Supplementary information for

Radiation-induced aerobic oxidation *via* solvent-derived peroxyl radicals

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1. General information

All available reagents and solvents were purchased from commercial suppliers and were used as received without further purification. The retention factor (R_f) of analytical thin-layer chromatography (TLC) was recorded by using the GF254 silica gel plate (0.23 mm coating, purchased from Yantai Huayang New Material Technology Co., Ltd). Plates were visualized by UV light or TLC stains (potassium permanganate or iodine). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 MHz Spectrometer (400 MHz for ^{1}H; 101 MHz for ^{13}C). ^{19}F NMR spectra were recorded on a Bruker AVANCE 500 MHz Spectrometer (471 MHz for ^{19}F). ^{31}P NMR spectra were recorded on a Bruker AVANCE 500 MHz or 600 MHz Spectrometer (202 MHz or 243 MHz for ^{31}P). For $CDCl_3$ solutions, the chemical shifts (δ) are reported as parts per million (ppm) referenced to residual protium or carbon of the solvents; $CHCl_3$ δ H (7.26 ppm) and $CDCl_3$ δ C (77.16 ppm). Coupling constants are reported in Hertz (Hz). Chemical shift multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet. High-resolution mass spectrometry (HRMS) was performed on a Waters Vion^{TM} IMS QTof Mass Spectrometer.

The reaction mixtures were purified by preparative thin-layer chromatography, preparative high performance liquid chromatography, or flash column chromatography. Preparative thin-layer chromatography purifications were performed on Silica Gel 60 GF254 plates (1 mm coating, purchased from Shanghai Haohong Scientific Co., Ltd). Preparative high performance liquid chromatography purifications were performed on a Waters 2545 Binary Gradient Module equipped with a Waters 2489 UV/Visible Detector and a Waters SunFire C18 OBD Prep Column (100 Å, 5 μm, 30 × 150 mm). Flash column chromatography purifications were performed on silica gel (200−300 mesh, purchased from Yantai Huayang New Material Technology Co., Ltd).

Gas chromatography-mass spectrometry (GC-MS) was performed on a SHIMADZU GCMS-QP2020 NX Gas Chromatograph-Mass Spectrometer. UV-visible absorption spectra were measured on a HITACHI U-3010 UV-VIS Spectrophotometer. Fluorescence spectra were measured on a HITACHI F-7000 FL Spectrophotometer.

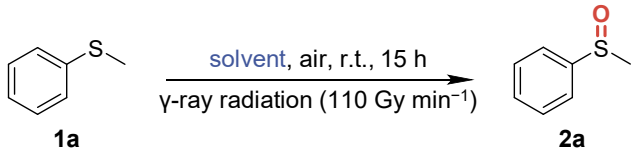
All reactants were irradiated with γ-rays from a ^{60}Co source (Department of Applied Chemistry of Peking University).

2. The optimization of reaction conditions

General procedure for the optimization of reaction conditions:

A 130 mL test tube was charged with 15 mL of solution containing **1a** (37.3 mg, 0.3 mmol). Then the test tube was sealed and exposed to ^{60}Co γ-ray radiation (dose rate: 110 Gy min^{-1}, measured using a Fricke dosimeter) at room temperature for a specific time. After the reaction, the reaction mixture was diluted and analyzed by GC-MS with 1,3,5-trimethoxybenzene as the internal standard.

Table S1 Evaluation of the solvent[a]

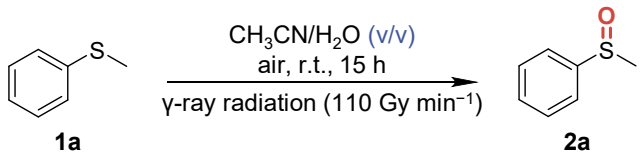


1a **2a**

Entry	Solvent	Yield of **2a** (%)[b]	Entry	Solvent	Yield of **2a** (%)[b]
1	CH_3CN	95	13	Acetone	75
2	Benzonitrile	49	14	Hexane	28
3	Phenylacetonitrile	34	15	Cyclohexane	22
4	Butyronitrile	72	16	DMF	21
5	Valeronitrile	32	17	DMA	16
6	CH_3OH	87	18	DMSO	Trace
7	EtOH	66	19	Benzene	20
8	*i*-PrOH	44	20	Toluene	24
9	Et_2O	25	21	CH_2Cl_2	n.d.
10	THF	18	22	$CHCl_3$	n.d.
11	1,4-Dioxane	17	23	CCl_4	n.d.
12	EtOAc	62			

[a] Reaction conditions: **1a** (0.3 mmol) in solvent (15 mL) with γ-ray radiation (dose rate: 110 Gy min^{-1}, measured using a Fricke dosimeter) at room temperature and under an air atmosphere for 15 h. [b] Determined by GC-MS using 1,3,5-trimethoxybenzene as the internal standard. EtOH = ethanol, *i*-PrOH = 2-propanol, Et_2O = diethyl ether, DMA = *N*,*N*-dimethylacetamide, $CHCl_3$ = trichloromethane, CCl_4 = tetrachloromethane. n.d. = no detected.

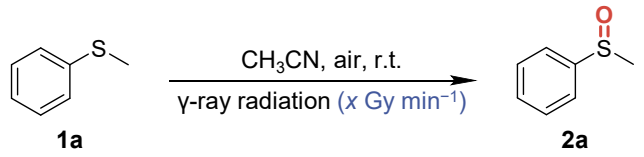
Table S2 Evaluation of the mixed solvent of CH_3CN and water[a]



Entry	Solvent	Yield of **2a** (%)[b]
1	CH_3CN	95
2	CH_3CN/H_2O (4/1)	72
3	CH_3CN/H_2O (3/2)	43
4	CH_3CN/H_2O (2/3)	19
5	CH_3CN/H_2O (1/4)	16

[a] Reaction conditions: **1a** (0.3 mmol) in the mixed solvent of CH_3CN and H_2O (15 mL) with γ-ray radiation (dose rate: 110 Gy min^{-1}, measured using a Fricke dosimeter) at room temperature and under an air atmosphere for 15 h. [b] Determined by GC-MS using 1,3,5-trimethoxybenzene as the internal standard.

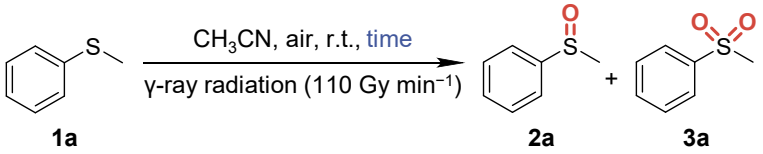
Table S3 Evaluation of the dose rate[a]



Entry	Dose rate (Gy min^{-1})	Time (h)	Yield of **2a** (%)[b]
1	110	15	95
2	220	7.5	94

[a] Reaction conditions: **1a** (0.3 mmol) in CH_3CN (15 mL) with γ-ray radiation (dose rate was measured using a Fricke dosimeter, and the absorbed dose was 99 kGy) at room temperature and under an air atmosphere. [b] Determined by GC-MS using 1,3,5-trimethoxybenzene as the internal standard.

Table S4 Evaluation of the reaction time[a]

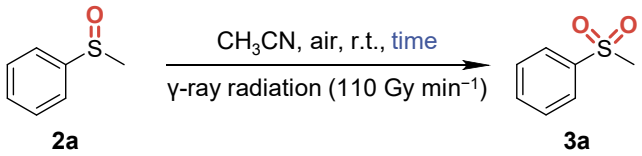


1a **2a** **3a**

Entry	Time (h)	Yield of **2a** (%)[b]	Yield of **3a** (%)[b]
1	2	27	n.d.
2	4	45	n.d.
3	6	60	n.d.
4	8	74	n.d.
5	15	95	n.d.
6	18	75	13
7	21	69	18
8	63	n.d.	48

[a] Reaction conditions: **1a** (0.3 mmol) in CH_3CN (15 mL) with γ-ray radiation (dose rate: 110 Gy min^{-1}, measured using a Fricke dosimeter) at room temperature and under an air atmosphere for different reaction times. [b] Determined by GC-MS using 1,3,5-trimethoxybenzene as the internal standard. n.d. = no detected.

Table S5 Transformation from **2a** to **3a**[a]



2a **3a**

Entry	Time (h)	Yield of **3a** (%)[b]
1	2	7
2	4	13
3	6	19
4	15	30

[a] Reaction conditions: **2a** (0.3 mmol) in CH_3CN (15 mL) with γ-ray radiation (dose rate: 110 Gy min^{-1}, measured using a Fricke dosimeter) at room temperature and under an air atmosphere for different reaction times. [b] Determined by GC-MS using 1,3,5-trimethoxybenzene as the internal standard.

3. Substrate scope studies

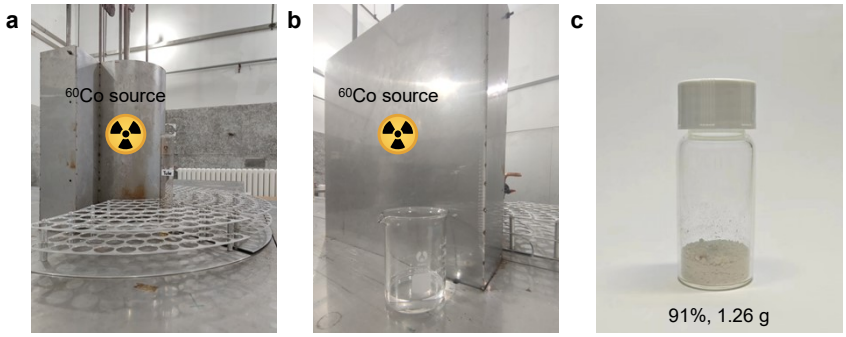


Fig. S1 Photographs of the reaction setups for radiation-induced aerobic oxidation and the gram-scale synthetic product **5g**. (a) The reaction setup for general procedures A and B. (b) The reaction setup for gram-scale synthesis of **5g**. (c) The gram-scale synthetic product **5g**.

General procedure A for the radiation-induced oxidation of sulfides:

A 130 mL test tube was charged with 15 mL of acetonitrile containing 0.3 mmol **1**. Then the test tube was sealed and exposed to ^{60}Co γ-ray radiation (dose rate: 110 Gy min^{-1}, measured using a Fricke dosimeter) at room temperature. Unless otherwise specified, the reaction time is 15 h. After the reaction, the solvent was removed on a rotary evaporator under reduced pressure, and the residue was purified by preparative thin-layer chromatography or preparative high performance liquid chromatography to afford the desired product **2**.

General procedure B for the radiation-induced oxidation of phosphorus(III) compounds:

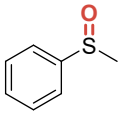
A 130 mL test tube was charged with 15 mL of acetonitrile containing 0.3 mmol **4**. Then the test tube was sealed and exposed to ^{60}Co γ-ray radiation (dose rate: 110 Gy min^{-1}, measured using a Fricke dosimeter) at room temperature. Unless otherwise specified, the reaction time is 3 h. After the reaction, the solvent was removed on a rotary evaporator under reduced pressure, and the residue was purified by preparative thin-layer chromatography to afford the desired product **5**.

Procedure for gram-scale synthesis of triphenylphosphine oxide (5g):

A 300 mL beaker was charged with 50 mL of acetonitrile containing **4g** (1.31 g, 5.0 mmol). Then the beaker was exposed to ^{60}Co γ-ray radiation (dose rate: 110 Gy min^{-1}, measured using a Fricke dosimeter) at room temperature for 6.5 h. After the reaction, the solvent was removed on a rotary evaporator under reduced pressure, and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) to obtain **5g** as a white solid (1.26 g, 91% yield).

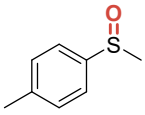
Characterization data for the products:

(methylsulfinyl)benzene (2a)



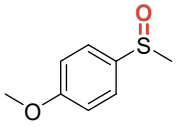
2a was prepared according to general procedure A using **1a** (37.3 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.39) to obtain **2a** as a colorless oil (38.3 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.62 (m, 2H), 7.55 – 7.48 (m, 3H), 2.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.83, 131.14, 129.46, 123.60, 44.08. HRMS (ESI): calculated for C_7H_8OS $[M+H]^+$: 141.0369, found: 141.0369.

1-methyl-4-(methylsulfinyl)benzene (2b)



2b was prepared according to general procedure A using **1b** (41.4 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.49) to obtain **2b** as a colorless oil (37.2 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.52 (m, 2H), 7.32 (d, J = 7.9 Hz, 2H), 2.69 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.65, 141.62, 130.15, 123.66, 44.13, 21.51. HRMS (ESI): calculated for $C_8H_{10}OS$ $[M+H]^+$: 155.0525, found: 155.0521.

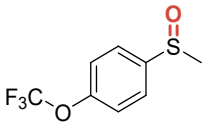
1-methoxy-4-(methylsulfinyl)benzene (2c)



2c was prepared according to general procedure A using **1c** (46.3 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.24) to obtain **2c** as a white solid (32.8 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.56 (m, 2H), 7.04 – 6.99 (m, 2H), 3.84 (s, 3H), 2.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.07, 136.74, 125.55, 114.95, 55.63, 44.12. HRMS (ESI):

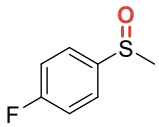
calculated for $C_8H_{10}O_2S$ $[M+H]^+$: 171.0474, found: 171.0473.

1-(methylsulfinyl)-4-(trifluoromethoxy)benzene (2d)



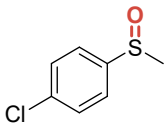
2d was prepared according to general procedure A using **1d** (62.5 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.26) to obtain **2d** as a white solid (51.3 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.68 (m, 2H), 7.38 (d, J = 8.4 Hz, 2H), 2.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.24 (d, J = 1.6 Hz), 144.28, 125.56, 121.91, 120.45 (q, J = 259.9 Hz), 44.23. ^{19}F NMR (471 MHz, $CDCl_3$) δ –57.83. HRMS (ESI): calculated for $C_8H_7F_3O_2S$ $[M+H]^+$: 225.0192, found: 225.0194.

1-fluoro-4-(methylsulfinyl)benzene (2e)



2e was prepared according to general procedure A using **1e** (42.6 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.29) to obtain **2e** as a colorless oil (39.4 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.61 (m, 2H), 7.25 – 7.18 (m, 2H), 2.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.43 (d, J = 251.4 Hz), 141.31 (d, J = 3.2 Hz), 125.94 (d, J = 8.9 Hz), 116.80 (d, J = 22.7 Hz), 44.30. ^{19}F NMR (471 MHz, $CDCl_3$) δ −108.67. HRMS (ESI): calculated for C_7H_7FOS $[M+H]^+$: 159.0274, found: 159.0275.

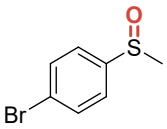
1-chloro-4-(methylsulfinyl)benzene (2f)



2f was prepared according to general procedure A using **1f** (47.6 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative high performance liquid chromatography [eluent A: 0.1% formic acid in water; eluent B: acetonitrile; flow rate: 30 mL

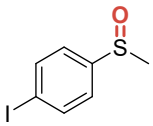
min^{-1}; ramp from 5% B (at min 2) to 95% B (at min 14)] to obtain **2f** as a colorless oil (48.9 mg, 93% yield). R_f = 0.38, hexane/ethyl acetate = 1:2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 2H), 7.53 – 7.48 (m, 2H), 2.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.38, 137.38, 129.79, 125.09, 44.19. HRMS (ESI): calculated for C_7H_7ClOS $[M+H]^+$: 174.9979, found: 174.9978.

1-bromo-4-(methylsulfinyl)benzene (2g)



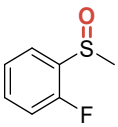
2g was prepared according to general procedure A using **1g** (60.9 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative high performance liquid chromatography [eluent A: 0.1% formic acid in water; eluent B: acetonitrile; flow rate: 30 mL min^{-1}; ramp from 5% B (at min 2) to 95% B (at min 14)] to obtain **2g** as a white solid (46.1 mg, 70% yield). R_f = 0.36, hexane/ethyl acetate = 1:2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.65 (m, 2H), 7.54 – 7.50 (m, 2H), 2.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.04, 132.71, 125.60, 125.28, 44.15. HRMS (ESI): calculated for C_7H_7BrOS $[M+H]^+$: 218.9474, found: 218.9475.

1-iodo-4-(methylsulfinyl)benzene (2h)



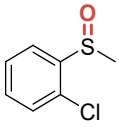
2h was prepared according to general procedure A using **1h** (75.0 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative high performance liquid chromatography [eluent A: 0.1% formic acid in water; eluent B: acetonitrile; flow rate: 30 mL min^{-1}; ramp from 5% B (at min 2) to 95% B (at min 14)] to obtain **2h** as a white solid (33.0 mg, 41% yield). R_f = 0.26, hexane/ethyl acetate = 1:2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 2H), 7.41 – 7.36 (m, 2H), 2.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.87, 138.61, 125.28, 97.51, 44.12. HRMS (ESI): calculated for C_7H_7IOS $[M+H]^+$: 266.9335, found: 266.9336.

1-fluoro-2-(methylsulfinyl)benzene (2i)



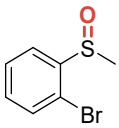
2i was prepared according to general procedure A using **1i** (42.6 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.50) to obtain **2i** as a colorless oil (42.3 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 1H), 7.52 – 7.46 (m, 1H), 7.42 – 7.37 (m, 1H), 7.14 – 7.09 (m, 1H), 2.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.60 (d, J = 246.8 Hz), 132.81 (d, J = 7.6 Hz), 125.55 (dd, J = 4.4, 2.9 Hz), 115.81 (d, J = 20.2 Hz), 42.25 (d, J = 1.8 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ −114.77. HRMS (ESI): calculated for C_7H_7FOS $[M+H]^+$: 159.0274, found: 159.0276.

1-chloro-2-(methylsulfinyl)benzene (2j)



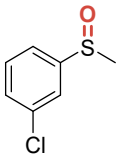
2j was prepared according to general procedure A using **1j** (47.6 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 1:2, R_f = 0.54) to obtain **2j** as a colorless oil (49.1 mg, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.93 (m, 1H), 7.56 – 7.51 (m, 1H), 7.47 – 7.42 (m, 1H), 7.40 – 7.37 (m, 1H), 2.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.44, 132.17, 129.92, 128.32, 125.45, 41.68. HRMS (ESI): calculated for C_7H_7ClOS $[M+H]^+$: 174.9979, found: 174.9978.

1-bromo-2-(methylsulfinyl)benzene (2k)



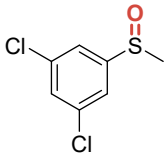
2k was prepared according to general procedure A using **1k** (60.9 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.49) to obtain **2k** as a colorless oil (38.1 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.93 (m, 1H), 7.61 – 7.55 (m, 2H), 7.40 – 7.34 (m, 1H), 2.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.50, 133.05, 132.39, 128.87, 125.82, 118.55, 42.03. HRMS (ESI): calculated for C_7H_7BrOS $[M+H]^+$: 218.9474, found: 218.9475.

1-chloro-3-(methylsulfinyl)benzene (2l)



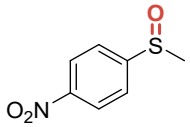
2l was prepared according to general procedure A using **1l** (47.6 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (petroleum ether/ethyl acetate = 1:2, R_f = 0.38) to obtain **2l** as a colorless oil (47.0 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.65 (m, 1H), 7.51 – 7.45 (m, 3H), 2.73 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.98, 135.84, 131.32, 130.72, 123.76, 121.73, 44.16. HRMS (ESI): calculated for C_7H_7ClOS $[M+H]^+$: 174.9979, found: 174.9978.

1,3-dichloro-5-(methylsulfinyl)benzene (2m)



2m was prepared according to general procedure A using **1m** (57.6 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.43) to obtain **2m** as a white solid (59.1 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 1.8 Hz, 2H), 7.47 – 7.45 (m, 1H), 2.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.52, 136.46, 131.22, 122.07, 44.17. HRMS (ESI): calculated for $C_7H_6Cl_2OS$ $[M+H]^+$: 208.9589, found: 208.9588.

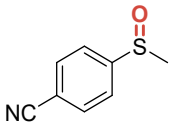
1-(methylsulfinyl)-4-nitrobenzene (2n)



2n was prepared according to general procedure A using **1n** (50.8 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.16) to obtain **2n** as a yellow solid (45.6 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 – 8.36 (m, 2H), 7.85 – 7.81 (m, 2H), 2.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.30, 149.59, 124.77, 124.60, 43.96. HRMS (ESI): calculated for $C_7H_7NO_3S$

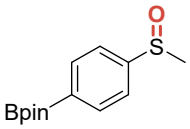
$[M+H]^+$: 186.0219, found: 186.0220.

4-(methylsulfinyl)benzonitrile (2o)



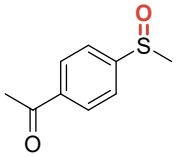
2o was prepared according to general procedure A using **1o** (44.7 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.41) to obtain **2o** as a white solid (40.1 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.81 (m, 2H), 7.78 – 7.74 (m, 2H), 2.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.61, 133.12, 124.43, 117.82, 114.95, 43.94. HRMS (ESI): calculated for C_7H_7NOS $[M+H]^+$: 166.0321, found: 166.0319.

4,4,5,5-tetramethyl-2-(4-(methylsulfinyl)phenyl)-1,3,2-dioxaborolane (2p)



2p was prepared according to general procedure A using **1p** (75.0 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.30) to obtain **2p** as a white solid (51.7 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.94 (m, 2H), 7.64 – 7.62 (m, 2H), 2.71 (s, 3H), 1.35 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.86, 135.69, 122.67, 84.38, 44.06, 25.01, 25.00. HRMS (ESI): calculated for $C_{13}H_{19}BO_3S$ $[M+H]^+$: 267.1221, found: 267.1224.

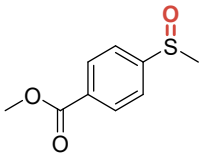
1-(4-(methylsulfinyl)phenyl)ethan-1-one (2q)



2q was prepared according to general procedure A using **1q** (49.9 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.25) to obtain **2q** as a white solid (41.9 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.07 (m, 2H), 7.75 – 7.71 (m, 2H), 2.75 (s, 3H), 2.64 (s,

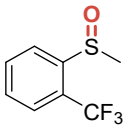
3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.14, 151.07, 139.20, 129.26, 123.86, 43.95, 26.92. HRMS (ESI): calculated for $C_9H_{10}O_2S$ $[M+H]^+$: 183.0474, found: 183.0473.

methyl 4-(methylsulfinyl)benzoate (2r)



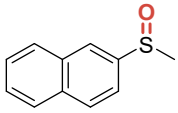
2r was prepared according to general procedure A using **1r** (54.7 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.24) to obtain **2r** as a white solid (15.8 mg, 27% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.17 (m, 2H), 7.73 – 7.70 (m, 2H), 3.94 (s, 3H), 2.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.14, 150.96, 132.73, 130.61, 123.63, 52.63, 43.97. HRMS (ESI): calculated for $C_9H_{10}O_3S$ $[M+H]^+$: 199.0423, found: 199.0424.

1-(methylsulfinyl)-2-(trifluoromethyl)benzene (2s)



2s was prepared according to general procedure A using **1s** (57.7 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.64) to obtain **2s** as a yellow solid (52.0 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 7.9 Hz, 1H), 7.86 – 7.81 (m, 1H), 7.74 – 7.71 (m, 1H), 7.65 – 7.60 (m, 1H), 2.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.99, 133.58, 131.20, 126.45 (d, J = 5.2 Hz), 126.45 (d, J = 15.8 Hz), 125.80 (q, J = 723.9 Hz), 124.70, 44.62. ^{19}F NMR (471 MHz, $CDCl_3$) δ −57.41. HRMS (ESI): calculated for $C_8H_7F_3OS$ $[M+H]^+$: 209.0242, found: 209.0242.

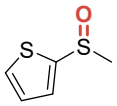
2-(methylsulfinyl)naphthalene (2t)



2t was prepared according to general procedure A using **1t** (52.2 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer

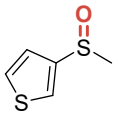
chromatography (hexane/ethyl acetate = 1:2, R_f = 0.20) to obtain **2t** as a white solid (30.1 mg, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 1.7 Hz, 1H), 7.98 (d, *J* = 8.6 Hz, 1H), 7.96 – 7.89 (m, 2H), 7.62 – 7.56 (m, 3H), 2.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.73, 134.56, 133.03, 129.76, 128.64, 128.18, 127.94, 127.50, 124.20, 119.54, 43.87. HRMS (ESI): calculated for $C_{11}H_{10}OS$ $[M+H]^+$: 191.0525, found: 191.0523.

2-(methylsulfinyl)thiophene (2u)



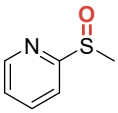
2u was prepared according to general procedure A using **1u** (39.0 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.32) to obtain **2u** as a yellow oil (34.5 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.49 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.12 (dd, *J* = 5.0, 3.7 Hz, 1H), 2.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.21, 131.09, 129.61, 127.59, 44.54. HRMS (ESI): calculated for $C_5H_6OS_2$ $[M+H]^+$: 146.9933, found: 146.9934.

3-(methylsulfinyl)thiophene (2v)



2v was prepared according to general procedure A using **1v** (39.0 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.21) to obtain **2v** as a yellow oil (37.0 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.51 (dd, *J* = 5.1, 3.0 Hz, 1H), 7.28 (dd, *J* = 5.1, 1.3 Hz, 1H), 2.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.00, 128.75, 125.72, 122.85, 43.18. HRMS (ESI): calculated for $C_5H_6OS_2$ $[M+H]^+$: 146.9933, found: 146.9934.

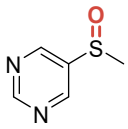
2-(methylsulfinyl)pyridine (2w)



2w was prepared according to general procedure A using **1w** (37.5 mg, 0.3 mmol) and acetonitrile (15

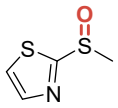
mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.36) to obtain **2w** as a colorless oil (21.7 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 – 8.60 (m, 1H), 8.04 – 8.01 (m, 1H), 7.97 – 7.92 (m, 1H), 7.40 – 7.36 (m, 1H), 2.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.13, 149.65, 138.28, 124.72, 119.41, 41.45. HRMS (ESI): calculated for C_6H_7NOS $[M+H]^+$: 142.0321, found: 142.0318.

5-(methylsulfinyl)pyrimidine (2x)



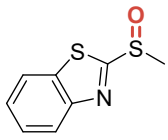
2x was prepared according to general procedure A using **1x** (37.8 mg, 0.3 mmol) and acetonitrile (15 mL). The reaction time is 30 h. After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (dichloromethane/methanol = 20:1, R_f = 0.34) to obtain **2x** as a white solid (25.8 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (s, 1H), 8.99 (s, 2H), 2.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.59, 153.27, 140.41, 43.77. HRMS (ESI): calculated for $C_5H_6N_2OS$ $[M+H]^+$: 143.0274, found: 143.0277.

2-(methylsulfinyl)thiazole (2y)



2y was prepared according to general procedure A using **1y** (39.4 mg, 0.3 mmol) and acetonitrile (15 mL). The reaction time is 30 h. After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.40) to obtain **2y** as a yellow oil (16.8 mg, 38% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 3.1 Hz, 1H), 7.67 (d, J = 3.1 Hz, 1H), 3.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.31, 144.87, 123.89, 43.44. HRMS (ESI): calculated for $C_4H_5NOS_2$ $[M+H]^+$: 147.9885, found: 147.9888.

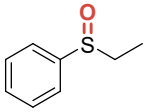
2-(methylsulfinyl)benzo[d]thiazole (2z)



2z was prepared according to general procedure A using **1z** (54.4 mg, 0.3 mmol) and acetonitrile (15

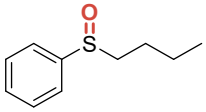
mL). The reaction time is 30 h. After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.58) to obtain **2z** as a white solid (23.6 mg, 40% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.05 (m, 1H), 8.02 – 7.99 (m, 1H), 7.60 – 7.54 (m, 1H), 7.52 – 7.47 (m, 1H), 3.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.55, 153.92, 136.14, 127.13, 126.42, 124.12, 122.48, 43.32. HRMS (ESI): calculated for $C_8H_7NOS_2$ $[M+H]^+$: 198.0042, found: 198.0044.

(ethylsulfinyl)benzene (2aa)



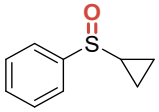
2aa was prepared according to general procedure A using **1aa** (41.4 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.38) to obtain **2aa** as a yellow solid (31.9 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 2H), 7.55 – 7.46 (m, 3H), 2.95 – 2.85 (m, 1H), 2.81 – 2.72 (m, 1H), 1.20 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.51, 131.05, 129.27, 124.32, 50.47, 6.11. HRMS (ESI): calculated for $C_8H_{10}OS$ $[M+H]^+$: 155.0525, found: 155.0525.

(butylsulfinyl)benzene (2ab)



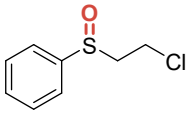
2ab was prepared according to general procedure A using **1ab** (46.9 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.56) to obtain **2ab** as a colorless oil (20.9 mg, 38% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 2H), 7.56 – 7.46 (m, 3H), 2.84 – 2.73 (m, 2H), 1.77 – 1.67 (m, 1H), 1.63 – 1.53 (m, 1H), 1.52 – 1.35 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.17, 131.04, 129.32, 124.16, 57.21, 24.27, 22.03, 13.78. HRMS (ESI): calculated for $C_{10}H_{14}OS$ $[M+H]^+$: 183.0838, found: 183.0838.

(cyclopropylsulfinyl)benzene (2ac)



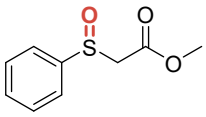
2ac was prepared according to general procedure A using **1ac** (45.1 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.46) to obtain **2ac** as a yellow solid (38.3 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.64 (m, 2H), 7.54 – 7.46 (m, 3H), 2.29 – 2.22 (m, 1H), 1.27 – 1.20 (m, 1H), 1.07 – 1.00 (m, 1H), 0.99 – 0.89 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.03, 131.05, 129.29, 124.15, 33.95, 3.55, 2.94. HRMS (ESI): calculated for $C_9H_{10}OS$ $[M+H]^+$: 167.0525, found: 167.0525.

(2-chloroethyl)sulfinyl)benzene (2ad)



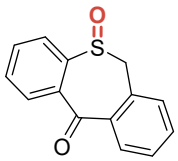
2ad was prepared according to general procedure A using **1ad** (51.8 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.59) to obtain **2ad** as a colorless oil (35.4 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.62 (m, 2H), 7.58 – 7.52 (m, 3H), 4.01 – 3.93 (m, 1H), 3.69 – 3.62 (m, 1H), 3.19 – 3.14 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.94, 131.56, 129.64, 124.03, 59.51, 36.80. HRMS (ESI): calculated for C_8H_9ClOS $[M+H]^+$: 189.0135, found: 189.0141.

methyl 2-(phenylsulfinyl)acetate (2ae)



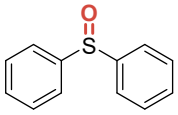
2ae was prepared according to general procedure A using **1ae** (54.7 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.50) to obtain **2ae** as a white solid (47.7 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.67 (m, 2H), 7.56 – 7.53 (m, 3H), 3.85 (d, J = 13.7 Hz, 1H), 3.71 (s, 3H), 3.67 (d, J = 13.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.33, 143.23, 131.97, 129.59, 124.25, 61.76, 52.92. HRMS (ESI): calculated for $C_9H_{10}O_3S$ $[M+H]^+$: 199.0423, found: 199.0424.

dibenzo[b,e]thiepin-11(6H)-one 5-oxide (2af)



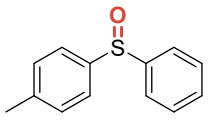
2af was prepared according to general procedure A using **1af** (67.9 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.52) to obtain **2af** as a white solid (59.3 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.14 (m, 2H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.79 – 7.74 (m, 1H), 7.64 – 7.58 (m, 2H), 7.51 – 7.47 (m, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 4.84 (d, *J* = 13.5 Hz, 1H), 4.28 (d, *J* = 13.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.44, 146.95, 138.12, 134.26, 134.03, 133.50, 132.65, 132.06, 131.47, 130.90, 129.20, 128.01, 124.38, 61.11. HRMS (ESI): calculated for $C_{14}H_{10}O_2S$ $[M+H]^+$: 243.0474, found: 243.0475.

sulfinyldibenzene (2ag)



2ag was prepared according to general procedure A using **1ag** (55.8 mg, 0.3 mmol) and acetonitrile (15 mL). The reaction time is 30 h. After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.75) to obtain **2ag** as a white solid (40.3 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.63 (m, 4H), 7.49 – 7.40 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.74, 131.17, 129.44, 124.90. HRMS (ESI): calculated for $C_{12}H_{10}OS$ $[M+H]^+$: 203.0525, found: 203.0523.

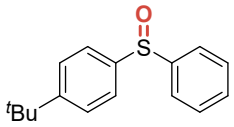
1-methyl-4-(phenylsulfinyl)benzene (2ah)



2ah was prepared according to general procedure A using **1ah** (60.1 mg, 0.3 mmol) and acetonitrile (15 mL). The reaction time is 30 h. After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:1, R_f = 0.72) to obtain **2ah** as a white solid (45.3 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 2H), 7.53 (d, *J* = 8.0 Hz,

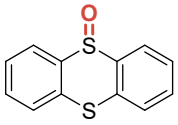
2H), 7.48 – 7.41 (m, 3H), 7.25 (d, J = 8.0 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.90, 142.57, 141.74, 130.98, 130.13, 129.36, 125.09, 124.78, 21.50. HRMS (ESI): calculated for $C_{13}H_{12}OS$ $[M+H]^+$: 217.0682, found: 217.0684.

1-(tert-butyl)-4-(phenylsulfinyl)benzene (2ai)



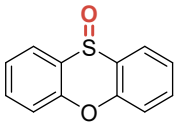
2ai was prepared according to general procedure A using **1ai** (72.7 mg, 0.3 mmol) and acetonitrile (15 mL). The reaction time is 30 h. After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:1, R_f = 0.80) to obtain **2ai** as a white solid (53.5 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.63 (m, 2H), 7.58 – 7.54 (m, 2H), 7.48 – 7.40 (m, 5H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.80, 145.72, 142.39, 130.97, 129.34, 126.50, 124.93, 124.84, 35.04, 31.24. HRMS (ESI): calculated for $C_{16}H_{18}OS$ $[M+H]^+$: 259.1151, found: 259.1151.

thianthrene 5-oxide (2aj)



2aj was prepared according to general procedure A using **1aj** (64.9 mg, 0.3 mmol) and acetonitrile (15 mL). The reaction time is 30 h. After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 4:1, R_f = 0.42) to obtain **2aj** as a white solid (44.2 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.92 (m, 2H), 7.64 – 7.61 (m, 2H), 7.58 – 7.53 (m, 2H), 7.45 – 7.40 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.56, 129.98, 129.15, 128.56, 124.62. HRMS (ESI): calculated for $C_{12}H_8OS_2$ $[M+H]^+$: 233.0089, found: 233.0089.

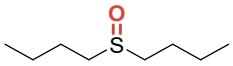
phenoxathiine 10-oxide (2ak)



2ak was prepared according to general procedure A using **1ak** (60.1 mg, 0.3 mmol) and acetonitrile (15 mL). The reaction time is 30 h. After steps of treatments as described, the mixture was purified by

preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.51) to obtain **2ak** as a white solid (47.6 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.92 (m, 2H), 7.65 – 7.60 (m, 2H), 7.45 – 7.36 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.64, 133.90, 131.19, 124.98, 123.84, 118.94. HRMS (ESI): calculated for $C_{12}H_8O_2S$ $[M+H]^+$: 217.0318, found: 217.0319.

1-(butylsulfinyl)butane (2al)

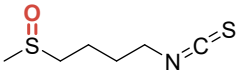


2al was prepared according to general procedure A using **1al** (43.8 mg, 0.3 mmol) and acetonitrile (15 mL). The reaction time is 7 h. After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (6% methanol in dichloromethane, R_f = 0.60) to obtain **2al** as a yellow oil (43.6 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.77 – 2.60 (m, 4H), 1.79 – 1.70 (m, 4H), 1.56 – 1.40 (m, 4H), 0.96 (t, J = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 51.99, 24.72, 22.17, 13.79. HRMS (ESI): calculated for $C_8H_{18}OS$ $[M+H]^+$: 163.1151, found: 163.1146.

tetrahydrothiophene 1-oxide (2am)

2am was prepared according to general procedure A using **1am** (26.4 mg, 0.3 mmol) and acetonitrile (15 mL). The reaction time is 7 h. After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (6% methanol in dichloromethane, R_f = 0.48) to obtain **2am** as a colorless oil (28.4 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.92 – 2.77 (m, 4H), 2.48 – 2.39 (m, 2H), 2.04 – 1.96 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 54.60, 25.60. HRMS (ESI): calculated for C_4H_8OS $[M+H]^+$: 105.0369, found: 105.0364.

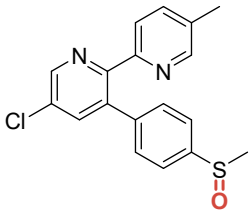
1-isothiocyanato-4-(methylsulfinyl)butane (2an)



2an was prepared according to general procedure A using **1an** (48.4 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (6% methanol in dichloromethane, R_f = 0.50) to obtain **2an** as a white solid (37.5 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.57 (t, J = 5.9 Hz, 2H), 2.75 – 2.65 (m, 2H), 2.57 (s, 3H),

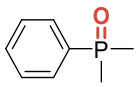
1.95 – 1.82 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 130.94, 53.53, 44.70, 38.79, 29.04, 20.14. HRMS (ESI): calculated for $C_6H_{11}NOS_2$ $[M+H]^+$: 178.0355, found: 178.0358.

5-chloro-5'-methyl-3-(4-(methylsulfinyl)phenyl)-2,2'-bipyridine (2ao)



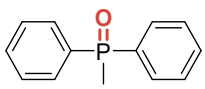
2ao was prepared according to general procedure A using **1ao** (98.0 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (dichloromethane/methanol = 20:1, R_f = 0.26) to obtain **2ao** as a white solid (53.6 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 2.4 Hz, 1H), 8.41 – 8.39 (m, 1H), 7.74 (d, *J* = 2.4 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.55 (dd, *J* = 8.1, 2.4 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.07 (d, *J* = 8.0 Hz, 1H), 2.75 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.40, 152.49, 149.94, 148.18, 145.96, 141.10, 138.13, 137.49, 136.06, 131.65, 131.18, 130.48, 124.24, 122.83, 44.03, 24.35. HRMS (ESI): calculated for $C_{18}H_{15}ClN_2OS$ $[M+H]^+$: 343.0666, found: 343.0666.

dimethyl(phenyl)phosphine oxide (5a)



5a was prepared according to general procedure B using **4a** (41.4 mg, 0.3 mmol) and acetonitrile (15 mL). The reaction time is 100 min. After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (dichloromethane/methanol = 20:1, R_f = 0.26) to obtain **5a** as a white solid (42.9 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.68 (m, 2H), 7.53 – 7.43 (m, 3H), 1.72 (d, *J* = 13.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.55 (d, *J* = 99.2 Hz), 131.80 (d, *J* = 2.8 Hz), 129.69 (d, *J* = 9.7 Hz), 128.79 (d, *J* = 11.7 Hz), 18.07 (d, *J* = 71.4 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 34.74. HRMS (ESI): calculated for $C_8H_{11}OP$ $[M+H]^+$: 155.0620, found: 155.0621.

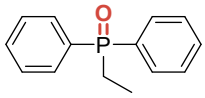
methyldiphenylphosphine oxide (5b)



5b was prepared according to general procedure B using **4b** (60.1 mg, 0.3 mmol) and acetonitrile (15

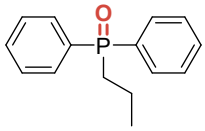
mL). The reaction time is 100 min. After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (dichloromethane/methanol = 20:1, R_f = 0.31) to obtain **5b** as a white solid (61.6 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.68 (m, 4H), 7.54 – 7.42 (m, 6H), 2.01 (d, *J* = 13.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.17 (d, *J* = 101.2 Hz), 131.85 (d, *J* = 2.7 Hz), 130.62 (d, *J* = 9.8 Hz), 128.75 (d, *J* = 11.8 Hz), 16.69 (d, *J* = 73.7 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 29.85. HRMS (ESI): calculated for $C_{13}H_{13}OP$ $[M+H]^+$: 217.0777, found: 217.0779.

ethyldiphenylphosphine oxide (5c)



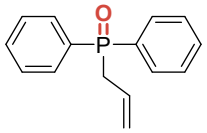
5c was prepared according to general procedure B using **4c** (64.3 mg, 0.3 mmol) and acetonitrile (15 mL). The reaction time is 100 min. After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (dichloromethane/methanol = 20:1, R_f = 0.32) to obtain **5c** as a white solid (65.4 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 4H), 7.53 – 7.43 (m, 6H), 2.32 – 2.23 (m, 2H), 1.24 – 1.15 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.93 (d, *J* = 97.7 Hz), 131.79 (d, *J* = 2.7 Hz), 130.99 (d, *J* = 9.2 Hz), 128.74 (d, *J* = 11.5 Hz), 22.78 (d, *J* = 72.9 Hz), 5.72 (d, *J* = 5.1 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 34.09. HRMS (ESI): calculated for $C_{14}H_{15}OP$ $[M+H]^+$: 231.0933, found: 231.0937.

diphenyl(propyl)phosphine oxide (5d)



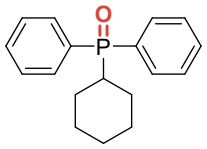
5d was prepared according to general procedure B using **4d** (68.5 mg, 0.3 mmol) and acetonitrile (15 mL). The reaction time is 220 min. After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (dichloromethane/methanol = 20:1, R_f = 0.33) to obtain **5d** as a white solid (66.1 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.68 (m, 4H), 7.51 – 7.40 (m, 6H), 2.28 – 2.20 (m, 2H), 1.70 – 1.57 (m, 2H), 1.02 – 0.97 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.16 (d, *J* = 98.9 Hz), 131.73 (d, *J* = 2.8 Hz), 130.86 (d, *J* = 9.3 Hz), 128.68 (d, *J* = 11.6 Hz), 31.87 (d, *J* = 72.0 Hz), 15.75 (d, *J* = 15.6 Hz), 15.34 (d, *J* = 3.9 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 32.19. HRMS (ESI): calculated for $C_{15}H_{17}OP$ $[M+H]^+$: 245.1090, found: 245.1094.

allyldiphenylphosphine oxide (5e)



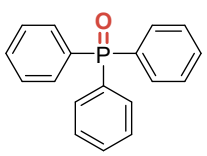
5e was prepared according to general procedure B using **4e** (67.9 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (dichloromethane/methanol = 20:1, R_f = 0.38) to obtain **5e** as a white solid (64.2 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 4H), 7.54 – 7.43 (m, 6H), 5.87 – 5.74 (m, 1H), 5.18 – 5.10 (m, 2H), 3.18 – 3.11 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.55 (d, *J* = 99.1 Hz), 131.95 (d, *J* = 2.8 Hz), 131.14 (d, *J* = 9.2 Hz), 128.69 (d, *J* = 11.7 Hz), 127.13 (d, *J* = 9.1 Hz), 121.14 (d, *J* = 11.7 Hz), 36.24 (d, *J* = 68.8 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 29.66. HRMS (ESI): calculated for $C_{15}H_{15}OP$ $[M+H]^+$: 243.0933, found: 243.0934.

cyclohexyldiphenylphosphine oxide (5f)



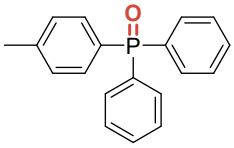
5f was prepared according to general procedure B using **4f** (80.5 mg, 0.3 mmol) and acetonitrile (15 mL). The reaction time is 100 min. After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (dichloromethane/methanol = 20:1, R_f = 0.39) to obtain **5f** as a white solid (78.7 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 4H), 7.51 – 7.42 (m, 6H), 2.28 – 2.18 (m, 1H), 1.84 – 1.69 (m, 5H), 1.59 – 1.47 (m, 2H), 1.32 – 1.19 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.26 (d, *J* = 94.4 Hz), 131.52 (d, *J* = 2.8 Hz), 131.21 (d, *J* = 8.7 Hz), 128.64 (d, *J* = 11.1 Hz), 37.33 (d, *J* = 73.1 Hz), 26.49 (d, *J* = 13.4 Hz), 25.89 (d, *J* = 1.5 Hz), 24.91 (d, *J* = 3.0 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 34.19. HRMS (ESI): calculated for $C_{18}H_{21}OP$ $[M+H]^+$: 285.1403, found: 285.1403.

triphenylphosphine oxide (5g)



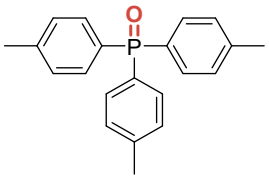
5g was prepared according to general procedure B using **4g** (78.7 mg, 0.3 mmol) and acetonitrile (15 mL). The reaction time is 100 min. After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.22) to obtain **5g** as a white solid (80.3 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.63 (m, 6H), 7.57 – 7.51 (m, 3H), 7.48 – 7.42 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.66 (d, *J* = 104.5 Hz), 132.22 (d, *J* = 9.9 Hz), 132.05 (d, *J* = 2.8 Hz), 128.61 (d, *J* = 12.1 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 29.00. HRMS (ESI): calculated for $C_{18}H_{15}OP$ $[M+H]^+$: 279.0933, found: 279.0939.

diphenyl(*p*-tolyl)phosphine oxide (5h)



5h was prepared according to general procedure B using **4h** (82.9 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (dichloromethane/methanol = 20:1, R_f = 0.53) to obtain **5h** as a white solid (80.8 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.63 (m, 4H), 7.58 – 7.50 (m, 4H), 7.47 – 7.42 (m, 4H), 7.28 – 7.25 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.53 (d, *J* = 2.8 Hz), 132.91 (d, *J* = 104.0 Hz), 132.19 (d, *J* = 10.3 Hz), 132.13 (d, *J* = 9.9 Hz), 131.90 (d, *J* = 2.8 Hz), 129.33 (d, *J* = 12.5 Hz), 129.24 (d, *J* = 107.1 Hz), 128.52 (d, *J* = 12.1 Hz), 21.68 (d, *J* = 1.4 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 29.18. HRMS (ESI): calculated for $C_{19}H_{17}OP$ $[M+H]^+$: 293.1090, found: 293.1091.

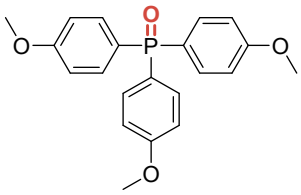
tri-*p*-tolylphosphine oxide (5i)



5i was prepared according to general procedure B using **4i** (91.3 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.24) to obtain **5i** as a white solid (84.8 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 6H), 7.25 – 7.21 (m, 6H), 2.38 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.28 (d, *J* = 2.9 Hz), 132.17 (d, *J* = 10.2 Hz), 130.35, 129.24 (d, *J* = 12.4 Hz), 21.68 (d, *J* = 1.3 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 29.16. HRMS (ESI): calculated for $C_{21}H_{21}OP$

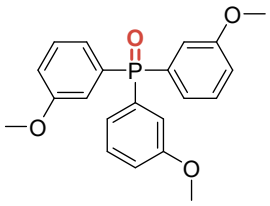
$[M+H]^+$: 321.1403, found: 321.1410.

tris(4-methoxyphenyl)phosphine oxide (5j)



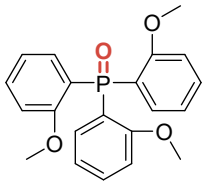
5j was prepared according to general procedure B using **4j** (105.7 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (dichloromethane/methanol = 20:1, R_f = 0.39) to obtain **5j** as a white solid (99.8 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 6H), 6.91 – 6.88 (m, 6H), 3.77 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.28 (d, J = 2.9 Hz), 133.81 (d, J = 11.2 Hz), 124.51 (d, J = 110.9 Hz), 113.94 (d, J = 13.1 Hz), 55.30. ^{31}P NMR (202 MHz, $CDCl_3$) δ 28.63. HRMS (ESI): calculated for $C_{21}H_{21}O_4P$ $[M+H]^+$: 369.1250, found: 369.1259.

tris(3-methoxyphenyl)phosphine oxide (5k)



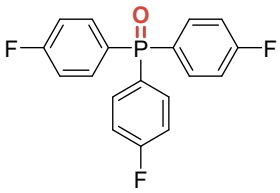
5k was prepared according to general procedure B using **4k** (105.7 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (dichloromethane/methanol = 20:1, R_f = 0.42) to obtain **5k** as a white solid (107.6 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 3H), 7.31 – 7.26 (m, 3H), 7.17 – 7.11 (m, 3H), 7.08 – 7.05 (m, 3H), 3.79 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.64 (d, J = 15.0 Hz), 133.74 (d, J = 103.6 Hz), 129.72 (d, J = 14.5 Hz), 124.41 (d, J = 10.2 Hz), 118.31 (d, J = 2.6 Hz), 116.80 (d, J = 10.8 Hz), 55.50. ^{31}P NMR (202 MHz, $CDCl_3$) δ 29.66. HRMS (ESI): calculated for $C_{21}H_{21}O_4P$ $[M+H]^+$: 369.1250, found: 369.1254.

tris(2-methoxyphenyl)phosphine oxide (5l)



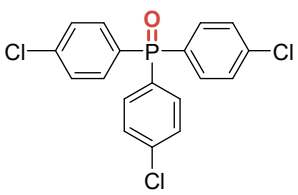
5l was prepared according to general procedure B using **4l** (105.7 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (dichloromethane/methanol = 20:1, R_f = 0.29) to obtain **5l** as a white solid (106.6 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 3H), 7.46 – 7.39 (m, 3H), 6.96 – 6.91 (m, 3H), 6.88 – 6.84 (m, 3H), 3.52 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.51 (d, *J* = 2.5 Hz), 134.44 (d, *J* = 8.8 Hz), 133.12 (d, *J* = 2.2 Hz), 121.31 (d, *J* = 110.2 Hz), 120.30 (d, *J* = 12.6 Hz), 111.28 (d, *J* = 6.6 Hz), 55.49. ^{31}P NMR (202 MHz, $CDCl_3$) δ 25.56. HRMS (ESI): calculated for $C_{21}H_{21}O_4P$ $[M+H]^+$: 369.1250, found: 369.1260.

tris(4-fluorophenyl)phosphine oxide (5m)



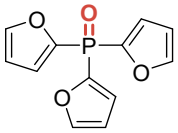
5m was prepared according to general procedure B using **4m** (94.9 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.36) to obtain **5m** as a white solid (93.3 mg, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.59 (m, 6H), 7.20 – 7.13 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.31 (dd, *J* = 254.4, 3.2 Hz), 134.58 (dd, *J* = 11.4, 8.8 Hz), 128.24 (dd, *J* = 108.3, 3.4 Hz), 116.23 (dd, *J* = 21.4, 13.4 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ −106.00. ^{31}P NMR (202 MHz, $CDCl_3$) δ 26.72. HRMS (ESI): calculated for $C_{18}H_{12}F_3OP$ $[M+H]^+$: 333.0651, found: 333.0651.

tris(4-chlorophenyl)phosphine oxide (5n)



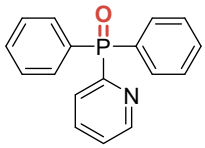
5n was prepared according to general procedure B using **4n** (109.7 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 1:2, R_f = 0.51) to obtain **5n** as a white solid (90.5 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 6H), 7.47 – 7.44 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.22 (d, *J* = 3.3 Hz), 133.42 (d, *J* = 10.8 Hz), 130.35 (d, *J* = 106.4 Hz), 129.24 (d, *J* = 12.9 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 26.82. HRMS (ESI): calculated for $C_{18}H_{12}Cl_3OP$ $[M+H]^+$: 380.9764, found: 380.9764.

tri(furan-2-yl)phosphine oxide (5o)



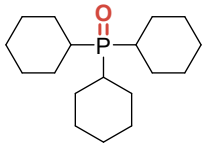
5o was prepared according to general procedure B using **4o** (69.6 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (dichloromethane/methanol = 20:1, R_f = 0.47) to obtain **5o** as a white solid (50.7 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.70 (m, 3H), 7.16 – 7.13 (m, 3H), 6.54 – 6.52 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.98 (d, *J* = 8.8 Hz), 146.06 (d, *J* = 158.5 Hz), 123.59 (d, *J* = 22.0 Hz), 111.16 (d, *J* = 9.3 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ −11.70. HRMS (ESI): calculated for $C_{12}H_9O_4P$ $[M+H]^+$: 249.0311, found: 249.0311.

diphenyl(pyridin-2-yl)phosphine oxide (5p)



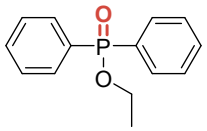
5p was prepared according to general procedure B using **4p** (79.0 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (dichloromethane/methanol = 20:1, R_f = 0.37) to obtain **5p** as a white solid (77.9 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.6 Hz, 1H), 8.27 (t, *J* = 6.8 Hz, 1H), 7.90 – 7.77 (m, 5H), 7.50 – 7.32 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.40 (d, *J* = 131.9 Hz), 150.17 (d, *J* = 19.1 Hz), 136.21 (d, *J* = 9.3 Hz), 132.22 (d,*J* = 104.4 Hz), 132.13 (d, *J* = 9.5 Hz), 131.93 (d, *J* = 2.9 Hz), 128.38 (d, *J* = 12.1 Hz), 128.36 (d, *J* = 20.0 Hz), 125.31 (d, *J* = 3.1 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 20.80. HRMS (ESI): calculated for $C_{17}H_{14}NOP$ $[M+H]^+$: 280.0886, found: 280.0886.

tricyclohexylphosphine oxide (5q)



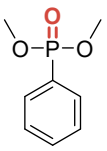
5q was prepared according to general procedure B using **4q** (84.1 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (dichloromethane/methanol = 20:1, R_f = 0.37) to obtain **5q** as a white solid (66.9 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.93 – 1.70 (m, 18H), 1.47 – 1.19 (m, 15H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 35.45 (d, *J* = 60.6 Hz), 27.04 (d, *J* = 11.6 Hz), 26.44 (d, *J* = 2.9 Hz), 26.25 (d, *J* = 1.5 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 50.25. HRMS (ESI): calculated for $C_{18}H_{33}OP$ $[M+H]^+$: 297.2342, found: 297.2345.

ethyl diphenylphosphinate (5r)



5r was prepared according to general procedure B using **4r** (69.1 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (dichloromethane/methanol = 20:1, R_f = 0.53) to obtain **5r** as a colorless oil (71.5 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 4H), 7.53 – 7.48 (m, 2H), 7.46 – 7.40 (m, 4H), 4.10 (p, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.19 (d, *J* = 2.9 Hz), 131.80 (d, *J* = 137.6 Hz), 131.74 (d, *J* = 10.2 Hz), 61.22 (d, *J* = 5.8 Hz), 16.61 (d, *J* = 6.7 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 31.28. HRMS (ESI): calculated for $C_{14}H_{15}O_2P$ $[M+H]^+$: 247.0882, found: 247.0879.

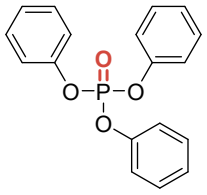
dimethyl phenylphosphonate (5s)



5s was prepared according to general procedure B using **4s** (51.0 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer

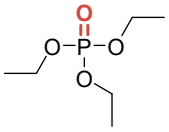
chromatography (dichloromethane/methanol = 20:1, R_f = 0.47) to obtain **5s** as a colorless oil (52.9 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.76 (m, 2H), 7.59 – 7.54 (m, 1H), 7.50 – 7.44 (m, 2H), 3.77 (s, 3H), 3.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.78 (d, *J* = 3.0 Hz), 132.02 (d, *J* = 9.9 Hz), 128.69 (d, *J* = 15.1 Hz), 127.05 (d, *J* = 188.6 Hz), 52.82 (d, *J* = 5.6 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 21.63. HRMS (ESI): calculated for $C_8H_{11}O_3P$ $[M+H]^+$: 187.0519, found: 187.0515.

triphenyl phosphate (5t)



5t was prepared according to general procedure B using **4t** (93.1 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 4:1, R_f = 0.46) to obtain **5t** as a white solid (90.4 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 6H), 7.27 – 7.19 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.59 (d, *J* = 7.4 Hz), 129.99, 125.73 (d, *J* = 1.4 Hz), 120.26 (d, *J* = 4.9 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ −17.71. HRMS (ESI): calculated for $C_{18}H_{15}O_4P$ $[M+H]^+$: 327.0781, found: 327.0785.

triethyl phosphate (5u)



5u was prepared according to general procedure B using **4u** (49.8 mg, 0.3 mmol) and acetonitrile (15 mL). After steps of treatments as described, the mixture was purified by preparative thin-layer chromatography (dichloromethane/methanol = 20:1, R_f = 0.66) to obtain **5u** as a colorless oil (52.1 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.14 – 4.05 (m, 6H), 1.35 – 1.30 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 63.73 (d, *J* = 5.8 Hz), 16.25 (d, *J* = 6.7 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ −0.92. HRMS (ESI): calculated for $C_6H_{15}O_4P$ $[M+H]^+$: 183.0781, found: 183.0783.

4. Mechanistic studies

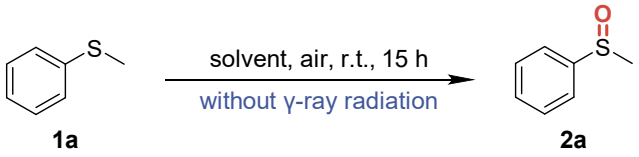
4.1 Control experiments

Procedures for control experiments:

A 130 mL test tube was charged with 15 mL of solvent containing **1a** (37.3 mg, 0.3 mmol). Then the test tube was sealed and placed without receiving ^{60}Co γ-ray radiation. After 15 h, the reaction mixture was diluted and analyzed by GC-MS with 1,3,5-trimethoxybenzene as the internal standard.

A 100 mL Schlenk vial was charged with 15 mL of solvent containing **1a** (37.3 mg, 0.3 mmol). Then the reaction mixture was degassed with three freeze-pump-thaw cycles and filled with high-purity (99.999%) argon. Then the Schlenk vial was sealed and exposed to ^{60}Co γ-ray radiation (dose rate: 110 Gy min^{-1}, measured using a Fricke dosimeter) at room temperature for 15 h. After the reaction, the reaction mixture was diluted and analyzed by GC-MS with 1,3,5-trimethoxybenzene as the internal standard.

Table S6 Evaluation of γ-ray radiation[a]

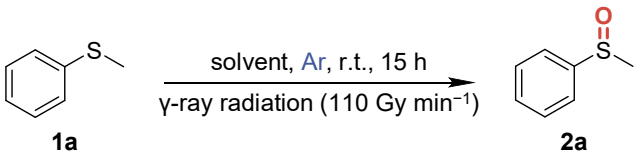


1a **2a**

Entry	Solvent	Yield of **2a** (%)[b]
1	CH_3CN	n.d.
2	CH_3OH	n.d.
3	Cyclohexane	n.d.
4	THF	n.d.

[a] Reaction conditions: **1a** (0.3 mmol) in solvent (15 mL) without γ-ray radiation at room temperature and under an air atmosphere for 15 h. [b] Determined by GC-MS using 1,3,5-trimethoxybenzene as the internal standard.

Table S7 Evaluation of the reaction atmosphere[a]



1a **2a**

Entry	Solvent	Yield of **2a** (%)[b]
1	CH_3CN	n.d.
2	CH_3OH	n.d.
3	Cyclohexane	n.d.
4	THF	n.d.

[a] Reaction conditions: **1a** (0.3 mmol) in solvent (15 mL) with γ-ray radiation (dose rate: 110 Gy min^{-1}, measured using a Fricke dosimeter) at room temperature and under an argon atmosphere for 15 h. [b] Determined by GC-MS using 1,3,5-trimethoxybenzene as the internal standard.

4.2 ROS detection using fluorescence probe DCFH

A stock solution of DCFH (10 mM in acetonitrile) was diluted in acetonitrile to a final concentration of 100 μM. A 5 mL glass vial was charged with 1 mL DCFH solution (100 μM in acetonitrile). Then the glass vial was sealed and exposed to ^{60}Co γ-ray radiation (dose rate: 110 Gy min^{-1}, measured using a Fricke dosimeter) at room temperature for different reaction times. After the reaction, the reaction mixture was transferred to the 1 cm path semi-micro polystyrene cuvette to record the fluorescence emission spectrum (Fig. S2).

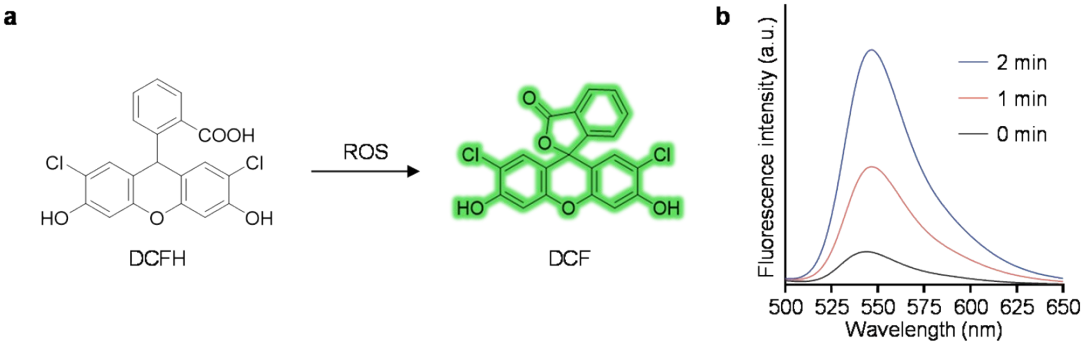


Fig. S2 ROS detection using fluorescence probe DCFH. (a) The mechanism of DCFH as the ROS fluorescent probe. (b) The fluorescence emission spectra (λ_{ex} = 485 nm) of DCFH (100 μM in acetonitrile) after receiving ^{60}Co γ-ray radiation at different times.

4.3 $O_2^{\cdot-}$ detection using $O_2^{\cdot-}$-specific probe NBT

A stock solution of NBT (1 mM in acetonitrile) was diluted in acetonitrile to a final concentration of 100 μM. A 5 mL glass vial was charged with 1 mL NBT solution (100 μM in acetonitrile). Then the glass vial was sealed and exposed to ^{60}Co γ-ray radiation (dose rate: 110 Gy min^{-1}, measured using a Fricke dosimeter) at room temperature for different reaction times. After the reaction, the reaction

mixture was diluted 5 times and transferred to the 1 cm path quartz cuvette to record the UV-visible absorption spectrum (Fig. S3).

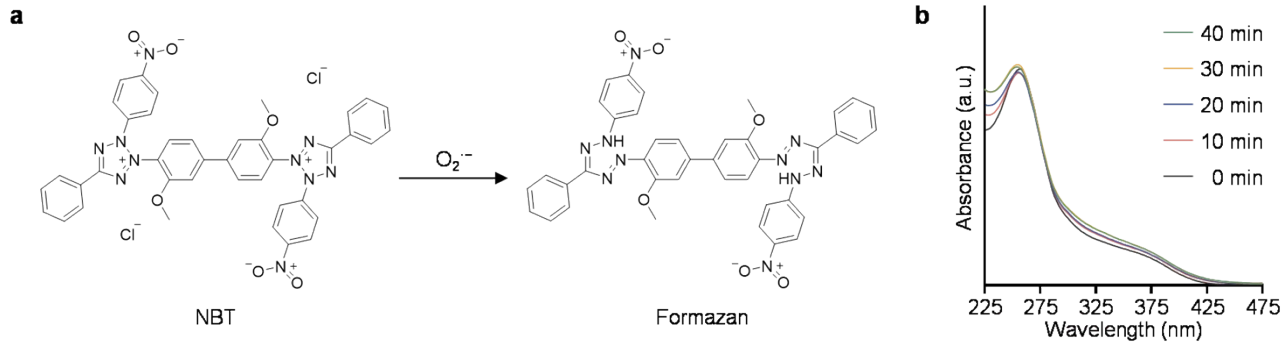


Fig. S3 $O_2^{\cdot-}$ detection using $O_2^{\cdot-}$-specific probe NBT. (a) The mechanism of NBT as the $O_2^{\cdot-}$-specific probe. (b) The UV-visible absorption spectra of NBT (100 μM in acetonitrile) after receiving ^{60}Co γ-ray radiation at different times.

4.4 Quenching experiments

General procedure for quenching experiments:

A 130 mL test tube was charged with 15 mL of solvent containing **1a** (37.3 mg, 0.3 mmol) and 0.6 mmol scavenger. Then the test tube was sealed and exposed to ^{60}Co γ-ray radiation (dose rate: 110 Gy min^{-1}, measured using a Fricke dosimeter) at room temperature for 15 h. After the reaction, the reaction mixture was diluted and analyzed by GC-MS with 1,3,5-trimethoxybenzene as the internal standard.

