Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Oxidative Mizoroki–Heck Reaction of Unprotected Cinnamylamines at Ambient Temperature Under Air

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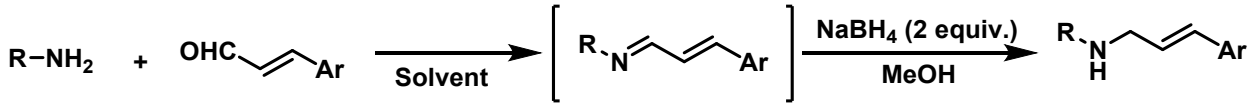
1. General Information

All the materials were obtained from Sigma-Aldrich Chemical Company, St. Louis, MO, USA, Combi-Blocks, San Diego, CA, USA, Oakwood Chemical, Estill, SC, USA, Alfa Aesar, Ward Hill, MA, USA, Acros Organic, Geel, Belgium, Ambeed, Inc., Arlington Heights, IL, USA, or TCI, Tokyo, Japan, and were used as received. Deuterated NMR solvents were obtained from Cambridge Isotope Laboratories, Inc., Andover, MA, and used without further purification. NMR spectra were recorded on either a Varian Inova 400 MHz NMR, 600 MHz NMR spectrometer or a Bruker Avance III 600 MHz NMR spectrometer and were processed using MestReNova by Mestrelab Research S.L. Proton (^{1}H) chemical shifts are reported in parts per million (δ) with respect to tetramethylsilane (TMS, δ=0), and referenced internally with respect to the protio solvent impurity.[1] Fluorine (^{19}F) chemical shifts are reported in parts per million (δ) and referenced internally with respect to hexafluorobenzene included in an insert tube (C_6F_6, δ= −164.9).[2] ESI mass spectra were recorded on an Agilent 6530 LC Q-TOF mass spectrometer using electrospray ionization with fragmentation voltage set at 115 V or lower for sensitive substrates, and processed with an Agilent MassHunter Operating System, or on a Waters SYNAPT G2-Si High Definition Mass Spectrometer. Scanning Electron Microscopy (SEM) and Scanning Transmission Electron Microscopy (STEM) data were collected on a JEOL JSM-7500F. Dynamic Light Scattering (DLS) was performed using a Litesizer 500 (Anton Paar) by diluting filtered reactions into methanol.

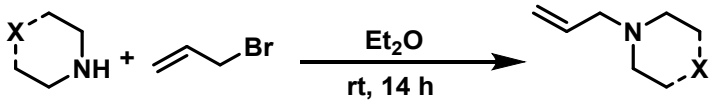
2. Synthesis of Cinnamylamine Substrates

A) Synthetic Procedure for Cinnamylamines:



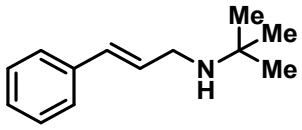
Method I: Amine (1 equiv.) and cinnamaldehyde (1 equiv.) were charged in an oven-dried 50 mL round bottom flask with 15 mL of chloroform and allowed to stir at 60 °C for 4 h, followed by filtration over Na_2SO_4. After evaporation *in vacuo*, the evacuated filtrate was dissolved in methanol (10 mL). To the solution was added sodium borohydride (2 equiv.) portion wise, followed by stirring at room temperature overnight. After completion, reaction was quenched with aq. NaOH solution. The aqueous layer was extracted with diethyl ether (2 × 25 mL), dried over Na_2SO_4, followed by concentration *in vacuo*. The crude product was purified by acid-base workup: first, the residue was acidified using 1.2 M hydrochloric $acid_{(aq)}$, followed by subsequent washing with diethyl ether (2 × 50 mL). Then the aqueous layer was basified with ammonium hydroxide solution and extracted with dichloromethane (2 × 50 mL). After drying over Na_2SO_4, the organic layer was concentrated *in vacuo* to give the secondary amine product.

Method II: Amine (1 equiv.) and cinnamaldehyde (1 equiv.) were charged in an oven dried 50 mL round bottom flask in 15 mL of methanol and allowed to stir at room temperature for 1 h, followed by addition of sodium borohydride (2 equiv.) portion wise, followed by stirring at room temperature overnight. After completion, reaction was quenched with aq. NaOH solution. The aqueous layer was extracted with diethyl ether (2 × 25 mL), dried over Na_2SO_4, followed by concentration *in vacuo*. The crude product was purified by acid-base workup: first, the residue was acidified using 1.2 M hydrochloric acid, followed by subsequent washing with diethyl ether (2 × 50 mL). Then the aqueous layer was basified with ammonium hydroxide solution and extracted with dichloromethane (2 × 50 mL). After drying over Na_2SO_4, the organic layer was concentrated *in vacuo* to give the secondary amine product.

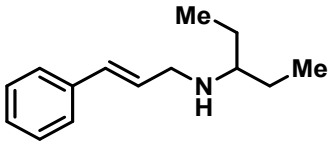


Method III: A solution of amine (5 mmol.) in diethyl ether (10 mL) was cooled to 0 °C, and allyl bromide (10 mmol.) was added dropwise to it. After stirring for 30 minutes, the reaction mixture was warmed to RT, and allowed to stir overnight. Ammonium $hydroxide_{(aq)}$ was added to convert the milky reaction mixture into a clear solution. The aqueous layer was extracted with diethyl ether (2 × 25 mL), dried over Na_2SO_4, followed by concentration *in vacuo* to give the tertiary amine products.

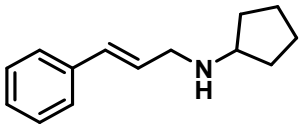
B) Characterization Data



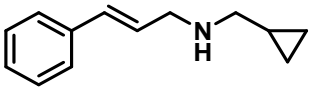
(*E*)-*N*-(*tert*-Butyl)-3-phenylprop-2-en-1-amine (A): Method II: *tert*-Butylamine (730 mg, 10 mmol) and cinnamaldehyde (1321 mg, 10 mmol) were used. Product recovered as pale-yellow oil (79% yield, 1.49 g), which gave spectral data consistent with that in the literature.[3]



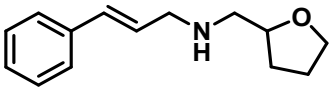
***N*-Cinnamylpentan-3-amine (B):** Method II: 3-Aminopentane (870 mg, 10 mmol) and cinnamaldehyde (1321 mg, 10 mmol) were used. Product recovered as yellow oil (88% yield, 1.78 g), which gave spectral data consistent with that in the literature.[3]



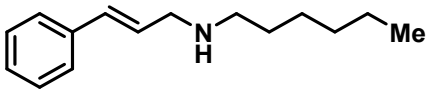
***N*-Cinnamylcyclopentanamine (C):** Method I: Cyclopentylamine (300 mg, 3.5 mmol) and cinnamaldehyde (462 mg, 3.5 mmol) were used. Product recovered as yellow oil (82% yield, 577 mg), which gave spectral data consistent with that in the literature.[3]



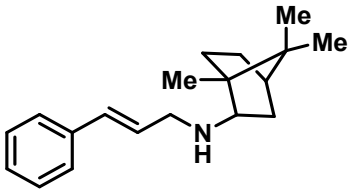
(*E*)-*N*-(Cyclopropylmethyl)-3-phenylprop-2-en-1-amine (D): Method II: Cyclopropylmethylamine (710 mg, 10 mmol) and cinnamaldehyde (1321 mg, 10 mmol) were used. Product recovered as yellow oil (51% yield, 955 mg), which gave spectral data consistent with that in the literature.[3]



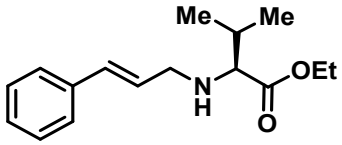
(*E*)-3-Phenyl-*N*-((tetrahydrofuran-2-yl)methyl)prop-2-en-1-amine (E): Method I: Tetrahydrofurfurylamine (300 mg, 2.97 mmol) and cinnamaldehyde (392 mg, 2.97 mmol) were used. Product recovered as colorless oil (75% yield, 483 mg), which gave spectral data consistent with that in the literature.[3]



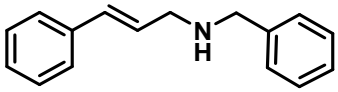
***N*-Cinnamylhexan-1-amine (F):** Method I: 1-Hexylamine (300 mg, 2.96 mmol) and cinnamaldehyde (392 mg, 2.96 mmol) were used. Product recovered as yellow oil (85% yield, 545 mg), which gave spectral data consistent with that in the literature.[3]



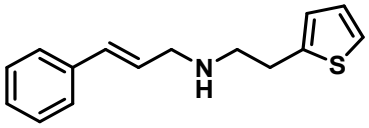
(2*R*,4*S*)-*N*-Cinnamyl-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine (G): Method I: (R)-(+)-Bornylamine (500 mg, 3.26 mmol) and cinnamaldehyde (432 mg, 3.26 mmol) were used. Product recovered as yellow oil (63% yield, 552 mg), which gave spectral data consistent with that in the literature.[3]



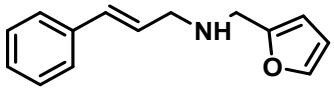
Ethyl cinnamyl-*L*-valinate (H): Method II: Ethyl valinate (1450 mg, 10 mmol) and cinnamaldehyde (1452 mg, 10 mmol) were used. Product recovered as colorless oil (79% yield, 2.06 g), which gave spectral data consistent with that in the literature.[3]



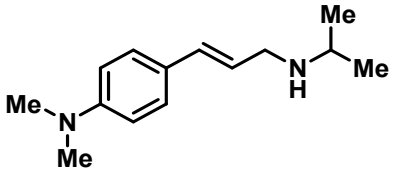
(*E*)-*N*-Benzyl-3-phenylprop-2-en-1-amine (I): Method I: Benzylamine (500 mg, 4.7 mmol) and cinnamaldehyde (616 mg, 4.7 mmol) were used. Product recovered as colorless oil (82% yield, 855 mg), which gave spectral data consistent with that in the literature.[3]



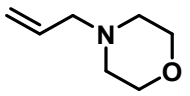
(*E*)-3-Phenyl-*N*-(2-(thiophen-2-yl)ethyl)prop-2-en-1-amine (J): Method II: Thiophene-2-ethylamine (300 mg, 2.38 mmol) and cinnamaldehyde (315 mg, 2.38 mmol) were used. Product recovered as colorless oil (56% yield, 1.28 g), which gave spectral data consistent with that in the literature.[3]



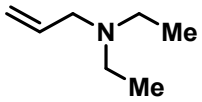
(*E*)-*N*-(Furan-2-ylmethyl)-3-phenylprop-2-en-1-amine (K): Method II: Furan-2-ylmethanamine (970 mg, 10 mmol) and cinnamaldehyde (1.32 g, 10 mmol) were used. Product recovered as yellow oil (60% yield, 1.27 g), which gave spectral data consistent with that in the literature.[3]



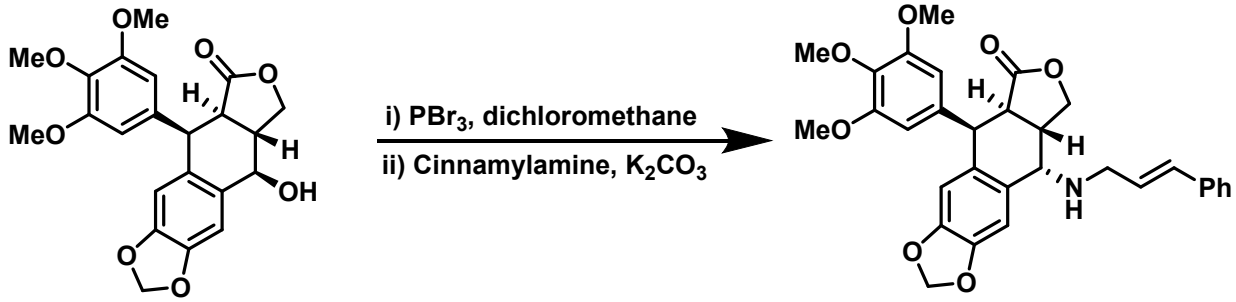
(*E*)-4-(3-(Isopropylamino)prop-1-en-1-yl)-*N*,*N*-dimethylaniline (L): Method I: Isopropylamine (591 mg, 10 mmol) and 4-*N*,*N*-dimethyl cinnamaldehyde (900 mg, 10 mmol) were used. Product recovered as colorless oil (54% yield, 600 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.4 Hz, 2H), 6.69 (d, *J* = 8.2 Hz, 2H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.13 (dt, *J* = 13.8, 6.5 Hz, 1H), 3.39 (d, *J* = 6.6 Hz, 2H), 2.96 (s, 6H), 2.94 – 2.87 (m, 1H), 1.11 (d, *J* = 6.3 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.4, 131.6, 127.6, 126.2, 124.8, 112.9, 50.3, 48.5, 41.0, 23.4. HRMS (ESI - MS): calcd. 217.1699 $[M-H]^+$ Found: 217.1783.



4-Allylmorpholine (M): Method III: Morpholine (870 mg, 5 mmol.) and allyl bromide (1.21 g, 10 mmol.) were used. Product recovered as a yellow oil (457 mg, 72% yield). Spectral data was consistent with that in the literature.[4]



***N*,*N*-Diethylprop-2-en-1-amine (N):** Method III: Diethylamine (365 mg, 5 mmol.) and allyl bromide (1.21 g, 10 mmol.) were used. Product recovered as a yellow oil (361 mg, 64% yield). Spectral data was consistent with that in the literature.[4]



(5*R*,5a*R*,8a*S*,9*R*)-9-(Cinnamylamino)-5-(3,4,5-trimethoxyphenyl)-5,8,8a,9-tetrahydrofuro[3',4':6,7]naphtho[2,3-d][1,3]dioxol-6(5a*H*)-one (O): To a solution of podophyllotoxin (1.0 g, 2.4 mmol, 1 equiv.) in dry dichloromethane (10 mL) was added PBr_3 (457 mg, 1.7 mmol, 0.70 equiv.) under nitrogen atmosphere at 0 °C, and the resulting reaction mixture was stirred at RT. After completion of the reaction (as monitored by TLC), the mixture was quenched by addition of water and extracted with dichloromethane (3 × 25 mL). The combined organic phase was washed with brine, and concentrated *in vacuo* to furnish the corresponding crude alkyl bromide. This bromide which was directly used in the next step without further purification. Then, method III was used. Product was purified over silica gel in hexanes/EtOAc (50:50) and recovered as a light yellow oil (383 mg, 30% yield). Unexpected stereochemistry of the amine center was determined through coupling constant analysis and comparison with similar structures in the literature.[3]

3. Optimization and Synthesis of γ-Arylated Cinnamylamines

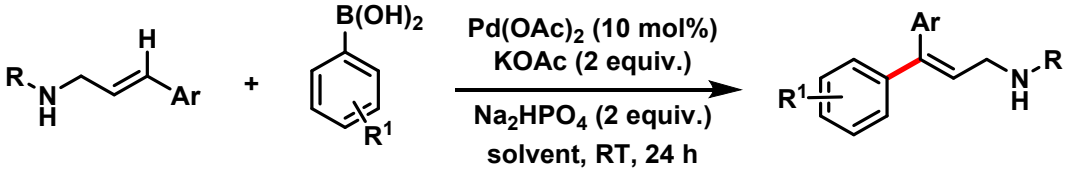
A. Optimization Controls:

Table *S*-1. Optimization of *E*-Selective γ-Arylation of *N*-*tert*-butylcinnamylamine.

In triplicate: A 7.5 mL vial was charged with $Pd(OAc)_2$ (3.4 mg, 0.015 mmol, 0.10 equiv), potassium acetate (30 mg, 0.3 mmol, 1 equiv), sodium biphosphate (43 mg, 0.30 mmol, 1.0 equiv), amine (0.15 mmol, 1 equiv), and boronic acid (0.3 mmol, 2 equiv), followed by addition of acetic acid (4 mL). The vial was then allowed to stir at 1200 rpm at RT (25 °C) for 24 h (this was controlled by setting the plate and monitoring with a thermometer and the built-in thermocouple). After the reaction, solvent was removed *in vacuo*, and the ^{1}HNMR yield measured using 1,1,2,2-tetrachloroethane as internal standard.

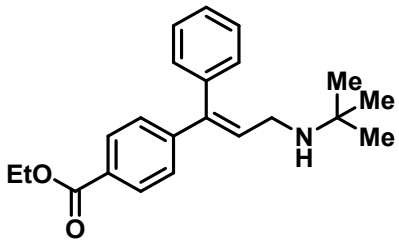
Entry	Reaction conditions	Yield(%)	Std. Dev. (%)
1	None	91	3
2	Without $Pd(OAc)_2$	0	0
3	$PdCl_2$	25	2
4	$Pd(CF_3CO_2)_2$	87	2
5	$Pd(PPh_3)_2Cl_2$	0	0
6	Without KOAc	69	6
7	Without Na_2HPO_4	70	4
8	LiOAc instead of KOAc	85	7
9	NaOAc instead of KOAc	75	5
10	$Mg(OAc)_2$•$4H_2O$	72	1
11	KH_2PO_4 instead of Na_2HPO_4	82	6
12	Cs_2CO_3 instead of Na_2HPO_4	81	7
13	$K_2S_2O_8$ instead of Na_2HPO_4	72	2
14	Na_3PO_4 instead of Na_2HPO_4	31	2
15	$KNaC_4H_4O_6$•$4H_2O$ instead of Na_2HPO_4	30	3
16	Stir at 300rpm	66	3
17	Stir at 600rpm	75	3
18	Stir at 900rpm	85	3
19	Stir at 1200rpm	90	5
20	HFIP: AcOH (0.8mL:0.2mL)	81	7
21	HFIP: AcOH (0.9mL:0.2mL)	84	3
22	HFIP: AcOH (0.5mL:0.5mL)	75	5

B. Procedure for Substrate Scope Study (Solvent AcOH-**Method A**, Solvent AcOH/HFIP-**Method B**):

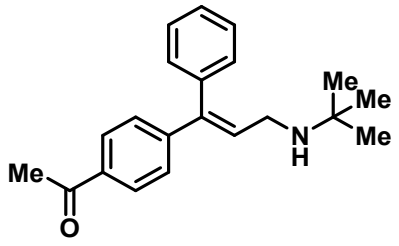


A 7.5 mL vial was charged with $Pd(OAc)_2$ (3.4 mg, 0.015 mmol, 0.10 equiv), potassium acetate (30 mg, 0.3 mmol, 1 equiv), Sodium biphosphate (43 mg, 0.30 mmol, 1.0 equiv), amine (0.15 mmol, 1 equiv), and boronic acid (0.3 mmol, 2 equiv.) in either acetic acid (**Method A**, 4 mL) or 1:3 acetic acid:HFIP (**Method B**, 1.2 mL). The vial was then allowed to stir at 1200 rpm at RT (25 °C) for 24 h (this was controlled by setting the plate and monitoring with a thermometer and the built-in thermocouple). After completion, the reaction mixture was basified using aq. sodium hydroxide solution (6 M). The reaction mixture was stirred for 15 minutes followed by extraction with dichloromethane (3 × 10 mL). The organic layer was washed with brine and dried over Na_2SO_4. The filtrate was concentrated *in vacuo* and then purified over silica-gel column chromatography.

C. Characterization Data:

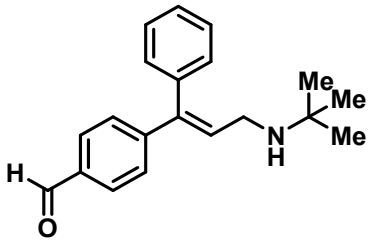


Ethyl (*E*)-4-(3-(*tert*-butylamino)-1-phenylprop-1-en-1-yl)benzoate (1a): Method A: Reaction mixture was chromatographed using 8:2 ethyl acetate/methanol. Product recovered as a colorless oil (123 mg, 81% yield), which gave spectral data consistent with that in the literature.[3] The *Z*/*E* ratio was determined as 1:20 from the NMR. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.18 – 7.15 (m, 2H), 6.29 (t, *J* = 6.9 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 3.27 (d, *J* = 6.8 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.05 (s, 9H).

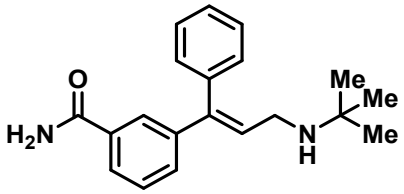


(*E*)-1-(4-(3-(*tert*-Butylamino)-1-phenylprop-1-en-1-yl)phenyl)ethan-1-one (1b): Method A: Reaction mixture was chromatographed using 8:2 ethyl acetate/methanol. Product recovered as a colorless oil (97 mg, 70% yield), which

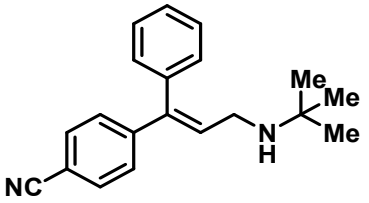
gave spectral data consistent with that in the literature.[3] The *Z*/*E* ratio was determined as *E*-exclusive from the NMR. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.39 – 7.35 (m, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.70 (t, *J* = 7.2 Hz, 1H), 3.57 (d, *J* = 5.2 Hz, 2H), 2.53 (s, 3H), 1.26 (s, 9H).



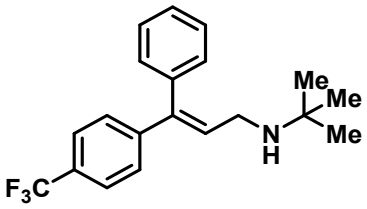
(*E*)-4-(3-(*tert*-Butylamino)-1-phenylprop-1-en-1-yl)benzaldehyde (1c): Method A: Reaction mixture was chromatographed using 8:2 ethyl acetate/methanol. Product recovered as a colorless oil (90 mg, 68% yield), which gave spectral data consistent with that in the literature.[3] The *Z*/*E* ratio was determined as *E*-exclusive from the NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.46 – 7.35 (m, 5H), 7.17 (d, *J* = 6.6 Hz, 2H), 6.36 (t, *J* = 6.7 Hz, 1H), 3.30 (d, *J* = 6.8 Hz, 2H), 1.06 (s, 9H).



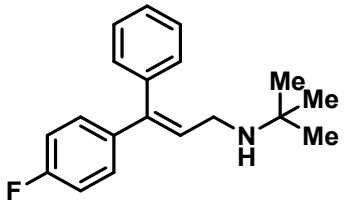
(*E*)-3-(3-(*tert*-Butylamino)-1-phenylprop-1-en-1-yl)benzamide (1d): Method A: Reaction mixture was chromatographed using 1:1 ethyl acetate/methanol. Product recovered as a yellow oil (55 mg, 40% yield), which gave spectral data consistent with that in the literature.[3] The *Z*/*E* ratio was determined as 1:>20 from the NMR. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.69 (d, *J* = 6.4 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.32 (q, *J* = 7.4 Hz, 3H), 7.16 (d, *J* = 7.2 Hz, 2H), 6.24 (t, *J* = 6.8 Hz, 1H), 6.17 (s, 1H), 5.89 (s, 1H), 3.27 (d, *J* = 6.8 Hz, 2H), 1.04 (s, 9H).



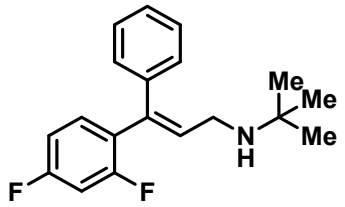
(*E*)-4-(3-(*tert*-Butylamino)-1-phenylprop-1-en-1-yl)benzonitrile (1e): Method A: Reaction mixture was chromatographed using 98:2 ethyl acetate/methanol. Product recovered as a yellow oil (69 mg, 53% yield). The *Z*/*E* ratio was determined as *E*-exclusive from the NMR. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.37 – 7.34 (m, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 6.29 (t, *J* = 7.0 Hz, 1H), 3.26 (d, *J* = 7.0 Hz, 2H), 1.04 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.7, 141.5, 138.5, 132.1, 132.0, 129.6, 128.6, 127.9, 127.9, 119.1, 110.6, 50.7, 42.0, 29.1. HRMS (ESI - MS): calcd. 291.1856 $[M+H]^+$ Found: 291.1877.



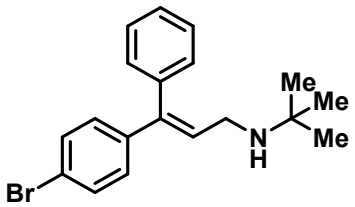
(*E*)-*N*-(*tert*-Butyl)-3-phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-amine (1f): Method A: Reaction mixture was chromatographed using 8:2 ethyl acetate/methanol. Product recovered as a colorless oil (121 mg, 81% yield), which gave spectral data consistent with that in the literature.[3] The *Z*/*E* ratio was determined as 1:>20 from the NMR. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 8.8 Hz, 3H), 7.17 (d, *J* = 7.0 Hz, 2H), 6.28 (t, *J* = 6.7 Hz, 1H), 3.29 (d, *J* = 6.8 Hz, 2H), 1.06 (s, 9H).



(*E*)-*N*-(*tert*-Butyl)-3-(4-fluorophenyl)-3-phenylprop-2-en-1-amine (1g): Method A: Reaction mixture was chromatographed using 98:2 ethyl acetate/methanol. Product recovered as a colorless oil (85 mg, 67% yield), which gave spectral data consistent with that in the literature.[3] The *Z*/*E* ratio was determined as 1:14 from the NMR. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (tt, *J* = 8.2, 1.6 Hz, 2H), 7.34 – 7.30 (m, 1H), 7.18 (ddd, *J* = 9.4, 8.4, 3.2 Hz, 4H), 6.93 (t, *J* = 8.8 Hz, 2H), 6.14 (t, *J* = 7.0 Hz, 1H), 3.25 (d, *J* = 7.0 Hz, 2H), 1.05 (s, 9H).

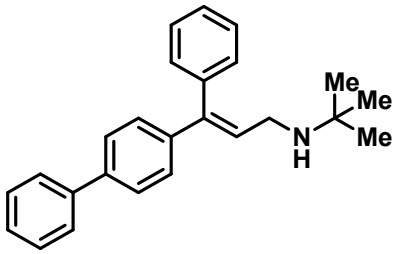


(*E*)-*N*-(*tert*-Butyl)-3-(2,4-difluorophenyl)-3-phenylprop-2-en-1-amine (1h): Method A: Reaction mixture was chromatographed using 8:2 ethyl acetate/methanol. Product recovered as a yellow oil (62 mg, 46% yield), which gave spectral data consistent with that in the literature.[3] The *Z*/*E* ratio was determined as 1:14 from the NMR. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.3 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.17 (d, *J* = 7.0 Hz, 2H), 7.14 (dd, *J* = 8.5, 6.8 Hz, 1H), 6.82 – 6.70 (m, 2H), 6.06 (t, *J* = 6.8 Hz, 1H), 3.35 (d, *J* = 6.9 Hz, 2H), 1.07 (s, 10H).

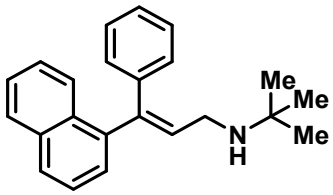


(*E*)-3-(4-Bromophenyl)-*N*-(*tert*-butyl)-3-phenylprop-2-en-1-amine (1i): Method B: Reaction mixture was chromatographed using 50:1 ethyl acetate/methanol. Product recovered as a colorless oil (40 mg, 26% yield), which gave spectral data consistent with that in the literature.[3] The *Z*/*E* ratio was determined as 1:>20 from the NMR. ^{1}H

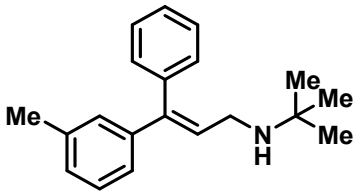
NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 5H), 7.16 (d, *J* = 7.0 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.21 (t, *J* = 6.8 Hz, 1H), 3.26 (d, *J* = 6.8 Hz, 2H), 1.06 (s, 9H).



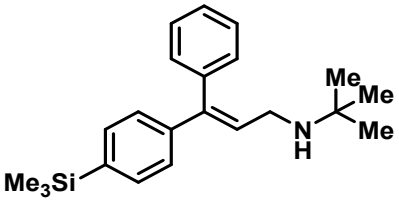
(*E*)-3-([1,1'-Biphenyl]-4-yl)-*N*-(tert-butyl)-3-phenylprop-2-en-1-amine (1j): Method B: Reaction mixture was chromatographed using 9:1 ethyl acetate/methanol. Product recovered as a colorless oil (97 mg, 63% yield), which gave spectral data consistent with that in the literature.[3] The *Z*/*E* ratio was determined as 1:16 from the NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.39 (dd, *J* = 14.6, 7.2 Hz, 4H), 7.32 (t, *J* = 8.4 Hz, 4H), 7.21 (d, *J* = 7.2 Hz, 2H), 6.26 (s, 1H), 3.26 (d, *J* = 6.8 Hz, 2H), 1.04 (s, 9H).



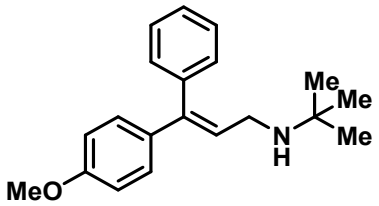
(*E*)-*N*-(*tert*-Butyl)-3-(naphthalen-1-yl)-3-phenylprop-2-en-1-amine (1k): Method A: Reaction mixture was chromatographed using 9:1 ethyl acetate/methanol. Product recovered as a yellow oil (61 mg, 43% yield), which gave spectral data consistent with that in the literature.[3] The *Z*/*E* ratio was determined as *E*-exclusive from the NMR. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.46 (d, *J* = 6.8 Hz, 1H), 7.38 – 7.26 (m, 7H), 7.24 – 7.21 (m, 1H), 6.27 (t, *J* = 7.2 Hz, 1H), 3.72 (d, *J* = 7.2 Hz, 2H), 1.18 (s, 9H).



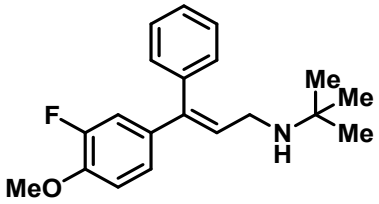
(*E*)-*N*-(*tert*-Butyl)-3-phenyl-3-(m-tolyl)prop-2-en-1-amine (1l): Method B: Reaction mixture was chromatographed using 50:1 ethyl acetate/methanol. Product recovered as a colorless oil (60 mg, 48% yield), which gave spectral data consistent with that in the literature.[3] The *Z*/*E* ratio was determined as 1:>20 from the NMR. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 7.0 Hz, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.07 (s, 1H), 7.06 – 7.00 (m, 2H), 6.22 (t, *J* = 6.8 Hz, 1H), 3.29 (d, *J* = 6.9 Hz, 2H), 2.28 (s, 3H), 1.07 (s, 9H).



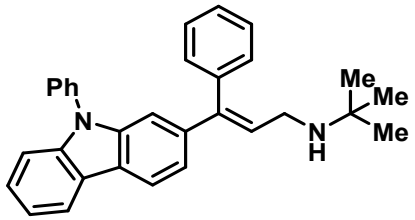
(*E*)-*N*-(*tert*-Butyl)-3-phenyl-3-(4-(trimethylsilyl)phenyl)prop-2-en-1-amine (1m): Method A: Reaction mixture was chromatographed using 1:1 ethyl acetate/hexanes. Product recovered as a yellow oil (96 mg, 63% yield). The *Z*/*E* ratio was determined as 1:7 from the NMR. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.32 (ddd, *J* = 7.4, 3.8, 1.2 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 7.0 Hz, 2H), 6.24 (t, *J* = 7.0 Hz, 1H), 3.25 (d, *J* = 7.0 Hz, 2H), 1.04 (s, 9H), 0.24 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.0, 142.5, 139.8, 139.4, 133.3, 129.8, 128.5, 128.3, 127.3, 126.7, 50.8, 42.1, 29.1, -1.0. HRMS (ESI - MS): calcd. 338.2299 $[M+H]^+$ Found: 338.2318.



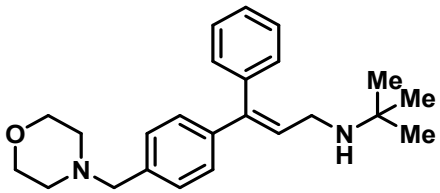
(*E*)-*N*-(*tert*-Butyl)-3-(4-methoxyphenyl)-3-phenylprop-2-en-1-amine (1n): Method A: Reaction mixture was chromatographed using 2:8 ethyl acetate/hexane. Product recovered as a yellow oil (100 mg, 75% yield), which gave spectral data consistent with that in the literature.[3] The *Z*/*E* ratio was determined as 1:16 from the NMR. ^{1}H NMR. (600 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 5H), 6.79 (d, *J* = 8.8 Hz, 2H), 6.13 (t, *J* = 7.0 Hz, 1H), 3.78 (s, 3H), 3.24 (d, *J* = 7.0 Hz, 2H), 1.05 (s, 9H).



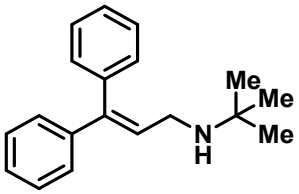
(*E*)-*N*-(*tert*-Butyl)-3-(3-fluoro-4-methoxyphenyl)-3-phenylprop-2-en-1-amine (1o): Method A: Reaction mixture was chromatographed using 95:5 ethyl acetate/methanol. Product recovered as a yellow oil (82 mg, 58% yield). The *Z*/*E* ratio was determined as *E*-exclusive from the NMR. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 7.0 Hz, 2H), 6.97 (dd, *J* = 12.9, 2.1 Hz, 1H), 6.94 (d, *J* = 8.6 Hz, 1H), 6.83 (t, *J* = 8.6 Hz, 1H), 6.14 (t, *J* = 7.0 Hz, 1H), 3.86 (s, 3H), 3.23 (d, *J* = 7.0 Hz, 2H), 1.04 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.15 (d, *J* = 244.9 Hz), 147.03 (d, *J* = 11.0 Hz), 139.2, 135.5, 129.7, 128.5, 127.6, 123.21 (d, *J* = 3.1 Hz), 115.2, 115.14 (d, *J* = 19.1 Hz), 112.9, 56.4, 41.8, 28.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -132.7. HRMS (ESI - MS): calcd. 314.1915 $[M-H]^+$ Found: 314.1926.



