Supporting Information for

Sequential Difunctionalization of 2-Iodobiphenyls by Exploiting the Reactivities of a Palladacycle and an Acyclic Arylpalladium Species

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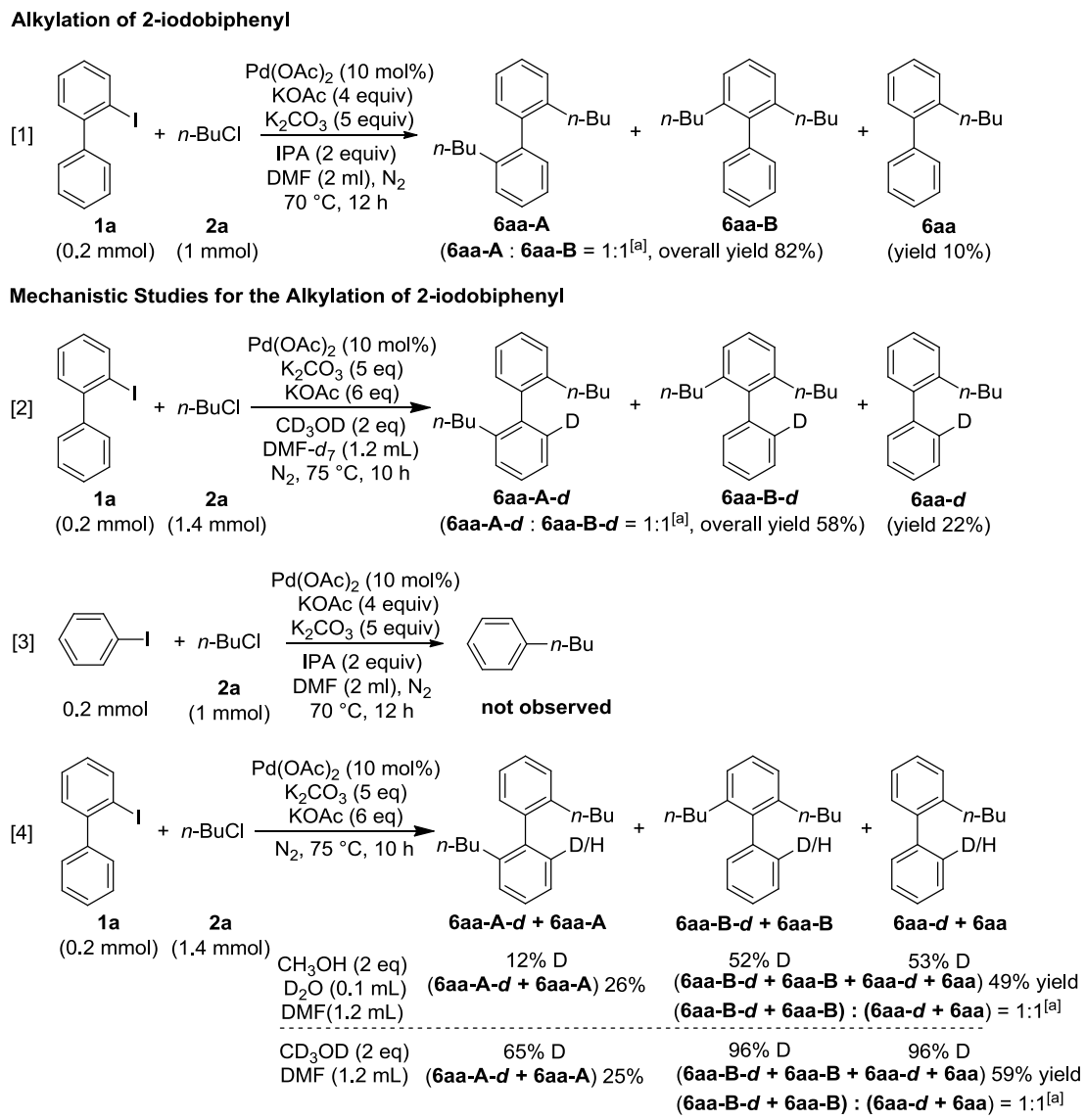
I. General Information

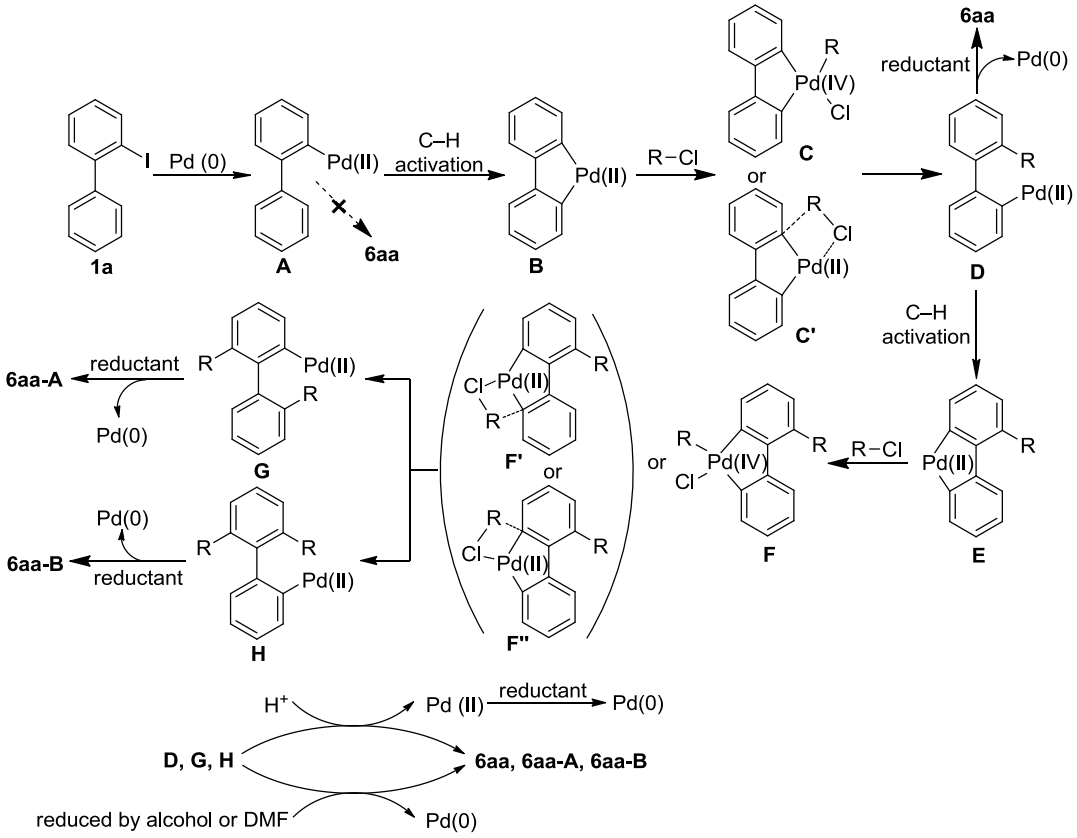
$Pd(OAc)_2$ was purchased from Strem Chemicals. All of the solvents were purified by distillation prior to use. Unless otherwise noted, the other commercial chemicals were used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker ARX400. High resolution mass spectra were measured on Bruker MicroTOF II ESI-TOF or EI-TOF (Agilent 6538 UHD) mass spectrometer. GC-MS data were tested with ThermoFisher Trace1300-ISQ (EI). ^1H NMR spectra were recorded in $CDCl_3$ and referenced to residual $CHCl_3$ at 7.26 ppm, and ^{13}C NMR spectra were referenced to the central peak of $CDCl_3$ at 77.0 ppm. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

II. Mechanistic Studies on the Pd-Catalyzed Alkylation of 2-Iodobiphenyl.



Scheme S1. Pd-Catalyzed alkylation of 2-iodobiphenyls with *n*-BuCl and mechanistic studies. [a] The ratios of **6aa-A** and **6aa-B** were determined by GC-MS and ^1H NMR. [b] Isolated yield.

When the alkylation reaction was carried out in the presence of CD_3OD and DMF-d_7, all of the products were fully deuterated at the 2 or 2' positions (**Scheme S1,** [2]). Furthermore, when iodobenzene was used, no alkylated products were observed (**Scheme S1,** [3]). All of these experimental results are consistent with a dibenzopalladacyclopentadiene intermediate, rather than a simple open-chain arylpalladium species as the reactive intermediate in the alkylation of 2-iodobiphenyl, even for the formation of monobutylated product **6aa**.



Scheme S2. Proposed mechanism for the alkylation of 2-iodobiphenyl with alkyl chloride.

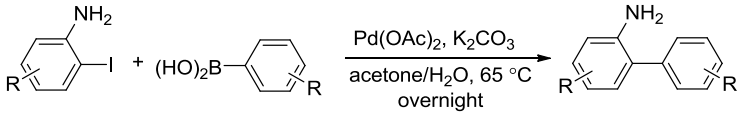
Based on the product distribution in the alkylation reaction and the mechanistic experiments, a mechanism for the alkylation of 2-iodobiphenyl with alkyl chloride can be proposed as shown in **Scheme S2**. The catalytic cycle starts with the oxidation addition of 2-iodobiphenyl to Pd(0). The resulting Pd(II) species **A** cleaves the 2'-C–H bond to form the key palladacycle **B**. The oxidative addition of the alkyl chloride to the Pd(II) in **B** forms Pd(IV) complex **C**, which then undergoes reductive elimination to afford intermediate **D**. It should be mentioned that a metathesis pathway cannot be ruled out for the formation of **D**. Intermediate **D** then generates monoalkylated product **6aa** following depalladation. Alternatively, **D** may undergo a second C-H activation to give alkylated dibenzometallacycle **E**. By following similar pathways to the formation of **D**, two isomeric intermediates **G** and **H** may be formed, which then form the corresponding dialkylated products.

Furthermore, to disambiguate the source of deuterium in products **6aa-*d***, **6aa-A-*d***, and

6aa-B-*d*, additional experiments were performed in the presence of D_2O or in a mixture of CD_3OD and DMF (**Scheme S1,** [4]). The products were deuterated in part, which means that CD_3 of methanol, DMF and hydroxy group acted as the deuterium source in the reaction. Therefore, intermediates **D**, **G**, and **H** form the final products *via* two competing pathways: direct protonation and reduction by an alcohol or DMF (**Scheme S2**).

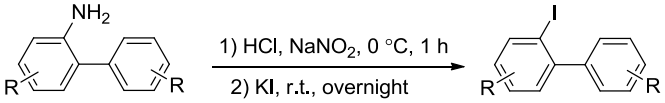
III. Experimental Procedures for the Synthesis of Substrates.

Preparation of 2-aminobiphenyls (1a' – 1k')[1]:



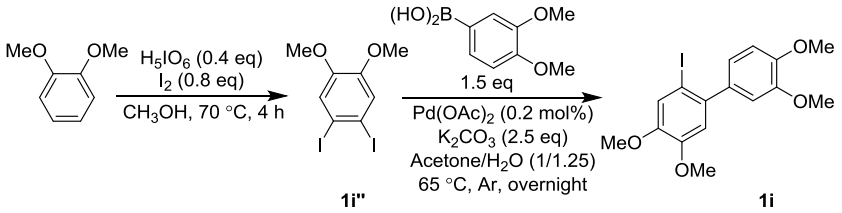
A 100 mL thick-walled ground flask equipped with PTFE stopcock on side-arm were added a magnetic stir-bar, substituted 2-iodoaniline (5.0 mmol), corresponding substituted phenylboronic acid (10.0 mmol, 2.0 equiv), and K_2CO_3 (12.5 mmol, 2.5 equiv, 1.73 g). The flask was equipped with a rubber septum and sealed up. The reaction flask was evacuated and back-filled with argon, followed by the addition of acetone (10.0 mL) and water (12.0 mL) with a gas-tight syringe. The reaction mixture was stirred and heated to 65 ℃. A solution of $Pd(OAc)_2$ (0.03 mmol, 0.6 mmol%, 6.7 mg) in acetone (2.0 mL) was then introduced to the reaction mixture with a gas-tight syringe. After the reaction mixture was stirred at 65 ℃ overnight, it was allowed to cool to room temperature. The reaction mixture was extracted with ethyl acetate (4 x 40 mL), and the combined organic phases were washed with 50 mL of water. The organic phases were dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ether and ethyl acetate) to give the corresponding substituted 2-aminobiphenyls (**1a'-1k'**).

Preparation of 2-iodobiphenyls (1a – 1k)[2]:



2-Aminobiphenyl (5.0 mmol) was added slowly to a stirred mixture of conc. HCl (36-38%; 6.5 mmol, 2.3 mL) and water (8.5 mL). An aqueous solution of $NaNO_2$ (20%; 7.5 mmol, 2.59g) was added to the reaction mixture below 5 ℃ within 10 min and stirred for 1 h at the same temperature. An aqueous solution of KI (10.0 mmol, 1.66 g) in water (10.0 mL) was added and the reaction mixture was stirred at room temperature overnight. Ethyl acetate (50 mL) was added to the reaction mixture and the organic phase was treated with saturated $NaHSO_3$ to decolorize. The aqueous phase was extracted with ethyl acetate (3 x 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ether) to give the desired compounds (**1a-1k**).

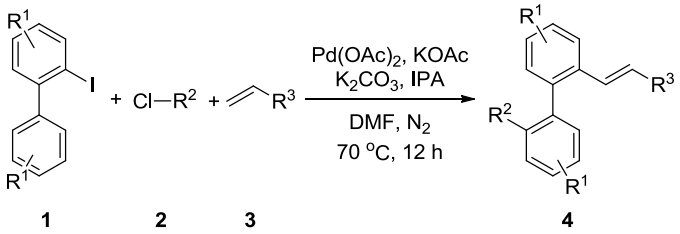
Preparation of 2-iodo-3',4,4',5-tetramethoxy-1,1'-biphenyl (1i):



In a round-bottom flask, a solution of H_5IO_6 (0.4 eq, 8.0 mmol, 1.83 g) in methanol (20 mL) was stirred for 15 min at 20 ℃. Iodine (0.8 eq, 16.0 mmol, 4.06 g) was then added to the solution and the mixture was stirred vigorously for another 10 min. Veratrol (20 mmol, 2.55 mL) was added to the mixture and stirred for 4 h at 70 ℃ (a white precipitate was formed during the reaction). After that, the reaction mixture was diluted with EtOAc (100 mL) and washed with saturated aqueous $NaHCO_3$ (30 mL) and brine (30 mL, twice). The organic phase was dried with Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was recrystallized to give the 1,2-diiodo-4,5-dimethoxybenzene (**1i"**, 5.5 g, 71%).[3]

The desired product **1i** was synthesized from the prepared 1,2-diiodo-4,5-dimethoxybenzene (1.95 g, 5.0 mmol) and (3,4-dimethoxyphenyl)boronic acid (1.365 g, 7.5 mmol) using the general procedure above. The product was obtained as a light yellow solid (1.15 g, 58% yield).

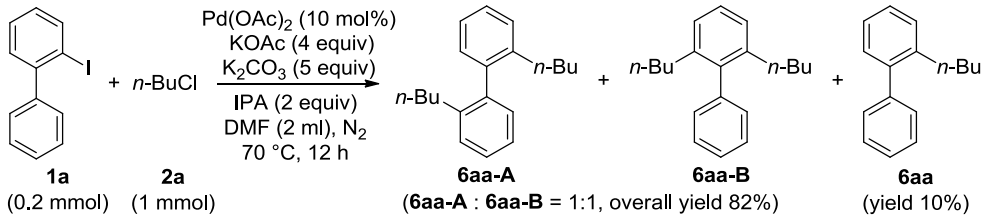
IV. General Procedure for the Sequential Difunctionalization of 2-Iodobiphenyls.



A 25 mL Schlenk tube equipped with a stir bar was charged with $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), KOAc (78.4 mg, 0.8 mmol, 4.0 equiv), K_2CO_3 (138.2 mg, 1.0 mmol, 5.0 equiv), IPA (30.6 μL, 0.4 mmol, 2.0 equiv), 2-iodobiphenyls (0.2 mmol, 1.0 equiv), alkyl chlorides (1.0 mmol, 5.0 equiv), alkenes (0.2 mmol, 1.0 equiv), and DMF (2 mL). The tube was evacuated and backfilled with N_2 (5 times). After the reaction mixture was stirred in a preheated oil bath (70 ℃) for 12 h, it was allowed to cool down to room temperature and diluted with ethyl acetate (10 mL). The reaction mixture was washed with saturated brine (10 mL, 3 times), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by preparative silica gel TLC to give the corresponding compounds.

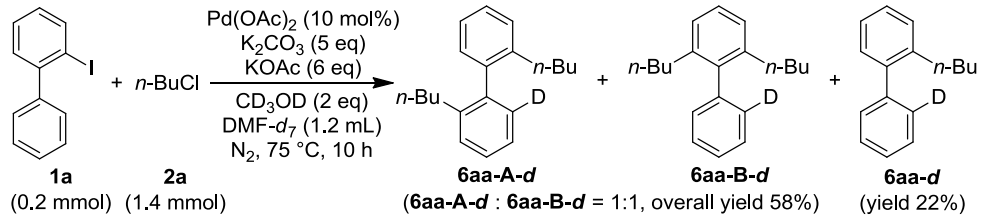
V. Experimental Procedures for the Pd-Catalyzed Alkylation of 2-Iodobiphenyls and Mechanistic Studies.

Pd-Catalyzed Alkylation of 2-Iodobiphenyls with *n*-BuCl:



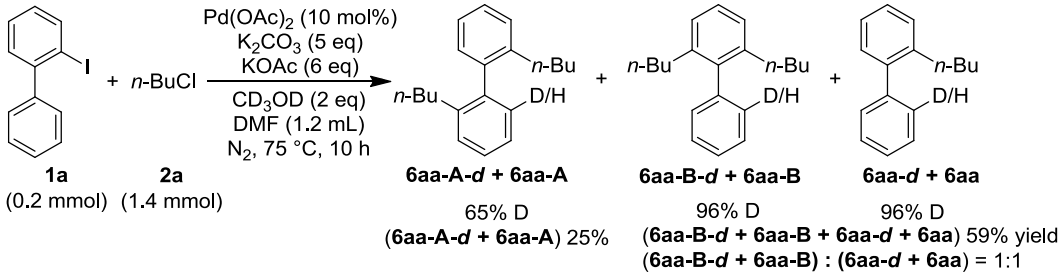
A 50 mL Schlenk-type tube (with a Teflon high pressure valve and side arm) equipped with a magnetic stir bar was charged with 2-iodobiphenyl (0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 10 mol%), K_2CO_3 (138.2 mg, 5.0 eq), KOAc (117.7 mg, 6.0 eq), followed by *n*-BuCl (146.2 uL, 7.0 eq), *i*-PrOH (30.6 uL, 2.0 eq), and DMF (1.2 mL) as the solvent. The reaction tube was backfilled with nitrogen and sealed. After the reaction mixture was stirred at 75 ℃ for 10 h, it was allowed to cool to ambient temperature. The reaction mixture was diluted with EtOAc (15 mL) and washed with saturated aqueous $NaHCO_3$ (3 mL) and brine (3 mL, twice). The organic phase was dried with Na_2SO_4, filtered, and concentrated *in vacuo*. The desired products were obtained by preparative thin-layer chromatograph (petroleum ether). The ratio of **6aa-A** and **6aa-B** was determined by GC-MS and ^{1}H NMR.

Pd-Catalyzed Alkylation of 2-Iodobiphenyls with *n*-BuCl in DMF-d_7 and CD_3OD:



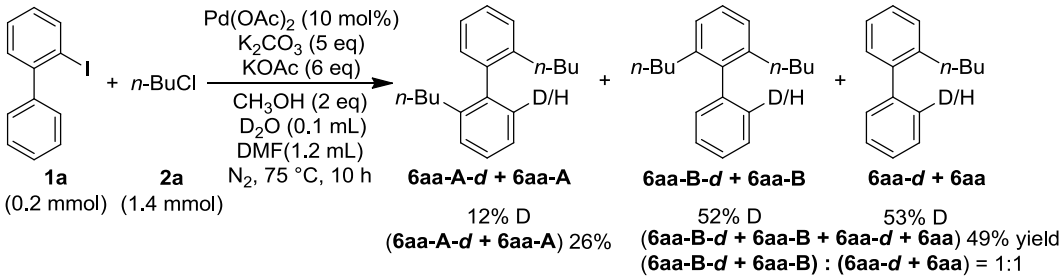
A 50 mL Schlenk-type tube (with a Teflon high pressure valve and side arm) equipped with a magnetic stir bar was charged with 2-iodo-1,1'-biphenyl (0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 10 mol%), K_2CO_3 (138.2 mg, 5.0 eq), KOAc (117.7 mg, 6.0 eq), followed by *n*-BuCl (146.2 uL, 7.0 eq), CD_3OD (16.2 uL, 2.0 eq), and DMF-d_7 (1.2 mL) as the solvent. The reaction tube was backfilled with nitrogen and sealed. After the reaction mixture was stirred at 75 ℃ for 10 h, it was allowed to cool to ambient temperature. The reaction mixture was diluted with EtOAc (15 mL) and washed with saturated aqueous $NaHCO_3$ (3 mL) and brine (3 mL, twice). The organic phase was dried with Na_2SO_4, filtered, and concentrated *in vacuo*. The desired products were obtained by preparative thin-layer chromatograph (petroleum ether). The ratio of **6aa-A-*d*** and **6aa-B-*d*** was determined by GC-MS and ^{1}H NMR.The extent of D incorporation was analyzed by ^{1}H NMR after purification.

Pd-Catalyzed Alkylation of 2-Iodobiphenyls with *n*-BuCl in CD_3OD:



A 50 mL Schlenk-type tube (with a Teflon high pressure valve and side arm) equipped with a magnetic stir bar was charged with 2-iodo-1,1'-biphenyl (0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 10 mol%), K_2CO_3 (138.2 mg, 5.0 eq), KOAc (117.7 mg, 6.0 eq), followed by *n*-BuCl (146.2 uL, 7.0 eq), CD_3OD (16.2 uL, 2.0 eq), and DMF (1.2 mL) as the solvent. The reaction tube was backfilled with nitrogen and sealed. After the reaction mixture was stirred at 75 ℃ for 10 h, it was allowed to cool to ambient temperature. The reaction mixture was diluted with EtOAc (15 mL) and washed with saturated aqueous $NaHCO_3$ (3 mL) and brine (3 mL, twice). The organic phase was dried with Na_2SO_4, filtered, and concentrated *in vacuo*. The desired products were obtained by preparative thin-layer chromatograph (petroleum ether). The ratio of **6aa-A(-*d*)** and **6aa-B(-*d*)** was determined by GC-MS and ^1H NMR. The extent of D incorporation was analyzed by ^1H NMR after purification.

Pd-Catalyzed Alkylation of 2-Iodobiphenyls with *n*-BuCl in the Presence of D_2O:



A 50 mL Schlenk-type tube (with a Teflon high pressure valve and side arm) equipped with a magnetic stir bar was charged with 2-iodo-1,1'-biphenyl (0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 10 mol%), K_2CO_3 (138.2 mg, 5.0 eq), KOAc (117.7 mg, 6.0 eq), followed by *n*-BuCl (146.2 uL, 7.0 eq), CH_3OH (16.2 uL, 2.0 eq), D_2O (0.1 mL), and DMF (1.2 mL) as the solvent. The reaction tube was backfilled with nitrogen and sealed. After the reaction mixture was stirred at 75 ℃ for 10 h, it was allowed to cool to ambient temperature. The reaction mixture was diluted with EtOAc (15 mL) and washed with saturated aqueous $NaHCO_3$ (3 mL) and brine (3 mL, twice). The organic phase was dried with Na_2SO_4, filtered, and concentrated *in vacuo*. The desired products were obtained by preparative thin-layer chromatograph (petroleum ether). The extent of D incorporation was analyzed by ^1H NMR after purification.

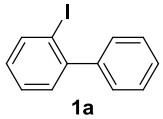
VI. References.

(1) T. I. Wallow, B. M. Novak, *J. Org. Chem.* **1994**, *59*, 5034.

(2) S. Y. Cho, A. C. Grimsdale, D. J. Jones, S. E. Watkins, A. B. Holmes, *J. Am. Chem. Soc.* **2007**, *129*, 11910.

(3) J. Lacour, D. Monchaud, G. Bernardinelli, F. Favarger, *Org. Lett.* **2001**, *3*, 1407.

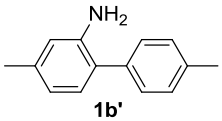
VII. Characterization of synthesized compounds.



1a

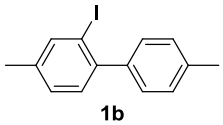
2-iodo-1,1'-biphenyl (1a): Purified by column chromatography on a silica gel column using petroleum ether as the eluent to give the title compound as a colorless liquid (1.26 g, 90% yield). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.98 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.39-7.48 (m, 4 H), 7.38-7.32 (m, 3 H), 7.06 (ddd, *J* = 9.2, 7.4, 1.8 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*): δ 146.58, 144.15, 139.44, 130.04, 129.23, 128.74, 128.07, 127.91, 127.60, 98.59. MS (EI): m/z = 280.01 ($[M]^{+}$).

The data are identical to: S. Y. Cho, A. C. Grimsdale, D. J. Jones, S. E. Watkins, A. B. Holmes, *J. Am. Chem. Soc.* **2007**, *129*, 11910.



1b'

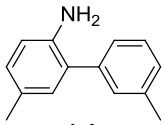
4,4'-dimethyl-[1,1'-biphenyl]-2-amine (1b'): Purified by column chromatography on a silica gel column using petroleum ether : ethyl acetate = 20:1 as the eluent to give the title compound as a yellow liquid (0.92 g, 93% yield). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.39 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 1H), 6.64 (s, 1H), 3.62 (br s, 2H), 2.44 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*): δ 143.30, 138.09, 136.51, 136.47, 130.27, 129.38, 128.91, 124.88, 119.49, 116.17, 21.13, 21.10. HRMS (ESI-TOF) *m/z*: calcd for $C_{14}H_{16}N^{+}$: 198.1277 $(M + H)^{+}$, found: 198.1275.



1b

2-iodo-4,4'-dimethyl-1,1'-biphenyl (1b): Purified by column chromatography on a silica gel column using petroleum ether as the eluent to give the title compound as a colorless liquid (1.28 g, 83% yield). ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 7.85 (d, *J* = 0.6 Hz, 1H), 7.32-7.26 (m, 3H), 7.25-7.21 (m, 3H), 2.41 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $(CD_3)_2CO$): δ145.31, 142.82,

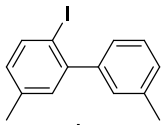
141.47, 140.51, 138.64, 131.42, 130.74, 130.73, 130.15, 99.58, 21.94, 21.11. MS (EI): m/z = 308.05 ($[M]^+$).



1c'

3',5-dimethyl-[1,1'-biphenyl]-2-amine (1c'): Purified by column chromatography on a silica gel column using petroleum ether : ethyl acetate = 20:1 as the eluent to give the title compound as a yellow liquid (0.94 g, 95% yield). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.36 (t, *J* = 7.5 Hz, 1H), 7.30-7.27 (m, 2H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.01-6.98 (m, 2H), 6.72 (d, *J* = 7.8 Hz, 1H), 3.60 (br s, 2H), 2.43 (s, H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*): δ 140.88, 139.55, 138.31, 130.85, 129.73, 128.84, 128.56, 127.81, 127.74, 127.72, 125.99, 115.70, 20.42, 20.37. HRMS (ESI-TOF) *m/z*: calcd for $C_{14}H_{16}N^+$: 198.1277 $(M + H)^+$, found: 198.1280.

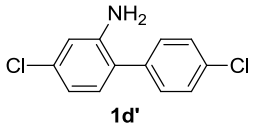
The data are identical to: J. M. Racowski, N. D. Ball, M. S. Sanford, *J. Am. Chem. Soc.* **2011**, *133*, 18022.



1c

2-iodo-3',5-dimethyl-1,1'-biphenyl (1c): Purified by column chromatography on a silica gel column using petroleum ether as the eluent to give the title compound as a colorless oil (1.23 g, 80% yield). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.15-7.13 (m, 3H), 6.86 (ddd, *J* = 8.0, 2.3, 0.6 Hz, 1H), 2.42 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*): δ 146.46, 144.13, 139.15, 138.01, 137.48, 131.00, 129.89, 129.64, 128.21, 127.72, 126.31, 94.43, 21.45, 20.86. MS (EI): m/z = 308.05 ($[M]^+$).

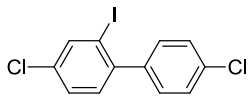
The data are identical to: J. M. Racowski, N. D. Ball, M. S. Sanford, *J. Am. Chem. Soc.* **2011**, *133*, 18022.



1d'

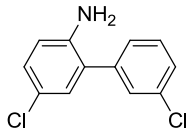
4,4'-dichloro-[1,1'-biphenyl]-2-amine (1d'): Purified by column chromatography on a silica gel column using petroleum ether : ethyl acetate = 20:1 as the eluent to give the title compound as a yellow liquid (1.12 g, 94% yield). ^{1}H NMR (400 MHz, Chloroform-*d*): δ7.43-7.40 (m, 2H), 7.36-7.33 (m, 2H), 6.99 (d, *J* = 8.0 Hz, 1 H), 6.77 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.74 (d, *J* = 2.0 Hz, 1H), 3.78 (br s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*): δ 144.54, 136.82, 134.25, 133.44, 131.30, 130.34, 129.12, 124.63, 118.62, 115.23. HRMS (ESI-TOF) *m/z*: calcd for $C_{12}H_{10}Cl_2N^+$:

238.0185 $(M + H)^+$, found: 238.0178.



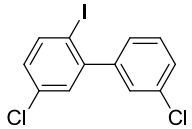
1d

4,4'-dichloro-2-iodo-1,1'-biphenyl (1d): Purified by column chromatography on a silica gel column using petroleum ether as the eluent to give the title compound as a colorless solid (1.47 g, 84% yield). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.95 (d, *J* = 2.1 Hz, 1 H), 7.42-7.38 (m, 2H), 7.37 (dd, *J* = 8.3, 2.1 Hz, 1 H), 7.26-7.22 (m, 2H), 7.19 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*): δ 143.90, 141.36, 138.82, 134.05, 133.93, 130.54, 130.36, 128.41, 128.33, 98.29. MS (EI): m/z = 347.96 $([M]^+)$.



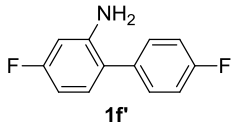
1e'

3',5-dichloro-[1,1'-biphenyl]-2-amine (1e'): Purified by column chromatography on a silica gel column using petroleum ether : ethyl acetate = 20:1 as the eluent to give the title compound as a yellow oil(1.07 g, 90% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (t, *J* = 1.8 Hz, 1H), 7.41-7.36 (m, 1H), 7.33 (ddt, *J* = 12.2, 7.2, 1.7 Hz, 2H), 7.15-7.04 (m, 2H), 6.69 (d, *J* = 8.5 Hz, 1H), 3.69 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.02, 140.04, 134.78, 130.19, 129.78, 129.01, 128.67, 127.78, 127.27, 127.06, 123.19, 116.81.



1e

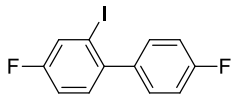
3',5-dichloro-2-iodo-1,1'-biphenyl (1e): Purified by column chromatography on a silica gel column using petroleum ether as the eluent to give the title compound as a yellow oil (1.4 g, 81% yield). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.86 (d, *J* = 8.5 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.31 (d, *J* = 2.1 Hz, 1H), 7.28 (d, *J* = 2.5 Hz, 1H), 7.21 (dt, *J* = 6.6, 1.8 Hz, 1H), 7.06 (dd, *J* = 8.5, 2.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 146.65, 144.50, 140.56, 134.56, 133.95, 129.90, 129.41, 129.37, 129.19, 128.23, 127.37, 95.27. MS (EI): m/z = 347.91 $([M]^+)$.



1f'

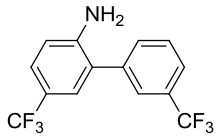
4,4'-difluoro-[1,1'-biphenyl]-2-amine (1f'): Purified by column chromatography on a silica gel

column using petroleum ether : ethyl acetate = 20:1 as the eluent to give the title compound as a yellow liquid (0.98 g, 96% yield). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.40-7.35 (m, 2 H), 7.17-7.10 (m, 2H), 7.02 (dd, *J* = 8.3, 6.5 Hz, 1 H), 6.55-6.44 (m, 2H), 3.82 (br s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.15 (d, *J* = 242.4 Hz), 162.03 (d, *J* = 244.9 Hz), 145.11 (d, *J* = 10.9 Hz), 134.49 (d, *J* = 3.3 Hz), 131.57 (d, *J* = 9.8 Hz), 130.79 (d, *J* = 7.9 Hz), 122.48 (d, *J* = 2.7 Hz), 115.75 (d, *J* = 21.2 Hz), 105.16 (d, *J* = 21.4 Hz), 102.02 (d, *J* = 24.6 Hz). HRMS (ESI-TOF) *m/z*: calcd for $C_{12}H_{10}F_2N^+$: 206.0776 $(M + H)^+$, found: 206.0776.



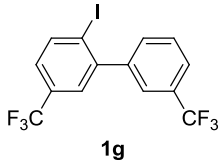
1f

4,4'-difluoro-2-iodo-1,1'-biphenyl (1f): Purified by column chromatography on a silica gel column using petroleum ether as the eluent to give the title compound as a colorless liquid (1.22 g, 77% yield). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.69 (dd, *J* = 8.2, 2.6 Hz, 1 H), 7.30-7.22 (m, 3 H), 7.14-7.08 (m, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*): δ 162.41 (d. *J* = 245.6 Hz), 161.26 (d, *J* = 250.2 Hz), 141.87 (d, *J* = 3.5 Hz), 139.19 (d, *J* = 3.4 Hz), 131.09 (d, *J* = 8.1 Hz), 130.55 (d, *J* = 8.0 Hz), 126.29 (d, *J* = 23.5 Hz), 115.25 (d, *J* = 20.8 Hz), 115.01 (d, *J* = 21.4 Hz), 98.07 (d, *J* = 8.0 Hz). MS (EI): m/z = 315.97 ($[M]^+$).



1g'

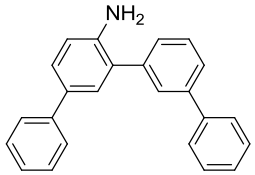
3',5-bis(trifluoromethyl)-[1,1'-biphenyl]-2-amine (1g'): Purified by column chromatography on a silica gel column using petroleum ether : ethyl acetate = 20:1 as the eluent to give the title compound as a yellow oil (1.41 g, 92% yield). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.72 (d, *J* = 2.1 Hz, 1H), 7.69-7.58 (m, 3H), 7.43 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.35 (d, *J* = 2.1 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 4.02 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 146.43, 138.92, 132.41 (d, *J* = 1.5 Hz), 131.57 (q, *J* = 32.4 Hz), 129.63, 127.59 (q, *J* = 3.8 Hz), 126.28 (q, *J* = 3.7 Hz), 125.81 (q, *J* = 3.8 Hz), 125.27, 124.66 (q, *J* = 3.8 Hz), 124.62 (q, *J* = 271.1Hz) 123.93 (q, *J* = 271.2 Hz), 120.56 (q, *J* = 32.9 Hz), 115.14.



1g

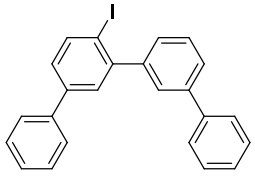
2-iodo-3',5-bis(trifluoromethyl)-1,1'-biphenyl (1g): Purified by column chromatography on a

silica gel column using petroleum ether as the eluent to give the title compound as a colorless oil (1.73 g, 83% yield). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.12 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.65-7.53 (m, 4H), 7.33 (dd, *J* = 8.3, 2.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 145.95 , 143.46 , 140.38, 132.54, 131.09 (q, *J* = 32.93Hz), 131.05 (q, *J* = 32.87 Hz) , 128.83, 126.36 (q, *J* = 3.7 Hz), 126.09 (q, *J* = 3.8 Hz), 125.85 (q, *J* = 3.7 Hz), 125.10 (q, *J* = 3.9 Hz), 123.92 (q, *J* = 272.6 Hz), 123.74 (q, *J* = 272.6 Hz), 102.62. MS (EI): m/z = 415.97 ([M]$^{+}$).



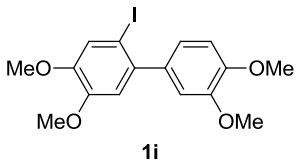
1h'

[1,1':3',1'':3'',1'''-quaterphenyl]-4'-amine (1h'): Purified by column chromatography on a silica gel column using petroleum ether : ethyl acetate = 20:1 as the eluent to give the title compound as a brown liquid (1.19 g, 74% yield). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.88 (s, 1H), 7.77-7.69 (m, 5H), 7.44-7.66 (m, 9H), 7.36-7.40 (m, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 3.95 (br s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*): δ 142.95, 141.69, 140.83, 140.66, 139.84, 131.51, 129.24, 129.02, 128.75, 128.60, 127.86, 127.82, 127.61, 127.39, 127.11, 127.06, 126.29, 126.24, 125.95, 115.96. HRMS (ESI-TOF) *m/z*: calcd for $C_{24}H_{20}N^{+}$: 322.1590 $(M + H)^{+}$, found: 322.1583.



1h

4'-iodo-1,1':3',1'':3'',1'''-quaterphenyl (1h): Purified by column chromatography on a silica gel column using petroleum ether as the eluent to give the title compound as a colorless solid (1.51 g, 70% yield). **1**H NMR (400 MHz, Chloroform-*d*): δ 8.04 (d, *J* = 8.2 Hz, 1H), 7.70-7.64 (m, 4H), 7.63-7.60 (m, 3H), 7.54 (dd, *J* = 7.7, 0.5 Hz, 1H), 7.49-7.43 (m, 4H), 7.41-7.35 (m, 3H), 7.30 (dd, *J* = 8.2, 2.3 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 146.84, 144.44, 141.37, 140.85, 140.82, 139.93, 139.75, 128.91, 128.82, 128.79, 128.48, 128.26, 128.11, 127.78, 127.52, 127.41, 127.20, 126.94, 126.42, 97.22.

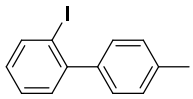


1i

2-iodo-3',4,4',5-tetramethoxy-1,1'-biphenyl (1i): Purified by column chromatography on a silica

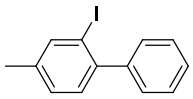
gel column using petroleum ether : ethyl acetate = 30:1 as the eluent to give the title compound as a colorless solid (1.5 g, 76% yield). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.32 (d, *J* = 1.2 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.83 (s, 1H), 3.93-3.85 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 148.89, 148.41, 148.23, 147.95, 138.87, 136.74, 121.52, 121.45, 112.93, 112.90, 110.40, 86.61, 56.09, 55.81, 55.73.

The data are identical to: A. Fürstner, J. W. J. Kennedy *Chem. Eur. J.* **2006**, *12*, 7398 – 7410.



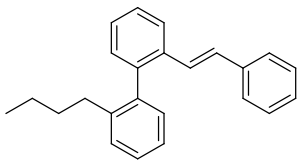
1j

2-Iodo-4'-methylbiphenyl (1j): Purified by column chromatography on a silica gel column using petroleum ether as the eluent to give the title compound as a colorless solid (1.32 g, 90% yield). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.97 (d, *J* = 7.9 Hz, 1H), 7.39 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.31 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.26 (s, 4H), 7.03 (td, *J* = 7.8, 1.7 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 146.59, 141.35, 139.45, 137.37, 130.13, 129.11, 128.63, 128.58, 128.08, 98.80, 21.28. MS (EI): $[M]^{+}$: 294.01.



1k

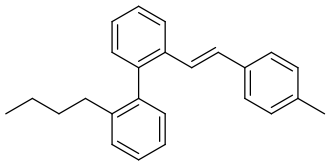
2-Iodo-4-methylbiphenyl (1k): Purified by column chromatography on a silica gel column using petroleum ether as the eluent to give the title compound as a colorless oil (1.30 g, 88% yield). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.82 (s, 1H), 7.48-7.38 (m, 3H), 7.37-7.31 (m, 2H), 7.21 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 144.04, 143.72, 139.90, 138.78, 129.67, 129.36, 128.93, 127.86, 127.43, 98.41, 20.43. MS (EI): $[M]^{+}$: 293.98.



4aaa

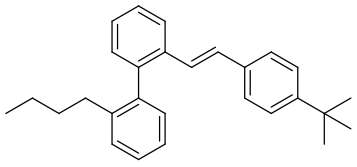
(*E*)-2-butyl-2'-styryl-1,1'-biphenyl (4aaa): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50:1 as the eluent to give the title compound as a colorless oil (50.0mg, 80%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.83 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.44-7.40 (ddd, *J* = 16.4, 8.1, 1.5 Hz, 2H), 7.37 – 7.32 (m, 3H), 7.32-7.28 (m, 4H), 7.24-7.14 (m, 3H), 7.07 (d, *J* = 16.4 Hz, 1H), 6.85 (d, *J* = 16.3 Hz, 1H), 2.53-2.38 (m, 2H), 1.46-1.39 (m, 2H), 1.23-1.13 (m, 2H), 0.74 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 141.03, 140.93, 140.18, 137.53, 135.61, 130.39, 130.25, 129.06, 128.95, 128.51, 127.49, 127.39, 127.38, 127.09,

127.04, 126.45, 125.41, 124.71, 32.77, 32.74, 22.37, 13.72. HRMS (ESI-TOF): m/z calcd for $C_{24}H_{25}^+$: 313.1951 $(M + H)^+$; found: 313.1903.



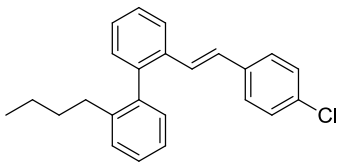
4aab

(*E*)-2-butyl-2'-(4-methylstyryl)-1,1'-biphenyl (4aab): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50:1 as the eluent to give the title compound as a colorless oil (56.2mg, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.79 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.42-7.32 (m, 3H), 7.32-7.24 (m, 2H), 7.24-7.19 (m, 2H), 7.19-7.15 (m, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 7.02 (d, *J* = 16.3 Hz, 1H), 6.76 (d, *J* = 16.3 Hz, 1H), 2.49-2.34 (m, 2H), 2.32 (s, 3H), 1.43-1.35 (m, 2H), 1.20-1.09 (m, 2H), 0.72 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 141.05, 140.78, 140.25, 137.28, 135.79, 134.78, 130.36, 130.26, 129.23, 128.97, 128.93, 127.43, 127.34, 126.83, 126.38, 126.13, 125.38, 124.60, 32.76, 32.74, 22.37, 21.19, 13.73. HRMS (ESI-TOF) *m/z*: calcd for $C_{25}H_{26}Na^+$: 349.1927 $(M + Na)^+$, found: 349.1917.



4aac

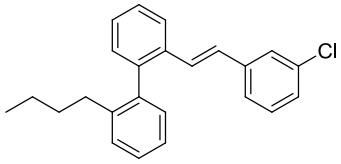
(*E*)-2-butyl-2'-(4-(tert-butyl)styryl)-1,1'-biphenyl (4aac): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50:1 as the eluent to give the title compound as a light yellow oil (59.7mg, 81%). ^{1}H NMR (400 MHz, Chloroform-*d*)**:** δ 7.78 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.38 (td, *J* = 7.6, 1.5 Hz, 1H), 7.35-7.27 (m, 5H), 7.26-7.19 (m, 4H), 7.15 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.02 (d, *J* = 16.3 Hz, 1H), 6.77 (d, *J* = 16.3 Hz, 1H), 2.48-2.34 (m, 2H), 1.43-1.34 (m, 2H), 1.30 (s, 9H), 1.19-1.09 (m, 2H), 0.71 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*)**:** δ 150.55, 141.04, 140.80, 140.25, 135.82, 134.81, 130.35, 130.27, 128.93, 128.81, 127.45, 127.34, 126.84, 126.38, 126.21, 125.45, 125.39, 124.63, 34.54, 32.79, 32.76, 31.24, 22.38, 13.73. HRMS (ESI-TOF) *m/z*: calcd for $C_{28}H_{32}Na^+$: 391.2396 $(M + Na)^+$, found: 391.2397.



4aad

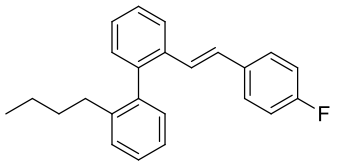
(*E*)-2-butyl-2'-(4-chlorostyryl)-1,1'-biphenyl (4aad): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50:1 as the eluent to give the title compound as a colorless oil (53.4mg, 77%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.76 (dd, *J* =

7.8, 1.3 Hz, 1H), 7.41-7.29 (m, 4H), 7.26-7.16 (m, 6H), 7.14 (dd, *J* = 7.4, 1.4 Hz, 1H), 6.96 (d, *J* = 16.3 Hz, 1H), 6.76 (d, *J* = 16.3 Hz, 1H), 2.46-2.32 (m, 2H), 1.41-1.34 (m, 2H), 1.18-1.08 (m, 2H), 0.70 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 141.02, 140.04, 136.03, 135.28, 132.95, 130.45, 130.22, 128.99, 128.68, 127.73, 127.71, 127.58, 127.57, 127.43, 127.29, 125.44, 124.71, 32.76, 32.72, 22.37, 13.72. HRMS (ESI-TOF) *m/z*: calcd for $C_{24}H_{23}NaCl^+$: 369.1380 $(M + Na)^+$, found: 369.1380.



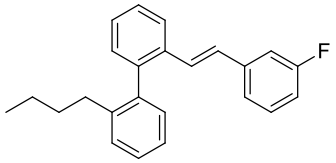
4aae

(*E*)-2-butyl-2'-(3-chlorostyryl)-1,1'-biphenyl (4aae): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50:1 as the eluent to give the title compound as a light yellow oil (53.4mg, 77%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.76 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.42-7.35 (m, 2H), 7.35 -7.31 (m, 2H), 7.28-7.12 (m, 7H), 6.94 (d, *J* = 16.4 Hz, 1H), 6.80 (d, *J* = 16.3 Hz, 1H), 2.50-2.32 (m, 2H), 1.42-1.35 (m, 2H), 1.19-1.10 (m, 2H), 0.71 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*)**:** δ 141.13, 140.97, 139.96, 139.45, 135.17, 134.45, 130.49, 130.19, 129.71, 129.03, 128.55, 127.73, 127.64, 127.44, 127.28, 126.50, 125.48, 124.90, 124.41, 32.78, 32.73, 22.38, 13.72. HRMS (EI-TOF) *m/z*: calcd for $C_{24}H_{23}Cl$: 346.1488 (M^+); found: 346.1482.



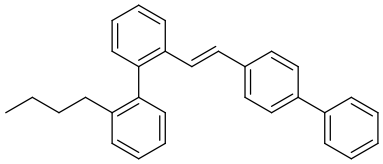
4aaf

(*E*)-2-butyl-2'-(4-fluorostyryl)-1,1'-biphenyl (4aaf): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50:1 as the eluent to give the title compound as a light yellow oil (58.2mg, 88%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.76 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.39 (td, *J* = 7.5, 1.5 Hz, 1H), 7.36-7.29 (m, 3H), 7.28-7.20 (m, 4H), 7.15 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.00-6.94 (m, 3H), 6.71 (d, *J* = 16.3 Hz, 1H), 2.48-2.34 (m, 2H), 1.42-1.35 (m, 2H), 1.19-1.09 (m, 2H), 0.71 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.40, 160.94, 141.03, 140.89, 140.13, 135.44, 133.70 (d, *J* = 3.4 Hz), 130.33 (d, *J* = 19.4 Hz), 128.97, 127.90 (d, *J* = 7.9 Hz), 127.82, 127.53, 127.41, 127.10, 126.85 (d, *J* = 2.5 Hz), 125.43, 124.61, 115.45 (d, *J* = 21.6 Hz), 32.77, 32.73, 22.37, 13.72. HRMS (ESI-TOF) *m/z*: calcd for $C_{24}H_{23}NaF^+$: 353.1676 $(M + Na)^+$, found: 353.1676.



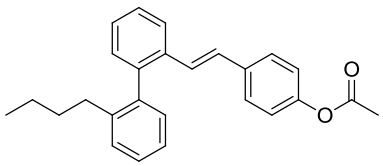
4aag

(*E*)-2-butyl-2'-(3-fluorostyryl)-1,1'-biphenyl (4aag): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50:1 as the eluent to give the title compound as a light yellow solid (54.2mg, 82%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.78 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.43-7.27 (m, 5H), 7.25-7.19 (m, 2H), 7.15 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.07-7.02 (m, 1H), 7.02-6.92 (m, 2H), 6.92-6.86 (m, 1H), 6.80 (d, *J* = 16.4 Hz, 1H), 2.49-2.33 (m, 2H), 1.43-1.34 (m, 2H), 1.19-1.10 (m, 2H), 0.71 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 164.26, 161.82, 141.06 (d, *J* = 16.7 Hz), 139.96, 139.88, 135.15, 130.33 (d, *J* = 27.3 Hz), 129.92 (d, *J* = 8.5 Hz), 129.03, 128.42, 127.88 (d, *J* = 2.7 Hz), 127.64, 127.42 (d, *J* = 1.6 Hz), 125.46, 124.82, 122.34 (d, *J* = 2.7 Hz), 114.15 (d, *J* = 21.6 Hz), 112.72 (d, *J* = 21.7 Hz), 32.78, 32.73, 22.37, 13.71. HRMS (ESI-TOF) *m/z*: calcd for $C_{24}H_{23}NaF^{+}$: 353.1676 $(M + Na)^{+}$, found: 353.1676.



