Supporting information

Rhodium(III)-Catalyzed direct C-H activation of 2-Aryl-3*H*-indoles: A strategy for 4-heteroaryl pyrazoles synthesis

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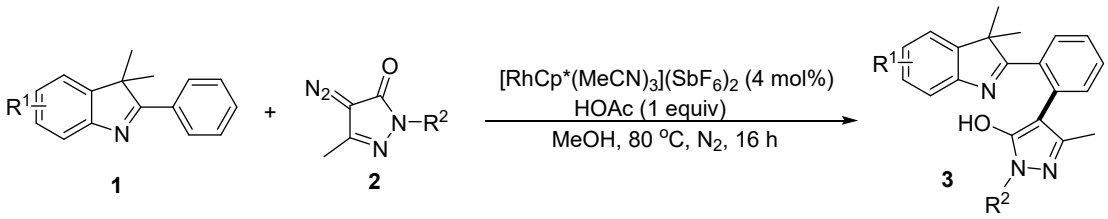
1. General Information

All chemicals were analytically pure and used directly after purchased. All solvents were used without any particular precautions to extrude moisture. ^{1}H NMR spectra were recorded on 400 MHz spectrometer, and ^{13}C NMR spectra were recorded on a 100 MHz spectrometer. All spectra were referenced to the solvent peaks (^{1}H: residual $CDCl_3$ = 7.26 ppm, ^{13}C: $CDCl_3$ = 77.00 ppm). High-resolution mass spectra (HRMS) were equipped with an ESI source and a TOF detector. Column chromatography was performed on silica gel (70-230 mesh ASTM) using the reported eluents. Thin-layer chromatography (TLC) was carried out on 4×15 cm plates with a layer thickness of 0.2 mm (silica gel 60 F254). 2-phenyl-3*H*-indoles[1] and diazopyrazolones[2] were synthesized according to the previously reported procedure.

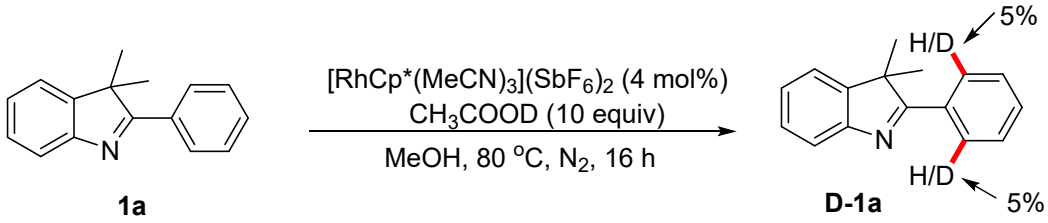
2. Typical procedure for synthesis of 3



To a tube equipped with magnetic stir bar, 2-phenyl-3*H*-indoles (**1**, 0.20 mmol), diazopyrazolones (**2**, 0.30 mmol), $[RhCp^*(MeCN)_3](SbF_6)_2$ (4 mol%), and HOAc (1 equiv.) in MeOH (2.0 mL) were added and stirred at 80 °C for 16 h under N_2 atmosphere. After removal of the solvent under reduced pressure, purification was performed by flash column chromatography on silica gel with petroleum ether/ethyl acetate (gradient mixture ratio from 20:1 to 10:1) as eluent to afford the corresponding products.

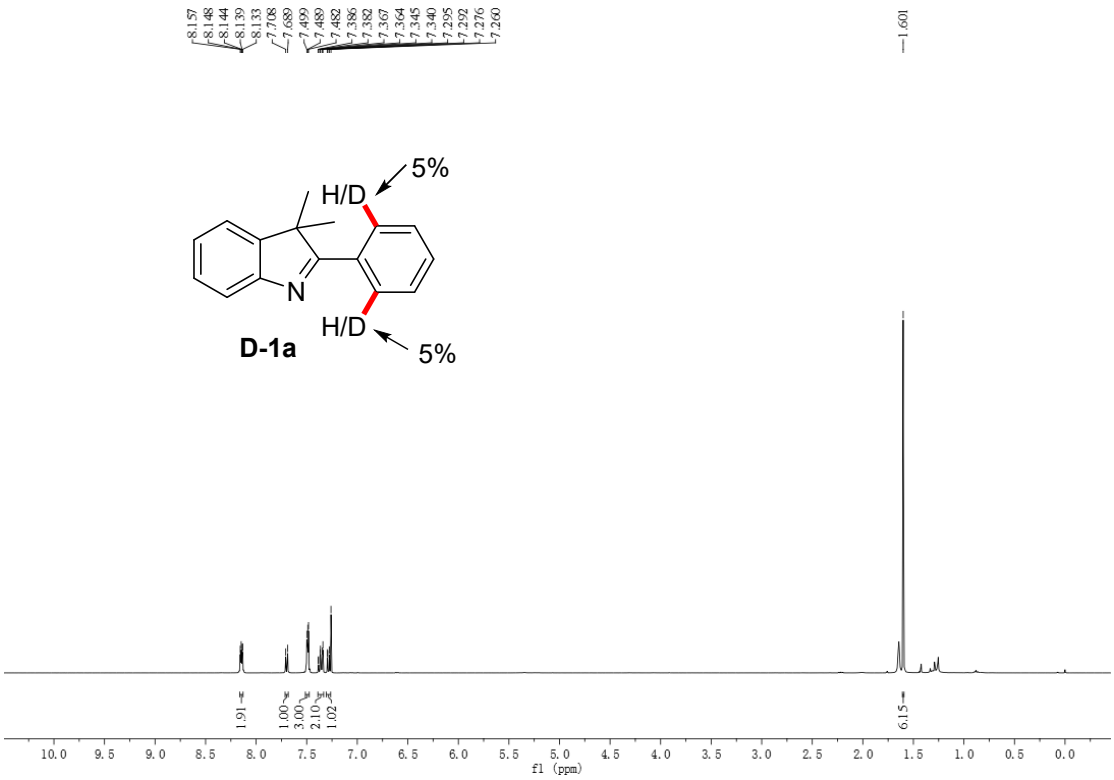
3. Mechanism Experiments

(1) H/D exchange

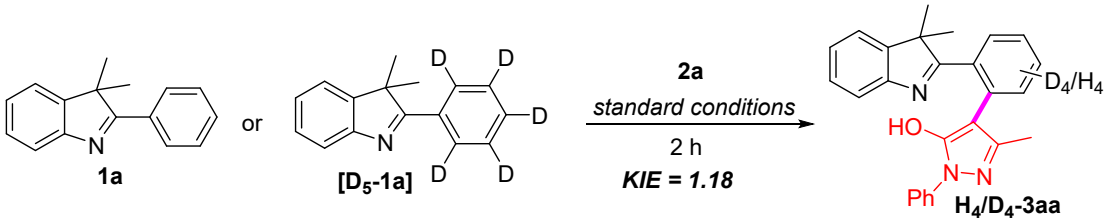


To a tube equipped with magnetic stir bar, 2-phenyl-3*H*-indole (**1a**, 0.20 mmol), $[RhCp^*(MeCN)_3](SbF_6)_2$ (4 mol%), and CH_3COOD (2.0 mmol, 10 equiv.) in MeOH (2.0 mL) were added and stirred at 80 °C for 16 h under N_2 atmosphere. After removal

of the solvent under reduced pressure, purification was performed by flash column chromatography on silica gel with petroleum ether/ethyl acetate (gradient mixture ratio from 30:1 to 20:1) as eluent to afford the corresponding products **D-1a**. The D-incorporation in **D-1a** was determined by ^{1}H-NMR spectroscopy.

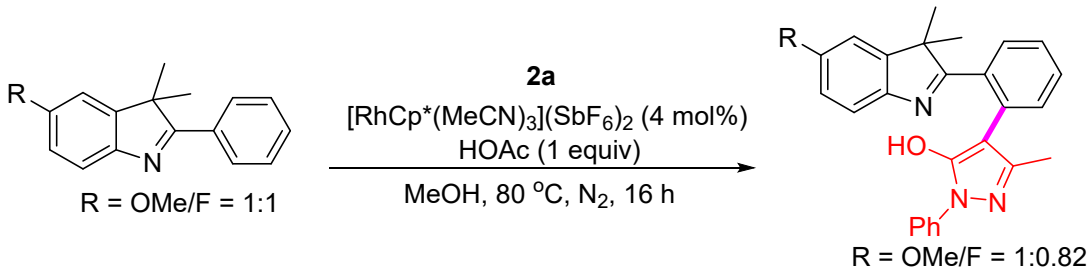


(2) General procedure for estimation of the KIE:



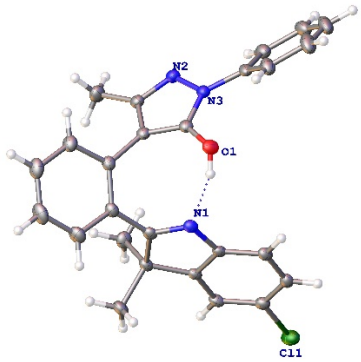
To two separated tube charged with 2-phenyl-3*H*-indole (**1a**, 0.20 mmol) or **D$_5$-1a** (0.20 mmol), diazopyrazolones (**2a**, 0.3 mmol), [RhCp*(MeCN)$_3$](SbF$_6$)$_2$ (4 mol%), and HOAc (1 equiv.) in MeOH (2.0 mL) were added and stirred at 80 °C for 2 h under N_2 atmosphere. After removal of the solvent under reduced pressure, purification was performed by flash column chromatography on silica gel with petroleum ether/ethyl acetate (gradient mixture ratio from 20:1 to 10:1) as eluent to afford the corresponding products **3aa** (31.4 mg, 40%) and **D$_4$-3aa** (26.9 mg, 34%).

(3) Intermolecular competition reaction with differently substituted 2-phenyl-3*H*-indoles



A suspension of 2-phenyl-3*H*-indole (**1f**, 0.2 mmol) and (**1g,** 0.2 mmol), **2a** (68.4 mg, 0.3 mmol), $[RhCp^*(MeCN)_3](SbF_6)_2$ (4 mol%), and HOAc (1 equiv.) in MeOH (2.0 mL) were added and stirred at 80 °C for 16 h under N_2 atmosphere. After removal of the solvent under reduced pressure, purification was performed by flash column chromatography on silica gel with petroleum ether/ethyl acetate (gradient mixture ratio from 20:1 to 10:1) as eluent to afford the corresponding products **3fa** and **3ga** at a ratio of 1:0.82.

4. The Crystal Structure of Product 3ha



X-ray molecular structure of 3ha

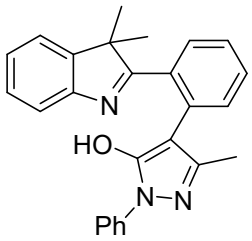
Table 1 Crystal data and structure refinement for exp_13844_auto.

Identification code	exp_13844_auto
Empirical formula	$C_{26}H_{22}ClN_3O$
Formula weight	427.91
Temperature/K	293.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.4744(9)
b/Å	16.0747(14)
c/Å	14.7594(11)
α/°	90
β/°	99.735(9)
γ/°	90

Volume/Å^3	2215.5(3)
Z	4
ρ_{calc}g/cm^3	1.283
μ/mm^{-1}	0.195
F(000)	896.0
Crystal size/mm^3	0.14 × 0.12 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.768 to 58.622
Index ranges	-12 ≤ h ≤ 10, -21 ≤ k ≤ 18, -14 ≤ l ≤ 19
Reflections collected	11487
Independent reflections	5140 [R_{int} = 0.0290, R_{sigma} = 0.0451]
Data/restraints/parameters	5140/0/283
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0542, wR_2 = 0.1094
Final R indexes [all data]	R_1 = 0.0873, wR_2 = 0.1247
Largest diff. peak/hole / e Å^{-3}	0.18/-0.23

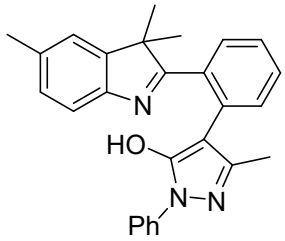
5. Characterization of compounds 3

4-(2-(3,3-dimethyl-3*H*-indol-2-yl)phenyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-ol (3aa)



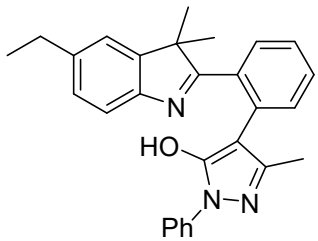
The compound prepared using $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (6.6 mg, 0.008 mmol), 3,3-dimethyl-2-phenyl-3*H*-indole (44.2 mg, 0.2 mmol), 4-diazo-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (60.0 mg, 0.3 mmol, 1.5 equiv.), and HOAc (12 mg, 0.2 mmol, 1 equiv.). After 16 h, it was cooled to room temperature and concentrated under reduced pressure. The reside was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **3aa** as a yellow liquid (56.6 mg, 72%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 12.46 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 8.3 Hz, 2H), 7.43 (dd, *J* = 17.7, 8.1 Hz, 4H), 7.38 - 7.27 (m, 3H), 7.22 (t, *J* = 7.4 Hz, 1H), 2.19 (s, 3H), 1.65 (s, 3H), 1.08 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 187.9, 173.1, 169.8, 163.1, 159.8, 150.6, 150.1, 146.8, 144.8, 138.9, 133.3, 132.9, 131.9, 129.7, 128.6, 127.9, 127.3, 126.4, 125.4, 121.7, 121.5, 104.2, 55.6, 23.5, 22.2, 12.9. **HRMS (ESI)**: Calcd for $C_{26}H_{23}N_3O$ $[M+H]^+$: 394.1914; found: 394.1915.

