. **HRMS** (ESI) m/z calcd for $C_{26}H_{32}C_{l2}NO_4(M+NH_4)^+$: 492.1702, found: 492.1695.



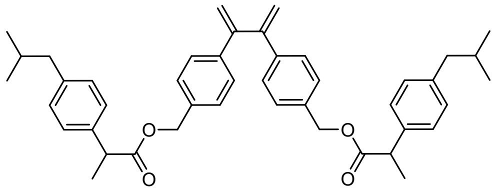
4-(3-(4-((((*Tert*-butoxycarbonyl)(methyl)carbamoyl)oxy)methyl)phenyl)buta-1,3-dien-2-yl)benzyl *N*-(*tert*-butoxycarbonyl)-*N*-methylglycinate (32). Colorless oil was obtained in 45% isolated yield, 41.3 mg, Rf = 0.2 (PE:EA=2:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.38 (dd, *J* = 8.2, 2.3 Hz, 4H), 7.26 (dt, *J* = 7.9, 4.0 Hz, 4H), 5.55 (d, *J* = 2.0 Hz, 2H), 5.32 (d, *J* = 2.0 Hz, 2H), 5.13 (d, *J* = 5.2 Hz, 4H), 3.96 (d, *J* = 38.8 Hz, 4H), 2.92 (d, *J* = 8.7 Hz, 6H), 1.46 (s, 9H), 1.34 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 169.8, 156.0, 155.3, 149.0, 140.2, 140.0, 134.7, 128.3, 128.1, 127.6, 127.6, 116.8, 66.3, 51.1, 50.3, 35.6, 28.3, 28.1. **HRMS** (ESI) m/z calcd for $C_{34}H_{48}N_3O_8(M+NH_4)^+$: 626.3435, found: 627.3452.



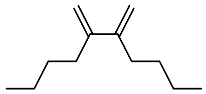
(Buta-1,3-diene-2,3-diylbis(4,1-phenylene))bis(methylene) bis(2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate) (33). Colorless oil was obtained in 45% isolated yield, 48.7 mg, Rf = 0.6 (PE:EA=2:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 7.6 Hz, 4H), 7.43 (t, *J* = 7.5 Hz, 4H), 7.38 – 7.31 (m, 8H), 7.16 (d, *J* = 8.1 Hz, 4H), 7.13 – 7.05 (m, 4H), 5.53 (s 2H), 5.29 (s, 2H), 5.08 (q, *J* = 12.6 Hz, 4H), 3.78 (q, *J* = 7.2 Hz, 2H), 1.53 (d, *J* = 7.2 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 173.8, 159.6 (d, J_{C-F}= 249.5 Hz), 149.0, 141.6 (d, J_{C-F}= 7.1 Hz), 139.9, 135.5, 135.0, 130.8 (d, J_{C-F}= 3.0 Hz), 128.9 (d, J_{C-F}= 3.0 Hz), 128.4, 127.9, 127.7, 127.5, 123.6, 123.5 (d, J_{C-F}= 3.0 Hz), 116.8, 115.2 (d, J_{C-F}= 24.2 Hz), 66.4, 45.0, 18.3. **^{19}F NMR** (377 MHz, Chloroform-*d*) δ -117.58. **HRMS** (ESI) m/z calcd for $C_{48}H_{44}F_2NO_4$ $(M+NH_4)^+$: 736.3232, found: 736.3227.



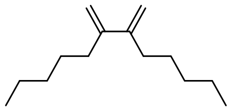
(Buta-1,3-diene-2,3-diylbis(4,1-phenylene))bis(methylene) bis(2-(6-methoxynaphthalen-2-yl)propanoate) (34). Colorless oil was obtained in 61% isolated yield, 63.2 mg, Rf = 0.5 (PE:EA=2:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.71 – 7.58 (m, 6H), 7.37 (dd, *J* = 8.5, 1.9 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 4H), 7.16 – 7.09 (m, 8H), 5.51 (d, *J* = 1.6 Hz, 2H), 5.27 (d, *J* = 1.6 Hz, 2H), 5.13 – 4.99 (m, 4H), 3.91 – 3.85 (m, 8H), 1.57 (d, *J* = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 174.4, 157.61, 149.1, 139.8, 135.5, 135.2, 133.7, 129.3, 128.9, 127.8, 127.5, 127.1, 126.2, 126.0, 118.9, 116.6, 105.5, 66.2, 55.3, 45.4, 18.5. **HRMS** (ESI) m/z calcd for $C_{46}H_{46}NO_6$ $(M+NH_4)^+$: 708.3319, found: 708.3303.



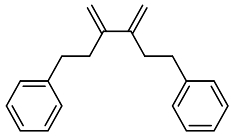
(Buta-1,3-diene-2,3-diylbis(4,1-phenylene))bis(methylene) bis(2-(4-isobutylphenyl)propanoate) (35). Colorless oil was obtained in 42% isolated yield, 40.7 mg, Rf = 0.5 (PE:EA=2:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.33 – 7.28 (m, 4H), 7.20 – 7.15 (m, 4H), 7.12 (d, *J* = 8.3 Hz, 4H), 7.07 (d, *J* = 8.2 Hz, 4H), 5.52 (d, *J* = 1.6 Hz, 2H), 5.28 (d, *J* = 1.6 Hz, 2H), 5.12 – 5.00 (m, 4H), 3.73 (q, *J* = 7.2 Hz, 2H), 2.44 (d, *J* = 7.2 Hz, 4H), 1.90 – 1.78 (m, 2H), 1.49 (d, *J* = 7.2 Hz, 6H), 0.89 (d, *J* = 6.6 Hz, 12H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 174.5, 149.1, 140.6, 139.7, 137.6, 135.3, 129.3, 127.6, 127.4, 127.2, 116.6, 66.0, 45.1, 45.0, 30.2, 22.4, 18.4. **HRMS** (ESI) m/z calcd for $C_{44}H_{54}NO_4(M+NH_4)^+$: 660.4048, found: 660.4042.



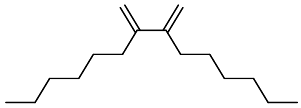
5,6-Dimethylenedecane (36)[5]**.** Colorless oil was obtained in 41% isolated yield, 10.3 mg, Rf = 0.5 (PE). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 5.07 – 5.03 (m, 2H), 4.93 – 4.89 (m, 2H), 2.23 (t, *J* = 7.4 Hz, 4H), 1.44 – 1.29 (m, 8H), 0.91 (t, *J* = 7.2 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 148.0, 111.2, 34.0, 30.9, 22.6, 14.0.



6,7-Dimethylenedodecane (37)[7]**.** Colorless oil was obtained in 41% isolated yield, 12.1 mg, Rf = 0.4 (PE). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 5.04 (s, 2H), 4.91 (s, 2H), 2.22 (t, *J* = 7.7 Hz, 4H), 1.48 – 1.40 (m, 4H), 1.33 – 1.26 (m, 8H), 0.89 (t, *J* = 7.2 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 148.1, 111.2, 34.2, 31.8, 28.4, 22.6, 14.1.

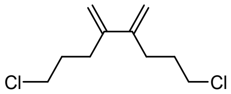


(3,4-Dimethylenehexane-1,6-diyl)dibenzene (38). Colorless oil was obtained in 41% isolated yield, 16.1 mg, Rf = 0.3 (PE). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 4H), 7.22 – 7.17 (m, 6H), 5.17 (s, 2H), 5.00 (s, 2H), 2.83 – 2.75 (m, 4H), 2.59 – 2.51 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.7, 142.2, 128.4, 128.3, 125.8, 112.2, 36.2, 35.2. **HRMS** (ESI) m/z calcd for $C_{20}H_{23}$ $(M+H)^+$: 263.1795, found: 263.1798.

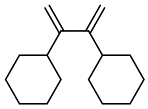


7,8-Dimethylenetetradecane (39)[5]**.** Colorless oil was obtained in 58% isolated yield, 19.3 mg, Rf = 0.4 (PE). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 5.04 (d, *J* = 1.6 Hz, 2H), 4.90 (s, 2H), 2.22 (t, *J*

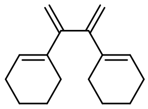
= 7.8 Hz, 4H), 1.45 – 1.39 (m, 4H), 1.34 – 1.26 (m, 12H), 0.88 (t, *J* = 6.9 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 148.07, 111.24, 34.30, 31.76, 29.22, 28.64, 22.66, 14.09.



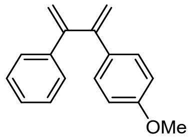
1,8-Dichloro-4,5-dimethyleneoctane (40). Colorless oil was obtained in 54% isolated yield, 16.8 mg, Rf = 0.3 (PE). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 5.14 (d, *J* = 0.9 Hz, 2H), 5.01 (s, 2H), 3.54 (t, *J* = 6.4 Hz, 6H), 2.44 – 2.37 (m, 4H), 1.96 – 1.88 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 145.5, 113.1, 44.6, 31.4, 31.2. **HRMS** (ESI) m/z calcd for $C_{10}H_{17}Cl_2$ $(M+H)^+$: 207.0701, found: 207.0690.



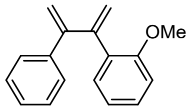
Buta-1,3-diene-2,3-diyldicyclohexane (41)^7. Colorless oil was obtained in 38% ^{1}H-NMR yield, Rf = 0.7 (PE). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.90 (s, 2H), 4.77 (s, 2H), 2.06 (dd, *J* = 13.1, 10.0 Hz, 2H), 1.83 – 1.73 (m, 9H), 1.69 (d, *J* = 13.5 Hz, 3H), 1.32 – 1.05 (m, 14H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 156.3, 108.3, 41.1, 32.9, 27.1, 26.7.



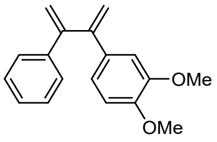
1,1'-(buta-1,3-diene-2,3-diyl)dicyclohex-1-ene (42)^5. Colorless oil was obtained in 38% ^{1}H-NMR yield, Rf = 0.7 (PE). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 5.75 – 5.70 (m, 2H), 5.10 (d, *J* = 1.9 Hz, 2H), 4.82 (d, *J* = 1.9 Hz, 2H), 2.18 (td, *J* = 6.3, 3.3 Hz, 4H), 2.08 (dp, *J* = 6.4, 3.4, 3.0 Hz, 4H), 1.71 – 1.63 (m, 4H), 1.58 – 1.51 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*). δ 151.6, 135.9, 127.6, 110.5, 26.0, 25.7, 23.1, 22.4.



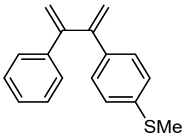
1-Methoxy-4-(3-phenylbuta-1,3-dien-2-yl)benzene (43)^8. Colorless oil was obtained in 25% ^{1}H-NMR yield, Rf = 0.6 (PE:DCM = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.41 – 7.36 (m, 2H), 7.34 – 7.29 (m, 2H), 7.27 – 7.18 (m, 3H), 6.80 – 6.75 (m, 2H), 5.53 (d, *J* = 1.8 Hz, 1H), 5.47 (d, *J* = 1.7 Hz, 1H), 5.31 (d, *J* = 1.7 Hz, 1H), 5.23 (d, *J* = 1.7 Hz, 1H), 3.74 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.2, 150.1, 149.3, 140.3, 132.7, 128.7, 128.3, 127.6, 127.5, 116.1, 114.9, 113.7, 55.3.



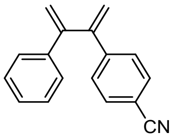
1-Methoxy-2-(3-phenylbuta-1,3-dien-2-yl)benzene (44). Colorless oil was obtained in 34% ^{1}H-NMR yield, Rf = 0.6 (PE:DCM = 3:1). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.34 - 7.28 (m, 3H), 7.27 - 7.23 (m, 2H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 5.34 (s, 1H), 5.28 (s, 1H), 5.21 (s, 1H), 4.99 (s, 1H), 3.79 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 157.1, 150.8, 147.6, 141.6, 131.1, 130.9, 128.9, 128.7, 128.0, 127.4, 120.6, 118.9, 115.5, 111.2, 55.8. **HRMS** (ESI) m/z calcd for $C_{17}H_{17}O$ $(M+H)^+$: 237.1274, found: 237.1273.



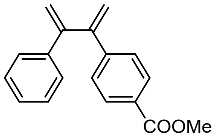
1,2-Dimethoxy-4-(3-phenylbuta-1,3-dien-2-yl)benzene (45). Colorless oil was obtained in 34% ^{1}H-NMR yield, Rf = 0.5 (PE:DCM = 1:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.41 – 7.36 (m, 2H), 7.23 (dd, *J* = 12.4, 7.4 Hz, 3H), 6.97 – 6.89 (m, 2H), 6.75 (d, *J* = 8.3 Hz, 1H), 5.54 (d, *J* = 1.7 Hz, 1H), 5.50 (d, *J* = 1.6 Hz, 1H), 5.34 (d, *J* = 1.8 Hz, 1H), 5.26 (d, *J* = 1.6 Hz, 1H), 3.81 (d, *J* = 8.2 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.1, 149.5, 148.7, 148.6, 140.4, 133.0, 128.3, 127.6, 127.5, 120.2, 116.2, 115.0, 110.9, 110.8, 55.9, 55.9. **HRMS** (ESI) m/z calcd for $C_{18}H_{19}O_2$ $(M+H)^+$: 267.1380, found: 267.1372.



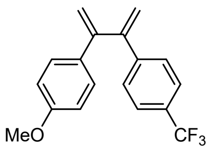
Methyl(4-(3-phenylbuta-1,3-dien-2-yl)phenyl)sulfane (46). Colorless oil was obtained in 32% ^{1}H-NMR yield, R_f = 0.6 (PE:DCM = 3:1). **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.38 (d, *J* = 7.4 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.25 - 7.19 (m, 3H), 7.14 (d, *J* = 8.2 Hz, 2H), 5.54 (d, *J* = 6.4 Hz, 2H), 5.32 (s, 1H), 5.29 (s, 1H), 2.45 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-d) δ 128.4, 128.0, 127.7, 127.5, 126.3, 116.4, 115.9, 15.8. **HRMS** (ESI) m/z calcd for $C_{17}H_{17}S$ $(M+H)^+$: 253.1046, found: 253.1033.



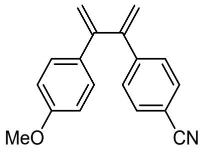
4-(3-Phenylbuta-1,3-dien-2-yl)benzonitrile (47)^8. Colorless oil was obtained in 40% ^{1}H-NMR yield, Rf = 0.6 (PE:DCM = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.31 (m, 2H), 7.30 – 7.24 (m, 3H), 5.64 (d, *J* = 1.4 Hz, 1H), 5.60 (d, *J* = 1.3 Hz, 1H), 5.48 (d, *J* = 1.3 Hz, 1H), 5.33 (t, *J* = 1.2 Hz, 1H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.0, 148.6, 144.8, 139.5, 132.3, 128.5, 128.2, 128.1, 127.5, 119.0, 117.2, 111.3.



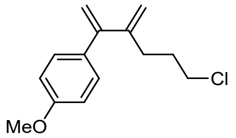
Methyl 4-(3-phenylbuta-1,3-dien-2-yl)benzoate (48)^6. White solid was obtained in 50% ^{1}H-NMR yield, Rf = 0.5 (PE:EA = 10:1).-**^{1}H NMR** (400 MHz, Chloroform-d) δ 7.93 (d, *J* = 7.9 Hz, 2H), 7.44 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.29 - 7.16 (m, 3H), 5.62 (s, 1H), 5.57 (s, 1H), 5.43 (s, 1H), 5.33 (s, 1H), 3.88 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.0, 149.5, 149.2, 144.9, 139.9, 129.7, 129.2, 128.4, 127.8, 127.6, 127.6, 118.1, 116.9, 52.2.



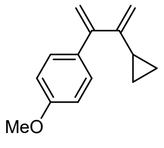
1-Methoxy-4-(3-(4-(trifluoromethyl)phenyl)buta-1,3-dien-2-yl)benzene (49)[9].White solid was obtained in 37% isolated yield, 16.9 mg, Rf = 0.5 (PE:EA = 5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.50 (dd, *J* = 8.6, 5.4 Hz, 4H), 7.30 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.9 Hz, 2H), 5.61 (s, 1H), 5.51 (s, 1H), 5.44 (s, 1H), 5.24 (s, 1H), 3.78 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.4, 149.1, 148.7, 132.2, 129.6 (q, $J_{C\text{-}F}$= 32.3 Hz), 128.7, 127.8, 125.3 (q, $J_{C\text{-}F}$= 4.0 Hz), 124.3 (q, $J_{C\text{-}F}$= 272.7 Hz), 117.9, 115.4, 113.8, 55.4. **^{19}F NMR** (377 MHz, Chloroform-*d*) δ -62.48.



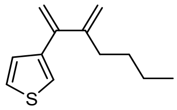
4-(3-(4-Methoxyphenyl)buta-1,3-dien-2-yl)benzonitrile (50). White solid was obtained in 47% isolated yield, 18.4 mg, Rf = 0.4 (PE:EA=5:1). m.p. 71-72 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.57 – 7.51 (m, 2H), 7.50 – 7.42 (m, 2H), 7.29 – 7.24 (m, 2H), 6.82 – 6.76 (m, 2H), 5.63 (d, *J* = 1.3 Hz, 1H), 5.52 (d, *J* = 1.5 Hz, 1H), 5.49 (d, *J* = 1.3 Hz, 1H), 5.24 (d, *J* = 1.5 Hz, 1H), 3.77 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.4, 148.7, 148.2, 144.7, 132.1, 131.7, 128.5, 128.0, 118.6, 115.5, 113.8, 111.0, 55.3. **HRMS** (ESI) m/z calcd for $C_{18}H_{16}ON$ $(M+H)^+$: 262.1226, found: 262.1221.



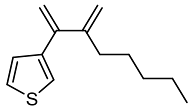
1-(6-Chloro-3-methylenehex-1-en-2-yl)-4-methoxybenzene (51). Colorless oil was obtained in 25% ^{1}H-NMR yield, Rf = 0.5 (PE:DCM = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.25 – 7.20 (m, 2H), 6.88 – 6.83 (m, 2H), 5.20 (d, *J* = 1.6 Hz, 1H), 5.15 (d, *J* = 1.5 Hz, 1H), 5.12 – 5.09 (m, 1H), 5.05 (d, *J* = 2.0 Hz, 1H), 3.81 (s, 3H), 3.53 (t, *J* = 6.6 Hz, 2H), 2.39 (dd, *J* = 7.4, 1.3 Hz, 2H), 1.94 – 1.85 (m, 2H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.3, 149. 8, 147.8, 133.3, 129.2, 116.3, 113.6, 113.0, 55.4, 44.6, 31.8, 31.1. **HRMS** (ESI) m/z calcd for $C_{14}H_{18}ClO$ $(M+H)^+$: 237.1041, found: 237.1033.



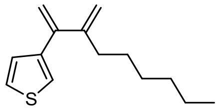
1-(3-Cyclopropylbuta-1,3-dien-2-yl)-4-methoxybenzene (52). Colorless oil was obtained in 37% ^{1}H-NMR yield, R_f = 0.6 (PE:DCM = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.32 - 7.20 (m, 2H), 6.90 - 6.81 (m, 2H), 5.41 (d, *J* = 1.8 Hz, 1H), 5.17 (d, *J* = 1.3 Hz, 1H), 4.96 (d, *J* = 1.2 Hz, 1H), 4.86 (d, *J* = 1.7 Hz, 1H), 3.82 (s, 3H), 1.54 - 1.45 (m, 1H), 0.75 - 0.67 (m, 2H), 0.52 - 0.47 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.1, 150.4, 134.0, 129.4, 113.5, 113.0, 112.4, 55.4, 15.2, 7.0. **HRMS** (ESI) m/z calcd for $C_{14}H_{17}O$ $(M+H)^+$: 201.1274, found: 201.1268.



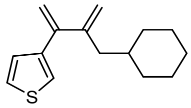
3-(3-Methylenehept-1-en-2-yl)thiophene (53). Colorless oil was obtained in 50% isolated yield, 14.4 mg, Rf = 0.6 (PE:DCM = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.27 – 7.23 (m, 1H), 7.16 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.09 (dd, *J* = 5.0, 1.3 Hz, 1H), 5.26 (d, *J* = 1.5 Hz, 1H), 5.18 (d, *J* = 1.6 Hz, 1H), 5.05 (d, *J* = 1.8 Hz, 1H), 5.02 (d, *J* = 2.0 Hz, 1H), 2.28 (t, *J* = 7.7 Hz, 2H), 1.49 – 1.39 (m, 3H), 1.36 – 1.29 (m, 3H), 0.90 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.2, 145.2, 142.2, 127.6, 124.9, 122.3, 114.5, 112.6, 34.6, 30.4, 22.4, 14.0. **HRMS** (ESI) m/z calcd for $C_{12}H_{17}S$ (M+H)$^+$: 193.1045, found: 193.1041.



3-(3-Methyleneoct-1-en-2-yl)thiophene (54). Colorless oil was obtained in 47% isolated yield, 14.5 mg, Rf = 0.6 (PE:DCM = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.25 (dd, *J* = 4.8, 3.2 Hz, 1H), 7.16 (dd, *J* = 3.1, 1.3 Hz, 1H), 7.09 (dd, *J* = 4.9, 1.3 Hz, 1H), 5.26 (s, 1H), 5.19 (s, 1H), 5.05 (s, 1H), 5.02 (s, 1H), 2.27 (t, *J* = 7.6 Hz, 2H), 1.50 – 1.40 (m, 2H), 1.32 – 1.28 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.2, 145.2, 142.2, 127.6, 124.9, 122.3, 114.5, 112.6, 34.8, 31.5, 27.9, 22.5, 14.1. **HRMS** (ESI) m/z calcd for $C_{13}H_{19}S$ (M+H)$^+$: 207.1202, found: 207.1197.

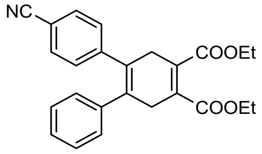


3-(3-Methylenenon-1-en-2-yl)thiophene (55). Colorless oil was obtained in 55% isolated yield, 18.2 mg, Rf = 0.6 (PE:DCM = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.25 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.16 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.09 (dd, *J* = 5.0, 1.2 Hz, 1H), 5.25 (d, *J* = 1.6 Hz, 1H), 5.18 (d, *J* = 1.6 Hz, 1H), 5.05 (d, *J* = 2.0 Hz, 1H), 5.01 (d, *J* = 2.0 Hz, 1H), 2.27 (t, *J* = 7.5 Hz, 2H), 1.50 – 1.40 (m, 2H), 1.30 – 1.29 (m, 6H), 0.88 – 0.86 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.2, 145.2, 142.2, 127.6, 124.9, 122.3, 114.5, 112.6, 34.9, 31.7, 29.0, 28.2, 22.6, 14.1. **HRMS** (ESI) m/z calcd for $C_{14}H_{21}S$ (M+H)$^+$: 221.1359, found: 221.1353.

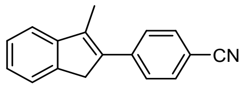


3-(3-(Cyclohexylmethyl)buta-1,3-dien-2-yl)thiophene (56). Colorless oil was obtained in 40% isolated yield, 13.9 mg, Rf = 0.6 (PE:DCM = 3:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.25 (dd, *J* = 5.0, 3.1 Hz, 1H), 7.16 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.09 (dd, *J* = 4.9, 1.3 Hz, 1H), 5.26 (d, *J* = 1.6 Hz, 1H), 5.17 (d, *J* = 1.6 Hz, 1H), 5.04 (d, *J* = 2.4 Hz, 1H), 5.01 (d, *J* = 2.3 Hz, 1H), 2.16 (d, *J* = 7.0 Hz, 2H), 1.80 – 1.58 (m, 8H), 1.42 (dtt, *J* = 14.6, 7.2, 3.6 Hz, 2H), 1.30 – 1.09 (m, 5H), 0.95 – 0.80 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 147.5, 145.2, 142.3, 127.6, 124.9, 122.3, 115.9, 112.9, 43.1, 35.9, 33.3, 26.6, 26.3. **HRMS** (ESI) m/z calcd for $C_{15}H_{21}S$ (M+H)$^+$: 233.1359, found:

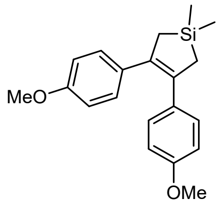
233.1352.



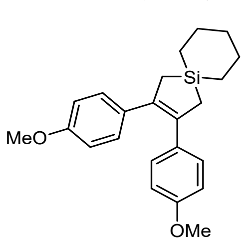
Diethyl 4-cyano-3',6'-dihydro-[1,1':2',1''-terphenyl]-4',5'-dicarboxylate (57). Yellow oil was obtained in 40% isolated yield, 32 mg, Rf = 0.4 (PE:EA=5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 7.8 Hz, 2H), 7.19 – 7.13 (m, 3H), 7.11 (d, *J* = 7.8 Hz, 2H), 7.00 – 6.94 (m, 2H), 4.27 (q, *J* = 7.2 Hz, 4H), 3.53 – 3.42 (m, 4H), 1.32 (t, *J* = 7.2 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.5, 167.4, 146.2, 140.2, 133.2, 132.7, 132.0, 131.7, 129.7, 129.3, 128.7, 128.5, 127.5, 118.9, 110.5, 61.6, 35.0, 34.2, 14.2. **HRMS** (ESI) m/z calcd for $C_{25}H_{24}NO_4$ (M+H)$^+$: 402.1700, found: 402.1704.



4-(3-Methyl-1*H*-inden-2-yl)benzonitrile (58). Colorless oil was obtained in 68% isolated yield, 78.2 mg, Rf = 0.5 (PE:EA=5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 7.3 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 3.75 (s, 2H), 2.35 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.9, 142.5, 142.3, 138.2, 138.2, 132.3, 128.7, 126.8, 125.9, 123.6, 119.8, 119.2, 109.9, 40.7, 12.4. **HRMS** (ESI) m/z calcd for $C_{17}H_{14}N$ (M+H)$^+$: 232.1121, found: 232.1116.



3,4-Bis(4-methoxyphenyl)-1,1-dimethyl-1*H*-silole (59). Colorless oil was obtained in 89% isolated yield, 57.8 mg, Rf = 0.4 (PE:EA=5:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 8.8 Hz, 4H), 6.87 (d, *J* = 8.8 Hz, 4H), 3.93 (s, 6H), 2.08 (s, 4H), 0.46 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.5, 136.5, 135.5, 129.9, 113.0, 55.1, 26.4, -1.9. **HRMS** (ESI) m/z calcd for $C_{20}H_{25}O_2Si$ (M+H)$^+$: 325.1618, found: 325.1619.



2,3-Bis(4-methoxyphenyl)-5-silaspiro[4.5]deca-1,3-diene (60). Colorless oil was obtained in 87% isolated yield, 63.4 mg, Rf = 0.4 (PE:EA=5:1)). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.04 – 6.97 (m, 4H), 6.70 – 6.65 (m, 4H), 3.74 (s, 6H), 1.91 (s, 4H), 1.81 – 1.67 (m, 4H), 1.51 – 1.41 (m, 2H), 0.88 – 0.79 (m, 4H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.7, 136.7, 135.7, 129.9, 113.1, 55.2, 30.0, 25.4, 24.3, 12.7. **HRMS** (ESI) m/z calcd for $C_{23}H_{29}O_2S$ (M+H)$^+$: 365.1931, found: 365.1931.

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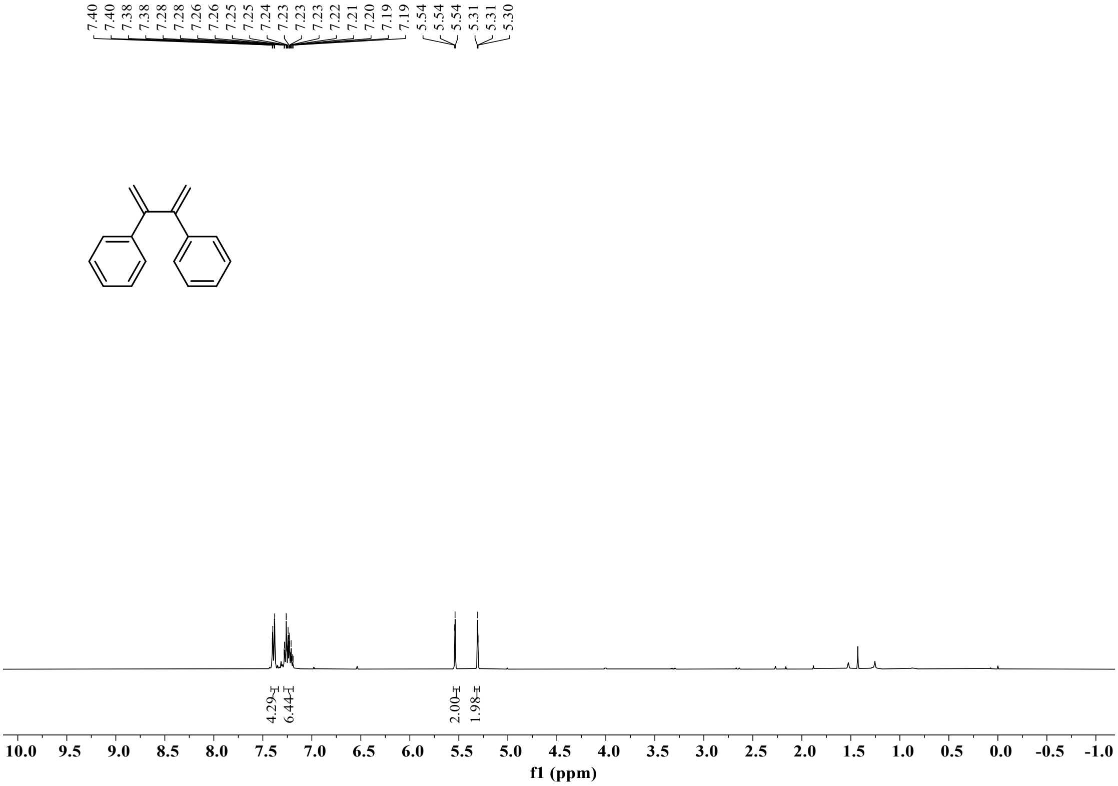
NMR spectra of products

^{1}H NMR Spectra of compound **3**



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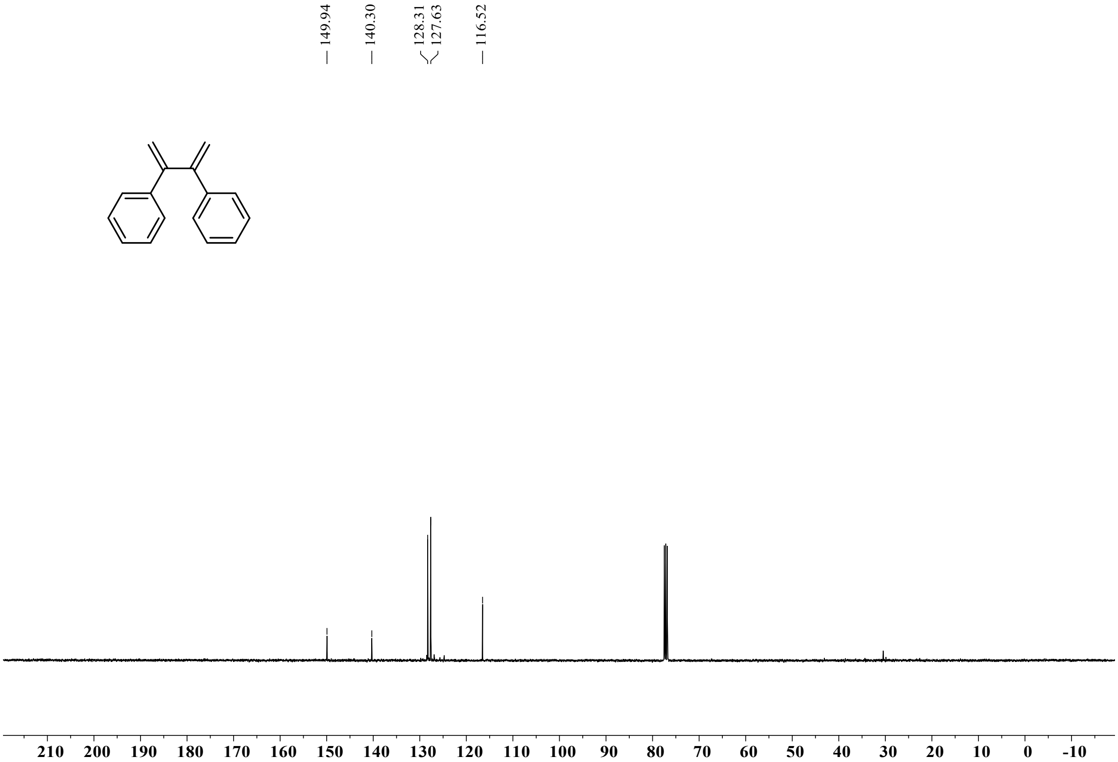

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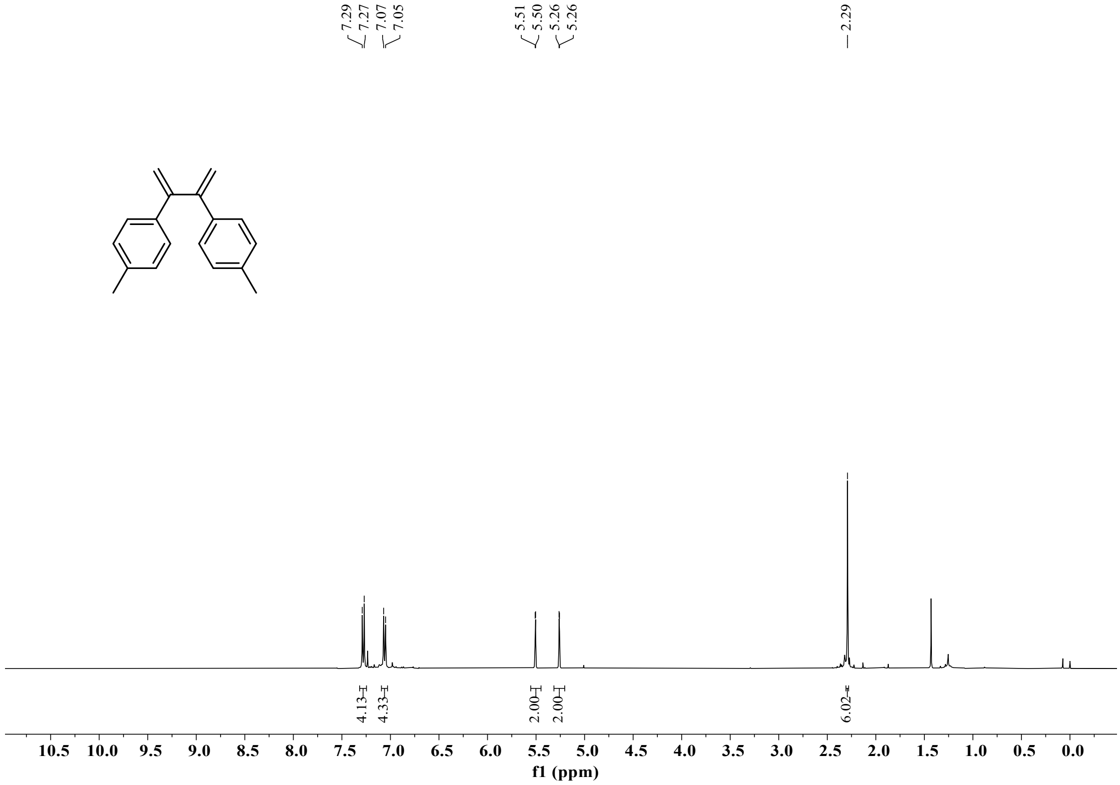

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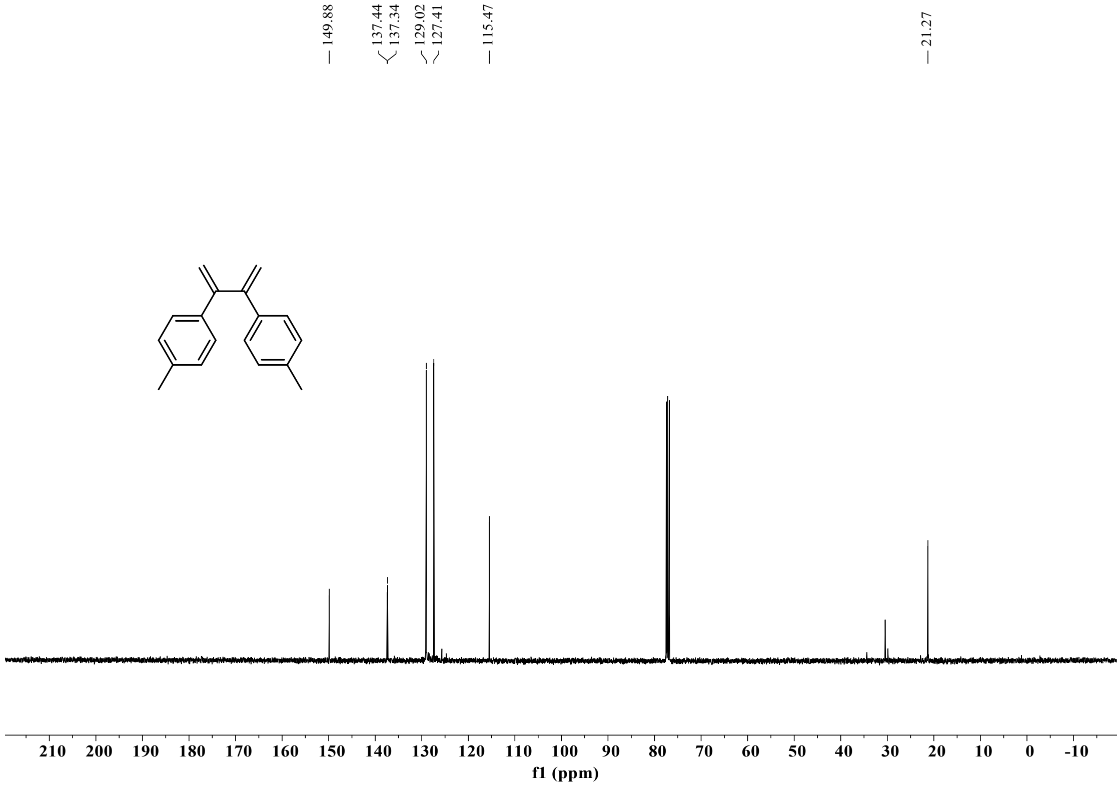

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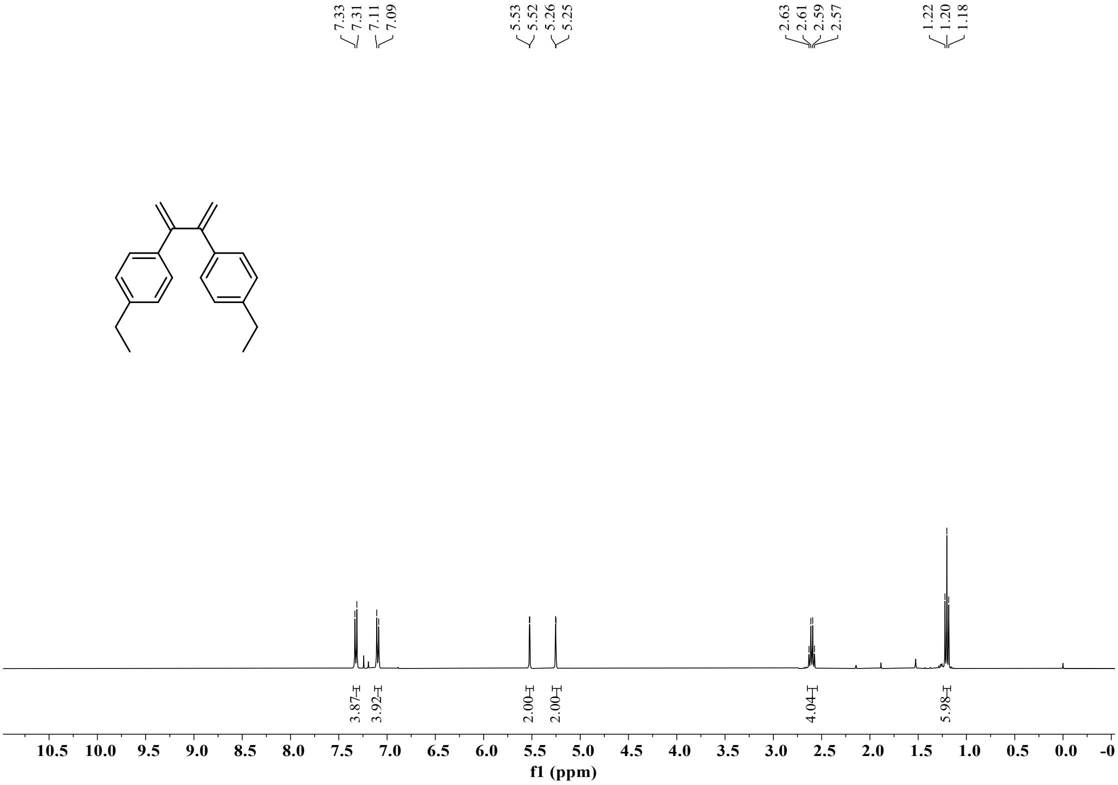

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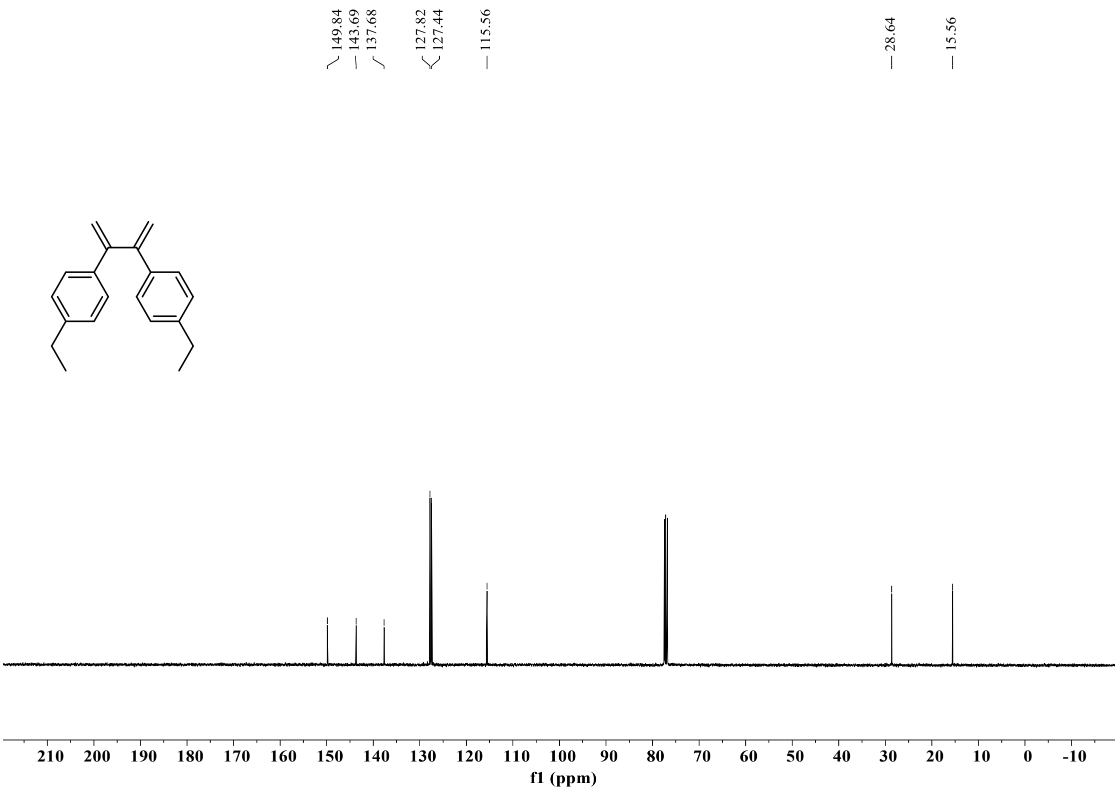