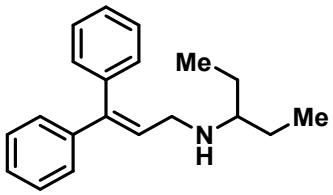
(*E*)-*N*-(*tert*-Butyl)-3-phenyl-3-(9-phenyl-9H-carbazol-2-yl)prop-2-en-1-amine (1p): Method A: Reaction mixture was chromatographed using 7:3 ethyl acetate/methanol. Product recovered as a pale-yellow liquid (108 mg, 56% yield). The *Z*/*E* ratio was determined as *E*-exclusive from the NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.7 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.66 – 7.51 (m, 4H), 7.50 – 7.30 (m, 8H), 7.30 – 7.18 (m, 2H, also contains $CDCl_3$ peak), 7.00 (d, *J* = 8.2 Hz, 1H), 6.21 (t, *J* = 7.0 Hz, 1H), 3.26 (d, *J* = 7.0 Hz, 2H), 1.03 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.9, 141.6, 141.2, 140.8, 140.2, 137.7, 130.1, 129.8, 128.3, 128.3, 127.6, 127.3, 126.0, 123.3, 122.7, 120.6, 120.4, 120.1, 119.8, 109.9, 108.2, 50.6, 42.1, 29.2. HRMS (ESI - MS): calcd. 431.2482 $[M+H]^+$ Found: 431.2482.



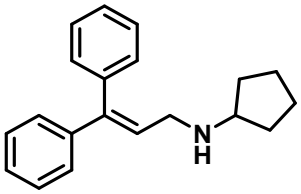
(*E*)-*N*-(*tert*-Butyl)-3-(4-(morpholinomethyl)phenyl)-3-phenylprop-2-en-1-amine (1q): Method A: Reaction mixture was chromatographed using 8:2 ethyl acetate/methanol. Product recovered as a pale yellow oil (85 mg, 52% yield). The *Z*/*E* ratio was determined as *E*-exclusive from the NMR. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.3 Hz, 2H), 7.32 (t, *J* = 6.0 Hz, 1H), 7.23–7.16 (m, 6H), 6.20 (t, *J* = 7.0 Hz, 1H), 3.70 (t, *J* = 4.4 Hz, 4H), 3.46 (s, 2H), 3.23 (d, *J* = 7.0 Hz, 2H), 2.43 (s, 4H), 1.03 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.7, 141.2, 139.8, 136.8, 129.8, 129.1, 128.3, 127.3, 127.3, 67.2, 63.7, 53.8, 50.7, 42.0, 29.2. HRMS (ESI - MS): calcd. 365.2587 $[M+H]^+$ Found: 365.2601.



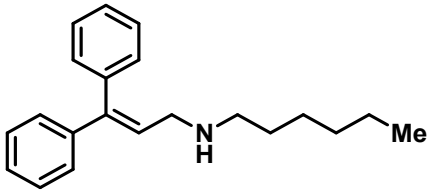
***N*-(*tert*-Butyl)-3,3-diphenylprop-2-en-1-amine (2a):** Method A: Reaction mixture was chromatographed using 19:1 ethyl acetate/methanol. Product recovered as a colorless oil (91 mg, 76% yield), which gave spectral data consistent with that in the literature.[3] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.2 Hz, 2H), 7.34 – 7.30 (m, 1H), 7.28 – 7.21 (m, 5H), 7.19 (d, *J* = 7.8 Hz, 2H), 6.20 (t, *J* = 6.8 Hz, 1H), 3.25 (d, *J* = 6.8 Hz, 2H), 1.04 (s, 9H).



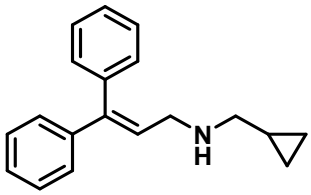
***N*-(3,3-Diphenylallyl)pentan-3-amine (2b):** Method A: Reaction mixture was chromatographed using 1:9 ethyl acetate/methanol. Product recovered as a yellow oil (89 mg, 71% yield), which gave spectral data consistent with that in the literature.[3] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.29 – 7.20 (m, 5H), 7.18 (d, *J* = 7.0 Hz, 2H), 6.19 (t, *J* = 7.0 Hz, 1H), 3.27 (d, *J* = 6.9 Hz, 2H), 2.35 (t, *J* = 6.0 Hz, 1H), 1.58 (s, 1H), 1.41 – 1.30 (m, 4H), 0.83 (t, *J* = 7.6 Hz, 6H).



***N*-(3,3-Diphenylallyl)cyclopentanamine (2c):** Method A: Reaction mixture was chromatographed using 9:1 ethyl acetate/methanol. Product recovered as a yellow oil (84 mg, 67% yield), which gave spectral data consistent with that in the literature.[3] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.2 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.29 – 7.21 (m, 5H), 7.20 – 7.16 (m, 2H), 6.21 (t, *J* = 6.8 Hz, 1H), 3.31 (d, *J* = 6.8 Hz, 2H), 3.07 (p, *J* = 6.8 Hz, 1H), 1.78 – 1.74 (m, 2H), 1.70 – 1.61 (m, 2H), 1.56 – 1.44 (m, 2H), 1.29 – 1.26 (m, 2H).

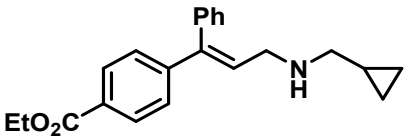


***N*-(3,3-Diphenylallyl)hexan-1-amine (2d):** Method A: Reaction mixture was chromatographed using 50:1 ethyl acetate/methanol. Product recovered as a colorless oil (55 mg, 42% yield), which gave spectral data consistent with that in the literature.[3] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.6 Hz, 2H), 7.32 (td, *J* = 7.0, 1.2 Hz, 1H), 7.29 – 7.21 (m, 5H), 7.17 (d, *J* = 7.8 Hz, 2H), 6.20 (t, *J* = 6.8 Hz, 1H), 3.33 (d, *J* = 6.8 Hz, 2H), 2.58 (t, *J* = 7.2 Hz, 2H), 1.44 (d, *J* = 6.4 Hz, 2H), 1.27 (d, *J* = 11.6 Hz, 6H), 0.87 (t, *J* = 5.9 Hz, 3H).

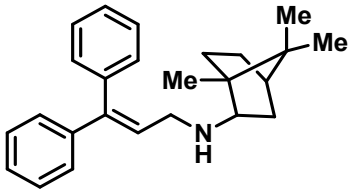


***N*-(Cyclopropylmethyl)-3,3-diphenylprop-2-en-1-amine (2e):** Method A: Reaction mixture was chromatographed using 9:1 ethyl acetate/methanol. Product recovered as a yellow oil (84 mg, 71% yield), which gave spectral data consistent with that in the literature.[3] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.2 Hz, 2H), 7.32 – 7.28 (m, 1H), 7.27

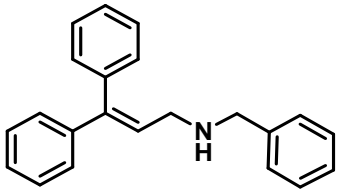
– 7.19 (m, 5H), 7.17 – 7.13 (m, 2H), 6.18 (t, *J* = 6.8 Hz, 1H), 3.32 (d, *J* = 6.8 Hz, 1H), 2.42 (d, *J* = 6.8 Hz, 2H), 2.00 (s, 1H), 0.92 – 0.86 (m, 1H), 0.46 – 0.39 (m, 2H), 0.08 – 0.03 (m, 2H).



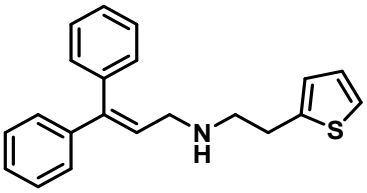
Ethyl (*E*)-4-(3-((cyclopropylmethyl)amino)-1-phenylprop-1-en-1-yl)benzoate (2f): Method A: Reaction mixture was chromatographed using 1:1 ethyl acetate/hexanes. Product recovered as a yellow oil (110 mg, 73% yield). The *Z*/*E* ratio was determined as 1:>20 from the NMR. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.33 (m, 3H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 6.4 Hz, 2H), 6.51 (t, *J* = 6.8 Hz, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 3.65 (d, *J* = 6.8 Hz, 2H), 2.64 (d, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.02 – 0.93 (m, 1H), 0.42 (d, *J* = 7.6 Hz, 2H), 0.18 (d, *J* = 4.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.4, 146.5, 145.3, 137.9, 129.9, 129.6, 129.6, 128.8, 128.3, 127.6, 61.1, 51.7, 45.8, 14.5, 7.8, 4.3. HRMS (ESI - MS): calcd. 336.1958 $[M+H]^+$ Found: 336.1977.



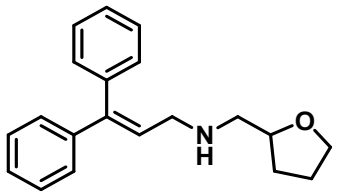
(2*R*,4*S*)-*N*-(3,3-Diphenylallyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine (2g): Method B: Reaction mixture was chromatographed using 99:1 ethyl acetate/methanol. Product recovered as a colorless oil (71 mg, 46% yield), which gave spectral data consistent with that in the literature.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (q, *J* = 6.4 Hz, 3H), 7.33 – 7.20 (m, 5H), 7.12 (d, *J* = 6.2 Hz, 2H), 6.59 (dd, *J* = 9.0, 5.8 Hz, 1H), 3.90 (dd, *J* = 13.8, 5.7 Hz, 1H), 3.81 – 3.55 (m, 2H), 3.01 (d, *J* = 7.5 Hz, 1H), 1.96 (dd, *J* = 11.5, 7.1 Hz, 1H), 1.64 (dd, *J* = 20.0, 7.9 Hz, 4H), 1.42 (d, *J* = 9.6 Hz, 1H), 1.32 – 1.21 (m, 1H), 1.07 (s, 3H), 0.83 (s, 3H), 0.75 (s, 3H).



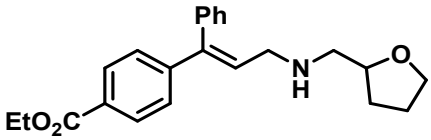
***N*-Benzyl-3,3-diphenylprop-2-en-1-amine (2h):** Method A: Reaction mixture was chromatographed using 8:2 ethyl acetate/methanol. Product recovered as a yellow oil (94 mg, 70% yield), which gave spectral data consistent with that in the literature.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 4H), 7.30 – 7.24 (m, 9H), 7.17 (dd, *J* = 7.8, 1.6 Hz, 2H), 6.23 (t, *J* = 6.8 Hz, 1H), 3.76 (s, 2H), 3.37 (d, *J* = 6.8 Hz, 2H).



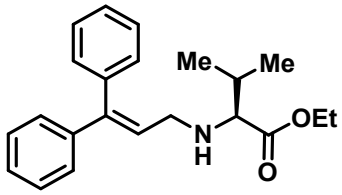
3,3-Diphenyl-*N*-(2-(thiophen-2-yl)ethyl)prop-2-en-1-amine (2i): Method A: Reaction mixture was chromatographed using 3:7 ethyl acetate/methanol. Product recovered as a yellow oil (43 mg, 30% yield), which gave spectral data consistent with that in the literature.[3] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.2 Hz, 2H), 7.32 (dd, *J* = 8.3, 6.2 Hz, 1H), 7.29 – 7.20 (m, 5H), 7.13 (dd, *J* = 8.3, 6.6 Hz, 3H), 6.92 (dd, *J* = 5.0, 3.4 Hz, 1H), 6.79 (d, *J* = 2.8 Hz, 1H), 6.16 (t, *J* = 6.8 Hz, 1H), 4.01 (s, 2H), 3.38 (d, *J* = 6.8 Hz, 2H), 3.00 (t, *J* = 6.8 Hz, 2H), 2.91 (t, *J* = 6.8 Hz, 2H).



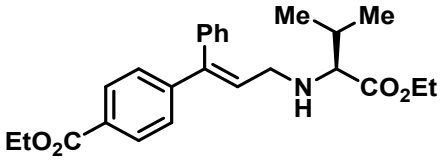
3,3-Diphenyl-*N*-((tetrahydrofuran-2-yl)methyl)prop-2-en-1-amine (2j): Method A: Reaction mixture was chromatographed using 7:3 ethyl acetate/methanol. Product recovered as a yellow oil (88 mg, 67% yield), which gave spectral data consistent with that in the literature.[3] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.2 Hz, 2H), 7.32 – 7.28 (m, 1H), 7.27 – 7.19 (m, 5H), 7.17 – 7.13 (m, 2H), 6.17 (t, *J* = 6.8 Hz, 1H), 3.94 (dt, *J* = 10.8, 3.6 Hz, 1H), 3.81 (dd, *J* = 15.0, 6.8 Hz, 1H), 3.71 (dd, *J* = 14.6, 7.6 Hz, 1H), 3.33 (d, *J* = 6.8 Hz, 1H), 2.65 (dd, *J* = 12.0, 3.7 Hz, 1H), 2.59 (dd, *J* = 12.0, 7.8 Hz, 1H), 1.96 – 1.81 (m, 4H), 1.50 (ddd, *J* = 15.7, 12.0, 7.6 Hz, 1H).



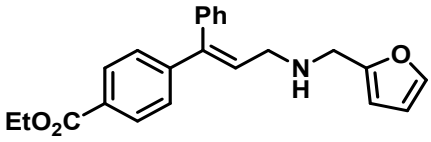
Ethyl (*E*)-4-(1-phenyl-3-(((tetrahydrofuran-2-yl)methyl)amino)prop-1-en-1-yl)benzoate (2k): Method A: Reaction mixture was chromatographed using 2:8 ethyl acetate/hexanes. Product recovered as a yellow oil (84 mg, 61% yield). The *Z*/*E* ratio was determined as 1:>20 from the NMR. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 2H), 7.33 – 7.29 (m, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 7.0 Hz, 2H), 6.28 (t, *J* = 6.7 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.95 (ddd, *J* = 10.9, 7.2, 3.6 Hz, 1H), 3.80 (dd, *J* = 14.8, 6.8 Hz, 1H), 3.70 (dd, *J* = 14.8, 7.2 Hz, 1H), 3.36 (d, *J* = 6.7 Hz, 2H), 2.67 (dd, *J* = 12.0, 3.6 Hz, 1H), 2.59 (dd, *J* = 12.0, 7.9 Hz, 1H), 1.99–1.79 (m, 4H), 1.53 – 1.44 (m, 1H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.5, 146.5, 142.7, 138.9, 129.7, 129.6, 129.5, 129.1, 128.4, 127.6, 127.3, 78.0, 67.9, 60.9, 53.8, 48.6, 29.3, 25.8, 14.4. HRMS (ESI - MS): calcd. 366.2064 $[M+H]^+$ Found: 366.2086.



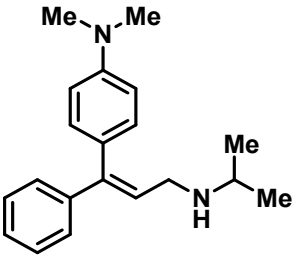
Ethyl (3,3-diphenylallyl)-*L*-valinate (2l): Method A: Reaction mixture was chromatographed using 1:19 ethyl acetate/hexanes. Product recovered as a yellow oil (94 mg, 62% yield), which gave spectral data consistent with that in the literature.[3] Conversion to the Mosher amide suggested >99% *ee* of the product. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.2 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.27 – 7.20 (m, 5H), 7.14 (d, *J* = 7.0 Hz, 2H), 6.11 (t, *J* = 6.8 Hz, 1H), 4.21 – 3.95 (m, 2H), 3.30 (dd, *J* = 13.6, 6.8 Hz, 1H), 3.16 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.95 (d, *J* = 5.8 Hz, 1H), 2.45 (s, 1H), 1.96 – 1.82 (m, 1H), 1.16 (t, *J* = 7.2 Hz, 3H), 0.92 (dd, *J* = 6.8, 3.4 Hz, 6H).



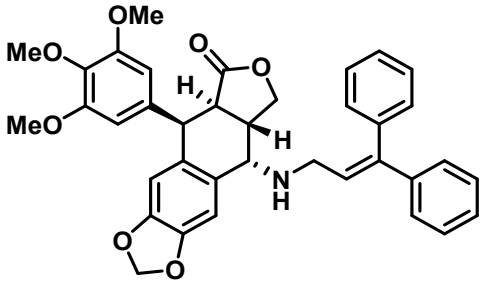
Ethyl (S,E)-4-(3-((1-ethoxy-3-methyl-1-oxobutan-2-yl)amino)-1-phenylprop-1-en-1-yl)benzoate (2m): Method A: Reaction mixture was chromatographed using 5:95 ethyl acetate/hexanes. Product recovered as a yellow oil (100 mg, 54% yield). The *Z*/*E* ratio was determined E exclusive from the NMR. Conversion to the Mosher amide suggested >99% *ee* of the product. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.34 – 7.30 (m, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 7.0 Hz, 2H), 6.22 (t, *J* = 6.8 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 4.16 – 4.00 (m, 2H), 3.32 (dd, *J* = 14.0, 6.8 Hz, 1H), 3.19 (dd, *J* = 14.0, 7.0 Hz, 1H), 2.93 (d, *J* = 5.8 Hz, 1H), 1.89 (dd, *J* = 13.0, 6.6 Hz, 1H), 1.67 (s, 1H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.17 (t, *J* = 7.2 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.3, 166.6, 146.6, 142.9, 139.0, 129.9, 129.8, 129.5, 129.2, 128.4, 127.6, 127.3, 66.9, 61.0, 60.5, 47.7, 31.8, 19.3, 18.7, 14.5, 14.4, 0.1. HRMS (ESI - MS): calcd. 410.2326 $[M+H]^+$ Found: 410.2323.



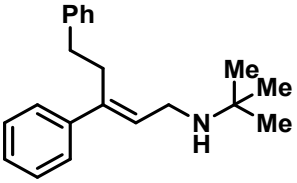
Ethyl (*E*)-4-(3-((furan-2-ylmethyl)amino)-1-phenylprop-1-en-1-yl)benzoate (2n): Method A: Reaction mixture was chromatographed using 2:8 ethyl acetate/hexanes. Product recovered as a yellow oil (94 mg, 58% yield). The *Z*/*E* ratio was determined as 1:>20 from the NMR. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.31 (m, 4H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 6.8 Hz, 2H), 6.27 (t, *J* = 6.8 Hz, 2H), 6.07 (d, *J* = 3.0 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 3.75 (s, 2H), 3.36 (d, *J* = 6.8 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6, 153.6, 146.6, 143.0, 141.9, 139.0, 129.8, 129.5, 129.3, 128.4, 127.6, 127.4, 110.2, 107.1, 61.0, 47.8, 45.8, 29.8, 14.4. HRMS (ESI - MS): calcd. 362.1751 $[M-H]^+$ Found: 362.1750.



(*Z*)-4-(3-(isopropylamino)-1-phenylprop-1-en-1-yl)-N,N-dimethylaniline (2o): Method A: Reaction mixture was chromatographed using 1:9 ethyl acetate/methanol. Product recovered as a faint purple oil (87 mg, 66% yield). The *Z*/*E* ratio was determined as 1:3 from the NMR. ^{1}H NMR (600 MHz, $CDCl_3$) (major + minor isomer) δ 7.36 (t, *J* = 7.2 Hz, 2H), 7.33 – 7.30 (m, 1H), 7.29 – 7.21 (m, 6H), 7.20 – 7.17 (m, 2H), 7.13 (d, *J* = 8.9 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.71 (d, *J* = 8.8 Hz, 2H), 6.61 (d, *J* = 8.9 Hz, 2H), 6.15 (t, *J* = 7.0 Hz, 1H), 6.11 (t, *J* = 6.9 Hz, 1H), 3.49 (d, *J* = 6.8 Hz, 2H), 3.36 (d, *J* = 7.2 Hz, 2H), 3.01 (dd, *J* = 14.2, 4.0 Hz, 1H), 2.98 (s, 9H), 2.95 (dd, *J* = 8.6, 4.8 Hz,12H), 2.92 (s, 6H), 1.10 (d, *J* = 6.4 Hz, 9H), 1.08 (d, *J* = 6.4 Hz, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.1, 147.9, 142.1, 130.7, 129.7, 128.5, 128.5, 128.2, 128.0, 127.9, 126.1, 118.6, 112.1, 112.0, 60.6, 48.3, 43.5, 40.5, 40.5, 23.5, 19.6, 19.5, 14.3. HRMS (ESI - MS): calcd. 295.2164 $[M-H]^+$ Found: 295.2189.

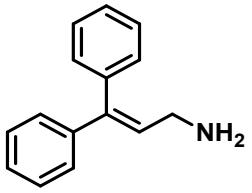


(5*R*,5a*R*,8a*S*,9*S*)-9-((3,3-Diphenylallyl)amino)-5-(3,4,5-trimethoxyphenyl)-5,8,8a,9-tetrahydrofuro[3',4':6,7]naphtho[2,3-d][1,3]dioxol-6(5a*H*)-one (2p): Method B: Reaction mixture was chromatographed using 7:3 ethyl acetate/hexanes. Product recovered as a colorless oil (152 mg, 56% yield), which gave spectral data consistent with that in the literature.[3] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.36 – 7.31 (m, 4H), 7.30 – 7.27 (m, 2H), 7.09 (s, 1H), 6.54 (s, 1H), 6.36 (s, 1H), 6.19 (s, 2H), 5.94 (d, *J* = 1.2 Hz, 1H), 5.91 (d, *J* = 1.2 Hz, 1H), 4.73 (d, *J* = 11.4 Hz, 1H), 4.64 (d, *J* = 11.4 Hz, 1H), 4.58 (d, *J* = 5.6 Hz, 1H), 4.38 (d, *J* = 3.0 Hz, 1H), 3.98 – 3.87 (m, 2H), 3.78 (s, 3H), 3.71 (s, 6H), 3.38 (dd, *J* = 14.0, 5.5 Hz, 1H), 2.80 – 2.69 (m, 1H).

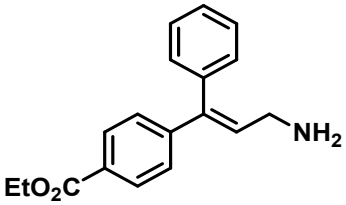


(*E*)-*N*-(*tert*-Butyl)-3,5-diphenylpent-2-en-1-amine (2q): Method A: Reaction mixture was chromatographed using 99:1 ethyl acetate/methanol. Product recovered as a yellow oil (120 mg, 41% yield). The *Z*/*E* ratio was determined as 1:20 from the NMR. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.30–7.26 (m,

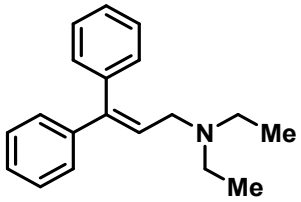
3H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 7.4 Hz, 2H), 5.80 (t, *J* = 7.0 Hz, 1H), 3.11 (d, *J* = 7.0 Hz, 2H), 2.83 (t, *J* = 7.4 Hz, 2H), 2.63 (t, *J* = 7.4 Hz, 2H), 1.07 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.3, 141.9, 128.8, 128.5, 128.5, 127.2, 126.7, 126.1, 51.1, 40.5, 34.7, 32.1, 28.8. HRMS (ESI - MS): calcd. 294.2216 $[M+H]^+$ Found: 294.2218.



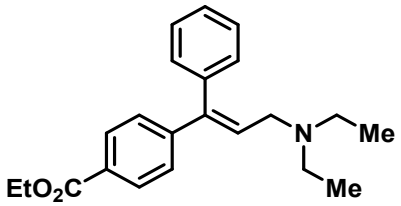
3,3-Diphenylprop-2-en-1-amine (3a): Method A: Reaction mixture was chromatographed using 2:8 ethyl acetate/hexanes. Product recovered as a yellow oil (64 mg, 68% yield), which gave spectral data consistent with that in the literature.[1] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (ddd, *J* = 7.5, 4.4, 1.2 Hz, 2H), 7.34 – 7.31 (m, 1H), 7.30 – 7.22 (m, 3H, also contains $CDCl_3$ peak), 7.17 (dd, *J* = 8.1, 1.2 Hz, 2H), 6.16 (t, *J* = 7.0 Hz, 1H), 3.36 (d, *J* = 7.0 Hz, 2H), 1.26 (br s, 2H).



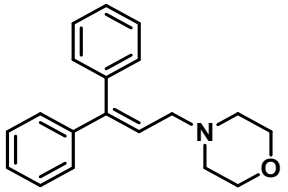
Ethyl (*E*)-4-(3-amino-1-phenylprop-1-en-1-yl)benzoate (3b): Method A: Reaction mixture was chromatographed using 2:8 ethyl acetate/hexanes. Product recovered as brown oil (95 mg, 62% yield). The *Z*/*E* ratio was determined as 1:7 from the ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.38 (dd, *J* = 8.0, 6.4 Hz, 2H), 7.36 – 7.33 (m, 1H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.16 – 7.12 (m, 2H), 6.25 (t, *J* = 6.9 Hz, 1H), 4.36 (dd, *J* = 14.3, 7.1 Hz, 2H), 3.39 (d, *J* = 6.9 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.5, 145.9, 144.4, 138.3, 129.8, 129.7, 129.6, 128.7, 128.1, 127.6, 126.9, 61.1, 40.1, 14.5. HRMS (ESI - MS): calcd. 282.1489 $[M+H]^+$ Found: 282.1410



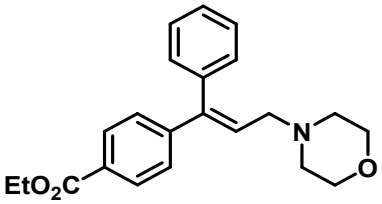
***N*,*N*-Diethyl-3,3-diphenylprop-2-en-1-amine (3c):** Method A: Reaction mixture was chromatographed using 98:2 ethyl acetate/methanol. Product recovered as a yellow oil (77 mg, 64% yield), which gave spectral data consistent with that in the literature.[1] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41–7.36 (m, 2H), 7.33 (ddd, *J* = 8.6, 4.4, 1.2 Hz, 1H), 7.29 – 7.22 (m, 5H, also contains $CHCl_3$ peak), 7.15 (dd, *J* = 8.1, 1.2 Hz, 2H), 6.25 (t, *J* = 6.8 Hz, 1H), 3.27 (d, *J* = 6.8 Hz, 2H), 2.63 (q, *J* = 7.2 Hz, 4H), 0.99 (s, 6H).



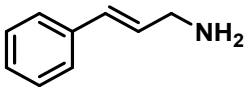
Ethyl (*E*)-4-(3-(diethylamino)-1-phenylprop-1-en-1-yl)benzoate (3d): Method A: Reaction mixture was chromatographed using 99:1 ethyl acetate/methanol. Product recovered as a brown oil (102 mg, 64% yield). The *Z*/*E* ratio was determined as *E*-exclusive from the NMR. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 6.8 Hz, 2H), 6.33 (t, *J* = 6.6 Hz, 1H), 4.41 – 4.31 (m, 3H), 3.18 (d, *J* = 6.6 Hz, 2H), 2.54 (q, *J* = 7.2 Hz, 4H), 1.38 (t, *J* = 7.2 Hz, 4H), 0.97 (t, *J* = 7.2 Hz, 7H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6, 146.7, 142.8, 139.2, 129.9, 129.6, 129.2, 128.5, 127.6, 127.3, 61.0, 51.9, 47.2, 14.5, 11.9. HRMS (ESI - MS): calcd. 338.2115 $[M-H]^+$ Found: 338.2093.



4-(3,3-Diphenylallyl)morpholine (3e): Method A: Reaction mixture was chromatographed using 99:1 ethyl acetate/methanol. Product recovered as a yellow oil (92 mg, 73% yield), which gave spectral data consistent with that in the literature.[5] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (ddd, *J* = 7.4, 4.2, 1.2 Hz, 2H), 7.33 (ddd, *J* = 8.6, 4.4, 1.2 Hz, 1H), 7.29 – 7.22 (m, 5H, also contains $CDCl_3$ peak), 7.16 (dd, *J* = 8.1, 1.2 Hz, 2H), 6.21 (t, *J* = 6.8 Hz, 1H), 3.72 (t, *J* = 4.6 Hz, 4H), 3.08 (d, *J* = 6.8 Hz, 2H), 2.46 (s, 4H).

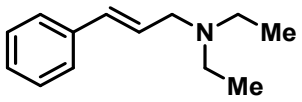


Ethyl (*E*)-4-(3-morpholino-1-phenylprop-1-en-1-yl)benzoate (3f): Method A: Reaction mixture was chromatographed using 3:7 ethyl acetate/hexanes. Product recovered as a yellow oil (79 mg, 50% yield). The *Z*/*E* ratio was determined as 1:>20 from the NMR. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 7.0 Hz, 2H), 6.30 (t, *J* = 6.8 Hz, 1H), 4.36 (q, *J* = 7.0 Hz, 2H), 3.72 (t, *J* = 4.4 Hz, 4H), 3.09 (d, *J* = 6.6 Hz, 2H), 2.45 (s, 4H), 1.38 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6, 146.4, 143.9, 139.0, 129.9, 129.6, 129.4, 128.6, 127.9, 127.7, 127.3, 67.1, 61.1, 57.8, 53.9, 14.5. HRMS (ESI - MS): calcd. 352.1907 $[M+H]^+$ Found: 352.1932.

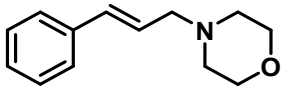


(*E*)-3-Phenylprop-2-en-1-amine (4a): Method A: Reaction mixture was chromatographed using 95:5 ethyl acetate/methanol. Product recovered as a yellow oil (28 mg, 47% yield), which gave spectral data consistent with that

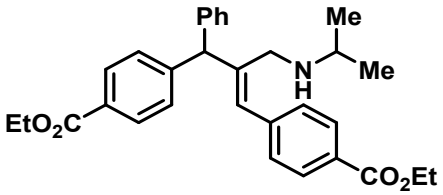
in the literature.[4] The *Z*/*E* ratio was determined as E-exclusive from the NMR. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 6.50 (d, *J* = 15.8 Hz, 1H), 6.33 (dt, *J* = 15.8, 5.8 Hz, 1H), 3.48 (d, *J* = 5.8 Hz, 2H), 1.22 (s, 2H).



(*E*)-*N*,*N*-Diethyl-3-phenylprop-2-en-1-amine (4b): Method A: Reaction mixture was chromatographed using 8:2 ethyl acetate/hexanes. Product recovered as brown oil (57 mg, 67% yield), which gave spectral data consistent with that in the literature.[3] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.20 (m, 1H), 6.51 (d, *J* = 15.8 Hz, 1H), 6.30 (dt, *J* = 15.8, 6.8 Hz, 1H), 3.26 (dd, *J* = 6.8, 1.4 Hz, 2H), 2.58 (q, *J* = 7.2 Hz, 4H), 1.06 (t, *J* = 7.2 Hz, 6H).



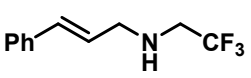
4-Cinnamylmorpholine (4c): Method A: Reaction mixture was chromatographed using 1:1 ethyl acetate/hexanes. Product recovered as a colorless oil (64 mg, 70% yield), which gave spectral data consistent with that in the literature.[3] The *Z*/*E* ratio was determined as *E*-exclusive from the NMR. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 6.54 (d, *J* = 15.8 Hz, 1H), 6.26 (dt, *J* = 15.8, 6.8 Hz, 1H), 3.74 (t, *J* = 4.6 Hz, 4H), 3.16 (dd, *J* = 6.8, 0.8 Hz, 2H), 2.51 (s, 4H).



Diethyl 4,4'-(2-((isopropylamino)methyl)-3-phenylprop-1-ene-1,3-diyl)(*Z*)-dibenzoate (5): Method A: Reaction mixture was chromatographed using 2:8 ethyl acetate/hexanes. Product recovered as a yellow oil (90 mg, 41% yield). Alkene was observed to be *Z*-selective based on the NMR, consistent with previous literature.[6] ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 11.2, 8.2 Hz, 4H), 7.39 – 7.29 (m, 6H), 7.28 – 7.21 (m, 3H), 6.15 (s, 1H), 5.39 (s, 1H), 4.37 (q, *J* = 7.2 Hz, 4H), 3.33 (s, 2H), 2.66 (s, 1H), 1.39 (dt, *J* = 12.9, 6.6 Hz, 6H), 0.93 (d, *J* = 3.6 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 166.6, 147.7, 142.0, 141.4, 129.8, 129.7, 129.6, 129.6, 129.0, 128.9, 128.8, 128.8, 127.0, 61.1, 61.1, 56.3, 49.0, 47.1, 29.9, 22.9, 14.5. HRMS (ESI - MS): calcd. 486.2639 $[M+H]^+$ Found: 486.2756.