3-methyl-1-phenyl-4-(2-(3,3,5-trimethyl-3*H*-indol-2-yl)phenyl)-1*H*-pyrazol-5-ol (3ba)



The compound prepared using $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (6.6 mg, 0.008 mmol), 3,3,5-trimethyl-2-phenyl-3*H*-indole (47.0 mg, 0.2 mmol), 4-diazo-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (60.0 mg, 0.3 mmol, 1.5 equiv.), and HOAc (12 mg, 0.2 mmol, 1 equiv.). After 16 h, it was cooled to room temperature and concentrated under reduced pressure. The reside was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **3ba** as a yellow liquid (50.5 mg, 62%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 7.8 Hz, 2H), 7.54 (t, *J* = 7.1 Hz, 2H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.42 (dt, *J* = 16.0, 8.0 Hz, 4H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.17 - 7.11 (m, 2H), 2.41 (s, 3H), 2.17 (s, 3H), 1.64 (s, 3H), 1.05 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 186.8, 150.7, 148.0, 146.8, 145.1, 138.9, 136.8, 133.5, 133.0, 132.1, 129.7, 128.6, 127.4, 126.4, 125.5, 122.4, 121.6, 119.2, 118.6, 104.3, 55.5, 23.6, 22.4, 21.5, 12.9. **HRMS (ESI)**: Calcd for $C_{27}H_{25}N_3O$ $[M+H]^+$: 408.2070; found: 408.2071.

4-(2-(5-ethyl-3,3-dimethyl-3*H*-indol-2-yl)phenyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-ol (3ca)

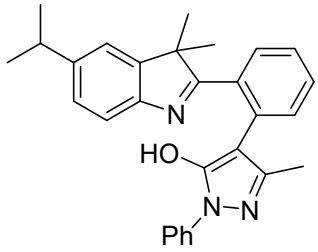


The compound prepared using $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (6.6 mg, 0.008 mmol), 5-ethyl-3,3-dimethyl-2-phenyl-3*H*-indole (49.8 mg, 0.2 mmol), 4-diazo-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (60.0 mg, 0.3 mmol, 1.5 equiv.), and HOAc (12 mg, 0.2 mmol, 1 equiv.). After 16 h, it was cooled to room temperature and concentrated under reduced pressure. The reside was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **3ca** as a pale yellow solid (53.1 mg, 63%). m.p. 112-114 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.8 Hz, 2H), 7.57 - 7.48 (m, 3H), 7.46 - 7.36 (m, 4H), 7.25 - 7.11 (m, 3H), 2.70 (q, *J* = 7.6 Hz, 2H), 2.16 (s, 3H), 1.64 (s, 3H),

1.28 - 1.23 (m, 3H), 1.05 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 186.9, 150.8, 148.2, 146.9, 145.1, 143.4, 138.9, 133.6, 133.1, 132.1, 129.7, 128.6, 127.6, 127.5, 126.5, 125.5, 121.7, 121.2, 119.4, 104.3, 55.6, 28.9, 23.7, 22.5, 15.9, 12.9. **HRMS (ESI)**: Calcd for $C_{28}H_{27}N_3O$ $[M+H]^+$: 422.2227; found: 422.2227.

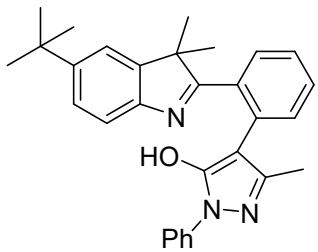
4-(2-(5-isopropyl-3,3-dimethyl-3*H*-indol-2-yl)phenyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-ol (3da)



The compound prepared using $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (6.6 mg, 0.008 mmol), 5-isopropyl-3,3-dimethyl-2-phenyl-3*H*-indole (52.6 mg, 0.2 mmol), 4-diazo-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (60.0 mg, 0.3 mmol, 1.5 equiv.), and HOAc (12 mg, 0.2 mmol, 1 equiv.). After 16 h, it was cooled to room temperature and concentrated under reduced pressure. The reside was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **3da** as a pale yellow solid (52.2 mg, 60%). m.p. 174-176 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.58 (s, 1H), 7.84 - 7.75 (m, 2H), 7.58 - 7.49 (m, 3H), 7.47 - 7.34 (m, 4H), 7.24 - 7.18 (m, 2H), 7.17 (d, *J* = 1.2 Hz, 1H), 2.97 (hept, *J* = 6.9 Hz, 1H), 2.16 (s, 3H), 1.66 (s, 3H), 1.27 (d, *J* = 6.9 Hz, 6H), 1.06 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 187.2, 150.8, 148.3, 148.1, 146.8, 145.1, 139.1, 133.5, 133.1, 132.1, 129.7, 128.6, 127.4, 126.4, 126.1, 125.4, 121.6, 119.7, 119.3, 104.3, 55.6, 34.3, 24.2, 23.8, 22.5, 13.0. **HRMS (ESI)**: Calcd for $C_{29}H_{29}N_3O$ $[M+H]^+$: 436.2383; found: 436.2383.

4-(2-(5-(tert-butyl)-3,3-dimethyl-3*H*-indol-2-yl)phenyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-ol (3ea)

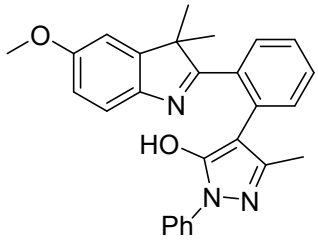


The compound prepared using $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (6.6 mg, 0.008 mmol), 5-(tert-

butyl)-3,3-dimethyl-2-phenyl-3*H*-indole (55.4 mg, 0.2 mmol), 4-diazo-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (60.0 mg, 0.3 mmol, 1.5 equiv.), and HOAc (12 mg, 0.2 mmol, 1 equiv.). After 16 h, it was cooled to room temperature and concentrated under reduced pressure. The reside was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **3ea** as a pale yellow liquid (55.7 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.64 (s, 1H), 7.80 (d, *J* = 7.9 Hz, 2H), 7.58 - 7.50 (m, 3H), 7.46 - 7.36 (m, 5H), 7.33 (d, *J* = 1.5 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 2.16 (s, 3H), 1.67 (s, 3H), 1.35 (s, 9H), 1.07 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 187.5, 150.8, 150.3, 147.9, 146.9, 144.7, 139.0, 133.6, 133.1, 132.2, 129.7, 128.6, 127.5, 126.4, 125.4, 125.2, 121.6, 118.9, 118.6, 104.4, 55.7, 35.0, 31.6, 23.9, 22.6, 13.0. **HRMS (ESI)**: Calcd for $C_{30}H_{31}N_3O$ $[M+H]^+$: 450.2540; found: 450.2540.

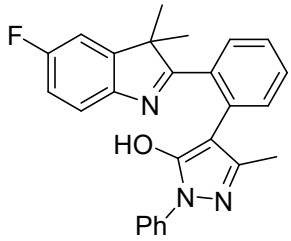
4-(2-(5-methoxy-3,3-dimethyl-3*H*-indol-2-yl)phenyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-ol (3fa)



The compound prepared using $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (6.6 mg, 0.008 mmol), 5-methoxy-3,3-dimethyl-2-phenyl-3*H*-indole (50.2 mg, 0.2 mmol), 4-diazo-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (60.0 mg, 0.3 mmol, 1.5 equiv.), and HOAc (12 mg, 0.2 mmol, 1 equiv.). After 16 h, it was cooled to room temperature and concentrated under reduced pressure. The reside was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4:1) to afford **3fa** as a pale yellow solid (57.5 mg, 68%). m.p. 118-120 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.57 - 7.48 (m, 3H), 7.46 - 7.36 (m, 4H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.90 - 6.79 (m, 2H), 3.82 (s, 3H), 2.16 (s, 3H), 1.63 (s, 3H), 1.05 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 185.8, 159.1, 150.7, 146.9, 146.7, 143.8, 138.9, 133.5, 133.0, 132.1, 129.7, 128.6, 127.5, 126.4, 125.5, 121.6, 120.2, 112.7, 108.3, 104.3, 55.7, 55.7, 23.8, 22.5, 12.9. **HRMS (ESI)**: Calcd for $C_{27}H_{25}N_3O_2$ $[M+H]^+$: 424.2020; found: 424.2019.

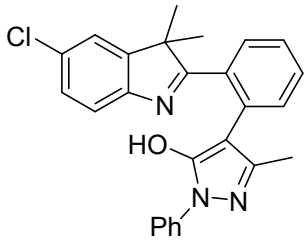
4-(2-(5-fluoro-3,3-dimethyl-3*H*-indol-2-yl)phenyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-ol (3ga)



The compound prepared using $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (6.6 mg, 0.008 mmol), 5-fluoro-3,3-dimethyl-2-phenyl-3*H*-indole (47.8 mg, 0.2 mmol), 4-diazo-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (60.0 mg, 0.3 mmol, 1.5 equiv.), and HOAc (12 mg, 0.2 mmol, 1 equiv.). After 16 h, it was cooled to room temperature and concentrated under reduced pressure. The reside was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **3ga** as a pale white solid (47.7 mg, 58%). m.p. 172-174 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.12 (s, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.54 (dd, *J* = 13.8, 7.4 Hz, 3H), 7.48 - 7.34 (m, 4H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.03 (dd, *J* = 14.6, 5.3 Hz, 2H), 2.16 (s, 3H), 1.63 (s, 3H), 1.05 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 188.0, 161.9 (d, *J* = 247.0 Hz), 150.4, 147.1 (d, $J_{C\text{-}F}$ = 6.7 Hz), 146.8, 146.22, 138.9, 133.1 (d, $J_{C\text{-}F}$ = 9.9 Hz), 131.9, 129.9, 128.6, 127.4, 126.5, 125.5, 121.5, 120.6 (d, $J_{C\text{-}F}$ = 8.3 Hz), 114.8 (d, $J_{C\text{-}F}$ = 24.0 Hz), 109.5 (d, $J_{C\text{-}F}$ = 24.6 Hz), 104.2, 56.1 (d, $J_{C\text{-}F}$ = 1.9 Hz), 23.5, 22.2, 13.1. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -114.23. **HRMS (ESI)**: Calcd for $C_{26}H_{22}FN_3O$ $[M+H]^+$: 412.1820; found: 412.1820.

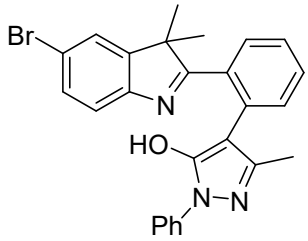
4-(2-(5-chloro-3,3-dimethyl-3*H*-indol-2-yl)phenyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-ol (3ha)



The compound prepared using $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (6.6 mg, 0.008 mmol), 5-chloro-3,3-dimethyl-2-phenyl-3*H*-indole (51.0 mg, 0.2 mmol), 4-diazo-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (60.0 mg, 0.3 mmol, 1.5 equiv.), and HOAc (12 mg, 0.2 mmol, 1 equiv.). After 16 h, it was cooled to room temperature and concentrated under reduced pressure. The reside was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **3ha** as a yellow solid (52.1 mg, 61%). m.p. 142-144 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.98 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.53 (dt, *J* = 14.4, 7.1 Hz, 3H), 7.42 (dt, *J* = 19.1, 7.7 Hz, 4H), 7.34 - 7.26 (m, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 2.15 (s, 3H), 1.64 (s, 3H), 1.05 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 188.6, 150.4, 148.8, 146.9, 138.9, 133.2, 132.0, 130.0, 128.7, 128.3, 127.4, 126.6, 125.6, 122.4, 121.6, 120.7, 104.1, 56.1, 23.5, 22.2, 13.0. **HRMS (ESI)**: Calcd for $C_{26}H_{22}ClN_3O$ $[M+H]^+$: 428.1524; found: 428.1524.

