Supporting Information for

Synthesis of Spiro-3*H*-indazoles via [3+2] Dipolar Cycloaddition of Arynes with 6-Diazocyclohex-2-en-1-one Derivatives and Fused-2*H*-indazoles by Subsequent Rearrangement

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1. General

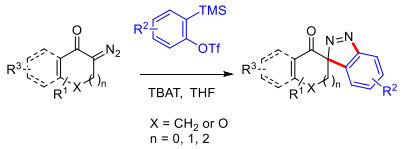
All isolated compounds were characterized on Varian 300, Bruker 400, JEOL 400 MHz spectrometers in $CDCl_3$, $(CD_3)_2CO$ or CD_3OD. Chemical shifts were reported as δ values relative to internal $CHCl_3$ (δ 7.26 for ^1H NMR and 77.16 for ^{13}C NMR), $(CH_3)_2CO$ (δ 2.05 for ^1H NMR and δ 29.84 for ^{13}C NMR) and MeOH (δ 3.31 for ^1H NMR and 49.15 for ^{13}C NMR). High-resolution mass spectra (HRMS) were obtained on a 4G mass spectrometer by using electrospray ionization (ESI) analyzed by quadrupole time-of- flight (QTof). All melting points were measured with the samples after column chromatography and uncorrected. Column chromatography was performed on silica gel. Anhydrous THF and toluene were distilled over sodium benzophenone ketyl under Ar. All other solvents and reagents were used as obtained from commercial sources without further purification.

2. General Experimental Procedure

General Procedure for the Preparation of 6-Diazocyclohex-2-en-1-one Derivatives

1a and **1c** were prepared according to the literature.[1] **1b** and **1d**–**u** were prepared according to the literature.[2]

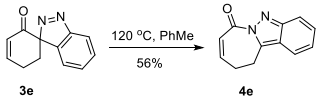
General Procedure for the Preparation of 3d–t.



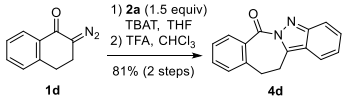
To a solution of diazo compound **1d** (52 mg, 0.30 mmol) and benzyne precursor **2a** (134 mg, 0.450 mmol, 1.5 equiv) in THF (3.0 mL) was added TBAT (243 mg, 0.450 mmol, 1.5 equiv) at 0 ^oC. Then the mixture was warmed to room temperature. After **1d** was completely depleted monitoring on TLC, the solvent was removed and the resulting residue was purified by flash column chromatography (PE:EA = 10:1) to give **3d** (69 mg, 93%) as a white solid.

3e–**t** were prepared following a similar method. Conditions: **1** (0.30 mmol), **2** (0.45 mmol, 1.5 equiv), TBAT (0.45 mmol, 1.5 equiv), solvent (3 mL), 0 to 20 ^oC, air.

Procedure for the Preparation of Fused-2*H*-indazole 4e–u

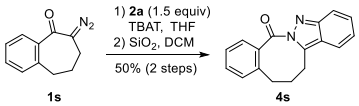


A solution of **3e** (48 mg, 0.24 mmol) in PhMe (2.4 mL) was heated to 110 ^oC and kept for 12 h. The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography (PE:EA = 1:2) to give **4e** (27 mg, 56%) as a light yellow oil.

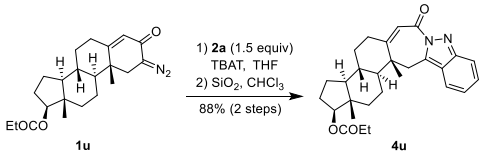


To a solution of diazo compound **1d** (52 mg, 0.30 mmol) and benzyne precursor **2a** (134 mg, 0.450 mmol, 1.5 equiv) in THF (3.0 mL) was added TBAT (243 mg, 0.450 mmol, 1.5 equiv) at 0 ^oC. Then the mixture was warmed to room temperature. After **1d** was completely depleted monitoring on TLC, the solvent was removed, and the resulting residue was redissolved in TFA/$CHCl_3$ (1 M, 1.0 mL) at room temperature and the solution was stirred for 5 min. After full conversion, the solvent was removed under reduced pressure and the resulting residue was purified by flash column chromatography (EA) to give **4d** (60 mg, 81% for two steps) as a light

yellow oil.

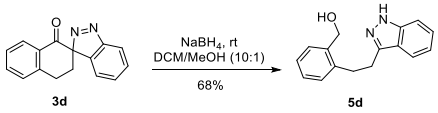


To a solution of diazo compound **1s** (59 mg, 0.32 mmol) and benzyne precursor **2a** (143 mg, 0.479 mmol, 1.5 equiv) in THF (3.2 mL) was added TBAT (259 mg, 0.480 mmol, 1.5 equiv) at 0 ^{o}C. Then the mixture was warmed to room temperature. After **1s** was completely depleted monitoring on TLC, the solvent was removed and the resulting residue was passed through a short silica gel column to get the crude spiro indazole **3s**. Then the crude product was redissolved in DCM (3 mL) and added SiO_2 (200 mg). The solution was stirred at room temperature. After full conversion, the solvent was removed under reduced pressure and the resulting residue was purified by flash column chromatography (PE:EA = 1:1) to give **4s** (42 mg, 50% for two steps) as a yellow oil.



To a solution of diazo compound **1u** (75 mg, 0.20 mmol) and benzyne precursor **2a** (89 mg, 0.30 mmol, 1.5 equiv) in THF (2.0 mL) was added TBAT (162 mg, 0.300 mmol, 1.5 equiv) at 0 ^{o}C. Then the mixture was warmed to room temperature. After **1u** was completely depleted monitoring on TLC, the solvent was removed and the resulting residue was passed through a short silica gel column to get the crude spiro indazole **3u**. Then the crude product was redissolved in $CHCl_3$ (2 mL) and added SiO_2 (125 mg). The solution was stirred at room temperature. After full conversion, the solvent was removed under reduced pressure and the resulting residue was purified by flash column chromatography (PE:EA = 1:2) to give **4u** (78 mg, 88% for two steps) as a yellow oil.

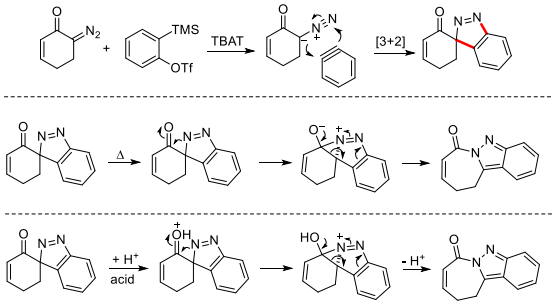
Procedure for the Preparation of 5d



To a solution of spiroindazole **3d** (19 mg, 0.080 mmol) in DCM/MeOH (2.0 mL, 10:1) was added $NaBH_4$ (ca. 5.0 mg, 0.13 mmol, 1.6 equiv) at room temperature. After the solution was stirred for 15 min, excess CH_3COCH_3 was added. Then the solvent was removed and the resulting residue was purified by flash column chromatography (EA) to give **5d** (13 mg, 68%) as a white solid.

3. Proposed Mechanisms for the Formation of Spiro-3*H*-indazoles and Fused-2*H*-indazoles

The mechanisms were proposed according to the literature.[3]



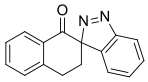
4. References

1. Y. Jiang, V. Z. Y. Khong, E. Lourdusamya and C.-M. Park, *Chem. Comm.*, 2012, **48**, 3133.

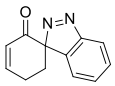
2. L. Zhao, J. Wang, H. Zheng, Y. Li, K.Yang, B. Cheng, X. Jin, X. Yao and H. Zhai, *Org. Lett.*, 2014, **16**, 6378.

3. (a) M. P. Sammes and A. R. Katritzky, *Adv. Heterocycl. Chem.*, 1983, **34**, 1; (b) Z. Liu, F. Shi, P. D. G. Martinez, C. Raminelli and R. C. Larock, *J. Org. Chem.*, 2008, **73**, 219; (c) D. Vuluga, J. Legros, B. Crousse and D. Bonnet-Delpon, *Green Chem.*, 2009, **11**, 156.

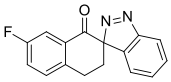
5. Characterization Data of Products.



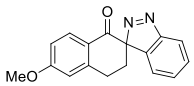
3d (69 mg, Y = 93%, R_f = 0.5 (PE:EA = 5:1)) was isolated as a white solid; mp 107−108 ℃. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.21 (d, J = 7.6 Hz, 1H), 7.94 (dd, J = 7.6, 0.6 Hz, 1H), 7.71 (td, J = 7.6, 1.2 Hz, 1H), 7.66−7.62 (m, 2H), 7.57−7.53 (m, 2H), 7.44 (t, J = 7.2 Hz, 1H), 3.75−3.68 (m, 1H), 3.42−3.34 (m, 1H), 2.69−2.62 (m, 1H), 2.53−2.46 (m, 1H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 189.3, 159.2, 145.4, 142.5, 135.3, 132.8, 130.9, 130.4, 130.4, 128.6, 127.9, 123.7, 122.4, 101.5, 32.2, 27.6; ESI-HRMS *m/z* calcd for $C_{16}H_{13}N_2O$ $[M + H]^+$ 249.1022, found 249.1021.



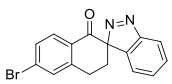
3e (47 mg, Y = 79%, R_f = 0.3 (PE:EA = 2:1)) was isolated as a white solid; mp 98−99 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) 8.17 (d, J = 7.5 Hz, 1H), 7.59−7.53 (m, 1H), 7.52−7.45 (m, 2H), 7.41−7.35 (m, 1H), 6.36 (dt, J = 10.2, 2.1 Hz, 1H), 3.15−3.02 (m, 1H), 2.81−2.69 (m, 1H), 2.50−2.42 (m, 1H), 2.38−2.29 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.3, 158.0, 152.1, 140.4, 130.2, 129.6, 129.6, 122.4, 122.2, 99.8, 31.0, 24.9; ESI-HRMS *m/z* calcd for $C_{12}H_{11}N_2O$ $[M + H]^+$ 199.0866, found 199.0864.



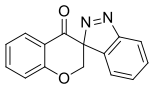
3f (64 mg, Y = 80%, R_f = 0.7 (PE:EA = 2:1)) was isolated as a white solid; mp 99−100 ℃. ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 8.23−8.20 (m, 1H), 7.69−7.63 (m, 3H), 7.60−7.48 (m, 3H), 3.75−3.65 (m, 1H), 3.43−3.34 (m, 1H), 2.75−2.65 (m, 1H), 2.52−2.44 (m, 1H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 188.7, 162.4 (d, J = 243.7 Hz), 159.3, 142.2, 141.6 (d, J = 2.3 Hz), 134.3 (d, J = 6.0 Hz), 132.8 (d, J = 7.5 Hz), 131.1, 130.5, 123.8, 122.7 (d, J = 21.8 Hz), 122.5, 113.9 (d, J = 21.8 Hz), 101.1, 32.3, 27.1; ESI-HRMS *m/z* calcd for $C_{16}H_{12}FN_2O$ $[M + H]^+$ 267.0928, found 267.0927.



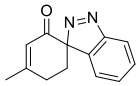
3g (65 mg, Y = 78%, R_f = 0.5 (PE:EA = 2:1)) was isolated as a yellow oil. ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 8.20−8.17 (m, 1H), 7.90 (d, J = 8.7 Hz, 1H), 7.65−7.61 (m, 1H), 7.61−7.58 (m, 1H), 7.55−7.50 (m, 1H), 7.06 (d, J = 2.4 Hz, 1H), 6.98 (dd, J = 8.7, 2.4 Hz, 1H), 3.95 (s, 3H), 3.72−3.62 (m, 1H), 3.39−3.29 (m, 1H), 2.63−2.44 (m, 2H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 187.6, 165.4, 159.2, 148.0, 142.8, 131.1, 130.8, 130.2, 126.2, 123.6, 122.3, 114.9, 113.7, 101.3, 56.1, 32.2, 27.9; ESI-HRMS *m/z* calcd for $C_{17}H_{15}N_2O_2$ $[M + H]^+$ 279.1128, found 279.1129.



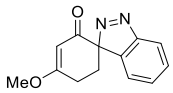
3h (93 mg, Y = 95%, R_f = 0.15 (DCM:PE = 1:1)) was isolated as a white solid; mp 103−104 ℃. ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 8.21 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 2.4 Hz, 1H), 7.86 (dd, J = 8.1, 2.1 Hz, 1H), 7.69−7.64 (m, 2H), 7.59−7.54 (m, 2H), 3.74−3.63 (m, 1H), 3.41−3.32 (m, 1H), 2.76−2.67 (m, 1H), 2.51−2.43 (m, 1H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 188.4, 159.3, 144.6, 142.1, 137.9, 134.4, 132.7, 131.1, 130.8, 130.5, 123.8, 122.5, 121.2, 101.1, 32.0, 27.3; ESI-HRMS *m/z* calcd For $C_{16}H_{12}BrN_2O$ $[M + H]^+$ 327.0128, found 327.0132.



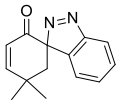
3i (51 mg, Y = 68%, R_f = 0.9 (DCM:EA = 30:1)) was isolated as a white solid; mp 112−113 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (d, J = 7.8 Hz, 1H), 7.95 (dd, J = 7.8, 1.2 Hz, 1H), 7.69−7.59 (m, 2H), 7.50−7.40 (m, 2H), 7.26−7.13 (m, 2H), 5.07 (d, J = 11.7 Hz, 1H), 4.45 (d, J = 11.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.2, 161.7, 158.7, 137.3, 137.2, 130.7, 130.4, 128.4, 122.8, 122.6, 122.6, 120.4, 118.5, 97.4, 70.8; ESI-HRMS *m/z* calcd for $C_{15}H_{11}N_2O_2$ $[M + H]^+$ 251.0815, found 251.0816.



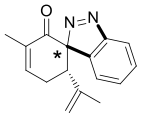
3j (55 mg, Y = 87%, R_f = 0.6 (PE:EA = 2:1)) was isolated as a white solid; mp 112−113 ℃. ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 8.16−8.13 (m, 1H), 7.63−7.58 (m, 2H), 7.55−7.50 (m, 1H), 6.14−6.12 (m, 1H), 3.05−2.94 (m, 1H), 2.83−2.73 (m, 1H), 2.49−2.41 (m, 1H), 2.38−2.30 (m, 1H), 2.21 (s, 3H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 189.1, 166.1, 159.0, 142.3, 130.7, 130.2, 126.4, 123.5, 122.2, 100.2, 31.2, 30.1, 24.5; ESI-HRMS *m/z* calcd for $C_{13}H_{12}N_2O + H^+$ $[M + H]^+$ 213.1022, found 213.1021.



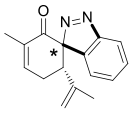
3k (45 mg, Y = 66%, R_f = 0.5 (PE:EA = 2:1)) was isolated as a red solid; mp 102−103 ℃. ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 8.14 (dd, J = 7.5, 0.6 Hz, 1H), 7.64−7.58 (m, 2H), 7.55−7.51 (m, 1H), 5.66 (s, 1H), 3.91 (s, 3H), 3.05−2.94 (m, 1H), 2.83−2.73 (m, 1H), 2.49−2.30 (m, 2H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 188.6, 180.0, 159.2, 142.8, 130.6, 130.1, 123.4, 122.2, 103.0, 100.3, 56.8, 29.9, 27.9; ESI-HRMS *m/z* calcd for $C_{13}H_{13}N_2O_2$ $[M + H]^+$ 229.0972, found 229.0971.



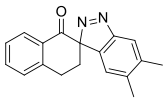
3l (60 mg, Y = 88%, R_f = 0.25 (PE:EA = 5:1)) was isolated as a white solid; mp 68−69 ℃. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.17−8.15 (m, 1H), 7.66−7.64 (m, 1H), 7.63−7.55 (m, 2H), 7.21 (d, *J* = 10.4 Hz, 1H), 6.16 (d, *J* = 10.0 Hz, 1H), 2.84 (d, *J* = 14.4 Hz, 1H), 1.72 (dd, *J* = 14.4, 2.0 Hz, 1H), 1.60 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 189.6, 162.0, 159.3, 143.7, 130.9, 130.0, 126.9, 123.8, 122.1, 102.4, 45.2, 34.7, 31.1, 29.0; ESI-HRMS *m/z* calcd for $C_{14}H_{15}N_2O$ $[M + H]^+$ 227.1179, found 227.1176.



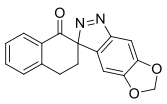
3m-a (32 mg, Y = 42%, R_f = 0.35 (PE:EA = 5:1), with low polarity) was isolated as a colorless oil. ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 8.12−8.09 (m, 1H), 7.66−7.63 (m, 1H), 7.58−7.54 (m, 2H), 7.33−7.30 (m, 1H), 4.63−4.60 (m, 1H), 4.50−4.47 (m, 1H), 3.83−3.76 (m, 1H), 3.52−3.39 (m, 1H), 2.80−2.68 (m, 1H), 1.83−1.81(m, 3H), 1.25−1.24 (m, 3H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 190.0, 160.6, 148.0, 143.8, 141.7, 136.1, 130.3, 129.9, 124.9, 121.9, 114.7, 106.4, 51.5, 32.0, 22.0, 16.5; ESI-HRMS *m/z* calcd for $C_{16}H_{17}N_2O$ $[M + H]^+$ 253.1335, found 253.1333.



3m-b (30 mg, Y = 39%, R_f = 0.25 (PE:EA = 5:1), with high polarity) was isolated as a colorless oil. ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 8.14−8.11 (m, 1H), 7.64−7.58 (m, 2H), 7.52−7.47 (m, 1H), 7.28−7.24 (m, 1H), 4.54−4.52 (m, 1H), 4.32 (br s, 1H), 4.12−4.07 (m, 1H), 3.09−2.96 (m, 1H), 2.87−2.75 (m, 1H), 1.82−1.80 (m, 3H), 1.38−1.36 (m, 3H); ^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 189.6, 159.2, 147.5, 143.0, 138.4, 134.9, 130.5, 130.4, 124.1, 122.4, 114.4, 102.7, 48.4, 30.3, 23.0, 16.3; ESI-HRMS *m/z* calcd for $C_{16}H_{17}N_2O$ $[M + H]^+$ 253.1335, found 253.1334.

