Supplementary Information (SI) for Organic Chemistry Frontiers.

Supplementary Information

Reactions of Ketosulfoxonium Ylides with Allylic Carbocations: Stereoselective Access to Highly-Substituted Cyclopropanes and α-Alkylated Ylides

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1 Materials and methods

Reaction Setup: Air sensitive reactions were performed in flame- or oven-dried glassware equipped with tightly fitted rubber septa and under an ultra-purified argon (>99.999%) atmosphere. Other reactions were performed with same glassware without the use of the argon atmosphere Analytical thin-layer chromatography (TLC) was conducted on aluminum plates with 0.2 mm of silica gel 60 F_{254} (Merck), with visualization by UV-Vis (254 nm) and treatment with Vaniline or $KMnO_4$ solution.

Solvents: THF was dried over 4 Å molecular sieves prior to use. When dry HFIP was used, it was distilled over 4 Å molecular sieve prior to use. All other solvents were used without any treatment.

Chemicals: All reagents available commercially were used without further purification.

Purification: Column flash chromatography was performed using silica gel 601 (particle size 0.063-0.210 mm) or using Biotage Isolera^{TM} Prime (Using Snap Ultra 10 g Cartrige). All of the yields refer to isolated products.

Microwave: Microwave experiments were performed in a microwave synthesis reactor (AntonPaar Monowave 300), powers from 0 to 850 W, and pressures from 0 to 30 bar, using sealed glass vials (6 mL).

NMR Spectroscopy: ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-*d*$_6$ solution on a 400 (Agilent Technologies, 400/54 Premium Shielded) or 500 MHz (Agilent Technologies, 500/54 Premium Shielded). The chemical shifts (δ) are given in part per million from the peak of tetramethylsilane (δ 0.00 ppm) as an internal standard in ^{1}H NMR or residual solvents from $CDCl_3$ (7.26 ppm) or DMSO-d$_6$ (2.50 ppm). Multiplicities are given as s (singlet), d (doublet), dd (doublet of doublets), t (triplet), td (triplet of doublets) and m (multiplet); coupling constants (*J*) are given in Hz. ^{13}C NMR spectra were recorded on 100 MHz or 125 MHz spectrometers, and chemical shifts (δ) are given from $CDCl_3$ (77.0 ppm) or DMSO-d$_6$ (39.5 ppm).

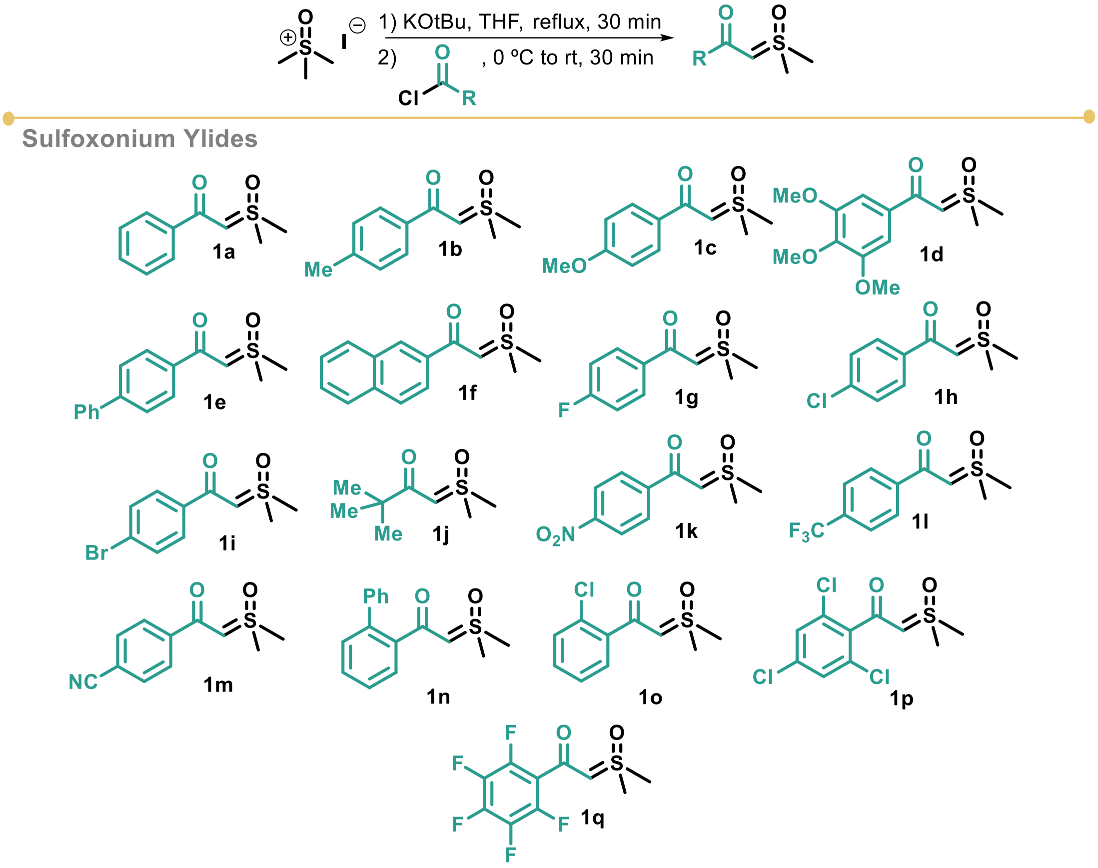
Infrared Spectroscopy (IR): IR spectra were obtained using Fourier-transform infrared spectroscopy (FT-IR) at 4.0 cm^{-1} resolution (Bruker, model ALPHA) and are reported in wavenumbers.

Melting Points (Mp): All melting points were determined in open glass capillaries using a digital melting point apparatus (Fisatom, model 430D). The values were uncorrected.

High-Resolution Mass Spectrosopy (HRMS): High-resolution mass spectra (HRMS) were recorded using Termo Scientific LQT Velos mass spectrometer and electron spray ionization (ESI/Orbitrap) or Bruker INCT-IF mass spectrometer and electron spray ionization (ESI/TOF/micrOTOF II models)

Single Crystal X-ray Diffraction (SCXRD): Single crystals were analyzed at 100 K on a Rigaku XtaLAB Synergy-S Dualflex diffractometer equipped with a HyPix-6000HE detector, using a Cu Kα radiation (λ = 1.54184 Å).

2 General procedure A: Synthesis of the Ketosulfoxonium Ylides

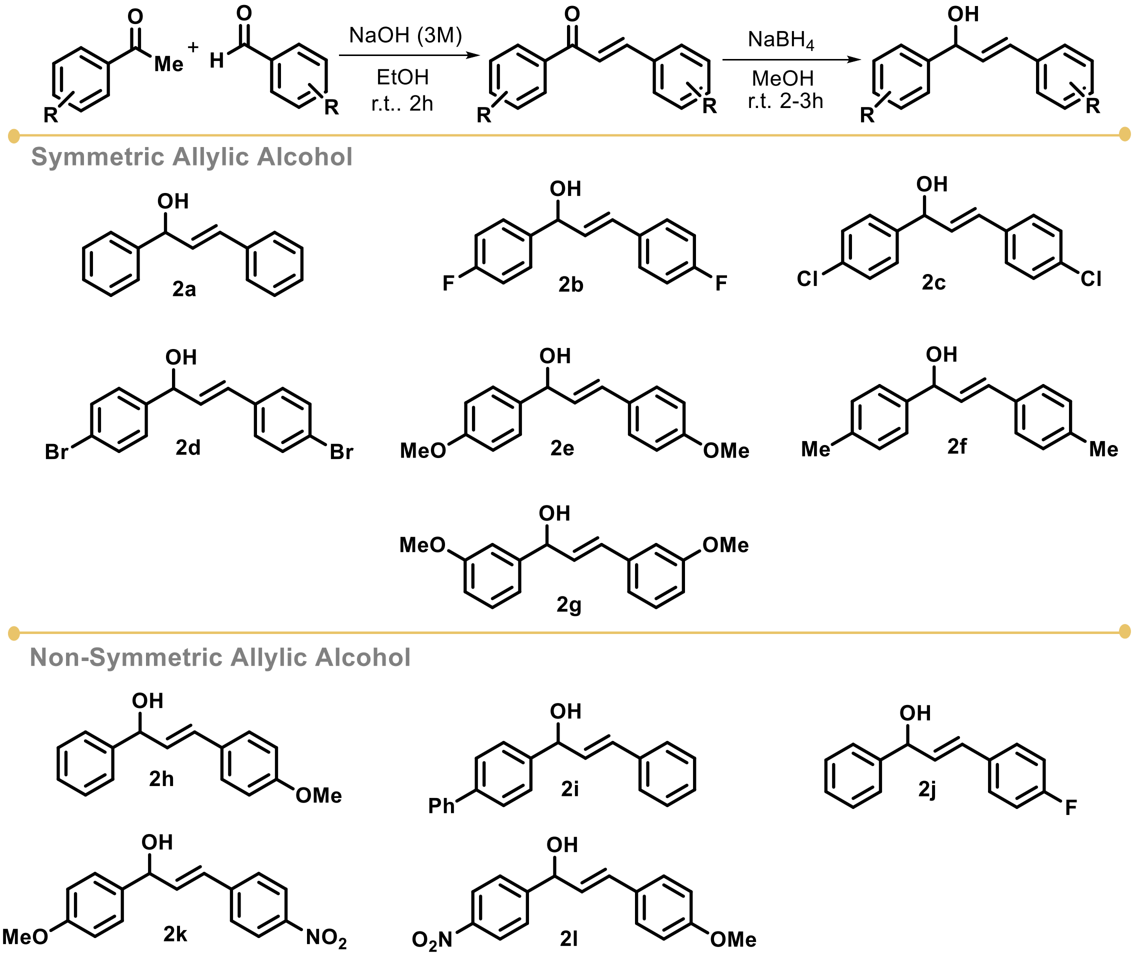


1a 1b 1c 1d 1e 1f 1g 1h 1i 1j 1k 1l 1m 1n 1o 1p 1q

This procedure was followed from literature with some modifications. To a 125 mL round bottom flask equipped with magnetic stir, trimethylsulfoxonium iodide (242.1 mg; 1.1 mmol; 1.1 eq) and potassium *tert*-butoxide (235.6 mg; 2.1 mmol; 2.1 eq), coupled with a condenser and dried under reduced pressure with support of hot-air pistol. Under Ar atmosphere, dry THF (4.5 mL) was added and stirred under reflux for 30 min. After cooling to rt, and under 0 °C bath, a solution of benzoyl chloride (1 mmol; 1 eq) in THF (1 mL; 1 M) was added dropwise, and the resultant solution was stirred at rt for further 30 min. After the elapsed time, the solvent was removed under reduced pressure, and to the solid, distilled water was added and the aqueous phase extracted with mixture of CH_2Cl_2: *i*PrOH (3:1; 3 x 10 mL). The organic phase was combined, dried over Na_2SO_4, filtered and the solvent removed under reduced pressure. The product was purified by recrystallization (EtOAc and hexanes)

The sulfoxonium ylides used in this paper were prepared from literature and the data characterization matches with reported data.[1,1,2,3,4,5,6,7,8]

3 General Procedure B: Synthesis of the Alcohols

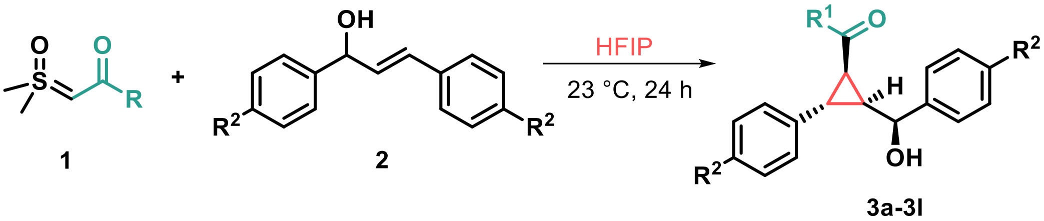


To a 50 mL round bottom flask, acetophenone (5 mmol; 1 eq), benzaldehyde (5 mmol; 1 eq) and EtOH (10mL) were added. After cooling the mixture to 0°C, aqueous solution of NaOH (2 M; 2 eq) was added to the solution dropwise. The resulted solution was stirred at rt until the completion of the starting material. The reactional mixture was filtered and the solid collected, furnishing the desired alcohol. In some cases, recrystallization was performed to ensure the pure chalcone, but usually the next step was performed without the purification.

To a 25 mL round bottom flask, the chalcone (2 mmol; 1 eq) and magnetic stir were added, followed by addition of MeOH (4 mL;0,5 M) (obs: in some cases, CH_2Cl_2 was added to solubilize the chalcone). $NaBH_4$ (2.4 mmol; 1.2 eq) was added in one portion at rt. After the consuption of ketone, the organic solvent was removed under reduced pressure, followed by addition of deionized water and extracted with EtOAc. After combining the organic solventes, Na_2SO_4 was added, filtered and the EtOAc removed under reduced pressure. The synthetized alcohols were previously reported.

The alcohols used in this paper were prepared from literature and the data characterization matches with reported data.[9,10,11,12,13,14,15,16,17]

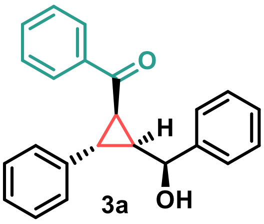
4 General Procedure C: Synthesis of Cyclopropanes via Sulfoxonium Ylides Addition to Allylic Carbocations



To a 4 mL vial, the sulfoxonium ylide **1** (0.1 mmol; 1 eq), the alcohol **2** (0.2 mmol; 2 eq) and the magnetic stir were added. After closing the flask with tightly fitted rubber septa, HFIP (200 μL, 0.5 M) was added, and the reaction was stirred at 23 °C for 24 h. After the elapsed time, $CHCl_3$ was added to the reaction and the solvent was removed under reduce pressure. The crude was transferred to the column chromathography (EtOAc:hexanes 15:85 → 20:80) to obtain the desired product **3**.

1 mmol scale: To a 10 mL round bottom flask, **2a** (420 mg; 2 mmol; 2 eq), **1a** (196.3 mg; 1 mmol; 1 eq) and HFIP (2 mL; 0.5 M) were added sequentially and the reaction maintained under stirring at 23 °C for 24 h. After elapsed time, $CHCl_3$ was added to the reaction, and the solvents removed under reduced pressure, repeating the procedure twice. The crude was transferred to column chromathography (EtOAc:hexanes 15:85 → 20:80) to provide **3** (167.5 mg; 0.51 mmol; 51 % yield) as a white solid

(±)((1*R*,2*S*,3*S*)-2-((*S*)-hydroxy(phenyl)methyl) - 3phenylcyclopropyl)(phenyl) methanone (**3a**)



3a

Prepared according to procedure C from chalcone **2a** and sulfoxonium ylide **1a**.

Column chromatography eluent: Hex/AcOEt 80:20.

White solid (36.3 mg; 56% yield)

m.p.: 128-129 °C

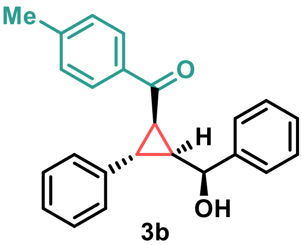
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 – 8.03 (m, 2H), 7.62 – 7.56 (m, 1H), 7.53 – 7.46 (m, 4H), 7.38 – 7.32 (m, 2H), 7.31 – 7.23 (m, 3H), 7.22 – 7.16 (m, 1H), 7.12 – 7.04 (m, 2H), 4.96 (d, *J* = 9.0 Hz, 1H), 3.18 – 3.08 (m, 2H), 2.56 (bs, 1H), 2.41 (td, *J* = 9.0, 7.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 198.5, 143.5, 139.2, 138.2, 133.1, 128.6, 128.6, 128.6, 128.3, 127.6, 126.8, 126.6, 125.8, 71.4, 40.7, 33.7, 32.0.

IR (neat, cm^{-1}): 3406, 3060, 3029, 2922, 1662, 1599, 1580, 1495, 1450, 1431, 1390, 1339, 1307, 1227, 1078, 1061, 1033, 1015, 953, 917, 744, 697,660.

HRMS (ESI-TOF): Calculated for $C_{23}H_{20}O_2Na$ $[M+Na]^+$ 351.13555, found 351.13409

(±)((1*R*,2*S*,3*S*)-2-((*S*)-hydroxy(phenyl)methyl)-3-phenylcyclopropyl)(*p*-tolyl)methanone (**3b**)



3b

Prepared according to procedure C from chalcone **2a** and sulfoxonium ylide **1b**.

Column chromatography eluent: Hex/AcOEt 80:20.

White solid (15 mg; 44% yield)

m.p.: 153-154 °C

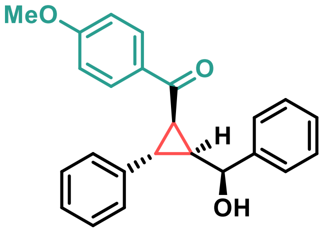
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 – 7.92 (m, 2H), 7.51 – 7.45 (m, 2H), 7.37 – 7.29 (m, 2H), 7.29 – 7.22 (m, 5H), 7.21 – 7.14 (m, 1H), 7.08 – 7.04 (m, 2H), 4.94 (dd, *J* = 9.1, 3.9 Hz, 1H), 3.12 – 3.05 (m, 2H), 2.64 (d, *J* = 3.9 Hz, 1H), 2.41 (s, 3H), 2.40 – 2.32 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 198.0, 144.1, 143.5, 139.3, 135.6, 129.3, 128.6, 128.6, 128.6, 128.5, 127.5, 126.7, 126.6, 125.8, 71.5, 40.5, 33.6, 31.9, 21.7.

IR (neat, cm^{-1}): 3424, 3060, 3029, 2922, 1659, 1606, 1573, 1522, 1495, 1452, 1432, 1410, 1372, 1344, 1235, 1207, 1180, 1078, 1060, 1031, 1014, 953, 916, 823, 752, 724, 698

HRMS (ESI-TOF): Calculated for $C_{24}H_{22}O_2Na$ $[M+Na]^+$ 365.15120, found 365.14877.

(±)((1*R*,2*S*,3*S*)-2-((*S*)-hydroxy(phenyl)methyl)-3-phenylcyclopropyl)(4-methoxyphenyl)methanone (**3c**)



3c

Prepared according to procedure C from chalcone **2a** and sulfoxonium ylide **1c**.

Column chromatography eluent: Hex/AcOEt 80:20.

White solid (19.4 mg; 54% yield)

m.p.: 150-151 °C

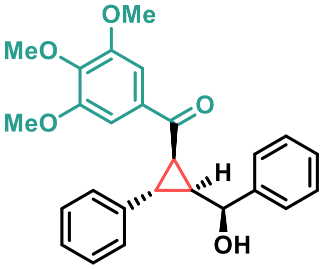
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 – 8.01 (m, 2H), 7.52 – 7.47 (m, 2H), 7.38 – 7.30 (m, 2H), 7.30 – 7.23 (m, 4H), 7.22 – 7.17 (m, 1H), 7.12 – 7.05 (m, 2H), 6.99 – 6.90 (m, 2H), 4.96 (dd, *J* = 8.8, 3.0 Hz, 1H), 3.88 (s, 3H), 3.11 – 3.01 (m, 2H), 2.77 (d, J = 4.0 Hz, 1H), 2.36 (td, J = 8.8, 6.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 197.0, 163.9, 143.7, 139.6, 131.2, 130.8, 128.8, 128.7, 127.6, 126.9, 126.7, 126.0, 114.0, 71.8, 55.7, 40.4, 33.6, 31.9.

IR (neat, cm^{-1}): 3443, 3060, 3029, 2925, 2852, 1653, 1600, 1575, 1511, 1496, 1456, 1428, 1372, 1341, 1311, 1260, 1239, 1170, 1114, 1079, 1060, 1020, 955, 841, 804, 781, 753, 698, 614.

HRMS (ESI-TOF): Calculated for $C_{24}H_{22}NaO_3$ $[M+Na]^+$ 381,1467, found 381.1461

(±)((1*R*,2*S*,3*S*)-2-((*S*)-hydroxy(phenyl)methyl)-3-phenylcyclopropyl)(3,4,5-trimethoxyphenyl)methanone (**3d**)



3d

Prepared according to procedure C from chalcone **2a** and sulfoxonium ylide **1d**.

Column chromatography eluent: Hex/AcOEt 80:20.

White solid (24.7 mg; 59% yield)

m.p.: 129-130 °C

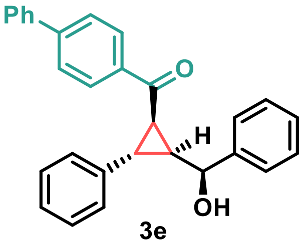
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 – 7.49 (m, 2H), 7.39 – 7.34 (m, 3H), 7.33 – 7.26 (m, 5H), 7.24 – 7.18 (m, 1H), 7.15 – 7.09 (m, 2H), 4.94 (d, *J* = 9.2 Hz, 1H), 3.93 (s, 3H), 3.87 (s, 6H), 3.08 – 2.98 (m, 2H), 2.92 (s, 1H), 2.42 (td, *J* = 8.9, 6.6 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 197.2, 153.1, 143.4, 142.8, 139.2, 133.1, 128.7, 128.6, 127.6, 126.9, 126.6, 125.8, 105.9, 71.8, 61.0, 56.2, 40.0, 33.9, 32.1.

IR (neat, cm^{-1}): 3061, 3027, 3003, 2936, 1667, 1583, 1502, 1455, 1414, 1334, 1232, 1194, 1156, 1127, 1073, 1026, 1003, 969, 920, 847, 749, 699.

HRMS (ESI-TOF): Calculated for $C_{26}H_{26}O_5Na$ $[M+Na]^+$ 441.16725, found 441.16519

(±)[1,1'-biphenyl]-4-yl((1*R*,2*S*,3*S*)-2-((S)-hydroxy(phenyl)methyl)-3-phenylcyclopropyl)methanone (**3e**)



3e

Prepared according to procedure C from chalcone **2a** and sulfoxonium ylide **1e**. Column chromatography eluent: Hex/AcOEt 85:15.

White solid (29.5 mg; 73% yield)

m.p.: 154-155 °C

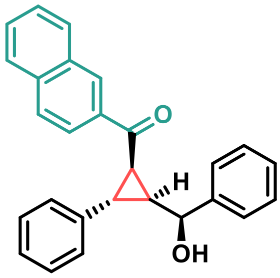
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 – 8.07 (m, 2H), 7.73 – 7.66 (m, 2H), 7.65 – 7.58 (m, 2H), 7.52 – 7.43 (m, 4H), 7.43 – 7.29 (m, 3H), 7.30 – 7.22 (m, 3H), 7.23 – 7.14 (m, 1H), 7.13 – 7.01 (m, 2H), 4.97 (d, J = 9.6 Hz, 1H), 3.15 (d, J = 7.7 Hz, 2H), 2.65 (s, 1H), 2.42 (dt, J = 9.1, 7.7 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 198.1, 146.0, 143.7, 140.0, 139.4, 136.9, 129.1, 129.1, 128.8, 128.7, 128.4, 127.7, 127.4, 126.9, 126.8, 126.0, 71.6, 40.8, 33.9, 32.2.

IR (neat, cm^{-1}): 3433, 3060, 3030, 2925, 2854, 1659, 1603, 1559, 1500, 1451, 1432, 1407, 1372, 1344, 1232, 1194, 1158, 1077, 1061, 1031, 1010, 953, 917, 843, 750, 697.

HRMS (ESI-TOF): Calculated for $C_{29}H_{24}O_2Na$ $[M+Na]^+$ 427.16685, found 427.16458

(±) ((1*R*,2*S*,3*S*)-2-((*S*)-hydroxy(phenyl)methyl)-3-phenylcyclopropyl)(naphthalen-2-yl)methanone (**3f**)



3f

Prepared according to procedure C from chalcone **2a** and sulfoxonium ylide **1f**. Column chromatography eluent: Hex/AcOEt 80:20.

White solid (22.7 mg; 60% yield)

m.p.: 154-155 °C

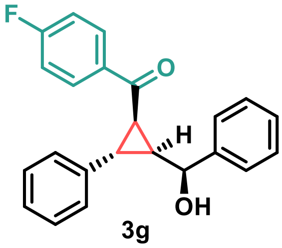
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1H), 8.10 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.02 – 7.84 (m, 3H), 7.65 – 7.54 (m, 2H), 7.53 – 7.47 (m, 2H), 7.38 – 7.31 (m, 2H), 7.31 – 7.24 (m, 3H), 7.24 – 7.17 (m, 1H), 7.15 – 7.07 (m, 2H), 5.00 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.27 (dd, *J* = 8.7, 5.3 Hz, 1H), 3.19 (dd, *J* = 6.6, 5.3 Hz, 1H), 2.60 (d, *J* = 3.4 Hz, 1H), 2.47 (td, *J* = 8.9, 6.7 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 198.3, 143.5, 139.3, 135.6, 135.4, 132.5, 130.2, 129.7, 128.6, 128.6, 128.5, 128.5, 127.8, 127.6, 126.8, 126.8, 126.7, 125.8, 124.0, 71.5, 40.7, 33.9, 32.1.

IR (neat, cm^{-1}): 3442, 3059, 3029, 2924, 1658, 1627, 1600, 1522, 1496, 1468, 1435, 1387, 1337, 1276, 1256, 1219, 1193, 1126, 1078, 1061, 945, 916, 866, 847, 816, 785, 753, 698.

HRMS (ESI-TOF): Calculated for $C_{27}H_{22}NaO_2$ $[M+Na]^+$ 401.15175, found 401.15548

(±)(4-fluorophenyl)((1*R*,2*S*,3*S*)-2-((*S*)-hydroxy(phenyl)methyl)-3-phenylcyclopropyl)methanone (**3g**)



3g

Prepared according to procedure C from chalcone **2a** and sulfoxonium ylide **1g**.

Column chromatography eluent: Hex/AcOEt 85:15.

White solid (26 mg; 76% yield)

m.p.: 123-124 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 – 8.01 (m, 2H), 7.53 – 7.40 (m, 2H), 7.38 – 7.28 (m, 2H), 7.28 – 7.21 (m, 3H), 7.21 – 7.17 (m, 1H), 7.16 – 7.10 (m, 1H), 7.08 – 7.01 (m, 2H), 4.90 (dd, *J* = 9.2, 4.0 Hz, 1H), 3.14 – 3.08 (m, 1H), 3.04 (dd, *J* = 8.8, 5.3 Hz, 1H), 2.52 (d, *J* = 4.0 Hz, 1H), 2.39 (td, *J* = 9.2, 6.6 Hz, 1H).

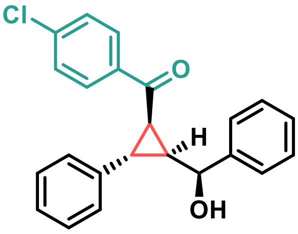
^{13}C NMR (101 MHz, $CDCl_3$): δ 196.7, 165.7 (d, *J* = 254.9 Hz), 143.4, 139.0, 134.5 (d, *J* = 3.0 Hz), 130.9 (d, *J* = 9.3 Hz), 128.6 (d, *J* = 1.4 Hz), 127.6, 126.8, 126.6, 125.7, 115.8, 115.5, 71.4, 40.5, 33.6, 31.8.

^{19}F NMR (376 MHz, $CDCl_3$): δ -105.16 (tt, *J* = 8.6, 5.4 Hz).

IR (neat, cm^{-1}): 3422, 3062, 3029, 2924, 2854, 1662, 1598, 1504, 1454, 1432, 1413, 1368, 1338, 1227, 1156, 1127, 1098, 1078. 1061, 1015, 954, 917, 842, 815, 785, 752, 698, 611.

HRMS (ESI-TOF): Calculated for $C_{23}H_{19}O_2FNa$ $[M+Na]^+$ 369.12613, found 369.12506

(±)(4-chlorophenyl)((1*R*,2*S*,3*S*)-2-((*S*)-hydroxy(phenyl)methyl)-3-phenylcyclopropyl)methanone (**3h**)



3h

Prepared according to procedure C from chalcone **2a** and sulfoxonium ylide **1h**. Column chromatography eluent: Hex/AcOEt 80:20.

White solid (26 mg; 57% yield)

m.p.: 166-167 °C

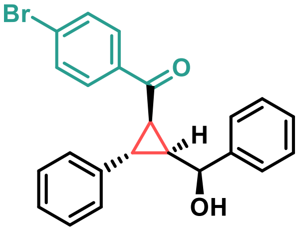
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 – 7.94 (m, 2H), 7.49 – 7.39 (m, 4H), 7.38 – 7.30 (m, 2H), 7.28 – 7.14 (m, 4H), 7.08 – 7.01 (m, 2H), 4.89 (dd, *J* = 9.2, 4.1 Hz, 1H), 3.16 – 3.08 (m, 1H), 3.04 (dd, *J* = 8.8, 5.3 Hz, 1H), 2.45 (d, *J* = 4.2 Hz, 1H), 2.40 (td, *J* = 9.0, 6.7 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 197.2, 143.4, 139.6, 139.0, 136.5, 129.7, 128.9, 128.6, 127.7, 126.9, 126.6, 125.8, 71.4, 40.7, 33.7, 32.0.

IR (neat, cm^{-1}): 3407, 3061, 3029, 2925, 1663, 1589, 1571, 1492, 1453, 1432, 1402, 1368, 1341, 1284, 1222, 1176, 1092, 1061, 1029, 1010, 953, 840, 824, 789, 753, 698.

HRMS (ESI-TOF): Calculated for $C_{23}H_{19}O_2ClNa$ $[M+Na]^+$ 385.09658, found 385.09402

(±)(4-bromophenyl)((1*R*,2*S*,3*S*)-2-((*S*)-hydroxy(phenyl)methyl)-3-phenylcyclopropyl)methanone (**3i**)



3i

Prepared according to procedure C from chalcone **2a** and sulfoxonium ylide **1i**. Column chromatography eluent: Hex/AcOEt 80:20.

White solid (24.3 mg; 60% yield)

m.p.: 172-173 °C

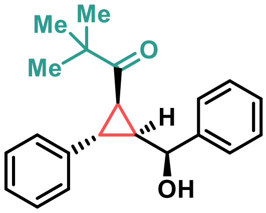
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 – 7.87 (m, 2H), 7.65 – 7.58 (m, 2H), 7.50 – 7.43 (m, 2H), 7.38 – 7.30 (m, 2H), 7.30 – 7.22 (m, 3H), 7.22 – 7.17 (m, 1H), 7.09 – 7.01 (m, 2H), 4.90 (dd, *J* = 9.2, 4.1 Hz, 1H), 3.13 (dd, *J* = 6.6, 5.3 Hz, 1H), 3.04 (dd, *J* = 8.8, 5.3 Hz, 1H), 2.44 (d, *J* = 4.3 Hz, 1H), 2.43 – 2.37 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 197.3, 143.4, 139.0, 136.9, 131.9, 129.8, 128.6, 128.3, 127.7, 126.9, 126.6, 125.8, 71.4, 40.7, 33.7, 32.0.

IR (neat, cm^{-1}): 3566, 3421, 3061, 3029, 1699, 1660, 1603, 1584, 1494, 1454, 1433, 1400, 1366, 1339, 1277, 1222, 1177, 1098, 1070, 1029, 1007, 952, 917, 878, 838, 821, 786, 753, 698, 676.

HRMS (ESI-TOF): Calculated for $C_{23}H_{19}O_2BrNa$ $[M+Na]^+$ 429.04606, found 429.04459

(±)1-((1*R*,2*S*,3*S*)-2-((S)-hydroxy(phenyl)methyl)-3-phenylcyclopropyl)-2,2-dimethylpropan-1-one (**3j**)



3j

Prepared according to procedure C from chalcone **2a** and sulfoxonium ylide **1j**. Column chromatography eluent: Hex/AcOEt 80:20.

White solid (25.6 mg; 83 % yield)

m.p.: 136-137 °C

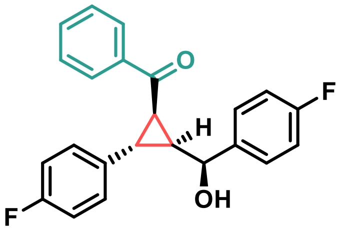
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 – 7.42 (m, 2H), 7.39 – 7.30 (m, 2H), 7.30 – 7.15 (m, 4H), 7.01 (dd, *J* = 6.9, 1.8 Hz, 2H), 4.97 (dd, *J* = 8.8, 4.9 Hz, 1H), 3.03 – 2.84 (m, 1H), 2.63 (dd, *J* = 8.7, 5.3 Hz, 1H), 2.56 (d, *J* = 5.0 Hz, 1H), 2.21 (td, *J* = 8.8, 6.7 Hz, 1H), 1.24 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 214.5, 144.1, 139.6, 128.7, 127.6, 126.8, 125.9, 70.7, 44.9, 40.5, 32.5, 32.0, 26.5.

IR (neat, cm^{-1}): 3441, 3061, 3028, 2970, 2931, 2870, 1682, 1602, 1541, 1494, 1476, 1452, 1395, 1367, 1341, 1318, 1278, 1226, 1197, 1097, 1074, 1058, 1030, 1013, 965, 920, 753, 722, 698.

HRMS (ESI-TOF): Calculated for $C_{21}H_{24}O_2Na$ [M+Na]$^+$ 331.16685, found 331.16617

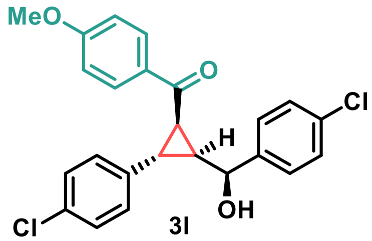
(±)((1*R*,2*S*,3*S*)-2-(4-fluorophenyl)-3-((*S*)-(4-fluorophenyl)(hydroxy)methyl)cyclopropyl)(phenyl)methanone (**3k**)



3k

Prepared according to procedure C from chalcone **2b** and sulfoxonium ylide **1a**.
Column chromatography eluent: Hex/AcOEt 80:20.
White solid (28.4 mg; 78% yield)
m.p.: 139-140 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 – 7.97 (m, 2H), 7.65 – 7.52 (m, 1H), 7.51 – 7.39 (m, 4H), 7.09 – 6.84 (m, 6H), 4.91 (dd, *J* = 9.1, 3.3 Hz, 1H), 3.12 – 3.02 (m, 2H), 2.60 (d, *J* = 4.0 Hz, 1H), 2.34 – 2.24 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 198.2, 163.2 (d, *J* = 44.1 Hz), 160.7 (d, *J* = 44.1 Hz), 139.2 (d, *J* = 3.1 Hz), 137.9, 134.6 (d, *J* = 3.1 Hz), 133.2, 128.6, 128.2, 128.1 (d, *J* = 8.0 Hz), 127.3 (d, *J* = 8.0 Hz), 115.5 (d, *J* = 8.2 Hz), 115.3 (d, *J* = 8.1 Hz), 70.6, 40.6, 33.5, 31.0.
^{19}F NMR (376 MHz, $CDCl_3$): δ -114.90 – -115.04 (m, 1F), -115.50 – -115.63 (m, 1F).
IR (neat, cm^{-1}): 3420, 3063, 2925, 1661, 1601, 1581, 1511, 1451, 1407, 1372, 1334, 1224, 1158, 1106, 1065, 1015, 955, 883, 835, 791, 747, 699, 653.
HRMS (ESI-TOF): Calculated for $C_{23}H_{18}O_2F_2Na$ [M+Na]$^+$ 387.11671, found 387.11548

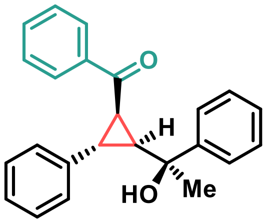
(±)((1R,2S,3S)-2-(4-chlorophenyl)-3-((S)-(4-chlorophenyl)(hydroxy)methyl)cyclopropyl) (4-methoxyphenyl)methanone (**3l**)



3l

Prepared according to procedure C from chalcone **2c** and sulfoxonium ylide **1c**.
Column chromatography eluent: Hex/AcOEt 80:20.
White solid (20 mg; 48% yield)
m.p.: 143-144 °C
^{1}H NMR (500 MHz, CDCl$_3$): δ 8.0 – 8.0 (m, 2H), 7.4 – 7.4 (m, 2H), 7.3 – 7.3 (m, 2H), 7.3 – 7.2 (m, 2H), 7.0 – 7.0 (m, 2H), 7.0 – 6.9 (m, 2H), 4.9 (dd, *J* = 9.3, 2.2 Hz, 1H), 3.9 (s, 3H), 3.0 – 3.0 (m, 2H), 2.9 (s, 1H), 2.2 (td, *J* = 8.8, 6.7 Hz, 1H).
^{13}C NMR (126 MHz, CDCl$_3$) δ 196.6, 164.0, 142.2, 137.8, 133.4, 132.8, 130.9, 130.8, 129.0, 128.9, 128.0, 127.2, 114.1, 71.0, 55.7, 40.2, 33.5, 31.1.
IR (neat, cm^{-1}): 3414, 2926, 2842, 1734, 1651, 1598, 1574, 1511, 1493, 1442, 1421, 1397, 1372, 1312, 1261, 1238, 1168, 1090, 1067, 1014, 957, 887, 815, 781, 739, 704.
HRMS (ESI-TOF): Calculated for $C_{24}H_{19}Cl_2O_2$ [M–OH]$^+$ 409.0757; found 409.0748

(±)((1*R*,2*S*,3*S*)-2-((*S*)-1-hydroxy-1-phenylethyl)-3-phenylcyclopropyl)(phenyl)methanone (**3m**)



3m

Prepared according to procedure C from chalcone **2n** and sulfoxonium ylide **1a**.
Column chromatography eluent: Hex/AcOEt 80:20.
White solid (15.8 mg; 46% yield)
m.p: 140-141 °C
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.72 – 7.60 (m, 2H), 7.55 – 7.50 (m, 2H), 7.49 – 7.41 (m, 1H), 7.40 – 7.33 (m, 2H), 7.33 – 7.26 (m, 4H), 7.24 – 7.17 (m, 2H), 7.10

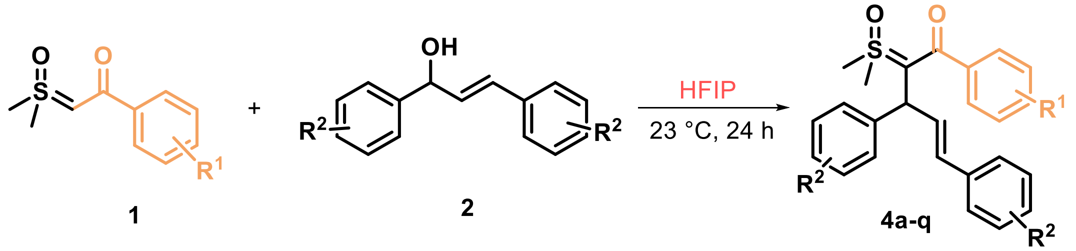
– 7.00 (m, 1H), 5.64 (d, *J* = 1.0 Hz, 1H), 3.56 (dd, *J* = 7.3, 5.5 Hz, 1H), 3.02 (dd, *J* = 8.8, 5.5 Hz, 1H), 2.70 (dd, *J* = 8.8, 7.3 Hz, 1H), 1.68 (d, *J* = 1.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 202.5, 149.1, 140.1, 138.3, 133.0, 128.7, 128.3, 127.9, 127.9, 127.0, 126.6, 126.4, 124.5, 71.9, 46.2, 34.8, 33.9, 33.2.

IR (neat, cm^{-1}): 3365, 3060, 3030, 2976, 2929, 2854, 1651, 1602, 1581, 1495, 1448, 1373, 1305, 1278, 1256, 1223, 1199, 1131, 1104, 1080, 1064, 1032, 1010, 967, 917, 763, 749, 699.

HRMS (ESI-TOF): Calculated for $C_{24}H_{21}O$ $[M–OH]^+$ 325.15869, found 325.15750

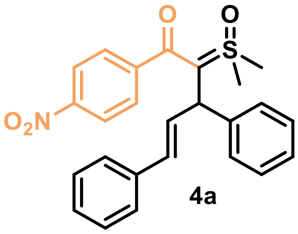
5 General Procedure D: Synthesis of α-Alkylated Sulfoxonium Ylides via Sulfoxonium Ylides Addition to Allylic Carbocation



To a 4 mL vial, the sulfoxonium ylide **1** (0.1 mmol; 1 eq), the alcohol **2** (0.2 mmol; 2 eq) and the magnetic stir were added. After closing the flask with tightly fitted rubber septa, HFIP (200 *μ*L, 0.5 M) was added, and the reaction was stirred at 23 °C for 24 h. After the elapsed time, $CHCl_3$ was added to the reaction and the solvent was removed under reduce pressure. The crude was transferred to the column chromathography (MeOH:$CHCl_3$ 1:99) to obtain the desired product **4**. For examples **4h**, **4i**, **4j**, and **4k**, 5 equivalents of t-BuOH were added to the reaction medium.

1 mmol scale: To a 10 mL round bottom flask, **2a** (420 mg; 2 mmol; 2 eq), **1a** (196.3 mg; 1 mmol; 1 eq), tBuOH (0.47 mL; 5 mmol; 5 eq) and HFIP (2 mL; 0.5 M) were added sequentially and the reaction maintained under stirring at 23 °C for 24 h. After elapsed time, $CHCl_3$ was added to the reaction, and the solvents removed under reduced pressure, repeating the procedure twice. The crude was transferred to column chromathography ($CHCl_3$:MeOH 95.5:0.5 → 98:2) to provide **4** (295.3 mg; 0.76 mmol; 76 % yield) as a white solid.

(*E*)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(4-nitrophenyl)-3,5-diphenylpent-4-en-1-one (**4a**)



4a

Prepared according to procedure D from chalcone **2a** and sulfoxonium ylide **1k**.

Column chromatography eluent: Chloroform/Methanol 99:1

Yellow solid (72.6 mg; 84% yield)

m.p.: 154-155 °C

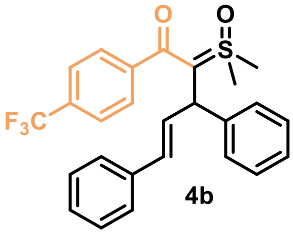
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 – 8.17 (m, 2H), 7.70 – 7.58 (m, 2H), 7.47 – 7.40 (m, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.23 (m, 6H), 7.23 – 7.18 (m, 1H), 6.74 (dd, *J* = 15.8, 8.3 Hz, 1H), 6.42 (d, *J* = 15.8 Hz, 1H), 4.85 (d, *J* = 8.3 Hz, 1H), 3.67 (s, 3H), 3.43 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 181.8, 148.1, 147.5, 143.4, 137.0, 131.5, 131.1, 128.7, 128.3, 128.2, 127.6, 127.5, 126.5, 126.4, 123.5, 86.9, 47.4, 44.2, 43.1.

IR (neat, cm^{-1}): 3025, 2922, 1729, 1668, 1600, 1522, 1449, 1390, 1347, 1311, 1194, 1102, 1072, 1014, 978, 941, 855, 747, 699.

HRMS (ESI-TOF): Calculated for $C_{25}H_{24}O_4NS$ $[M+Na]^+$ 434.14206, found 434.14035

(*E*)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-3,5-diphenyl-1-(4-(trifluoromethyl)phenyl)pent-4-en-1-one (**4b**)



4b

Prepared according to procedure D from chalcone **2a** and sulfoxonium ylide **1l**.

Column chromatography eluent: Chloroform/Methanol 99:1

White solid (28.7 mg; 63% yield)

m.p.: 169-170 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 – 7.55 (m, 3H), 7.45 – 7.37 (m, 2H), 7.37 – 7.29 (m, 2H), 7.28 – 7.20 (m, 5H), 7.19 – 7.14 (m, 1H), 6.74 (dd, *J* = 15.8, 8.3 Hz, 1H), 6.41 (d, *J* = 15.9 Hz, 1H), 4.87 (d, *J* = 8.3 Hz, 1H), 3.62 (s, 3H), 3.37 (s, 3H).

