Supporting Information for:

Photo-Induced Imino Functionalizations of Alkenes via Intermolecular Charge Transfer

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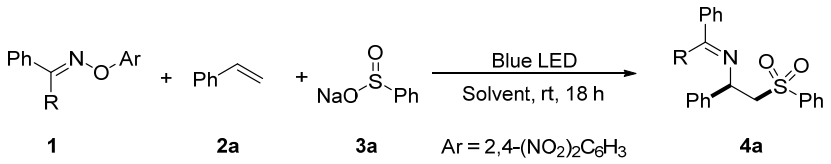
Table of Contents

1. **General experimental details**

All the reagents were commercially available and were used without further purification unless otherwise stated. Solvents were treated prior to use according to the standard methods. Unless otherwise stated, all reactions were conducted under inert atmosphere using standard Schlenk techniques or in an argon-filled glove-box. ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ on 400 MHz or 700 MHz instrument with tetramethylsilane (TMS) as internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, m = multiplet), coupling constant (Hz), and integration. Flash column chromatography was performed on commercially available silica gel (200-300 mesH). All reactions were monitored by TLC, GC-FID, GC-MS or NMR analysis. HRMS data was obtained with Micromass HPLC-Q-TOF mass spectrometer (ESI) or Agilent 6540 Accurate-MS spectrometer (Q-TOF).

2. Screening of reaction conditions of sulfonylimination

Yields were determined by HPLC analysis of the crude product mixtures using anthracene as internal standard.



1 **2a** **3a** Ar = 2,4-$(NO_2)_2C_6H_3$ **4a**

Table S1. Effect of Substituent[a]

Entry	R	Yield of **4a** (%)
1	H	--
2	Me	--
3	Ph	74

[a]Conditions: **1a** (0.12 mmol), **2a** (0.10 mmol), **3a** (0.18 mmol), MeCN (1.0 mL), Blue LED, rt, 18 h.

Table S2. Effect of Solvent[a]

Entry	Solvent	Yield of **4a** (%)
1	MeCN	74
2	THF	21
3	DMSO	46
4	DCM	5
5	DMF	43
6	EA	40
7	NMP	28
8	MeOH	16
9	MTBE	--

[a]Conditions: **1a** (0.12 mmol), **2a** (0.10 mmol), **3a** (0.18 mmol), MeCN (1.0 mL), Blue LED, rt, 18 h.

Table S3. Effect of Substrate Ratio[a]

Entry	**1a**:**3a**	Yield of **4a** (%)
1	1.2:1.5	62
2	1.2:1.8	74
3	1.0:1.0	43
4	1.0:1.5	57
5	1.8:1.5	58
6	1.5:1.5	64

[a]Conditions: **1a** (x mmol), **2a** (0.10 mmol), **3a** (y mmol), MeCN (1.0 mL), Blue LED, rt, 18 h.

Table S4. Effect of Reaction Concentration[a]

Entry	[Con.]	Yield of **4a** (%)
1	0.1 M	74
2	0.2 M	61
3	0.05 M	56

[a]Conditions: **1a** (0.12 mmol), **2a** (0.10 mmol), **3a** (0.18 mmol), MeCN (x mL), Blue LED, rt, 18 h.

Table S5. Effect of Mixed Solvent[a]

Entry	Solvent	Yield of **4a** (%)
1	MeCN/DMSO = 9:1	88
2	MeCN/DMF = 9:1	70
3	MeCN/THF = 9:1	54
4	MeCN/NMP = 9:1	76
5	MeCN/DCM = 9:1	72
6	MeCN/EtOH = 9:1	65
7	MeCN/EA = 9:1	49
8	MeCN/DMSO = 2:1	77
9	MeCN/DMSO = 1:1	71

[a]Conditions: **1a** (0.12 mmol), **2a** (0.10 mmol), **3a** (0.18 mmol), Solvent (1.0 mL), Blue LED, rt, 18 h.

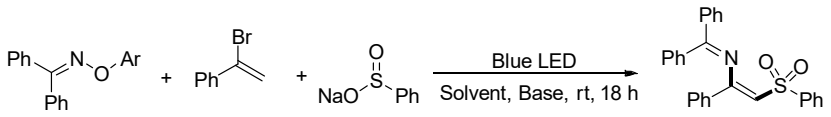
Table S6. Effect of Light Source[a]

Entry	Light Source	Yield of **4a** (%)
1	Kessil light 390 nm	76
2	Kessil light 427 nm	78
3	Kessil light 456 nm	65
4	Blue LED light box	88
5	Without light	--

[a]Conditions: **1a** (0.12 mmol), **2a** (0.10 mmol), **3a** (0.18 mmol), MeCN/DMSO = 9:1 (1.0 mL), Blue LED, rt, 18 h.

3. Screening of reaction conditions of vinylsulfonylimination

Yields were determined by HPLC analysis of the crude product mixtures using anthracene as internal standard.



1a **2aa** **3a** Ar = 2,4-$(NO_2)_2C_6H_3$ **28a**

Table S7. Effect of Base[a]

Entry	Base	Yield of **28a** (%)
1	w/o base	15[b]
2	Cs_2CO_3	71(68[b])
3	Na_2CO_3	59
4	Li_2CO_3	23
5	K_2CO_3	38
6	CsF	22
7	KOAc	42
8	$LiOH·H_2O$	44
9	K_3PO_4	50
10	CsOAc	20

[a]Conditions: **1a** (0.12 mmol), **2a** (0.10 mmol), **3a** (0.18 mmol), Base (0.10 mmol), MeCN (1.0 mL), Blue LED, rt, 18 h; [b]Isolated yield.

Table S8. Effect of the Amount of Base[a]

Entry	Cs_2CO_3(x mmol)	Yield of **28a** (%)
1	0.12	69
2	0.05	58
3	0.25	51

[a]Conditions: **1a** (0.12 mmol), **2a** (0.10 mmol), **3a** (0.18 mmol), MeCN (1.0 mL), Blue LED, rt, 18 h.

Table S9. Effect of Solvent[a]

Entry	Solvent	Yield of **28a** (%)
1	MeCN	71
2	DMF	69
3	THF	22
4	EtOH	47
5	EA	67
6	DMSO	62

[a]Conditions: **1a** (0.12 mmol), **2a** (0.10 mmol), **3a** (0.18 mmol), Cs_2CO_3 (0.10 mmol), Solvent (1.0 mL), Blue LED, rt, 18 h.

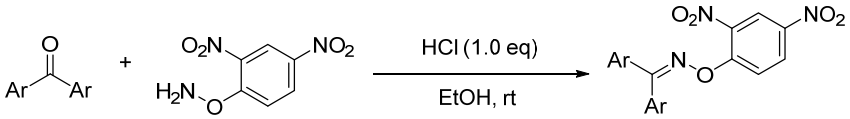
Table S10. Effect of Mixed Solvent[a]

Entry	Solvent	Yield of **28a** (%)
1	MeCN/DMSO = 9:1	62
2	MeCN/DMF = 9:1	60
3	MeCN/EA = 9:1	57
4	MeCN/DMF = 4:1	61
5	MeCN/EA = 4:1	59
6	MeCN/DMSO = 4:1	70

[a]Conditions: **1a** (0.12 mmol), **2a** (0.10 mmol), **3a** (0.18 mmol), Cs_2CO_3 (0.10 mmol), Solvent (1.0 mL), Blue LED, rt, 18 h.

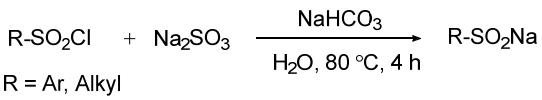
4. Procedure for the synthesis of substrates

General procedure A for the condensation of diaryl ketone with O-aryl-hydroxylamines



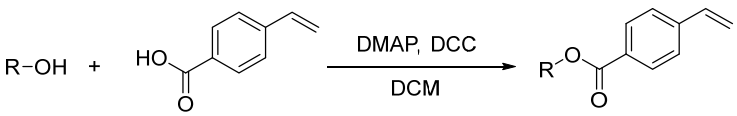
O-aryl oximes were synthesized according to modified literature procedures.[1] A solution of diaryl ketone (1.5 equiv.) in EtOH (0.1 M) was treated with the O-arylhydroxylamine (1.0 equiv.). Then HCl (1.0 equiv.) was added into the solution and stirred at room temperature overnight. Then the reaction mixture was filtered and the filter cake was washed with cold *n*-pentane. The product was dried at 60 °C for 3 h.

General procedure B for the synthesis of sodium sulfinates

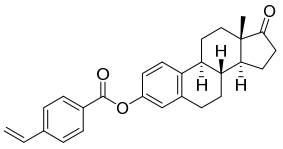


Known sodium sulfinates were synthesized according to literature procedures.[2] A solution of sodium sulfite (1.26 g, 10.0 mmol) and sodium bicarbonate (0.84 g, 10.0 mmol) in H_2O (5 mL) was treated with sulphonyl chloride (5.0 mmol) and stirred at 80 °C for 4 h. Water was removed by rotary evaporator. Then the remaining solid was dissolved and recrystallized by ethanol to get a white solid.

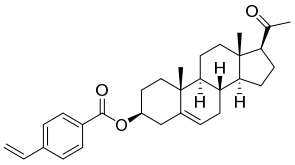
General procedure C for the synthesis of complex alkenes



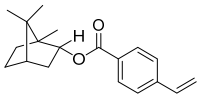
Complex alkenes were synthesized according to literature procedures.[3] 4-Vinylbenzoic acid (1.0 equiv.) was added to a mixture of corresponding alcohol (1.0 equiv.), DMAP (1.0 equiv.) and DCC (1.0 equiv.) in CH_2Cl_2 (0.2 M) at room temperature and then stirred overnight. Next, the reaction mixture was filtered, concentrated on a rotary evaporator and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give a white solid.



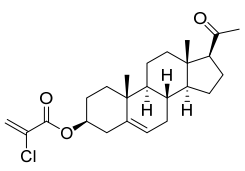
(8R,9S,13S,14S)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 4-vinylbenzoate (5aa): Prepared according to the general procedure C, known compound,[3] white solid, 507.4 mg, 42% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 1H), 6.99 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.95 (d, *J* = 2.4 Hz, 1H), 6.79 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.91 (d, *J* = 17.7 Hz, 1H), 5.42 (d, *J* = 11.0 Hz, 1H), 3.02 – 2.82 (m, 2H), 2.51 (dd, *J* = 18.9, 8.6 Hz, 1H), 2.46 – 2.40 (m, 1H), 2.32 (td, *J* = 10.7, 3.5 Hz, 1H), 2.21 – 2.12 (m, 1H), 2.12 – 1.94 (m, 3H), 1.70 – 1.43 (m, 6H), 0.92 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 165.21,148.85, 142.54, 138.08, 137.43, 135.96, 130.48, 128.73, 126.47, 126.27, 121.72, 118.89, 116.92, 50.47, 47.98, 44.20, 38.05, 35.88, 31.59, 29.45, 26.39, 25.80, 21.62, 13.87.



(3S,8S,9S,10R,13S,14S,17S)-17-Acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-vinylbenzoate (5ab): Prepared according to the general procedure C, known compound,[4] white solid, 898.9 mg, 67% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 6.75 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.86 (d, *J* = 17.6 Hz, 1H), 5.42 (d, *J* = 4.4 Hz, 1H), 5.38 (d, *J* = 11.0 Hz, 1H), 4.95 – 4.70 (m, 1H), 2.55 (t, *J* = 8.9 Hz, 1H), 2.47 (d, *J* = 7.8 Hz, 2H), 2.24 – 2.16 (m, 1H), 2.13 (s, 3H), 2.09 – 1.96 (m, 3H), 1.93 (dt, *J* = 13.2, 3.4 Hz, 1H), 1.82 – 1.32 (m, 9H), 1.31 – 1.12 (m, 3H), 1.07 (s, 3H), 0.65 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 209.55, 165.77, 141.79, 139.68, 136.07, 129.91, 129.85, 126.03, 122.46, 116.37, 74.42, 63.70, 56.86, 49.92, 44.01, 38.82, 38.19, 37.06, 36.68, 31.85, 31.81, 31.57, 27.87, 24.50, 22.85, 21.07, 19.39, 13.25.

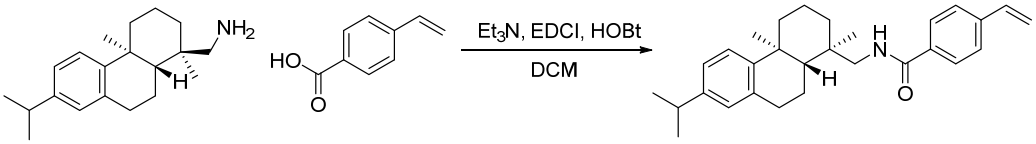


(1S,2R,4S)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 4-vinylbenzoate (5ac): Prepared according to the general procedure C, white solid, known compound,[5] 333.4 mg, 59% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 6.76 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.86 (d, *J* = 17.6 Hz, 1H), 5.38 (d, *J* = 10.9 Hz, 1H), 5.11 (dt, *J* = 9.9, 3.2 Hz, 1H), 2.57 – 2.37 (m, 1H), 2.18 – 2.09 (m, 1H), 1.86 – 1.76 (m, 1H), 1.74 (t, *J* = 4.5 Hz, 1H), 1.47 – 1.37 (m, 1H), 1.36 – 1.27 (m, 1H), 1.12 (dd, *J* = 13.8, 3.4 Hz, 1H), 0.97 (s, 3H), 0.92 (s, 3H), 0.91(s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.59, 141.79, 136.08, 130.04, 129.82, 126.08, 116.36, 80.50, 49.11, 47.89, 45.01, 36.93, 28.11, 27.42, 19.75, 18.94, 13.64.

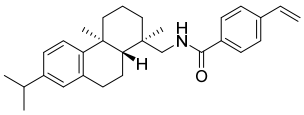


(3S,8S,9S,10R,13S,14S,17S)-17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-chloroacrylate (5ad): Prepared according to the general procedure, white solid, melting point: 152 – 154 °C, 362.5 mg, 45% yield, R_f = 0.5 (PE/EA = 9/1). **^{1}H NMR** (700 MHz, Chloroform-*d*) δ 6.51 (d, *J* = 1.3 Hz, 1H), 5.99 (d, *J* = 1.3 Hz, 1H), 5.40 (d, *J* = 4.4 Hz, 1H), 4.75 – 4.69 (m, 1H), 2.54 (t, *J* = 9.0 Hz, 1H), 2.41 (d, *J* = 7.7 Hz, 2H), 2.21 – 2.14 (m, 1H), 2.13 (s, 3H), 2.07 – 1.99 (m, 2H), 1.97 – 1.88 (m, 2H), 1.74 – 1.55 (m, 6H), 1.53 – 1.42 (m, 3H), 1.28 – 1.14 (m, 3H), 1.04 (s, 3H), 0.64 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 209.59, 161.33, 139.23, 131.98, 125.40, 122.80, 76.33, 63.66, 56.81, 49.83, 43.99,

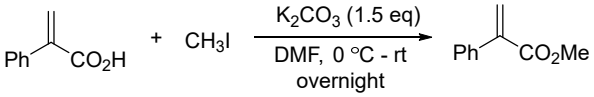
38.77, 37.84, 36.91, 36.60, 31.80, 31.78, 31.60, 27.57, 24.49, 22.82, 21.05, 19.33. **HRMS** calculated for $C_{24}H_{34}ClO_3$ $[M+H]^+$ 405.2191, found 405.2190.



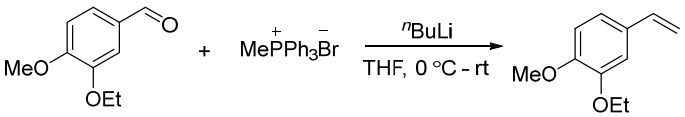
Complex alkene was synthesized according to literature procedures.[6] A reaction tube equipped with a magnetic stir bar was charged with Dehydroabietylamine (1.5 mmol), 4-vinylbenzoic acid (1.5 mmol), EDCl (1.8 mmol), HOBt (1.8 mmol), triethylamine (3.75 mmol) and DCM (15 mL). The resulting mixture was stirred at room temperature for 10 h, then added 25 mL water and 10 mL saturated brine solution to the mixture and extracted with DCM for 3 times (3 × 25 mL). The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) to give product as white solid.



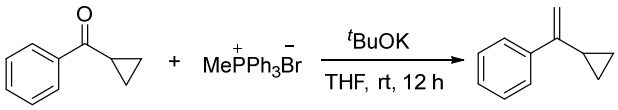
N-(((1R,4aS,10aR)-7-Isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-4-vinylbenzamide (5ad): white solid, melting point: 170 – 171 ºC, 412.6 mg, 66% yield, R_f = 0.4 (PE/EA = 9/1), **^{1}H NMR** (700 MHz, Chloroform-*d*) δ 7.71 – 7.66 (m, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 1H), 6.99 (dd, *J* = 8.1, 1.6 Hz, 1H), 6.91 – 6.85 (m, 1H), 6.73 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.09 (t, *J* = 5.7 Hz, 1H), 5.81 (d, *J* = 18.1 Hz, 1H), 5.34 (d, *J* = 11.3 Hz, 1H), 3.42 (dd, *J* = 13.7, 6.3 Hz, 1H), 3.35 (dd, *J* = 13.7, 6.6 Hz, 1H), 2.93 (dd, *J* = 17.0, 6.1 Hz, 1H), 2.85 – 2.79 (m, 2H), 2.30 (d, *J* = 12.6 Hz, 1H), 1.98 (dd, *J* = 13.2, 7.4 Hz, 1H), 1.84 – 1.73 (m, 2H), 1.71 – 1.67 (m, 1H), 1.55 – 1.47 (m, 2H), 1.42 – 1.33 (m, 2H), 1.27 – 1.17 (m, 9H), 1.01 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.26, 147.03, 145.64, 140.56, 135.95, 134.76, 133.90, 127.15, 126.97, 126.35, 124.25, 123.90, 115.88, 50.33, 45.88, 38.38, 37.72, 37.60, 36.44, 33.43, 30.47, 25.47, 23.99, 23.98, 19.12, 18.83, 18.67; **HRMS** calculated for $C_{29}H_{38}NO$ $[M+H]^+$ 416.2948, found 416.2952.



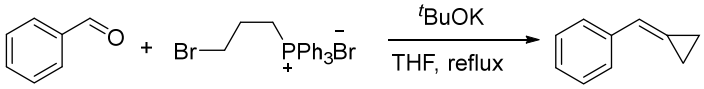
Known alkene was synthesized according to literature procedures.[7] A flame dried 50 mL round bottom flask was charged with a magnetic stir bar, 2-phenylacrylic acid (5.0 mmol, 1.0 equiv., 0.741 g) and anhydrous potassium carbonate (K_2CO_3, 1.5 equiv., 7.5 mmol, 1.04 g). The flask was then evacuated and backfilled with N_2 three times. 10 mL of DMF (0.5 mol/L) was added. The reaction mixture was stirred at room temperature for 5 min before cooling to 0 °C in an ice bath. Methyl iodide (1.05 equiv., 5.25 mmol, 0.745 g, 0.33 mL) was added dropwise to the reaction mixture under N_2. After addition, the solution was gradually warmed to room temperature and stirred overnight. The reaction was quenched by adding brine and extracted with diethyl ether in a separatory funnel. The combined organic phase was washed with brine, saturated sodium thiosulfate ($Na_2S_2O_3$) and washed with brine again. The organic phase was collected and dried over anhydrous sodium sulfate. Crude product was purified by silica gel flash chromatography (hexane to 8% EtOAc in hexane). The title compound was obtained as a colorless oil, 0.718 g, 89% yield and stored in a − 20 °C freezer.



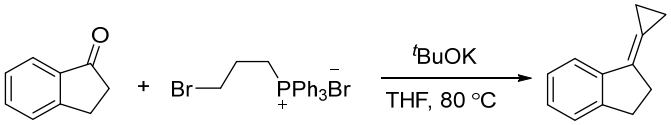
Known alkene was synthesized according to literature procedures.[8] To a flame-dried round-bottom flask, methyltriphenylphosphonium bromide (6.0 mmol) in THF (40 mL) was added ^{n}BuLi (2.4 mL, 2.5 M in THF, 6.0 mmol) slowly at 0 °C under N_2. After stirring for 20 min, 3-ethoxy-4-methoxybenzaldehyde (5.0 mmol) was added. The reaction mixture was then warmed to room temperature and stirred for another 12 hours. After the starting material was consumed completely which was detected by TLC, the reaction mixture was quenched with sat. NH_4Cl aq. (15 mL) and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over Na_2SO_4, concentrated in vacuo and purified by flash chromatography on silica gel with *n*-pentene or *n*-hexane to afford the alkene product.



Known radical probe was synthesized according to literature procedures.[8] To a flame-dried round-bottom flask, methyltriphenylphosphonium bromide (20.0 mmol) in THF (20 mL) was added potassium *tert*-butoxide (20.0 mmol) at 0 °C under N_2. After stirring for 20 min, ketone (15.0 mmol) was added. The reaction mixture was then warmed to room temperature and stirred for another 12 hours. After the starting material was consumed completely which was detected by TLC, the reaction mixture was quenched with sat. NH_4Cl aq. (15 mL) and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over Na_2SO_4, concentrated in vacuo and purified by flash chromatography on silica gel with *n*-hexane to afford corresponding product.

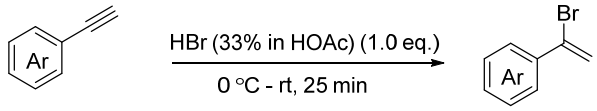


Known radical probe was synthesized according to literature procedures.[9] To a suspension of 1-bromopropyl-3-triphenylphoshonium bromide (1.5 equiv.) in THF (2 M) under argon atmosphere was added a solution of *t*-BuOK (3 equiv.) in THF (1 M *t*-BuOK in THF) via cannula, and the reaction mixture turned to bright orange. The reaction mixture was then heated at reflux with an oil bath for 90 min and the benzaldehyde (1 equiv.) was added. The reflux was continued for 2 h, and the reaction mixture was cooled down to room temperature. The reaction mixture was then poured in a large Erlenmeyer containing a large amount of pentane and the precipitates were filtered. The filtrate was concentrated and the residue was purified on a silica gel chromatography.



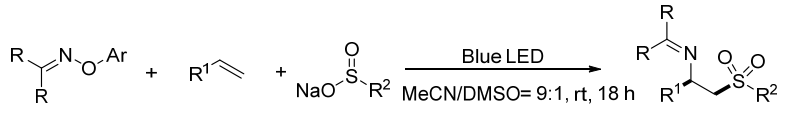
Known alkene was synthesized according to literature procedures.[10] (3-bromopropyl)triphenylphosphonium bromide (1.5 equiv.) and potassium *tert*-butoxide (3 equiv.) were suspended in THF at 0 °C. After 15 min the ketone (1.0 equiv.) was added and the reaction was stirred at 80 °C (oil bath as heat source) for 8 h. After the mixture was cooled and the reaction was quenched by addition of sat. NH_4Cl aq. and extracted with MTBE 3 times and then combined the

organic phases. The organic phases were dried over anhydrous Na_2SO_4, the solvent was removed and the residue was purified by column chromatography.

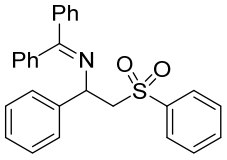


Known alpha bromoolefins were synthesized according to literature procedures.[11] Under strict exclusion of moisture, HBr (1.0 equiv., 33% solution in acetic acid) was added dropwise with cooling (ice/water bath) to arylacetylene (1.0 equiv.). After stirring at room temperature for 25 min, water (40 mL) and CH_2Cl_2 (25 mL) were added to the dark blue reaction mixture. This mixture was vigorously shaken until the color changed from blue to yellow-green, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$ (2×25 mL), water (25 mL) and dried ($MgSO_4$). After filtration and removal ofall volatile materials in vacuo (rotary evaporator), the residue was chromatographed on SiO_2 (PE/EA= 5:1) to give the title compounds and stored in a – 20 °C freezer.

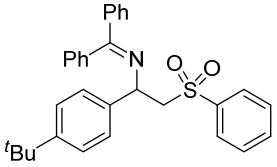
5. General procedure: photo-induced sulfonylimination of alkenes



In a glove box, an oven-dried 4 mL vial was charged with O-aryl oxime (0.12 mmol), alkene (0.10 mmol), sodium sulfinate (0.18 mmol), MeCN (0.9 mL) and DMSO (0.1 mL) at room temperature. The reaction tube was sealed with a Teflon screw cap, removed from the glove box. Then, the reaction mixture was stirred at rt under Blue LED for 18 hours. And the crude reaction mixture was purified by column chromatography on silica gel using petroleum ether and ethyl acetate to afford the corresponding product.

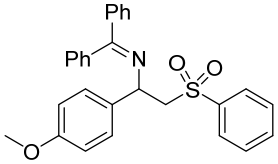


(±)-1,1-Diphenyl-N-(1-phenyl-2-(phenylsulfonyl)ethyl)methanimine (4a): Prepared according to the general procedure, colorless oil, 36.3 mg, corrected weight: 35.1 mg, 82% yield (accompanied by a small amount of inseparable alkenyl sulfone compound, the yield of the product has been adjusted accordingly), R_f = 0.3 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 – 7.73 (m, 2H), 7.51 – 7.45 (m, 1H), 7.44 – 7.31 (m, 8H), 7.25 – 7.23 (m, 2H), 7.23 – 7.17 (m, 3H), 7.08 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.03 – 6.97 (m, 2H), 5.03 (dd, *J* = 9.3, 2.8 Hz, 1H), 4.08 (dd, *J* = 14.4, 9.3 Hz, 1H), 3.49 (dd, *J* = 14.4, 2.9 Hz, 1H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 169.22, 142.18, 140.54, 139.23, 136.20, 133.13, 130.29, 129.03, 128.79, 128.74, 128.71, 128.29, 127.92, 127.85, 127.79, 127.58, 126.89, 64.56, 61.41. **HRMS** calculated for $C_{27}H_{24}NO_2S$ $[M+H]^+$ 426.1522, found 426.1523.

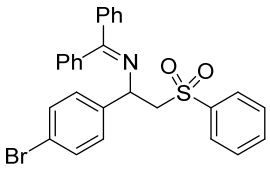


(±)-N-(1-(4-(*tert*-Butyl)phenyl)-2-(phenylsulfonyl)ethyl)-1,1-diphenylmethanimine (4b): Prepared according to the general procedure, colorless oil, 47.2 mg, corrected weight: 44.4 mg, 92% yield (accompanied by a small amount of inseparable alkenyl sulfone compound, the yield of the product

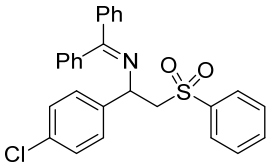
has been adjusted accordingly), R_f = 0.35 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.45 – 7.31 (m, 8H), 7.28 – 7.18 (m, 4H), 7.05 (d, *J* = 5.8 Hz, 2H), 7.01 (d, *J* = 8.1 Hz, 2H), 5.11 – 4.78 (m, 1H), 4.05 (dd, *J* = 14.3, 9.2 Hz, 1H), 3.49 (dd, *J* = 14.4, 2.9 Hz, 1H), 1.26 (s, 9H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 168.82, 150.44, 140.56, 139.36, 138.93, 136.21, 133.04, 130.19, 128.96, 128.79, 128.67, 128.24, 127.94, 127.89, 127.81, 126.54, 125.57, 64.40, 61.08, 34.49, 31.33. **HRMS** calculated for $C_{31}H_{32}NO_2S$ $[M+H]^+$ 482.2148, found 482.2156.



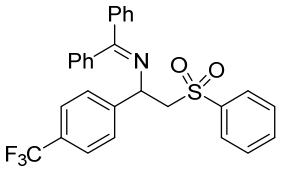
(±)-N-(1-(4-Methoxyphenyl)-2-(phenylsulfonyl)ethyl)-1,1-diphenylmethanimine (4c): Prepared according to the general procedure, white solid, melting point: 121 – 122 °C, 37.5 mg, 82% yield, R_f = 0.15 (PE/EA = 9/1). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.79 – 7.70 (m, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.44 – 7.31 (m, 8H), 7.27 – 7.20 (m, 2H), 7.02 (d, *J* = 6.5 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.74 (d, *J* = 8.7 Hz, 2H), 4.98 (dd, *J* = 9.2, 3.0 Hz, 1H), 4.04 (dd, *J* = 14.4, 9.2 Hz, 1H), 3.74 (s, 3H), 3.47 (dd, *J* = 14.4, 3.1 Hz, 1H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 168.86, 158.87, 140.58, 139.27, 136.23, 134.28, 133.05, 130.22, 128.98, 128.73, 128.66, 128.27, 127.96, 127.90, 127.81, 127.78, 114.05, 64.59, 60.79, 55.25. **HRMS** calculated for $C_{28}H_{26}NO_3S$ $[M+H]^+$ 456.1628, found 456.1633.



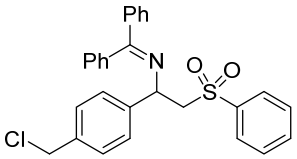
(±)-N-(1-(4-Bromophenyl)-2-(phenylsulfonyl)ethyl)-1,1-diphenylmethanimine (4d): Prepared according to the general procedure, colorless oil, 45.9 mg, corrected weight: 42.4 mg, 84% yield (accompanied by a small amount of inseparable alkenyl sulfone compound, the yield of the product has been adjusted accordingly), R_f = 0.3 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 – 7.72 (m, 2H), 7.53 – 7.47 (m, 1H), 7.47 – 7.30 (m, 10H), 7.28 – 7.19 (m, 2H), 7.03 – 6.92 (m, 4H), 4.99 (dd, *J* = 8.9, 3.2 Hz, 1H), 4.01 (dd, *J* = 14.4, 9.0 Hz, 1H), 3.47 (dd, *J* = 14.4, 3.3 Hz, 1H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 169.75, 141.03, 140.38, 138.95, 136.00, 133.20, 131.83, 130.49, 129.06, 128.85, 128.79, 128.66, 128.41, 127.89, 127.88, 127.62, 121.47, 64.22, 60.8. **HRMS** calculated for $C_{27}H_{23}BrNO_2S$ $[M+H]^+$ 504.0627, found 504.0627.



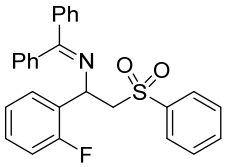
(±)-N-(1-(4-Chlorophenyl)-2-(phenylsulfonyl)ethyl)-1,1-diphenylmethanimine (4e): Prepared according to the general procedure, colorless oil, 36.6 mg, corrected weight: 34.9 mg, 76% yield (accompanied by a small amount of inseparable alkenyl sulfone compound, the yield of the product has been adjusted accordingly), R_f = 0.3 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.75 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.54 – 7.47 (m, 1H), 7.47 – 7.33 (m, 8H), 7.29 – 7.22 (m, 2H), 7.21 – 7.14 (m, 2H), 7.02 (d, *J* = 8.5 Hz, 2H), 7.00 (d, *J* = 6.9 Hz, 2H), 5.01 (dd, *J* = 9.0, 3.2 Hz, 1H), 4.02 (dd, *J* = 14.9, 9.6 Hz, 1H), 3.47 (dd, *J* = 14.4, 3.3 Hz, 1H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 169.72, 140.51, 140.39, 138.93, 136.00, 133.33, 133.19, 130.49, 130.07, 129.05, 128.88, 128.84, 128.79, 128.40, 128.30, 127.88, 127.62, 64.27, 60.75. **HRMS** calculated for $C_{27}H_{23}ClNO_2S$ $[M+H]^+$ 460.1133, found 460.1139.



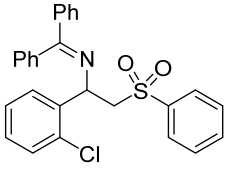
(±)-1,1-Diphenyl-N-(2-(phenylsulfonyl)-1-(4-(trifluoromethyl)phenyl)ethyl)methanimine (4f): Prepared according to the general procedure, colorless oil, 42.3 mg, corrected weight: 38.1 mg, 77% yield (accompanied by a small amount of inseparable alkenyl sulfone compound, the yield of the product has been adjusted accordingly), R_f = 0.3 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.74 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.54 – 7.33 (m, 11H), 7.31 – 7.15 (m, 4H), 6.99 (d, *J* = 6.5 Hz, 2H), 5.10 (dd, *J* = 8.8, 3.5 Hz, 1H), 4.03 (dd, *J* = 14.4, 8.8 Hz, 1H), 3.51 (dd, *J* = 14.4, 3.5 Hz, 1H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 170.11, 145.86, 140.29, 138.86, 135.95, 133.28, 130.59, 129.8 (q, *J* = 31.4 Hz), 129.08, 128.92, 128.81, 128.47, 127.93, 127.86, 127.57, 127.40, 125.67 (q, *J* = 3.7 Hz), 123.96 (q, *J* = 272.9 Hz), 64.08, 61.05; **^{19}F NMR** (375 MHz, Chloroform-*d*) δ -62.57. **HRMS** calculated for $C_{28}H_{23}F_3NO_2S$ $[M+H]^+$ 494.1396, found 494.1399.



(±)-N-(1-(4-(Chloromethyl)phenyl)-2-(phenylsulfonyl)ethyl)-1,1-diphenylmethanimine (4g): Prepared according to the general procedure, colorless oil, 36.3 mg, corrected weight: 34.6 mg, 73% yield (accompanied by a small amount of inseparable alkenyl sulfone compound, the yield of the product has been adjusted accordingly), R_f = 0.25 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 7.5 Hz, 2H), 7.55 – 7.31 (m, 9H), 7.24 (d, *J* = 9.0 Hz, 4H), 7.09 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 6.4 Hz, 2H), 5.12 – 4.90 (m, 1H), 4.51 (s, 2H), 4.19 – 3.96 (m, 1H), 3.48 (dd, *J* = 14.4, 3.1 Hz, 1H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 169.46, 142.29, 140.43, 139.13, 136.81, 136.08, 133.19, 130.41, 129.05, 128.98, 128.81, 128.37, 127.88, 127.74, 127.32, 64.31, 61.10, 45.87. **HRMS** calculated for $C_{28}H_{25}ClNO_2S$ $[M+H]^+$ 474.1289, found 474.1295.

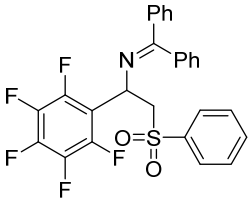


(±)-N-(1-(2-Fluorophenyl)-2-(phenylsulfonyl)ethyl)-1,1-diphenylmethanimine (4h): Prepared according to the general procedure, yellow oil, 38.7 mg, corrected weight: 37.4 mg, 84% yield (accompanied by a small amount of inseparable alkenyl sulfone compound, the yield of the product has been adjusted accordingly), R_f = 0.3 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.82 – 7.68 (m, 2H), 7.53 – 7.45 (m, 3H), 7.44 – 7.32 (m, 7H), 7.31 – 7.22 (m, 2H), 7.20 – 7.15 (m, 1H), 7.10 – 6.96 (m, 3H), 6.94 – 6.85 (m, 1H), 5.27 (dd, *J* = 8.9, 2.8 Hz, 1H), 4.03 (dd, *J* = 14.5, 9.6 Hz, 1H), 3.57 (dd, *J* = 14.4, 3.1 Hz, 1H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 170.23, 159.01 (d, *J* = 247.4 Hz), 140.29, 139.09, 135.95, 133.12, 130.48, 129.07 (d, *J* = 8.2 Hz), 128.96, 128.92, 128.85 (d, *J* = 8.0 Hz), 128.39, 127.97, 127.91, 127.54, 124.45 (d, *J* = 3.4 Hz), 115.48 (d, *J* = 21.7 Hz), 62.72, 55.08; **^{19}F NMR** (375 MHz, Chloroform-*d*) δ -117.34. **HRMS** calculated for $C_{27}H_{23}FNO_2S$ $[M+H]^+$ 444.1428, found 444.1434.

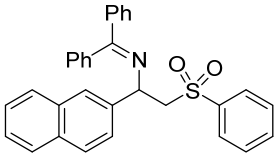


(±)-N-(1-(2-Chlorophenyl)-2-(phenylsulfonyl)ethyl)-1,1-diphenylmethanimine (4i): Prepared according to the general procedure, yellow oil, 37.3 mg, corrected weight: 35.4 mg, 77% yield (accompanied by a small amount of inseparable alkenyl sulfone compound, the yield of the product has been adjusted accordingly), R_f = 0.32 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 7.4 Hz, 2H), 7.60 – 7.47 (m, 4H), 7.43 – 7.34 (m, 6H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.24 – 7.09 (m, 3H), 6.96 (d, *J* = 6.8 Hz, 2H), 5.34 (d, *J* = 9.5 Hz, 1H), 4.07 – 3.76 (m, 1H), 3.48 (dd, *J* = 14.4, 1.9 Hz, 1H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 170.37, 140.14, 136.19, 133.14,

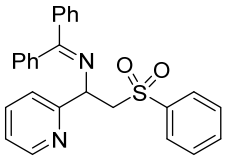
131.46, 130.43, 129.51, 129.17, 129.03, 129.02, 128.96, 128.80, 128.61, 128.39, 128.18, 127.91, 127.71, 127.33, 62.62, 57.86. **HRMS** calculated for $C_{27}H_{23}ClNO_2S$ $[M+H]^+$ 460.1133, found 460.1137.



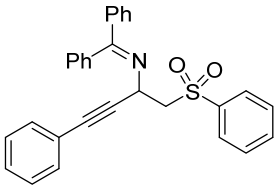
(±)-N-(1-(Perfluorophenyl)-2-(phenylsulfonyl)ethyl)-1,1-diphenylmethanimine (4j): Prepared according to the general procedure, yellow oil, 47.5 mg, corrected weight: 42.8 mg, 83% yield (accompanied by a small amount of inseparable alkenyl sulfone compound, the yield of the product has been adjusted accordingly), R_f = 0.35 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.72 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.59 – 7.52 (m, 1H), 7.47 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.44 – 7.34 (m, 6H), 7.29 – 7.22 (m, 2H), 6.94 (d, *J* = 6.7 Hz, 2H), 5.38 (t, *J* = 6.9 Hz, 1H), 3.96 (dd, *J* = 14.6, 7.8 Hz, 1H), 3.83 (dd, *J* = 14.6, 6.0 Hz, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 171.79, 146.30 – 146.12 (m), 144.01 – 143.34 (m), 142.30 – 142.00 (m), 139.47, 138.95 – 138.53 (m), 138.44, 136.64 – 135.75 (m), 135.29, 133.60, 131.04, 129.16, 129.10, 128.89, 128.80, 128.08, 127.82, 126.79, 59.89, 51.80; **^{19}F NMR** (375 MHz, Chloroform-*d*) δ -139.77 (d, *J* = 15.6 Hz), -154.47 (t, *J* = 21.0 Hz), -161.66 – -161.80 (m). **HRMS** calculated for $C_{27}H_{19}F_5NO_2S$ $[M+H]^+$ 516.1051, found 516.1055.



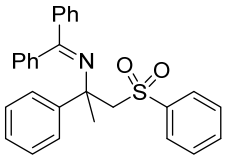
(±)-N-(1-(Naphthalen-2-yl)-2-(phenylsulfonyl)ethyl)-1,1-diphenylmethanimine (4k): Prepared according to the general procedure, colorless oil, 20.7 mg, 44% yield, R_f = 0.3 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 – 7.74 (m, 3H), 7.77 – 7.68 (m, 2H), 7.51 – 7.31 (m, 11H), 7.29 – 7.25 (m, 4H), 7.02 (d, *J* = 6.5 Hz, 2H), 5.20 (d, *J* = 8.0 Hz, 1H), 4.15 (dd, *J* = 12.6, 8.8 Hz, 1H), 3.58 (dd, *J* = 14.4, 2.7 Hz, 1H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 171.22, 140.48, 133.34, 133.10, 132.80, 128.99, 128.88, 128.59, 128.32, 127.93, 127.88, 127.82, 127.63, 126.20, 126.03, 125.79, 124.74, 64.41, 61.57. **HRMS** calculated for $C_{31}H_{26}NO_2S$ $[M+H]^+$ 476.1679, found 476.1681.



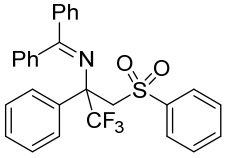
(±)-1,1-Diphenyl-N-(2-(phenylsulfonyl)-1-(pyridin-2-yl)ethyl)methanimine (4l): Prepared according to the general procedure, yellow oil, 26.2 mg, 61% yield, R_f = 0.1 (PE/EA = 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.52 – 8.42 (m, 1H), 7.84 – 7.71 (m, 2H), 7.56 (td, *J* = 7.7, 1.8 Hz, 1H), 7.51 – 7.46 (m, 3H), 7.43 – 7.34 (m, 6H), 7.31 – 7.24 (m, 2H), 7.15 – 7.06 (m, 4H), 5.22 (dd, *J* = 8.0, 4.1 Hz, 1H), 4.10 – 3.93 (m, 2H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 170.67, 159.77, 149.41, 140.51, 139.21, 136.78, 135.93, 133.09, 130.51, 129.05, 128.98, 128.92, 128.46, 127.92, 127.76, 126.37, 122.52, 122.04, 62.63, 62.27. **HRMS** calculated for $C_{26}H_{23}N_2O_2S$ $[M+H]^+$ 427.1475, found 427.1481.



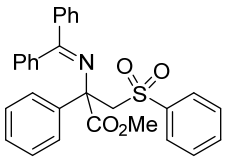
(±)-1,1-Diphenyl-N-(4-phenyl-1-(phenylsulfonyl)but-3-yn-2-yl)methanimine (4m): Prepared according to the general procedure, yellow oil, 25.7 mg, 57% yield, R_f = 0.2 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 – 7.76 (m, 2H), 7.56 – 7.47 (m, 4H), 7.44 – 7.34 (m, 7H), 7.33 – 7.30 (m, 2H), 7.29 – 7.22 (m, 5H), 4.90 (dd, *J* = 8.8, 3.6 Hz, 1H), 4.06 (dd, *J* = 14.5, 8.8 Hz, 1H), 3.69 (dd, *J* = 14.5, 3.6 Hz, 1H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 171.79, 140.21, 138.94, 135.67, 133.39, 131.71, 130.71, 129.20, 129.14, 129.09, 128.56, 128.52, 128.22, 128.07, 128.01, 127.93, 122.39, 86.65, 84.90, 61.92, 50.11. **HRMS** calculated for $C_{29}H_{24}NO_2S$ $[M+H]^+$ 450.1522, found 450.1527.



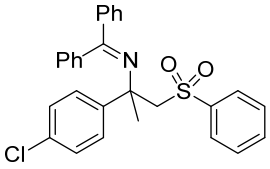
(±)-1,1-Diphenyl-N-(2-phenyl-1-(phenylsulfonyl)propan-2-yl)methanimine (4n): Prepared according to the general procedure, colorless oil, 36.0 mg, corrected weight: 34.6 mg, 82% yield (accompanied by a small amount of inseparable alkenyl sulfone compound, the yield of the product has been adjusted accordingly), R_f = 0.25 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.41 – 7.34 (m, 4H), 7.30 – 7.14 (m, 4H), 7.11 – 7.05 (m, 7H), 6.62 – 6.42 (m, 2H), 4.18 (d, *J* = 14.4 Hz, 1H), 3.75 (d, *J* = 14.4 Hz, 1H), 1.69 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.33, 146.52, 141.73, 140.88, 138.23, 132.75, 130.00, 128.92, 128.45, 128.19, 127.83, 127.71, 127.68, 127.38, 127.06, 126.32, 71.86, 63.62, 24.19. **HRMS** calculated for $C_{28}H_{26}NO_2S$ $[M+H]^+$ 440.1679, found 440.1684.



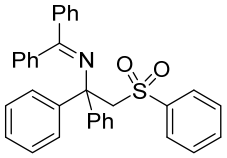
(±)-1,1-Diphenyl-N-(1,1,1-trifluoro-2-phenyl-3-(phenylsulfonyl)propan-2-yl)methanimine (4o): Prepared according to the general procedure, colorless oil, 46.3 mg, corrected weight: 39.4 mg, 80% yield (accompanied by a small amount of inseparable alkenyl sulfone compound, the yield of the product has been adjusted accordingly), R_f = 0.2 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 7.4 Hz, 2H), 7.68 – 7.63 (m, 2H), 7.62 – 7.55 (m, 1H), 7.52 – 7.40 (m, 4H), 7.38 – 7.26 (m, 6H), 7.23 – 7.13 (m, 1H), 7.06 (t, *J* = 7.8 Hz, 2H), 6.76 (d, *J* = 7.5 Hz, 2H), 4.10 (d, *J* = 15.0 Hz, 1H), 3.61 (d, *J* = 15.0 Hz, 1H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 171.41, 141.38, 141.08, 139.27, 137.23, 133.50, 130.78, 129.25, 128.92, 128.67 (q, *J* = 274.2 Hz), 128.62, 128.35, 128.26, 128.03, 127.86, 127.64, 68.69 (q, *J* = 27.2 Hz), 57.57; **^{19}F NMR** (375 MHz, Chloroform-*d*) δ -74.13. **HRMS** calculated for $C_{28}H_{23}F_3NO_2S$ $[M+H]^+$ 494.1396, found 494.1400.



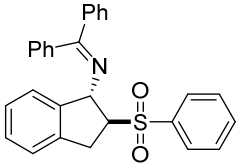
(±)-Methyl 2-((diphenylmethylene)amino)-2-phenyl-3-(phenylsulfonyl) propanoate (4o): Prepared according to the general procedure, colorless oil, 34.4 mg, 71% yield, R_f = 0.15 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.68 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.60 – 7.55 (m, 2H), 7.45 – 7.36 (m, 2H), 7.36 – 7.19 (m, 9H), 7.15 – 7.10 (m, 3H), 6.97 – 6.90 (m, 2H), 4.31 (d, *J* = 14.8 Hz, 1H), 4.19 (d, *J* = 14.8 Hz, 1H), 3.41 (s, 3H); **^{13}C NMR** (175 MHz, Chloroform-*d*) δ 172.07, 170.89, 141.13, 140.55, 140.48, 137.07, 133.03, 130.69, 129.09, 128.58, 128.54, 128.45, 128.38, 127.95, 127.79, 127.78, 127.56, 126.01, 68.67, 64.53, 52.64. **HRMS** calculated for $C_{29}H_{26}NO_4S$ $[M+H]^+$ 484.1577, found 484.1583.



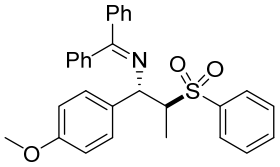
(±)-N-(2-(4-Chlorophenyl)-1-(phenylsulfonyl)propan-2-yl)-1,1-diphenyl methanimine (4p): Prepared according to the general procedure, colorless oil, 40.4 mg, corrected weight: 37.2 mg, 78% yield (accompanied by a small amount of inseparable alkenyl sulfone compound, the yield of the product has been adjusted accordingly), R_f = 0.3 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 7.6 Hz, 2H), 7.55 – 7.47 (m, 1H), 7.43 – 7.32 (m, 5H), 7.28 – 7.18 (m, 3H), 7.10 (t, *J* = 7.6 Hz, 2H), 7.00 – 6.93 (m, 4H), 6.62 – 6.45 (m, 2H), 4.11 (d, *J* = 14.3 Hz, 1H), 3.85 (d, *J* = 14.3 Hz, 1H), 1.70 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.69, 144.29, 141.33, 140.61, 138.01, 132.97, 132.79, 130.23, 128.92, 128.41, 128.11, 127.99, 127.90, 127.84, 127.74, 127.61, 127.48, 71.46, 63.03, 24.25. **HRMS** calculated for $C_{28}H_{25}ClNO_2S$ $[M+H]^+$ 474.1289, found 474.1295.



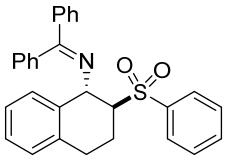
(±)-N-(1,1-Diphenyl-2-(phenylsulfonyl)ethyl)-1,1-diphenylmethanimine (4r): Prepared according to the general procedure, colorless oil, 29.3 mg, 58% yield, R_f = 0.27 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.76 – 7.62 (m, 2H), 7.49 (dd, *J* = 8.4, 1.1 Hz, 2H), 7.44 – 7.38 (m, 1H), 7.40 – 7.31 (m, 3H), 7.22 – 7.15 (m, 3H), 7.15 – 7.08 (m, 6H), 7.08 – 7.00 (m, 6H), 6.62 (d, *J* = 7.1 Hz, 2H), 4.33 (s, 2H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 169.48, 147.30, 141.58, 140.73, 138.36, 132.65, 130.27, 129.78, 128.90, 128.77, 128.68, 128.61, 128.47, 128.23, 127.97, 127.95, 127.88, 127.65, 127.54, 127.34, 127.18, 126.32, 66.05, 65.41. **HRMS** calculated for $C_{33}H_{28}NO_2S$ $[M+H]^+$ 502.1835, found 502.1840.



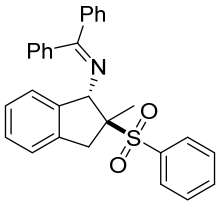
(±)-1,1-Diphenyl-N-(2-(phenylsulfonyl)-2,3-dihydro-1H-inden-1-yl)methanimine (4s): Prepared according to the general procedure, white solid, melting point: 73 – 74 °C, 34.5 mg, 79% yield, R_f = 0.25 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 7.4 Hz, 2H), 7.59 (d, *J* = 7.3 Hz, 2H), 7.56 – 7.47 (m, 4H), 7.46 – 7.35 (m, 5H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.21 – 7.12 (m, 3H), 7.07 – 7.02 (m, 1H), 5.61 (d, *J* = 7.2 Hz, 1H), 4.43 (q, *J* = 8.8 Hz, 1H), 3.35 – 3.17 (m, 2H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 170.31, 141.71, 139.73, 138.88, 138.43, 135.91, 133.61, 130.43, 129.15, 129.11, 129.05, 128.69, 128.63, 128.53, 128.34, 128.04, 127.44, 124.60, 124.29, 71.18, 66.67, 33.40. **HRMS** calculated for $C_{28}H_{24}NO_2S$ $[M+H]^+$ 438.1522, found 438.1524.



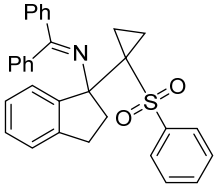
(±)-N-(1-(4-Methoxyphenyl)-2-(phenylsulfonyl)propyl)-1,1-diphenylmethanimine (4t): Prepared according to the general procedure, white solid, melting point: 147 – 148 °C, 40.5 mg, 86% yield, R_f = 0.2 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.70 – 7.65 (m, 2H), 7.54 (d, *J* = 7.5 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.40 – 7.28 (m, 8H), 7.04 – 6.92 (m, 4H), 6.74 (d, *J* = 8.8 Hz, 2H), 5.15 (d, *J* = 2.6 Hz, 1H), 3.76 (s, 3H), 3.49 – 3.23 (m, 1H), 1.54 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 158.63, 138.71, 132.99, 130.19, 128.92, 128.72, 128.23, 128.10, 127.90, 127.87, 126.43, 113.83, 67.70, 62.55, 55.22, 9.14. **HRMS** calculated for $C_{29}H_{28}NO_3S$ $[M+H]^+$ 470.1784, found 470.1789.



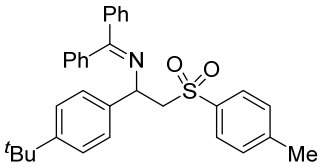
(±)-1,1-Diphenyl-N-(2-(phenylsulfonyl)-1,2,3,4-tetrahydronaphthalen-1-yl)methanimine (4u): Prepared according to the general procedure, yellow oil, 25.5 mg, 56% yield, R_f = 0.2 (PE/EA = 9/1). **^{1}H NMR** (700 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 7.3 Hz, 2H), 7.48 – 7.42 (m, 6H), 7.38 – 7.30 (m, 5H), 7.28 – 7.21 (m, 2H), 7.14 (t, *J* = 7.1 Hz, 1H), 7.12 – 7.04 (m, 2H), 6.90 (d, *J* = 7.9 Hz, 1H), 5.17 (d, *J* = 6.7 Hz, 1H), 3.94 – 3.78 (m, 1H), 2.98 (ddd, *J* = 15.2, 8.5, 6.2 Hz, 1H), 2.88 (dt, *J* = 16.3, 6.0 Hz, 1H), 2.52 – 2.40 (m, 1H), 2.21 – 2.14 (m, 1H); **^{13}C NMR** (175 MHz, Chloroform-*d*) δ 168.87, 139.83, 139.41, 136.35, 135.74, 135.19, 132.99, 130.22, 128.96, 128.91, 128.75, 128.46, 128.35, 128.34, 128.20, 127.86, 127.43, 127.29, 126.26, 65.55, 59.80, 27.47, 21.58. **HRMS** calculated for $C_{29}H_{26}NO_2S$ $[M+H]^+$ 452.1679, found 452.1684.



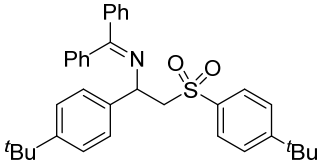
(±)-N-(2-Methyl-2-(phenylsulfonyl)-2,3-dihydro-1*H*-inden-1-yl)-1,1-diphenyl methanimine (4v): Prepared according to the general procedure, white solid, melting point: 185 – 186 ºC, 26.7 mg, 59% yield, R_f = 0.45 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.70 – 7.58 (m, 4H), 7.56 – 7.45 (m, 6H), 7.42 – 7.31 (m, 5H), 7.21 – 7.16 (m, 2H), 7.15 – 7.11 (m, 1H), 7.05 – 7.00 (m, 1H), 5.68 (s, 1H), 3.62 (d, *J* = 15.6 Hz, 1H), 2.81 (d, *J* = 15.6 Hz, 1H), 1.70 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 170.43, 141.75, 138.23, 136.67, 135.97, 133.42, 130.28, 130.08, 129.13, 129.02, 128.76, 128.54, 128.52, 128.02, 127.97, 127.21, 124.70, 124.44, 74.86, 67.39, 41.40, 16.85. **HRMS** calculated for $C_{29}H_{26}NO_2S$ $[M+H]^+$ 452.1679, found 452.1684.



(±)-N-(2-Methyl-2-(phenylsulfonyl)-2,3-dihydro-1*H*-inden-1-yl)-1,1-diphenyl methanimine (4w): Prepared according to the general procedure, white solid, melting point: 177 – 178 ºC, 18.7 mg, corrected weight: 17.9 mg, 37% yield (accompanied by a small amount of inseparable O-aryl oxime compound, the yield of the product has been adjusted accordingly), R_f = 0.5 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.34 – 7.26 (m, 4H), 7.25 – 7.19 (m, 2H), 7.15 – 7.03 (m, 5H), 7.00 – 6.90 (m, 2H), 6.87 (dt, *J* = 8.1, 4.2 Hz, 1H), 6.68 (d, *J* = 7.6 Hz, 1H), 6.40 (d, *J* = 4.0 Hz, 2H), 6.30-6.12 (m, 2H), 3.26 (ddd, *J* = 14.7, 10.7, 4.3 Hz, 1H), 2.99 (ddd, *J* = 15.9, 10.6, 4.9 Hz, 1H), 2.27 (ddd, *J* = 14.7, 10.6, 5.1 Hz, 1H), 2.22 – 2.12 (m, 1H), 2.07 (ddd, *J* = 10.2, 6.2, 4.3 Hz, 1H), 1.87 – 1.80 (m, 1H), 1.80 – 1.71 (m, 1H), 1.71 – 1.64 (m, 1H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 146.61, 145.46, 141.66, 141.52, 137.16, 131.59, 129.88, 128.18, 128.04, 127.91, 127.32, 127.24, 126.73, 126.00, 125.18, 124.33, 72.16, 51.85, 40.09, 30.61, 12.18, 9.19. **HRMS** calculated for $C_{31}H_{28}NO_2S$ $[M+H]^+$ 478.1835, found 478.1837.

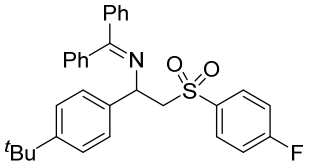


(±)-N-(1-(4-(*tert*-Butyl)phenyl)-2-tosylethyl)-1,1-diphenylmethanim ine (5a): Prepared according to the general procedure, colorless oil, 47.6 mg, corrected weight: 45.0 mg, 91% yield (accompanied by a small amount of inseparable alkenyl sulfone compound, the yield of the product has been adjusted accordingly), R_f = 0.4 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.43 – 7.38 (m, 5H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.25 – 7.09 (m, 4H), 7.14 (d, *J* = 8.2 Hz, 2H), 7.05 – 7.03 (m, 2H), 7.01 (d, *J* = 8.3 Hz, 2H), 5.00 (dd, *J* = 9.2, 2.8 Hz, 1H), 4.04 (dd, *J* = 14.3, 9.3 Hz, 1H), 3.47 (dd, *J* = 14.4, 2.9 Hz, 1H), 2.32 (s, 3H), 1.26 (s, 9H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 168.63, 150.40, 143.96, 139.37, 139.04, 137.62, 136.18, 132.44, 130.14, 130.07, 129.58, 128.78, 128.65, 128.30, 128.24, 127.93, 127.73, 126.53, 125.54, 64.42, 61.11, 34.48, 31.34, 21.56. **HRMS** calculated for $C_{32}H_{34}NO_2S$ $[M+H]^+$ 496.2305, found 496.2310.

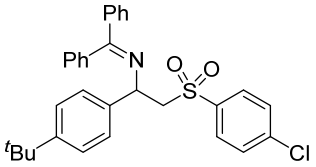


(±)-N-(1-(4-(*tert*-Butyl)phenyl)-2-((4-(*tert*-butyl)phenyl)sulfonyl)eth yl)-1,1-diphenylmethanimine (5b): Prepared according to the general procedure, colorless oil, 58.1 mg, corrected weight: 51.7 mg, 96% yield (accompanied by a small amount of inseparable alkenyl sulfone compound, the yield of the product has been adjusted accordingly), R_f = 0.5 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 8.5 Hz, 2H), 7.50 – 7.31 (m, 9H), 7.28 – 7.20 (m, 4H), 7.04 (d, *J* = 8.2 Hz, 4H), 5.03 (dd, *J* = 9.4, 2.4 Hz, 1H), 4.13 – 4.00 (m, 1H),

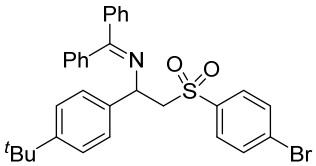
3.46 (dd, *J* = 14.4, 2.6 Hz, 1H), 1.27 (s, 9H), 1.26 (s, 9H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 156.90, 150.40, 139.23, 137.57, 136.20, 130.11, 130.07, 128.77, 128.65, 128.20, 127.97, 127.84, 127.80, 126.51, 125.96, 125.55, 64.60, 61.09, 35.10, 34.49, 31.34, 31.05. **HRMS** calculated for $C_{35}H_{40}NO_2S$ $[M+H]^+$ 538.2774, found 538.2782.



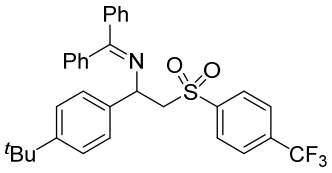
(±)-N-(1-(4-(*tert*-Butyl)phenyl)-2-((4-fluorophenyl)sulfonyl)ethyl)-1,1-diphenylmethanimine (5c): Prepared according to the general procedure, yellow oil, 50.4 mg, corrected weight: 46.5 mg, 93% yield (accompanied by a small amount of inseparable alkenyl sulfone compound, the yield of the product has been adjusted accordingly), R_f = 0.5 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.75 – 7.70 (m, 2H), 7.46 – 7.60 (m, 5H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.30 – 7.18 (m, 4H), 7.05 (d, *J* = 6.2 Hz, 2H), 7.01 – 6.97 (m, 4H), 5.00 (dd, *J* = 9.1, 3.1 Hz, 1H), 4.03 (dd, *J* = 14.5, 9.1 Hz, 1H), 3.52 (dd, *J* = 14.5, 3.1 Hz, 1H), 1.26 (s, 9H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 168.91, 165.36 (d, *J* = 255.5 Hz), 150.57, 139.15, 138.57, 136.62 (d, *J* = 3.0 Hz), 136.08, 130.80, 130.70, 130.38, 128.71, 128.31, 127.86, 127.84, 126.56, 125.58, 116.16 (d, *J* = 22.6 Hz), 64.42, 61.15, 34.49, 31.32; **^{19}F NMR** (375 MHz, Chloroform-*d*) δ -104.56. **HRMS** calculated for $C_{31}H_{31}FNO_2S$ $[M+H]^+$ 500.2054, found 500.2058.



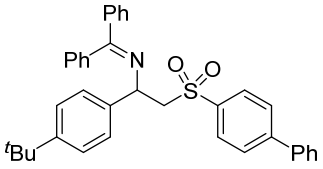
(±)-N-(1-(4-(*tert*-Butyl)phenyl)-2-((4-chlorophenyl)sulfonyl)ethyl)-1,1-diphenylmethanimine (5d): Prepared according to the general procedure, colorless oil, 51.3 mg, corrected weight: 48.2 mg, 93% yield (accompanied by a small amount of inseparable alkenyl sulfone compound, the yield of the product has been adjusted accordingly), R_f = 0.47 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.68 – 7.61 (m, 2H), 7.44 – 7.34 (m, 6H), 7.32 – 7.16 (m, 6H), 7.07 – 7.01 (m, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 5.00 (dd, *J* = 9.2, 3.2 Hz, 1H), 4.03 (dd, *J* = 14.5, 9.2 Hz, 1H), 3.52 (dd, *J* = 14.6, 3.3 Hz, 1H), 1.26 (s, 9H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 168.92, 150.61, 139.71, 139.08, 138.48, 136.04, 130.41, 130.08, 129.40, 129.22, 128.73, 128.66, 128.32, 128.30, 127.87, 127.78, 126.56, 125.59, 64.31, 61.16, 34.50, 31.33. **HRMS** calculated for $C_{31}H_{31}ClNO_2S$ $[M+H]^+$ 516.1759, found 516.1763.



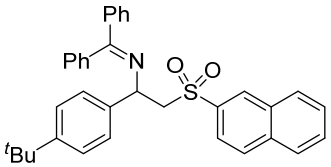
(±)-N-(2-((4-Bromophenyl)sulfonyl)-1-(4-(*tert*-butyl)phenyl)ethyl)-1,1-diphenylmethanimine (5e): Prepared according to the general procedure, yellow oil, 49.0 mg, corrected weight: 45.2 mg, 81% yield (accompanied by a small amount of inseparable alkenyl sulfone compound, the yield of the product has been adjusted accordingly), R_f = 0.47 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.5 Hz, 2H), 7.48 – 7.32 (m, 8H), 7.30 – 7.24 (m, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 6.1 Hz, 2H), 6.98 (d, *J* = 8.3 Hz, 2H), 4.99 (dd, *J* = 9.2, 3.2 Hz, 1H), 4.04 (dd, *J* = 14.1, 9.0 Hz, 1H), 3.52 (dd, *J* = 14.6, 3.3 Hz, 1H), 1.27 (s, 9H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 168.09, 150.62, 139.62, 138.98, 138.46, 136.01, 132.21, 130.45, 130.07, 129.47, 128.74, 128.66, 128.32, 127.89, 127.77, 126.55, 125.59, 64.27, 61.15, 34.50, 31.33. **HRMS** calculated for $C_{31}H_{31}BrNO_2S$ $[M+H]^+$ 560.1253, found 560.1260.



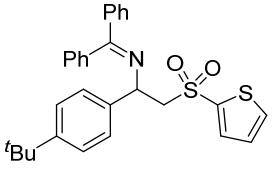
(±)-N-(1-(4-(*tert*-Butyl)phenyl)-2-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)-1,1-diphenylmethanimine (5f): Prepared according to the general procedure, colorless oil, 40.6 mg, corrected weight: 38.0 mg, 69% yield (accompanied by a small amount of inseparable alkenyl sulfone compound, the yield of the product has been adjusted accordingly), R_f = 0.5 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.45 – 7.40 (m, 3H), 7.39 – 7.28 (m, 3H), 7.24 – 7.19 (m, 4H), 7.03 (d, *J* = 6.0 Hz, 2H), 6.98 (d, *J* = 8.2 Hz, 2H), 5.04 (dd, *J* = 9.5, 2.9 Hz, 1H), 4.33 – 3.92 (m, 1H), 3.55 (dd, *J* = 14.6, 3.1 Hz, 1H), 1.26 (s, 9H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 150.73, 144.16, 138.80, 138.26, 137, 61, 132.44, 130.52, 130.07, 128.78, 128.51, 128.35, 128.12 (q, *J* = 35.9 Hz), 127.89, 127.70, 126.53, 126.04 (q, *J* =3.7 Hz), 125.71 (q, *J* = 273.2 Hz), 125.62, 64.23, 61.13, 34.50, 31.29; **^{19}F NMR** (375 MHz, Chloroform-*d*) δ -63.06. **HRMS** calculated for $C_{32}H_{31}F_3NO_2S$ $[M+H]^+$ 550.2022, found 550.2022.



(±)-N-(1-(4-(*tert*-Butyl)phenyl)-2-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)-1,1-diphenylmethanimine (5g): Prepared according to the general procedure, colorless oil, 37.0 mg, corrected weight: 33.8 mg, 61% yield (accompanied by a small amount of inseparable alkenyl sulfone compound, the yield of the product has been adjusted accordingly), R_f = 0.25 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.53 – 7.37 (m, 10H), 7.30 – 7.18 (m, 5H), 7.11 – 7.00 (m, 4H), 5.05 (d, *J* = 8.0 Hz, 1H), 4.20 – 4.05 (m, 1H), 3.52 (dd, *J* = 14.4, 2.7 Hz, 1H), 1.26 (s, 9H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 168.75, 150.49, 146.01, 139.25, 130.16, 128.96, 128.70, 128.50, 128.45, 128.26, 127.92, 127.82, 127.58, 127.39, 126.53, 125.58, 64.54, 61.16, 34.48, 31.31. **HRMS** calculated for $C_{37}H_{36}NO_2S$ $[M+H]^+$ 558.2461, found 558.2462.

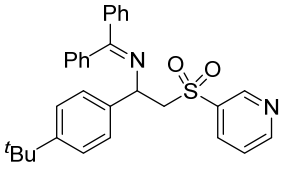


(±)-N-(1-(4-(*tert*-Butyl)phenyl)-2-(naphthalen-2-ylsulfonyl)ethyl)-1,1-diphenylmethanimine (5h): Prepared according to the general procedure, colorless oil, 48.8 mg, corrected weight: 42.9 mg, 81% yield (accompanied by a small amount of inseparable alkenyl sulfone compound, the yield of the product has been adjusted accordingly), R_f = 0.25 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.28 (s, 1H), 7.83 (dd, *J* = 8.3, 2.9 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.62 – 7.56 (m, 1H), 7.54 – 7.47 (m, 1H), 7.44 – 7.37 (m, 3H), 7.28 (d, *J* = 7.5 Hz, 2H), 7.23 – 7.15 (m, 3H), 7.07 – 7.00 (m, 6H), 5.05 (d, *J* = 6.6 Hz, 1H), 4.16 – 4.10 (m, 1H), 3.59 (dd, *J* = 14.5, 3.1 Hz, 1H), 1.23 (s, 9H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 168.72, 150.42, 138.89, 137.46, 136.22, 135.05, 132.12, 130.10, 129.67, 129.33, 129.29, 128.89, 128.65, 128.53, 128.23, 127.88, 127.84, 127.65, 127.36, 126.55, 125.52, 122.74, 64.36, 61.21, 34.45, 31.28. **HRMS** calculated for $C_{35}H_{34}NO_2S$ $[M+H]^+$ 532.2305, found 532.2310.

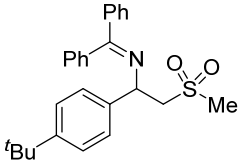


(±)-N-(1-(4-(*tert*-Butyl)phenyl)-2-(thiophen-2-ylsulfonyl)ethyl)-1,1-diphenylmethanimine (5i): Prepared according to the general procedure, colorless oil, 47.9 mg, corrected weight: 44.6 mg, 91% yield (accompanied by a small amount of inseparable alkenyl sulfone compound, the yield of the product has been adjusted accordingly), R_f = 0.25 (PE/EA = 9/1). **^{1}H**

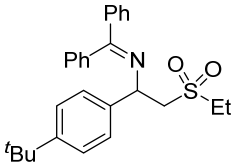
NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.49 (m, 3H), 7.47 – 7.39 (m, 4H), 7.37 – 7.32 (m, 1H), 7.31 – 7.21 (m, 4H), 7.11 – 7.02 (m, 4H), 6.94 (dd, *J* = 4.9, 3.8 Hz, 1H), 5.06 (dd, *J* = 9.1, 2.9 Hz, 1H), 4.13 (dd, *J* = 13.7, 8.9 Hz, 1H), 3.58 (dd, *J* = 14.4, 2.9 Hz, 1H), 1.27 (s, 9H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 169.04, 150.53, 141.80, 139.47, 138.86, 136.25, 133.83, 133.44, 130.25, 128.84, 128.69, 128.26, 127.99, 127.88, 127.58, 126.59, 125.63, 65.84, 61.24, 34.51, 31.34. **HRMS** calculated for $C_{29}H_{30}NO_2S_2$ $[M+H]^+$ 488.1712, found 488.1718.



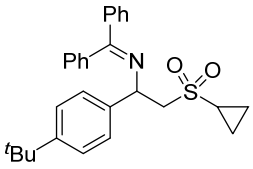
(±)-N-(1-(4-(*tert*-Butyl)phenyl)-2-(pyridin-3-ylsulfonyl)ethyl)-1,1-diphenylmethanimine (5j): Prepared according to the general procedure, yellow oil, 46.2 mg, corrected weight: 43.5 mg, 90% yield (accompanied by a small amount of inseparable alkenyl sulfone compound, the yield of the product has been adjusted accordingly), R_f = 0.1 (PE/EA = 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.05 – 8.91 (m, 1H), 8.70 – 8.60 (m, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.31 (m, 6H), 7.29 – 7.17 (m, 5H), 7.13 – 6.95 (m, 4H), 5.04 (dd, *J* = 9.2, 3.1 Hz, 1H), 4.19 – 4.04 (m, 1H), 3.57 (dd, *J* = 14.6, 3.3 Hz, 1H), 1.26 (s, 9H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 153.42, 150.69, 148.93, 138.23, 137.11, 135.68, 130.51, 128.83, 128.67, 128.37, 127.90, 127.70, 126.55, 125.65, 123.42, 64.59, 61.07, 34.50, 31.30. **HRMS** calculated for $C_{30}H_{31}N_2O_2S$ $[M+H]^+$ 483.2101, found 483.2103.



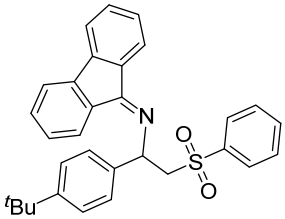
(±)-N-(1-(4-(*tert*-Butyl)phenyl)-2-(methylsulfonyl)ethyl)-1,1-diphenylmethanimine (5k): Prepared according to the general procedure, colorless oil, 31.2 mg, 74% yield, R_f = 0.1 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.72 – 7.64 (m, 2H), 7.45 – 7.36 (m, 4H), 7.38 – 7.29 (m, 2H), 7.30 – 7.24 (m, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 7.04 – 6.99 (m, 2H), 5.02 (dd, *J* = 10.0, 3.0 Hz, 1H), 3.99 – 3.81 (m, 1H), 3.32 – 3.25 (m, 1H), 2.87 (s, 3H), 1.29 (s, 9H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 150.73, 138.89, 138.41, 135.92, 130.67, 128.74, 128.61, 128.36, 128.25, 127.57, 126.61, 125.67, 63.14, 61.30, 43.14, 34.54, 31.33. **HRMS** calculated for $C_{26}H_{30}NO_2S$ $[M+H]^+$ 420.1992, found 420.1997.



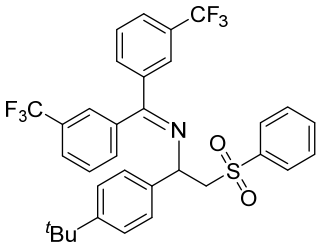
(±)-N-(1-(4-(*tert*-Butyl)phenyl)-2-(ethylsulfonyl)ethyl)-1,1-diphenylmethanimine (5l): Prepared according to the general procedure, colorless oil, 39.3 mg, corrected weight: 38.6 mg, 89% yield (accompanied by a small amount of inseparable alkenyl sulfone compound, the yield of the product has been adjusted accordingly), R_f = 0.1 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.71 – 7.62 (m, 2H), 7.46 – 7.31 (m, 6H), 7.30 – 7.22 (m, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 7.05 – 6.99 (m, 2H), 5.02 (dd, *J* = 9.9, 2.8 Hz, 1H), 4.03 – 3.81 (m, 1H), 3.28 – 3.14 (m, 1H), 3.01 (dq, *J* = 14.8, 7.4 Hz, 1H), 2.89 (dq, *J* = 14.3, 7.5 Hz, 1H), 1.38 (t, *J* = 7.4 Hz, 3H), 1.29 (s, 9H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 150.66, 139.02, 138.65, 135.96, 130.58, 128.70, 128.60, 128.33, 128.21, 127.60, 126.58, 125.64, 61.10, 60.03, 49.15, 34.53, 31.33, 6.82. **HRMS** calculated for $C_{27}H_{32}NO_2S$ $[M+H]^+$ 434.2148, found 434.2155.



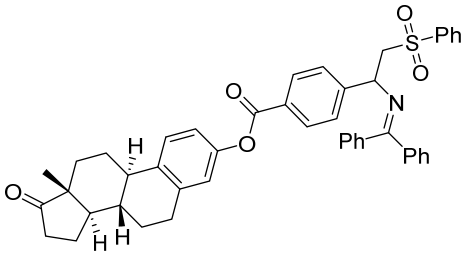
(±)-N-(1-(4-(*tert*-Butyl)phenyl)-2-(cyclopropylsulfonyl)ethyl)-1,1-diphenylmethanimine (5m): Prepared according to the general procedure, colorless oil, 43.8 mg, corrected weight: 42.3 mg, 95% yield (accompanied by a small amount of inseparable alkenyl sulfone compound, the yield of the product has been adjusted accordingly), R_f = 0.15 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.74 – 7.61 (m, 2H), 7.45 – 7.36 (m, 4H), 7.33 (d, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 7.10 – 7.04 (m, 2H), 5.08 (dd, *J* = 9.6, 3.1 Hz, 1H), 4.00 – 3.81 (m, 1H), 3.35 (dd, *J* = 14.4, 3.1 Hz, 1H), 2.30 (tt, *J* = 8.0, 4.9 Hz, 1H), 1.29 (s, 9H), 1.27 – 1.20 (m, 1H), 1.18 – 1.08 (m, 1H), 1.01 – 0.91 (m, 1H), 0.90 – 0.81 (m, 1H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 150.60, 138.88, 136.12, 130.42, 128.70, 128.67, 128.31, 128.14, 127.76, 126.68, 125.62, 62.34, 61.17, 34.53, 31.35, 5.70, 5.31, 4.85. **HRMS** calculated for $C_{28}H_{32}NO_2S$ $[M+H]^+$ 446.2148, found 446.2153.



(±)-N-(1-(4-(*tert*-Butyl)phenyl)-2-(phenylsulfonyl)ethyl)-9H-fluoren-9-imine (5n): Prepared according to the general procedure, yellow oil, 30.9 mg, 64% yield, R_f = 0.2 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 7.7 Hz, 1H), 7.70 – 7.64 (m, 2H), 7.58 (d, *J* = 7.4 Hz, 1H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.34 – 7.27 (m, 4H), 7.27 – 7.20 (m, 3H), 7.19 – 7.10 (m, 3H), 6.18 (dd, *J* = 9.1, 2.5 Hz, 1H), 4.14 (dd, *J* = 14.4, 9.1 Hz, 1H), 3.75 (dd, *J* = 14.5, 2.5 Hz, 1H), 1.25 (s, 9H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 163.46, 150.70, 143.85, 140.87, 139.85, 137.98, 132.86, 131.61, 131.41, 131.15, 128.70, 128.27, 128.14, 127.87, 127.71, 126.31, 125.85, 123.07, 120.24, 119.07, 65.47, 60.04, 34.51, 31.28. **HRMS** calculated for $C_{31}H_{20}NO_2S$ $[M+H]^+$ 480.1992, found 480.1993.

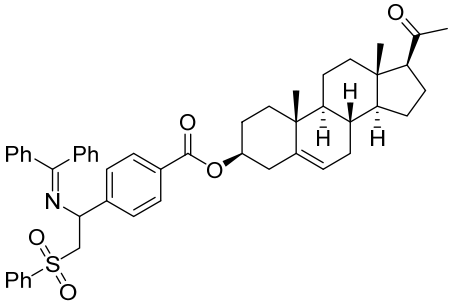


(±)-N-(1-(4-(*tert*-Butyl)phenyl)-2-(phenylsulfonyl)ethyl)-1,1-bis(3-(trifluoromethyl)phenyl)methanimine (5o): Prepared according to the general procedure, yellow oil, 39.7 mg, corrected weight: 37.9 mg, 61% yield (accompanied by a small amount of inseparable alkenyl sulfone compound, the yield of the product has been adjusted accordingly), R_f = 0.25 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 – 7.72 (m, 4H), 7.65 (t, *J* = 7.9 Hz, 2H), 7.53 – 7.43 (m, 2H), 7.43 – 7.34 (m, 4H), 7.28 – 7.23 (m, 2H), 7.16 (s, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 4.91 (dd, *J* = 9.8, 2.2 Hz, 1H), 4.16 (dd, *J* = 14.4, 9.8 Hz, 1H), 3.46 (dd, *J* = 14.4, 2.4 Hz, 1H), 1.27 (s, 9H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 166.04, 151.10, 140.46, 139.14, 138.08, 136.08, 133.36, 132.19, 131.54, 130.56-130.31 (m), 131.20, 129.28, 129.04, 128.60, 127.75, 127.28 – 127.06 (m), 126.38, 126.13 – 125.83 (m), 125.90, 125.09 – 124.64 (m), 124.82 (q, *J* = 274.1), 64.06, 61.57, 34.53, 31.23. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -62.53, -62.82. **HRMS** calculated for $C_{33}H_{30}F_6NO_2S$ $[M+H]^+$ 618.1896, found 618.1899.

