Supporting Information

DBU-Mediated [3+2] Annulation of 3-Hydroxyisoindolinones with Vinylsulfonium Salts: An Efficient Approach to Functionalized Oxazolo[2,3-a]isoindolones

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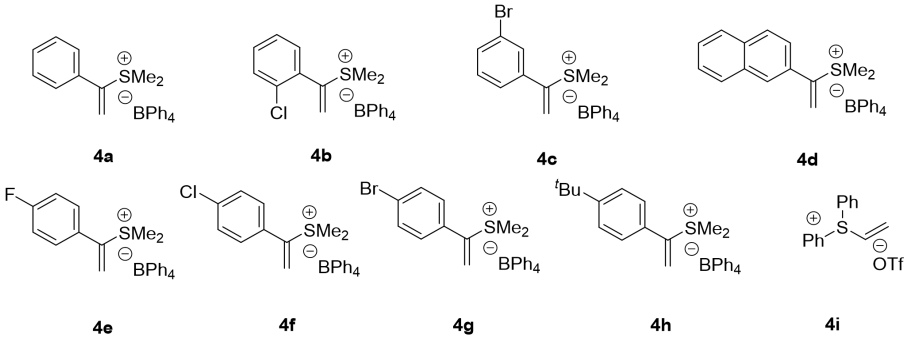
1. General Information

All reactions were performed under air atmospheres in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents were purified and dried according to standard methods prior to use. Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. The reactions were monitored through thin layer chromatography (TLC) on silica gel-precoated glass plates. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). ^{1}H NMR and ^{13}C NMR were recorded on a Bruker AVIII 400 (400 MHz) spectrometer with $CDCl_3$ as the solvent. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton ($CDCl_3$: δ 7.26 ppm), carbon ($CDCl_3$: δ 77.07 ppm) and tetramethylsilane (TMS δ 0.00). Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), m (multiplet). Coupling constants *J* are reported in Hz. HRMS data were obtained on LCMS–IT–TOF (Shimadzu, Kyoto, JP) with ESI resource. Single crystal X–ray data were collected on a Bruker APEXII X–ray diffractometer equipped with a CMOS PHOTON 100 detector with a Mo Kα X–ray source (Kα = 0.71073 Å). Melting points were recorded on a Tianjin University of Science and Technology X–4 melting point apparatus.

2. Synthesis of Substrates

3-hydroxy-3-arylisoindolin-1-one compounds **1**[1] and aryl thianthrenium salts **2**[2] and *α*-Aryl tetraphenylborate vinylsulfonium salts **4** [3] were synthesized according to the previous procedures.



References

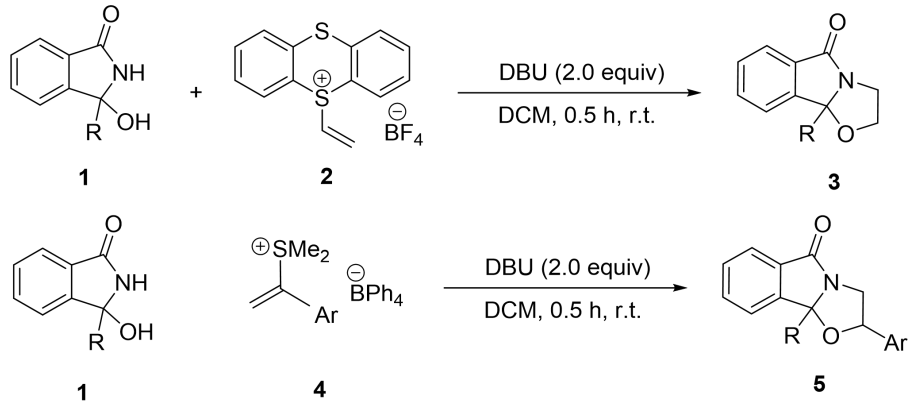
[1] E. C.Wang, H. F. Chen, P. K. Feng, Y. L. Lin, M. K. Hsu, *Tetrahedron Lett.*, **2002**, *43*, 9163–9165.

[2] J. Chen, J. Li, M. B. Plutschack, F. Berger, T. Ritter, *Angew. Chem., Int. Ed.,* **2020**, *59*, 5616–5620.

[3] J. V. Matlock, S. P. Fritz, S. A. Harrison, D. M. Coe, E. M. McGarrigle, V. K. Aggarwal, *J. Org. Chem.,* **2014**, *79*, 10226–10239.

3. Synthesis and Characterization Data of 3a-3p, and 5a-5r

3.1 General Procedure for Synthesis of 3 and 5



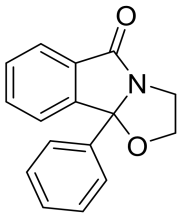
1 2 3

1 4 5

The 3-hydroxy-3-arylisoindolin-1-ones **1** (0.2 mmol), vinylsulfonium salts **2** or **4** (0.4 mmol, 2.0 equiv) and DCM (2.0 mL) were added to a 10 mL dry sealed tube at air atmosphere. Then DBU (0.4 mmol, 2.0 equiv) were added in one portion. This solution was stirred at room temperature for 0.5 h until the complete consumption of **1** monitored by TLC. The reaction mixture was filtered with Celite, and eluted with DCM. The filtrate was concentrated and the residue was purified by flash column chromatography (petroleum ether: EtOAc = 5:1) on silica gel to afford corresponding products **3** or **5**.

3.2 Characterization Data of 3a-3p and 5a-5r

9b-Phenyl-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (3a)

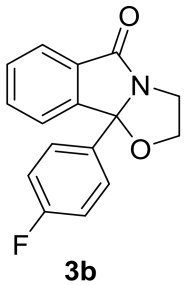


3a

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 94% yield (47.2 mg). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a white solid. **Mp:** 134 – 136 °C **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 1H), 7.61 – 7.59 (m, 2H), 7.52 – 7.47

(m, 2H), 7.42 – 7.34 (m, 3H), 7.29 (dd, *J* = 6.3, 2.5 Hz, 1H), 4.41 – 4.35 (m, 1H), 4.17 – 4.09 (m, 2H), 3.31 – 3.25 (m, 1H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 174.0, 146.8, 138.0, 133.2, 131.2, 130.1, 128.8, 128.8, 125.8, 124.3, 123.6, 100.4, 70.2, 41.5. **HRMS** (ESI) *m*/*z* calcd for $C_{16}H_{14}NO_2^+$ ($[M+H]^+$): 252.1019, found 252.1013.

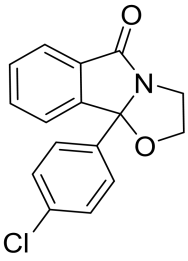
9b-(4-Fluorophenyl)-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (3b)



3b

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 80% yield (43.1 mg). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.77 (m, 1H), 7.60 – 7.55 (m, 2H), 7.53 – 7.47 (m, 2H), 7.28 – 7.26 (m, 1H), 7.08 (t, *J* = 8.6 Hz, 2H), 4.40 – 4.33 (m, 1H), 4.17 – 4.10 (m, 2H), 3.30 – 3.23 (m, 1H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 173.9, 163.1 (d, *J* = 247.6 Hz), 146.7, 133.9 (d, *J* = 3.0 Hz), 133.3, 131.1, 130.3, 127.7 (d, *J* = 8.3 Hz), 124.4, 123.5, 115.8 (d, *J* = 21.8 Hz), 100.1, 70.2, 41.6. **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ-113.18 (s). **HRMS** (ESI) *m*/*z* calcd for $C_{16}H_{13}FNO_2^+$ ($[M+H]^+$): 270.0925, found 270.0928.

9b-(4-Chlorophenyl)-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (3c)

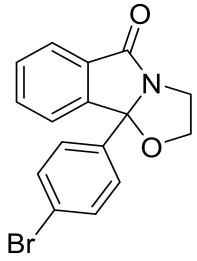


3c

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 88% yield (50.2 mg). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.77 (m, 1H), 7.56 – 7.47 (m, 4H), 7.38 – 7.32 (m, 2H), 7.29 – 7.24 (m, 1H), 4.38 – 4.34 (m, 1H), 4.16 – 4.09 (m, 2H), 3.29 – 3.22 (m, 1H). **^{13}C {^{1}H} NMR** (101

MHz, $CDCl_3$) δ 173.8, 146.4, 136.8, 134.8, 133.4, 131.1, 130.3, 129.0, 127.3, 124.4, 123.5, 100.0, 70.3, 41.6. **HRMS** (ESI) *m*/*z* calcd for $C_{16}H_{13}ClNO_2^+$ ([M+H]$^+$): 286.0629, found 286.0631.

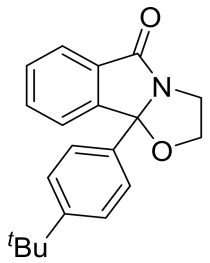
9b-(4-Bromophenyl)-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (3d)



3d

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 89% yield (58.6 mg). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.79 (m, 1H), 7.53 – 7.45 (m, 6H), 7.28 – 7.24 (m, 1H), 4.36 (d, *J* = 5.6 Hz, 1H), 4.15 – 4.09 (m, 2H), 3.28 – 3.21 (m, 1H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 173.8, 146.4, 137.3, 133.4, 132.0, 131.1, 130.4, 127.7, 124.4, 123.5, 123.1, 100.1, 70.3, 41.6. **HRMS** (ESI) *m*/*z* calcd for $C_{16}H_{13}BrNO_2^+$ ([M+H]$^+$): 330.0124, found 330.0128.

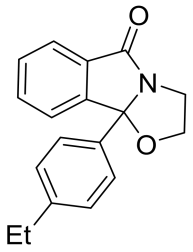
9b-(4-(*tert*-Butyl)phenyl)-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (3e)



3e

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 72% yield (44.2 mg). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.77 (m, 1H), 7.53 – 7.44 (m, 4H), 7.41 – 7.39 (m, 2H), 7.33 – 7.30 (m, 1H), 4.38 – 4.32 (m, 1H), 4.16 – 4.08 (m, 2H), 3.32 – 3.25 (m, 1H), 1.31 (s, 9H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 174.0, 151.8, 146.9, 134.9, 133.2, 131.2, 130.0, 125.7, 125.5, 124.3, 123.6, 100.4, 70.2, 41.5, 34.6, 31.3. **HRMS** (ESI) *m*/*z* calcd for $C_{20}H_{22}NO_2^+$ ([M+H]$^+$): 308.1645, found 308.1643.

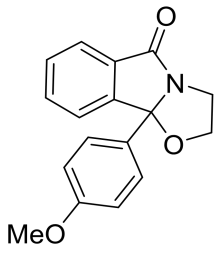
9b-(4-Ethylphenyl)-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (3f)



3f

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 87% yield (48.6 mg). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.76 (m, 1H), 7.51 – 7.44 (m, 4H), 7.32 – 7.28 (m, 1H), 7.23 – 7.21 (m, 2H), 4.39 – 4.33 (m, 1H), 4.16 – 4.06 (m, 2H), 3.31 – 3.24 (m, 1H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 174.0, 146.9, 145.0, 135.1, 133.2, 131.2, 130.0, 128.3, 125.8, 124.3, 123.6, 100.5, 70.2, 41.5, 28.6, 15.4. **HRMS** (ESI) *m*/*z* calcd for $C_{18}H_{18}NO_2^+$ ($[M+H]^+$): 280.1332, found 280.1336.

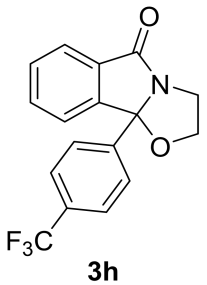
9b-(4-Methoxyphenyl)-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (3g)



3g

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 90% yield (50.6 mg). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.77 (m, 1H), 7.52 – 7.47 (m, 4H), 7.30 – 7.28 (m, 1H), 6.93 – 6.89 (m, 2H), 4.39 – 4.33 (m, 1H), 4.16 – 4.08 (m, 2H), 3.81 (s, 3H), 3.31 – 3.24 (m, 1H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 174.0, 160.0, 147.0, 133.2, 131.1, 130.0, 129.8, 127.1, 124.3, 123.5, 114.1, 100.4, 70.2, 55.3, 41.5. **HRMS** (ESI) *m*/*z* calcd for $C_{17}H_{16}NO_3^+$ ($[M+H]^+$): 282.1125, found 282.1121.

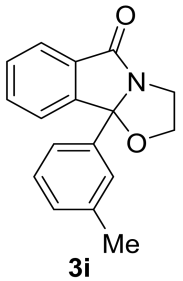
9b-(4-(Trifluoromethyl)phenyl)-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (3h)



3h

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 56% yield (35.7 mg). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 – 7.73 (m, 1H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.47 – 7.43 (m, 2H), 7.21 – 7.17 (m, 1H), 4.35 – 4.29 (m, 1H), 4.12 – 4.04 (m, 2H), 3.22 – 3.15 (m, 1H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 173.8, 146.1, 142.4, 133.5, 131.3, 131.1, 130.9, 130.5, 126.3, 125.9 (q, *J* = 3.7 Hz), 124.6, 123.5, 100.0, 70.4, 41.7. **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -62.66 (s). **HRMS** (ESI) *m*/*z* calcd for $C_{17}H_{13}F_3NO_2^+$ ([M+H]$^+$): 320.0893, found 320.0898.

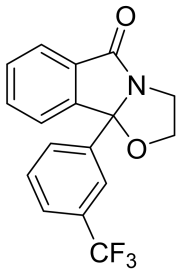
9b-(*m*-Tolyl)-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (3i)



3i

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 85% yield (45.1 mg). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.77 (m, 1H), 7.51 – 7.46 (m, 2H), 7.43 – 7.39 (m, 2H), 7.31 – 7.26 (m, 2H), 7.16 (d, *J* = 7.5 Hz, 1H), 4.39 – 4.34 (m, 1H), 4.17 – 4.08 (m, 2H), 3.31 – 3.25 (m, 1H), 2.35 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 174.0, 146.9, 138.6, 137.9, 133.2, 131.2, 130.1, 129.6, 128.7, 126.3, 124.3, 123.6, 122.8, 100.5, 70.2, 41.5, 21.5. **HRMS** (ESI) *m*/*z* calcd for $C_{17}H_{16}NO_2^+$ ([M+H]$^+$): 266.1176, found 266.1170.

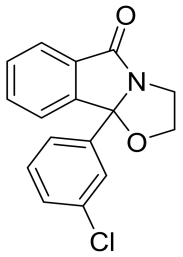
9b-(3-(Trifluoromethyl)phenyl)-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (3j)



3j

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 69% yield (44.0 mg). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 2.1 Hz, 1H), 7.85 – 7.80 (m, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.64 – 7.62 (m, 1H), 7.55 – 7.51 (m, 3H), 7.28 – 7.26 (m, 1H), 4.40 – 4.36 (m, 1H), 4.18 – 4.13 (m, 2H), 3.30 – 3.24 (m, 1H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 173.9, 146.2, 139.6, 133.5, 131.1, 130.5, 129.5, 129.3, 125.8 (q, *J* = 3.7 Hz), 124.6, 124.2, 123.5, 122.7 (q, *J* = 3.7 Hz), 122.4, 99.9, 70.3, 41.7. **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -62.54 (s). **HRMS** (ESI) *m*/*z* calcd for $C_{17}H_{13}F_3NO_2^+$ ($[M+H]^+$): 320.0893, found 320.0896.

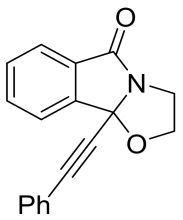
9b-(3-Chlorophenyl)-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (3k)



3k

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 70% yield (39.9 mg). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.79 (m, 1H), 7.62 – 7.61 (m, 1H), 7.55 – 7.50 (m, 2H), 7.50 – 7.46 (m, 1H), 7.36 – 7.32 (m, 2H), 7.30 – 7.27 (m, 1H), 4.40 – 4.34 (m, 1H), 4.18 – 4.11 (m, 2H), 3.32 – 3.24 (m, 1H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 173.8, 146.3, 140.4, 134.9, 133.4, 131.1, 130.4, 130.2, 129.1, 126.1, 124.5, 124.1, 123.5, 99.9, 70.3, 41.6. **HRMS** (ESI): *m*/*z* calcd for $C_{16}H_{13}ClNO_2^+$ $[M+H]^+$ 286.0629, found 286.0633.

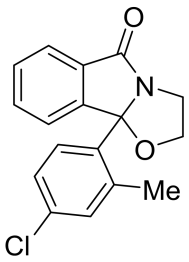
9b-(Phenylethynyl)-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (3l)



3l

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 75% yield (41.3 mg). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.78 (m, 2H), 7.67 (td, *J* = 7.5, 1.2 Hz, 1H), 7.58 (td, *J* = 7.5, 1.0 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.36 – 7.30 (m, 3H), 4.54 (td, *J* = 8.1, 6.5 Hz, 1H), 4.39 (td, *J* = 8.2, 5.1 Hz, 1H), 4.09 – 4.06 (m, 1H), 3.63 – 3.61 (m, 1H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 172.6, 143.9, 133.6, 132.0, 131.2, 131.0, 129.3, 128.4, 124.3, 123.6, 121.4, 92.3, 86.3, 83.6, 70.3, 42.0. **HRMS** (ESI): *m*/*z* calcd for $C_{18}H_{14}NO_2^+$ $[M+H]^+$ 276.1019, found 276.1016.

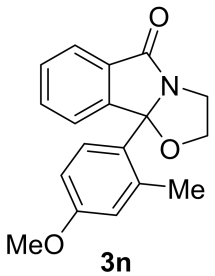
9b-(4-Chloro-2-methylphenyl)-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (3m)



3m

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 75% yield (44.9 mg). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a white solid. **Mp:** 76 – 78 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.77 (m, 2H), 7.55 – 7.50 (m, 2H), 7.27 – 7.19 (m, 2H), 7.14 (d, *J* = 2.3 Hz, 1H), 4.37 (q, *J* = 6.3 Hz, 1H), 4.20 – 4.13 (m, 2H), 3.22 – 3.14 (m, 1H), 2.06 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 173.9, 145.7, 138.5, 134.6, 133.6, 133.5, 132.2, 131.7, 130.5, 128.6, 126.2, 124.3, 123.3, 100.3, 70.0, 41.3, 20.1. **HRMS** (ESI) *m*/*z* calcd for $C_{17}H_{15}ClNO_2^+$ ($[M+H]^+$): 300.0786, found 300.0781.

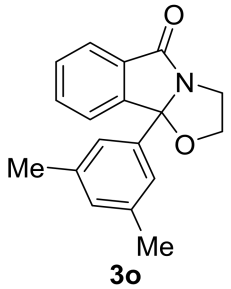
9b-(4-Methoxy-2-methylphenyl)-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (3n)



3n

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 63% yield (37.2 mg). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.79 (m, 1H), 7.74 (d, *J* = 8.6 Hz, 1H), 7.51 – 7.49 (m, 2H), 7.23 – 7.21 (m, 1H), 6.80 – 6.78 (m, 1H), 6.68 (d, *J* = 2.7 Hz, 1H), 4.38 – 4.35 (m, 1H), 4.19 – 4.13 (m, 2H), 3.80 (s, 3H), 3.23 – 3.16 (m, 1H), 2.06 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 174.0, 159.9, 146.4, 138.1, 133.3, 131.7, 130.2, 128.5, 126.9, 124.2, 123.4, 118.1, 110.8, 100.6, 70.0, 55.2, 41.1, 20.5. **HRMS** (ESI) *m*/*z* calcd for $C_{18}H_{18}NO_3^+$ ([M+H]$^+$): 296.1281, found 296.1285.

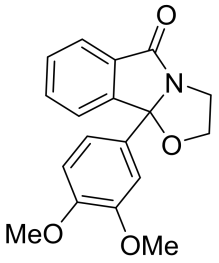
9b-(3,5-Dimethylphenyl)-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (3o)



3o

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 81% yield (45.2 mg). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$)δ 7.82 – 7.77 (m, 1H), 7.52 – 7.46 (m, 2H), 7.35 – 7.29 (m, 1H), 7.23 – 7.16 (m, 2H), 7.00 – 6.97 (m, 1H), 4.40 – 4.33 (m, 1H), 4.17 – 4.08 (m, 2H), 3.33 – 3.25 (m, 1H), 2.32 (d, J = 0.8 Hz, 6H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 174.0, 146.9, 138.5, 137.8, 133.2, 131.2, 130.5, 130.1, 124.23, 123.5, 123.4, 100.5, 70.2, 41.5, 21.4. **HRMS** (ESI) *m*/*z* calcd for $C_{18}H_{18}NO_2^+$ ([M+H]$^+$): 280.1332, found 280.1334.

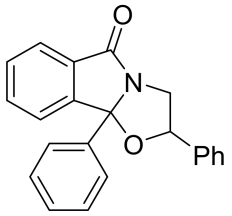
9b-(3,4-Dimethoxyphenyl)-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (3p)



3p

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 82% yield (51.0 mg). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a white solid. **Mp:** 150 – 152 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 – 7.77 (m, 1H), 7.52 – 7.45 (m, 2H), 7.33 – 7.28 (m, 1H), 7.19 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.05 (d, *J* = 2.1 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 4.40 – 4.34 (m, 1H), 4.17 – 4.08 (m, 2H), 3.87 (s, 3H), 3.86 (s, 3H), 3.33 – 3.26 (m, 1H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 174.1, 149.4, 149.3, 146.8, 133.2, 131.0, 130.2, 130.1, 124.3, 123.4, 118.2, 111.2, 108.7, 100.4, 70.2, 56.0, 56.0, 41.6. **HRMS** (ESI) *m*/*z* calcd for $C_{18}H_{18}NO_4^+$ ($[M+H]^+$): 312.1230, found 312.1233.

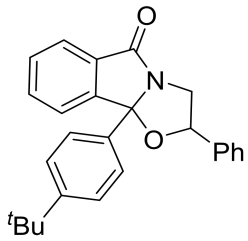
2,9b-Diphenyl-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (5a)



5a

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 81% yield (53.0 mg, 9:1 dr). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a light-yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7.87 (m, 1H), 7.73 – 7.70 (m, 2H), 7.55 – 7.51 (m, 2H), 7.49 – 7.43 (m, 3H), 7.39 – 7.37 (m, 1H), 7.34 – 7.30 (m, 3H), 7.21 (dd, *J* = 7.4, 2.2 Hz, 2H), 5.37 (dd, *J* = 7.8, 6.4 Hz, 1H), 4.02 (dd, *J* = 11.2, 6.4 Hz, 1H), 3.71 (dd, *J* = 11.2, 7.8 Hz, 1H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 173.7, 146.5, 139.4, 137.9, 133.3, 131.2, 130.2, 129.0, 128.7, 128.5, 126.2, 125.8, 124.5, 123.9, 101.3, 84.3, 49.3, 29.7. **HRMS** (ESI) *m*/*z* calcd for $C_{22}H_{18}NO_2^+$ ($[M+H]^+$): 328.1332, found 328.1334.

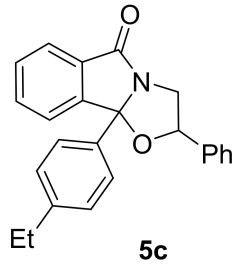
9b-(4-(*tert*-Butyl)phenyl)-2-phenyl-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (5b)



5b

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 95% yield (72.8 mg, 13:1 dr). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a yellow solid. **Mp:** 60 – 62 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7.87 (m, 1H), 7.65 – 7.63 (m, 2H), 7.54 (dd, *J* = 5.6, 3.1 Hz, 2H), 7.50 – 7.47 (m, 2H), 7.42 – 7.40 (m, 1H), 7.31 – 7.28 (m, 3H), 7.23 – 7.21 (m, 2H), 5.38 (dd, *J* = 7.8, 6.4 Hz, 1H), 4.01 (dd, *J* = 11.2, 6.4 Hz, 1H), 3.73 (dd, *J* = 11.1, 7.8 Hz, 1H), 1.38 (s, 9H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 173.7, 152.0, 146.6, 139.6, 134.8, 133.2, 131.3, 130.1, 128.7, 128.5, 126.2, 125.9, 125.5, 124.4, 124.0, 101.3, 84.2, 49.3, 34.7, 31.4. **HRMS** (ESI) *m*/*z* calcd for $C_{26}H_{26}NO_2^+$ ([M+H]$^+$): 384.1958, found 384.1961.

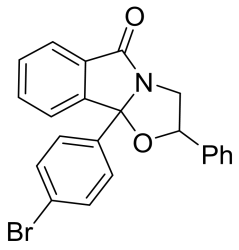
9b-(4-Ethylphenyl)-2-phenyl-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (5c)



5c

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 88% yield (62.5 mg, 13:1 dr). It was purified by flash chromatography (V_{PE}:V_{EA}=5:1) to afford a white solid. **Mp:** 53 – 55 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 1H), 7.65 – 7.62 (m, 2H), 7.54 (dd, *J* = 5.6, 3.1 Hz, 2H), 7.42 – 7.38 (m, 1H), 7.30 – 7.28 (m, 5H), 7.23 – 7.21 (m, 2H), 5.38 (dd, *J* = 7.8, 6.4 Hz, 1H), 4.02 (dd, *J* = 11.2, 6.4 Hz, 1H), 3.72 (dd, *J* = 11.1, 7.8 Hz, 1H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.32 – 1.28 (m, 3H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 173.7, 146.6, 145.2, 139.5, 135.1, 133.2, 131.2, 130.2, 128.7, 128.5, 128.5, 126.2, 125.8, 124.4, 123.9, 101.4, 84.2, 49.3, 28.6, 15.5. **HRMS** (ESI) *m*/*z* calcd for $C_{24}H_{22}NO_2^+$ ([M+H]$^+$): 356.1645, found 356.1646.

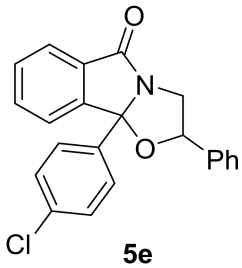
9b-(4-Bromophenyl)-2-phenyl-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (5d)



5d

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 79% yield (64.0 mg, 10:1 dr). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.80 (m, 1H), 7.52 – 7.46 (m, 6H), 7.29 – 7.27 (m, 1H), 7.25 – 7.19 (m, 3H), 7.13 – 7.11 (m, 2H), 5.28 (dd, *J* = 7.8, 6.3 Hz, 1H), 3.94 (dd, *J* = 11.3, 6.4 Hz, 1H), 3.61 (dd, *J* = 11.3, 7.9 Hz, 1H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 173.5, 146.0, 139.2, 137.2, 133.4, 132.2, 131.1, 130.5, 128.8, 128.6, 127.7, 126.2, 124.6, 123.8, 123.2, 100.9, 84.4, 49.3. **HRMS** (ESI) *m*/*z* calcd for $C_{22}H_{17}BrNO_2^+$ ([M+H]$^+$): 406.0437, found 406.0435.

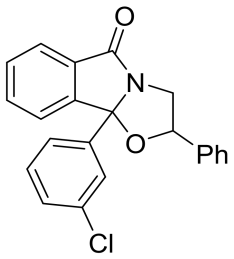
9b-(4-Chlorophenyl)-2-phenyl-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (5e)



5e

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 74% yield (53.4 mg, 10:1 dr). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a white foam. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.79 (m, 1H), 7.60 – 7.57 (m, 2H), 7.51 – 7.47 (m, 2H), 7.38 – 7.35 (m, 2H), 7.29 – 7.26 (m, 1H), 7.24 – 7.21 (m, 3H), 7.13 – 7.10 (m, 2H), 5.28 (dd, *J* = 7.8, 6.4 Hz, 1H), 3.94 (dd, *J* = 11.2, 6.4 Hz, 1H), 3.61 (dd, *J* = 11.2, 7.8 Hz, 1H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 173.5, 146.1, 139.2, 136.6, 135.0, 133.4, 131.1, 130.5, 129.2, 128.8, 128.6, 127.4, 126.2, 124.6, 123.8, 100.9, 84.4, 49.3. **HRMS** (ESI) *m*/*z* calcd for $C_{22}H_{17}ClNO_2^+$ ([M+H]$^+$): 362.0942, found 362.0945.

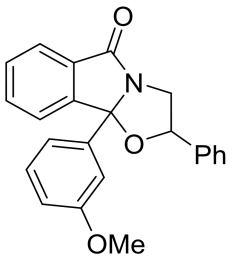
9b-(3-Chlorophenyl)-2-phenyl-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (5f)



5f

Prepared according to the general procedure (reaction time: 0.5 h) as described above in 78% yield (56.3 mg, 7:1 dr). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7.85 (m, 1H), 7.71 – 7.68 (m, 1H), 7.59 – 7.54 (m, 3H), 7.40 – 7.33 (m, 3H), 7.31 – 7.27 (m, 3H), 7.19 – 7.17 (m, 2H), 5.35 (dd, *J* = 7.8, 6.3 Hz, 1H), 4.00 (dd, *J* = 11.2, 6.4 Hz, 1H), 3.69 (dd, *J* = 11.2, 7.9 Hz, 1H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 173.5, 145.9, 140.3, 139.2, 135.1, 133.4, 131.1, 130.5, 130.4, 129.2, 128.8, 128.6, 126.2, 126.1, 124.6, 124.1, 123.9, 100.7, 84.4, 49.3. **HRMS** (ESI) *m*/*z* calcd for $C_{22}H_{17}ClNO_2^+$ ($[M+H]^+$): 362.0942, found 362.0943.

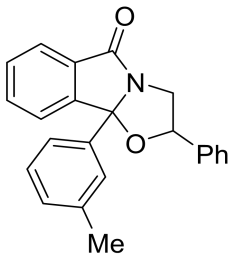
9b-(3-Methoxyphenyl)-2-phenyl-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (5g)



5g

Prepared according to the asymmetric procedure (reaction time: 0.5 h) as described above in 73% yield (54.5 mg, 7:1 dr). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a white solid. **Mp:** 125 – 127 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.83 (m, 1H), 7.52 – 7.50 (m, 2H), 7.38 – 7.27 (m, 5H), 7.24 – 7.16 (m, 4H), 6.94 – 6.91 (m, 1H), 5.34 (dd, *J* = 7.8, 6.5 Hz, 1H), 3.97 (dd, *J* = 11.2, 6.4 Hz, 1H), 3.81 (s, 3H), 3.69 (dd, *J* = 11.2, 7.8 Hz, 1H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 173.7, 160.2, 146.3, 139.6, 139.4, 133.3, 131.2, 130.3, 130.2, 128.8, 128.6, 126.2, 124.5, 123.9, 118.1, 114.5, 111.3, 101.2, 84.3, 55.4, 49.4. **HRMS** (ESI) *m*/*z* calcd for $C_{24}H_{24}NO_3^+$ ($[M+H]^+$): 374.1751, found 374.1753.

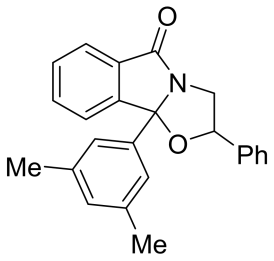
2-Phenyl-9b-(*m*-tolyl)-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (5h)



5h

Prepared according to the asymmetric procedure (reaction time: 0.5 h) as described above in 57% yield (38.9 mg, 10:1 dr). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7.85 (m, 1H), 7.55 – 7.49 (m, 4H), 7.39 – 7.29 (m, 4H), 7.28 – 7.27 (m, 1H), 7.23 – 7.19 (m, 3H), 5.35 (dd, *J* = 7.8, 6.4 Hz, 1H), 3.99 (dd, *J* = 11.1, 6.4 Hz, 1H), 3.70 (dd, *J* = 11.2, 7.8 Hz, 1H), 2.40 (s, 3H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 173.7, 146.6, 139.5, 138.8, 137.8, 133.2, 131.3, 130.2, 129.8, 128.9, 128.7, 128.5, 126.4, 126.2, 124.5, 123.9, 122.9, 101.3, 84.2, 49.3, 21.6. **HRMS** (ESI) *m*/*z* calcd for $C_{23}H_{20}NO_2^+$ ([M+H]$^+$): 342.1489, found 342.1492.

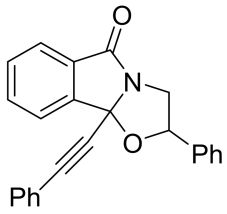
9b-(3,5-Dimethylphenyl)-2-phenyl-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (5i)



5i

Prepared according to the asymmetric procedure (reaction time: 0.5 h) as described above in 61% yield (43.3 mg, 13:1 dr). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.83 (m, 1H), 7.55 – 7.50 (m, 2H), 7.38 (dd, *J* = 5.8, 2.8 Hz, 1H), 7.33 – 7.27 (m, 5H), 7.23 – 7.18 (m, 2H), 7.03 (s, 1H), 5.35 (dd, *J* = 7.8, 6.5 Hz, 1H), 3.96 (dd, *J* = 11.1, 6.5 Hz, 1H), 3.70 (dd, *J* = 11.1, 7.8 Hz, 1H), 2.35 (s, 6H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 173.7, 146.6, 139.5, 138.7, 137.7, 133.2, 131.2, 130.6, 130.1, 128.7, 128.5, 126.2, 124.4, 123.9, 123.4, 101.3, 84.2, 49.3, 21.4. **HRMS** (ESI) *m*/*z* calcd for $C_{24}H_{22}NO_2^+$ ([M+H]$^+$): 356.1645, found 356.1642.