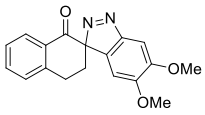


3n (71 mg, Y = 86%, R_f = 0.24 (PE:EA = 5:1)) was isolated as a white solid; mp 140−141 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 1H), 7.95 (s, 1H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.16 (s, 1H), 3.75−3.67 (m, 1H), 3.34−3.27 (m, 1H), 2.60−2.54 (m, 1H), 2.48−2.41 (m, 1H), 2.38 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3, 157.5, 144.1, 139.7, 139.1, 138.5, 134.5, 132.1, 129.3, 128.6, 127.2, 123.4, 122.8, 99.7, 31.9, 27.2, 20.5, 20.3; ESI-HRMS *m/z* calcd for $C_{18}H_{17}N_2O$ $[M + H]^+$ 277.1335, found 277.1336.

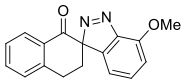


3o (70 mg, Y = 80%, R_f = 0.40 (PE:EA = 3:1)) was isolated as a light yellow solid; mp 189−190 ℃.

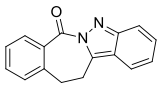
^{1}H NMR (400 MHz, $(CD_3)_2CO$) 7.93 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.71−7.67 (m, 1H), 7.62 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.48−7.41 (m, 1H), 7.14 (s, 1H), 6.21 (br s, 1H), 6.21 (br s, 1H), 3.79−3.71 (m, 1H), 3.40−3.25 (m, 1H), 2.84−2.75 (m, 1H), 2.31−2.25 (m, 1H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) *δ* 189.4, 154.5, 151.6, 150.1, 145.6, 139.3, 135.2, 134.0, 133.1, 130.4, 128.5, 127.8, 104.0, 102.3, 101.1, 32.8, 28.0; ESI-HRMS *m/z* calcd for $C_{17}H_{13}N_2O_3$ $[M + H]^+$ 293.0921, found 293.0918.



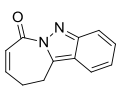
3p (65 mg, Y = 70%, R_f = 0.15 (PE:EA = 3:1)) was isolated as a light yellow solid; mp 178−179 ℃. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) *δ* 7.93 (d, *J* = 8.0 Hz, 1H), 7.74 (s, 1H), 7.70−7.66 (m, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.29 (s, 1H), 3.97 (s, 3H), 3.85 (s, 3H), 3.81−3.71 (m, 1H), 3.35−3.29 (m, 1H), 2.82−2.75 (m, 1H), 2.26−2.20 (m, 1H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) *δ* 189.8, 153.5, 152.8, 151.4, 145.6, 136.9, 135.1, 133.2, 130.3, 128.5, 127.8, 106.2, 104.7, 101.5, 56.5, 56.5, 32.9, 28.0; ESI-HRMS *m/z* calcd for $C_{18}H_{17}N_2O_3$ $[M + H]^+$ 309.1234, found 309.1233.



3q (77 mg, Y = 92%, R_f = 0.35 (PE:EA = 3:1)) was isolated as a yellow solid; mp 118−119 ℃. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) *δ* 7.94 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.70 (td, *J* = 7.6, 1.2 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.50−7.43 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.13 (dd, *J* = 7.2, 0.4 Hz 1H), 4.17 (s, 3H), 3.75−3.67 (m, 1H), 3.40−3.33 (m, 1H), 2.68−2.61 (m, 1H), 2.49−2.42 (m, 1H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) *δ* 189.8, 154.3, 148.5, 146.0, 145.9, 135.8, 133.4, 133.4, 130.9, 129.1, 128.4, 116.0, 114.7, 101.8, 57.9, 32.9, 28.0; ESI-HRMS *m/z* calcd for $C_{17}H_{15}N_2O_2$ $[M + H]^+$ 279.1128, found 279.1130.

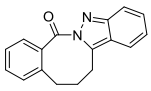


4d (60 mg, Y = 81% for two steps, R_f = 0.45 (PE:EA = 2:1)) was isolated as a light yellow oil. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) *δ* 7.98 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.52−7.44 (m, 2H), 7.40−7.38 (m, 1H), 7.35−7.31 (m, 2H), 7.08 (t, *J* =7.2, 1H), 3.52−3.48 (m, 2H), 3.32−3.28 (m, 2H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) *δ* 169.1, 146.3, 144.5, 142.3, 132.8, 132.1, 131.7, 130.9, 127.0, 126.9, 123.0, 121.1, 120.5, 110.8, 34.8, 30.0; ESI-HRMS *m/z* calcd for $C_{16}H_{13}N_2O$ $[M + H]^+$ 249.1022, found 249.1023.

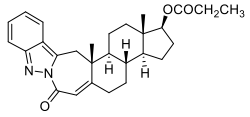


4e (27 mg, Y = 56%, R_f = 0.43 (PE:EA = 1:1)) was isolated as a light yellow oil. ^{1}H NMR (300

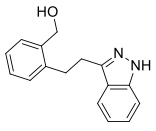
MHz, $CDCl_3$) δ 7.68 (d, J = 9.0 Hz, 1H), 7.49 (d, J = 8.7 Hz, 1H), 7.32−7.27 (m, 1H), 7.07−7.01 (m, 1H), 6.99−6.93 (m, 1H), 6.45 (dt, J = 12.3, 1.5 Hz, 1H), 3.43−3.39 (m, 2H), 2.74−2.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 150.2, 148.2, 136.4, 129.6, 125.5, 123.5, 121.0, 120.5, 119.3, 27.0, 23.3; ESI-HRMS *m/z* calcd for $C_{12}H_{11}N_2O$ $[M + H]^+$ 199.0866, found 199.0865.



4s (42 mg, Y = 50% for two steps, R_f = 0.1 (PE:EA = 5:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J = 7.6, 1.2 Hz, 1H), 7.74 (d, J = 9.2 Hz, 1H), 7.61 (dt, J = 8.8, 1.2 Hz, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.45 (dt, J = 8.8, 1.2 Hz, 1H), 7.35−7.31 (m, 1H), 7.27−7.26 (m, 1H), 7.06−7.02 (m, 1H), 2.91 (br s, 2H), 2.70 (t, J = 6.4 Hz, 2H), 2.00−1.94 (m, 2H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 166.6, 150.9, 139.8, 139.1, 135.1, 134.5, 132.6, 130.4, 130.3, 127.9, 123.8, 122.2, 122.0, 119.6, 32.1, 31.6, 21.9; ESI-HRMS *m/z* calcd for $C_{17}H_{15}N_2O$ $[M + H]^+$ 263.1179, found 263.1178.



4u (78 mg, Y = 88% for two steps, R_f = 0.40 (PE:EA = 1:1)) was isolated as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, J = 8.7 Hz, 1H), 7.49 (d, J = 8.7 Hz, 1H), 7.32−7.27 (m, 1H), 7.08−7.03 (m, 1H), 6.28 (s, 1H), 4.63 (t, J = 8.1 Hz, 1H), 3.59 (d, J = 15.0 Hz, 1H), 3.12 (d, J = 15.0 Hz, 1H), 2.58−2.39 (m, 2H), 2.34 (q, J = 7.5 Hz, 2H), 2.27−2.14 (m, 1H), 1.96−1.81 (m, 3H), 1.74−1.49 (m, 4H), 1.45−1.33 (m, 1H), 1.30−1.06 (m, 3H), 1.15 (t, J = 7.5 Hz, 4H), 1.01 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 169.8, 163.2, 150.2, 133.2, 129.2, 123.4, 122.3, 120.1, 119.3, 119.2, 82.1, 51.8, 50.5, 43.5, 42.6, 36.8, 36.6, 35.6, 33.7, 31.8, 27.8, 27.7, 23.5, 21.7, 18.7, 12.2, 9.3; ESI-HRMS *m/z* calcd for $C_{28}H_{35}N_2O_3$ $[M + H]^+$ 447.2642, found 447.2641.



5d (13 mg, Y = 68%, R_f = 0.5 (PE:EA = 1:1)) was isolated as a white solid; mp 132−133 ℃. ^{1}H NMR (400 MHz, CD_3OD) δ 7.62 (d, J = 8.0 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.35−7.31 (m, 2H), 7.17−7.15 (m, 3H), 7.06 (t, J = 7.2 Hz, 1H), 4.63 (s, 2H), 3.28−3.24 (m, 2H), 3.17−3.13 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ 147.2, 142.8, 141.1, 140.1, 130.7, 129.7, 128.9, 127.9, 127.5, 123.1, 121.3, 121.3, 111.2, 63.2, 33.4, 29.9; ESI-HRMS *m/z* calcd for $C_{16}H_{17}N_2O$ $[M + H]^+$ 253.1335, found 253.1334.

6. NMR spectra

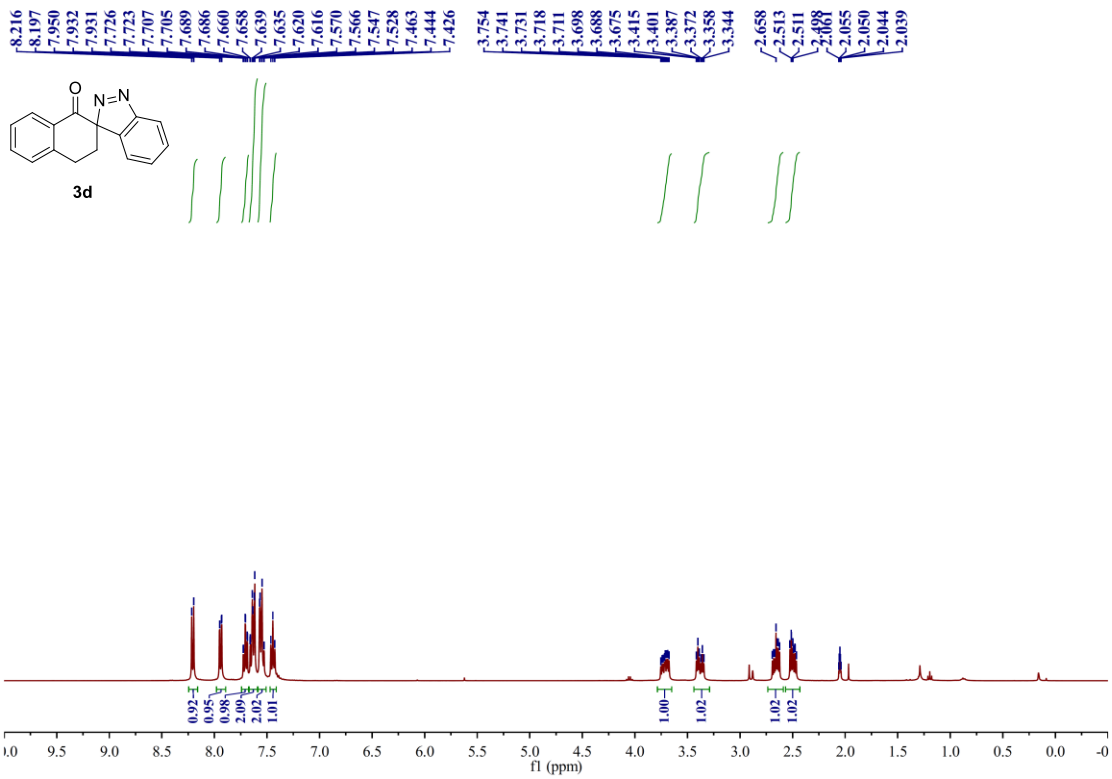


Fig. S1. ^{1}H NMR of compound **3d** (400 MHz, $(CD_3)_2CO$).

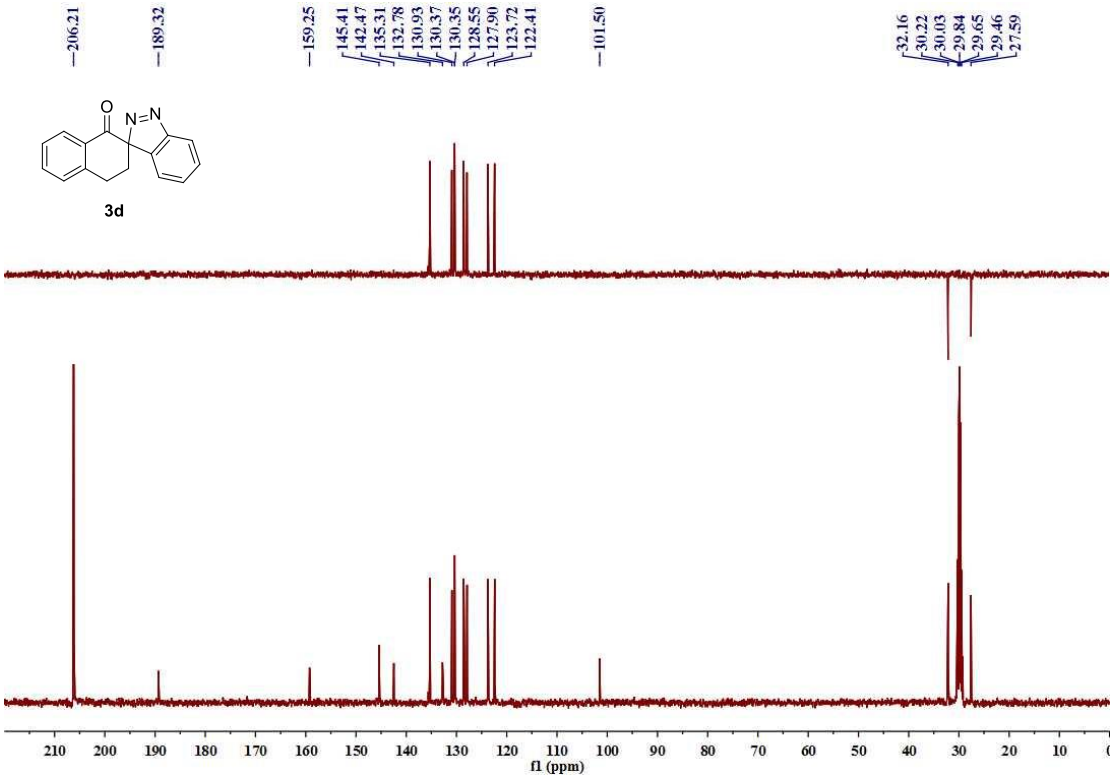


Fig. S2. ^{13}C and DEPT-135 NMR of compound **3d** (100 MHz, $(CD_3)_2CO$).

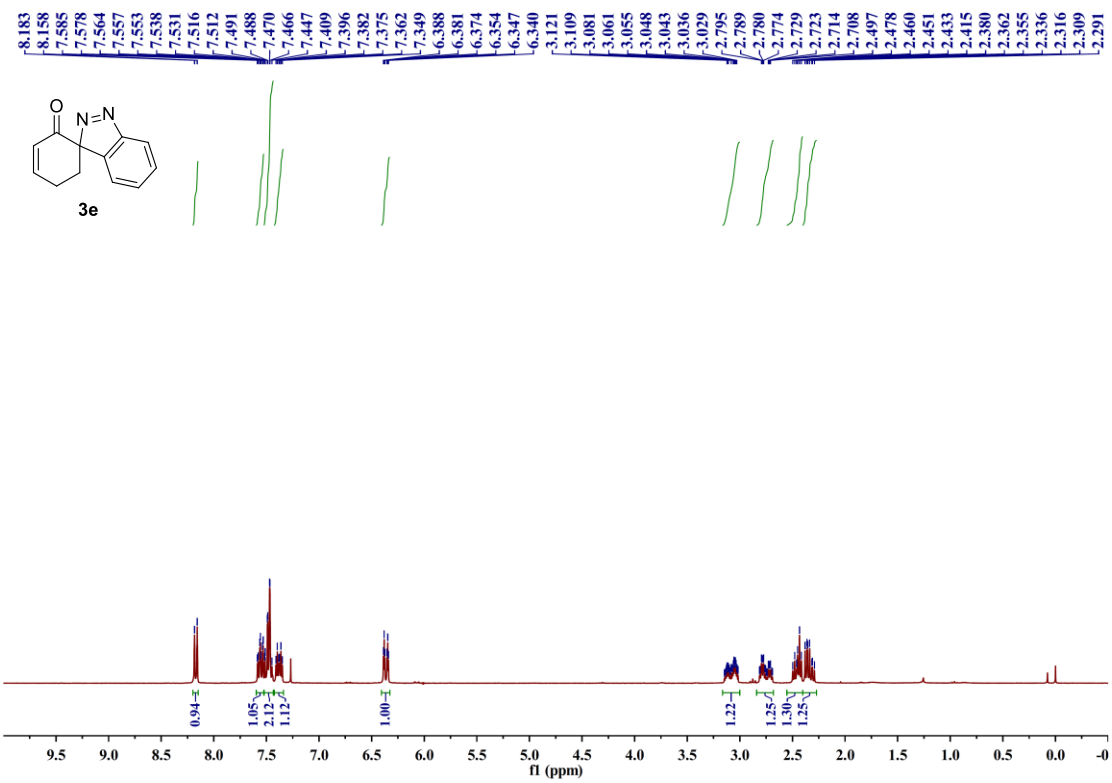


Fig. S3. ^{1}H NMR of compound **3e** (300 MHz, $CDCl_3$).

