Supporting Information

Access to Spiro-bicyclo[2.1.1]hexanes via $BF_3{\cdot}Et_2O$-Catalyzed Formal [2π + 2σ] Cycloaddition of Bicyclo[1.1.0]butanes with Benzofuran-derived Oxa(aza)dienes

Jia-Yi Su,‡[a] Jian Zhang,‡[b] Zhi-Yun Xin,[b] Hao Li,*[a] Hanliang Zheng,*[b] and Wei-Ping Deng*[b]

[a] *State Key Laboratory of Bioreactor Engineering, Shanghai Key Laboratory of New Drug Design, School of Pharmacy, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China.*

[b] *Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Department of Chemistry and Materials Science, Zhejiang Normal University, Jinhua 321004, China.*

Contents

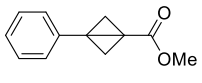
1. General information

^{1}H NMR spectra were recorded on a Bruker DPX 400 MHz or 600 MHz spectrometer in $CDCl_3$. Chemical shifts were reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The spectra are interpreted as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, dtd = doublet of triplet of doublets, brs = broad signals, coupling constant (s) *J* are reported in Hz and relative integrations are reported. ^{13}C NMR spectra were recorded on a Bruker DPX 400 MHz or 600 MHz spectrometer in $CDCl_3$. Chemical shifts were reported in ppm with the internal chloroform signal at 77.16 ppm as a standard. ^{19}F NMR (376 MHz) spectra were recorded on a Bruker DPX 400 MHz spectrometer in $CDCl_3$ and referenced relative to $CFCl_3$. Melting points were obtained in open capillary tubes using SGW X-4 micro melting point apparatus which were uncorrected. High-resolution mass spectra (HRMS) were recorded on a JEOC AccuTOF LC-plus 4G mass spectrometer using ESI (electrospray ionization). Anhydrous CH_2Cl_2 was distilled from calcium hydride. Anhydrous toluene was distilled from sodium/benzophenone. Other anhydrous solvents (<30 ppm water, *Karl-Fischer* titration) were purchased from J&K and stored over molecular sieves under an argon atmosphere. Lewis acids were purchased from Laajoo, Adamas and Bide chemical company. Bicyclo[1.1.0]butanes (BCBs),[1] benzofuran-derived oxadienes,[2] (benzo)furan-derived azadienes[3,4] and other *α*,*β*-unsaturated compounds[5] were synthesized according to the literature and spectral data of them were in accordance with those reported in the literature.

2. Synthesis and Spectral Characterization of BCBs

BCBs **1** were synthesized according to the literature and spectral data of them was in accordance with those reported in the literatures.[1]

These BCBs are stable at -20 ℃ and can be stored for several months without decomposition.



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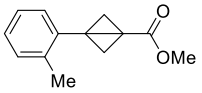

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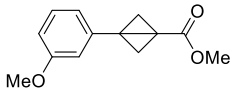

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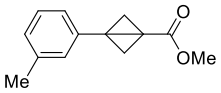

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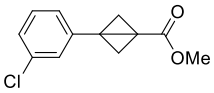

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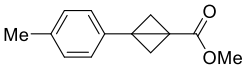

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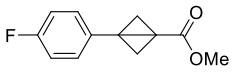

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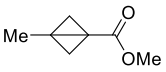

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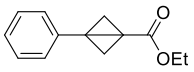

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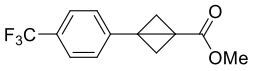

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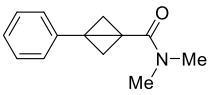

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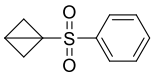

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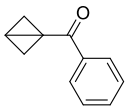

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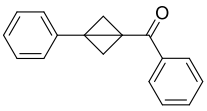

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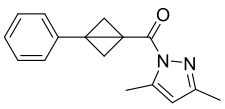
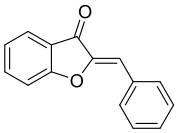


1o

3. Synthesis and Spectral Characterization of Benzofuran-derived Oxadienes

Benzofuran-derived Oxadienes **2** were synthesized according to the literature and spectral data of them was in accordance with those reported in the literatures.[2]



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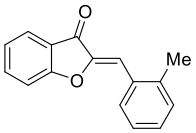

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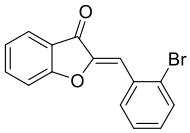

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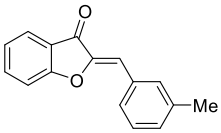

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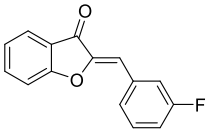

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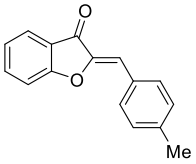

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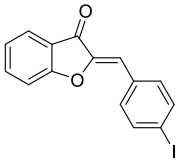

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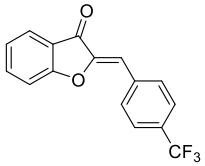

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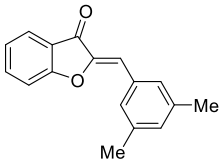

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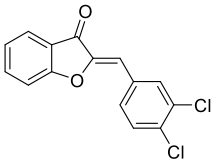

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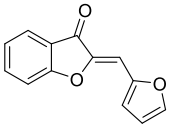

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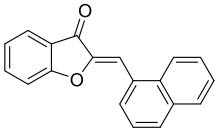

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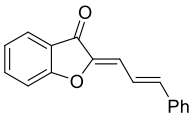

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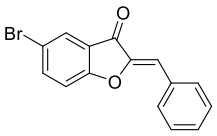

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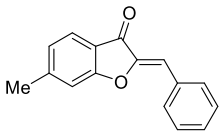

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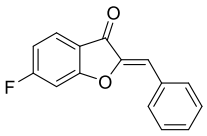

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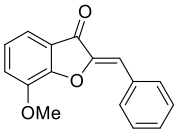

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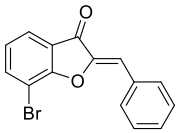

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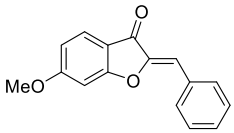

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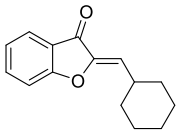
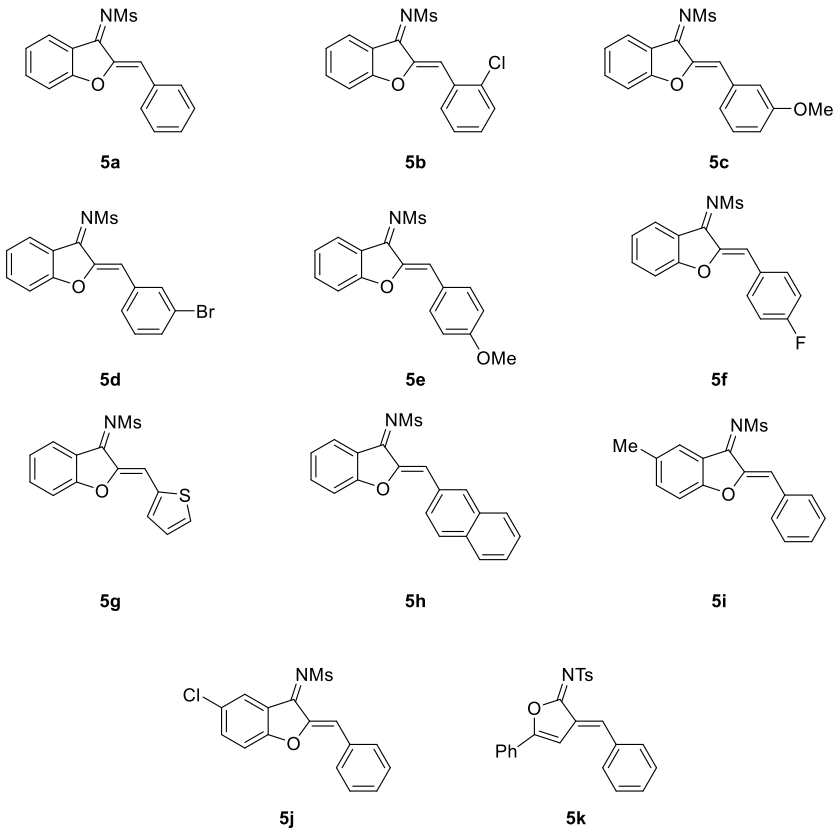


2t

4. Synthesis and Spectral Characterization of (Benzo)furan-derived Azadienes

(Benzo)furan-derived Azadienes **5** were synthesized according to the literature and spectral data of them was in accordance with those reported in the literatures.[3,4]



5a **5b** **5c**

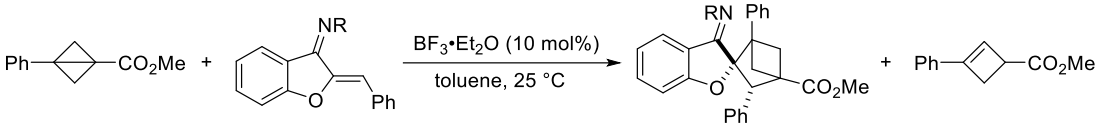
5d **5e** **5f**

5g **5h** **5i**

5j **5k**

5. Optimization studies

Table S1. Screening of benzofuran-derived azadienes of [2π + 2σ] cycloadditions

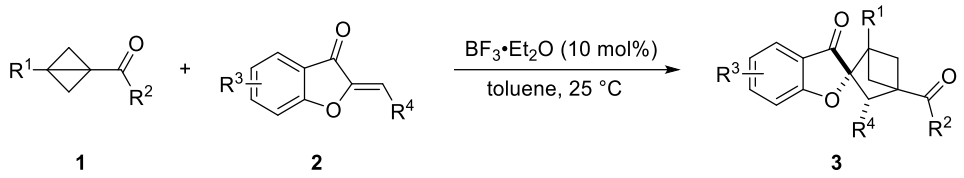


1a **5** **6** **4a**

Entry[a]	R	Yield of **6** (%)[b]	Yield of **4a** (%)[b]	Recovery of **5** (%)[b]
1	Ts	33	40	-
2	Ns	27	42	8
3	Ms	99	42	-
4[c]	Ms	98	30	-
5[d]	Ms	89	23	7
6[e]	Ms	99	25	-
7[f]	Ms	85	26	10

[a] Reaction conditions: **1a** (0.20 mmol), **5** (0.10 mmol), $BF_3 \cdot Et_2O$ (0.01 mmol, 10 mol%), toluene (2.0 mL), N_2 atmosphere, 25 °C, 10 mins. [b] Isolated yield. [c] with **1a** (0.17 mmol). [d] with **1a** (0.15 mmol). [e] toluene (1.5 mL) and the solution of **1a** (0.30 M in toluene, 0.15 mmol) was added dropwise within 5 mins. [f] toluene (1.5 mL) and the solution of **1a** (0.24 M in toluene, 0.12 mmol) was added dropwise within 5 mins.

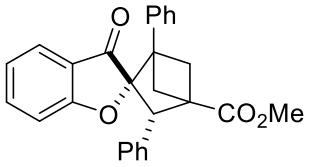
6. General procedure for the formal [2π + 2σ] cycloaddition



1 2 3

General procedure A:

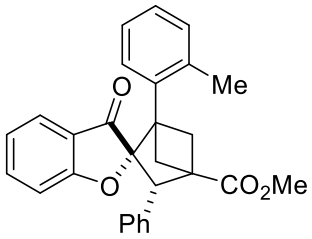
Under a nitrogen atmosphere, BCBs **1** (0.60 mmol, 3.0 equiv.) and benzofuran-derived oxadienes **2** (0.20 mmol, 1.0 equiv.) were added sequentially into a flame-dried Schlenk tube equipped with a magnetic stir bar. The tube was evacuated and back-filled with nitrogen for five times. Then the anhydrous toluene (4.0 mL) was added via syringe sequentially. Then, $BF_3 \cdot Et_2O$ (2.8 mg, 0.02 mmol, 10 mol%) was added and the mixture was stirred at 25 ℃ until **2** was consumed (monitored by TLC) (10 mins were enough in all examples). Then, the reaction mixture was quenched with water and extracted with ethyl acetate for three times. The resulted filtrate was separated. The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by column chromatography (petroleum ether/ethyl acetate) to give the corresponding products **3**.



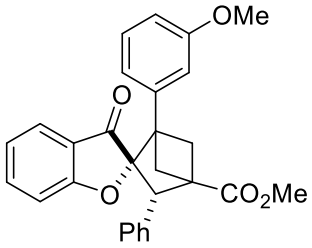
methyl 3-oxo-1',3'-diphenyl-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (3a): Following the general procedure **A**, compound **3a** was obtained as a white solid in 83% yield (68.1 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate = 10/1); m.p. = 161-163 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.36 (ddd, *J* = 8.5, 7.1, 1.5 Hz, 1H), 7.23 – 7.14 (m, 3H), 7.13 – 7.03 (m, 5H), 7.00 – 6.93 (m, 2H), 6.91 – 6.84 (m, 1H), 6.69 (d, *J* = 8.4 Hz, 1H), 4.34 (d, *J* = 2.3 Hz, 1H), 3.67 (s, 3H), 3.39 (dd, *J* = 9.5, 7.1 Hz, 1H), 3.13 (dd, *J* = 9.5, 7.6 Hz, 1H), 2.53 (dd, *J* = 7.6, 2.4 Hz, 1H), 2.29 (d, *J* = 7.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.3, 172.1, 171.6, 138.0, 137.0, 136.2, 128.4(2C), 128.1(2C), 127.7(2C), 127.4, 126.9, 126.4(2C), 123.9, 121.7(2), 121.6(5), 112.8, 95.9, 58.5, 58.4, 52.1, 49.9, 44.5, 43.1; **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{22}O_4Na$ $[M+Na]^+$: 433.1411, found: 433.1407.

In the reaction for preparation of **3a**, **methyl 3-phenylcyclobut-2-ene-1-carboxylate (4a)** was obtained as a colorless oil in 62% yield (35.0 mg); $\mathbf{R}_f$ = 0.80 (petroleum ether/ethyl acetate = 10/1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 4H), 7.30 – 7.26 (m, 1H), 6.28 (d, *J* =

1.4 Hz, 1H), 3.72 (s, 3H), 3.69 – 3.65 (m, 1H), 3.08 (dd, *J* = 12.9, 4.8 Hz, 1H), 3.01 (dd, *J* = 12.9, 2.1 Hz, 1H).[6]

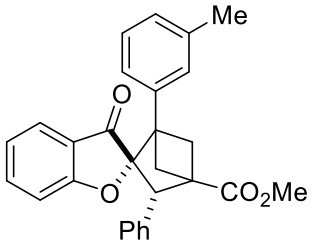


methyl 3-oxo-3'-phenyl-1'-(*o*-tolyl)-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (3b): Following the general procedure **A**, compound **3b** was obtained as a white solid in 83% yield (70.5 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1); $\mathbf{R}_f$ = 0.35 (petroleum ether/ethyl acetate = 10/1); m.p. = 158-159 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 1H), 7.39 – 7.31 (m, 1H), 7.24 – 7.13 (m, 3H), 7.08 – 7.01 (m, 1H), 7.00 – 6.90 (m, 4H), 6.90 – 6.82 (m, 2H), 6.69 (d, *J* = 8.4 Hz, 1H), 4.36 (d, *J* = 2.3 Hz, 1H), 3.67 (s, 3H), 3.48 (dd, *J* = 9.6, 7.1 Hz, 1H), 3.26 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.65 (dd, *J* = 7.6, 2.4 Hz, 1H), 2.35 – 2.27 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.5, 172.1, 171.4, 137.9, 136.7, 136.2, 135.1, 131.0, 128.4(2C), 128.2(2C), 127.7, 127.4, 126.9, 125.5, 124.0, 121.8, 121.5, 112.5, 97.2, 59.1, 58.1, 52.1, 50.2, 46.0, 44.4, 20.6; **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{24}O_4Na$ $[M+Na]^+$: 447.1567, found: 447.1561.

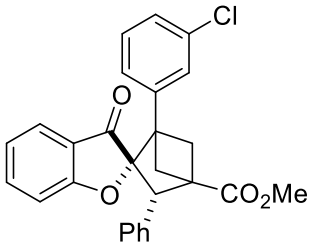


methyl 1'-(3-methoxyphenyl)-3-oxo-3'-phenyl-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (3c): Following the general procedure **A**, compound **3c** was obtained as a white solid in 86% yield (75.8 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate = 10/1); m.p. = 164-166 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 1H), 7.40 – 7.33 (m, 1H), 7.23 – 7.13 (m, 3H), 7.04 – 6.93 (m, 3H), 6.92 – 6.84 (m, 1H), 6.73 – 6.67 (m, 2H), 6.66 – 6.63 (m, 1H), 6.63 – 6.58 (m, 1H), 4.33 (d, *J* = 2.2 Hz, 1H), 3.67 (s, 3H), 3.64 (s, 3H), 3.36 (dd, *J* = 9.5, 7.1 Hz, 1H), 3.11 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.52 (dd, *J* = 7.5, 2.3 Hz, 1H), 2.28 (d, *J* = 7.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.2, 172.1, 171.6, 159.2, 138.5, 138.0, 136.2, 129.1, 128.4(2C), 127.7(2C), 126.9, 124.0, 121.8, 121.7, 118.9, 113.2, 112.7,

111.9, 95.8, 58.5, 58.3, 55.2, 52.1, 49.7, 44.6, 43.2; **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{24}O_5Na$ $[M+Na]^+$: 463.1516, found: 463.1508.

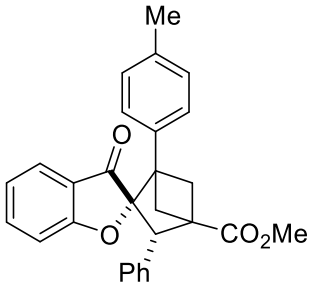


methyl 3-oxo-3'-phenyl-1'-(*m*-tolyl)-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (3d): Following the general procedure **A**, compound **3d** was obtained as a white solid in 85% yield (72.2 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate = 10/1); m.p. = 159-160 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 1H), 7.38 – 7.32 (m, 1H), 7.23 – 7.13 (m, 3H), 7.00 – 6.93 (m, 3H), 6.93 – 6.82 (m, 4H), 6.69 (d, *J* = 8.4 Hz, 1H), 4.33 (d, *J* = 2.3 Hz, 1H), 3.66 (s, 3H), 3.36 (dd, *J* = 9.6, 7.1 Hz, 1H), 3.12 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.51 (dd, *J* = 7.6, 2.4 Hz, 1H), 2.27 (d, *J* = 7.1 Hz, 1H), 2.16 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.3, 172.1, 171.6, 137.9, 137.6, 136.9, 136.3, 128.4(2C), 128.1, 127.9, 127.7(2C), 127.2, 126.9, 123.9, 123.5, 121.7(1), 121.6(9), 112.7, 95.9, 58.5, 58.4, 52.1, 49.9, 44.5, 43.2, 21.4; **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{24}O_4Na$ $[M+Na]^+$: 447.1567, found: 447.1563.

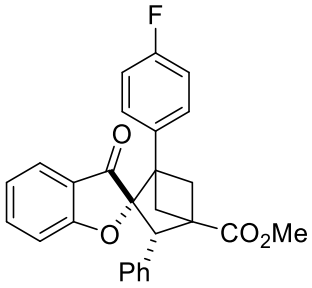


methyl 1'-(3-chlorophenyl)-3-oxo-3'-phenyl-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (3e): Following the general procedure **A**, compound **3e** was obtained as a white solid in 69% yield (61.4 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate = 10/1); m.p. = 167-169 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 1H), 7.43 – 7.34 (m, 1H), 7.24 – 7.14 (m, 3H), 7.12 – 7.07 (m, 1H), 7.07 – 6.92 (m, 5H), 6.95 – 6.86 (m, 1H), 6.75 – 6.68 (m, 1H), 4.33 (d, *J* = 2.2 Hz, 1H), 3.67 (s, 3H), 3.36 (dd, *J* = 9.5, 7.2 Hz, 1H), 3.12 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.52 (dd, *J* = 7.5, 2.4 Hz, 1H), 2.28 (d, *J* = 7.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.9, 171.8, 171.5, 139.0, 138.2, 135.9, 134.0, 129.4, 128.4(2C),

127.7(2C), 127.6, 127.0, 126.8, 124.6, 124.0, 121.9, 121.5, 112.8, 95.6, 58.4, 57.8, 52.2, 49.9, 44.4, 43.2; **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{21}ClO_4Na$ $[M+Na]^+$: 467.1021, found: 467.1020.

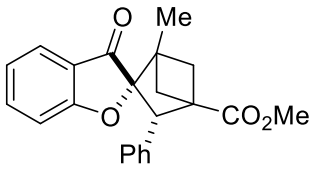


methyl 3-oxo-3'-phenyl-1'-(*p*-tolyl)-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (3f): Following the general procedure **A**, compound **3f** was obtained as a white solid in 85% yield (72.2 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate = 10/1); m.p. = 156-157 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) 7.50 – 7.45 (m, 1H), 7.38 – 7.32 (m, 1H), 7.22 – 7.13 (m, 3H), 7.02 – 6.93 (m, 4H), 6.93 – 6.84 (m, 3H), 6.68 (d, *J* = 8.4 Hz, 1H), 4.32 (d, *J* = 2.2 Hz, 1H), 3.66 (s, 3H), 3.37 (dd, *J* = 9.6, 7.1 Hz, 1H), 3.11 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.49 (dd, *J* = 7.6, 2.3 Hz, 1H), 2.26 (d, *J* = 7.1 Hz, 1H), 2.15 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.4, 172.1, 171.6, 137.9, 136.9, 136.3, 134.0, 128.8(2C), 128.4(2C), 127.7(2C), 126.9, 126.3(2C), 123.9, 121.7, 121.6, 112.7, 95.9, 58.7, 58.2, 52.1, 49.9, 44.7, 43.2, 21.1; **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{24}O_4Na$ $[M+Na]^+$: 447.1567, found: 447.1562.

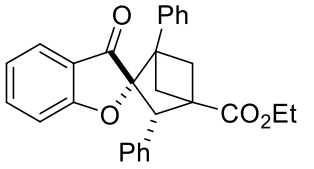


methyl 1'-(4-fluorophenyl)-3-oxo-3'-phenyl-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (3g): Following the general procedure **A**, compound **3g** was obtained as a white solid in 69% yield (59.1 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate = 10/1); m.p. = 162-164 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 1H), 7.42 – 7.33 (m, 1H), 7.25 – 7.13 (m, 3H), 7.12 – 7.01 (m, 2H), 7.01 – 6.91 (m, 2H), 6.94 – 6.86 (m, 1H), 6.83 – 6.72 (m, 2H), 6.69 (d, *J* = 8.4 Hz, 1H), 4.33 (d, *J* = 2.3 Hz, 1H), 3.67 (s, 3H), 3.37 (dd, *J* = 9.6, 7.1 Hz, 1H), 3.11 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.50 (dd, *J* = 7.6, 2.3 Hz, 1H), 2.27 (d, *J* =

7.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.2, 171.9, 171.5, 162.1 (d, J_{C-F} = 245.9 Hz), 138.2, 136.1, 132.8 (d, J_{C-F} = 3.2 Hz), 128.4(2C), 128.1 (d, J_{C-F} = 8.1 Hz)(2C), 127.7(2C), 127.0, 124.0, 121.9, 121.6, 115.0 (d, J_{C-F} = 21.3 Hz)(2C), 112.7, 95.8, 58.4, 57.7, 52.2, 49.8, 44.5, 43.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.83; **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{21}FO_4Na$ $[M+Na]^+$: 451.1317, found: 451.1319.

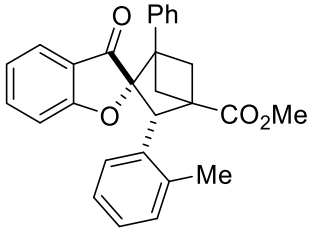


methyl (2*S*,3'*S*)-1'-methyl-3-oxo-3'-phenyl-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (3h): Following the general procedure **A**, compound **3h** was obtained as colorless oil in 16% yield (11.1 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate = 10/1); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 1H), 7.30 – 7.19 (m, 6H), 7.10 – 7.05 (m, 2H), 4.80 (d, *J* = 1.2 Hz, 1H), 3.64 (s, 3H), 2.77 – 2.71 (m, 2H), 2.70 – 2.65 (m, 1H), 2.53 – 2.48 (m, 1H), 1.65 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 174.7, 153.1, 138.2, 136.5, 135.6, 128.6(2C), 128.4(2C), 127.8, 124.7, 123.5, 122.2, 118.6, 111.3, 79.2, 52.1, 49.3, 45.4, 42.0, 36.9, 27.5; **HRMS** (ESI-TOF, m/z): calcd for $C_{22}H_{20}O_4Na$ $[M+Na]^+$: 371.1254, found: 371.1256.

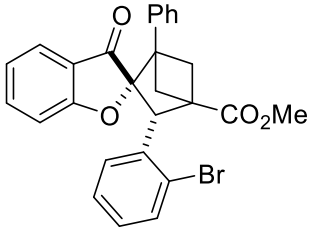


ethyl 3-oxo-1',3'-diphenyl-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (3i): Following the general procedure **A**, compound **3i** was obtained as a white solid in 84% yield (71.3 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate = 10/1); m.p. = 164-166 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.35 (ddd, *J* = 8.6, 7.2, 1.5 Hz, 1H), 7.24 – 7.16 (m, 3H), 7.13 – 7.02 (m, 5H), 7.02 – 6.97 (m, 2H), 6.91 – 6.83 (m, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 4.33 (d, *J* = 2.2 Hz, 1H), 4.18 – 4.08 (m, 2H), 3.38 (dd, *J* = 9.6, 7.1 Hz, 1H), 3.14 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.51 (dd, *J* = 7.6, 2.3 Hz, 1H), 2.28 (d, *J* = 7.1 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.4, 171.6, 171.6, 138.0, 137.0, 136.2, 128.3(2C), 128.1(2C), 127.9(2C), 127.3, 126.9, 126.5(2C), 123.9, 121.7(0), 121.6(8),

112.8, 96.0, 60.9, 58.6, 58.3, 50.1, 44.5, 43.1, 14.2; **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{24}O_4Na$ $[M+Na]^+$: 447.1567, found: 447.1564.

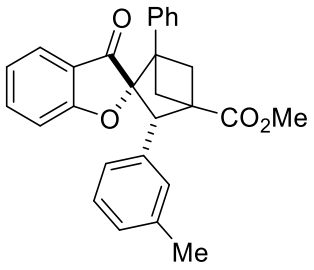


methyl 3-oxo-1'-phenyl-3'-(*o*-tolyl)-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (3j): Following the general procedure **A**, compound **3j** was obtained as a white solid in 78% yield (66.1 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1); $\mathbf{R}_f$ = 0.45 (petroleum ether/ethyl acetate = 10/1); m.p. = 157-159 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 1H), 7.37 – 7.27 (m, 2H), 7.23 – 7.14 (m, 1H), 7.15 – 7.07 (m, 1H), 7.09 – 6.96 (m, 6H), 6.86 – 6.76 (m, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 4.42 (d, *J* = 2.1 Hz, 1H), 3.65 (s, 3H), 3.39 (dd, *J* = 9.5, 7.1 Hz, 1H), 3.22 (dd, *J* = 9.6, 7.5 Hz, 1H), 2.57 (dd, *J* = 7.5, 2.3 Hz, 1H), 2.25 (d, *J* = 7.2 Hz, 1H), 1.79 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.6, 172.2, 171.7, 137.8, 137.6, 136.6, 134.9, 130.6, 128.0(2C), 127.4, 126.9, 126.3(2C), 126.1, 125.9, 123.8, 121.7, 121.4, 112.7, 95.9, 58.7, 54.9, 52.1, 50.3, 43.9, 43.4, 19.9; **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{24}O_4Na$ $[M+Na]^+$: 447.1567, found: 447.1565.

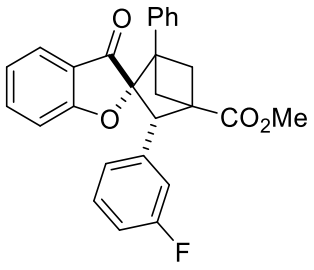


methyl 3'-(2-bromophenyl)-3-oxo-1'-phenyl-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (3k): Following the general procedure **A**, compound **3k** was obtained as a white solid in 77% yield (75.4 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate = 10/1); m.p. = 170-171 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 3H), 7.35 – 7.29 (m, 2H), 7.12 – 7.06 (m, 1H), 7.06 – 7.00 (m, 5H), 6.85 – 6.79 (m, 1H), 6.69 (d, *J* = 8.3 Hz, 1H), 4.55 (d, *J* = 2.2 Hz, 1H), 3.68 (s, 3H), 3.46 (dd, *J* = 9.5, 7.2 Hz, 1H), 3.14 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.56 (dd, *J* = 7.6, 2.3 Hz, 1H), 2.27 (d, *J* = 7.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.0, 172.0, 171.5, 137.3, 136.5(3), 136.4(6), 133.1, 128.5, 128.1, 128.0(2C), 127.4(1), 127.3(6), 126.4(2C), 126.2, 123.8, 122.2, 121.7, 112.4, 95.1, 58.6, 57.1, 52.3, 50.3, 43.5, 43.1;

HRMS (ESI-TOF, m/z): calcd for $C_{27}H_{21}Br^{79}O_4Na$ $[M+Na]^+$: 511.0516, found: 511.0515; calcd for $C_{27}H_{21}Br^{81}O_4Na$ $[M+Na]^+$: 513.0495, found: 513.0498.

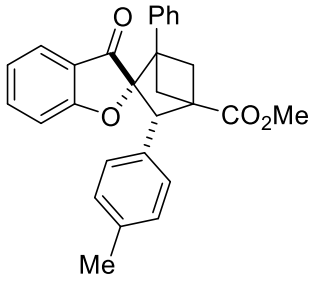


methyl 3-oxo-1'-phenyl-3'-(*m*-tolyl)-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (3l): Following the general procedure **A**, compound **3l** was obtained as a white solid in 76% yield (64.5 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate = 10/1); m.p. = 157-159 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 1H), 7.39 – 7.30 (m, 1H), 7.14 – 7.02 (m, 6H), 6.99 – 6.95 (m, 1H), 6.90 – 6.82 (m, 1H), 6.80 – 6.75 (m, 1H), 6.75 – 6.72 (m, 1H), 6.72 – 6.68 (m, 1H), 4.30 (d, *J* = 2.3 Hz, 1H), 3.67 (s, 3H), 3.38 (dd, *J* = 9.5, 7.1 Hz, 1H), 3.13 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.52 (dd, *J* = 7.5, 2.4 Hz, 1H), 2.28 (d, *J* = 7.1 Hz, 1H), 2.18 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.4, 172.1, 171.6, 137.9(0), 137.8(8), 137.0, 136.1, 128.5, 128.2, 128.0(2C), 127.7, 127.3, 126.4(2C), 124.7, 123.9, 121.7, 121.6, 112.8, 95.9, 58.5, 58.3, 52.1, 49.9, 44.6, 43.1, 21.5; **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{24}O_4Na$ $[M+Na]^+$: 447.1567, found: 447.1567.

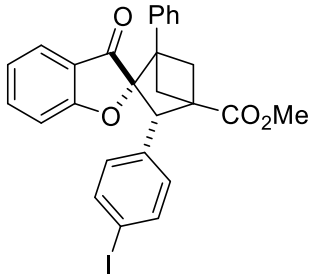


methyl 3'-(3-fluorophenyl)-3-oxo-1'-phenyl-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (3m): Following the general procedure **A**, compound **3m** was obtained as a white solid in 72% yield (61.7 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate = 10/1); m.p. = 163-165 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 1H), 7.41 – 7.32 (m, 1H), 7.18 – 7.11 (m, 1H), 7.11 – 7.03 (m, 5H), 6.92 – 6.83 (m, 2H), 6.78 – 6.68 (m, 3H), 4.31 (d, *J* = 2.2 Hz, 1H), 3.68 (s, 3H), 3.36 (dd, *J* = 9.6, 7.2 Hz, 1H), 3.12 (dd, *J* = 9.6, 7.7 Hz, 1H), 2.53 (dd, *J* = 7.7, 2.3 Hz, 1H), 2.30 (d, *J* = 7.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ

202.0, 171.7, 171.5, 162.8 (d, J_{C-F} = 245.6 Hz), 138.8 (d, J_{C-F} = 7.3 Hz), 138.2, 136.7, 129.8 (d, J_{C-F} = 8.4 Hz), 128.1(2C), 127.5, 126.4(2C), 124.0, 123.7 (d, J_{C-F} = 2.9 Hz), 121.9, 121.5, 114.7 (d, J_{C-F} = 22.0 Hz), 114.0 (d, J_{C-F} = 21.0 Hz), 112.7, 95.6, 58.4, 58.0 (d, J_{C-F} = 1.8 Hz), 52.2, 50.0, 44.5, 43.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.94; **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{21}FO_4Na$ $[M+Na]^+$: 451.1317, found: 451.1316.

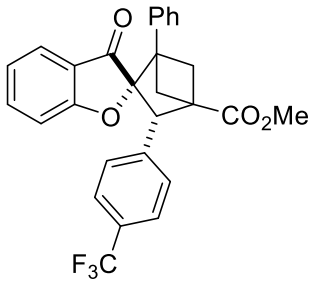


methyl 3-oxo-1'-phenyl-3'-(*p*-tolyl)-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (3n): Following the general procedure **A**, compound **3n** was obtained as a white solid in 75% yield (63.7 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate = 10/1); m.p. = 153-155 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.35 (ddd, *J* = 8.5, 7.2, 1.5 Hz, 1H), 7.13 – 7.01 (m, 5H), 7.05 – 6.97 (m, 2H), 6.90 – 6.82 (m, 3H), 6.75 – 6.69 (m, 1H), 4.31 (d, *J* = 2.3 Hz, 1H), 3.66 (s, 3H), 3.38 (dd, *J* = 9.6, 7.1 Hz, 1H), 3.12 (dd, *J* = 9.6, 7.5 Hz, 1H), 2.51 (dd, *J* = 7.5, 2.3 Hz, 1H), 2.30 – 2.24 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.4, 172.1, 171.6, 137.9, 137.0, 136.5, 133.1, 129.1(2C), 128.0(2C), 127.6(2C), 127.3, 126.4(2C), 123.9, 121.7(2C), 112.8, 95.9, 58.4, 58.2, 52.1, 50.0, 44.5, 43.1, 21.2; **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{24}O_4Na$ $[M+Na]^+$: 447.1567, found: 447.1567.

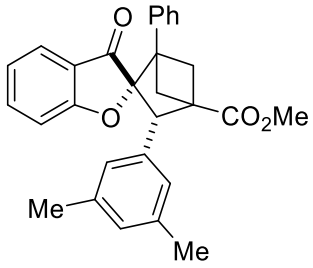


methyl 3'-(4-iodophenyl)-3-oxo-1'-phenyl-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (3o): Following the general procedure **A**, compound **3o** was obtained as a white solid in 76% yield (81.5 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1); $\mathbf{R}_f$ = 0.35 (petroleum ether/ethyl acetate = 10/1); m.p. = 178-180 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) 7.55 – 7.49 (m, 2H), 7.47 – 7.43 (m, 1H), 7.42 – 7.36 (m, 1H), 7.14 – 7.01 (m, 5H), 6.92 – 6.84 (m, 1H), 6.77 – 6.70 (m, 3H), 4.25

(d, *J* = 2.2 Hz, 1H), 3.67 (s, 3H), 3.36 (dd, *J* = 9.6, 7.2 Hz, 1H), 3.07 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.51 (dd, *J* = 7.7, 2.3 Hz, 1H), 2.29 (d, *J* = 7.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.0, 171.8, 171.5, 138.2, 137.5(2C), 136.7, 136.0, 129.8(2C), 128.1(2C), 127.5, 126.4(2C), 124.0, 121.9, 121.5, 112.8, 95.6, 92.5, 58.5, 57.9, 52.2, 49.9, 44.5, 43.0; **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{21}IO_4Na$ $[M+Na]^+$: 559.0377, found: 559.0373.

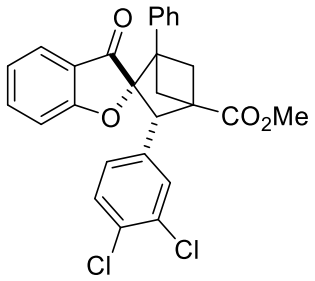


methyl 3-oxo-1'-phenyl-3'-(4-(trifluoromethyl)phenyl)-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (3p): Following the general procedure **A**, compound **3p** was obtained as a white solid in 72% yield (68.9 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate = 10/1); m.p. = 167-169 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 3H), 7.42 – 7.32 (m, 1H), 7.14 – 7.02 (m, 7H), 6.93 – 6.85 (m, 1H), 6.69 (dd, *J* = 8.4, 0.8 Hz, 1H), 4.40 – 4.35 (m, 1H), 3.69 (s, 3H), 3.39 (dd, *J* = 9.6, 7.2 Hz, 1H), 3.10 (dd, *J* = 9.6, 7.7 Hz, 1H), 2.56 (dd, *J* = 7.7, 2.3 Hz, 1H), 2.32 (d, *J* = 7.3 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.8, 171.7, 171.4, 140.4 (d, J_{C-F} = 1.4 Hz), 138.3, 136.5, 129.2 (q, J_{C-F} = 32.5 Hz), 128.1(2C), 128.1(2C), 127.5, 126.4(2C), 125.4 (q, J_{C-F} = 3.7 Hz)(2C), 124.2 (d, J_{C-F} = 272.1 Hz), 124.0, 122.0, 121.5, 112.7, 95.6, 58.5, 58.0, 52.3, 49.9, 44.5, 43.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.52; **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{21}F_3O_4Na$ $[M+Na]^+$: 501.1258, found: 501.1260.

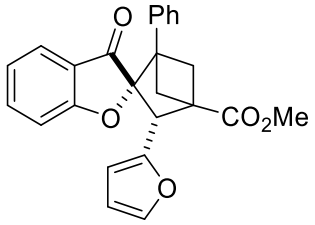


methyl 3'-(3,5-dimethylphenyl)-3-oxo-1'-phenyl-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (3q): Following the general procedure **A**, compound **3q** was obtained as a white solid in 70% yield (61.4 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1); $\mathbf{R}_f$ = 0.45 (petroleum ether/ethyl acetate = 10/1); m.p. = 168-169 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 1H), 7.40 – 7.31

(m, 1H), 7.16 – 7.00 (m, 5H), 6.91 – 6.81 (m, 1H), 6.81 – 6.77 (m, 1H), 6.75 – 6.68 (m, 1H), 6.56 – 6.51 (m, 2H), 4.26 (d, *J* = 2.3 Hz, 1H), 3.67 (s, 3H), 3.37 (dd, *J* = 9.6, 7.1 Hz, 1H), 3.11 (dd, *J* = 9.5, 7.5 Hz, 1H), 2.51 (dd, *J* = 7.6, 2.4 Hz, 1H), 2.27 (d, *J* = 7.1 Hz, 1H), 2.15 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.5, 172.2, 171.7, 137.8, 137.7(2C), 137.1, 136.0, 128.6, 128.0(2C), 127.3, 126.5(2C), 125.5(2C), 123.9, 121.8, 121.6, 112.8, 96.0, 58.5, 58.3, 52.1, 49.8, 44.6, 43.1, 21.4(2C); **HRMS** (ESI-TOF, m/z): calcd for $C_{29}H_{26}O_4Na$ $[M+Na]^+$: 461.1724, found: 461.1726.

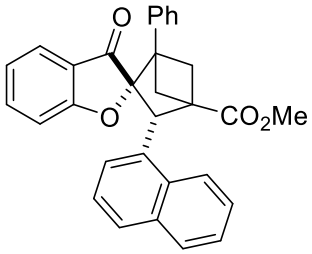


methyl 3'-(3,4-dichlorophenyl)-3-oxo-1'-phenyl-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (3r): Following the general procedure **A**, compound **3r** was obtained as a white solid in 68% yield (65.2 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate = 10/1); m.p. = 175-177 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 1H), 7.45 – 7.35 (m, 1H), 7.29 – 7.23 (m, 1H), 7.15 – 7.10 (m, 1H), 7.13 – 7.04 (m, 5H), 6.94 – 6.85 (m, 1H), 6.82 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 4.24 (d, *J* = 2.2 Hz, 1H), 3.69 (s, 3H), 3.35 (dd, *J* = 9.6, 7.3 Hz, 1H), 3.08 (dd, *J* = 9.7, 7.7 Hz, 1H), 2.53 (dd, *J* = 7.7, 2.3 Hz, 1H), 2.30 (d, *J* = 7.3 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.7, 171.5, 171.4, 138.3, 136.6, 136.5, 132.5, 131.1, 130.3, 129.8, 128.2(2C), 127.6, 127.5, 126.4(2C), 124.1, 122.1, 121.4, 112.8, 95.4, 58.4, 57.5, 52.3, 50.1, 44.5, 43.0; **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{20}Cl_2O_4Na$ $[M+Na]^+$: 501.0631, found: 501.0626.

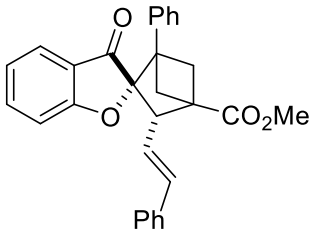


methyl 3'-(furan-2-yl)-3-oxo-1'-phenyl-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (3s): Following the general procedure **A**, compound **3s** was obtained as a white solid in 64% yield (51.3 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate

= 10/1); m.p. = 149-151 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.43 (m, 1H), 7.43 – 7.37 (m, 1H), 7.26 – 7.24 (m, 1H), 7.14 – 7.03 (m, 5H), 6.92 – 6.84 (m, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.27 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.15 (d, *J* = 3.2 Hz, 1H), 4.27 (d, *J* = 2.2 Hz, 1H), 3.69 (s, 3H), 3.35 (dd, *J* = 9.6, 7.3 Hz, 1H), 3.19 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.44 (dd, *J* = 7.5, 2.3 Hz, 1H), 2.27 (d, *J* = 7.3 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.8, 171.7, 171.4, 150.7, 142.1, 138.0, 136.7, 128.1(2C), 127.4, 126.5(2C), 124.0, 121.8, 121.3, 112.7, 110.1, 107.7, 95.2, 58.7, 52.6, 52.2, 49.8, 43.9, 43.4; **HRMS** (ESI-TOF, m/z): calcd for $C_{25}H_{20}O_5Na$ $[M+Na]^+$: 423.1203, found: 423.1203.

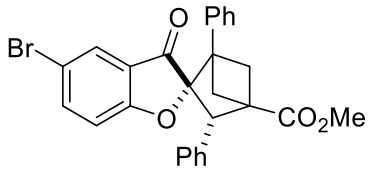


methyl 3'-(naphthalen-1-yl)-3-oxo-1'-phenyl-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (3t): Following the general procedure **A**, compound **3t** was obtained as a white solid in 60% yield (55.3 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate = 10/1); m.p. = 162-164°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 2H), 7.52 – 7.37 (m, 4H), 7.25 – 7.19 (m, 1H), 7.14 – 6.97 (m, 7H), 6.76 – 6.68 (m, 1H), 6.30 (d, *J* = 8.4 Hz, 1H), 4.96 (d, *J* = 2.1 Hz, 1H), 3.66 (s, 3H), 3.56 (dd, *J* = 9.5, 7.2 Hz, 1H), 3.28 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.63 (dd, *J* = 7.6, 2.2 Hz, 1H), 2.36 (d, *J* = 7.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.3, 172.4, 171.9, 137.6, 136.7, 133.7, 132.9, 132.5, 128.6, 128.0(2C), 127.7, 127.4, 126.4(2C), 125.6, 125.5, 125.3, 123.6(3), 123.6(0), 123.2, 121.8, 121.4, 112.3, 96.0, 58.6, 54.7, 52.2, 50.1, 44.1, 43.3; **HRMS** (ESI-TOF, m/z): calcd for $C_{31}H_{24}O_4Na$ $[M+Na]^+$: 483.1567, found: 483.1565.

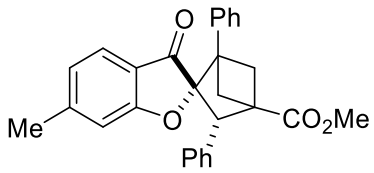


methyl (2*S*,3'*S*)-3-oxo-1'-phenyl-3'-((*E*)-styryl)-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (3u): Following the general procedure **A**, compound **3u** was obtained as colorless oil in 41% yield (35.8 mg); purified by silica gel column

chromatography (petroleum ether/ethyl acetate = 20/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 7.7, 1.3 Hz, 2H), 7.39 – 7.17 (m, 5H), 7.17 – 7.04 (m, 5H), 6.97 (dd, *J* = 8.6, 1.2 Hz, 1H), 6.89 – 6.82 (m, 1H), 6.44 – 6.30 (m, 2H), 3.74 (dd, *J* = 8.4, 2.2 Hz, 1H), 3.68 (s, 3H), 3.31 (dd, *J* = 9.5, 7.3 Hz, 1H), 3.01 (dd, *J* = 9.5, 7.7 Hz, 1H), 2.34 (dd, *J* = 7.7, 2.3 Hz, 1H), 2.22 (d, *J* = 7.3 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.2, 171.5(2), 171.5(1), 138.0, 137.0, 136.9, 134.5, 128.6(2C), 128.1(2C), 127.7, 127.4, 126.6(2C), 126.5(2C), 123.9, 123.8, 121.8, 121.6, 112.9, 96.2, 58.6, 57.8, 52.0, 51.2, 43.2, 42.6; **HRMS** (ESI-TOF, m/z): calcd for $C_{29}H_{24}O_4Na$ $[M+Na]^+$: 459.1567, found: 459.1569.