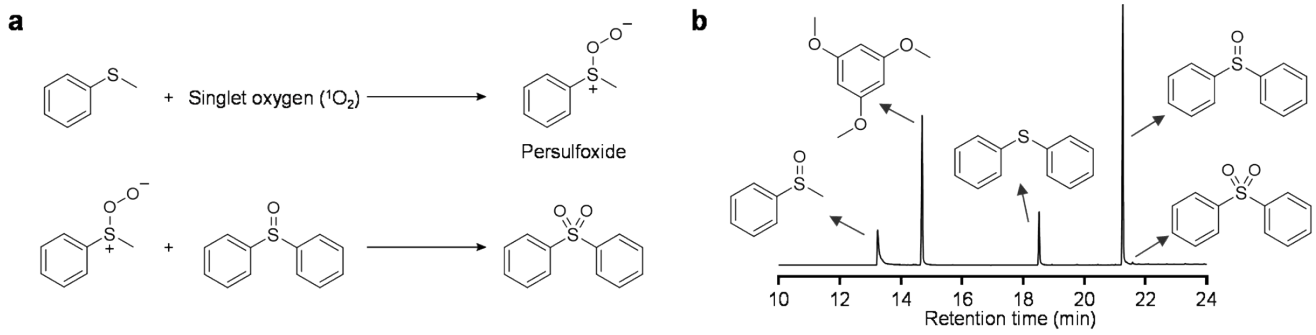


Fig. S4 (a) The mechanism of Ph_2SO as the persulfoxide scavenger. (b) GC-MS chromatogram of the quenching experiment with Ph_2SO as the persulfoxide scavenger.

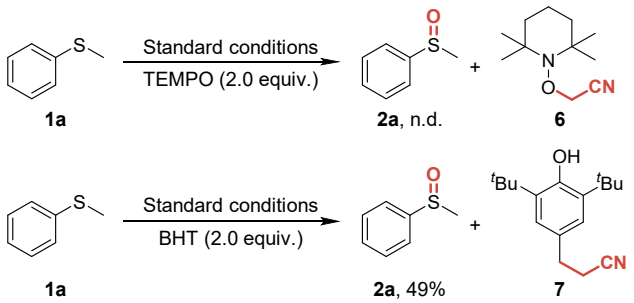


Fig. S5 Radical trapping experiments with TEMPO or BHT as the radical scavenger. Standard conditions: **1a** (0.3 mmol) in CH_3CN (15 mL) with γ-ray radiation (dose rate: 110 Gy min^{-1}, measured using a Fricke dosimeter) at room temperature and under an air atmosphere for 15 h.

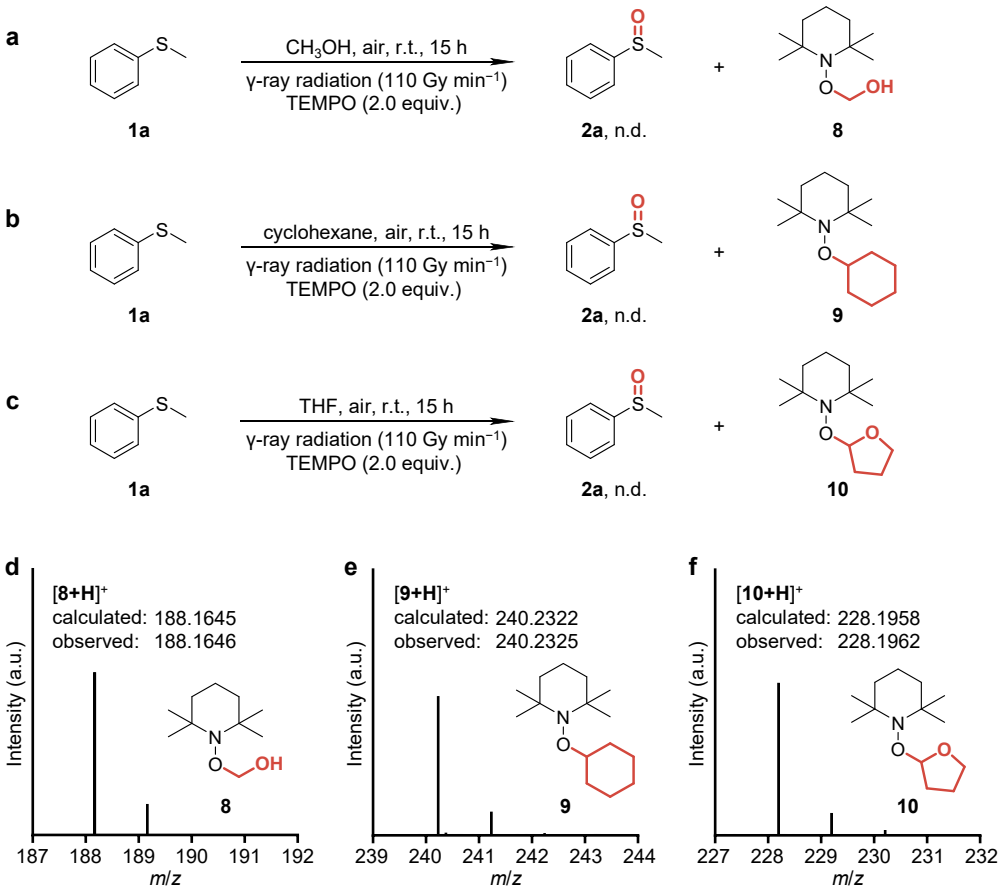


Fig. S6 Radical trapping experiments with TEMPO as the radical scavenger. Reaction conditions: **1a** (0.3 mmol) and TEMPO (0.6 mmol) in (a) CH_3OH, (b) cyclohexane, or (c) THF (15 mL) with γ-ray radiation (dose rate: 110 Gy min^{-1}, measured using a Fricke dosimeter) at room temperature and under an air atmosphere for 15 h. High-resolution mass spectrometry of the adducts between TEMPO and (d) $\cdot CH_2OH$, (e) $\cdot C_6H_{11}$, or (f) $\cdot C_4H_7O$.

4.5 Kinetic studies with CD_3CN as the solvent

A 10 mL glass vial was charged with 1 mL **1a** solution (1 mM in CD_3CN or CH_3CN). Then the glass vial was sealed and exposed to ^{60}Co γ-ray radiation (dose rate: 110 Gy min^{-1}, measured using a Fricke dosimeter) at room temperature for different reaction times. After the reaction, the reaction mixture was analyzed by GC-MS with 1,3,5-trimethoxybenzene as the internal standard.

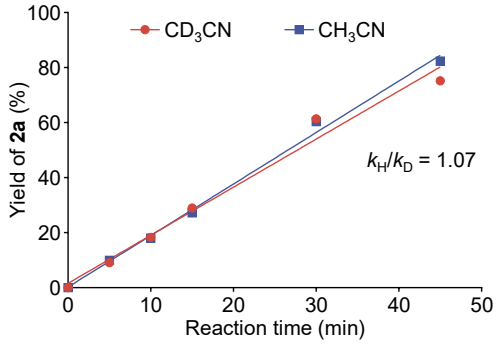


Fig. S7 Kinetic studies with CD_3CN as the solvent.

5. Computational studies

5.1 Computational details

All density functional theory (DFT)[1] calculations were performed with the Gaussian 16 (A.03) program[2] to investigate the detailed mechanism. Geometry optimizations were carried out in the solution phase by using the B3LYP functional[3], where Grimme D3 correction[4] was utilized for the empirical dispersion. The 6-311+G(d,p) basis sets were used for all atoms.[5] The solvent effect was considered with the solvation model based on density (SMD).[6] Frequency calculations were performed for each species to make sure that all of the stationary points are minima with no imaginary frequencies or transition states with only one imaginary frequency, and to provide the thermal correction to free energies at 298.15 K and 1 atm pressure. Intrinsic reaction coordinate (IRC) calculations were carried out on each transition state to confirm that the transition state connects the reactant and product in the specific step.[7] In each step, the Gibbs energy difference between the transition state and the reactant is defined as the Gibbs activation energy ($\Delta G^{\neq}$), and the Gibbs energy difference between the product and the reactant is defined as the Gibbs reaction energy (ΔG). All energies reported here are in kcal mol^{-1}. The calculated optimized structures are illustrated by CYLview.[8]

5.2 Radiolysis of CH_3CN in the presence of O_2

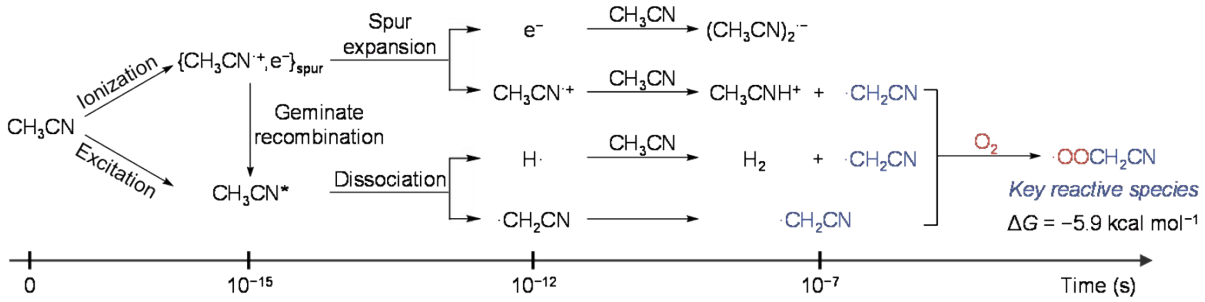


Fig. S8 Radiolysis of CH_3CN in the presence of O_2.

5.3 Intrinsic reaction coordinate (IRC) analysis

Intrinsic reaction coordinate (IRC) calculations were carried out on each transition state in Fig. 4b and 5a to confirm that the transition state connects the reactant and product in the specific step.

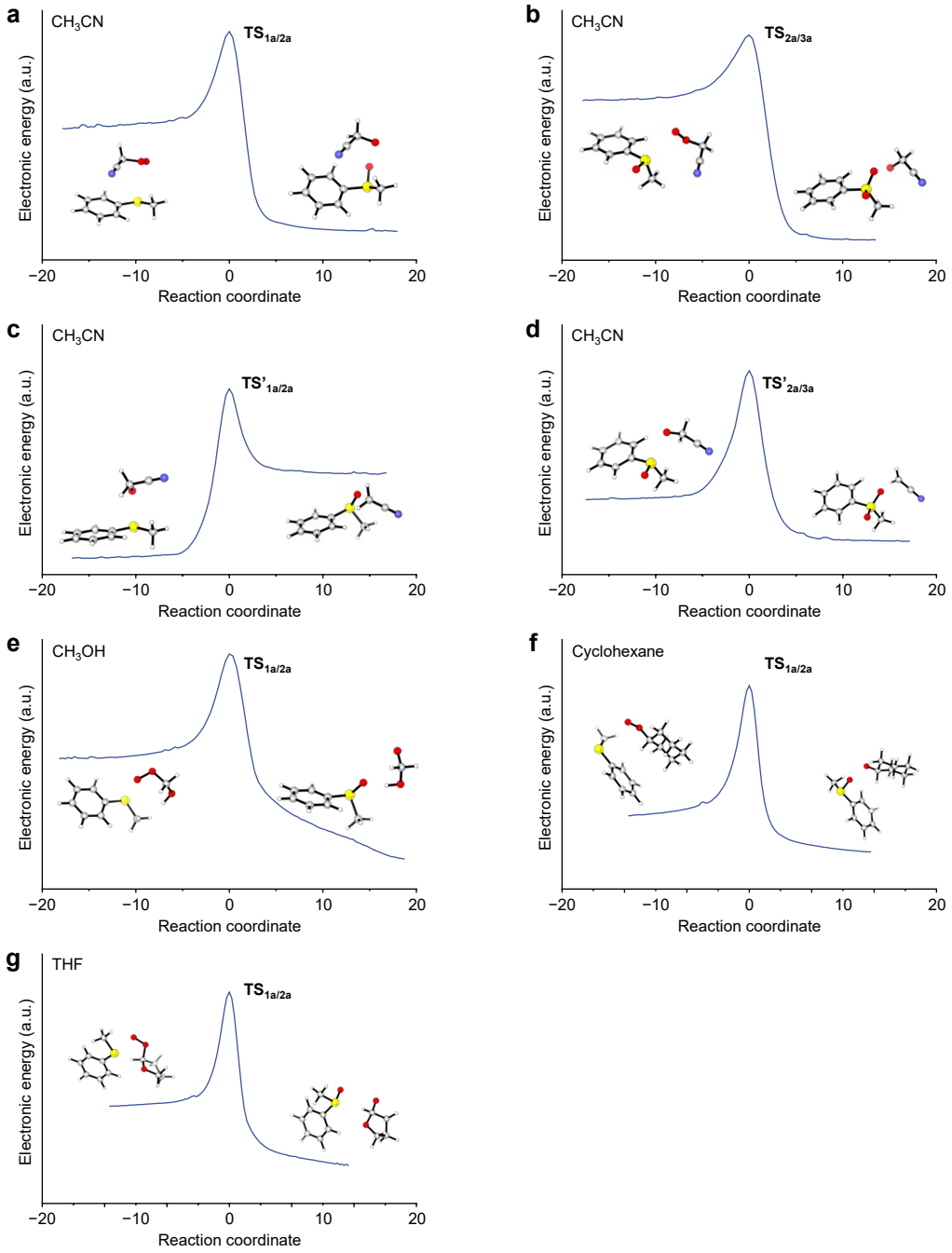


Fig. S9 The intrinsic reaction coordinate of (a) $\mathbf{TS_{1a/2a}}$, (b) $\mathbf{TS_{2a/3a}}$, (c) $\mathbf{TS'_{1a/2a}}$, (d) $\mathbf{TS'_{2a/3a}}$ in Fig. 4b, and the intrinsic reaction coordinate of $\mathbf{TS_{1a/2a}}$ in (e) CH_3OH, (f) cyclohexane, (g) THF in Fig. 5a.

5.4 Distortion-interaction analysis

Distortion-interaction analysis was performed on transition states. Each transition state structure was separated into two fragments according to the reactants, followed by the calculation of single-point energies. For each fragment, the distortion energy refers to the electronic energy change of the fragment from the equilibrium geometry to the transition state geometry. The total distortion energy of both two fragments is denoted as $\Delta E^{\neq}_{dist}$, and the distortion energies of **1a**, **2a**, ·$OOCH_2CN$, ·OCH_2CN, ·$OOCH_2OH$, ·OOCy and ·OOTHF are denoted as $\Delta E^{\neq}_{dist,1a}$, $\Delta E^{\neq}_{dist,2a}$, $\Delta E^{\neq}_{dist,\cdot OOCH_2CN}$, $\Delta E^{\neq}_{dist,\cdot OCH_2CN}$, $\Delta E^{\neq}_{dist,\cdot OOCH_2OH}$, $\Delta E^{\neq}_{dist,\cdot OOCy}$ and $\Delta E^{\neq}_{dist,\cdot OOTHF}$, respectively. The interaction energy ($\Delta E^{\neq}_{int}$) refers to the energy released when the two fragments form a complete transition state. The activation energy, $\Delta E^{\neq}$, is the sum of $\Delta E^{\neq}_{dist}$ and $\Delta E^{\neq}_{int}$. $\Delta E^{\neq}_{dist}$ and $\Delta E^{\neq}_{int}$ are calculated by the following formula:

$$\Delta E^{\neq}_{dist} = \Delta E^{\neq}_{dist,1} + \Delta E^{\neq}_{dist,2} = [E_1(\mathrm{TS}) - E_1(\mathrm{free})] + [E_2(\mathrm{TS}) - E_2(\mathrm{free})]$$

$$\Delta E^{\neq}_{int} = E_{total}(\mathrm{TS}) - E_1(\mathrm{TS}) - E_2(\mathrm{TS})$$

where $\Delta E^{\neq}_{dist,1}$ represents the distortion energy of fragment 1, $\Delta E^{\neq}_{dist,2}$ represents the distortion energy of fragment 2, E_1(TS) represents the electronic energy of fragment 1 in the transition state, E_2(TS) represents the electronic energy of fragment 2 in the transition state, E_1(free) represents the electronic energy of fragment 1 in the equilibrium geometry, E_2(free) represents the electronic energy of fragment 2 in the equilibrium geometry, and E_{total}(TS) represents the electronic energy of the transition state.

Table S8 Electronic energies (in Hartree) of transition states and their fragments calculated at the B3LYP-D3/6-311+G(d,p)/SMD level of theory[a]

Structure	Solvent	E_{total}(TS)	E_1(TS)	E_2(TS)	E_1(free)	E_2(free)
TS$_{1a/2a}$	CH_3CN	−952.4250269	−669.8900135	−282.5109065	−669.8908703	−282.5528384
TS$_{2a/3a}$	CH_3CN	−1027.629723	−745.0961987	−282.5192667	−745.0992411	−282.5528384
TS'$_{1a/2a}$	CH_3CN	−877.2204265	−669.8891680	−207.3206557	−669.8908703	−207.3678981
TS'$_{2a/3a}$	CH_3CN	−952.4346035	−745.0963317	−207.3308854	−745.0992411	−207.3678981
TS$_{1a/2a}$	CH_3OH	−935.4169493	−669.8885823	−265.5030638	−669.8892758	−265.5463318
TS$_{1a/2a}$	Cyclohexane	−1055.594718	−669.8866184	−385.6941520	−669.8878345	−385.7411525
TS$_{1a/2a}$	THF	−1052.172191	−669.8890719	−382.2691512	−669.8895635	−382.3182354

[a] Fragment 1 is related to sulfide or sulfoxide, and fragment 2 is related to solvent-derived radical.

6. NMR spectra

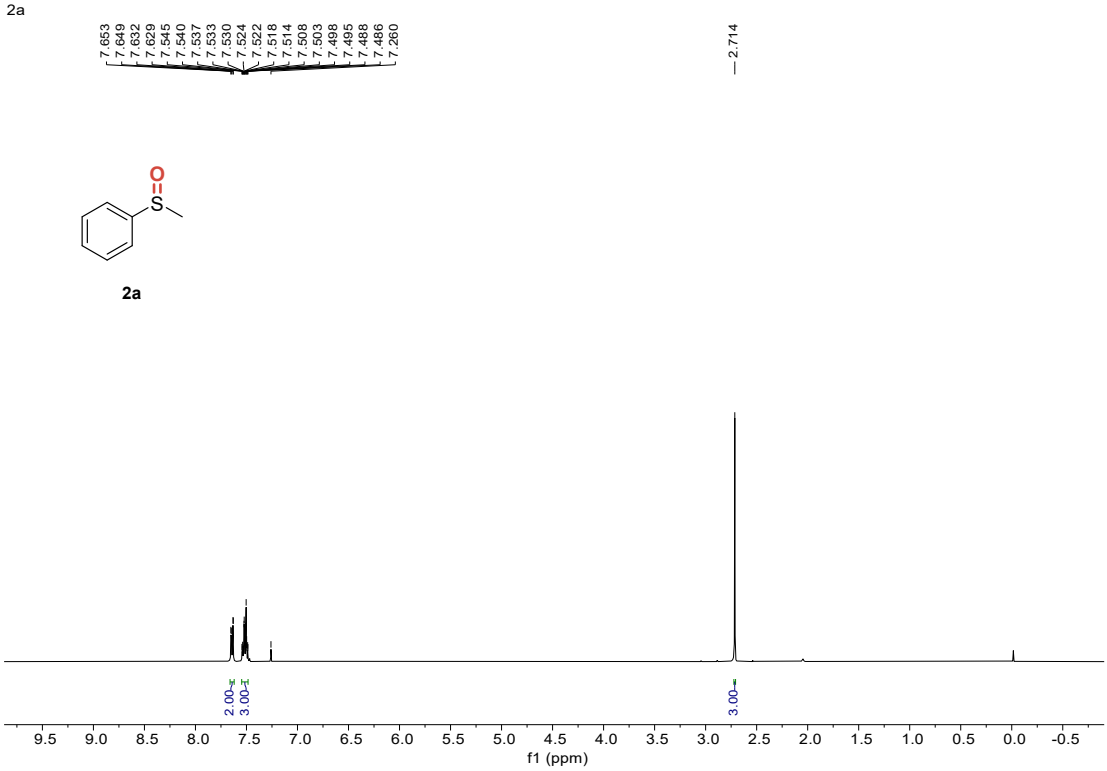


Fig. S10 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2a**.

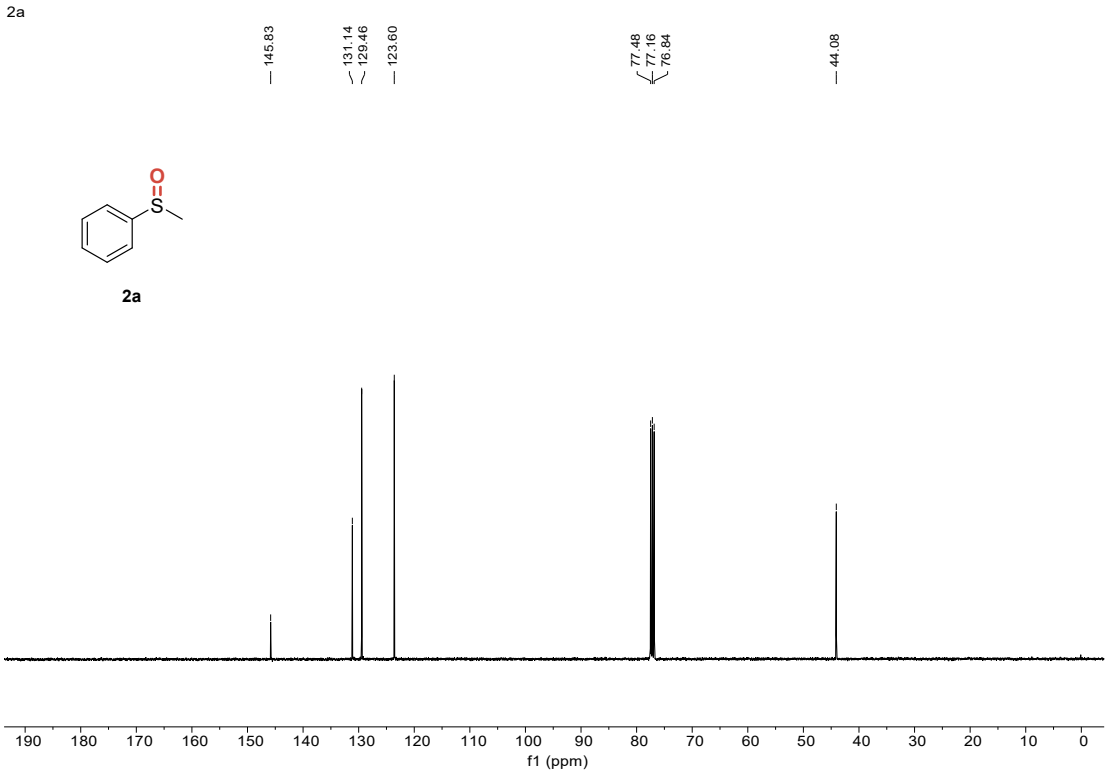


Fig. S11 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2a**.

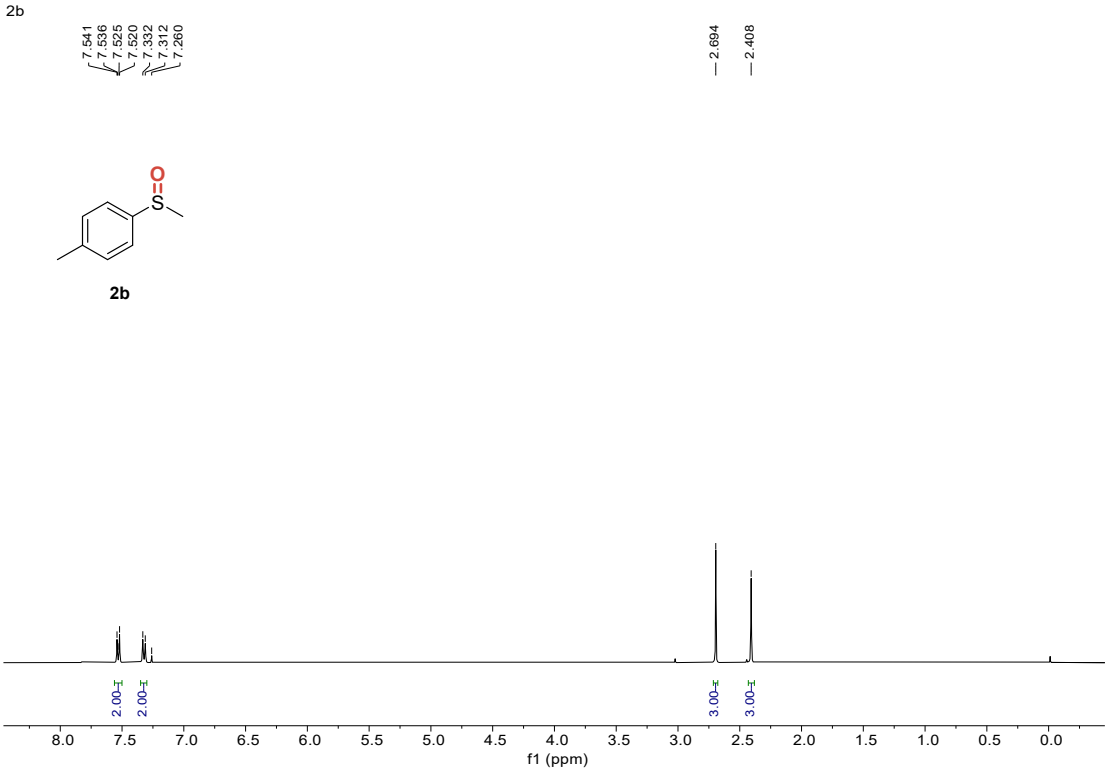


Fig. S12 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2b**.

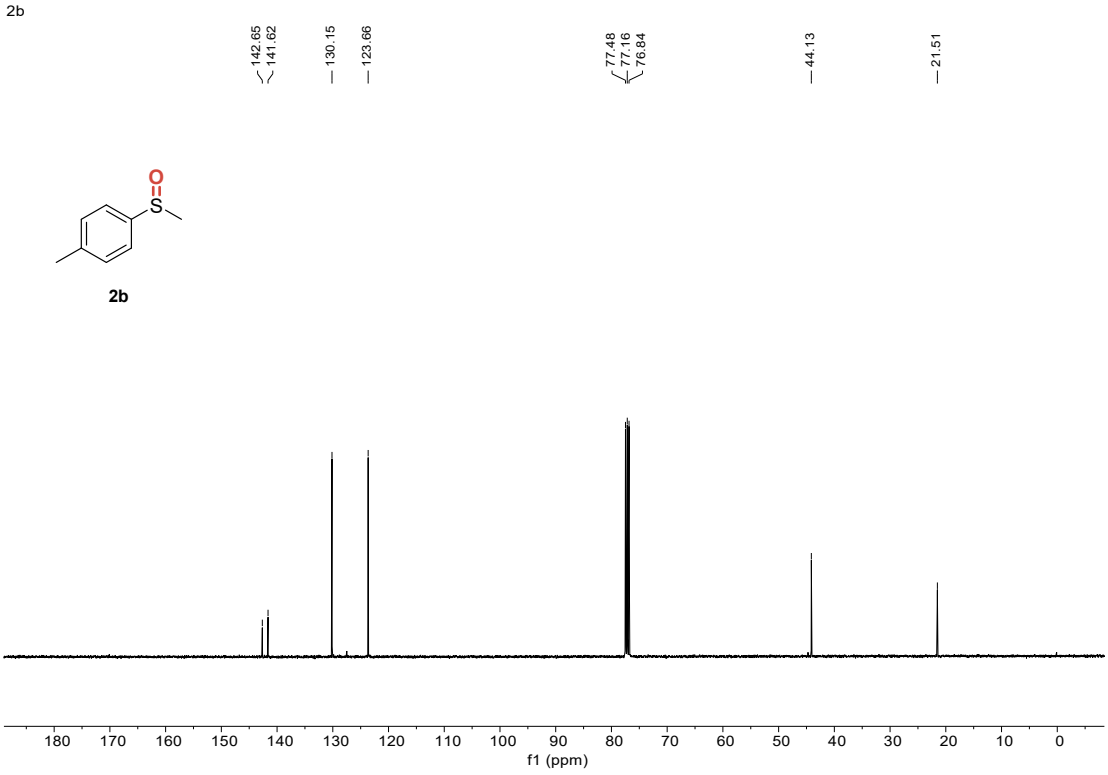


Fig. S13 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2b**.

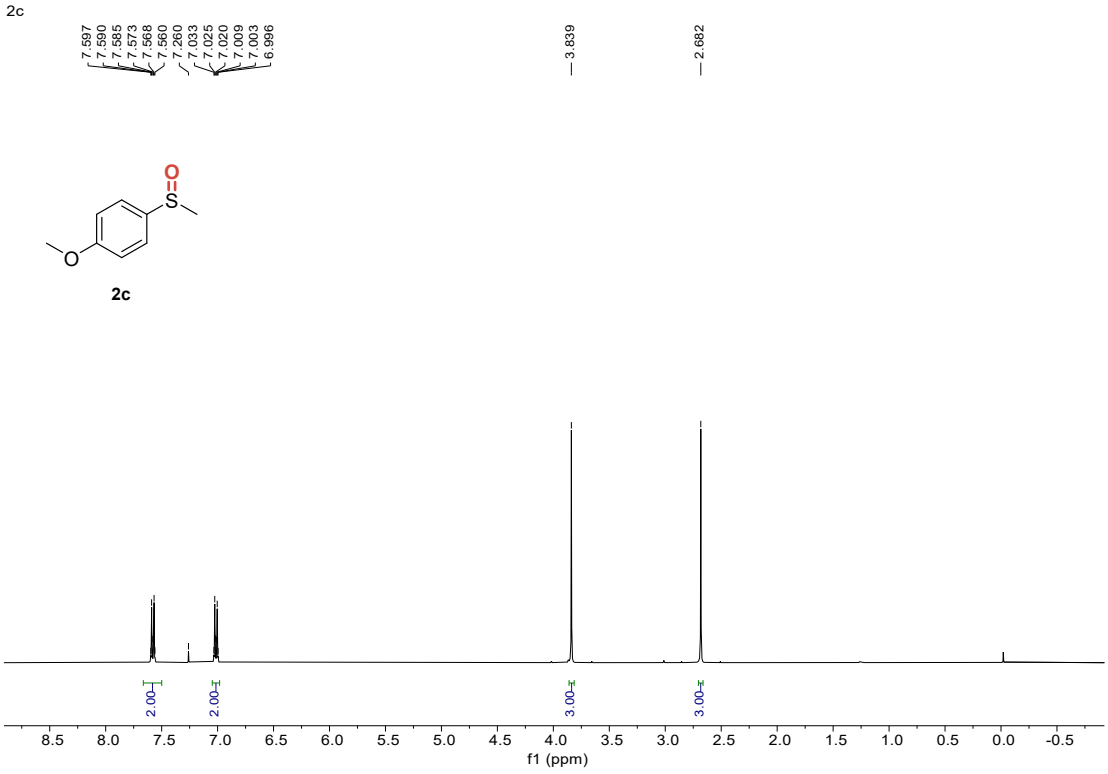


Fig. S14 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2c**.

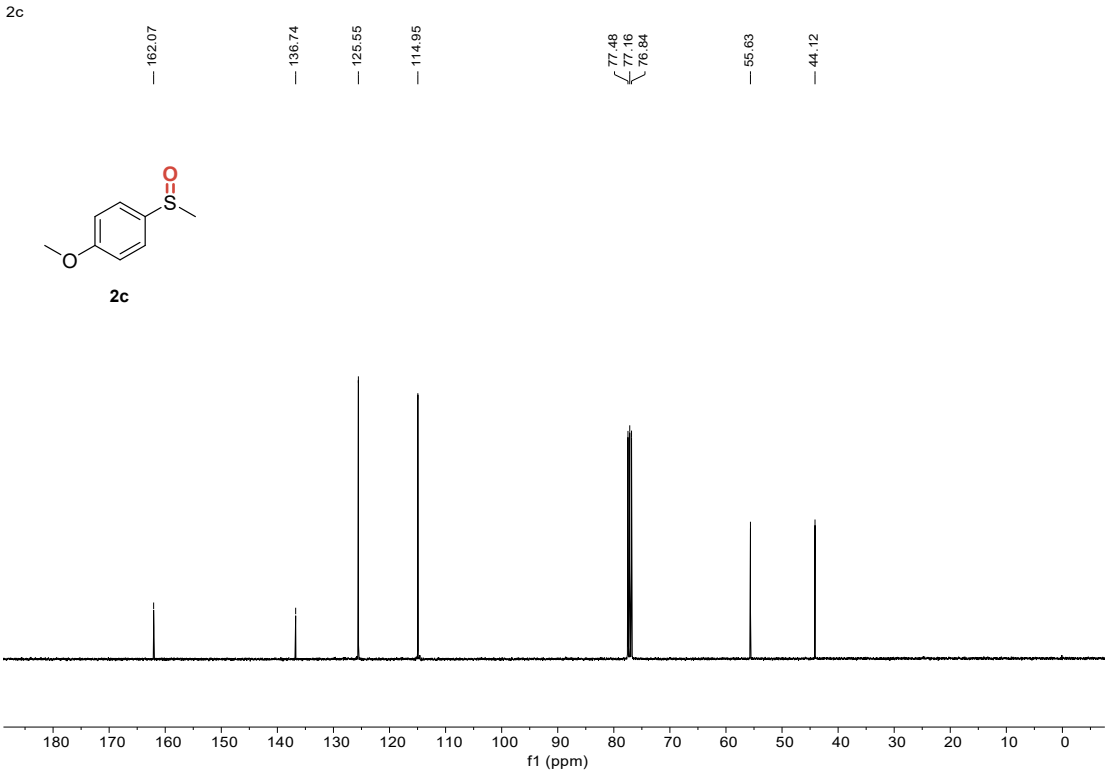


Fig. S15 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2c**.

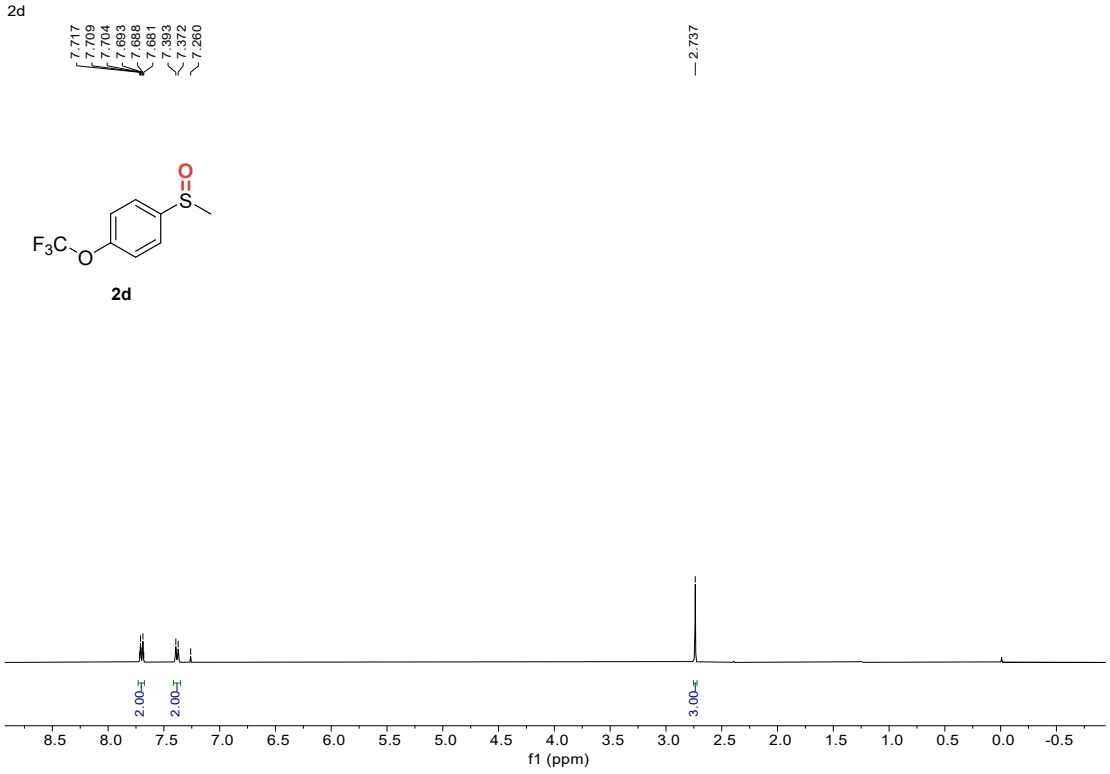


Fig. S16 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2d**.

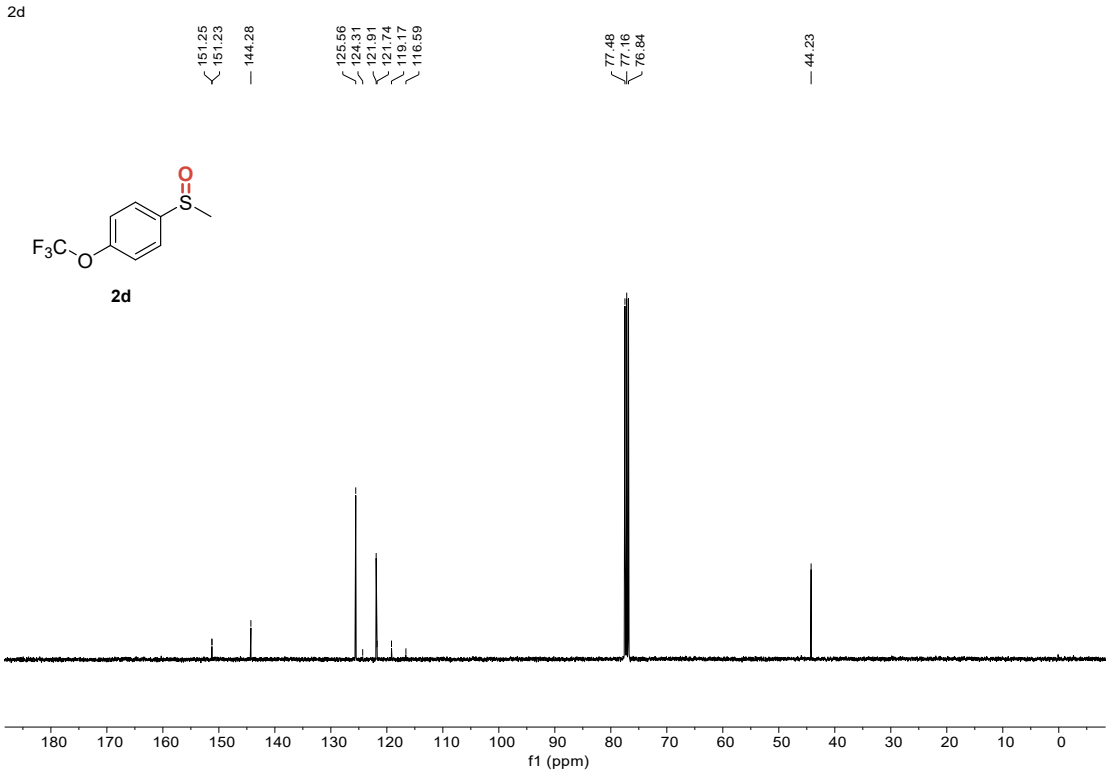


Fig. S17 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2d**.

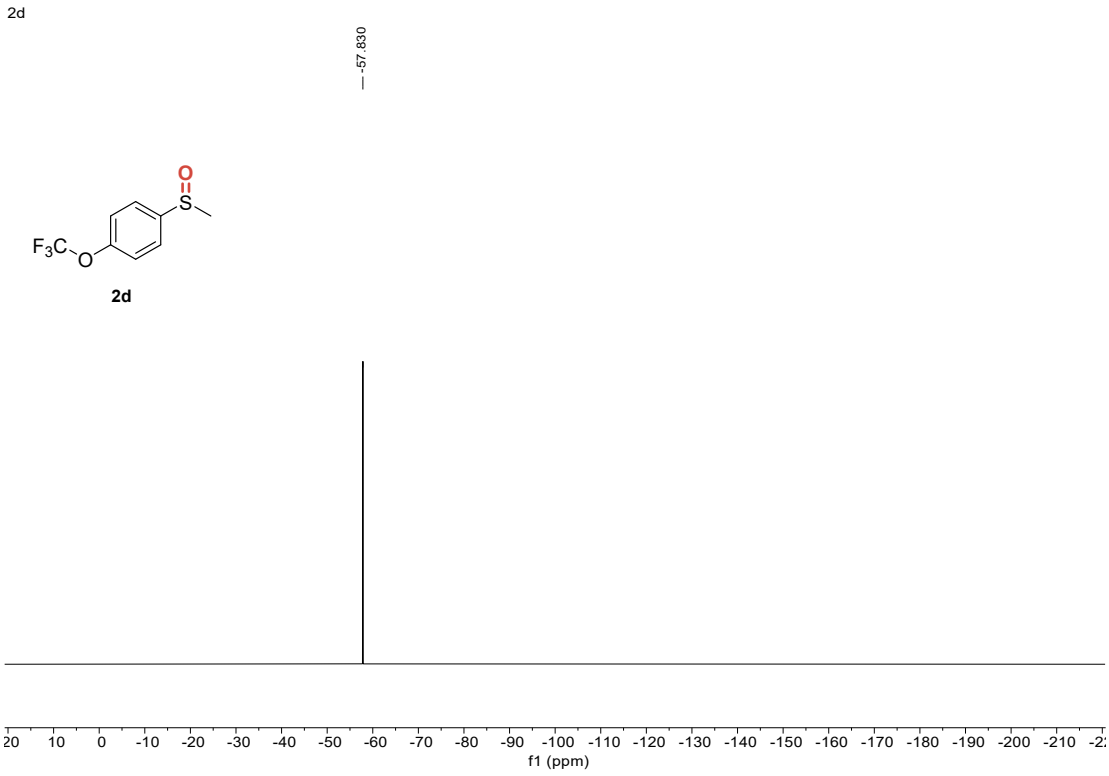


Fig. S18 ^{19}F NMR spectrum (471 MHz, $CDCl_3$) of **2d**.

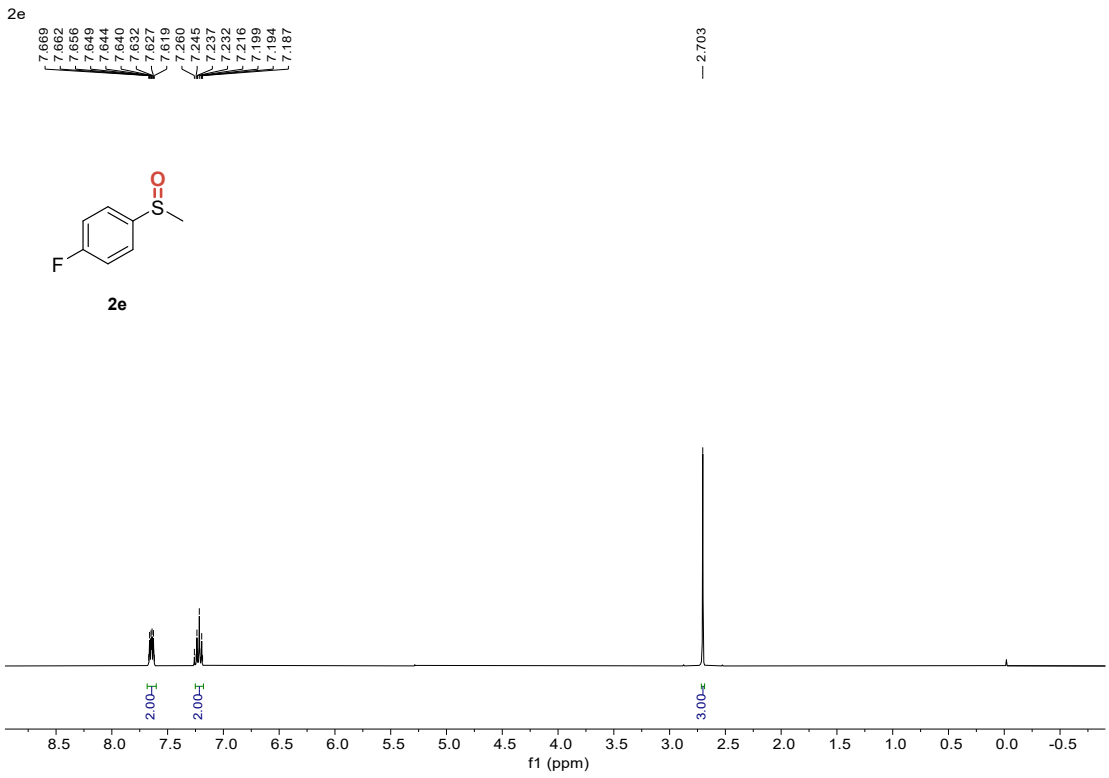


Fig. S19 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2e**.

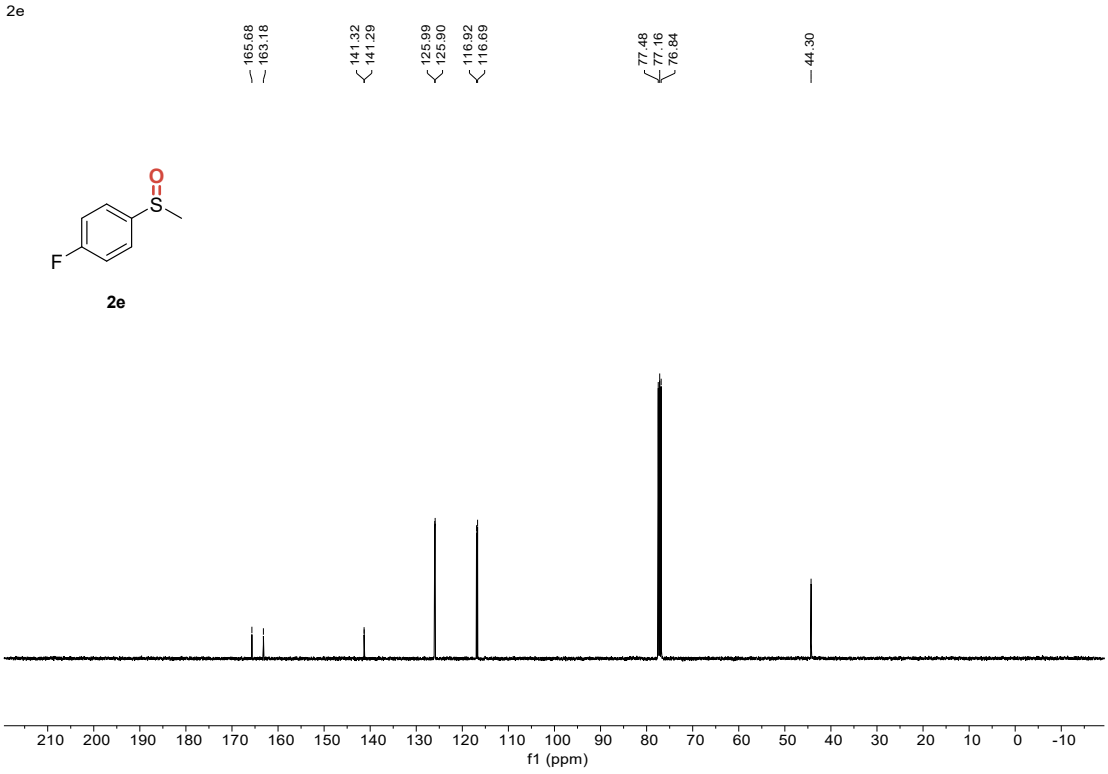


Fig. S20 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2e**.

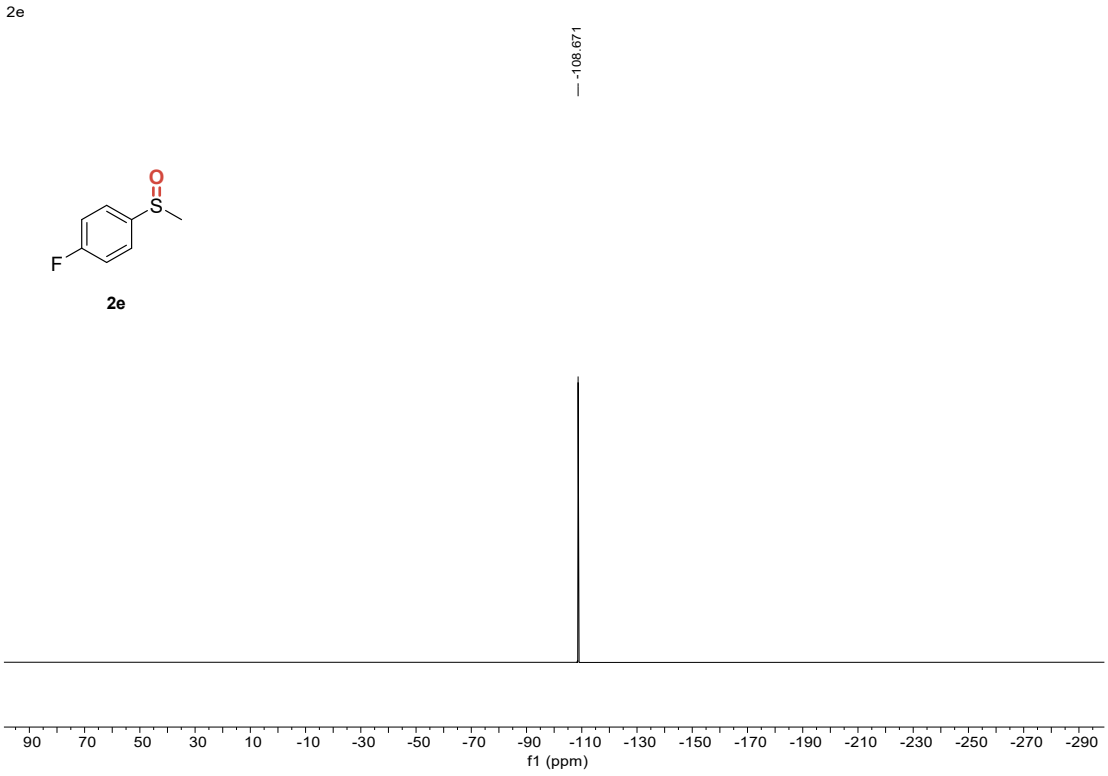


Fig. S21 ^{19}F NMR spectrum (471 MHz, $CDCl_3$) of **2e**.

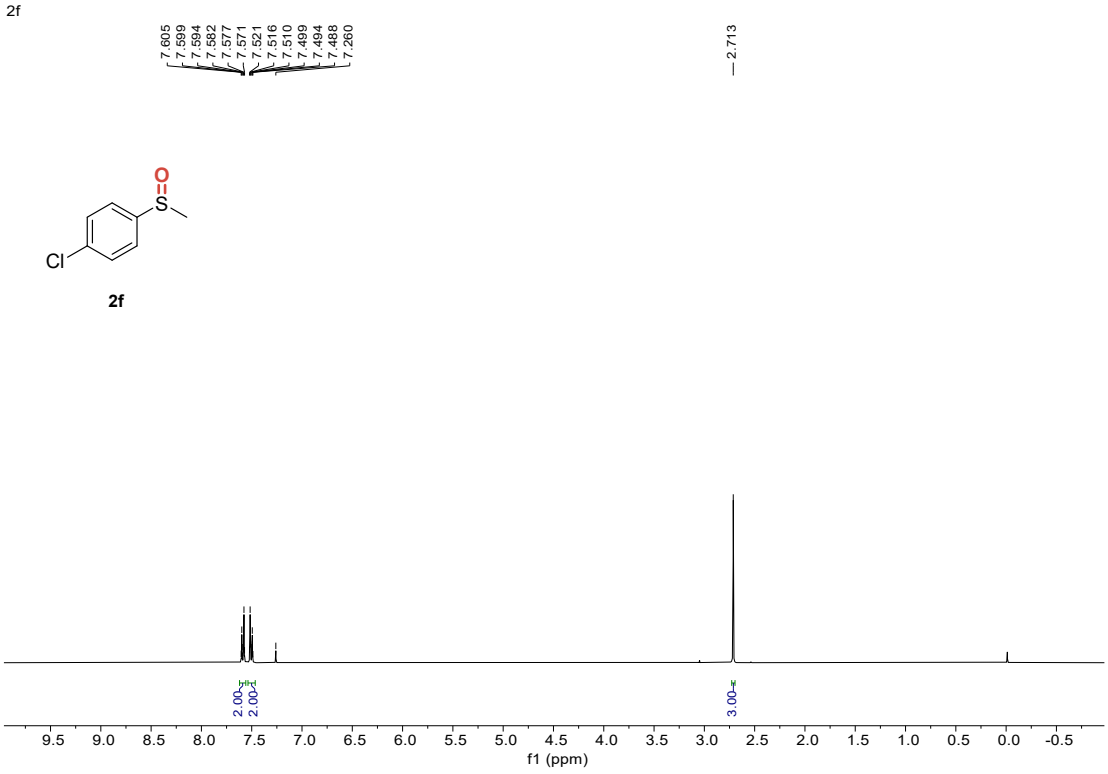


Fig. S22 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2f**.

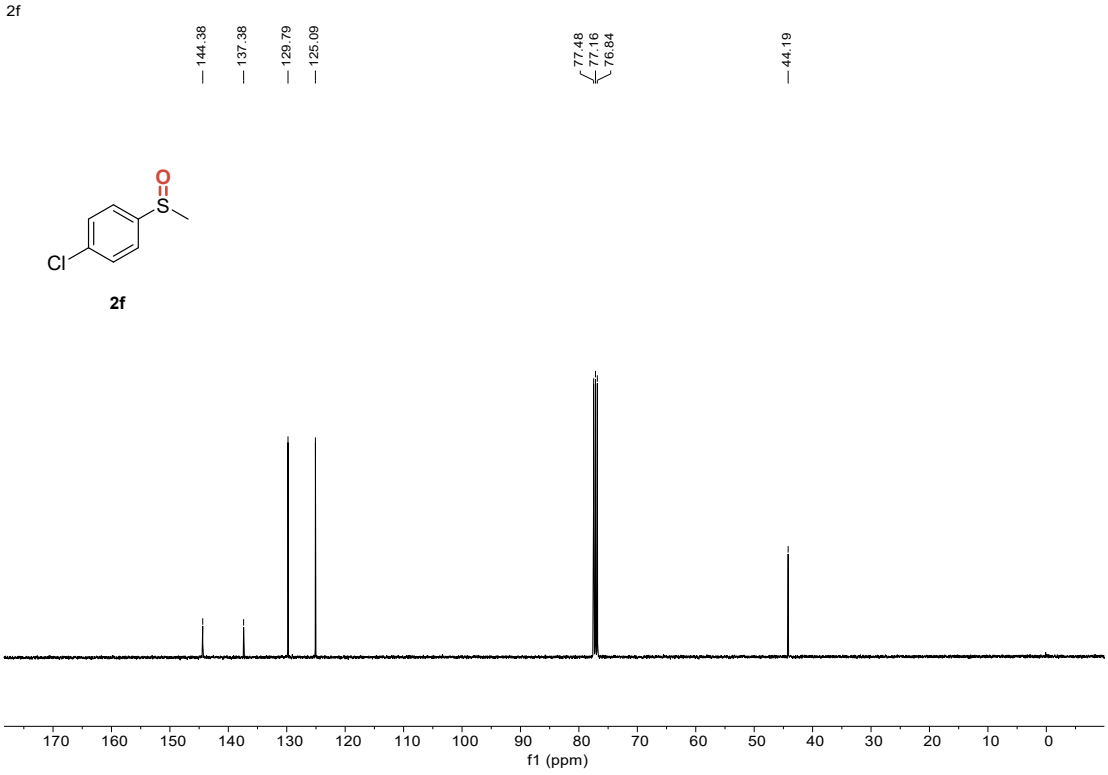


Fig. S23 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2f**.

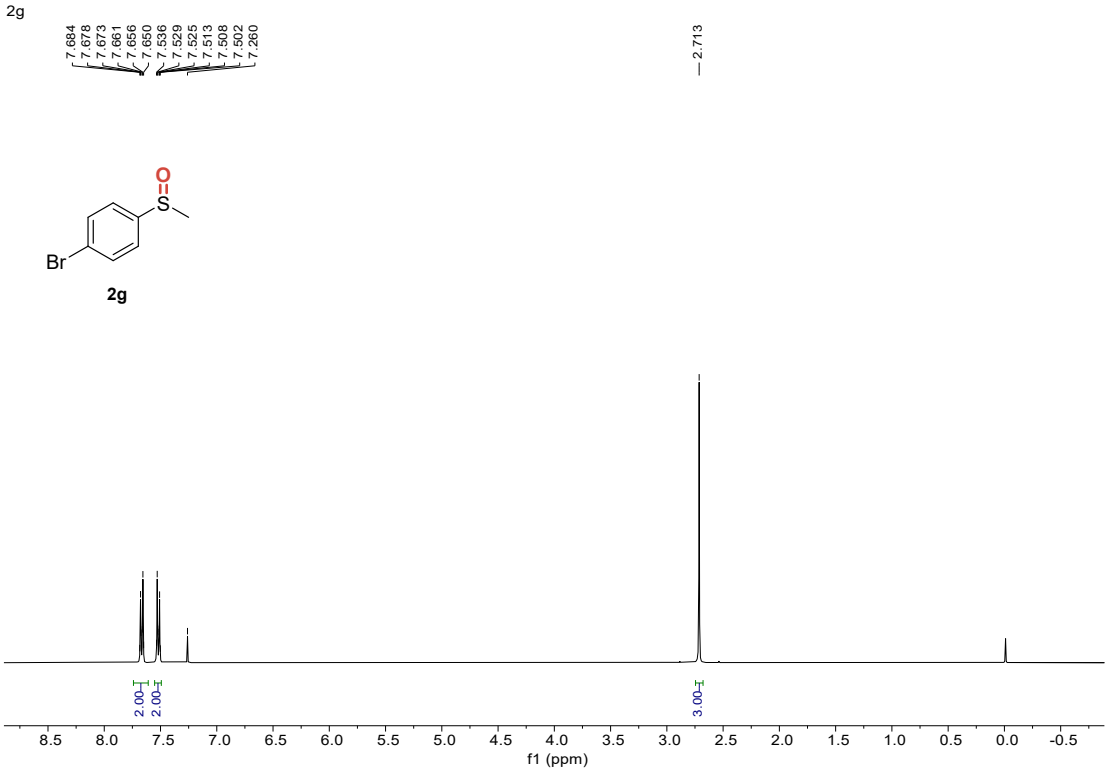


Fig. S24 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2g**.

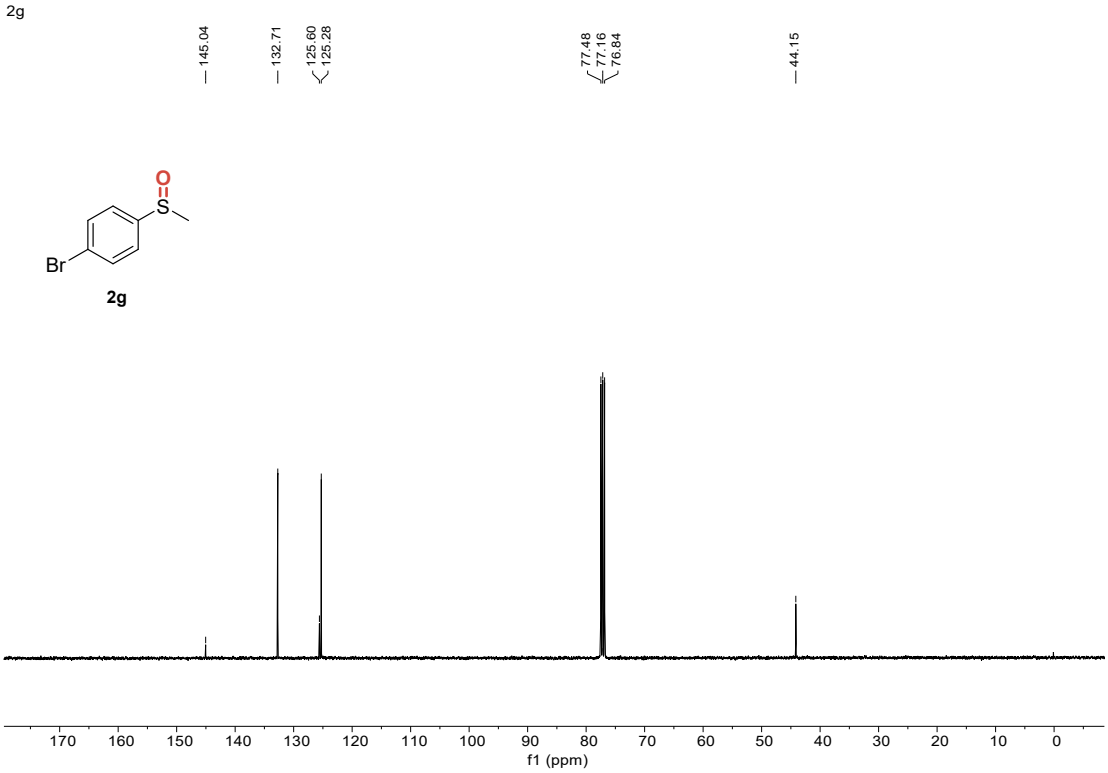


Fig. S25 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2g**.

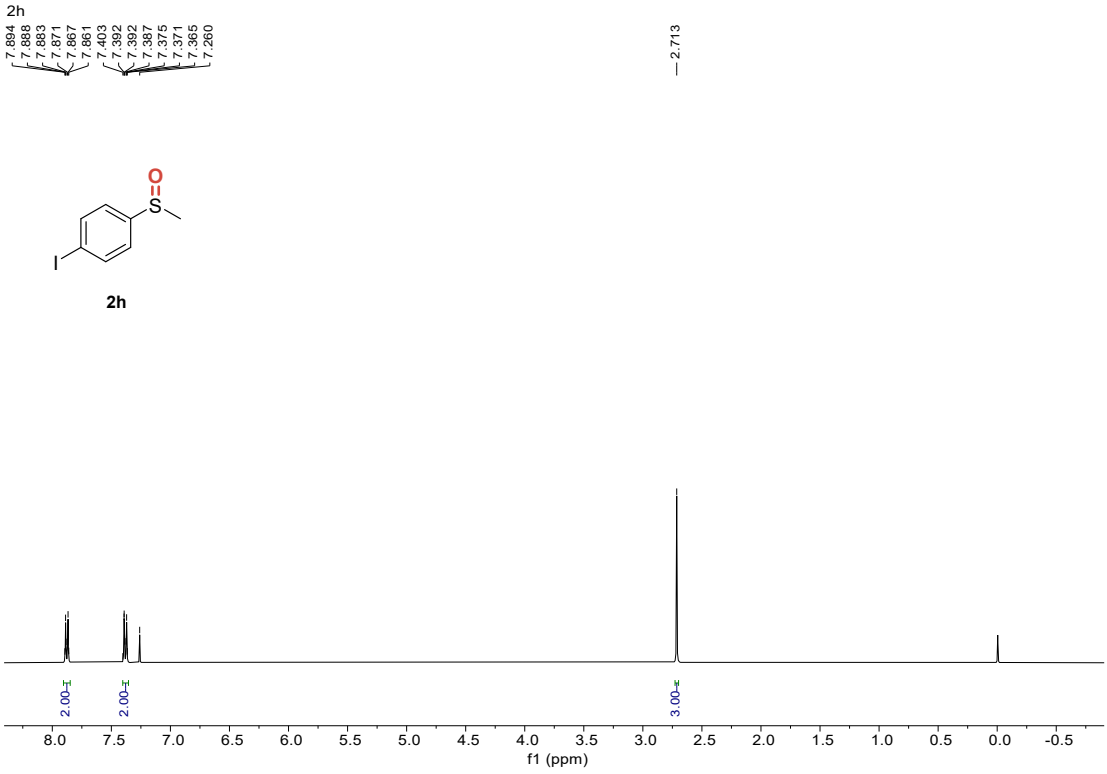


Fig. S26 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2h**.

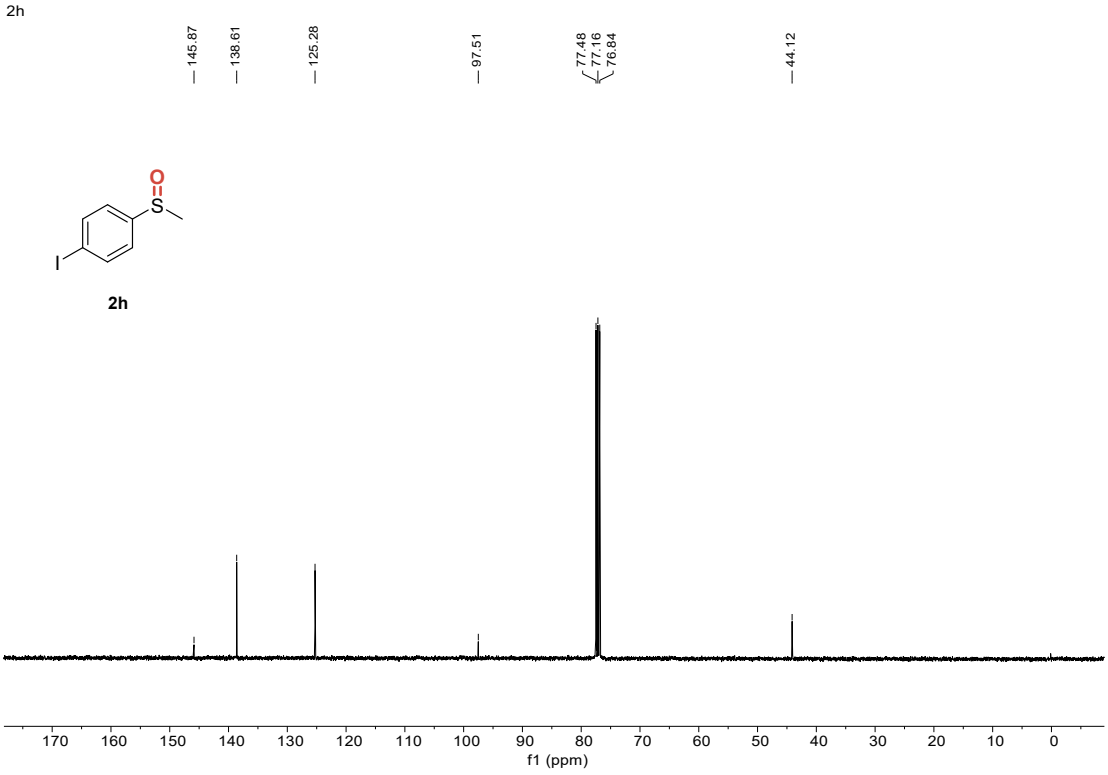


Fig. S27 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2h**.