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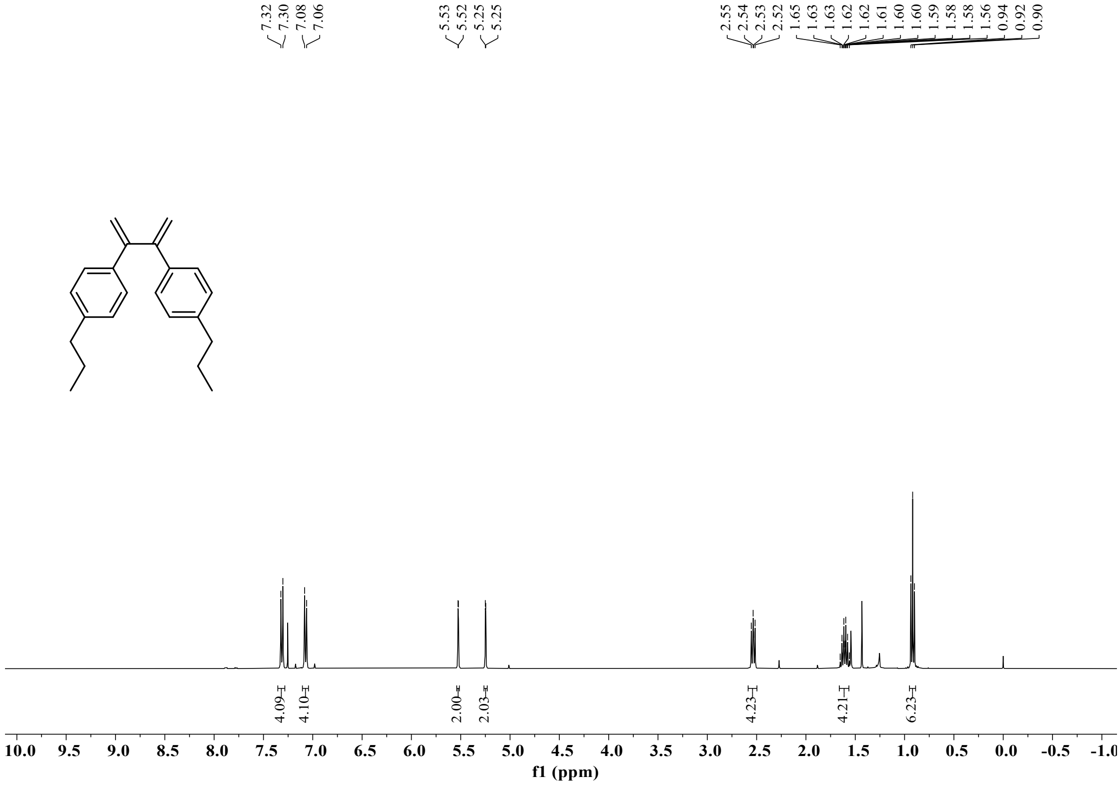

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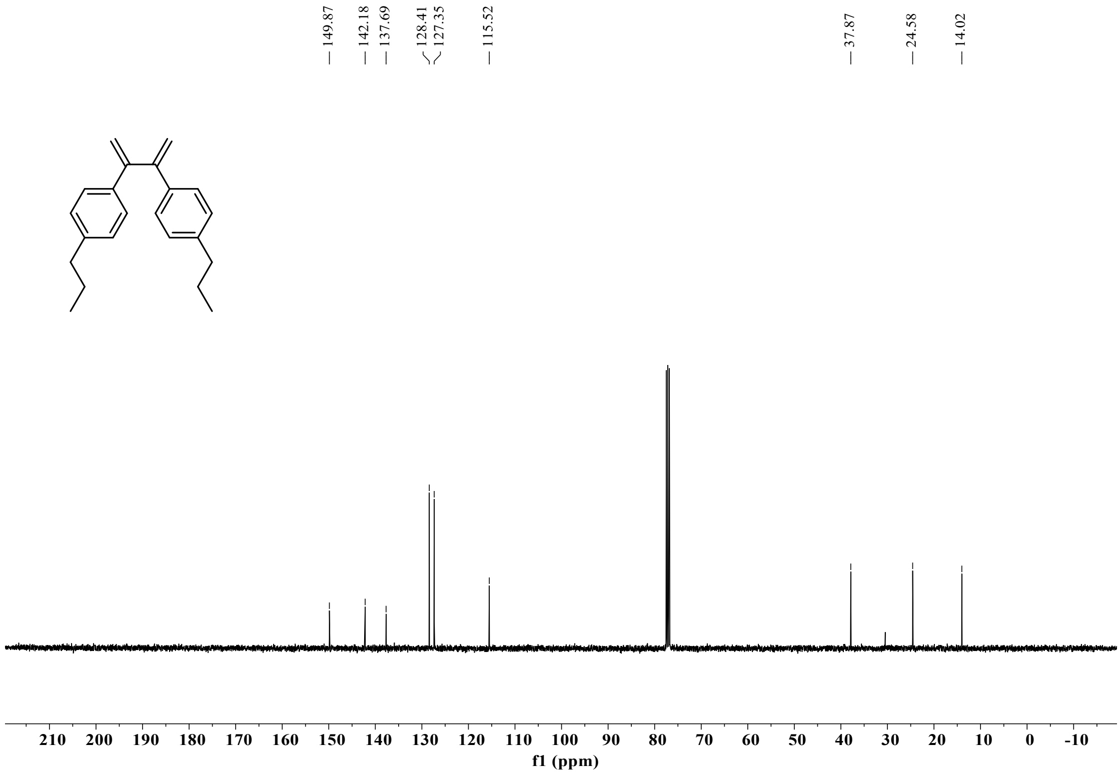

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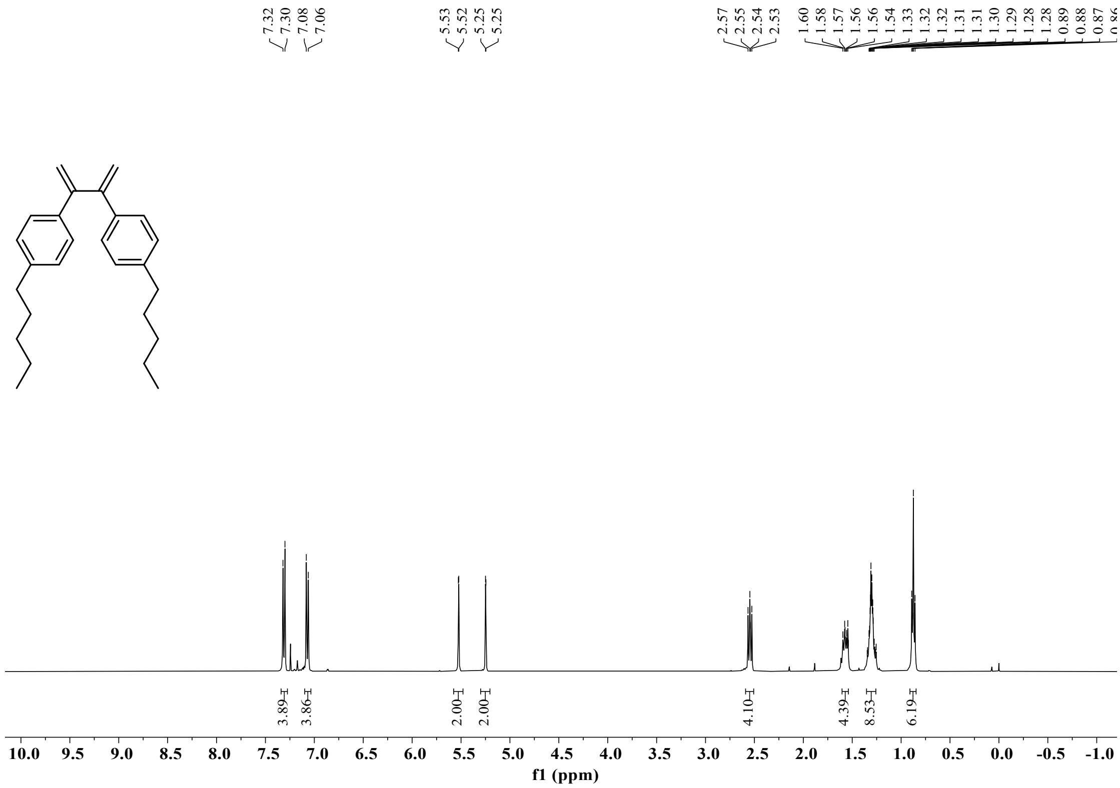

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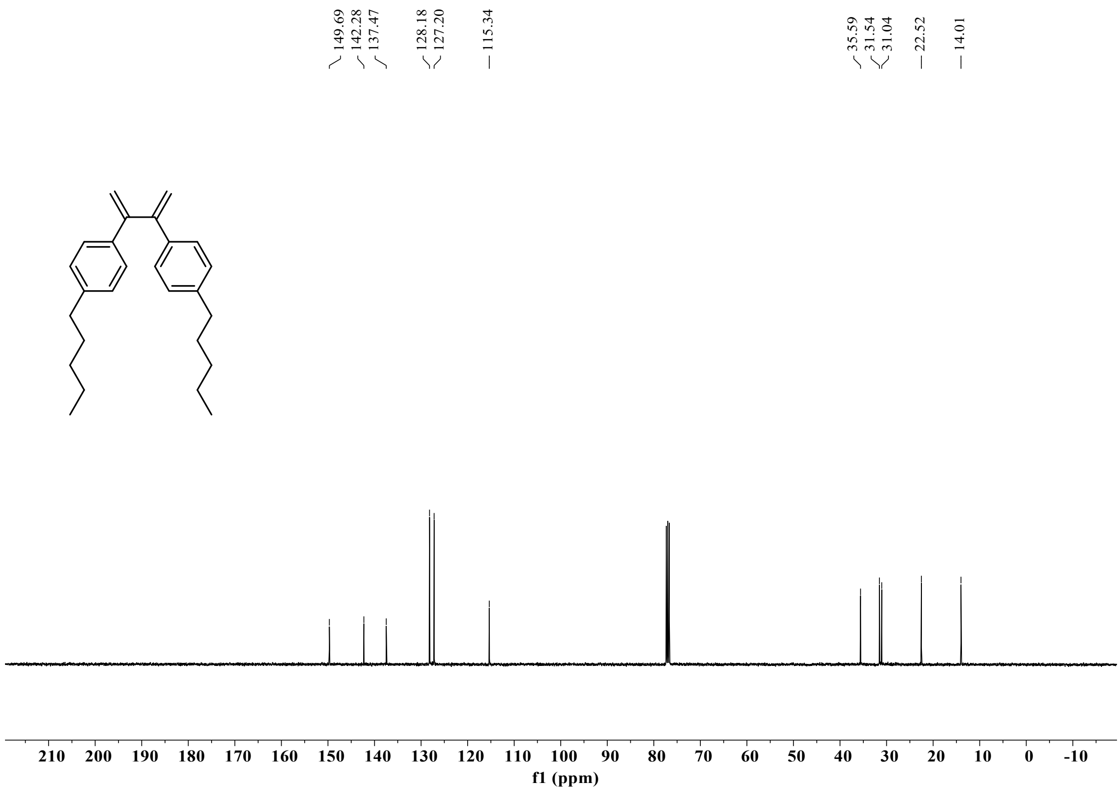

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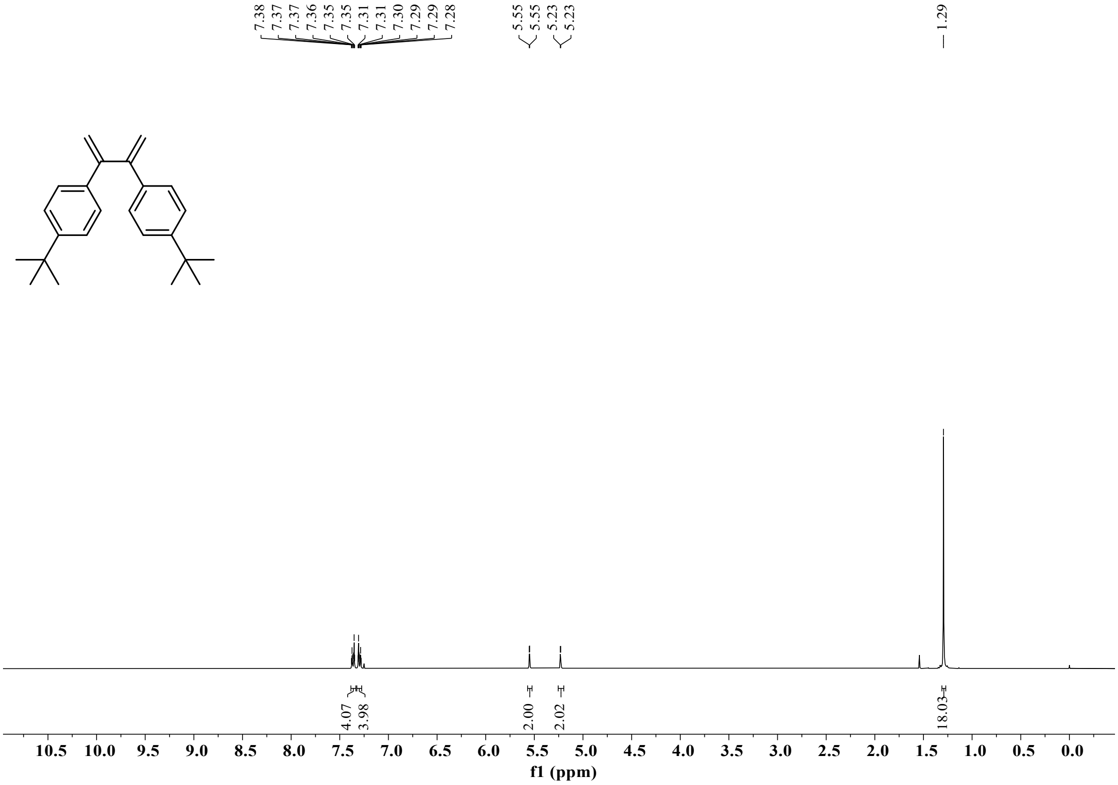

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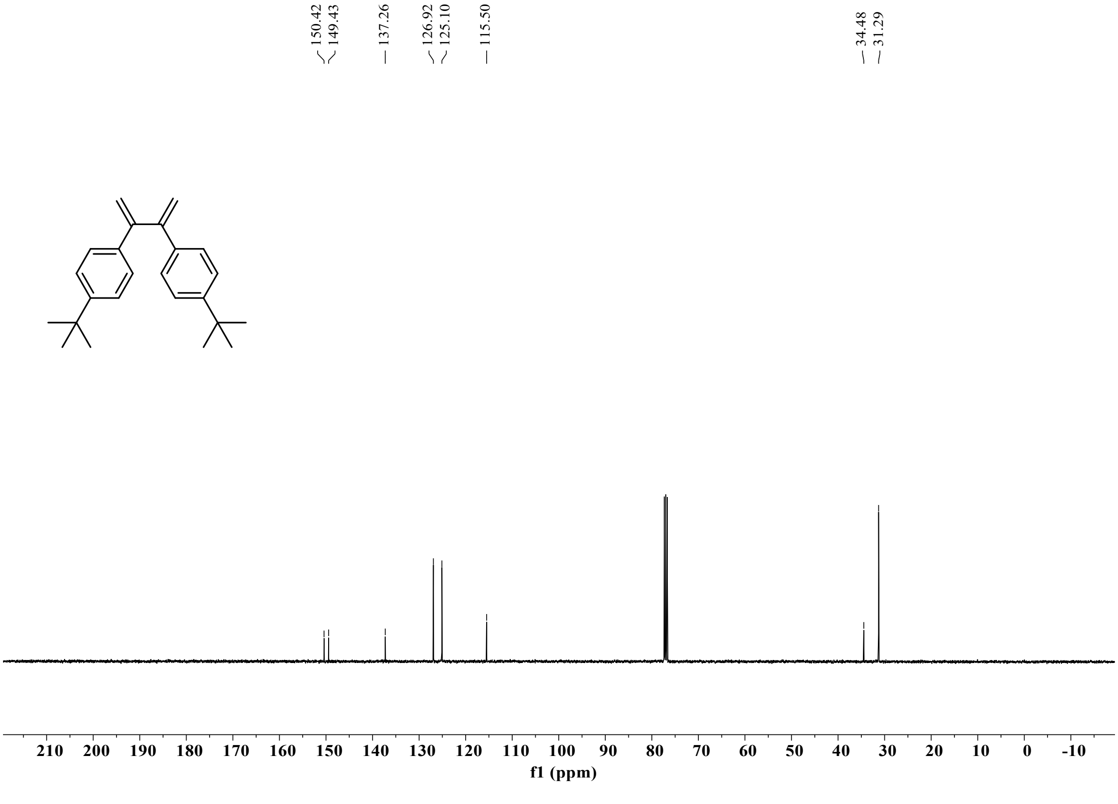

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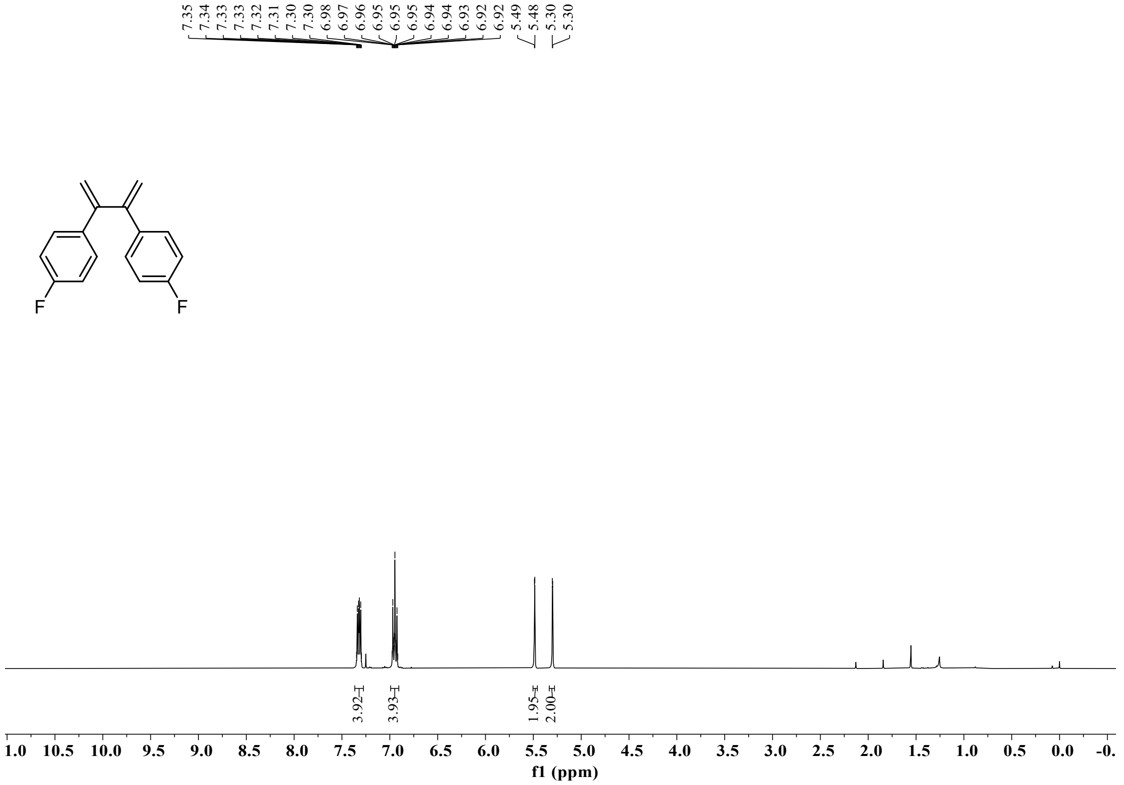

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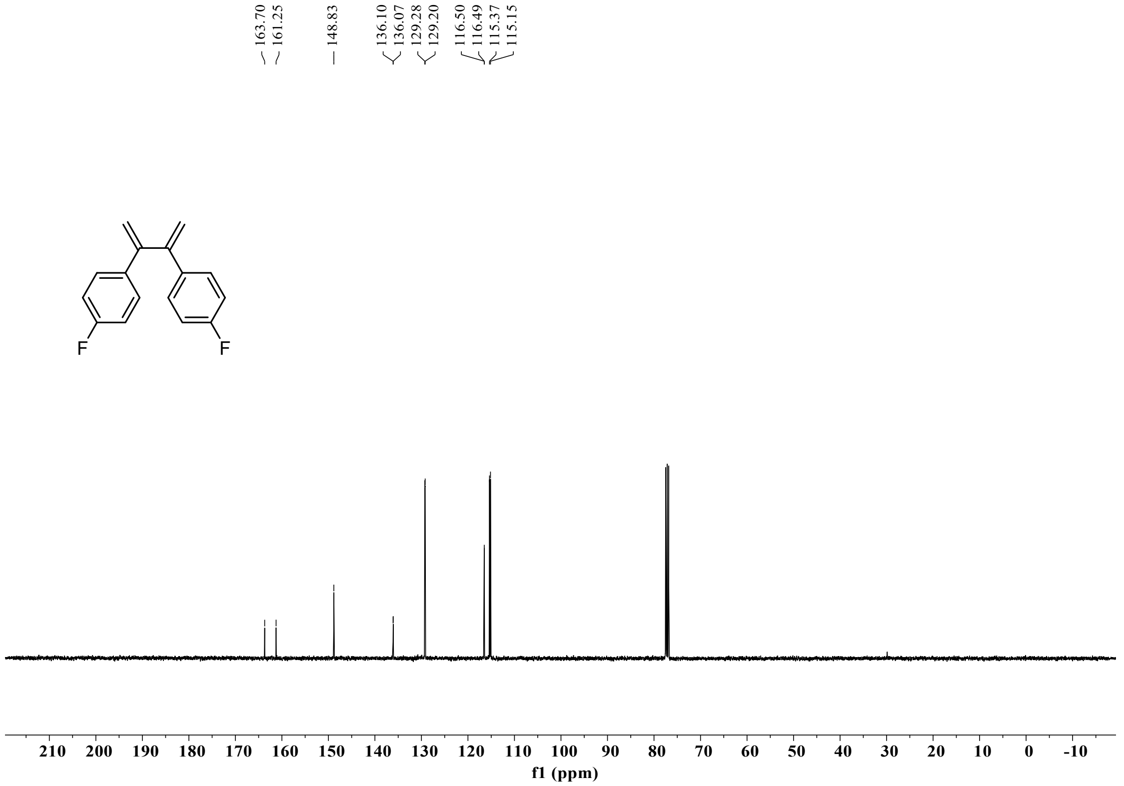

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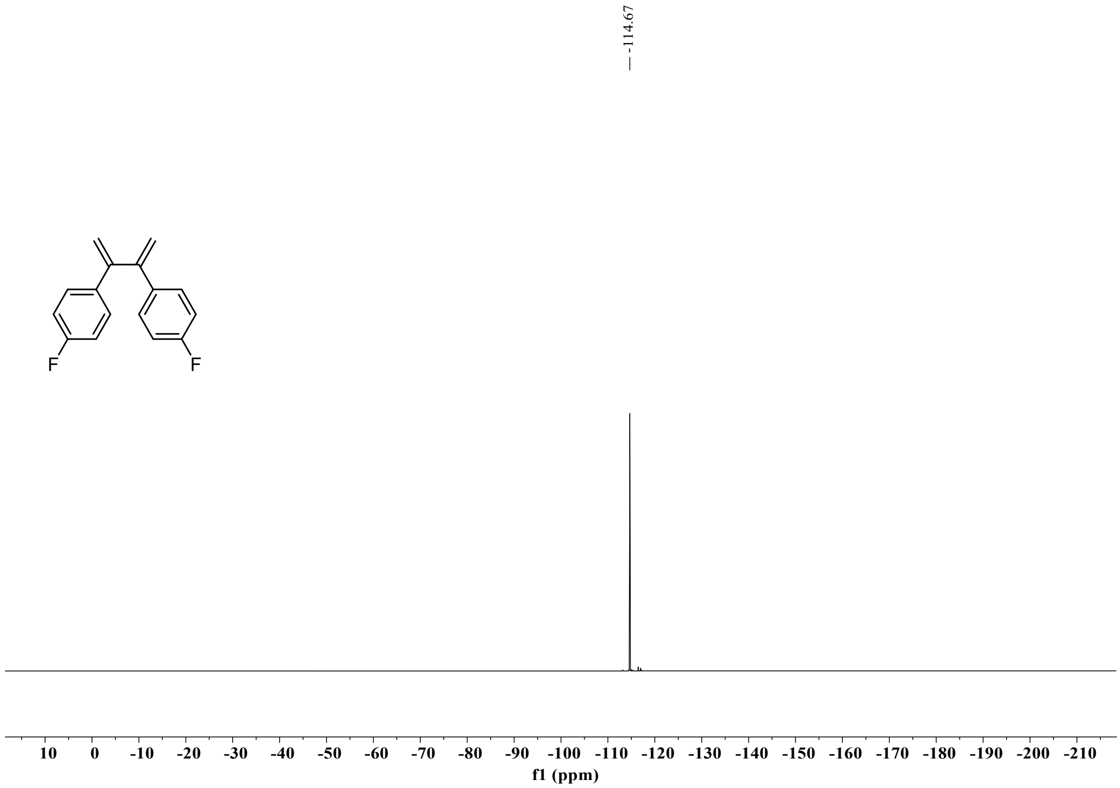

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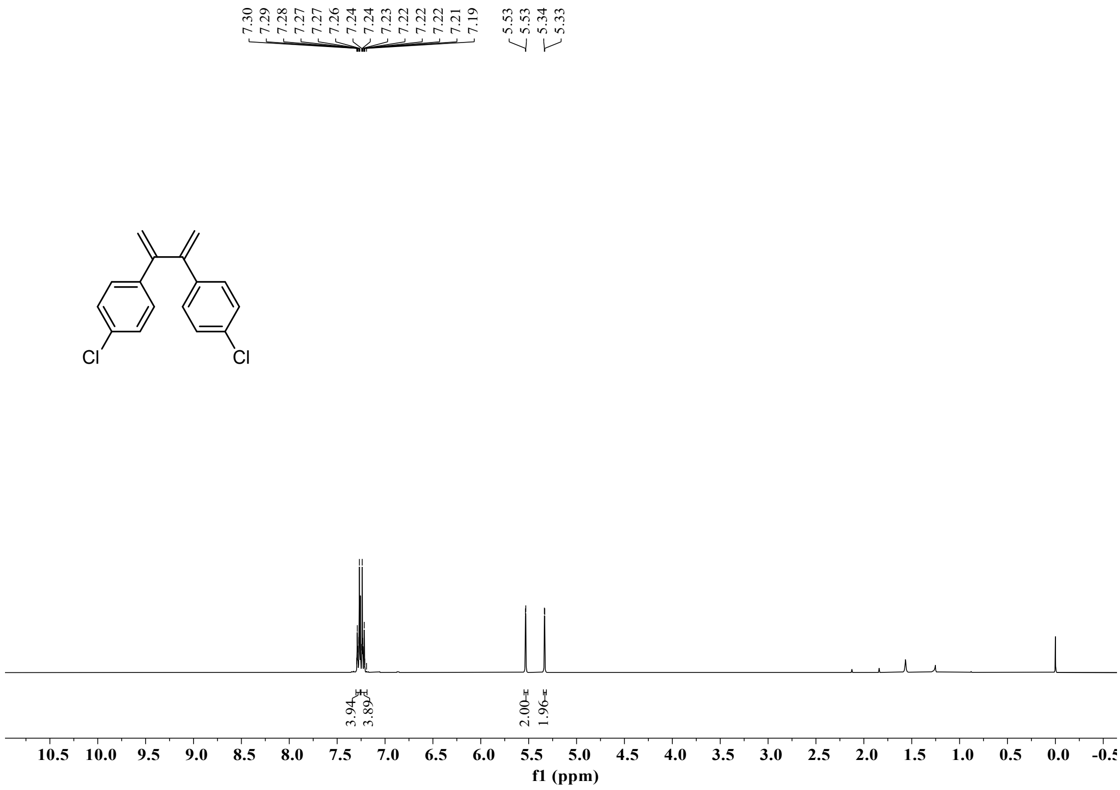

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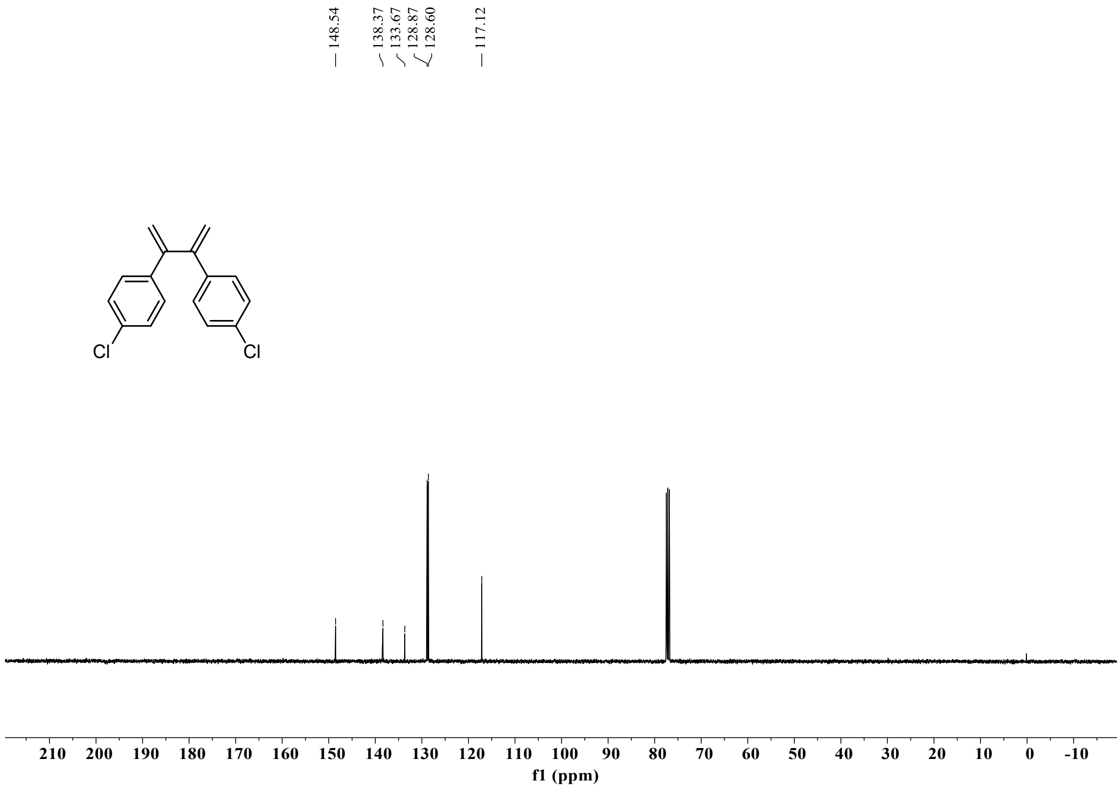

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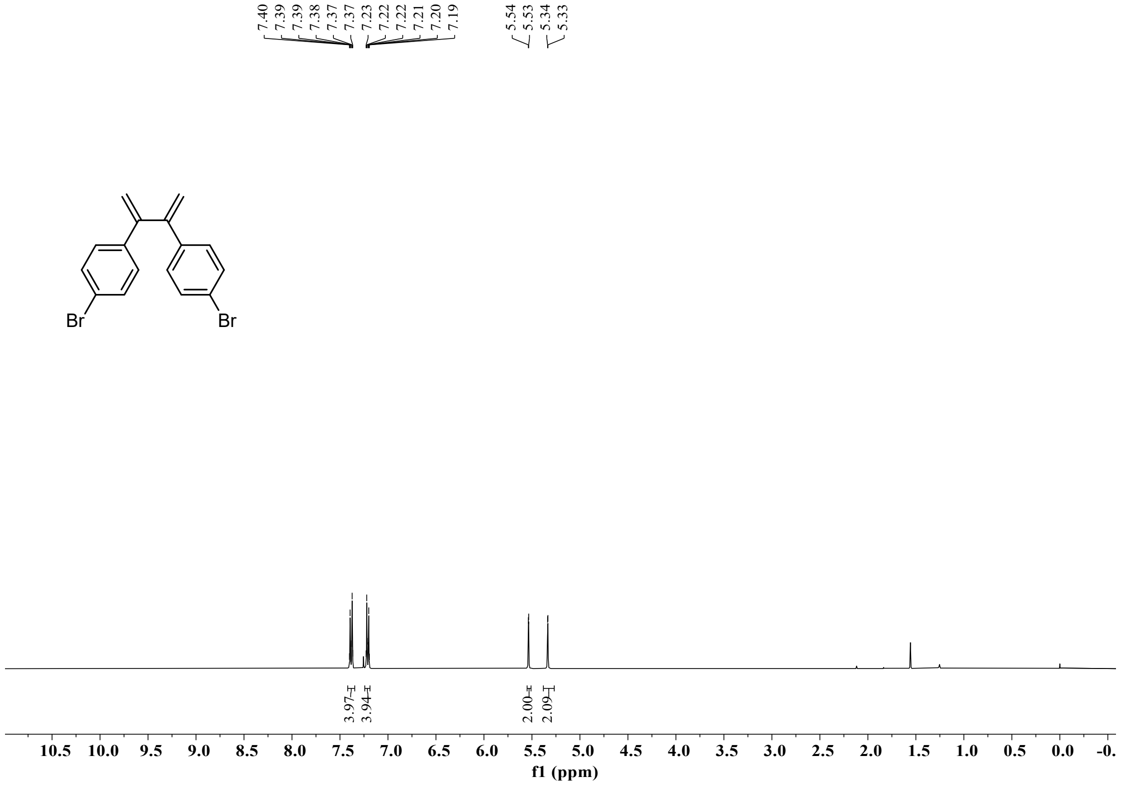

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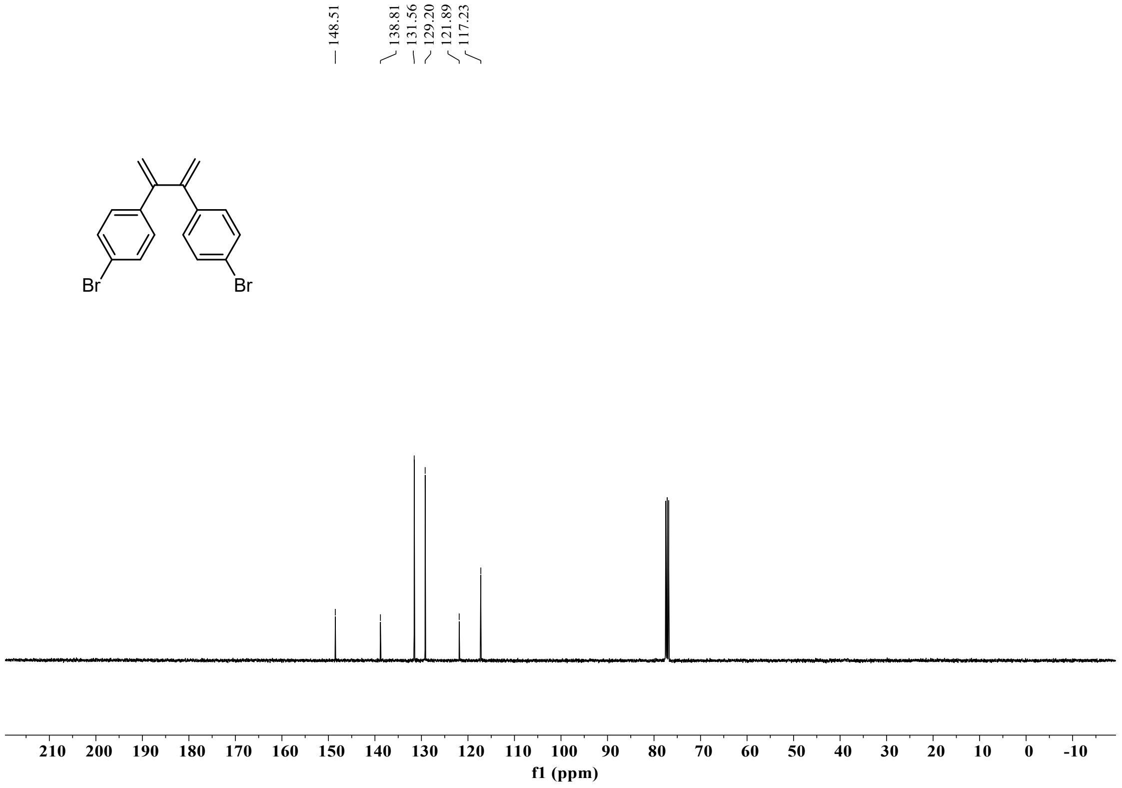

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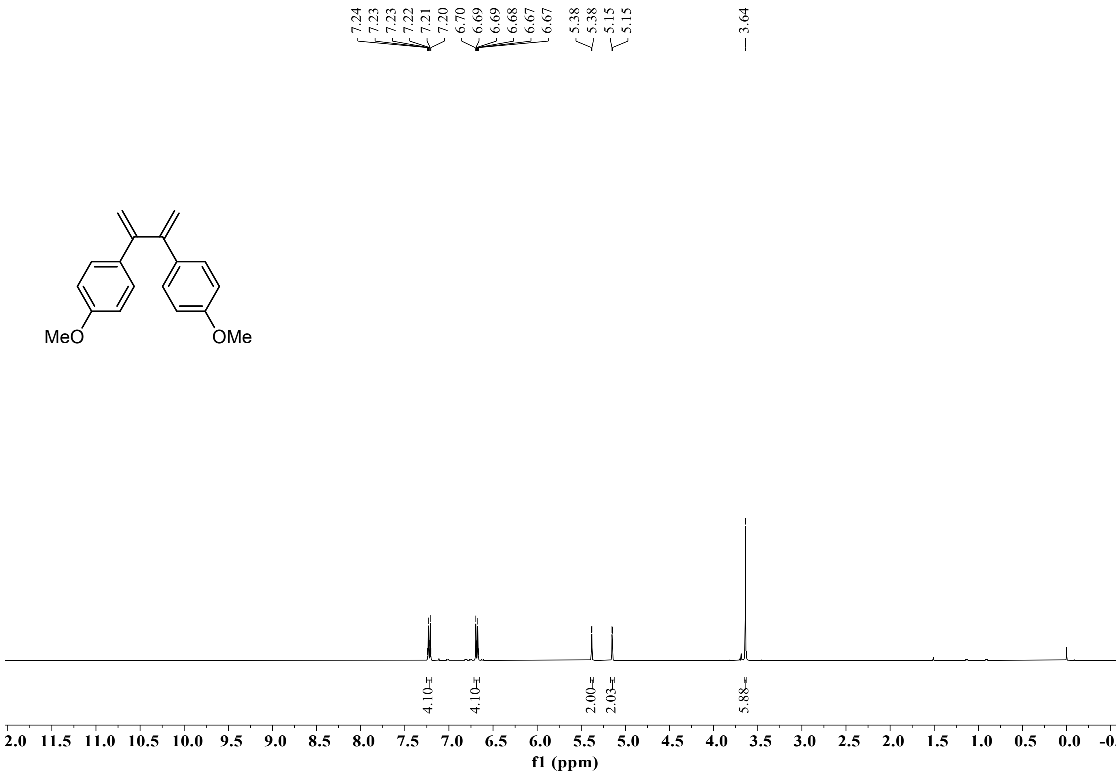

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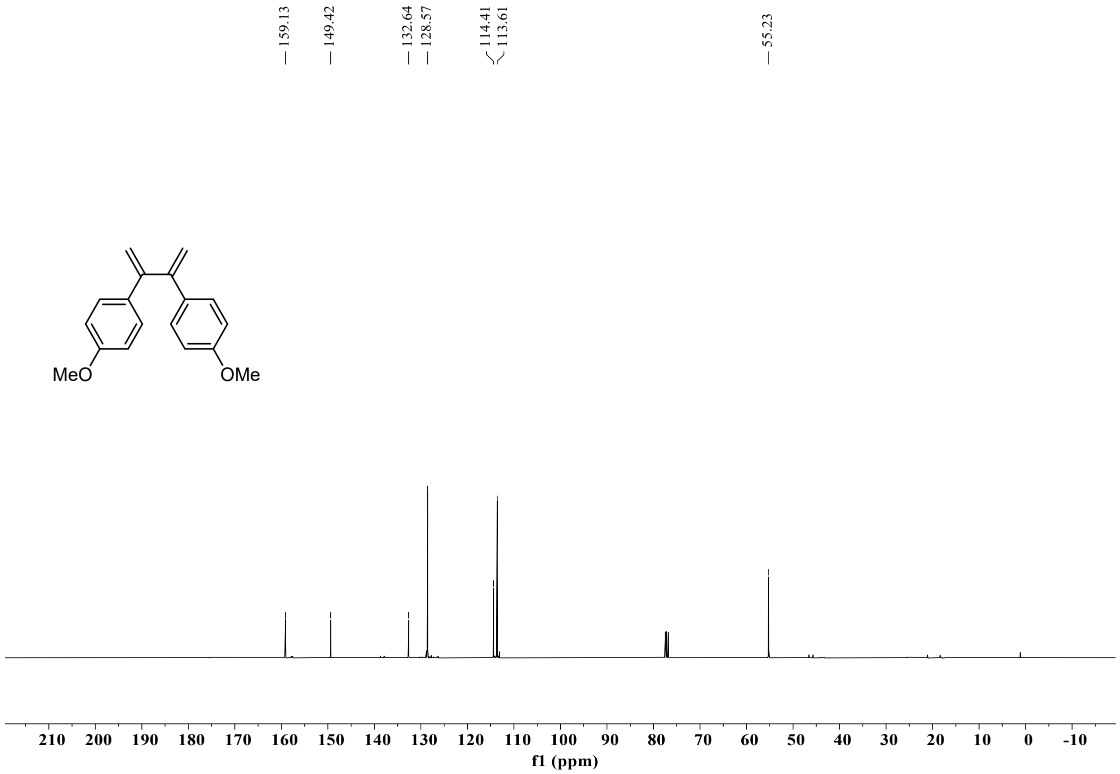

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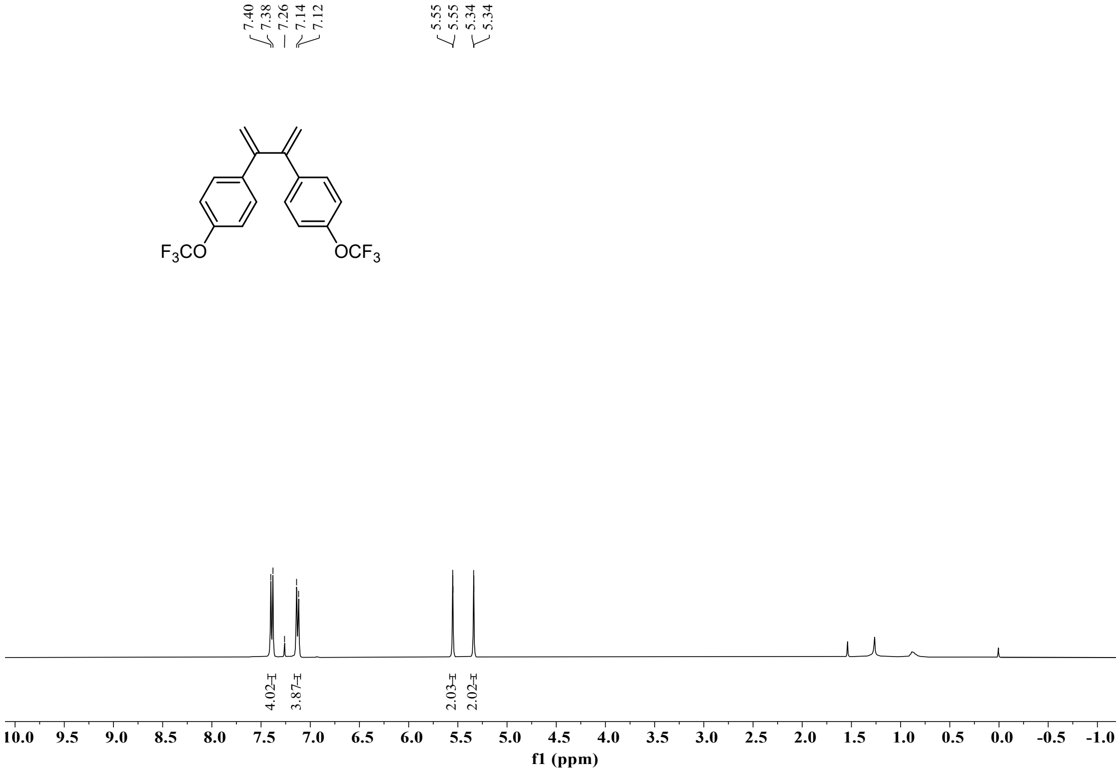