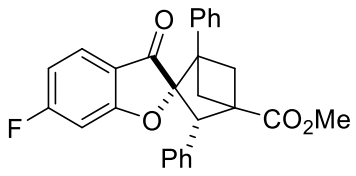


methyl 5-bromo-3-oxo-1',3'-diphenyl-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (3v): Following the general procedure **A**, compound **3v** was obtained as a white solid in 86% yield (84.2 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate = 10/1); m.p. = 169-171 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 2.2, 0.5 Hz, 1H), 7.42 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.24 – 7.15 (m, 3H), 7.14 – 7.05 (m, 5H), 7.00 – 6.90 (m, 2H), 6.60 (dd, *J* = 8.8, 0.5 Hz, 1H), 4.33 (d, *J* = 2.3 Hz, 1H), 3.67 (s, 3H), 3.34 (dd, *J* = 9.6, 7.2 Hz, 1H), 3.11 (dd, *J* = 9.6, 7.7 Hz, 1H), 2.53 (dd, *J* = 7.6, 2.4 Hz, 1H), 2.29 (d, *J* = 7.7 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.9, 171.9, 170.2, 140.5, 136.6, 135.9, 128.5(2C), 128.2(2C), 127.7(2C), 127.6, 127.1, 126.5, 126.4(2C), 123.3, 114.5, 114.3, 96.9, 58.8, 58.5, 52.2, 49.9, 44.6, 43.1; **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{21}Br^{79}O_4Na$ $[M+Na]^+$: 511.0516, found: 511.0513; calcd for $C_{27}H_{21}Br^{81}O_4Na$ $[M+Na]^+$: 513.0495, found: 513.0498.

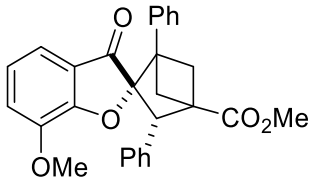


methyl 6-methyl-3-oxo-1',3'-diphenyl-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (3w): Following the general procedure **A**, compound **3w** was obtained as a white solid in 44% yield (37.4 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate = 10/1); m.p. = 159-161 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.9 Hz, 1H), 7.24 –

7.14 (m, 3H), 7.14 – 7.02 (m, 5H), 6.97 (dd, *J* = 7.6, 1.9 Hz, 2H), 6.68 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.48 (s, 1H), 4.33 (d, *J* = 2.2 Hz, 1H), 3.66 (s, 3H), 3.39 (dd, *J* = 9.5, 7.1 Hz, 1H), 3.12 (dd, *J* = 9.6, 7.5 Hz, 1H), 2.51 (dd, *J* = 7.5, 2.4 Hz, 1H), 2.27 (d, *J* = 7.2 Hz, 1H), 2.23 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.6, 172.2, 172.1, 150.0, 137.1, 136.4, 128.4(2C), 128.0(2C), 127.8(2C), 127.3, 126.8, 126.5(2C), 123.5, 123.4, 119.3, 112.7, 96.0, 58.4, 58.3, 52.1, 49.9, 44.6, 43.1, 22.6; **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{24}O_4Na$ $[M+Na]^+$: 447.1567, found: 447.1560.

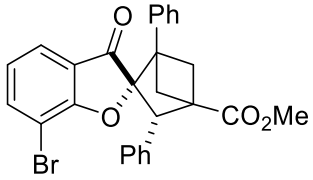


methyl 6-fluoro-3-oxo-1',3'-diphenyl-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (3x): Following the general procedure **A**, compound **3x** was obtained as a white solid in 85% yield (72.8 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate = 10/1); m.p. = 161-163 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 8.5, 5.8 Hz, 1H), 7.24 – 7.18 (m, 3H), 7.14 – 7.04 (m, 5H), 7.00 – 6.94 (m, 2H), 6.64 – 6.55 (m, 1H), 6.37 (dd, *J* = 9.2, 2.1 Hz, 1H), 4.34 (d, *J* = 2.3 Hz, 1H), 3.67 (s, 3H), 3.36 (dd, *J* = 9.6, 7.1 Hz, 1H), 3.11 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.53 (dd, *J* = 7.6, 2.4 Hz, 1H), 2.29 (d, *J* = 7.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.2, 172.9 (d, J_{C-F} = 15.2 Hz), 171.9, 169.3 (d, J_{C-F} = 258.1 Hz), 136.7, 136.0, 128.5(2C), 128.2(2C), 127.6(2C), 127.5, 127.1, 126.4(2C), 125.9 (d, J_{C-F} = 12.2 Hz), 118.3 (d, J_{C-F} = 1.5 Hz), 110.7 (d, J_{C-F} = 24.5 Hz), 100.1 (d, J_{C-F} = 26.0 Hz), 97.3, 58.4(4), 58.4(2), 52.2, 49.9, 44.5, 43.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -96.76; **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{21}FO_4Na$ $[M+Na]^+$: 451.1317, found: 451.1319.

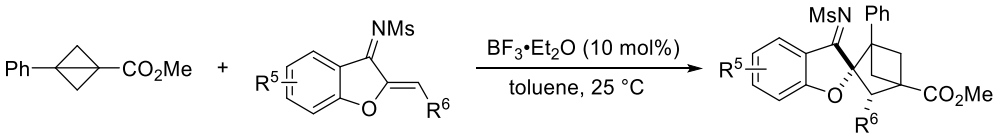


methyl 7-methoxy-3-oxo-1',3'-diphenyl-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (3y): Following the general procedure **A**, compound **3y** was obtained as a white solid in 65% yield (57.3 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1); $\mathbf{R}_f$ = 0.35 (petroleum ether/ethyl acetate = 10/1); m.p. = 165-167℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 – 7.04 (m, 9H), 7.03 – 6.96 (m, 2H), 6.91 – 6.85 (m, 1H), 6.78 (t, *J* = 7.7 Hz, 1H), 4.32 (d, *J* = 2.2 Hz, 1H), 3.66 (s, 3H), 3.50

(s, 3H), 3.38 (dd, *J* = 9.6, 7.1 Hz, 1H), 3.21 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.53 (dd, *J* = 7.6, 2.3 Hz, 1H), 2.30 (d, *J* = 7.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.3, 172.0, 161.9, 145.8, 136.9, 136.2, 128.4(2C), 128.1(2C), 127.8(2C), 127.4, 126.9, 126.4(2C), 123.3, 122.2, 121.9, 115.9, 96.3, 58.9, 58.3, 57.3, 52.1, 50.0, 44.7, 43.2; **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{24}O_5Na$ $[M+Na]^+$: 463.1516, found: 463.1516.



methyl 7-bromo-3-oxo-1',3'-diphenyl-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (3z): Following the general procedure **A**, compound **3z** was obtained as a white solid in 87% yield (85.1 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate = 10/1); m.p. = 168-170 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.37 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.26 – 7.14 (m, 3H), 7.16 – 7.09 (m, 4H), 7.12 – 6.99 (m, 3H), 6.79 – 6.70 (m, 1H), 4.32 (d, *J* = 2.2 Hz, 1H), 3.65 (s, 3H), 3.33 (dd, *J* = 9.6, 7.0 Hz, 1H), 3.26 (dd, *J* = 9.6, 7.4 Hz, 1H), 2.53 (dd, *J* = 7.5, 2.4 Hz, 1H), 2.32 (d, *J* = 7.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.6, 171.7, 167.9, 140.2, 136.6, 135.6, 128.4(2C), 128.2(2C), 128.0(2C), 127.5, 127.2, 126.3(2C), 123.1, 122.8(4), 122.7(5), 106.1, 97.1, 58.9, 58.3, 52.1, 50.4, 44.5, 43.2; **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{21}Br^{79}O_4Na$ $[M+Na]^+$: 511.0516, found: 511.0514; calcd for $C_{27}H_{21}Br^{81}O_4Na$ $[M+Na]^+$: 513.0495, found: 513.0500.

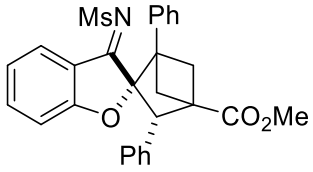


1a **5** **6**

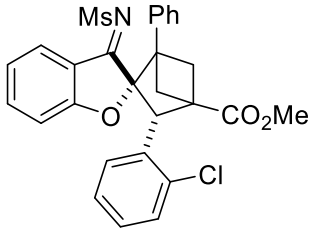
General procedure B:

Under a nitrogen atmosphere, benzofuran-derived azadienes **5** (0.20 mmol, 1.0 equiv.) was added into a flame-dried Schlenk tube equipped with a magnetic stir bar. The tube was evacuated and back-filled with nitrogen for five times. Then the anhydrous toluene (3.0 mL) were added via syringe sequentially. Then, $BF_3 \cdot Et_2O$ (2.8 mg, 0.02 mmol, 10 mol%) was added and the mixture was stirred at 25 °C. Then, BCB **1a** (0.30 mmol, 1.5 equiv.) in toluene (1.0 mL) was added dropwise during 5 minutes. Until **5** was consumed (monitored by TLC) (10 minutes were enough in all examples). Then, the reaction mixture was quenched with water and

extracted with ethyl acetate for three times. The resulted filtrate was separated. The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by column chromatography (petroleum ether/ethyl acetate) to give the corresponding products **6**.

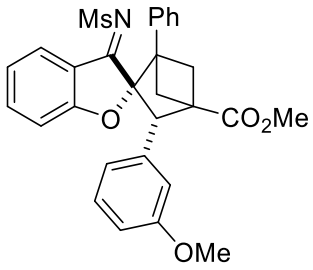


methyl (*Z*)-3-((methylsulfonyl)imino)-1',3'-diphenyl-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (6a): Following the general procedure **B**, compound **6a** was obtained as a white solid in 99% yield (96.5 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate = 4/1); m.p. = 171-173 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 – 8.18 (m, 1H), 7.35 – 7.30 (m, 1H), 7.23 – 7.16 (m, 3H), 7.13 – 7.03 (m, 5H), 7.01 – 6.96 (m, 2H), 6.89 – 6.83 (m, 1H), 6.64 – 6.57 (m, 1H), 4.41 (d, *J* = 2.4 Hz, 1H), 3.69 (s, 3H), 3.42 (dd, *J* = 9.8, 7.3 Hz, 1H), 3.39 (s, 3H), 3.21 (dd, *J* = 9.7, 7.6 Hz, 1H), 2.58 (dd, *J* = 7.6, 2.5 Hz, 1H), 2.31 (d, *J* = 7.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.4, 171.9, 169.9, 138.9, 136.4, 135.9, 130.2, 128.5(2C), 128.1(2C), 127.7, 127.5(2C), 127.1, 126.4(2C), 122.1, 118.1, 112.0, 98.1, 61.4, 60.4, 52.2, 49.6, 44.8, 43.7, 43.4; **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{25}NO_5SNa$ $[M+Na]^+$: 510.1346, found: 510.1350.

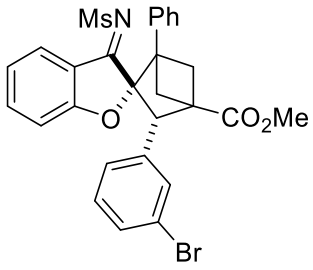


methyl (*Z*)-3'-(2-chlorophenyl)-3-((methylsulfonyl)imino)-1'-phenyl-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (6b): Following the general procedure **B**, compound **6b** was obtained as a white solid in 90% yield (94.0 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1); $\mathbf{R}_f$ = 0.45 (petroleum ether/ethyl acetate = 4/1); m.p. = 179-181 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) 8.17 – 8.10 (m, 1H), 7.38 – 7.13 (m, 5H), 7.09 – 6.99 (m, 5H), 6.88 – 6.77 (m, 1H), 6.66 – 6.59 (m, 1H), 4.60 (d, *J* = 2.4 Hz, 1H), 3.70 (s, 3H), 3.53 (dd, *J* = 9.6, 7.2 Hz, 1H), 3.39 (s, 3H), 3.18 (dd, *J* = 9.7, 7.7 Hz, 1H), 2.62 (dd, *J* = 7.6, 2.5 Hz, 1H), 2.30 (d, *J* = 7.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$)

δ 182.7, 171.8, 169.9, 138.2, 135.9, 135.6, 134.7, 130.3, 129.8, 128.3, 128.0(2C), 127.7, 127.6, 126.7, 126.3(2C), 121.9, 118.4, 111.6, 97.2, 60.6, 57.7, 52.3, 49.6, 43.8, 43.5, 43.4; **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{24}ClNO_5SNa$ $[M+Na]^+$: 544.0956, found: 544.0955.

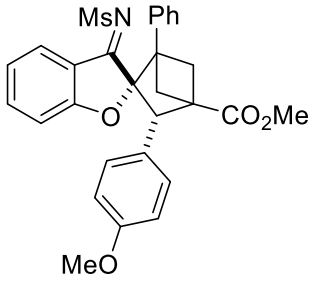


methyl (*Z*)-3'-(3-methoxyphenyl)-3-((methylsulfonyl)imino)-1'-phenyl-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (6c): Following the general procedure **B**, compound **6c** was obtained as a white solid in 85% yield (88.0 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1); $\mathbf{R}_f$ = 0.30 (petroleum ether/ethyl acetate = 4/1); m.p. = 176-178 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 – 8.19 (m, 1H), 7.39 – 7.30 (m, 1H), 7.16 – 7.02 (m, 6H), 6.92 – 6.83 (m, 1H), 6.75 – 6.68 (m, 1H), 6.65 (d, *J* = 8.5 Hz, 1H), 6.59 – 6.52 (m, 1H), 6.54 – 6.48 (m, 1H), 4.37 (d, *J* = 2.4 Hz, 1H), 3.71 (s, 3H), 3.60 (s, 3H), 3.46 – 3.37 (m, 4H), 3.20 (dd, *J* = 9.7, 7.6 Hz, 1H), 2.57 (dd, *J* = 7.6, 2.5 Hz, 1H), 2.30 (d, *J* = 7.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.3, 171.8, 169.9, 159.5, 138.8, 137.3, 136.3, 130.2, 129.4, 128.0(2C), 127.6, 126.3(2C), 121.9, 119.8, 118.1, 112.8, 112.7, 111.9, 98.0, 61.4, 60.2, 55.0, 52.1, 49.4, 44.8, 43.6, 43.3; **HRMS** (ESI-TOF, m/z): calcd for $C_{29}H_{27}NO_6SNa$ $[M+Na]^+$: 540.1452, found: 540.1452.

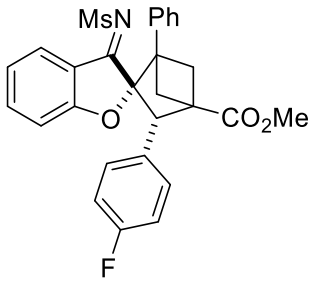


methyl (*Z*)-3'-(3-bromophenyl)-3-((methylsulfonyl)imino)-1'-phenyl-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (6d): Following the general procedure **B**, compound **6d** was obtained as a white solid in 96% yield (108.8 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1); $\mathbf{R}_f$ = 0.35 (petroleum ether/ethyl acetate = 4/1); m.p. = 188-189 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.40 – 7.28 (m, 2H), 7.21 – 7.18 (m, 1H), 7.14 – 7.01 (m, 6H), 6.93 – 6.83 (m, 2H), 6.66 (d, *J* = 8.4 Hz, 1H), 4.34 (d, *J* = 2.4 Hz, 1H), 3.70 (s, 3H), 3.44 – 3.35 (m, 4H), 3.19

(dd, J = 9.7, 7.8 Hz, 1H), 2.58 (dd, J = 7.7, 2.5 Hz, 1H), 2.31 (d, J = 7.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.0, 171.5, 169.7, 139.0, 138.2, 136.0, 130.4(2C), 130.3, 130.0, 128.1(2C), 127.8, 126.8, 126.4(2C), 122.5, 122.2, 118.0, 112.0, 97.8, 60.6, 60.4, 52.3, 49.6, 44.7, 43.6, 43.4; **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{24}Br^{79}NO_5SNa$ $[M+Na]^+$: 588.0451, found: 588.0454; calcd for $C_{28}H_{24}Br^{81}NO_5SNa$ $[M+Na]^+$: 590.0431, found: 590.0436.

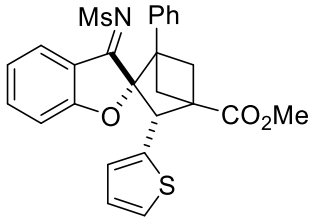


methyl (*Z*)-3'-(4-methoxyphenyl)-3-((methylsulfonyl)imino)-1'-phenyl-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (6e): Following the general procedure **B**, compound **6e** was obtained as a white solid in 83% yield (85.9 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate = 4/1); m.p. = 179-180 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (dd, J = 8.6, 1.2 Hz, 1H), 7.38 – 7.31 (m, 1H), 7.15 – 7.03 (m, 5H), 6.97 – 6.91 (m, 2H), 6.90 – 6.84 (m, 1H), 6.76 – 6.70 (m, 2H), 6.66 (d, J = 8.2 Hz, 1H), 4.33 (d, J = 2.3 Hz, 1H), 3.75 (s, 3H), 3.69 (s, 3H), 3.44 – 3.36 (m, 4H), 3.21 (dd, J = 9.7, 7.6 Hz, 1H), 2.55 (dd, J = 7.6, 2.5 Hz, 1H), 2.28 (d, J = 7.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.6, 172.0, 169.9, 158.6, 138.8, 136.5, 130.2, 128.8(2C), 128.1(2C), 127.9, 127.7, 126.4(2C), 122.1, 118.1, 113.8(2C), 112.1, 98.2, 61.1, 60.4, 55.3, 52.2, 49.9, 44.9, 43.7, 43.4; **HRMS** (ESI-TOF, m/z): calcd for $C_{29}H_{27}NO_6SNa$ $[M+Na]^+$: 540.1452, found: 540.1452.

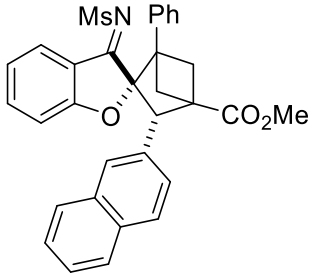


methyl (*Z*)-3'-(4-fluorophenyl)-3-((methylsulfonyl)imino)-1'-phenyl-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (6f): Following the general procedure **B**, compound **6f** was obtained as a white solid in 94% yield (95.0 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate = 4/1); m.p. = 176-178 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 – 8.17 (m,

1H), 7.39 – 7.30 (m, 1H), 7.16 – 7.02 (m, 5H), 7.03 – 6.94 (m, 2H), 6.94 – 6.83 (m, 3H), 6.64 (d, *J* = 8.4 Hz, 1H), 4.36 (d, *J* = 2.3 Hz, 1H), 3.69 (s, 3H), 3.45 – 3.35 (m, 4H), 3.19 (dd, *J* = 9.7, 7.7 Hz, 1H), 2.57 (dd, *J* = 7.6, 2.5 Hz, 1H), 2.31 (d, *J* = 7.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.2, 171.7, 169.8, 161.8 (d, J_{C-F} = 245.8 Hz), 139.0, 136.2, 131.6 (d, J_{C-F} = 3.3 Hz), 130.3, 129.3 (d, J_{C-F} = 8.0 Hz)(2C), 128.1(2C), 127.8, 126.4(2C), 122.2, 118.0, 115.4 (d, J_{C-F} = 21.4 Hz)(2C), 112.0, 97.9, 60.8, 60.4, 52.2, 49.8, 44.8, 43.6, 43.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.17; **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{24}FNO_5SNa$ $[M+Na]^+$: 528.1252, found: 528.1255.

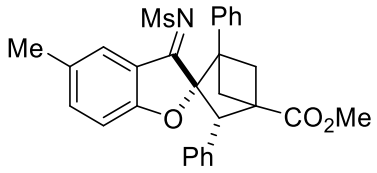


methyl (*Z*)-3-((methylsulfonyl)imino)-1'-phenyl-3'-(thiophen-2-yl)-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (6g): Following the general procedure **B**, compound **6g** was obtained as a white solid in 67% yield (66.1 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate = 4/1); m.p. = 165-167 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.42 – 7.34 (m, 1H), 7.19 (dd, *J* = 4.7, 1.7 Hz, 1H), 7.16 – 7.04 (m, 5H), 6.94 – 6.79 (m, 4H), 4.58 (d, *J* = 2.4 Hz, 1H), 3.65 (s, 3H), 3.44 – 3.35 (m, 4H), 3.27 (dd, *J* = 9.8, 7.9 Hz, 1H), 2.49 (dd, *J* = 7.9, 2.5 Hz, 1H), 2.27 (d, *J* = 7.3 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.0, 171.1, 169.8, 138.9, 137.6, 136.1, 130.3, 128.1(2C), 127.8, 127.1, 126.5(2C), 126.2, 125.5, 122.3, 118.0, 112.1, 97.2, 60.7, 57.7, 52.1, 51.9, 44.0, 43.6, 43.4; **HRMS** (ESI-TOF, m/z): calcd for $C_{26}H_{23}NO_5S_2Na$ $[M+Na]^+$: 516.0910, found: 516.0919.

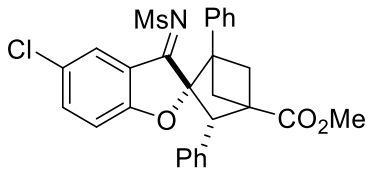


methyl (*Z*)-3-((methylsulfonyl)imino)-3'-(naphthalen-2-yl)-1'-phenyl-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (6h): Following the general procedure **B**, compound **6h** was obtained as a white solid in 90% yield (96.8 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1); $\mathbf{R}_f$ = 0.35 (petroleum

ether/ethyl acetate = 4/1); m.p. = 175-177 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 – 8.18 (m, 1H), 7.79 – 7.69 (m, 2H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.56 (d, *J* = 1.7 Hz, 1H), 7.49 – 7.39 (m, 2H), 7.31 – 7.23 (m, 1H), 7.15 – 7.03 (m, 5H), 6.97 (dd, *J* = 8.5, 1.9 Hz, 1H), 6.85 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 1H), 6.55 – 6.50 (m, 1H), 4.57 (d, *J* = 2.4 Hz, 1H), 3.68 (s, 3H), 3.48 (dd, *J* = 9.7, 7.1 Hz, 1H), 3.42 (s, 3H), 3.33 (dd, *J* = 9.7, 7.6 Hz, 1H), 2.66 (dd, *J* = 7.6, 2.5 Hz, 1H), 2.35 (d, *J* = 7.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.4, 172.0, 169.9, 138.9, 136.3, 133.7, 133.4, 132.5, 130.2, 128.0(9)(2C), 128.0(6)(2C), 127.7(3), 127.6(5), 126.5, 126.4(2C), 126.2, 125.9, 125.5, 122.1, 118.0, 112.0, 98.1, 61.3, 60.7, 52.2, 49.7, 44.8, 43.7, 43.4; **HRMS** (ESI-TOF, m/z): calcd for $C_{32}H_{27}NO_5SNa$ $[M+Na]^+$: 560.1503, found: 560.1501.

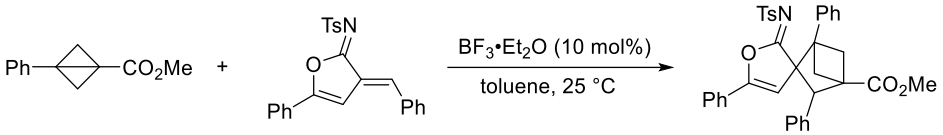


methyl (*Z*)-5-methyl-3-((methylsulfonyl)imino)-1',3'-diphenyl-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (6i): Following the general procedure **B**, compound **6i** was obtained as a white solid in 84% yield (84.3 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate = 4/1); m.p. = 167-169 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 1H), 7.23 – 7.13 (m, 3H), 7.17 – 7.03 (m, 6H), 6.97 (dd, *J* = 7.5, 2.0 Hz, 2H), 6.51 (d, *J* = 8.5 Hz, 1H), 4.39 (d, *J* = 2.4 Hz, 1H), 3.68 (s, 3H), 3.43 (dd, *J* = 9.7, 7.1 Hz, 1H), 3.38 (s, 3H), 3.20 (dd, *J* = 9.7, 7.7 Hz, 1H), 2.57 (dd, *J* = 7.6, 2.5 Hz, 1H), 2.30 (d, *J* = 7.1 Hz, 1H), 2.20 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.5, 172.0, 168.6, 140.6, 136.5, 135.9, 131.6, 129.3, 128.4(2C), 128.1(2C), 127.7, 127.5(2C), 127.0, 126.4(2C), 118.0, 111.6, 98.2, 61.6, 60.3, 52.2, 49.5, 44.9, 43.7, 43.4, 21.0; **HRMS** (ESI-TOF, m/z): calcd for $C_{29}H_{27}NO_5SNa$ $[M+Na]^+$: 524.1503, found: 524.1489.



methyl (*Z*)-5-chloro-3-((methylsulfonyl)imino)-1',3'-diphenyl-3*H*-spiro[benzofuran-2,2'-bicyclo[2.1.1]hexane]-4'-carboxylate (6j): Following the general procedure **B**, compound **6j** was obtained as a white solid in 99% yield (103.4 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate = 4/1); m.p. = 176-178 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 2.3

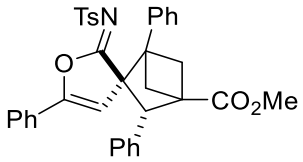
Hz, 1H), 7.31 – 7.23 (m, 1H), 7.26 – 7.16 (m, 3H), 7.18 – 7.07 (m, 3H), 7.07 (dd, *J* = 7.5, 2.1 Hz, 2H), 6.97 (dd, *J* = 7.6, 2.0 Hz, 2H), 6.58 (d, *J* = 8.9 Hz, 1H), 4.39 (d, *J* = 2.4 Hz, 1H), 3.69 (s, 3H), 3.44 – 3.34 (m, 4H), 3.19 (dd, *J* = 9.7, 7.7 Hz, 1H), 2.59 (dd, *J* = 7.7, 2.5 Hz, 1H), 2.31 (d, *J* = 7.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.2, 171.8, 168.2, 138.9, 136.1, 135.6, 129.3, 128.6(2C), 128.2(2C), 127.9, 127.5(2C), 127.2(7), 127.2(5), 126.3(2C), 119.0, 113.2, 99.1, 61.8, 60.6, 52.2, 49.6, 44.9, 43.7, 43.4; **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{24}ClNO_5SNa$ $[M+Na]^+$: 544.0956, found: 544.0963.



1a **5k** **6k**

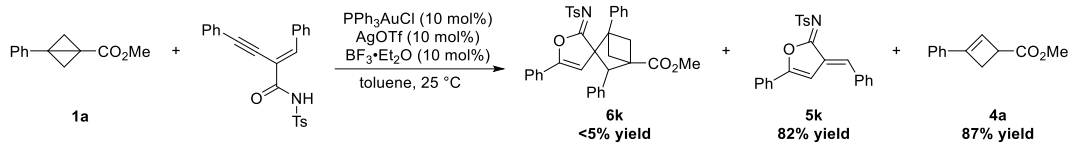
General procedure C:

Under a nitrogen atmosphere, BCB **1a** (0.40 mmol, 2.0 equiv.) and furan-derived azadiene **5k** (0.20 mmol, 1.0 equiv.) were added sequentially into a flame-dried Schlenk tube equipped with a magnetic stir bar. The tube was evacuated and back-filled with nitrogen for five times. Then the anhydrous toluene (4.0 mL) was added via syringe sequentially. Then, $BF_3 \cdot Et_2O$ (2.8 mg, 0.02 mmol, 10 mol%) was added and the mixture was stirred at 25 ℃ until **5k** was consumed (monitored by TLC). Then, the reaction mixture was quenched with water and extracted with ethyl acetate for three times. The resulted filtrate was separated. The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by column chromatography (petroleum ether/ethyl acetate = 20:1) to give the corresponding product **6k**.



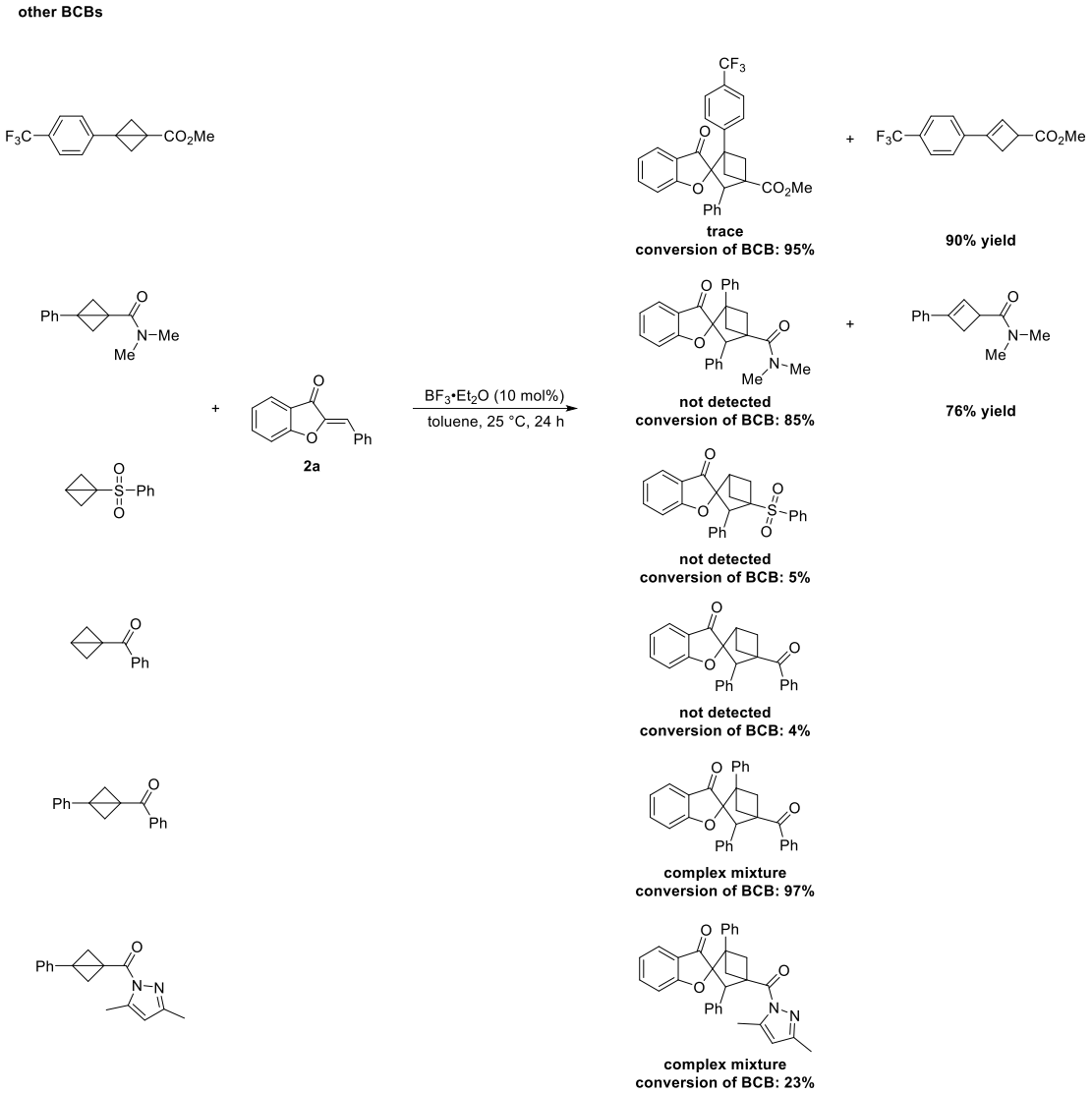
methyl (*E*)-1,3,5'-triphenyl-2'-(tosylimino)-2'*H*-spiro[bicyclo[2.1.1]hexane-2,3'-furan]-4-carboxylate (6k): Following the general procedure **C,** compound **6k** was obtained as a white solid in 84% yield (99.1 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1); $\mathbf{R}_f$ = 0.35 (petroleum ether/ethyl acetate = 10/1); m.p. = 164-165 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.19 (m, 5H), 7.20 – 7.16 (m, 1H), 7.15 – 7.10 (m, 2H), 7.10 – 6.99 (m, 5H), 6.93 – 6.87 (m, 2H), 5.21 (s, 1H), 4.44 (d, *J* = 2.0 Hz, 1H), 3.65 (s, 3H), 3.53 (dd, *J* = 9.7, 7.4 Hz, 1H), 2.72 (dd, *J* = 9.7, 8.0 Hz, 1H), 2.56 (dd, *J* = 8.0, 2.2 Hz, 1H), 2.45 (s, 3H), 2.19 (d, *J* = 7.3 Hz, 1H); **^{13}C NMR**

(100 MHz, $CDCl_3$) δ 175.6, 172.0, 153.3, 144.0, 138.3, 137.9, 137.2, 130.0, 129.6(2C), 128.9(2C), 128.6(2C), 128.1(2C), 127.8(2C), 127.6, 127.3(2C), 127.2, 127.0, 126.1(2C), 125.2(2C), 104.3, 68.0, 61.0, 60.4, 52.2, 50.3, 45.1, 43.0, 21.8; **HRMS** (ESI-TOF, m/z): calcd for $C_{36}H_{31}NO_5SNa$ $[M+Na]^+$: 612.1816, found: 612.1819.

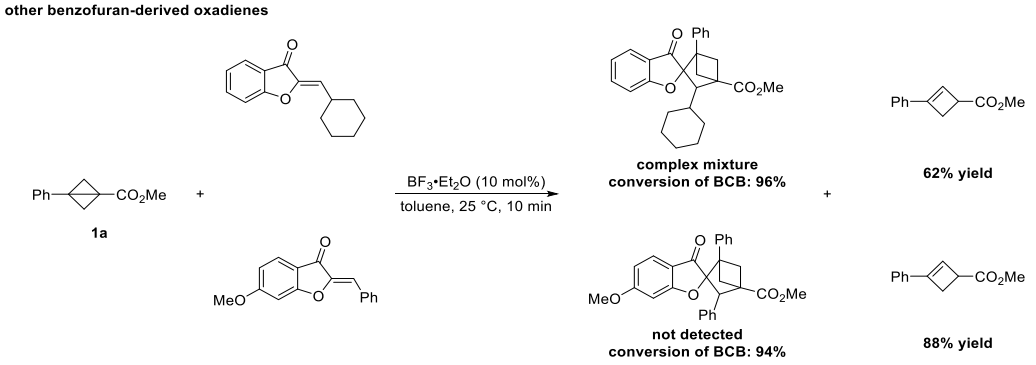


Under a nitrogen atmosphere, Ph_3PAuCl (9.9 mg, 0.02 mmol, 10 mol%) and AgOTf (5.1 mg, 0.02 mmol, 10 mol%) were added sequentially into a flame-dried Schlenk tube equipped with a magnetic stir bar. The tube was evacuated and back-filled with nitrogen for five times. Then the anhydrous toluene (4.0 mL) was added via syringe sequentially. In case of turbidity (AgCl precipitation) in the solution of tube, the allylenamide (80.3 mg, 0.20 mmol, 1.0 equiv) was added and stirred for 30 seconds. Then, BCB **1a** (37.6 mg, 0.40 mmol, 2.0 equiv.) and $BF_3 \cdot Et_2O$ (2.8 mg, 0.02 mmol, 10 mol%) was added and the mixture was stirred at 25 ℃. After 10 mins, **1a** was consumed (monitored by TLC). Then, the solvent was evaporated, and analyzed by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. Only trace amount (<5% yield) of the desired product **6k** was detected. However, the furan-derived azadiene **5k** could generate in high yield (82% yield) and most of the BCB **1a** transformed into the·cyclobutene **4a** (87% yield).

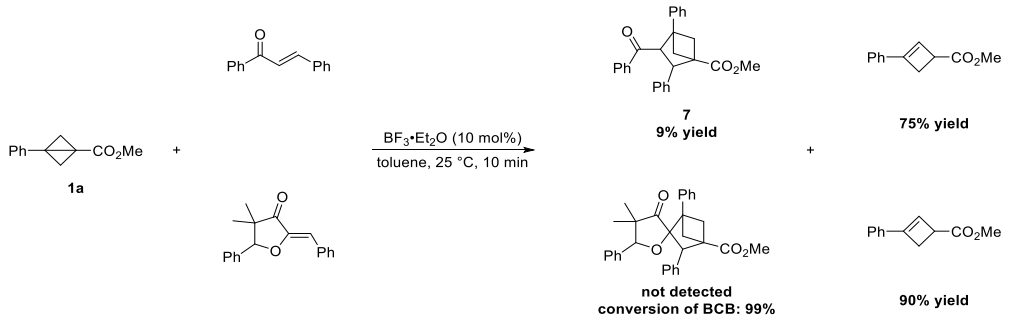
Following the general procedure **A**, The BCB containing the trifluoromethyl group gave only trace amount of the desired products with the cyclobutene as byproduct. *N*,*N*-dimethyl-3-phenylbicyclo[1.1.0]butane-1-carboxamide, monosubstituted BCB sulfone and monosubstituted BCB ketone have been evaluated and the reactions didn't occur. Moreover, disubstituted BCB ketone and BCB containing an acyl pyrazole group gave complex reaction mixtures.

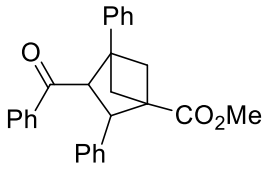


Benzofuran-derived oxadiene with aliphatic group (cyclohexyl) gave a complex reaction mixture. The 6-OMe substituted benzofuran-derived oxadiene failed to give the desire product and gave cyclobutene **4a** as byproduct.



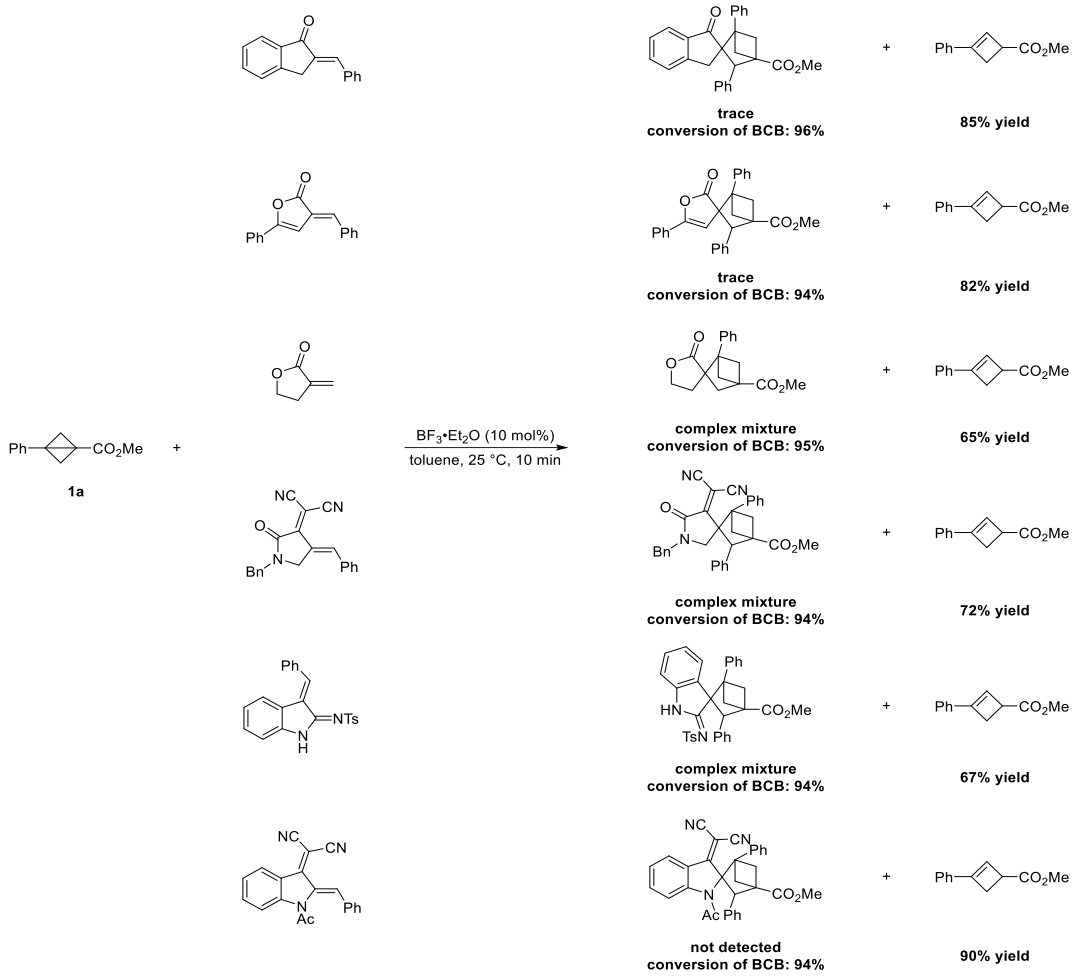
In addition, acyclic oxadiene afforded ideal product in 9% yield. Encouragely, monocyclic oxadiene without dearomatization driving force was investigated, but no target product was observed.



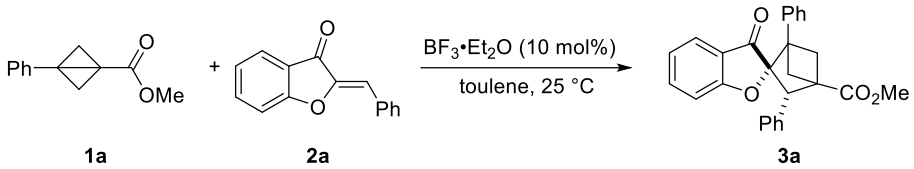


methyl 3-benzoyl-2,4-diphenylbicyclo[2.1.1]hexane-1-carboxylate (7): Following the general procedure **A,** compound **7** was obtained as a white solid in 9% yield (7.1 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50/1); $\mathbf{R}_f$ = 0.40 (petroleum ether/ethyl acetate = 20/1); m.p. = 121-123 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 2H), 7.37 – 7.20 (m, 6H), 7.19 – 7.01 (m, 7H), 4.37 (dd, *J* = 4.9, 1.9 Hz, 1H), 4.23 (dd, *J* = 4.9, 1.7 Hz, 1H), 3.64 (s, 3H), 3.08 (dd, *J* = 9.6, 6.8 Hz, 1H), 2.70 (dd, *J* = 9.6, 7.4 Hz, 1H), 2.34 (dd, *J* = 7.4, 1.9 Hz, 1H), 2.19 (dd, *J* = 6.8, 1.7 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.4, 172.7, 141.2, 140.3, 137.9, 132.8, 128.8(2C), 128.4(2C), 128.3(2C), 128.2(2C), 127.6(2C), 126.9, 125.9(2C), 59.1, 55.5, 52.5, 52.0, 51.8, 45.2, 43.9; **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{24}O_3Na$ $[M+Na]^+$: 419.1618, found: 419.1620.

To further expand the substrate scope of $BF_3{\cdot}Et_2O$-Catalyzed formal [2π + 2σ] cycloaddition reaction, several other *α,β*-unsaturated compounds were tested following the general procedure **A**.



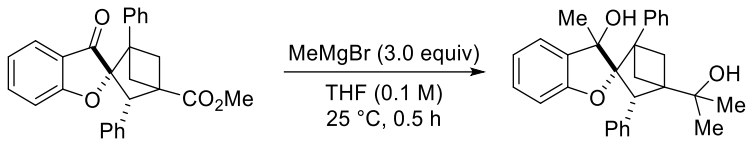
7. Scale-up experiment



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

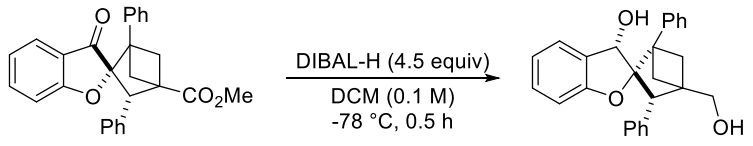
Under a nitrogen atmosphere, BCB **1a** (1.13 g, 6.0 mmol, 3.0 equiv.) and benzofuran-derived oxadiene **2a** (0.44 g, 2.0 mmol, 1.0 equiv.) were added sequentially into a flame-dried Schlenk flask equipped with a magnetic stir bar. The flask was evacuated and back-filled with nitrogen for five times. Then the anhydrous toluene (40.0 mL) was added via syringe sequentially. Then, $BF_3 \cdot Et_2O$ (28.4 mg, 0.2 mmol, 10 mol%) was added and the mixture was stirred at 25 ℃. After completion (10 mins), the reaction mixture was quenched with water and extracted with ethyl acetate for three times. The resulted filtrate was separated. The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by column chromatography (petroleum ether/ethyl acetate = 20:1) to give the corresponding product **3a** in 81% yield (665 mg).