4aah

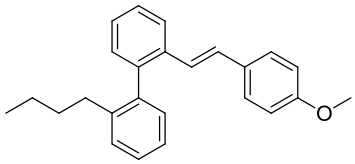
(*E*)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)-2'-butyl-1,1'-biphenyl (4aah): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50:1 as the eluent to give the title compound as a light yellow solid (70.6mg, 91%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.82 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.62-7.56 (m, 2H), 7.55-7.50 (m, 2H), 7.50-7.40 (m, 3H), 7.39-7.28 (m, 7H), 7.24 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.18 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.08 (d, *J* = 16.4 Hz, 1H), 6.87 (d, *J* = 16.3 Hz, 1H), 2.54-2.37 (m, 2H), 1.45-1.38 (m, 2H), 1.21-1.12 (m, 2H), 0.73 (t, *J* = 7.3 Hz, 3H). ^{13}CNMR (101 MHz, Chloroform-*d*)**:** δ 141.06, 140.96, 140.64, 140.18, 140.12, 136.60, 135.62, 130.43, 130.28, 128.98, 128.74, 128.56, 127.52, 127.40, 127.24, 127.20, 127.17, 127.08, 126.88, 126.83, 125.44, 124.72, 32.78, 32.76, 22.38, 13.74. HRMS (EI-TOF) *m/z*: calcd for $C_{30}H_{28}$: 388.2191 (M^{+}); found: 388.2192.



4aai

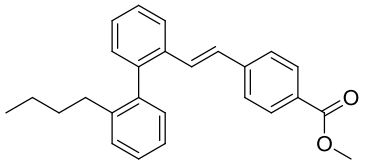
(*E*)-4-(2-(2'-butyl-[1,1'-biphenyl]-2-yl)vinyl)phenyl acetate (4aai): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50:1 as the eluent to give the title compound as a light yellow solid (68.9mg, 93%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.76 (dd,

J = 7.9, 1.3 Hz, 1H), 7.41-7.26 (m, 6H), 7.24 (dd, J = 6.7, 2.1 Hz, 1H), 7.21 (dd, J = 7.6, 1.5 Hz, 1H),, 7.14 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.02-6.95 (m, 3H), 6.74 (d, *J* = 16.3 Hz, 1H), 2.47-2.34 (m, 2H), 2.29 (s, 3H), 1.41-1.34 (m, 2H), 1.19-1.08 (m, 2H), 0.71 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*)**:** δ 169.41, 149.86, 141.02, 140.95, 140.10, 135.47, 135.37, 130.40, 130.21, 128.98, 128.02, 127.52, 127.39, 127.36, 127.12, 125.43, 124.70, 121.63, 32.77, 32.73, 22.36, 21.09, 13.71. HRMS (ESI-TOF) *m/z*: calcd for $C_{26}H_{26}NaO_2^+$: 393.1825 $(M + Na)^+$, found: 393.1828.



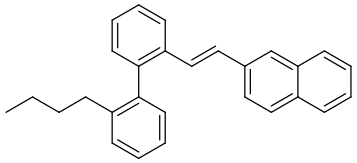
4aaj

(*E*)-2-butyl-2'-(4-methoxystyryl)-1,1'-biphenyl (4aaj): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50:1 as the eluent to give the title compound as a colorless oil (48.6mg, 71%). ^{1}H NMR (400 MHz, Chloroform-*d*)**:** δ 7.77 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.40-7.31 (m, 3H), 7.29 (td, *J* = 7.6, 1.3 Hz, 2H), 7.25-7.20 (m, 3H), 7.15 (dd, *J* = 7.2, 1.3 Hz, 1H), 6.98 (d, *J* = 16.3 Hz, 1H), 6.83-6.79 (m, 2H), 6.67 (d, *J* = 16.3 Hz, 1H), 3.79 (s, 3H), 2.48-2.34 (m, 2H), 1.43-1.35 (m, 2H), 1.19-1.10 (m, 2H), 0.71 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 159.12, 141.06, 140.64, 140.32, 135.89, 130.40, 130.36, 130.27, 128.92, 128.52, 127.65, 127.41, 127.33, 126.65, 125.38, 125.02, 124.44, 113.98, 55.26, 32.76, 32.74, 22.38, 13.73. HRMS (EI-TOF) *m/z*: calcd for $C_{25}H_{26}O$: 342.1984 (M^+); found: 342.1980.



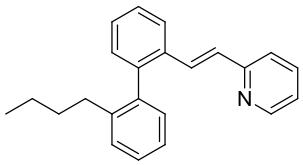
4aak

Methyl (*E*)-4-(2-(2'-butyl-[1,1'-biphenyl]-2-yl)vinyl)benzoate (4aak): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50:1 as the eluent to give the title compound as a yellow oil (38.5mg, 52%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.96-7.90 (m, 2H), 7.79 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.43-7.35 (m, 2H), 7.34-7.29 (m, 4H), 7.26-7.21 (m, 2H), 7.14 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.03 (d, *J* = 16.3 Hz, 1H), 6.90 (d, *J* = 16.4 Hz, 1H), 3.89 (s, 3H), 2.47-2.32 (m, 2H), 1.41-1.34 (m, 2H), 1.17-1.08 (m, 2H), 0.69 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 166.82, 142.01, 141.32, 141.00, 139.90, 135.07, 130.50, 130.22, 129.89, 129.64, 129.03, 128.69, 127.95, 127.65, 127.47, 126.23, 125.46, 124.88, 52.01, 32.76, 32.72, 22.36, 13.71. HRMS (ESI-TOF) *m/z*: calcd for $C_{26}H_{26}NaO_2^+$: 393.1825 $(M + Na)^+$, found: 393.1829.



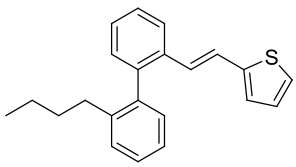
4aal

(*E*)-2-(2-(2'-butyl-[1,1'-biphenyl]-2-yl)vinyl)naphthalene (4aal): Purified by preparative thin-layer chromatograph using petroleum ether as the eluent to give the title compound as a colorless solid (67.4mg, 93%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.85 (d, *J* = 7.8 Hz, 1H), 7.77 (t, *J* = 7.6, 5.9, 1.7 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.47-7.27 (m, 8H), 7.25-7.16 (m, 3H), 6.93 (d, *J* = 16.3 Hz, 1H), 2.51-2.36 (m, 2H), 1.48-1.35 (m, 2H), 1.19-1.10 (m, 2H), 0.70 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 141.08, 141.00, 140.19, 135.66, 135.06, 133.58, 132.89, 130.46, 130.29, 129.18, 129.00, 128.15, 127.91, 127.61, 127.54, 127.45, 127.43, 127.11, 126.61, 126.22, 125.78, 125.45, 124.71, 123.38, 32.78, 32.76, 22.38, 13.74. HRMS (ESI-TOF) *m/z*: calcd for $C_{28}H_{26}Na^{+}$: 385.1927 $(M + Na)^{+}$, found: 385.1897.



4aam

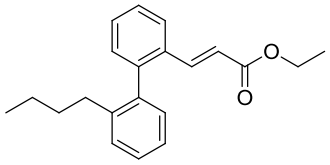
(*E*)-2-(2-(2'-butyl-[1,1'-biphenyl]-2-yl)vinyl)pyridine (4aam): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50:1 as the eluent to give the title compound as a colorless oil (28.8mg, 46%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.50 (d, *J* = 4.8 Hz, 1H), 7.83 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.55 (td, *J* = 7.7, 1.8 Hz, 1H), 7.40 (td, *J* = 7.6, 1.5 Hz, 1H), 7.37-7.29 (m, 3H), 7.25-7.04 (m, 7H), 2.47-2.33 (m, 2H), 1.43-1.32 (m, 2H), 1.15-1.08 (m, 2H), 0.69 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 156.10, 149.39, 141.40, 141.05, 140.04, 136.25, 135.05, 131.17, 130.51, 130.27, 129.28, 128.98, 127.72, 127.55, 127.48, 125.45, 125.43, 121.80, 120.93, 32.78, 32.74, 22.38, 13.70. HRMS (ESI-TOF) *m/z*: calcd for $C_{23}H_{23}NNa^{+}$: 336.1723 $(M + Na)^{+}$, found: 336.1729.



4aan

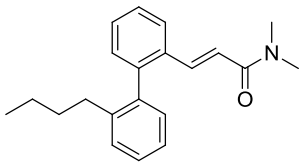
(*E*)-2-(2-(2'-butyl-[1,1'-biphenyl]-2-yl)vinyl)thiophene (4aan): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50:1 as the eluent to give the title compound as a colorless oil (33.7mg, 53%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.72 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.38 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.38 -7.27 (m, 3H), 7.30-7.20 (m, 1H), 7.20 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.17-7.06 (m, 3H), 6.94-6.92 (m, 2H), 6.62 (d, *J* = 16.1 Hz, 1H), 2.49-2.32 (m, 2H), 1.43-1.36 (m, 2H), 1.20-1.08 (m, 2H), 0.72 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz,

Chloroform-*d*): δ 143.19, 140.98, 140.81, 139.99, 135.25, 130.42, 130.24, 128.94, 127.53, 127.44, 127.37, 127.03, 126.85, 125.61, 125.41, 124.49, 124.22, 122.04, 32.74, 32.70, 22.37, 13.74. HRMS (ESI-TOF) *m/z*: calcd for $C_{22}H_{23}S^+$: 319.1515 $(M + H)^+$, found: 319.1492.



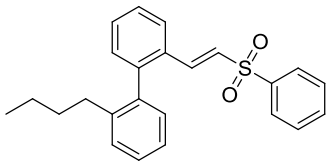
4aao

Ethyl (*E*)-3-(2'-butyl-[1,1'-biphenyl]-2-yl)acrylate (4aao): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20:1 as the eluent to give the title compound as a light yellow oil (32.6mg, 53%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.75-7.67 (m, 1H), 7.44-7.35 (m, 3H), 7.34-7.27 (m, 2H), 7.24-7.20 (m, 2H), 7.07 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.43-2.25 (m, 2H), 1.40-1.32 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.13 (q, *J* = 7.3 Hz, 2H), 0.72 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 166.82, 143.03, 142.75, 140.77, 139.12, 133.01, 130.74, 130.07, 129.48, 129.11, 127.90, 127.51, 126.00, 125.51, 118.80, 60.27, 32.73, 32.70, 22.34, 14.20, 13.72. HRMS (ESI-TOF) *m/z*: calcd for $C_{21}H_{24}NaO_2^+$: 331.1669 $(M + Na)^+$, found: 331.1679.



4aap

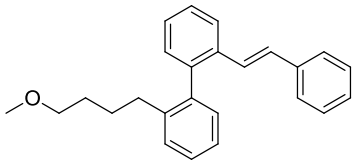
(*E*)-3-(2'-butyl-[1,1'-biphenyl]-2-yl)-N,N-dimethylacrylamide (4aap): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20:1 as the eluent to give the title compound as a colorless solid (38.1mg, 62%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.67-7.63 (m, 1H), 7.40-7.34 (m, 3H), 7.32-7.27 (m, 2H), 7.23-7.19 (m, 2H), 7.08 (d, *J* = 7.1 Hz 1H), 6.54 (d, *J* = 15.6 Hz, 1H), 2.96 (s, 3H),2.95 (s, 3H), 2.43-2.26 (m, 2H), 1.42-1.30 (m, 2H), 1.18-1.09 (m, 2H), 0.72 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 166.68, 141.99, 140.68, 140.59, 139.81, 133.86, 130.78, 129.91, 129.14, 128.67, 127.74, 127.39, 127.23, 125.64, 119.00, 37.20, 35.68, 32.73, 32.71, 22.39, 13.70. HRMS (ESI-TOF) *m/z*: calcd for $C_{21}H_{25}NNaO^+$:330.1828 $(M + Na)^+$, found: 330.1834.



4aaq

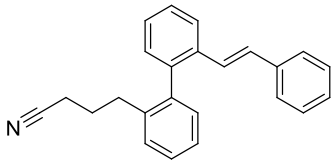
(*E*)-2-butyl-2'-(2-(phenylsulfonyl)vinyl)-1,1'-biphenyl (4aaq): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50:1 as the eluent to give the title

compound as a yellow oil (42.1mg, 56%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.81-7.76 (m, 2H), 7.62-7.55 (m, 2H), 7.50 (t, *J* = 8.3, 6.9 Hz, 2H), 7.46-7.31 (m, 4H), 7.28-7.20 (m, 3H), 7.02 (dd, *J* = 7.5, 1.4 Hz, 1H), 6.62 (d, *J* = 15.5 Hz, 1H), 2.34-2.13 (m, 2H), 1.35-1.22 (m, 2H), 1.12-1.03 (m, 2H), 0.69 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 142.93, 141.22, 140.60, 140.55, 138.53, 133.15, 131.12, 130.81, 130.33, 129.90, 129.26, 129.13, 128.48, 128.25, 127.68, 127.54, 127.03, 125.68, 32.69, 32.59, 22.26, 13.65. HRMS (ESI-TOF) *m/z*: calcd for $C_{24}H_{24}NaO_2S^+$: 399.1389 $(M + Na)^+$, found: 399.1400.



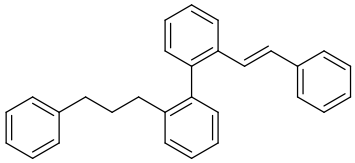
4aba

(*E*)-2-(4-methoxybutyl)-2'-styryl-1,1'-biphenyl (4aba): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50:1 as the eluent to give the title compound as a colorless solid (49.3mg, 72%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.79 (d, *J* = 7.9 Hz, 1H), 7.40 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.37-7.34 (m, 1H), 7.34-7.29 (m, 3H), 7.28-7.26 (m, 4H), 7.24-7.19 (m, 2H), 7.19-7.12 (m, 1H), 7.03 (d, *J* = 16.3 Hz, 1H), 6.80 (d, *J* = 16.3 Hz, 1H), 3.19 (s, 3H), 3.14 (t, *J* = 6.3 Hz, 2H), 2.51-2.36 (m, 2H), 1.49-1.38 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 140.82, 140.56, 140.17, 137.48, 135.61, 130.38, 130.26, 129.13, 128.95, 128.53, 127.56, 127.42, 127.10, 127.00, 126.46, 125.56, 124.73, 72.43, 58.37, 32.74, 29.20, 27.01. HRMS (ESI-TOF) *m/z*: calcd for $C_{25}H_{26}NaO^+$: 365.1876 $(M + Na)^+$, found: 365.1872.



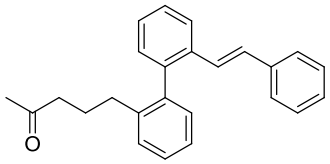
4aca

(*E*)-4-(2'-styryl-[1,1'-biphenyl]-2-yl)butanenitrile (4aca): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50:1 as the eluent to give the title compound as a light yellow solid (41.4mg, 64%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.80 (d, *J* = 7.8 Hz, 1H), 7.45-7.26 (m, 9H), 7.24-7.18 (m, 3H), 7.04 (d, *J* = 16.3 Hz, 1H), 6.77 (d, *J* = 16.3 Hz, 1H), 2.65-2.52 (m, 2H), 2.10 (t, *J* = 7.2 Hz, 2H), 1.74-1.66 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 140.39, 140.08, 138.09, 137.24, 135.52, 130.54, 130.14, 129.68, 129.13, 128.58, 127.89, 127.80, 127.61, 127.33, 126.51, 126.43, 125.03, 119.30, 32.05, 26.03, 16.57. HRMS (ESI-TOF) *m/z*: calcd for $C_{23}H_{23}NNa^+$: 336.1723 $(M + Na)^+$, found: 336.1729.



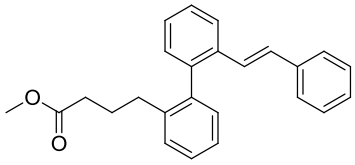
4ada

(*E*)-2-(3-phenylpropyl)-2'-styryl-1,1'-biphenyl (4ada): Purified by preparative thin-layer chromatograph using petroleum ether as the eluent to give the title compound as a colorless solid (53.2mg, 71%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.78 (d, *J* = 7.8 Hz, 1H), 7.42-7.34 (m, 2H), 7.33-7.27 (m, 6H), 7.22-7.16 (m, 5H), 7.16 -7.08 (m, 2H), 7.01 (d, *J* = 16.3 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 2H), 6.82 (d, *J* = 16.3 Hz, 1H), 2.55-2.39 (m, 4H), 1.77-1.69 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 142.12, 140.76, 140.56, 140.24, 137.48, 135.58, 130.36, 130.30, 129.20, 129.03, 128.54, 128.18, 128.11, 127.57, 127.44, 127.12, 126.98, 126.48, 125.63, 125.46, 124.82, 35.56, 32.89, 32.05. HRMS (ESI-TOF) *m/z*: calcd for $C_{29}H_{26}Na^{+}$: 397.1927 $(M + Na)^{+}$, found: 397.1927.



4aea

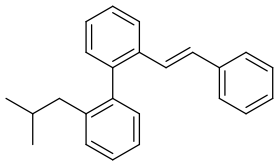
(*E*)-5-(2'-styryl-[1,1'-biphenyl]-2-yl)pentan-2-one (4aea): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50:1 as the eluent to give the title compound as a light yellow oil (35.4mg, 52%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.79 (d, *J* = 7.8 Hz, 1H), 7.41-7.36 (m, 2H), 7.33-7.26 (m, 7H), 7.21-7.16 (m, 3H), 7.02 (d, *J* = 16.3 Hz, 1H), 6.79 (d, *J* = 16.3 Hz, 1H), 2.48-2.35 (m, 2H), 2.23-2.16 (m, 2H), 1.90 (s, 3H), 1.71-1.64 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 208.74, 140.62, 140.26, 139.78, 137.37, 135.54, 130.33, 129.29, 128.97, 128.57, 127.70, 127.56, 127.53, 127.19, 126.82, 126.44, 125.86, 124.81, 43.18, 32.24, 29.47, 24.48. HRMS (ESI-TOF) *m/z*: calcd for $C_{25}H_{24}NaO^{+}$: 363.1719 $(M + Na)^{+}$, found: 363.1719.



4afa

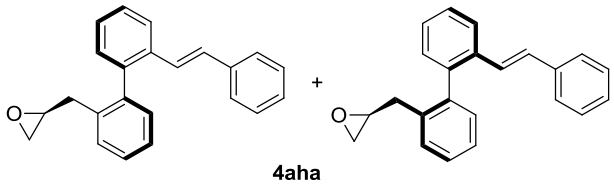
Methyl (*E*)-4-(2'-styryl-[1,1'-biphenyl]-2-yl)butanoate （4afa）: Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50:1 as the eluent to give the title compound as a colorless oil (52.1mg, 73%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.81-7.77 (m, 1H), 7.40 (td, *J* = 7.6, 1.2 Hz, 1H), 7.37-7.24 (m, 8H), 7.22-7.16 (m, 3H), 7.03 (d, *J* = 16.3 Hz, 1H), 6.79 (d, *J* = 16.3 Hz, 1H), 3.53 (s, 3H), 2.53-2.39 (m, 2H), 2.13 (t, *J* = 7.5 Hz, 2H), 1.78-1.70 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 173.72, 140.56, 140.30, 139.58, 137.42, 135.60, 130.36, 130.32, 129.30, 129.04, 128.53, 127.67, 127.52, 127.46, 127.16, 126.84, 126.46, 125.87,

124.82, 51.33, 33.55, 32.31, 25.69. HRMS (ESI-TOF) *m/z*: calcd for $C_{25}H_{24}NaO_2^+$: 379.1669 $(M + Na)^+$, found: 379.1674.



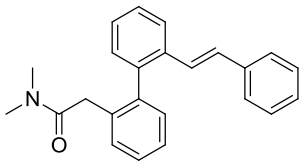
4aga

(*E*)-2-isobutyl-2'-styryl-1,1'-biphenyl (4aga): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50:1 as the eluent to give the title compound as a yellow oil (33.7mg, 54%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.81 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.45-7.24 (m, 9H), 7.28-7.14 (m, 3H), 7.04 (d, *J* = 16.4 Hz, 1H), 6.82 (d, *J* = 16.3 Hz, 1H), 2.43-2.26 (m, 1H), 1.74-1.64 (m, 1H), 0.75 (d, *J* = 6.5 Hz, 3H), 0.71 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 141.01, 140.54, 139.90, 137.57, 135.55, 130.55, 130.37, 129.74, 128.95, 128.53, 127.38, 127.33, 127.27, 127.08, 126.98, 126.44, 125.48, 124.67, 42.36, 29.14, 22.56, 22.38. HRMS (ESI-TOF) *m/z*: calcd for $C_{24}H_{25}^+$: 313.1951 $(M + H)^+$, found: 313.1972.



4aha

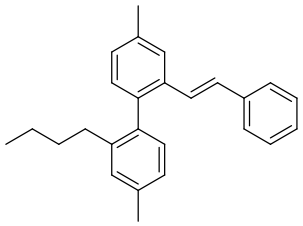
(*E*)-2-((2'-styryl-[1,1'-biphenyl]-2-yl)methyl)oxirane (4aha): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50:1 as the eluent to give the title compound as a light yellow oil (43.6mg, 70%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.79 (ddd, *J* = 7.3, 5.7, 1.3 Hz, 1H), 7.46-7.39 m, 3H), 7.37-7.27 (m, 6H) , 7.25-7.19 (m, 3H), 7.03 (d, *J* = 16.3 Hz, 1H), 6.79 (d, *J* = 16.3 Hz, 0.5H), 6.78 (d, *J* = 16.3 Hz, 0.5H), 2.99-2.88 (m, 1H), 2.82-2.75 (m, 1H), 2.63-2.51 (m, 2H), 2.25 (dd, *J* = 5.0, 2.6 Hz, 0.5H), 2.19 (dd, *J* = 4.9, 2.7 Hz, 0.5H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 140.66, 140.63, 140.36, 140.29, 137.30, 135.80, 135.70, 135.64, 135.57, 130.41, 130.28, 130.23, 129.69, 129.68, 129.65, 129.56, 128.57, 128.55, 127.84, 127.82, 127.76, 127.56, 127.28, 127.22, 126.65, 126.64, 126.55, 126.52, 126.47, 126.45, 124.97, 124.95, 52.05, 51.93, 47.33, 47.25, 36.32, 36.15. HRMS (ESI-TOF) *m/z*: calcd for $C_{23}H_{20}NaO^+$: 335.1406 $(M + Na)^+$, found: 335.1402.



4aia

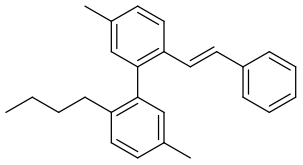
(*E*)-*N*,*N*-dimethyl-2-(2'-styryl-[1,1'-biphenyl]-2-yl)acetamide (4aia): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 20:1 as the eluent to give the title

compound as a light yellow solid (23.9mg, 35%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.79 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.42-7.38 (m, 3H), 7.35-7.26 (m, 6H), 7.22-7.17 (m, 3H), 7.03 (d, *J* = 16.3 Hz, 1H), 6.78 (d, *J* = 16.3 Hz, 1H), 3.49-3.38 (m, 2H), 2.79 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 171.10, 140.19, 140.12, 137.17, 135.77, 133.92, 130.36, 130.16, 129.67, 129.44, 128.57, 127.94, 127.82, 127.62, 127.28, 126.66, 126.54, 126.45, 124.84, 38.09, 37.25, 35.44. HRMS (ESI-TOF) *m/z*: calcd for $C_{24}H_{23}NNaO^{+}$: 364.1672 $(M + Na)^{+}$, found: 364.1677.



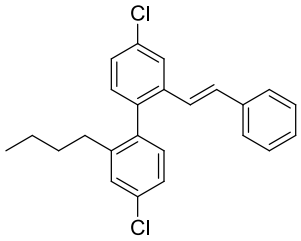
4baa

(*E*)-2-butyl-4,4'-dimethyl-2'-styryl-1,1'-biphenyl (4baa): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50:1 as the eluent to give the title compound as a colorless oil (37.4mg, 55%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.60 (s, 1H), 7.33-7.26 (m, 4H), 7.21 (d, *J* = 6.6 Hz, 1H), 7.14-7.11 (m, 2H), 7.09 (d, *J* = 7.7 Hz, 1H), 7.06-7.00 (m, 3H), 6.82 (d, *J* = 16.3 Hz, 1H), 2.46 (s, 3H), 2.42 (s, 3H), 2.40-2.33 (m, 2H), 1.42-1.34 (m, 2H), 1.19-1.10 (m, 2H), 0.72 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 141.04, 138.31, 137.78, 137.26, 136.83, 136.70, 135.56, 130.59, 130.44, 129.70, 128.69, 128.54, 128.03, 127.47, 127.32, 126.52, 126.19, 125.26, 32.95, 32.80, 22.51, 21.39, 21.34, 13.84. HRMS (EI-TOF) *m/z*: calcd for $C_{26}H_{28}$: 340.2191 (M^{+}); found: 340.2193.



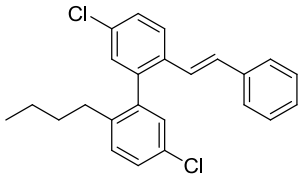
4caa

(*E*)-2-butyl-5,5'-dimethyl-2'-styryl-1,1'-biphenyl (4caa): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50:1 as the eluent to give the title compound as a colorless oil (40.8mg, 60%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.31-7.25 (m, 3H), 7.28-7.10 (m, 5H), 7.05-6.95 (m, 3H), 6.81 (d, *J* = 16.3 Hz, 1H), 2.40 (s, 3H), 2.36 (s, 3H), 2.43-2.29 (m, 2H), 1.43-1.35 (m, 2H), 1.21-1.10 (m, 2H), 0.72 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 141.09, 140.18, 137.92, 137.79, 136.81, 134.70, 132.74, 131.03, 130.82, 128.73, 128.48, 128.13, 128.11, 127.93, 127.15, 127.12, 126.37, 124.48, 32.83, 32.25, 22.35, 21.19, 20.95, 13.75.HRMS (EI-TOF) *m/z*: calcd for $C_{26}H_{28}$: 340.2191 (M^{+}); found: 340.2195.



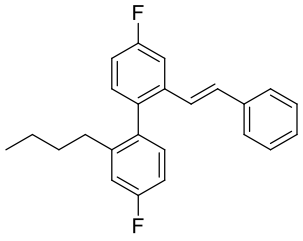
4daa

(*E*)-2-butyl-4,4'-dichloro-2'-styryl-1,1'-biphenyl (4daa): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50:1 as the eluent to give the title compound as a colorless oil (34.3mg, 45%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.75 (d, *J* = 2.1 Hz, 1H), 7.33-7.26 (m, 6H), 7.23 (dd, *J* = 8.2, 2.1 Hz, 2H), 7.1-7.00 (m, 3H), 6.66 (d, *J* = 16.2 Hz, 1H), 2.42-2.28 (m, 2H), 1.40-1.33 (m, 2H), 1.18-1.09 (m, 2H), 0.72 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 143.13, 137.92, 137.49, 136.80, 133.69, 133.55, 131.61, 131.48, 130.81, 129.03, 128.67, 128.01, 127.08, 126.64, 125.77, 125.29, 124.78, 32.64, 32.50, 22.31, 13.70. HRMS (EI-TOF) *m/z*: calcd for $C_{24}H_{22}Cl_2$: 380.1099 (M^+); found: 380.1096.



4eaa

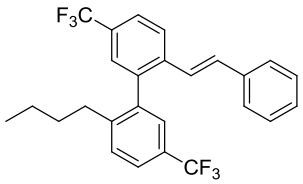
(*E*)-2-butyl-5,5'-dichloro-2'-styryl-1,1'-biphenyl (4eaa): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50:1 as the eluent to give the title compound as a colorless oil (31.3mg, 41%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.71 (d, *J* = 8.5 Hz, 1H), 7.37 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.33 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.29-7.28 (m, 4H), 7.25-7.21 (m, 2H), 7.18 (d, *J* = 2.3 Hz, 1H), 7.15 (d, *J* = 2.3 Hz, 1H), 7.02 (d, *J* = 16.3 Hz, 1H), 6.68 (d, *J* = 16.3 Hz, 1H), 2.43-2.25 (m, 2H), 1.40-1.32 (m, 2H), 1.21 -1.06 (m, 2H), 0.71 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 140.86, 140.50, 139.59, 137.00, 134.21, 132.73, 131.16, 130.38, 130.18, 129.99, 129.69, 128.63, 128.07, 128.05, 127.84, 126.56, 126.13, 125.28, 32.56, 32.06, 22.26, 13.66. HRMS (EI-TOF) *m/z*: calcd for $C_{24}H_{22}Cl_2$ (M^+): 380.1099; found: 380.1103.



4faa

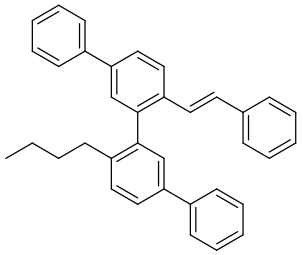
(*E*)-2-butyl-4,4'-difluoro-2'-styryl-1,1'-biphenyl (4faa): Purified by preparative thin-layer

chromatograph using petroleum ether : ethyl acetate = 50:1 as the eluent to give the title compound as a colorless oil (28.6mg, 41%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.46 (dd, *J* = 10.4, 2.7 Hz, 1H), 7.30-7.29 (m, 3H), 7.25-7.21 (m, 1H), 7.16-6.91 (m, 7H), 6.69 (dd, *J* = 16.3, 1.8 Hz, 1H), 2.43-2.28 (m, 2H), 1.41-1.34 (m, 2H), 1.21-1.10 (m, 2H), 0.72 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 162.36 (d, *J* = 245.8 Hz) , 143.80 (d, *J* = 7.2 Hz), 137.96 (d, *J* = 7.6 Hz), 136.90, 135.76 (d, *J* = 3.2 Hz), 135.08 (d, *J* = 3.2 Hz), 132.04 (d, *J* = 8.2 Hz), 131.83 (d, *J* = 8.0 Hz), 129.20 (d *J* = 255.3 Hz), 128.65 , 128.61, 126.60, 126.51, 125.78 (d, *J* = 2.6 Hz), 115.52 (d, *J* = 20.9 Hz), 114.11 (d, *J* = 21.5 Hz), 112.44 (d, *J* = 21.1 Hz), 111.10 (d, *J* = 22.1 Hz), 32.79, 32.41, 22.28, 13.68 . HRMS (ESI-TOF): m/z calcd for $C_{24}H_{23}F_2^+$: 349.1762 $(M + H)^+$; found: 349.1792.



4gaa

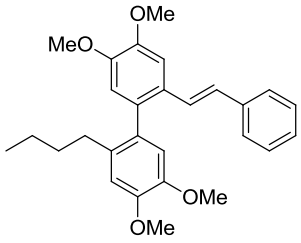
(*E*)-2-butyl-2'-styryl-5,5'-bis(trifluoromethyl)-1,1'-biphenyl (4gaa): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50:1 as the eluent to give the title compound as a colorless oil (67.3mg, 75%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.90 (d, *J* = 8.3 Hz, 1H), 7.68-7.63 (m, 2H), 7.47-7.44 (m, 3H), 7.33-7.27 (m, 4H), 7.27-7.22 (m, 1H), 7.13 (d, *J* = 16.3 Hz, 1H), 6.70 (d, *J* = 16.3 Hz, 1H), 2.49-2.34 (m, 2H), 1.44-1.34 (m, 2H), 1.18-1.09 (m, 2H), 0.69 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 145.35, 139.53, 139.42, 139.26, 136.57, 132.34, 129.68, 129.08 (q, *J* = 32.6 Hz), 128.72, 128.33, 128.23 (q, *J* = 32.9 Hz), 127.17 (q, *J* = 3.7 Hz), 126.80 (d, *J* = 3.7 Hz), 126.76, 125.39, 124.97 (q, *J* = 3.7 Hz), 124.86, 124.83 (q, *J* = 3.8 Hz), 124.15 (q, *J* = 271.90 Hz), 124.06 (q, *J* = 271.21 Hz), 32.64, 32.47, 22.26, 13.55. HRMS (EI-TOF) *m/z*: calcd for $C_{26}H_{22}F_6$: 448.1626 (M^+); found: 448.1620.



4haa

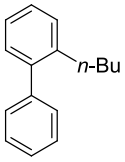
(*E*)-4'-butyl-6''-styryl-1,1':3',1'':3'',1'''-quaterphenyl (4haa): Purified by preparative thin-layer chromatograph using petroleum ether as the eluent to give the title compound as a colorless solid (80.8mg, 87%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.90 (d, *J* = 8.2 Hz, 1H), 7.69-7.61 (m, 6H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.50 (d, *J* = 2.1 Hz, 1H), 7.49=7.36 (m, 6H), 7.36-7.27 (m, 5H), 7.24-7.17 (m, 1H), 7.12 (d, *J* = 16.3 Hz, 1H), 6.92 (d, *J* = 16.3 Hz, 1H), 2.57-2.43 (m, 2H), 1.52-1.41 (m,

2H), 1.24-1.13 (m, 2H), 0.72 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 141.28, 140.68, 140.60, 140.43, 140.33, 139.68, 138.27, 137.50, 134.73, 129.49, 129.26, 129.02, 128.81, 128.71, 128.56, 127.48, 127.38, 127.08, 126.95, 126.89, 126.55, 126.51, 126.20, 126.11, 125.21, 32.83, 32.48, 22.40, 13.75. HRMS (EI-TOF) *m/z*: calcd for $C_{36}H_{32}$: 464.2504 (M^+); found: 464.2500.



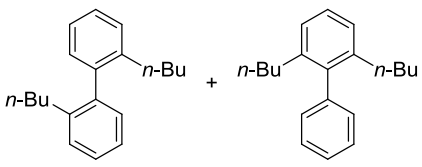
4iaa

(*E*)-2-butyl-4,4',5,5'-tetramethoxy-2'-styryl-1,1'-biphenyl (4iaa): Purified by preparative thin-layer chromatograph using petroleum ether : ethyl acetate = 50:1 as the eluent to give the title compound as a colorless solid (34.6mg, 40%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.29-7.26 (m, 5H), 7.21-7.16 (m, 1H), 6.91 (d, *J* = 16.3 Hz, 1H), 6.81 (s, 1H), 6.78 (d, *J* = 16.3 Hz, 1H), -6.71 (s, 1H), 6.67 (s, 1H), 4.02 (s, 3H), 3.96 (s, 3H), 3.88 (s, 3H), 3.83 (s, 3H), 2.41-2.27 (m, 2H), 1.43-1.35 (m, 2H), 1.20-1.11 (m, 2H), 0.72 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 148.26, 148.09, 146.36, 137.71, 133.88, 133.77, 131.83, 128.55, 128.45, 127.13, 126.98, 126.90, 126.23, 113.59, 113.42, 111.96, 107.08, 55.99, 55.97, 55.92, 33.31, 32.51, 22.45, 13.83. HRMS (ESI-TOF) *m/z*: calcd for $C_{28}H_{33}O_4^+$: 433.2373 $(M + H)^+$, found: 433.2366.



6aa

2-butyl-1,1'-biphenyl (6aa): Purified by preparative thin-layer chromatograph using petroleum ether as the eluent to give the title compound as a colorless oil. ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.45-7.41 (m, 2H), 7.37-7.34 (m, 1H), 7.33-7.27 (m, 4H), 7.23 (td, *J* = 7.3, 1.6 Hz, 1H), 7.16 (dd, *J* = 7.5, 1.3 Hz, 1H), 2.60-2.57 (m, 2H), 1.45-1.40 (m, 2H), 2.22-1.15 (m, 2H), 0.76 (t, *J* = 7.4 Hz, 3H). MS (EI): $[M]^+$: 210.15.



6aa-A **6aa-B**

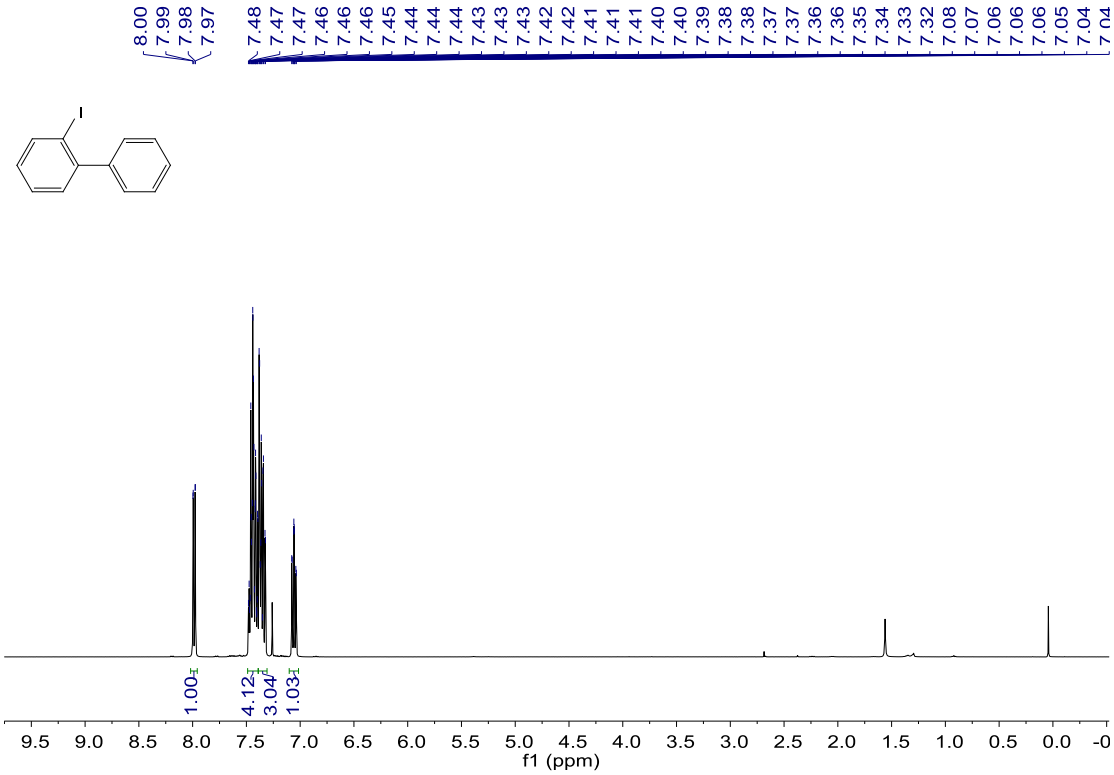
2,2'-dibutyl-1,1'-biphenyl (6aa-A) and 2,6-dibutyl-1,1'-biphenyl (6aa-B): Purified by

preparative thin-layer chromatograph using petroleum ether as the eluent to give the title compound as a colorless oil. ^{1}H NMR (600 MHz, Acetone-d_6): **2,2'-dibutyl-1,1'-biphenyl (6aa-A):** δ 7.34-7.27 (m, 4H), 7.24-7.20 (m, 2H), 7.08 (dd, *J* = 7.5, 0.9 Hz, 2H), 2.44-2.38 (m, 2H), 2.44-2.38 (m, 2H), 2.34-2.28 (m, 2H), 1.43-1.34 (m, 4H), 1.19-1.10 (m, 4H), 0.75 (t, *J* = 6.4 Hz, 6H). MS (EI): $[M]^+$: 266.22. **2,6-dibutyl-1,1'-biphenyl (6aa-B):** δ 7.46-7.42 (m, 2H), 7.38-7.34 (m, 1H), 7.23-7.19 (m, 1H), 7.19-7.15 (m, 2H), 7.12 (d, *J* = 7.6 Hz, 2H), 2.32-2.28 (m, 4H), 1.43-1.34 (m, 4H), 1.19-1.10 (m, 4H), 0.72 (t, *J* = 6.4 Hz, 6H). MS (EI): $[M]^+$: 266.22.

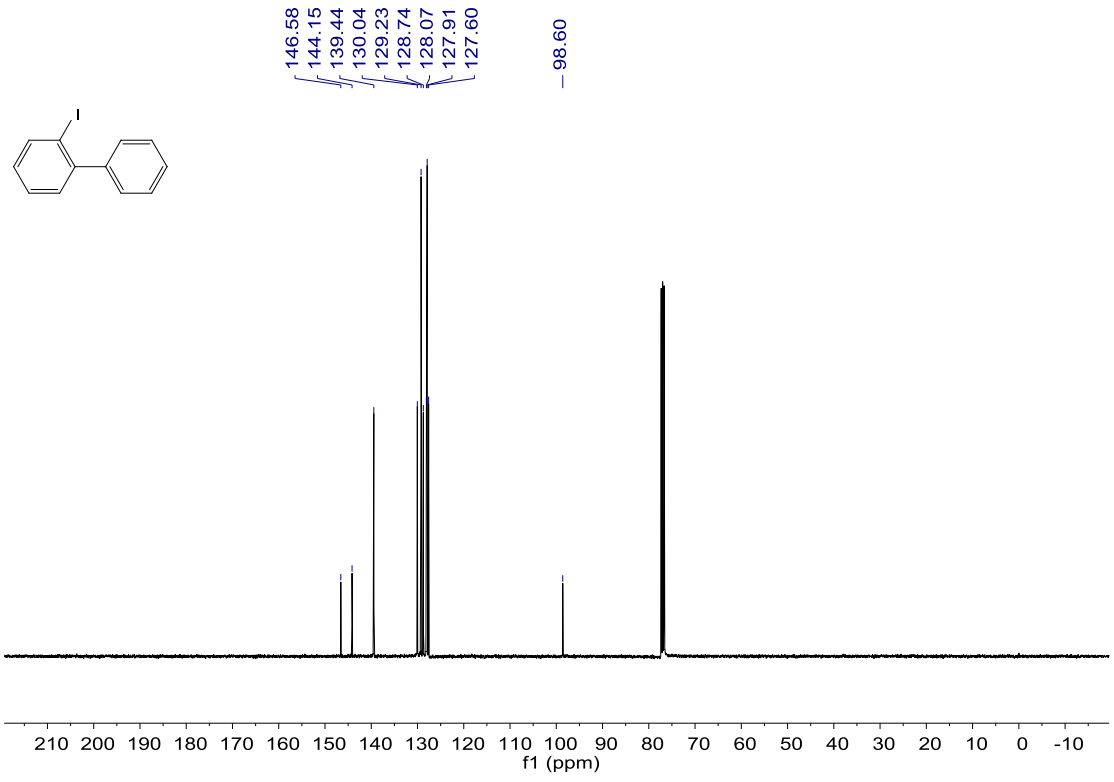
VII. NMR Spectra

2-iodobiphenyl (1a)

^{1}H NMR

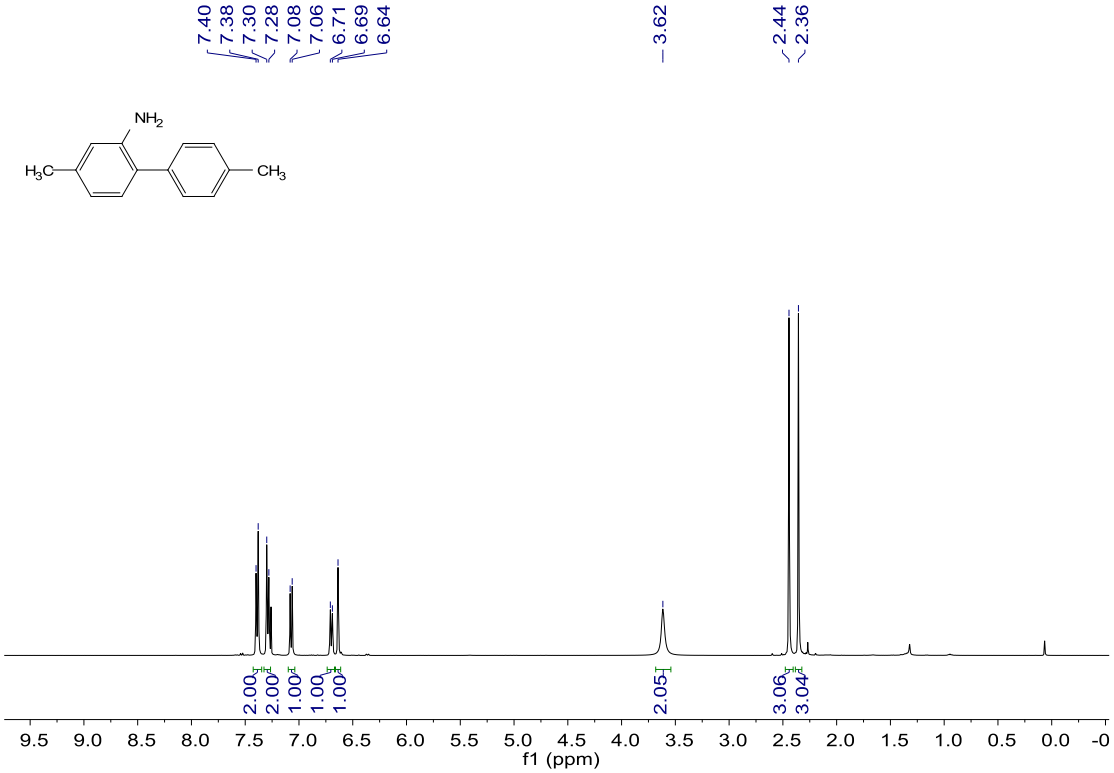


^{13}C NMR

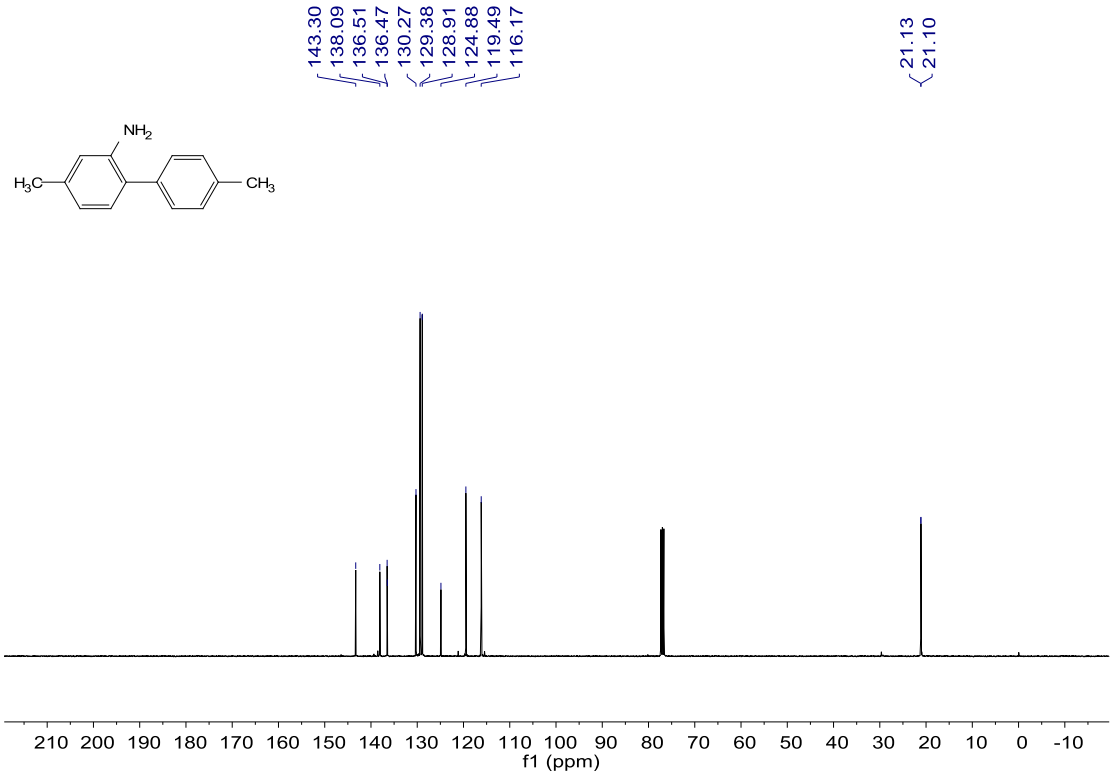


4,4’-dimethyl-2-aminobiphenyl (1b’)