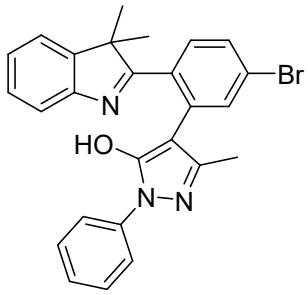
4-(2-(5-bromo-3,3-dimethyl-3*H*-indol-2-yl)phenyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-ol (3ia)



The compound prepared using $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (6.6 mg, 0.008 mmol), 5-bromo-3,3-dimethyl-2-phenyl-3*H*-indole (59.8 mg, 0.2 mmol), 4-diazo-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (60.0 mg, 0.3 mmol, 1.5 equiv.), and HOAc (12 mg, 0.2 mmol, 1 equiv.). After 16 h, it was cooled to room temperature and concentrated under reduced pressure. The reside was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **3ia** as a pale yellow solid (63.1 mg, 67%). m.p. 177-179 °C.

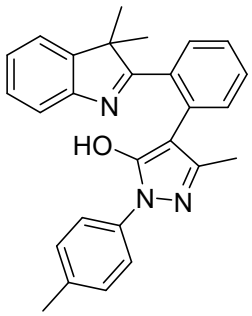
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.92 (s, 1H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.54 (dd, *J* = 16.3, 7.8 Hz, 2H), 7.49 - 7.32 (m, 7H), 7.21 (t, *J* = 7.3 Hz, 1H), 2.15 (s, 3H), 1.64 (s, 3H), 1.05 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 188.6, 150.3, 149.3, 146.8, 138.9, 133.2, 131.9, 131.2, 130.0, 128.7, 127.3, 126.6, 126.6, 125.6, 125.3, 121.6, 121.2, 118.7, 118.6, 104.2, 56.1, 23.5, 22.2, 13.0. **HRMS (ESI)**: Calcd for $C_{26}H_{22}BrN_3O$ $[M+H]^+$: 472.1019; found: 472.1017.

4-(5-bromo-2-(3,3-dimethyl-3*H*-indol-2-yl)phenyl)-3-methyl-1-phenyl-1*H* pyrazol-5-ol (3la)



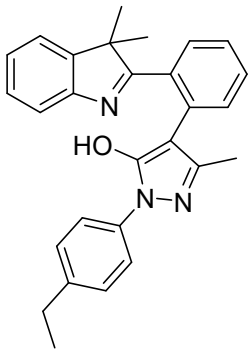
The compound prepared using $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (6.6 mg, 0.008 mmol), 2-(4-bromophenyl)-3,3-dimethyl-3*H*-indole (59.8 mg, 0.2 mmol), 4-diazo-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (60.0 mg, 0.3 mmol, 1.5 equiv.), and HOAc (12 mg, 0.2 mmol, 1 equiv.). After 16 h, it was cooled to room temperature and concentrated under reduced pressure. The reside was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **3la** as a yellow liquid (71.6 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.44 (s, 1H), 7.75 (d, *J* = 7.9 Hz, 2H), 7.58 (q, *J* = 4.8 Hz, 3H), 7.45 – 7.28 (m, 6H), 7.22 (t, *J* = 7.4 Hz, 1H), 2.17 (s, 3H), 1.63 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9, 150.7, 149.9, 146.5, 144.6, 138.7, 135.7, 134.2, 132.1, 129.60, 128.8, 128.6, 128.1, 126.9, 126.8, 125.6, 124.1, 121.7, 121.6, 119.7, 103.1, 55.6, 23.5, 22.2, 13.0. **HRMS (ESI)**: Calcd for $C_{26}H_{22}BrN_3O$ $[M+H]^+$: 472.1019; found: 472.1017.

4-(2-(3,3-dimethyl-3*H*-indol-2-yl)phenyl)-3-methyl-1-(*p*-tolyl)-1*H*-pyrazol-5-ol (3ab)



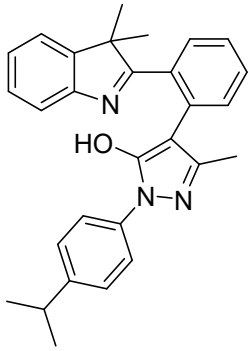
The compound prepared using $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (6.6 mg, 0.008 mmol), 3,3-dimethyl-2-phenyl-3*H*-indole (44.2 mg, 0.2 mmol), 4-diazo-5-methyl-2-(p-tolyl)-2,4-dihydro-3*H*-pyrazol-3-one (64.2 mg, 0.3 mmol, 1.5 equiv.), and HOAc (12 mg, 0.2 mmol, 1 equiv.). After 16 h, it was cooled to room temperature and concentrated under reduced pressure. The reside was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **3ab** as a yellow liquid (57.0 mg, 70%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 12.27 (s, 1H), 7.66 - 7.51 (m, 5H), 7.43 (dd, *J* = 9.9, 8.0 Hz, 2H), 7.38 - 7.27 (m, 3H), 7.20 (d, *J* = 8.2 Hz, 2H), 2.36 (s, 3H), 2.16 (s, 3H), 1.64 (s, 3H), 1.06 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 188.1, 150.5, 150.2, 146.5, 144.9, 136.5, 135.2, 133.4, 133.0, 132.1, 129.8, 129.2, 128.0, 127.4, 126.7, 126.4, 121.7, 121.7, 119.7, 104.1, 55.7, 23.6, 22.4, 20.9, 13.0. **HRMS (ESI)**: Calcd for $C_{27}H_{25}N_3O$ $[M+H]^+$: 408.2070; found: 408.2070.

4-(2-(3,3-dimethyl-3*H*-indol-2-yl)phenyl)-1-(4-ethylphenyl)-3-methyl-1*H*-pyrazol-5-ol (3ac)



The compound prepared using $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (6.6 mg, 0.008 mmol), 3,3-dimethyl-2-phenyl-3*H*-indole (44.2 mg, 0.2 mmol), 4-diazo-2-(4-ethylphenyl)-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (68.4 mg, 0.3 mmol, 1.5 equiv.), and HOAc (12 mg, 0.2 mmol, 1 equiv.). After 16 h, it was cooled to room temperature and concentrated under reduced pressure. The reside was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **3ac** as a yellow liquid (56.4 mg, 67%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.61 (t, *J* = 9.1 Hz, 3H), 7.54 (dd, *J* = 7.0, 3.9 Hz, 2H), 7.43 (dd, *J* = 11.7, 7.7 Hz, 2H), 7.37 - 7.27 (m, 3H), 7.22 (d, *J* = 8.2 Hz, 2H), 2.65 (q, *J* = 7.5 Hz, 2H), 2.15 (s, 3H), 1.64 (s, 3H), 1.25 (d, *J* = 7.8 Hz, 3H), 1.06 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 187.5, 150.5, 150.2, 146.6, 144.9, 141.7, 136.6, 133.4, 133.0, 132.1, 129.8, 128.1, 128.0, 127.4, 126.7, 126.4, 121.9, 121.7, 119.7, 104.1, 55.7, 28.4, 23.6, 22.4, 15.5, 12.9. **HRMS (ESI)**: Calcd for $C_{28}H_{27}N_3O$ $[M+H]^+$: 422.2227; found: 422.2227.

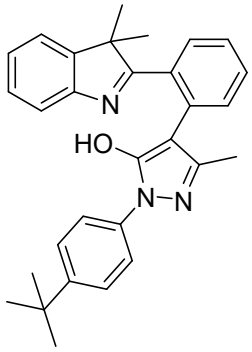
4-(2-(3,3-dimethyl-3*H*-indol-2-yl)phenyl)-1-(4-isopropylphenyl)-3-methyl-1*H*-pyrazol-5-ol (3ad)



The compound prepared using $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (6.6 mg, 0.008 mmol), 3,3-dimethyl-2-phenyl-3*H*-indole (44.2 mg, 0.2 mmol), 4-diazo-2-(4-isopropylphenyl)-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (72.6 mg, 0.3 mmol, 1.5 equiv.), and HOAc (12 mg, 0.2 mmol, 1 equiv.). After 16 h, it was cooled to room temperature and concentrated under reduced pressure. The reside was purified by silica gel column chromatography

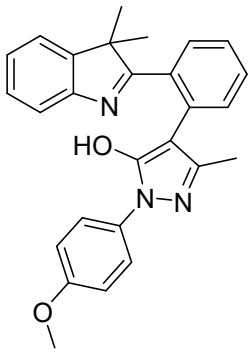
(petroleum ether/ethyl acetate = 10:1) to afford **3ad** as a yellow liquid (53.9 mg, 62%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 - 7.57 (m, 3H), 7.57 - 7.51 (m, 2H), 7.47 - 7.39 (m, 2H), 7.34 (ddd, *J* = 19.0, 10.7, 4.4 Hz, 3H), 7.24 (d, *J* = 8.5 Hz, 2H), 2.91 (dp, *J* = 14.1, 7.0 Hz, 1H), 2.17 (d, *J* = 17.5 Hz, 3H), 1.64 (s, 3H), 1.25 (d, *J* = 6.9 Hz, 6H), 1.05 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 188.4, 150.4, 150.3, 146.6, 146.3, 144.9, 136.6, 133.5, 133.0, 132.1, 129.8, 128.1, 127.4, 126.7, 126.6, 126.4, 121.9, 121.7, 119.7, 104.1, 55.7, 33.7, 23.9, 23.6, 22.4, 12.9. **HRMS (ESI)**: Calcd for $C_{29}H_{29}N_3O$ $[M+H]^+$: 436.2383; found: 436.2381.

1-(4-(*tert*-butyl)phenyl)-4-(2-(3,3-dimethyl-3*H*-indol-2-yl)phenyl)-3-methyl-1*H*-pyrazol-5-ol (3ae)



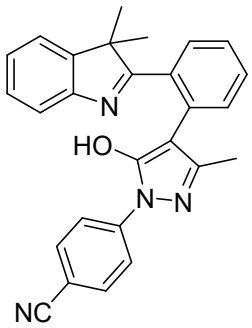
The compound prepared using $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (6.6 mg, 0.008 mmol), 3,3-dimethyl-2-phenyl-3*H*-indole (44.2 mg, 0.2 mmol), 2-(4-(tert-butyl)phenyl)-4-diazo-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (76.8 mg, 0.3 mmol, 1.5 equiv.), and HOAc (12 mg, 0.2 mmol, 1 equiv.). After 16 h, it was cooled to room temperature and concentrated under reduced pressure. The reside was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **3ae** as a yellow liquid (53.0 mg, 59%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.62 (dd, *J* = 7.8, 5.7 Hz, 3H), 7.57 -7.50 (m, 2H), 7.47 - 7.26 (m, 7H), 2.15 (s, 3H), 1.64 (s, 3H), 1.33 (s, 9H), 1.06 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 188.8, 150.4, 150.3, 148.6, 146.6, 144.9, 136.3, 133.5, 133.0, 132.1, 129.8, 128.1, 127.4, 126.7, 126.4, 125.6, 121.7, 121.5, 119.7, 104.1, 55.7, 34.4, 31.3, 23.6, 22.4, 12.9. **HRMS (ESI)**: Calcd for $C_{30}H_{31}N_3O$ $[M+H]^+$: 450.2540; found: 450.2540.