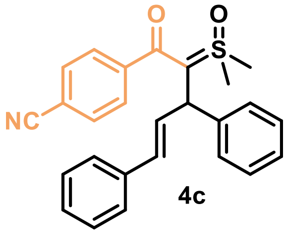
^{13}C NMR (126 MHz, $CDCl_3$): δ 182.9, 144.8, 143.7, 137.2, 131.4 (d, *J* = 11.4 Hz),, 128.6, 128.2, 127.6, 127.5, 127.5, 126.4, 126.3, 125.2 (q, *J* = 3.8 Hz), 86.2, 47.7, 44.4, 43.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.72.

IR (neat, cm^{-1}): 3025, 2923, 1598, 1517, 1496, 1449, 1403, 1324, 1192, 1167, 1124, 1066, 1014, 978, 940, 854, 768, 748, 698.

HRMS (ESI-TOF): Calculated for $C_{26}H_{24}O_2F_3S$ [M+Na]$^+$ 457.14436, found 457.14270

(*E*)-4-(2-(dimethyl(oxo)- λ^6-sulfaneylidene)-3,5-diphenylpent-4-enoyl)benzonitrile (**4c**



4c

Prepared according to procedure D from chalcone **2a** and sulfoxonium ylide **1m**.

Column chromatography eluent: Chloroform/Methanol 99:1

White solid (39.3 mg; 95% yield)

m.p.: 153-154 °C

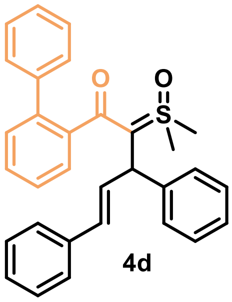
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 – 7.61 (m, 2H), 7.59 – 7.53 (m, 2H), 7.44 – 7.38 (m, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.27 (d, J = 3.8 Hz, 4H), 7.19 (td, J = 5.9, 2.5 Hz, 1H), 6.73 (dd, J = 15.9, 8.2 Hz, 1H), 6.40 (d, J = 15.8 Hz, 1H), 4.84 (d, J = 8.2 Hz, 1H), 3.64 (d, J = 0.9 Hz, 3H), 3.40 (d, J = 0.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 182.3, 145.8, 143.6, 137.2, 132.2, 131.6, 131.3, 128.8, 128.4, 128.1, 127.8, 127.6, 126.6, 126.5, 118.7, 112.9, 86.9, 47.6, 44.4, 43.2.

IR (neat, cm^{-1}): 3025, 2923, 2228, 1598, 1513, 1493, 1449, 1383, 1305, 1193, 1100, 1072, 1016, 984, 940, 917, 852, 748, 698.

HRMS (ESI-TOF): Calculated for $C_{26}H_{24}O_2NS$ [M+Na]$^+$ 414.15223, found 414.15021

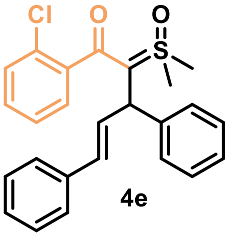
(*E*)-1-([1,1'-biphenyl]-2-yl)-2-(dimethyl(oxo)- λ^6-sulfaneylidene)-3,5-diphenylpent-4-en-1-one (**4d**)



4d

Prepared according to procedure D from chalcone **2a** and sulfoxonium ylide **1n**.
Column chromatography eluent: Chloroform/Methanol 99:1
White solid (32.5 mg; 70% yield)
m.p.: 112-113 °C
^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.6 – 7.5 (m, 2H), 7.5 – 7.4 (m, 2H), 7.4 – 7.2 (m, 10H), 7.1 (dq, *J* = 14.1, 7.2 Hz, 2H), 7.0 (s, 2H), 6.3 (dd, *J* = 15.8, 8.2 Hz, 1H), 5.9 (d, *J* = 15.8 Hz, 1H), 4.4 (d, *J* = 8.2 Hz, 1H), 3.5 (s, 3H), 3.4 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d$_6$): δ 183.1, 143.7, 141.2, 140.1, 137.8, 137.0, 131.4, 129.2, 129.1, 128.8, 128.1, 127.6 (d, *J* = 4.6 Hz), 127.5, 127.4, 127.0, 126.7, 126.6, 126.4, 125.7, 125.2, 84.9, 78.8, 47.1, 42.7 (d, *J* = 19.1 Hz).
IR (neat, cm^{-1}): 3056, 3024, 2922, 2852, 1598, 1509, 1494, 1448, 1384, 1347, 1303, 1192, 1121, 1092, 1074, 1014, 975, 939, 919, 859, 767, 745, 699, 654.
HRMS (ESI-TOF): Calculated for $C_{31}H_{29}O_2S$ [M+Na]$^+$ 465.18828, found 465.18671
Obs.: *NMR analysis in CDCl$_3$ at room temperature led to spectra with low resolution and broadened signals. In this case, DMSO-d$_6$ was used and the experiment run at 60 °C.*

(*E*)-1-(2-chlorophenyl)-2-(dimethyl(oxo)- λ^6-sulfaneylidene)-3,5-diphenylpent-4-en-1-one (**4e**)



4e

Prepared according to procedure D from chalcone **2a** and sulfoxonium ylide **1o**.
Column chromatography eluent: Chloroform/Methanol 99:1
White solid (33 mg; 79% yield)

m.p.: 159-160 °C

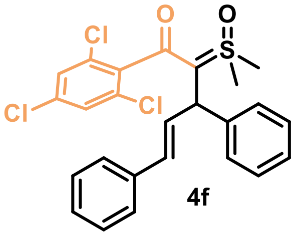
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 3H), 7.33 – 7.28 (m, 4H), 7.27 – 7.11 (m, 7H), 6.66 (dd, *J* = 15.8, 8.7 Hz, 1H), 6.31 (d, *J* = 15.8 Hz, 1H), 4.61 (d, *J* = 8.6 Hz, 1H), 3.64 (s, 3H), 3.49 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 181.7, 143.8, 140.5, 137.4, 131.1, 131.0, 129.8, 129.3, 128.5, 128.1, 128.1, 127.4, 127.3, 126.4, 126.3, 126.1, 86.4, 47.1, 44.2, 43.3.

IR (neat, cm^{-1}): 3057, 3025, 2922, 1597, 1568, 1517, 1470, 1448, 1431, 1385, 1304, 1193, 1111, 1073, 1045, 1014, 975, 941, 918, 860, 766, 747, 698.

HRMS (ESI-TOF): Calculated for $C_{25}H_{24}O_2ClS$ $[M+Na]^+$ 423.11800, found 423.11636

(*E*)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-3,5-diphenyl-1-(2,4,6-trichlorophenyl)pent-4-en-1-one (**4f**)



4f

Prepared according to procedure D from chalcone **2a** and sulfoxonium ylide **1p**.
Column chromatography eluent: Chloroform/Methanol 99:1
White solid (47.5 mg; 97% yield)

m.p.: 150-151 °C

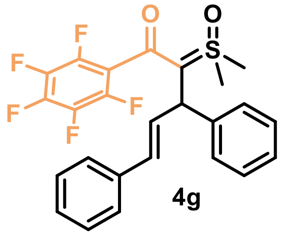
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.19 (m, 11H), 7.21 – 7.13 (m, 1H), 6.60 (dd, *J* = 15.8, 9.0 Hz, 1H), 6.28 (d, *J* = 15.8 Hz, 1H), 4.49 (d, *J* = 9.0 Hz, 1H), 3.61 (s, 3H), 3.57 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.8, 143.1, 137.9, 137.4, 134.3, 133.2, 133.0, 131.3, 130.3, 128.6, 128.2, 128.1, 128.1, 127.5, 127.3, 126.4, 126.3, 86.8, 48.0, 43.8, 43.7.

IR (neat, cm^{-1}): 3058, 3026, 2923, 1700, 1650, 1598, 1576, 1527, 1494, 1449, 1370, 1306, 1258, 1193, 1115, 1080, 1058, 1016, 973, 941, 918, 863, 813, 799, 765, 747, 729, 698.

HRMS (ESI-TOF): Calculated for $C_{25}H_{21}Cl_3NaO_2S$ $[M+Na]^+$ 513.0226, found 513.0227

(*E*)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(perfluorophenyl)-3,5-diphenylpent-4-en-1-one (**4g**)



4g

Prepared according to procedure D from chalcone **2a** and sulfoxonium ylide **1q**.

Column chromatography eluent: Chloroform/Methanol 99:1

White solid (45.9 mg; 96% yield)

m.p.: 171-172 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 4H), 7.29 – 7.21 (m, 5H), 7.20 – 7.13 (m, 1H), 6.60 (dd, *J* = 15.8, 8.1 Hz, 1H), 6.36 (d, *J* = 15.8 Hz, 1H), 4.72 (d, *J* = 8.1 Hz, 1H), 3.64 (s, 3H), 3.54 (s, 3H).

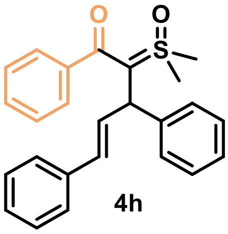
^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 142.2, 137.0, 131.6, 130.2, 128.6, 128.2, 127.6, 127.3, 126.5, 126.3, 89.8, 45.4, 43.6, 42.9.

^{19}F NMR (470 MHz, $CDCl_3$) δ -140.68 (dd, *J* = 23.9, 6.3 Hz, 1F), -142.06 (dd, *J* = 24.1, 6.1 Hz, 1F), -155.00 (t, *J* = 20.6 Hz, 1F), -161.38 (dtd, *J* = 45.1, 23.6, 8.6 Hz, 2F).

IR (neat, cm^{-1}): 3026, 2924, 1652, 1598, 1537, 1515, 1493, 1449, 1413, 1382, 1306, 1199, 1137, 1093, 1017, 985, 940, 908, 855, 808, 767, 746, 698, 655.

HRMS (ESI-TOF): Calculated for $C_{25}H_{20}O_2F_5S$ $[M+H]^+$ 479.10987, found 479.10809

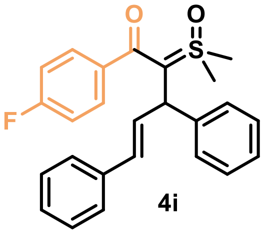
(E)-2-(dimethyl(oxo)- λ^6-sulfaneylidene)-1,3,5-triphenylpent-4-en-1-one (**4h**)



4h

Prepared according to procedure D from chalcone **2a** and sulfoxonium ylide **1a**.
Column chromatography eluent: Chloroform/Methanol 99:1
White solid (32.2 mg; 83% yield)
m.p.: 154-155 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.6 – 7.5 (m, 2H), 7.5 – 7.3 (m, 11H), 7.3 – 7.1 (m, 2H), 6.8 (dd, J = 15.9, 8.4 Hz, 1H), 6.4 (d, J = 15.9 Hz, 1H), 5.0 (d, J = 8.4 Hz, 1H), 3.6 (d, J = 0.9 Hz, 3H), 3.3 (d, J = 0.8 Hz, 3H)
^{13}C NMR (126 MHz, $CDCl_3$): δ 184.8, 144.2, 141.3, 137.5, 131.8, 131.1, 129.4, 128.6, 128.2, 128.1, 127.6, 127.3, 127.3, 126.4, 126.1, 85.5, 48.1, 44.6, 43.3.
IR (neat, cm^{-1}): 3389, 3080, 3056, 3024, 2922, 1598, 1581, 1500, 1447, 1384, 1304, 1191, 1100, 1072, 1016, 976, 939, 918, 762, 746, 698, 656.
HRMS (ESI-TOF): Calculated for $C_{25}H_{25}O_2S$ $[M+H]^+$ 389.15698, found 389.15642.

(*E*)-2-(dimethyl(oxo)- λ^6-sulfaneylidene)-1-(4-fluorophenyl)-3,5-diphenylpent-4-en-1-one (**4i**)



4i

Prepared according to procedure D from chalcone **2a** and sulfoxonium ylide **1g**.
Column chromatography eluent: Chloroform/Methanol 99:1
White solid (26.4 mg; 63% yield)
m.p.: 142-143 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.6 – 7.5 (m, 2H), 7.5 – 7.4 (m, 2H), 7.4 – 7.3 (m, 6H), 7.3 – 7.1 (m, 2H), 7.1 – 7.0 (m, 2H), 6.8 (dd, *J* = 15.9, 8.3 Hz, 1H), 6.5 – 6.4 (m, 1H), 5.0 (d, *J* = 8.3 Hz, 1H), 3.6 (d, *J* = 0.8 Hz, 3H), 3.3 (d, *J* = 0.9 Hz, 3H).

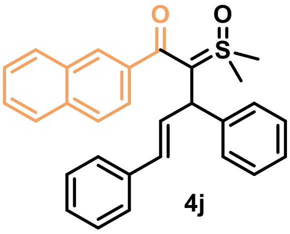
^{13}C NMR (101 MHz, CDCl$_3$): δ 183.6, 164.8, 162.3, 144.1, 137.4, 131.6 (d, *J* = 40.3 Hz), 129.6 (d, *J* = 8.4 Hz), 128.8, 128.3, 127.7, 127.6, 126.5, 126.4, 115.2 (d, *J* = 21.5 Hz), 48.2, 44.7, 43.4, 31.1, 29.9.

^{19}F NMR (376 MHz, CDCl$_3$): δ -111.4.

IR (neat, cm^{-1}): 3025, 2960, 2923, 2853, 1598, 1493, 1449, 1380, 1303, 1261, 1221, 1189, 1155, 1095, 1072, 1013, 976, 939, 917, 847, 803, 750, 696.

HRMS (ESI-TOF): Calculated for $C_{25}H_{24}FO_2S$ [M+H]$^+$ 407.5234, found 407.1473

(*E*)-2-(dimethyl(oxo)- λ^6-sulfaneylidene)-1-(naphthalen-2-yl)-3,5-diphenylpent-4-en-1-one (**4j**)



4j

Prepared according to procedure D from chalcone **2a** and sulfoxonium ylide **1f**.

Column chromatography eluent: Chloroform/Methanol 99:1

Yellowish oil (24.6 mg; 56% yield)

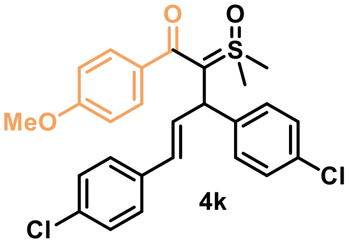
^{1}H NMR (400 MHz, CDCl$_3$): δ 8.0 – 8.0 (m, 1H), 7.9 – 7.8 (m, 2H), 7.8 – 7.7 (m, 1H), 7.7 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.6 – 7.4 (m, 4H), 7.4 – 7.3 (m, 6H), 7.2 – 7.1 (m, 2H), 6.8 (dd, *J* = 15.9, 8.5 Hz, 1H), 6.5 (d, *J* = 15.8 Hz, 1H), 5.1 (d, *J* = 8.5 Hz, 1H), 3.7 (d, *J* = 0.8 Hz, 3H), 3.4 (d, *J* = 0.9 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 184.8, 144.3, 128.8, 128.7, 128.3, 128.1, 127.9, 127.8, 127.5, 127.2, 126.8, 126.5, 126.4, 126.3, 125.2, 86.1, 48.4, 44.8, 43.4, 29.8.

IR (neat, cm^{-1}): 3364, 3056, 3024, 2923, 2853, 1717, 1651, 1629, 1598, 1577, 1558, 1513, 1492, 1450, 1390, 1287, 1231, 1191, 1129, 1097, 1072, 1017, 977, 940, 915, 864, 826, 749, 698.

HRMS (ESI-TOF): Calculated for $C_{29}H_{27}O_2S$ [M+H]$^+$ 439.1732, found 439.1722

(E)-3,5-bis(4-chlorophenyl)-2-(dimethyl(oxo)-l6-sulfaneylidene)-1-(4-methoxyphenyl)pent-4-en-1-one (**4k**)



4k

Prepared according to procedure D from chalcone **2c** and sulfoxonium ylide **1c**.

Column chromatography eluent: Chloroform/Methanol 99:1

Yellowish oil (16.5 mg; 34% yield)

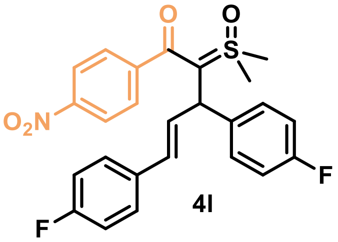
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.5 (d, *J* = 8.7 Hz, 2H), 7.4 – 7.2 (m, 8H), 6.9 – 6.8 (m, 2H), 6.7 (dd, *J* = 15.9, 8.2 Hz, 1H), 6.4 (d, *J* = 15.8 Hz, 1H), 5.0 (d, *J* = 8.1 Hz, 1H), 3.8 (s, 3H), 3.6 (s, 3H), 3.3 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 184.6, 161.0, 142.8, 135.8, 132.2, 132.1, 130.4, 129.2, 128.9, 128.8, 128.4, 127.7, 127.2, 127.1, 113.6, 55.5, 48.0, 43.9, 31.7, 29.9.

IR (neat, cm^{-1}): 3027, 2922, 2852, 1662, 1604, 1578, 1487, 1383, 1302, 1249, 1190, 1170, 1090, 1013, 978, 940, 870, 830, 797, 758, 736, 703.

HRMS (ESI-TOF): Calculated for $C_{26}H_{25}Cl_2O_3S$ [M+H]$^+$ 487.0896, found 487.0897

(*E*)-2-(dimethyl(oxo)- λ^6-sulfaneylidene)-3,5-bis(4-fluorophenyl)-1-(4-nitrophenyl)pent-4-en-1-one (**4l**)



4l

Prepared according to procedure D from chalcone **2b** and sulfoxonium ylide **1k**.

Column chromatography eluent: Chloroform/Methanol 99:1

Yellow solid (44.6 mg; 95% yield)

m.p.: 164-165 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.3 – 8.2 (m, 2H), 7.7 – 7.6 (m, 2H), 7.4 – 7.3 (m, 2H), 7.2 (dddd, *J* = 8.4, 6.2, 3.1, 2.0 Hz, 2H), 7.1 – 6.9 (m, 4H), 6.6 (dd, *J* = 15.8, 8.2 Hz, 1H), 6.4 (dd, *J* = 15.9, 1.0 Hz, 1H), 4.8 (dt, *J* = 8.2, 1.1 Hz, 1H), 3.6 (d, *J* = 0.9 Hz, 3H), 3.4 (d, *J* = 0.9 Hz, 3H).

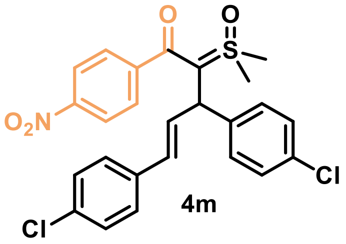
^{13}C NMR (126 MHz, $CDCl_3$): δ 181.8, 163.5, 162.5, 161.5, 160.6, 148.3, 147.5, 139.2 (d, *J* = 3.0 Hz), 133.1 (d, *J* = 3.1 Hz), 130.7 (d, *J* = 2.4 Hz), 130.6, 129.1 (d, *J* = 7.7 Hz), 128.3, 128.0 (d, *J* = 8.1 Hz), 123.7, 115.7 (d, *J* = 21.5 Hz), 115.2 (d, *J* = 21.3 Hz), 47.1, 44.4, 43.3.

^{19}F NMR (470 MHz, $CDCl_3$): δ -114.1 (ddd, J = 13.9, 8.8, 5.2 Hz), -116.4 (tt, J = 9.0, 4.9 Hz).

IR (neat, cm^{-1}): 3030, 2924, 2852, 1734, 1601, 1523, 1507, 1389, 1347, 1308, 1223, 1192, 1159, 1104, 1015, 979, 941, 857, 836, 736, 703.

HRMS (ESI-TOF): Calculated for $C_{25}H_{22}O_4NF_2S$ $[M+H]^+$ 470.12321, found 470.12210

(*E*)-3,5-bis(4-chlorophenyl)-2-(dimethyl(oxo)- λ^6-sulfaneylidene)-1-(4-nitrophenyl)pent-4-en-1-one (**4m**)



4m

Prepared according to procedure D from chalcone **2c** and sulfoxonium ylide **1k**.

Column chromatography eluent: Chloroform/Methanol 99:1

Yellow solid (36.7 mg; 73% yield)

m.p.: 180-181 °C

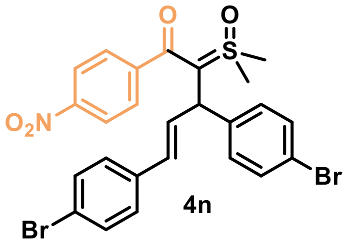
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.3 – 8.2 (m, 2H), 7.6 – 7.6 (m, 2H), 7.3 – 7.2 (m, 6H), 7.2 – 7.2 (m, 2H), 6.7 (dd, *J* = 15.8, 8.2 Hz, 1H), 6.3 (dd, *J* = 15.8, 1.1 Hz, 1H), 4.8 (d, *J* = 8.2 Hz, 1H), 3.6 (d, *J* = 0.8 Hz, 3H), 3.4 (d, *J* = 0.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 182.0, 148.4, 147.3, 142.0, 135.4, 133.6, 132.5, 131.4, 130.8, 129.0, 128.9, 128.6, 128.3, 127.7, 123.8, 86.5, 47.3, 44.5, 43.5

IR (neat, cm^{-1}): 3026, 2923, 1600, 1522, 1489, 1403, 1347, 1309, 1193, 1091, 1013, 979, 940, 857, 828, 739, 716, 702.

HRMS (ESI-TOF): Calculated for $C_{25}H_{22}O_4NCl_2S$ $[M+H]^+$ 502.06466, found 502.06262

(*E*)-3,5-bis(4-bromophenyl)-2-(dimethyl(oxo)- λ^6-sulfaneylidene)-1-(4-nitrophenyl)pent-4-en-1-one (**4n**)



4n

Prepared according to procedure D from chalcone **2d** and sulfoxonium ylide **1k**.

Column chromatography eluent: Chloroform/Methanol 99:1

Yellow solid (20.7 mg; 35% yield)

m.p.: 151-152 °C

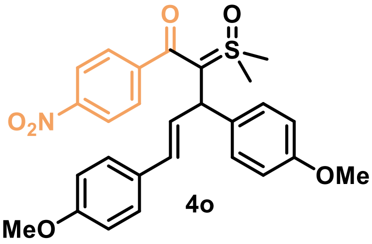
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.2 (d, *J* = 8.7 Hz, 2H), 7.6 – 7.6 (m, 2H), 7.5 – 7.4 (m, 4H), 7.2 (d, *J* = 8.8 Hz, 2H), 7.1 (d, *J* = 8.3 Hz, 2H), 6.7 (dd, *J* = 15.8, 8.2 Hz, 1H), 6.3 (d, *J* = 15.8 Hz, 1H), 4.7 (d, *J* = 8.2 Hz, 1H), 3.6 (s, 3H), 3.4 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 181.8, 148.2, 147.1, 142.3, 135.6, 131.8, 131.4, 131.2, 130.7, 129.1, 128.1, 127.8, 123.6, 121.5, 120.4, 47.2, 44.3, 43.3, 29.7.

IR (neat, cm^{-1}):3363, 3024, 2922, 1728, 1600, 1523, 1486, 1400, 1347, 1323, 1194, 1106, 1071, 1011, 979, 941, 857, 825, 740, 707.

HRMS (ESI-TOF): Calculated for $C_{25}H_{22}Br_2NO_4S$ [M+H]$^+$ 591,31400, found 591.95941

(*E*)-2-(dimethyl(oxo)- λ^6-sulfaneylidene)-3,5-bis(4-methoxyphenyl)-1-(4-nitrophenyl)pent-4-en-1-one (**4o**)



4o

Prepared according to procedure D from chalcone **2e** and sulfoxonium ylide **1k**.

Column chromatography eluent: Chloroform/Methanol 99:1

Yellow solid (21.7 mg; 44% yield)

m.p.: 169-170 °C

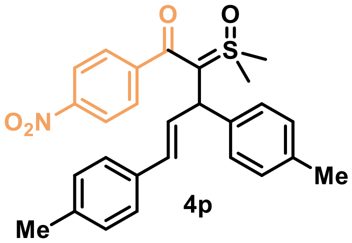
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 8.7 Hz, 1H), 7.68 – 7.55 (m, 1H), 7.33 (d, J = 8.6 Hz, 2H), 7.22 – 7.10 (m, 2H), 6.93 – 6.84 (m, 2H), 6.84 – 6.76 (m, 2H), 6.56 (dd, J = 15.8, 8.1 Hz, 1H), 6.33 (d, J = 15.6 Hz, 1H), 4.75 (d, J = 8.1 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 3.64 (d, J = 0.8 Hz, 3H), 3.42 (d, J = 0.8 Hz, 3H).

^{13}C NMR (126 MHz, CDCl$_3$): δ 181.5, 159.3, 158.1, 148.1, 147.6, 135.5, 130.7, 129.8, 129.2, 128.5, 128.3, 127.5, 123.5 (d, J = 4.8 Hz), 114.1, 113.6, 87.3, 55.4, 55.3, 46.8, 44.2, 43.1.

IR (neat, cm^{-1}): 3025, 2922, 2851, 1606, 1509, 1464, 1388, 1346, 1301, 1248, 1177, 1089, 1029, 979, 940, 857, 832, 737, 702.

HRMS (ESI-TOF): Calculated for $C_{27}H_{28}O_6NS$ $[M+H]^+$ 494.16318, found 494.16138

(*E*)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(4-nitrophenyl)-3,5-di-p-tolylpent-4-en-1-one (**4p**)



4p

Prepared according to procedure D from chalcone **2f** and sulfoxonium ylide **1k**.

Column chromatography eluent: Chloroform/Methanol 99:1

Yellow solid (19.8 mg; 43% yield)

m.p: 179-180 °C

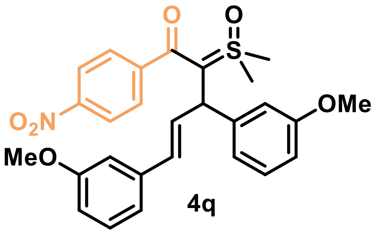
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.31 – 8.03 (m, 2H), 7.70 – 7.53 (m, 2H), 7.37 – 7.20 (m, 2H), 7.19 – 7.09 (m, 4H), 7.09 – 6.98 (m, 2H), 6.63 (dd, *J* = 15.8, 8.2 Hz, 1H), 6.33 (d, *J* = 15.8 Hz, 1H), 4.76 (d, *J* = 8.2 Hz, 1H), 3.62 (s, 3H), 3.42 (s, 3H), 2.33 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 181.6, 148.0, 147.6, 140.4, 137.4, 136.0, 134.2, 131.2, 130.3, 129.3, 129.0, 128.2, 127.3, 126.2, 123.4, 87.1, 47.1, 44.1, 43.1, 21.1, 20.9.

IR (neat, cm^{-1}): 3021, 2922, 2856, 1729, 1601, 1522, 1455, 1383, 1346, 1311, 1193, 1091, 1014, 978, 941, 857, 822, 805, 731, 704.

HRMS (ESI-TOF): Calculated for $C_{27}H_{28}O_4NS$ $[M+H]^+$ 462.17336, found 462.17169

(*E*)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-3,5-bis(3-methoxyphenyl)-1-(4-nitrophenyl)pent-4-en-1-one (**4q**)



4q

Prepared according to procedure D from chalcone **2g** and sulfoxonium ylide **1k**.

Column chromatography eluent: Chloroform/Methanol 99:1

Yellow solid (39.4 mg; 80% yield)

m.p: 160-161 °C

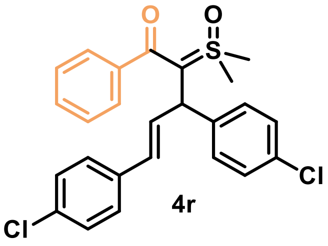
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.10 (m, 2H), 7.61 – 7.54 (m, 2H), 7.24 (t, *J* = 3.9 Hz, 1H), 7.22 – 7.14 (m, 1H), 6.97 (d, *J* = 7.7 Hz, 1H), 6.92 – 6.89 (m, 1H), 6.87 – 6.83 (m, 1H), 6.82 – 6.76 (m, 2H), 6.71 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.66 (dd, *J* = 15.8, 8.2 Hz, 1H), 6.34 (d, *J* = 15.7 Hz, 1H), 4.77 (d, *J* = 8.2 Hz, 1H), 3.80 (s, 3H), 3.74 (s, 3H), 3.62 (s, 3H), 3.46 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 181.7, 159.9, 159.6, 148.0, 147.5, 145.1, 138.4, 131.4, 131.4, 129.7, 129.3, 128.2, 123.5, 119.8, 119.0, 114.0, 113.0, 111.9, 111.0, 86.9, 55.3, 55.2, 47.2, 44.1, 43.1.

IR (neat, cm^{-1}): 3006, 2924, 2836, 1726, 1665, 1600, 1582, 1522, 1487, 1453, 1433, 1389, 1346, 1312, 1289, 1261, 1192, 1157, 1103, 1085, 1044, 1014, 979, 940, 860, 821, 782, 740, 697.

HRMS (ESI-TOF): Calculated for $C_{27}H_{28}O_6NS$ [M+H]$^+$ 494.16318, found 494.16086

(*E*)-3,5-bis(4-chlorophenyl)-2-(dimethyl(oxo)- λ^6-sulfaneylidene)-1-phenylpent-4-en-1-one (**4r**)



4r

Prepared according to procedure D from chalcone **2c** and sulfoxonium ylide **1a**.

Column chromatography eluent: Chloroform/Methanol 99:1

Yellow solid (14.2 mg; 31% yield)

m.p: 115-116 °C

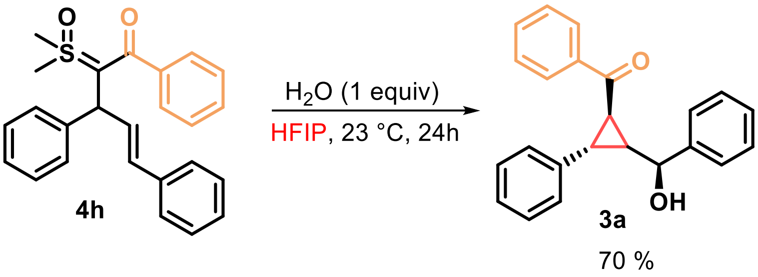
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H), 7.42 – 7.34 (m, 3H), 7.34 – 7.28 (m, 4H), 7.25 – 7.20 (m, 4H), 6.71 (dd, J = 15.8, 8.3 Hz, 1H), 6.37 (dd, J = 15.9, 1.1 Hz, 1H), 4.92 (d, J = 8.3 Hz, 1H), 3.61 (d, J = 0.9 Hz, 3H), 3.37 (d, J = 0.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 184.9, 142.6, 141.0, 135.7, 133.1, 132.0, 131.9, 130.2, 129.6, 128.9, 128.8, 128.3, 127.6, 127.2, 84.7, 47.5, 44.6, 43.5, 29.7.

IR (neat, cm^{-1}): 3027, 2923, 1653, 1597, 1578, 1557, 1489, 1439, 1401, 1306, 1239, 1192, 1091, 1014, 977, 941, 870, 829, 783, 739, 701.

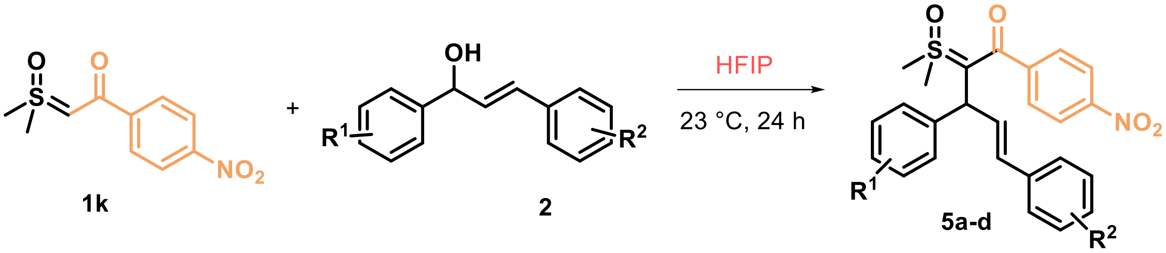
HRMS (ESI-TOF): Calculated for $C_{25}H_{23}O_2Cl_2S$ $[M+H]^+$ 457.07903, found 457.07809

6 Conversion of Sulfoxonium Ylide to Cyclopropane



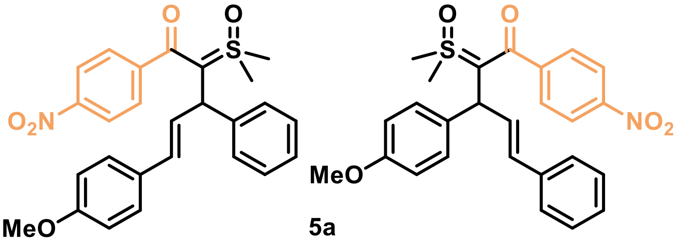
To a 4 mL vial, the α-alkylated sulfoxonium ylide **4h** (38.8 mg; 0.1 mmol; 1 eq), H_2O (18 uL; 0.1 mmol; 1 eq) and HFIP (200 μL; 0.5 M) were added sequentially. After closing the flask with tightly fitted rubber septa, the result mixture was stirred at 23 °C for 24 h under Ar. After the elapsed time, $CHCl_3$ was added to the reaction and the solvent removed under reduced pressure. The crude was purified by column chromathography (EtOAc:hexanes 15:85), furnishing the product (23 mg; 70 % yield) as white solid.

7 General Procedure E: Synthesis of α-Alkylated Sulfoxonium Ylides via Sulfoxonium Ylides Addition to Non-Symmetric Allylic Carbocation



To a 4 mL vial, the sulfoxonium ylide **1** (0.1 mmol; 1 eq), the alcohol **2** (0.2 mmol; 2 eq) and the magnetic stir were added. After closing the flask with tightly fitted rubber septa, HFIP (200 *μ*L, 0.5 M) was added, and the reaction was stirred at 23 °C for 24 h. After the elapsed time, $CHCl_3$ was added to the reaction and the solvent was removed under reduce pressure. The crude was transferred to the column chromathography (MeOH:$CHCl_3$ 1:99) to obtain the desired product **5**.

(*E*)-2-(dimethyl(oxo)- λ^6-sulfaneylidene)-5-(4-methoxyphenyl)-1-(4-nitrophenyl)-3-phenylpent-4-en-1-one (**5a**)



5a

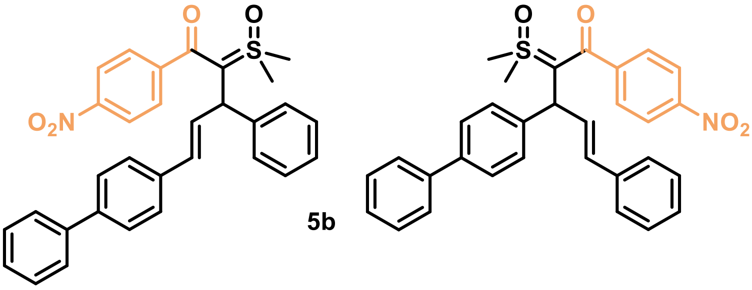
Prepared according to procedure E from chalcone **2h** and sulfoxonium ylide **1k**.
Column chromatography eluent: Chloroform/Methanol 99:1
Yellow solid (14.8 mg; 32% yield), 1:1 regioisomers
m.p: 150-151 °C
^{1}H NMR (400 MHz, $CDCl_3$): 8.24 – 8.15 (m, 4H), 7.62 (dq, *J* = 9.0, 2.3 Hz, 4H), 7.44 – 7.37 (m, 2H), 7.37 – 7.31 (m, 5H), 7.27 (d, *J* = 4.7 Hz, 6H), 7.20 – 7.12 (m, 3H), 6.92 – 6.85 (m, 2H), 6.84 – 6.79 (m, 2H), 6.71 (dd, *J* = 15.9, 8.1 Hz, 1H), 6.57 (dd, *J* = 15.8, 8.2 Hz, 1H), 6.44 – 6.30 (m, 2H), 4.79 (dd, *J* = 11.2, 8.2 Hz, 2H), 3.82 (s, 3H), 3.78 (s, 4H), 3.65 (d, *J* = 0.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 181.8, 181.7, 159.4, 158.3, 148.2, 148.2, 147.7, 143.8, 137.2, 135.4, 131.6, 131.4, 131.1, 129.9, 129.1, 128.8, 128.7, 128.4, 128.4, 127.7, 127.6, 127.6, 126.5, 126.5, 114.3, 113.8, 87.3, 55.5, 55.4, 47.5, 47.0, 44.4, 44.3, 43.2, 29.8.

IR (neat, cm^{-1}): 3027, 2925, 1604, 1511, 1401, 1347, 1307, 1248, 1193, 1097, 1014, 979, 940, 856, 832, 737, 701

HRMS (ESI-TOF): Calculated for $C_{26}H_{25}NNaO_5S$ [M+Na]$^+$ 486.1351, found 486.1344

(*E*)-5-([1,1'-biphenyl]-4-yl)-2-(dimethyl(oxo)- λ^6-sulfaneylidene)-1-(4-nitrophenyl)-3-phenylpent-4-en-1-one (**5b**)



5b

Prepared according to procedure E from chalcone **2i** and sulfoxonium ylide **1k**.

Column chromatography eluent: Chloroform/Methanol 99:1

Yellow solid (45.9 mg; 90% yield); 1:1 regioisomers

m.p.: 120-121 °C

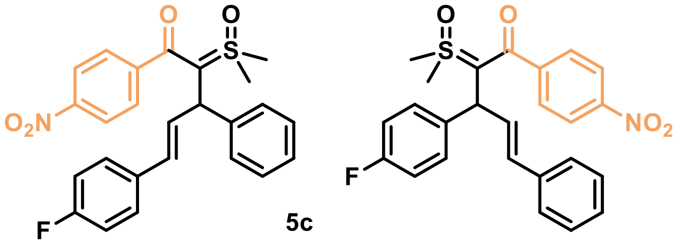
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.3 – 8.2 (m, 2H), 7.7 – 7.5 (m, 4H), 7.5 – 7.4 (m, 4H), 7.4 – 7.3 (m, 3H), 7.3 – 7.3 (m, 2H), 6.8 (ddd, *J* = 15.8, 8.2, 5.8 Hz, 1H), 6.4 (dd, *J* = 16.0, 4.8 Hz, 1H), 4.9 – 4.8 (m, 1H), 3.7 (dd, *J* = 1.5, 0.8 Hz, 3H), 3.5 (d, *J* = 0.8 Hz, 1H), 3.4 (d, *J* = 0.8 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 182.0 (d, *J* = 2.5 Hz), 148.2, 147.7 (d, *J* = 1.9 Hz), 143.5, 142.6, 140.8, 140.7, 140.6, 139.5, 137.1, 136.1, 131.7, 131.4, 131.2 (d, *J* = 1.7 Hz), 129.0 (d, *J* = 3.1 Hz), 128.9, 128.5, 128.4, 128.0, 127.8, 127.6, 127.5, 127.4, 127.1, 127.1 (d, *J* = 1.8 Hz), 126.9, 126.6, 126.5, 123.7 (d, *J* = 1.8 Hz), 87.0 (d, *J* = 10.5 Hz), 47.6, 44.4 (d, *J* = 1.8 Hz), 43.3, 43.2.

IR (neat, cm^{-1}): 3027, 2919, 2850, 1600, 1522, 1488, 1448, 1386, 1347, 1311, 1266, 1194, 1097, 1013, 980, 940, 857, 838, 760, 736, 699.

HRMS (ESI-TOF): Calculated for $C_{31}H_{27}NNaO_4S$ [M+Na]$^+$ 532.1558, found 532.1551

(*E*)-2-(dimethyl(oxo)- λ^6-sulfaneylidene)-5-(4-fluorophenyl)-1-(4-nitrophenyl)-3-phenylpent-4-en-1-one (**5c**)



5c

Prepared according to procedure E from chalcone **2j** and sulfoxonium ylide **1k**.
Column chromatography eluent: Chloroform/Methanol 99:1
Yellow solid (37.9 mg; 84% yield); 1.3:1 regioisomers

m.p.: 159-160 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.2 – 8.2 (m, 4H), 7.7 – 7.6 (m, 4H), 7.4 – 7.3 (m, 6H), 7.3 (dd, *J* = 1.7, 1.1 Hz, 1H), 7.2 – 7.2 (m, 3H), 7.1 – 6.9 (m, 4H), 6.7 (ddd, *J* = 19.1, 15.8, 8.2 Hz, 2H), 6.4 – 6.3 (m, 2H), 4.8 (dd, *J* = 10.0, 8.0 Hz, 2H), 3.7 – 3.6 (m, 6H), 3.4 (d, *J* = 0.8 Hz, 3H), 3.4 (d, *J* = 0.8 Hz, 3H).

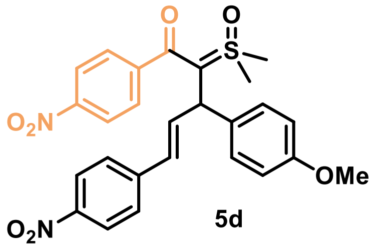
^{13}C NMR (101 MHz, $CDCl_3$): δ 181.8 (d, *J* = 2.6 Hz), 163.6, 162.7, 161.2, 160.3, 148.2 (d, *J* = 6.1 Hz), 147.5 (d, *J* = 10.7 Hz), 143.4, 139.3 (d, *J* = 3.3 Hz), 136.9, 133.2 (d, *J* = 3.2 Hz), 131.8, 131.0 (d, *J* = 6.0 Hz), 130.4, 129.1, 129.0, 128.8, 128.5, 128.3 (d, *J* = 4.3 Hz), 128.0, 127.9 (d, *J* = 3.1 Hz), 127.5, 126.6, 126.5, 123.7 (d, *J* = 5.0 Hz), 115.7 (d, *J* = 21.7 Hz), 115.2 (d, *J* = 21.3 Hz), 86.9 (d, *J* = 10.9 Hz), 47.5, 47.0, 44.3 (d, *J* = 3.9 Hz), 43.3, 43.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ -114.4 (tt, *J* = 8.6, 5.3 Hz), -116.5 (ddd, *J* = 13.1, 9.2, 5.3 Hz).

IR (neat, cm^{-1}): 3027, 2923, 2852, 1600, 1522, 1507, 1449, 1387, 1347, 1310, 1223, 1193, 1159, 1101, 1014, 979, 940, 857, 835, 757, 737, 701.

HRMS (ESI-TOF): Calculated for $C_{25}H_{22}FNNaO_4S$ [M+Na]$^+$ 429.1300, found 429.1291

(*E*)-2-(dimethyl(oxo)- λ^6-sulfaneylidene)-3-(4-methoxyphenyl)-1,5-bis(4-nitrophenyl)pent-4-en-1-one (**5d**)



5d

Prepared according to procedure E from chalcone **2k** and sulfoxonium ylide **1k**.

Column chromatography eluent: Chloroform/Methanol 99:1

Yellow solid (36.6 mg; 72% yield); 10:1 regioisomers

m.p.: 158-159 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.3 – 8.1 (m, 4H), 7.7 – 7.6 (m, 2H), 7.6 – 7.4 (m, 2H), 7.2 – 7.1 (m, 2H), 6.9 (dt, *J* = 16.7, 8.4 Hz, 1H), 6.8 (d, *J* = 8.8 Hz, 1H), 6.5 (d, *J* = 15.9 Hz, 1H), 4.8 (d, *J* = 8.1 Hz, 1H), 3.8 (s, 3H), 3.7 (d, *J* = 0.8 Hz, 3H), 3.4 (d, *J* = 0.9 Hz, 3H).

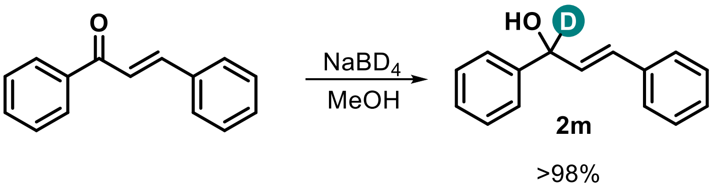
^{13}C NMR (101 MHz, $CDCl_3$): δ 182.0, 158.5, 148.4, 147.4, 147.1, 143.7, 136.9, 134.6, 129.4, 128.7, 128.4, 127.0, 124.3, 123.7, 114.0, 86.5, 55.4, 47.3, 44.7, 43.2.

IR (neat, cm^{-1}): 3009, 2925, 2851, 1599, 1512, 1462, 1388, 1344, 1305, 1249, 1191, 1109, 1016, 980, 940, 858, 830, 738, 704.