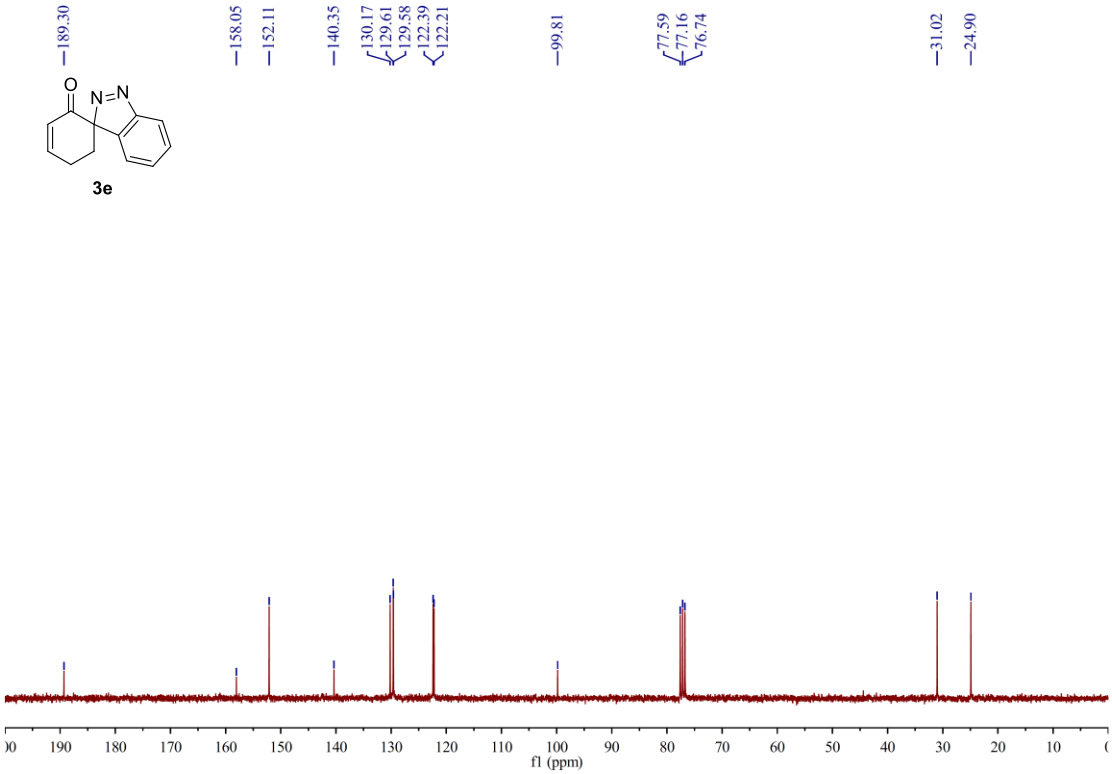


Fig. S4. ^{13}C NMR of compound **3e** (75 MHz, $CDCl_3$).

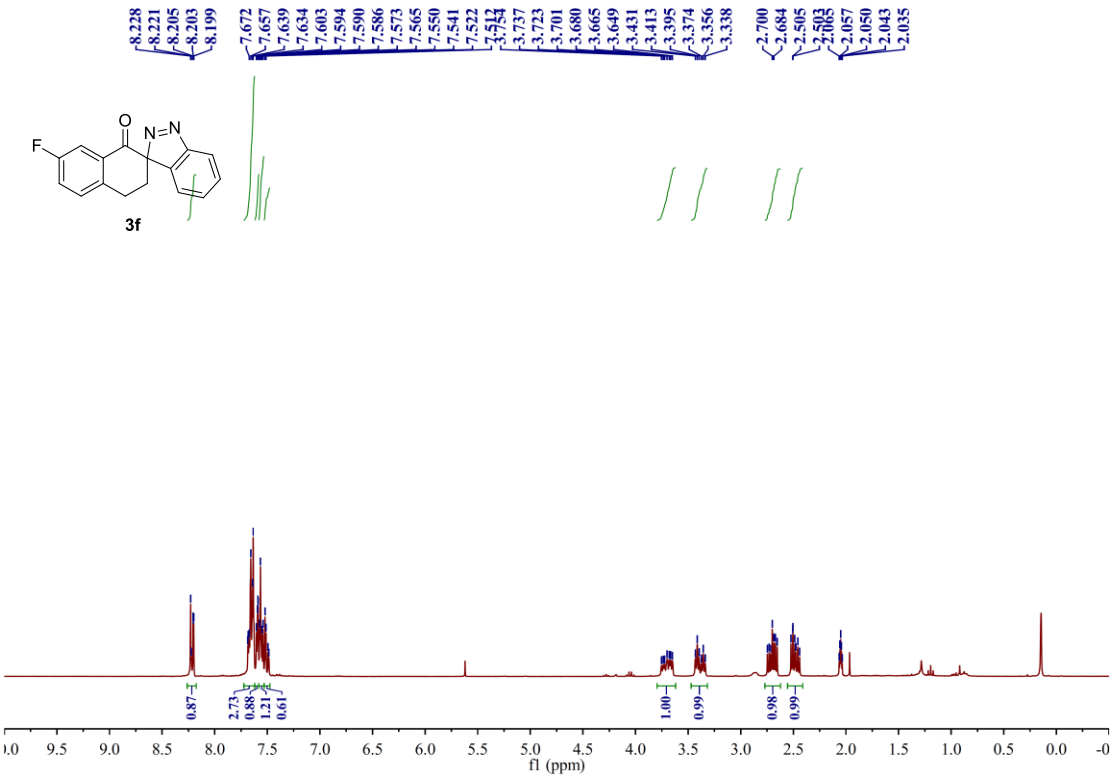


Fig. S5 ^{1}H NMR of compound **3f** (300 MHz, $(CD_3)_2CO$).

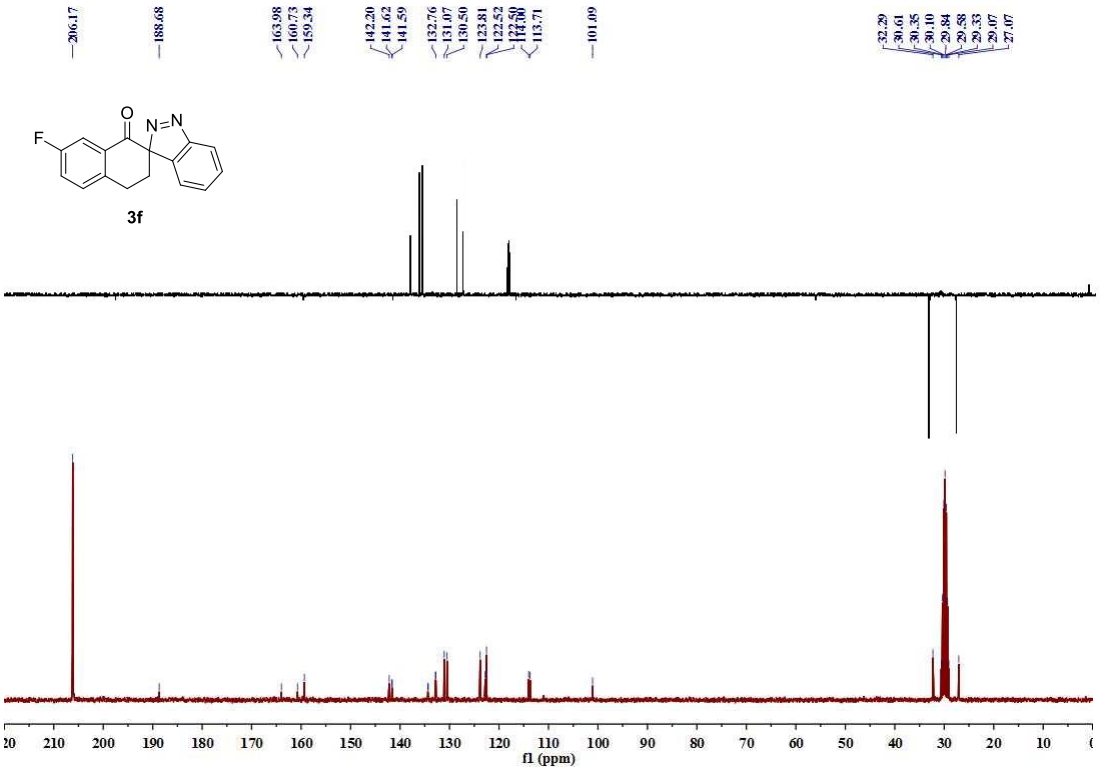


Fig. S6. ^{13}C and DEPT-135 NMR of compound **3f** (75 MHz, $(CD_3)_2CO$).

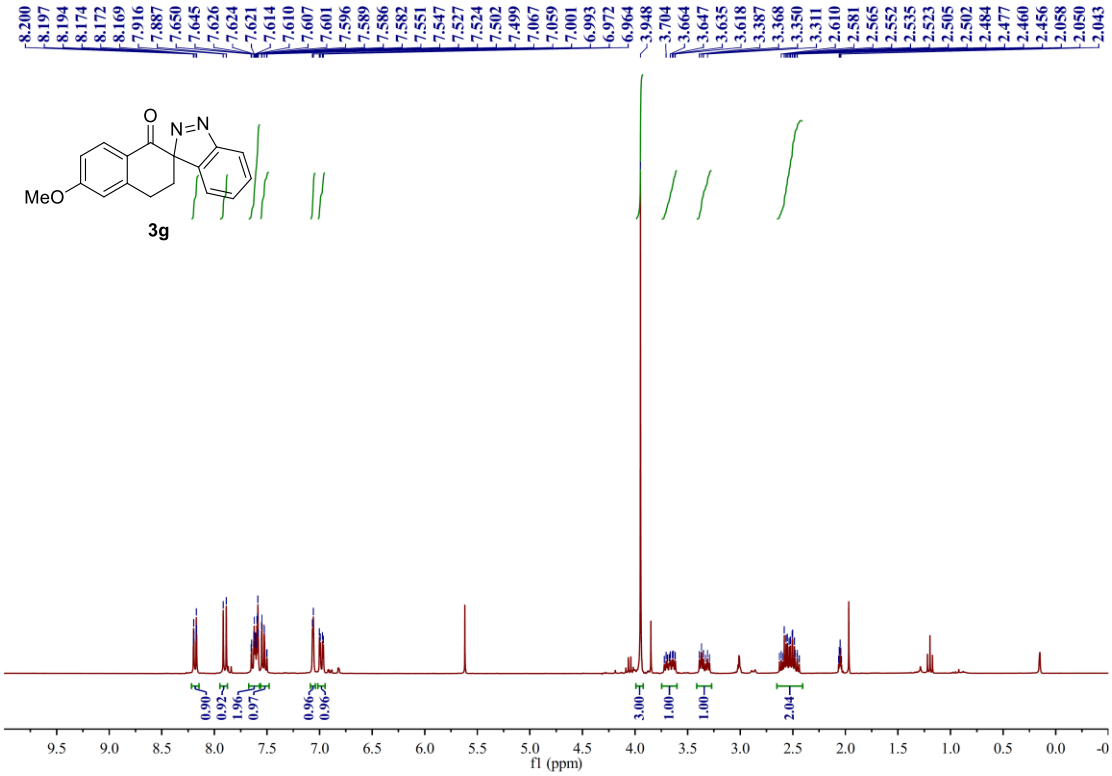


Fig. S7. ^{1}H NMR of compound **3g** (300 MHz, $(CD_3)_2CO$).

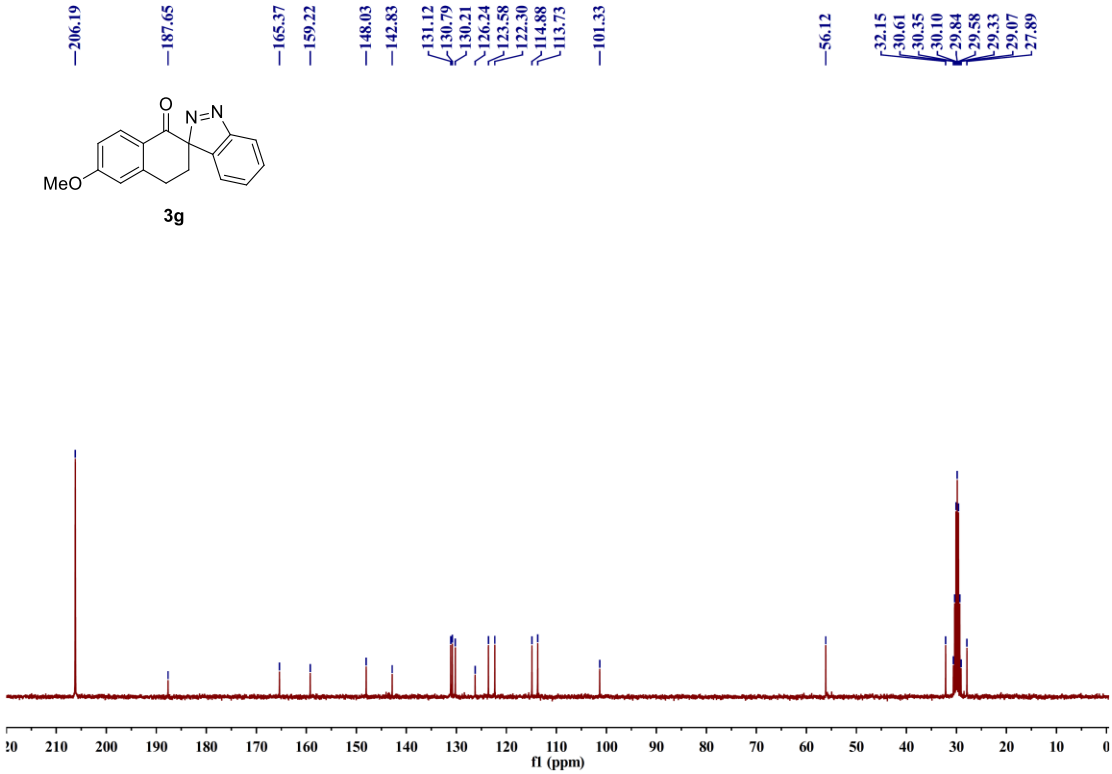


Fig. S8. ^{13}C NMR of compound **3g** (75 MHz, $(CD_3)_2CO$).

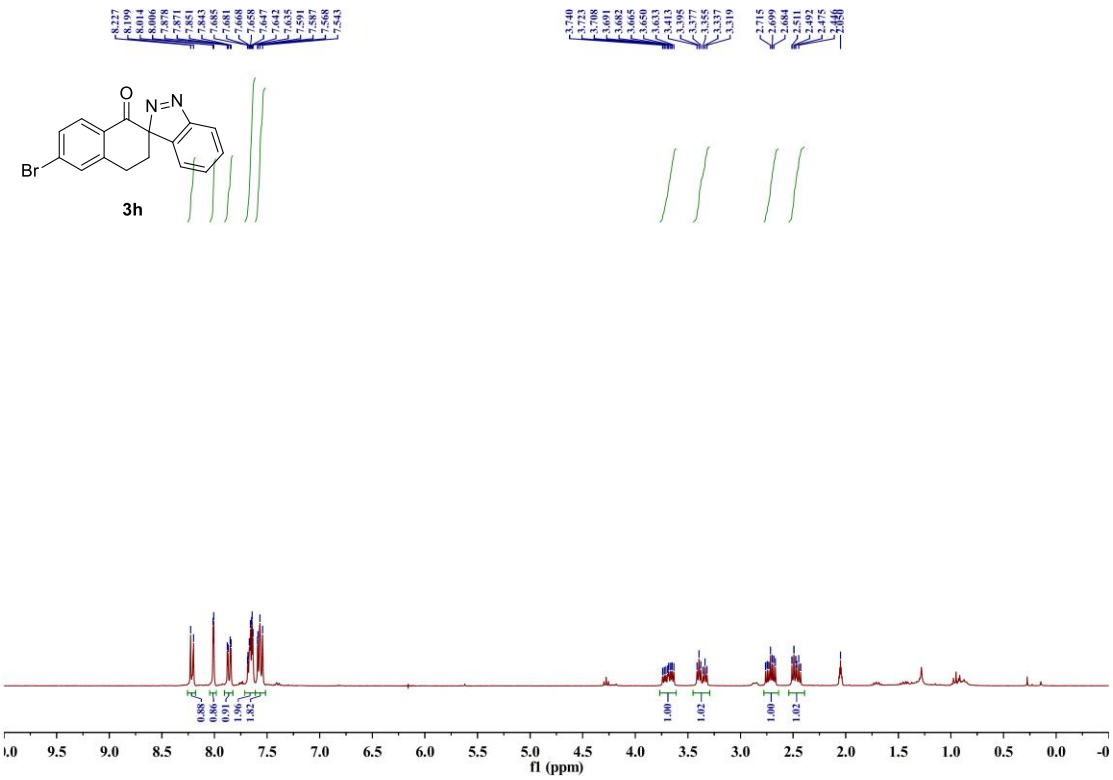


Fig. S9. ^{1}H NMR of compound **3h** (300 MHz, $(CD_3)_2CO$).