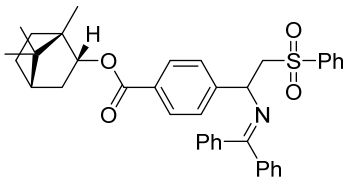


(8S,9R,13R,14R)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 4-(1-((diphenylmethylene)amino)-2-(phenylsulfonyl)ethyl)benzoate (6a): Prepared according to the general procedure, colorless oil, 56.2 mg, 78% yield, 1:1 *d.r.*, R_f = 0.1 (PE/EA = 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 7.6 Hz, 2H), 7.52

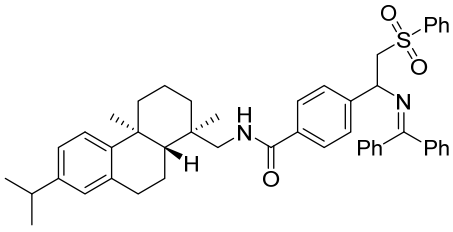
(t, *J* = 7.4 Hz, 1H), 7.48 – 7.36 (m, 8H), 7.35 – 7.21 (m, 5H), 7.01 (d, *J* = 6.5 Hz, 2H), 6.98 – 6.90 (m, 2H), 5.13 (d, *J* = 7.0 Hz, 1H), 4.33 – 3.89 (m, 1H), 3.51 (dd, *J* = 14.4, 3.0 Hz, 1H), 3.07 – 2.82 (m, 2H), 2.50 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.45 – 2.38 (m, 1H), 2.30 (td, *J* = 10.8, 3.5 Hz, 1H), 2.21 – 2.11 (m, 1H), 2.11 – 1.94 (m, 4H), 1.68 – 1.41 (m, 7H), 0.91 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 165.02, 148.76, 138.12, 137.51, 133.32, 130.66, 129.13, 128.48, 127.94, 127.63, 127.19, 126.49, 121.65, 118.82, 61.20, 50.45, 47.97, 44.19, 38.03, 35.88, 31.58, 29.45, 26.37, 25.80, 21.62, 13.87. **HRMS** calculated for $C_{46}H_{44}NO_5S$ $[M+H]^+$ 722.2935, found 722.2939.



(3S,8S,9S,10R,13S,14S,17S)-17-Acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(1-((diphenylmethylene)amino)-2-(phenylsulfonyl)ethyl)benzoate (6b): Prepared according to the general procedure, colorless oil, 60.0 mg, 78% yield, 1:1 *d.r.*, R_f = 0.1 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.45 – 7.36 (m, 8H), 7.28 – 7.24 (m, 2H), 7.17 (d, *J* = 7.4 Hz, 2H), 6.99 (d, *J* = 6.4 Hz, 2H), 5.45 – 5.37 (m, 1H), 5.09 (d, *J* = 7.4 Hz, 1H), 4.90 – 4.77 (m, 1H), 4.22 – 3.98 (m, 1H), 3.48 (dd, *J* = 14.4, 2.8 Hz, 1H), 2.54 (t, *J* = 8.9 Hz, 1H), 2.48 – 2.40 (m, 2H), 2.23 – 2.15 (m, 1H), 2.12 (s, 3H), 2.08 – 1.86 (m, 4H), 1.76 – 1.58 (m, 5H), 1.58 – 1.39 (m, 4H), 1.32 – 1.17 (m, 3H), 1.06 (s, 3H), 0.64 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 209.53, 165.58, 140.34, 139.60, 133.25, 130.04, 129.08, 128.41, 127.92, 127.63, 126.89, 122.51, 74.52, 63.68, 61.18, 56.84, 49.90, 43.99, 38.80, 38.15, 37.03, 36.67, 31.84, 31.80, 31.57, 27.84, 24.50, 22.85, 21.07, 19.38, 13.25. **HRMS** calculated for $C_{49}H_{54}NO_5S$ $[M+H]^+$ 768.3717, found 768.3718.

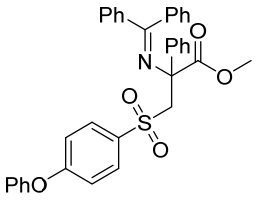


(1S,2R,4S)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 4-(1-((diphenylmethylene)amino)-2-(phenylsulfonyl)ethyl)benzoate (6c): Prepared according to the general procedure, colorless oil, 48.2 mg, 80% yield, 1:1 *d.r.*, R_f = 0.5 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.81 – 7.71 (m, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.46 – 7.34 (m, 8H), 7.28 – 7.23 (m, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.00 (d, *J* = 6.5 Hz, 2H), 5.12 – 5.05 (m, 2H), 4.06 (dd, *J* = 14.4, 9.0 Hz, 1H), 3.50 (dd, *J* = 14.4, 3.1 Hz, 1H), 2.52 – 2.39 (m, 1H), 2.13 – 2.03 (m, 1H), 1.83-1.75 (m, 1H), 1.75 – 1.71 (m, 1H), 1.43 – 1.35 (m, 1H), 1.33 – 1.26 (m, 1H), 1.14 – 1.03 (m, 1H), 0.95 (s, 3H), 0.92 – 0.87 (m, 6H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 169.92, 166.41, 146.93, 140.36, 138.94, 135.99, 133.22, 130.49, 130.17, 129.98, 129.07, 128.84, 128.79, 128.41, 127.90, 127.88, 127.62, 126.93, 80.61, 80.59, 64.17, 61.19, 49.11, 49.08, 47.89, 44.98, 36.93, 36.89, 28.09, 27.39, 19.73, 18.92, 13.63, 13.61. **HRMS** calculated for $C_{38}H_{40}NO_4S$ $[M+H]^+$ 606.2673, found 606.2676.

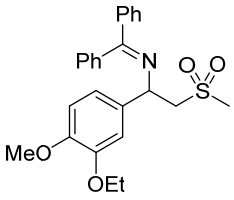


4-(1-((Diphenylmethylene)amino)-2-(phenylsulfonyl)ethyl)-N-(((1R,4aS,10aR)-7-isopropyl-1,4a,10a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)benzamide (6d): Prepared according to the general procedure, colorless oil, 50.1 mg, 68% yield, 1:1 *d.r.*, R_f =

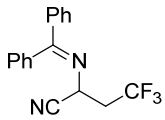
0.15 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 7.7 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.48 – 7.34 (m, 9H), 7.26 (d, *J* = 7.2 Hz, 2H), 7.16 – 7.13 (m, 3H), 6.98 – 6.97 (m, 3H), 6.87 (d, *J* = 3.6 Hz, 1H), 6.09 (t, *J* = 5.8 Hz, 1H), 5.06 (d, *J* = 7.5 Hz, 1H), 4.05 (s, 1H), 3.50 – 3.37 (m, 2H), 3.26 (dt, *J* = 13.5, 5.7 Hz, 1H), 2.91 (dd, *J* = 17.0, 6.0 Hz, 1H), 2.82-2.74 (m, 2H), 2.28 (d, *J* = 13.0 Hz, 1H), 1.96 (dd, *J* = 12.9, 7.0 Hz, 1H), 1.85 – 1.61 (m, 4H), 1.53 – 1.42 (m, 2H), 1.41 – 1.29 (m, 2H), 1.22 – 1.84 (m, 9H), 0.98 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.15, 167.10, 147.03, 145.66, 140.30, 134.77, 133.25, 129.07, 128.43, 127.89, 127.67, 127.34, 127.19, 126.96, 124.24, 123.91, 61.08, 50.21, 45.66, 45.61, 38.37, 37.76, 37.57, 36.43, 36.39, 33.42, 30.45, 25.46, 23.98, 19.11, 18.89, 18.65. **HRMS** calculated for $C_{48}H_{53}N_2O_3S$ $[M+H]^+$ 737.3771, found 737.3778.



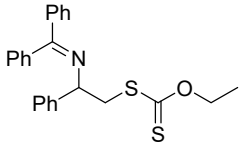
Methyl 2-((diphenylmethylene)amino)-3-((4-phenoxyphenyl)sulfonyl) -2-phenylpropanoate (9): Prepared according to the general procedure, colorless oil, 29.6 mg, 51% yield, R_f = 0.25 (PE/EA = 2/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.67 – 7.55 (m, 4H), 7.42 – 7.38 (m, 2H), 7.37 – 7.30 (m, 6H), 7.27 (d, *J* = 9.4 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.19 – 7.15 (m, 3H), 7.04 – 6.96 (m, 4H), 6.77 – 6.69 (m, 2H), 4.31 (d, *J* = 14.8 Hz, 1H), 4.21 (d, *J* = 14.8 Hz, 1H), 3.40 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 172.09, 170.92, 161.94, 154.96, 141.26, 140.54, 137.07, 133.82, 130.98, 130.75, 130.13, 129.02, 128.55, 128.38, 128.01, 127.85, 127.83, 127.51, 126.03, 124.96, 120.34, 116.94, 68.46, 64.62, 52.64. **HRMS** calculated for $C_{35}H_{30}NO_5S$ $[M+H]^+$ 576.1839, found 576.1841.



N-(1-(3-Ethoxy-4-methoxyphenyl)-2-(methylsulfonyl)ethyl)-1,1-diphenylm ethanimine (13): Prepared according to the general procedure, colorless oil, 29.5 mg, 67% yield, R_f = 0.25 (PE/EA = 2/1). **^{1}H NMR** (700 MHz, Chloroform-*d*) δ 7.71 – 7.63 (m, 2H), 7.43 – 7.38 (m, 4H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.01 (d, *J* = 6.6 Hz, 2H), 6.76 (d, *J* = 8.3 Hz, 1H), 6.70 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.60 (d, *J* = 1.8 Hz, 1H), 4.96 (dd, *J* = 9.9, 3.1 Hz, 1H), 4.03 – 3.96 (m, 2H), 3.88 (dd, *J* = 14.7, 9.9 Hz, 1H), 3.84 (s, 3H), 3.28 (dd, *J* = 14.8, 2.2 Hz, 1H), 2.88 (s, 3H), 1.43 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (175 MHz, Chloroform-*d*) δ 170.14, 148.69, 148.27, 138.92, 136.02, 134.12, 130.67, 128.69, 128.51, 128.36, 128.26, 127.50, 119.04, 111.56, 111.42, 64.27, 63.33, 61.31, 55.93, 43.15, 14.76. **HRMS** calculated for $C_{25}H_{28}NO_4S$ $[M+H]^+$ 438.1734, found 438.1738.



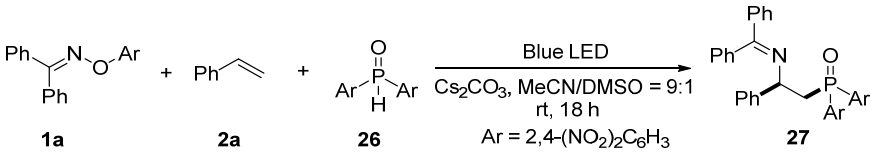
2-((Diphenylmethylene)amino)-4,4,4-trifluorobutanenitrile (27a): Prepared according to the general procedure, colorless oil., known compound[12], 16.6 mg, 55% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.66 – 7.62 (m, 2H), 7.56 – 7.52 (m, 2H), 7.52 – 7.44 (m, 2H), 7.41 – 7.33 (m, 2H), 7.20 – 7.25 (m, 2H), 4.55 (dd, *J* = 7.7, 5.3 Hz, 1H), 2.95 – 2.72 (m, 2H). **^{19}F NMR** (375 MHz, Chloroform-*d*) δ -63.93.



S-(2-((diphenylmethylene)amino)-2-phenylethyl) O-ethyl carbonodithioate (27b): Prepared according to the general procedure, colorless oil, 17.2 mg, 42% yield, R_f = 0.8 (PE/EA = 25/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.75 – 7.64 (m, 2H), 7.43 – 7.29 (m, 10H), 7.29 – 7.21 (m, 1H), 7.05 (d, *J* = 5.2 Hz, 2H), 4.81 – 4.68 (m, 1H), 4.56 – 4.45 (m, 2H), 3.74 – 3.58 (m, 1H), 3.56 – 3.36 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*)

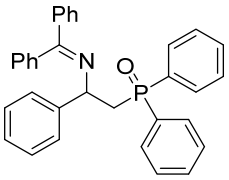
δ 214.25, 152.88, 148.70, 146.94, 130.25, 128.77, 128.60, 128.28, 128.05, 127.88, 127.39, 127.05, 69.72, 64.18, 44.32, 13.76. **HRMS** calculated for $C_{24}H_{24}NOS_2$ $[M+H]^+$ 406.1294, found 406.1294.

6. General procedure: photo-induced phosphinoylimination of alkenes

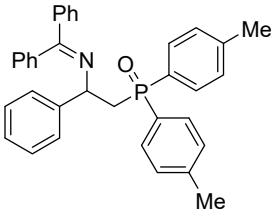


1a **2a** **26** **27**

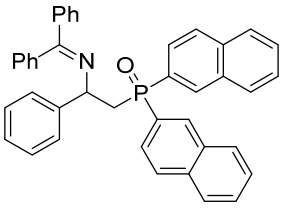
In a glove box, an oven-dried 4 mL vial was charged with O-aryl oxime (0.12 mmol), alkene (0.10 mmol), diarylphosphine oxide (0.18 mmol), Cs_2CO_3 (0.10 mmol), MeCN (0.9 mL) and DMSO (0.1 mL) at room temperature. The reaction tube was sealed with a Teflon screw cap, removed from the glove box. Then, the reaction mixture was stirred at rt under Blue LED for 18 hours. And the crude reaction mixture was purified by column chromatography on silica gel using petroleum ether and ethyl acetate to afford the corresponding products.



(2-((Diphenylmethylene)amino)-2-phenylethyl)diphenylphosphine oxide (27c): Prepared according to the general procedure, yellow oil, 23.1 mg, 48% yield, R_f = 0.3 (PE/EA = 1/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.86 – 7.72 (m, 2H), 7.68 – 7.59 (m, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.42 – 7.28 (m, 9H), 7.28 – 7.21 (m, 3H), 7.21 – 7.11 (m, 6H), 6.69 – 6.83 (m, 2H), 5.09 (td, *J* = 9.1, 3.3 Hz, 1H), 3.42 – 3.15 (m, 1H), 2.78 (ddd, *J* = 14.9, 13.4, 3.4 Hz, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 171.27, 145.04, 136.29, 134.63 (d, *J* = 97.3 Hz), 133.59 (d, *J* = 99.0 Hz), 132.45, 131.30 (d, *J* = 2.6 Hz), 131.04, 130.99, 130.95, 130.36, 130.27, 130.09, 129.84, 128.58, 128.51, 128.46, 128.41, 128.35 (d, *J* = 10.5 Hz), 128.13, 127.65 (d, *J* = 11.1 Hz), 126.97, 126.80, 60.53 (d, *J* = 3.3 Hz), 40.38 (d, *J* = 67.3 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 28.44. **HRMS** calculated for $C_{33}H_{29}NOP$ $[M+H]^+$ 486.1981, found 486.1974.



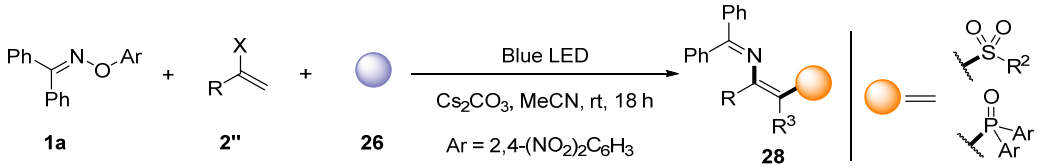
(2-((Diphenylmethylene)amino)-2-phenylethyl)di-p-tolylphosphine oxide (27d): Prepared according to the general procedure, yellow oil, 23.5 mg, 46% yield, R_f = 0.3 (PE/EA = 1/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.72 – 7.62 (m, 2H), 7.58 – 7.48 (m, 2H), 7.40 – 7.32 (m, 3H), 7.30 – 7.06 (m, 14H), 7.02 – 6.94 (m, 2H), 5.17 – 4.98 (m, 1H), 4.00 – 3.11 (m, 1H), 2.80 – 2.67 (m, 1H), 2.32 (s, 3H), 2.26 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.66, 145.24, 141.59 (d, *J* = 2.7 Hz), 141.28 (d, *J* = 2.6 Hz), 139.37, 136.35, 131.65 (d, *J* = 100.3 Hz), 131.01 (d, *J* = 9.8 Hz), 130.30 (d, *J* = 9.5 Hz), 129.70, 129.23, 129.11, 128.99, 128.60, 128.43, 128.27, 128.10, 127.77, 127.45, 126.86, 126.79, 60.53 (d, *J* = 3.6 Hz), 40.53 (d, *J* = 71.1 Hz), 21.51, 21.50. **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 28.66. **HRMS** calculated for $C_{35}H_{33}NOP$ $[M+H]^+$ 514.2294, found 514.2290.



(2-((Diphenylmethylene)amino)-2-phenylethyl)di(naphthalen-2-yl)phosphine oxide (27e): Prepared according to the general procedure, yellow oil, 19.4 mg, 33% yield, R_f = 0.3 (PE/EA = 1/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.44 (d, *J* = 13.4 Hz, 1H), 8.29 (d, *J* = 13.2 Hz, 1H), 7.86 – 7.71 (m, 7H), 7.69 – 7.62 (m, 1H), 7.61 – 7.42 (m, 6H), 7.35

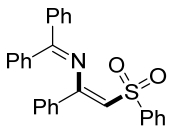
– 7.27 (m, 2H), 7.23 – 7.17 (m, 3H), 7.16 – 7.03 (m, 4H), 6.95 (d, *J* = 6.8 Hz, 2H), 6.90 – 6.81 (m, 2H), 5.18 (t, *J* = 7.0 Hz, 1H), 3.66 – 3.33 (m, 1H), 2.99 (td, *J* = 14.9, 3.4 Hz, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 168.05, 145.07 (d, *J* = 11.9 Hz), 139.00, 136.34, 134.45 (d, *J* = 2.3 Hz), 134.36 (d, *J* = 2.4 Hz), 132.86 (d, *J* = 8.3 Hz), 132.68 (d, *J* = 12.8 Hz), 132.52 (d, *J* = 12.7 Hz), 132.20, 132.09 (d, *J* = 8.5 Hz), 131.39, 131.22, 130.40, 129.76, 128.83 (d, *J* = 3.8 Hz), 128.50, 128.42 (d, *J* = 11.6 Hz), 128.31, 128.18, 128.08, 127.75, 127.71, 127.68, 127.48 (d, *J* = 94.2 Hz), 127.33, 126.85, 126.83, 126.66, 126.04 (d, *J* = 10.9 Hz), 125.50 (d, *J* = 10.2 Hz), 60.70 (d, *J* = 3.6 Hz), 40.28 (d, *J* = 70.1 Hz). **^{31}P NMR** (162 MHz, Chloroform-*d*) δ 28.88. **HRMS** calculated for $C_{41}H_{33}NOP$ $[M+H]^+$ 586.2294, found 586.2298.

7. General procedure: construction of (Z)-β-amino vinylsulfones and vinylphosphines

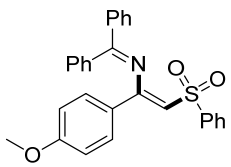


Procedure 7A: construction of (Z)-β-amino vinylsulfones. In a glove box, an oven-dried 4 mL vial was charged with O-aryl oxime **1a** (0.12 mmol), alkene **2"** (0.10 mmol), sodium sulfinate (0.18 mmol), Cs_2CO_3 (0.10 mmol), MeCN (1.0 mL) at room temperature. The reaction tube was sealed with a Teflon screw cap, removed from the glove box. Then, the reaction mixture was stirred at rt under Blue LED for 18 hours. And the crude reaction mixture was purified by column chromatography on silica gel using petroleum ether and ethyl acetate to afford the corresponding products.

Procedure 7B: construction of (Z)-β-amino vinylphosphines. In a glove box, an oven-dried 4 mL vial was charged with O-aryl oxime **1a** (0.12 mmol), alkene **2"** (0.10 mmol), diarylphosphine oxide (0.18 mmol), Cs_2CO_3 (0.15 mmol), MeCN (0.9 mL) and DMSO (0.1 mL) at room temperature. The reaction tube was sealed with a Teflon screw cap, removed from the glove box. Then, the reaction mixture was stirred at rt under Blue LED for 18 hours. And the crude reaction mixture was purified by column chromatography on silica gel using petroleum ether and ethyl acetate to afford the corresponding products.

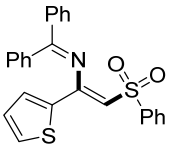


(Z)-1,1-Diphenyl-N-(1-phenyl-2-(phenylsulfonyl)vinyl)methanimine (28a): Prepared according to the general procedure 7A, white solid, melting point: 129 – 131 °C, 28.7 mg, 68% yield, R_f = 0.3 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 – 7.85 (m, 2H), 7.59 – 7.51 (m, 1H), 7.50 – 7.45 (m, 4H), 7.45 – 7.36 (m, 4H), 7.34 – 7.26 (m, 4H), 7.25 – 7.09 (m, 5H), 6.06 (s, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 169.55, 159.66, 142.28, 136.90, 136.37, 132.75, 130.61, 130.29, 129.23, 128.60, 128.54, 128.06, 127.93, 126.56, 108.86. **HRMS** calculated for $C_{27}H_{22}NO_2S$ $[M+H]^+$ 424.1366, found 424.1376.

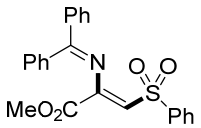


(Z)-N-(1-(4-methoxyphenyl)-2-(phenylsulfonyl)vinyl)-1,1-diphenylmethanimine (28b): Prepared according to the general procedure 7A, yellow oil, 37.4 mg, 82% yield, R_f = 0.2 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.89 – 7.83 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.52 – 7.46 (m, 4H), 7.46 – 7.37 (m, 4H), 7.36 – 7.28 (m, 4H), 7.19 (d, *J* = 8.9 Hz, 2H), 6.70 (d, *J* = 8.9 Hz, 2H),

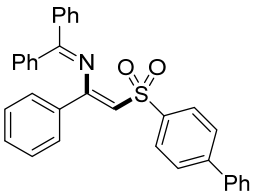
5.98 (s, 1H), 3.74 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 169.23, 161.24, 159.21, 142.60, 136.91, 132.49, 130.47, 129.21, 128.50, 128.20, 128.09, 127.98, 127.78, 113.87, 106.61, 55.32. **HRMS** calculated for $C_{28}H_{24}NO_3S$ $[M+H]^+$ 454.1471, found 454.1479.



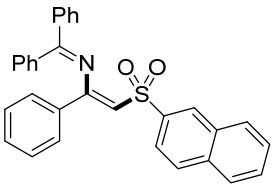
(Z)-1,1-Diphenyl-N-(2-(phenylsulfonyl)-1-(thiophen-2-yl)vinyl)methanimine (28c): Prepared according to the general procedure 7A, yellow oil, 21.5 mg, 50% yield, R_f = 0.3 (PE/EA = 9/1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.82 (m, 2H), 7.62 – 7.52 (m, 5H), 7.47 – 7.40 (m, 4H), 7.40 – 7.32 (m, 4H), 7.27 – 7.23 (m, 1H), 7.05 (dd, *J* = 3.8, 1.1 Hz, 1H), 6.87 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.08 (s, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 170.49, 153.04, 142.42, 138.01, 136.73, 132.65, 130.72, 129.49, 128.82, 128.58, 128.04, 127.97, 127.78, 127.69, 106.76. **HRMS** calculated for $C_{25}H_{20}NO_2S_2$ $[M+H]^+$ 430.0930, found 430.0936.



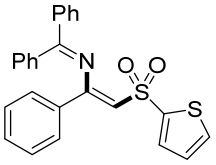
Methyl (Z)-2-((diphenylmethylene)amino)-3-(phenylsulfonyl)acrylate (28d): Prepared according to the general procedure 7A, yellow oil, 23.7 mg, 58% yield, R_f = 0.3 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 – 7.83 (m, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.54 – 7.49 (m, 5H), 7.48 – 7.39 (m, 7H), 6.67 (s, 1H), 3.53 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 171.81, 161.81, 146.65, 140.45, 136.83, 133.44, 131.05, 129.49, 128.66, 128.54, 128.21, 120.08, 53.03. **HRMS** calculated for $C_{23}H_{20}NO_4S$ $[M+H]^+$ 406.1108, found 406.1120.



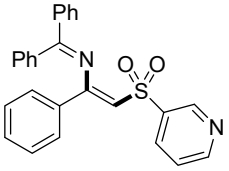
(Z)-N-(2-([1,1'-Biphenyl]-4-ylsulfonyl)-1-phenylvinyl)-1,1-diphenylmethanimine (28e): Prepared according to the general procedure 7A, yellow oil, 20.1 mg, 40% yield, R_f = 0.3 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.54 – 7.45 (m, 6H), 7.45 – 7.39 (m, 3H), 7.36 – 7.30 (m, 4H), 7.29 – 7.14 (m, 5H), 6.10 (s, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 169.56, 159.56, 145.54, 140.86, 139.72, 136.90, 136.39, 130.56, 130.20, 129.23, 129.02, 128.48, 128.46, 128.35, 128.01, 127.41, 127.23, 126.57, 108.98. **HRMS** calculated for $C_{33}H_{26}NO_2S$ $[M+H]^+$ 500.1679, found 500.1673.



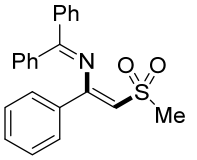
(Z)-N-(2-(Naphthalen-2-ylsulfonyl)-1-phenylvinyl)-1,1-diphenylmethanimine (28f): Prepared according to the general procedure 7A, yellow solid, melting point: 96 – 98 °C, 31.5 mg, 67% yield, R_f = 0.3 (PE/EA = 9/1). ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.40 (s, 1H), 7.93 – 7.89 (m, 3H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.49 – 7.44 (m, 4H), 7.43 – 7.38 (m, 2H), 7.32 – 7.27 (m, 4H), 7.22 (t, *J* = 6.7 Hz, 1H), 7.18 – 7.12 (m, 4H), 6.15 (s, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 169.50, 159.70, 138.81, 136.87, 136.27, 135.05, 131.98, 130.57, 130.18, 129.74, 129.53, 129.23, 128.86, 128.60, 128.44, 128.04, 127.86, 127.06, 126.55, 123.24, 109.16. **HRMS** calculated for $C_{31}H_{24}NO_2S$ $[M+H]^+$ 474.1522, found 474.1522.



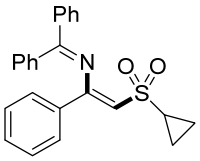
(Z)-1,1-Diphenyl-N-(1-phenyl-2-(thiophen-2-ylsulfonyl)vinyl)methanimine (28g): Prepared according to the general procedure 7A, yellow oil, 26.1 mg, 61% yield, R_f = 0.3 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.63 – 7.58 (m, 2H), 7.63 – 7.58 (m, 4H), 7.44 – 7.38 (m, 2H), 7.63 – 7.58 (m, 4H), 7.29 – 7.15 (m, 6H), 7.06 (dd, *J* = 4.9, 3.9 Hz, 1H), 6.09 (s, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 169.70, 159.87, 143.89, 136.94, 136.47, 132.86, 132.53, 130.55, 130.30, 129.24, 128.52, 128.01, 127.13, 126.59, 108.89. **HRMS** calculated for $C_{25}H_{20}NO_2S_2$ $[M+H]^+$ 430.0930, found 430.0925.



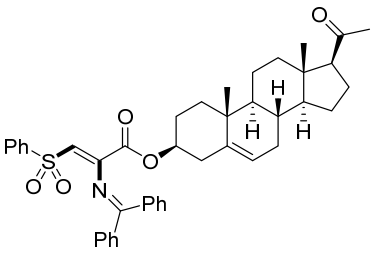
(Z)-1,1-Diphenyl-N-(1-phenyl-2-(pyridin-3-ylsulfonyl)vinyl)methanimine (28h): Prepared according to the general procedure 7A, yellow oil, 30.1 mg, 71% yield, R_f = 0.2 (PE/EA = 5/1). **^{1}H NMR** (700 MHz, Chloroform-*d*) δ 9.11 (s, 1H), 8.81 (d, *J* = 3.6 Hz, 1H), 8.12 (d, *J* = 7.9 Hz, 1H), 7.50 – 7.47 (m, 4H), 7.45 – 7.41 (m, 2H), 7.38 (dd, *J* = 7.7, 5.0 Hz, 1H), 7.36 – 7.32 (m, 4H), 7.28 – 7.25 (m, 1H), 7.20 – 7.15 (m, 4H), 6.11 (s, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 170.15, 160.85, 153.10, 148.90, 136.72, 135.86, 135.76, 130.83, 130.53, 129.20, 128.54, 128.14, 126.60, 123.18, 108.58. **HRMS** calculated for $C_{26}H_{21}N_2O_2S$ $[M+H]^+$ 425.1318, found 425.1322.



(Z)-N-(2-(Methylsulfonyl)-1-phenylvinyl)-1,1-diphenylmethanimine (28i): Prepared according to the general procedure 7A, white solid, melting point: 95 – 97 °C, 20.3 mg, 56% yield, R_f = 0.25 (PE/EA = 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.54 – 7.46 (m, 4H), 7.43 – 7.37 (m, 2H), 7.35 – 7.31 (m, 3H), 7.31 – 7.27 (m, 2H), 7.27 – 7.20 (m, 4H), 5.95 (s, 1H), 3.06 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 170.34, 160.67, 136.44, 130.62, 130.31, 129.15, 128.58, 128.08, 126.52, 108.81, 42.20. **HRMS** calculated for $C_{22}H_{20}NO_2S$ $[M+H]^+$ 362.1209, found 362.1212.

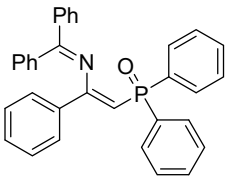


(Z)-N-(2-(Cyclopropylsulfonyl)-1-phenylvinyl)-1,1-diphenylmethanimine (28j): Prepared according to the general procedure 7A, white solid, melting point: 155 – 157 °C, 24.8 mg, 64% yield, R_f = 0.25 (PE/EA = 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.55 – 7.45 (m, 4H), 7.43 – 7.36 (m, 2H), 7.36 – 7.29 (m, 7H), 7.28 – 7.21 (m, 2H), 5.89 (s, 1H), 2.63 (tt, *J* = 8.1, 4.9 Hz, 1H), 1.27 – 1.19 (m, 2H), 0.98 – 0.91 (m, 2H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 169.86, 160.22, 137.04, 136.96, 130.45, 130.20, 129.17, 128.59, 128.01, 126.53, 107.06, 31.73, 4.74. **HRMS** calculated for $C_{24}H_{22}NO_2S$ $[M+H]^+$ 388.1366, found 388.1367.

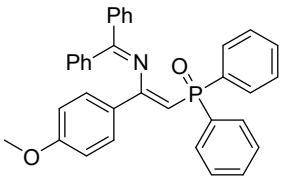


(3S,8S,9S,10R,13S,14S,17S)-17-Acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-chloroacrylate (28k): Prepared according to the general procedure 7A, yellow oil, 41.0 mg, 59% yield, R_f = 0.3 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 – 7.83 (m, 2H), 7.64 – 7.58 (m, 1H), 7.55 – 7.45 (m, 7H), 7.44 – 7.37 (m, 5H), 6.68 (s, 1H), 5.26 (d, *J* = 5.1 Hz, 1H), 4.42 – 4.33 (m, 1H), 2.51 (t, *J* = 8.9 Hz, 1H), 2.21 – 2.14 (m, 1H), 2.13 – 1.90 (m, 8H), 1.77 (dt, *J* = 13.3, 3.4 Hz, 1H), 1.71 – 1.50 (m, 6H), 1.50 – 1.39 (m, 3H), 1.38 – 1.30 (m, 1H), 1.15 – 1.00 (m, 2H), 0.94 (s, 3H), 0.61 (s, 3H). **^{13}C**

NMR (100 MHz, Chloroform-*d*) δ 209.51, 171.35, 160.42, 147.15, 140.44, 139.00, 137.00, 133.36, 130.99, 129.69, 128.64, 128.58, 128.15, 122.76, 120.10, 76.35, 63.63, 56.76, 49.77, 43.94, 38.72, 37.42, 36.73, 36.48, 31.73, 31.69, 31.55, 27.13, 24.45, 22.82, 20.98, 19.23, 13.21. **HRMS** calculated for $C_{43}H_{48}NO_5S$ $[M+H]^+$ 690.3248, found 690.3242.



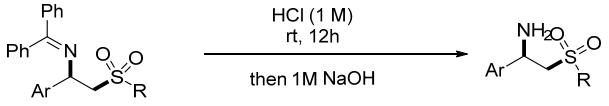
(Z)-(2-((Diphenylmethylene)amino)-2-phenylvinyl)diphenylphosphine oxide (28l): Prepared according to the general procedure 7B, yellow oil, 18.8 mg, 39% yield, R_f = 0.3 (PE/EA = 1/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 – 7.72 (m, 4H), 7.44 – 7.38 (m, 2H), 7.38 – 7.27 (m, 9H), 7.25 – 7.15 (m, 10H), 5.72 (d, *J* = 16.5 Hz, 1H). **^{13}C NMR** (100MHz, Chloroform-*d*) δ 168.58, 164.12, 138.65 (d, *J* = 13.8 Hz), 137.07, 135.03 (d, *J* = 106.2 Hz), 131.12 (d, *J* = 9.8 Hz), 130.89 (d, *J* = 2.7 Hz), 129.89, 129.36, 129.11, 128.30, 128.18, 127.65, 126.27, 98.67 (d, *J* = 108.9 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 19.73. **HRMS** calculated for $C_{33}H_{27}NOP$ $[M+H]^+$ 484.1825, found 484.1832.



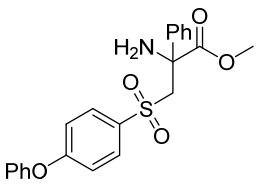
(Z)-(2-((Diphenylmethylene)amino)-2-(4-methoxyphenyl)vinyl)diphenylphosphine oxide (28m): Prepared according to the general procedure 7B, yellow oil, 22.2 mg, 43% yield, R_f = 0.2 (PE/EA = 1/1). **^{1}H NMR** (700 MHz, Chloroform-*d*) δ 7.80 – 7.70 (m, 4H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.35 – 7.27 (m, 8H), 7.27 – 7.21 (m, 6H), 7.21 – 7.15 (m, 4H), 6.75 (d, *J* = 8.9 Hz, 1H), 3.78 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 168.27, 163.67, 160.59, 137.14, 135.25 (d, *J* = 106.0 Hz), 131.10 (d, *J* = 9.7 Hz), 130.80 (d, *J* = 2.3 Hz), 129.84, 113.65, 96.08 (d, *J* = 111.4 Hz), 55.32. **^{31}P NM**R (162 MHz, Chloroform-*d*) δ 19.79. **HRMS** calculated for $C_{34}H_{29}NO_2P$ $[M+H]^+$ 514.1930, found 514.1930.

8. Pharmaceutical synthesis

8.1 General procedure for hydrolysis of sulfonylimination product

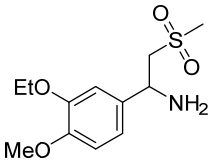


Synthesized according to literature procedures.[13] Sulfonylimination product (1.0 equiv.) was added to a mixture of MeOH (1.0 mL) and 1 M HCl aq. (6.2 equiv.). The reaction mixture was stirred at room temperature for 12 h and concentrated in vacuo. Then the residue was added water and adjusted PH = 13 with 1 M NaOH aq. And the crude reaction mixture was purified by column chromatography on silica gel using petroleum ether and ethyl acetate to afford the corresponding products.



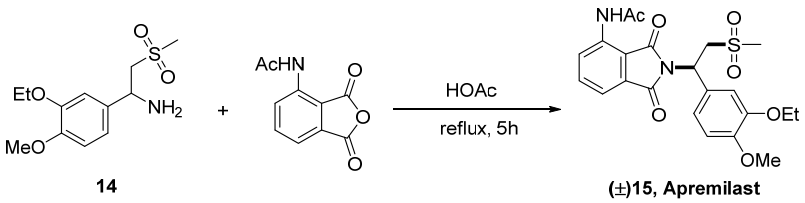
Methyl 2-amino-3-((4-phenoxyphenyl)sulfonyl)-2-phenylpropanoate (10): Prepared according to the general procedure, colorless oil, 28.0 mg, 99% yield, R_f = 0.25 (PE/EA = 2/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.81 – 7.77 (m, 2H), 7.50 – 7.45 (m, 2H), 7.44 – 7.38 (m, 2H), 7.33 – 7.27 (m, 3H), 7.25 – 7.20 (m, 1H), 7.06 (d, *J* = 7.7 Hz, 2H), 7.01 (d, *J* = 8.9 Hz, 2H), 4.17

(d, *J* = 14.3 Hz, 1H), 3.77 (d, *J* = 14.3 Hz, 1H), 3.78 (s, 3H), 2.66 (s, 2H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.43, 162.45, 154.90, 134.52, 130.24, 130.11, 128.82, 128.44, 125.24, 125.16, 120.41, 117.55, 65.59, 62.86, 53.23. **HRMS** calculated for $C_{22}H_{22}NO_5S$ $[M+H]^+$ 412.1213, found 412.1217.



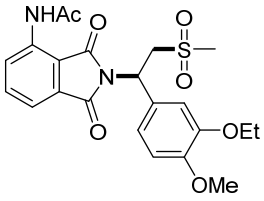
1-(3-Ethoxy-4-methoxyphenyl)-2-(methylsulfonyl)ethan-1-amine (14): Prepared according to the general procedure, colorless oil, 23.9 mg, 99% yield, R_f = 0.1 (EA). **^{1}H NMR** (700 MHz, Chloroform-*d*) δ 6.93 (d, *J* = 2.0 Hz, 1H), 6.91 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 4.60 (dd, *J* = 9.5, 3.2 Hz, 1H), 4.11 (qd, *J* = 7.0, 1.4 Hz, 2H), 3.87 (s, 3H), 3.34 (dd, *J* = 14.2, 9.6 Hz, 1H), 3.24 (dd, *J* = 14.1, 3.2 Hz, 1H), 1.93 (s, 2H), 2.91 (s, 3H), 1.47 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (175 MHz, Chloroform-*d*) δ 149.09, 148.73, 135.47, 118.25, 111.63, 110.67, 64.46, 63.13, 56.03, 50.97, 42.46, 14.80. **HRMS** calculated for $C_{12}H_{20}NO_4S$ $[M+H]^+$ 274.1108, found 274.1111.

8.2 Synthesis of (±) Apremilast



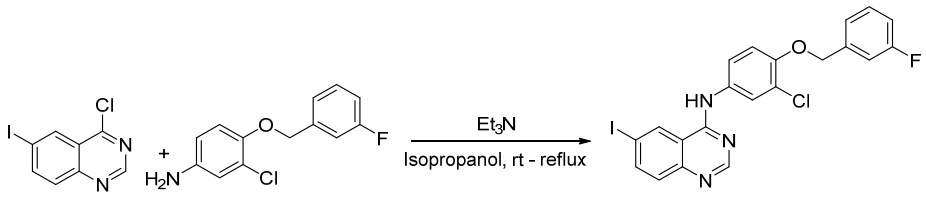
14 (±)15, Apremilast

Known compound was synthesized according to literature procedures.[14] Compound **14** (0.07 mmol), 3-acetamidophthalic anhydride (0.07 mmol), and glacial acetic acid (1.0 mL). The mixture was refluxed 5 h and then cooled to rt. The solvent was removed in vacuo, and the residue was dissolved in ethyl acetate. The resulting solution was washed with water, saturated aqueous $NaHCO_3$, brine and dried over sodium sulphate. The solvent was evaporated in vacuo. And the crude reaction mixture was purified by column chromatography on silica gel using petroleum ether and ethyl acetate to afford the corresponding products.



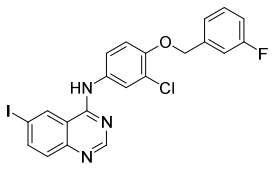
N-(2-(1-(3-Ethoxy-4-methoxyphenyl)-2-(methylsulfonyl)ethyl)-1,3-dioxoisoindolin-4-yl)acetamide (15): Known compound[14], white solid, 28.9 mg, 89% yield. **^{1}H NMR** (700 MHz, Chloroform-*d*) δ 9.46 (s, 1H), 8.75 (d, *J* = 8.4 Hz, 1H), 7.69 – 7.61 (m, 1H), 7.51 – 7.47 (m, 1H), 7.10 (m, 2H), 6.84 (d, *J* = 8.3 Hz, 1H), 5.87 (dd, *J* = 10.5, 4.4 Hz, 1H), 4.56 (dd, *J* = 14.3, 10.6 Hz, 1H), 4.11 (q, *J* = 7.0 Hz, 2H), 3.85 (s, 3H), 3.73 (dd, *J* = 14.4, 4.4 Hz, 1H), 2.88 (s, 3H), 2.26 (s, 3H), 1.47 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (175 MHz, Chloroform-*d*) δ 169.53, 169.22, 167.52, 149.77, 148.67, 137.64, 136.15, 131.07, 129.26, 125.00, 120.33, 118.27, 115.15, 112.43, 111.48, 64.56, 55.97, 54.51, 48.58, 41.67, 24.98, 14.72.

8.3 Synthesis of (±) Lapatinib analogue

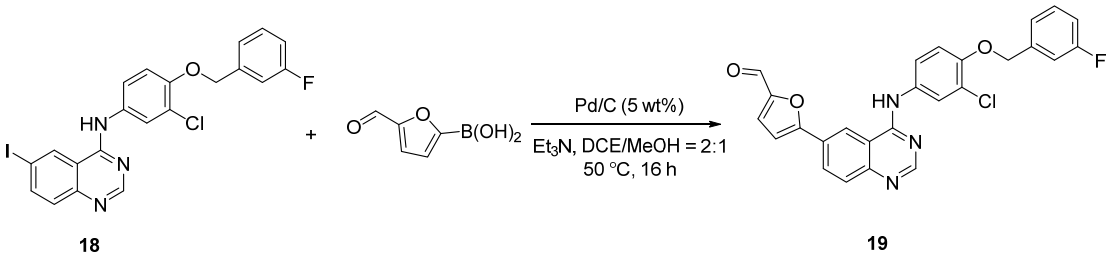


18

Known compound was synthesized according to literature procedures.[15] To a round bottle, isopropanol (35 mL), 3-chloro-4-((3-fluorobenzyl)oxy)aniline (1.51 g, 6.0 mmol), 4-cholo-6-iodo-quinazoline (1.45 g, 5.0 mmol) and triethylamine (0.84 mL, 6.0 mmol) was added. The resulting reaction mixture was stirred at room temperature for 6 h and then reflux for another 3 h. After cooling to room temperature, the yellow solid was collected by suck filtration, washed with isopropanol, water and ether sequentially, and dried at 50 ºC to afford compound **18** as white solid with 90% yield.

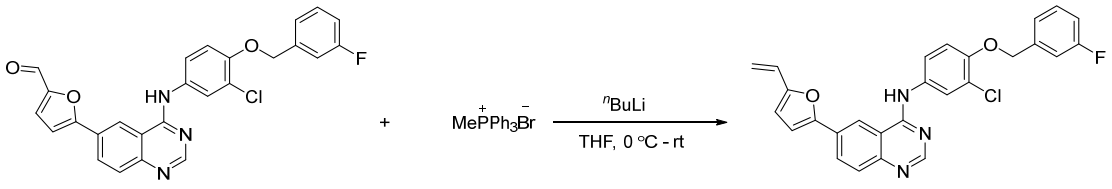


N-(3-Chloro-4-((3-fluorobenzyl)oxy)phenyl)-6-iodoquinazolin-4-amine (18): Known compound,[15] white solid, 2.266g, 90% yield, **^{1}H NMR** (400 MHz, DMSO-d^6) δ 9.85 (s, 1H), 8.95 (s, 1H), 8.61 (s, 1H), 8.13 – 8.08 (m, 1H), 8.03 (d, J = 2.6 Hz, 1H), 7.75 (dd, J = 9.0, 2.6 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.51 – 7.44 (m, 1H), 7.36 – 7.25 (m, 3H), 7.19 (td, J = 8.8, 2.4 Hz, 1H), 5.26 (s, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 162.66 (d, J = 243.7 Hz), 156.76, 155.26, 150.20, 149.19, 141.77, 140.09 (d, J = 7.5 Hz), 133.43, 131.81, 131.00 (d, J = 8.3 Hz), 130.24, 124.40, 123.76 (d, J = 2.4 Hz), 122.56, 121.51, 117.27, 115.15 (d, J = 20.9 Hz), 114.72, 114.48 (d, J = 21.9 Hz), 92.00, 69.86; **^{19}F NMR** (375 MHz, DMSO-d^6) δ -112.95. **HRMS** calculated for $C_{21}H_{15}ClFIN_3O$ $[M+H]^+$ 505.9927, found 505.9932.



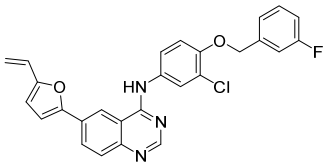
18 **19**

To a round bottle, dichloroethane (30 mL), methanol (15 mL), compound **18** (1.01g, 2 mmol), 5-formyl-furan-2-boronic acid (0.42g, 3.0 mmol), palladium on carbon (5%, 0.13g), triethylamine (1.11 mL, 8.0 mmol) were added, and were heated to 50 ºC and stirred for 16 h. Palladium on carbon was filtered off through celite, and the filtrate was concentrated, the residue was added ethyl acetate (120 mL), tetrahydrofuran (60 mL), water (20 mL) and saturated aqueous sodium bicarbonate (20 mL), stirred for 15 minutes. The organic layer was washed with saturated brine, dried over anhydrous sodium sulfate, concentrated, and dried in vacuo to give an orange solid **19** with 95% yield**.** The analytical data matches with reported values.[16]

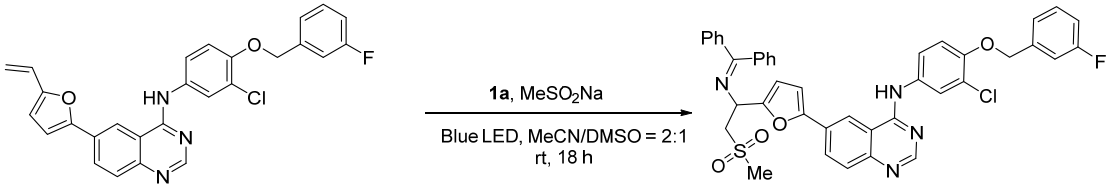


19 **20**

To a flame-dried round-bottom flask, methyltriphenylphosphonium bromide (6.0 mmol) in THF (40 mL) was added ^{n}BuLi (2.4 mL, 2.5 M in THF, 6.0 mmol) slowly at 0 ºC under N_2. After stirring for 20 min, compound **19** (5.0 mmol) was added. The reaction mixture was then warmed to room temperature and stirred for another 12 hours. After the starting material was consumed completely which was detected by TLC, the reaction mixture was quenched with sat. NH_4Cl aq. (15 mL) and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over Na_2SO_4, concentrated in vacuo and purified by flash chromatography on silica gel using DCM and ethyl acetate to afford the alkene product.

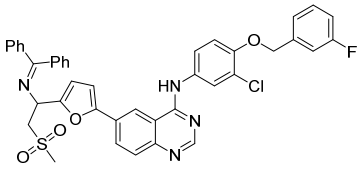


N-(3-Chloro-4-((3-fluorobenzyl)oxy)phenyl)-6-(5-vinylfuran-2-yl)quinazolin-4-amine (20): according to the step 2, yellow solid, melting point: 152 – 153 ºC, 186.6 mg, 79% yield, R_f = 0.5 (DCM/EA = 9/1), **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.70 (s, 1H), 8.11 (s, 1H), 8.06 – 8.01 (m, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.83 – 7.78 (m, 1H), 7.61 (s, 1H), 7.52 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.35 (td, *J* = 8.0, 6.0 Hz, 1H), 7.22 (t, *J* = 9.2 Hz, 2H), 7.02 (td, *J* = 8.3, 7.7, 2.0 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 6.77 (d, *J* = 3.4 Hz, 1H), 6.55 (dd, *J* = 17.5, 11.3 Hz, 1H), 6.40 (d, *J* = 3.4 Hz, 1H), 5.80 (d, *J* = 17.5 Hz, 1H), 5.25 (d, *J* = 11.3 Hz, 1H), 5.13 (s, 2H). **^{13}C NMR** (175 MHz, Chloroform-*d*) δ 163.00 (d, *J* = 246.3 Hz), 157.60, 154.67, 153.69, 151.86, 151.23, 149.36, 139.01 (d, *J* = 7.4 Hz), 132.00, 130.18 (d, *J* = 8.2 Hz), 129.32, 129.22, 125.07, 124.77, 123.59, 122.43 (d, *J* = 2.7 Hz), 122.15, 115.19, 114.93 (d, *J* = 21.1 Hz), 114.33, 114.18, 113.97 (d, *J* = 22.2 Hz), 113.29, 110.60, 108.62, 70.39; **^{19}F NMR** (375 MHz, Chloroform-*d*) δ -112.58. **HRMS** calculated for $C_{27}H_{20}ClFN_3O_2$ $[M+H]^+$ 472.1223, found 472.1226.



20 **21, Lapatinib analogue**

In a glove box, a sealed tube was charged with O-aryl oxime **1a** (0.12 mmol), alkene **20** (0.05 mmol), $MeSO_2Na$ (0.10 mmol), MeCN (0.67 mL), DMSO (0.33 mL) at room temperature. The reaction tube was sealed with a Teflon screw cap, removed from the glove box. Then, the reaction mixture was stirred at rt under Blue LED for 18 hours. And the crude reaction mixture was purified by column chromatography on silica gel using MeOH and DCM to afford the corresponding product**.**



N-(3-Chloro-4-((3-fluorobenzyl)oxy)phenyl)-6-(5-(1-((diphenylmethylene)amino)-2-(methylsulfonyl)ethyl)furan-2-yl)quinazolin-4-amine (21): yellow solid, melting point: 152 – 153 ºC, 21.1 mg, 18.8 mg (accompanied by a small amount of petroleum ether, the yield of the product has been adjusted accordingly) , 52% yield, R_f = 0.5 (DCM/MeOH = 15/1), **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.61 (s, 1H), 8.21 (s, 1H), 7.94 – 7.77 (m, 3H), 7.68 (d, *J* = 7.5 Hz, 2H), 7.55 (d, *J* = 10.7 Hz, 1H), 7.50 – 39 (m, 4H), 7.37 – 7.32 (m, 3H), 7.22 – 7.15 (m, 4H), 7.06 – 6.83 (m, 3H), 6.70 (d, *J* = 3.0 Hz, 1H), 6.15 (d, *J* = 3.0 Hz, 1H), 5.27 (dd, *J* = 9.6, 2.8 Hz, 1H), 5.09 (s, 2H), 3.99 (dd, *J* = 14.3, 9.8 Hz, 1H), 3.66 (d, *J* = 13.9 Hz, 1H), 2.95 (s, 3H); **^{13}C NMR** (175 MHz, Chloroform-*d*) δ 196.86, 172.59, 163.01 (d, *J* = 246.4 Hz), 157.70, 154.83, 153.12, 152.37, 151.18, 149.40, 139.05 (d, *J* = 7.3 Hz), 138.62, 137.58, 135.45, 132.45, 132.10, 131.17, 130.20 (d, *J* = 8.2 Hz), 130.07, 129.29, 129.06, 128.93, 128.78, 128.61, 128.57, 128.40, 128.29, 127.48, 125.12, 123.52, 122.46 (d, *J* = 2.7 Hz), 122.25, 115.24, 114.94 (d, *J* = 21.1 Hz), 114.59, 114.32, 114.00 (d, *J* = 22.2 Hz), 109.53, 107.43, 70.40, 59.96, 56.11, 43.37; **^{19}F NMR** (375 MHz, Chloroform-*d*) δ -112.57. **HRMS** calculated for $C_{41}H_{32}ClFN_4O_4S$ $[M+H]^+$ 731.1890, found 731.1904.

9. Mechanistic studies

9.1 UV-vis absorption experiments

UV−vis spectroscopic measurements were performed in MeCN/DMSO= 9:1 at 6.7 × 10^{-3} M concentration for each species.

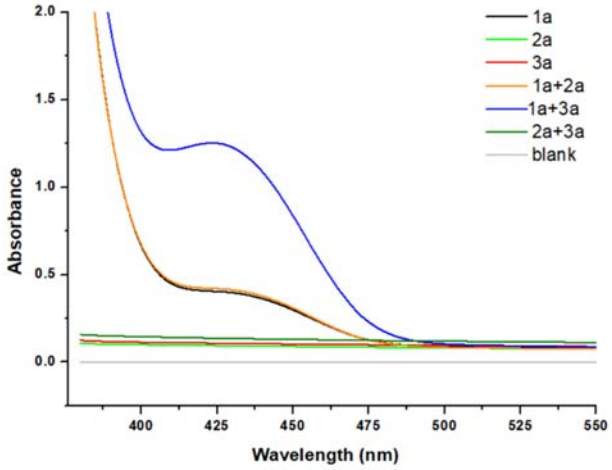
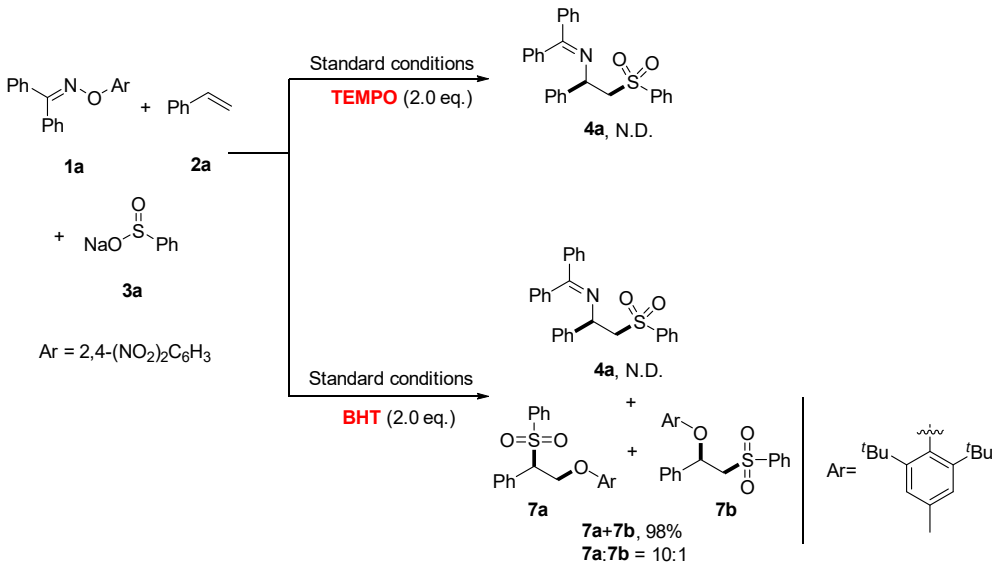


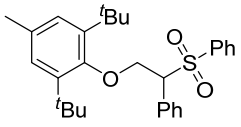
Figure S1. UV-vis absorption spectra of 1a, 2a, 3a and combinations of them

9.2 Radical inhibition and capture experiment



In a glove box, an oven-dried 4 mL vial was charged with O-aryl oxime **1a** (0.12 mmol), alkene **2a** (0.10 mmol), sodium sulfinate **3a** (0.18 mmol), radical scavenger TEMPO or BHT (0.20 mmol, 2.0 equiv.), MeCN (0.9 mL) and DMSO (0.1 mL) at room temperature. The reaction tube was sealed with a Teflon screw cap, removed from the glove box. Then, the reaction mixture was stirred at rt under Blue LED for 18 hours. And the crude reaction mixture was purified by column chromatography on silica gel using petroleum ether and ethyl acetate failed to afford the corresponding product **4a**, and in the presence of BHT, sulfonyletherification of olefin (**7a**:**7b** = 10:1) was formed mainly. The adduct was

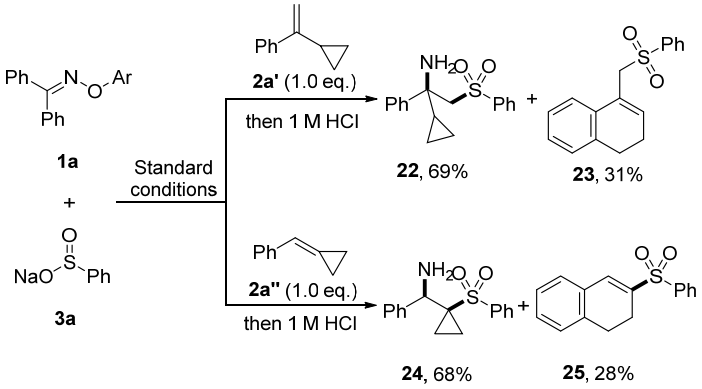
confirmed by NMR.



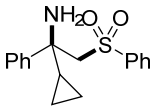
7a

1,3-*di-tert*-Butyl-5-methyl-2-(2-phenyl-2-(phenylsulfonyl)ethoxy)benzene (7a): colorless oil, (**7a**+**7b**) = 45.7 mg, 98% yield, R_f = 0.5 (PE/EA = 9/1), **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.55 – 7.51 (m, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.32 – 7.24 (m, 2H), 7.18 – 7.04 (m, 3H), 6.92 – 6.83 (m, 2H), 6.46 (d, *J* = 3.0 Hz, 1H), 6.35 (d, *J* = 3.0 Hz, 1H), 3.46 (dd, *J* = 14.3, 10.6 Hz, 1H), 3.35 – 3.21 (m, 1H), 3.25 (dd, *J* = 14.4, 1.6 Hz, 1H), 1.25 (s, 9H), 1.13 (s, 9H), 1.05 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 185.55, 148.74, 147.77, 144.19, 142.37, 139.14, 136.55, 133.27, 128.89, 128.05, 127.80, 127.51, 57.45, 49.57, 42.70, 34.97, 34.95, 29.42, 29.37, 24.90. **HRMS** calculated for $C_{29}H_{36}NaO_3S$ $[M+Na]^+$ 487.2277, found 487.2294.

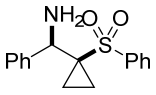
9.3 Radical clock experiment



In a glove box, an oven-dried 4 mL vial was charged with O-aryl oxime **1a** (0.12 mmol), alkene **2a'** or **2a''** (0.10 mmol), sodium sulfinate **3a** (0.18 mmol), MeCN (0.9 mL) and DMSO (0.1 mL) at room temperature. The reaction tube was sealed with a Teflon screw cap, removed from the glove box. Then, the reaction mixture was stirred at rt under Blue LED for 18 hours. And the crude reaction mixture was purified by column chromatography on silica gel using petroleum ether and ethyl acetate to afford the mixture. Then the product mixture was acidic hydrolysis with 1M hydrochloric acid and then adjusted to PH = 13 by 1M sodium hydroxide. And the crude mixture was purified by column chromatography on silica gel using petroleum ether and ethyl acetate to afford the corresponding products.

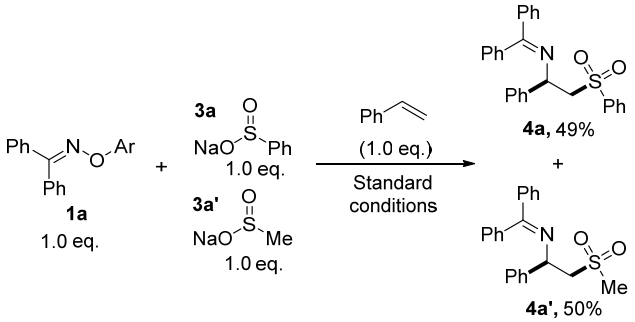


1-Cyclopropyl-1-phenyl-2-(phenylsulfonyl)ethan-1-amine (22): Prepared according to the general procedure, colorless oil, 20.7 mg, 69% yield, R_f = 0.15 (PE/EA = 2/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.69 – 7.60 (m, 2H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 4H), 7.22 – 7.13 (m, 3H), 3.79 (d, *J* = 14.5 Hz, 1H), 3.64 (d, *J* = 14.5 Hz, 1H), 2.13 (s, 2H), 1.49 – 1.40 (m, 1H), 0.61 – 0.51 (m, 2H), 0.40 (tt, *J* = 8.7, 5.6 Hz, 1H), 0.22 (ddd, *J* = 11.7, 9.4, 5.6 Hz, 1H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 141.54, 138.75, 130.72, 126.57, 125.67, 125.11, 124.68, 123.49, 65.38, 54.53, 19.85, -0.00, -1.24. **HRMS** calculated for $C_{17}H_{20}NO_2S$ $[M+H]^+$ 302.1209, found 302.1212.

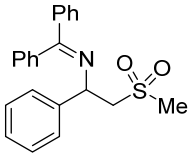


Phenyl(1-(phenylsulfonyl)cyclopropyl)methanamine (24): Prepared according to the general procedure, colorless oil, 19.5 mg, 68% yield, R_f = 0.12 (PE/EA = 2/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.96 – 7.84 (m, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 2H), 7.22 – 7.14 (m, 3H), 6.94 (dd, *J* = 6.6, 2.9 Hz, 2H), 4.68 (s, 1H), 2.08 (s, 2H), 1.88 – 1.59 (m, 1H), 1.38 (ddd, *J* = 10.6, 7.5, 5.2 Hz, 1H), 1.17 (ddd, *J* = 9.4, 7.6, 5.5 Hz, 1H), 0.29 (ddd, *J* = 9.5, 6.8, 5.3 Hz, 1H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 139.70, 138.90, 133.58, 129.21, 128.70, 128.36, 127.86, 126.87, 53.26, 47.79, 13.84, 6.78. **HRMS** calculated for $C_{16}H_{18}NO_2S$ $[M+H]^+$ 288.1053, found 288.1058.

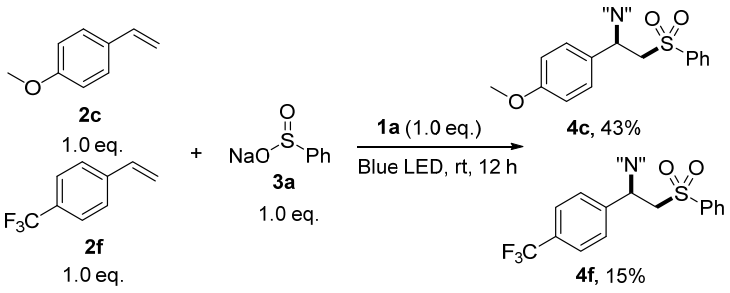
9.4 Competition experiment



In a glove box, an oven-dried 4 mL vial was charged with O-aryl oxime **1a** (0.10 mmol), styrene (0.10 mmol), sodium sulfinate **3a** (0.10 mmol), **3a'** (0.10 mmol), MeCN (0.9 mL) and DMSO (0.1 mL) at room temperature. The reaction tube was sealed with a Teflon screw cap, removed from the glove box. Then, the reaction mixture was stirred at rt under Blue LED for 18 hours. And the crude reaction mixture was purified by column chromatography on silica gel using petroleum ether and ethyl acetate to afford the corresponding products **4a** with 49% yield and **4a'** with 50% yield.



N-(2-(Methylsulfonyl)-1-phenylethyl)-1,1-diphenylmethanimine (4a'): colorless oil, 19.0 mg, corrected weight: 18.2 mg (accompanied by a small amount of inseparable alkenyl sulfone compound, the yield of the product has been adjusted accordingly), 50% yield, R_f = 0.12 (PE/EA = 9/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 7.3 Hz, 2H), 7.46 – 7.32 (m, 6H), 7.29 – 7.21 (m, 3H), 7.14 (d, *J* = 7.5 Hz, 2H), 7.04 – 6.95 (m, 2H), 5.05 (dd, *J* = 10.0, 2.9 Hz, 1H), 3.91 (t, *J* = 11.6 Hz, 1H), 3.34 – 3.24 (m, 1H), 2.89 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 141.63, 138.86, 135.93, 130.71, 128.80, 128.73, 128.55, 128.39, 128.27, 127.74, 127.42, 126.93, 63.27, 61.61, 43.19. **HRMS** calculated for $C_{22}H_{22}NO_2S$ $[M+H]^+$ 364.1366, found 364.1368.



In a glove box, an oven-dried 4 mL vial was charged with O-aryl oxime **1a** (0.10 mmol), sodium

sulfinate **3a** (0.10 mmol), alkene **2c** (0.10 mmol), **2f** (0.10 mmol), MeCN (0.9 mL) and DMSO (0.1 mL) at room temperature. The reaction tube was sealed with a Teflon screw cap, removed from the glove box. Then, the reaction mixture was stirred at rt under Blue LED for 12 hours. The yields were determined by ^{1}H NMR spectroscopy using mesitylene as the internal standard.

9.5 Determination of the binding ratio by Job's Plot

Job's plot was performed according to the literature method.[17] O-aryl oxime **1a** (0.125 mmol) was dissolved in DMSO-*d6* (3.0 mL) to give a stock solution at 0.042 mol/L concentration. Similarly, sodium benzosulfonate **3a** (0.125 mmol) was added to DMSO-*d6* (3.0 mL) solution to provide a 0.042 mol/L solution. Then, the solutions of **1a** and **3a** were added to the NMR tube based on the specific ratio in Table S11. The ^{1}H(Ar-H) chemical shift of free **1a** solution (0.042 mol/L) is 8.1946 ppm. The job's plot had a maximum when X (**1a**) equals to 0.5, suggesting that the binding stoichiometry between **1a** and **3a** is 1:1.

Table S11. ^{1}H NMR experimental data for Job's plot

Entry	V (**1a**, mL)	V (**3a**, mL)	X (**1a**)	δ(^{1}H(Ar-H), ppm)	Δδ(ppm)	Δδ*X (**1a**)*10^{-3}
1	0.45	0.05	0.9	8.1965	0.0019	1.71
2	0.40	0.10	0.8	8.1974	0.0028	2.24
3	0.35	0.15	0.7	8.1989	0.0043	3.01
4	0.30	0.20	0.6	8.1998	0.0052	3.12
5	0.25	0.25	0.5	8.2013	0.0067	3.35
6	0.20	0.30	0.4	8.2027	0.0081	3.24
7	0.15	0.35	0.3	8.2036	0.0090	2.70
8	0.10	0.40	0.2	8.2048	0.0102	2.04
9	0.05	0.45	0.1	8.2059	0.0113	1.13

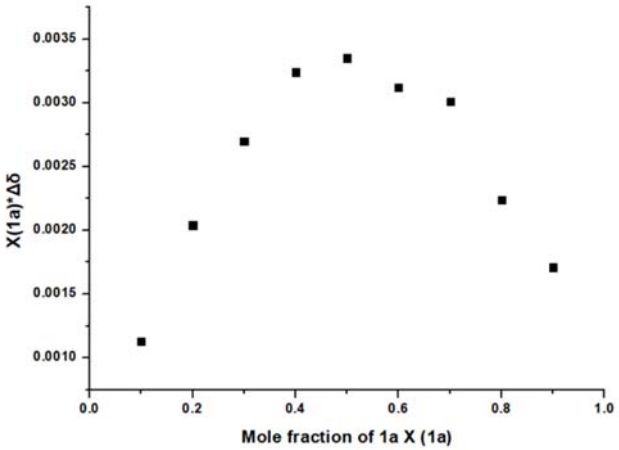


Figure S2. Job's plot for the determination of binding stoichiometry between 1a and 3a

9.6 ^{1}H NMR Titrations of 1a with 3a

1a (0.03 mmol, 10.9 mg) and **3a** were thoroughly mixed in DMSO-*d6* (0.5 mL), then the resulted mixture was injected into an NMR tube. The ^{1}H NMR (400 MHz, DMSO-*d6*, 25 °C) spectra of the $6.0*10^{-2}$ M DMSO-*d6* solution of **1a** with increasing concentration of **3a** (corresponding concentration from bottom to top is 0.0, $1.5*10^{-2}$, $3.0*10^{-2}$, $6.0*10^{-2}$, $9.0*10^{-2}$, $1.2*10^{-1}$, $3.0*10^{-1}$, were recorded and shown in Figure S3.

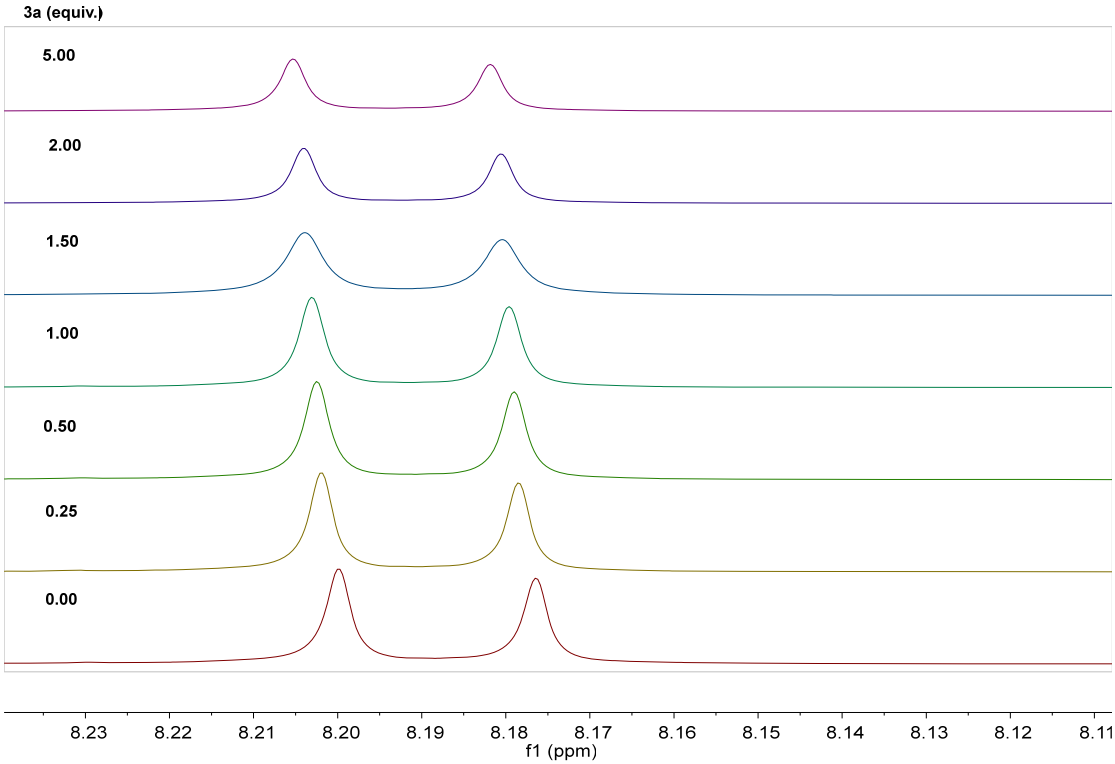


Figure S3. ^{1}H NMR spectra of 1a ($6.0*10^{-2}$ M) titrated with increasing equivalents of 3a (0-5 equiv.) in DMSO-*d6* (400 MHz, 298 K).

9.7 Determination of the association constant of the EDA complex

The association constant of the EDA complex formed between **1a** and **3a** was determined via UV/vis spectroscopy using the Benesi-Hildebrand methodology.[18] The absorbance of a constant concentration of **3a** ($2.9*10^{-3}$ M in DMSO) with increasing amounts of **1a** (M = $1.4*10^{-3}$, $2.9*10^{-3}$, $4.3*10^{-3}$, $5.7*10^{-3}$, $7.1*10^{-3}$, $1.1*10^{-2}$) was recorded at 430 nm. Plotting the reciprocal concentration of **1a** against the reciprocal of the absorbance ΔA (with $\Delta A = A - A_0$) resulted in a straight line, the intercept of which was divided by its slope to obtain the association constant (K_{EDA} = 3.65 M^{-1})

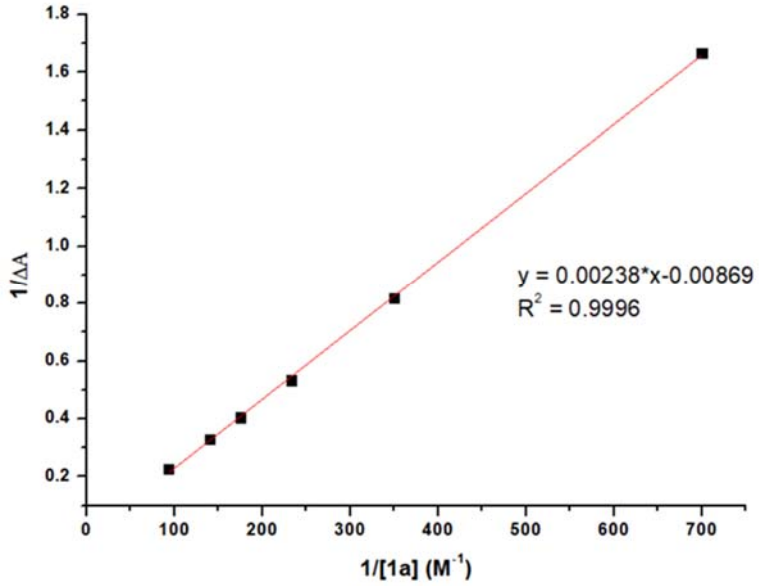


Figure S4. Benesi-Hildebrand plot for a solution of 3a in DMSO ($2.9*10^{-3}$ M) with increasing amounts of 1a recorded at 430 nm.

9.8 Theoretical calculations

The geometry optimizations were performed with the Gaussian 16[22] using B3LYP[19]/def2svp[20] method in the gas phase at room temperature. Gas-phase Hessian matrix calculations were applied to the characterization of all minima (without imaginary frequency) and transition states (with only one imaginary frequency). Thermochemical parameters such as internal energy, enthalpy, entropy, Gibbs free energy and thermal corrections (entropy and enthalpy, 298.15 K (room temperature), 1 atm) were obtained from these calculations. To further improve the accuracy of energies, single point energies were carried out using the B3LYP-D3[21]/def2tzvp[22] method, with SMD[23] solvation model (in acetonitrile). The 3D diagrams of optimized structures were generated with CYLview[23] software. Multiwfn[24] software package was used to plot isosurface map of spin density and it was further visualized by VMD.[25] Distances in structural figures are shown in Å and energies are in kcal/mol.