^{1}H NMR

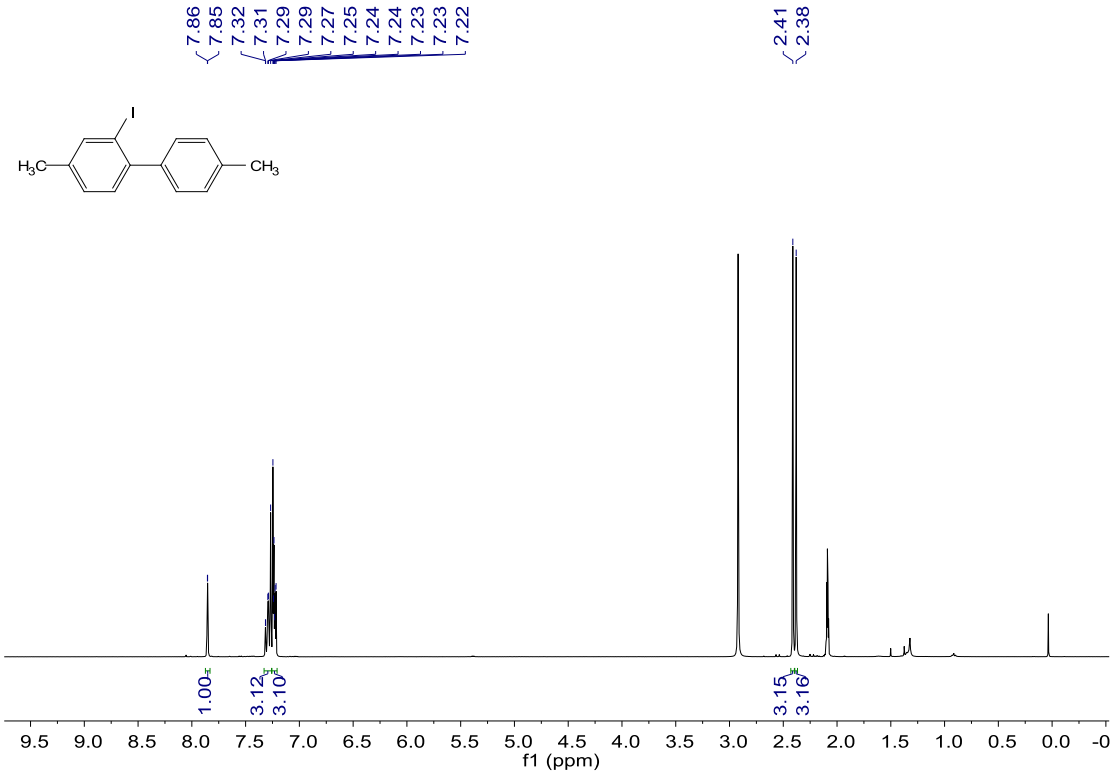


^{13}C NMR

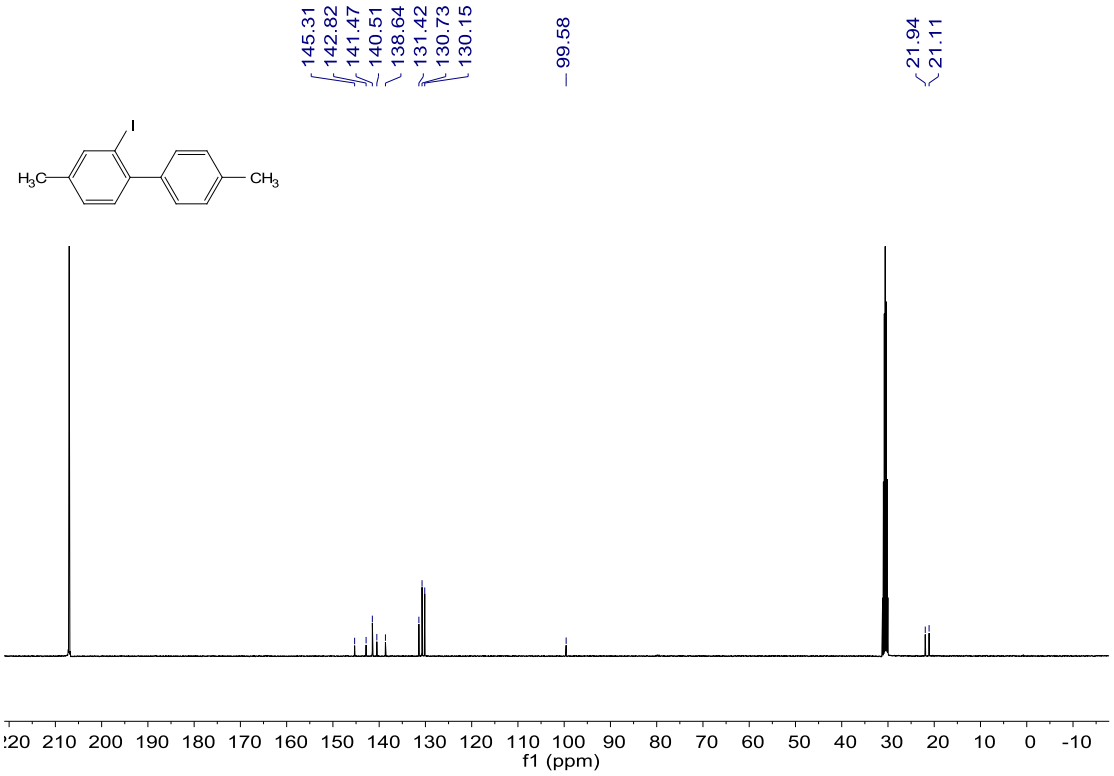


4,4’-dimethyl-2-iodobiphenyl (1b)

^{1}H NMR

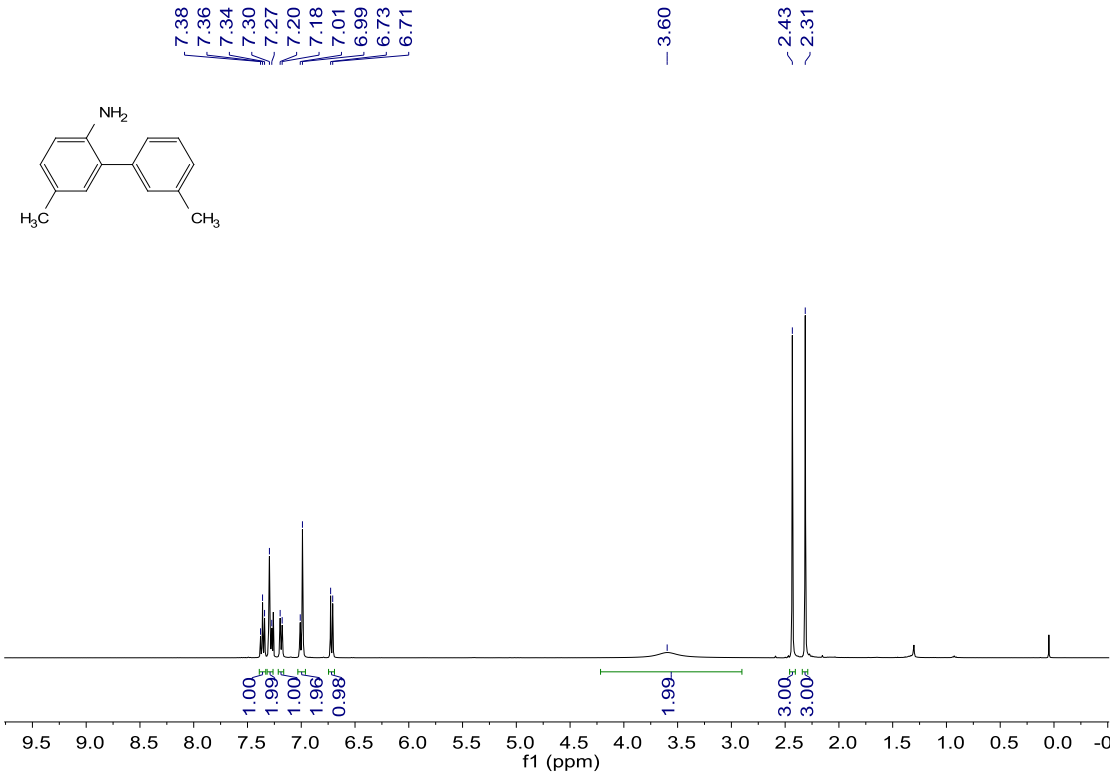


^{13}C NMR

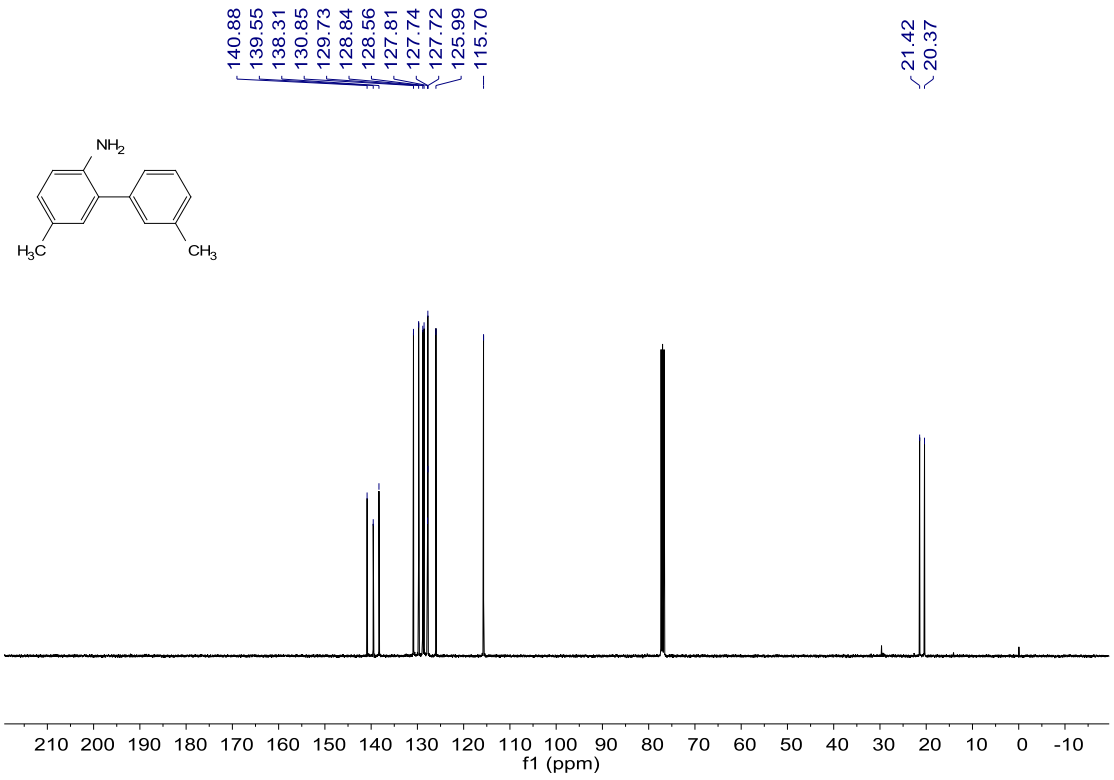


5,3'-dimethyl-2-aminobiphenyl (1c')

^{1}H NMR

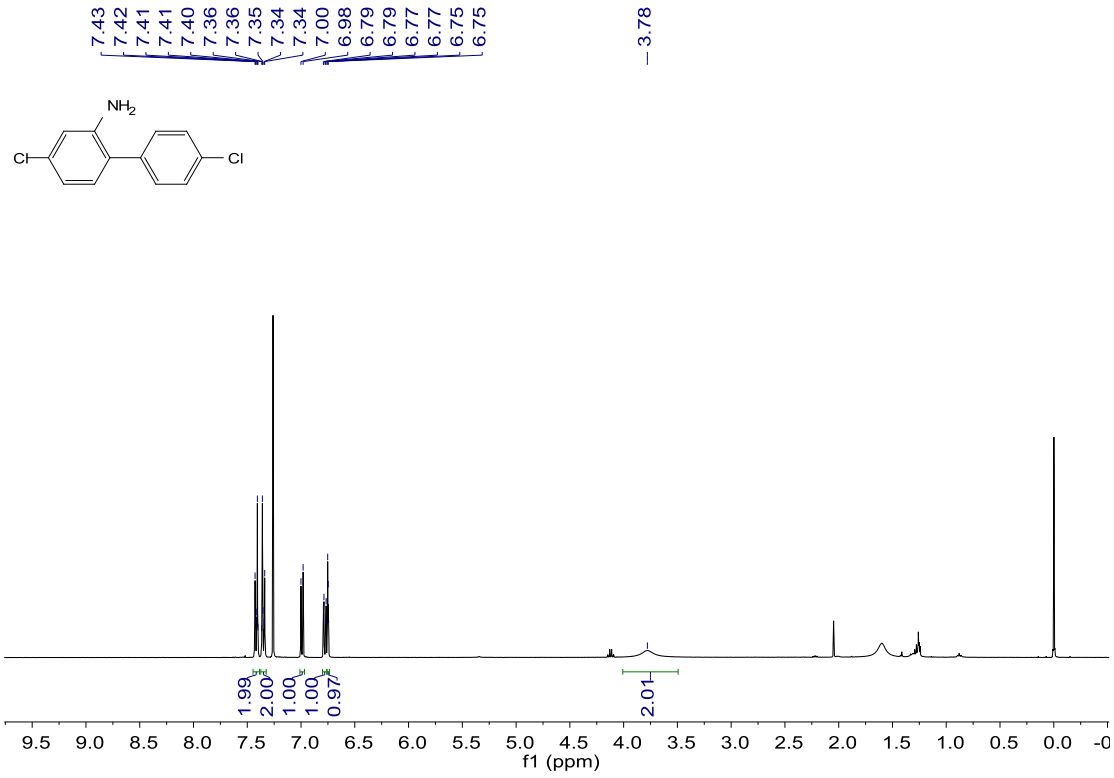


^{13}C NMR

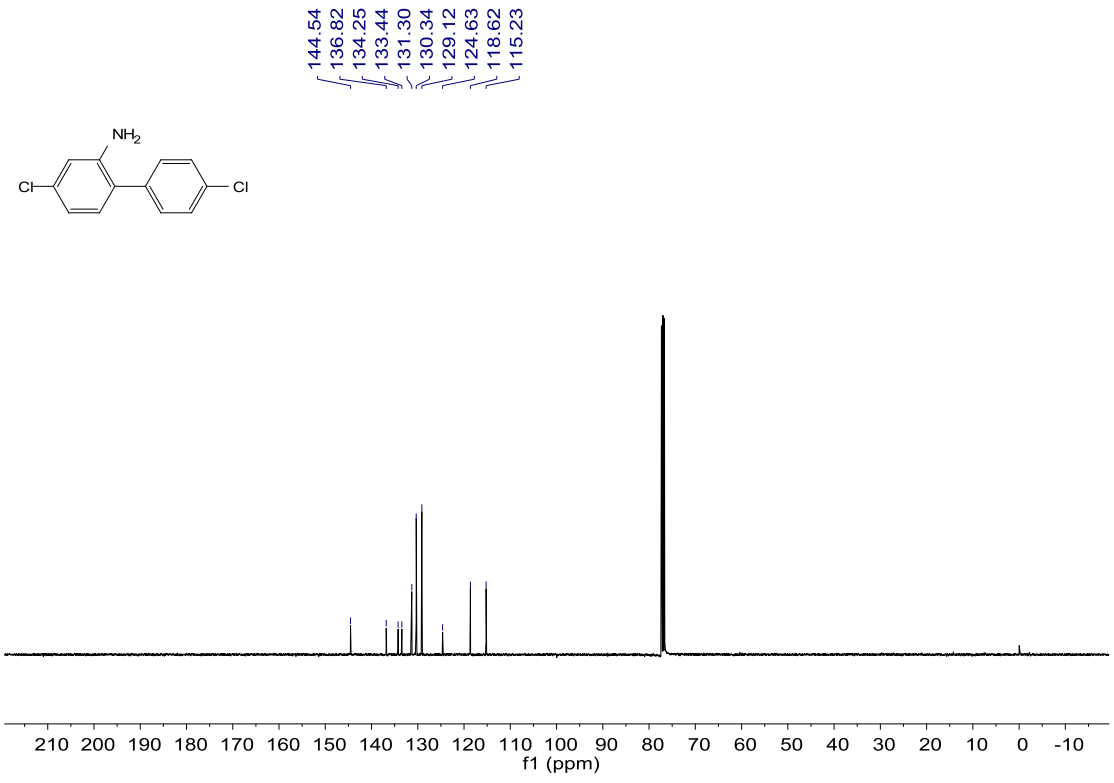


4,4’-dichloro-2-aminobiphenyl (1d’)

^{1}H NMR

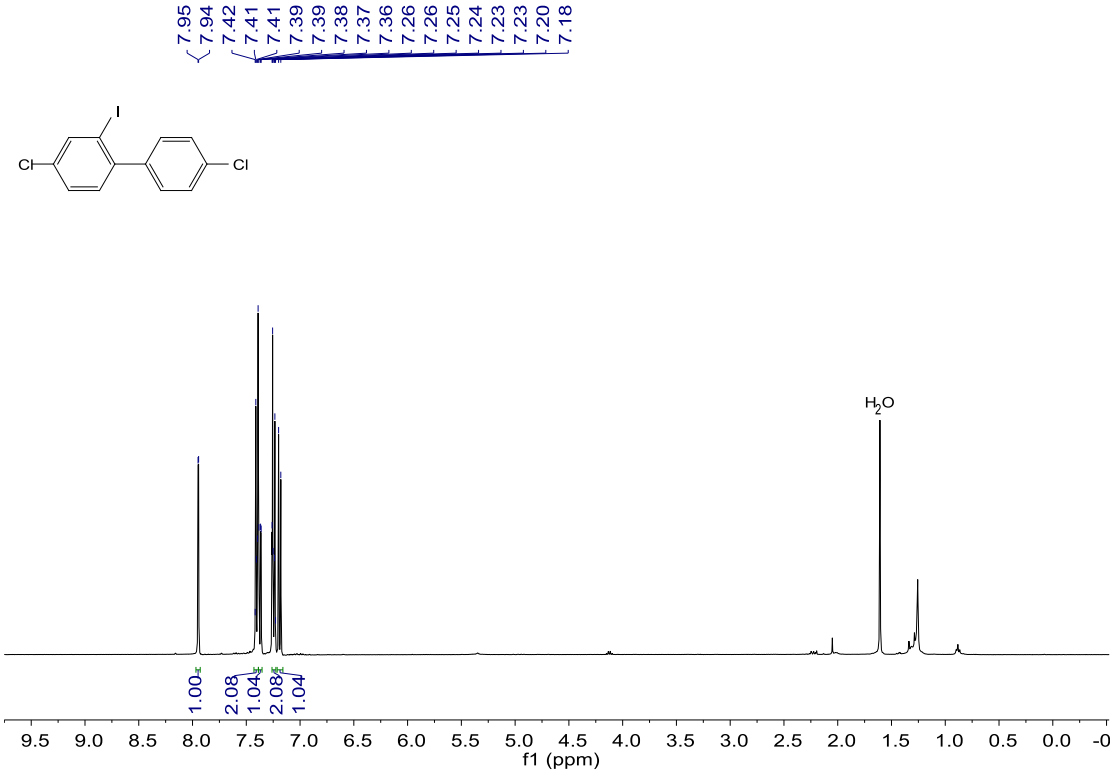


^{13}C NMR

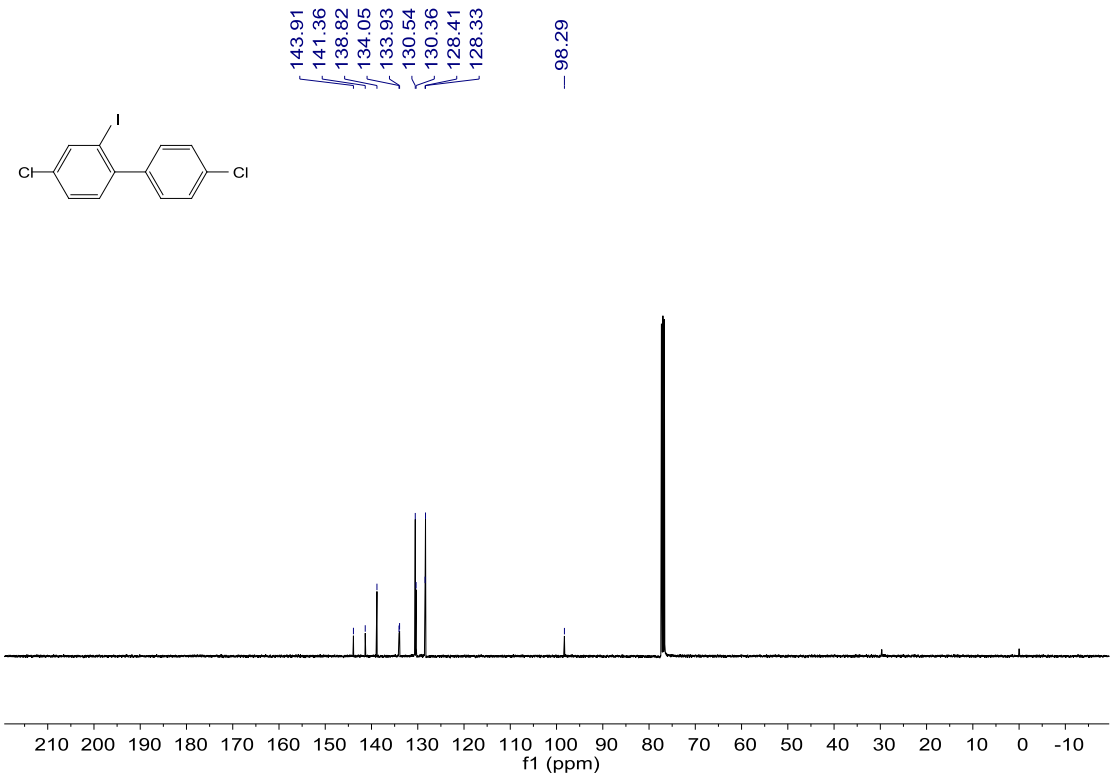


4,4’-dichloro-2-iodobiphenyl (1d)

^{1}H NMR

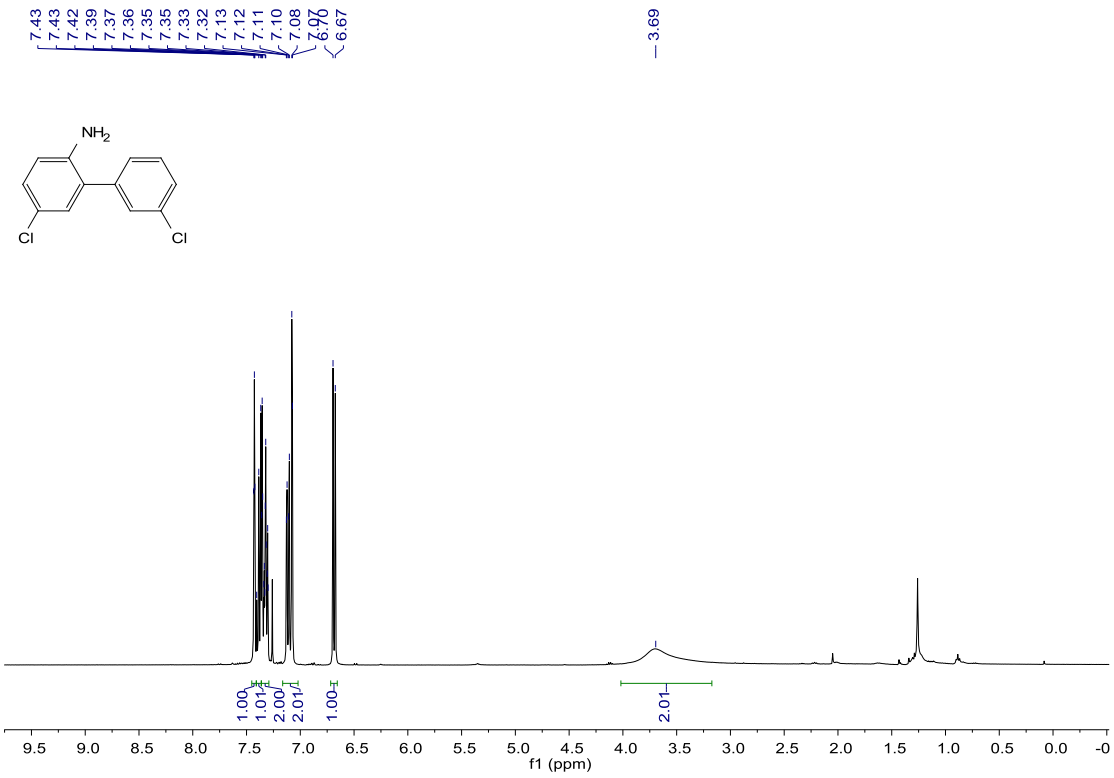


^{13}C NMR

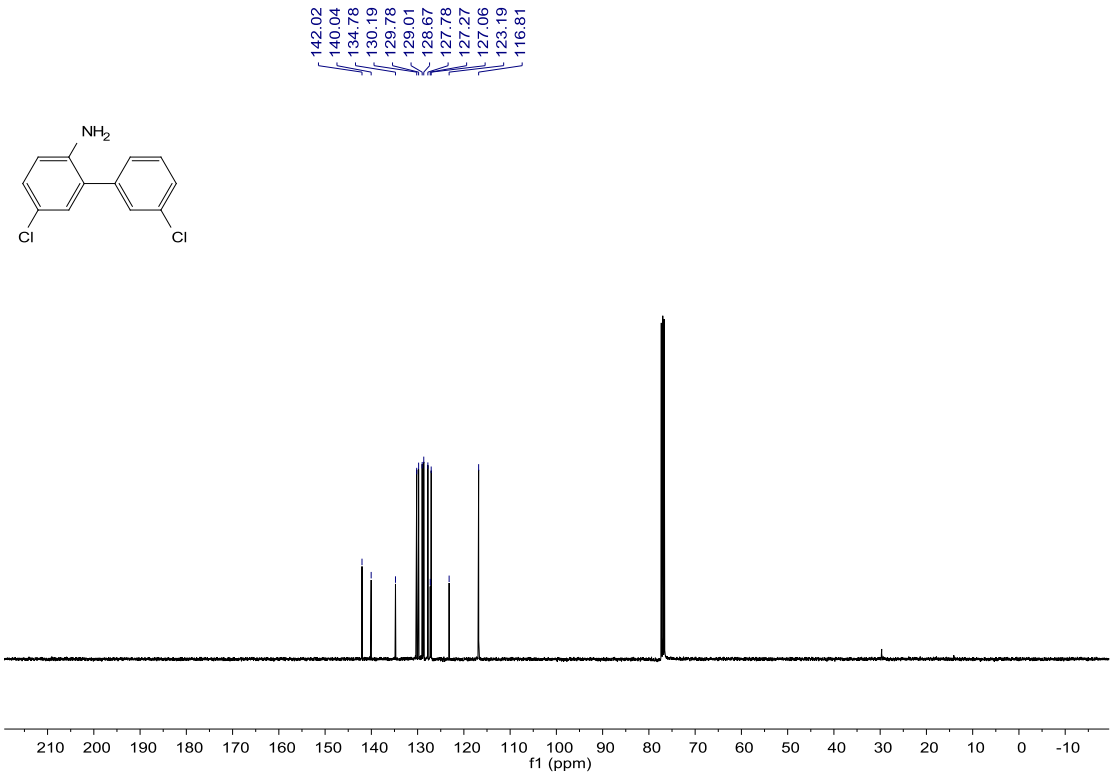


3',5-dichloro-[1,1'-biphenyl]-2-amine(1e')

^{1}H NMR

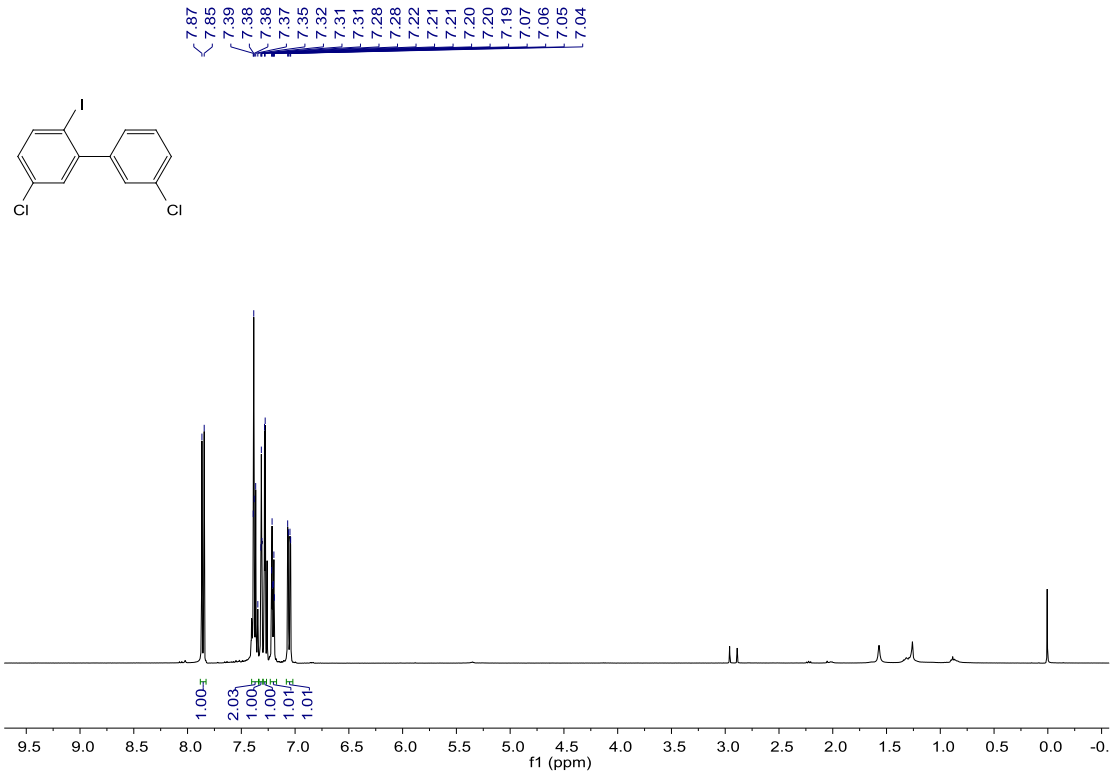


^{13}C NMR

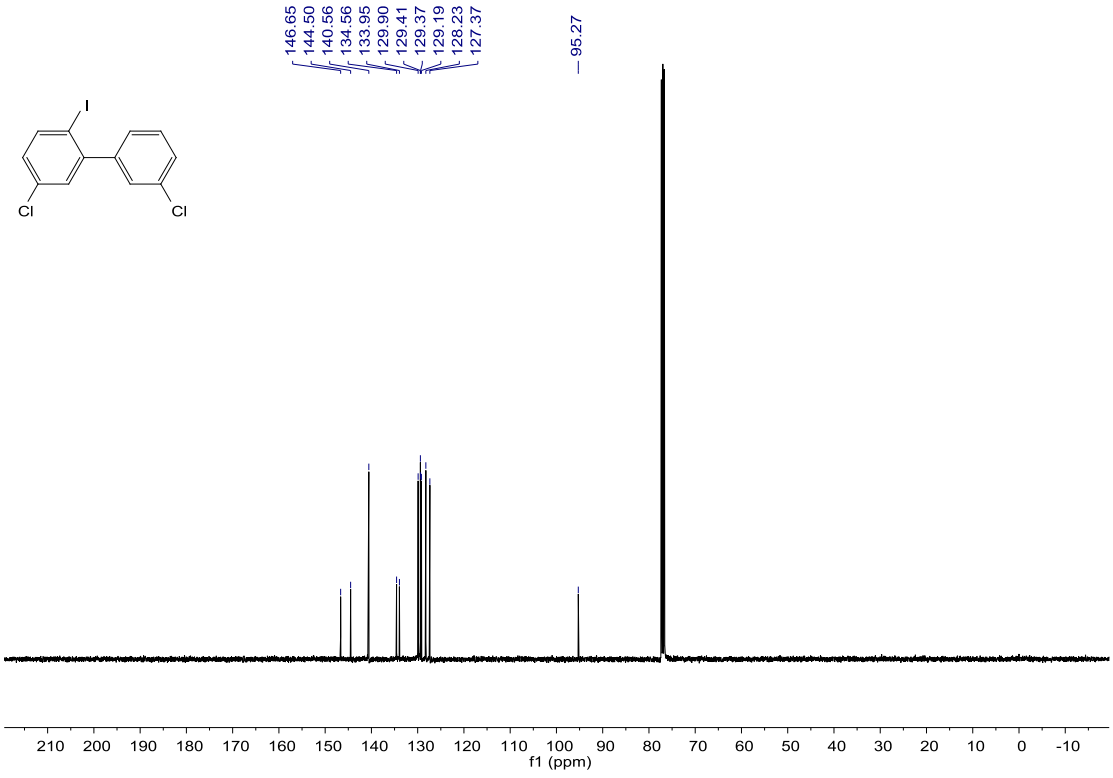


3',5-dichloro-2-iodo-1,1'-biphenyl(1e)

^{1}HNMR

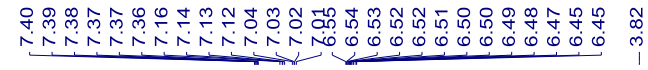


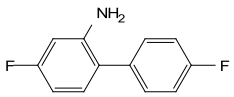
^{13}C NMR

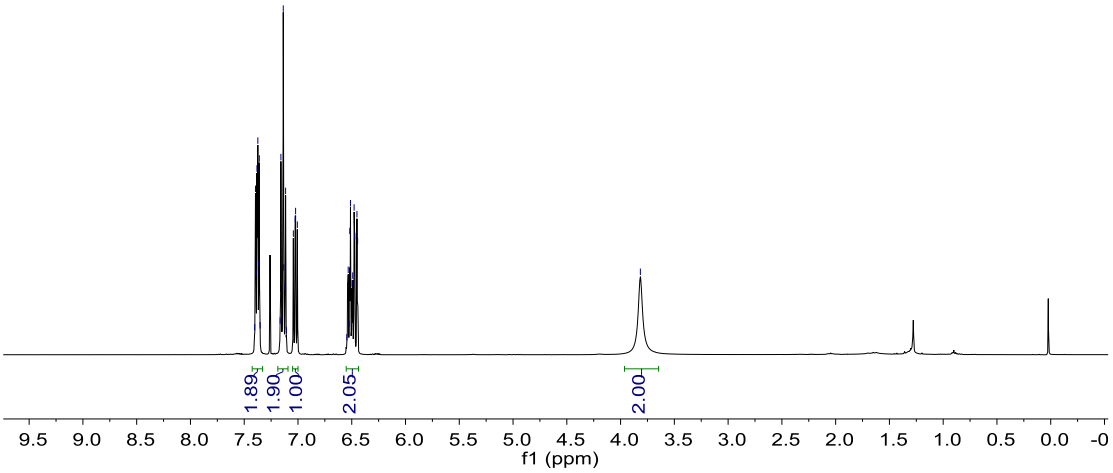


4,4'-difluoro-2-aminobiphenyl (1f')

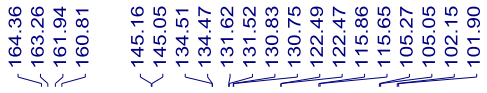
^{1}H NMR

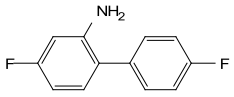


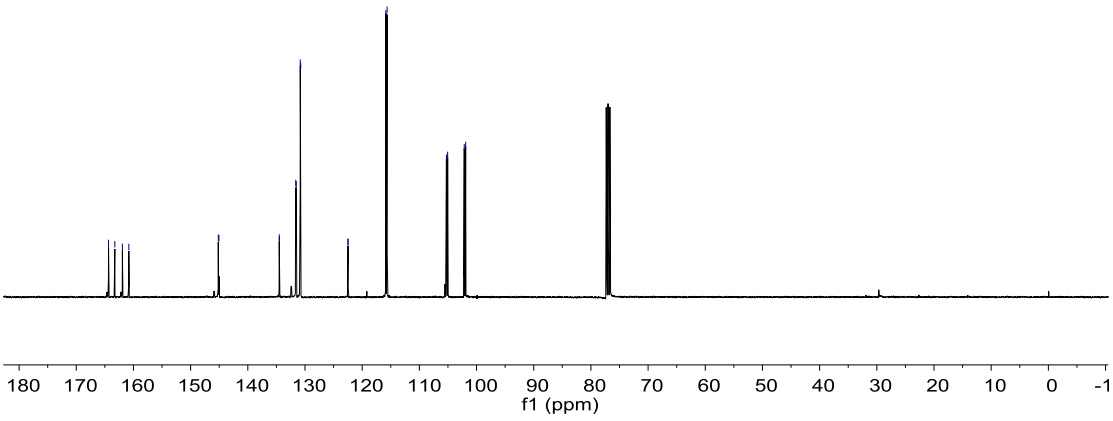




^{13}C NMR

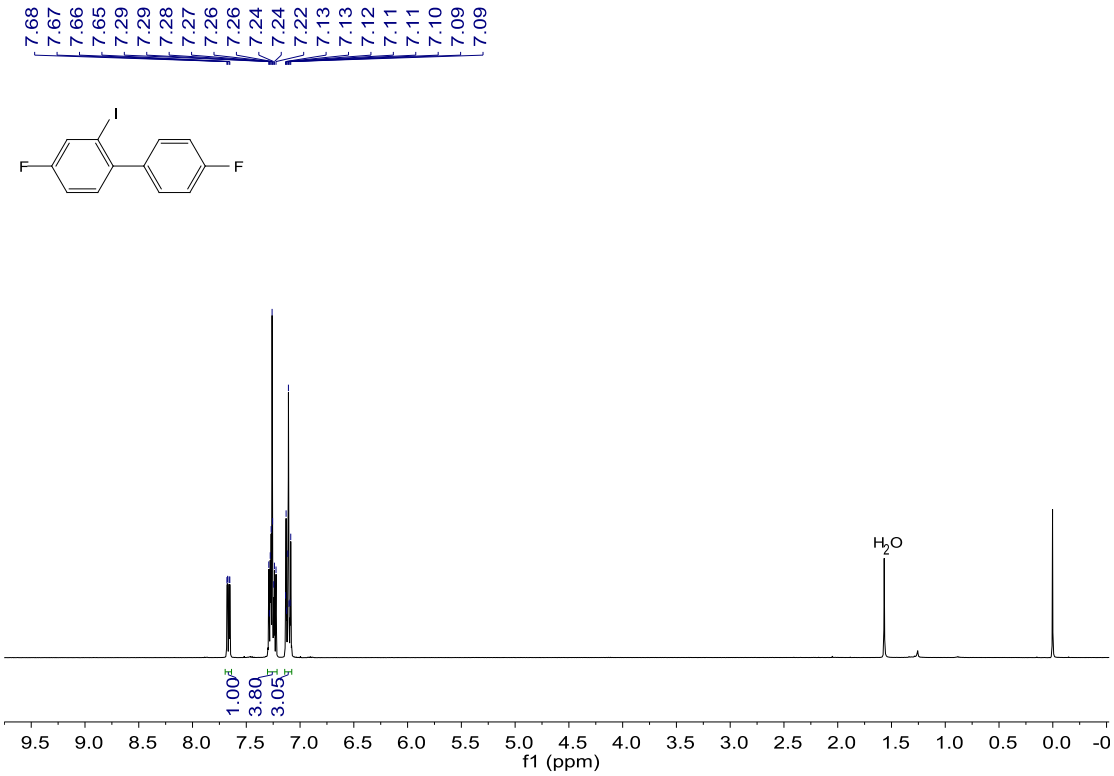




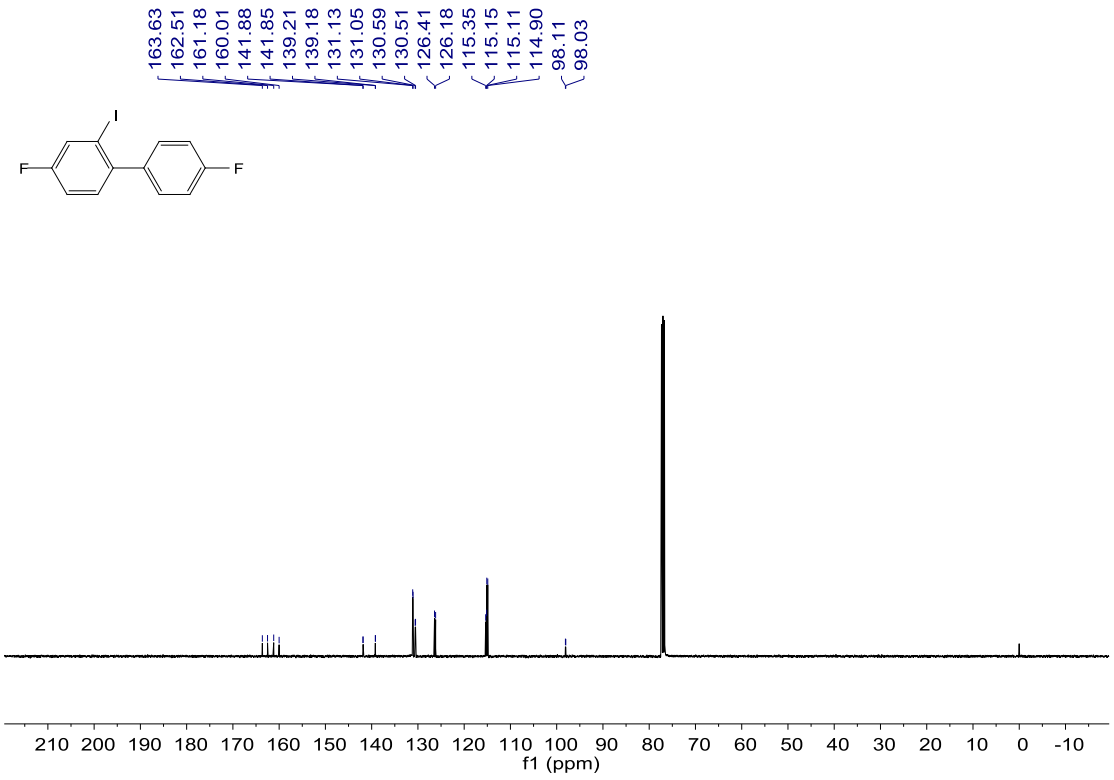


4,4’-difluoro-2-iodobiphenyl (1f)

^{1}H NMR

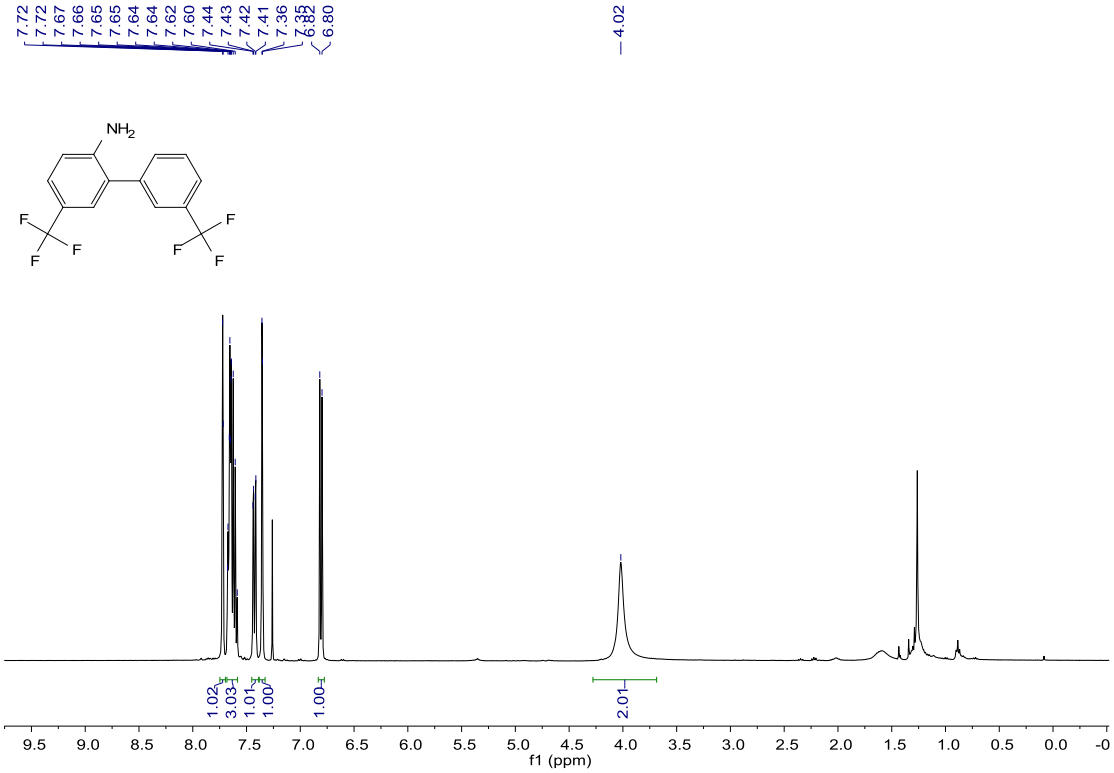


^{13}C NMR

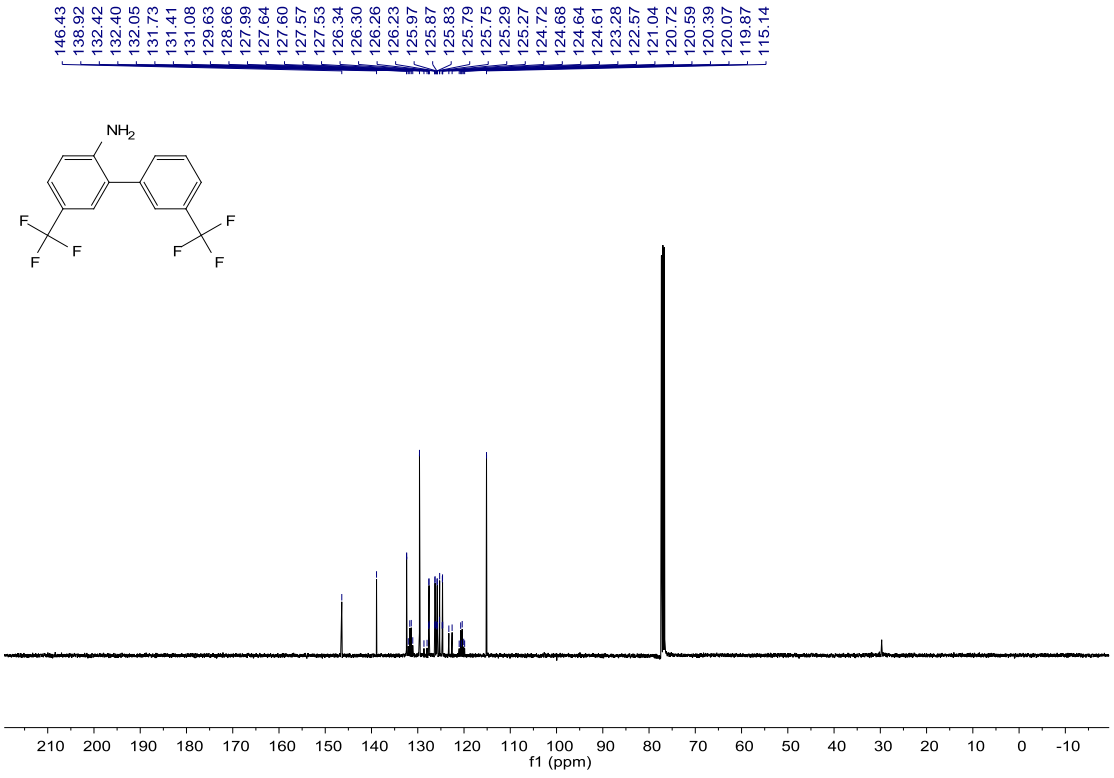


3',5-bis(trifluoromethyl)-[1,1'-biphenyl]-2-amine(1g')