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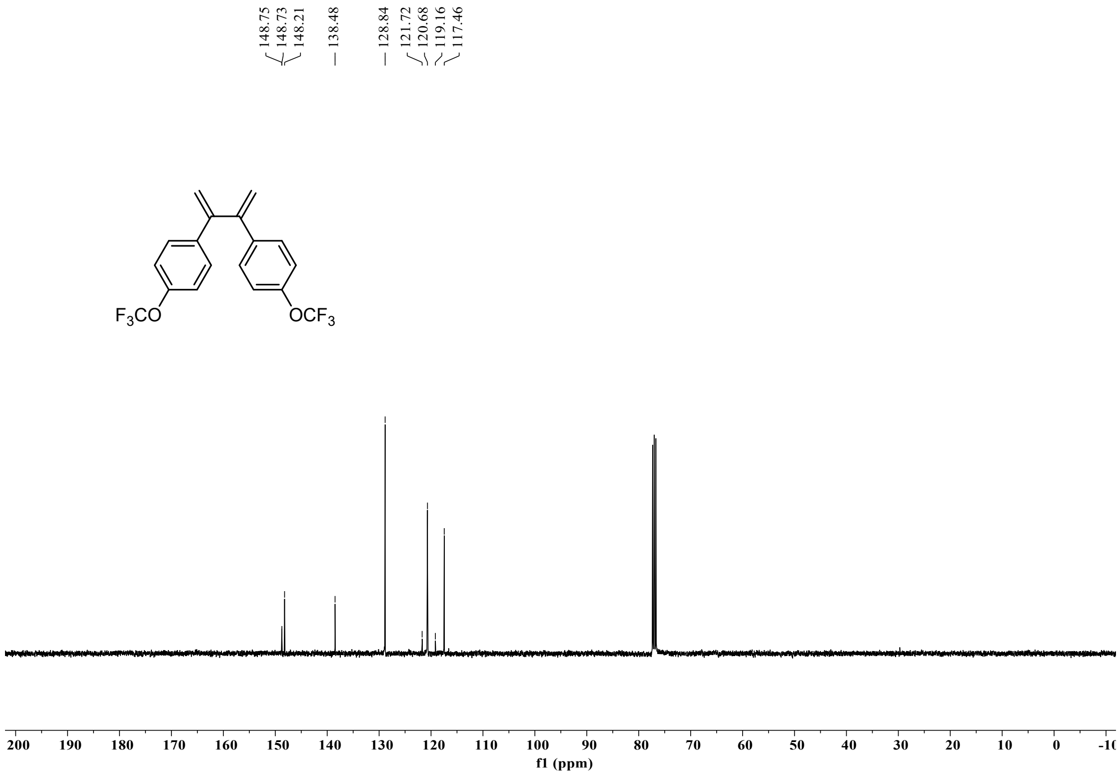

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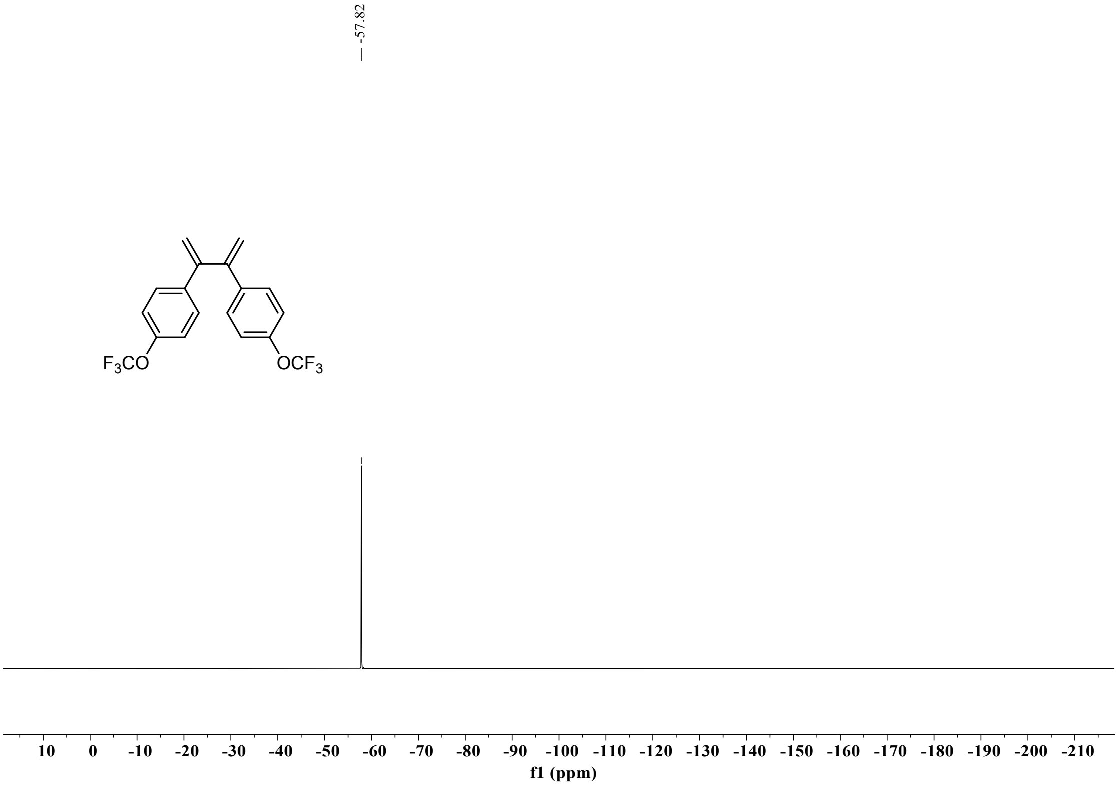

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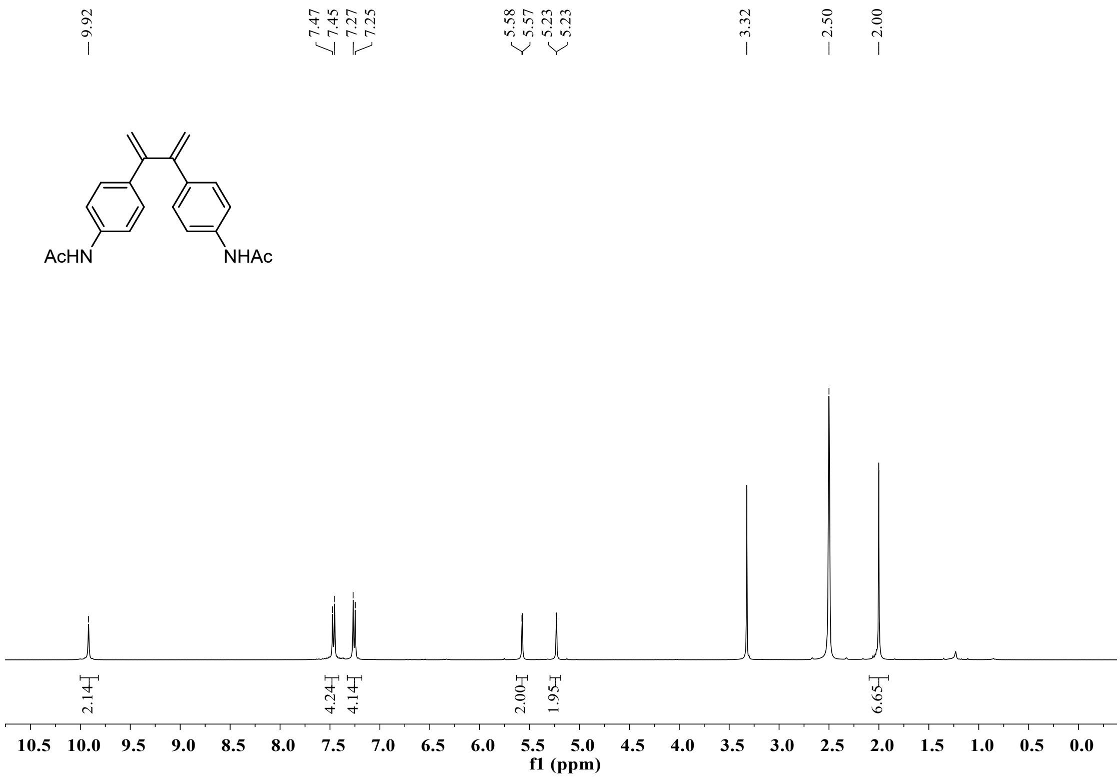

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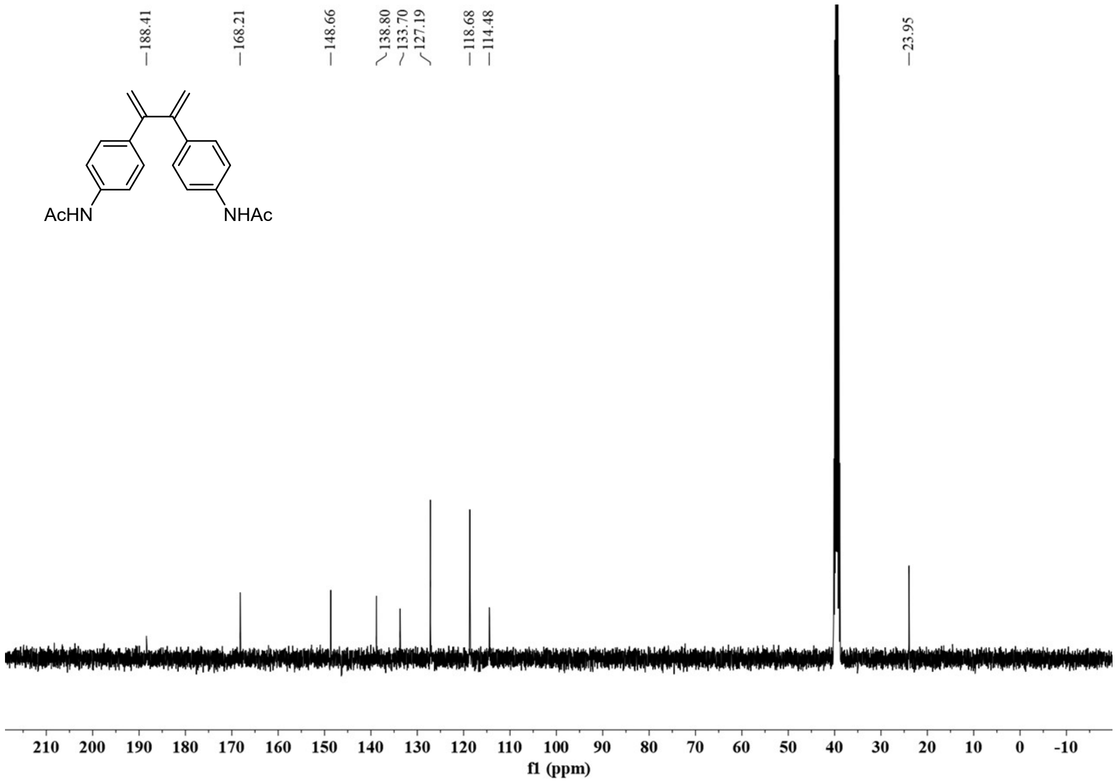

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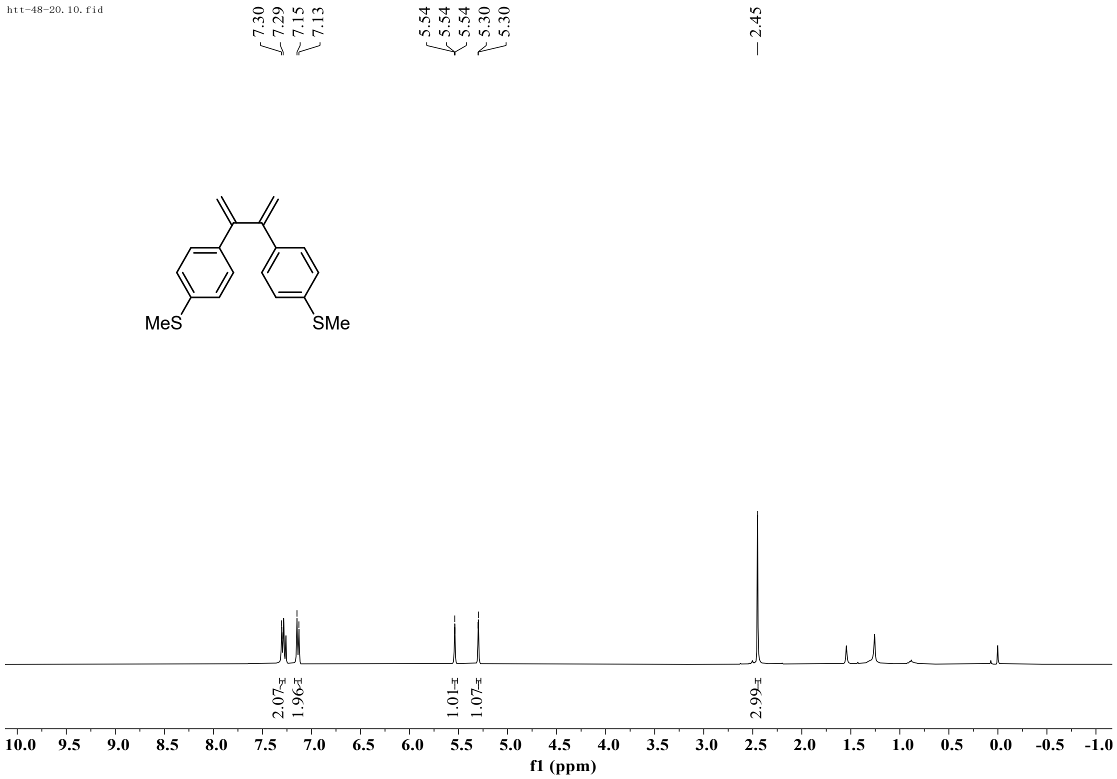

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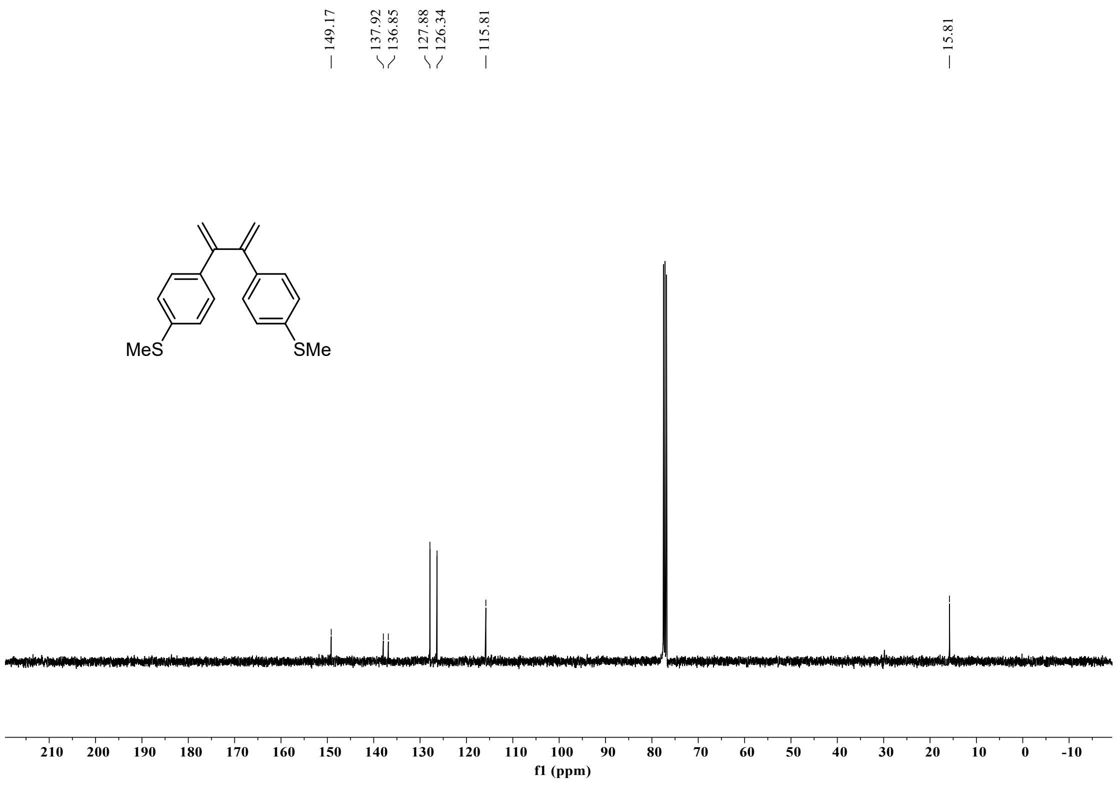

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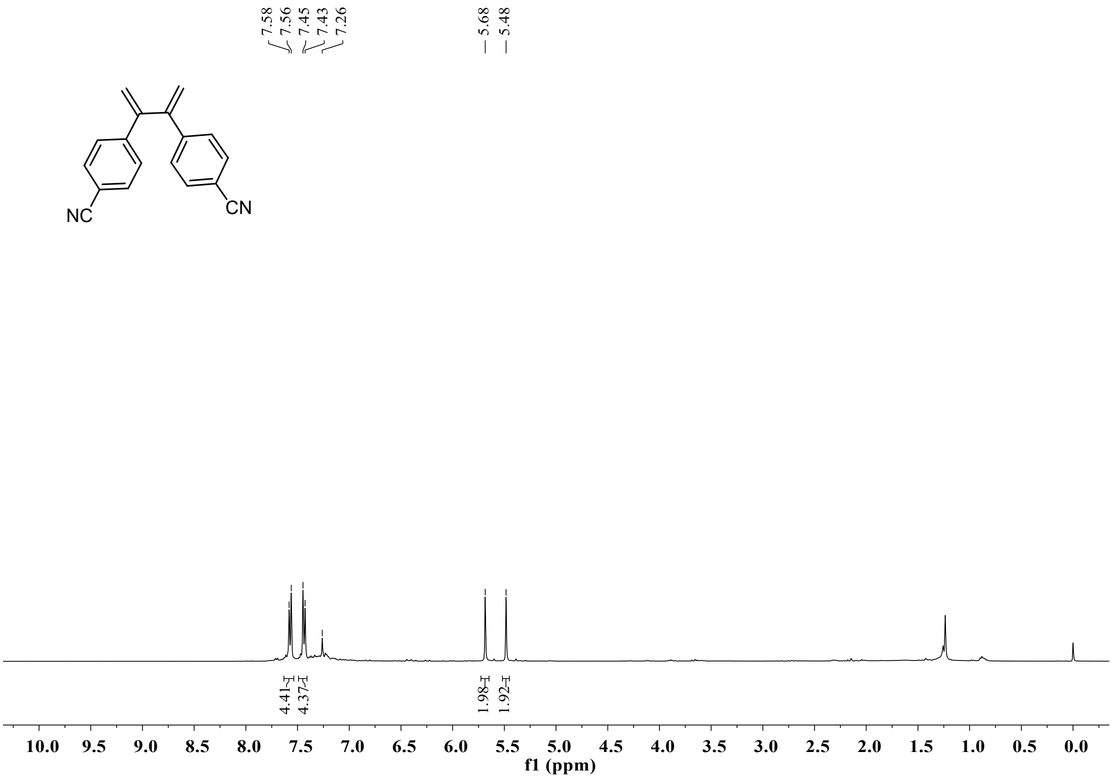

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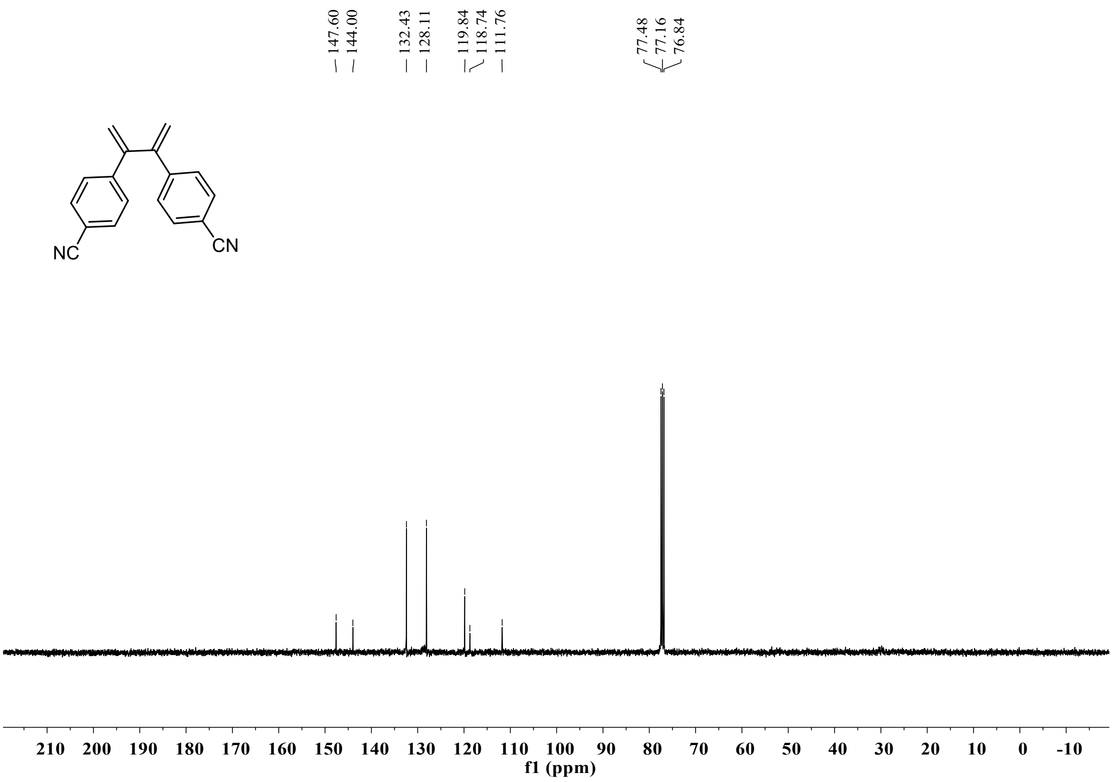

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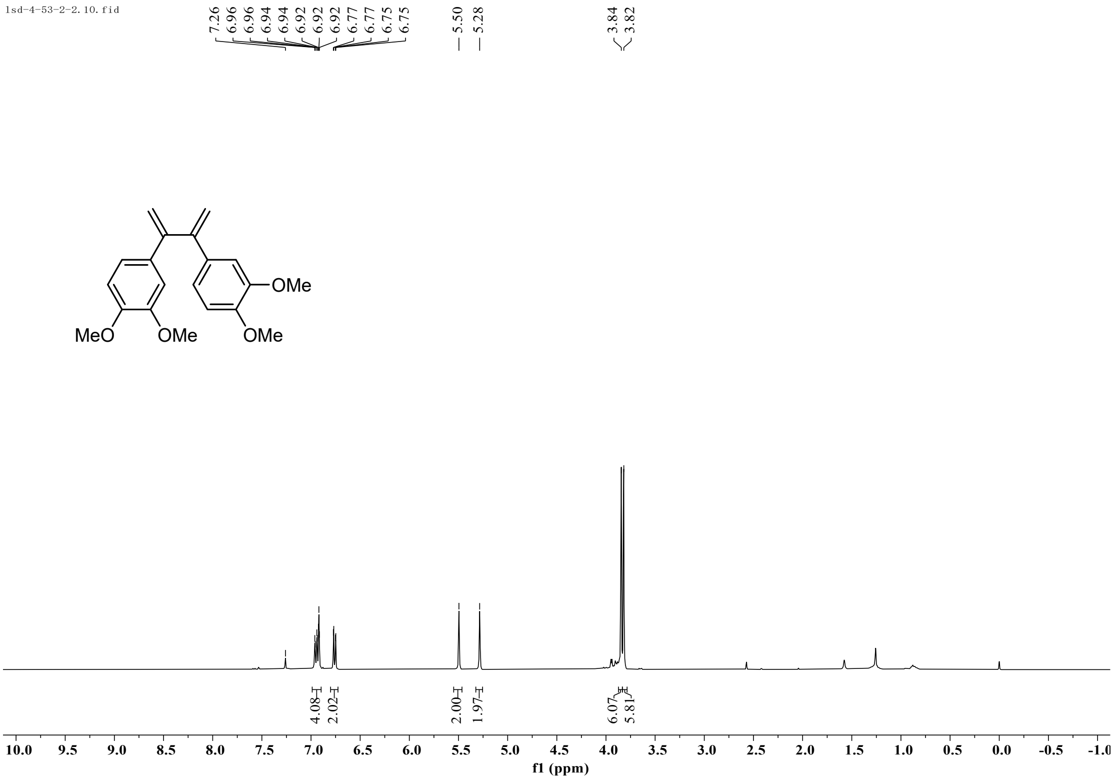

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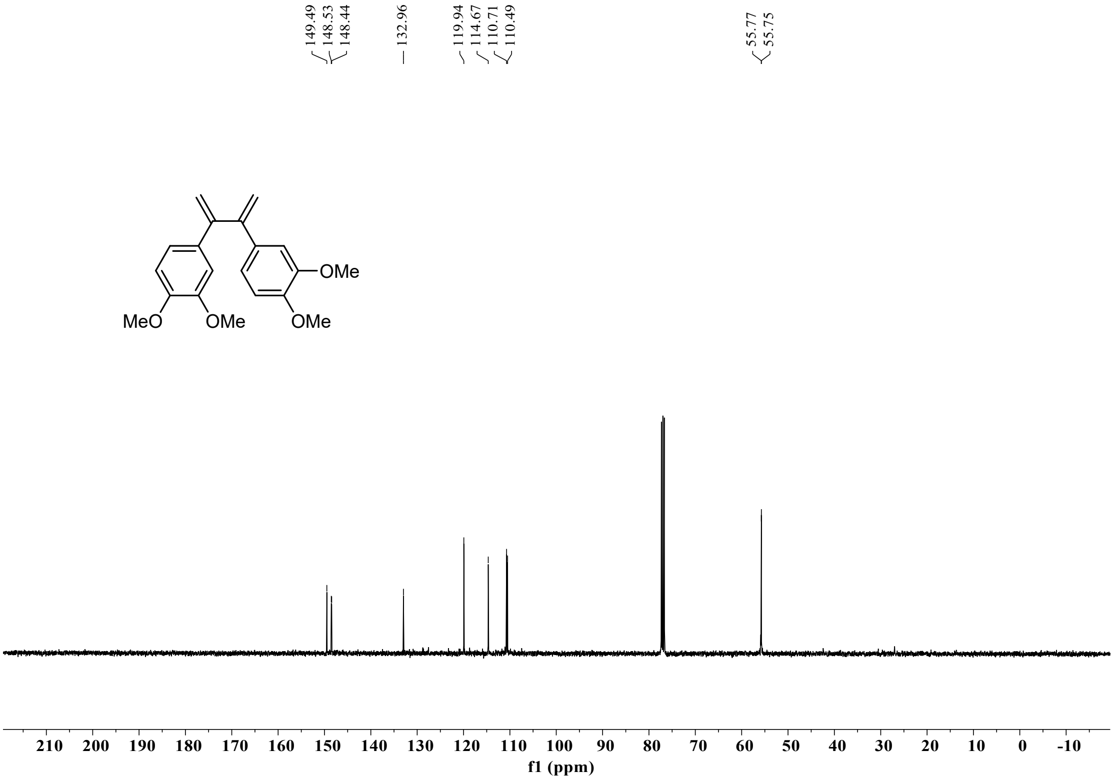

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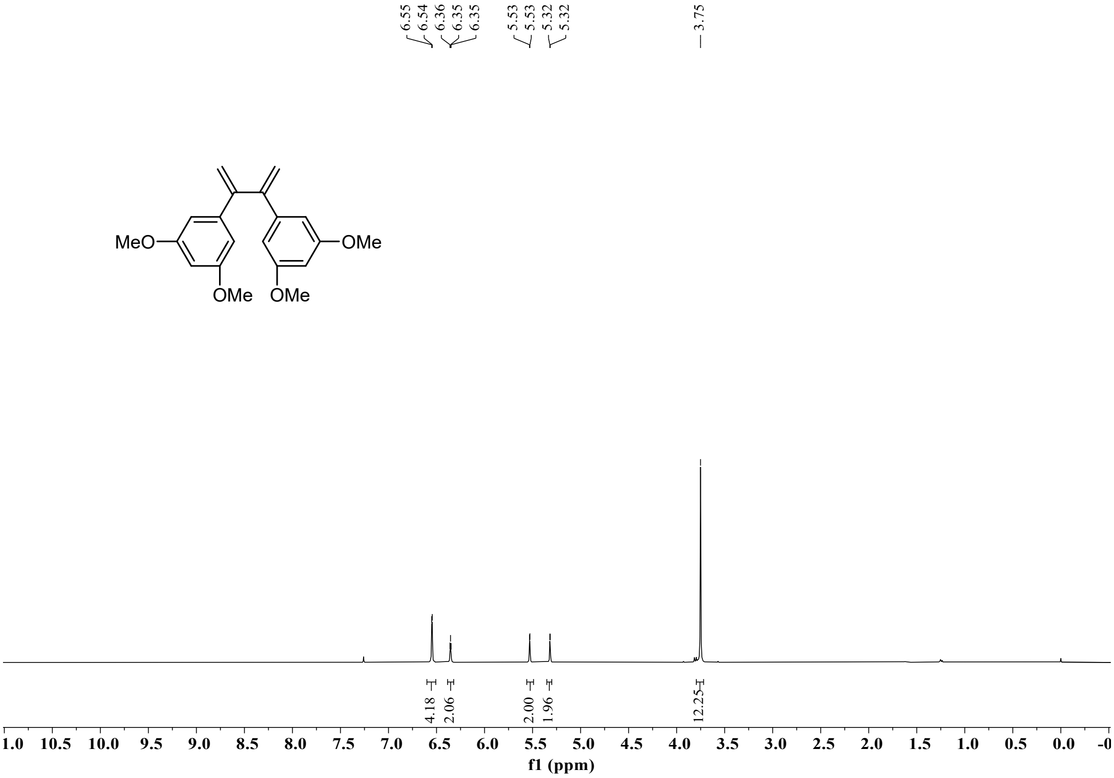

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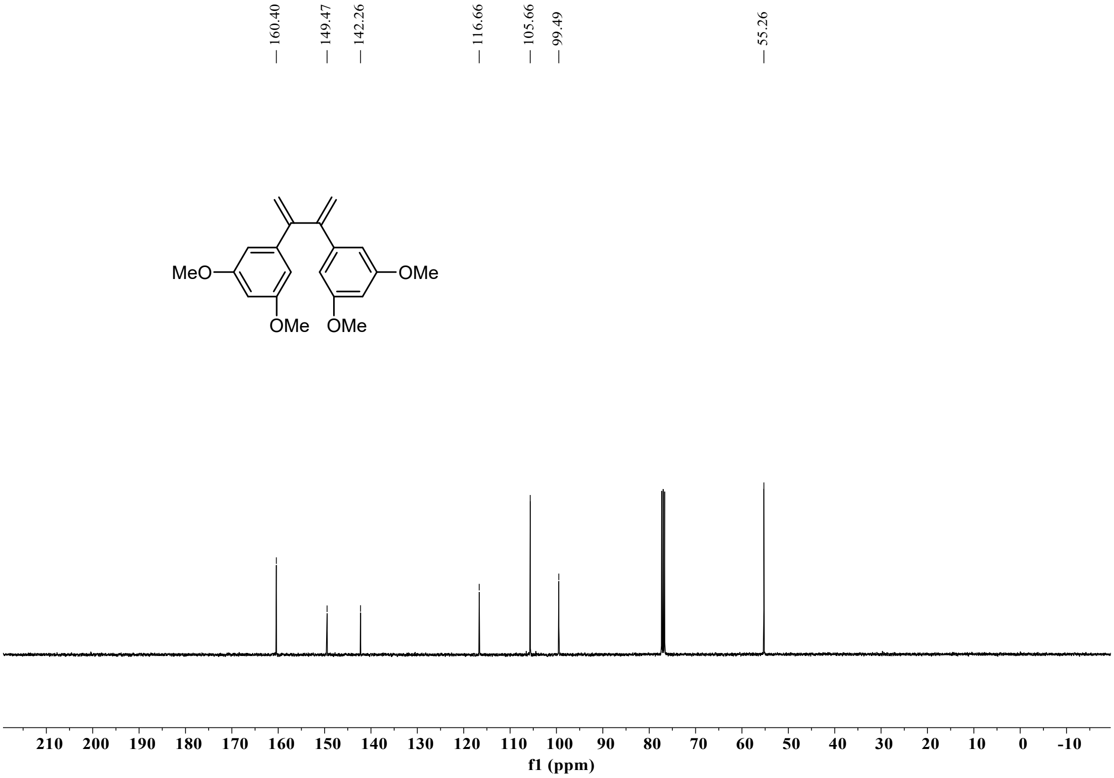

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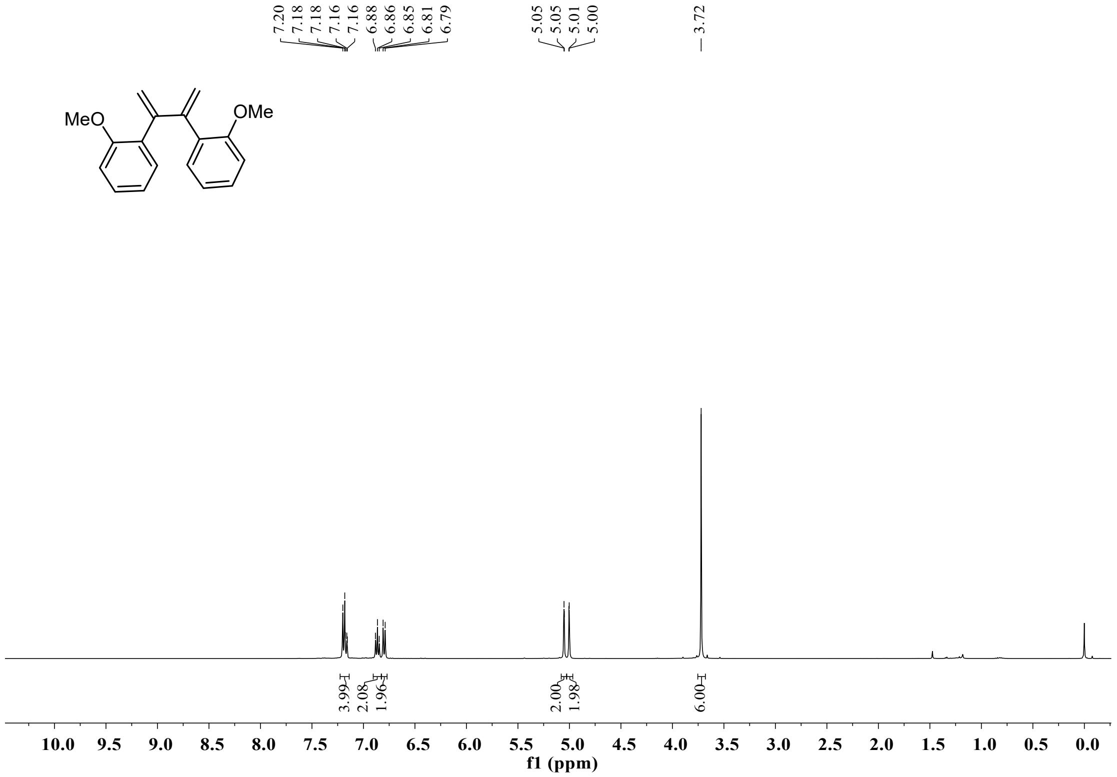

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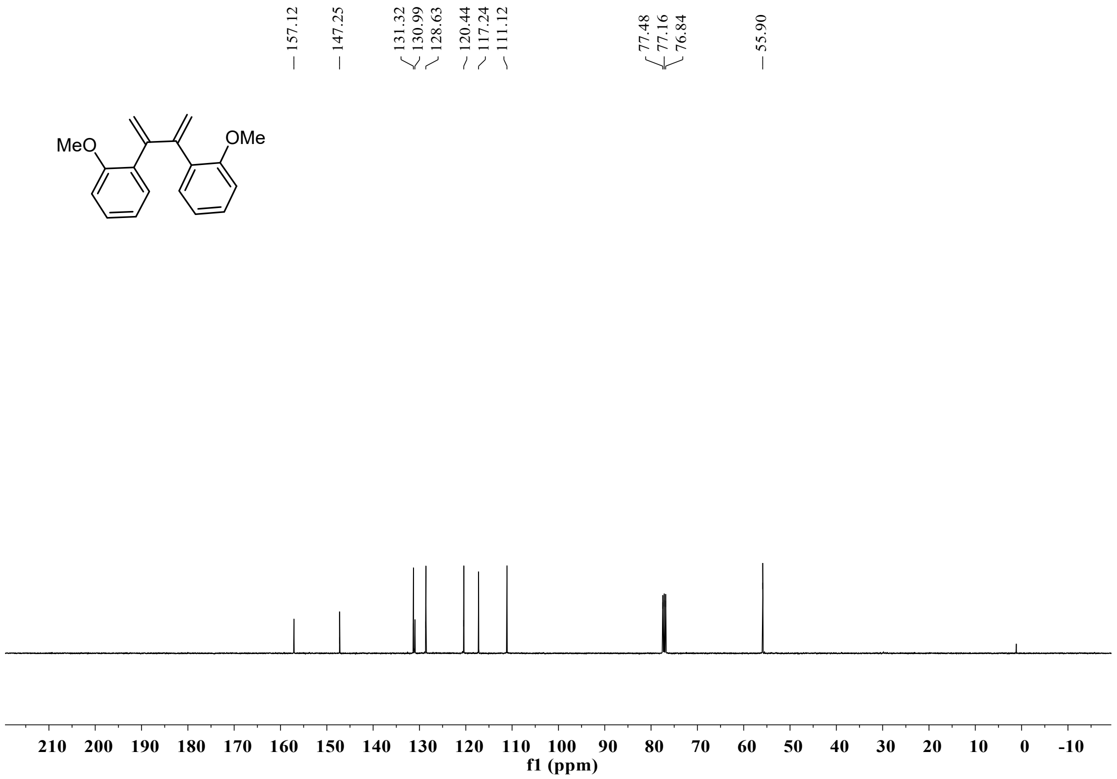

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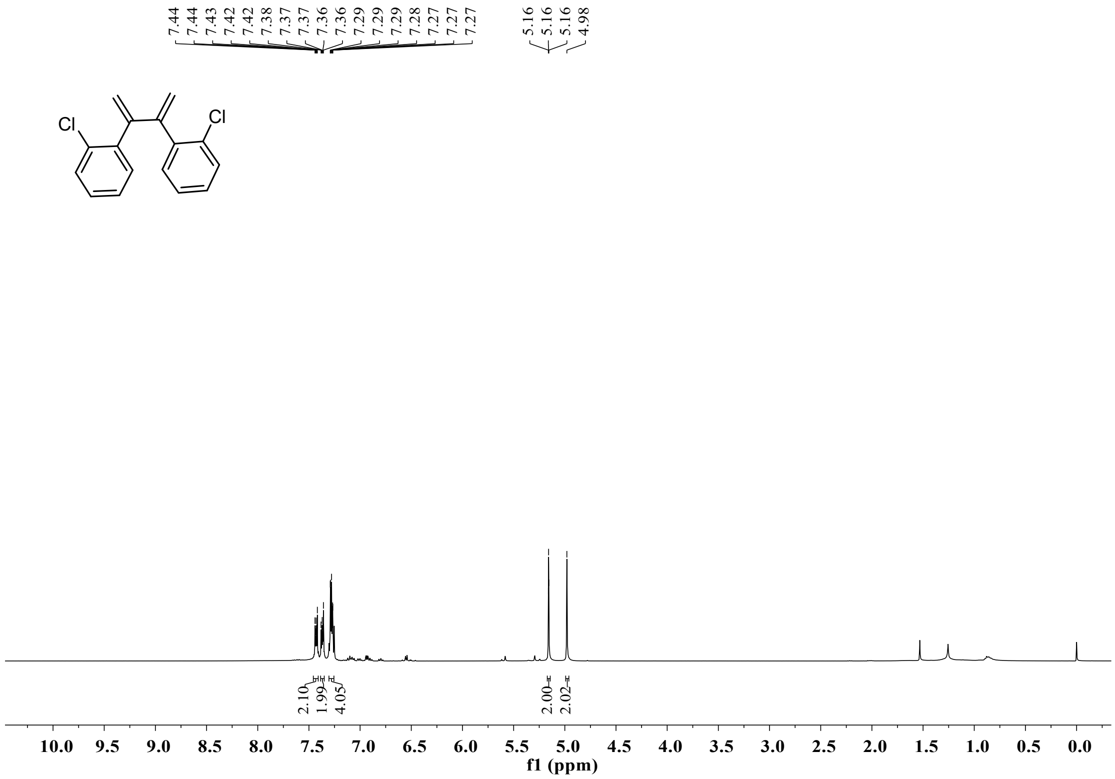

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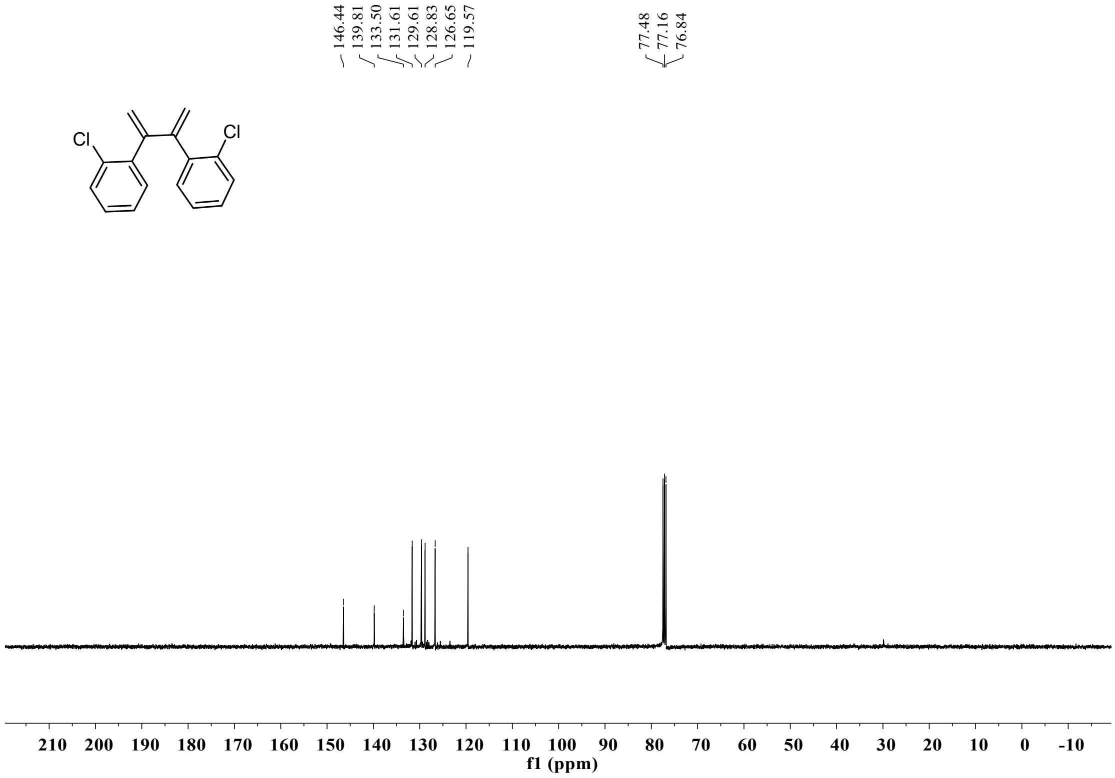