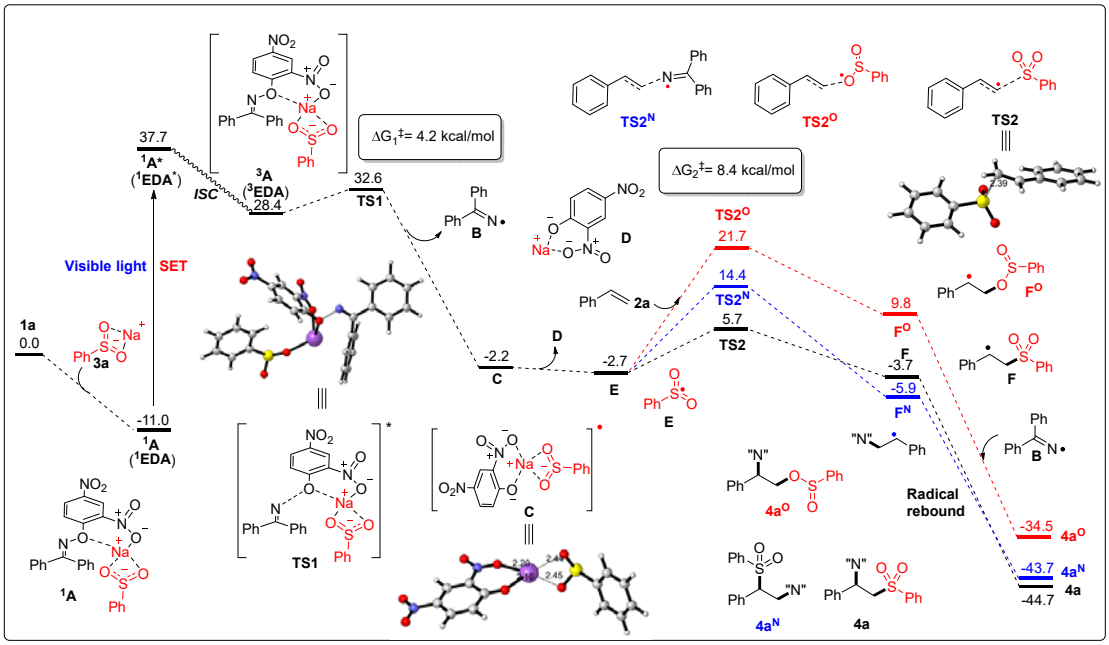
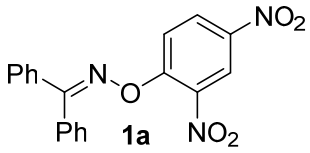


Figure S5. Calculated energy diagram for possible mechanism

Cartesian coordinates (xyz format) and energies of all the structures involved in each reaction mechanism studied calculated at the B3LYP/Def2TZVP-SMD(Acetonitrile)//B3LYP/def2svp level of theory



Cartesian Coordinates:

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C	0.30835000	-0.25234600	-0.06670400	H	-1.51632900	-6.21005100	0.60090700
C	0.88022800	0.98815900	0.27830800	N	2.36486500	-1.37490000	0.08865900
C	0.16553200	2.17071300	0.09714900	O	3.03885100	-2.57870700	0.38703200
C	-1.13058400	2.13779900	-0.43083900	C	4.35326900	-2.54731900	0.09508000
C	-1.70705500	0.91286600	-0.77650700	C	4.92078400	-1.93265200	-1.04268700
H	-1.44983900	-1.22632200	-0.87693500	C	5.21013500	-3.18300700	1.01115300
H	1.88916500	1.00857300	0.69251000	C	6.30203800	-1.88751000	-1.21865600
H	0.61990100	3.12540100	0.37364600	C	6.58549100	-3.18538900	0.82153900
H	-1.69000700	3.06636300	-0.56996700	H	4.75736200	-3.65158600	1.88650800
H	-2.71619300	0.87967000	-1.19449900	C	7.11824400	-2.51981100	-0.28738000
C	1.08261900	-1.51328500	0.09482500	H	6.73185600	-1.38604000	-2.08442800
C	0.37162700	-2.81689000	0.23897700	H	7.25988200	-3.66945300	1.52739200
C	0.66016100	-3.88499500	-0.62891000	N	4.09985100	-1.41136300	-2.15008600
C	-0.60678900	-2.98296900	1.23349100	O	4.49289300	-0.40541700	-2.71047200
C	-0.02415300	-5.09481700	-0.50115900	O	3.12020800	-2.06487500	-2.47101300
H	1.41472300	-3.75401100	-1.40648000	N	8.57933000	-2.49145600	-0.48197400
C	-1.27473600	-4.20235000	1.36930400	O	9.26560600	-3.06364200	0.34947000
H	-0.84026200	-2.15496500	1.90697400	O	9.00583800	-1.89910100	-1.45926700
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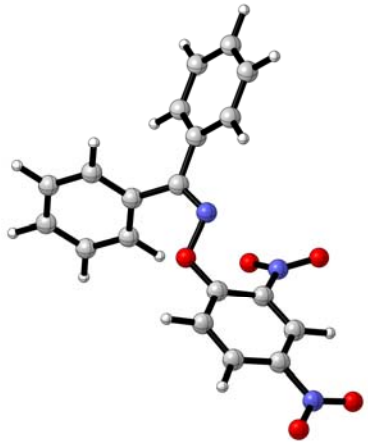

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

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H_corr: 0.316017 Hartree

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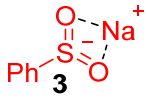
S: 161.54 Cal/Mol-Kelvin

H: -1272.260967 Hartree

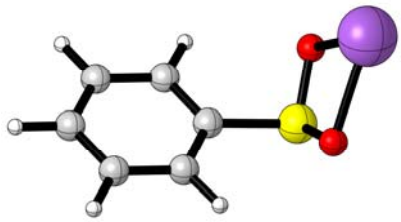
G: -1272.33772 Hartree



3

Cartesian Coordinates:

C	-2.68670000	0.09781800	0.27484700	H	-0.88448100	-1.04469000	0.71036700
C	-1.30818100	-0.07636300	0.43373800	H	-0.25314200	3.07366600	-0.35316400
C	-0.45052100	1.00457100	0.21048900	H	-2.73098400	3.39263000	-0.62651200
C	-0.95097100	2.25363600	-0.16795800	H	-4.27602200	1.47912600	-0.22285700
C	-2.33057700	2.42070700	-0.32499100	S	1.35387800	0.79928600	0.48729400
C	-3.19781200	1.34529700	-0.10103200	O	1.95098800	1.72916500	-0.60966100
H	-3.36509400	-0.74353700	0.44151900	O	1.58338900	-0.66487000	0.00946900
Na	2.50353000	0.01666000	-1.85574900				



Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

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H_corr: 0.109669 Hartree

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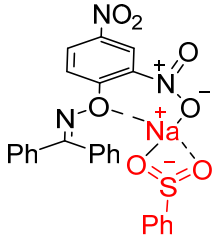
S: 96.638 Cal/Mol-Kelvin

H: -942.767708 Hartree

G: -942.813623 Hartree



^{1}A/^{1}A*

Cartesian Coordinates:

C	3.38286900	-2.08237200	3.53031000	C	3.74688700	-1.84508800	4.85848400
C	4.28758700	-1.82806700	2.48359400	H	2.38564200	-2.46487100	3.30827300
C	5.56617300	-1.32392100	2.80105300	H	6.27094900	-1.11670100	1.99530000
C	5.92480000	-1.09091300	4.12564400	H	6.92019200	-0.70325100	4.35596400
C	5.01707700	-1.35120300	5.16083600	H	5.30224000	-1.16740200	6.19966900

H	3.03116300	-2.04779100	5.65876800
C	3.89395900	-2.07454200	1.07122800
C	2.57365400	-2.71354500	0.76579900
C	1.50628500	-1.95366600	0.25897700
C	2.40805500	-4.09609400	0.96145100
C	0.28942200	-2.56983800	-0.05175600
H	1.63297900	-0.88143700	0.09486800
C	1.19088800	-4.70887900	0.64330900
H	3.24529600	-4.69704900	1.32106900
C	0.13016700	-3.94779500	0.13746900
H	-0.53264600	-1.97221000	-0.45232600
H	1.07885400	-5.78729900	0.77497200
H	-0.81641200	-4.43029200	-0.11678700
N	4.73961700	-1.72139000	0.16511100
O	4.26155800	-1.95161200	-1.13568400
C	5.22721100	-1.94255100	-2.08314300
C	4.86033100	-1.70977700	-3.43109500
C	6.58418000	-2.15015500	-1.78588200
C	5.81562800	-1.68809000	-4.44703300
C	7.53523700	-2.14855500	-2.79496400
H	6.86411700	-2.33933500	-0.75254000
C	7.14124000	-1.92328500	-4.11805800
H	5.52122600	-1.50518000	-5.47861100
H	8.58651800	-2.33886200	-2.58056000
N	3.47040900	-1.48427400	-3.83439400
O	2.58004100	-2.04122400	-3.19022700
O	3.26745500	-0.77327300	-4.79599200
N	8.14719700	-1.96390500	-5.19249100
O	9.29581100	-2.22832400	-4.87336900
O	7.76864600	-1.73501500	-6.32882000
Na	2.65661200	-3.92141400	-1.88172100
O	2.80295600	-5.87303700	-2.94992400
O	4.64640800	-4.97756900	-1.51704100
S	4.23124600	-6.16958600	-2.42530200
C	5.26092900	-5.85560600	-3.92339500
C	6.64161700	-5.68252300	-3.77878600
C	4.66575200	-5.82001200	-5.18571700
C	7.43182000	-5.45736000	-4.91022400
H	7.08714400	-5.70574600	-2.78071700
C	5.45981000	-5.58697400	-6.31523300
H	3.58475700	-5.96253600	-5.25881400
C	6.84009200	-5.40402000	-6.17902700
H	8.51012500	-5.30881700	-4.80485200
H	4.99947500	-5.54846900	-7.30656500
H	7.45785700	-5.21809700	-7.06129900

^{1}A

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 0.322605 Hartree

H_corr: 0.427751 Hartree

SCF: -2215.491484 Hartree

S: 221.296 Cal/Mol-Kelvin

H: -2215.063733 Hartree

G: -2215.168879 Hartree

^{1}A*

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 0.322605 Hartree

H_corr: 0.427751 Hartree

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S: 221.296 Cal/Mol-Kelvin

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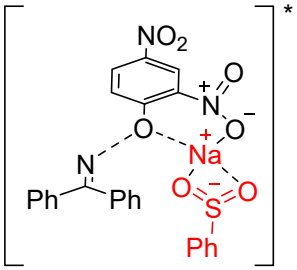
G: -2215.091337 Hartree



TS1

Cartesian Coordinates:

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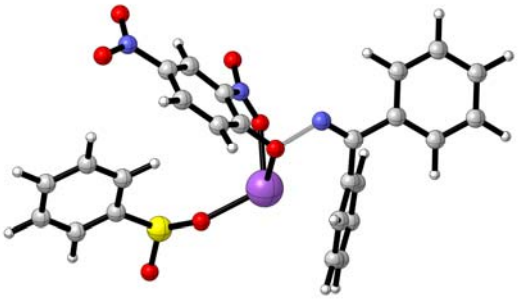
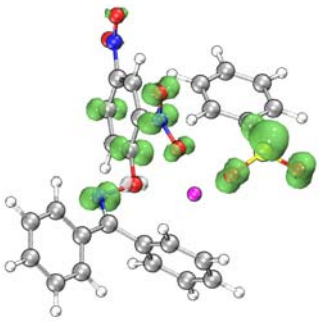
C	2.02375200	0.69405700	2.04199800	H	3.78510400	-0.97450000	-3.46159400
C	1.88647100	1.58327000	3.10629600	C	6.16867900	-3.10047000	-2.27421400
C	0.65331700	2.19639600	3.36022000	H	5.97587200	-4.36851100	-0.54622300
C	-0.44400100	1.91165700	2.54348700	H	6.13875800	-1.72727600	-3.95999700
H	-1.17573700	0.80272900	0.84393900	N	3.47457500	-4.01805100	0.05581800
H	2.98043100	0.21033200	1.83819500	O	2.20795800	-4.08418800	0.01558700
H	2.74586400	1.79660900	3.74683600	O	4.12484700	-4.60206300	0.92760200
H	0.54849800	2.89209300	4.19661300	N	7.50212700	-3.59312300	-2.58322200
H	-1.40903200	2.38757300	2.73519300	O	7.94707600	-3.34200500	-3.70569400
C	1.08188300	-0.53072300	0.05379000	O	8.10386500	-4.23813300	-1.73395000
C	-0.12911900	-1.25117700	-0.46627300	Na	0.82849100	-3.62609000	-1.60195800
C	-0.78783700	-2.18756500	0.34962200	O	0.40186800	-7.01704000	-4.72246600
C	-0.58288200	-1.04647900	-1.78097100	O	1.14632800	-4.94300300	-3.37672400
C	-1.86531700	-2.92803400	-0.15223900	S	1.43577800	-6.31345500	-3.92163400
H	-0.43713900	-2.35366200	1.37050000	C	2.96049100	-6.22743100	-4.88812600
C	-1.66882400	-1.77737900	-2.27561300	C	3.94843700	-5.30422700	-4.53035400
H	-0.06626900	-0.32740300	-2.41950600	C	3.13824200	-7.16980800	-5.90728800
C	-2.30745600	-2.72573000	-1.46578800	C	5.14996300	-5.31232900	-5.24504900
H	-2.35975500	-3.66436400	0.48611700	H	3.78516800	-4.58530100	-3.72624800
H	-2.01290100	-1.61144400	-3.29939300	C	4.34341100	-7.15698400	-6.61134500
H	-3.14966800	-3.30198000	-1.85630000	H	2.34502800	-7.87919100	-6.14813200
N	2.25746000	-0.66815100	-0.42211300	C	5.34443400	-6.23635100	-6.27807800
O	2.27003600	-1.85921200	-1.60608500	H	5.93825300	-4.60072200	-4.98663900
C	3.50776200	-2.30868300	-1.80737100	H	4.50062700	-7.87166800	-7.42253400
C	4.15212800	-3.28843000	-0.95791600	H	6.29008800	-6.24070300	-6.82527300
C	4.27333100	-1.74329100	-2.85861300				





Spin Density Plot

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

Imaginary Frequency: -666.2351 cm-1

G_corr: 0.316432 Hartree

H_corr: 0.423631 Hartree

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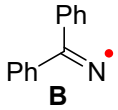
S: 225.618 Cal/Mol-Kelvin

H: -2214.992124 Hartree

G: -2215.099323 Hartree



Cartesian Coordinates:

C	-1.05769000	-0.31611700	-0.50529700	C	0.34431900	-3.02033300	0.10521700
C	0.21549400	-0.65159100	-0.99613600	C	0.86062800	-3.68640300	1.23078800
C	0.77242000	0.11268400	-2.03674300	C	-0.75601500	-3.57193100	-0.57254600
C	0.06503800	1.18591600	-2.57993800	C	0.28140900	-4.87642400	1.67310300
C	-1.20263200	1.51400200	-2.08736500	H	1.71582600	-3.25590000	1.75555000
C	-1.76013600	0.76259400	-1.04836700	C	-1.32938300	-4.76651600	-0.12953500
H	-1.49529400	-0.89500500	0.31074900	H	-1.15800300	-3.06988500	-1.45508000
H	1.76191800	-0.14987000	-2.41626600	C	-0.81466500	-5.41977900	0.99439200
H	0.50426200	1.76855100	-3.39367800	H	0.68606000	-5.38193700	2.55359700
H	-1.75628300	2.35425900	-2.51407500	H	-2.18201000	-5.18947800	-0.66690700
H	-2.74779500	1.01790100	-0.65595200	H	-1.26819200	-6.35144800	1.34217700
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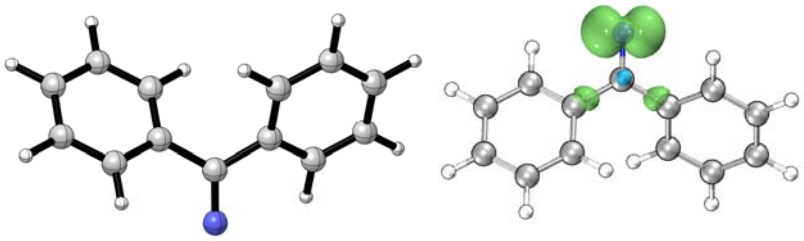

Spin Density Plot

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Pressure: 1.0 Atm

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H_corr: 0.202508 Hartree

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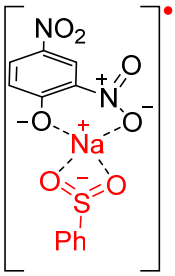
S: 106.389 Cal/Mol-Kelvin

H: -556.16712 Hartree

G: -556.217669 Hartree



C

Cartesian Coordinates:

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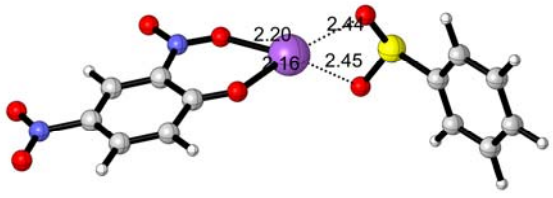
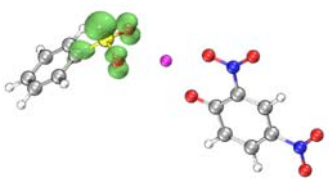
C	5.86980500	-2.88267100	-0.39343500	O	1.38828700	-4.07270100	-3.10018100
C	6.07115000	-3.94508600	0.59559000	O	3.30984900	-5.20457200	-4.28783800
C	6.80495200	-1.77460300	-0.28300900	S	1.85558300	-4.80337500	-4.33620700
C	7.07995800	-3.87268900	1.55848500	C	1.66459100	-3.65656000	-5.73416800
C	7.79614700	-1.71743600	0.66284200	C	2.50399700	-3.80739400	-6.84079900
H	6.66970100	-0.97319100	-1.01210400	C	0.63880000	-2.70921000	-5.68664000
C	7.93118000	-2.77812800	1.58865700	C	2.31930500	-2.95169500	-7.92969300
H	7.19952600	-4.67547300	2.28316900	H	3.29404600	-4.56054000	-6.83617900
H	8.48702600	-0.87647400	0.72468000	C	0.47108800	-1.86359400	-6.78610400
N	5.23339700	-5.12883800	0.64581400	H	0.00587200	-2.62448200	-4.80142600
O	4.39413900	-5.31812400	-0.24873100	C	1.30596100	-1.98663900	-7.90272200
O	5.37980200	-5.91422000	1.56618700	H	2.97319800	-3.03810200	-8.80063300
N	8.98750100	-2.72444200	2.59883100	H	-0.31322500	-1.10327800	-6.76721400
O	9.71838200	-1.74227800	2.59729300	H	1.16583200	-1.32375600	-8.75990500
O	9.07928200	-3.65885600	3.38265600				





Spin Density Plot

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 0.138673 Hartree

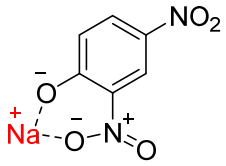
H_corr: 0.220553 Hartree

SCF: -1659.075868 Hartree

S: 172.332 Cal/Mol-Kelvin

H: -1658.855315 Hartree

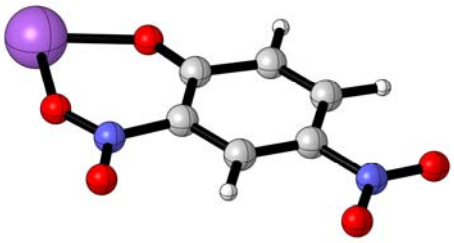
G: -1658.937195 Hartree



D

Cartesian Coordinates:

O	3.02263100	-3.24654100	-0.84804900	H	6.89763800	-1.19176200	-1.84984300
C	4.27682300	-3.17369500	-0.71262100	N	4.56990900	-5.15362000	0.86917800
C	5.10818800	-4.05887400	0.10178200	O	3.33769800	-5.37343700	0.85730300
C	5.01251300	-2.13550200	-1.40604500	O	5.32112400	-5.85554300	1.52347600
C	6.50178700	-3.89281800	0.18616100	N	8.56964100	-2.71660700	-0.40957000
C	6.37107900	-1.98326100	-1.31614200	O	9.08122100	-1.80101700	-1.04213700
H	4.40884500	-1.46380700	-2.01989100	O	9.18819100	-3.50201700	0.29545400
C	7.12027500	-2.87499900	-0.50906800	Na	1.58923000	-4.54443400	-0.05151400
H	7.09160800	-4.56886700	0.80122700				



Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 0.059863 Hartree

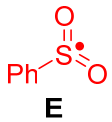
H_corr: 0.112209 Hartree

SCF: -878.606786 Hartree

S: 110.171 Cal/Mol-Kelvin

H: -878.494577 Hartree

G: -878.546923 Hartree

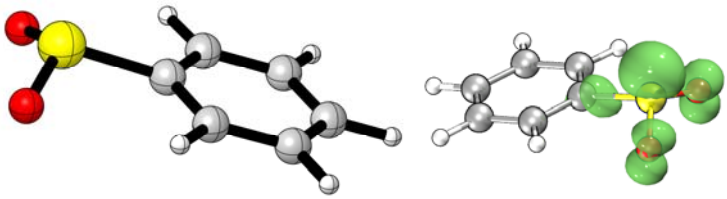


E

Cartesian Coordinates:

O	1.01442900	-5.17918600	-3.30229400	C	1.66490500	-2.95240200	-5.19516100
O	3.56825400	-5.47957100	-2.88594000	C	4.30923600	-2.05409600	-5.51033000
S	2.41774600	-5.22911100	-3.79714000	H	4.87767100	-3.81666700	-4.36588800
C	2.74239200	-3.65852400	-4.65536800	C	1.92755300	-1.77218300	-5.89550900
C	4.06522600	-3.23653100	-4.80698900	H	0.64605900	-3.31591500	-5.05028000

C	3.24459000	-1.32628700	-6.05376000	H	1.09887600	-1.19732100	-6.31596900
H	5.33550700	-1.69887300	-5.63090000	H	3.44285700	-0.40343500	-6.60437300



Spin Density Plot

Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 0.064891 Hartree

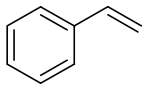
H_corr: 0.107098 Hartree

SCF: -780.455953 Hartree

S: 88.833 Cal/Mol-Kelvin

H: -780.348855 Hartree

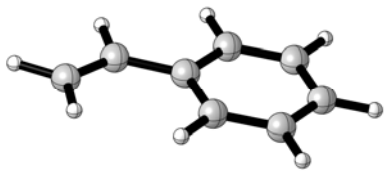
G: -780.391062 Hartree



2

Cartesian Coordinates:

C	-0.84903400	-0.03087500	-0.00006200	H	0.98962600	3.39148700	-0.00115100
C	0.54705100	0.01078500	0.00057100	H	-1.47697400	3.31883700	-0.00226200
C	1.24211100	1.23530700	0.00018800	H	-2.67700000	1.12961200	-0.00158400
C	0.48347000	2.42356900	-0.00084000	C	2.71611900	1.22035500	0.00089900
C	-0.90973600	2.38428200	-0.00146700	C	3.54733400	2.27312700	0.00071800
C	-1.58439900	1.15690500	-0.00108700	H	3.15900300	0.21724700	0.00166000
H	-1.36381400	-0.99519400	0.00025100	H	4.63076600	2.13117000	0.00131100
H	1.11647300	-0.92314500	0.00137400	H	3.19120600	3.30712900	-0.00001900



Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 0.102063 Hartree

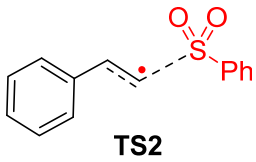
H_corr: 0.140947 Hartree

SCF: -309.802062 Hartree

S: 81.84 Cal/Mol-Kelvin

H: -309.661115 Hartree

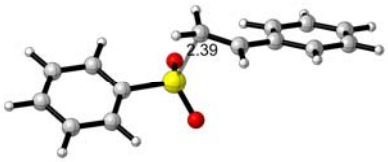
G: -309.699999 Hartree



TS2

Cartesian Coordinates:

C	-1.63194900	-0.70175300	0.42161800	C	2.53307500	3.79523300	0.76871200
C	-0.68222000	0.19043700	-0.08253700	H	0.82211900	2.96960500	1.74964700
C	-1.06260100	1.51548500	-0.31451400	C	3.18524400	4.80059200	-0.04610500
C	-2.35787600	1.97014200	-0.05116600	H	3.18339600	3.01600700	1.17985500
C	-3.29669700	1.06597400	0.45256300	C	4.59680700	4.90138000	-0.02834900
C	-2.93408900	-0.26460900	0.69094300	C	2.46303100	5.69219600	-0.87724900
H	-1.35595500	-1.74425400	0.59879900	C	5.25757900	5.86873200	-0.78104800
H	0.33506900	-0.12907000	-0.31687500	H	5.17055000	4.20965800	0.59471000
H	-2.62022700	3.00872300	-0.26141900	C	3.12974800	6.65184400	-1.63428200
H	-4.31742900	1.40053700	0.65390500	H	1.37876900	5.59697900	-0.96590200
H	-3.67263800	-0.96699600	1.08537900	C	4.52649200	6.75191900	-1.58498200
S	0.18317500	2.69145200	-0.90226600	H	6.34806200	5.93402500	-0.74698200
O	-0.54286400	3.80746400	-1.56526400	H	2.55681600	7.32278700	-2.27925700
O	1.22476100	1.92192600	-1.61873700	H	5.04380400	7.50801500	-2.18092100
C	1.17423400	3.70367000	1.01988900	H	0.51901600	4.56309900	0.85843500



Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

Imaginary Frequency: -255.8622 cm^{-1}

G_corr: 0.186518 Hartree

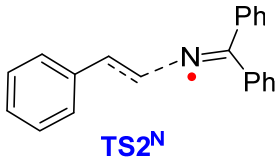
H_corr: 0.248974 Hartree

SCF: -1090.264171 Hartree

S: 131.449 Cal/Mol-Kelvin

H: -1090.015197 Hartree

G: -1090.077653 Hartree

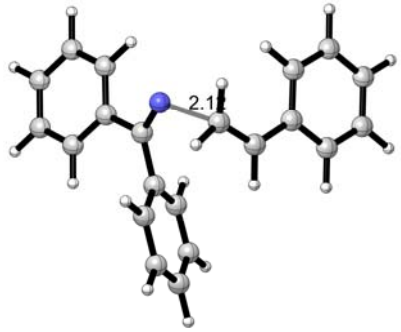


TS2^{N}

Cartesian Coordinates:

C	-0.12026500	3.85858600	0.86028900	C	1.17864400	4.02793400	1.28807000

H	-0.90148500	3.65957000	1.59471700	C	-0.00211000	-2.79201300	-0.42405700
C	2.29901600	4.47673600	0.47576300	H	0.06821100	-1.67379100	1.42065100
H	1.42264500	3.74836400	2.31764300	C	0.00039300	-1.48659100	-2.46011000
C	3.55749700	4.69032700	1.08485900	H	0.07000000	0.66341600	-2.19897200
C	2.19610000	4.70771900	-0.91684500	C	-0.02639400	-2.73145300	-1.81965200
C	4.65477900	5.12993700	0.34604200	H	-0.02499600	-3.75994100	0.08339000
H	3.66224500	4.50827300	2.15821200	H	-0.01311000	-1.43282500	-3.55188000
C	3.29492000	5.14389100	-1.65339200	H	-0.06299700	-3.65157200	-2.40864400
H	1.24741400	4.52600400	-1.42582400	C	0.60597400	0.85727000	1.90543500
C	4.52990300	5.36140600	-1.02835800	C	1.94025900	0.50440000	2.16372800
H	5.61490500	5.29168000	0.84335200	C	-0.24280700	1.15610000	2.98220300
H	3.19157200	5.31223300	-2.72875400	C	2.42300600	0.48048000	3.47457800
H	5.38913500	5.70383500	-1.61053800	H	2.60449500	0.25903800	1.33154200
H	-0.46327600	4.30043300	-0.07415000	C	0.23814100	1.11784100	4.29424900
N	-0.33798400	1.96989400	-0.07377400	H	-1.28711200	1.41193300	2.78783600
C	0.09445900	0.91843000	0.49059600	C	1.57374000	0.78689100	4.54316900
C	0.07664200	-0.36306200	-0.30424200	H	3.46731100	0.21792700	3.66270200
C	0.05201200	-1.61639100	0.33059700	H	-0.43392800	1.34693000	5.12535800
C	0.04933700	-0.31230300	-1.71039000	H	1.95090900	0.76156200	5.56870100



Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

Imaginary Frequency: -401.7732 cm^{-1}

G_corr: 0.27343 Hartree

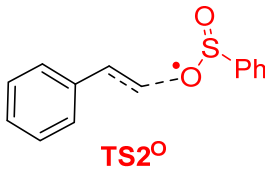
H_corr: 0.344305 Hartree

SCF: -866.163719 Hartree

S: 149.168 Cal/Mol-Kelvin

H: -865.819414 Hartree

G: -865.890289 Hartree

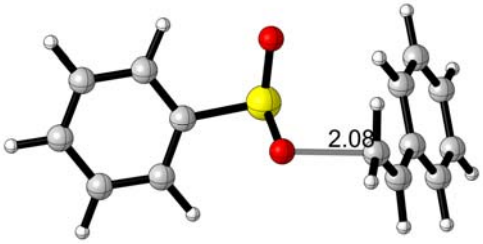


TS2^{O}

Cartesian Coordinates:

C	-1.84211800	2.21504600	0.23152900	C	0.06916600	1.26034400	-0.86961600
C	-0.45309700	2.07930100	0.12992100	C	-0.75278400	0.57820100	-1.77023700

C	-2.13746100	0.72641700	-1.66119100	C	4.30485500	-0.75640000	-2.53906100
C	-2.68147600	1.54341800	-0.66226100	H	4.11706800	-1.53330100	-3.28772900
H	-2.26818000	2.84957300	1.01306700	C	4.86457200	0.47980400	-3.04122300
H	0.23215800	2.58793600	0.81147300	C	5.27888900	0.54473400	-4.39559400
H	-0.31561200	-0.07090400	-2.53165100	C	5.02030800	1.64239300	-2.24191800
H	-2.79558600	0.19645800	-2.35461300	C	5.84015600	1.70297500	-4.92266500
H	-3.76571600	1.65491600	-0.58112400	H	5.15785000	-0.33896900	-5.02813000
S	1.89771600	1.17482900	-1.01833100	C	5.57902000	2.80036100	-2.77758100
O	1.96460900	-0.41909600	-0.98624800	H	4.67639300	1.65355700	-1.20580600
O	2.44624300	1.80690000	0.22666800	C	5.99559200	2.83724700	-4.11405600
C	3.94112100	-1.02471300	-1.23570200	H	6.15782300	1.72799500	-5.96805000
H	3.62036800	-2.02892200	-0.96224000	H	5.68391000	3.68688300	-2.14743000
H	4.25533700	-0.38591900	-0.40951000	H	6.43377500	3.74923600	-4.52719300



Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

Imaginary Frequency: -387.9671 cm^{-1}

G_corr: 0.186363 Hartree

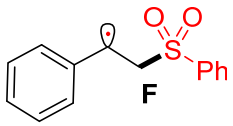
H_corr: 0.248375 Hartree

SCF: -1090.238515 Hartree

S: 130.515 Cal/Mol-Kelvin

H: -1089.99014 Hartree

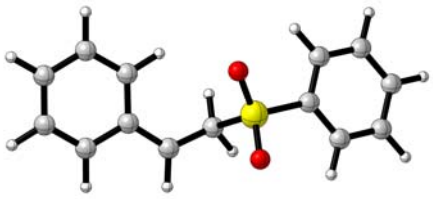
G: -1090.052152 Hartree



Cartesian Coordinates:

C	-1.97206200	-0.46303500	0.76549800	H	-4.14790300	2.09673600	0.13511500
C	-0.79446800	0.10995700	0.27863700	H	-4.09146800	-0.19880500	1.10036800
C	-0.84116300	1.40533500	-0.24529700	S	0.67908500	2.15399200	-0.86609900
C	-2.03457600	2.13018600	-0.30898500	O	0.29963300	3.18960700	-1.84250400
C	-3.20534800	1.54577100	0.18155900	O	1.60401200	1.06863100	-1.22336300
C	-3.17262900	0.25479800	0.72029800	C	1.39994700	3.01957800	0.62728800
H	-1.95438400	-1.47660800	1.17354100	C	2.79335300	3.45180200	0.38940200
H	0.14992000	-0.43799800	0.28049900	H	1.33509600	2.26858500	1.42765900
H	-2.03880700	3.12588400	-0.75659900	C	3.19323000	4.68014800	-0.20226600

H	3.57973000	2.74626500	0.66874300	H	1.20844300	5.37944700	-0.77885900
C	4.58047000	5.01039100	-0.25982200	C	4.08398700	7.13444400	-1.31061900
C	2.27063700	5.62444100	-0.74257900	H	6.08090400	6.44401000	-0.82750500
C	5.01261400	6.21403200	-0.79949900	H	1.99069000	7.52903400	-1.69899100
H	5.30757600	4.29671900	0.13704200	H	4.42529500	8.08071400	-1.73735400
C	2.71577900	6.82523900	-1.28213300	H	0.69940900	3.84209900	0.83372300



Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 0.189898 Hartree

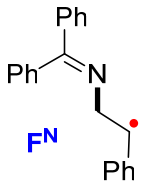
H_corr: 0.250622 Hartree

SCF: -1090.282585 Hartree

S: 127.806 Cal/Mol-Kelvin

H: -1090.031963 Hartree

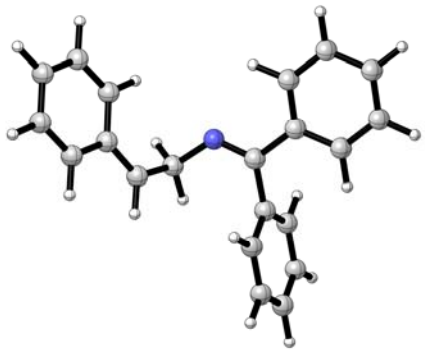
G: -1090.092687 Hartree



Cartesian Coordinates:

C	0.78831700	3.32830300	1.19673500	C	0.22927000	-1.50254600	0.35789700
C	2.20998100	3.82300800	1.20584500	C	0.25535900	0.05937000	-1.48950000
H	0.46061700	3.16087700	2.23719700	C	0.08790000	-2.56289400	-0.54283000
C	2.86035900	4.45735900	0.11745300	H	0.27896400	-1.71136200	1.42789500
H	2.79109300	3.65627900	2.11828300	C	0.11341000	-0.99756800	-2.38518400
C	4.20266200	4.92430100	0.25706500	H	0.32718800	1.09035000	-1.83841100
C	2.22392200	4.66787800	-1.14340400	C	0.02818100	-2.31502700	-1.91560800
C	4.85598000	5.56686100	-0.78594700	H	0.02593700	-3.58741700	-0.16687700
H	4.71526700	4.77186600	1.21115200	H	0.06864700	-0.79662700	-3.45891400
C	2.88850200	5.31207300	-2.18006100	H	-0.08334400	-3.14373400	-2.61979300
H	1.21139400	4.29159400	-1.29752900	C	0.43125500	0.67888500	2.31993300
C	4.20489200	5.76941400	-2.01338900	C	1.61862400	0.61161500	3.06653500
H	5.88281200	5.91683800	-0.64957800	C	-0.79473000	0.47717100	2.97470700
H	2.38068600	5.45809600	-3.13736300	C	1.58038900	0.35078300	4.43962000
H	4.72058300	6.27481300	-2.83359900	H	2.57844900	0.76086500	2.56510800
H	0.13083700	4.10708700	0.76781700	C	-0.83250100	0.22397300	4.34884300
N	0.63602400	2.14704000	0.35119400	H	-1.72512800	0.52117100	2.40235400
C	0.47273500	0.97587100	0.84141300	C	0.35496900	0.15860800	5.08440500
C	0.31382900	-0.17662000	-0.10199100	H	2.51276200	0.29781700	5.00779200

H	-1.79425200	0.07529600	4.84671400	H	0.32515900	-0.04286600	6.15822300



Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 0.276192 Hartree

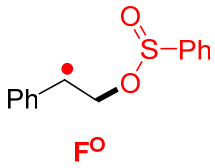
H_corr: 0.346765 Hartree

SCF: -866.198952 Hartree

S: 148.532 Cal/Mol-Kelvin

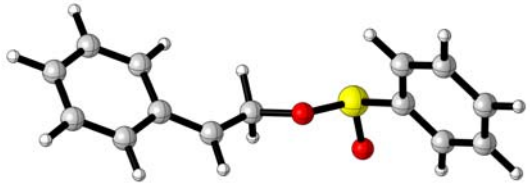
H: -865.852187 Hartree

G: -865.92276 Hartree



Cartesian Coordinates:

C	-2.46254900	0.43557400	0.23726100	H	3.86934100	-0.04506900	-0.39605200
C	-1.11382200	0.29155000	0.57772100	H	3.97592000	1.66770300	-0.88540400
C	-0.18977900	1.20511600	0.07297700	C	3.80659800	0.25505000	-2.51741000
C	-0.57866900	2.26457100	-0.75227400	H	3.17805200	-0.56064200	-2.88719700
C	-1.92811400	2.39977300	-1.08540800	C	4.82362700	0.75530300	-3.36655700
C	-2.86806000	1.48705800	-0.59060800	C	4.99141400	0.18837300	-4.66848700
H	-3.19853600	-0.27603900	0.61999000	C	5.71758800	1.80804500	-3.00013300
H	-0.75924700	-0.51797900	1.22023400	C	5.97521900	0.64247800	-5.53515000
H	0.16428000	2.96391200	-1.14315100	H	4.32253700	-0.61972500	-4.97663300
H	-2.24813700	3.21791400	-1.73551900	C	6.69899300	2.25452500	-3.87668400
H	-3.92337200	1.59868800	-0.85226700	H	5.63314800	2.27351900	-2.01617700
S	1.54085100	1.03248700	0.59736800	C	6.83945300	1.67986000	-5.14904500
O	2.07189100	0.80398800	-1.00953700	H	6.07670200	0.18865400	-6.52454700
O	1.62522900	-0.25343500	1.34789000	H	7.36821800	3.06233000	-3.56861700
C	3.50192500	0.70082300	-1.13092100	H	7.61409800	2.03599600	-5.83226100



Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 0.185639 Hartree

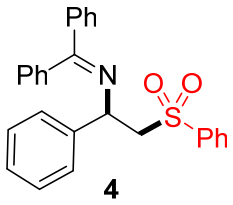
H_corr: 0.249987 Hartree

SCF: -1090.256699 Hartree

S: 135.43 Cal/Mol-Kelvin

H: -1090.006712 Hartree

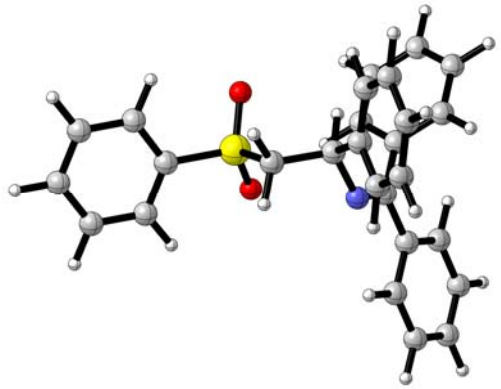
G: -1090.07106 Hartree



4

Cartesian Coordinates:

C	-1.96124200	0.39081300	0.49288000	H	4.37027600	7.55282000	2.04734000
C	-0.56691300	0.47739500	0.51711800	H	4.03819100	5.18693900	5.64108400
C	0.05383900	1.53589100	-0.15237900	H	4.32827700	7.40691900	4.53943200
C	-0.68055100	2.49158100	-0.86014100	N	4.31668000	1.77175000	2.13916800
C	-2.07429000	2.39316600	-0.87690900	C	5.32034700	1.16032000	1.63193700
C	-2.71177200	1.34807300	-0.19903800	C	5.86006000	-0.03606600	2.35067000
H	-2.46314800	-0.43138400	1.00876700	C	7.00635700	-0.71116100	1.89622400
H	0.04236200	-0.26966600	1.02971200	C	5.21299000	-0.51237600	3.50749600
H	-0.15772900	3.28332100	-1.40038300	C	7.49720600	-1.82584300	2.58285300
H	-2.66408100	3.12985700	-1.42781900	H	7.52024000	-0.36395200	0.99856800
H	-3.80206700	1.27428200	-0.21695700	C	5.70192800	-1.62355300	4.18974000
S	1.85341300	1.65117200	-0.13106500	H	4.31805200	0.00918500	3.84876300
O	2.27097400	2.43097900	-1.30958100	C	6.84862800	-2.28519200	3.73083000
O	2.38247200	0.29398000	0.09180300	H	8.39050600	-2.33731000	2.21528000
C	2.20424100	2.68161700	1.33526800	H	5.18632200	-1.98168900	5.08484700
C	3.71901500	2.93390000	1.51122100	H	7.23127100	-3.15787200	4.26670400
H	1.78424000	2.16862900	2.21219500	C	6.00557200	1.57236200	0.35300700
H	1.66481300	3.62108500	1.15206600	C	7.09359400	2.45955200	0.39363000
H	4.13341600	3.15528500	0.51192300	C	5.56783800	1.07678700	-0.88563300
C	3.91803200	4.17834600	2.37735700	C	7.73577500	2.84486900	-0.78660000
C	4.08930100	5.42957000	1.76645500	H	7.43893500	2.84862300	1.35525500
C	3.90327000	4.10347800	3.77834000	C	6.21305700	1.46602400	-2.06326900
C	4.23340800	6.58584600	2.53860800	H	4.70795900	0.40499500	-0.92226800
H	4.11595300	5.49770200	0.67492600	C	7.29746200	2.34693700	-2.01757200
C	4.04864900	5.25955400	4.55020800	H	8.58096200	3.53688300	-0.74337500
H	3.79172300	3.12916600	4.25731500	H	5.85847300	1.08221400	-3.02316000
C	4.21198600	6.50422700	3.93406100	H	7.79862800	2.64897000	-2.94090400



Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 0.370089 Hartree

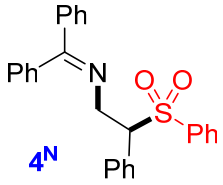
H_corr: 0.459237 Hartree

SCF: -1646.745812 Hartree

S: 187.629 Cal/Mol-Kelvin

H: -1646.286575 Hartree

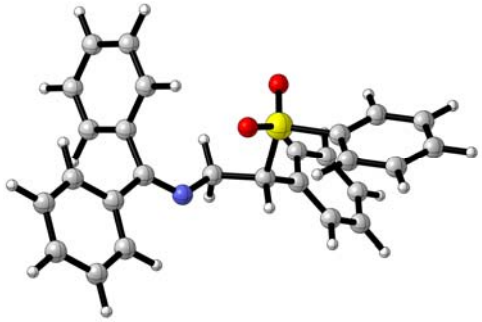
G: -1646.375723 Hartree



Cartesian Coordinates:

C	-1.91168300	0.21005200	0.46143400	C	5.83593300	0.02783200	2.34741300
C	-0.53018700	0.41516100	0.42899100	C	6.86327500	-0.81830000	1.89487200
C	-0.02522800	1.48762800	-0.31285500	C	5.27927900	-0.20981100	3.61912400
C	-0.86166000	2.33992500	-1.03834200	C	7.32035100	-1.87367100	2.69010600
C	-2.24129600	2.12145900	-0.99968300	H	7.30435200	-0.65739400	0.90983200
C	-2.76406100	1.06302400	-0.24888700	C	5.73869900	-1.25841800	4.41230600
H	-2.32313500	-0.62475100	1.03405000	H	4.48020400	0.44963600	3.96061400
H	0.15648900	-0.25362500	0.95173400	C	6.76243000	-2.09629600	3.95070000
H	-0.42847200	3.14908600	-1.62829300	H	8.11628100	-2.52479900	2.31953700
H	-2.90987500	2.77771600	-1.56208000	H	5.29832400	-1.42678500	5.39880000
H	-3.84394500	0.89620500	-0.22339400	H	7.12228700	-2.91937500	4.57377200
S	1.75841500	1.73708600	-0.37082500	C	6.08409400	1.49962400	0.25527000
O	2.07370300	2.52502600	-1.57683100	C	7.30949800	2.18068400	0.34882900
O	2.39110400	0.41967000	-0.16921600	C	5.58803000	1.15301200	-1.01260400
C	2.16152500	2.78161100	1.11758600	C	8.02359800	2.51724900	-0.80415000
C	3.70257500	2.89484700	1.20987700	H	7.70621900	2.44671700	1.33243900
H	1.81858200	2.17093100	1.96507400	C	6.30943400	1.48658100	-2.16334300
H	4.13129800	3.09284900	0.21113500	H	4.63066200	0.63361800	-1.09086600
N	4.26596000	1.76432300	1.90475200	C	7.52556400	2.16838200	-2.06362300
C	5.31805900	1.15350400	1.50687500	H	8.97350300	3.05149700	-0.71794700

H	5.91200700	1.21446800	-3.14447100	C	1.09506700	6.32404200	0.15036300
H	8.08491500	2.42898200	-2.96594200	H	2.54382100	4.90877200	-0.59449100
C	1.43036800	4.10055700	1.07827900	C	0.07681800	6.57029400	1.07737100
C	0.40365800	4.35715300	2.00141800	H	-1.06222700	5.76478200	2.73210300
C	1.76767400	5.10006700	0.14798600	H	1.36788800	7.09095100	-0.57914200
C	-0.26828600	5.58239500	2.00339200	H	-0.44601900	7.53018300	1.07717000
H	0.13091800	3.58846700	2.72973500	H	3.89951000	3.79107900	1.82524400



Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 0.371001 Hartree

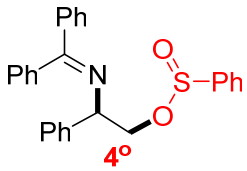
H_corr: 0.459238 Hartree

SCF: -1646.745102 Hartree

S: 185.711 Cal/Mol-Kelvin

H: -1646.285864 Hartree

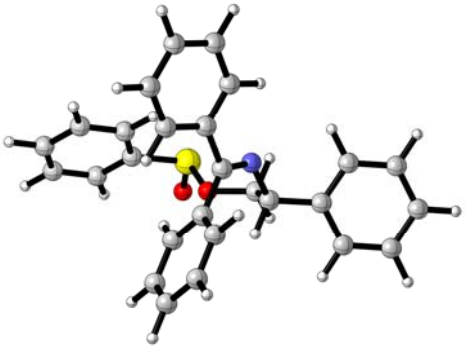
G: -1646.374101 Hartree



Cartesian Coordinates:

C	-1.96427200	-0.20625200	-0.07104600	O	2.74720000	-0.29906400	0.22030400
C	-0.73052400	0.34942200	-0.42467400	C	4.15697500	-0.12896800	0.37830600
C	0.29921000	0.35694800	0.51517000	C	4.72746100	-1.35950400	1.10424300
C	0.12539400	-0.16181500	1.80231500	H	4.37073400	0.77744100	0.97262900
C	-1.11150000	-0.71292100	2.14537700	H	4.64109100	-0.02545600	-0.60758900
C	-2.15365200	-0.73479100	1.20999100	H	4.51554300	-2.23921500	0.47243900
H	-2.78025000	-0.22526300	-0.79802200	C	6.24306500	-1.21729200	1.21687400
H	-0.54470100	0.77392700	-1.41421500	N	4.11636300	-1.43995000	2.41536500
H	0.94704000	-0.14938500	2.52269100	C	7.07683500	-1.86729500	0.29540300
H	-1.25971900	-1.12968900	3.14461000	C	6.82852100	-0.41228400	2.20654800
H	-3.12040100	-1.16501400	1.48393800	C	3.41518700	-2.43986400	2.79968000
S	1.86744900	1.15343500	0.05569000	C	8.46525500	-1.71353200	0.35456200
O	1.73787400	1.51677800	-1.38184400	H	6.63414400	-2.50552500	-0.47492700

C	8.21596700	-0.25931700	2.26816600	C	2.75153600	-1.36796300	6.38895200
H	6.18677800	0.08448700	2.93656800	H	4.07037700	-0.74248300	4.78729300
C	2.84040500	-2.40102000	4.18486500	C	3.45451600	-6.04543600	1.57257900
C	3.13109700	-3.66620000	1.96980500	H	4.33054800	-4.96131100	3.22336300
C	9.03909400	-0.90805700	1.34196000	C	2.06397700	-4.75293800	0.07495200
H	9.10003800	-2.22953800	-0.37055800	H	1.88311200	-2.64411700	0.53053100
H	8.65801700	0.36890900	3.04615600	C	1.74563900	-2.26125600	6.77959800
C	1.83137400	-3.29362900	4.58888000	H	0.50046100	-3.92116500	6.16949300
C	3.29022500	-1.43491200	5.10570100	H	3.11810100	-0.61622600	7.09299900
C	3.69572200	-4.90018300	2.33551500	C	2.63415700	-5.97523400	0.44205300
C	2.31275200	-3.60216800	0.82956900	H	3.90697300	-6.99682000	1.86423200
H	10.12451100	-0.78903000	1.39235800	H	1.42286600	-4.69024500	-0.80812500
C	1.28668300	-3.22120400	5.87492300	H	1.32396300	-2.20836500	7.78675500
H	1.46233000	-4.04693500	3.89092800	H	2.44066300	-6.87221400	-0.15193200



Temperature: 298.15 Kelvin

Pressure: 1.0 Atm

G_corr: 0.367898 Hartree

H_corr: 0.459009 Hartree

SCF: -1646.727325 Hartree

S: 191.761 Cal/Mol-Kelvin

H: -1646.268316 Hartree

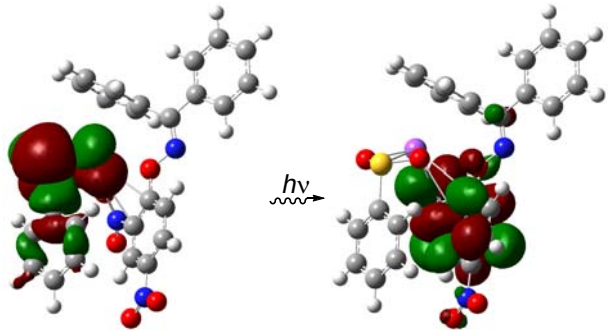
G: -1646.359427 Hartree

9.9 Time dependent density functional theory (TDDFT) calculation

Ground state geometry of the EDA complex was optimized at the B3LYP/def2-SVP level of theory. Using this geometry, single point time dependent density functional theory (TDDFT) calculation was then performed using the B3LYP-D3/def2tzvp method, with SMD solvation model (in acetonitrile). The first 10 excited states of the EDA complex (composed of **1a** and **3a**) are reported below.

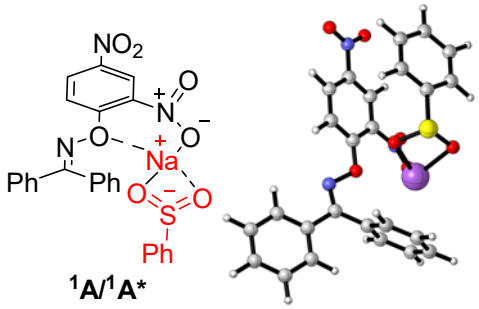
State 1	**2.1100 eV; 587.60 nm**	***f* = 0.0047**
136 → 137	0.70673	
State 2	**2.4734 eV; 501.27 nm**	***f* = 0.0008**
136 → 138	0.70652	
State 3	**3.0587 eV; 405.35 nm**	***f* = 0.0840**
135 → 137	0.69580	
State 4	**3.1944 eV; 388.13 nm**	***f* = 0.0023**
134 → 137	0.70454	
State 5	**3.3454 eV; 370.61 nm**	***f* = 0.0022**
133 → 137	0.70512	
State 6	**3.4335 eV; 361.10 nm**	***f* = 0.0193**
134 → 138	0.62186	
135 → 138	-0.25179	
136 → 139	-0.20967	
State 7	**3.4465 eV; 359.74 nm**	***f* = 0.0142**
134 → 138	0.17269	
135 → 138	-0.12652	
136 → 139	0.67175	
State 8	**3.4620 eV; 358.13 nm**	***f* = 0.2146**
133 → 138	0.17858	
134 → 138	0.27760	
135 → 139	0.61062	
State 9	**3.5347 eV; 350.76 nm**	***f* = 0.0012**
131 → 137	0.69729	
State 10	**3.5540 eV; 348.86 nm**	***f* = 0.0184**
131 → 137	0.69729	
133 → 138	0.67644	
135 → 138	-0.18260	

TDDFT Analysis



donor orbital
HOMO

acceptor orbital
LUMO



^{1}A/^{1}A*

TDDFT analysis strongly suggests that upon visible light excitation of complex **A**, a charge-transfer type excited state is populated.

10. X-ray crystallographic data

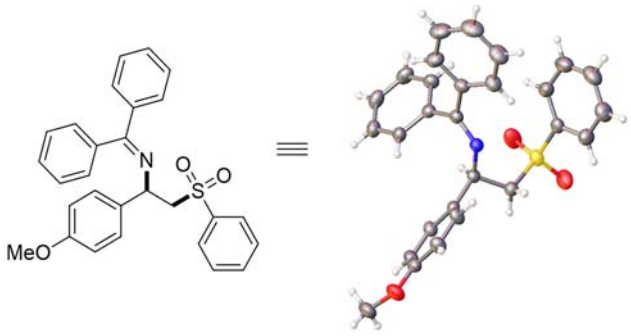


Table S12 Crystal data and structure refinement for 4c.

Identification code	4c
Empirical formula	$C_{28}H_{25}NO_3S$
Formula weight	455.55
Temperature/K	299.5
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.7117(3)
b/Å	9.2350(2)
c/Å	18.8993(4)
α/°	90.00
β/°	100.4340(10)
γ/°	90.00
Volume/Å^3	2353.60(9)
Z	4
ρ_{calc}g/cm^3	1.286
μ/mm^{-1}	1.460
F(000)	960.0
Crystal size/mm^3	0.17 × 0.16 × 0.12
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	10.54 to 150.86
Index ranges	-16 ≤ h ≤ 17, -10 ≤ k ≤ 11, -23 ≤ l ≤ 23
Reflections collected	19113
Independent reflections	4765 [R_{int} = 0.0510, R_{sigma} = 0.0461]
Data/restraints/parameters	4765/0/299
Goodness-of-fit on F^2	1.132
Final R indexes [I>=2σ (I)]	R_1 = 0.0512, wR_2 = 0.1459
Final R indexes [all data]	R_1 = 0.0688, wR_2 = 0.1641
Largest diff. peak/hole / e Å^{-3}	0.33/-0.52

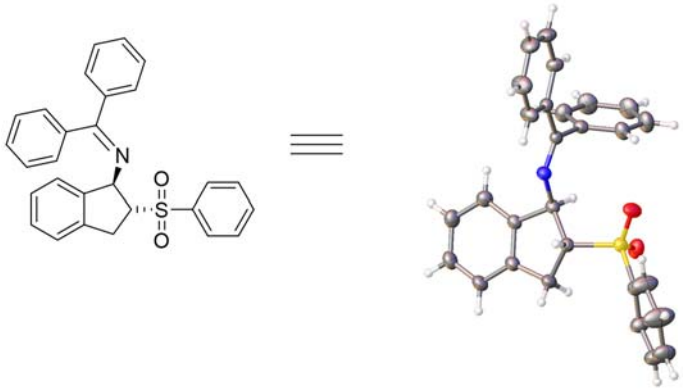


Table S13 Crystal data and structure refinement for 4s.

Identification code	4s
Empirical formula	$C_{28}H_{23}NO_2S$
Formula weight	437.53
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.8707(9)
b/Å	9.3692(5)
c/Å	17.0525(10)
α/°	90.00
β/°	107.269(7)
γ/°	90.00
Volume/Å^3	2268.8(2)
Z	4
ρ_{calc}g/cm^3	1.281
μ/mm^{-1}	1.460
F(000)	920.0
Crystal size/mm^3	0.16 × 0.13 × 0.11
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.22 to 134.06
Index ranges	-17 ≤ h ≤ 17, -11 ≤ k ≤ 9, -20 ≤ l ≤ 20
Reflections collected	14379
Independent reflections	4025 [R_{int} = 0.0699, R_{sigma} = 0.0525]
Data/restraints/parameters	4025/0/289
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0630, wR_2 = 0.1698
Final R indexes [all data]	R_1 = 0.0797, wR_2 = 0.1884
Largest diff. peak/hole / e Å^{-3}	0.36/-0.34

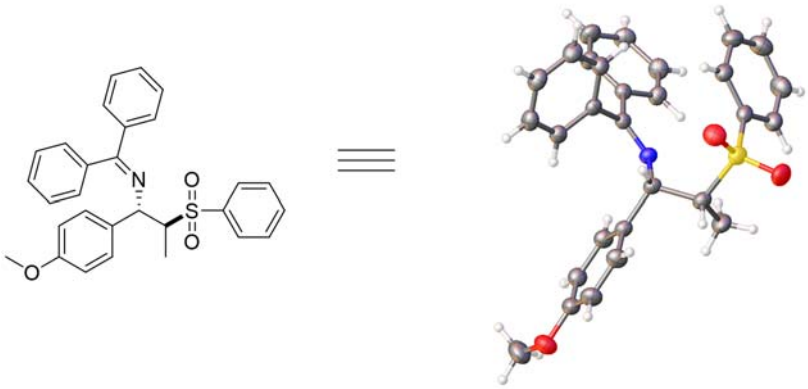
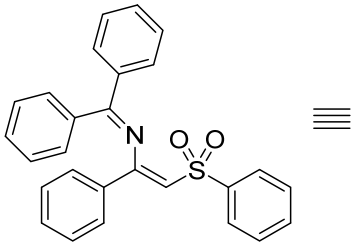


Table S14 Crystal data and structure refinement for 4t.

Identification code	4t
Empirical formula	$C_{29}H_{27}NO_3S$
Formula weight	469.58
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.7617(6)
b/Å	21.2431(10)
c/Å	9.2655(4)
α/°	90.00
β/°	100.383(4)
γ/°	90.00
Volume/Å^3	2470.7(2)
Z	4
ρ_{calc}g/cm^3	1.262
μ/mm^{-1}	1.405
F(000)	992.0
Crystal size/mm^3	0.17 × 0.15 × 0.12
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.04 to 134.38
Index ranges	$-15 \le h \le 15$, $-24 \le k \le 25$, $-10 \le l \le 11$
Reflections collected	17849
Independent reflections	4407 [R_{int} = 0.0483, R_{sigma} = 0.0274]
Data/restraints/parameters	4407/0/309
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0454, wR_2 = 0.1190
Final R indexes [all data]	R_1 = 0.0573, wR_2 = 0.1303
Largest diff. peak/hole / e Å^{-3}	0.28/-0.29



28a

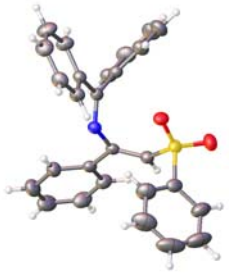


Table S15 Crystal data and structure refinement for28a.

Identification code	28a
Empirical formula	$C_{27}H_{21}NO_2S$
Formula weight	423.51
Temperature/K	294.8
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.2324(6)
b/Å	9.0288(4)
c/Å	19.0515(9)
α/°	90
β/°	96.874(2)
γ/°	90
Volume/Å^3	2259.77(18)
Z	4
ρ_{calc}g/cm^3	1.245
μ/mm^{-1}	0.166
F(000)	888.0
Crystal size/mm^3	0.25 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5 to 55.34
Index ranges	-17 ≤ h ≤ 17, -11 ≤ k ≤ 11, -21 ≤ l ≤ 24
Reflections collected	52161
Independent reflections	5226 [R_{int} = 0.0573, R_{sigma} = 0.0297]
Data/restraints/parameters	5226/0/280
Goodness-of-fit on F^2	0.901
Final R indexes [I>=2σ (I)]	R_1 = 0.0439, wR_2 = 0.1144
Final R indexes [all data]	R_1 = 0.0765, wR_2 = 0.1393
Largest diff. peak/hole / e Å^{-3}	0.19/-0.33

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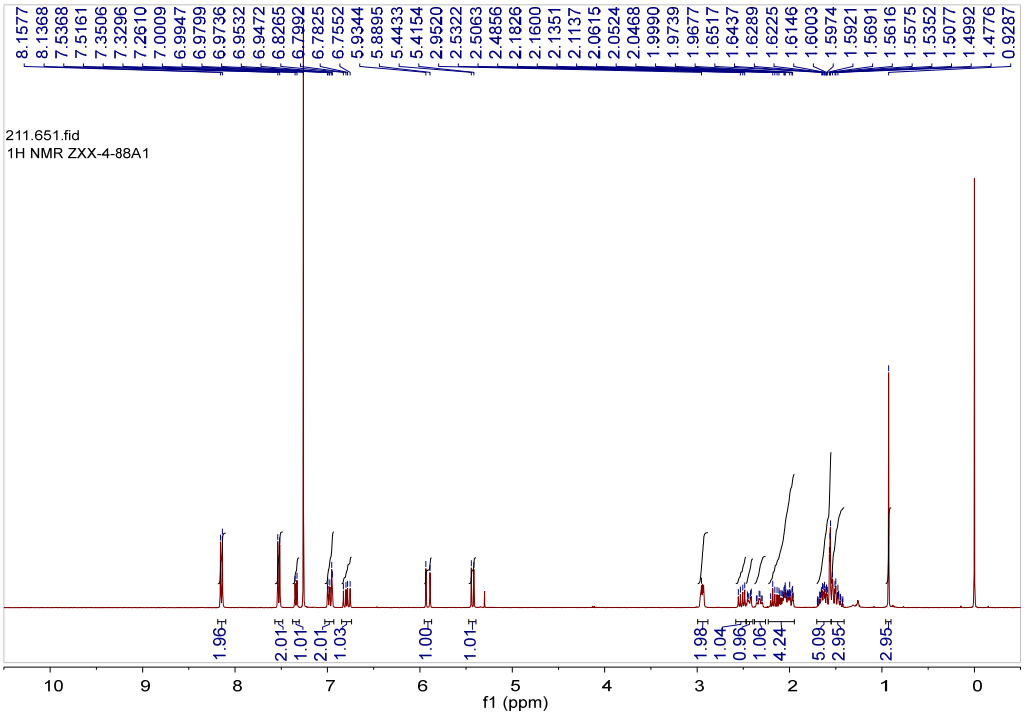
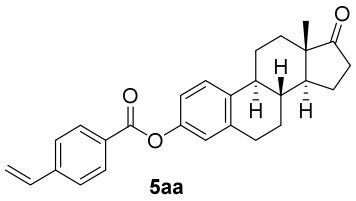
12. Copy of NMR spectra