^{1}HNMR

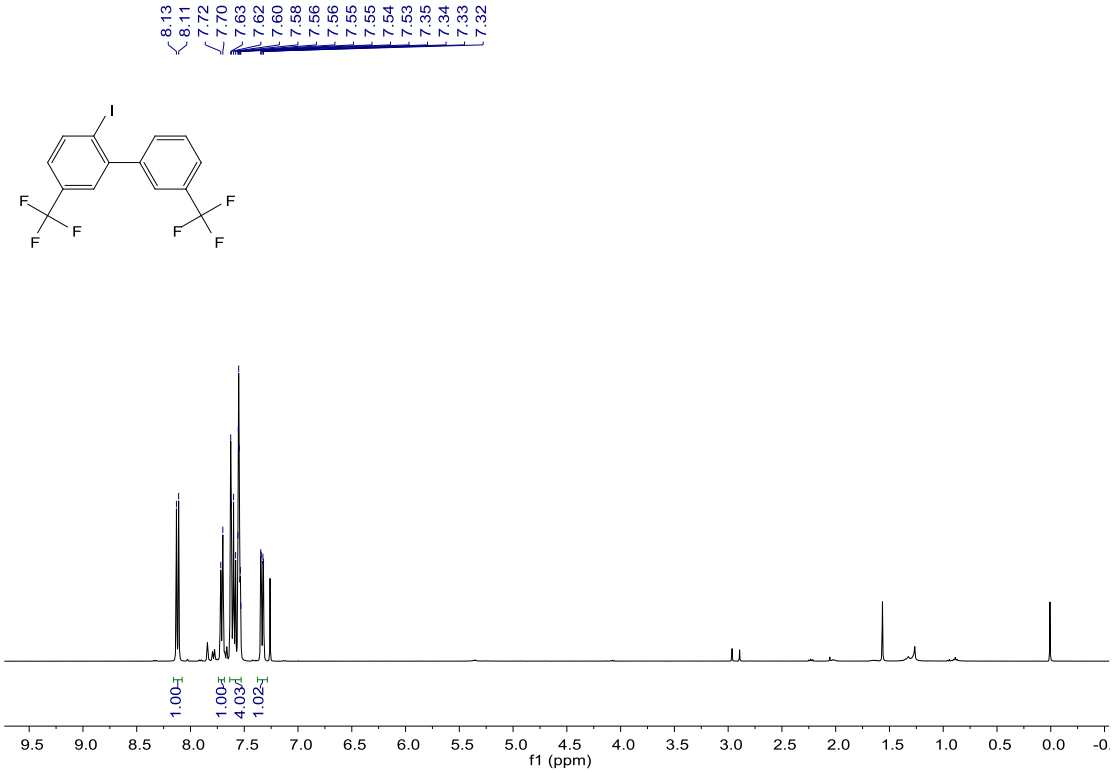


^{13}CNMR

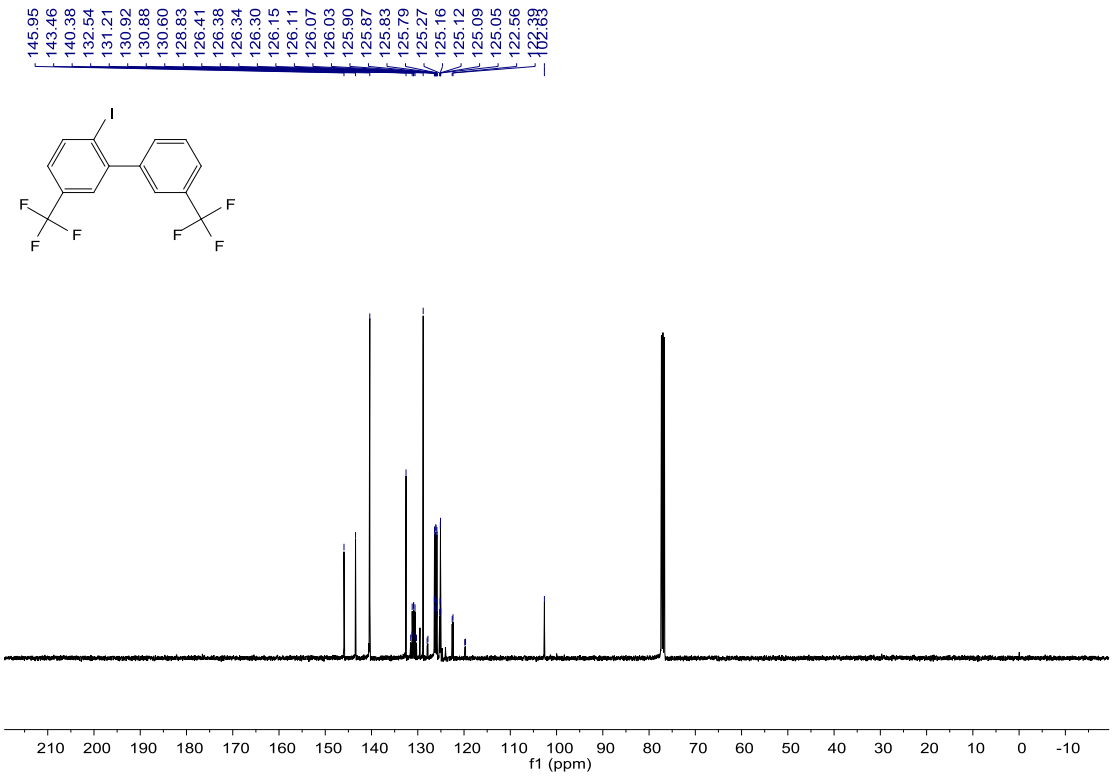


2-iodo-3',5-bis(trifluoromethyl)-1,1'-biphenyl(1g)

^{1}HNMR

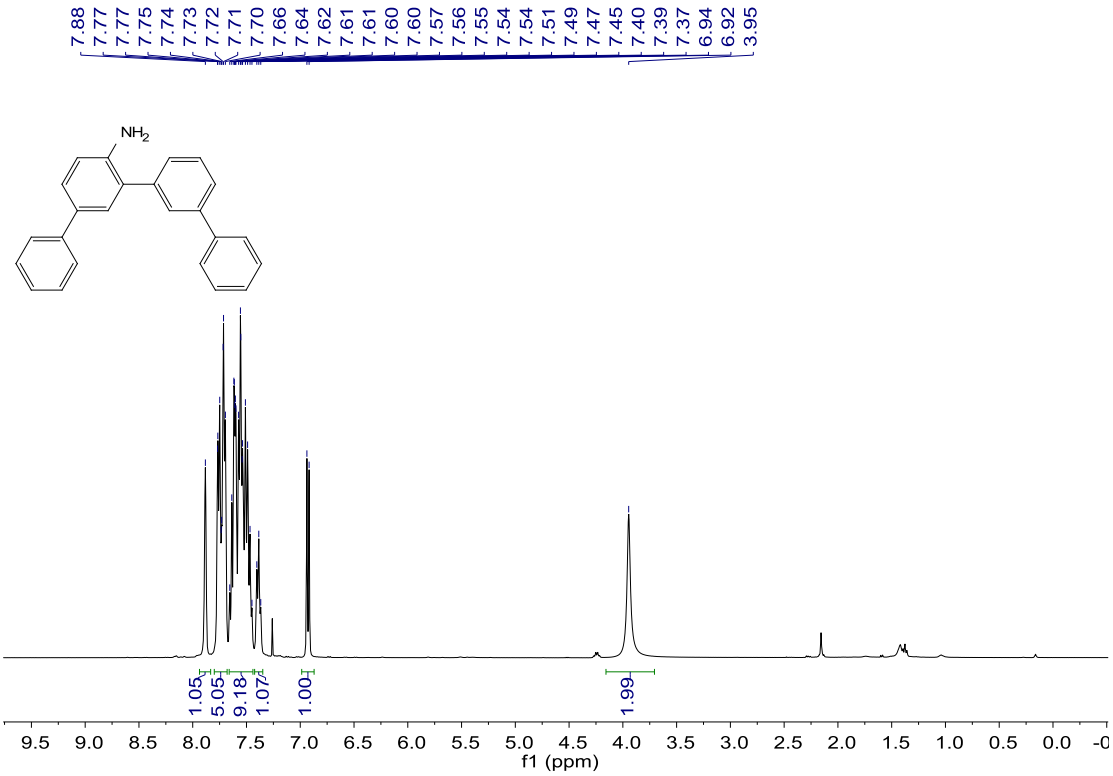


^{13}CNMR

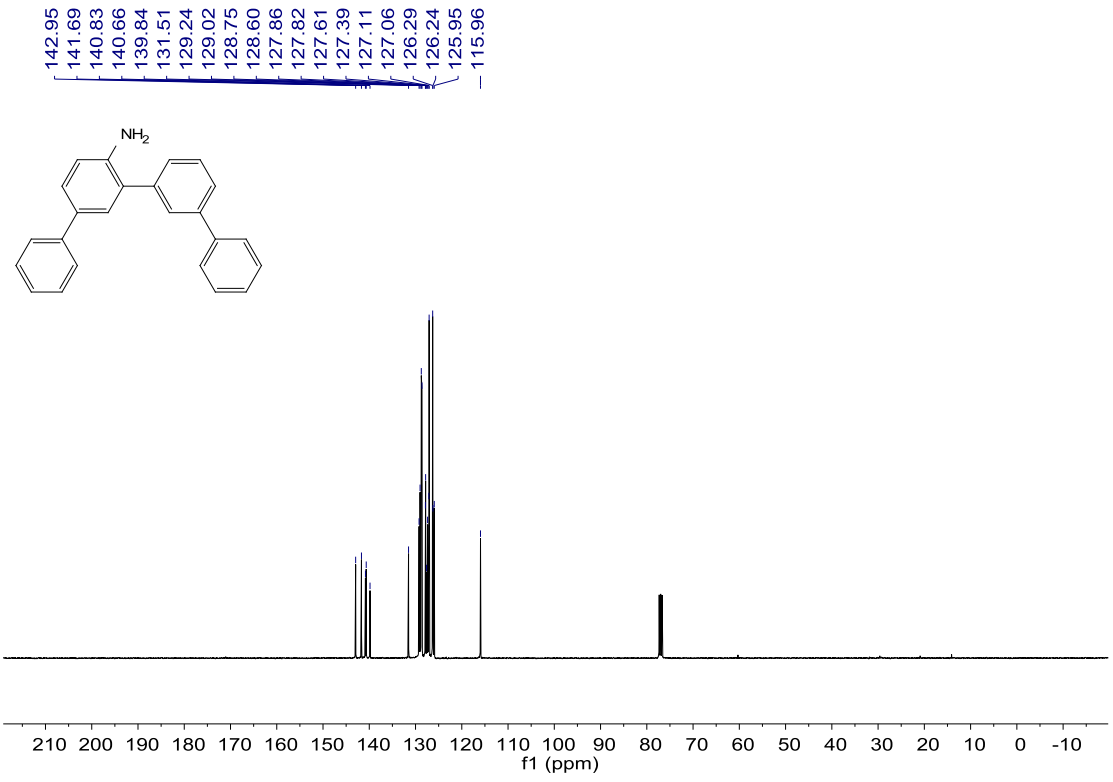


5,3'-diphenyl-2-aminobiphenyl (1h')

^{1}H NMR

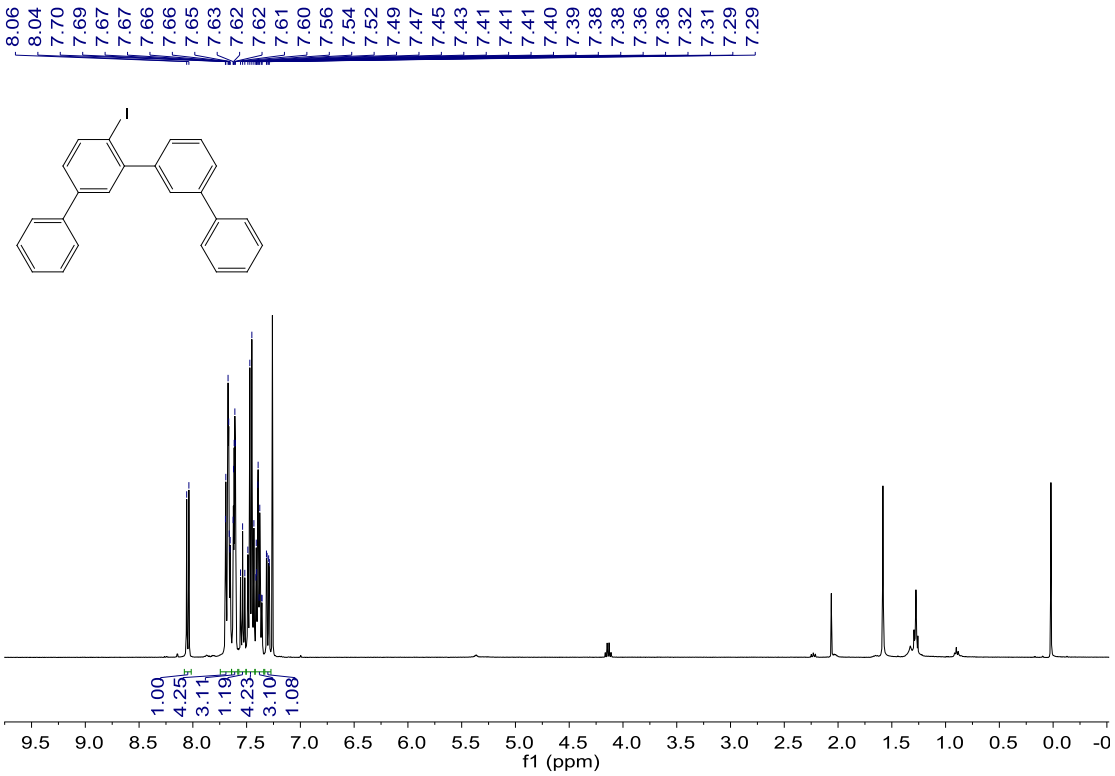


^{13}C NMR

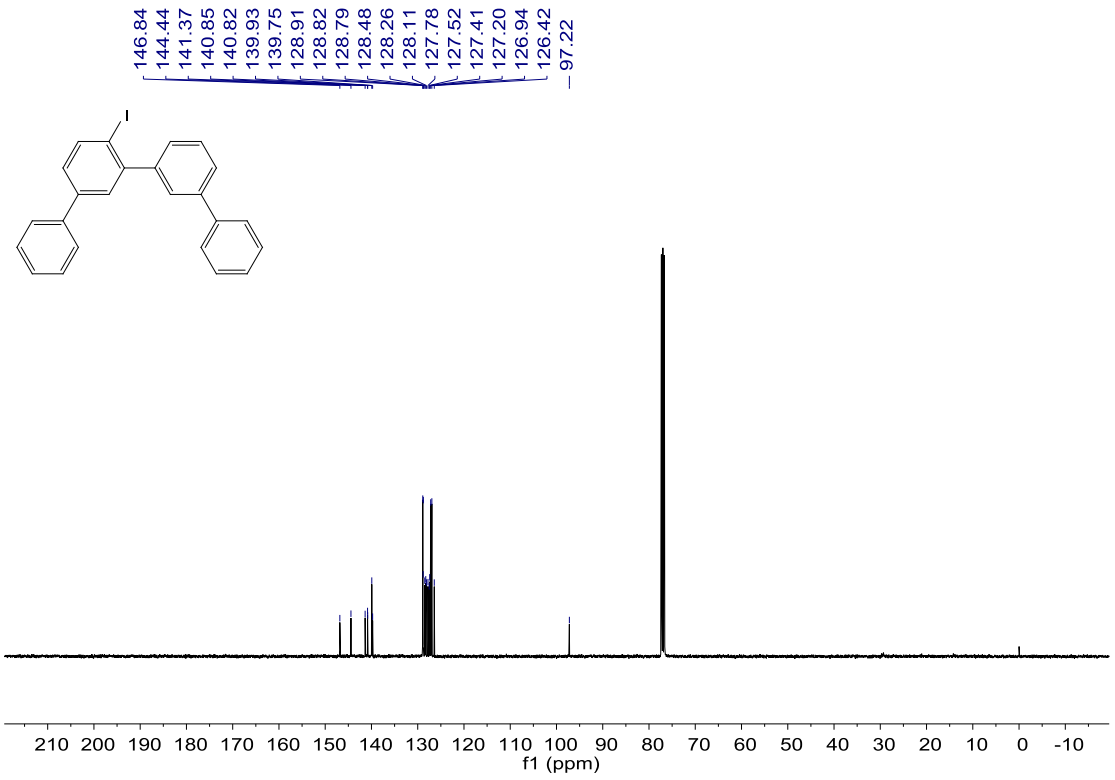


5,3'-diphenyl-2-iodobiphenyl (1h)

^{1}H NMR

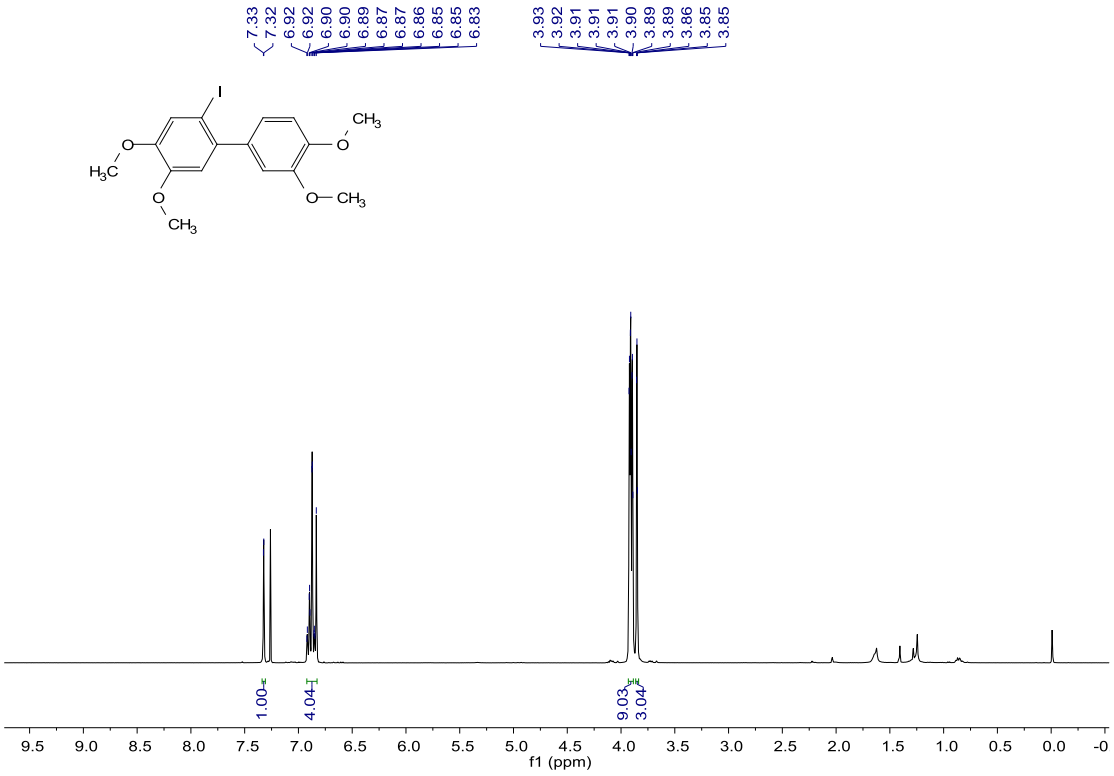


^{13}C NMR

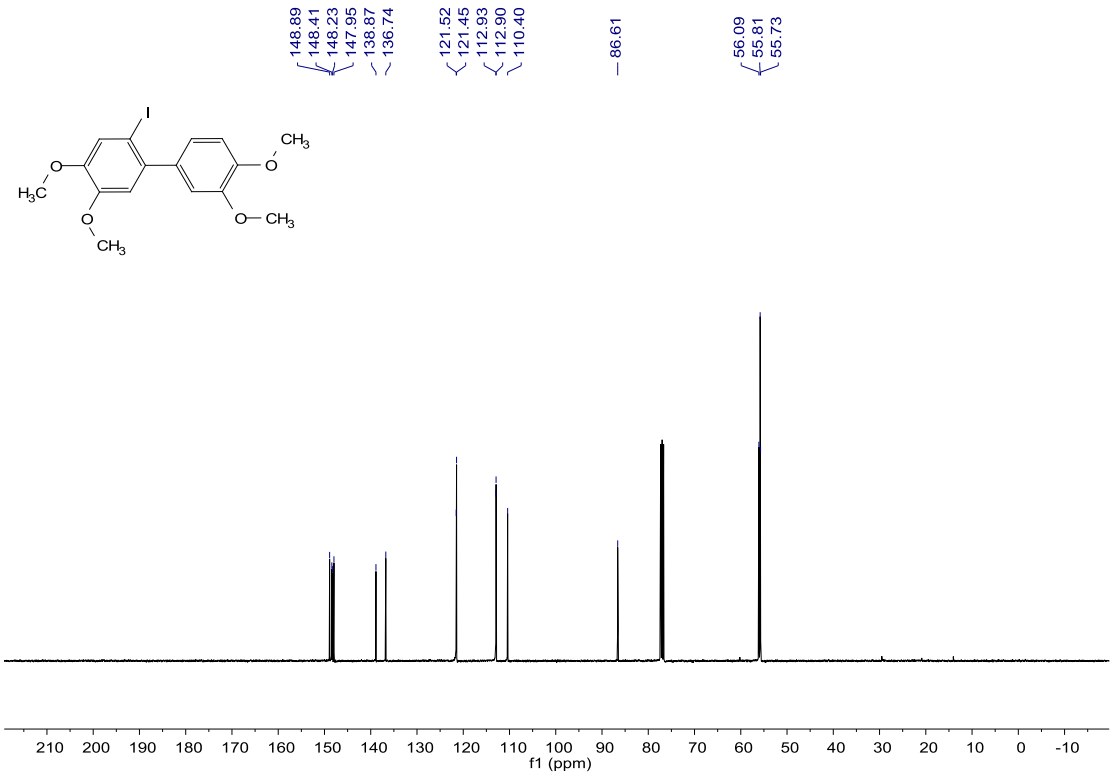


2-iodo-3',4,4',5-tetramethoxy-1,1'-biphenyl(1i)

^{1}HNMR

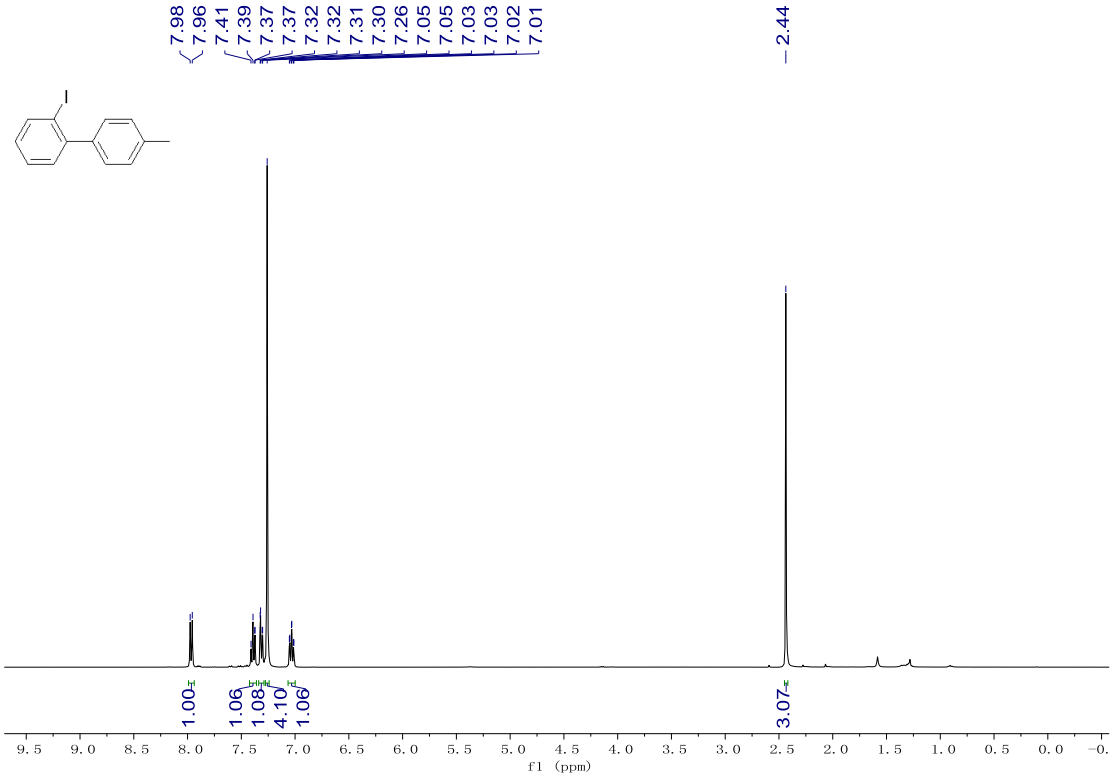


^{13}CNMR

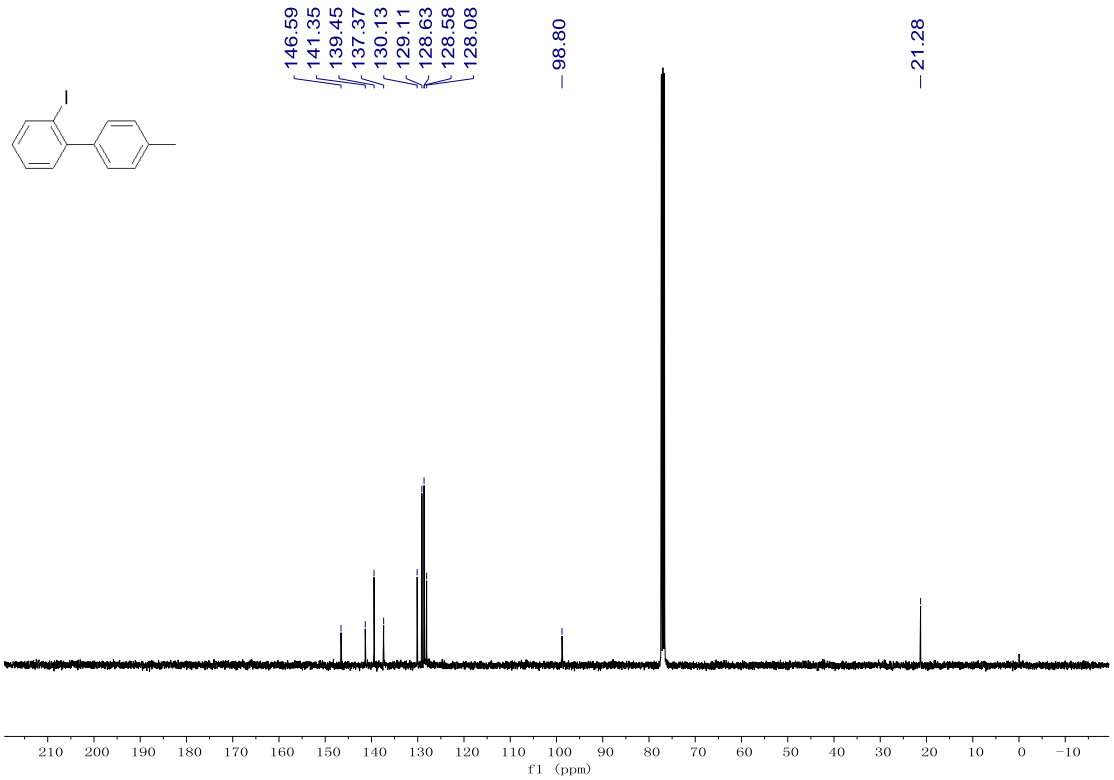


2-iodo-4’-methylbiphenyl (1j):

^{1}H NMR

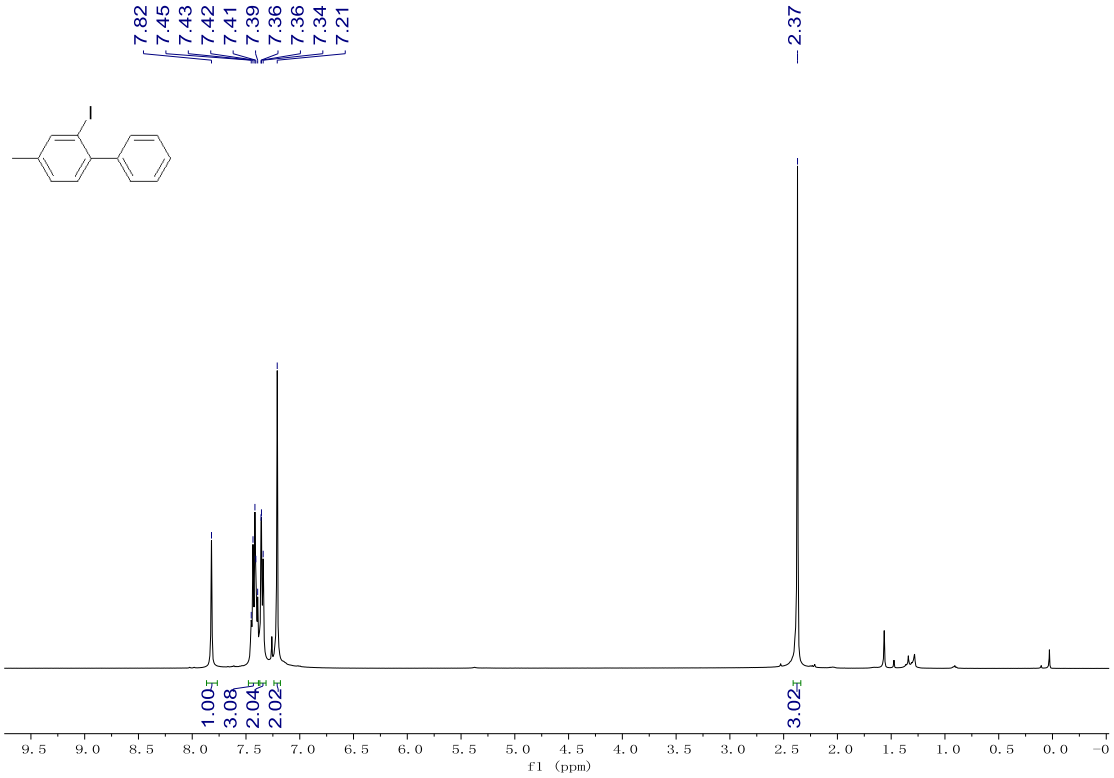


^{13}C NMR

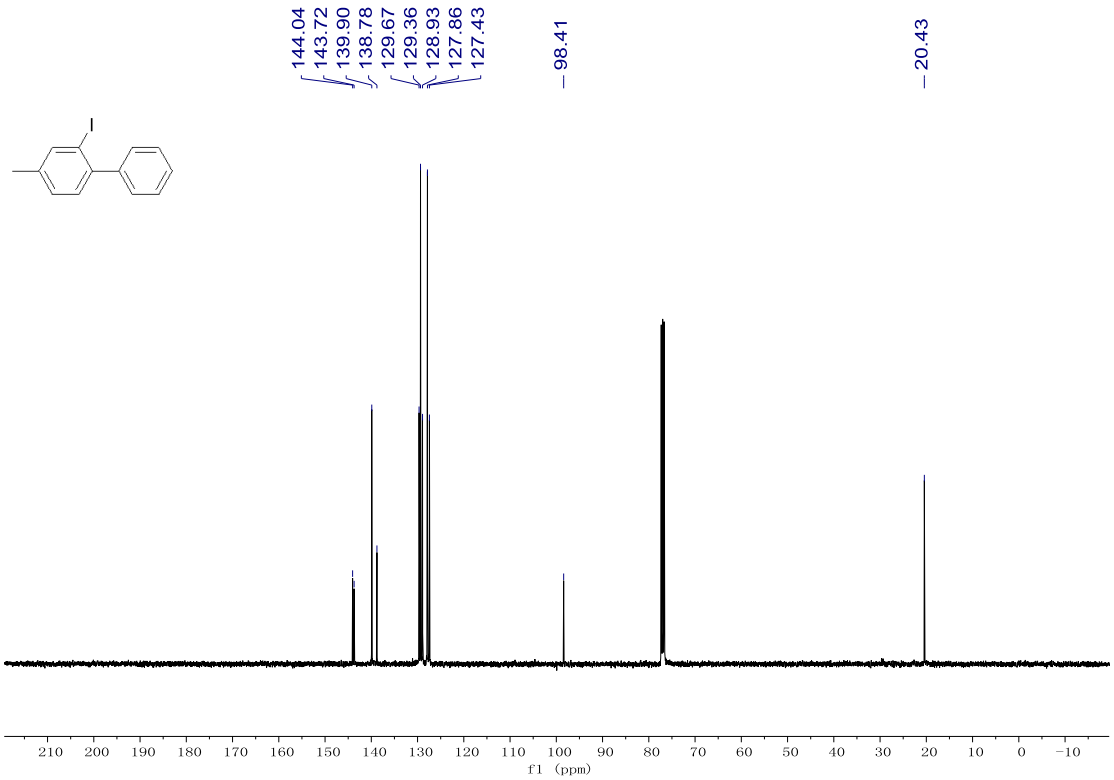


2-iodo-4-methylbiphenyl (1k):

^{1}H NMR

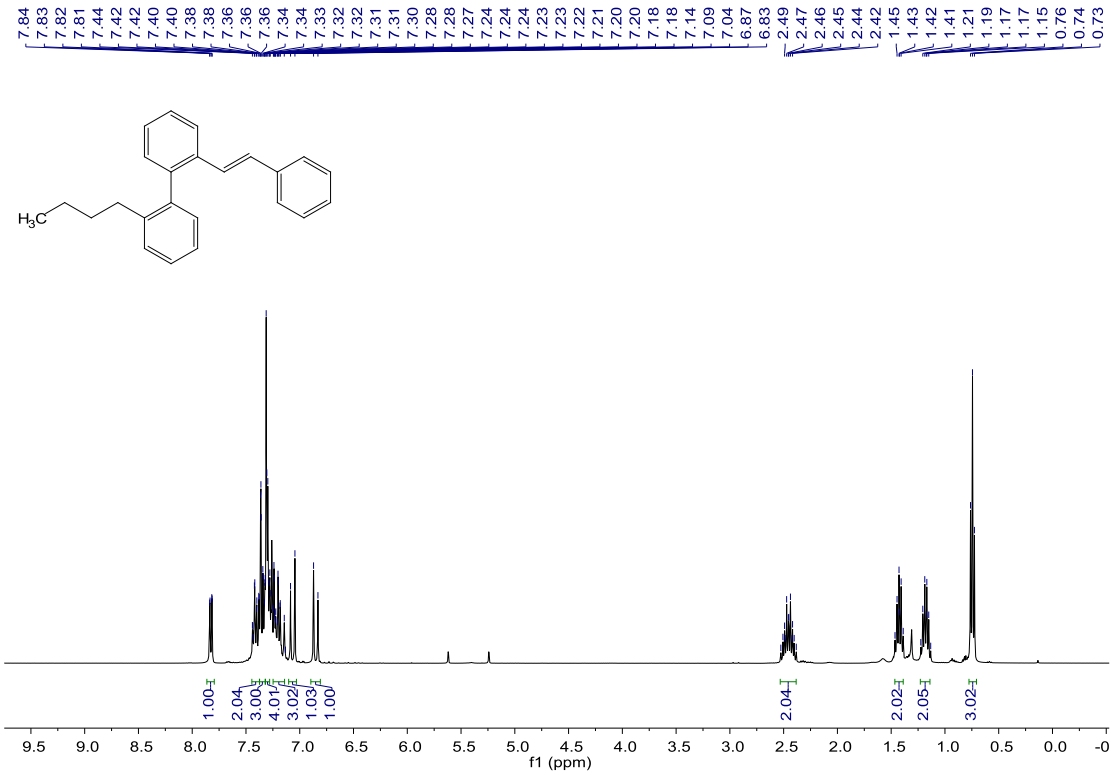


^{13}C NMR

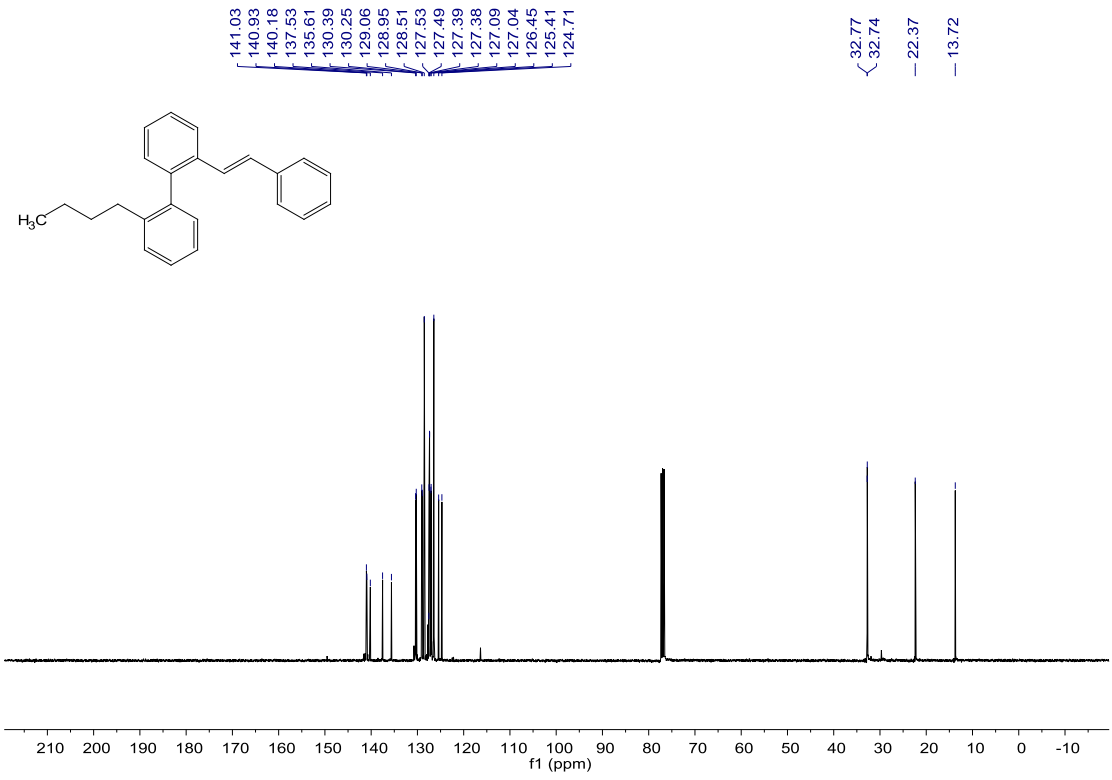


(*E*)-2-butyl-2'-styryl-1,1'-biphenyl(4aaa)

^{1}HNMR

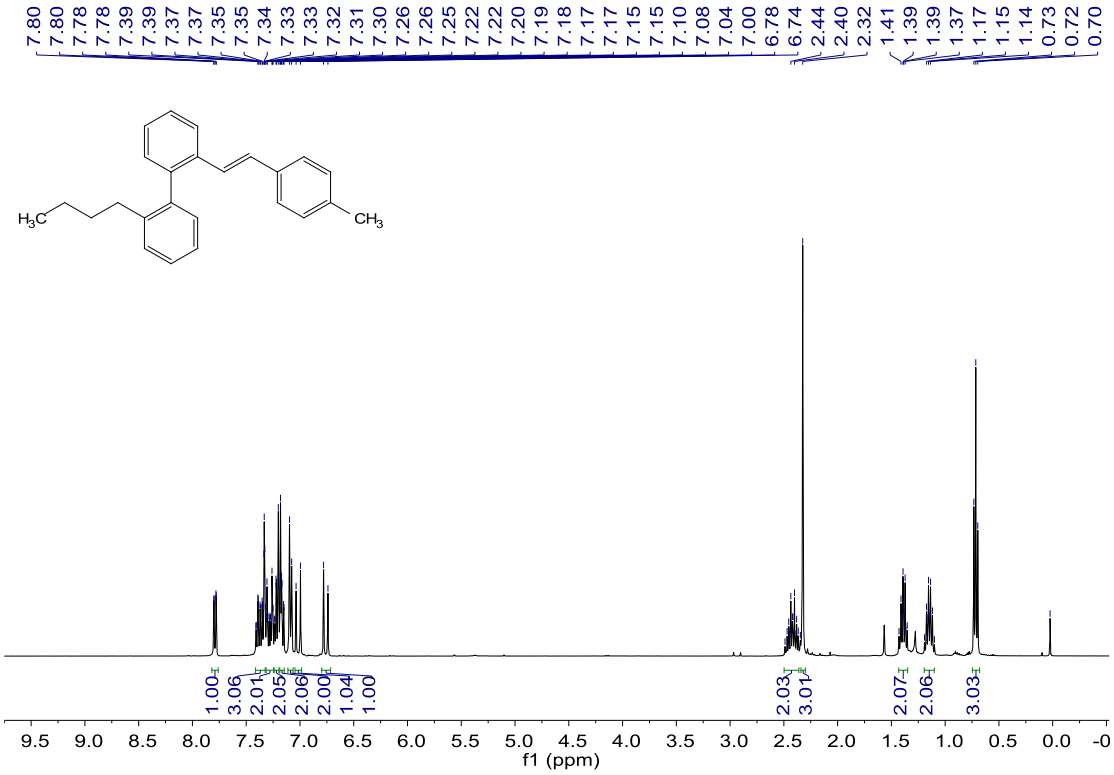


^{13}CNMR

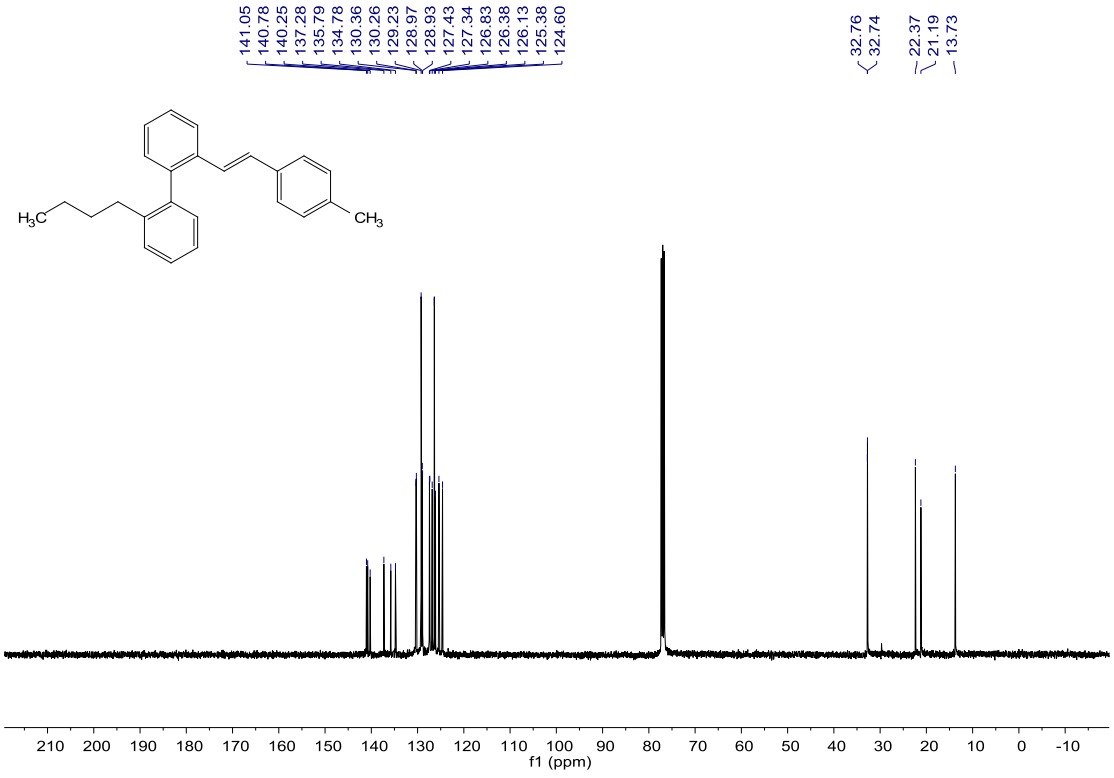


(*E*)-2-butyl-2'-(4-methylstyryl)-1,1'-biphenyl(4aab)

^{1}HNMR

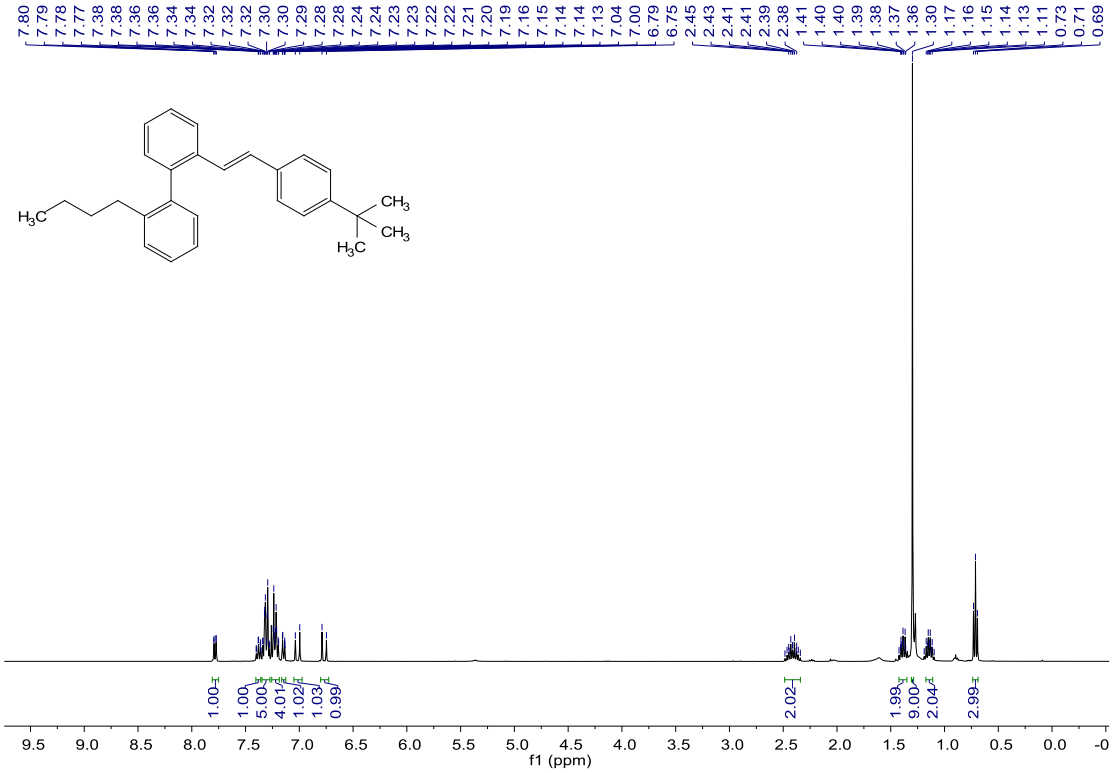


^{13}CNMR

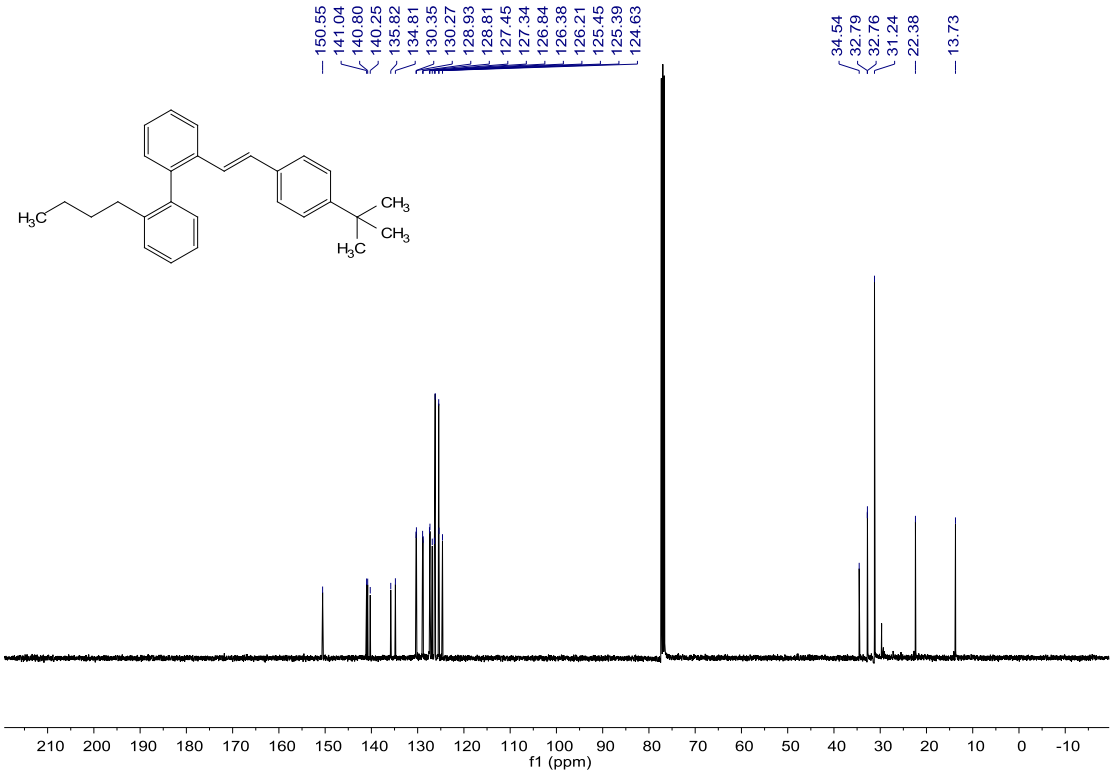


(*E*)-2-butyl-2'-(4-(tert-butyl)styryl)-1,1'-biphenyl(4aac)