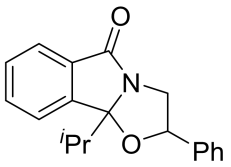
2-Phenyl-9b-(phenylethynyl)-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (5j)



5j

Prepared according to the asymmetric procedure (reaction time: 0.5 h) as described above in 83% yield (60.9 mg, 9:1 dr). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a yellow foam. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 – 7.74 (m, 2H), 7.60 (td, *J* = 7.5, 1.2 Hz, 1H), 7.54 – 7.50 (m, 1H), 7.45 – 7.41 (m, 2H), 7.29 – 7.25 (m, 3H), 7.22 – 7.17 (m, 3H), 7.14 – 7.12 (m, 2H), 5.74 (t, *J* = 7.2 Hz, 1H), 3.96 – 3.79 (m, 2H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 172.4, 143.7, 138.5, 133.6, 132.1, 131.4, 131.1, 129.3, 128.8, 128.7, 128.5, 126.4, 124.5, 123.9, 121.4, 92.8, 86.7, 84.6, 83.6, 49.4. **HRMS** (ESI) *m*/*z* calcd for $C_{25}H_{22}NO_2^+$ ([M+H]$^+$): 368.1645, found 368.1647.

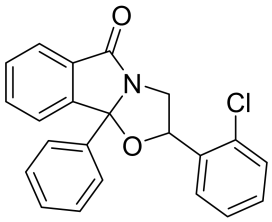
9b-Isopropyl-2-phenyl-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (5k)



5k

Prepared according to the asymmetric procedure (reaction time: 0.5 h) as described above in 62% yield (36.3 mg, 2:1 dr). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a yellow foam. **^{1}H NMR** (400 MHz, $CDCl_3$, mixture of diastereomers) δ 7.85 – 7.83 (m, 0.3H), 7.77 (dt, *J* = 7.4, 1.0 Hz, 0.7H), 7.66 – 7.51 (m, 3H), 7.41 – 7.35 (m, 1.3H), 7.32 – 7.28 (m, 0.3H), 7.19 – 7.15 (m, 2H), 6.98 – 6.94 (m, 1.4H), 5.57 (dd, *J* = 7.7, 4.2 Hz, 0.7H), 5.29 (t, *J* = 7.7 Hz, 0.3H), 4.86 (t, *J* = 8.5 Hz, 0.3H), 4.40 (dd, *J* = 8.7, 7.0 Hz, 0.3H), 4.04 (dd, *J* = 11.5, 4.2 Hz, 0.7H), 3.86 (dd, *J* = 11.5, 7.7 Hz, 0.7H), 2.59 – 2.49 (m, 0.7H), 2.35 – 2.17 (m, 0.3H), 1.25 (d, *J* = 7.0 Hz, 1H), 1.15 (d, *J* = 6.9 Hz, 2H), 0.95 (d, *J* = 6.8 Hz, 2H), 0.71 (d, *J* = 6.8 Hz, 1H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$, mixture of diastereomers) δ 174.5, 173.4, 145.8, 144.6, 141.1, 140.5, 133.3, 132.8, 132.7, 130.2, 130.0, 128.8, 128.6, 128.0, 127.4, 125.6, 125.5, 124.6, 124.4, 123.4, 123.2, 104.8, 104.6, 84.0, 75.8, 57.9, 50.4, 34.1, 32.1, 17.6, 17.3, 17.2, 16.6. **HRMS** (ESI) *m*/*z* calcd for $C_{19}H_{20}NO_2^+$ ([M+H]$^+$): 294.1489, found 294.1493.

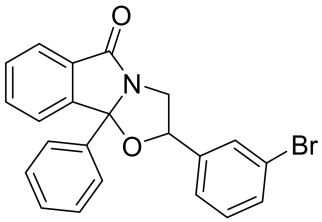
2-(2-Chlorophenyl)-9b-phenyl-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one



5l

Prepared according to the asymmetric procedure (reaction time: 0.5 h) as described above in 87% yield (62.8 mg, >20:1 dr). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a white solid. **Mp:** 104 – 106 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.81 (m, 1H), 7.69 – 7.66 (m, 2H), 7.58 – 7.52 (m, 2H), 7.47 – 7.38 (m, 4H), 7.33 – 7.30 (m, 1H), 7.20 – 7.09 (m, 3H), 5.70 (dd, *J* = 7.9, 5.4 Hz, 1H), 3.98 (dd, *J* = 11.4, 5.4 Hz, 1H), 3.83 (dd, *J* = 11.4, 7.9 Hz, 1H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 173.3, 146.6, 138.2, 137.8, 133.3, 131.4, 131.1, 130.3, 129.4, 129.1, 129.0, 129.0, 127.1, 126.4, 125.8, 124.5, 123.9, 101.2, 81.2, 48.2. **HRMS** (ESI) *m*/*z* calcd for $C_{22}H_{17}ClNO_2^+$ ([M+H]$^+$): 362.0942, found 362.0945.

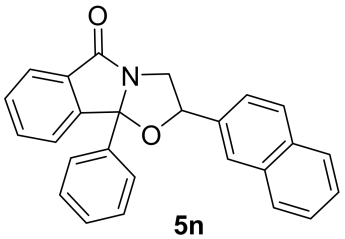
2-(3-Bromophenyl)-9b-phenyl-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (5m)



5m

Prepared according to the asymmetric procedure (reaction time: 0.5 h) as described above in 82% yield (66.4 mg, 2.3:1 dr). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a light-yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.84 (m, 1H), 7.69 – 7.66 (m, 2H), 7.56 – 7.51 (m, 2H), 7.46 – 7.33 (m, 6H), 7.19 – 7.07 (m, 2H), 5.30 (dd, *J* = 7.8, 6.3 Hz, 0.7H), 5.08 (dd, *J* = 9.7, 5.8 Hz, 0.3H), 4.61 (dd, *J* = 12.0, 5.8 Hz, 0.3H), 3.95 (dd, *J* = 11.2, 6.3 Hz, 0.7H), 3.68 (dd, *J* = 11.2, 7.8 Hz, 0.7H), 3.11 (dd, *J* = 12.0, 9.7 Hz, 0.3H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 174.1, 173.6, 148.4, 146.3, 141.8, 140.6, 139.8, 137.7, 133.8, 133.4, 131.6, 131.5, 131.1, 130.5, 130.4, 130.2, 130.1, 129.9, 129.2, 129.1, 129.0, 128.9, 128.8, 125.8, 125.5, 125.3, 124.6, 124.6, 124.4, 123.9, 123.8, 122.7, 122.7, 101.4, 100.7, 83.3, 82.7, 50.4, 49.2. **HRMS** (ESI) *m*/*z* calcd for $C_{22}H_{17}BrNO_2^+$ ([M+H]$^+$): 406.0437, found 406.0439.

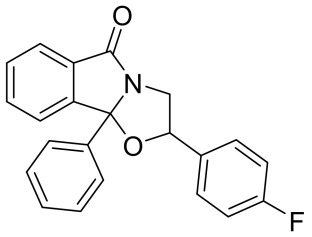
2-(Naphthalen-2-yl)-9b-phenyl-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (5n)



5n

Prepared according to the asymmetric procedure (reaction time: 0.5 h) as described above in 86% yield (64.9 mg, 20:1 dr). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a white solid. **Mp:** 120 – 122 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 – 7.88 (m, 1H), 7.81 – 7.77 (m, 2H), 7.76 – 7.72 (m, 3H), 7.65 (d, *J* = 1.7 Hz, 1H), 7.56 – 7.53 (m, 2H), 7.50 – 7.43 (m, 5H), 7.41 – 7.39 (m, 1H), 7.28 (dd, *J* = 8.6, 1.8 Hz, 1H), 5.52 (dd, *J* = 7.8, 6.4 Hz, 1H), 4.10 (dd, *J* = 11.2, 6.4 Hz, 1H), 3.76 (dd, *J* = 11.2, 7.8 Hz, 1H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 173.7, 146.6, 138.0, 136.7, 133.4, 133.3, 133.1, 131.3, 130.3, 129.0, 129.0, 128.0, 127.8, 126.4, 126.3, 125.9, 125.6, 124.5, 124.0, 123.6, 101.4, 84.5, 49.3. **HRMS** (ESI) *m*/*z* calcd for $C_{26}H_{20}NO_2^+$ ([M+H]$^+$): 378.1489, found 378.1493.

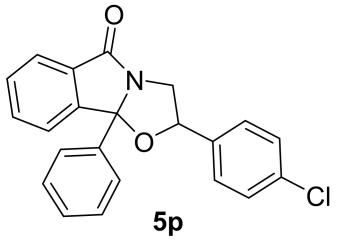
2-(4-Fluorophenyl)-9b-phenyl-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (5o)



5o

Prepared according to the asymmetric procedure (reaction time: 0.5 h) as described above in 74% yield (51.1 mg, 11:1 dr). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a yellow solid. **Mp:** 99 – 101 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.83 (m, 1H), 7.70 – 7.67 (m, 2H), 7.55 – 7.51 (m, 2H), 7.47 – 7.40 (m, 3H), 7.36 – 7.33 (m, 1H), 7.19 – 7.14 (m, 2H), 7.01 – 6.94 (m, 2H), 5.32 (dd, *J* = 7.8, 6.2 Hz, 1H), 3.96 (dd, *J* = 11.2, 6.3 Hz, 1H), 3.67 (dd, *J* = 11.2, 7.8 Hz, 1H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 173.6, 162.7 (d, *J* = 247.1 Hz), 146.4, 137.8, 135.3 (d, *J* = 3.3 Hz), 133.3, 131.1, 130.3, 129.1, 129.0, 128.0 (d, *J* = 8.3 Hz), 125.8, 124.5, 123.9, 115.7 (d, *J* = 21.6 Hz), 101.3, 83.6, 49.3. **^{19}F {^{1}H} NMR** (376 MHz, $CDCl_3$) δ -113.33 (s). **HRMS** (ESI) *m*/*z* calcd for $C_{22}H_{17}FNO_2^+$ ([M+H]$^+$): 346.1238, found 346.1241.

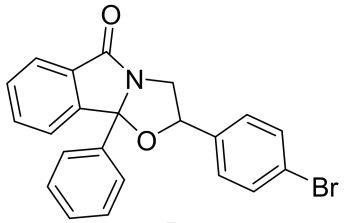
2-(4-Chlorophenyl)-9b-phenyl-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (5p)



5p

Prepared according to the asymmetric procedure (reaction time: 0.5 h) as described above in 74% yield (53.4 mg, 10:1 dr). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a white solid. **Mp:** 83 – 85 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 5.7, 3.1 Hz, 1H), 7.60 – 7.58 (m, 2H), 7.45 (dd, *J* = 5.6, 3.0 Hz, 2H), 7.38 – 7.31 (m, 3H), 7.27 (dd, *J* = 5.6, 2.9 Hz, 1H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 5.23 (dd, *J* = 7.8, 6.1 Hz, 1H), 3.87 (dd, *J* = 11.2, 6.1 Hz, 1H), 3.58 (dd, *J* = 11.2, 7.8 Hz, 1H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 173.6, 146.4, 138.2, 137.7, 134.3, 133.4, 131.1, 130.3, 129.1, 129.0, 128.9, 127.5, 125.8, 124.5, 123.9, 101.4, 83.5, 49.2. **HRMS** (ESI) *m*/*z* calcd for $C_{22}H_{17}ClNO_2^+$ ([M+H]$^+$): 362.0942, found 362.0943.

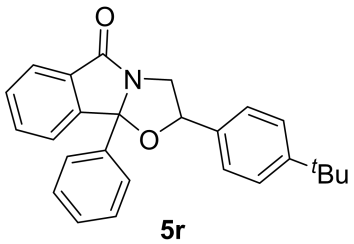
2-(4-Bromophenyl)-9b-phenyl-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (5q)



5q

Prepared according to the asymmetric procedure (reaction time: 0.5 h) as described above in 79% yield (64.0 mg, 12:1 dr). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a white foam. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.82 (m, 1H), 7.69 – 7.66 (m, 2H), 7.53 (dd, *J* = 5.6, 3.0 Hz, 2H), 7.46 – 7.39 (m, 5H), 7.36 – 7.33 (m, 1H), 7.06 – 7.03 (m, 2H), 5.30 (dd, *J* = 7.8, 6.1 Hz, 1H), 3.95 (dd, *J* = 11.2, 6.1 Hz, 1H), 3.67 (dd, *J* = 11.3, 7.9 Hz, 1H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 173.6, 146.4, 138.7, 137.7, 133.4, 131.9, 131.1, 130., 129.1, 129.0, 127.8, 125.8, 124.5, 123.9, 122.4, 101.4, 83.5, 49.2. **HRMS** (ESI) *m*/*z* calcd for $C_{22}H_{17}BrNO_2^+$ ([M+H]$^+$): 406.0437, found 406.0439.

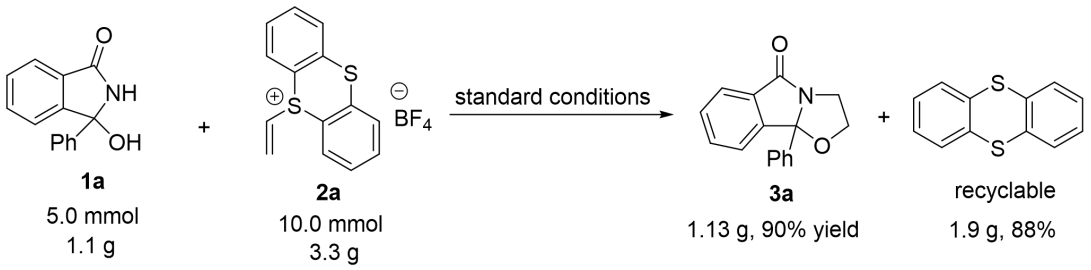
2-(4-(*tert*-Butyl)phenyl)-9b-phenyl-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (5r)



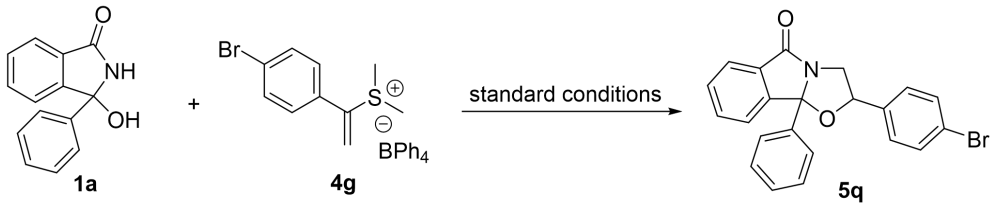
5r

Prepared according to the asymmetric procedure (reaction time: 0.5 h) as described above in 95% yield (72.8 mg, 14:1 dr). It was purified by flash chromatography (V_{PE}:V_{EA} = 5:1) to afford a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.85 (m, 1H), 7.71 – 7.69 (m, 2H), 7.54 – 7.49 (m, 2H), 7.47 – 7.40 (m, 3H), 7.35 – 7.31 (m, 3H), 7.16 – 7.14 (m, 2H), 5.32 (dd, *J* = 7.8, 6.5 Hz, 1H), 4.02 (dd, *J* = 11.2, 6.5 Hz, 1H), 3.67 (dd, *J* = 11.2, 7.8 Hz, 1H), 1.28 (s, 9H). **^{13}C {^{1}H} NMR** (101 MHz, $CDCl_3$) δ 173.7, 151.7, 146.5, 138.0, 136.3, 133.2, 131.3, 130.2, 129.0, 128.9, 126.2, 125.8, 125.7, 124.5, 123.9, 101.2, 84.3, 49.1, 34.6, 31.3. **HRMS** (ESI) *m*/*z* calcd for $C_{26}H_{20}NO_2^+$ ($[M+H]^+$): 384.1958, found 384.1961.

4. Scaled-up Synthesis of the Products 3a and 5q

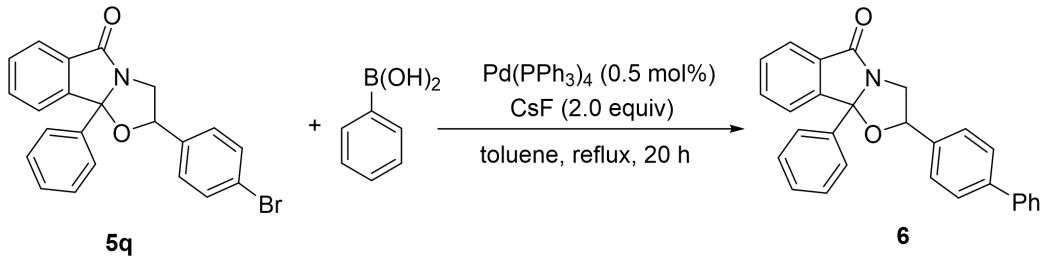


The compound **1a** (1.1 g, 5 mmol), vinylsulfonium salt **2a** (3.3 g, 10.0 mmol.) and DCM (50.0 mL) were added to a 100 mL dry sealed tube. Then DBU (1.52 g, 10.0 mmol) were added in one portion. This solution was stirred at room temperature for 0.5 h until the complete consumption of compound **1a** monitored by TLC. The reaction mixture was filtered with Celite, and eluted with dichloromethane. The filtrate was concentrated and the residue was purified by flash column chromatography (petroleum ether: EtOAc = 5:1) on silica gel to afford corresponding product **3a** in 90% yield (1.13 g). Meanwhile, thianthrene, a recyclable product of substrate 2, was isolated in 88% yield.



The compound **1a** (675 mg, 3.0 mmol), vinylsulfonium salt **4g** (3.38 g, 6.0 mmol.) and DCM (30.0 mL) were added to a 100 mL dry sealed tube. Then DBU (609 mg, 4.0 mmol) were added in one portion. This solution was stirred at room temperature for 0.5 h until the complete consumption of compound **1a** monitored by TLC. The reaction mixture was filtered with Celite, and eluted with dichloromethane. The filtrate was concentrated and the residue was purified by flash column chromatography (petroleum ether: EtOAc = 5:1) on silica gel to afford corresponding product **5q** in 76% yield (926.3 mg).

5. Transformation of the Product 5q and Control Experiment



Under nitrogen atmosphere, compound **5q** (0.2 mmol), phenylboric acid (0.24 mmol), CsF (0.4 mmol), and $Pd(PPh_3)_4$ (0.5 mol%) were successively added to a 10 mL dried sealed tube, followed by the addition of 2.0 mL of toluene. The resulting mixture was stirred at 100 °C in an oil bath for 20 h, and then the reaction mixture was directly subjected to flash column chromatography on silica gel (eluting with PE : EA = 5:1) to afford the corresponding product **6** as a yellow solid (69.3 mg, dr = 20:1, 86% yield), **Mp:** 102 – 104 °C.

2-([1,1'-Biphenyl]-4-yl)-9b-phenyl-2,3-dihydrooxazolo[2,3-*a*]isoindol-5(9b*H*)-one (6)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 5.9, 2.9 Hz, 1H), 7.71 – 7.69 (m, 2H), 7.54 – 7.49 (m, 6H), 7.44 – 7.39 (m, 4H), 7.38 – 7.29 (m, 3H), 7.26 – 7.23 (m, 2H), 5.37 (dd, *J* = 7.8, 6.4 Hz, 1H), 4.03 (dd, *J* = 11.2, 6.4 Hz, 1H), 3.70 (dd, *J* = 11.2, 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 146.5, 141.5, 140.7, 138.4, 137.9, 133.3, 131.3, 130.3, 129.0, 128.8, 127.5, 127.5, 127.1, 126.7, 125.9,

124.5, 123.9, 101.4, 84.1, 49.3. HRMS (ESI): *m*/*z* calcd for $C_{28}H_{22}NO_2^+$ $[M+H]^+$ 404.1645, found 404.1647.

6. X-Ray Single Crystal Data of Products 3p and 5a

Samples preparation for single crystal 3p and 5a: Pure **3p** (**or 5a**) (20 mg) was dissolved in 1.0 mL of ethyl acetate with a 10 mL of test tube, and then 4.0 mL of *n*-hexane was added to the test tube slowly. The test tube was sealed with a parafilm and kept standing for 3-5 days, and the single crystal **3p** (**or 5a**) appeared at the bottom of the test tube.

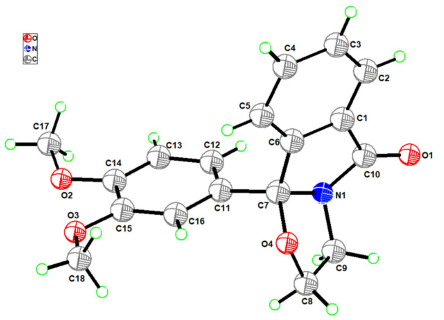


Figure S1. X-Ray structure of **3p**

CCDC number	2417187
Empirical formula	$C_{18}H_{17}O_4$
Formula weight	311.16
Temperature/K	293.0
Crystal system	triclinic
Space group	P-1
a/Å	8.4269(8)
b/Å	10.2708(11)
c/Å	10.7625(12)
α/°	112.254(4)
β/°	110.239(4)
γ/°	97.809(4)
Volume/Å^3	769.74(14) Å^3
Z	2
ρ_{calc}g/cm^3	1.335
μ/mm^{-1}	0.089
F(000)	328.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.538 to 55.036
Index ranges	-10≤h≤10, -12≤k≤13, -13≤l≤13
Reflections collected	7305
Independent reflections	3503 [R_{int} = 0.0326, R_{sigma} = 0.0474]
Data/restraints/parameters	3503/0/210
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0688, wR_2 = 0.1984
Final R indexes [all data]	R_1 = 0.0930, wR_2 = 0.2203
Largest diff. peak/hole / e Å^{-3}	0.40/-0.54

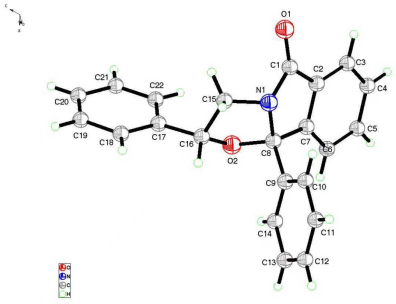


Figure S2. X-Ray structure of **5a**

CCDC number	2540289
Empirical formula	$C_{22}H_{17}NO_2$
Formula weight	327.36
Temperature/K	293.0
Crystal system	monoclinic
Space group	C2/m
a/Å	18.236(3)
b/Å	9.0230(19)
c/Å	13.095(4)
α/°	90
β/°	128.825(4)
γ/°	90
Volume/Å^3	1678.6(7)
Z	4
ρ_{calc}g/cm^3	1.295
μ/mm^{-1}	0.083
F(000)	688.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.992 to 52.878
Index ranges	-22≤h≤22, -11≤k≤9, -16≤l≤16
Reflections collected	7182
Independent reflections	1833 [R_{int} = 0.0465, R_{sigma} = 0.0422]
Data/restraints/parameters	1833/0/190
Goodness-of-fit on F^2	1.086
Final R indexes [I>=2σ (I)]	R_1 = 0.0533, wR_2 = 0.1169
Final R indexes [all data]	R_1 = 0.0862, wR_2 = 0.1344
Largest diff. peak/hole / e Å^{-3}	0.12/-0.12

7. NMR Spectra of Products 3a-3p, 5a-5r and 6

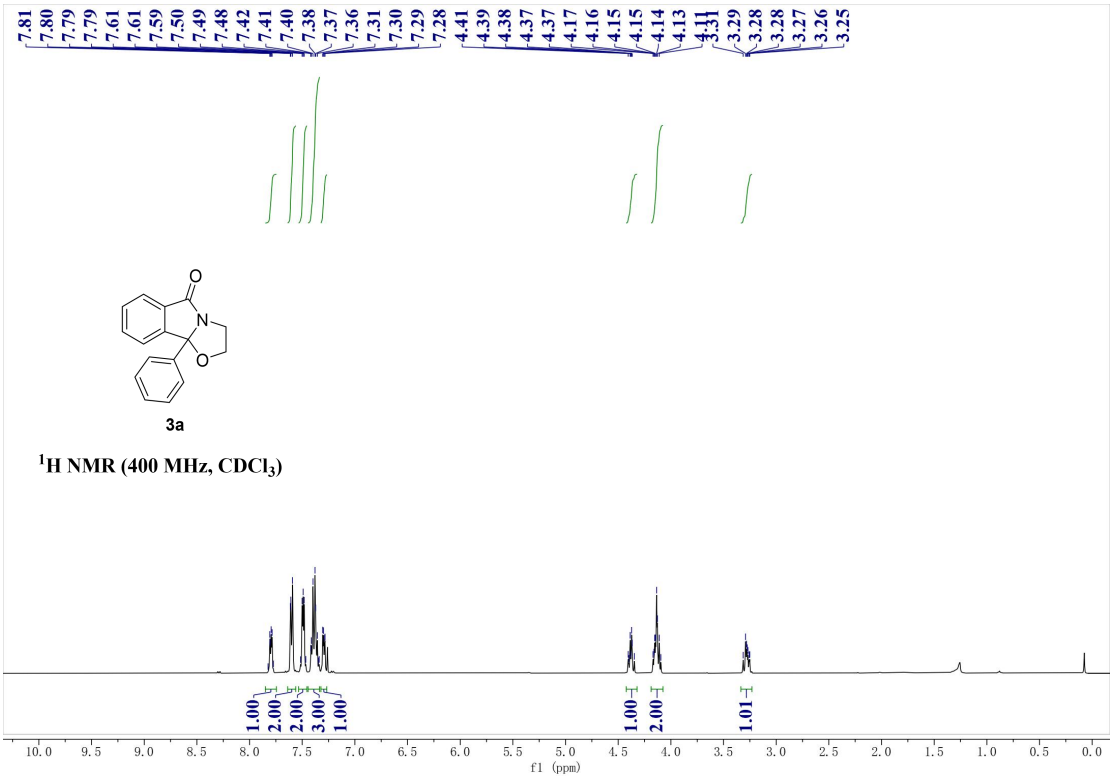


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3a**

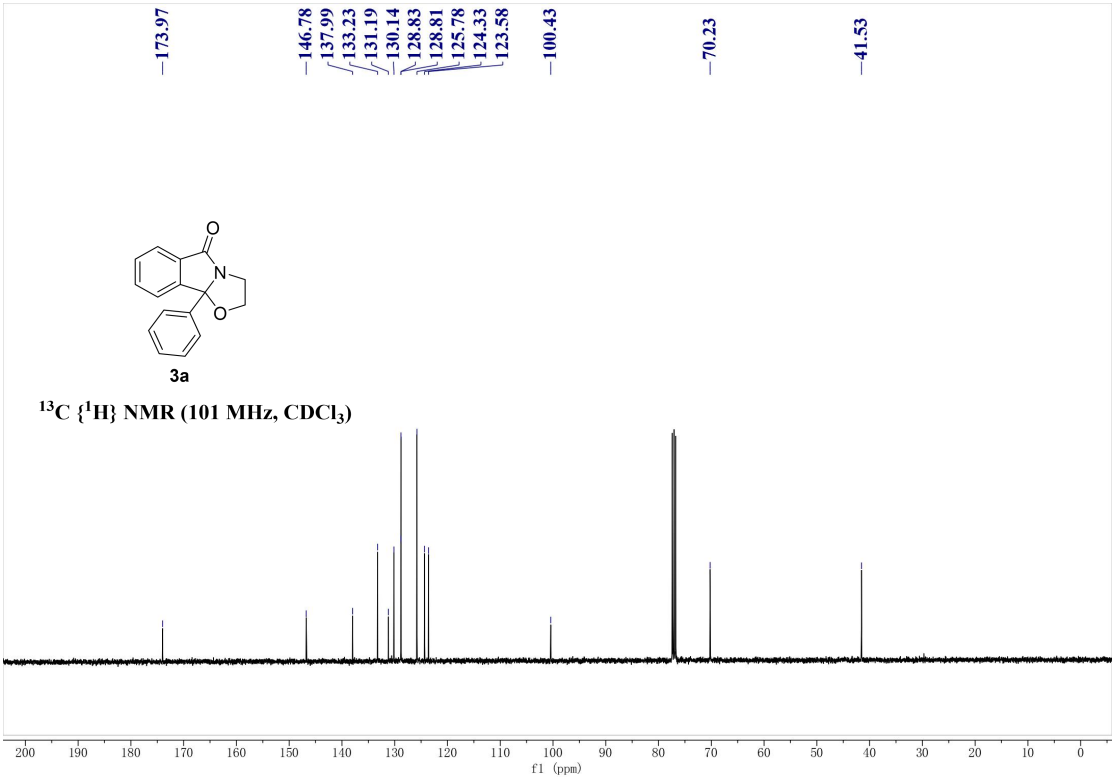


Figure S4. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **3a**

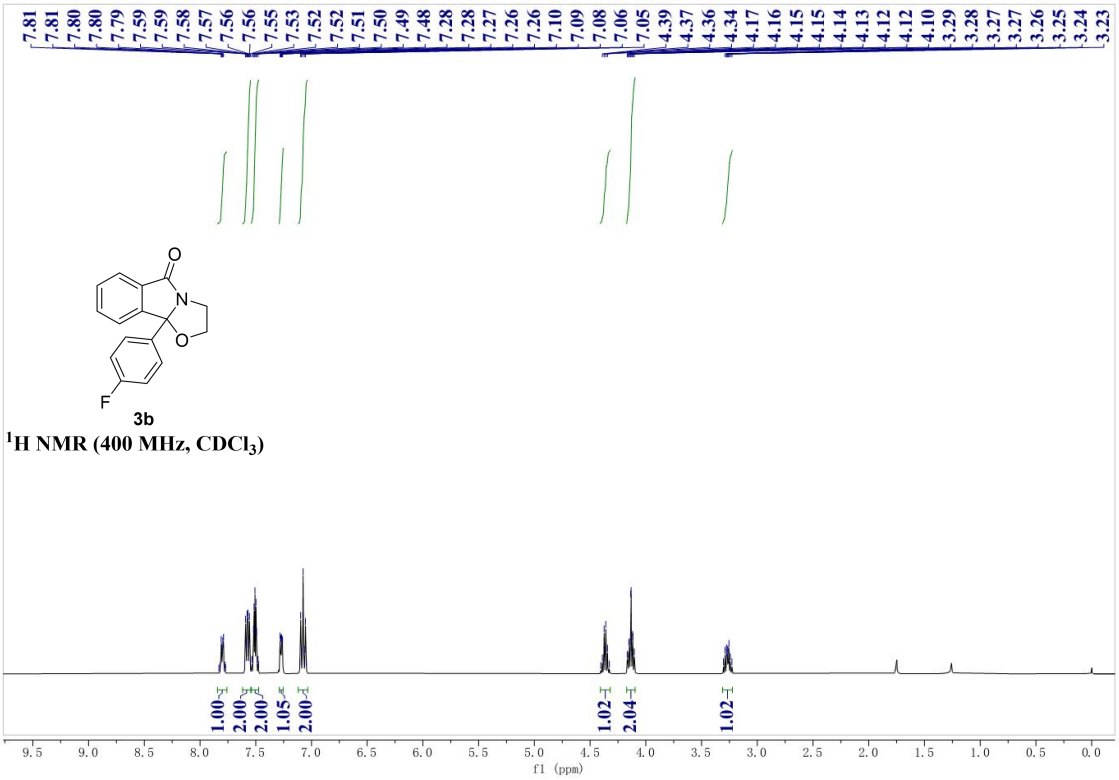


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3b**

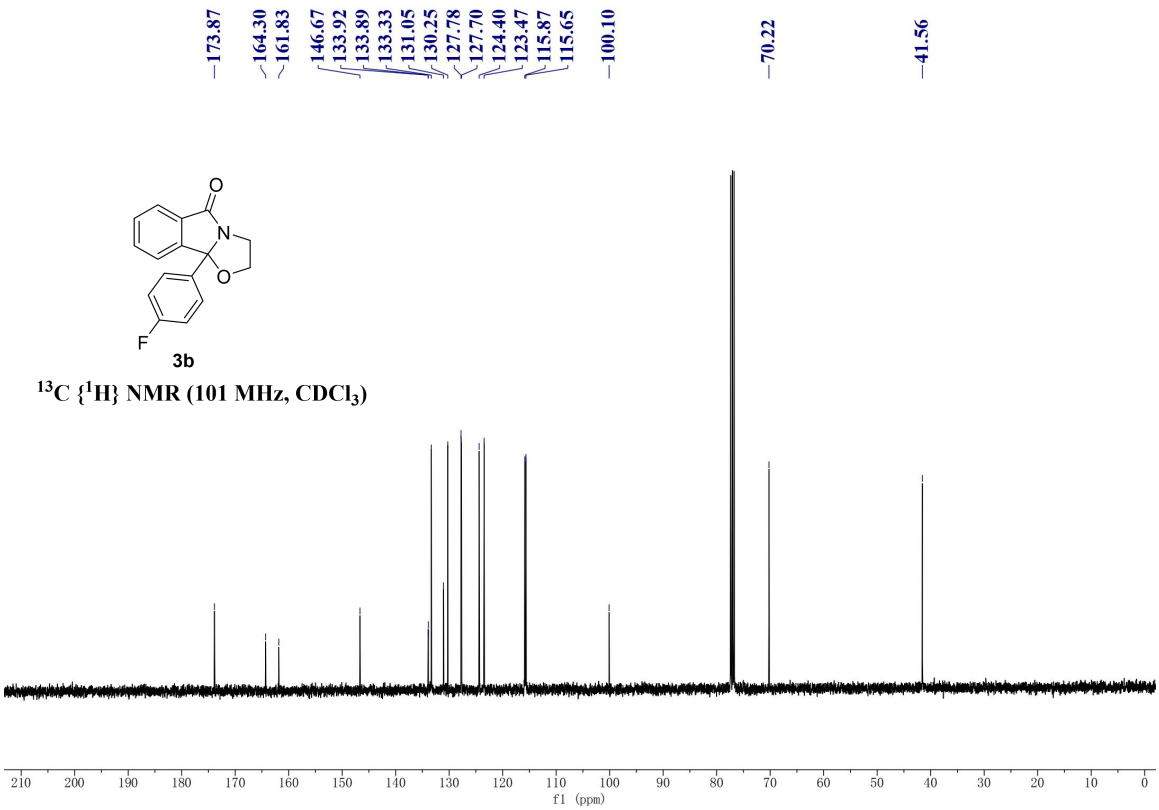


Figure S6. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **3b**

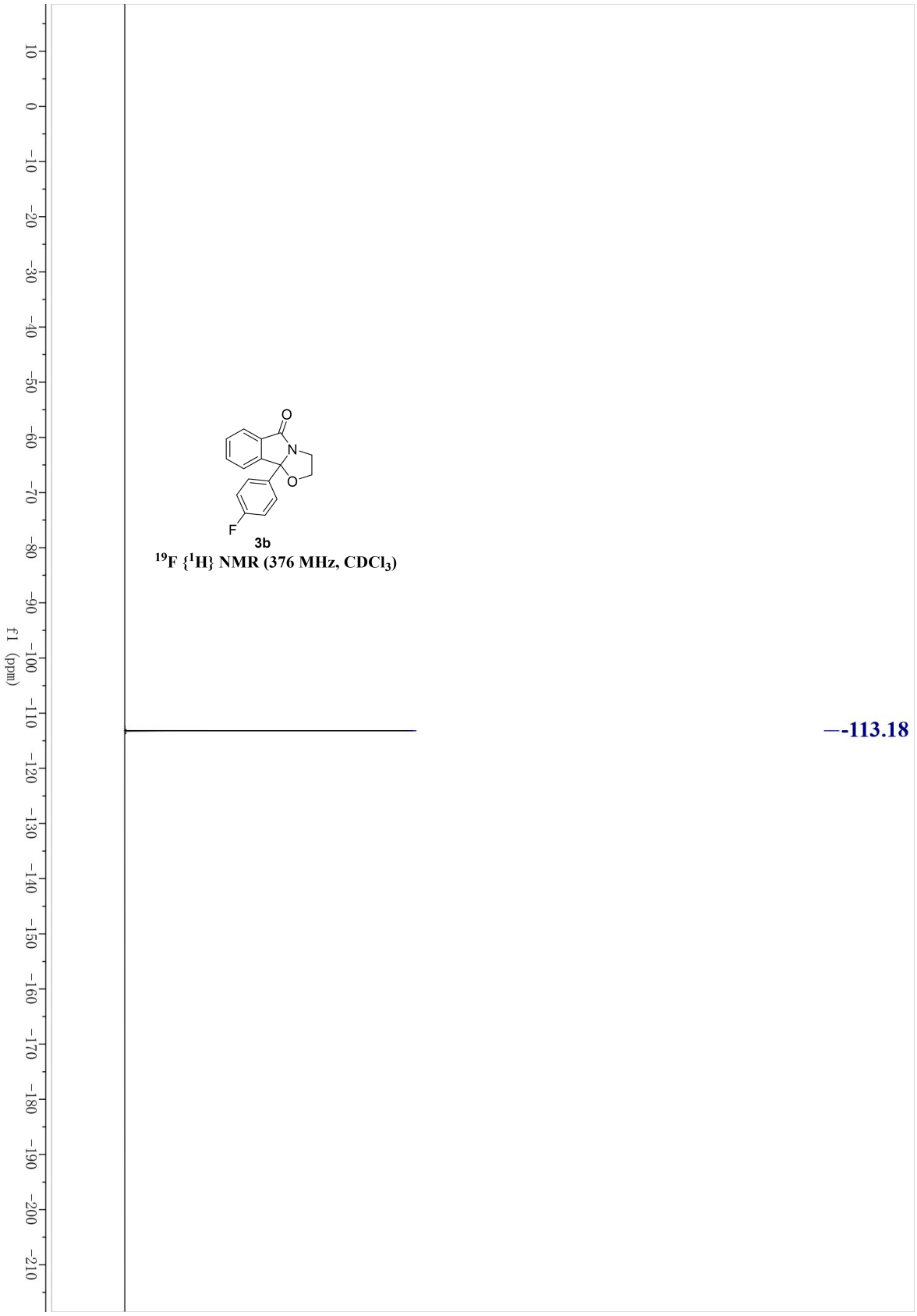


Figure S7. ^{19}F $\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) spectra of compound **3b**