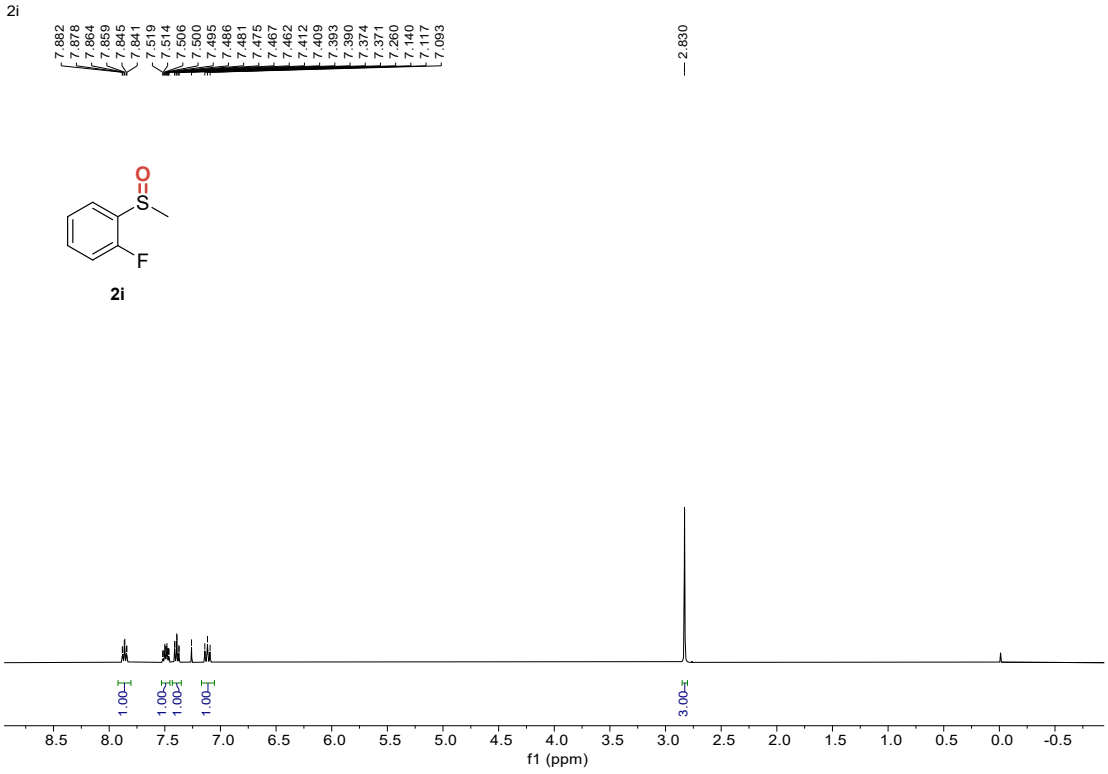


Fig. S28 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2i**.

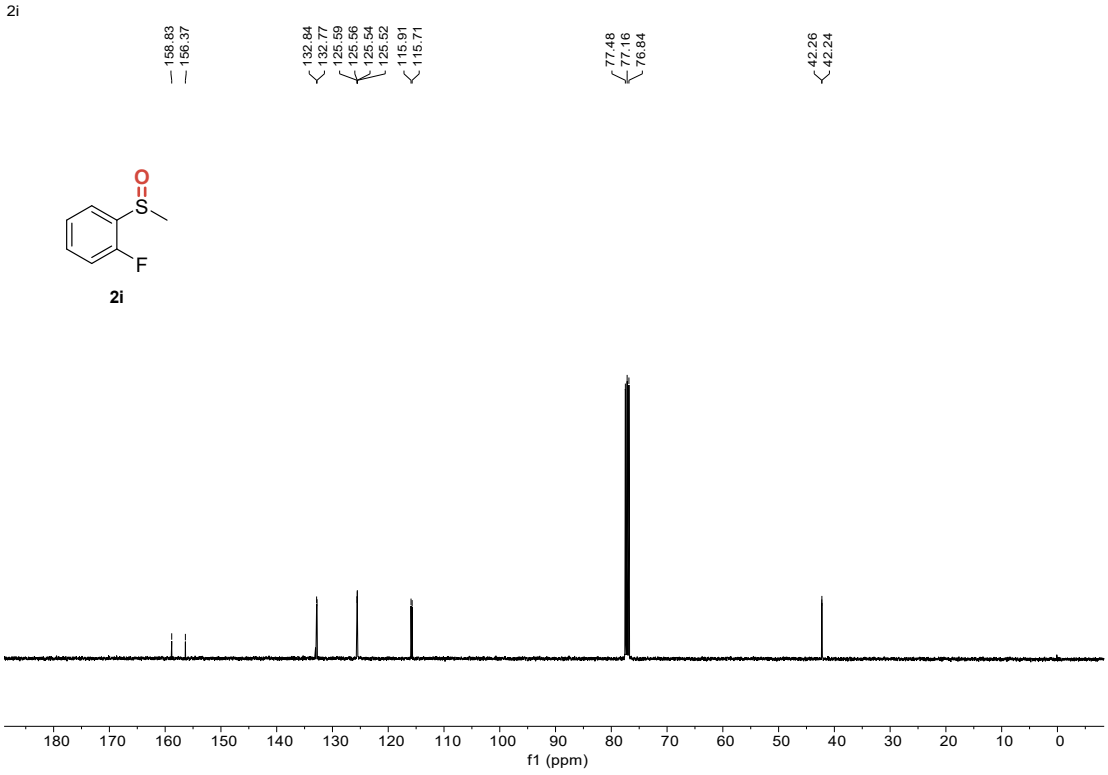


Fig. S29 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2i**.

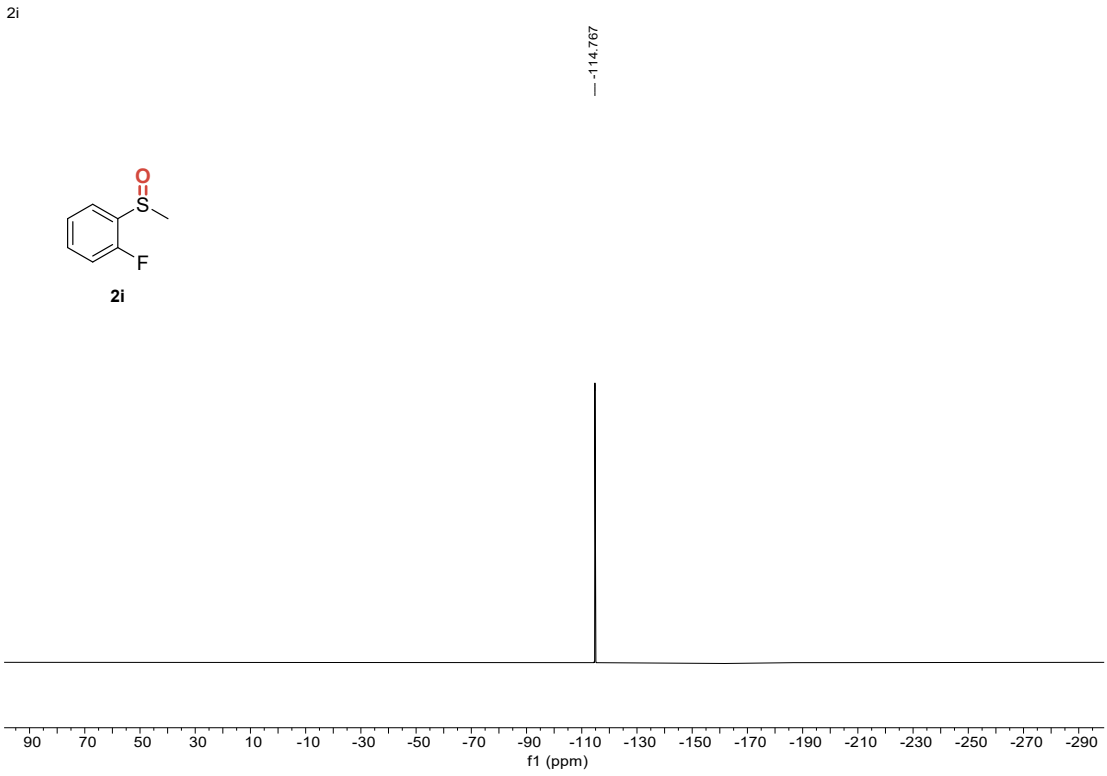


Fig. S30 ^{19}F NMR spectrum (471 MHz, $CDCl_3$) of **2i**.

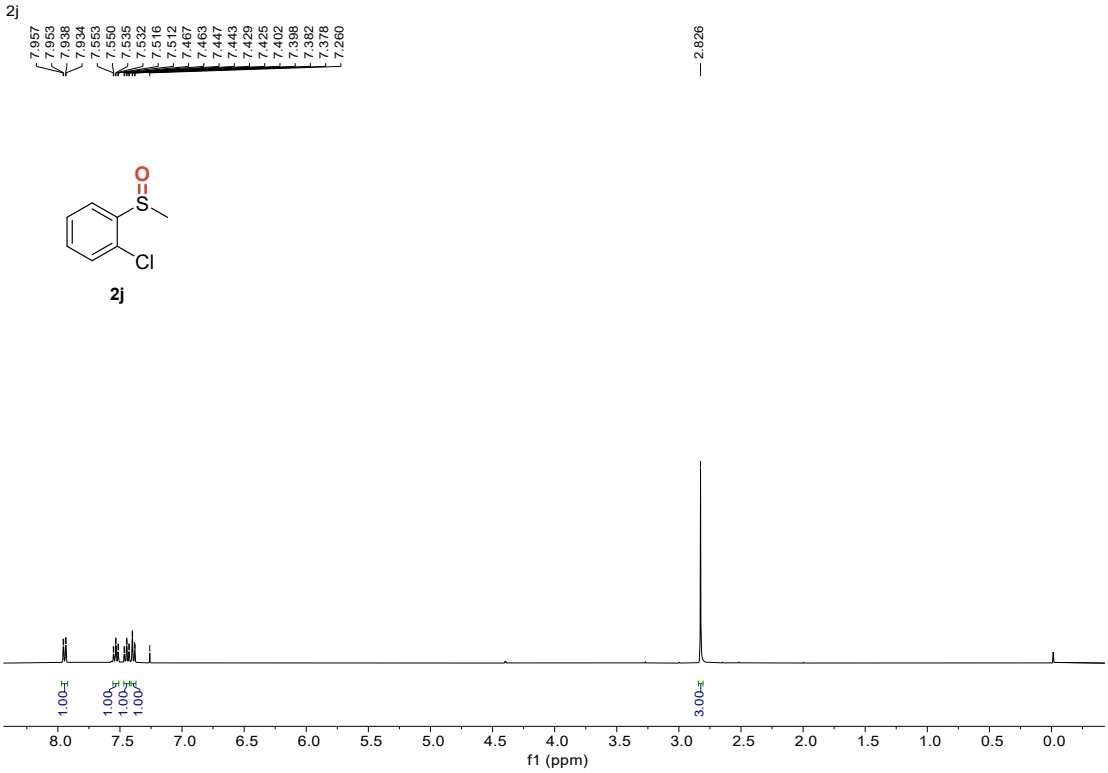


Fig. S31 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2j**.

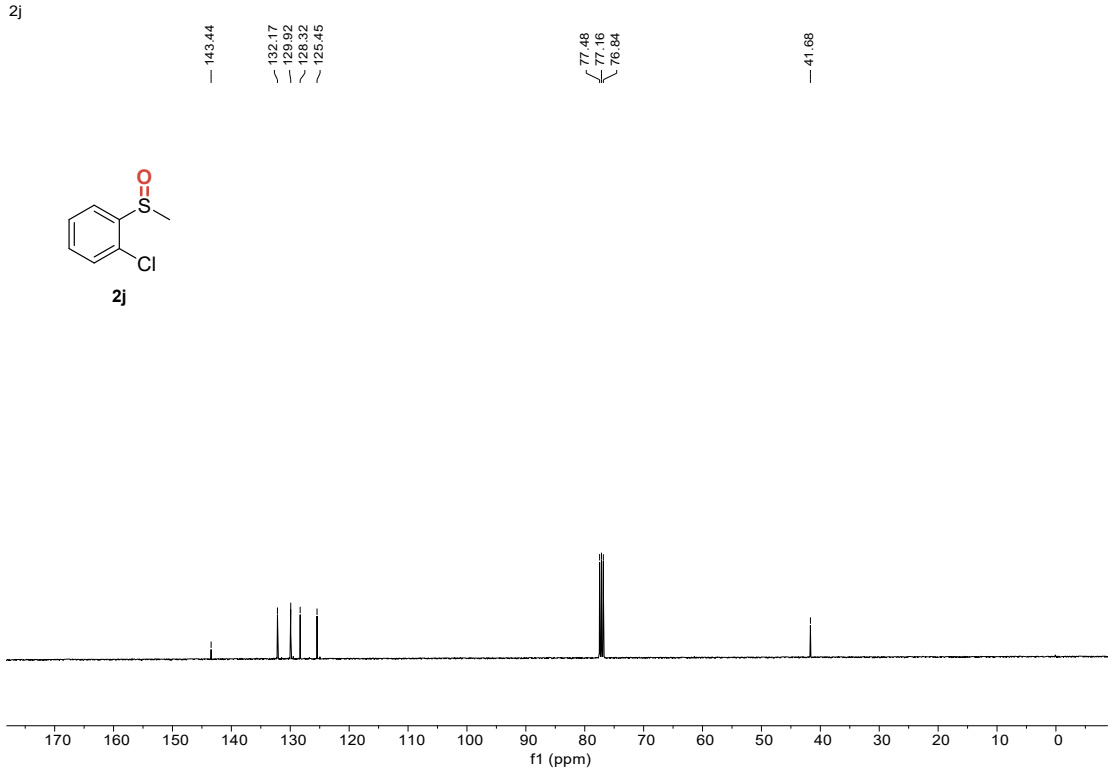


Fig. S32 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2j**.

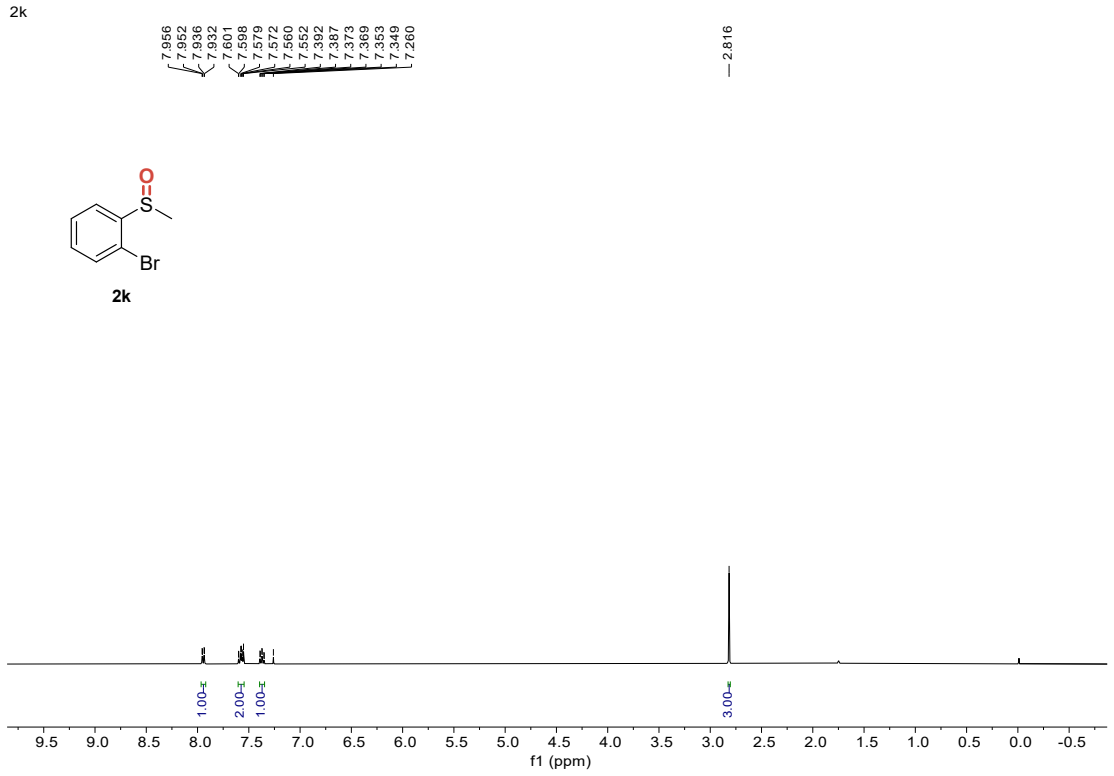


Fig. S33 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2k**.

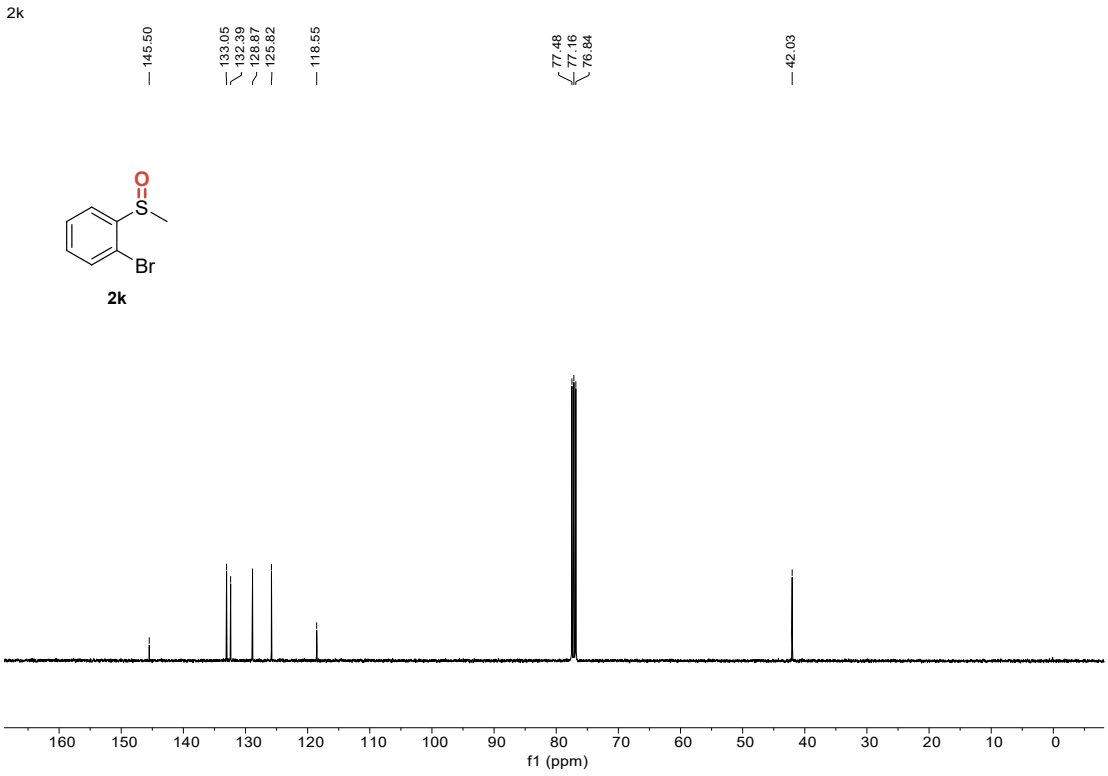


Fig. S34 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2k**.

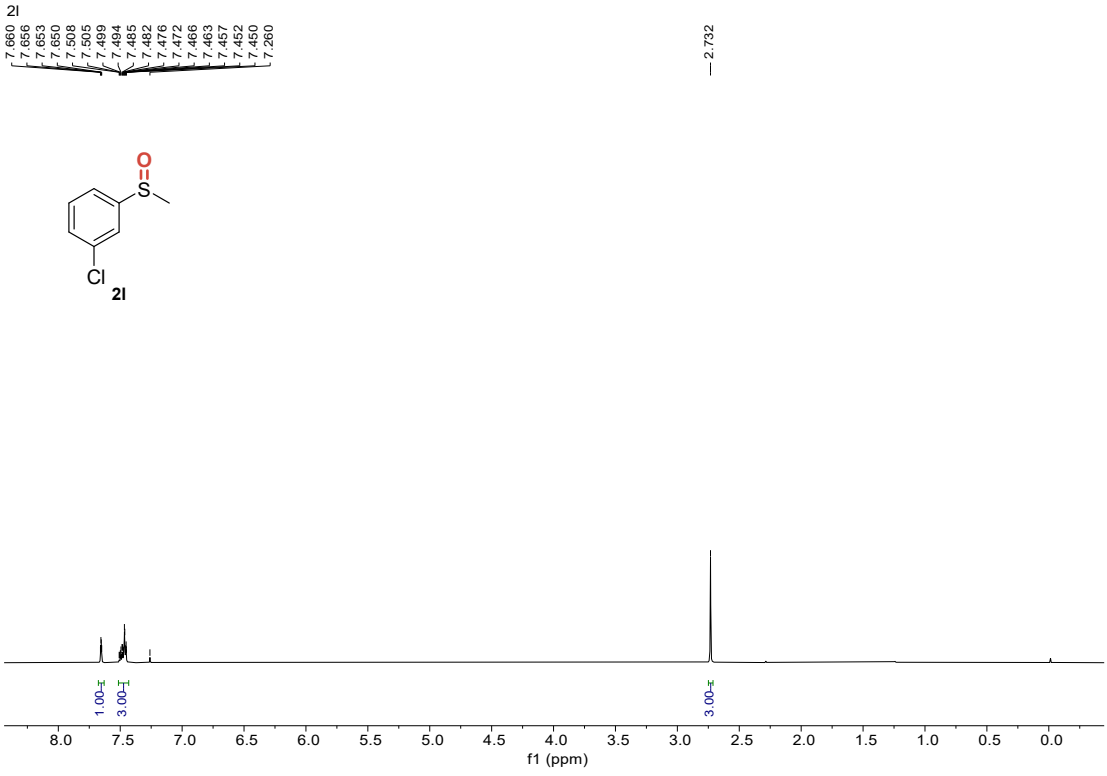


Fig. S35 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2l**.

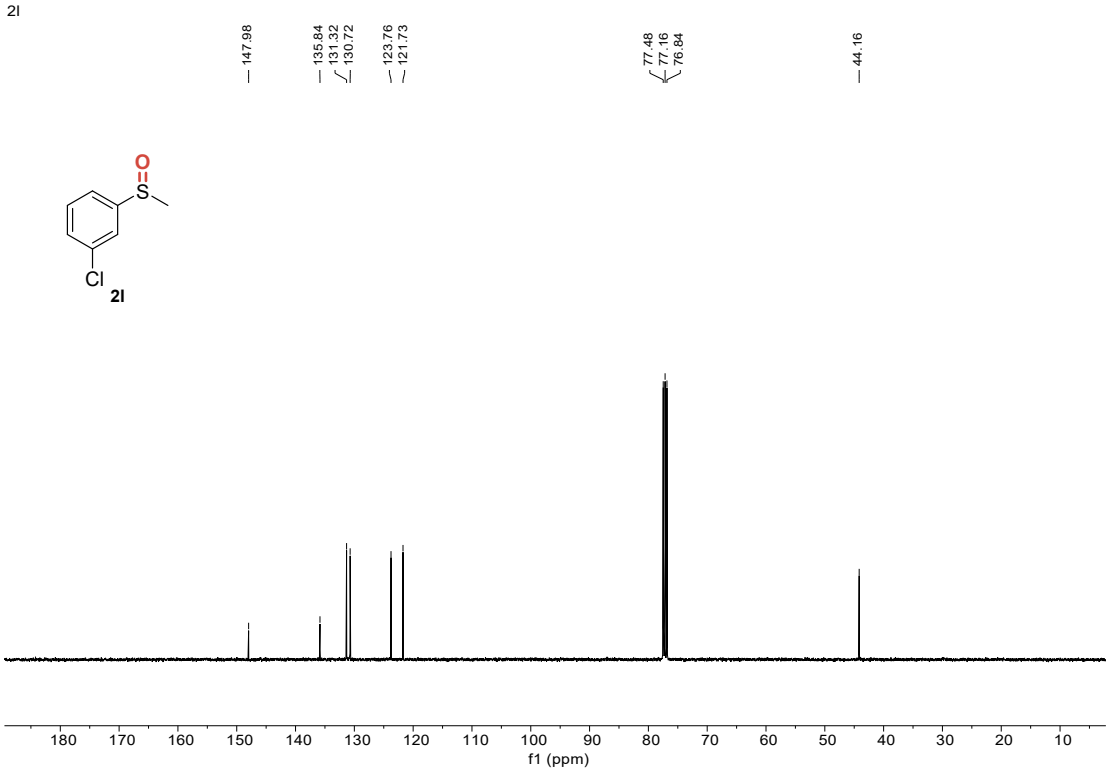


Fig. S36 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2l**.

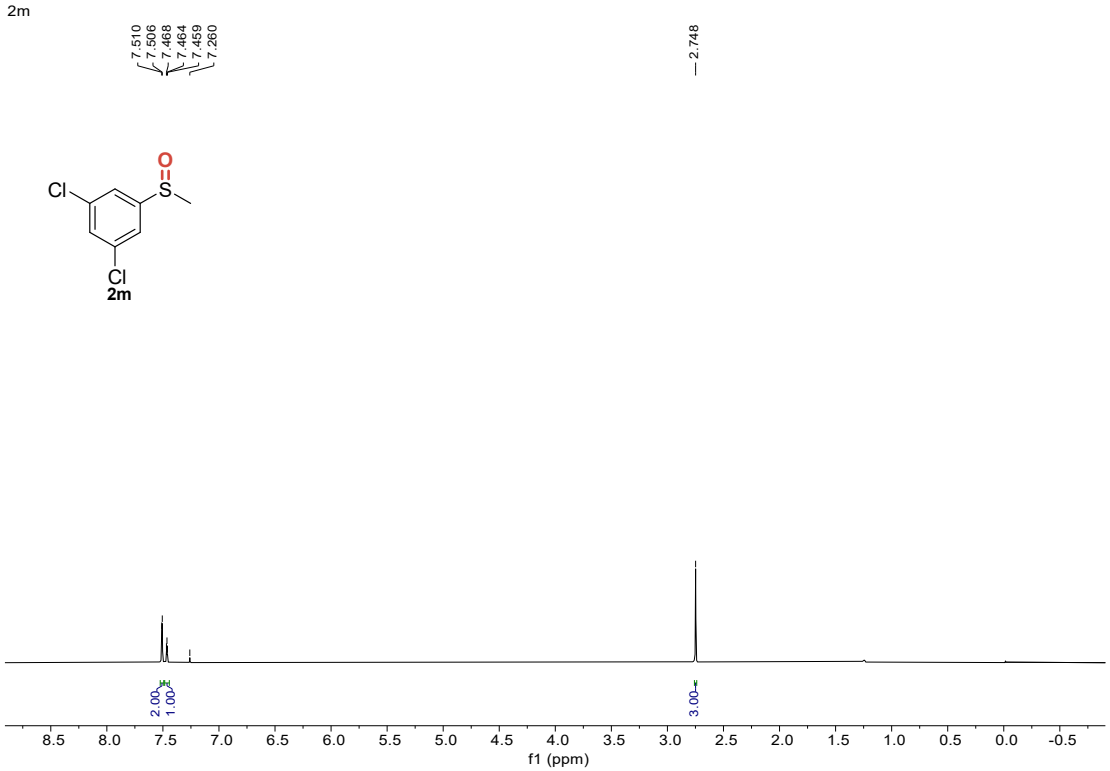


Fig. S37 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2m**.

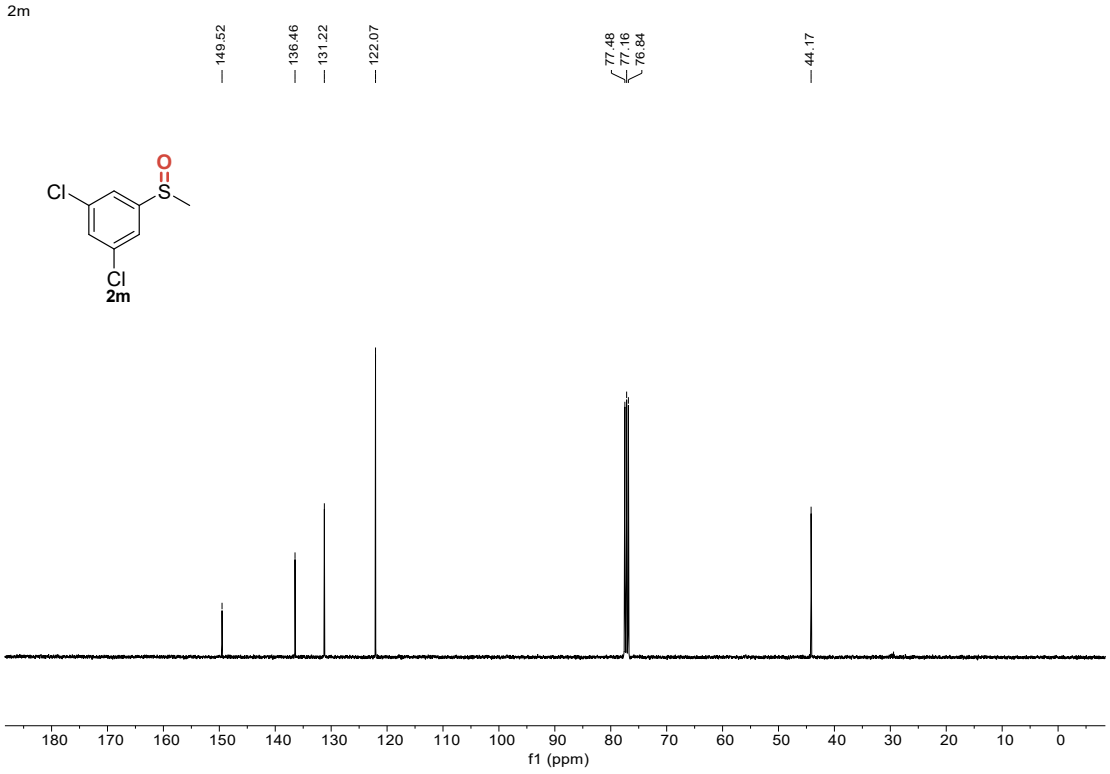


Fig. S38 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2m**.

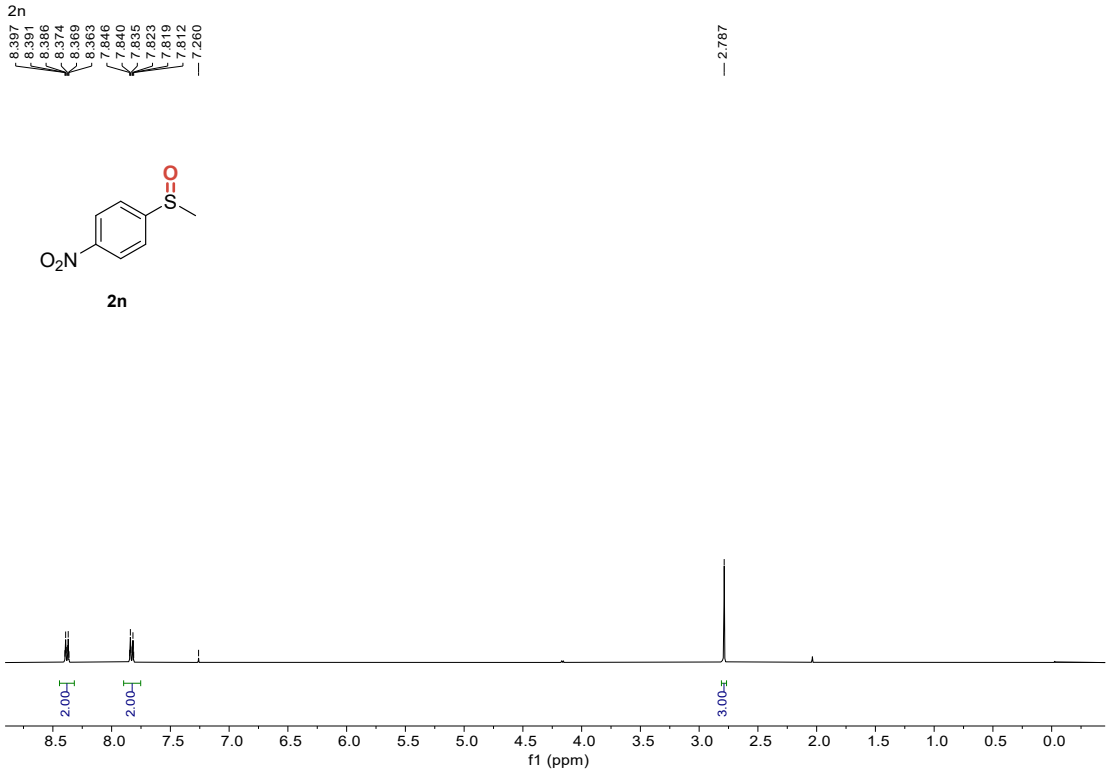


Fig. S39 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2n**.

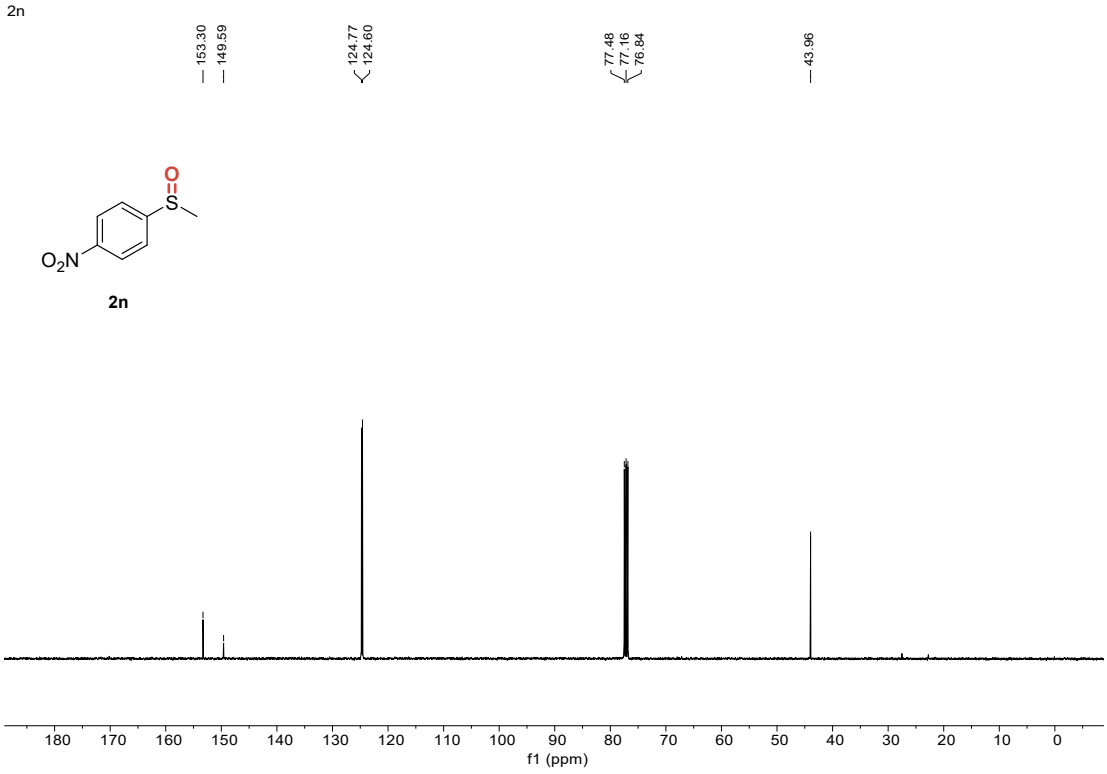


Fig. S40 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2n**.

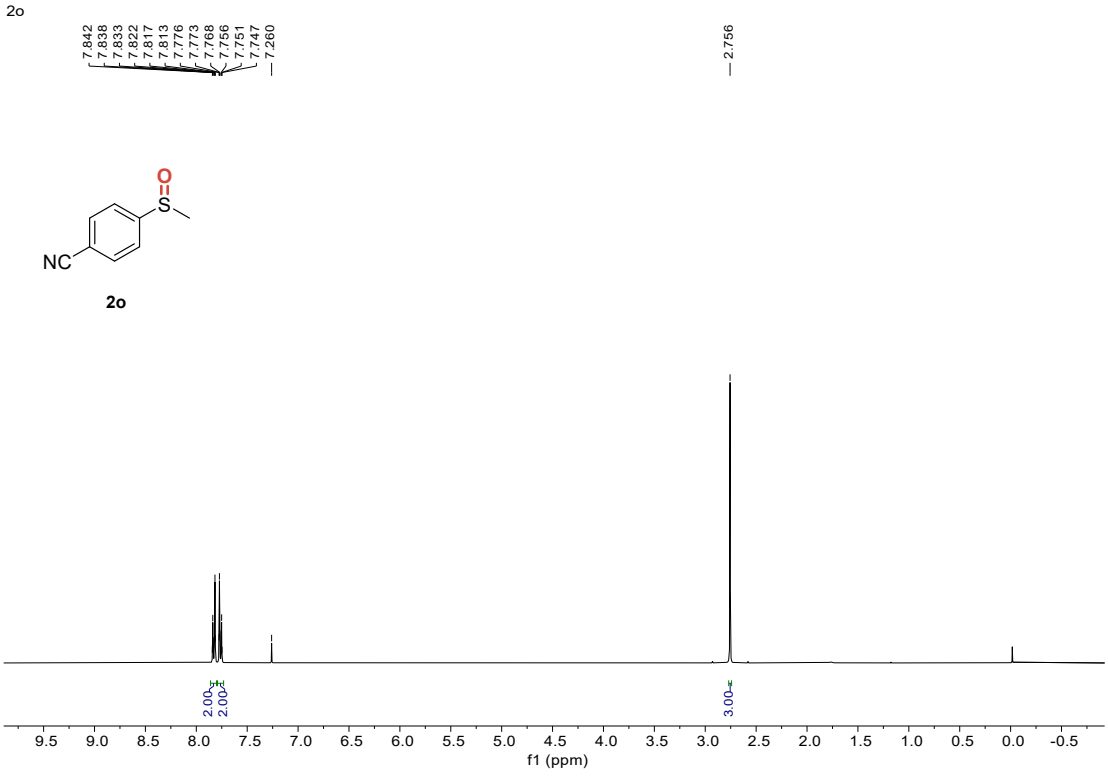


Fig. S41 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2o**.

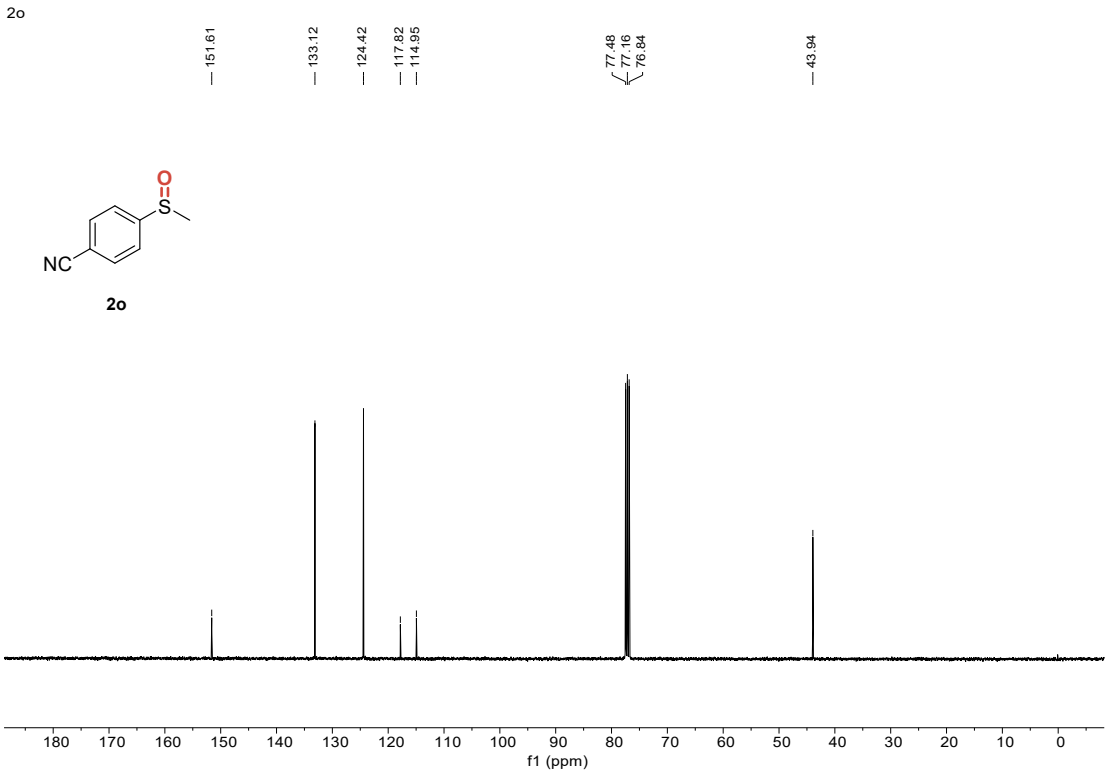


Fig. S42 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2o**.

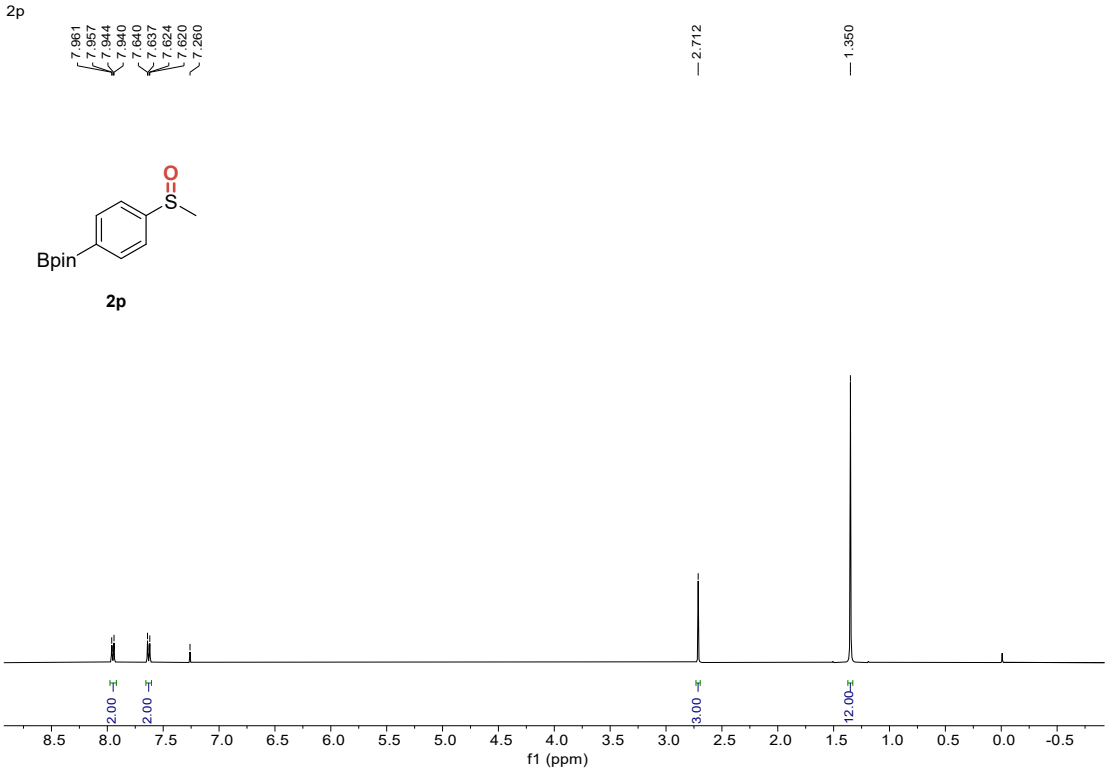


Fig. S43 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2p**.

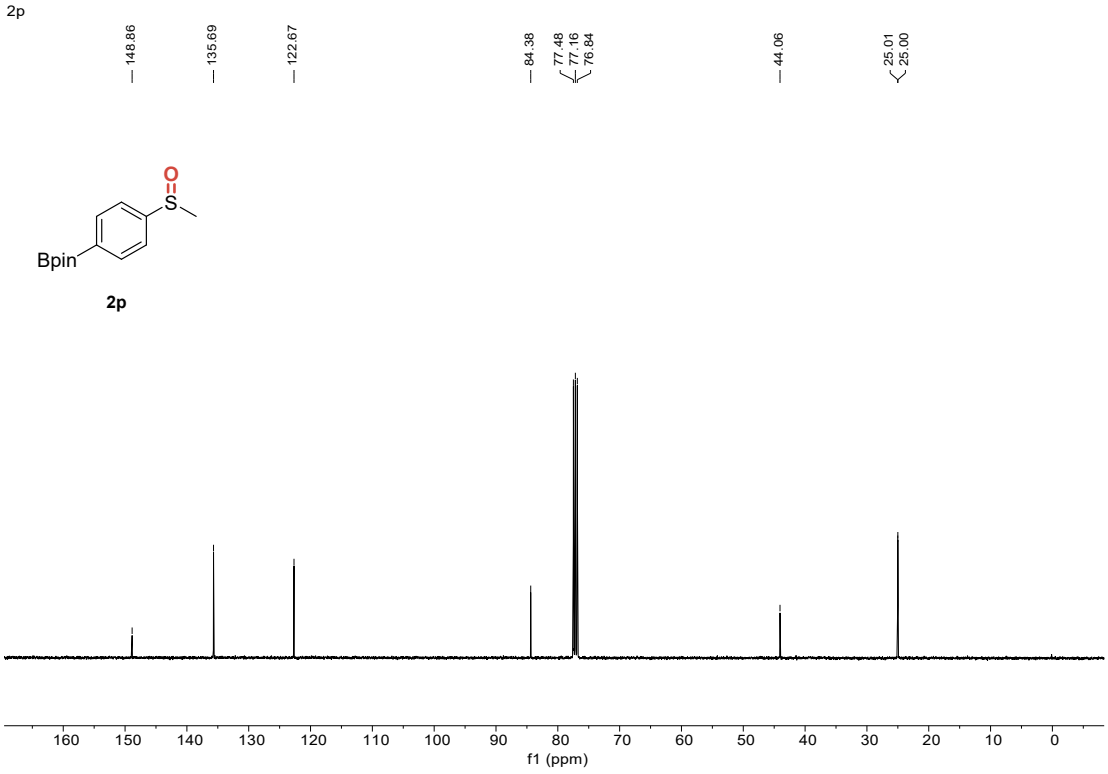


Fig. S44 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2p**.

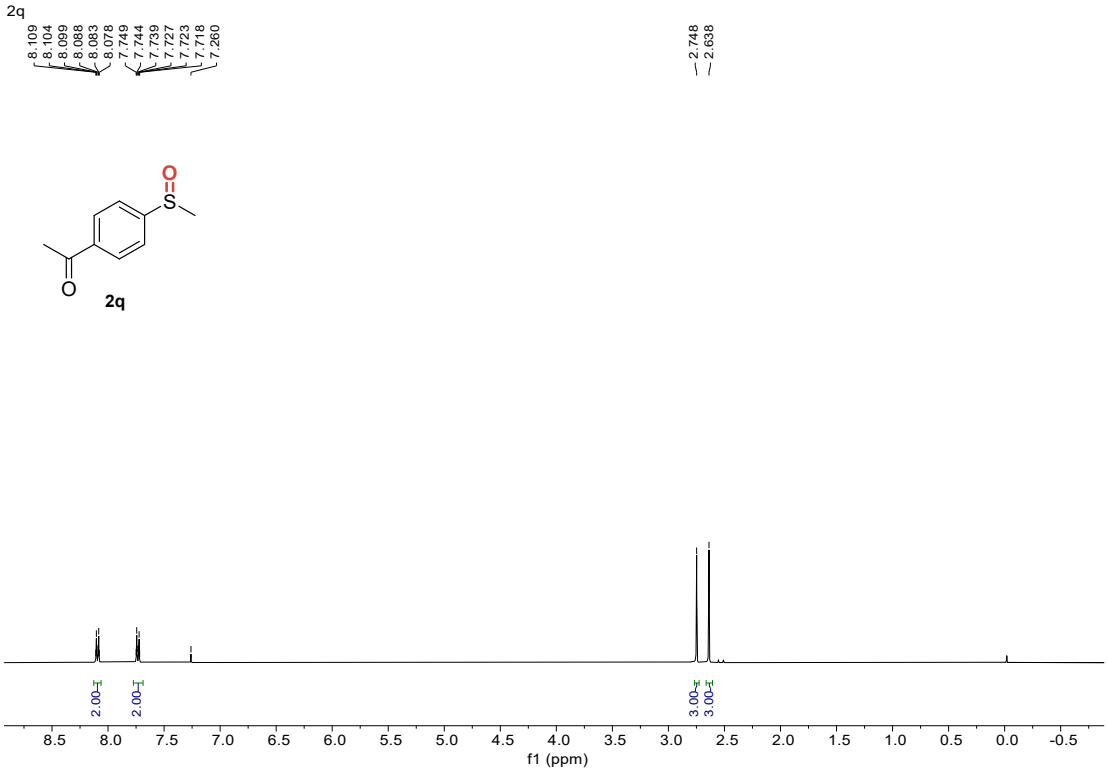


Fig. S45 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2q**.

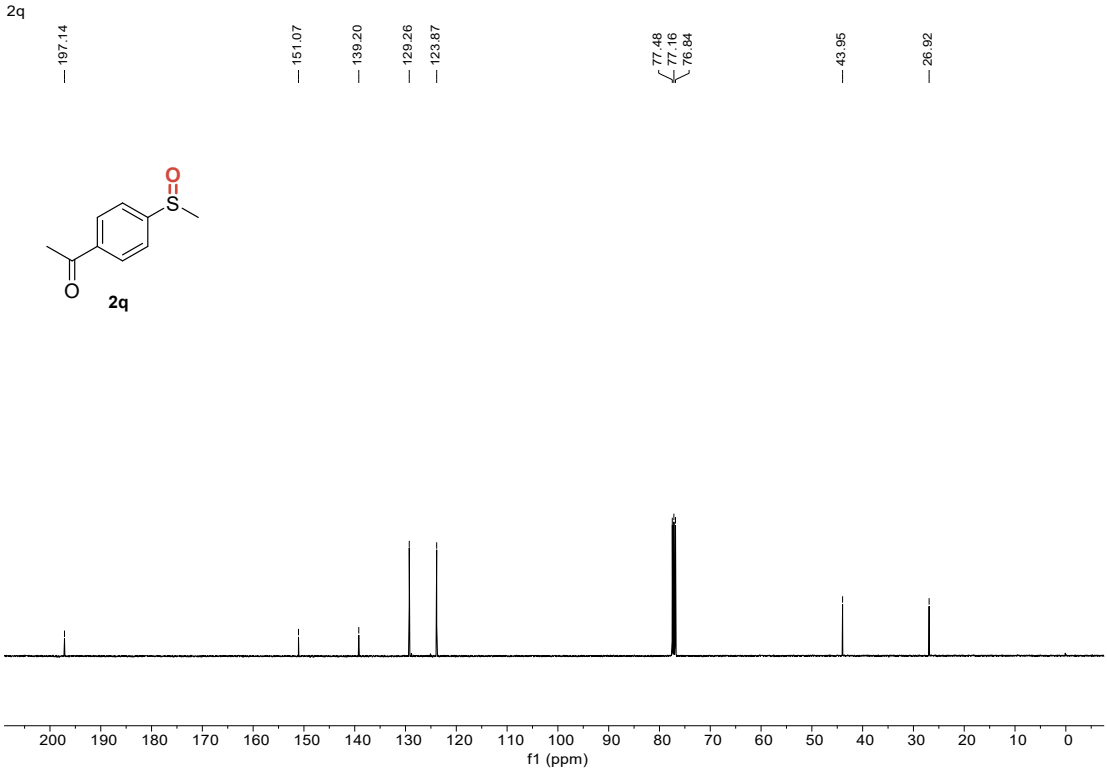


Fig. S46 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2q**.

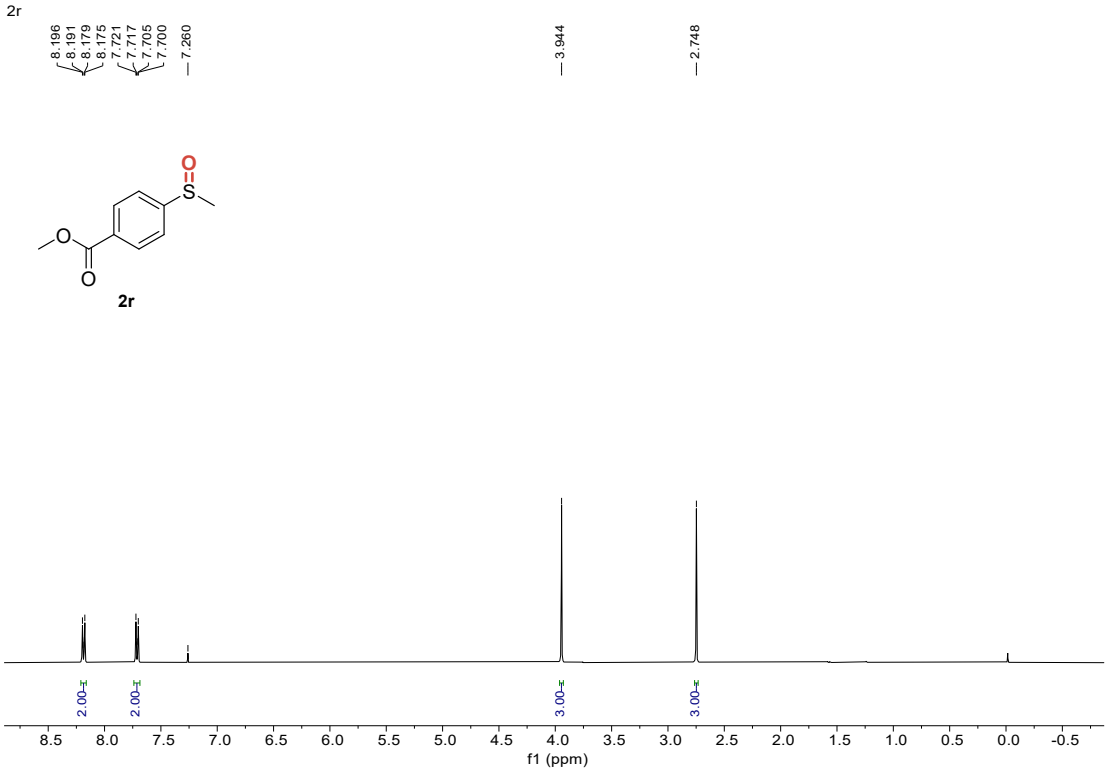


Fig. S47 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2r**.

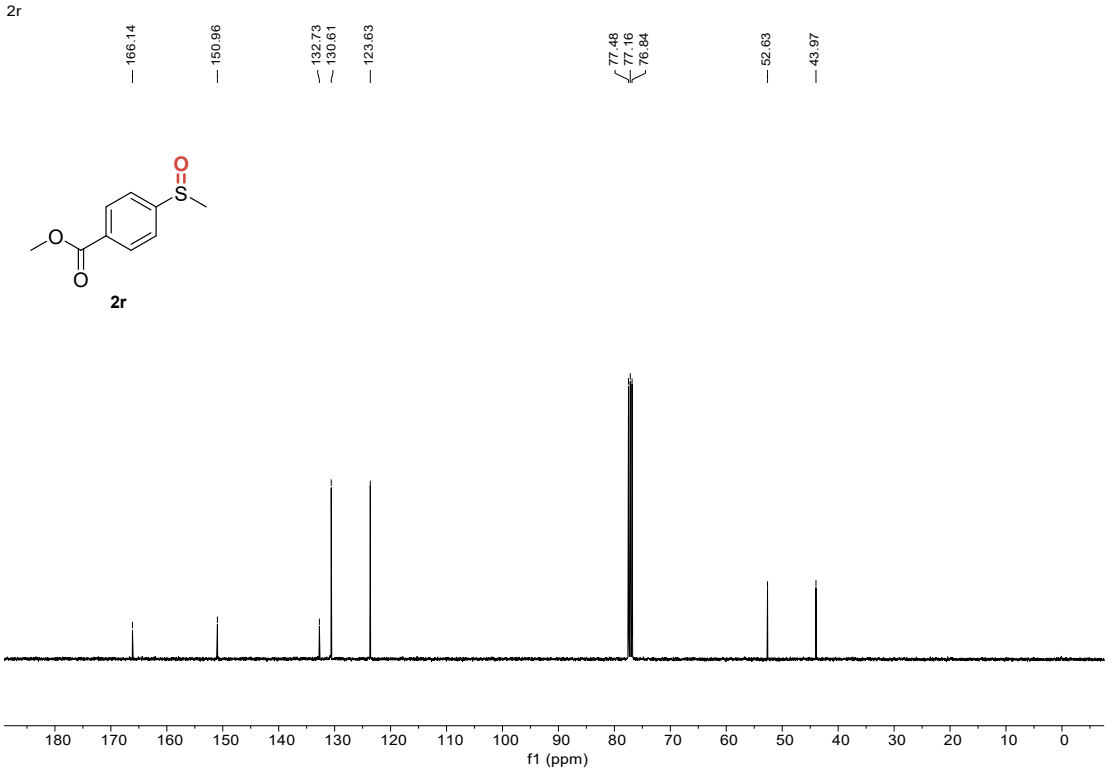


Fig. S48 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2r**.

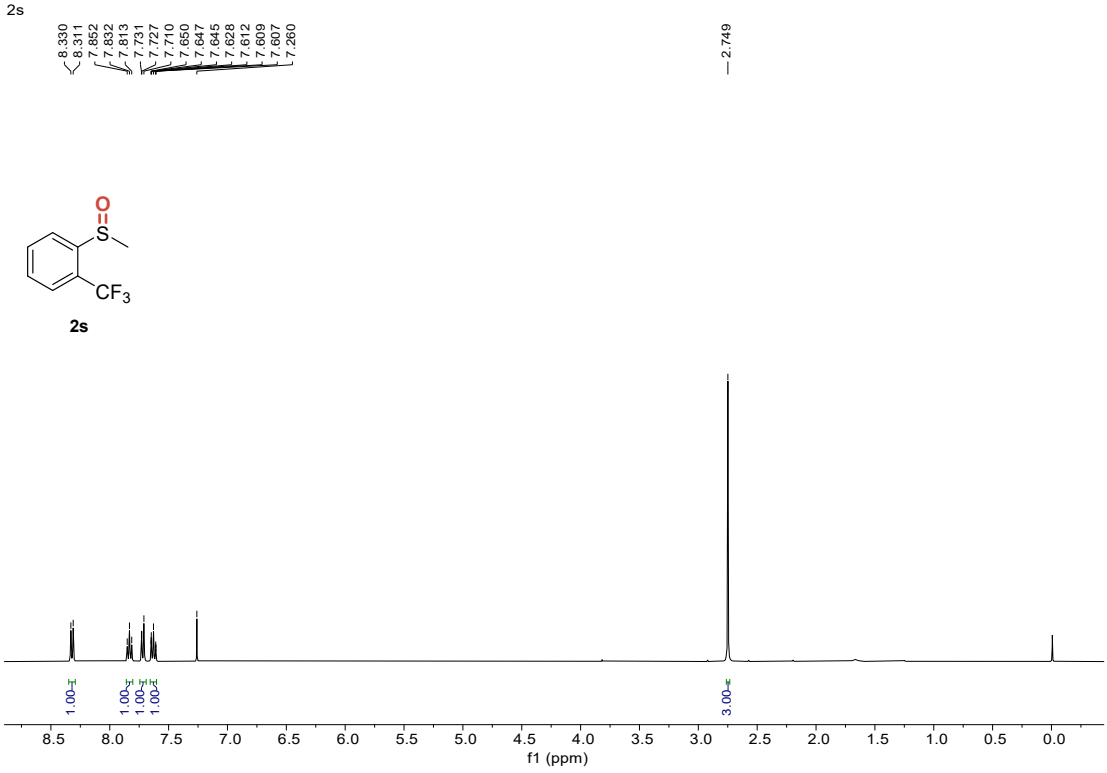


Fig. S49 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2s**.

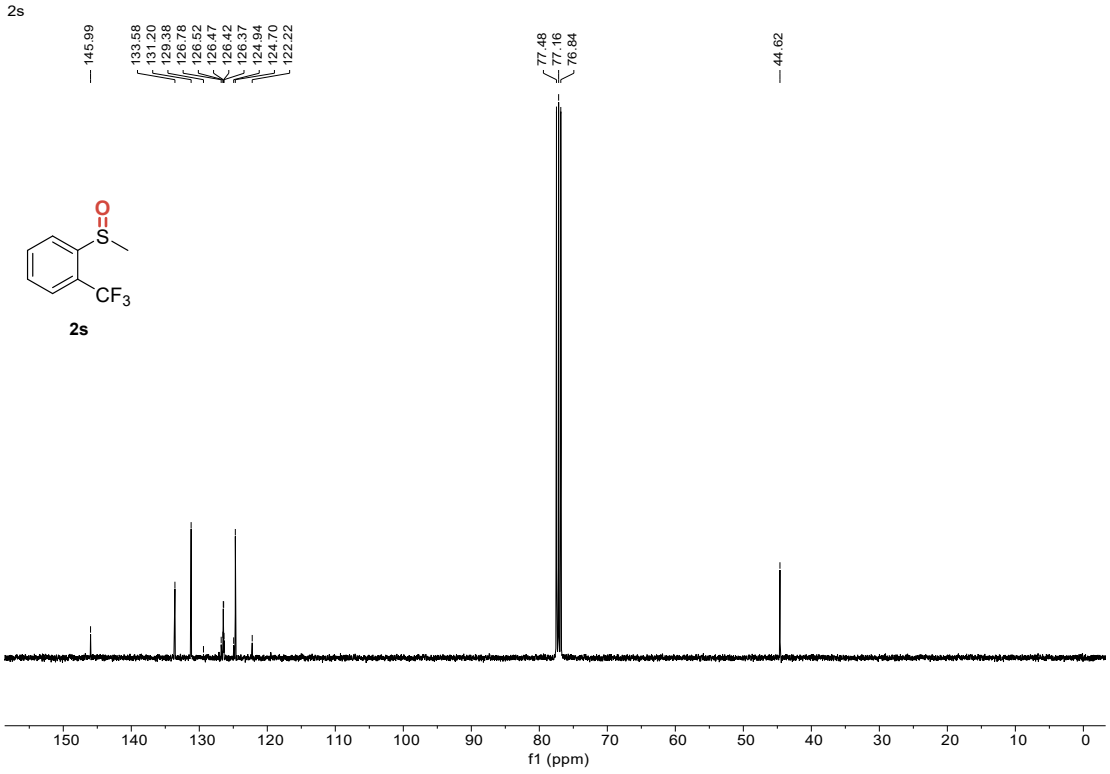


Fig. S50 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2s**.

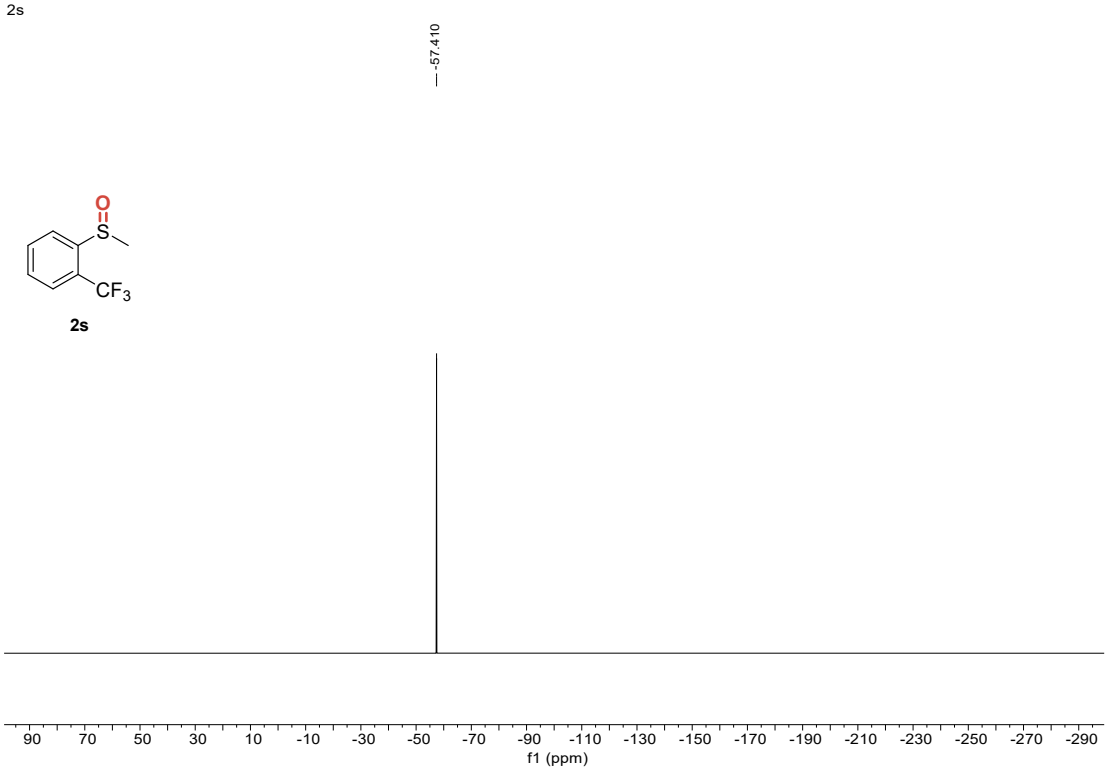


Fig. S51 ^{19}F NMR spectrum (471 MHz, $CDCl_3$) of **2s**.