D. Inefficient Substrates:

Cinnamyl amine substrates:



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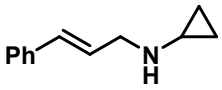

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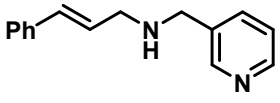

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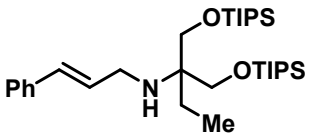

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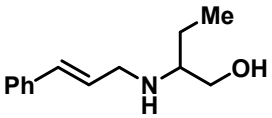

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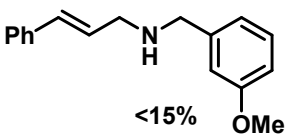

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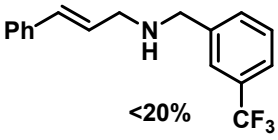

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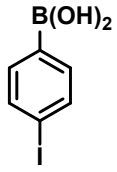

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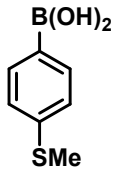

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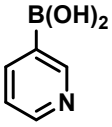

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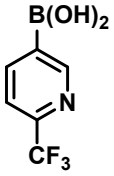

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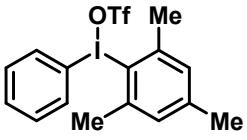

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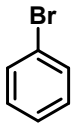

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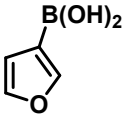

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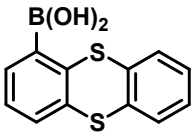

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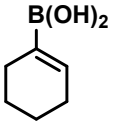

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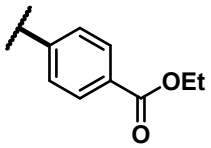
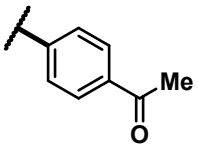
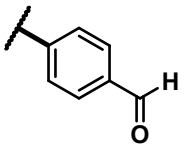
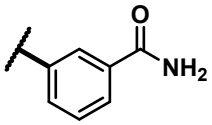
E. Comparison Table of Stereoselectivity with ref 3:

				
This work	**E/Z= 20:1**	**Only E Observed**	**Only E Observed**	**E/Z= >20:1**
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	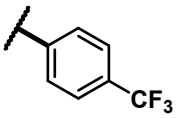	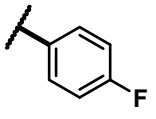	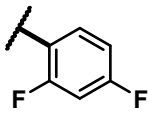	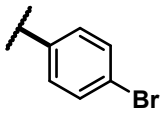
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	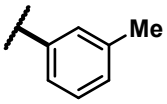	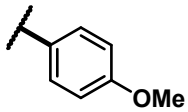	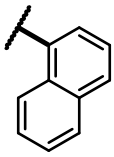	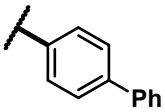
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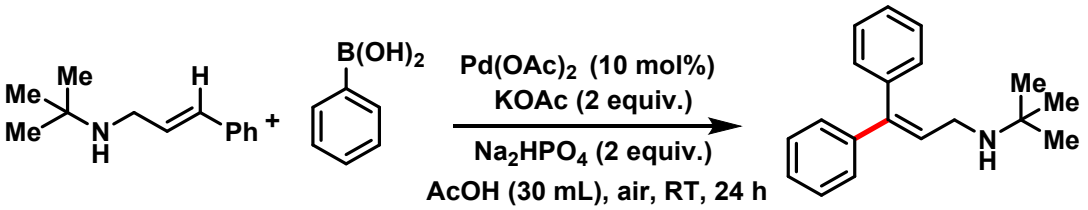
Previous report (ref.2)	**E/Z= 10:1**	**E/Z= 2:1**	**E/Z= 10:1**	**E/Z= 6:1**

4. Reaction Scale-up:



A 100 mL round bottom flask was charged with $Pd(OAc)_2$ (100.8 mg, 0.45 mmol, 0.10 equiv), potassium acetate (883 mg, 9.0 mmol, 2 equiv), disodium phosphate (1277 mg, 9.0 mmol, 2.0 equiv), phenyl boronic acid (1097 mg, 4.5 mmol, 2.0 equiv), and allylamine (840 mg, 4.5 mmol, 1.0 equiv) in 30 mL of acetic acid. The reaction mixture was stirred for 24 h at room temperature. After reaction completion, mixture was basified with sodium hydroxide solution (6 M). The reaction mixture was stirred for 10 minutes followed by extraction with dichloromethane (3 × 20 mL). The organic layer was washed with brine and dried over Na_2SO_4. The solvent was concentrated *in vacuo,* and the reaction mixture purified over silica-gel column chromatography using 19:1 ethyl acetate/methanol to produce a colorless oil in 57%.

5. Analytical Data of Pd Nano Particles:

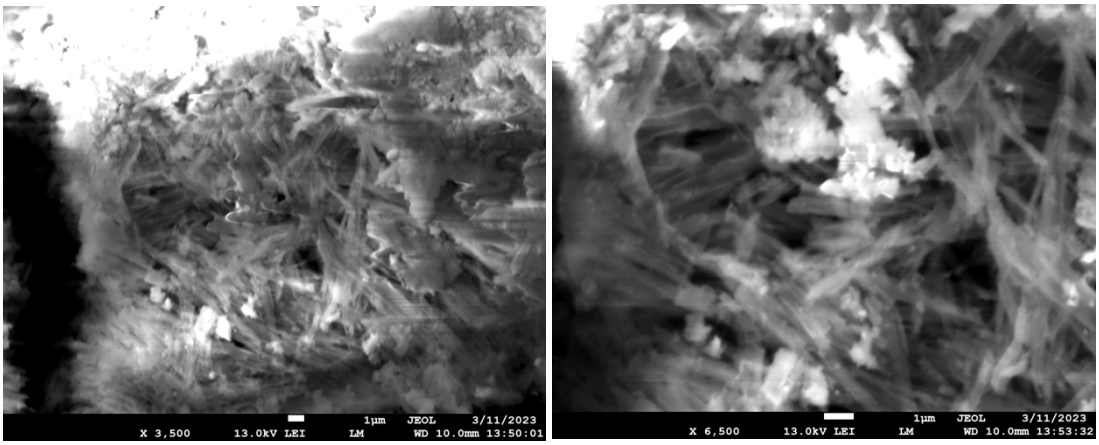


Figure *S*-1: SEM images of presumed Pd-NPs in 1µm range

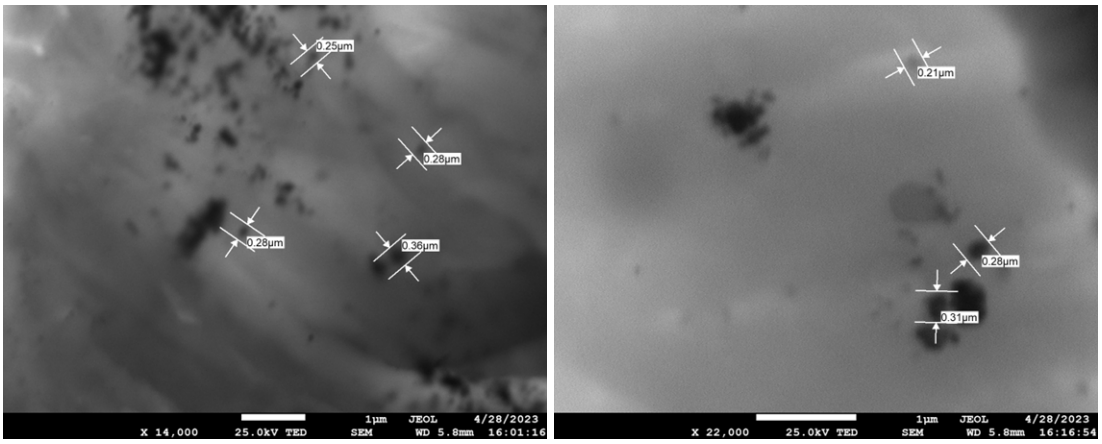


Figure *S*-2: High-magnification ABF-STEM images characterizing the presumed Pd nano particles.

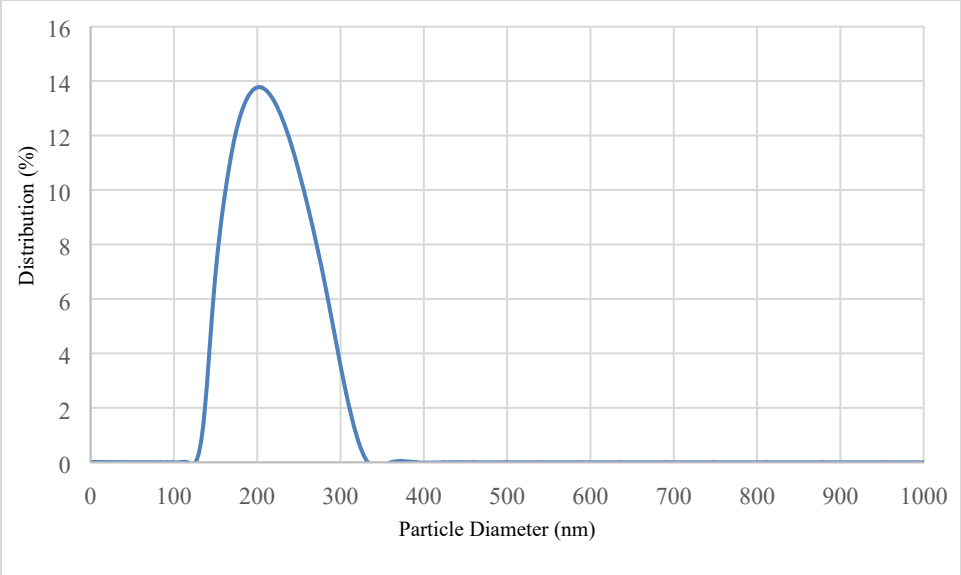


Figure *S*-3: Dynamic Light Scattering (DLS) data of presumed Pd-NPs size distribution

Figure *S*-2 shows STEM images of the sample prepared *in situ* during the oxidative Mizoroki–Heck reaction, followed by filteration, which was recorded in the bright-field high-resolution (ABF) mode. The above depicted images show the round shaped Pd-nano particles with consistent sizes for single particles. Dynamic Light Scattering-DLS data (**Figure *S*-3**) of Pd nano particle size distribution also strengthened the STEM results showing similar particle size distribution.

6. NMR (^{1}H and ^{13}C) Spectra of Compounds

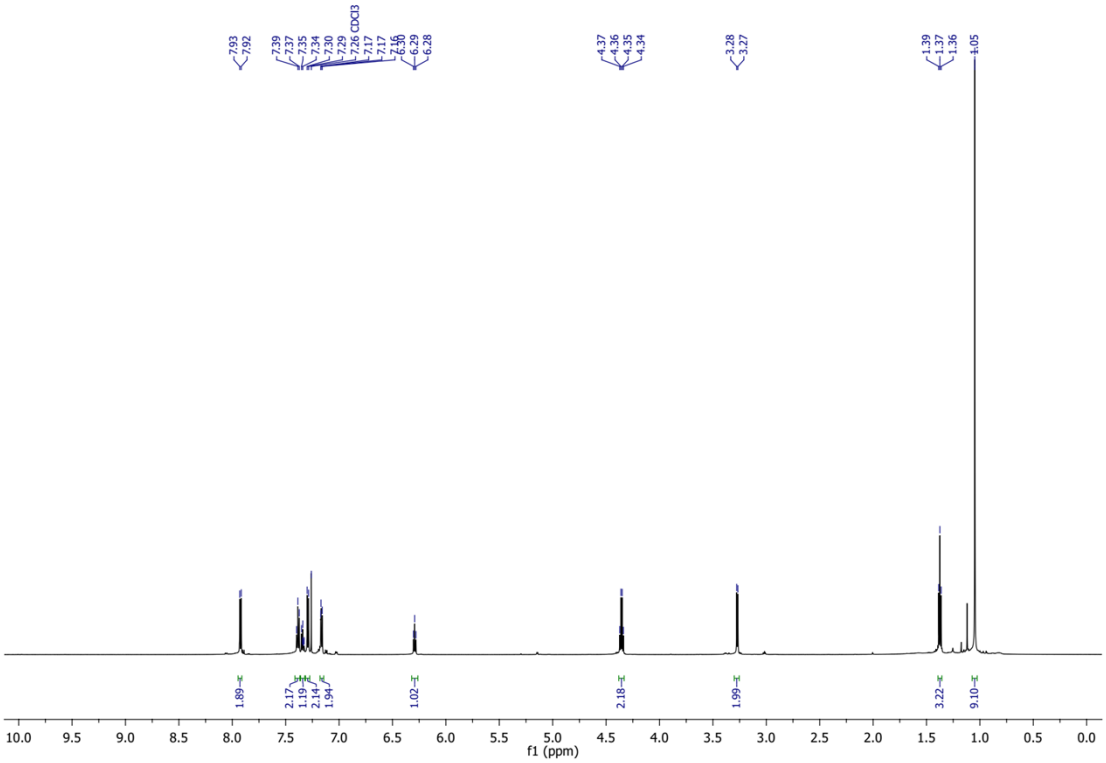


***Figure S*-4.** ^{1}H NMR spectrum of **1a** ($CDCl_3$, 600 MHz, 298 K)

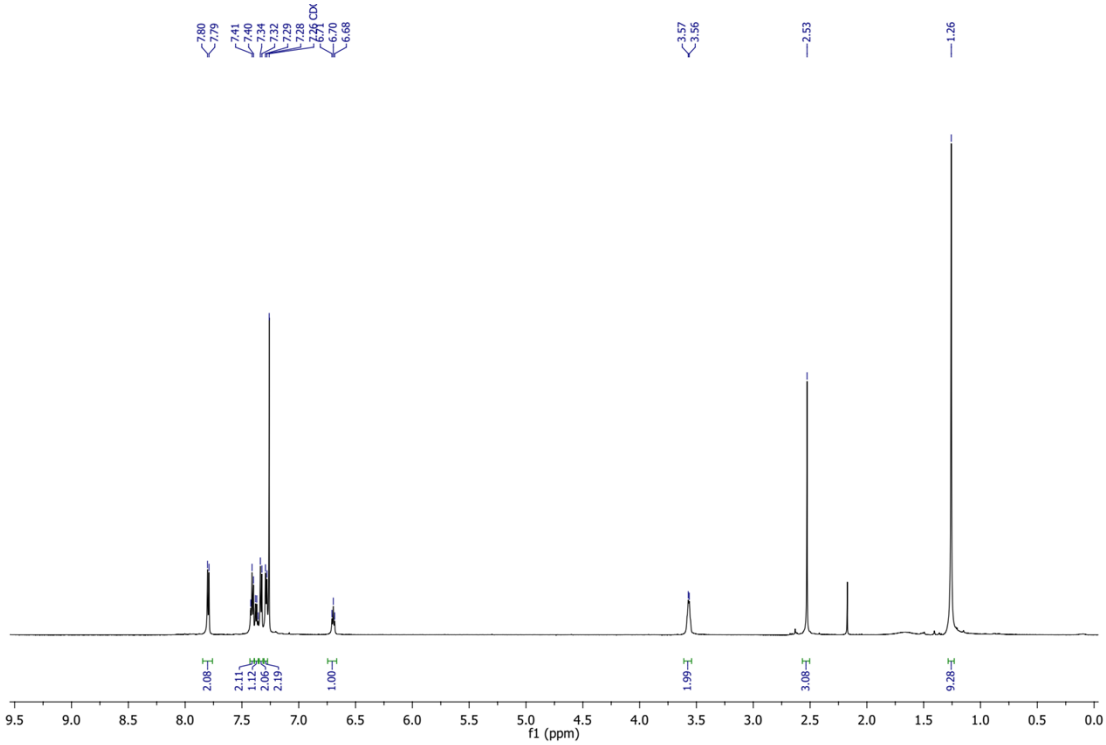


***Figure S*-5.** ^{1}H NMR spectrum of **1b** ($CDCl_3$, 600 MHz, 298 K)

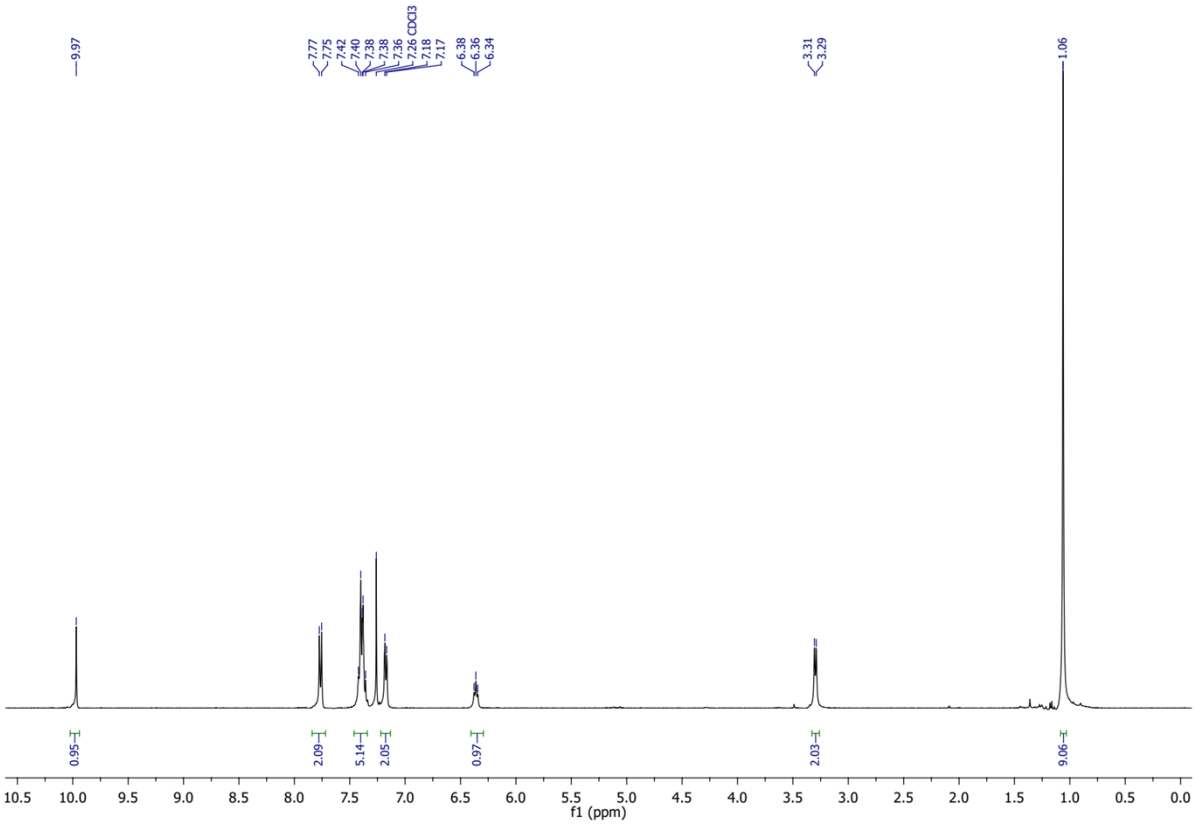


Figure S-6. ^{1}H NMR spectrum of **1c** ($CDCl_3$, 400 MHz, 298 K)

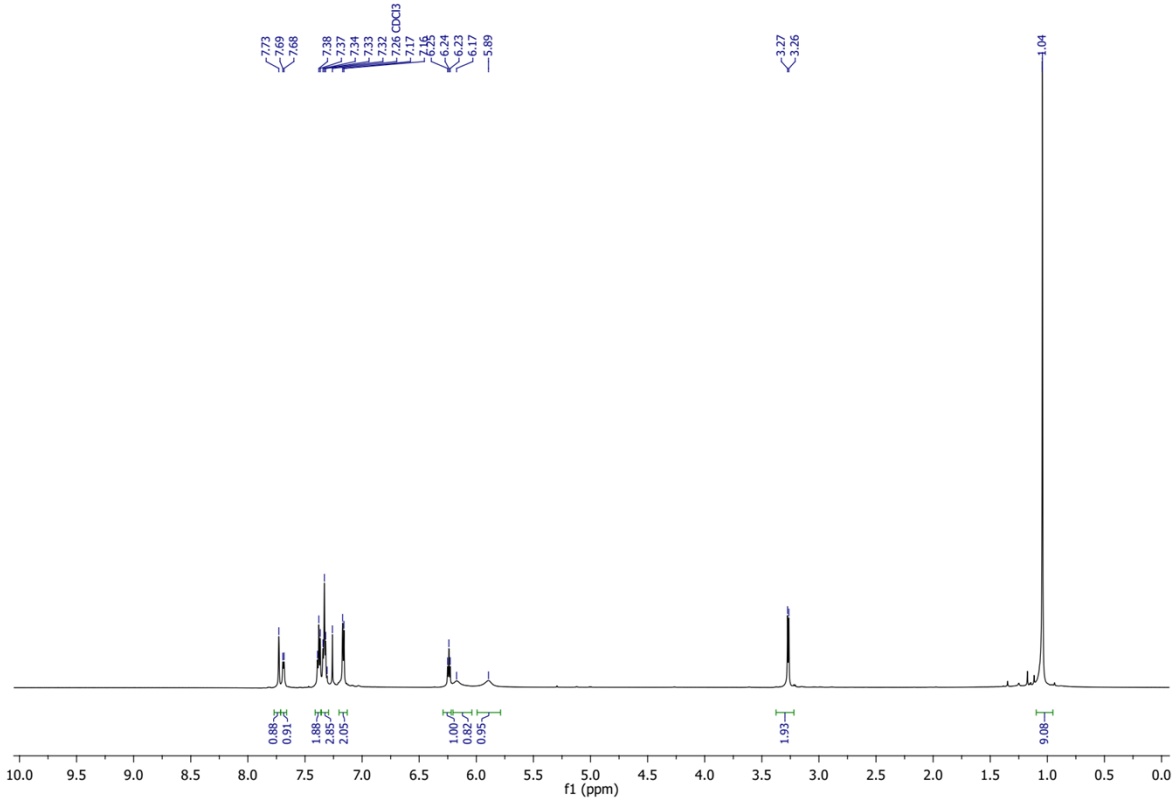


Figure S-7. ^{1}H NMR spectrum of **1d** ($CDCl_3$, 600 MHz, 298 K)

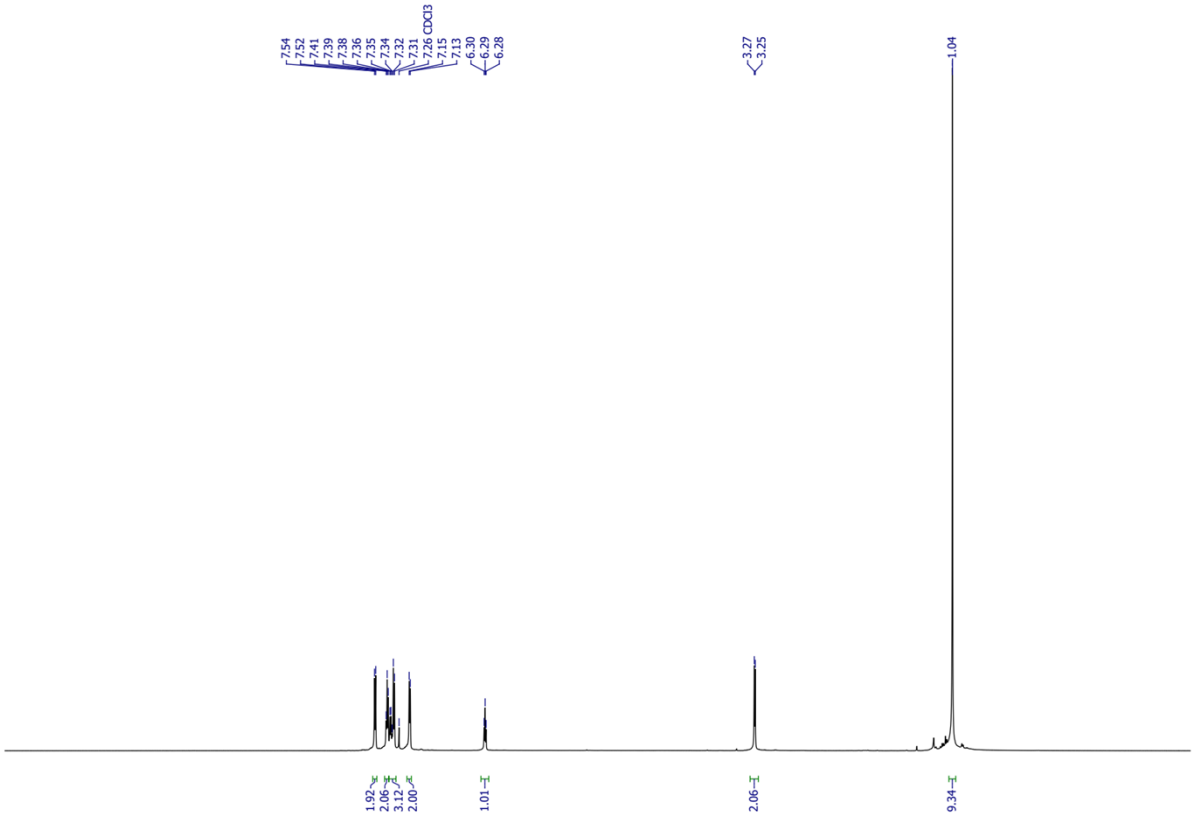


Figure S-8. ^{1}H NMR spectrum of **1e** ($CDCl_3$, 600 MHz, 298 K)

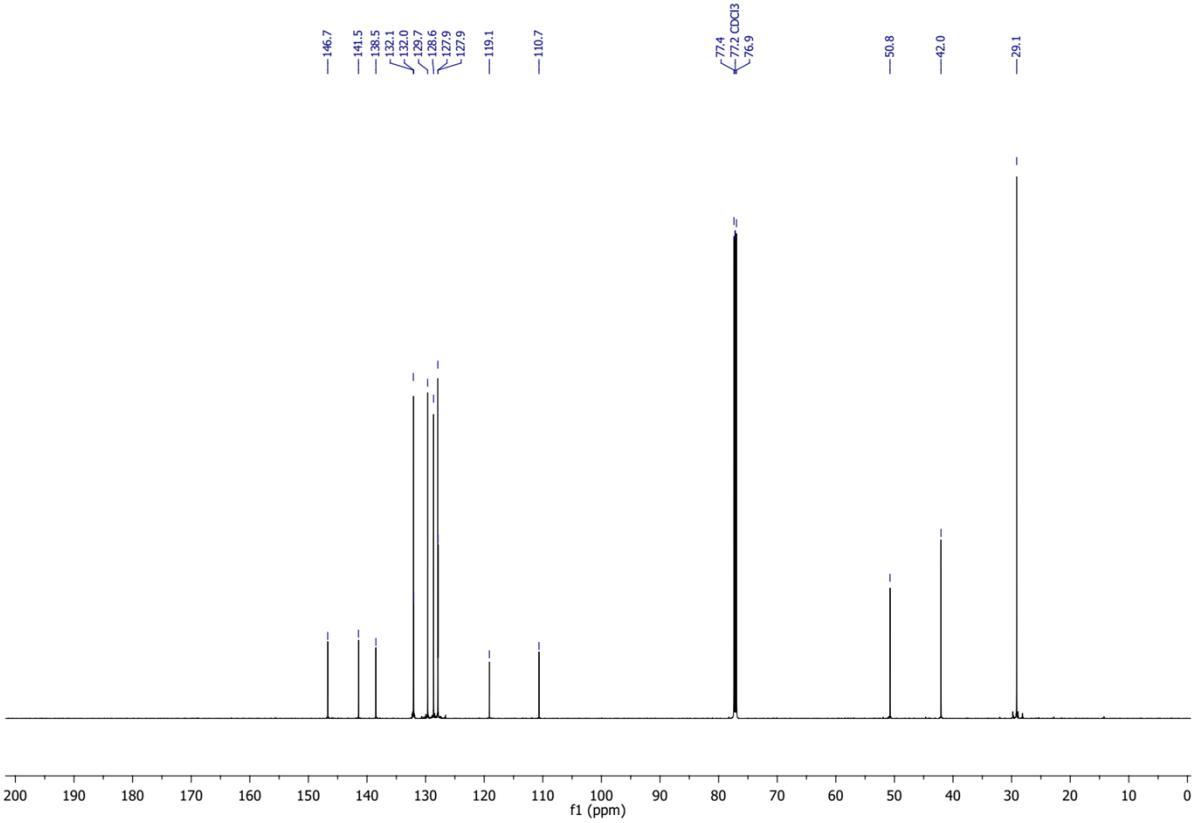


Figure S-9. ^{13}C NMR spectrum of **1e** ($CDCl_3$, 151 MHz, 298 K)