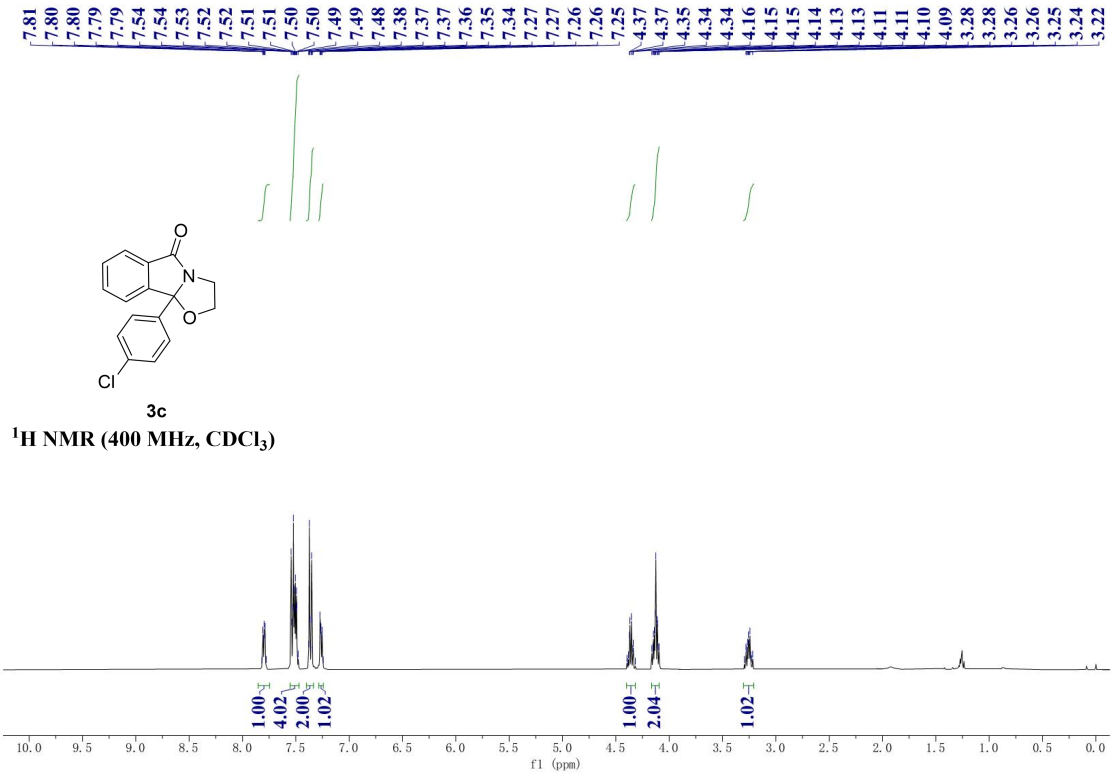


Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3c**

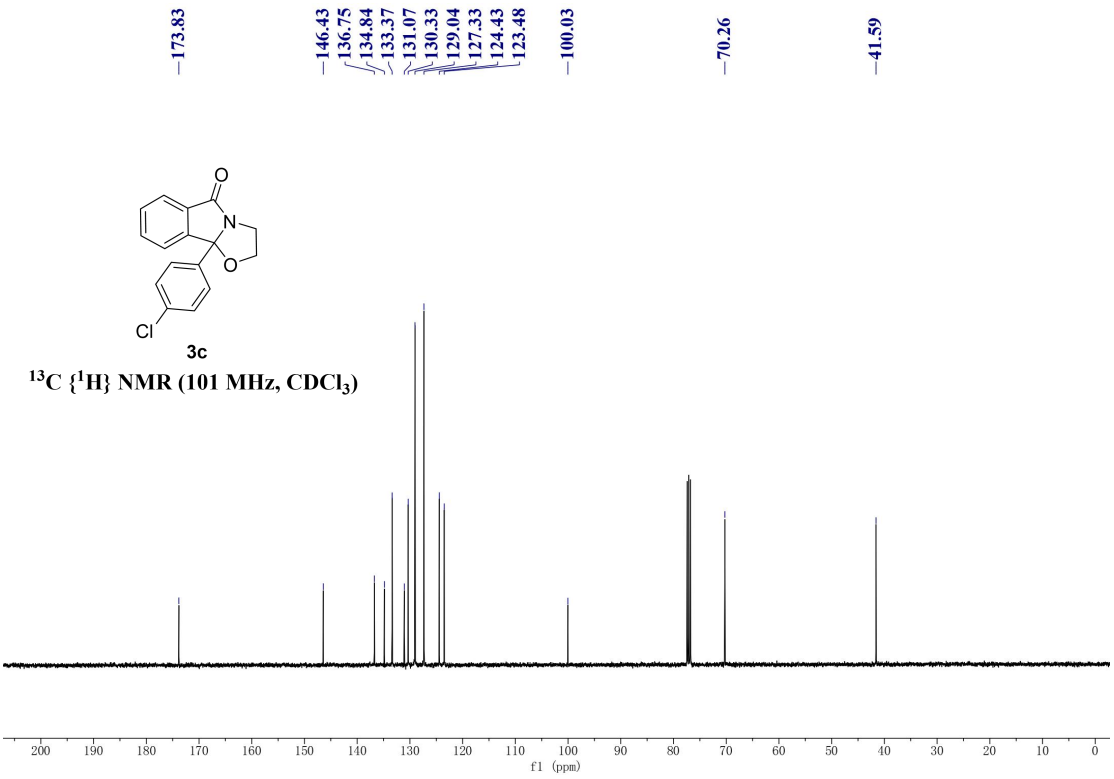


Figure S9. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **3c**

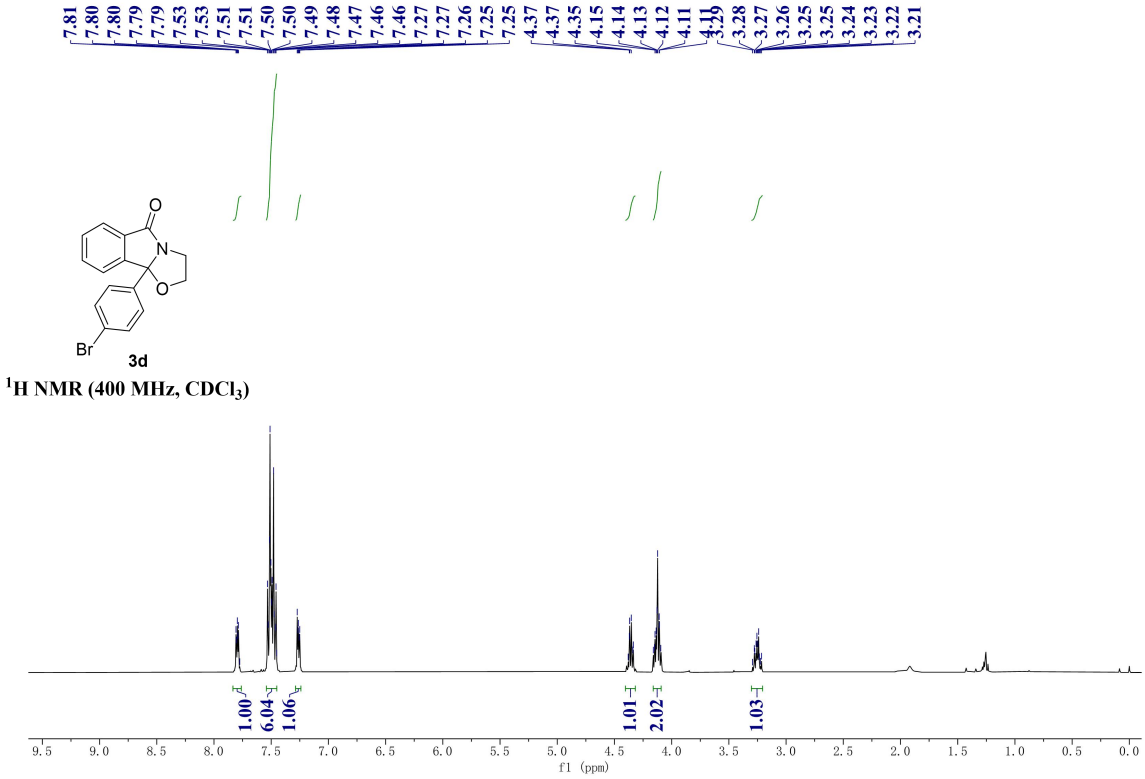


Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3d**

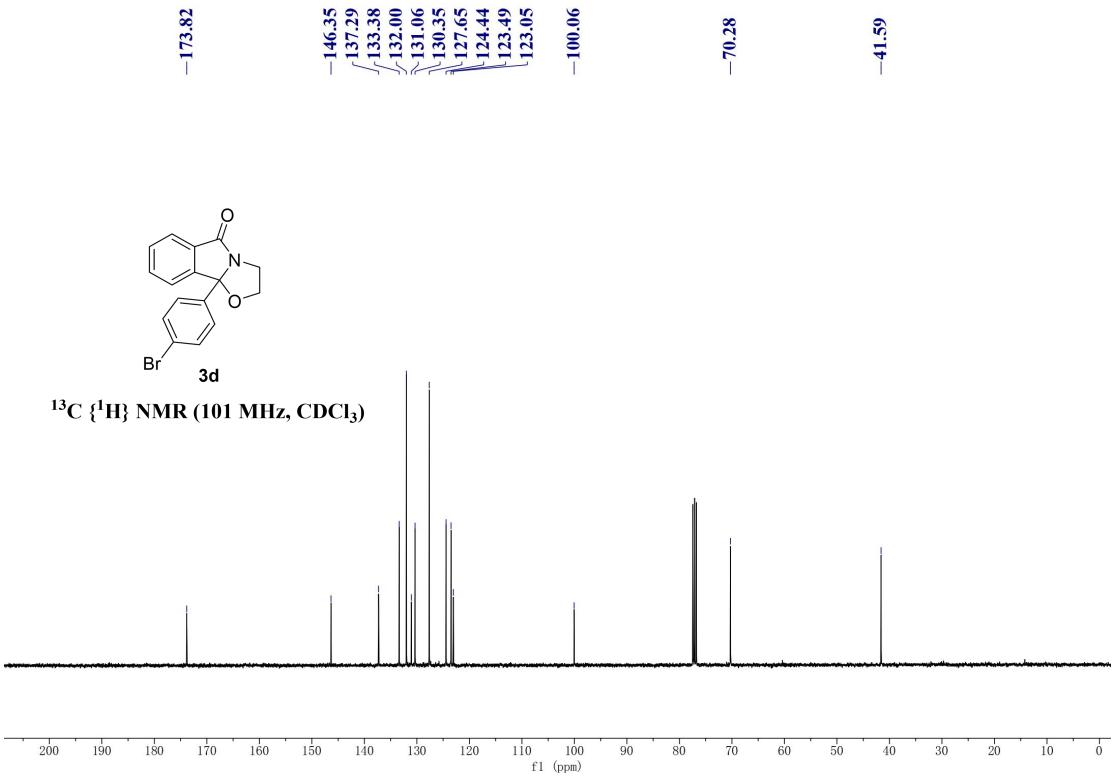


Figure S11. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **3d**

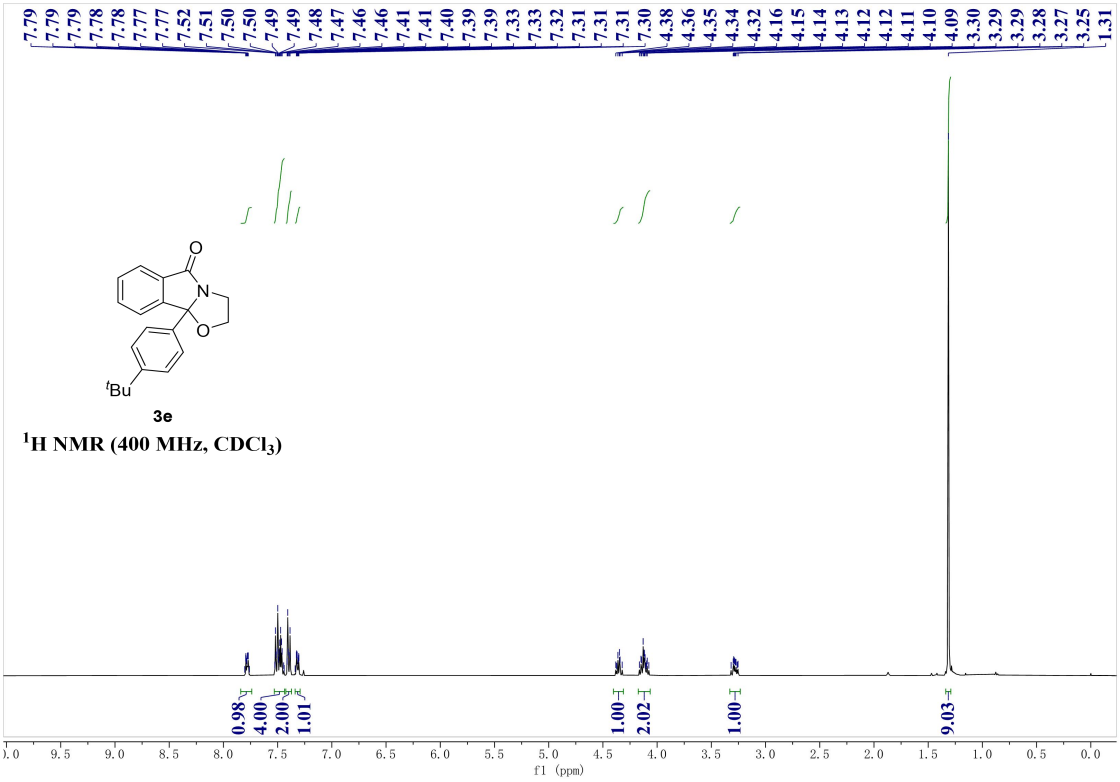


Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3e**

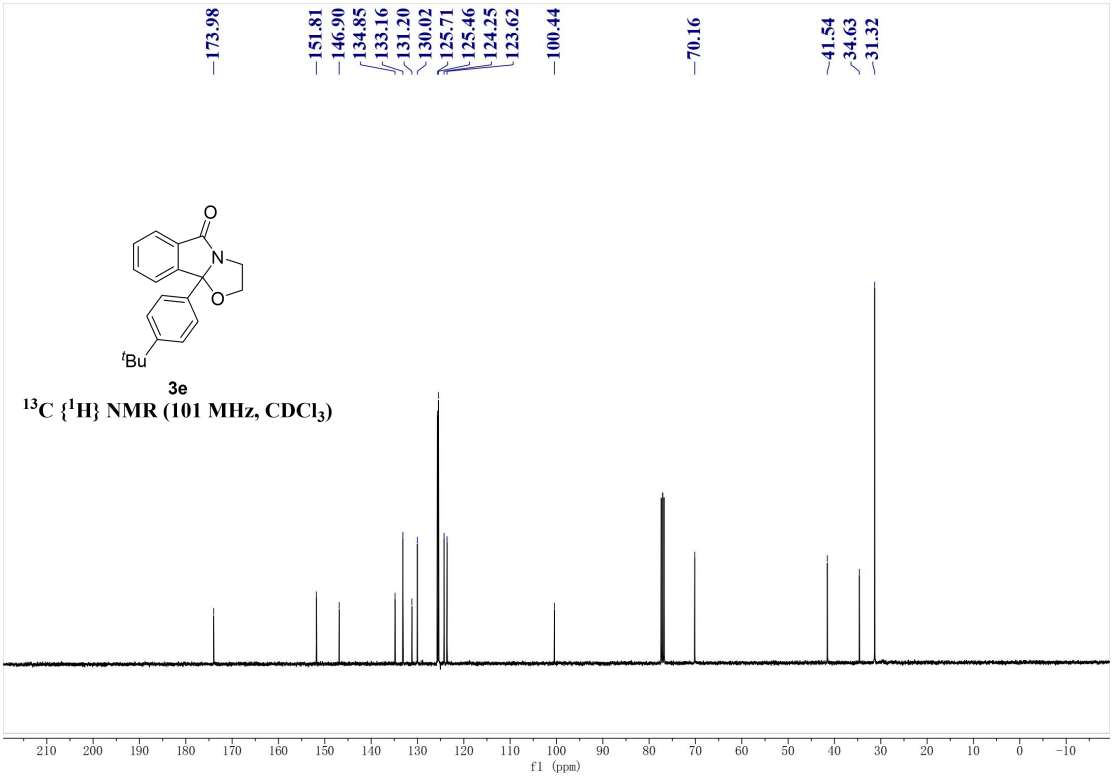


Figure S13. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **3e**

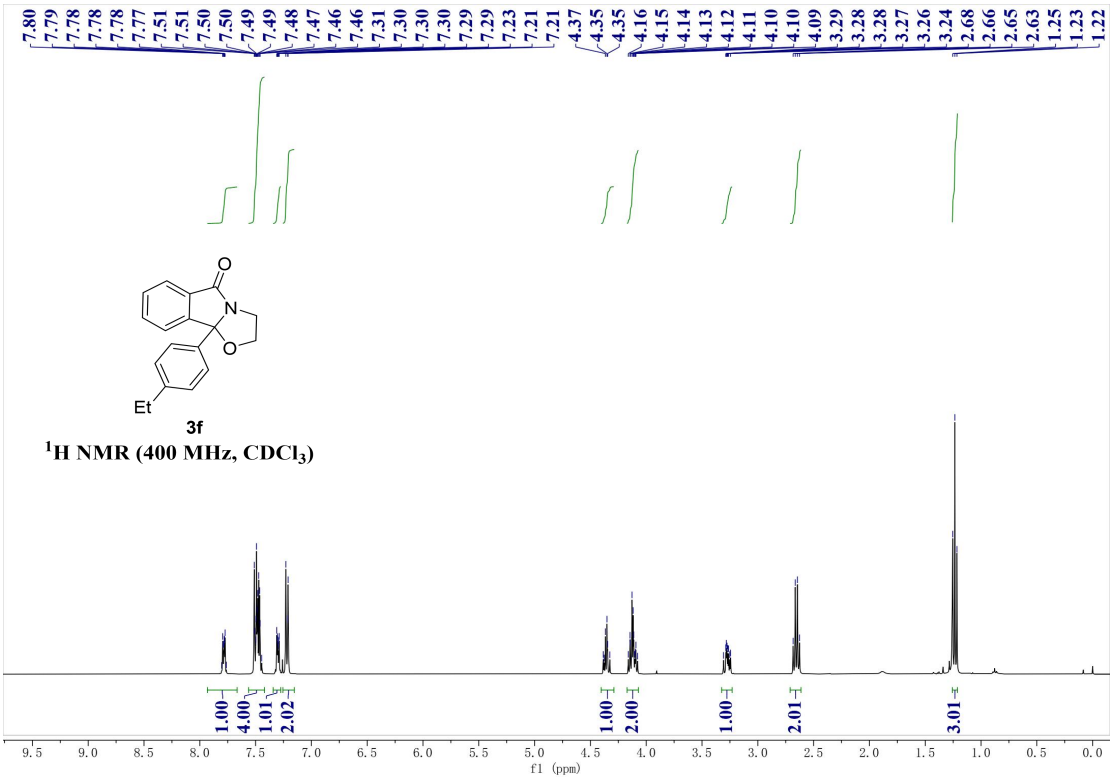


Figure S14. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3f**

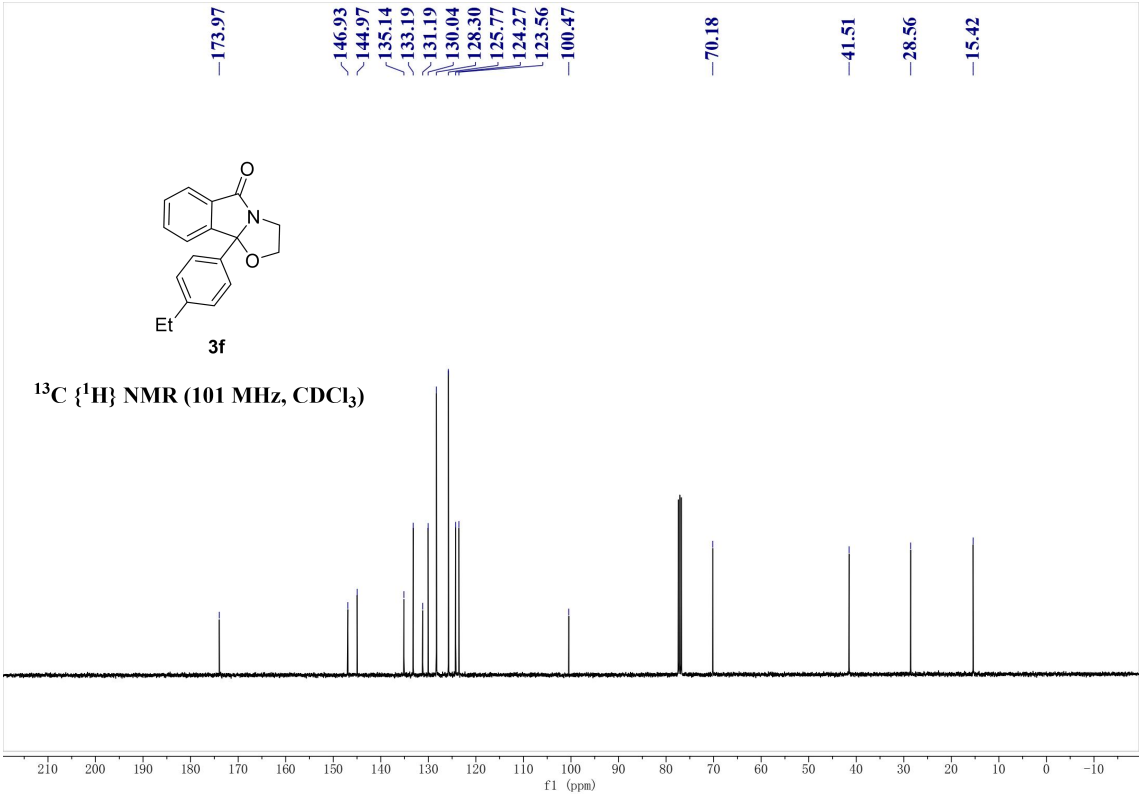


Figure S15. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **3f**

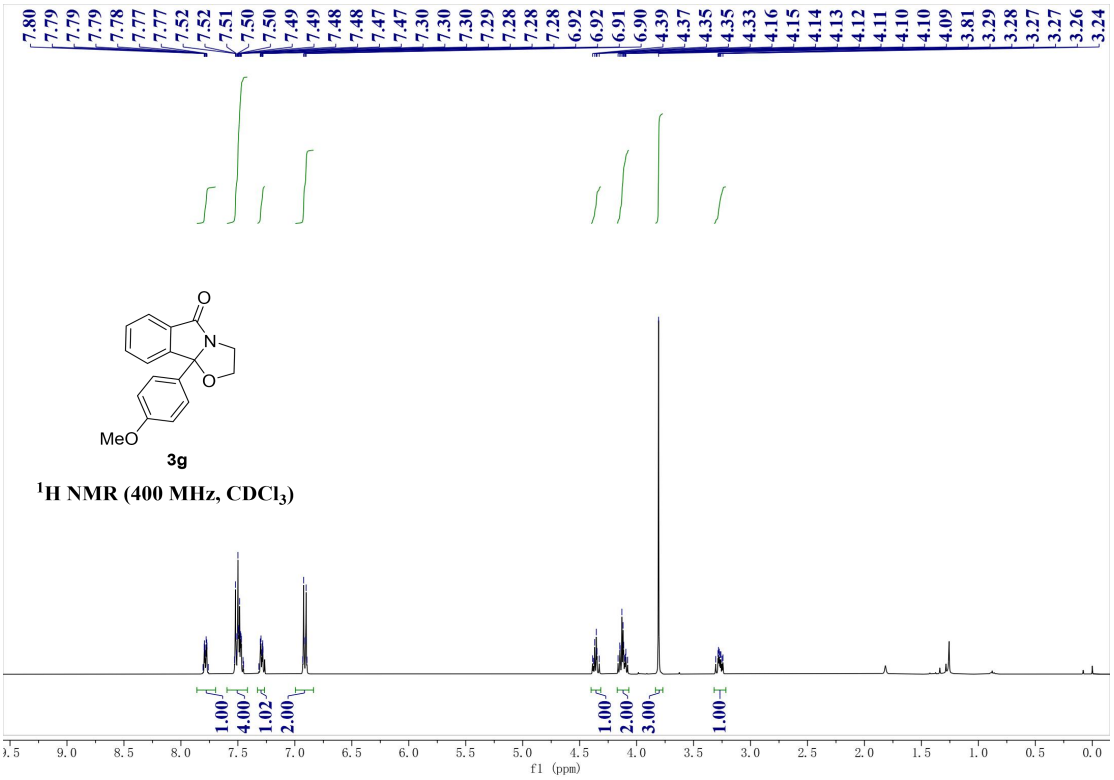


Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3g**

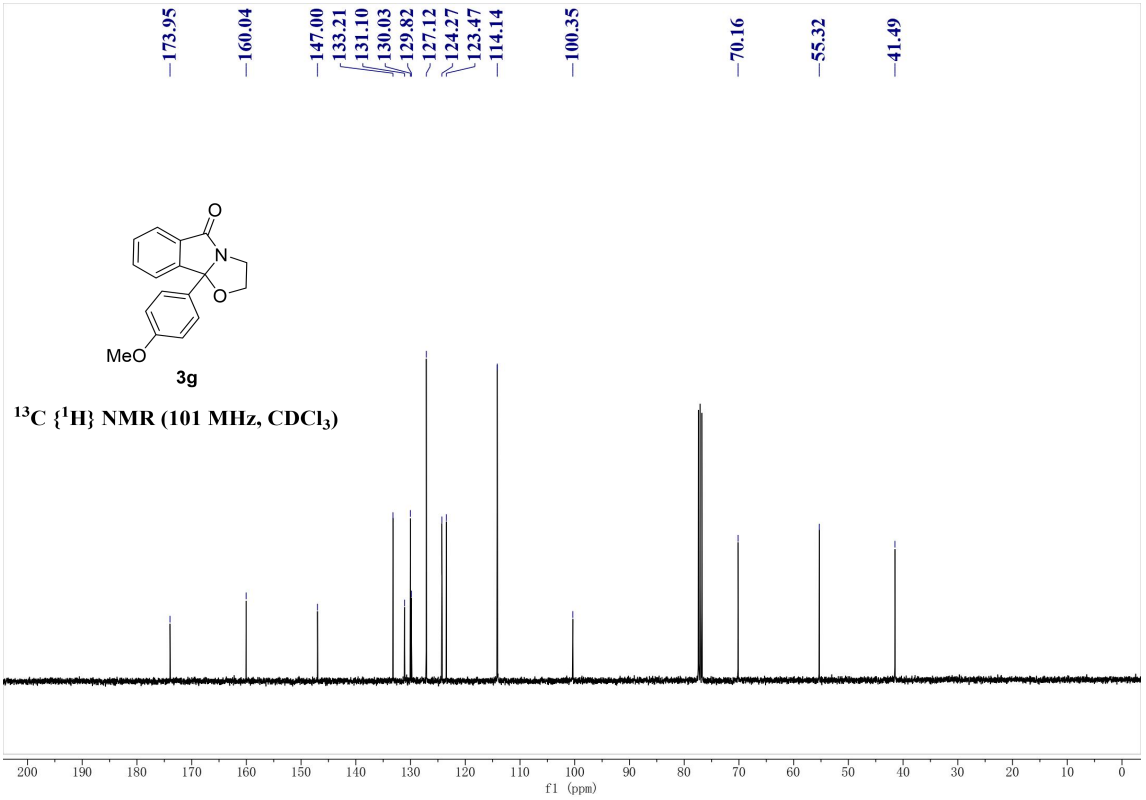


Figure S17. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **3g**

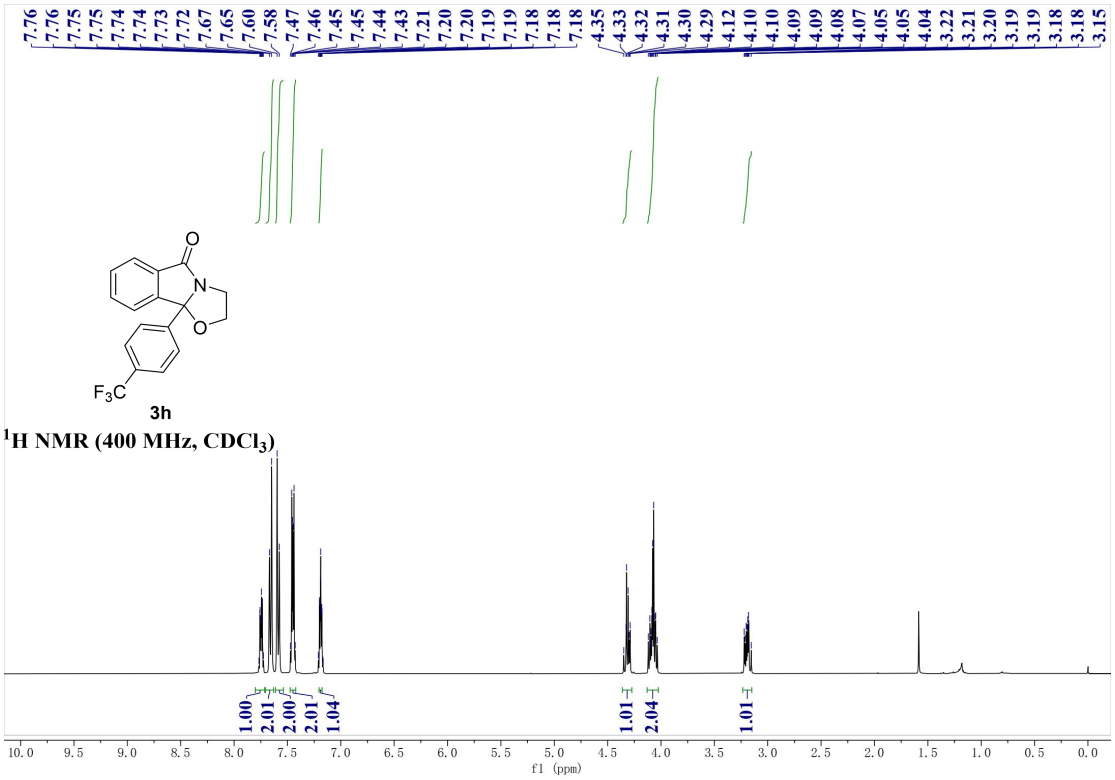


Figure S18. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3h**

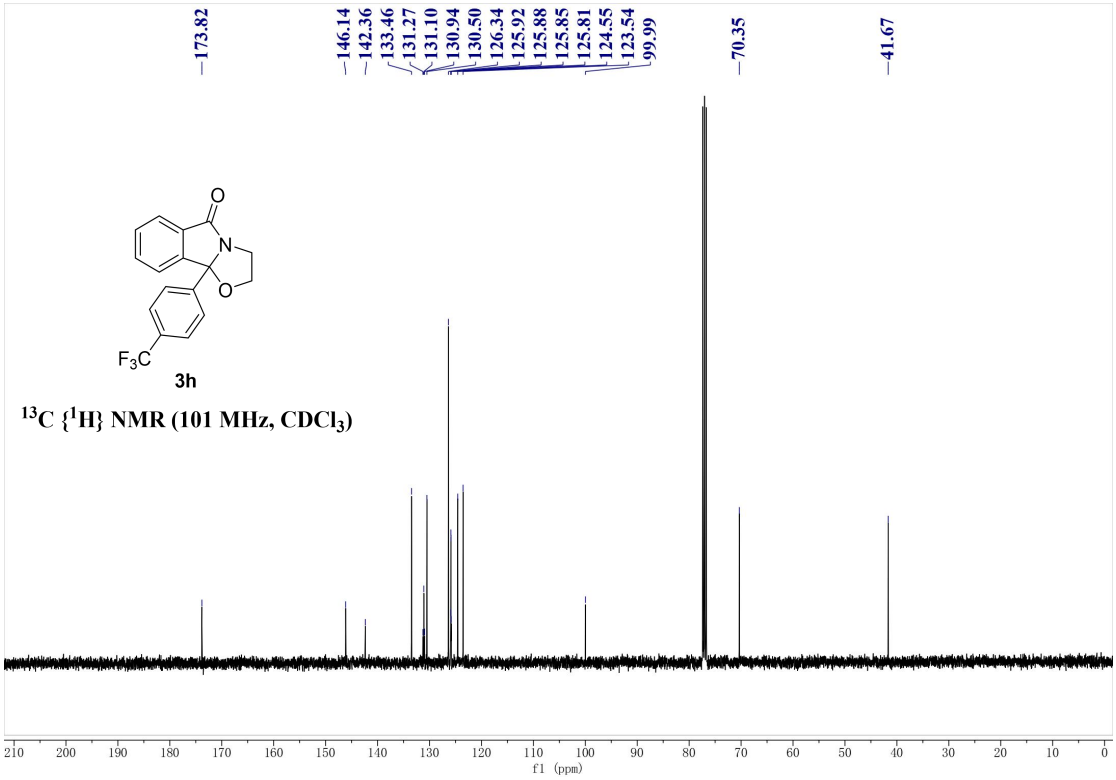