8. Synthetic transformations of products



3a **8**

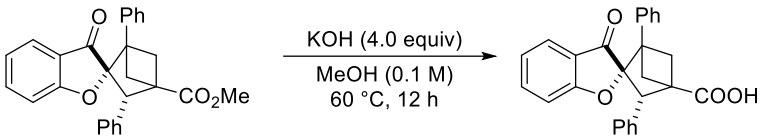
A flame-dried Schlenk tube was charged compound **3a** (82.1 mg, 0.2 mmol, 1.0 equiv.). Then purged with nitrogen. Anhydrous THF (2.0 mL) was added via syringe to the reaction tube. Then MeMgBr (0.2 mL, 0.6 mmol, 3.0 equiv., 3.0 M in Et_2O) was added dropwise. The resultant solution was stirred at 25 ℃ for 30 minutes. Then the reaction mixture was quenched with saturated NH_4Cl aqueous solution and extracted with ethyl acetate for three times. The combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4:1) to give the corresponding product **8** as a white solid in 83% yield (70.8 mg, dr > 20:1). m.p. = 152-154 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (brs, 2H), 7.34 – 7.25 (m, 4H), 7.27 – 7.18 (m, 1H), 7.14 – 6.94 (m, 4H), 6.85 (dd, *J* = 7.4, 1.4 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.64 – 6.56 (m, 1H), 3.92 (d, *J* = 2.4 Hz, 1H), 3.20 (dd, *J* = 9.6, 7.5 Hz, 1H), 2.31 (dd, *J* = 9.6, 7.0 Hz, 1H), 2.13 (d, *J* = 7.0 Hz, 1H), 2.08 (d, *J* = 1.1 Hz, 1H), 1.94 (dd, *J* = 7.5, 2.5 Hz, 1H), 1.56 (s, 3H), 1.18 (s, 1H), 1.15 (s, 3H), 0.96 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.4, 141.3, 138.7, 133.6, 132.1(2C), 129.5, 128.4(2C), 128.1(2C), 127.3(2C), 127.3, 126.7, 122.3, 120.6, 109.6, 101.3, 83.0, 71.4, 56.9, 56.0, 53.9, 42.7, 42.6, 28.7, 26.6(1), 26.5(5); **HRMS** (ESI-TOF, m/z): calcd for $C_{29}H_{30}O_3Na$ $[M+Na]^+$: 449.2088, found: 449.2089.



3a **9**

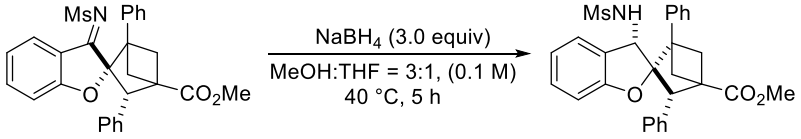
A flame-dried Schlenk tube was charged **3a** (82.1 mg, 0.2 mmol, 1.0 equiv.) and purged with nitrogen. Anhydrous DCM (2.0 mL) was added via syringe to the reaction tube. The mixture was cooled to -78℃. Then DIBAL-H (0.6 mL, 0.9 mmol, 1.5 M in toluene) was added dropwise. The resultant solution was stirred at -78 ℃ for 30 minutes. After the lreaction was completed, the mixture was warmed to room temperature and saturated aqueous Roche salt (5.0 mL) was added slowly to quench the reaction, and the resulting mixture was stirred overnight. The reaction mixture was extracted with DCM for three times. The combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude

mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1:1) to give the corresponding product **9** as a white solid in 90% yield (69.2 mg). m.p. = 135-137 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 2H), 7.23 – 7.07 (m, 9H), 7.03 – 6.95 (m, 1H), 6.78 – 6.69 (m, 1H), 6.42 (d, *J* = 8.1 Hz, 1H), 5.45 (d, *J* = 11.0 Hz, 1H), 3.78 – 3.65 (m, 2H), 3.49 (d, *J* = 2.3 Hz, 1H), 3.09 – 2.98 (m, 1H), 2.29 – 2.23 (m, 2H), 1.90 (dd, *J* = 7.3, 2.3 Hz, 1H), 1.32 (s, 1H), 1.20 (d, *J* = 11.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.8, 141.3, 137.0, 130.5, 129.6(2C), 129.1, 128.3(2C), 127.8(2C), 127.3(2C), 126.7, 126.6, 125.1, 120.7, 110.0, 98.4, 81.0, 62.8, 62.2, 54.7, 51.2, 43.9, 43.2; **HRMS** (ESI-TOF, m/z): calcd for $C_{26}H_{24}O_3Na$ $[M+Na]^+$: 407.1618, found: 407.1615.



3a **10**

3a (82.1 mg, 0.2 mmol, 1.0 equiv.) was dissolved in MeOH (2.0 mL), then 1 M KOH solution (0.8 mL, 0.8 mmol, 4.0 equiv.) was added. The reaction mixture was stirred at 60 ℃ for 12 hours. After the reaction was completed, then ethyl acetate (3 mL) was added to extract the reaction solution and the organic phase was removed. Acidified the aqueous phase with 2 M HCl to pH = 1, then the reaction mixture was quenched with saturated NH_4Cl aqueous solution and extracted with ethyl acetate for three times. The combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (DCM/MeOH = 20:1) to give the corresponding product **10** as a white solid in 93% yield (73.7 mg). m.p. = 141-143 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.77 (brs, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.39 – 7.31 (m, 1H), 7.22 – 6.95 (m, 10H), 6.91 – 6.83 (m, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 4.35 (s, 1H), 3.47 – 3.32 (m, 1H), 3.20 – 3.06 (m, 1H), 2.49 (d, *J* = 7.5 Hz, 1H), 2.31 (d, *J* = 7.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.3, 177.6, 171.6, 138.0, 136.8, 136.0, 128.4(2C), 128.1(2C), 127.8(2C), 127.4, 127.0, 126.4(2C), 124.0, 121.7, 121.6, 112.7, 95.9, 58.4, 58.3, 49.9, 44.8, 42.9; **HRMS** (ESI-TOF, m/z): calcd for $C_{26}H_{20}O_4Na$ $[M+Na]^+$: 419.1254, found: 419.1256.



6a **11**

A flame-dried Schlenk tube was charged **6a** (97.5 mg, 0.2 mmol, 1.0 equiv) and purged

with nitrogen. Anhydrous MeOH and THF (3:1 v:v, 2.0 mL) was added via syringe to the reaction tube. The mixture was stirred at 0 ℃ (ice bath) for 2.0 minutes. Then $NaBH_4$ (22.7 mg, 0.6 mmol, 3.0 equiv) was added in three portions. The resultant solution was warmed to 40 ℃ and stirred for 5 hours. After the reaction was completed, the reaction mixture was quenched with water and extracted with ethyl acetate for three times. The combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4:1) to give the corresponding product **11** as colorless oil in 91% yield (89.1 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 7.26 – 7.08 (m, 7H), 7.10 – 6.97 (m, 3H), 6.84 – 6.76 (m, 1H), 6.45 (d, *J* = 8.1 Hz, 1H), 5.60 (d, *J* = 10.3 Hz, 1H), 4.12 – 4.01 (m, 2H), 3.61 (s, 3H), 3.12 (dd, *J* = 9.5, 7.5 Hz, 1H), 3.03 (s, 3H), 2.74 (dd, *J* = 9.5, 7.3 Hz, 1H), 2.56 (d, *J* = 7.3 Hz, 1H), 2.31 (dd, *J* = 7.5, 2.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.3, 158.3, 139.6, 136.6, 130.7, 128.6(2C), 128.1(2C), 128.0(2C), 127.4(2C), 127.2, 126.8, 126.4, 124.2, 121.2, 110.3, 95.9, 63.7, 63.5, 55.1, 52.0, 49.5, 45.4, 44.9, 42.7; **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{27}NO_5SNa$ $[M+Na]^+$: 512.1503, found: 512.1504.

9. Crystallographic data for compounds 3a, 6a and 9

Preparations:

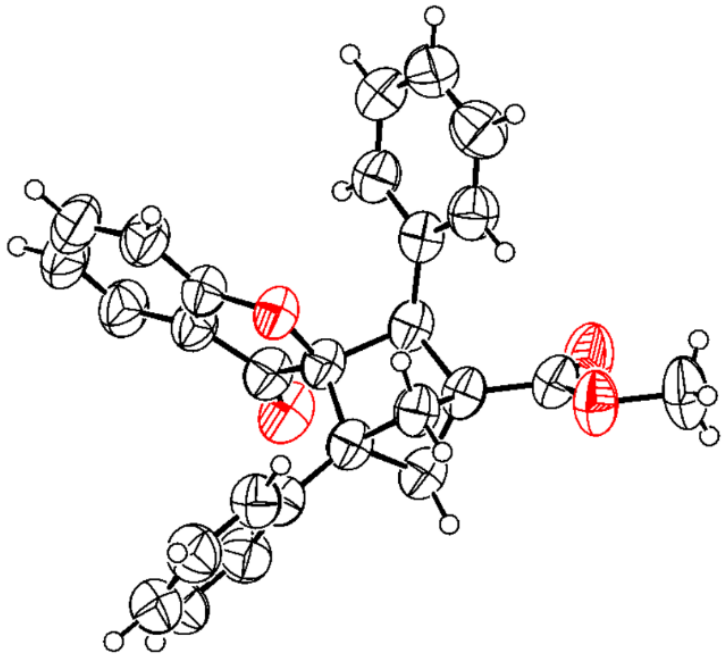
The corresponding compound (20.0 mg) was dissolved in 5.0 mL CH_2Cl_2 or acetone. The solution was filtered by millipore filter and transferred to a vial. Then, drops of hexane were added subsequently. A single crystal was obtained by natural volatilization at room temperature.

Crystals of **3a**, **6a** and **9** were prepared through the above method.

Methods:

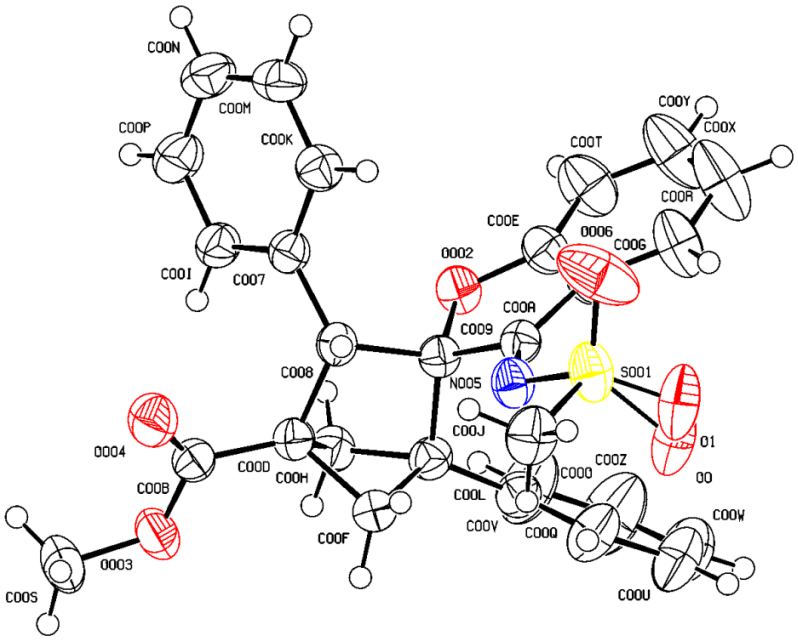
The data set was collected by a Bruker APEX-II CCD at 293(2) K equipped with micro-focus Cu radiation source (Kα = 1.54178 Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL program package.

Date of 3a: Details of the X-ray experiments and crystal data are summarized below. CCDC 2331074 contains the supplementary crystallographic data, and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.



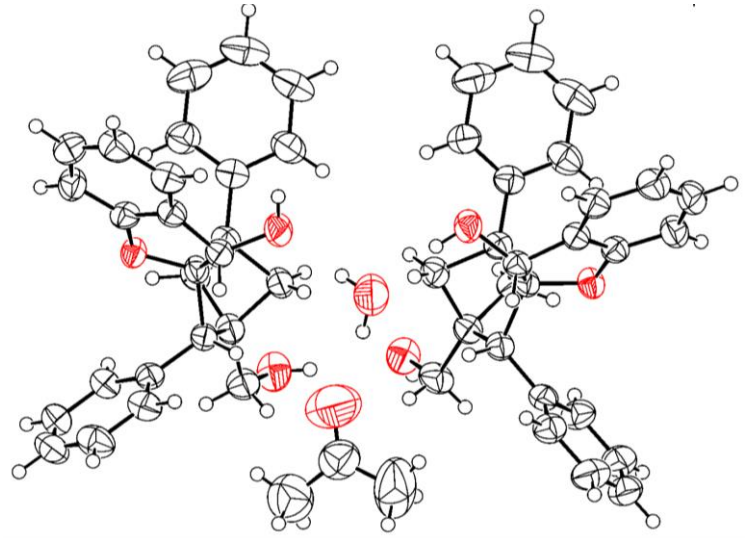
Ellipsoids are drawn at the 30% probability level

Date of 6a: Details of the X-ray experiments and crystal data are summarized below. CCDC 2331076 contains the supplementary crystallographic data, and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.



Ellipsoids are drawn at the 30% probability level

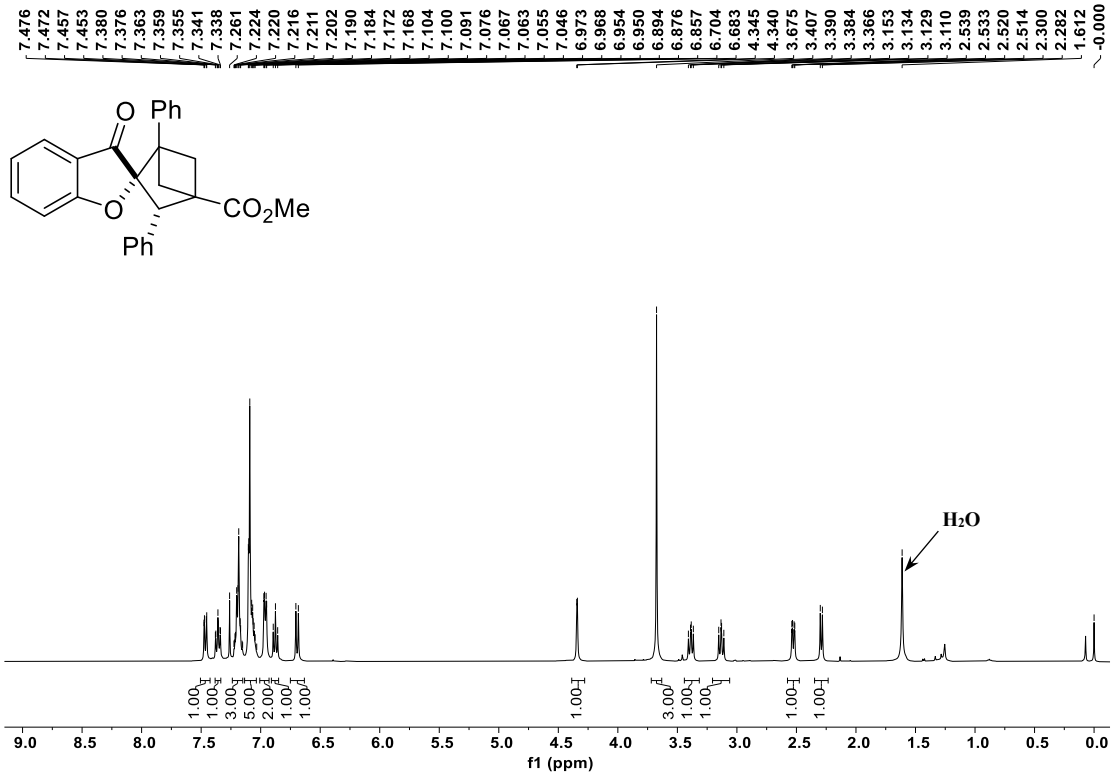
Date of 9: Details of the X-ray experiments and crystal data are summarized below. CCDC 2356085 contains the supplementary crystallographic data, and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.



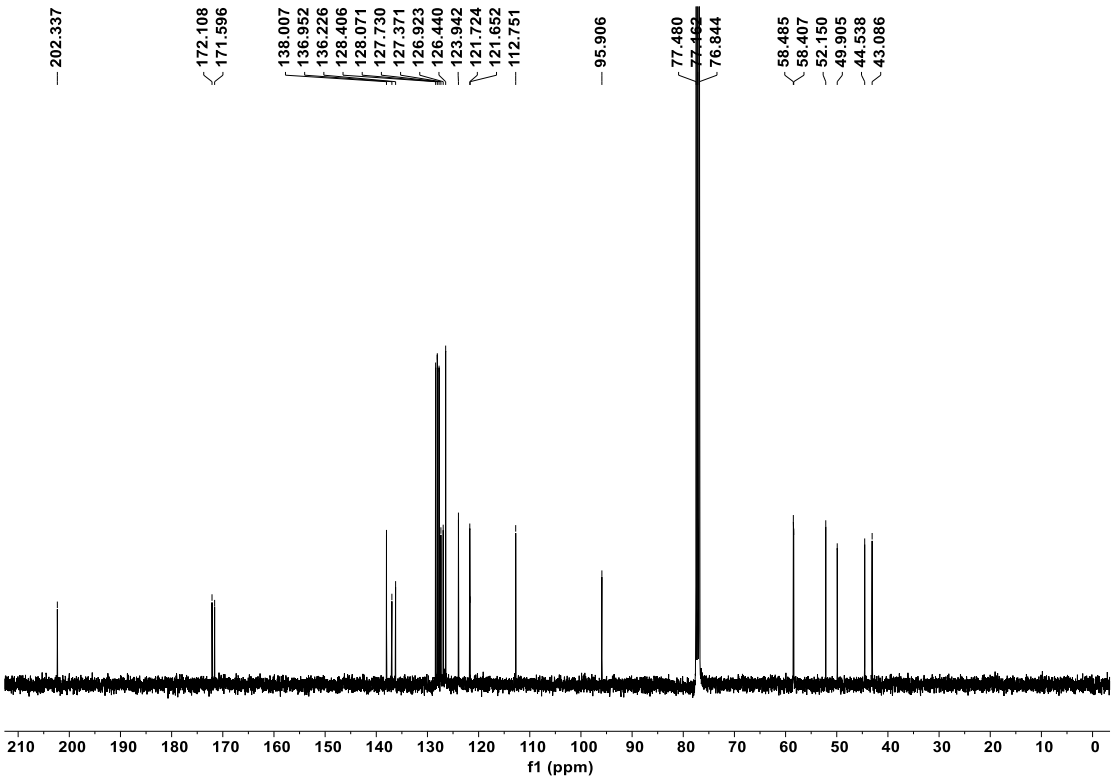
Ellipsoids are drawn at the 30% probability level

10. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra

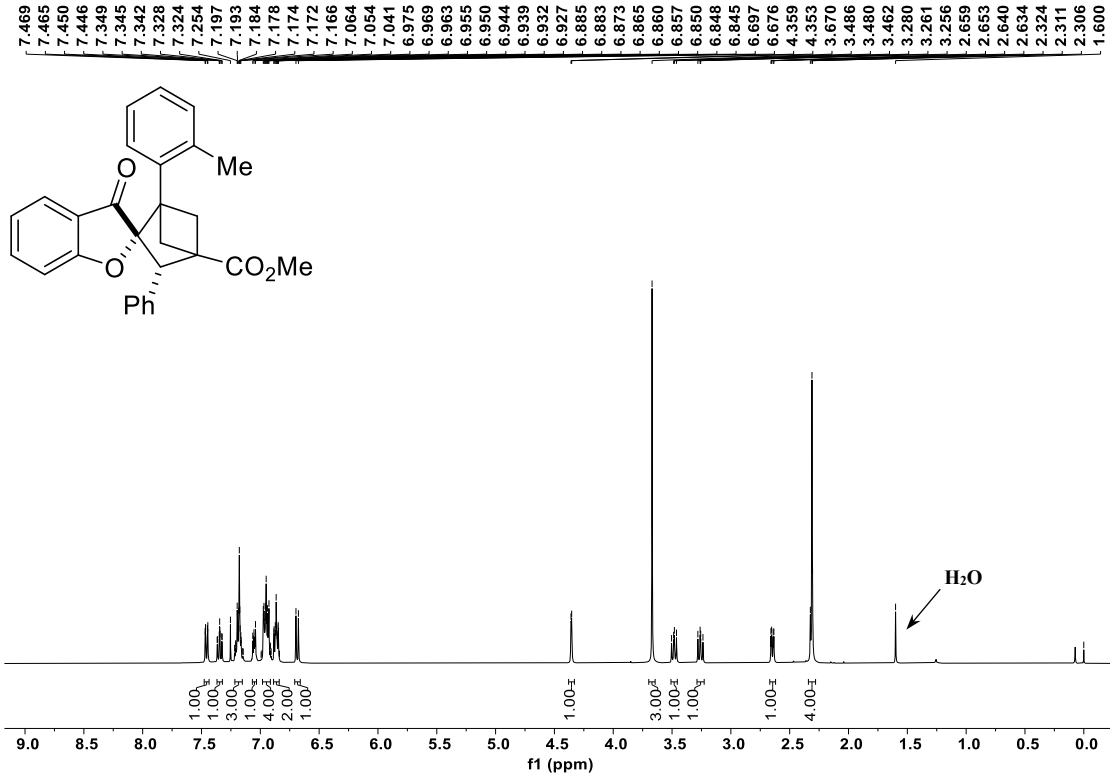
^{1}H NMR of **3a** in $CDCl_3$ (400 MHz)



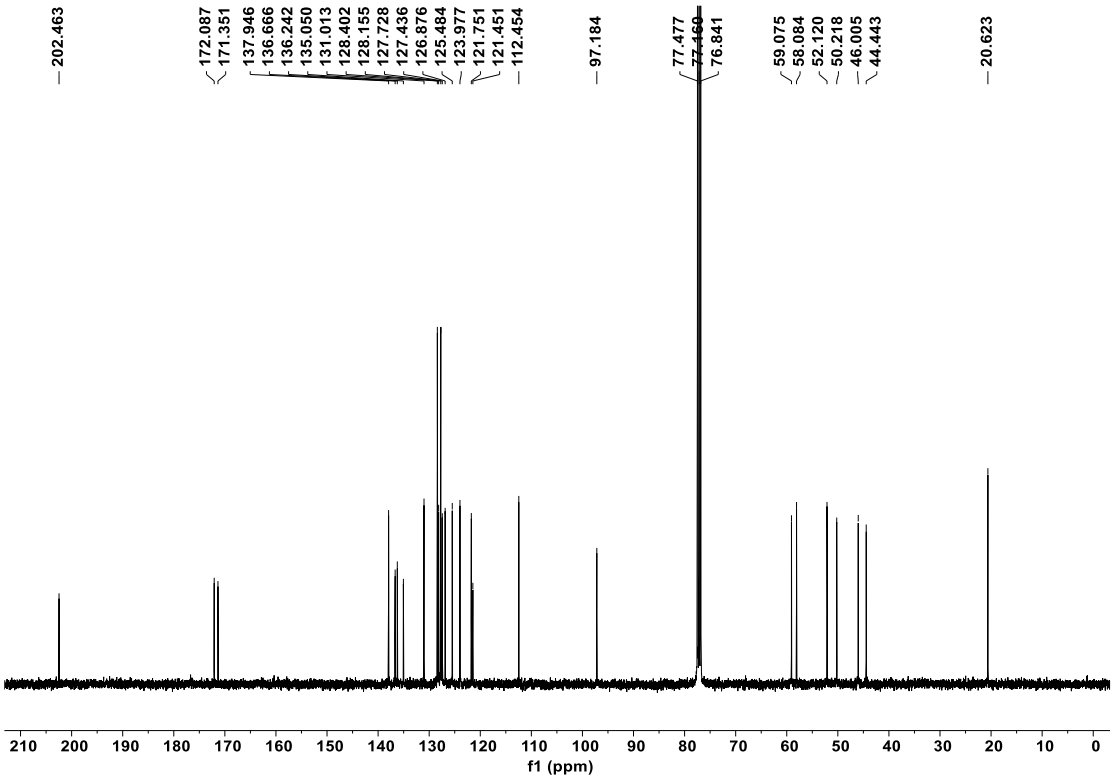
^{13}C NMR of **3a** in $CDCl_3$ (100 MHz)



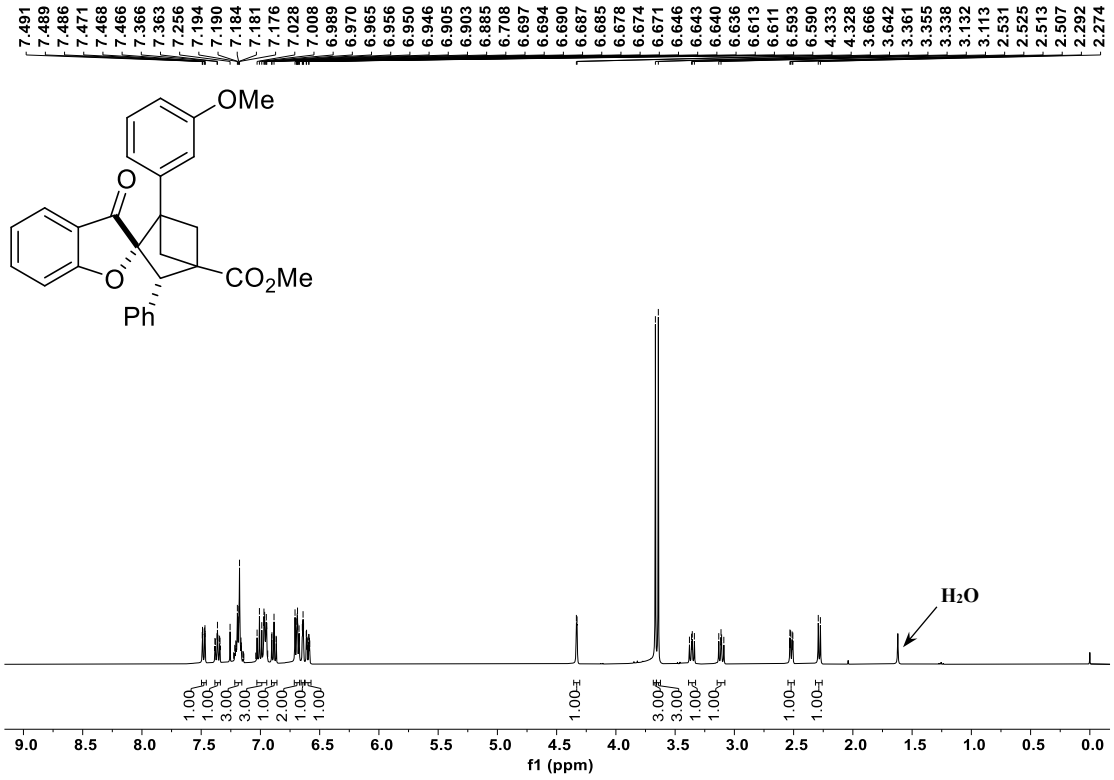
^{1}H NMR of **3b** in $CDCl_3$ (400 MHz)



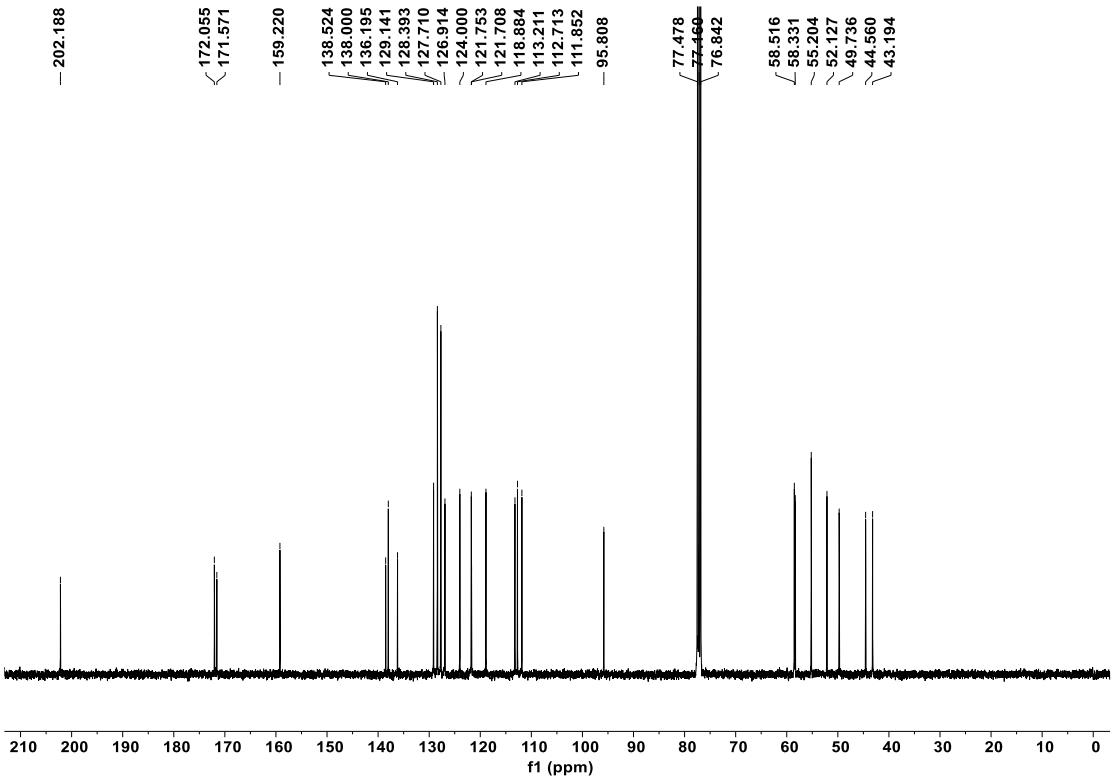
^{13}C NMR of **3b** in $CDCl_3$ (100 MHz)



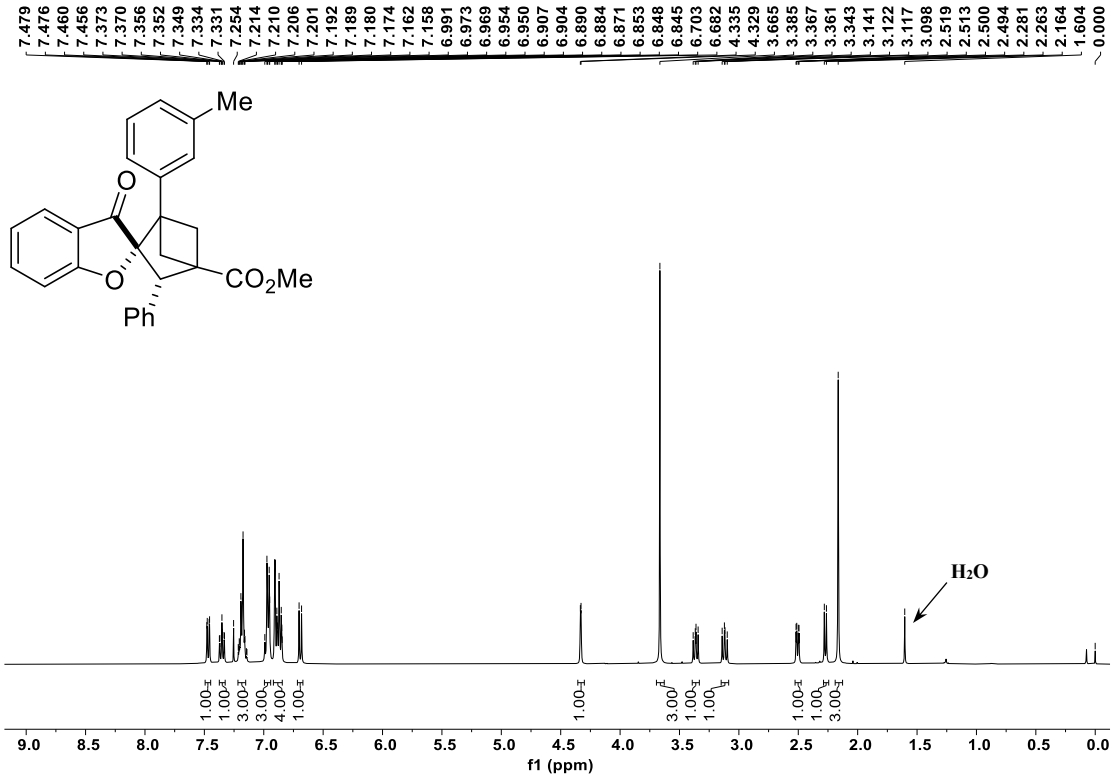
^{1}H NMR of **3c** in $CDCl_3$ (400 MHz)



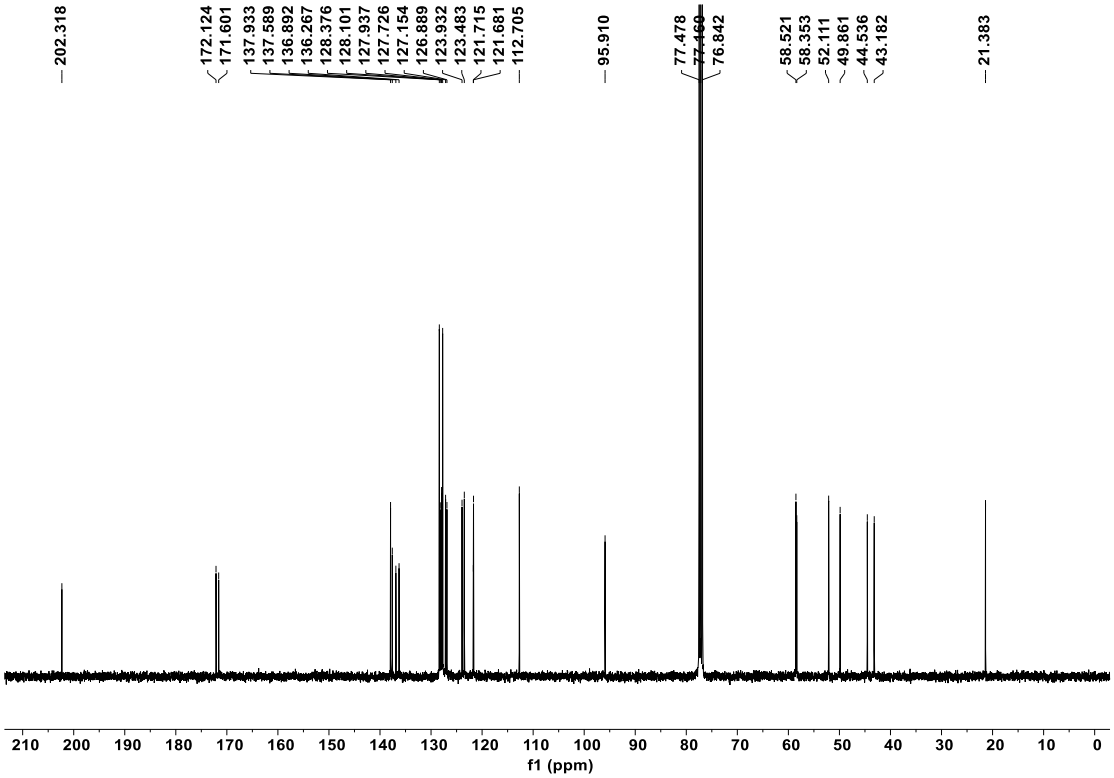
^{13}C NMR of **3c** in $CDCl_3$ (100 MHz)



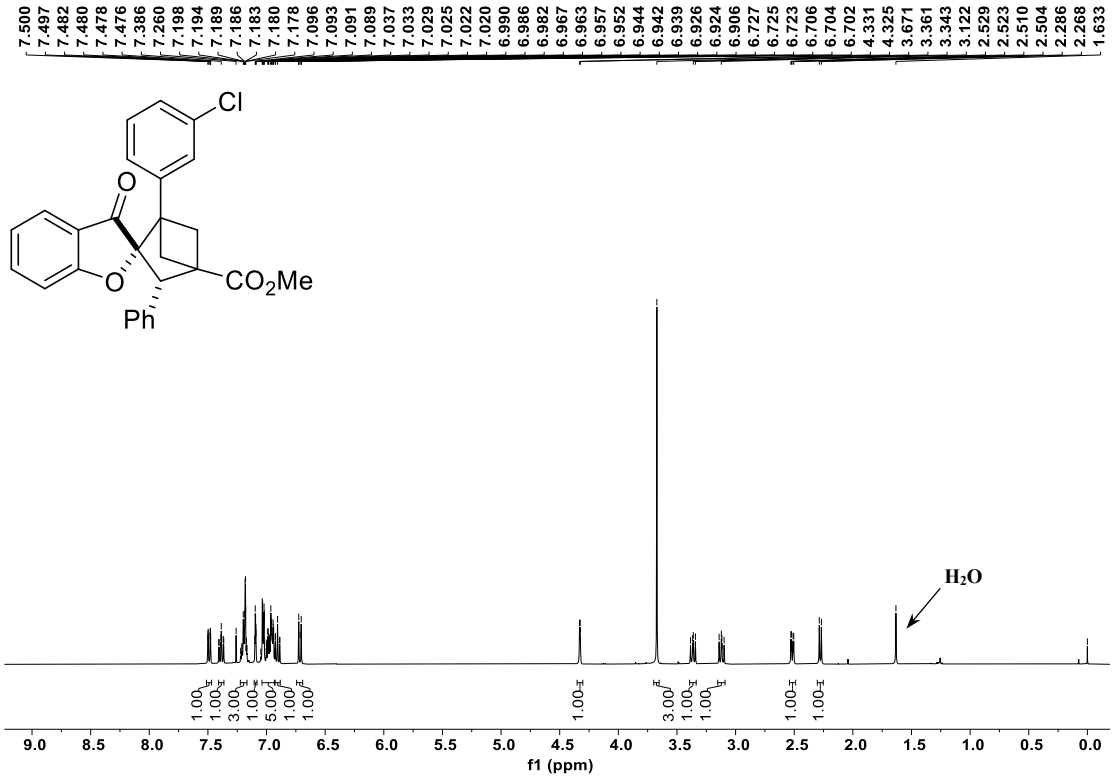
^{1}H NMR of **3d** in $CDCl_3$ (400 MHz)



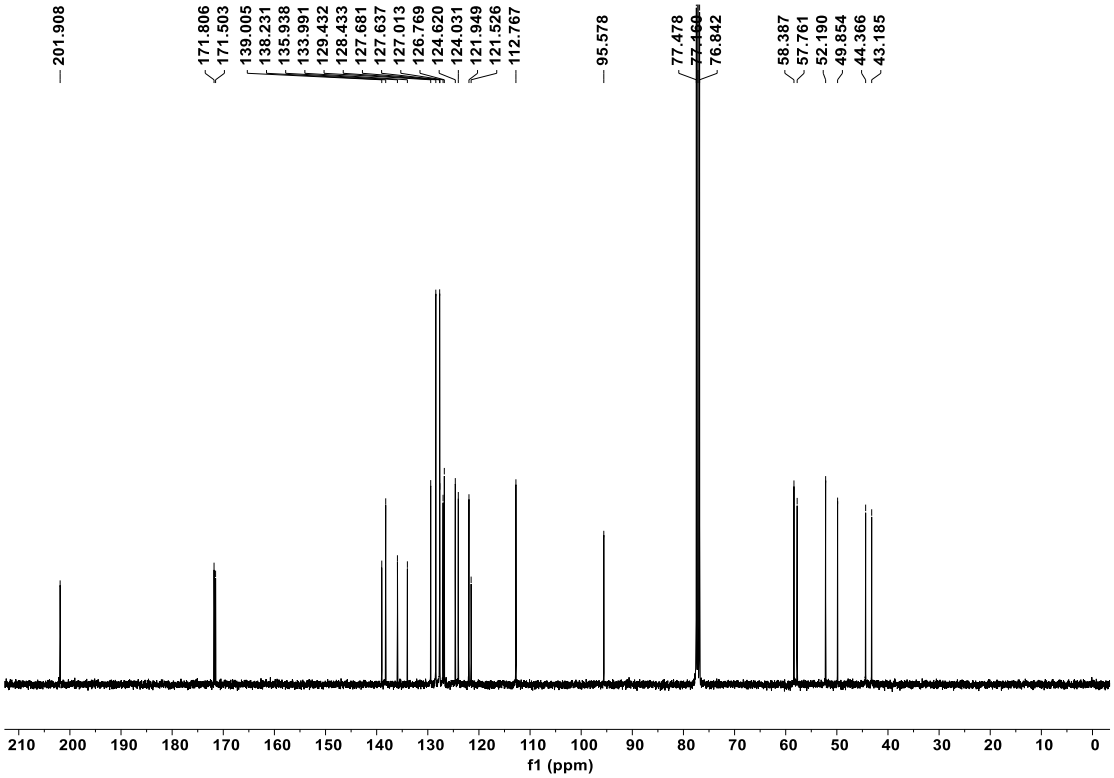
^{13}C NMR of **3d** in $CDCl_3$ (100 MHz)



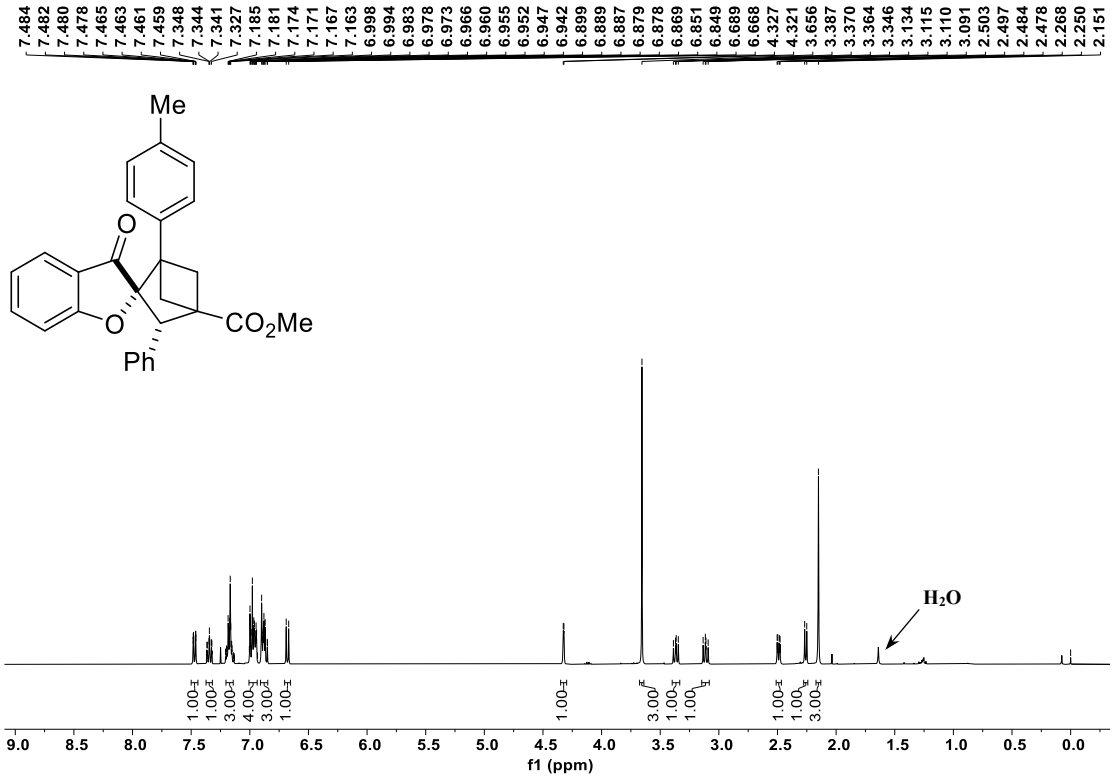
^{1}H NMR of **3e** in $CDCl_3$ (400 MHz)