^{1}HNMR

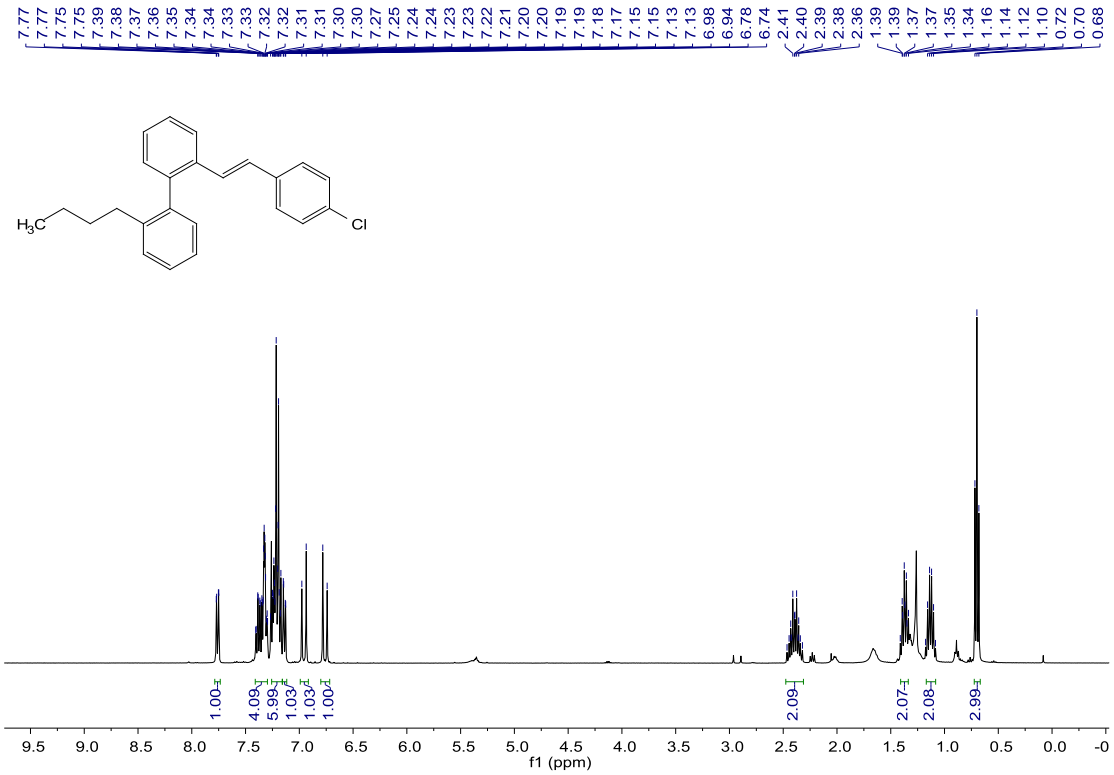


^{13}CNMR

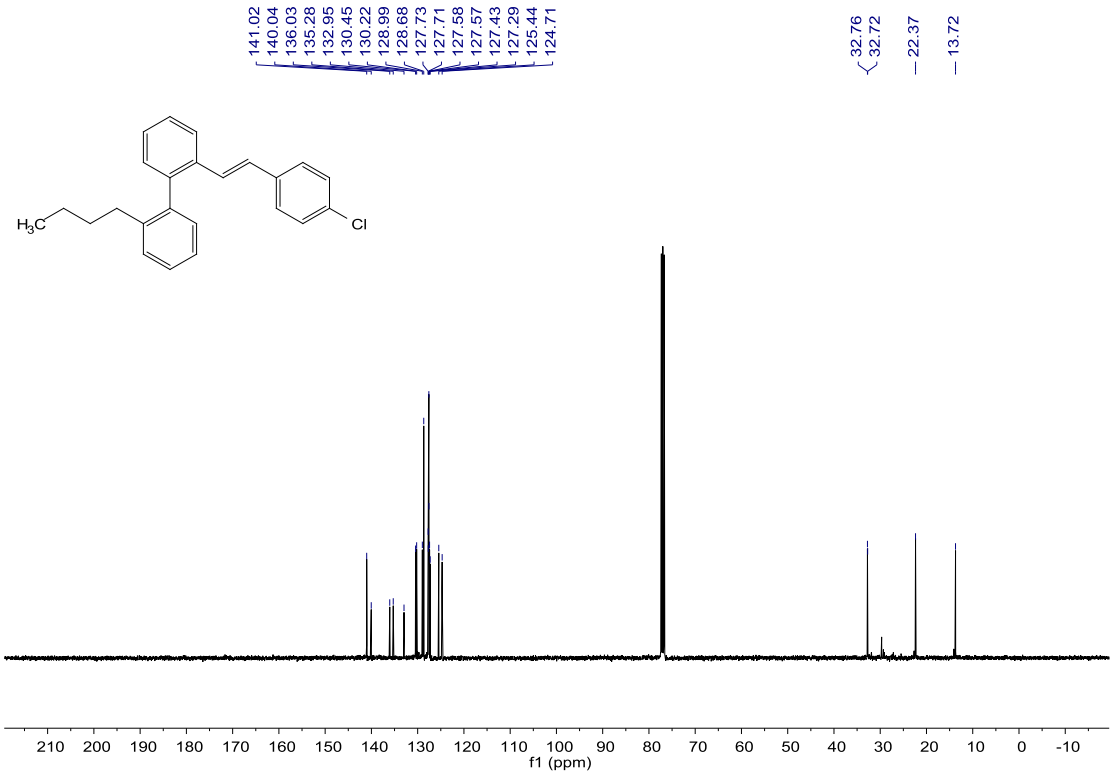


(*E*)-2-butyl-2'-(4-chlorostyryl)-1,1'-biphenyl(4aad)

^{1}HNMR

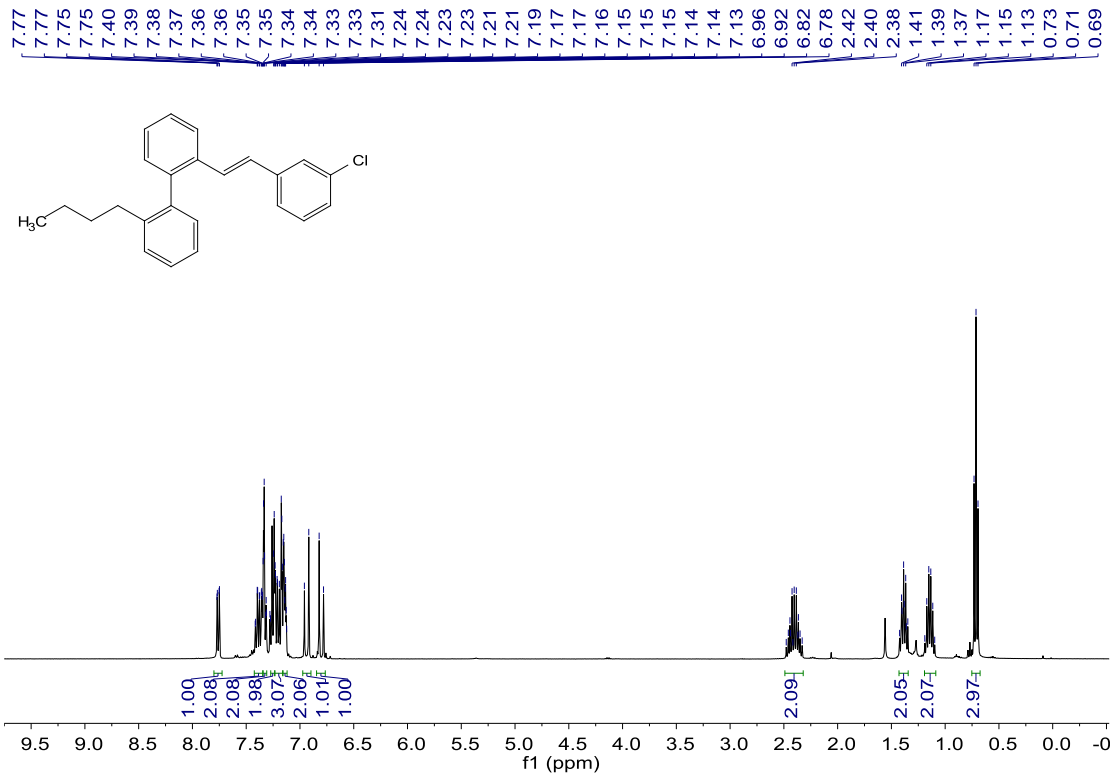


^{13}CNMR

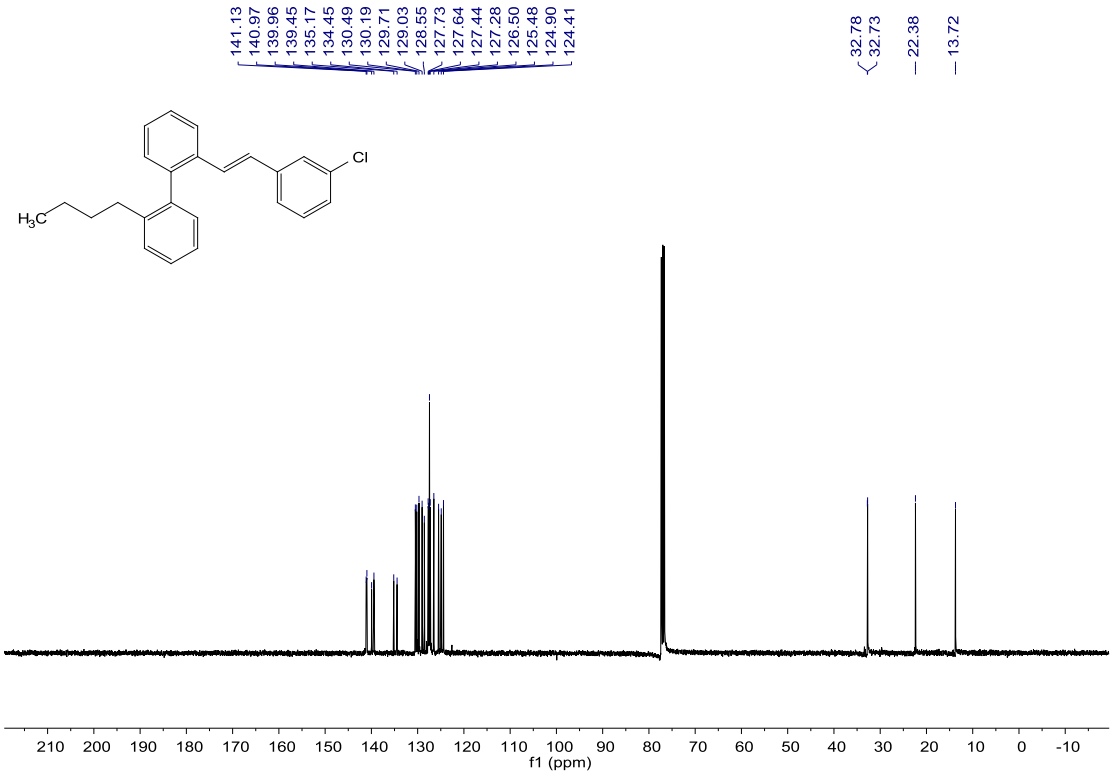


(*E*)-2-butyl-2'-(3-chlorostyryl)-1,1'-biphenyl(4aae)

^{1}HNMR

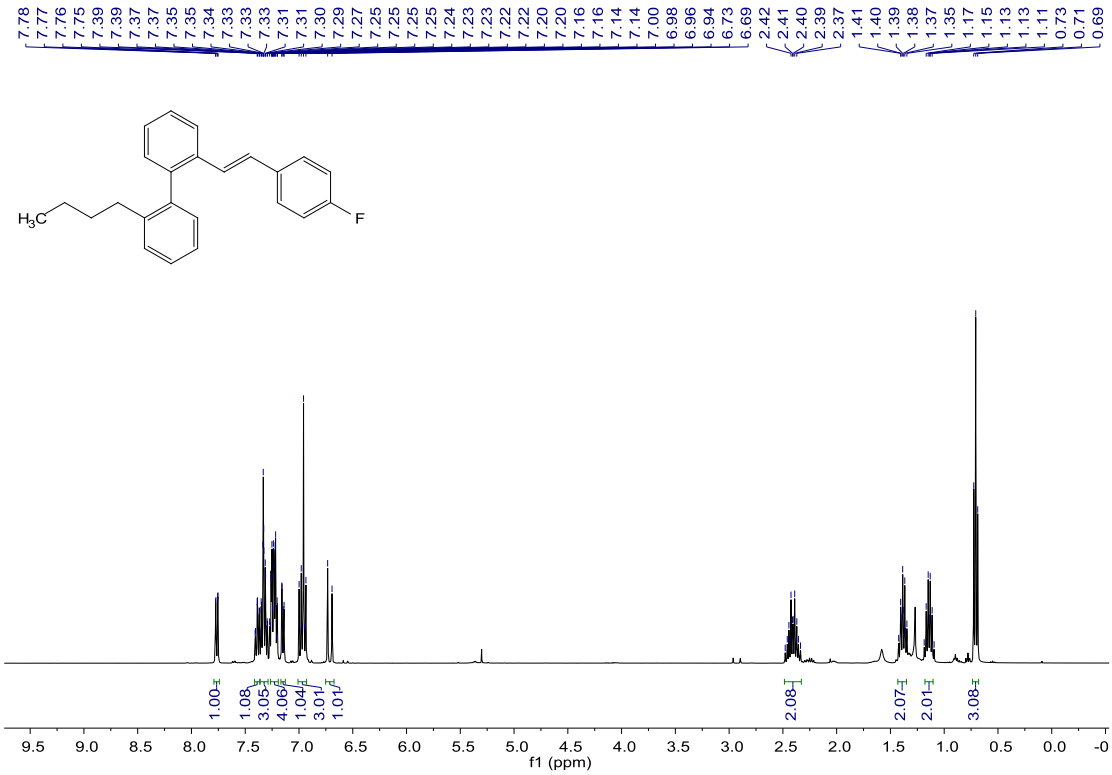


^{13}CNMR

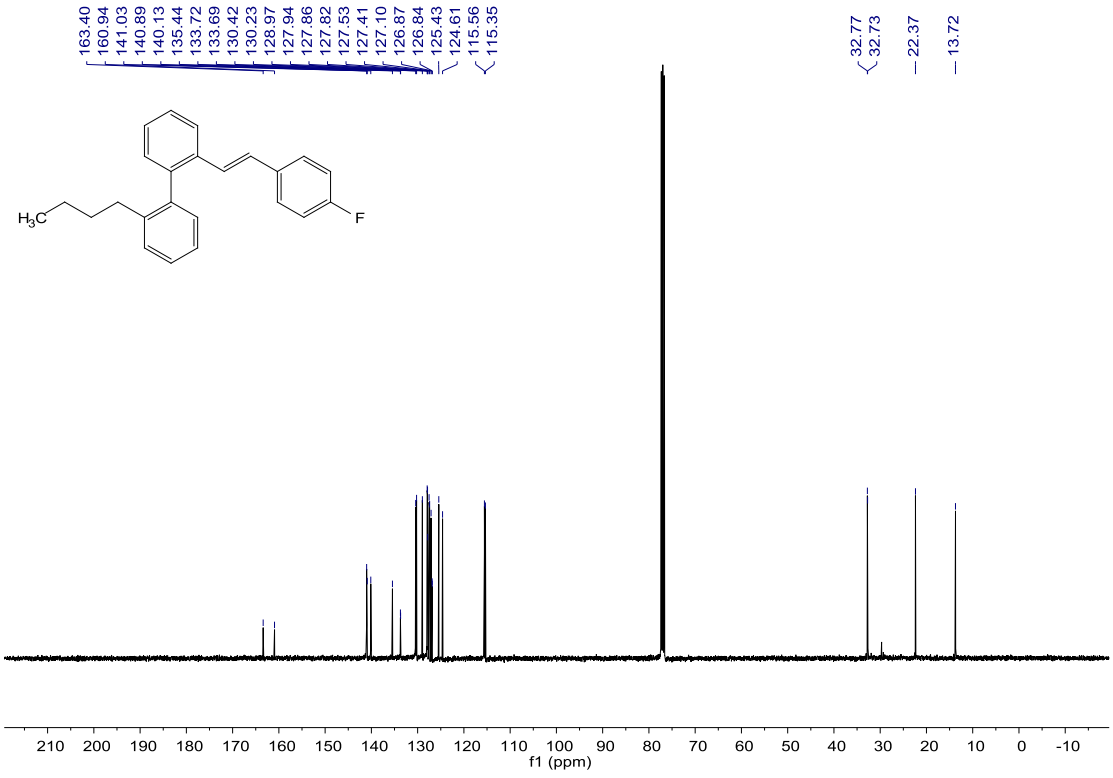


(*E*)-2-butyl-2'-(4-fluorostyryl)-1,1'-biphenyl(4aaf)

^{1}HNMR

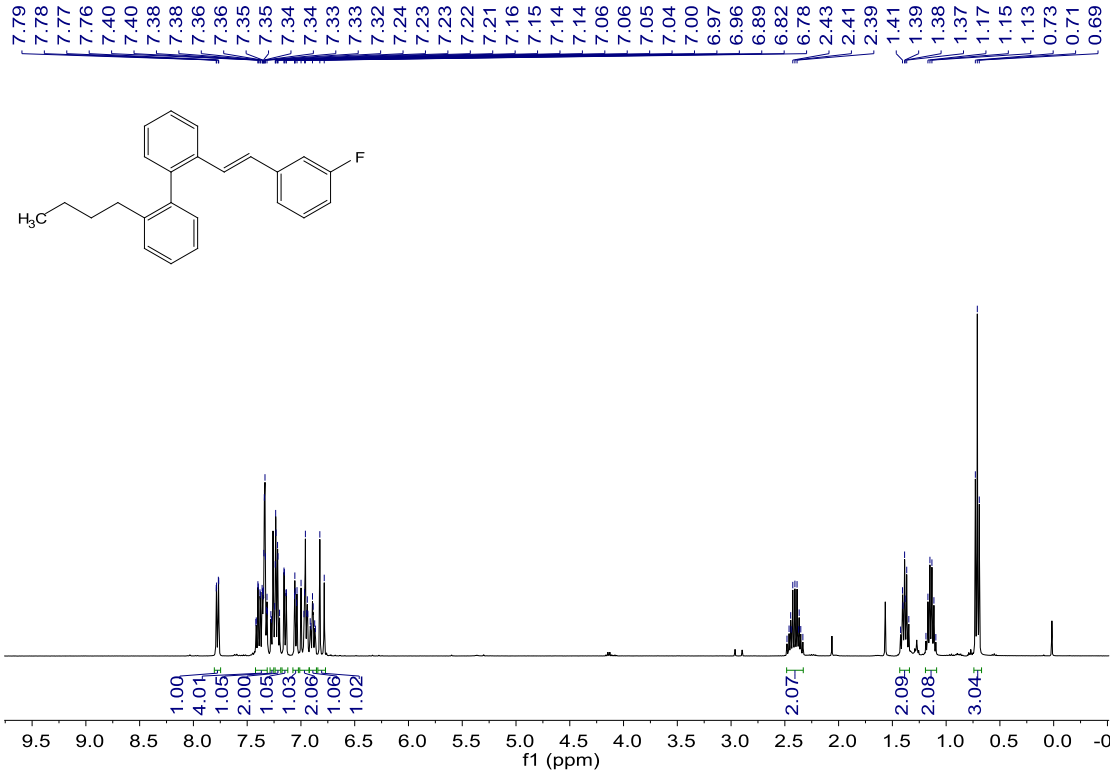


^{13}CNMR



(*E*)-2-butyl-2'-(3-fluorostyryl)-1,1'-biphenyl(4aag)

^{1}HNMR



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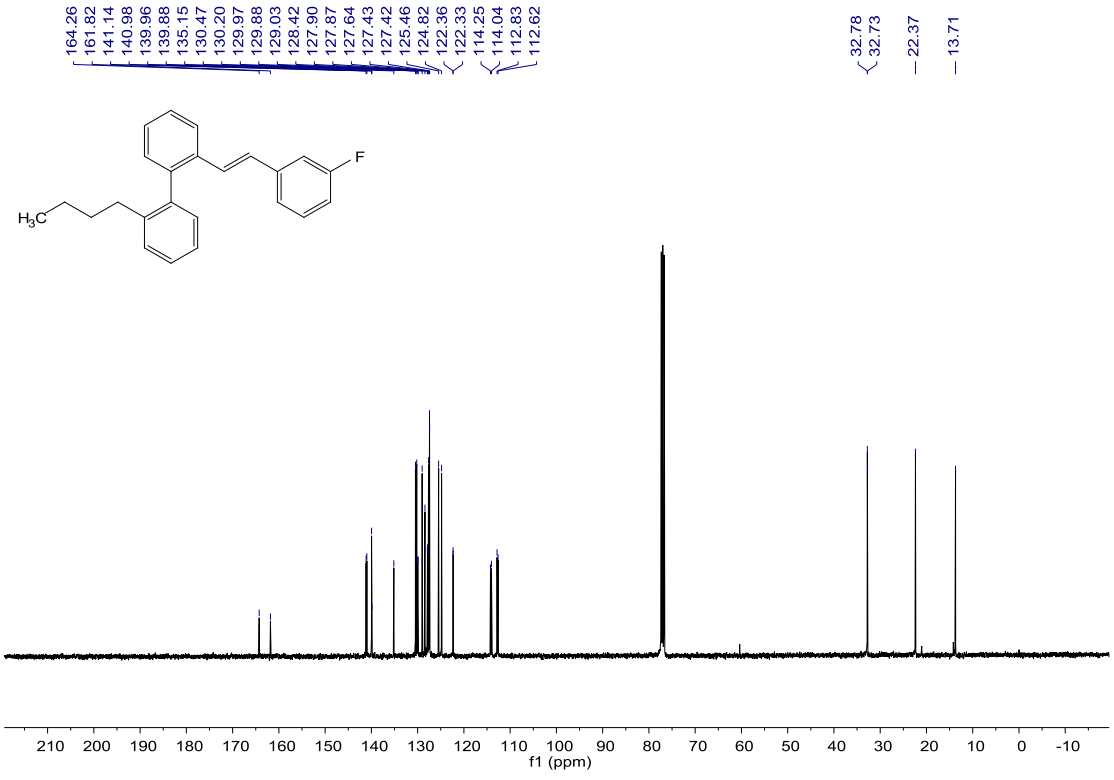
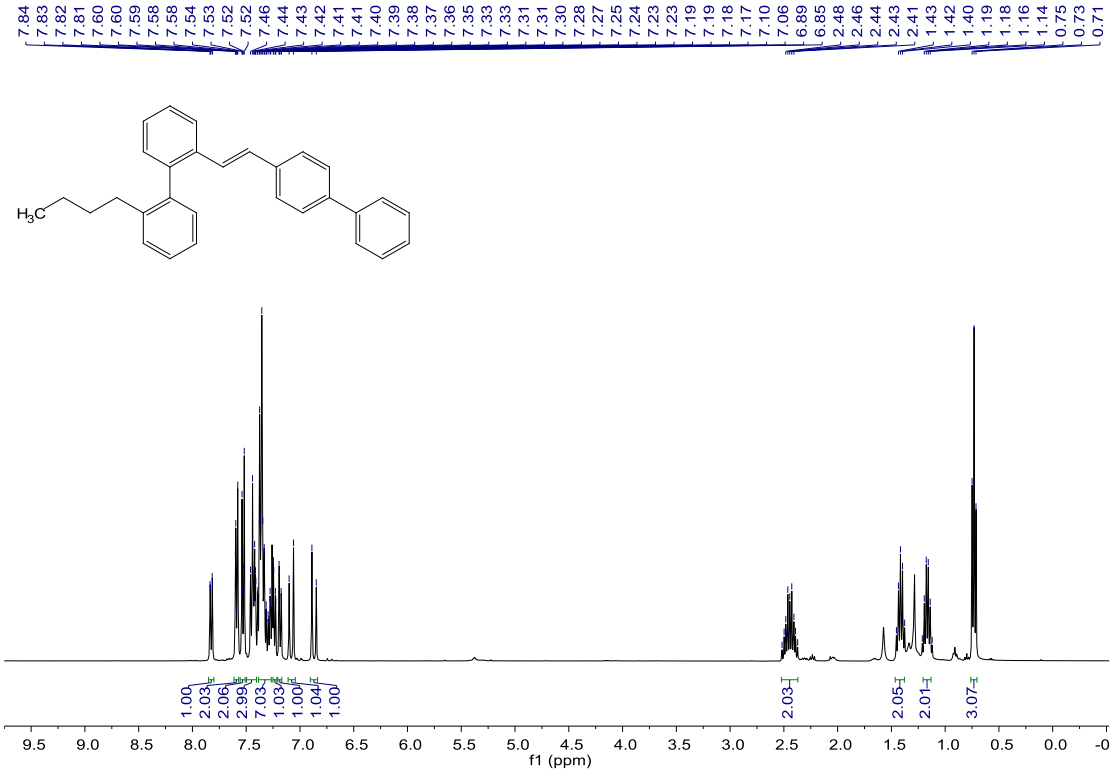


(*E*)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)-2'-butyl-1,1'-biphenyl(4aah)

^{1}HNMR



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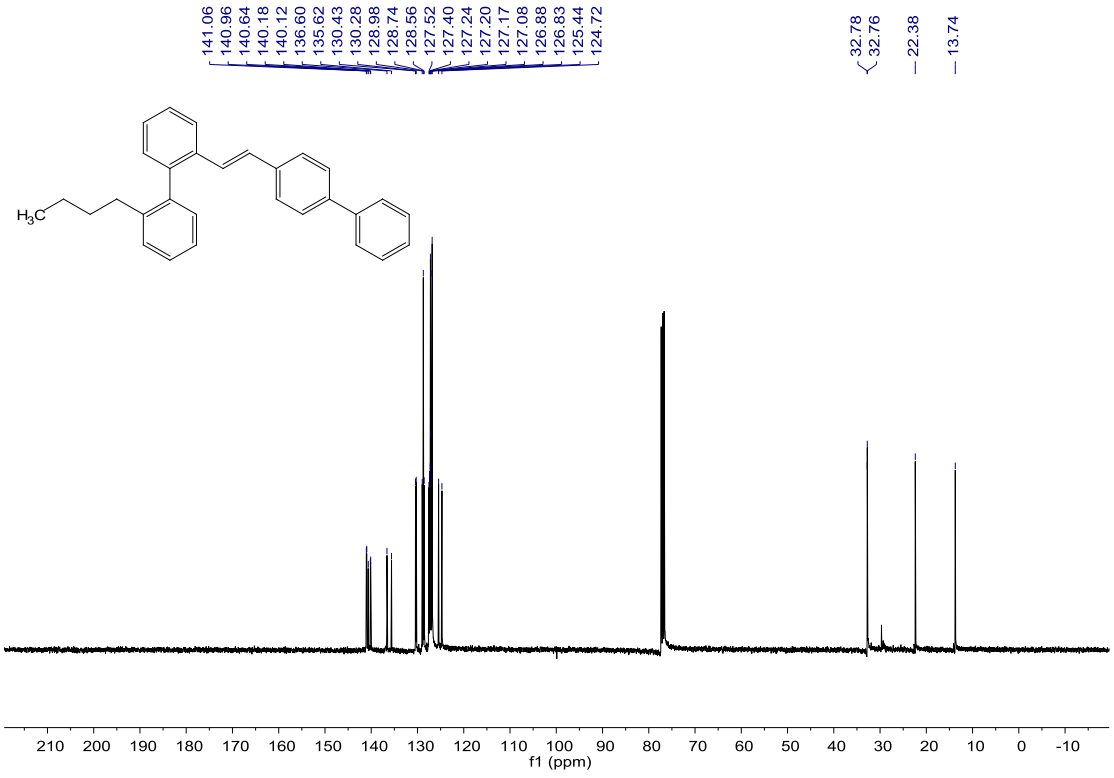
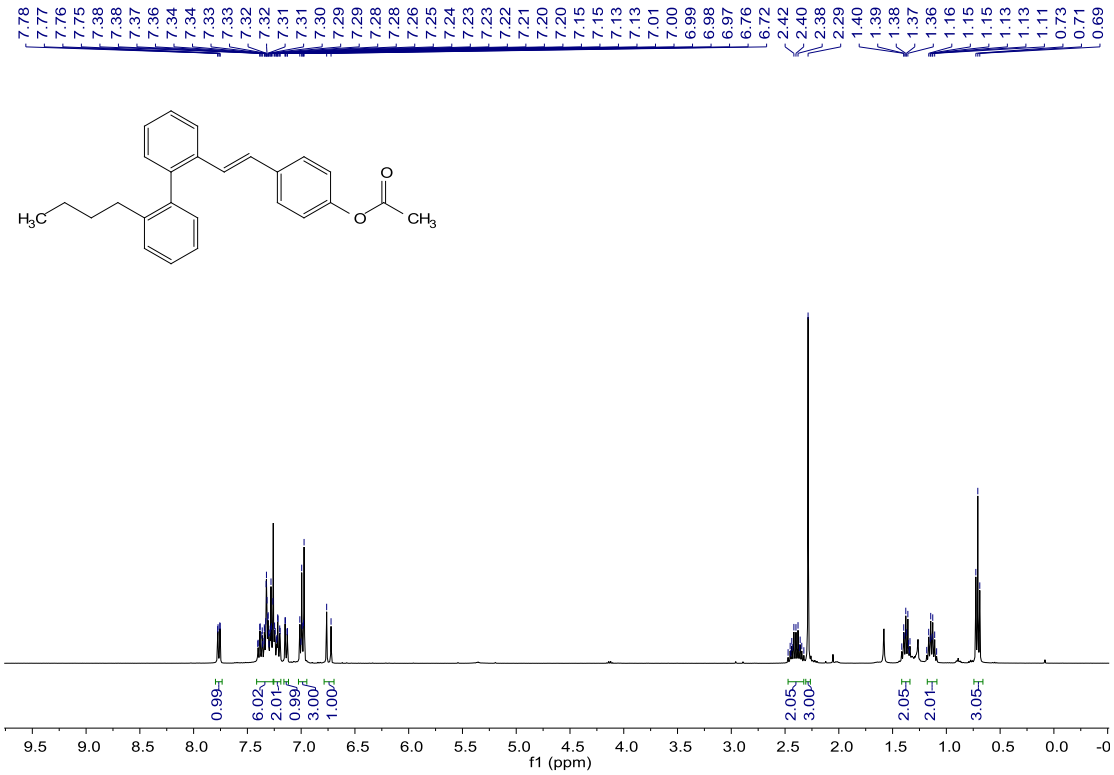


(*E*)-4-(2-(2'-butyl-[1,1'-biphenyl]-2-yl)vinyl)phenyl acetate (4aai)

^{1}HNMR



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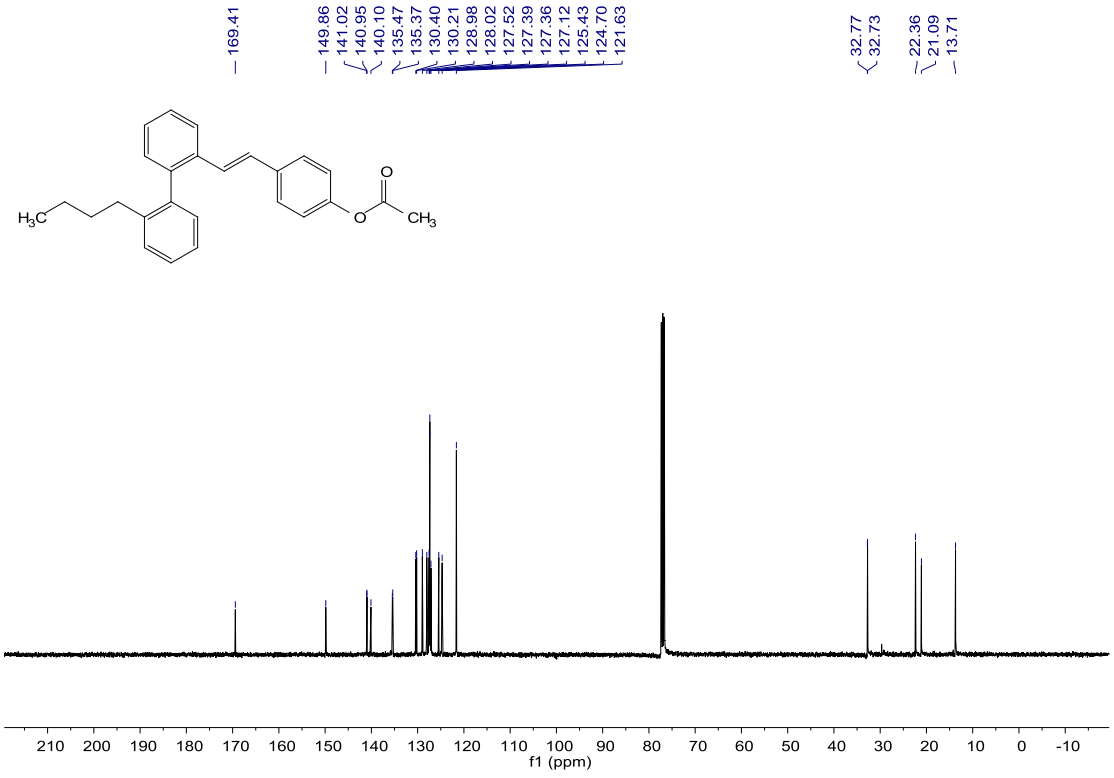
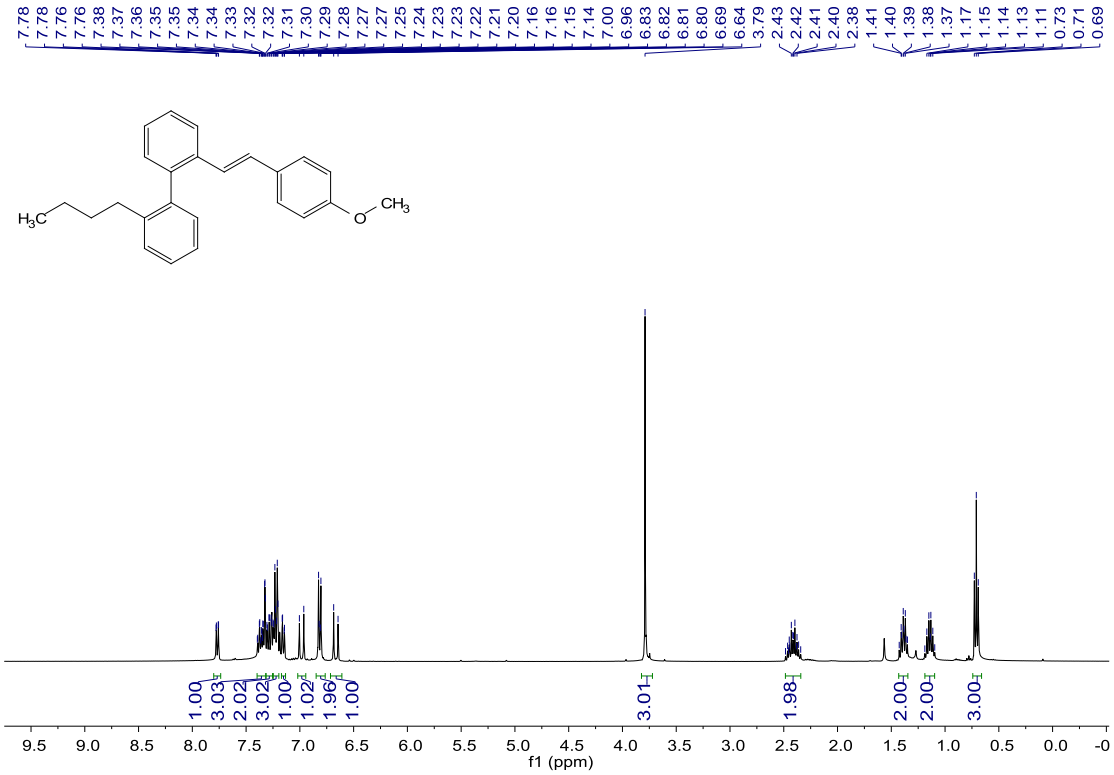


(*E*)-2-butyl-2'-(4-methoxystyryl)-1,1'-biphenyl(4aaj)

^{1}HNMR



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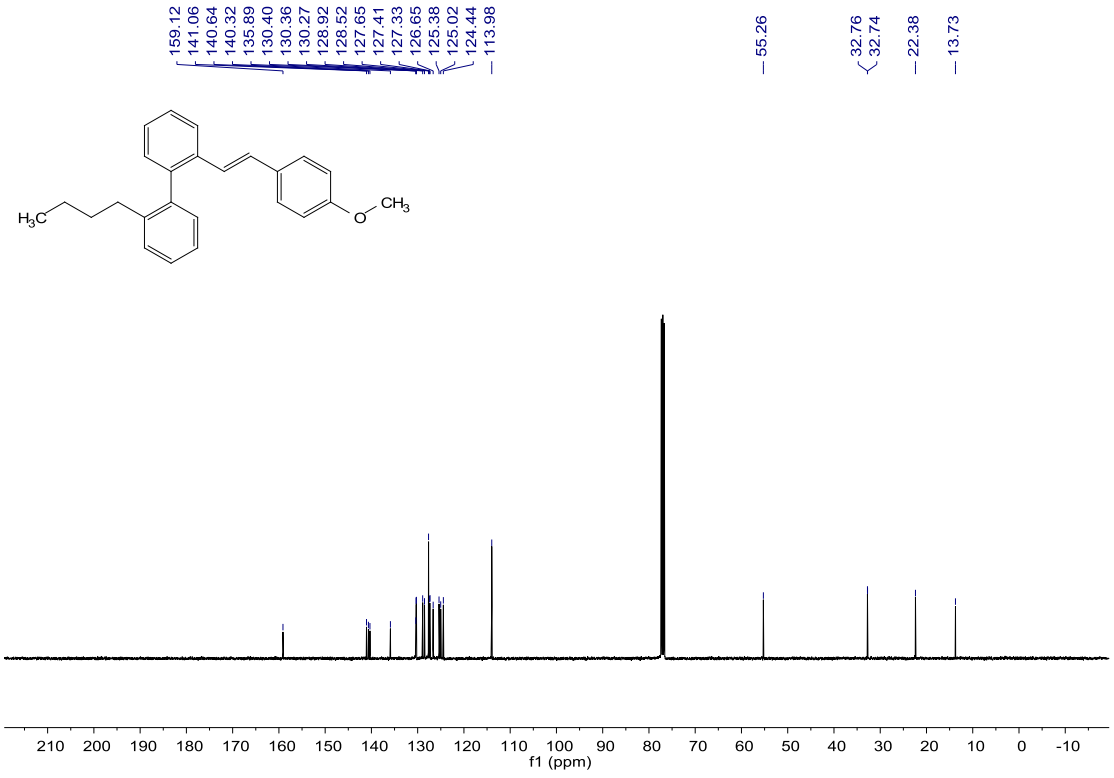
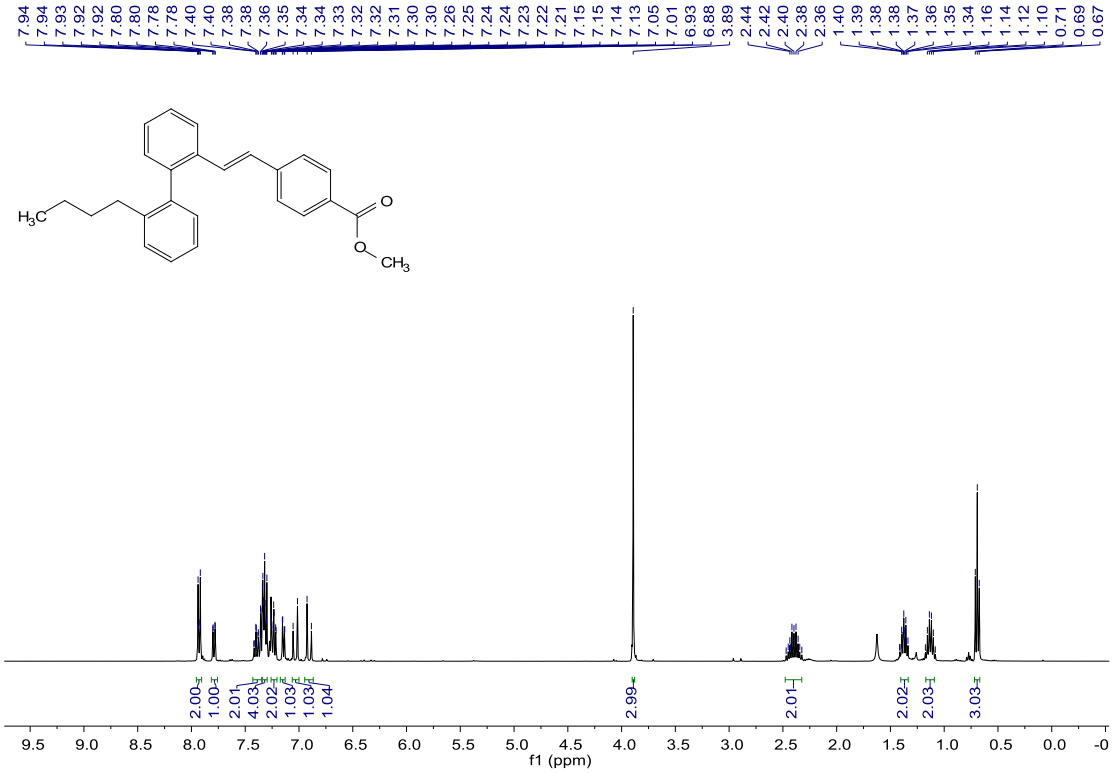


Methyl (*E*)-4-(2-(2'-butyl-[1,1'-biphenyl]-2-yl)vinyl)benzoate(4aak)

^{1}HNMR



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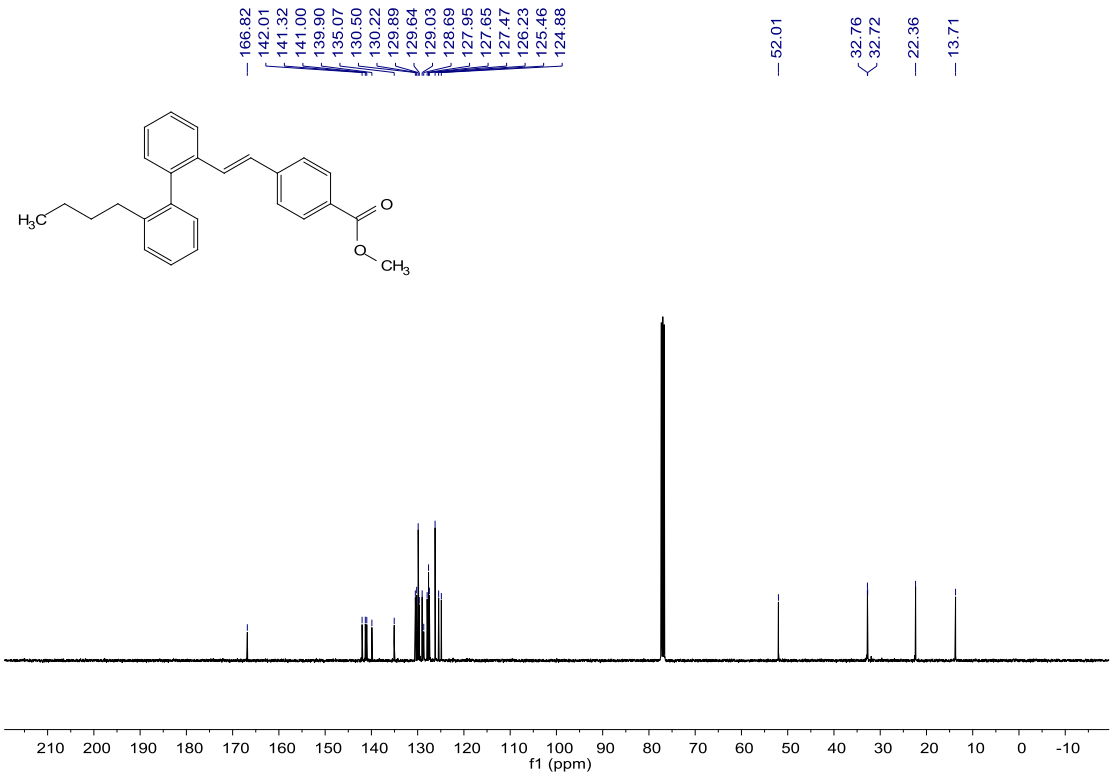
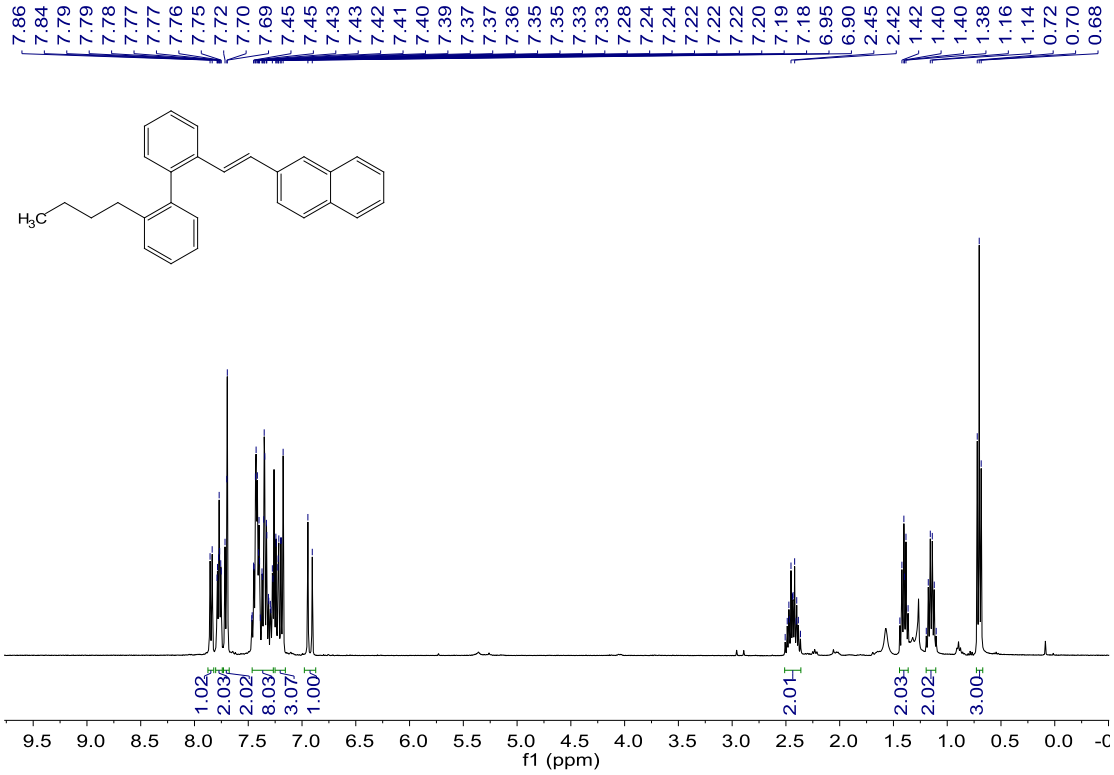
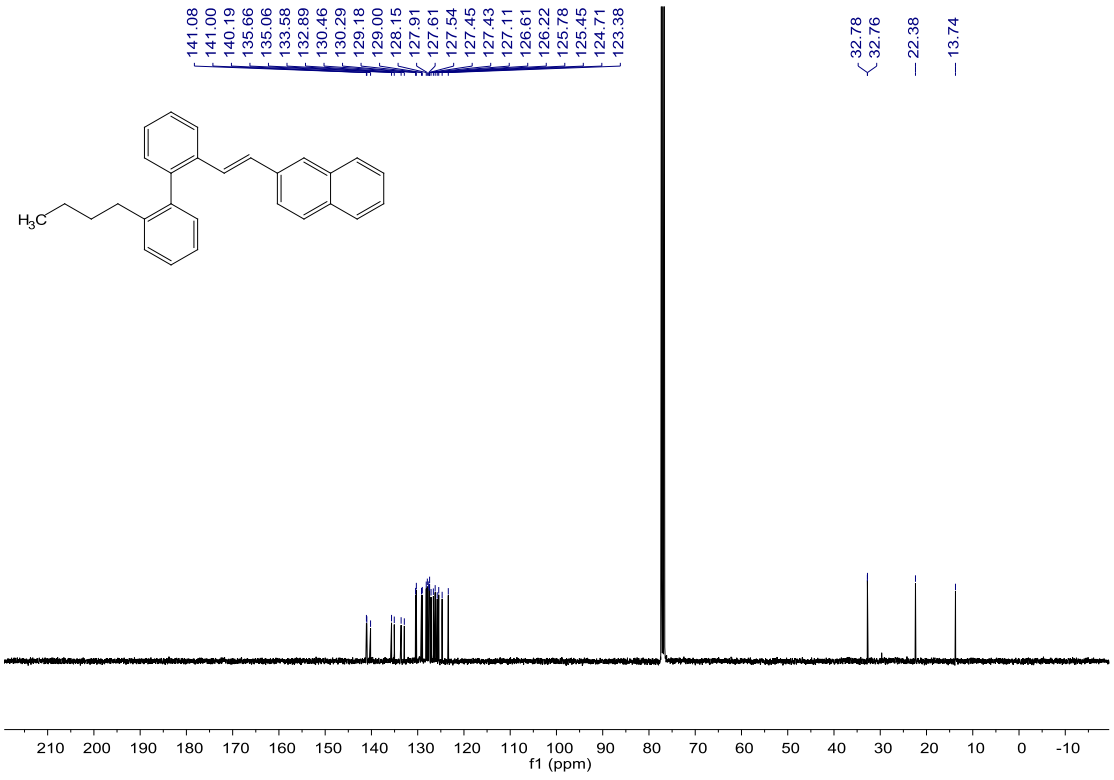


(*E*)-2-(2-(2'-butyl-[1,1'-biphenyl]-2-yl)vinyl)naphthalene(4aal)