Figure S19. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **3h**

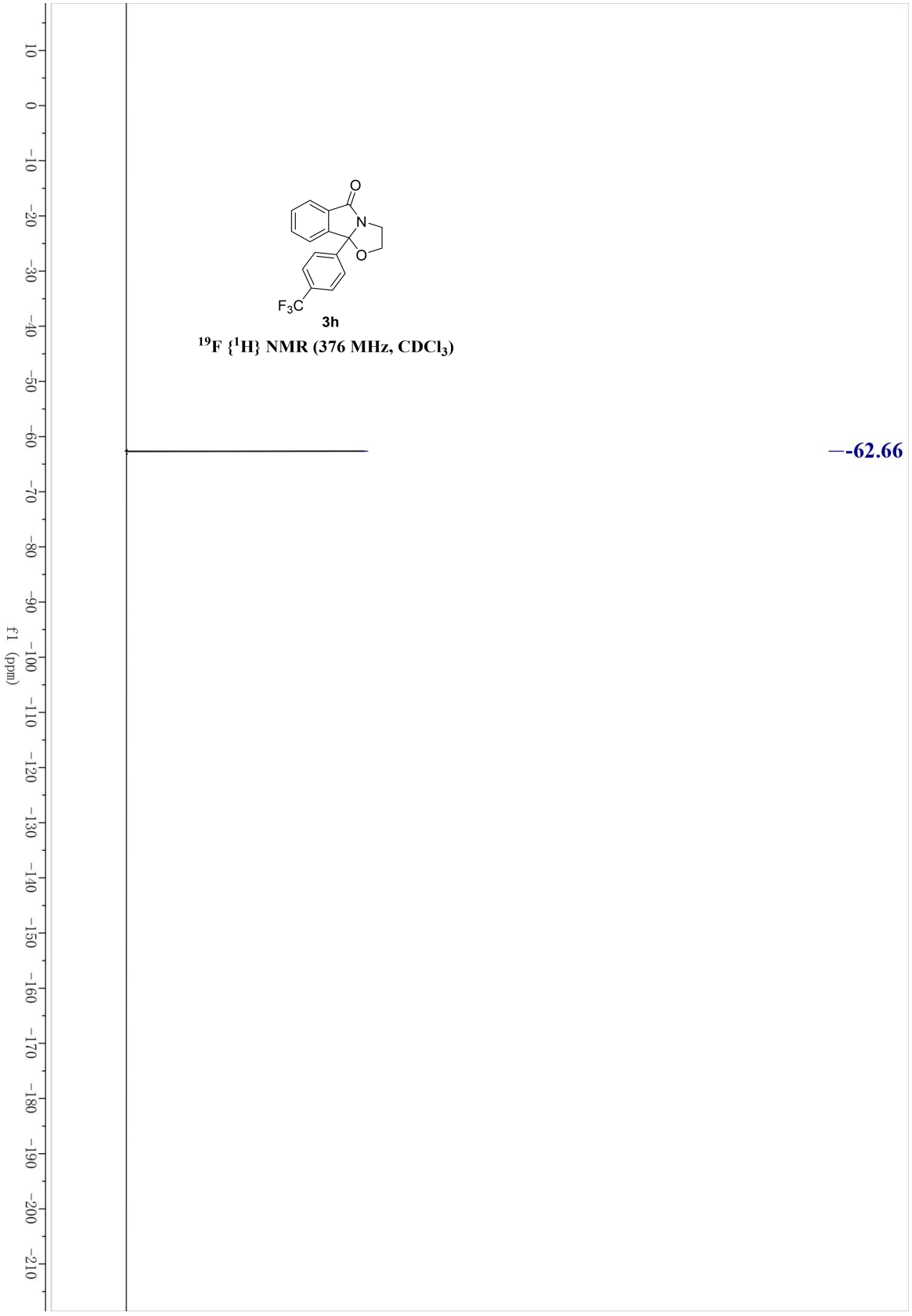


Figure S20. ^{19}F $\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) spectra of compound **3h**

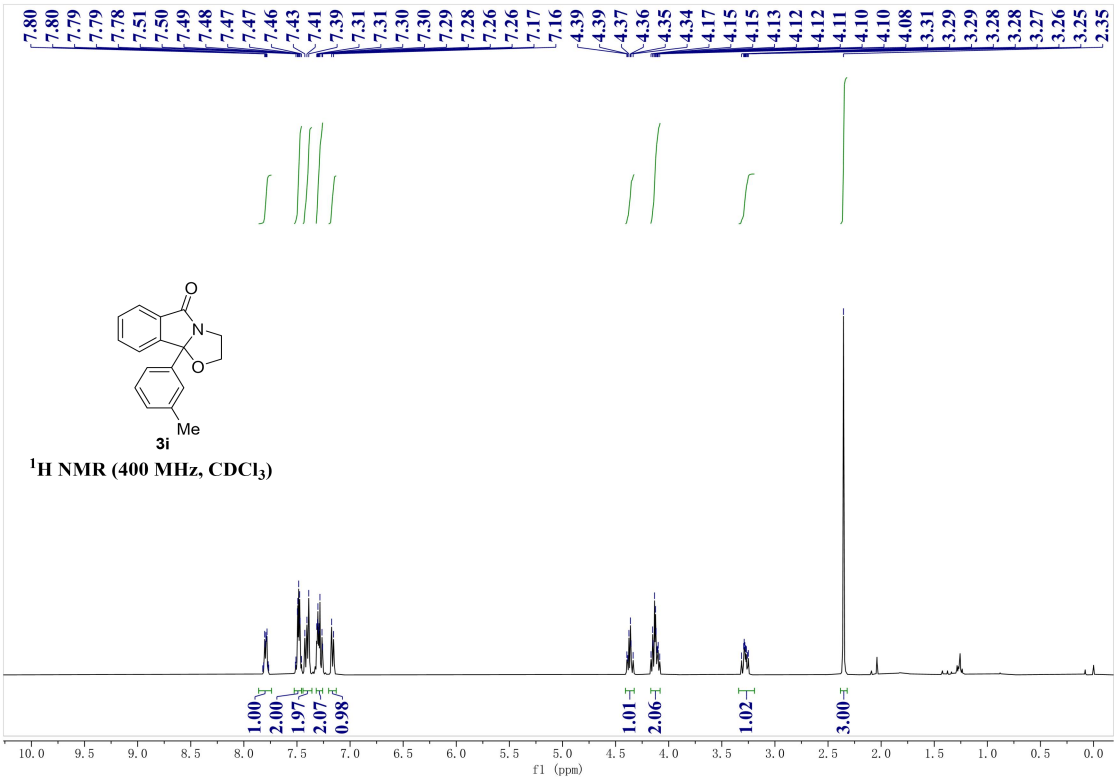


Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3i**

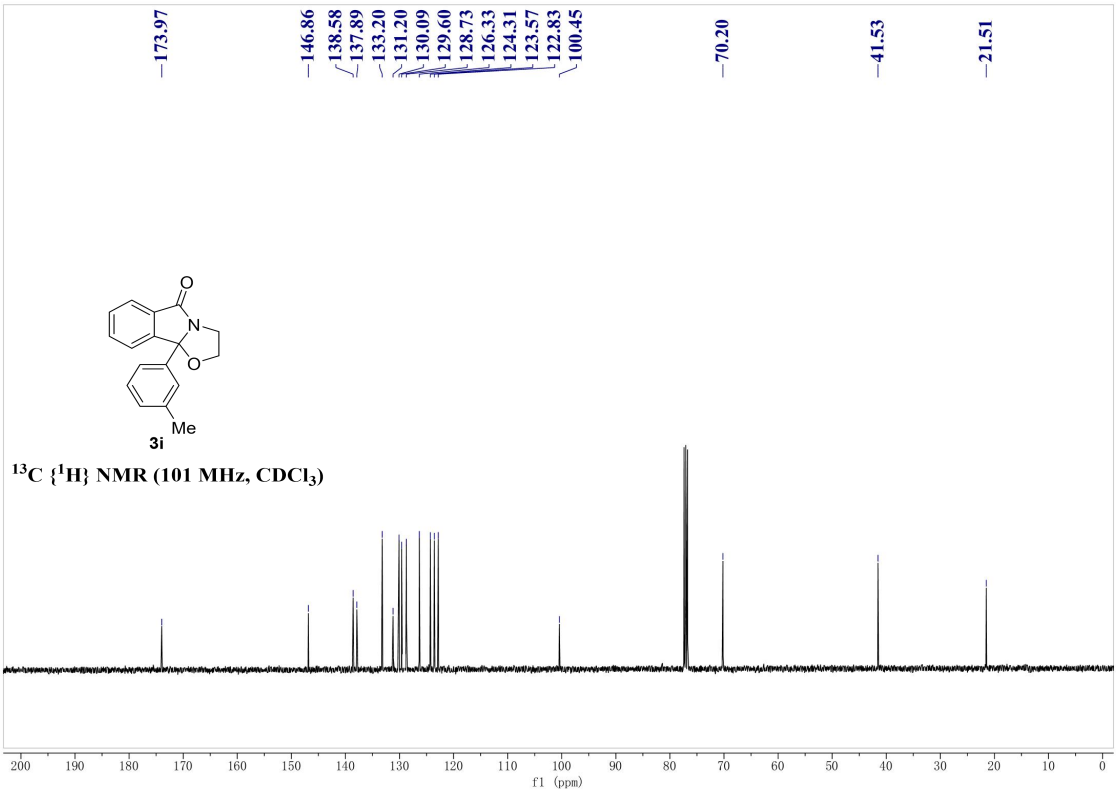


Figure S22. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **3i**

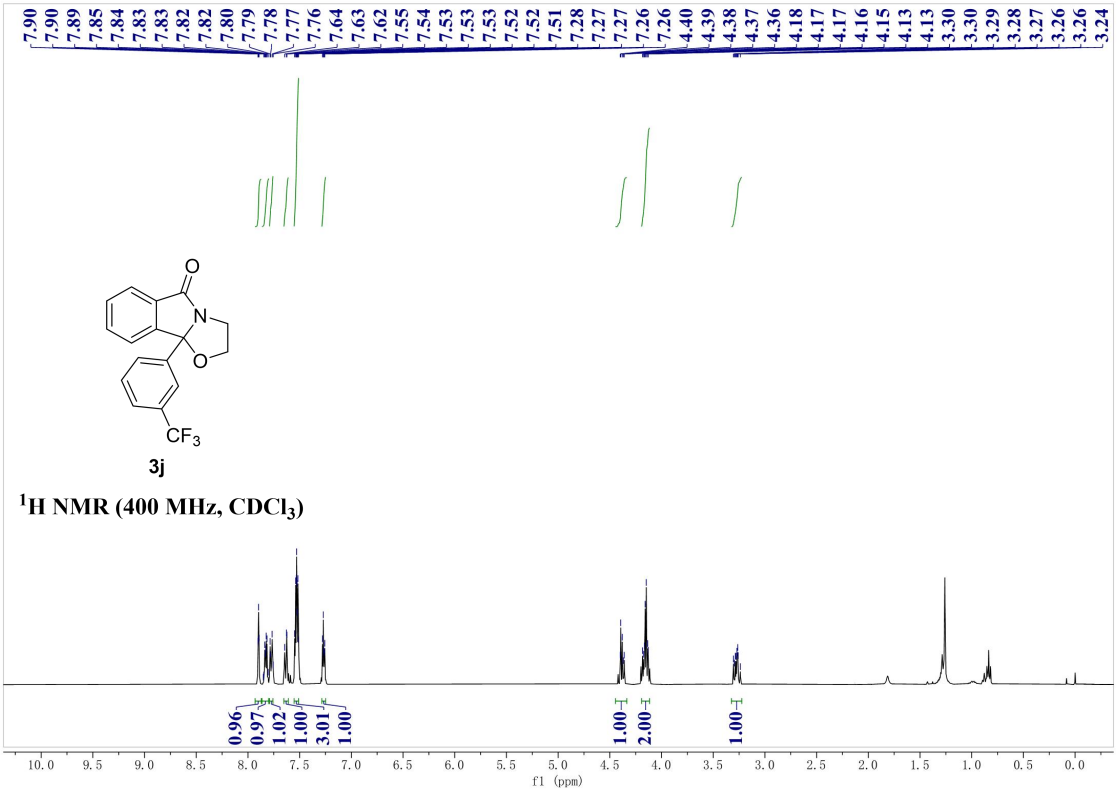


Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3j**

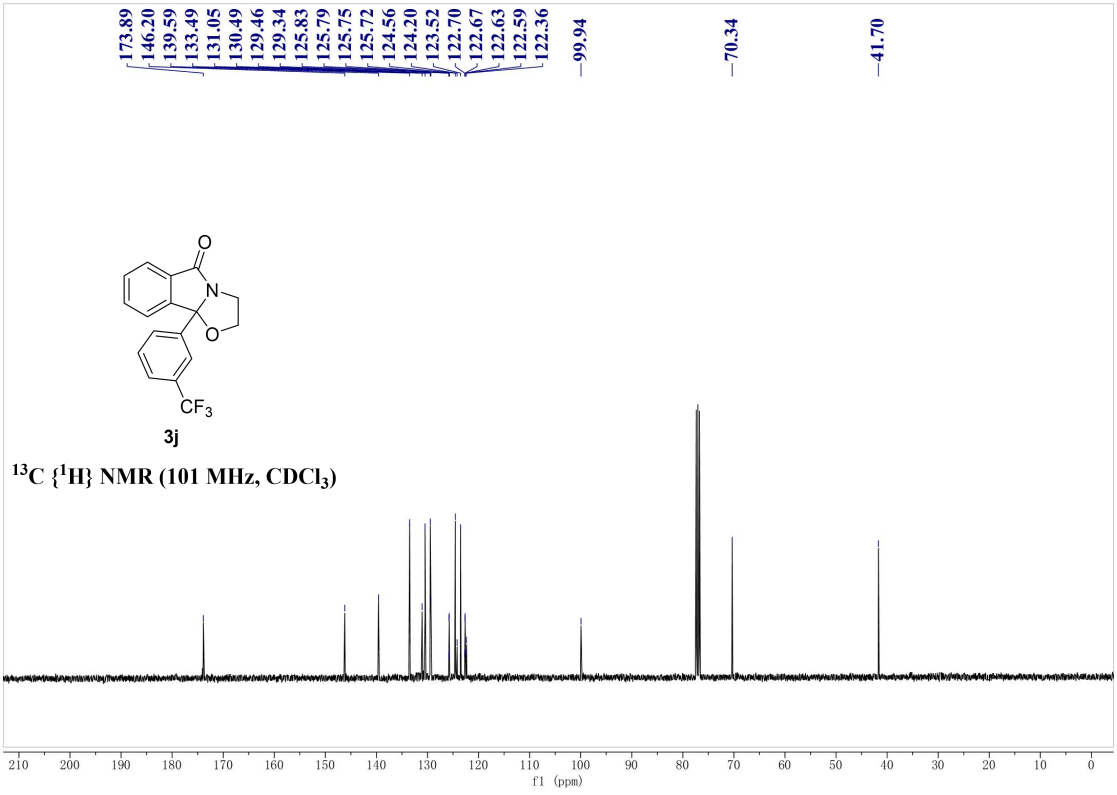


Figure S24. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **3j**

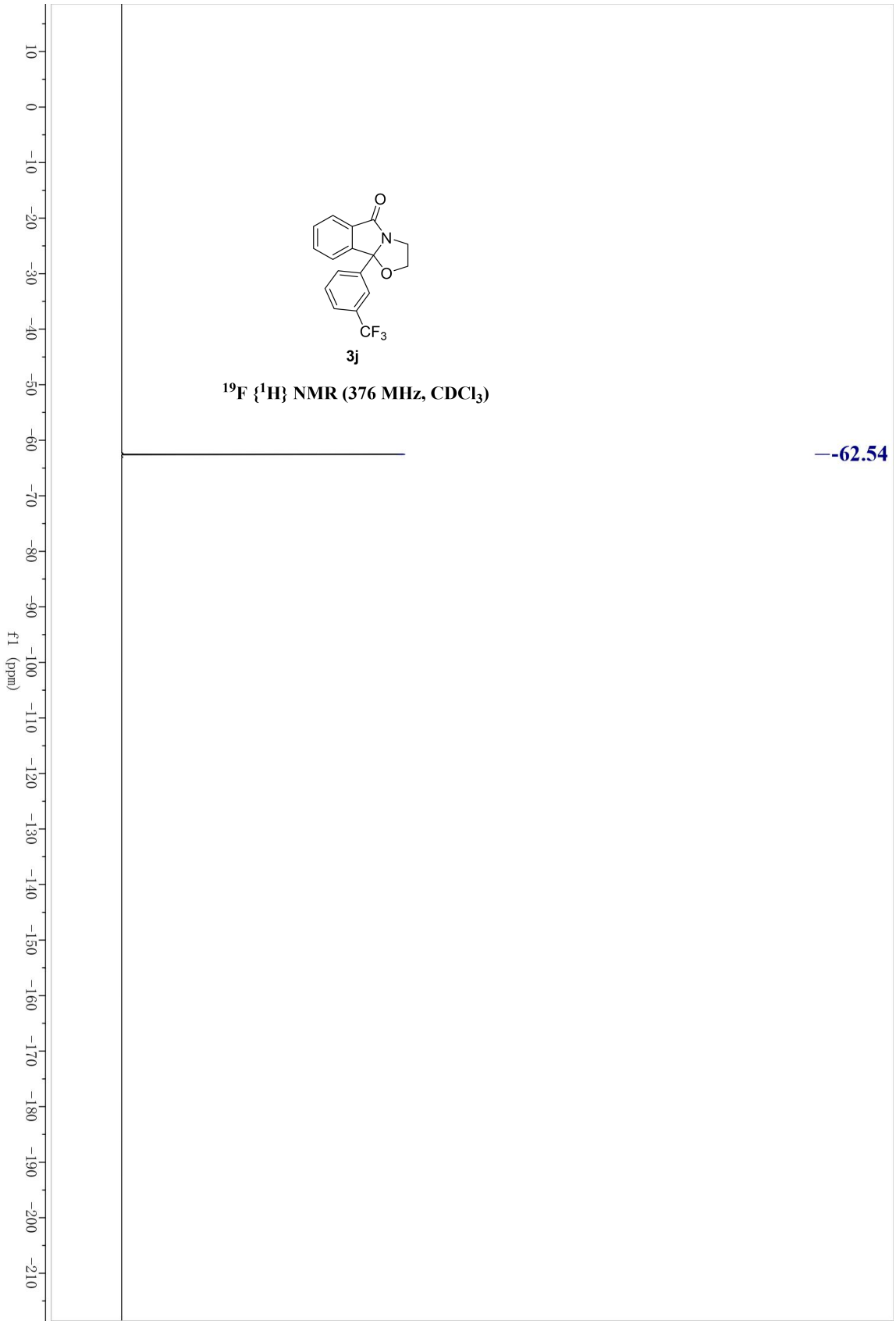


Figure S25. ^{19}F $\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) spectra of compound **3j**

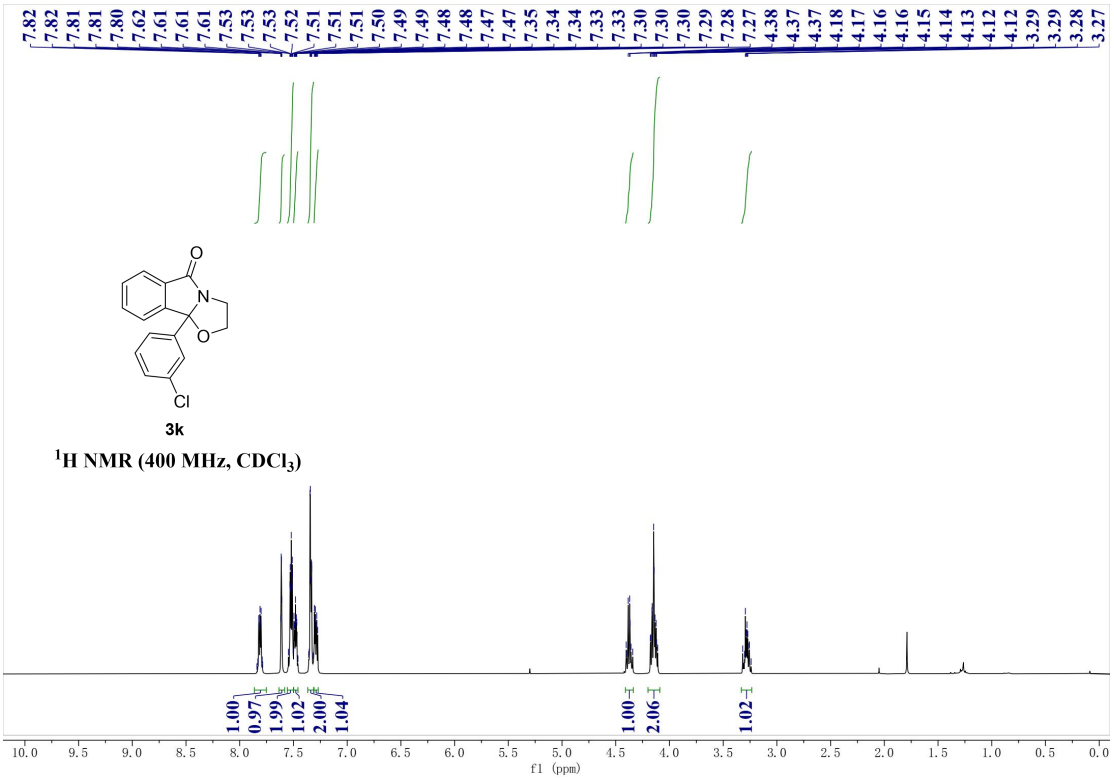


Figure S26. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3k**

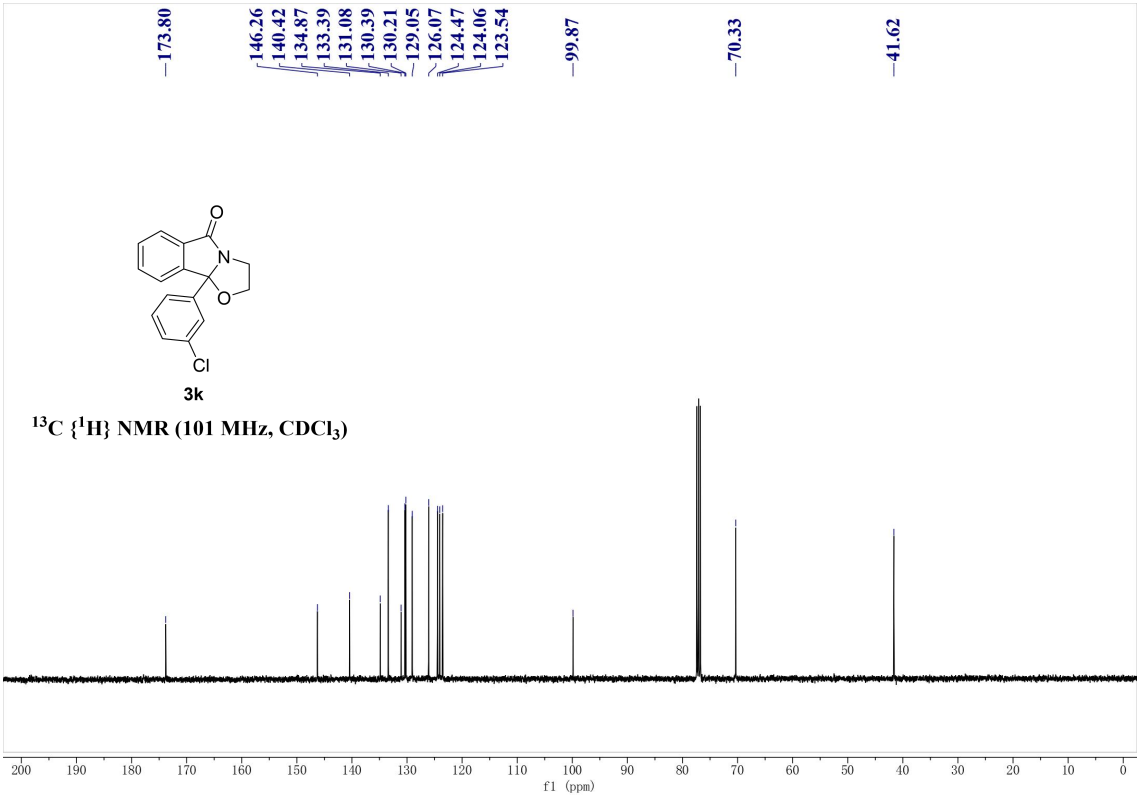


Figure S27. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **3k**

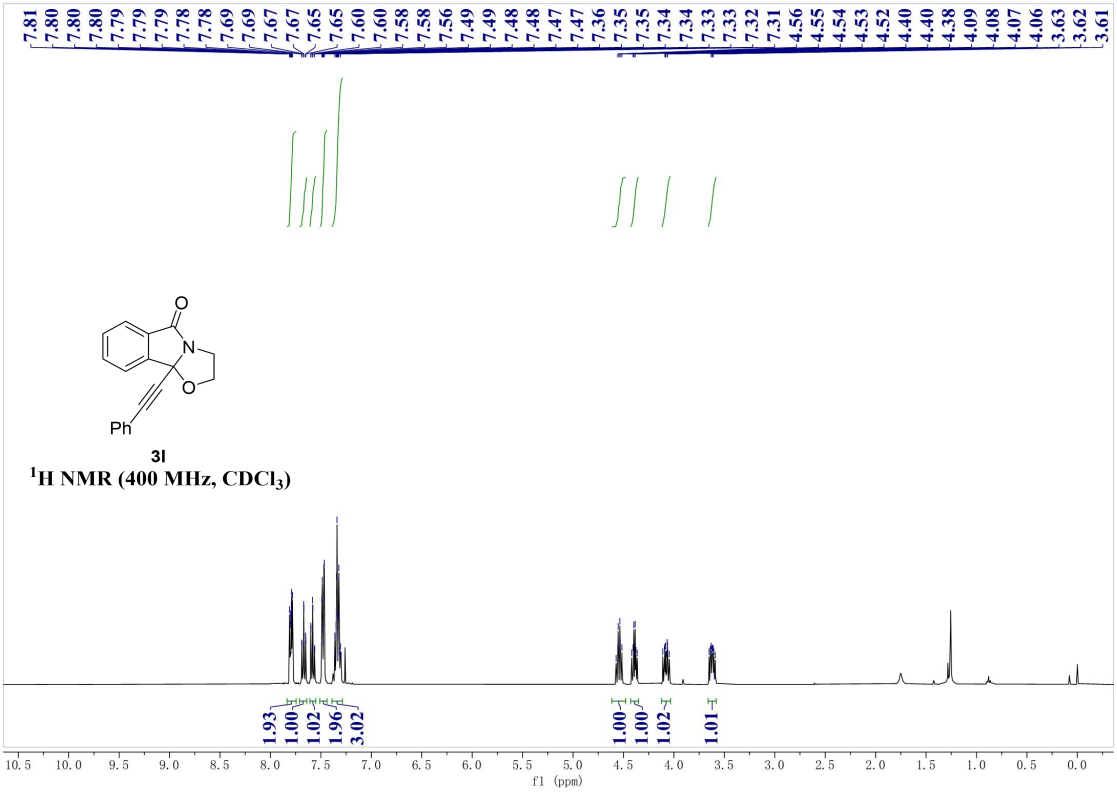


Figure S28. ^{1}H NMR (400 MHz, CDCl$_3$) spectra of compound **3l**

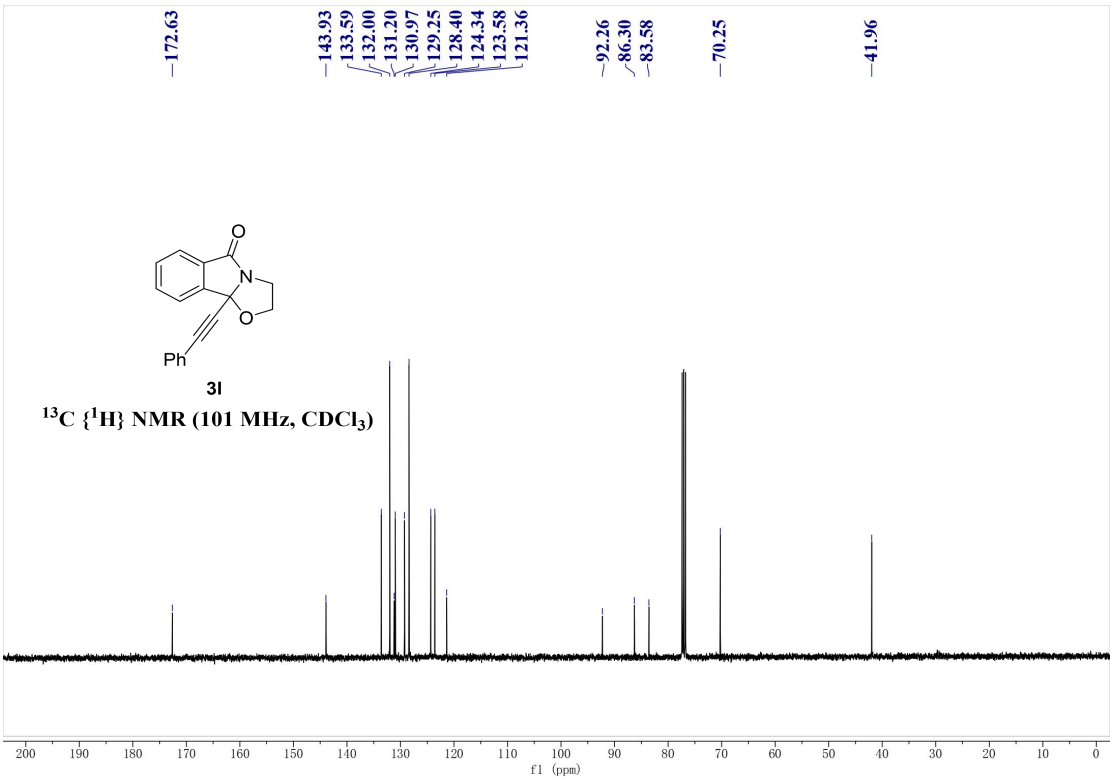


Figure S29. ^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$) spectra of compound **3l**