HRMS (ESI-TOF): Calculated for $C_{26}H_{25}O_7N_2S$ $[M+H]^+$, 509.13825, found 509.13617

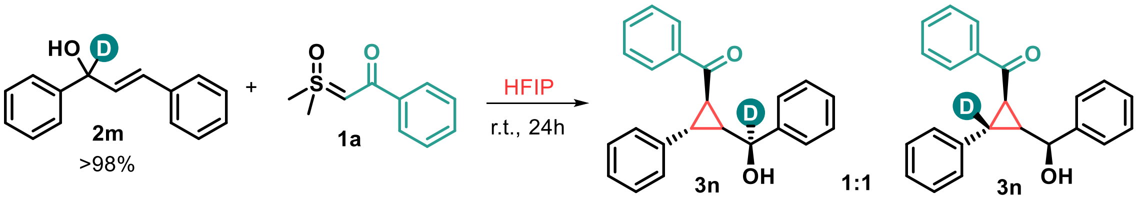
8 Experiments Involving Deuterated Substrates

8.1 Deuterated Alcohol Synthesis



To a 10 mL round bottom flask, the ketone (200 mg; 0.84 mmol; 1 eq) and MeOH (4 mL) were added, followed by the addition of $NaBD_4$ (42 mg; 1 mmol; 1.2 eq). The reaction mixture was stirred at 23 °C for 2h, followed by solvent removal under reduced pressure. After extraction with EtOAc, the deuterated alcohol **2m** was obtained in quantitative yield. The spectroscopic data was matched with literature.[18]

8.2 Synthesis of Cyclopropanes via Sulfoxonium Ylides Addition to Deuterated Allylic Carbocation



To a 4 mL vial flask, the alcohol **2m** (42 mg; 0.2 mmol; 2 eq) and the sulfoxonium ylide **1a** (24 mg; 0.1 mmol; 1 eq) were added, followed by addition of HFIP (200 μL; 0.5 M). The reaction mixture was stirred at 23 °C for 24h, followed by $CHCl_3$ addition and solvent removal under reduced pressure. The crude was purified by column chromathography (EtOAc:hexanes 15:85), furnishing the product **3n** (23 mg; 74 % yield) as a mixture of regioisomers (1:1).

m.p.: 125-126 °C

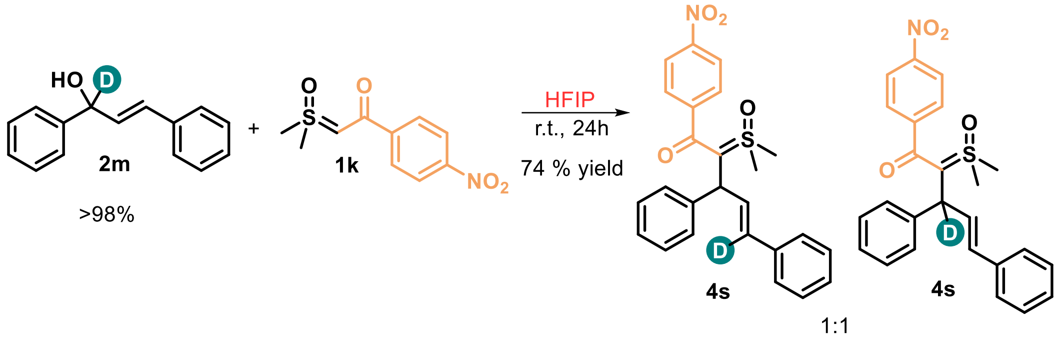
^{1}H NMR (400 MHz $CDCl_3$): δ 8.08 – 8.01 (m, 4H), 7.62 – 7.52 (m, 2H), 7.53 – 7.44 (m, 6H), 7.34 (t, *J* = 7.4 Hz, 3H), 7.25 (td, *J* = 7.8, 2.5 Hz, 5H), 7.19 (d, *J* = 7.1 Hz, 1H), 7.07 (dt, *J* = 8.0, 1.3 Hz, 4H), 4.96 (d, *J* = 9.2 Hz, 1H), 3.13 (s, 1H), 3.11 (dd, *J* = 5.1, 3.7 Hz, 2H), 2.56 (d, *J* = 12.1 Hz, 2H), 2.44 – 2.35 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 198.7, 143.7, 143.6, 139.4, 139.3, 138.3, 133.3, 128.8, 128.7 (d, *J* = 1.9 Hz), 128.5, 127.7 (d, *J* = 1.8 Hz), 126.9, 126.8 (d, *J* = 3.5 Hz), 126.0, 71.5, 40.8, 33.8 (d, *J* = 4.9 Hz), 32.2, 29.8 (d, *J* = 4.1 Hz).

IR (neat, cm^{-1}): 3430, 3060, 3028, 2923, 1662, 1600, 1580, 1495, 1449, 1426, 1369, 1278, 1224, 1180, 1092, 1040, 1020, 933, 940, 698, 656.

HRMS (ESI-TOF): Calculated for $C_{23}H_{19}DNaO_2$ [M+Na]$^+$ 352.1424, found 352.1425

8.3 Synthesis of α-Alkylated Sulfoxonium Ylides via Sulfoxonium Ylides Addition to Deuterated Allylic Carbocation



To a 4 mL vial flask, the alcohol **2m** (42 mg; 0.2 mmol; 2 eq) and the sulfoxonium ylide **1k** (24 mg; 0.1 mmol; 1 eq) were added, followed by addition of HFIP (200 μL; 0.5 M). The reaction mixture was stirred at 23 °C for 24h, followed by $CHCl_3$ addition and solvent removal under reduced pressure. The crude was purified by column chromathography (MeOH:$CHCl_3$ 1:99), furnishing the product **4s** (32.1 mg; 74 % yield) as a mixture of regioisomers (1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 – 8.14 (m, 2H), 7.64 – 7.56 (m, 2H), 7.42 – 7.12 (m, 10H), 6.71 (d, J = 3.8 Hz, 1H), 6.39 (d, J = 15.8 Hz, 1H), 4.82 (d, J = 8.6 Hz, 0H), 3.64 (d, J = 0.8 Hz, 3H), 3.40 (t, J = 0.8 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 181.77 (d, J = 1.6 Hz), 148.07, 147.55, 143.41, 143.36, 136.98, 136.91, 131.47, 131.07, 131.01, 128.69, 128.32, 128.22, 127.64, 127.47 (d, J = 2.0 Hz), 126.47 (d, J = 1.8 Hz), 126.34 (d, J = 2.5 Hz), 123.51, 86.92, 86.87, 47.33, 44.22 (d, J = 1.3 Hz), 43.04 (d, J = 1.6 Hz).
IR (neat, cm^{-1}): 3024, 2922, 1599, 1522, 1448, 1386, 1347, 1310, 1197, 1101, 1015, 976, 941, 859, 839, 740, 699.
HRMS (ESI-TOF): Calculated for $C_{25}H_{23}DNO_4S$ $[M+H]^+$ 435.14888, found 435.14383

9 Density Functional Theory Computational Studies

For the complete mechanism characterization, a conformational search was initially performed on the reactants, intermediates and transition states using

CREST software at the xTB-GFN2 level,[19] to identify the lowest energy conformers. All Density Functional Theory (DFT) calculations were conducted using the ORCA software, version 5.0.4.[20,21] Geometry optimizations were performed at the M06-2X/def2-SVP level of theory, with thermal corrections derived from vibrational frequency analyses. To improve the accuracy of electronic energies, single-point calculations were subsequently carried out at the M06-2X/def2-TZVP level to improve electronic properties. Furthermore, Conductor-like Polarizable Continuum Model (CPCM) implicit solvation model was used to account for the solvent effects. For HFIP, a dielectric constant of 16.7 was used based on literature data.[22,23] The final Gibbs free energy for each step was determined by summing the electronic energy (E_{el}) at the M06-2X/def2-TZVP level and the thermal corrections ($E_{thermal}$) at the M06-2X/def2-SVP level, as described by the following equation:

$$G = E_{el} + E_{thermal}$$

Moreover, to confirm energy minima, we assured no imaginary frequencies. For the transition states (TS), the frequency related to the transition state must be imaginary, indicating a saddle point of the potential energy surface. Therefore, to assert that the TS were in fact the TS of interest, we verified if the imaginary frequency was related to the bond breaking/forming and, to further validate the TS, an Intrinsic Reaction Coordinate (IRC) calculation was performed. The XYZ structures of all species (intermediates, TS, reactants and products), as well as all IRCs are provided as supplementary materials. The complete mechanism involving the lowest energy conformers can be seen in Figure S1.

For the identification of the **I-2** lowest energy conformers, considering both stereochemistries (*iso1* and *iso2*), four conformers of each stereoisomer were considered for the TS characterization, and the **I-2**, **TS2** and **I-3** energies of each conformer is shown in Figure S2 for R = H, respectively. Moreover, for the characterization of the lowest energy conformers of **I-6**, we considered the attack of water from both faces of **I-5**, yielding **I-6a**, **I-6b**, in which the **I-6a** has the lowest energy and was therefore considered in the reaction mechanism shown in **Figure S3**.

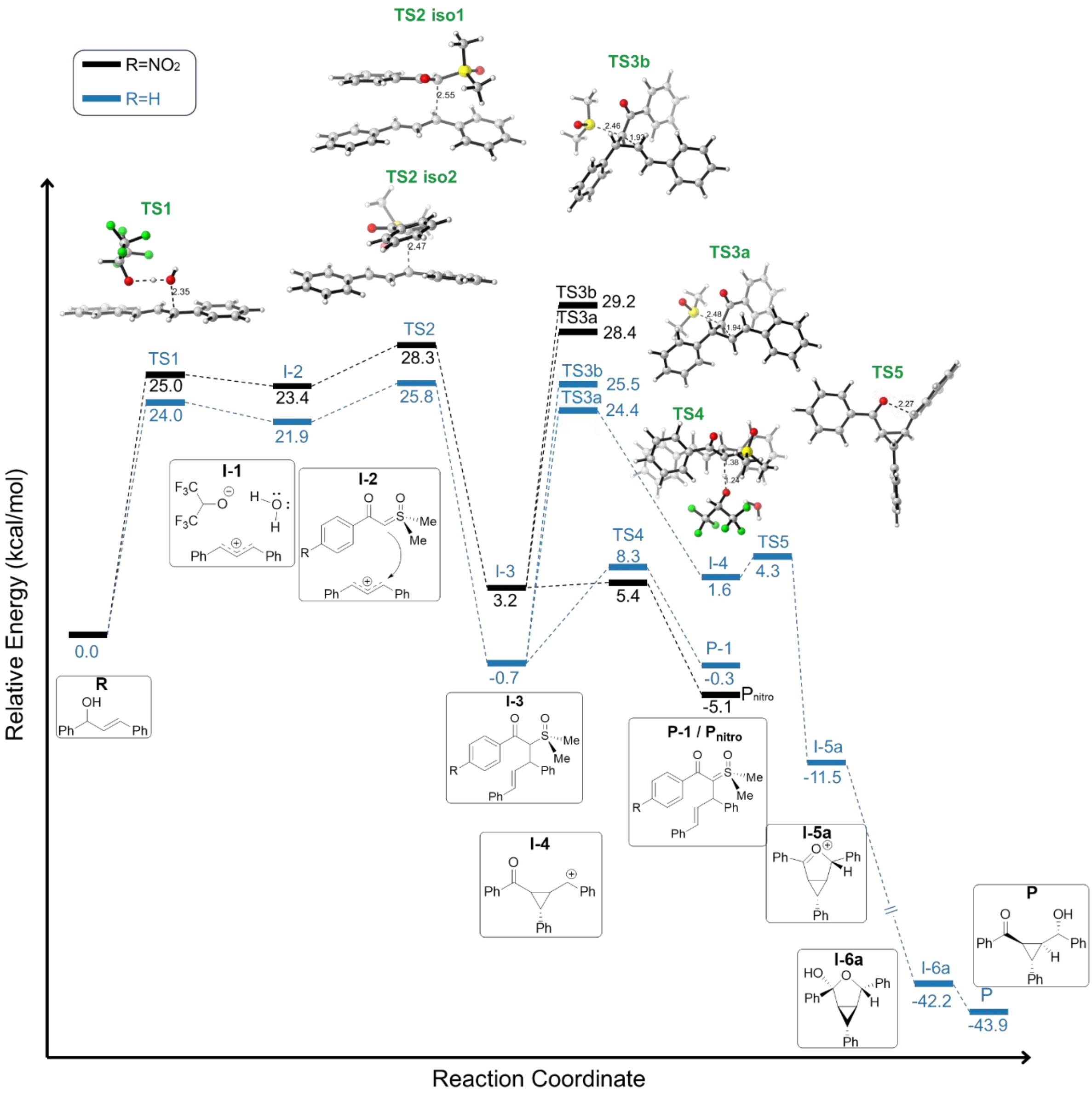


Figure S1: Complete reaction mechanism. All calculations were performed at the M06-2X-def2-TZVP[CPCM/κ=16.7]//M06-2X/def2-SVP[CPCM/κ=16.7] level of theory.

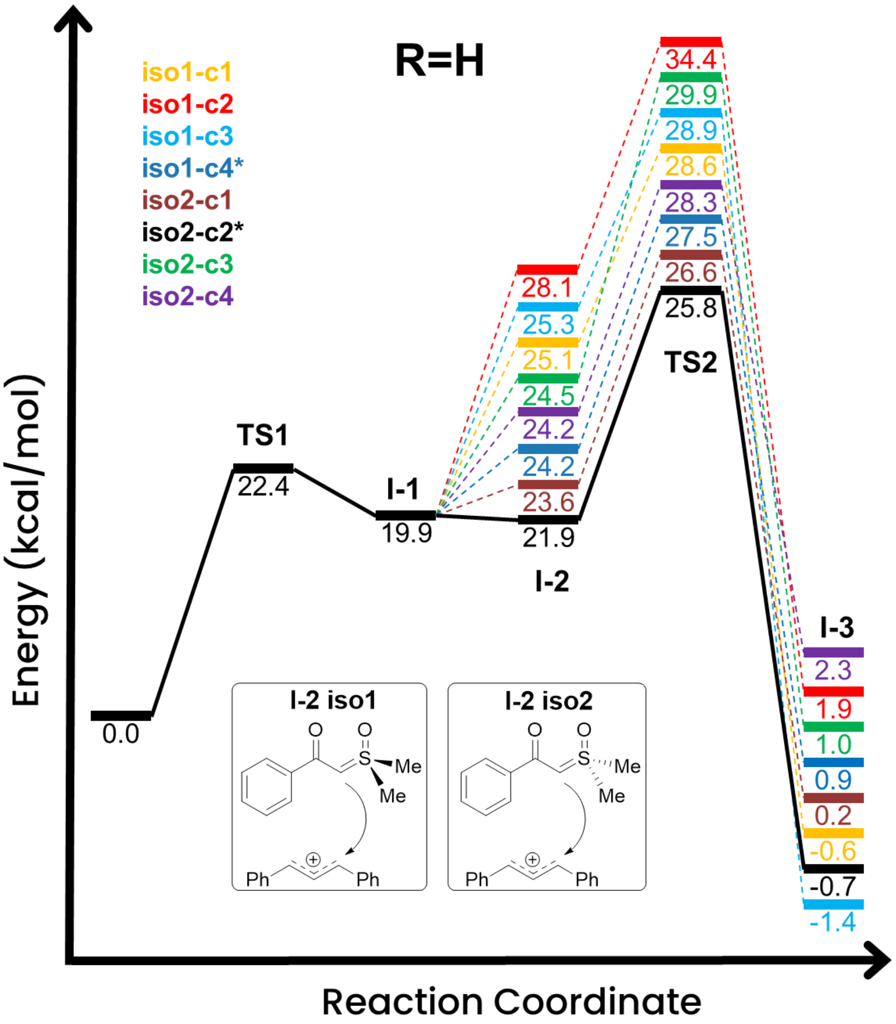


Figure S2: Relative energies for all **I-2** intermediates isomers. Lowest energy conformers for each stereoisomer (**iso1-c4** and **iso2-c2**) are marked with an asterisk (*). All calculations were performed at the M06-2X-def2-TZVP[CPCM/κ=16.7]//M06-2X/def2-SVP[CPCM/κ=16.7] level of theory.

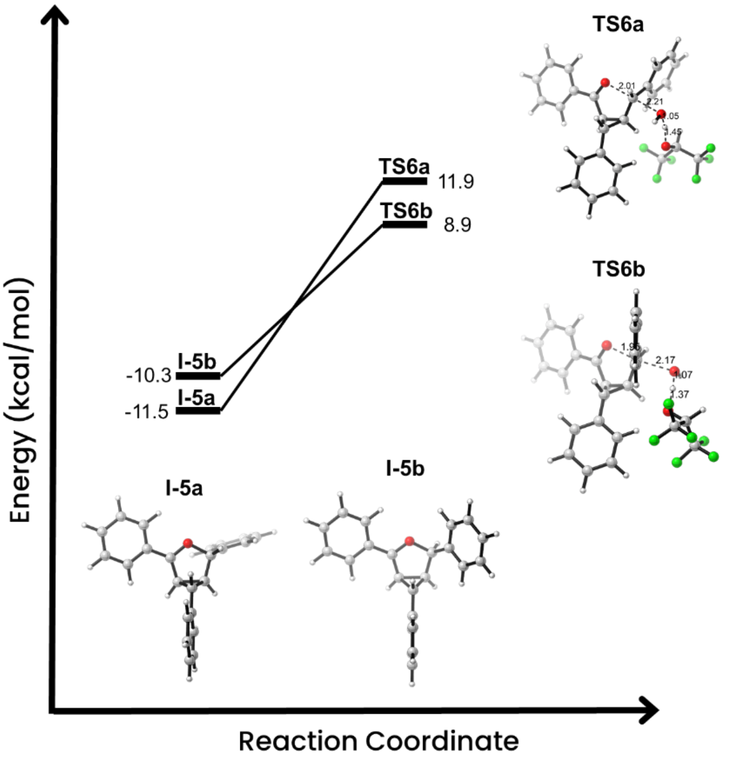


Figure S3: Relative energies for all **I-5a** and **I-5b** intermediates, as well as **TS6a** and **TS6b** transition states. All calculations were performed at the M06-2X-def2-TZVP[CPCM/κ=16.7]//M06-2X/def2-SVP[CPCM/κ=16.7] level of theory.

10 NCI Analysis

To gain a better insight of the interactions at the **TS3** step, which is critical for the determination of the observed stereochemistry, a Non-Covalent Index (NCI) analysis was carried out using NCIPLOT package.[24] This analysis is based on the reduced electron density gradient and is able to capture non-covalent interactions. In NCI plots, cold colors (e.g., blue) represent strong intermolecular attraction, such as hydrogen bonds, green colors represent weak van der Waals interactions, while hot colors (e.g., red) represent repulsive interactions. The plots for **TS3a** and **TS3b** for R = H are shown in Figure S4.

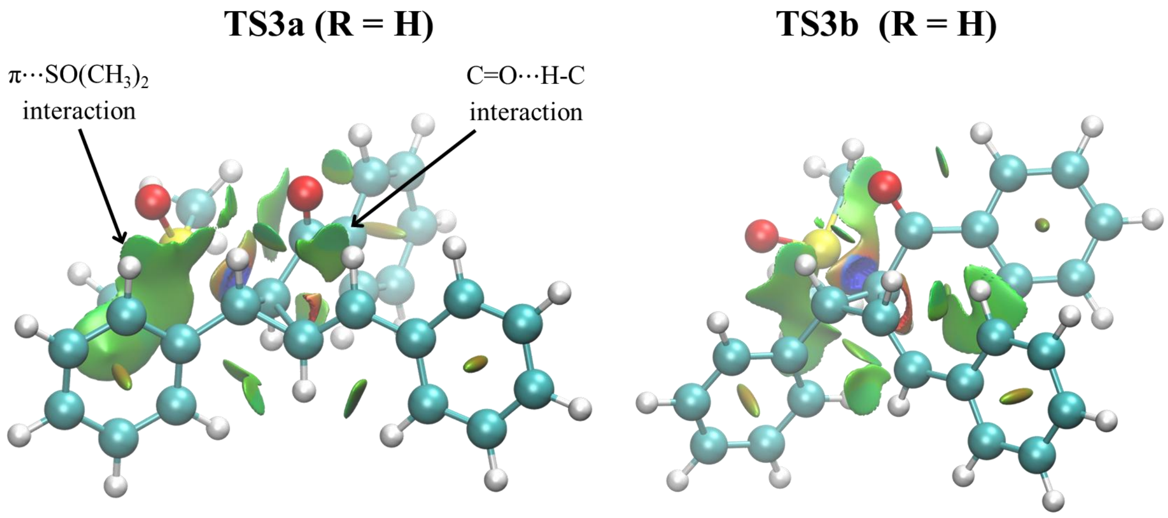
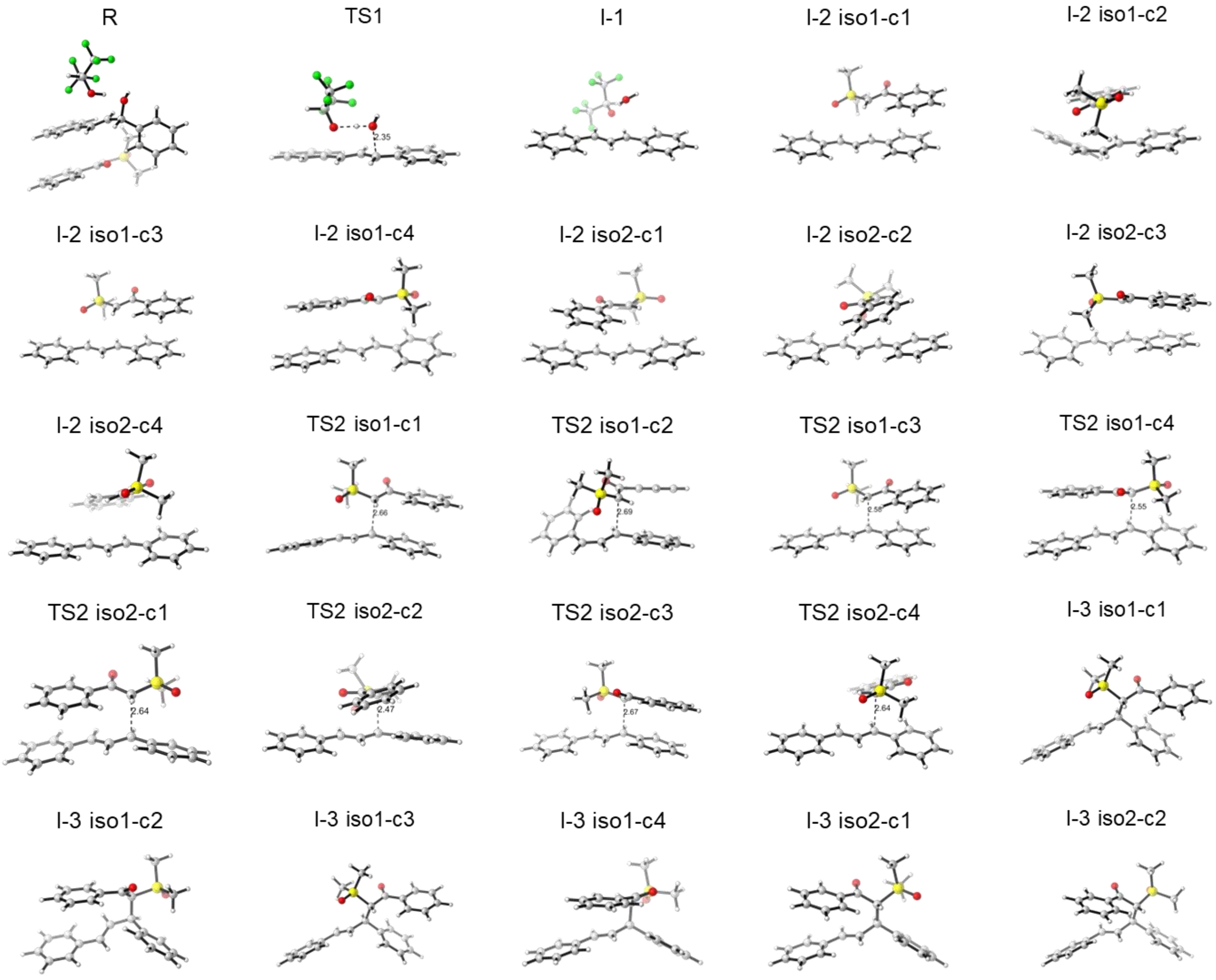


Figure S4: NCI analysis for **TS3a** and **TS3b** for R = H.

11 3D structures

All 3D structures of each step calculated in this computational study are shown in Figures S5 and S6, for R=H, and S7 for R=NO_2.



R, TS1, I-1, I-2 iso1-c1, I-2 iso1-c2

I-2 iso1-c3, I-2 iso1-c4, I-2 iso2-c1, I-2 iso2-c2, I-2 iso2-c3

I-2 iso2-c4, TS2 iso1-c1, TS2 iso1-c2, TS2 iso1-c3, TS2 iso1-c4

TS2 iso2-c1, TS2 iso2-c2, TS2 iso2-c3, TS2 iso2-c4, I-3 iso1-c1

I-3 iso1-c2, I-3 iso1-c3, I-3 iso1-c4, I-3 iso2-c1, I-3 iso2-c2

Figure S5: 3D structures for R = H.

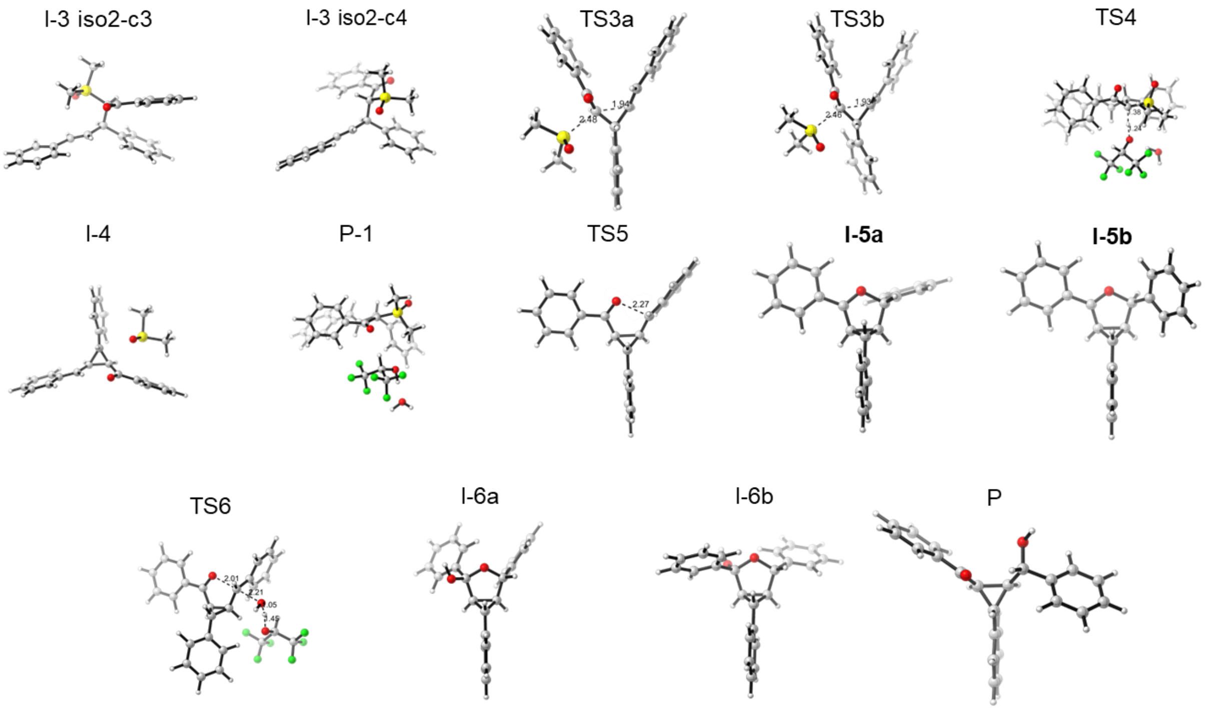


Figure S6: 3D structures for R = H.

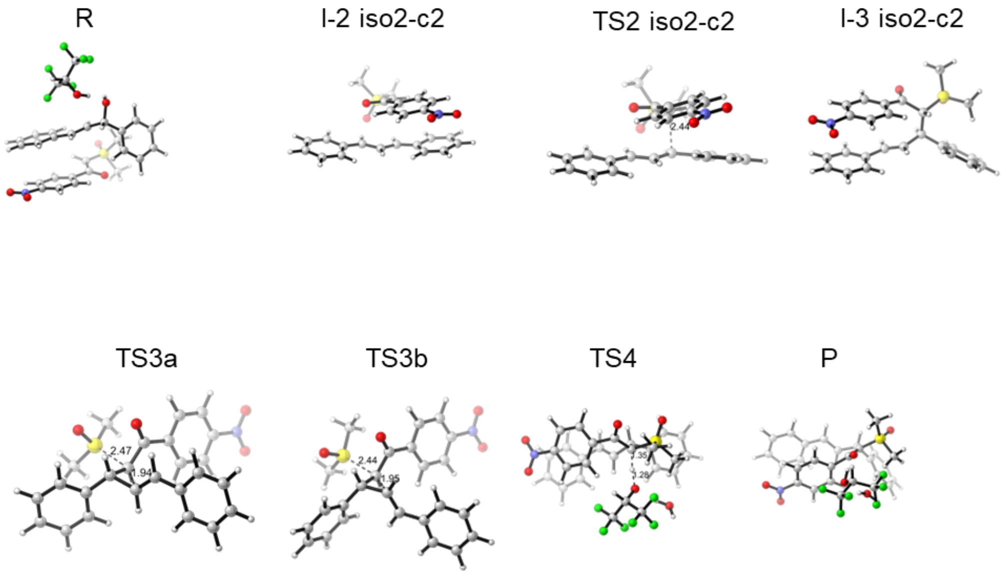


Figure S7: 3D structures for R=NO_2.

12 Computational Data Availability

The XYZ structures of all species presented in this study are shared as supporting files inside a folder called "structures". Inside this folder, all structures corresponding to R = H and R = NO_2 are separated into their respective folders and all Intrinsic Reaction Coordinate (IRC) XYZ trajectories are also provided. Furthermore, all single point energies, thermal energy corrections as well as lowest frequencies (and TS frequencies) are shared inside a datashee in xlsx format, called computational_energies_and_frequencies.xlsx.

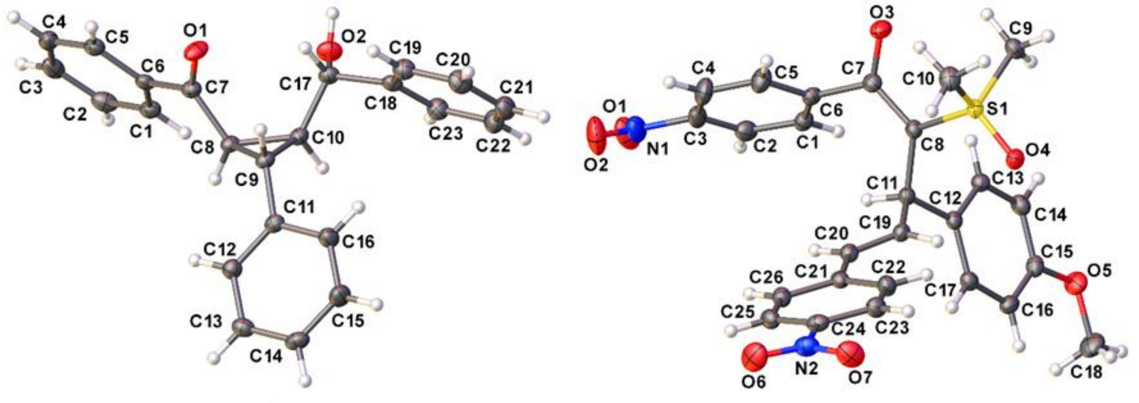
13 Single crystal X-ray diffraction (SCXRD)

Data collection and reduction, cell refinement and multi-scan absorption correction were performed using the CrysAlisPro program[25]. The structures were solved by the intrinsic phasing method from the SHELXT-2018/2[26] and refined by the least-squares method from the SHELXL-2019/2[27], both included in Olex2 program[28]. The non-hydrogen atoms were refined considering anisotropic displacement parameters, while the hydrogen atoms were refined at idealized positions using the riding model. Olex2 was also used to generate graphical illustrations. Table S1 summarizes some information concerning the data collection and refinement parameters of the elucidated structures. The Crystallographic Information Files (CIF) of **3a** and **5e** have been deposited in the Cambridge Structural Database (CSD) with CCDC numbers 2453810 and 2453811, respectively. Copies of the data can be obtained free of charge from www.ccdc.cam.ac.uk.

Table S1. Crystal data and structure refinement for **3a** and **5d**

	3a	**5d**
Molecular formula	$C_{23}H_{20}O_2$	$C_{26}H_{24}N_2O_7S$
Formula weight (g mol^{-1})	328.39	508.53
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	P-1
a (Å)	15.7894(1)	10.5928(2)
b (Å)	5.4472(1)	11.1713(2)
c (Å)	20.0645(1)	11.7801(2)
α (°)	90	105.275(2)
β (°)	90.387(1)	113.211(2)
γ (°)	90	91.778(2)
Volume (Å^3)	1725.66(2)	1221.53(4)
Z	4	2
ρ_{calc} (g/cm^3)	1.264	1.383
μ (mm^{-1})	0.623	1.604
T_{min}/T_{max}	0.586/1.000	0.952/1.000
2θ range for data collection (°)	11.208 to 140.144	9.19 to 140.144
Index ranges	-16, 19; -6, 6; -24, 24	-12, 12; -8, 13; -14 , 14
Reflections collected	40821	25405
Independent Ref./R_{int}	3284/0.0455	4629/0.0288
Goodness-on-fit on F^2	1.033	1.081
R_1/wR_2 [I >2σ(I)]	0.0371/0.0938	0.0314/0.0813
R_1/wR_2 (all data)	0.0388/0.0953	0.0339/0.0850
$\Delta\rho_{max}$; $\Delta\rho_{min}$ (e Å^{-3})	0.28/–0.24	0.29/–0.40

SCXRD technique was used to elucidate the crystal structure of **3a** and **5e**, with the ORTEP representations of the asymmetric unities shown in Figure S8.



3a **5d**

Figure S8: ORTEP type illustrations of the asymmetric unities of **3a** and **5d** with atomic labelling and 50% probability ellipsoids.

X-ray data indicate that the crystal structure of **3a** is composed of a racemic mixture, since it crystallized in the centrosymmetric monoclinic $P2_1/n$ space group. The structure of **3a** has the hydroxy(phenyl)methyl and phenylmethanone groups *cis*-positioned to each other with respect to the cyclopropane ring, while these substituents show a *trans* disposition in relation to the phenyl substituent. The C7–O1 (1.2217(14) Å) and C17–O2 (1.2217(14) Å) bonds have a character of double and single bonds, respectively. The crystal structure of **3a** is stabilized by the intermolecular hydrogen bonds O2–H2···O2' (dD···A = 2.8695(12) Å and <D–H···A = 163.28(4)º) that involve the hydroxyl group from different molecules, and by π···π stacking interactions (3.766 Å) between the phenylmethanone rings from neighboring molecules. These intermolecular interactions allow the organization of the **3a** molecules in a two-dimensional arrangement (Figure S9).

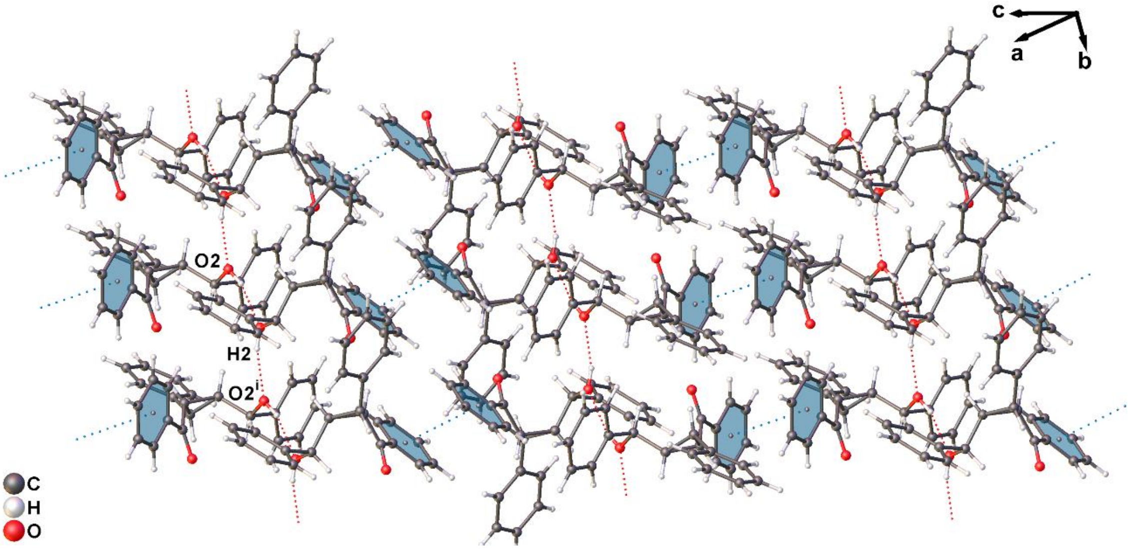


Figure S9: Two-dimensional network formed for **3a** through the hydrogen bonds viewed in the [-111] direction. The symmetry operator ^{i}1.5-X, 0.5+Y, 1.5-Z was used to generate equivalent molecules.

Compound **5d** crystallizes in the triclinic P-1 space group, also showing the crystallization of a racemic mixture. It was observed that the S1–C8 (1.7151(13) Å) and C7–O3 (1.2600(16) Å) bonds in **5d** are longer than the expected for double bonds, while the C7–C8 (1.3992(18) Å) bond is shorter than the observed for a typical single bond, being indicative that it has a contribution of the enol tautomer for the structure of **5d** in solid state. The C19–C20 bond (1.3286(18) Å) has the character of a double bond and shows the substituents in a *trans* conformation, as verified by the spectroscopic analyses. A possible π-hole interaction involving the *O*-carbonyl atom from one molecule of **5d** and one nitro group from a neighbor molecule is observed in the crystal structure of **5d**, with O3···N2^{i} distance of 2.888(1) Å. This interaction organizes the molecules of the ylide in the crystal packing through a one-dimensional chain (Figure S10).

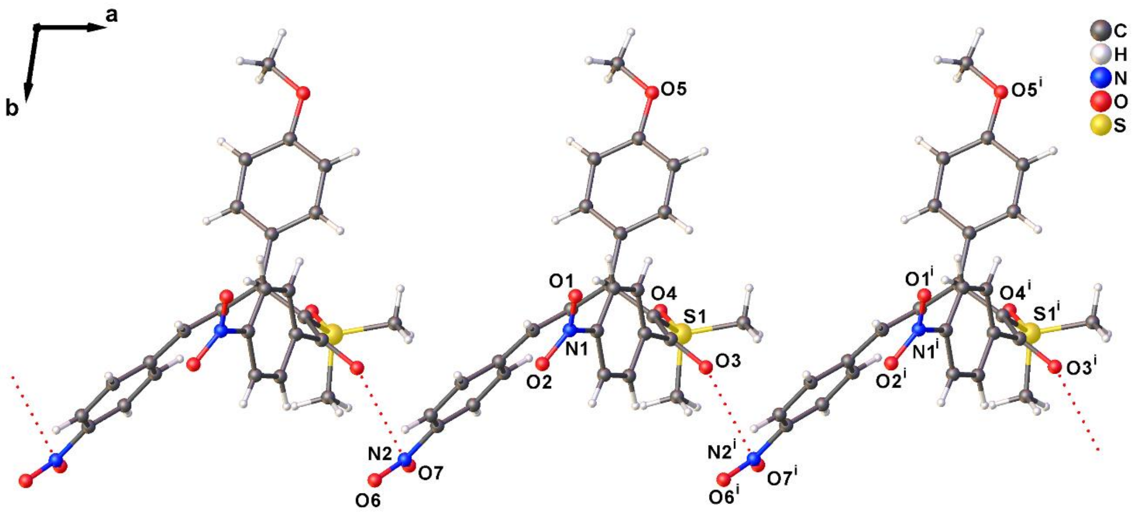


Figure S10: One-dimensional chain formed for **5d** through the π-hole interactions viewed in the [001] direction.

14 ^{1}H, ^{13}C and ^{19}F NMR spectra

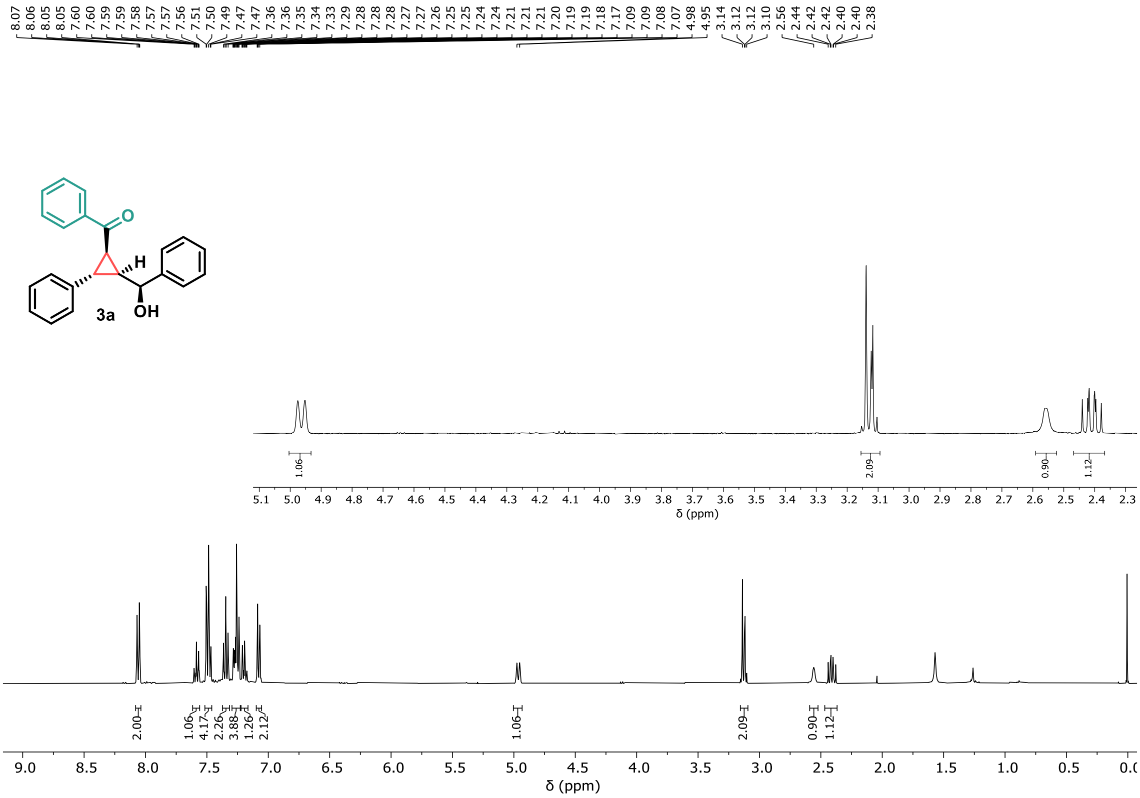


Figure S11: ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3a**.