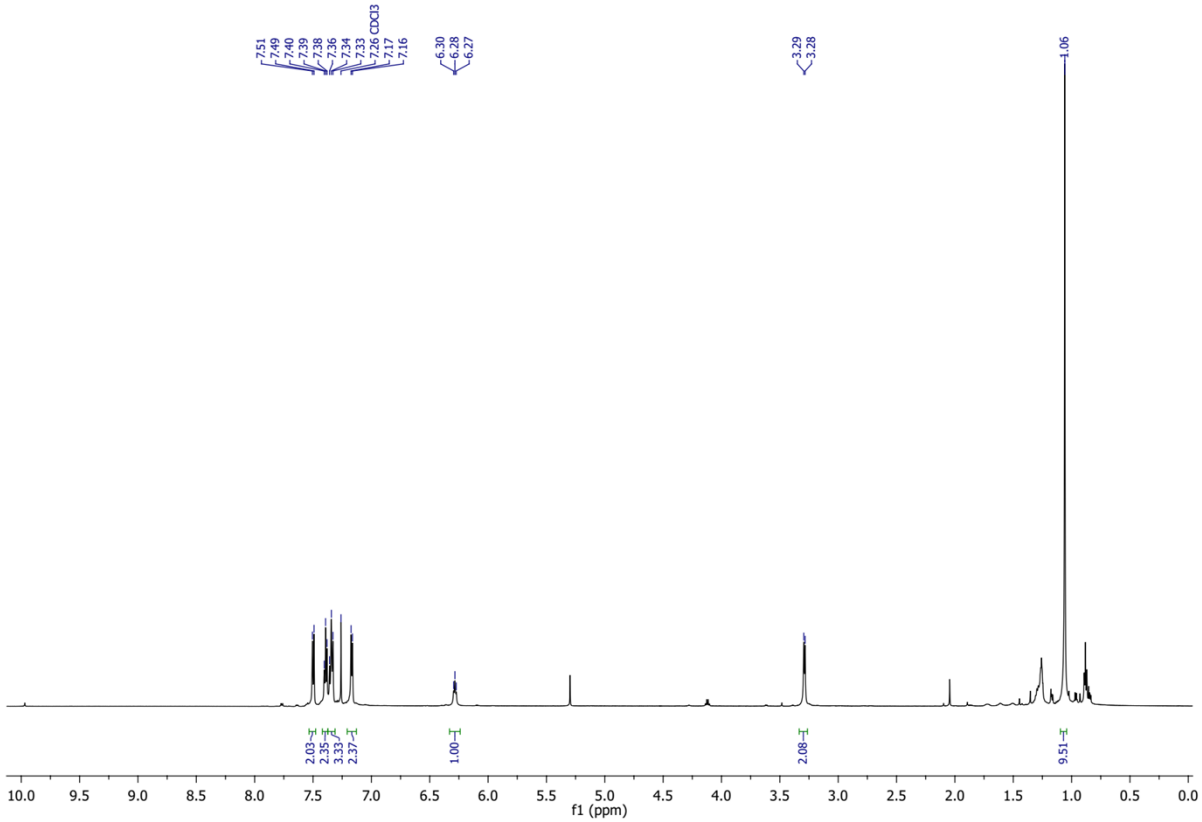


***Figure S*-10.** ^{1}H NMR spectrum of **1f** ($CDCl_3$, 600 MHz, 298 K)

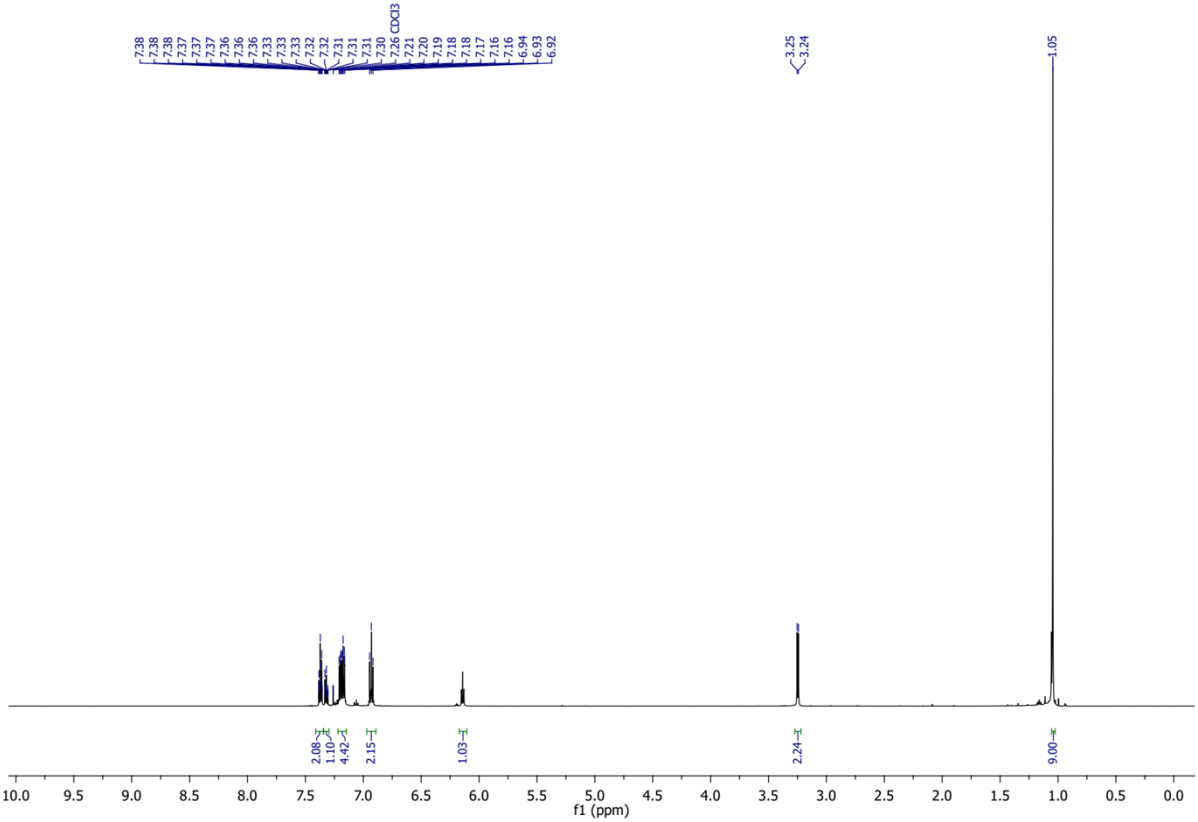


***Figure S*-11.** ^{1}H NMR spectrum of **1g** ($CDCl_3$, 600 MHz, 298 K)

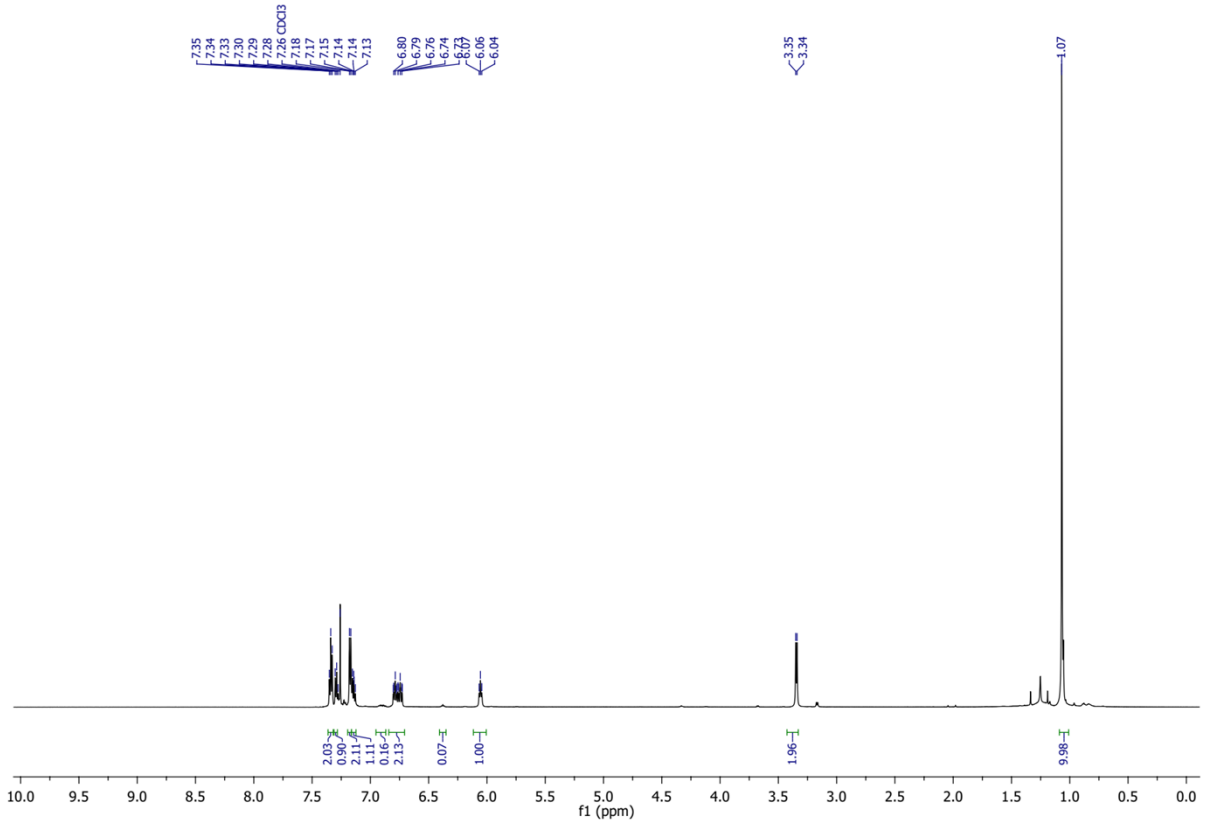


***Figure S*-12.** ^{1}H NMR spectrum of **1h** ($CDCl_3$, 600 MHz, 298 K)

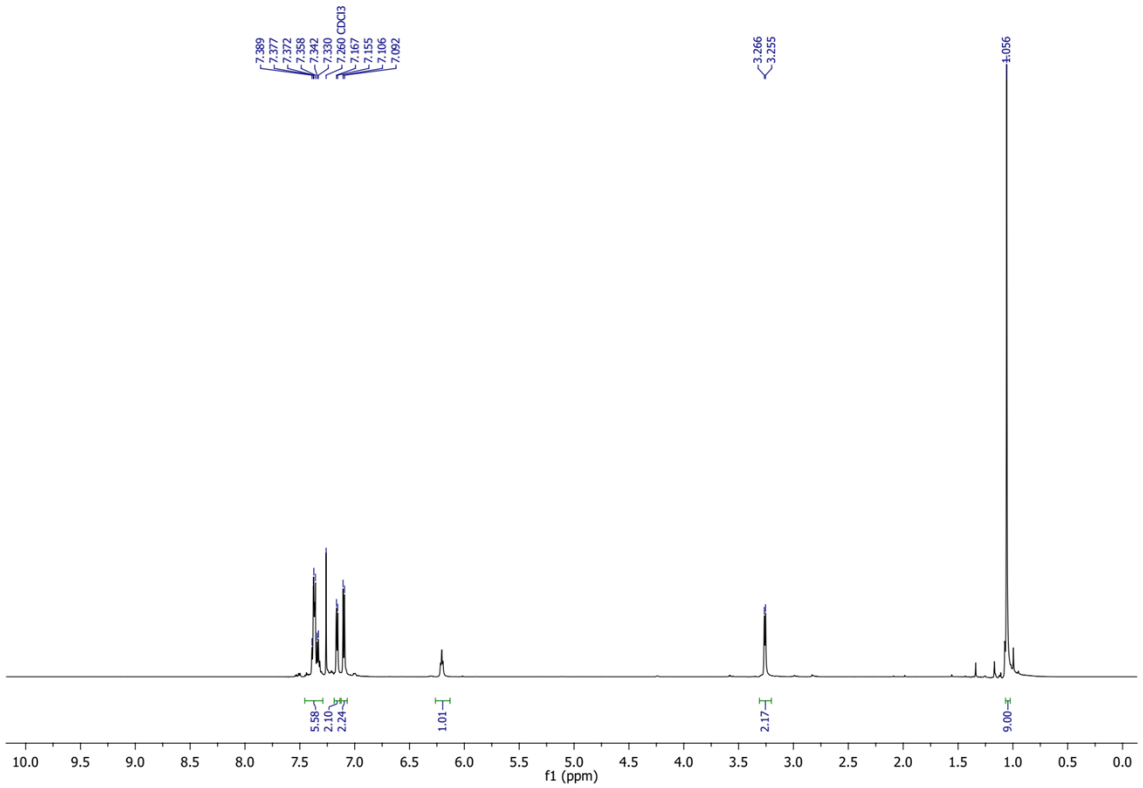


***Figure S*-13.** ^{1}H NMR spectrum of **1i** ($CDCl_3$, 600 MHz, 298 K)

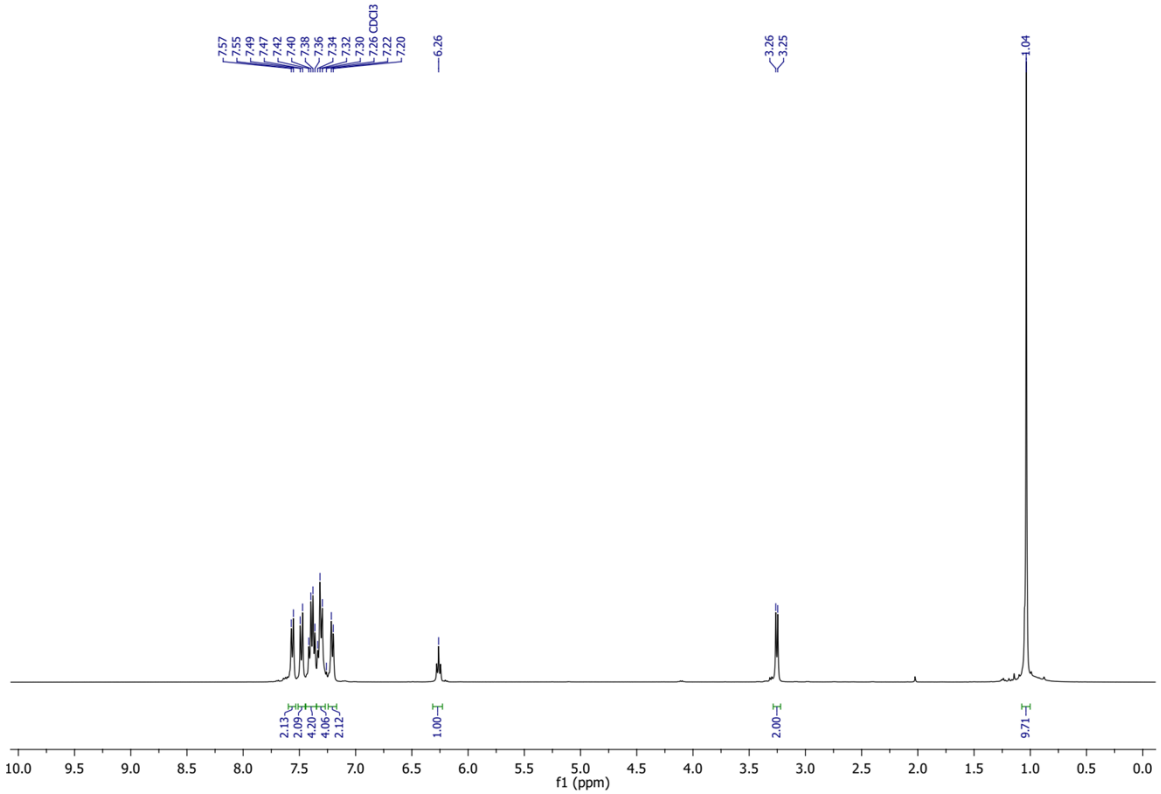


***Figure S*-14.** ^{1}H NMR spectrum of **1j** ($CDCl_3$, 400 MHz, 298 K)

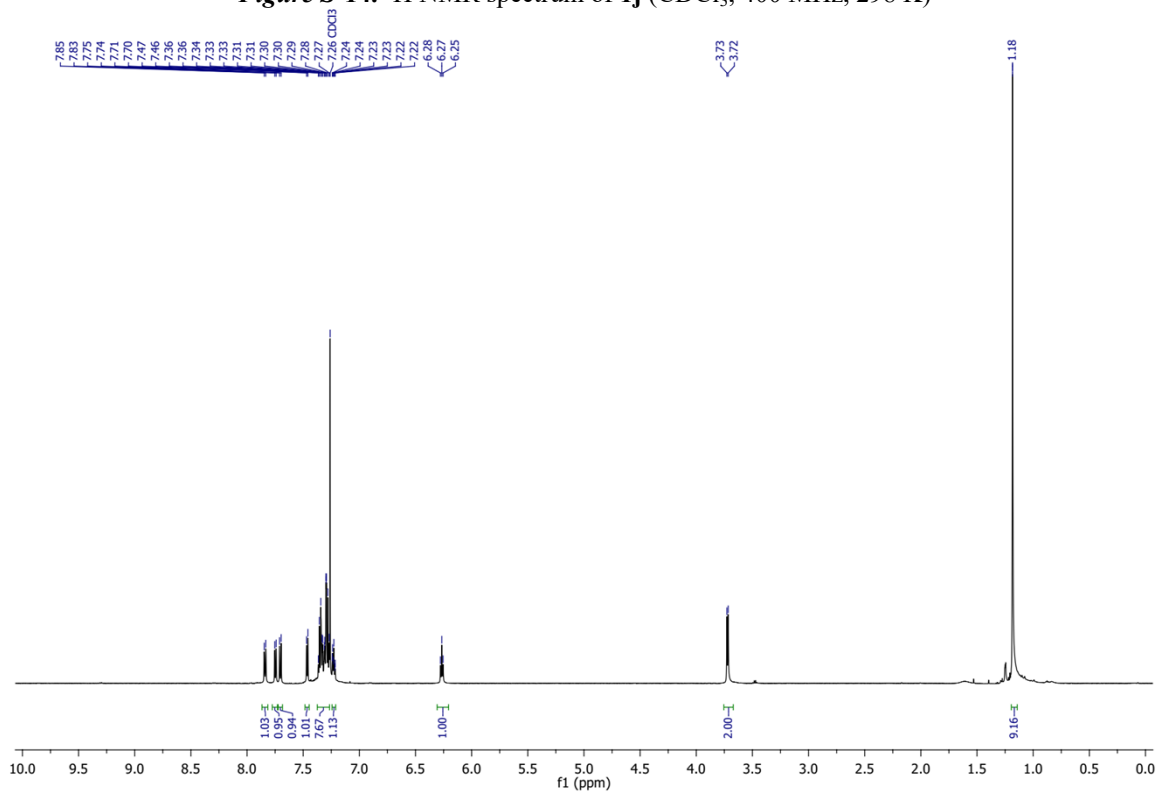


***Figure S*-15.** ^{1}H NMR spectrum of **1k** ($CDCl_3$, 600 MHz, 298 K)

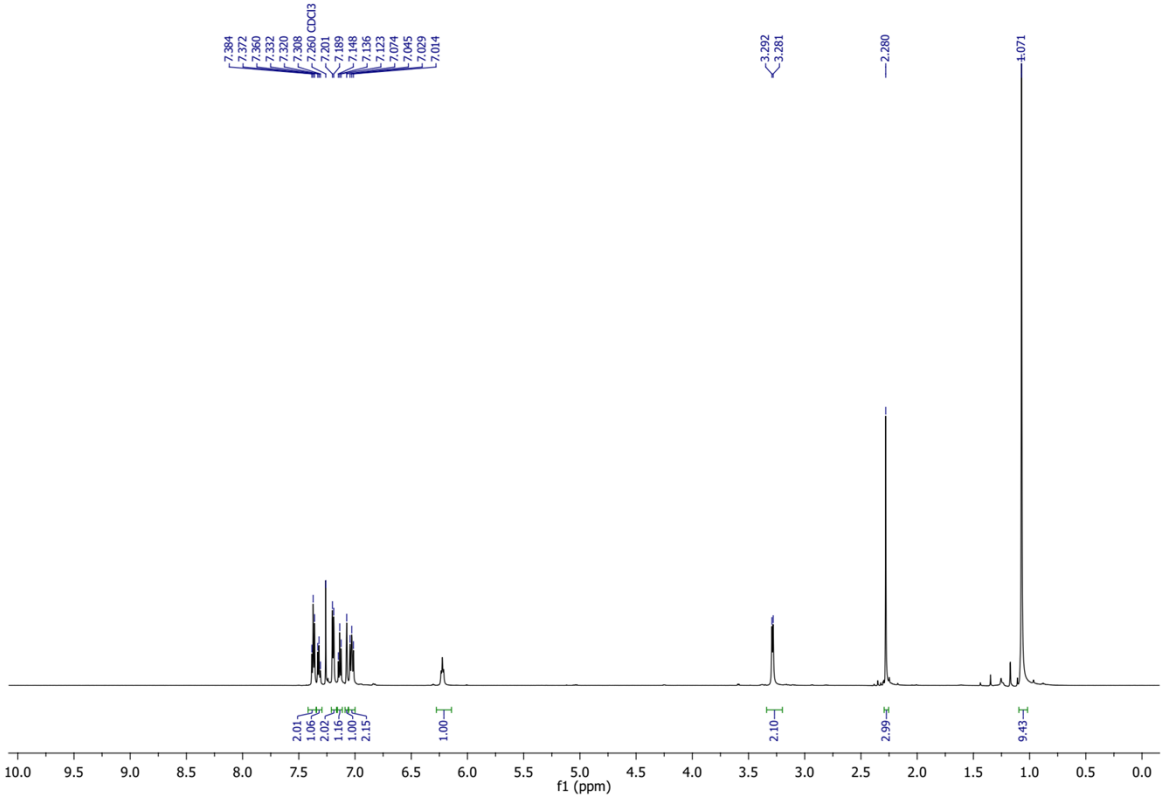


***Figure S*-16.** ^{1}H NMR spectrum of **1l** ($CDCl_3$, 600 MHz, 298 K)

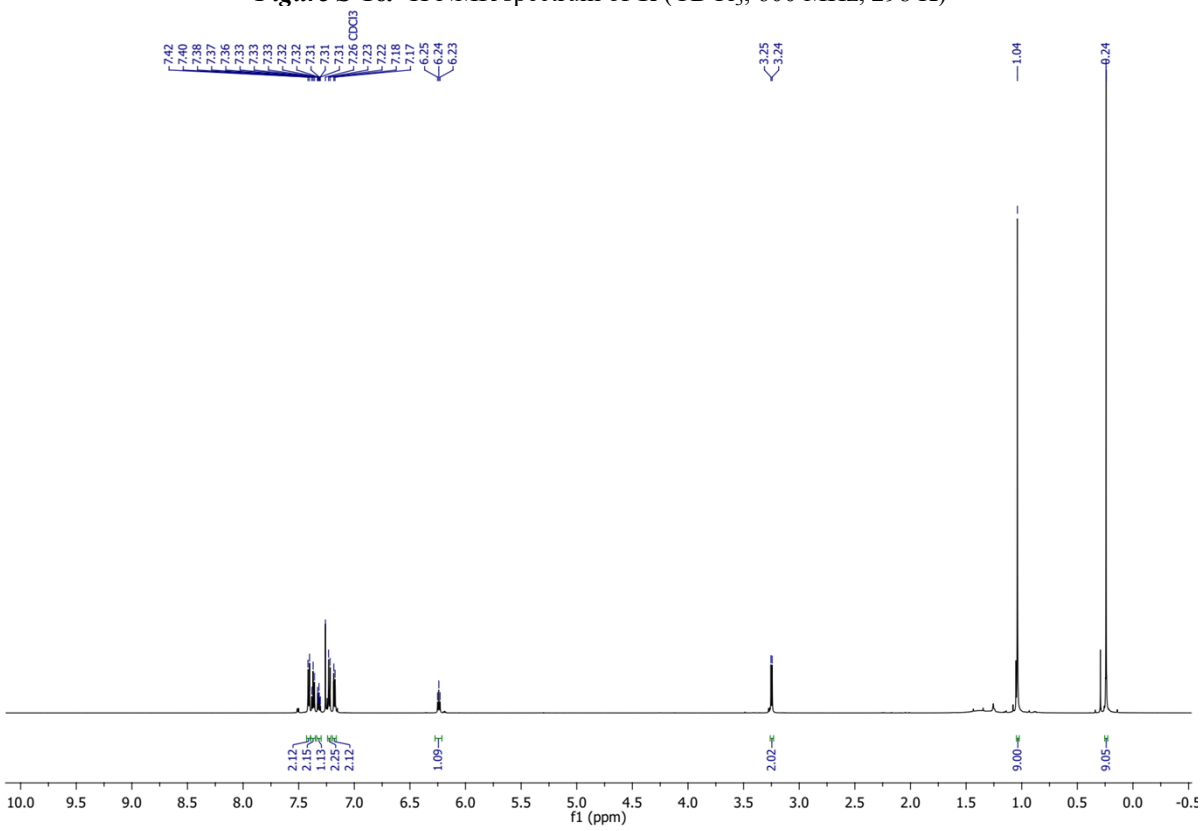


***Figure S*-17.** ^{1}H NMR spectrum of **1m** ($CDCl_3$, 600 MHz, 298 K)

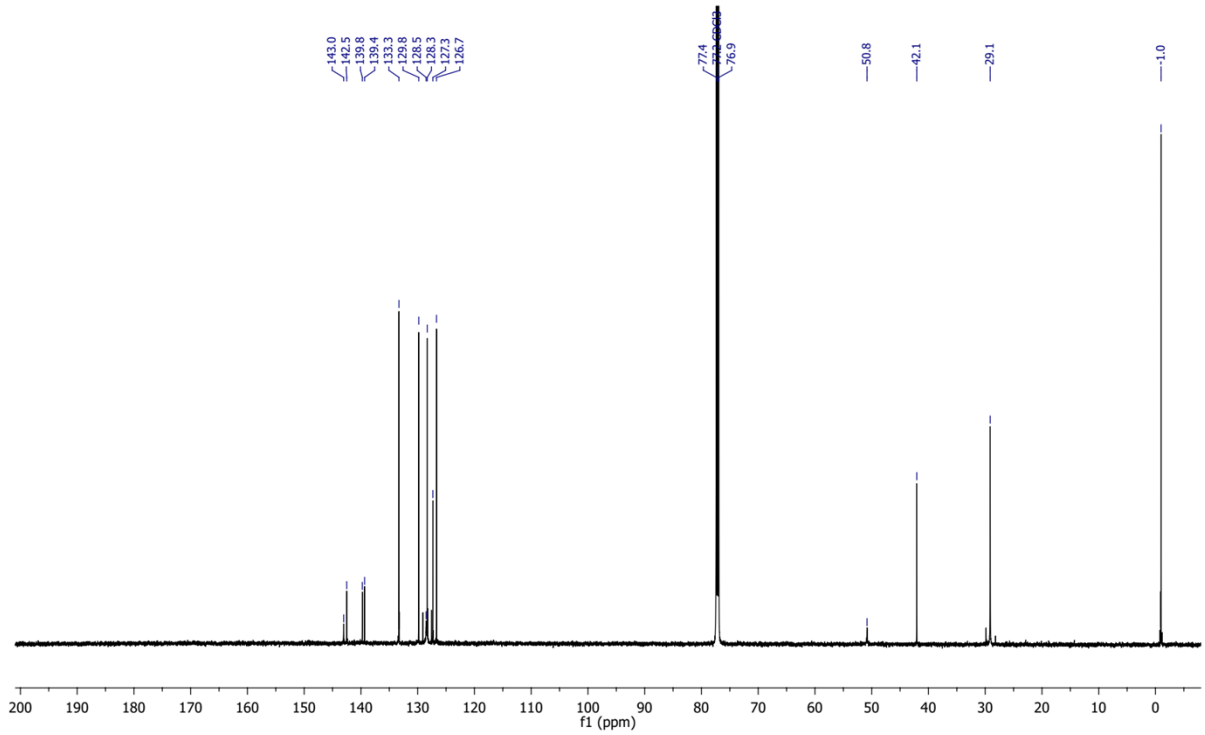


***Figure S*-18.** ^{13}C NMR spectrum of **1m** ($CDCl_3$, 151 MHz, 298 K)

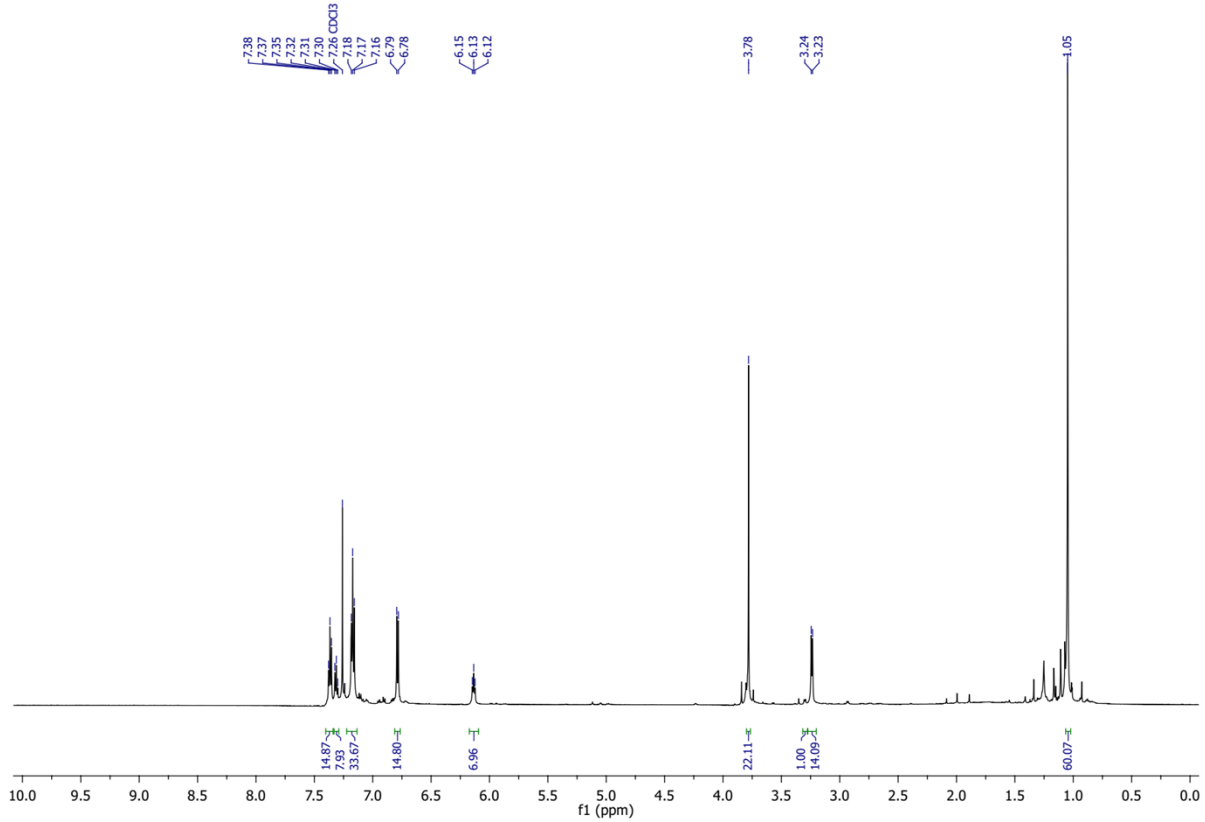


***Figure S*-19.** ^{1}H NMR spectrum of **1n** ($CDCl_3$, 600 MHz, 298 K)

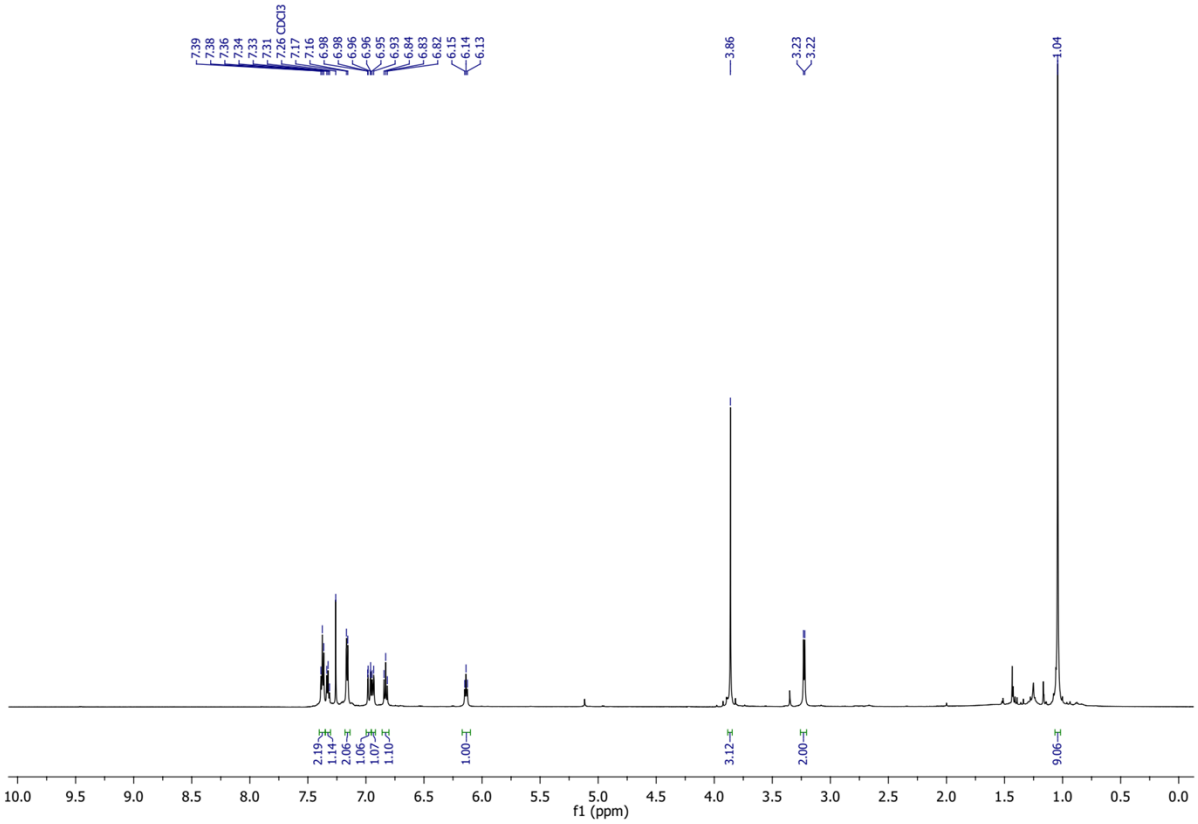


***Figure S*-20.** ^{1}H NMR spectrum of **1o** ($CDCl_3$, 600 MHz, 298 K)

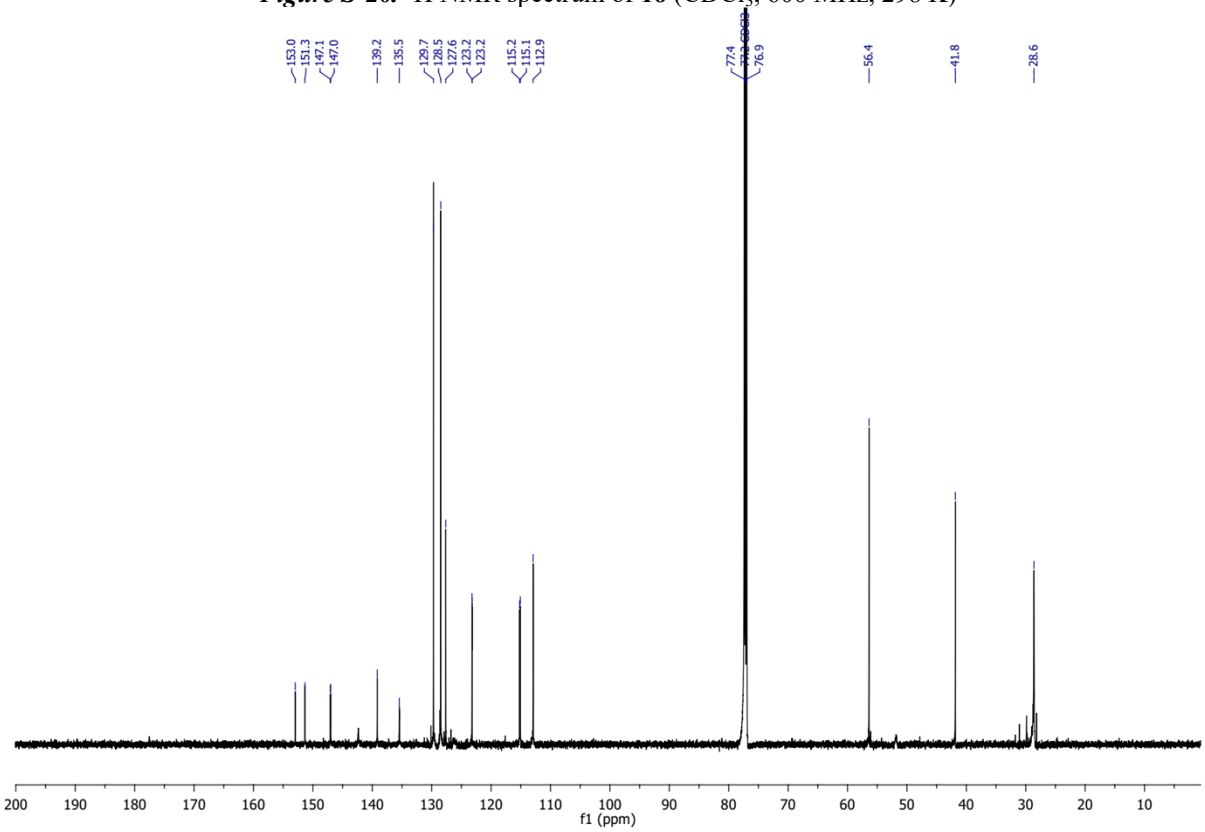


***Figure S*-21.** ^{13}C NMR spectrum of **1o** ($CDCl_3$, 151 MHz, 298 K)

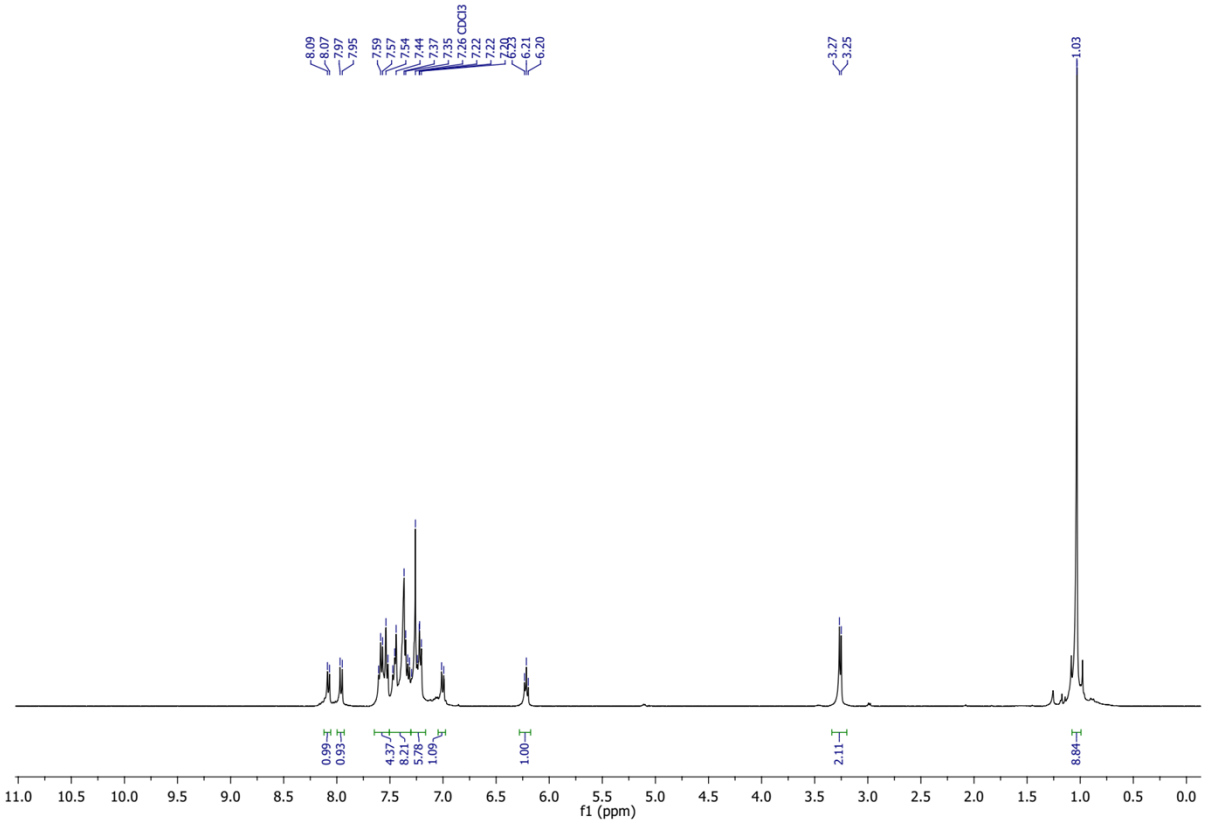


Figure S-22. ^{1}H NMR spectrum of **1p** ($CDCl_3$, 400 MHz, 298 K)