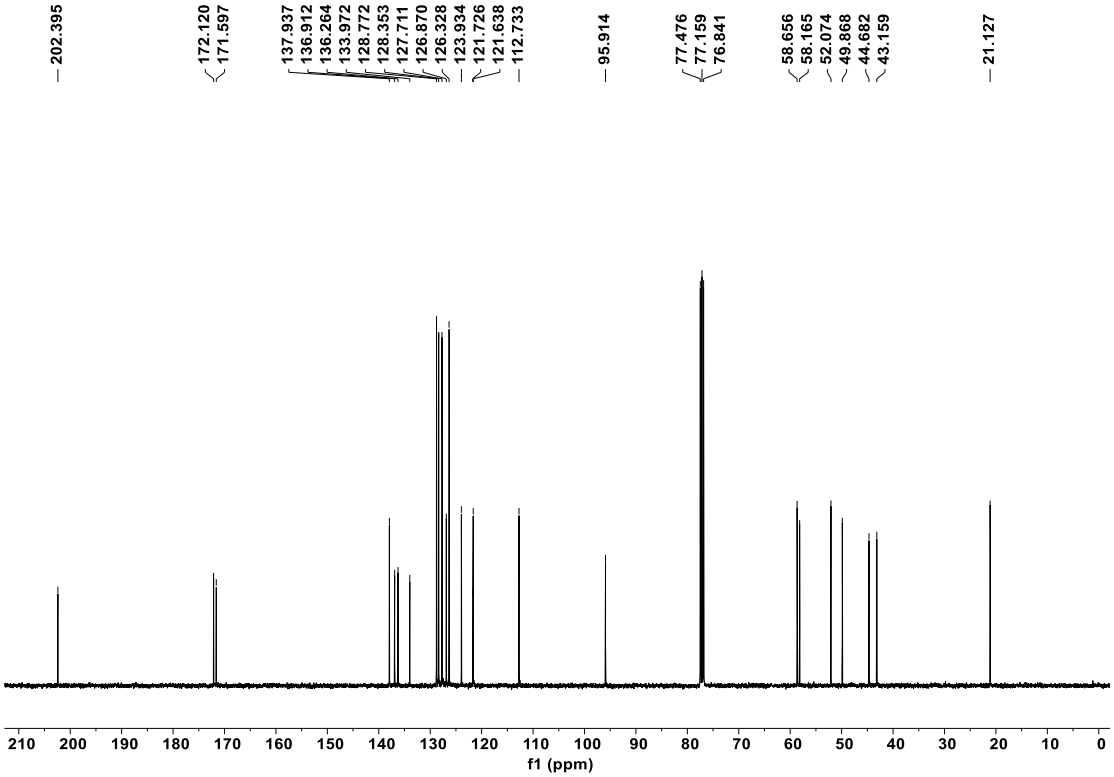
^{13}C NMR of **3e** in $CDCl_3$ (100 MHz)



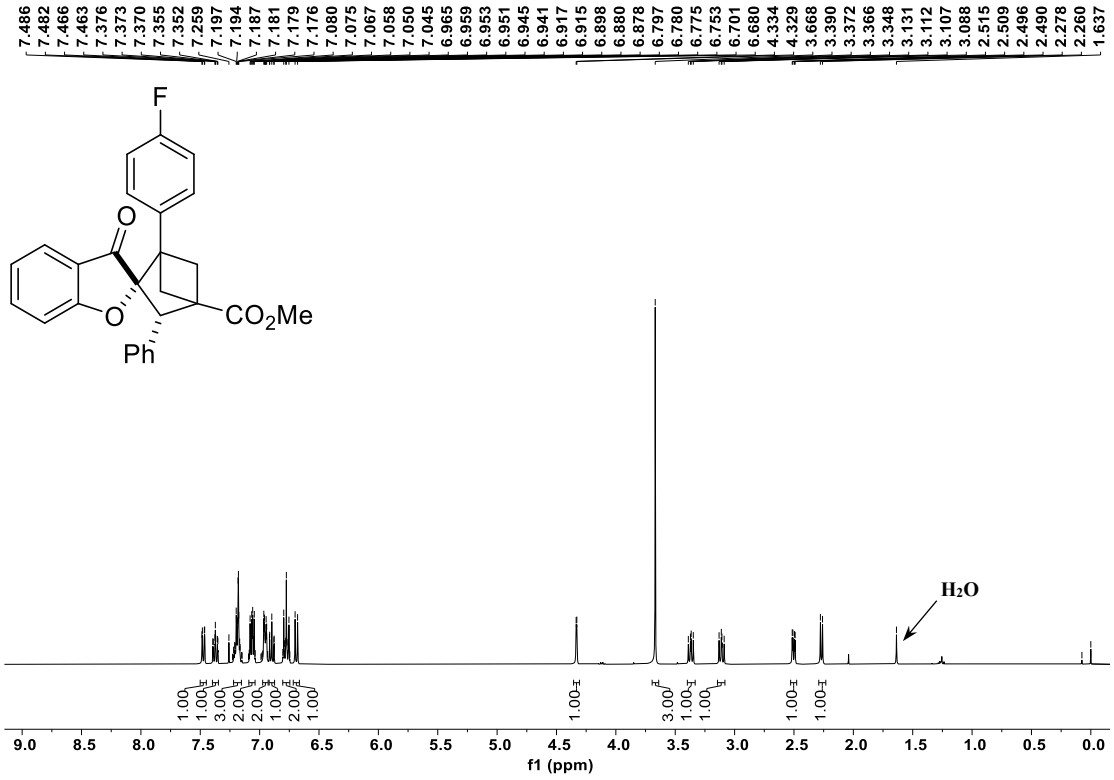
^{1}H NMR of **3f** in $CDCl_3$ (400 MHz)



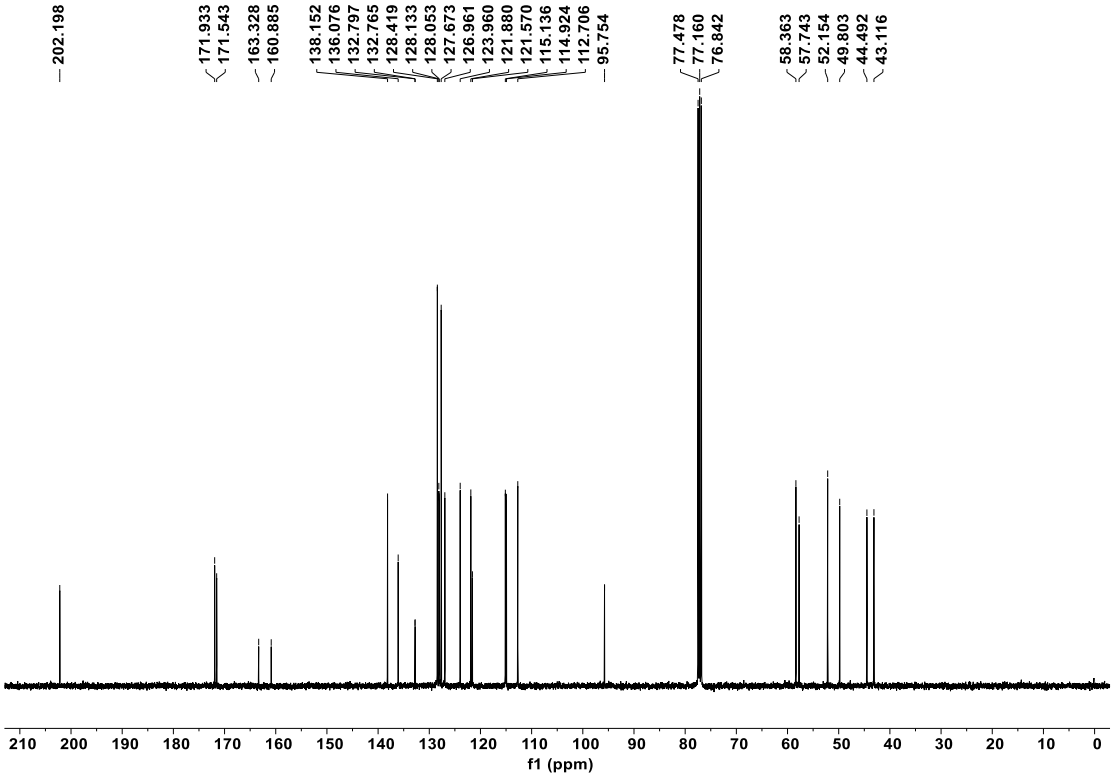
^{13}C NMR of **3f** in $CDCl_3$ (100 MHz)



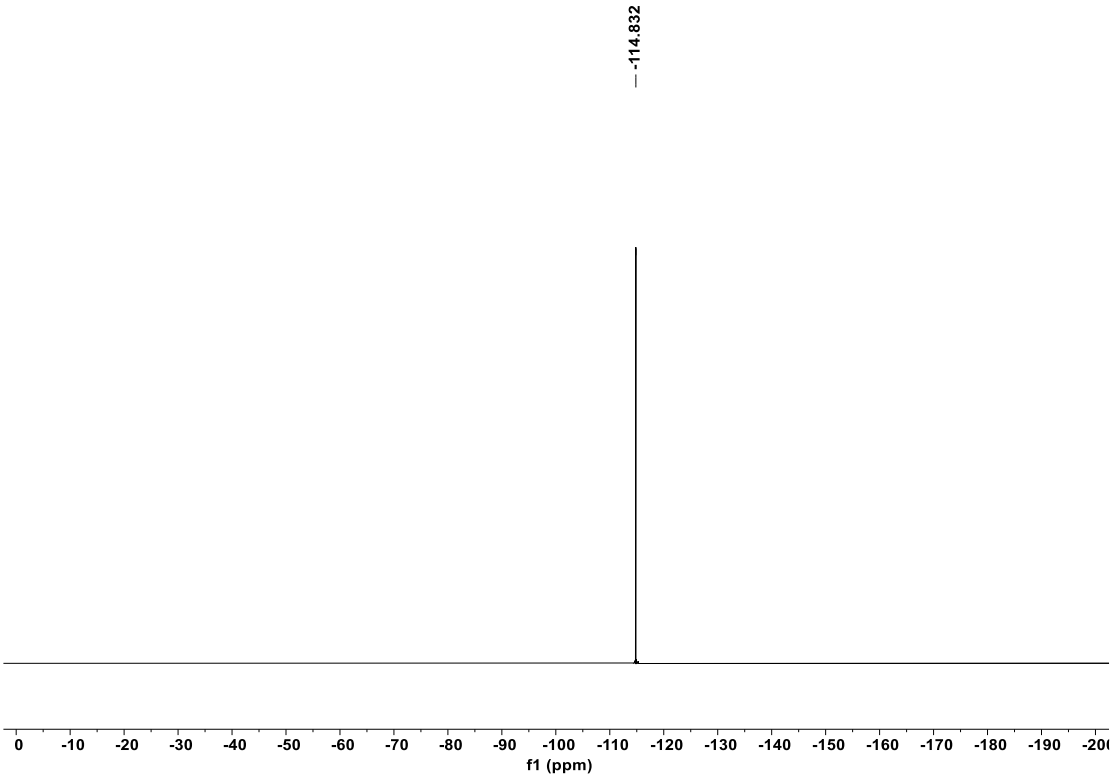
^{1}H NMR of **3g** in $CDCl_3$ (400 MHz)



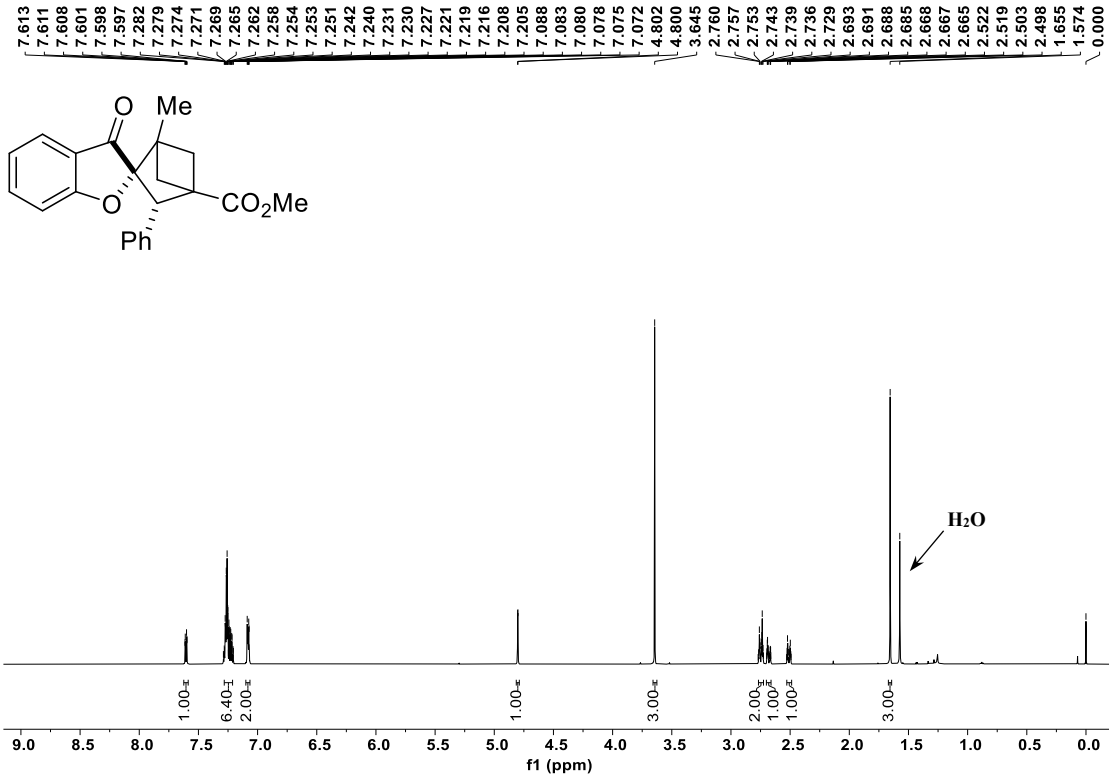
^{13}C NMR of **3g** in $CDCl_3$ (100 MHz)



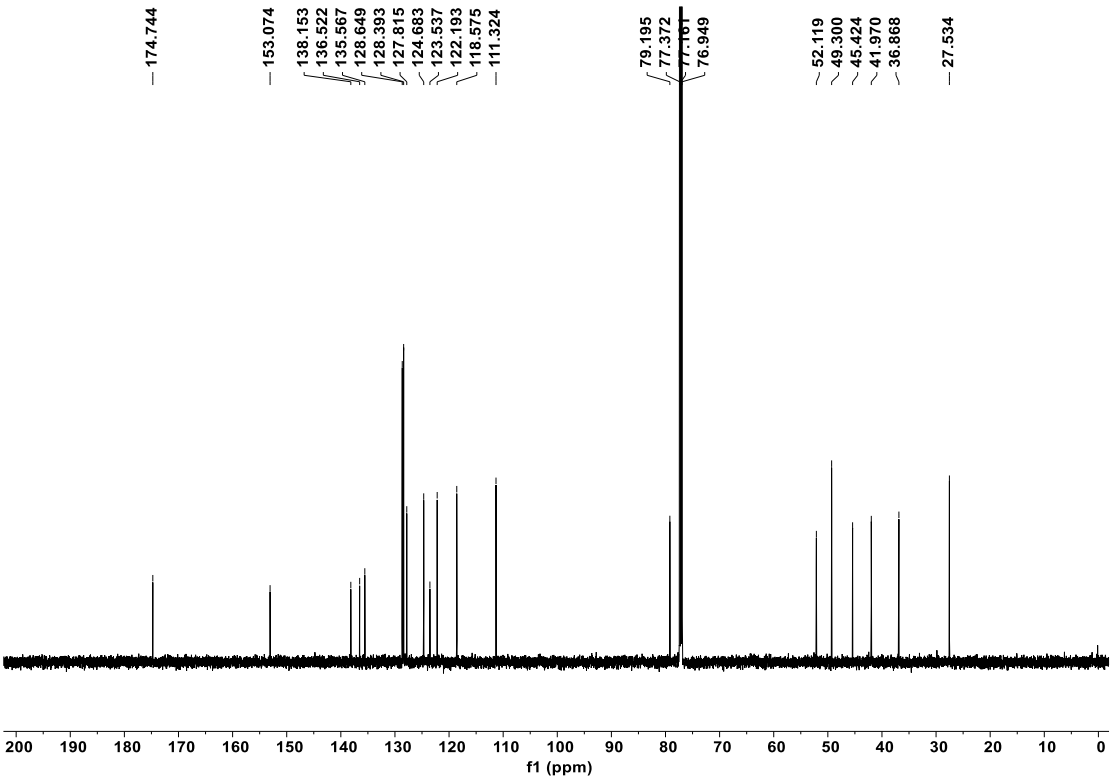
^{19}F NMR of **3g** in $CDCl_3$ (376 MHz)



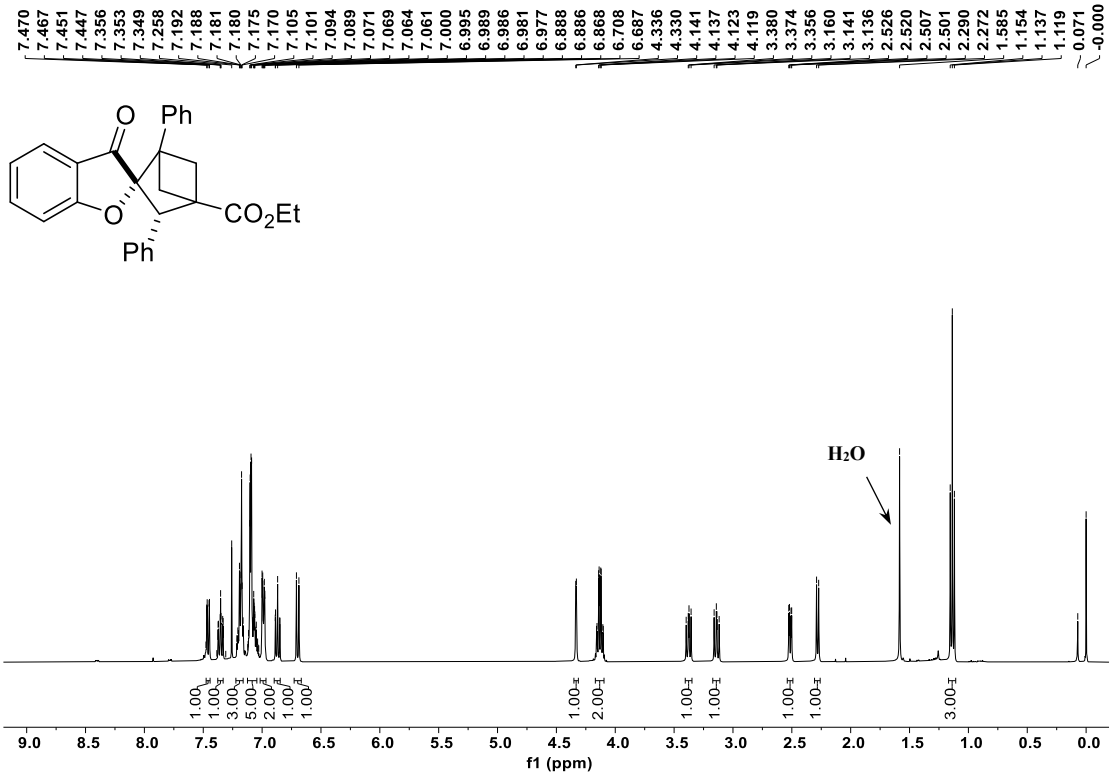
^{1}H NMR of **3h** in $CDCl_3$ (600 MHz)



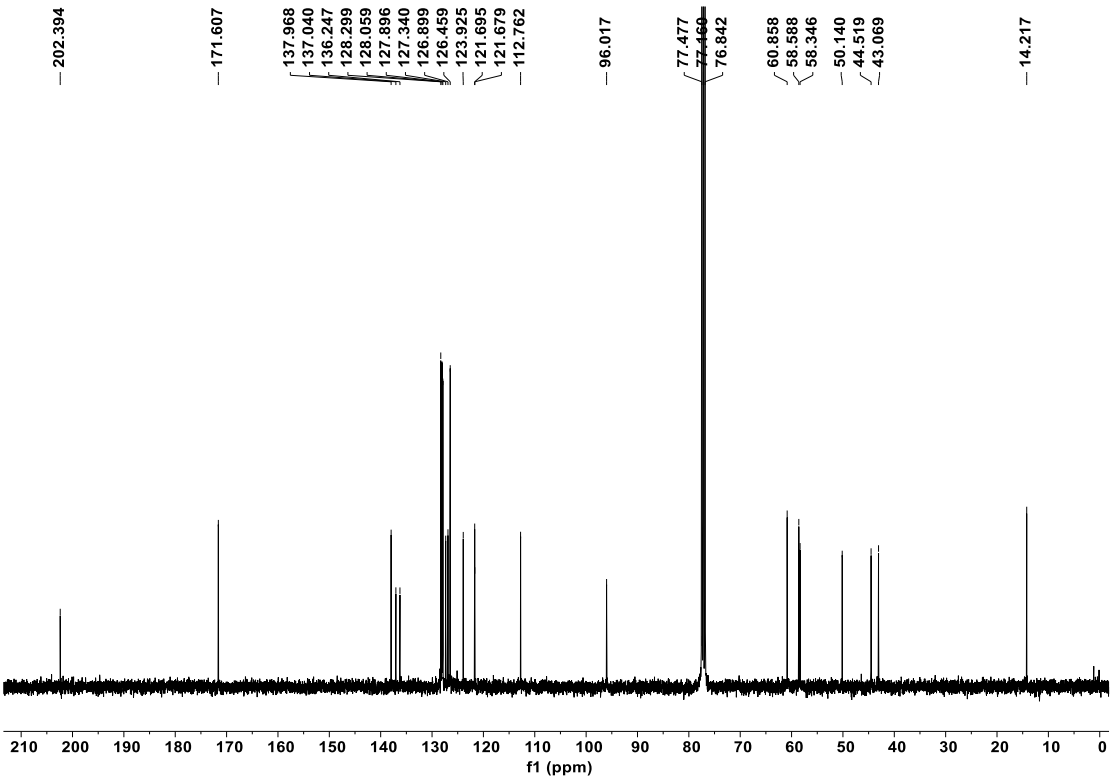
^{13}C NMR of **3h** in $CDCl_3$ (150 MHz)



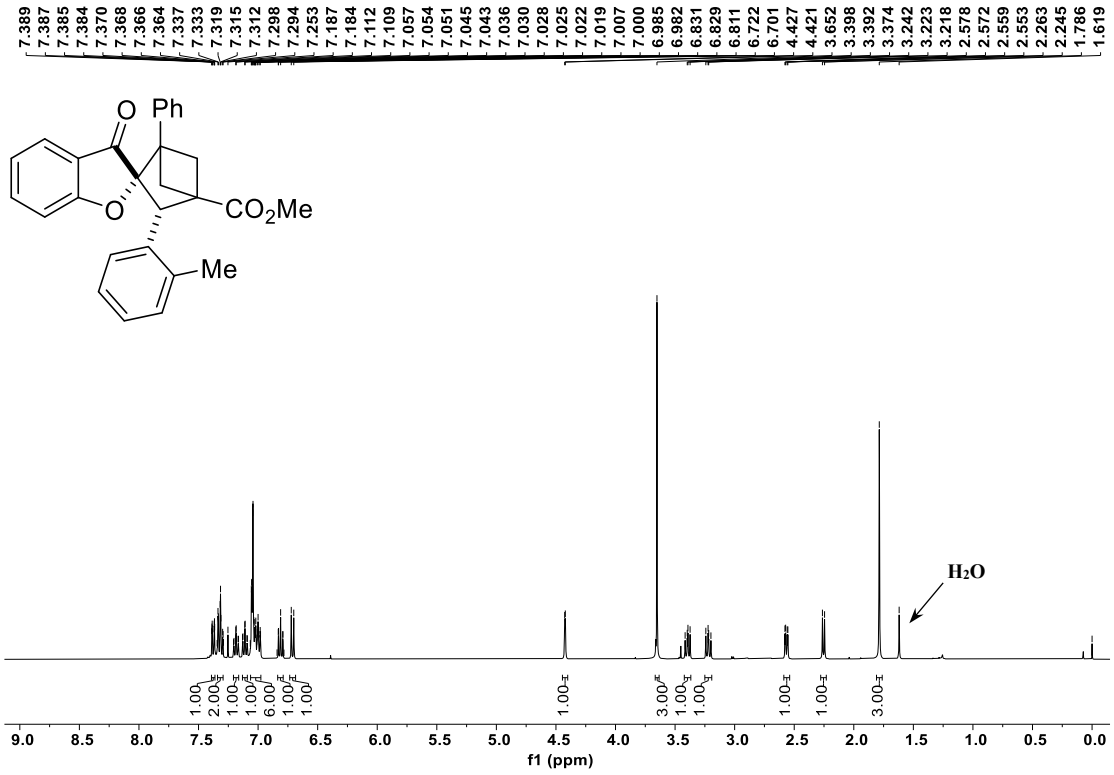
^{1}H NMR of **3i** in $CDCl_3$ (400 MHz)



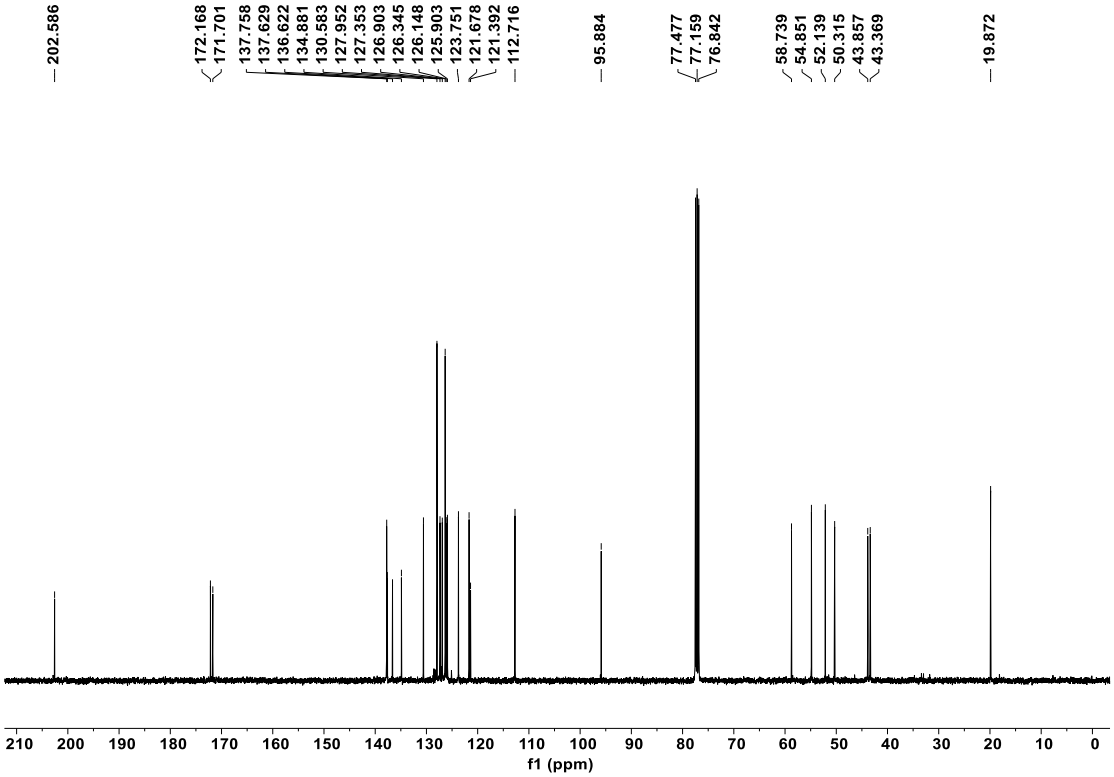
^{13}C NMR of **3i** in $CDCl_3$ (100 MHz)



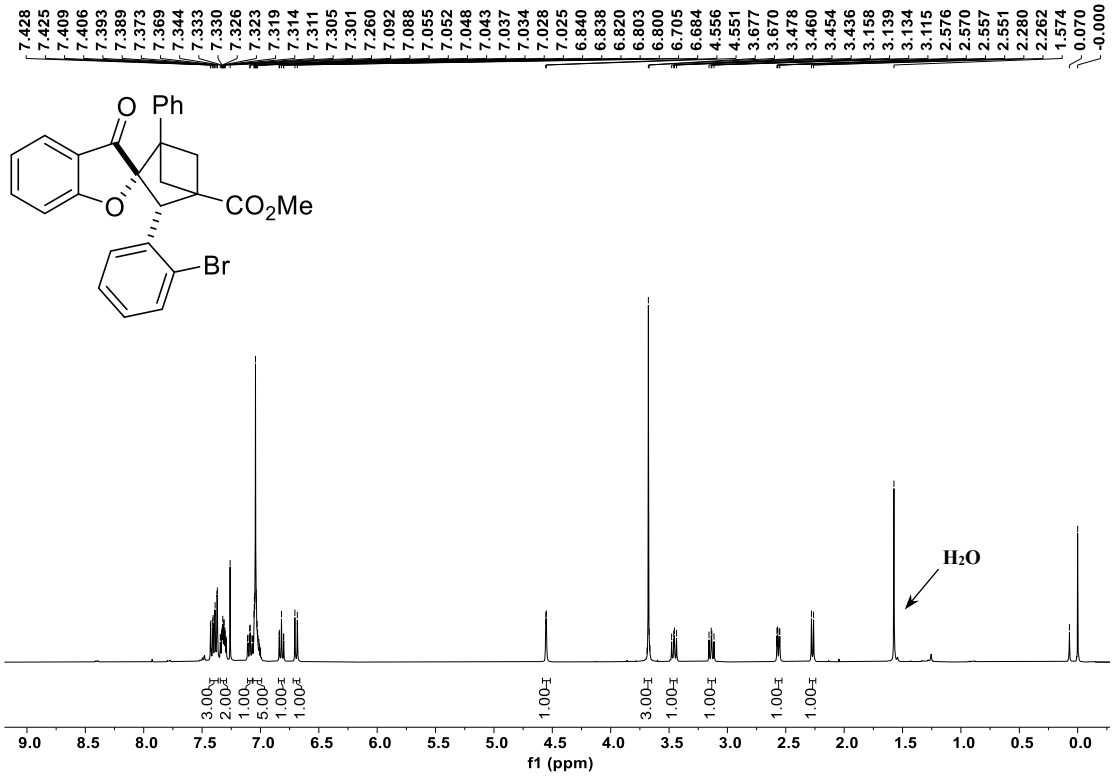
^{1}H NMR of **3j** in $CDCl_3$ (400 MHz)



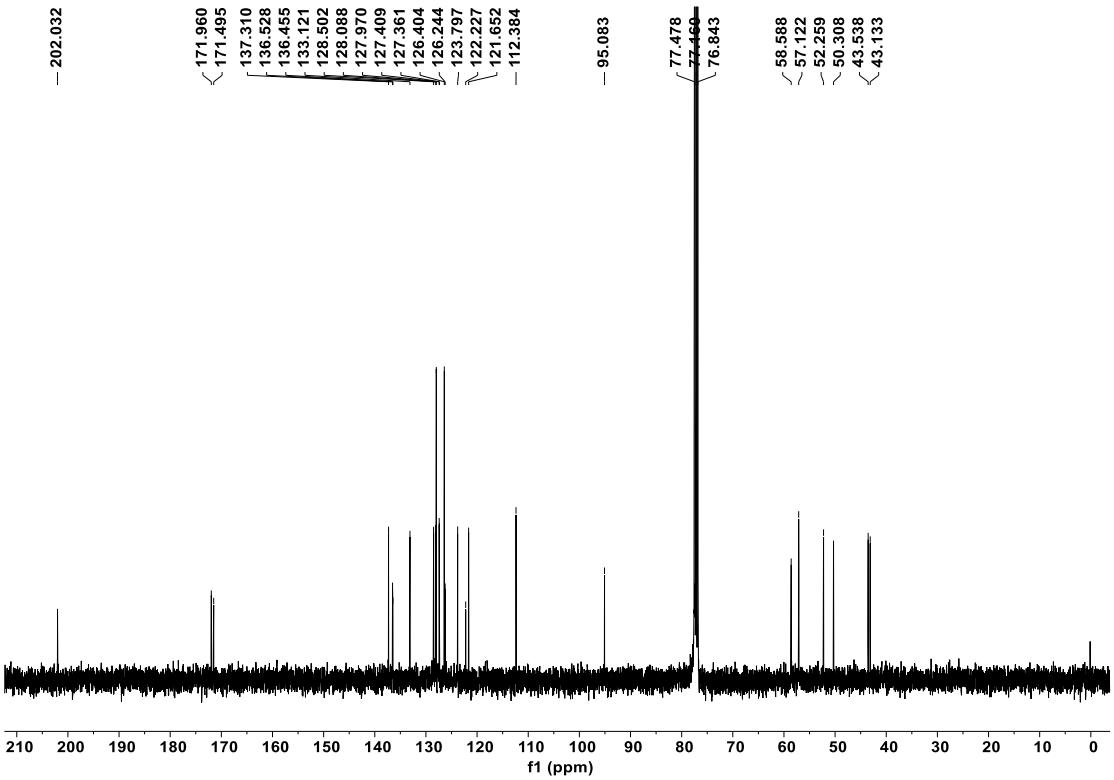
^{13}C NMR of **3j** in $CDCl_3$ (100 MHz)



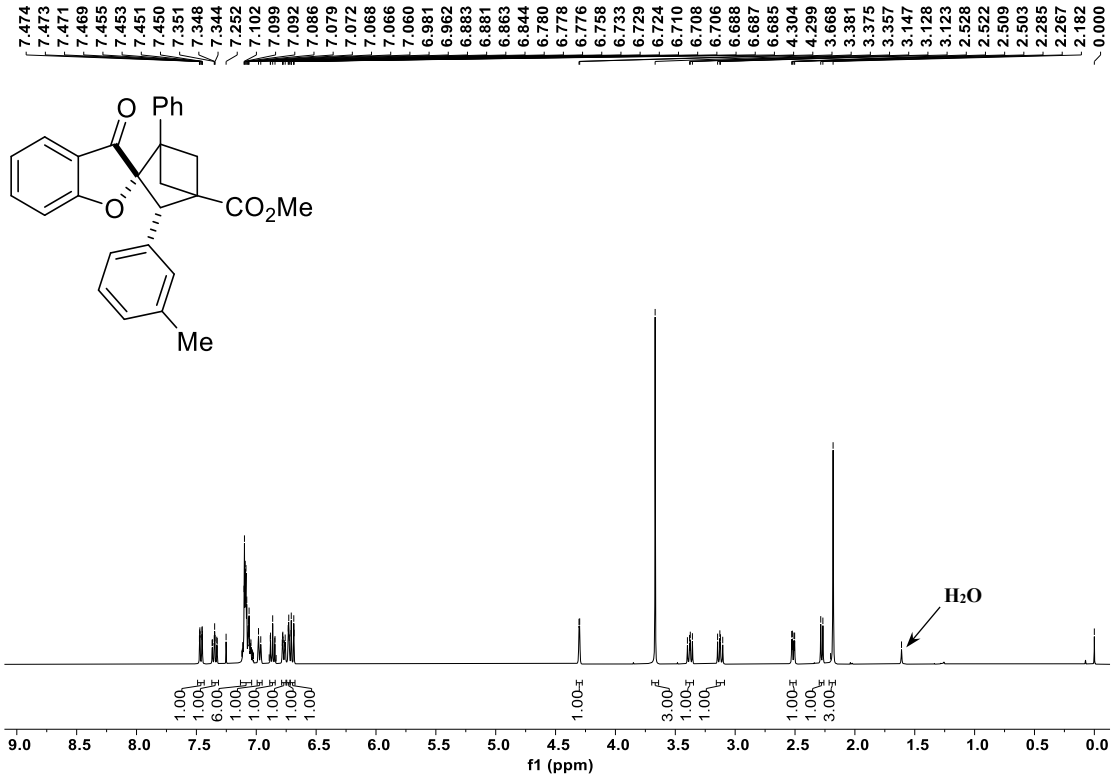
^{1}H NMR of **3k** in $CDCl_3$ (400 MHz)



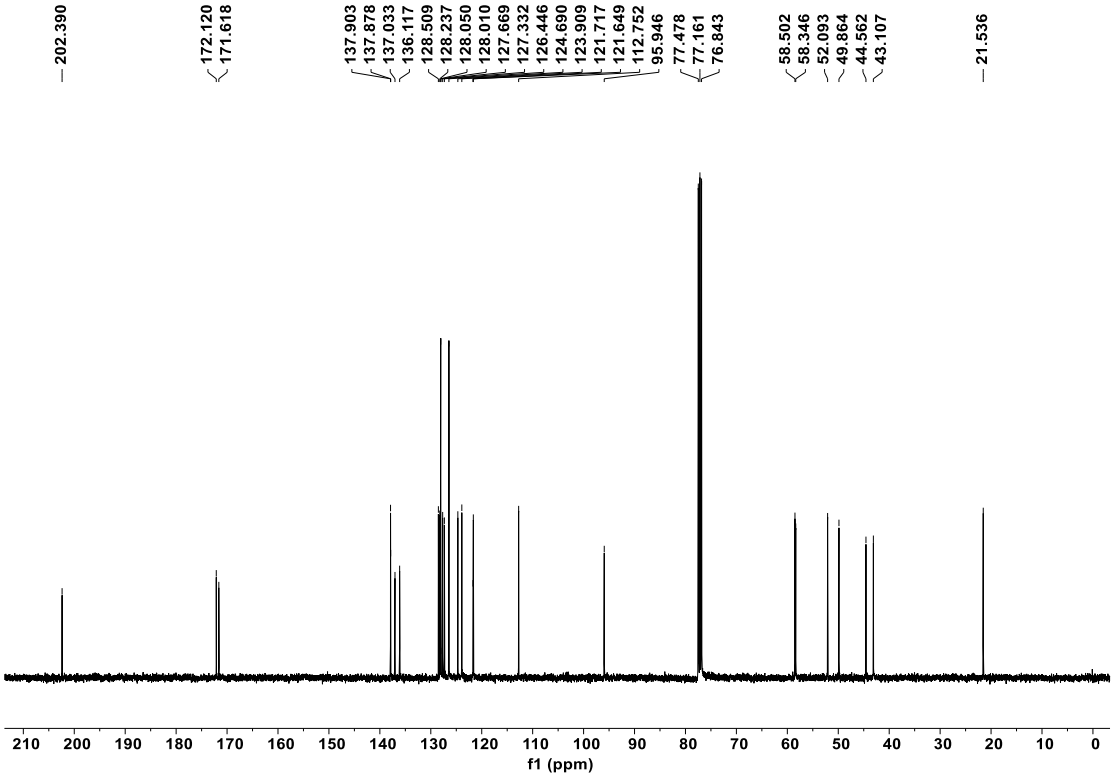
^{13}C NMR of **3k** in $CDCl_3$ (100 MHz)



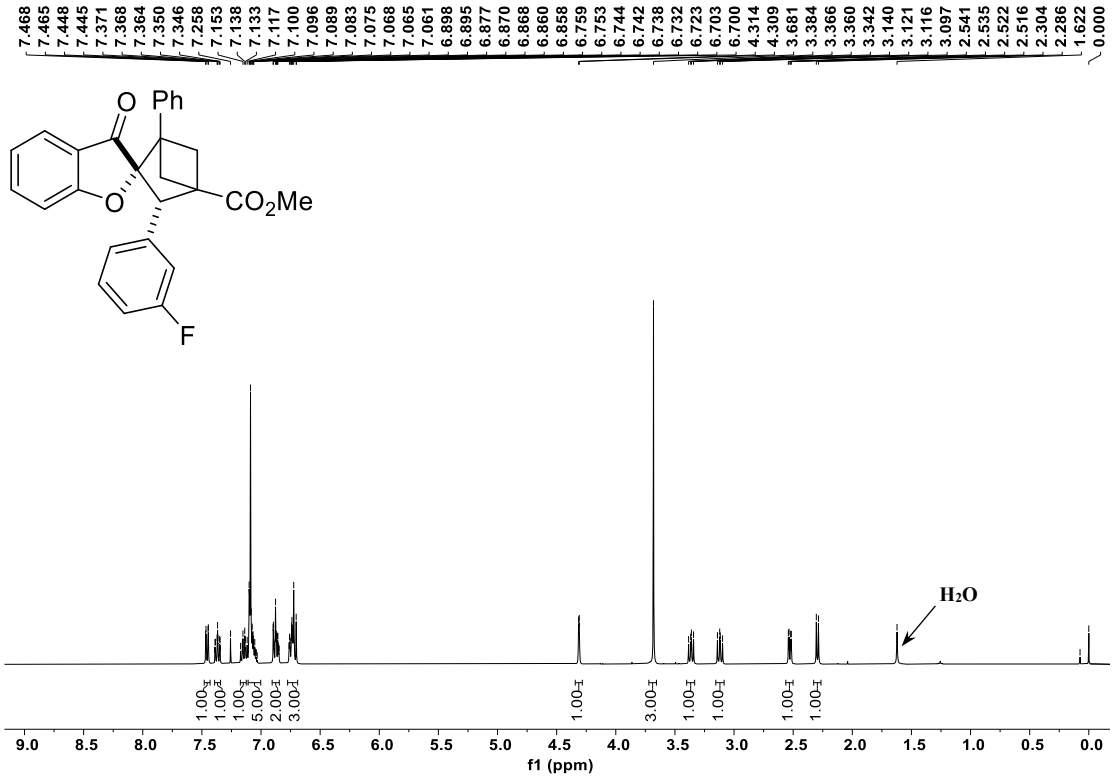
^{1}H NMR of **3l** in $CDCl_3$ (400 MHz)



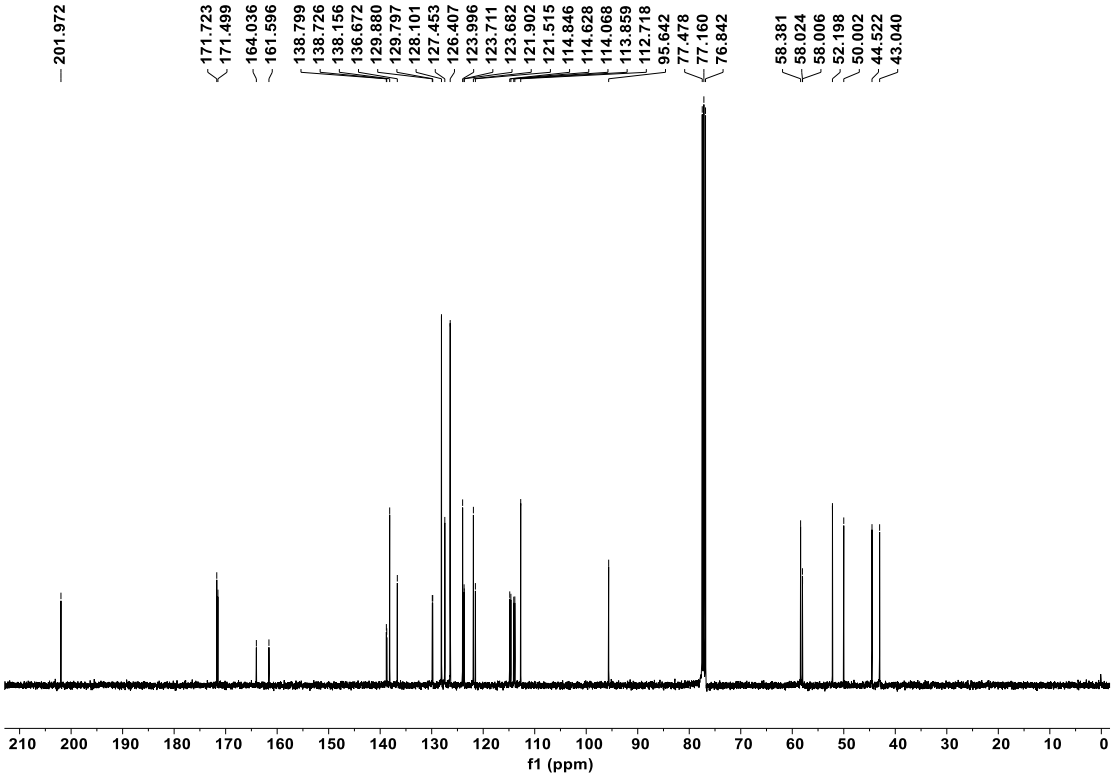
^{13}C NMR of **3l** in $CDCl_3$ (100 MHz)



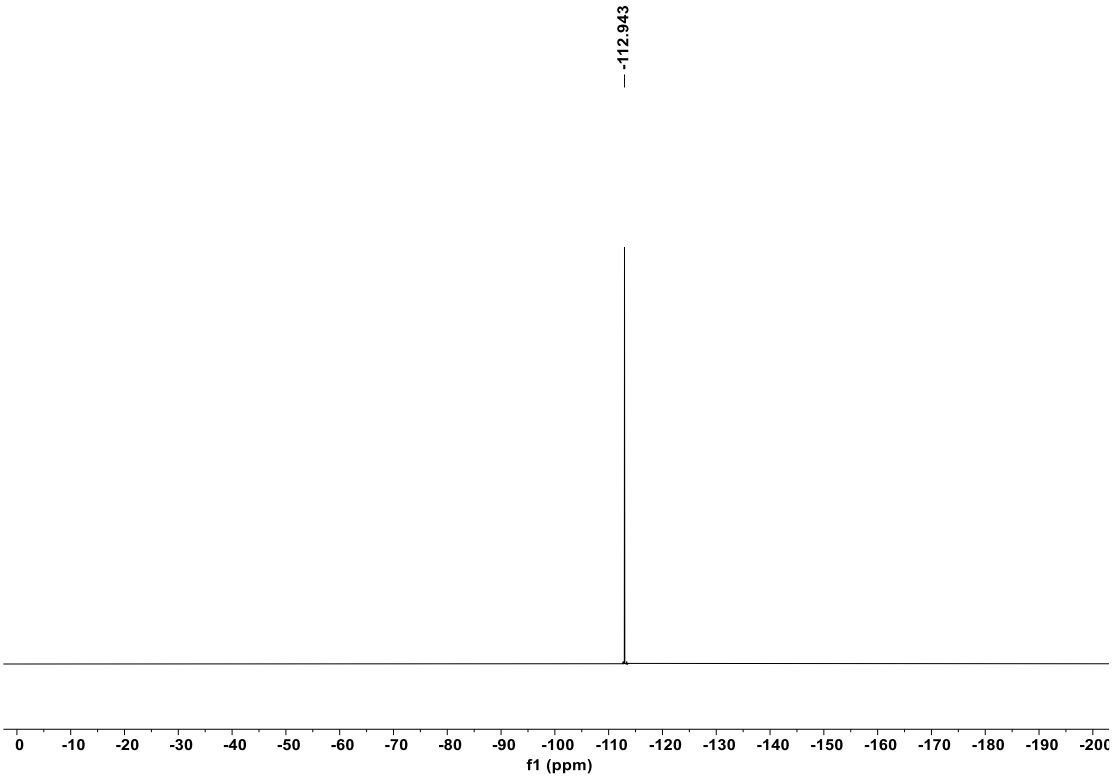
^{1}H NMR of **3m** in $CDCl_3$ (400 MHz)