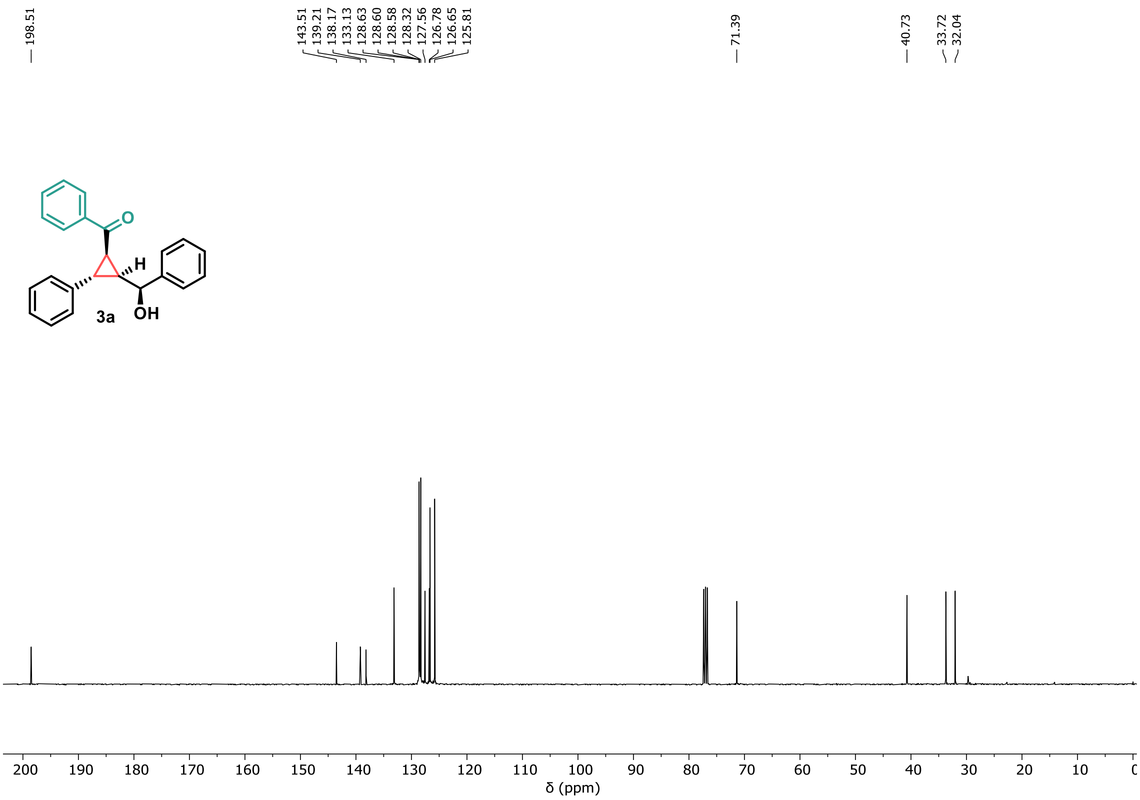


Figure S12: ^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **3a**.

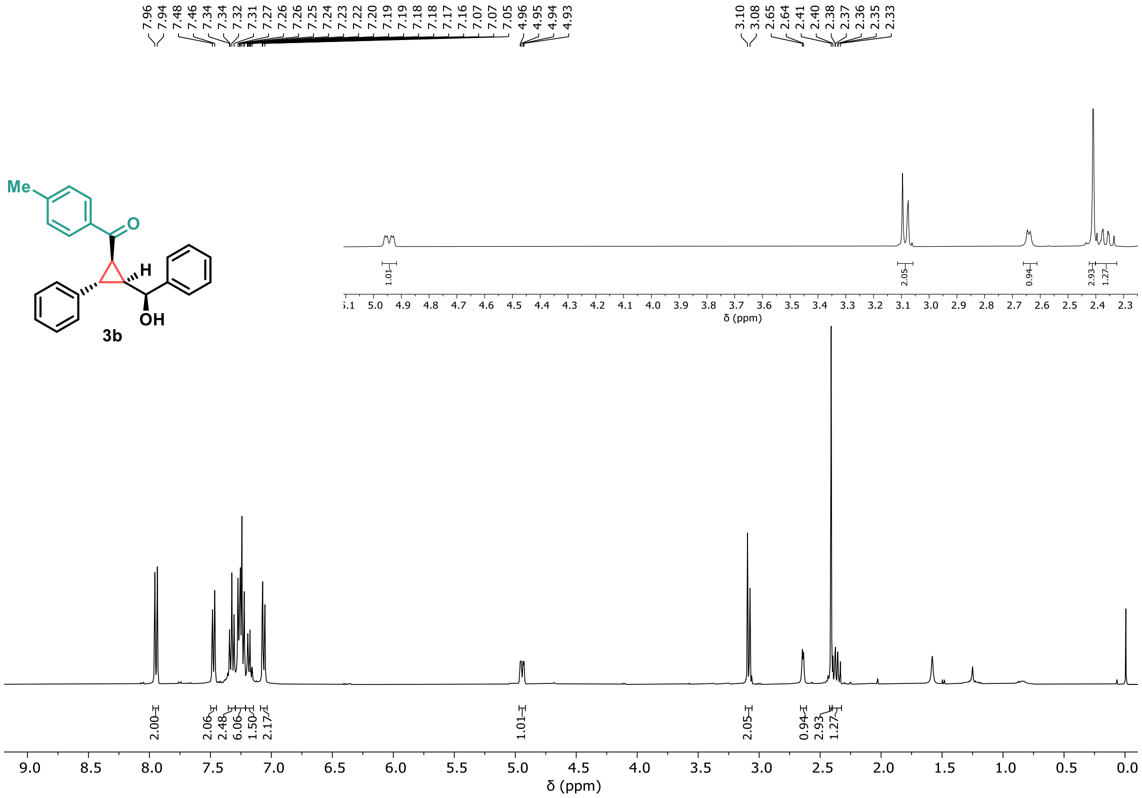


Figure S13: ^{1}H NMR spectra (400 MHz, CDCl$_3$) of compound **3b**.

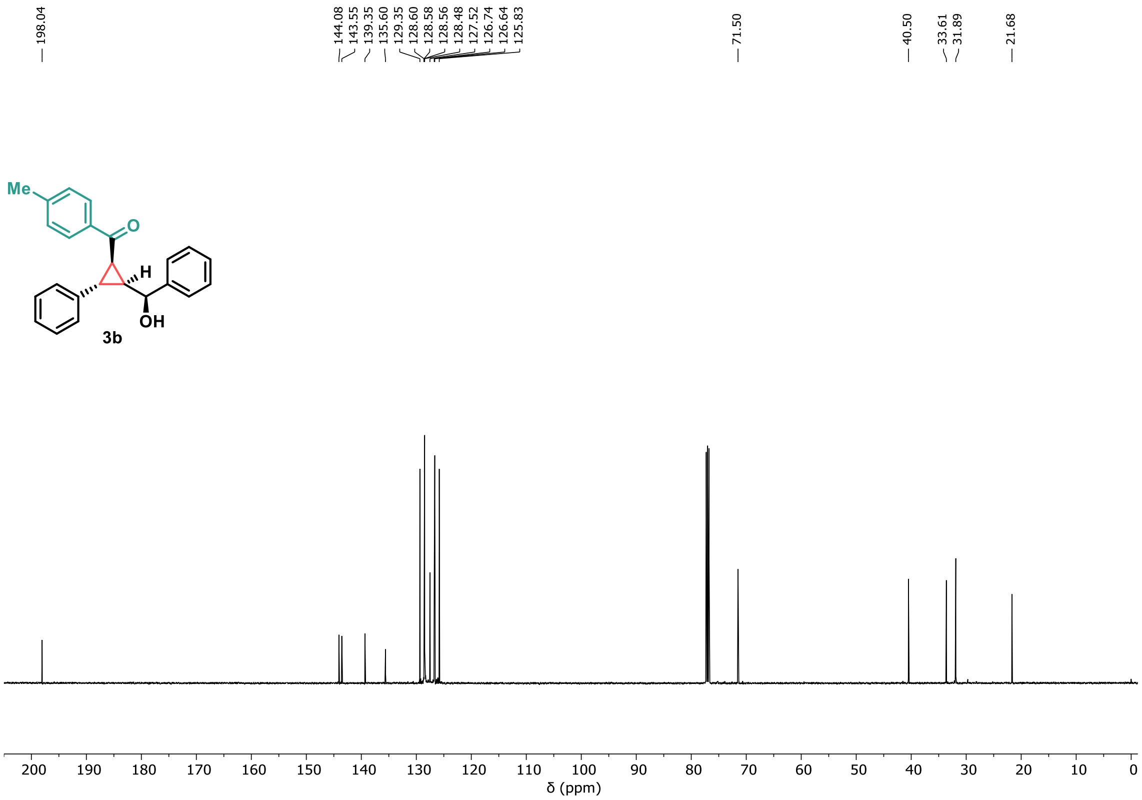


Figure S14: ^{13}C NMR spectra (101 MHz, CDCl$_3$) of compound **3b**.

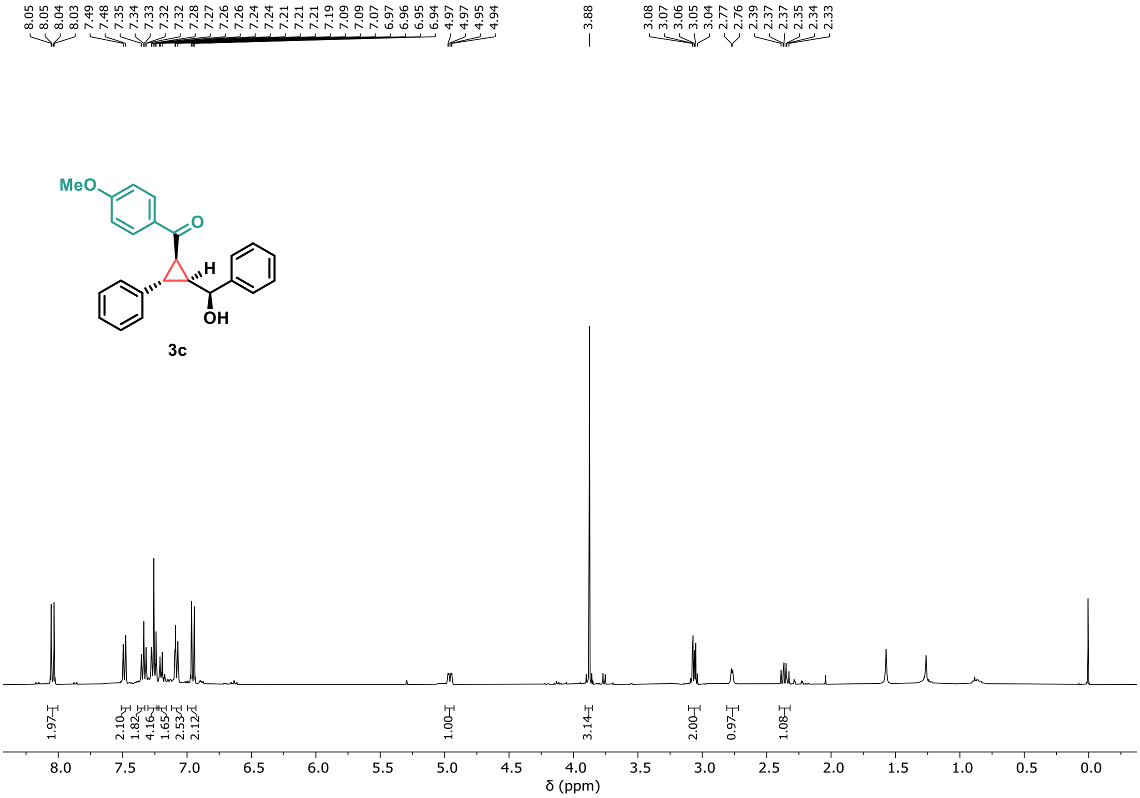


Figure S15: ^{1}H NMR (400 MHz, CDCl$_3$) of compound **3c**.

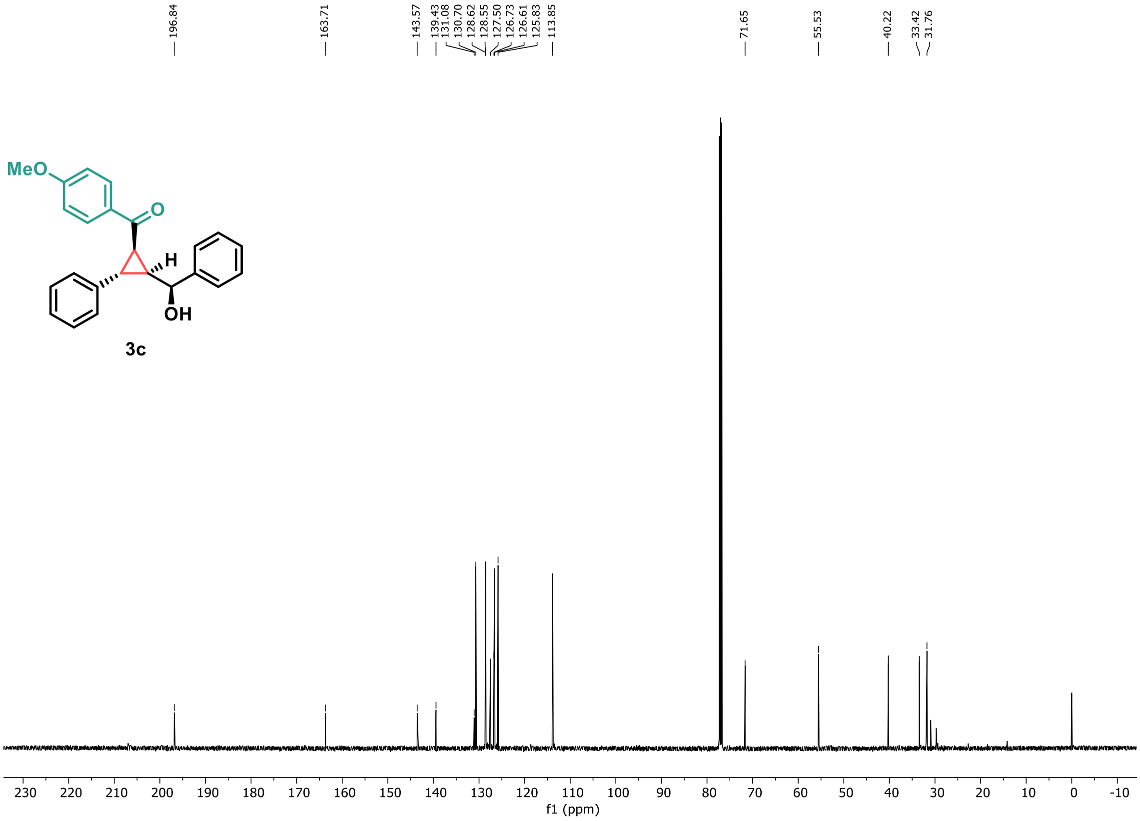


Figure S16: ^{13}C NMR spectra (126 MHz, CDCl$_3$) of compound **3c**.

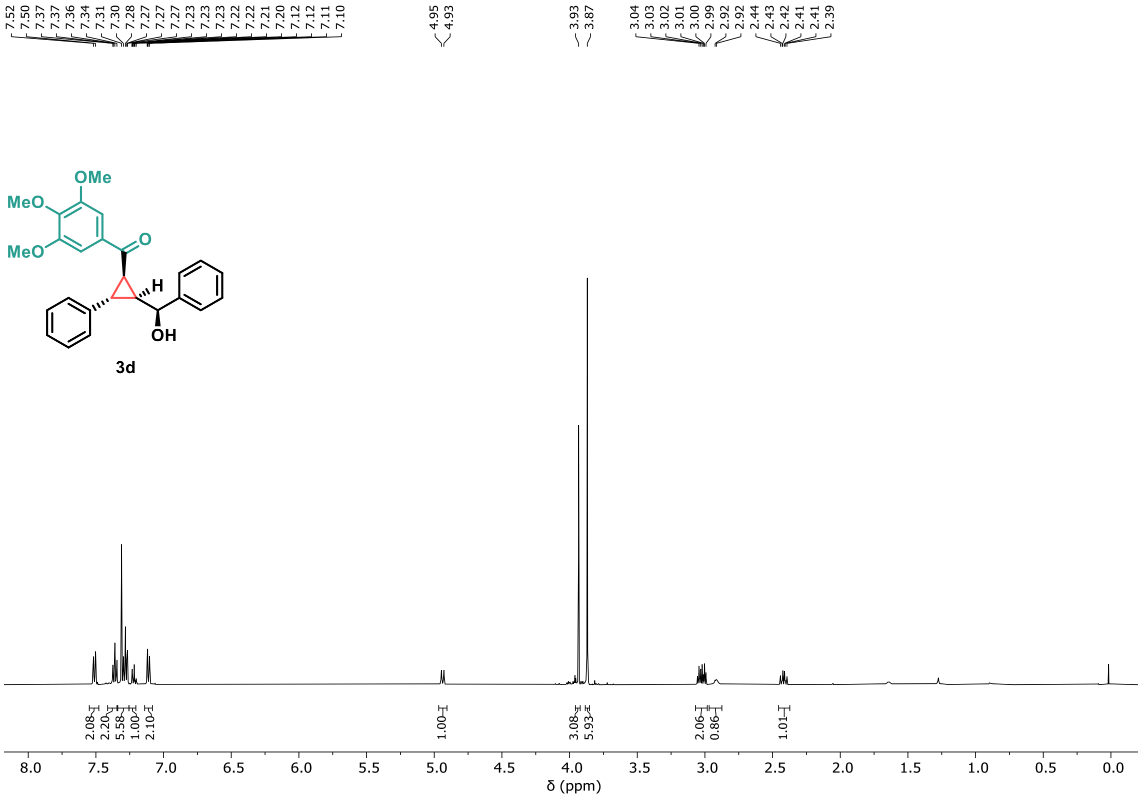


Figure S1: ^{1}H NMR spectra (500 MHz, $CDCl_3$) of compound **3d**.

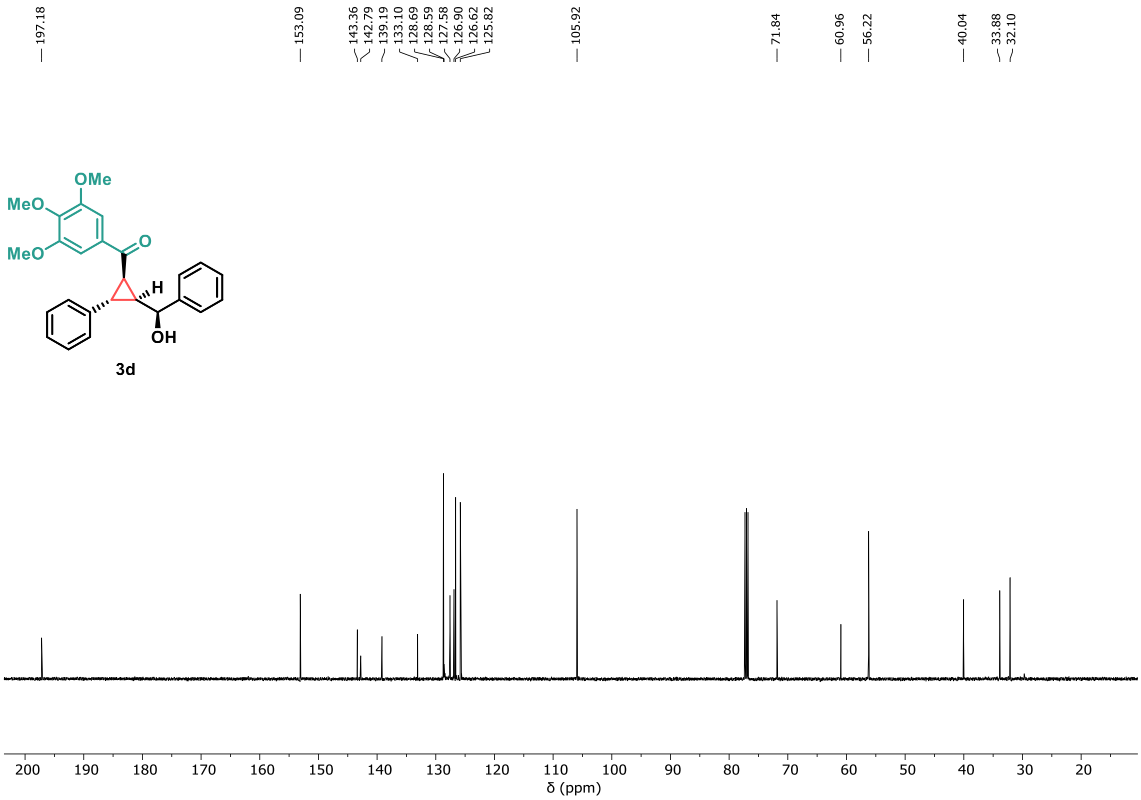


Figure S2: ^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **3d**.

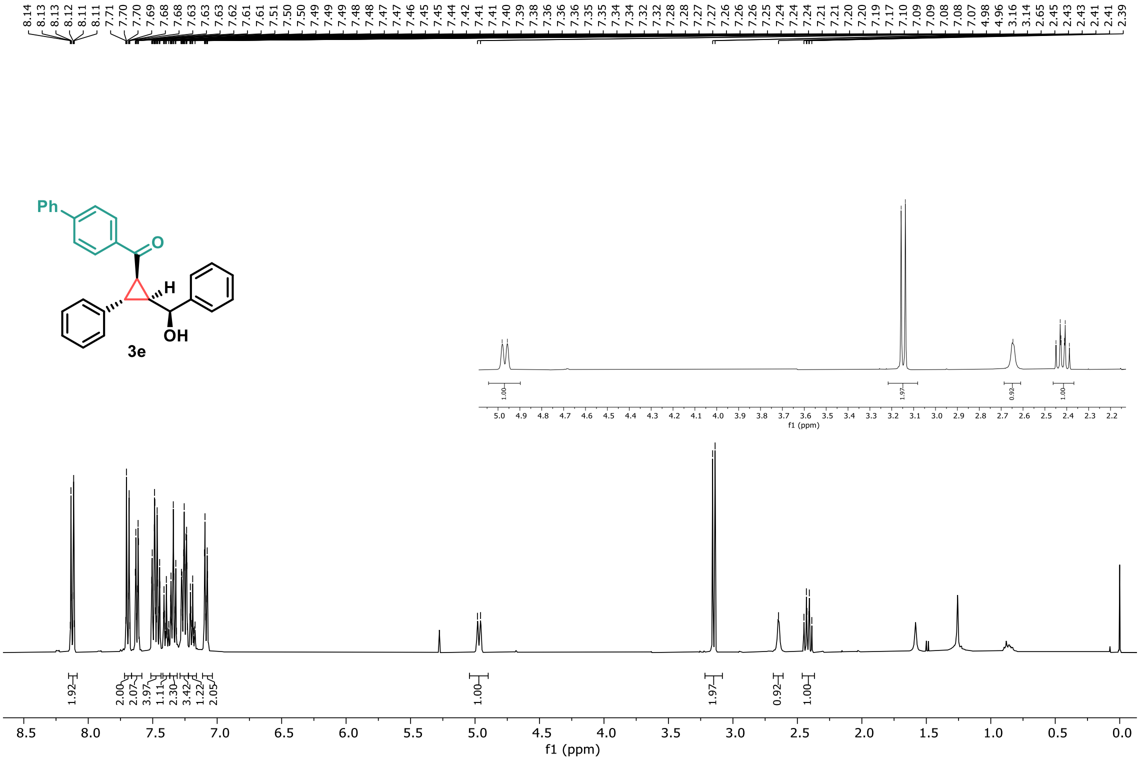


Figure S3: ^{1}H NMR spectra (400 MHz, CDCl$_3$) of compound **3e**.

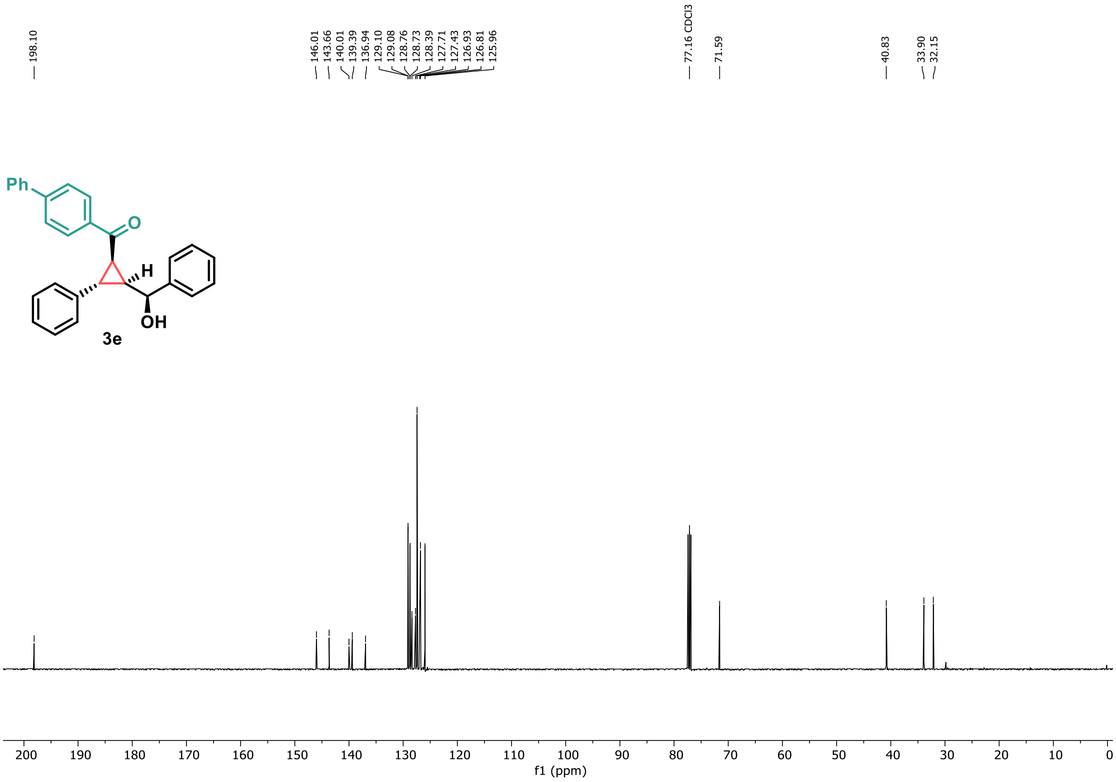


Figure S20: ^{13}C NMR spectra (101 MHz, CDCl$_3$) of compound **3e**.

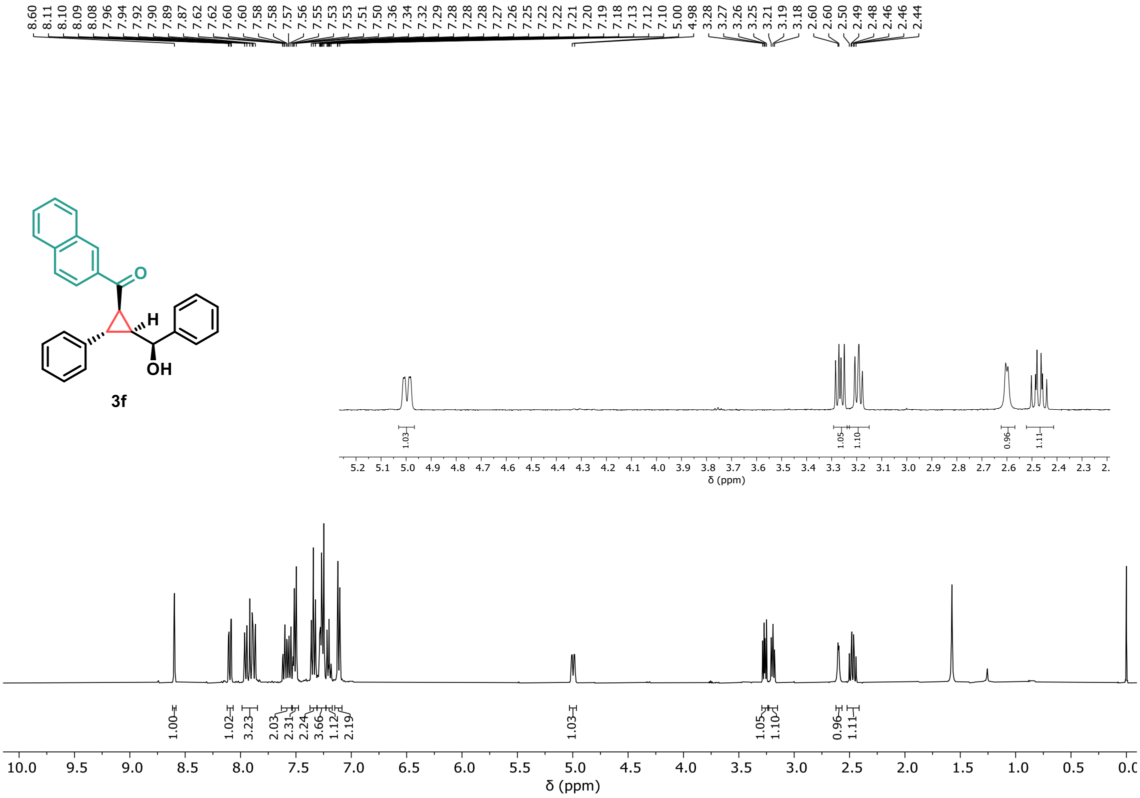


Figure S21: ^{1}H NMR spectra (400 MHz, CDCl$_3$) of compound **3f**.

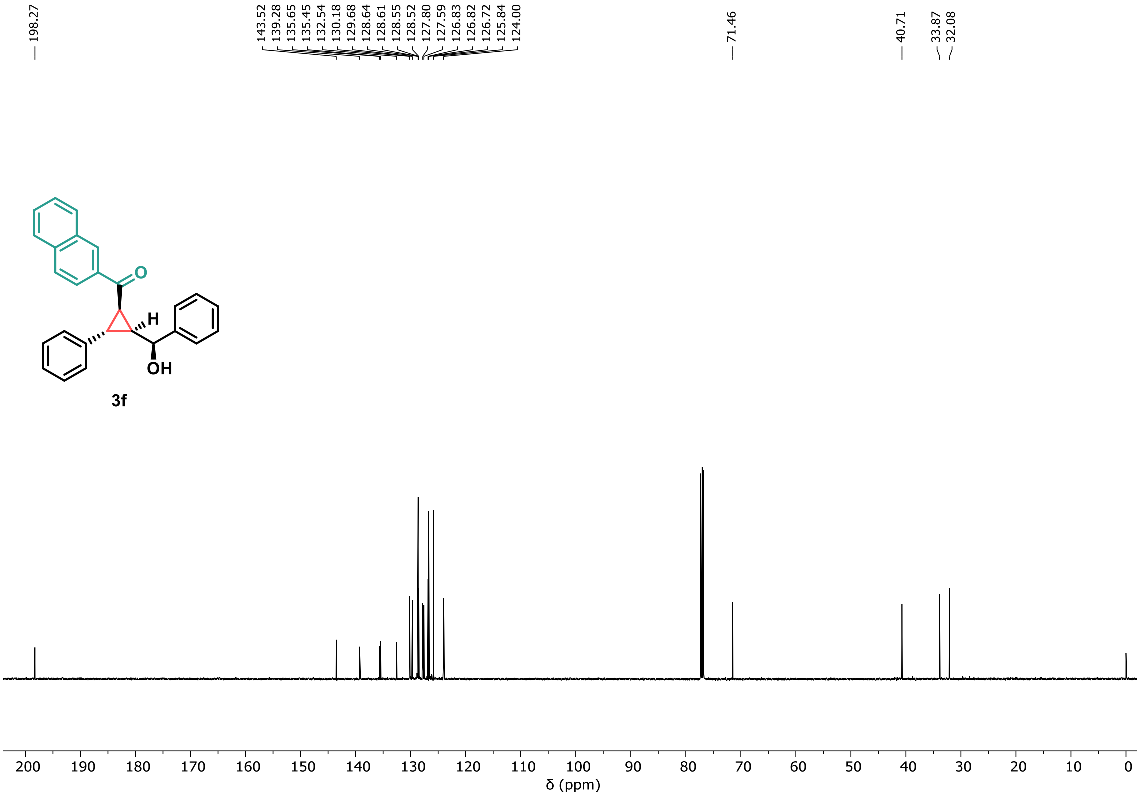


Figure S22: ^{13}C NMR spectra (126 MHz, CDCl$_3$) of compound **3f**.

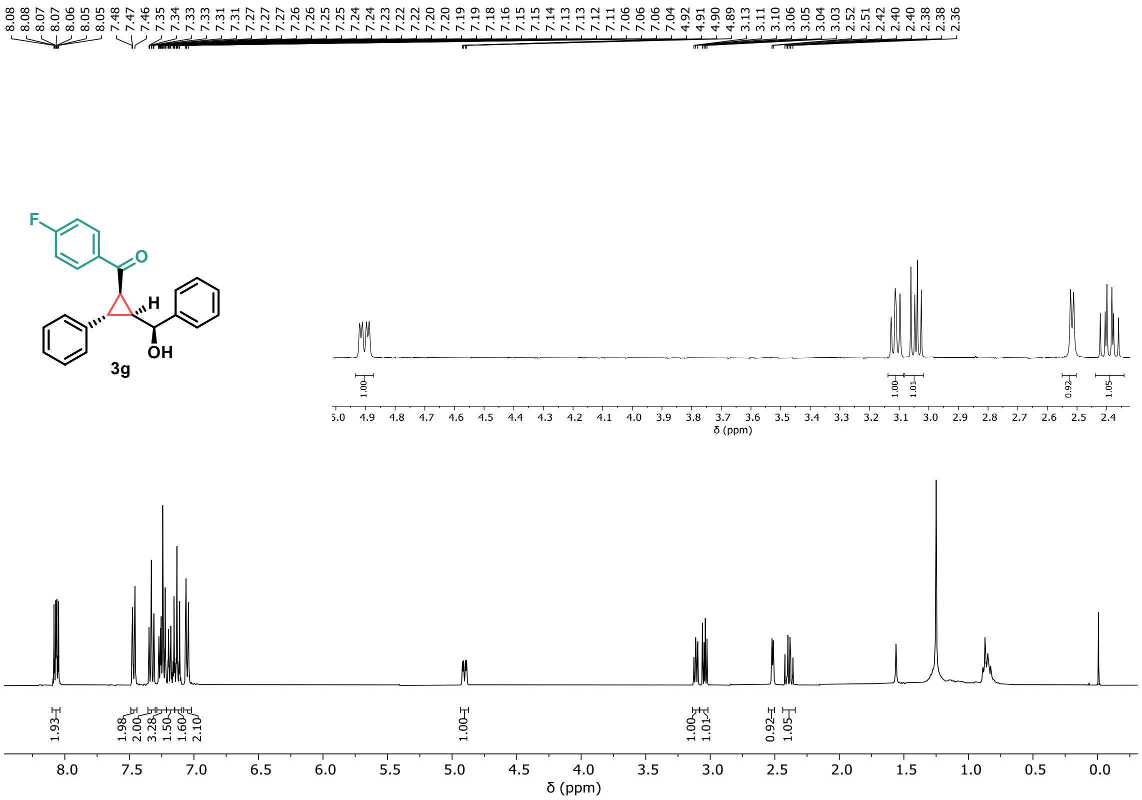


Figure S23: ^{1}H NMR spectra (400 MHz, CDCl$_3$) of compound **3g**.

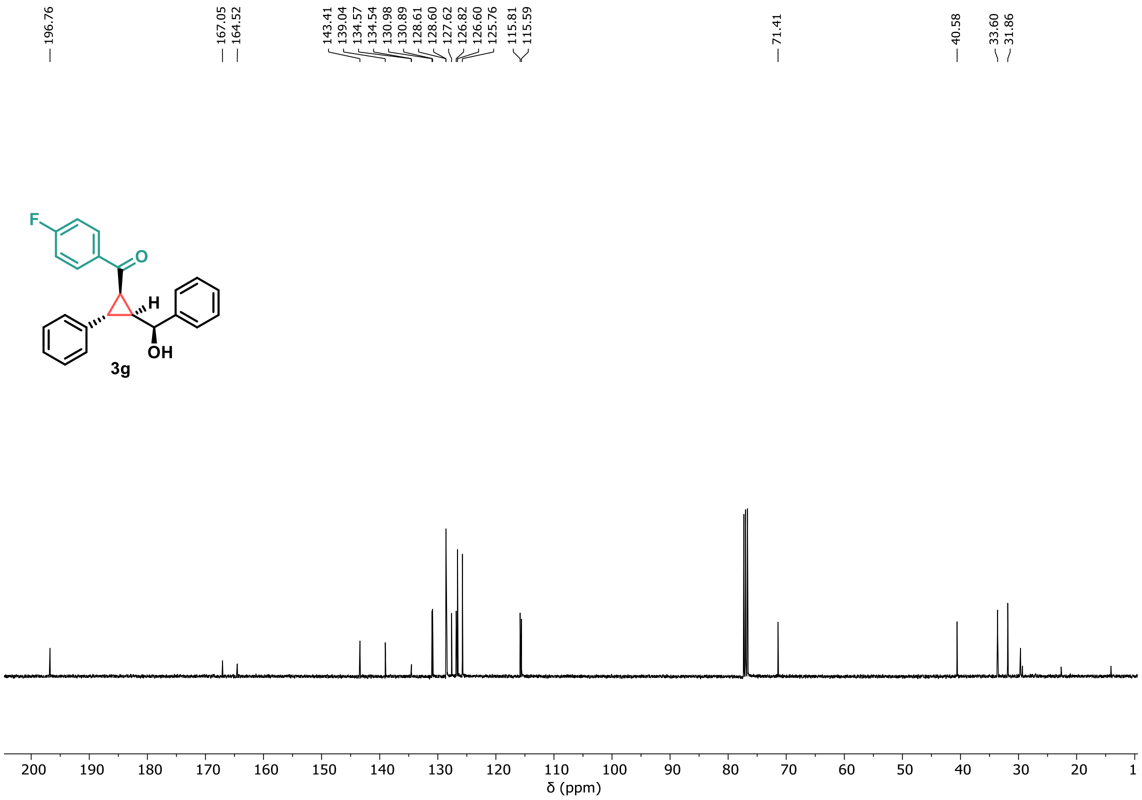


Figure S24: ^{13}C NMR spectra (101 MHz, CDCl$_3$) of compound **3g**.

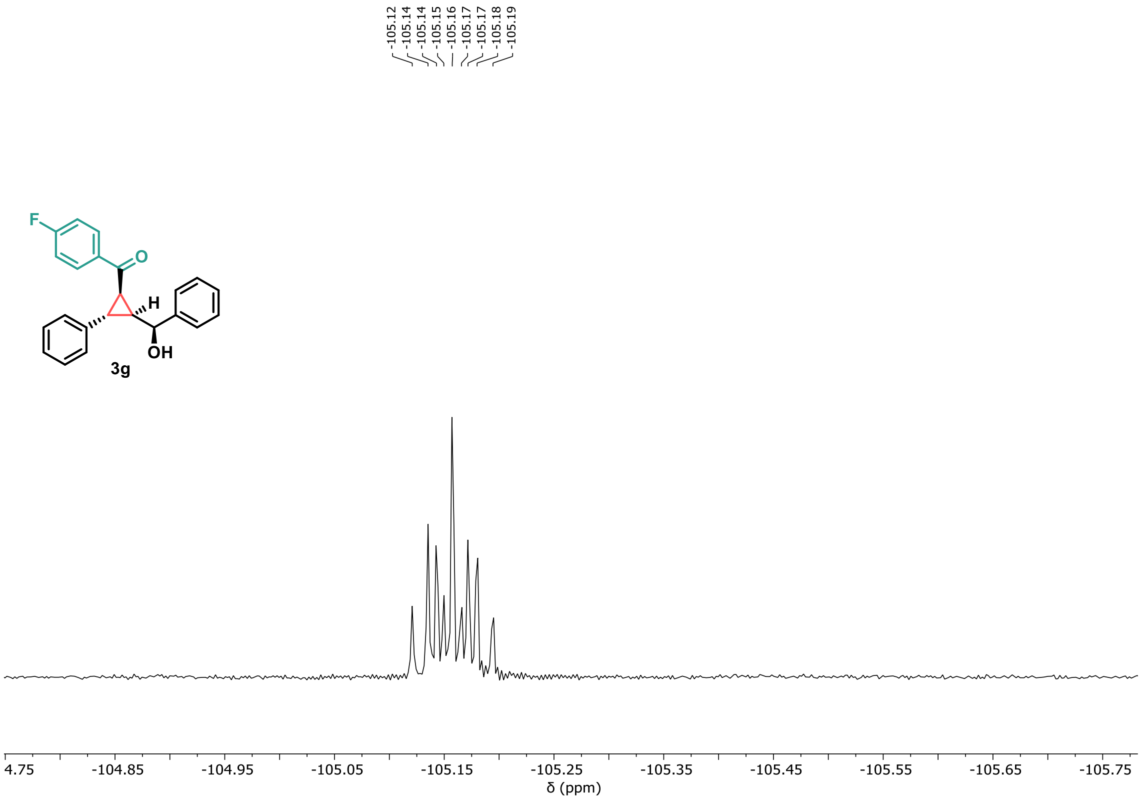


Figure S25: ^{19}F NMR spectra (376 MHz, CDCl$_3$) of compound **3g**.

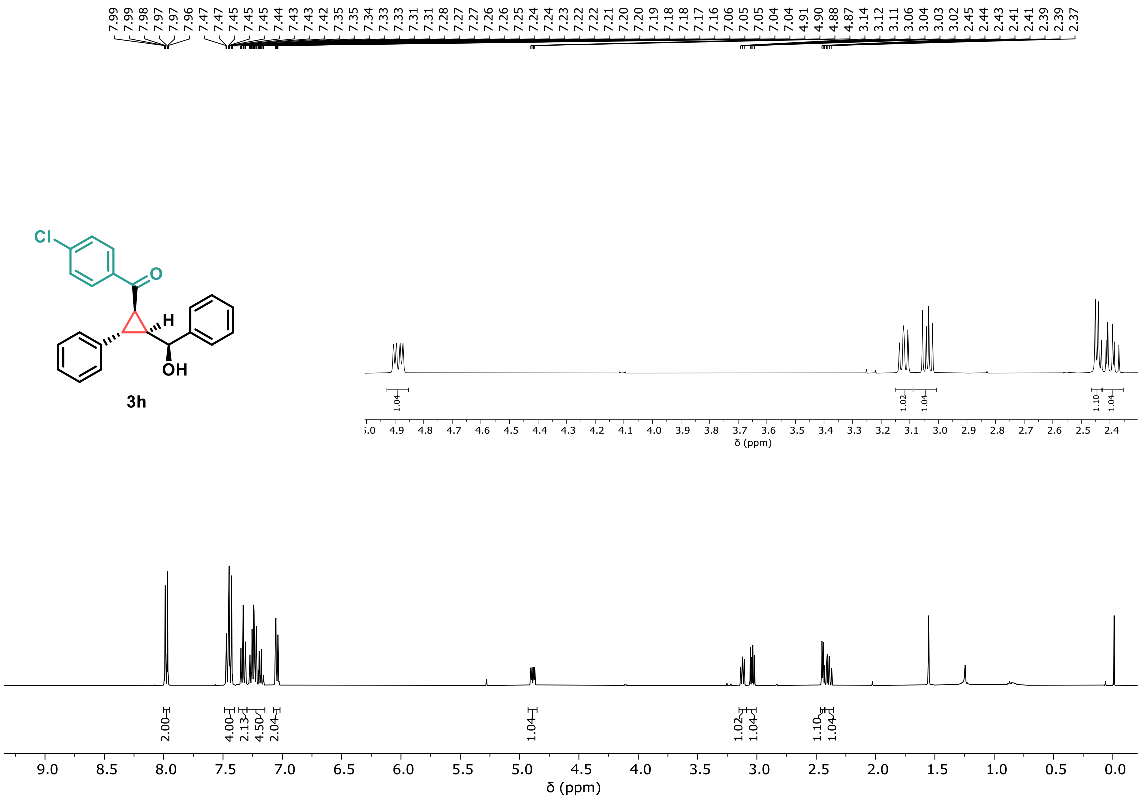


Figure S26: ^{1}H NMR spectra (400 MHz, CDCl$_3$) of compound **3h**.