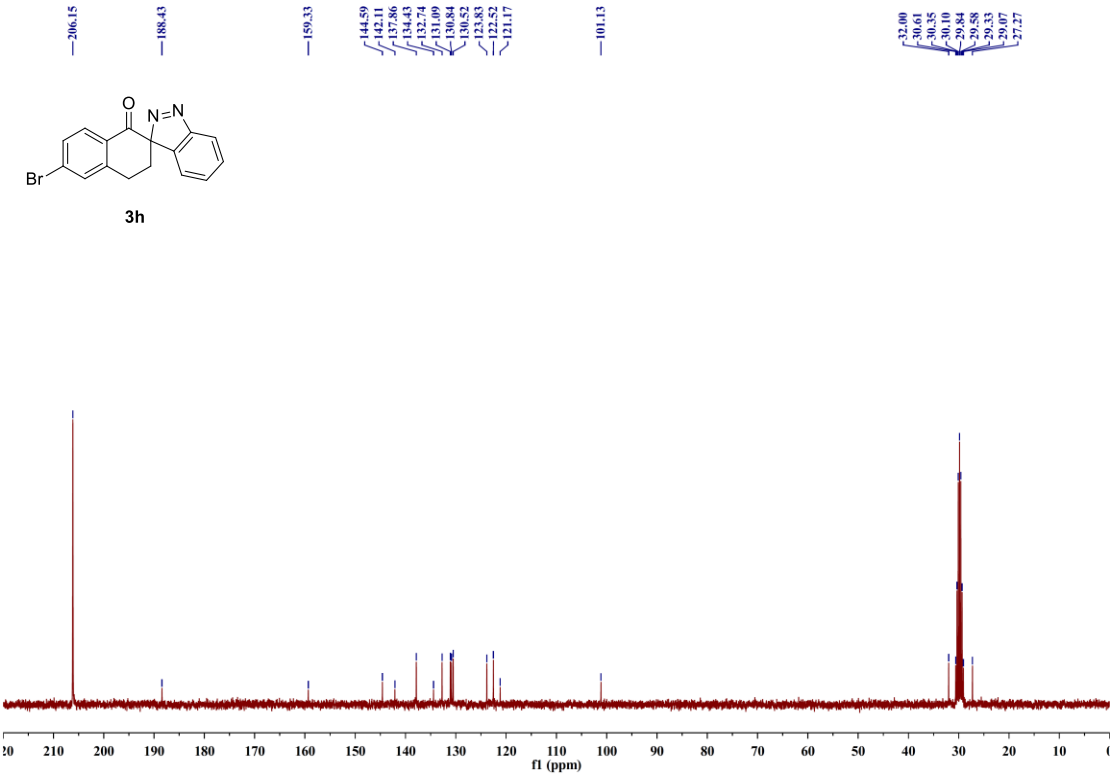


Fig. S10. ^{13}C NMR of compound **3h** (75 MHz, $(CD_3)_2CO$).

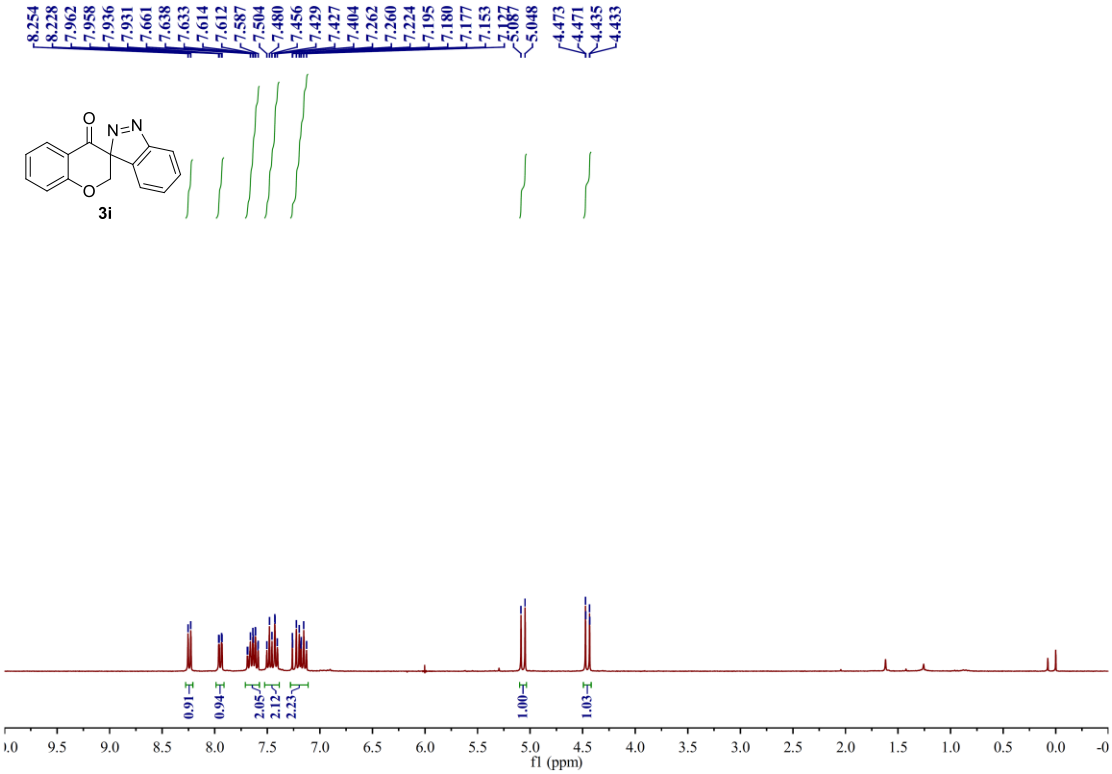


Fig. S11. ^{1}H NMR of compound **3i** (300 MHz, $CDCl_3$).

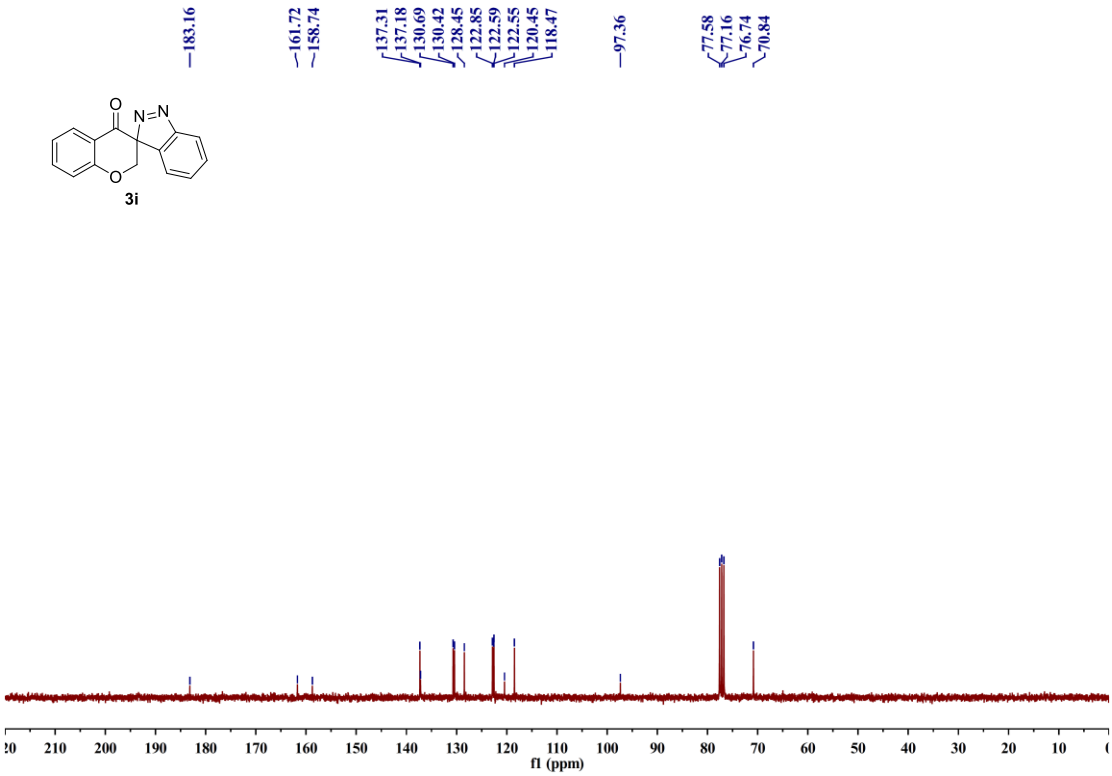


Fig. S12. ^{13}C NMR of compound **3i** (75 MHz, $CDCl_3$).

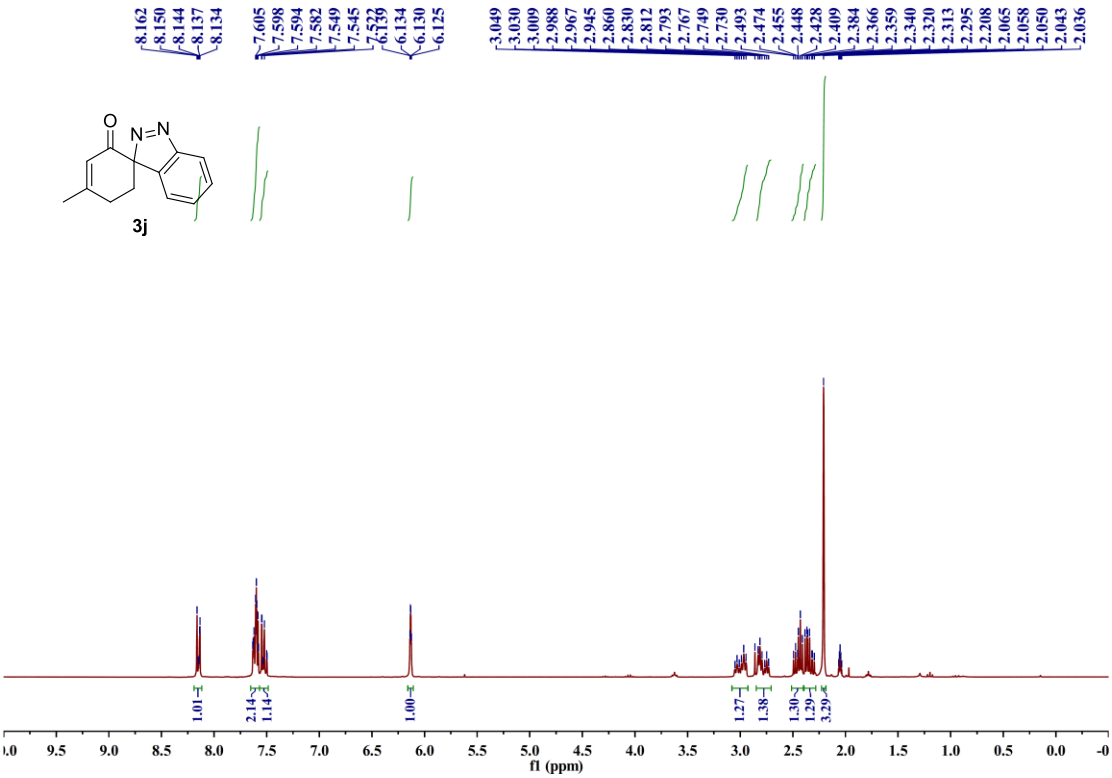


Fig. S13. ^{1}H NMR of compound **3j** (300 MHz, $(CD_3)_2CO$).

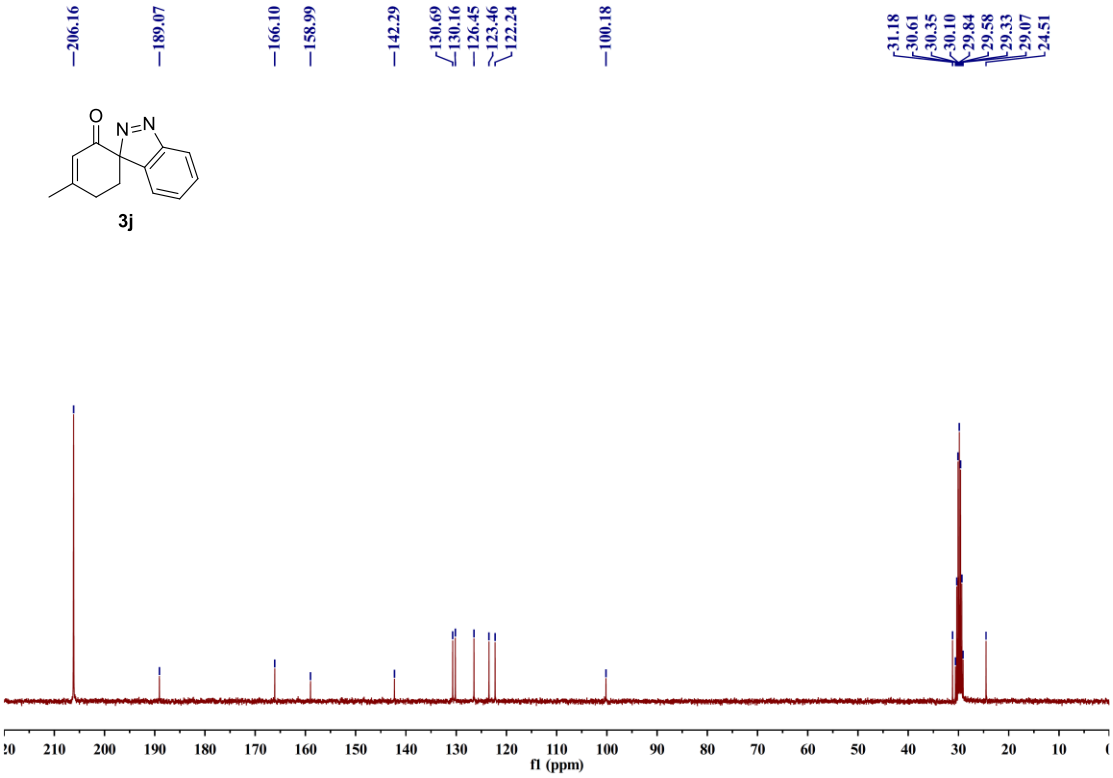


Fig. S14. ^{13}C NMR of compound **3j** (75 MHz, $(CD_3)_2CO$).

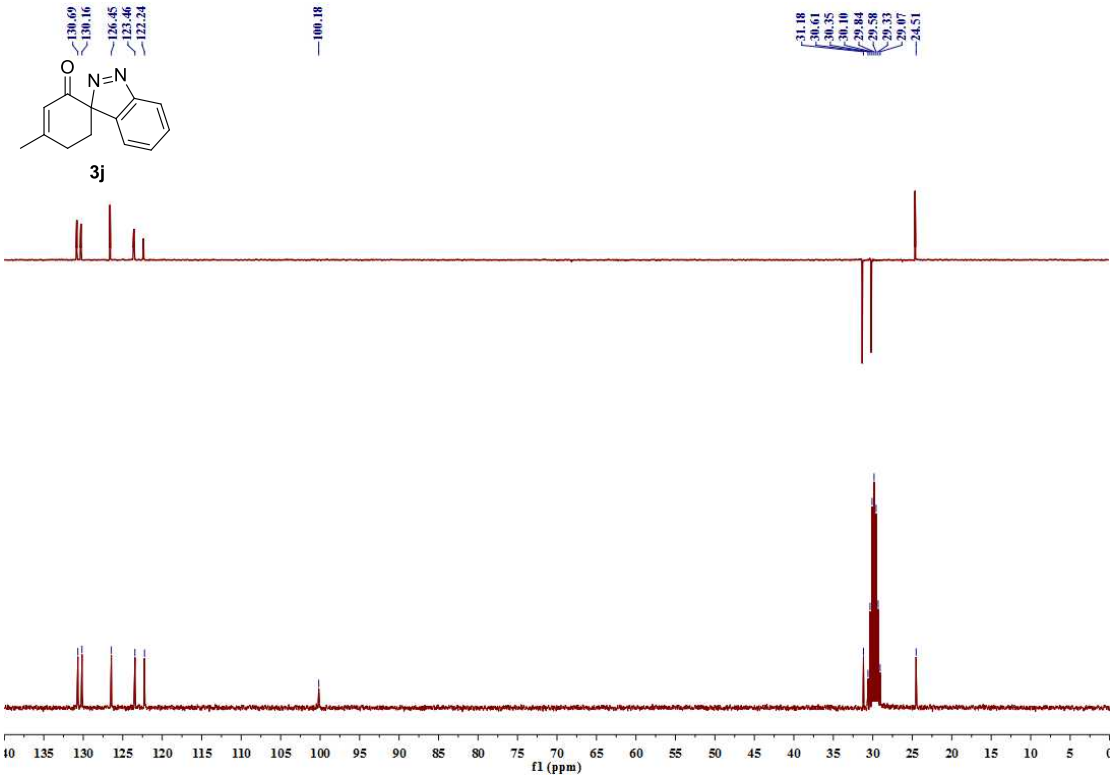


Fig. S15. ^{13}C and DEPT-135 NMR of compound **3j** (75 MHz, $(CD_3)_2CO$)

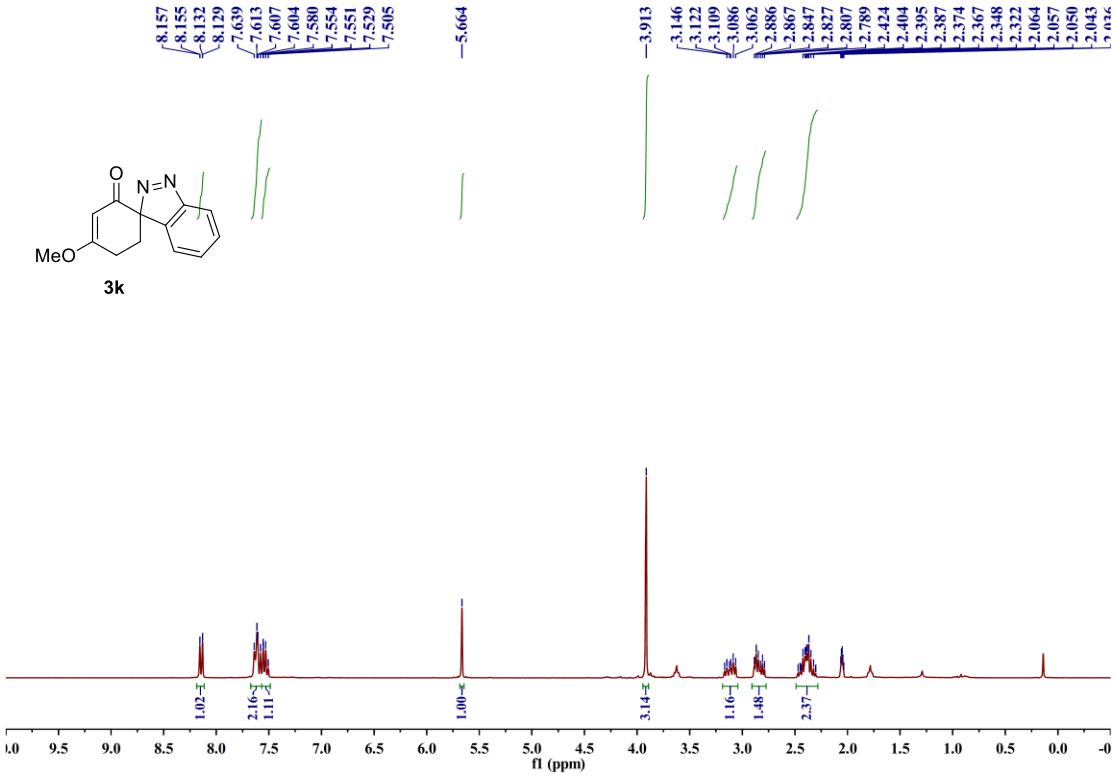


Fig. S16. ^{1}H NMR of compound **3k** (300 MHz, $(CD_3)_2CO$).