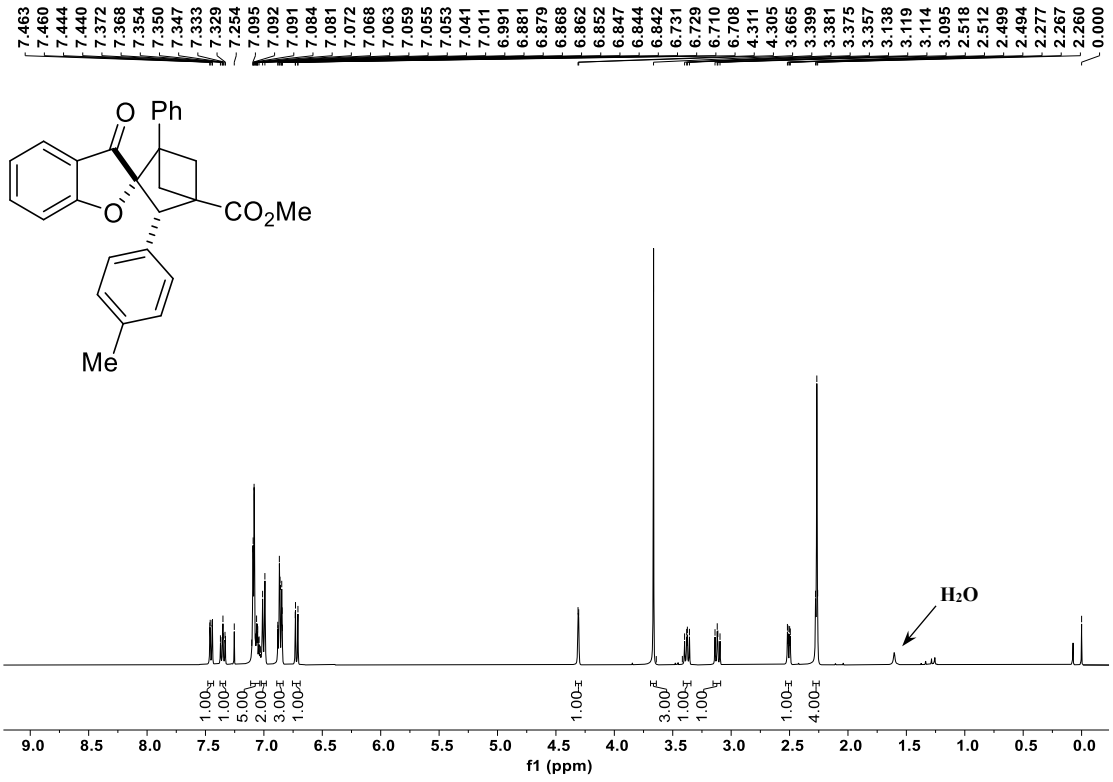
^{13}C NMR of **3m** in $CDCl_3$ (100 MHz)



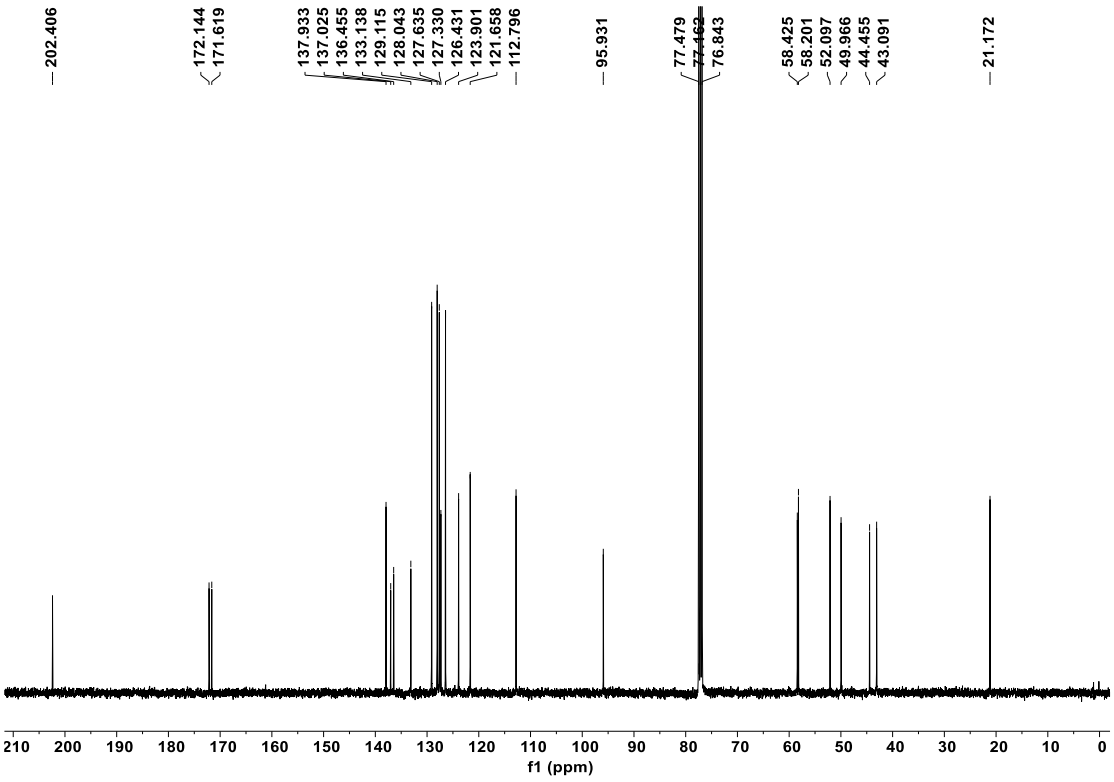
^{19}F NMR of **3m** in $CDCl_3$ (376 MHz)



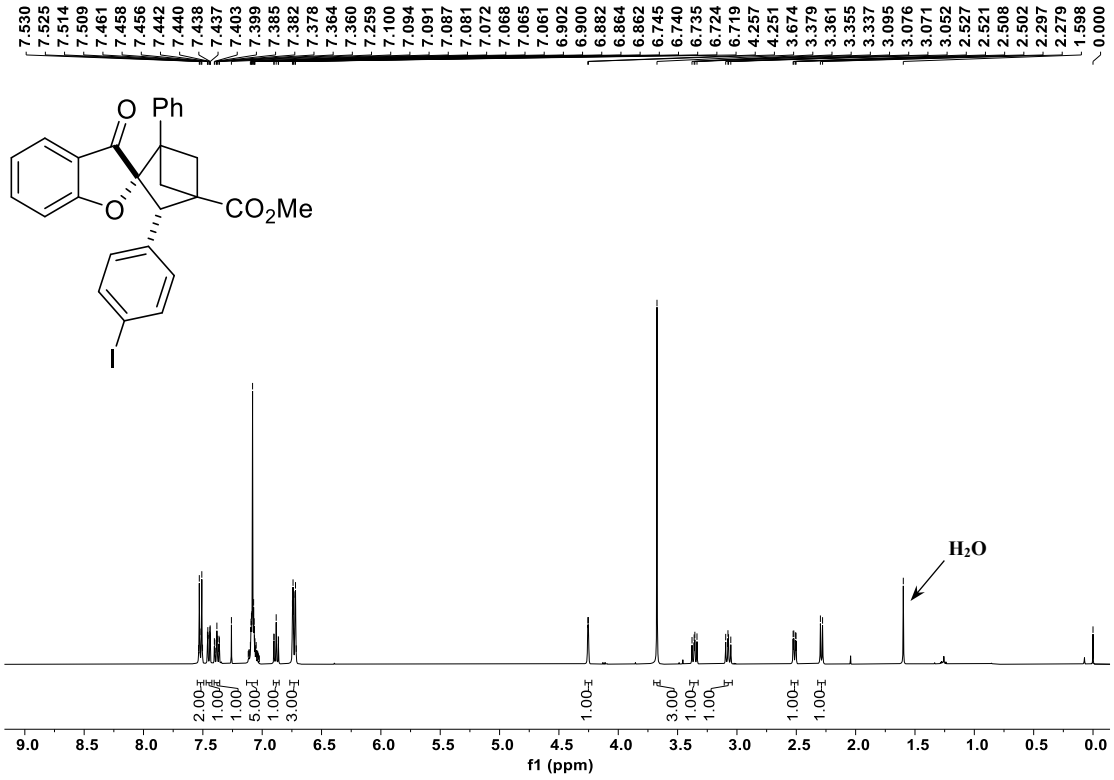
^{1}H NMR of **3n** in $CDCl_3$ (400 MHz)



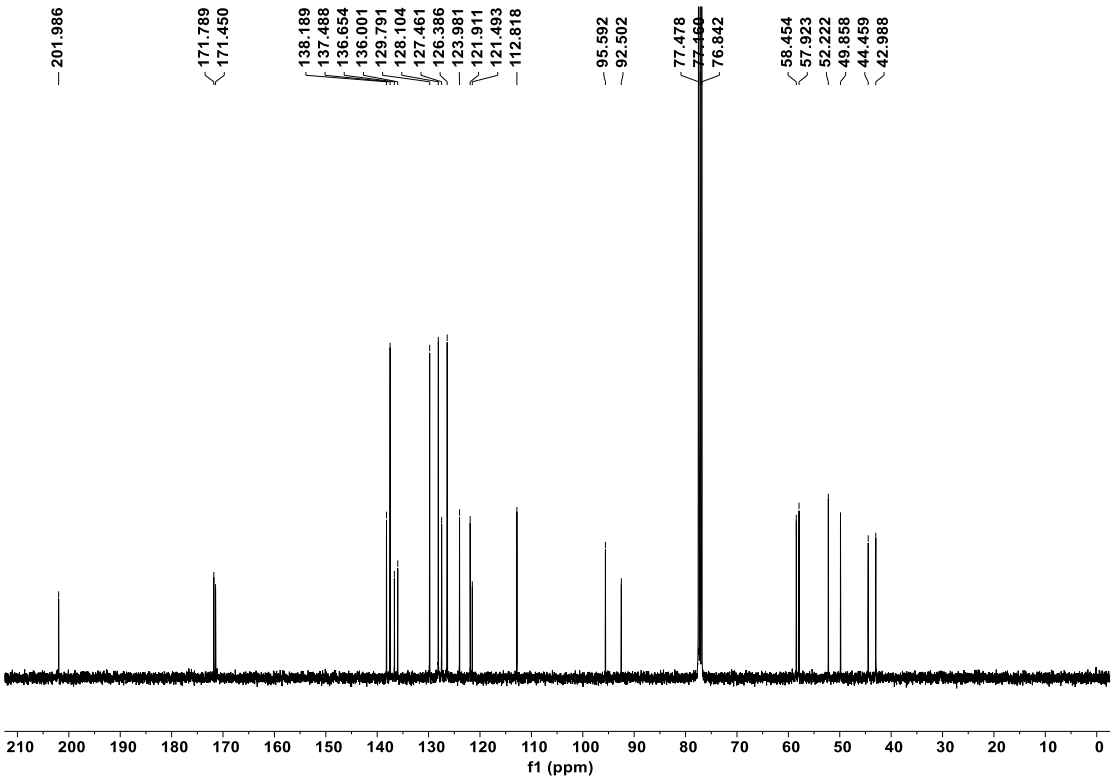
^{13}C NMR of **3n** in $CDCl_3$ (100 MHz)



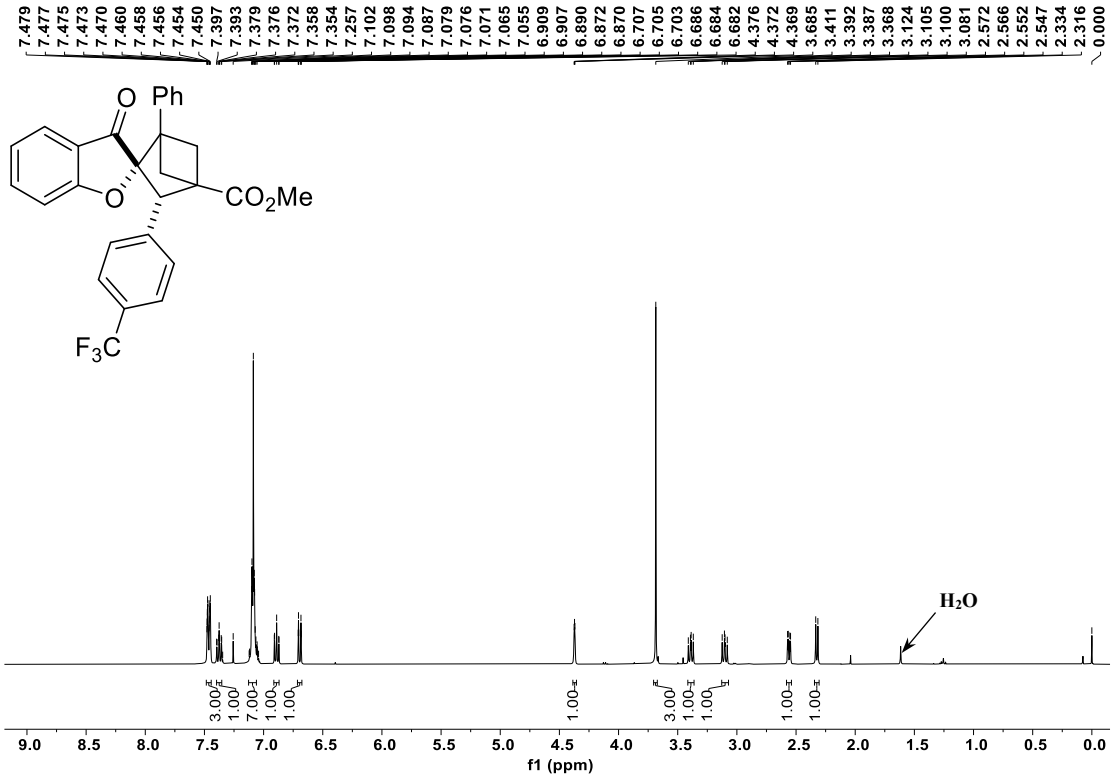
^{1}H NMR of **3o** in $CDCl_3$ (400 MHz)



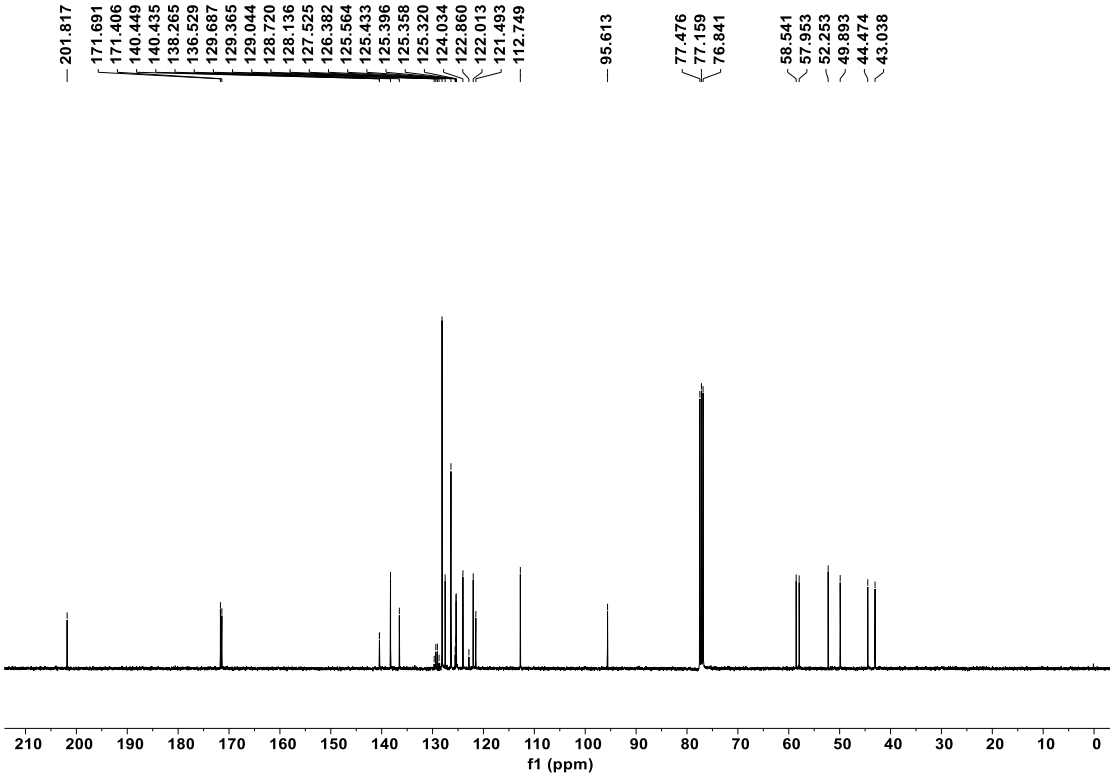
^{13}C NMR of **3o** in $CDCl_3$ (100 MHz)



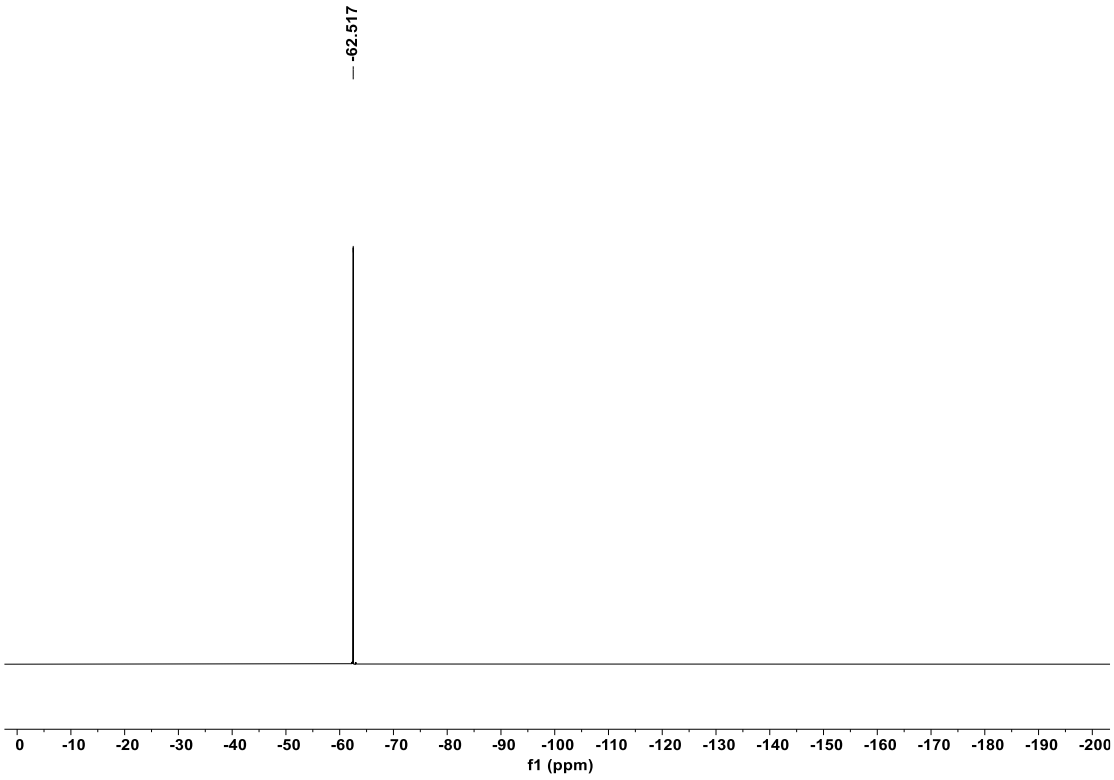
^{1}H NMR of **3p** in $CDCl_3$ (400 MHz)



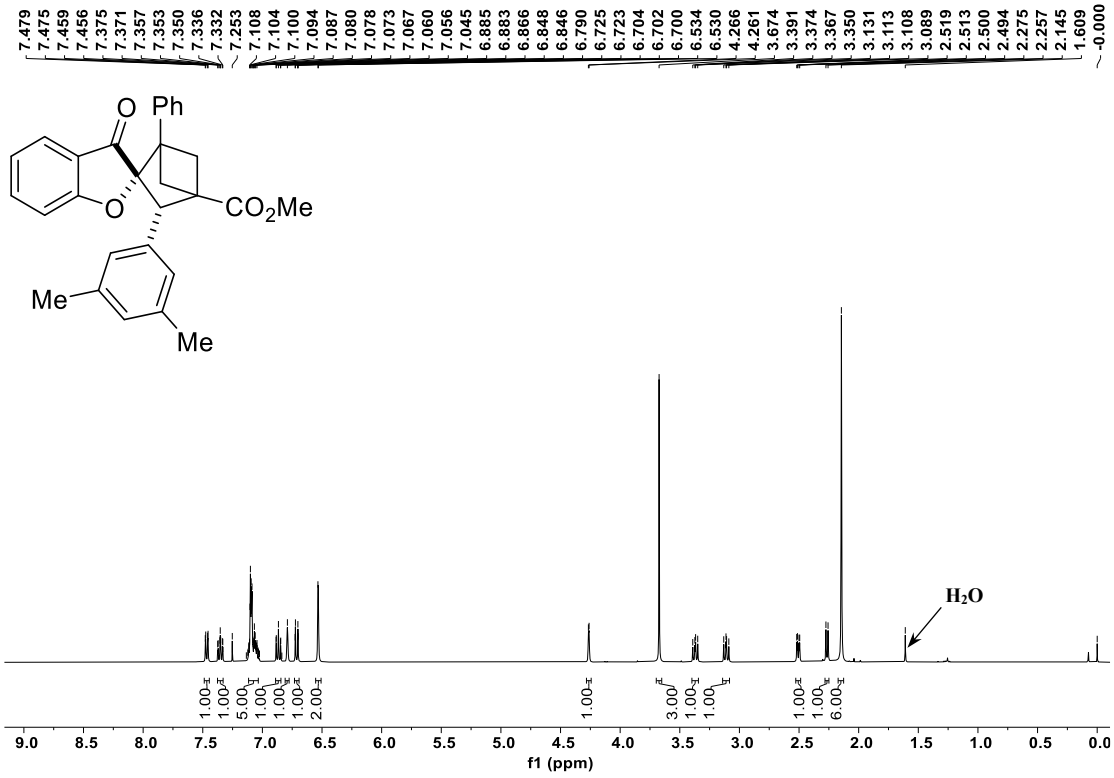
^{13}C NMR of **3p** in $CDCl_3$ (100 MHz)



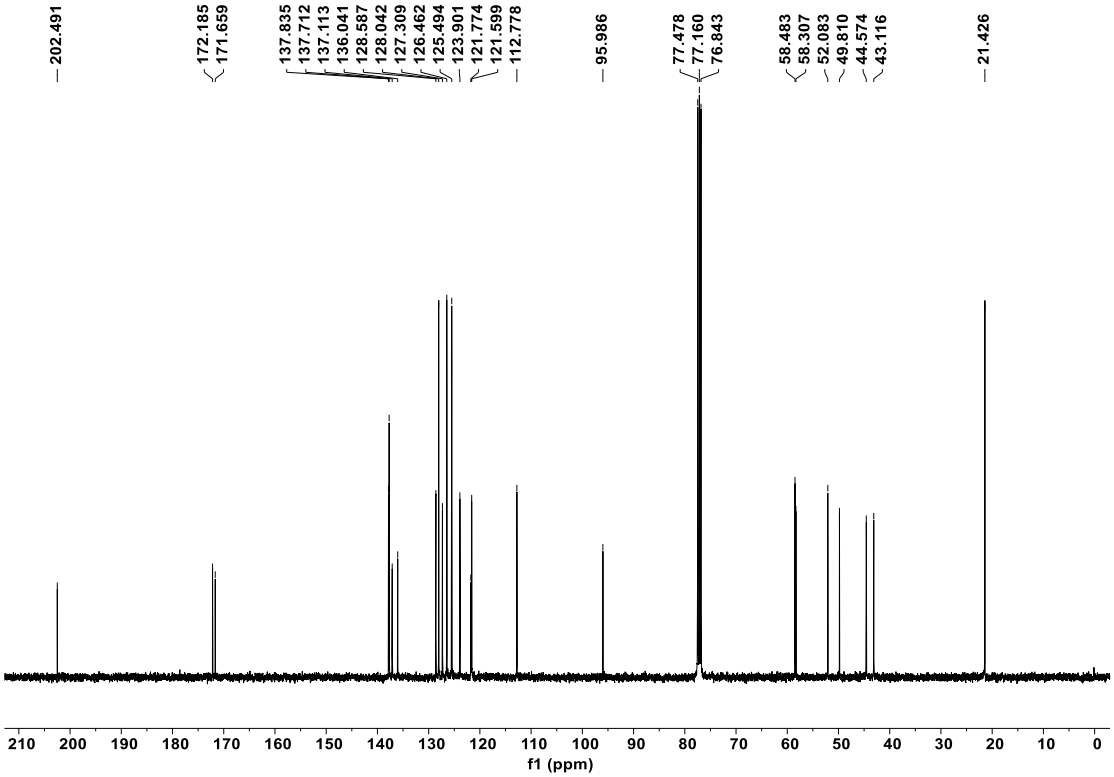
^{19}F NMR of **3p** in $CDCl_3$ (376 MHz)



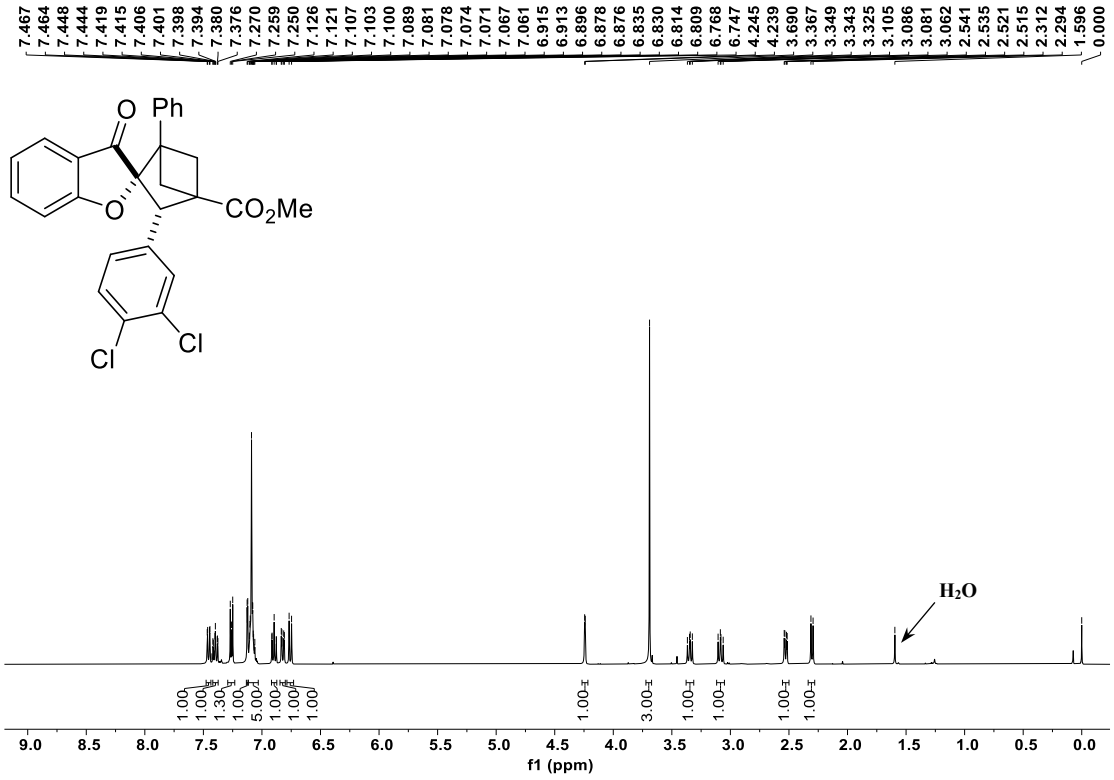
^{1}H NMR of **3q** in $CDCl_3$ (400 MHz)



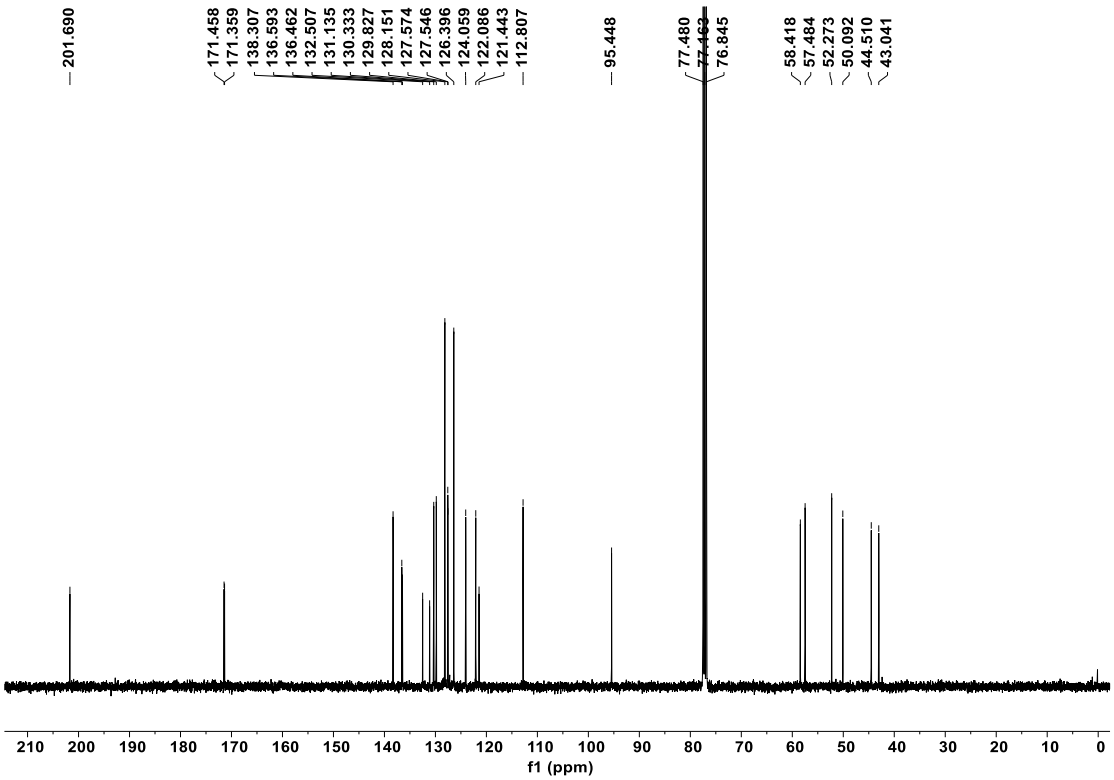
^{13}C NMR of **3q** in $CDCl_3$ (100 MHz)



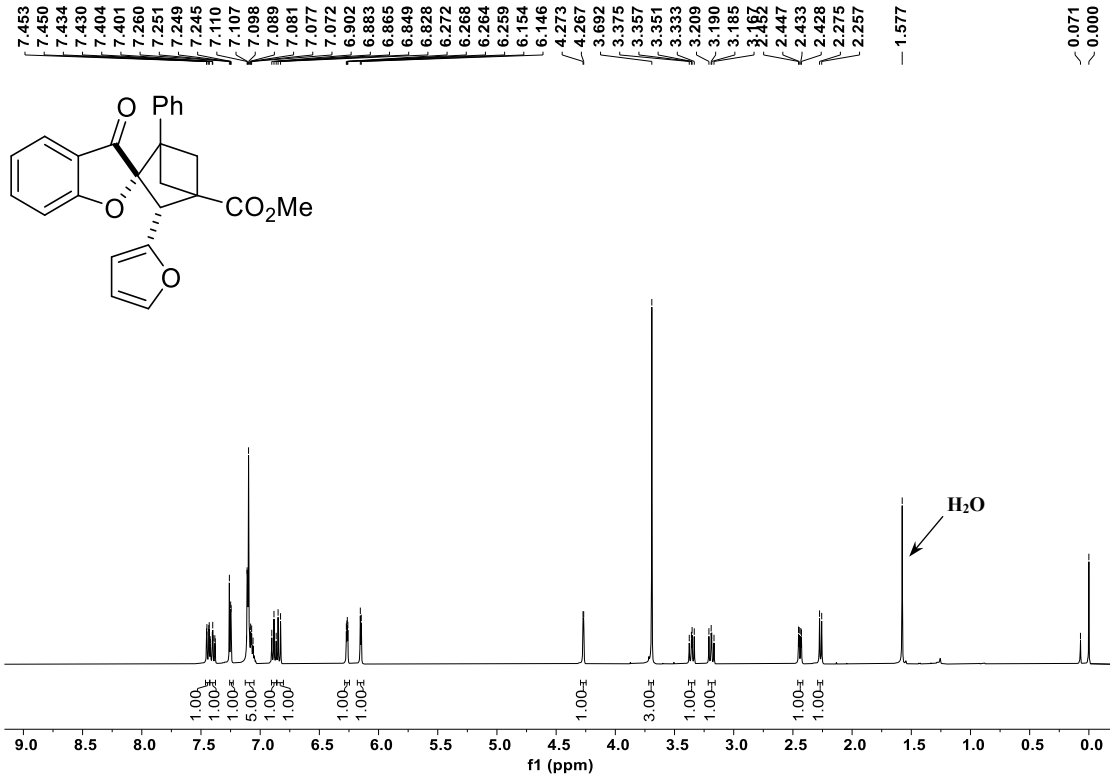
^{1}H NMR of **3r** in $CDCl_3$ (400 MHz)



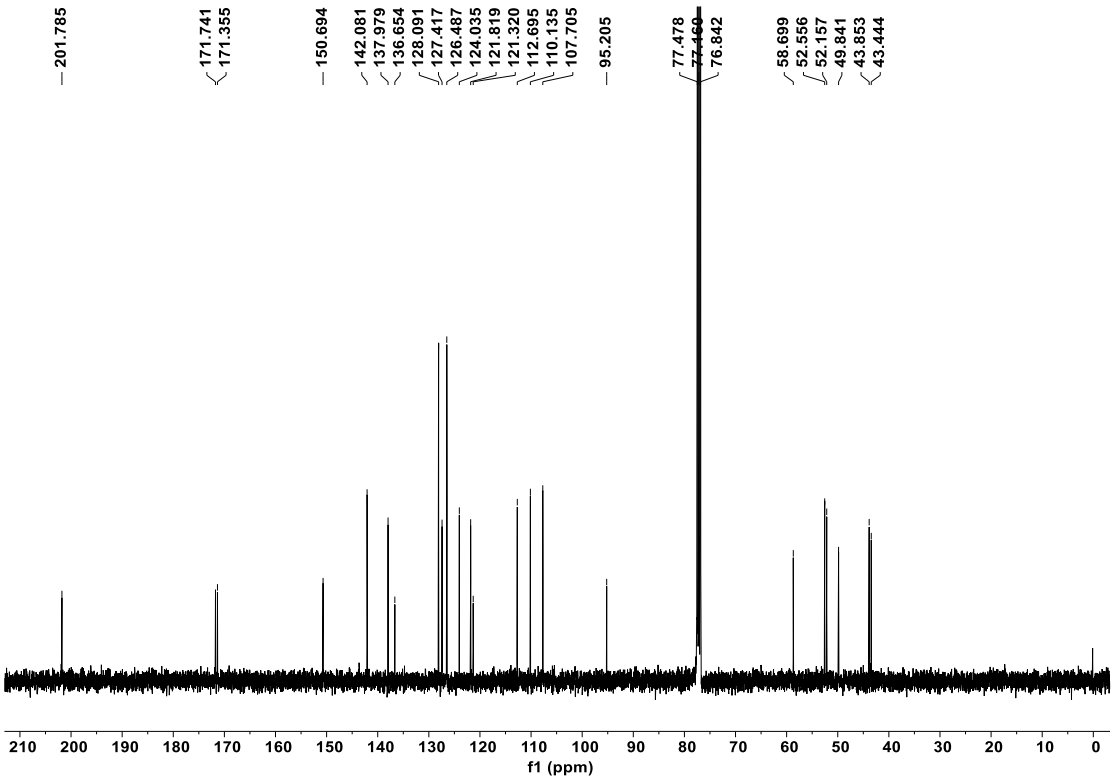
^{13}C NMR of **3r** in $CDCl_3$ (100 MHz)



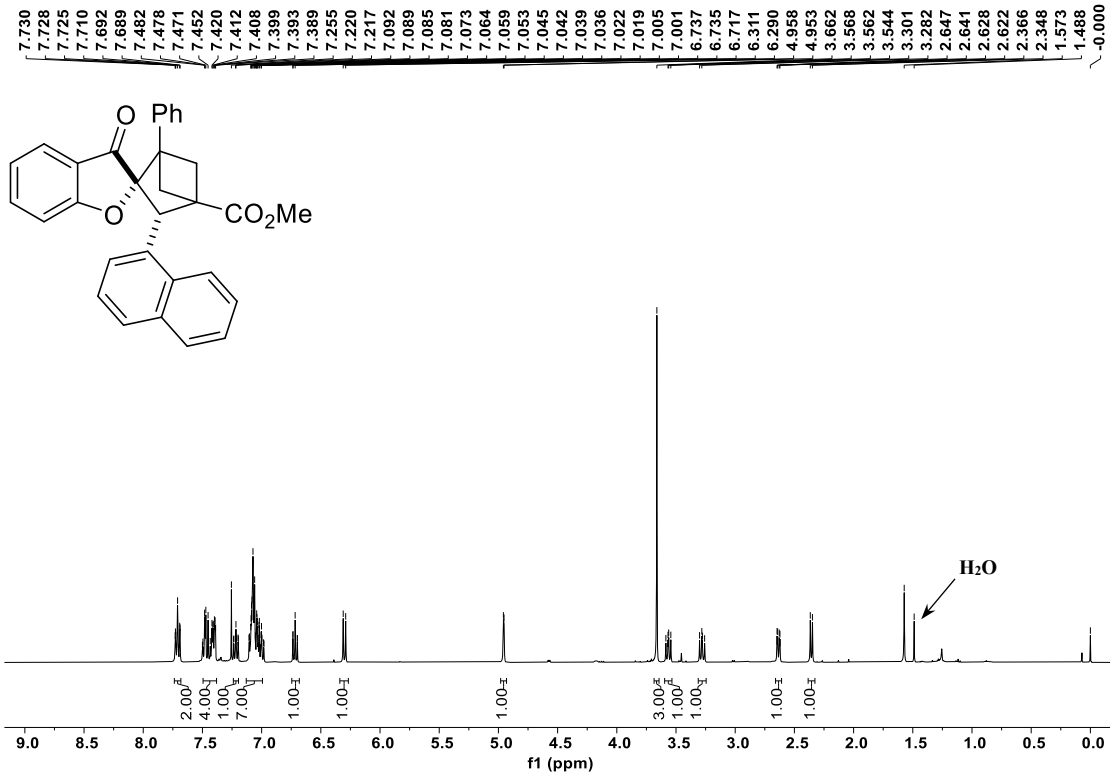
^{1}H NMR of **3s** in $CDCl_3$ (400 MHz)



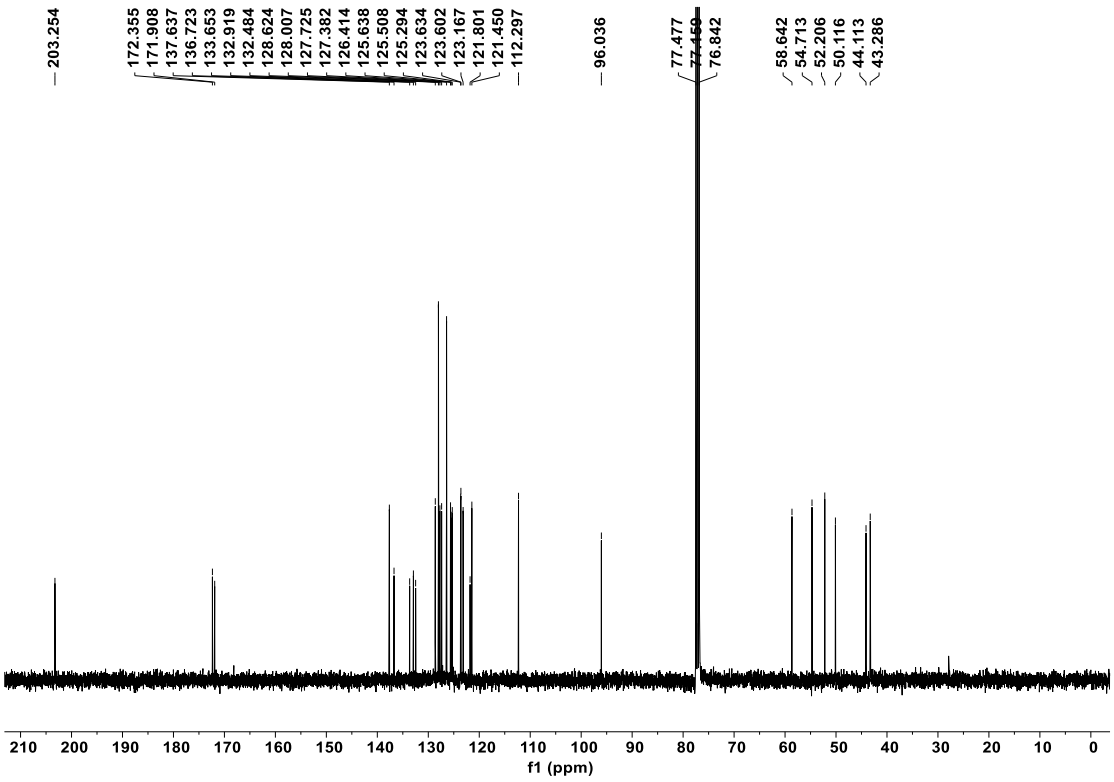
^{13}C NMR of **3s** in $CDCl_3$ (100 MHz)



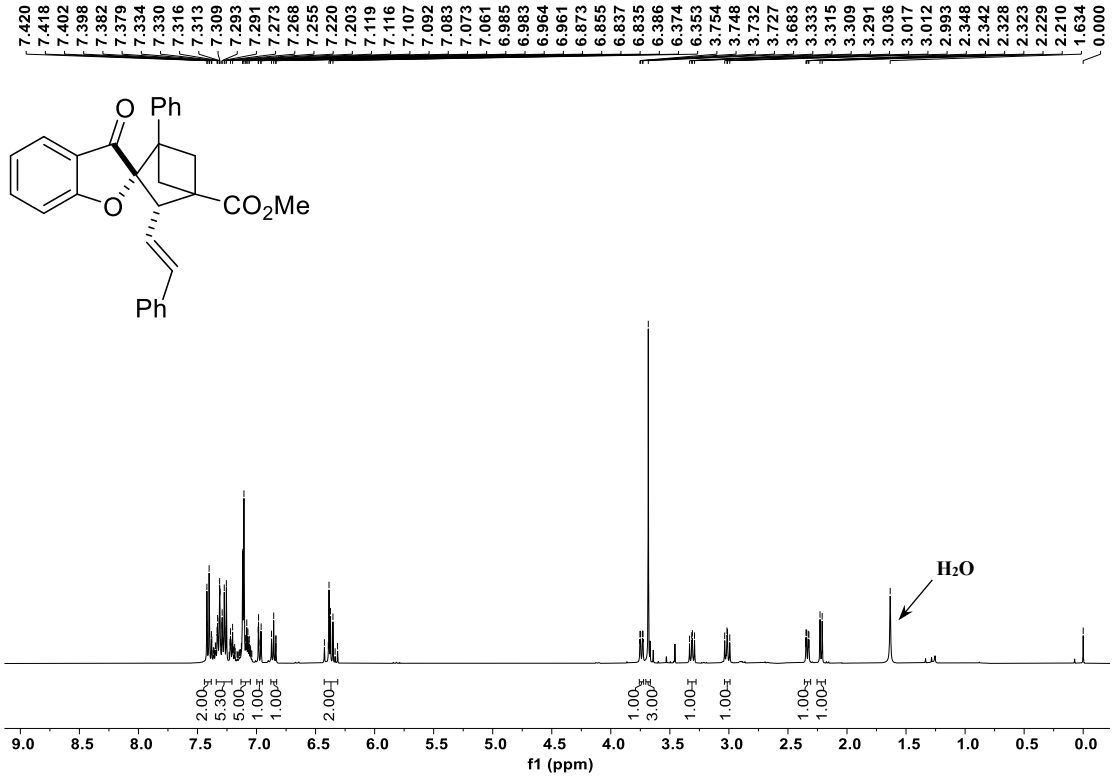
^{1}H NMR of **3t** in $CDCl_3$ (400 MHz)