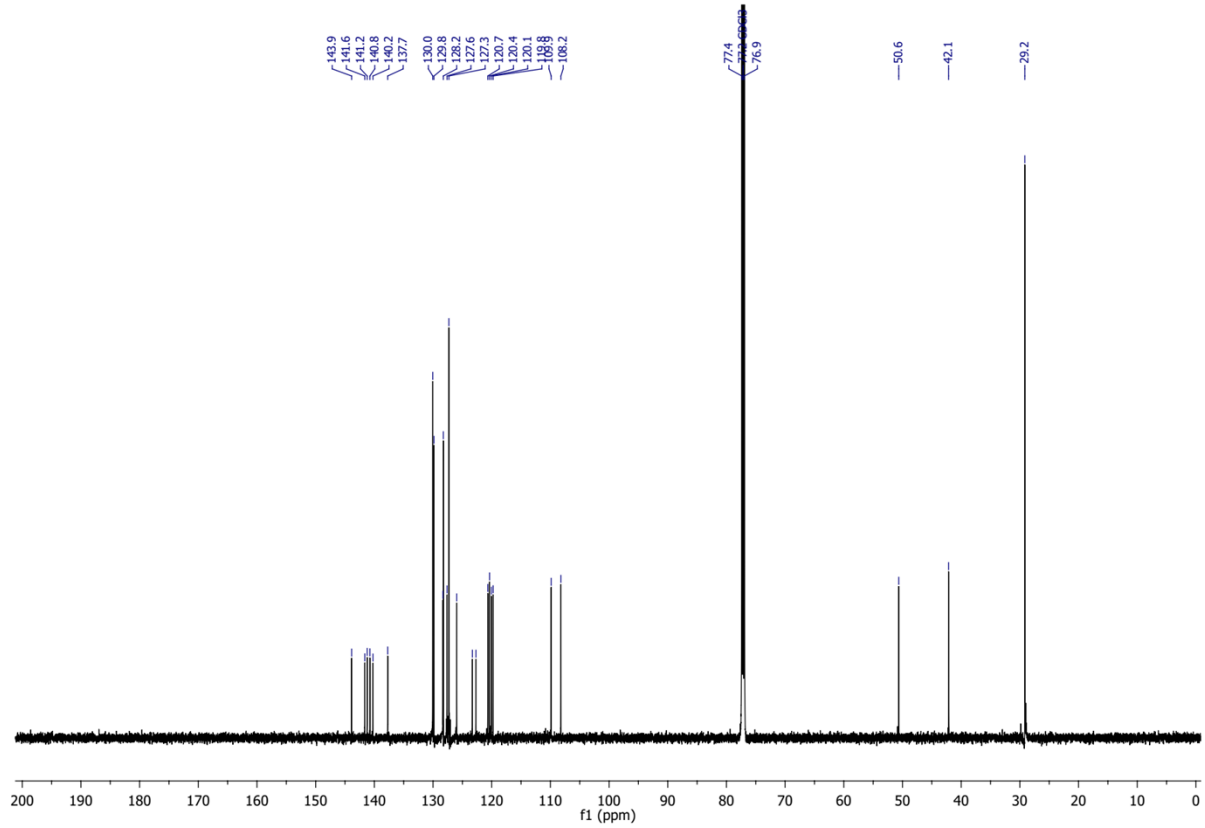


Figure S-23. ^{13}C NMR spectrum of **1p** ($CDCl_3$, 151 MHz, 298 K)

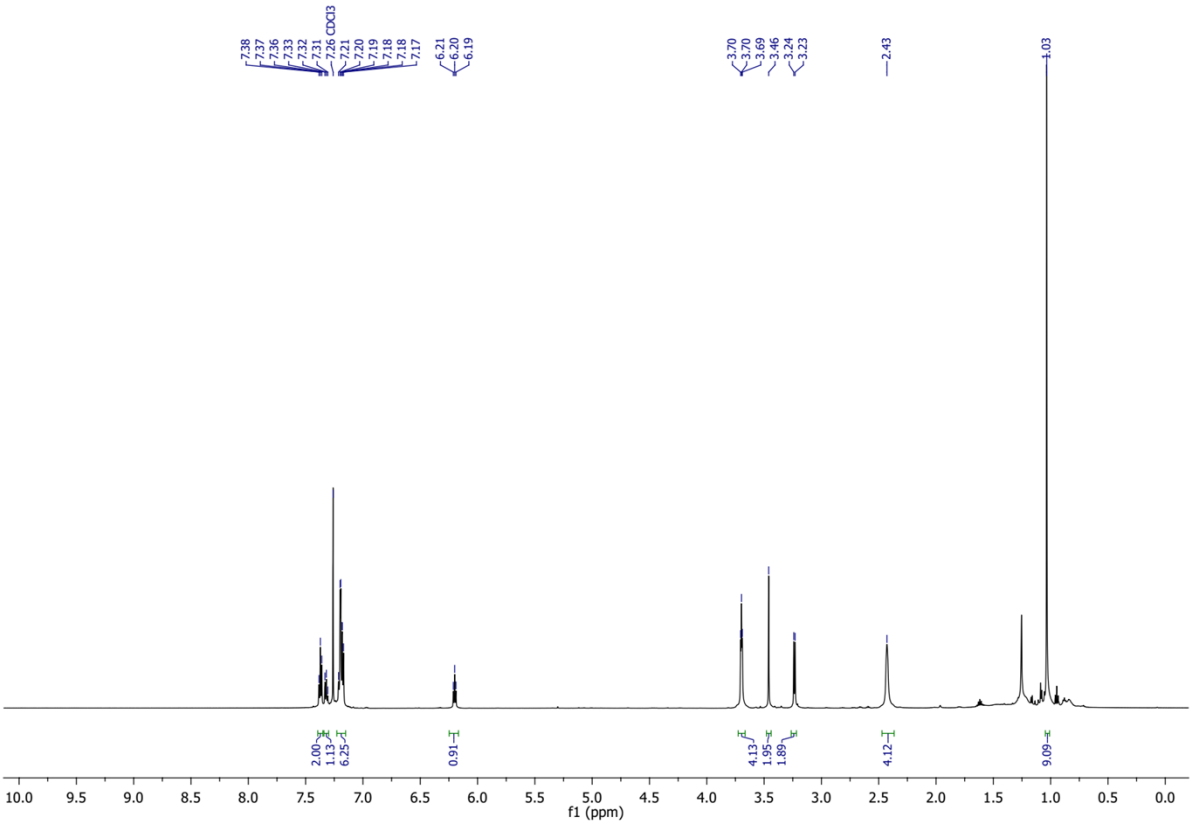


Figure S-24. ^{1}H NMR spectrum of **1q** ($CDCl_3$, 600 MHz, 298 K)

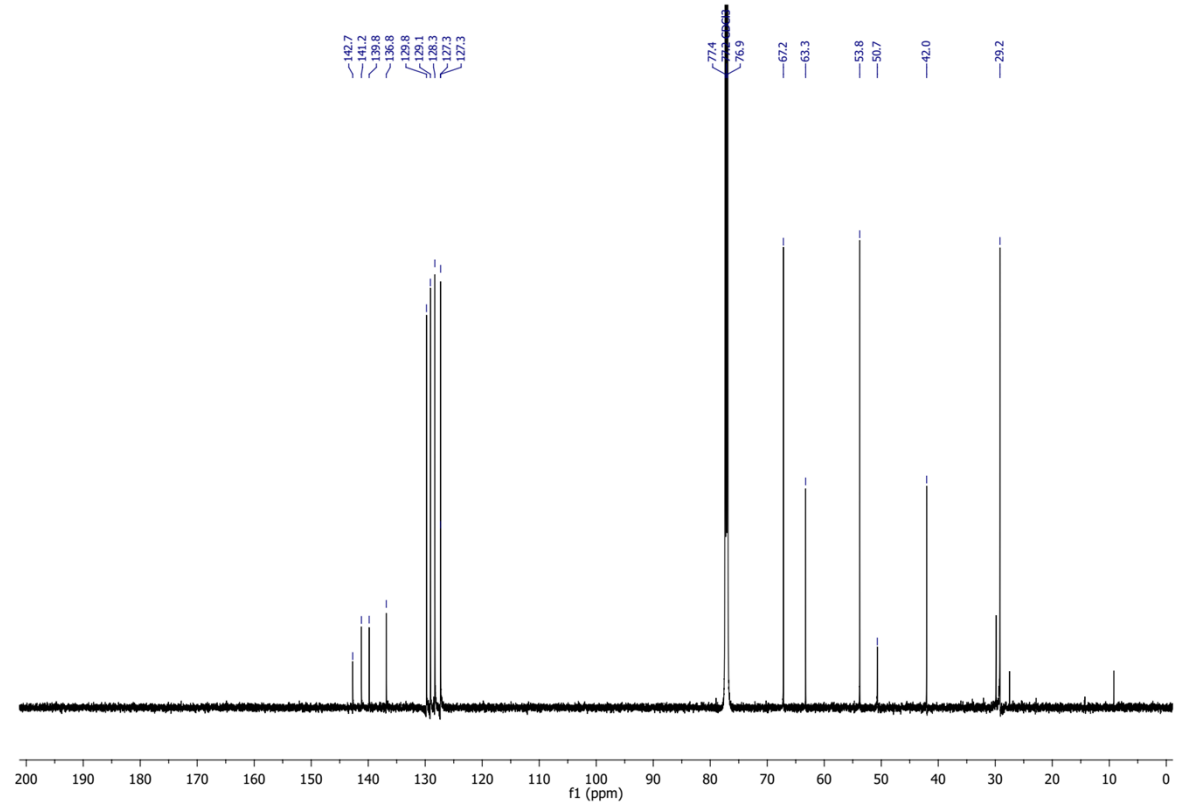


Figure S-25. ^{13}C NMR spectrum of **1q** ($CDCl_3$, 151 MHz, 298 K)

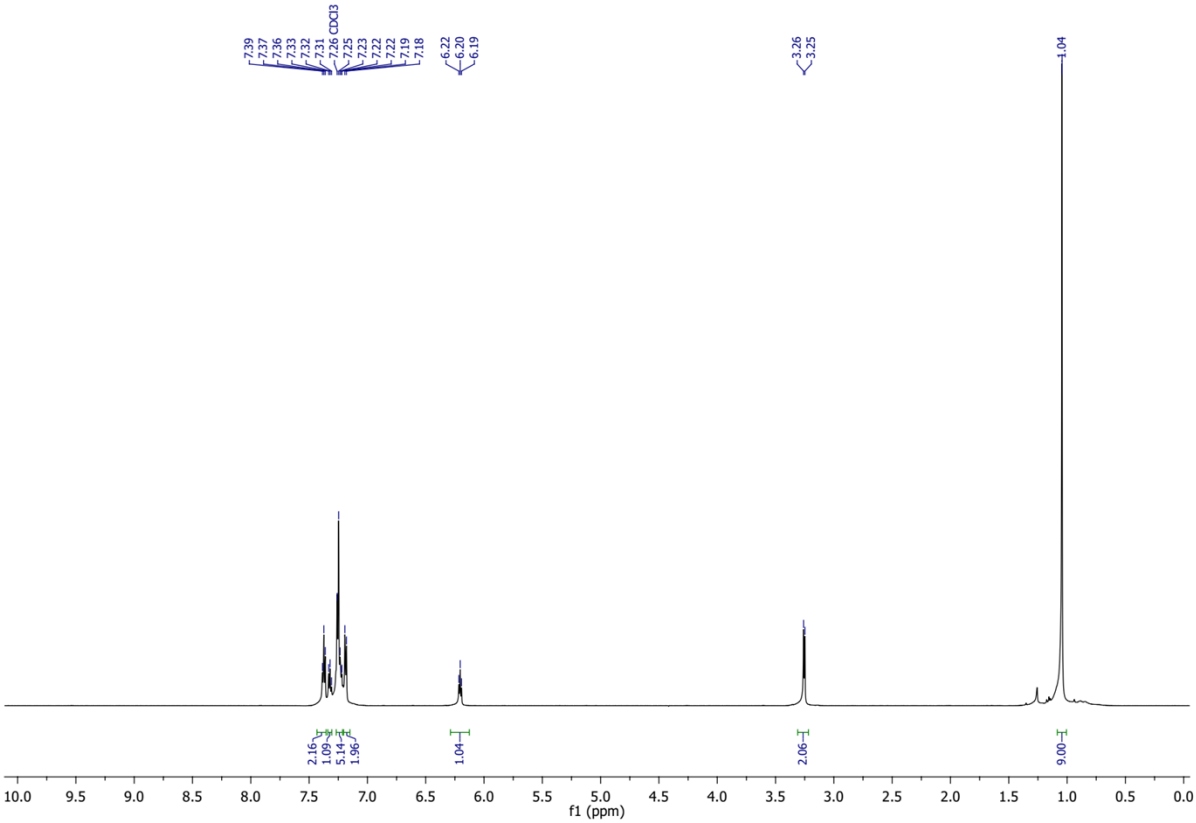


Figure S-26. ^{1}H NMR spectrum of **2a** ($CDCl_3$, 600 MHz, 298 K)

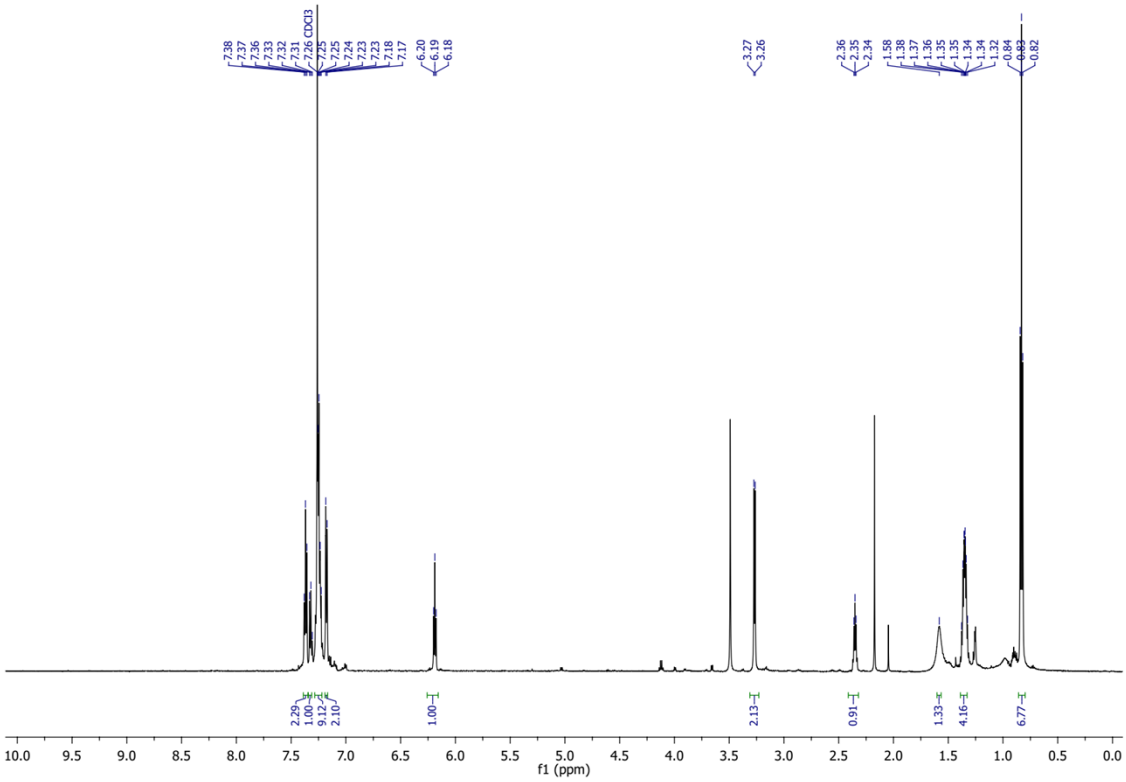


Figure S-27. ^{1}H NMR spectrum of **2b** ($CDCl_3$, 600 MHz, 298 K)

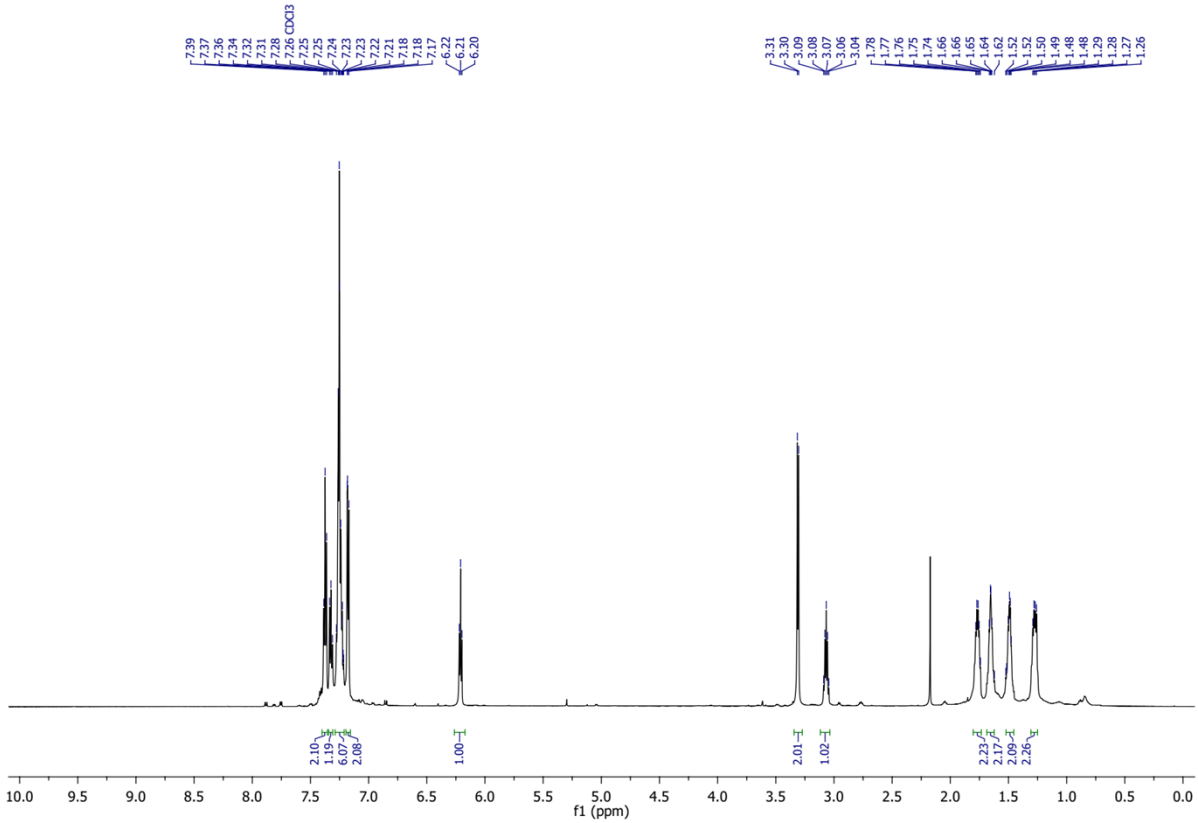


Figure S-28. ^{1}H NMR spectrum of **2c** ($CDCl_3$, 600 MHz, 298 K)

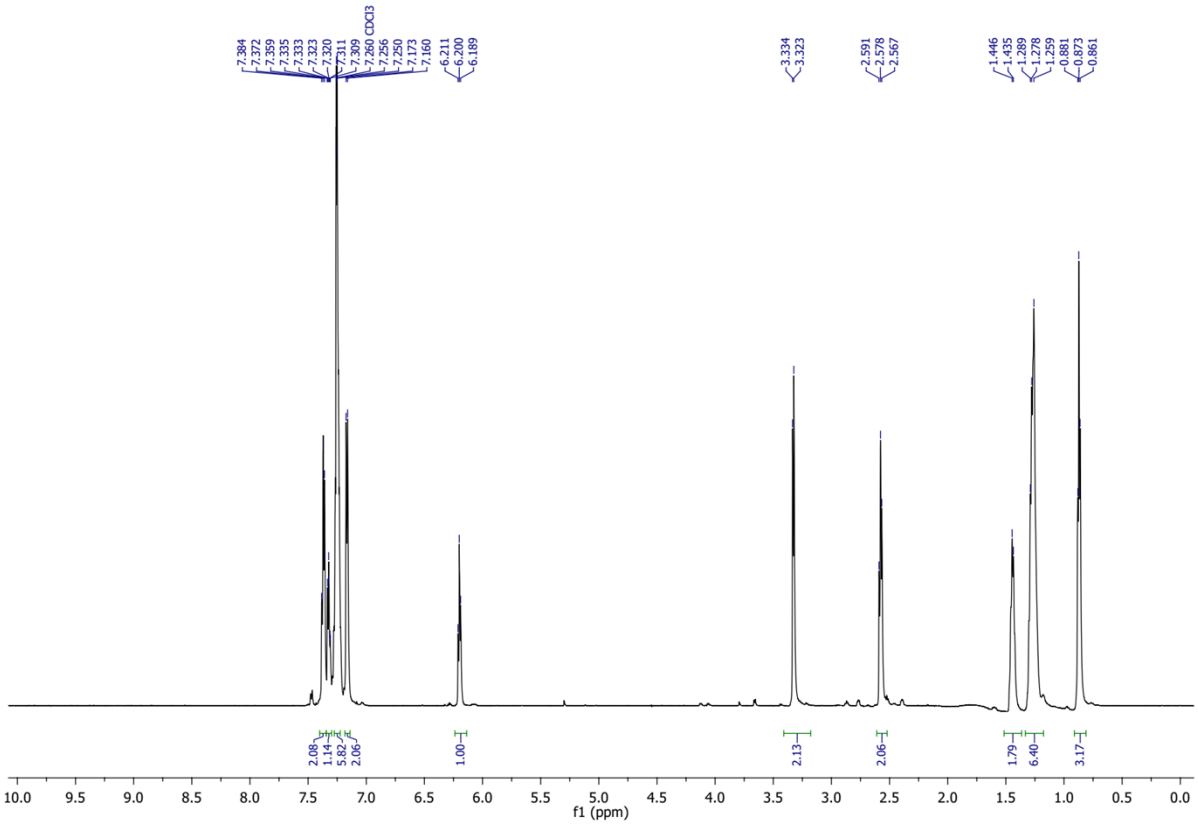


Figure S-29. ^{1}H NMR spectrum of **2d** ($CDCl_3$, 600 MHz, 298 K)

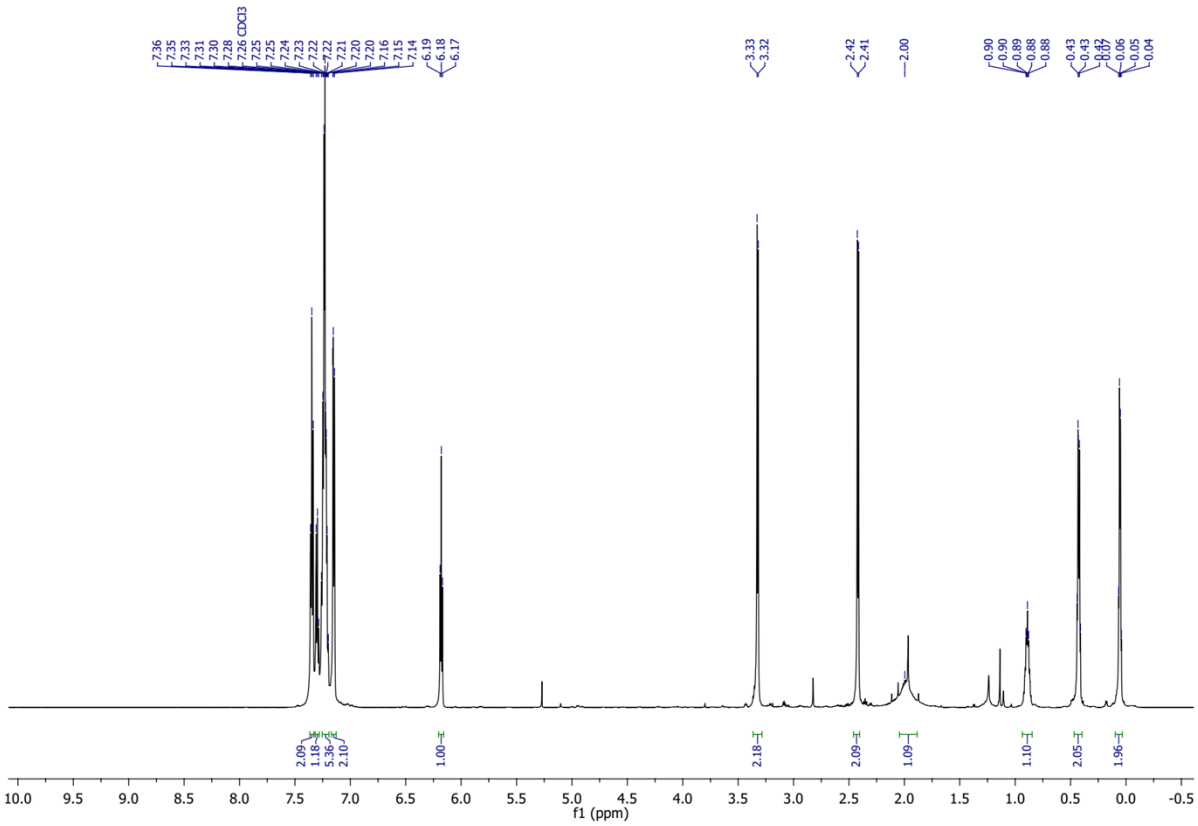


***Figure S*-30.** ^{1}H NMR spectrum of **2e** ($CDCl_3$, 600 MHz, 298 K)

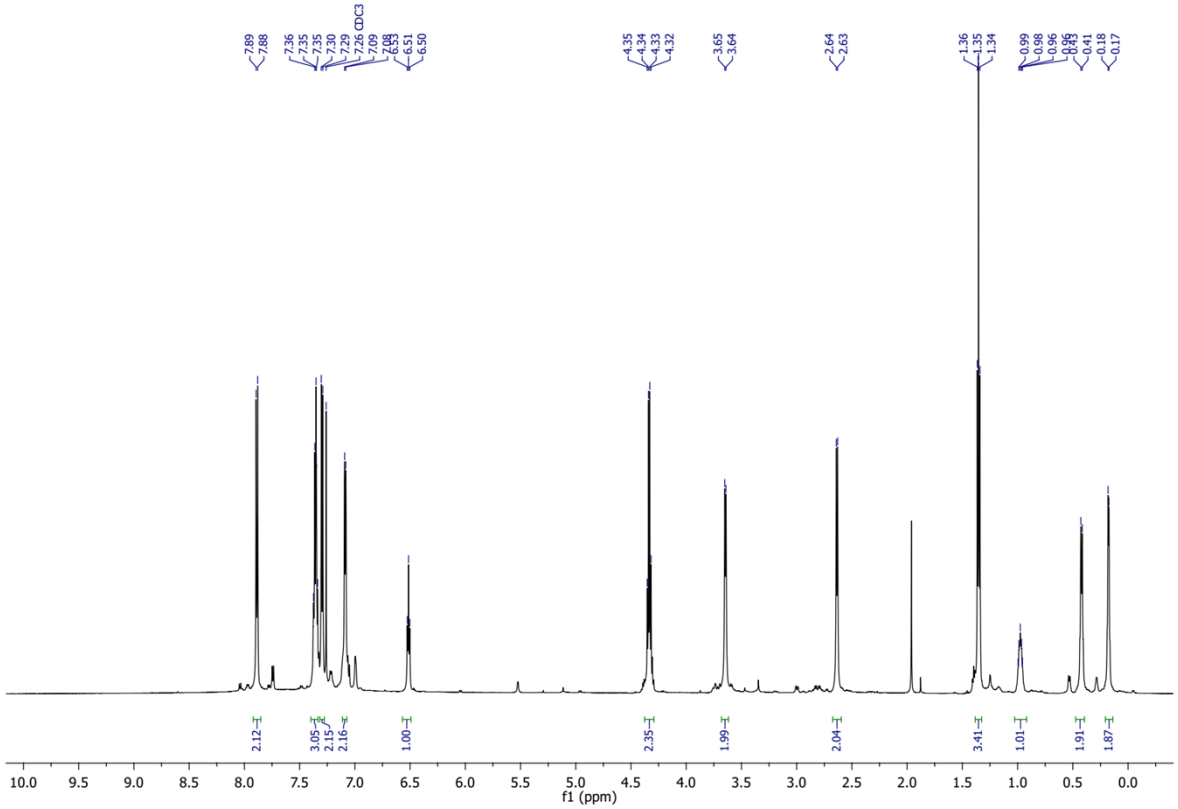


***Figure S*-31.** ^{1}H NMR spectrum of **2f** ($CDCl_3$, 600 MHz, 298 K)

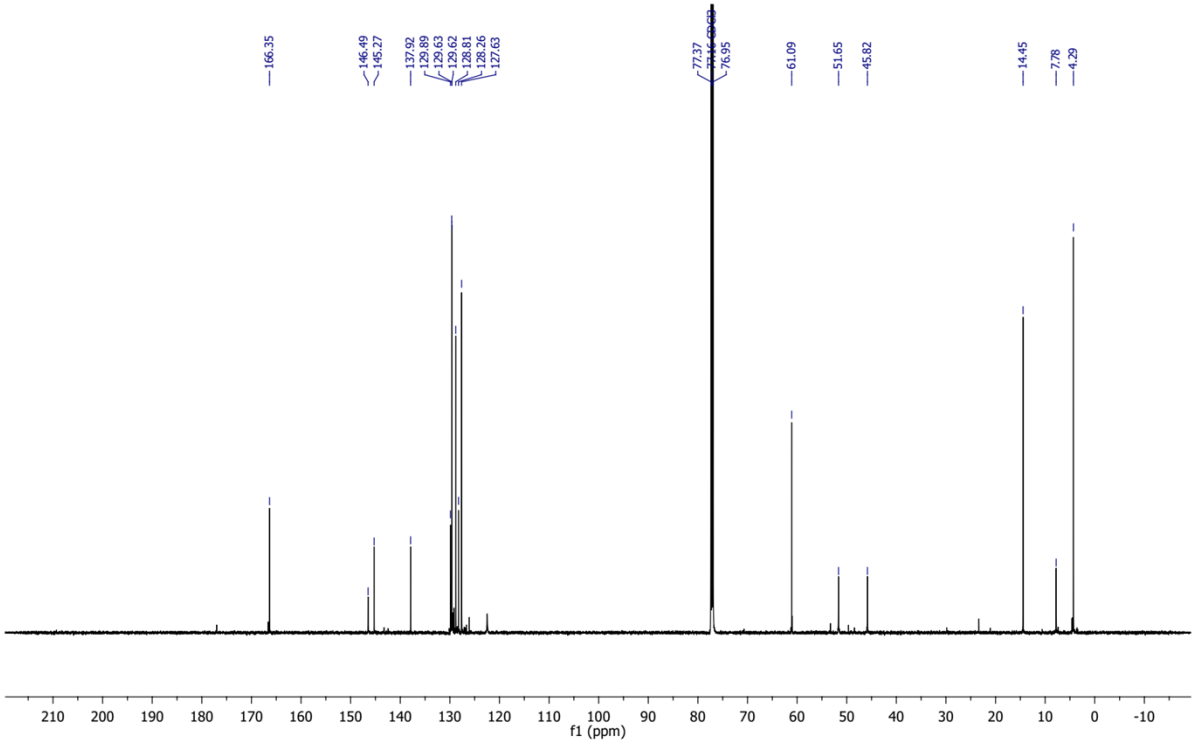


Figure S-32. ^{13}C NMR spectrum of **2f** ($CDCl_3$, 151 MHz, 298 K)