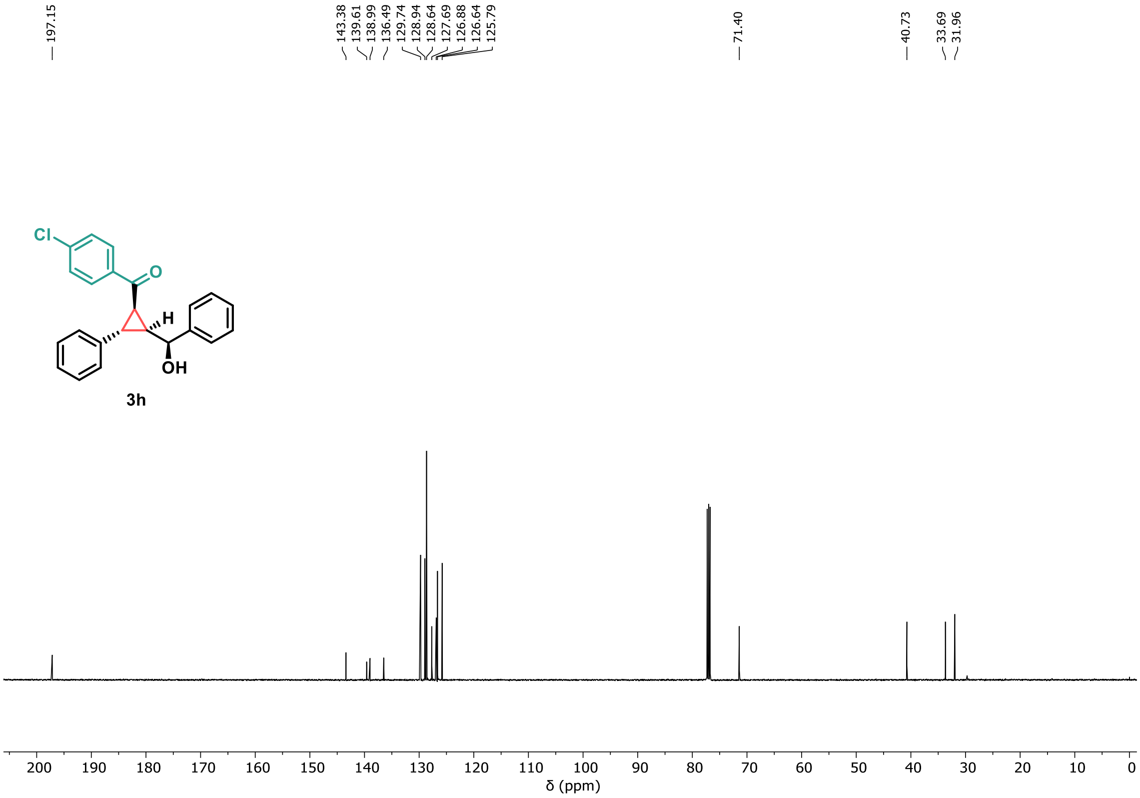


Figure S4: ^{13}C NMR spectra (126 MHz, CDCl$_3$) of compound **3h**.

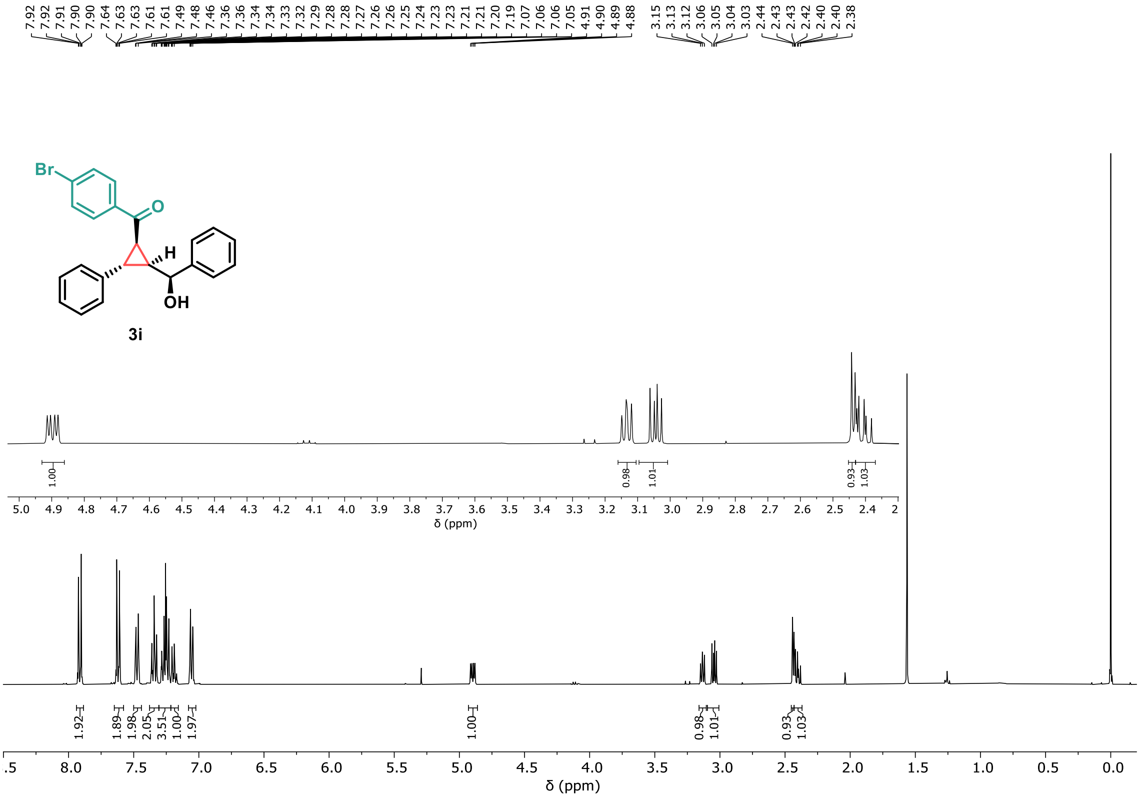


Figure S5: ^{1}H NMR spectra (400 MHz, CDCl$_3$) of compound **3i**.

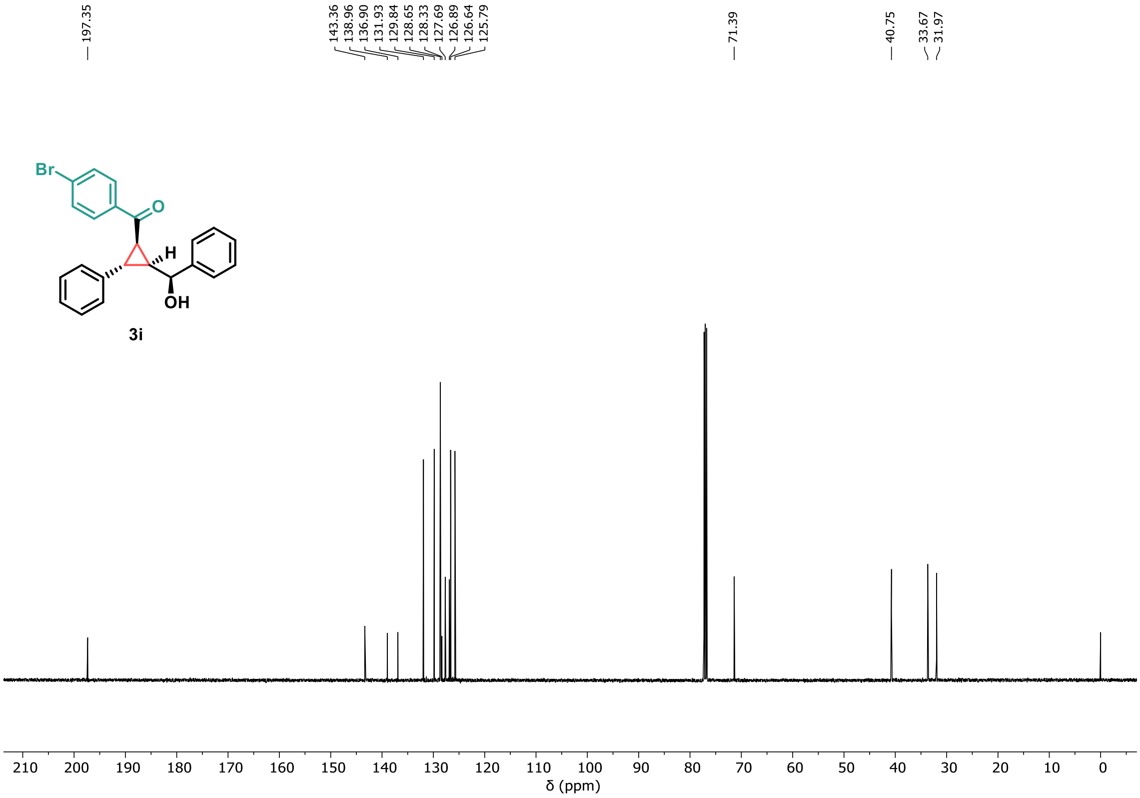


Figure S6: ^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **3i**.

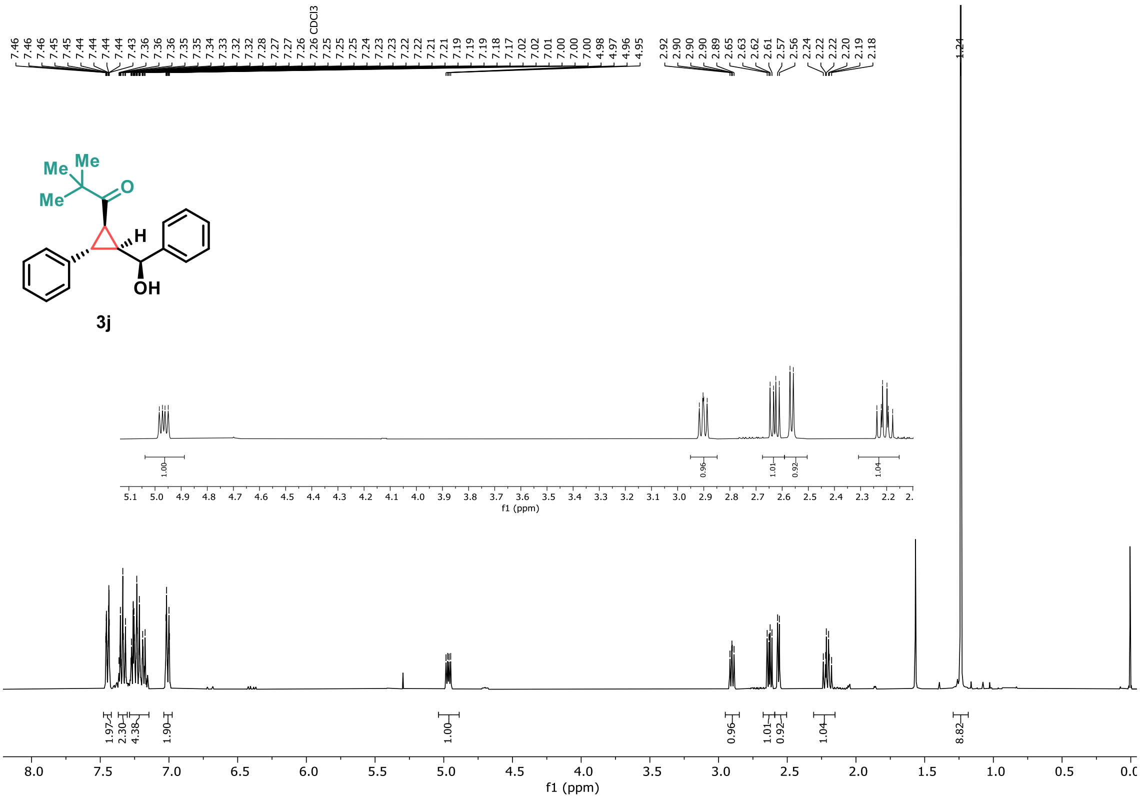


Figure S30: ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **3j**.

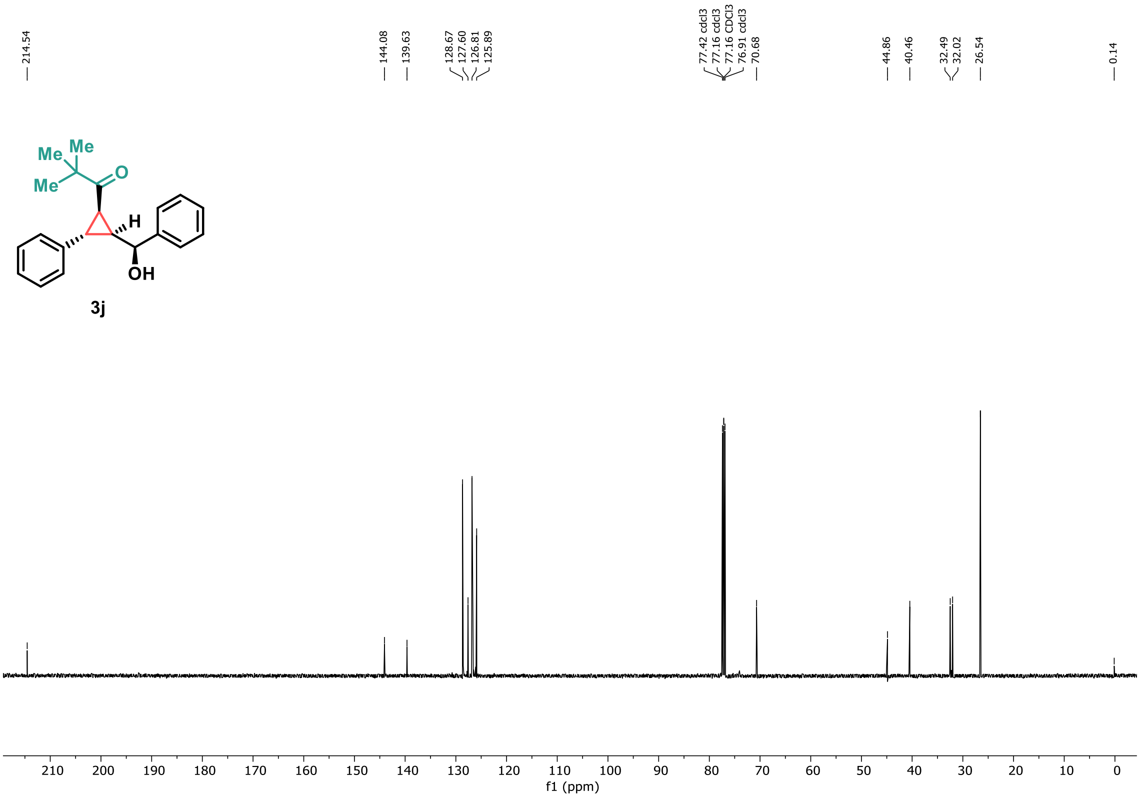


Figure S31: ^{13}C NMR spectra (101 MHz, CDCl$_3$) of compound **3j**.

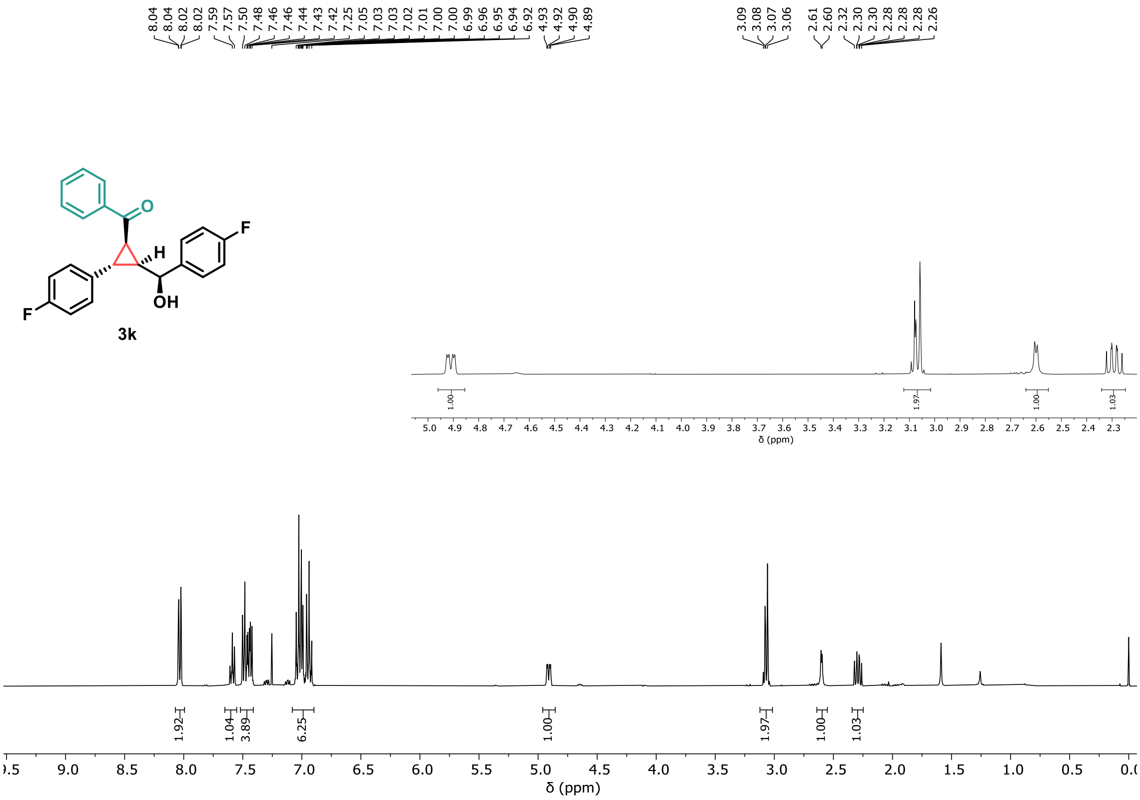


Figure S32: ^{1}H NMR spectra (400 MHz, CDCl$_3$) of compound **3k**.

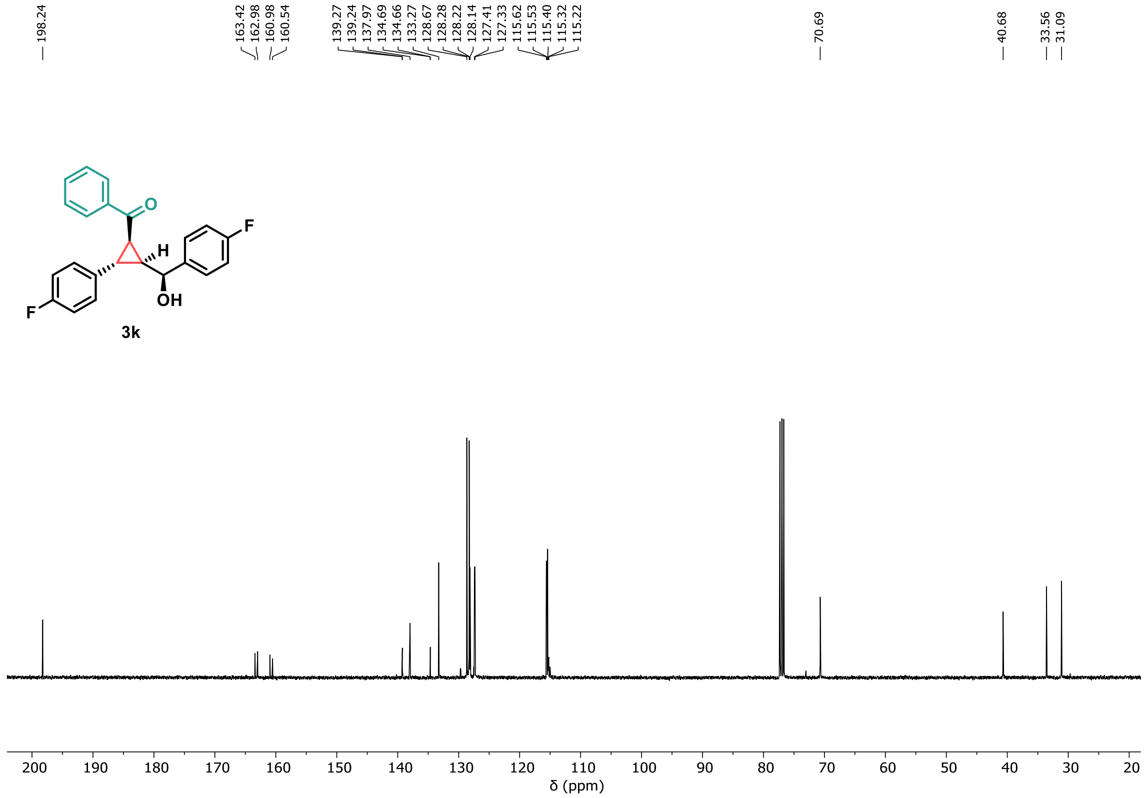


Figure S33: ^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **3k**.

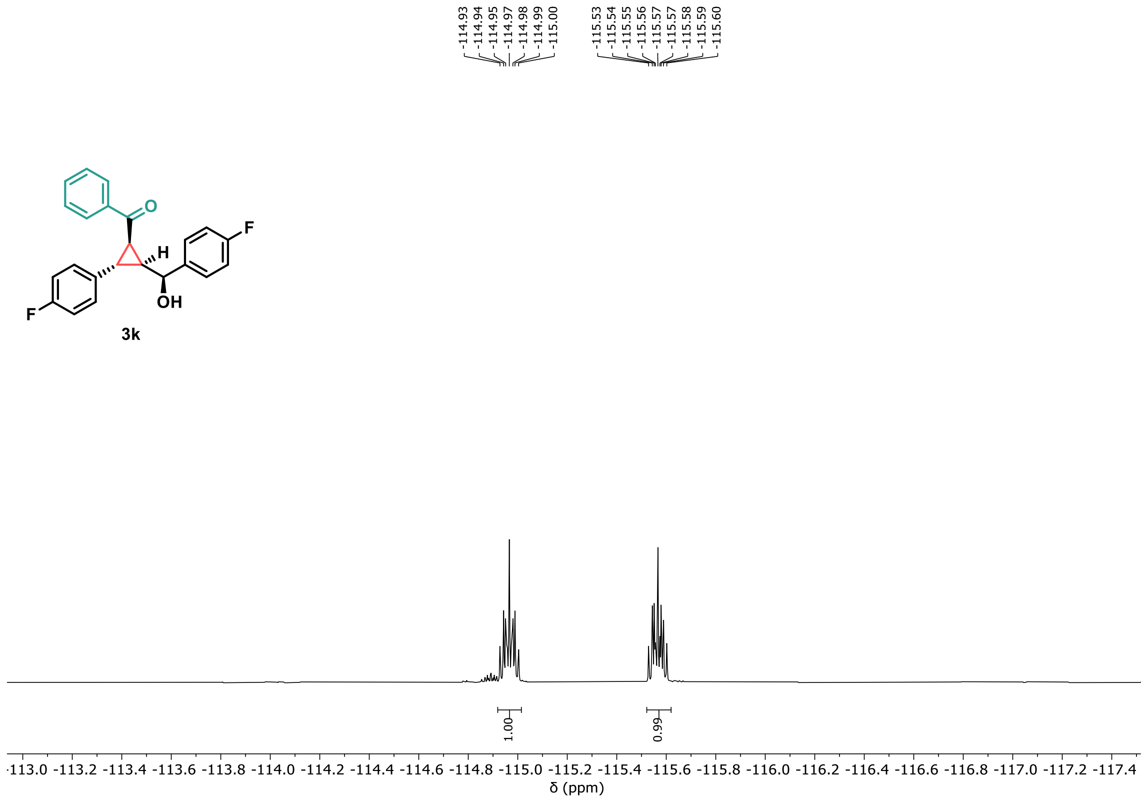


Figure S34: ^{19}F NMR spectra (376 MHz, $CDCl_3$) of compound **3k**.

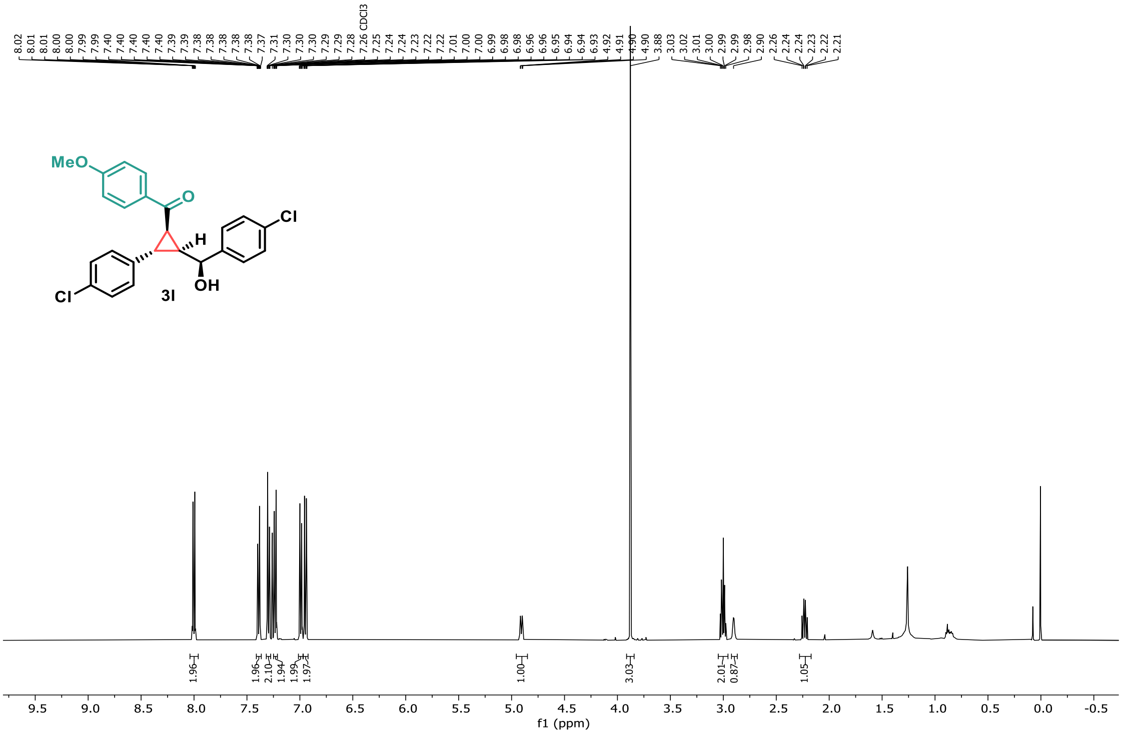


Figure S35: ^{1}H NMR spectra (500 MHz, $CDCl_3$) of compound **3l**.

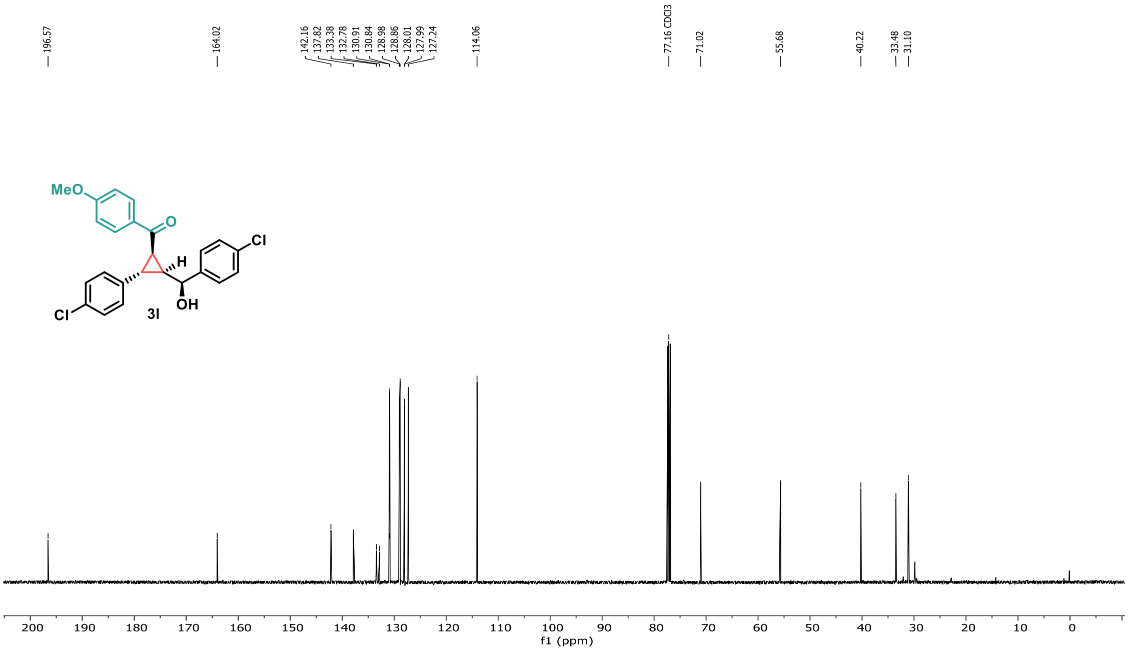


Figure S36: ^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **3l**.

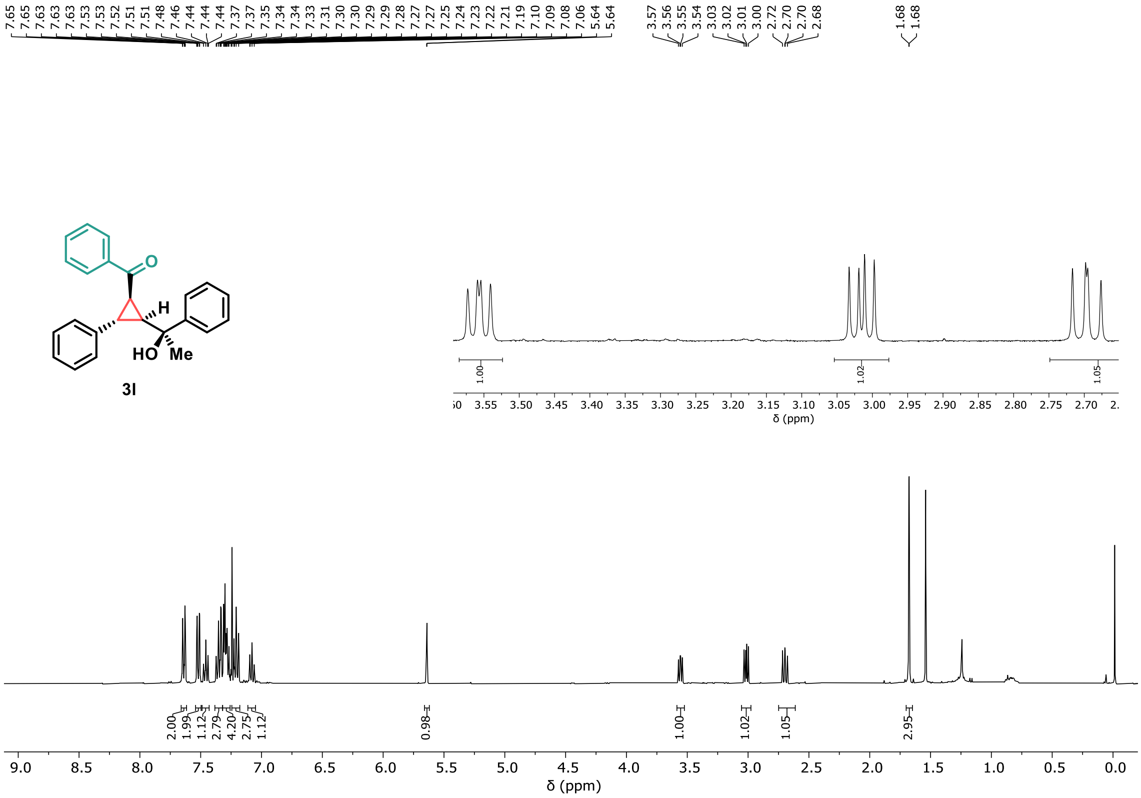


Figure S37: ^{1}H NMR spectra (400 MHz, CDCl$_3$) of compound **3m**.

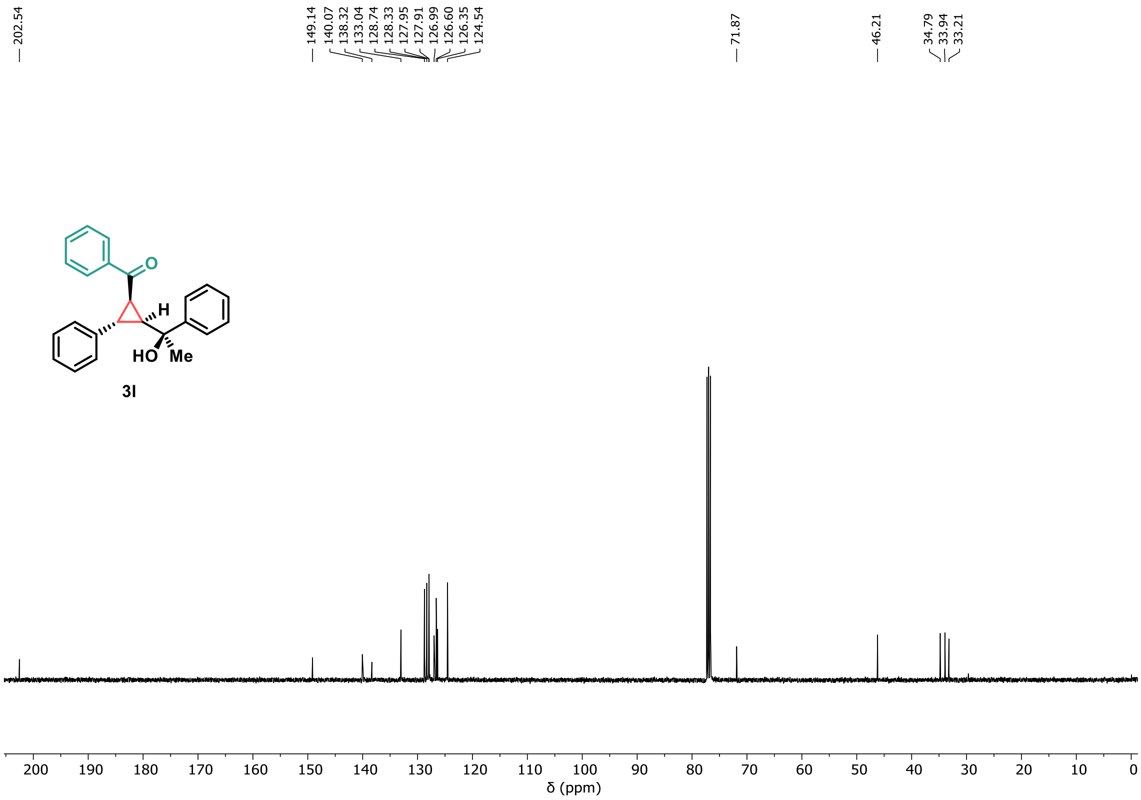


Figure S38: ^{13}C NMR spectra (101 MHz, CDCl$_3$) of compound **3m**.

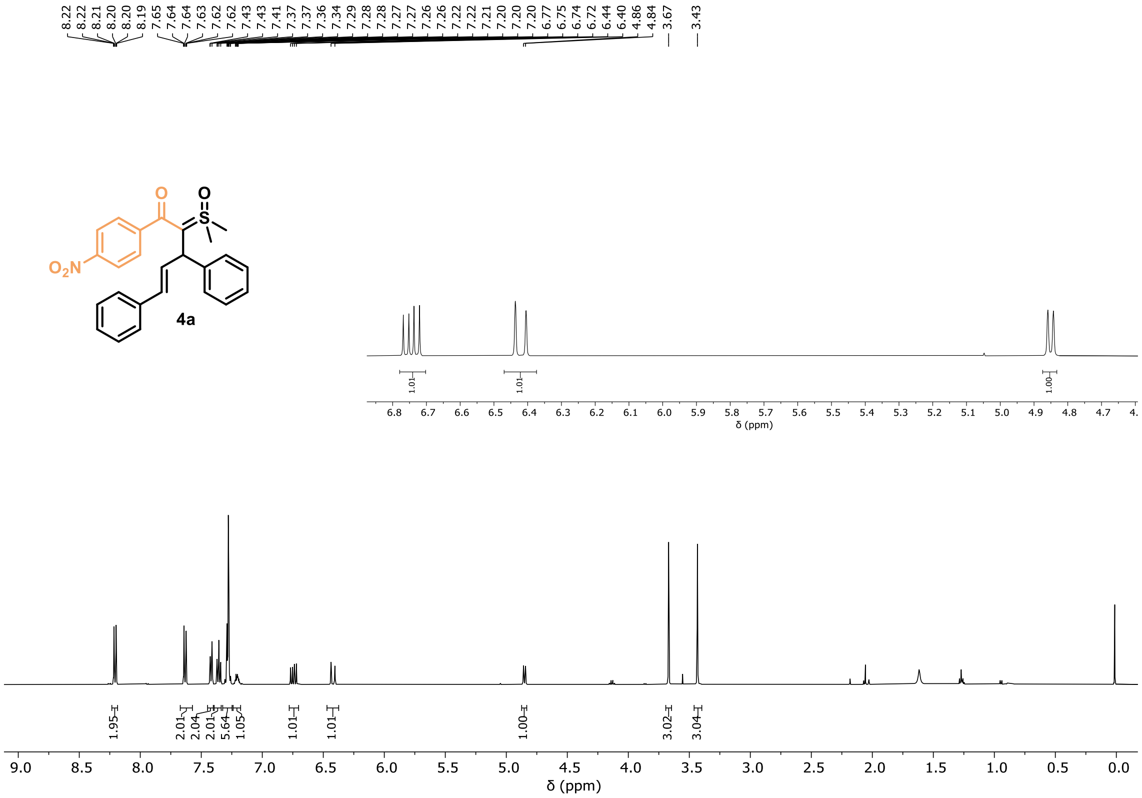


Figure S7: ^{1}H NMR spectra (500 MHz, CDCl$_3$) of compound **4a**.

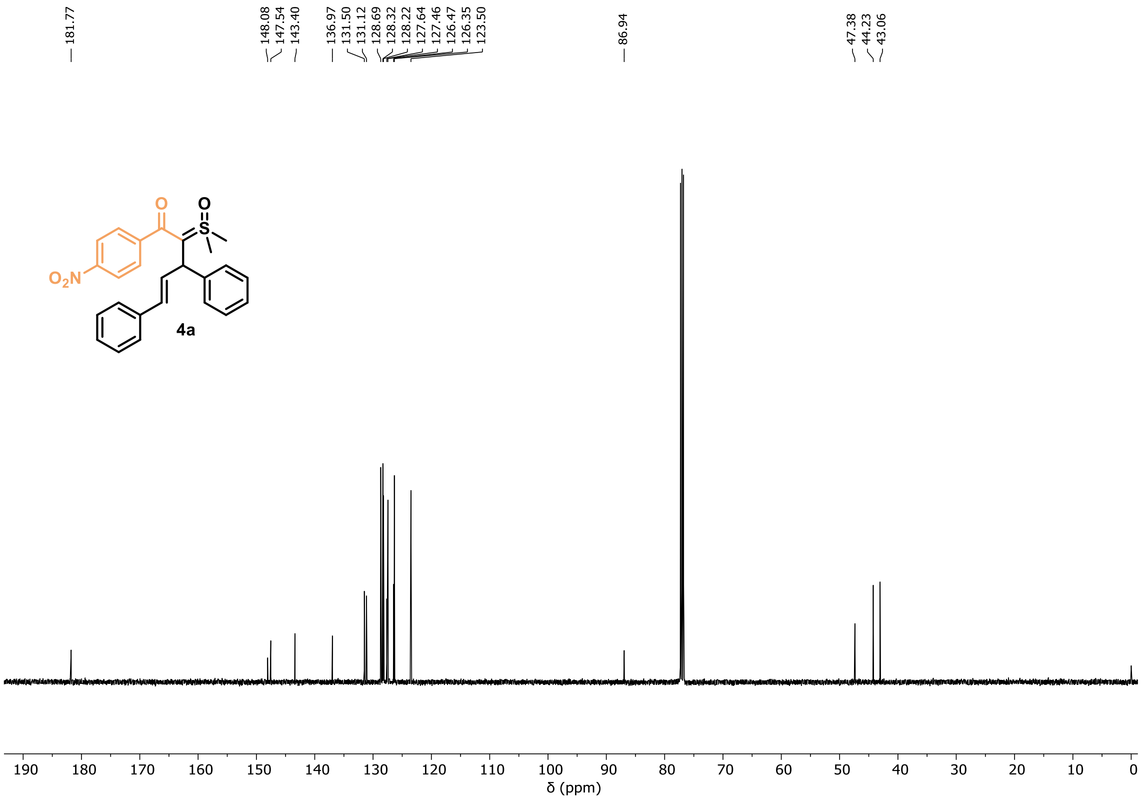


Figure S40: ^{13}C NMR spectra (126 MHz, CDCl$_3$) of compound **4a**.

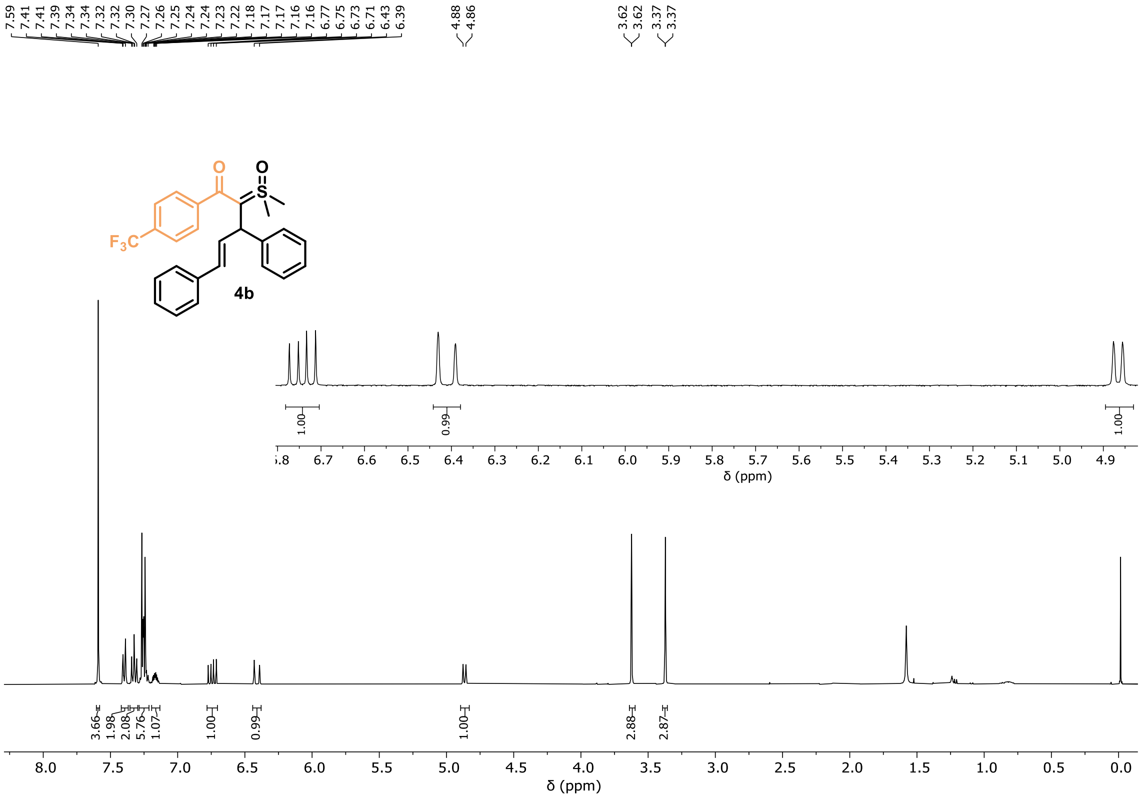


Figure S41: ^1H NMR spectra (400 MHz, $CDCl_3$) of compound **4b**.

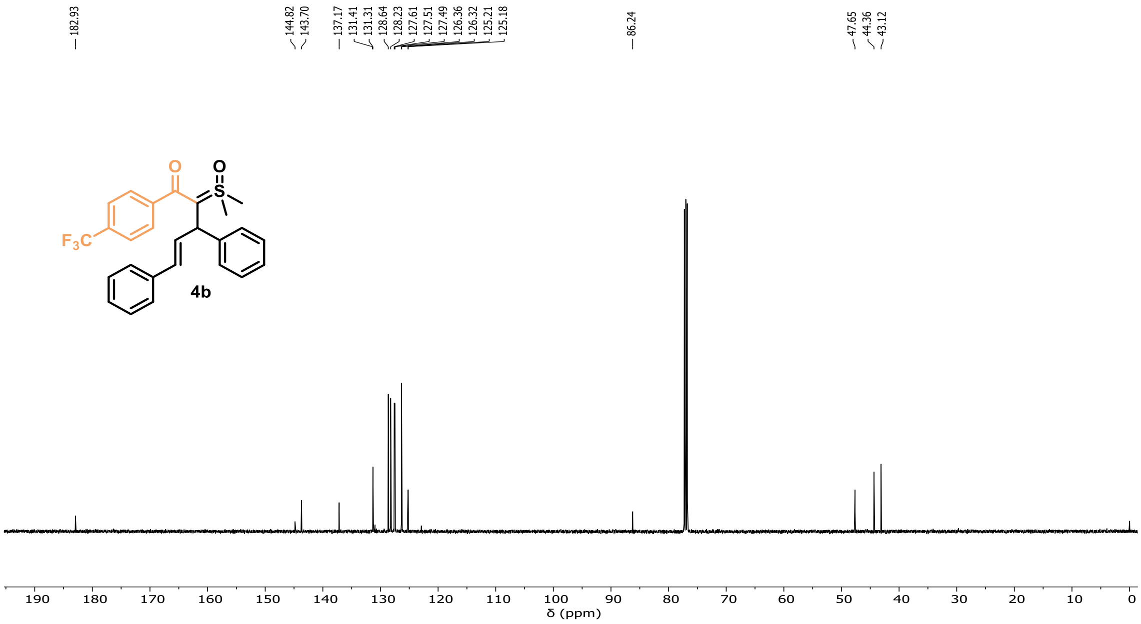


Figure S42: ^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **4b**.