4-(2-(3,3-dimethyl-3*H*-indol-2-yl)phenyl)-1-(4-methoxyphenyl)-3-methyl-1*H*-pyrazol-5-ol (3af)



The compound prepared using [Cp*Rh(MeCN)$_3$](SbF$_6$)$_2$ (6.6 mg, 0.008 mmol), 3,3-dimethyl-2-phenyl-3*H*-indole (44.2 mg, 0.2 mmol), 4-diazo-2-(4-methoxyphenyl)-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (69.0 mg, 0.3 mmol, 1.5 equiv.), and HOAc (12 mg, 0.2 mmol, 1 equiv.). After 16 h, it was cooled to room temperature and concentrated under reduced pressure. The reside was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4:1) to afford **3af** as a yellow liquid (53.3 mg, 63%). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.63 - 7.57 (m, 3H), 7.54 (t, *J* = 6.6 Hz, 2H), 7.42 (dd, *J* = 11.8, 7.6 Hz, 2H), 7.37 - 7.26 (m, 3H), 6.92 (d, *J* = 9.0 Hz, 2H), 3.82 (s, 3H), 2.15 (s, 3H), 1.64 (s, 3H), 1.06 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 187.7, 157.6, 150.3, 150.2, 146.4, 144.9, 133.4, 133.0, 132.1, 132.1, 129.8, 128.1, 127.4, 126.7, 126.4, 123.6, 121.7, 119.6, 113.8, 103.9, 55.7, 55.4, 23.6, 22.4, 12.9. **HRMS (ESI)**: Calcd for $C_{27}H_{25}N_3O_2$ $[M+H]^+$: 424.2020; found: 424.2020.

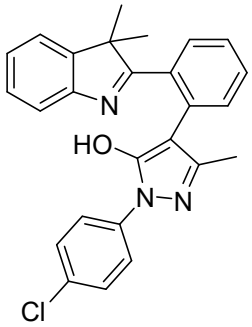
4-(4-(2-(3,3-dimethyl-3*H*-indol-2-yl)phenyl)-5-hydroxy-3-methyl-1*H*-pyrazol-1-yl)benzonitrile (3ag)



The compound prepared using [Cp*Rh(MeCN)$_3$](SbF$_6$)$_2$ (6.6 mg, 0.008 mmol), 3,3-dimethyl-2-phenyl-3*H*-indole (44.2 mg, 0.2 mmol), 4-(4-diazo-3-methyl-5-oxo-4,5-dihydro-1*H*-pyrazol-1-yl)benzonitrile (67.5 mg, 0.3 mmol, 1.5 equiv.), and HOAc (12 mg, 0.2 mmol, 1 equiv.). After 16 h, it was cooled to room temperature and concentrated under reduced pressure. The reside was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4:1) to afford **3ag** as a pale yellow solid (44.3 mg, 53%). m.p. 196-198 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.7 Hz, 2H), 7.67 (d, *J* = 8.7 Hz, 2H), 7.57 (dt, *J* = 7.5, 6.1 Hz, 3H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.41 - 7.27 (m, 4H), 2.15 (s, 3H), 1.66 (s, 3H), 1.12 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 187.5, 151.8, 149.6, 148.7, 144.8, 142.6, 133.2, 132.9, 132.8, 131.4, 130.1, 128.2, 127.5, 126.9, 126.8, 121.8, 120.4, 119.4, 118.9, 107.8, 104.9, 55.7, 23.5, 22.5, 13.1. **HRMS (ESI)**: Calcd for $C_{27}H_{22}N_4O$ $[M+H]^+$: 419.1866; found: 419.1866

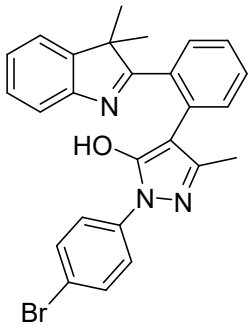
1-(4-chlorophenyl)-4-(2-(3,3-dimethyl-3*H*-indol-2-yl)phenyl)-3-methyl-1*H*-pyrazol-5-ol (3ah)



The compound prepared using $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (6.6 mg, 0.008 mmol), 3,3-dimethyl-2-phenyl-3*H*-indole (44.2 mg, 0.2 mmol), 2-(4-chlorophenyl)-4-diazo-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (70.2 mg, 0.3 mmol, 1.5 equiv.), and HOAc (12 mg, 0.2 mmol, 1 equiv.). After 16 h, it was cooled to room temperature and concentrated under reduced pressure. The reside was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **3ah** as a yellow liquid (39.3 mg, 46%).

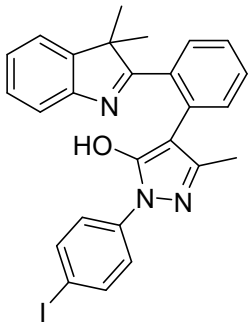
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.69 (s, 1H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.55 (t, *J* = 8.3 Hz, 3H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.38 - 7.27 (m, 5H), 2.14 (s, 3H), 1.66 (s, 3H), 1.06 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 184.6, 150.9, 150.0, 147.3, 144.9, 137.6, 133.3, 133.1, 131.9, 130.7, 129.9, 128.7, 128.1, 127.4, 126.8, 126.6, 122.4, 121.8, 119.6, 104.4, 55.7, 23.7, 22.3, 13.0. **HRMS (ESI)**: Calcd for $C_{26}H_{22}ClN_3O$ $[M+H]^+$: 428.1524; found: 428.1524.

1-(4-bromophenyl)-4-(2-(3,3-dimethyl-3*H*-indol-2-yl)phenyl)-3-methyl-1*H*-pyrazol-5-ol (3ai)



The compound prepared using [Cp*Rh(MeCN)$_3$](SbF$_6$)$_2$ (6.6 mg, 0.008 mmol), 3,3-dimethyl-2-phenyl-3*H*-indole (44.2 mg, 0.2 mmol), 2-(4-bromophenyl)-4-diazo-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (83.4 mg, 0.3 mmol, 1.5 equiv.), and HOAc (12 mg, 0.2 mmol, 1 equiv.). After 16 h, it was cooled to room temperature and concentrated under reduced pressure. The reside was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **3ai** as a yellow liquid (37.7 mg, 40%). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 12.72 (s, 1H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.60 - 7.48 (m, 5H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.37 - 7.26 (m, 3H), 2.14 (s, 3H), 1.66 (s, 3H), 1.06 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 188.0, 150.9, 150.0, 147.3, 144.9, 138.1, 133.3, 133.0, 131.8, 131.7, 129.9, 128.1, 127.4, 126.8, 126.6, 122.7, 121.8, 119.6, 118.5, 104.5, 55.7, 23.7, 22.5, 13.0. **HRMS (ESI)**: Calcd for $C_{26}H_{22}BrN_3O$ $[M+H]^+$: 472.1019; found: 472.1019.

4-(2-(3,3-dimethyl-3*H*-indol-2-yl)phenyl)-1-(4-iodophenyl)-3-methyl-1*H*-pyrazol-5-ol (3aj)

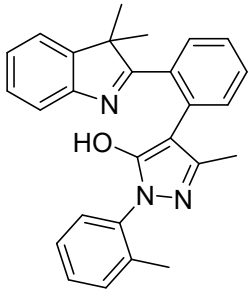


The compound prepared using [Cp*Rh(MeCN)$_3$](SbF$_6$)$_2$ (6.6 mg, 0.008 mmol), 3,3-dimethyl-2-phenyl-3*H*-indole (44.2 mg, 0.2 mmol), 4-diazo-2-(4-iodophenyl)-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (97.8 mg, 0.3 mmol, 1.5 equiv.), and HOAc (12 mg, 0.2 mmol, 1 equiv.). After 16 h, it was cooled to room temperature and concentrated under reduced pressure. The reside was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **3aj** as a pale yellow solid (51.9 mg, 50%). m.p. 168-170 °C.

^{1}H NMR (400 MHz, CDCl$_3$) δ 12.67 (s, 1H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.8

Hz, 2H), 7.55 (t, *J* = 8.9 Hz, 3H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.37 - 7.26 (m, 3H), 2.14 (s, 3H), 1.66 (s, 3H), 1.06 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 188.5, 150.9, 149.9, 147.4, 144.8, 138.8, 137.6, 133.3, 133.0, 131.8, 129.9, 128.1, 127.4, 126.8, 126.6, 122.9, 121.8, 119.6, 104.5, 89.5, 55.7, 23.6, 22.3, 13.1. **HRMS (ESI)**: Calcd for $C_{26}H_{22}IN_3O$ $[M+H]^+$: 520.0880; found: 520.0879.

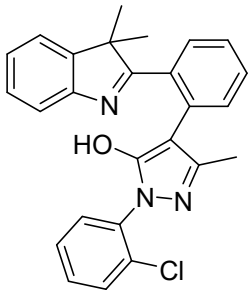
4-(2-(3,3-dimethyl-3*H*-indol-2-yl)phenyl)-3-methyl-1-(o-tolyl)-1*H*-pyrazol-5-ol (3ak)



The compound prepared using $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (6.6 mg, 0.008 mmol), 3,3-dimethyl-2-phenyl-3*H*-indole (44.2 mg, 0.2 mmol), 4-diazo-5-methyl-2-(o-tolyl)-2,4-dihydro-3*H*-pyrazol-3-one (64.2 mg, 0.3 mmol, 1.5 equiv.), and HOAc (12 mg, 0.2 mmol, 1 equiv.). After 16 h, it was cooled to room temperature and concentrated under reduced pressure. The reside was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **3ak** as a pale yellow liquid (63.5 mg, 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 12.4, 4.4 Hz, 2H), 7.51 - 7.40 (m, 3H), 7.38 - 7.30 (m, 3H), 7.25 (dt, *J* = 14.9, 5.2 Hz, 4H), 2.18 (s, 3H), 1.82 (s, 3H), 1.62 (s, 3H), 1.06 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 188.7, 150.6, 150.4, 146.4, 144.9, 137.3, 135.7, 133.6, 132.8, 132.1, 130.4, 129.6, 128.5, 127.9, 127.8, 127.4, 126.7, 126.3, 126.2, 121.6, 119.9, 102.5, 55.8, 23.6, 22.1, 17.2, 13.0. **HRMS (ESI)**: Calcd for $C_{27}H_{25}N_3O$ $[M+H]^+$: 408.2070; found: 408.2070.

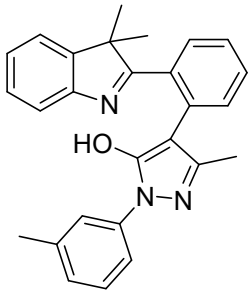
1-(2-chlorophenyl)-4-(2-(3,3-dimethyl-3*H*-indol-2-yl)phenyl)-3-methyl-1*H*-pyrazol-5-ol (3al)



The compound prepared using [Cp*Rh(MeCN)$_3$](SbF$_6$)$_2$ (6.6 mg, 0.008 mmol), 3,3-dimethyl-2-phenyl-3*H*-indole (44.2 mg, 0.2 mmol), 2-(2-chlorophenyl)-4-diazo-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (70.2 mg, 0.3 mmol, 1.5 equiv.), and HOAc (12 mg, 0.2 mmol, 1 equiv.). After 16 h, it was cooled to room temperature and concentrated under reduced pressure. The reside was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **3al** as a white solid (64.1 mg, 75%). m.p. 195-197 °C.

^{1}H NMR (400 MHz, CDCl$_3$) δ 11.81 (s, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.49 - 7.39 (m, 5H), 7.39 - 7.27 (m, 5H), 2.19 (s, 3H), 1.60 (s, 3H), 1.06 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 188.7, 151.2, 150.5, 147.4, 144.8, 136.1, 133.7, 132.7, 132.1, 131.8, 129.8, 129.7, 129.6, 129.6, 127.7, 127.6, 127.2, 126.6, 126.4, 121.5, 120.4, 102.9, 55.8, 23.7, 22.1, 13.1. **HRMS (ESI)**: Calcd for $C_{26}H_{22}ClN_3O$ $[M+H]^+$: 428.1524; found: 428.1524.

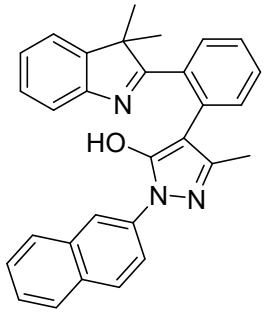
4-(2-(3,3-dimethyl-3*H*-indol-2-yl)phenyl)-3-methyl-1-(m-tolyl)-1*H*-pyrazol-5-ol (3am)



The compound prepared using [Cp*Rh(MeCN)$_3$](SbF$_6$)$_2$ (6.6 mg, 0.008 mmol), 3,3-dimethyl-2-phenyl-3*H*-indole (44.2 mg, 0.2 mmol), 4-diazo-5-methyl-2-(m-tolyl)-2,4-dihydro-3*H*-pyrazol-3-one (64.2 mg, 0.3 mmol, 1.5 equiv.), and HOAc (12 mg, 0.2 mmol, 1 equiv.). After 16 h, it was cooled to room temperature and concentrated under reduced pressure. The reside was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **3am** as a yellow liquid (40.7 mg, 50%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 12.38 (s, 1H), 7.57 (td, *J* = 13.3, 7.0 Hz, 5H), 7.43 (dd, *J* = 11.4, 7.7 Hz, 2H), 7.38 - 7.27 (m, 4H), 7.03 (d, *J* = 7.5 Hz, 1H), 2.38 (s, 3H), 2.16 (s, 3H), 1.65 (s, 3H), 1.06 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 188.1, 150.6, 150.2, 146.7, 144.9, 138.8, 138.5, 133.5, 133.1, 132.1, 129.8, 128.4, 128.0, 127.4, 126.7, 126.4, 126.4, 122.5, 121.7, 119.7, 118.9, 104.2, 55.7, 23.6, 22.3, 21.4, 13.0. **HRMS (ESI)**: Calcd for $C_{27}H_{25}N_3O$ $[M+H]^+$: 408.2070; found: 408.2070.