^{1}HNMR

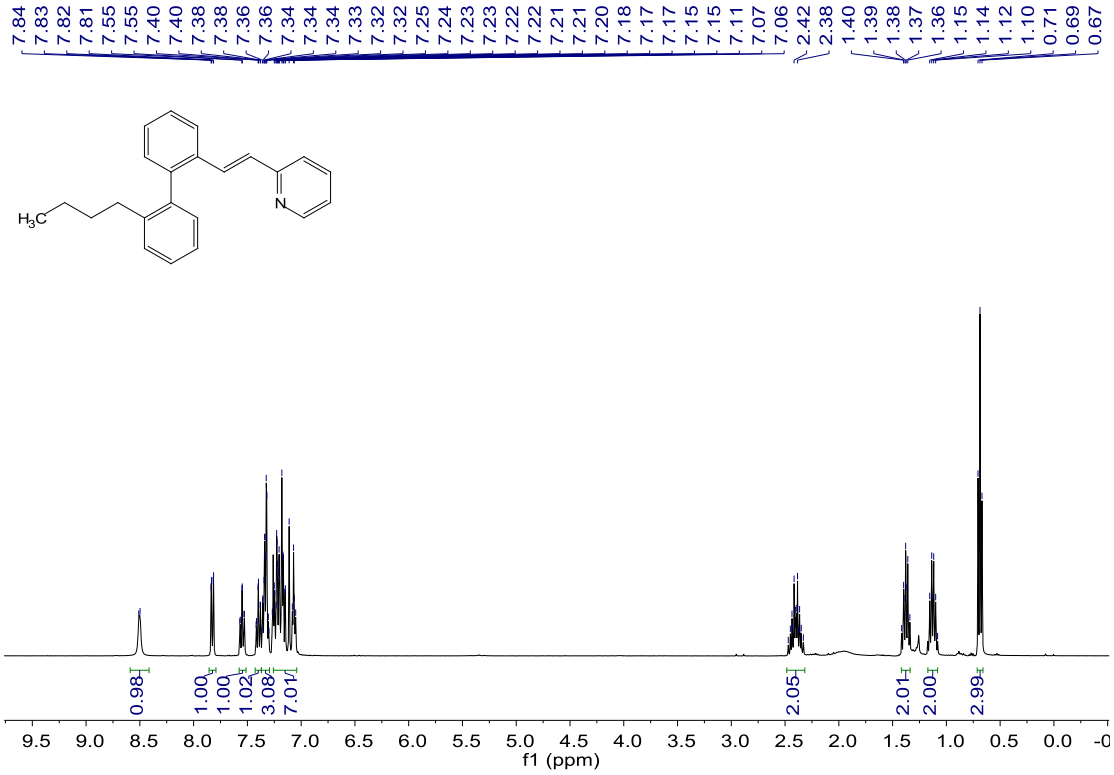


^{13}CNMR



(*E*)-2-(2-(2'-butyl-[1,1'-biphenyl]-2-yl)vinyl)pyridine(4aam)

^{1}HNMR



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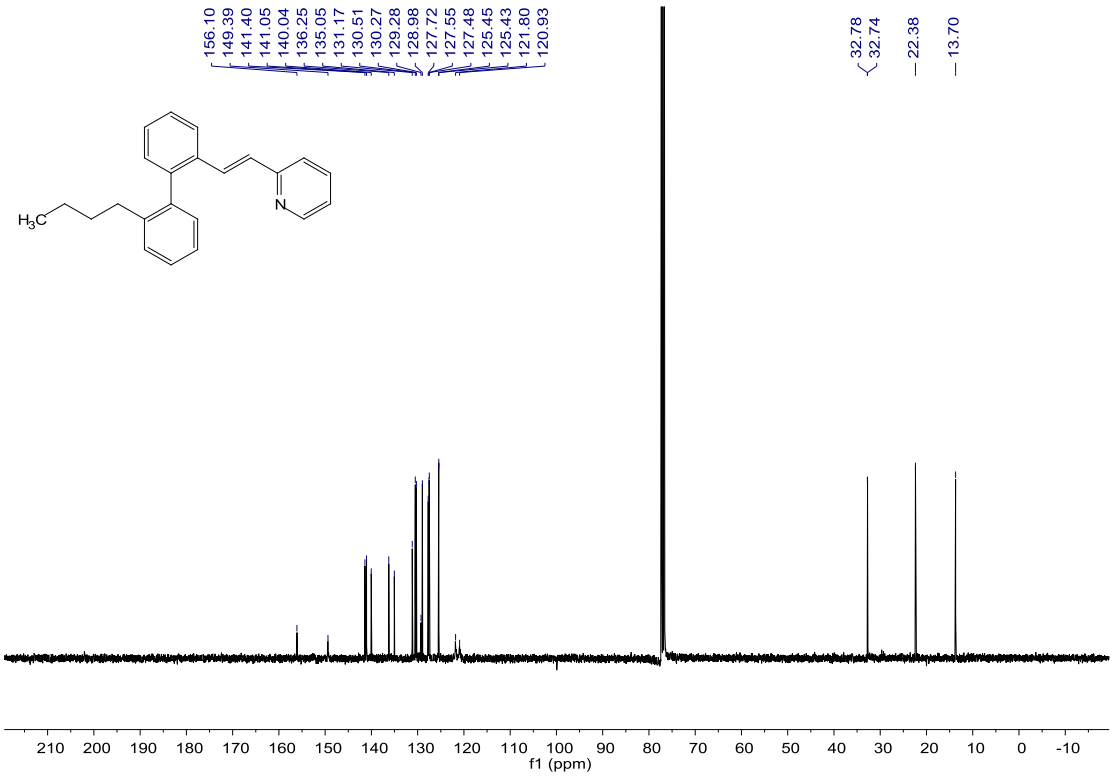
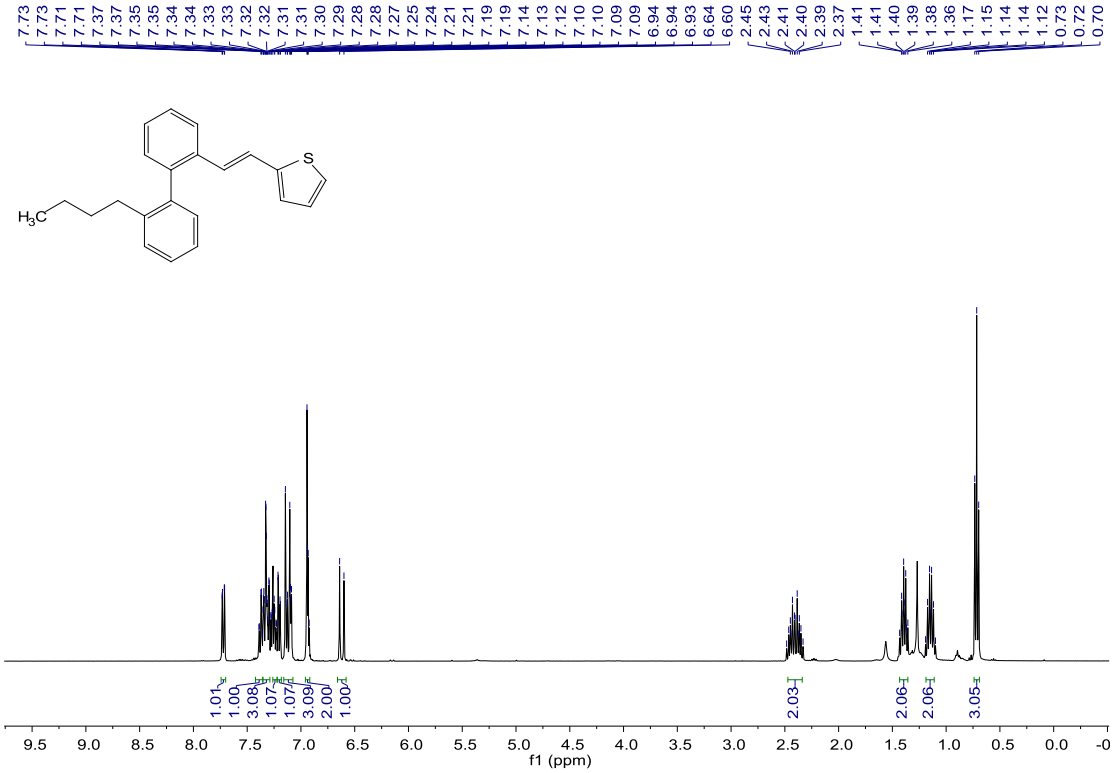


(*E*)-2-(2-(2'-butyl-[1,1'-biphenyl]-2-yl)vinyl)thiophene(4aan)

^{1}HNMR



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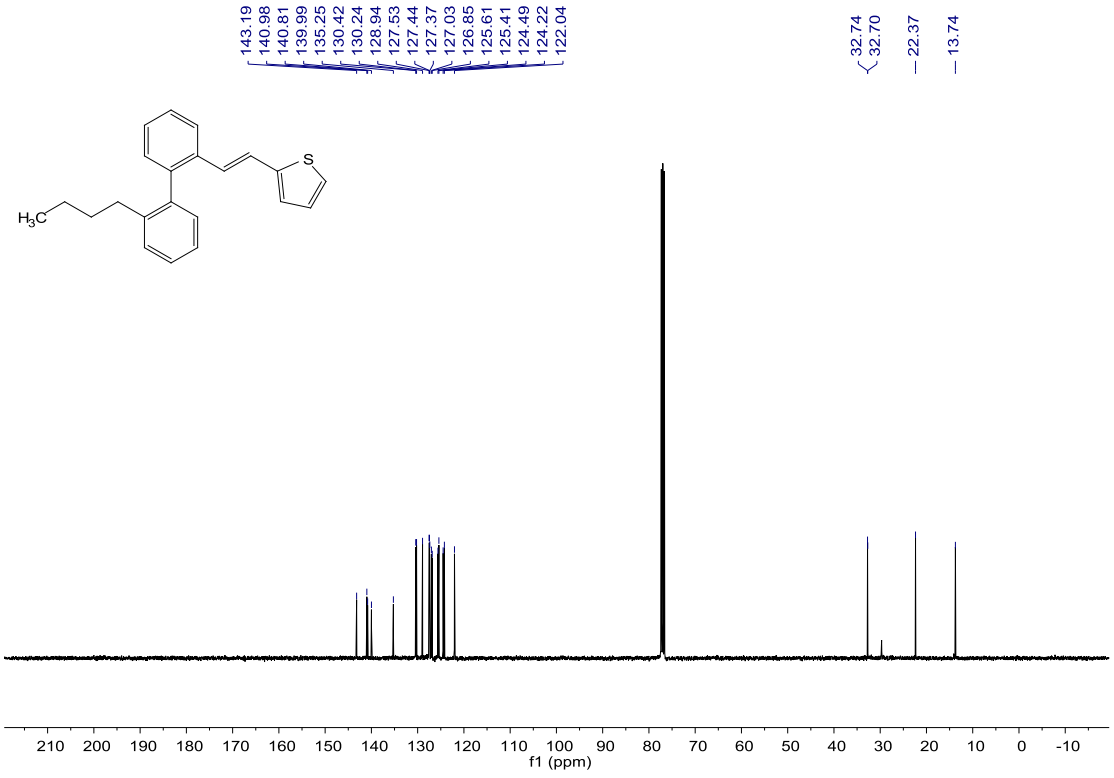
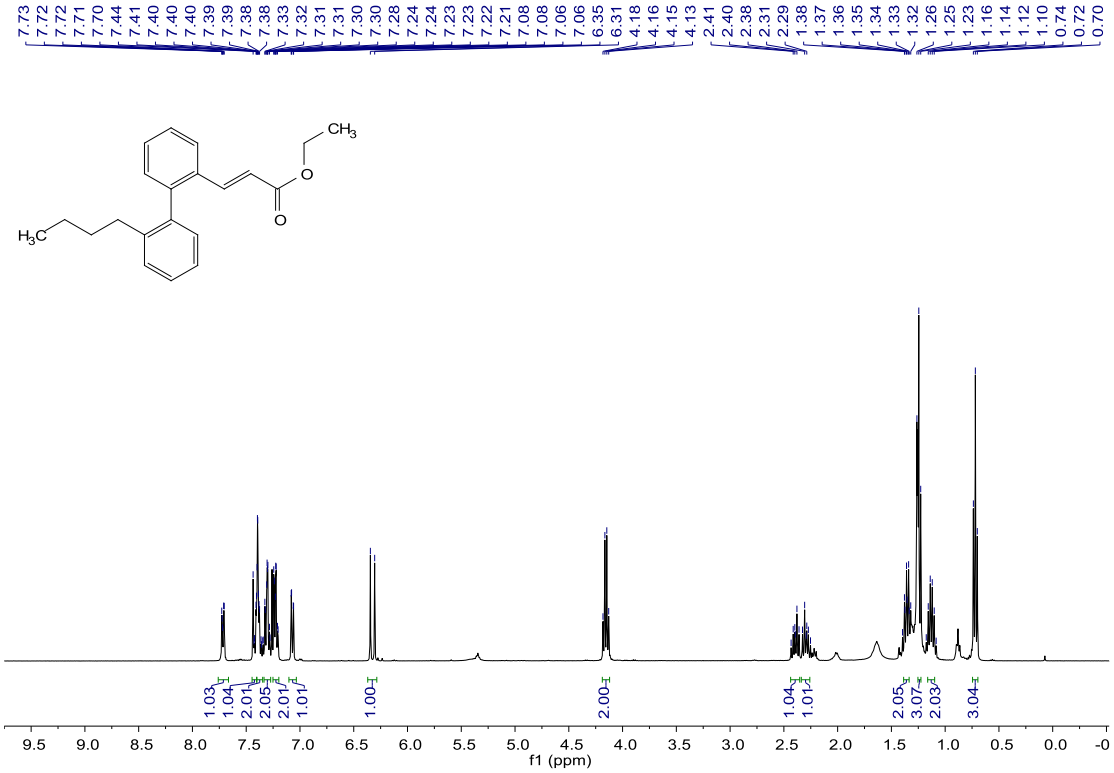


Ethyl (*E*)-3-(2'-butyl-[1,1'-biphenyl]-2-yl)acrylate(4aao)

^{1}HNMR



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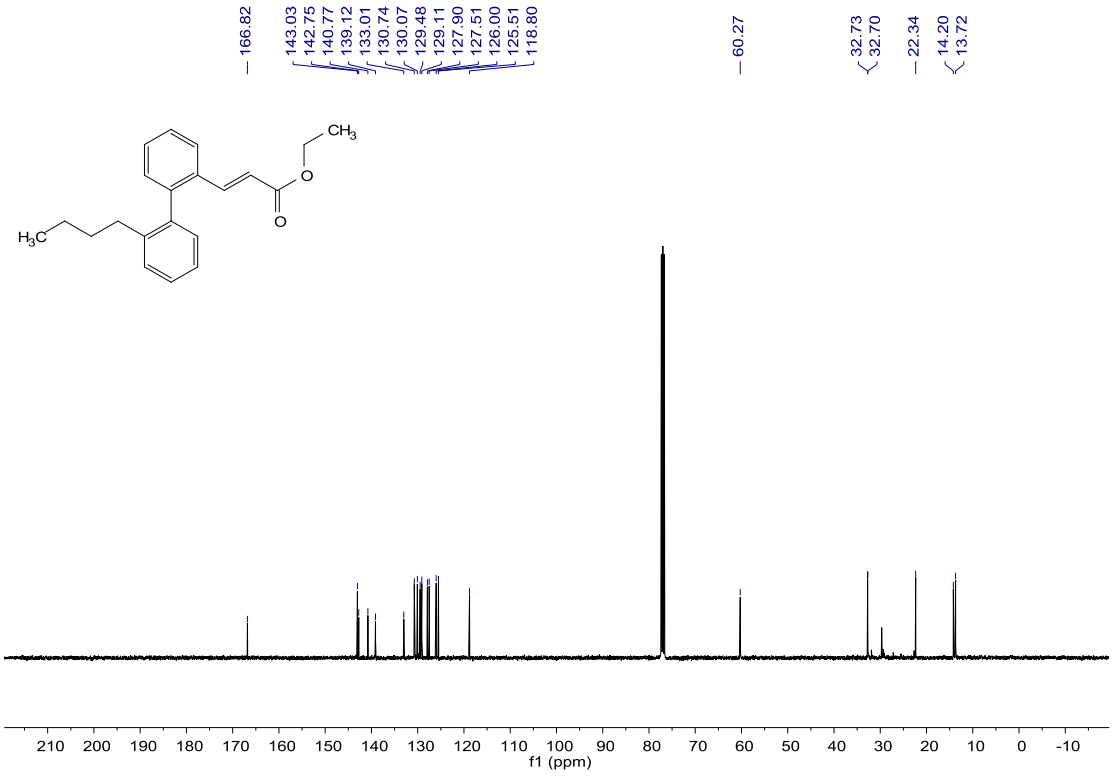
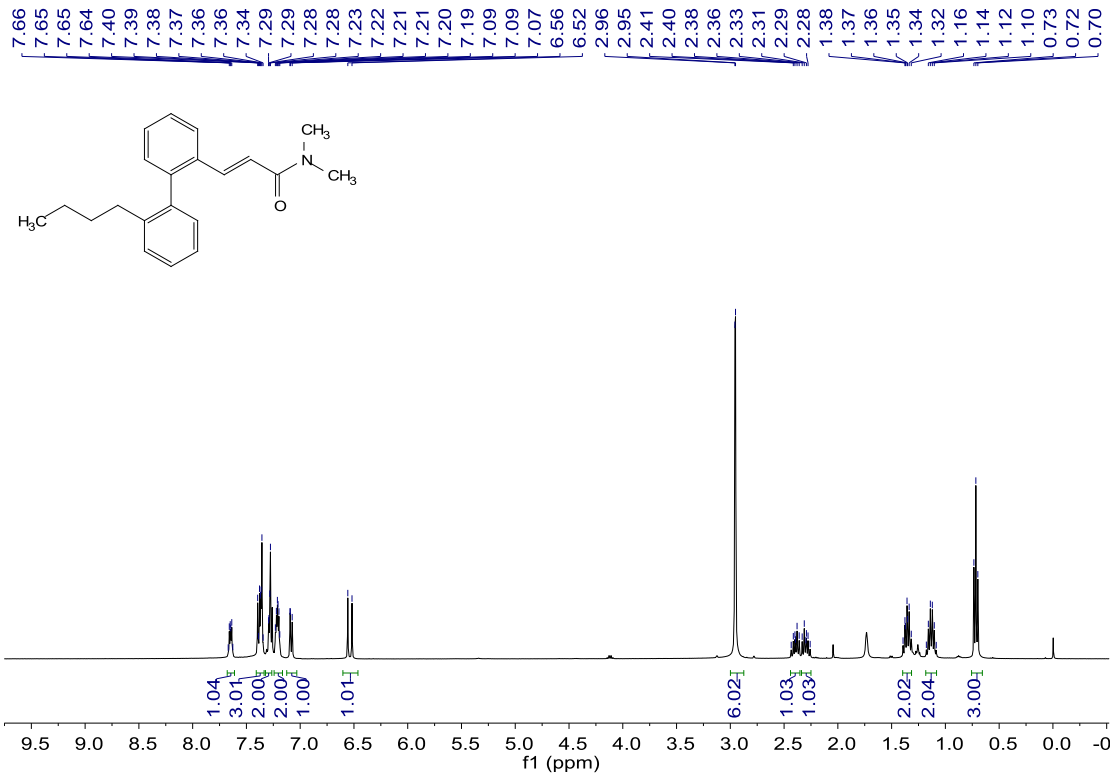


(*E*)-3-(2'-butyl-[1,1'-biphenyl]-2-yl)-N,N-dimethylacrylamide(4aap)

^{1}HNMR



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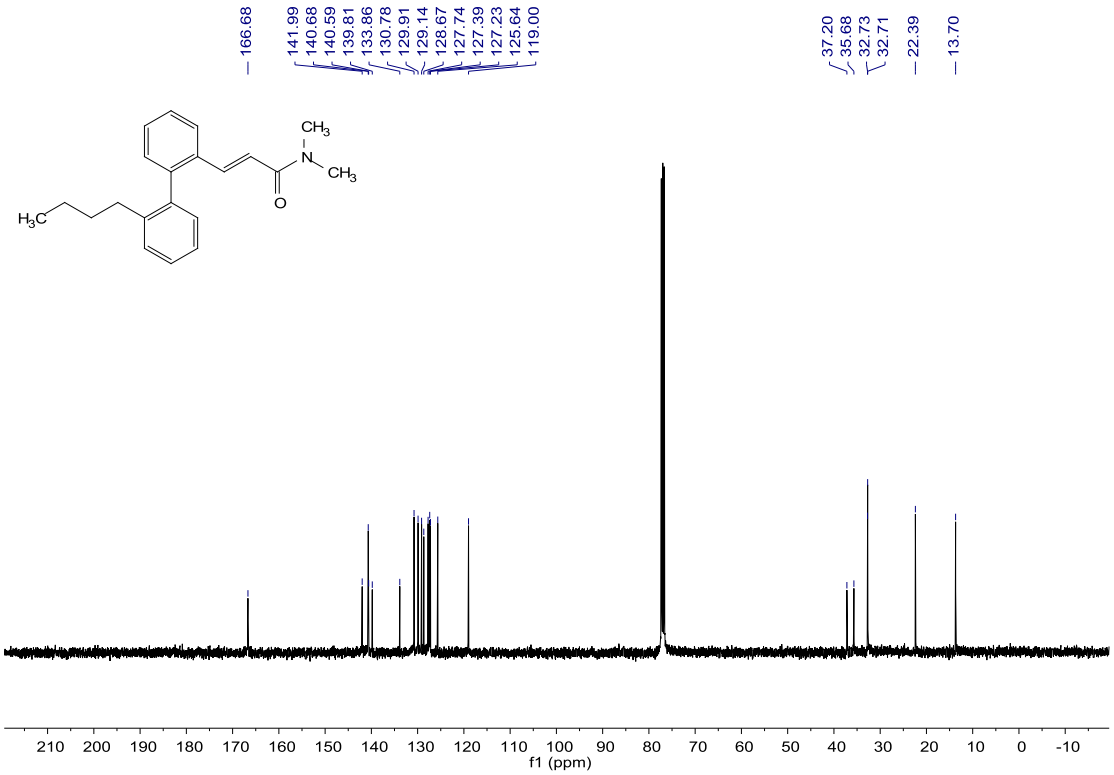
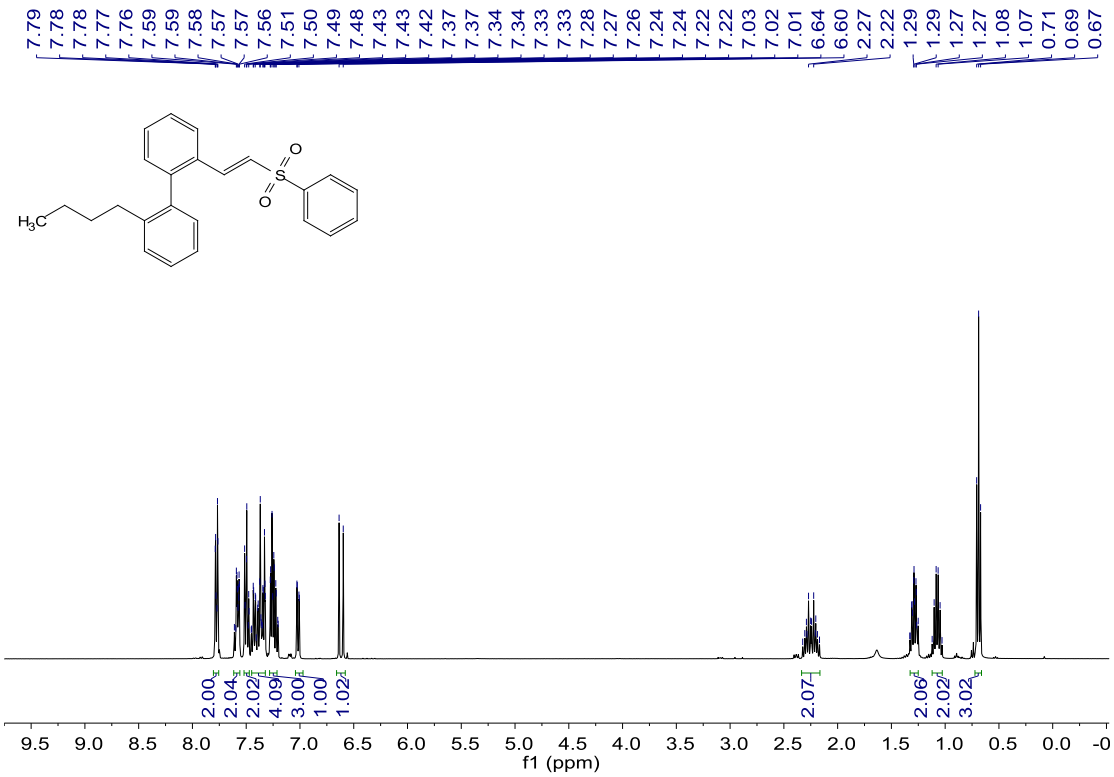


(*E*)-2-butyl-2'-(2-(phenylsulfonyl)vinyl)-1,1'-biphenyl(4aaq)

^{1}HNMR



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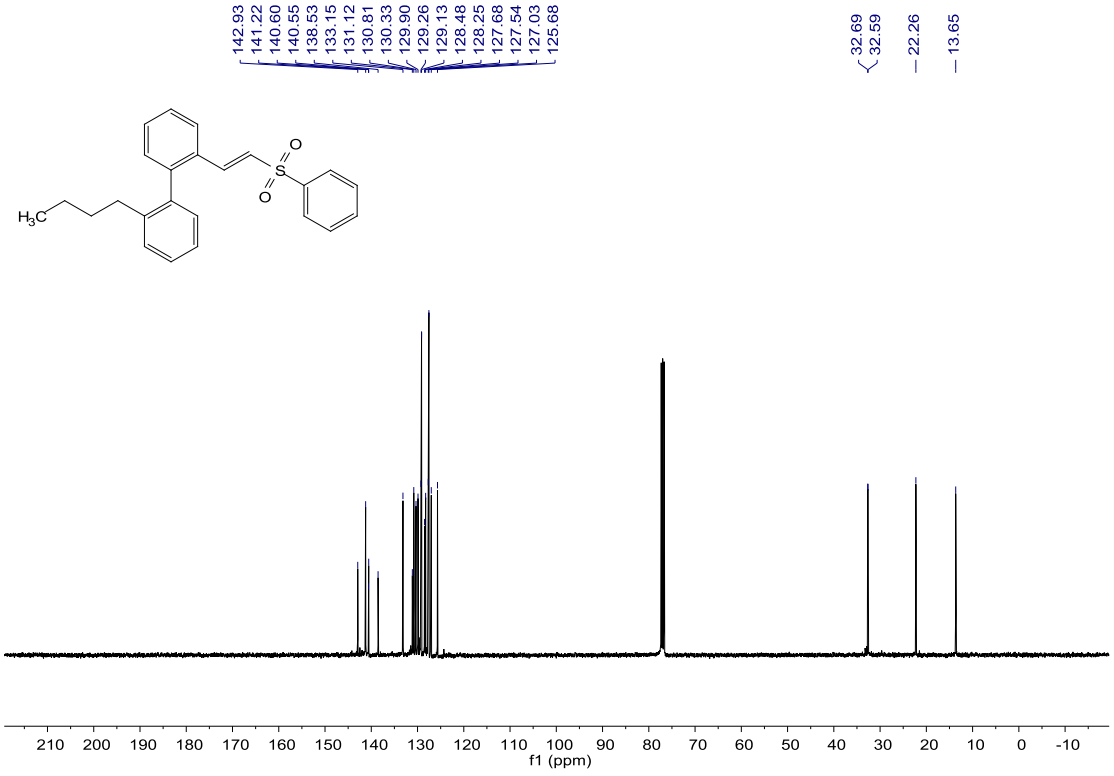
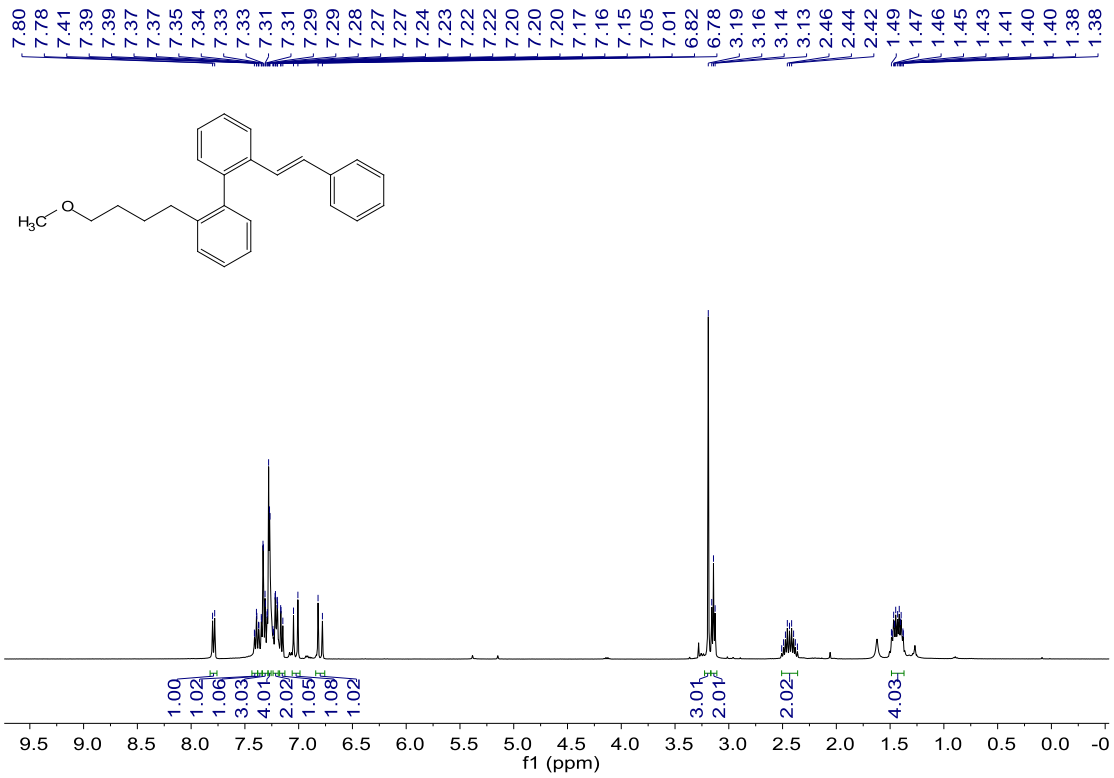


(*E*)-2-(4-methoxybutyl)-2'-styryl-1,1'-biphenyl(4aba)

^{1}HNMR



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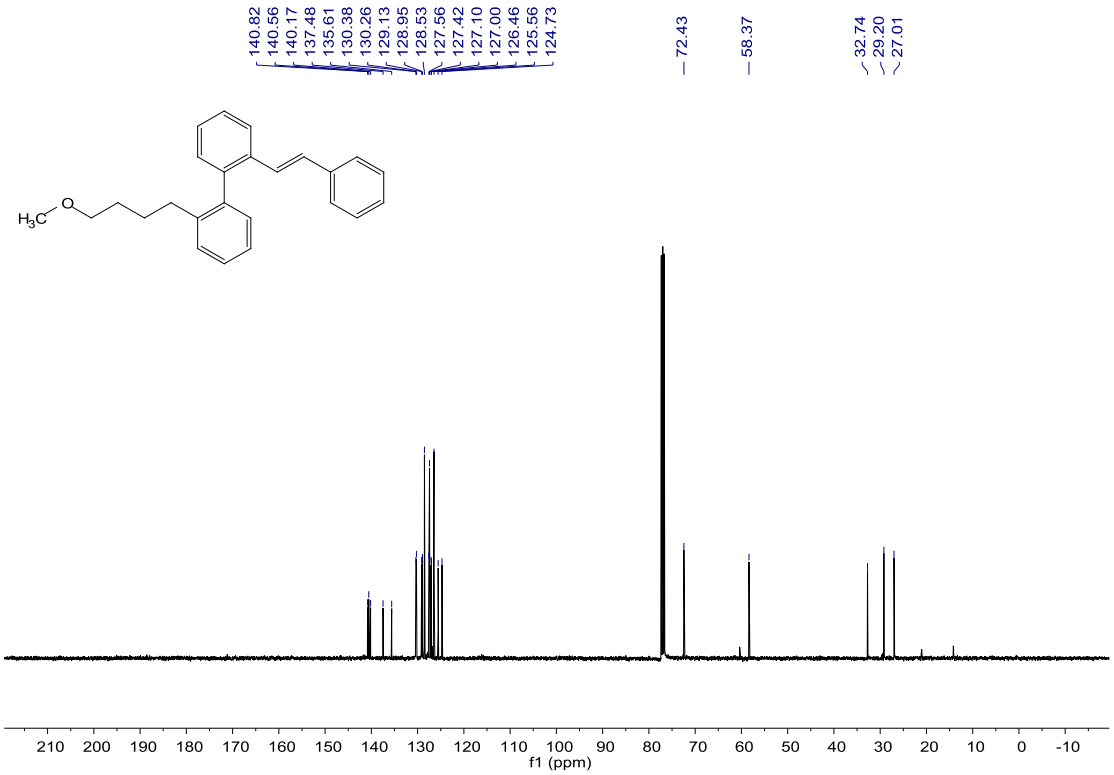
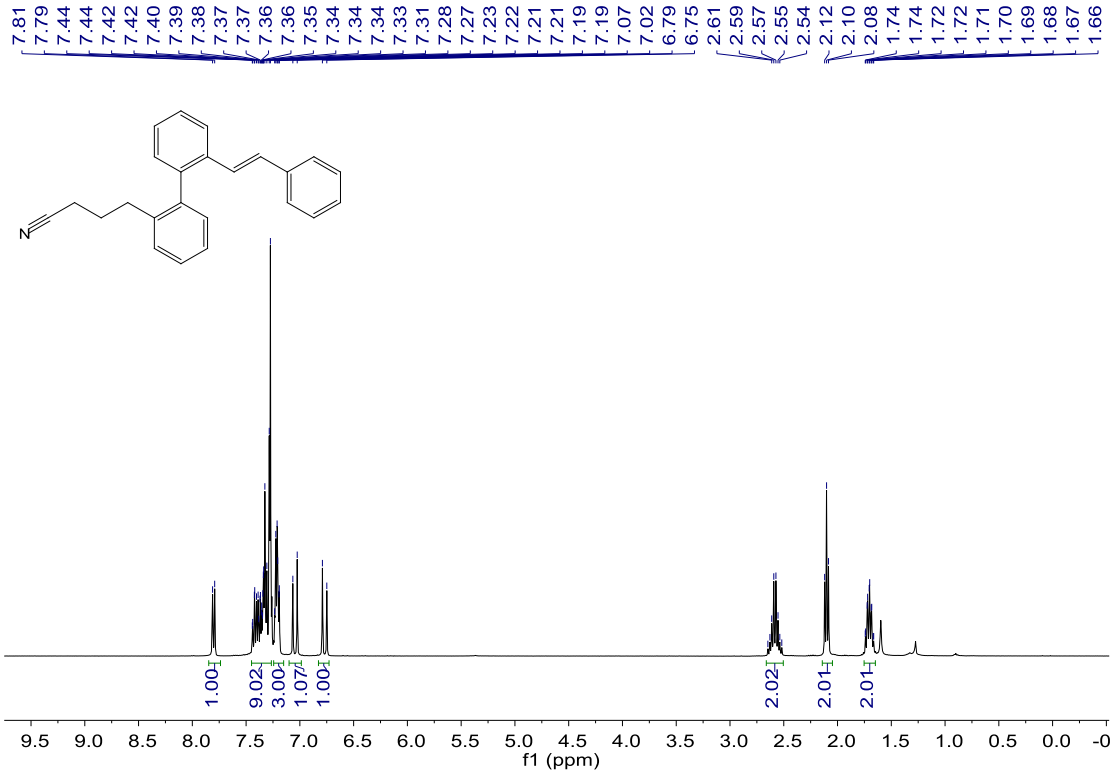


(*E*)-4-(2'-styryl-[1,1'-biphenyl]-2-yl)butanenitrile(4aca)

^{1}HNMR



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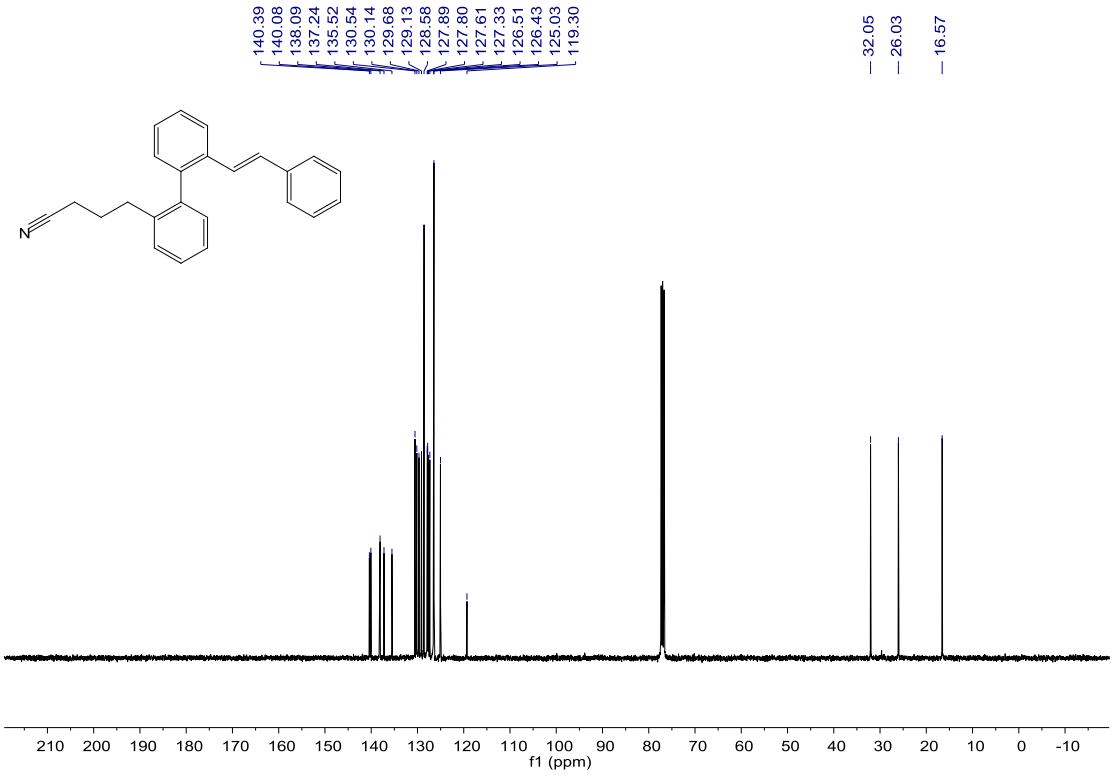
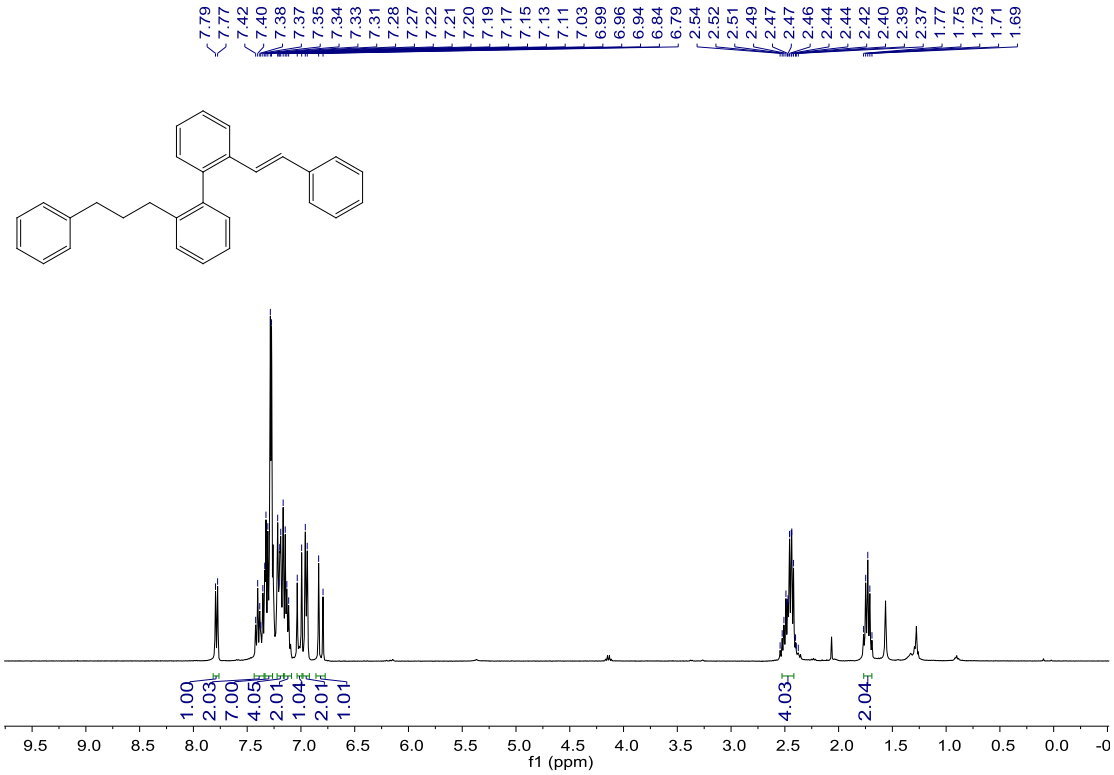


(*E*)-2-(3-phenylpropyl)-2'-styryl-1,1'-biphenyl(4ada)

^{1}HNMR



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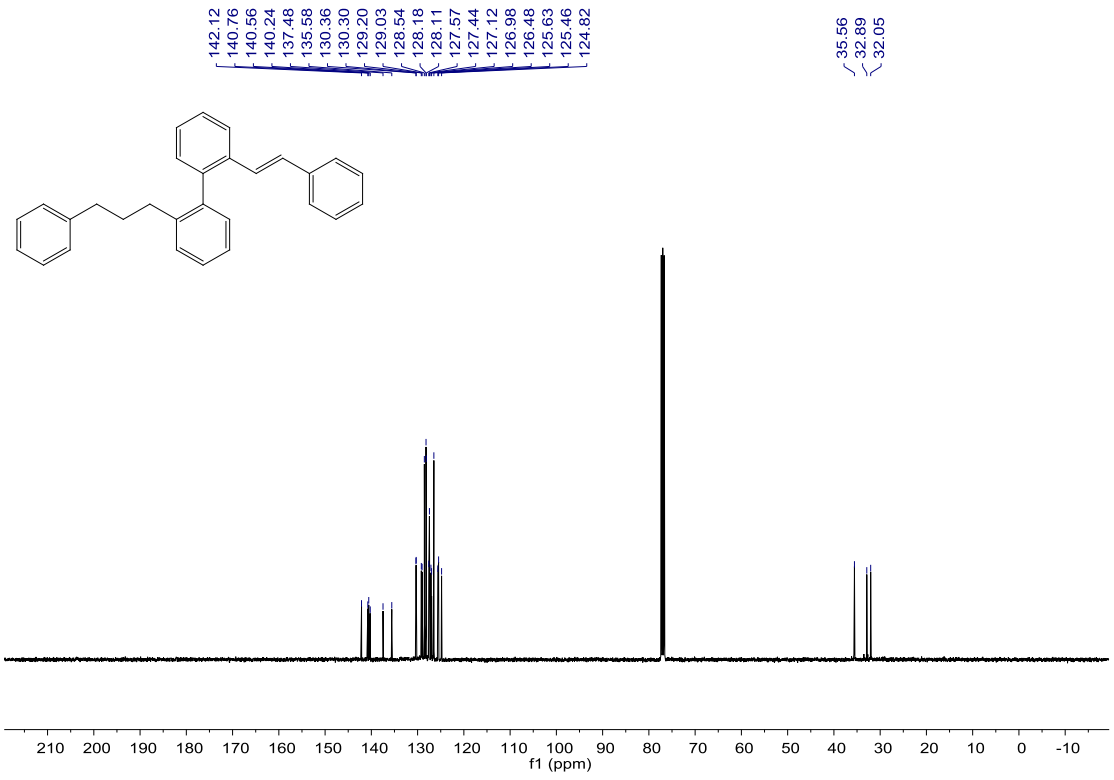
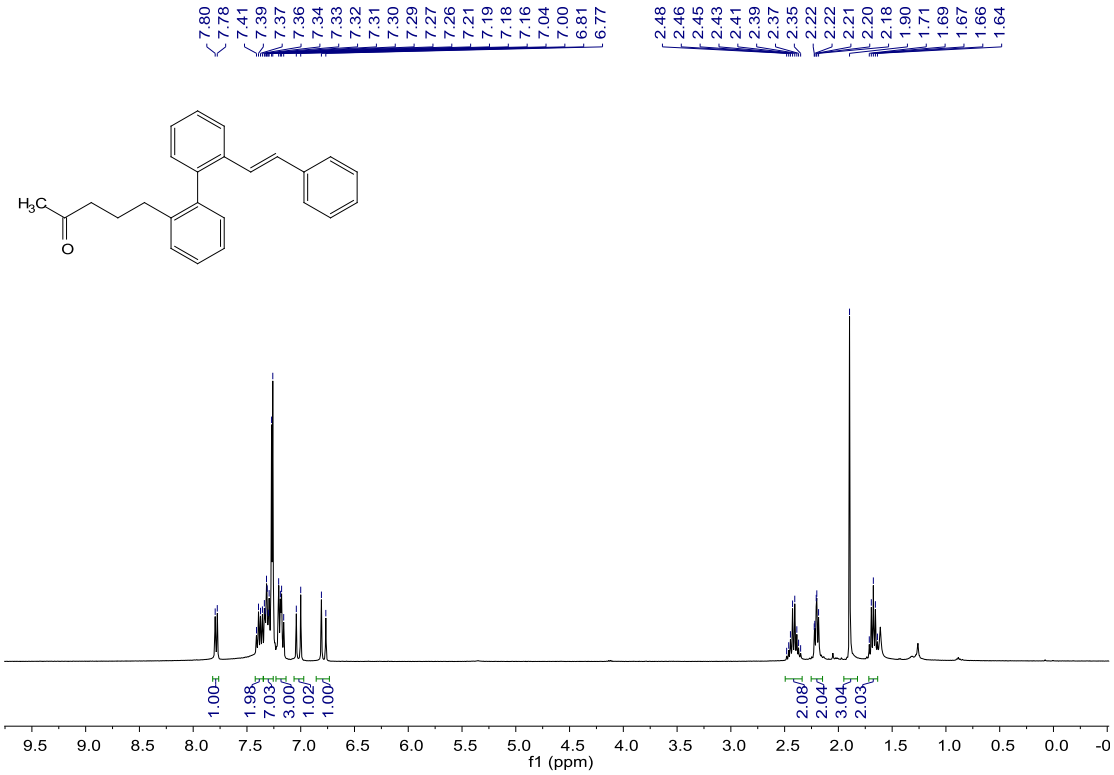


(*E*)-5-(2'-styryl-[1,1'-biphenyl]-2-yl)pentan-2-one(4aea)

^{1}HNMR



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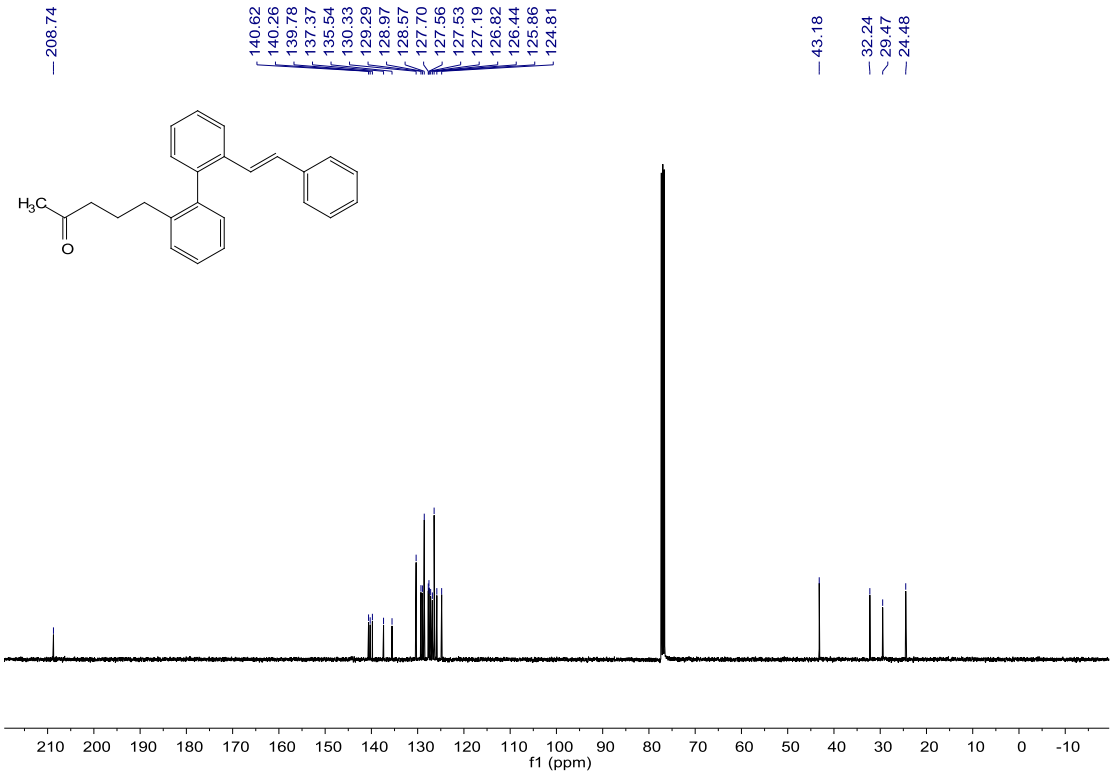
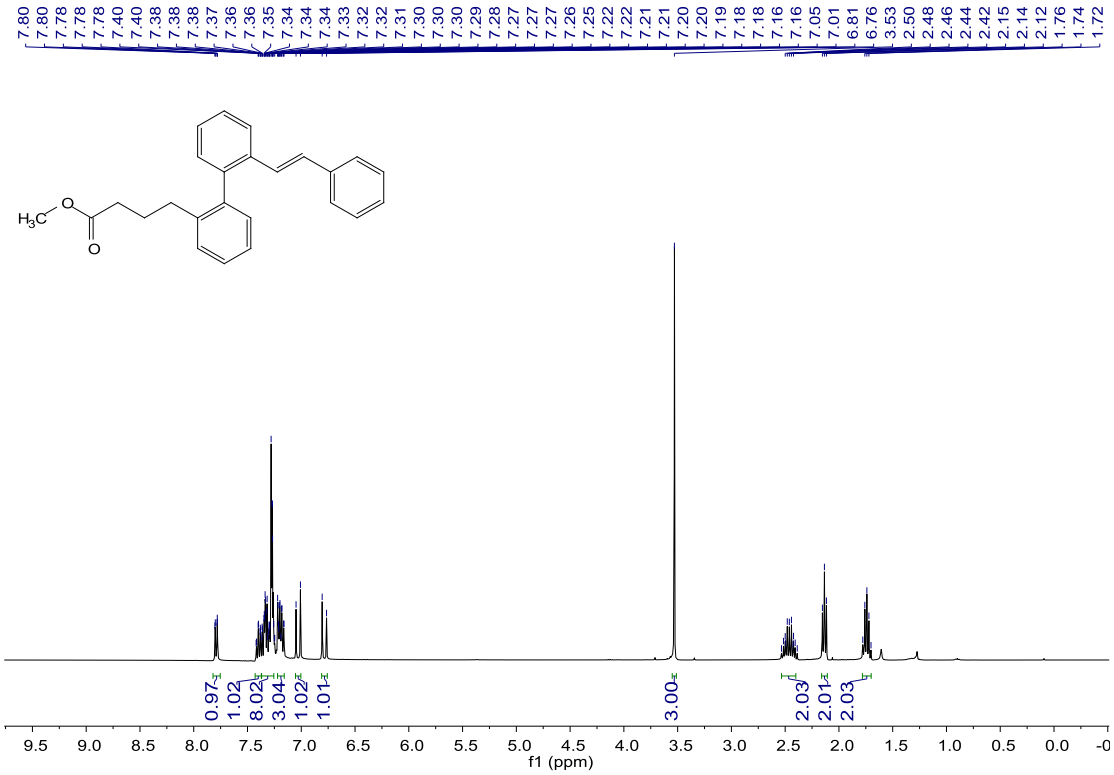