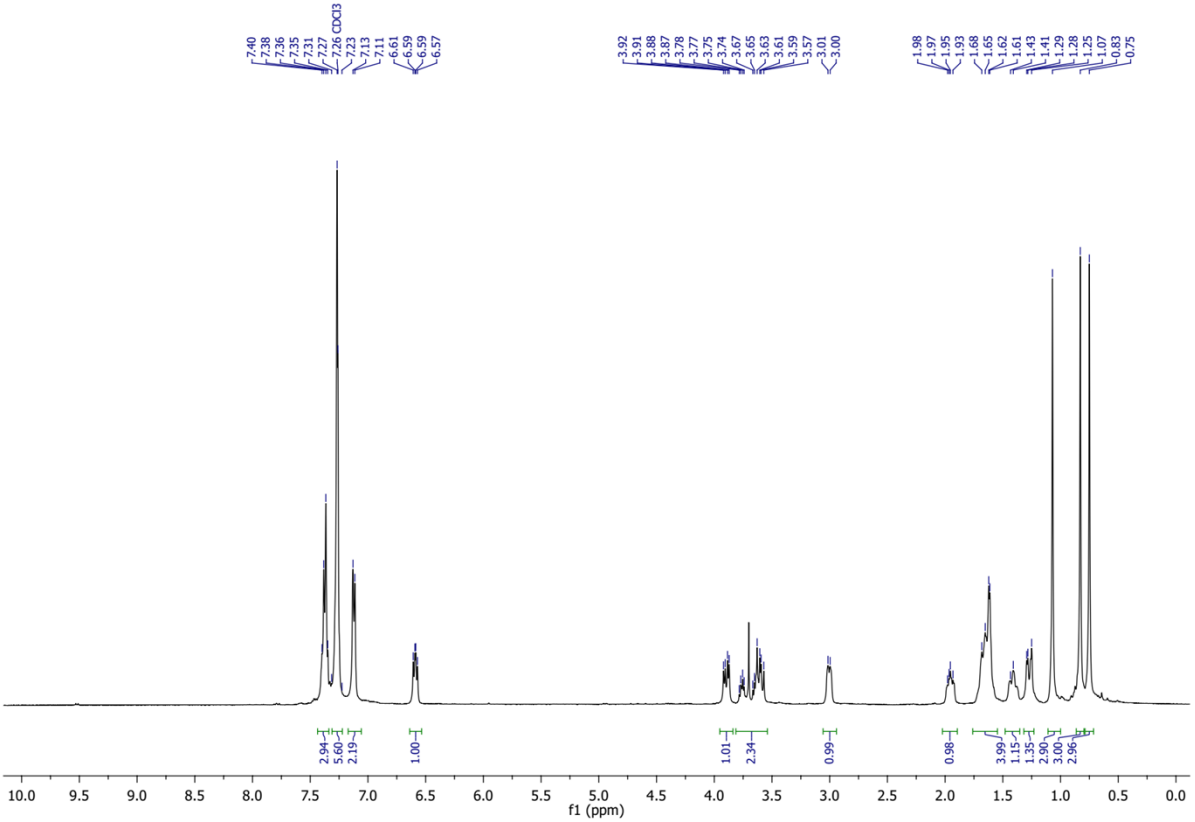


Figure S-33. ^{1}H NMR spectrum of **2g** ($CDCl_3$, 400 MHz, 298 K)

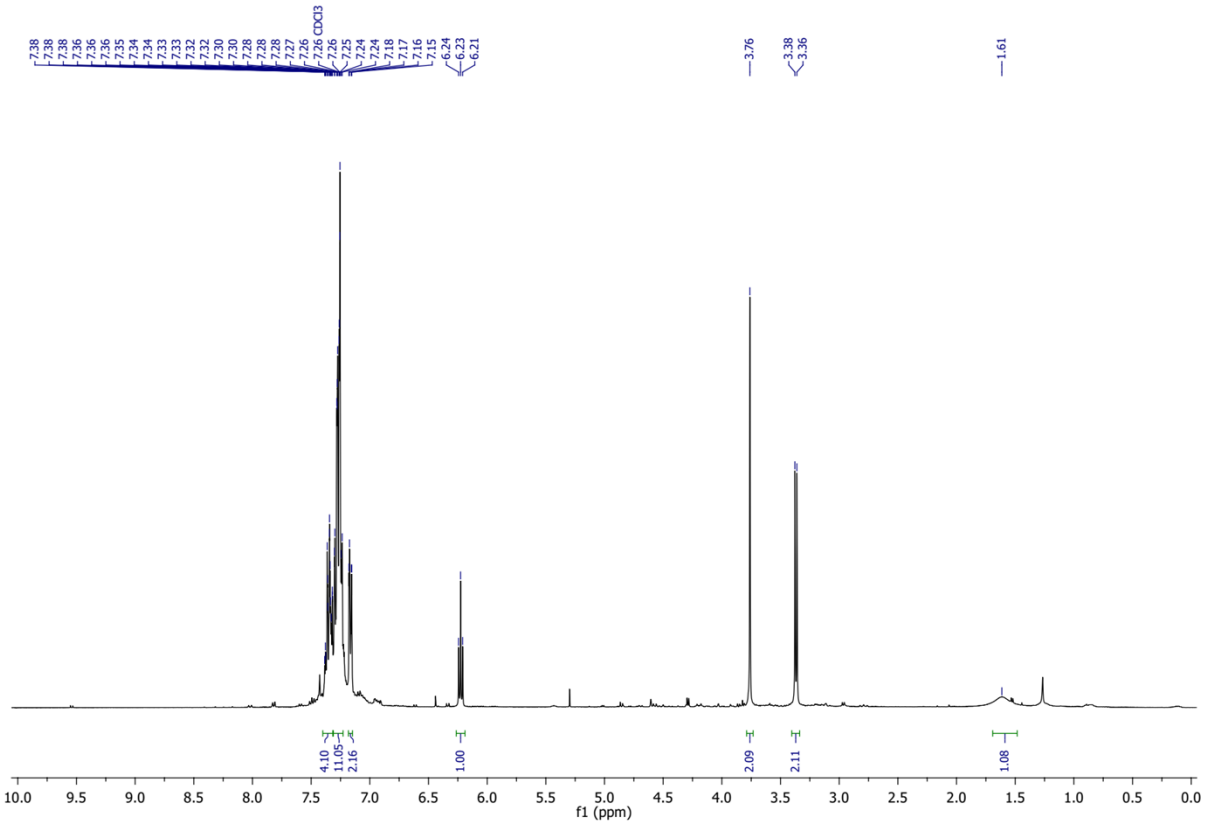


***Figure S*-34.** ^{1}H NMR spectrum of **2h** ($CDCl_3$, 400 MHz, 298 K)

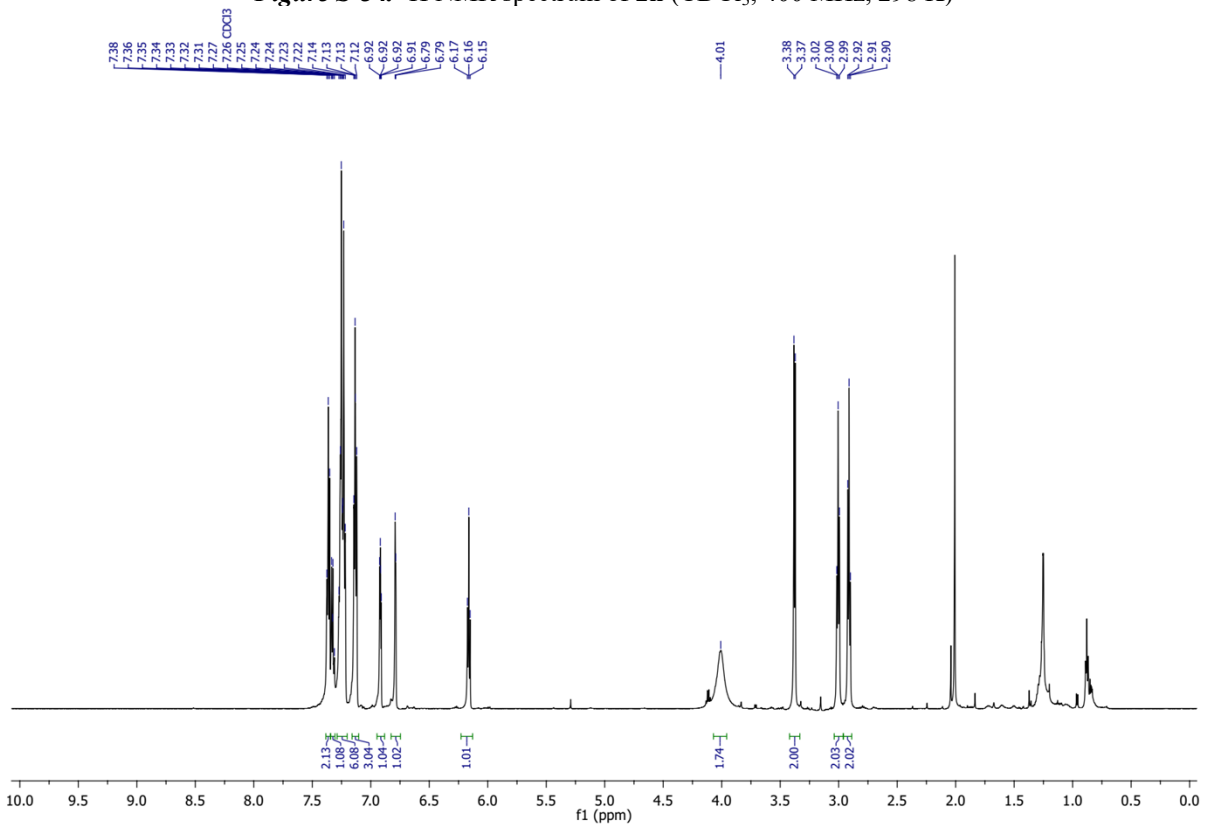


***Figure S*-35.** ^{1}H NMR spectrum of **2i** ($CDCl_3$, 600 MHz, 298 K)

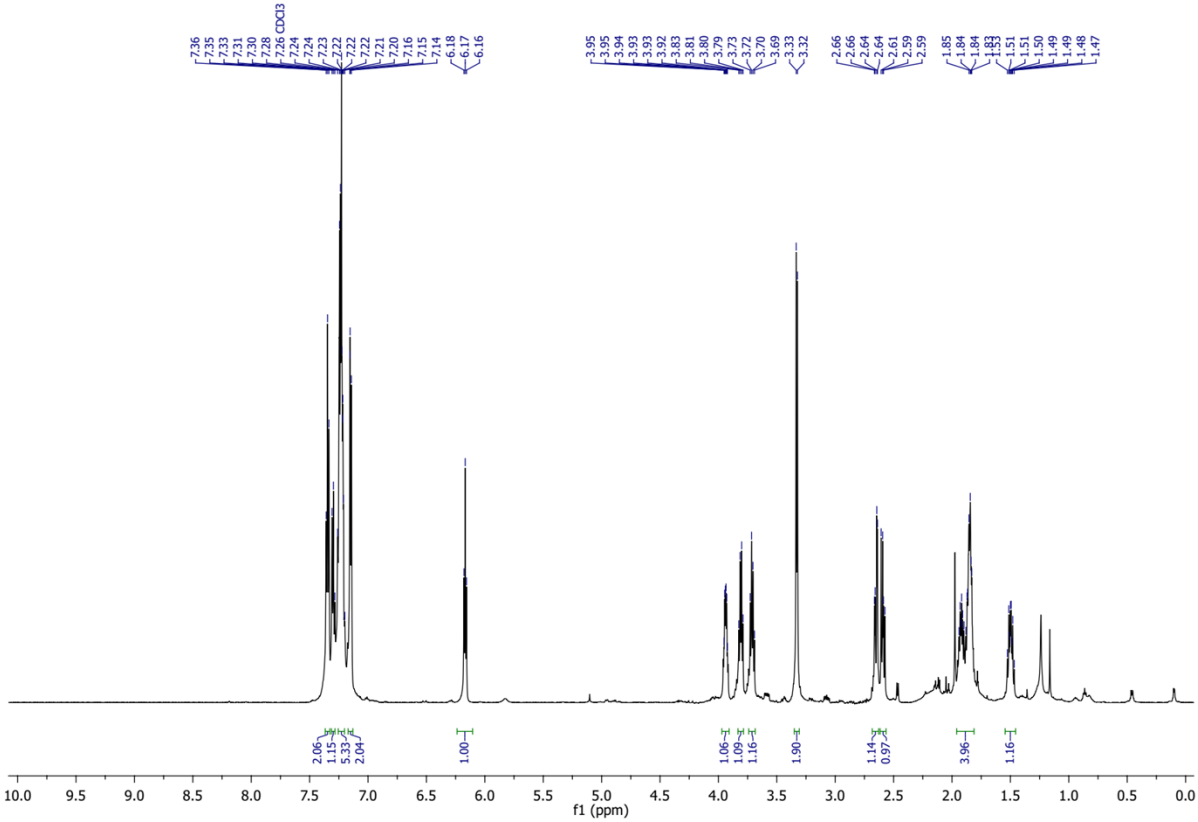


***Figure S*-36.** ^{1}H NMR spectrum of **2j** ($CDCl_3$, 600 MHz, 298 K)

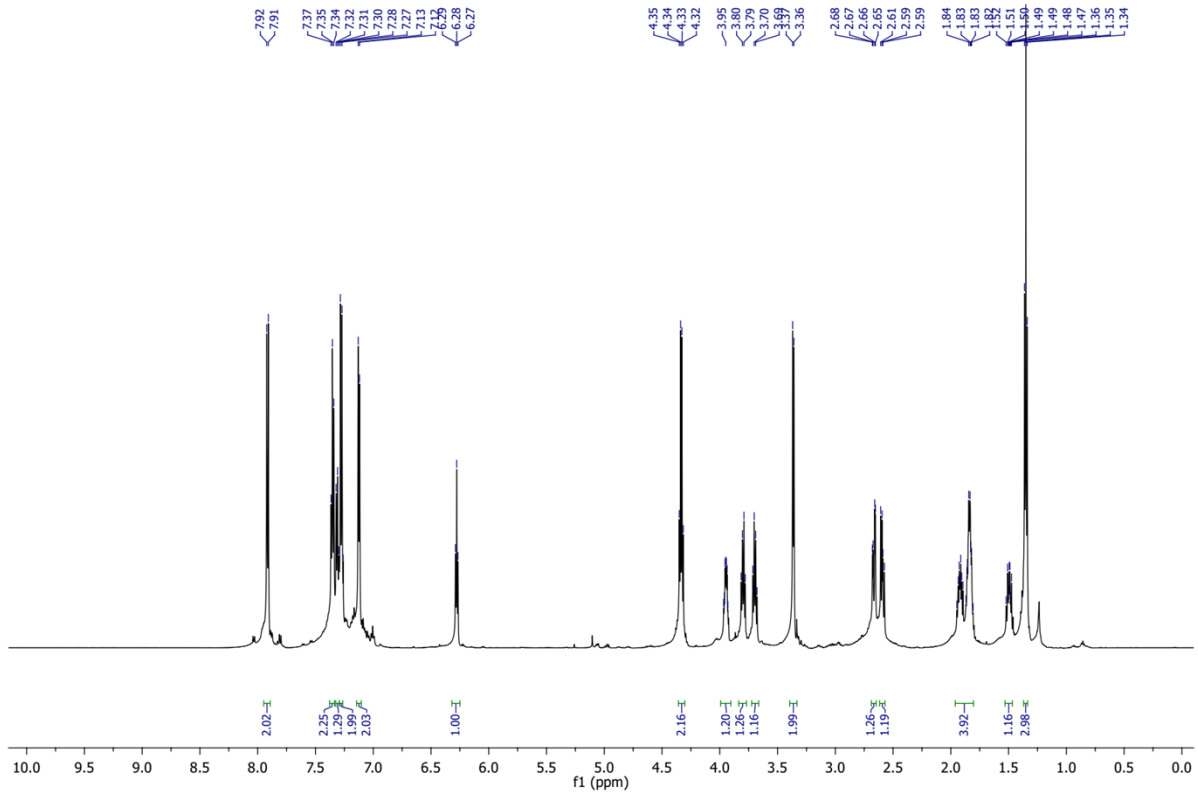


***Figure S*-37.** ^{1}H NMR spectrum of **2k** ($CDCl_3$, 600 MHz, 298 K)

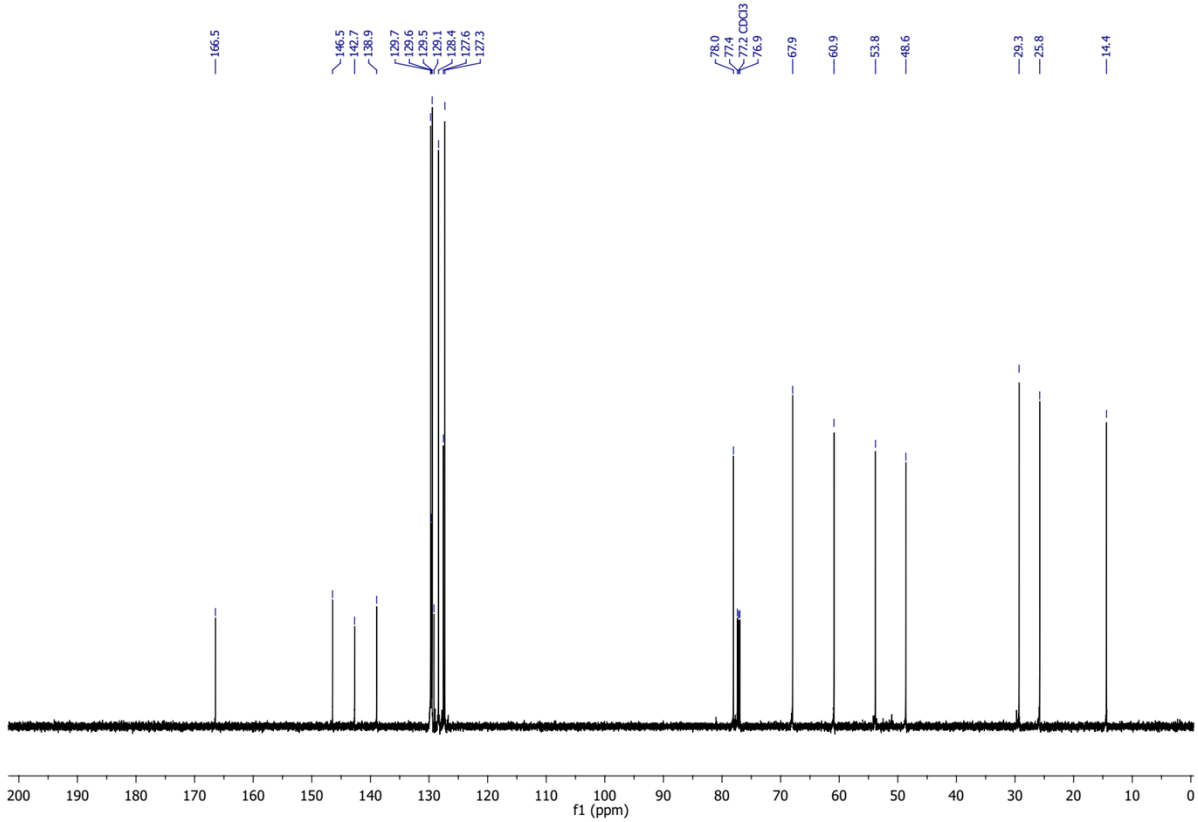


Figure S-38. ^{13}C NMR spectrum of **2k** ($CDCl_3$, 151 MHz, 298 K)

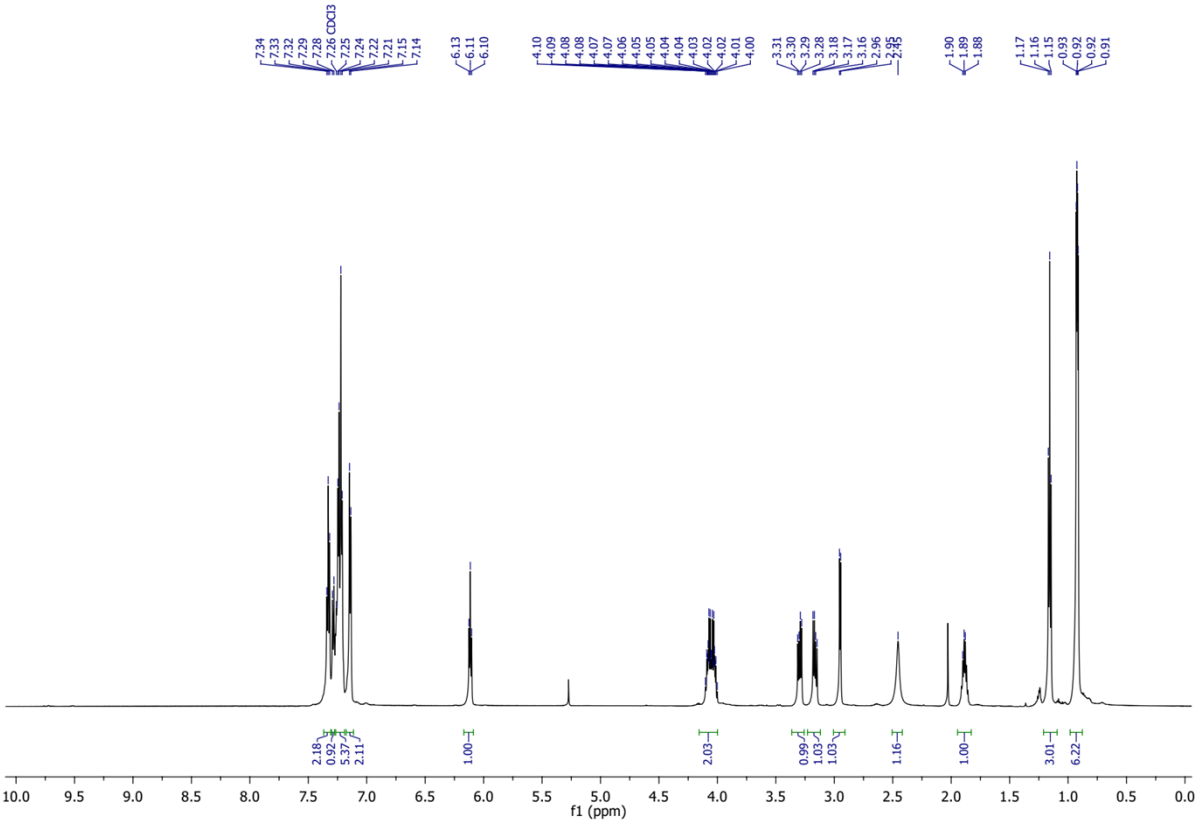


Figure S-39. ^{1}H NMR spectrum of **2l** ($CDCl_3$, 600 MHz, 298 K)

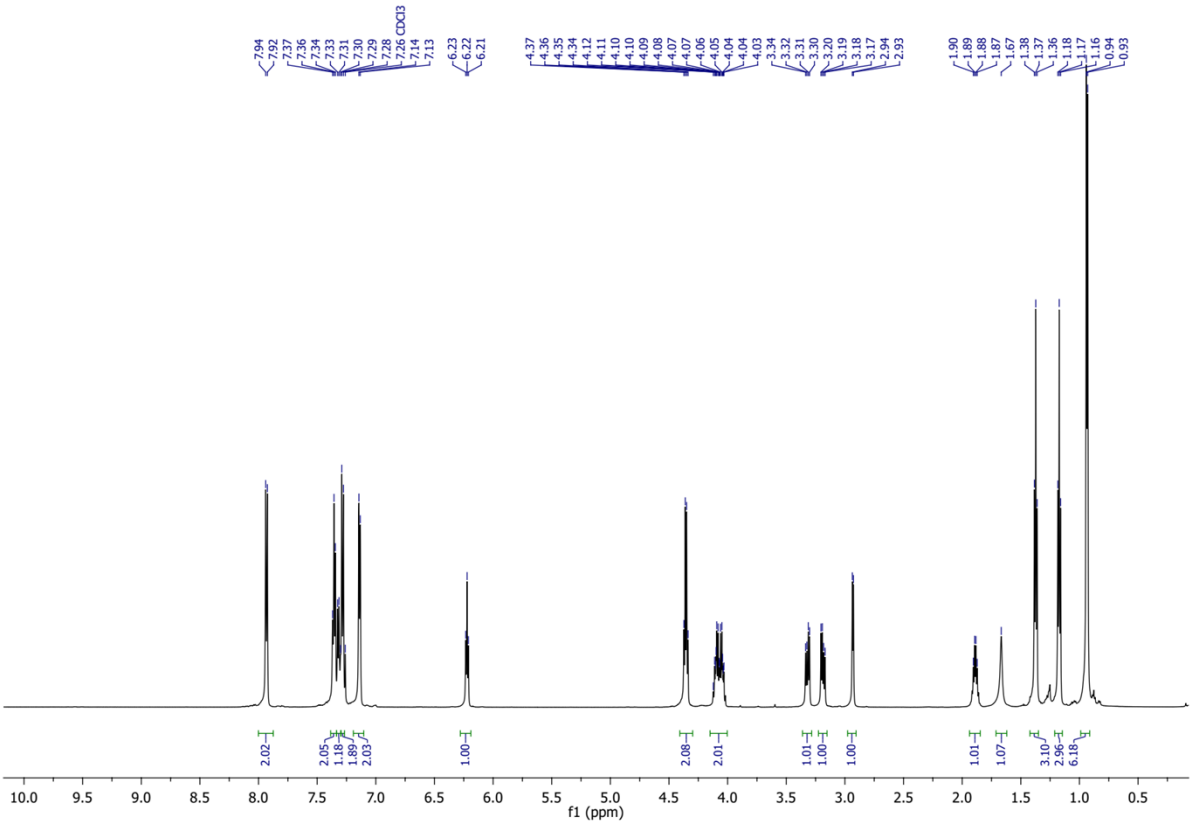


***Figure S*-40.** ^{1}H NMR spectrum of **2m** ($CDCl_3$, 600 MHz, 298 K)

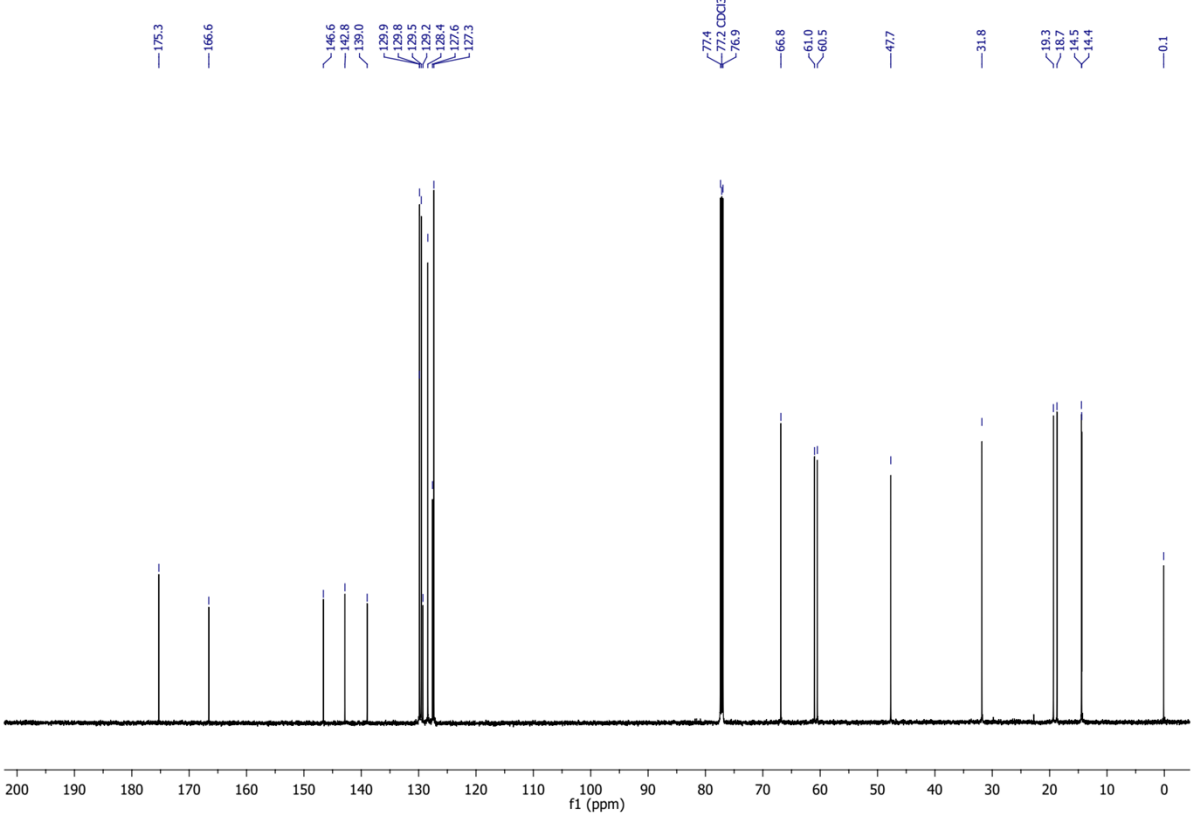


***Figure S*-41.** ^{13}C NMR spectrum of **2m** ($CDCl_3$, 151 MHz, 298 K)

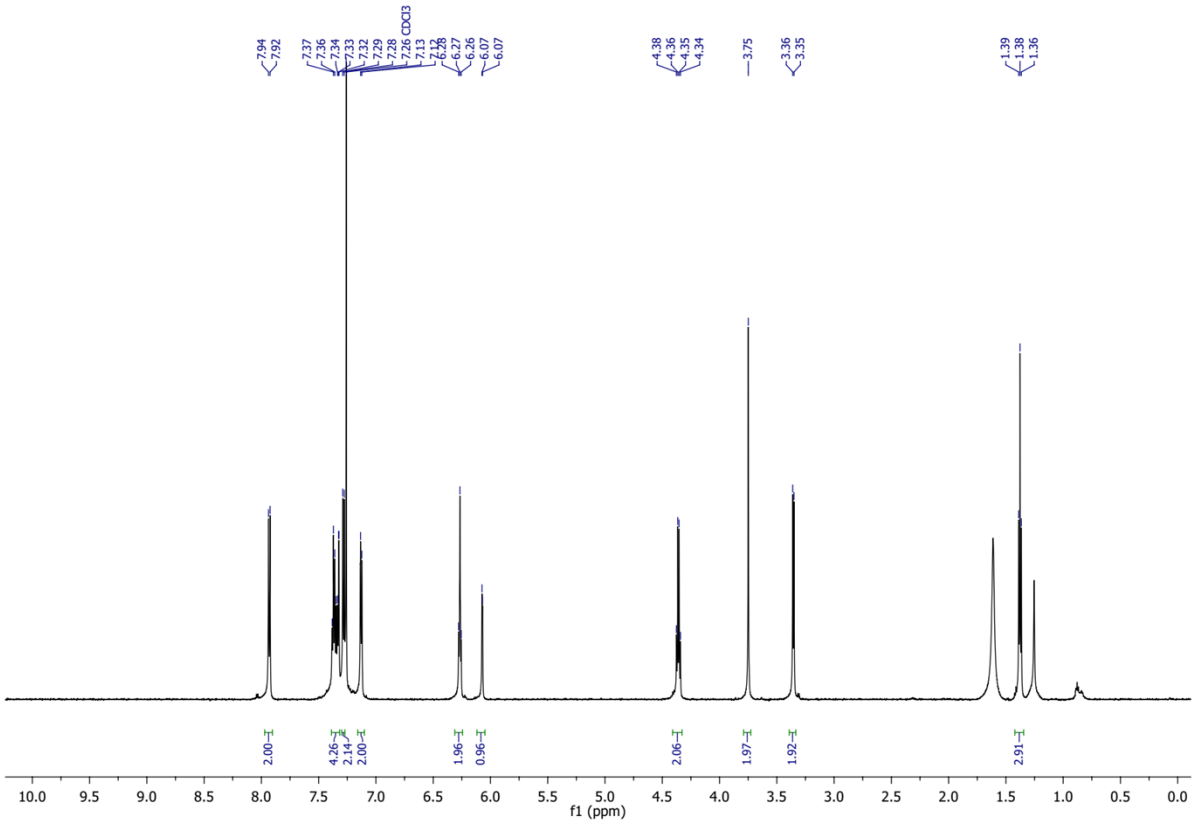


Figure S-42. ^{1}H NMR spectrum of **2n** ($CDCl_3$, 600 MHz, 298 K)

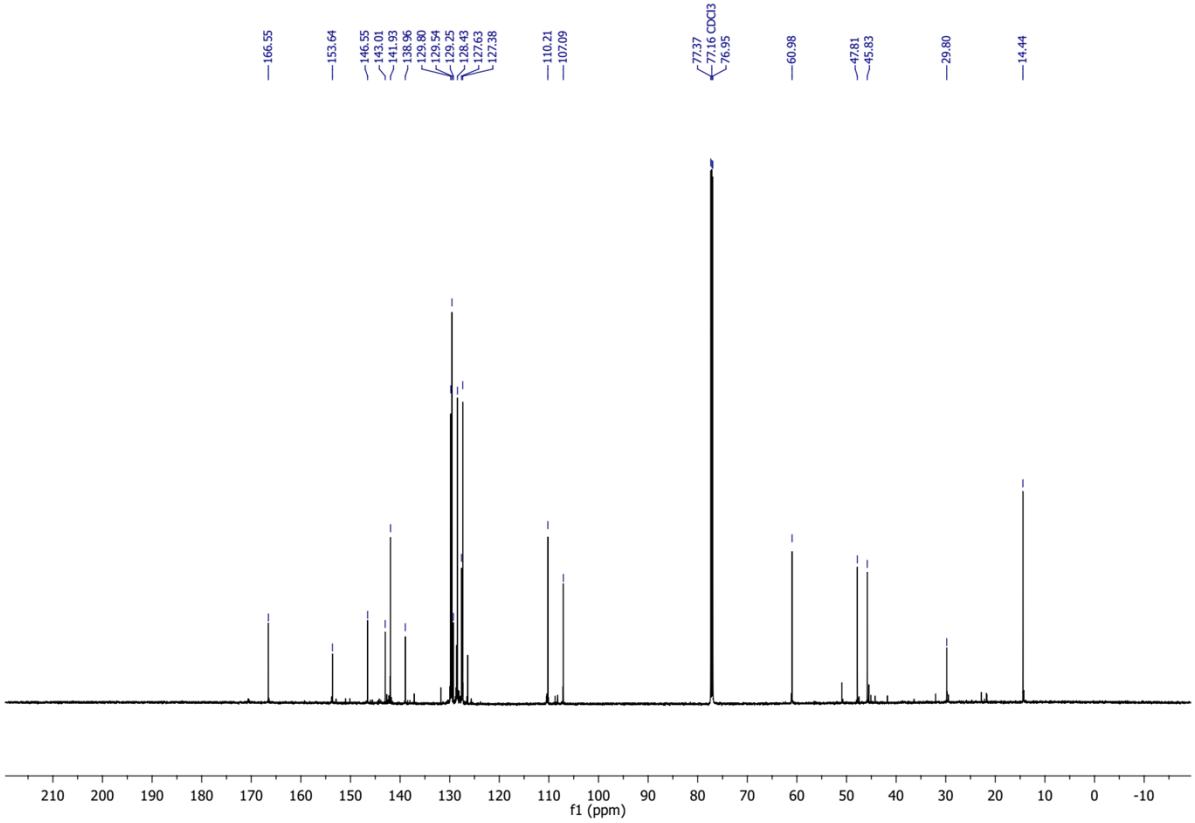


Figure S-43. ^{13}C NMR spectrum of **2n** ($CDCl_3$, 151 MHz, 298 K)