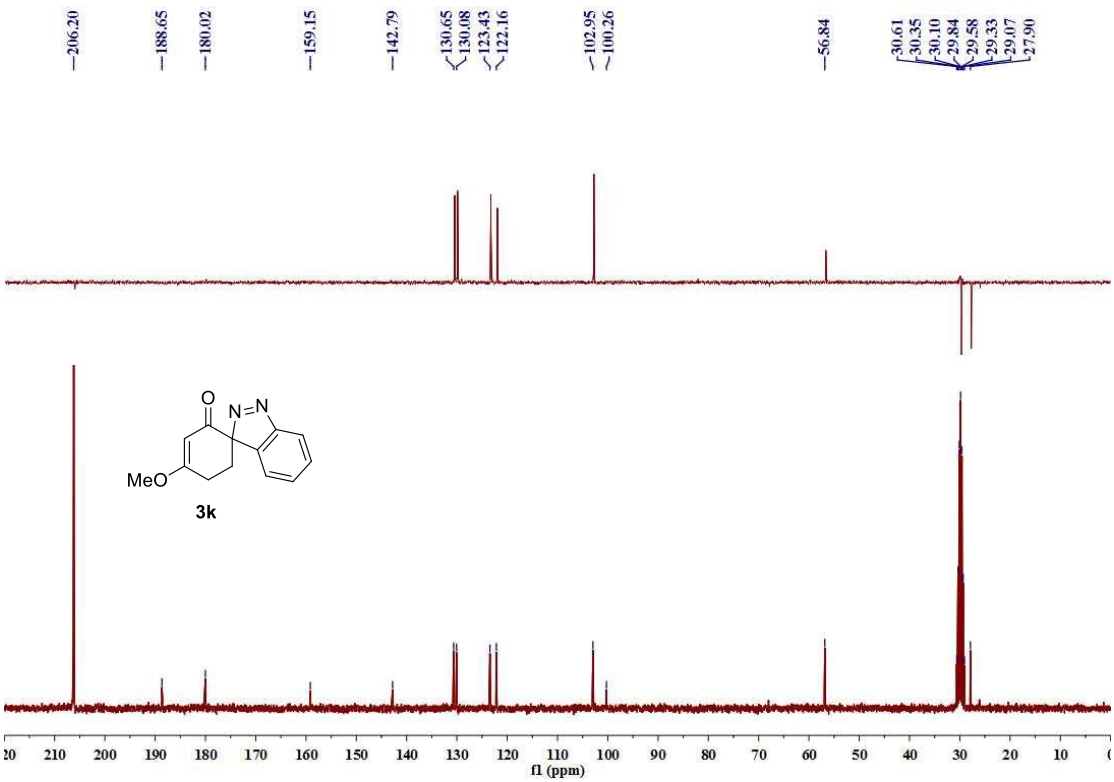


Fig. S17. ^{13}C and DEPT-135 NMR of compound **3k** (75 MHz, $(CD_3)_2CO$).

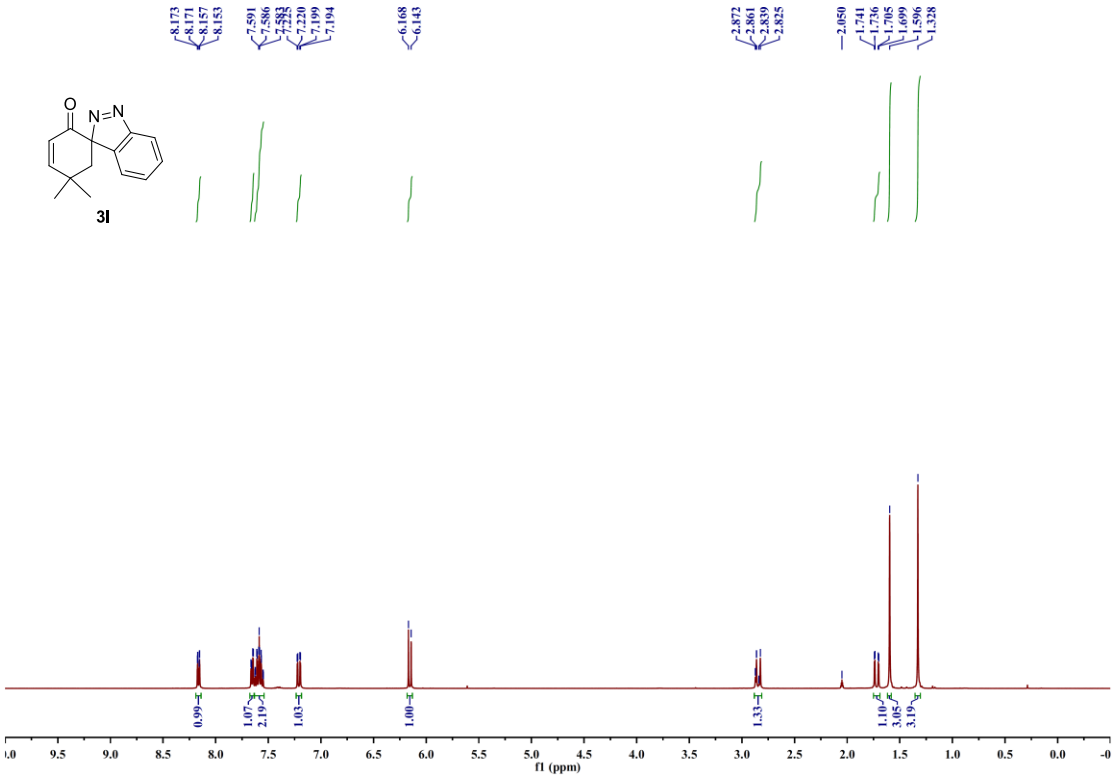


Fig. S18. ^{1}H NMR of compound **3l** (400 MHz, $(CD_3)_2CO$).

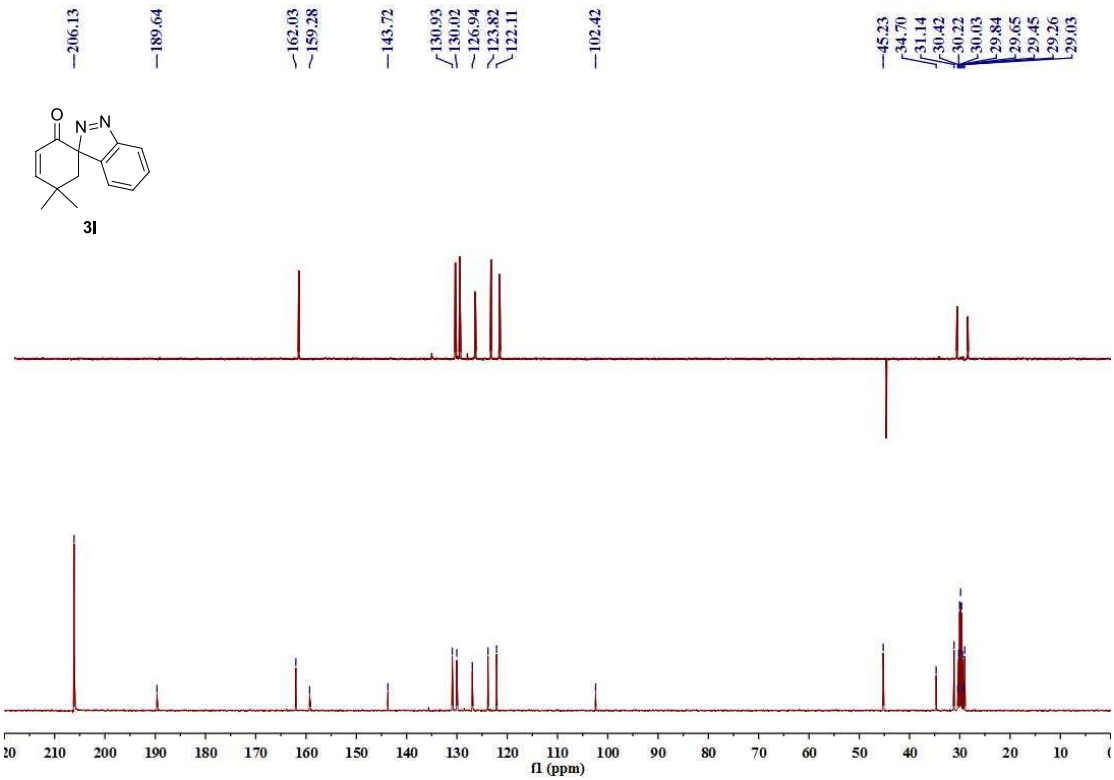


Fig. S19. ^{13}C and DEPT-135 NMR of compound **3l** (100 MHz, $(CD_3)_2CO$).

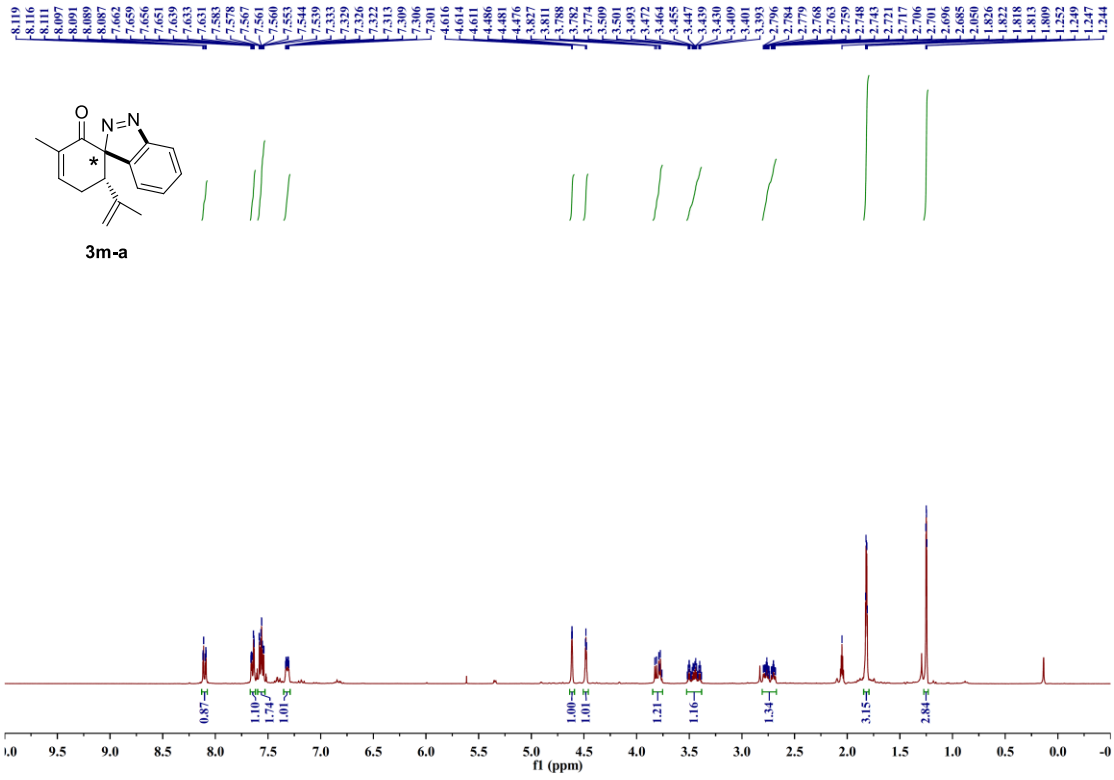


Fig. S20. ^{1}H NMR of compound **3m-a** (300 MHz, $(CD_3)_2CO$).

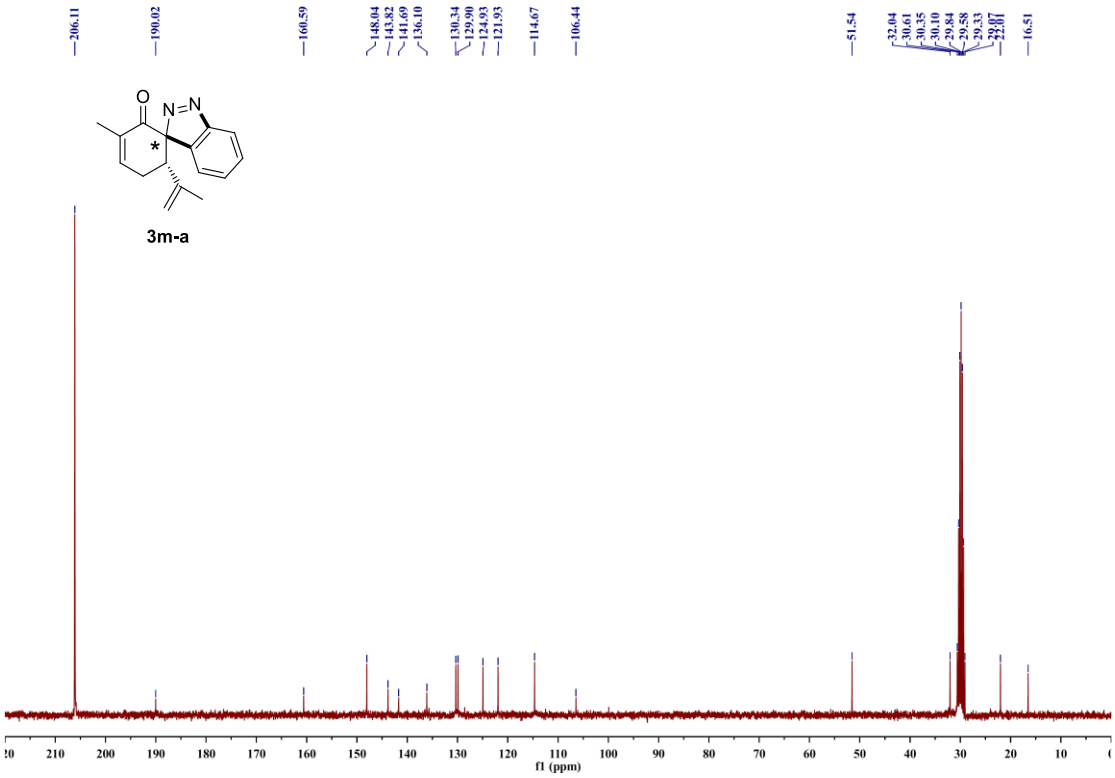


Fig. S21. ^{13}C NMR of compound **3m-a** (75 MHz, $(CD_3)_2CO$).

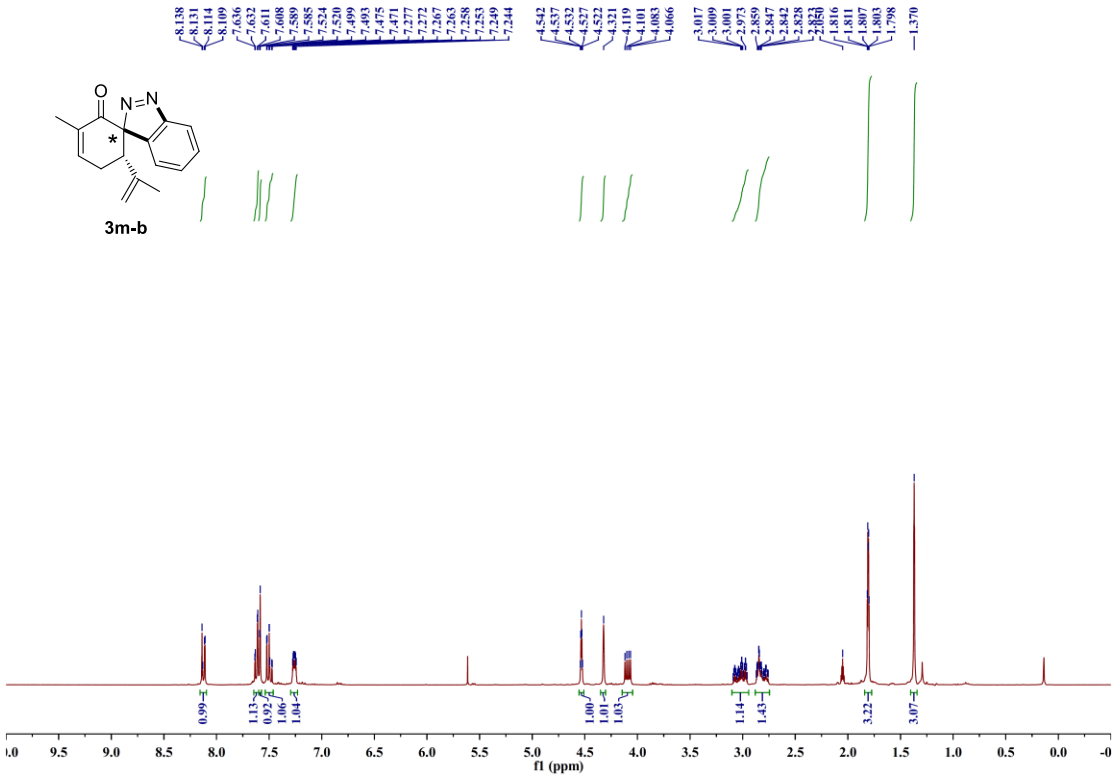


Fig. S22. ^{1}H NMR of compound **3m-b** (300 MHz, $(CD_3)_2CO$).