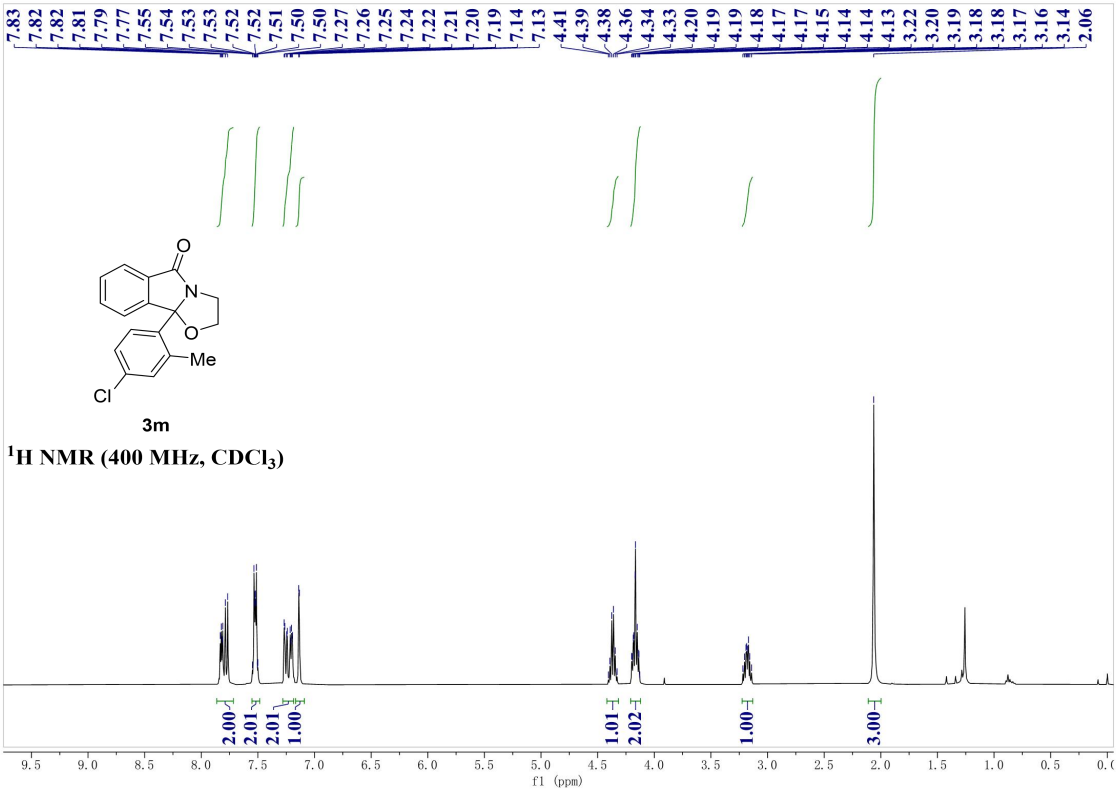


Figure S30. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3m**

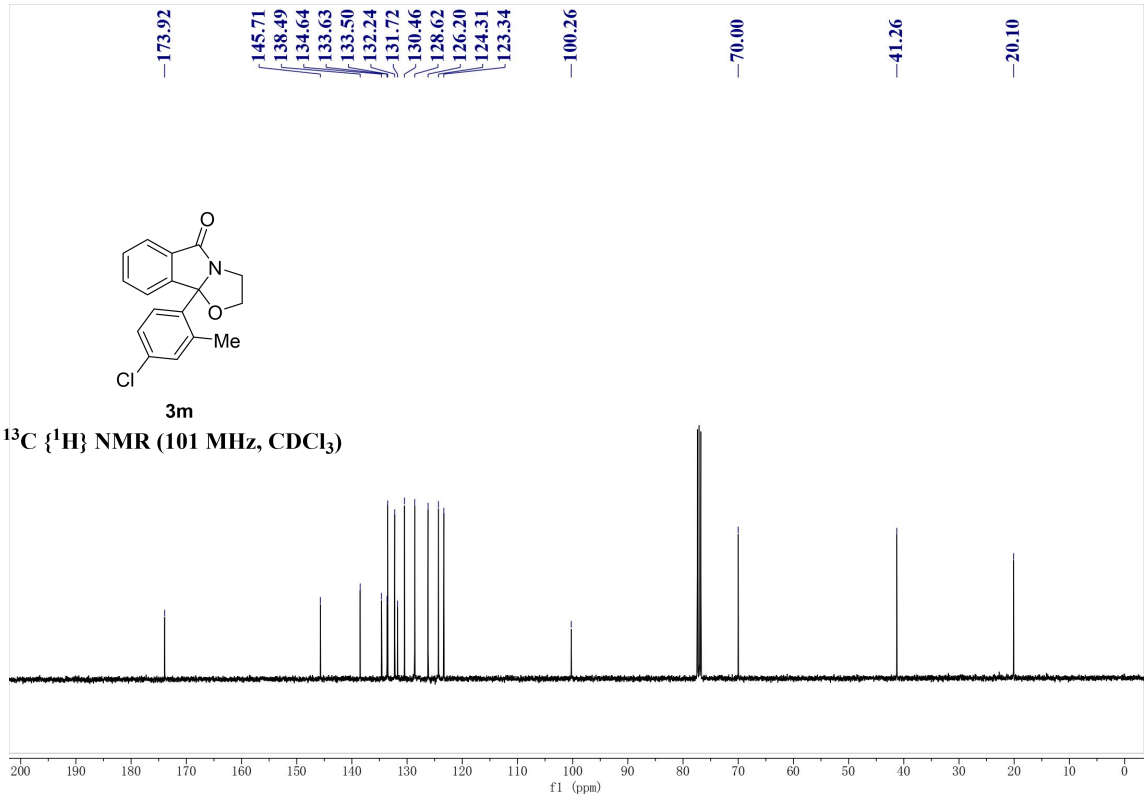


Figure S31. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **3m**

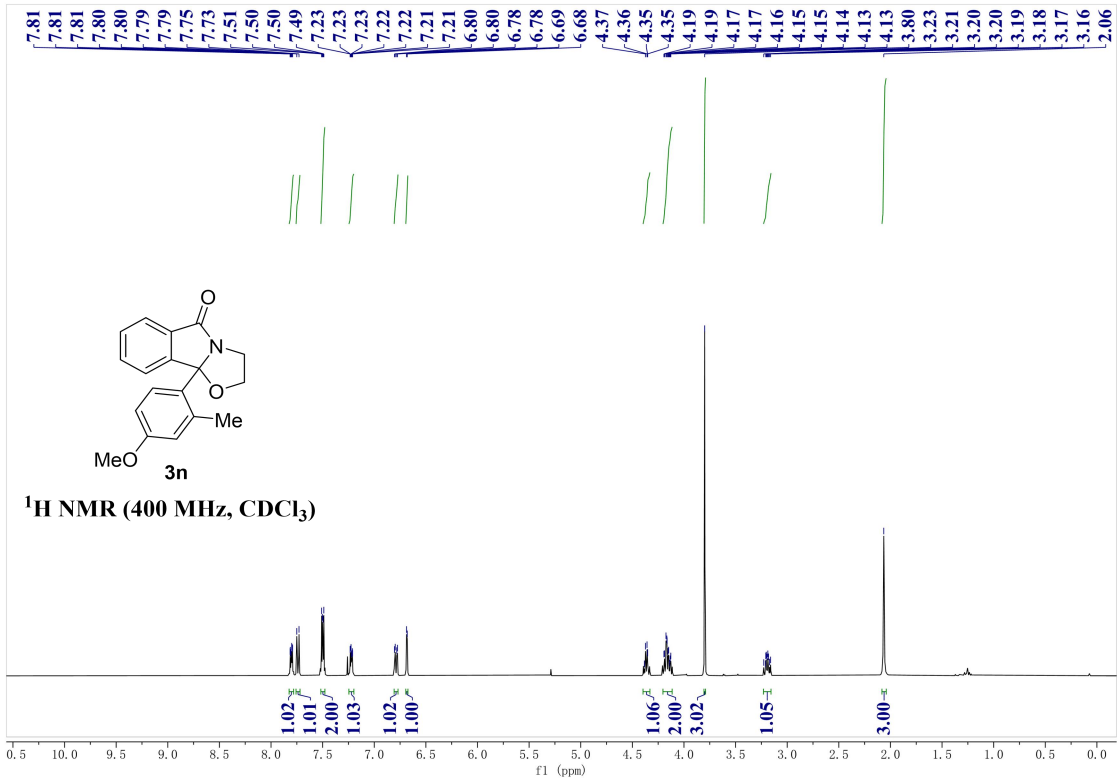


Figure S32. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3n**

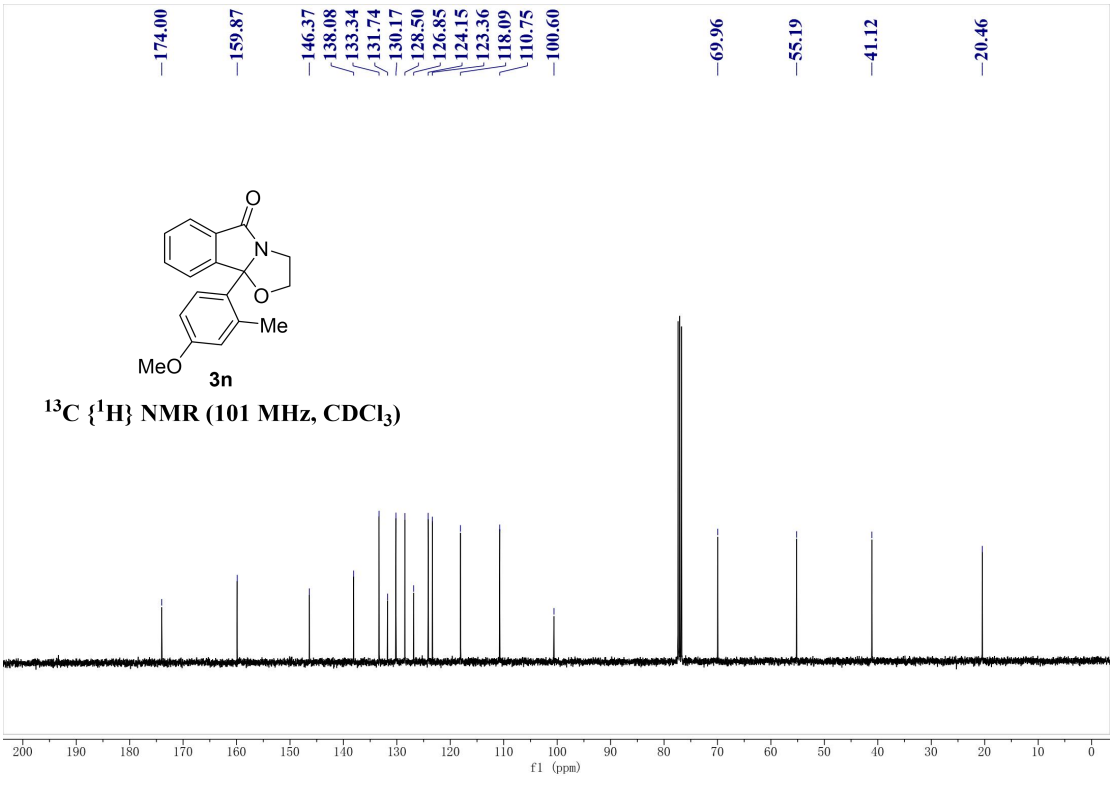


Figure S33. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **3n**

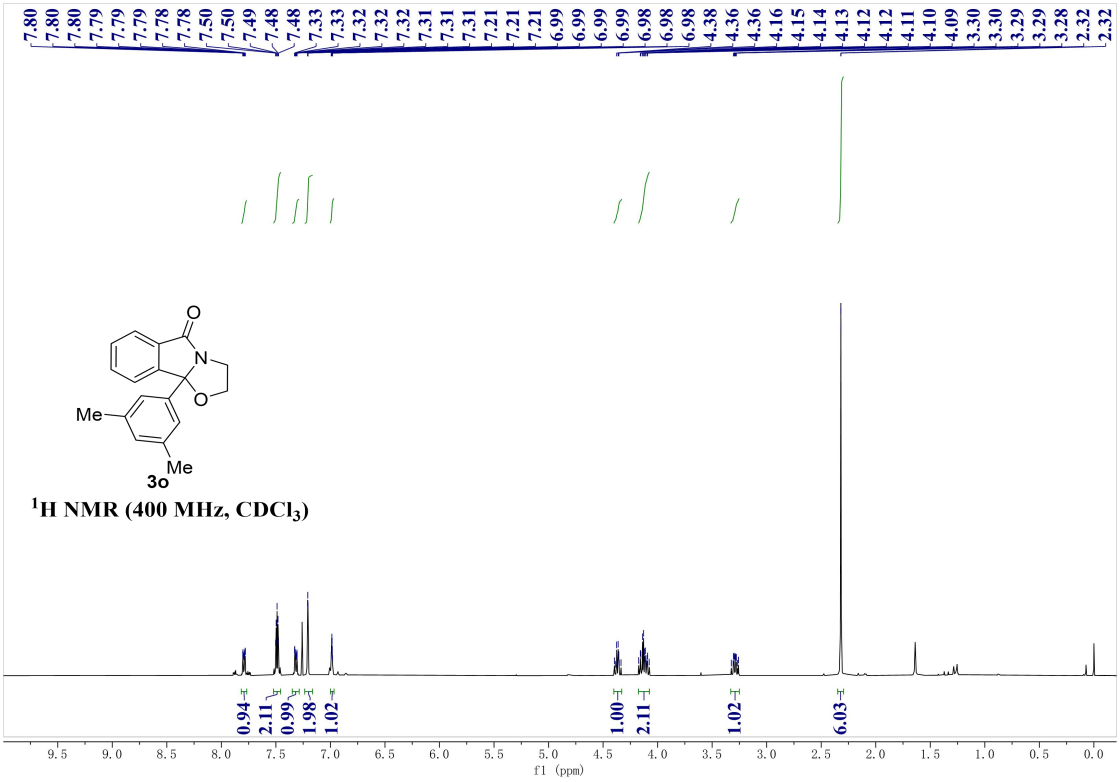


Figure S34. ^{1}H NMR (400 MHz, CDCl$_3$) spectra of compound **3o**

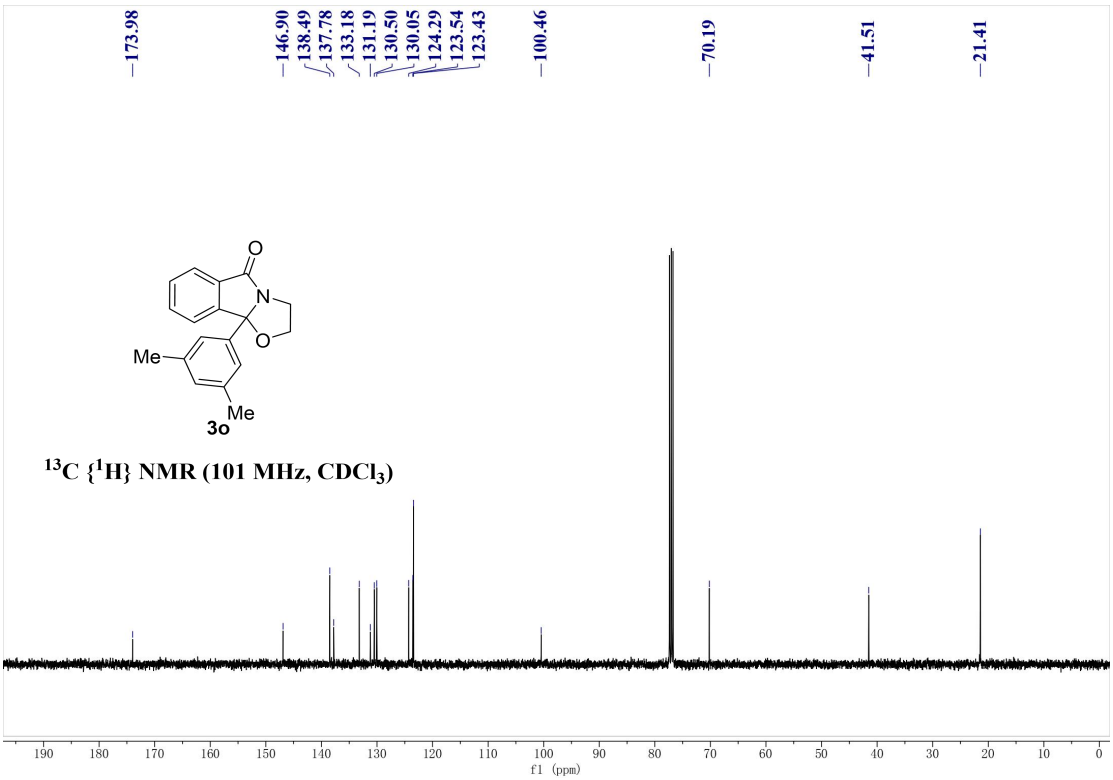


Figure S35. ^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$) spectra of compound **3o**