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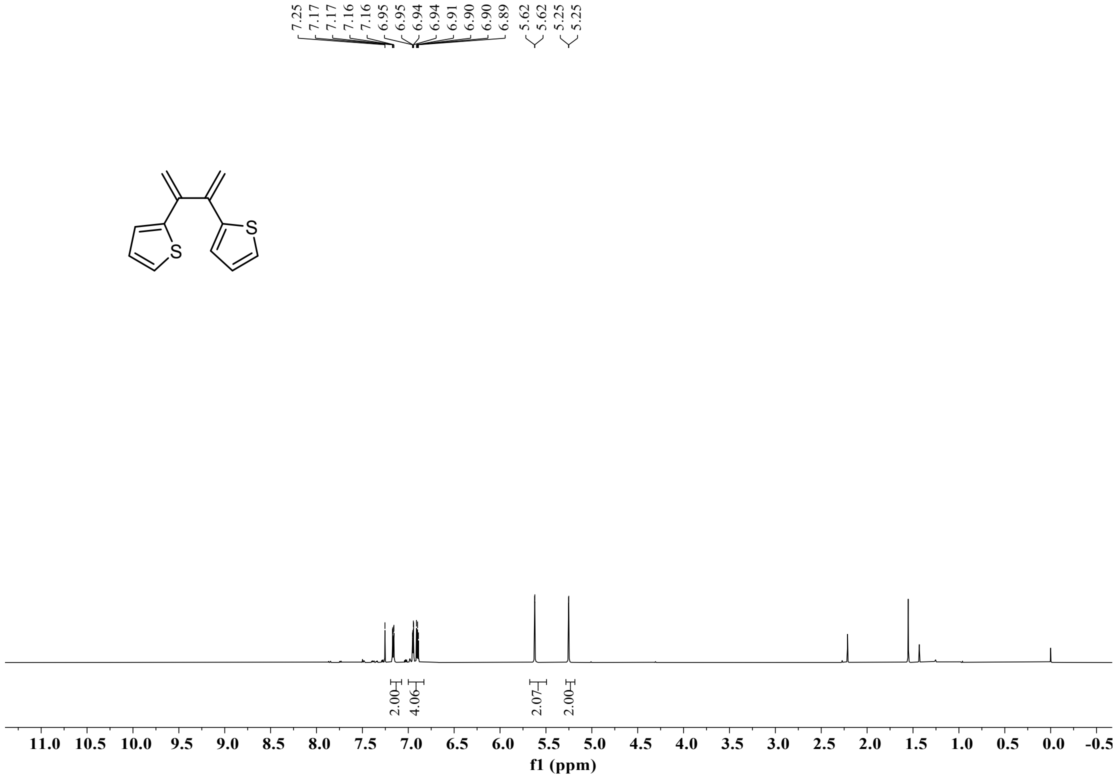

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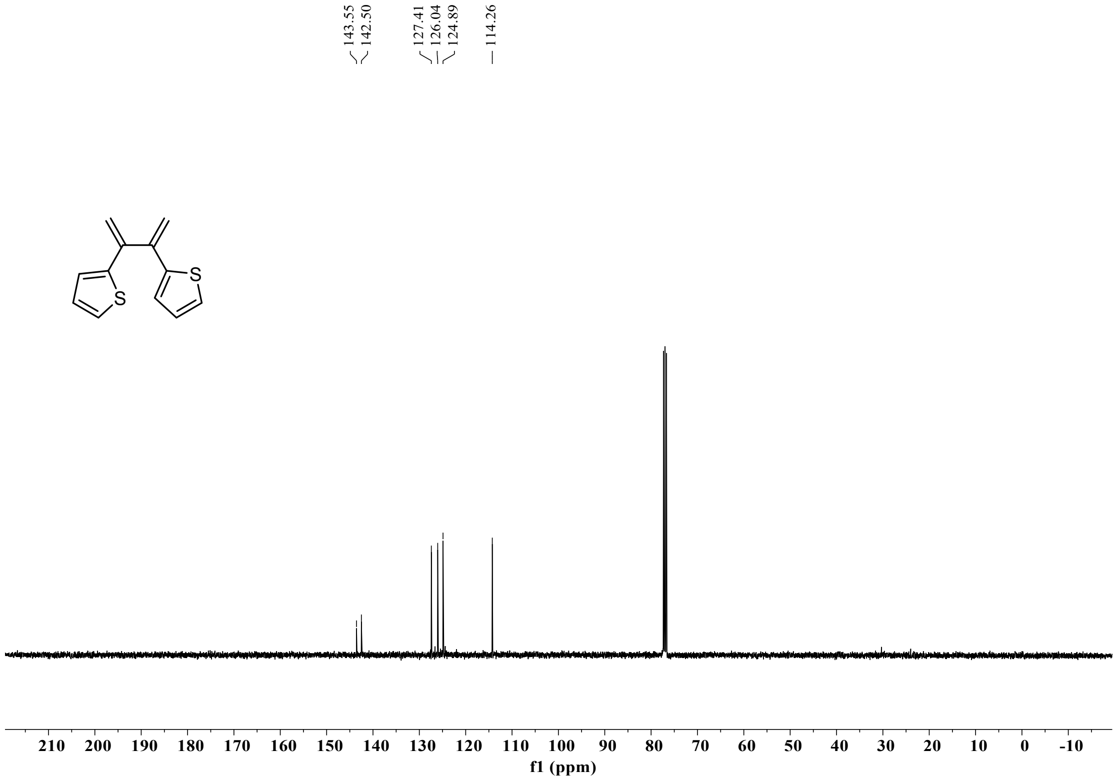

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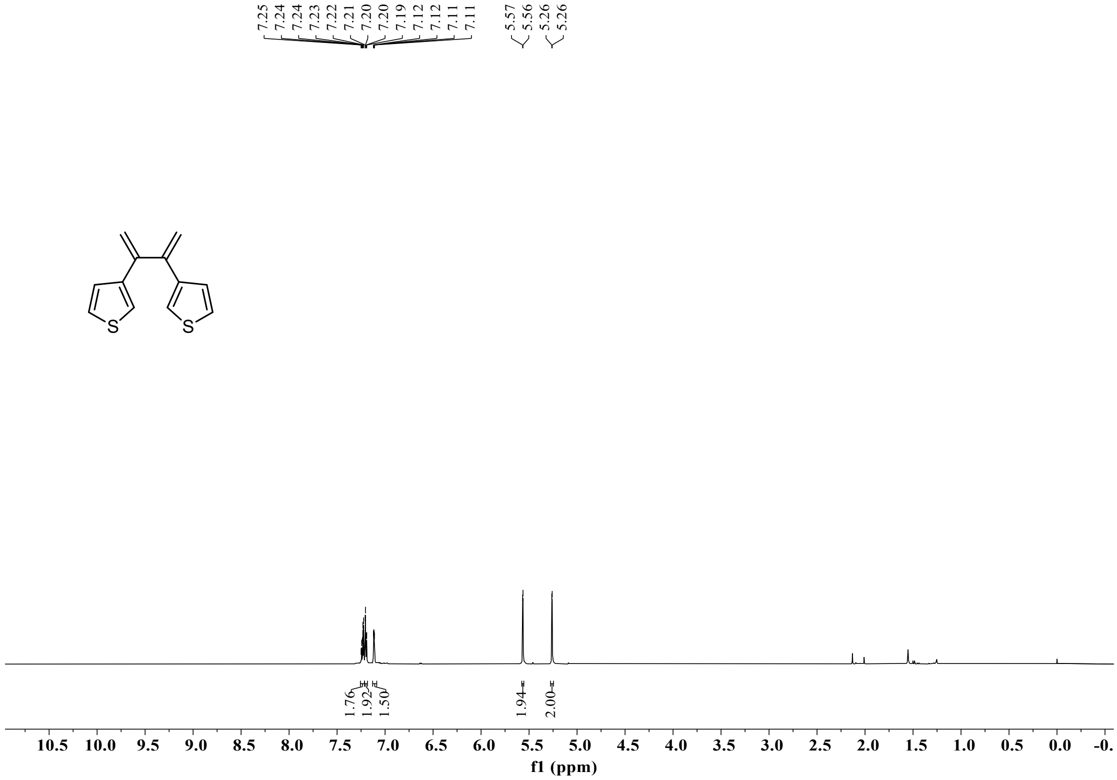

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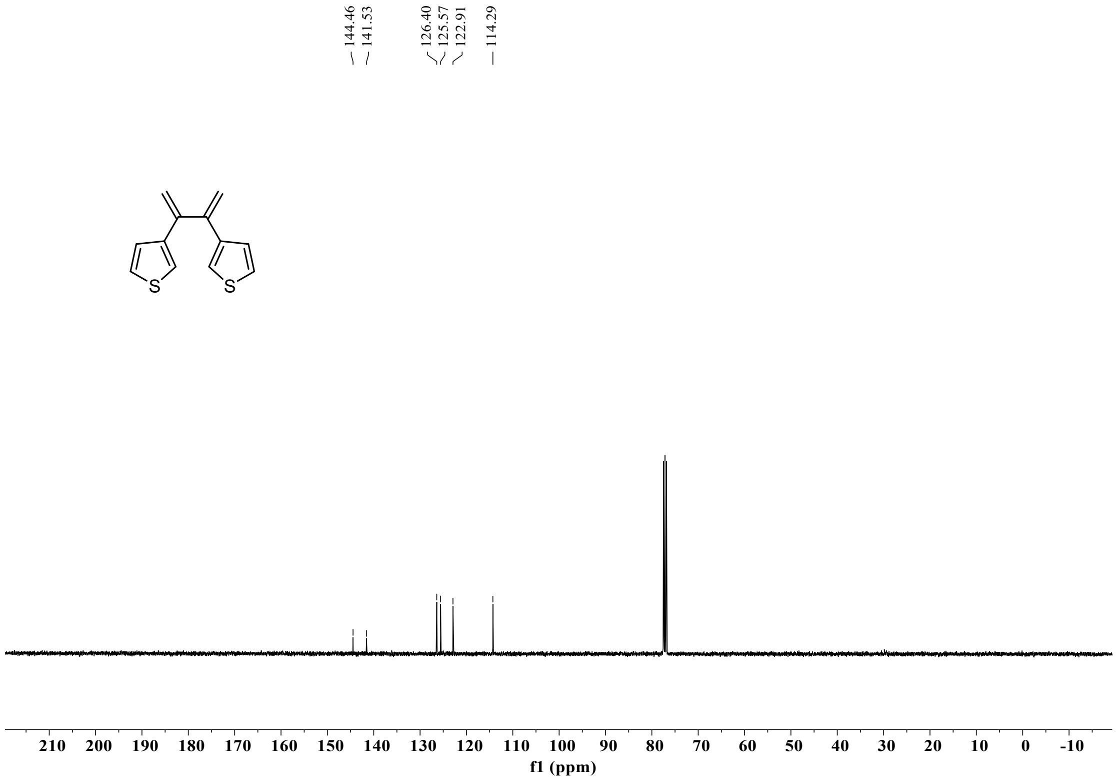

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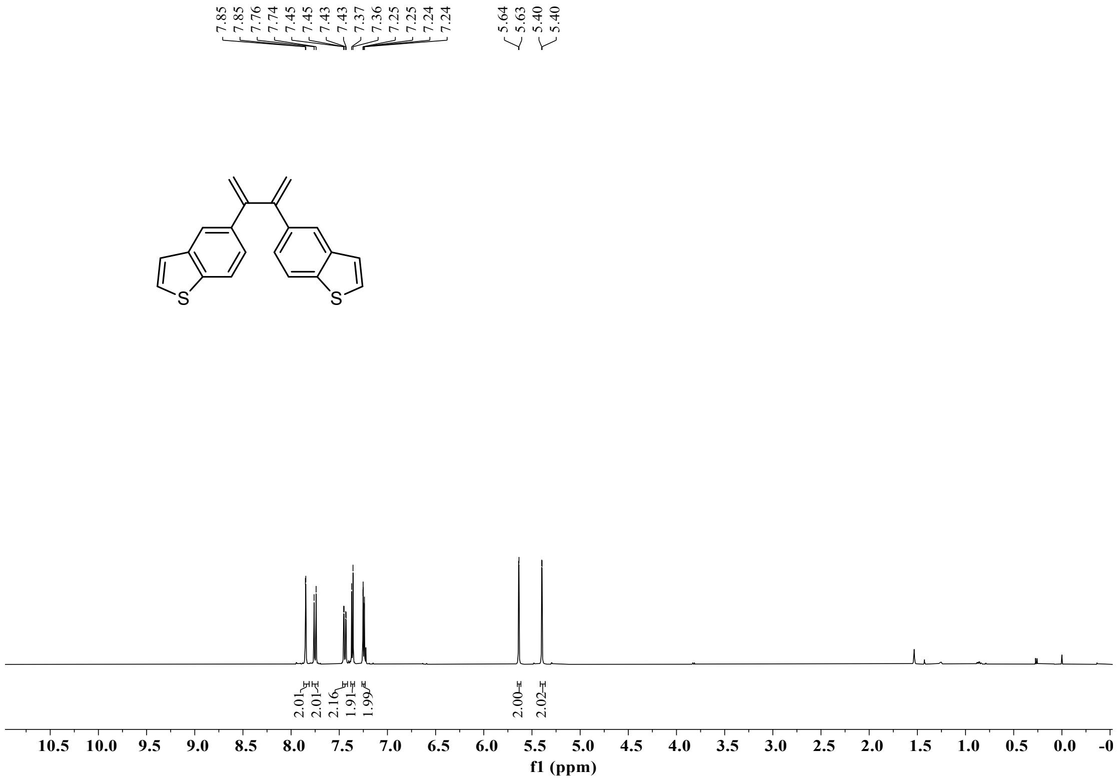

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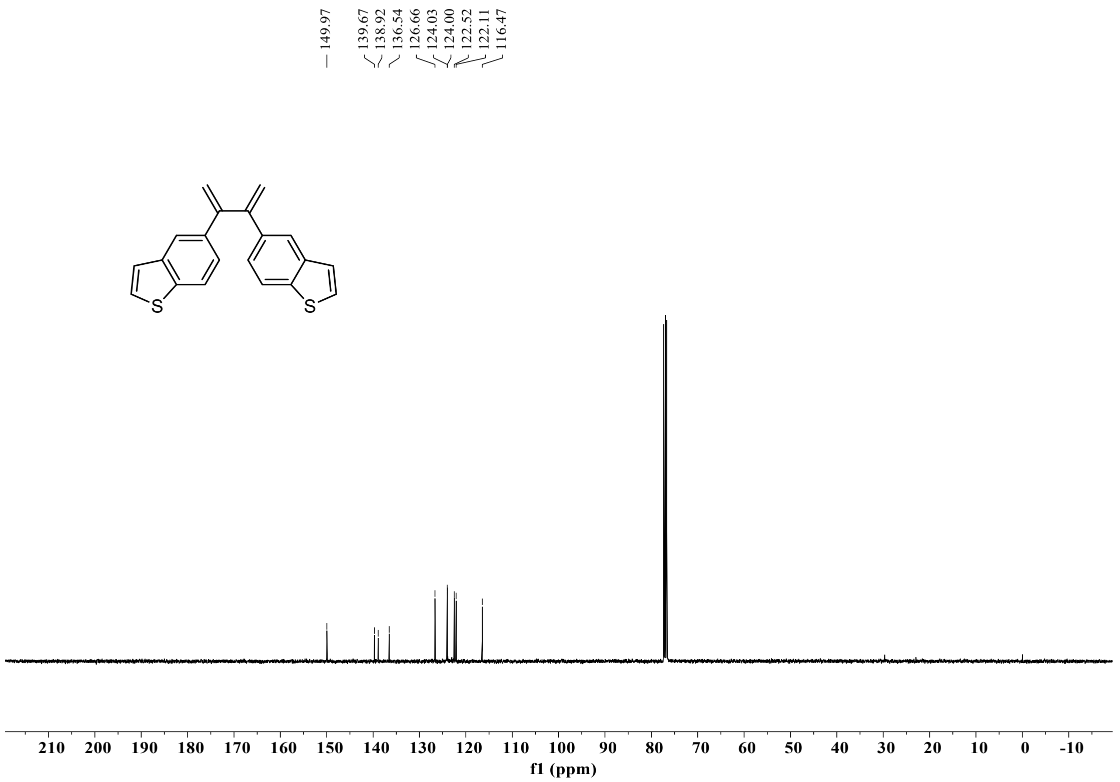

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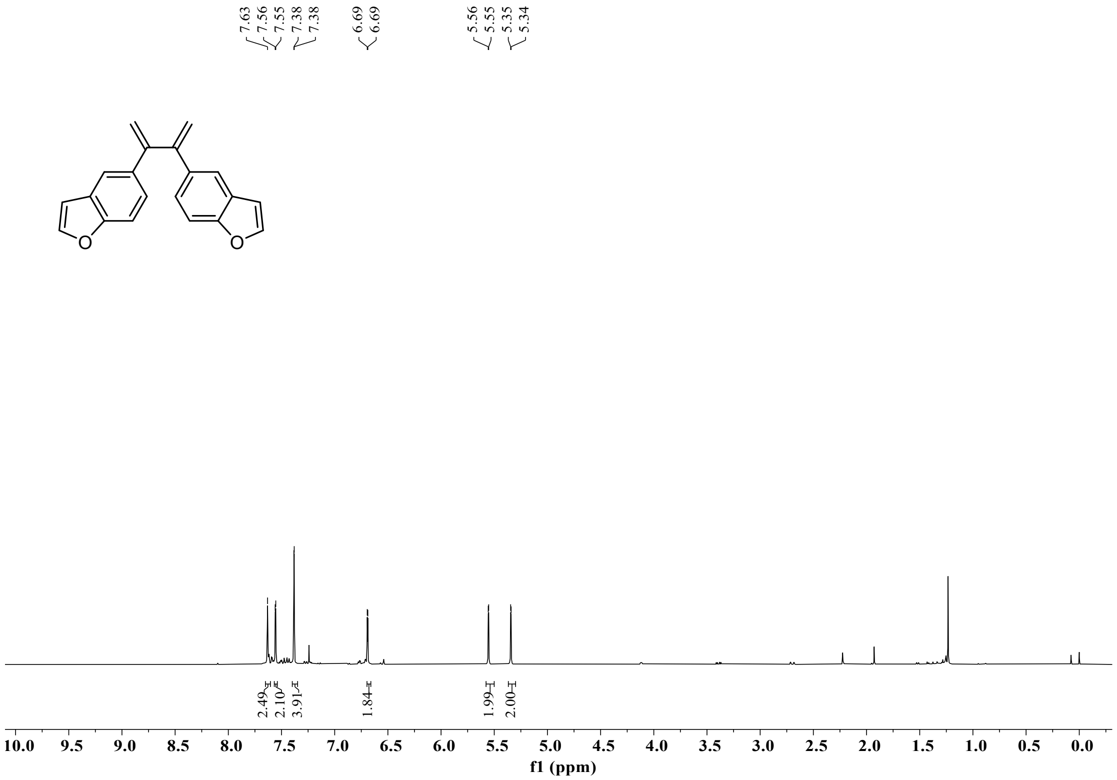

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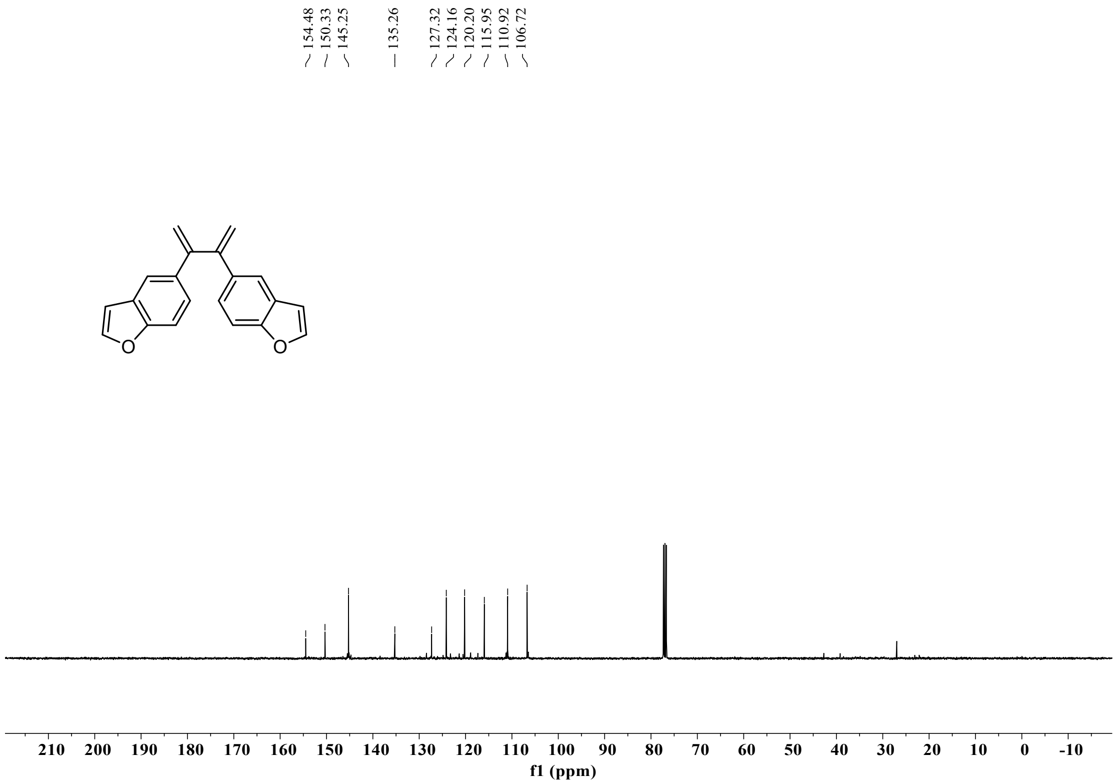

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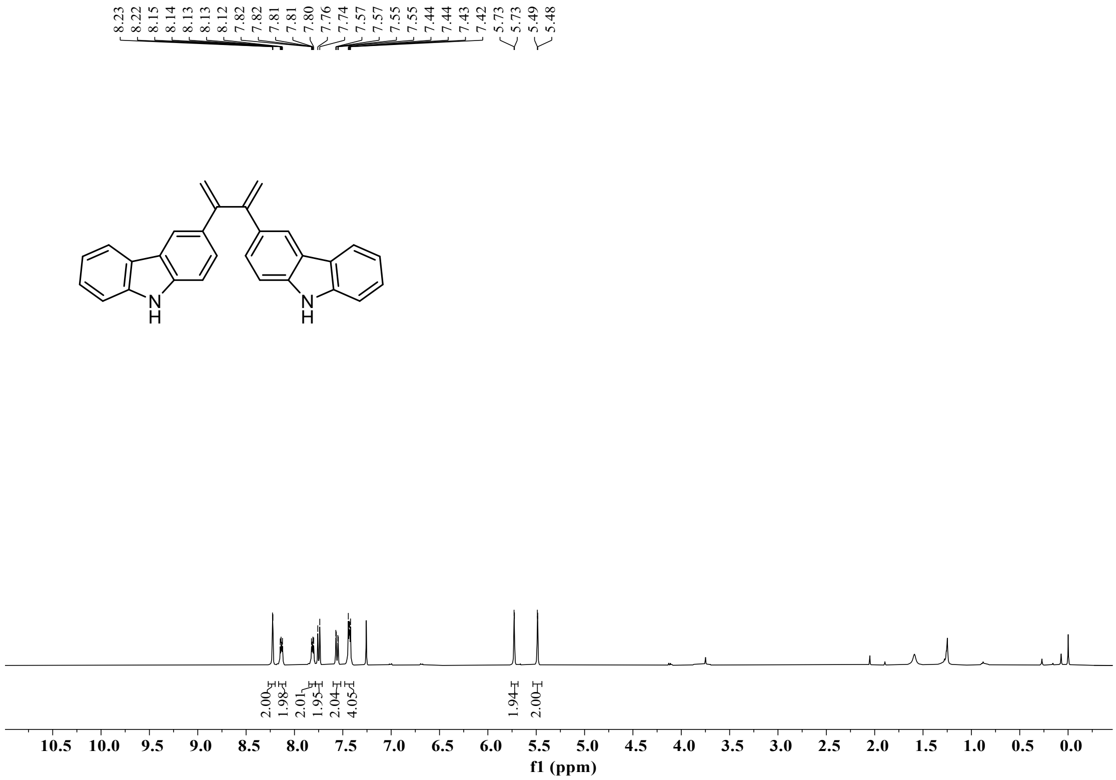

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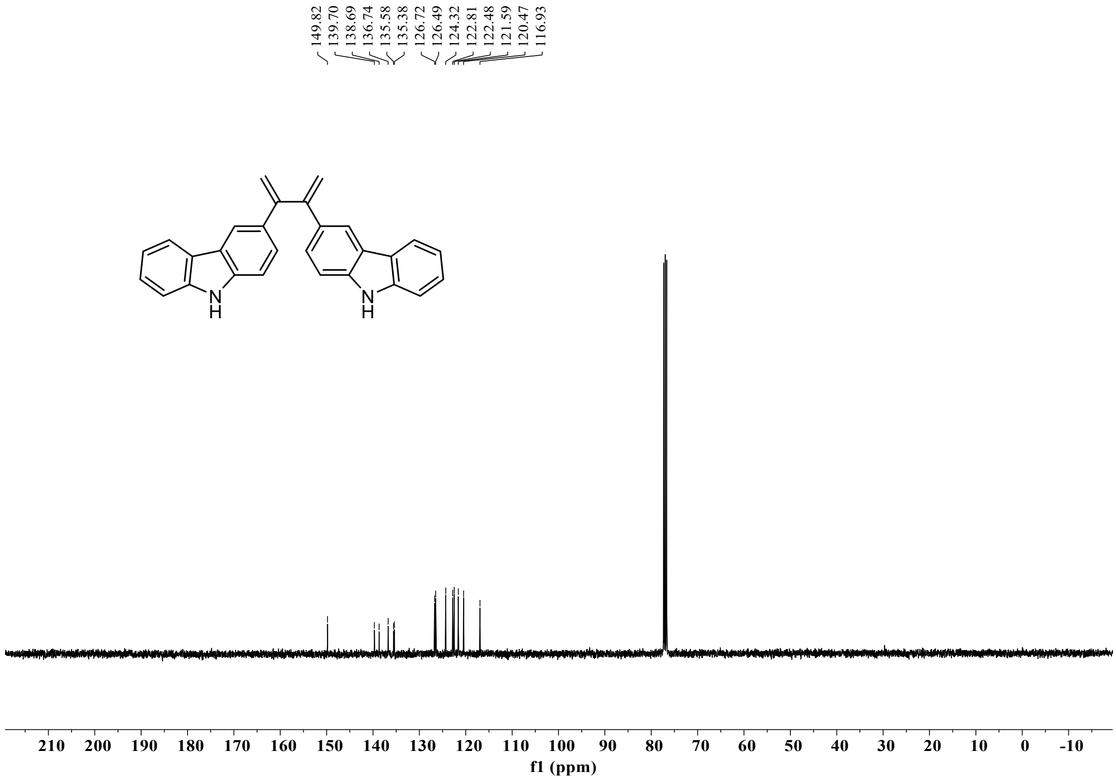

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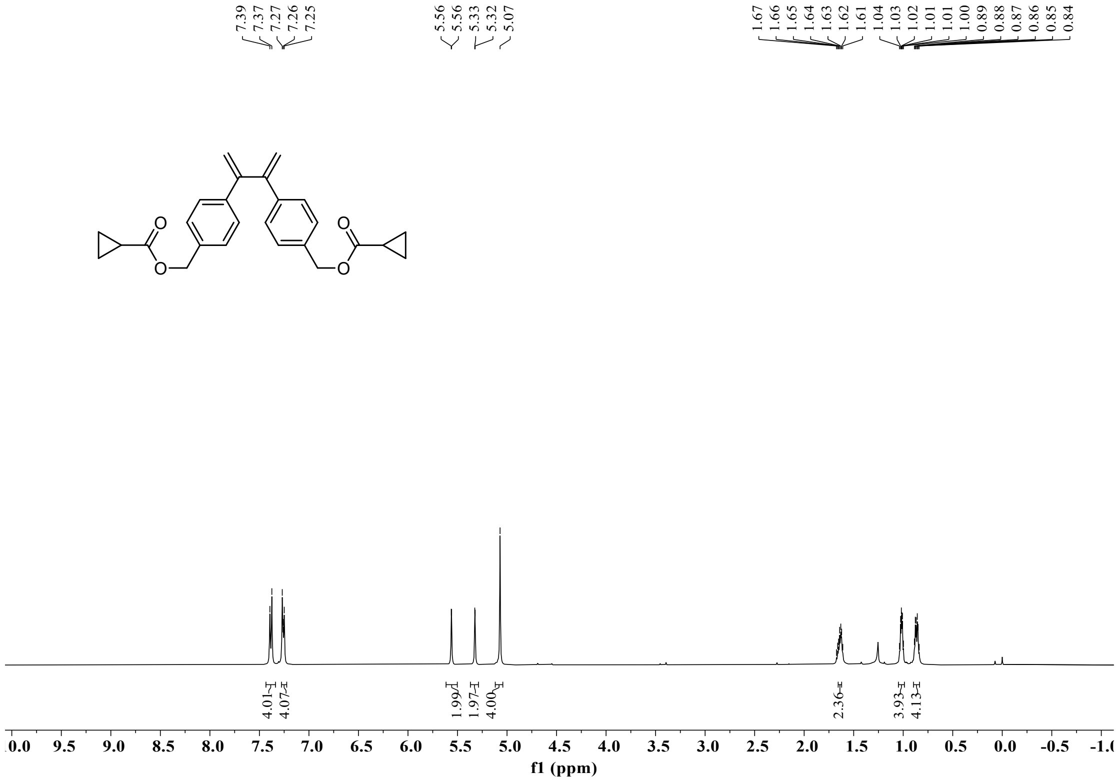
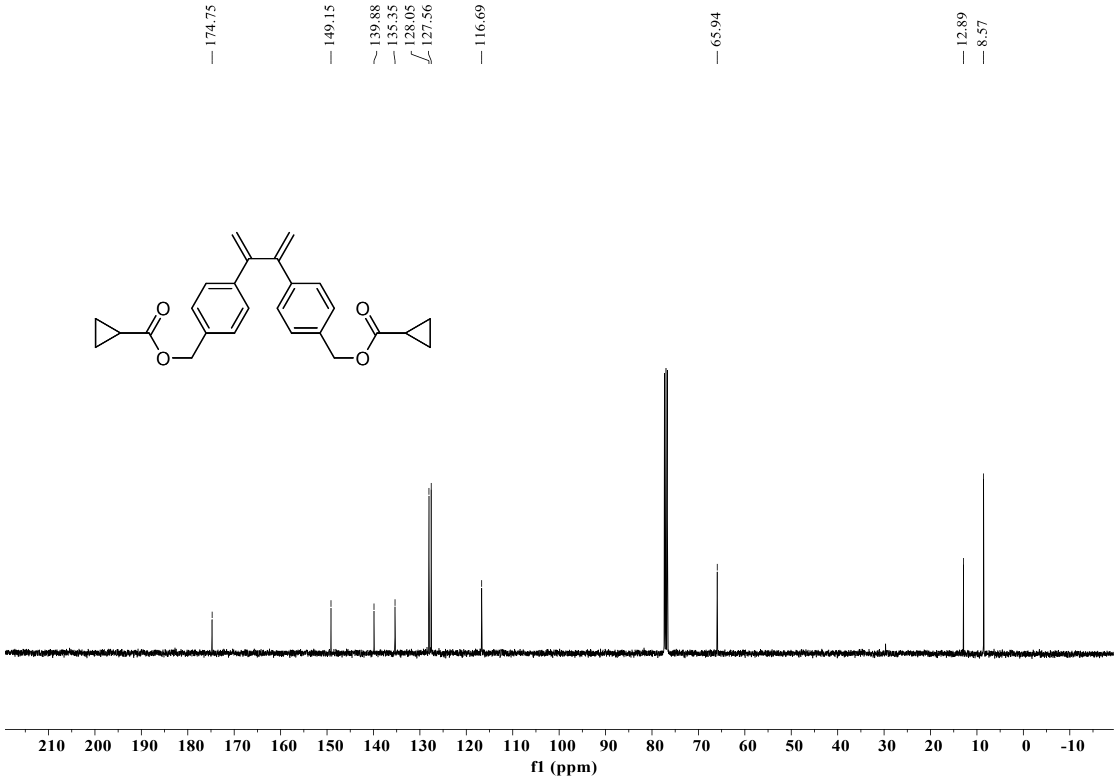
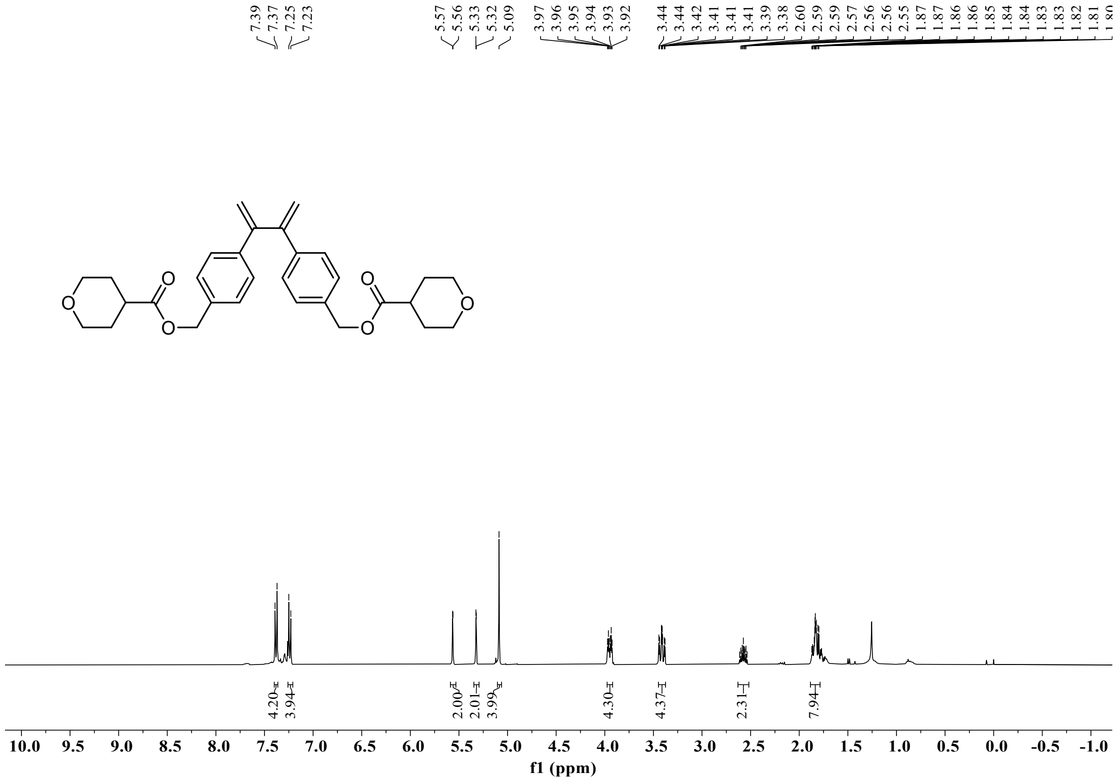


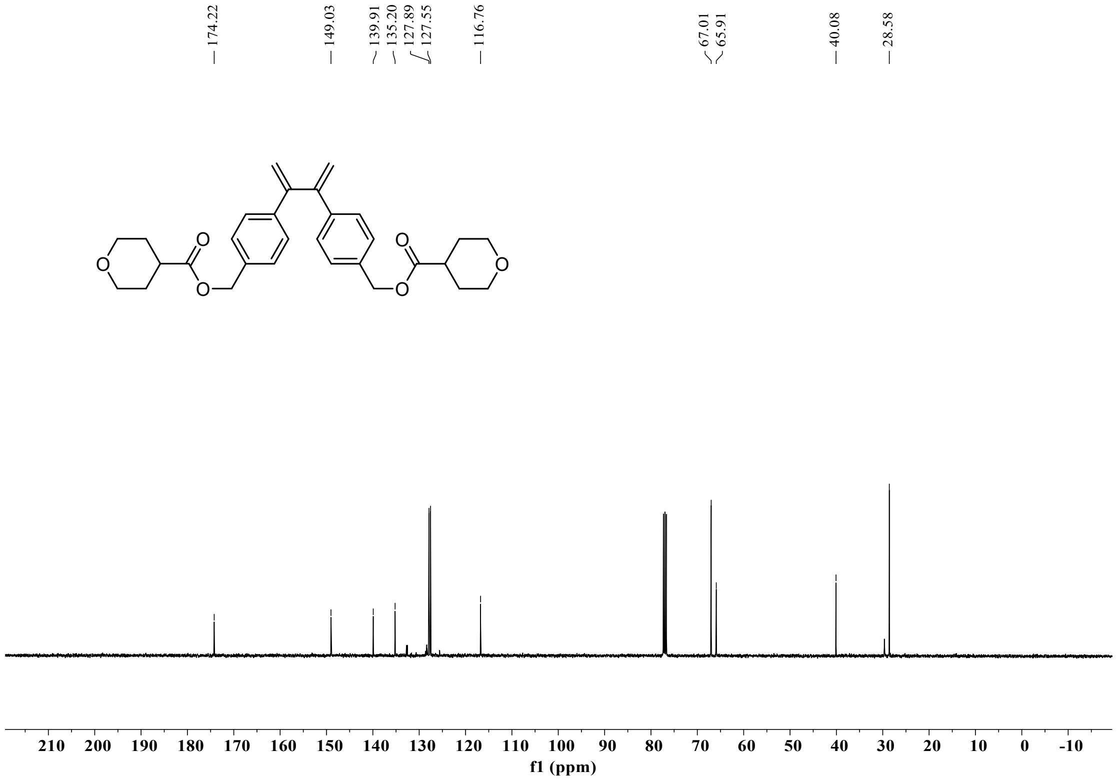
^{13}C NMR Spectra of compound **26**



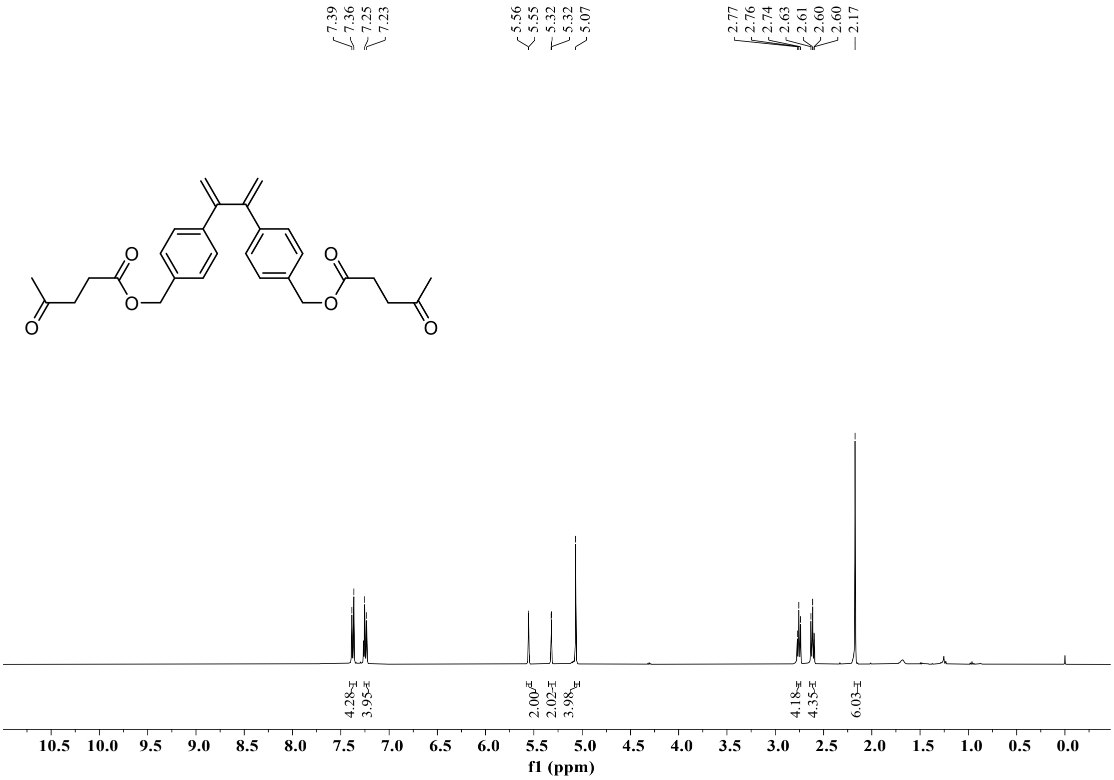
^{1}H NMR Spectra of compound **27**



^{13}C NMR Spectra of compound **27**



^{1}H NMR Spectra of compound **28**



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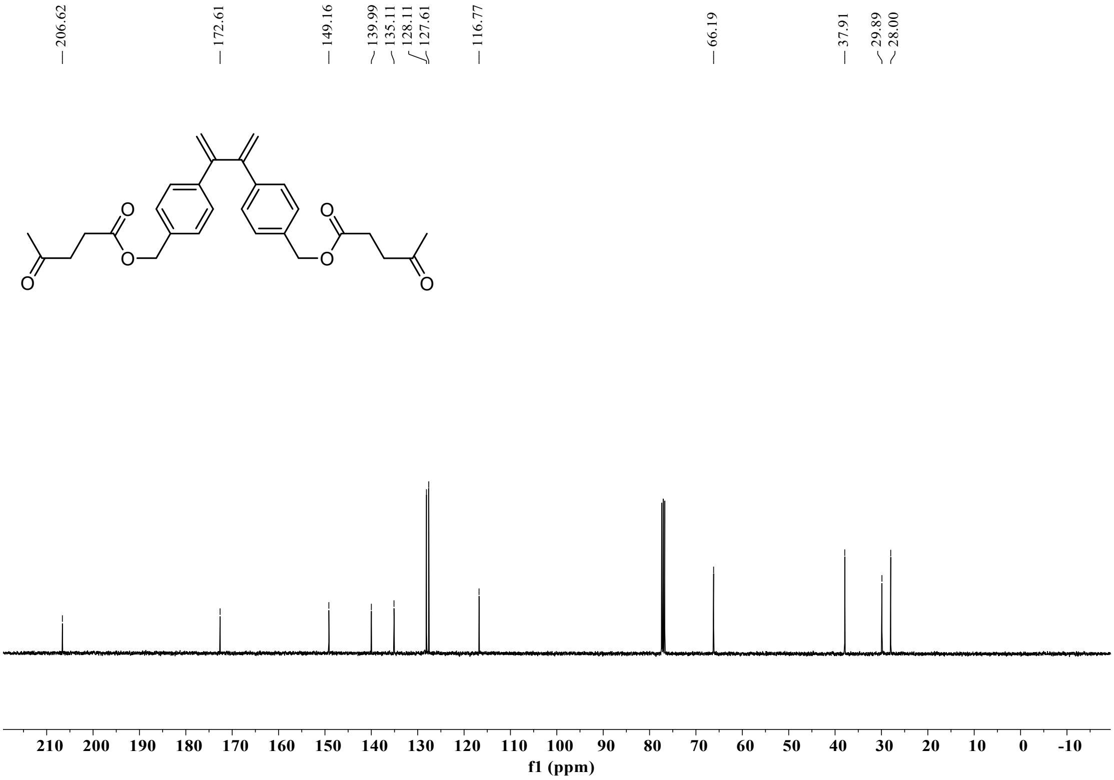