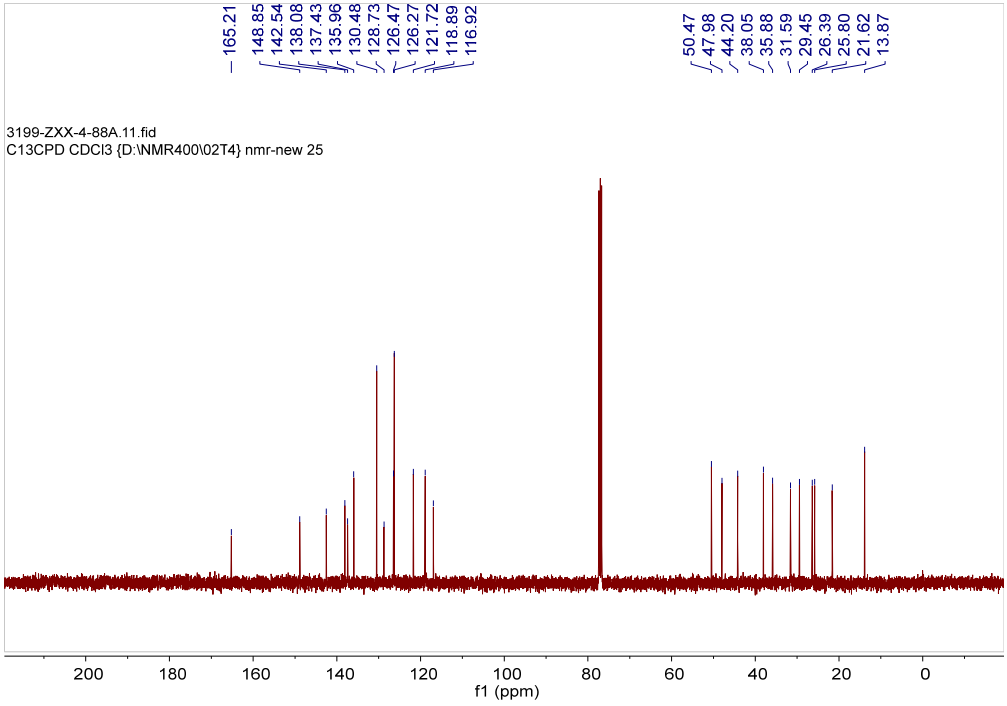


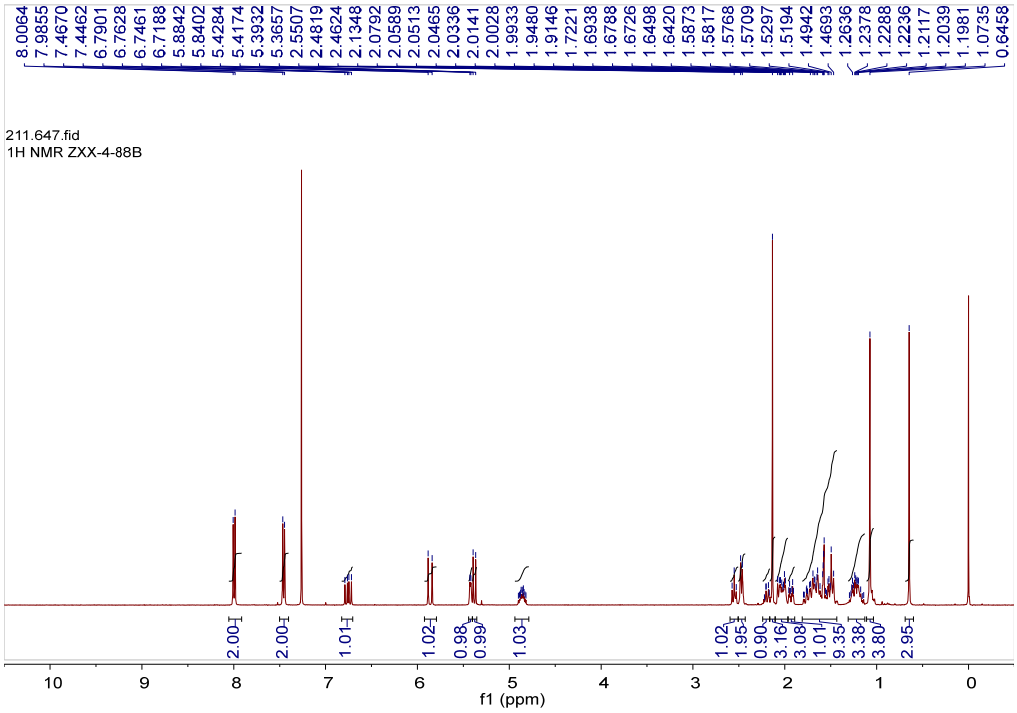


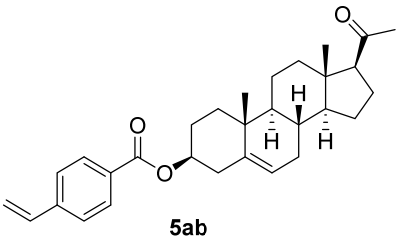
5aa

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



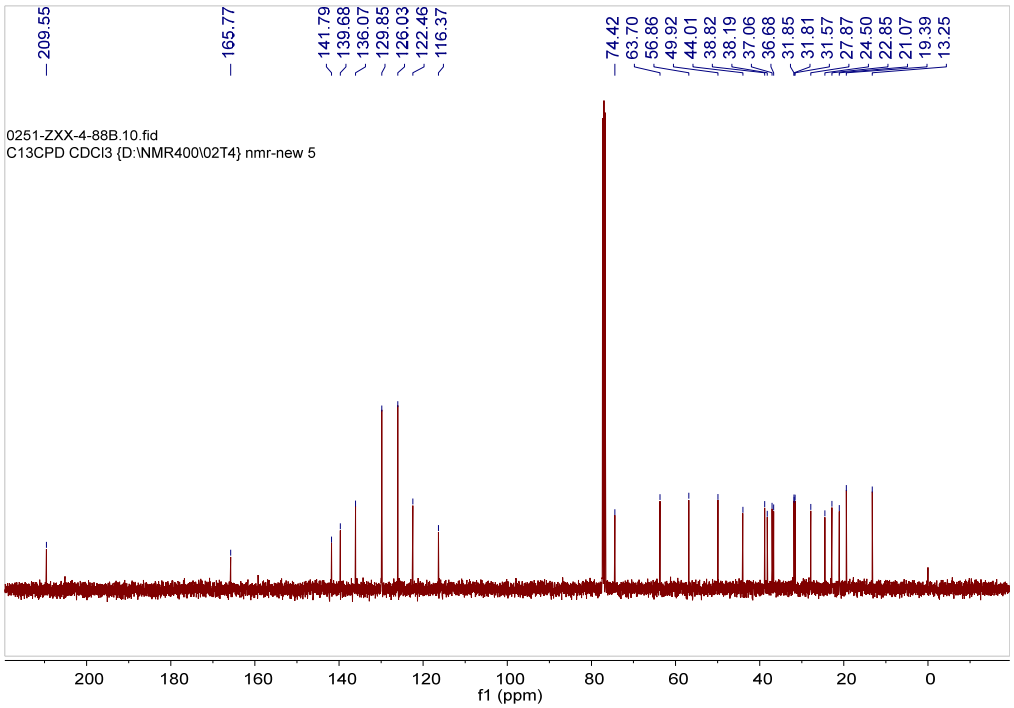


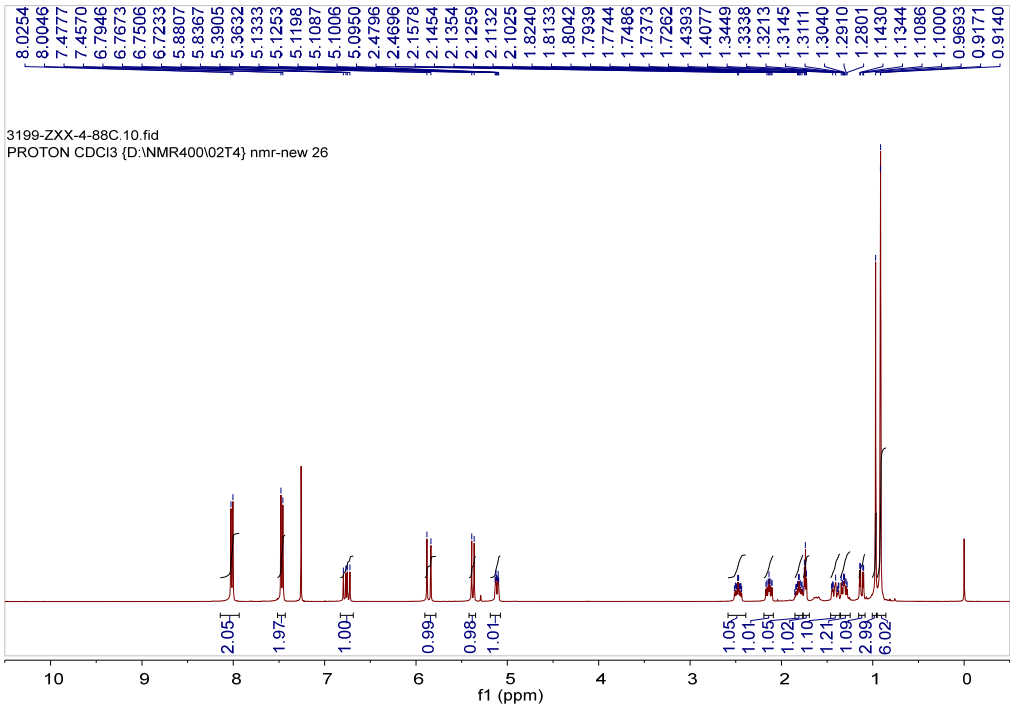


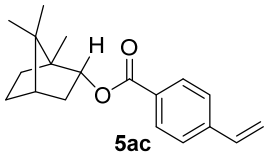
5ab

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



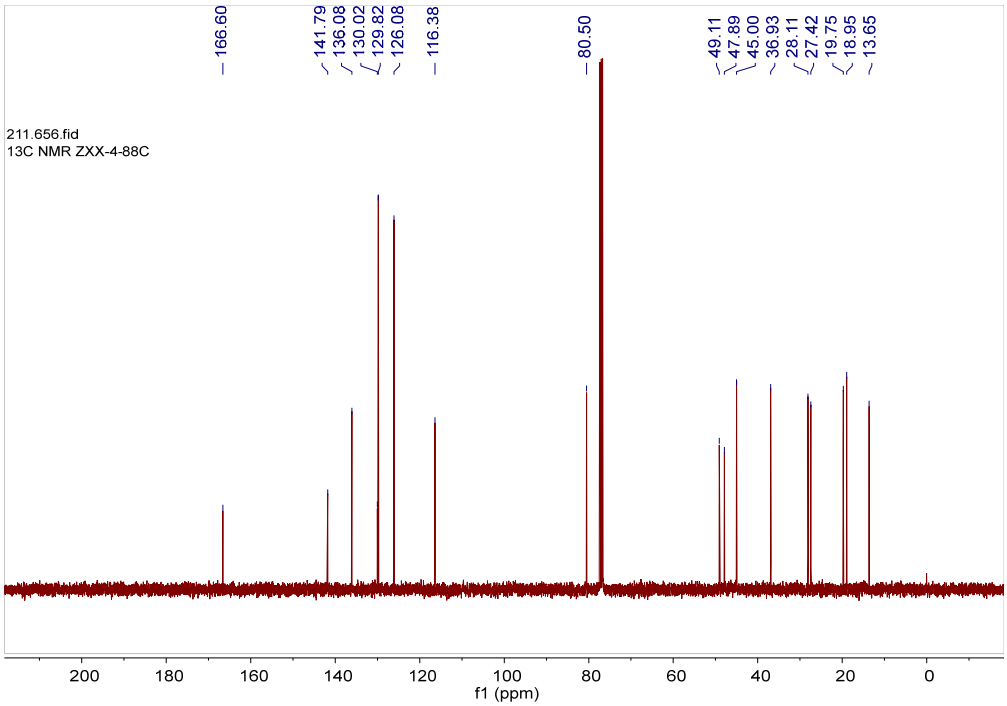


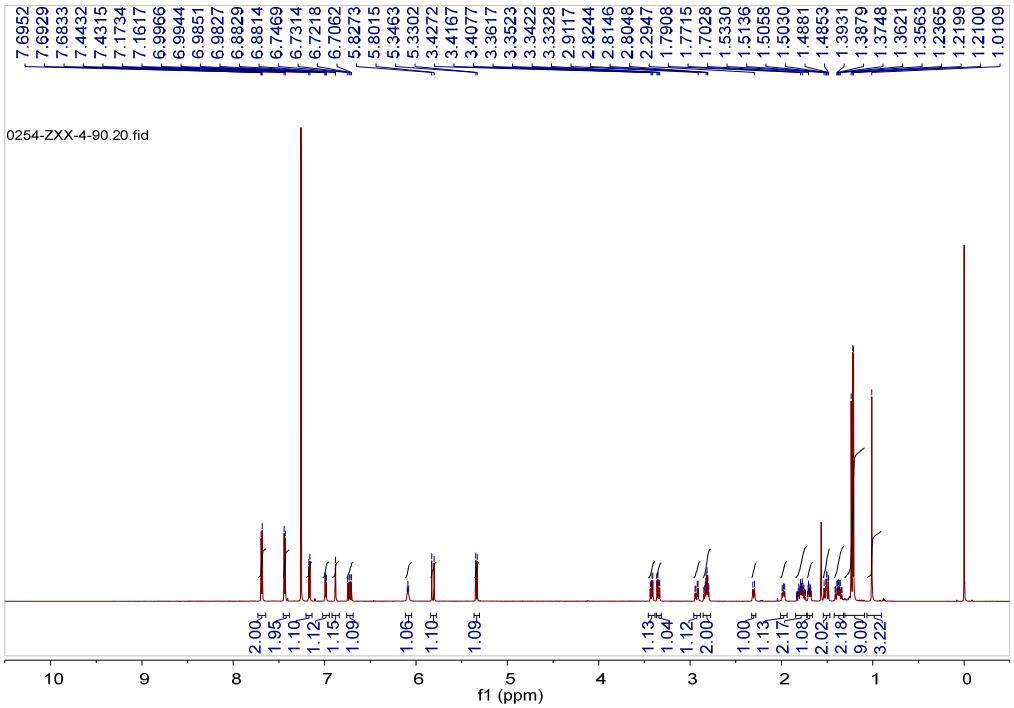


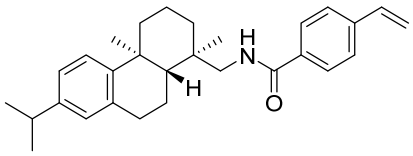
5ac

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



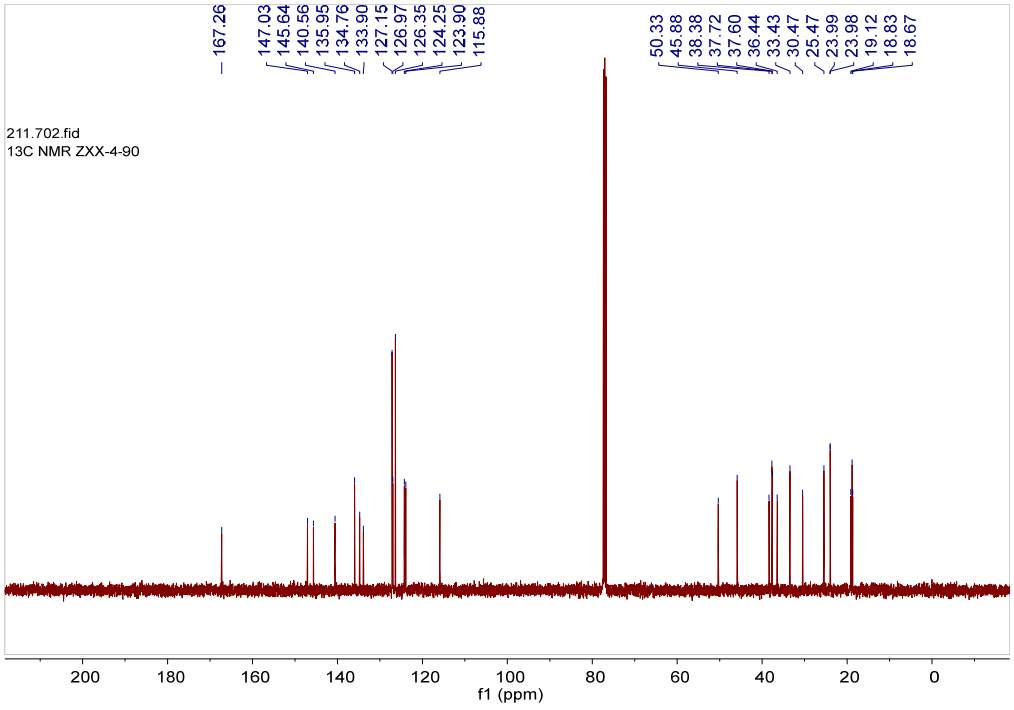


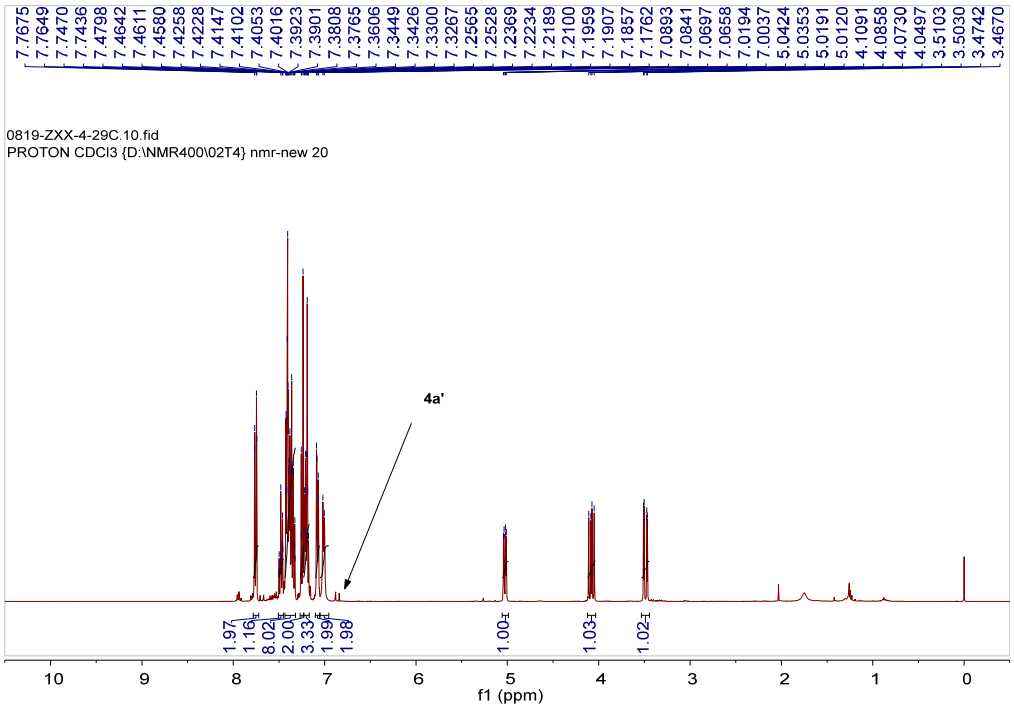


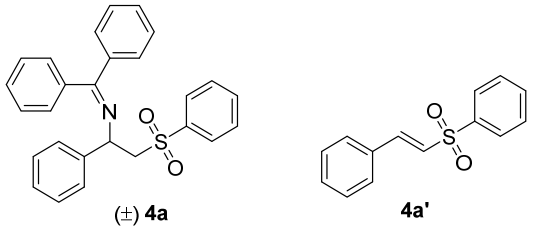
5ad

^{1}H NMR (700 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



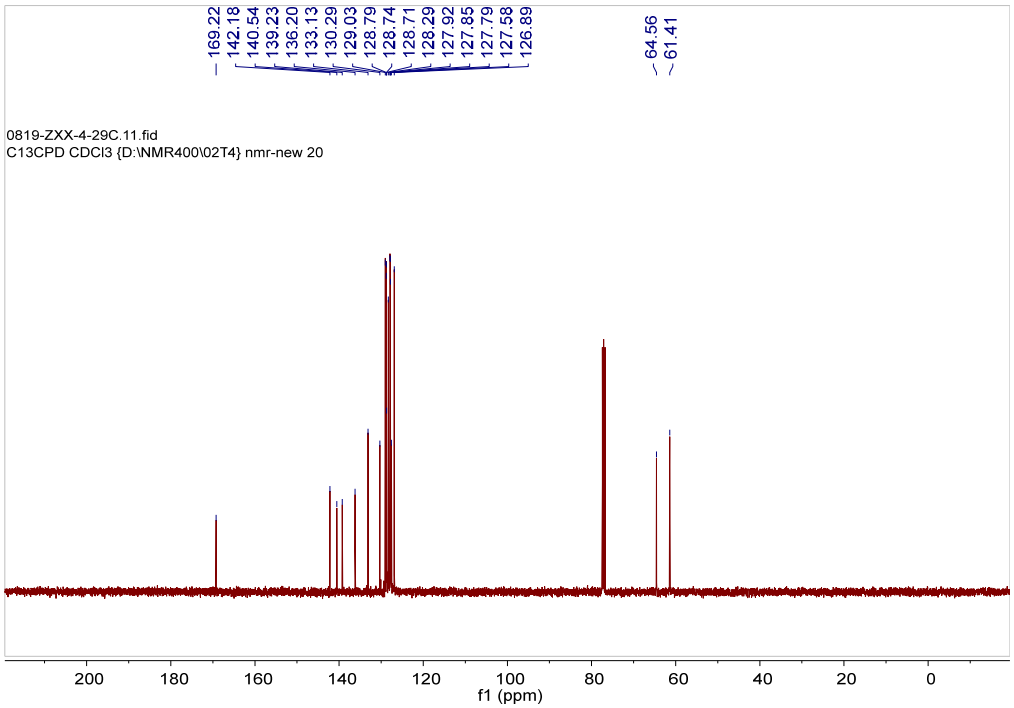


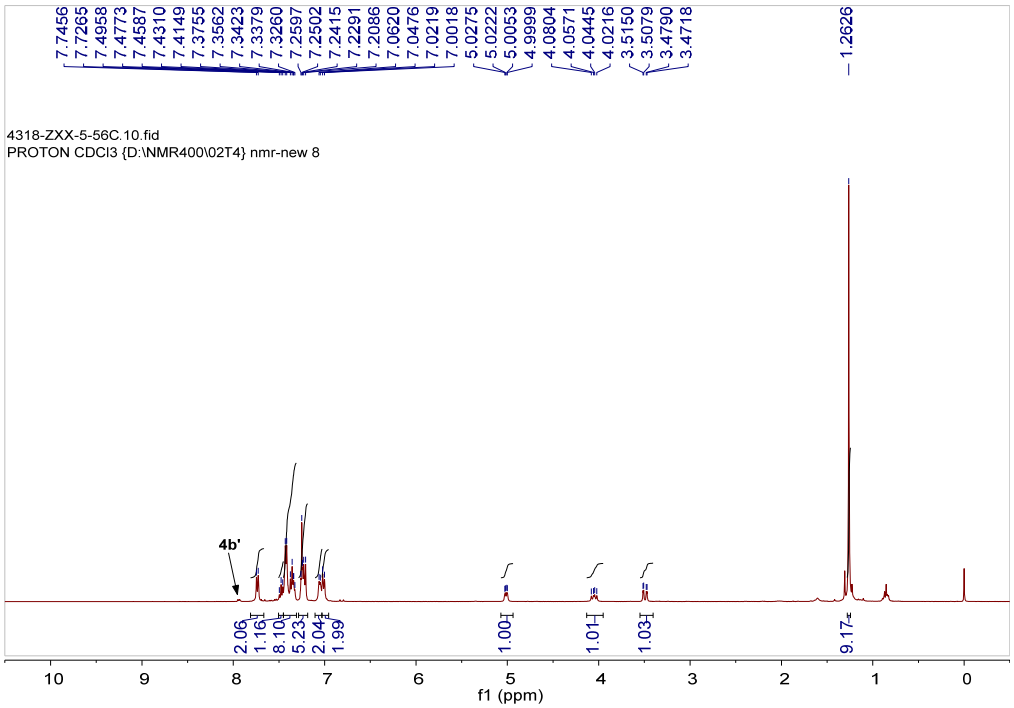


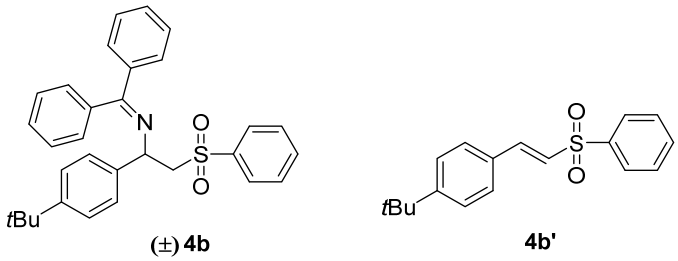
(±) **4a** **4a'**

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



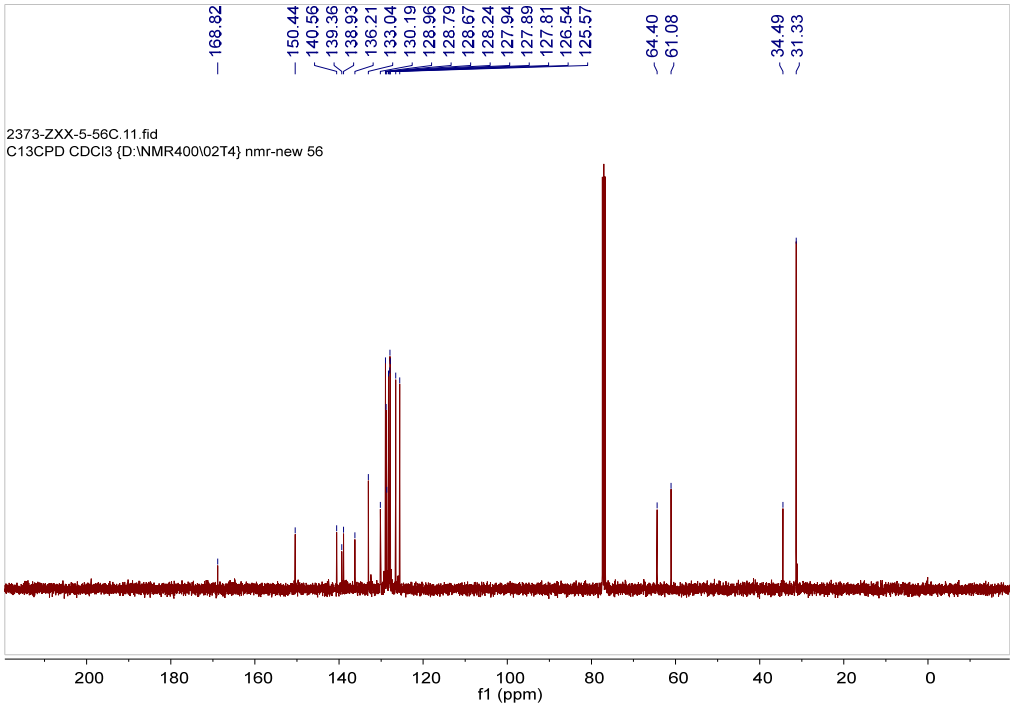


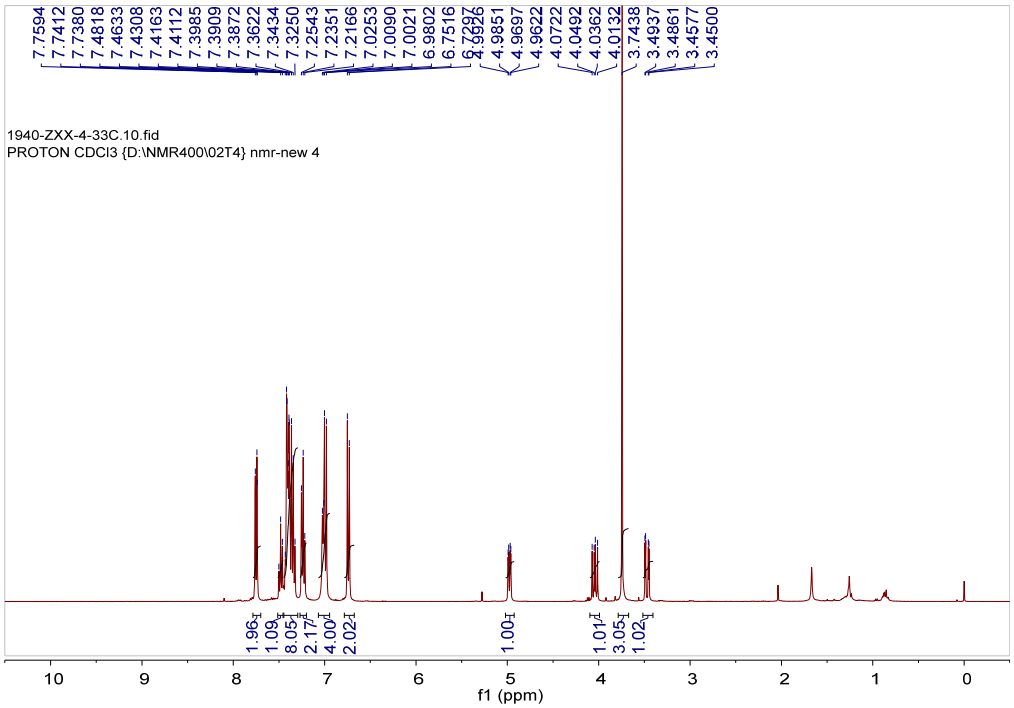


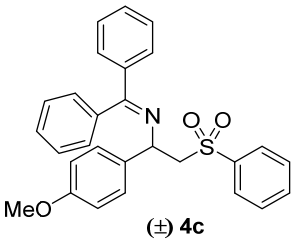
(±) **4b** **4b'**

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



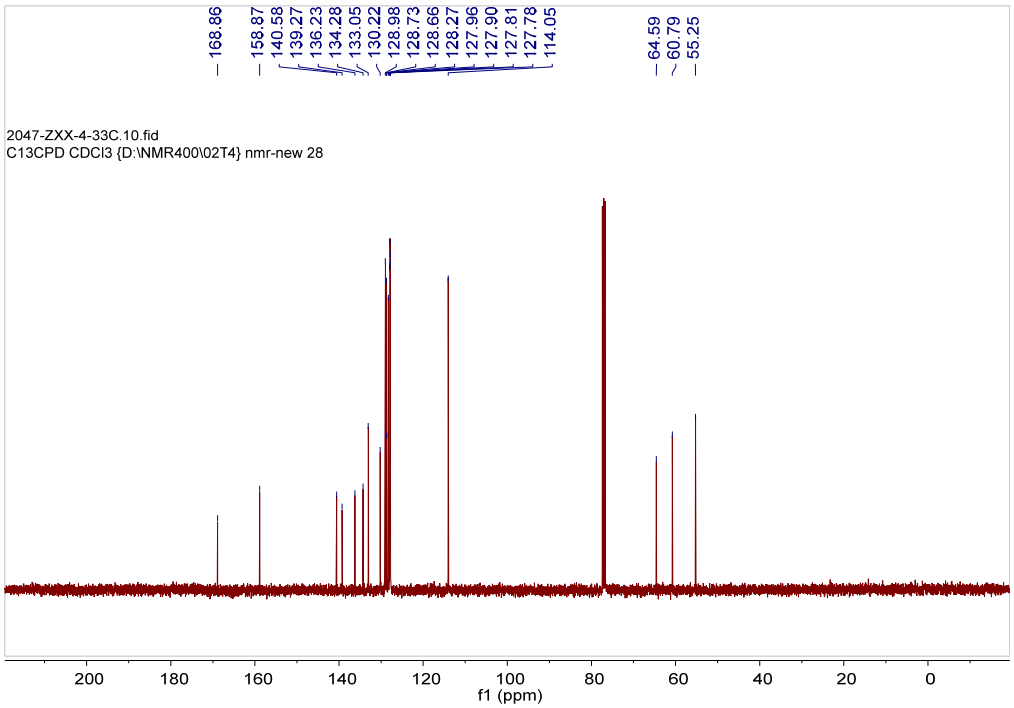


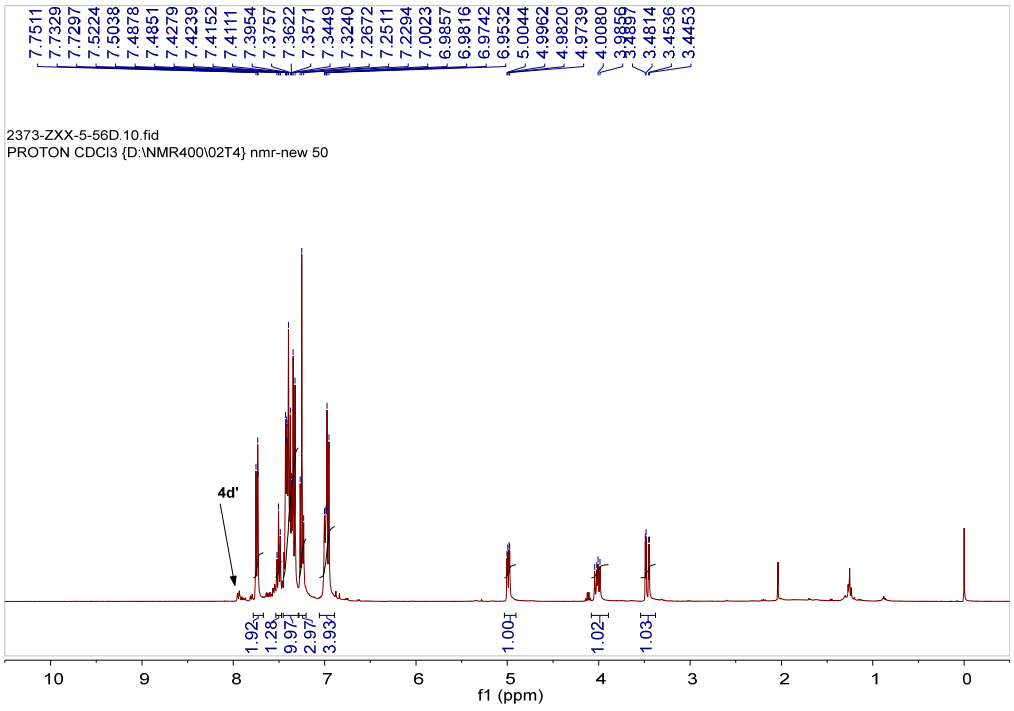


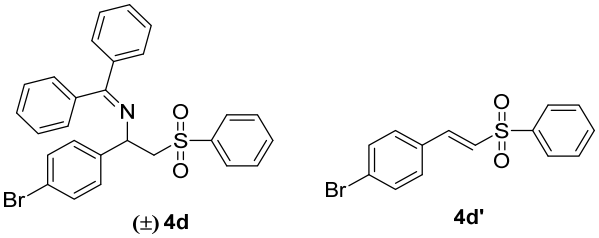
(±) 4c

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



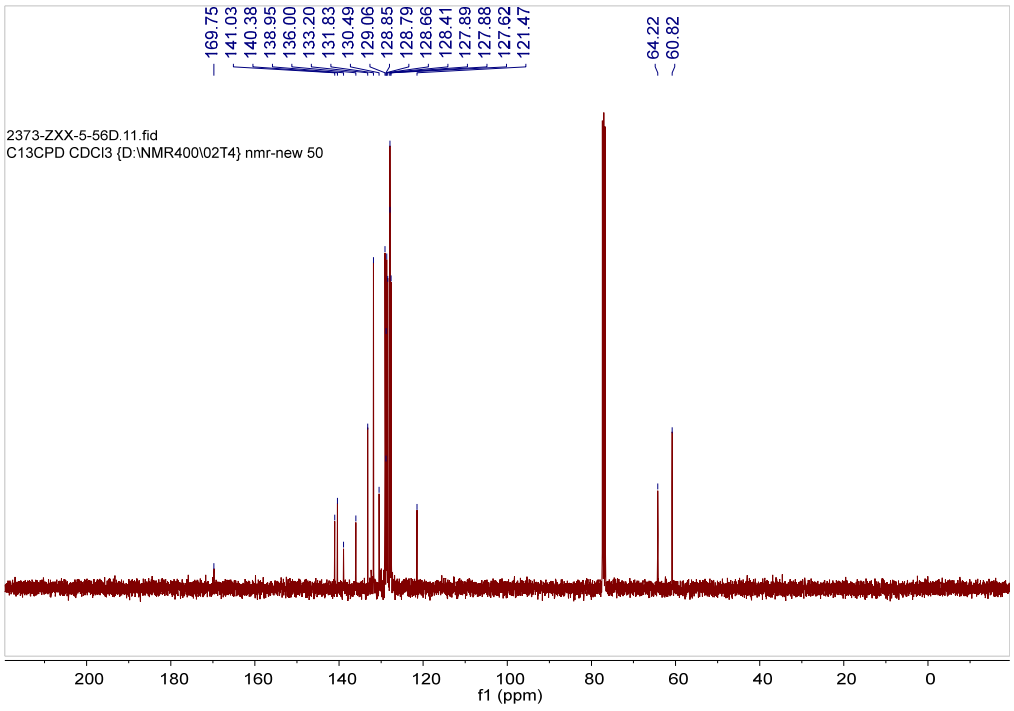


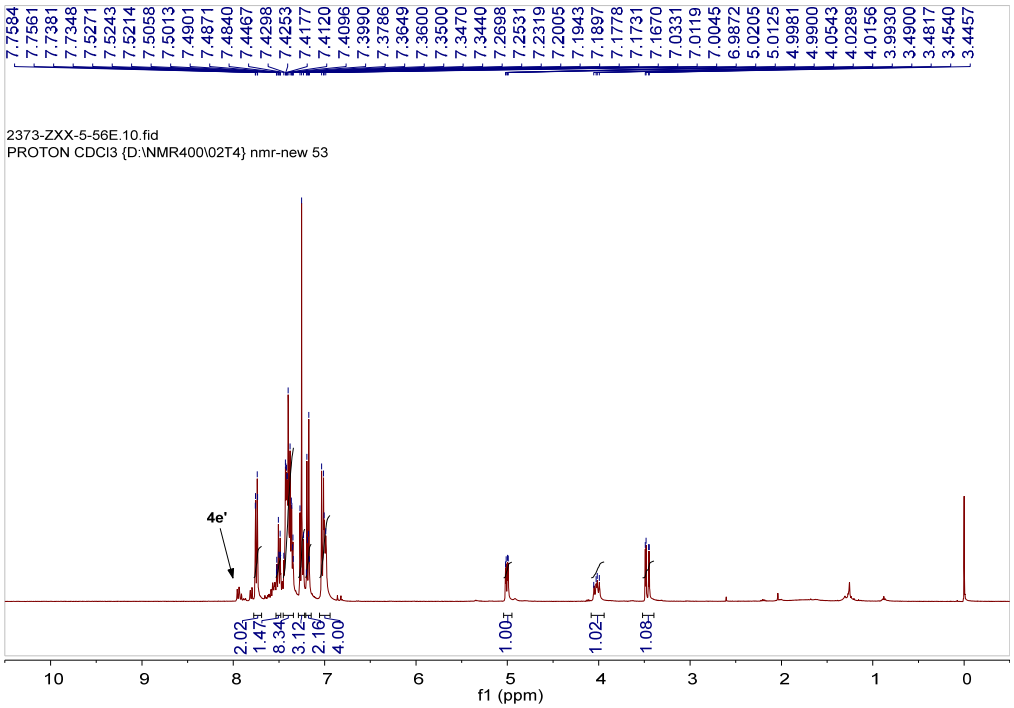


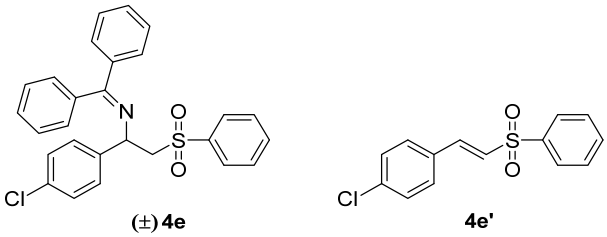
(±) **4d** **4d'**

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



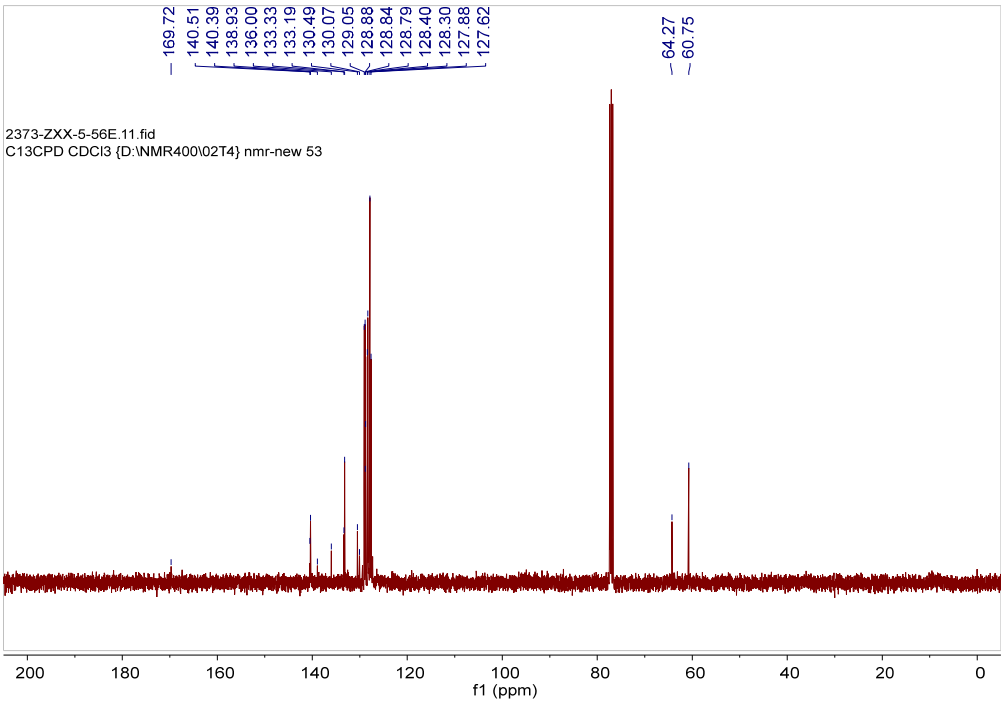


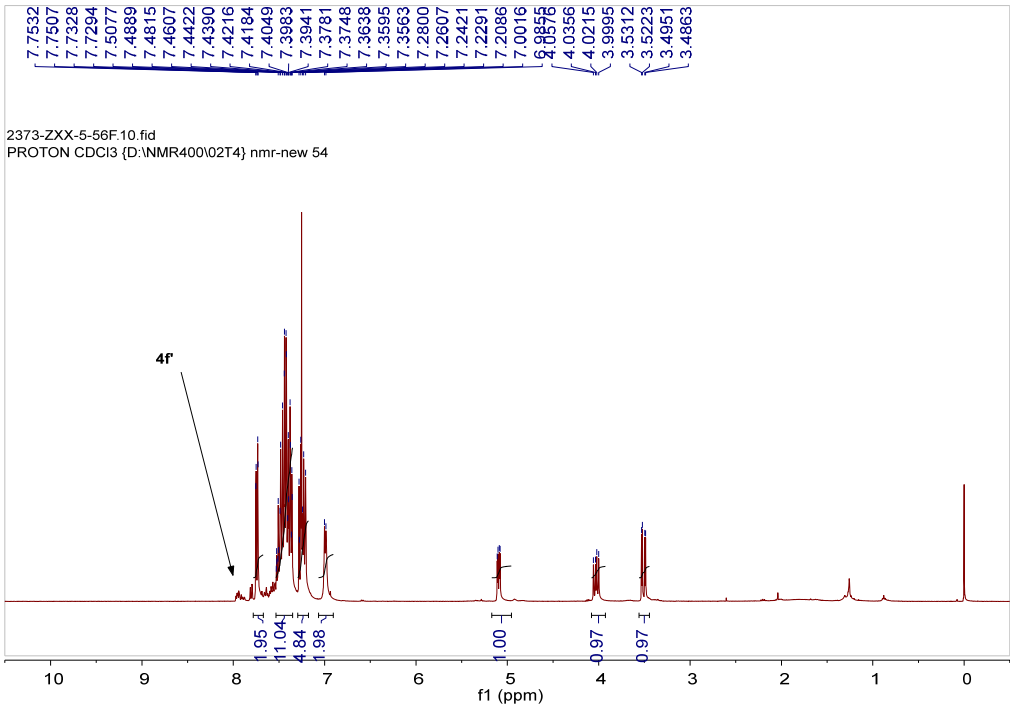


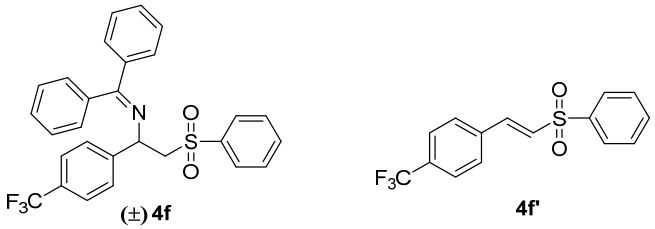
(±) **4e** **4e'**

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



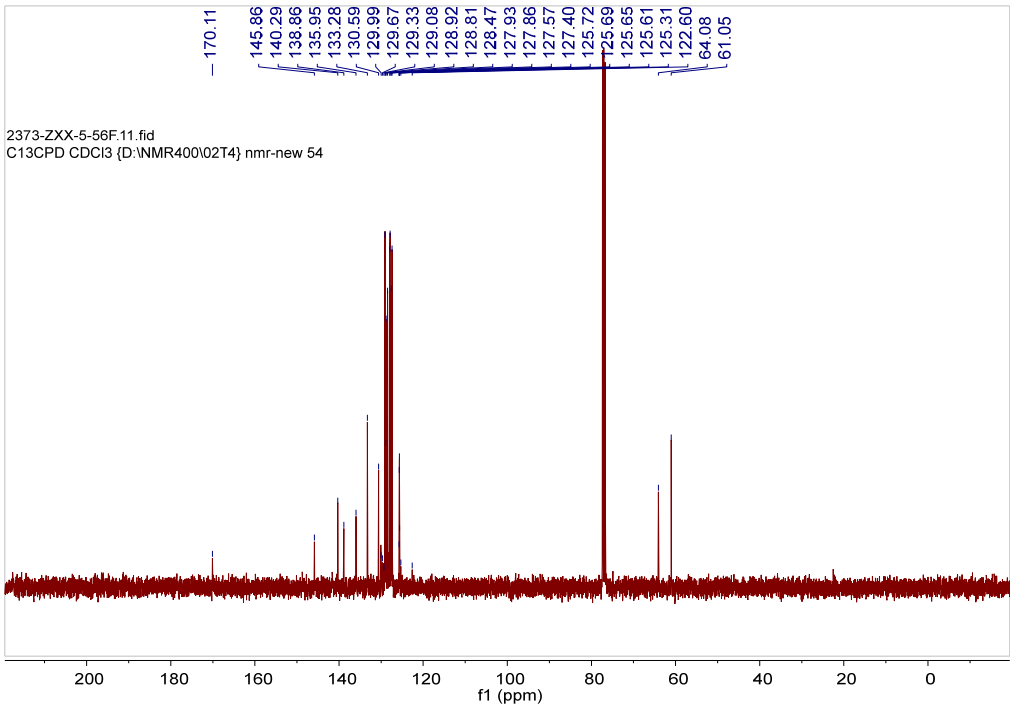


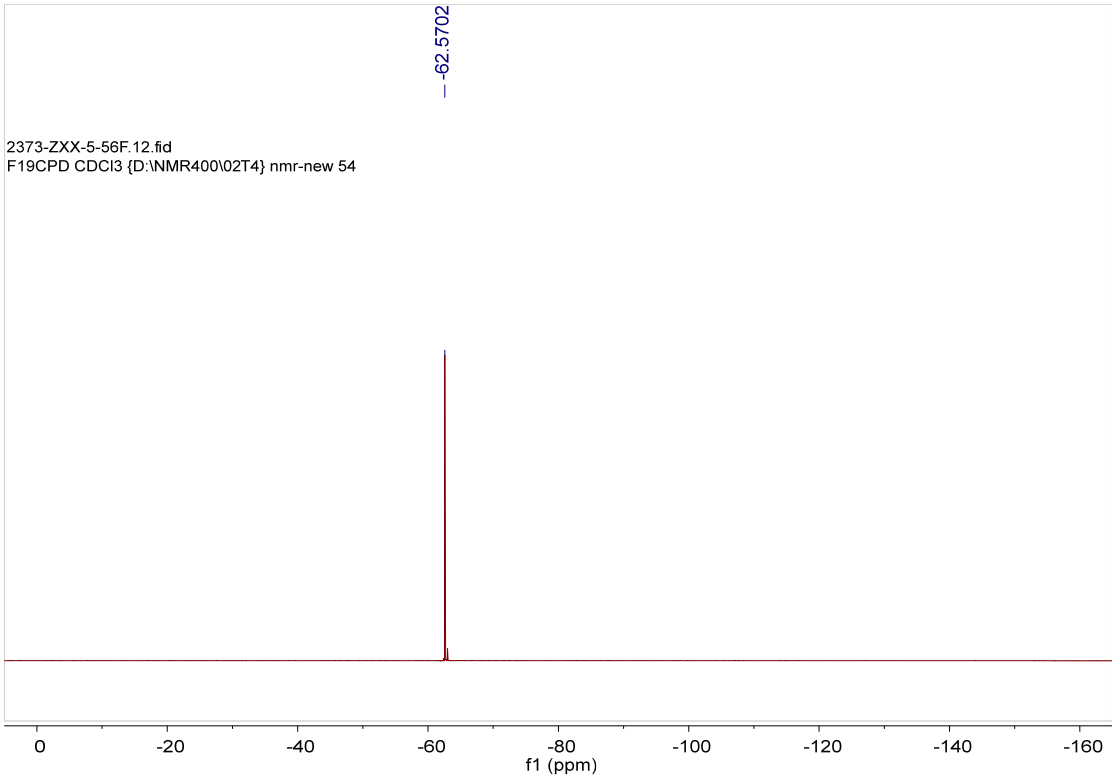


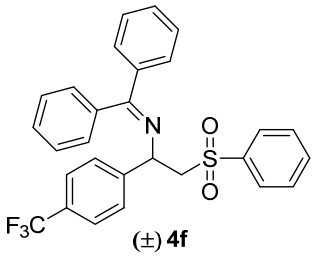
(±) **4f** **4f'**

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)

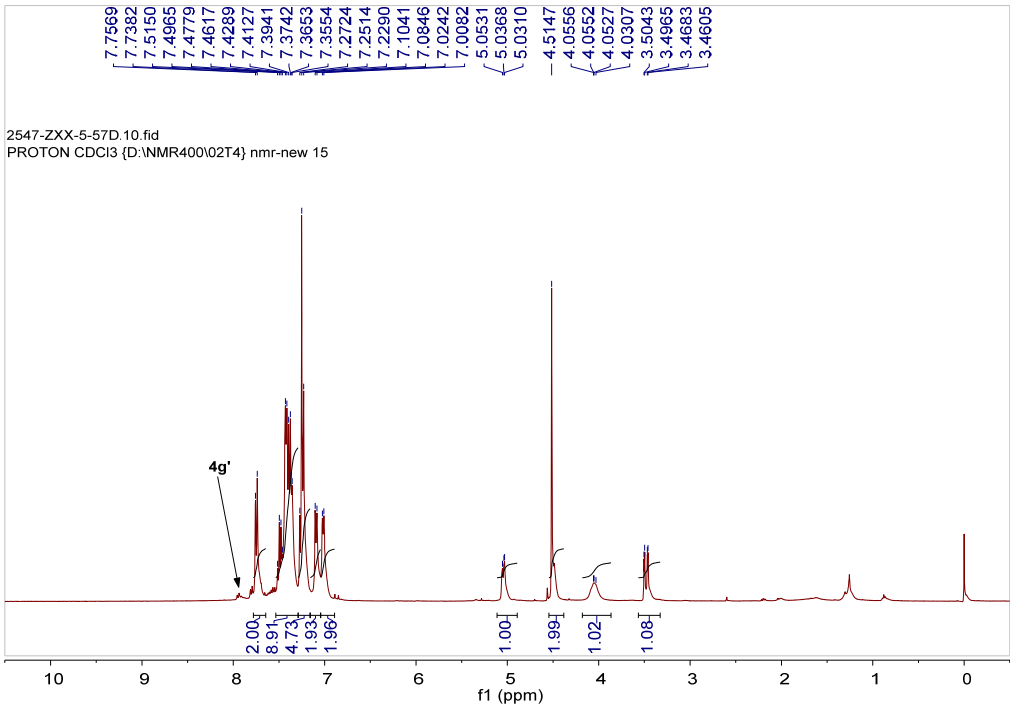


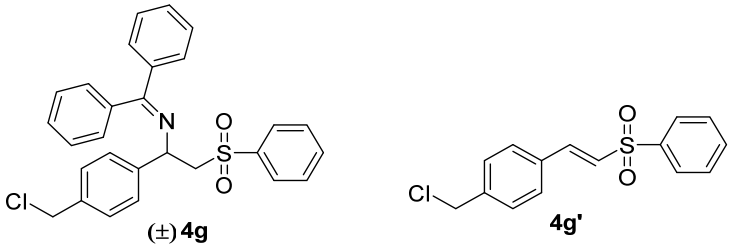




(±) **4f**

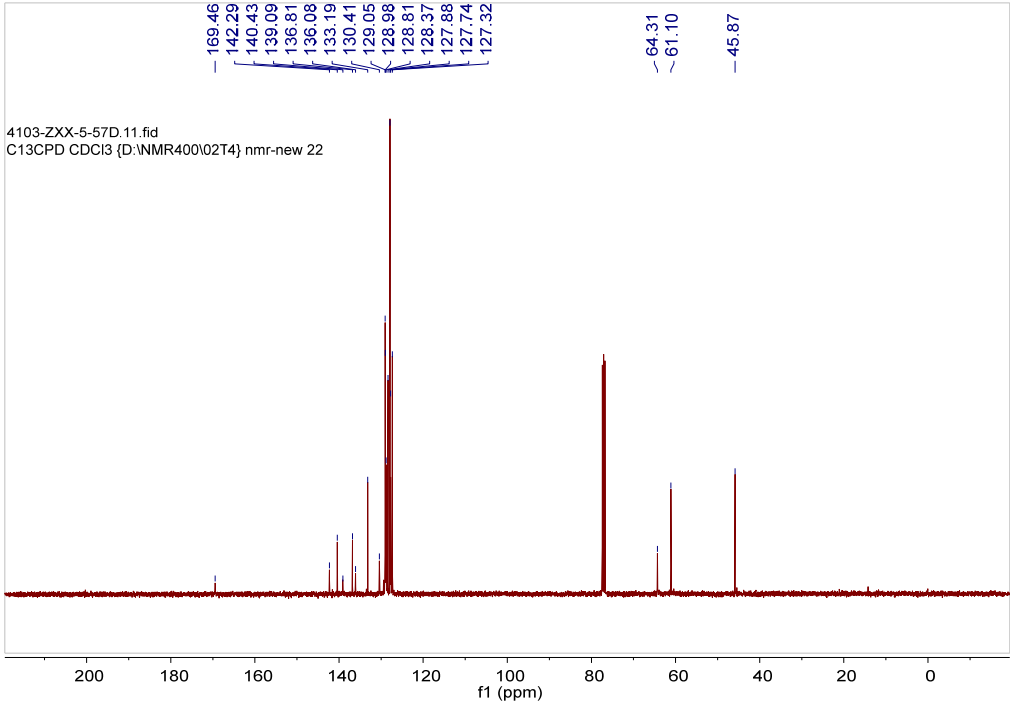
^{19}F NMR (375 MHz, Chloroform-*d*)

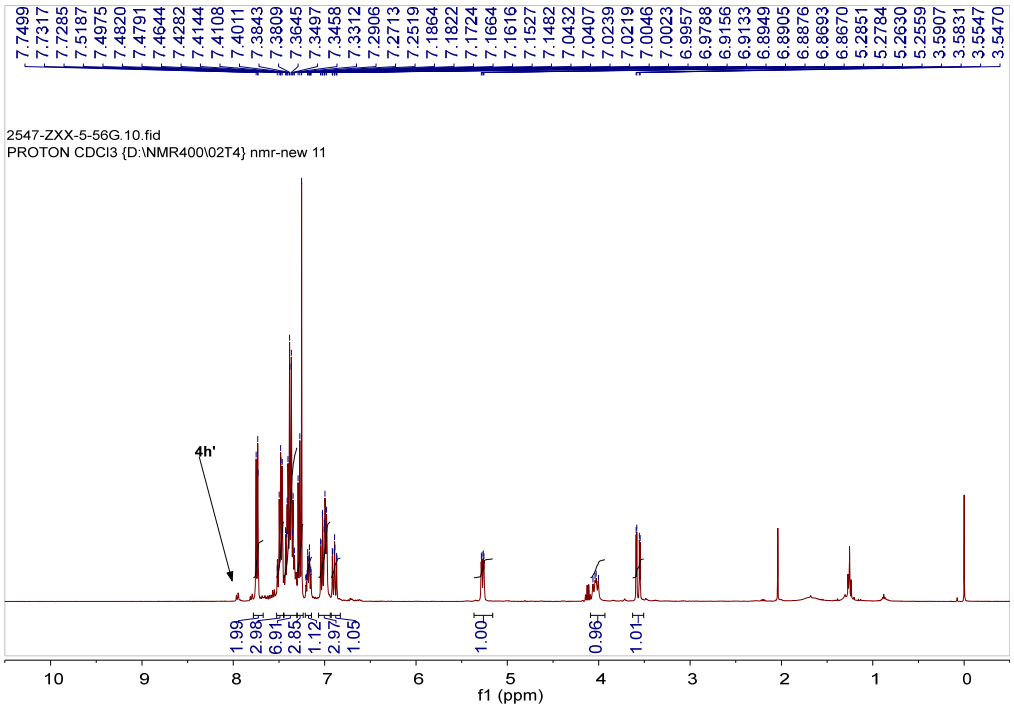


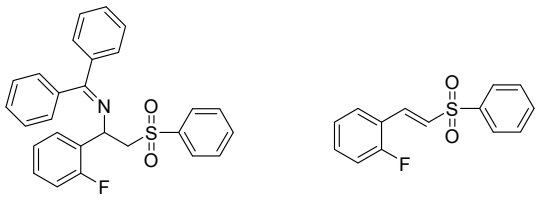


^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)

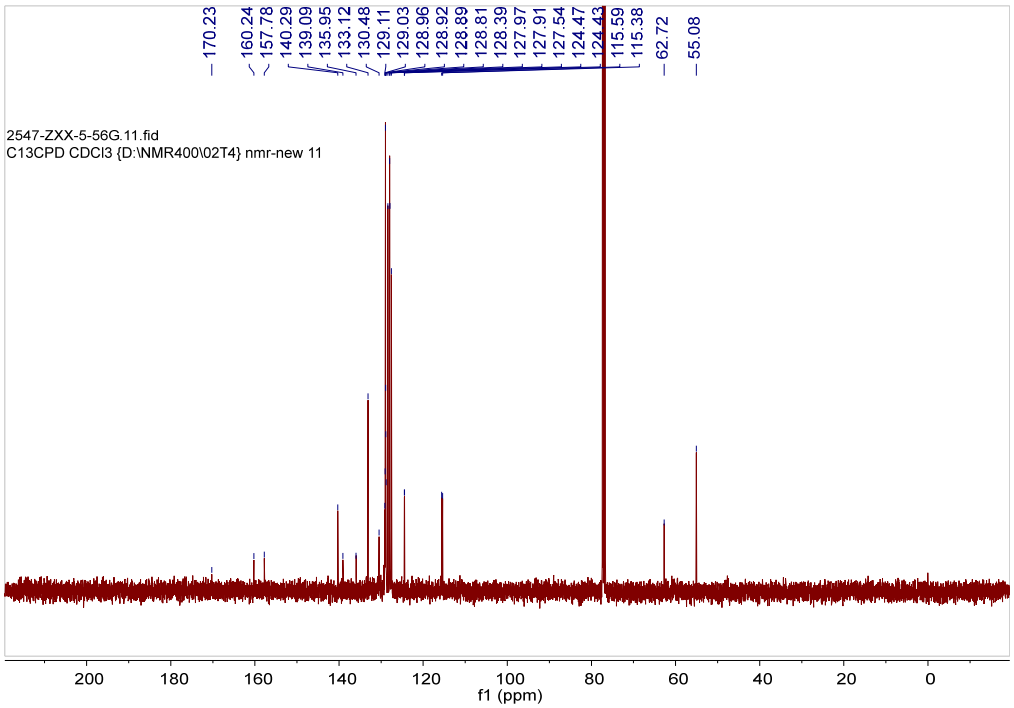


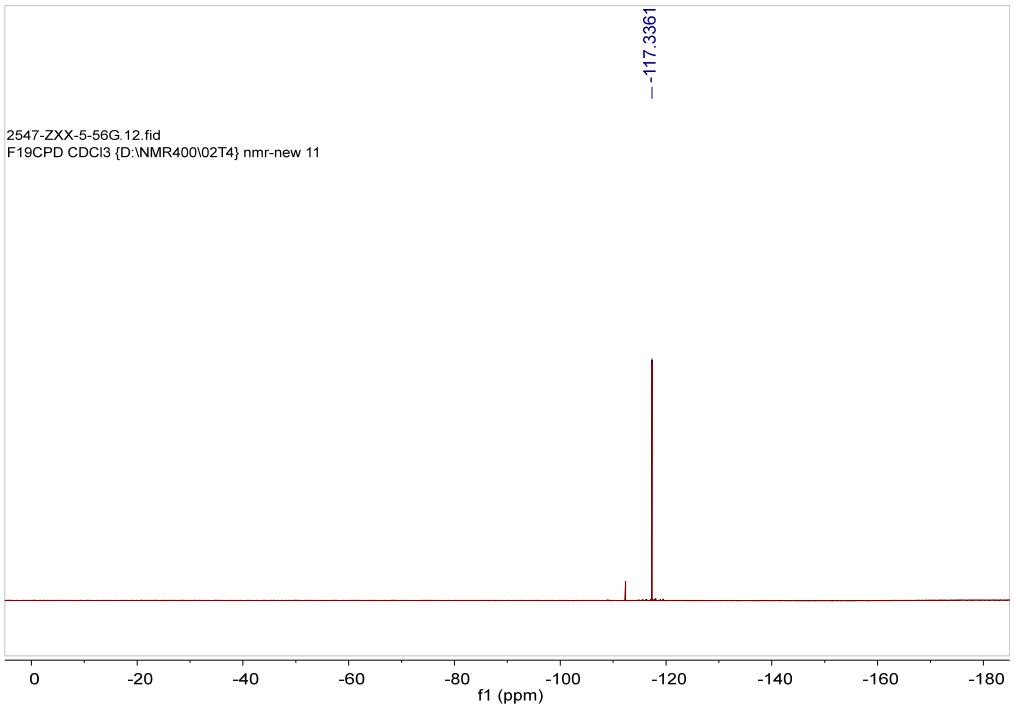


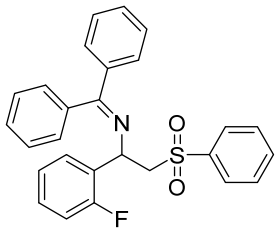


^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)

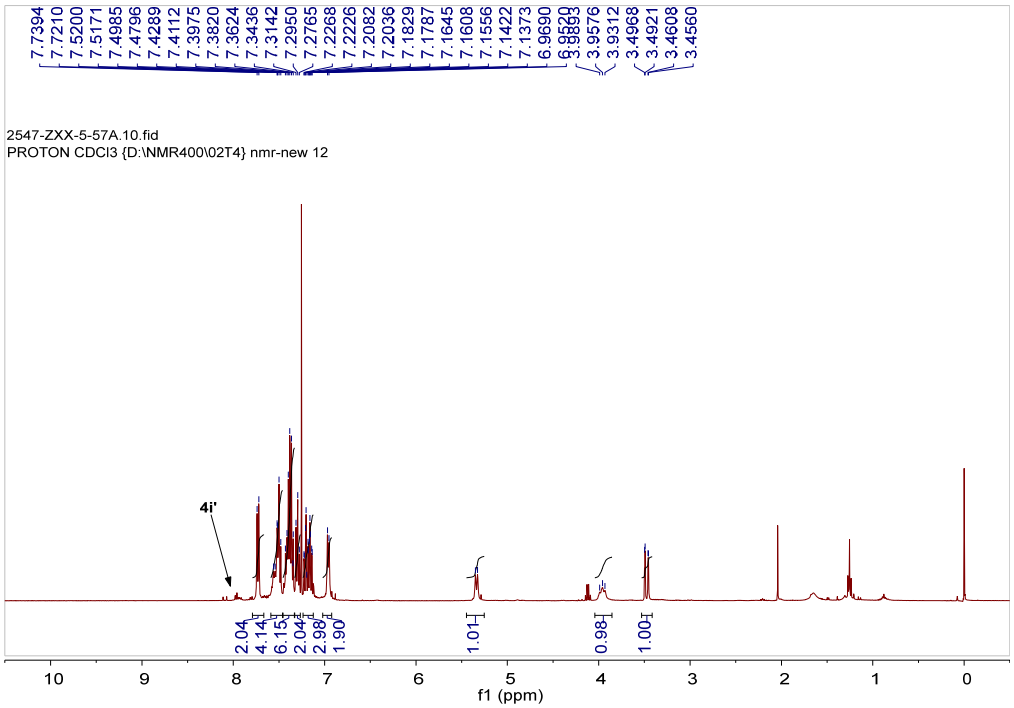


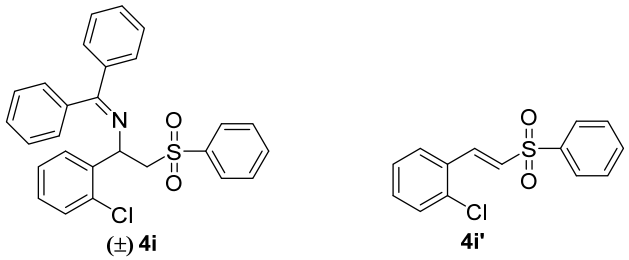




(±) 4h

^{19}F NMR (375 MHz, Chloroform-*d*)



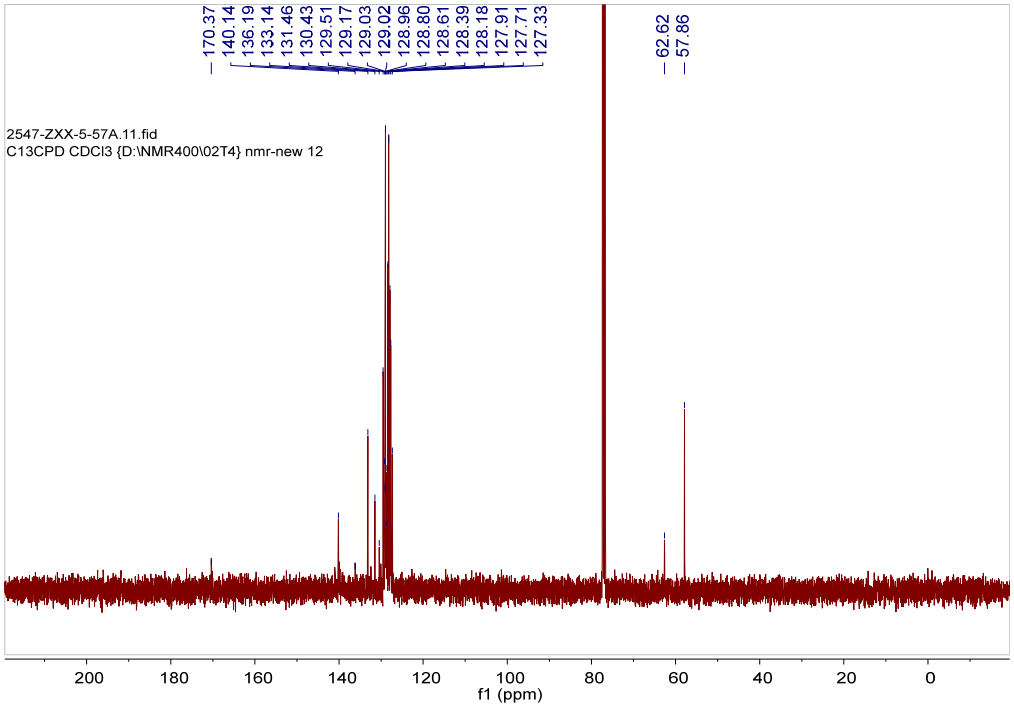


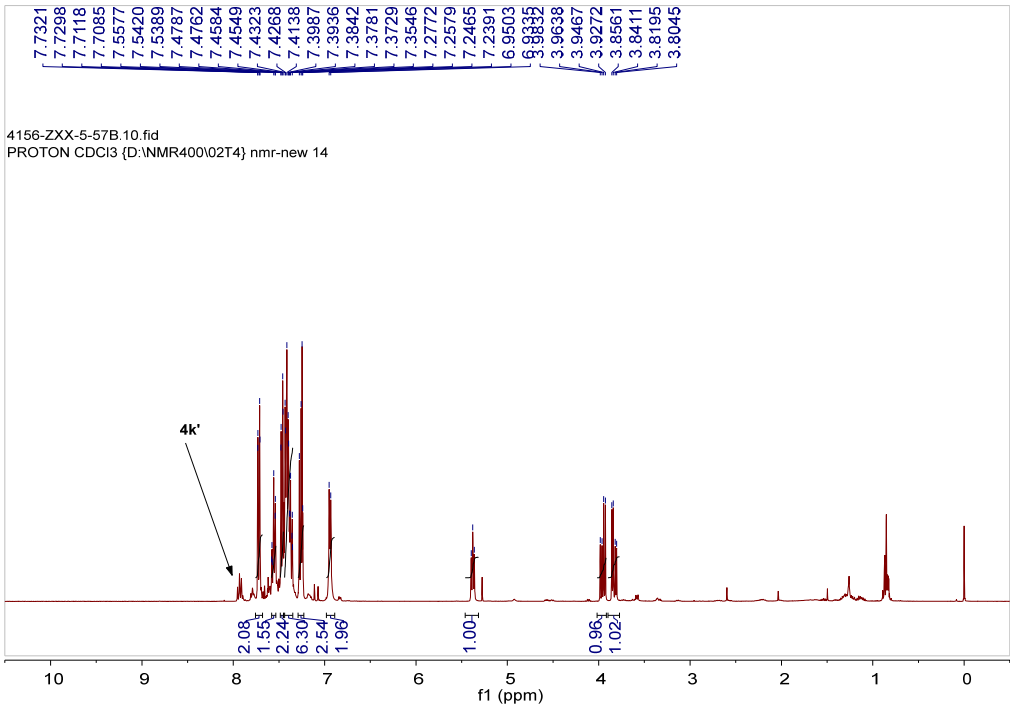
(±) **4i**

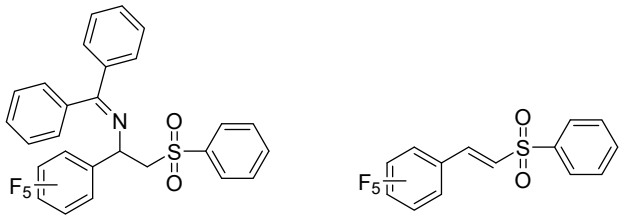
4i'

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



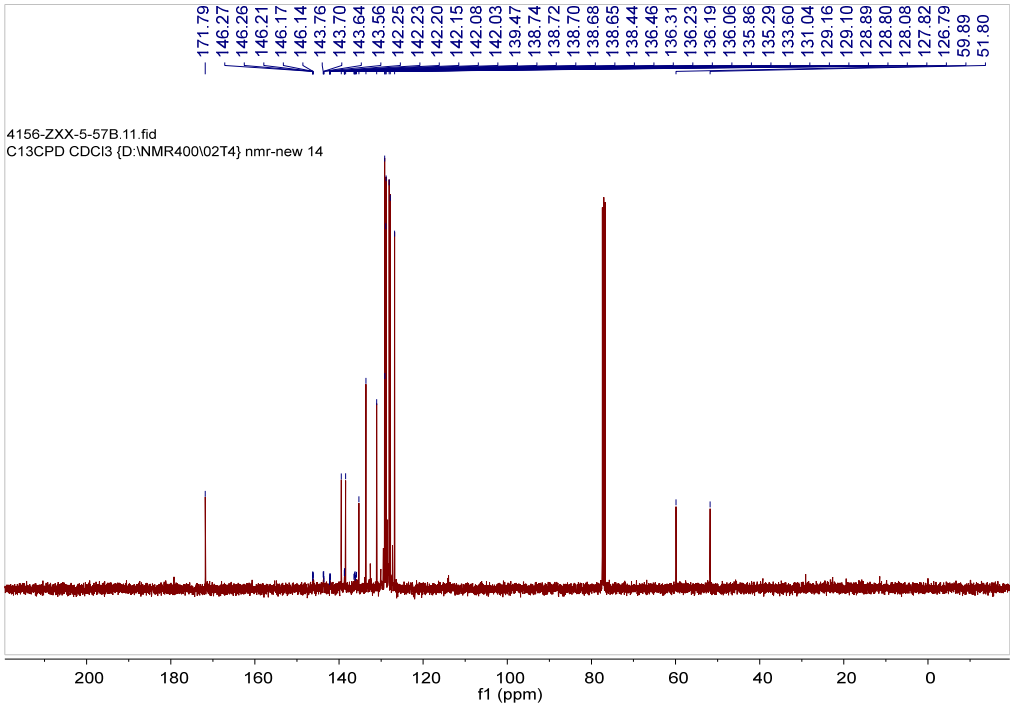


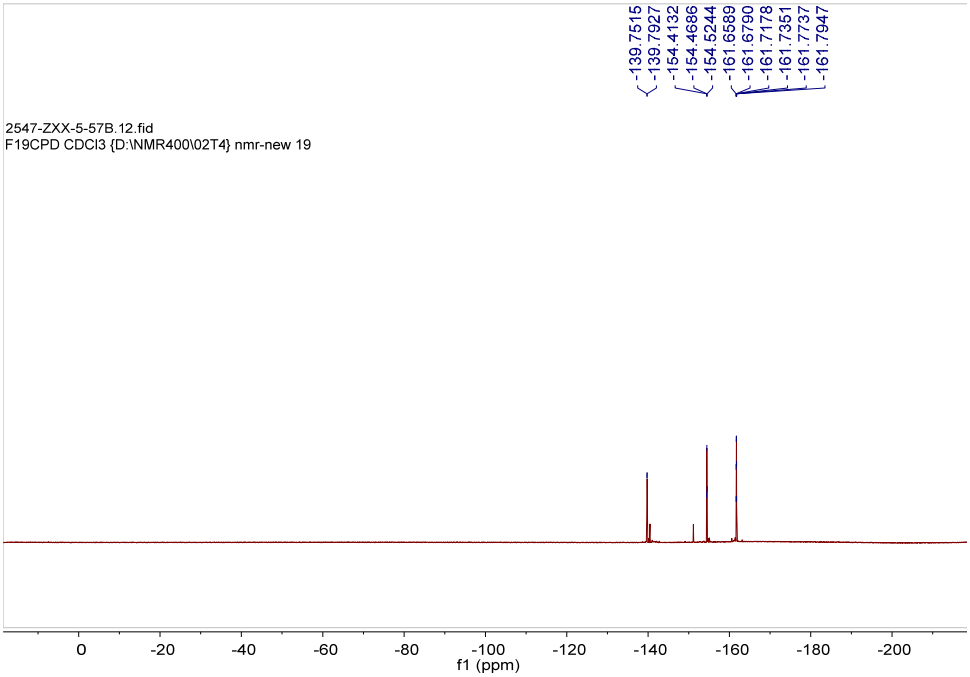


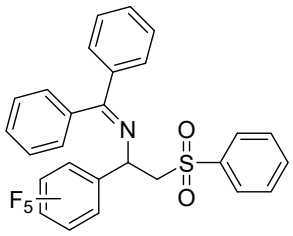
(±) **4k** **4k'**

[1]H NMR (400 MHz, Chloroform-*d*)

[13]C NMR (100 MHz, Chloroform-*d*)

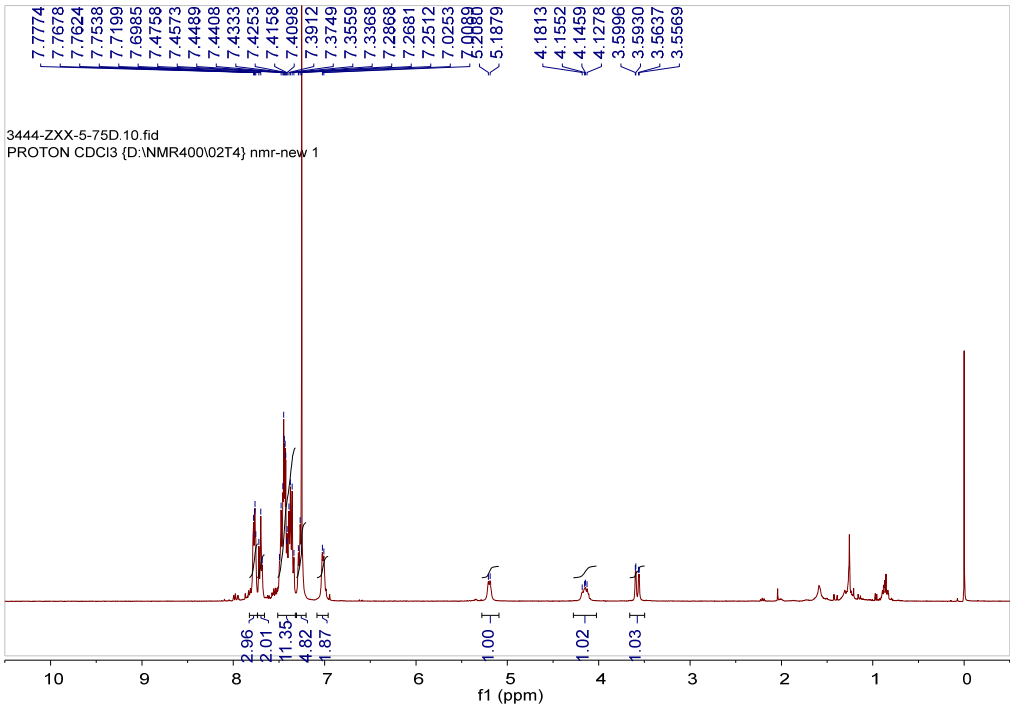


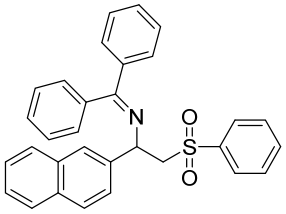




(±) 4k

^{19}F NMR (375 MHz, Chloroform-*d*)

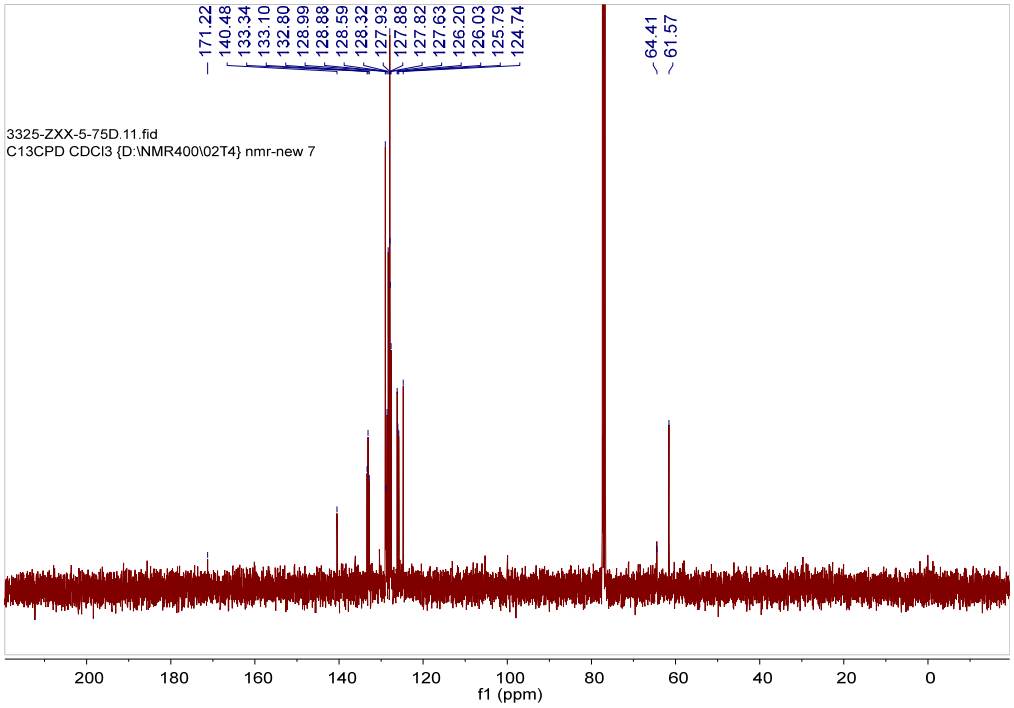


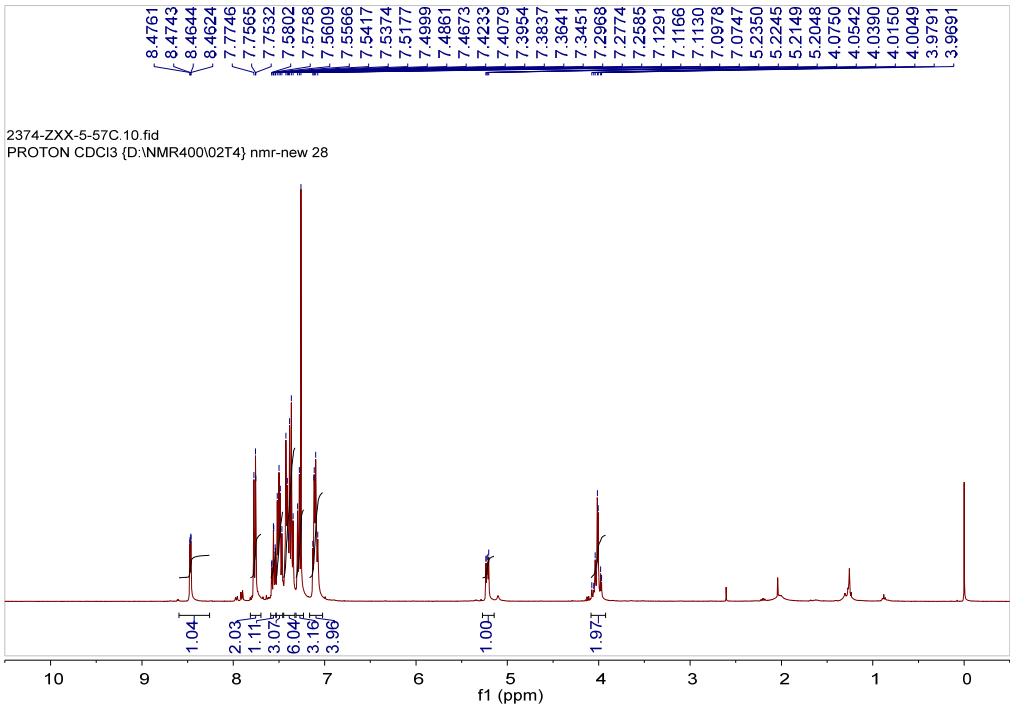


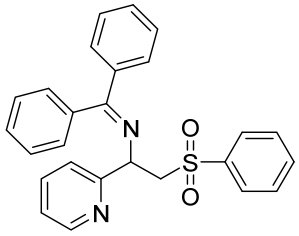
(±)**4k**

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



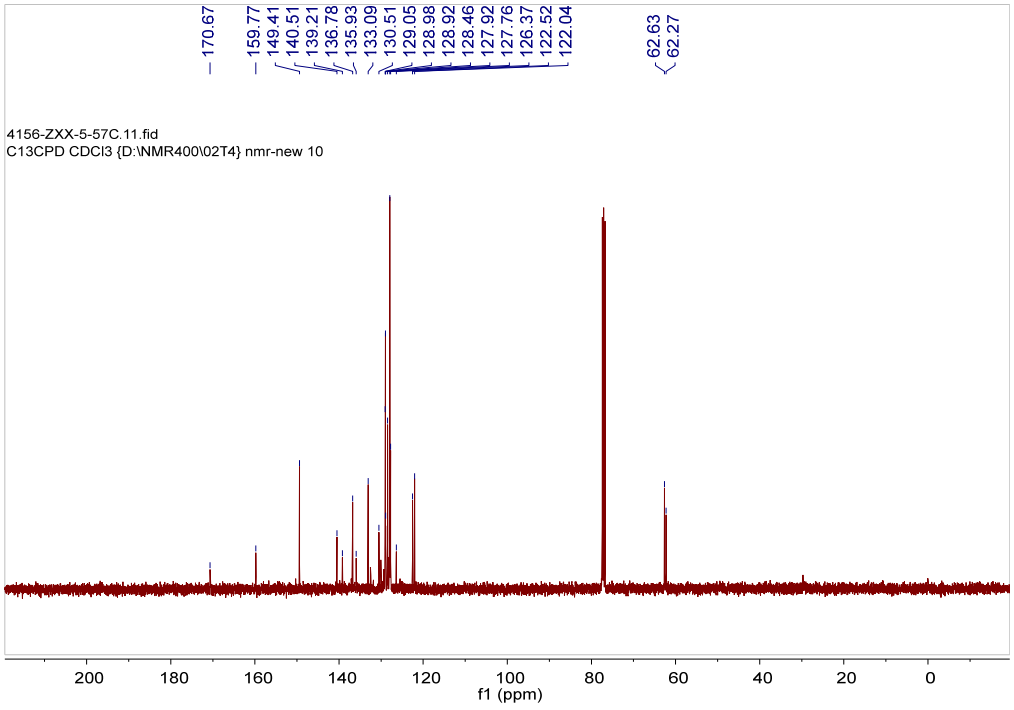


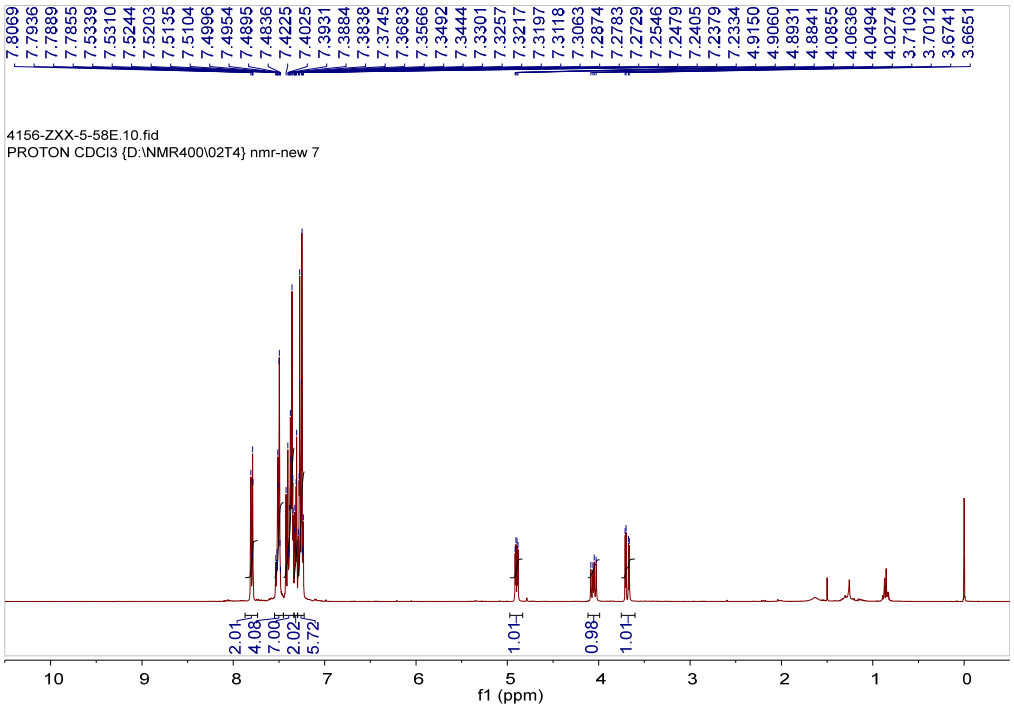


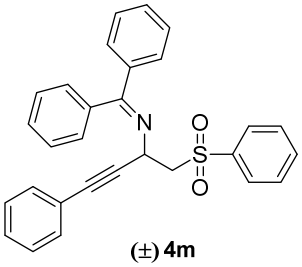
(±) 4l

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



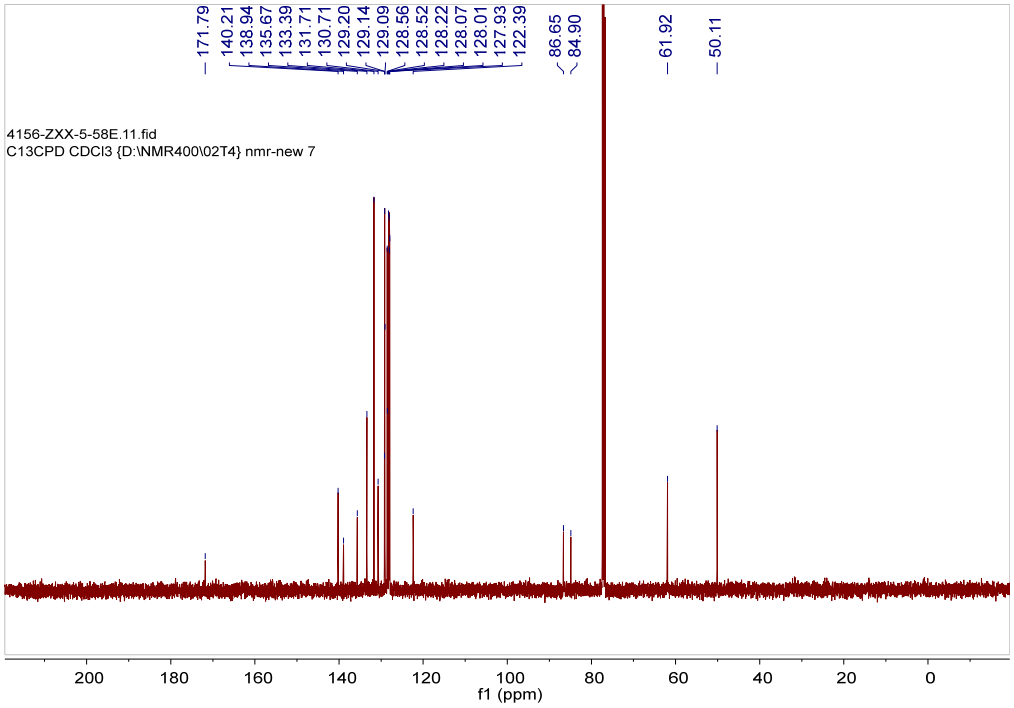


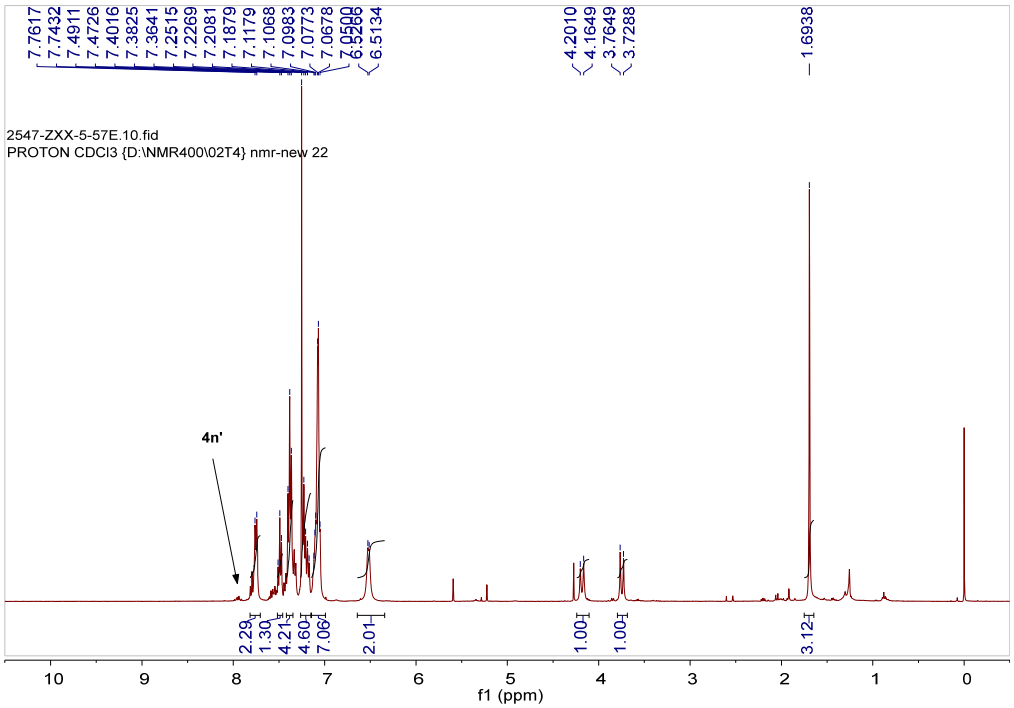


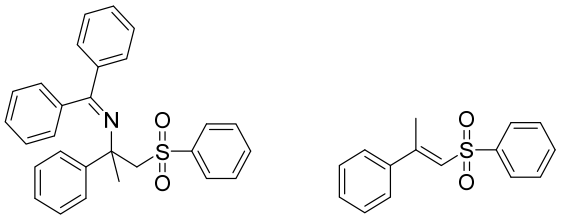
(±) **4m**

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



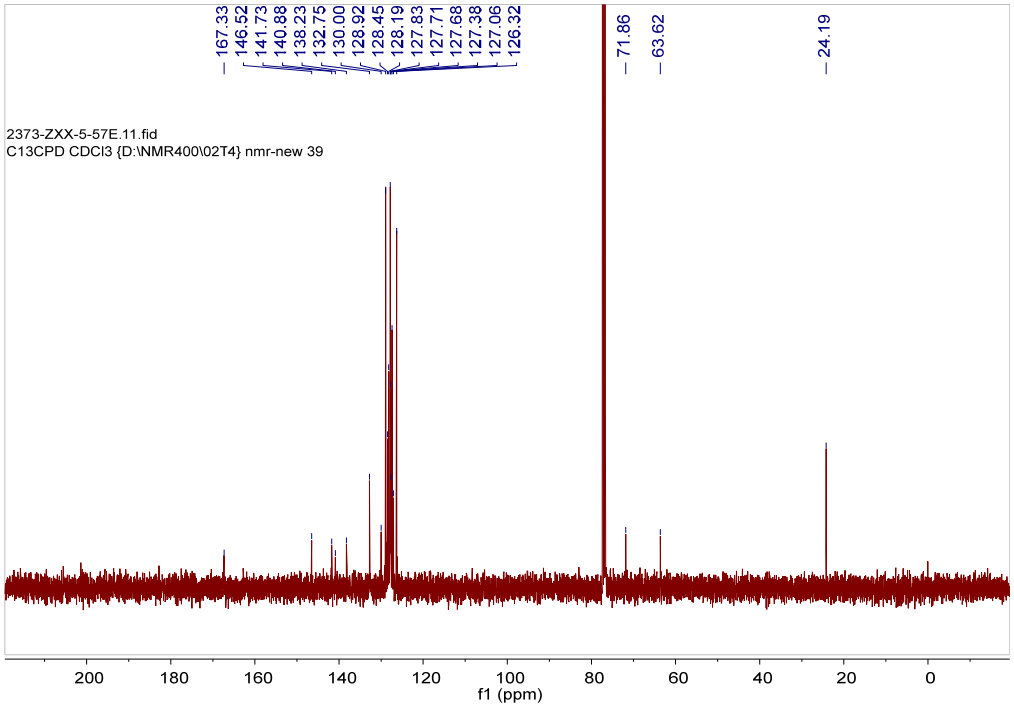


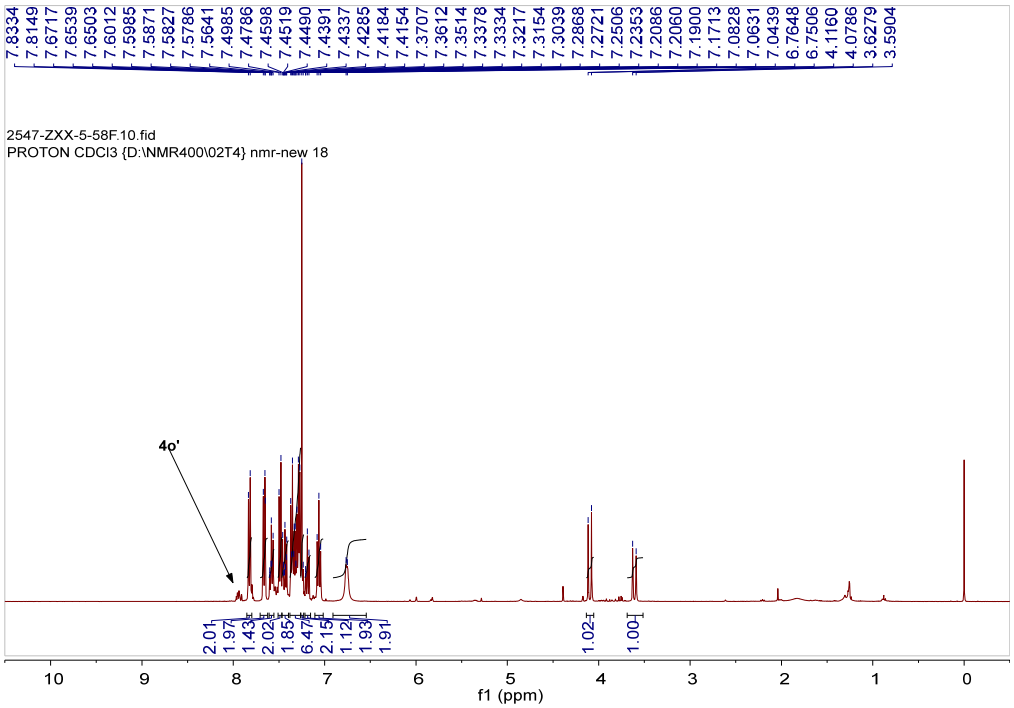


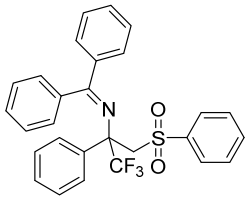
(±)**4n** **4n'**

^{1}H NMR (400 MHz, Chloroform-*d*)

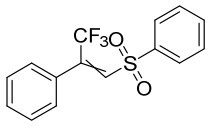
^{13}C NMR (100 MHz, Chloroform-*d*)