Methyl (*E*)-4-(2'-styryl-[1,1'-biphenyl]-2-yl)butanoate(4afa)

^{1}HNMR



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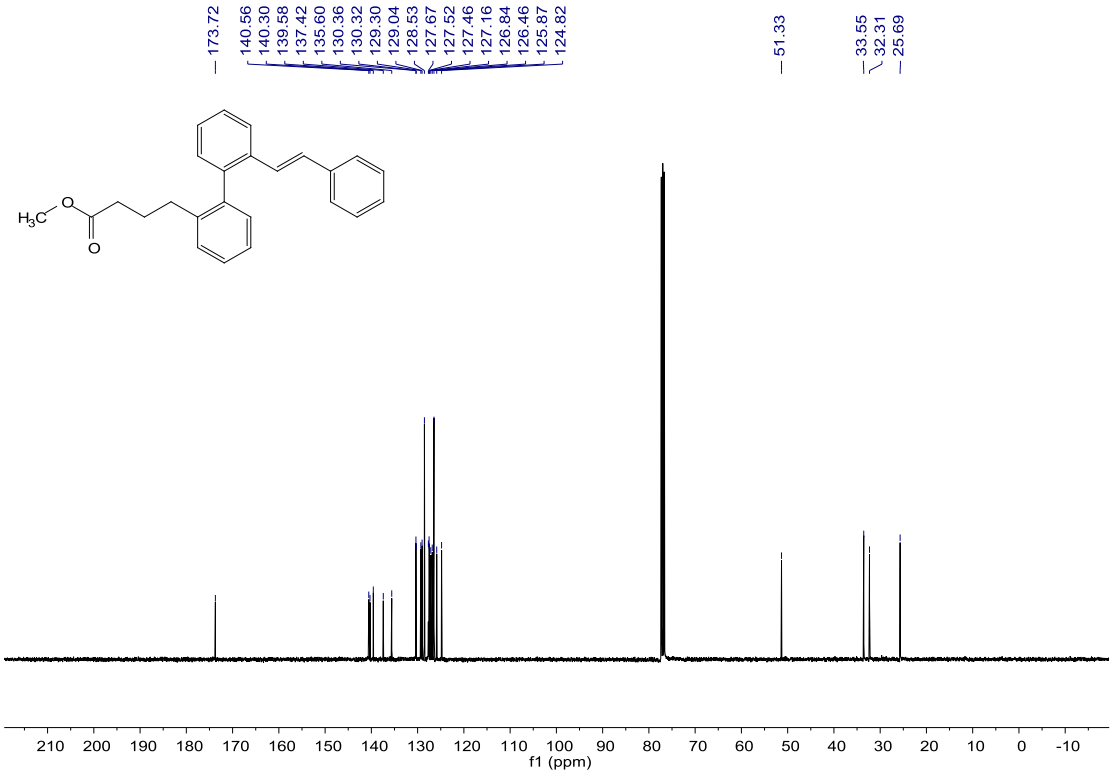
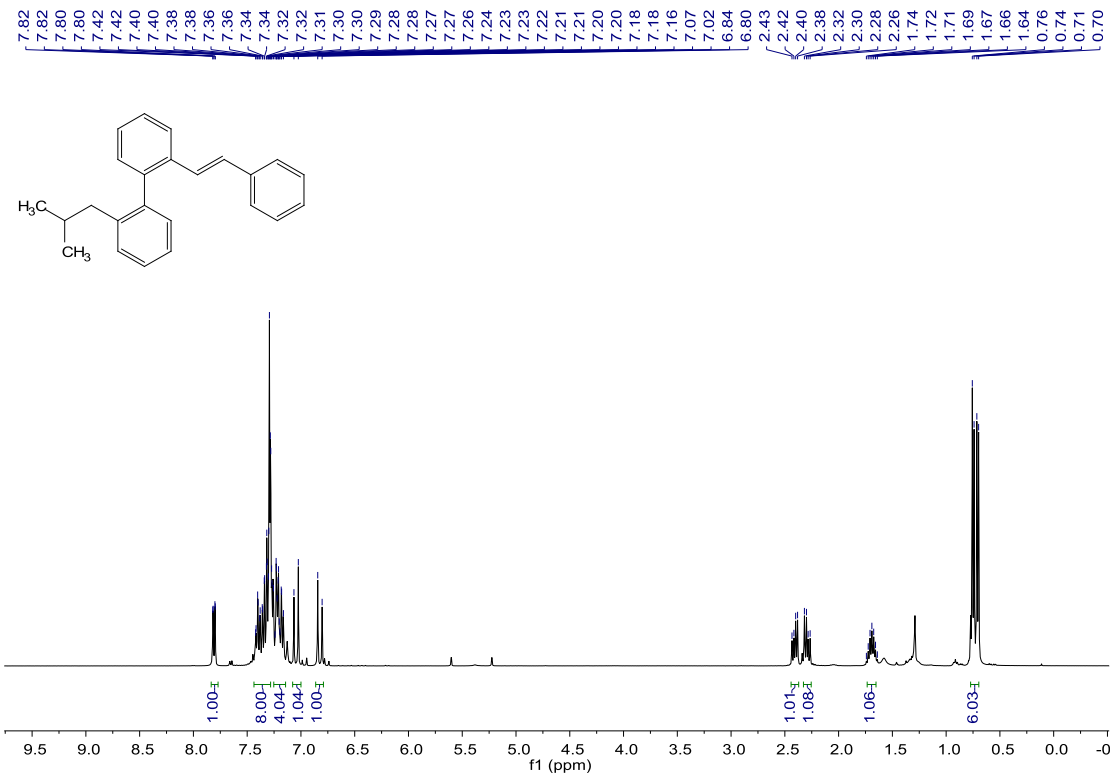


(*E*)-2-isobutyl-2'-styryl-1,1'-biphenyl(4aga)

^{1}HNMR



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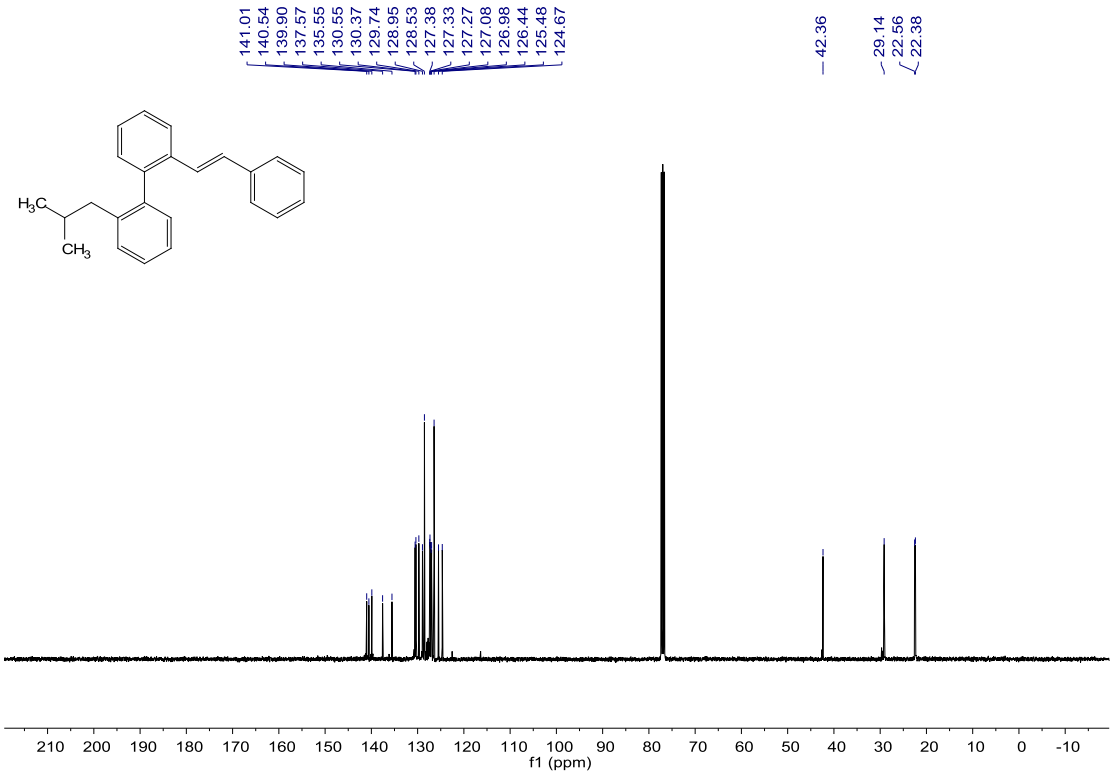
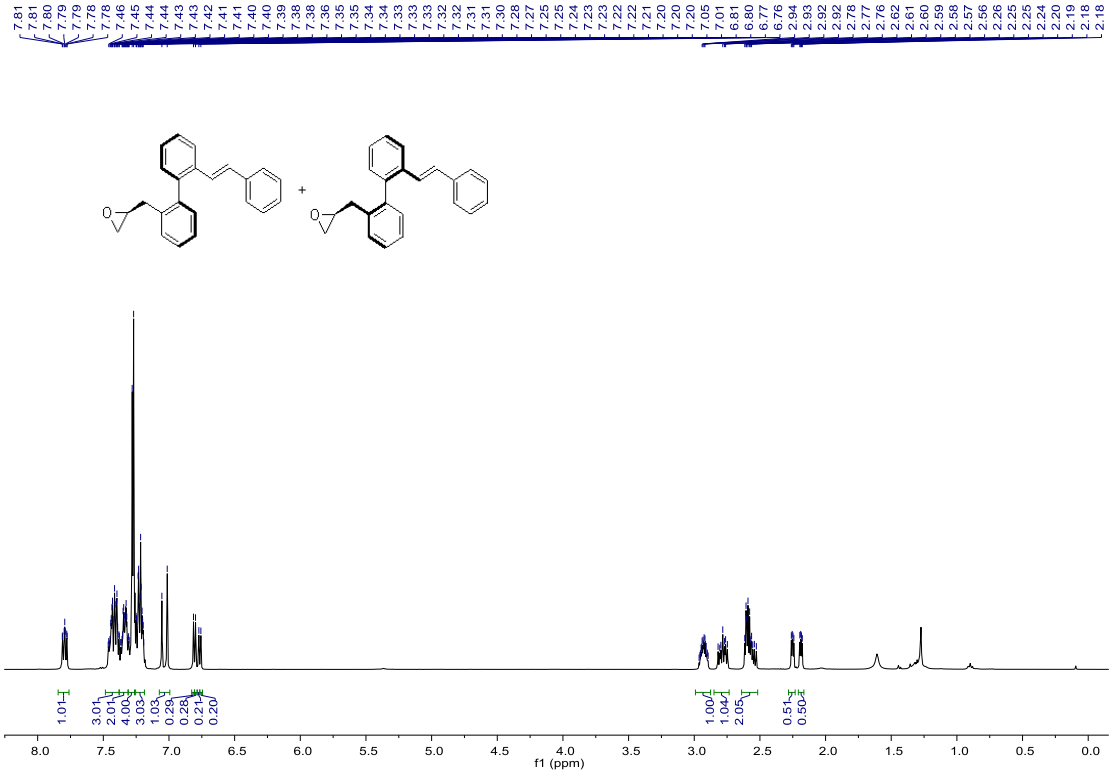


(*S*,*E*)-2-((2'-styryl-[1,1'-biphenyl]-2-yl)methyl)oxirane(4aha)

^{1}HNMR



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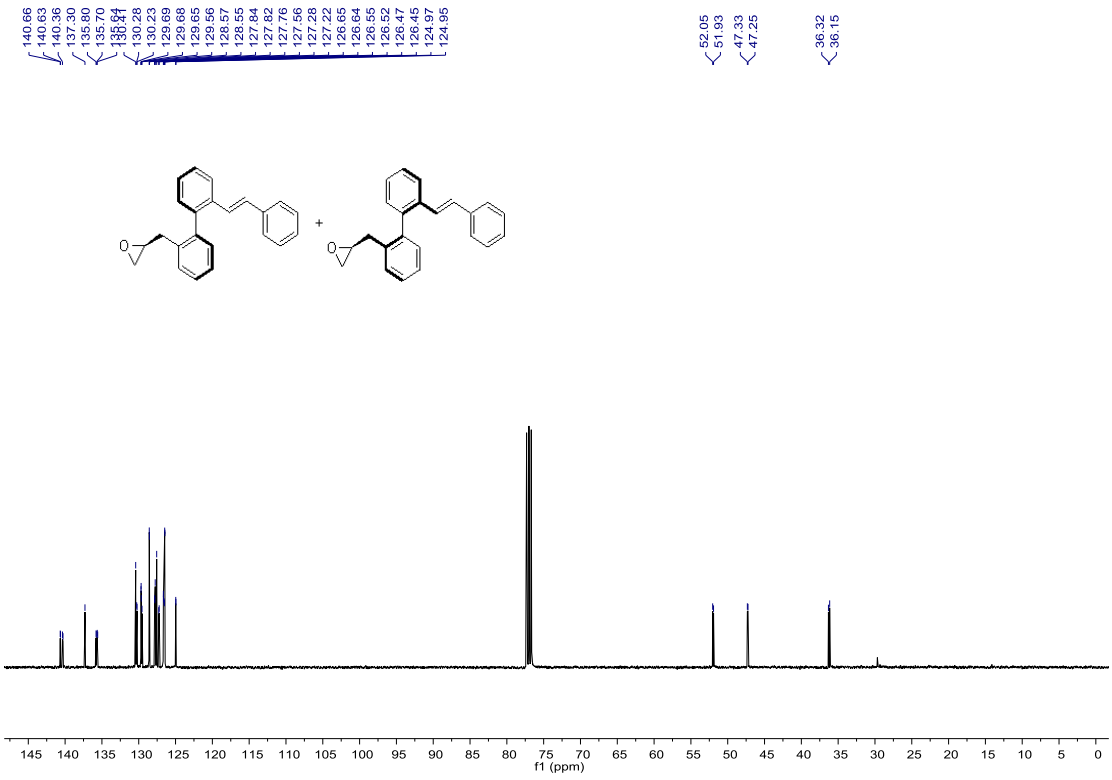
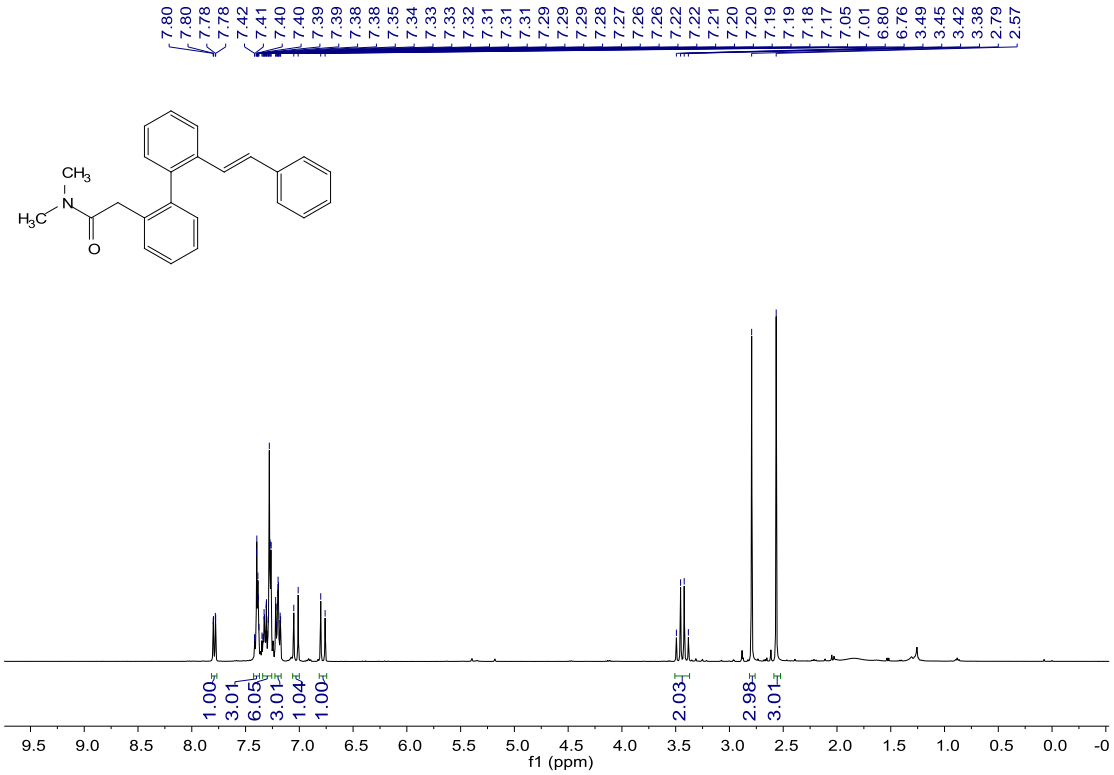


(*E*)-*N*,*N*-dimethyl-2-(2'-styryl-[1,1'-biphenyl]-2-yl)acetamide(4aia)

^{1}HNMR



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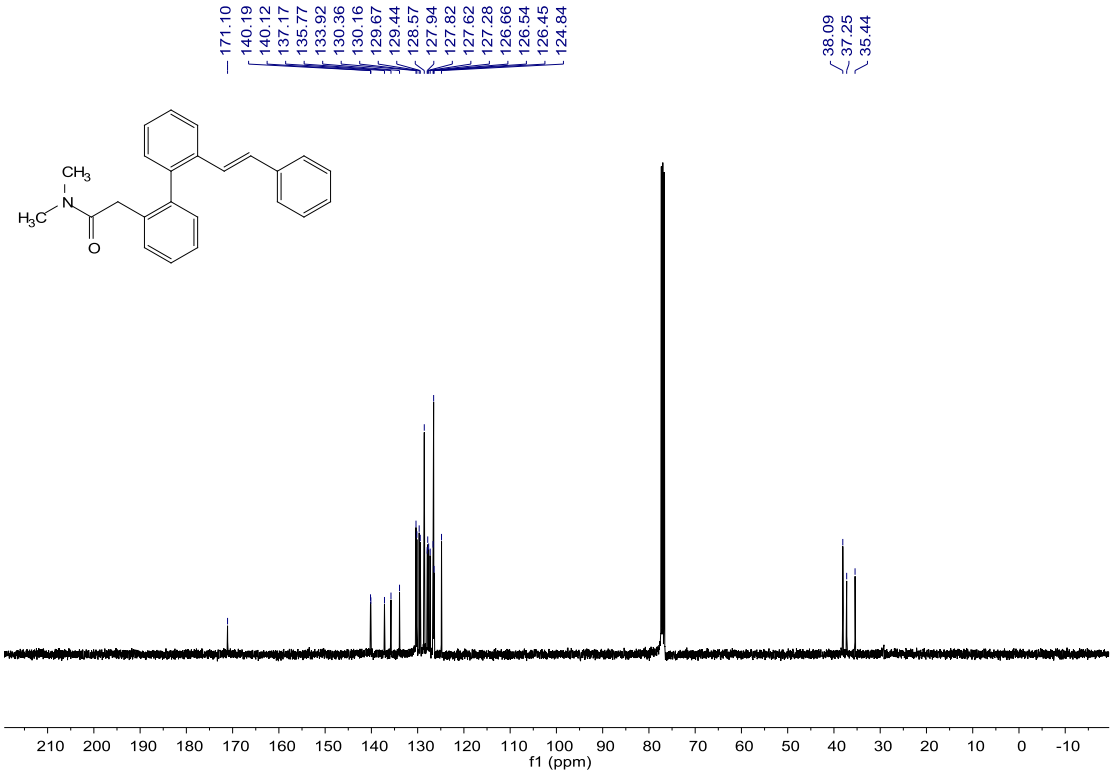
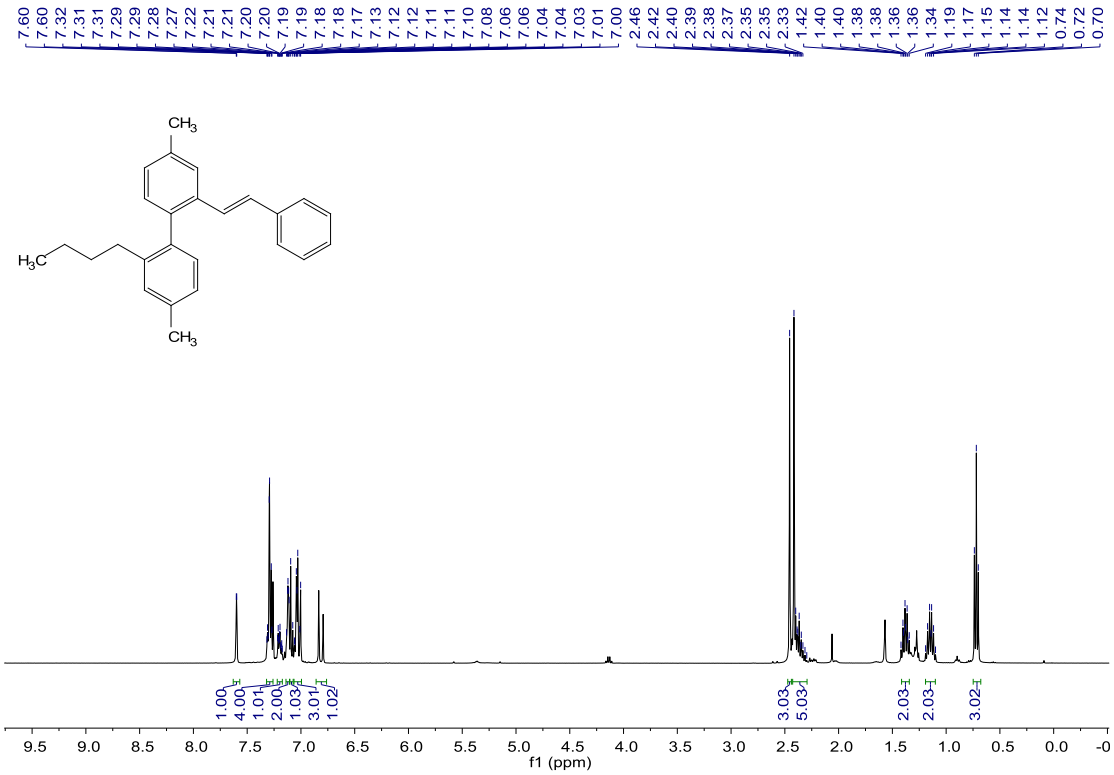
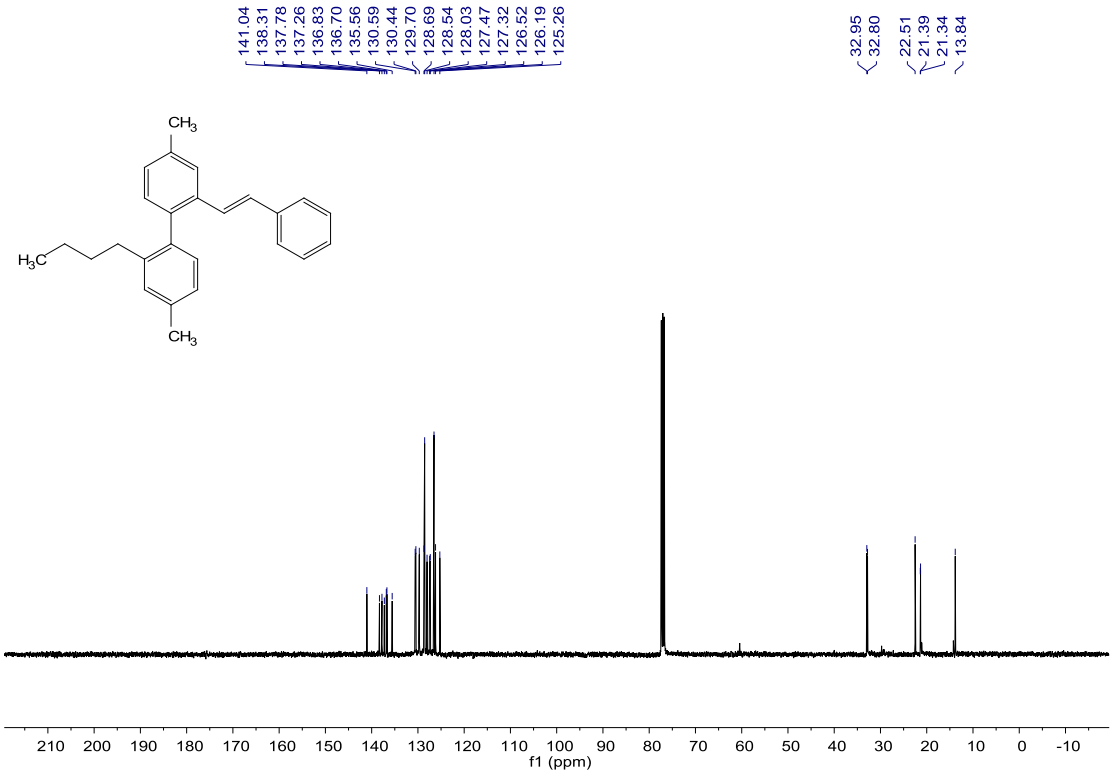


(*E*)-2-butyl-4,4'-dimethyl-2'-styryl-1,1'-biphenyl(4baa)

^{1}HNMR

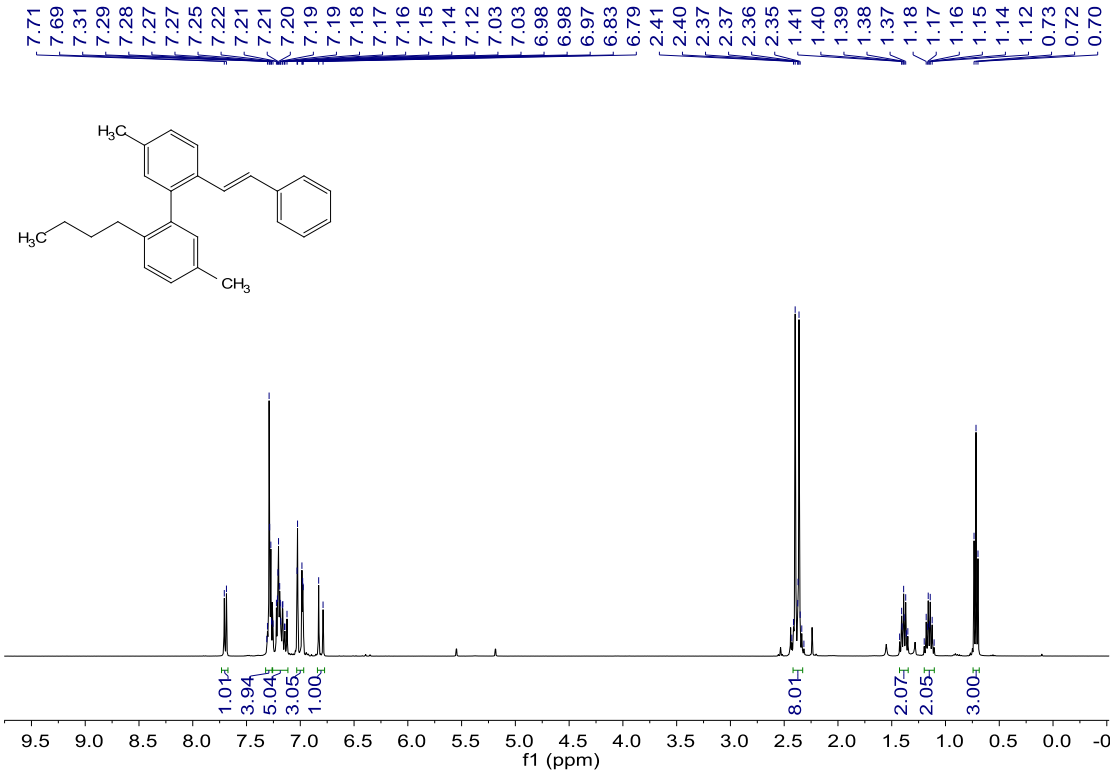


^{13}CNMR



(*E*)-2-butyl-5,5'-dimethyl-2'-styryl-1,1'-biphenyl(4caa)

^{1}HNMR



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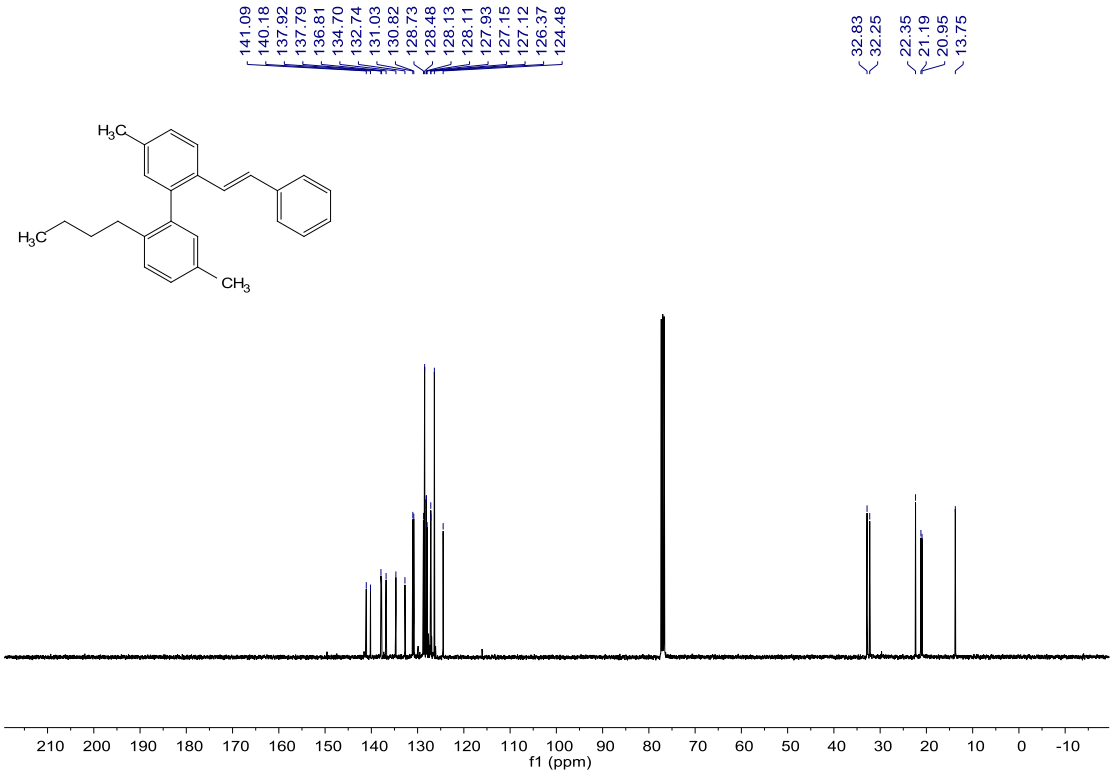
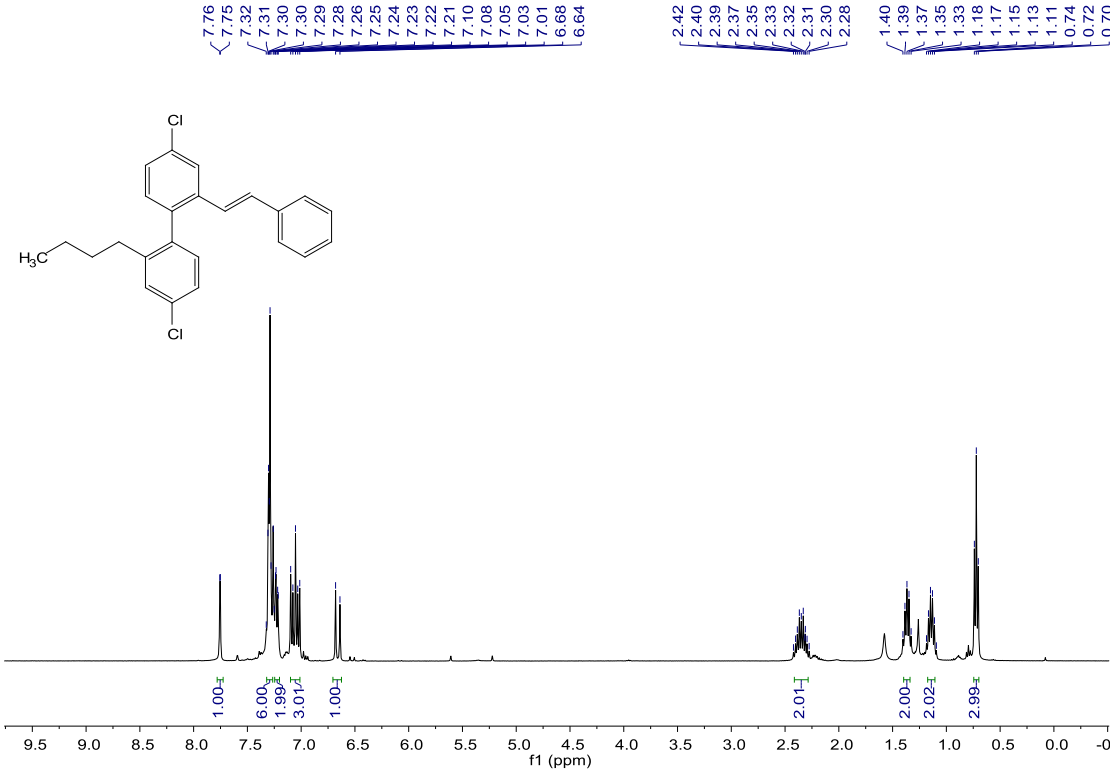


(*E*)-2-butyl-4,4'-dichloro-2'-styryl-1,1'-biphenyl(4daa)

^{1}HNMR



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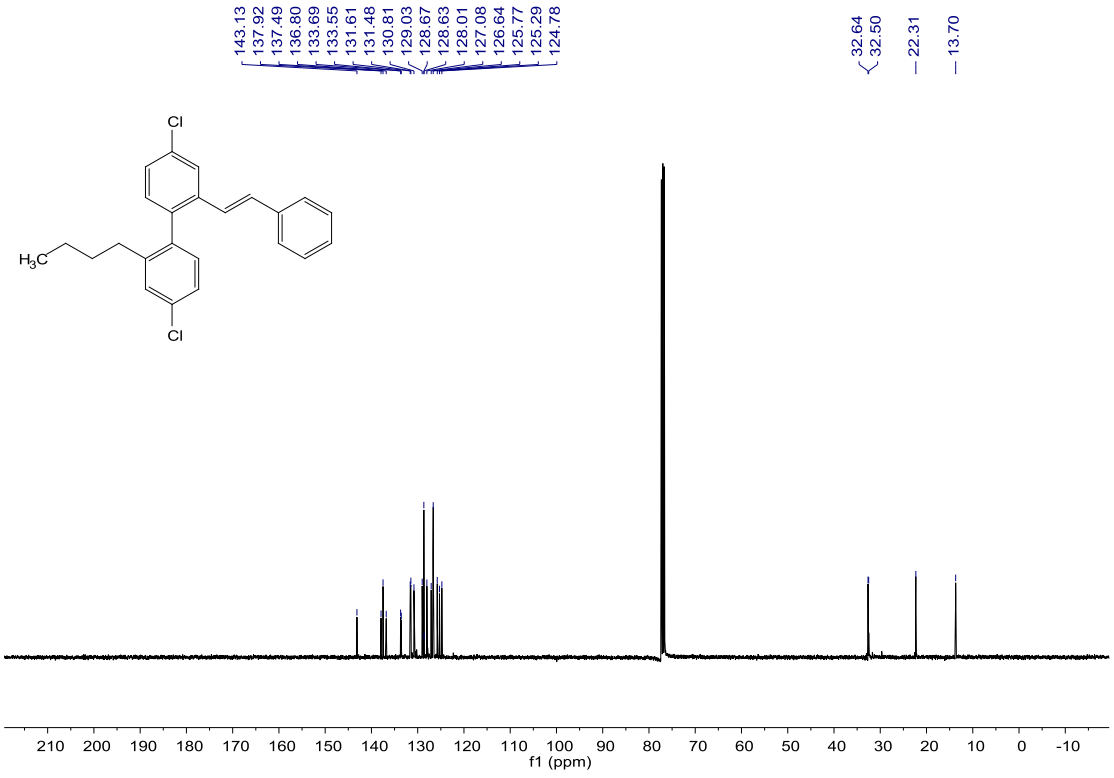
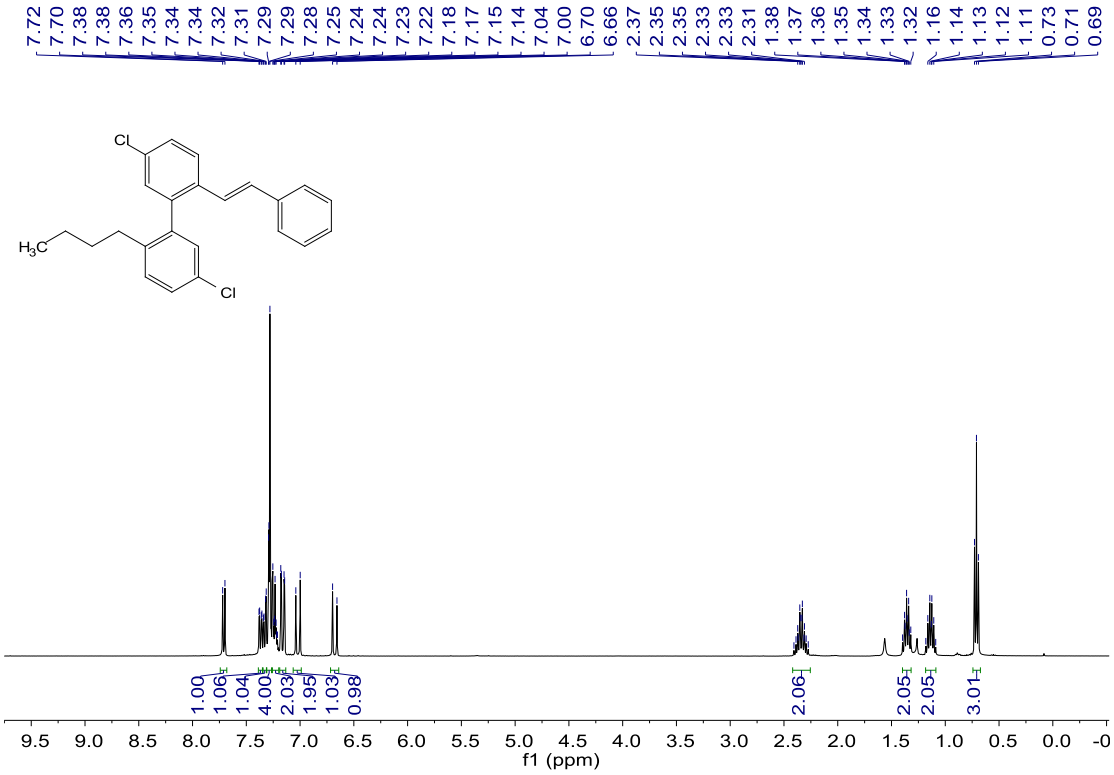


(*E*)-2-butyl-5,5'-dichloro-2'-styryl-1,1'-biphenyl(4eaa)

^{1}HNMR



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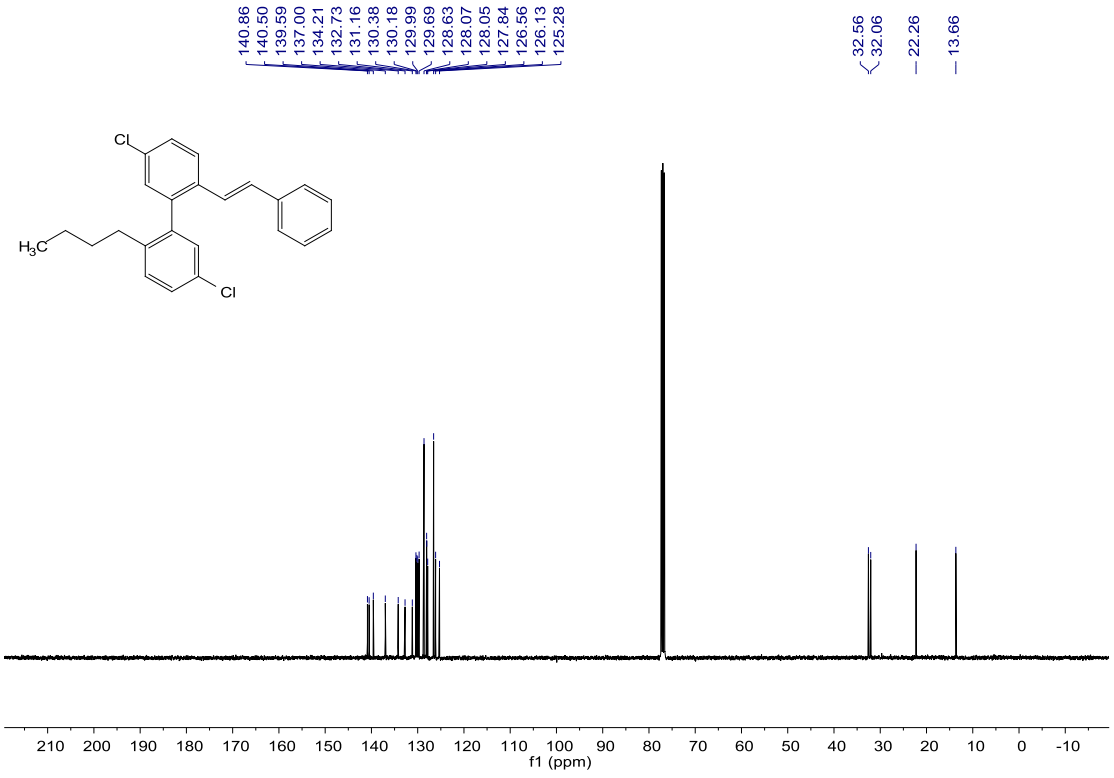
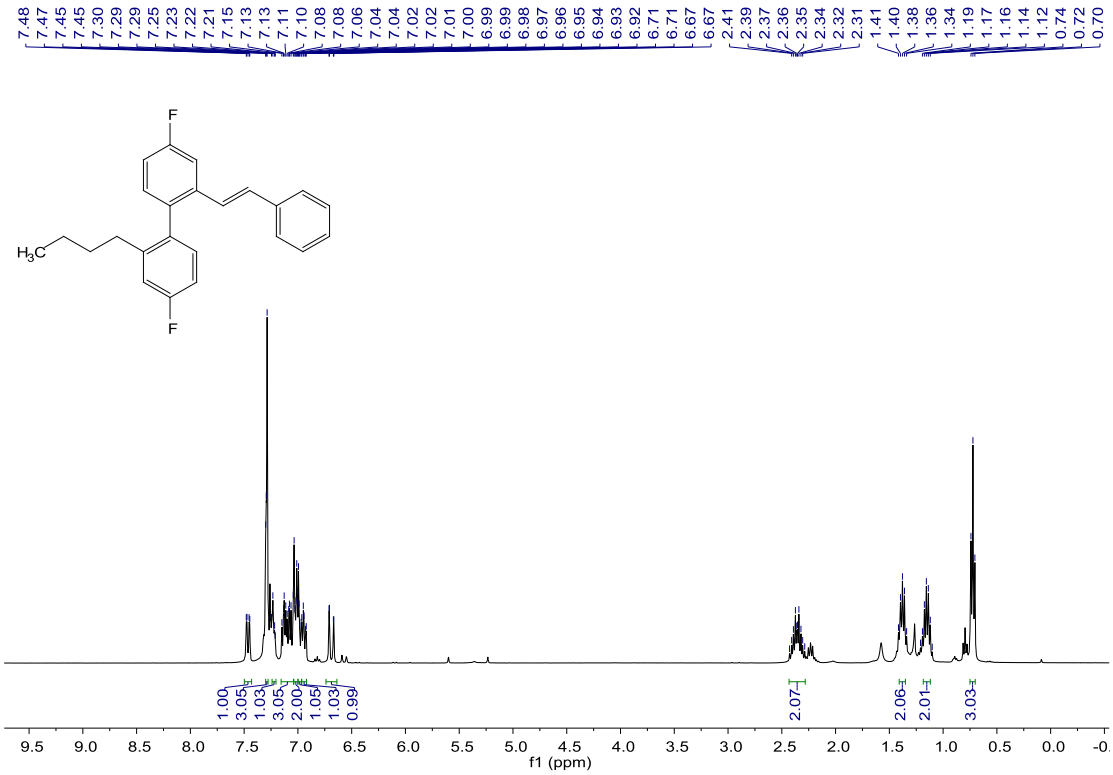


(*E*)-2-butyl-4,4'-difluoro-2'-styryl-1,1'-biphenyl(4faa)