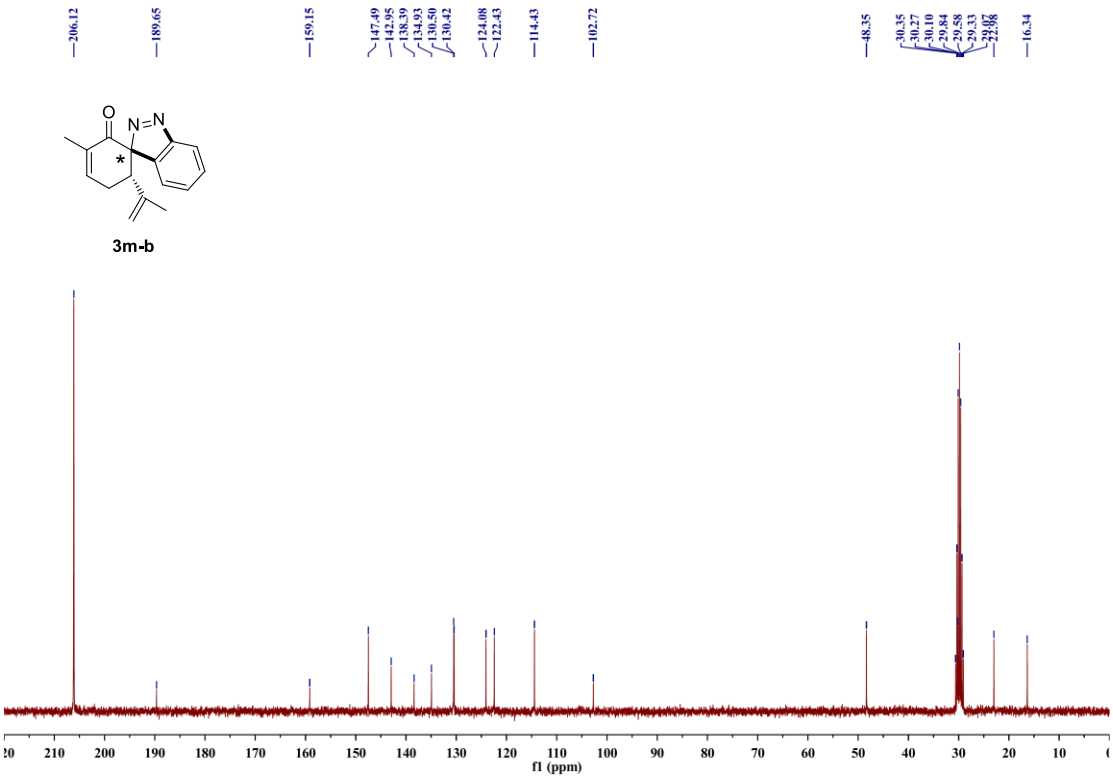


Fig. S23. ^{13}C NMR of compound **3m-b** (75 MHz, $(CD_3)_2CO$).

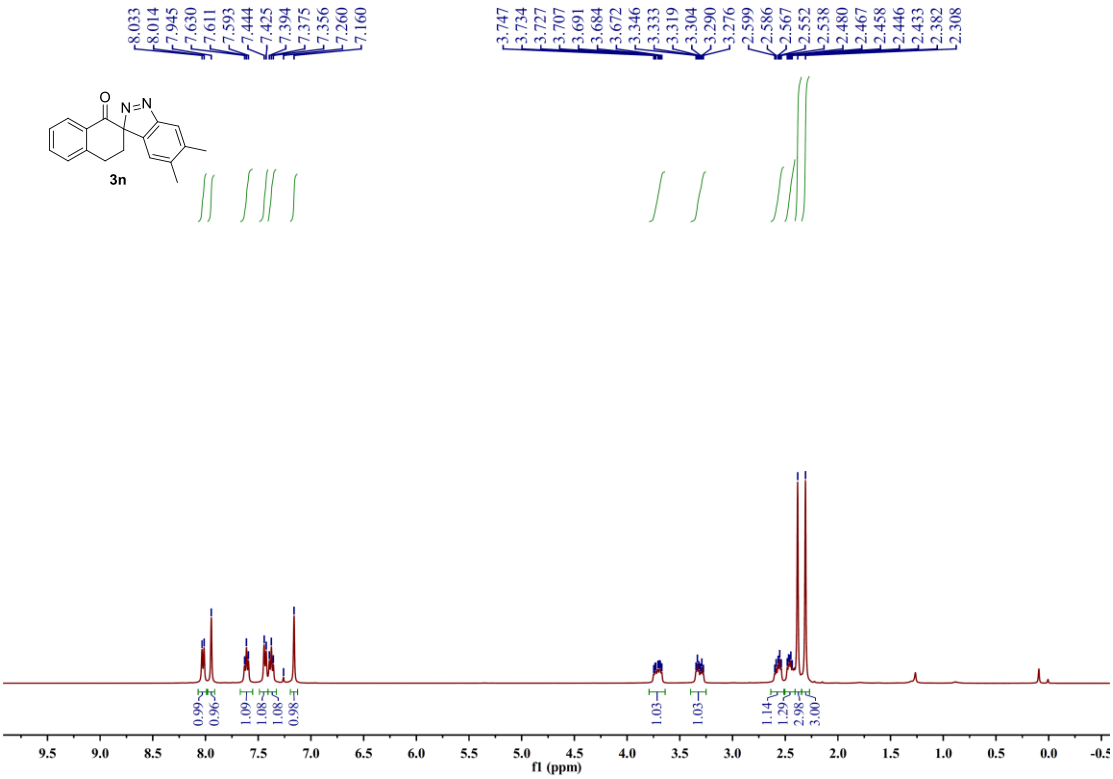


Fig. S24. ^{1}H NMR of compound **3n** (400 MHz, $CDCl_3$).

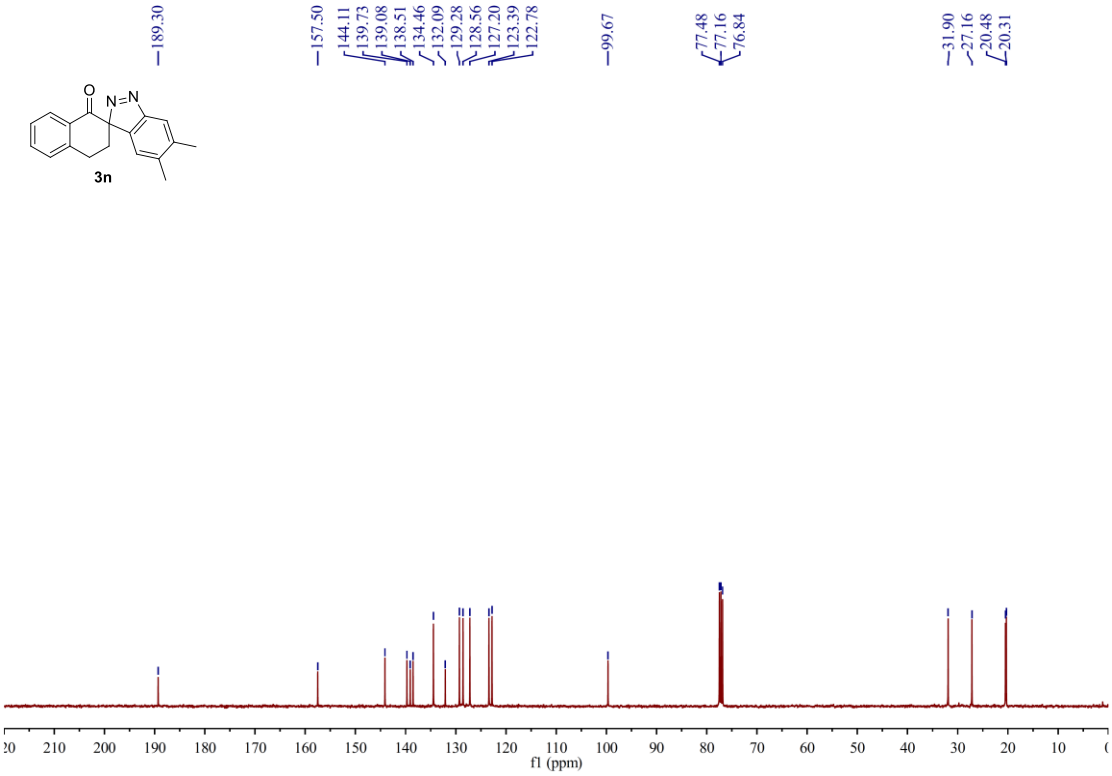


Fig. S25. ^{13}C NMR of compound **3n** (100 MHz, $CDCl_3$).

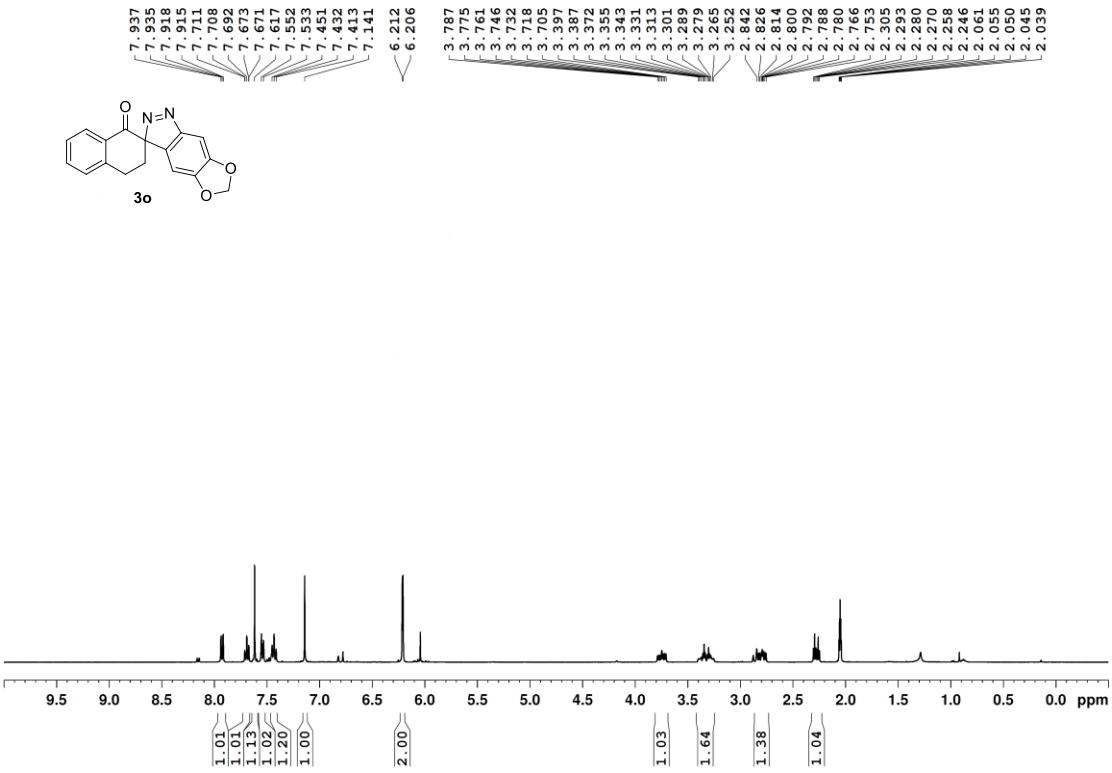


Fig. S26. ^{1}H NMR of compound **3o** (400 MHz, $(CD_3)_2CO$).

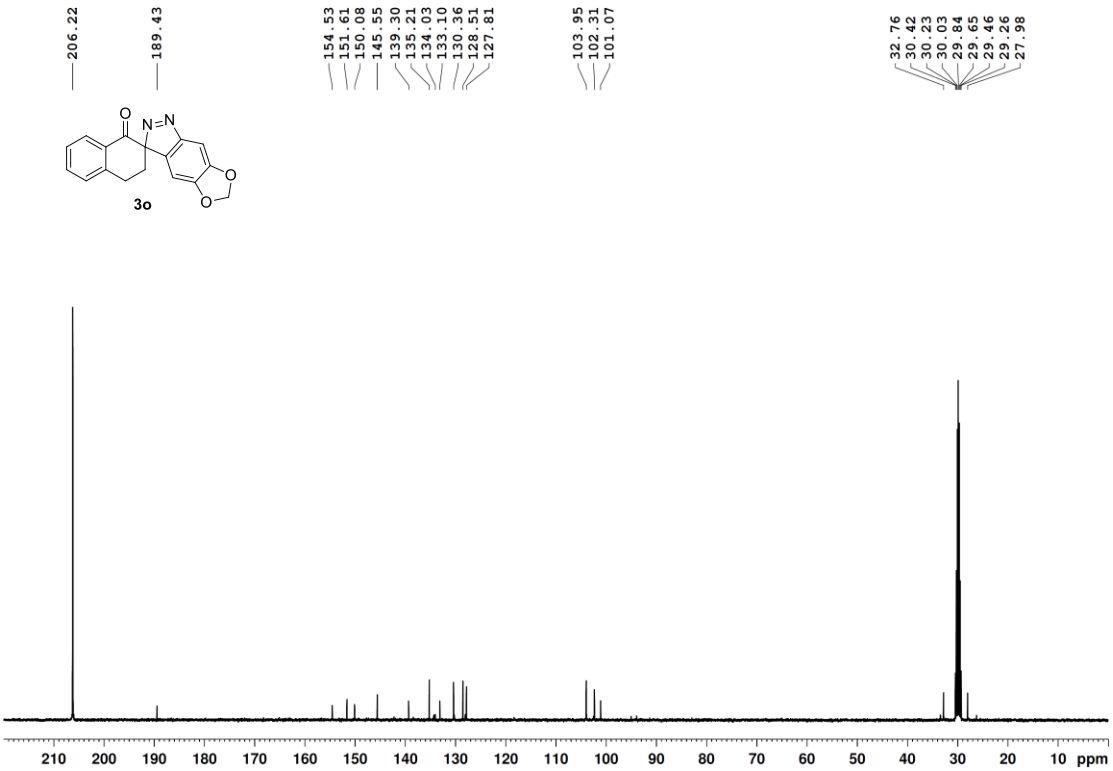


Fig. S27. ^{13}C NMR of compound **3o** (100 MHz, $(CD_3)_2CO$).

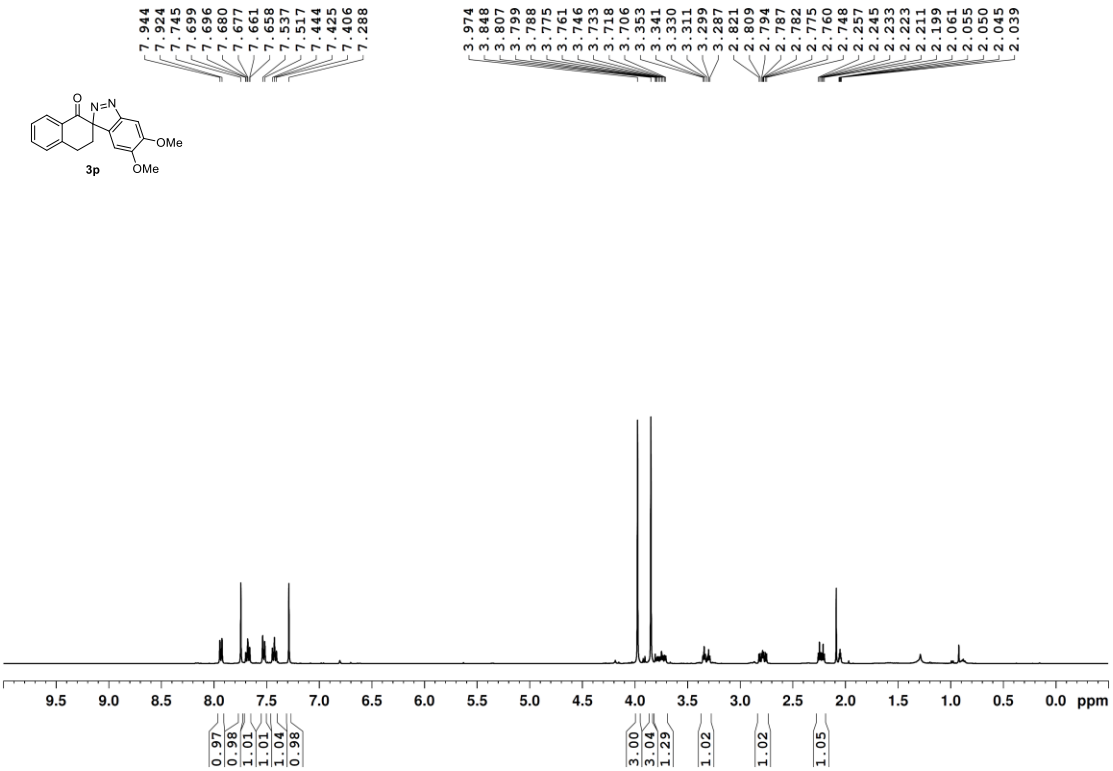


Fig. S28. ^{1}H NMR of compound **3p** (400 MHz, $(CD_3)_2CO$).