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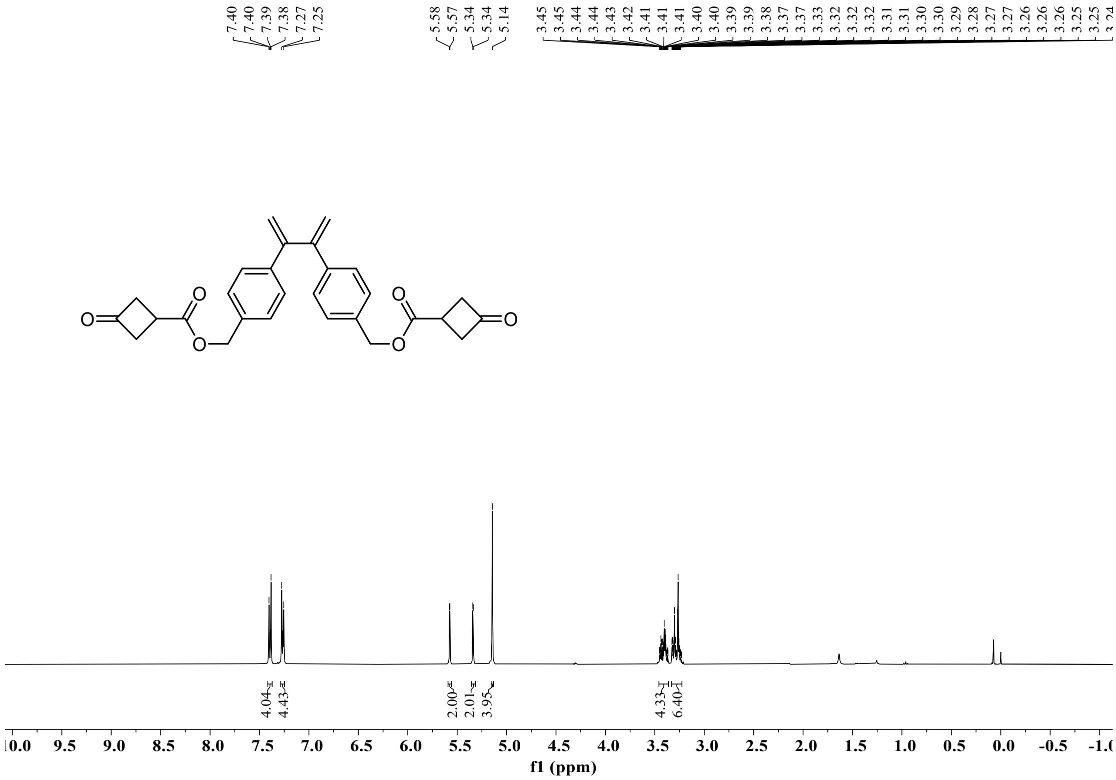

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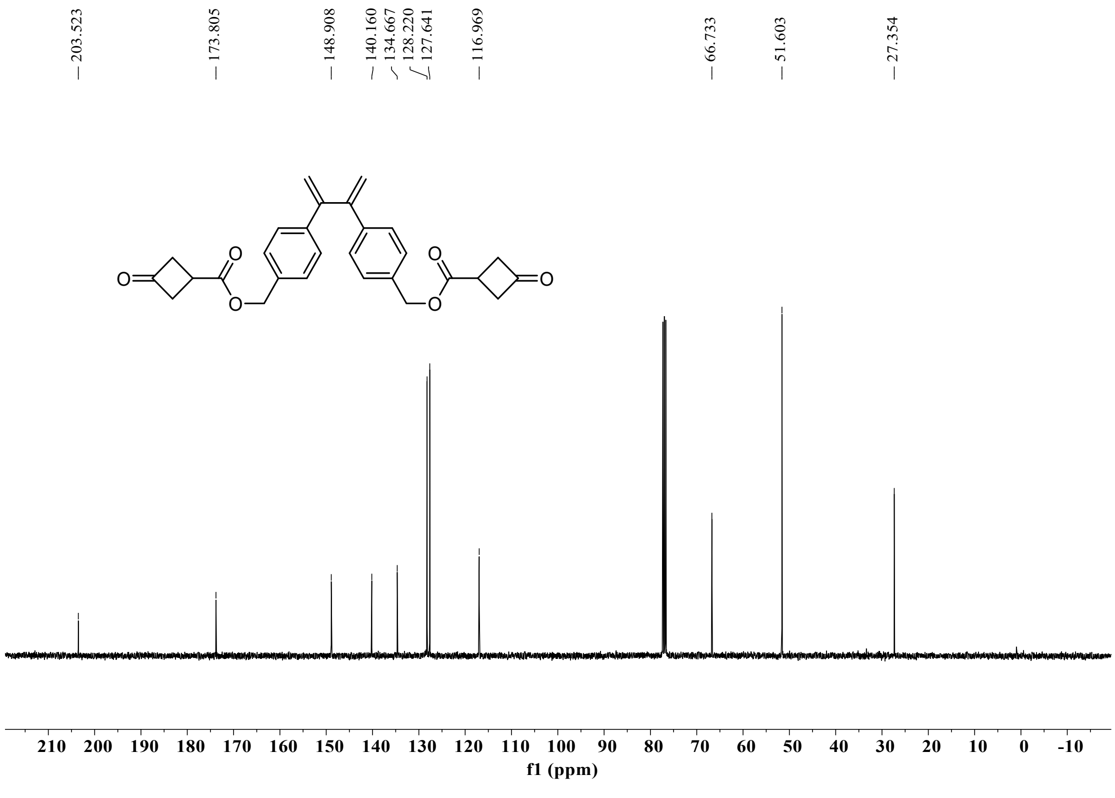

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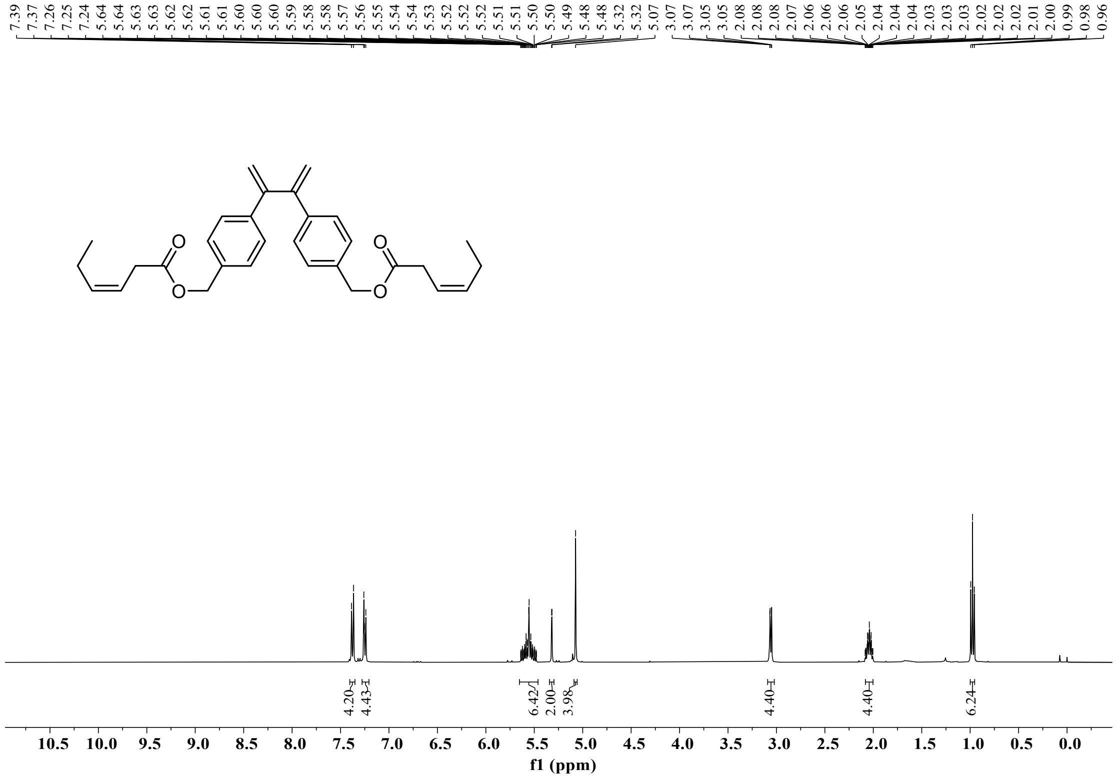
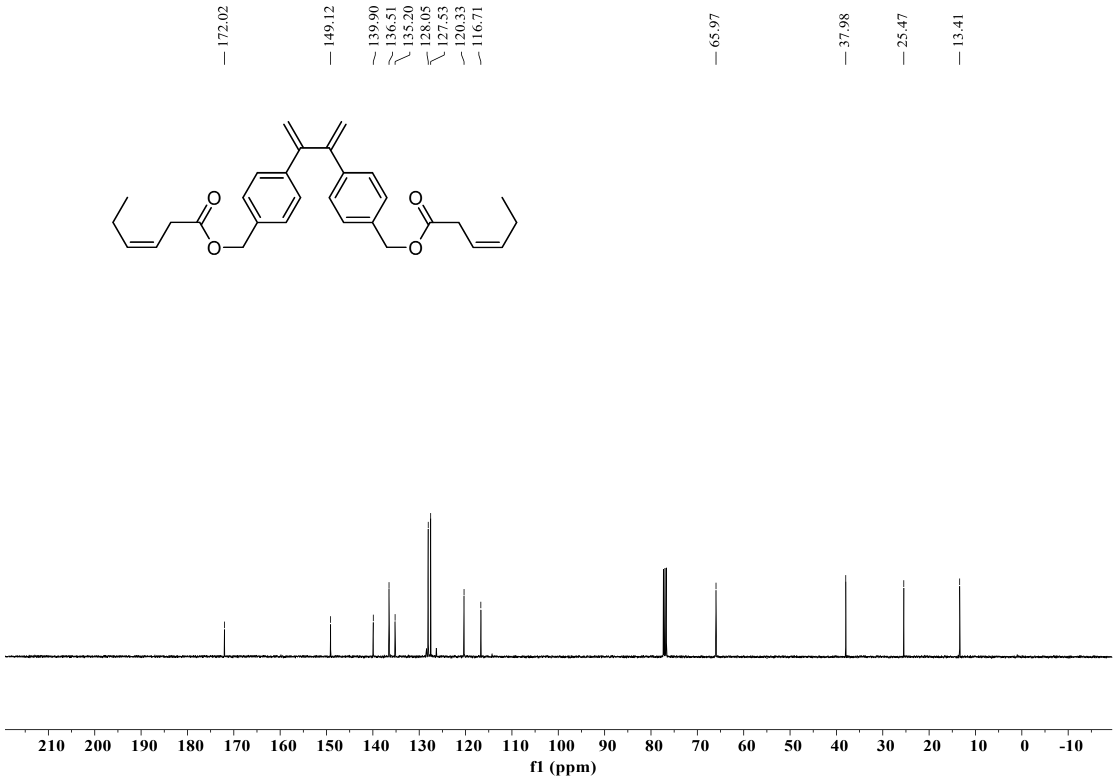
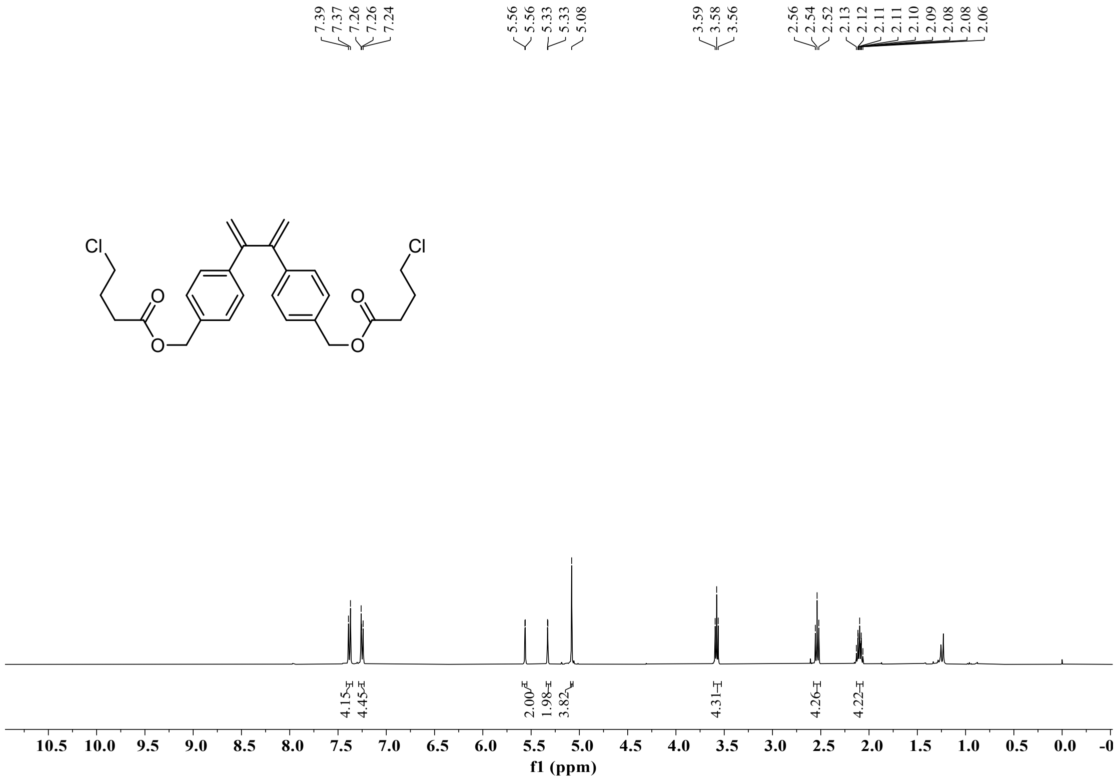


^{13}C NMR Spectra of compound 3**0**



^{1}H NMR Spectra of compound **31**



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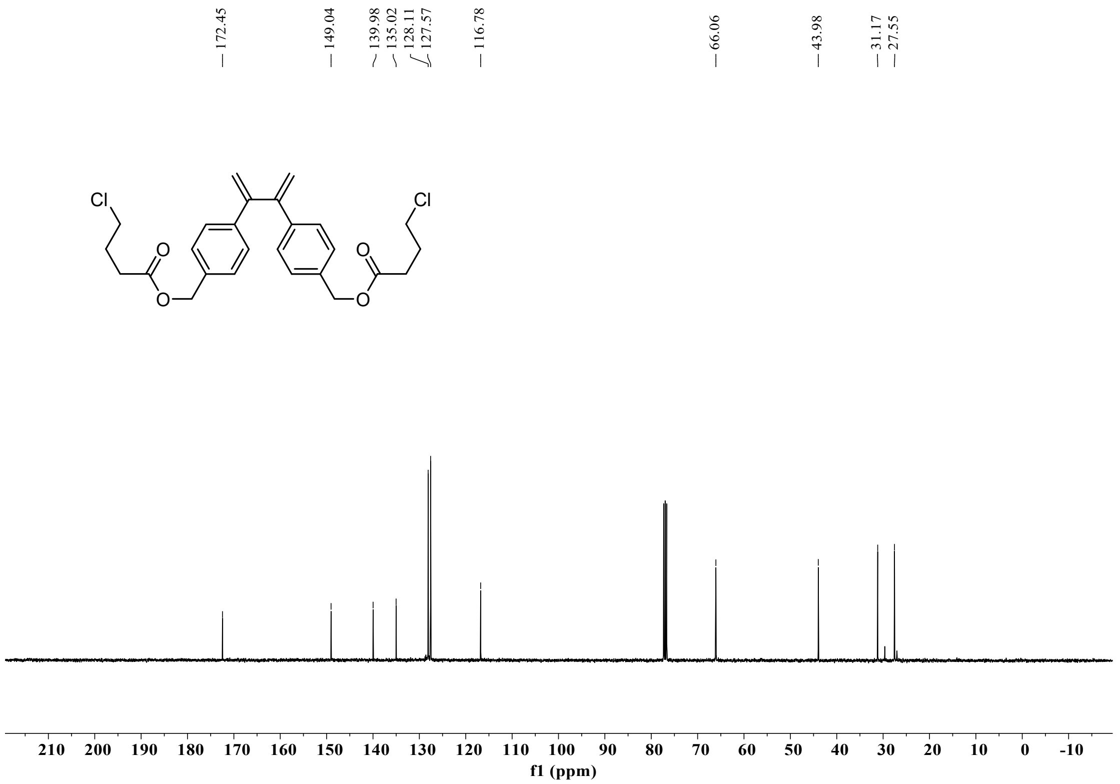

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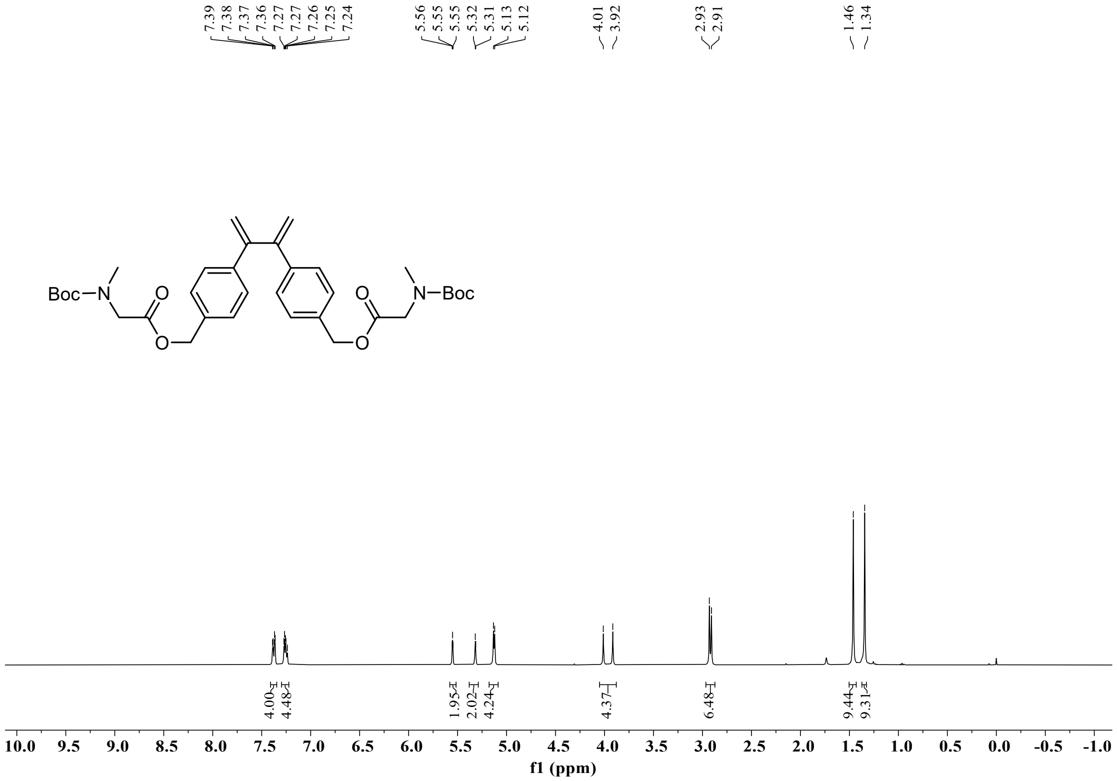

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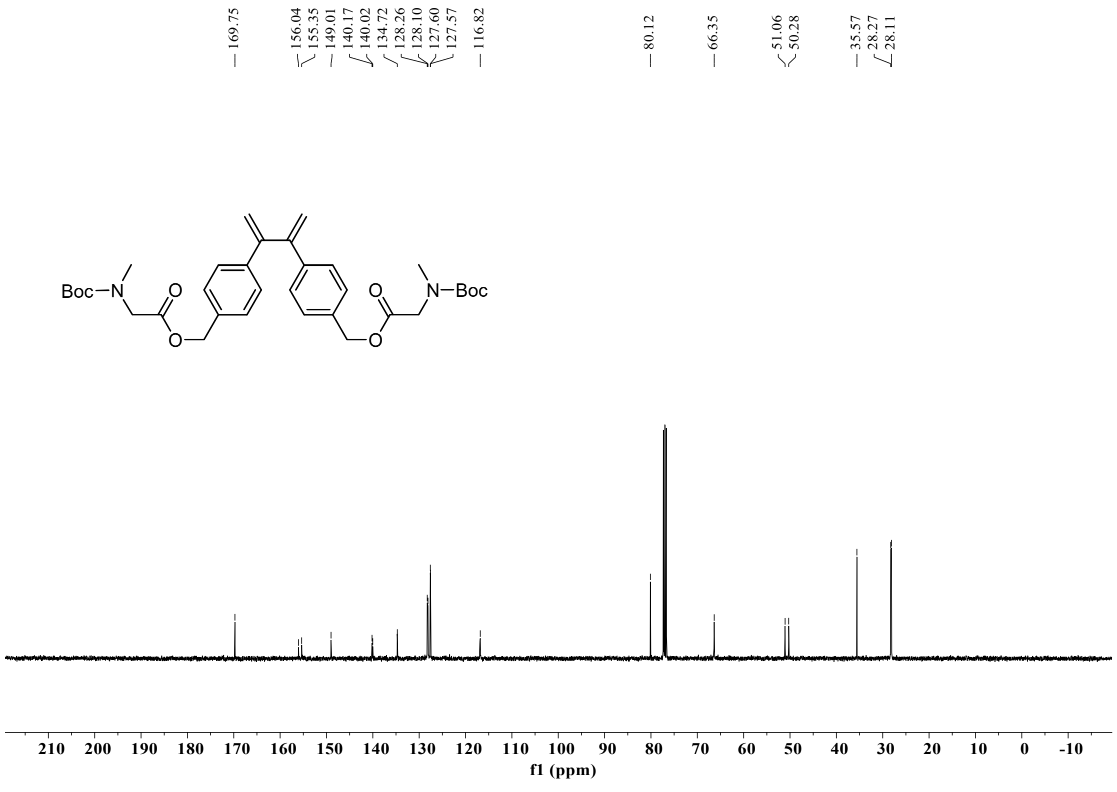

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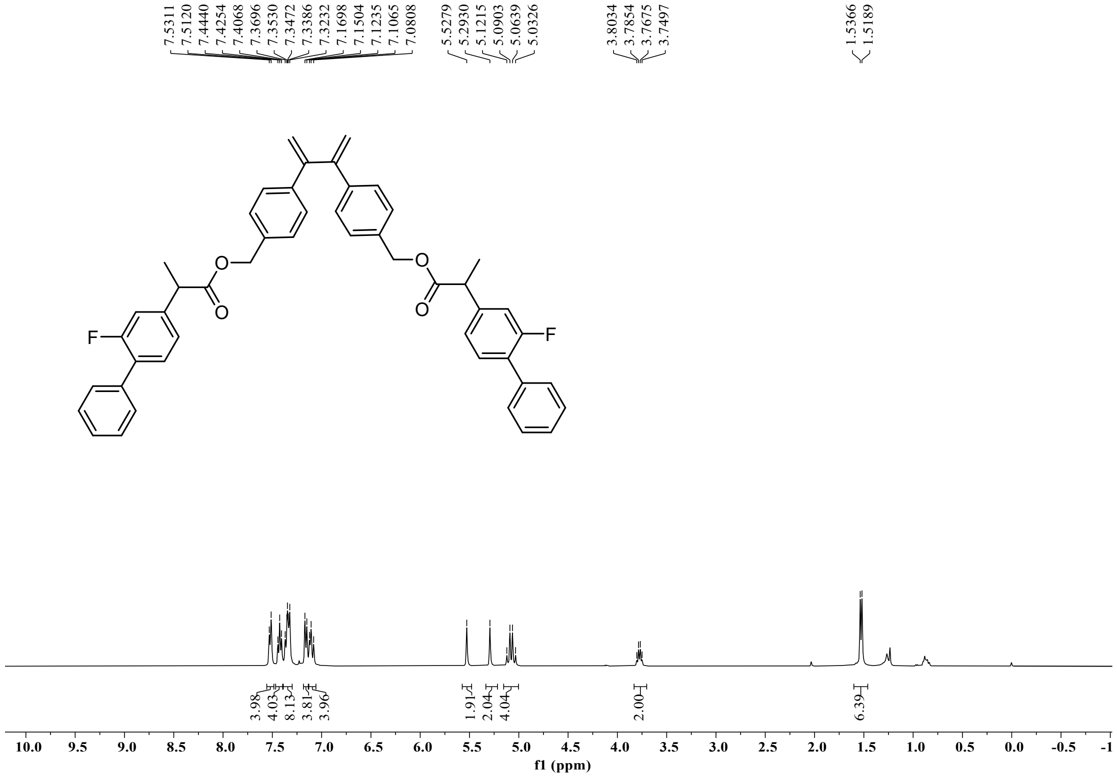

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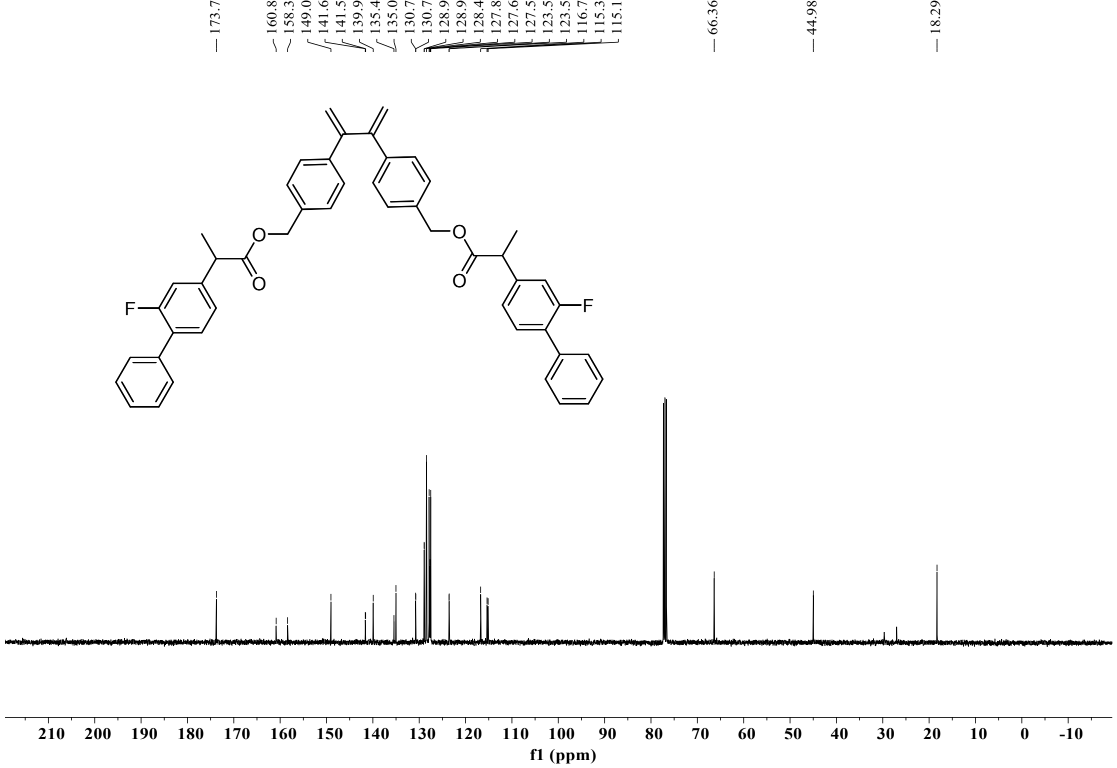
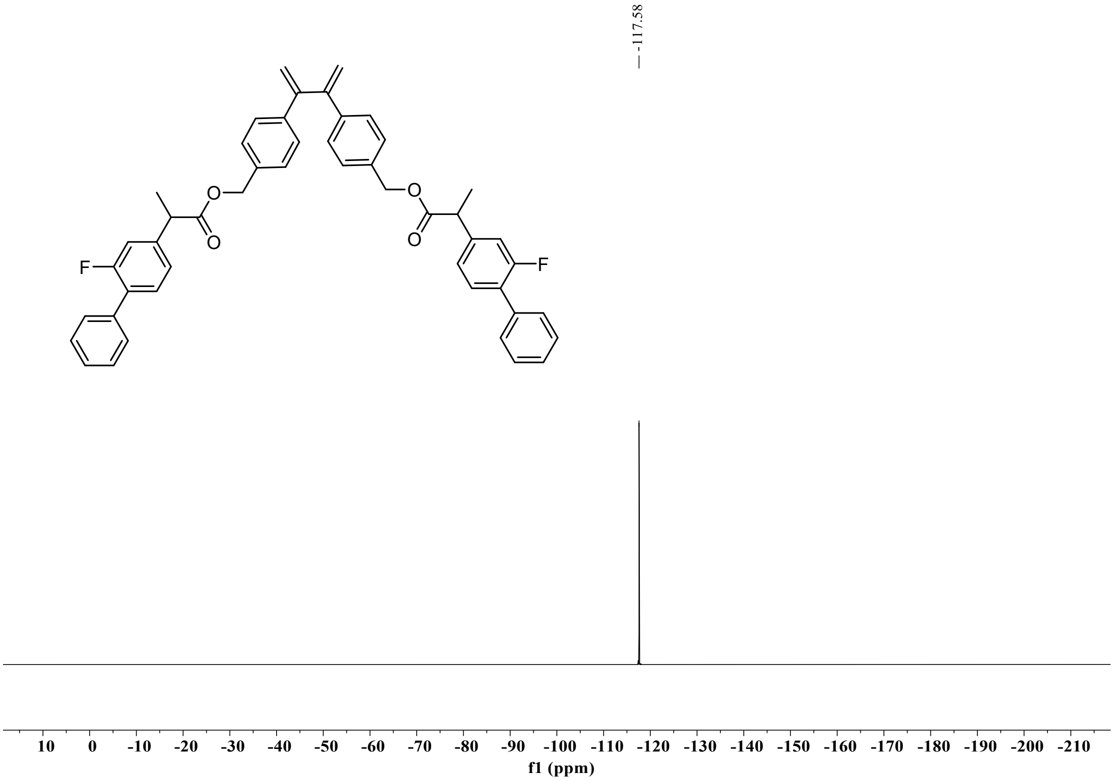


^{19}F NMR Spectra of compound **33**



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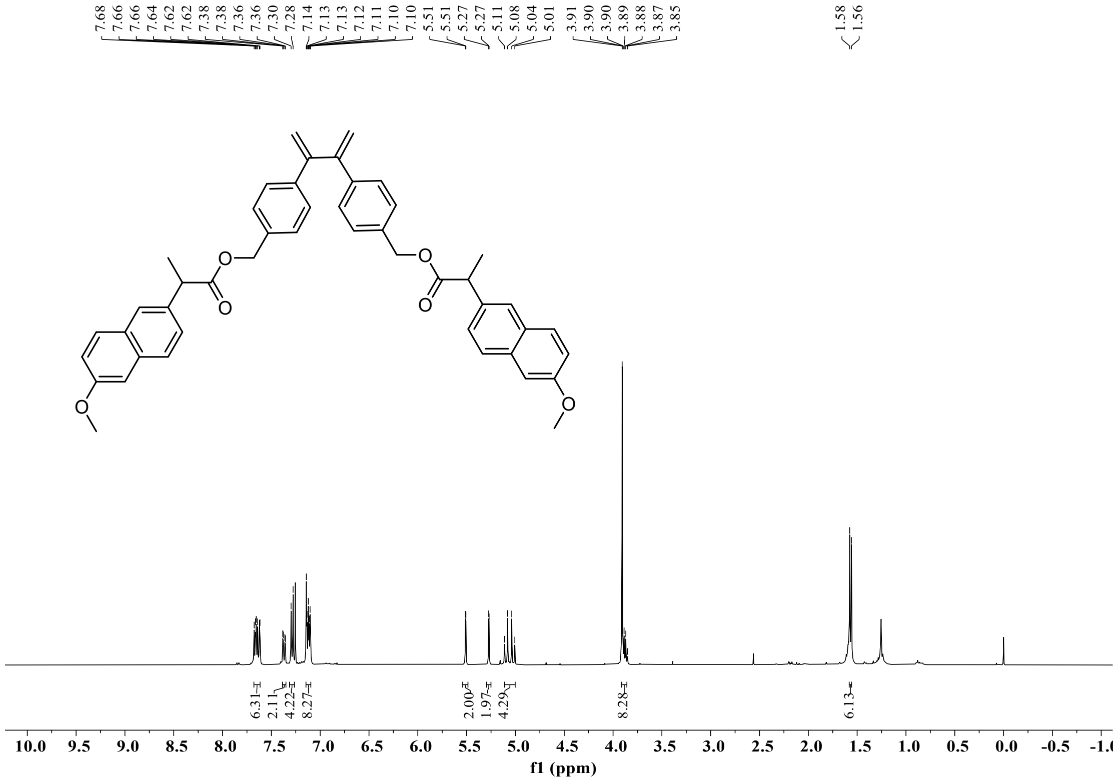

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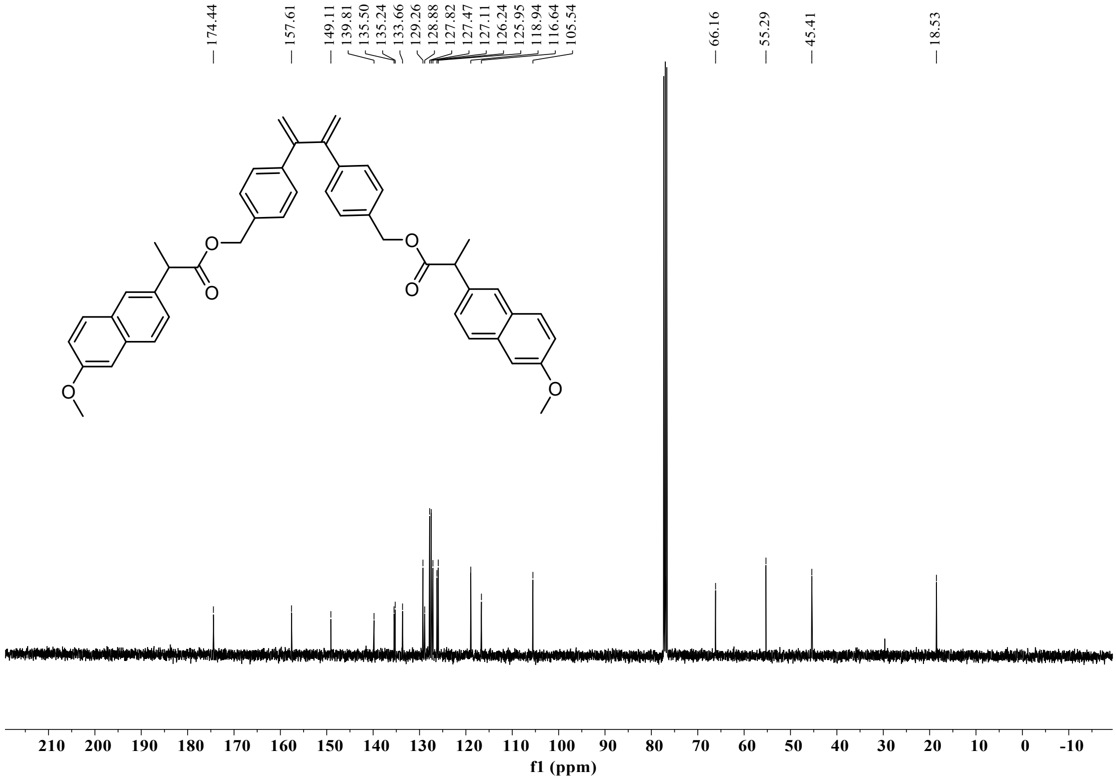

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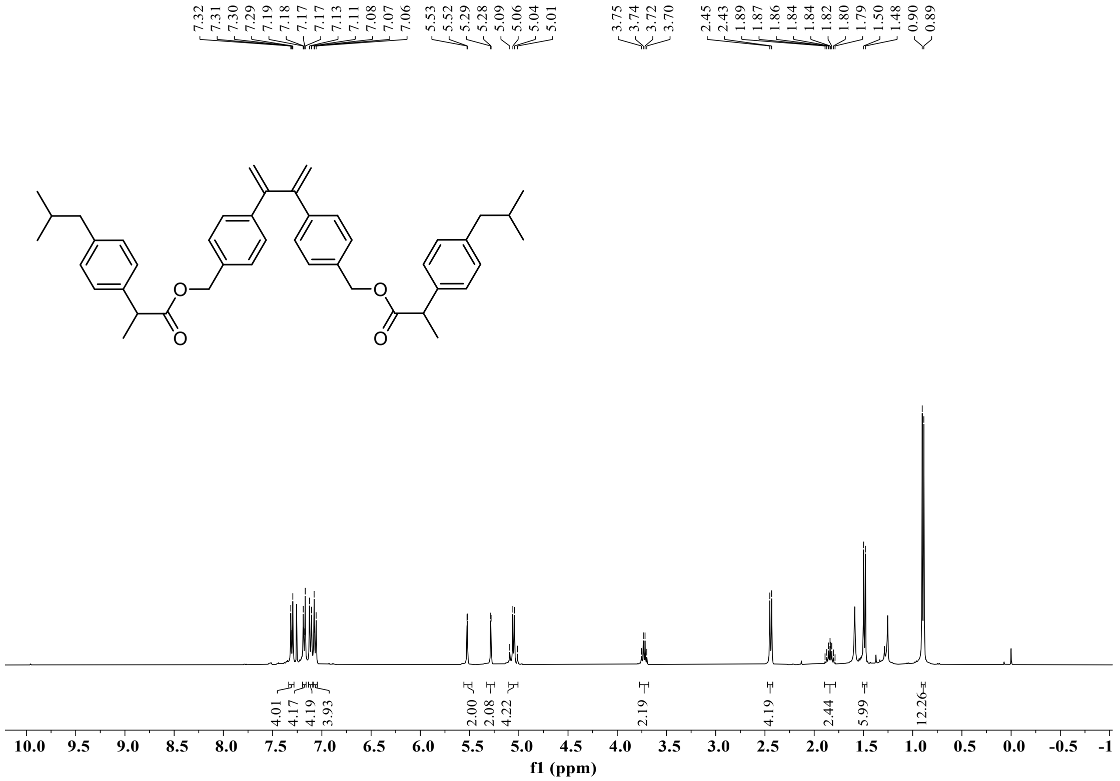

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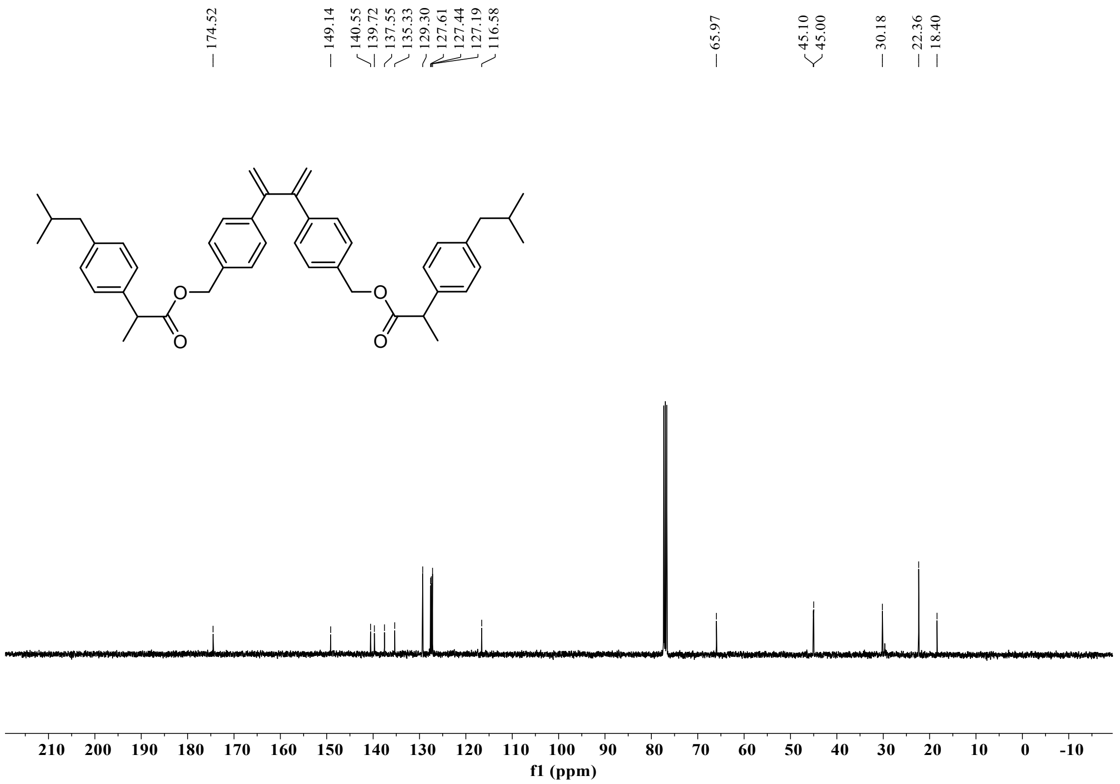

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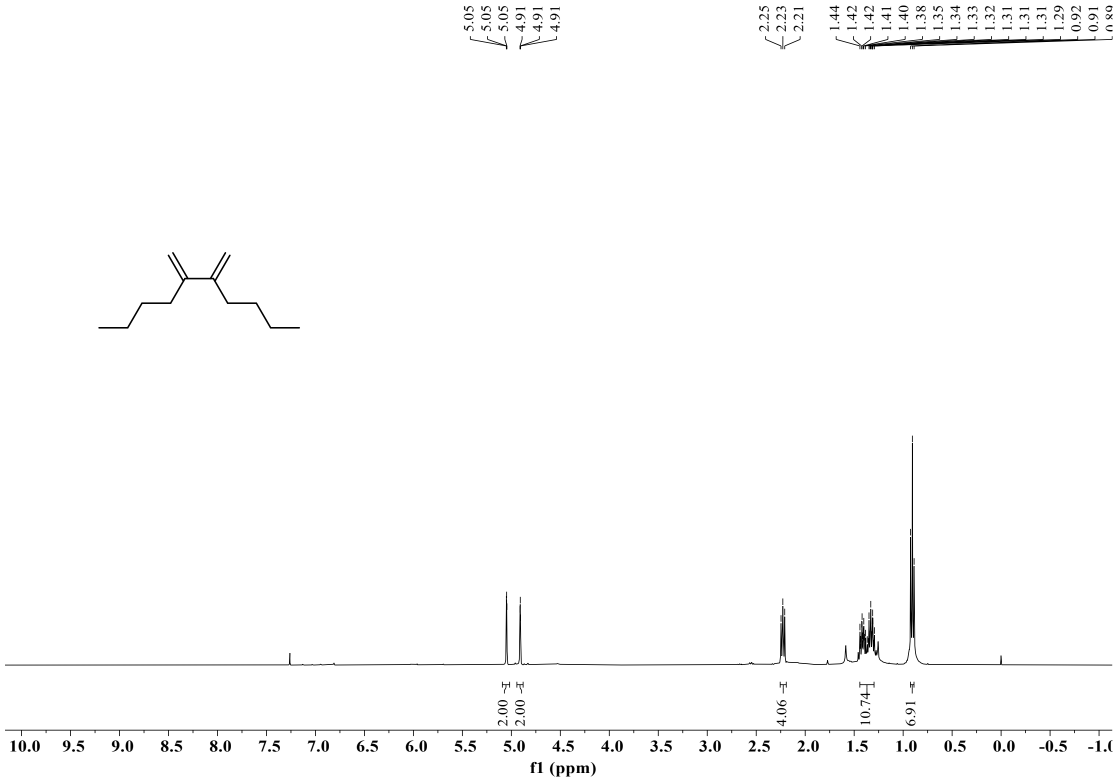