^{1}HNMR



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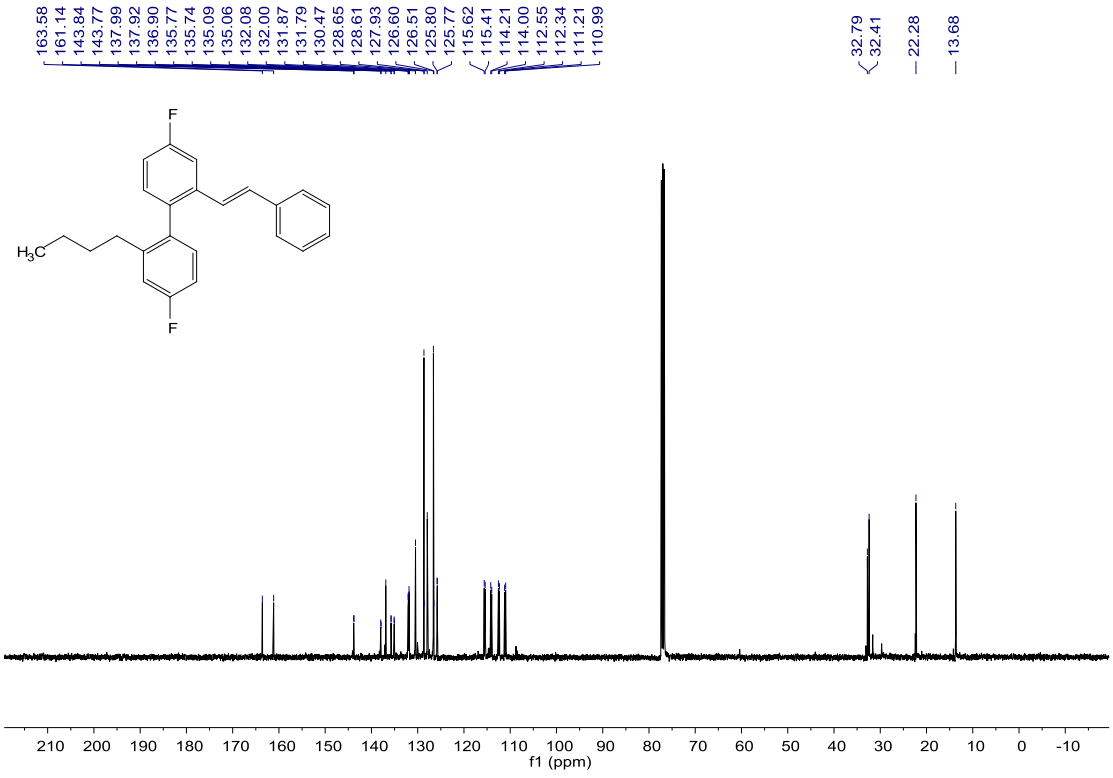
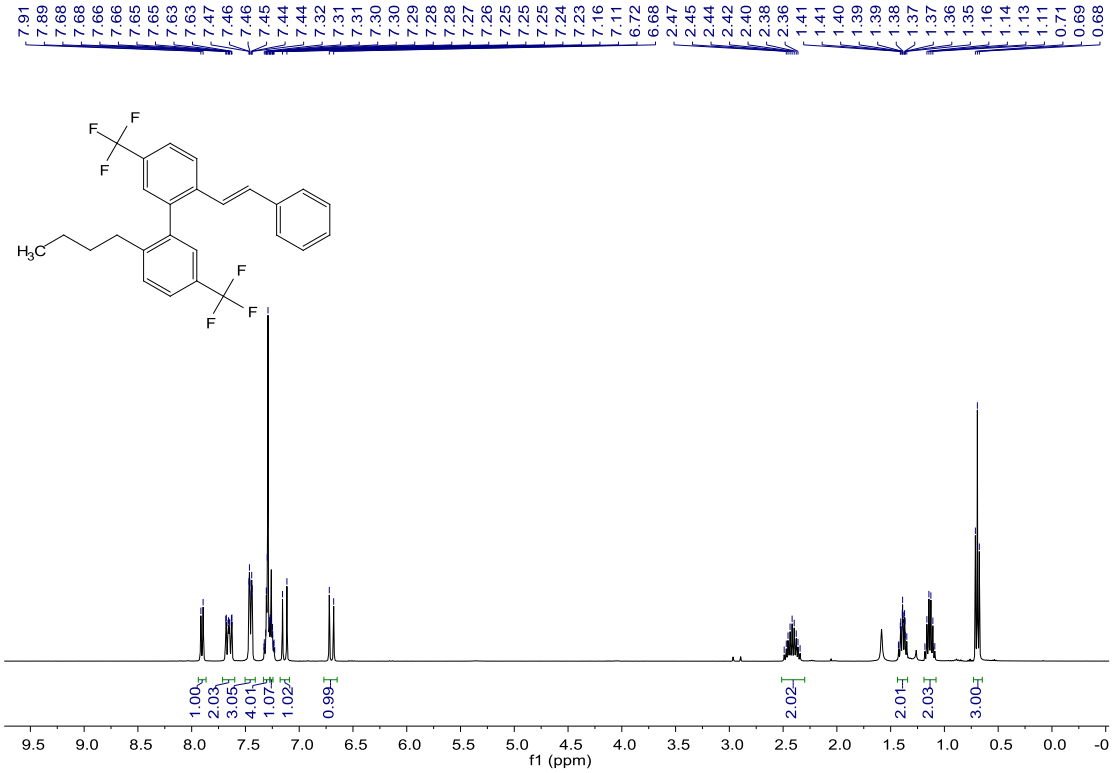
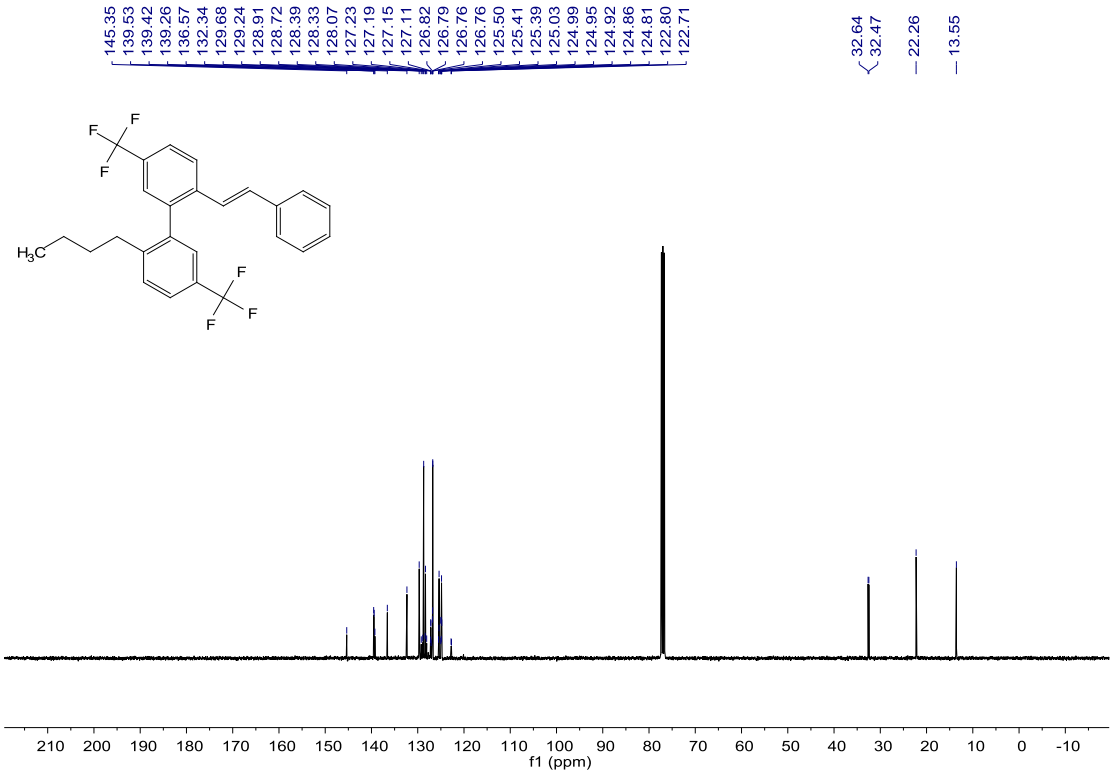


(*E*)-2-butyl-2'-styryl-5,5'-bis(trifluoromethyl)-1,1'-biphenyl(4gaa)

^{1}HNMR

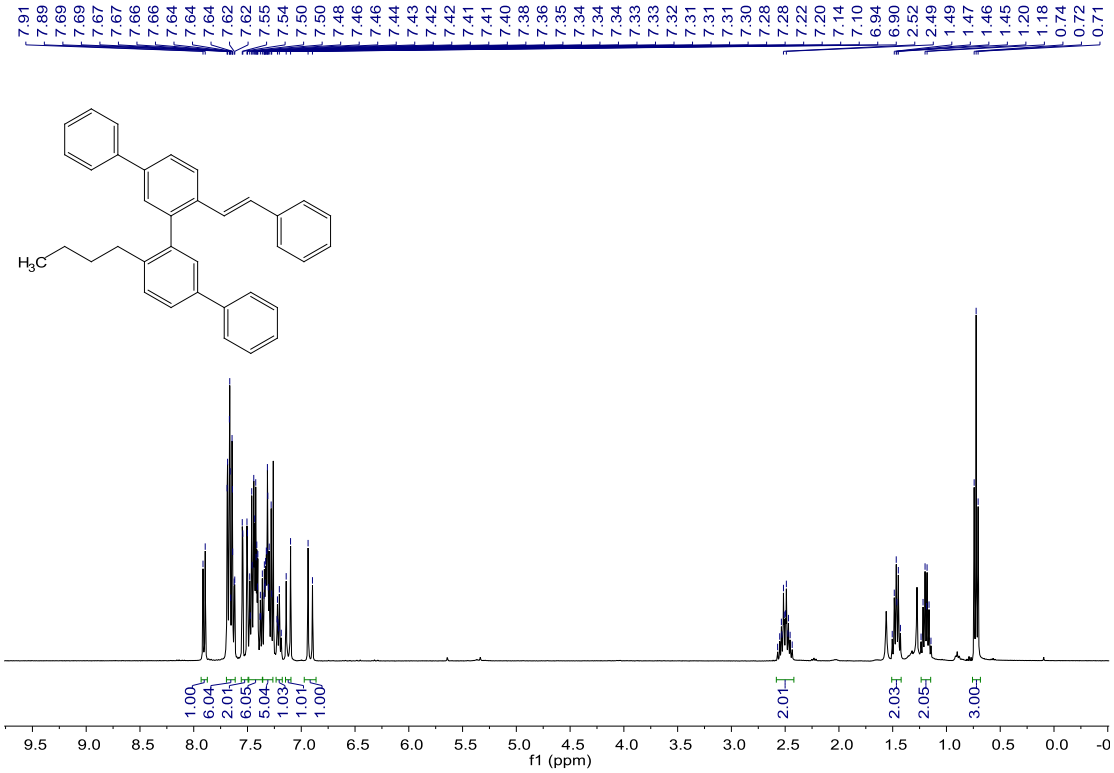


^{13}CNMR

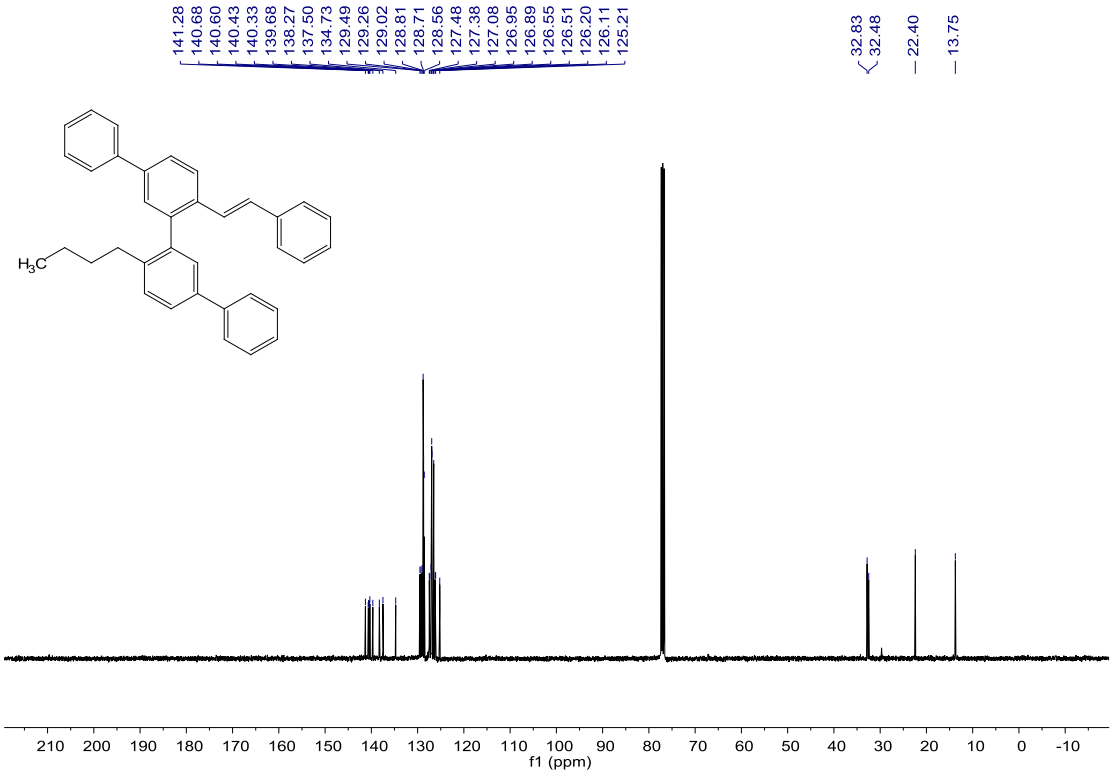


(*E*)-4'-butyl-6''-styryl-1,1':3',1'':3'',1'''-quaterphenyl(4haa)

^{1}HNMR

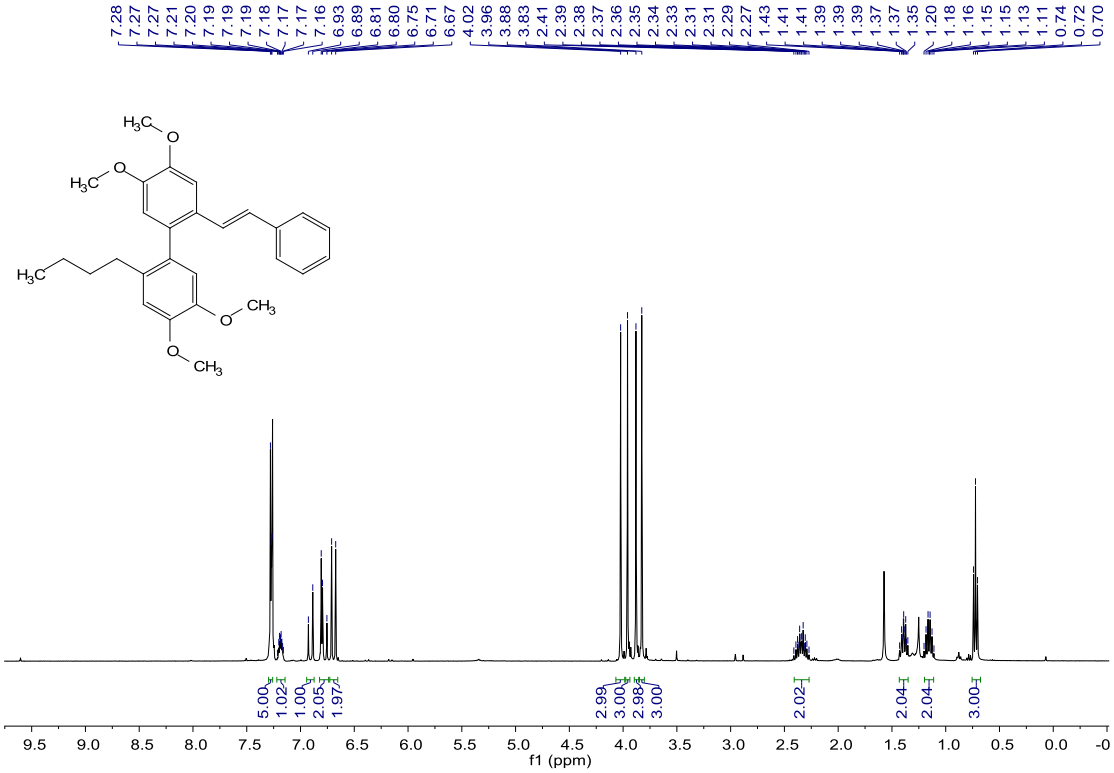


^{13}CNMR

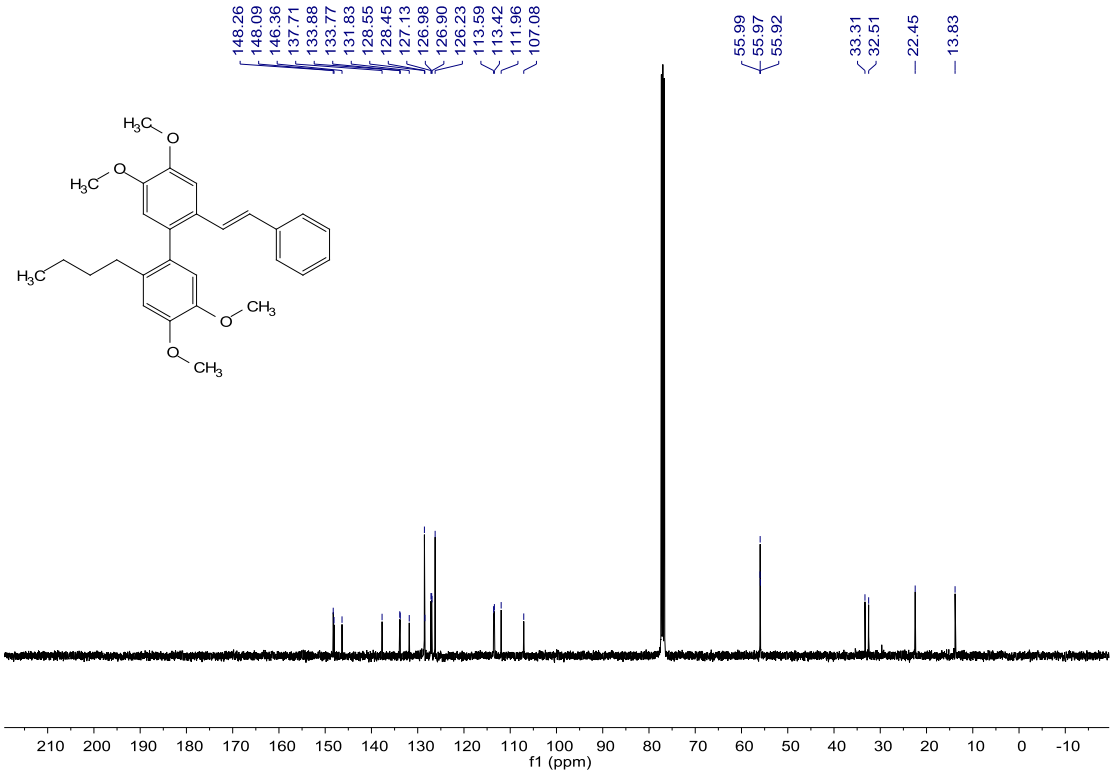


(*E*)-2-butyl-4,4',5,5'-tetramethoxy-2'-styryl-1,1'-biphenyl(4iaa)

^{1}HNMR

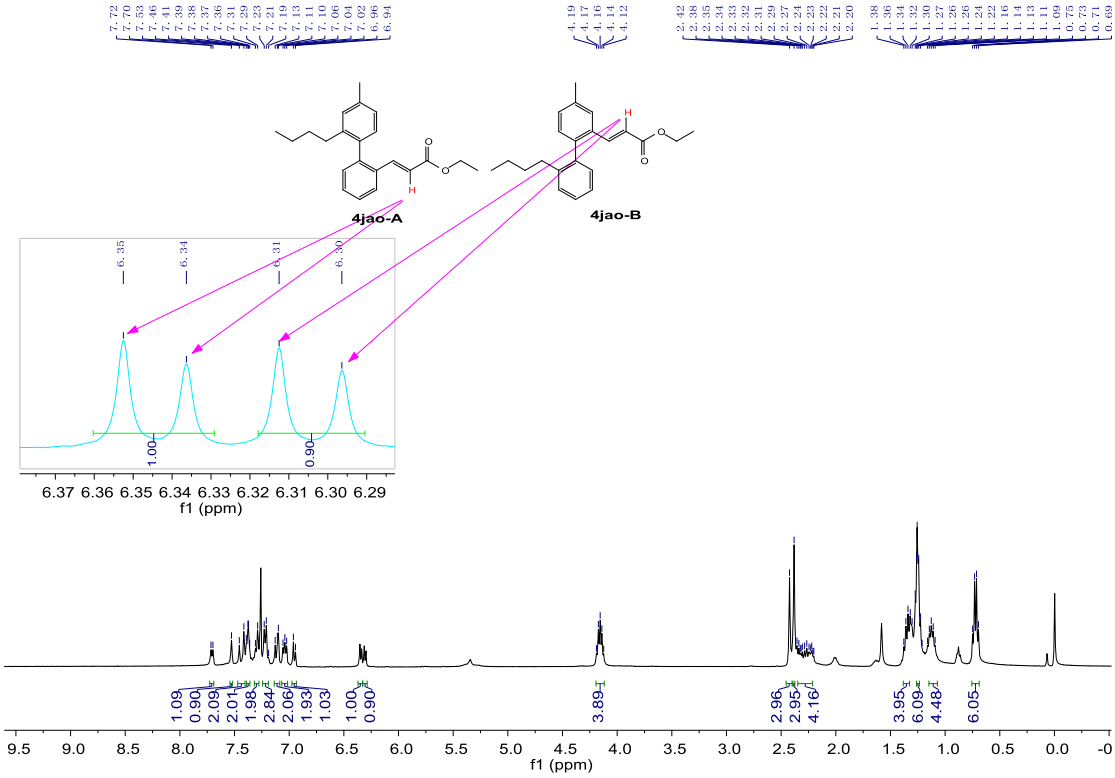


^{13}CNMR



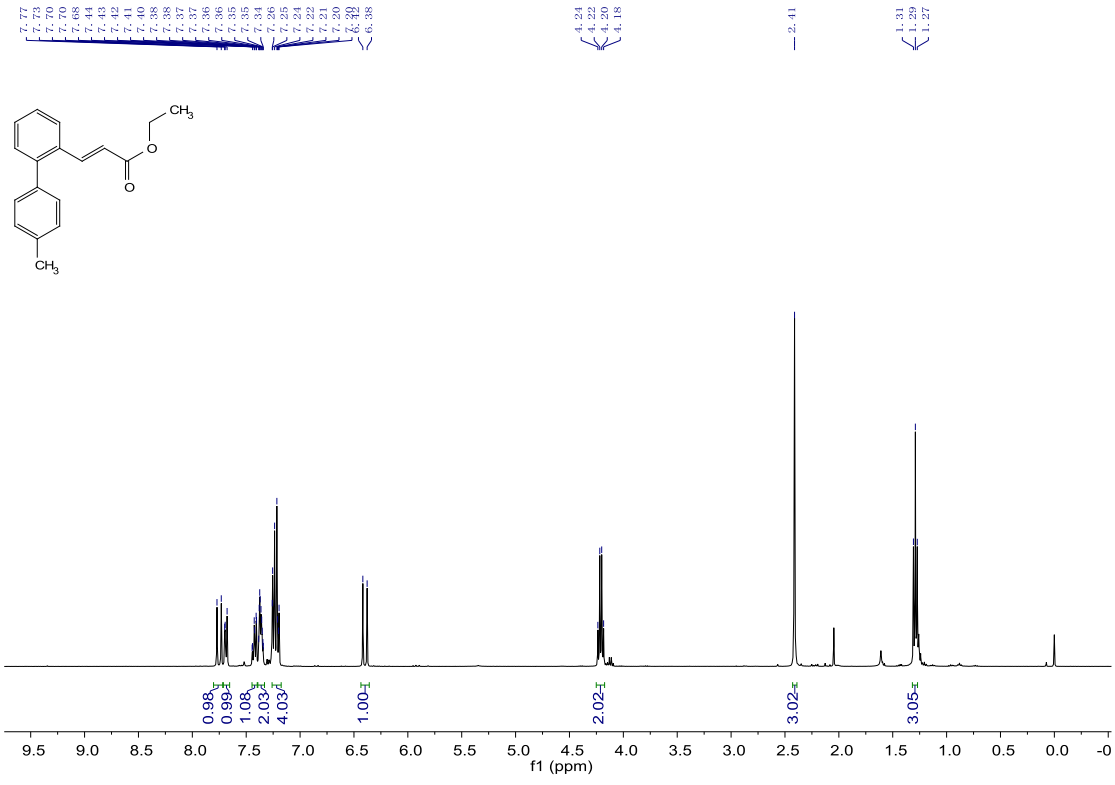
4jao-A and **4jao-B** (The products obtained in the reaction of 2-iodo-4'-methylbiphenyl (**1j**), Scheme 2 in the manuscript)

^{1}HNMR



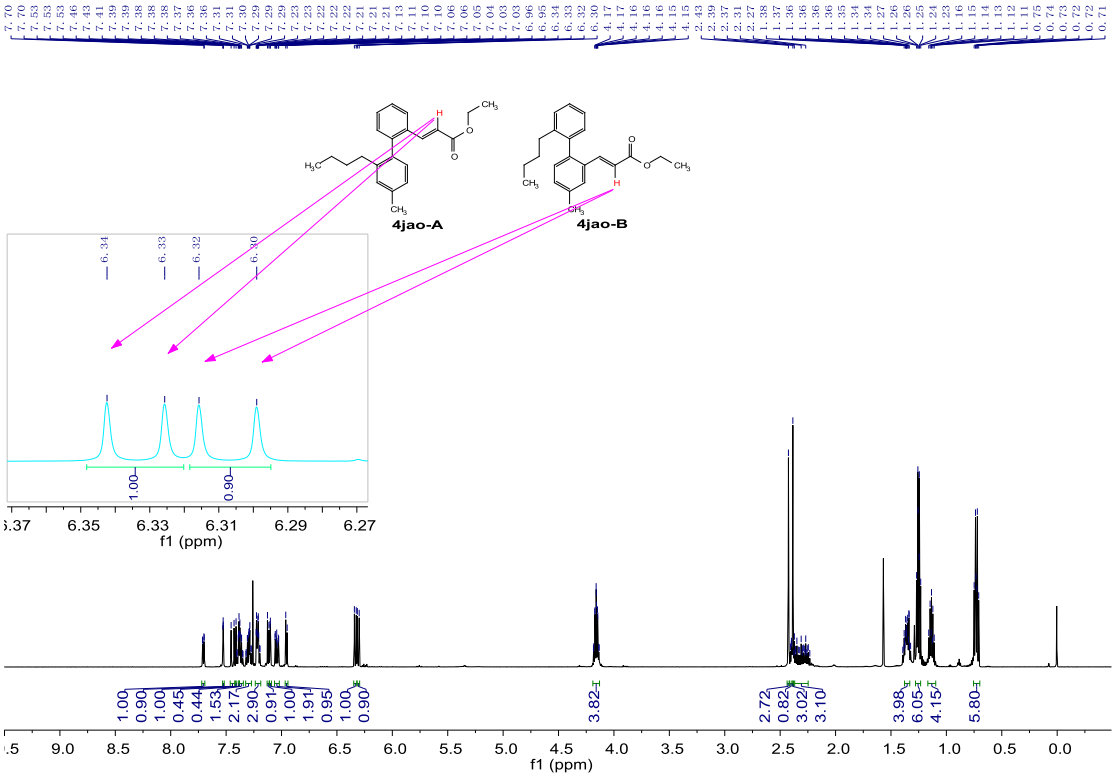
(*E*)-ethyl 3-(4'-methylbiphenyl-2-yl)acrylate(5jo-A)

^{1}HNMR



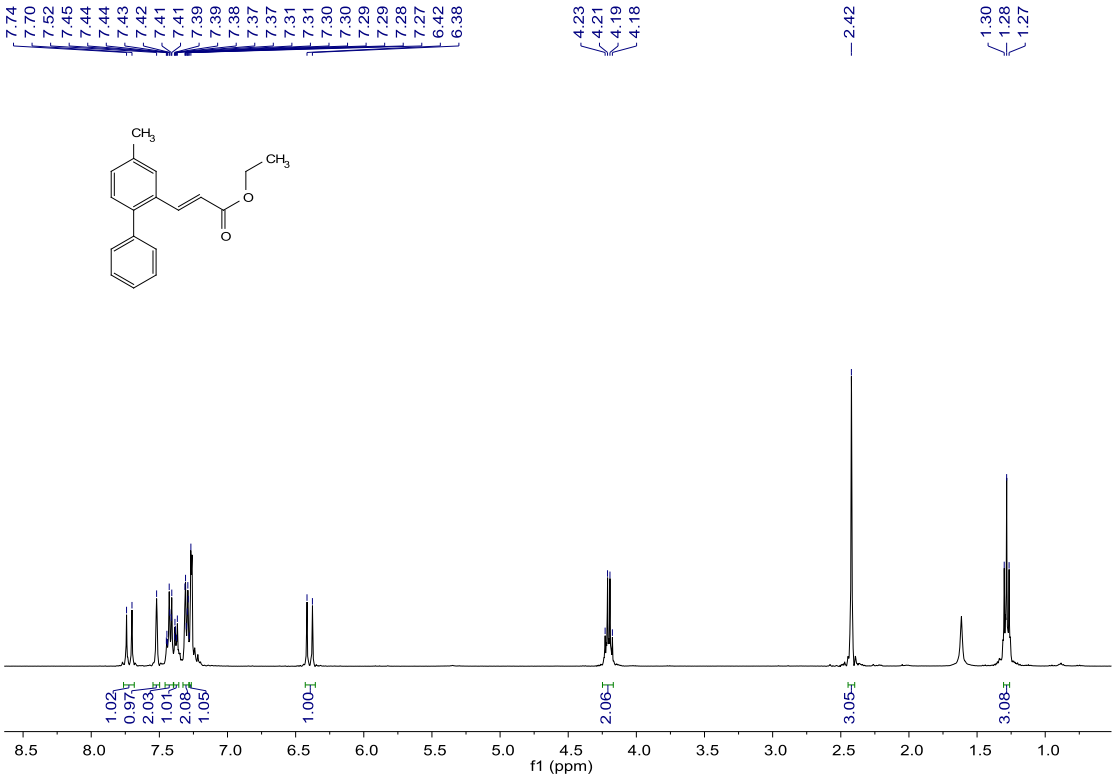
4jao-A and **4jao-B** (The products obtained in the reaction of 2-iodo-4-methylbiphenyl (**1k**), Scheme 2 in the manuscript)

^{1}HNMR (600 MHz, Chloroform-*d*)



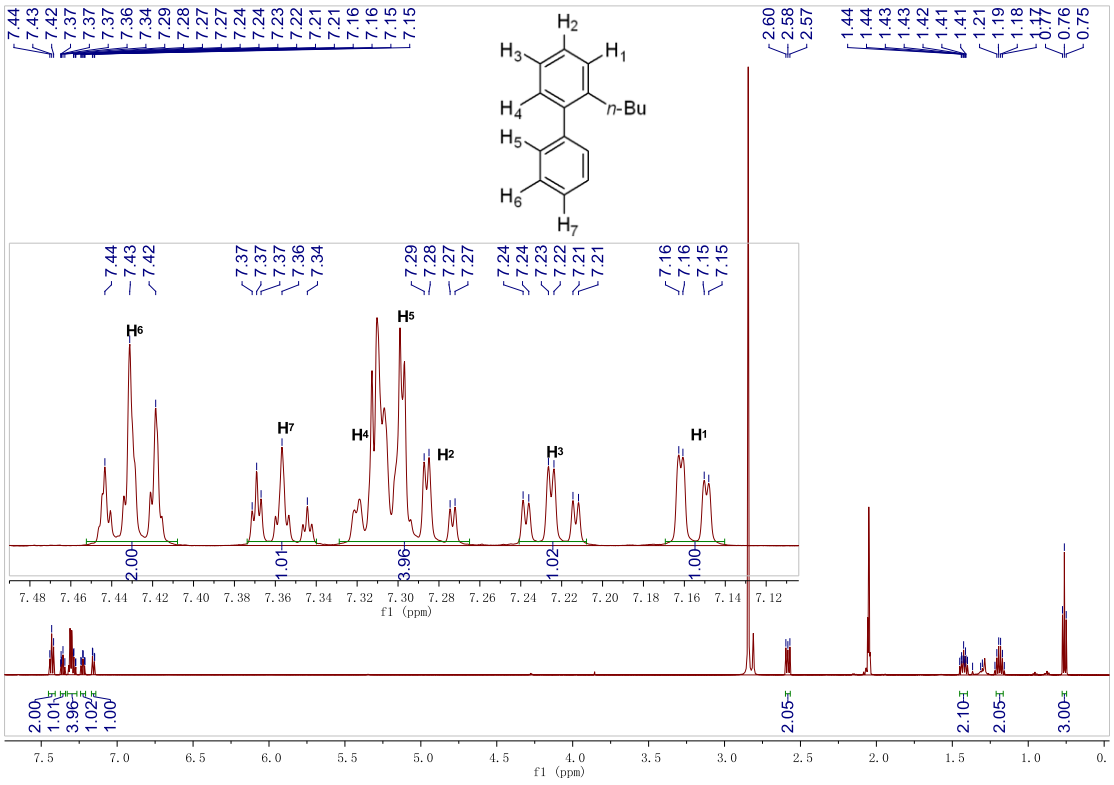
(*E*)-ethyl 3-(4-methylbiphenyl-2-yl)acrylate(5jo-B)

^{1}HNMR



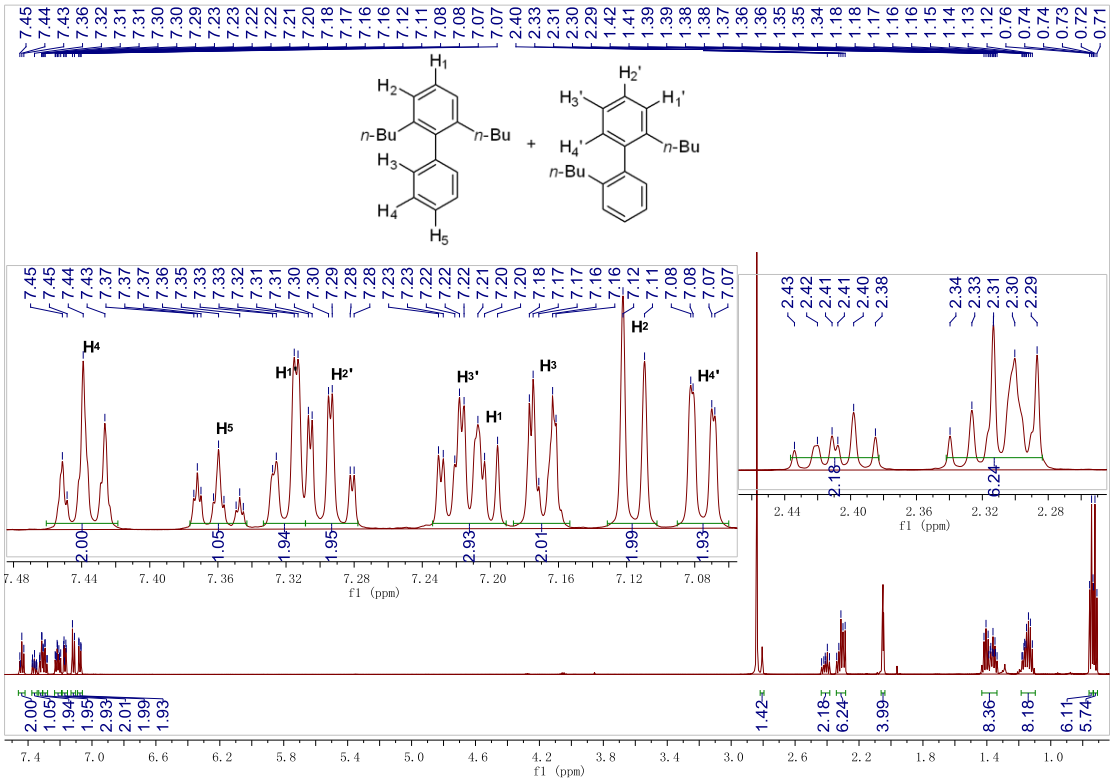
2-butyl-1,1'-biphenyl (6aa)

^{1}H NMR (600 MHz, acetone-d_6)



2,2'-dibutyl-1,1'-biphenyl (6aa-A) and 2,6-dibutyl-1,1'-biphenyl (6aa-B)

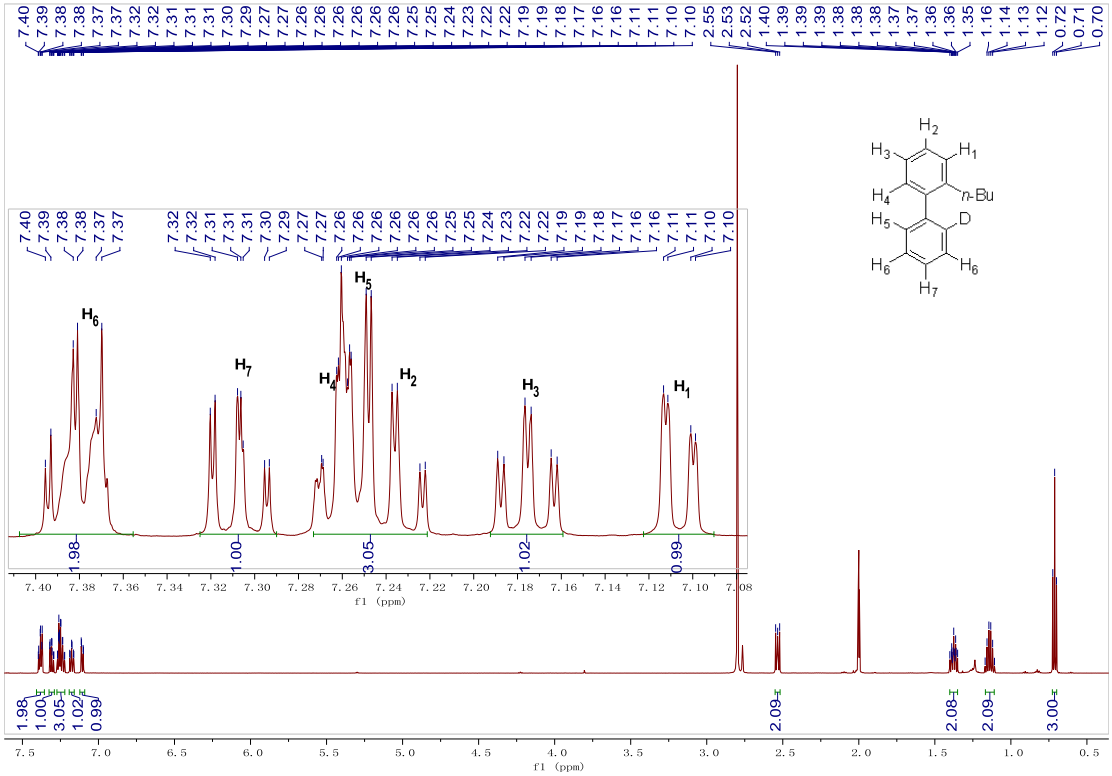
^{1}H NMR (600 MHz, acetone-d_6)



Reaction in DMF-d_7 and CD_3OD:

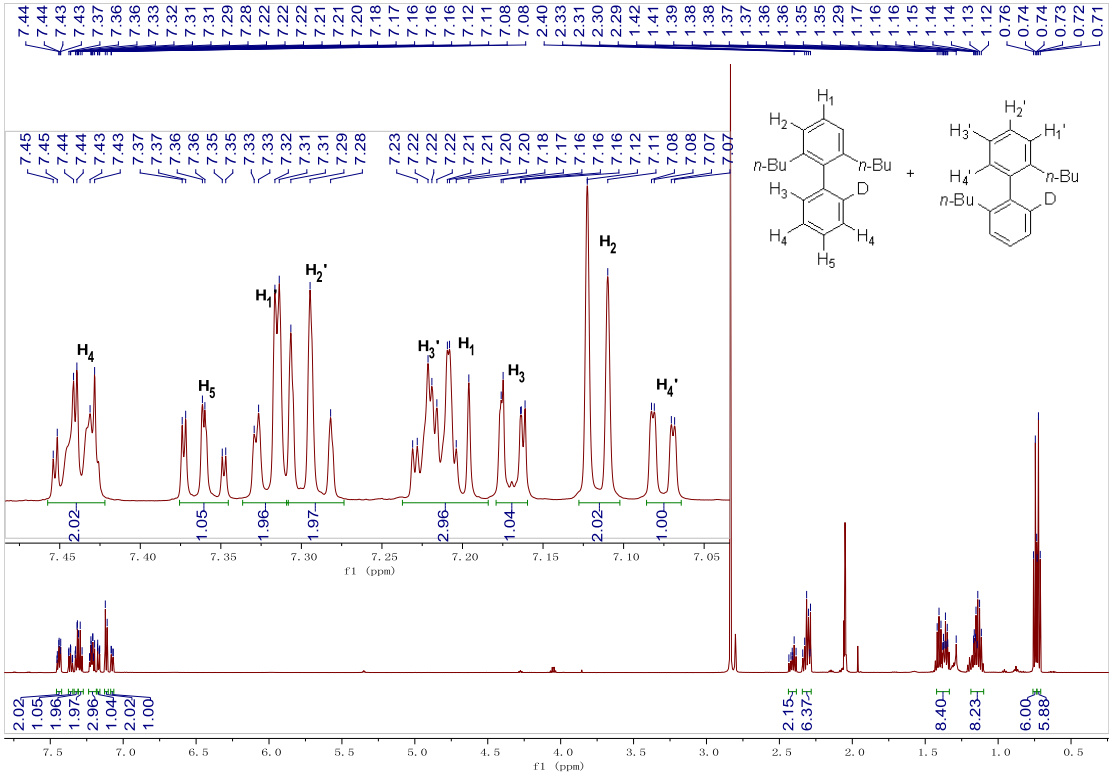
2-butyl-1,1'-biphenyl (6aa-*d*)

^{1}H NMR (600 MHz, acetone-d_6)



2,2'-dibutyl-1,1'-biphenyl (6aa-A-*d*) and 2,6-dibutyl-1,1'-biphenyl (6aa-B-*d*)

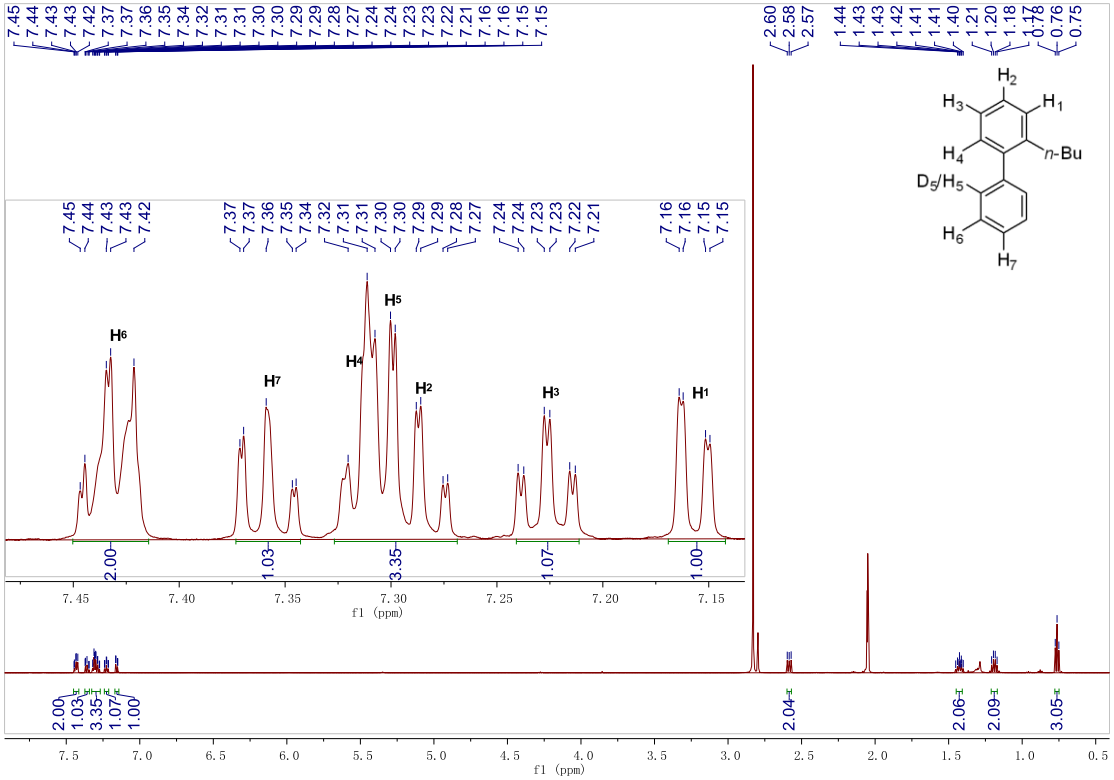
^{1}H NMR (600 MHz, acetone-d_6)



Reaction in DMF and CD_3OD:

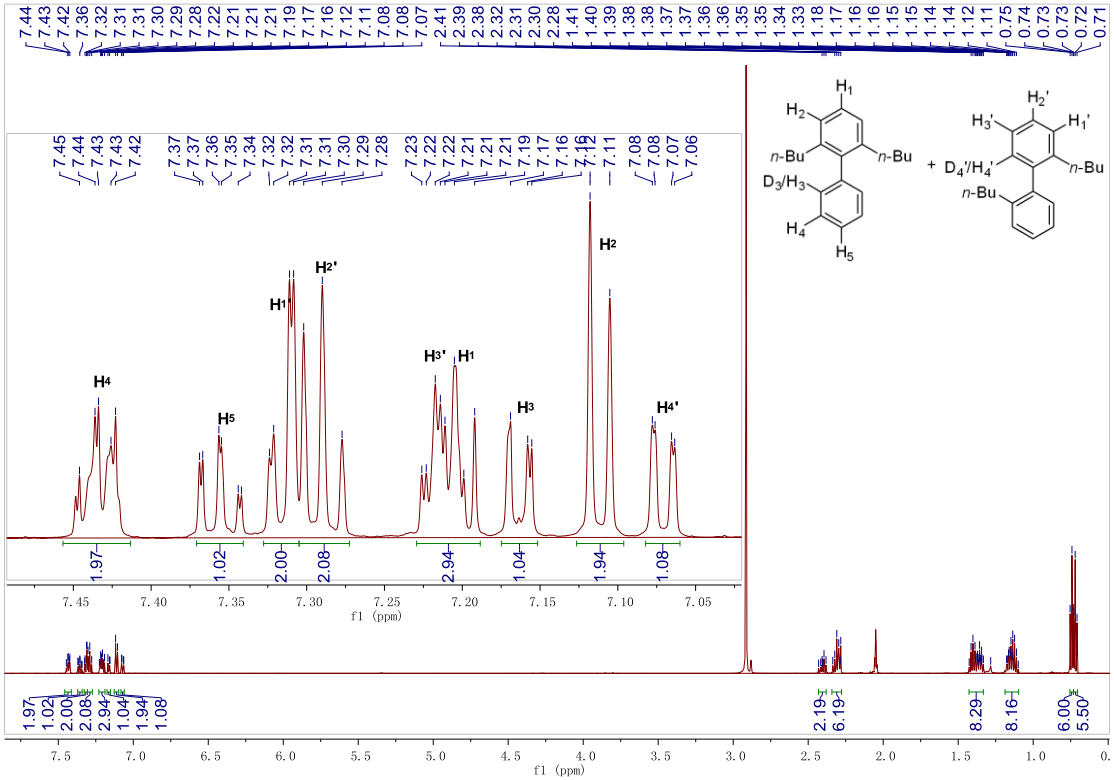
2-butyl-1,1'-biphenyl (6aa + 6aa-*d*)

^{1}H NMR (600 MHz, acetone-d_6)



2,2'-dibutyl-1,1'-biphenyl (6aa-A + 6aa-A-*d*) and **2,6-dibutyl-1,1'-biphenyl (6aa-B + 6aa-B-*d*)**

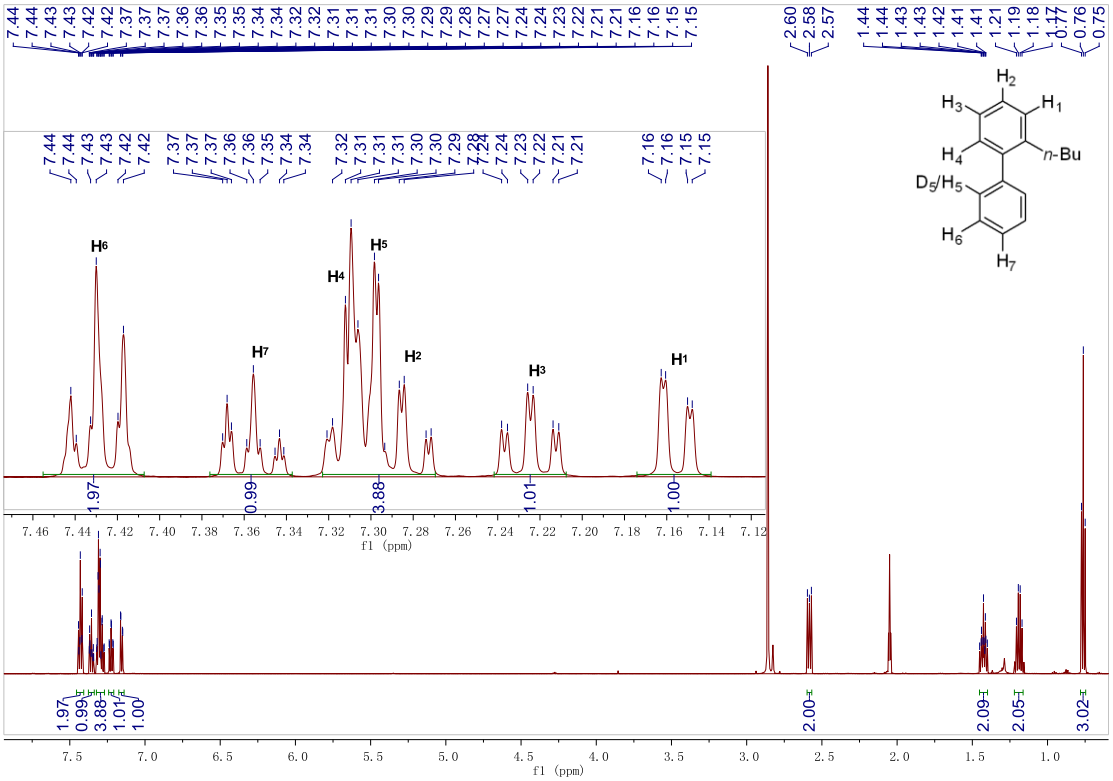
^{1}H NMR (600 MHz, acetone-d_6)



Reaction in the presence of D_2O:

2-butyl-1,1'-biphenyl (6aa + 6aa-*d*)

^{1}H NMR (600 MHz, acetone-d_6)



2,2'-dibutyl-1,1'-biphenyl (6aa-A + 6aa-A-*d*) and 2,6-dibutyl-1,1'-biphenyl (6aa-B + 6aa-B-*d*)

^{1}H NMR (600 MHz, acetone-d_6)