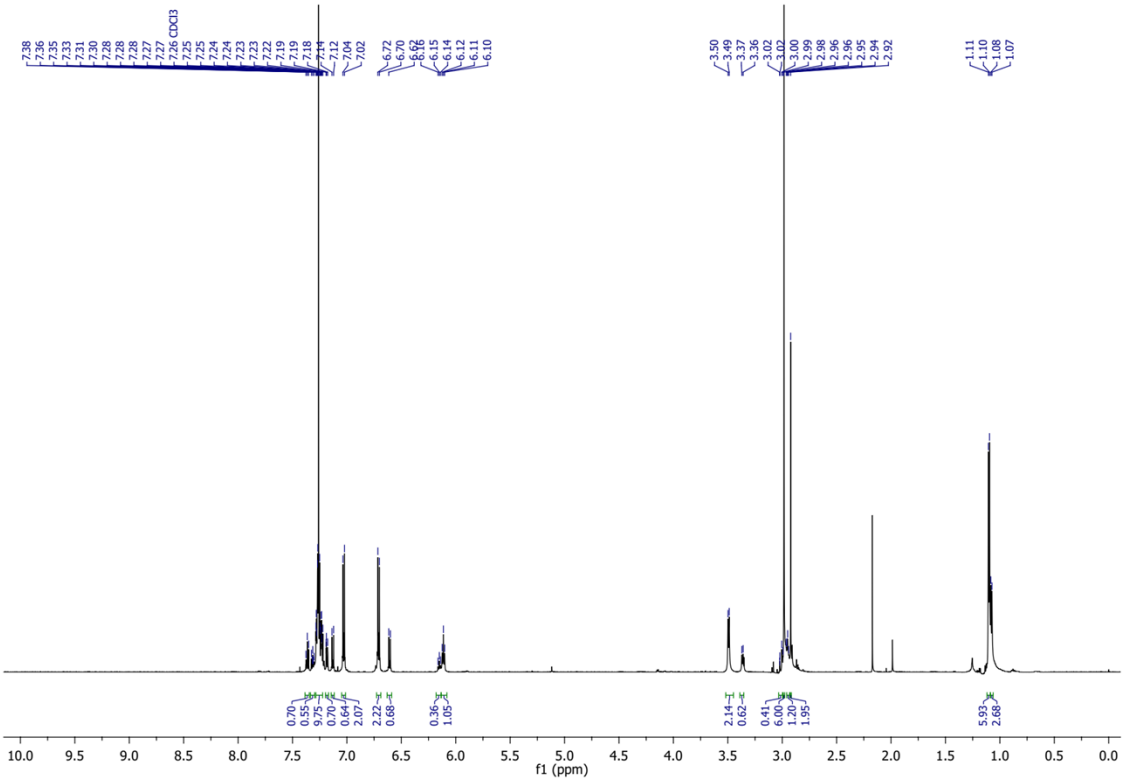


***Figure S*-44.** ^{13}C NMR spectrum of **2o** ($CDCl_3$, 600 MHz, 298 K)

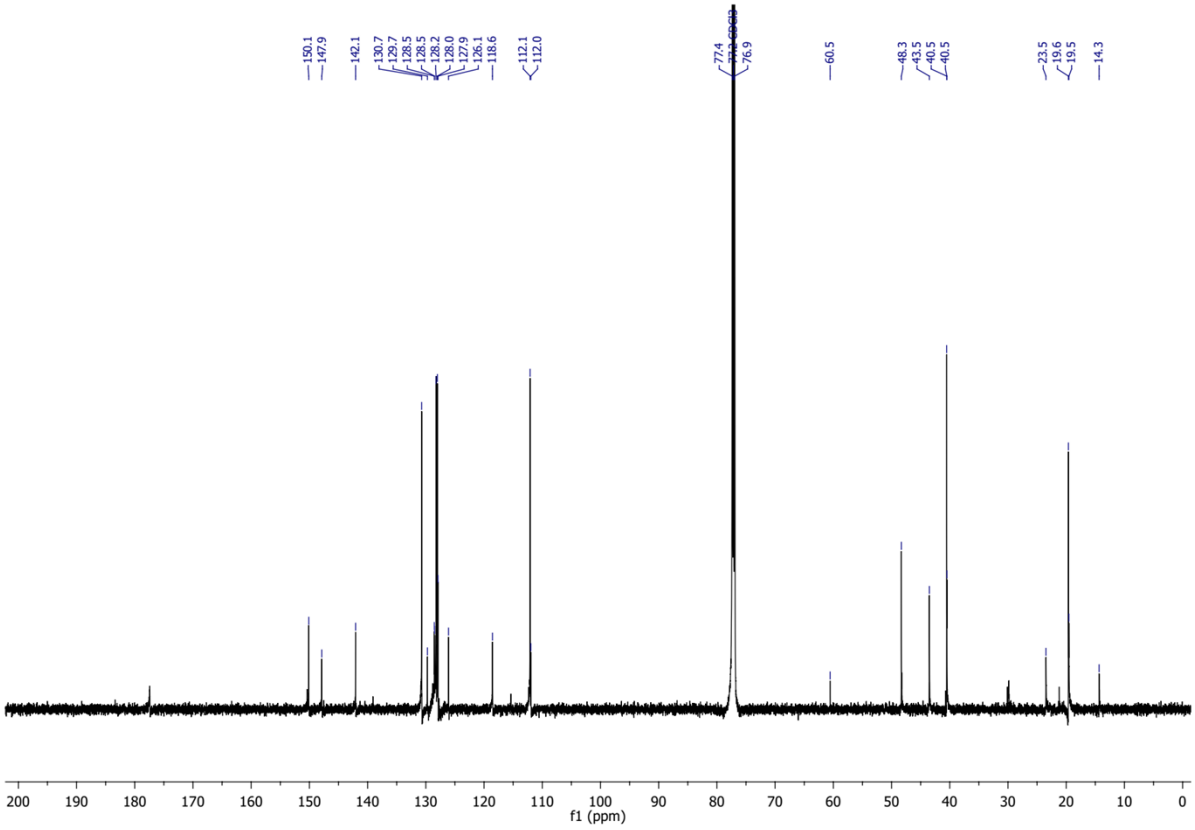


***Figure S*-45.** ^{13}C NMR spectrum of **2o** ($CDCl_3$, 151 MHz, 298 K)

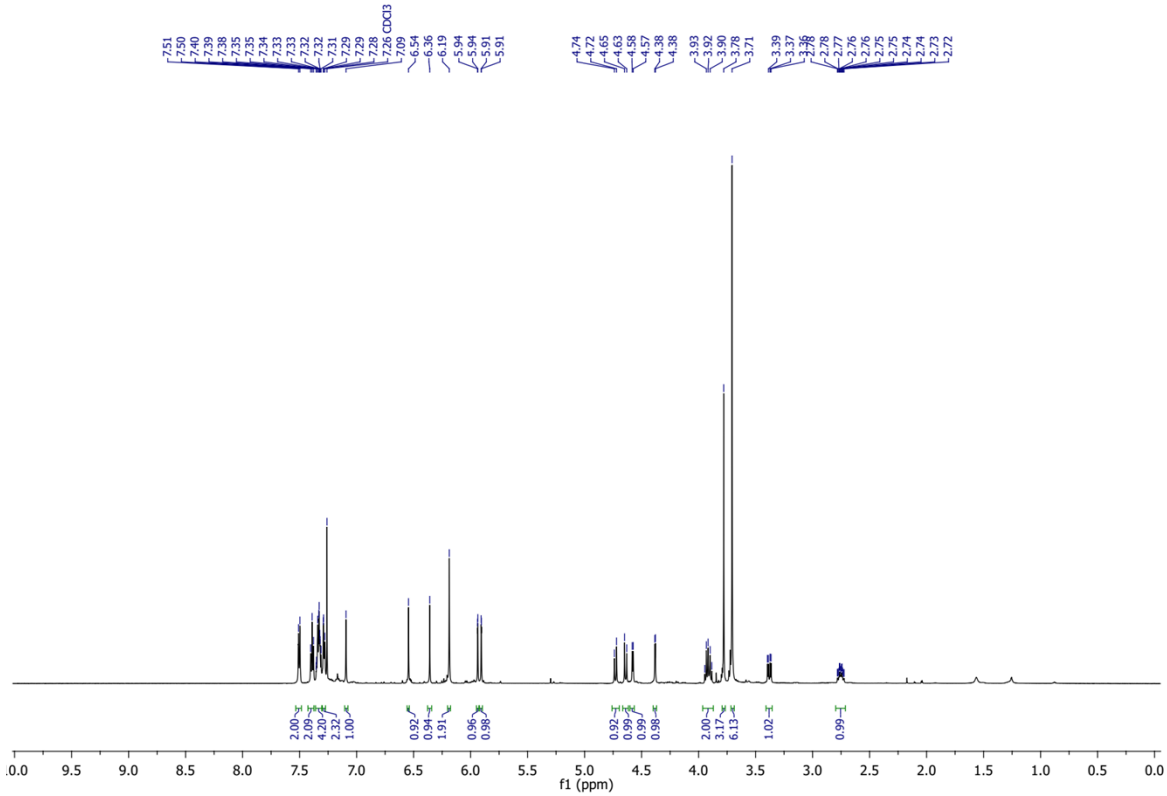


***Figure S*-46.** ^{1}H NMR spectrum of **2p** ($CDCl_3$, 600 MHz, 298 K)

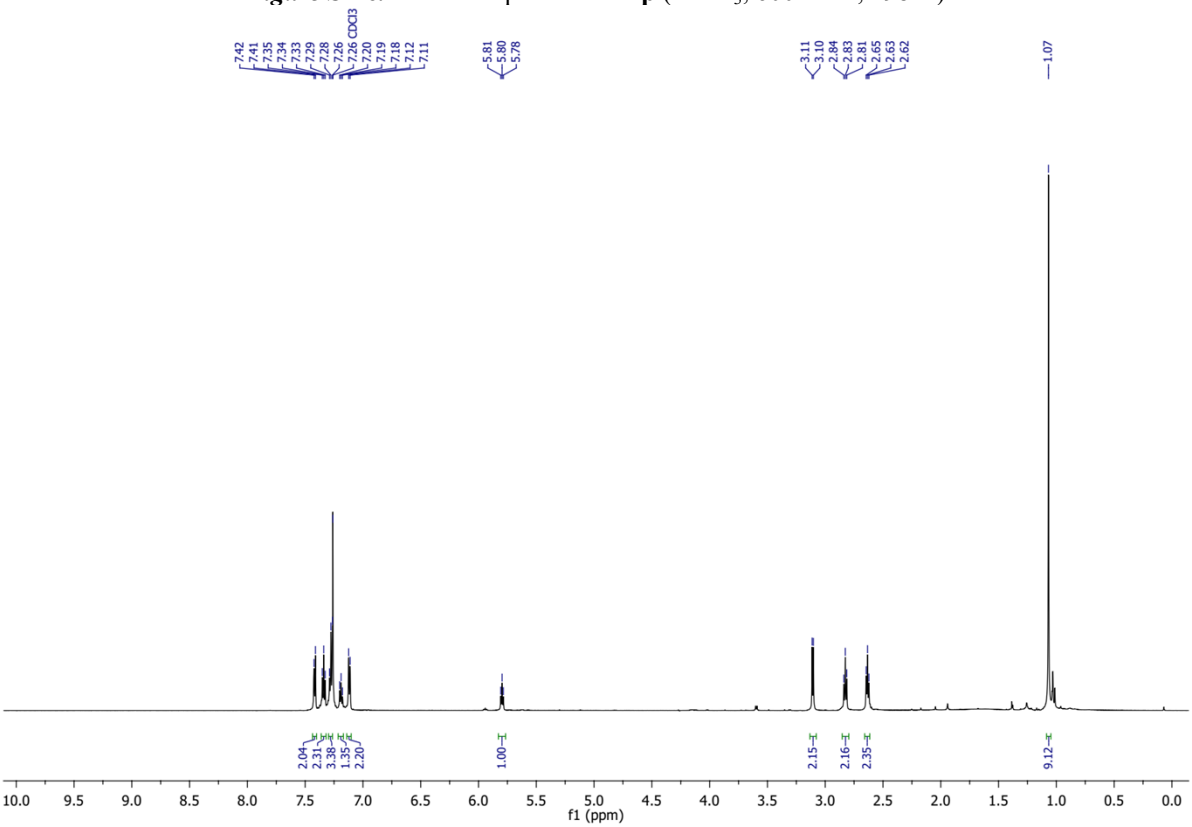


***Figure S*-47.** ^{1}H NMR spectrum of **2q** ($CDCl_3$, 600 MHz, 298 K)

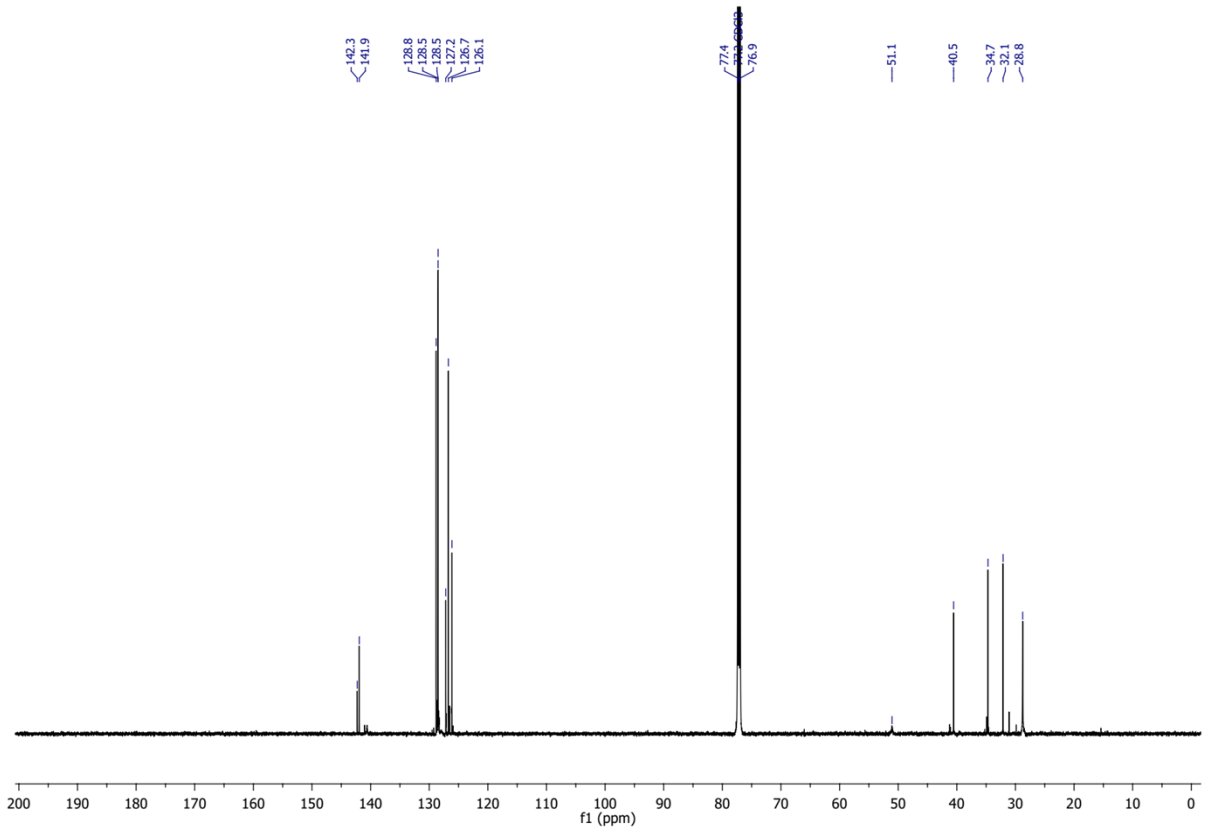


Figure S-48. ^{13}C NMR spectrum of **2q** ($CDCl_3$, 151 MHz, 298 K)

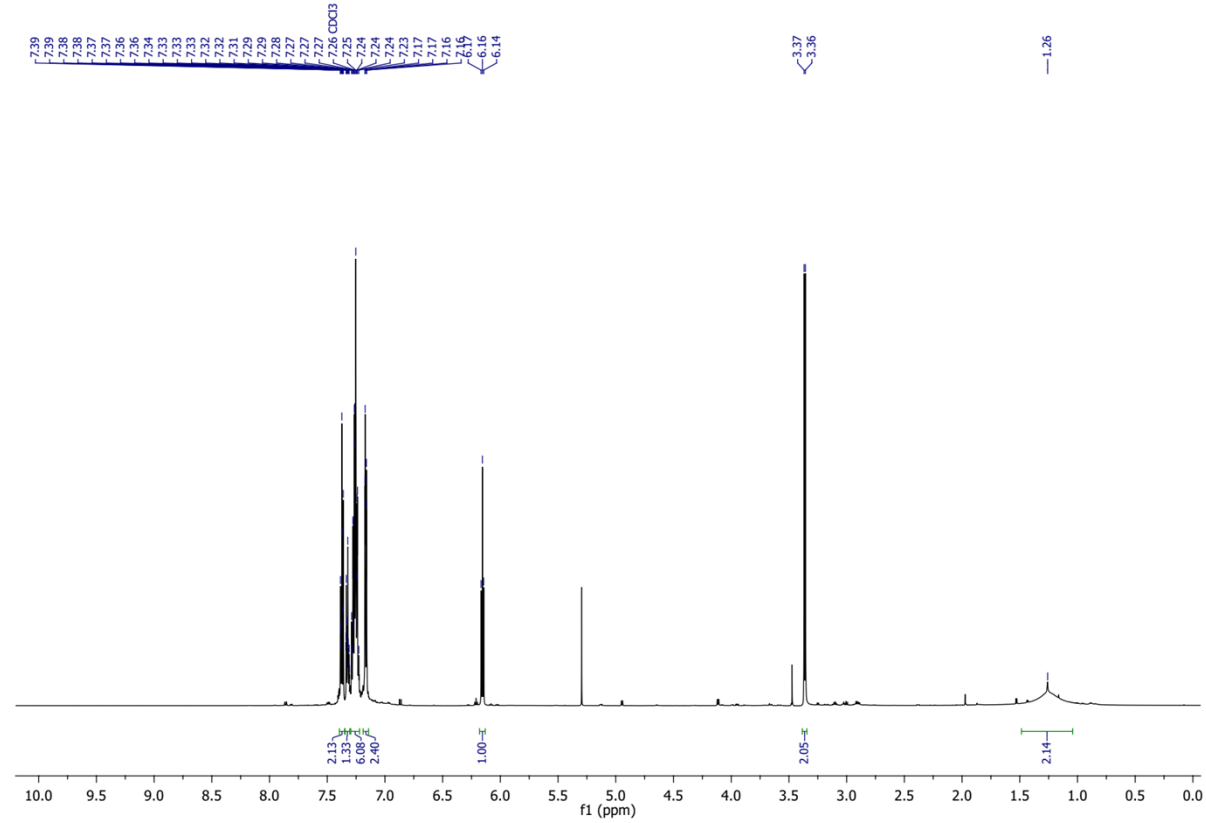


Figure S-49. ^{1}H NMR spectrum of **3a** ($CDCl_3$, 600 MHz, 298 K)

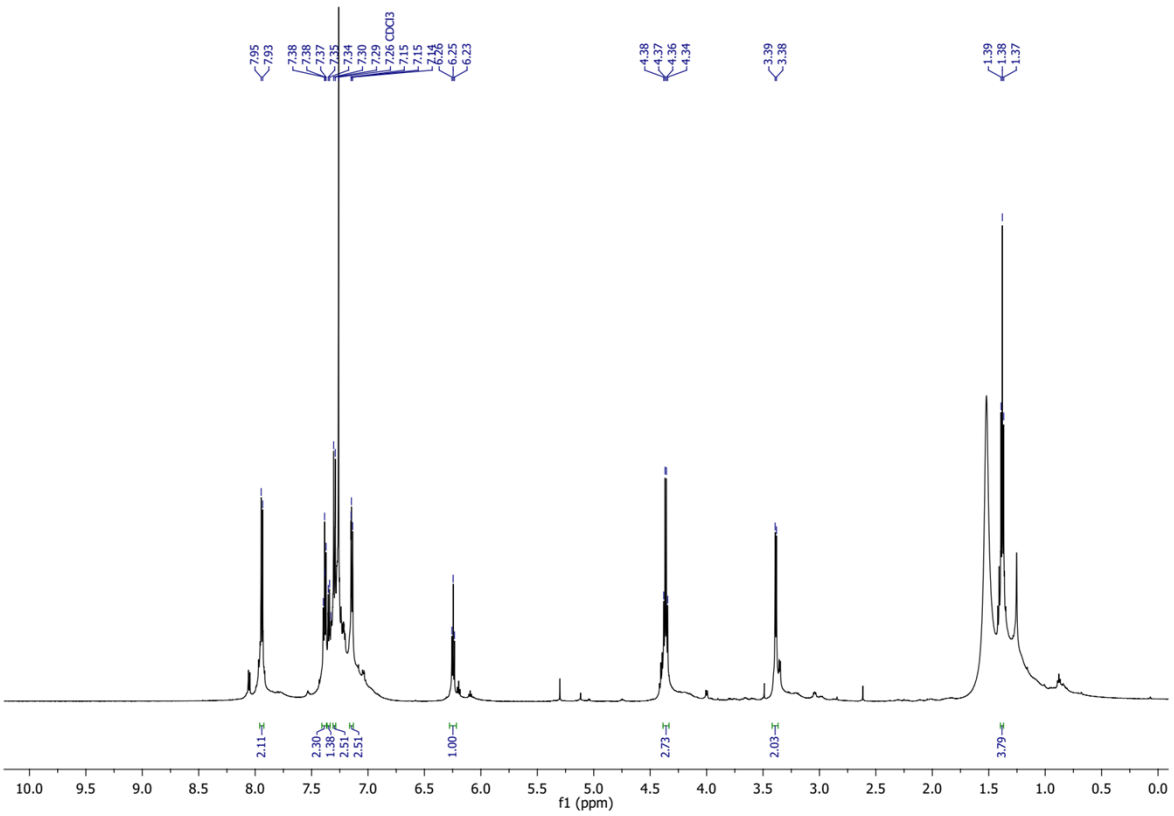


***Figure S*-50.** ^{1}H NMR spectrum of **3b** ($CDCl_3$, 600 MHz, 298 K)

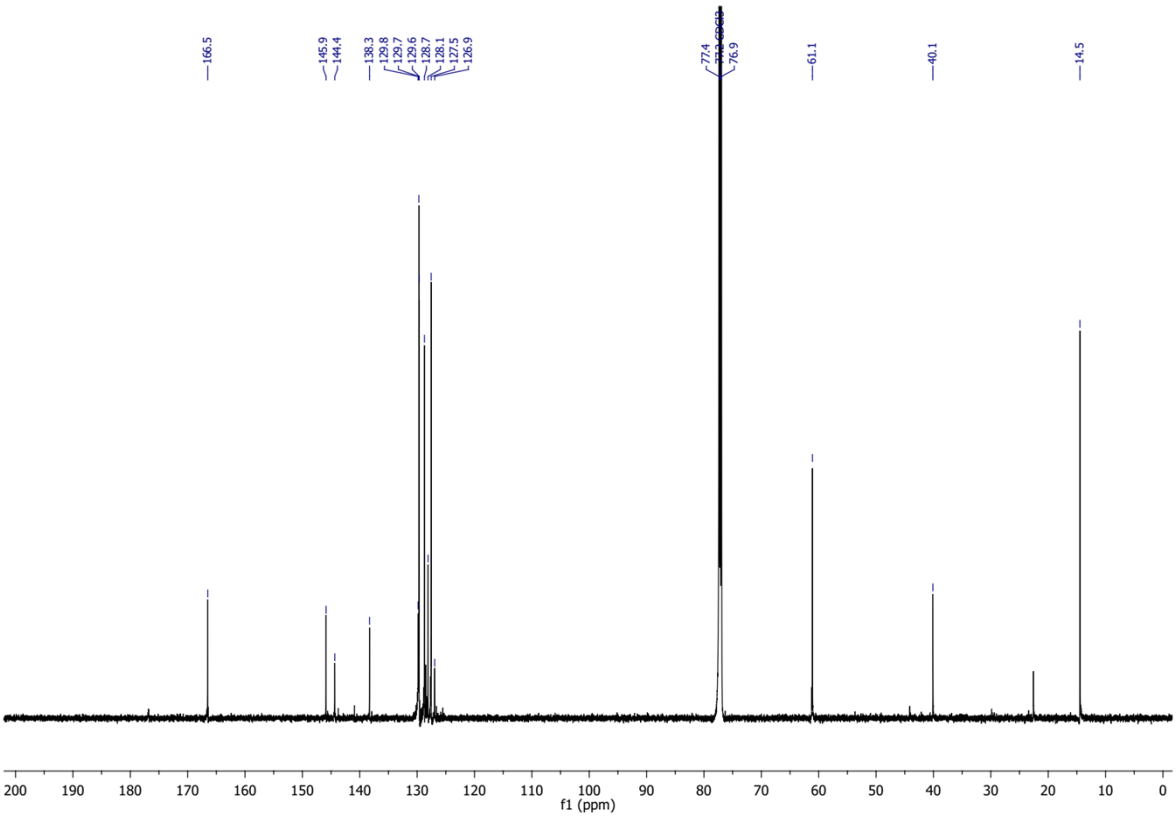


***Figure S*-51.** ^{13}C NMR spectrum of **3b** ($CDCl_3$, 151 MHz, 298 K)

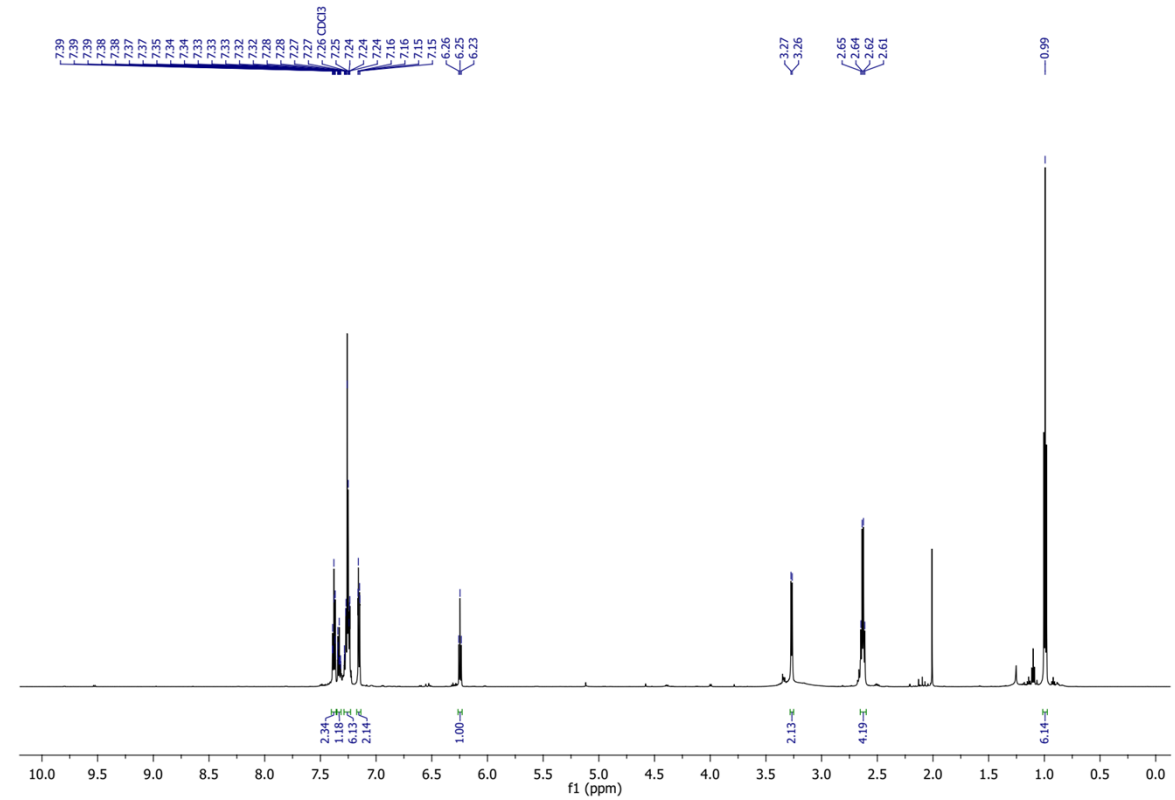


***Figure S*-52.** ^{1}H NMR spectrum of **3c** ($CDCl_3$, 600 MHz, 298 K)

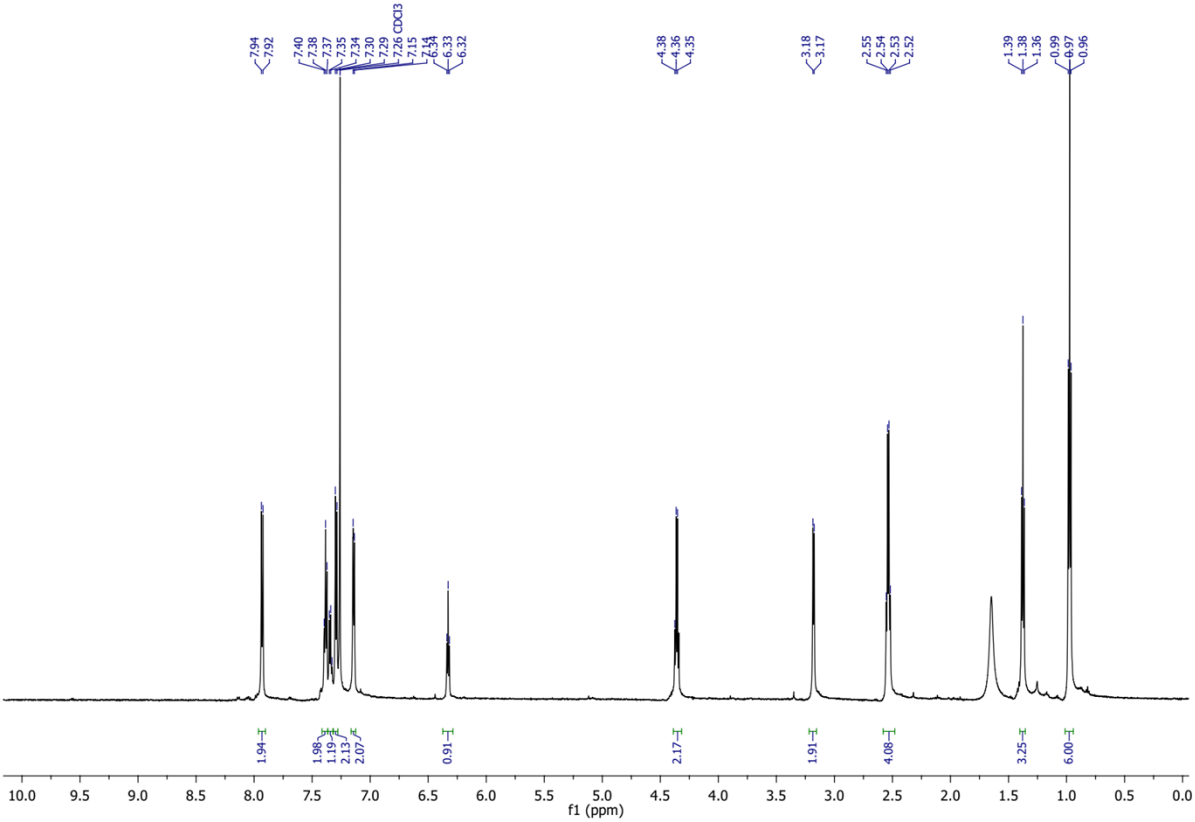


***Figure S*-53.** ^{1}H NMR spectrum of **3d** ($CDCl_3$, 600 MHz, 298 K)

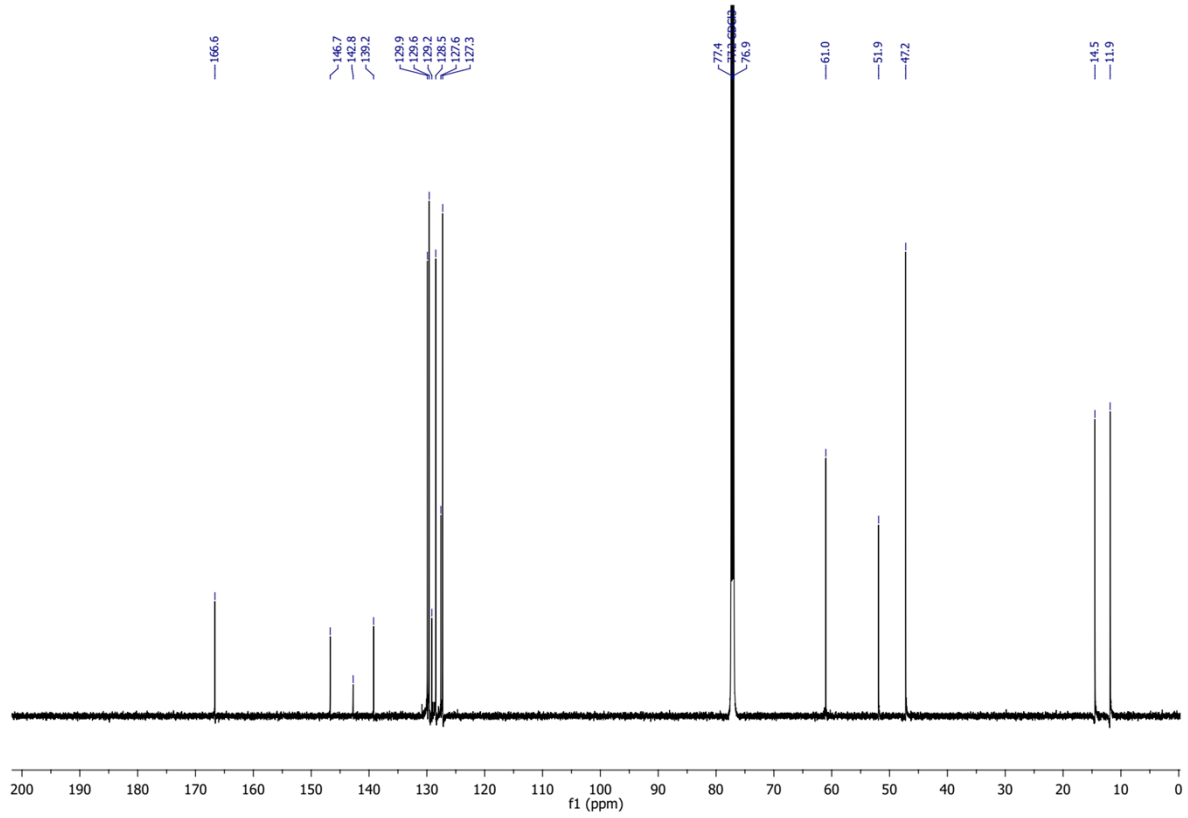


Figure S-54. ^{13}C NMR spectrum of **3d** ($CDCl_3$, 151 MHz, 298 K)