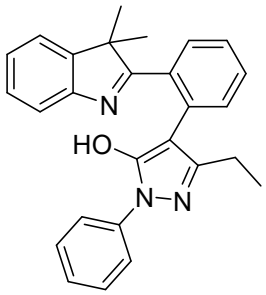
4-(2-(3,3-dimethyl-3*H*-indol-2-yl)phenyl)-3-methyl-1-(naphthalen-2-yl)-1*H*-pyrazol-5-ol (3an)



The compound prepared using $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (6.6 mg, 0.008 mmol), 3,3-dimethyl-2-phenyl-3*H*-indole (44.2 mg, 0.2 mmol), 4-diazo-5-methyl-2-(naphthalen-2-yl)-2,4-dihydro-3*H*-pyrazol-3-one (75.0 mg, 0.3 mmol, 1.5 equiv.), and HOAc (12 mg, 0.2 mmol, 1 equiv.). After 16 h, it was cooled to room temperature and concentrated under reduced pressure. The reside was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **3an** as a white solid (53.2 mg, 60%). m.p. 170-172 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.63 (s, 1H), 8.25 (s, 1H), 8.03 (d, *J* = 8.9 Hz, 1H), 7.91 - 7.81 (m, 3H), 7.64 - 7.54 (m, 3H), 7.47 (dd, *J* = 17.5, 7.4 Hz, 4H), 7.36 - 7.27 (m, 3H), 2.22 (s, 3H), 1.66 (s, 3H), 1.09 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 188.1, 151.0, 150.1, 147.1, 144.8, 136.6, 133.5, 133.0, 132.0, 131.3, 129.8, 128.4, 128.1, 128.1, 127.5, 127.4, 126.7, 126.5, 126.2, 125.4, 121.7, 120.9, 119.6, 118.9, 104.4, 55.7, 23.6, 22.3, 13.1. **HRMS (ESI)**: Calcd for $C_{30}H_{25}N_3O$ $[M+H]^+$: 444.2070; found: 444.2070.

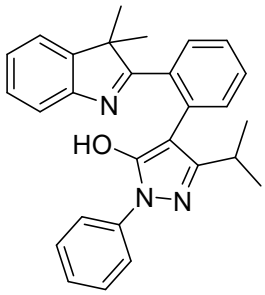
4-(2-(3,3-dimethyl-3H-indol-2-yl)phenyl)-3-ethyl-1-phenyl-1H-pyrazol-5-ol (3ao)



The compound prepared using $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (6.6 mg, 0.008 mmol), 3,3-dimethyl-2-phenyl-3*H*-indole (44.2 mg, 0.2 mmol), 4-diazo-5-ethyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (64.2 mg, 0.3 mmol, 1.5 equiv.), and HOAc (12 mg, 0.2 mmol, 1 equiv.). After 16 h, it was cooled to room temperature and concentrated under reduced pressure. The reside was purified by silica gel column chromatography

(petroleum ether/ethyl acetate = 10:1) to afford **3ao** as a yellow liquid (52.9 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.78 (s, 1H), 7.82 (d, *J* = 7.7 Hz, 2H), 7.65 – 7.57 (m, 2H), 7.57 – 7.51 (m, 1H), 7.47 – 7.28 (m, 7H), 7.21 (t, *J* = 7.4 Hz, 1H), 2.62 (qd, *J* = 7.5, 3.4 Hz, 2H), 1.69 (s, 3H), 1.28 (s, 3H), 1.11 (d, *J* = 3.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.7, 152.2, 150.7, 150.0, 144.9, 139.1, 133.2, 132.3, 129.8, 128.60, 128.0, 127.4, 126.7, 126.3, 125.4, 124.4, 123.9, 121.6, 119.7, 103.3, 55.7, 23.9, 22.6, 20.8, 13.3. **HRMS (ESI)**: Calcd for $C_{27}H_{25}N_3O$ [M+H]$^+$: 408.2070; found: 408.2070.

4-(2-(3,3-dimethyl-3H-indol-2-yl)phenyl)-3-isopropyl-1-phenyl-1H-pyrazol-5-ol (3ap)



The compound prepared using [Cp*Rh(MeCN)$_3$](SbF$_6$)$_2$ (6.6 mg, 0.008 mmol), 3,3-dimethyl-2-phenyl-3*H*-indole (44.2 mg, 0.2 mmol), 4-diazo-5-isopropyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (68.4 mg, 0.3 mmol, 1.5 equiv.), and HOAc (12 mg, 0.2 mmol, 1 equiv.). After 16 h, it was cooled to room temperature and concentrated under reduced pressure. The reside was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford **3ap** as a yellow liquid (61.5 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.78 (s, 1H), 7.86 (d, *J* = 7.9 Hz, 2H), 7.62 (d, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.36 (m, 5H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 2.97 (dd, *J* = 13.1, 6.4 Hz, 1H), 1.72 (s, 3H), 1.42 (d, *J* = 6.5 Hz, 3H), 1.15 (s, 3H), 1.02 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.5, 155.8, 150.4, 150.1, 145.0, 139.3, 133.5, 132.6, 129.7, 128.58, 128.0, 127.5, 126.8, 126.3, 125.3, 121.7, 121.6, 119.7, 103.0, 55.7, 31.5, 23.0, 22.7, 22.6, 14.1. **HRMS (ESI)**: Calcd for $C_{28}H_{27}N_3O$ [M+H]$^+$: 422.2227; found: 422.2226.

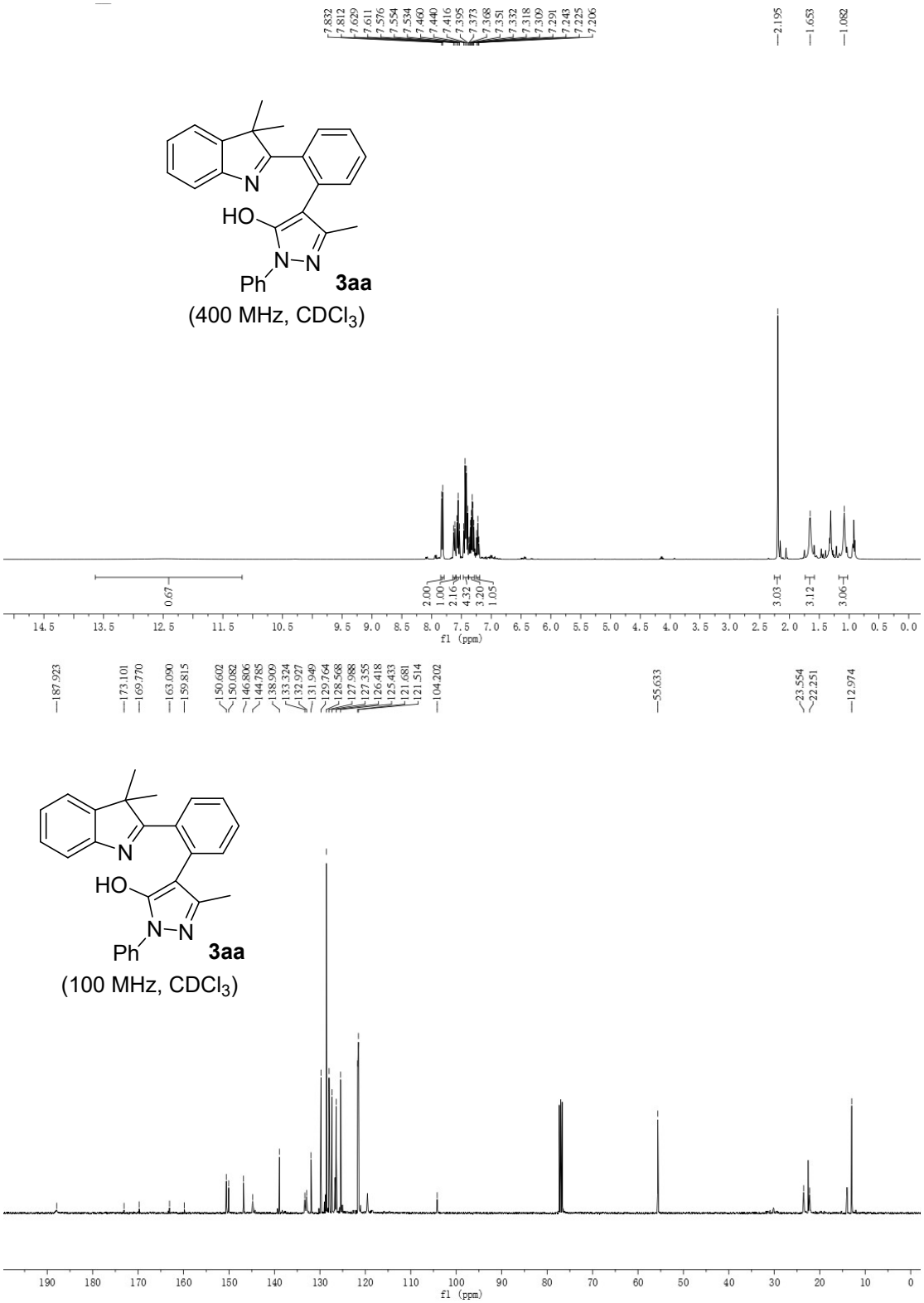
6. References

1. Gao, J.; Luo, K.; Wei, X.; Wang, H.; Liu, H.; Zhou, Z. Rh(III)-Catalyzed Successive C-H Activations of 2-Phenyl-3*H*-indoles and Cyclization Cascades to Construct Highly Fused Indole Heteropolycycles. *Org. Lett*. **2023**, *25*, 3341-3346.

2. F. Fang, S. Hu, C. Li, Q. Wang, R. Wang, X. Han, Y. Zhou, H. Liu, Catalytic System-

Controlled Divergent Reaction Strategies for the Construction of Diversified Spiropyrazolone Skeletonsfrom Pyrazolidinones and Diazopyrazolones, *Angew. Chem. Int. Ed.* **2021**, *60*, 21327−21333.