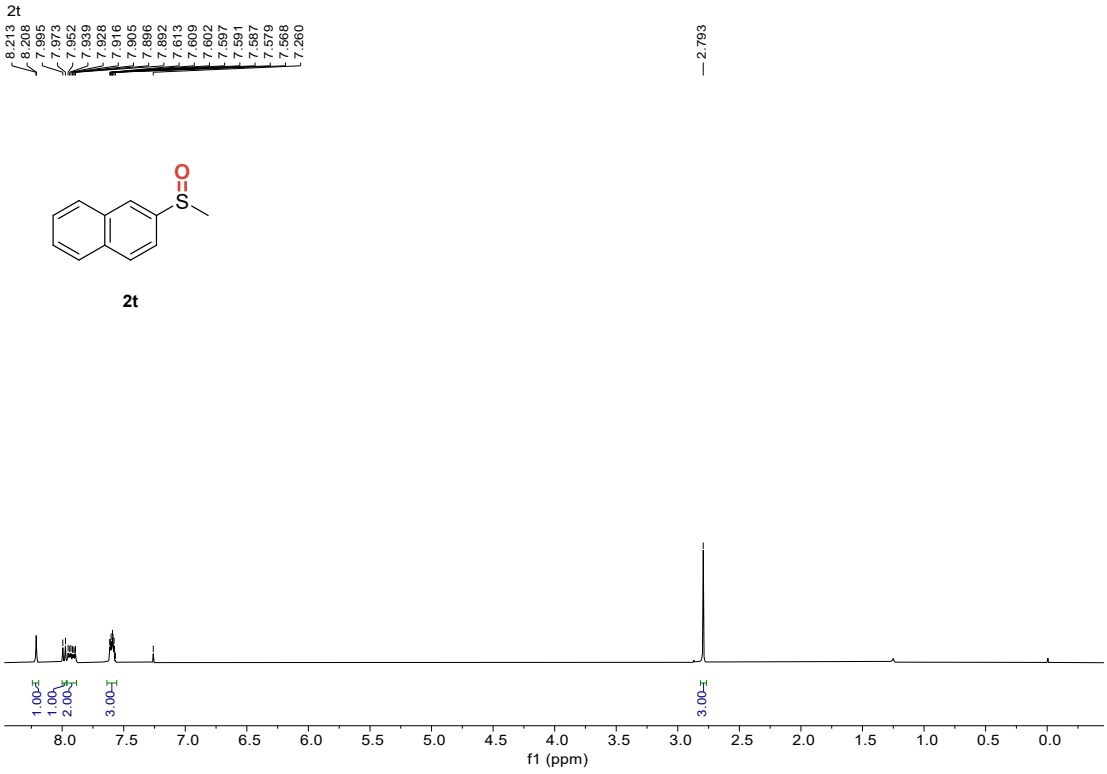


Fig. S52 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2t**.

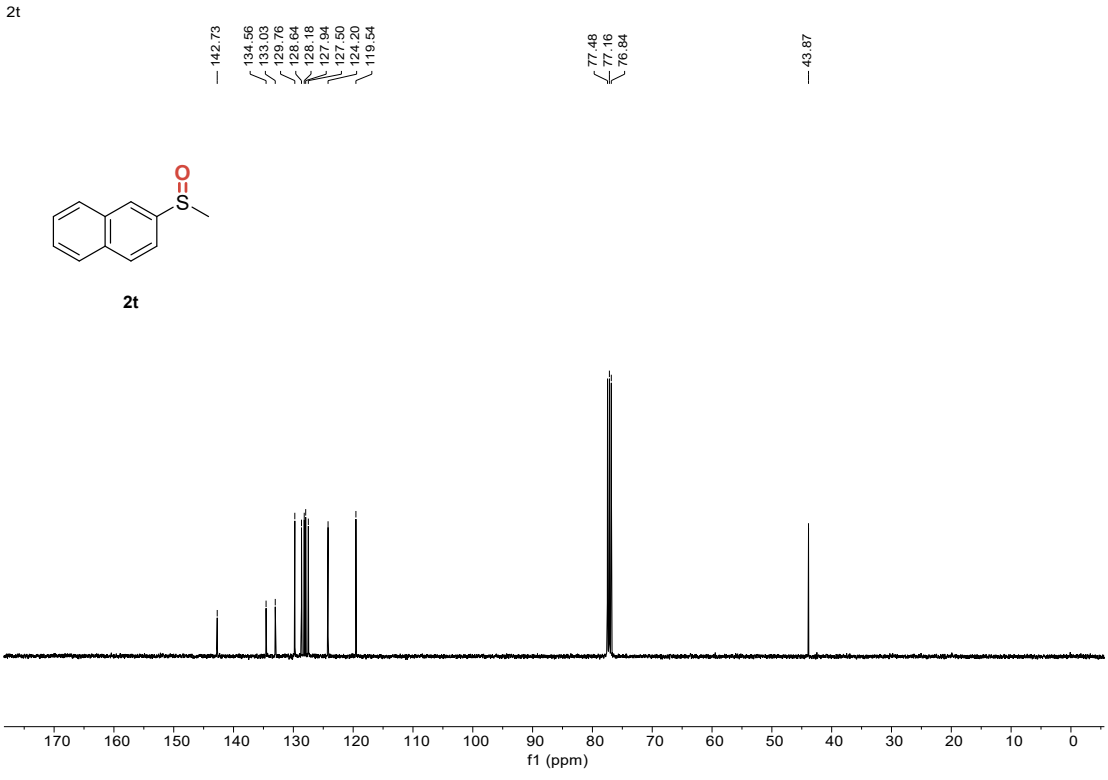


Fig. S53 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2t**.

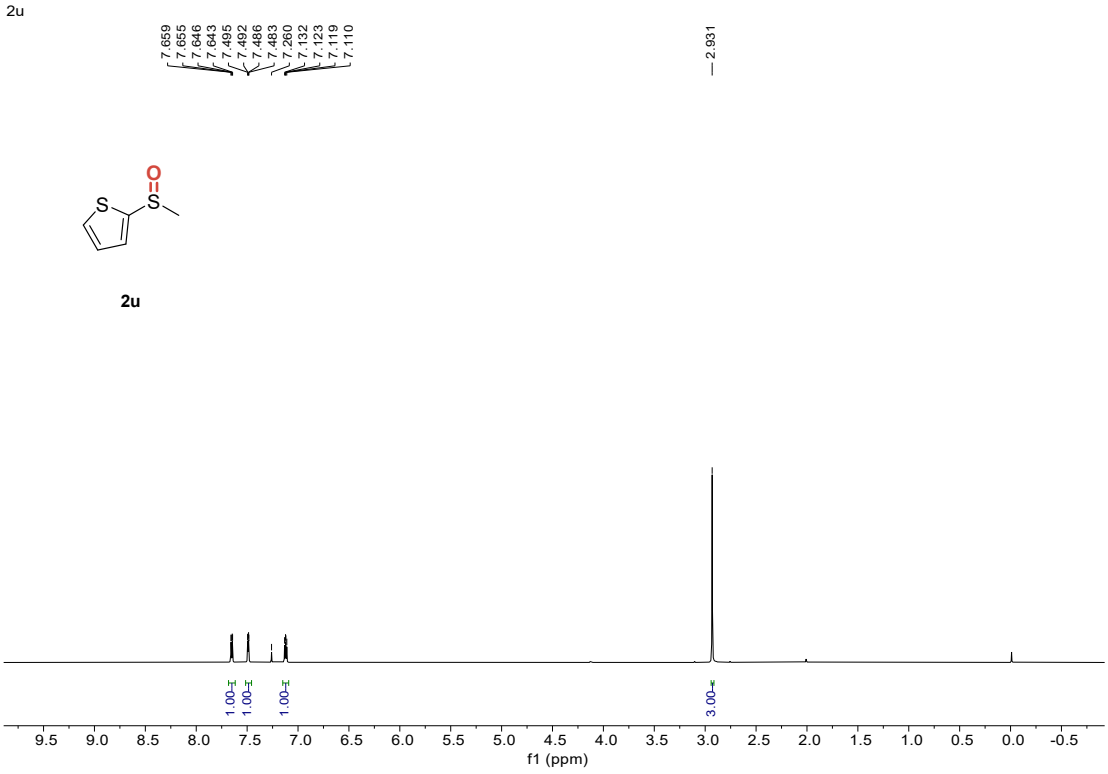


Fig. S54 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2u**.

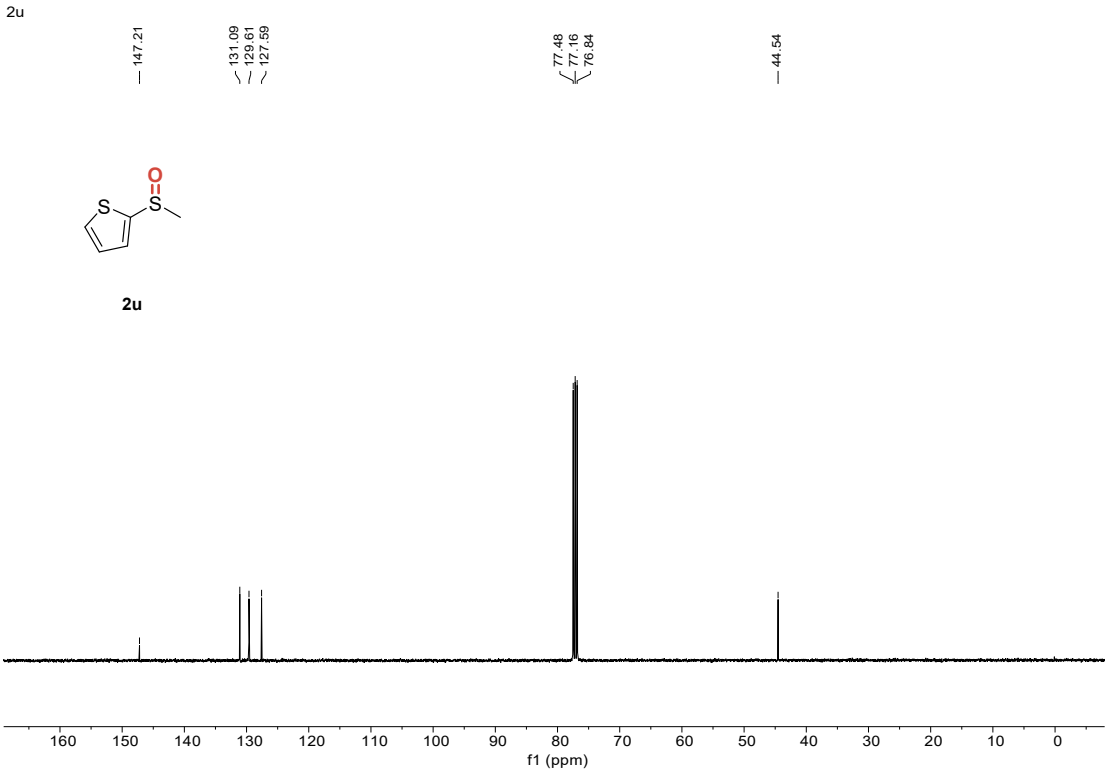


Fig. S55 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2u**.

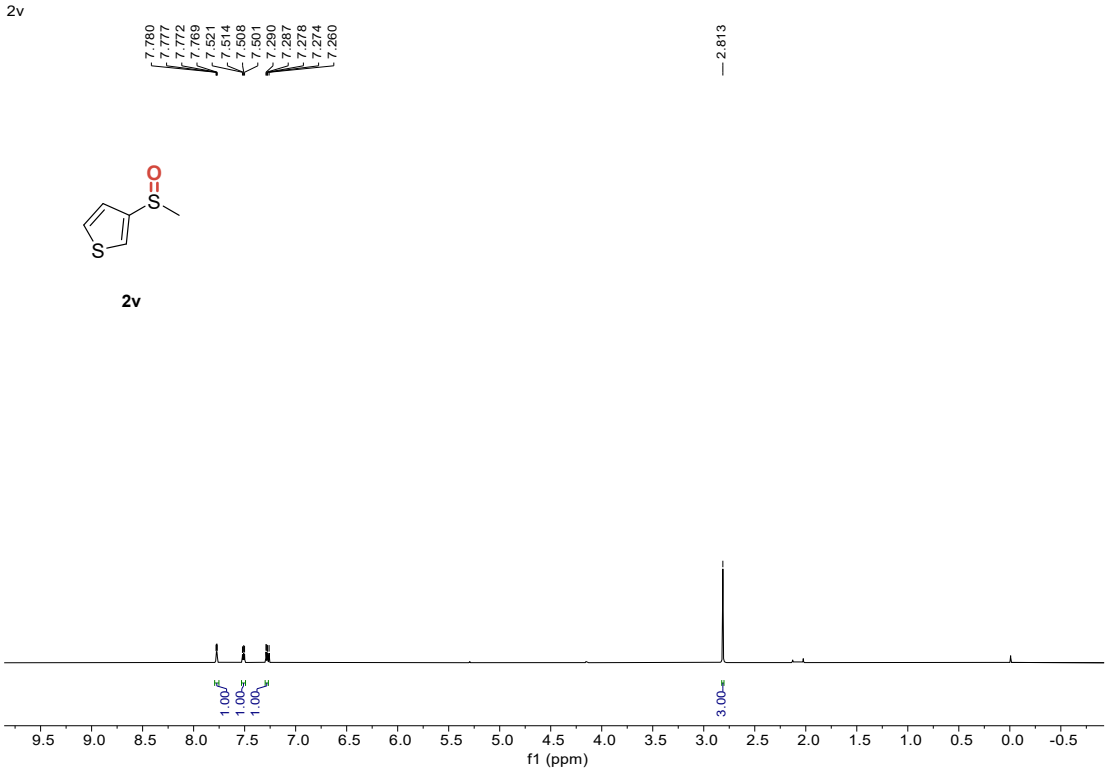


Fig. S56 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2v**.

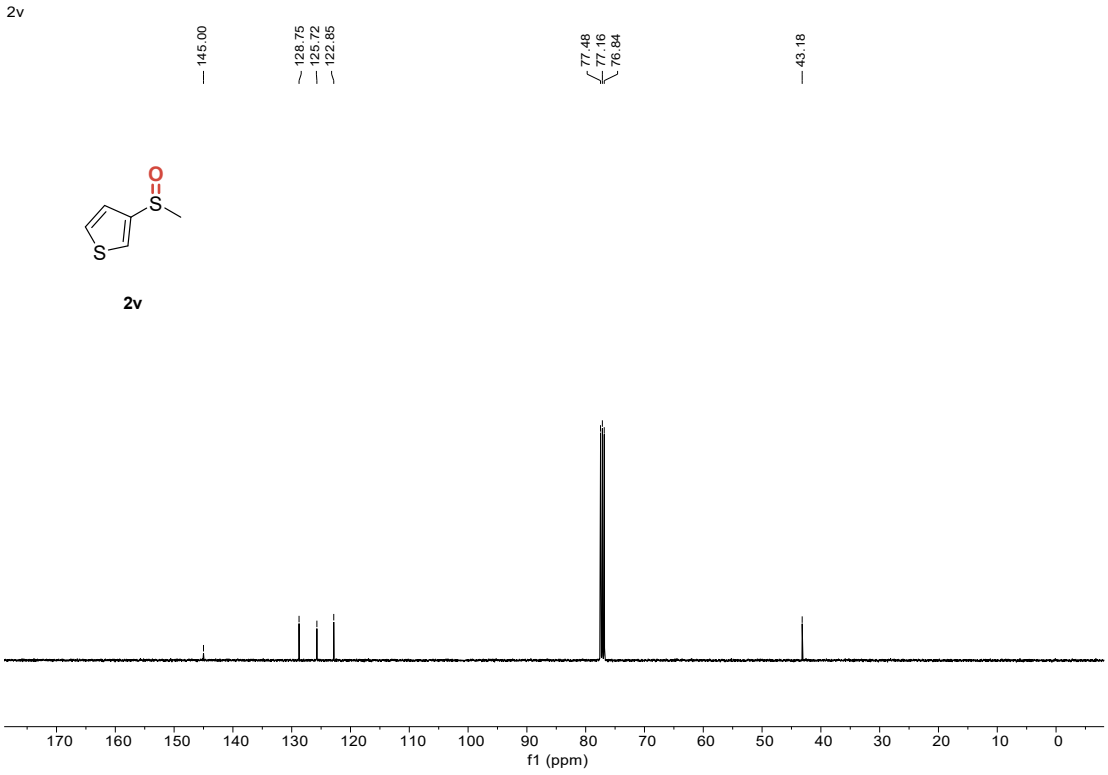


Fig. S57 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2v**.

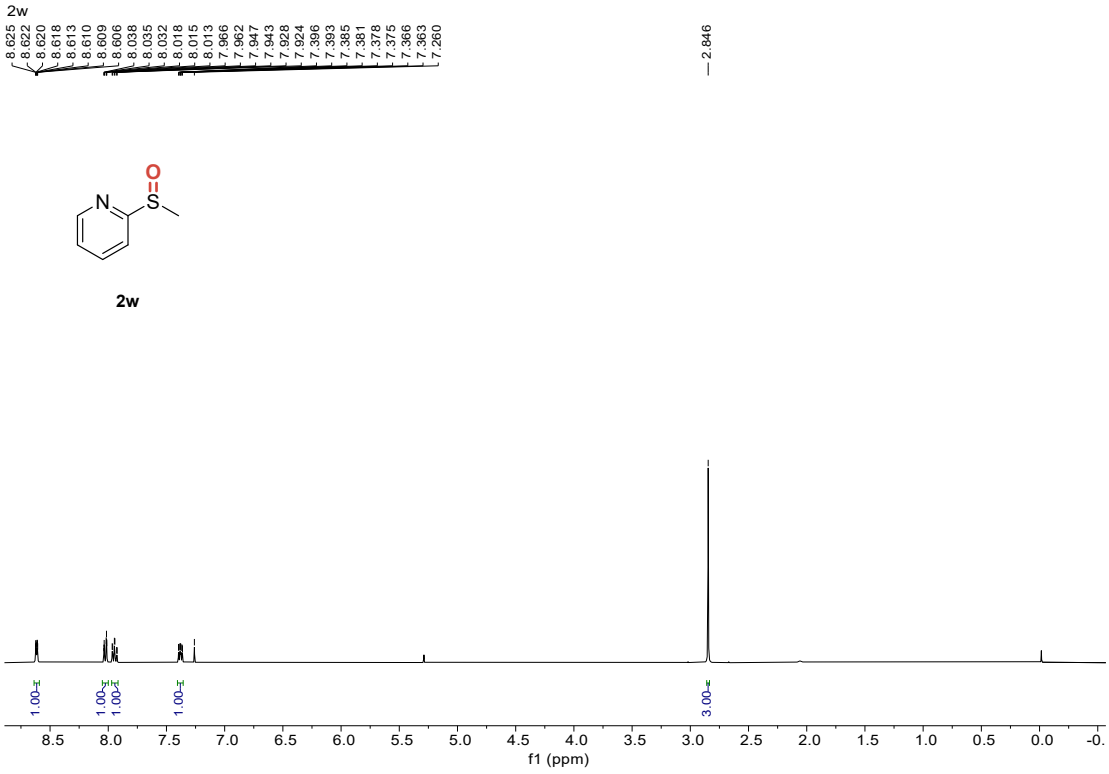


Fig. S58 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2w**.

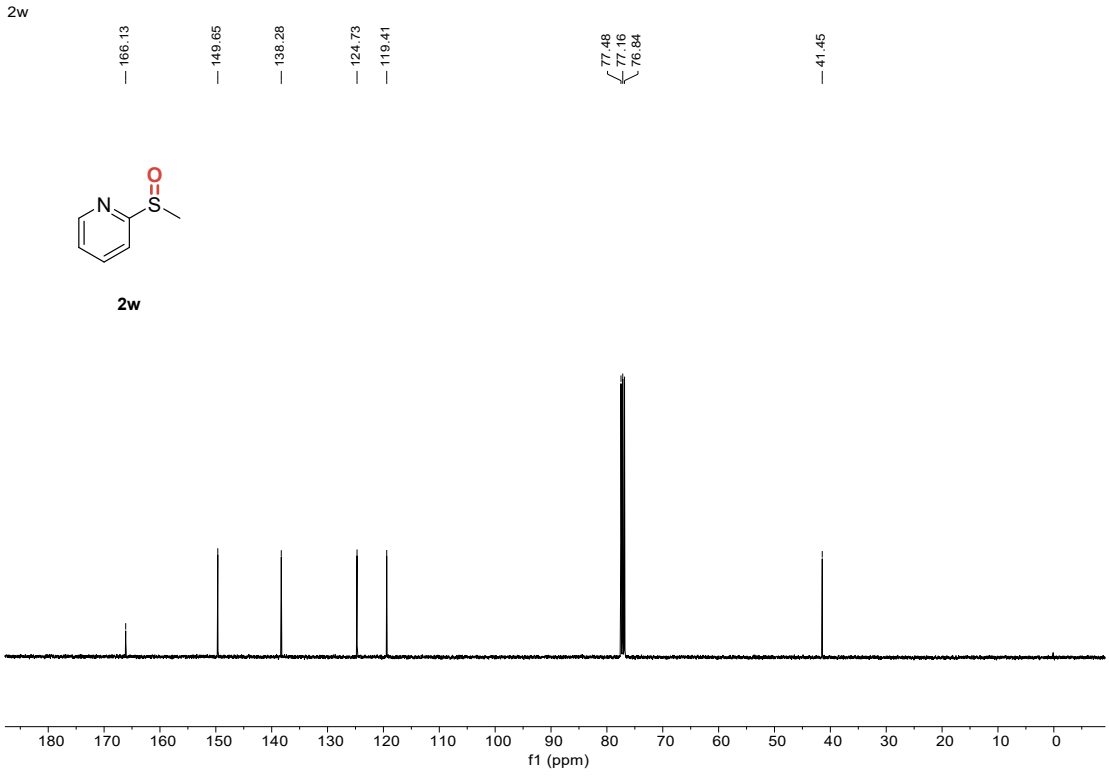


Fig. S59 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2w**.

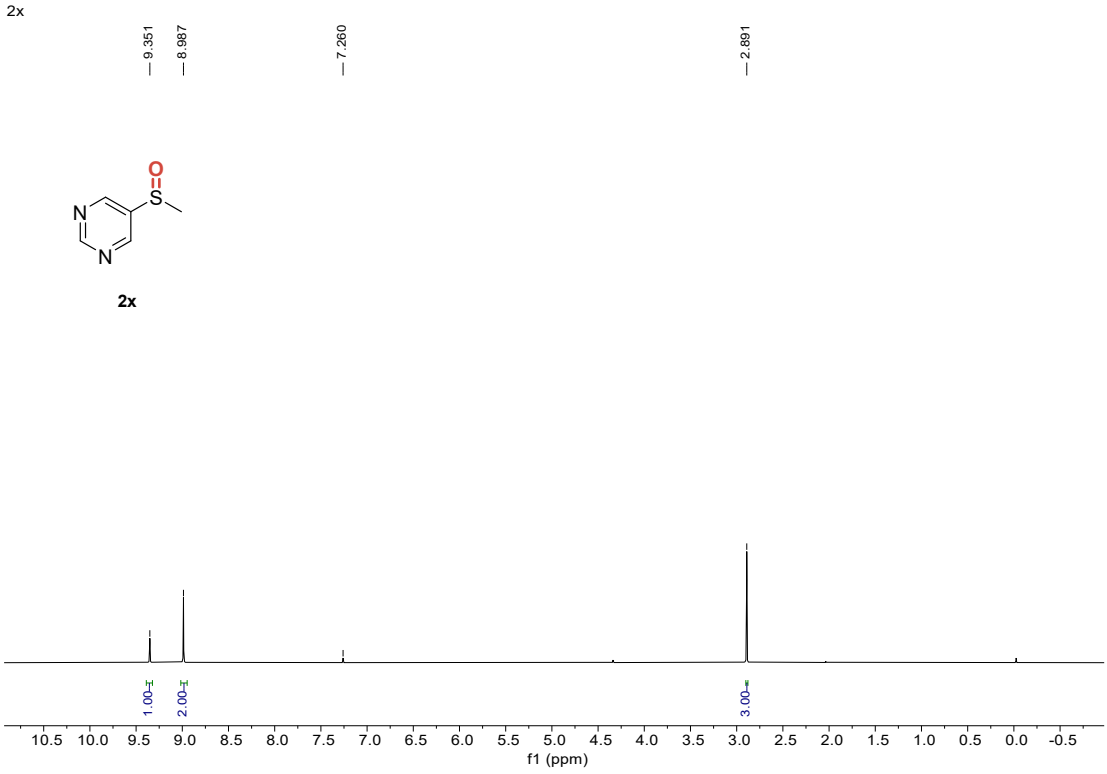


Fig. S60 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2x**.

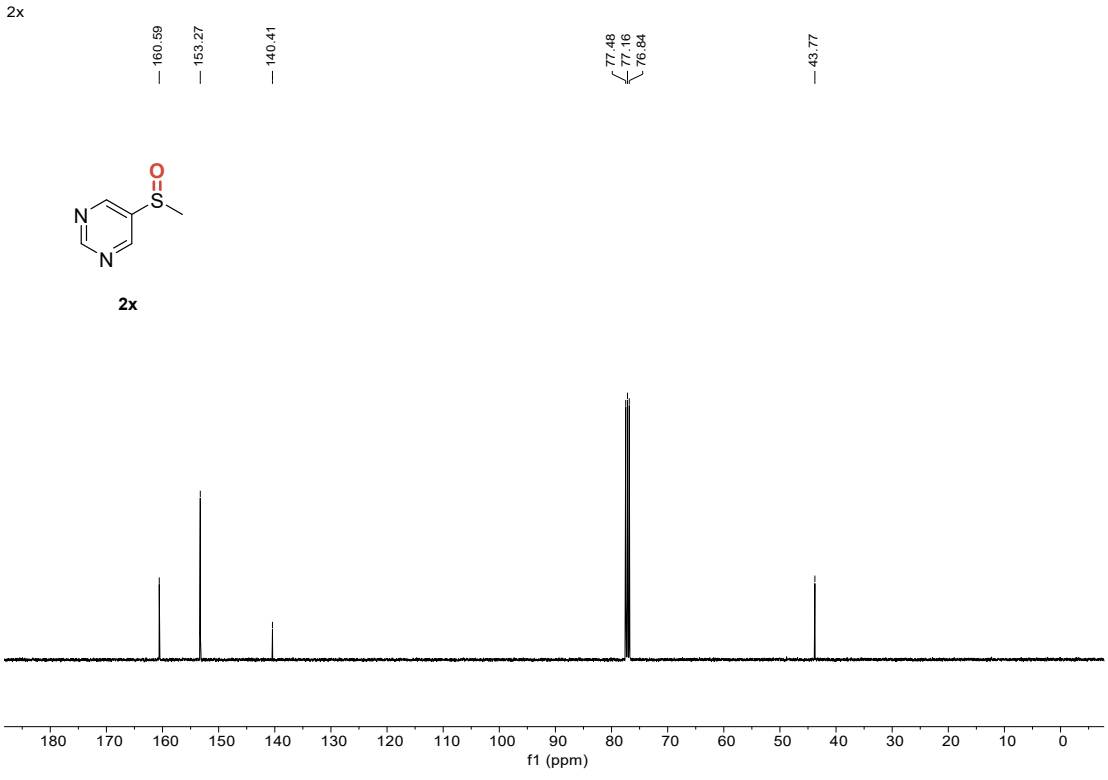


Fig. S61 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2x**.

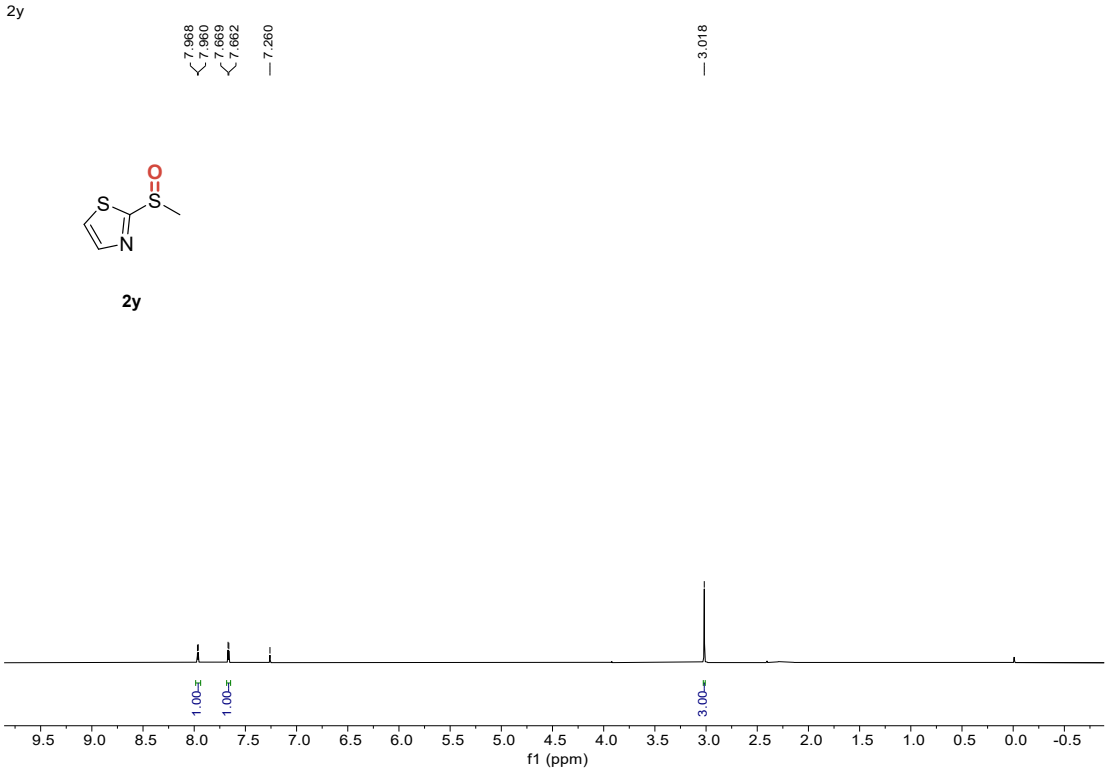


Fig. S62 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2y**.

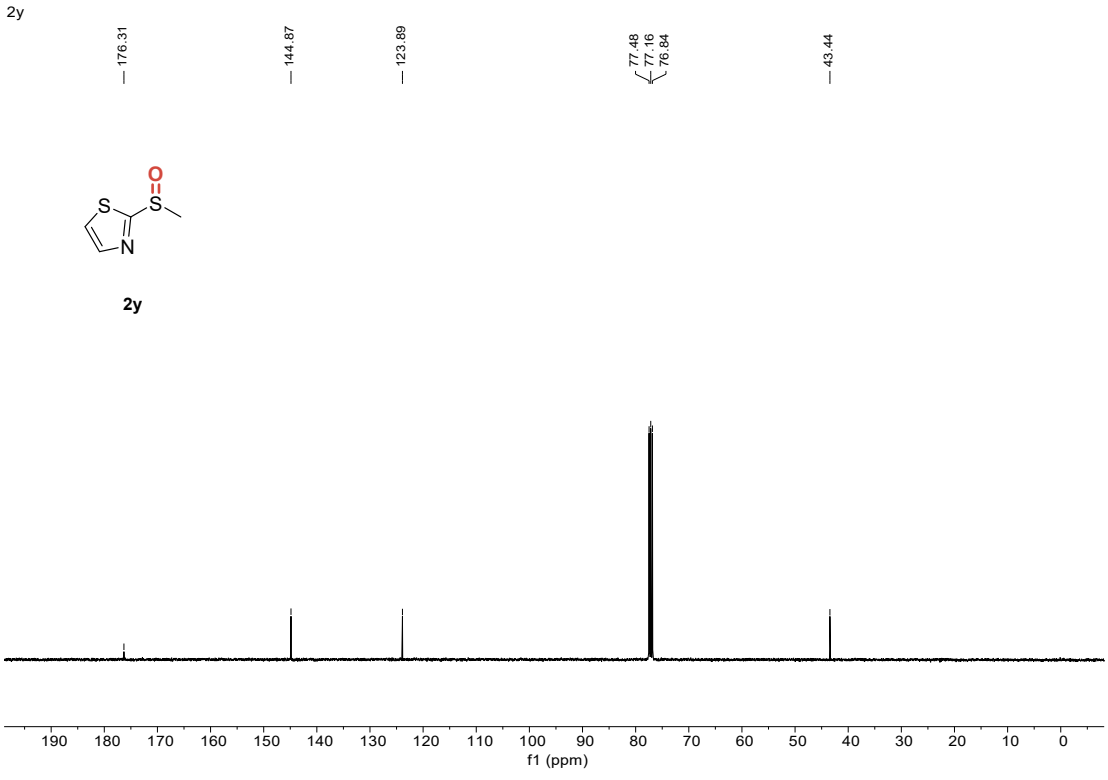


Fig. S63 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2y**.

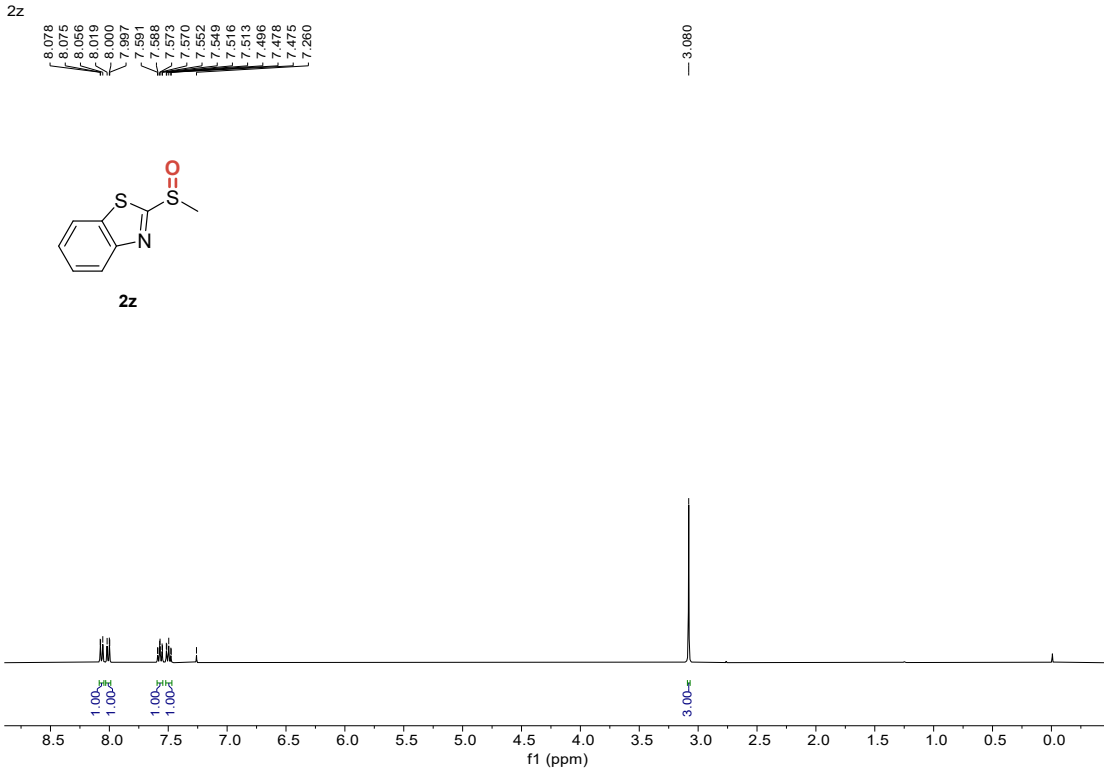


Fig. S64 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2z**.

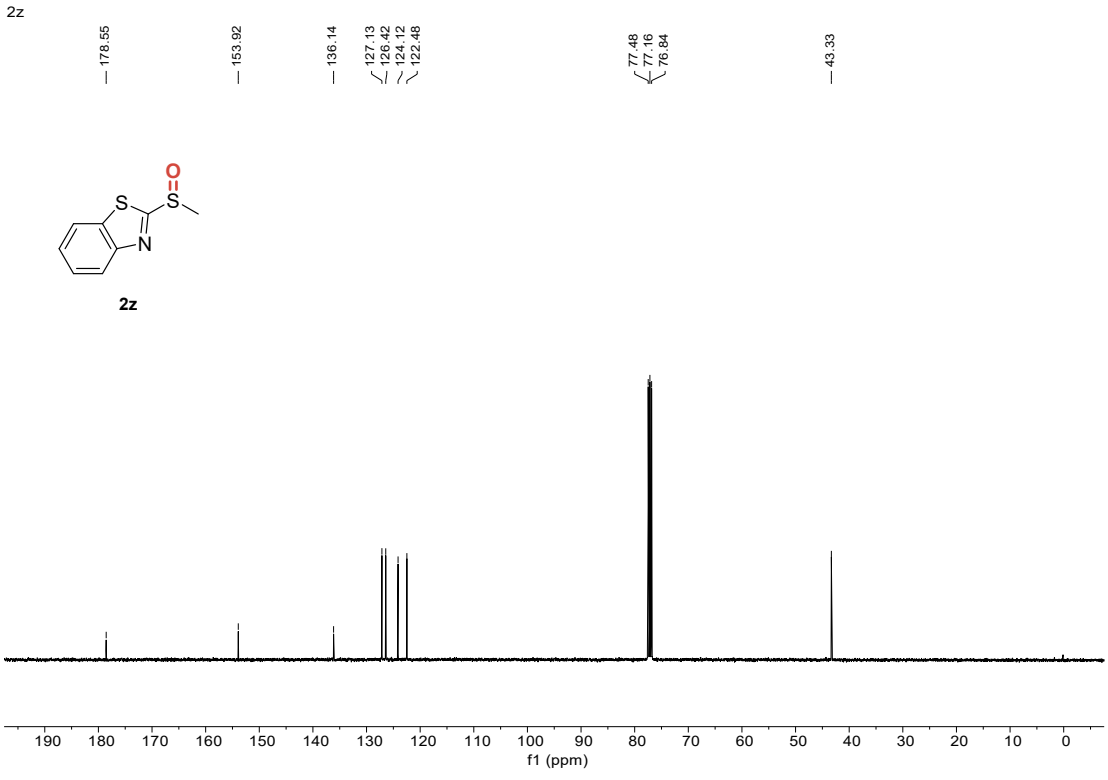


Fig. S65 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2z**.

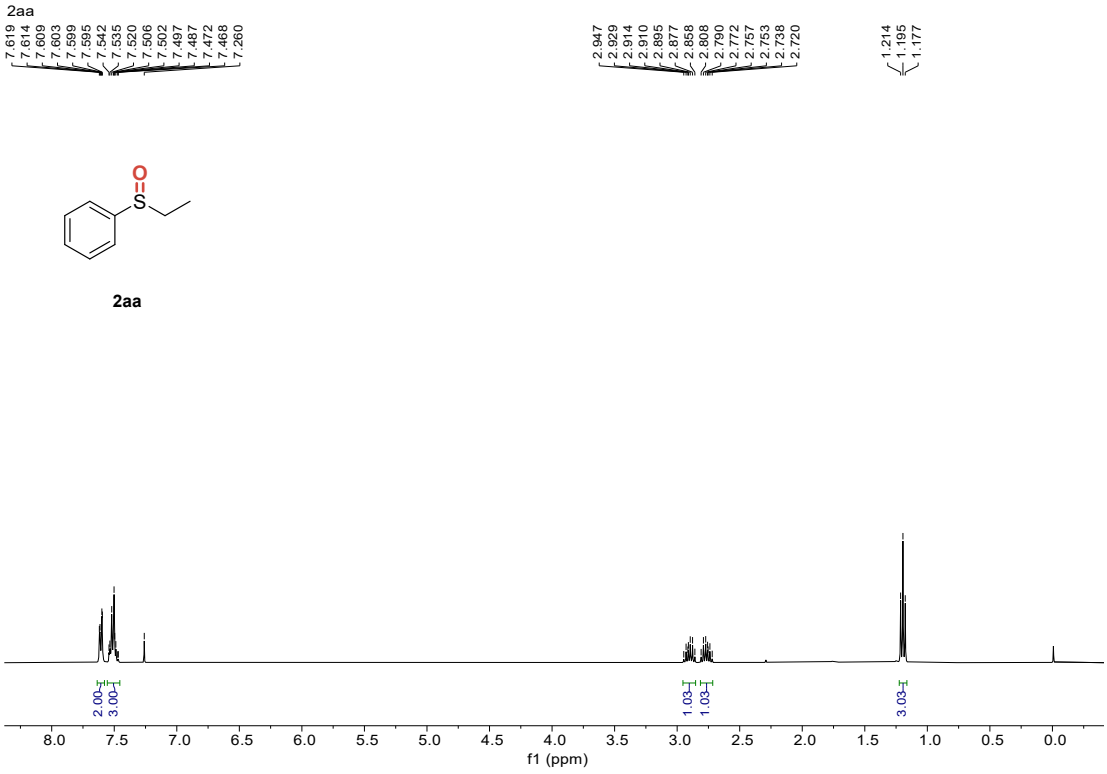


Fig. S66 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2aa**.

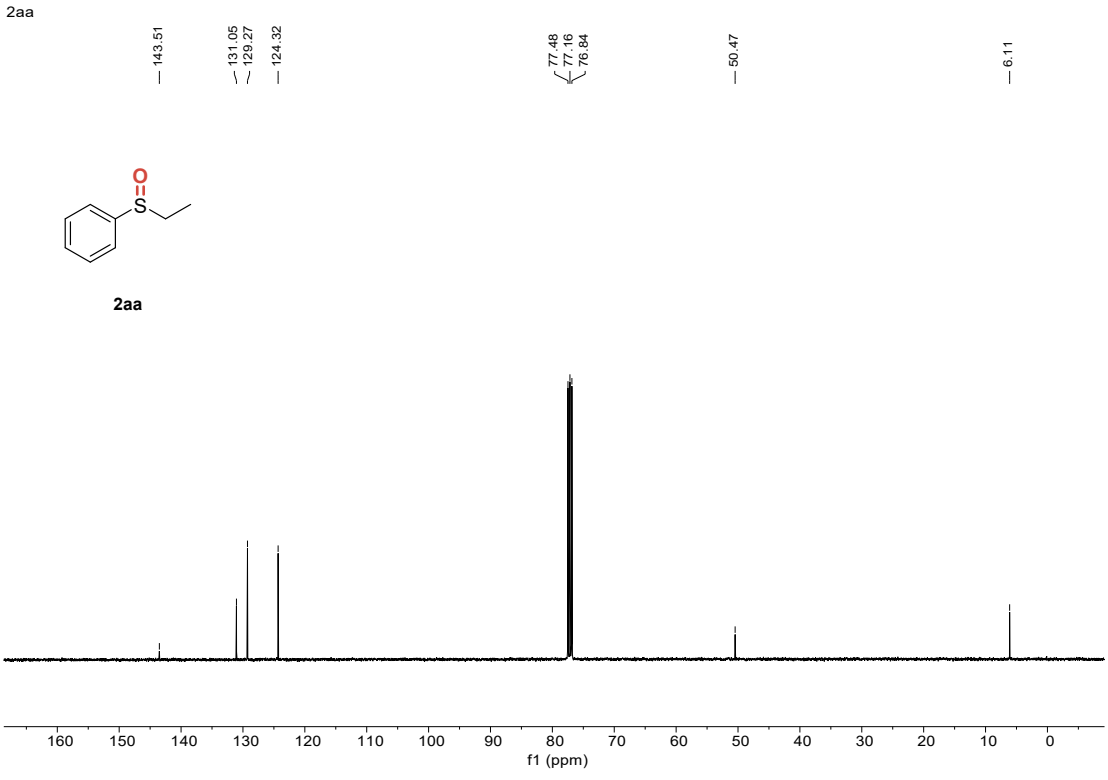


Fig. S67 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2aa**.

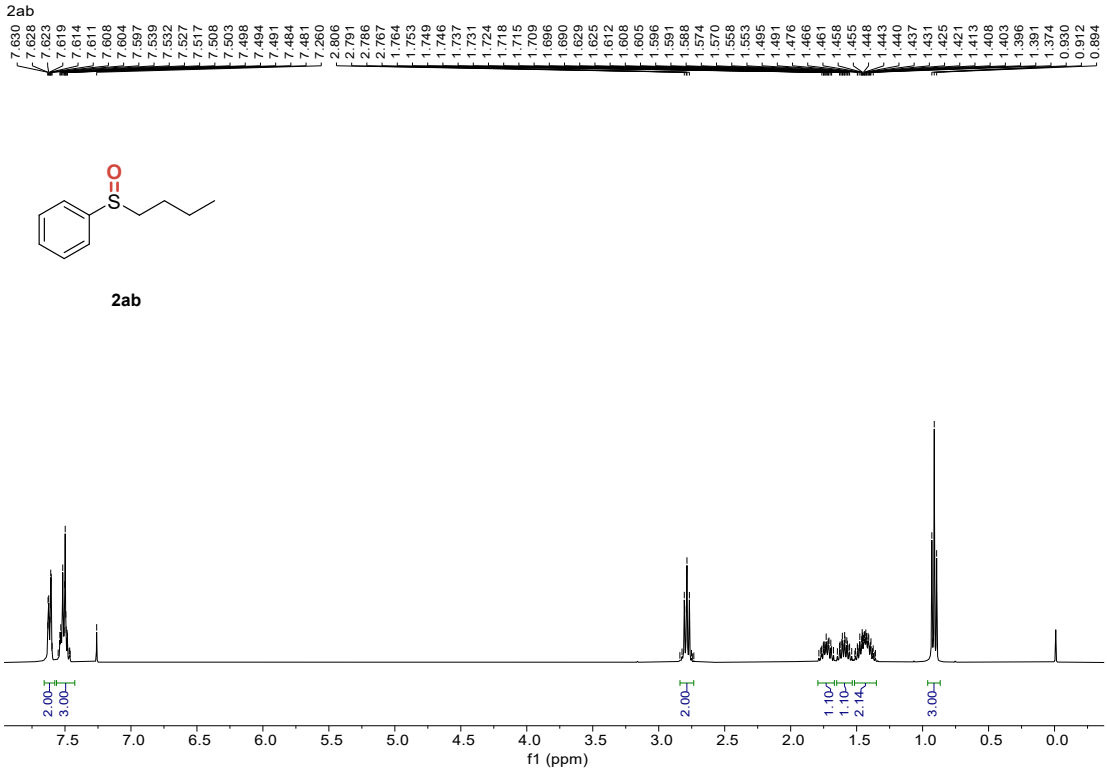


Fig. S68 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2ab**.

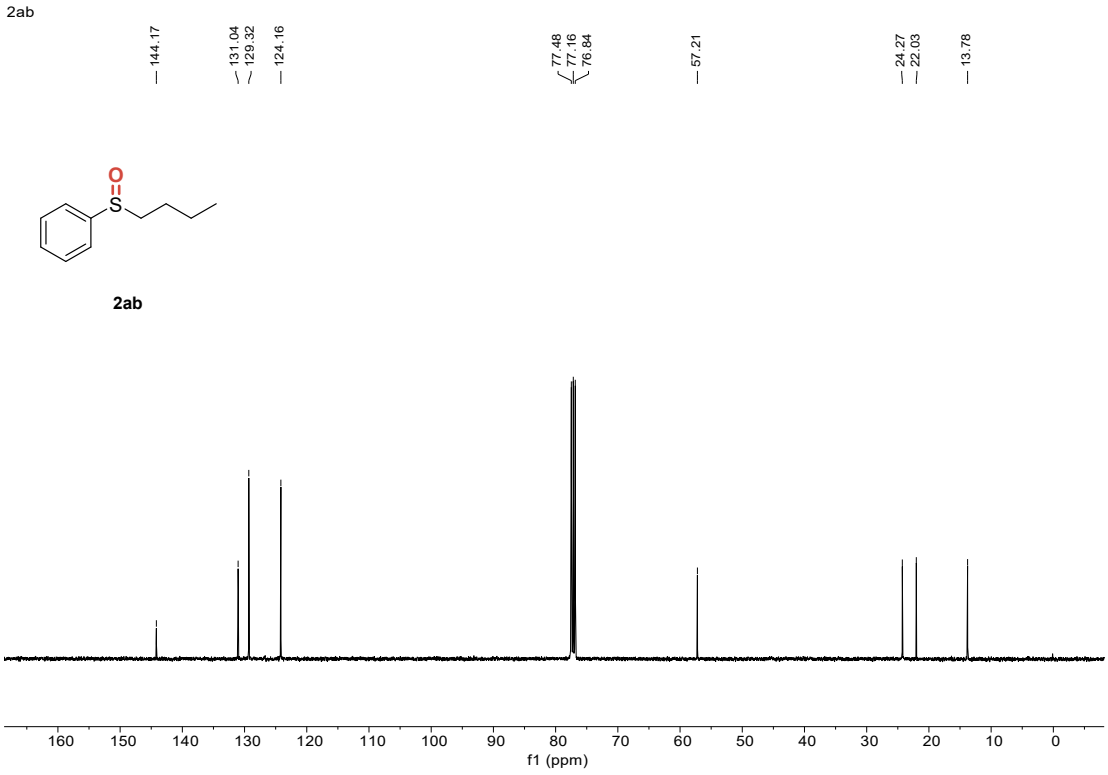


Fig. S69 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2ab**.

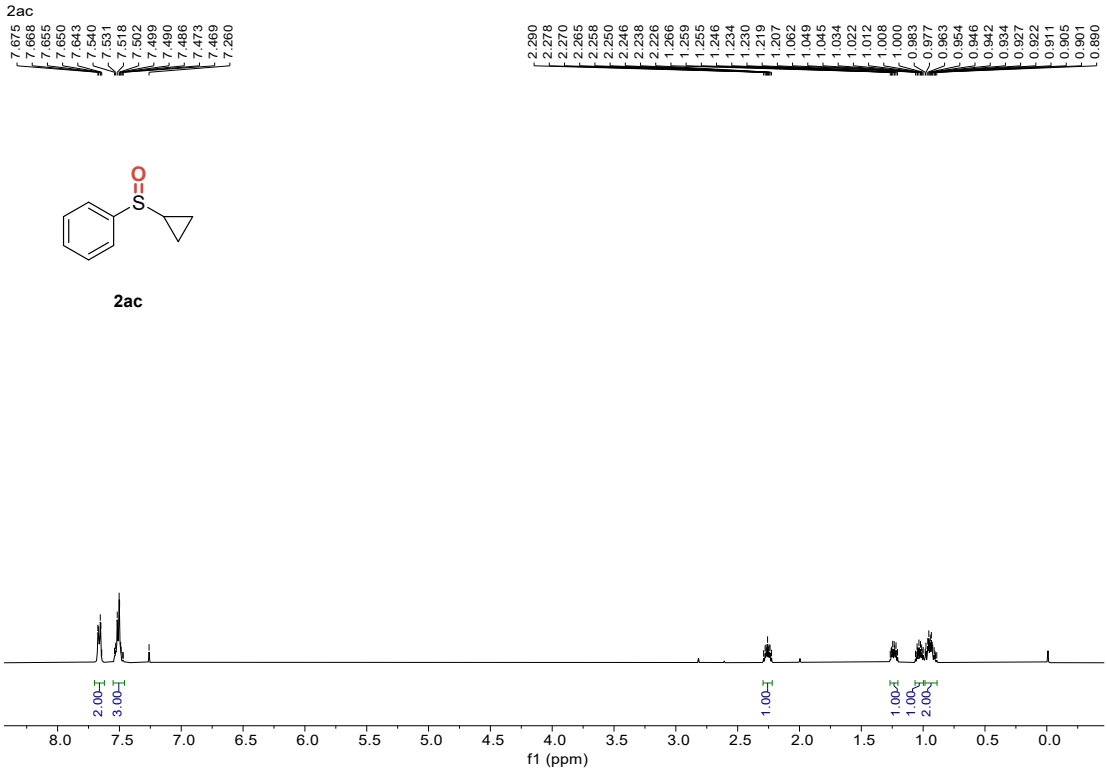


Fig. S70 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2ac**.

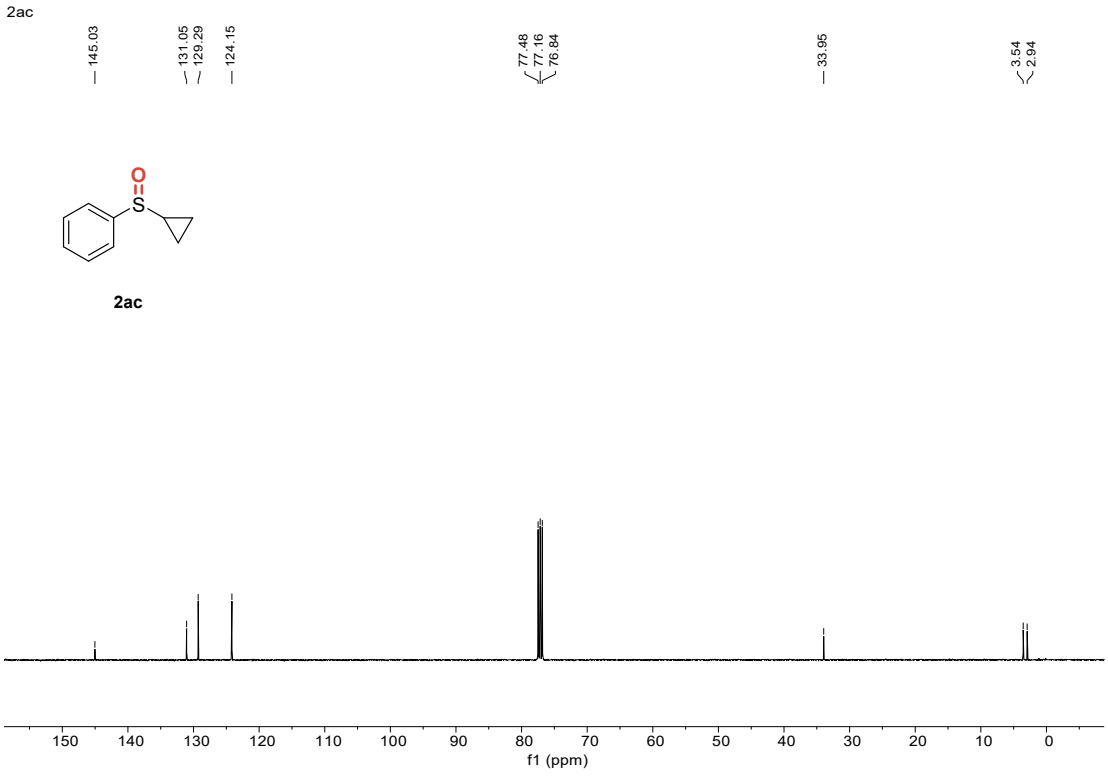


Fig. S71 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2ac**.

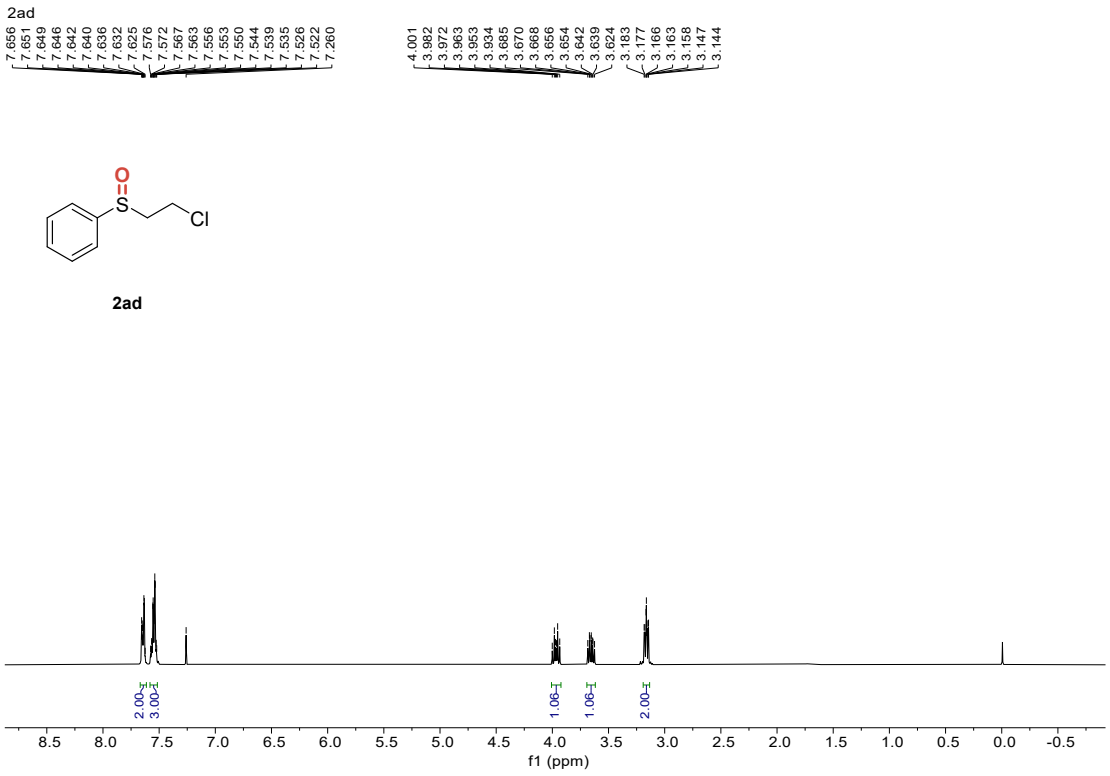


Fig. S72 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2ad**.

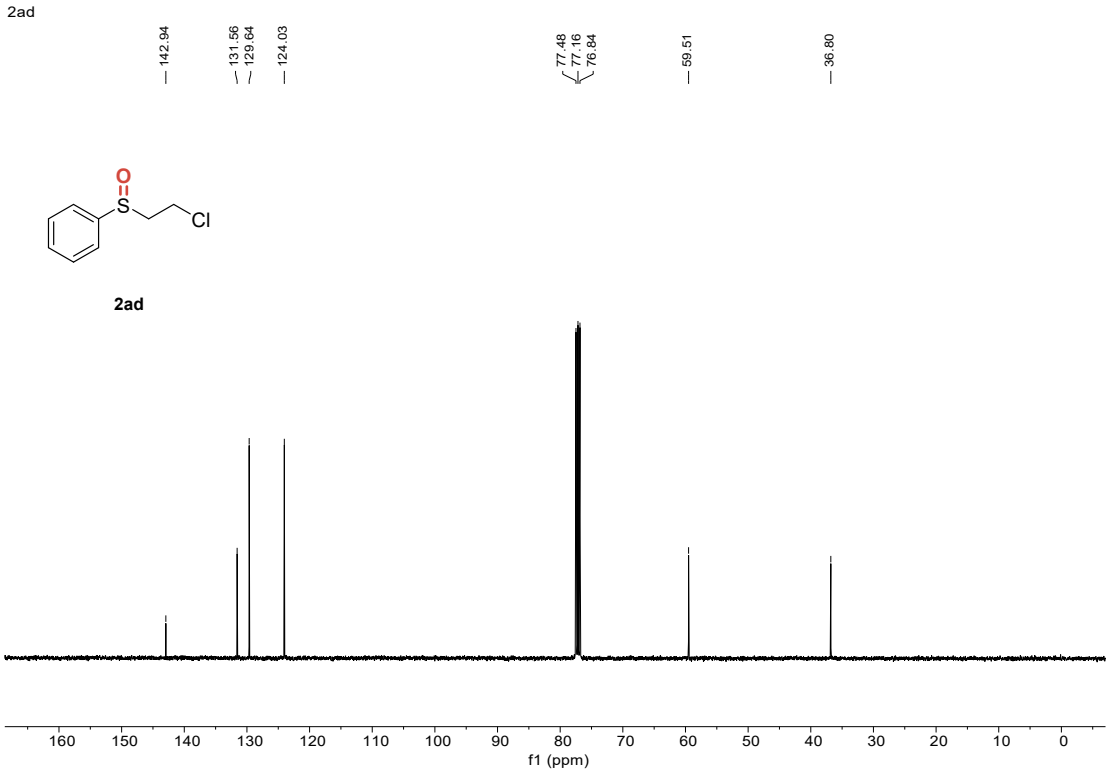


Fig. S73 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2ad**.

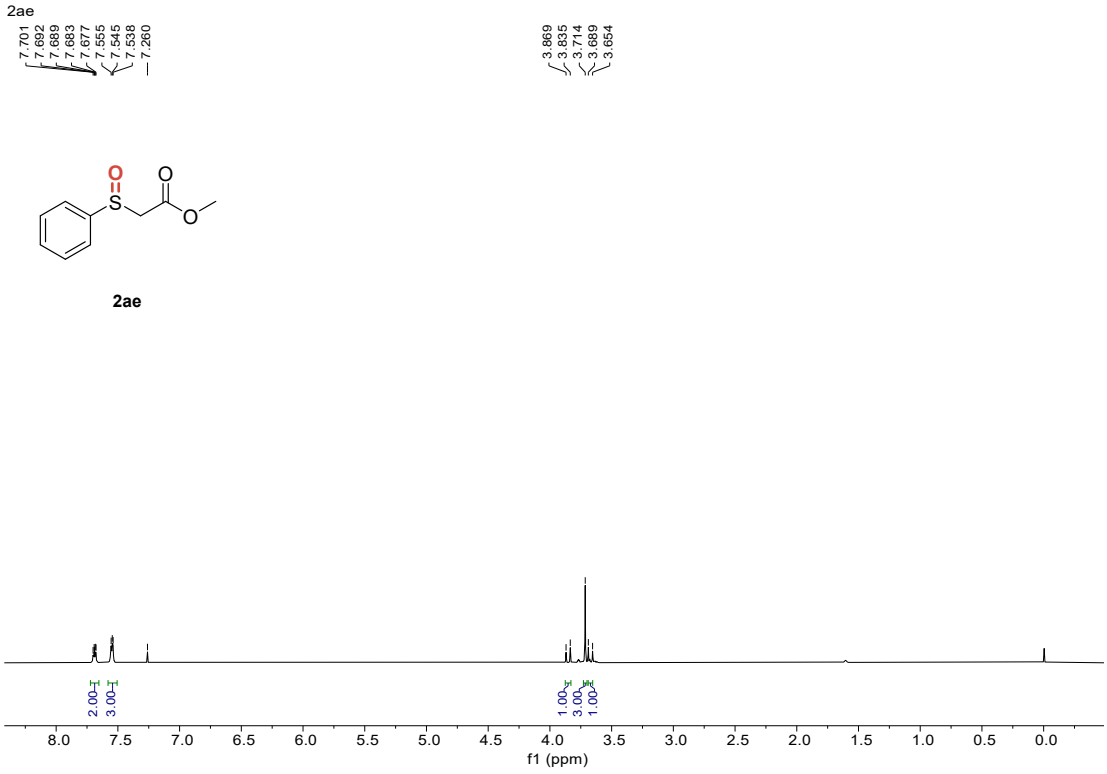


Fig. S74 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2ae**.

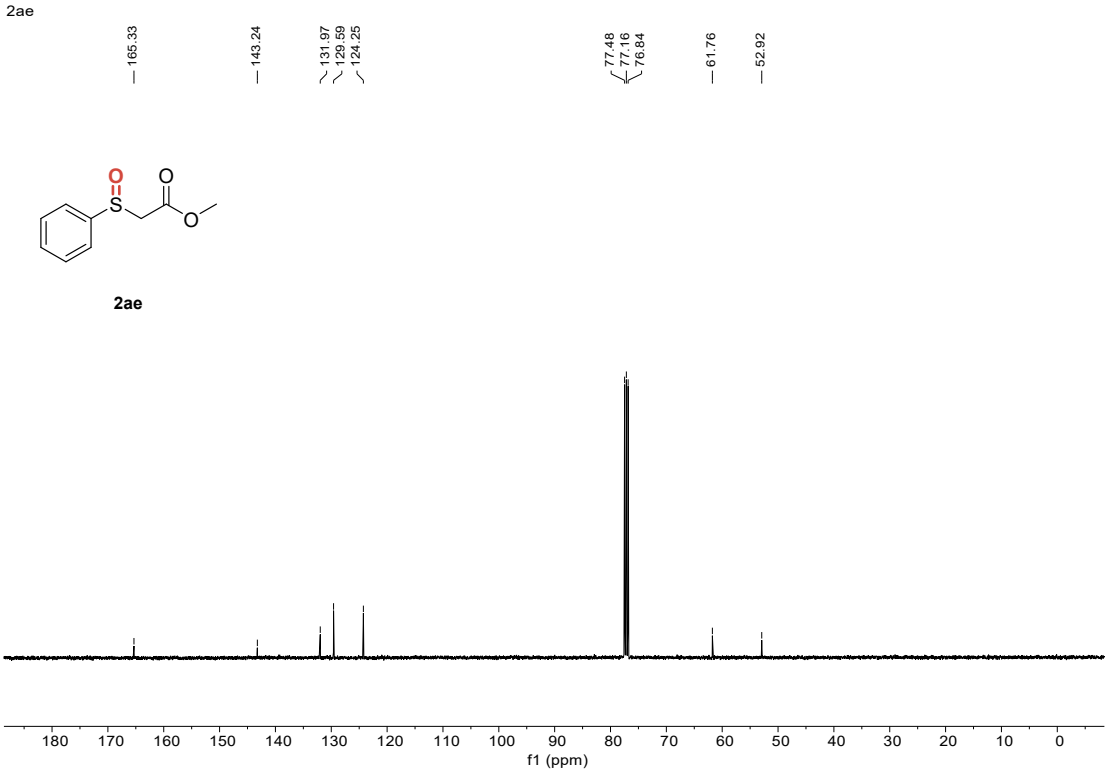


Fig. S75 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2ae**.