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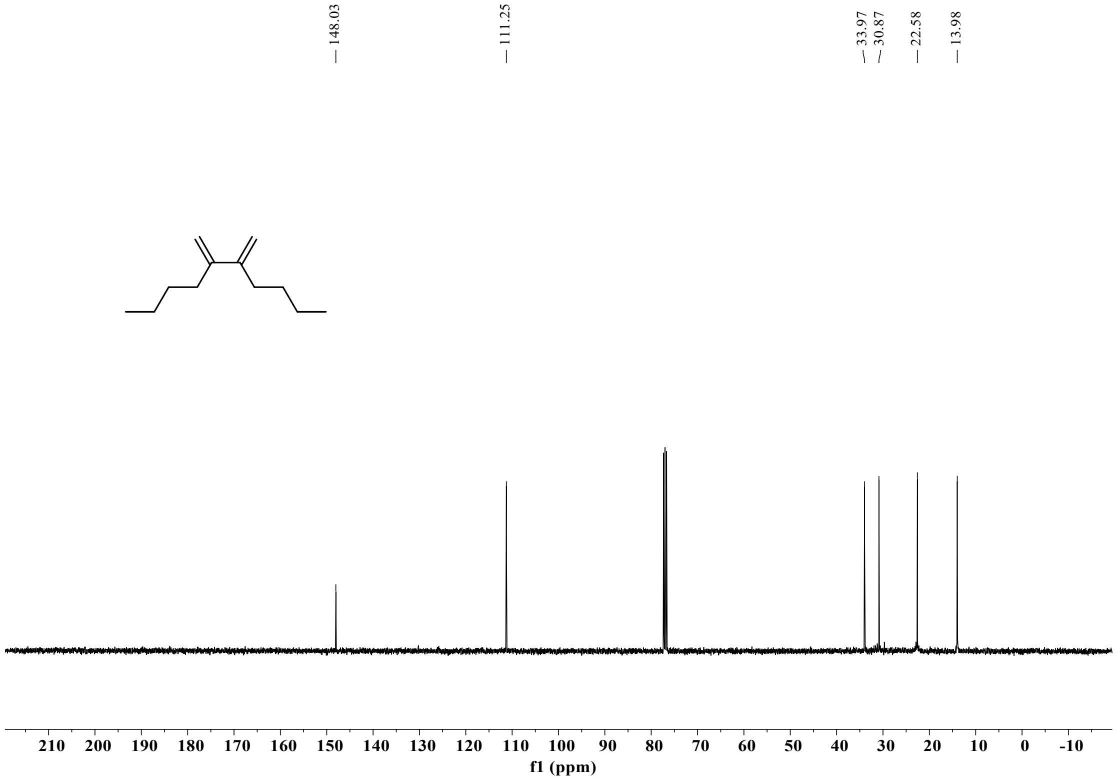

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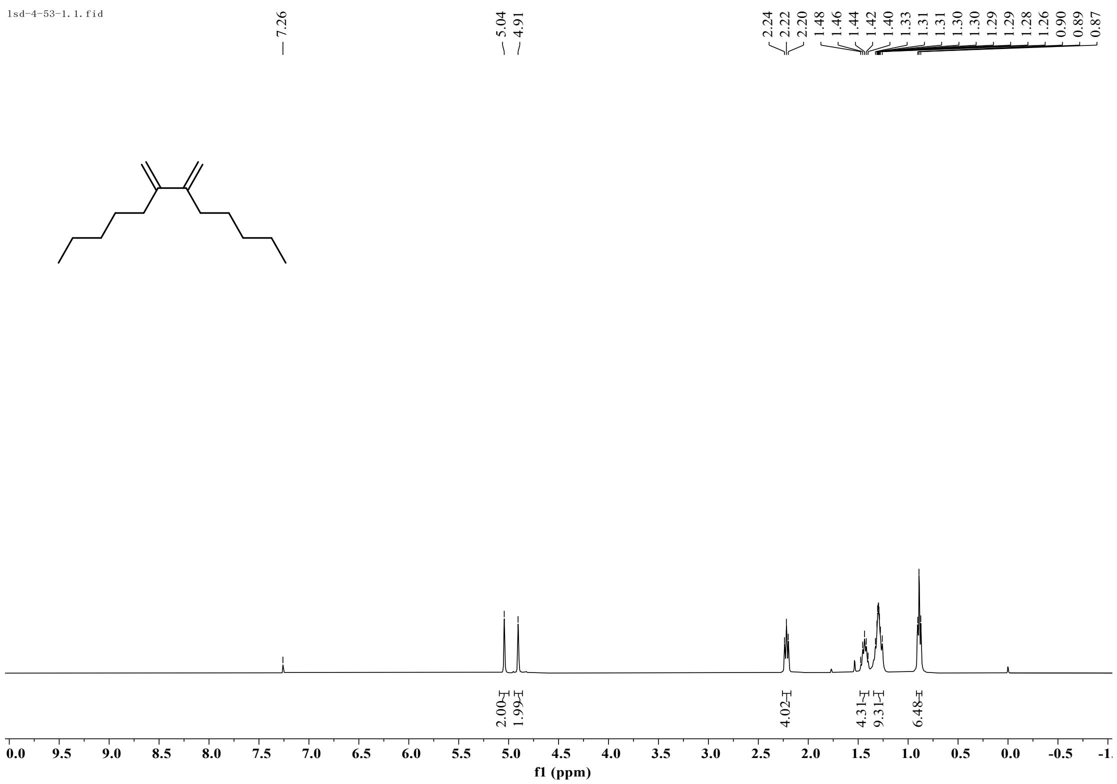

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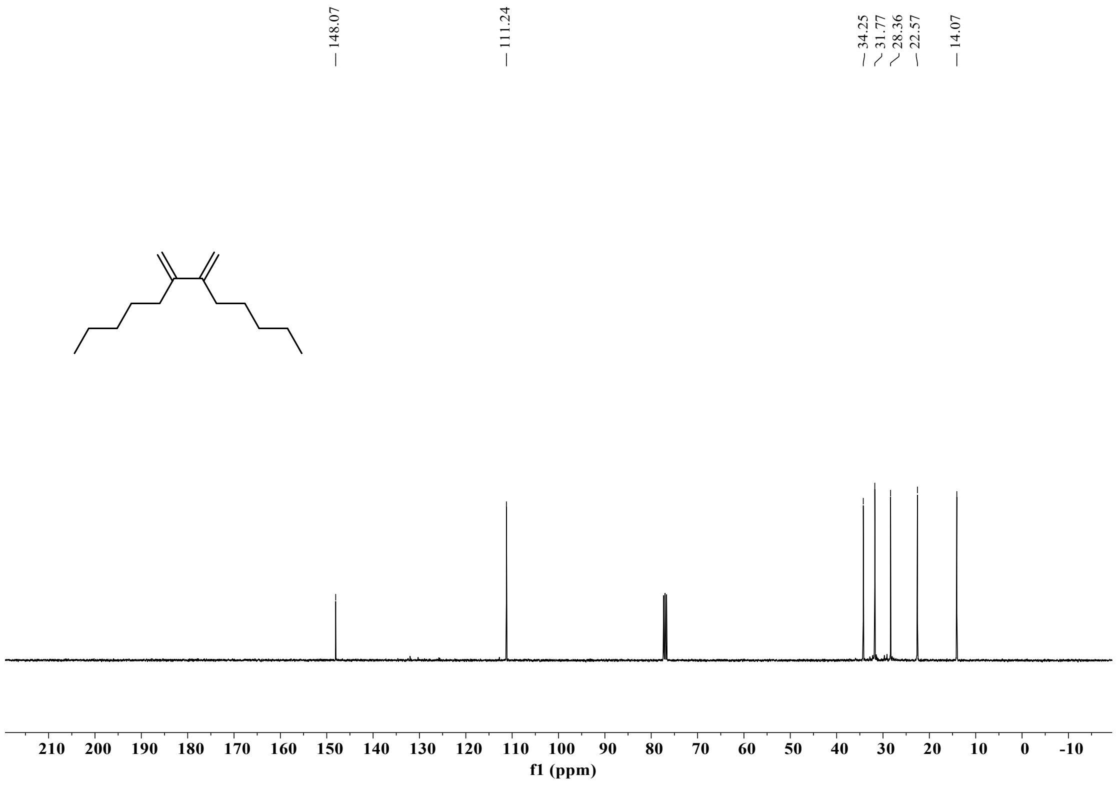

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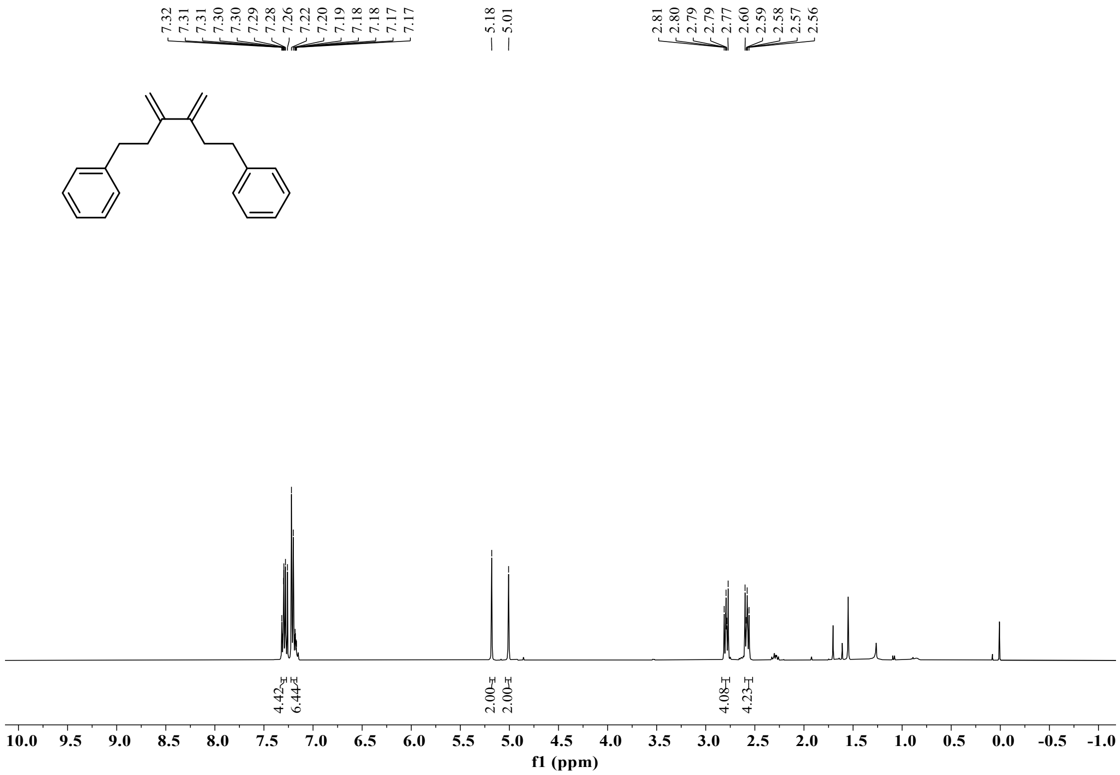

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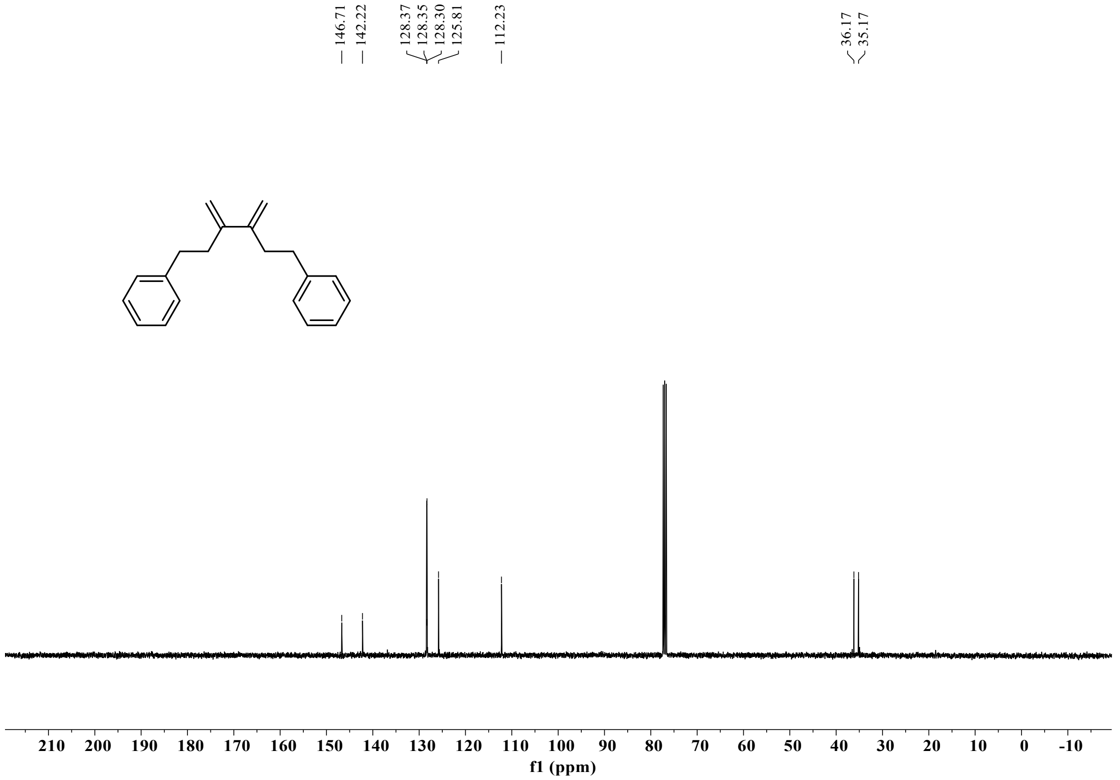

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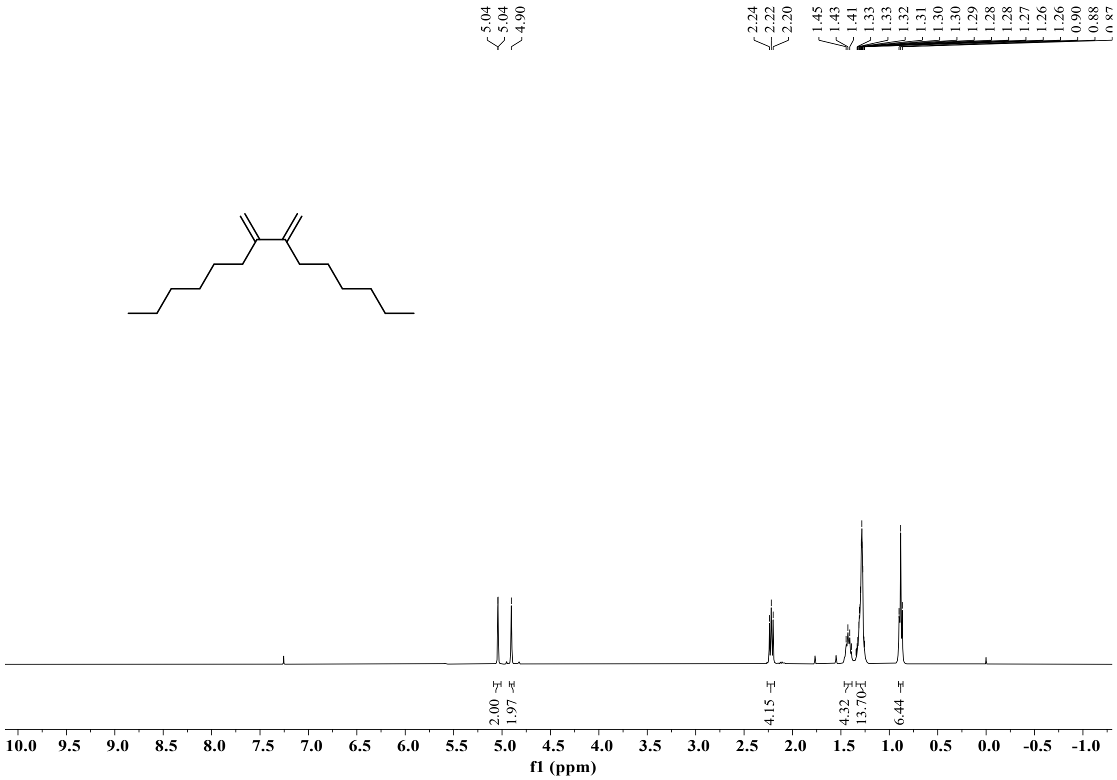

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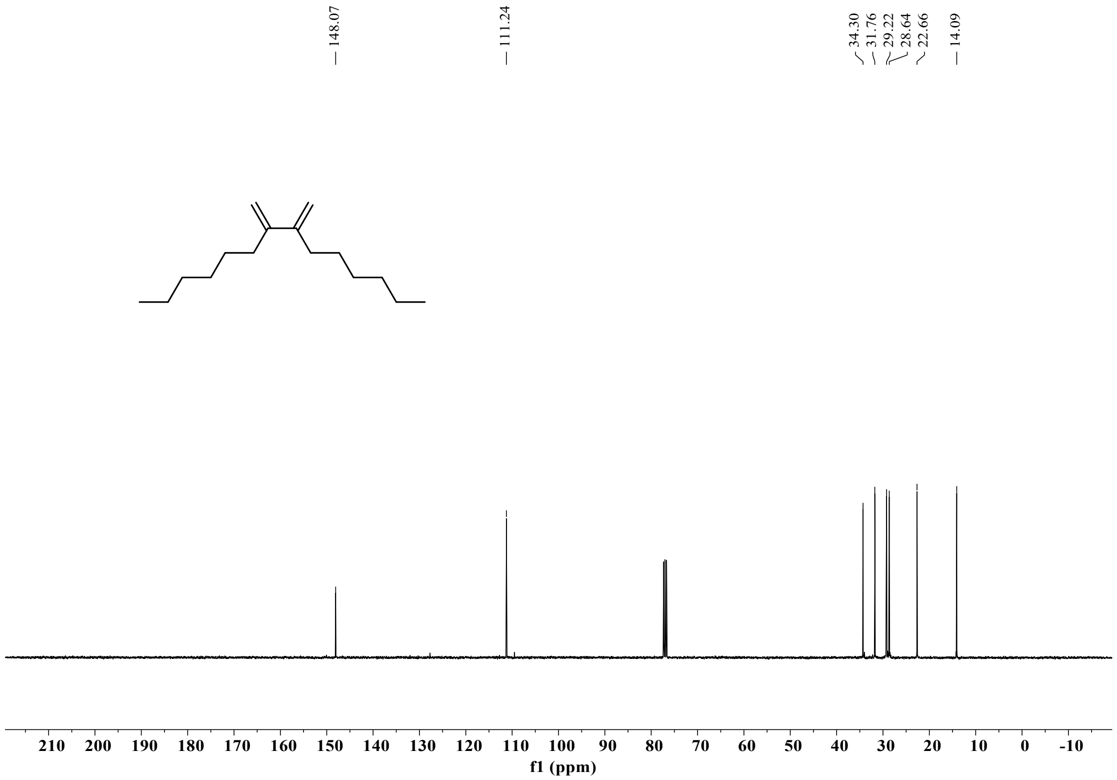

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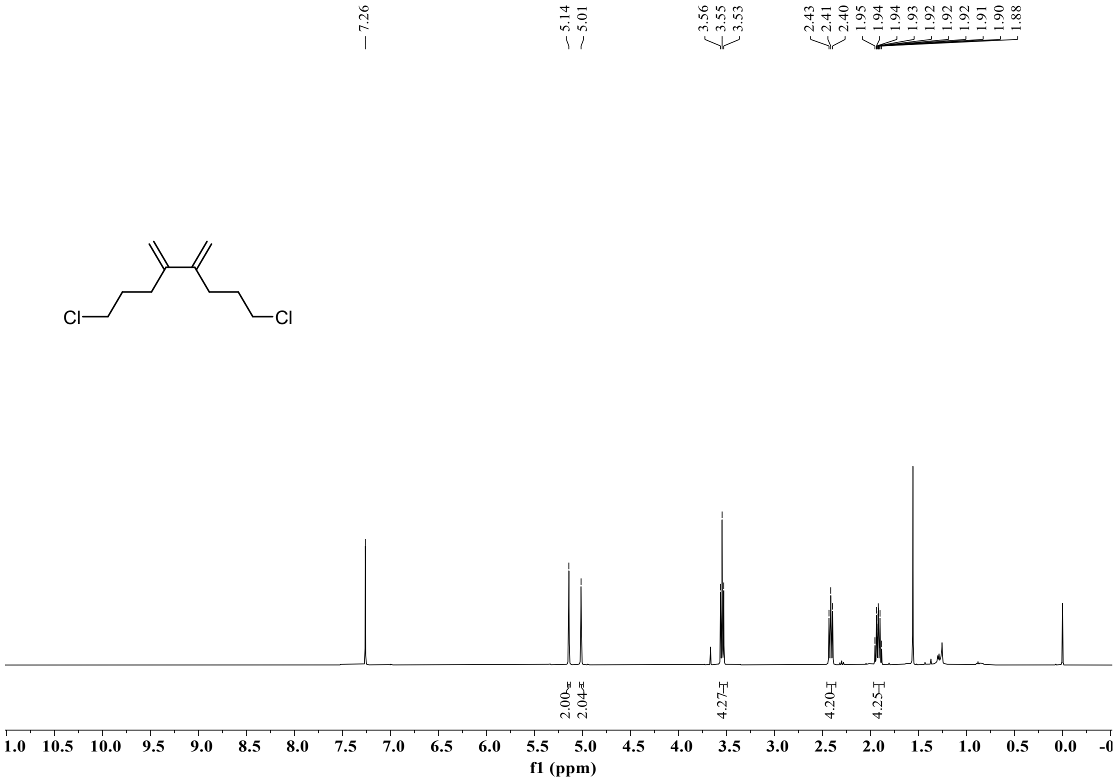

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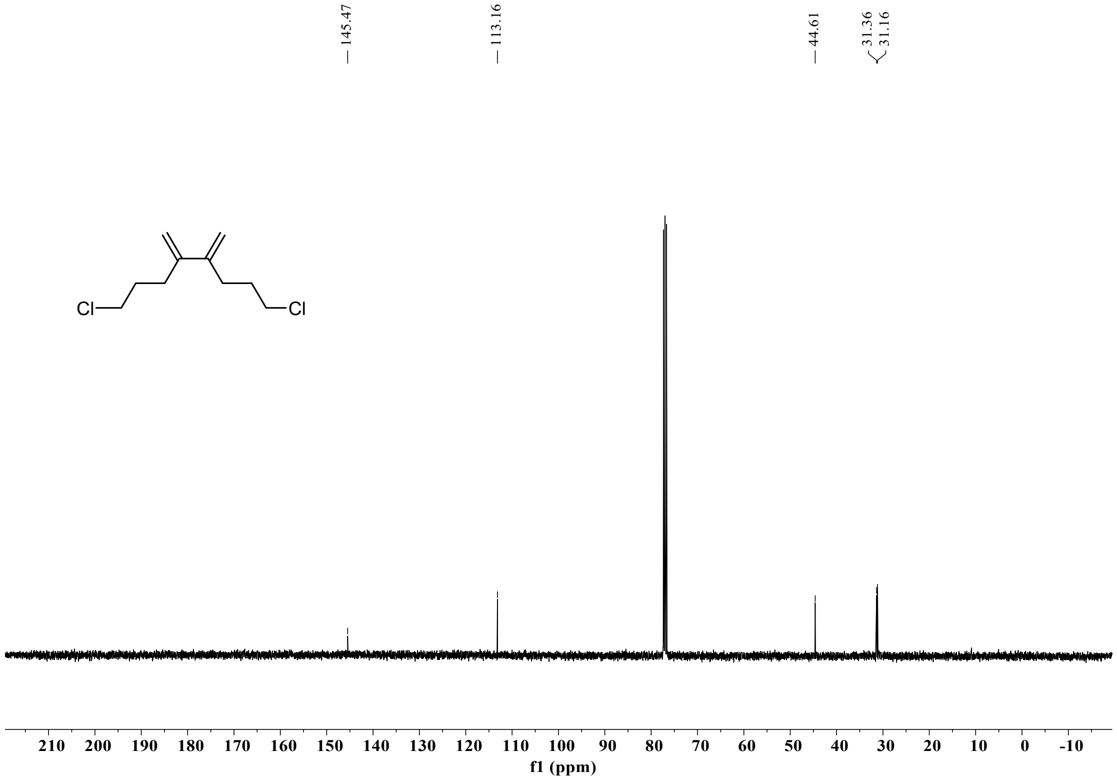

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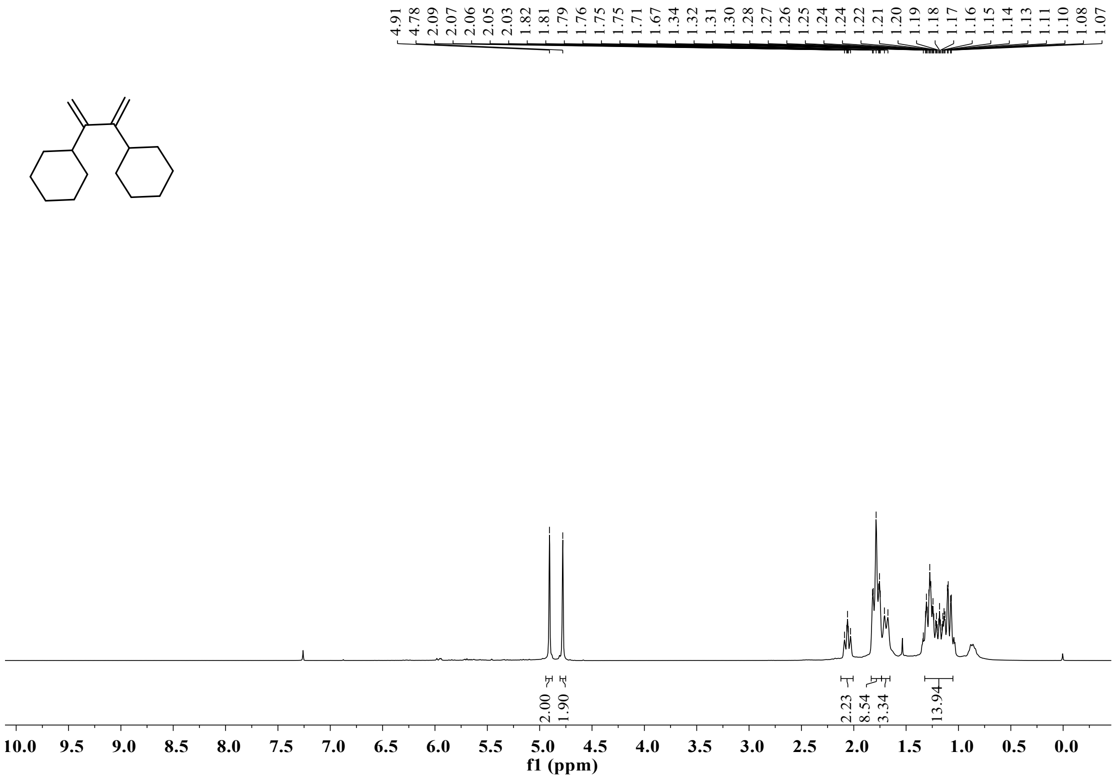

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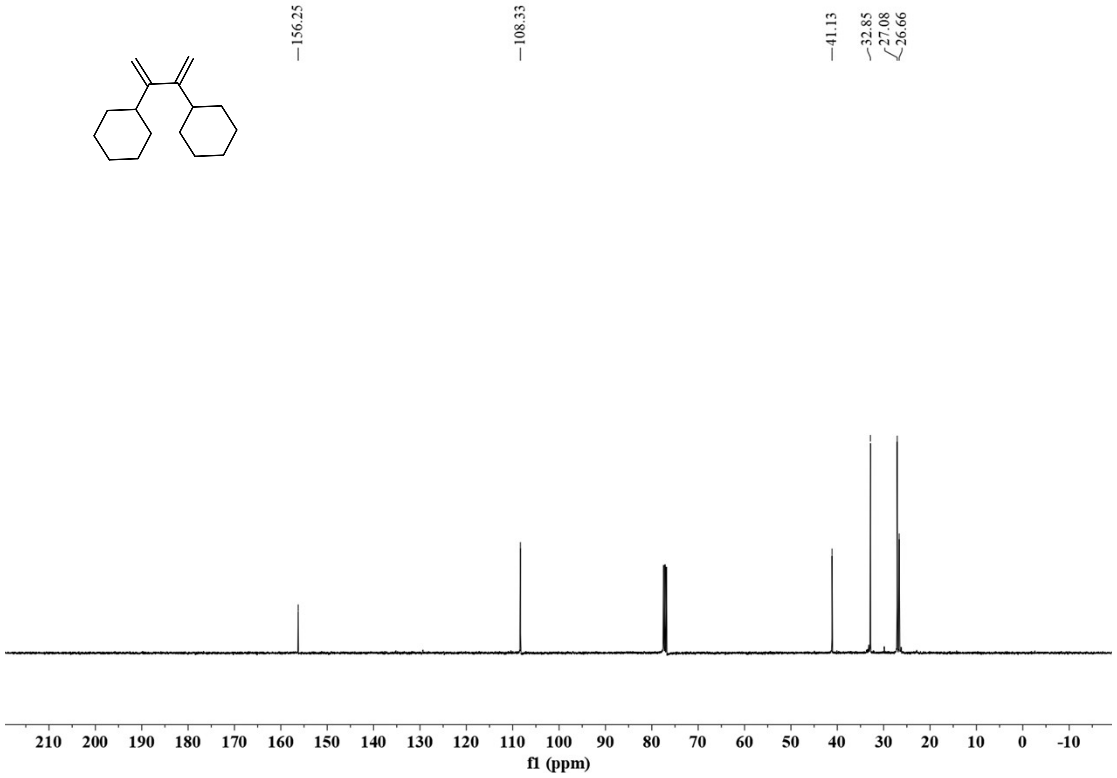

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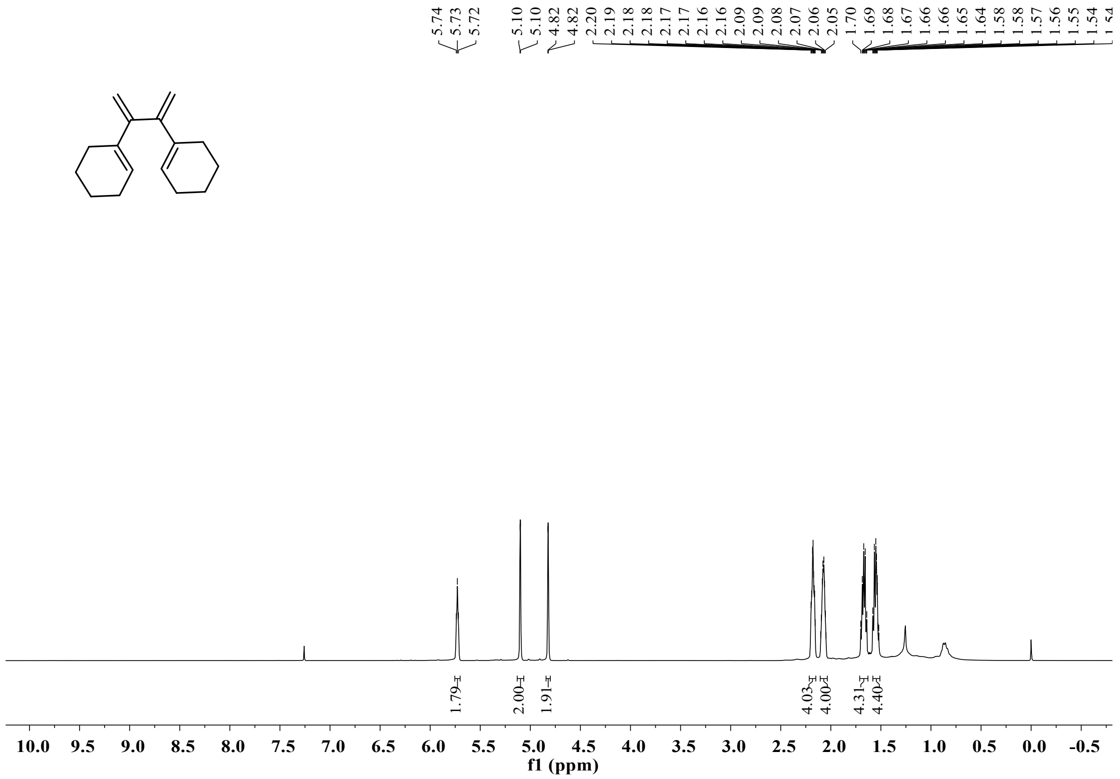

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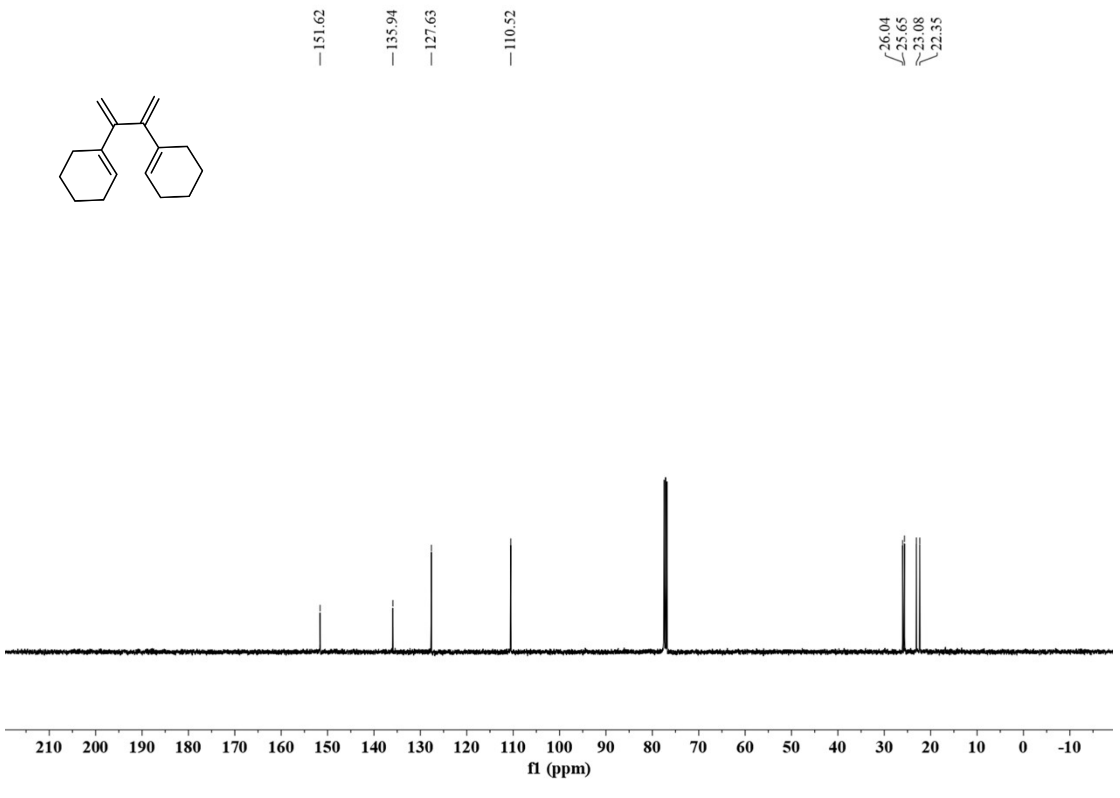

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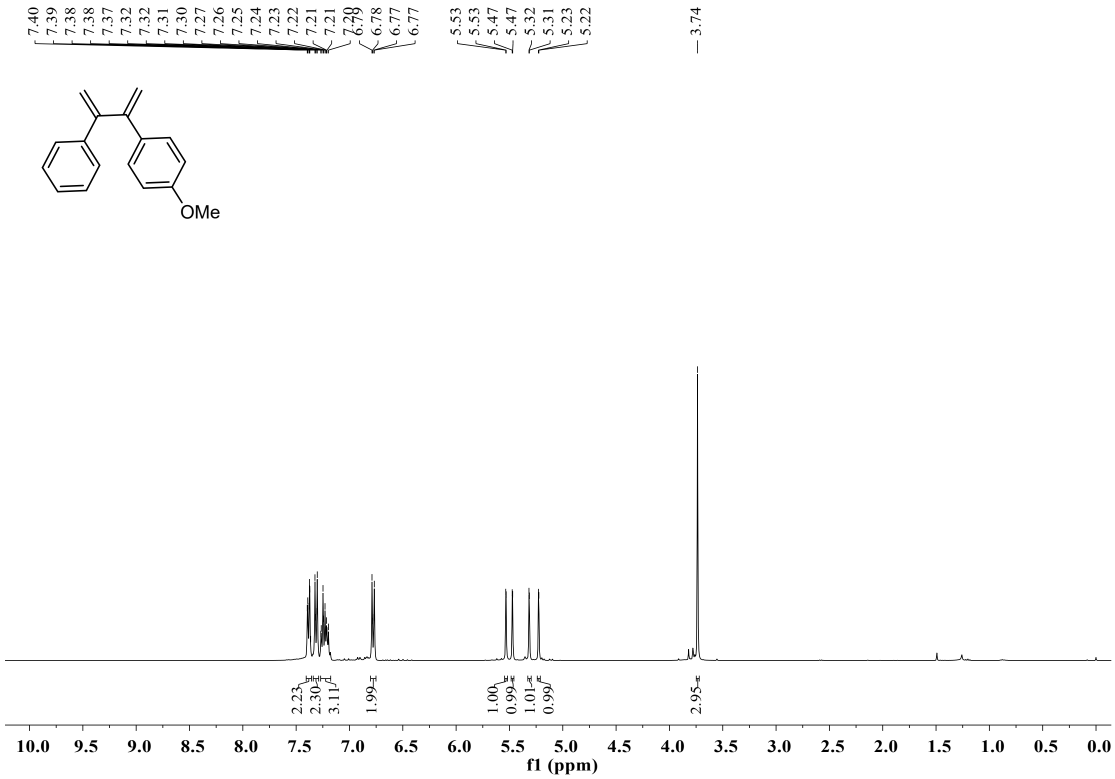

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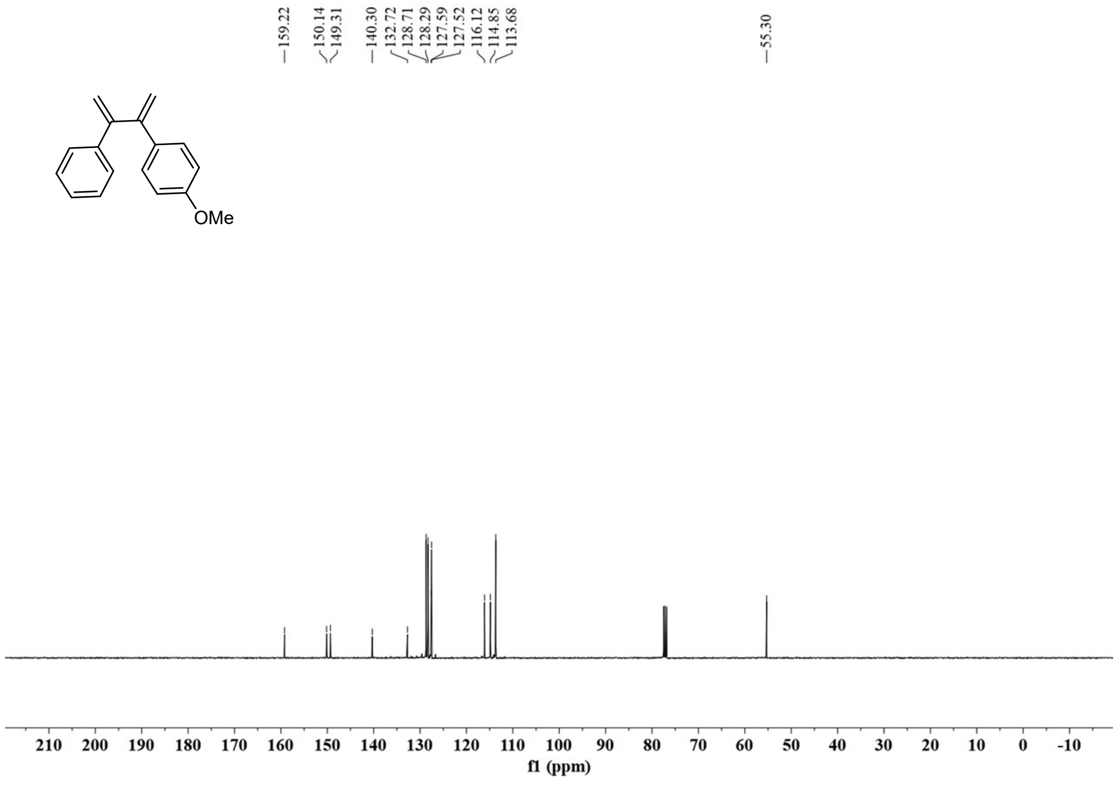

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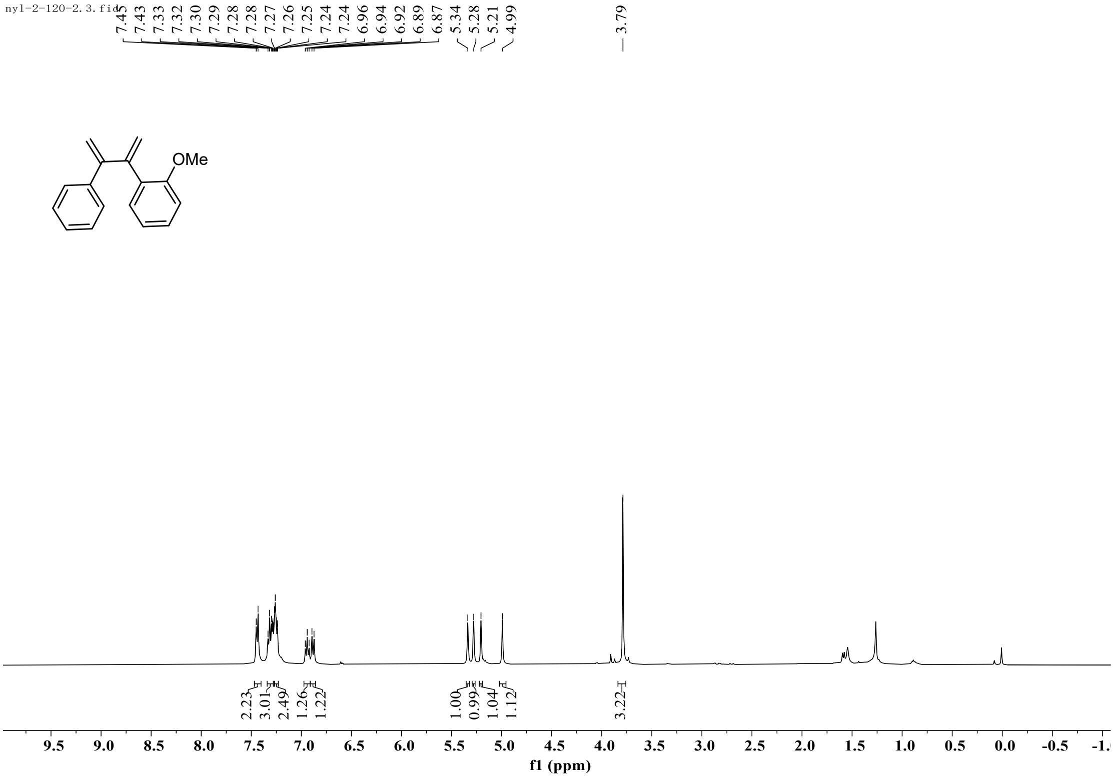