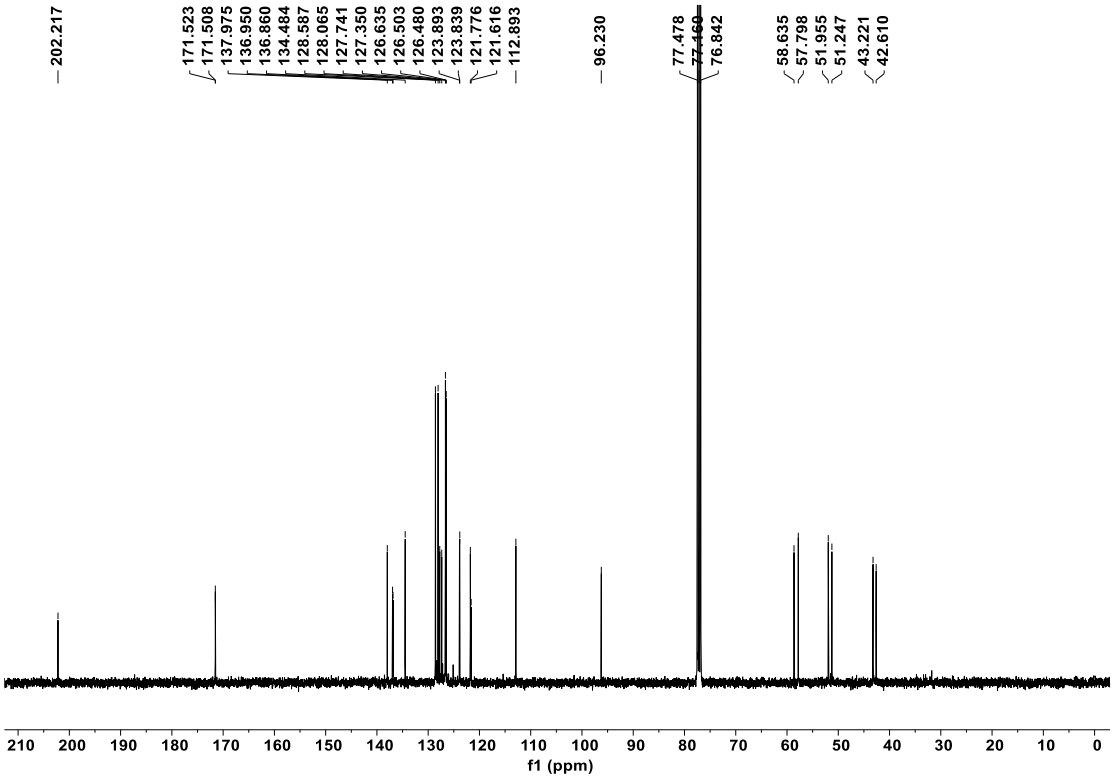
^{13}C NMR of **3t** in $CDCl_3$ (100 MHz)



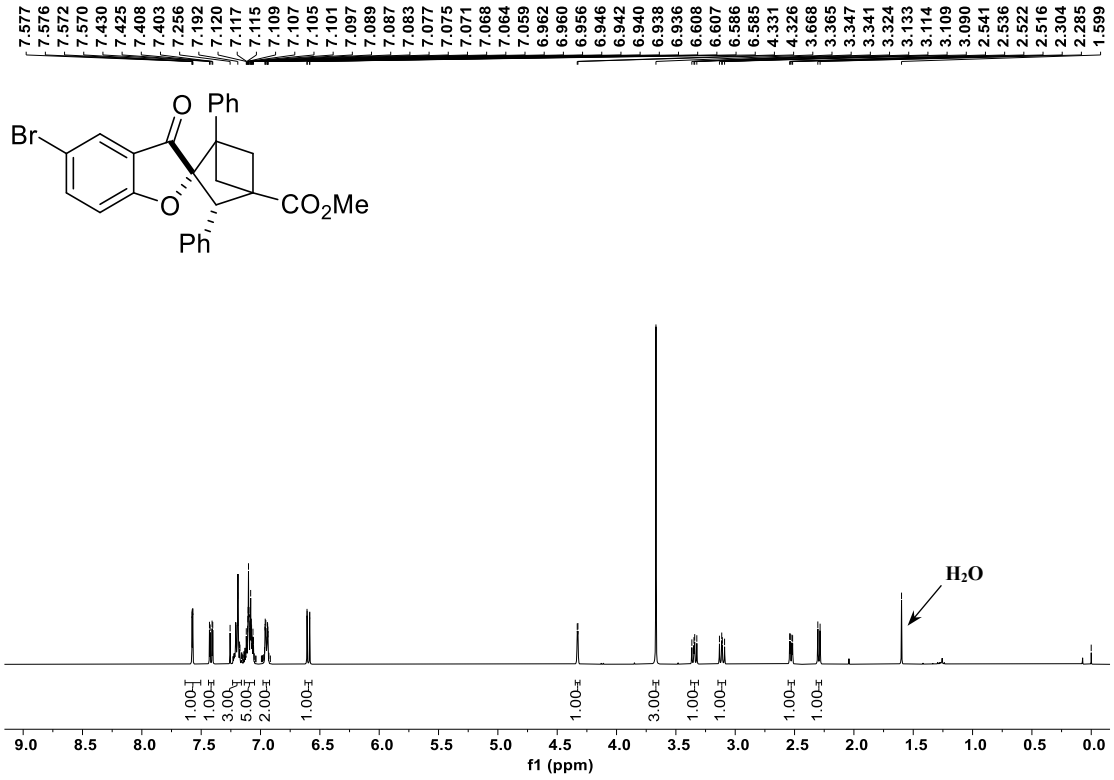
^{1}H NMR of **3u** in $CDCl_3$ (400 MHz)



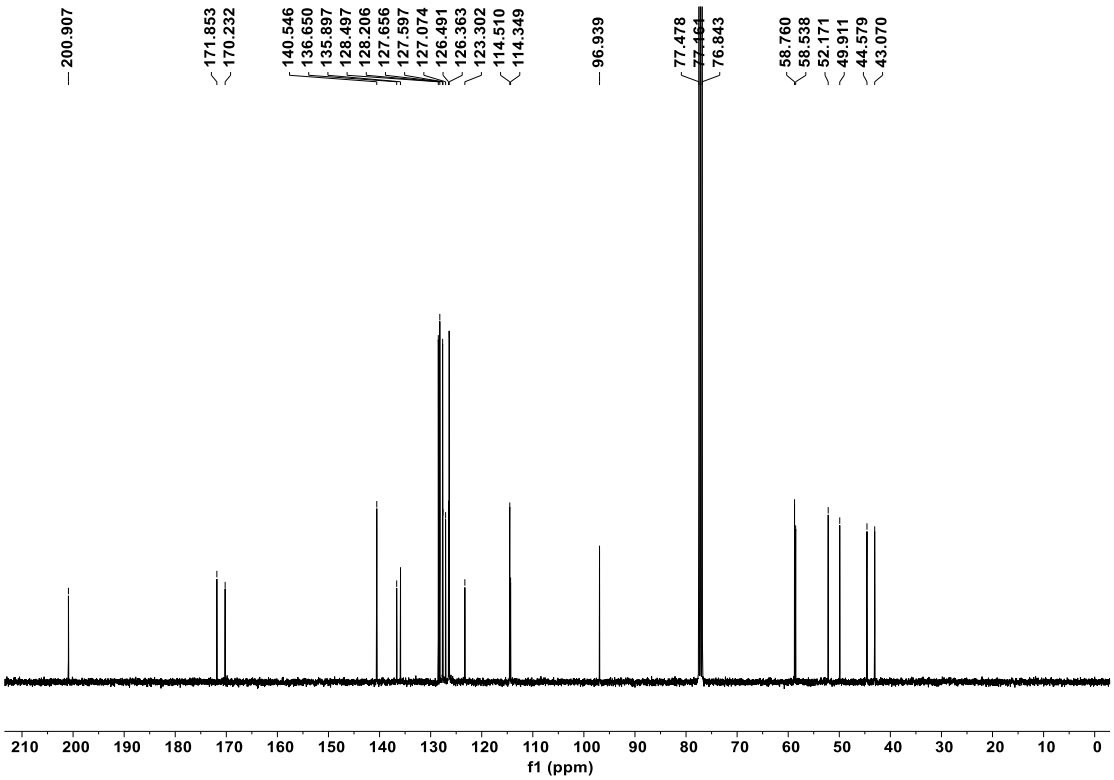
^{13}C NMR of **3u** in $CDCl_3$ (100 MHz)



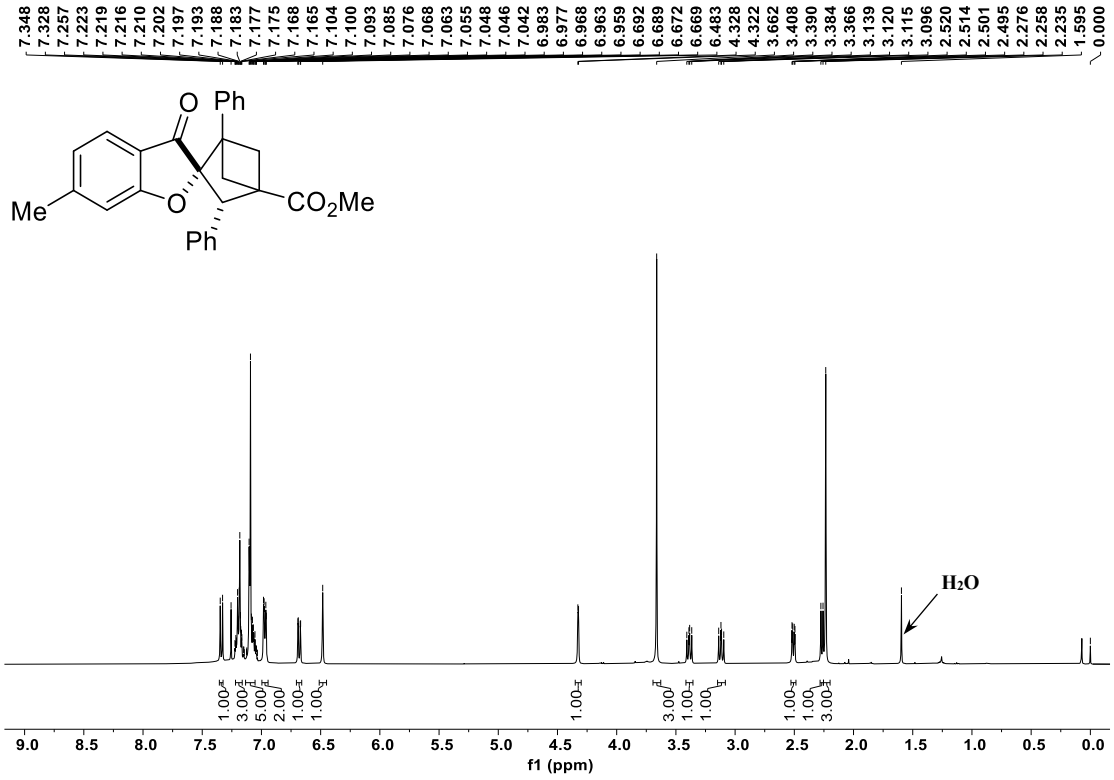
^{1}H NMR of **3v** in $CDCl_3$ (400 MHz)



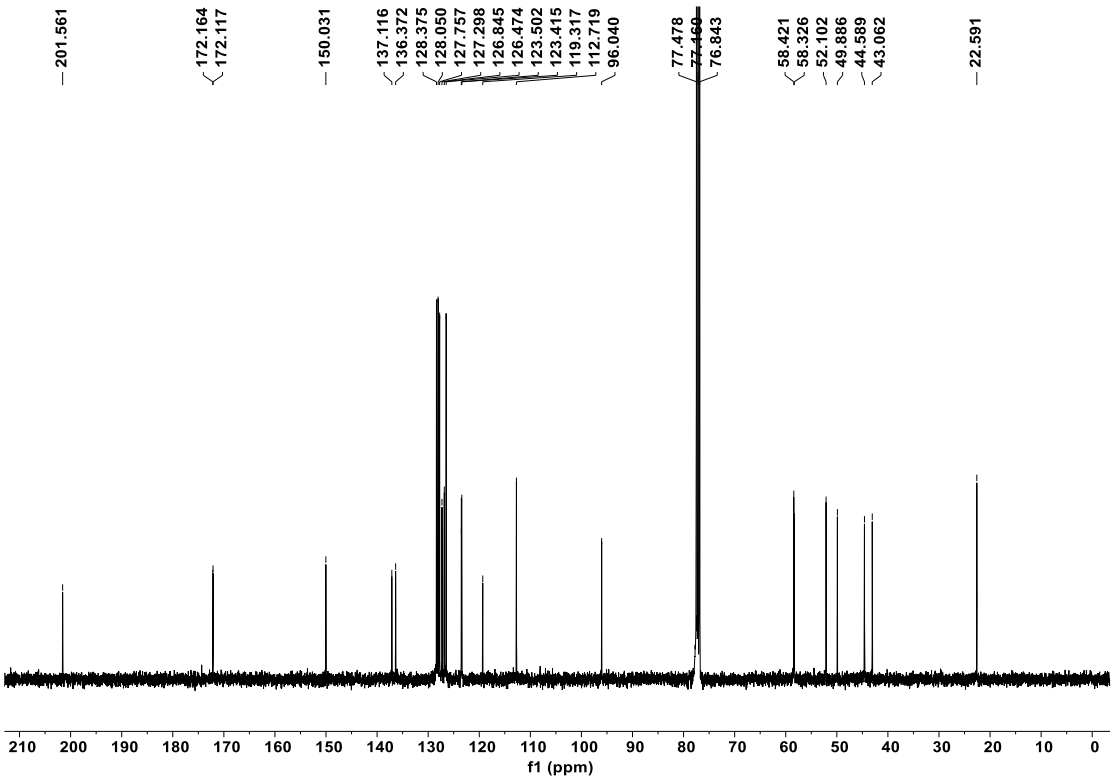
^{13}C NMR of **3v** in $CDCl_3$ (100 MHz)



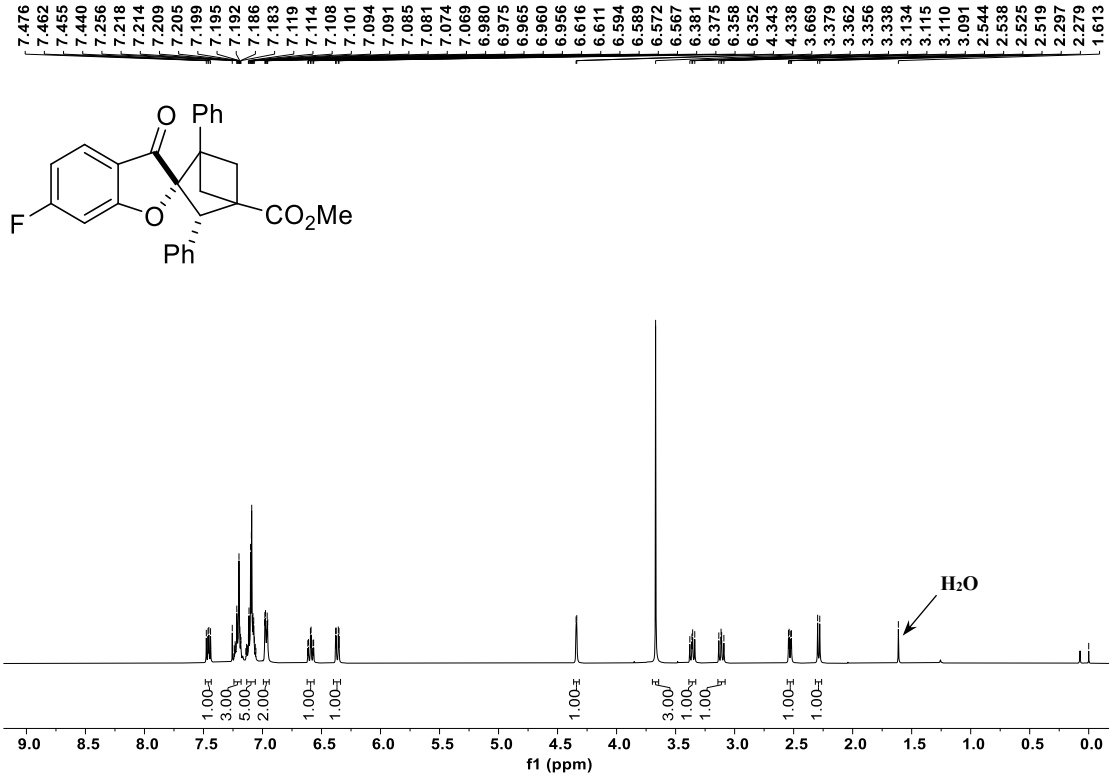
^{1}H NMR of **3w** in $CDCl_3$ (400 MHz)



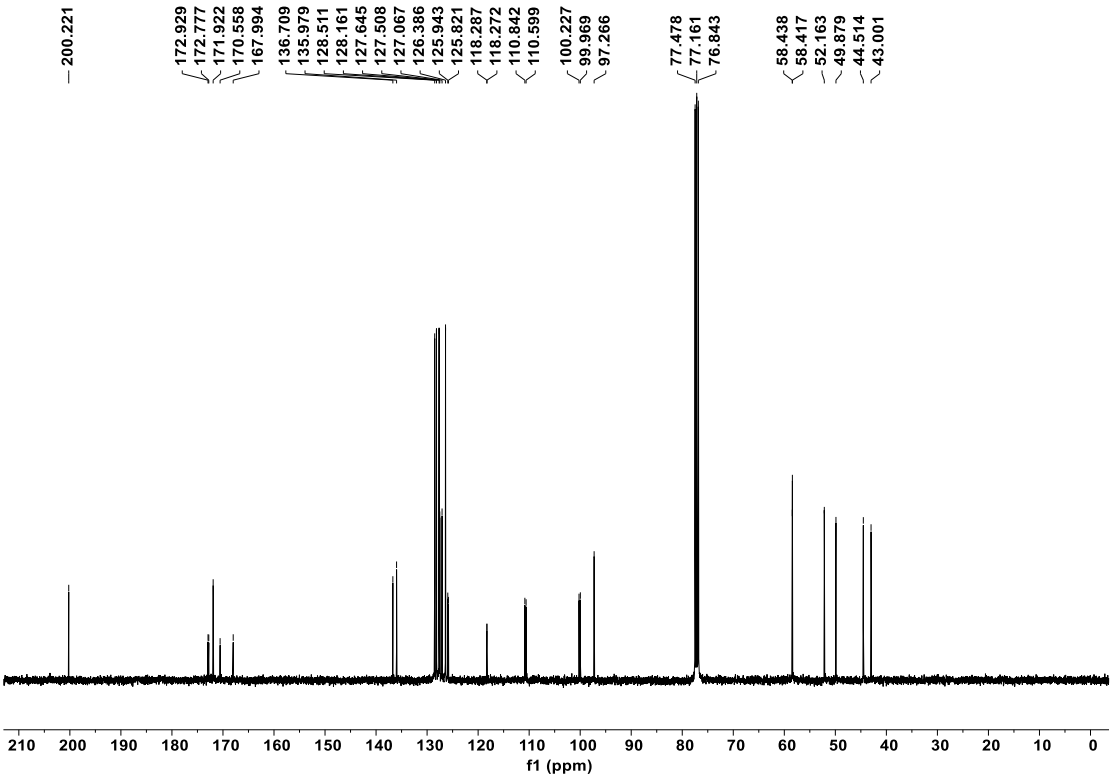
^{13}C NMR of **3w** in $CDCl_3$ (100 MHz)



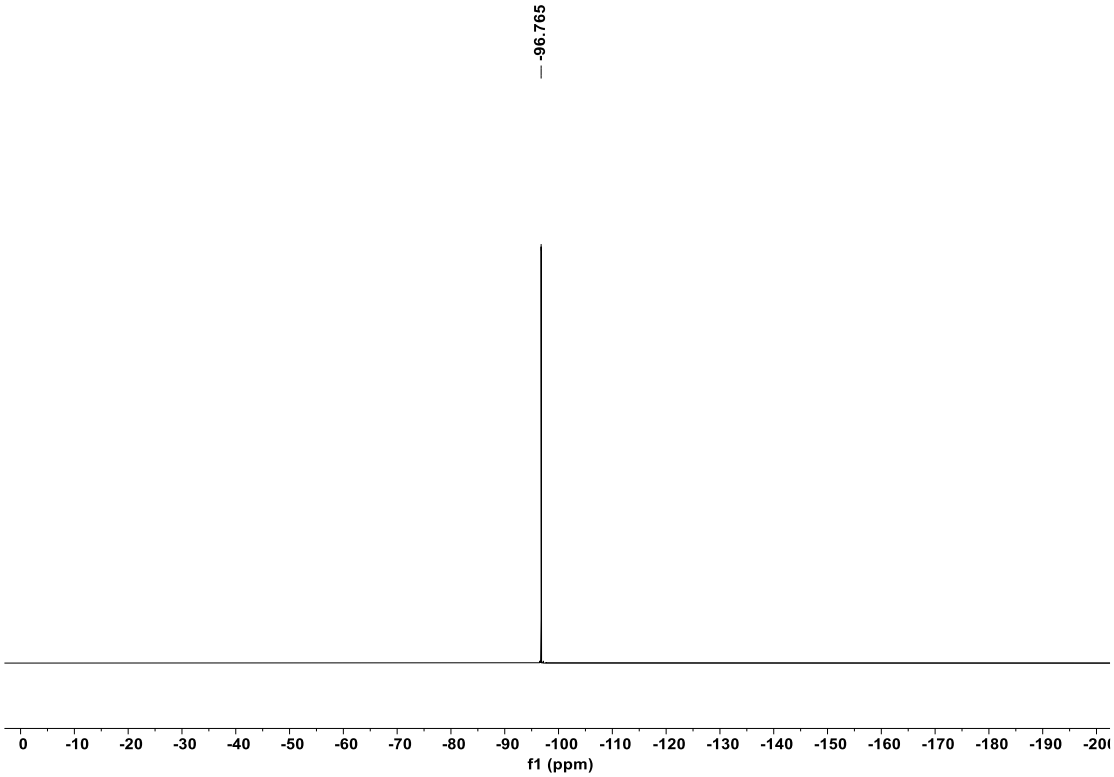
^{1}H NMR of **3x** in $CDCl_3$ (400 MHz)



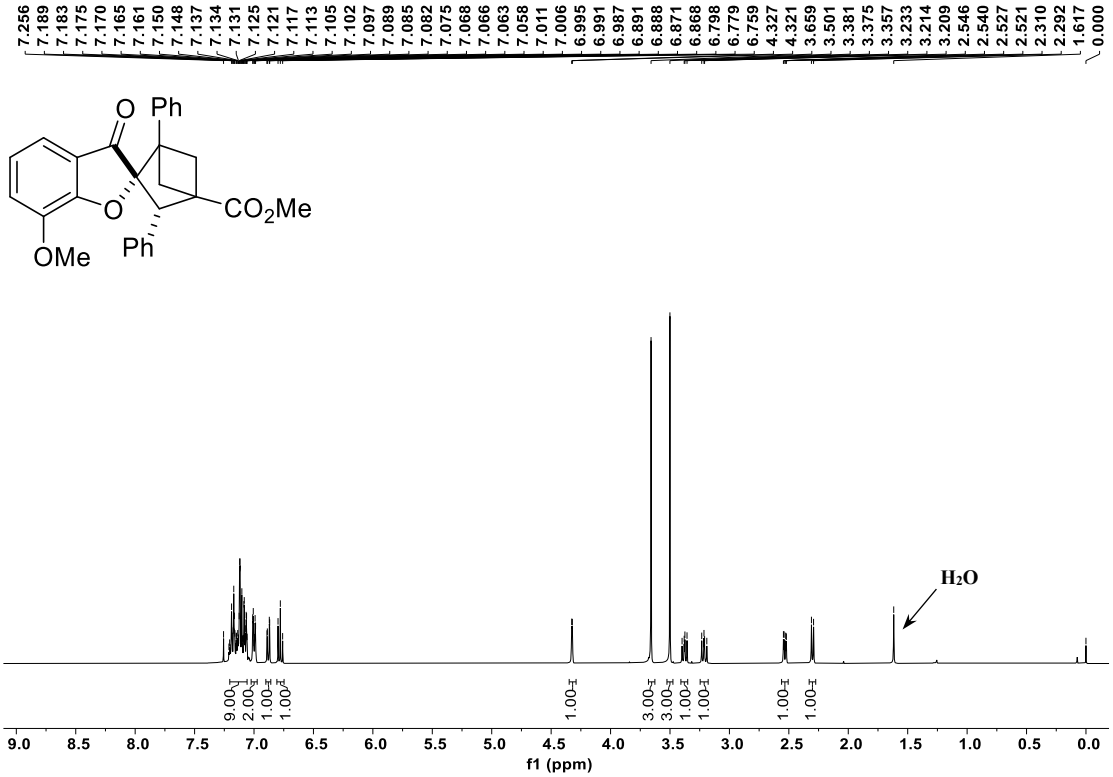
^{13}C NMR of **3x** in $CDCl_3$ (100 MHz)



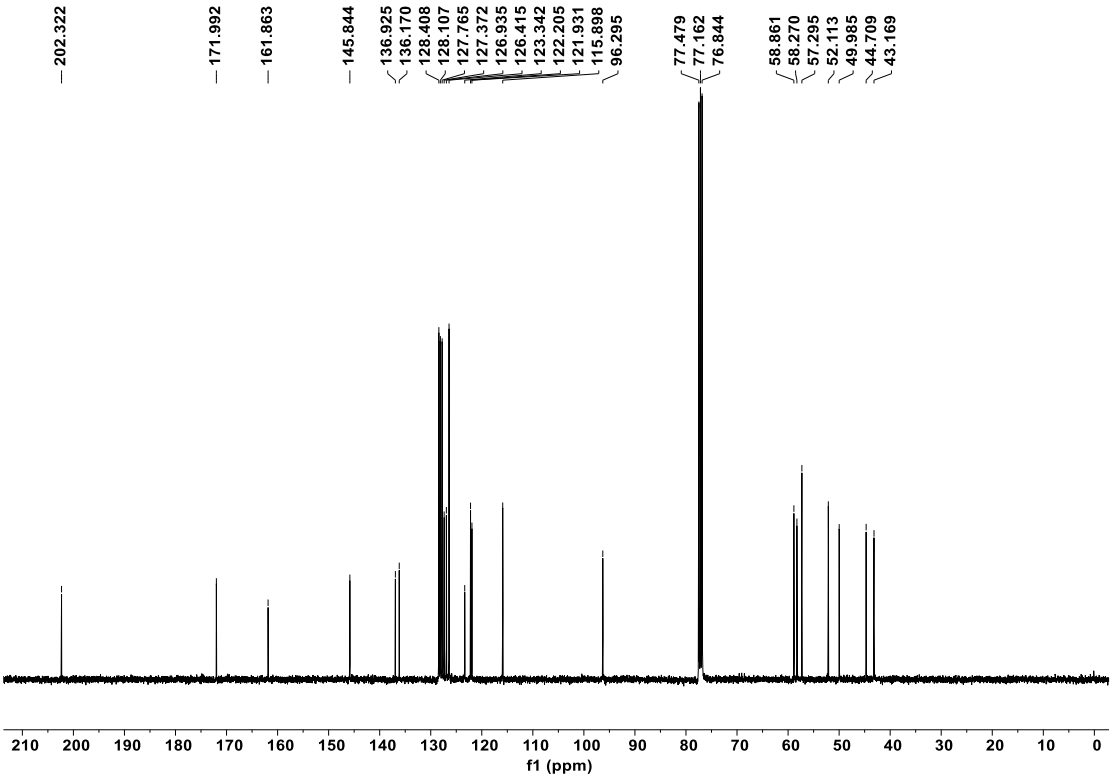
^{19}F NMR of **3x** in $CDCl_3$ (376 MHz)



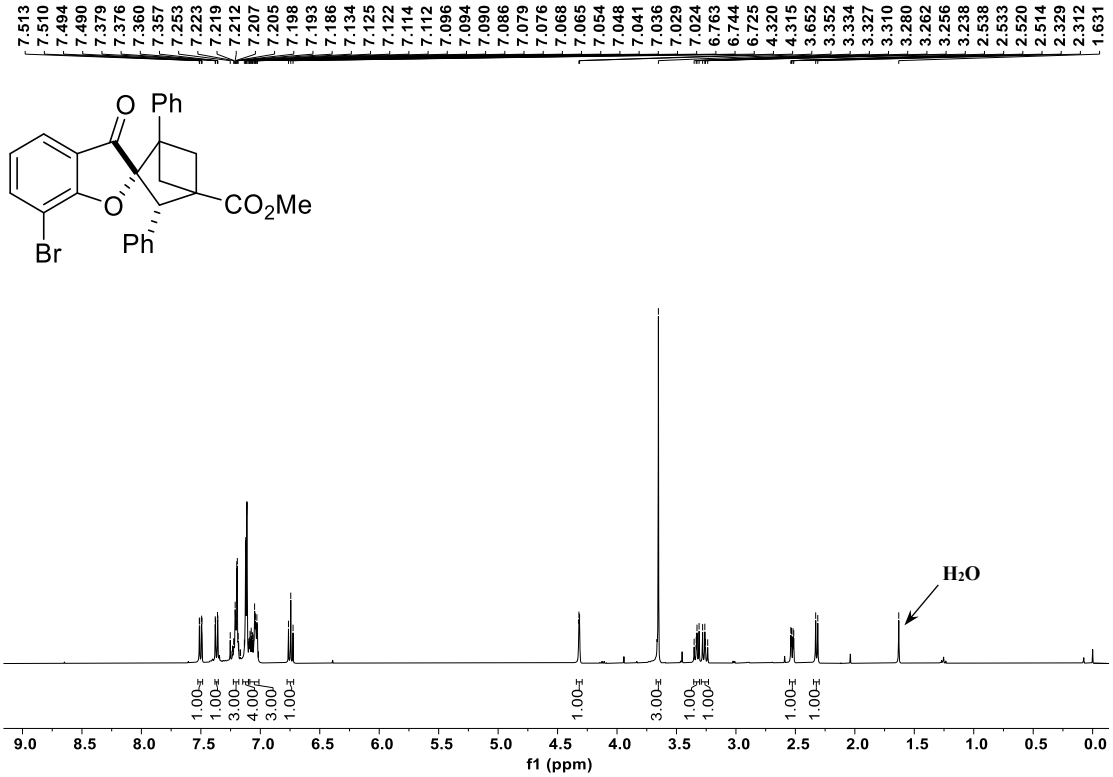
^{1}H NMR of **3y** in $CDCl_3$ (400 MHz)



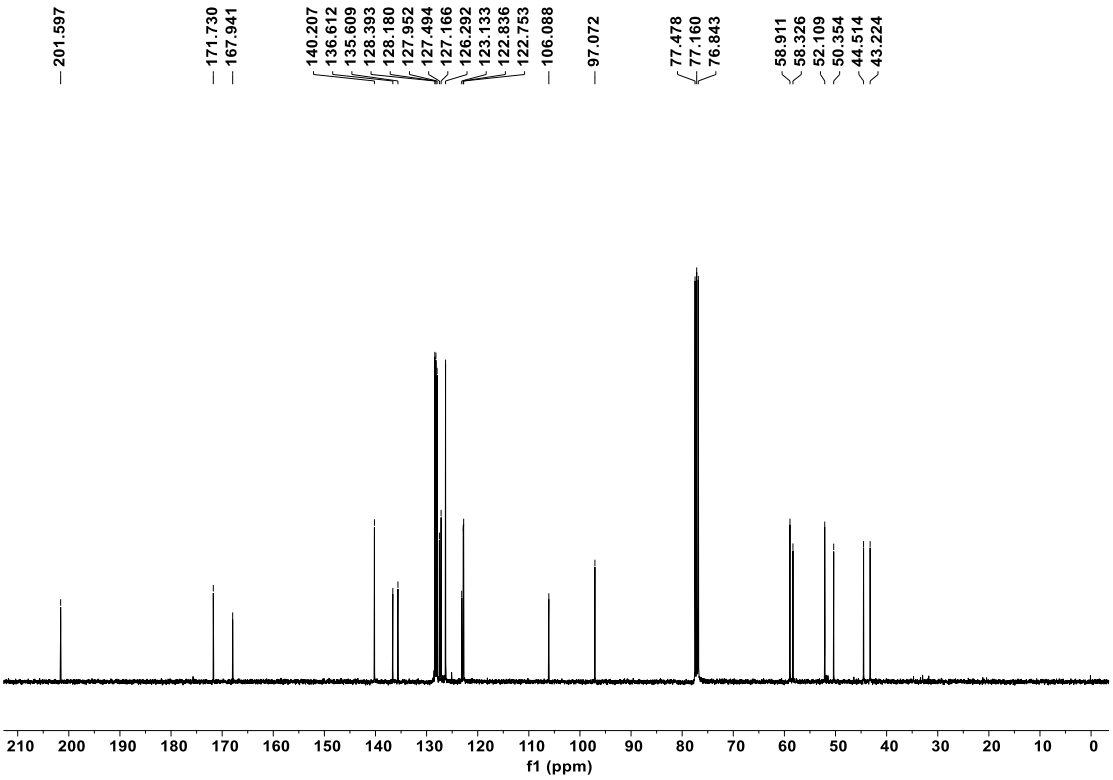
^{13}C NMR of **3y** in $CDCl_3$ (100 MHz)



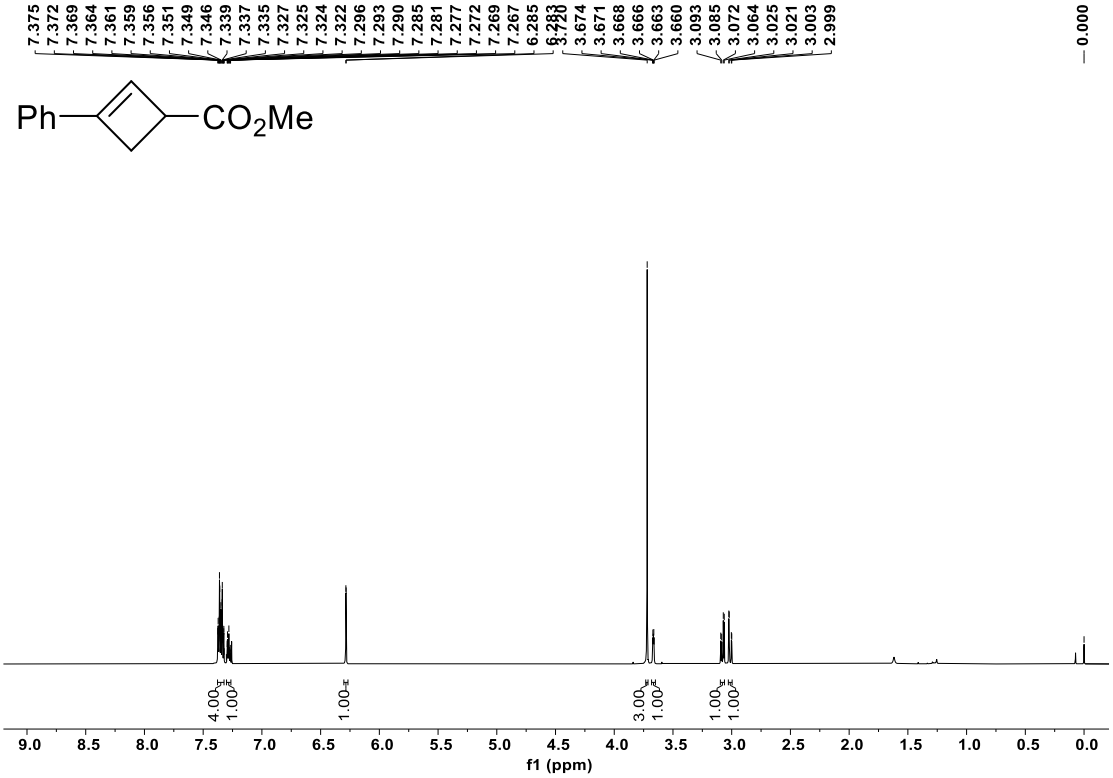
^{1}H NMR of **3z** in $CDCl_3$ (400 MHz)



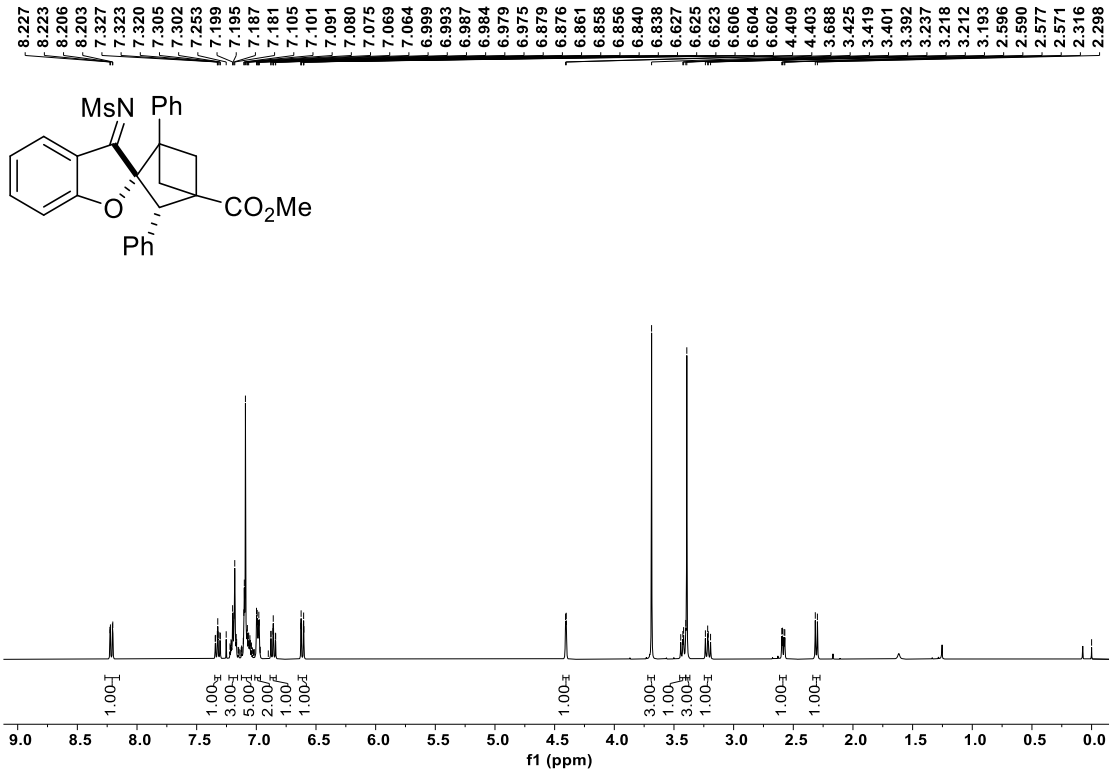
^{13}C NMR of **3z** in $CDCl_3$ (100 MHz)



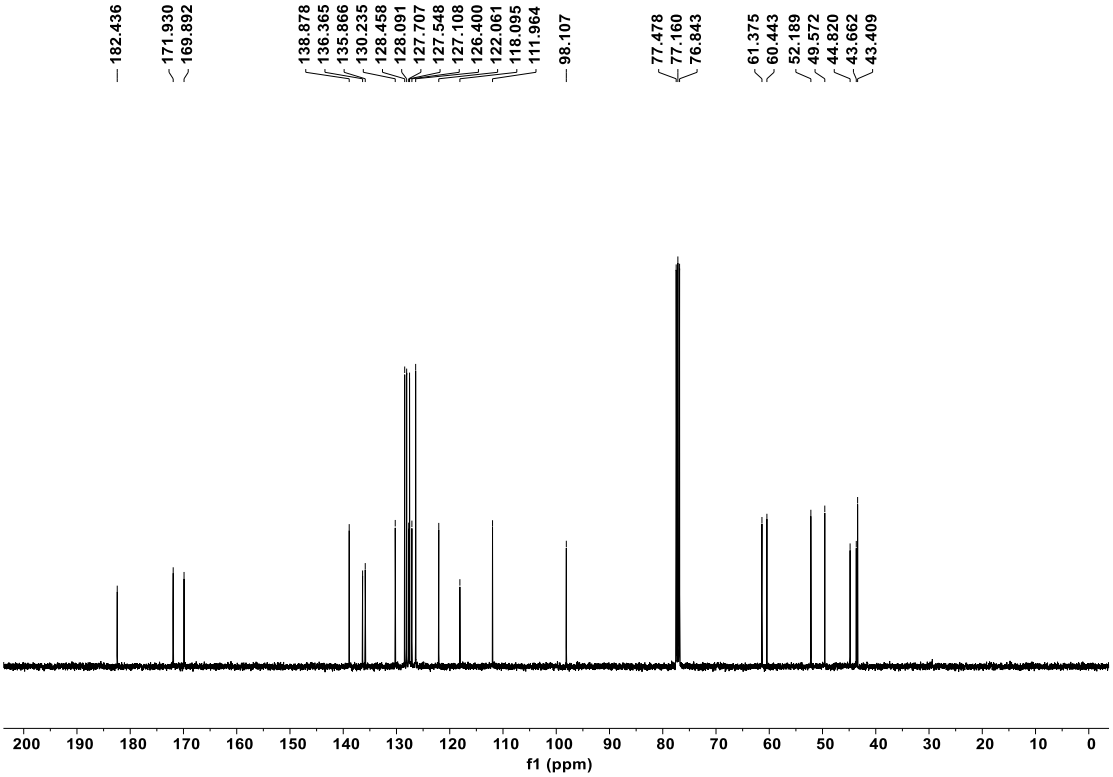
^{1}H NMR of **4a** in $CDCl_3$ (600 MHz)



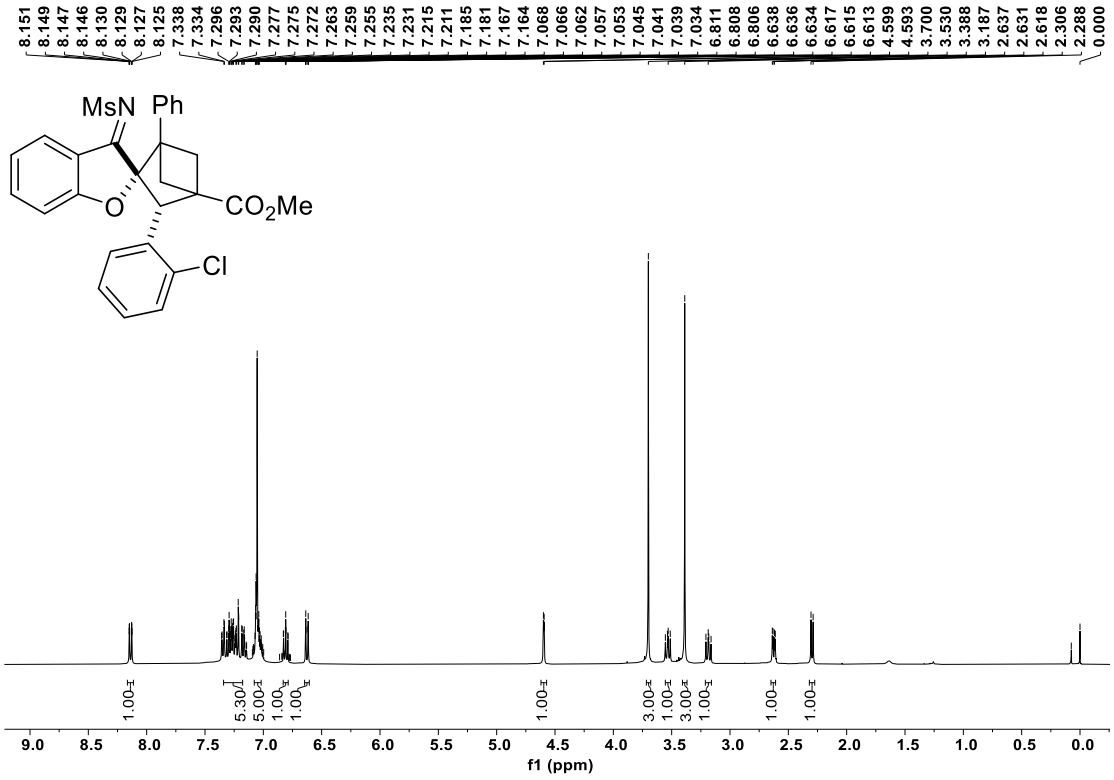
^{1}H NMR of **6a** in $CDCl_3$ (400 MHz)