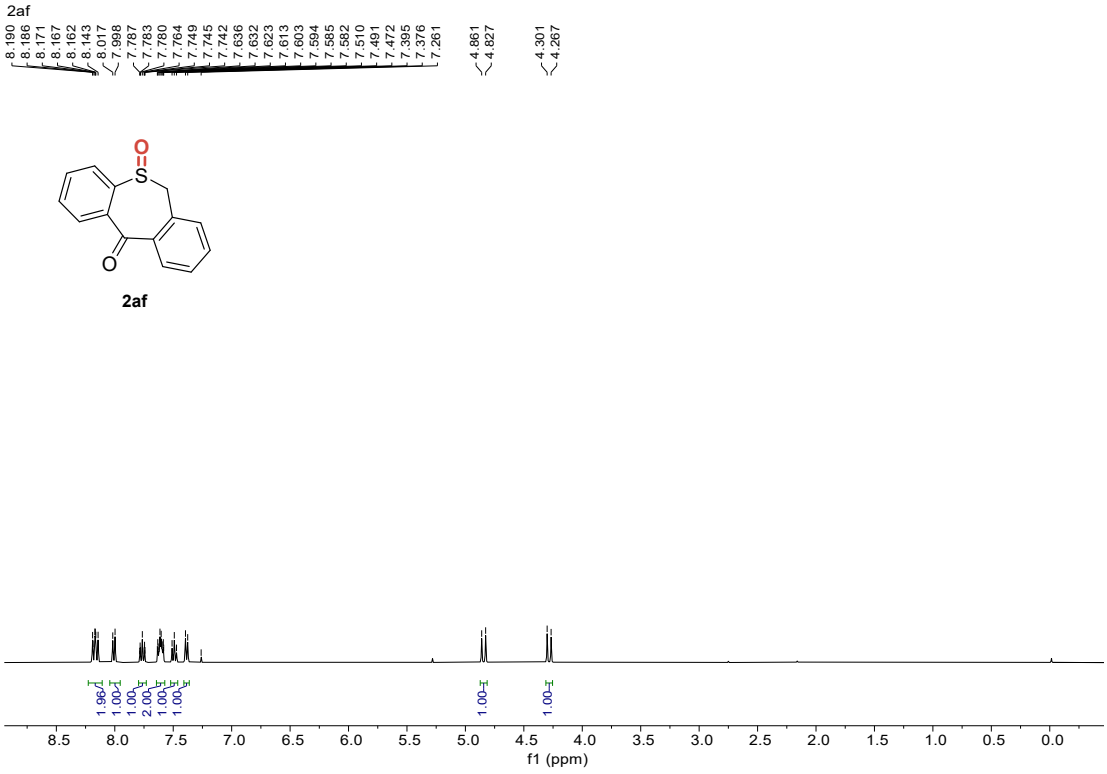


Fig. S76 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2af**.

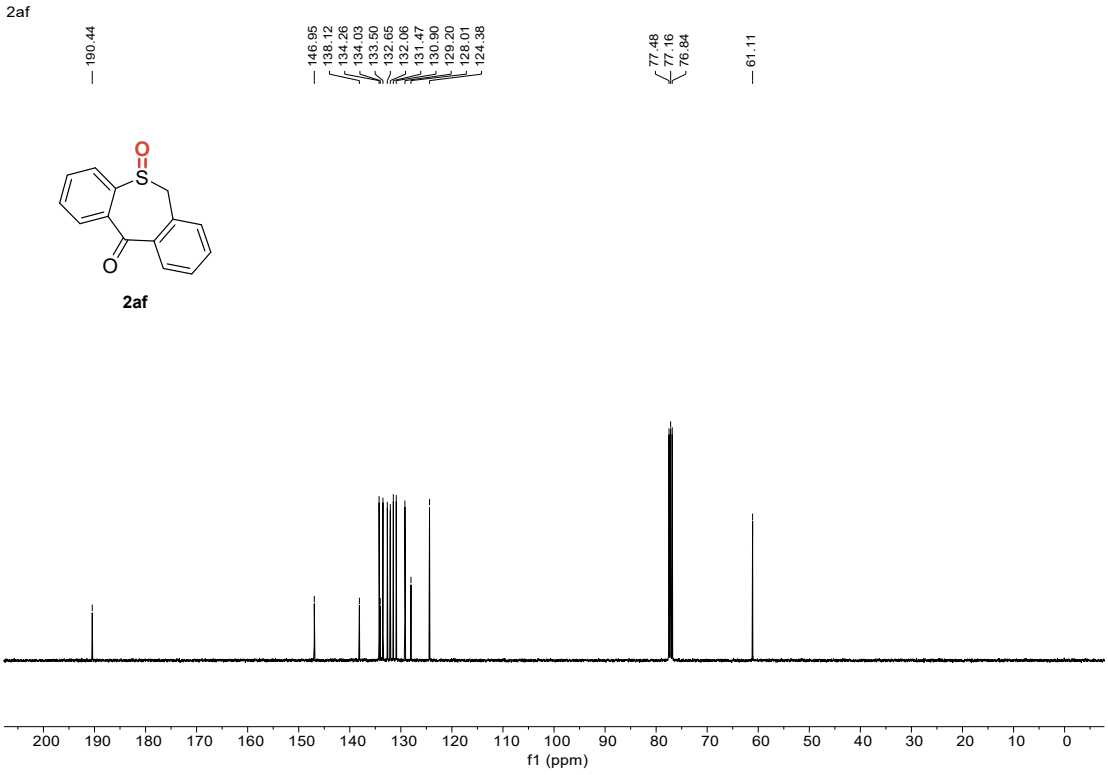


Fig. S77 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2af**.

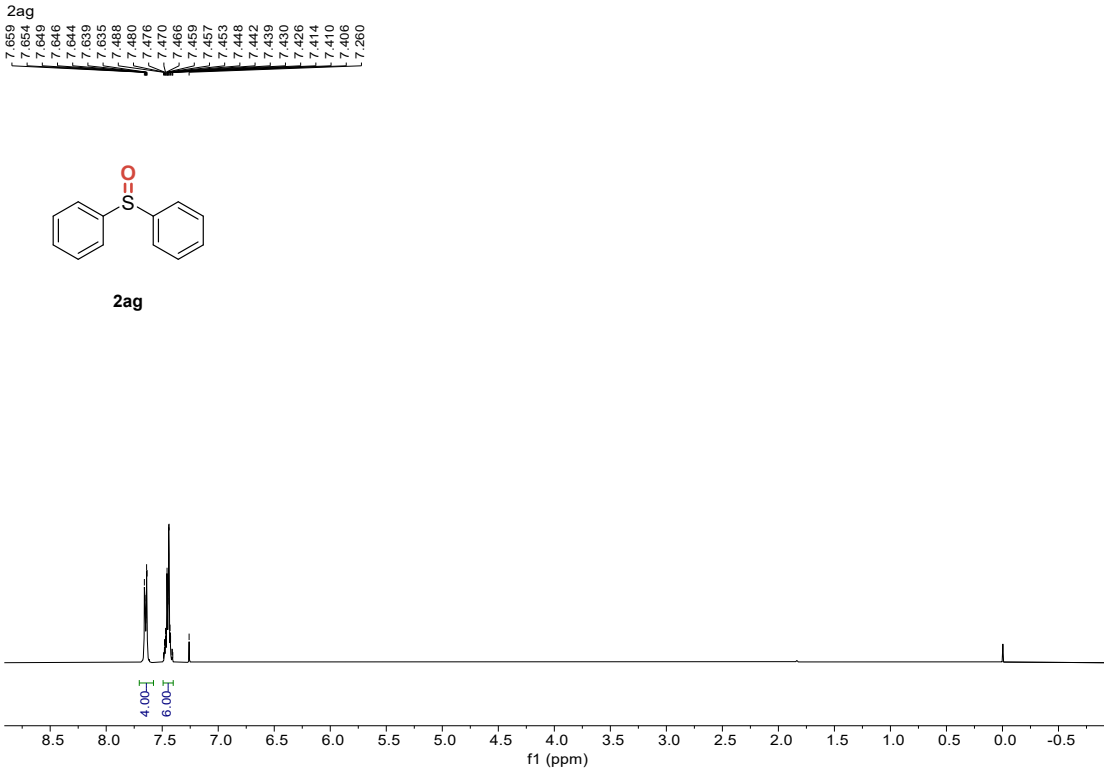


Fig. S78 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2ag**.

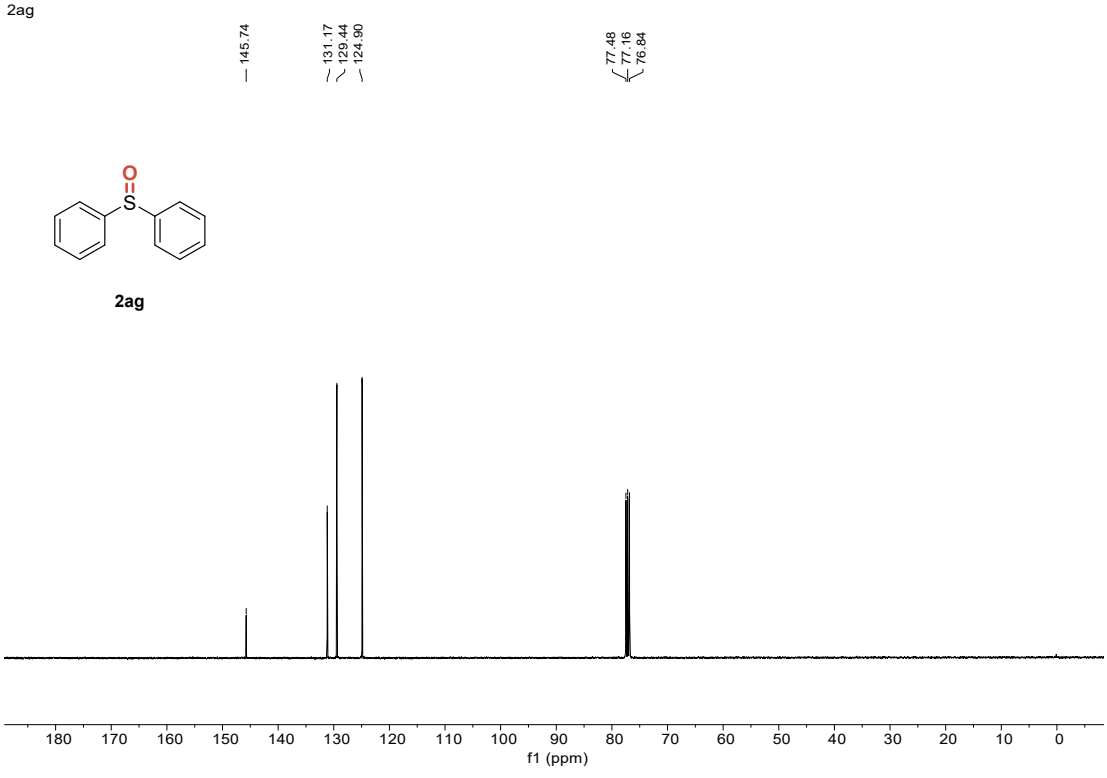


Fig. S79 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2ag**.

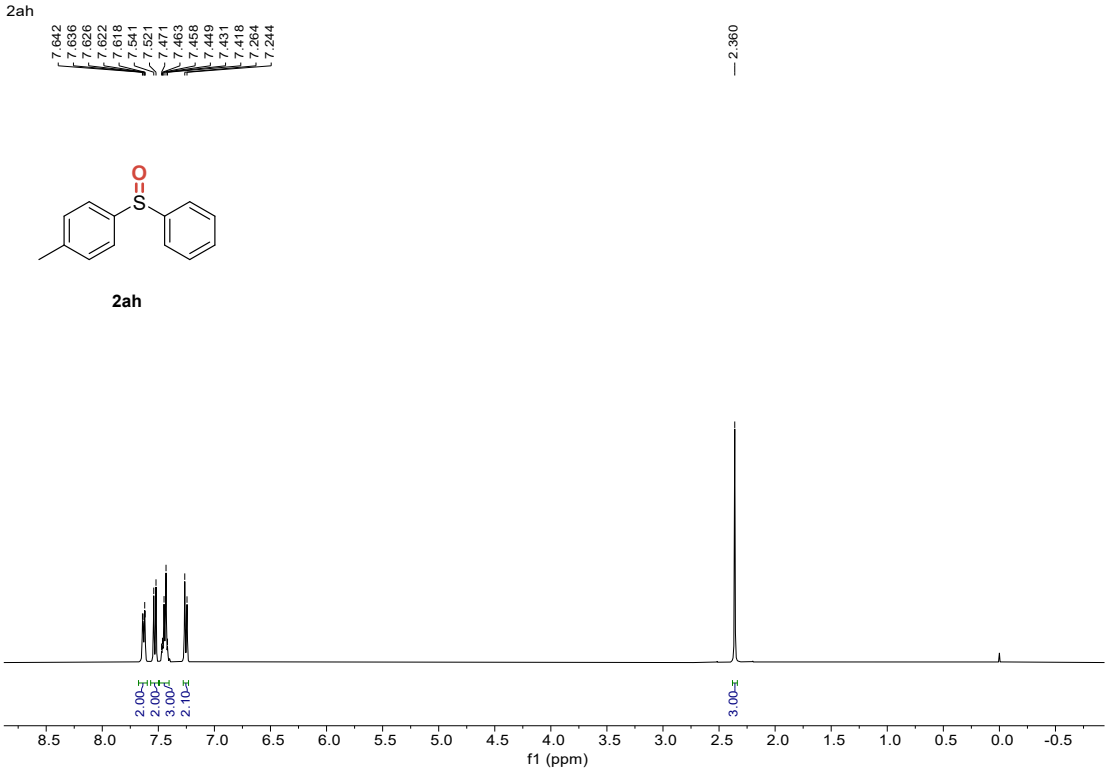


Fig. S80 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2ah**.

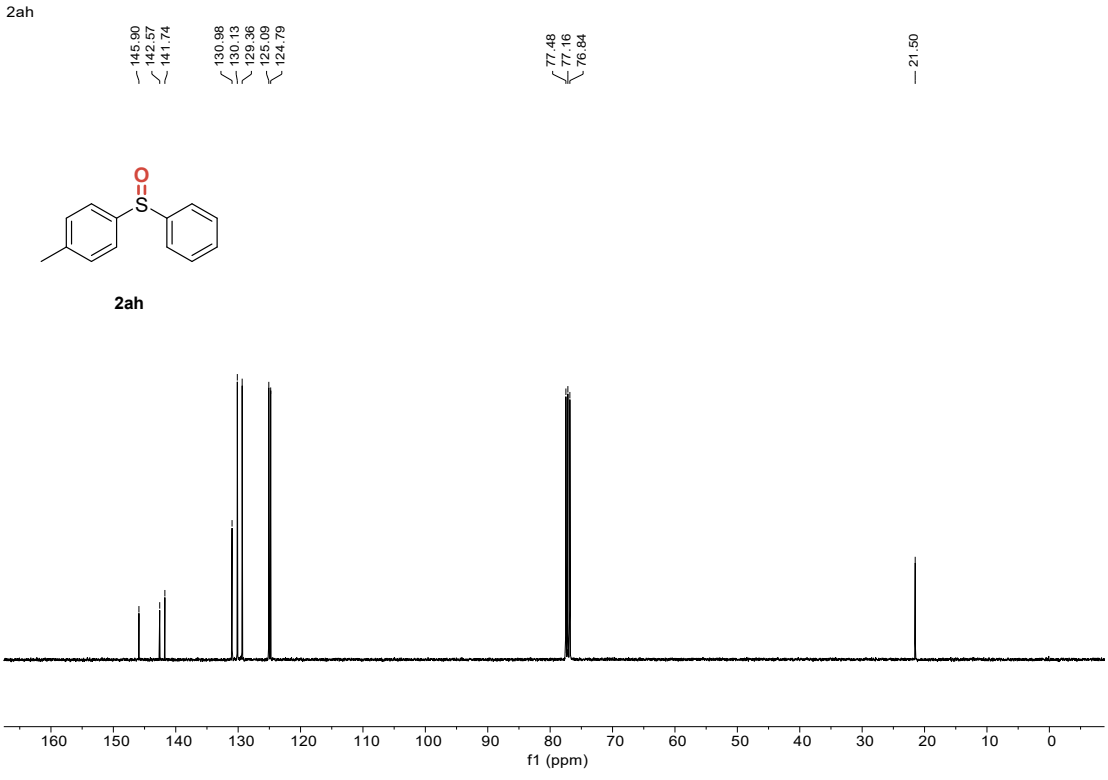


Fig. S81 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2ah**.

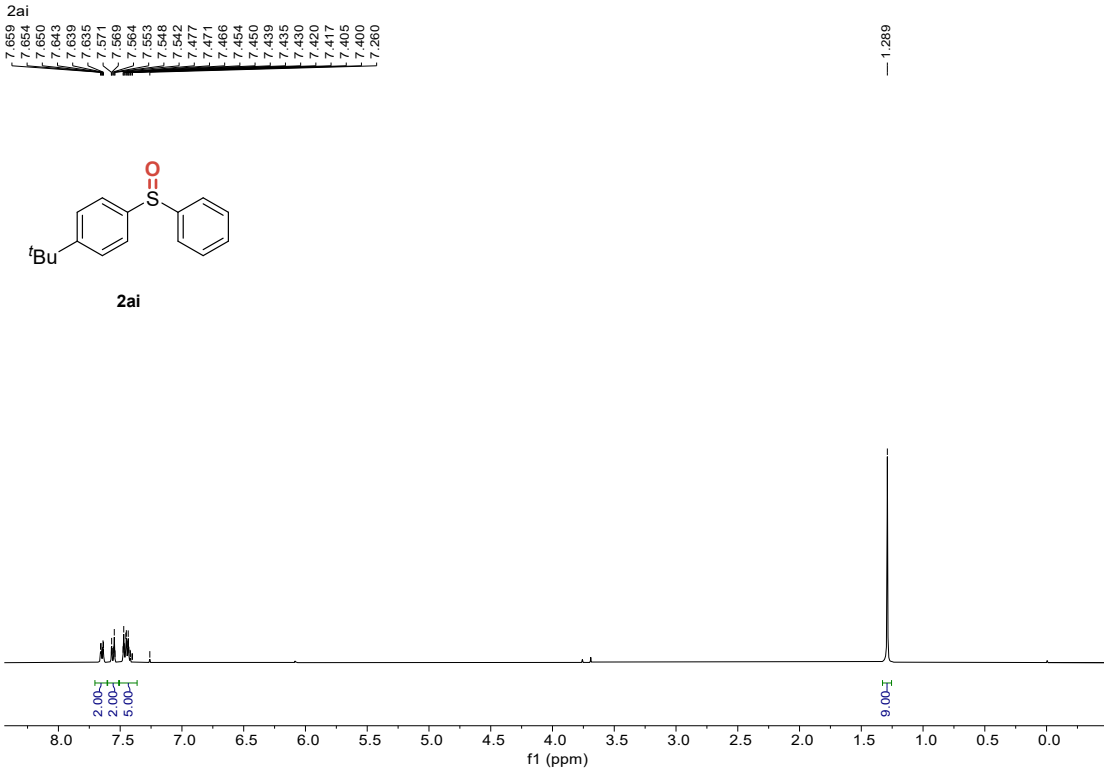


Fig. S82 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2ai**.

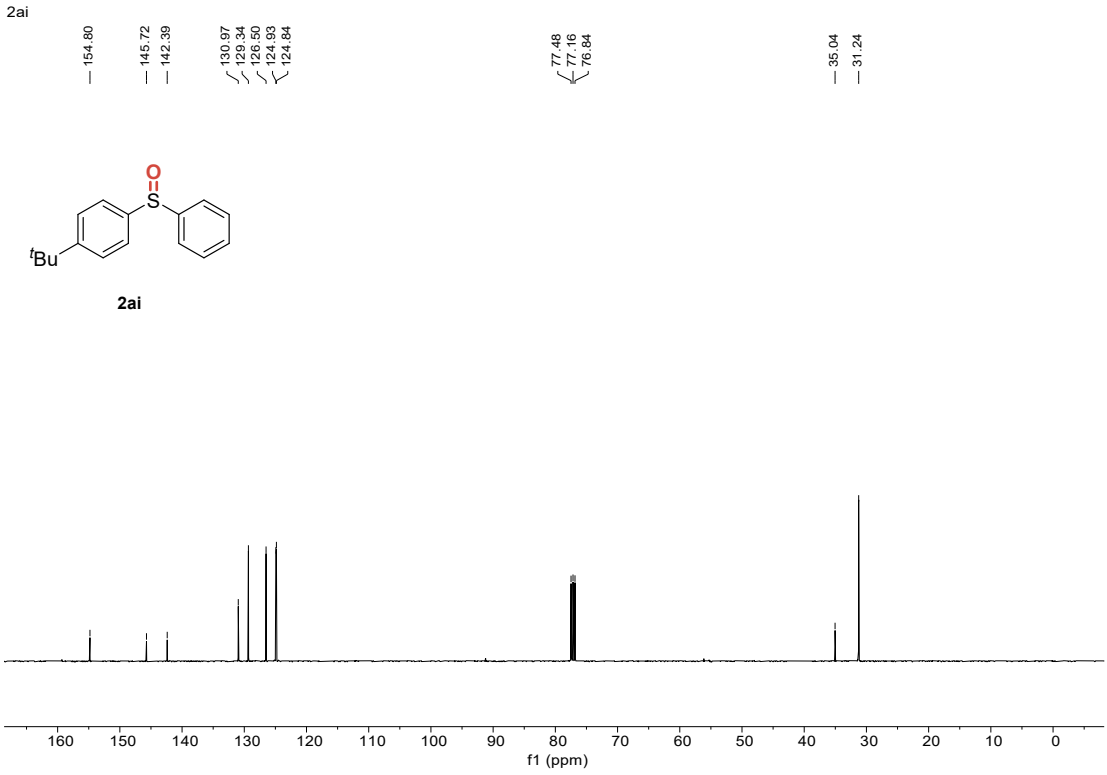


Fig. S83 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2ai**.

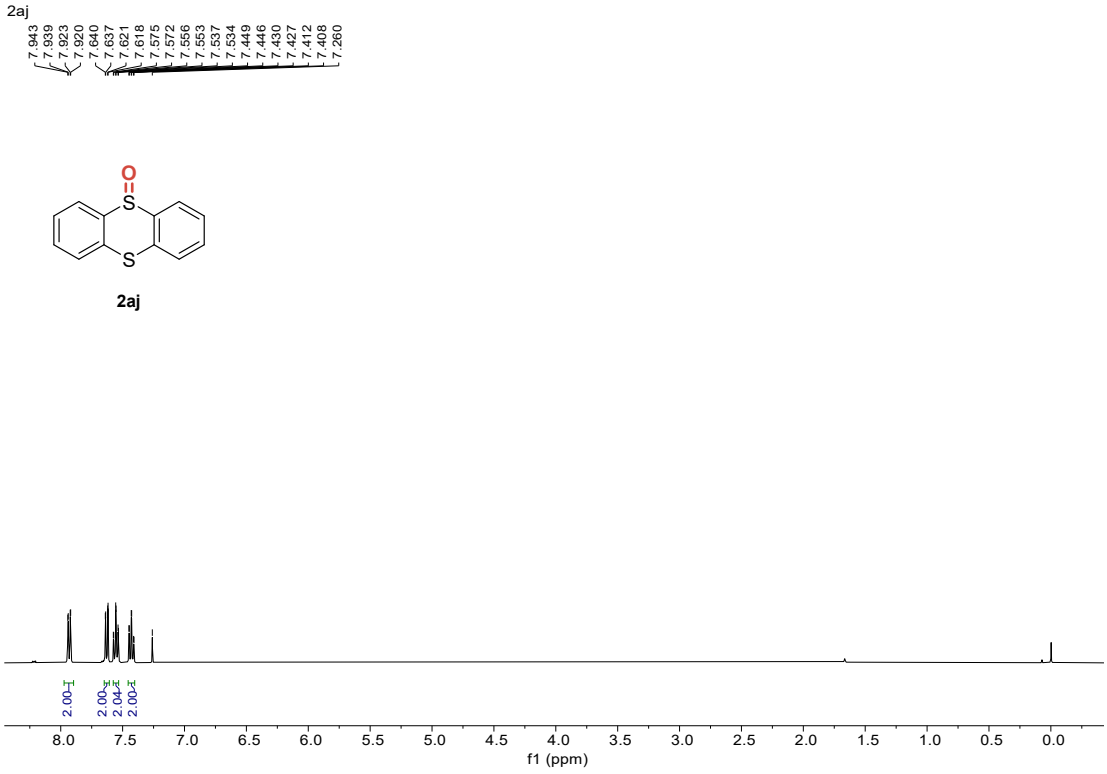


Fig. S84 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2aj**.

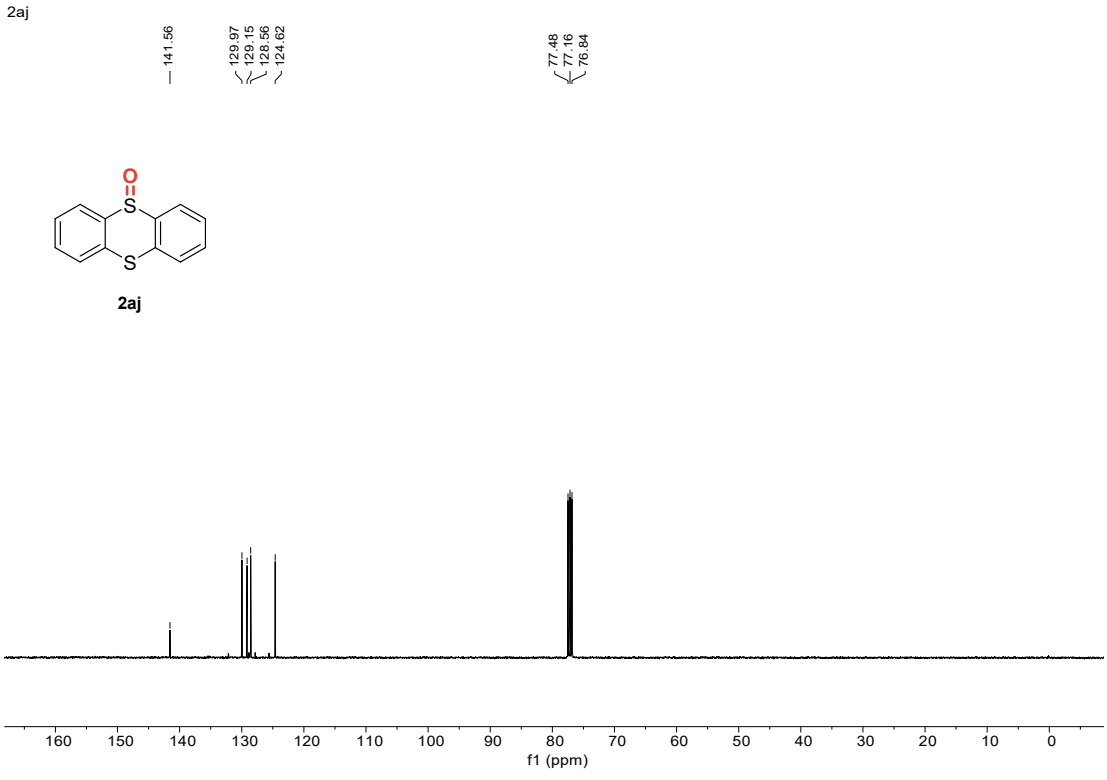


Fig. S85 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2aj**.

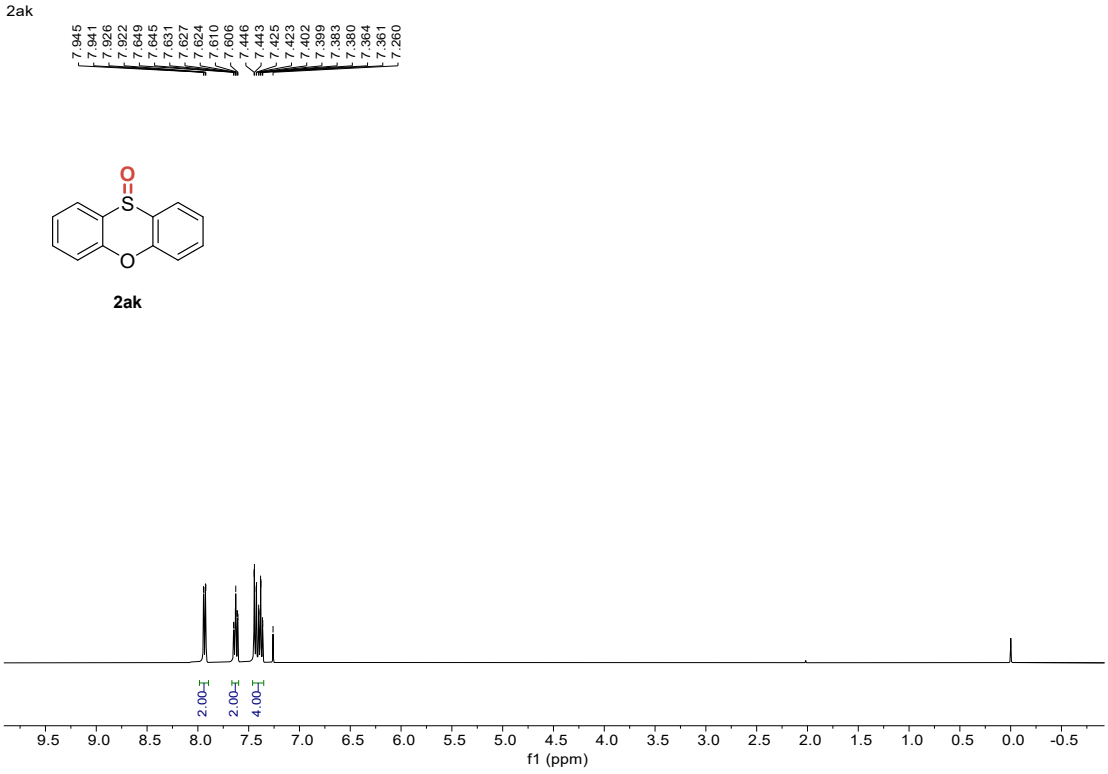


Fig. S86 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2ak**.

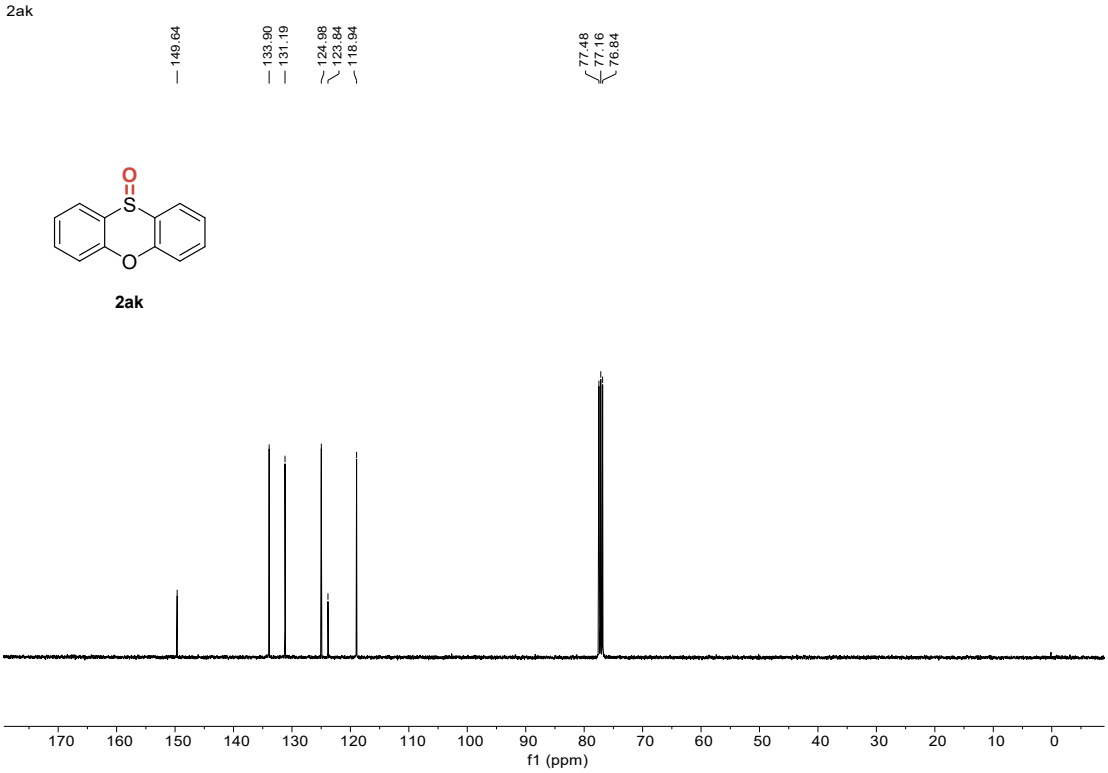


Fig. S87 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2ak**.

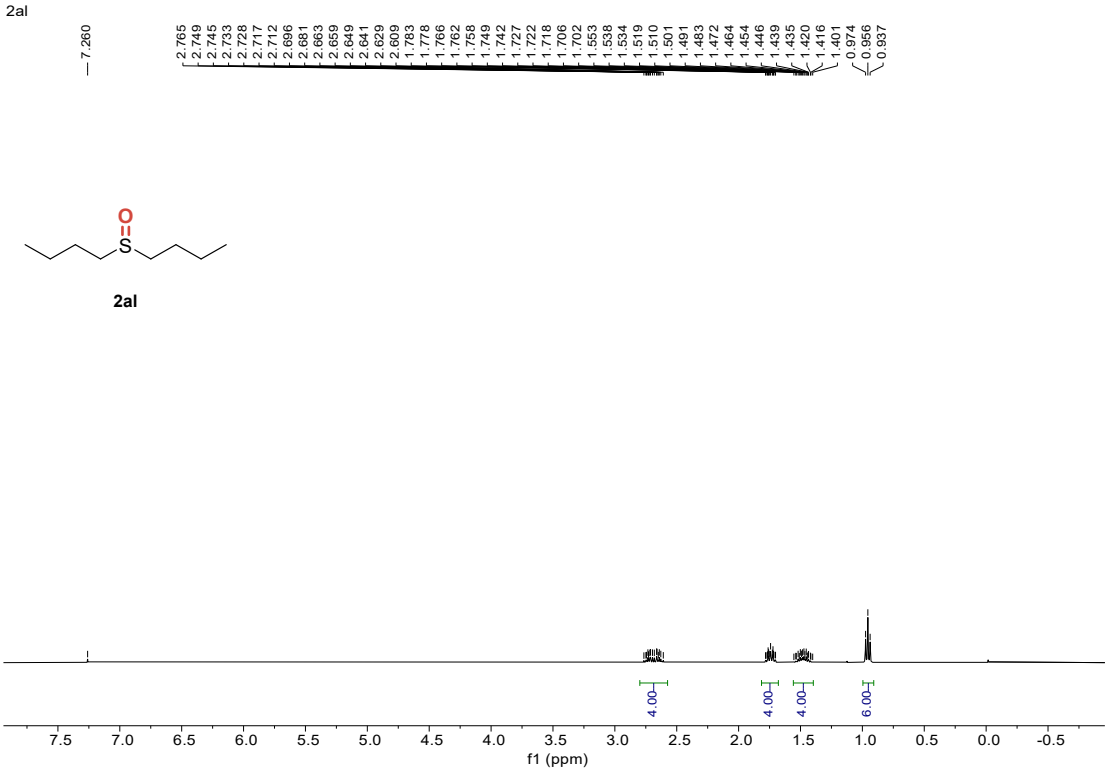


Fig. S88 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2al**.

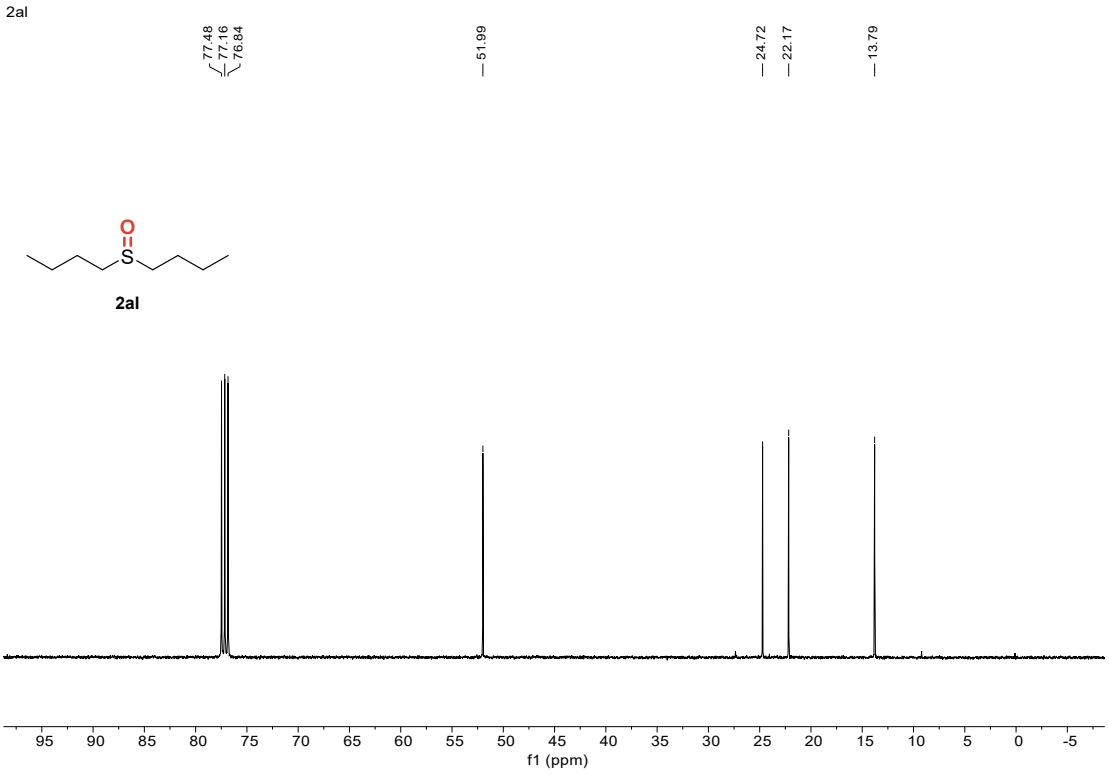


Fig. S89 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2al**.

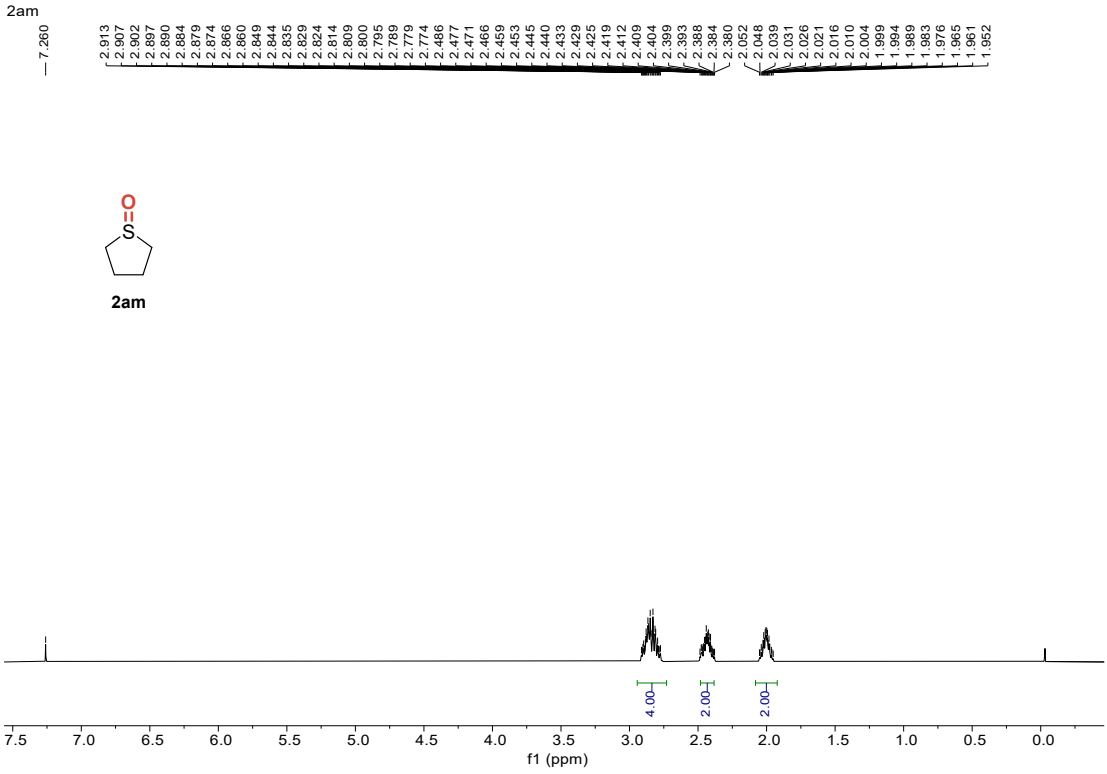


Fig. S90 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2am**.

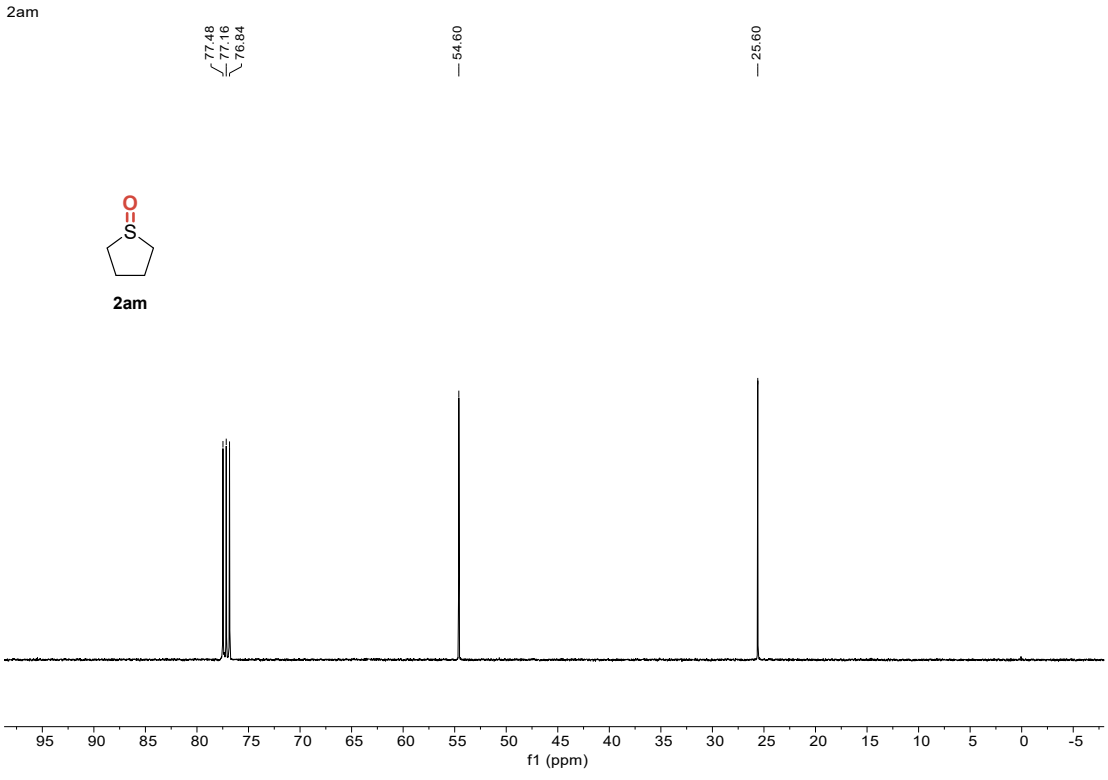


Fig. S91 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2am**.

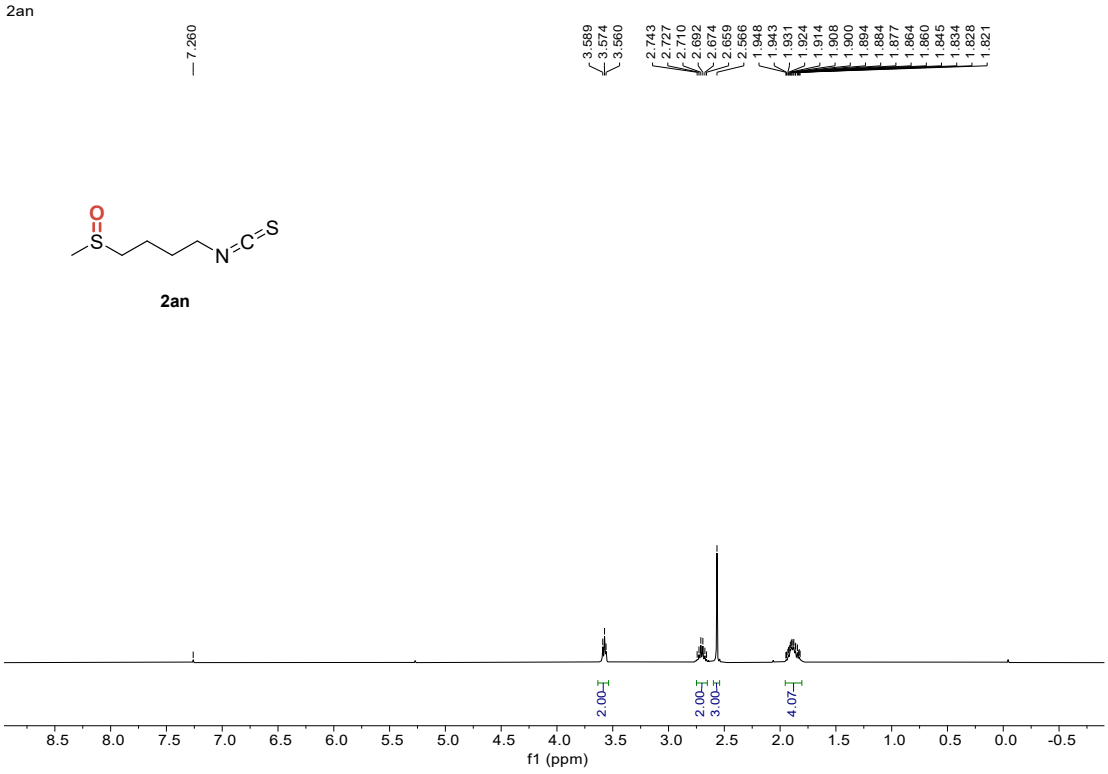


Fig. S92 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2an**.

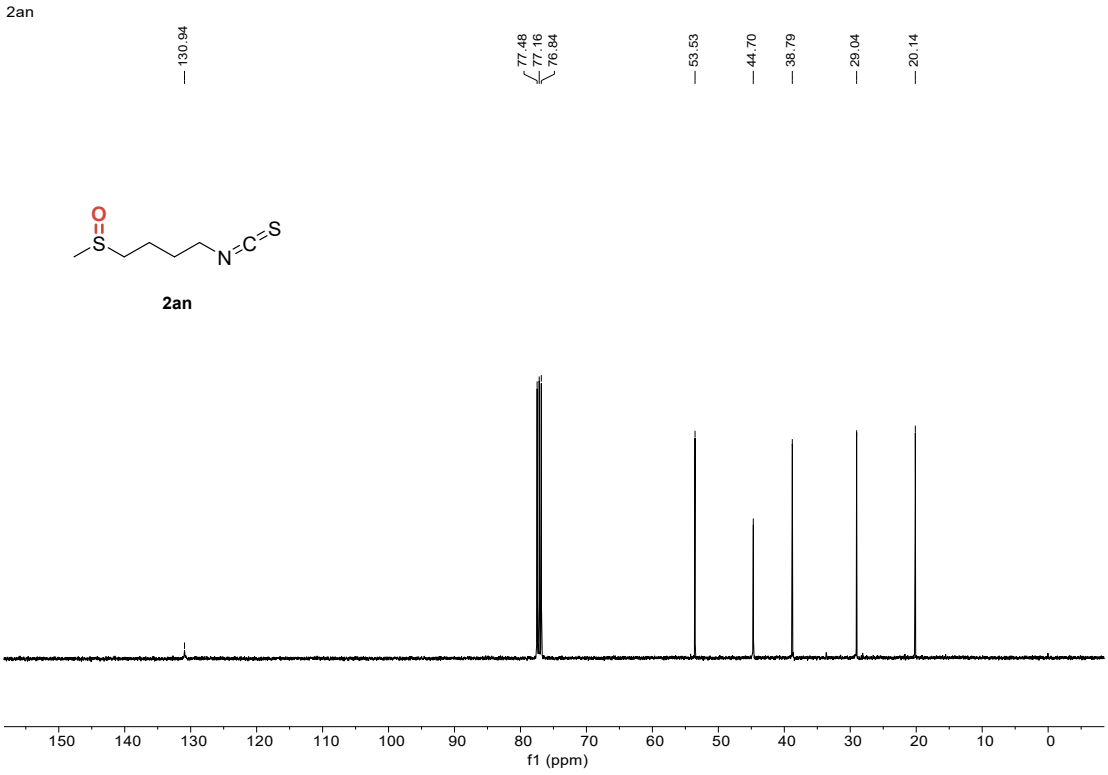


Fig. S93 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2an**.

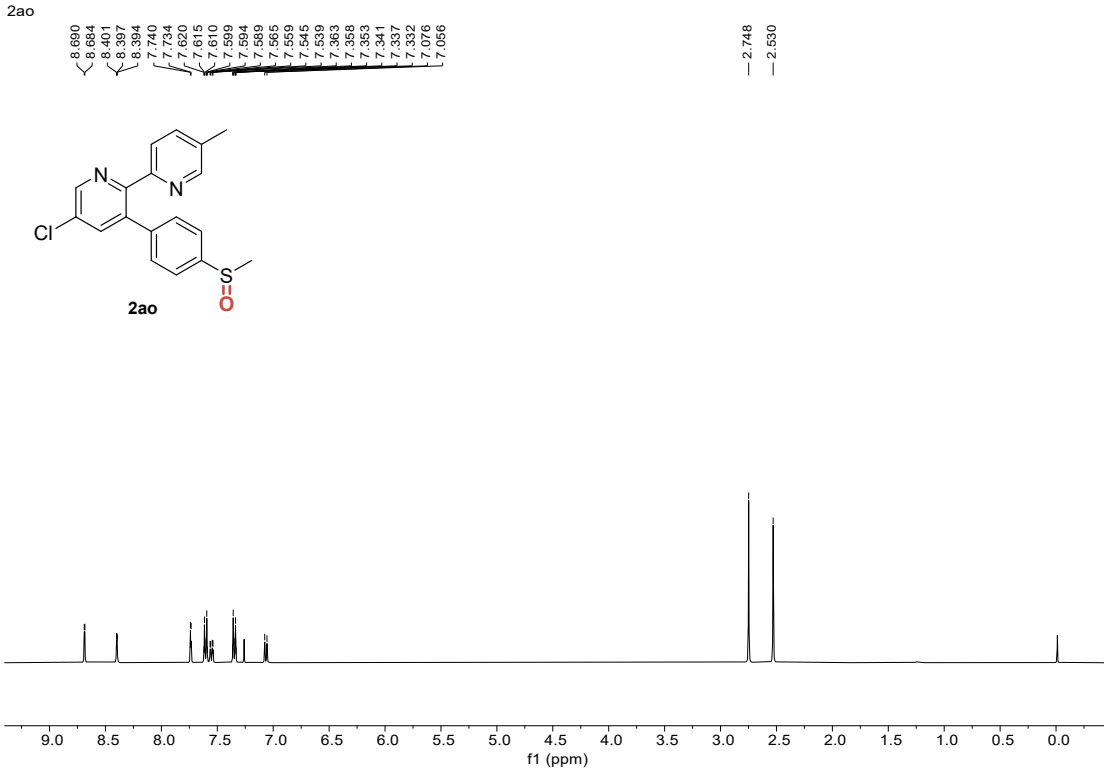


Fig. S94 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2ao**.

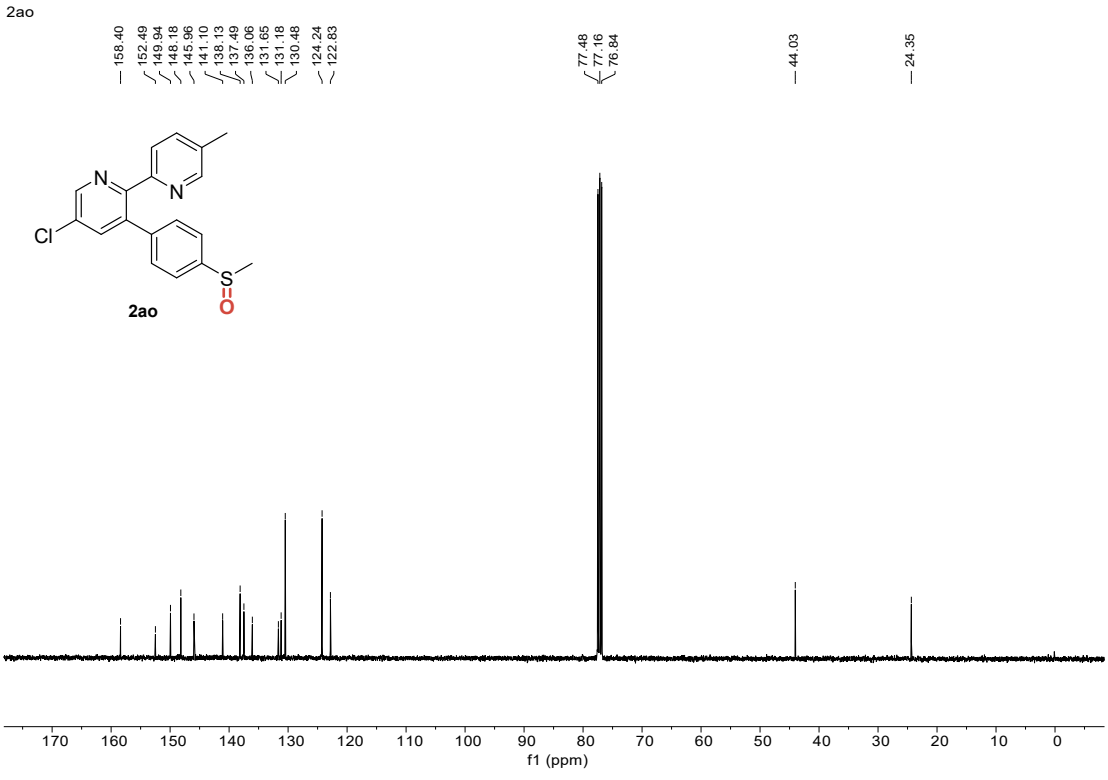


Fig. S95 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2ao**.

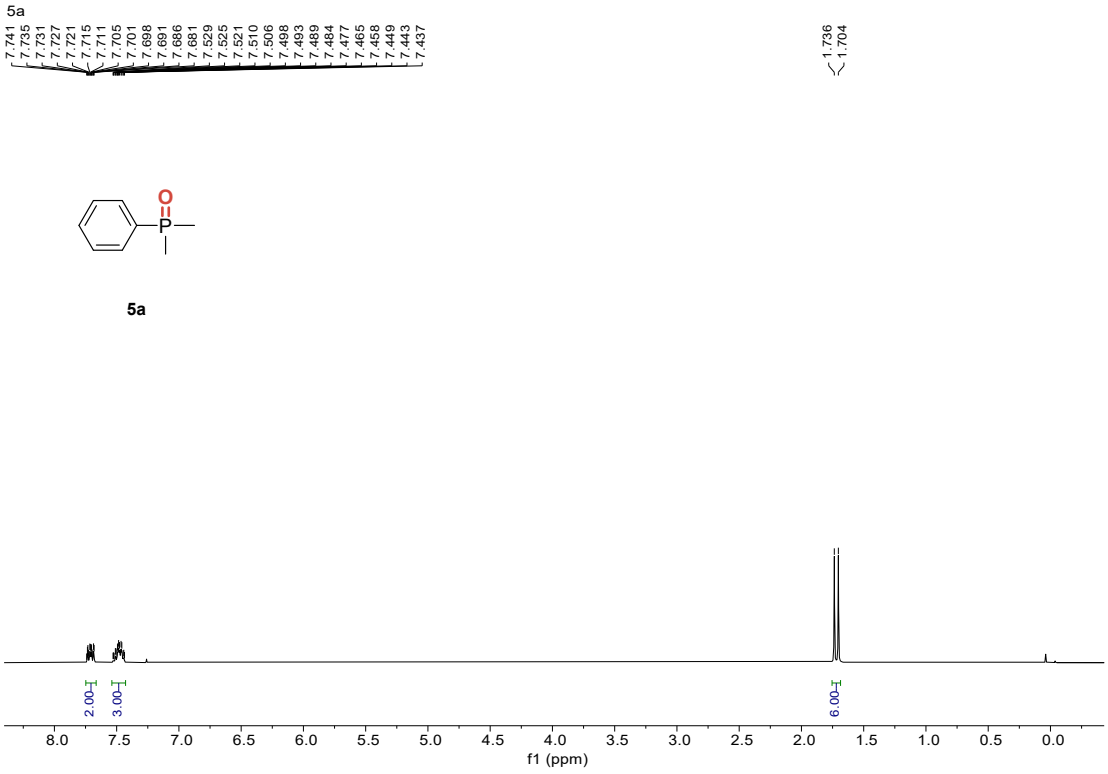


Fig. S96 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5a**.

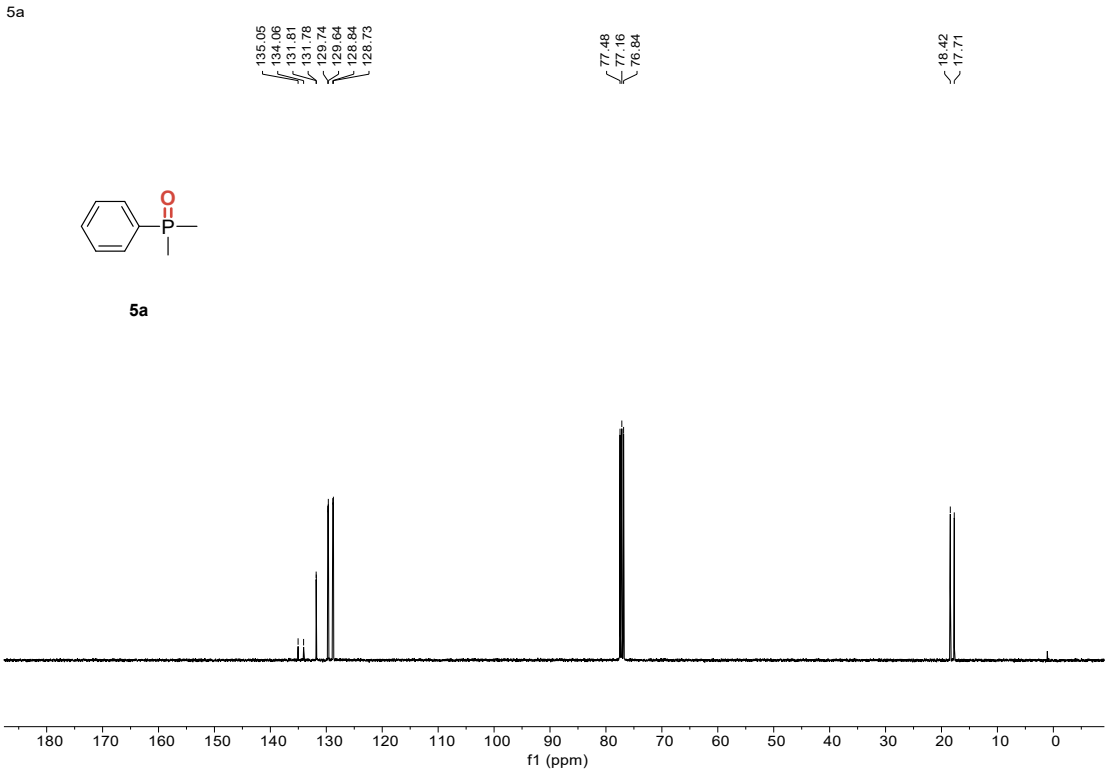


Fig. S97 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5a**.

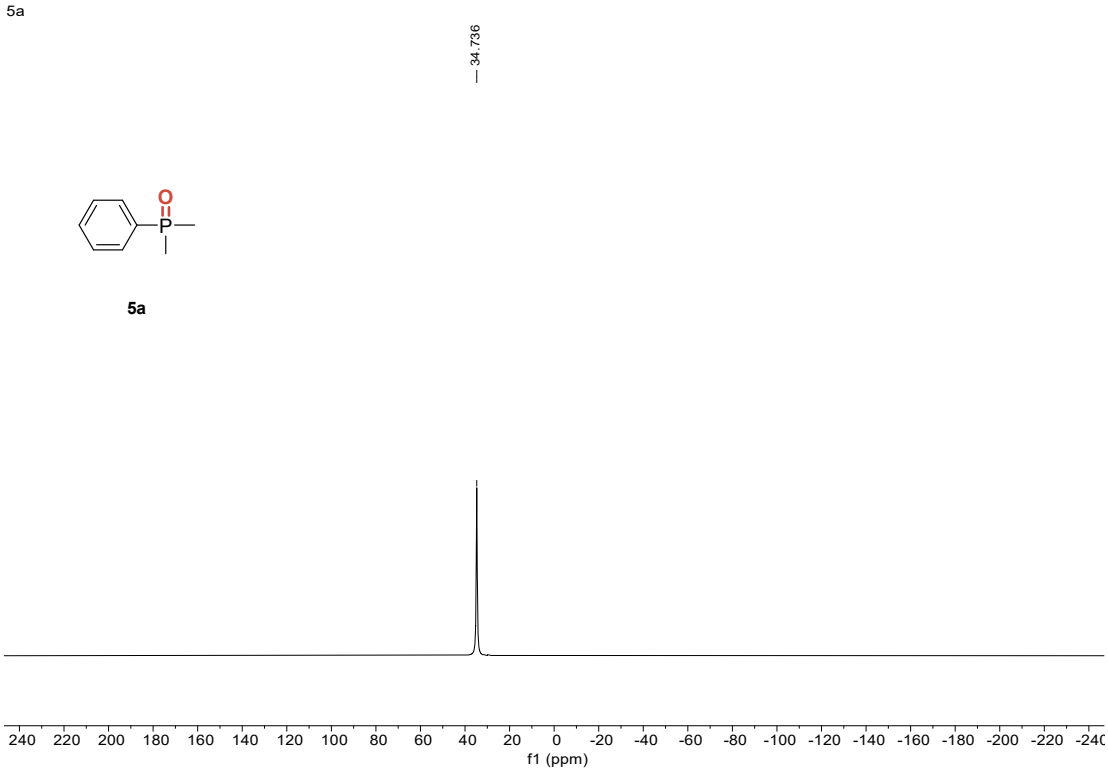


Fig. S98 ^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **5a**.

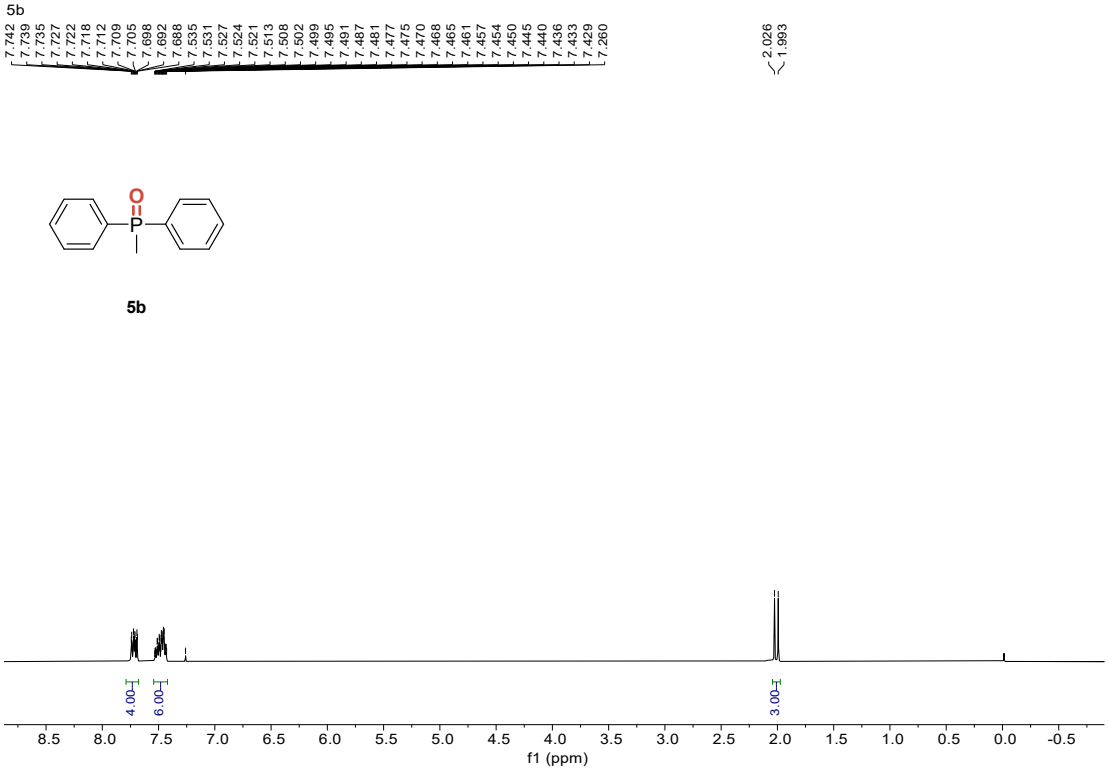


Fig. S99 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5b**.