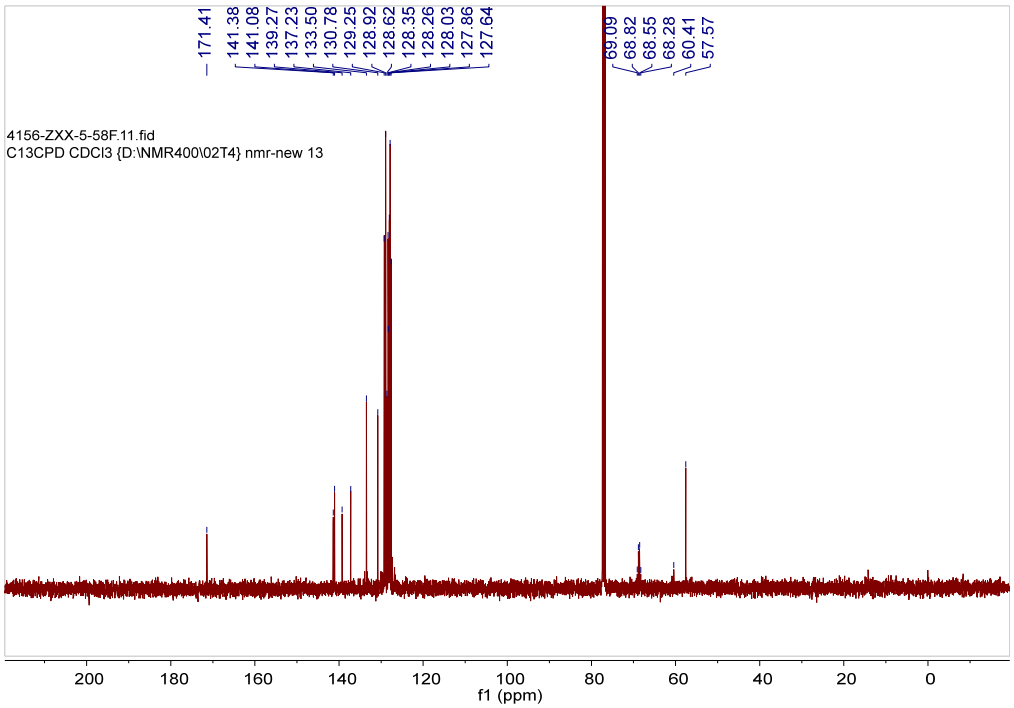
(±) **4o**

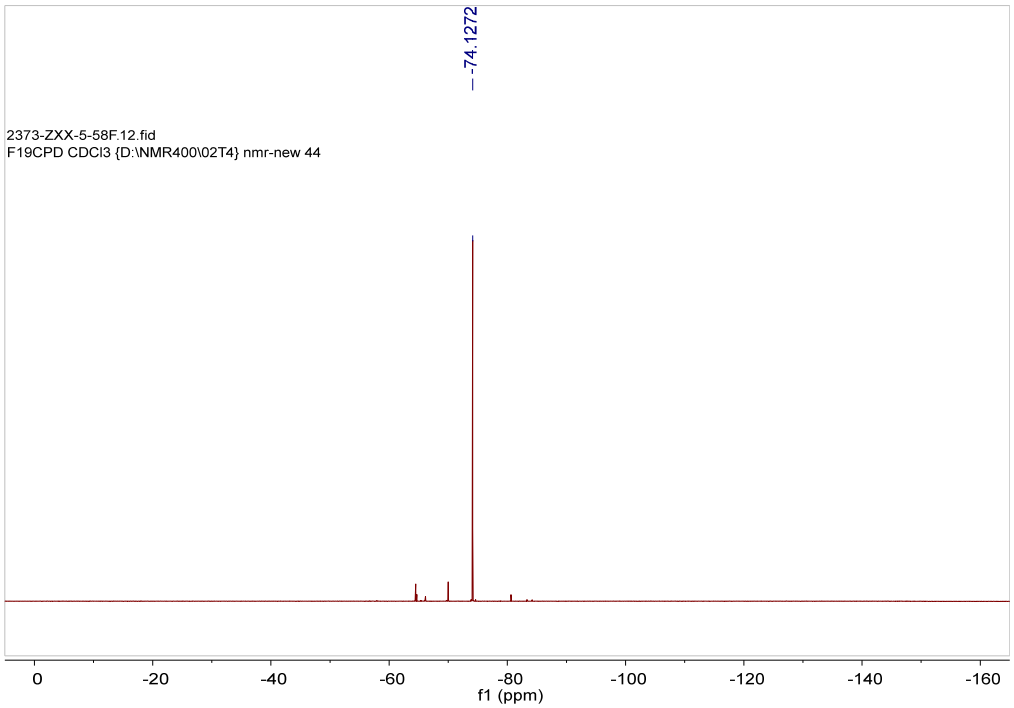


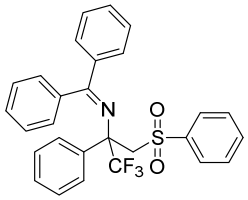
4o'

^{1}H NMR (400 MHz, Chloroform-*d*)

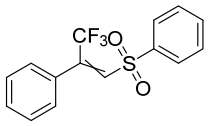
^{13}C NMR (100 MHz, Chloroform-*d*)





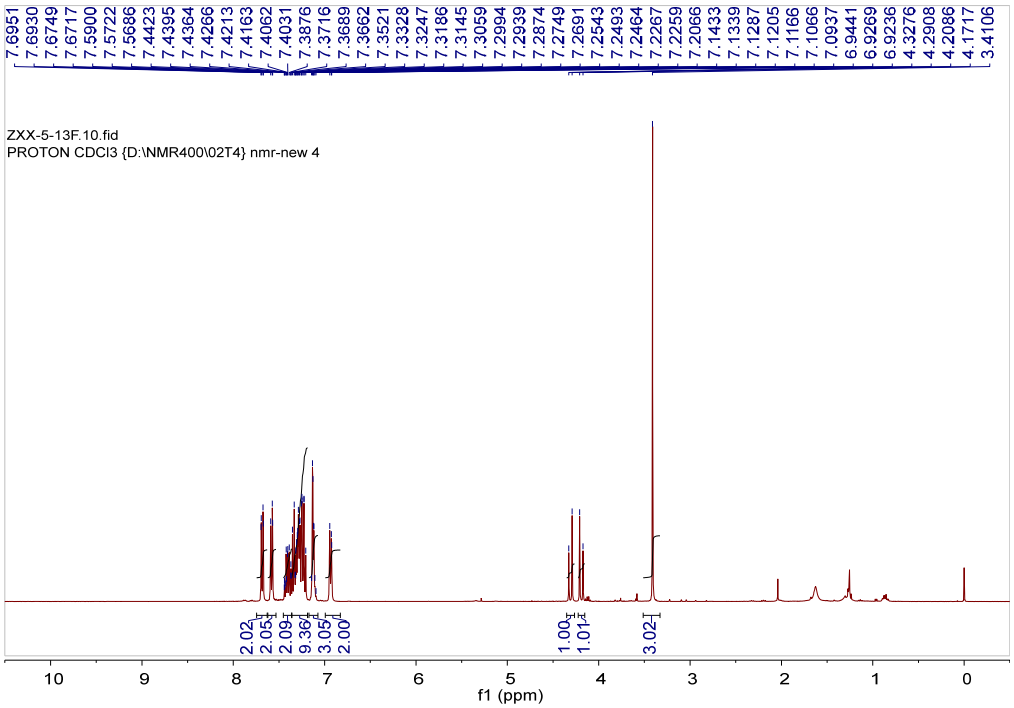


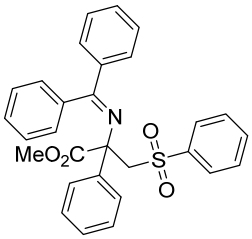
(±)**4o**



4o'

^{19}F NMR (375 MHz, Chloroform-*d*)

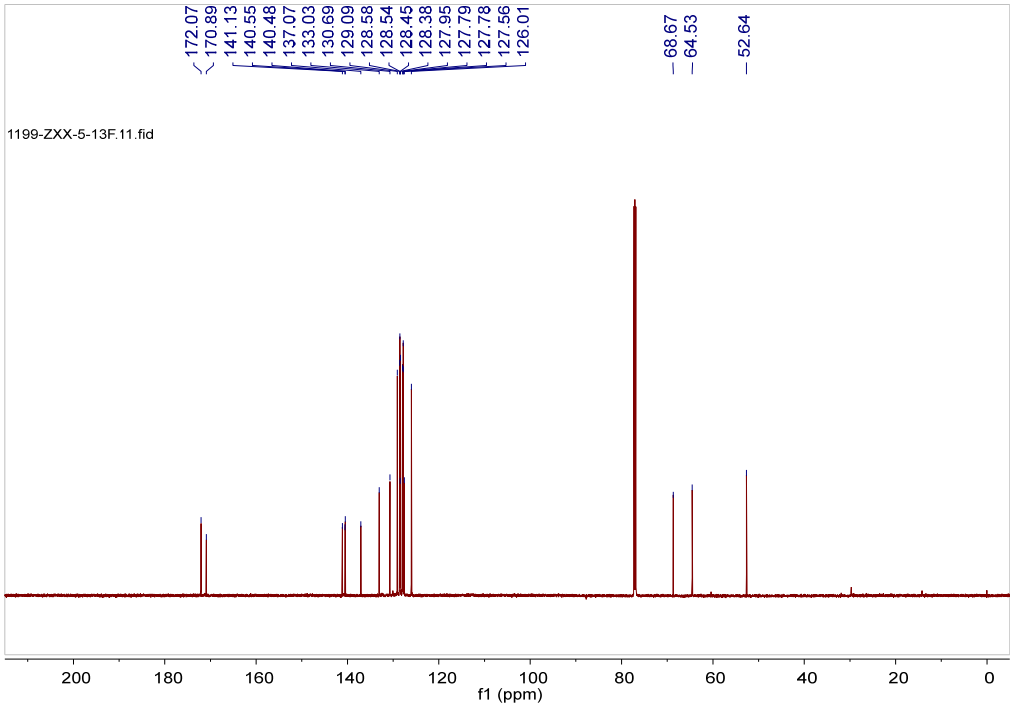


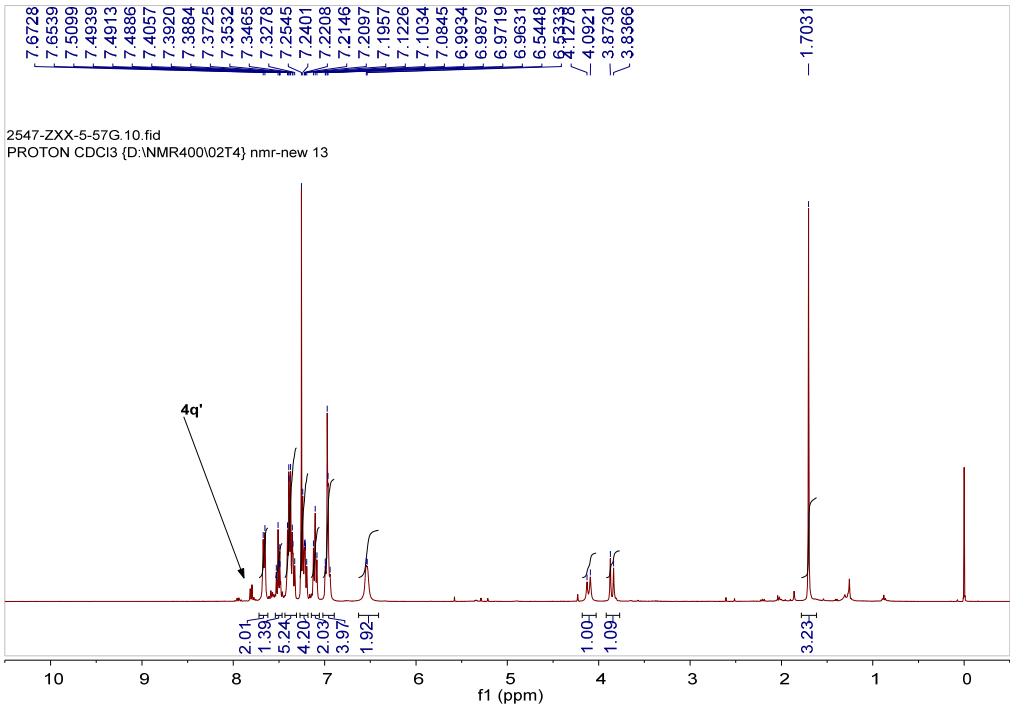


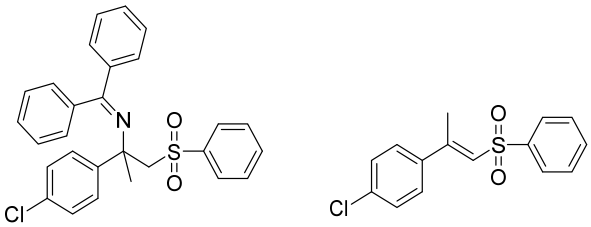
(±) **4p**

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (175 MHz, Chloroform-*d*)



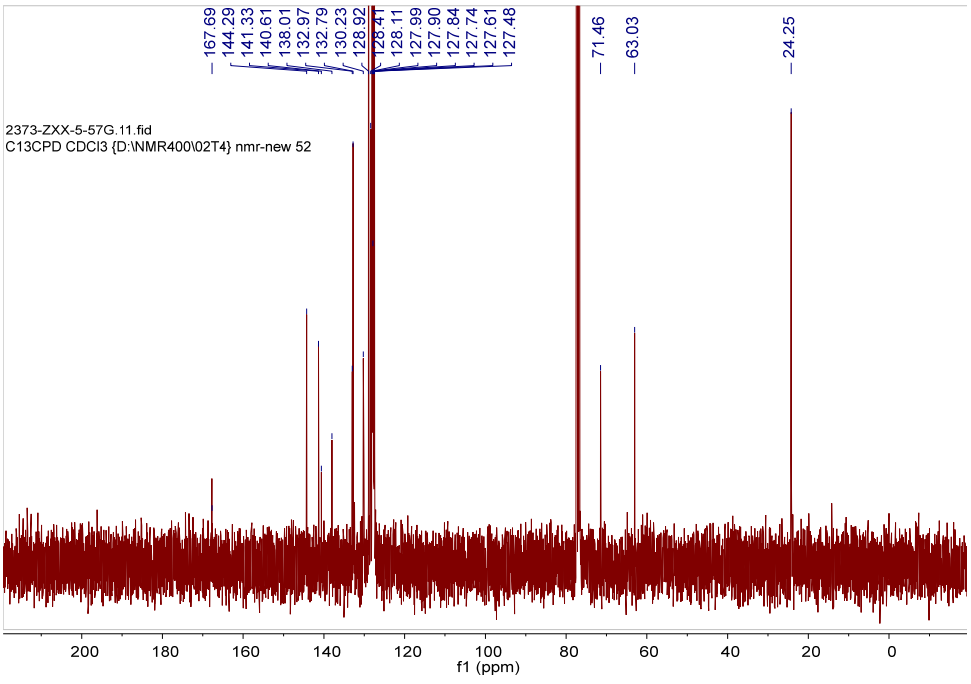


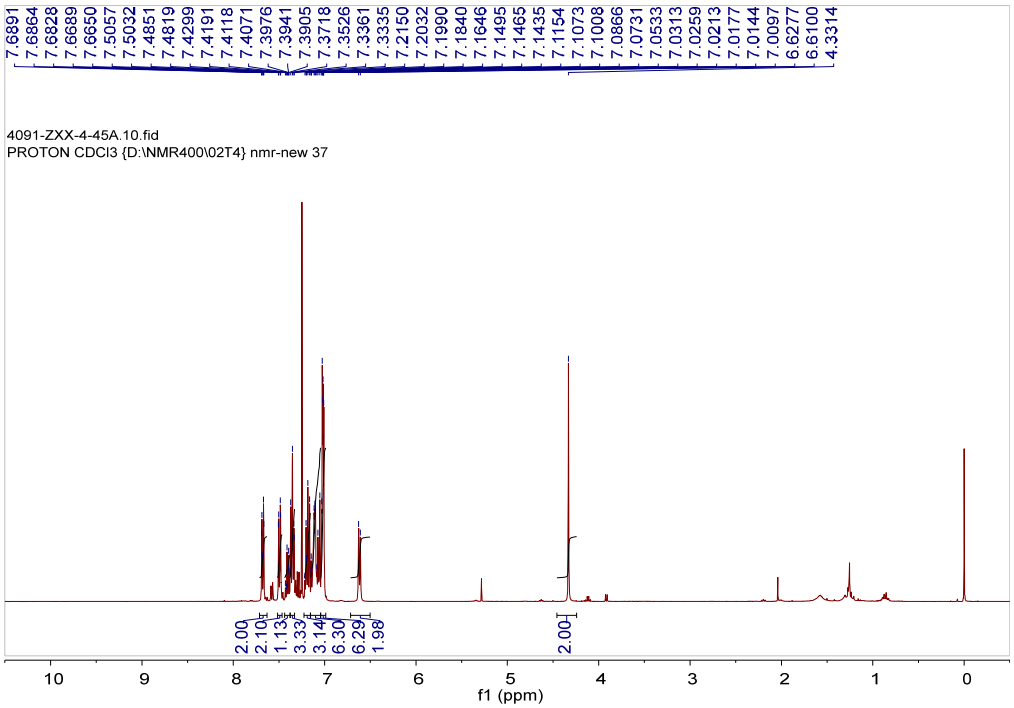


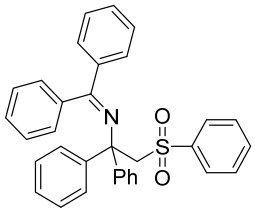
(±) **4q** **4q'**

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



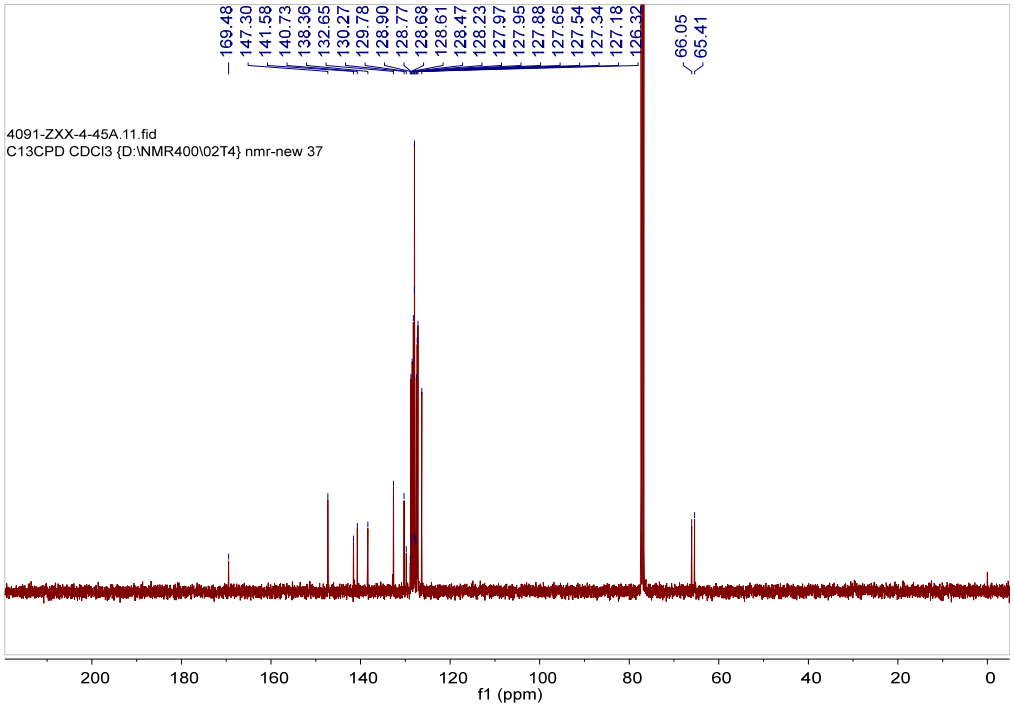


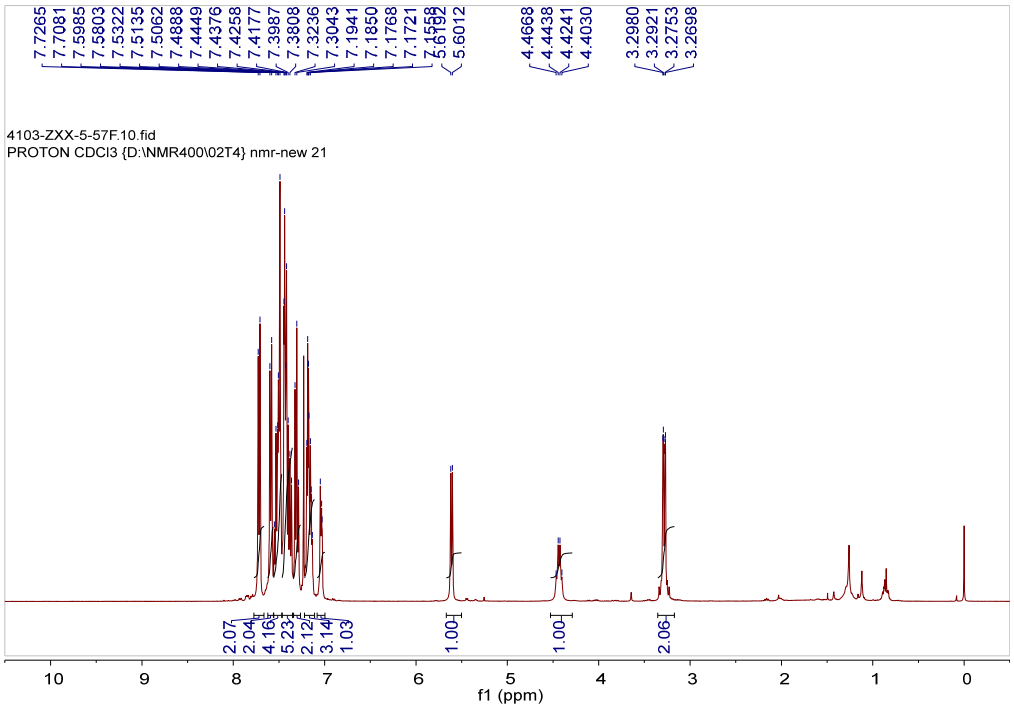


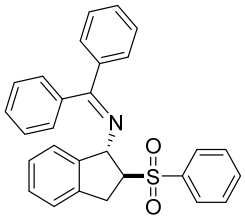
(±) **4r**

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



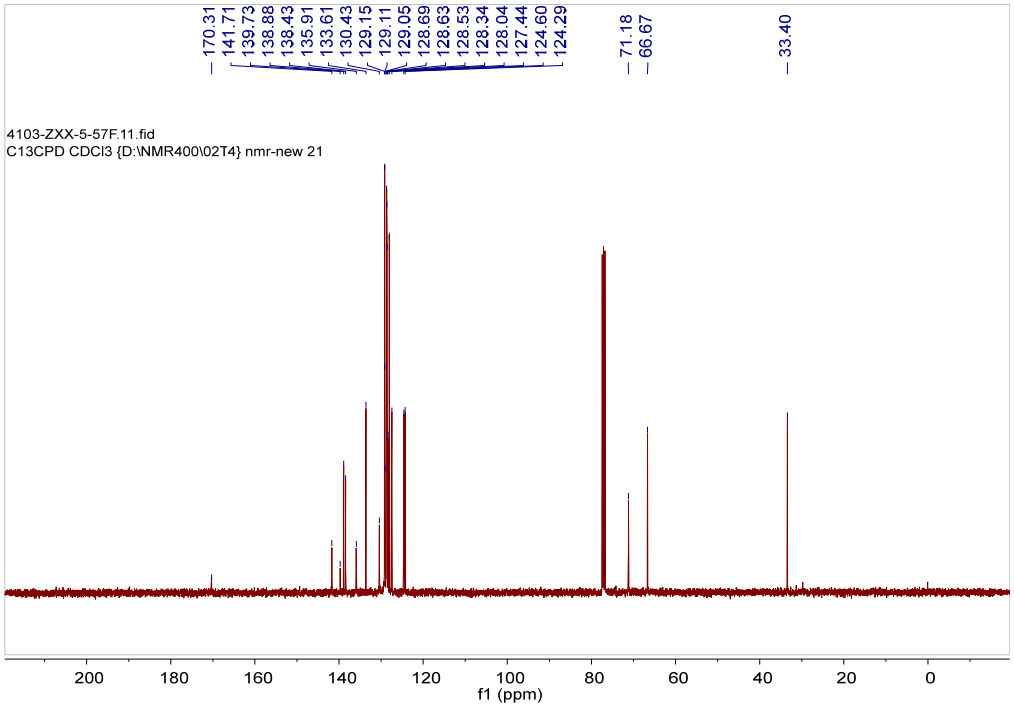


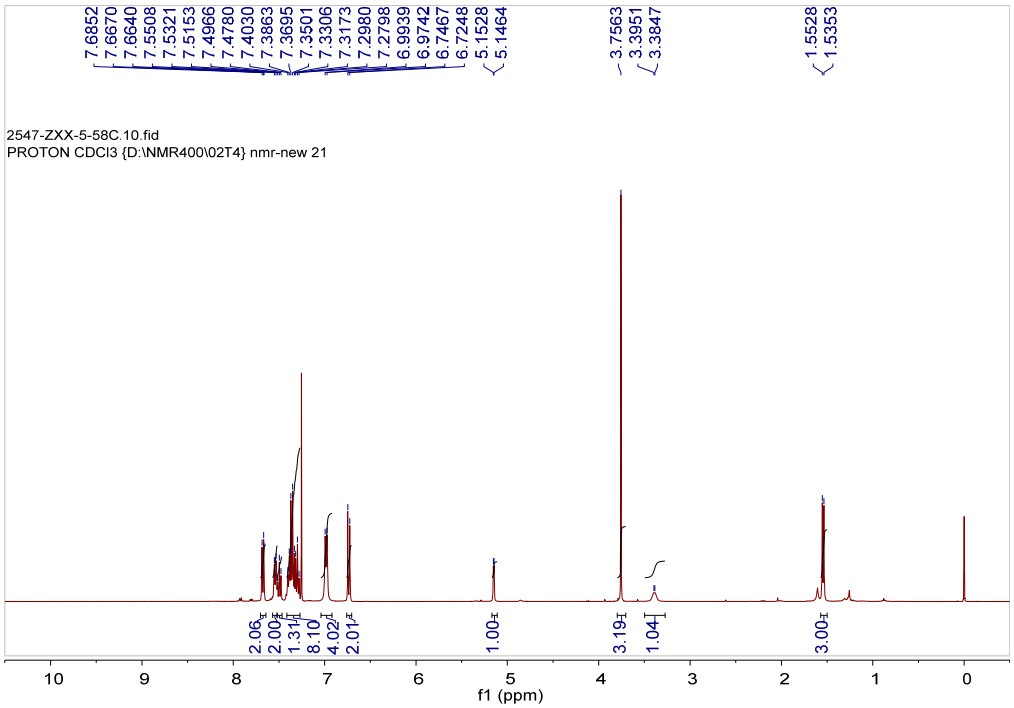


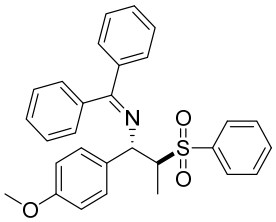
(±) **4s**

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



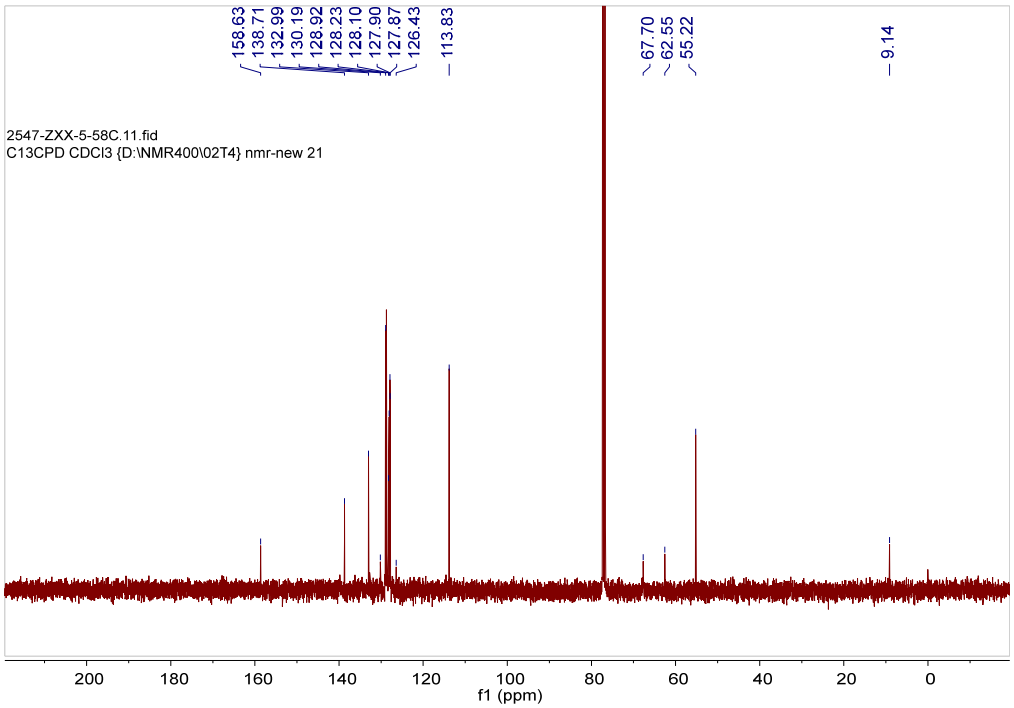


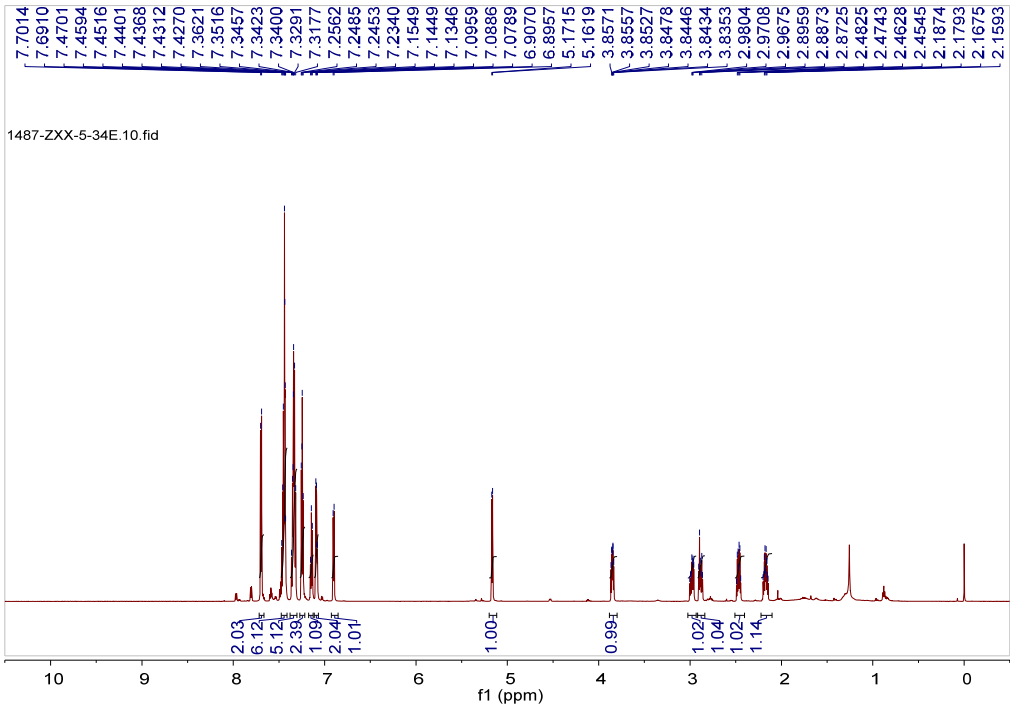


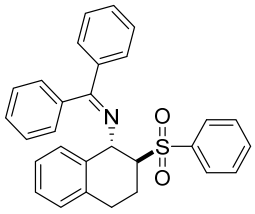
(±) **4t**

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



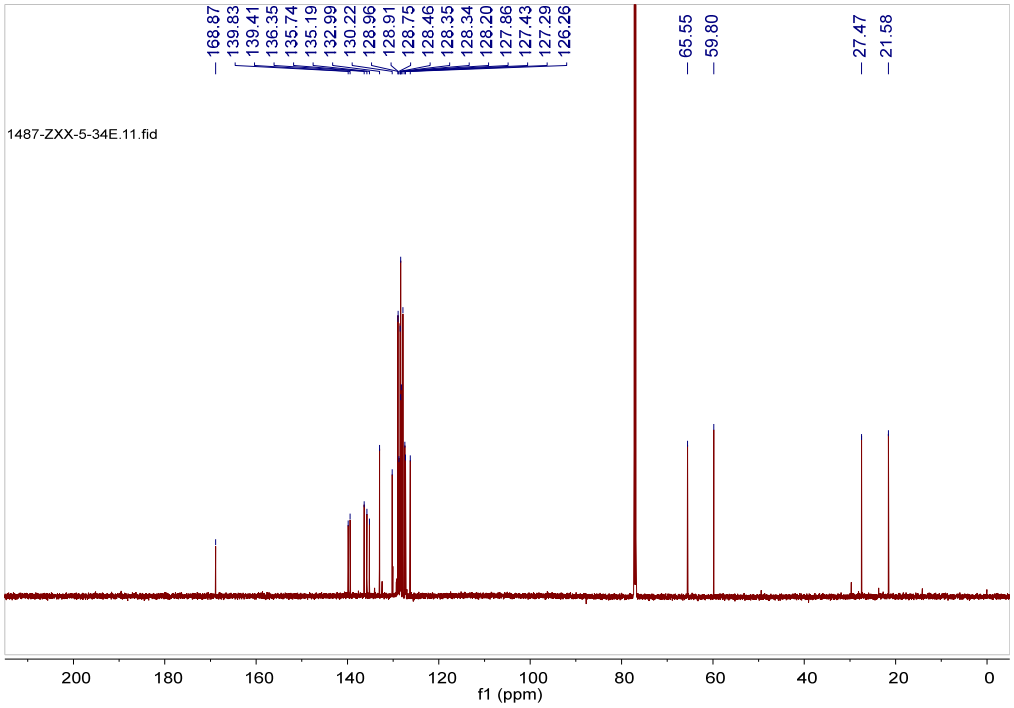


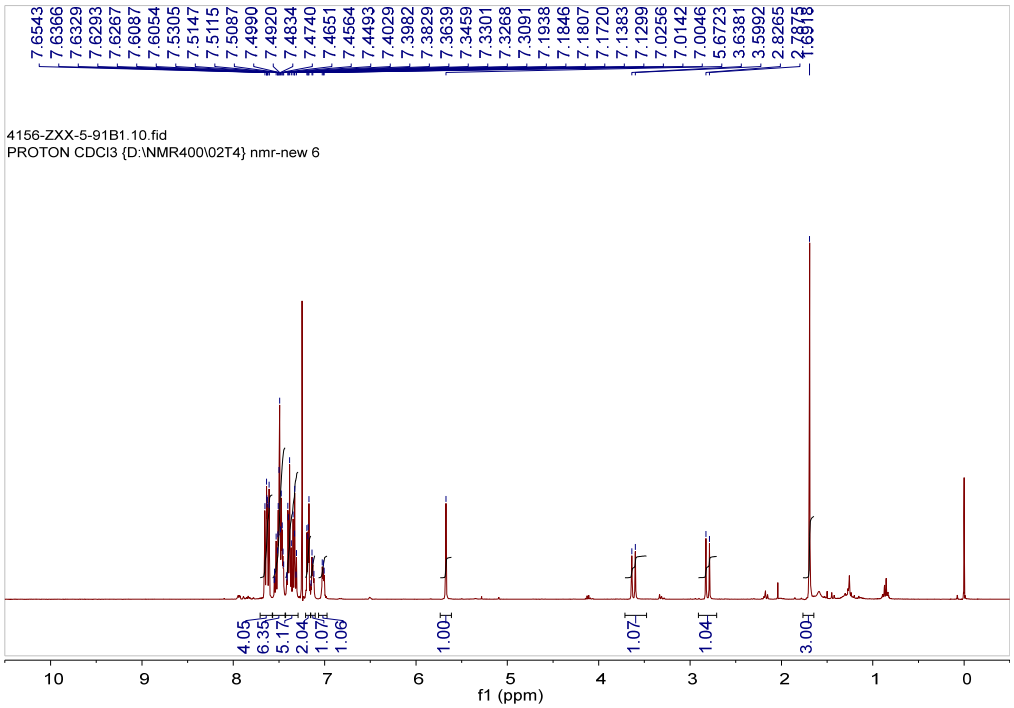


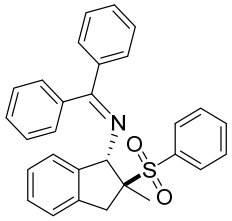
(±) **4u**

^{1}H NMR (700 MHz, Chloroform-*d*)

^{13}C NMR (175 MHz, Chloroform-*d*)



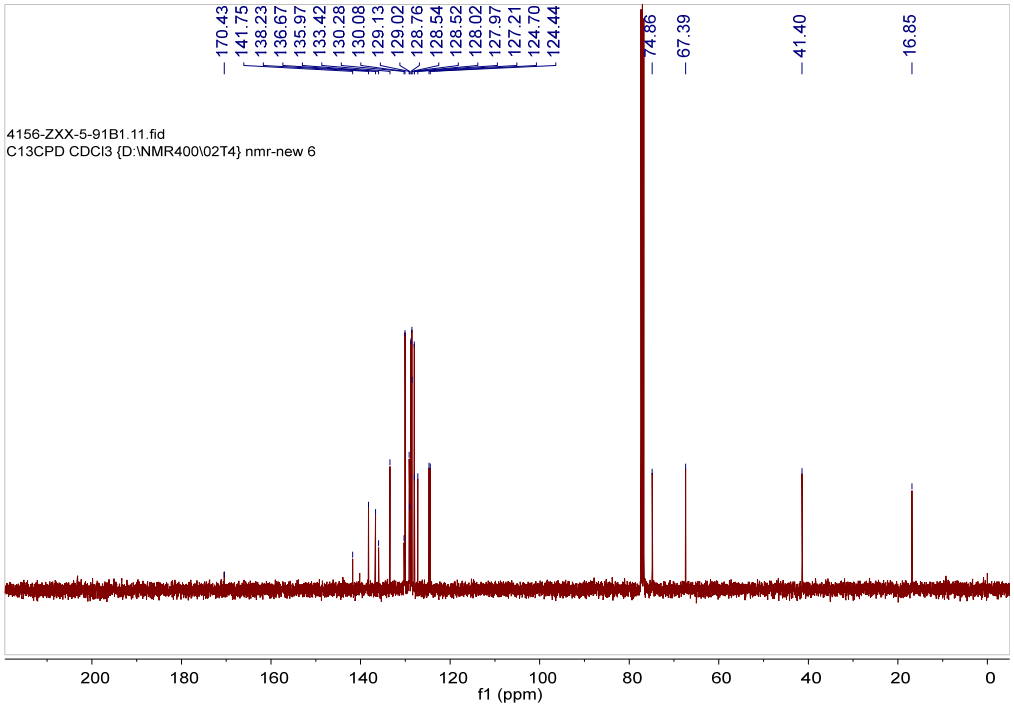


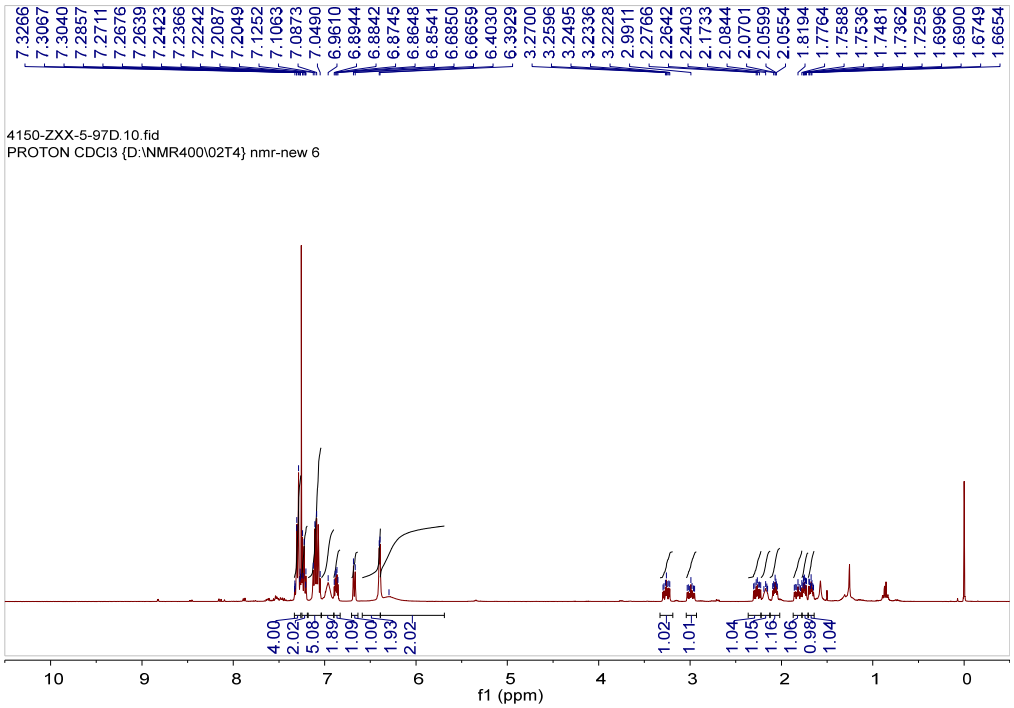


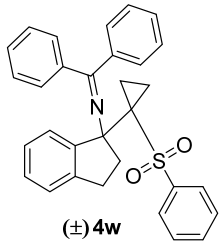
(±) **4v**

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



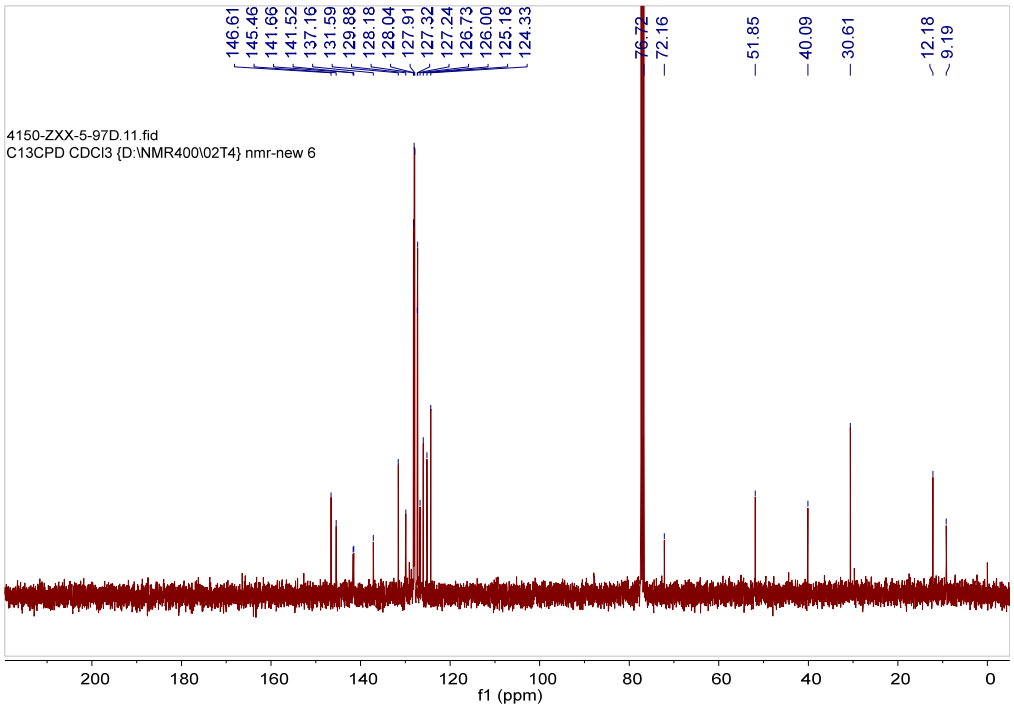


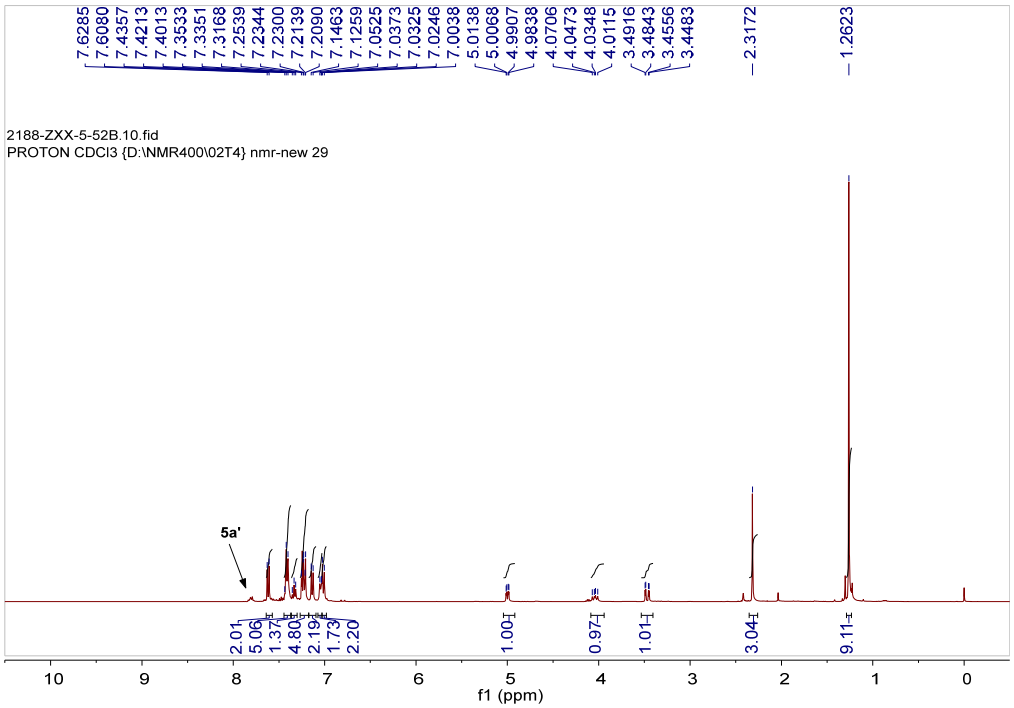


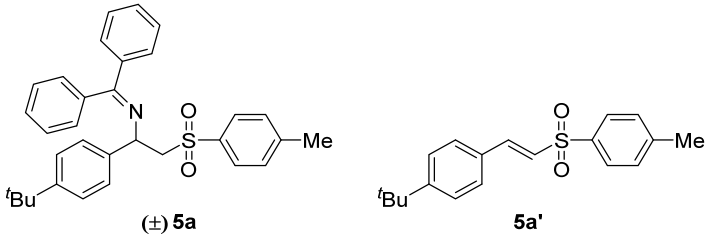
(±) **4w**

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



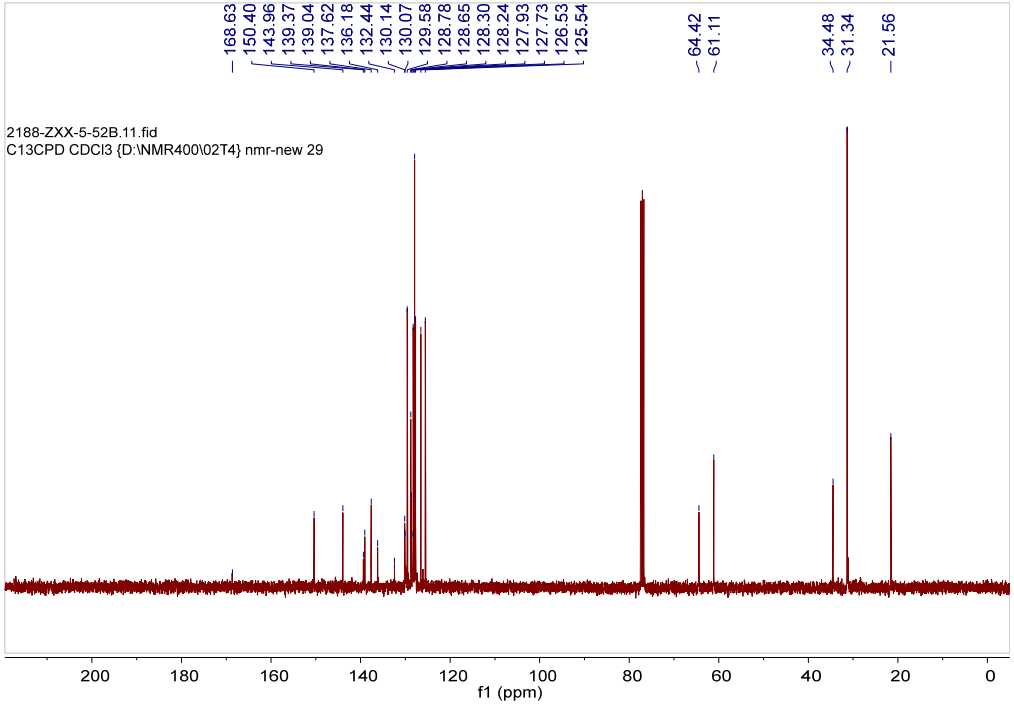


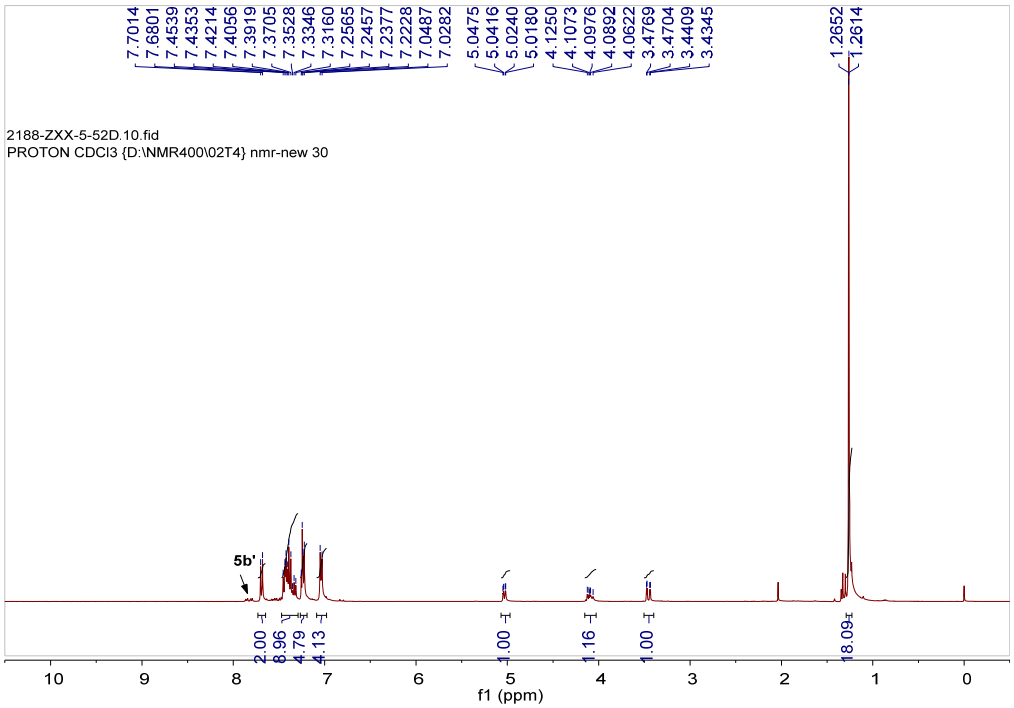


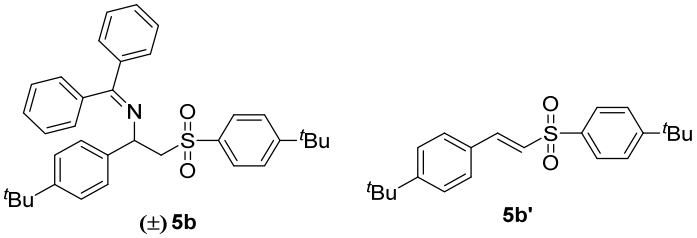
(±) **5a** **5a'**

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



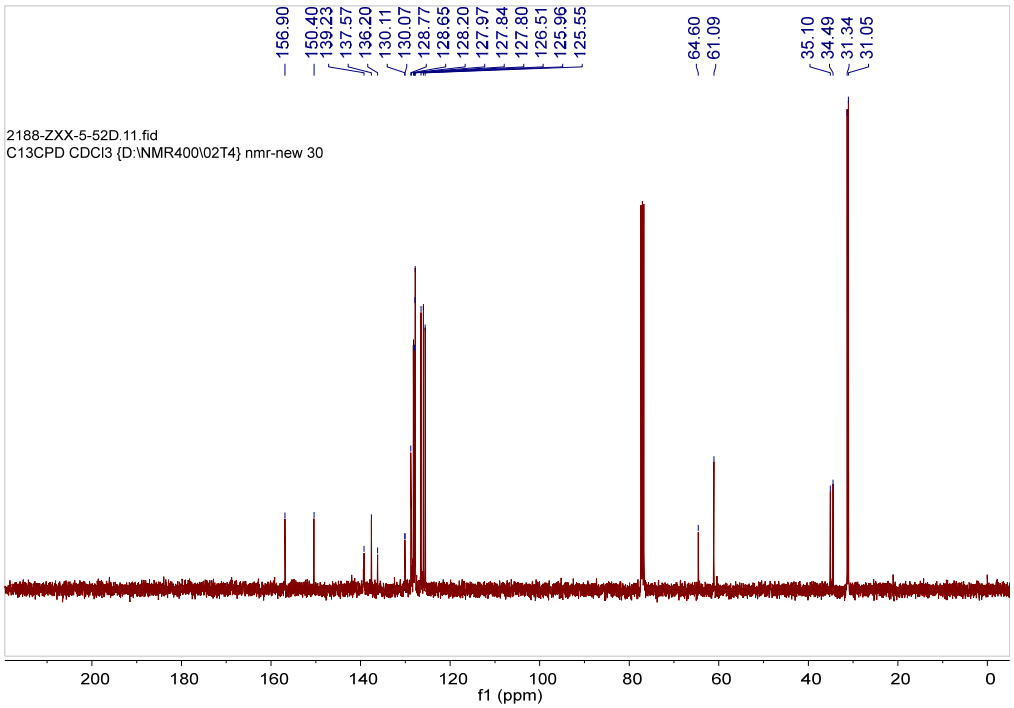


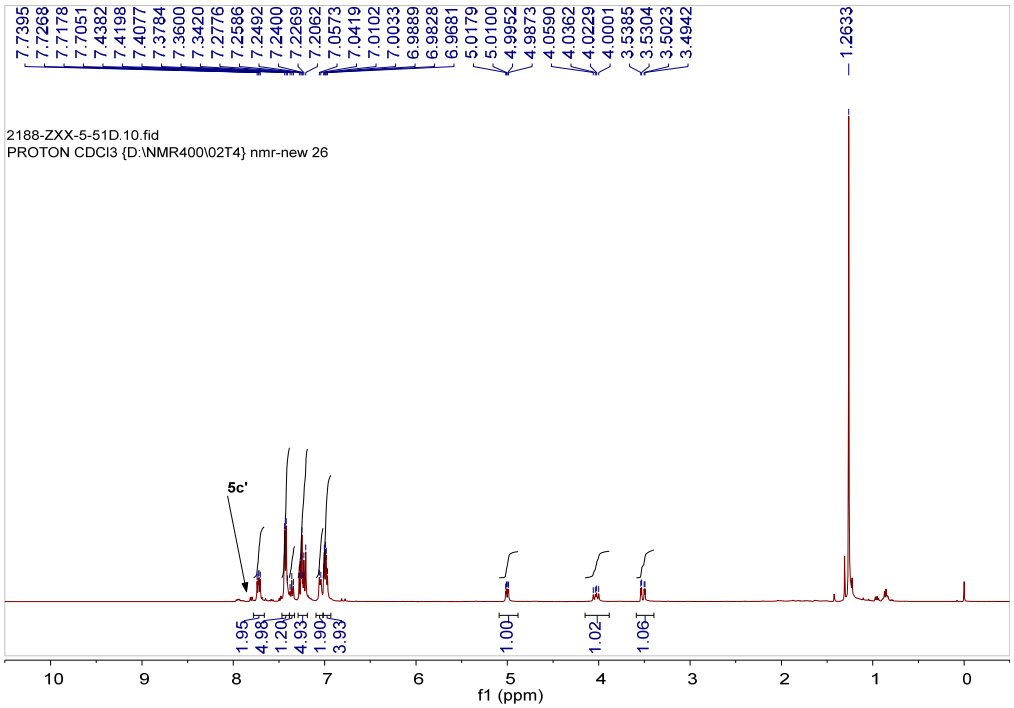


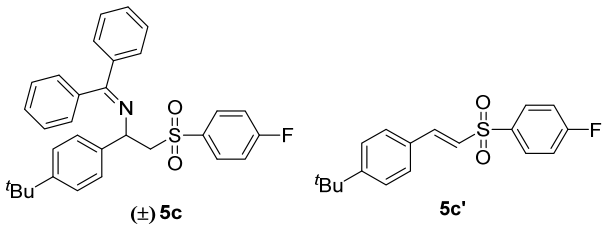
(±) **5b** **5b'**

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)

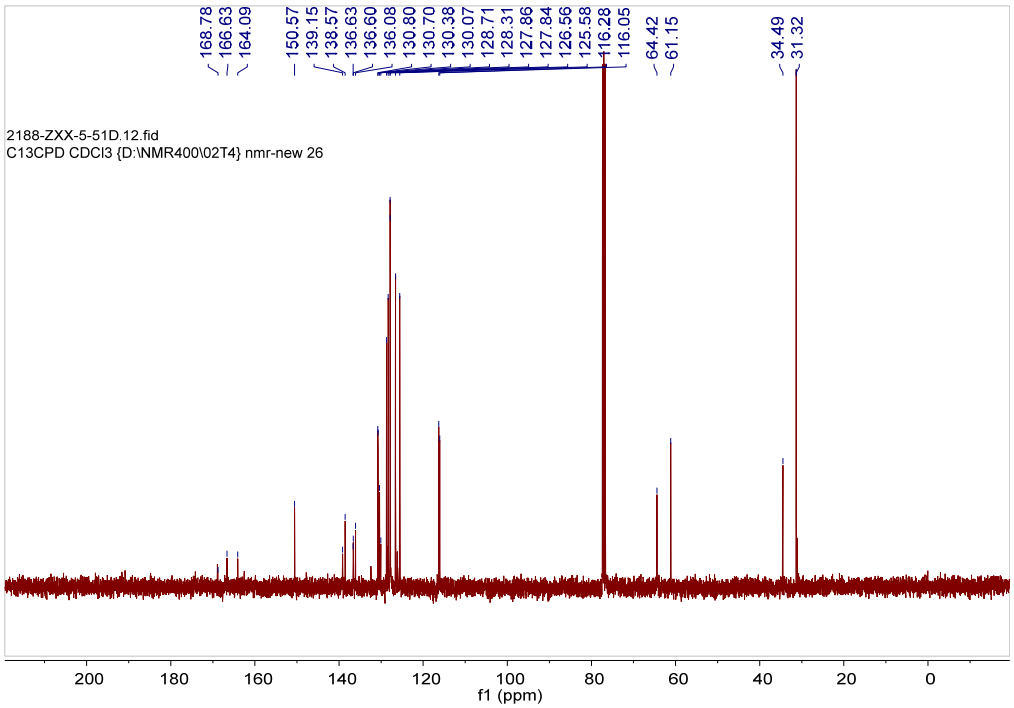


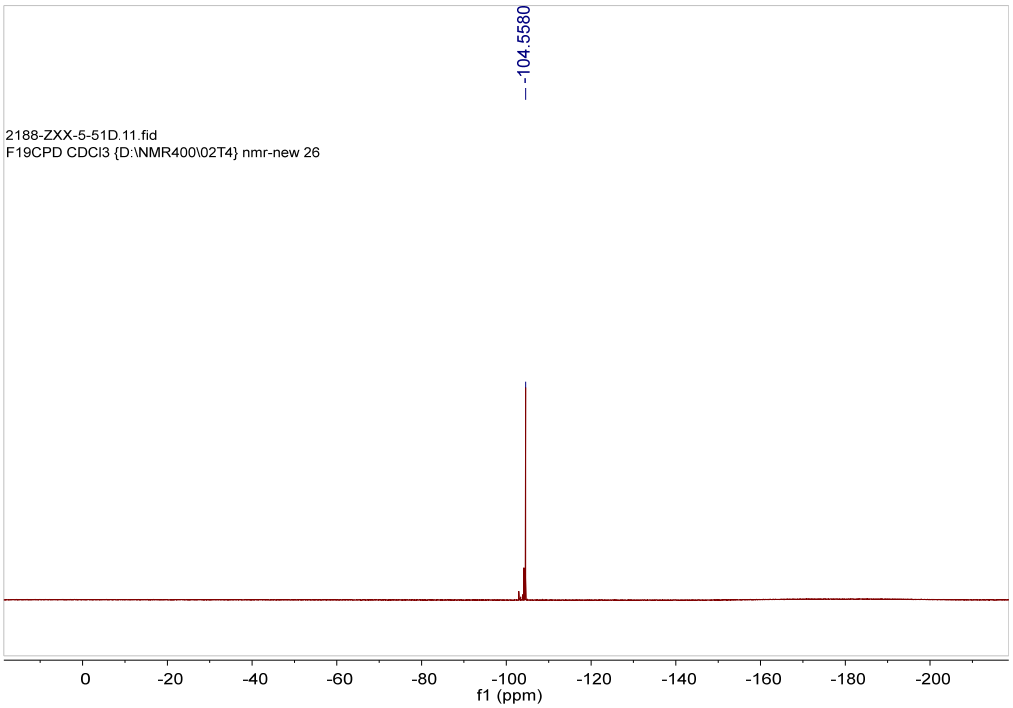


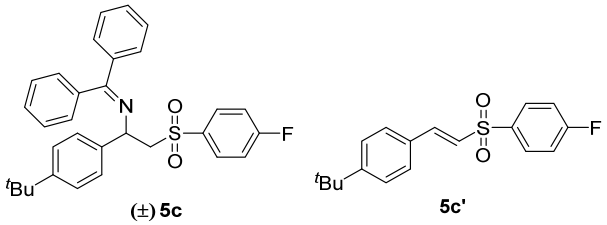


^{1}H NMR (400 MHz, Chloroform-*d*)

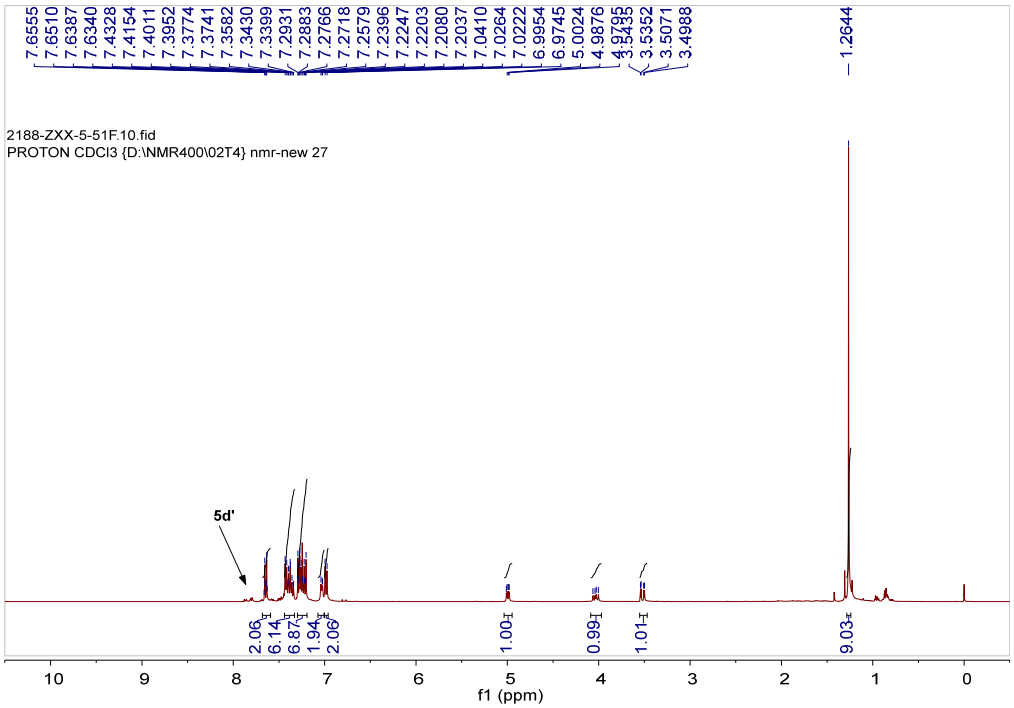
^{13}C NMR (100 MHz, Chloroform-*d*)

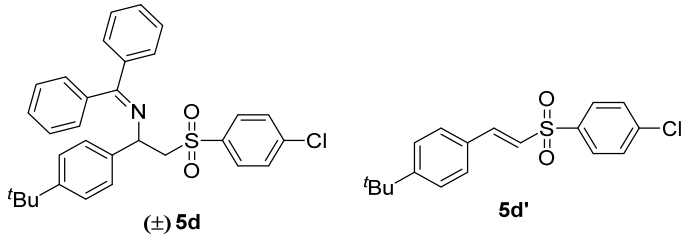






^{19}F NMR (375 MHz, Chloroform-*d*)

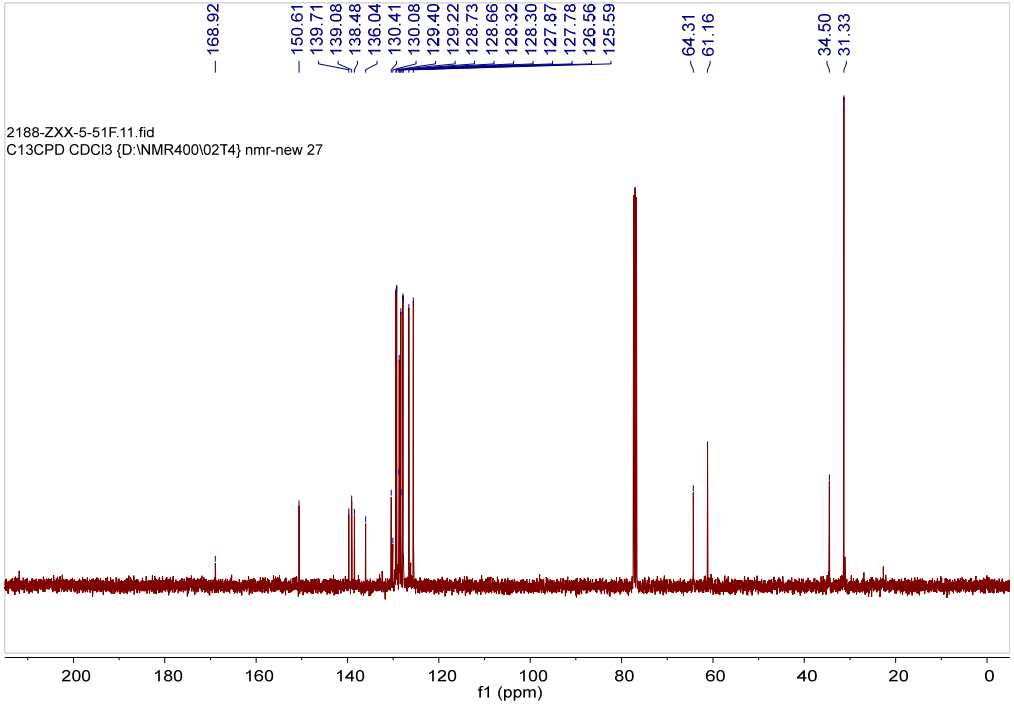


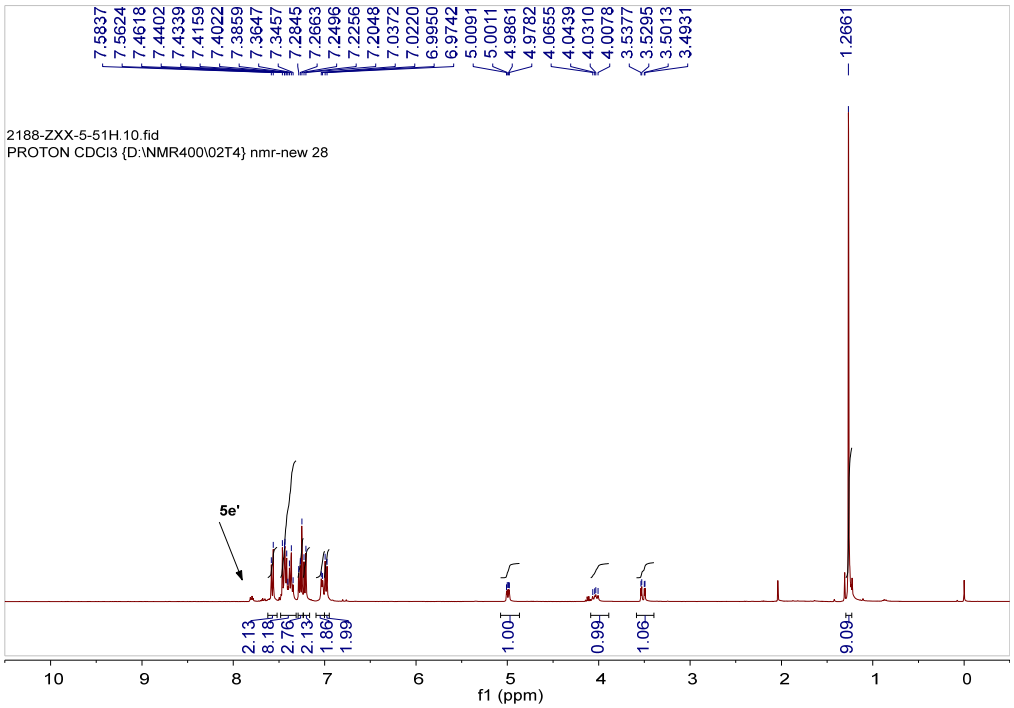


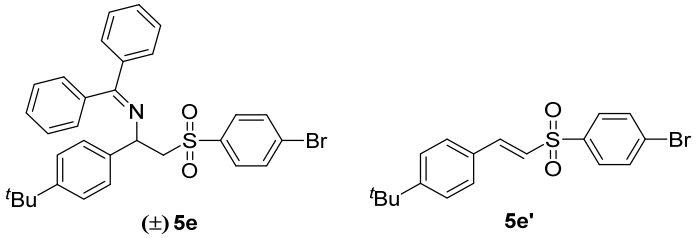
(±) **5d** **5d'**

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



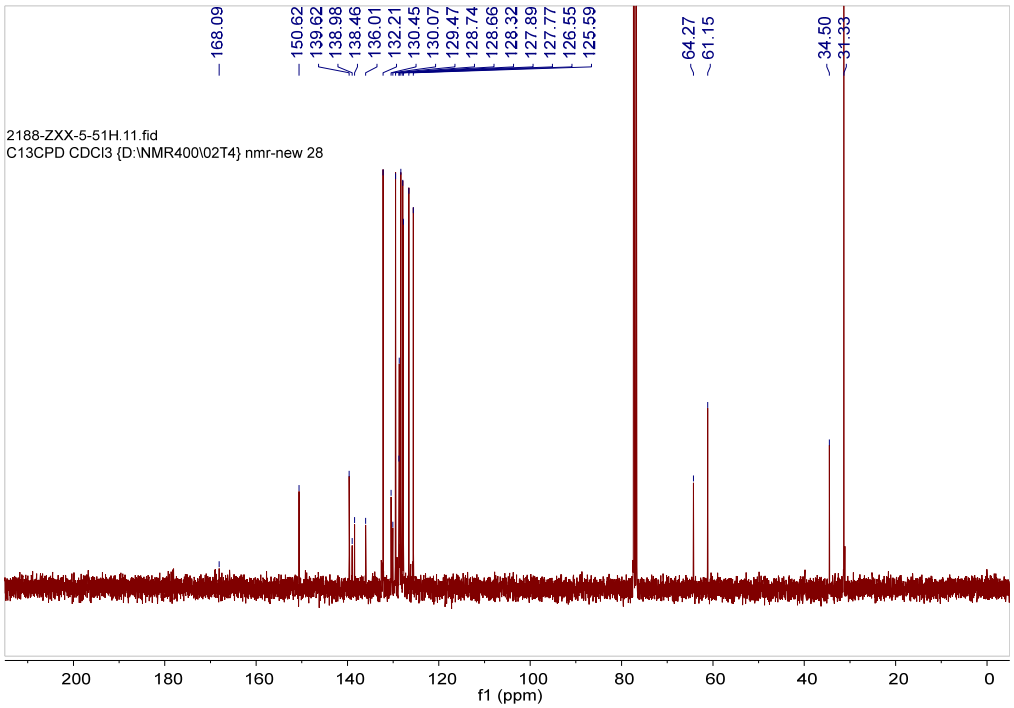


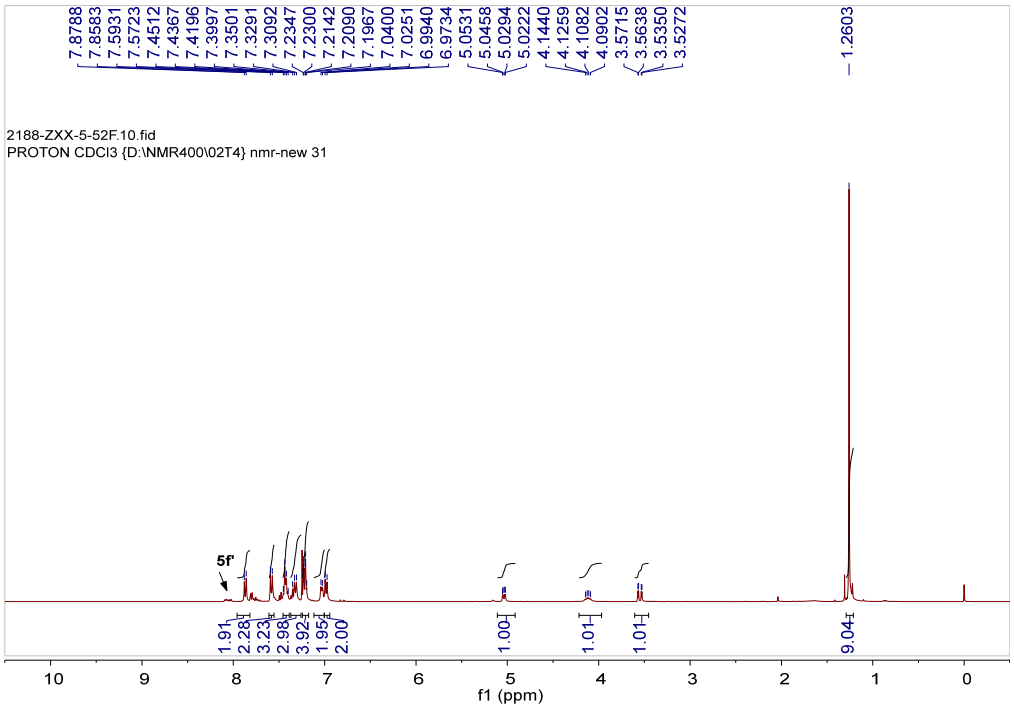


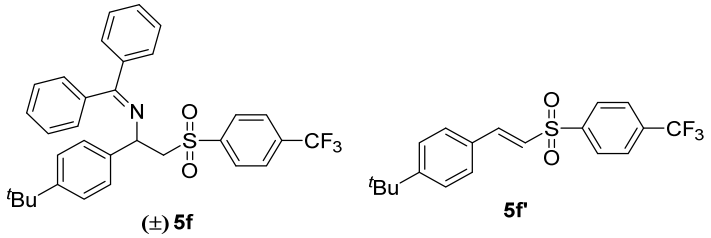
(±) **5e** **5e'**

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



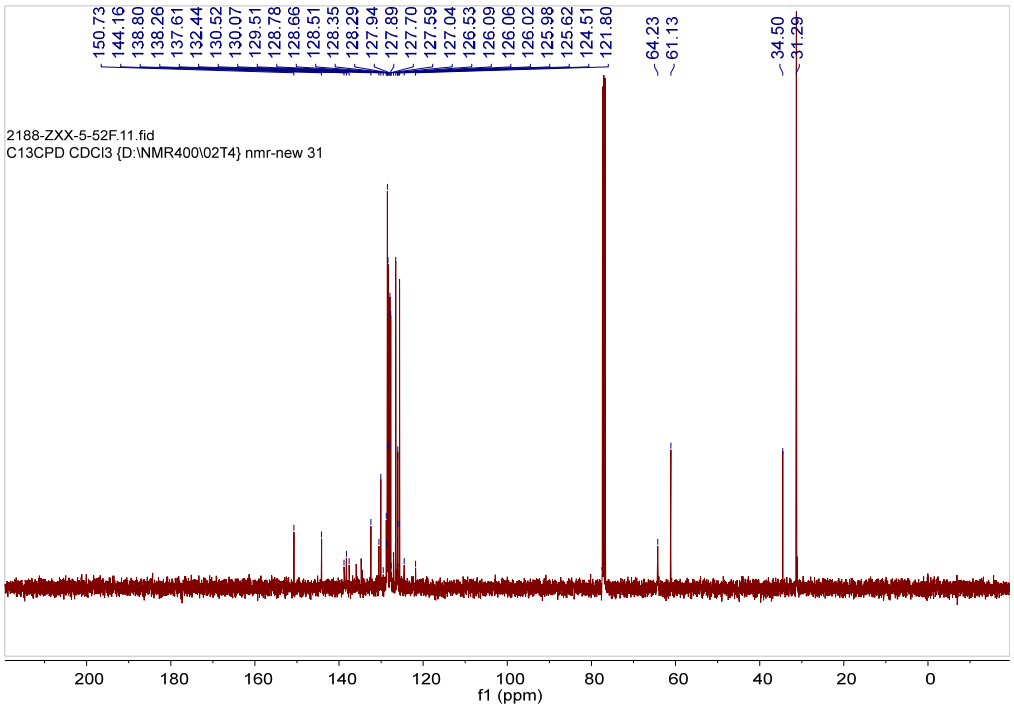


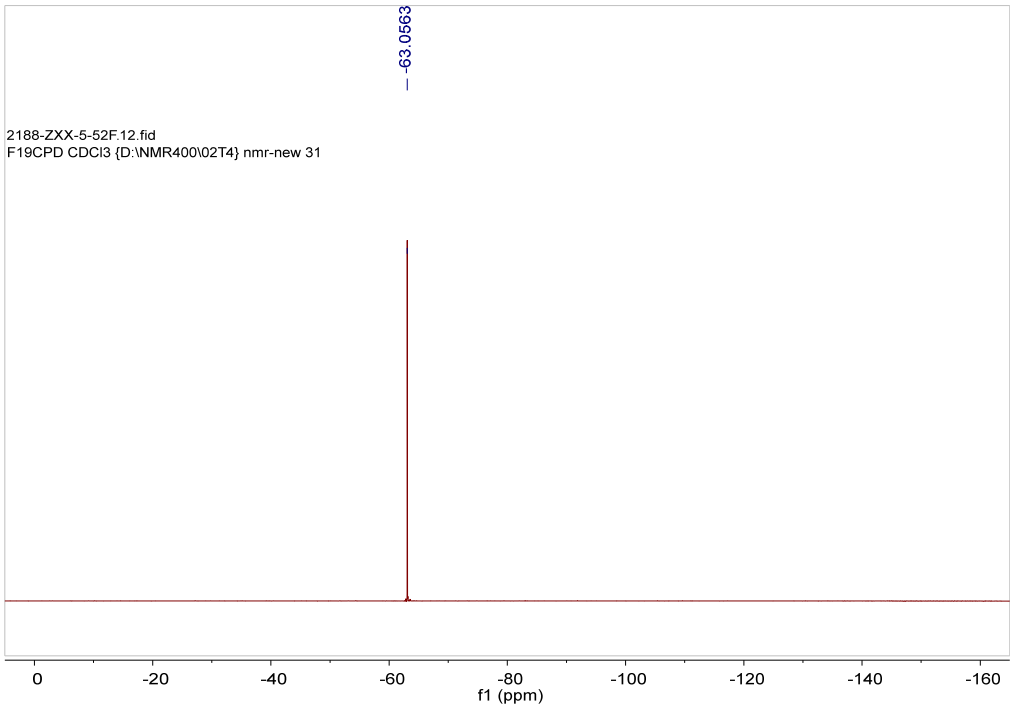


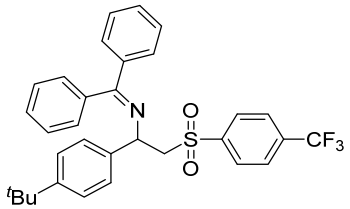
(±) **5f** **5f'**

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)