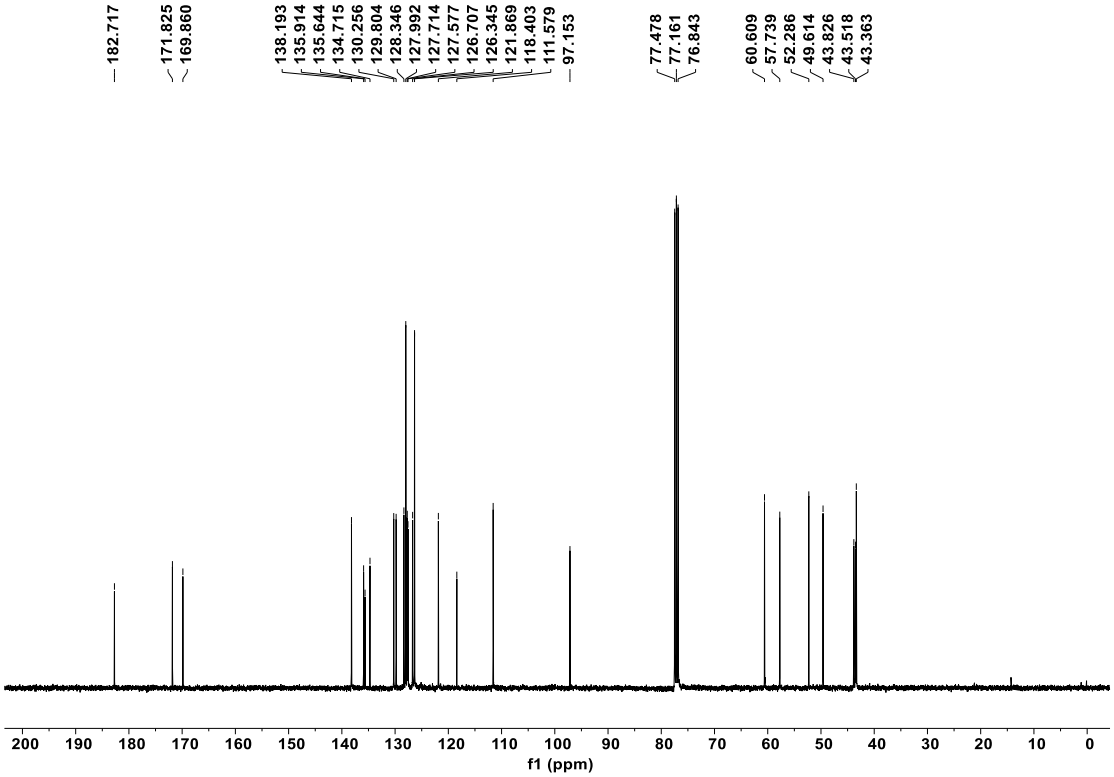
^{13}C NMR of **6a** in $CDCl_3$ (100 MHz)



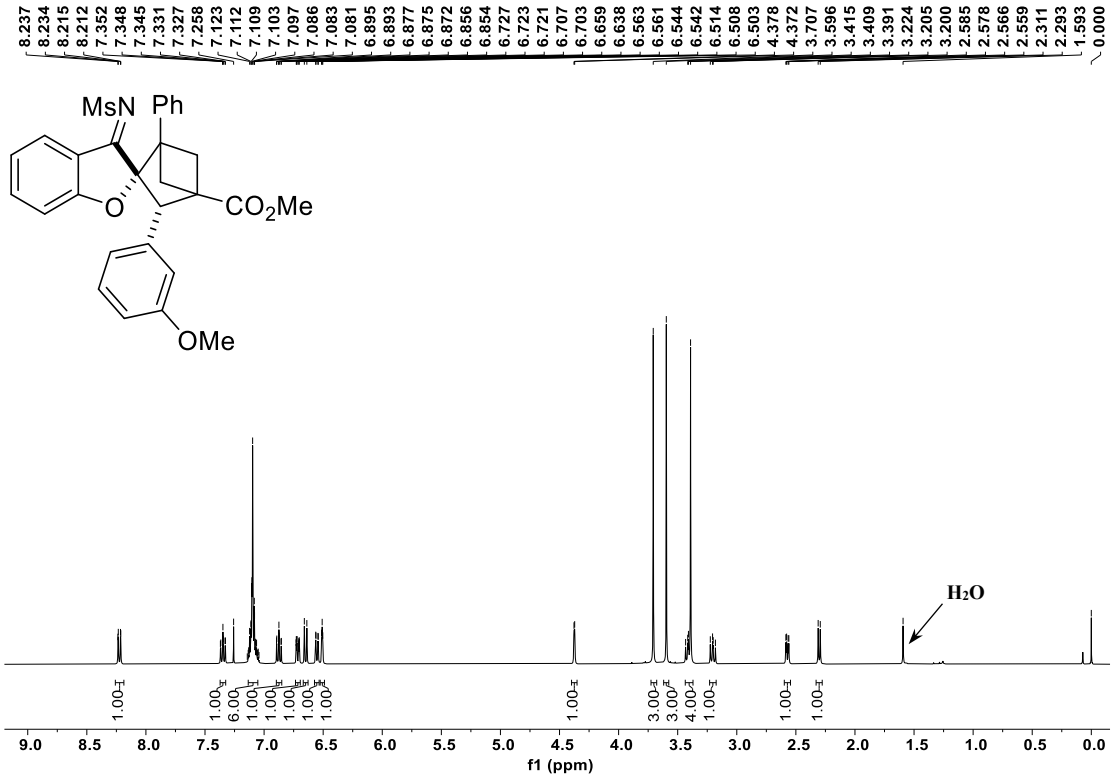
^{1}H NMR of **6b** in $CDCl_3$ (400 MHz)



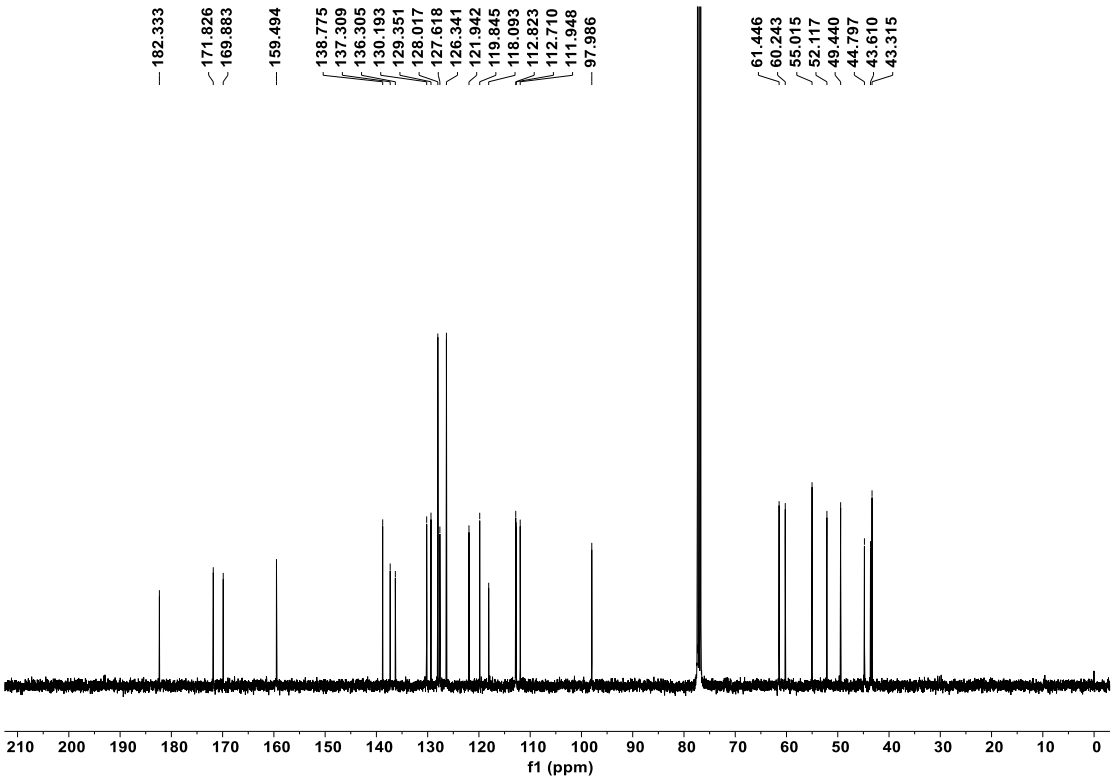
^{13}C NMR of **6b** in $CDCl_3$ (100 MHz)



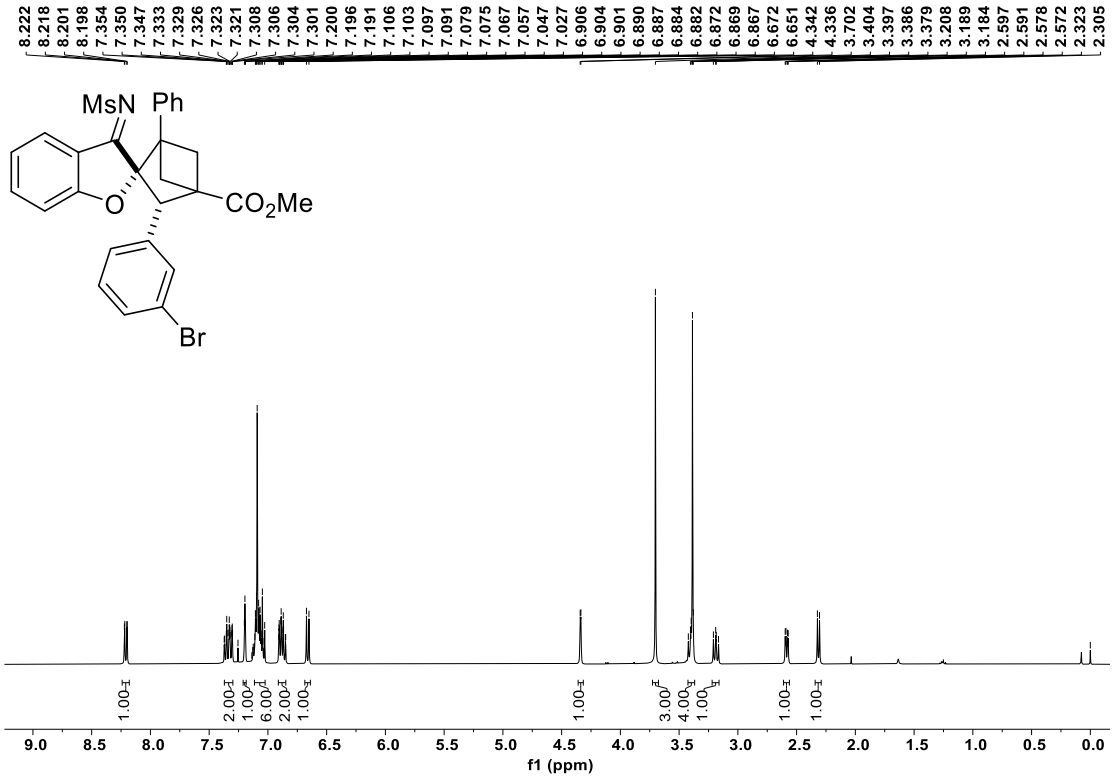
^{1}H NMR of **6c** in $CDCl_3$ (400 MHz)



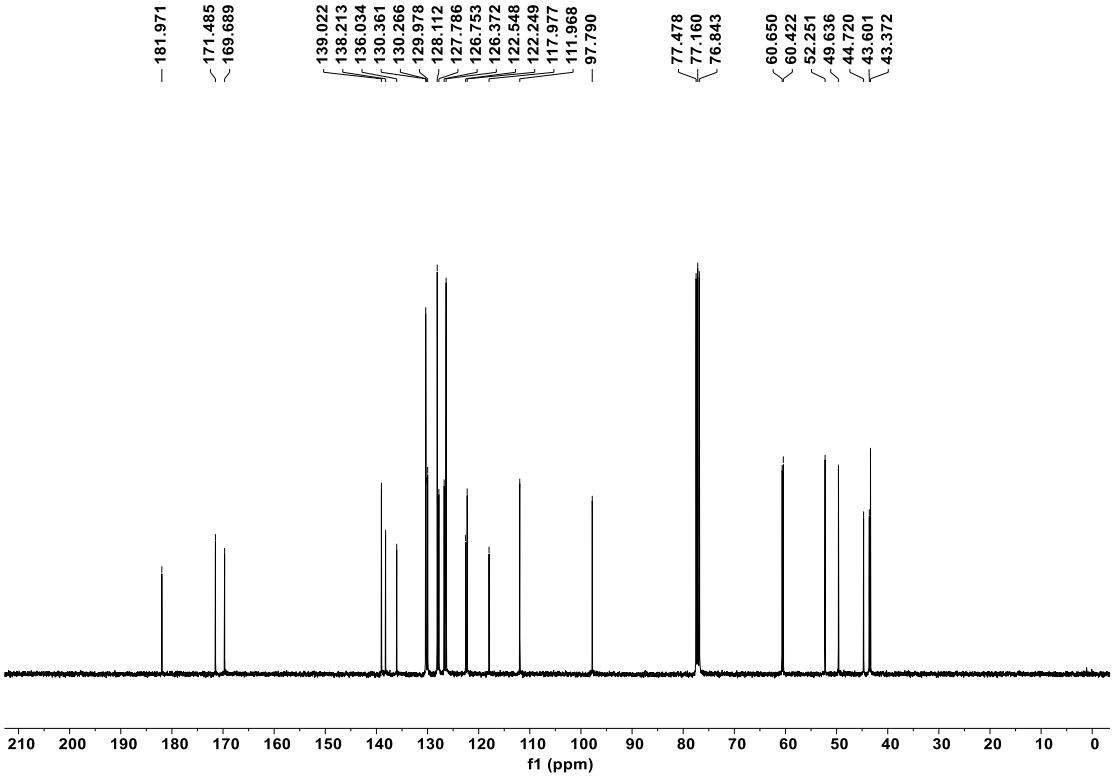
^{13}C NMR of **6c** in $CDCl_3$ (100 MHz)



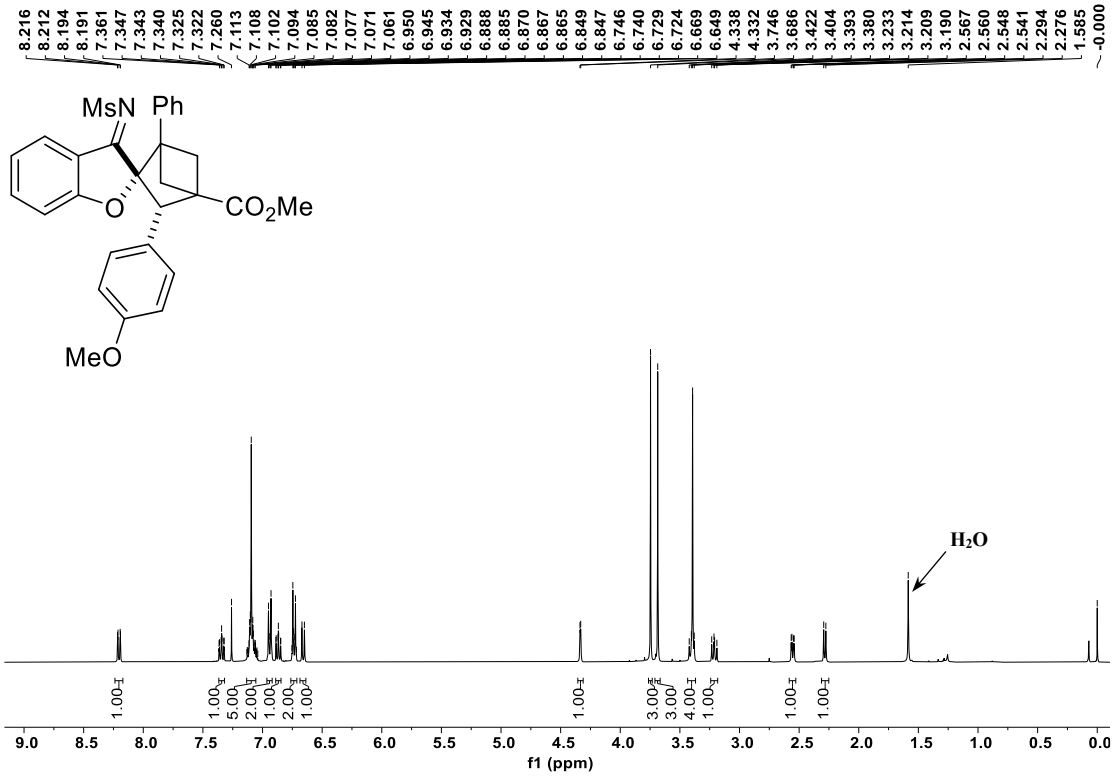
^{1}H NMR of **6d** in $CDCl_3$ (400 MHz)



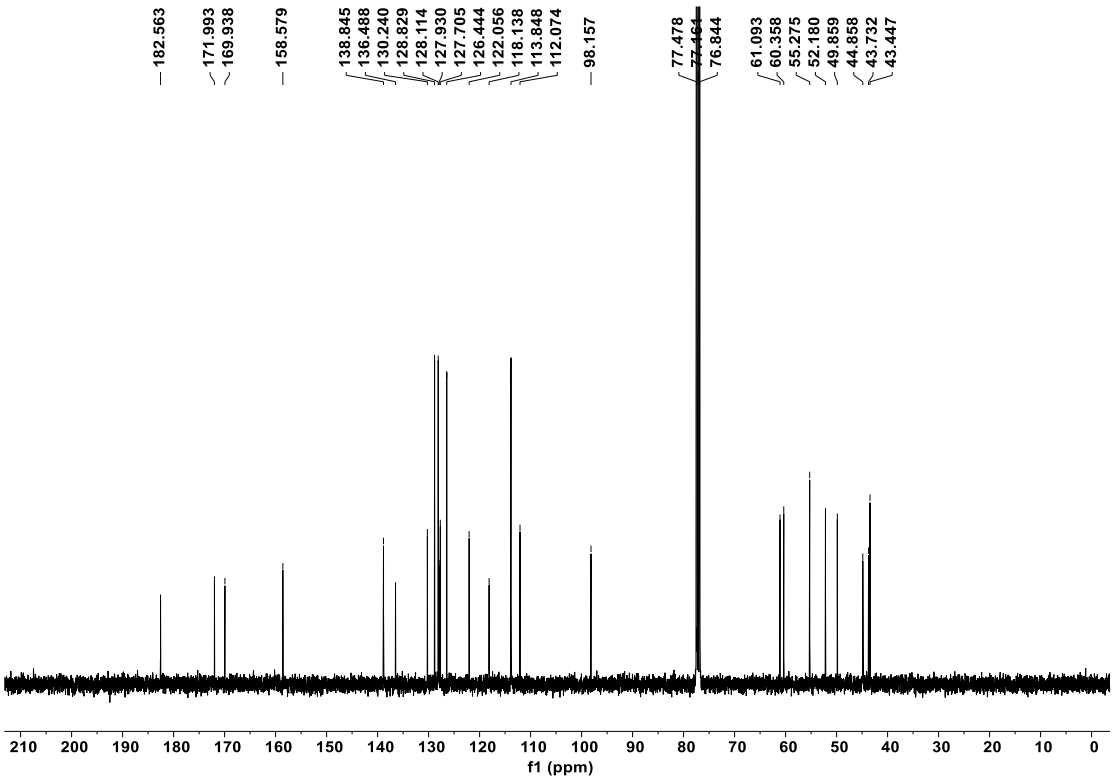
^{13}C NMR of **6d** in $CDCl_3$ (100 MHz)



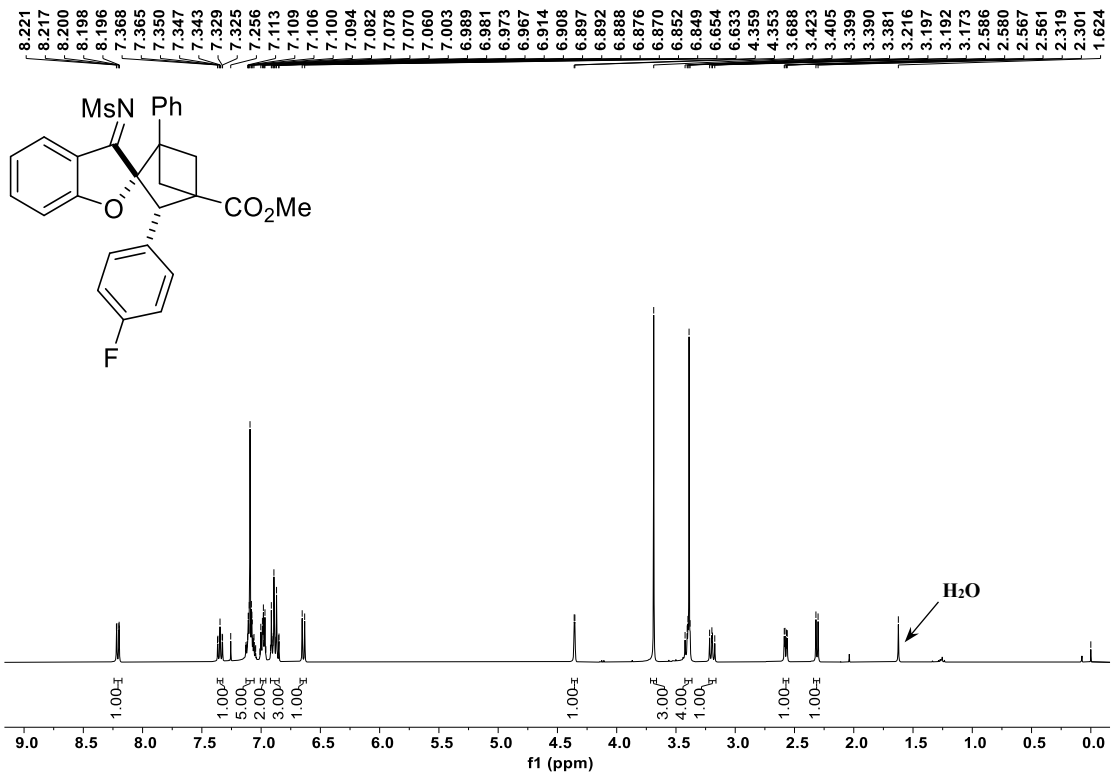
^{1}H NMR of **6e** in $CDCl_3$ (400 MHz)



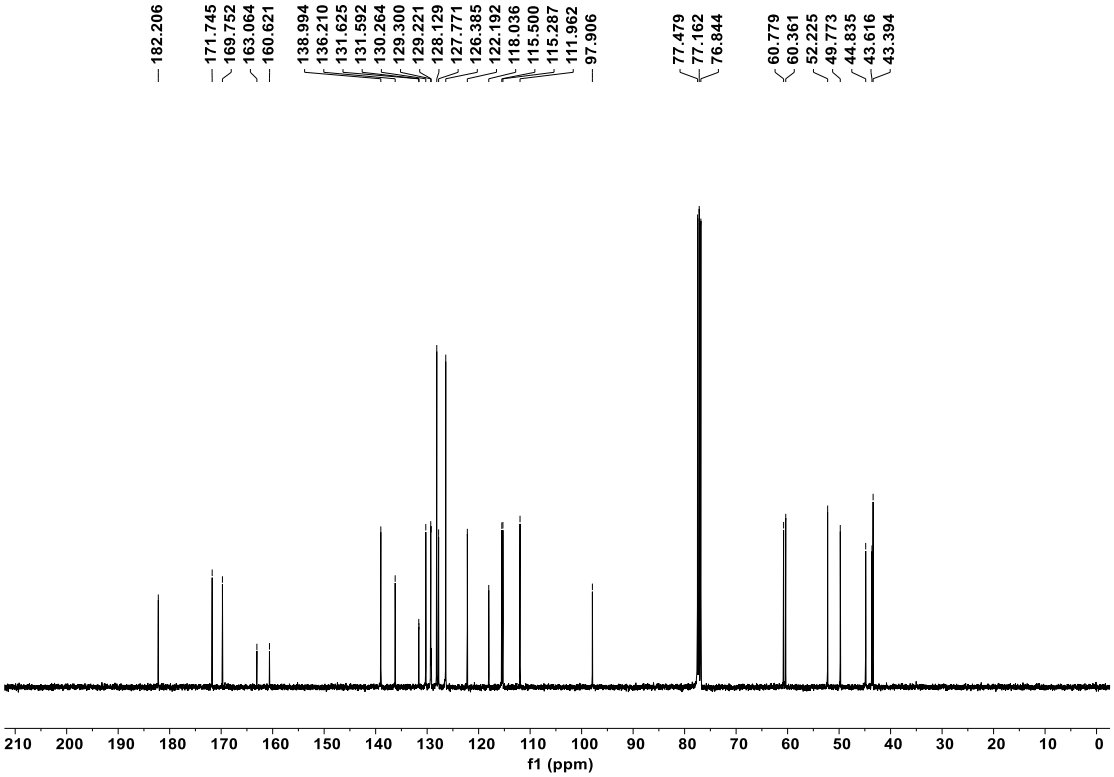
^{13}C NMR of **6e** in $CDCl_3$ (100 MHz)



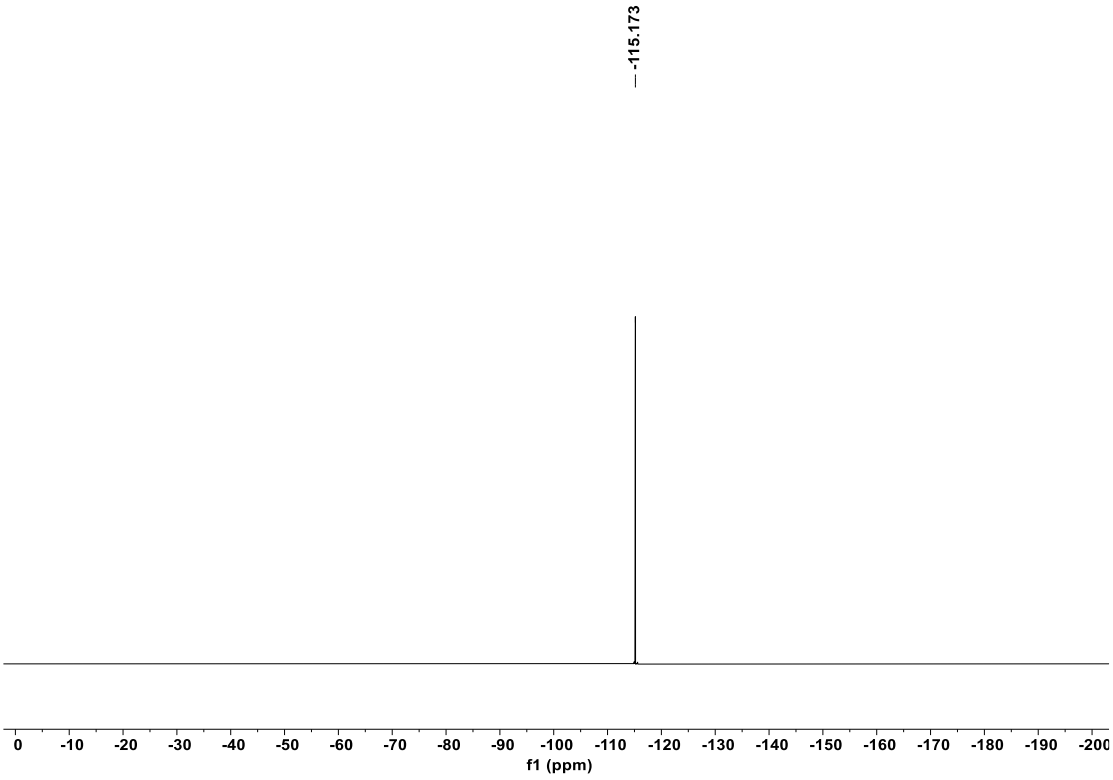
^{1}H NMR of **6f** in $CDCl_3$ (400 MHz)



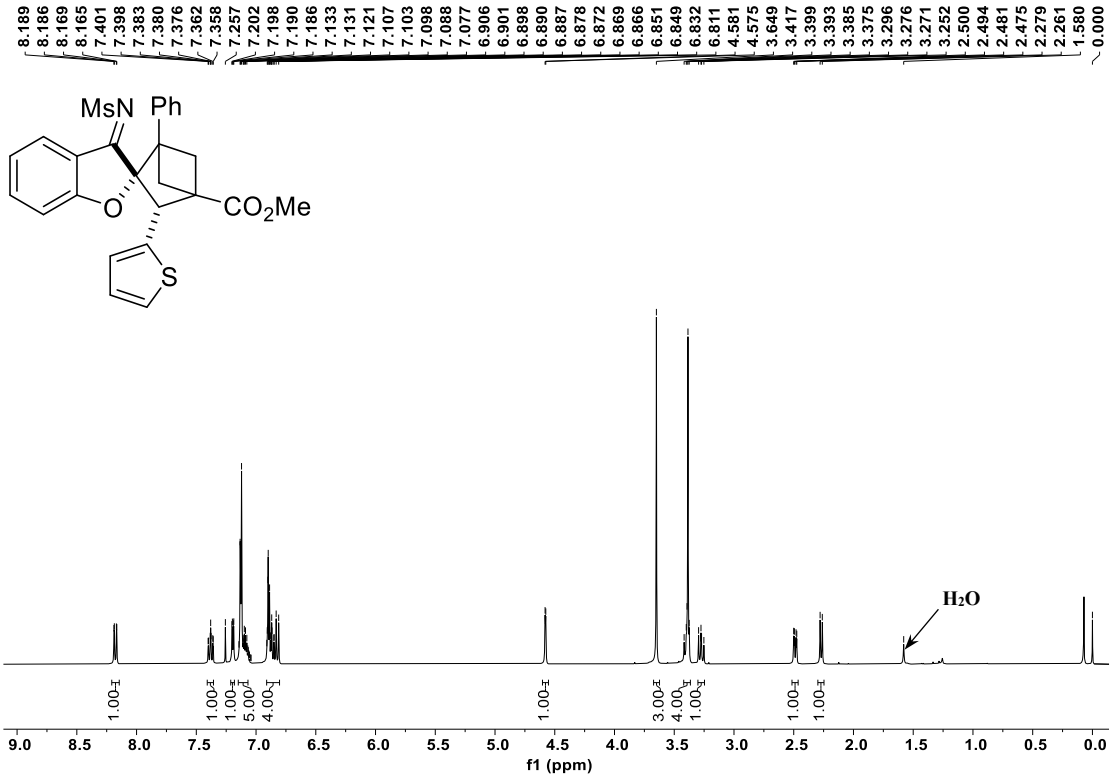
^{13}C NMR of **6f** in $CDCl_3$ (100 MHz)



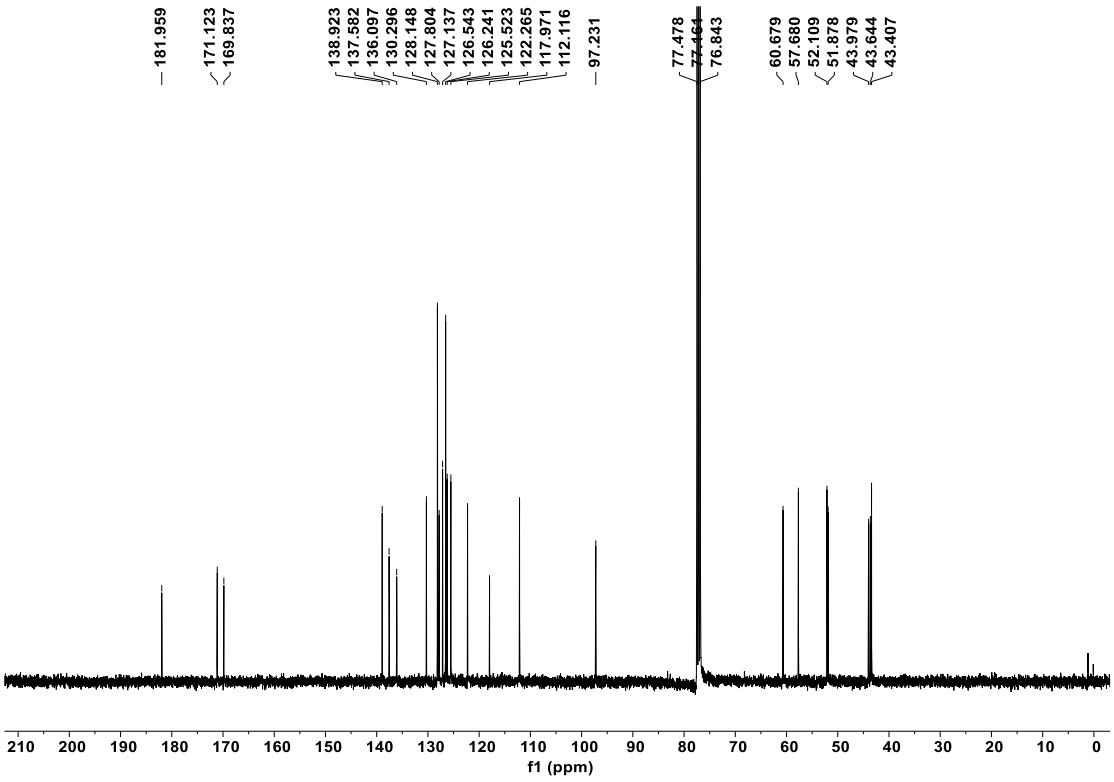
^{19}F NMR of **6f** in $CDCl_3$ (376 MHz)



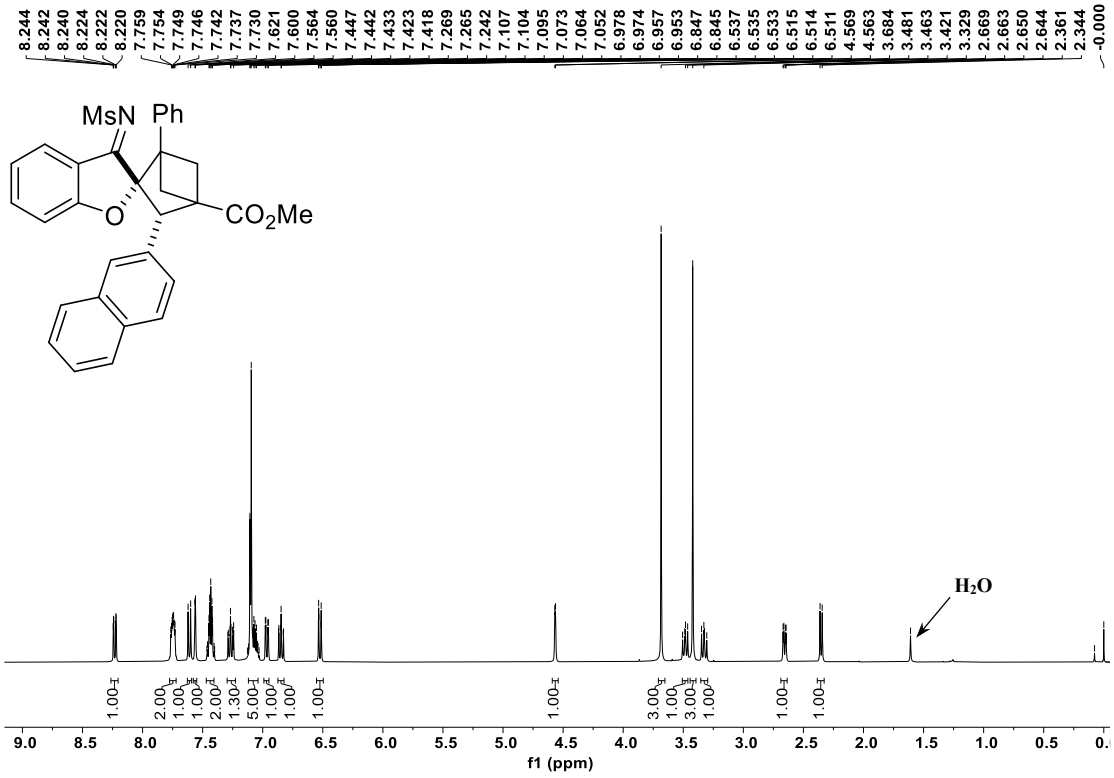
^{1}H NMR of **6g** in $CDCl_3$ (400 MHz)



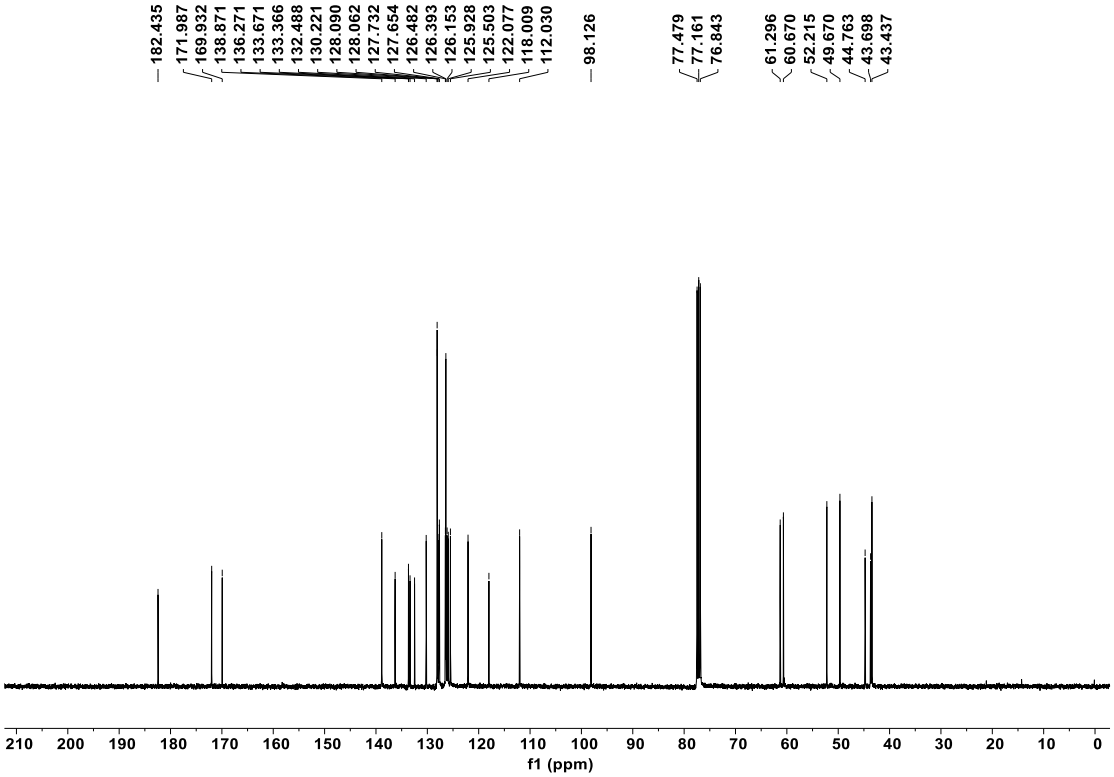
^{13}C NMR of **6g** in $CDCl_3$ (100 MHz)



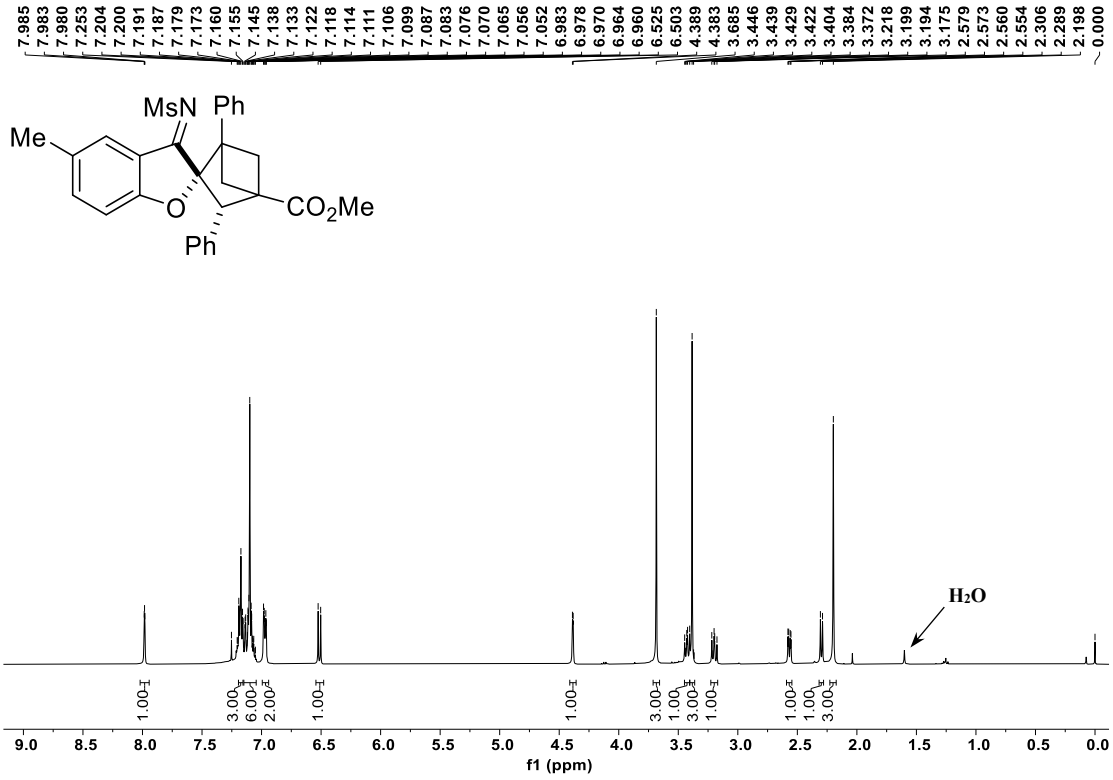
^{1}H NMR of **6h** in $CDCl_3$ (400 MHz)



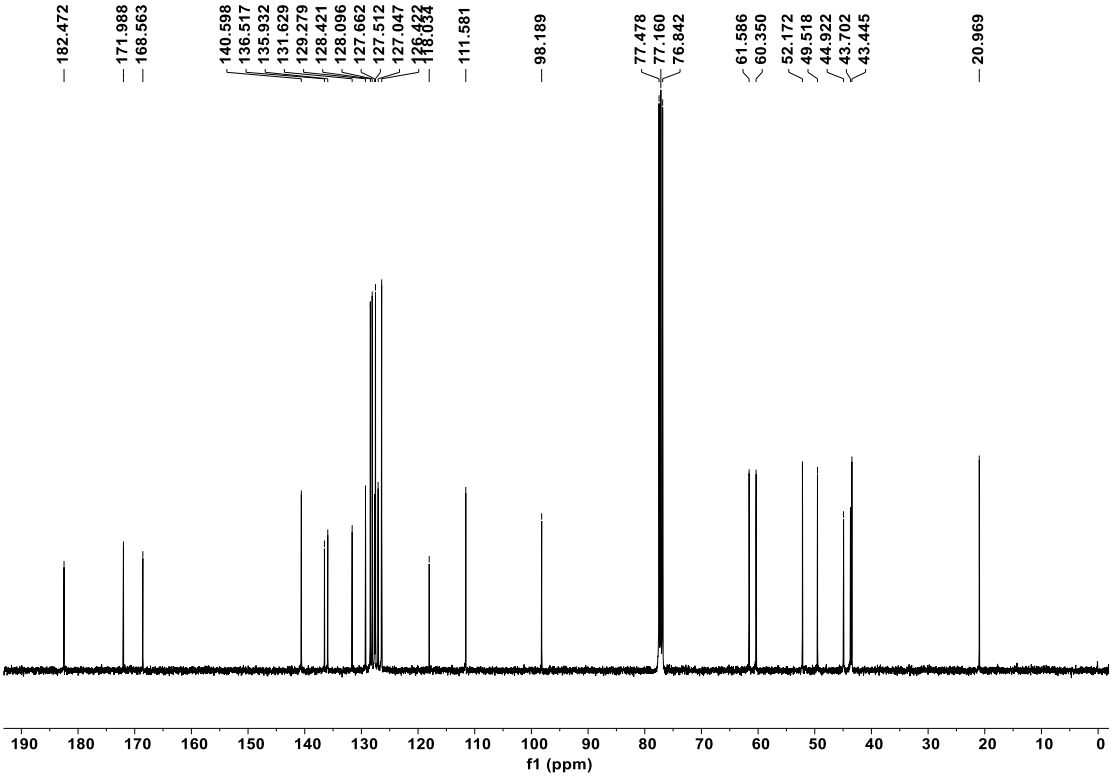
^{13}C NMR of **6h** in $CDCl_3$ (100 MHz)