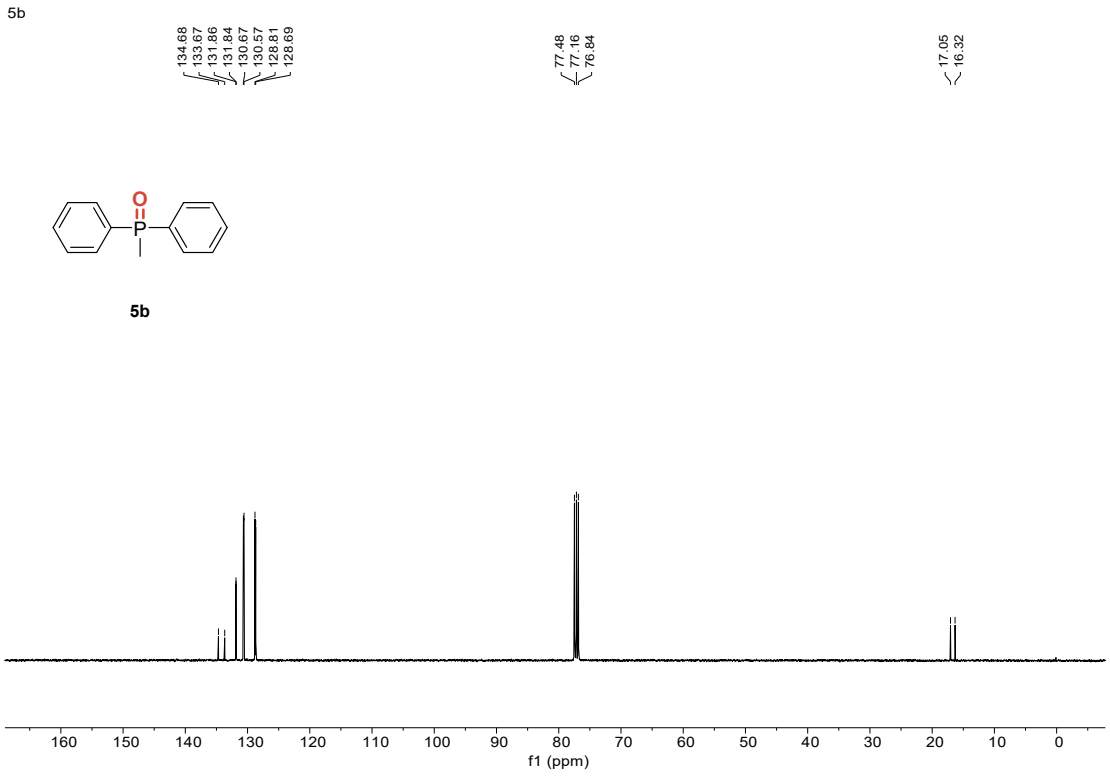


Fig. S100 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5b**.

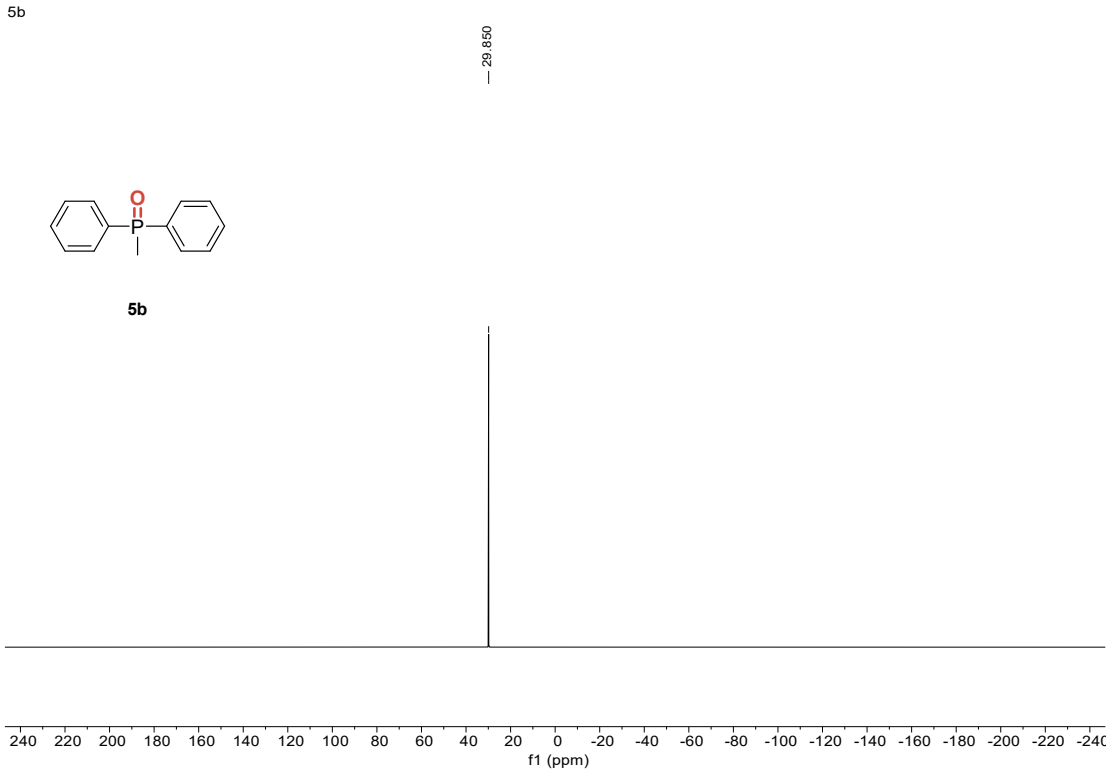


Fig. S101 ^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **5b**.

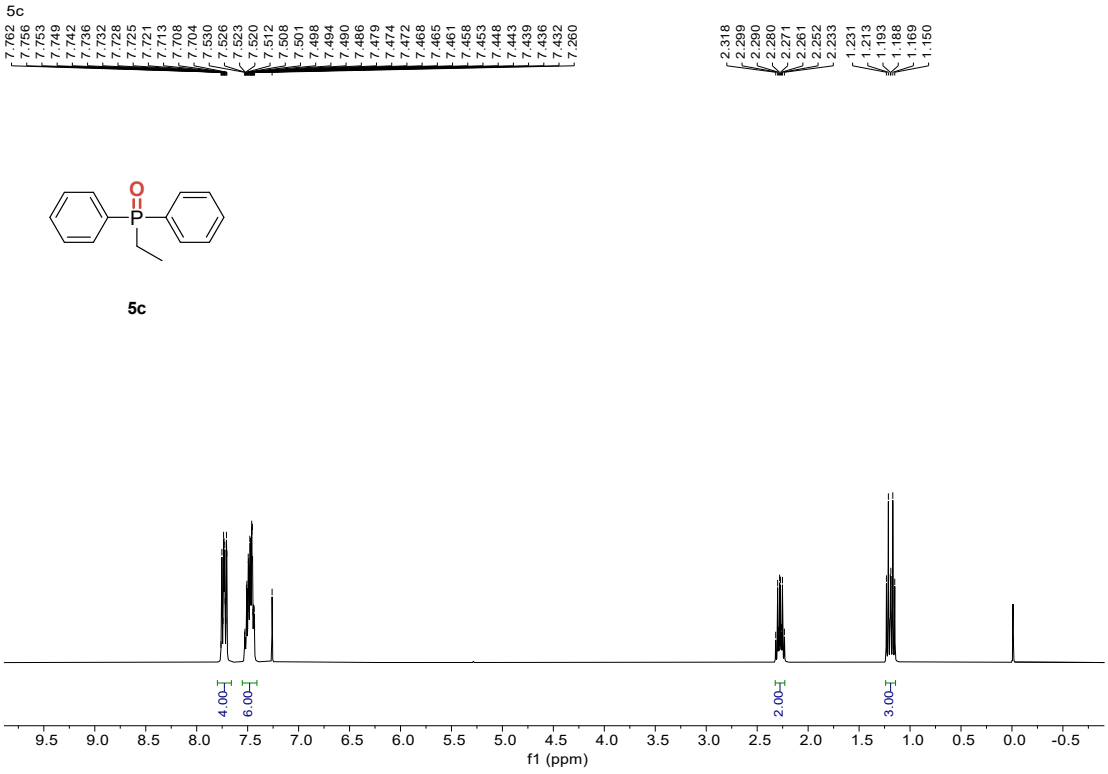


Fig. S102 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5c**.

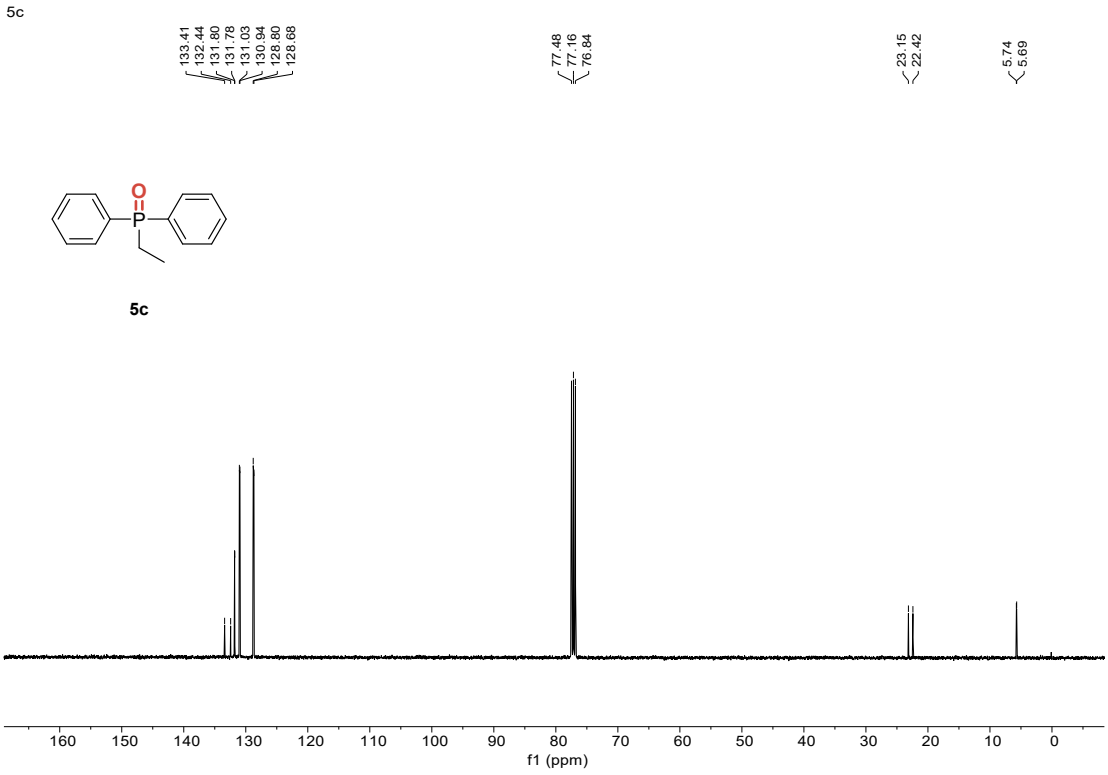


Fig. S103 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5c**.

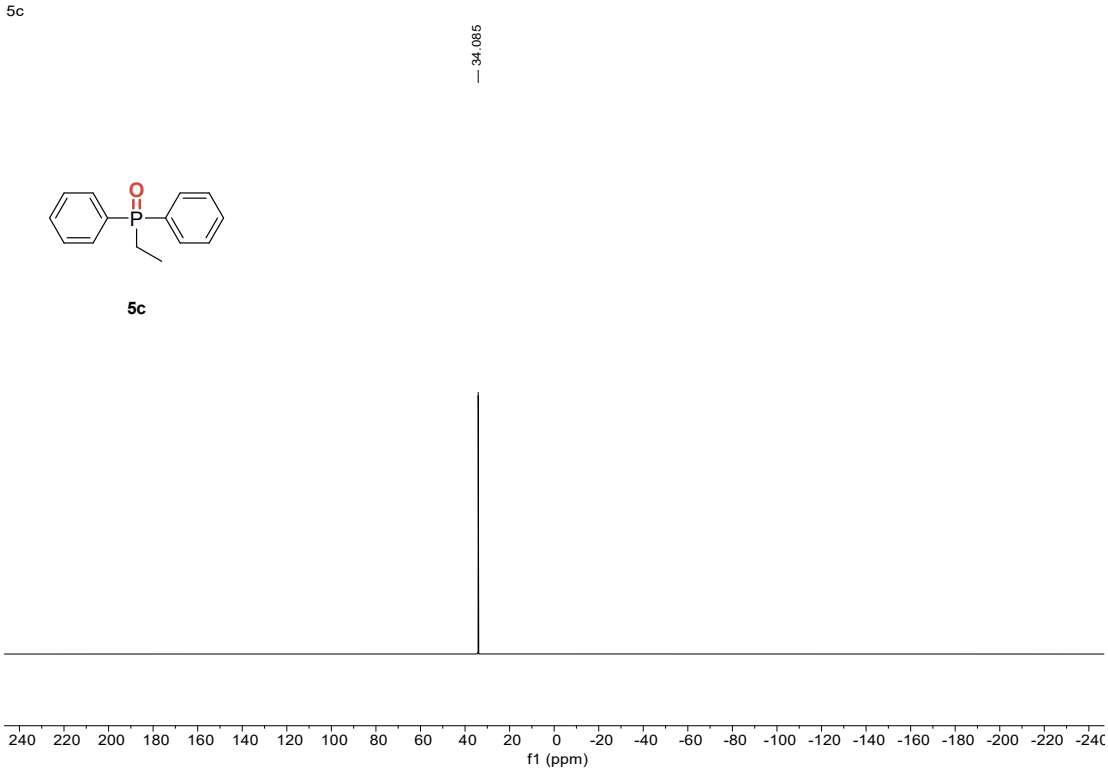


Fig. S104 ^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **5c**.

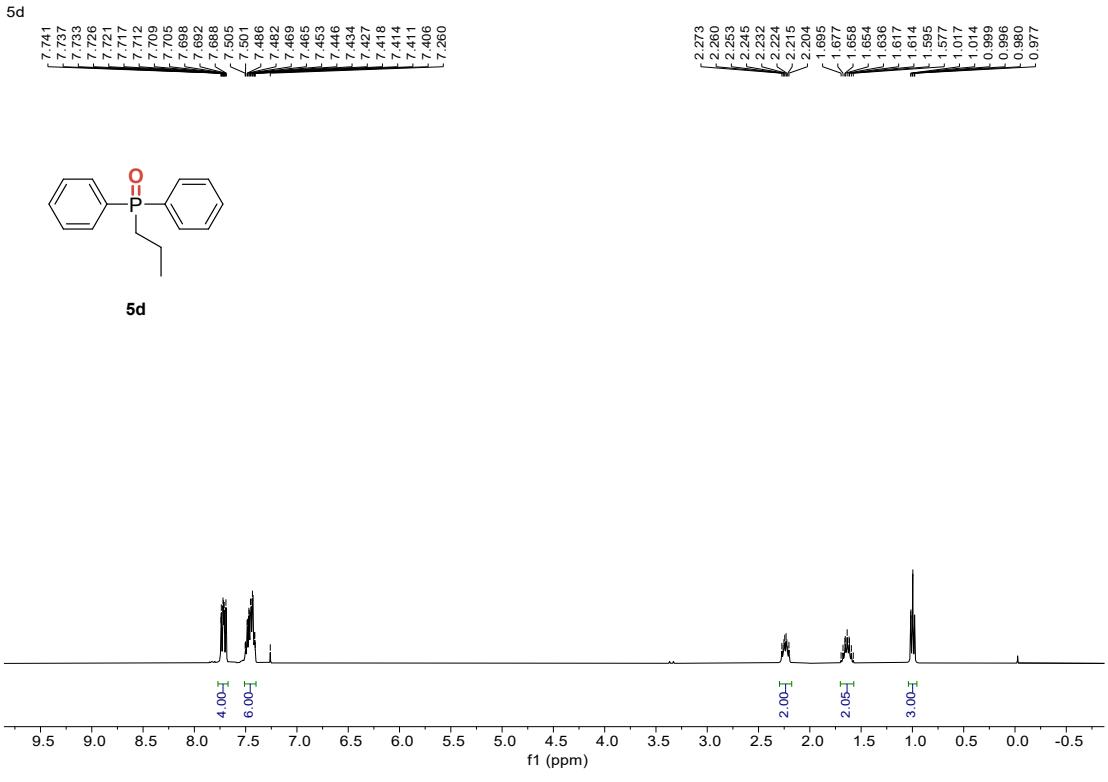


Fig. S105 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5d**.

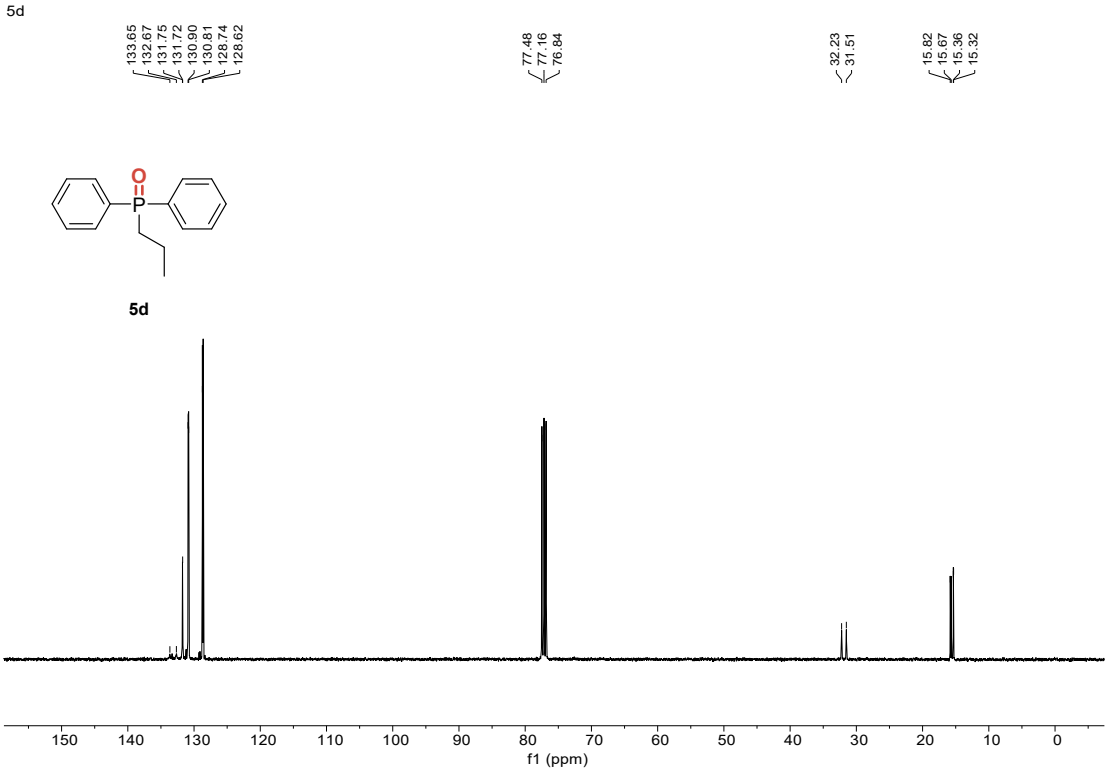


Fig. S106 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5d**.

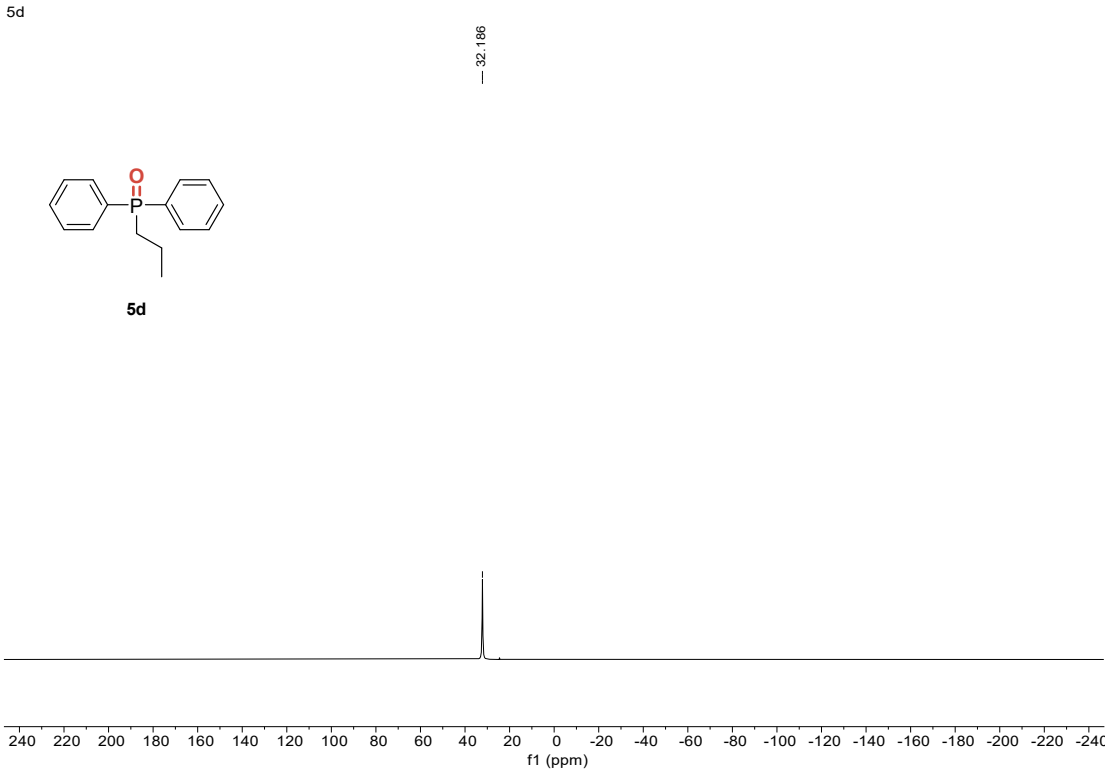


Fig. S107 ^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **5d**.

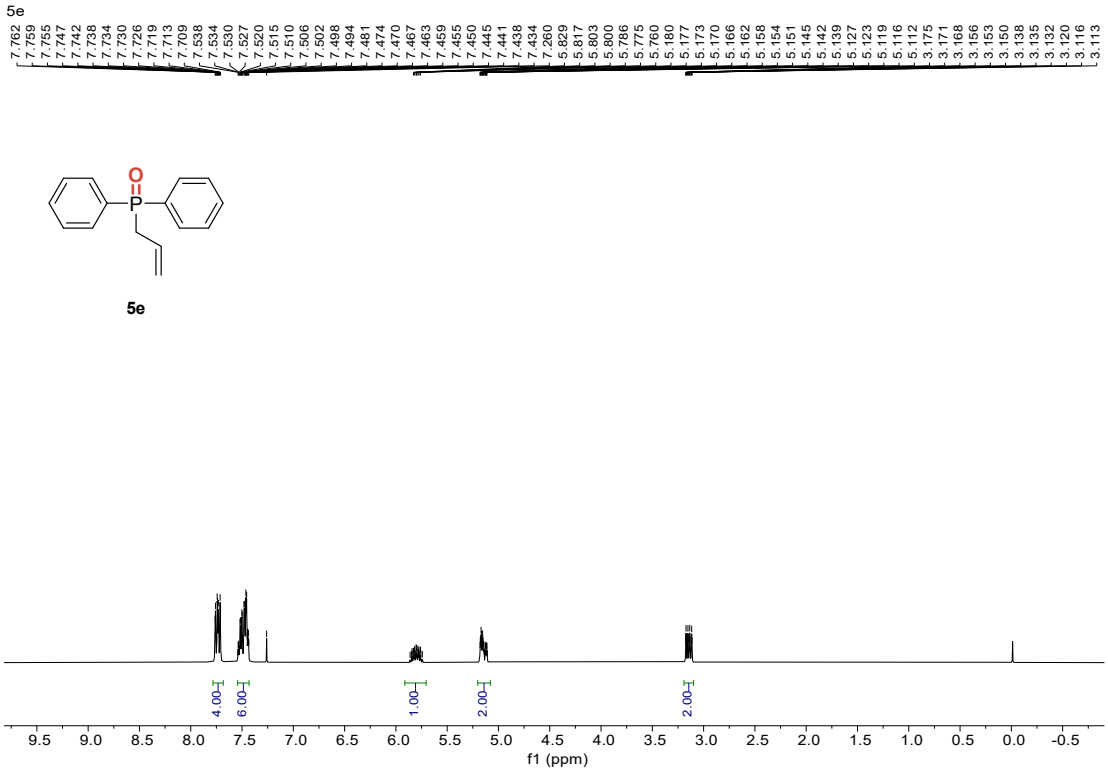


Fig. S108 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5e**.

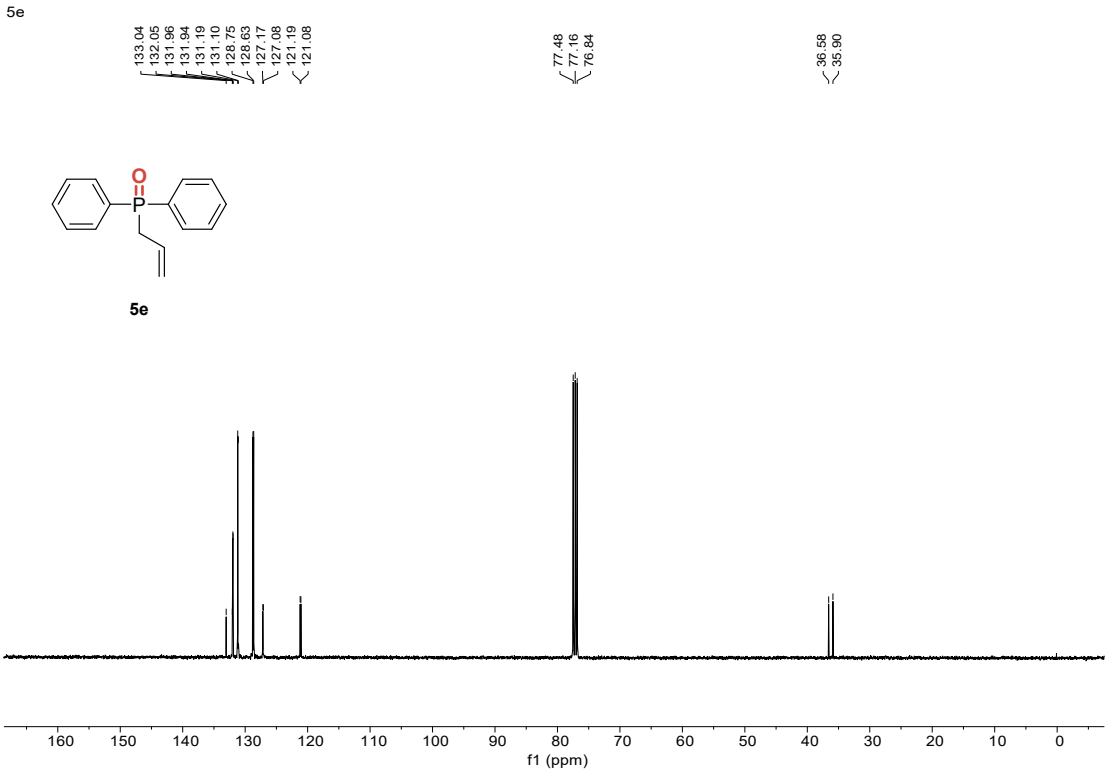


Fig. S109 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5e**.

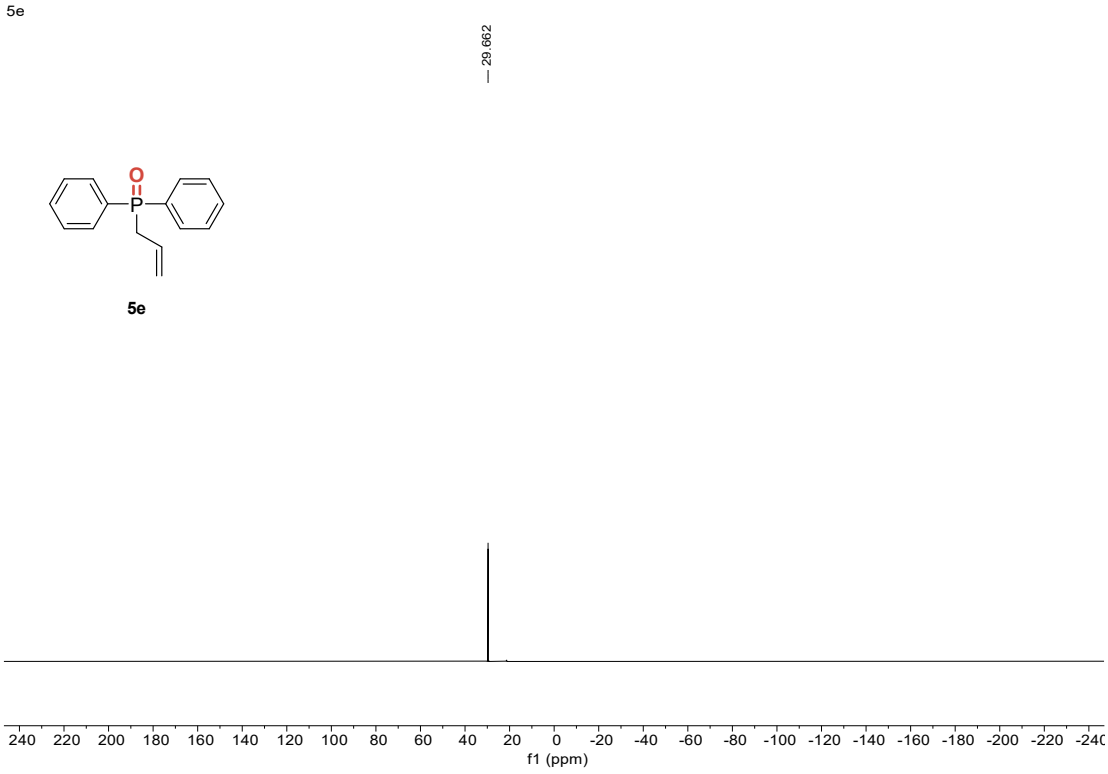


Fig. S110 ^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **5e**.

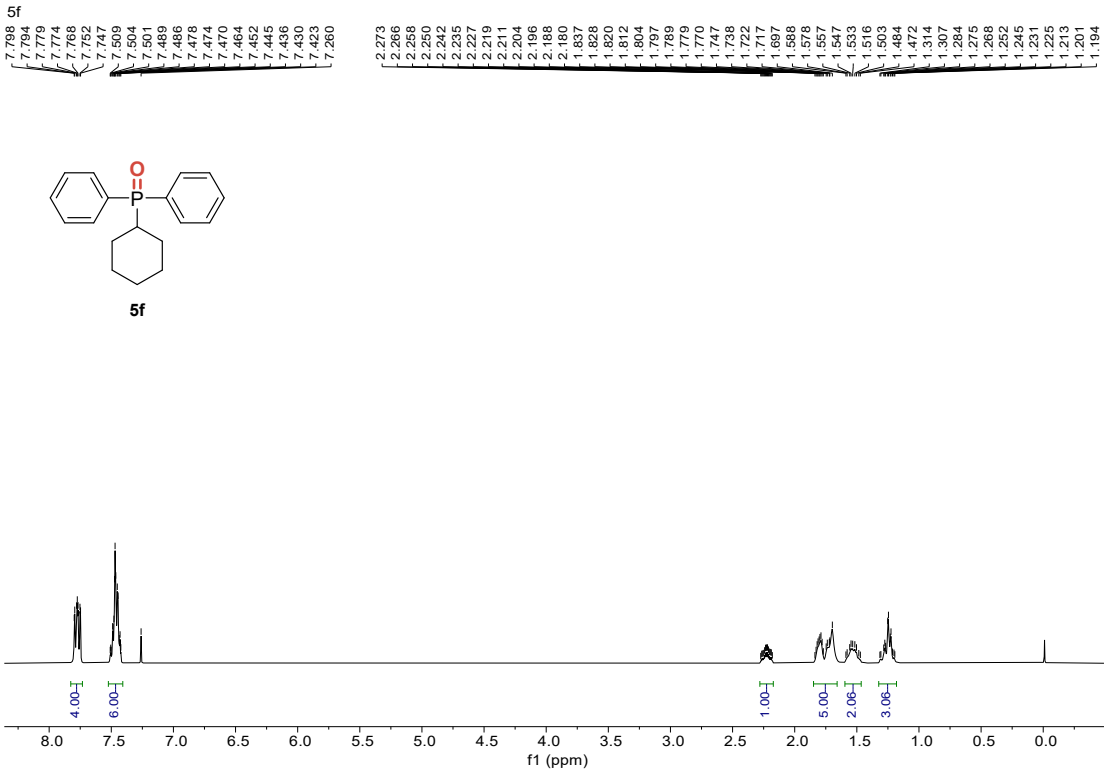


Fig. S111 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5f**.

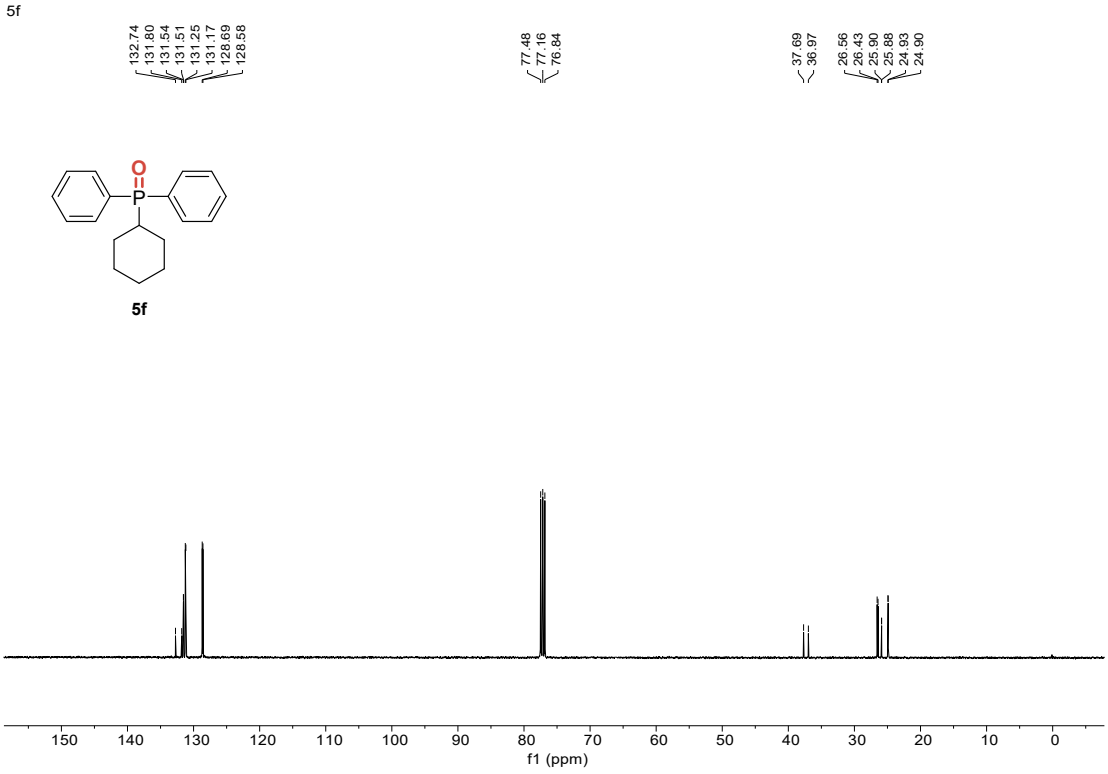


Fig. S112 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5f**.

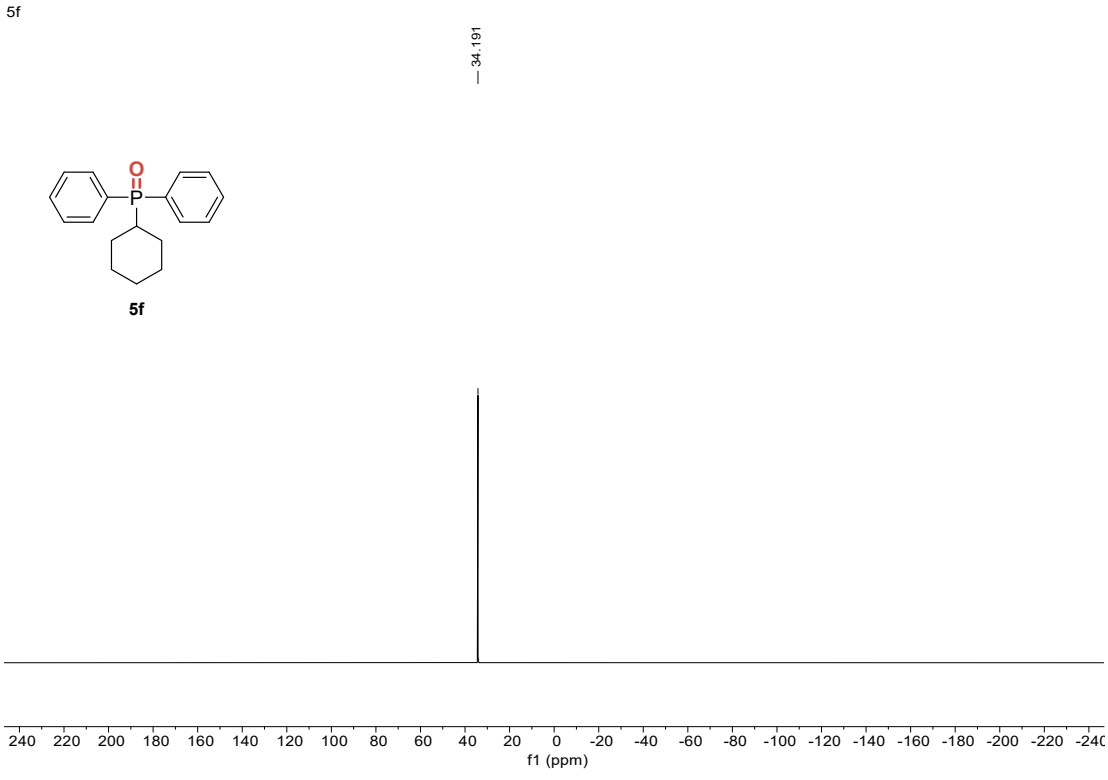


Fig. S113 ^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **5f**.

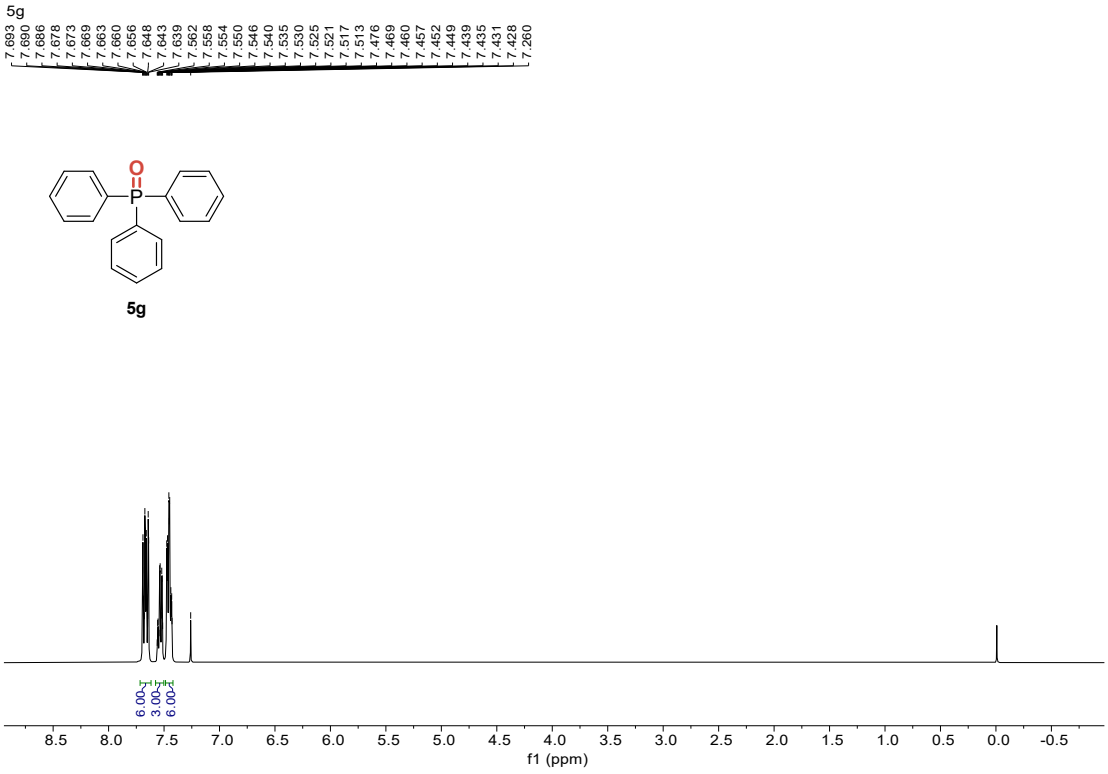


Fig. S114 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5g**.

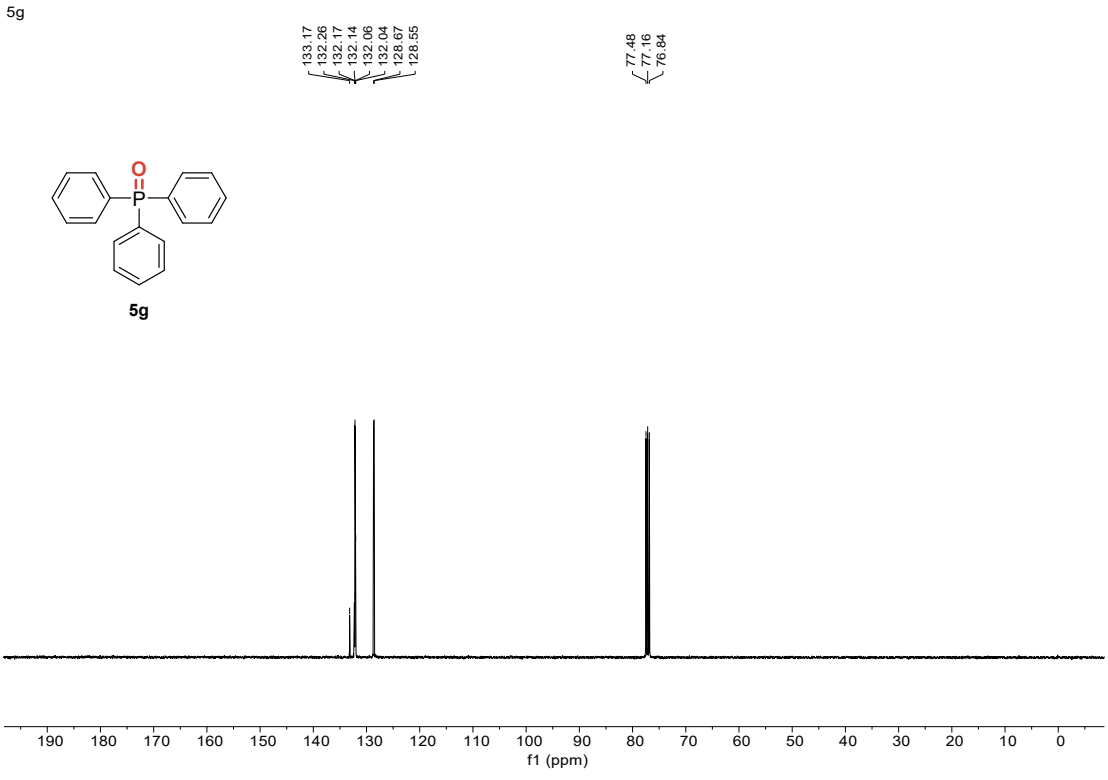


Fig. S115 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5g**.

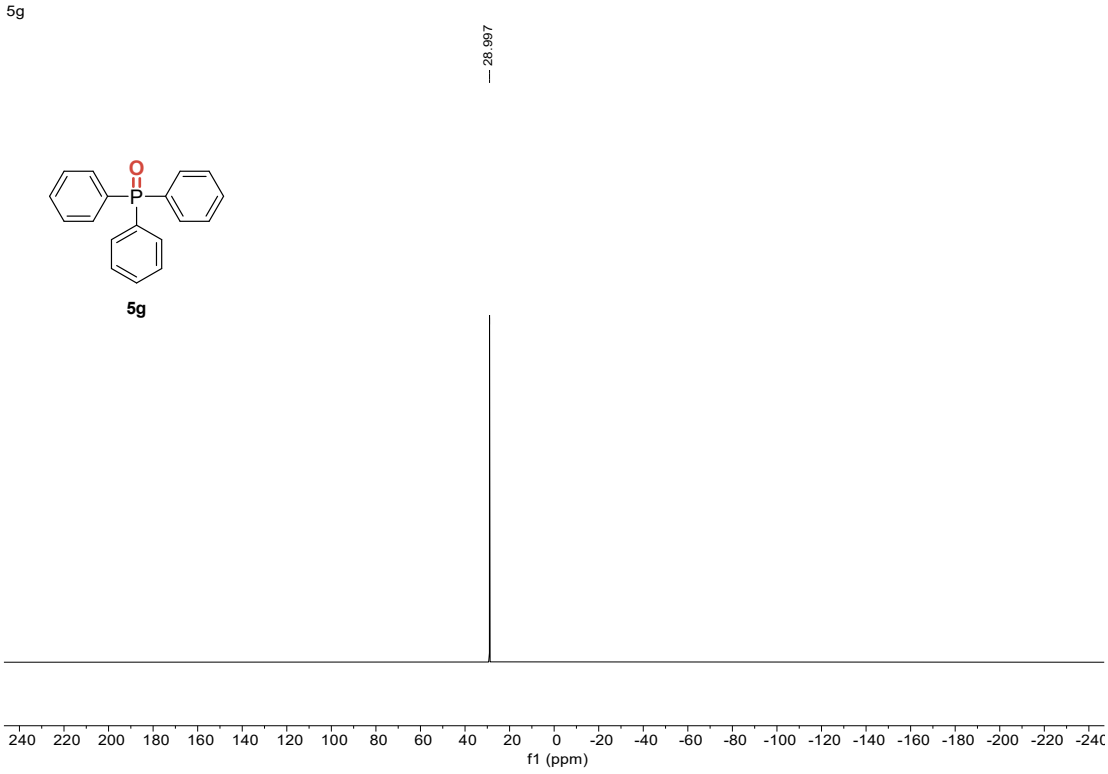


Fig. S116 ^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **5g**.

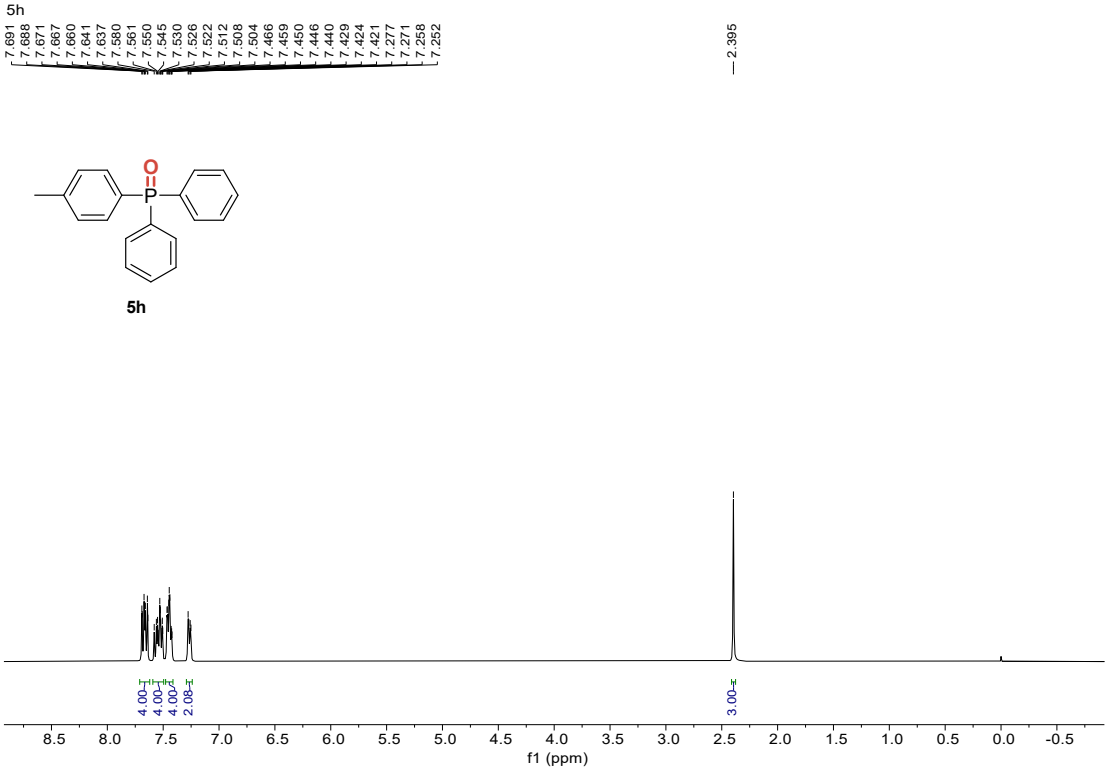


Fig. S117 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5h**.

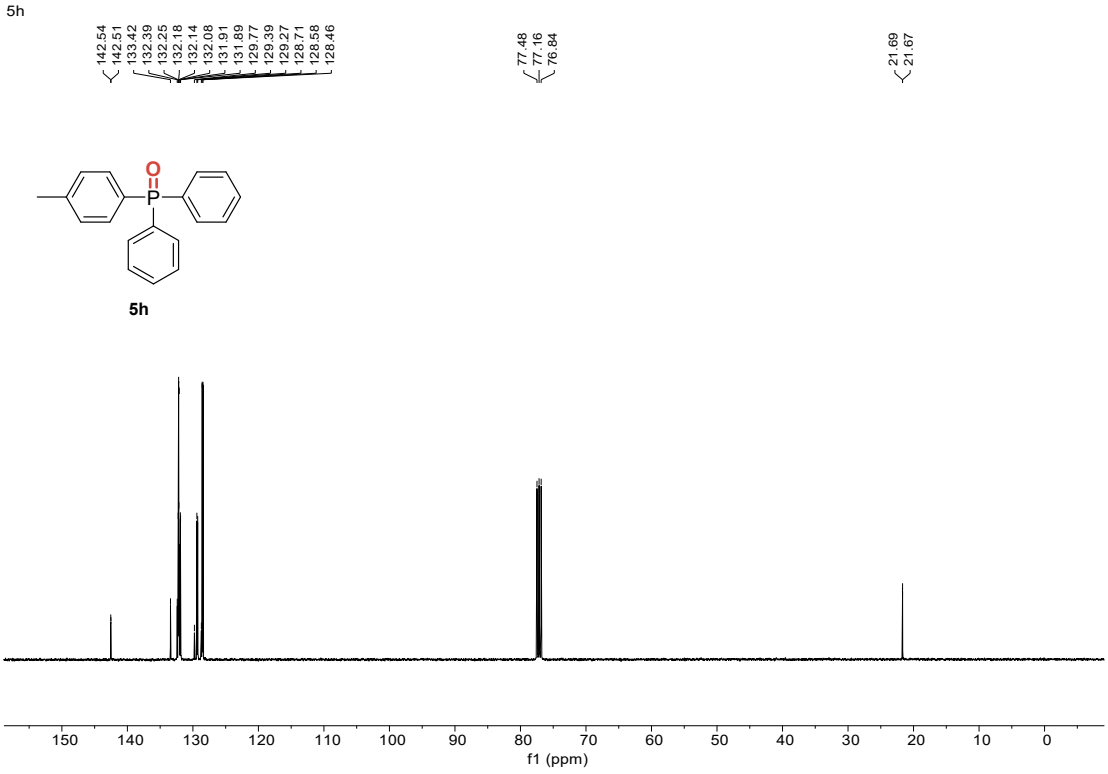


Fig. S118 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5h**.

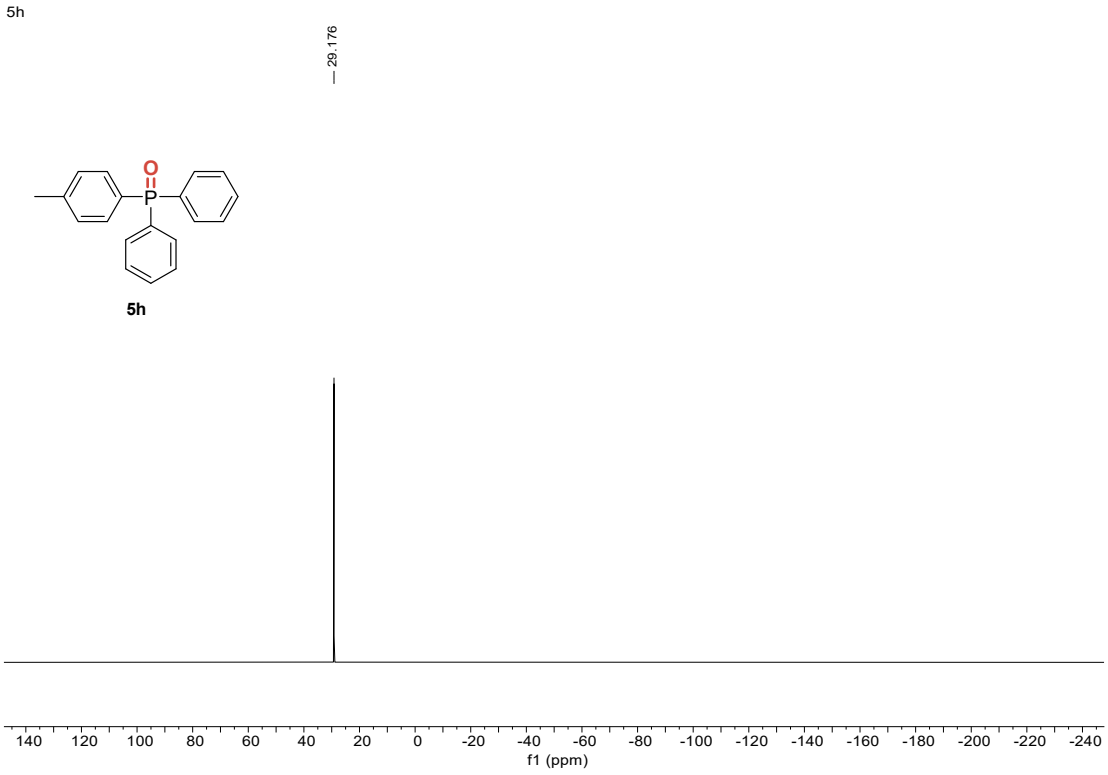


Fig. S119 ^{31}P NMR spectrum (243 MHz, $CDCl_3$) of **5h**.

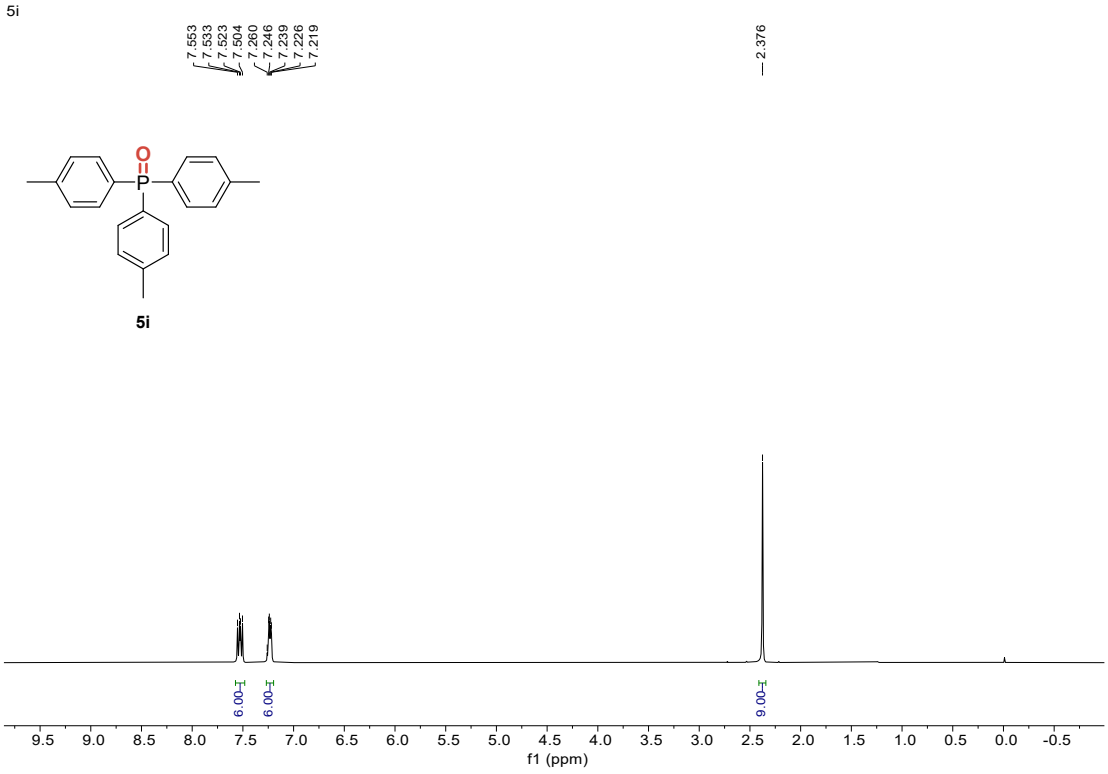


Fig. S120 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5i**.

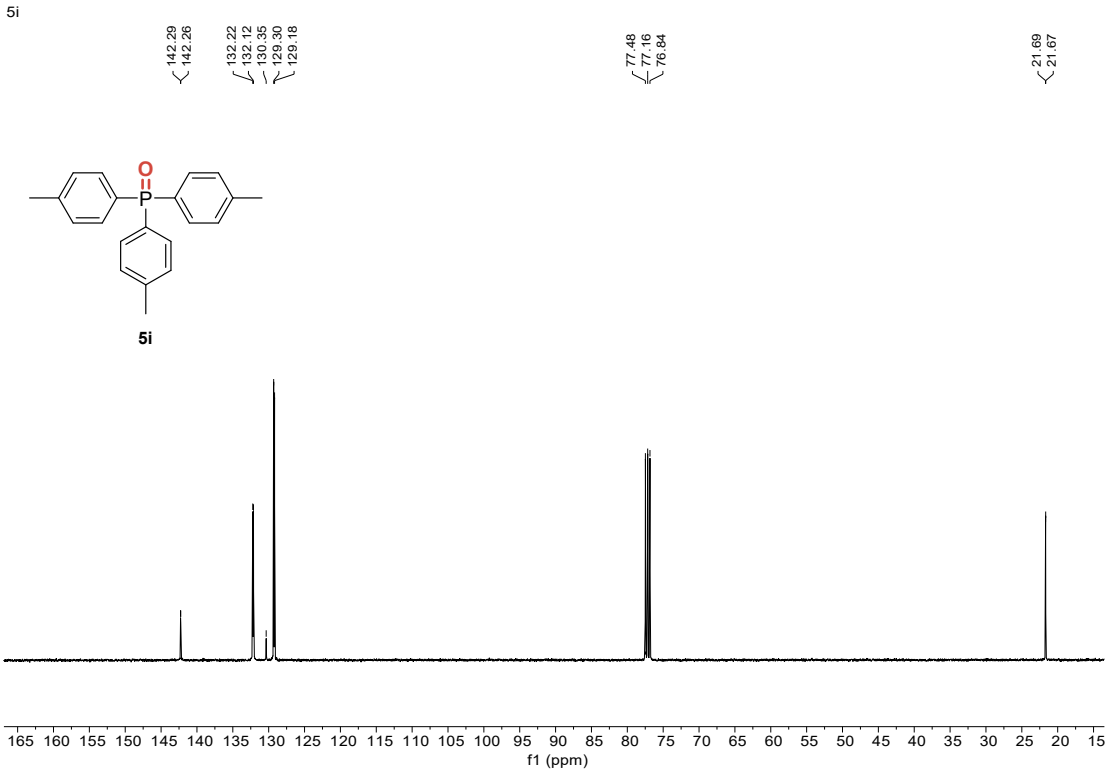


Fig. S121 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5i**.

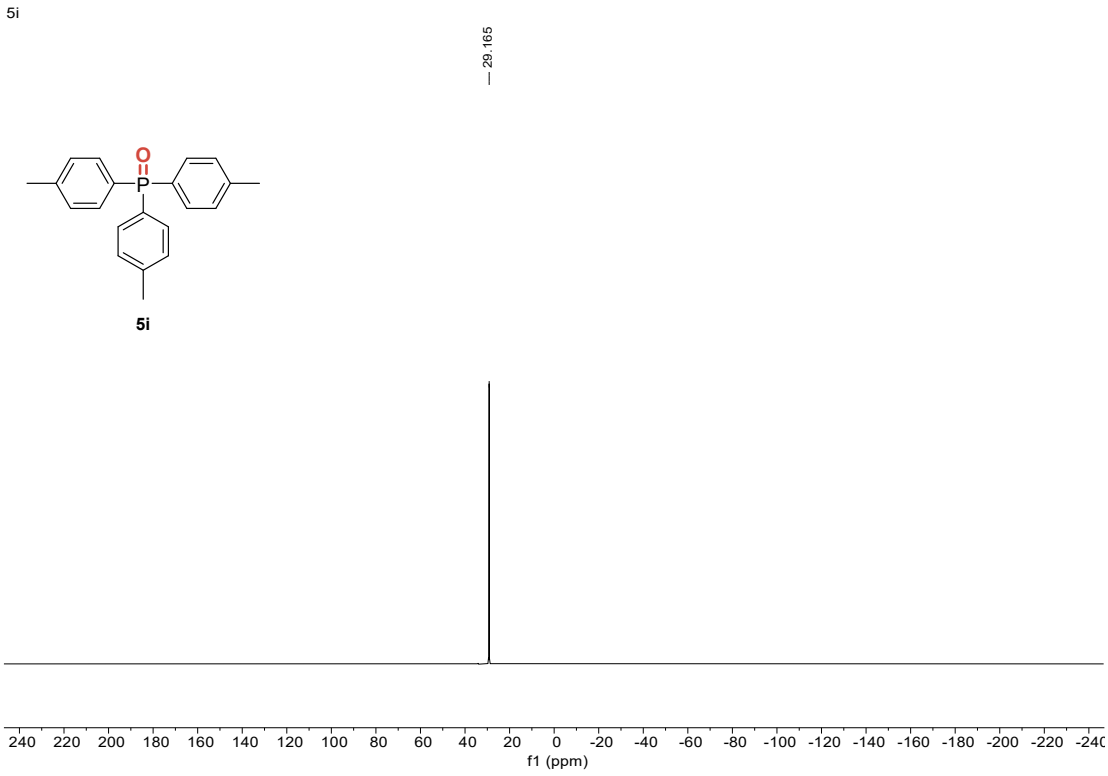


Fig. S122 ^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **5i**.

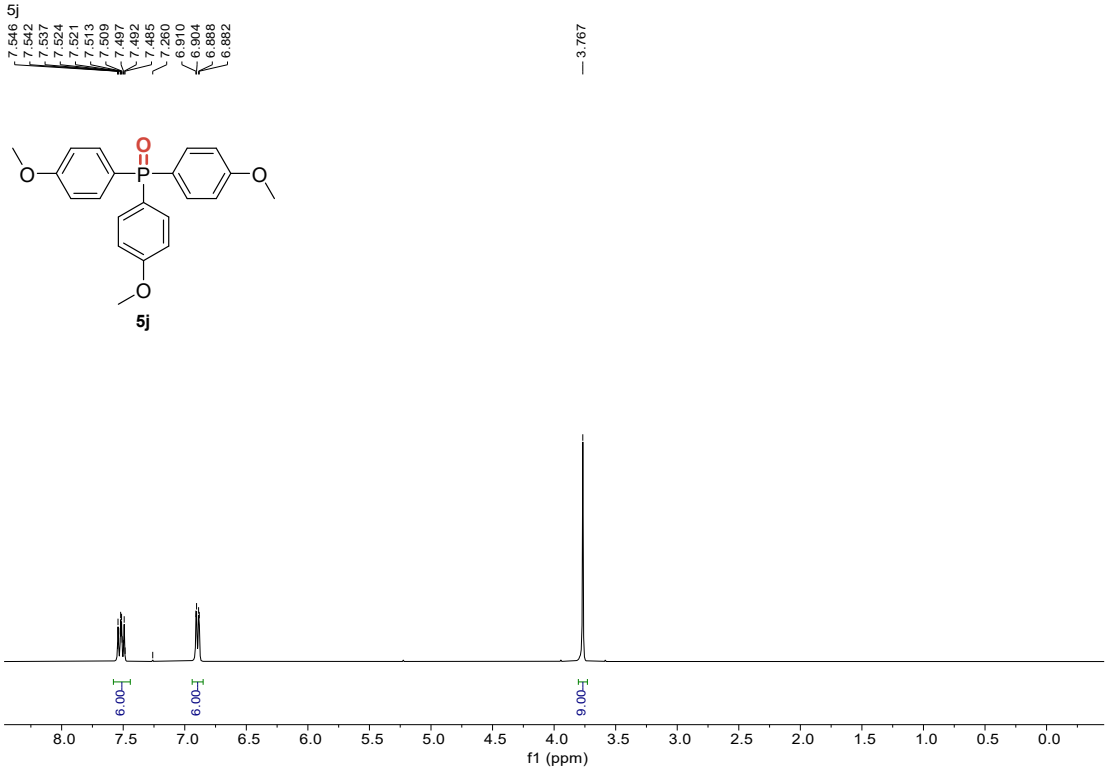


Fig. S123 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5j**.