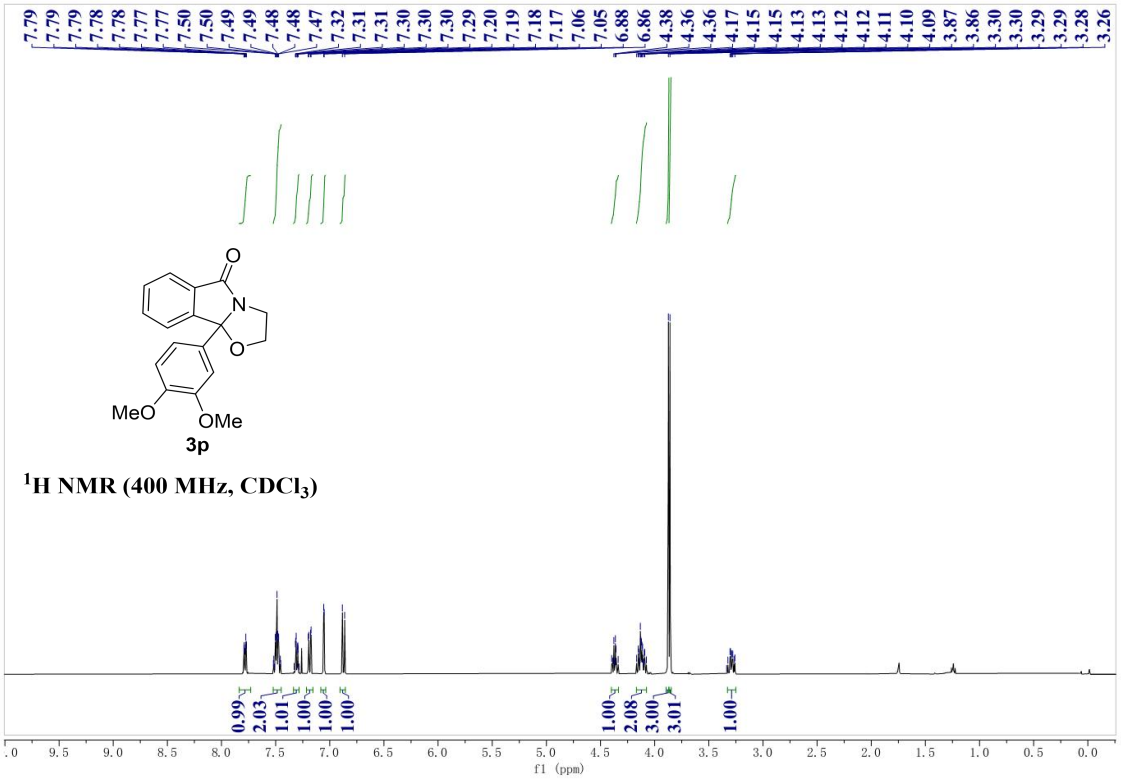


Figure S36. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3p**

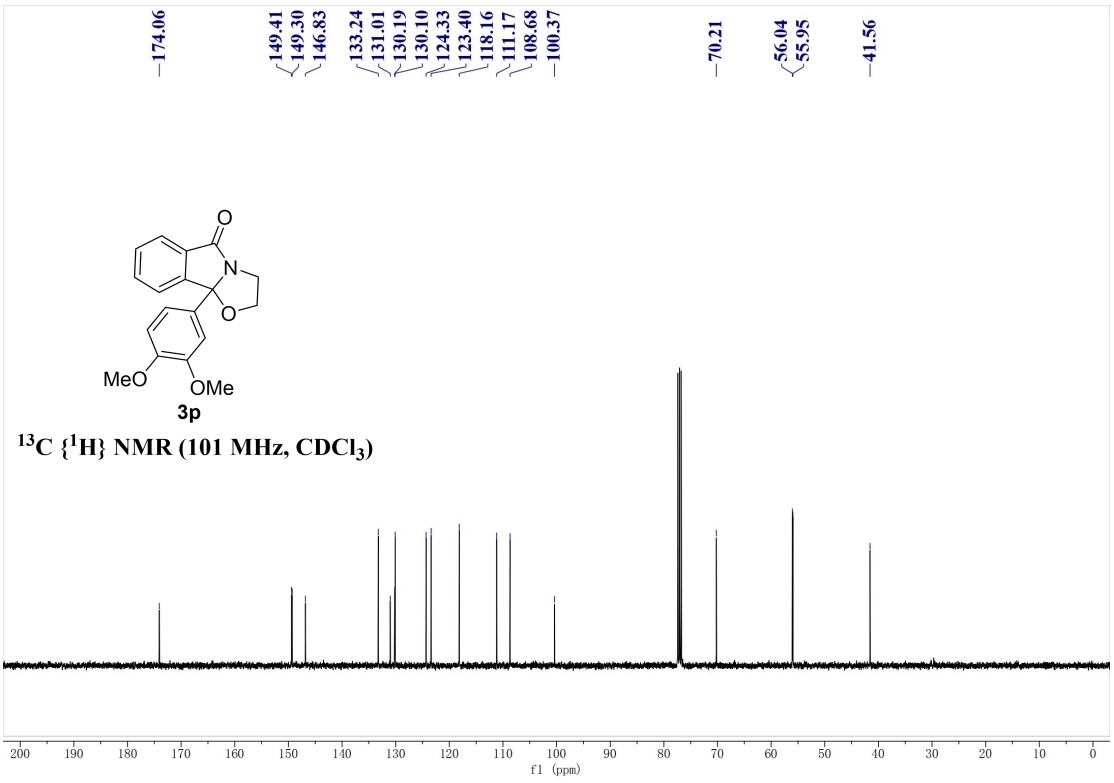


Figure S37. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **3p**

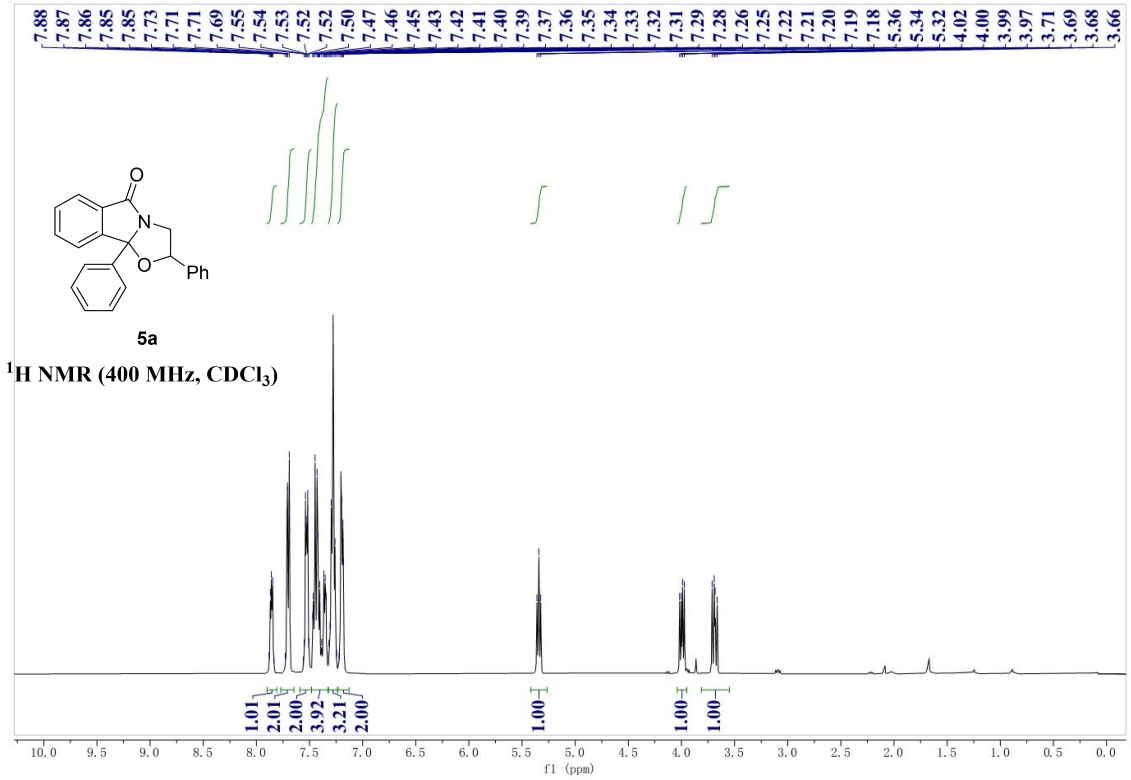


Figure S38. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **5a**

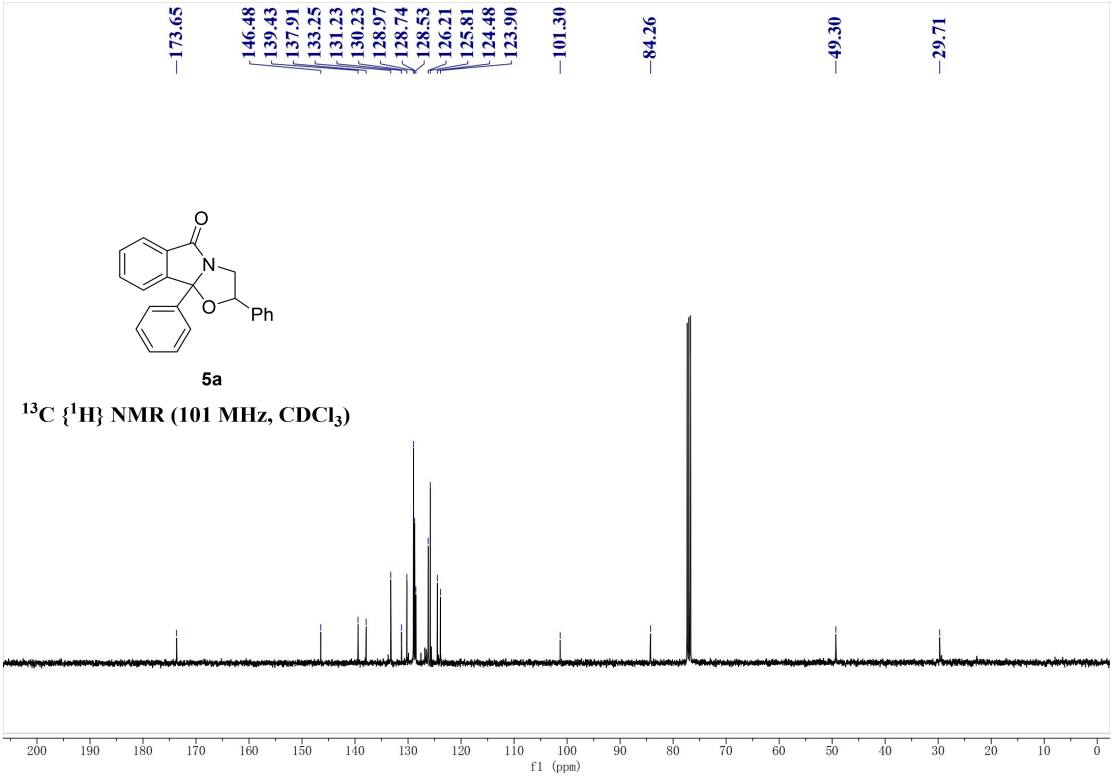


Figure S39. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **5a**

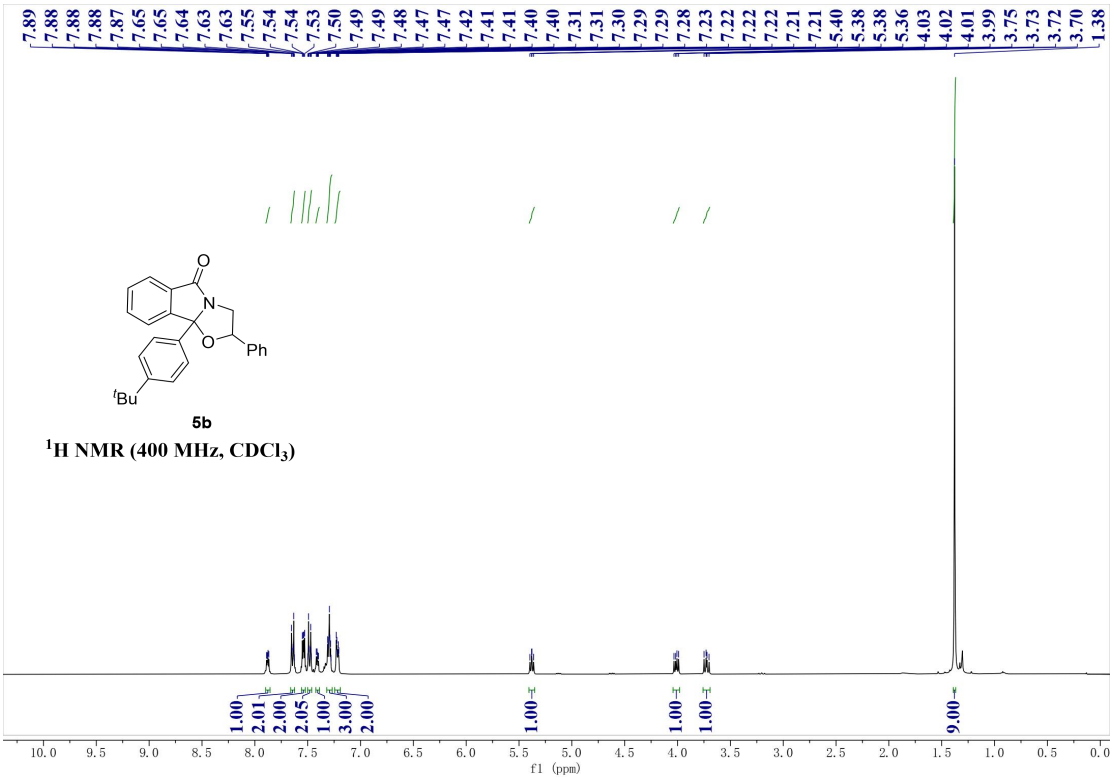


Figure S40. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **5b**

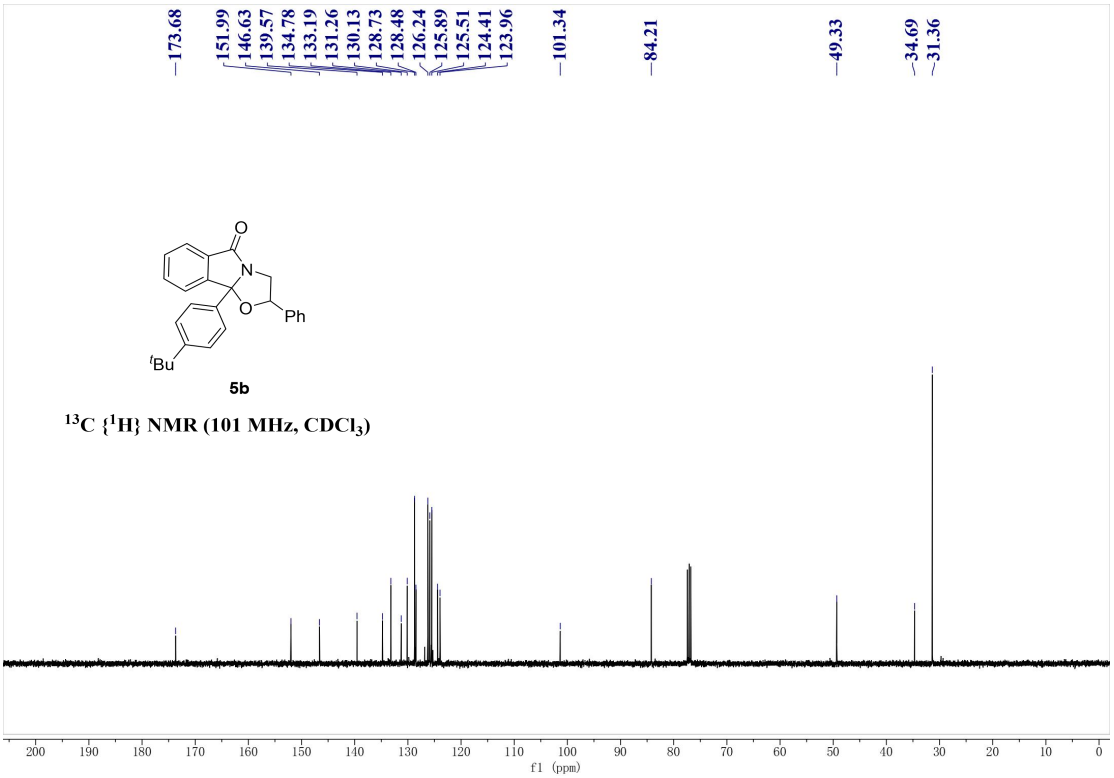


Figure S41. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **5b**

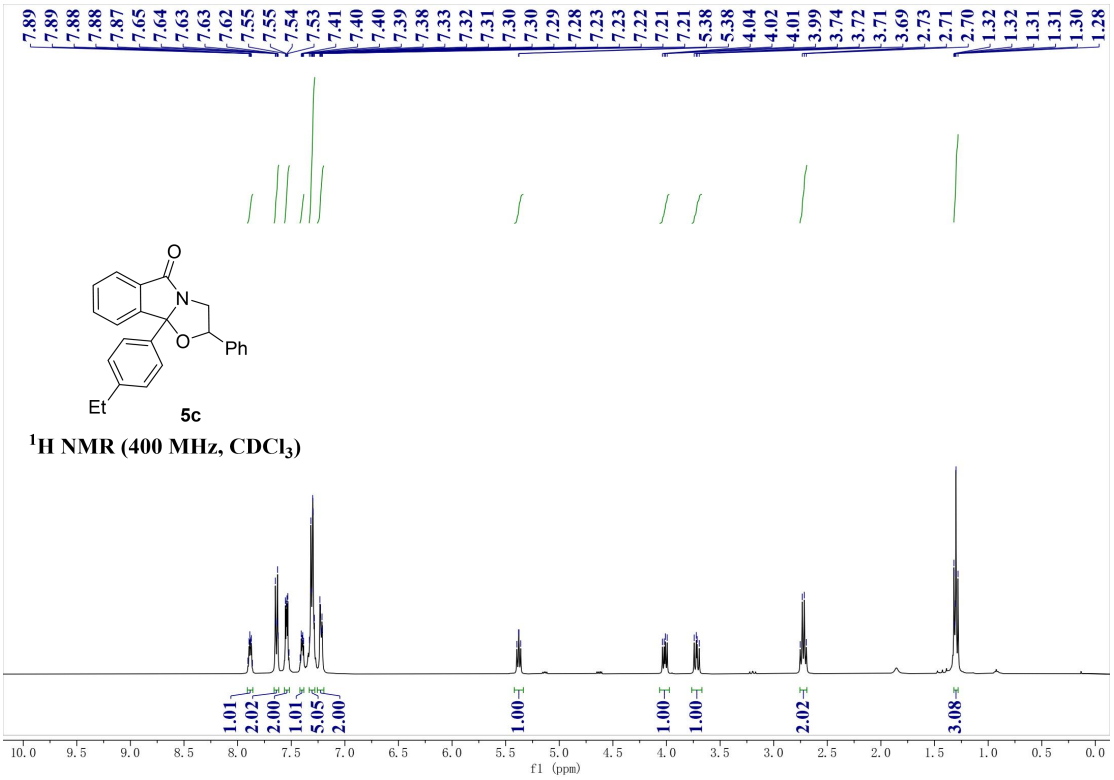


Figure S42. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **5c**

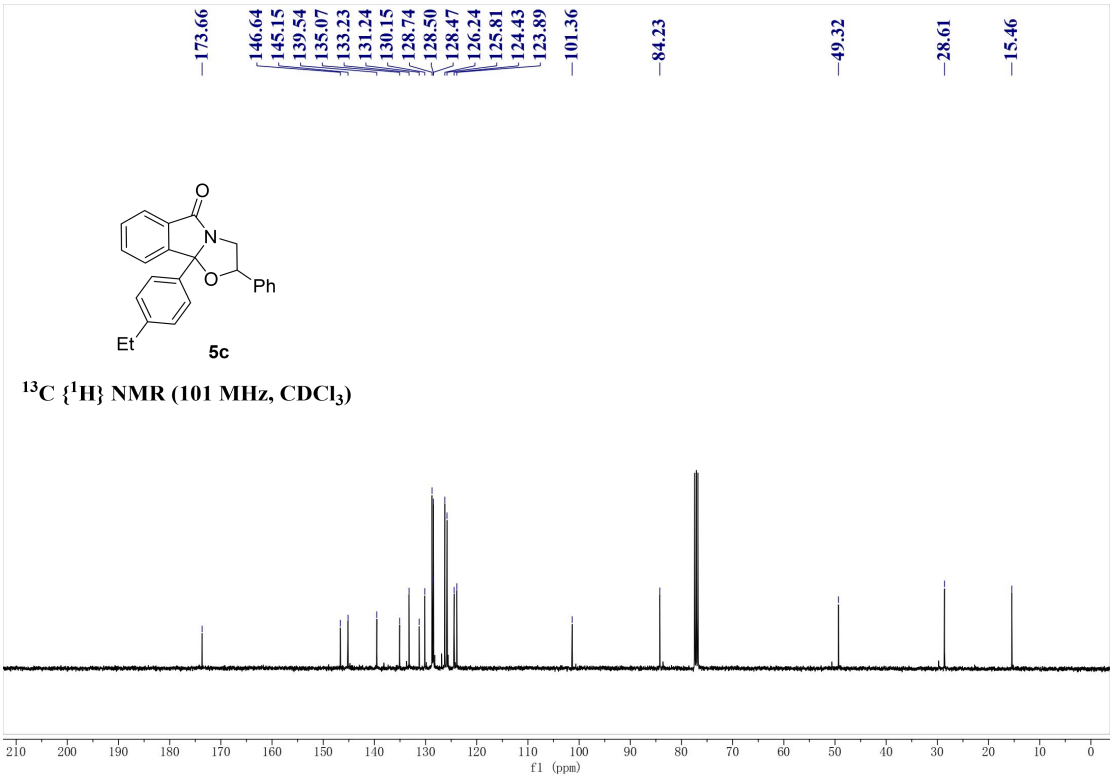


Figure S43. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **5c**

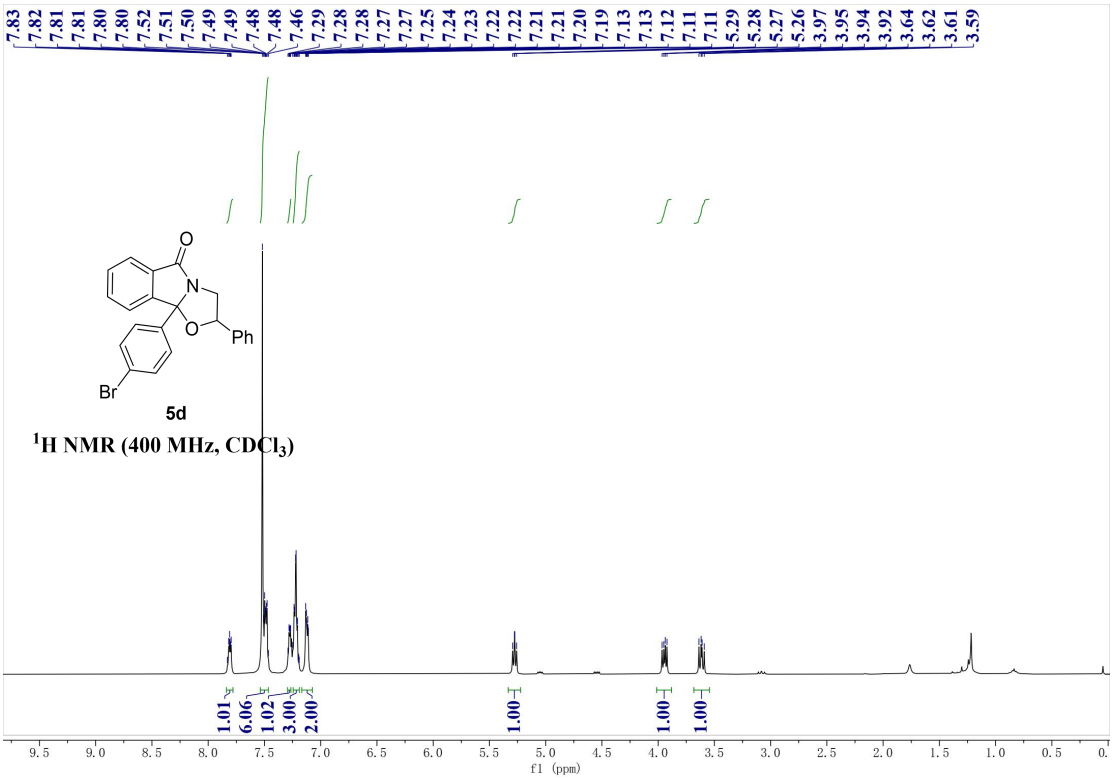


Figure S44. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **5d**

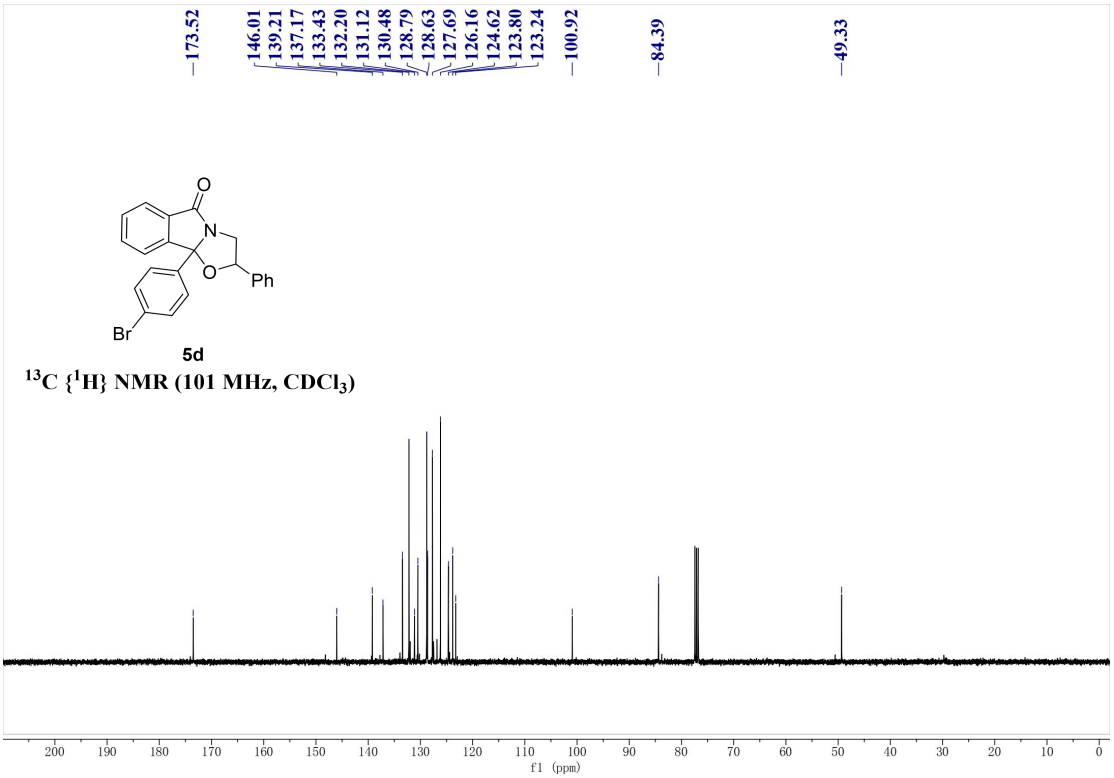


Figure S45. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **5d**

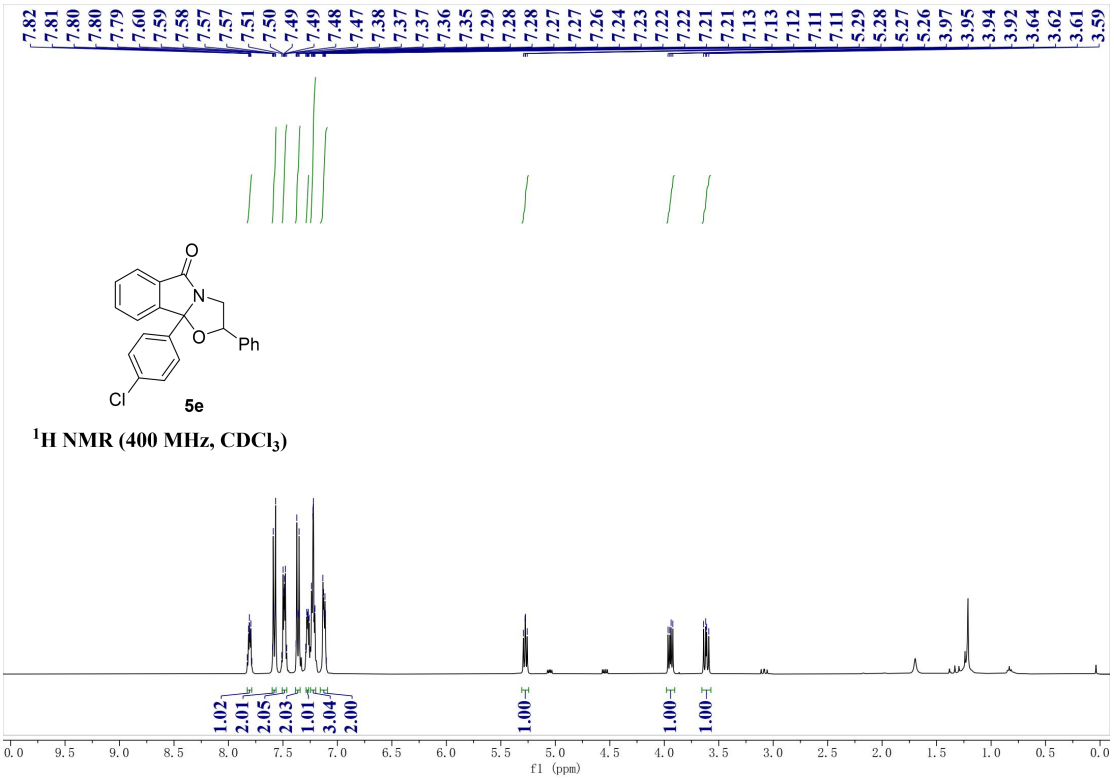


Figure S46. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **5e**

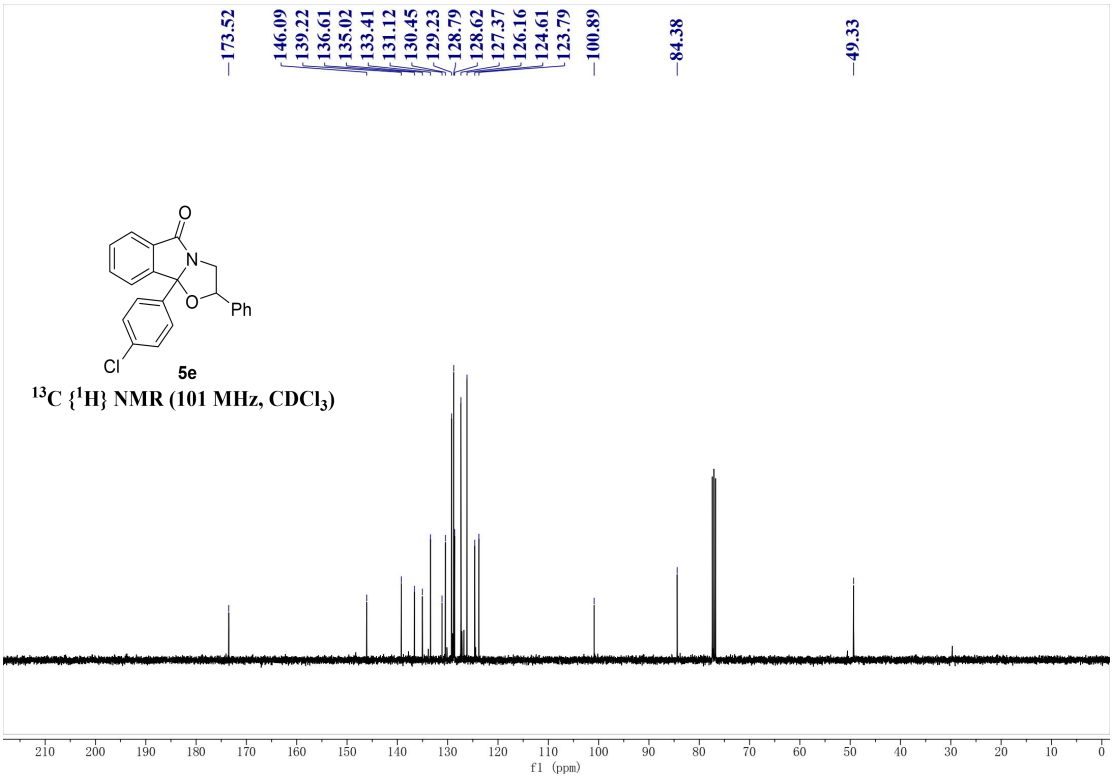


Figure S47. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **5e**

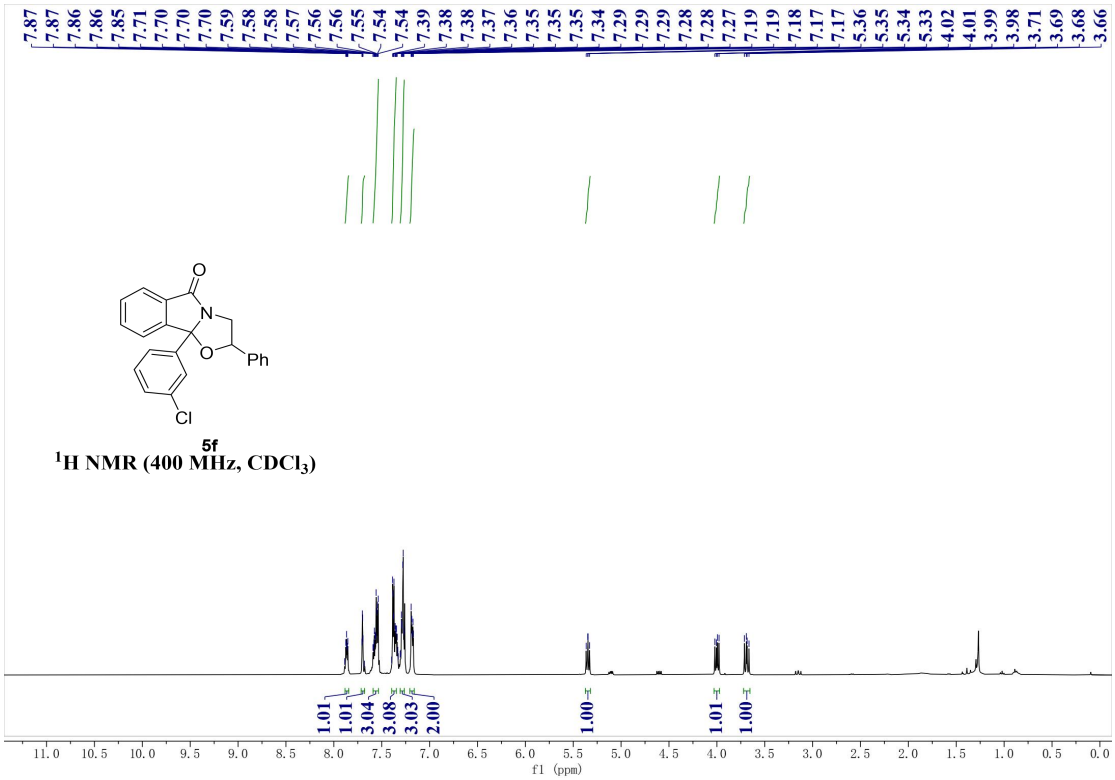


Figure S48. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **5f**

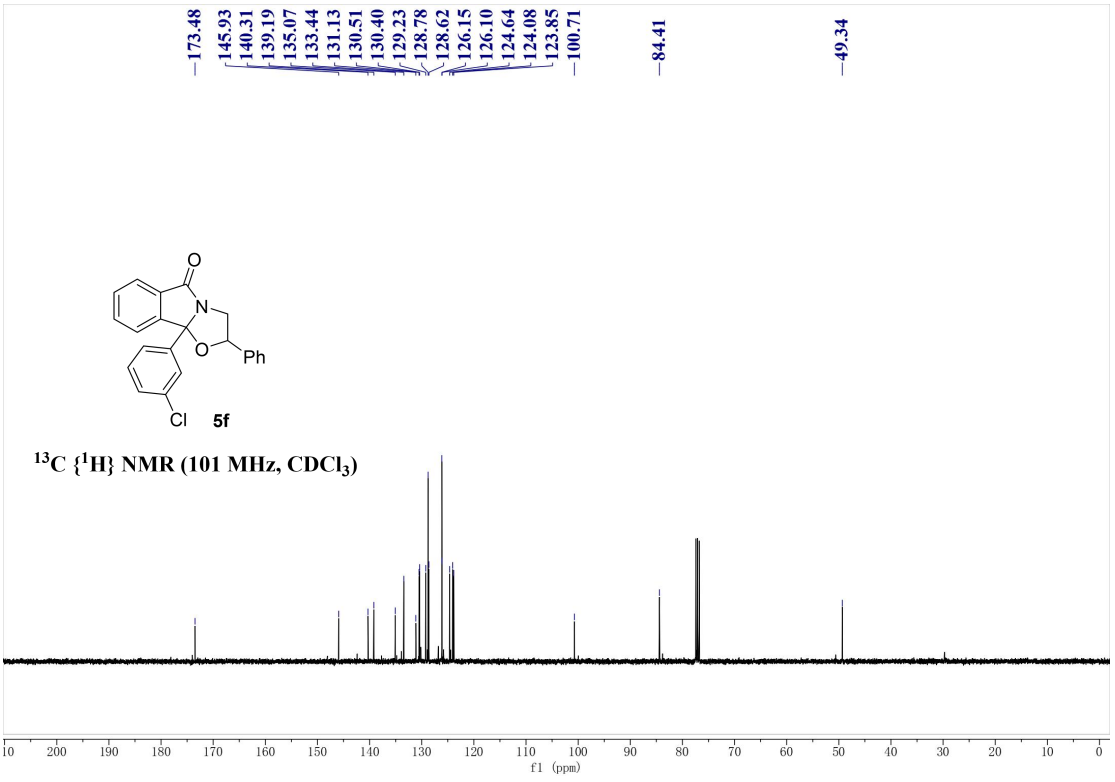


Figure S49. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **5f**

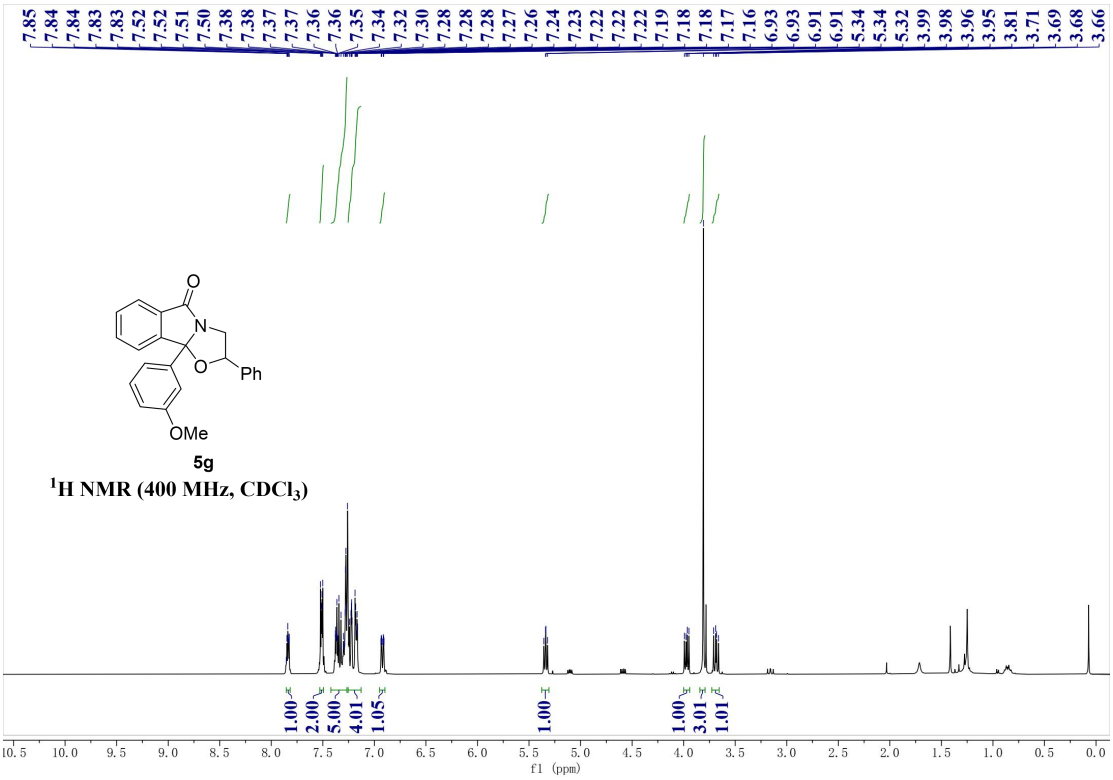