7. Copies of ^{1}H, ^{13}C, and ^{19}F NMR of products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7.416
7.395
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7.351
7.332
7.318
7.309
7.291
7.243
7.225
7.206
2.195
1.653
1.082
HO
N
N
N
Ph
3aa
(400 MHz, CDCl3)
0.67
2.00
1.00
2.16
4.32
3.20
1.05
3.03
3.12
3.06
f1 (ppm)
187.923
173.101
169.770
163.090
159.815
150.602
150.082
146.806
144.785
138.909
133.324
132.927
131.949
129.764
128.568
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127.355
126.418
125.433
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121.514
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HO
N
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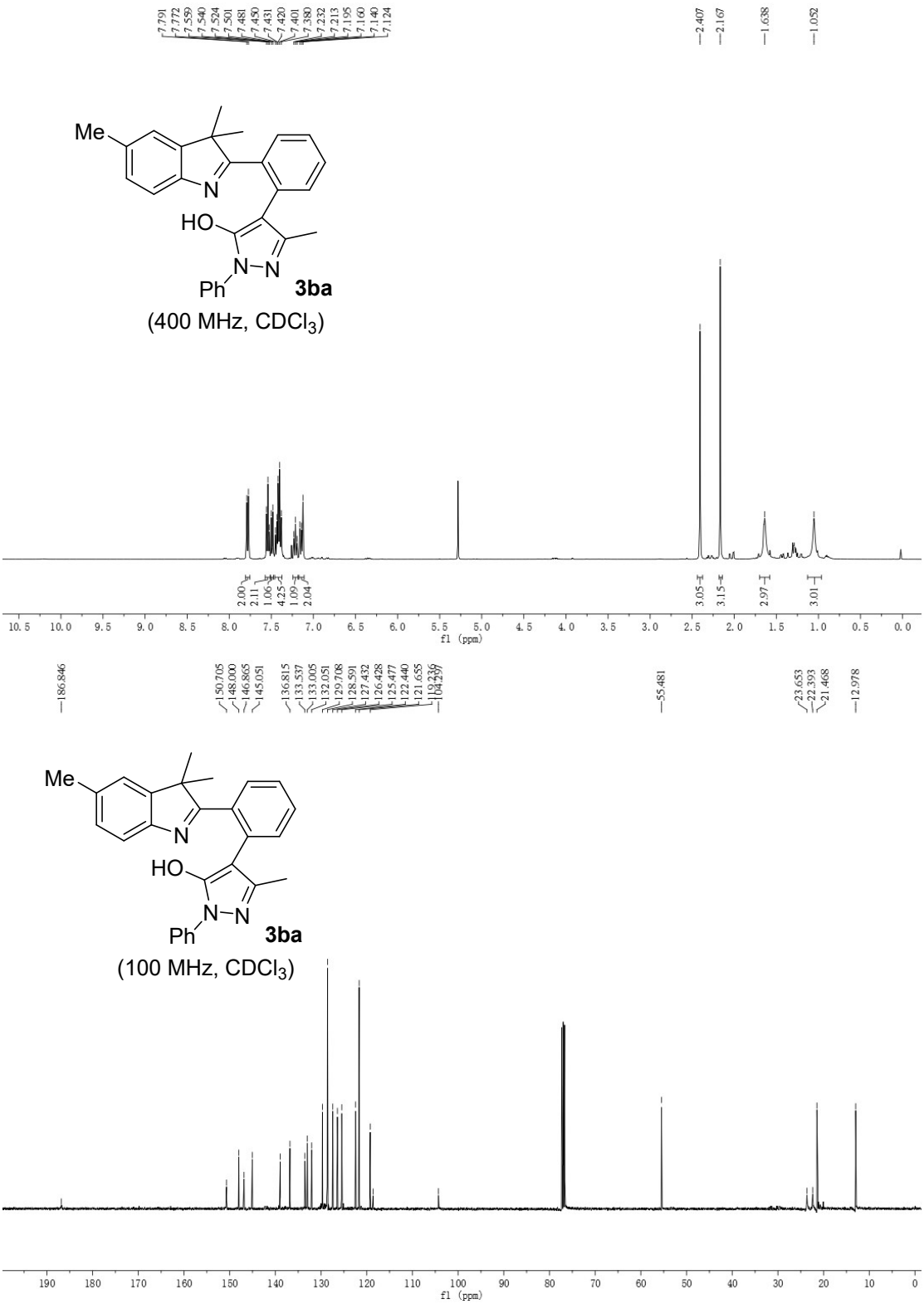
N
Ph
3aa
(100 MHz, CDCl3)
f1 (ppm)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7.540
7.524
7.501
7.481
7.450
7.431
7.420
7.401
7.380
7.232
7.213
7.195
7.160
7.140
7.124
2.407
2.167
1.638
1.052
Me
N
HO
N–N
Ph
3ba
(400 MHz, CDCl3)
2.00
2.11
1.06
4.25
1.09
2.04
3.05
3.15
2.97
3.01
f1 (ppm)
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146.865
145.051
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129.708
128.591
127.432
126.428
125.477
122.440
121.655
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Me
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HO
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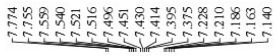
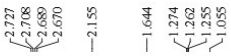
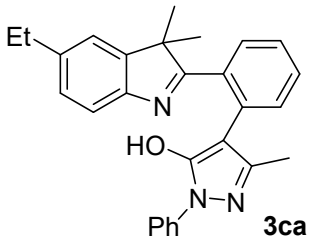
Ph
3ba
(100 MHz, CDCl3)
f1 (ppm)

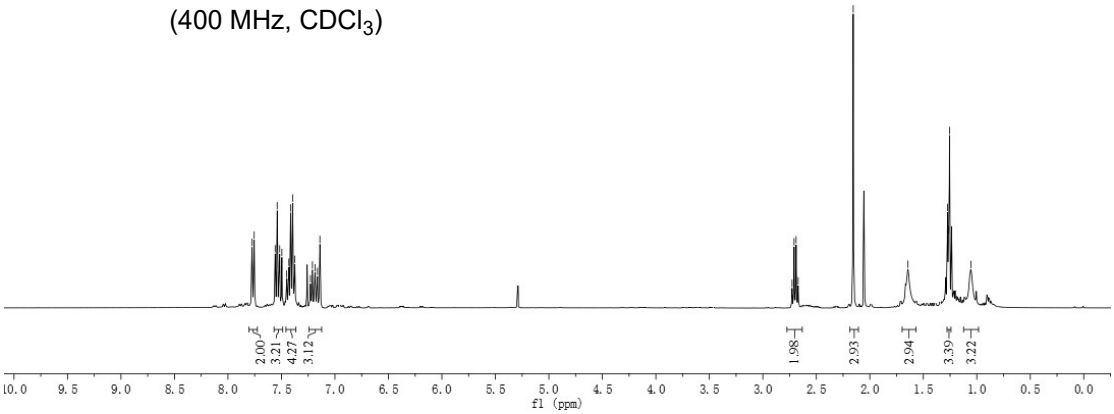


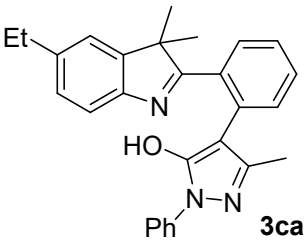




3ca

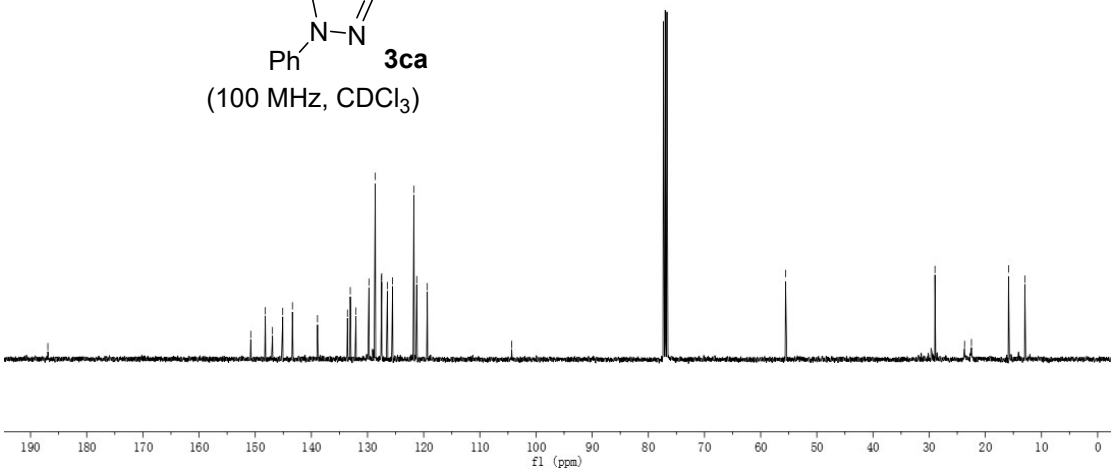
(400 MHz, $CDCl_3$)

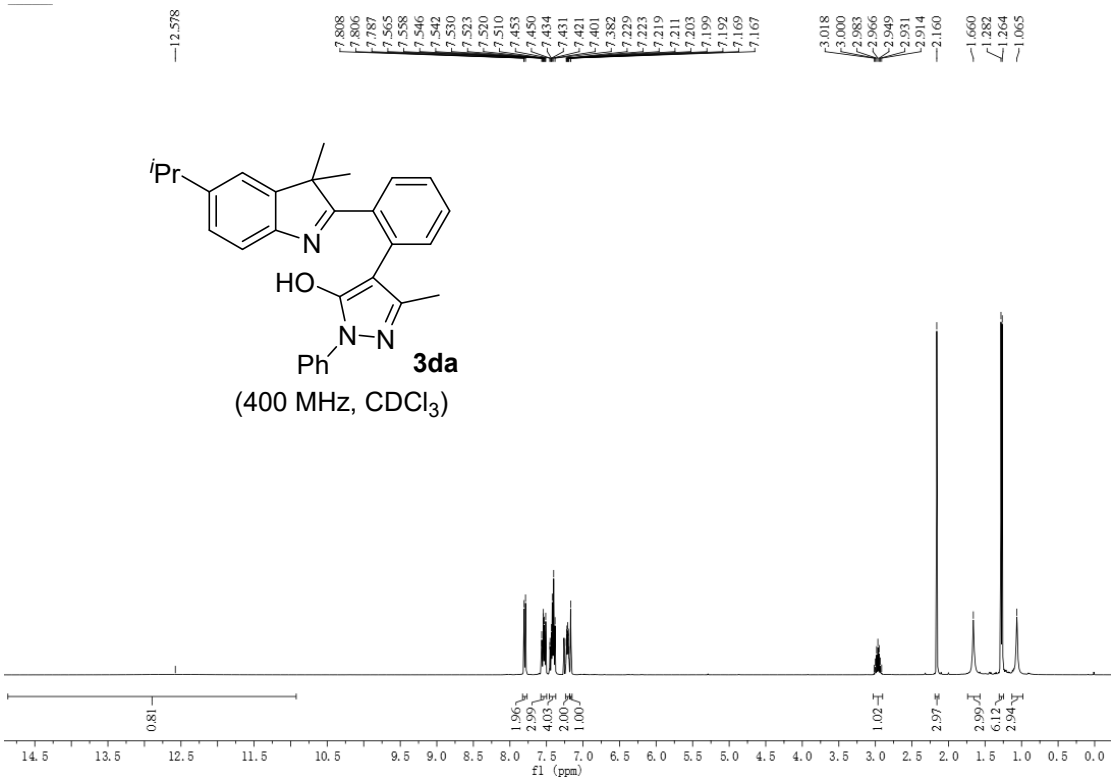




3ca

(100 MHz, $CDCl_3$)