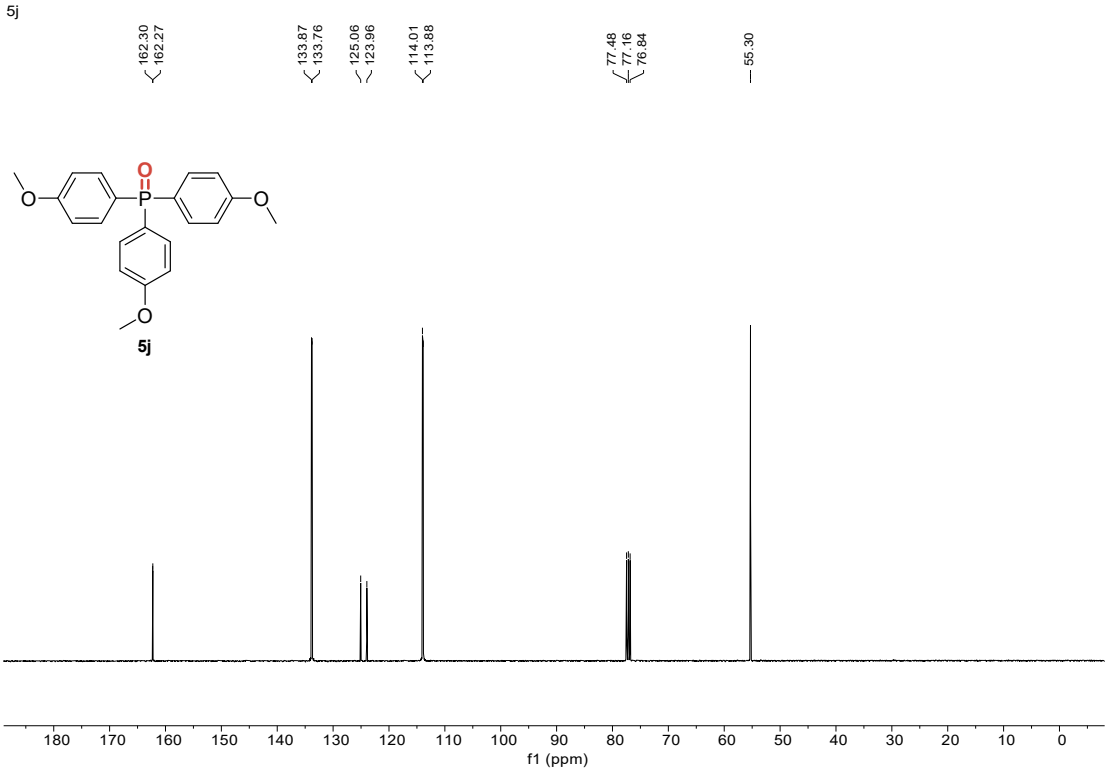


Fig. S124 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5j**.

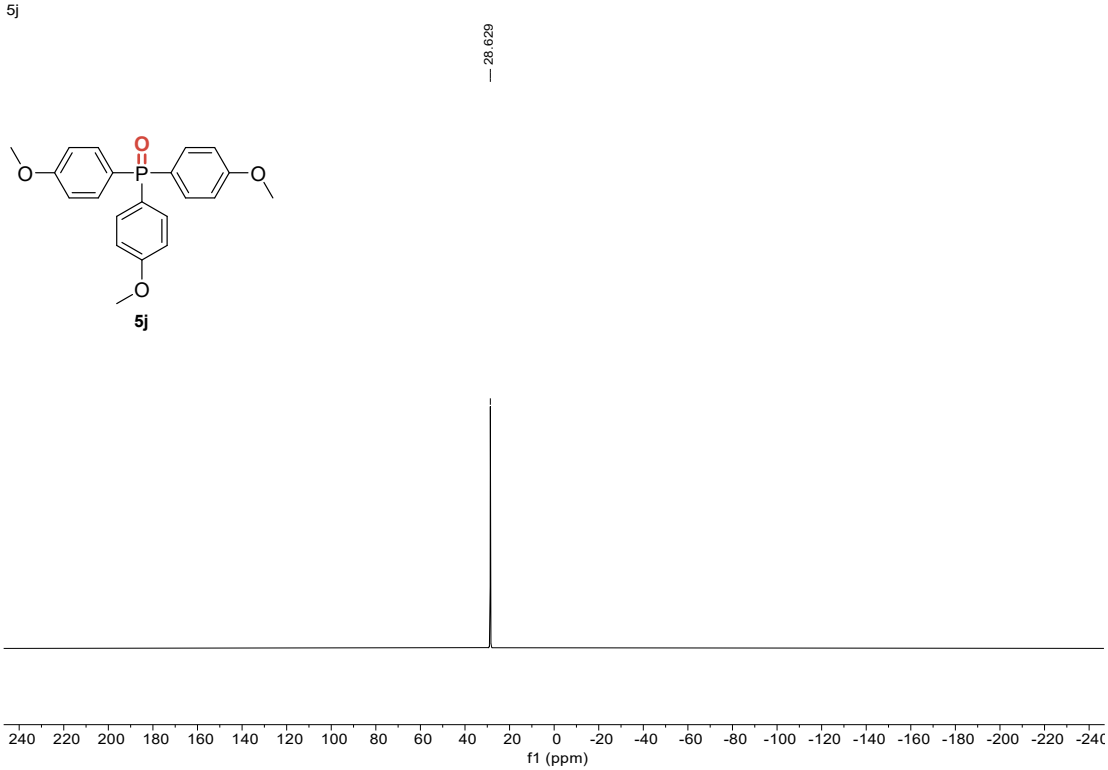


Fig. S125 ^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **5j**.

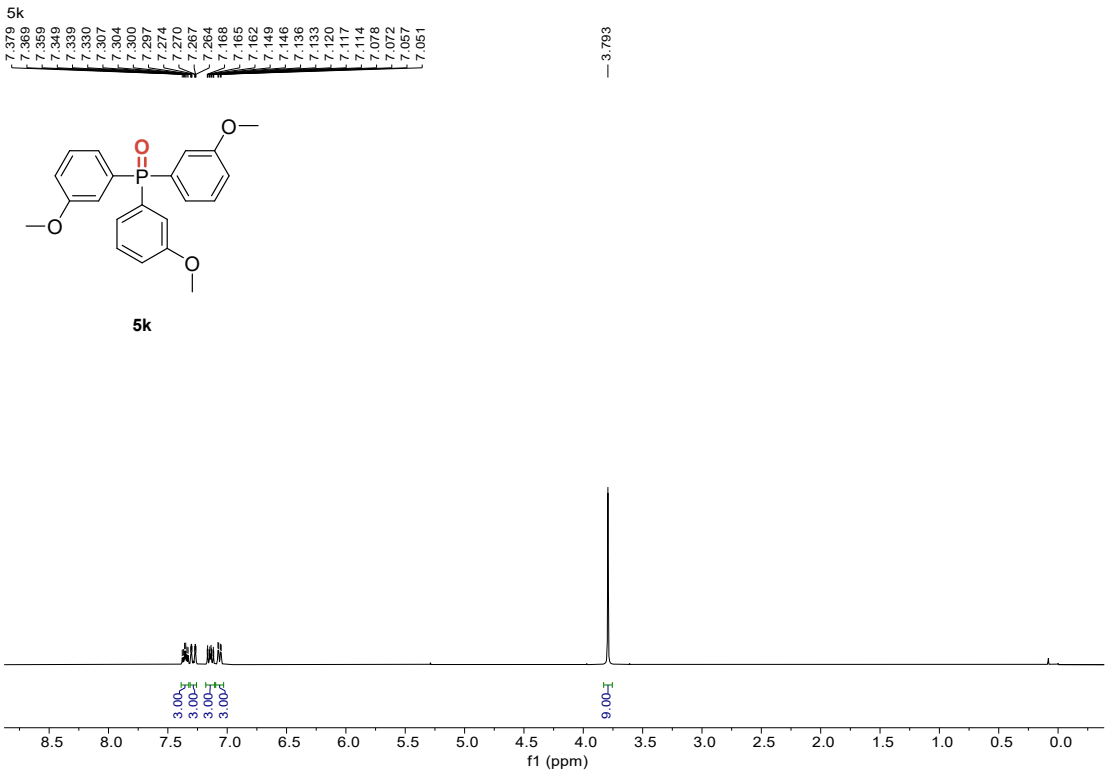


Fig. S126 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5k**.

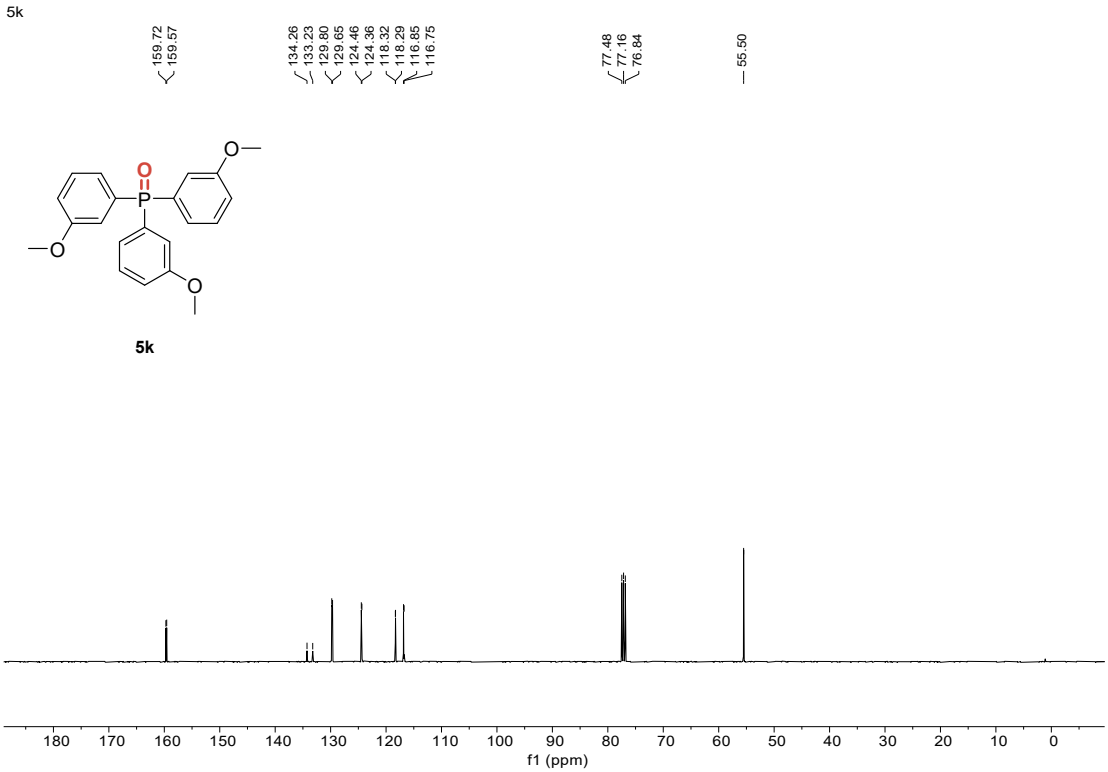


Fig. S127 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5k**.

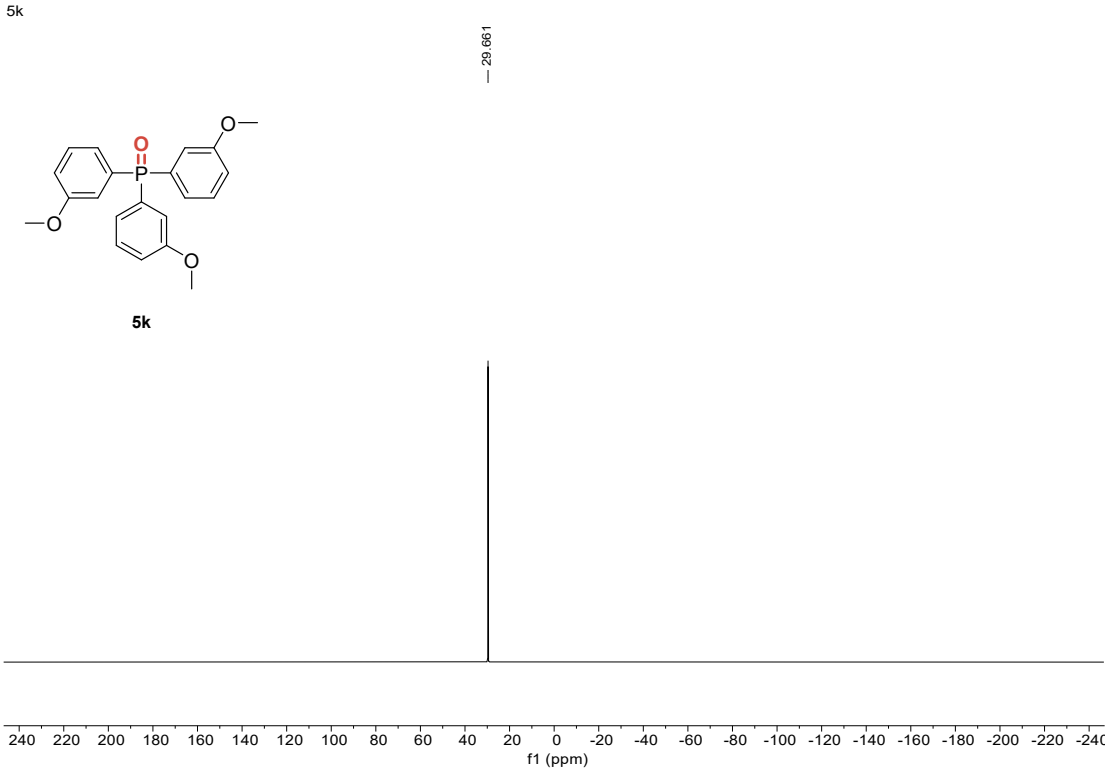


Fig. S128 ^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **5k**.

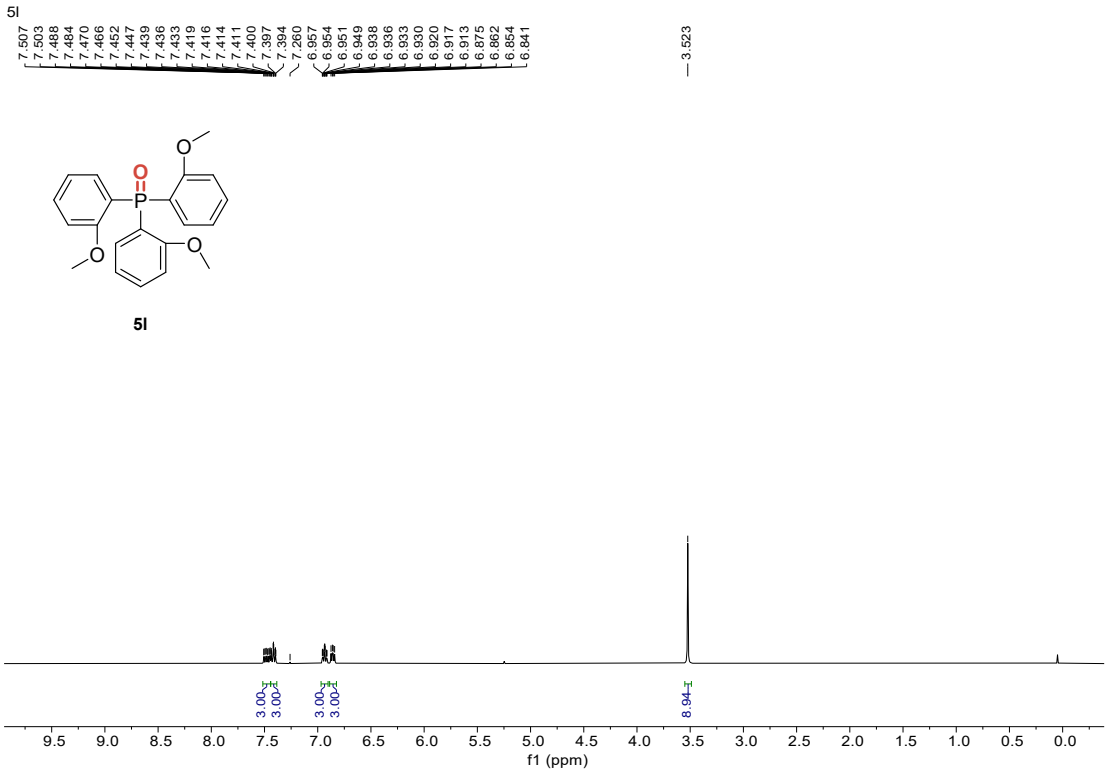


Fig. S129 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5l**.

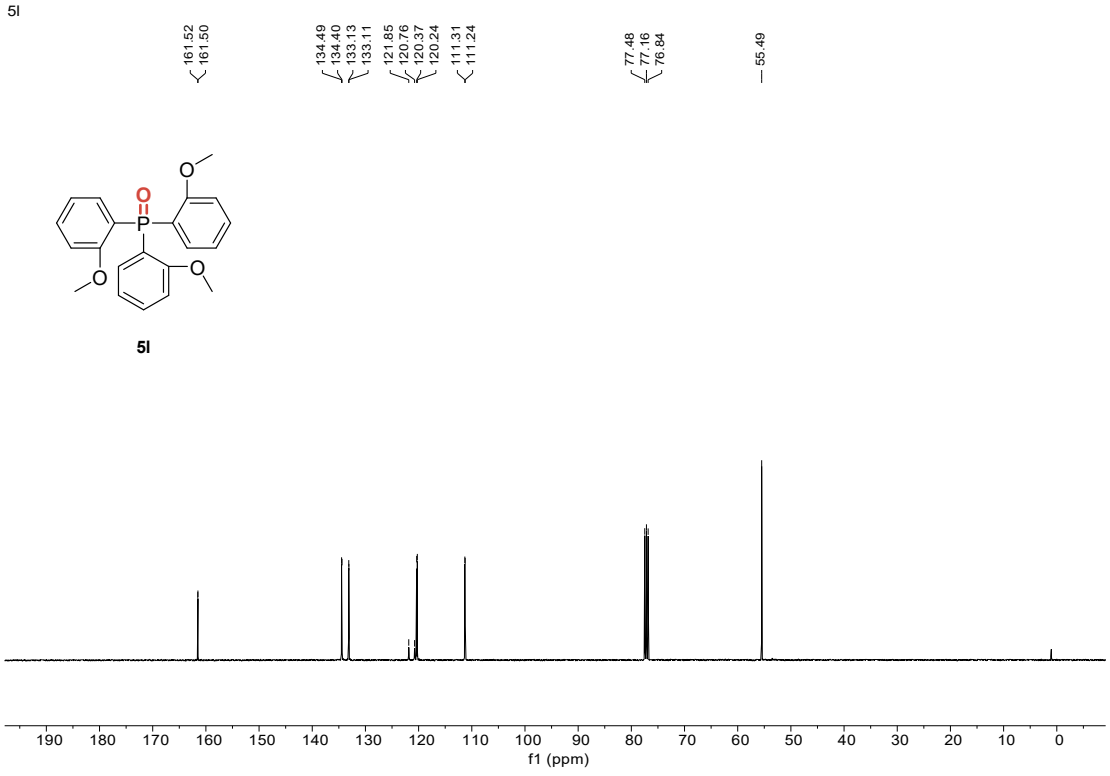


Fig. S130 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5l**.

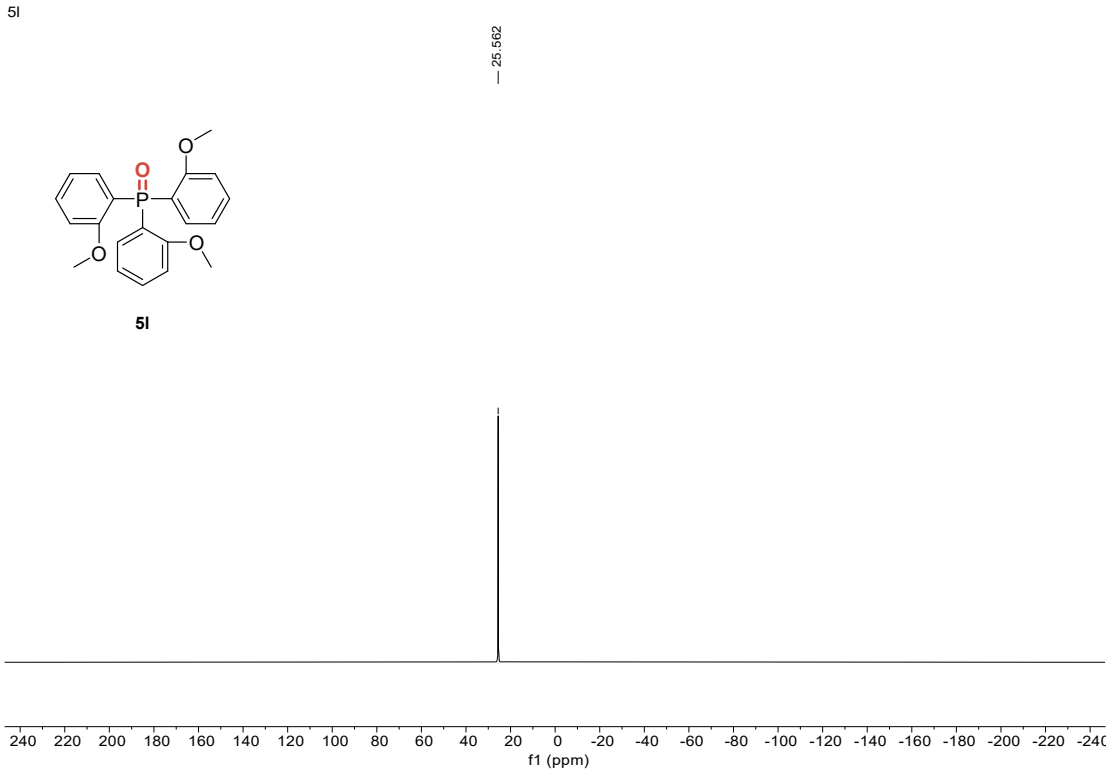


Fig. S131 ^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **5l**.

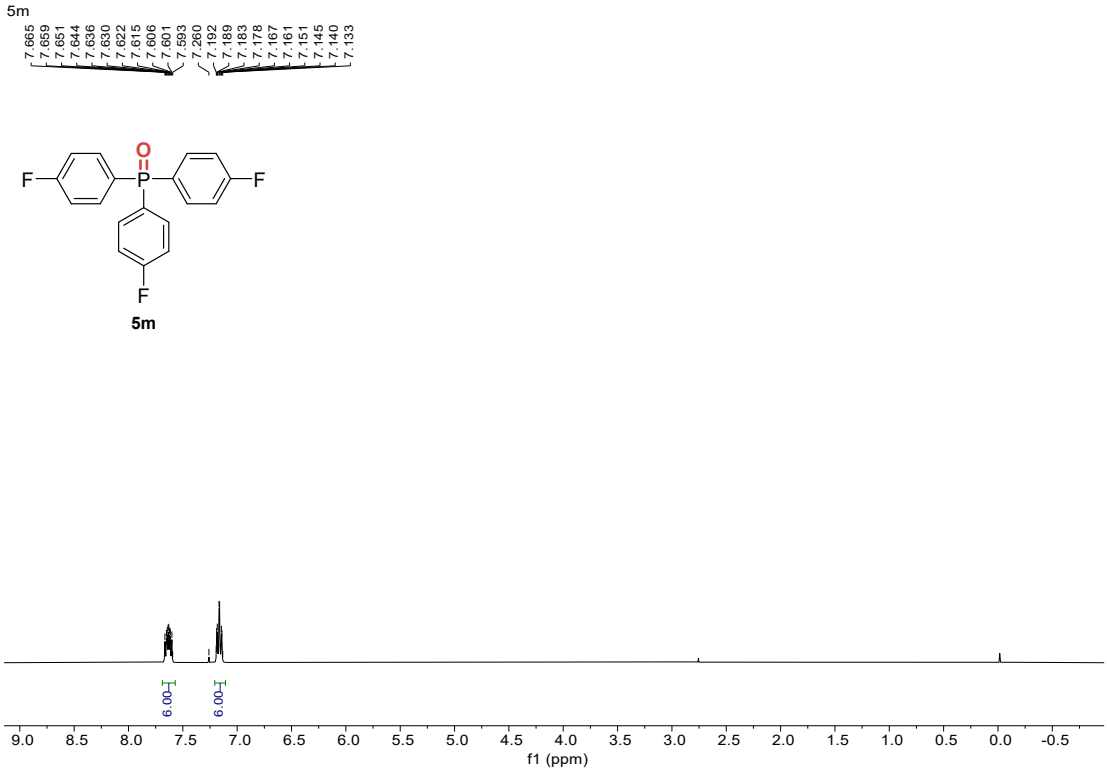


Fig. S132 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5m**.

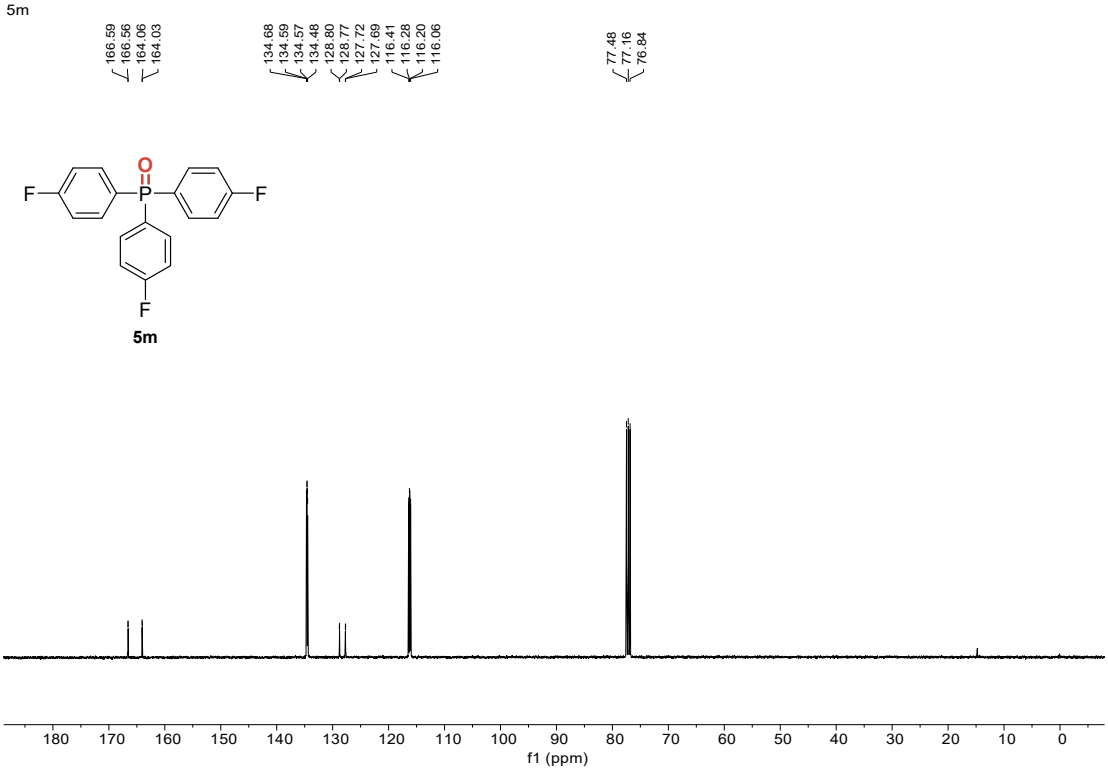


Fig. S133 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5m**.

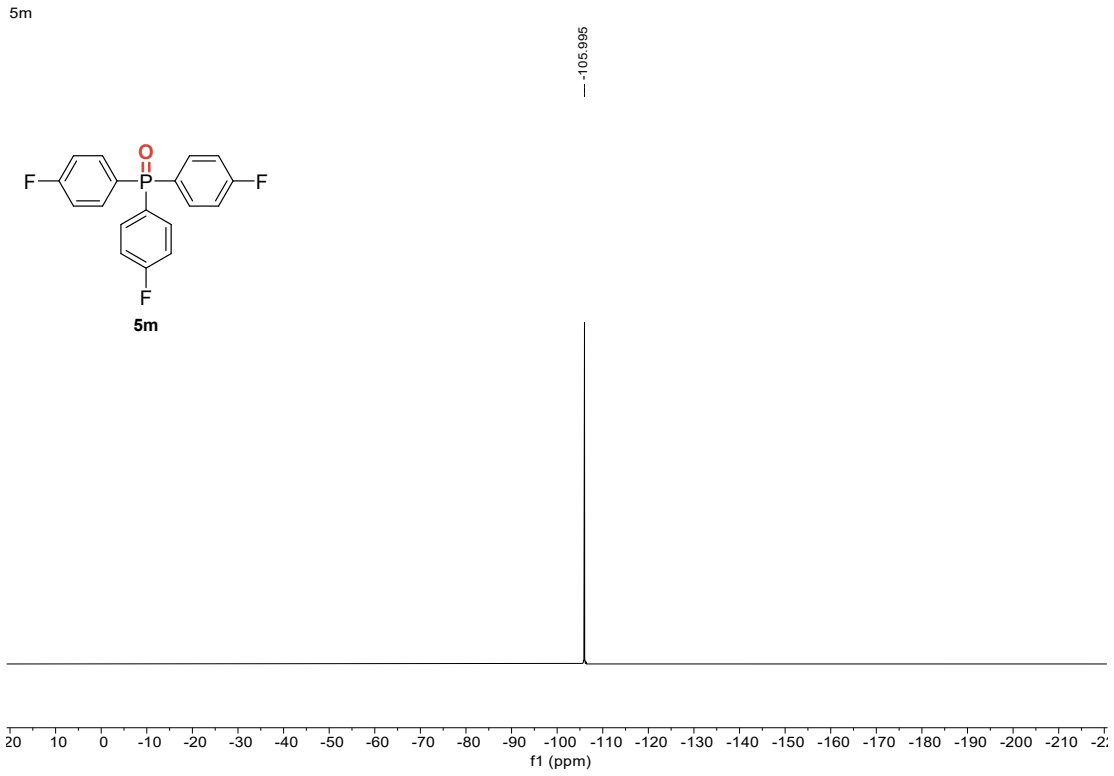


Fig. S134 ^{19}F NMR spectrum (471 MHz, $CDCl_3$) of **5m**.

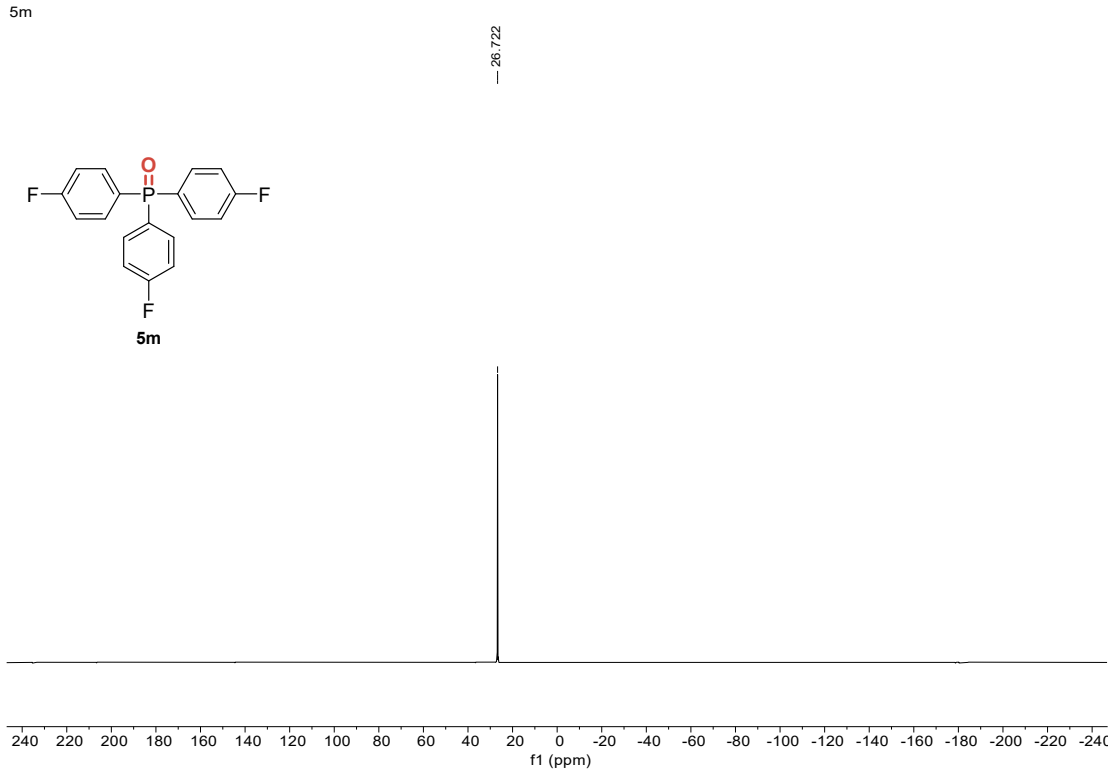


Fig. S135 ^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **5m**.

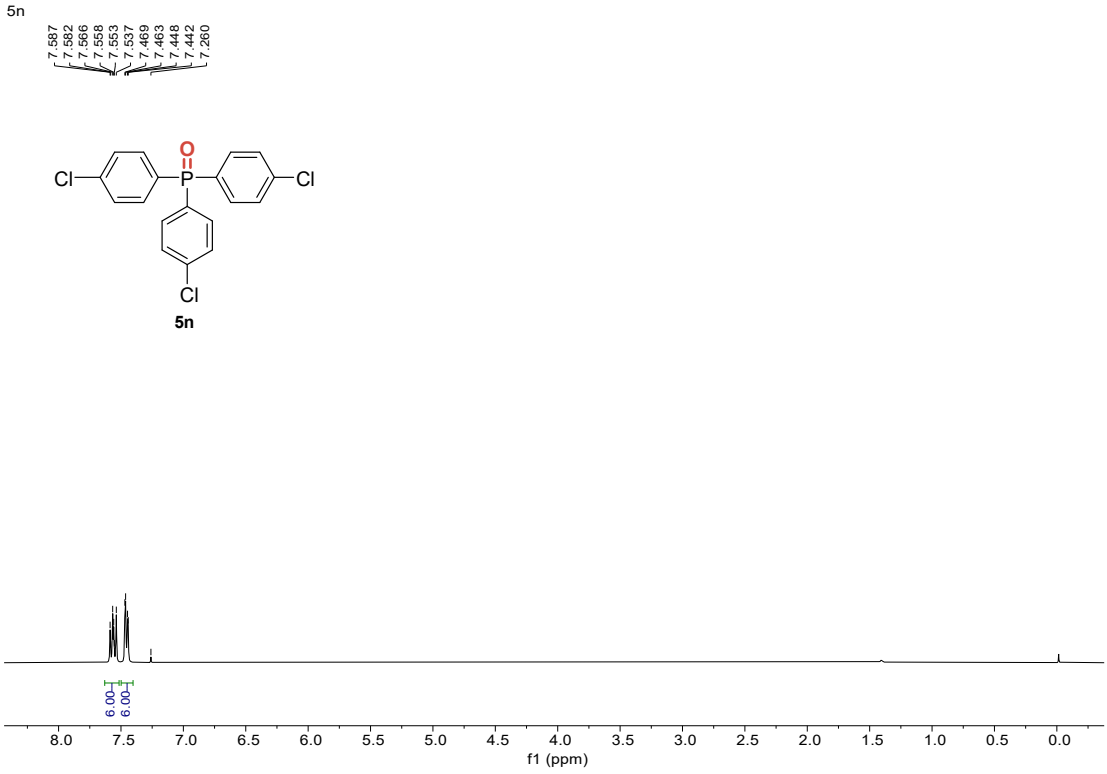


Fig. S136 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5n**.

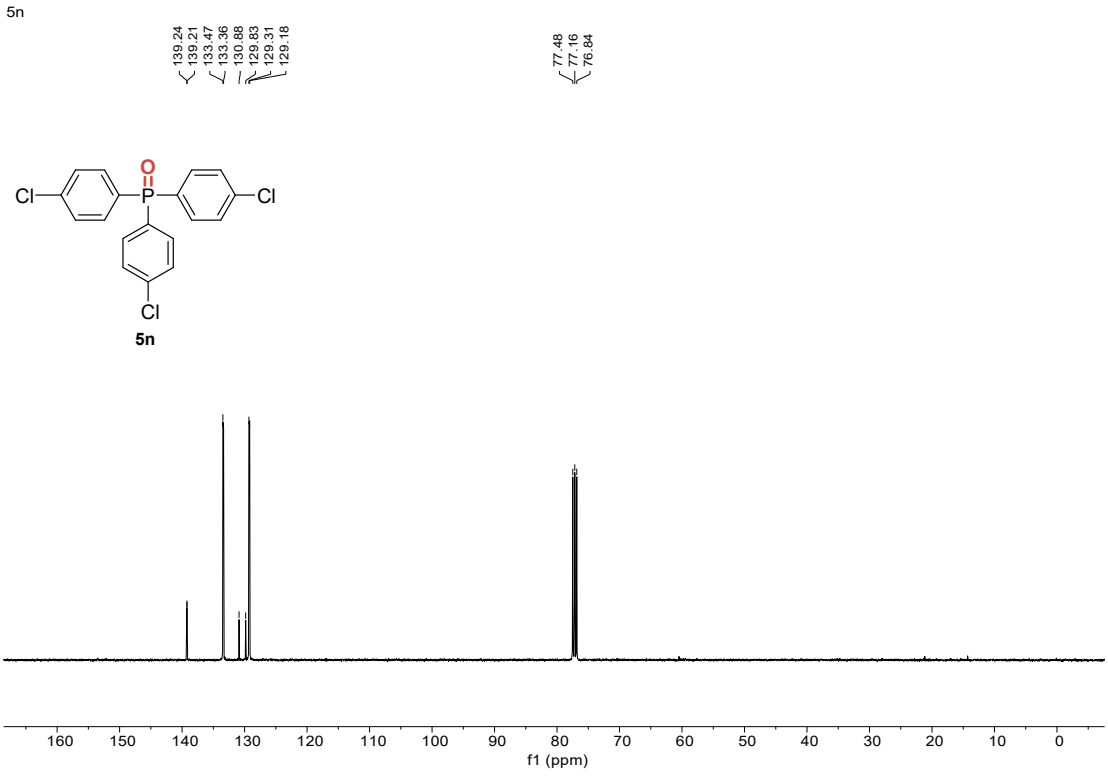


Fig. S137 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5n**.

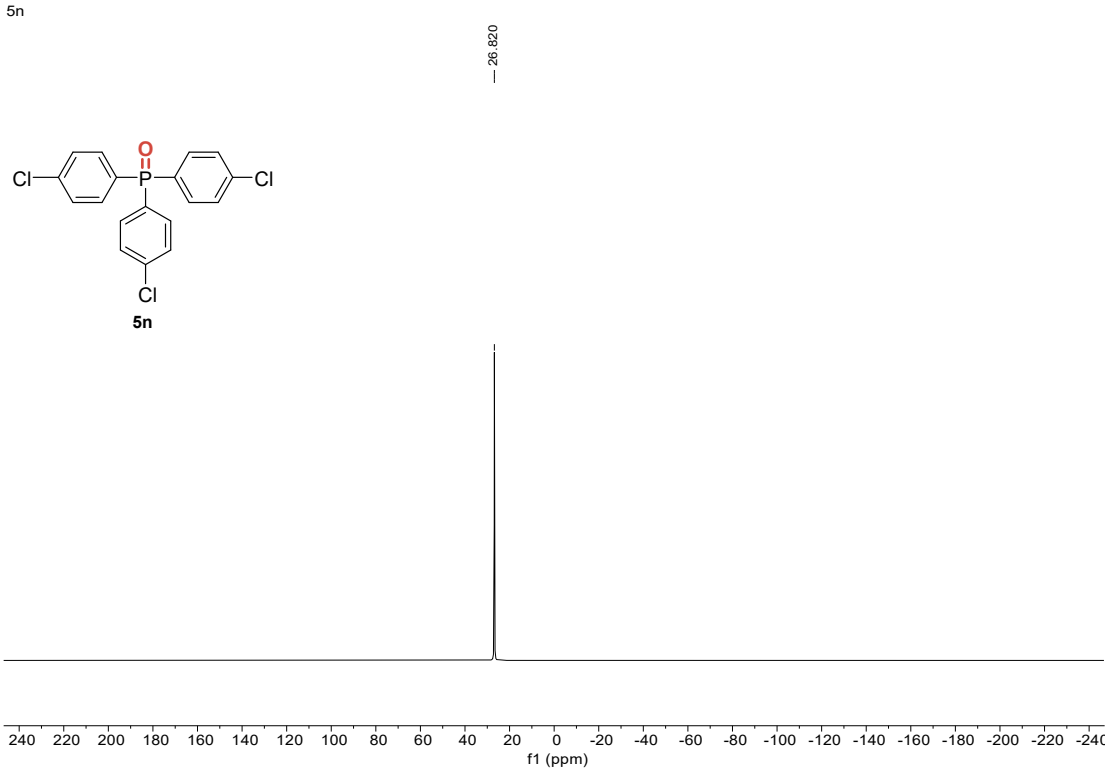


Fig. S138 ^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **5n**.

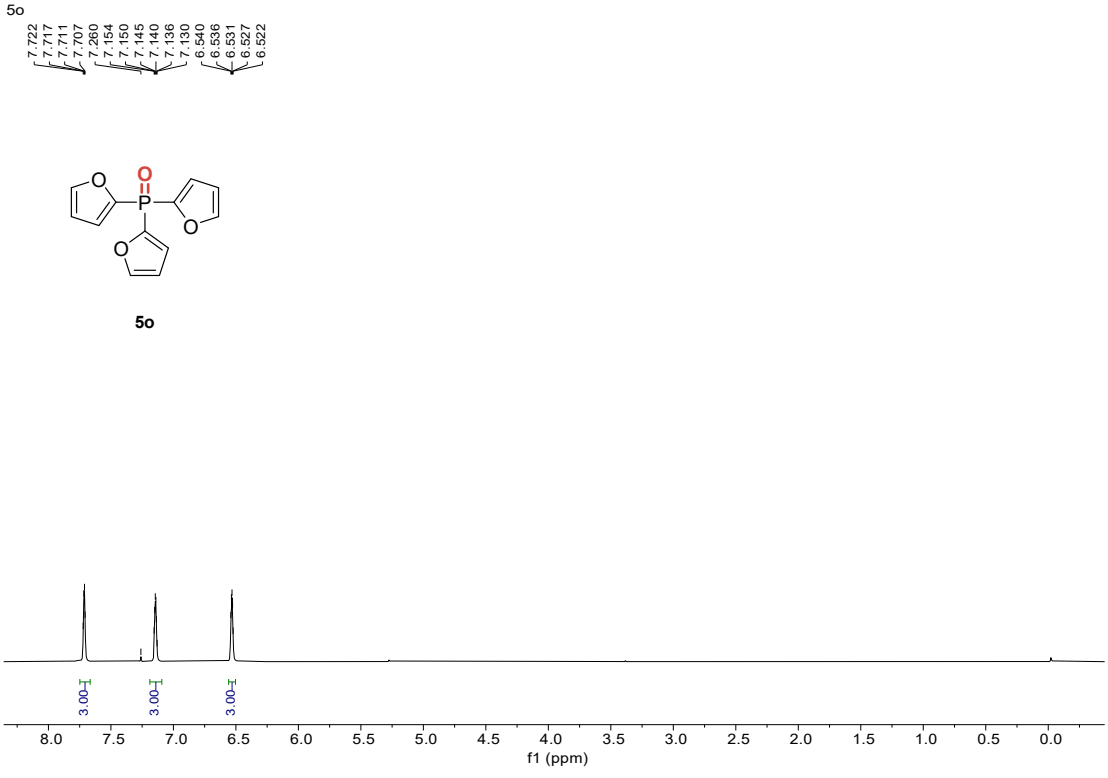


Fig. S139 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5o**.

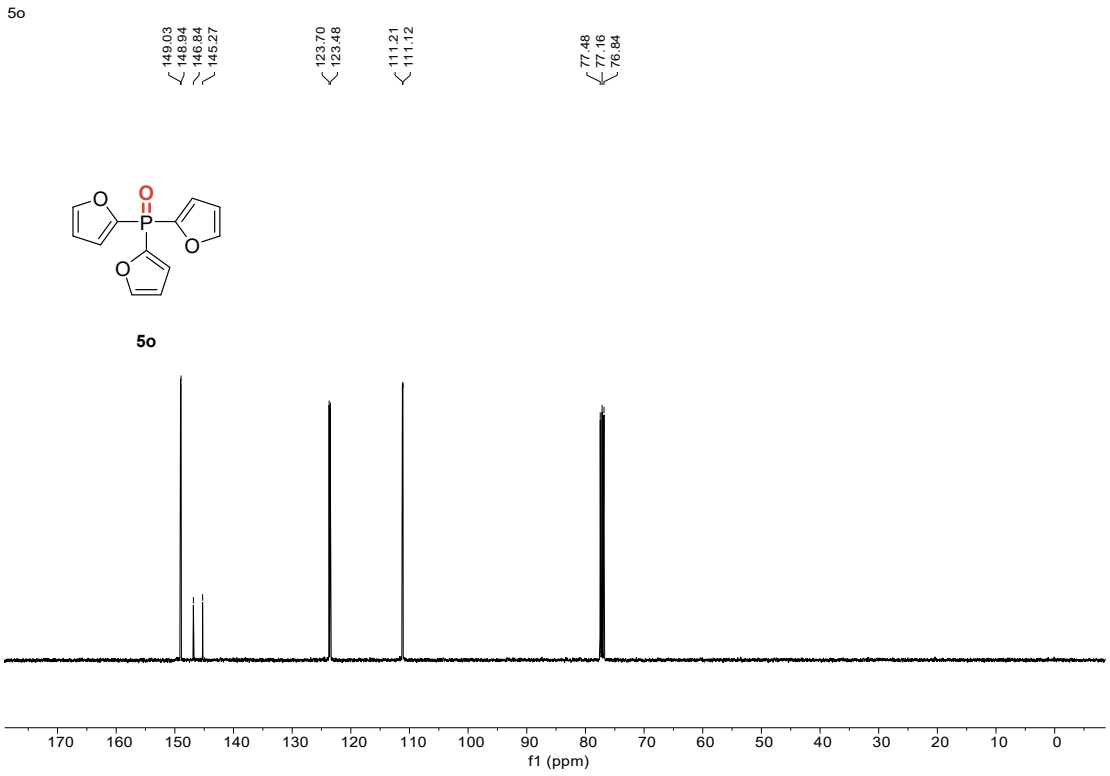


Fig. S140 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5o**.

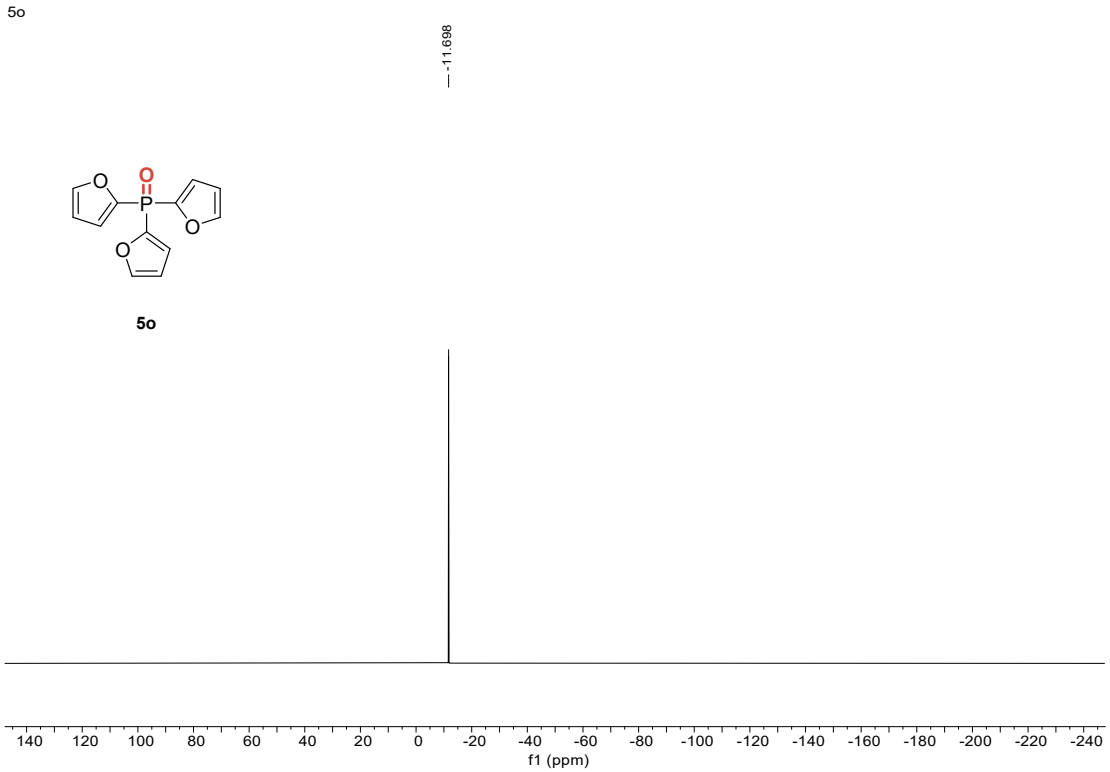


Fig. S141 ^{31}P NMR spectrum (243 MHz, $CDCl_3$) of **5o**.

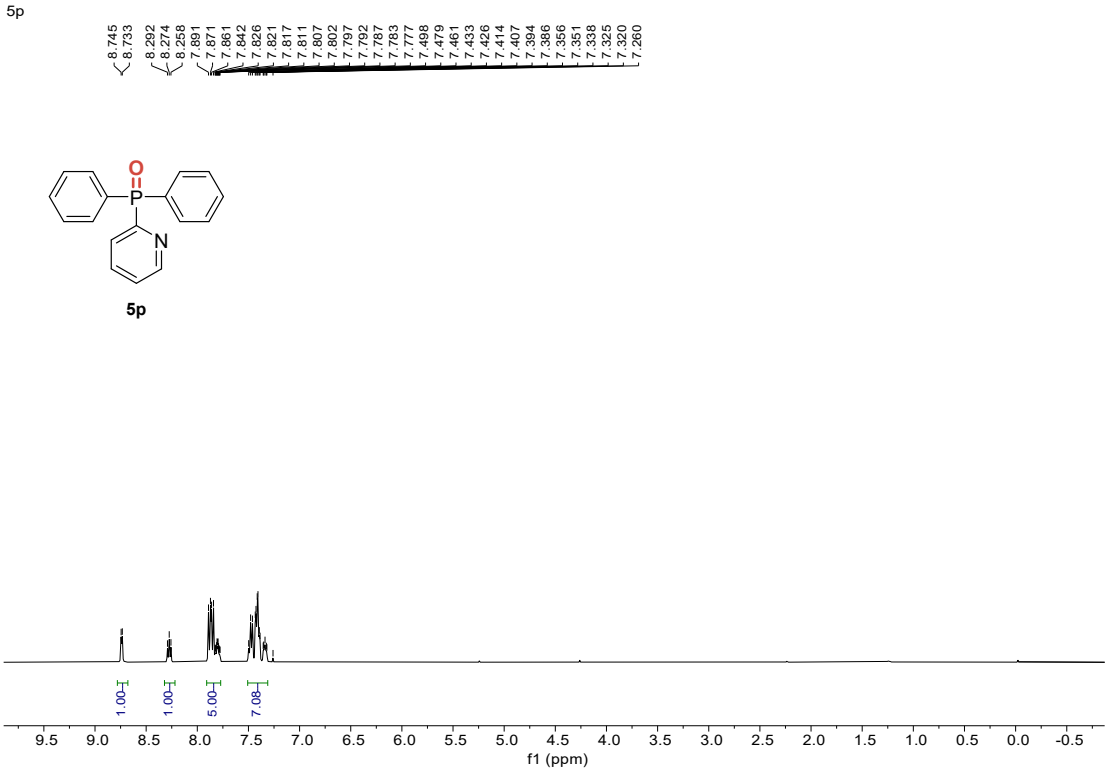


Fig. S142 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5p**.

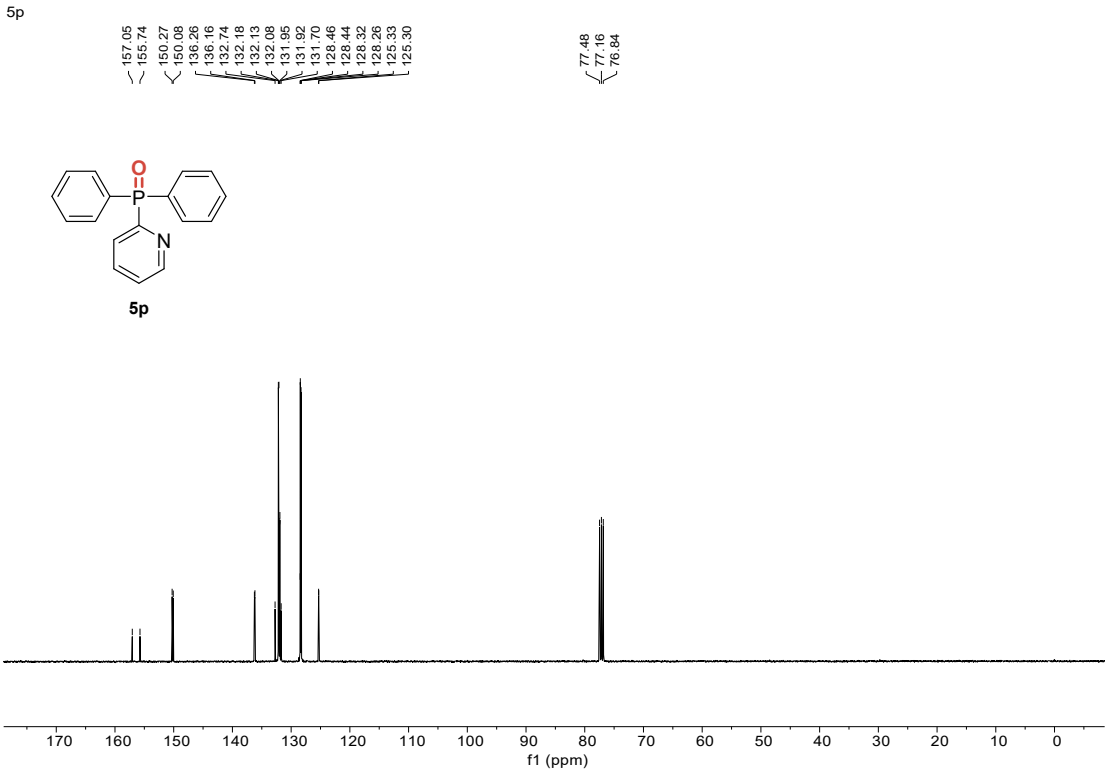


Fig. S143 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5p**.

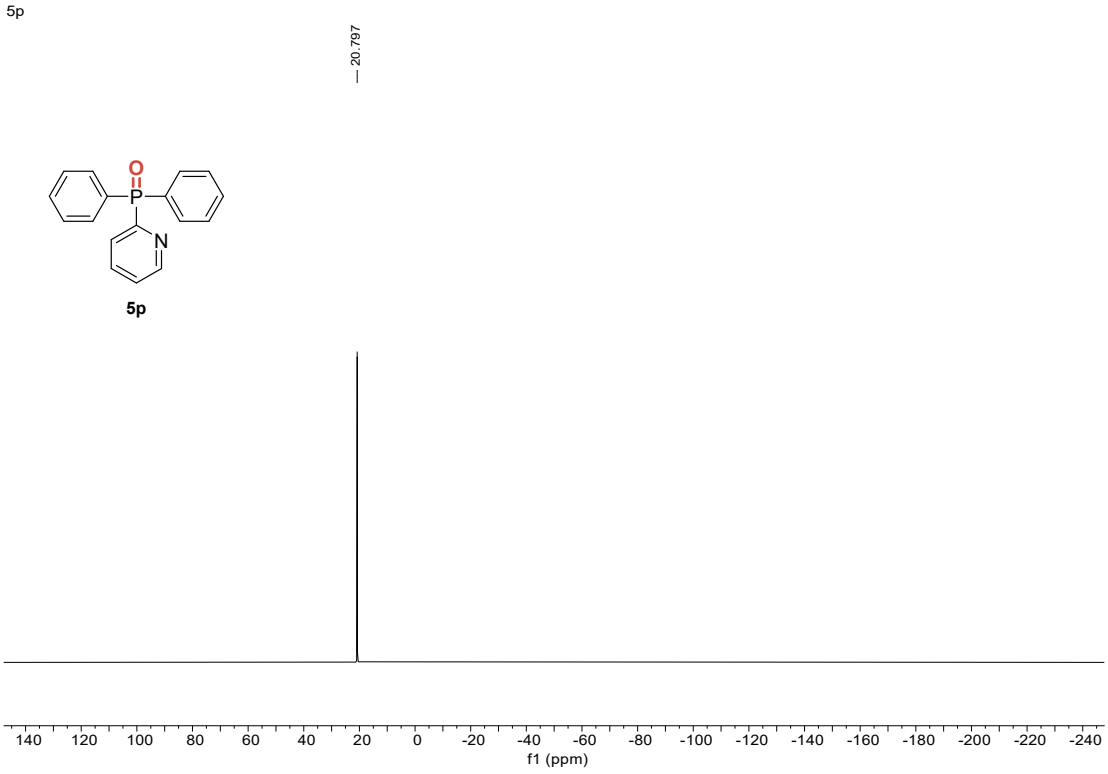


Fig. S144 ^{31}P NMR spectrum (243 MHz, $CDCl_3$) of **5p**.

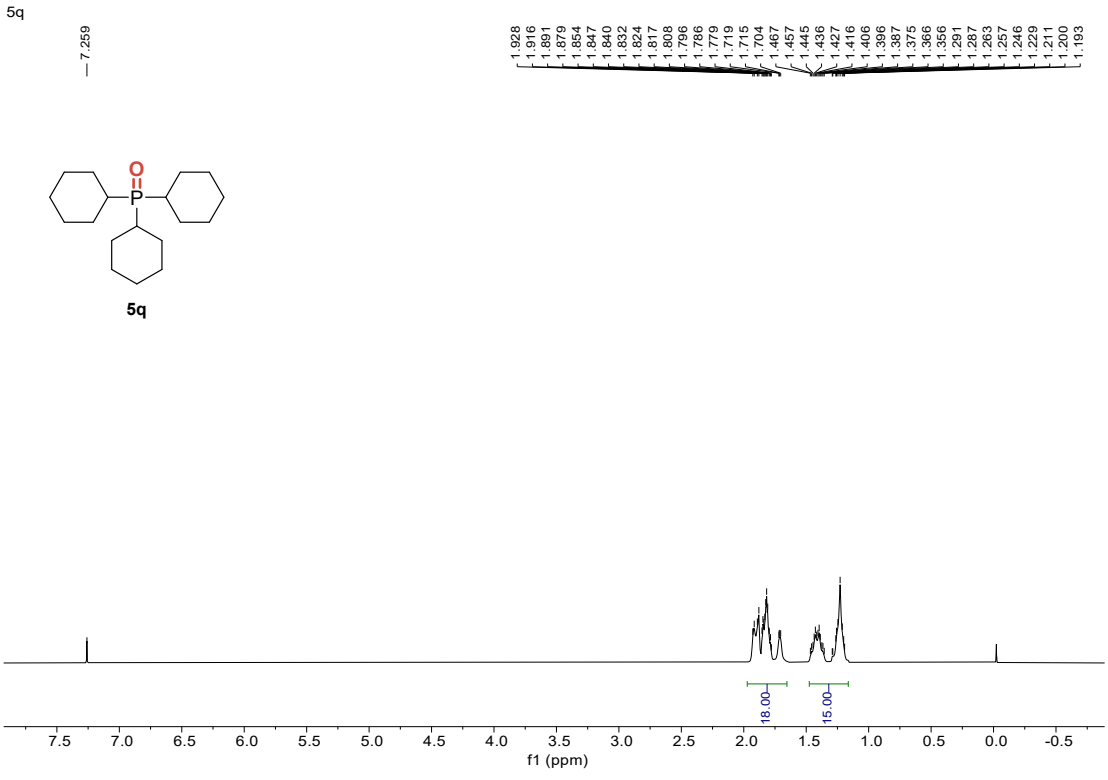


Fig. S145 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5q**.

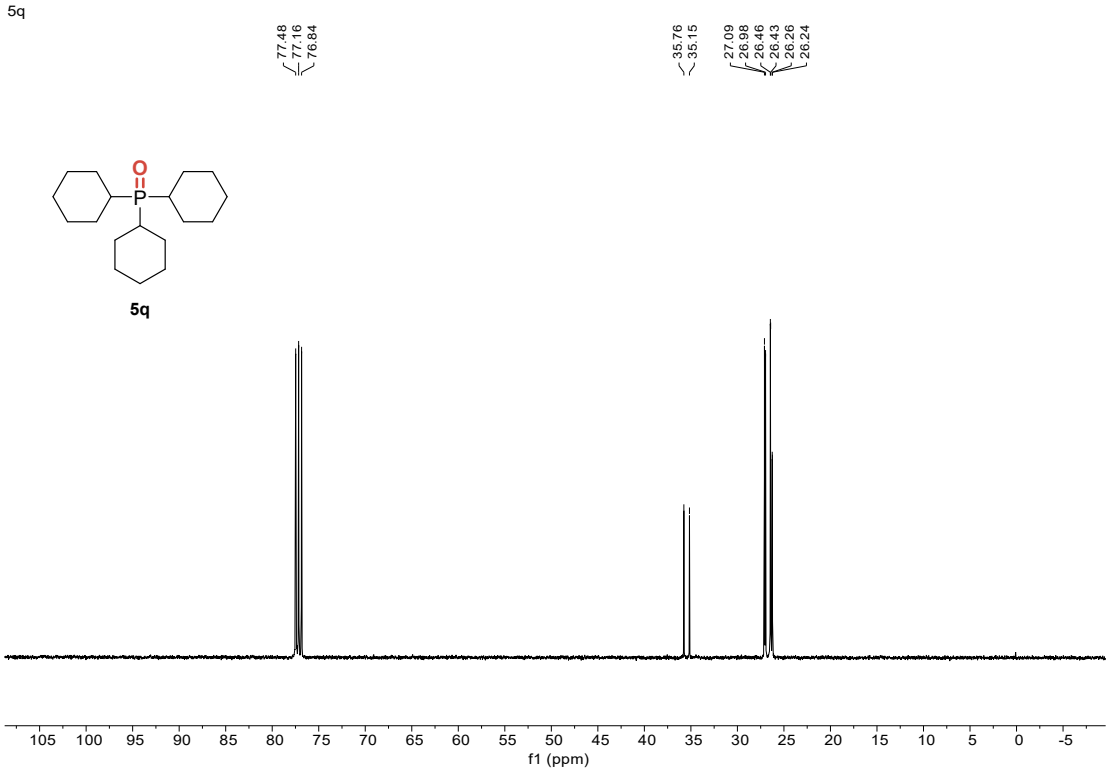


Fig. S146 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5q**.

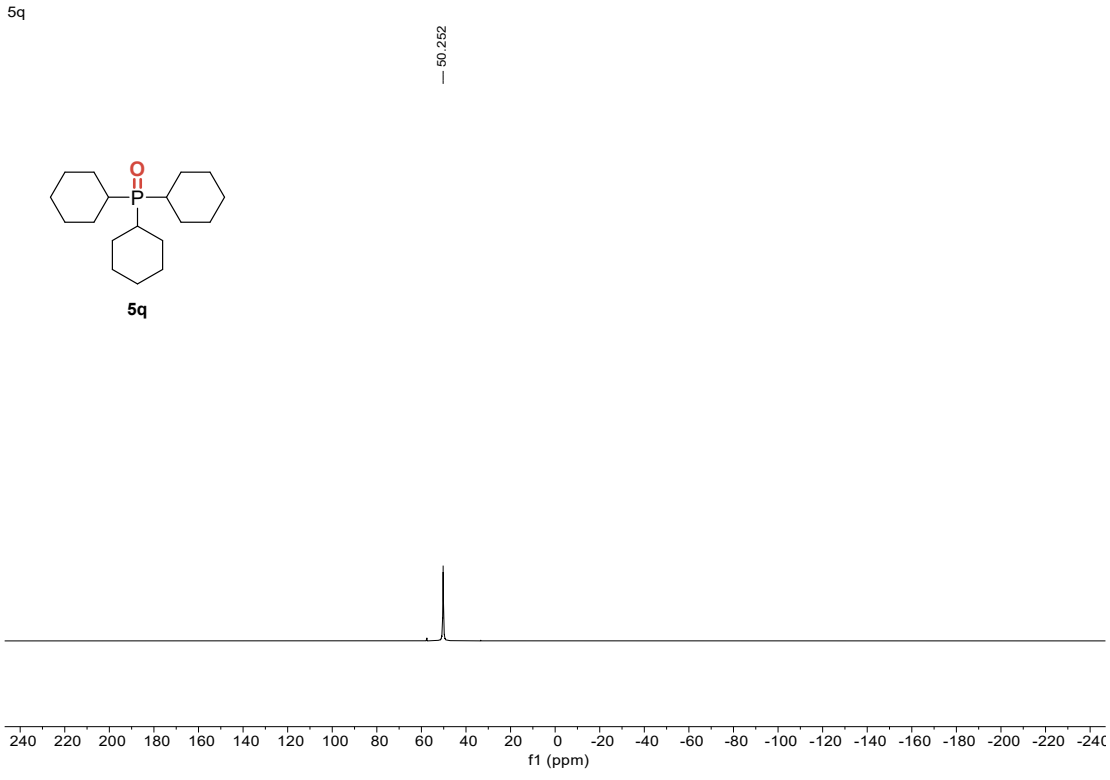


Fig. S147 ^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **5q**.