Figure S50. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **5g**

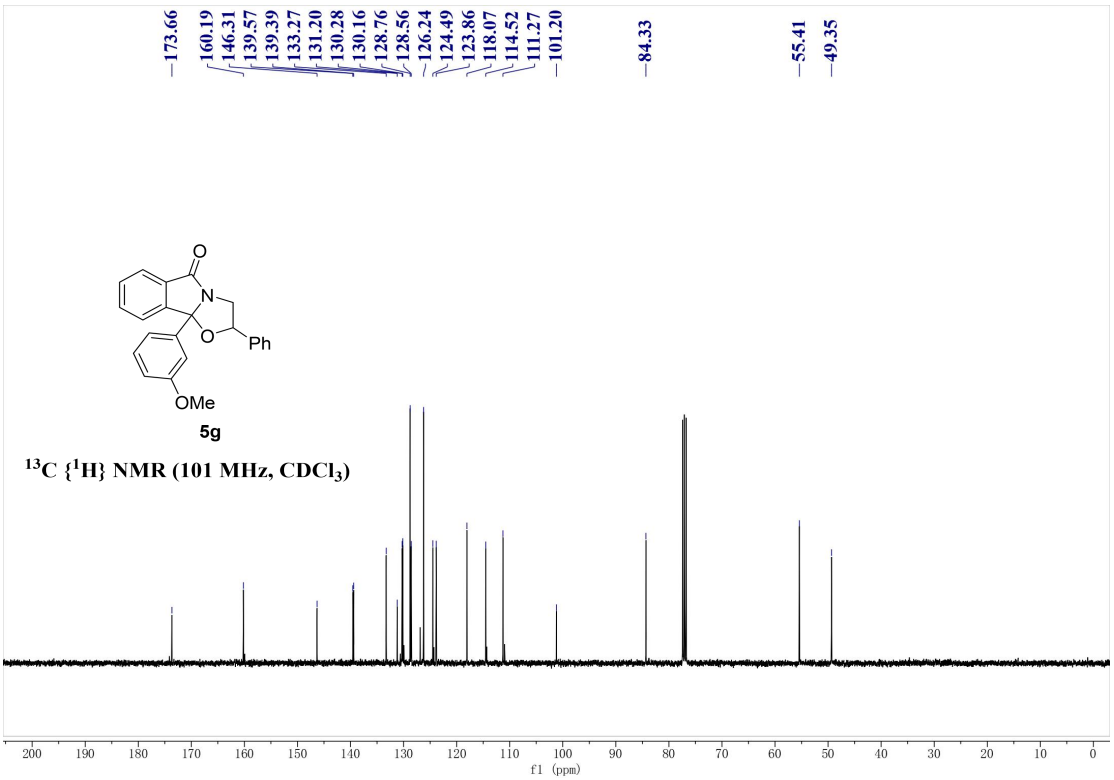


Figure S51. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **5g**

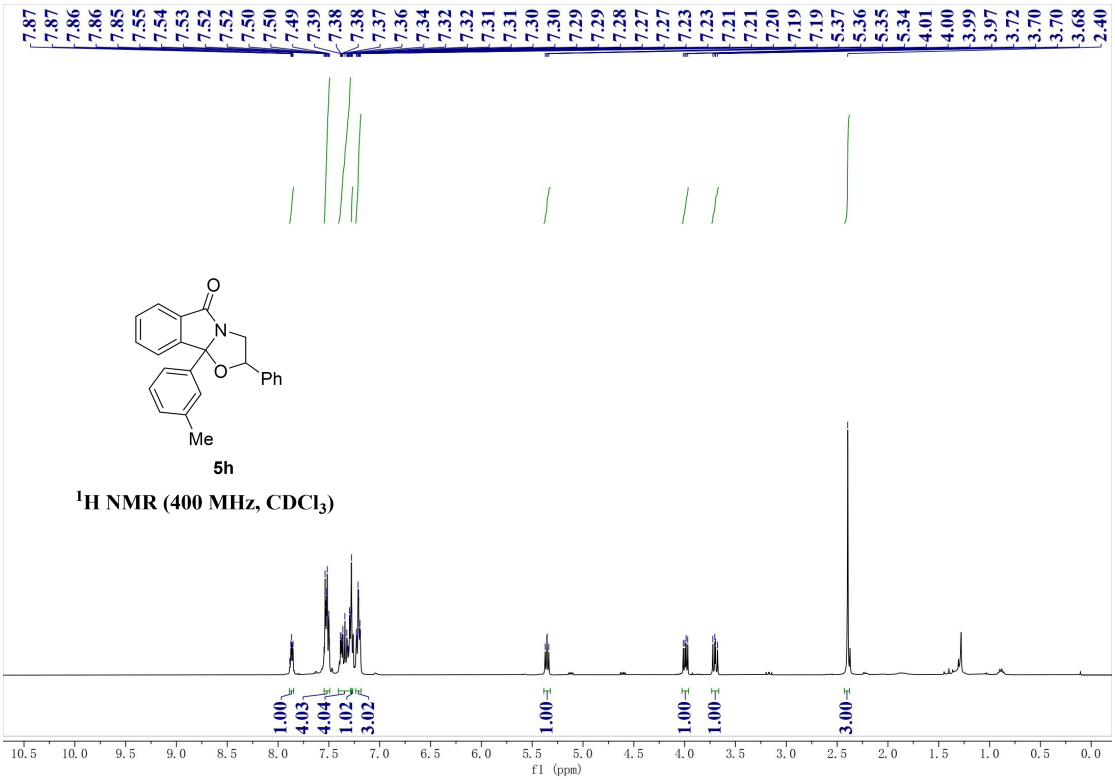


Figure S52. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **5h**

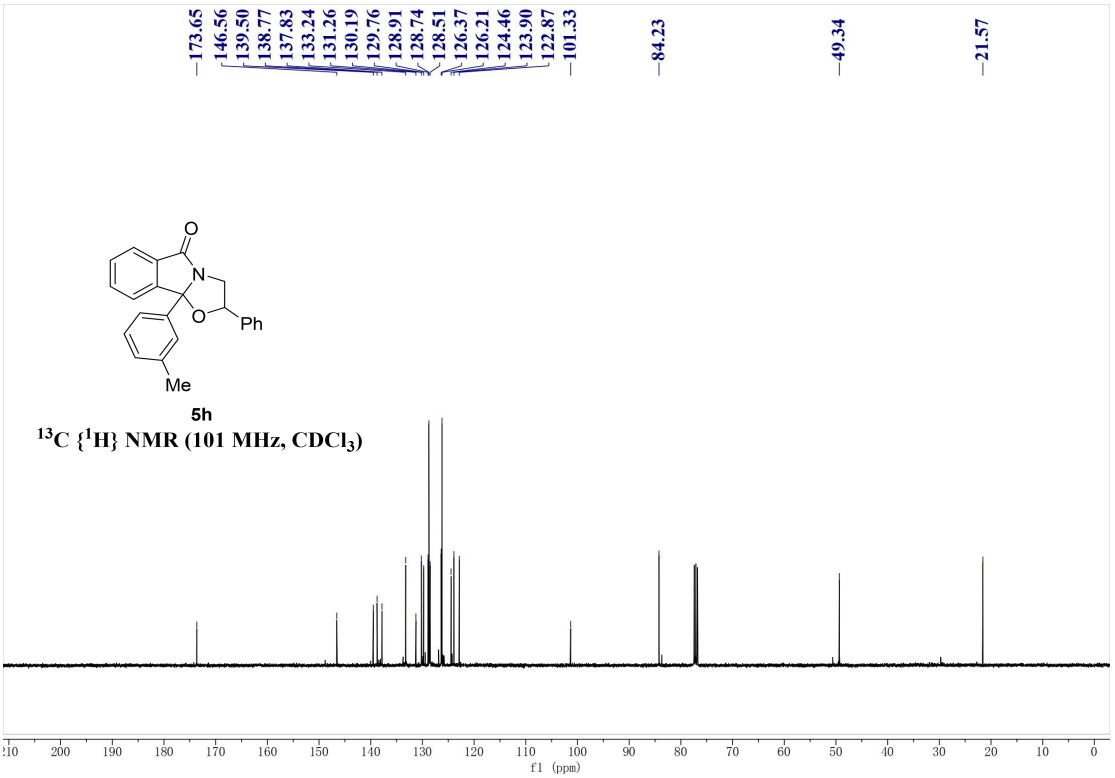


Figure S53. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **5h**

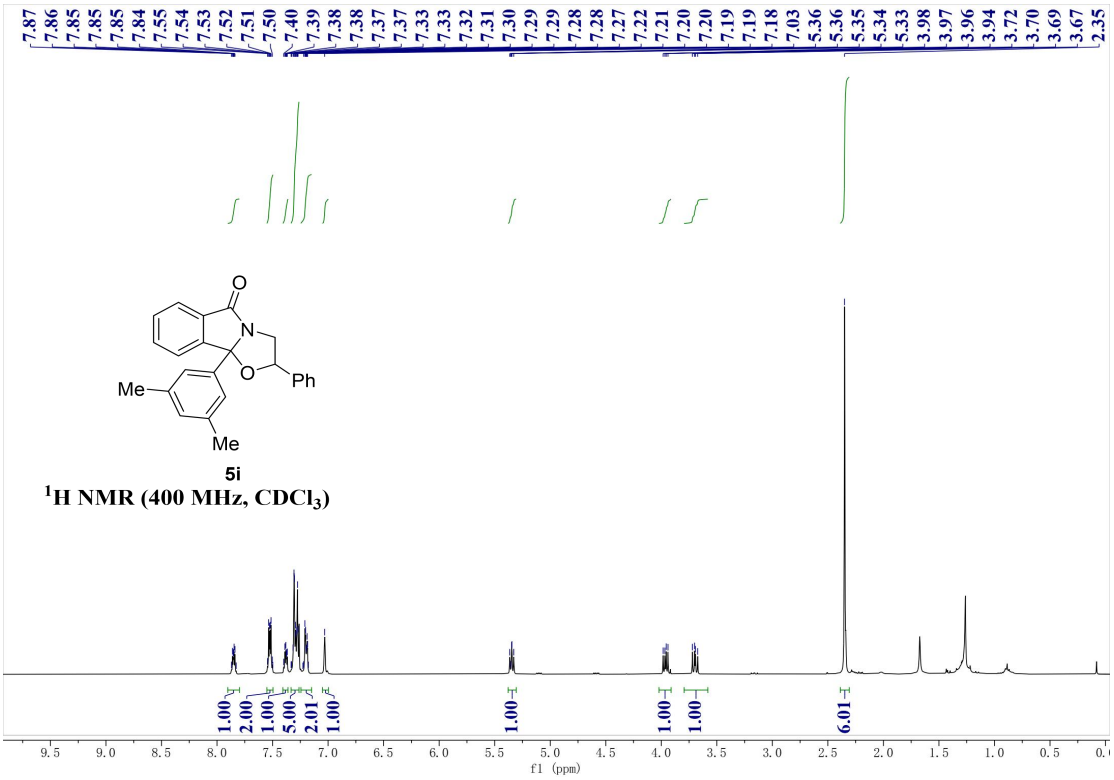


Figure S54. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **5i**

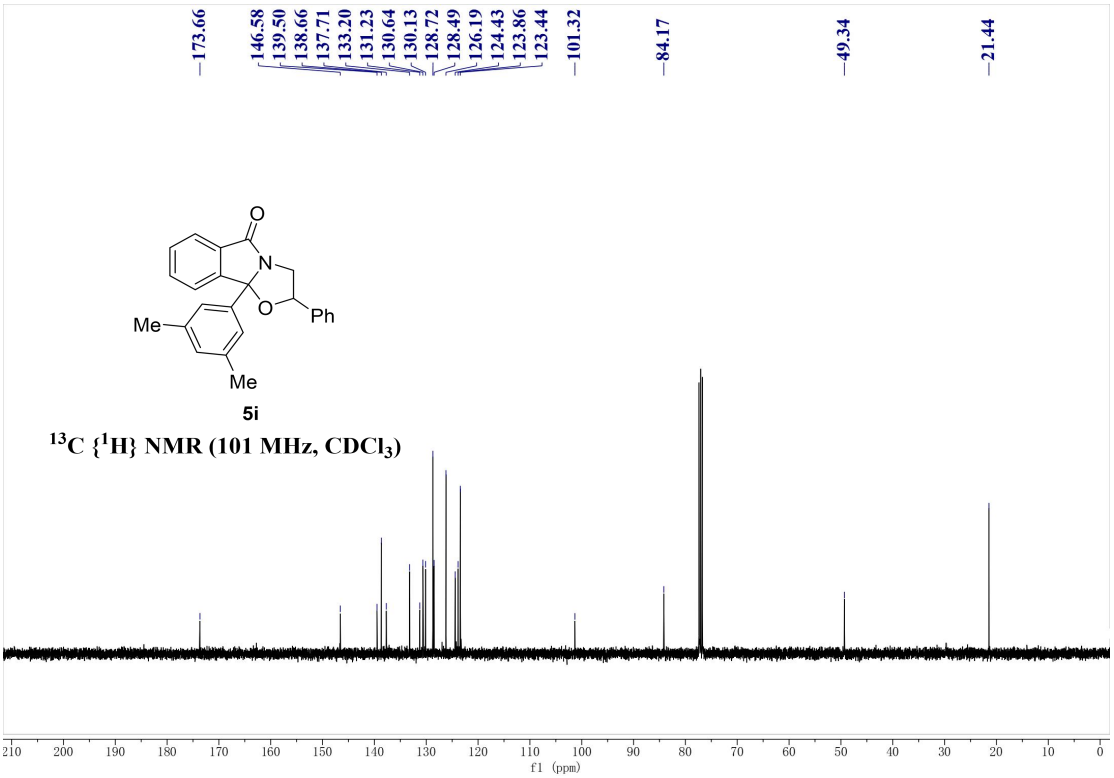


Figure S55. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **5i**

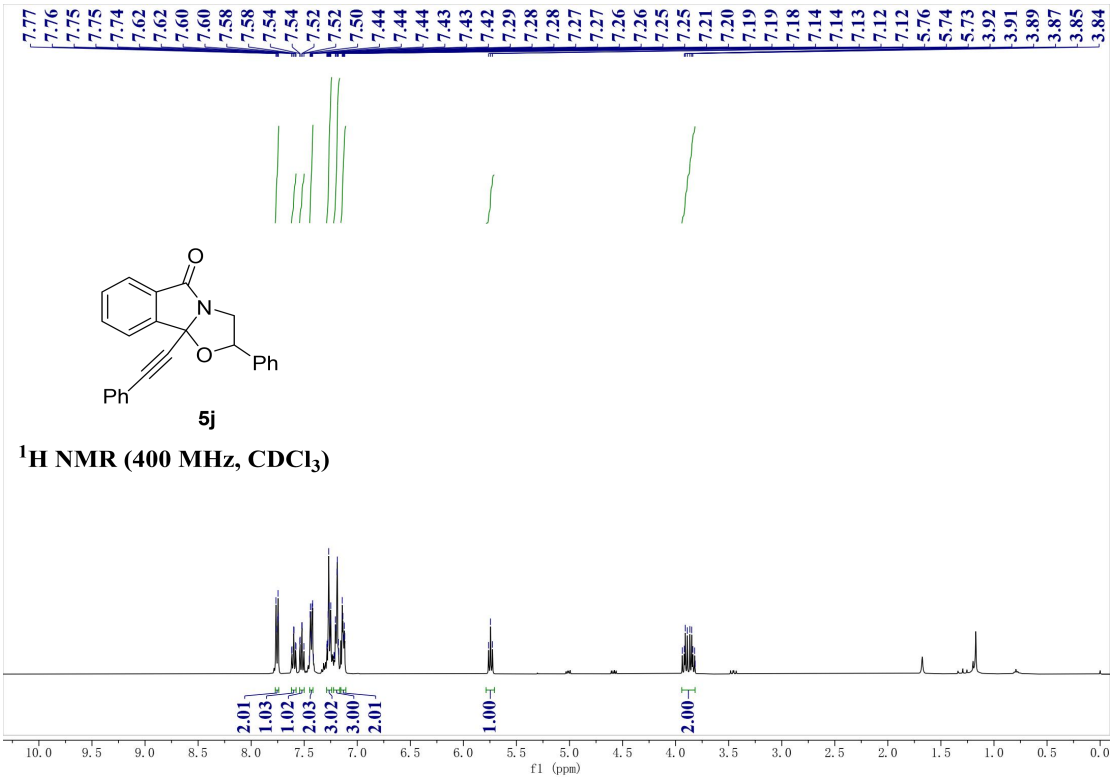


Figure S56. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **5j**

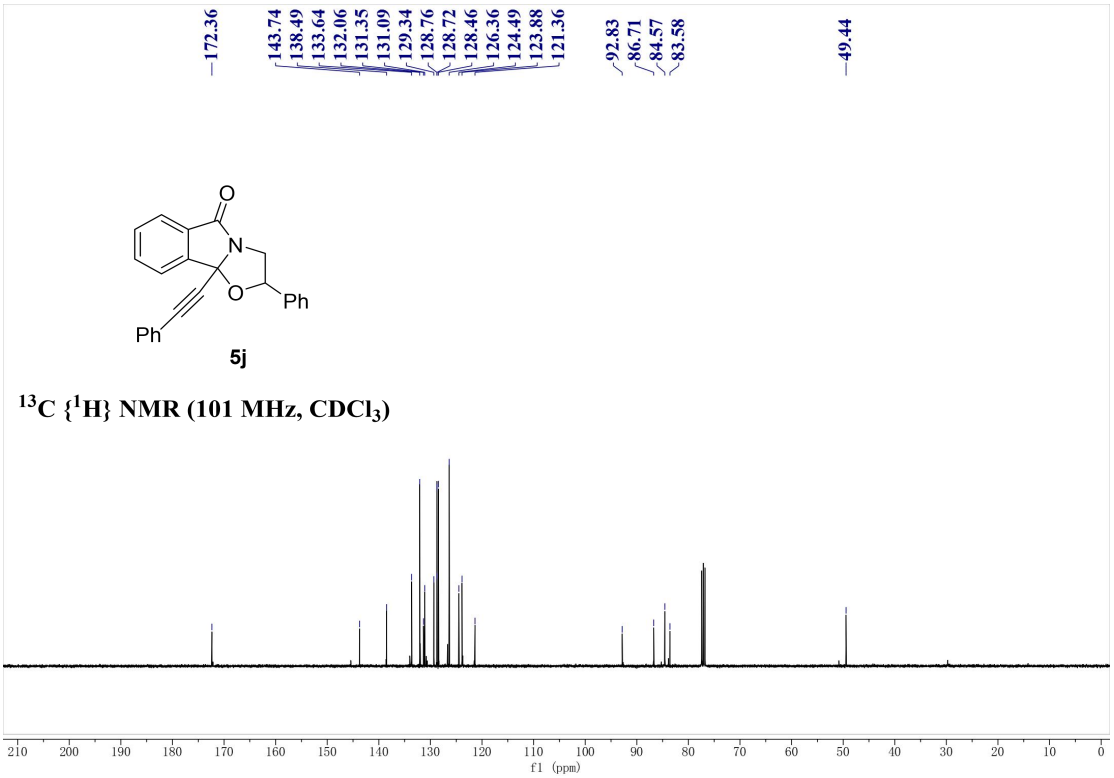


Figure S57. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **5j**

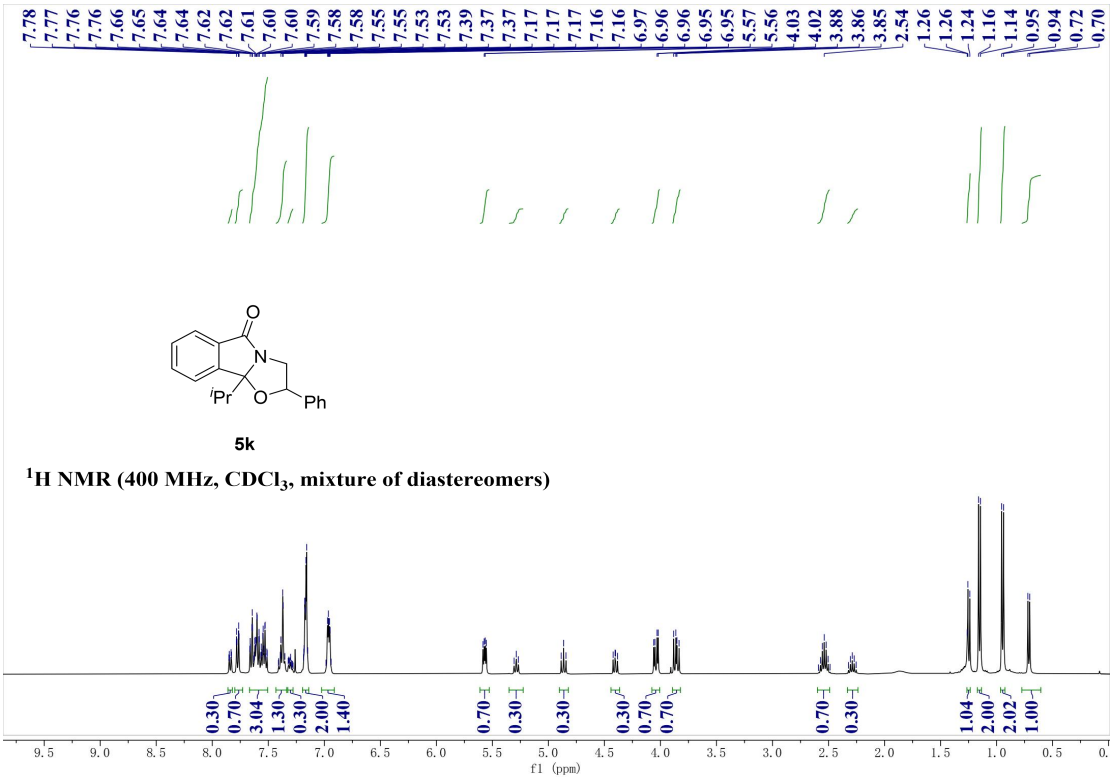


Figure S58. ^{1}H NMR (400 MHz, $CDCl_3$, mixture of diastereomers) spectra of compound **5k**

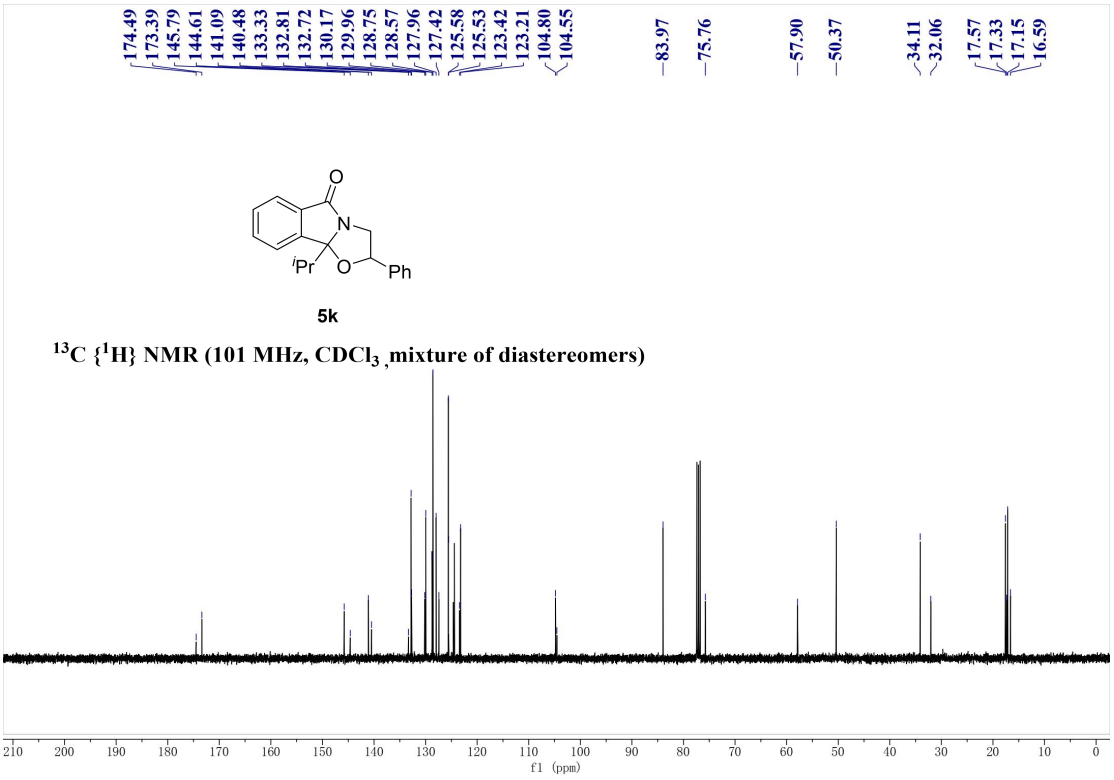


Figure S59. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, mixture of diastereomers) spectra of compound **5k**

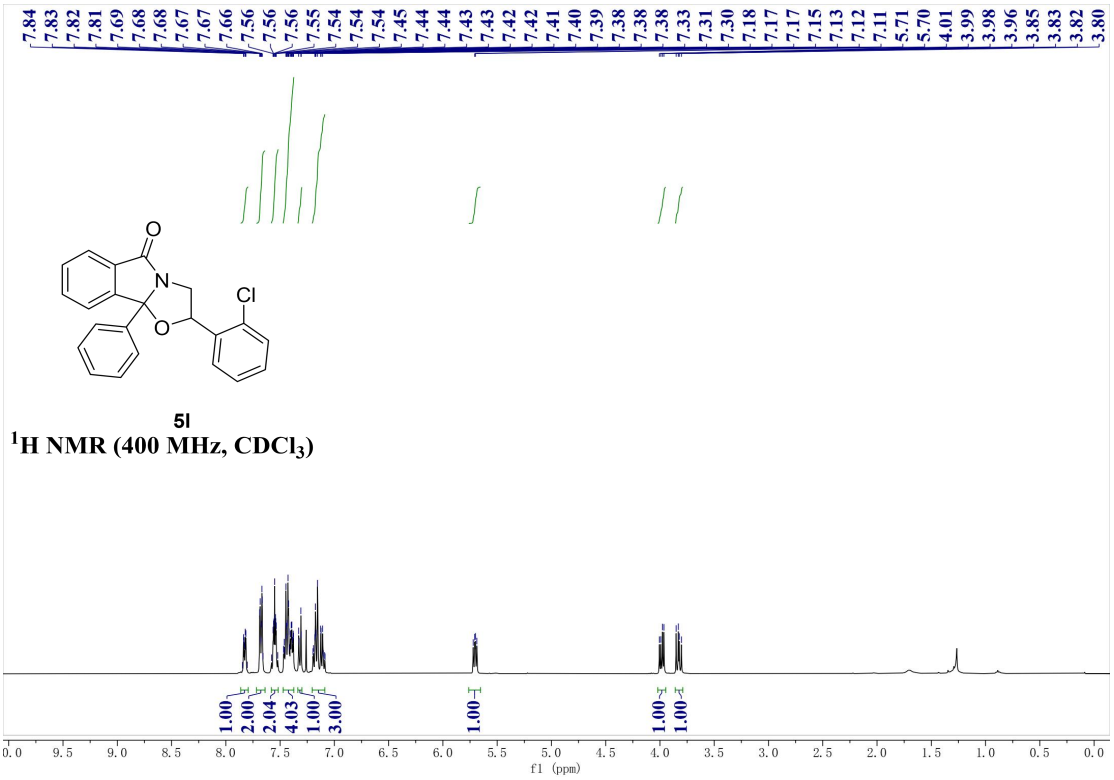


Figure S60. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **5l**

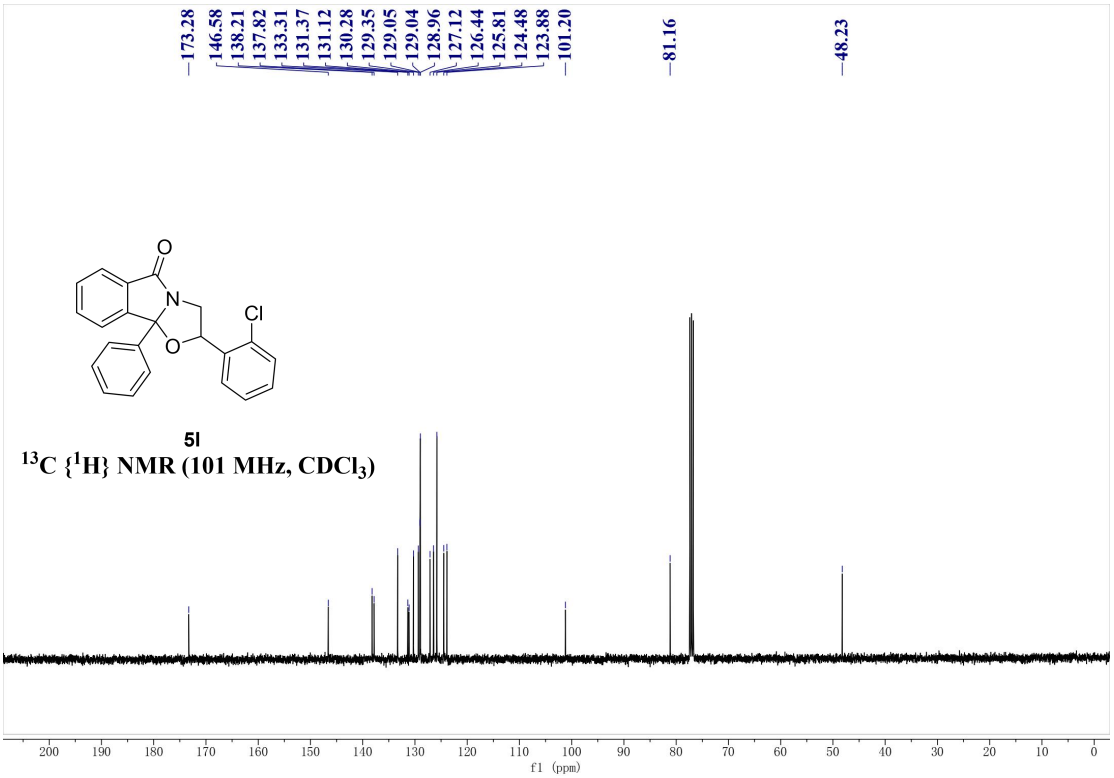


Figure S61. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **5l**

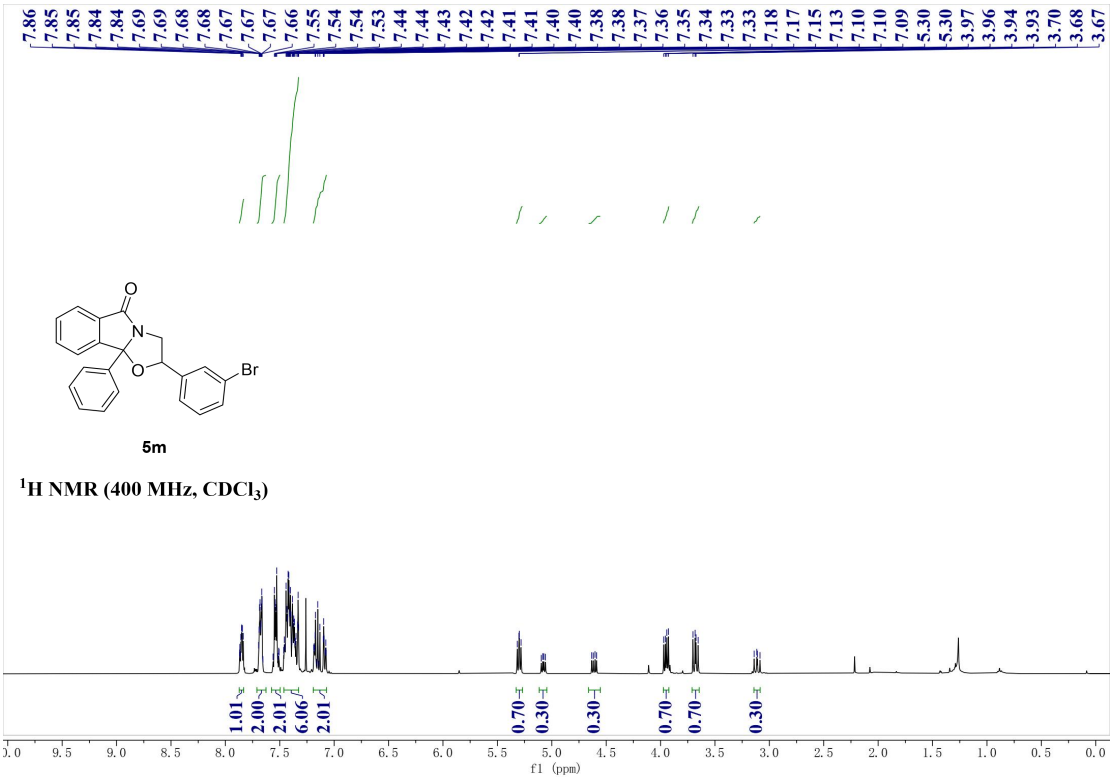


Figure S62. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **5m**

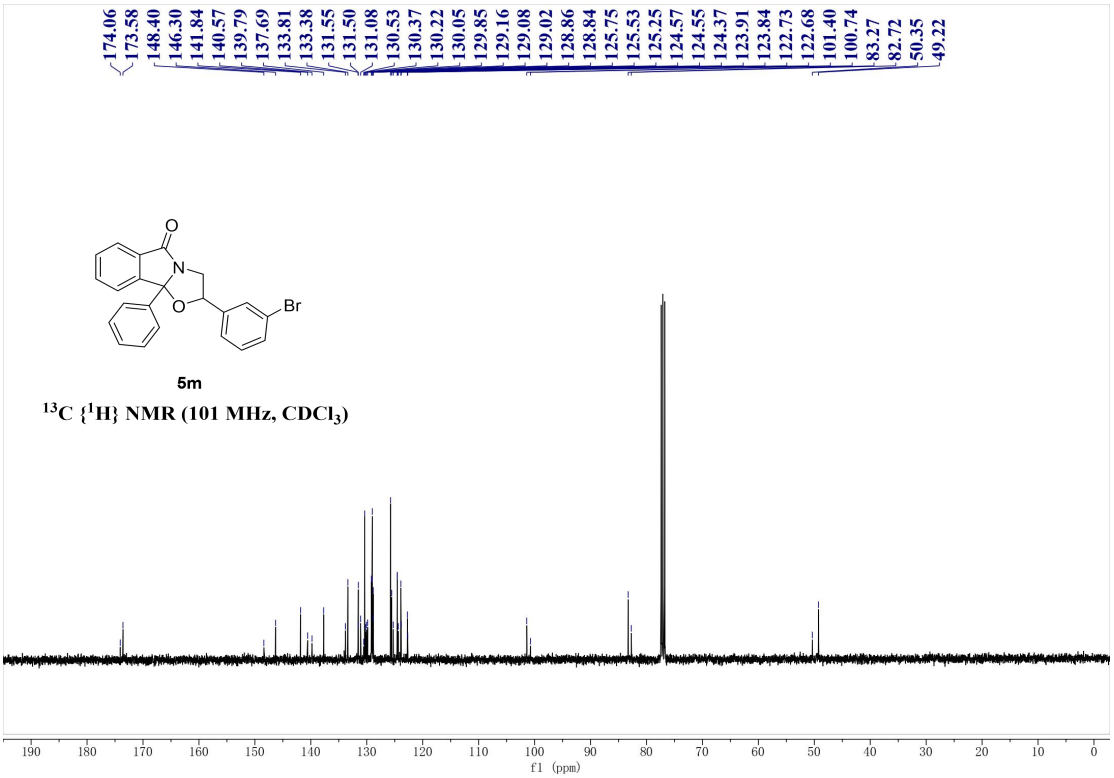
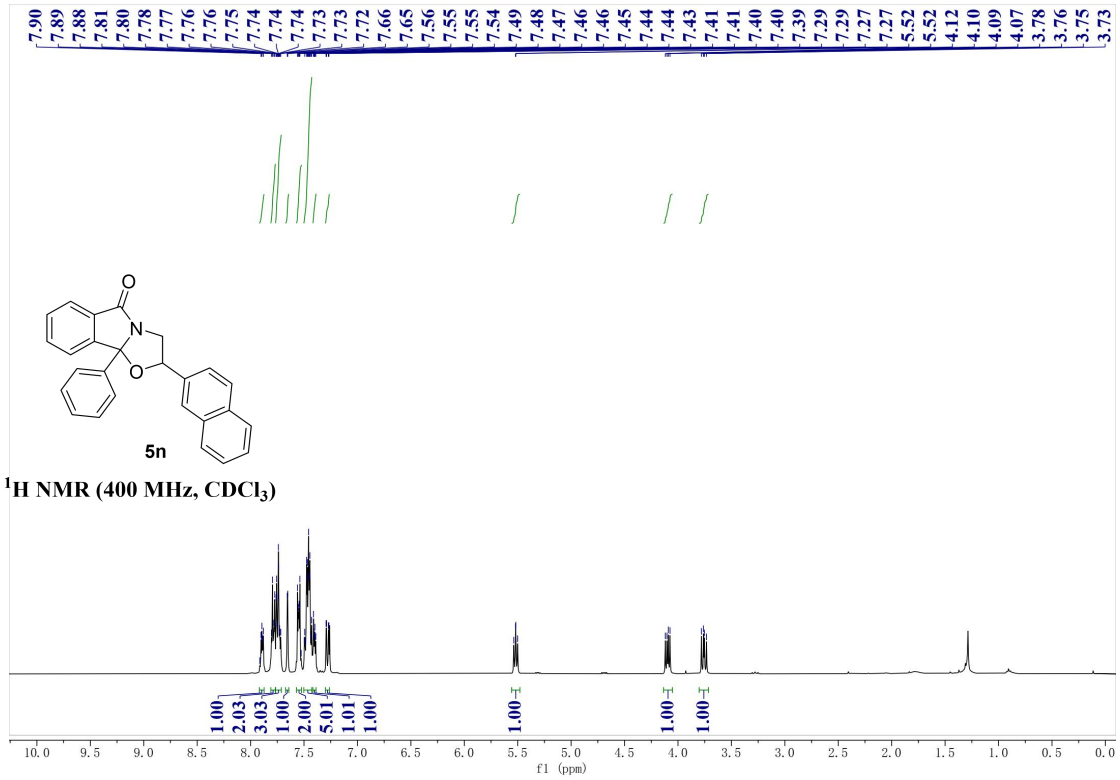
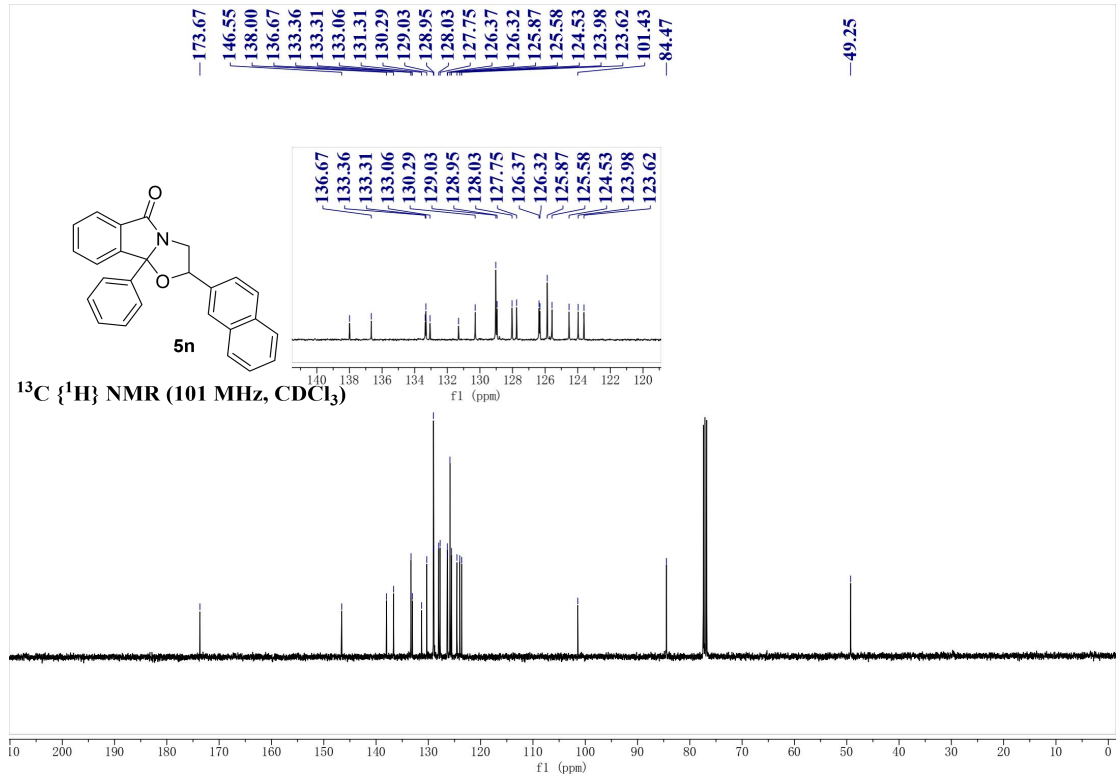