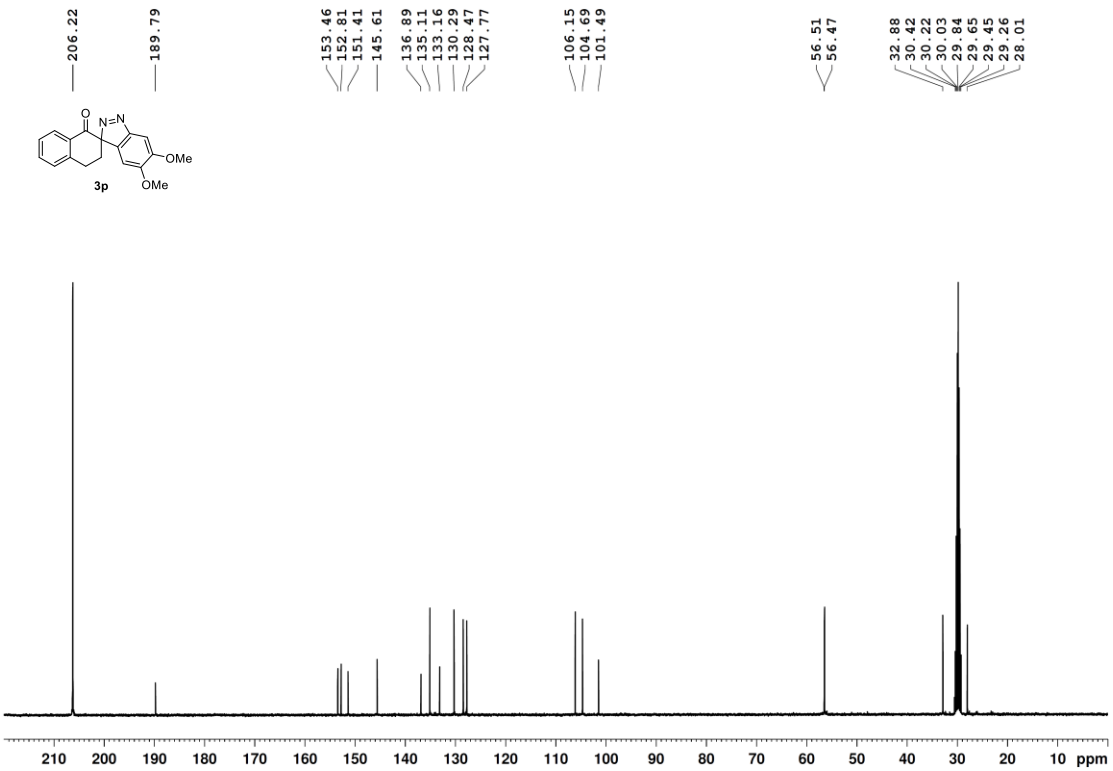


Fig. S29. ^{13}C NMR of compound **3p** (100 MHz, $(CD_3)_2CO$).

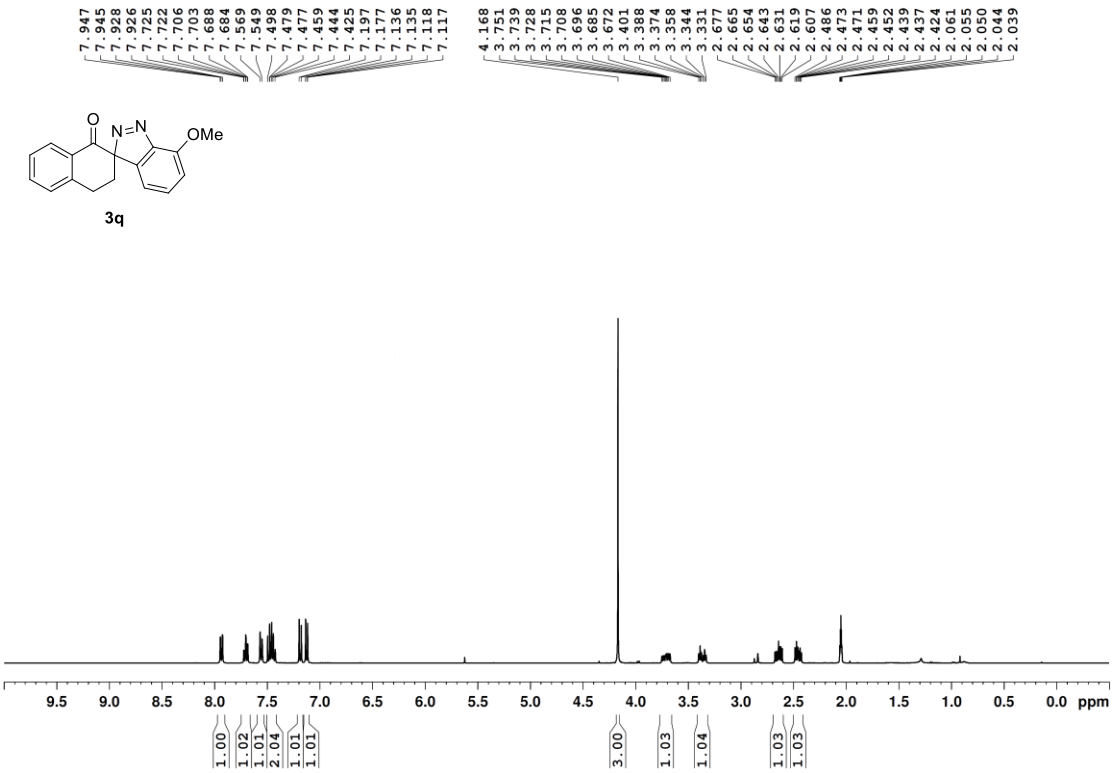


Fig. S30. ^{1}H NMR of compound **3q** (400 MHz, $(CD_3)_2CO$).

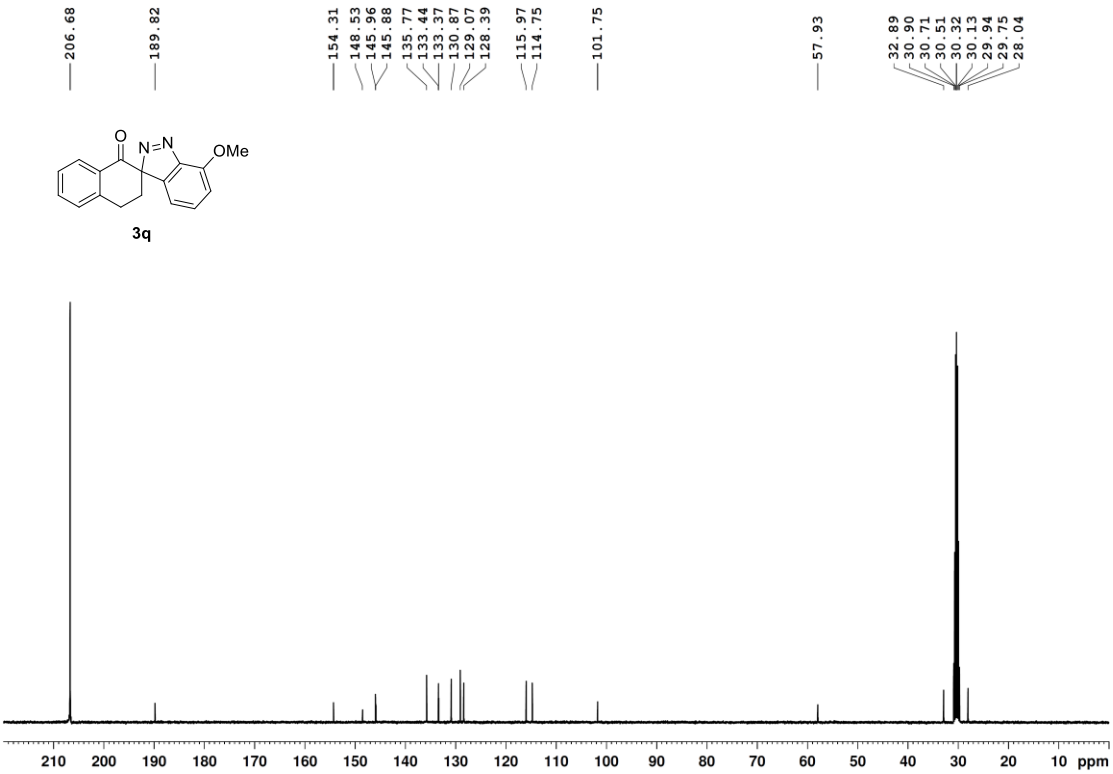


Fig. S31. ^{13}C NMR of compound **3q** (100 MHz, $(CD_3)_2CO$).

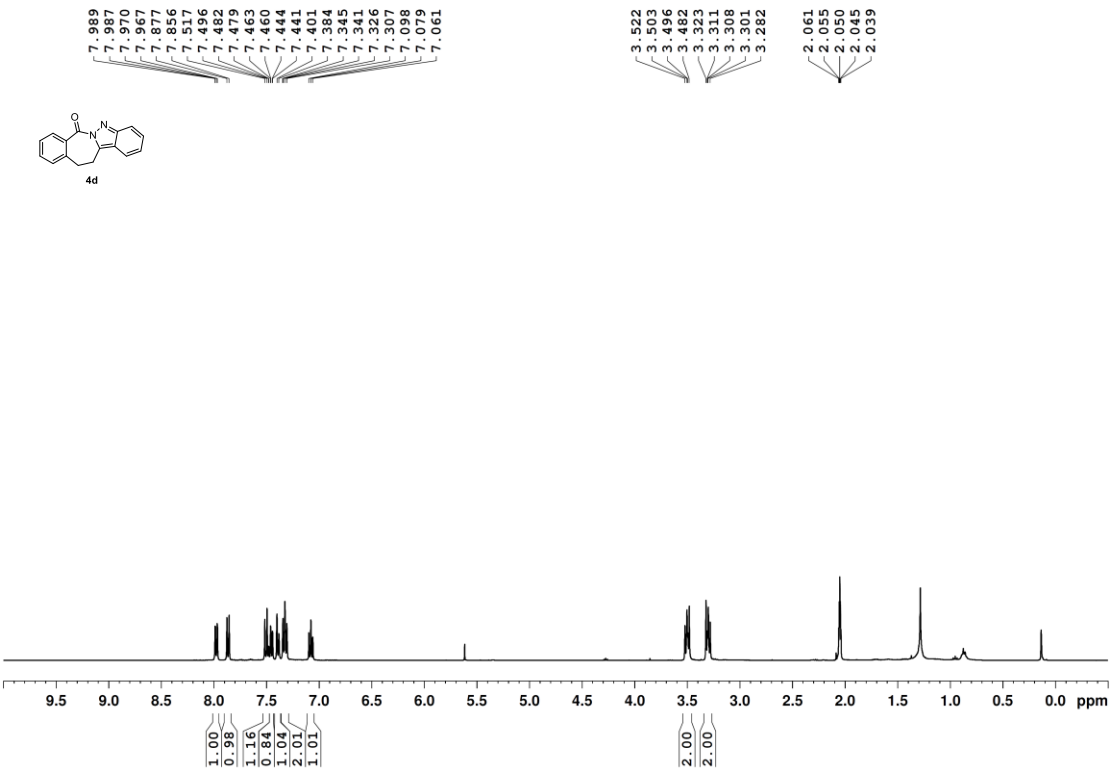


Fig. S32. ^{1}H NMR of compound **4d** (400 MHz, $(CD_3)_2CO$).

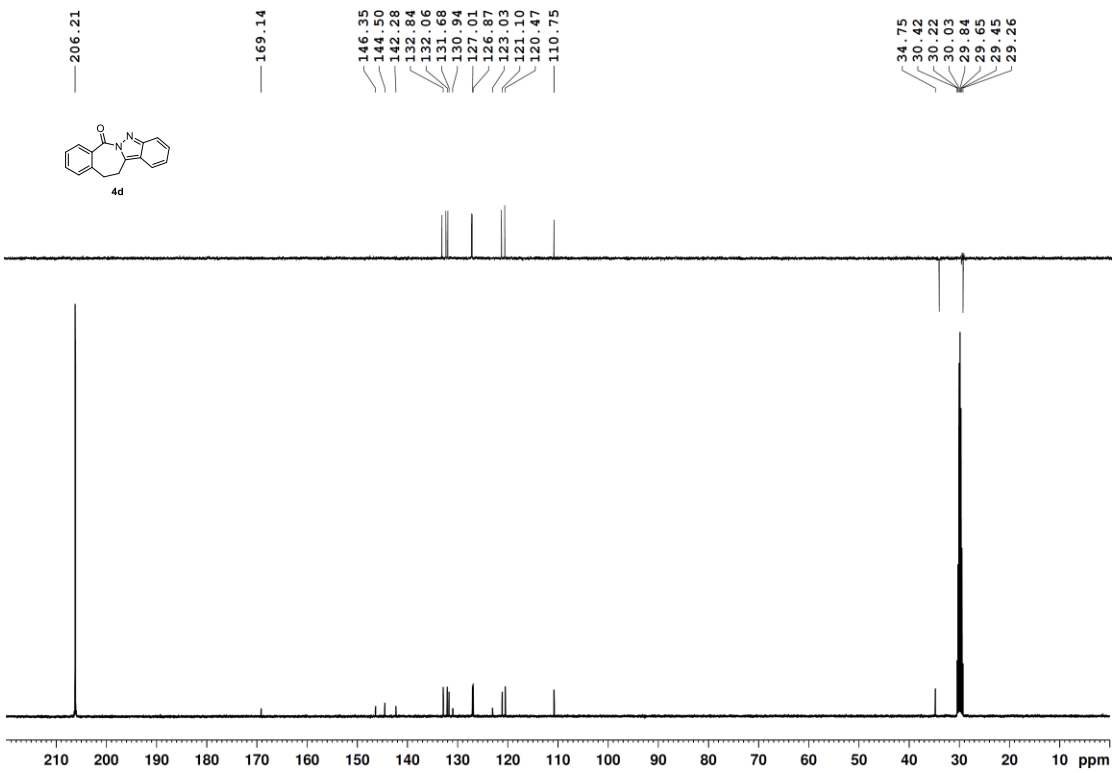


Fig. S33. ^{13}C and DEPT-135 NMR of compound **4d** (100 MHz, $(CD_3)_2CO$).

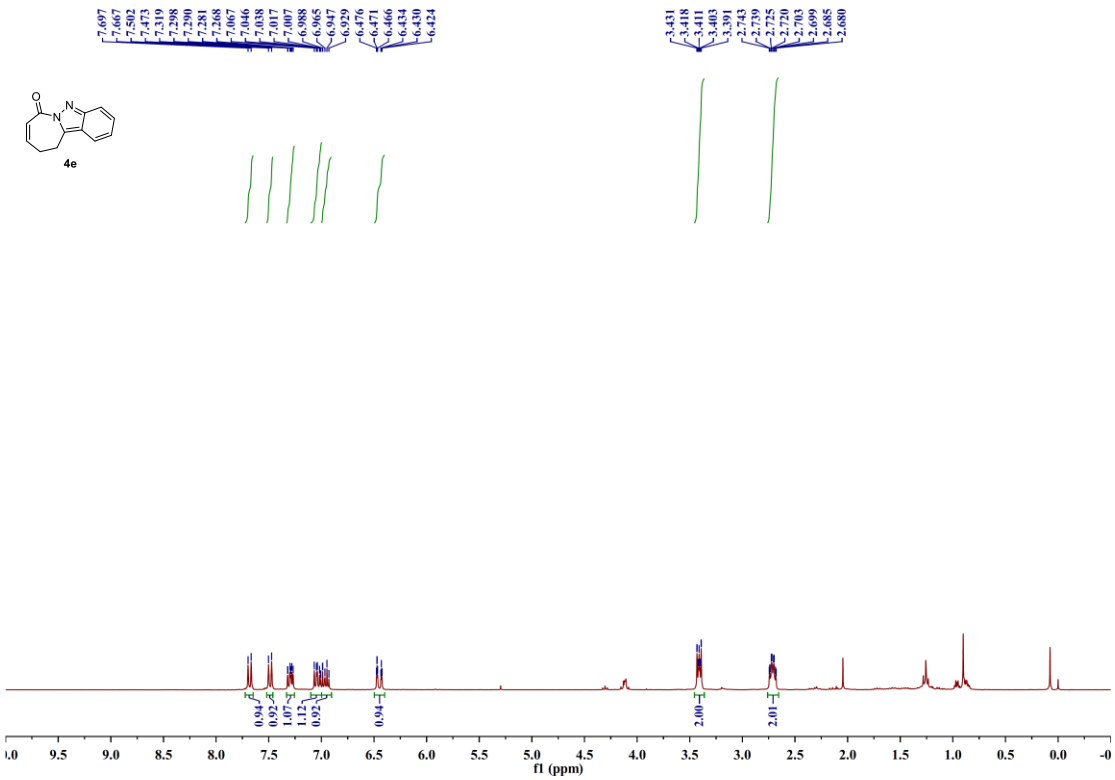


Fig. S34. ^{1}H NMR of compound **4e** (300 MHz, $CDCl_3$).

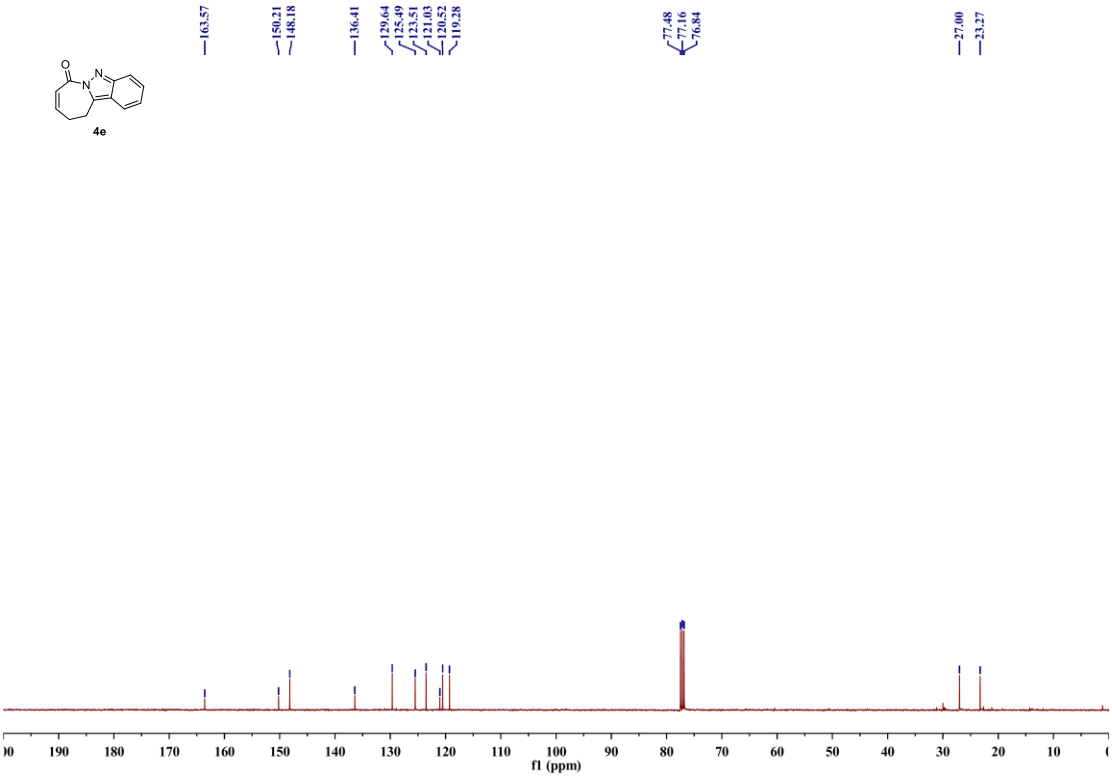


Fig. S35. ^{13}C NMR of compound **4e** (100 MHz, $CDCl_3$).