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7.523
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7.450
7.434
7.431
7.421
7.401
7.382
7.229
7.223
7.219
7.211
7.203
7.199
7.192
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7.167
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3.000
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2.966
2.949
2.931
2.914
2.160
1.660
1.282
1.264
1.065
iPr
N
HO
N–N
Ph
3da
(400 MHz, CDCl3)
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4.03
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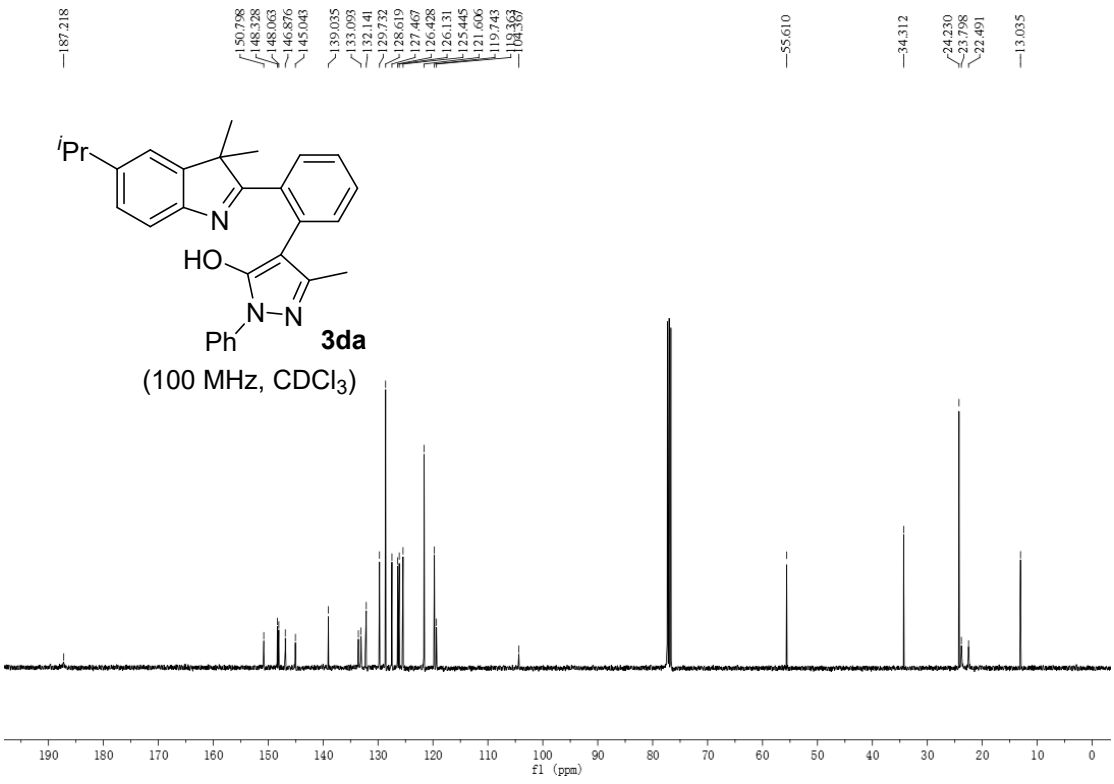
1.00
1.02
2.97
2.99
6.12
2.94
f1 (ppm)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126.428
126.131
125.445
121.606
119.743
104.369
55.610
34.312
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Ph
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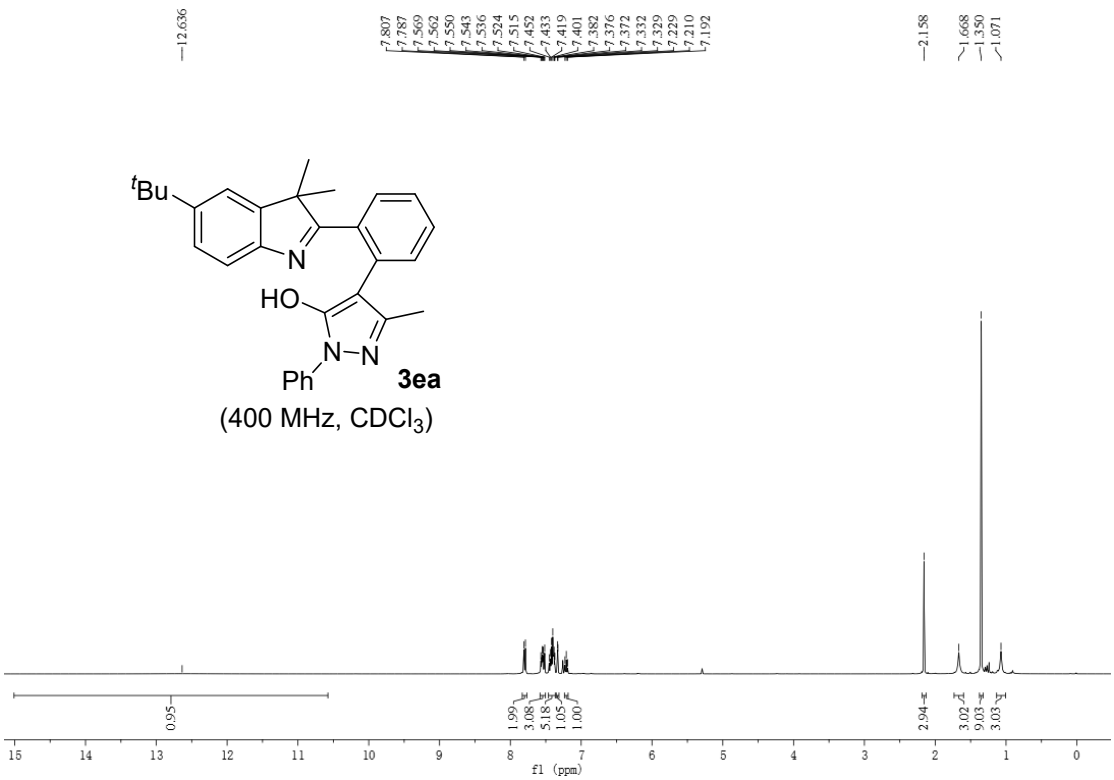
(100 MHz, CDCl3)
f1 (ppm)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7.433
7.419
7.401
7.382
7.376
7.372
7.332
7.329
7.229
7.210
7.192
2.158
1.668
1.350
1.071
tBu
N
HO
N–N
Ph
3ea
(400 MHz, CDCl3)
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3.08
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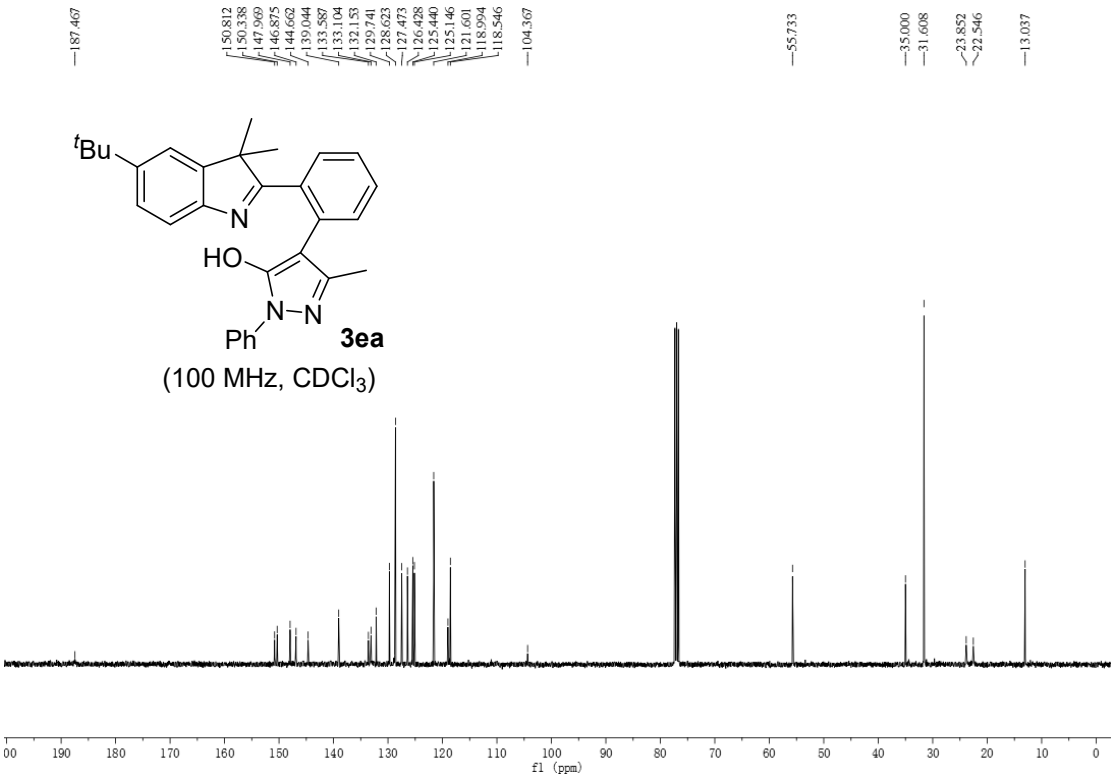
1.05
1.00
2.94
3.02
9.03
3.03
f1 (ppm)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126.428
125.440
125.146
121.601
118.994
118.546
104.367
55.733
35.000
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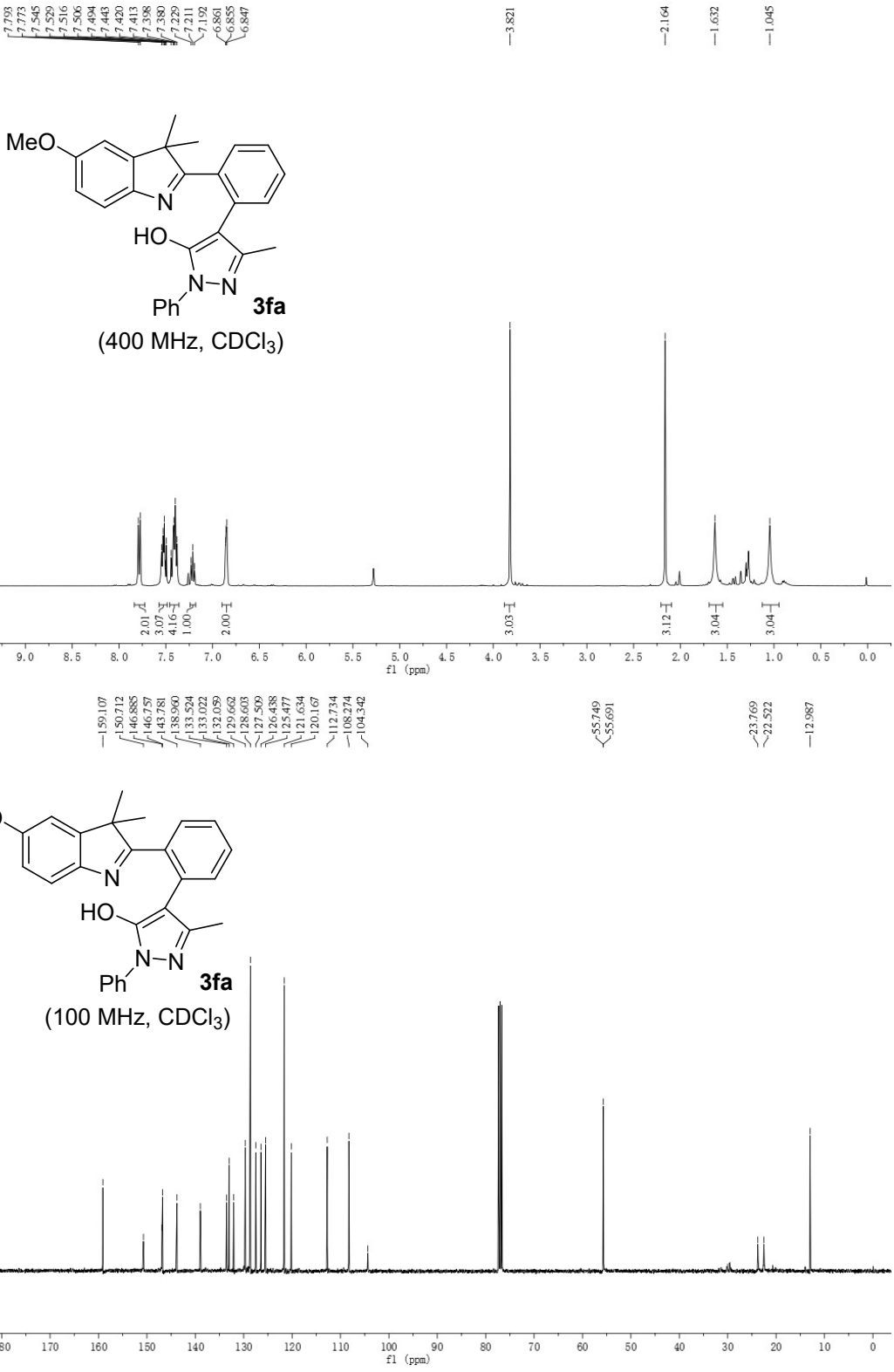
Ph
3ea
(100 MHz, CDCl3)
f1 (ppm)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7.413
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7.380
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7.211
7.192
6.861
6.855
6.847
3.821
2.164
1.632
1.045
MeO
N
HO
N–N
Ph
3fa
(400 MHz, CDCl3)
2.01
3.07
4.16
1.00
2.00
3.03
3.12
3.04
3.04
f1 (ppm)
185.775
159.107
150.712
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146.757
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127.509
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55.749
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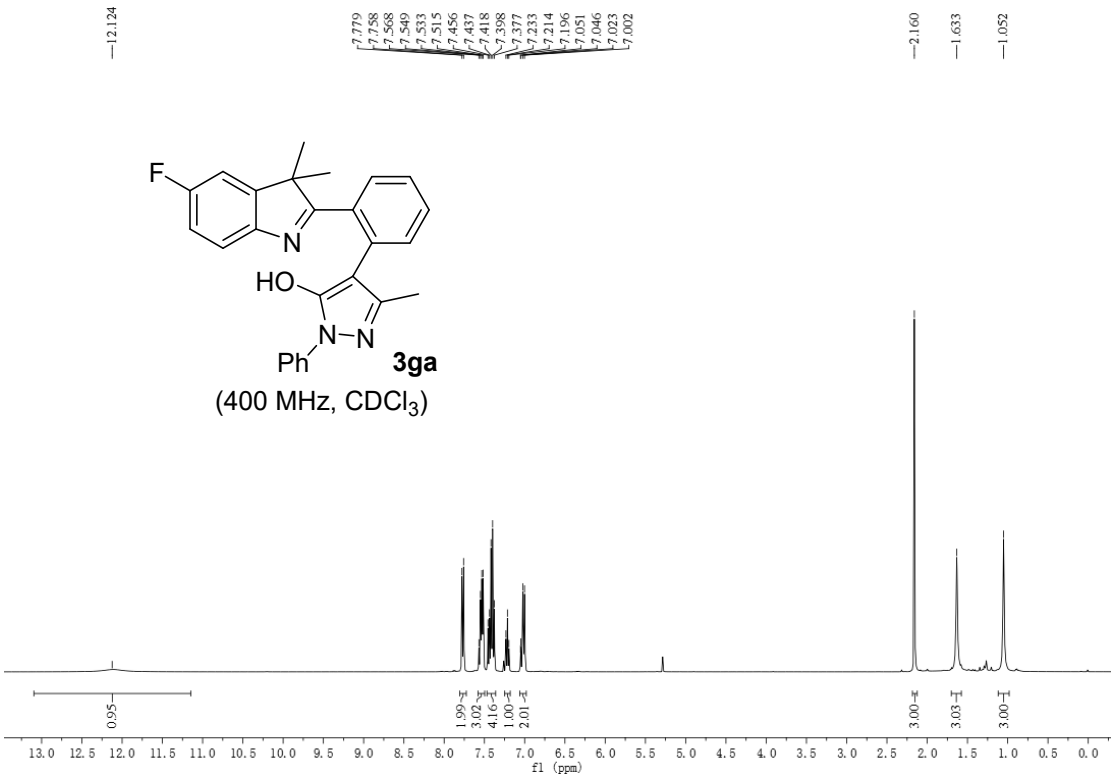
HO
N–N
Ph
3fa
(100 MHz, CDCl3)
f1 (ppm)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7.046
7.023
7.002
2.160
1.633
1.052
F
N
HO
N–N
Ph
3ga
(400 MHz, CDCl3)
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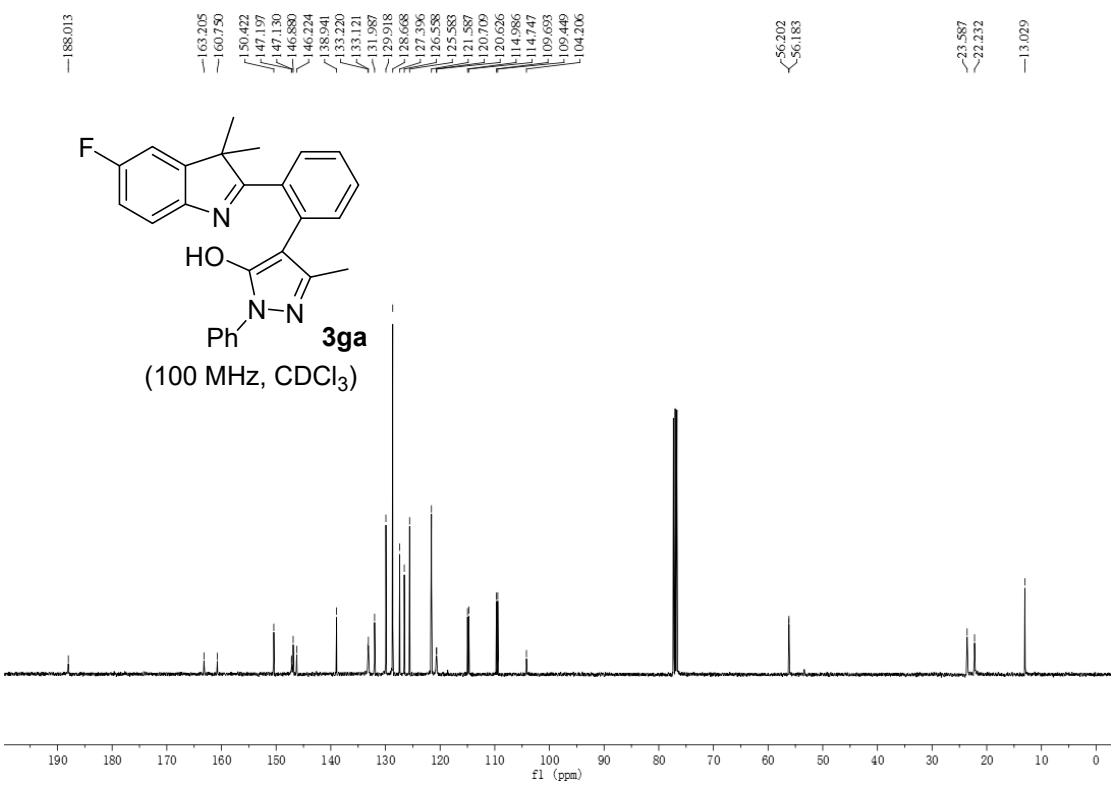
3.00
3.03
3.00
f1 (ppm)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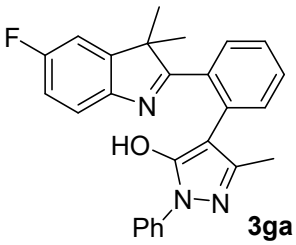
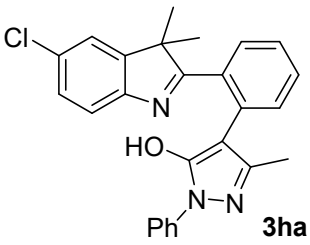
126.588
125.583
121.587
120.709
120.626
114.986
114.747
109.693
109.449
104.206
56.202
56.183
23.587
22.232
13.029
F
N
HO
N–N
Ph
3ga
(100 MHz, CDCl3)
f1 (ppm)