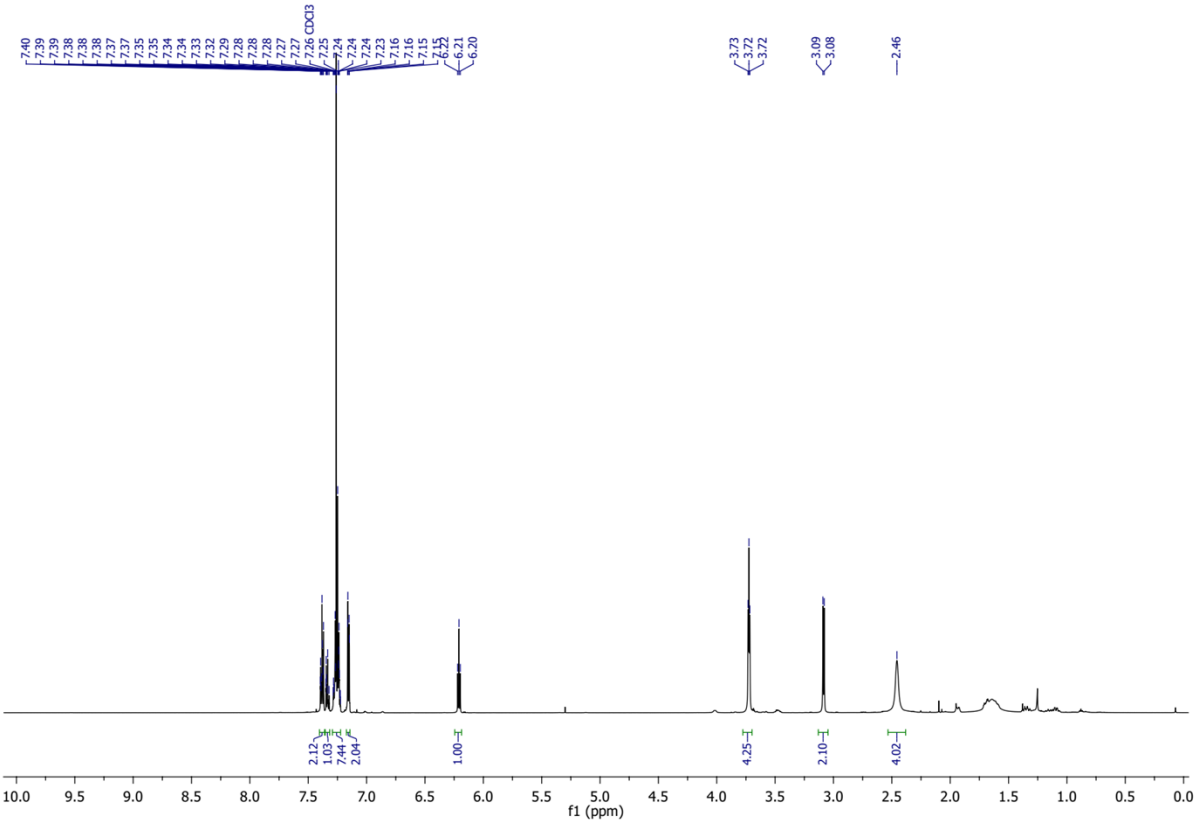


Figure S-55. ^{1}H NMR spectrum of **3e** ($CDCl_3$, 600 MHz, 298 K)

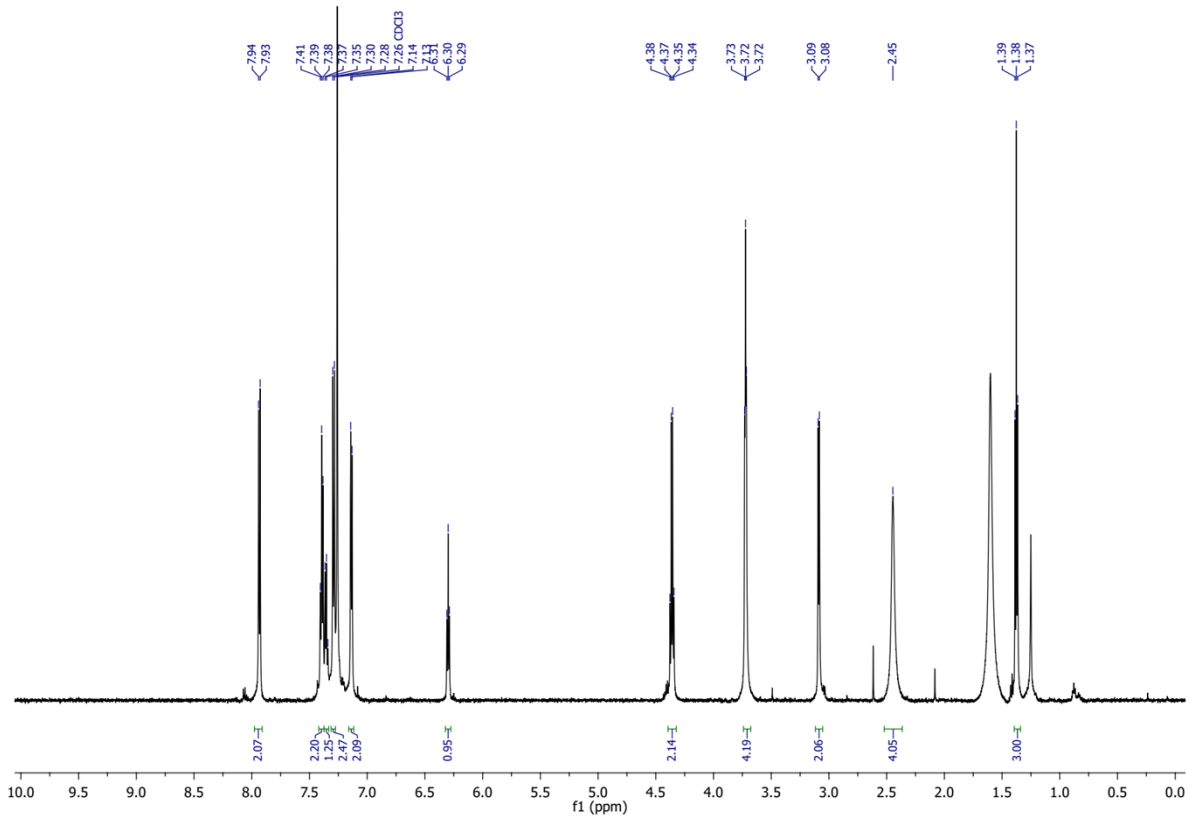


***Figure S*-56.** ^{1}H NMR spectrum of **3f** ($CDCl_3$, 600 MHz, 298 K)

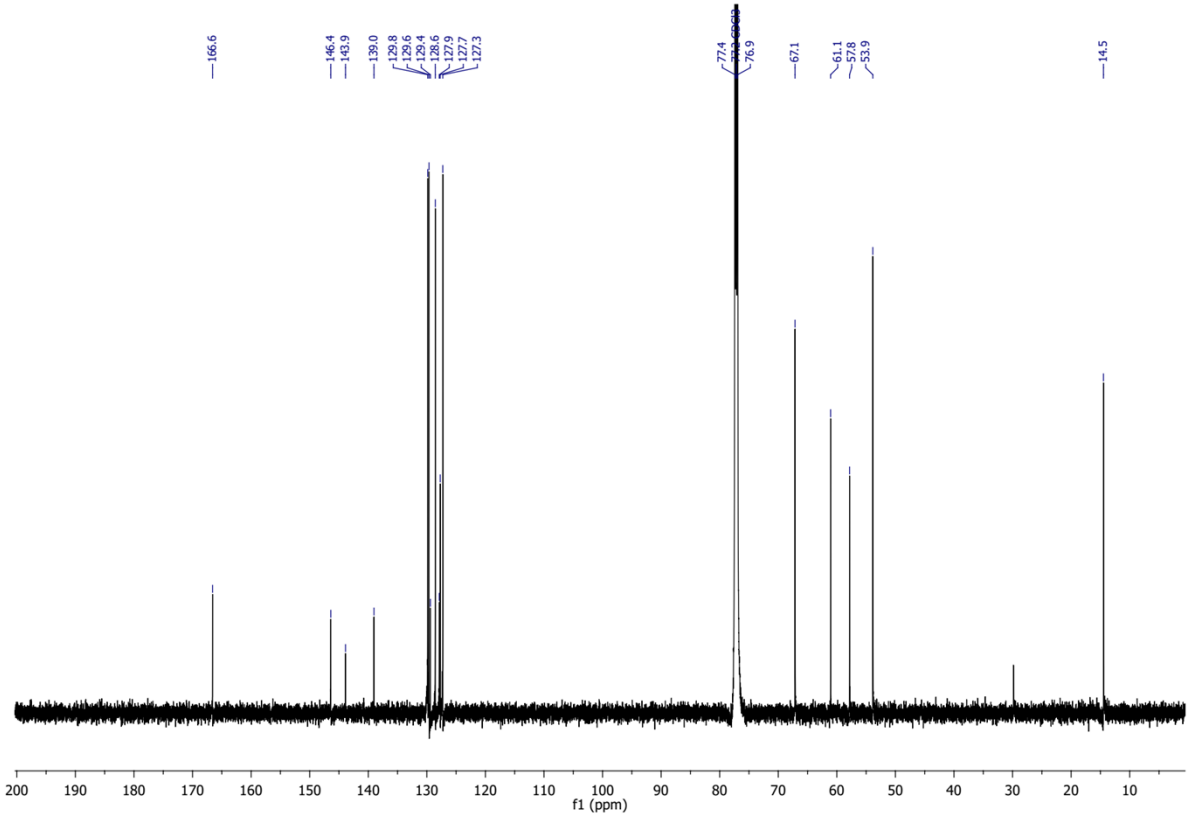


***Figure S*-57.** ^{1}H NMR spectrum of **3f** ($CDCl_3$, 600 MHz, 298 K)

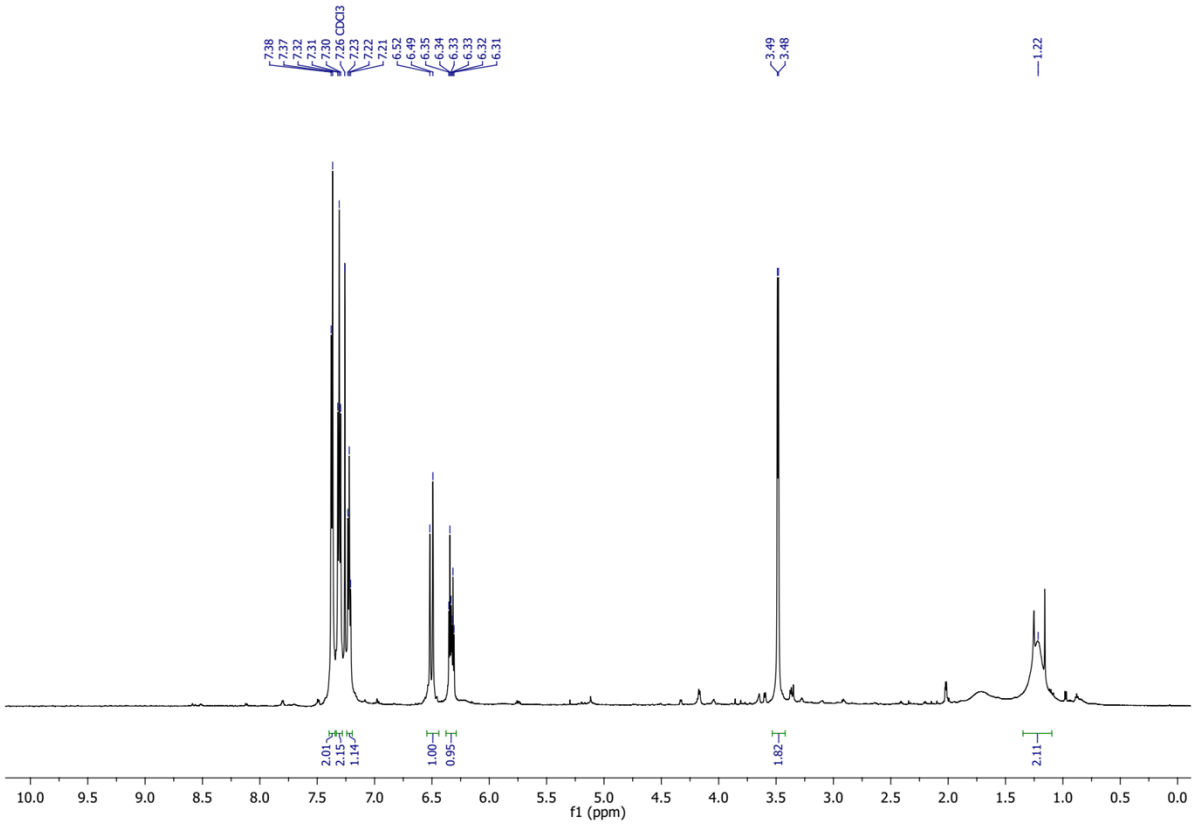


***Figure S*-58.** ^{1}H NMR spectrum of **4a** ($CDCl_3$, 600 MHz, 298 K)

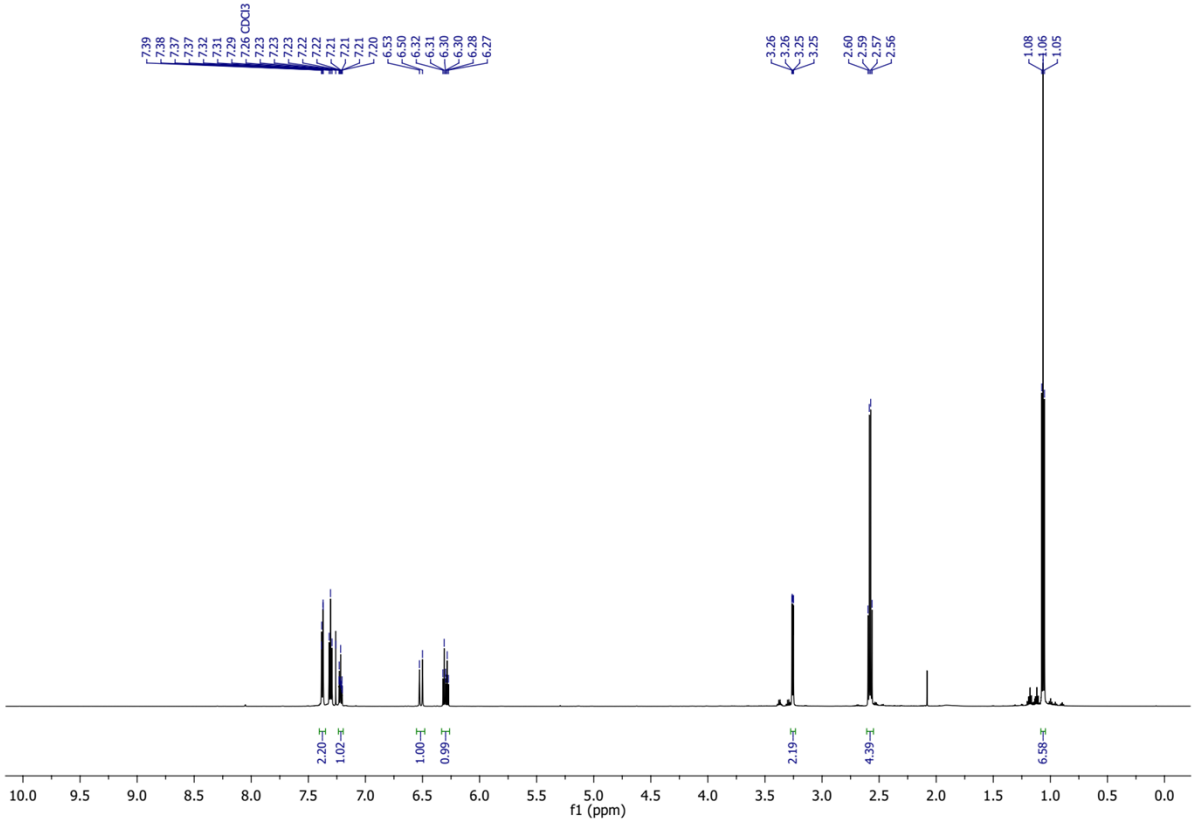


***Figure S*-59.** ^{1}H NMR spectrum of **4b** ($CDCl_3$, 600 MHz, 298 K)

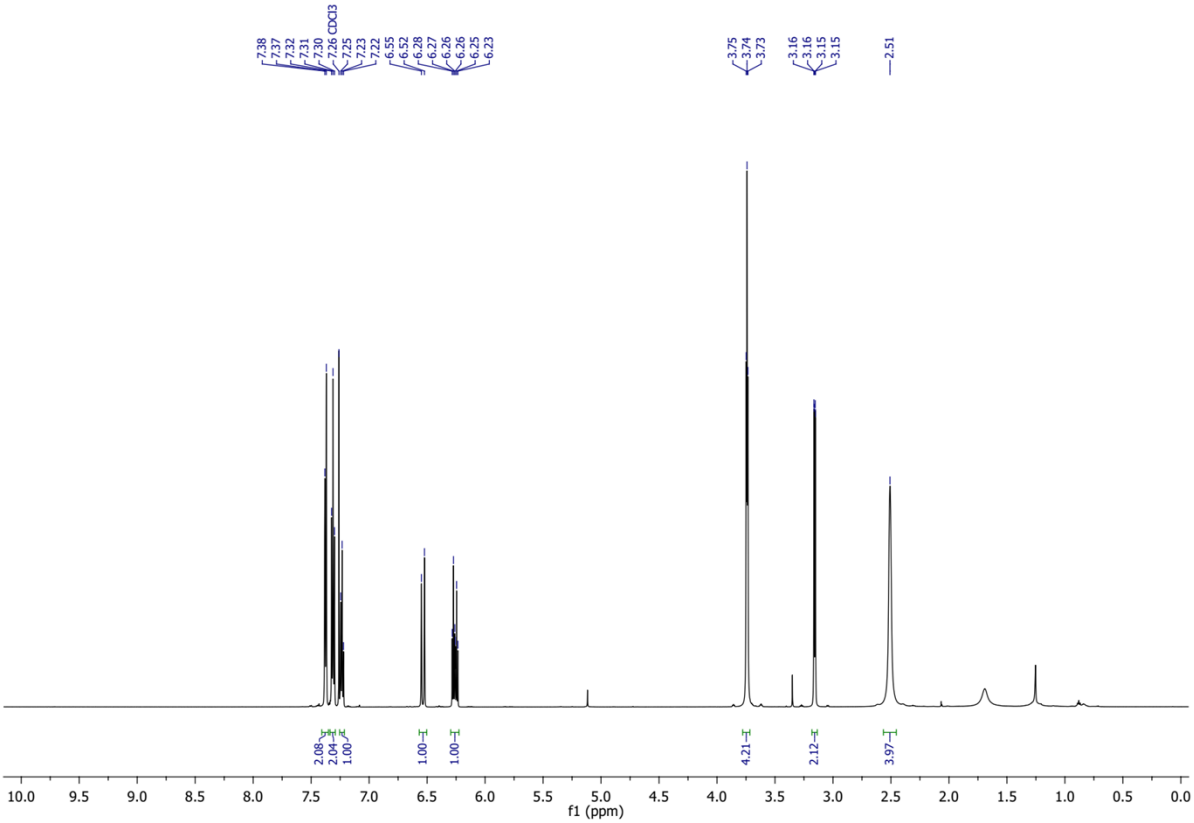


***Figure S*-60.** ^{1}H NMR spectrum of **4c** ($CDCl_3$, 600 MHz, 298 K)

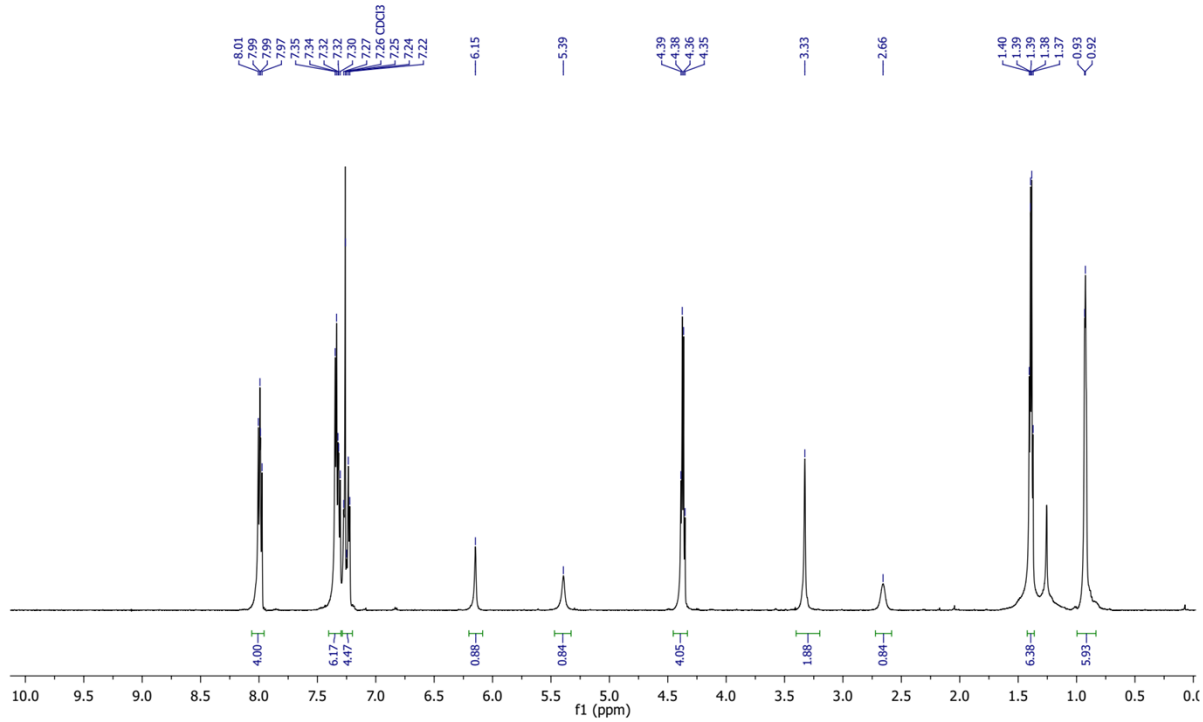


***Figure S*-61.** ^{1}H NMR spectrum of **5** ($CDCl_3$, 600 MHz, 298 K)

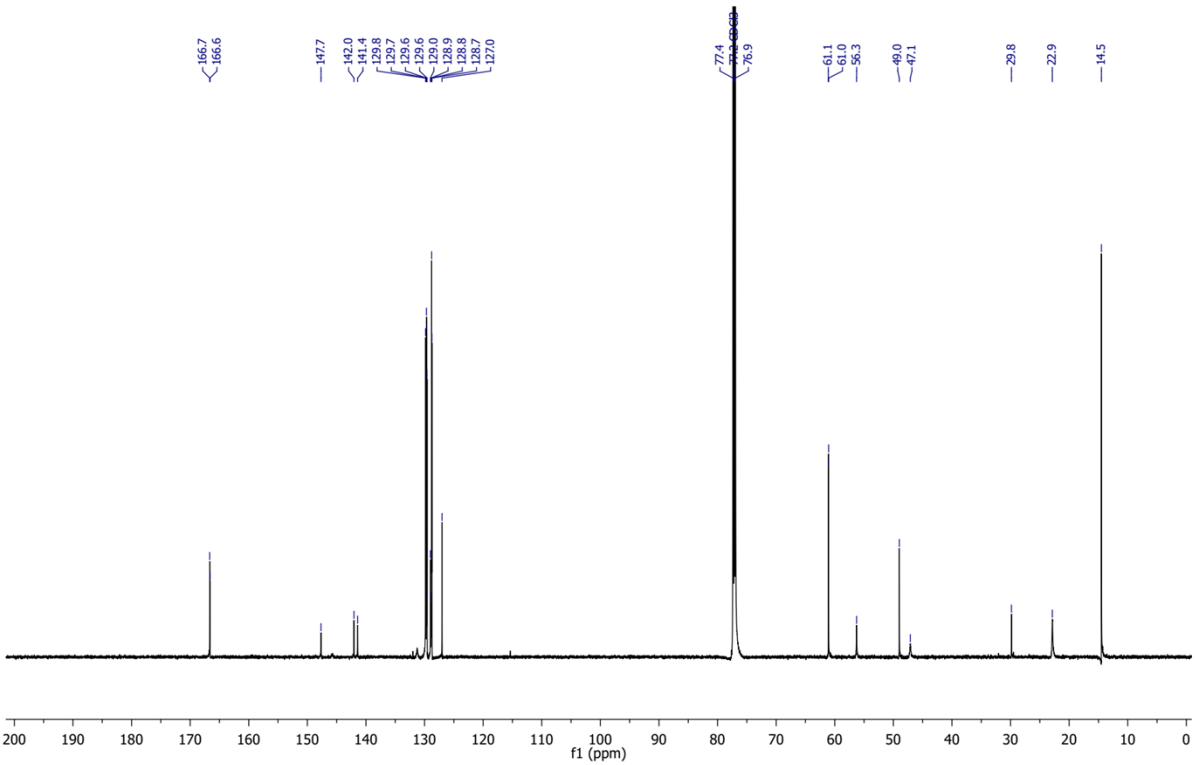


***Figure S*-62.** ^{13}C NMR spectrum of **5** ($CDCl_3$, 151 MHz, 298 K)

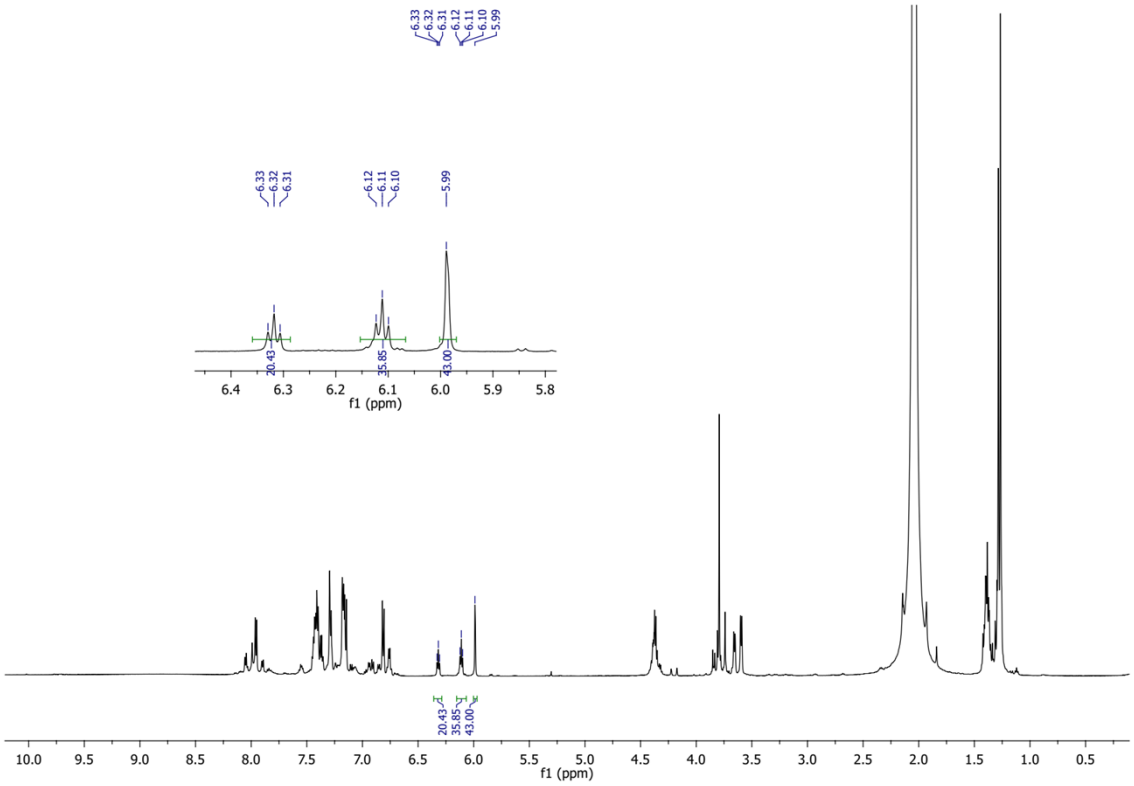


***Figure S*-63.** ^{1}H NMR spectrum of **Scheme 5b** ($CDCl_3$, 600 MHz, 298 K)

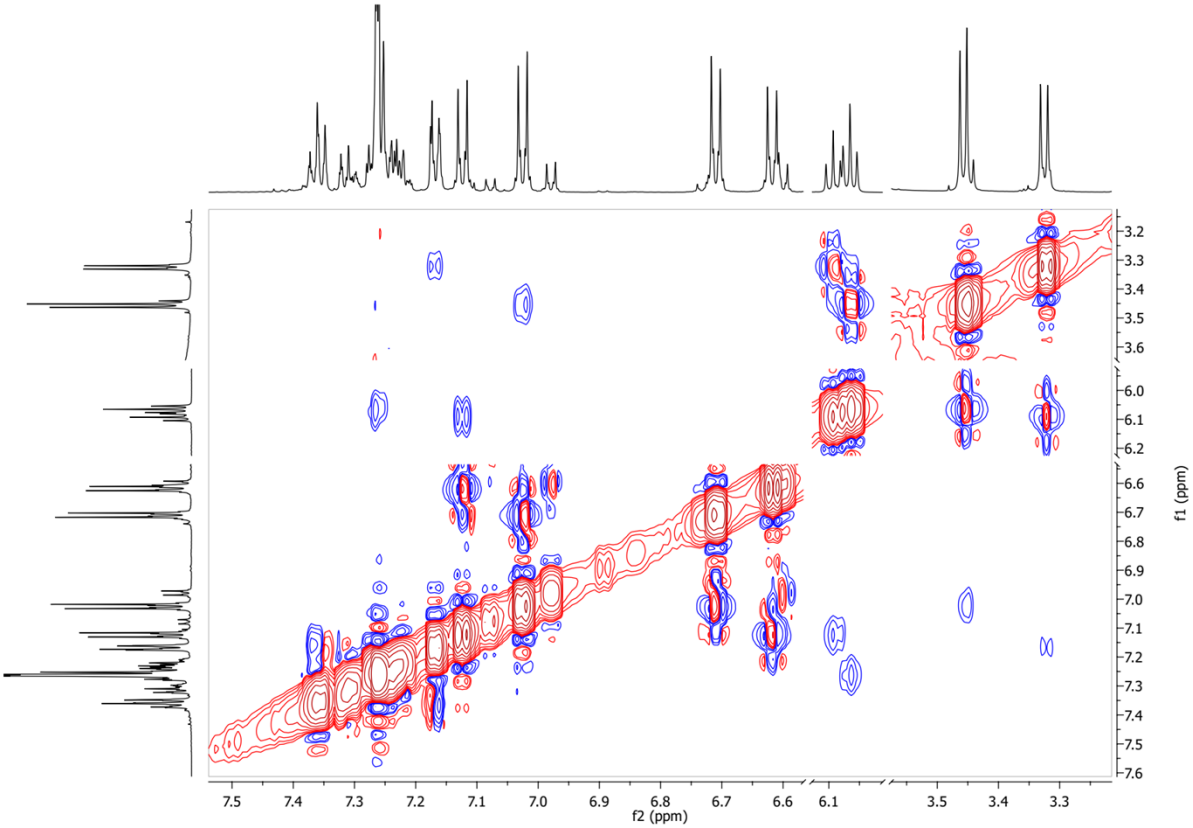


***Figure S*-64.** NOESY spectrum of **2o** (CDCl3, 600 MHz, 298 K)

7. References

[1] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176-2179.

[2] C. P. Rosenau, B. J. Jelier, A. D. Gossert and A. Togni, *Angew. Chem. Int. Ed.*, 2018, **57**, 9528-9533.

[3] V. G. Landge, J. M. Maxwell, P. Chand-Thakuri, M. Kapoor, E. T. Diemler, M. C. Young, *JACS Au*, 2021, **1**, 13-22.

[4] V. G. Landge, A. L. Bonds, T. A. Mncwango, C. B. Mather, Y. Saleh, H. L. Fields, F. Lee, M. C. Young, *Org. Chem. Front.,* 2022, **9**, 1967-1974.

[5] S. H. Nazari, N. Timpos-Flores, K. G. Forson, J. E. Bourdeau and D. J. Michaelis, C–N Bond Formation from Allylic Alcohols via Cooperative Nickel and Titanium Catalysis. *J. Org. Chem.*, 2018, **83**, 10646-10654.

[6] V. G. Landge, A. J. Grant, Y. Fu, A. M. Rabon, J. L. Payton and M. C. Young, Palladium-Catalyzed γ,γ'-Diarylation of Free Alkenyl Amines. *J. Am. Chem. Soc.*, 2021, **143**, 10352-10360.