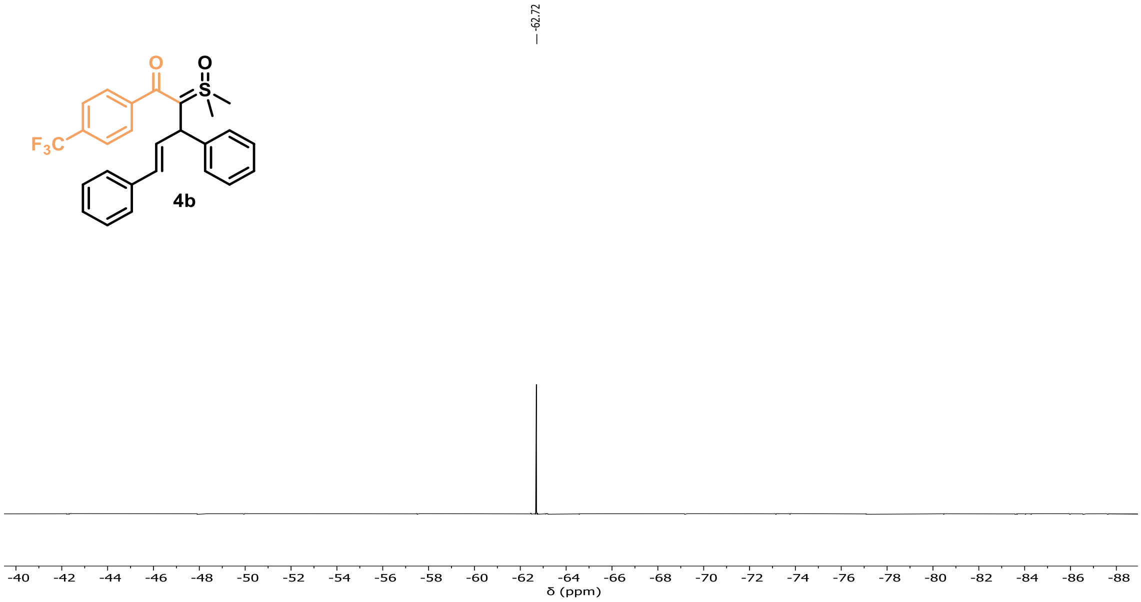


Figure S43: ^{19}F NMR spectra (376 MHz, $CDCl_3$) of compound **4b**.

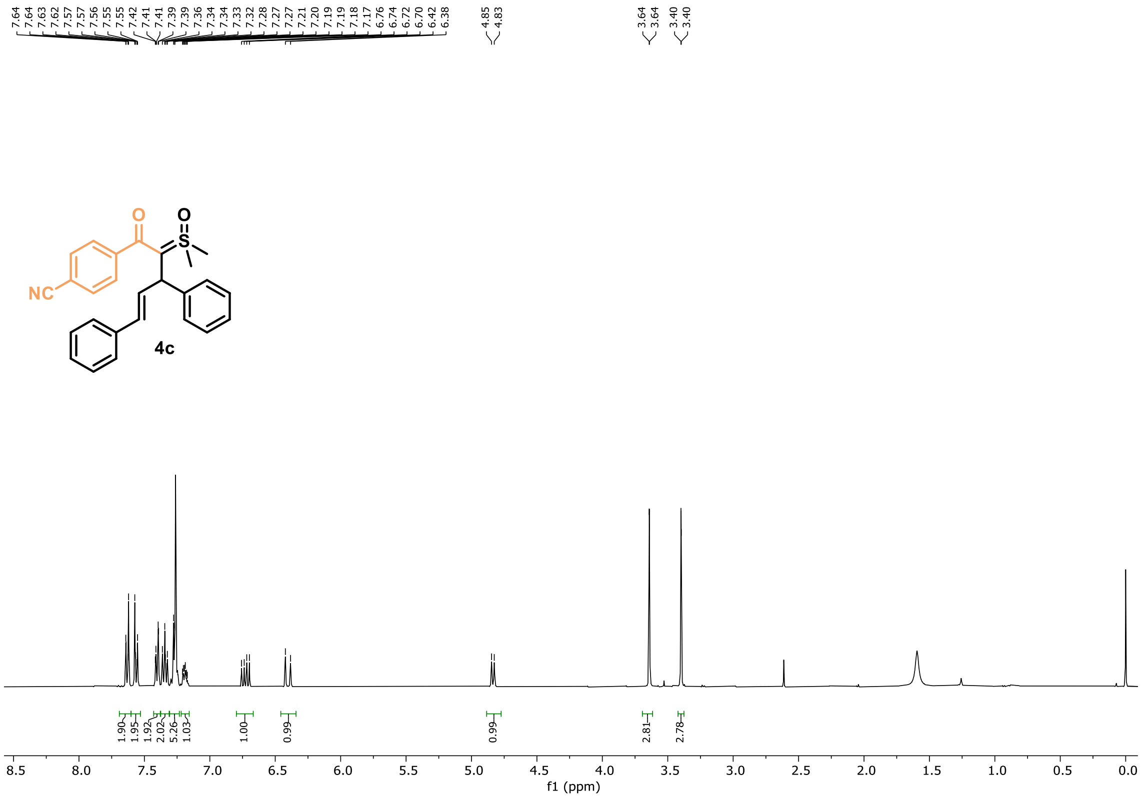


Figure S44: ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **4c**.

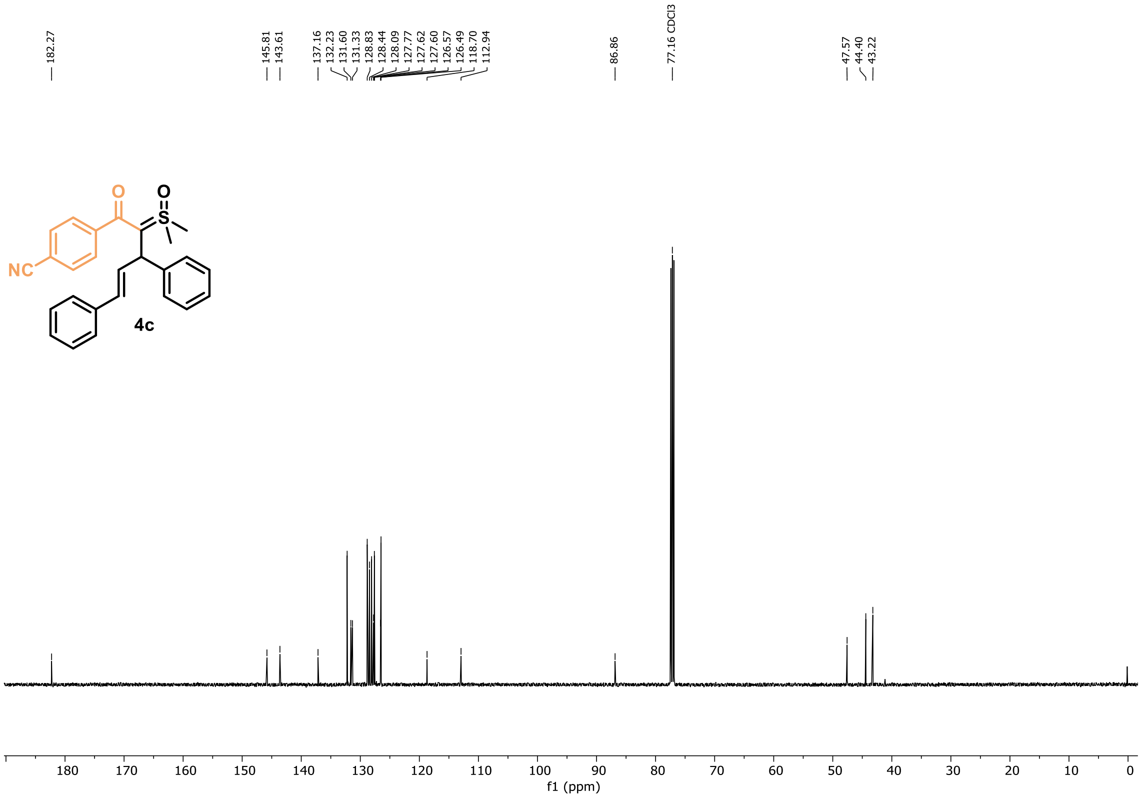


Figure S45: ^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **4c**.

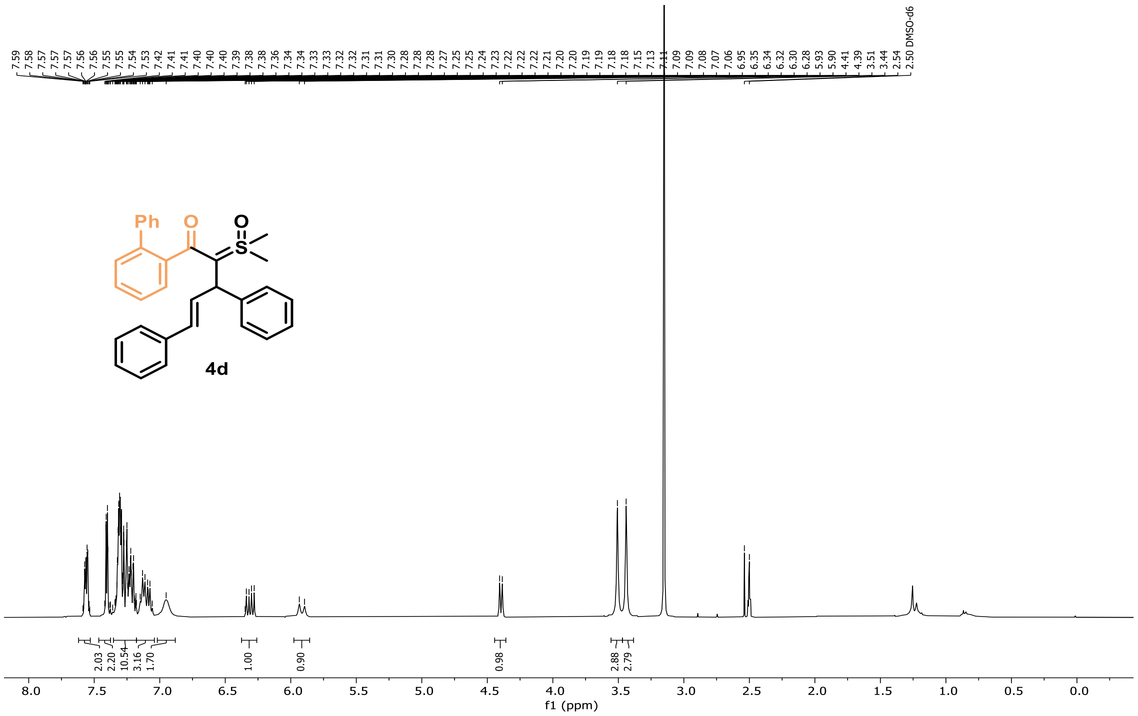


Figure S46: ^{1}H NMR spectra (400 MHz, DMSO-d_6, 60 °C) of compound **4d**

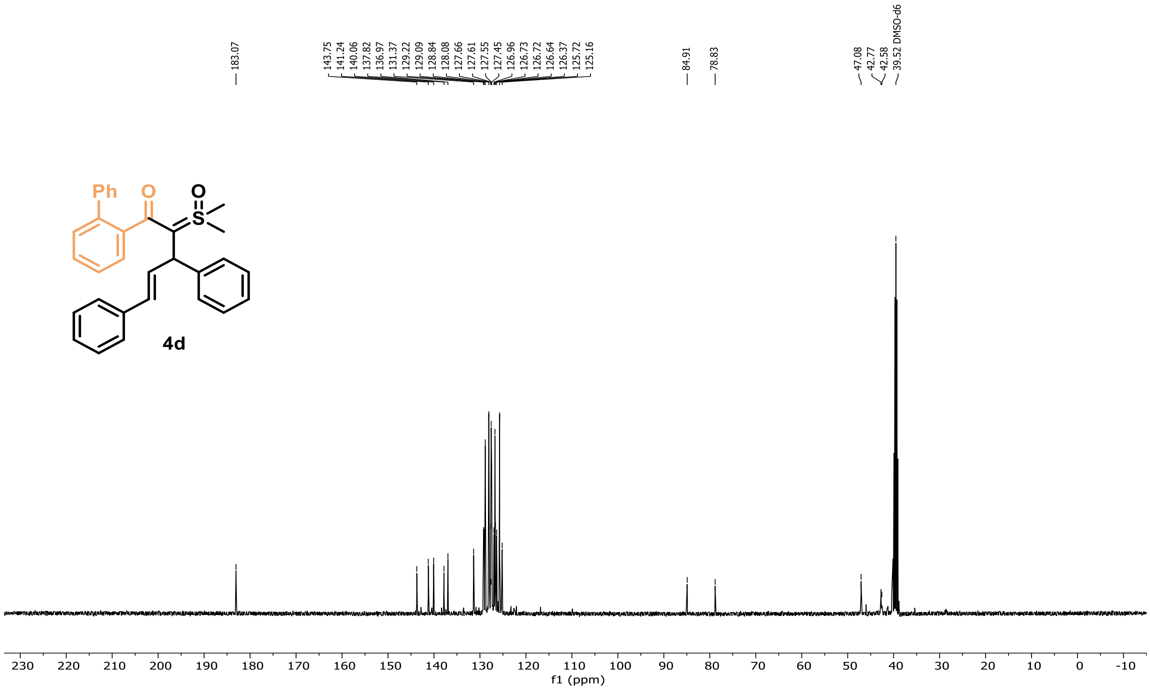


Figure S47: ^{13}C NMR spectra (101 MHz, DMSO-d$_6$, 60 °C) of compound **4d**

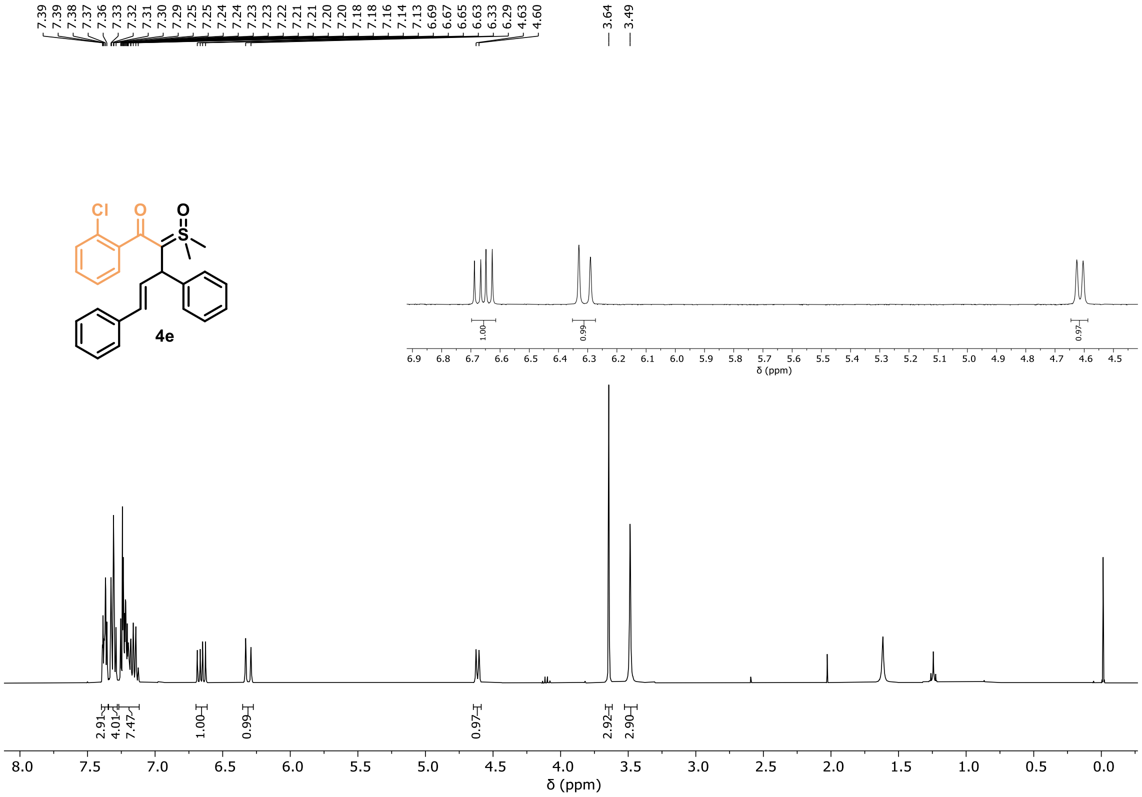


Figure S48: ^{1}H NMR spectra (400 MHz, CDCl$_3$) of compound **4e**.

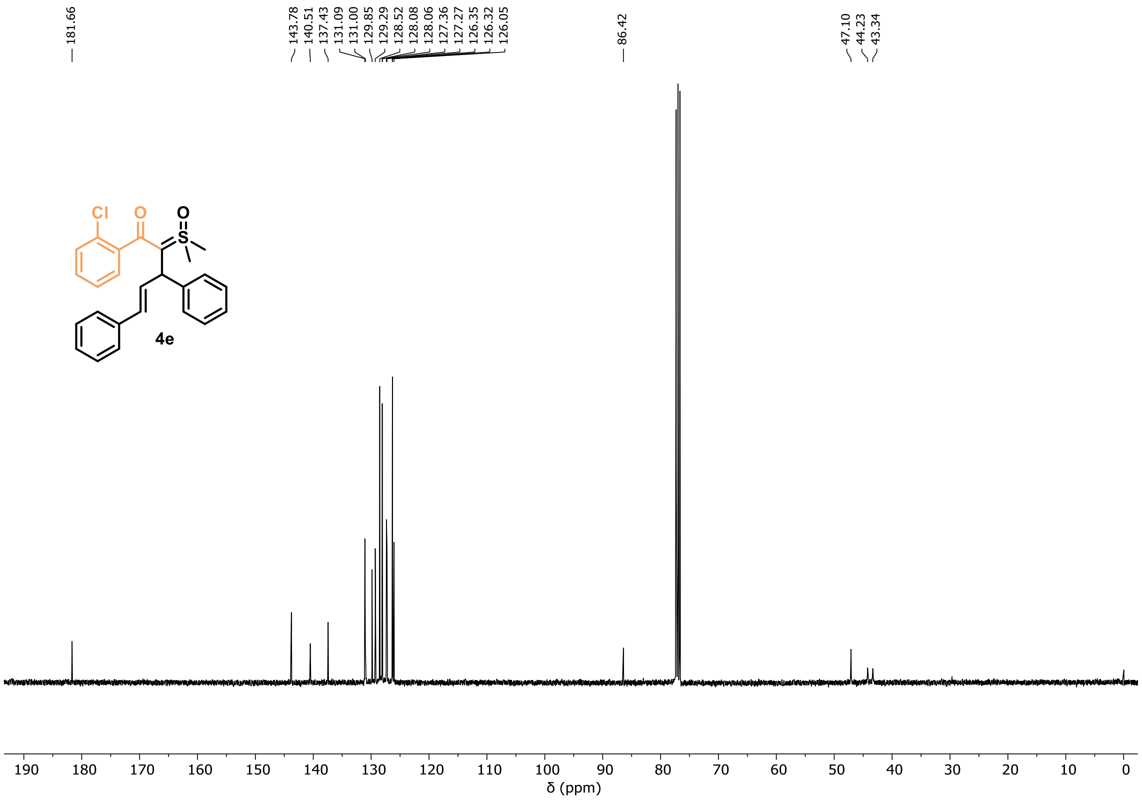


Figure S49: ^{13}C NMR spectra (126 MHz, CDCl$_3$) of compound **4e**.

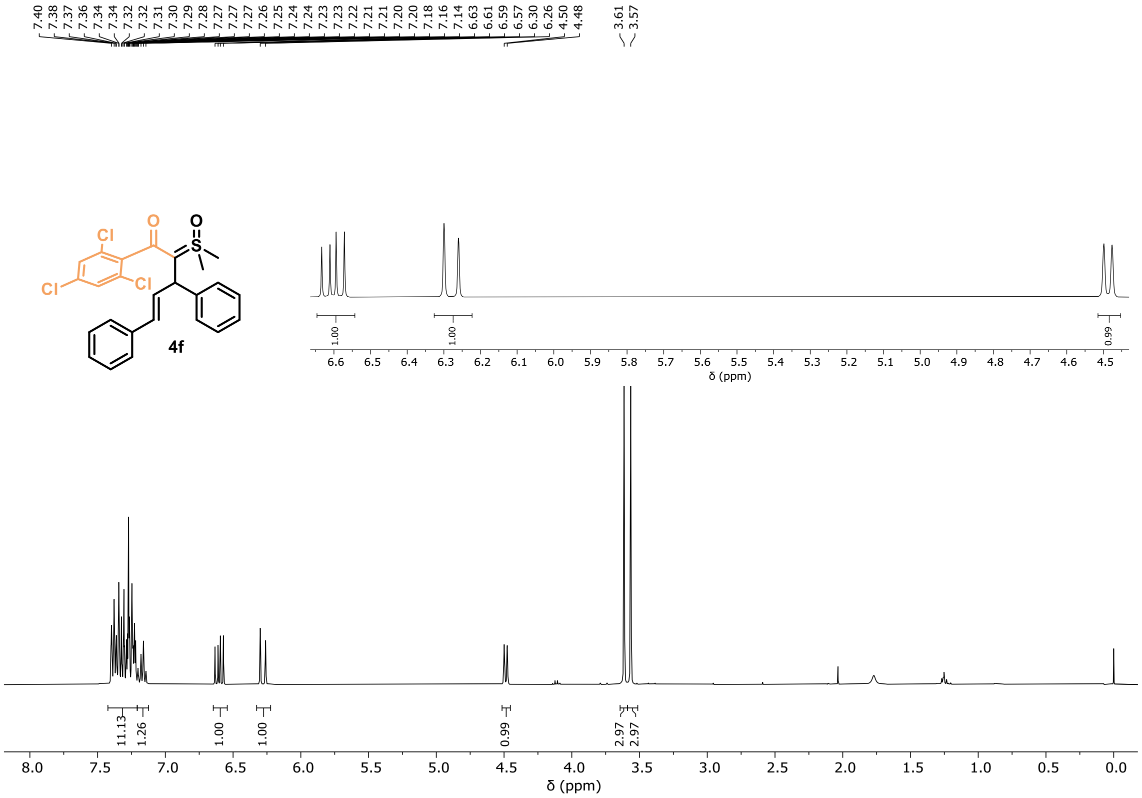


Figure S50: ^{1}H NMR spectra (400 MHz, CDCl$_3$) of compound **4f**.

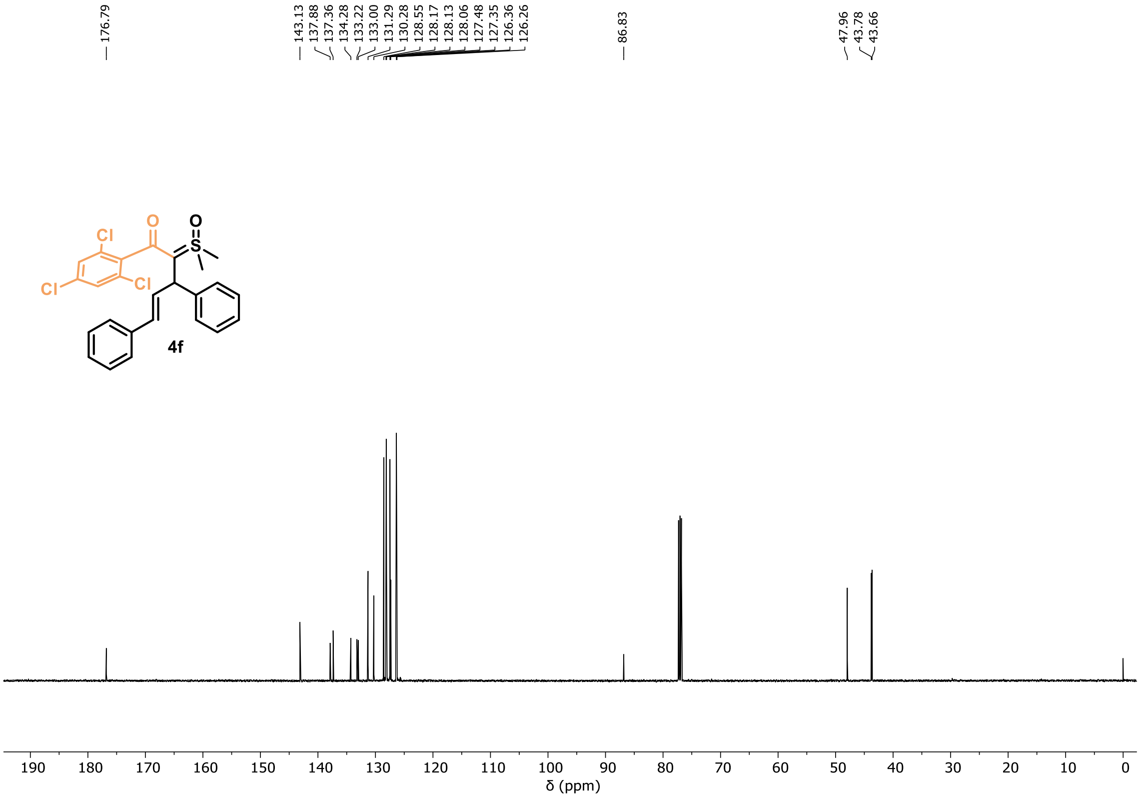


Figure S51: ^{13}C NMR spectra (126 MHz, CDCl3) of compound **4f**.

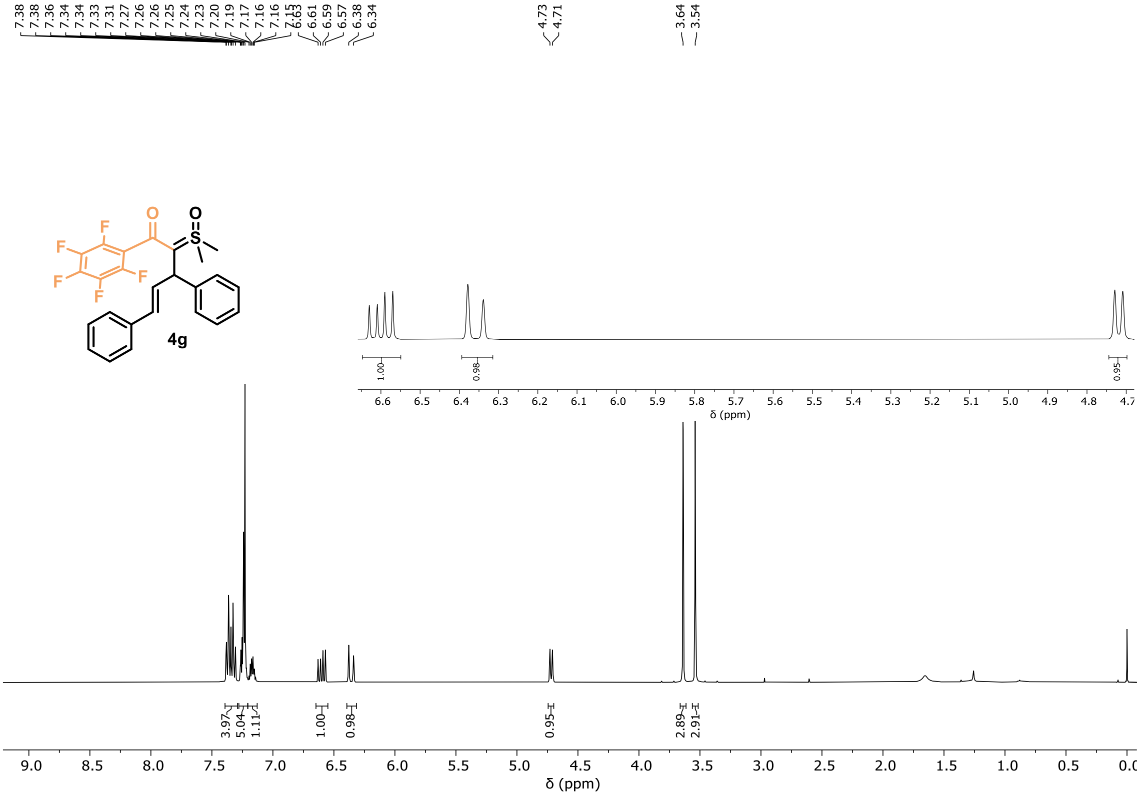


Figure S52: ^{1}H NMR spectra (400 MHz, CDCl3) of compound **4g**.

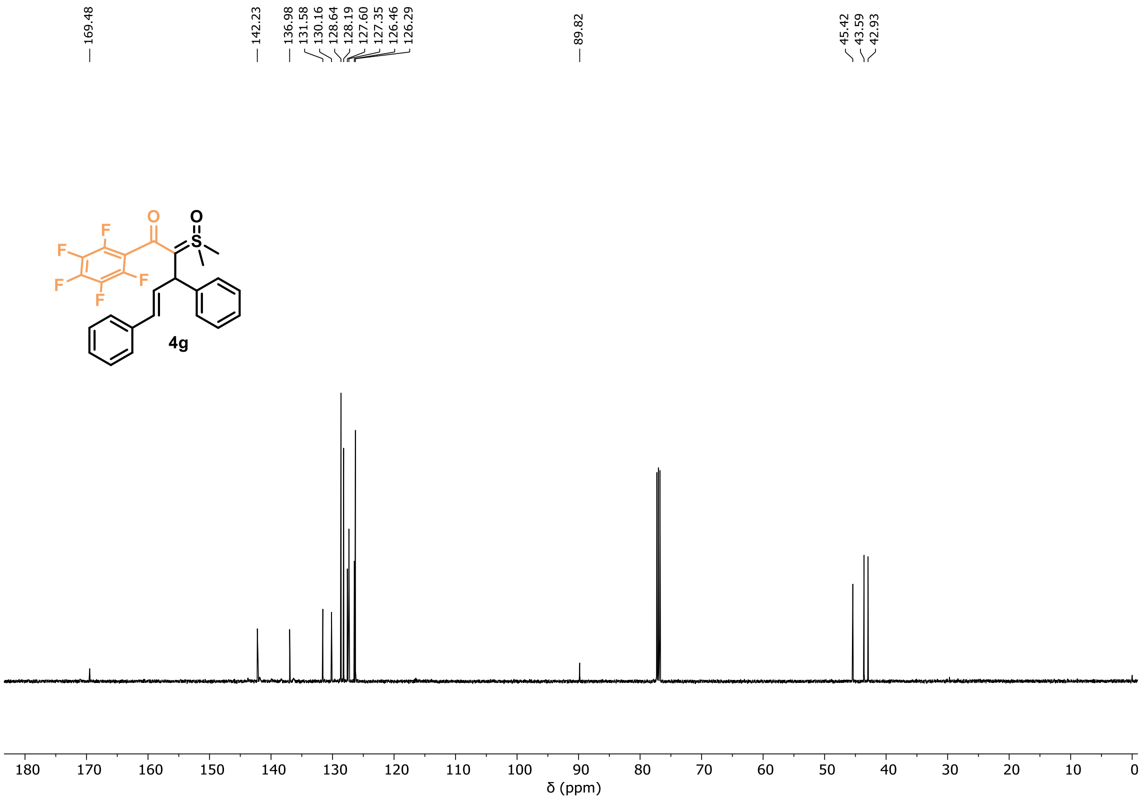


Figure S53: ^{13}C NMR spectra (126 MHz, CDCl$_3$) of compound **4g**.

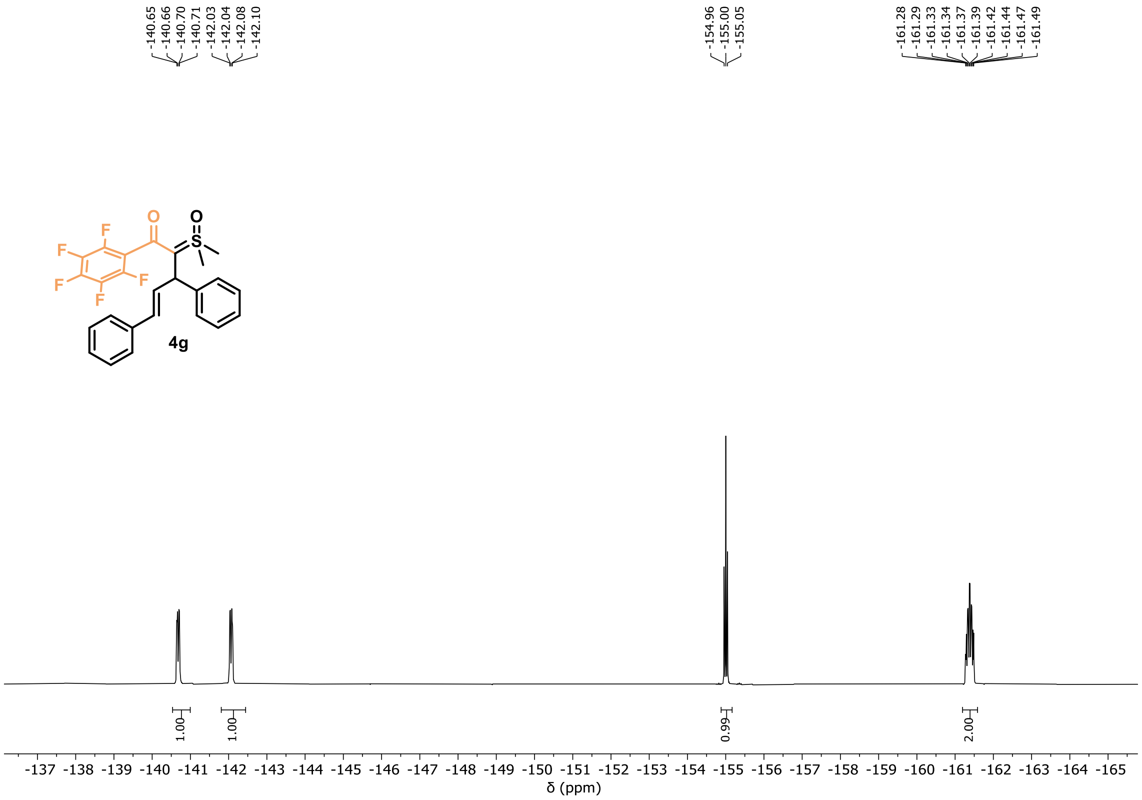


Figure S54: ^{19}F NMR spectra (470 MHz, CDCl$_3$) of compound **4g**.

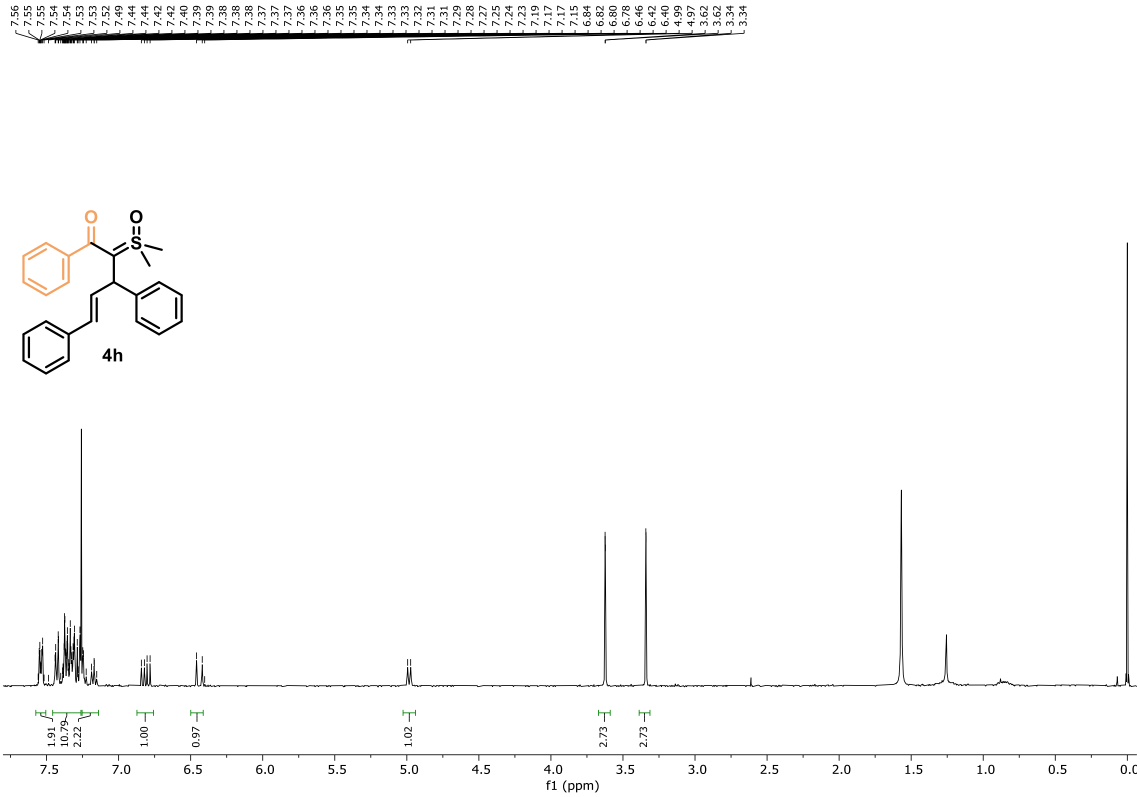


Figure S55: ^{1}H NMR spectra (400 MHz, CDCl$_3$) of compound **4h**

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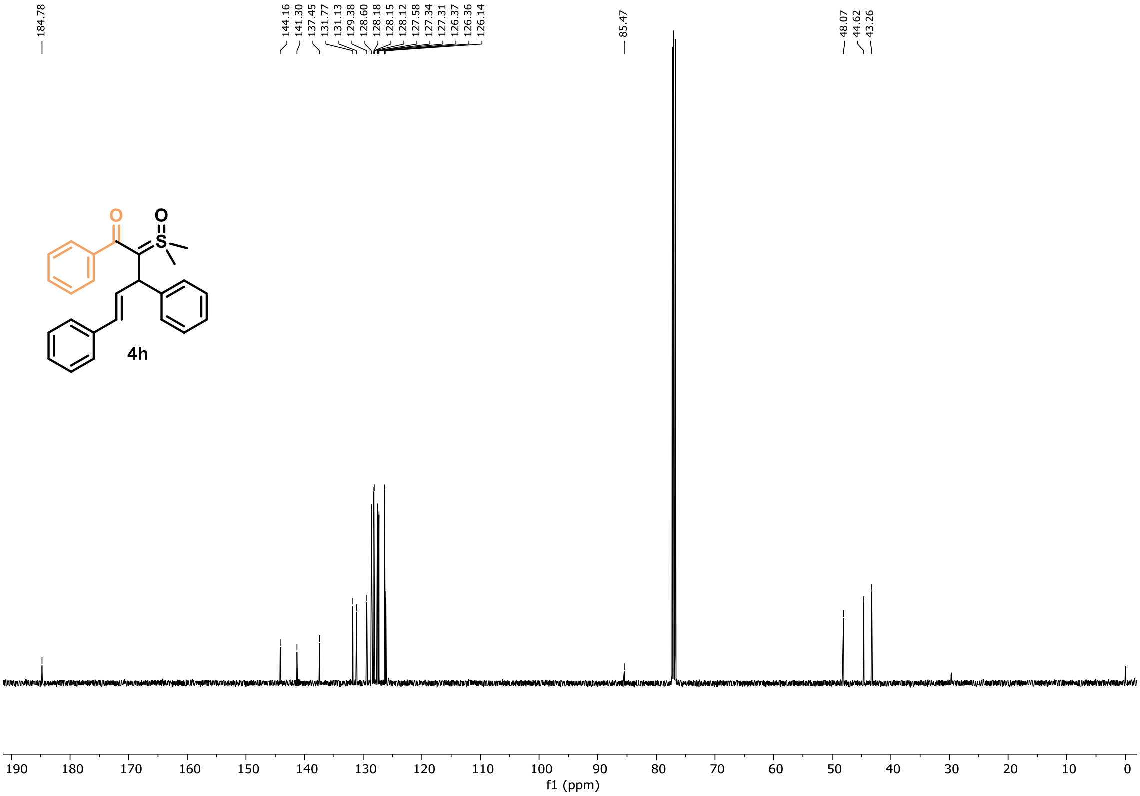

Figure S56: ^{13}C NMR spectra (126 MHz, CDCl$_3$) of compound **4h**.

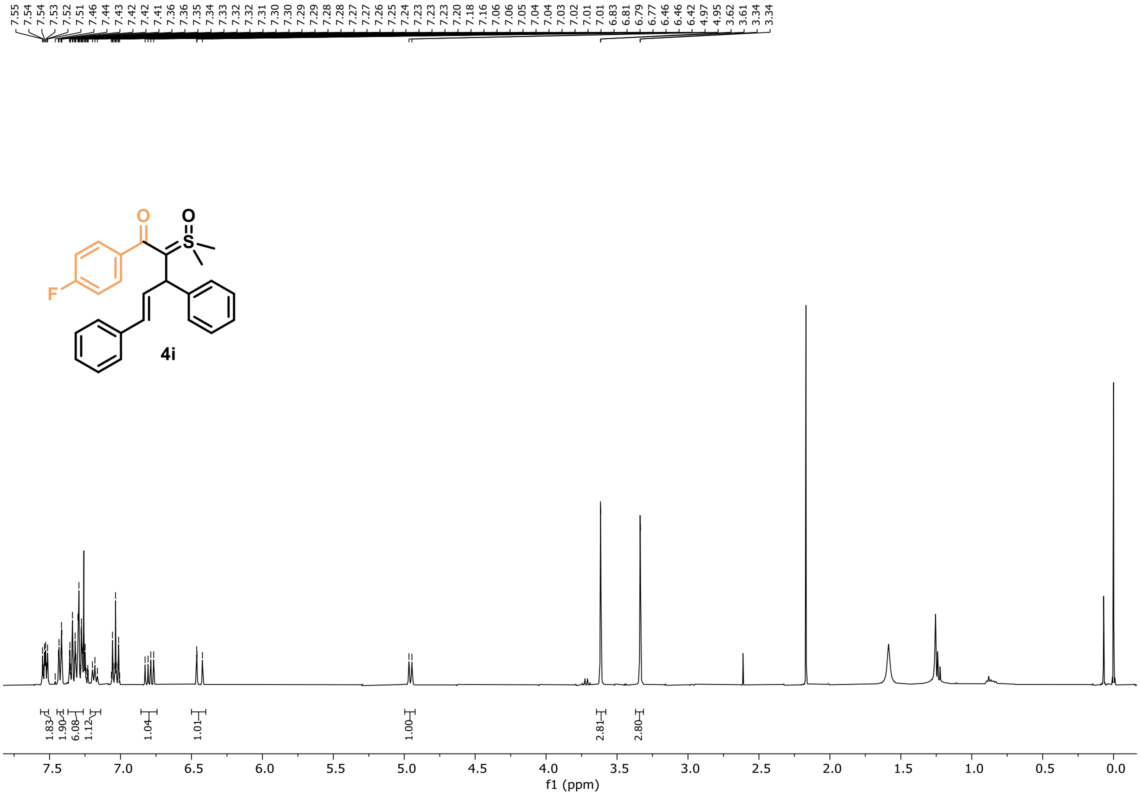

Figure S57: ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **4i**.