Figure S63. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **5m**



^{1}H NMR (400 MHz, $CDCl_3$)

Figure S64. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **5n**



^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)

Figure S65. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **5n**

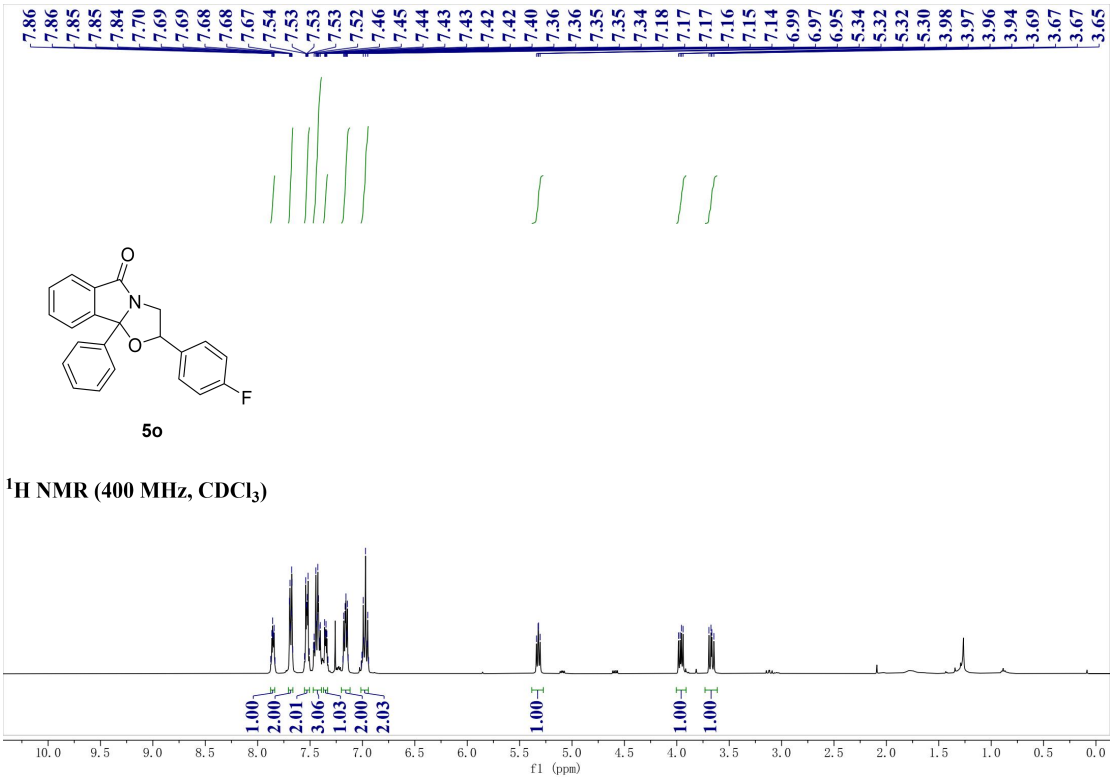


Figure S66. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **5o**

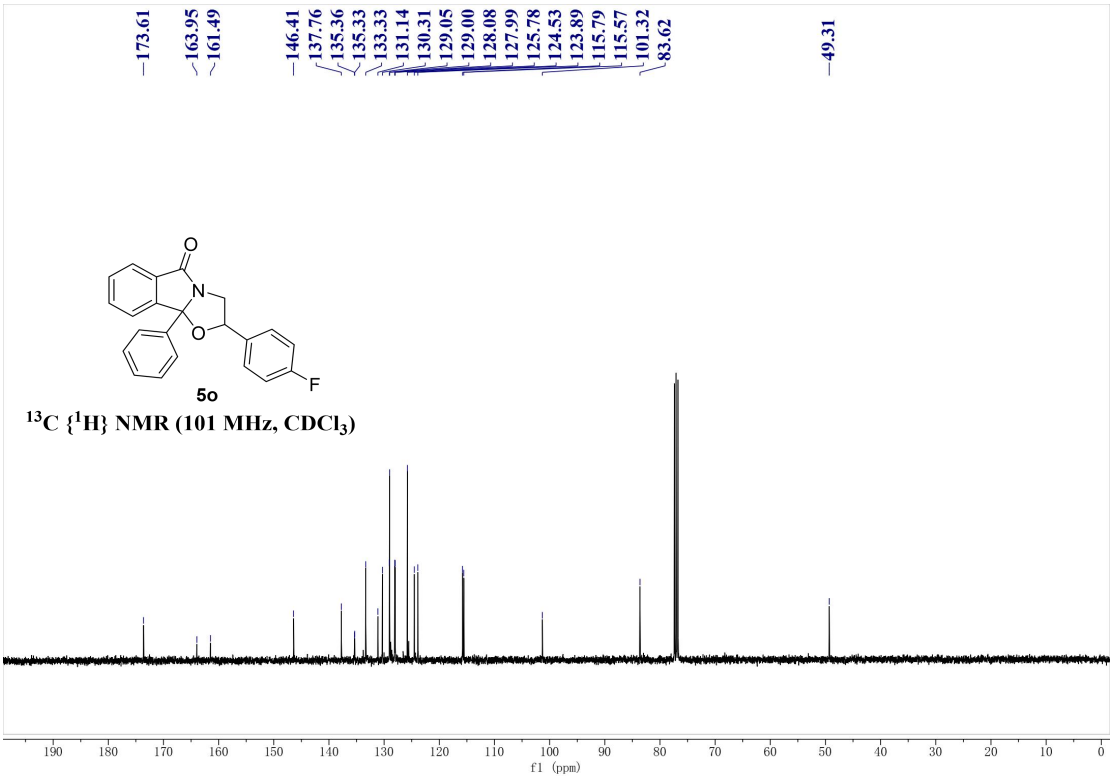


Figure S67. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **5o**

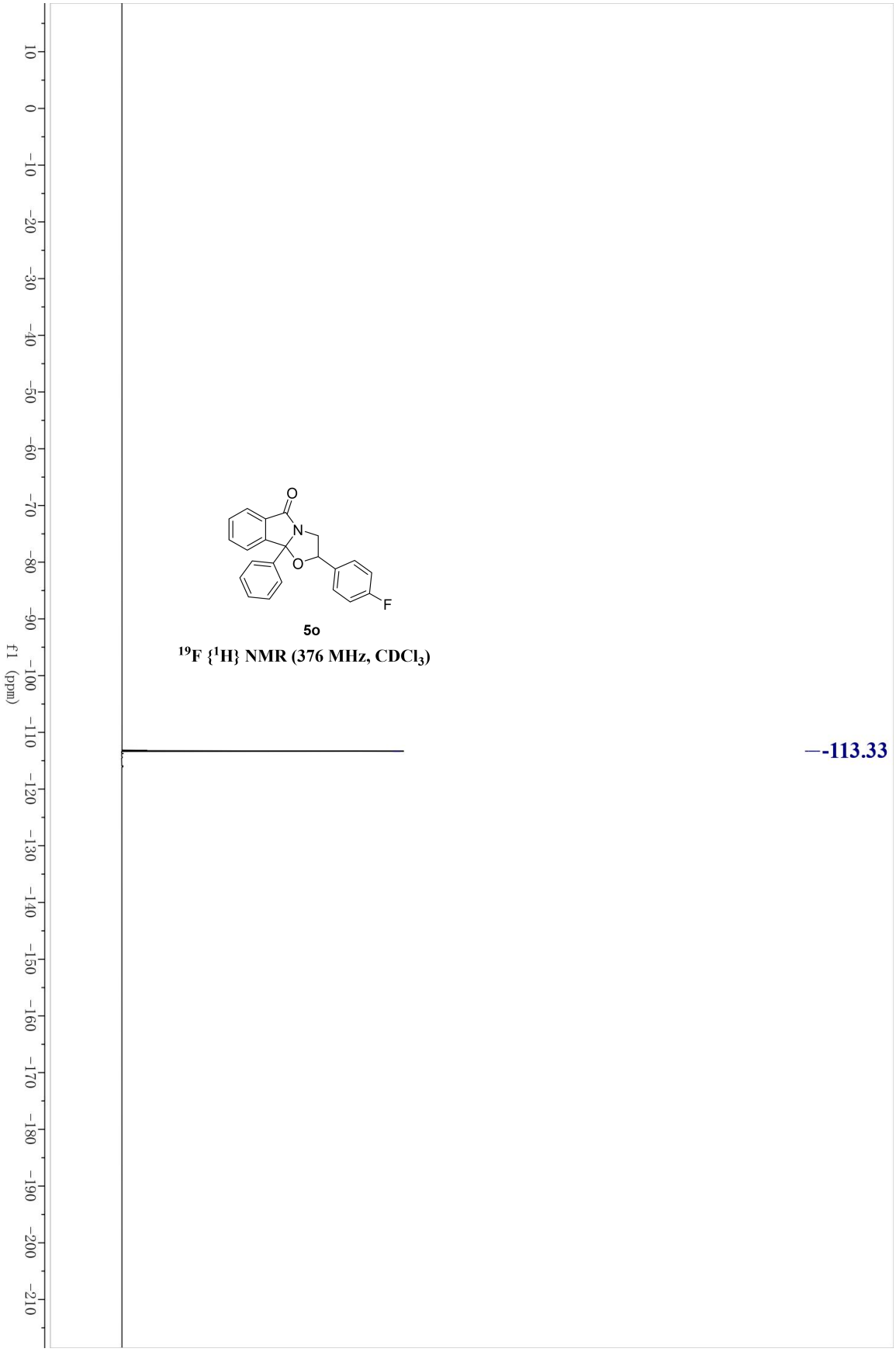


Figure S68. ^{19}F $\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) spectra of compound **5o**

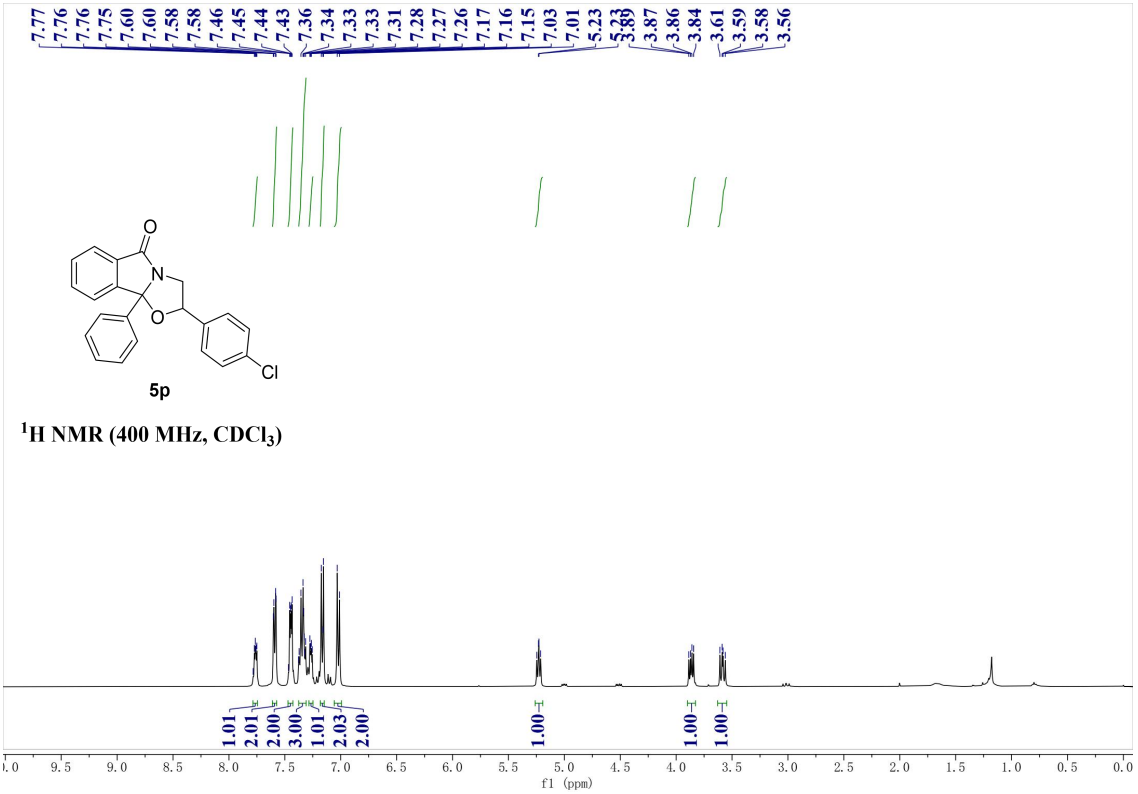


Figure S69. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **5p**

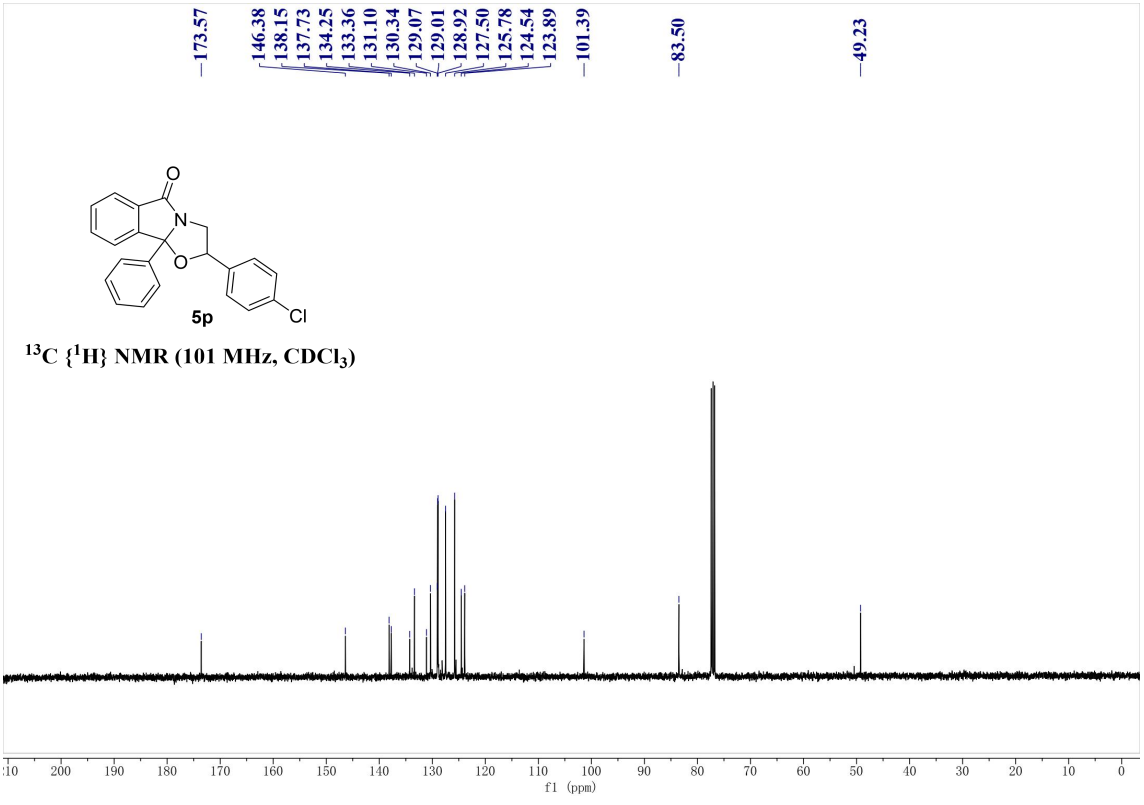


Figure S70. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **5p**

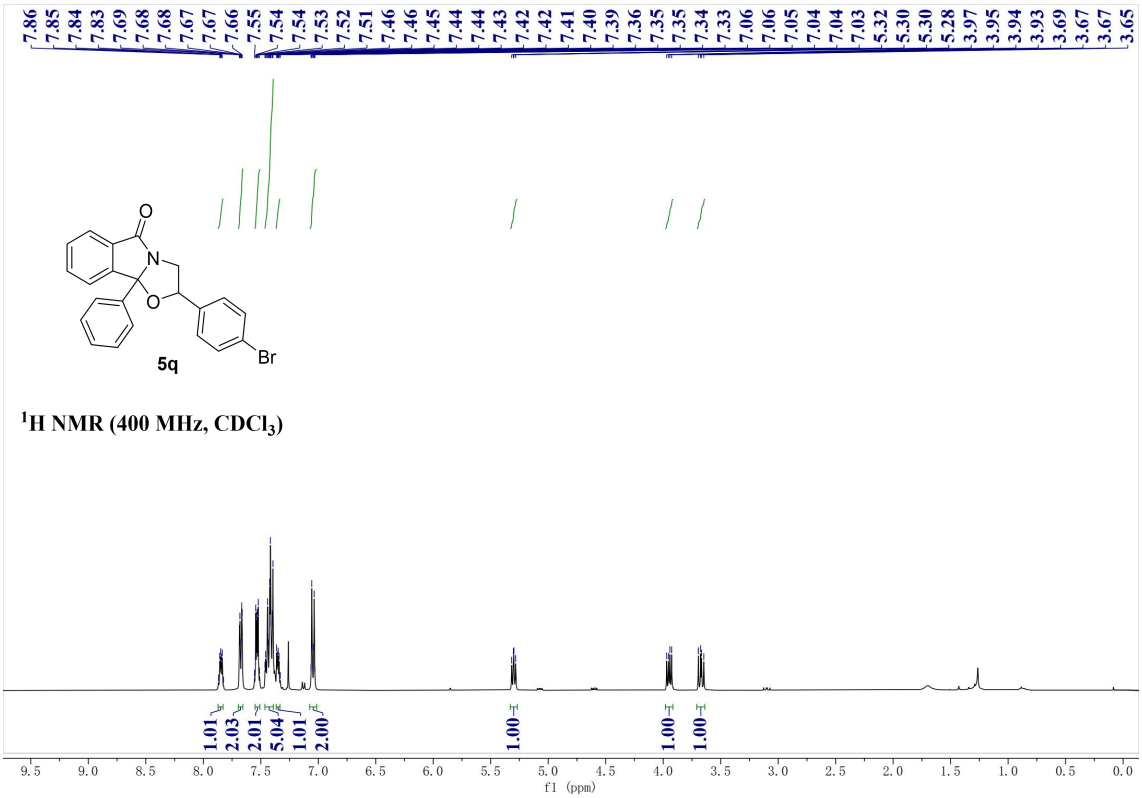


Figure S71. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **5q**

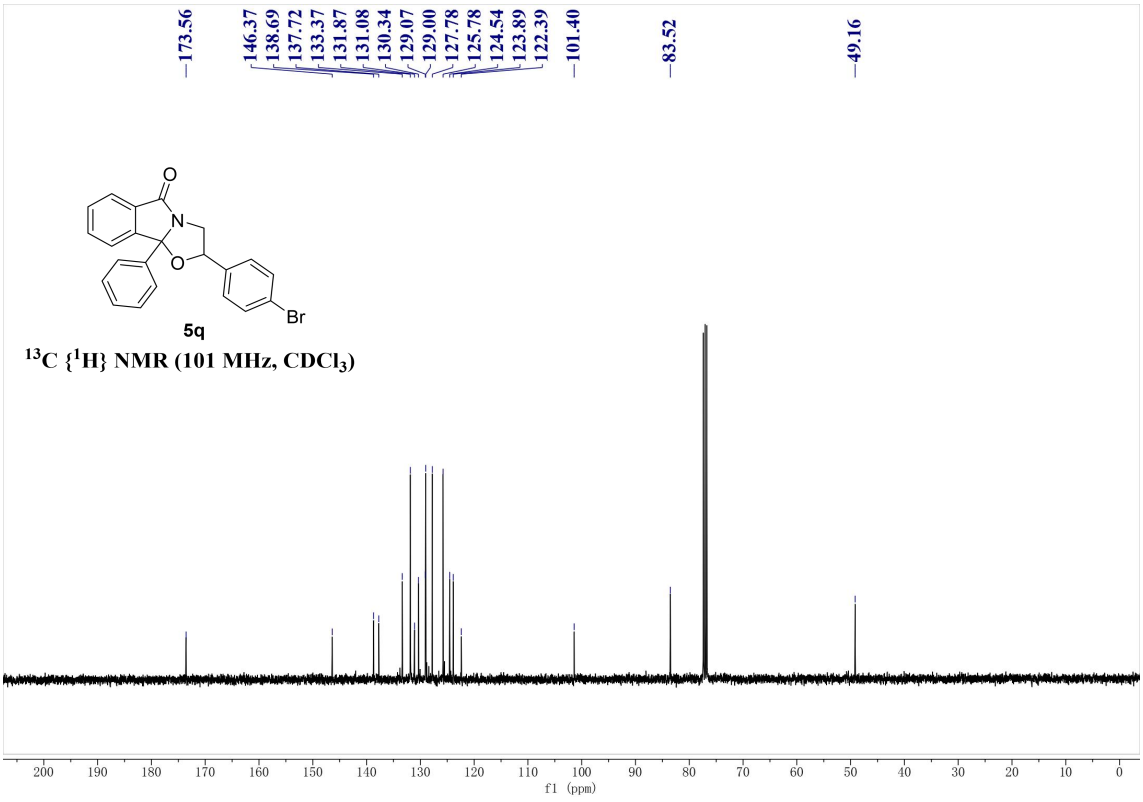


Figure S72. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **5q**

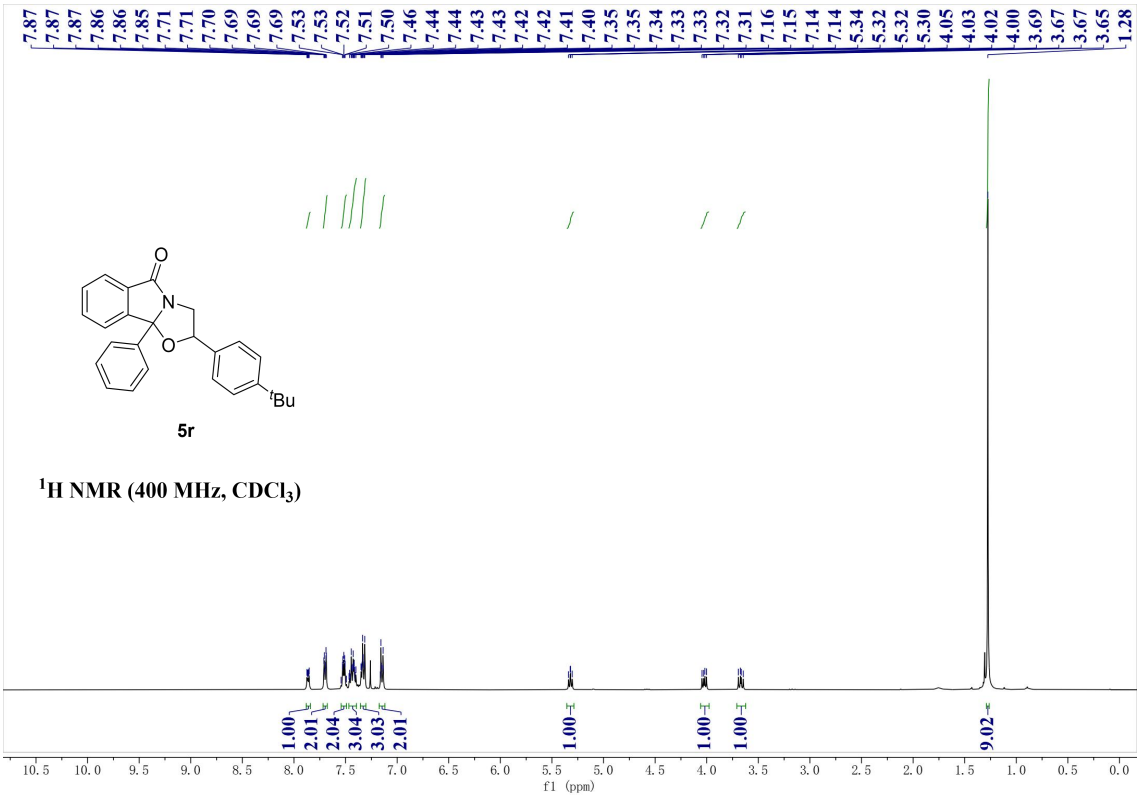


Figure S73. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **5r**

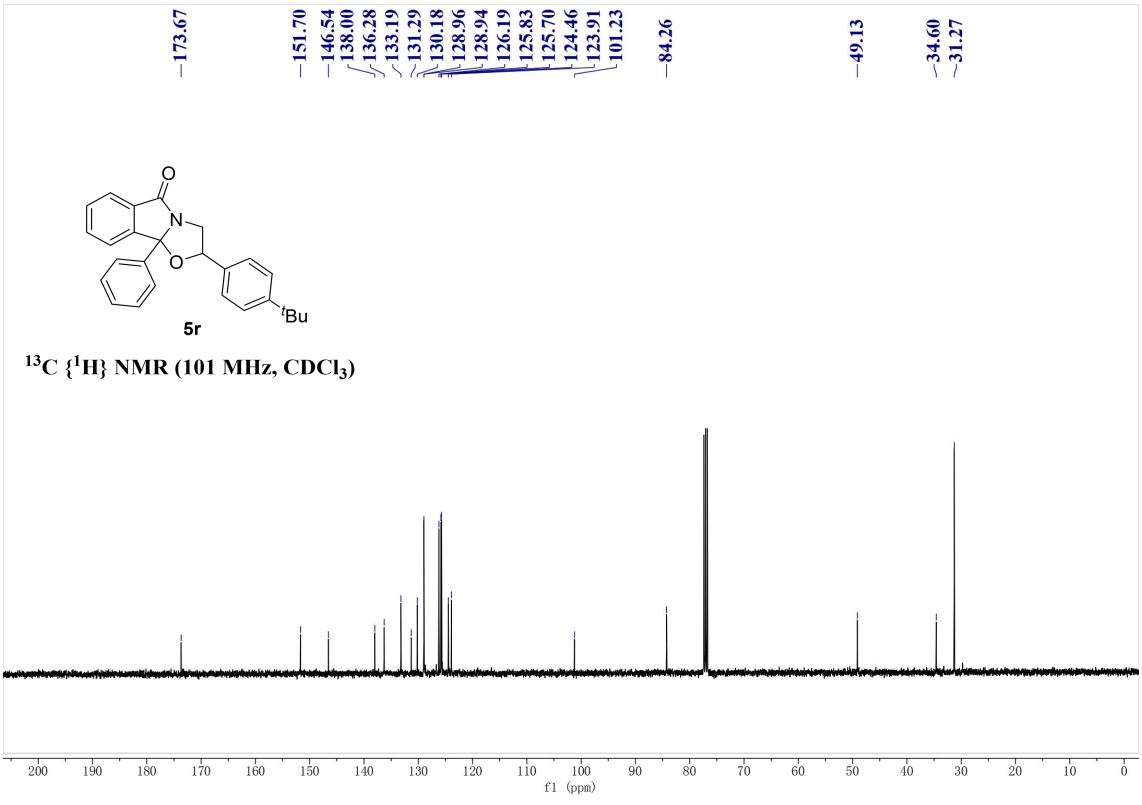


Figure S74. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **5r**

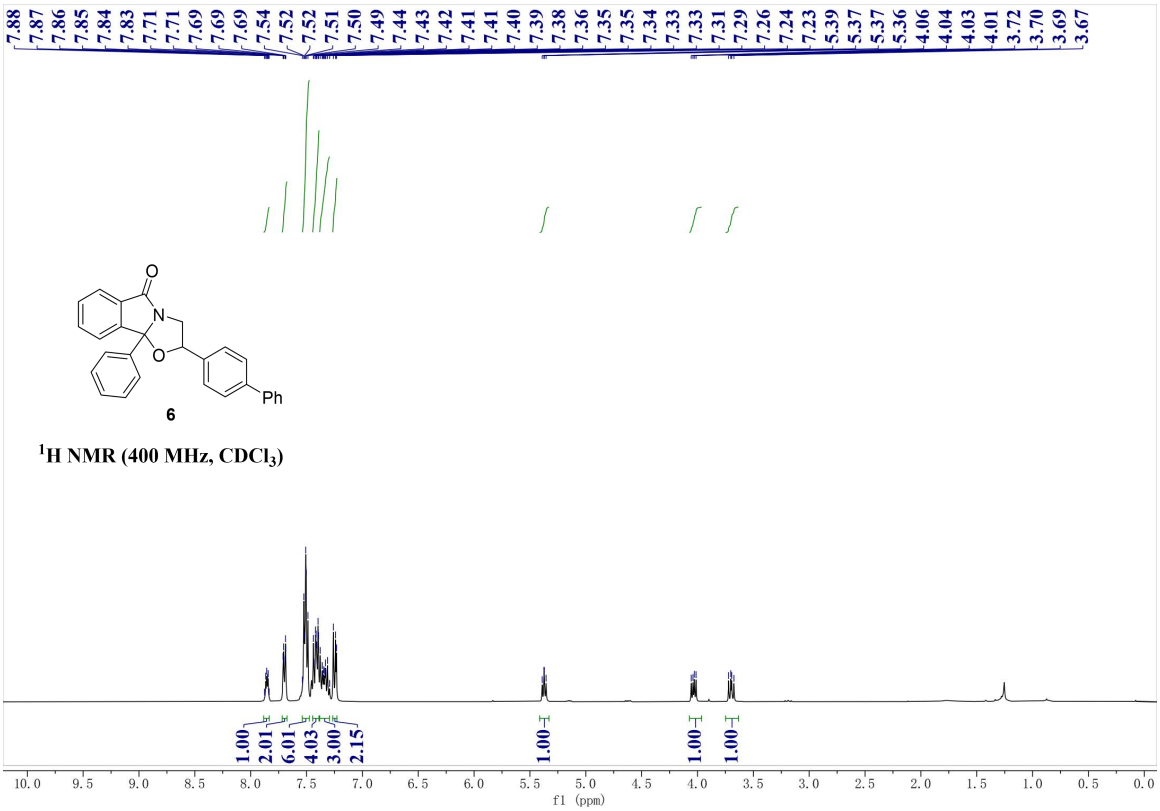


Figure S75. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **6**

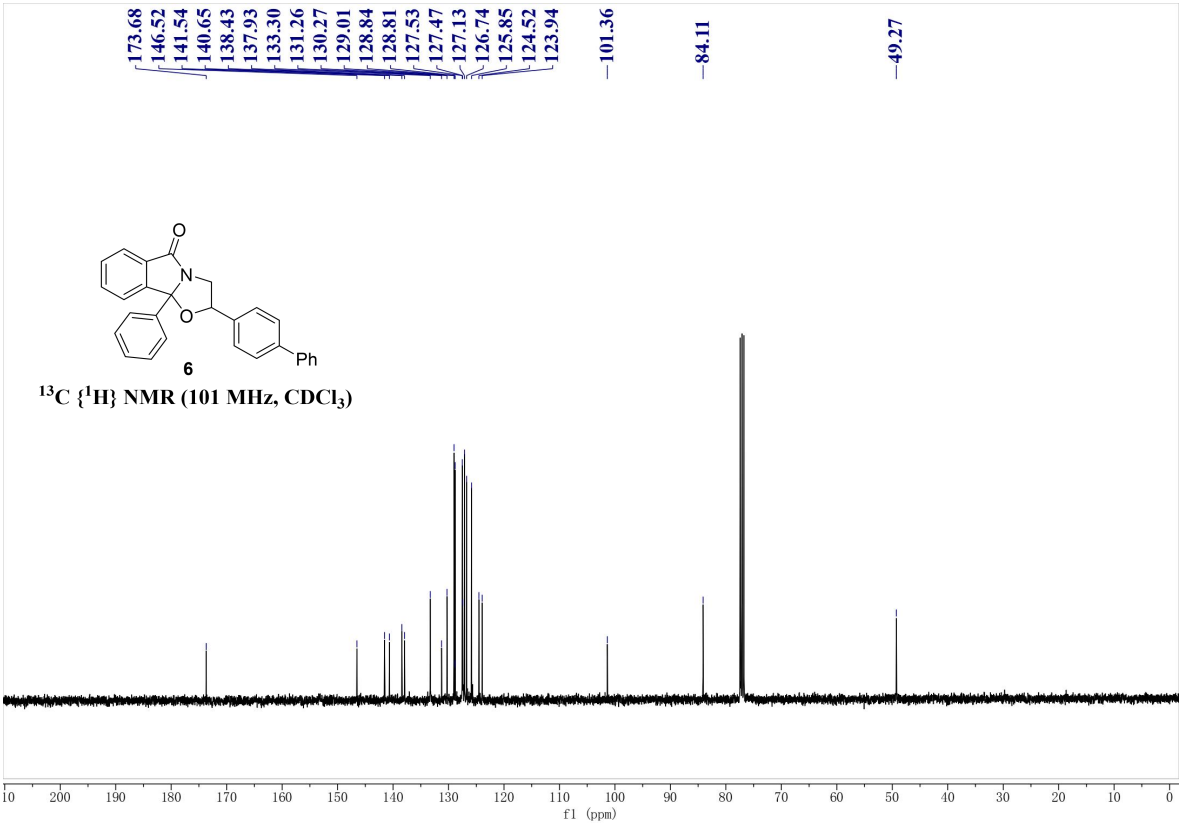


Figure S76. ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) spectra of compound **6**