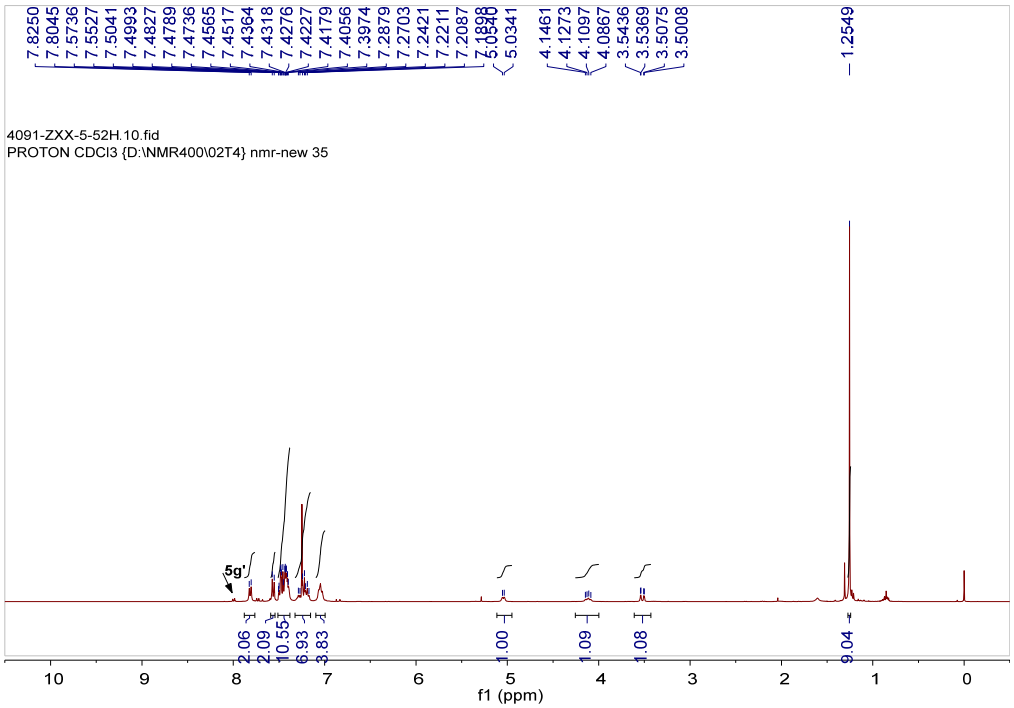


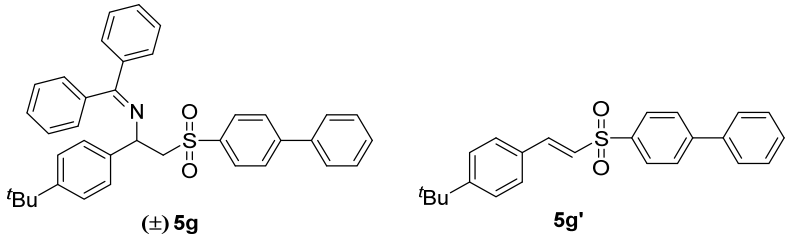




(±) **5f**

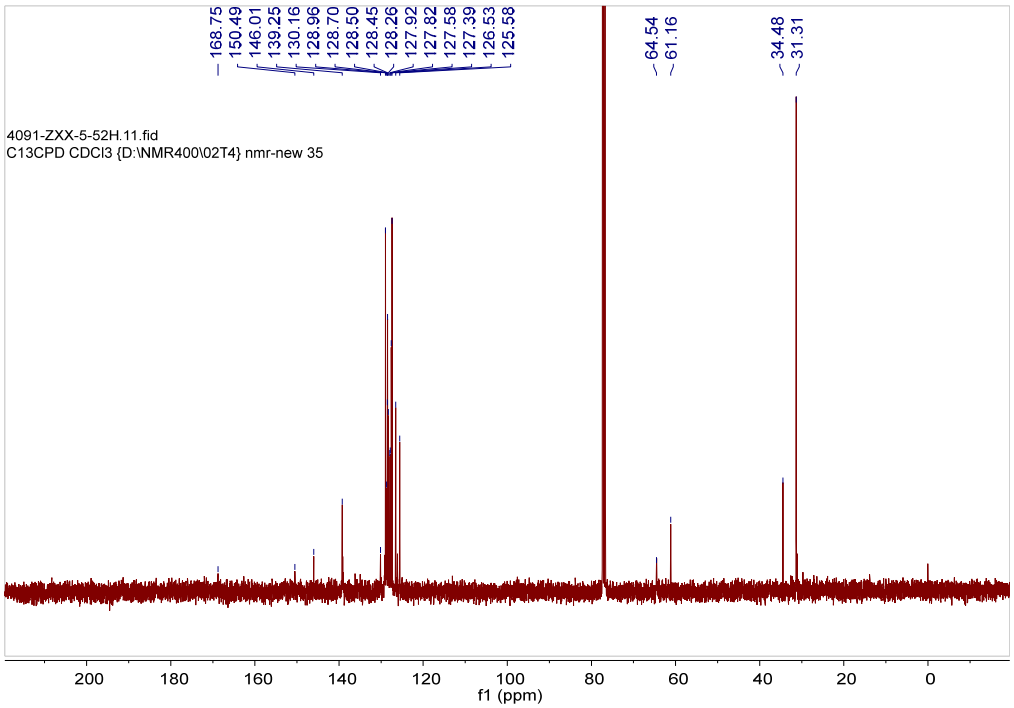
^{19}F NMR (375 MHz, Chloroform-*d*)

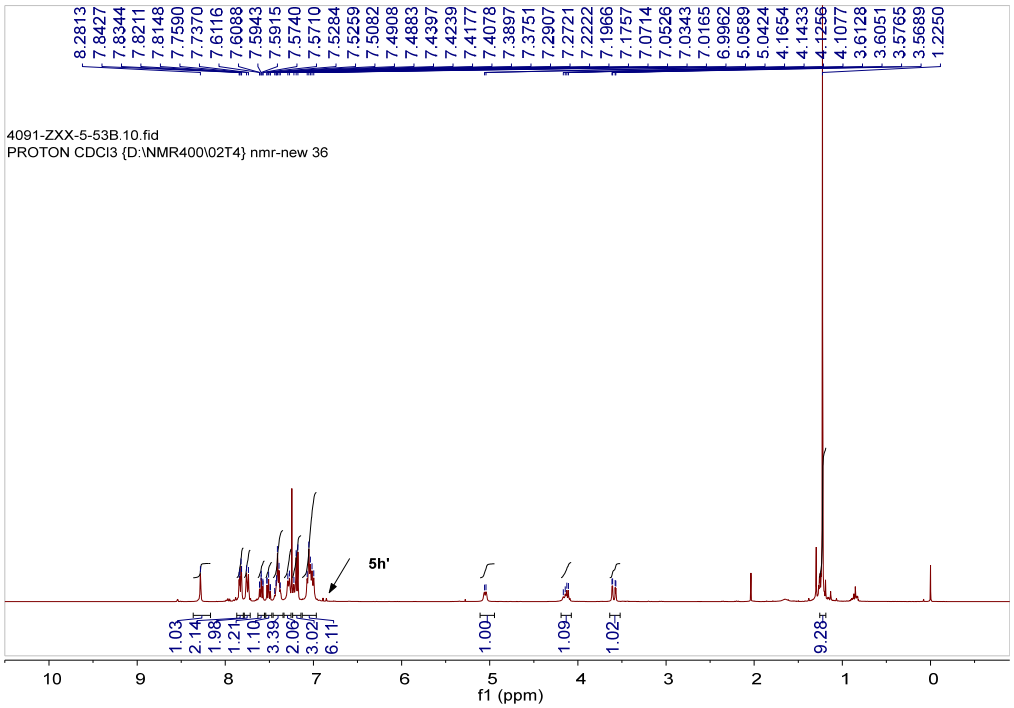


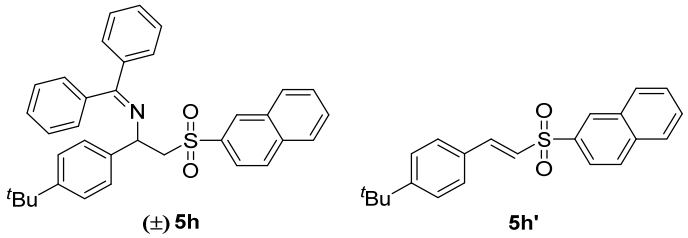


^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



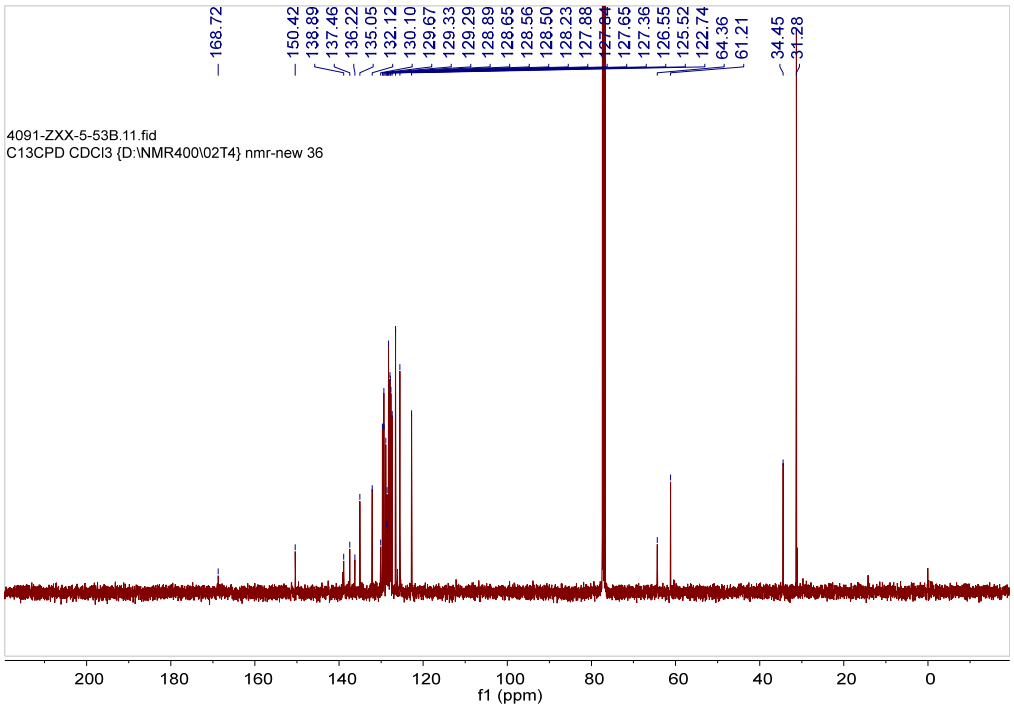


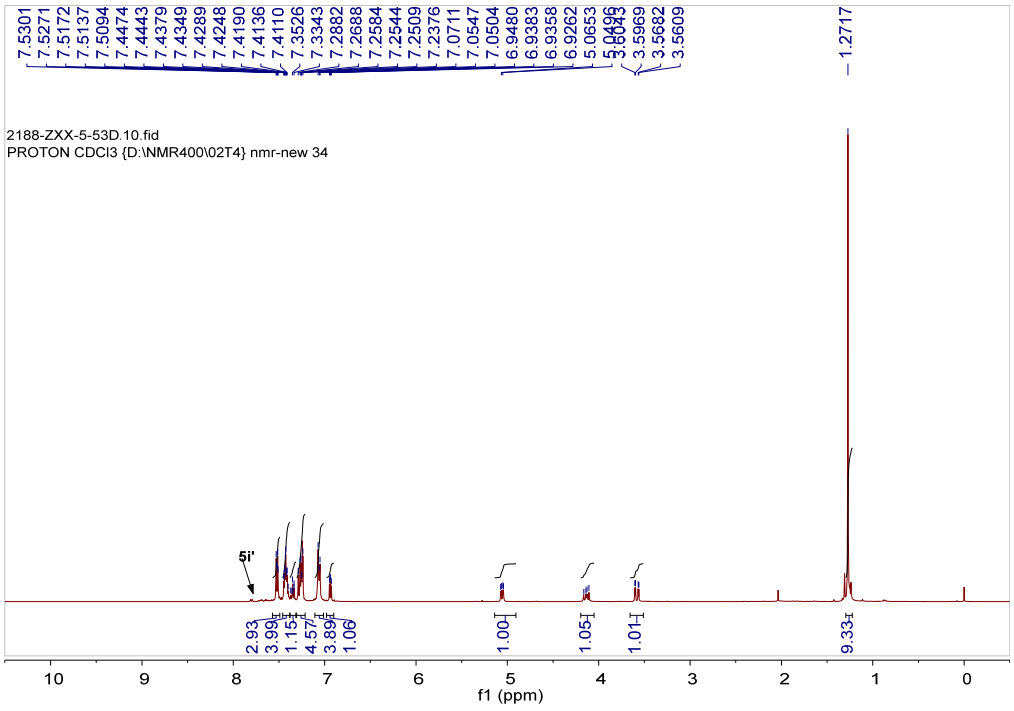


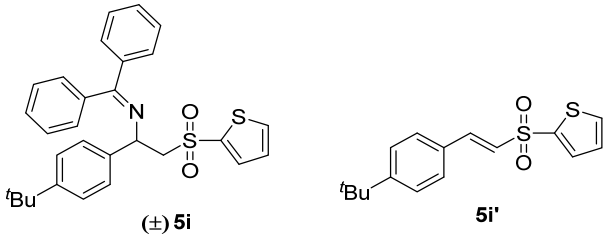
(±) **5h** **5h'**

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)





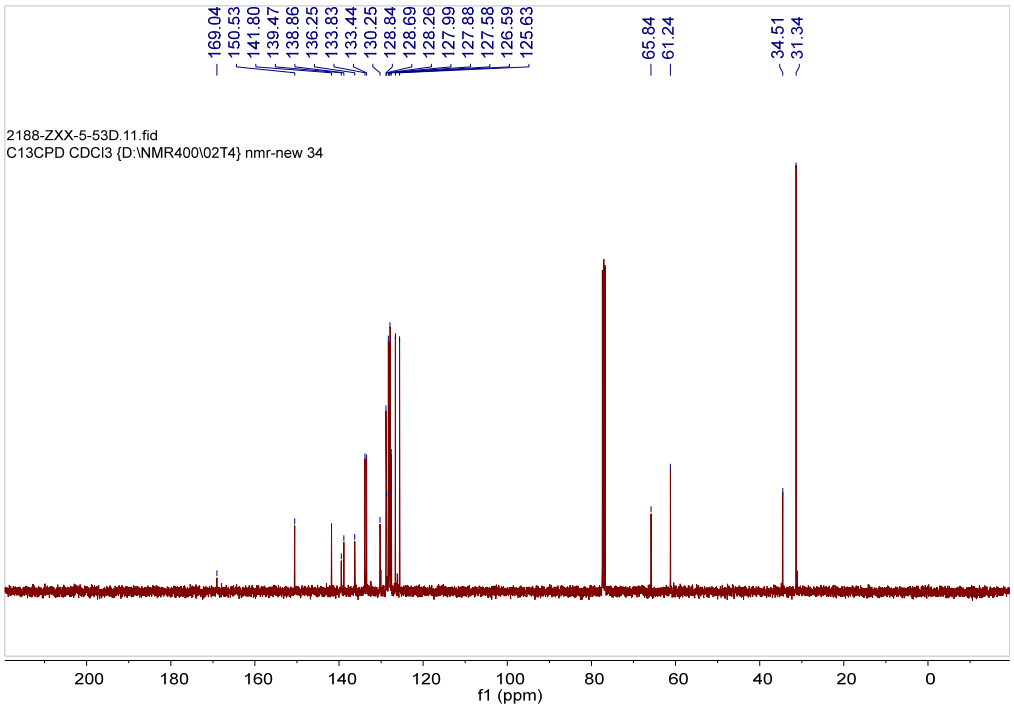


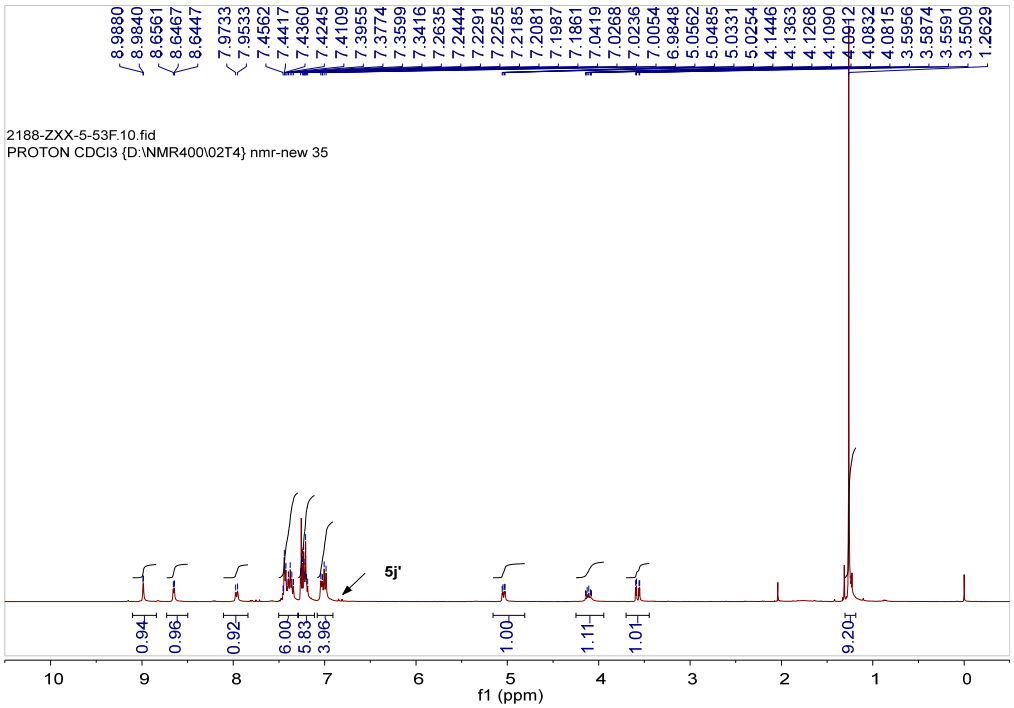
(±) **5i**

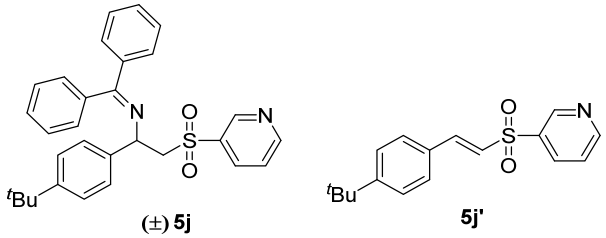
5i'

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)

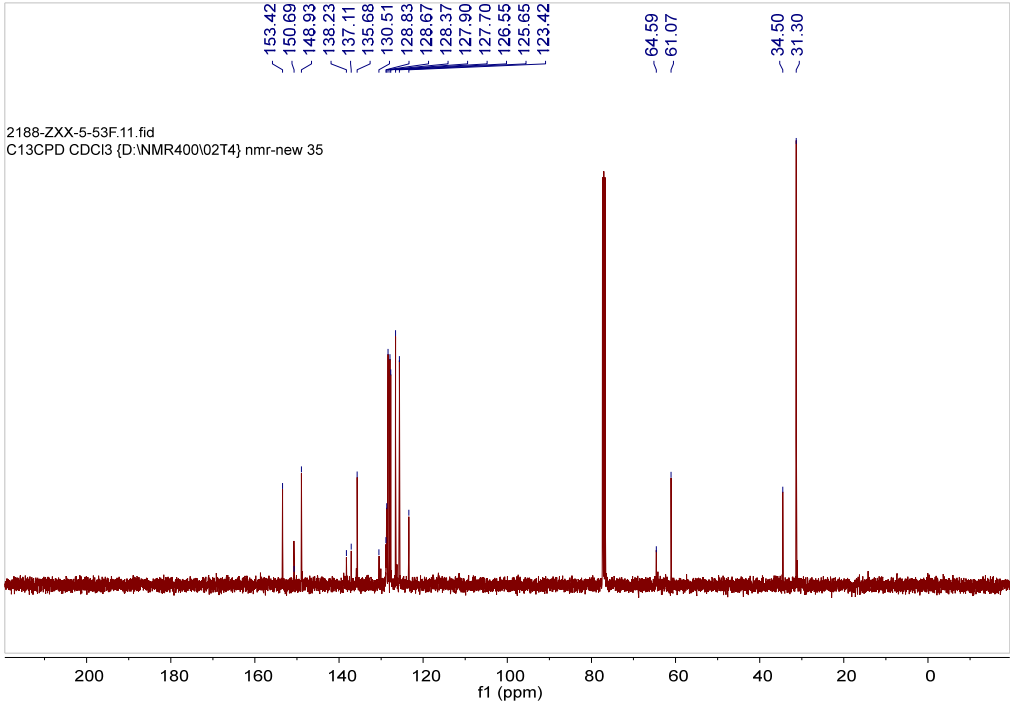


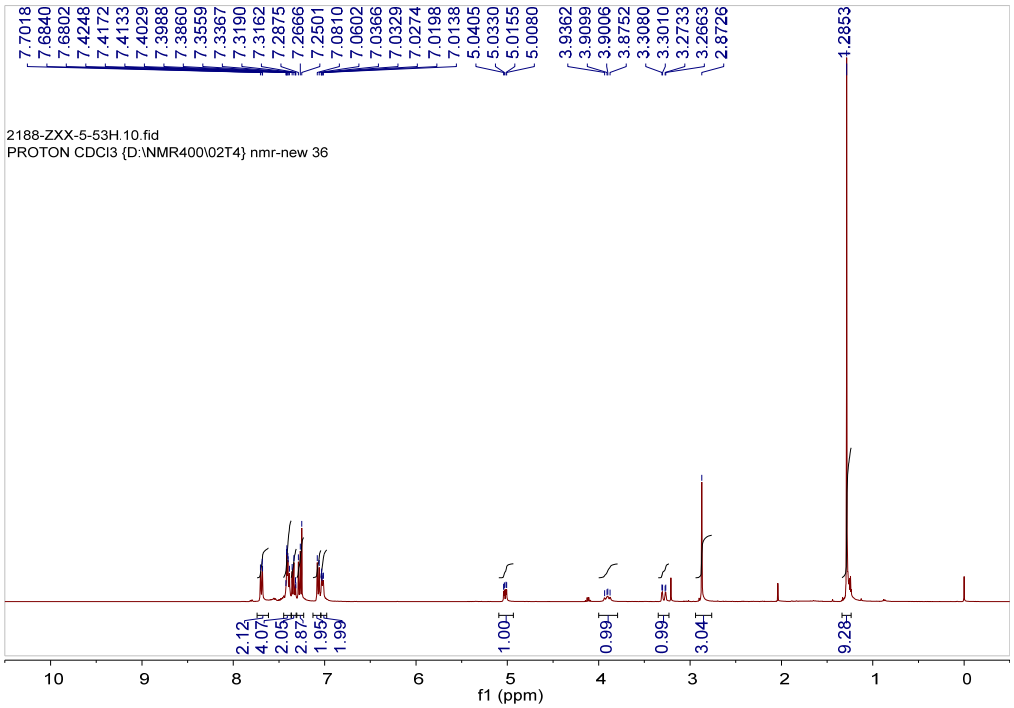


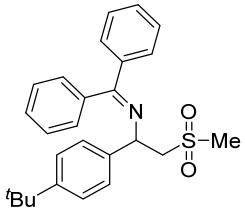


^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



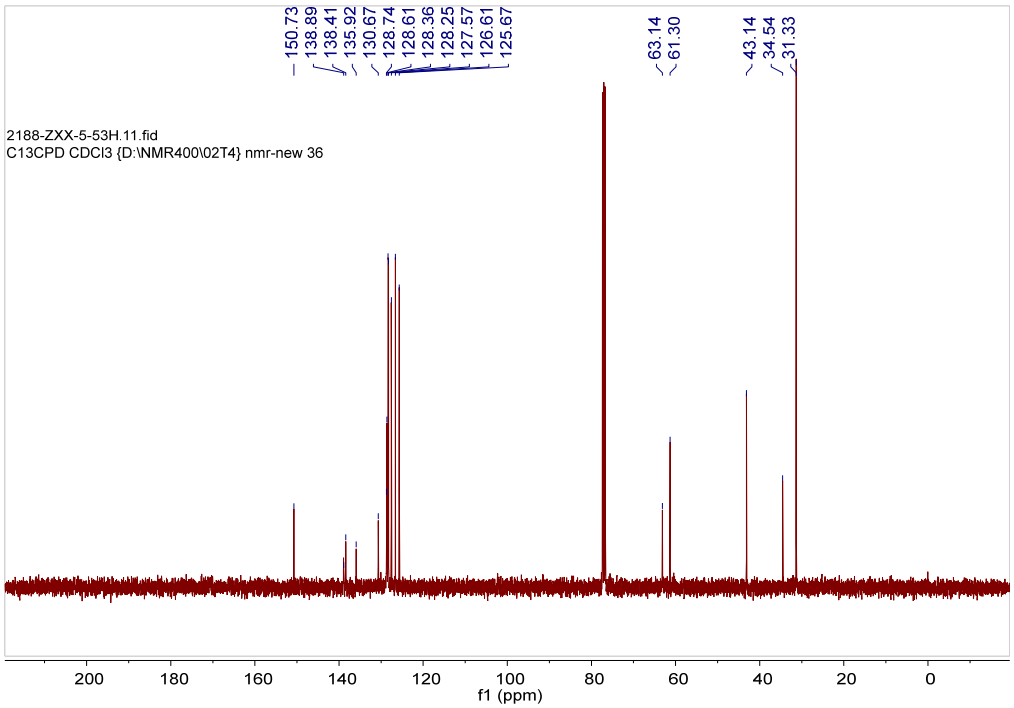


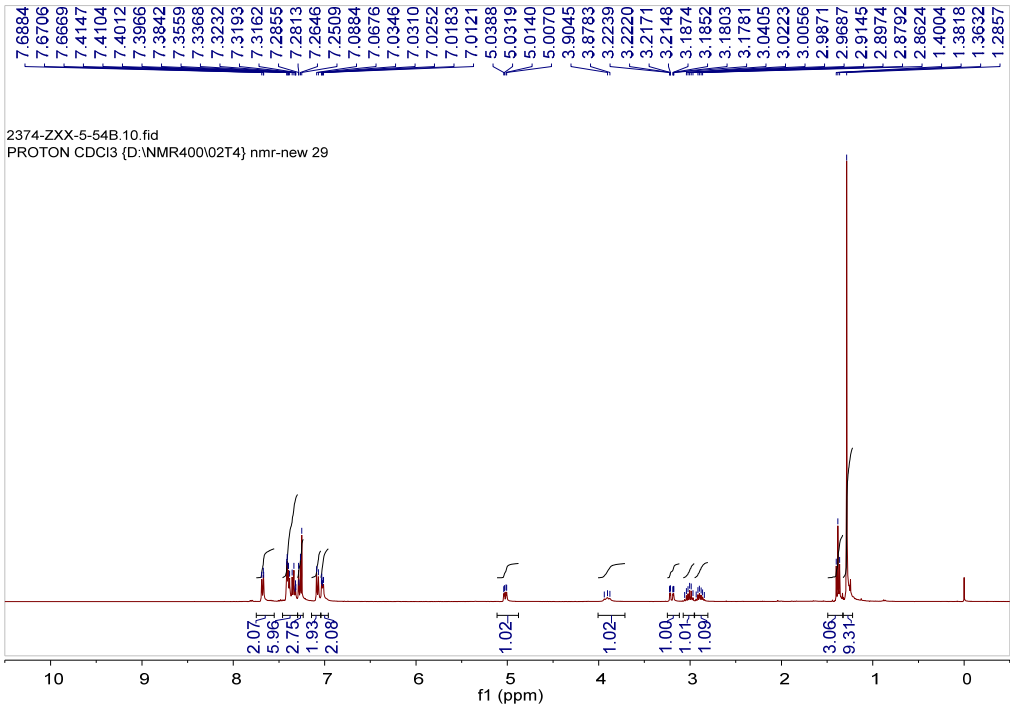


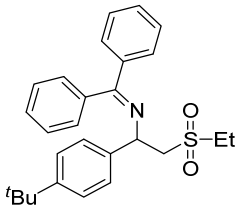
(±) **5k**

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



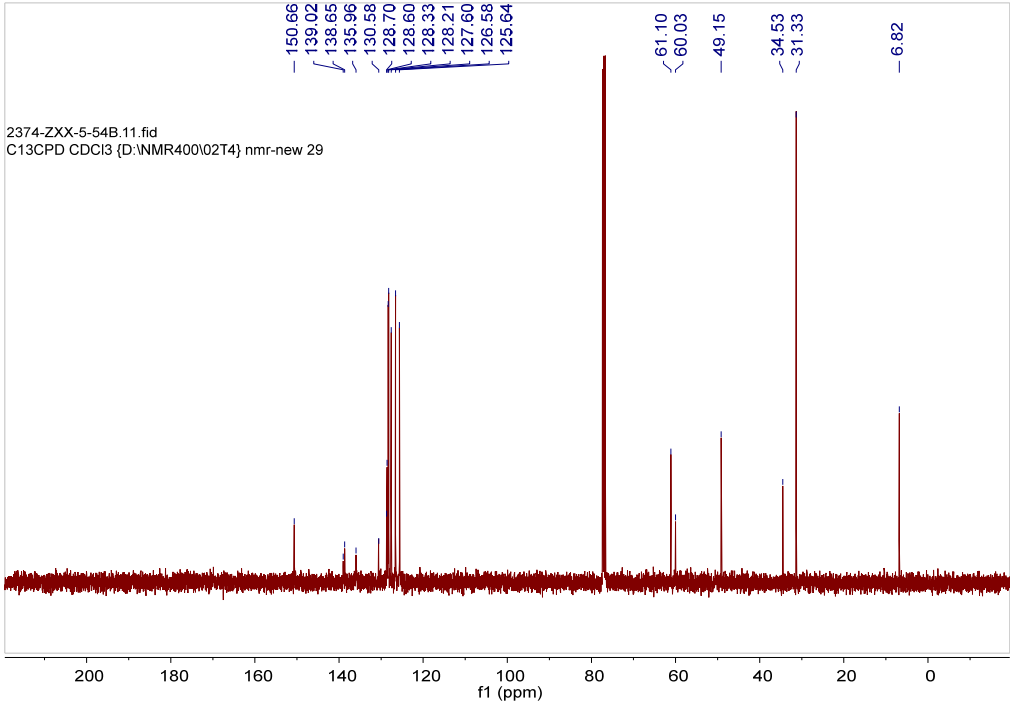


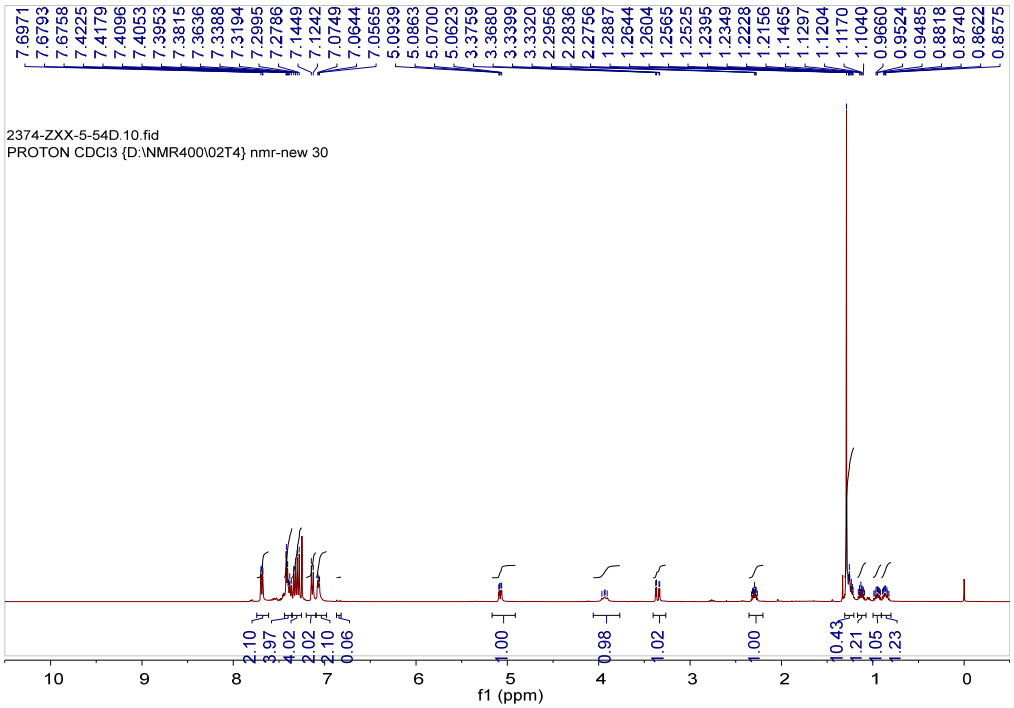


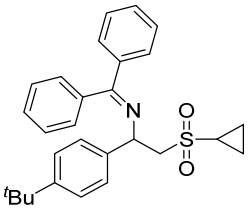
(±) **5l**

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



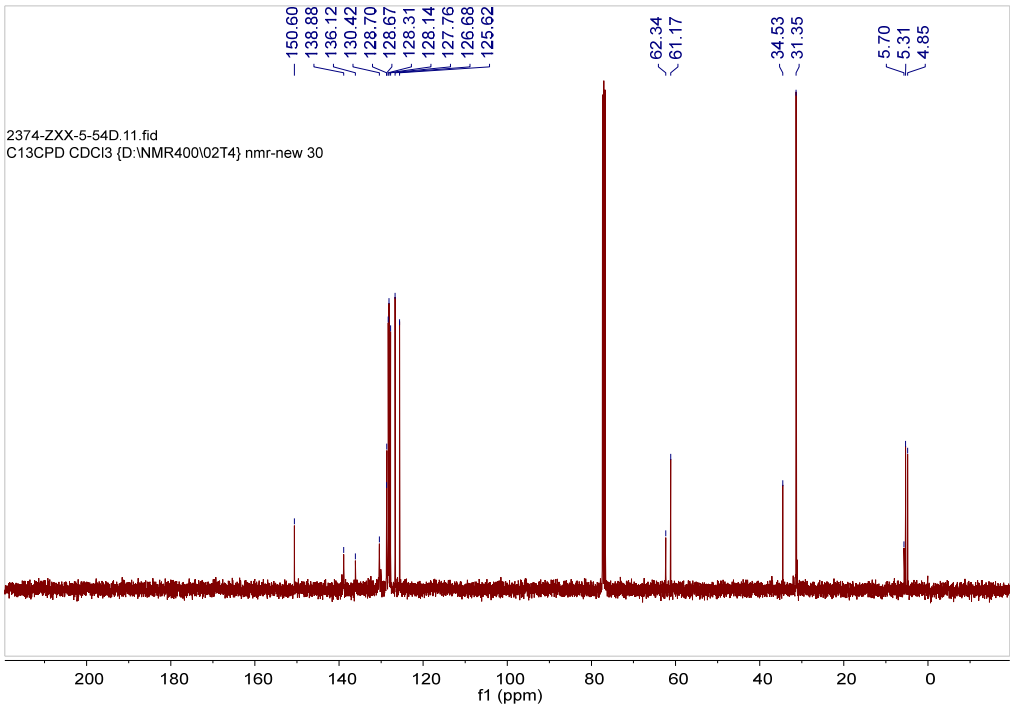


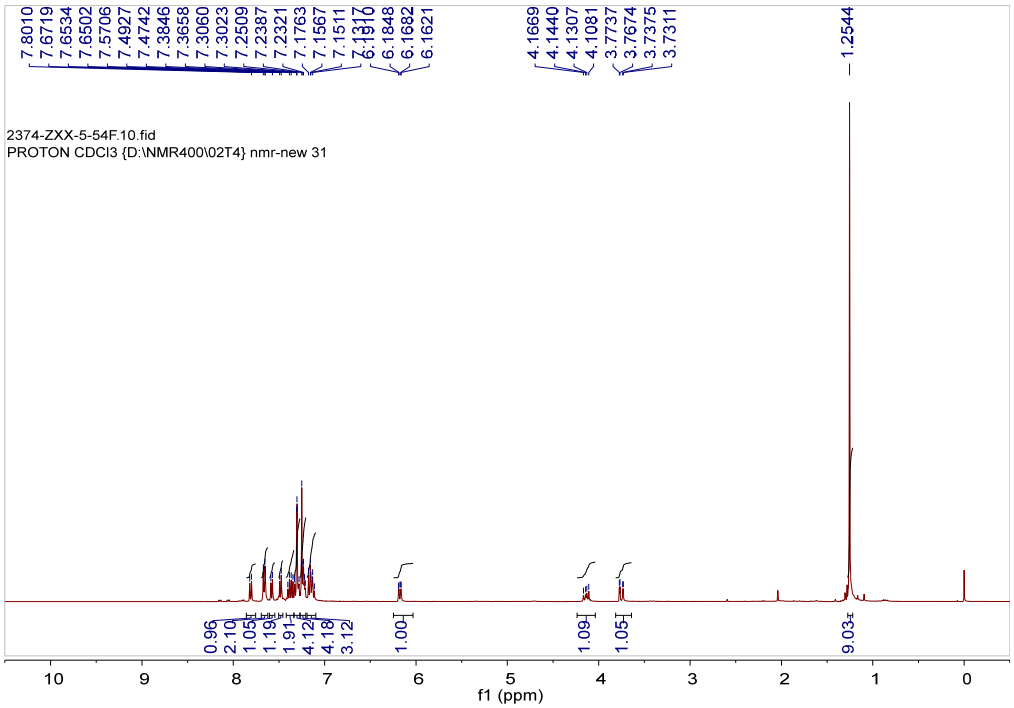


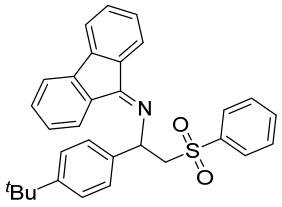
(±) **5m**

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



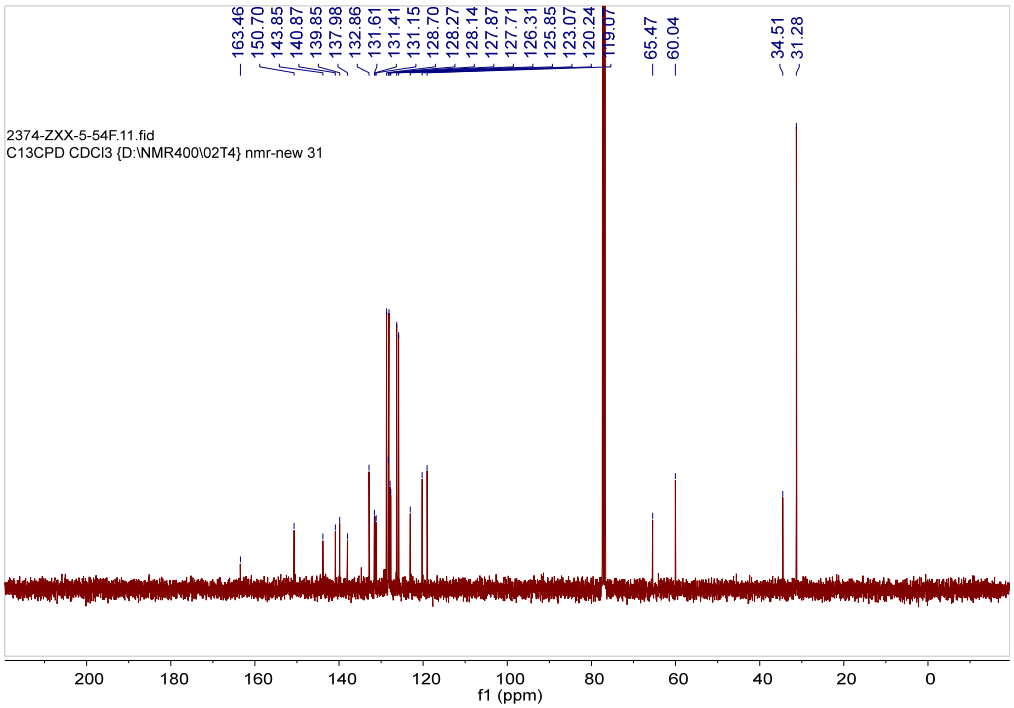


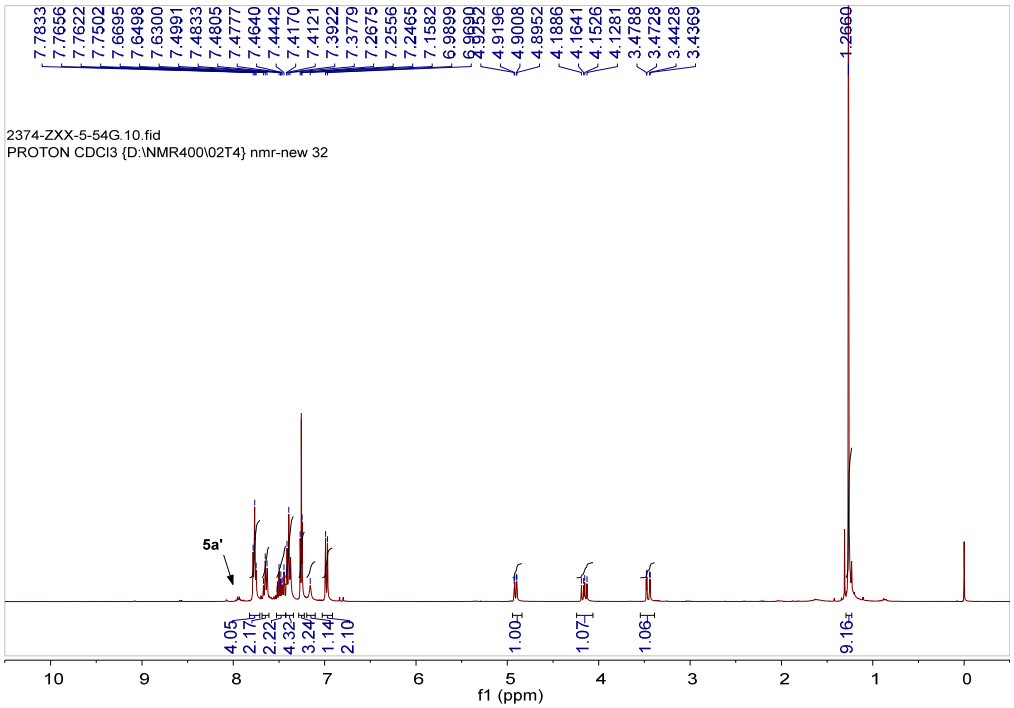


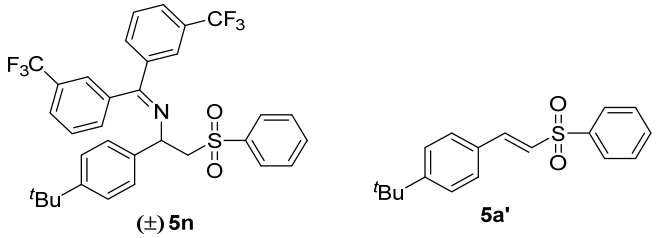
(±) **5n**

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)

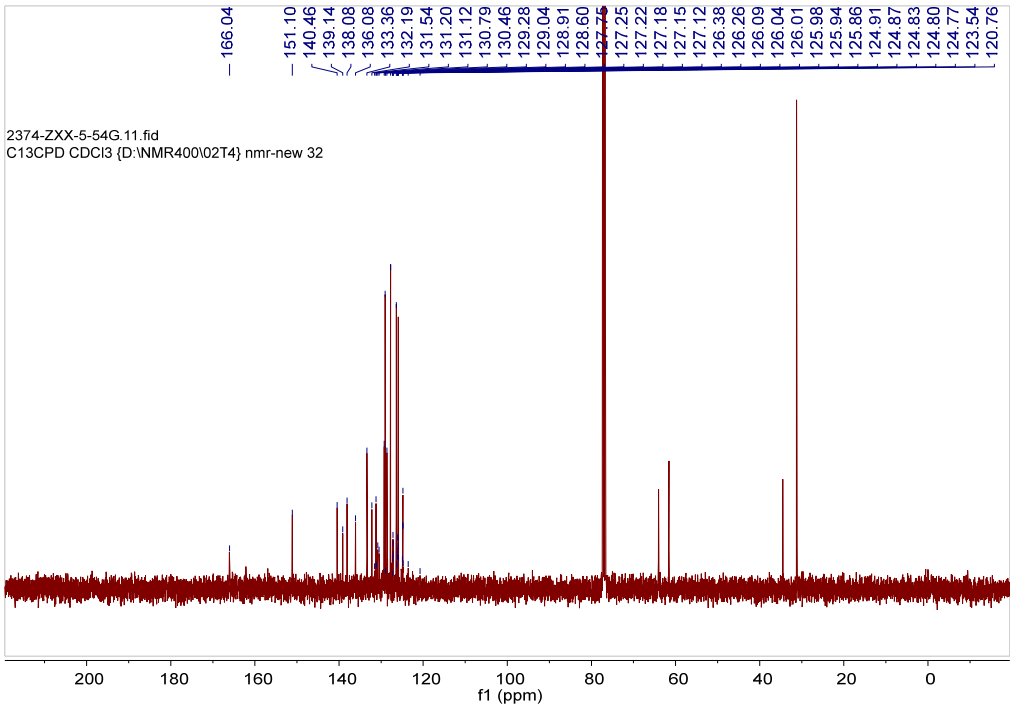


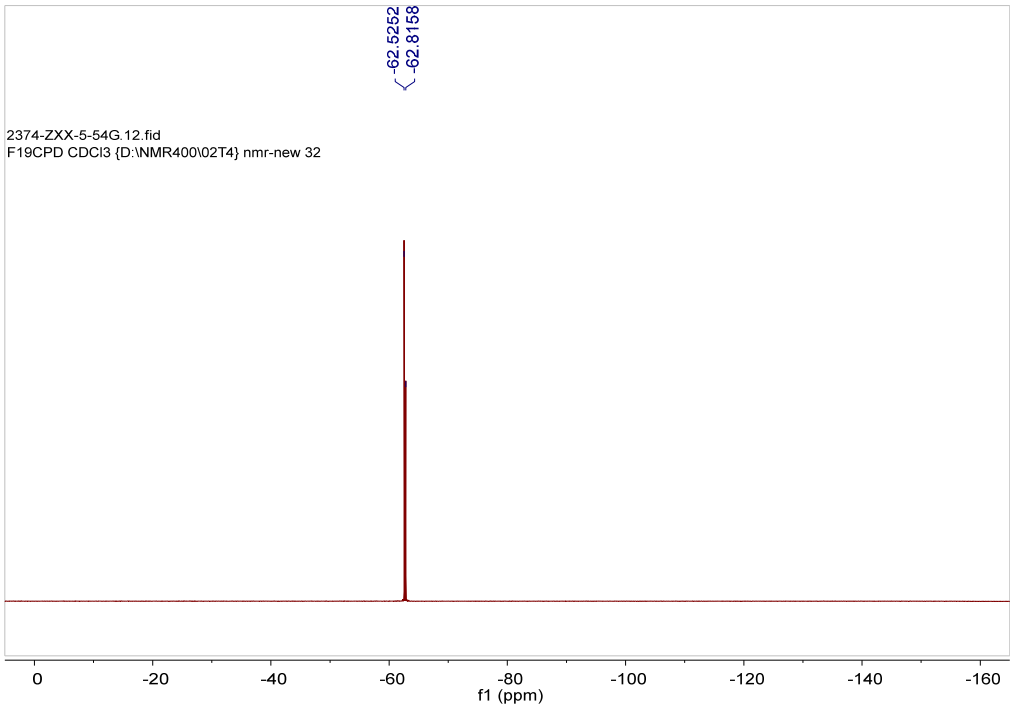


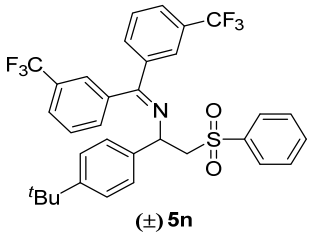


^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)

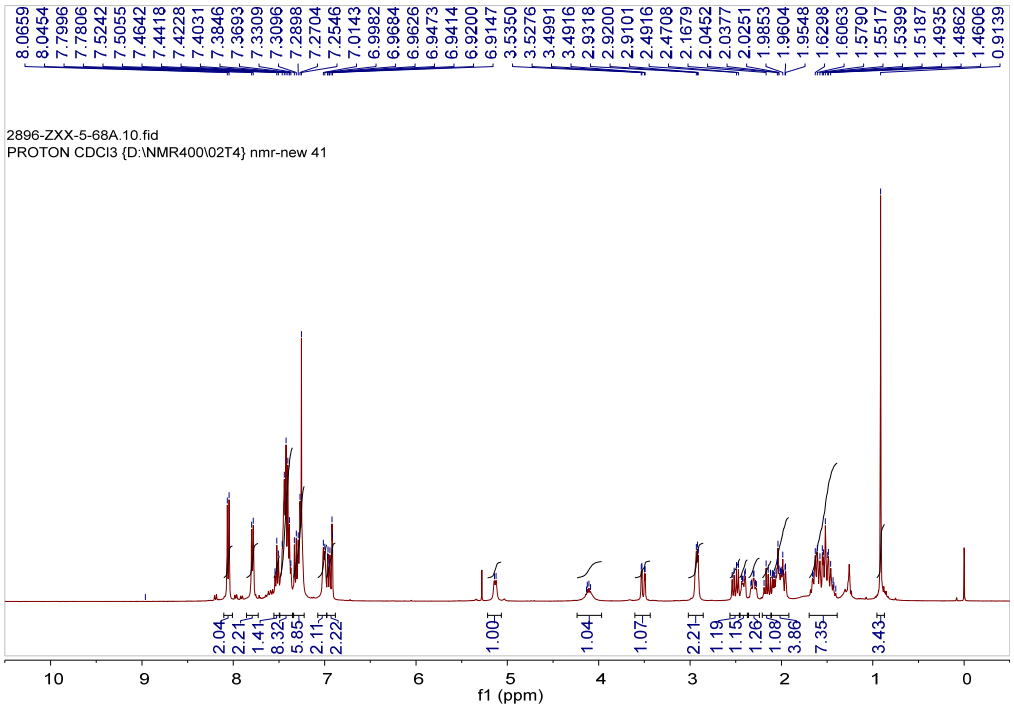


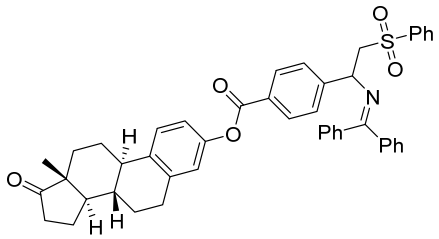




(±) **5n**

^{19}F NMR (375 MHz, Chloroform-*d*)

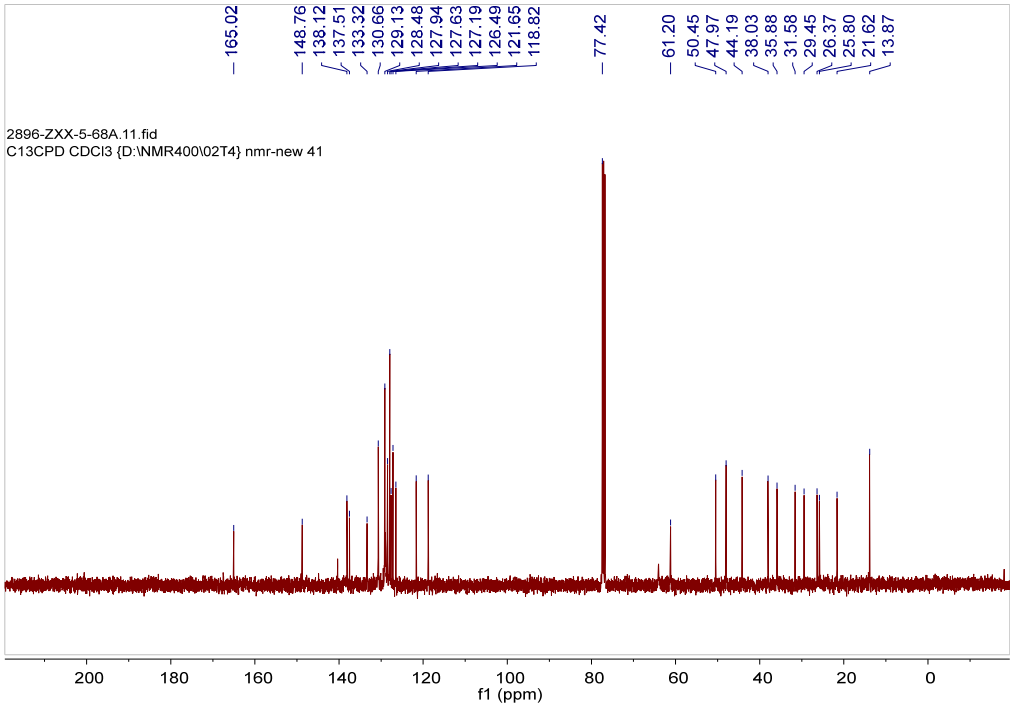


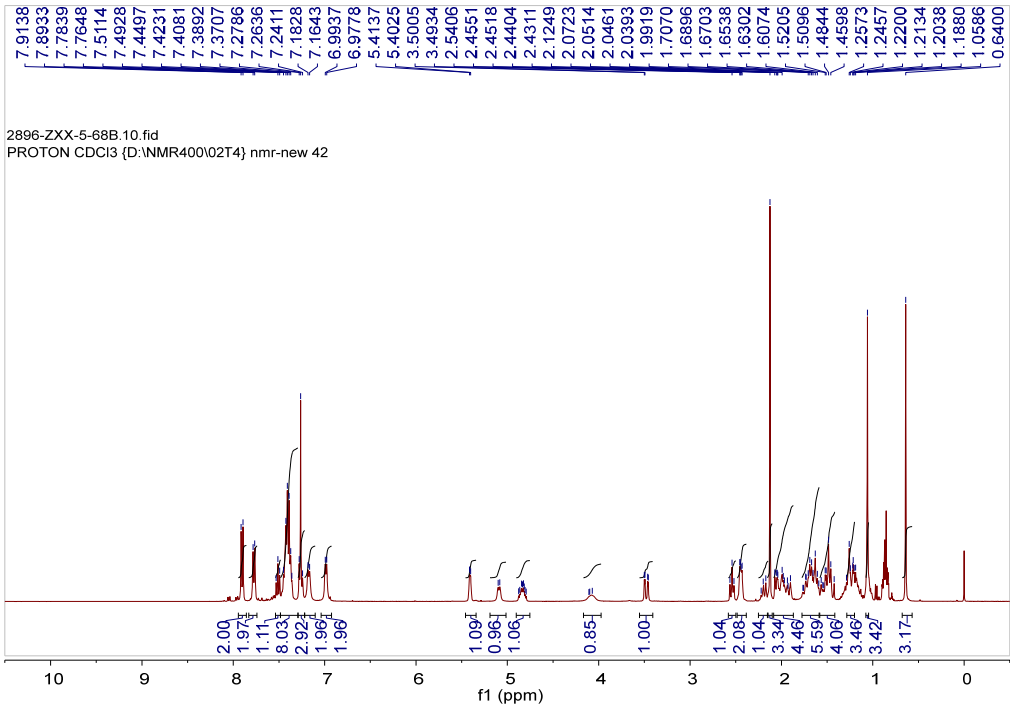


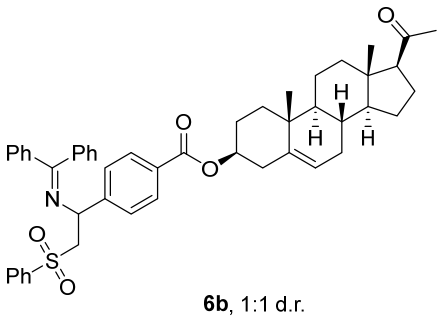
6a, 1:1 d.r.

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



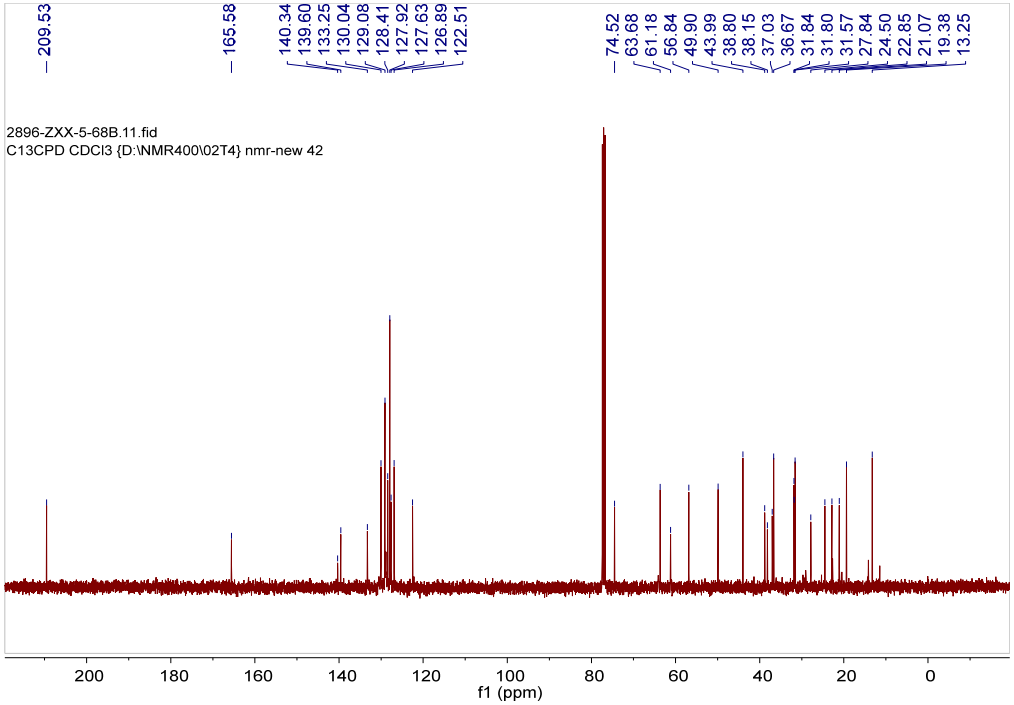


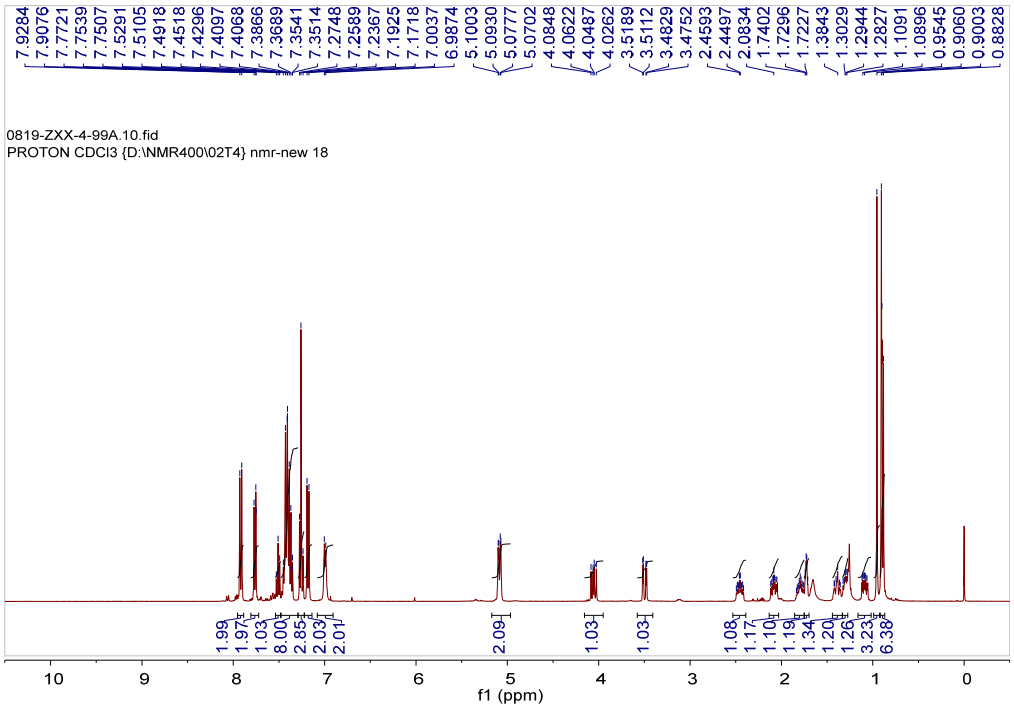


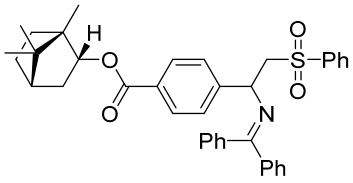
6b, 1:1 d.r.

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



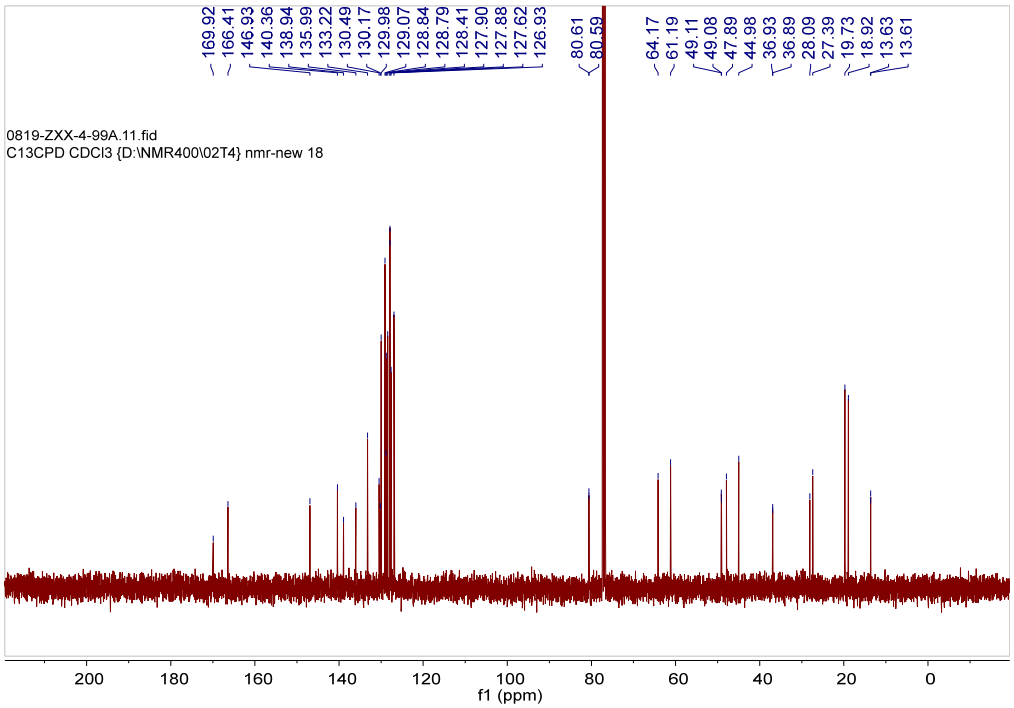


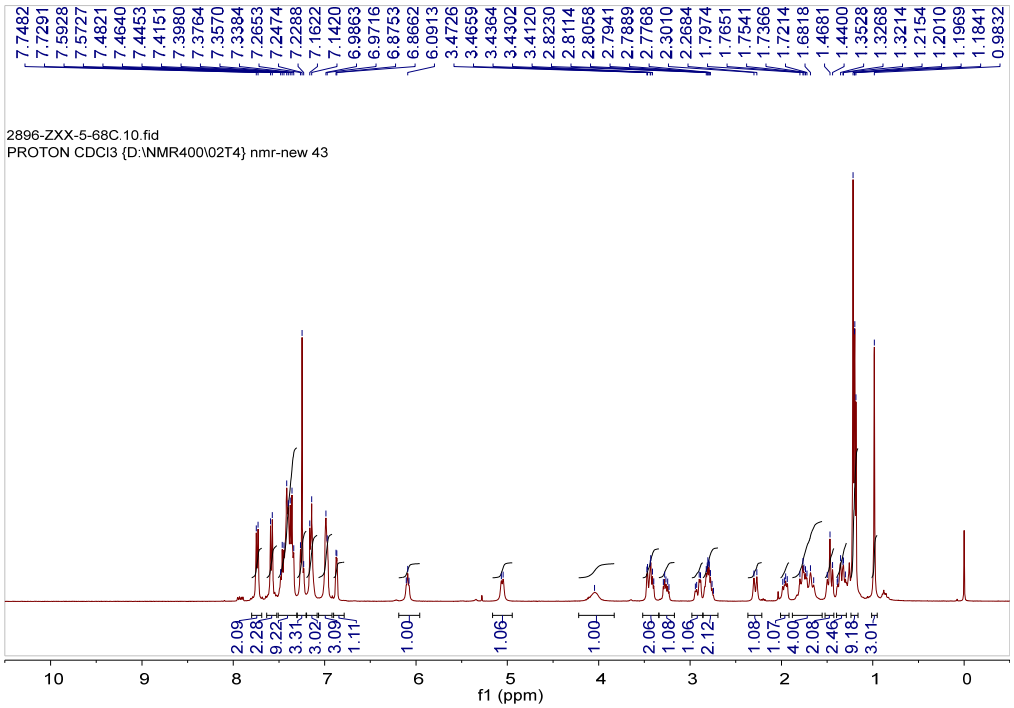


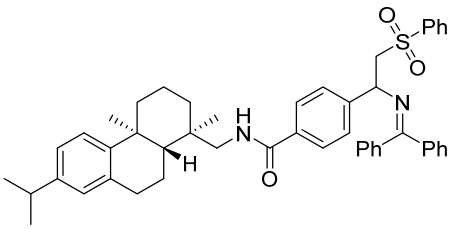
6c, 1:1 d.r.

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



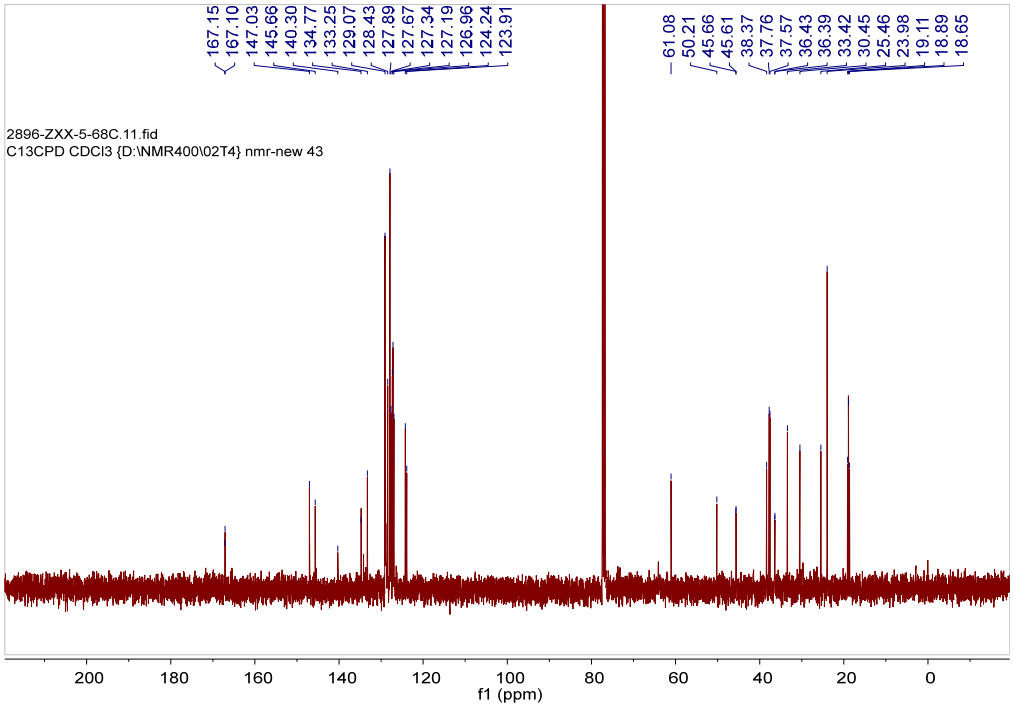


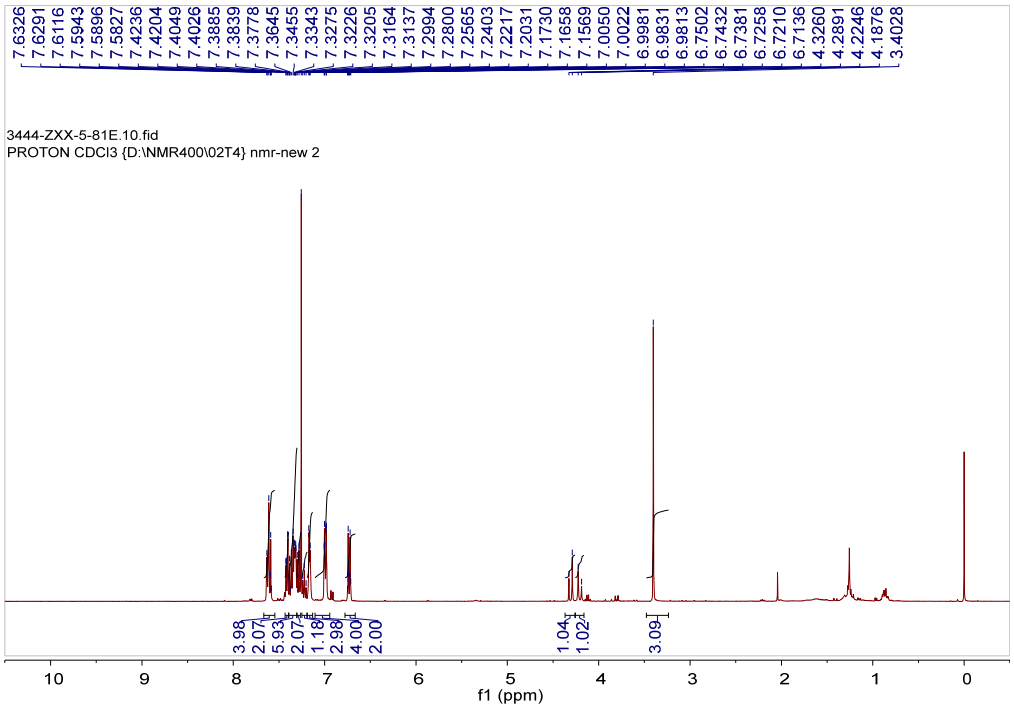


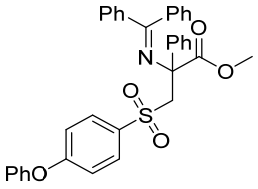
6d, 1:1 d.r.