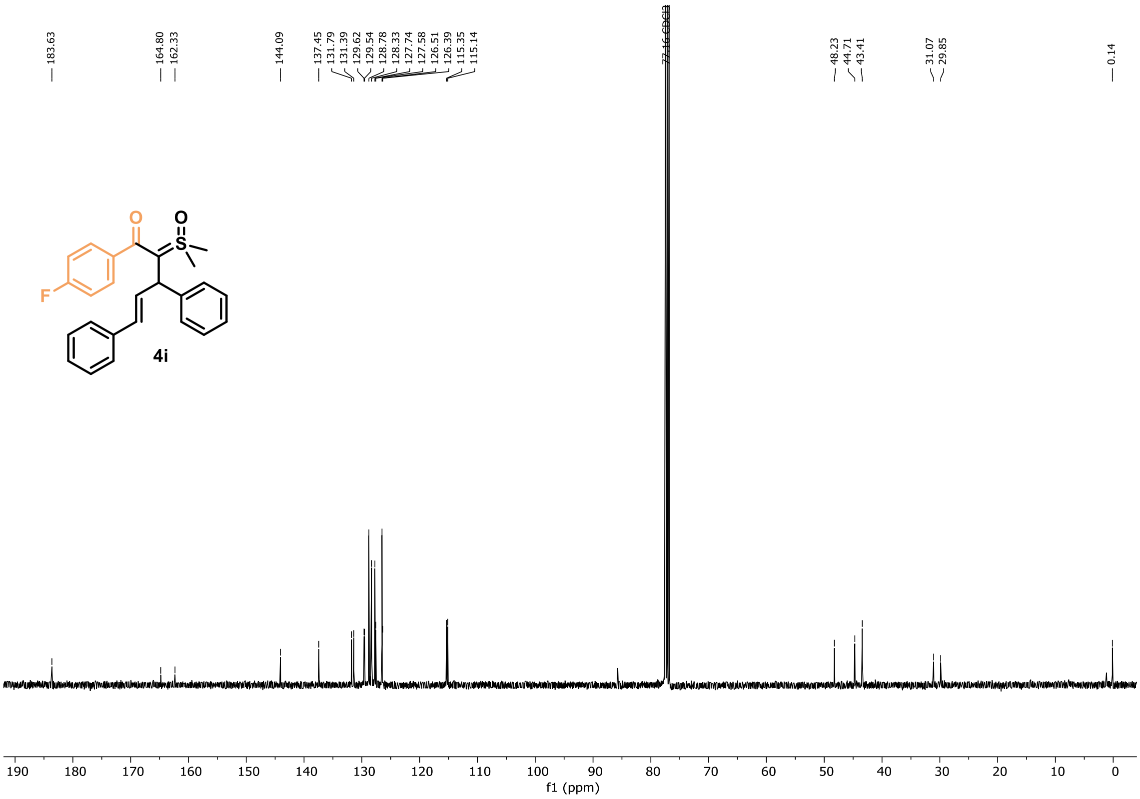

Figure S58: ^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **4i**.

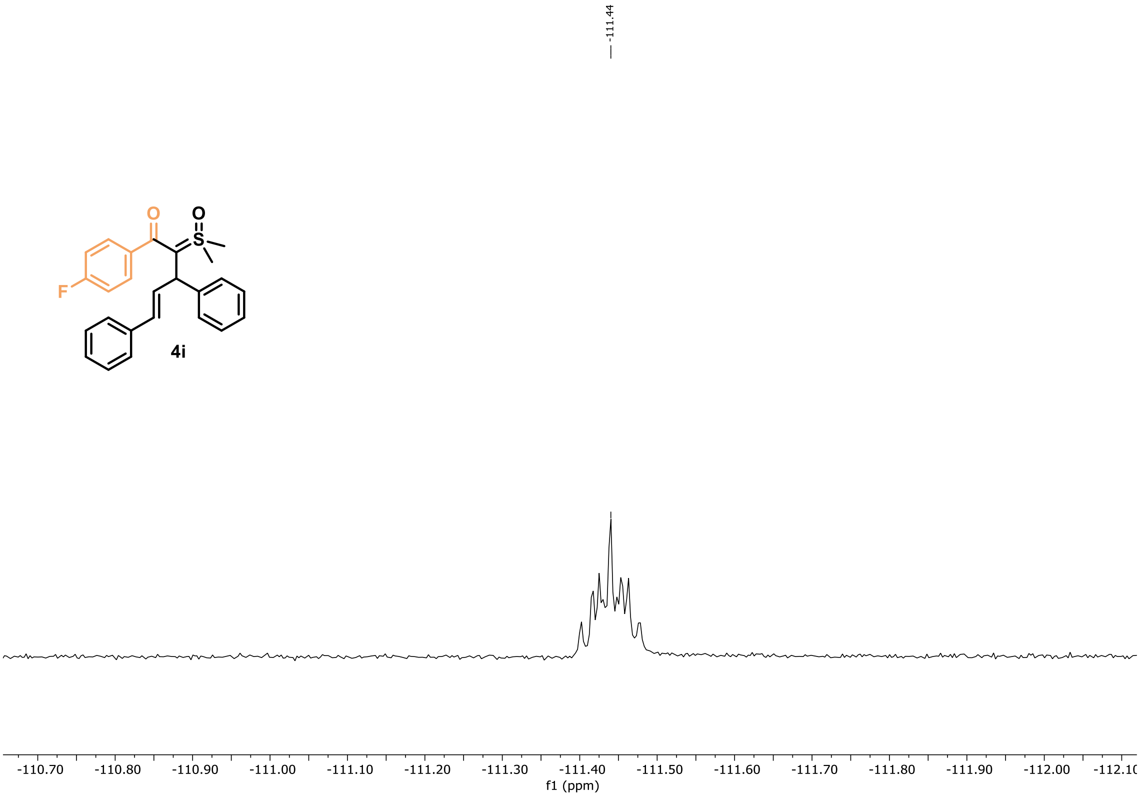

Figure S59: ^{19}F NMR spectra (376 MHz, CDCl$_3$) of compound **4i**.

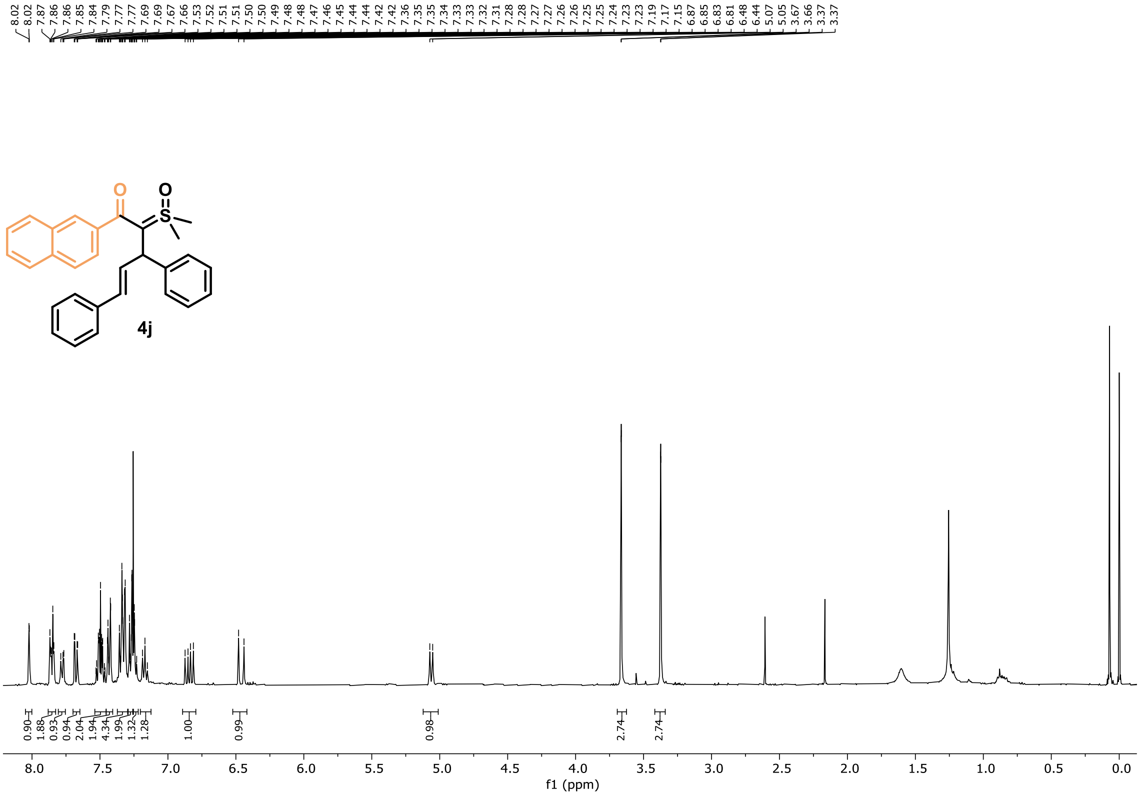

Figure S60: ^{1}H NMR spectra (400 MHz, CDCl$_3$) of compound **4j.**

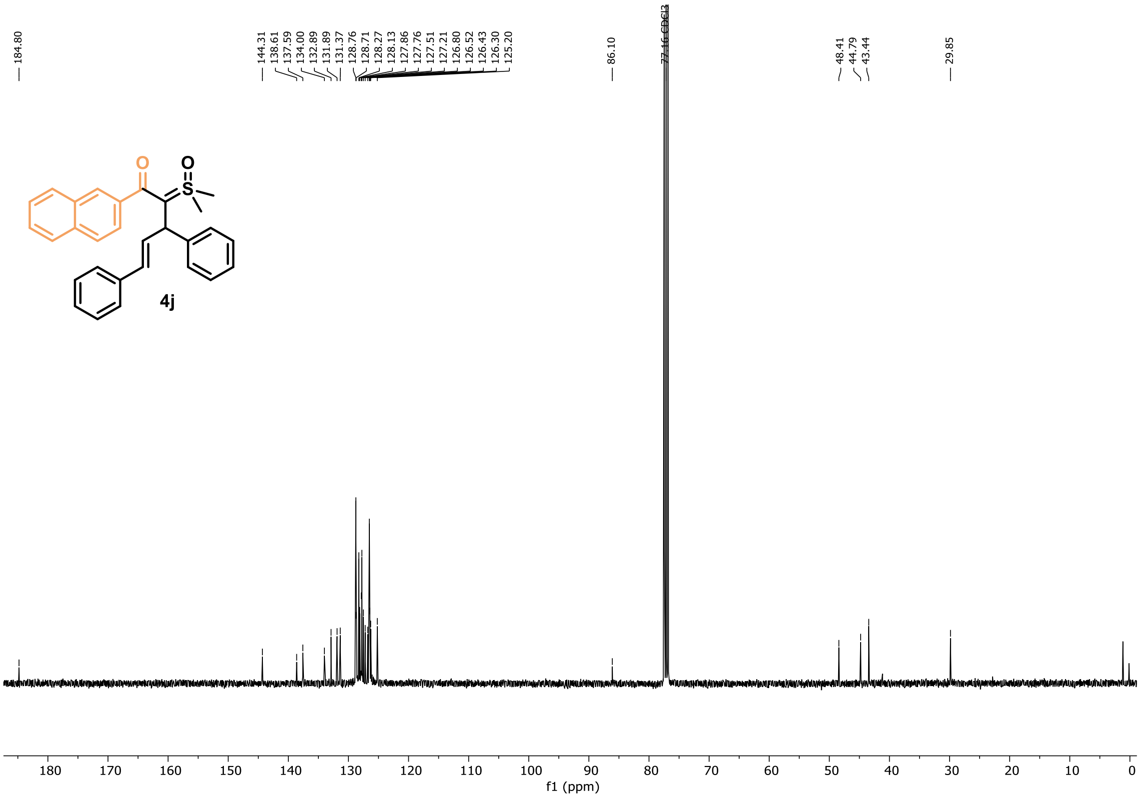

Figure S61: ^{13}C NMR spectra (101 MHz, CDCl$_3$) of compound **4j**.-

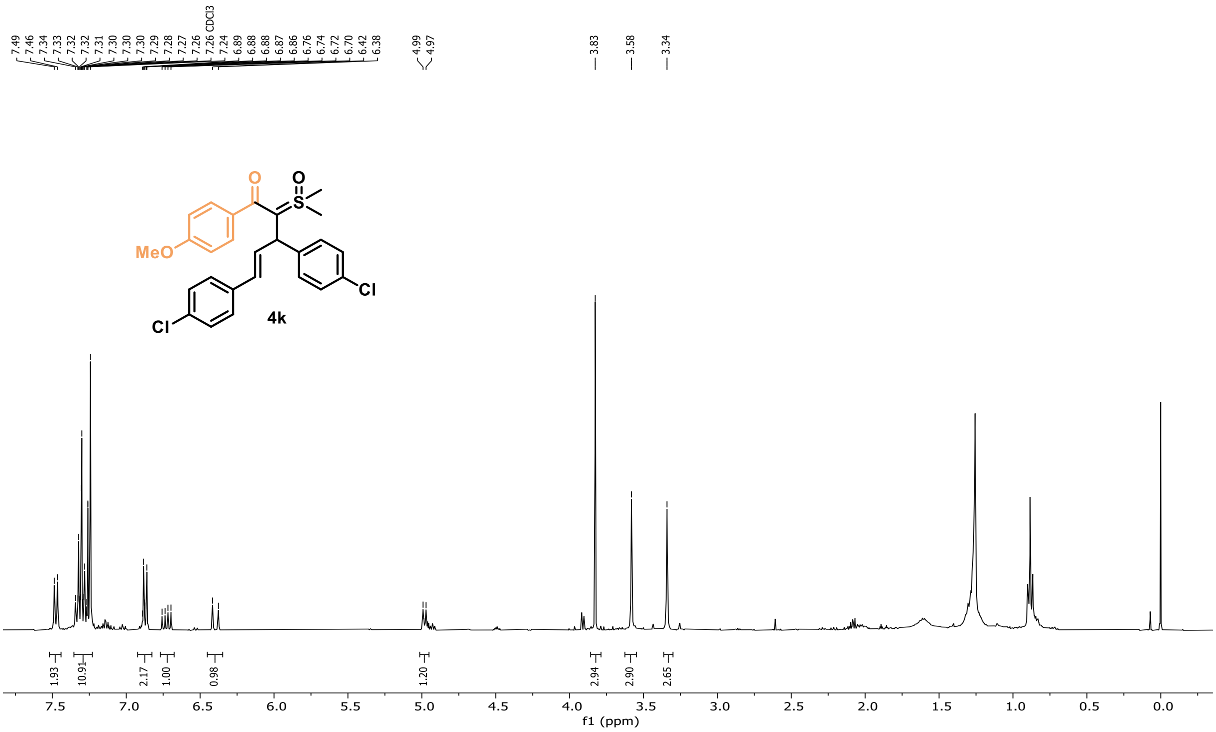

Figure S62: ^{1}H NMR spectra (400 MHz, CDCl$_3$) of compound **4k**

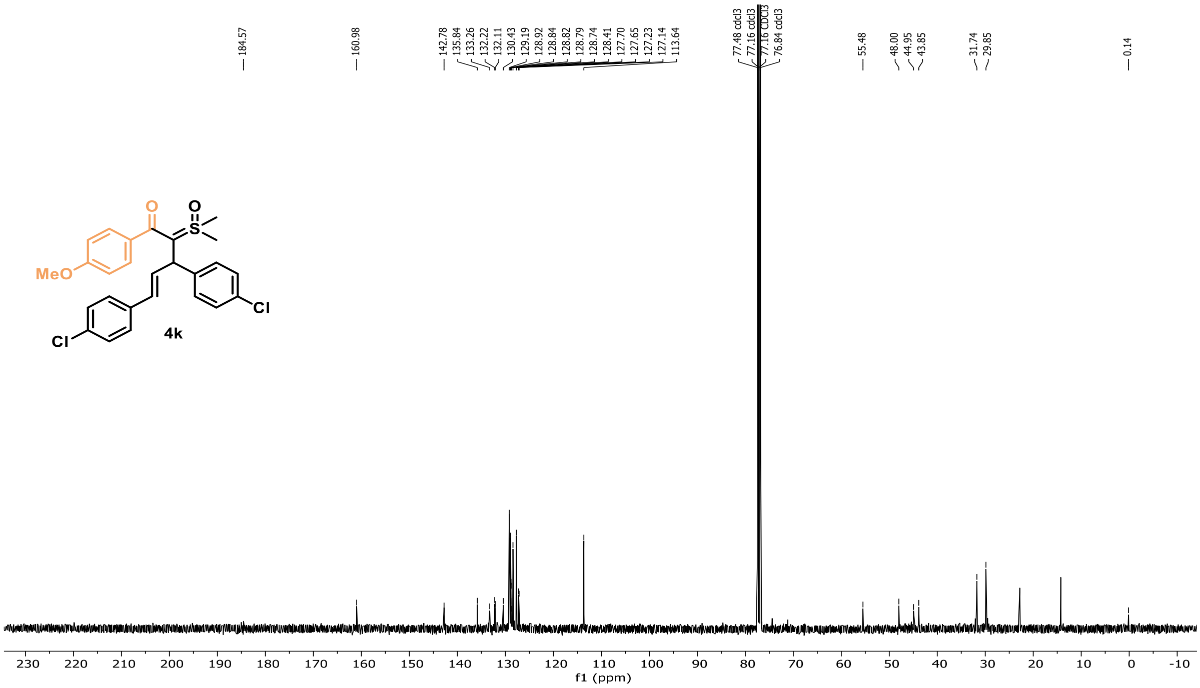

Figure S63: ^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **4k**.-

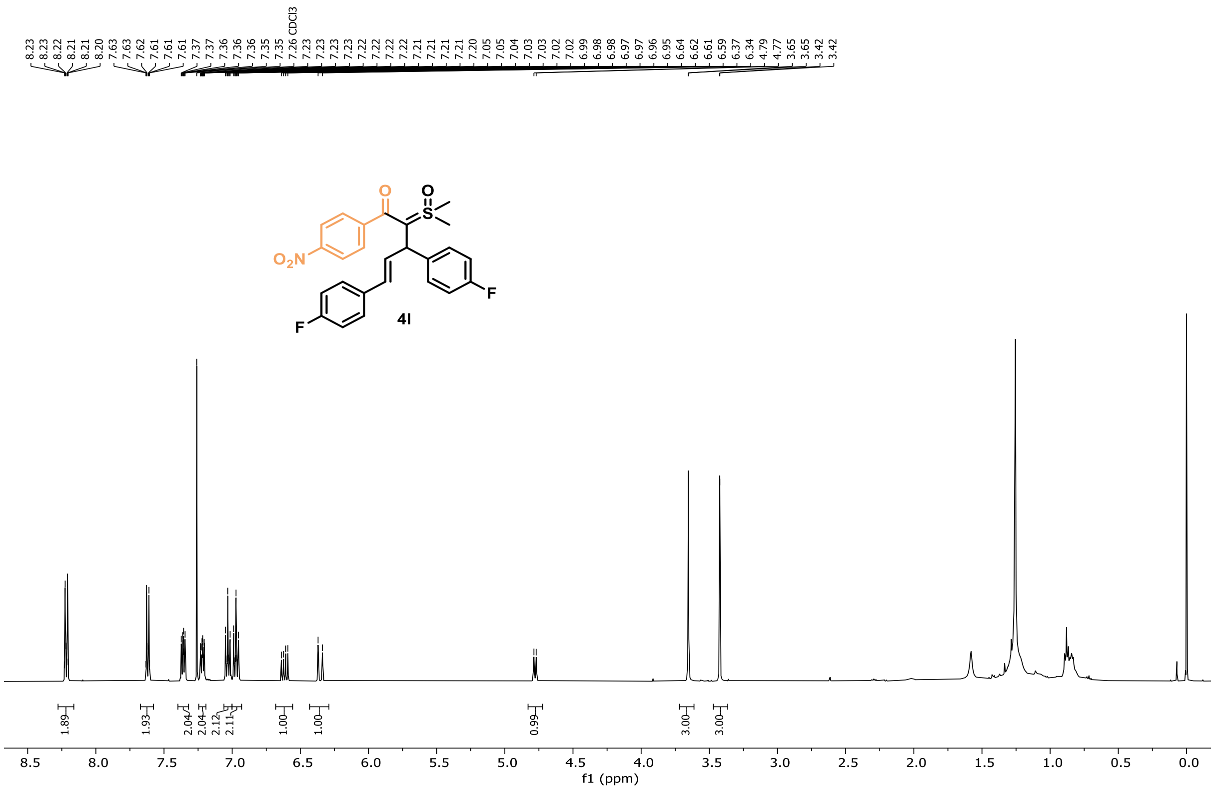

Figure S64: ^{1}H NMR spectra (500 MHz, $CDCl_3$) of compound **4l**

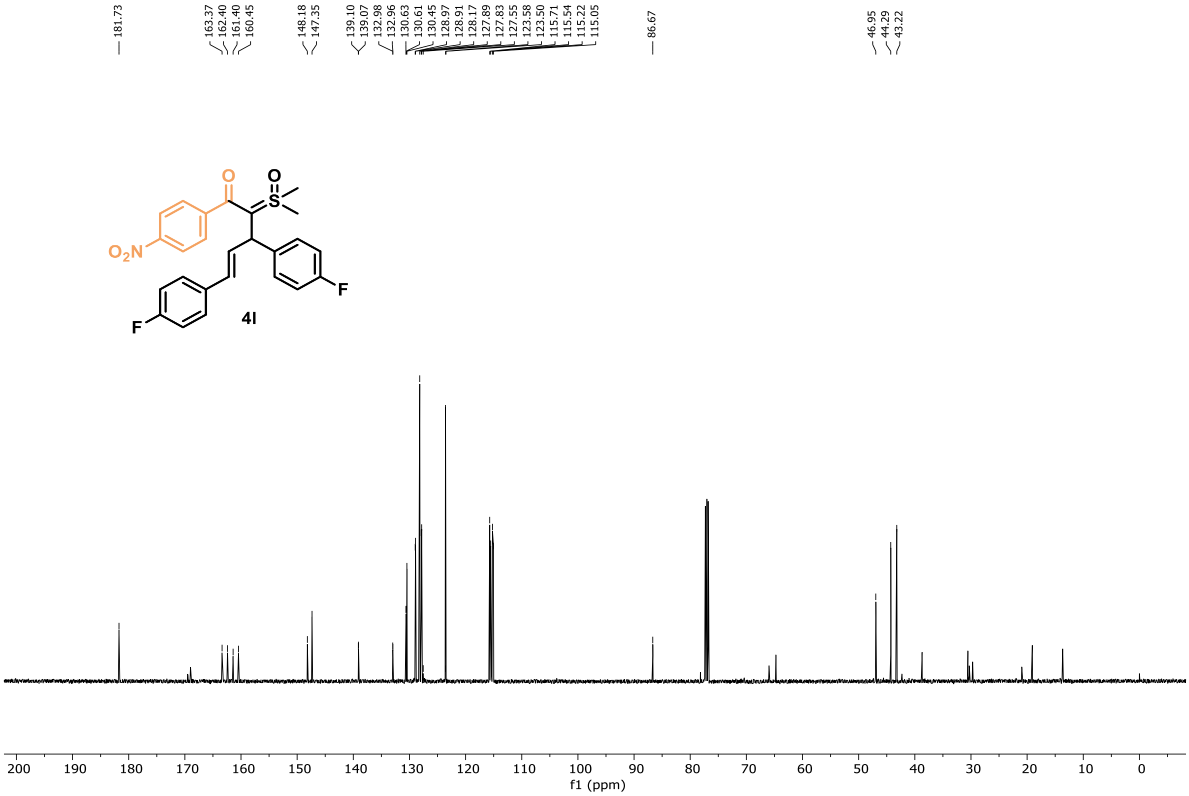

Figure S65: ^{13}C NMR spectra (126 MHz, CDCl$_3$) of compound **4l**.-

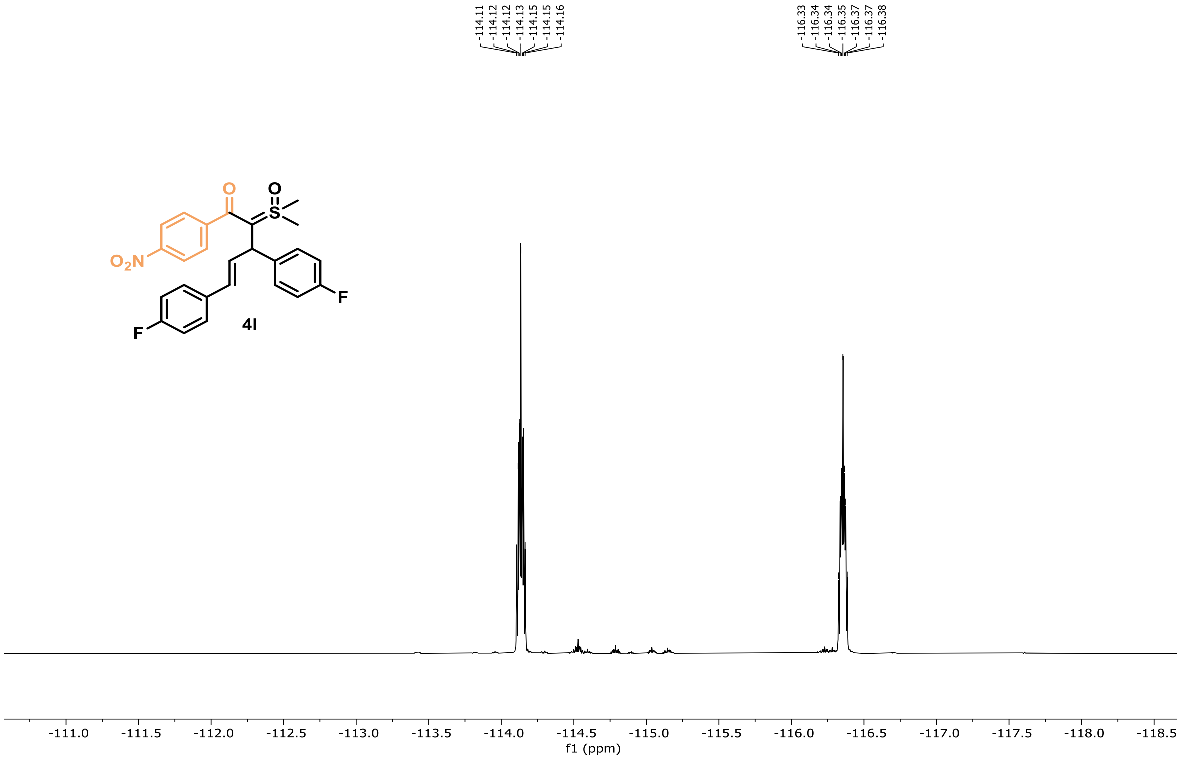

Figure S66: ^{19}F NMR spectra (470 MHz, CDCl$_3$) of compound **4l**.

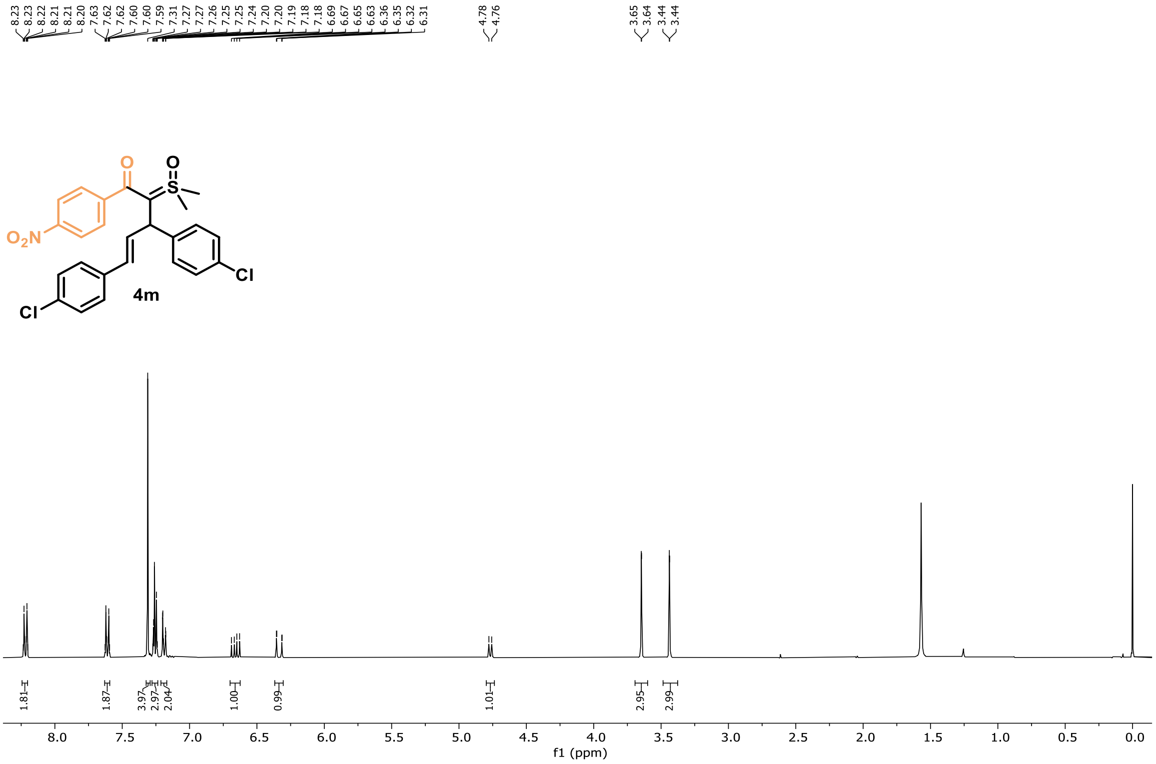

Figure S67: ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **4m**.

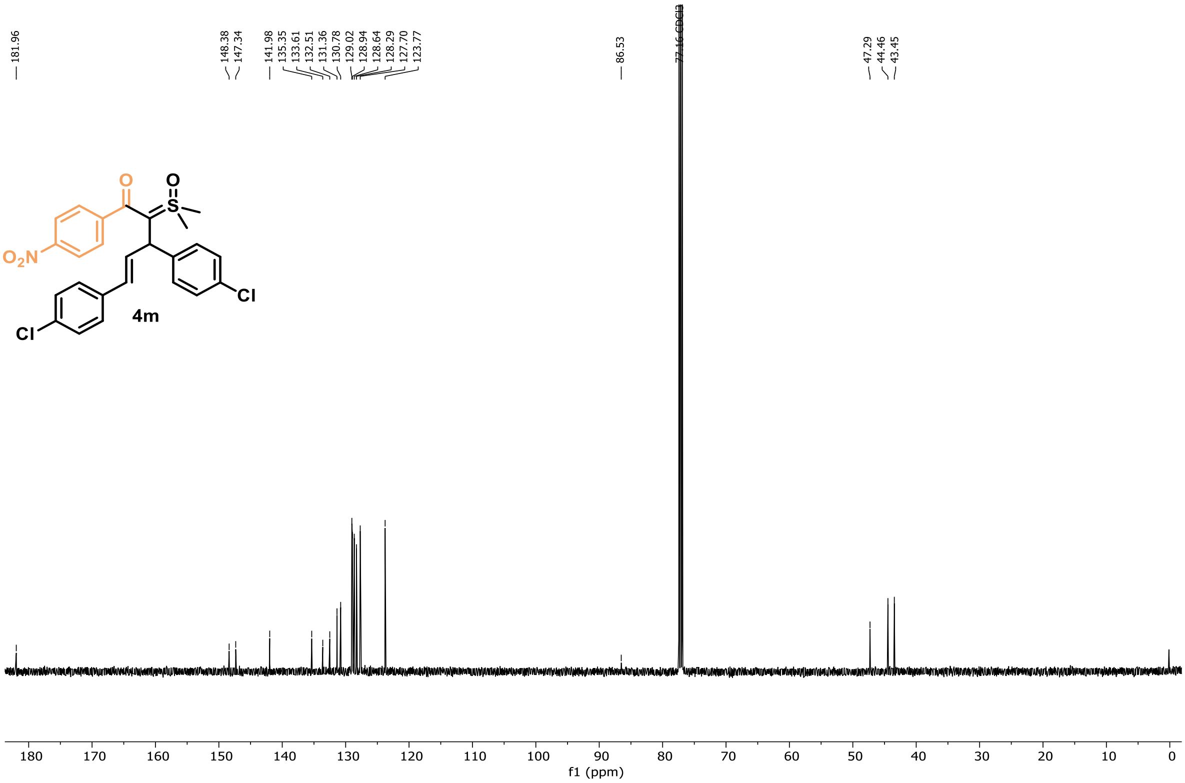

Figure S68: ^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **4m**.

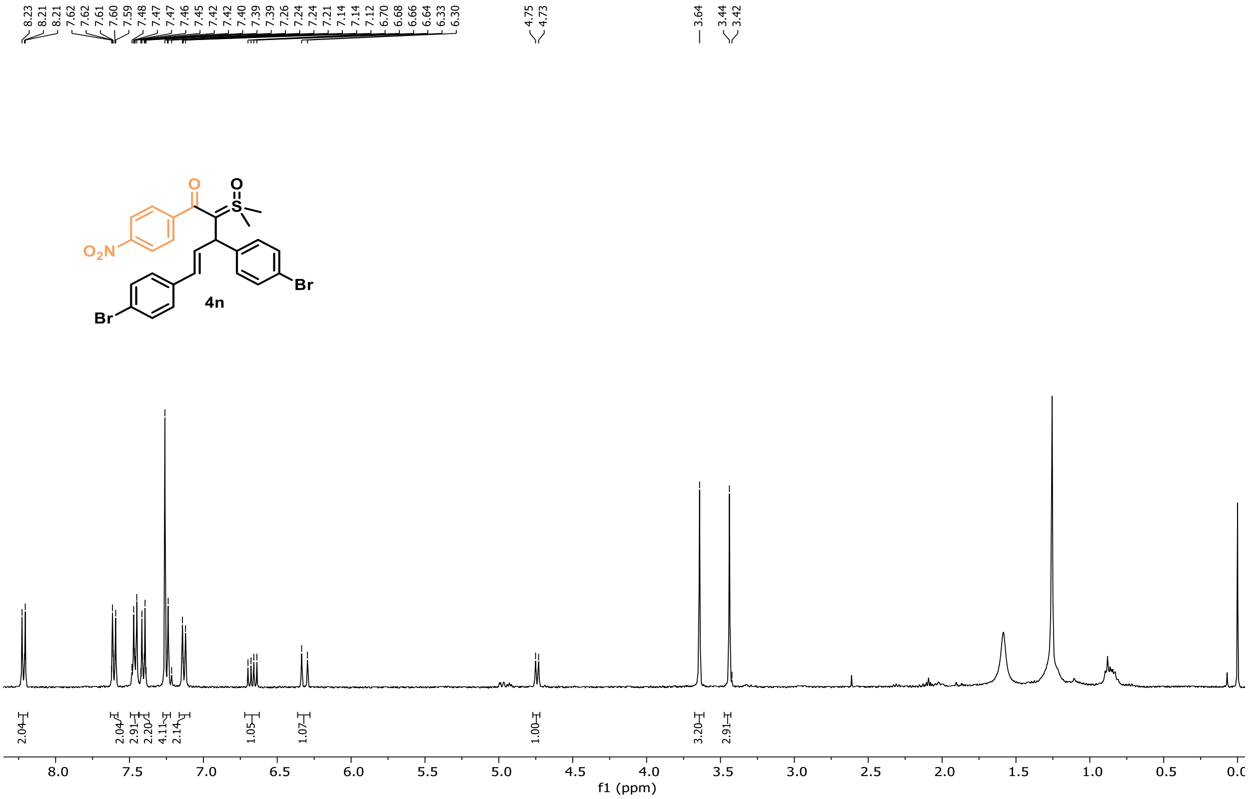

Figure S69: ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **4n**.

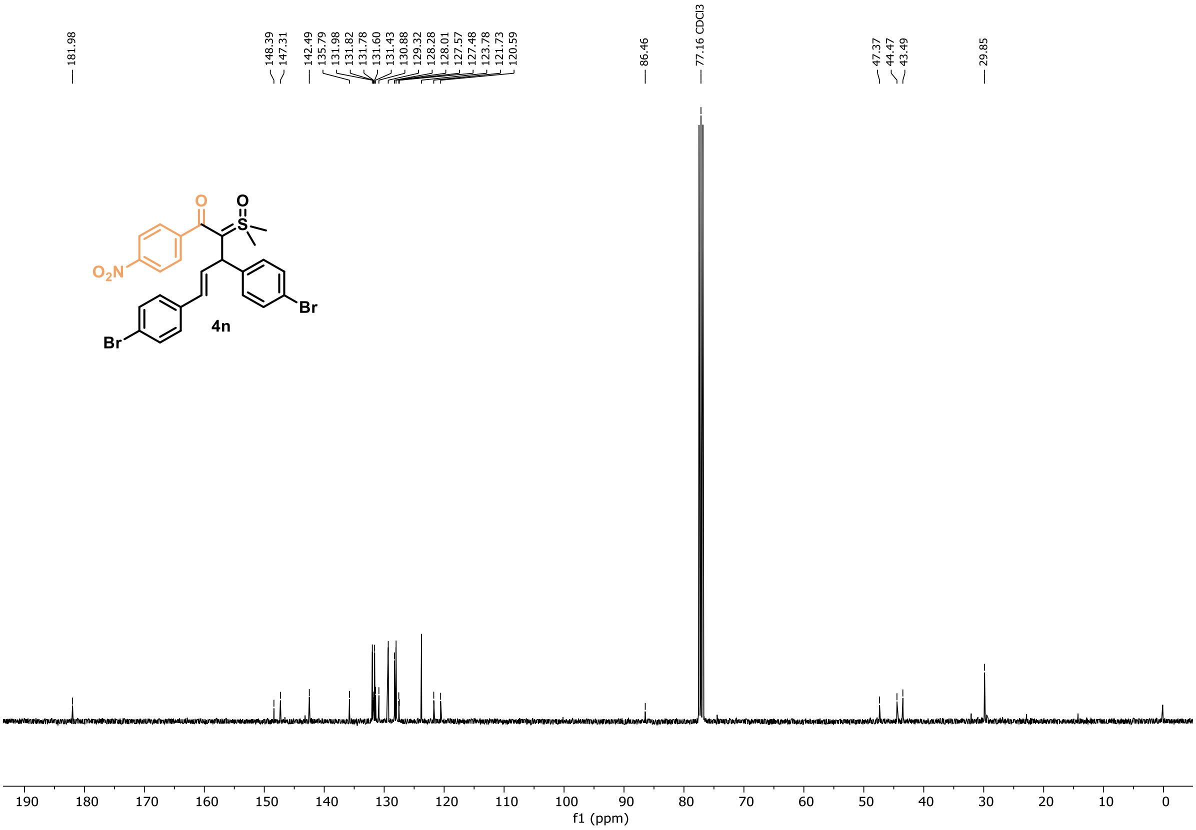

Figure S70: ^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **4n**.

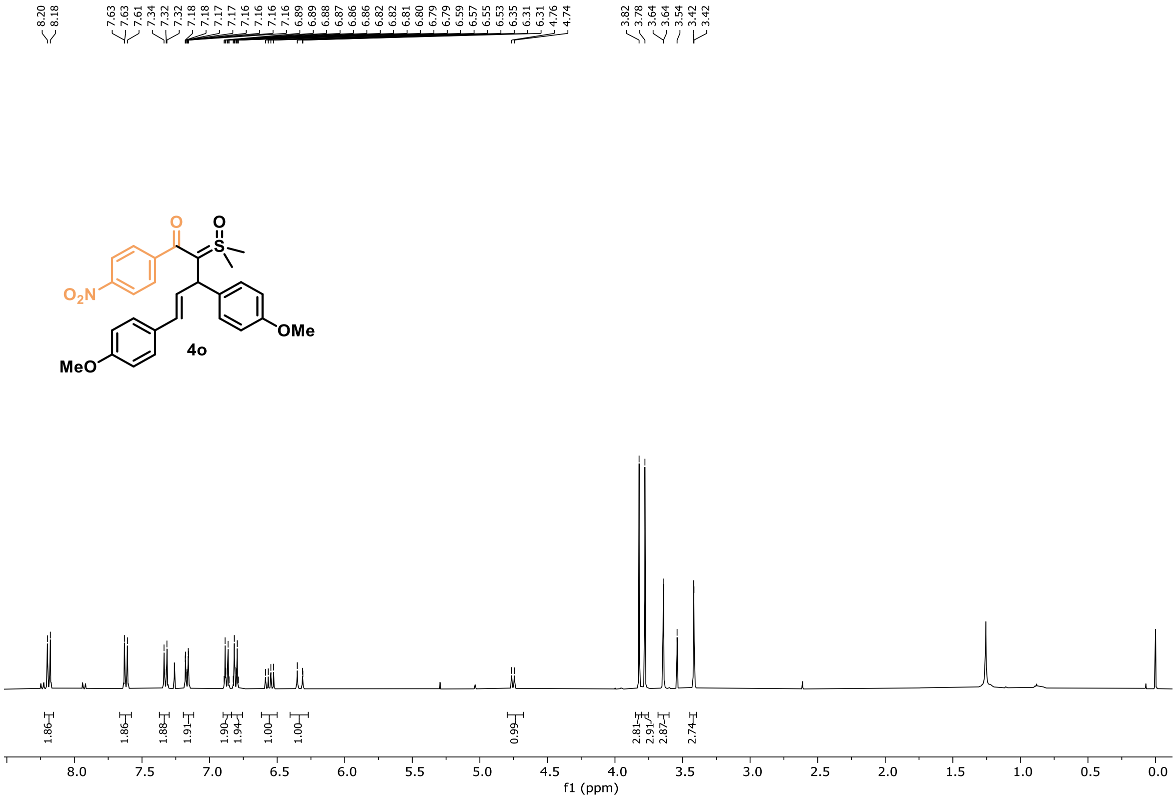

Figure S71: ^{1}H NMR spectra (400 MHz, CDCl$_3$) of compound **4o**.

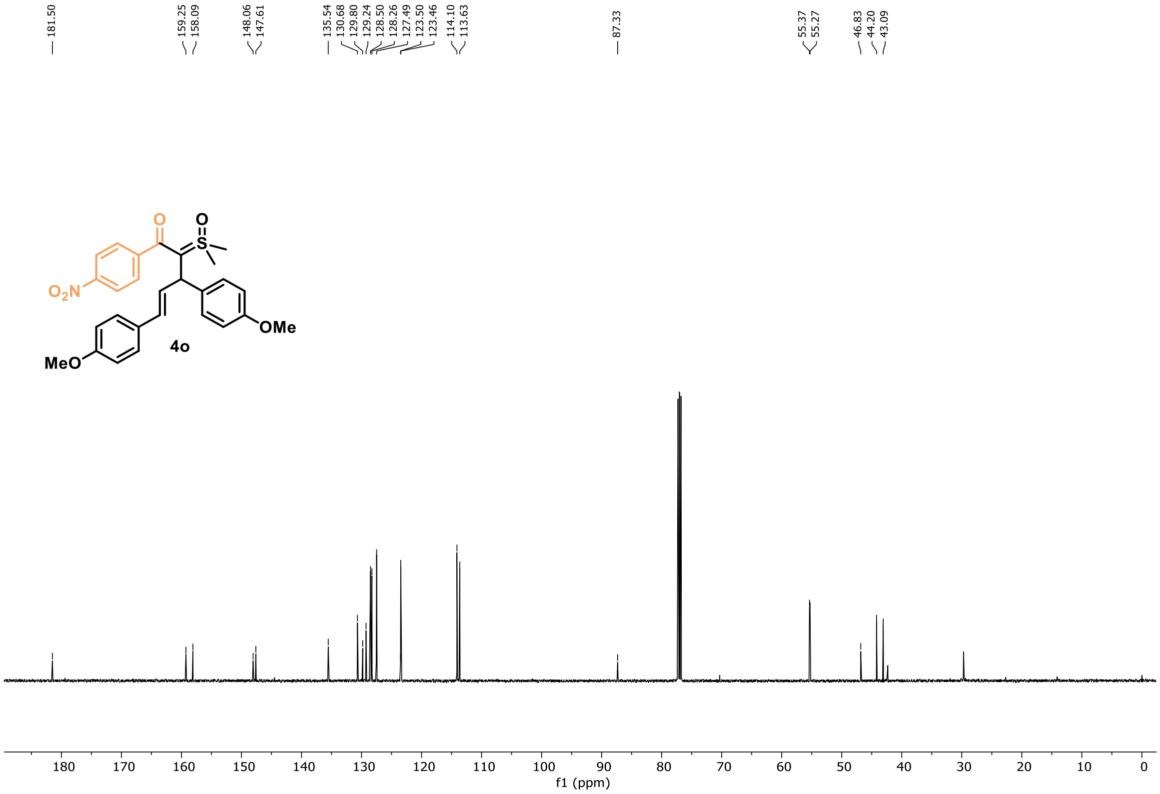

Figure S72: ^{13}C NMR spectra (101 MHz, CDCl$_3$) of compound **4o**.