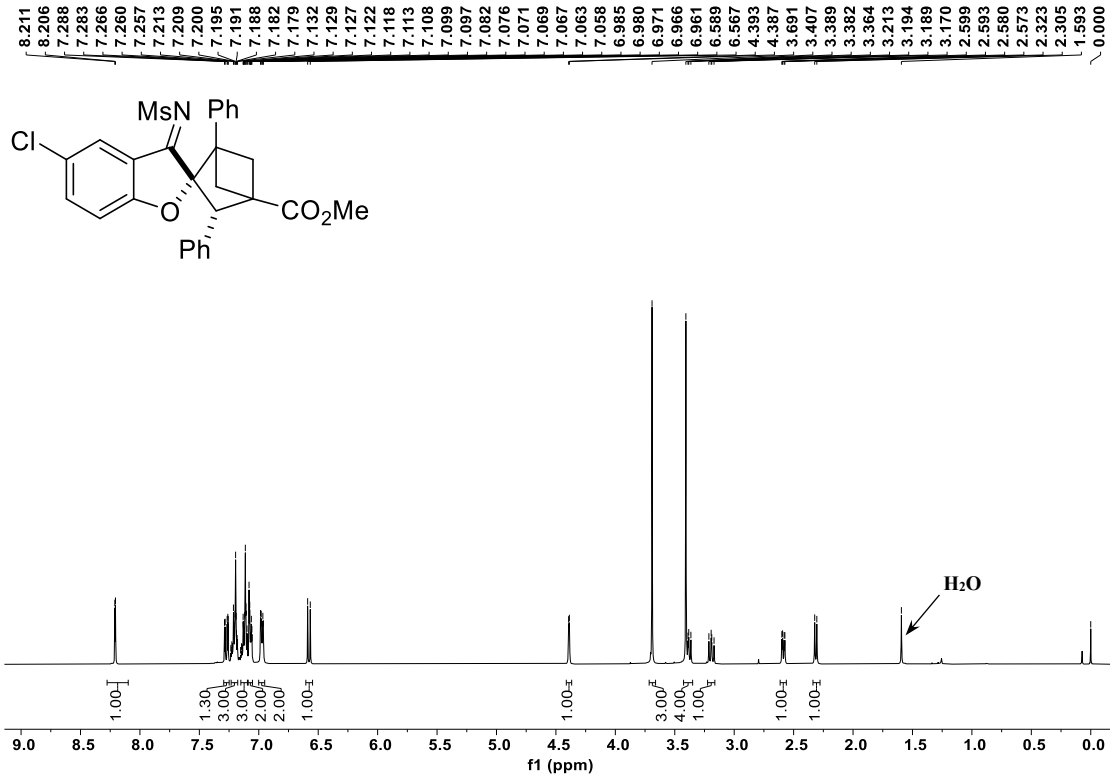
^{1}H NMR of **6i** in $CDCl_3$ (400 MHz)



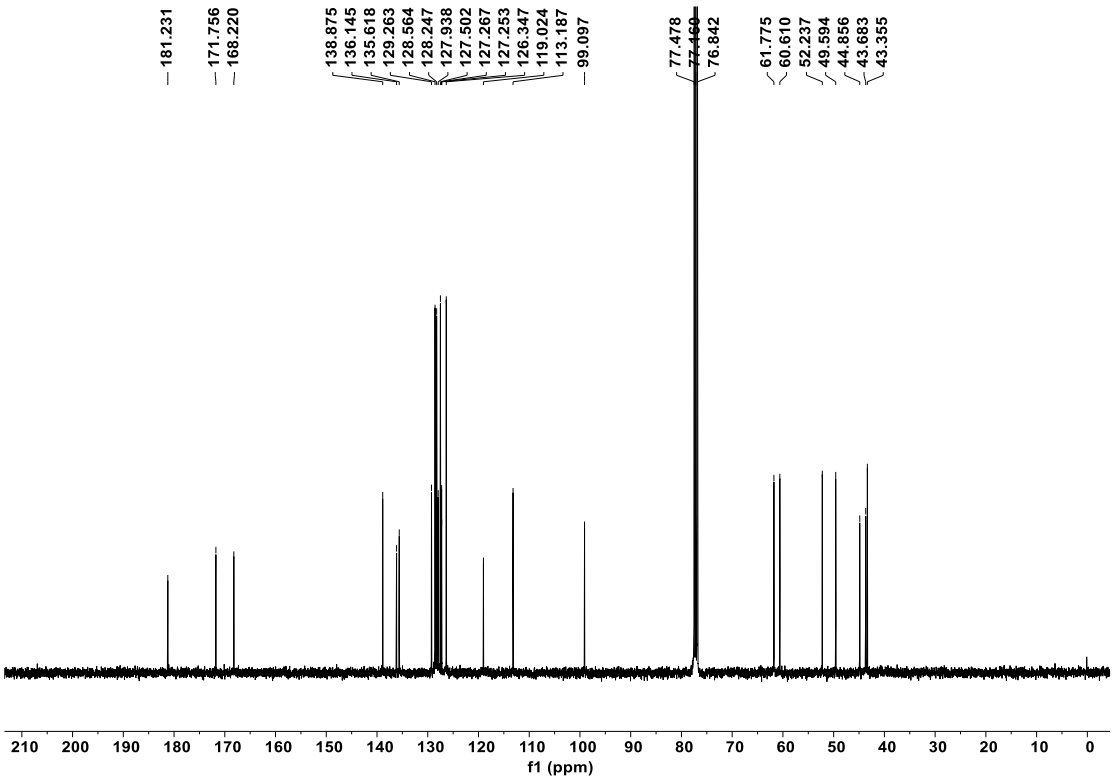
^{13}C NMR of **6i** in $CDCl_3$ (100 MHz)



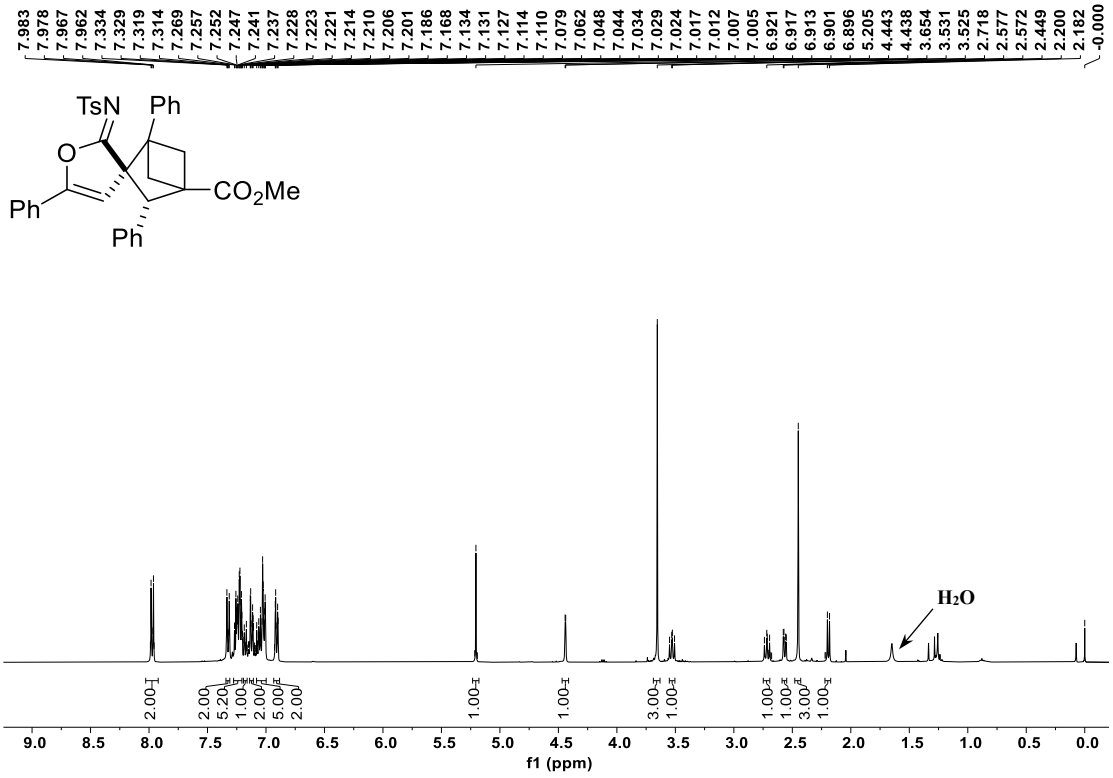
^{1}H NMR of **6j** in $CDCl_3$ (400 MHz)



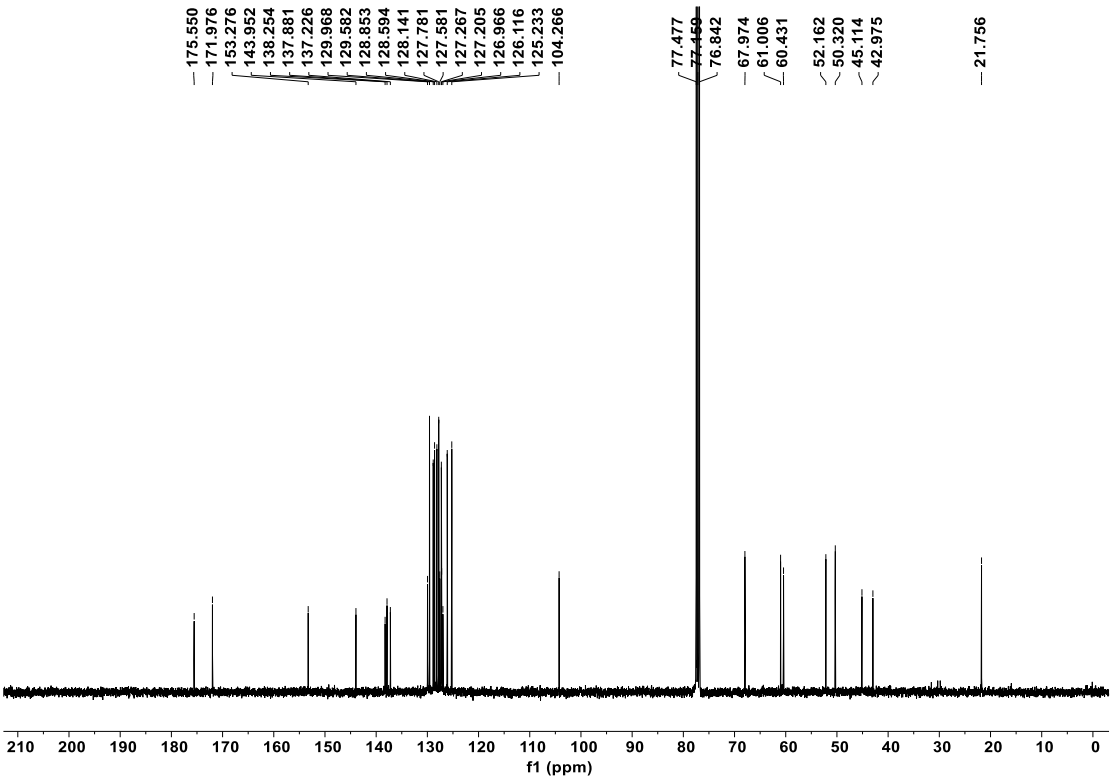
^{13}C NMR of **6j** in $CDCl_3$ (100 MHz)



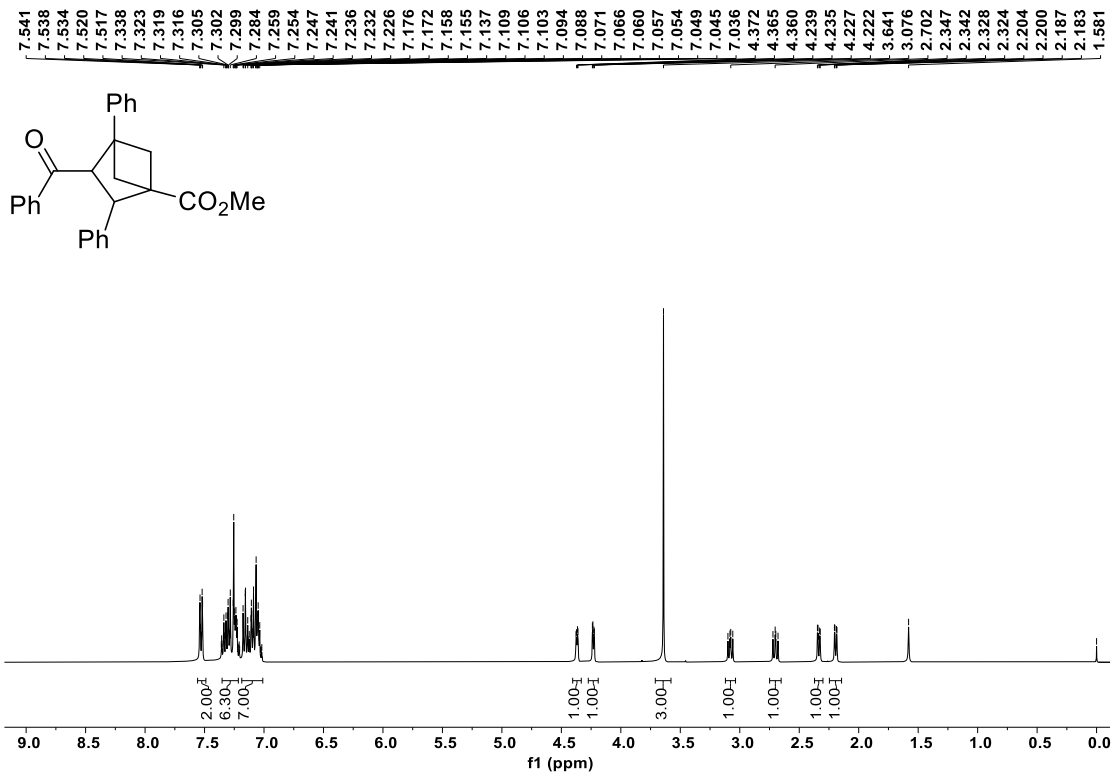
^{1}H NMR of **6k** in $CDCl_3$ (400 MHz)



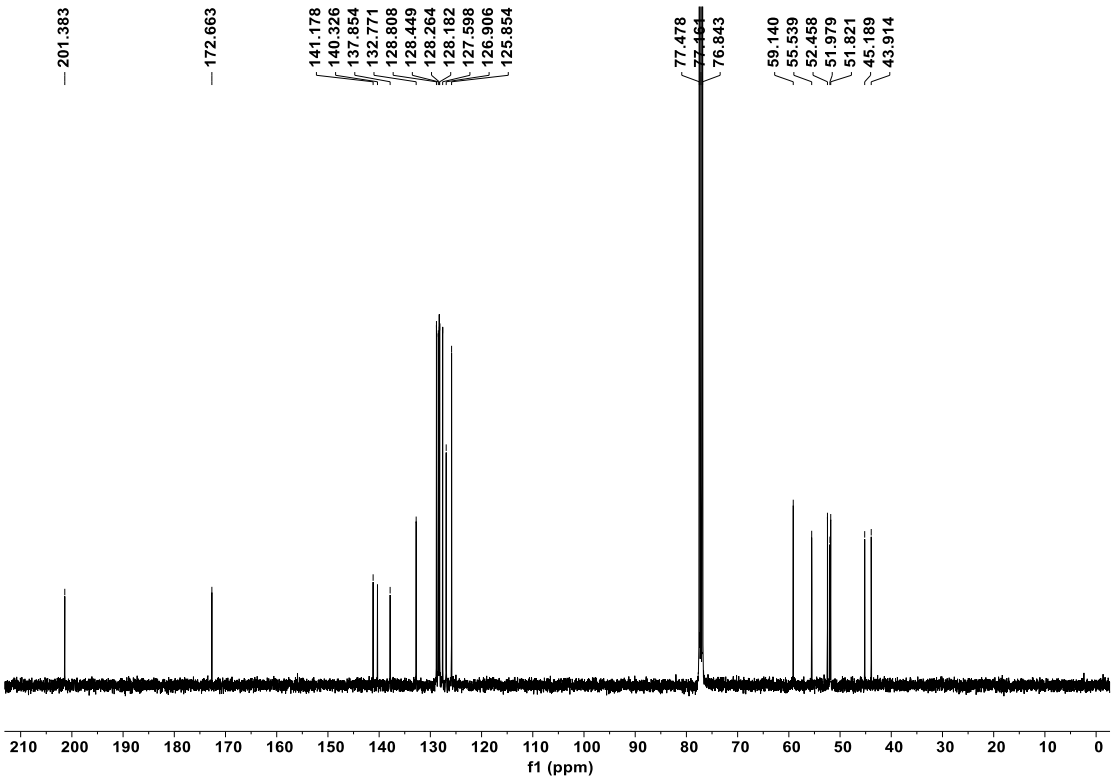
^{13}C NMR of **6k** in $CDCl_3$ (100 MHz)



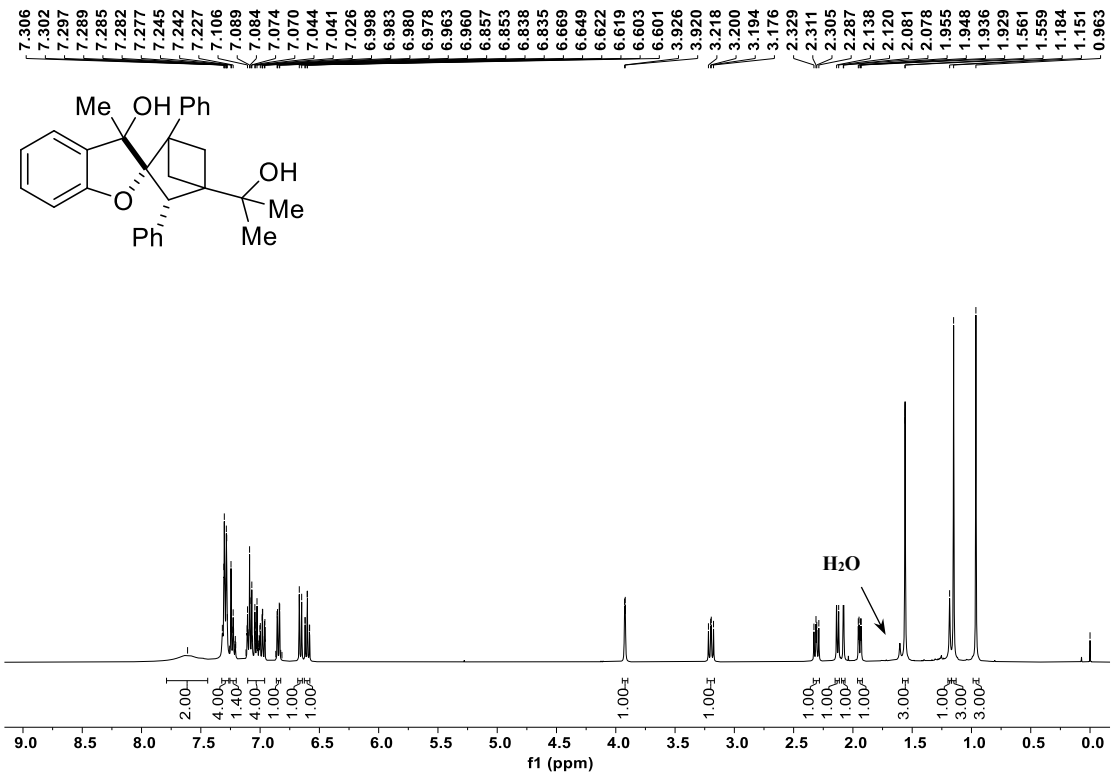
^{1}H NMR of **7** in $CDCl_3$ (400 MHz)



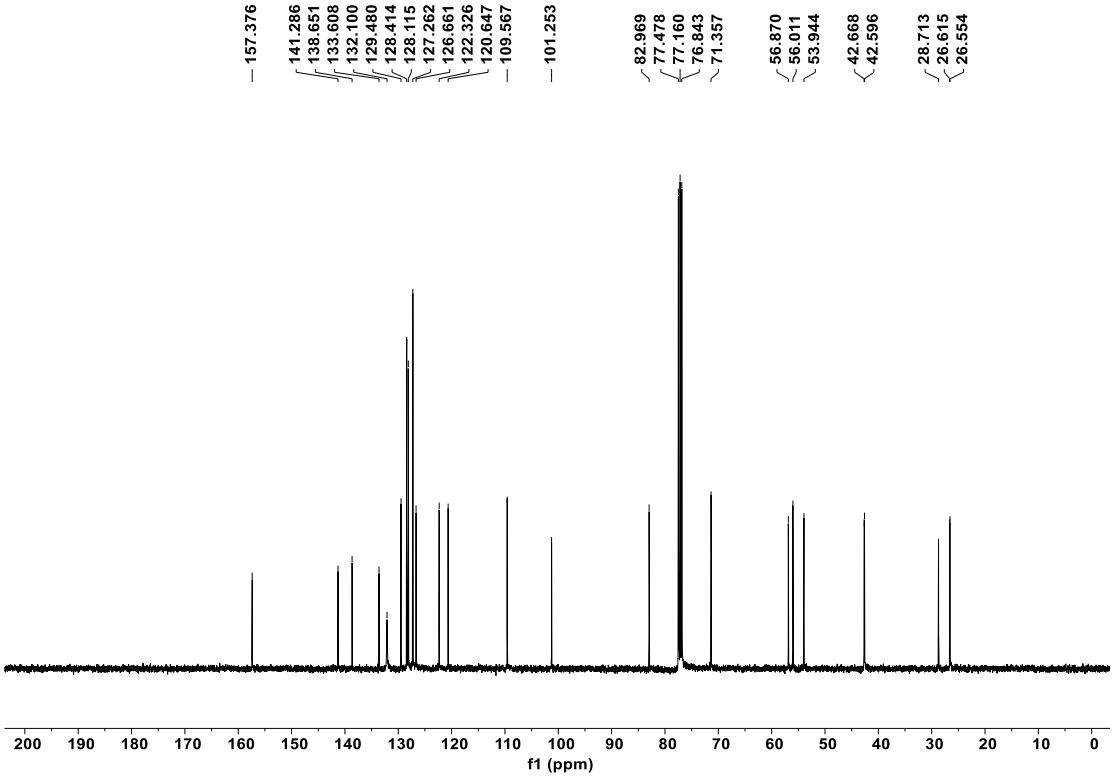
^{13}C NMR of **7** in $CDCl_3$ (100 MHz)



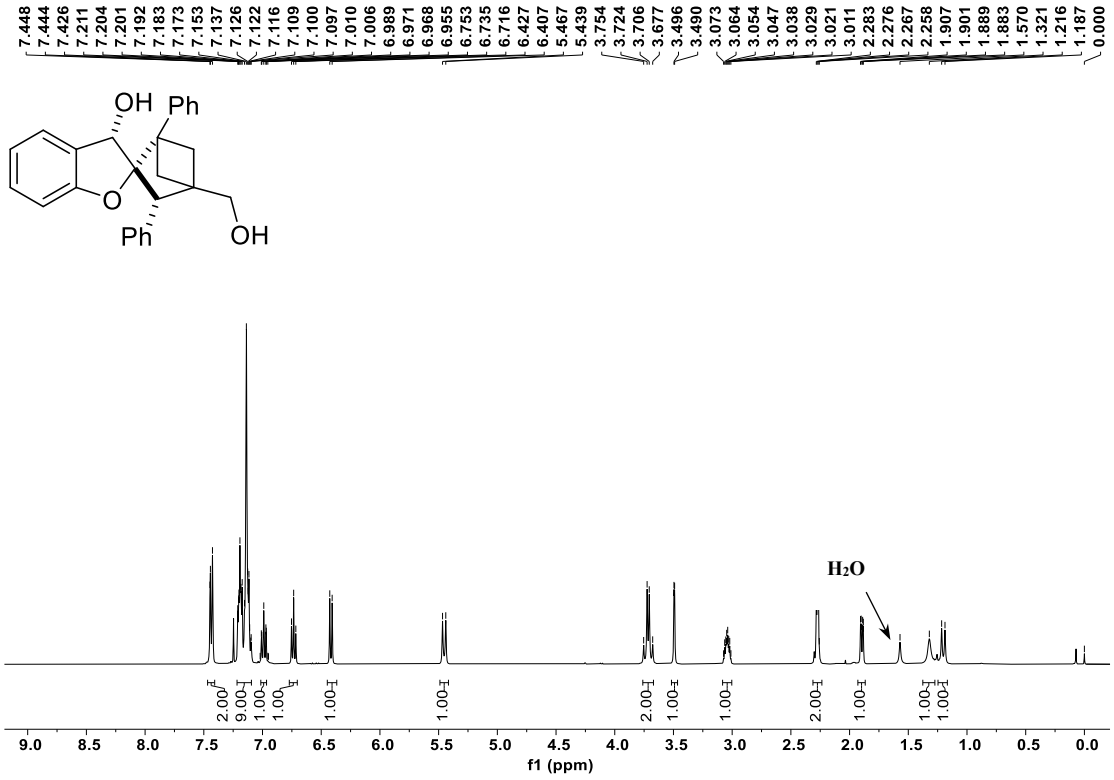
^{1}H NMR of **8** in $CDCl_3$ (400 MHz)



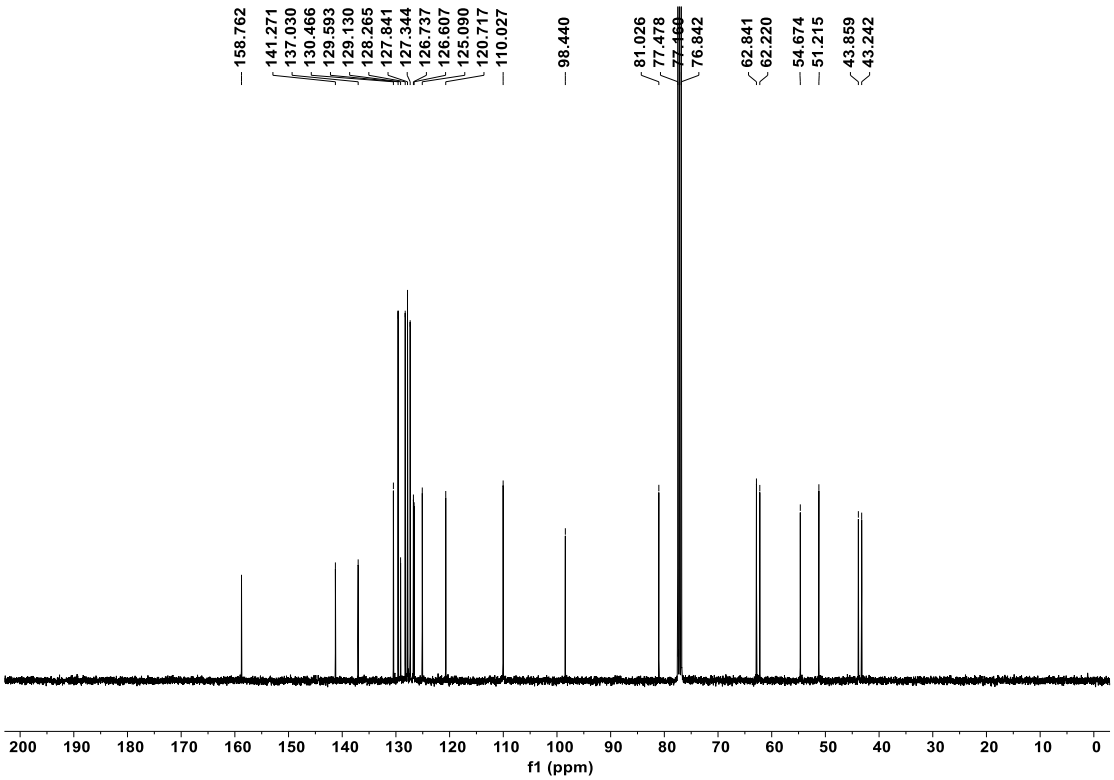
^{13}C NMR of **8** in $CDCl_3$ (100 MHz)



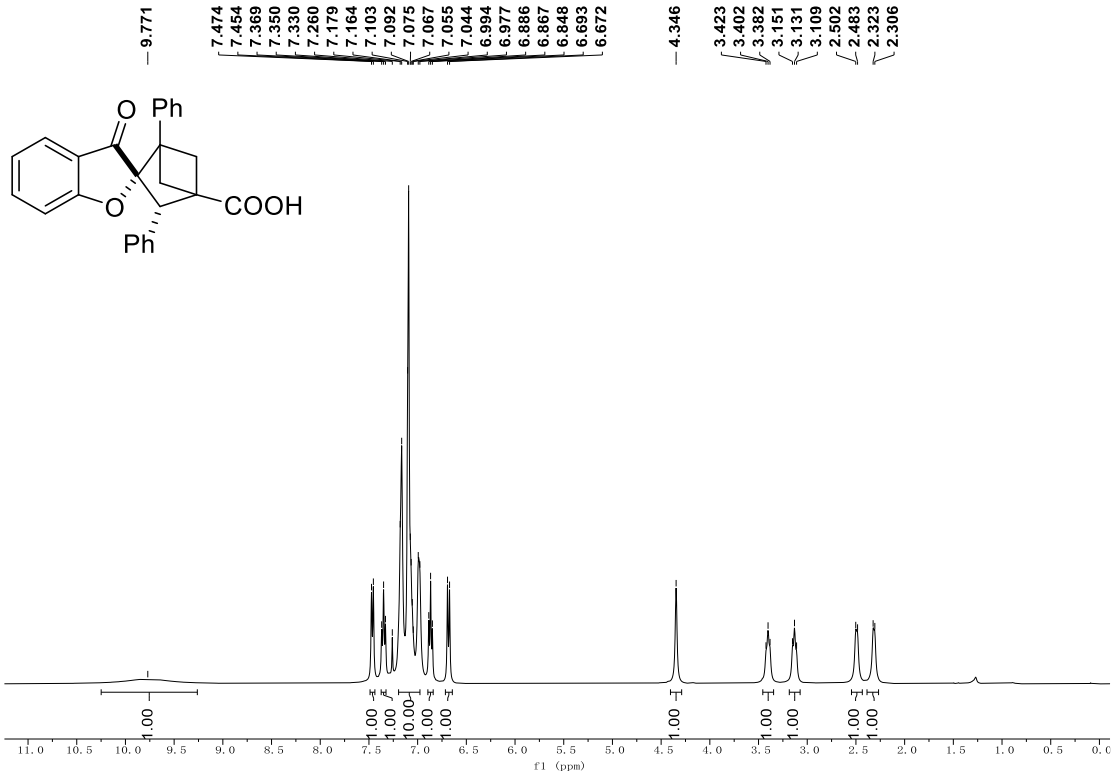
^{1}H NMR of **9** in $CDCl_3$ (400 MHz)



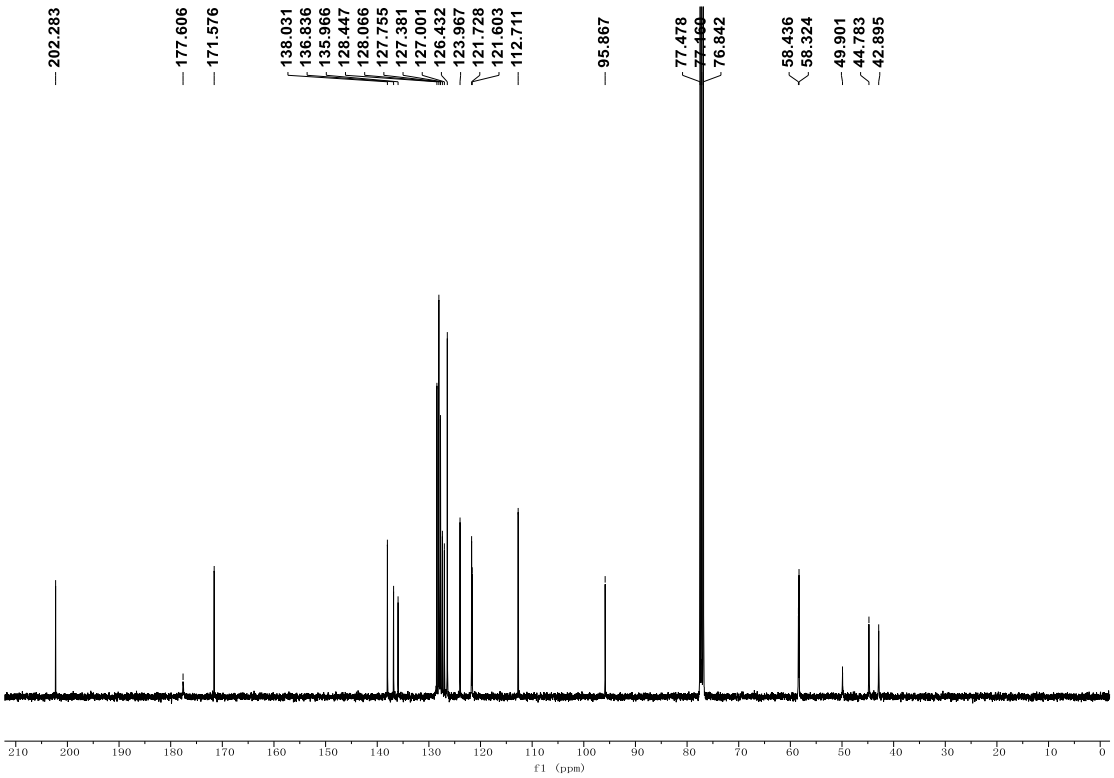
^{13}C NMR of **9** in $CDCl_3$ (100 MHz)



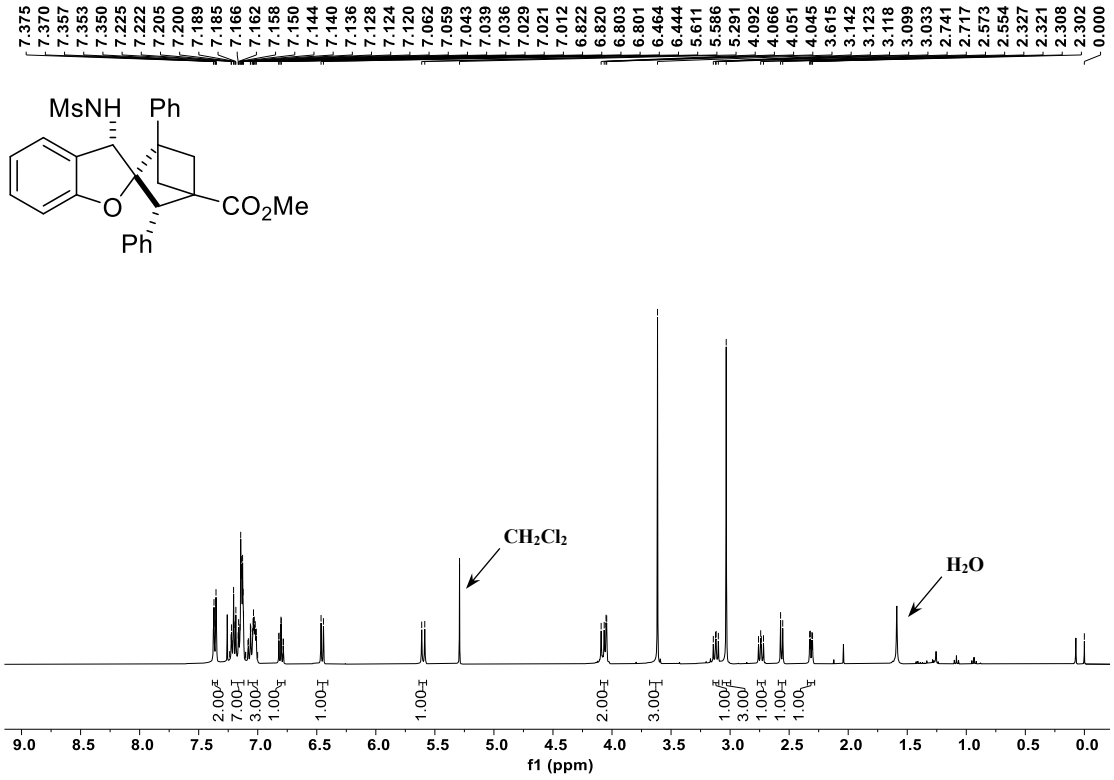
^{1}H NMR of **10** in $CDCl_3$ (400 MHz)



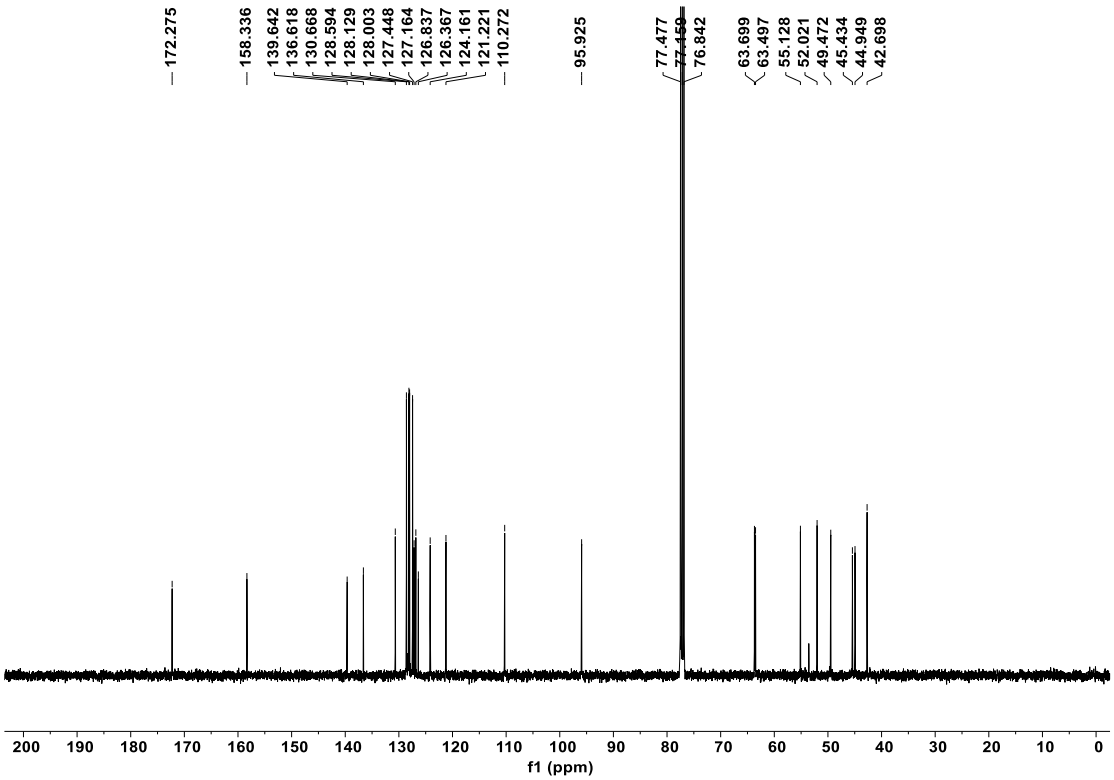
^{13}C NMR of **10** in $CDCl_3$ (100 MHz)



^{1}H NMR of **11** in $CDCl_3$ (400 MHz)



^{13}C NMR of **11** in $CDCl_3$ (100 MHz)



11. References

[1] (a) Ma, X.; Sloman, D. L.; Han, Y.; Bennett, D. J. A Selective Synthesis of 2,2-Difluorobicyclo[1.1.1]pentane Analogues: "BCP-F_2". *Org. Lett.* **2019**, *21*, 7199–7203. (b) Livingstone, K.; Siebold, K.; Meyer, S.; Martin-Heras, V.; Daniliuc, C. G.; Gilmour, R. Skeletal Ring Contractions via I(I)/I(III) Catalysis: Stereoselective Synthesis of *cis*-α,α-Difluorocyclopropanes. *ACS Catal*. **2022**, *12*, 14507–14516. (c) Wang, M.; Huang, Y.; Li, C.; Lu, P. Diastereoselective Synthesis of 1,1,3,3-Tetrasubstituted Cyclobutanes Enabled by Cycloaddition of Bicyclo[1.1.0]butanes. *Org. Chem. Front.* **2022**, *9*, 2149–2153. (d) Guo, R.; Chang, Y.; Herter, L.; Salome, C.; Braley, S. E.; Fessard, T. C.; Brown, M. K. Strain-Release [2π + 2σ] Cycloadditions for the Synthesis of Bicyclo[2.1.1]hexanes Initiated by Energy Transfer. *J. Am. Chem. Soc.* **2022**, *144*, 7988–7994. (e) Jung, M.; Lindsay, V. N. G. One-Pot Synthesis of Strain-Release Reagents from Methyl Sulfones. *J. Am. Chem. Soc.* **2022**, *144*, 4764–4769. (f) Lin, S.; Chen, Y.-H.; Liu, H.; Xiang, S.; Tan, B. Enantioselective Synthesis of Chiral Cyclobutenes Enabled by Brønsted Acid-Catalyzed Isomerization of BCBs. *J. Am. Chem. Soc.* **2023**, *145*, 21152–21158. (g) Liang, Y.; Paulus, F.; Daniliuc, C. G.; Glorius, F. Catalytic Formal [2π + 2σ] Cycloaddition of Aldehydes with Bicyclobutanes: Expedient Access to Polysubstituted 2-Oxabicyclo[2.1.1]hexanes. *Angew. Chem. Int. Ed.* **2023**, *62*, e202305043. (h) Ren, H.; Li, T.; Xing, J.; Li, Z.; Zhang, Y.; Yu, X.; Zheng, J. Ti-Catalyzed Formal [2π + 2σ] Cycloadditions of Bicyclo[1.1.0]butanes with 2-Azadienes to Access Aminobicyclo[2.1.1]hexanes. *Org. Lett*. **2024**, doi: org/10.1021/acs.orglett.4c00421.

[2] (a) Sim, H. M.; Loh, K. Y.; Yeo, W. K.; Lee, C. Y. Go, M. L. Aurones as Modulators of ABCG2 and ABCB1: Synthesis and Structure-Activity Relationships. *ChemMedChem.* **2011**, *6*, 713–724. (b) Wang, Z.-P.; Xiang, S.; Shao, P.-L.; He, Y. Catalytic Asymmetric [3 + 2] Cycloaddition Reaction between Aurones and Isocyanoacetates: Access to Spiropyrrolines via Silver Catalysis. *J. Org. Chem.* **2018**, *83*, 10995–11007.

[3] Tang, X.; Zheng, W.; Yao, W.; Ullah, N.; Lu, Y. Enantioselective Phosphine-Catalyzed Formal [4 + 4] Annulation of *α,β*-Unsaturated Imines and Allene Ketones: Construction of Eight-Membered Rings. *Angew. Chem. Int. Ed*. **2017**, *56*, 14222–14226.

[4] Yang W.-L.; Shen, J.-H.; Zhao Z.-H.; Wang, Z.; Deng, W.-P. Stereoselective Synthesis of

Functionalized Azepines via Gold and Palladium Relay Catalysis. *Org. Chem. Front.* **2022**, *9*, 4685–4691.

[5] (a) Liu, H.; Zhang, Q.; Wang, L.; Tong, X. PPh_3-Catalyzed Reactions of Alkyl Propiolates with N-Tosylimines: A Facile Synthesis of Alkyl 2-[aryl(tosylimino)methyl]acrylate and an Insight into the Reaction Mechanism. *Chem. Eur. J.* **2010**, *16*, 1968–1972. (b) Park, S.; Kadayat, T. M.; Jun, K.-Y.; Magar, T. B. T.; Bist, G.; Shrestha, A.; Lee, E.-S.; Kwon, Y. Novel 2-Aryl-4-(4′-hydroxyphenyl)-*5H*-indeno[1,2-*b*]pyridines as Potent DNA Non-intercalative Topoisomerase Catalytic Inhibitors. *Eur. J. Med. Chem*. **2017**, *125*, 14–28. (c) Chen, C.; Wen, S.; Geng, M.; Jin, S.; Zhang, Z.; Dong, X.-Q.; Zhang, X. A New Ferrocenyl Bisphosphorus Ligand for the Asymmetric Hydrogenation of α-Methylene-γ-keto-carboxylic Acids. *Chem. Commun.* **2017**, *53*, 9785–9788. (d) Gu, B.-Q.; Yang, W.-L.; Wu, S.-X.; Wang, Y.-B.; Deng, W.-P. Organocatalytic Asymmetric Synthesis of Tetrahydrocarbazoles via an Inverse-electron-demand Diels-Alder Reaction of 2,3-Indole-dienes with Enals. *Org. Chem. Front.* **2018**, *5*, 3430–3434. (e) Wu, S.-X.; Gu, B.-Q.; Xu, H.; Zheng, X.; Luo, X.; Deng, W.-P. Organocatalytic Asymmetric Inverse-Electron-Demand Diels-Alder Reaction of Pyrrolidone-Dienes with Enals. *Adv. Synth. Catal*. **2019**, *361*, 4302–4313. (f) Moriyama, K.; Oka, Y. Enantioselective Cascade Michael/Hemiaminal Formation of *α,β*-Unsaturated Iminoindoles with Aldehydes Using a Chiral Aminomethylpyrrolidine Catalyst Bearing a $SO_2C_6F_5$ Group as a Strongly Electron Withdrawing Arylsulfonyl Group. *ACS Catal*. **2022**, *12*, 7436–7442.

[6] Lin S.-L., Chen Y.-H., Liu H.-H., Xiang S.-H., Tan B. Enantioselective Synthesis of Chiral Cyclobutenes Enabled by Brønsted Acid-Catalyzed Isomerization of BCBs. *J. Am. Chem. Soc.* **2023**, *145*, 21152–21158.