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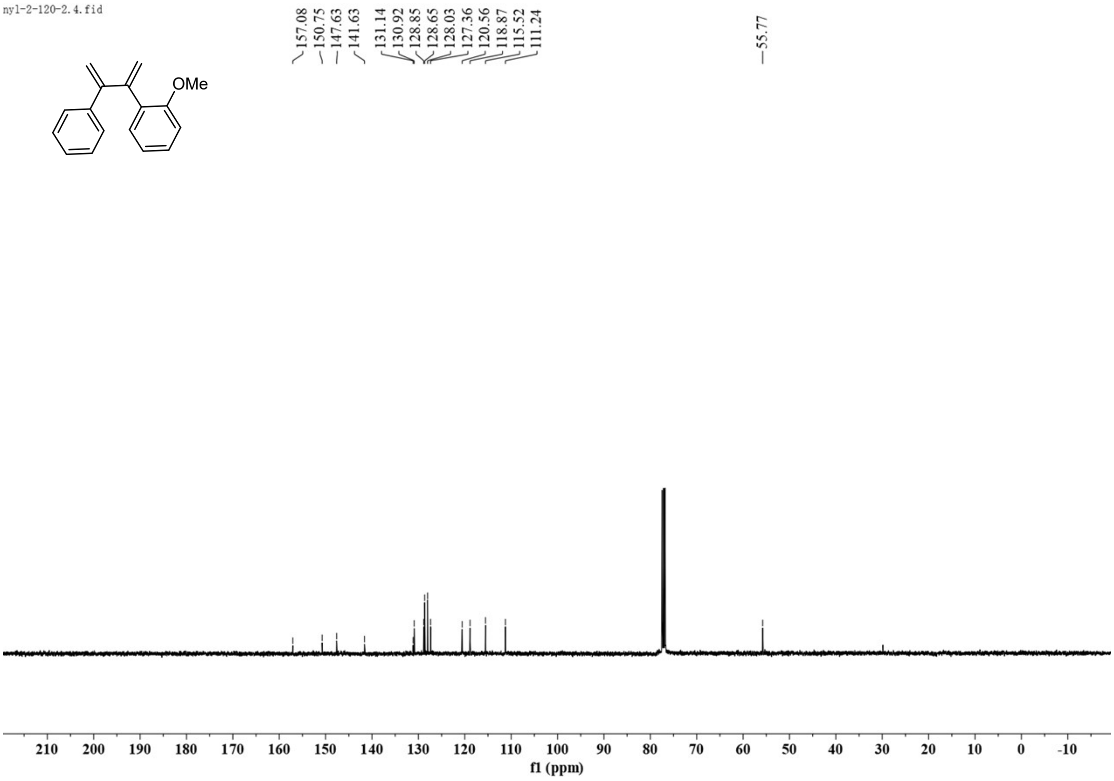

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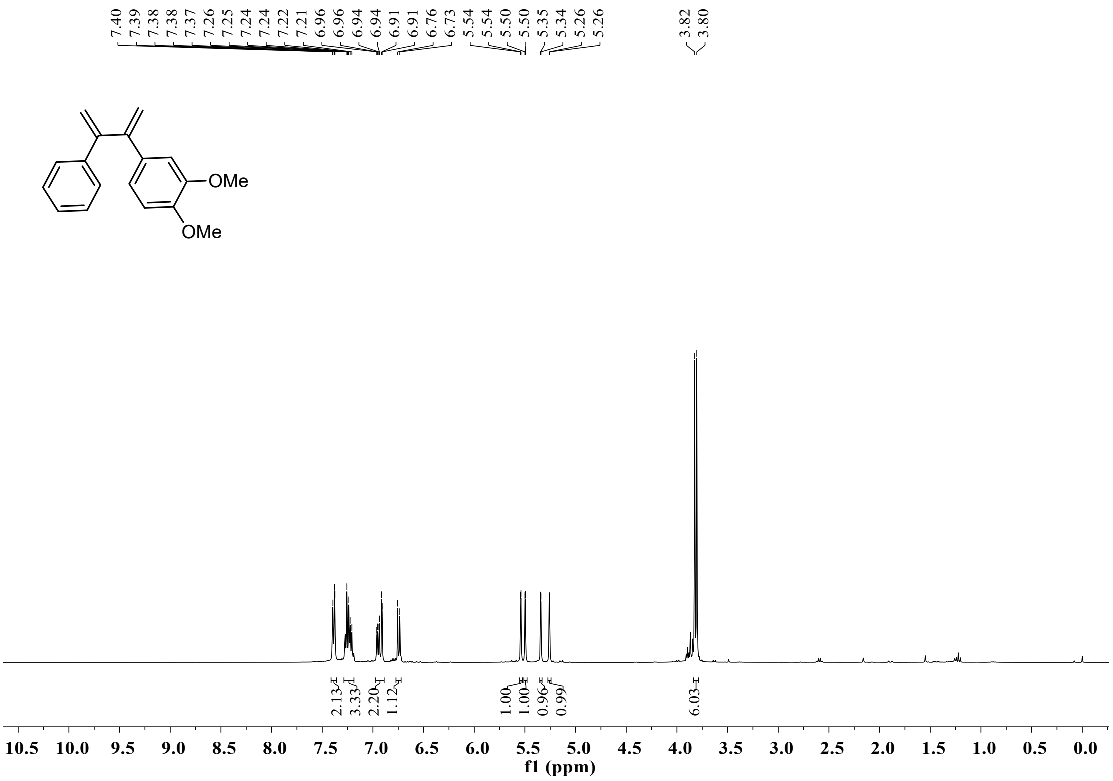

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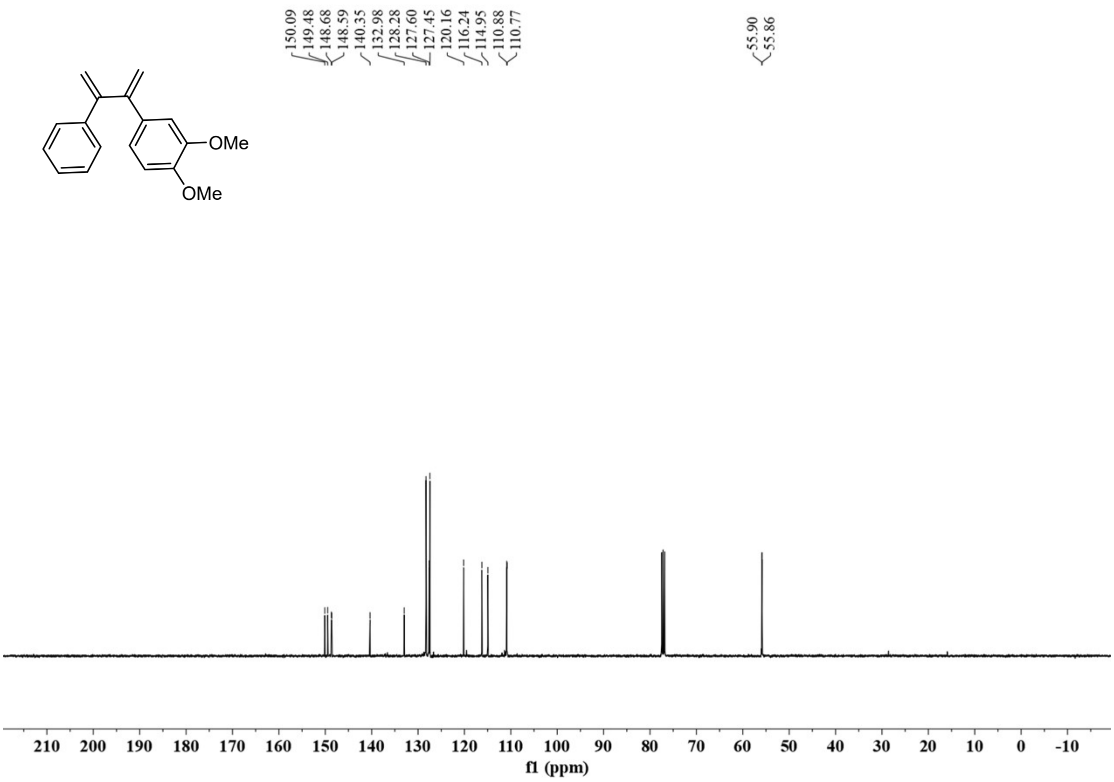

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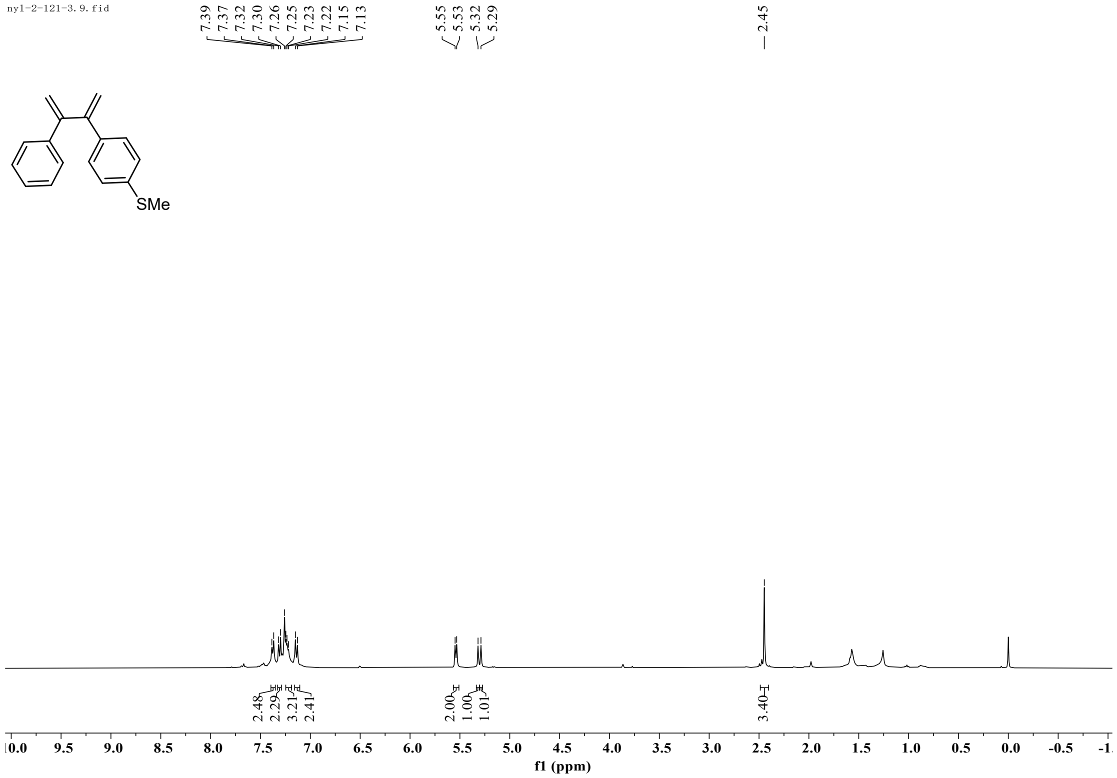

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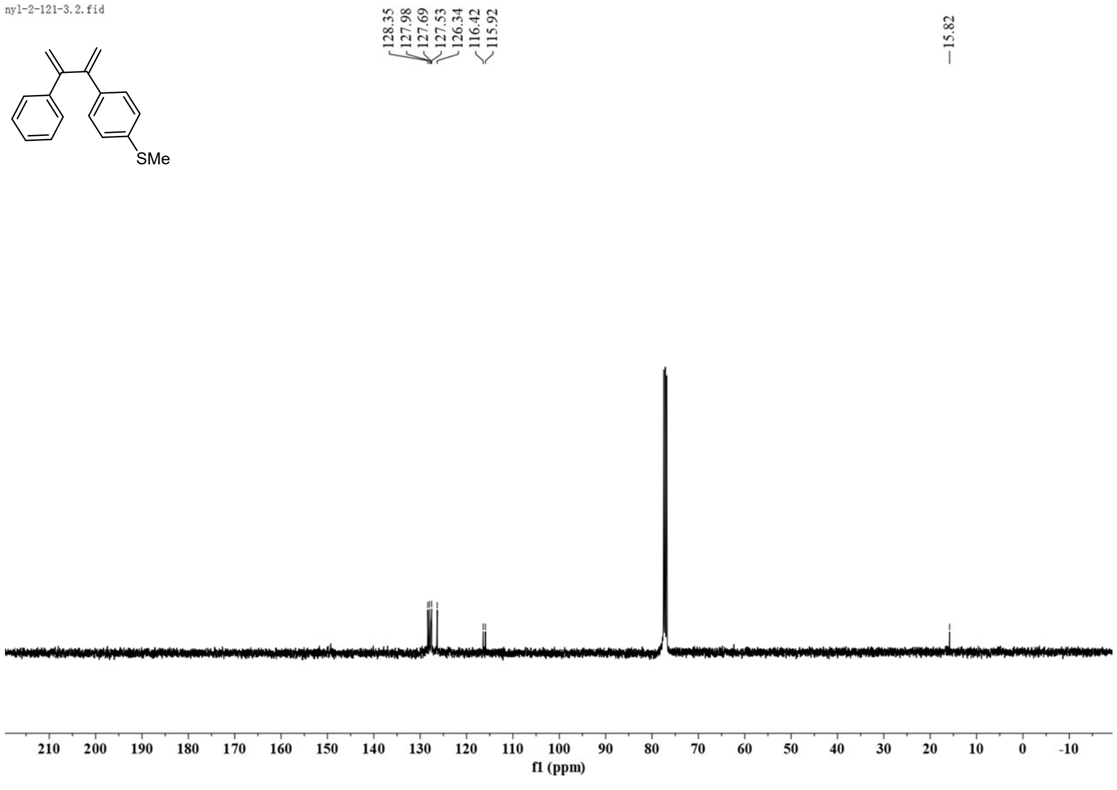

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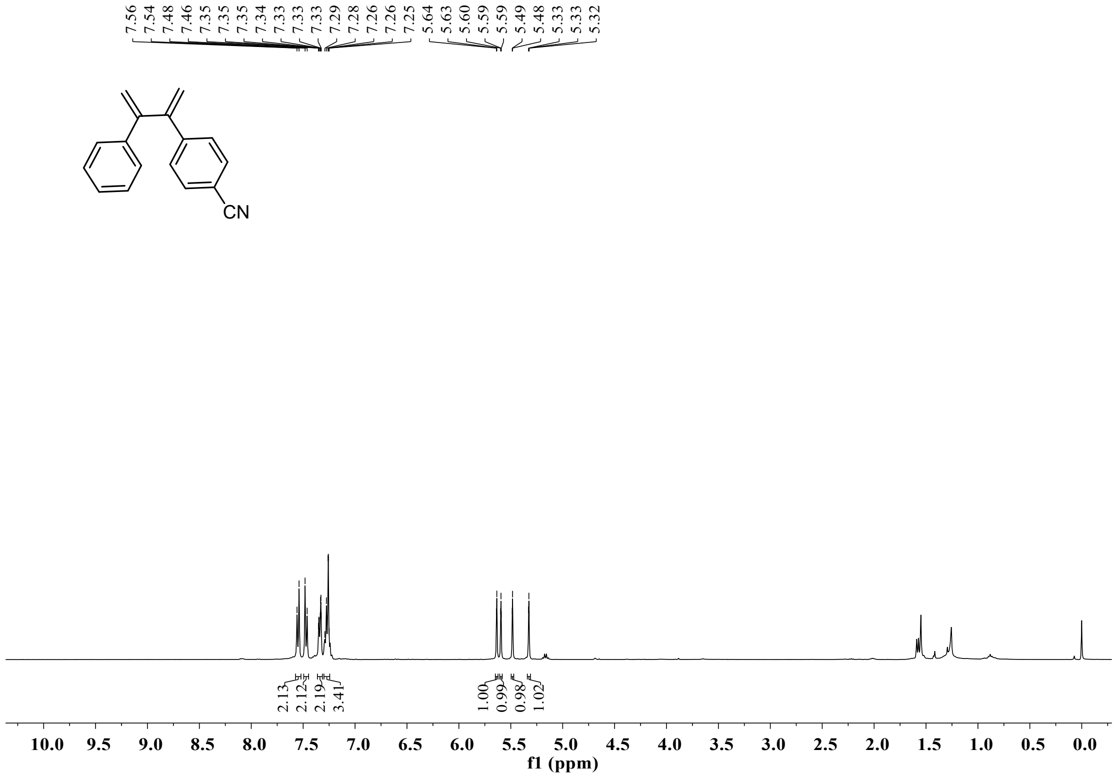

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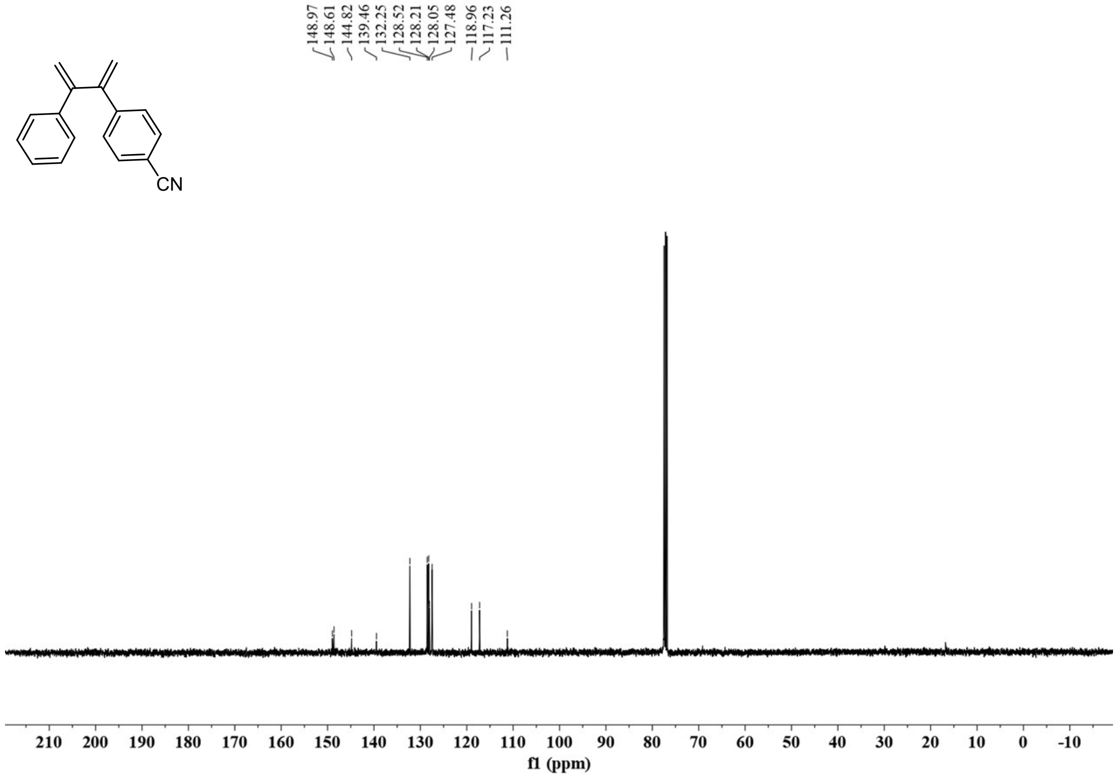

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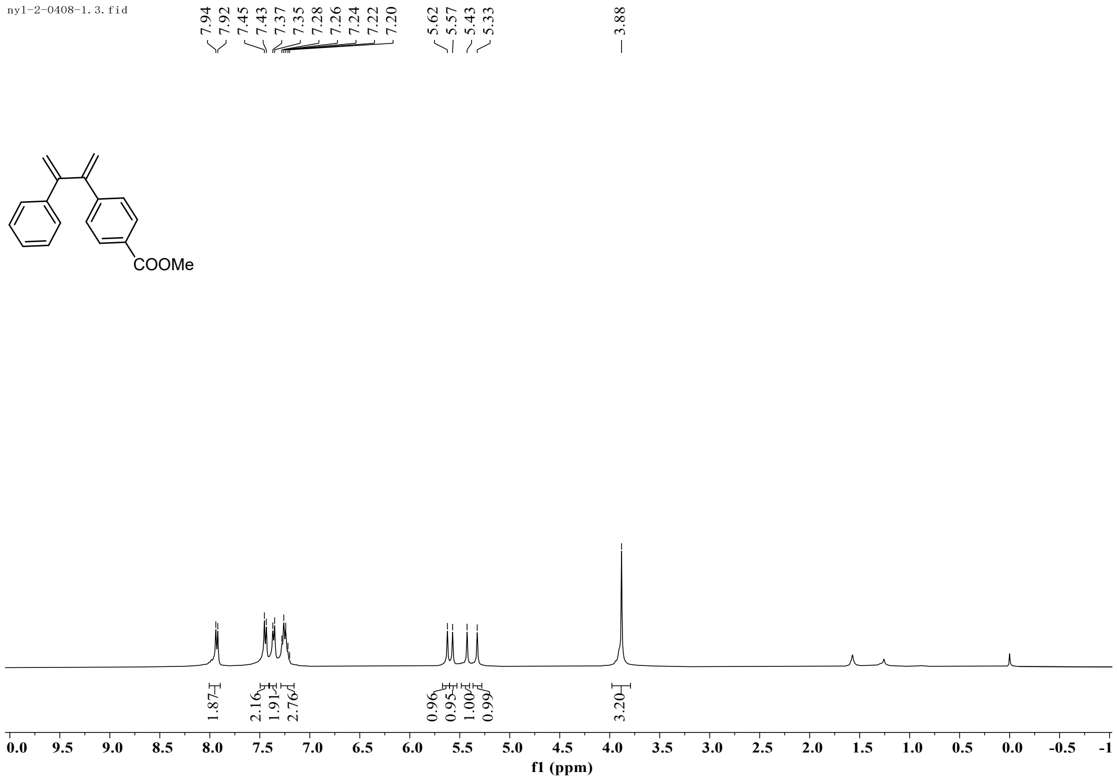

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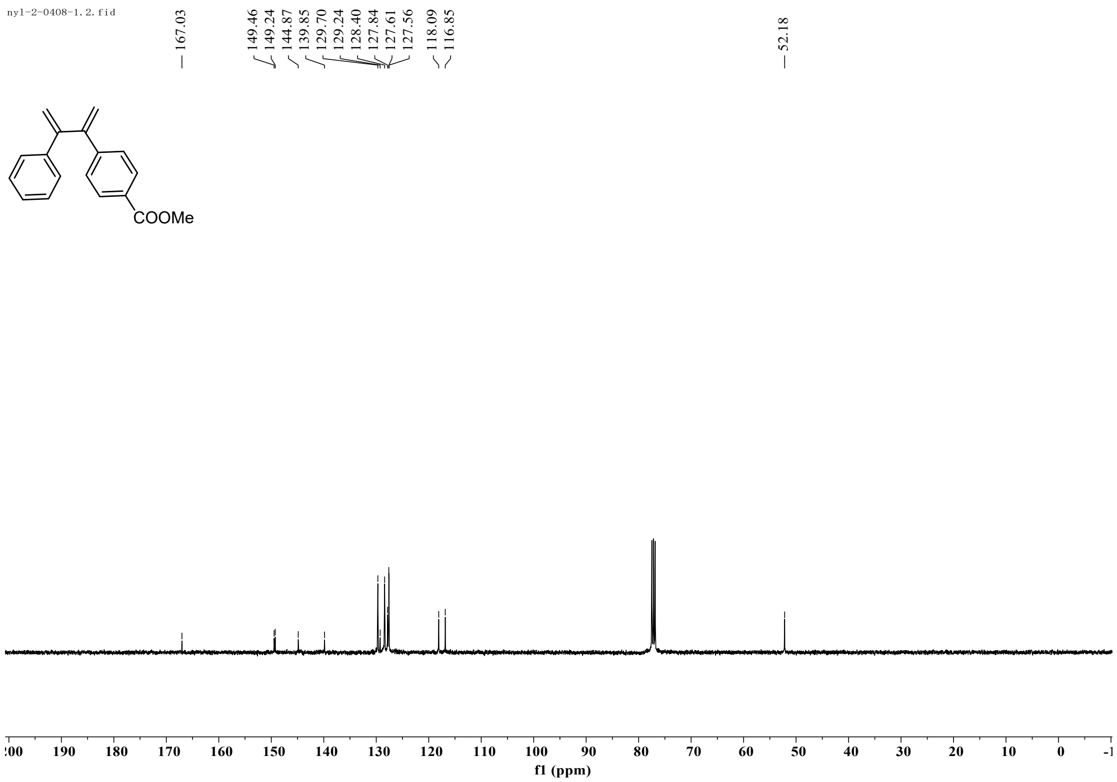

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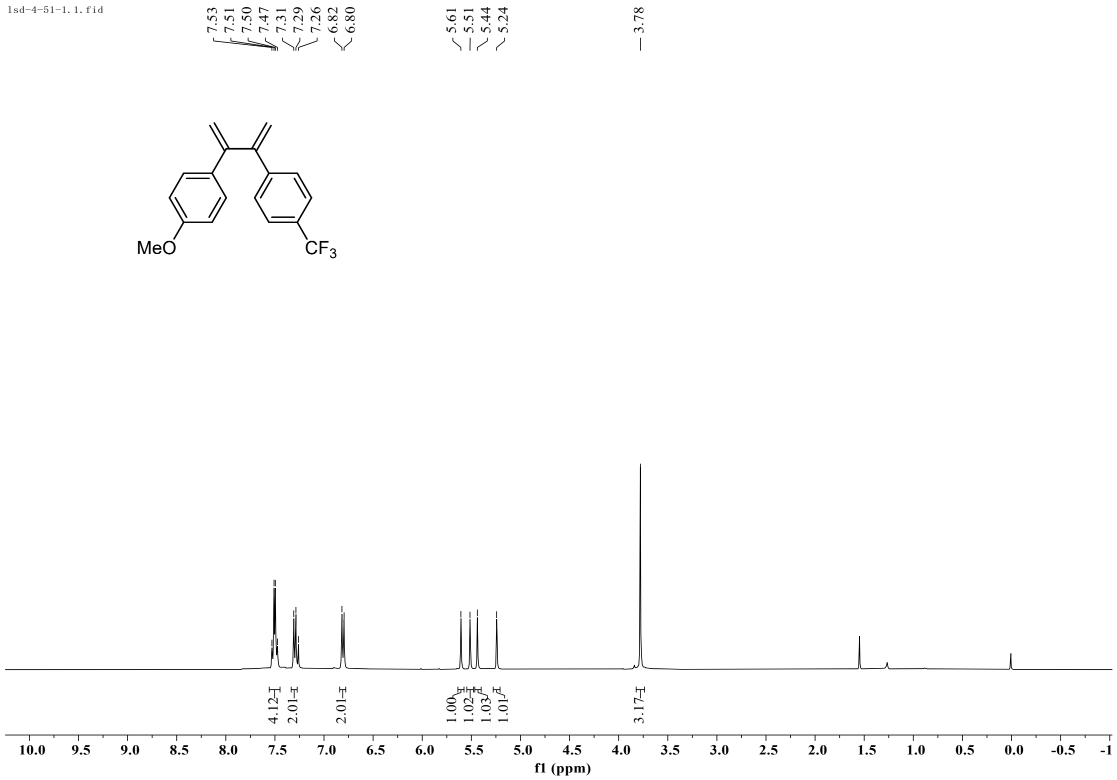

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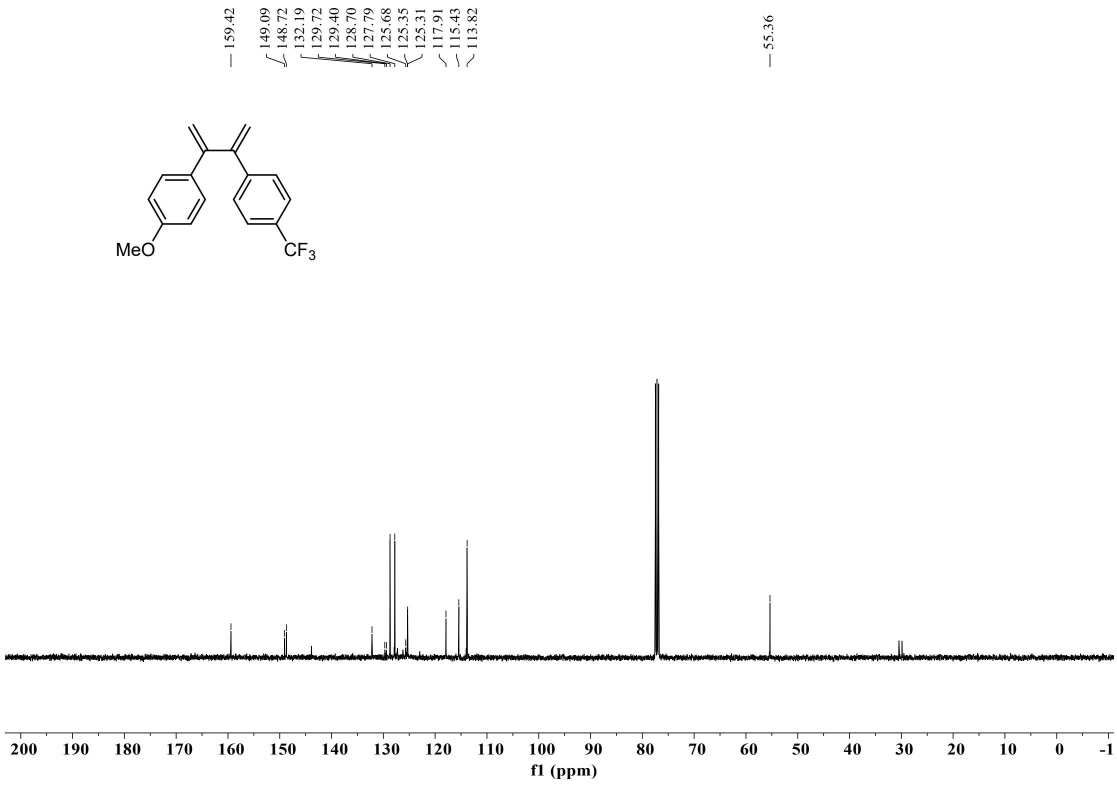
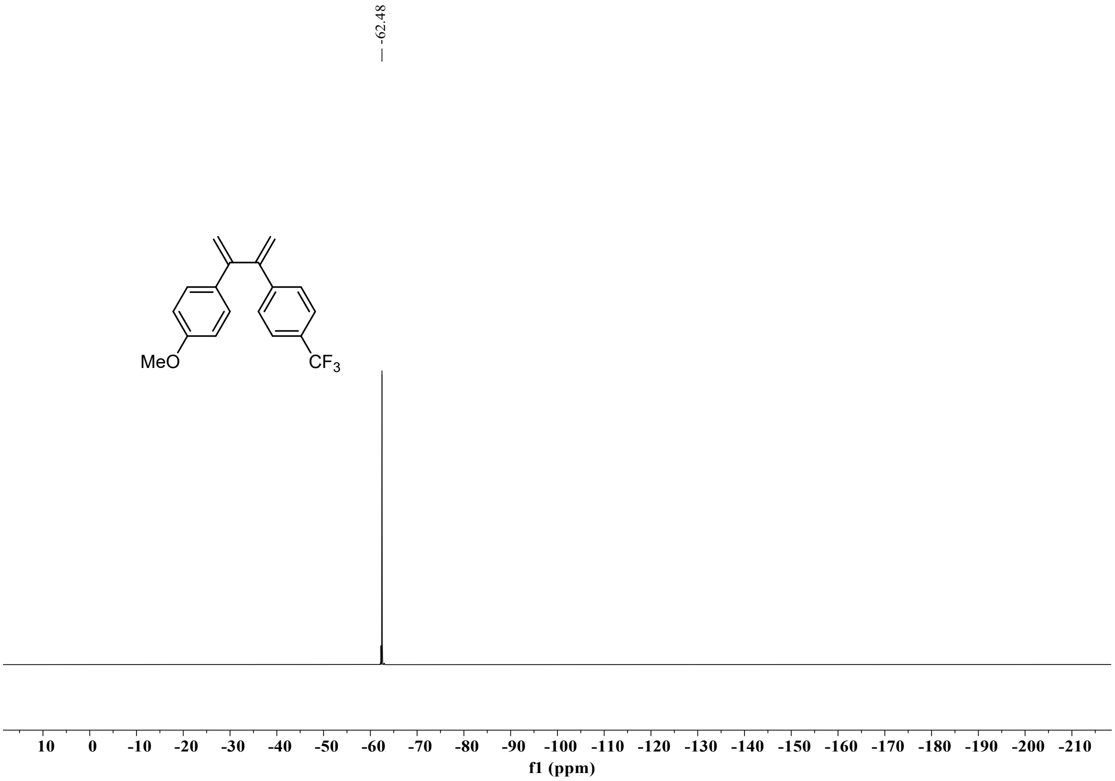


^{19}F NMR Spectra of compound **49**



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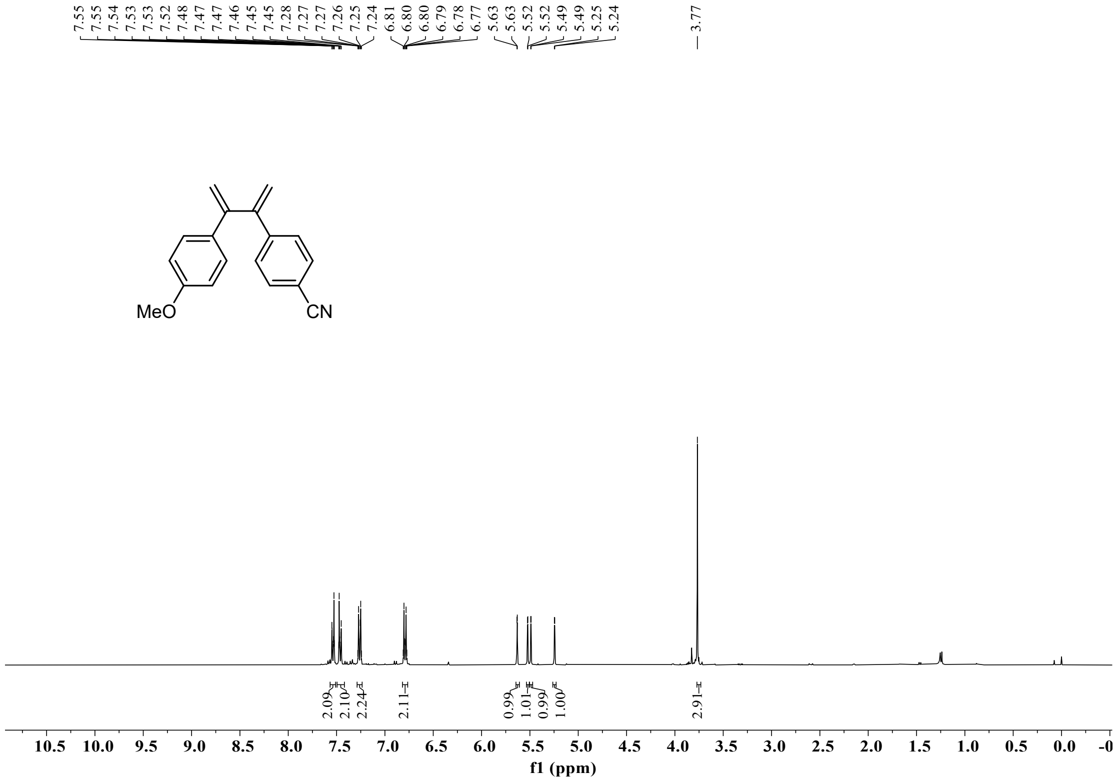

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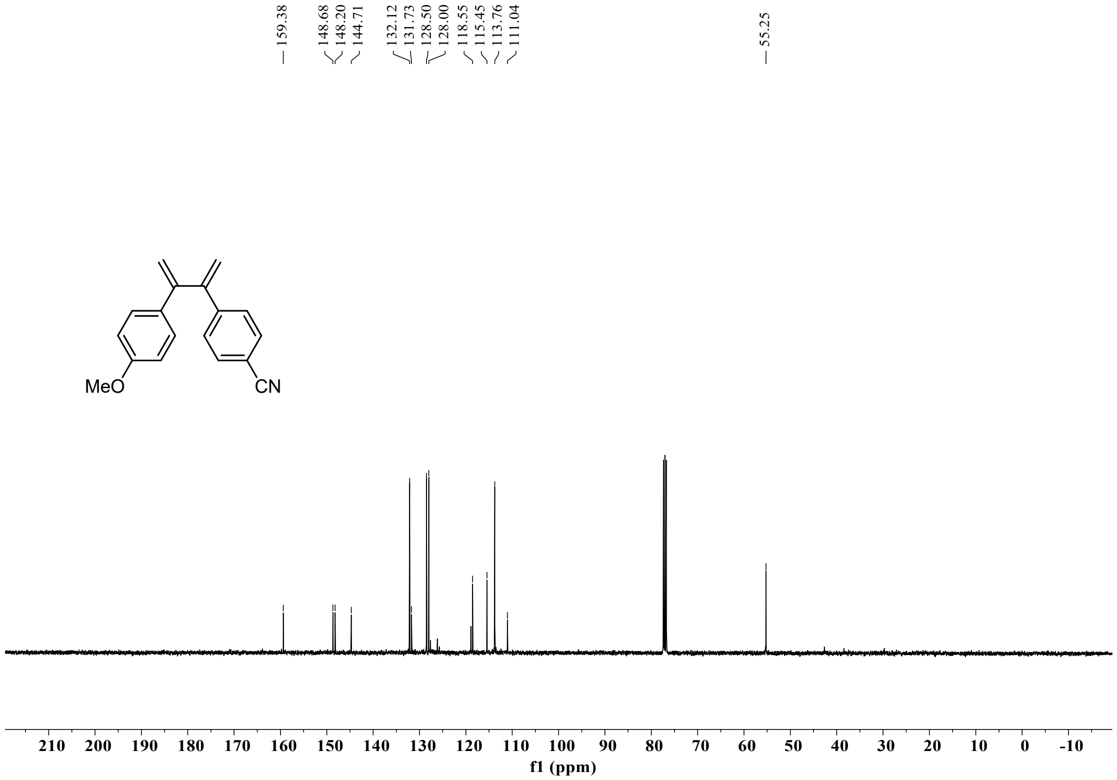

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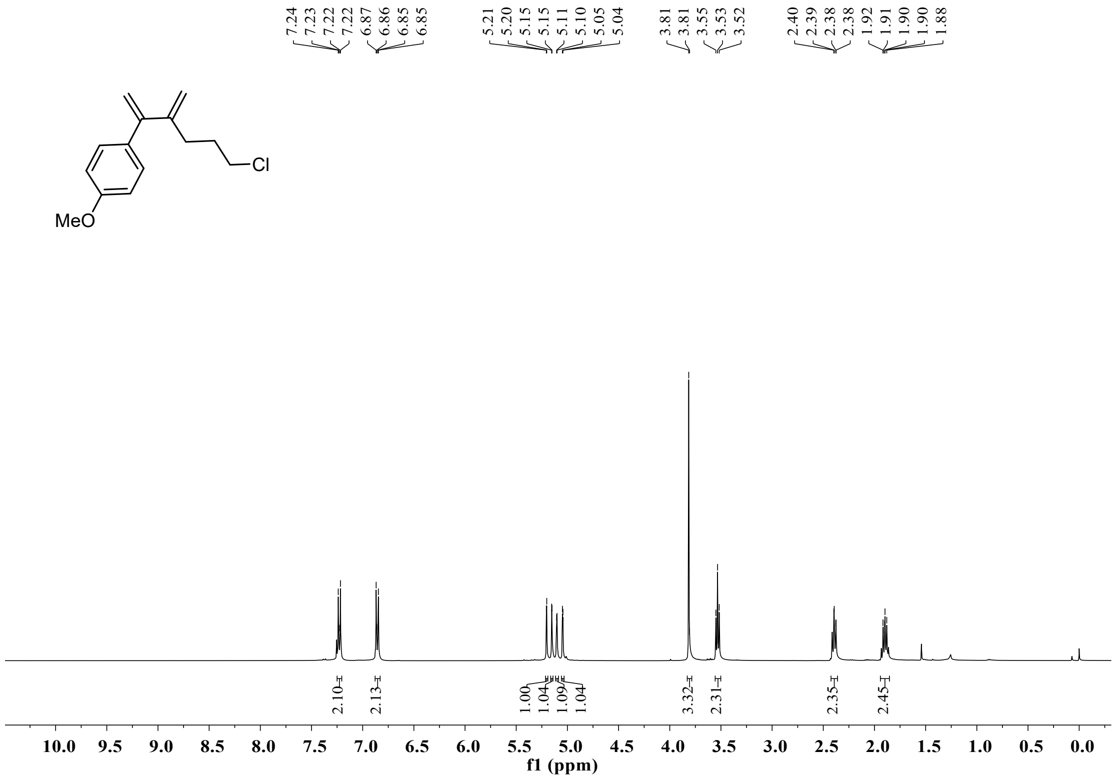

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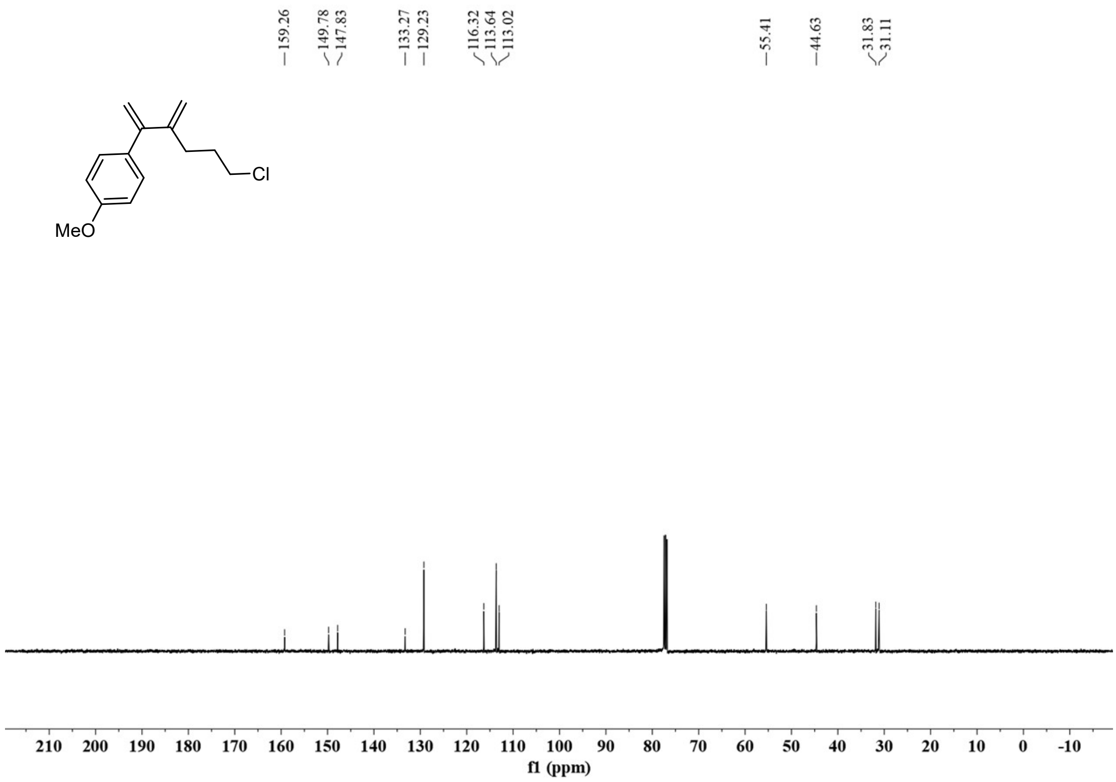

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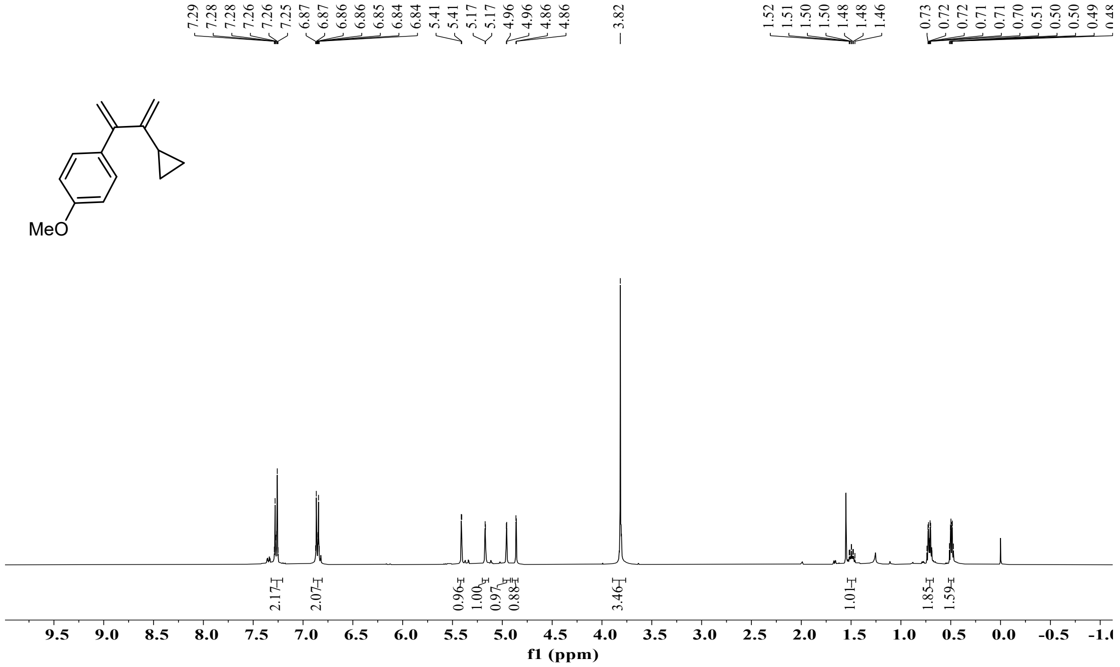