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



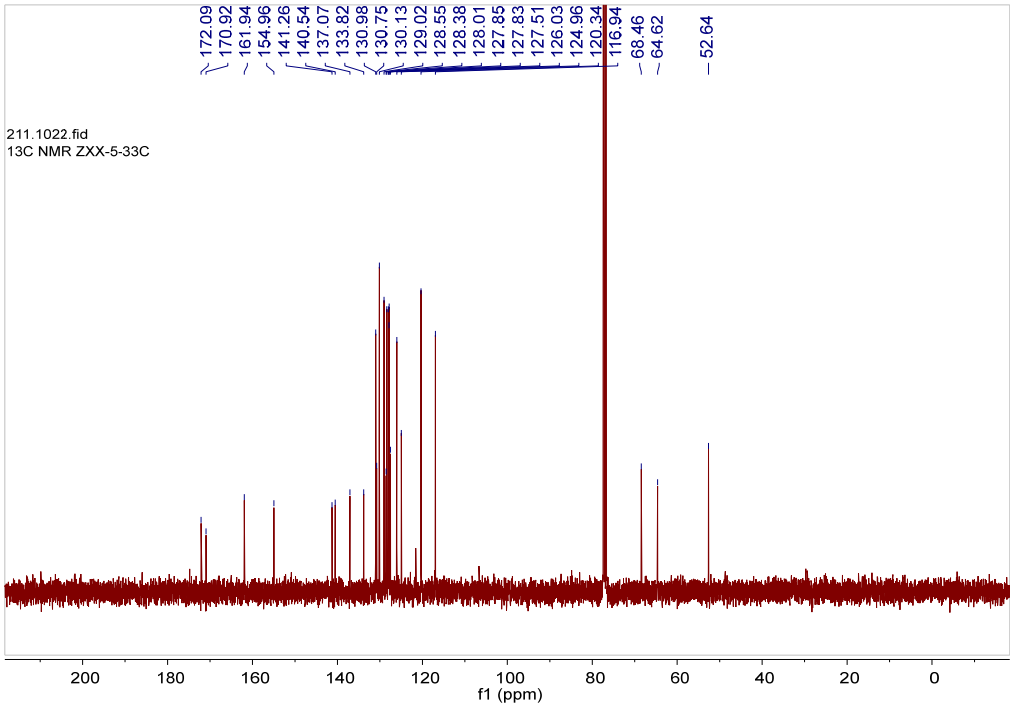


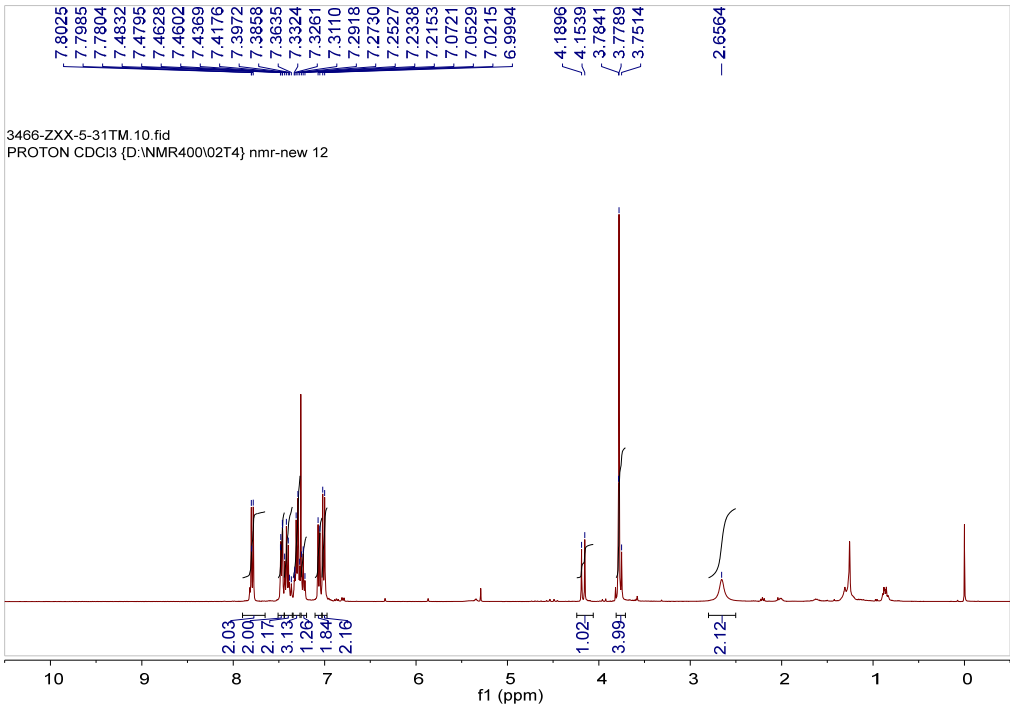


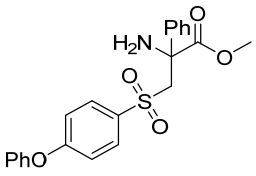
(±) **9**

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



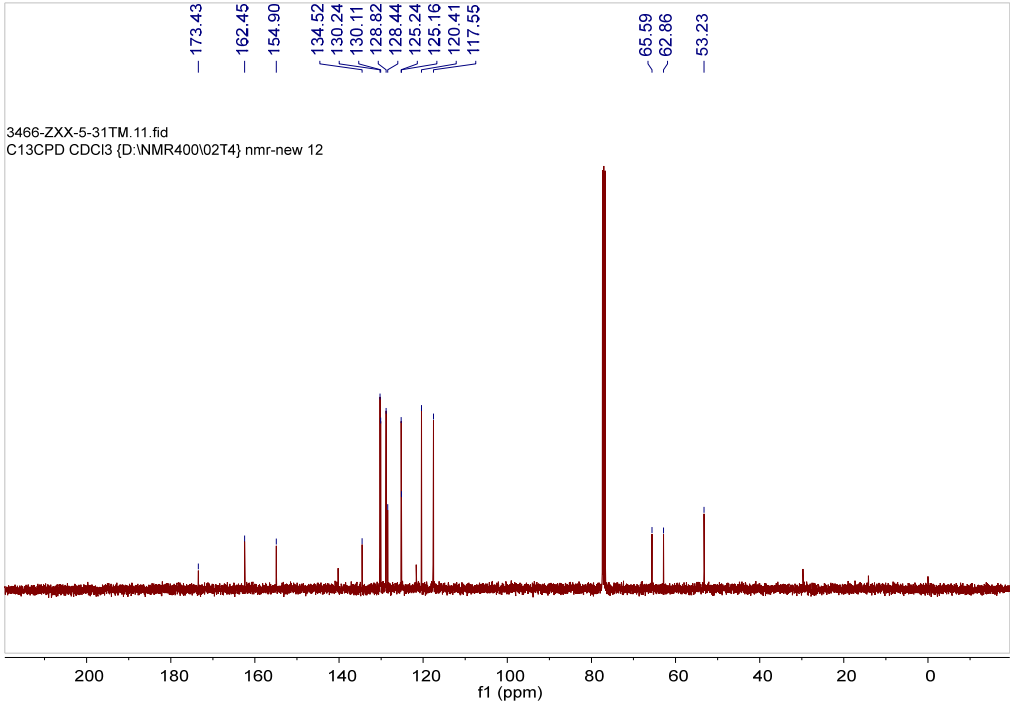


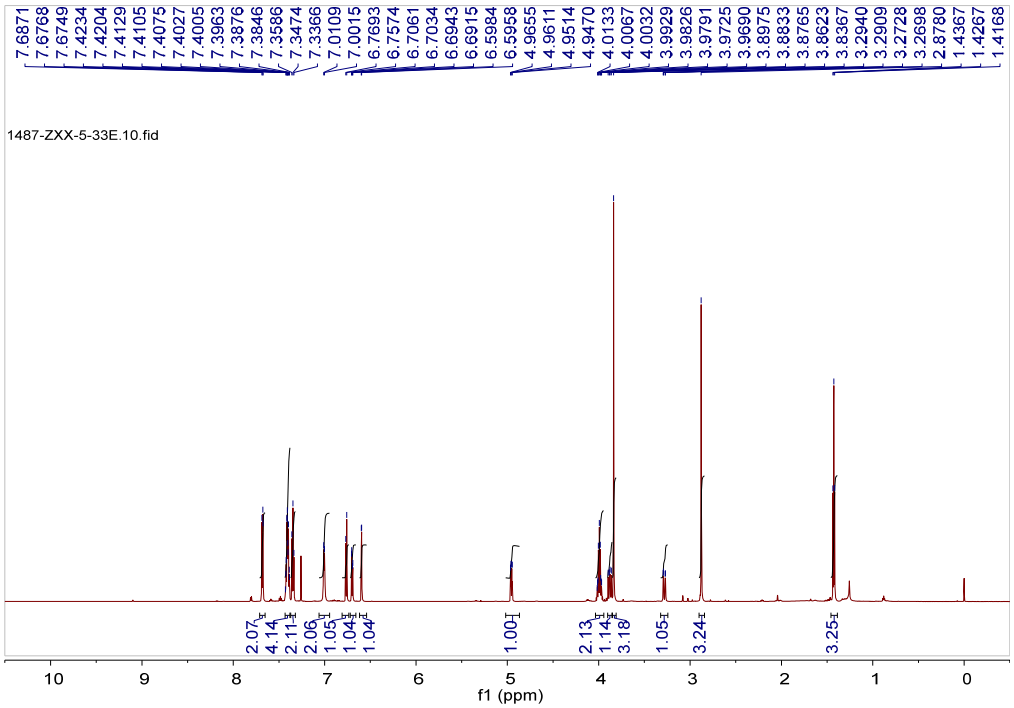


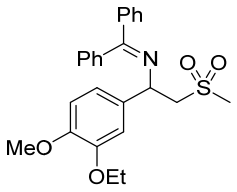
(±)10, Matrix metalloprotease inhibitor precursor

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



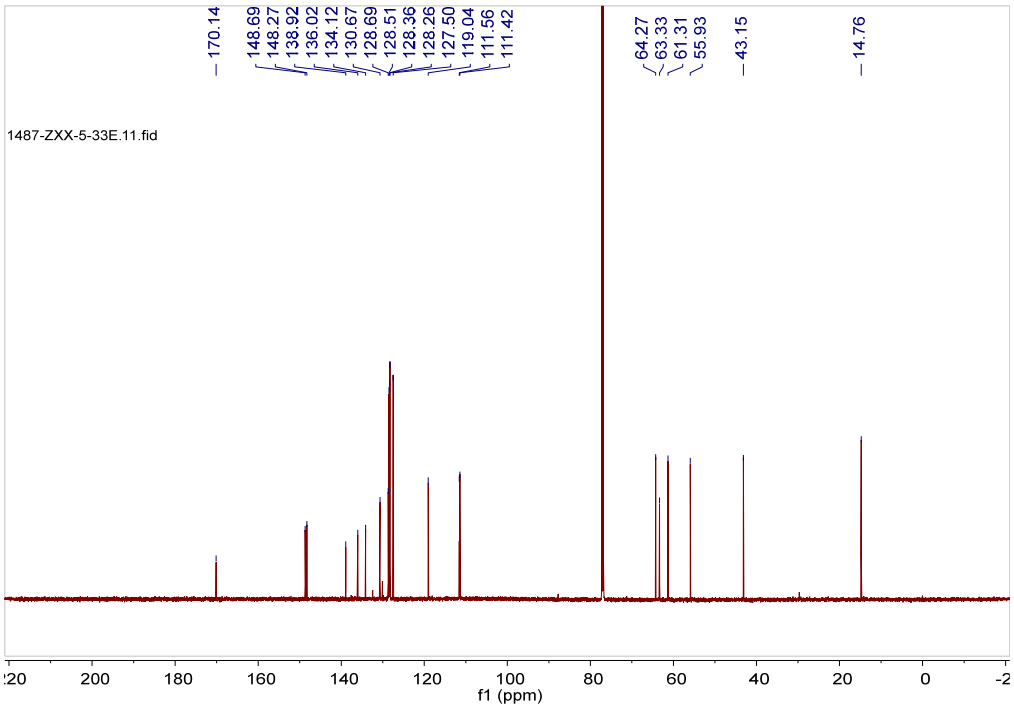


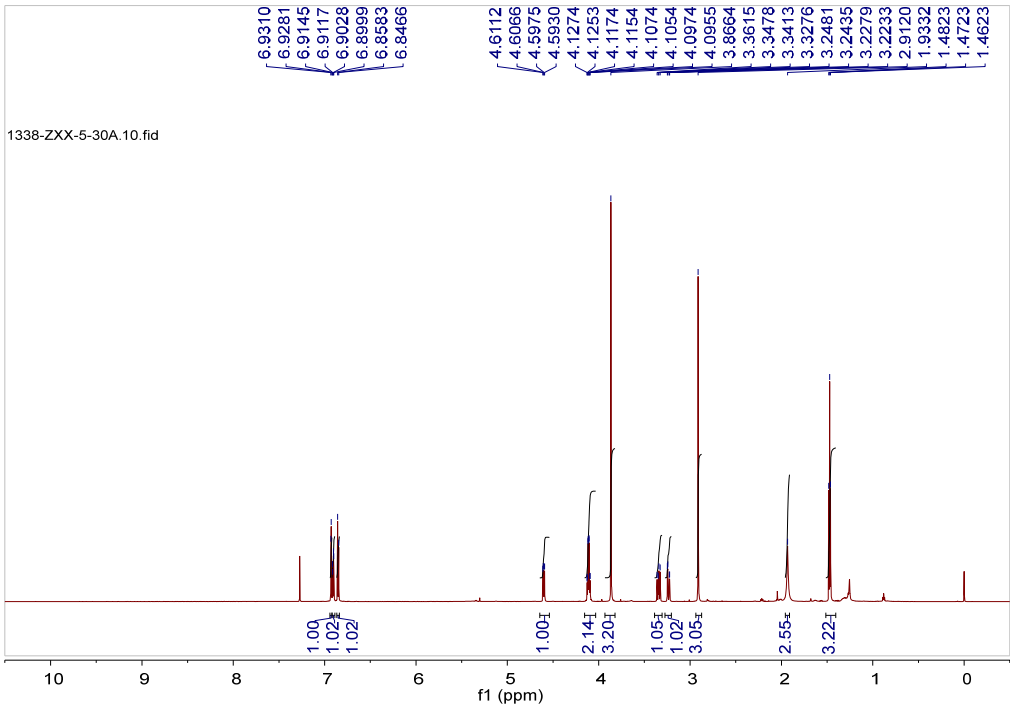


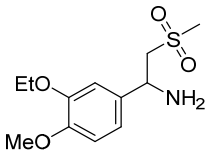
(±) **13**

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (175 MHz, Chloroform-*d*)



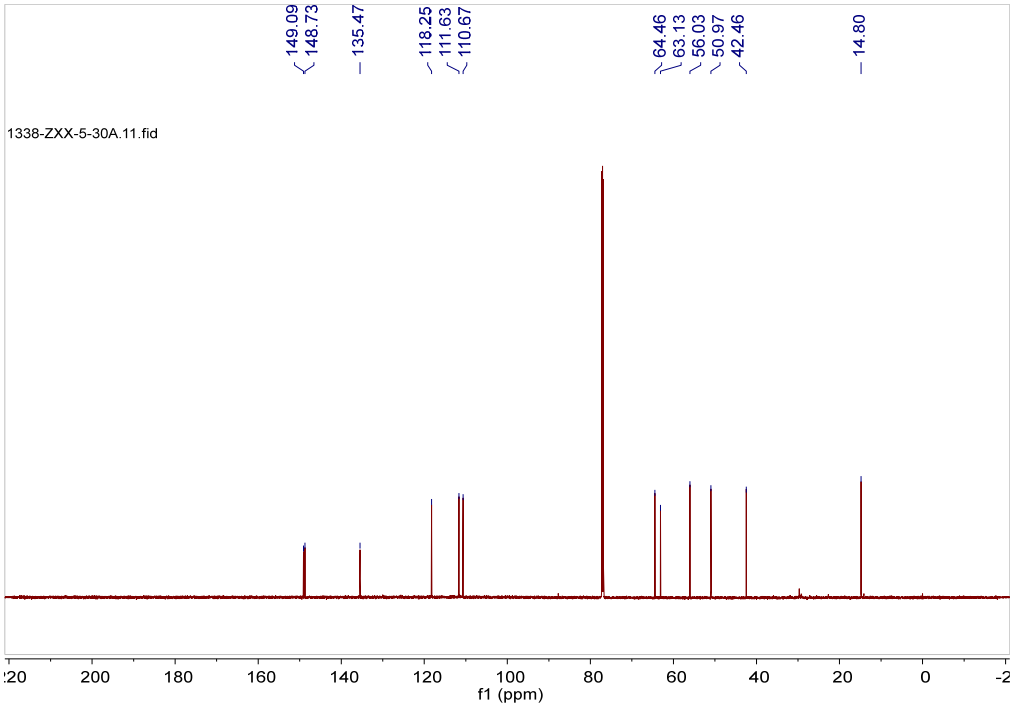


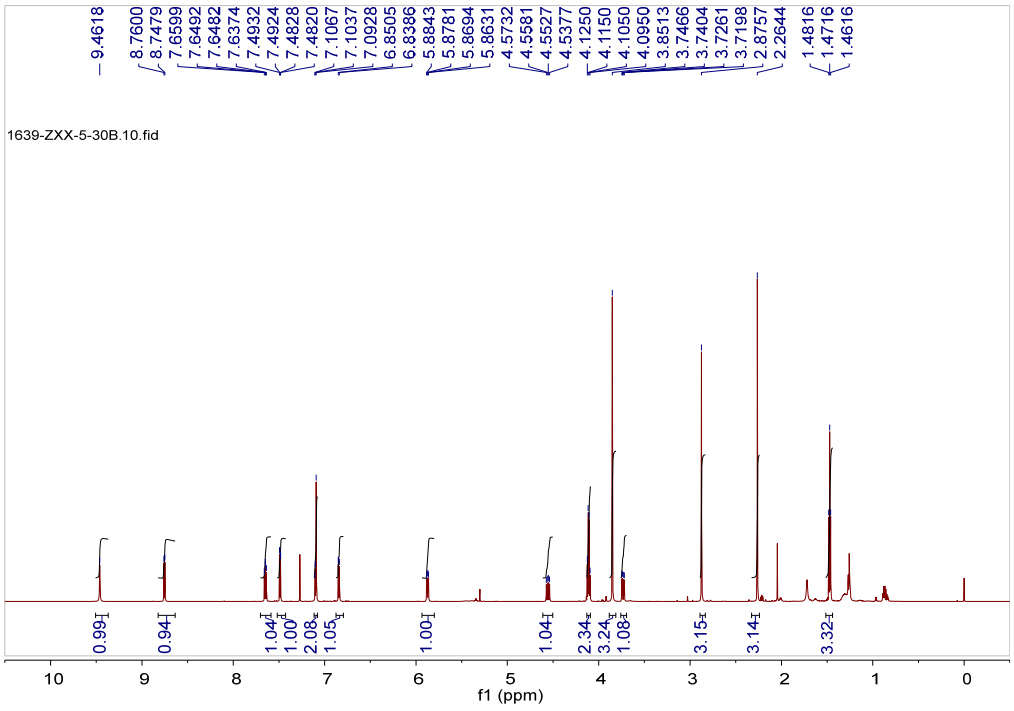


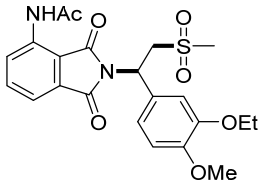
(±) **14**

^{1}H NMR (700 MHz, Chloroform-*d*)

^{13}C NMR (175 MHz, Chloroform-*d*)



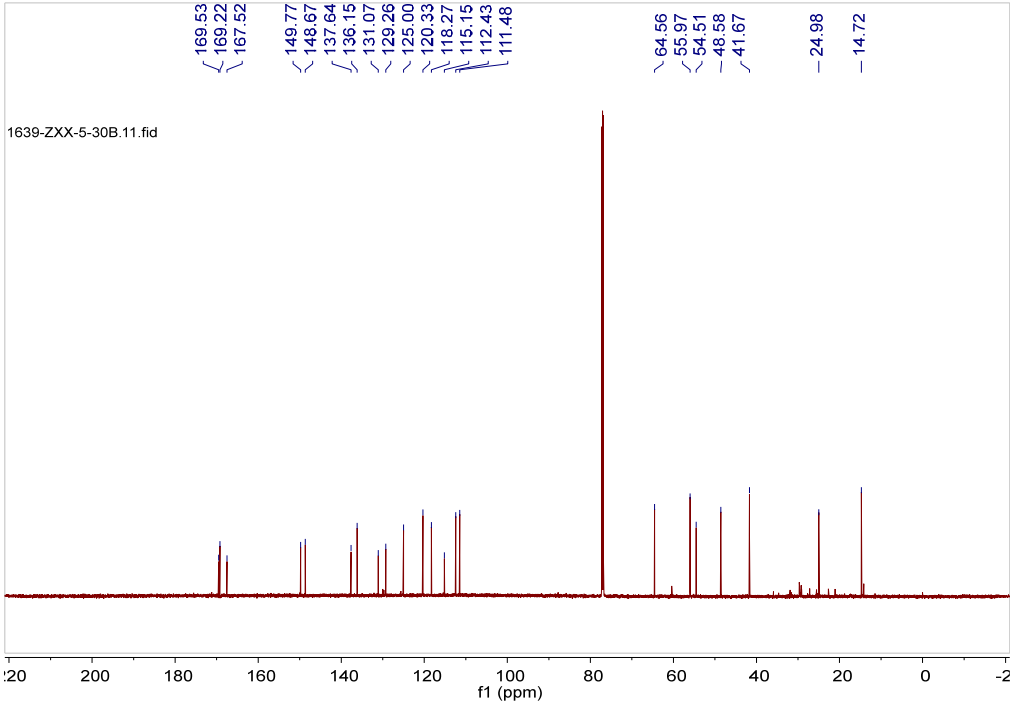


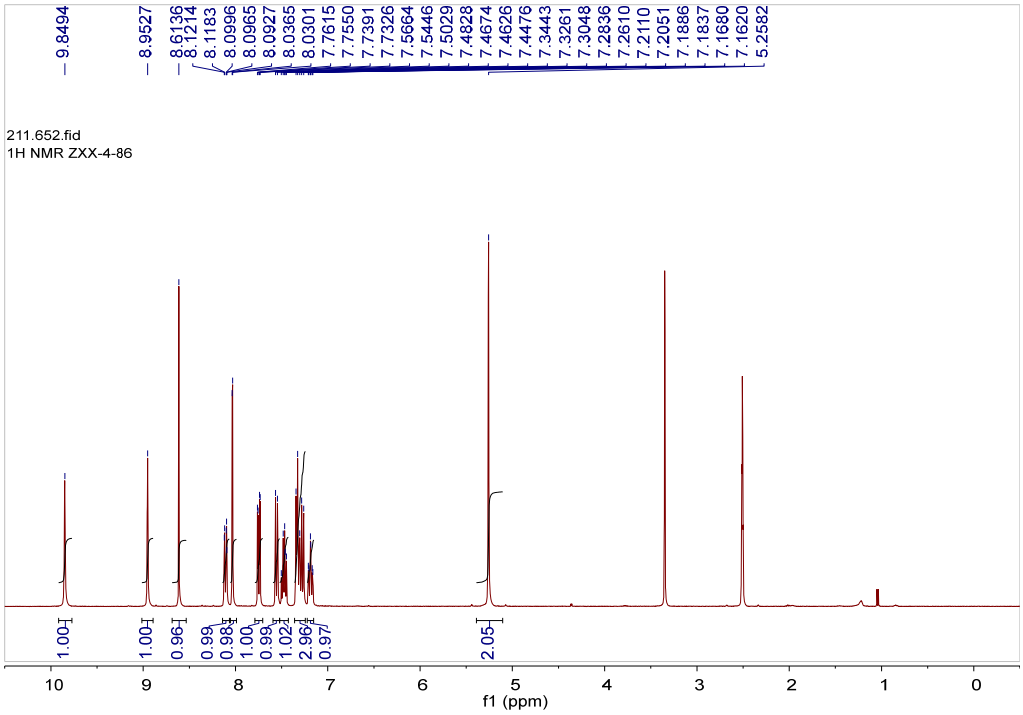


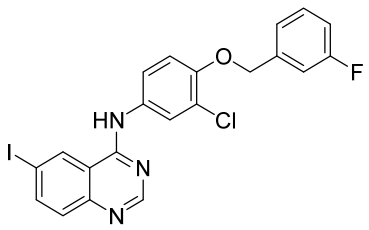
(±)15, Apremilast

^{1}H NMR (700 MHz, Chloroform-*d*)

^{13}C NMR (175 MHz, Chloroform-*d*)



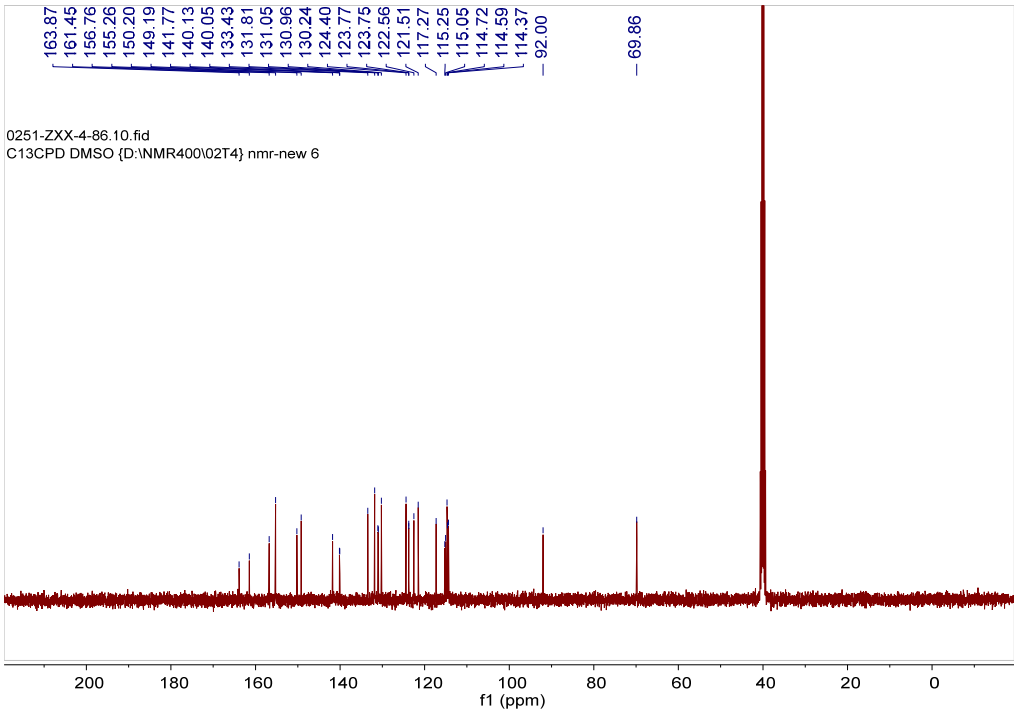


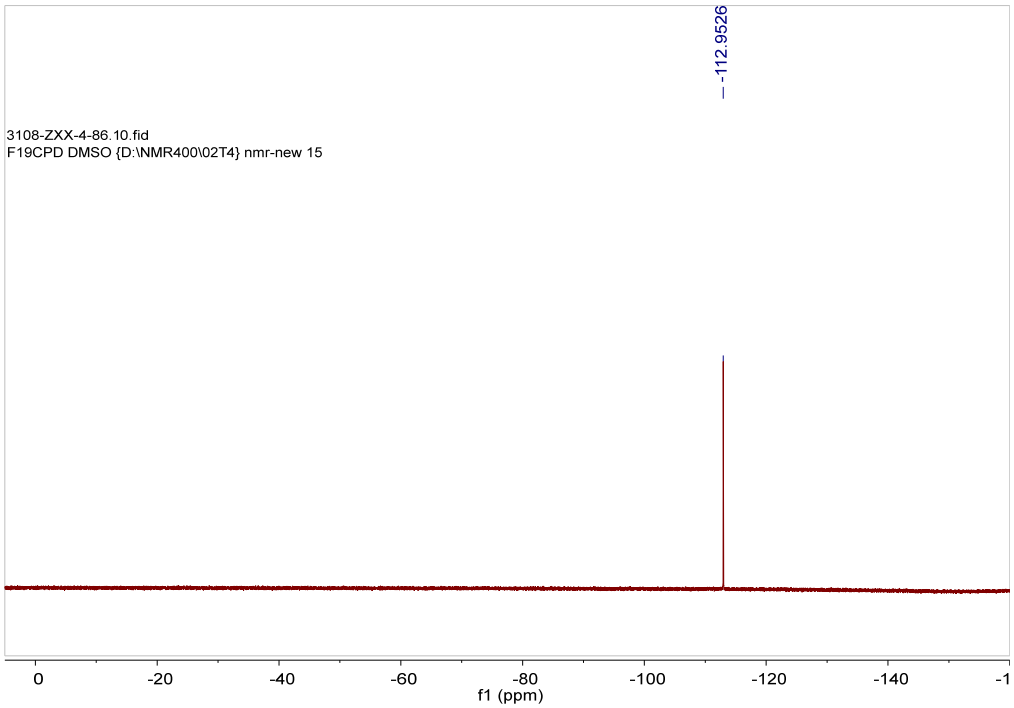


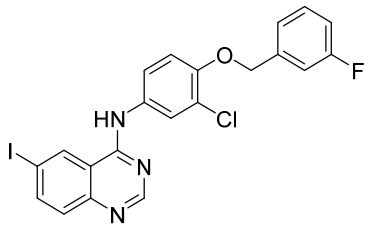
18

^{1}H NMR (400 MHz, DMSO-d^{6})

^{13}C NMR (100 MHz, DMSO-d^{6})

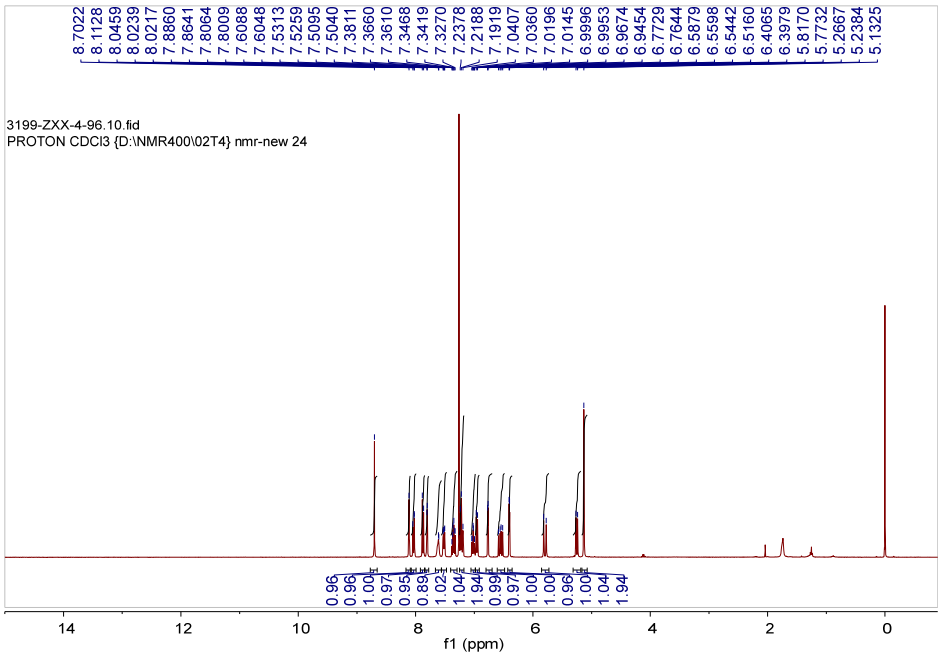


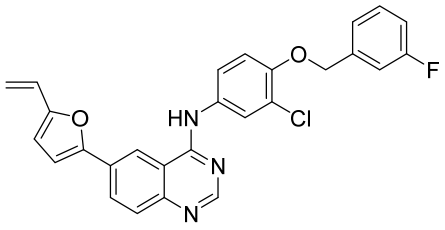




18

^{19}FNMR (375 MHz, DMSO-*d*^{6})

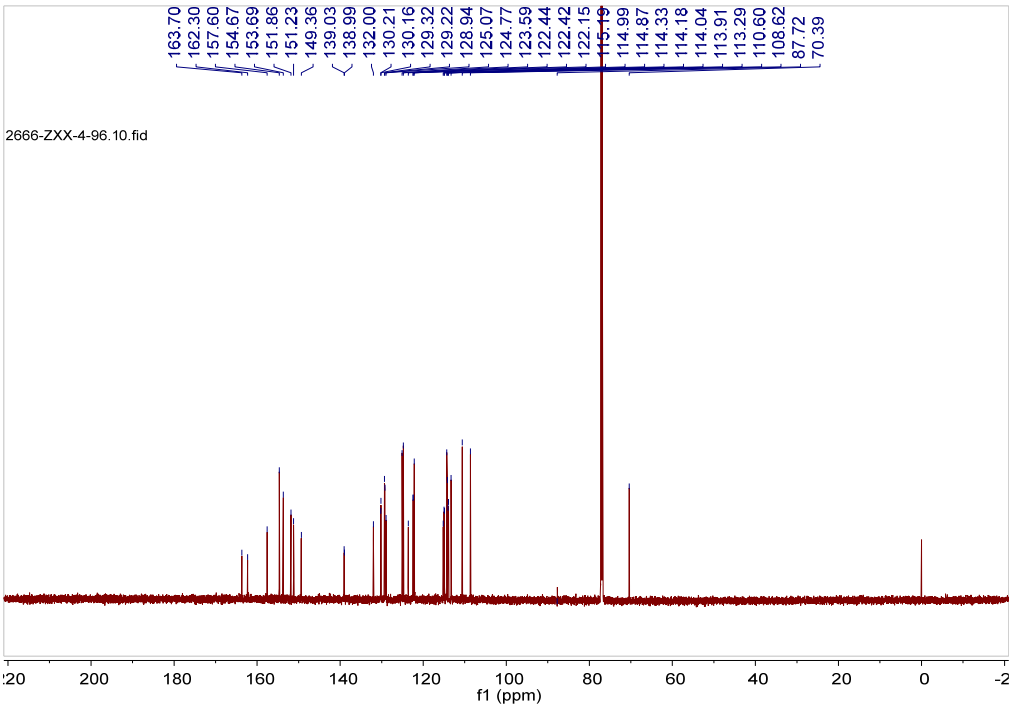


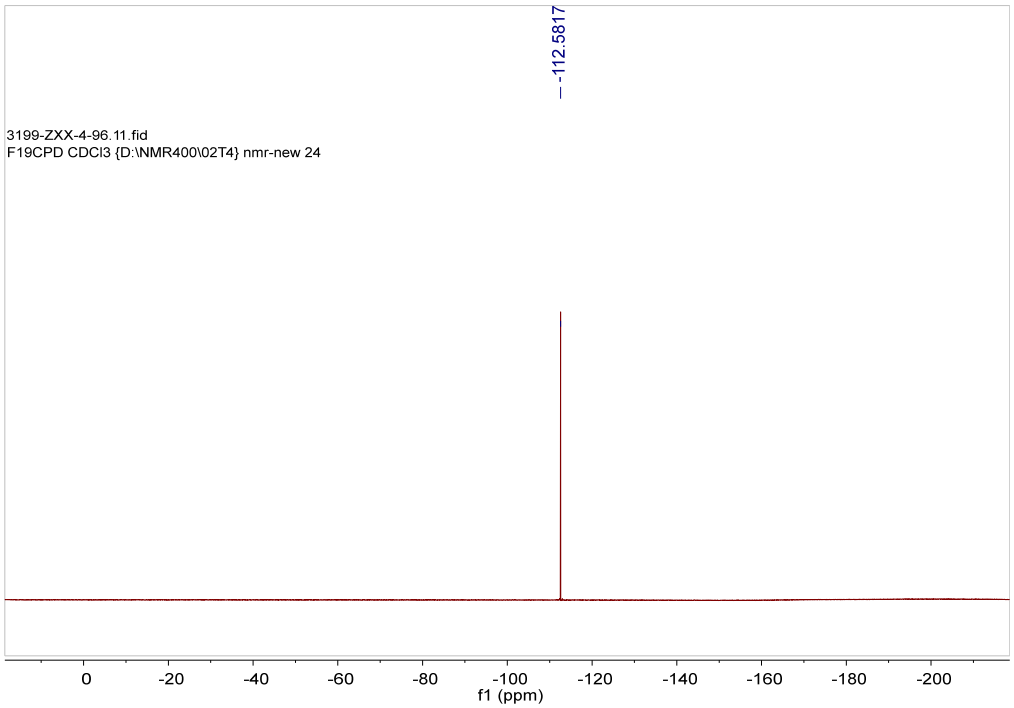


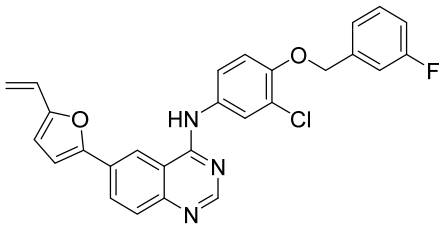
20

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (175 MHz, Chloroform-*d*)

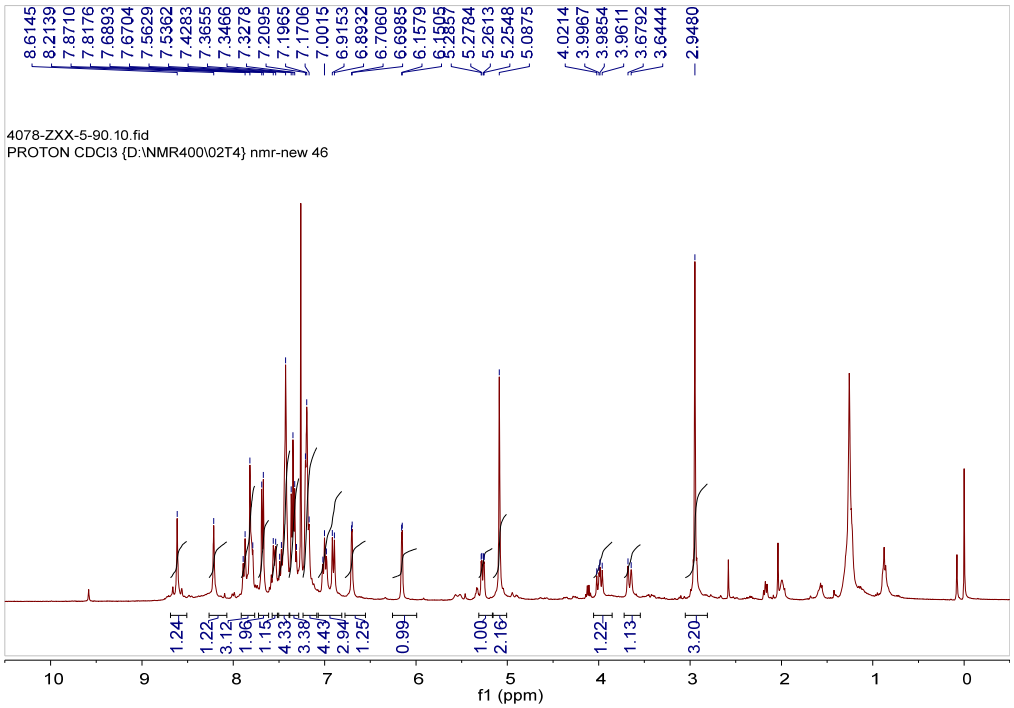


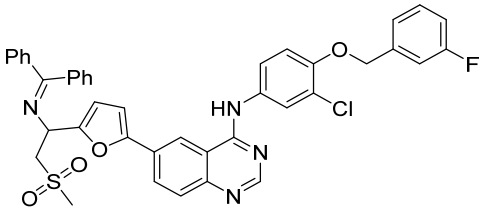




20

^{19}FNMR (375 MHz, Chloroform-*d*)

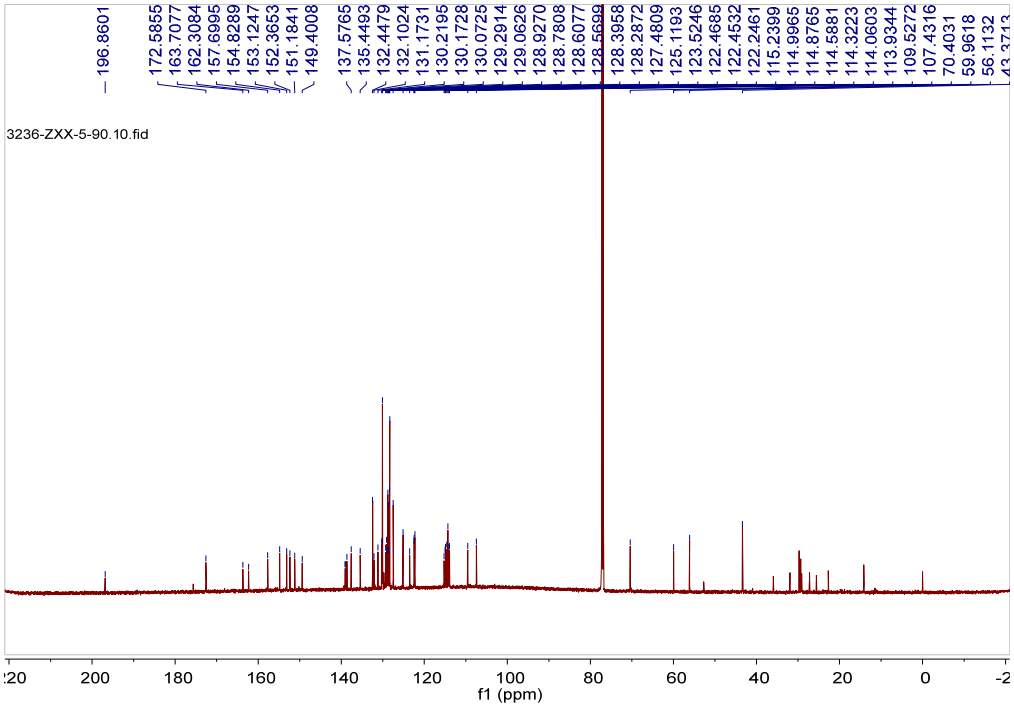


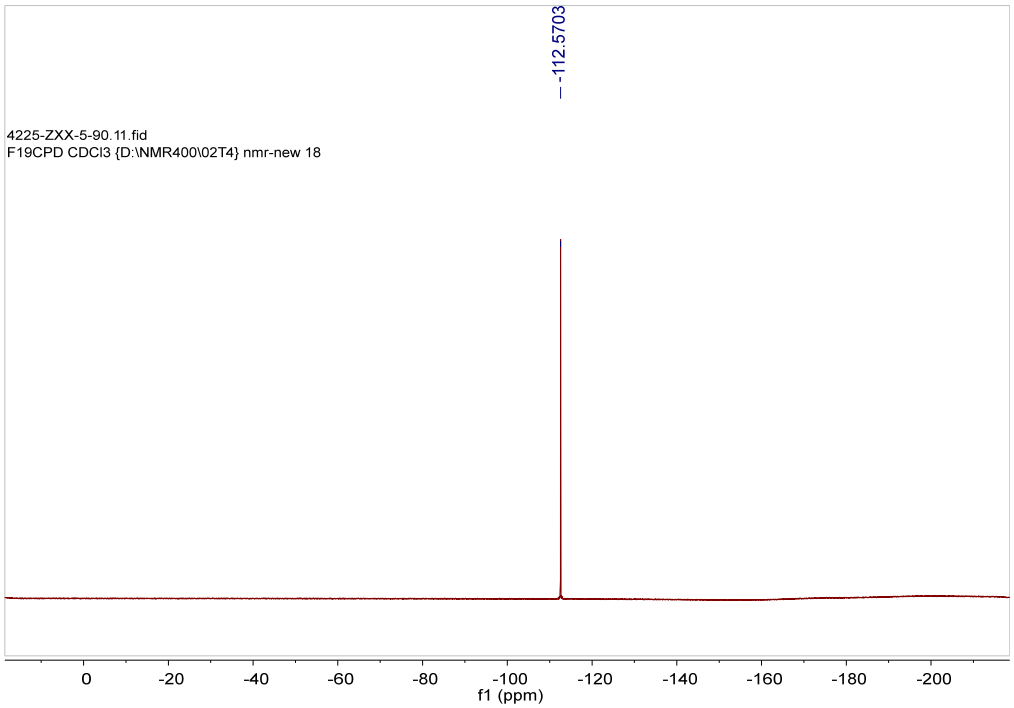


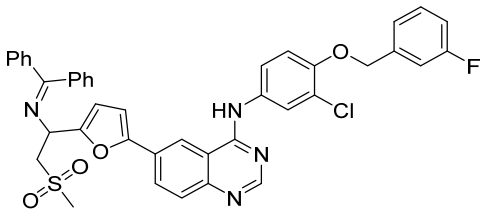
(±) 21, Lapatinib analogue

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (175 MHz, Chloroform-*d*)

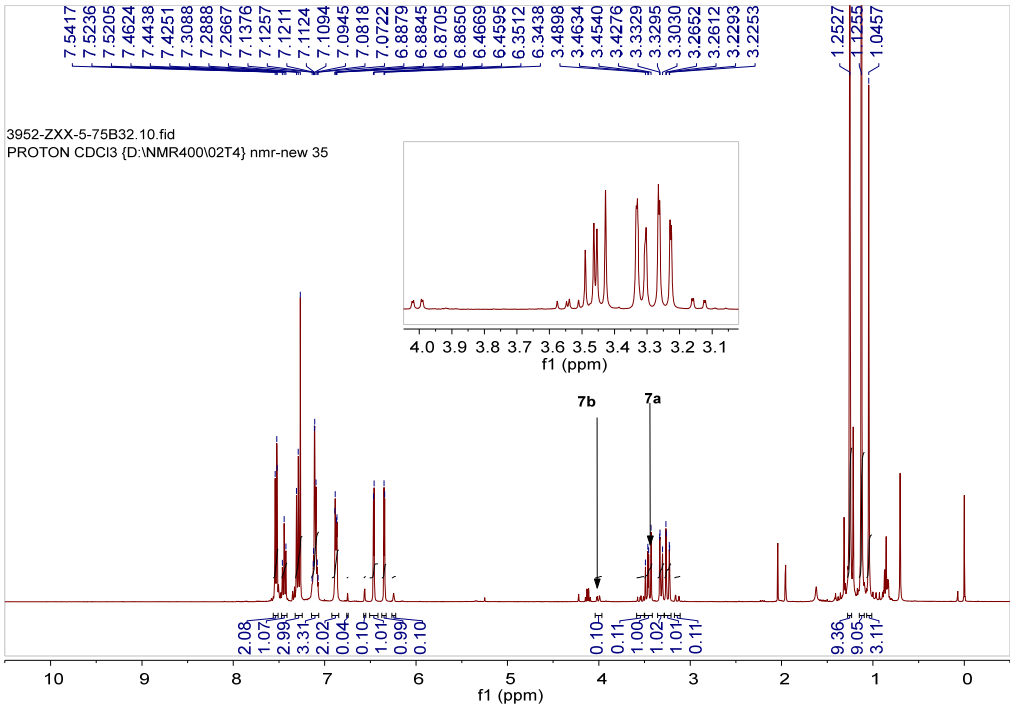


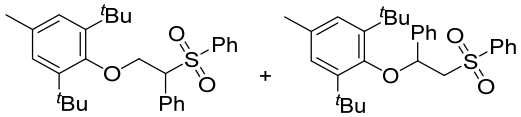




(±) 21, Lapatinib analogue

^{19}F NMR (375 MHz, Chloroform-*d*)

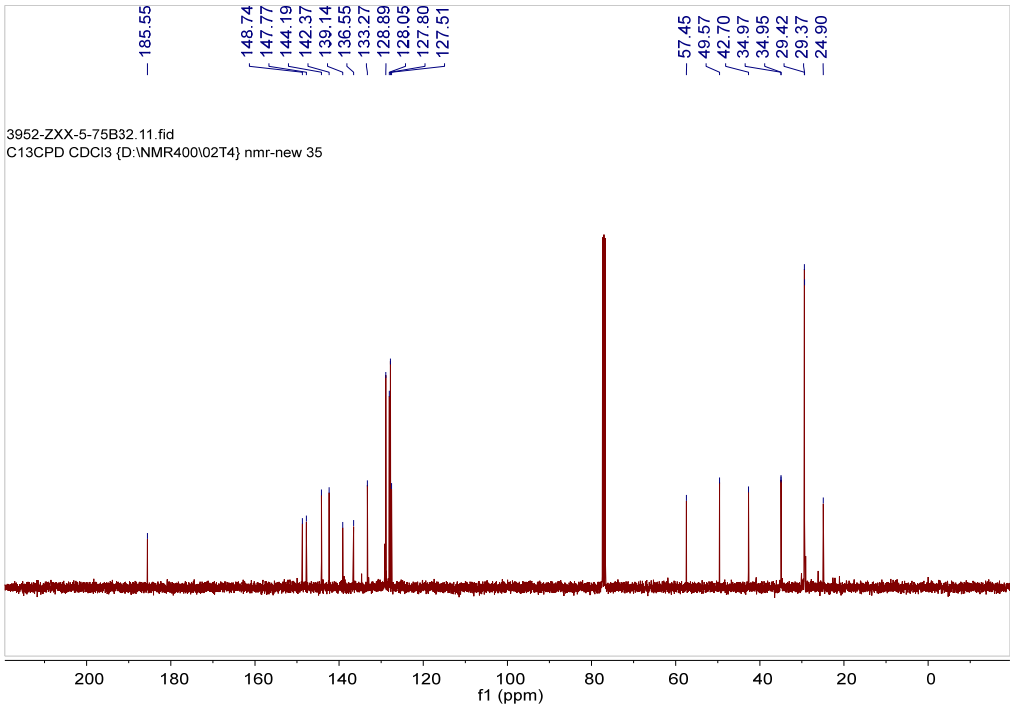


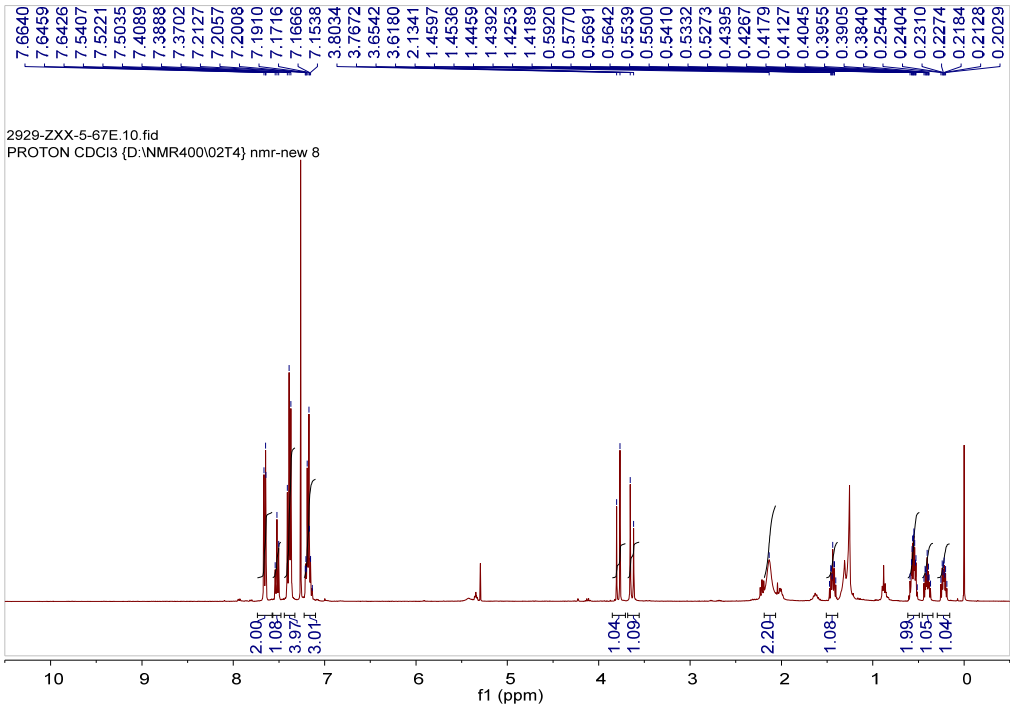


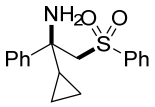
7a **7b**

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



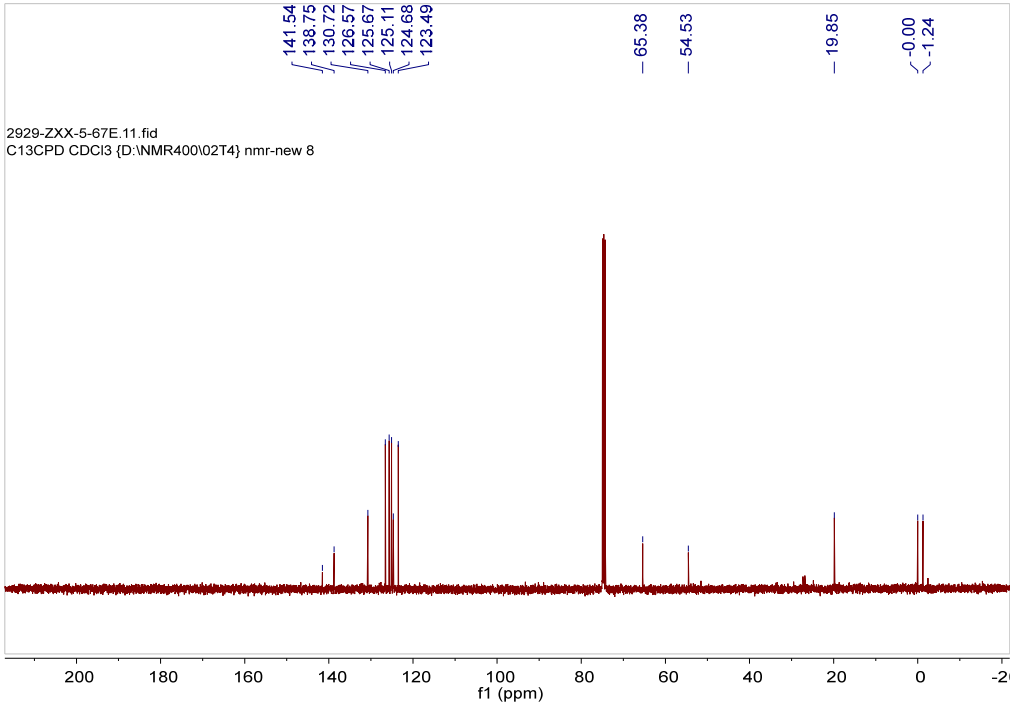


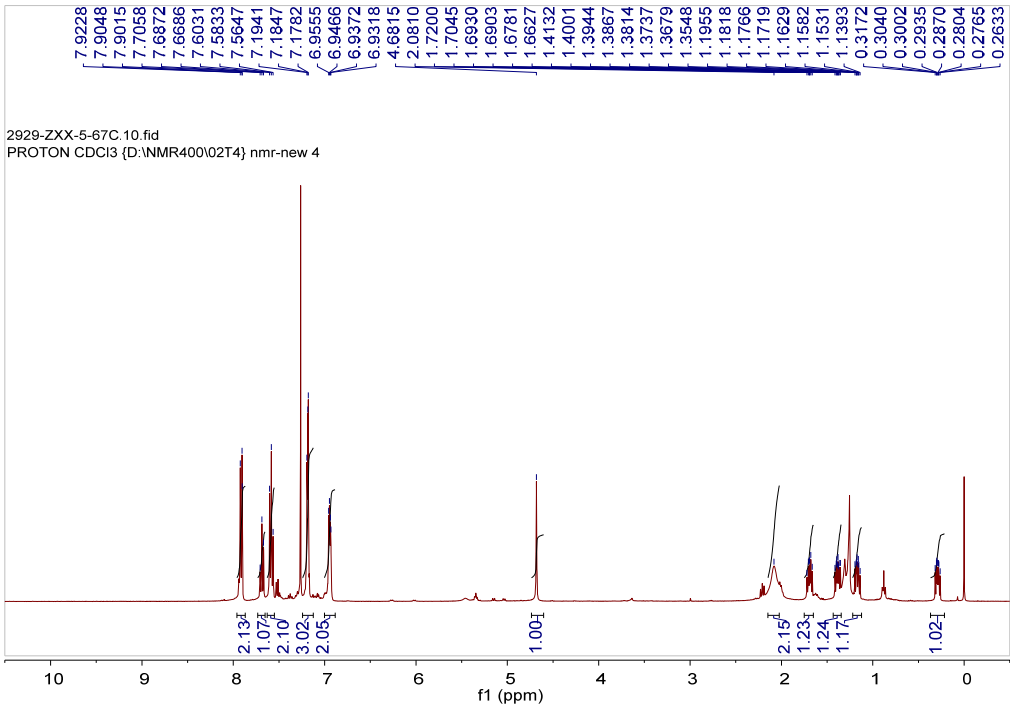


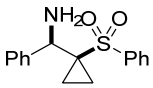
(±) 22

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



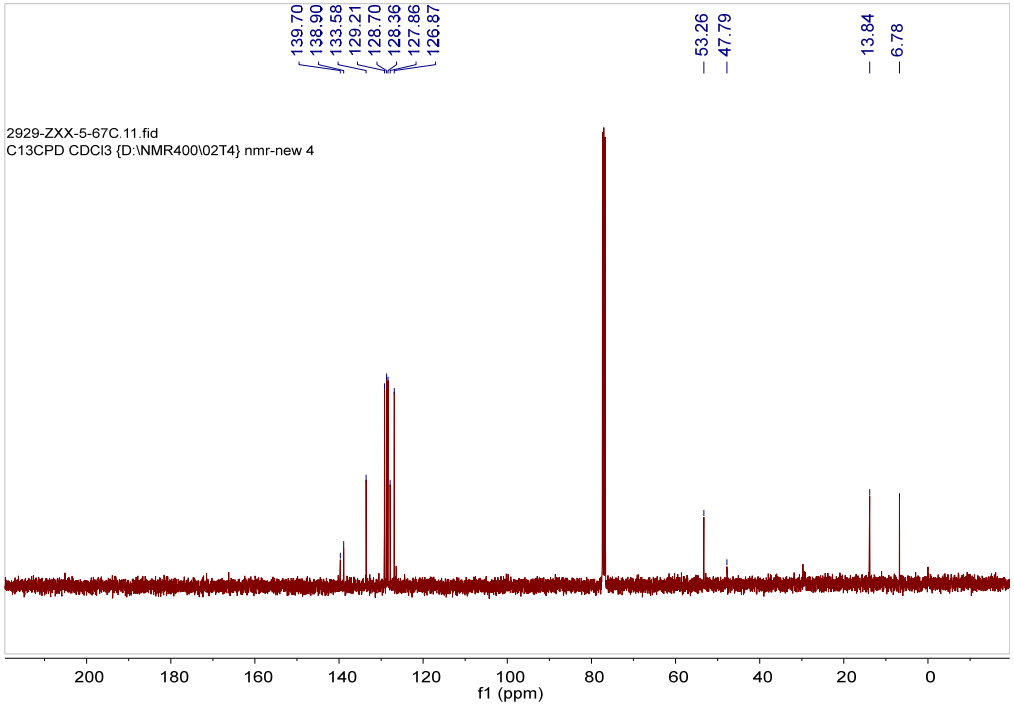


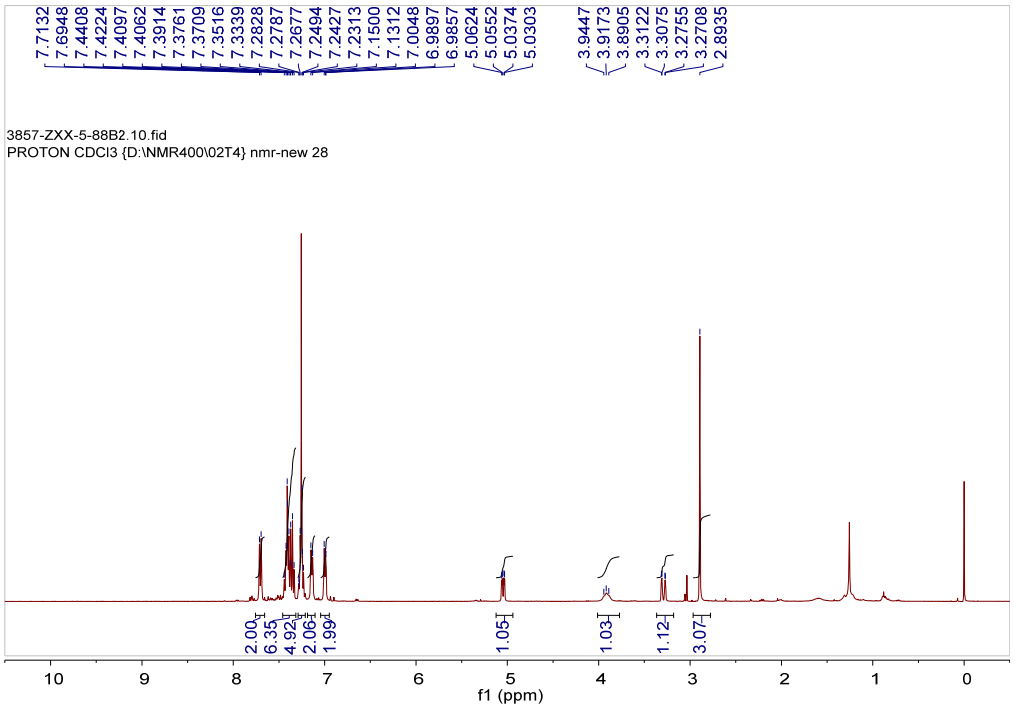


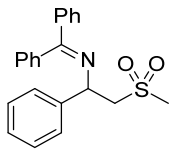
(±) 24

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



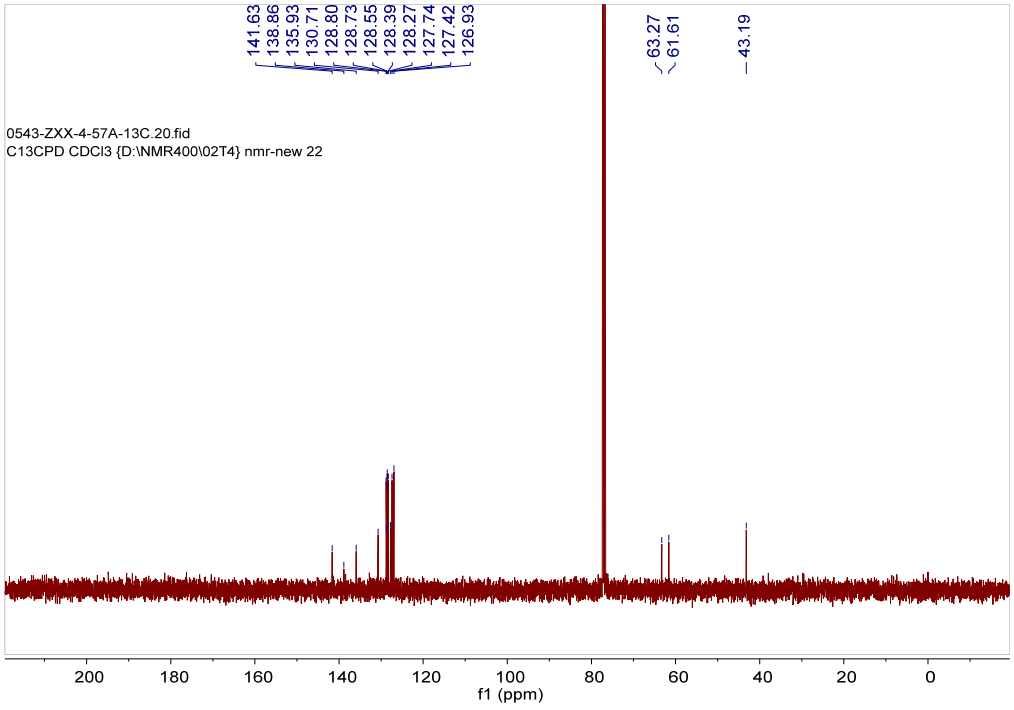


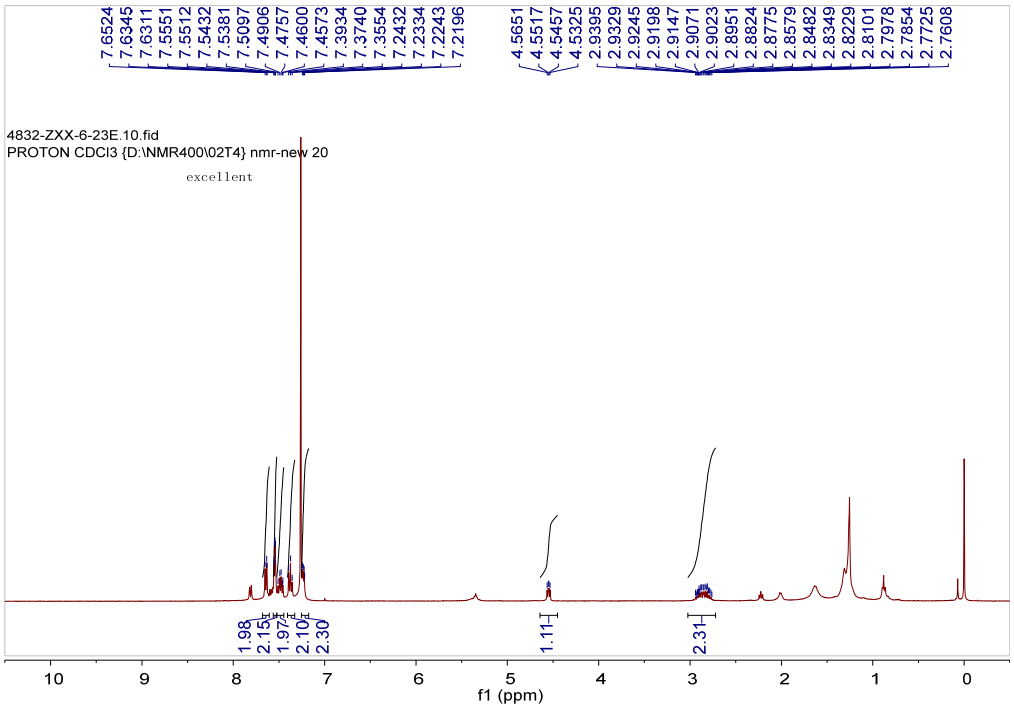


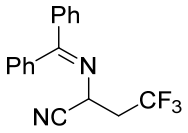
(±) 4a'

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (175 MHz, Chloroform-*d*)



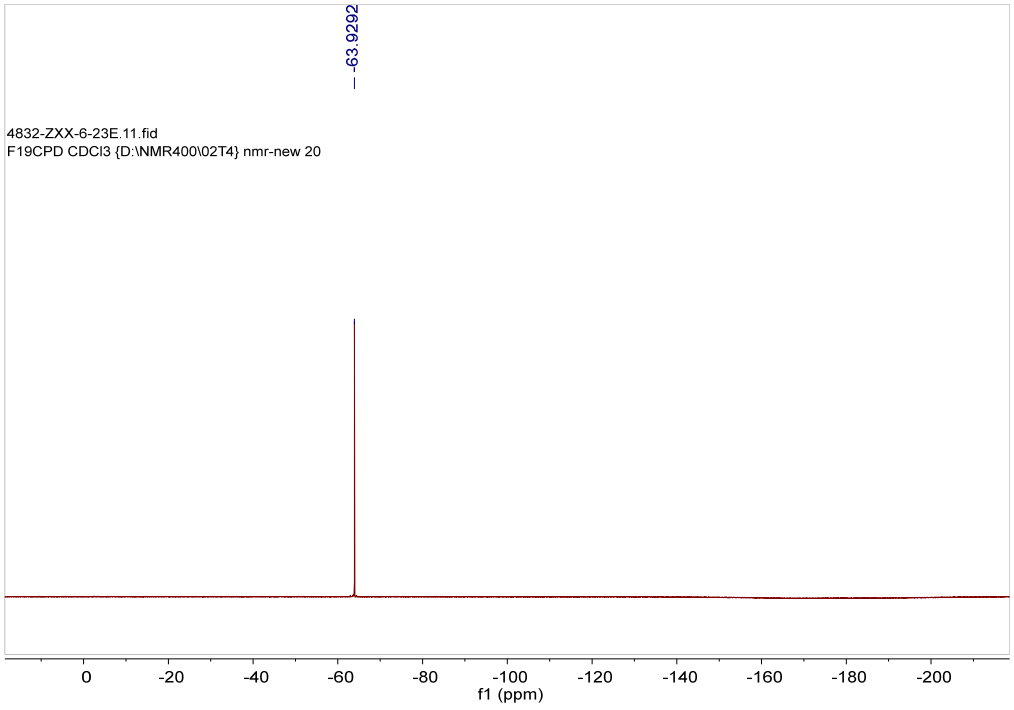


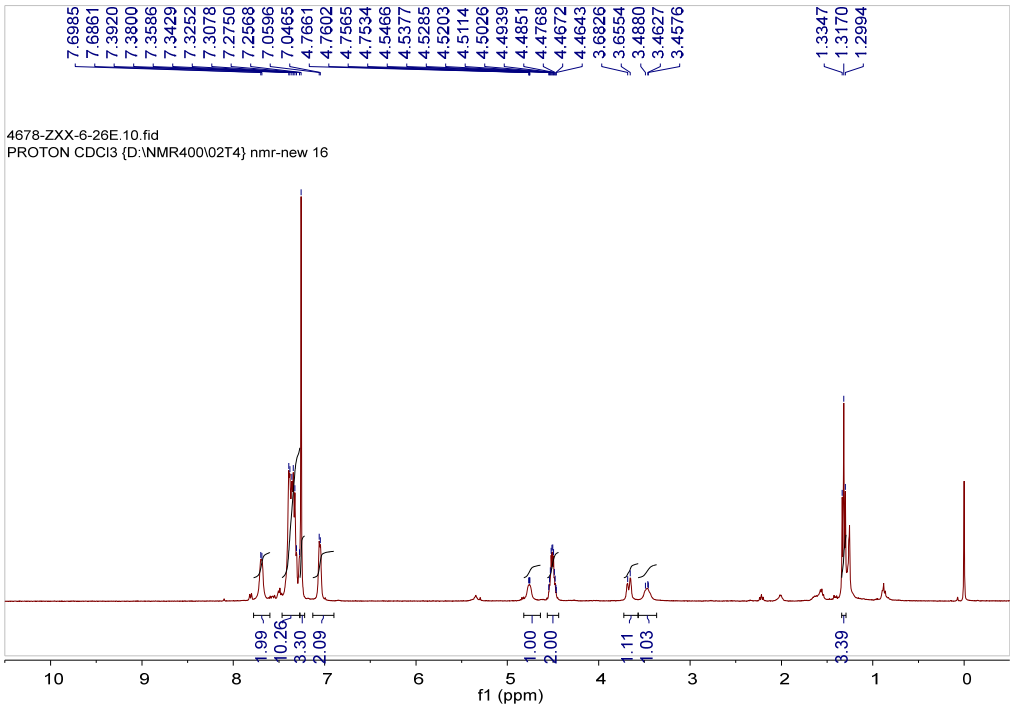


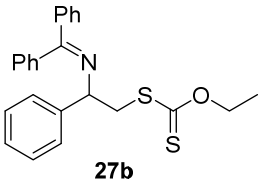
27a

^{1}H NMR (400 MHz, Chloroform-*d*)

^{19}F NMR (375 MHz, Chloroform-*d*)



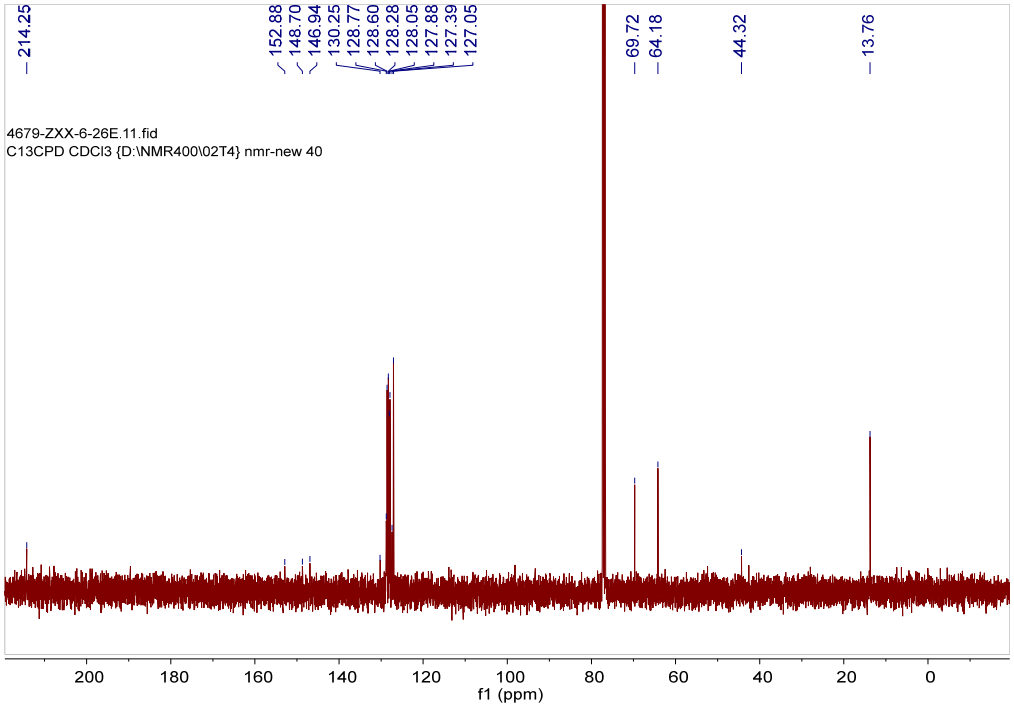


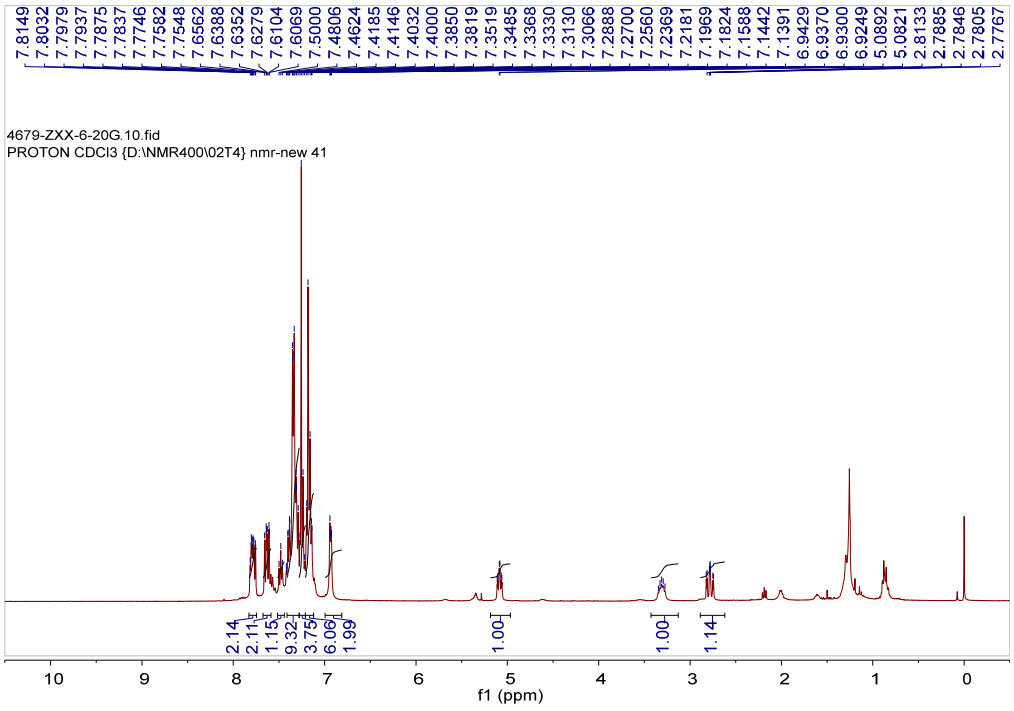


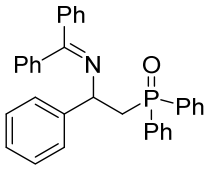
27b

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



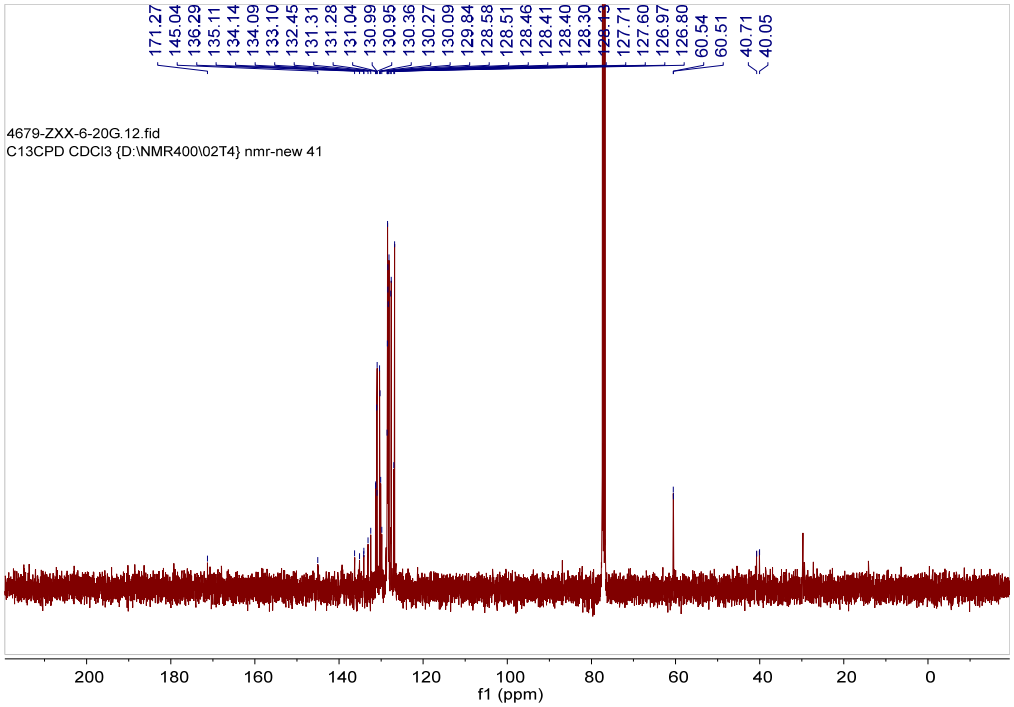


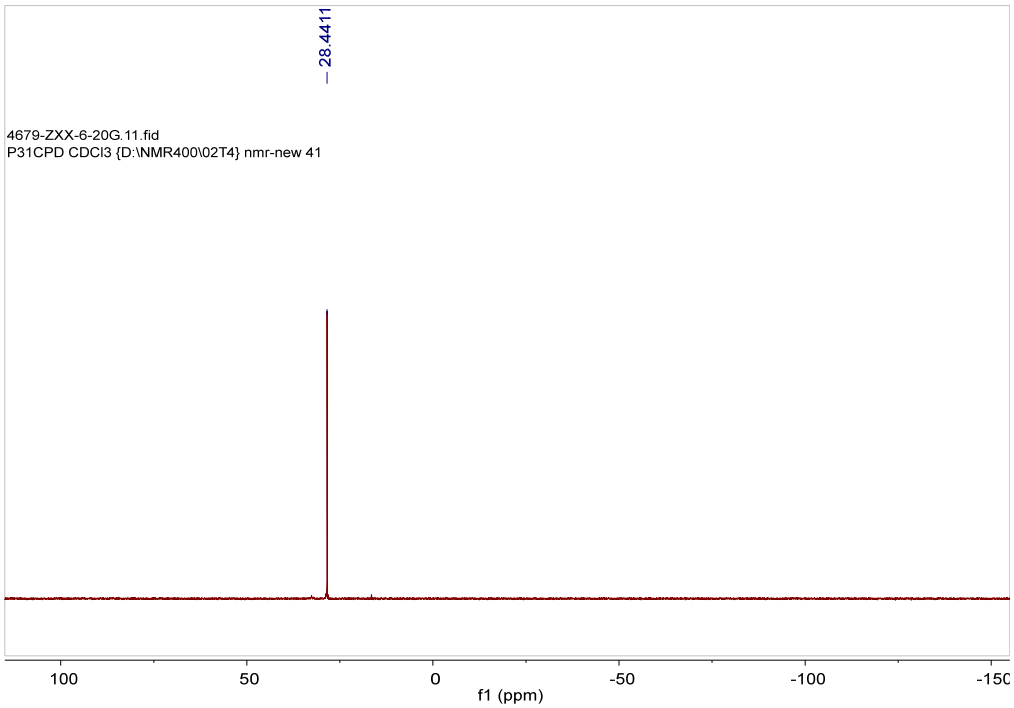


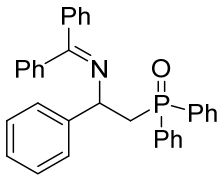
27c

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)

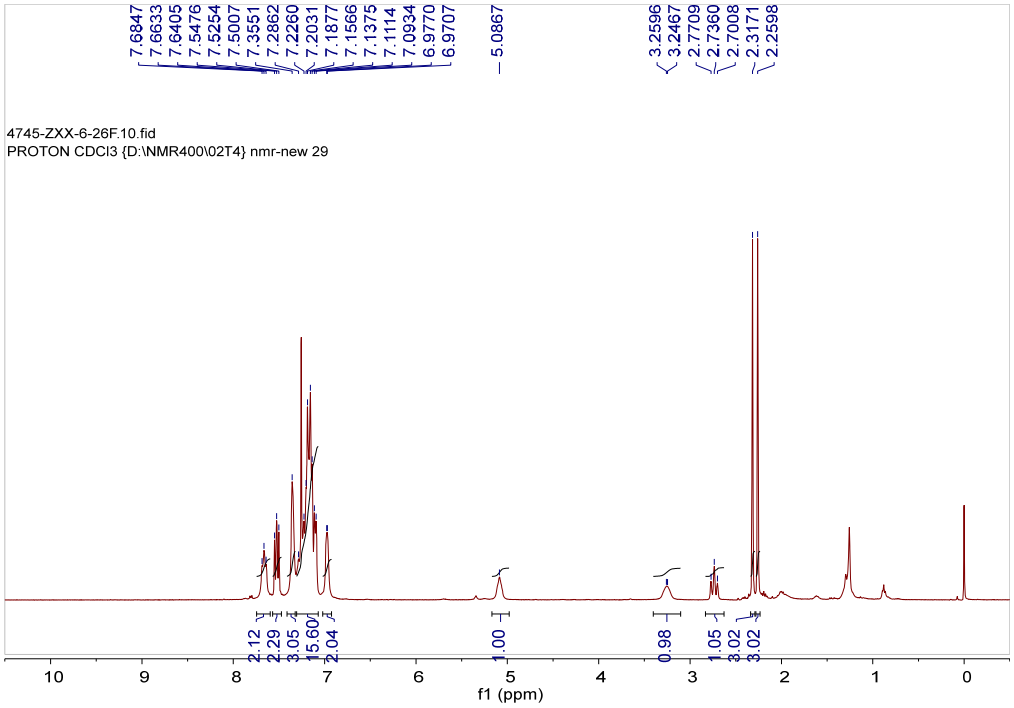


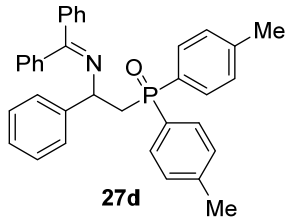




27c

^{31}P NMR (162 MHz, Chloroform-*d*)

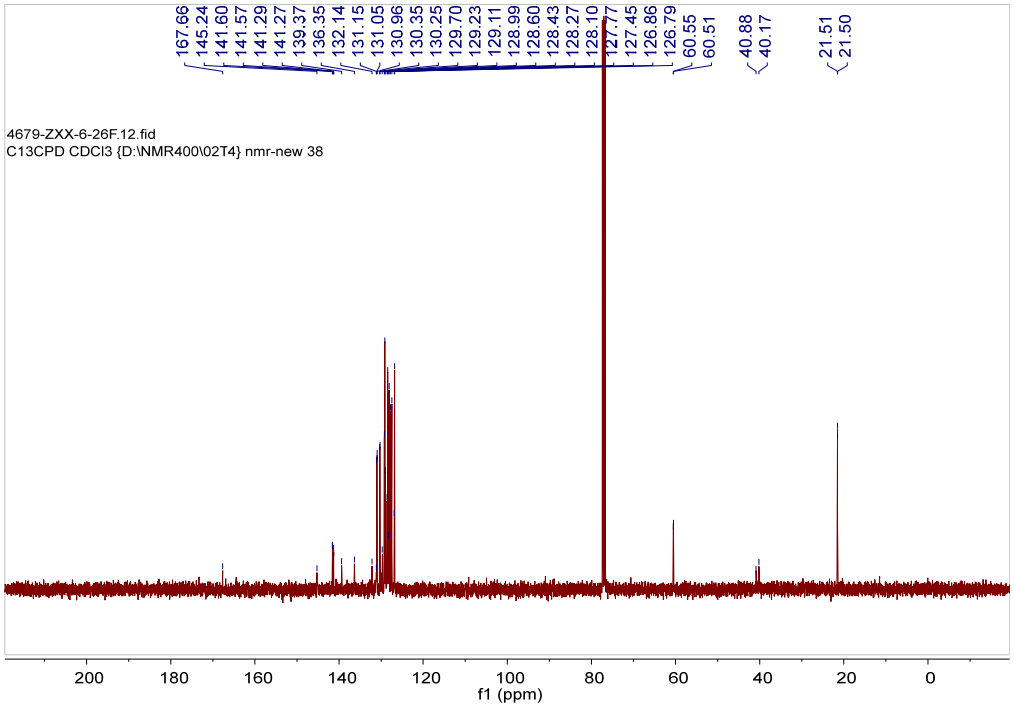


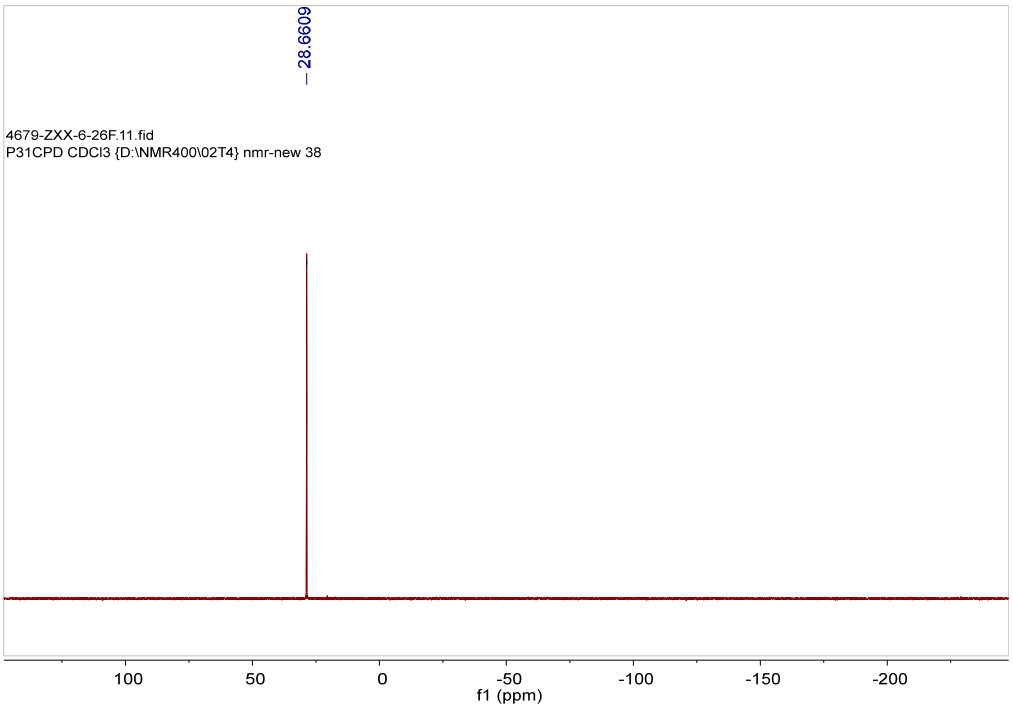


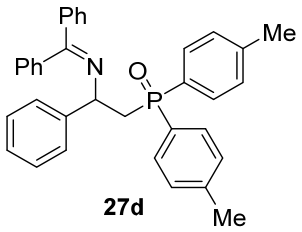
27d

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)