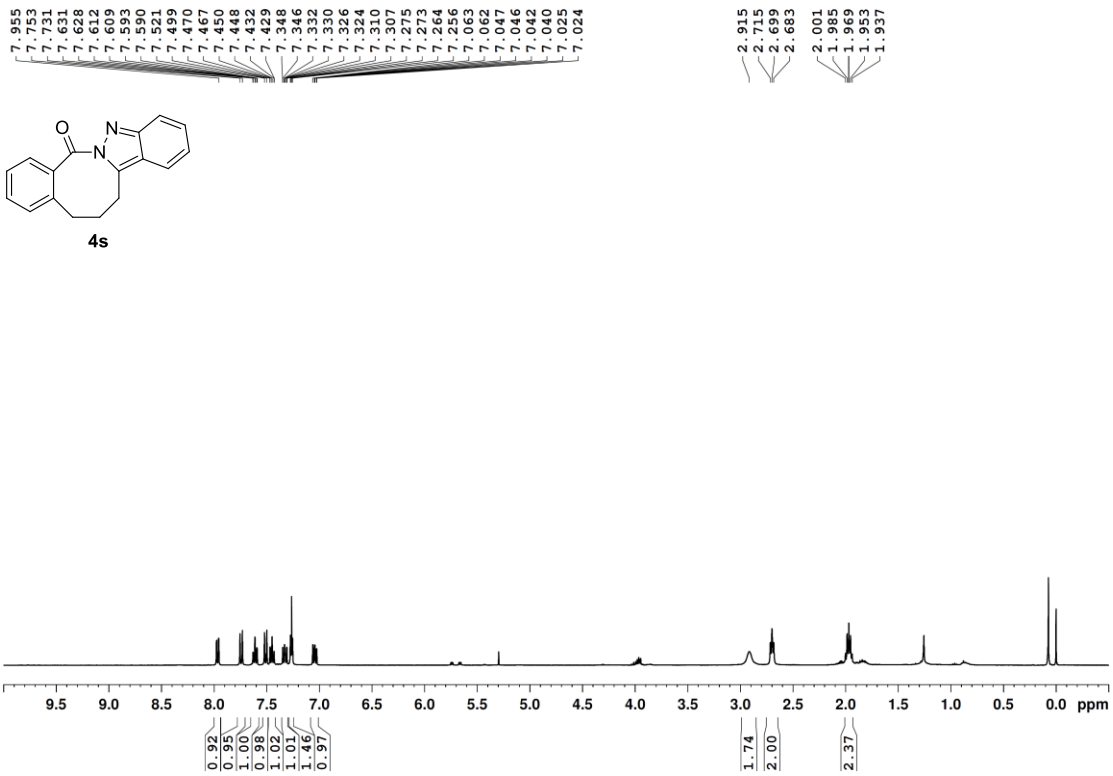


Fig. S36. ^{1}H NMR of compound **4s** (400 MHz, $CDCl_3$).

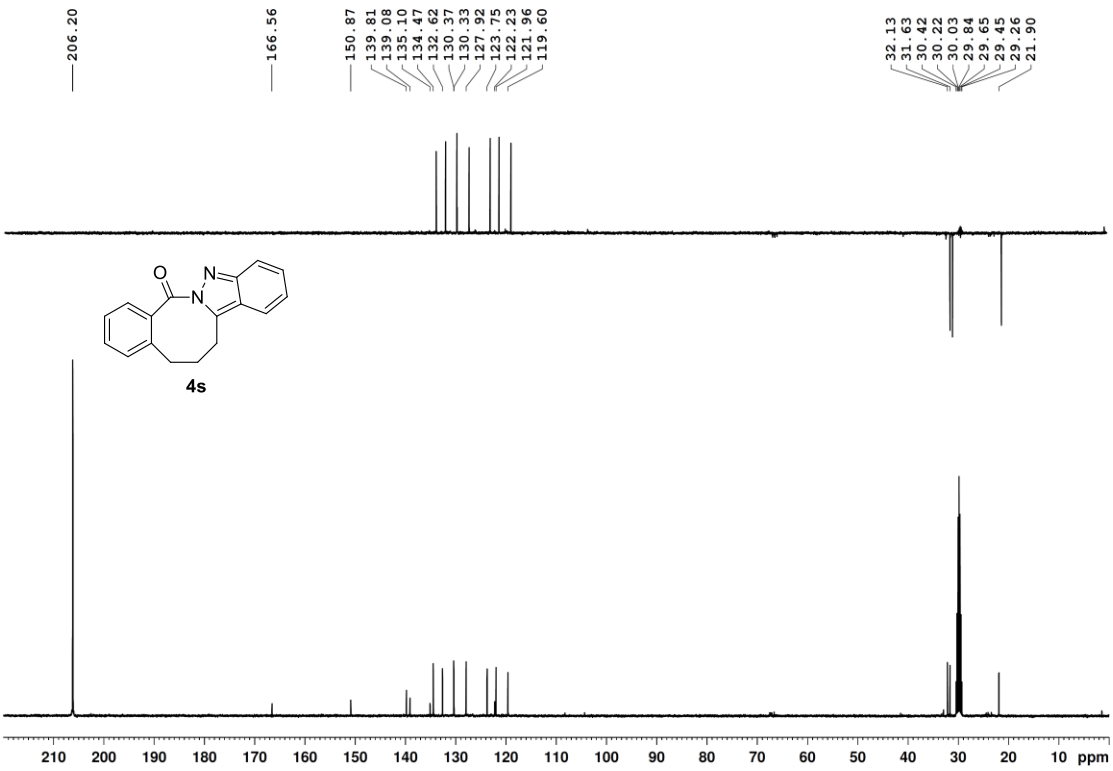


Fig. S37. ^{13}C and DEPT-135 NMR of compound **4s** (100 MHz, $(CD_3)_2CO$).

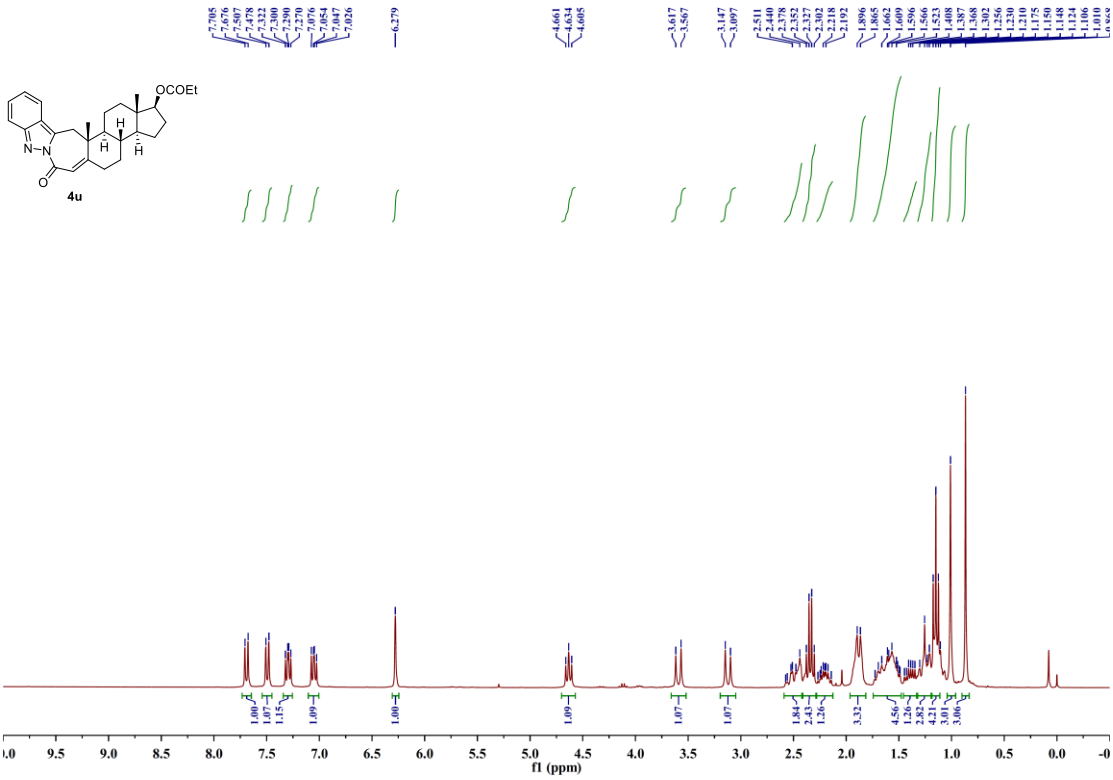


Fig. S38. ^{1}H NMR of compound **4u** (300 MHz, $CDCl_3$).

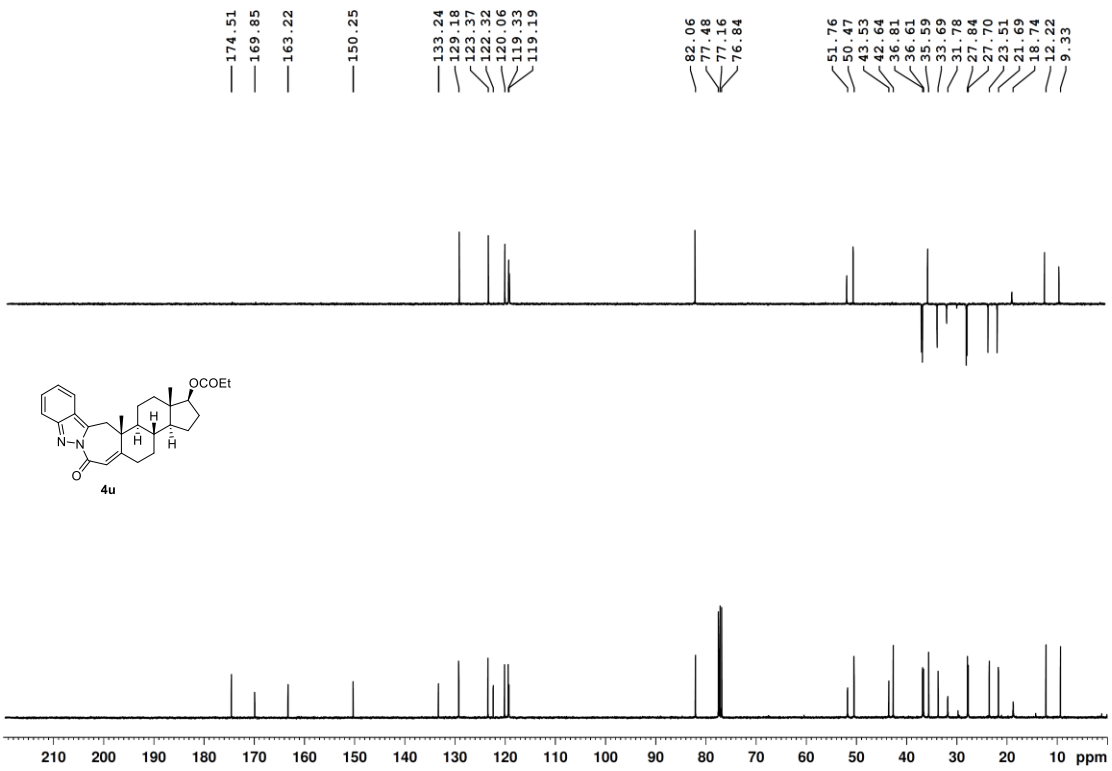


Fig. S39. ^{13}C and DEPT-135 NMR of compound **4u** (100 MHz, $CDCl_3$).

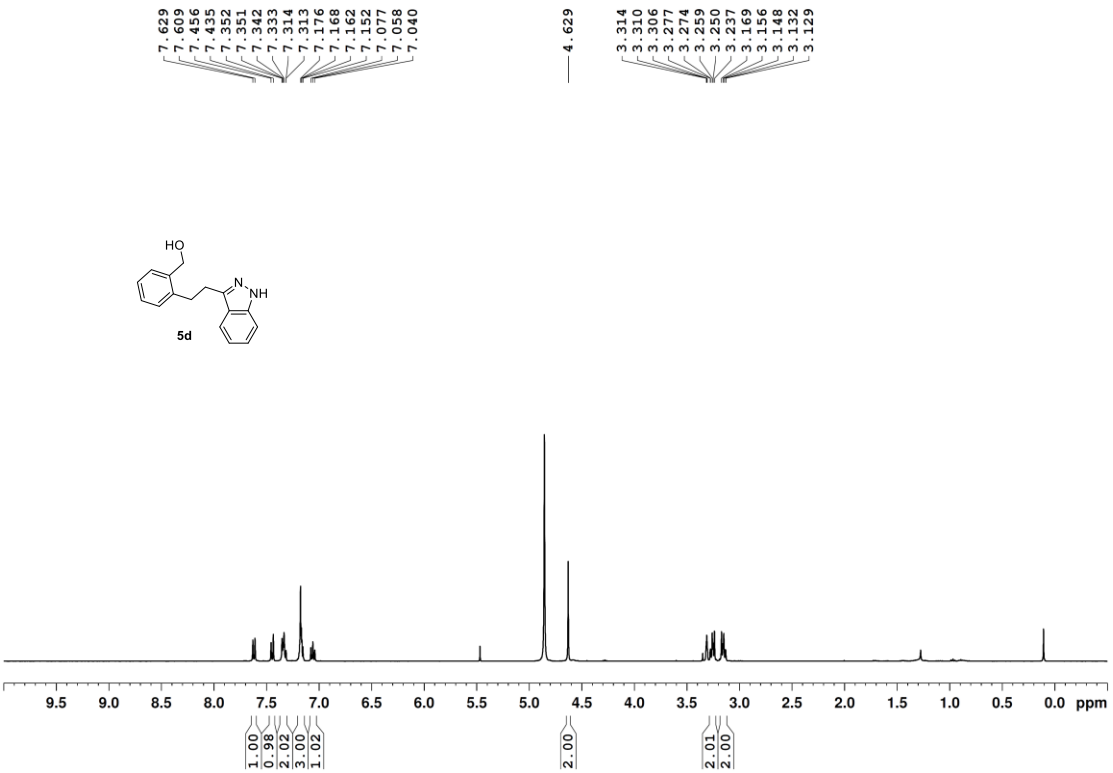


Fig. S40. ^{1}H NMR of compound **5d** (400 MHz, CD_3OD).

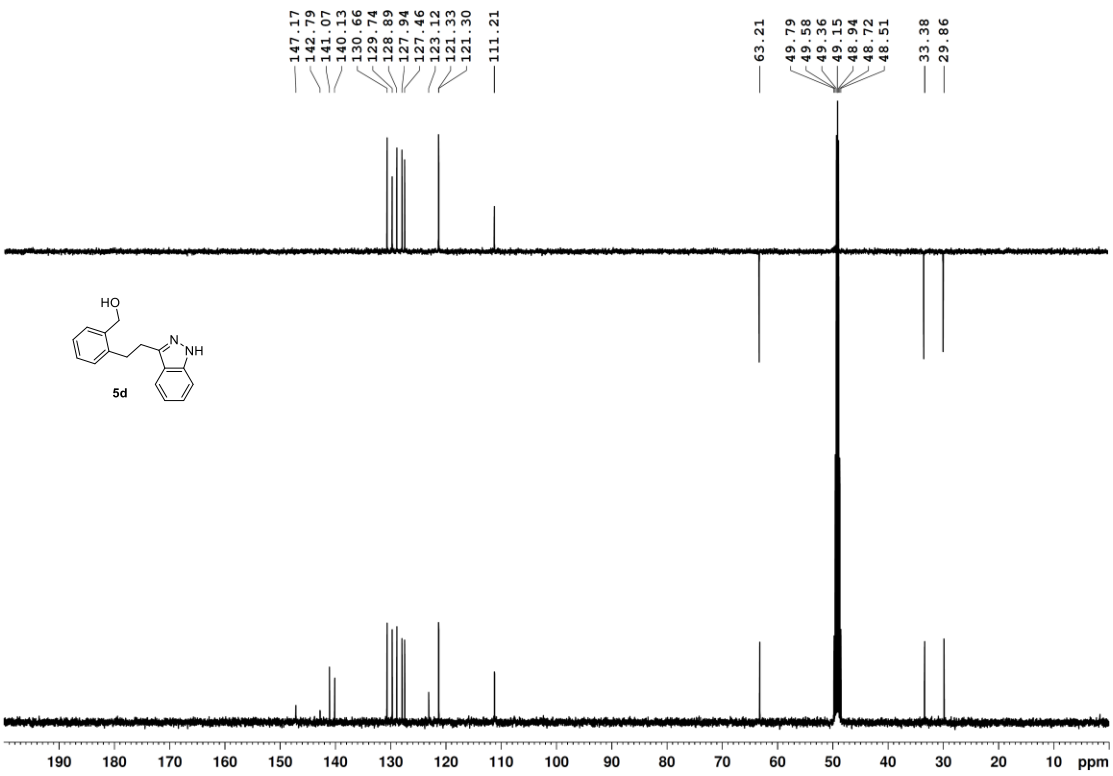


Fig. S41. ^{13}C and DEPT-135 NMR of compound **5d** (100 MHz, CD_3OD).