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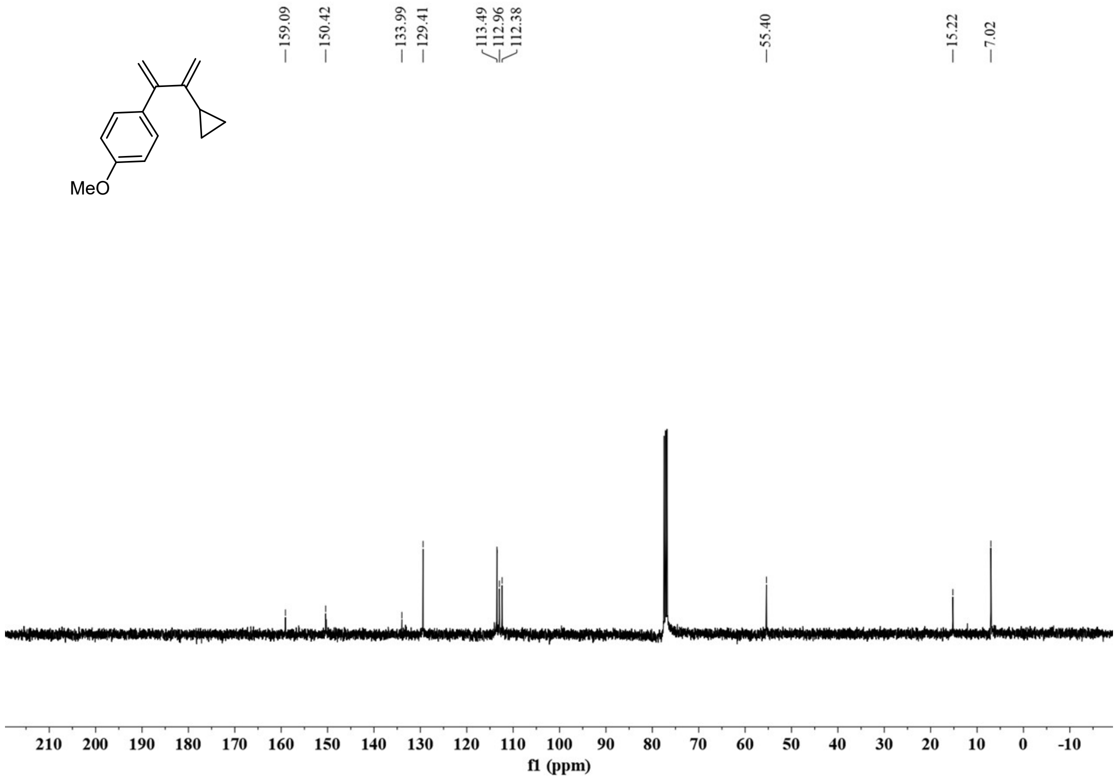

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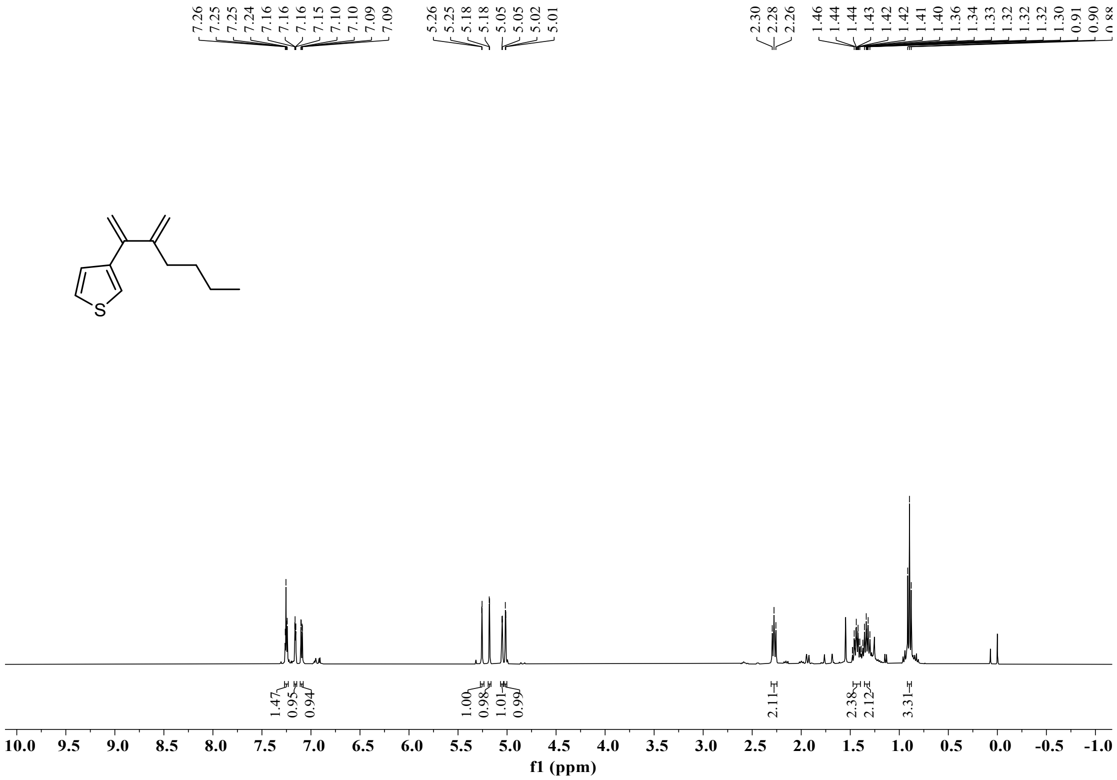

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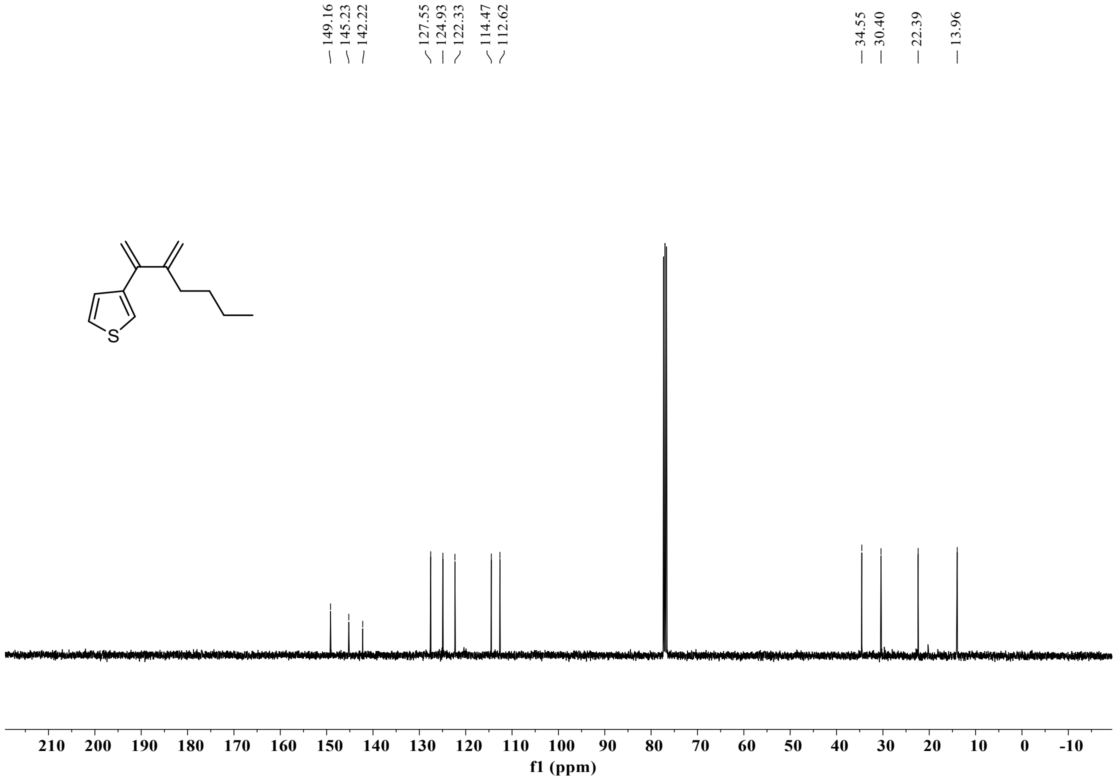

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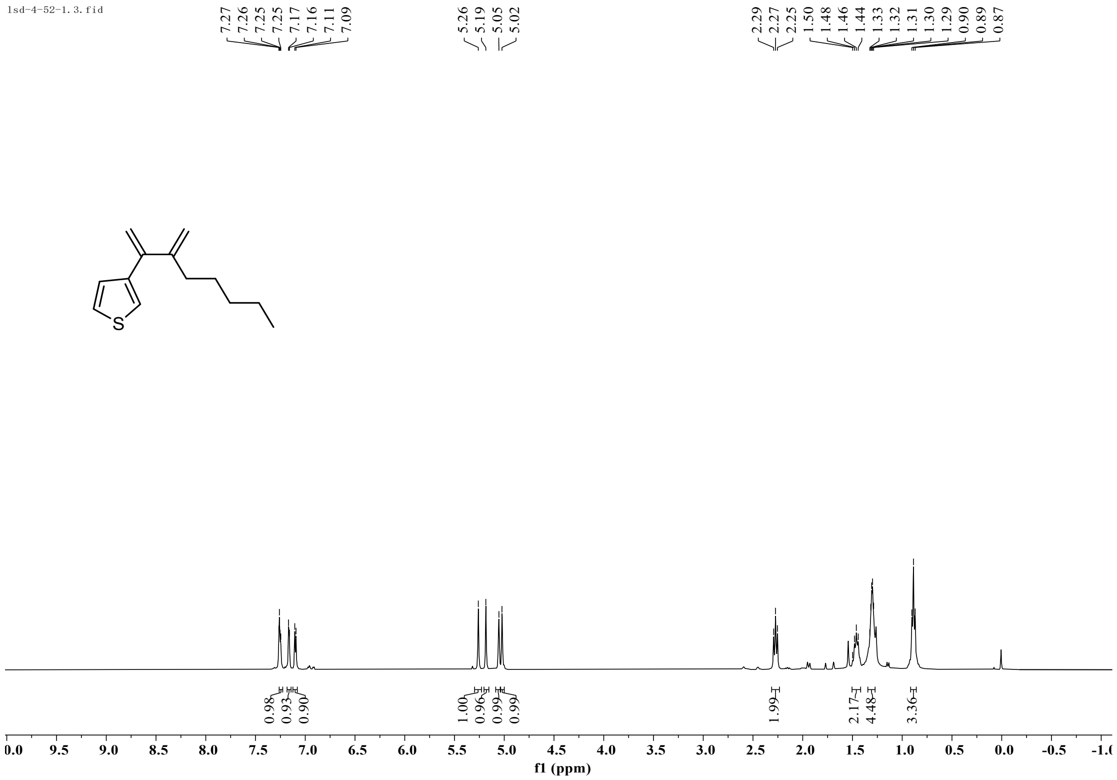

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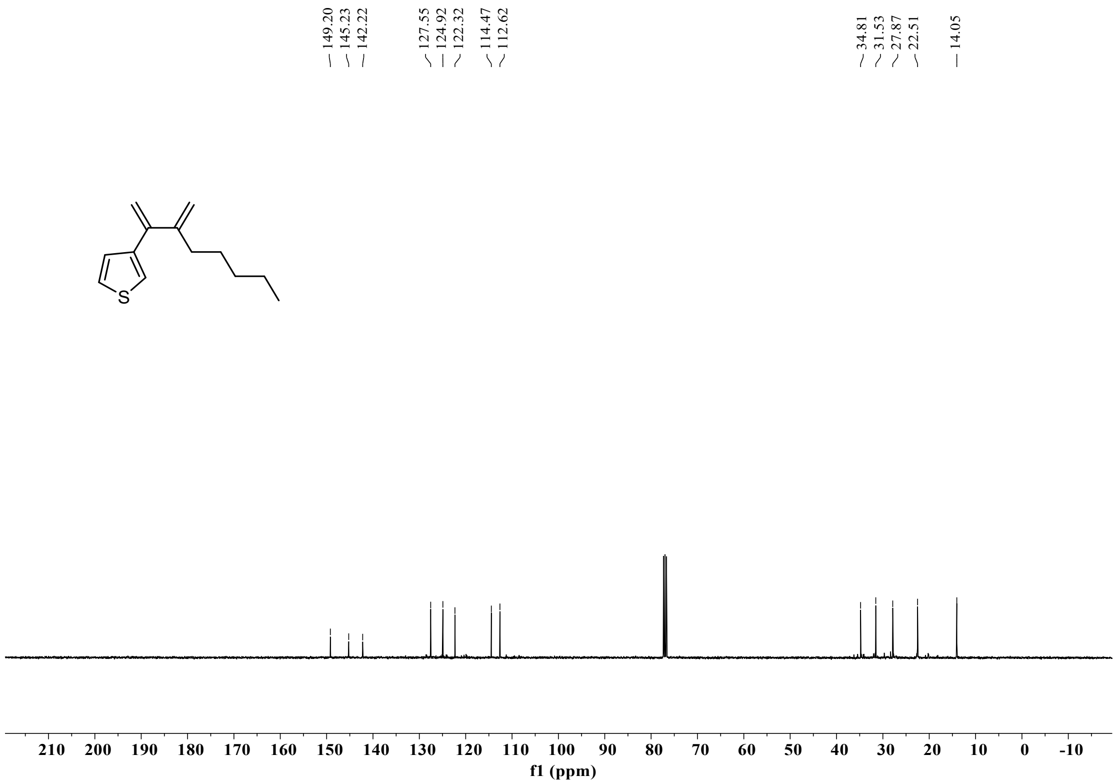

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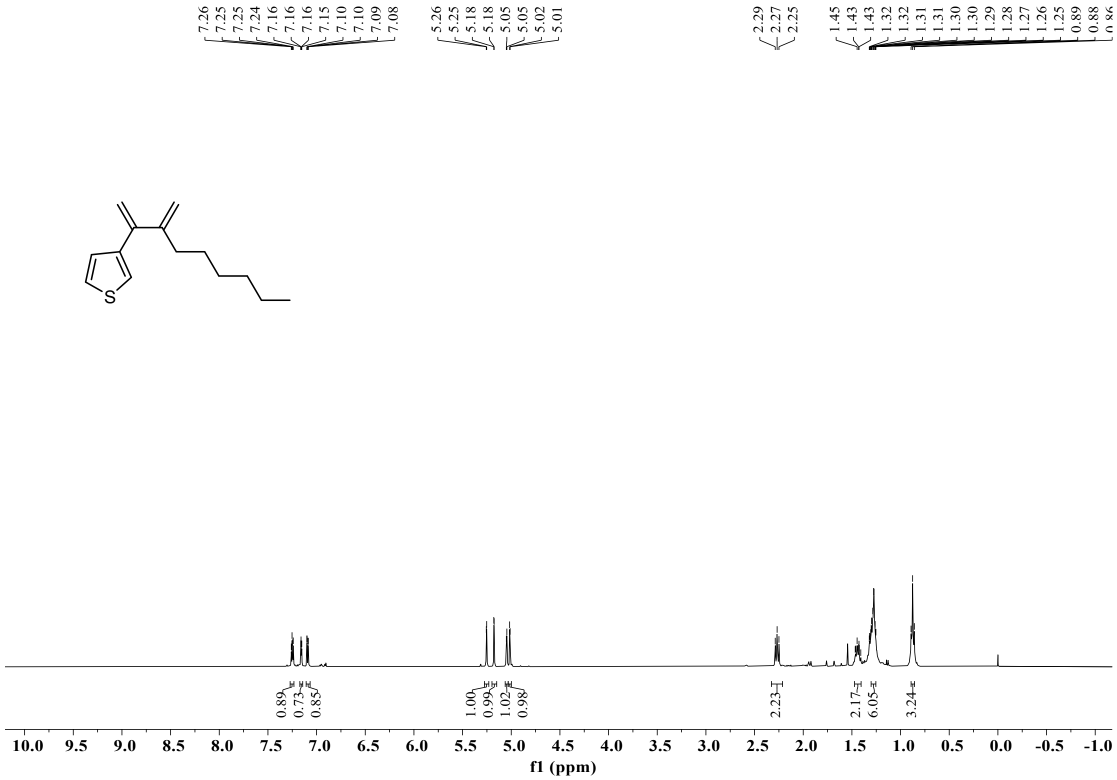

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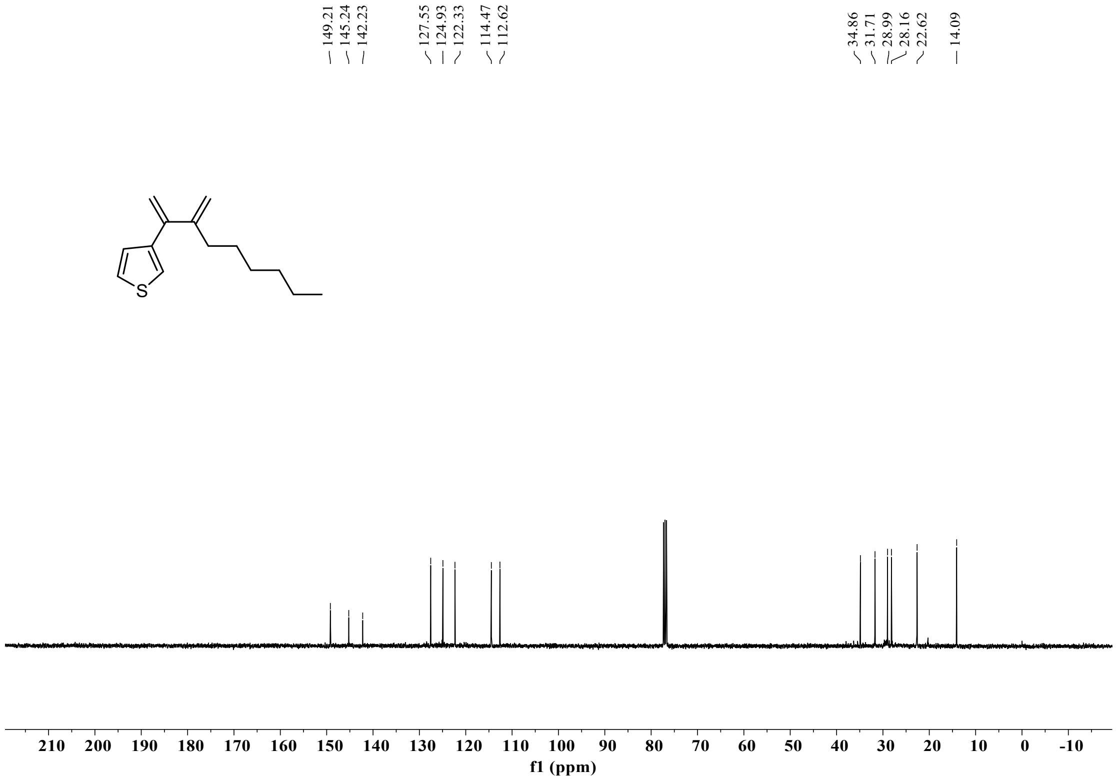

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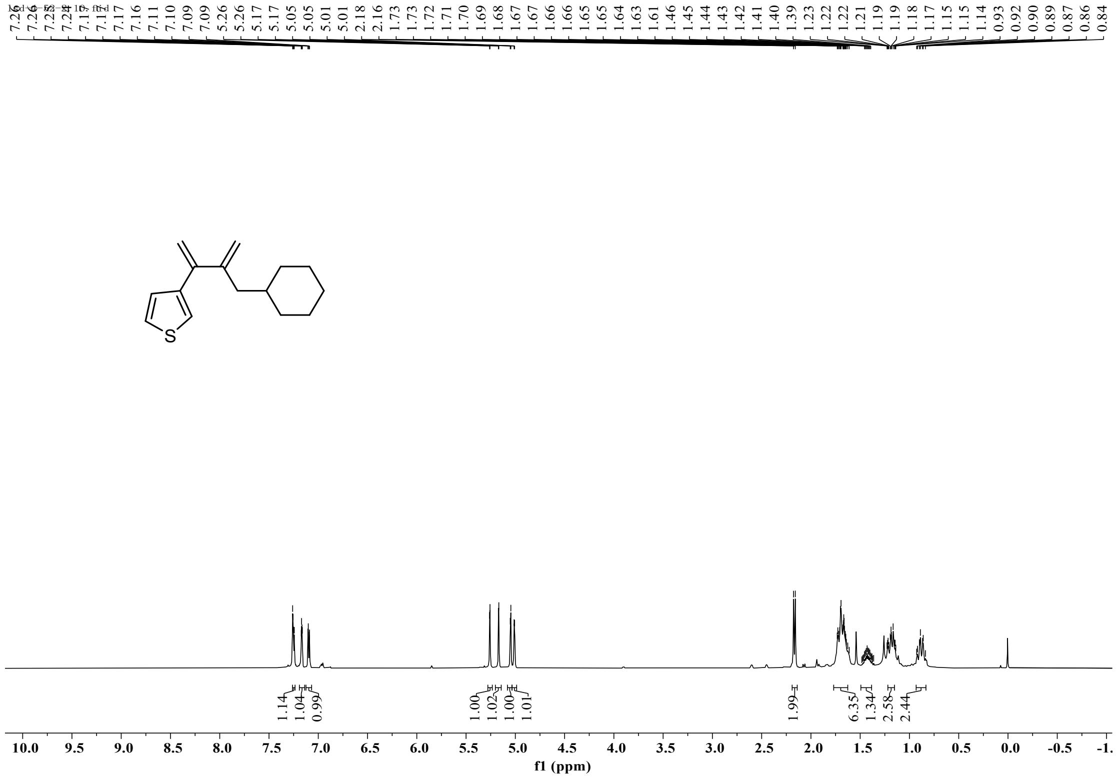

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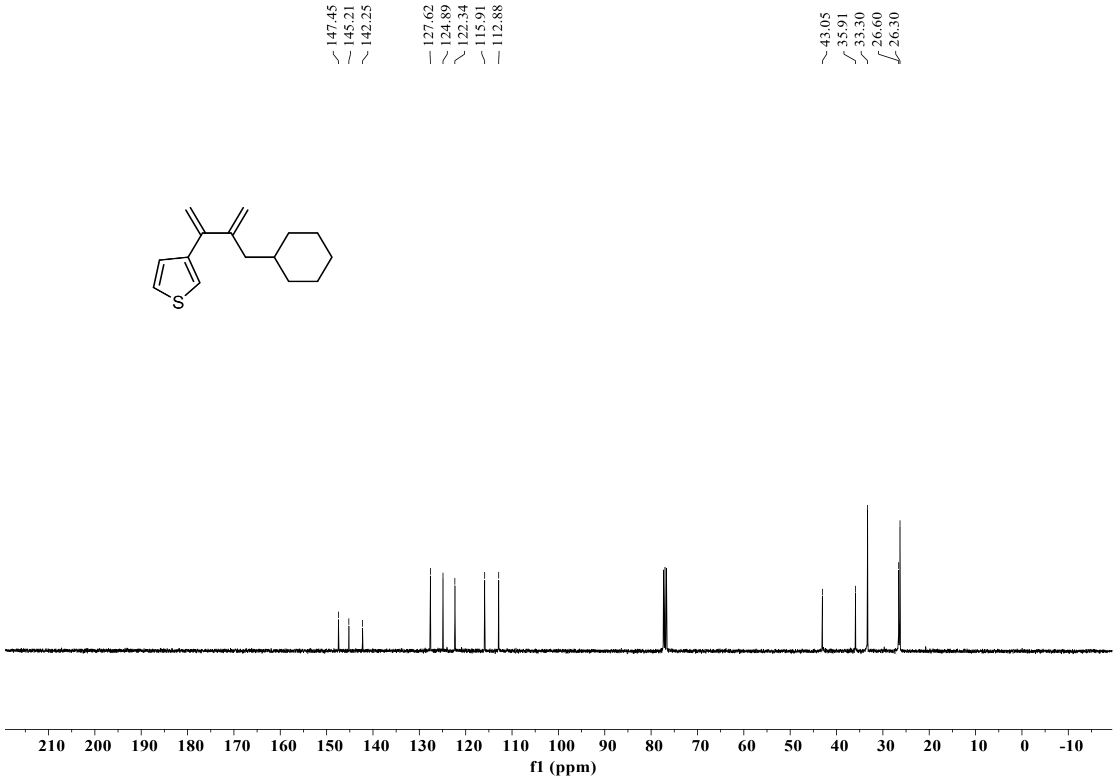

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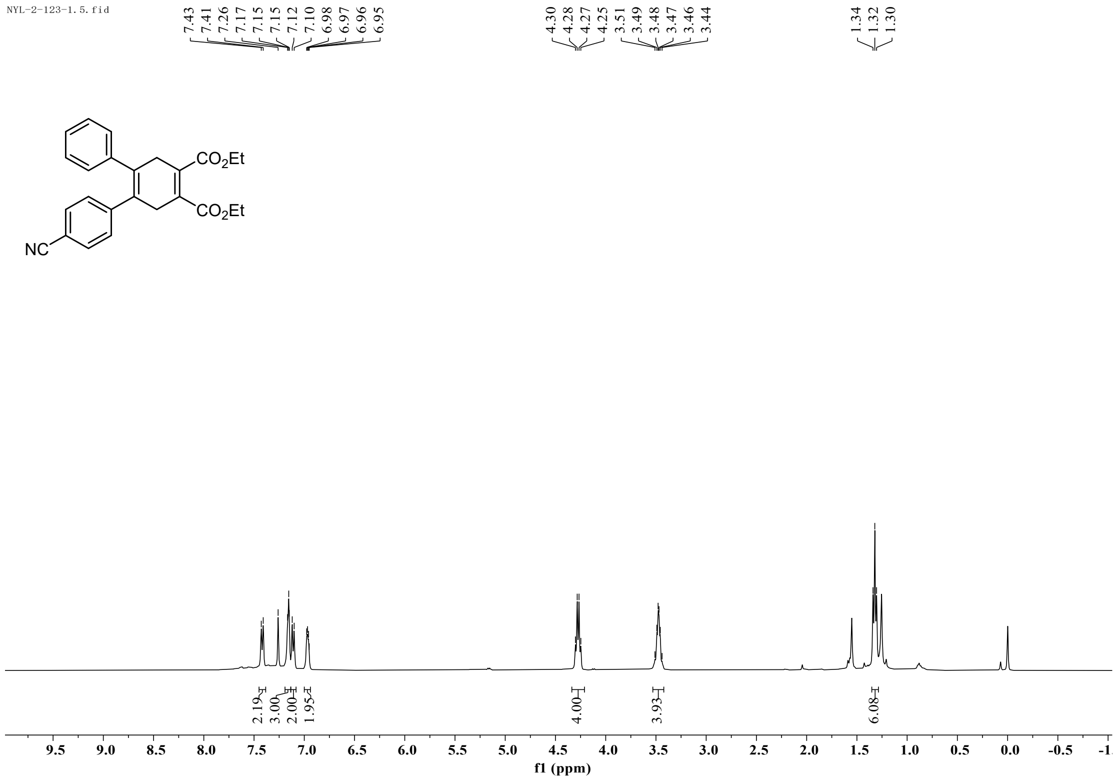

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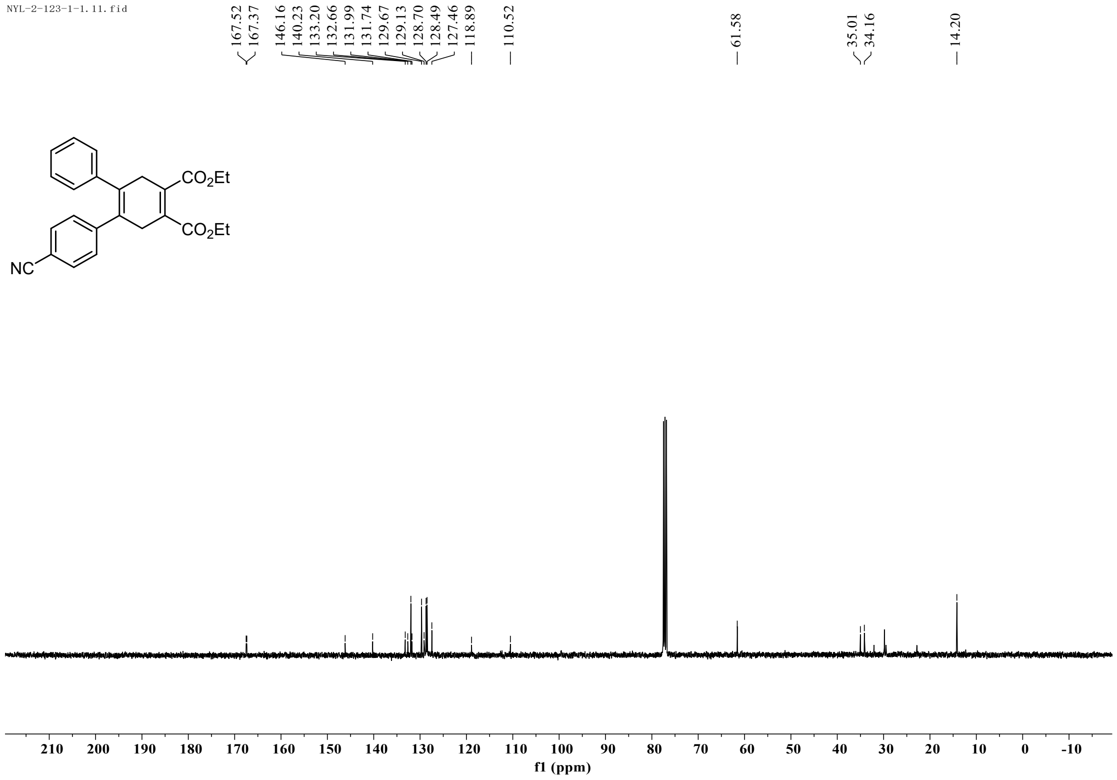
^{13}C NMR Spectra of compound **57**



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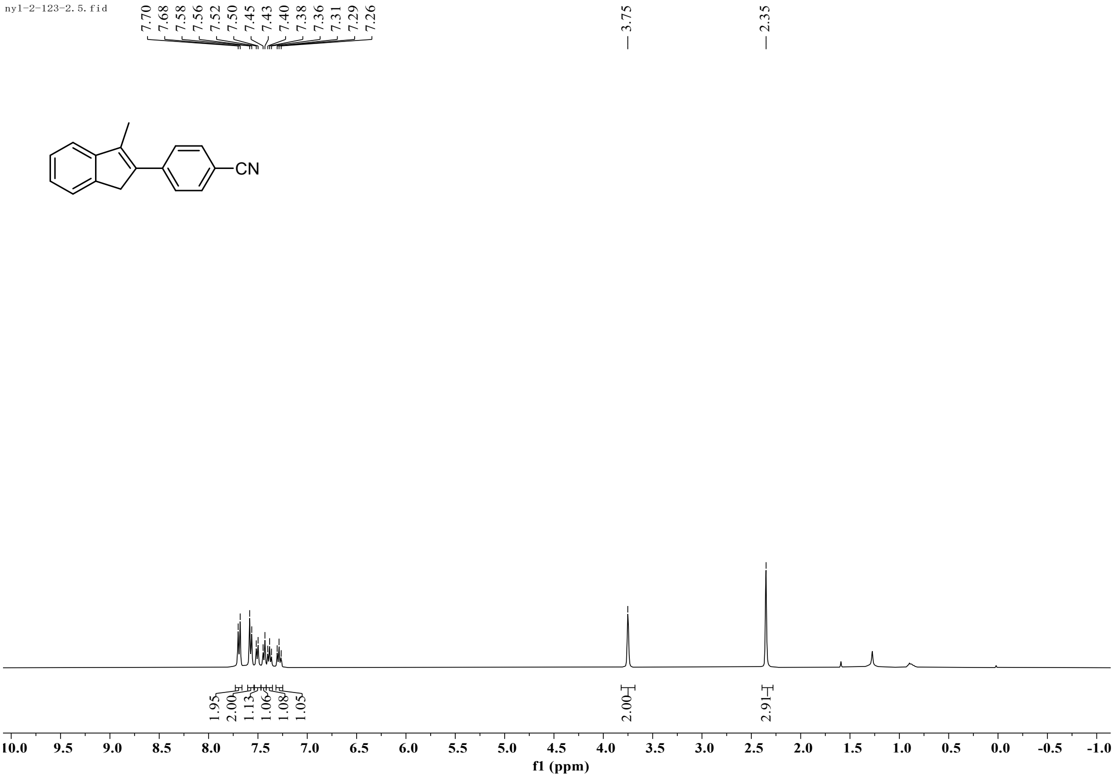

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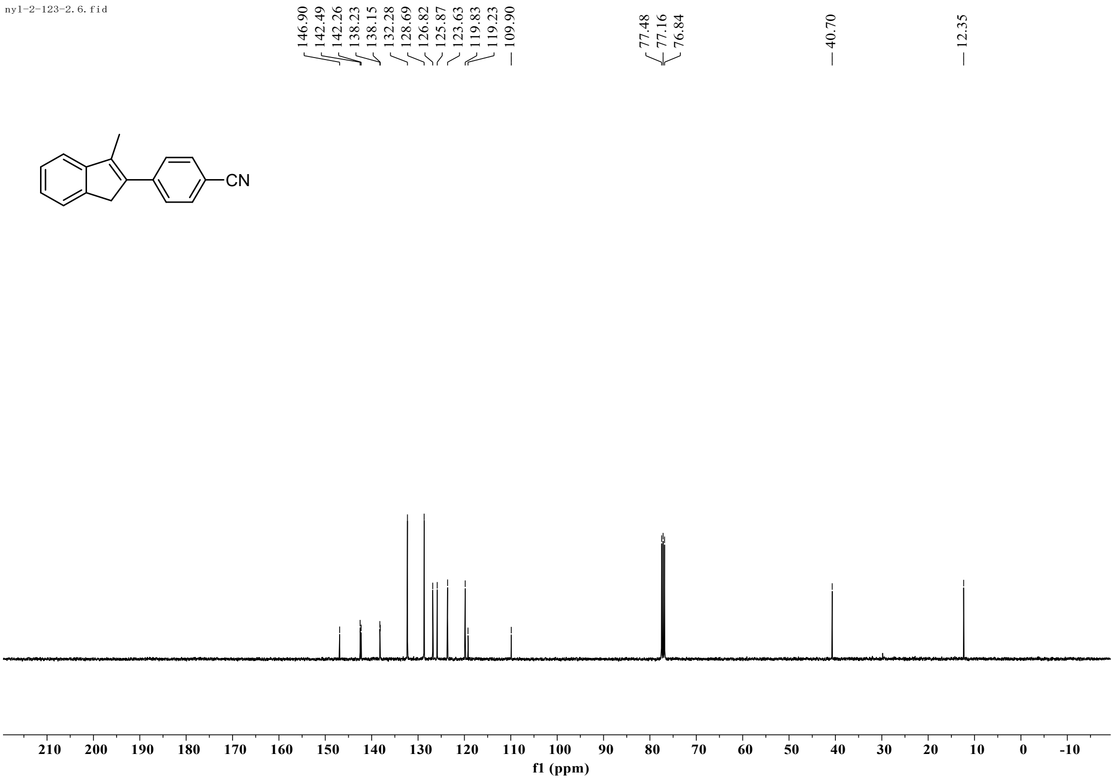
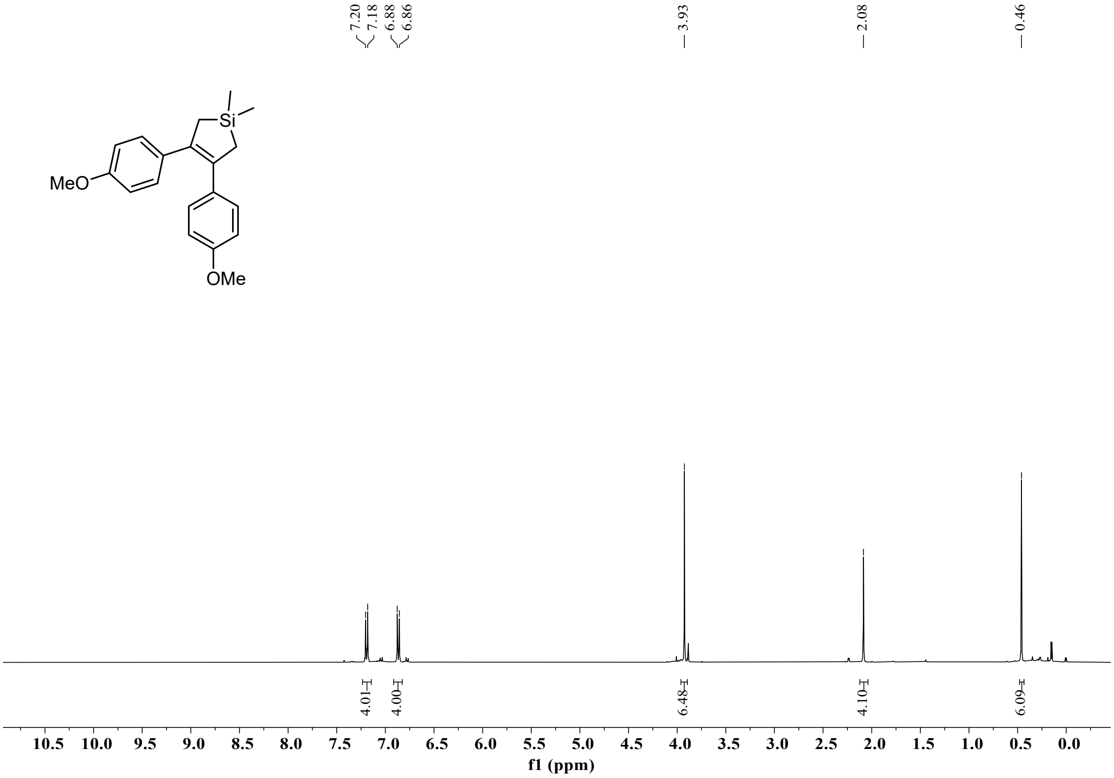
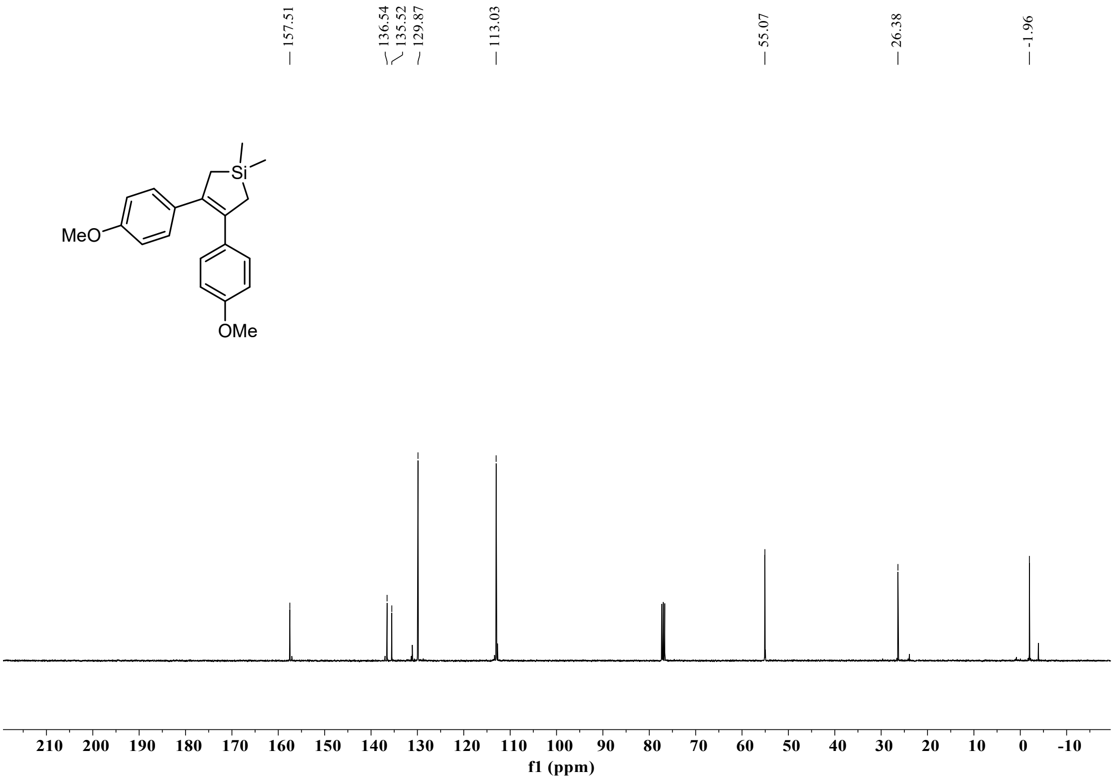


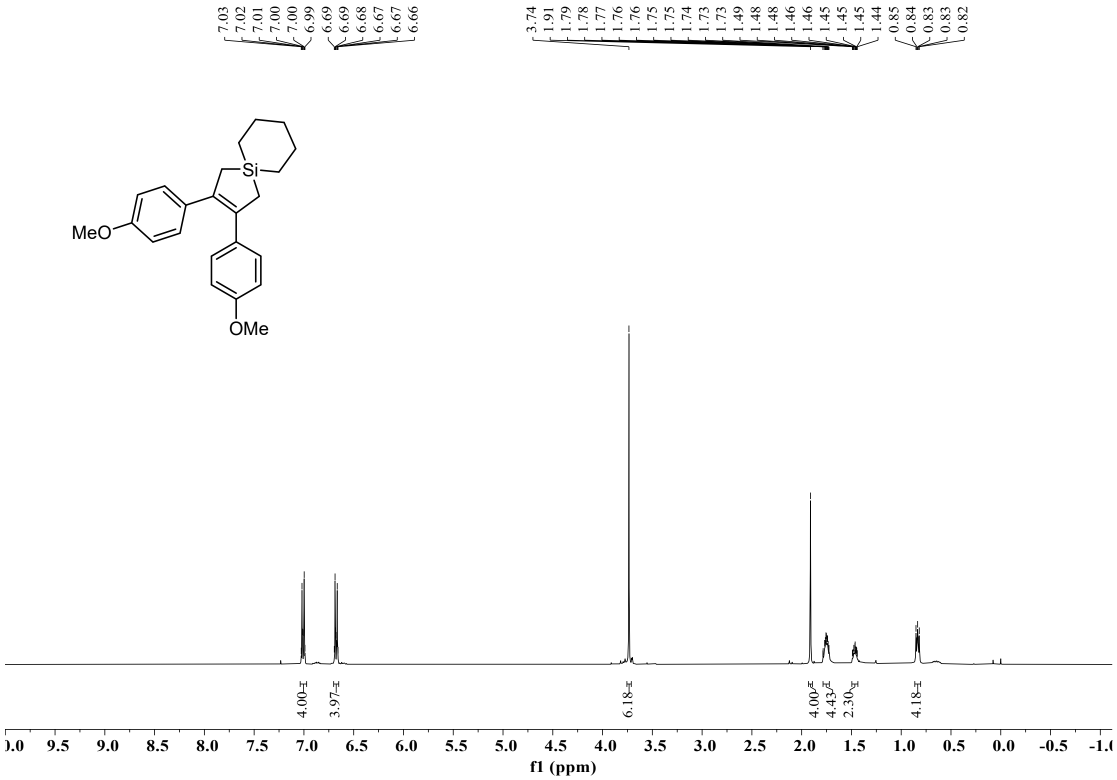
^{1}H NMR Spectra of compound **59**



^{13}C NMR Spectra of compound **59**



^{1}H NMR Spectra of compound **60**



^{13}C NMR Spectra of compound **60**