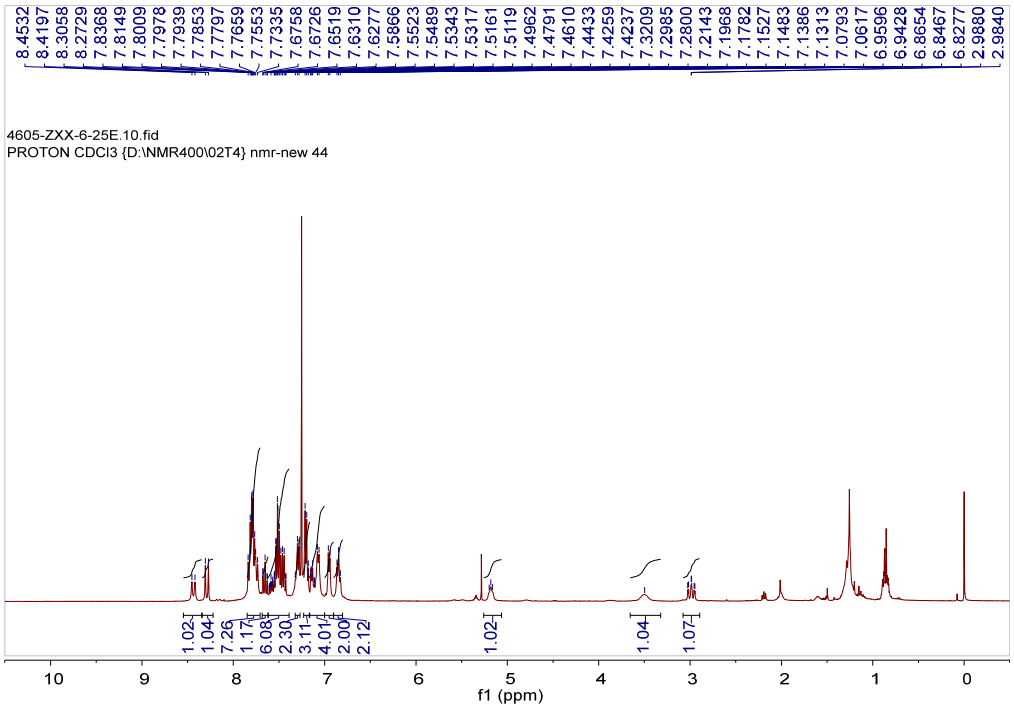


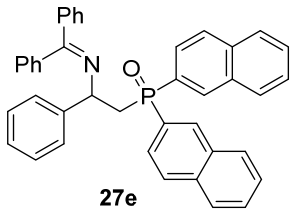




27d

^{31}P NMR (162 MHz, Chloroform-*d*)

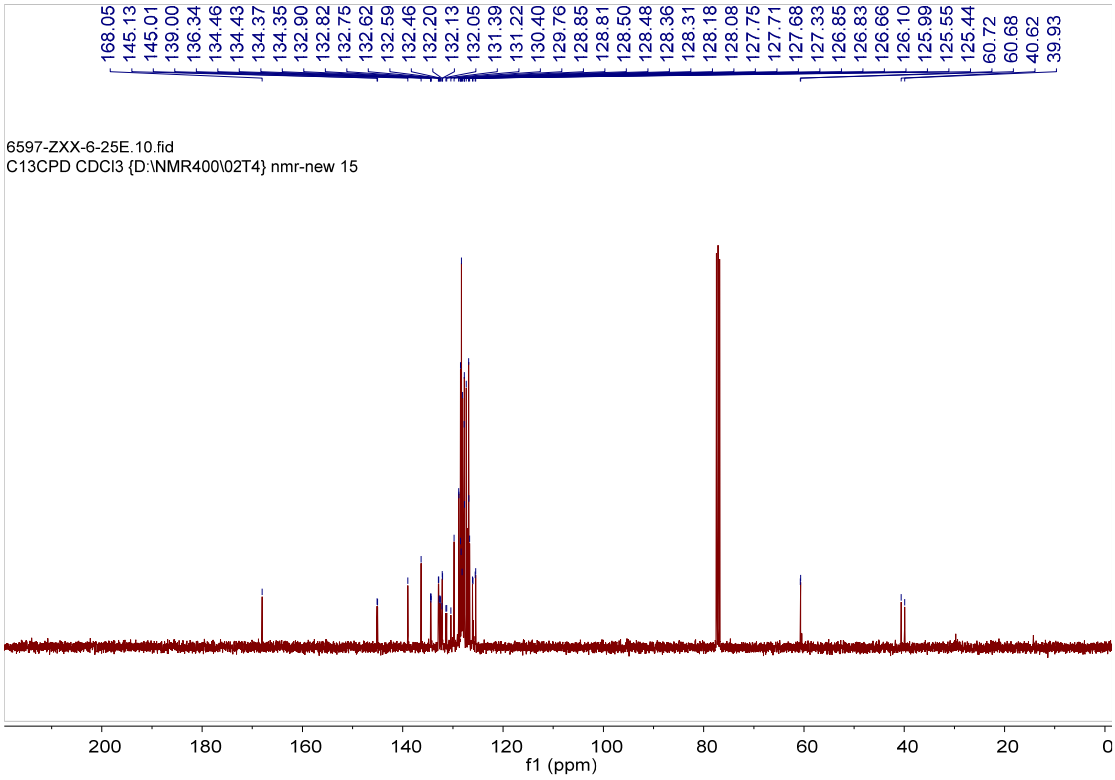


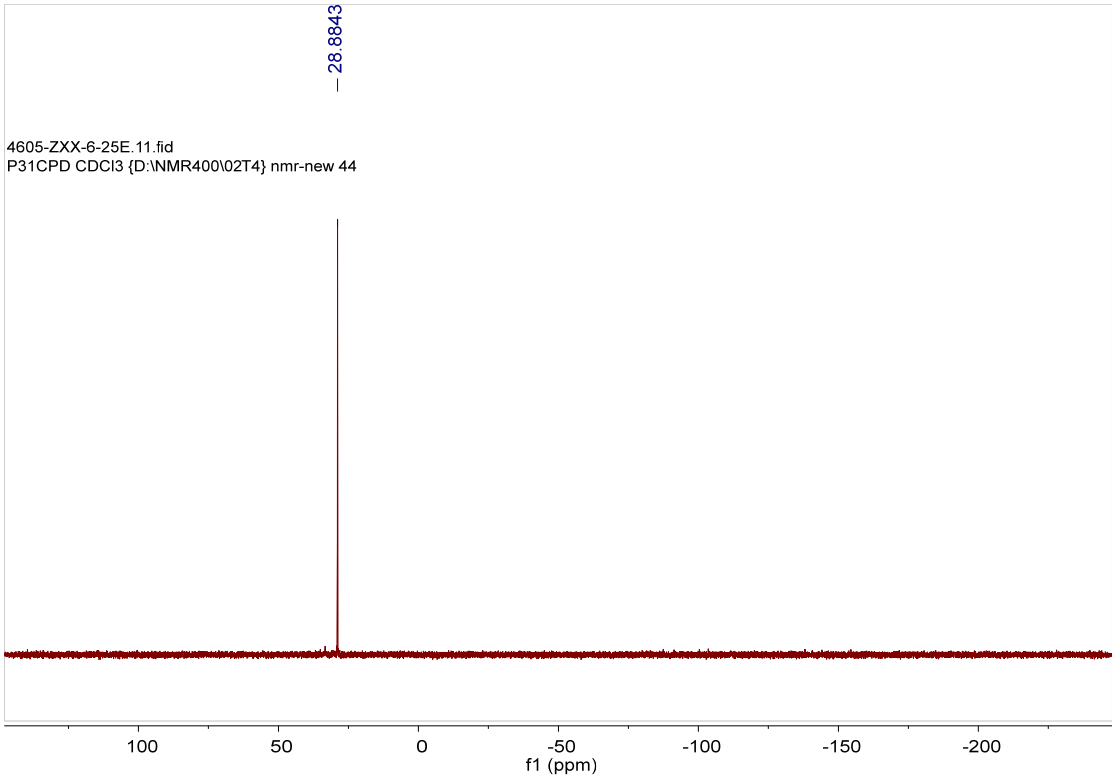


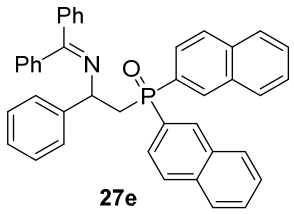
27e

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)

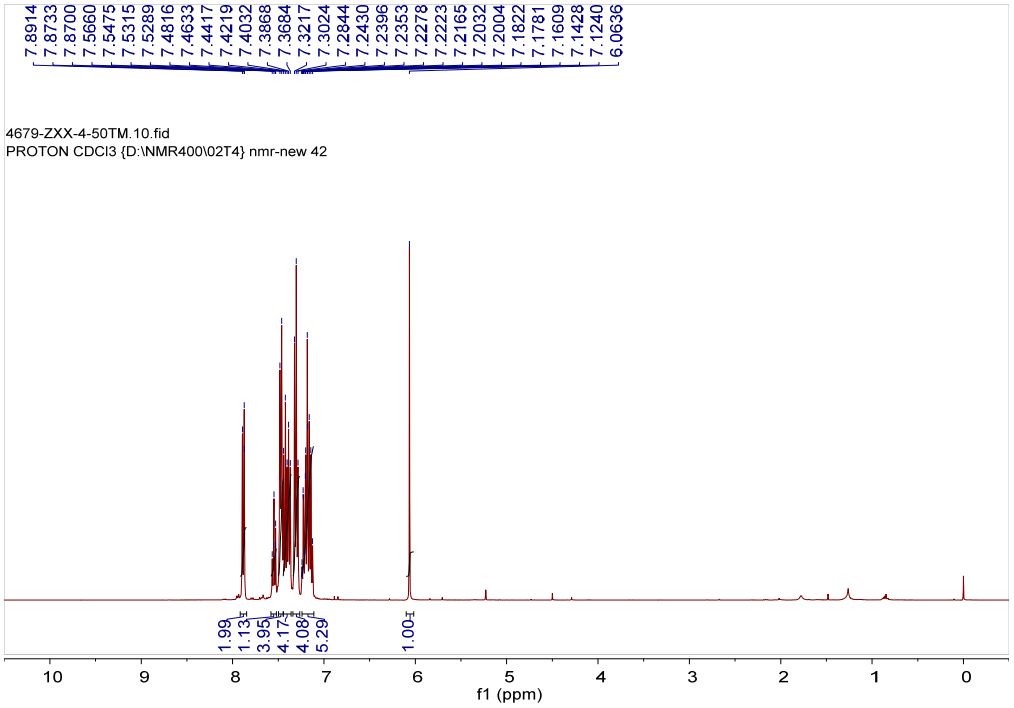


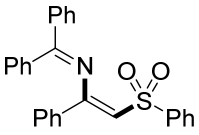




27e

^{31}P NMR (162 MHz, Chloroform-*d*)

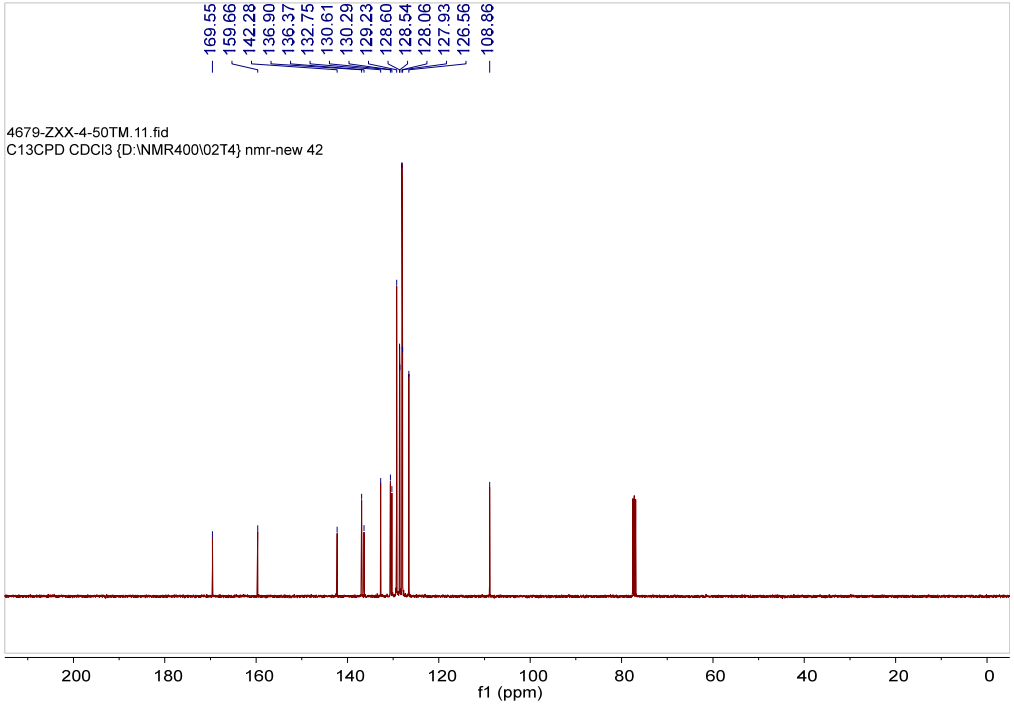


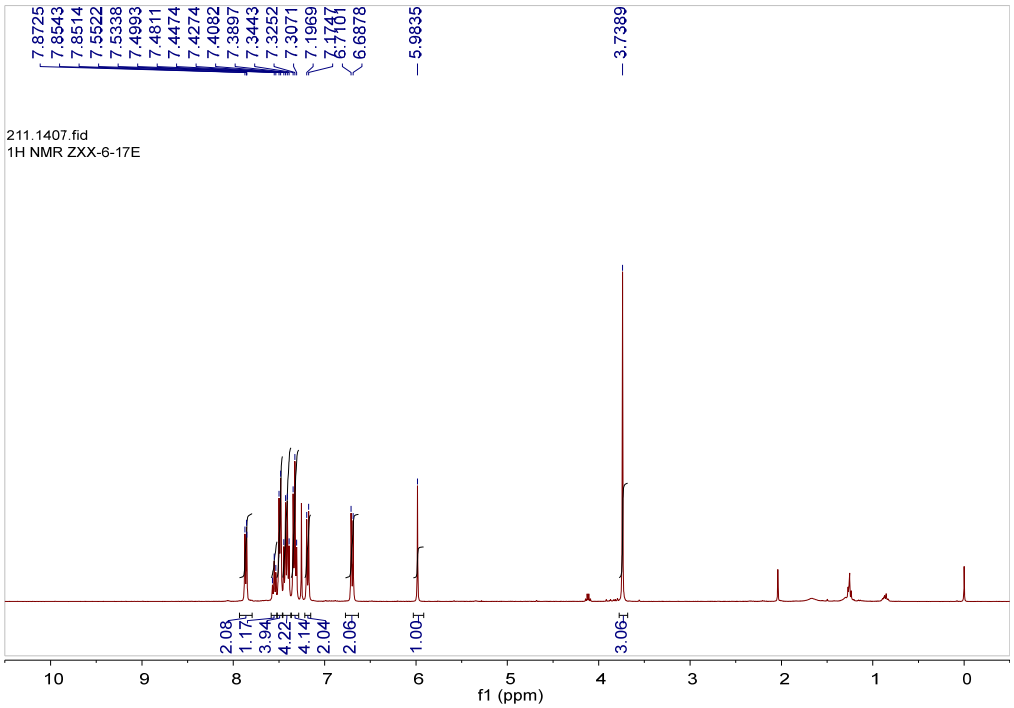


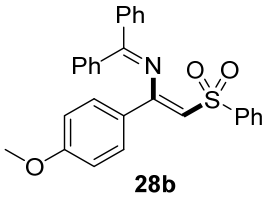
28a

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



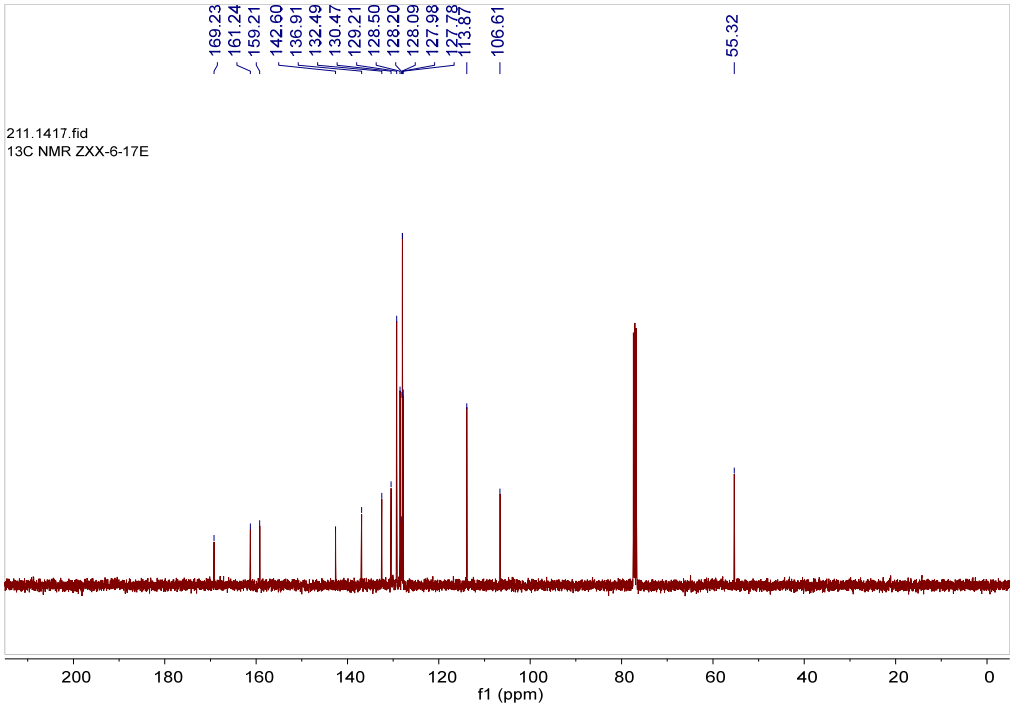


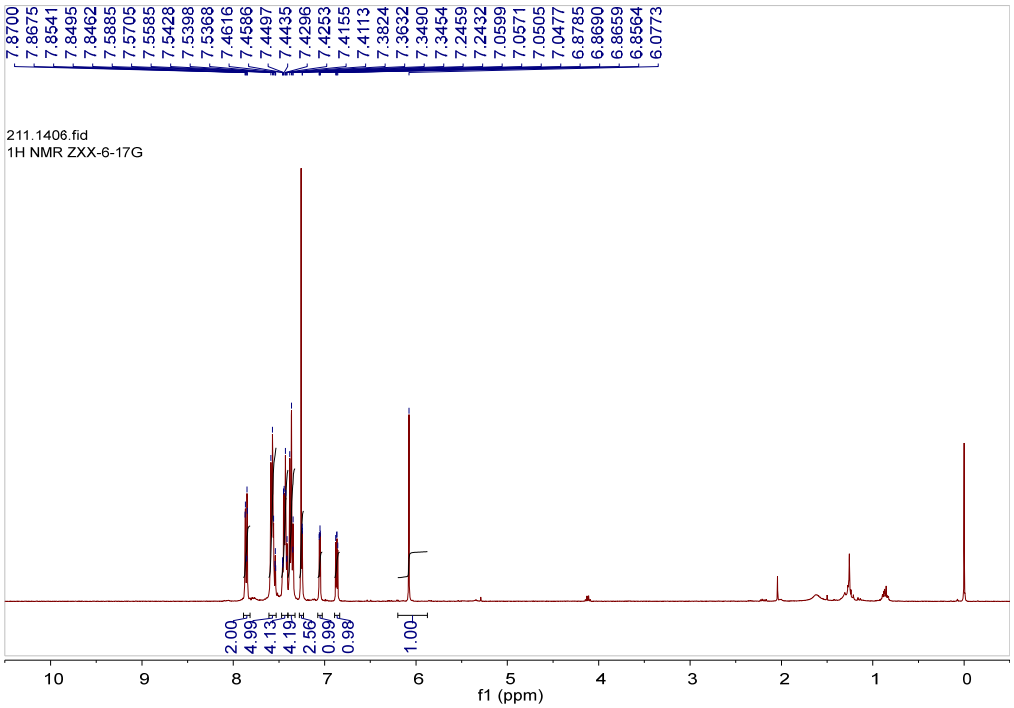


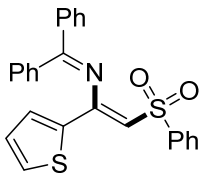
28b

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



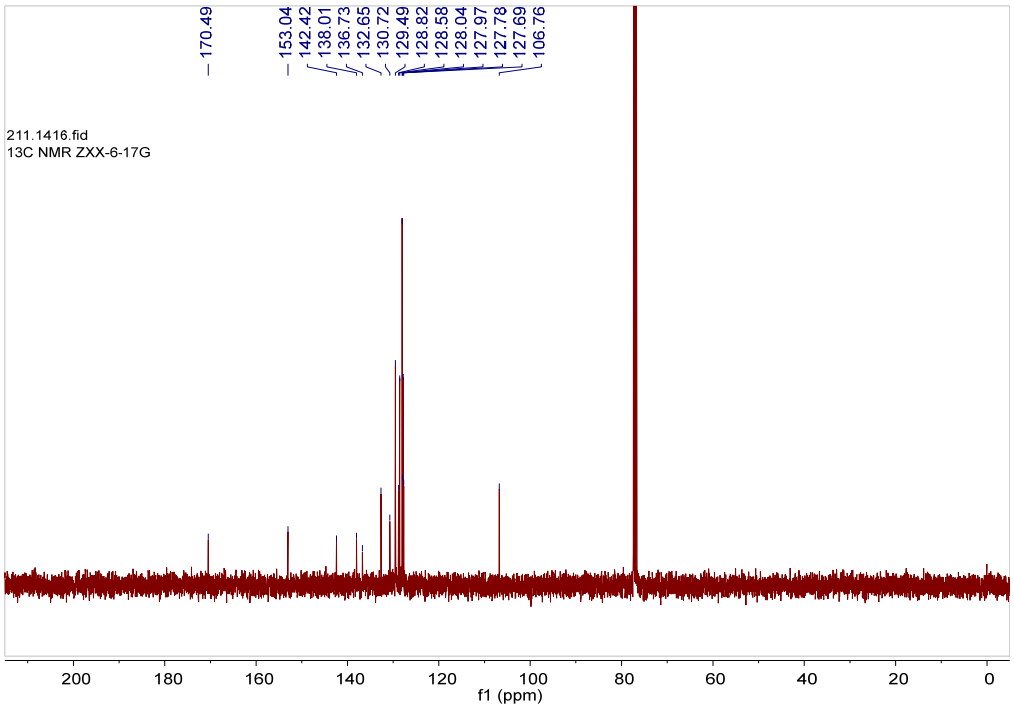


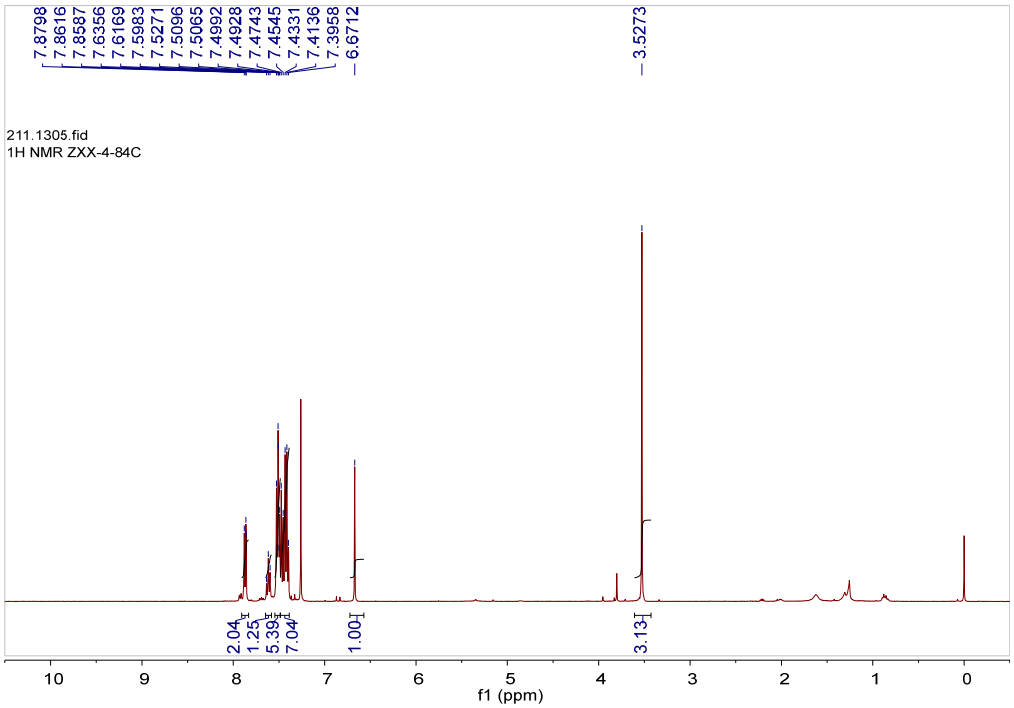


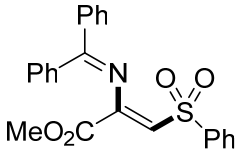
28c

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



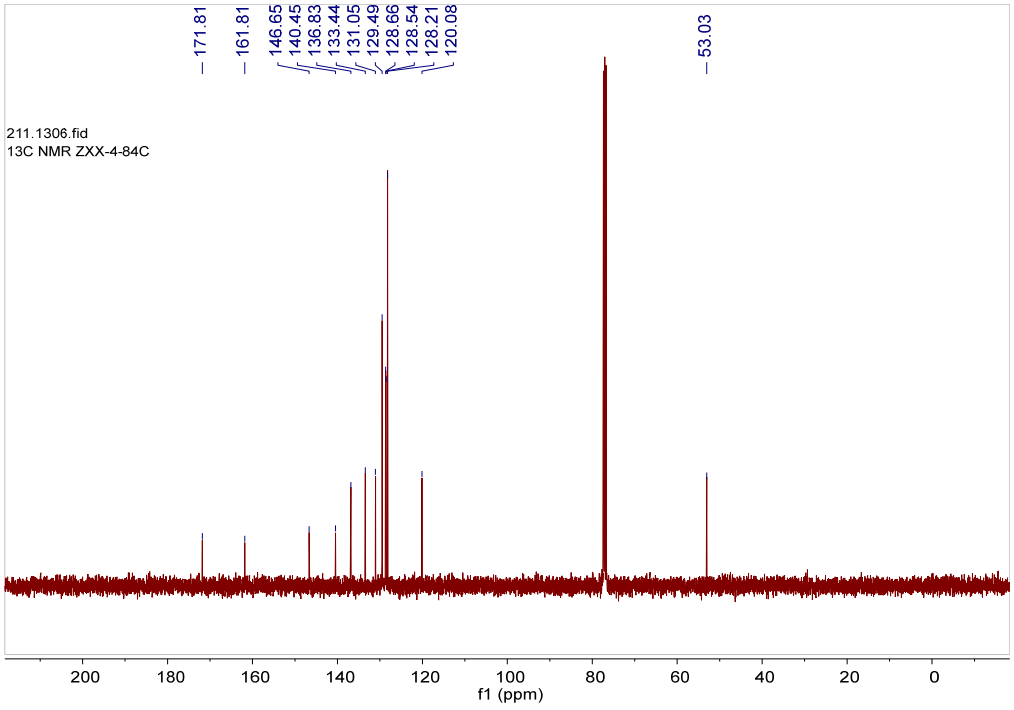


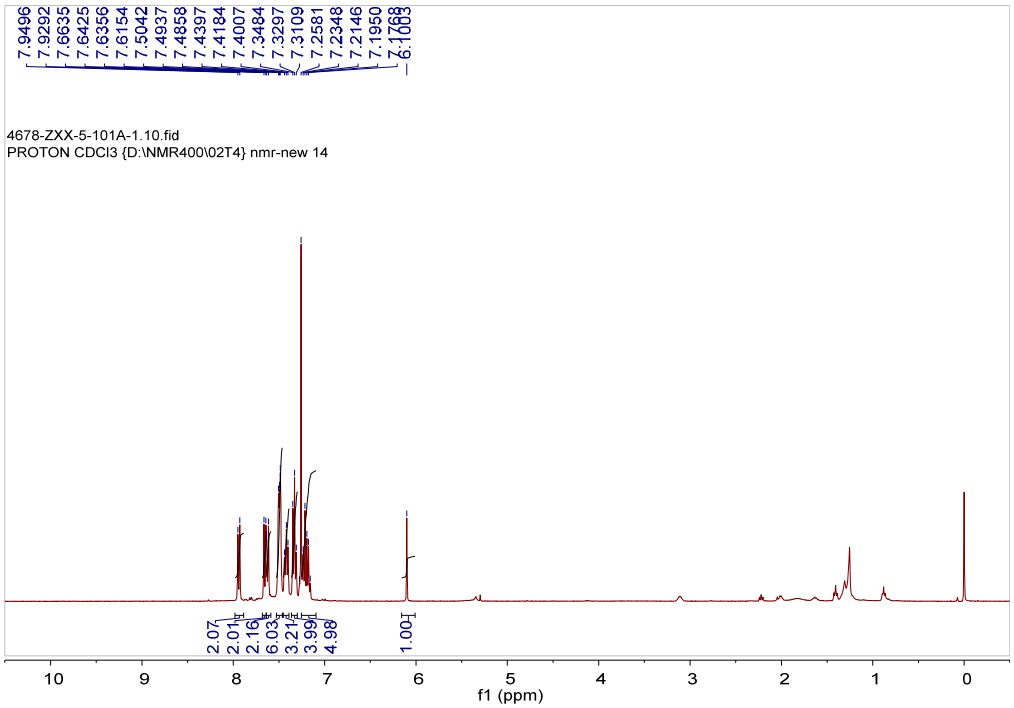


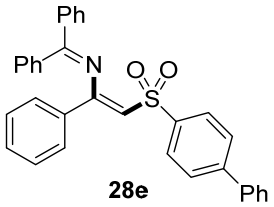
28d

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



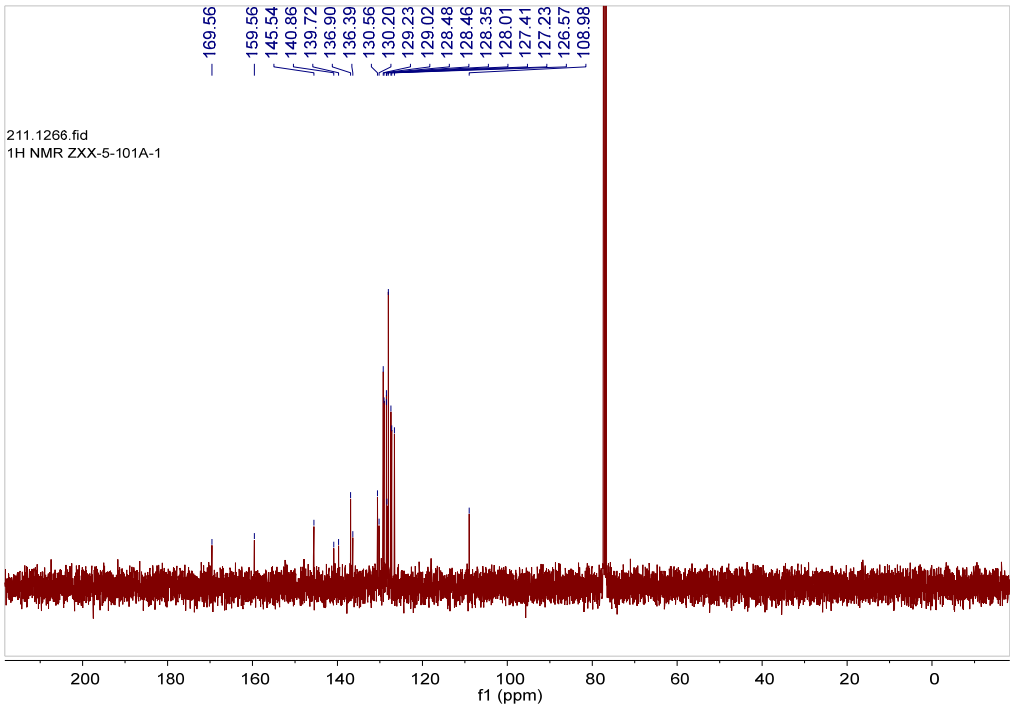


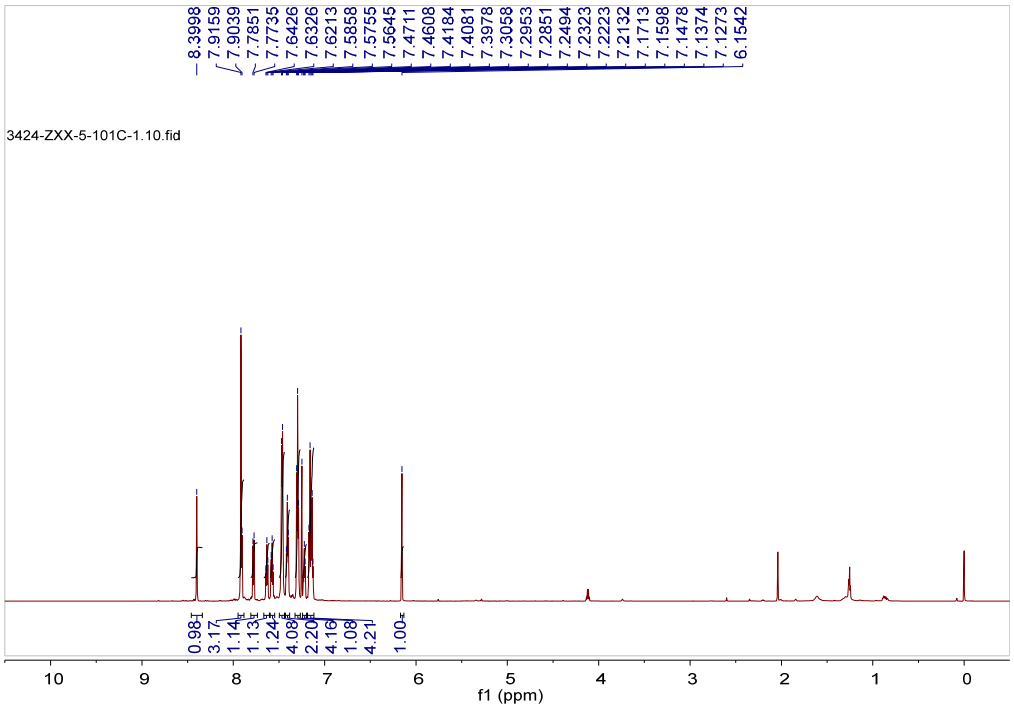


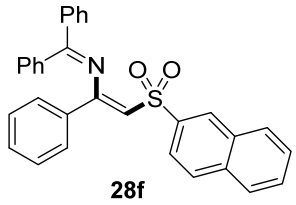
28e

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



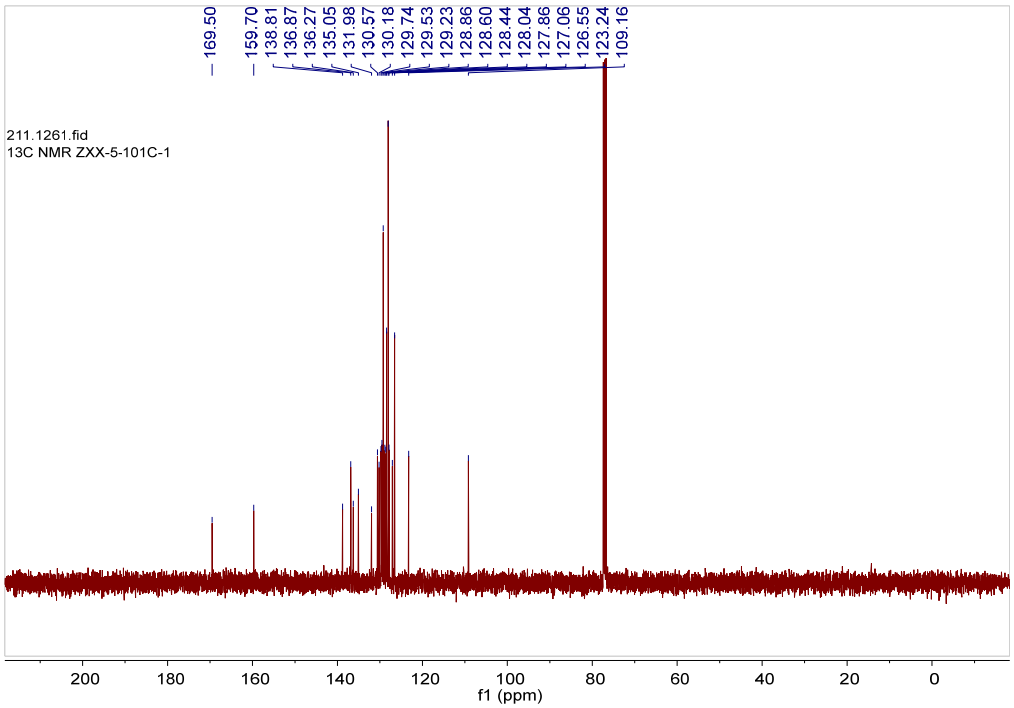


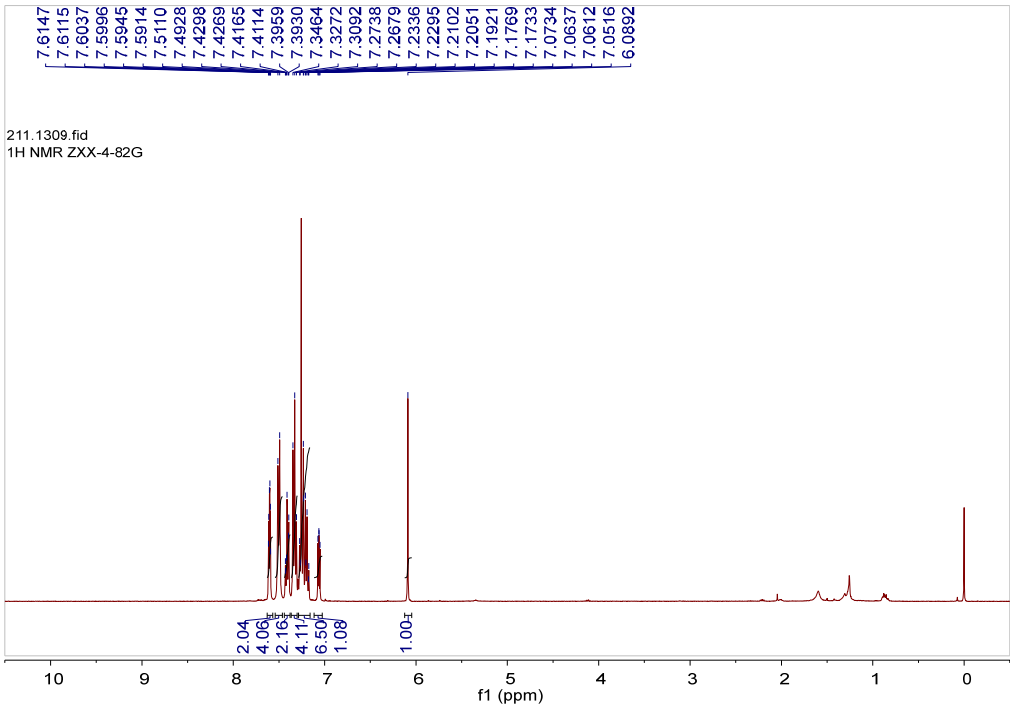


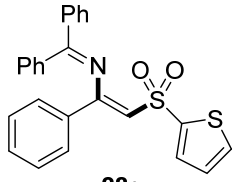
28f

^{1}H NMR (700 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



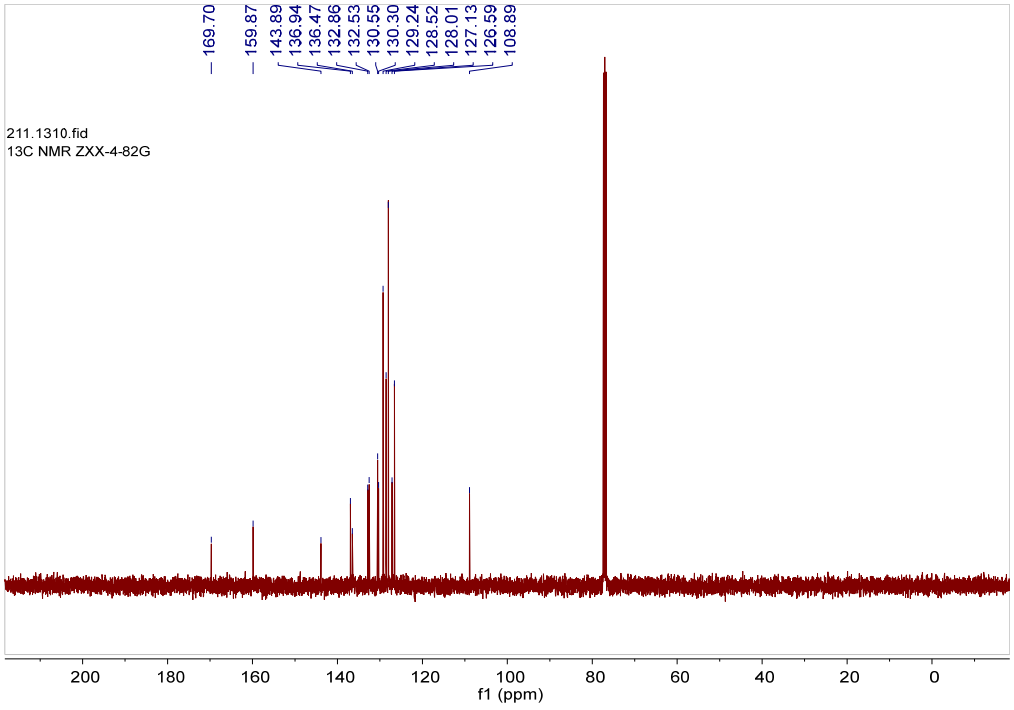


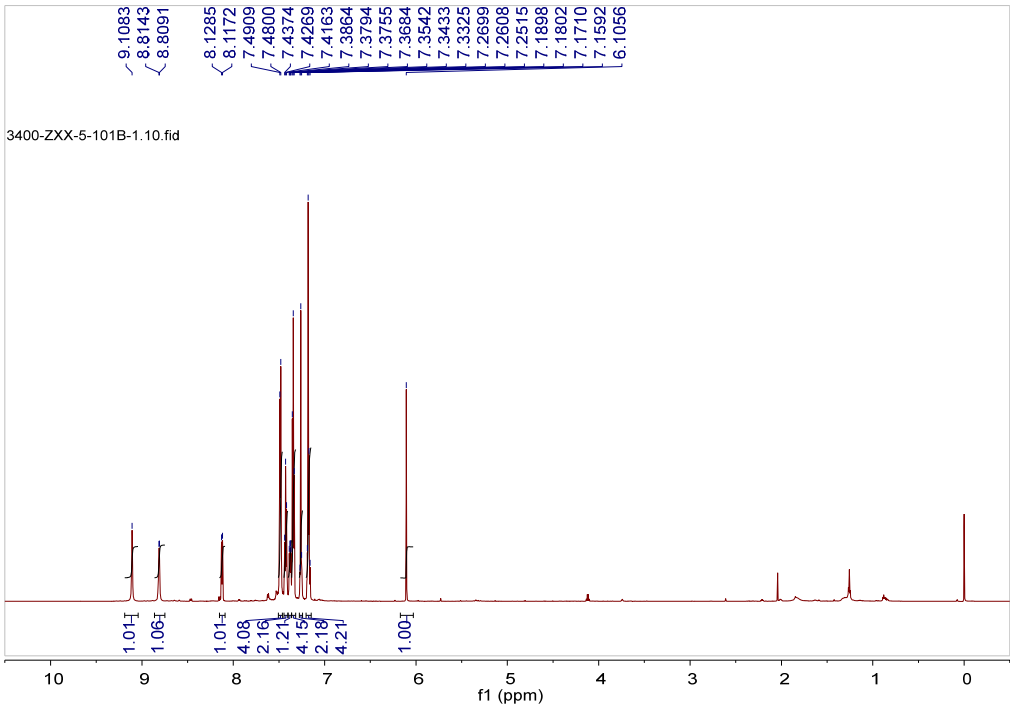


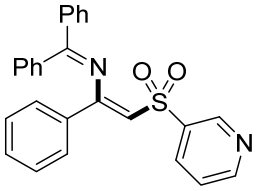
28g

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



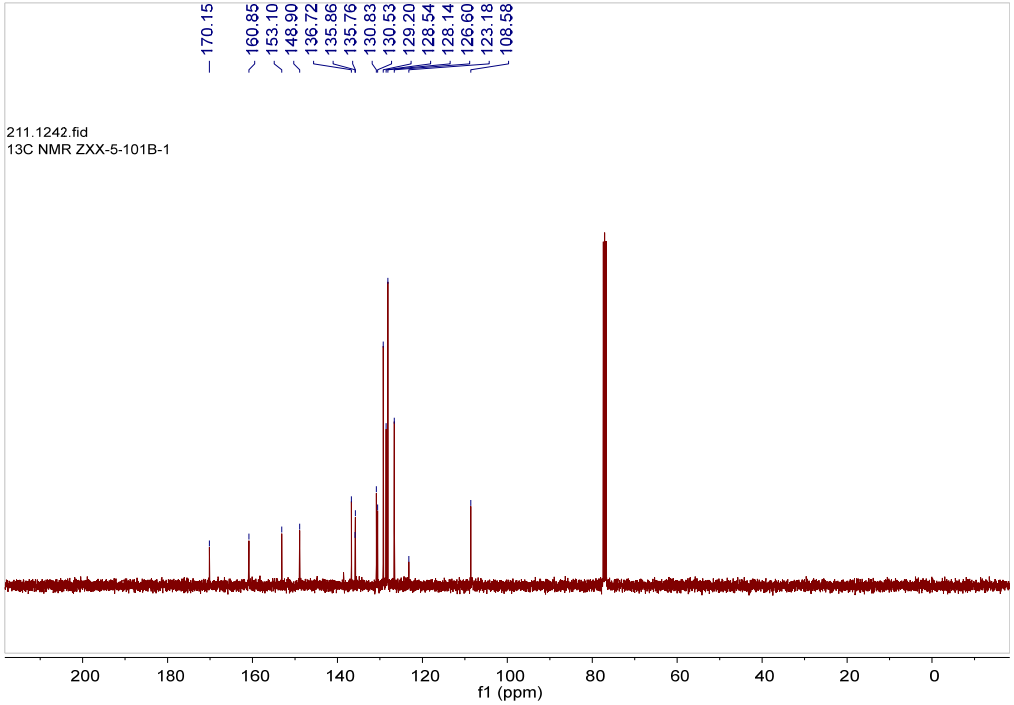


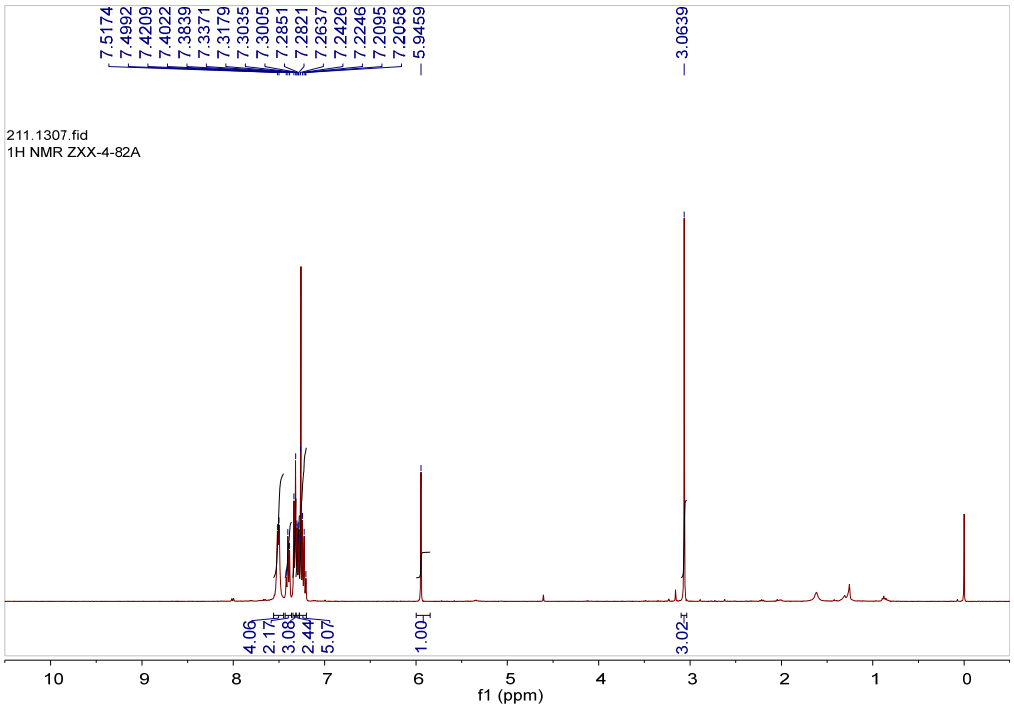


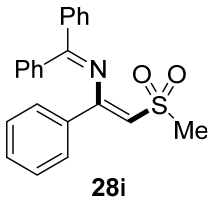
28h

^{1}H NMR (700 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



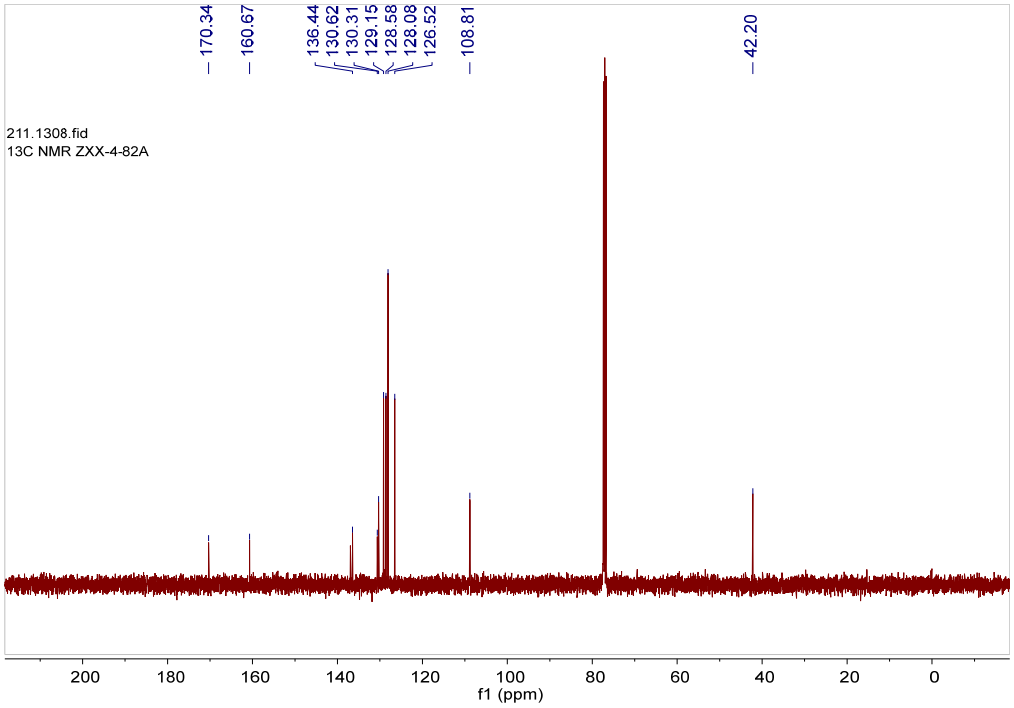


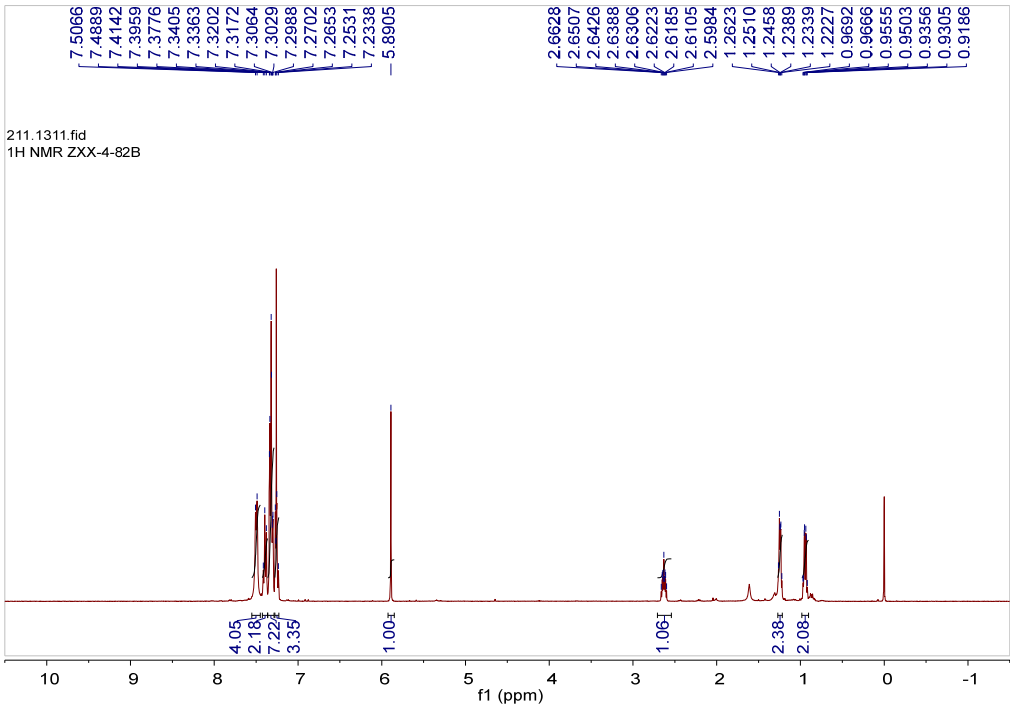


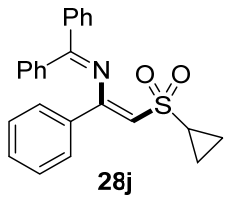
28i

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



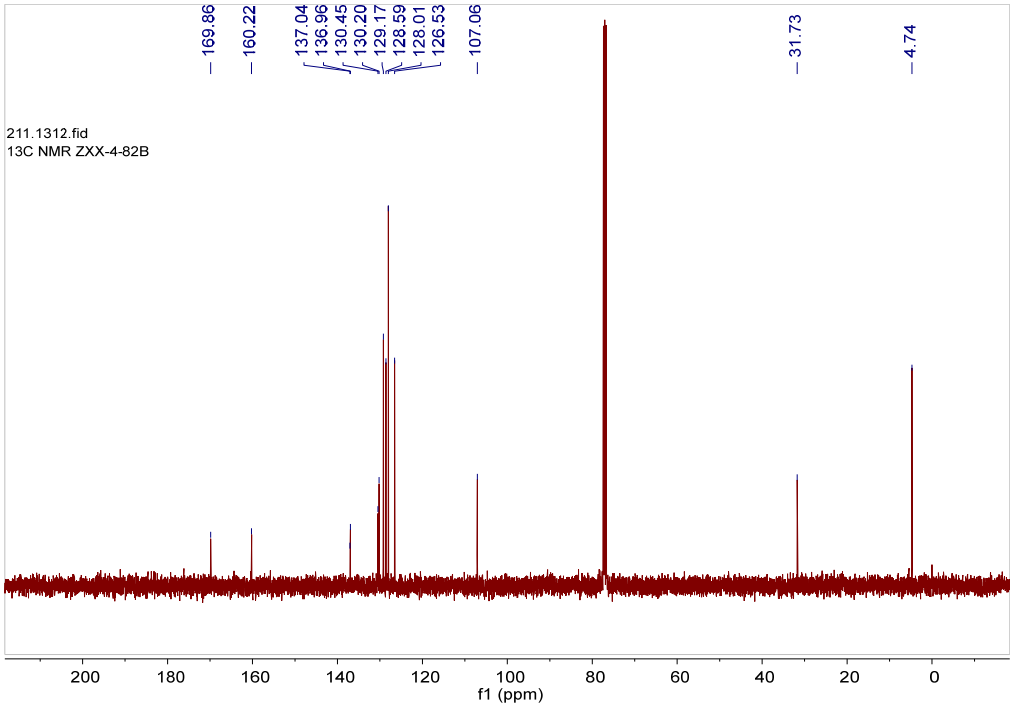


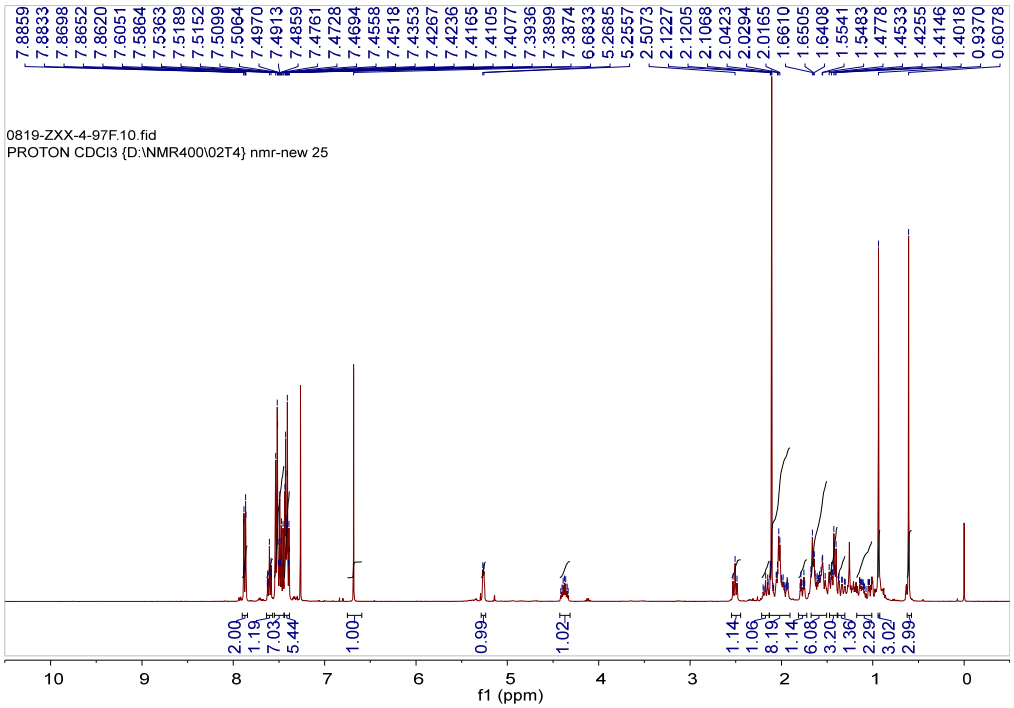


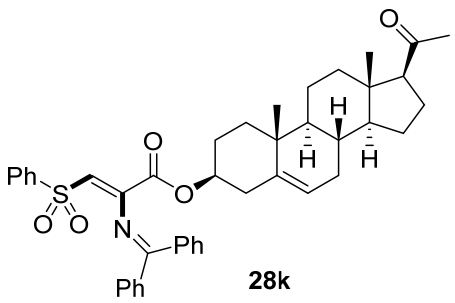
28j

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



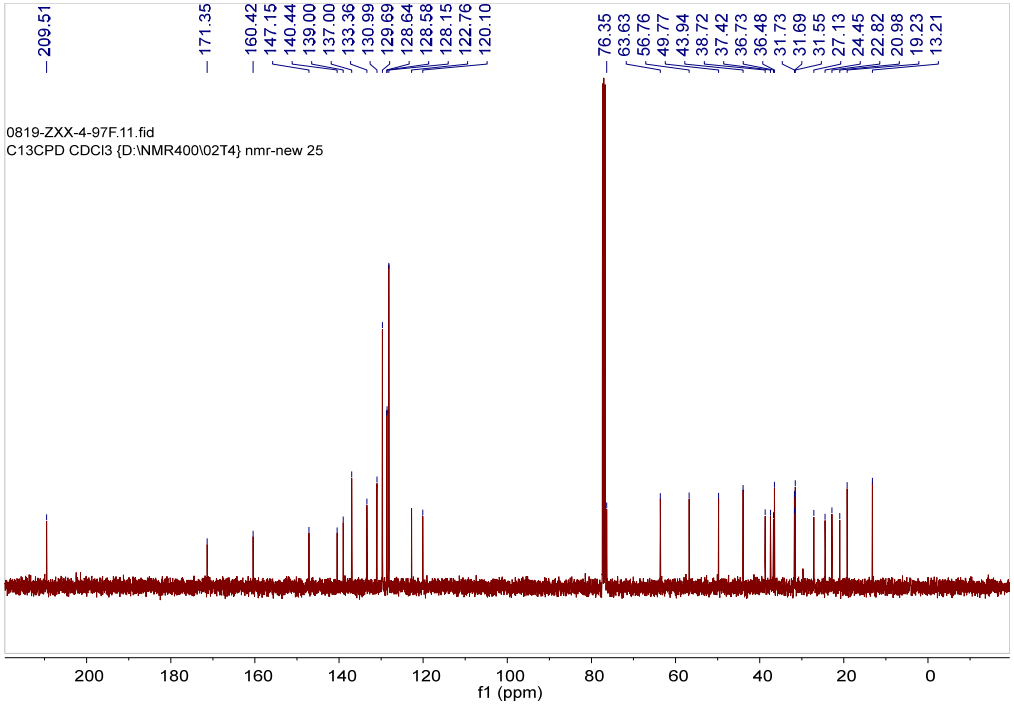


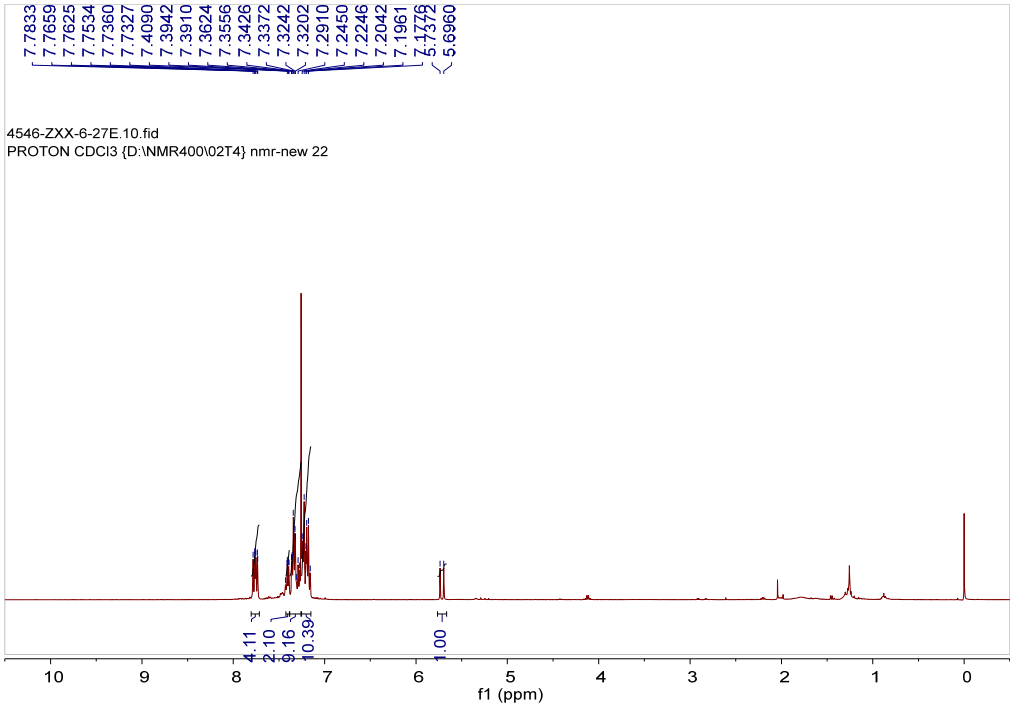


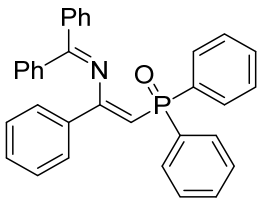
28k

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)



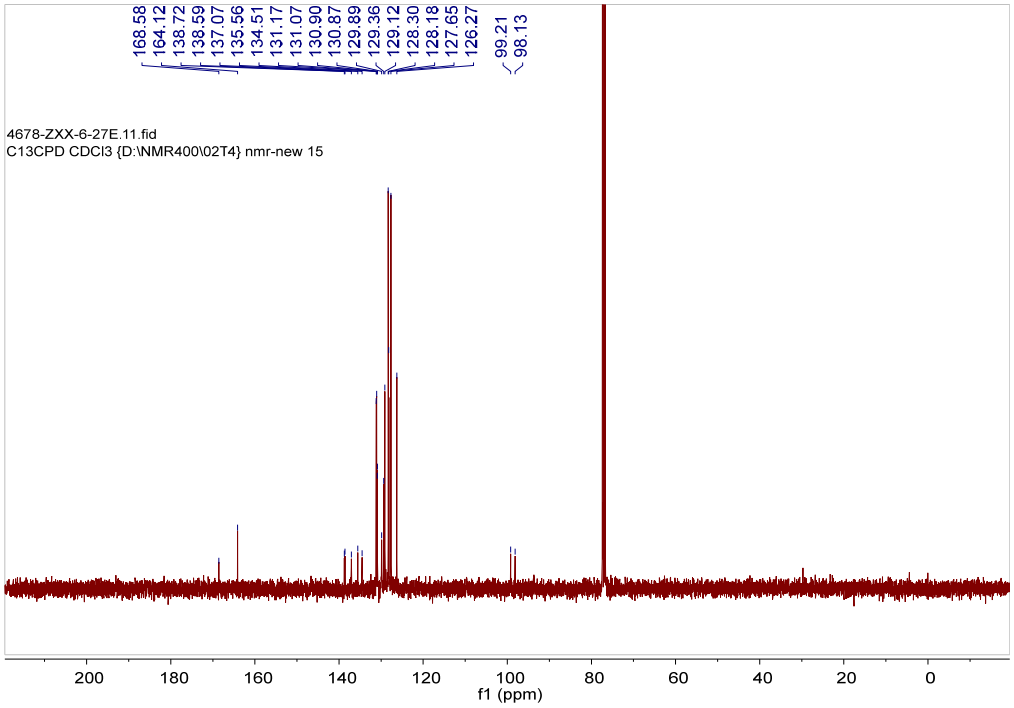


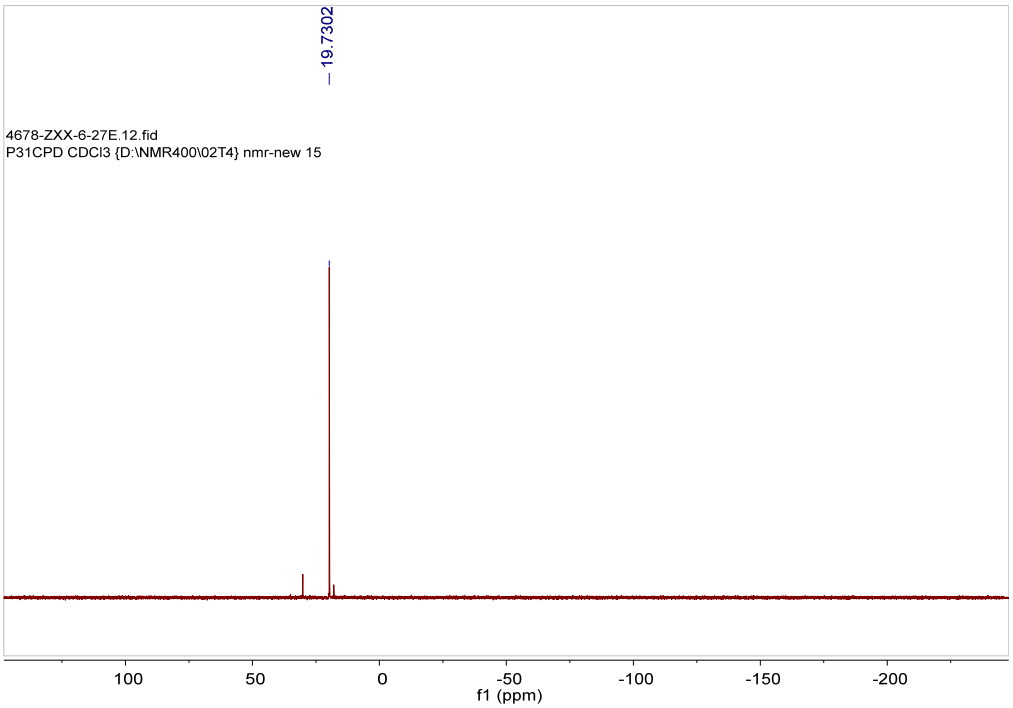


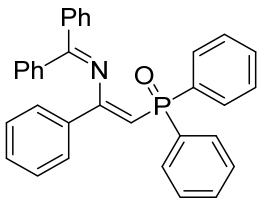
28l

^{1}H NMR (400 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)

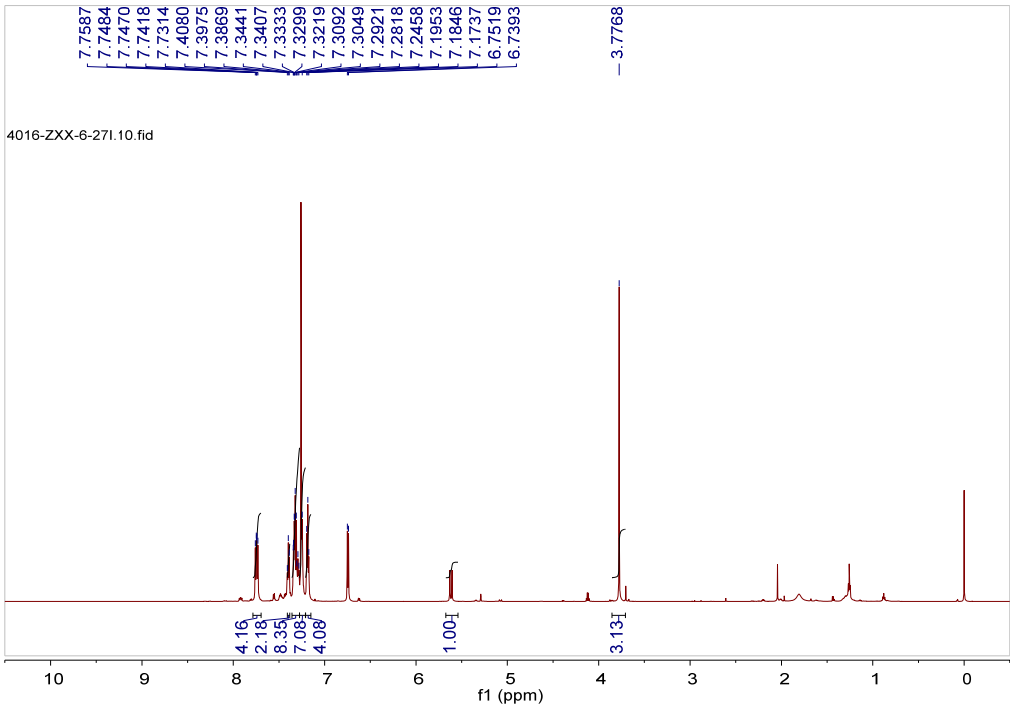


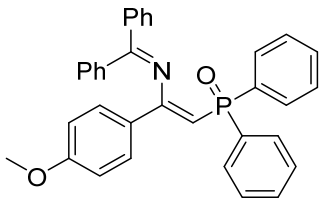




28l

^{31}P NMR (162 MHz, Chloroform-*d*)

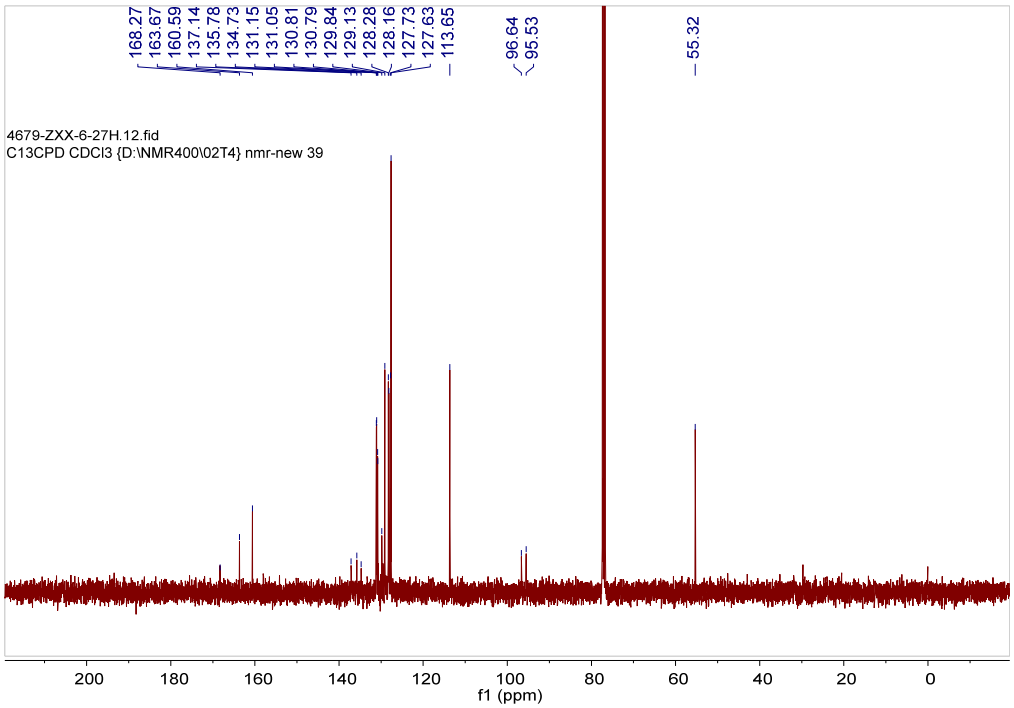


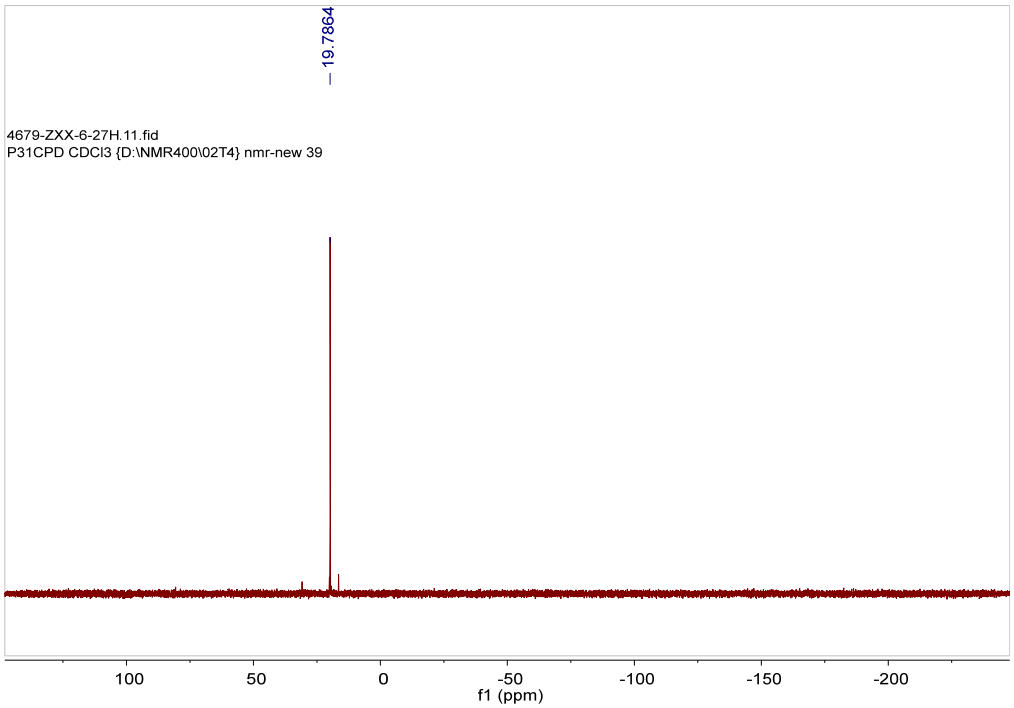


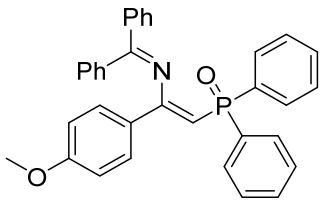
28m

^{1}H NMR (700 MHz, Chloroform-*d*)

^{13}C NMR (100 MHz, Chloroform-*d*)







28m

^{31}P NMR (162 MHz, Chloroform-*d*)