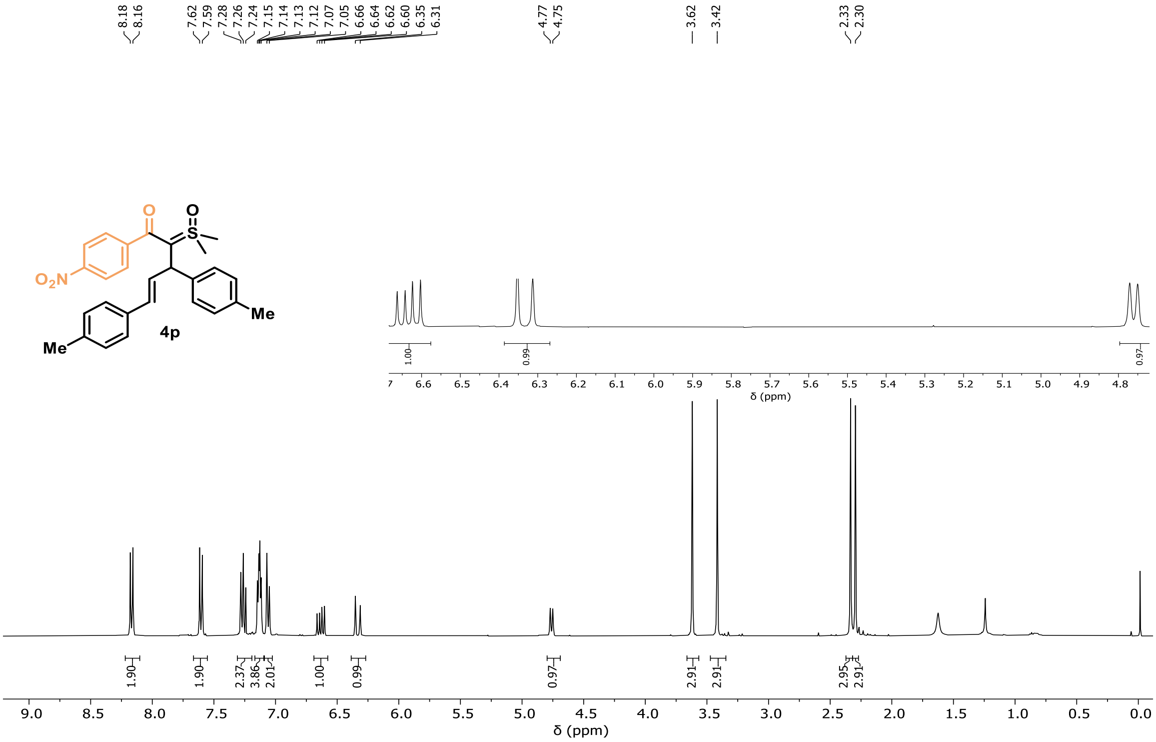

Figure S73: ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **4p**.

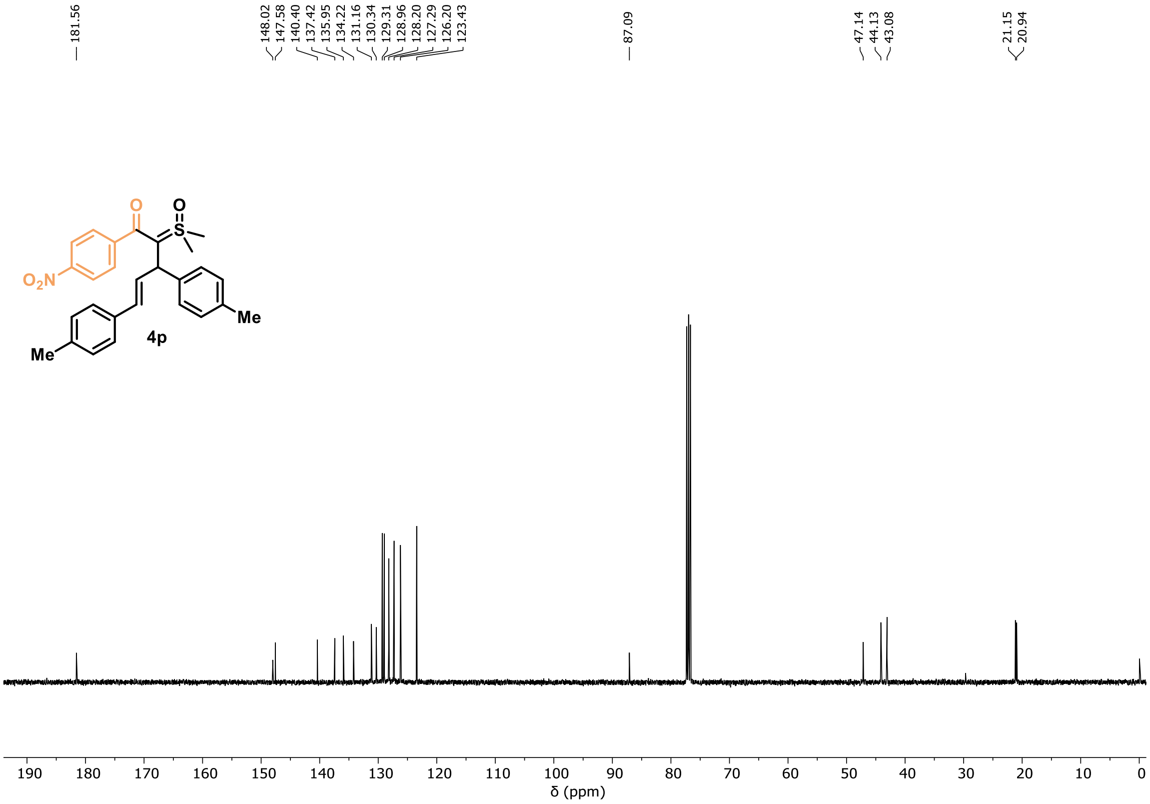

Figure S74: ^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **4p**.

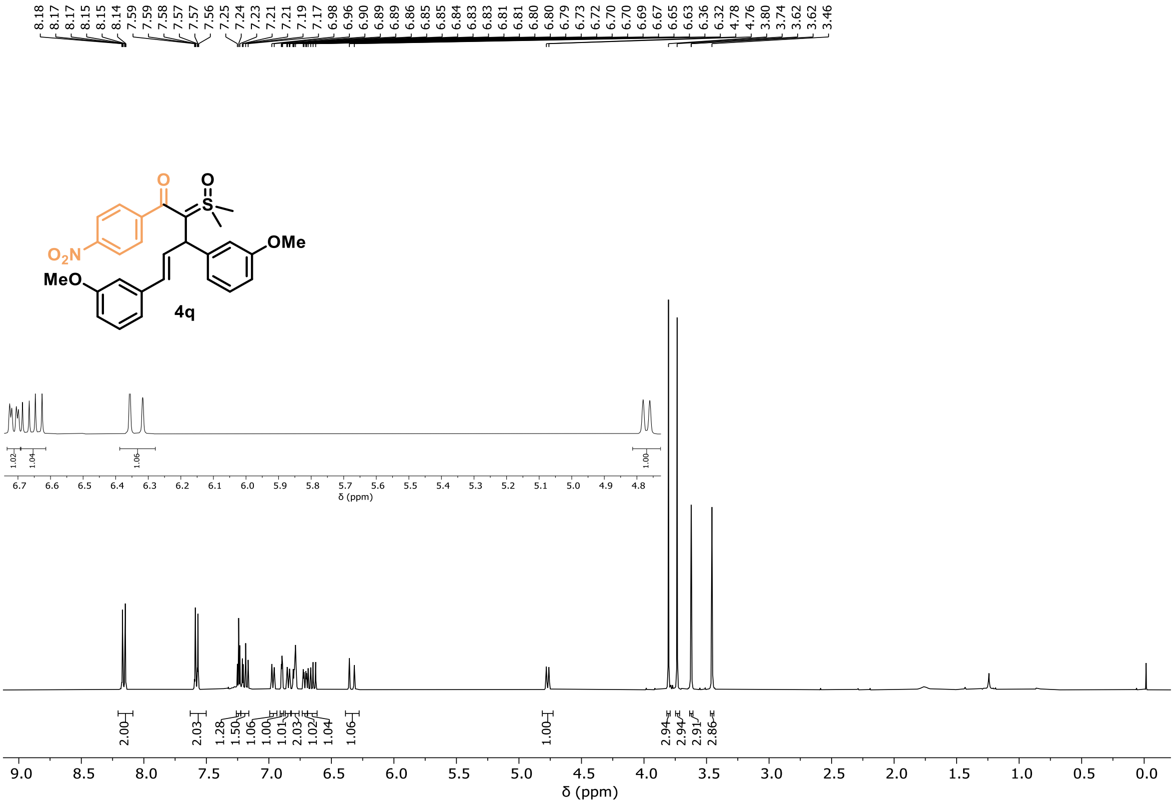

Figure S75: ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **4q.**

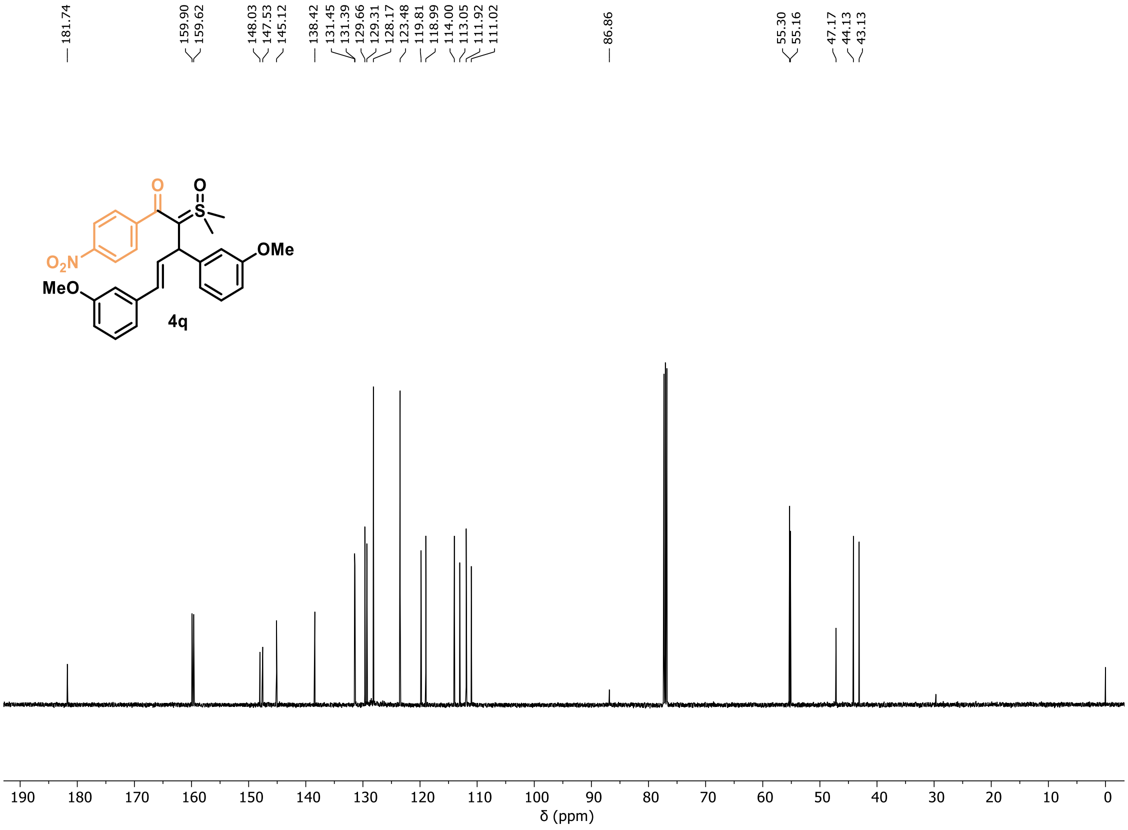

Figure S76: ^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **4p**.

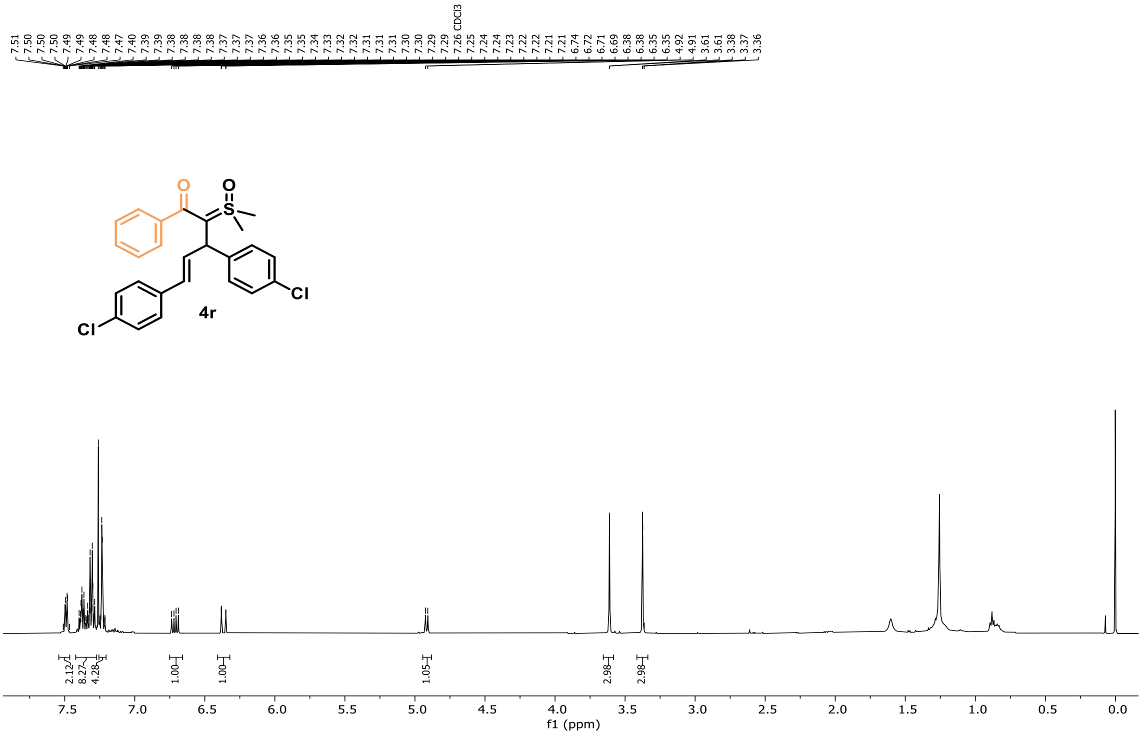

Figure S77: ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **4r**.

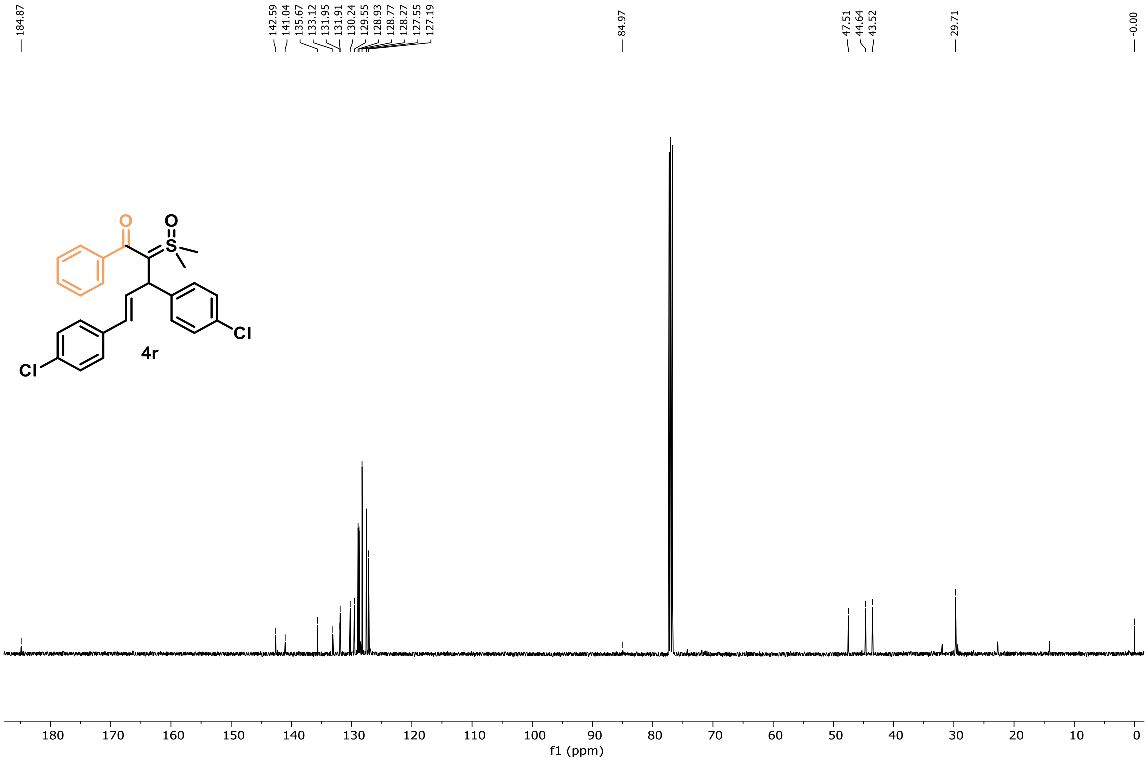

Figure S78: ^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **4r**.

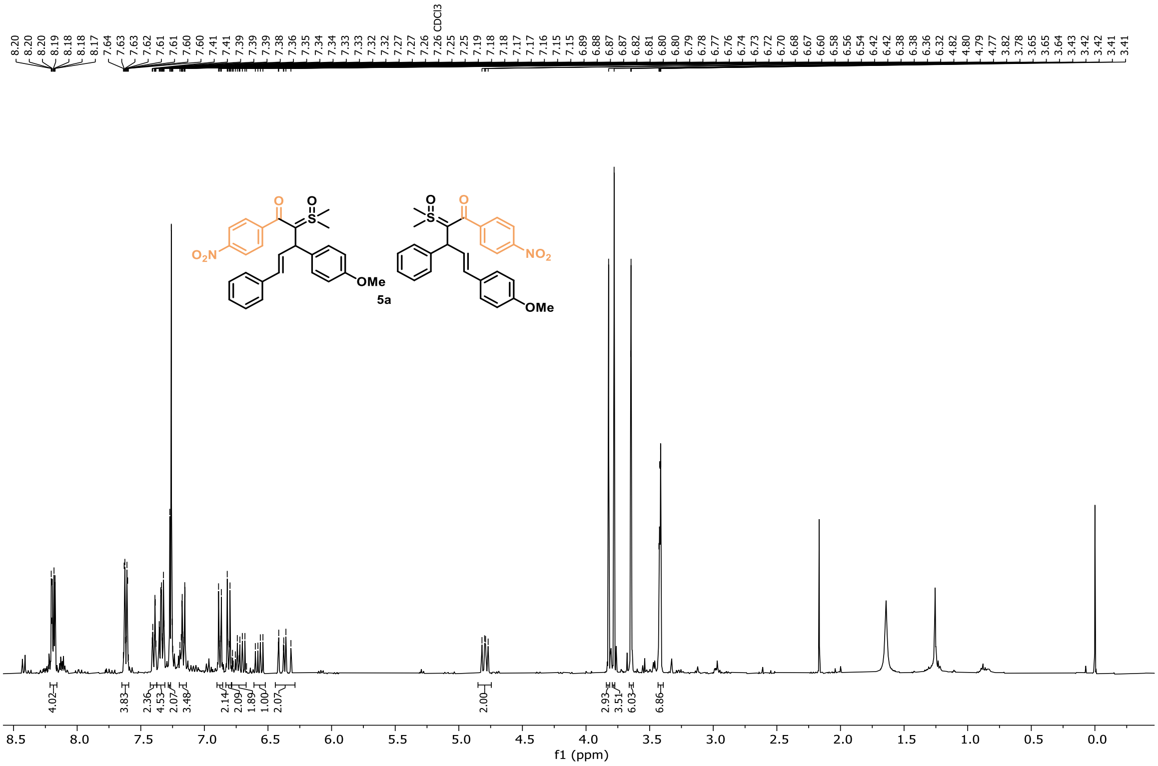

Figure S79: ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5a**.

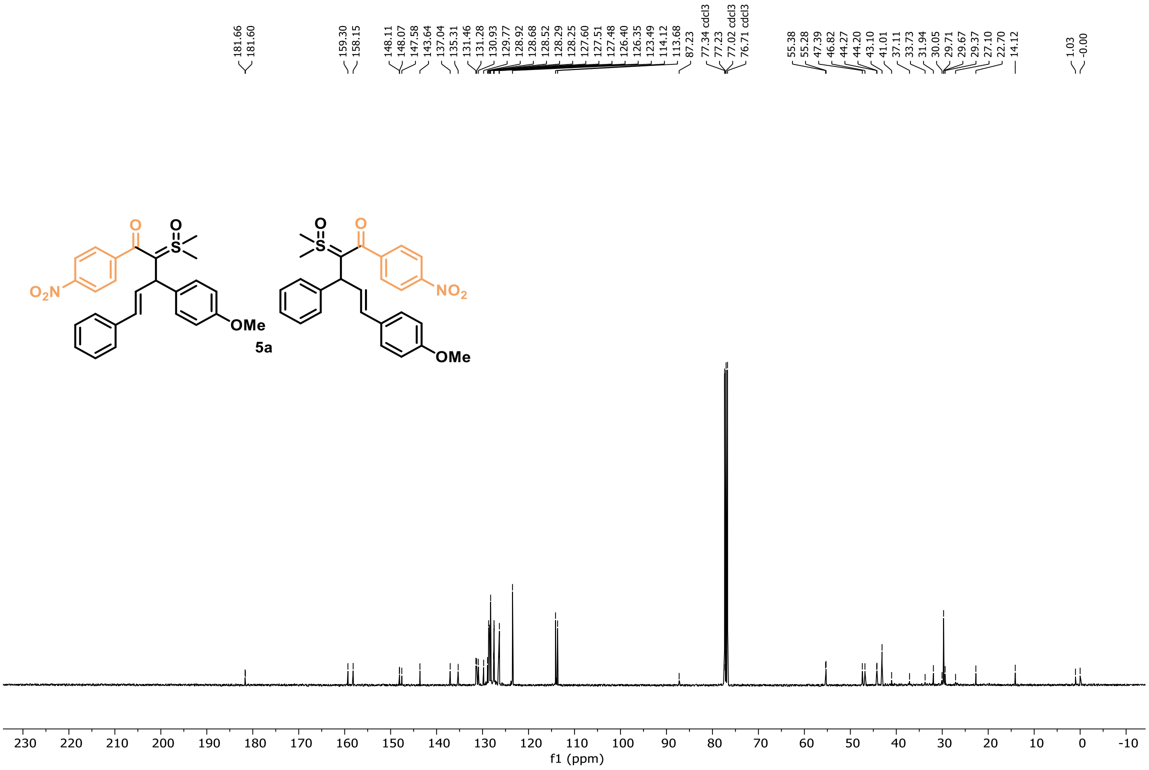

Figure S80: ^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5a**.

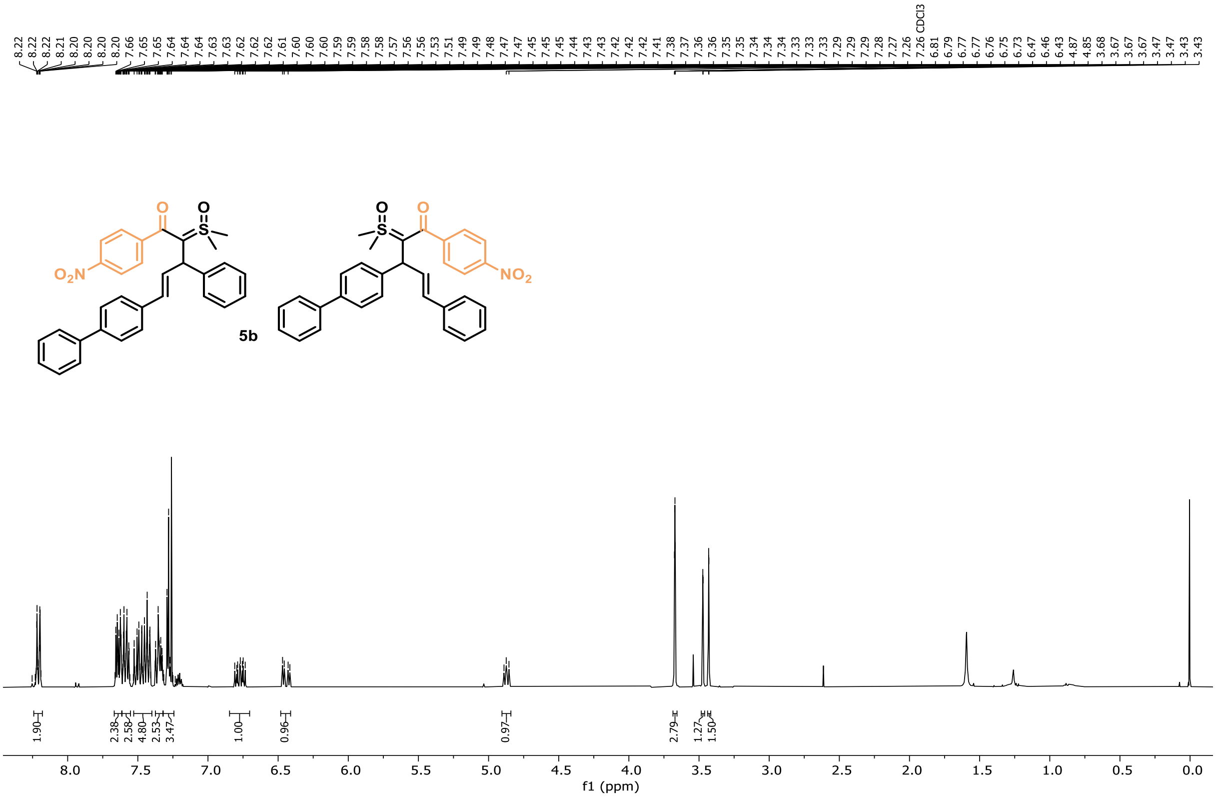

Figure S81: ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5b**.

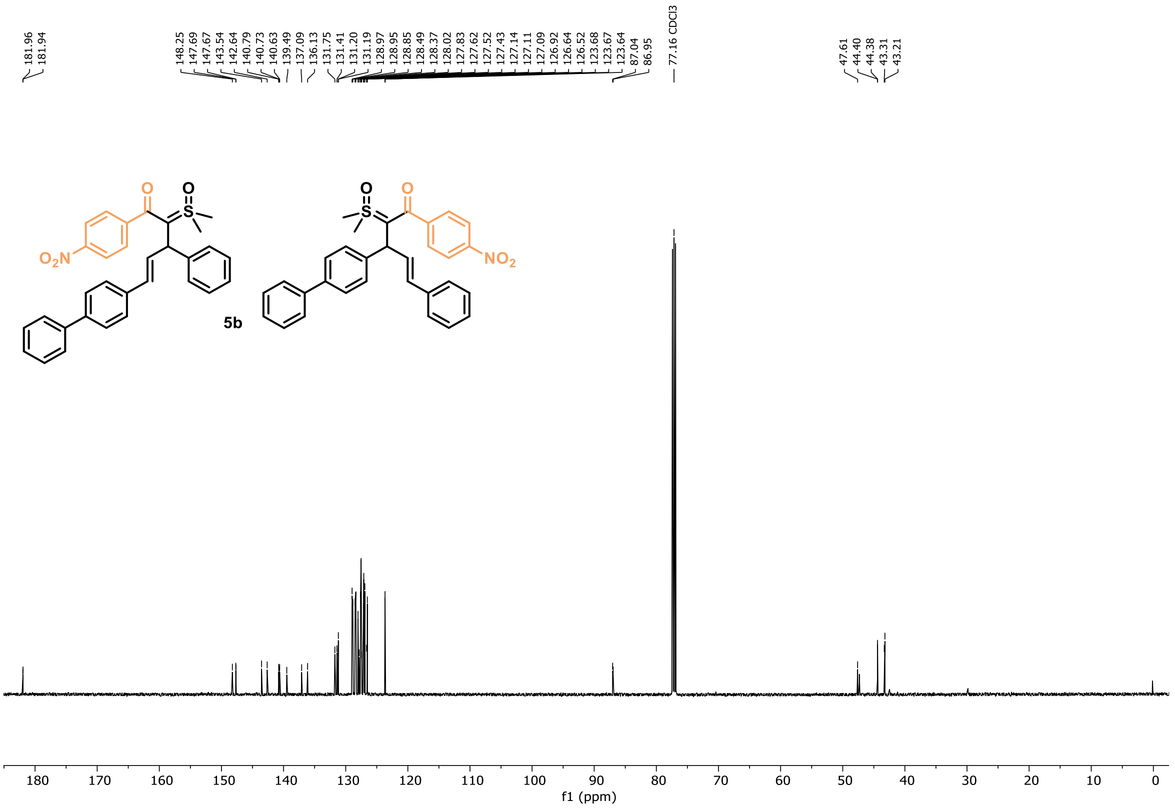

Figure S82: ^{13}C NMR spectra (126 MHz, $CDCl_3$) of compound **5b**.

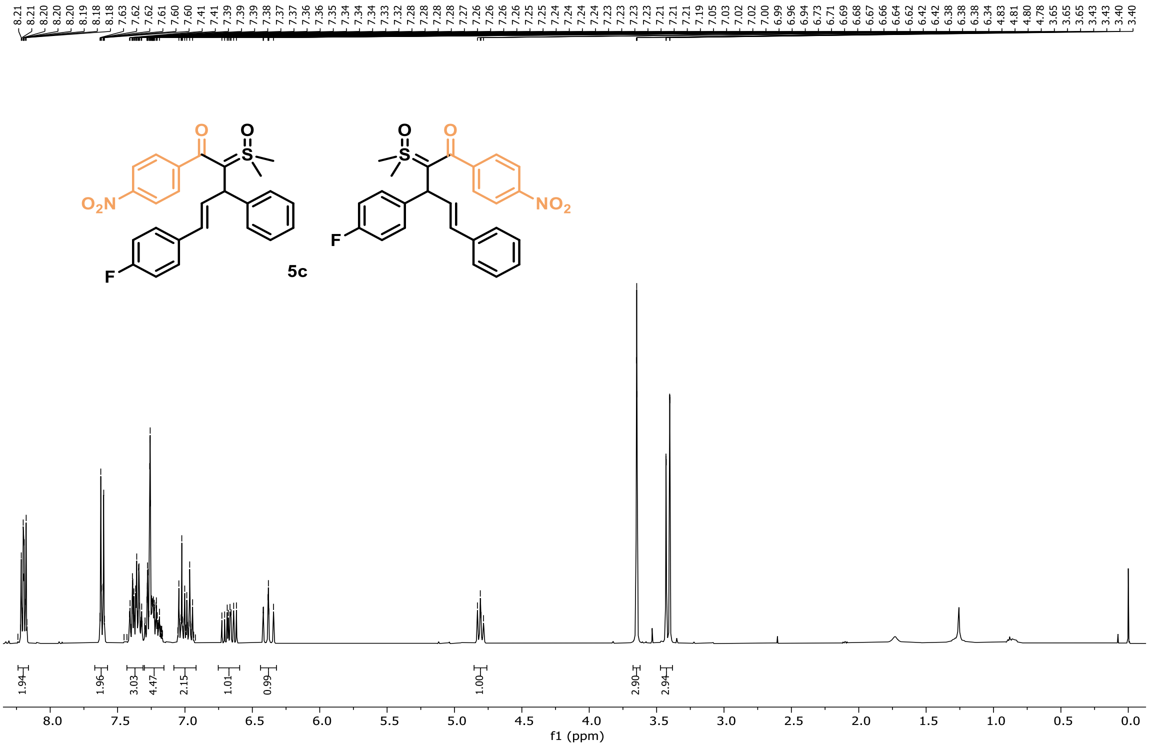

Figure S83: ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5c**.

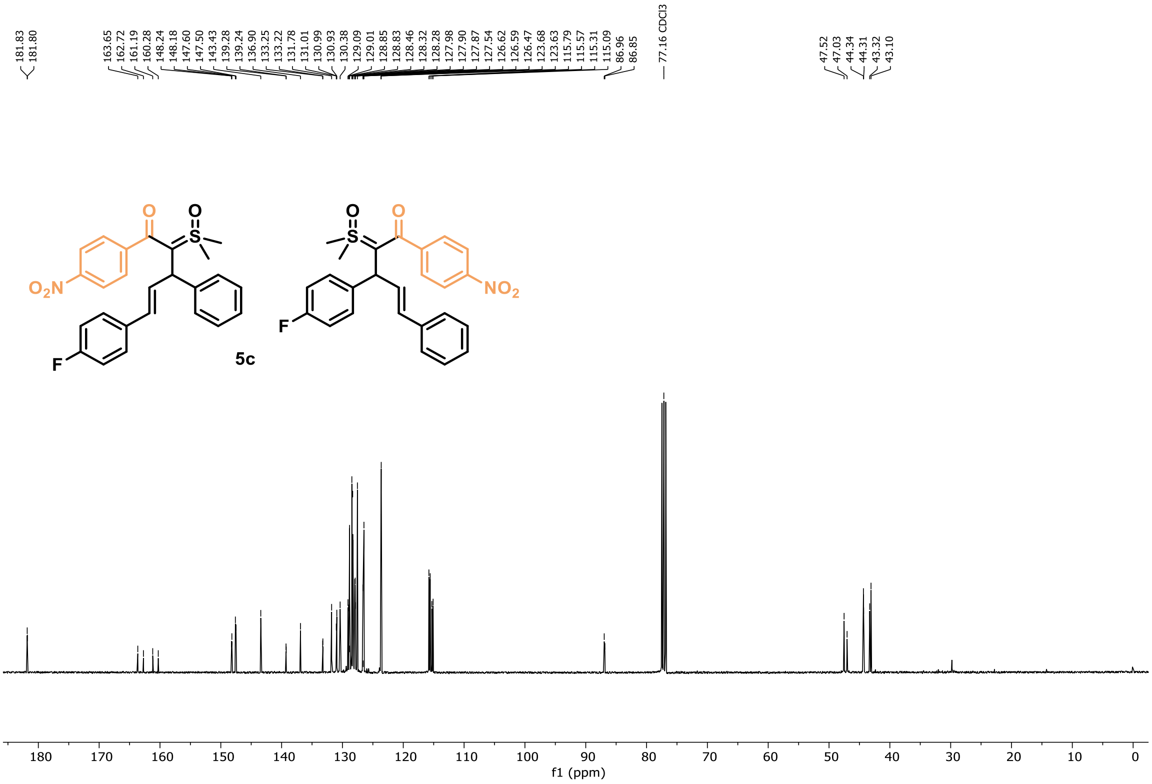

Figure S84: ^{13}C NMR spectra (101 MHz, $CDCl_3$) of compound **5c**.

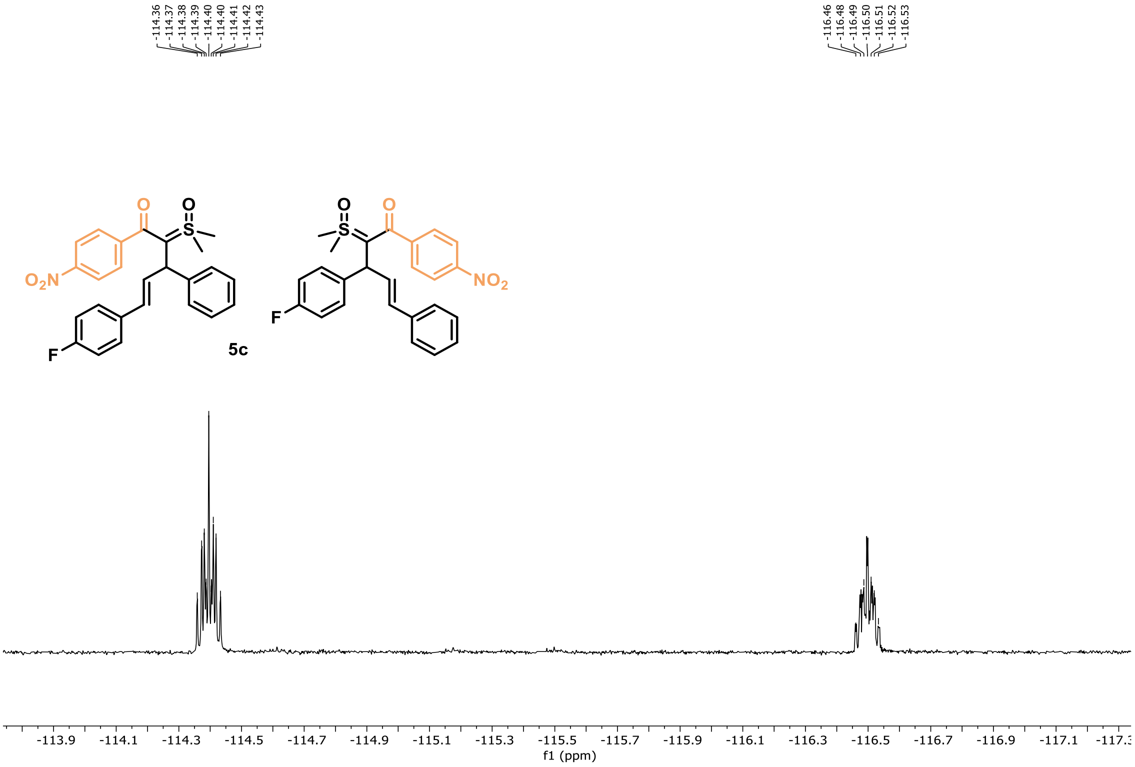

Figure S85: ^{19}F NMR spectra (376 MHz, $CDCl_3$) of compound **5c**.

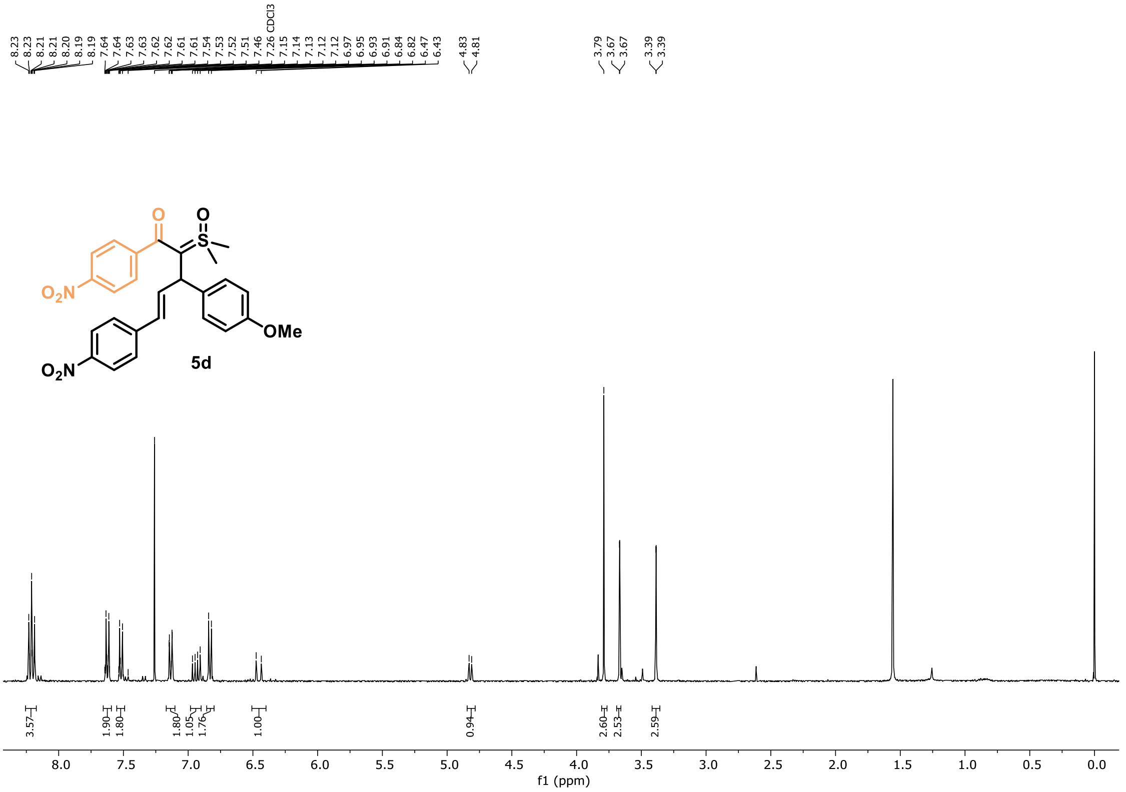

Figure S86: ^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5d**.

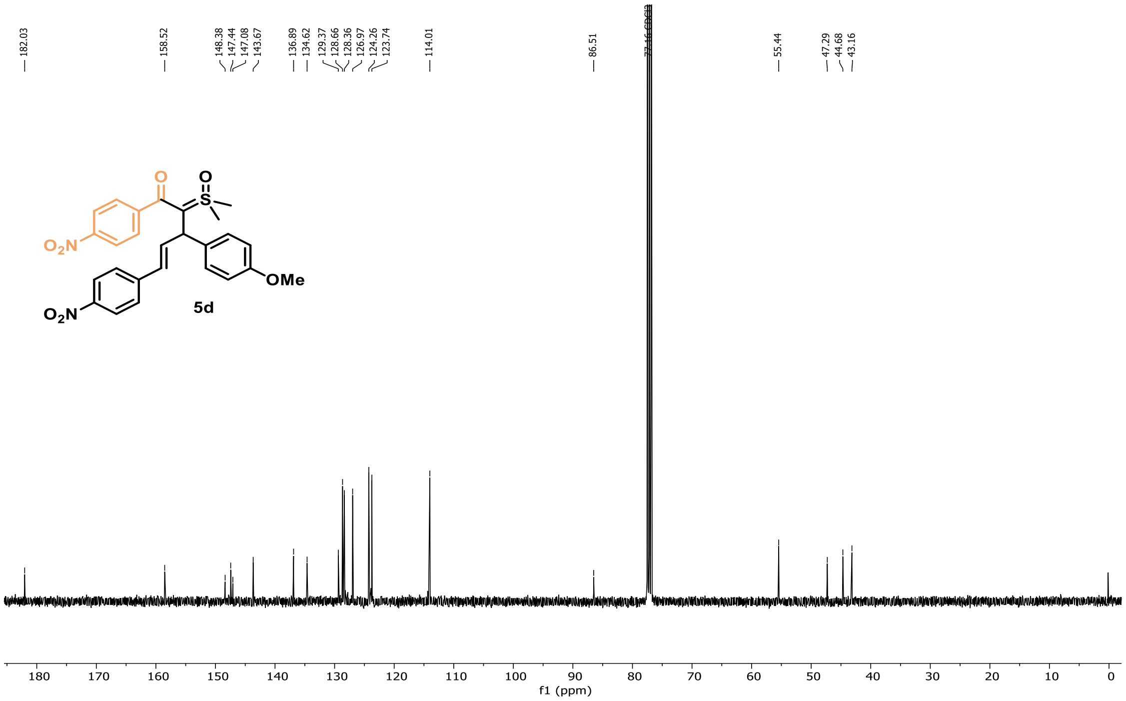

Figure S87: ^{13}C NMR spectra (101 MHz, CDCl$_3$) of compound **5d**.

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