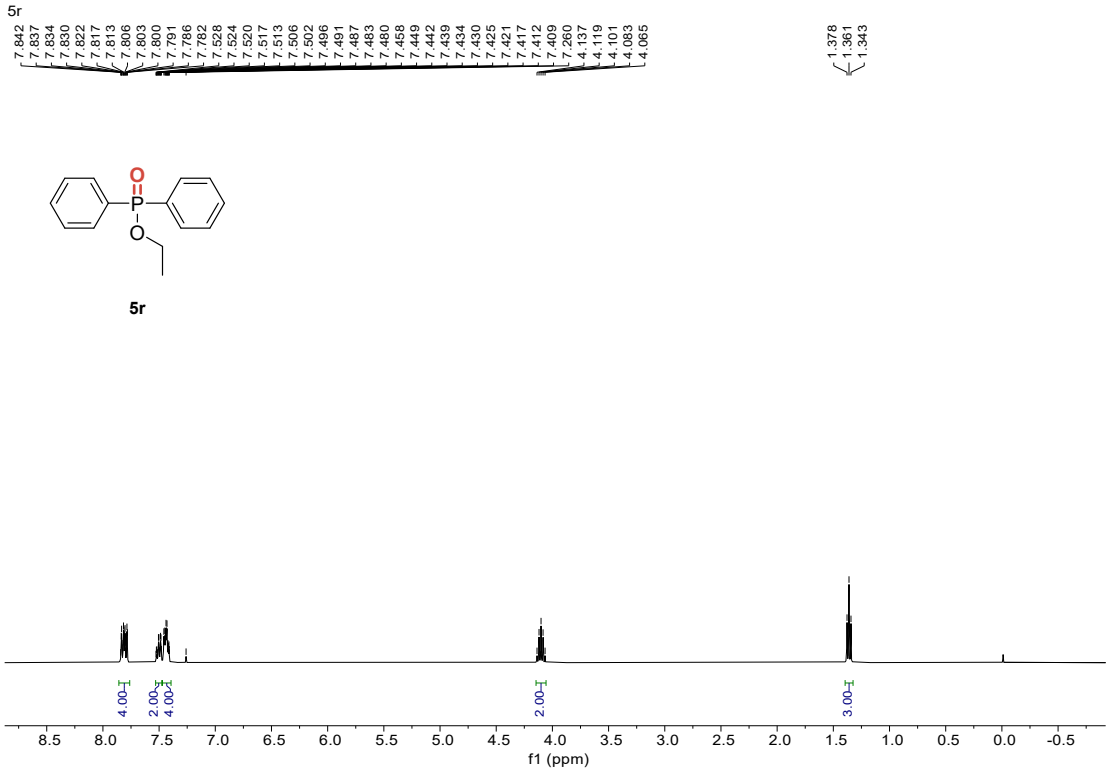


Fig. S148 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5r**.

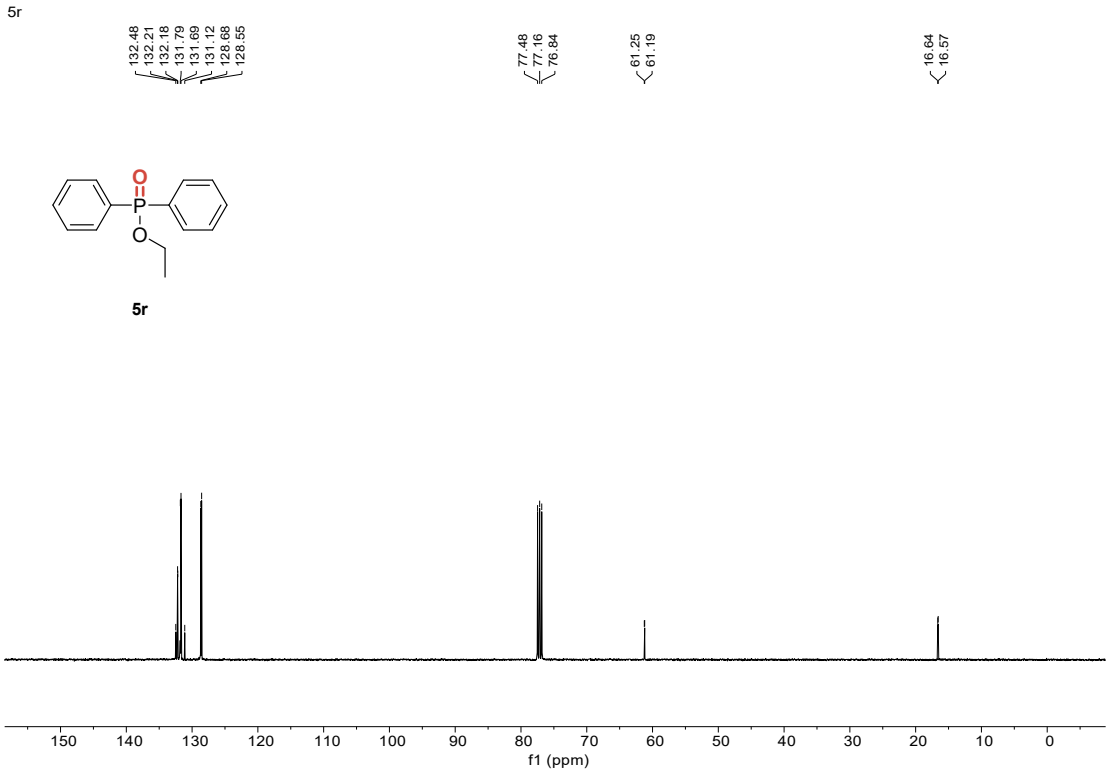


Fig. S149 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5r**.

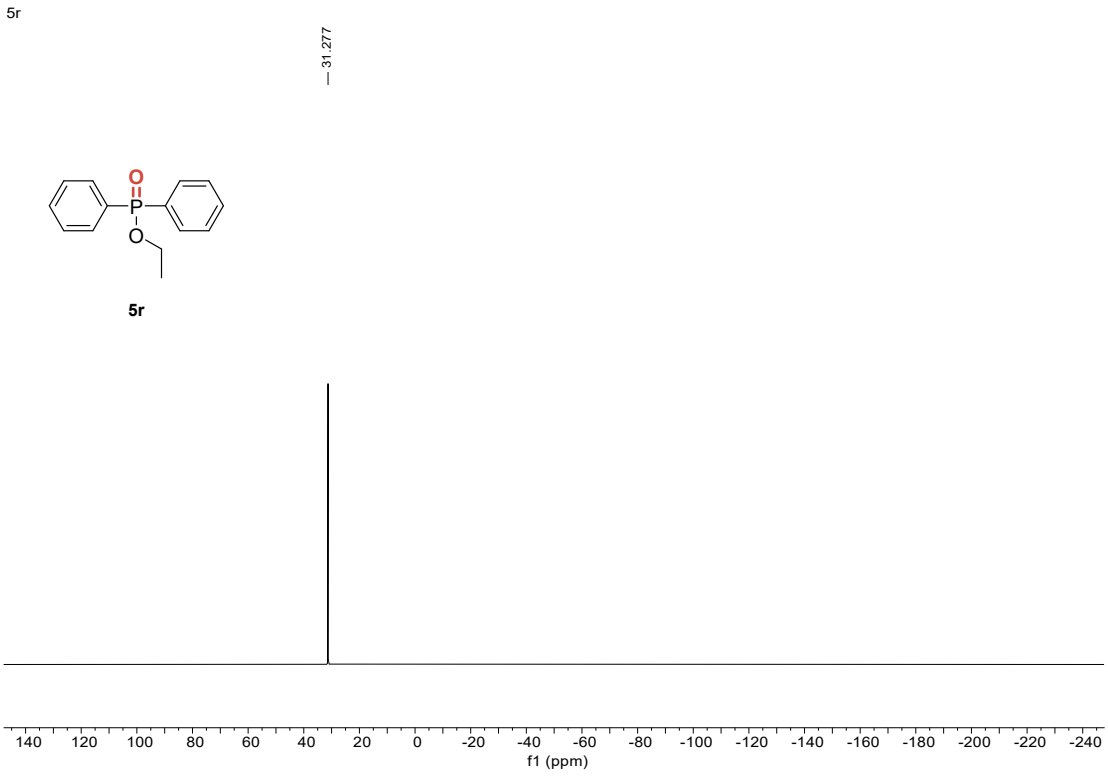


Fig. S150 ^{31}P NMR spectrum (243 MHz, $CDCl_3$) of **5r**.

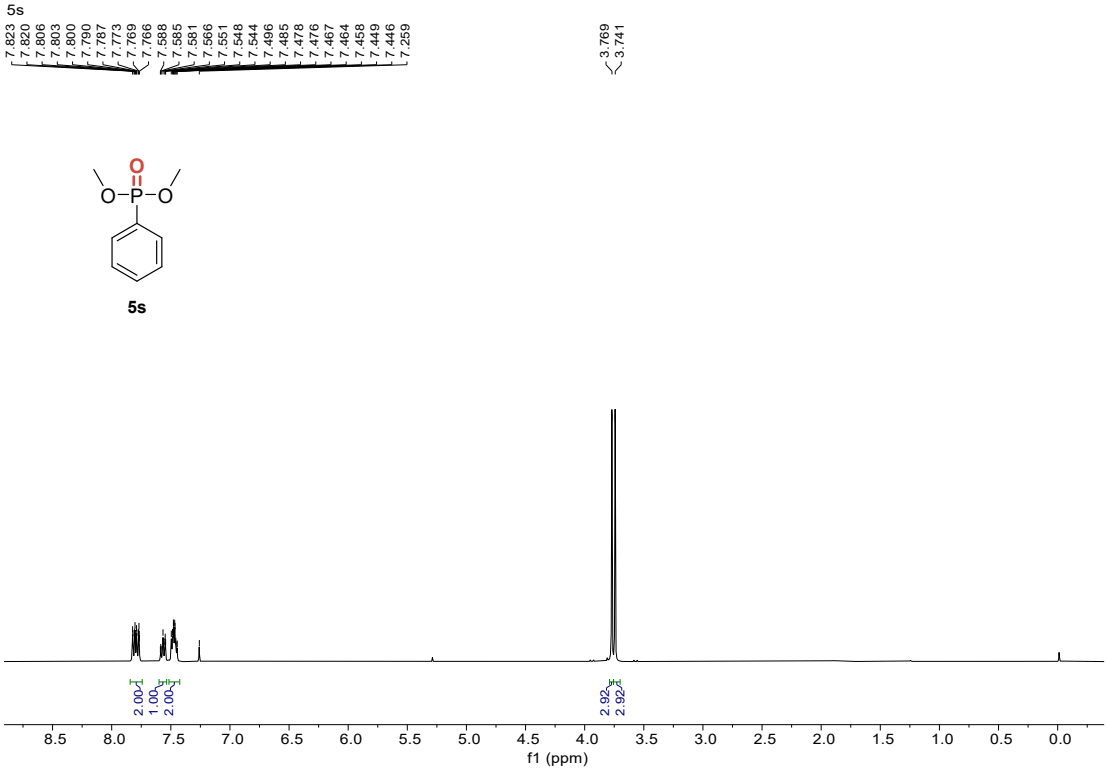


Fig. S151 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5s**.

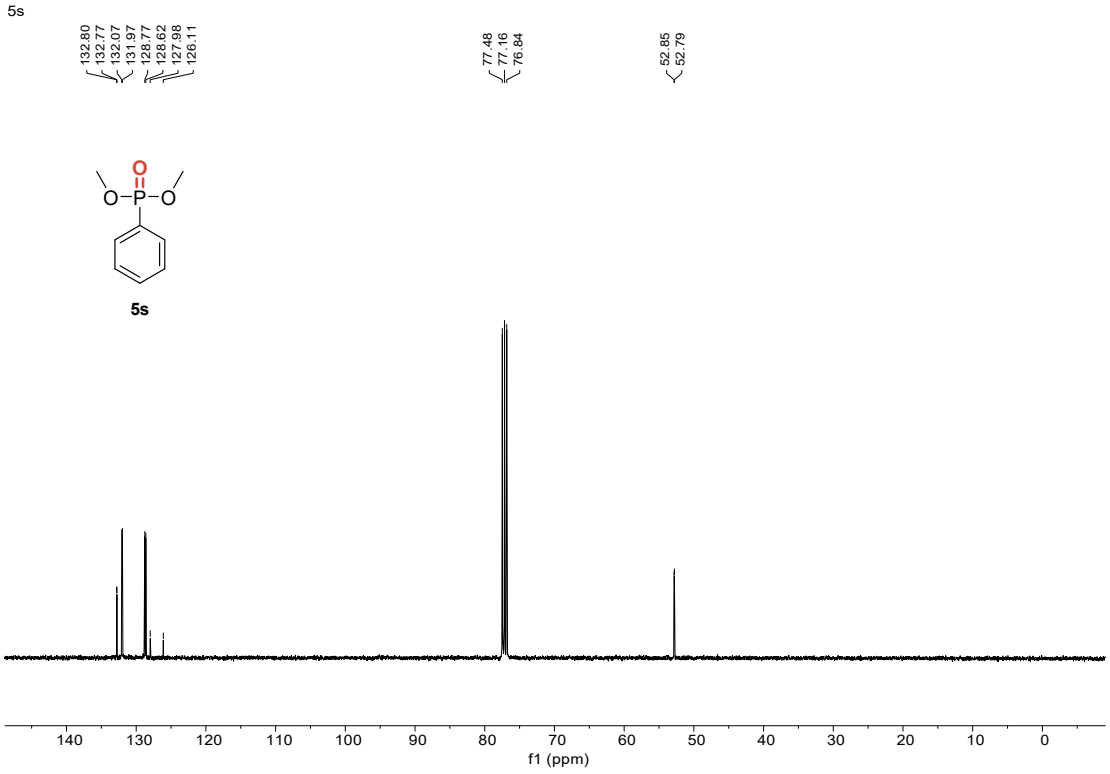


Fig. S152 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5s**.

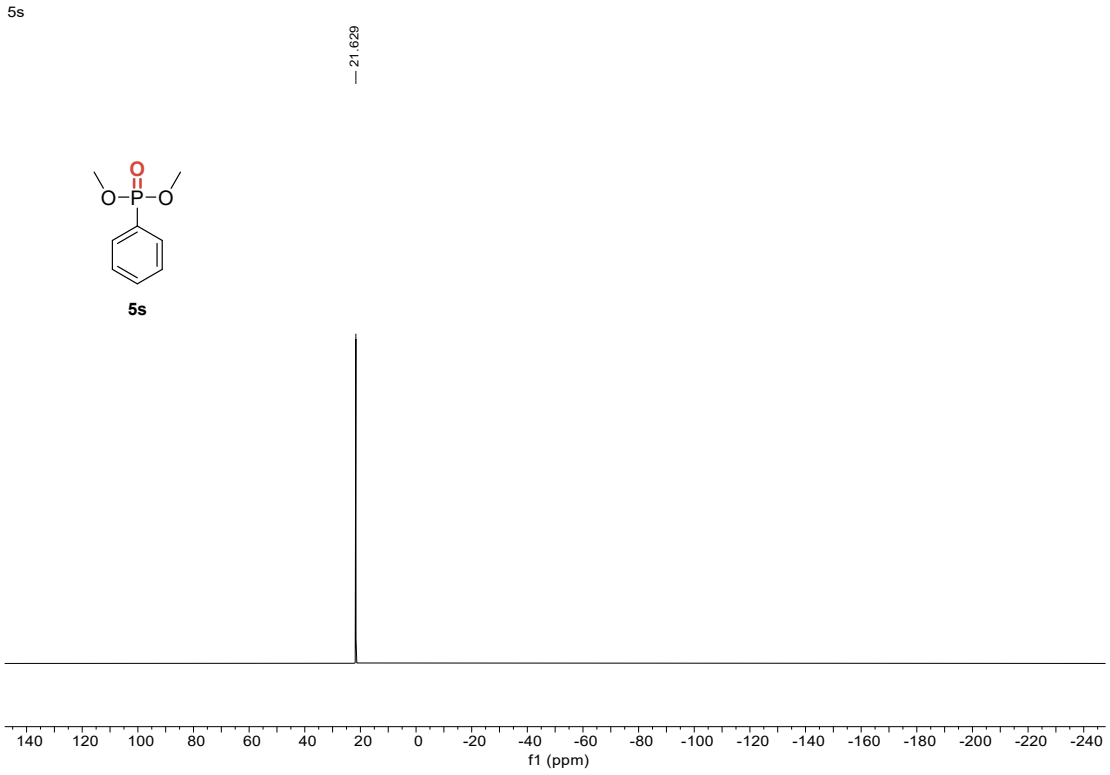


Fig. S153 ^{31}P NMR spectrum (243 MHz, $CDCl_3$) of **5s**.

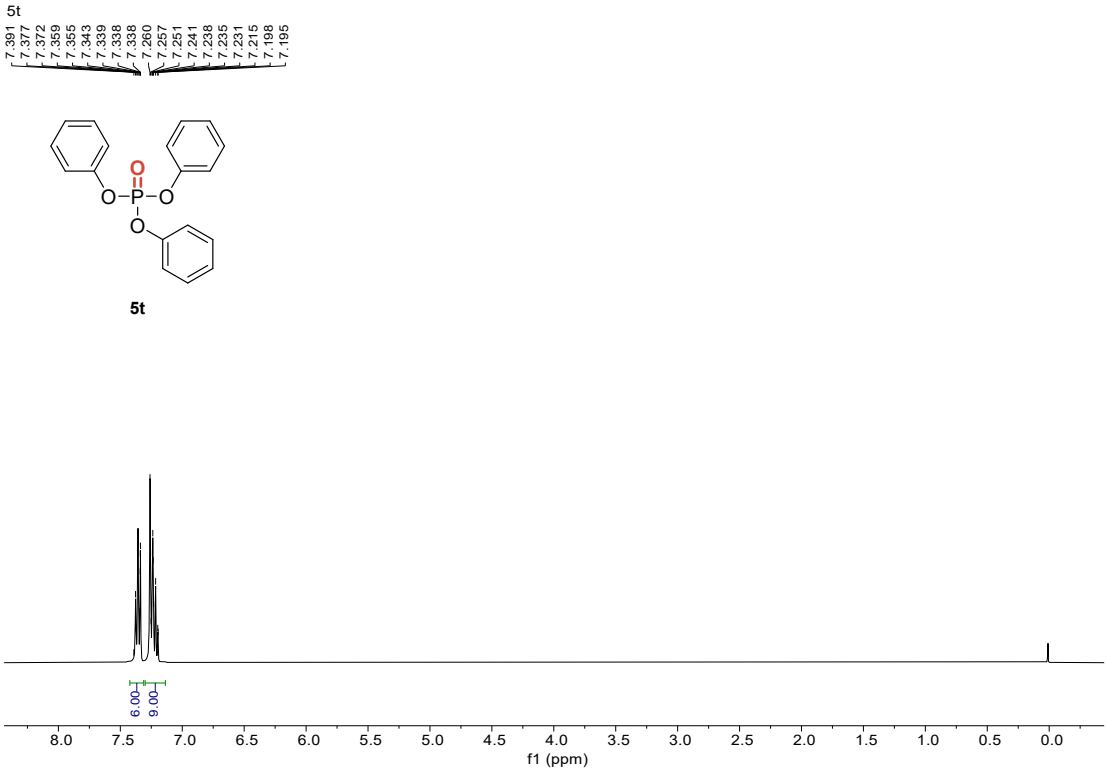


Fig. S154 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5t**.

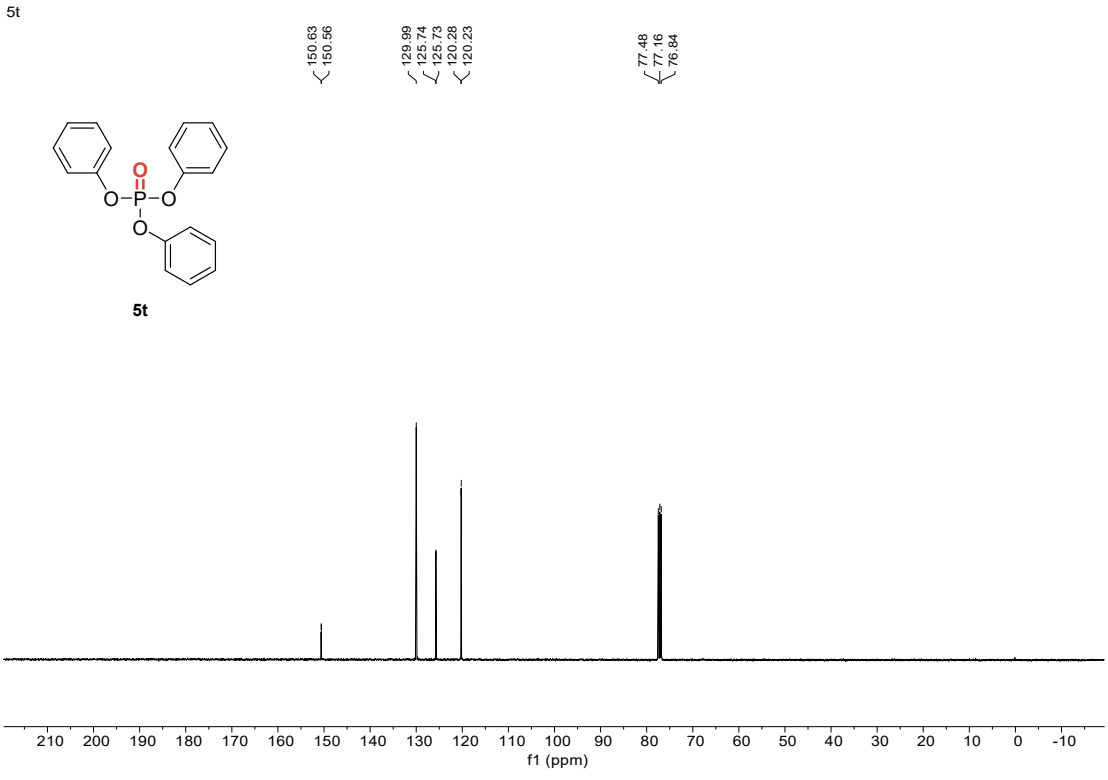


Fig. S155 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5t**.

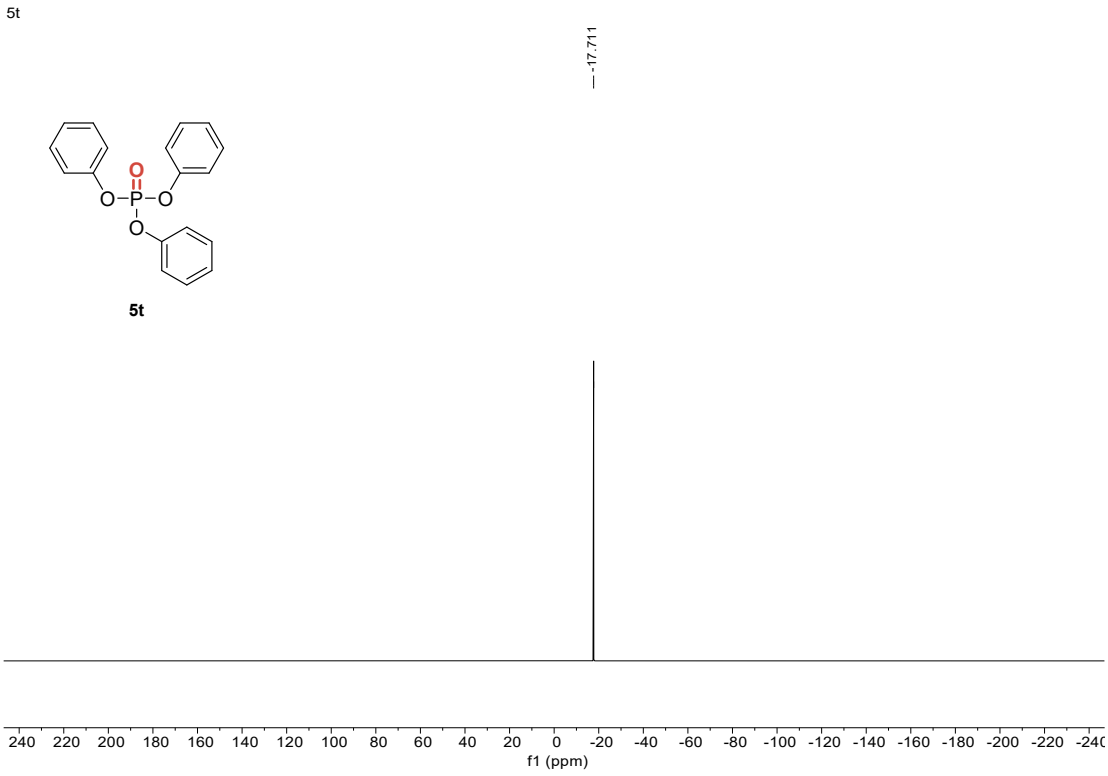


Fig. S156 ^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **5t**.

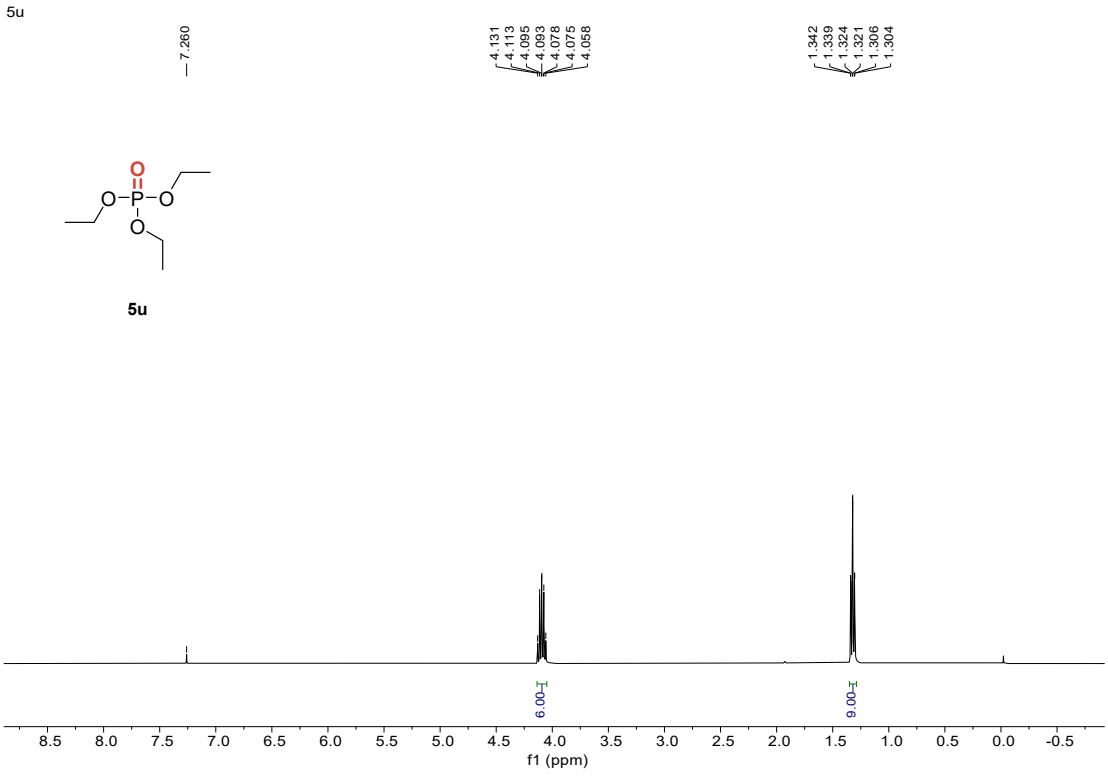


Fig. S157 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5u**.

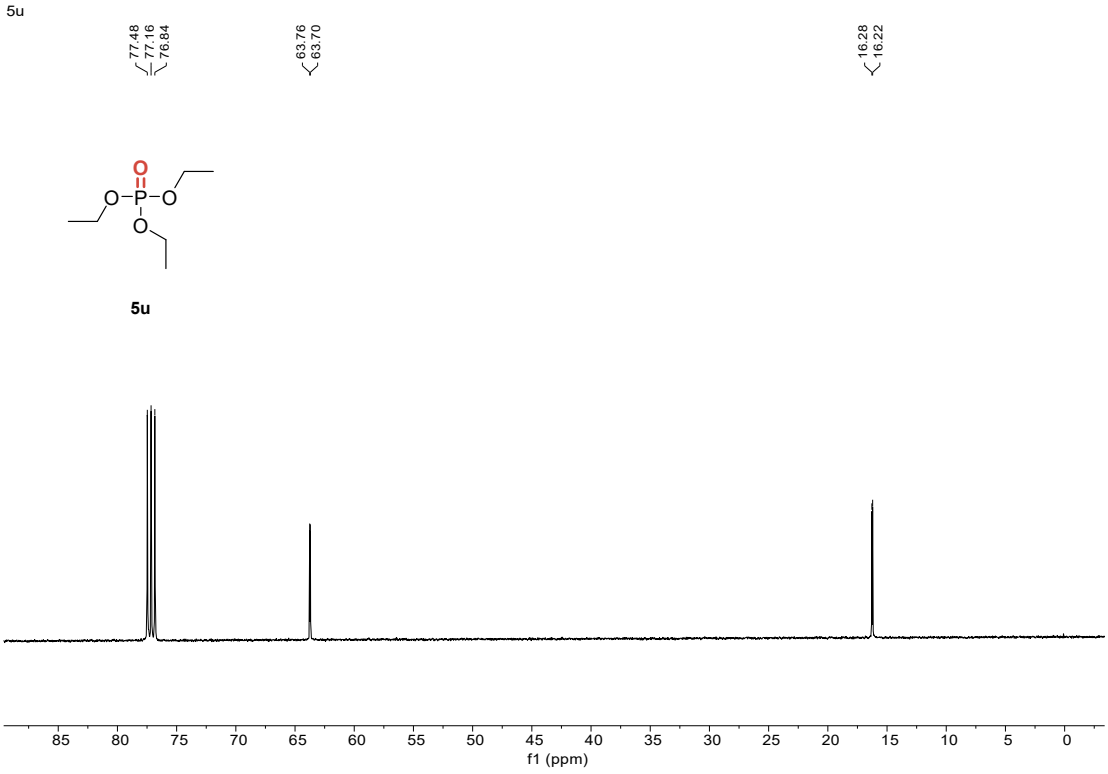


Fig. S158 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5u**.

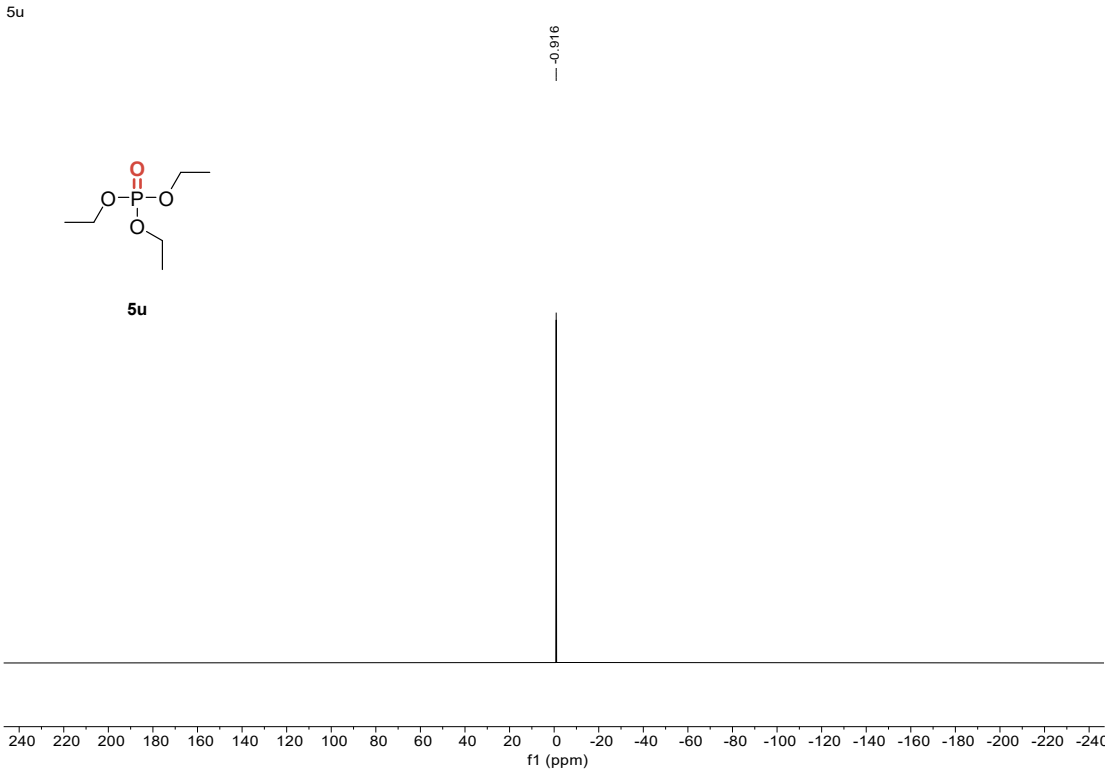


Fig. S159 ^{31}P NMR spectrum (202 MHz, $CDCl_3$) of **5u**.

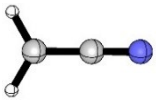
7. Cartesian coordinates of all the optimized geometries

Following geometries are optimized at the B3LYP-D3/6-311+G(d,p)/SMD(acetonitrile) level of theory:

O_2

G = −150.390994 a.u., *E* = −150.374754 a.u.

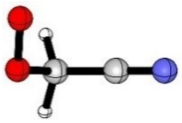
O	0.000000000	0.000000000	0.602698000
O	0.000000000	0.000000000	-0.602698000



·CH_2CN

G = −132.139786 a.u., *E* = −132.146550 a.u.

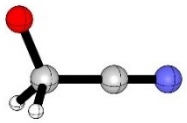
C	0.000056000	-1.191779000	0.000000000
H	0.000119000	-1.728029000	0.940406000
H	0.000119000	-1.728029000	-0.940406000
C	0.000000000	0.186696000	0.000000000
N	-0.000082000	1.355223000	0.000000000



·$OOCH_2CN$

G = −282.540159 a.u., *E* = −282.552838 a.u.

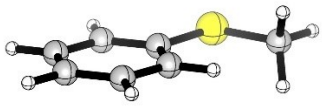
C	-0.017191000	0.892170000	0.205190000
H	-0.234439000	1.053102000	1.261904000
H	0.096983000	1.845448000	-0.311720000
C	1.178179000	0.074754000	0.039559000
N	2.125745000	-0.565482000	-0.093547000
O	-1.172255000	0.249755000	-0.426431000
O	-1.541330000	-0.842470000	0.205950000



·OCH_2CN

G = −207.358482 a.u., *E* = −207.367898 a.u.

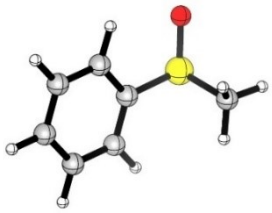
C	0.647160000	0.497820000	-0.000001000
H	0.844536000	1.157922000	-0.866300000
H	0.844527000	1.157924000	0.866304000
C	-0.774208000	0.095045000	0.000000000
N	-1.879153000	-0.231800000	0.000000000
O	1.528413000	-0.531305000	0.000001000



1a

G = −669.794920 a.u., *E* = −669.890870 a.u.

C	2.633638000	0.354293000	0.000030000
C	2.199315000	-0.973293000	-0.000087000
C	0.841032000	-1.271189000	-0.000107000
C	-0.108373000	-0.237744000	0.000052000
C	0.324263000	1.092287000	0.000077000
C	1.690520000	1.379016000	0.000040000
H	3.692786000	0.583623000	0.000139000
H	2.920822000	-1.782756000	-0.000195000
H	0.516271000	-2.306277000	-0.000246000
H	-0.386722000	1.907345000	-0.000079000
H	2.011995000	2.414678000	-0.000017000
S	-1.823931000	-0.722180000	0.000129000
C	-2.715678000	0.864735000	-0.000170000
H	-3.774552000	0.601829000	-0.000335000
H	-2.493141000	1.443969000	0.896255000
H	-2.492867000	1.443844000	-0.896597000

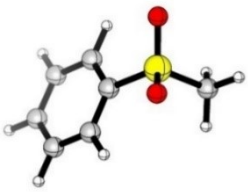


2a

G = −745.001307 a.u., *E* = −745.099241 a.u.

C	-2.865898000	0.090128000	0.163630000
C	-2.081497000	1.225940000	0.360235000
C	-0.699715000	1.163944000	0.177099000
C	-0.125678000	-0.044410000	-0.196815000
C	-0.895129000	-1.186446000	-0.411272000
C	-2.273516000	-1.113886000	-0.222794000
H	-3.939247000	0.142678000	0.304744000
H	-2.542656000	2.161868000	0.654155000
H	-0.070485000	2.034711000	0.317649000
H	-0.433505000	-2.118318000	-0.719981000
H	-2.884038000	-1.995024000	-0.382467000
C	2.092099000	-1.015063000	1.065662000
H	3.177244000	-1.124960000	1.081663000

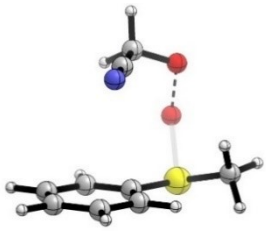
H	1.744698000	-0.433090000	1.920117000
H	1.615453000	-1.996048000	1.036004000
S	1.673766000	-0.115779000	-0.466265000
O	2.206037000	1.307426000	-0.295764000



3a

$G = -820.236353$ a.u., $E = -820.338588$ a.u.

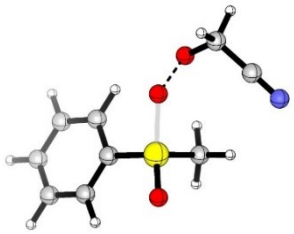
C	3.082725000	-0.000082000	0.076452000
C	2.390753000	-1.210755000	0.034122000
C	1.000566000	-1.218196000	-0.050322000
C	0.326418000	0.000068000	-0.092353000
C	1.000675000	1.218252000	-0.050036000
C	2.390870000	1.210658000	0.034385000
H	4.164568000	-0.000142000	0.141430000
H	2.931423000	-2.149180000	0.062956000
H	0.451478000	-2.150243000	-0.089863000
H	0.451654000	2.150344000	-0.089342000
H	2.931626000	2.149028000	0.063420000
C	-1.968779000	-0.001103000	1.564734000
H	-3.059899000	-0.001407000	1.573004000
H	-1.575120000	-0.900965000	2.036463000
H	-1.575606000	0.898369000	2.037617000
O	-1.910325000	1.269783000	-0.767830000
S	-1.468378000	0.000132000	-0.158626000
O	-1.910356000	-1.268654000	-0.769615000



$TS_{1a/2a}$

$G = -952.297876$ a.u., $E = -952.425027$ a.u.

C	-3.153929000	0.674477000	-0.116770000
C	-2.718811000	-0.057561000	0.986692000
C	-1.544554000	-0.803315000	0.922664000
C	-0.810369000	-0.811976000	-0.265363000
C	-1.242579000	-0.087679000	-1.382003000
C	-2.414266000	0.656657000	-1.299853000
H	-4.065212000	1.257639000	-0.055929000
H	-3.290119000	-0.046547000	1.907471000
H	-1.216571000	-1.360141000	1.789538000
H	-0.664187000	-0.096398000	-2.298214000
H	-2.746261000	1.225540000	-2.160353000
C	1.189602000	-2.155351000	1.219408000
H	2.180850000	-2.598178000	1.127017000
H	1.234181000	-1.249405000	1.821522000
H	0.498841000	-2.882893000	1.644070000
S	0.689070000	-1.745556000	-0.468483000
C	2.055296000	1.975139000	-0.286363000
H	1.690809000	1.991405000	-1.318833000
H	2.720384000	2.837904000	-0.150709000
C	0.904952000	2.161953000	0.618419000
N	0.021877000	2.315064000	1.344214000
O	2.790910000	0.821928000	-0.002543000
O	2.069960000	-0.405621000	-0.822497000

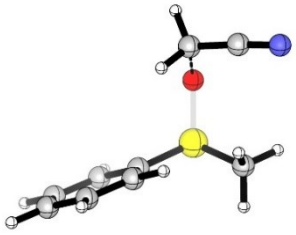


$TS_{2a/3a}$

$G = -1027.499079$ a.u., $E = -1027.629723$ a.u.

C	-4.021515000	-0.932853000	0.163217000
C	-3.878220000	0.428936000	-0.099964000
C	-2.608666000	0.988881000	-0.223823000
C	-1.499868000	0.159238000	-0.078301000
C	-1.619290000	-1.206538000	0.173613000
C	-2.895845000	-1.746551000	0.300993000
H	-5.011893000	-1.362332000	0.258509000
H	-4.752538000	1.059642000	-0.208030000
H	-2.480274000	2.044177000	-0.427059000
H	-0.740930000	-1.831116000	0.260979000
H	-3.009291000	-2.805362000	0.500872000
C	0.736390000	0.922027000	1.469226000
H	1.720966000	1.387170000	1.457501000
H	0.027867000	1.512781000	2.049611000
H	0.790361000	-0.104430000	1.825504000
S	0.131180000	0.907270000	-0.228631000
O	-0.042933000	2.341234000	-0.660152000
C	3.351457000	-1.410857000	-0.430054000
H	3.455181000	-1.416917000	-1.519736000
H	3.948040000	-2.236776000	-0.024192000
C	3.899659000	-0.146378000	0.086717000

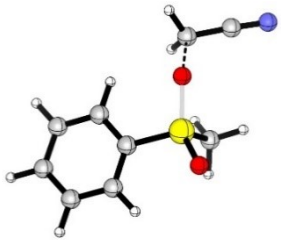
N	4.311382000	0.849893000	0.495450000
O	2.027911000	-1.632226000	-0.019537000
O	1.138689000	-0.589988000	-0.839530000



TS'$_{1a/2a}$

G = −877.097207 a.u., *E* = −877.220426 a.u.

C	3.409822000	1.097486000	-0.012301000
C	3.353289000	-0.133611000	0.643816000
C	2.189338000	-0.893587000	0.606296000
C	1.074196000	-0.412127000	-0.091375000
C	1.119116000	0.824700000	-0.743916000
C	2.294070000	1.570256000	-0.703928000
H	4.319801000	1.685207000	0.014522000
H	4.217676000	-0.506139000	1.180807000
H	2.147158000	-1.853557000	1.108046000
H	0.258890000	1.208654000	-1.274912000
H	2.333997000	2.526465000	-1.212502000
C	-1.218937000	-1.052528000	-1.608628000
H	-2.127495000	-1.654566000	-1.610784000
H	-1.473261000	0.002736000	-1.672166000
H	-0.568266000	-1.349859000	-2.431174000
S	-0.378913000	-1.434327000	-0.048709000
C	-2.123648000	0.974976000	1.193044000
H	-1.285162000	1.604679000	0.916119000
H	-2.356141000	0.974839000	2.251848000
C	-3.241205000	1.066163000	0.338590000
N	-4.136751000	1.066544000	-0.406512000
O	-1.447946000	-0.675675000	1.078193000



TS'$_{2a/3a}$

G = −952.307007 a.u., *E* = −952.434603 a.u.

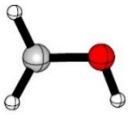
C	3.650840000	1.104033000	0.183175000
C	3.569625000	-0.288714000	0.182214000
C	2.335813000	-0.918832000	0.043189000
C	1.192897000	-0.131010000	-0.089201000
C	1.255015000	1.260987000	-0.099640000
C	2.496525000	1.875100000	0.042436000
H	4.614221000	1.588862000	0.288963000
H	4.466411000	-0.887628000	0.288150000
H	2.259757000	-1.998693000	0.035344000
H	0.359996000	1.854000000	-0.225497000
H	2.560477000	2.956732000	0.036107000
C	-1.012552000	-1.058687000	1.411987000
H	-2.010047000	-1.496174000	1.367344000
H	-0.331448000	-1.697695000	1.973329000
H	-1.043626000	-0.054694000	1.832552000
S	-0.387455000	-0.967346000	-0.274810000
O	-0.119759000	-2.397584000	-0.676992000
C	-2.385809000	1.483422000	-0.226939000
H	-2.402645000	2.172235000	-1.064753000
H	-1.835659000	1.852104000	0.633017000
C	-3.655183000	0.936285000	0.097412000
N	-4.670898000	0.439075000	0.355982000
O	-1.433353000	0.215015000	-0.888917000

Following geometries are optimized at the B3LYP-D3/6-311+G(d,p)/SMD(methanol) level of theory:

O_2

G = −150.387376 a.u., *E* = −150.371153 a.u.

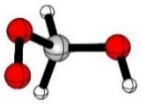
O	0.000000000	0.000000000	0.601989000
O	0.000000000	0.000000000	-0.601989000



·CH_2OH

G = −115.097617 a.u., *E* = −115.111425 a.u.

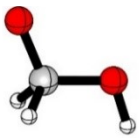
C	-0.688517000	0.027467000	0.056087000
H	-1.107513000	1.007716000	-0.137902000
H	-1.244514000	-0.886338000	-0.104227000
O	0.672164000	-0.127674000	-0.015463000
H	1.105822000	0.735211000	0.029309000



·$OOCH_2OH$

G = −265.526068 a.u., *E* = −265.546332 a.u.

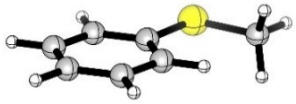
C	-0.604031000	0.544331000	0.277500000
H	-0.445070000	0.503074000	1.355311000
H	-0.978706000	1.506791000	-0.064009000
O	-1.411946000	-0.462936000	-0.205203000
H	-1.247954000	-1.278433000	0.288416000
O	0.745995000	0.482025000	-0.339052000
O	1.452941000	-0.518766000	0.138665000



·OCH_2OH

G = −190.346666 a.u., *E* = −190.361908 a.u.

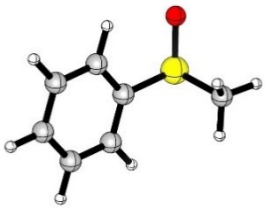
C	-0.106693000	0.426313000	0.000063000
H	-0.137295000	1.119699000	-0.876920000
H	-0.137562000	1.119368000	0.877329000
O	1.085902000	-0.329535000	0.000122000
H	1.838771000	0.278803000	-0.000938000
O	-1.201371000	-0.304934000	-0.000104000



1a

G = −669.793317 a.u., *E* = −669.889276 a.u.

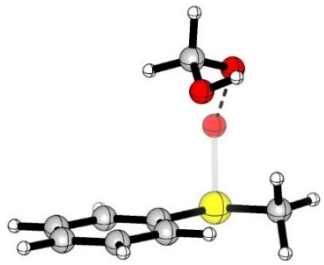
C	-2.633638000	0.354293000	-0.000030000
C	-2.199315000	-0.973293000	0.000087000
C	-0.841032000	-1.271189000	0.000107000
C	0.108373000	-0.237744000	-0.000052000
C	-0.324263000	1.092287000	-0.000077000
C	-1.690520000	1.379016000	-0.000040000
H	-3.692786000	0.583623000	-0.000139000
H	-2.920822000	-1.782756000	0.000195000
H	-0.516271000	-2.306277000	0.000246000
H	0.386722000	1.907345000	0.000079000
H	-2.011995000	2.414678000	0.000017000
S	1.823931000	-0.722180000	-0.000129000
C	2.715678000	0.864735000	0.000170000
H	3.774552000	0.601829000	0.000335000
H	2.493141000	1.443969000	-0.896255000
H	2.492867000	1.443844000	0.896597000



2a

G = −745.003455 a.u., *E* = −745.101631 a.u.

C	-2.864718000	0.090702000	0.165530000
C	-2.080240000	1.226501000	0.359750000
C	-0.698884000	1.165027000	0.176140000
C	-0.126675000	-0.044090000	-0.198463000
C	-0.895671000	-1.186507000	-0.411653000
C	-2.273434000	-1.113525000	-0.220285000
H	-3.937923000	0.143901000	0.308097000
H	-2.540405000	2.163227000	0.652700000
H	-0.075548000	2.039403000	0.317740000
H	-0.435387000	-2.118579000	-0.721758000
H	-2.884072000	-1.994906000	-0.378276000
C	2.099193000	-0.983271000	1.085637000
H	3.185045000	-1.086540000	1.099812000
H	1.750150000	-0.379299000	1.923918000
H	1.628272000	-1.967465000	1.084533000
S	1.668423000	-0.133447000	-0.466033000
O	2.207210000	1.300798000	-0.321270000



$TS_{1a/2a}$

G = −935.281518 a.u., *E* = −935.416949 a.u.

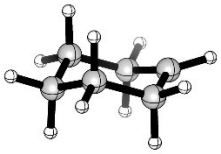
C	-3.209779000	0.874150000	0.020108000
C	-2.490157000	0.611867000	1.184821000
C	-1.329536000	-0.156128000	1.141982000
C	-0.900885000	-0.671356000	-0.084115000
C	-1.618457000	-0.414454000	-1.259721000
C	-2.770433000	0.360734000	-1.201080000
H	-4.109730000	1.476473000	0.062560000
H	-2.827486000	1.009530000	2.134883000
H	-0.778983000	-0.344170000	2.053065000
H	-1.277995000	-0.812477000	-2.208915000
H	-3.324502000	0.563127000	-2.110187000
C	1.278874000	-1.748537000	1.378263000
H	2.211857000	-2.298644000	1.257335000
H	1.479238000	-0.743506000	1.744787000
H	0.610426000	-2.293884000	2.044202000
S	0.553255000	-1.667186000	-0.273863000
O	1.883193000	-0.440654000	-1.048783000
C	1.973642000	1.924908000	-0.361994000
H	2.635636000	2.798154000	-0.446832000
H	1.203934000	1.955051000	-1.136160000
O	1.286391000	1.945225000	0.879046000
H	1.932742000	2.084702000	1.584096000
O	2.804562000	0.819616000	-0.518588000

Following geometries are optimized at the B3LYP-D3/6-311+G(d,p)/SMD(cyclohexane) level of theory:

O_2

G = −150.388369 a.u., *E* = −150.372124 a.u.

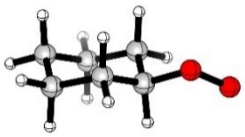
O	0.000000000	0.000000000	0.602845000
O	0.000000000	0.000000000	-0.602845000



·Cy

G = −235.184710 a.u., *E* = −235.309598 a.u.

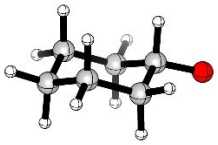
C	-0.000032000	1.410193000	0.263832000
C	1.265997000	0.709733000	-0.243175000
C	1.284803000	-0.776872000	0.163570000
C	0.000060000	-1.461778000	-0.165954000
C	-1.284745000	-0.776972000	0.163505000
C	-1.266060000	0.709674000	-0.243108000
H	2.131973000	-1.292133000	-0.298153000
H	1.301866000	0.781867000	-1.336498000
H	2.160136000	1.211752000	0.139365000
H	-0.000007000	1.409516000	1.361801000
H	-0.000060000	2.458980000	-0.049023000
H	0.000102000	-2.504125000	-0.463685000
H	-2.131843000	-1.292263000	-0.298322000
H	-1.458955000	-0.825589000	1.254609000
H	-1.302072000	0.781933000	-1.336416000
H	-2.160190000	1.211574000	0.139609000
H	1.458908000	-0.825377000	1.254692000



·OOCy

G = −385.608341 a.u., *E* = −385.741152 a.u.

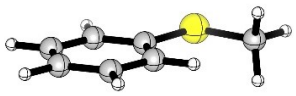
C	2.233368000	0.209974000	-0.207334000
C	1.327208000	1.376914000	0.202615000
C	-0.114944000	1.160021000	-0.276914000
C	-0.640881000	-0.174410000	0.234846000
C	0.229206000	-1.347414000	-0.187497000
C	1.673855000	-1.128959000	0.287485000
H	-0.768981000	1.965531000	0.064812000
H	1.335625000	1.477945000	1.294784000
H	1.707945000	2.318885000	-0.201553000
H	2.317087000	0.184768000	-1.300821000
H	3.243908000	0.361856000	0.183146000
H	-0.774413000	-0.149445000	1.319573000
H	-0.176776000	-2.277853000	0.217843000
H	0.207241000	-1.427406000	-1.280077000
H	1.701064000	-1.150398000	1.383837000
H	2.298938000	-1.957118000	-0.057247000
H	-0.144290000	1.149598000	-1.372518000
O	-1.982417000	-0.429858000	-0.324785000
O	-2.916861000	0.295717000	0.253412000



·OCy

G = −310.422326 a.u., *E* = −310.550899 a.u.

C	1.816794000	-0.000257000	-0.260783000
C	1.101191000	1.265068000	0.224963000
C	-0.372289000	1.280436000	-0.201291000
C	-1.102846000	0.000490000	0.245760000
C	-0.372811000	-1.280294000	-0.201222000
C	1.100702000	-1.265351000	0.224849000
H	-0.893227000	2.151260000	0.204817000
H	1.160937000	1.315053000	1.319796000
H	1.604456000	2.158802000	-0.155775000
H	1.846104000	-0.000208000	-1.357720000
H	2.856099000	-0.000525000	0.081799000
H	-1.115567000	-0.000300000	1.363133000
H	-0.894199000	-2.150627000	0.205278000
H	-0.443087000	-1.339592000	-1.293637000
H	1.160536000	-1.315544000	1.319656000
H	1.603537000	-2.159232000	-0.156141000
H	-0.442325000	1.339653000	-1.293749000
O	-2.433463000	0.000088000	-0.053889000

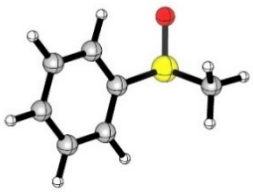


1a

G = −669.791672 a.u., *E* = −669.887834 a.u.

C	-2.632981000	0.350538000	-0.000083000
C	-2.195077000	-0.974782000	-0.000077000
C	-0.837361000	-1.268795000	-0.000021000
C	0.110014000	-0.234703000	0.000021000

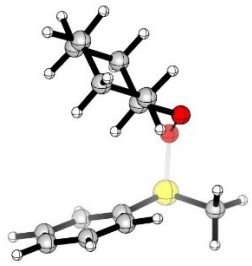
C	-0.327442000	1.092828000	0.000007000
C	-1.693318000	1.376531000	-0.000041000
H	-3.692418000	0.577167000	-0.000117000
H	-2.914656000	-1.785672000	-0.000110000
H	-0.507939000	-2.301995000	-0.000011000
H	0.380539000	1.910200000	0.000037000
H	-2.017824000	2.411087000	-0.000047000
S	1.823732000	-0.721717000	0.000082000
C	2.712006000	0.864982000	0.000012000
H	3.771539000	0.605289000	0.000380000
H	2.493270000	1.445712000	-0.896933000
H	2.492728000	1.446092000	0.896579000



2a

$G = -744.994082$ a.u., $E = -745.092405$ a.u.

C	-2.863638000	0.097212000	0.166623000
C	-2.072765000	1.227950000	0.361515000
C	-0.692531000	1.158893000	0.176056000
C	-0.125340000	-0.052233000	-0.197425000
C	-0.902414000	-1.188090000	-0.412338000
C	-2.279558000	-1.109133000	-0.222019000
H	-3.936456000	0.156025000	0.308157000
H	-2.528990000	2.166566000	0.654011000
H	-0.052218000	2.023168000	0.308465000
H	-0.447153000	-2.120218000	-0.729951000
H	-2.896324000	-1.985413000	-0.383905000
C	2.087330000	-1.013366000	1.071453000
H	3.172897000	-1.115934000	1.096243000
H	1.737359000	-0.426611000	1.921365000
H	1.615945000	-1.997013000	1.051236000
S	1.676941000	-0.114818000	-0.470578000
O	2.199673000	1.301139000	-0.294946000



$TS_{1a/2a}$

$G = -1055.347802$ a.u., $E = -1055.594718$ a.u.

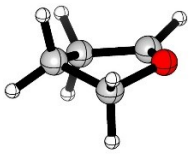
C	-1.877899000	-2.988478000	-0.229744000
C	-2.325954000	-2.484889000	0.991957000
C	-2.442435000	-1.113255000	1.183229000
C	-2.103853000	-0.239420000	0.143914000
C	-1.644153000	-0.736245000	-1.078561000
C	-1.541059000	-2.112613000	-1.259795000
H	-1.790592000	-4.058363000	-0.376627000
H	-2.588125000	-3.160933000	1.797085000
H	-2.791892000	-0.720299000	2.131009000
H	-1.358333000	-0.066432000	-1.877317000
H	-1.185206000	-2.498556000	-2.207821000
C	-2.301022000	2.269626000	-1.126229000
H	-3.130061000	1.839990000	-1.687698000
H	-2.483600000	3.327334000	-0.938236000
H	-1.344422000	2.152720000	-1.635395000
S	-2.188973000	1.495035000	0.505369000
O	-0.383635000	1.954707000	0.745554000
C	4.070219000	-0.860279000	0.190641000
C	3.204515000	-0.509227000	1.406612000
C	2.386076000	0.764077000	1.159535000
C	1.534324000	0.639039000	-0.104941000
C	2.402026000	0.308042000	-1.325594000
C	3.222589000	-0.967079000	-1.082664000
H	1.730556000	0.982810000	2.005465000
H	2.522457000	-1.343727000	1.615596000
H	3.830041000	-0.388564000	2.296700000
H	4.829404000	-0.079953000	0.052504000
H	4.609628000	-1.797315000	0.363723000
H	0.814570000	-0.179562000	0.031317000
H	1.763010000	0.195534000	-2.206557000
H	3.074436000	1.151838000	-1.519815000
H	2.539507000	-1.820964000	-0.989482000
H	3.860275000	-1.168290000	-1.949479000
H	3.057083000	1.623221000	1.037845000
O	0.829209000	1.829438000	-0.400415000

Following geometries are optimized at the B3LYP-D3/6-311+G(d,p)/SMD(tetrahydrofuran) level of theory:

O_2

G = −150.394530 a.u., *E* = −150.378292 a.u.

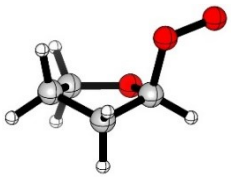
O	0.000000000	0.000000000	0.602698000
O	0.000000000	0.000000000	-0.602698000



·C_4H_7O

G = −231.808131 a.u., *E* = −231.882525 a.u.

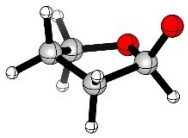
C	-1.143727000	0.379356000	-0.173816000
O	-0.767554000	-0.989987000	0.116716000
C	0.592690000	-1.095456000	-0.044418000
C	1.243797000	0.254044000	-0.137793000
C	0.078584000	1.206252000	0.215295000
H	-1.364506000	0.460837000	-1.244059000
H	-2.044229000	0.599946000	0.398472000
H	1.023062000	-1.986960000	0.394306000
H	2.095335000	0.357900000	0.541372000
H	1.615482000	0.457591000	-1.150822000
H	0.066322000	1.408574000	1.289243000
H	0.120895000	2.156828000	-0.317847000



·OOTHF

G = −382.237966 a.u., *E* = −382.318235 a.u.

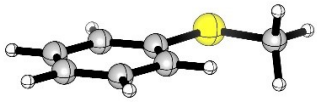
C	-1.497119000	-0.966348000	-0.213656000
O	-0.214900000	-1.087914000	0.477073000
C	0.364529000	0.151713000	0.628514000
C	-0.715820000	1.196925000	0.434054000
C	-1.637774000	0.510288000	-0.585415000
H	-1.483150000	-1.634884000	-1.074721000
H	-2.268981000	-1.295842000	0.485815000
H	0.949927000	0.189906000	1.545441000
H	-1.222531000	1.341965000	1.391426000
H	-0.317055000	2.155661000	0.103764000
H	-2.670418000	0.852410000	-0.516919000
H	-1.282197000	0.687799000	-1.602351000
O	1.365219000	0.376230000	-0.474144000
O	2.501121000	-0.244878000	-0.242108000



·OTHF

G = −307.052684 a.u., *E* = −307.129051 a.u.

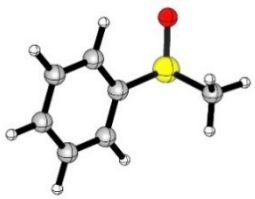
C	1.350454000	-0.711975000	0.019294000
O	0.001943000	-1.201105000	-0.139394000
C	-0.900985000	-0.119335000	-0.356692000
C	-0.018818000	1.188442000	-0.391654000
C	1.211574000	0.755798000	0.407360000
H	1.842414000	-1.321218000	0.778753000
H	1.889525000	-0.824786000	-0.929010000
H	-1.379625000	-0.253458000	-1.348826000
H	0.232431000	1.396089000	-1.432636000
H	-0.557752000	2.037190000	0.023937000
H	2.097821000	1.338845000	0.150689000
H	1.025539000	0.853361000	1.479699000
O	-1.877407000	-0.036846000	0.540337000



1a

G = −669.793548 a.u., *E* = −669.889563 a.u.

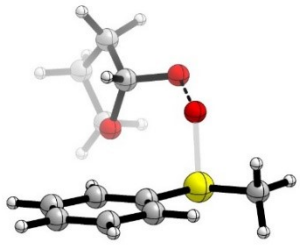
C	-2.633568000	0.352908000	-0.000076000
C	-2.197922000	-0.973822000	0.000127000
C	-0.839829000	-1.270234000	0.000118000
C	0.108855000	-0.236563000	-0.000085000
C	-0.325556000	1.092544000	-0.000288000
C	-1.691693000	1.378089000	-0.000280000
H	-3.692881000	0.581286000	-0.000065000
H	-2.918716000	-1.783898000	0.000283000
H	-0.513668000	-2.304779000	0.000274000
H	0.383989000	1.908793000	-0.000466000
H	-2.014318000	2.413395000	-0.000444000
S	1.823878000	-0.721921000	-0.000013000
C	2.714947000	0.864550000	0.000376000
H	3.774088000	0.602539000	-0.000671000
H	2.493288000	1.444930000	-0.895757000
H	2.494766000	1.443646000	0.897701000



2a

G = −744.998996 a.u., *E* = −745.097042 a.u.

C	-2.865194000	0.092610000	0.164357000
C	-2.078666000	1.226596000	0.361081000
C	-0.697400000	1.162231000	0.177329000
C	-0.125369000	-0.046742000	-0.196929000
C	-0.897452000	-1.186578000	-0.412176000
C	-2.275474000	-1.111944000	-0.223365000
H	-3.938456000	0.147240000	0.305360000
H	-2.538242000	2.163387000	0.654744000
H	-0.064526000	2.030849000	0.315380000
H	-0.438403000	-2.118457000	-0.724899000
H	-2.888141000	-1.991324000	-0.384703000
C	2.088608000	-1.015910000	1.067556000
H	3.173881000	-1.124105000	1.088039000
H	1.739600000	-0.433886000	1.921352000
H	1.613561000	-1.997734000	1.039332000
S	1.675187000	-0.114901000	-0.467247000
O	2.205428000	1.305110000	-0.295722000



$TS_{1a/2a}$

G = −1051.977395 a.u., *E* = −1052.172191 a.u.

C	3.227852000	-2.351373000	0.345021000
C	3.852495000	-1.122078000	0.548169000
C	3.190757000	0.066871000	0.247870000
C	1.893257000	0.012415000	-0.267798000
C	1.255547000	-1.218086000	-0.474136000
C	1.928855000	-2.394317000	-0.163650000
H	3.749235000	-3.270995000	0.583615000
H	4.860836000	-1.082079000	0.943719000
H	3.691016000	1.011056000	0.413629000
H	0.238600000	-1.243060000	-0.849219000
H	1.435333000	-3.346909000	-0.318316000
C	1.993066000	2.840597000	-0.228310000
H	1.390243000	3.730651000	-0.406592000
H	2.265559000	2.783466000	0.824269000
H	2.876754000	2.860933000	-0.867627000
S	0.929209000	1.447742000	-0.680337000
O	-0.346718000	1.539213000	0.783499000
C	-3.236065000	-0.587926000	-1.271686000
O	-1.963713000	-0.540862000	-0.611457000
C	-2.176423000	-0.075293000	0.731076000
C	-3.653625000	-0.403081000	1.068522000
C	-4.192760000	-1.094101000	-0.196331000
H	-3.520639000	0.413005000	-1.621008000
H	-3.140796000	-1.247940000	-2.135066000
H	-1.448839000	-0.608962000	1.348113000
H	-3.718919000	-1.028320000	1.959595000
H	-4.186567000	0.529077000	1.267720000
H	-4.108087000	-2.180523000	-0.108643000
H	-5.234697000	-0.844660000	-0.406000000
O	-2.003834000	1.291601000	0.856049000

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