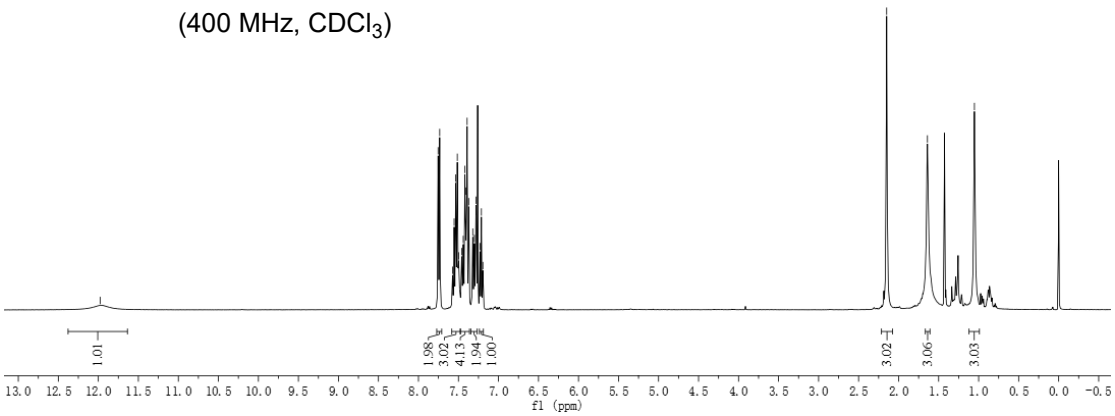
3ga

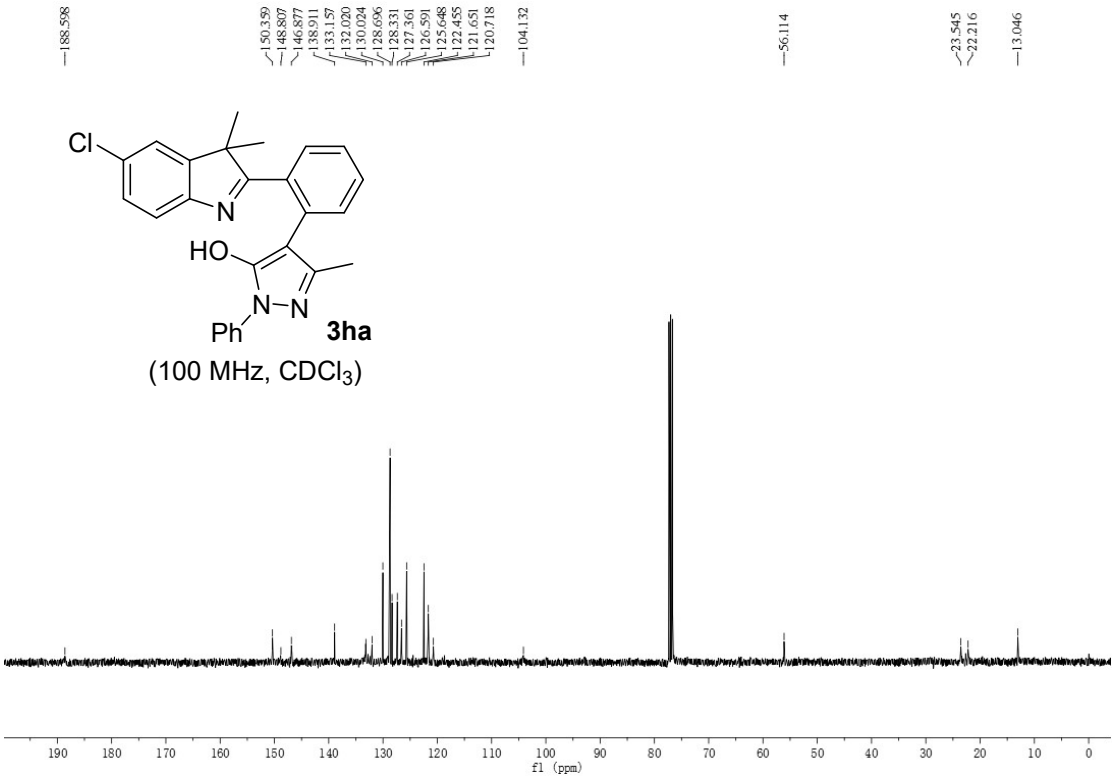
(376 MHz, $CDCl_3$)

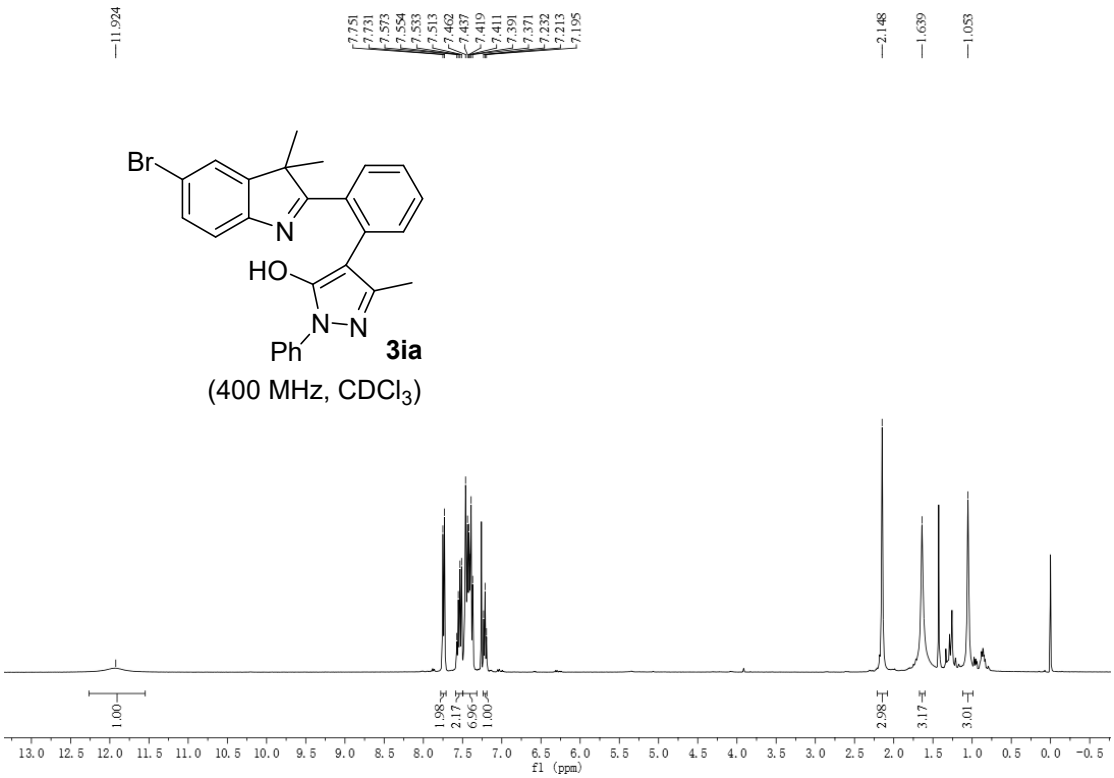


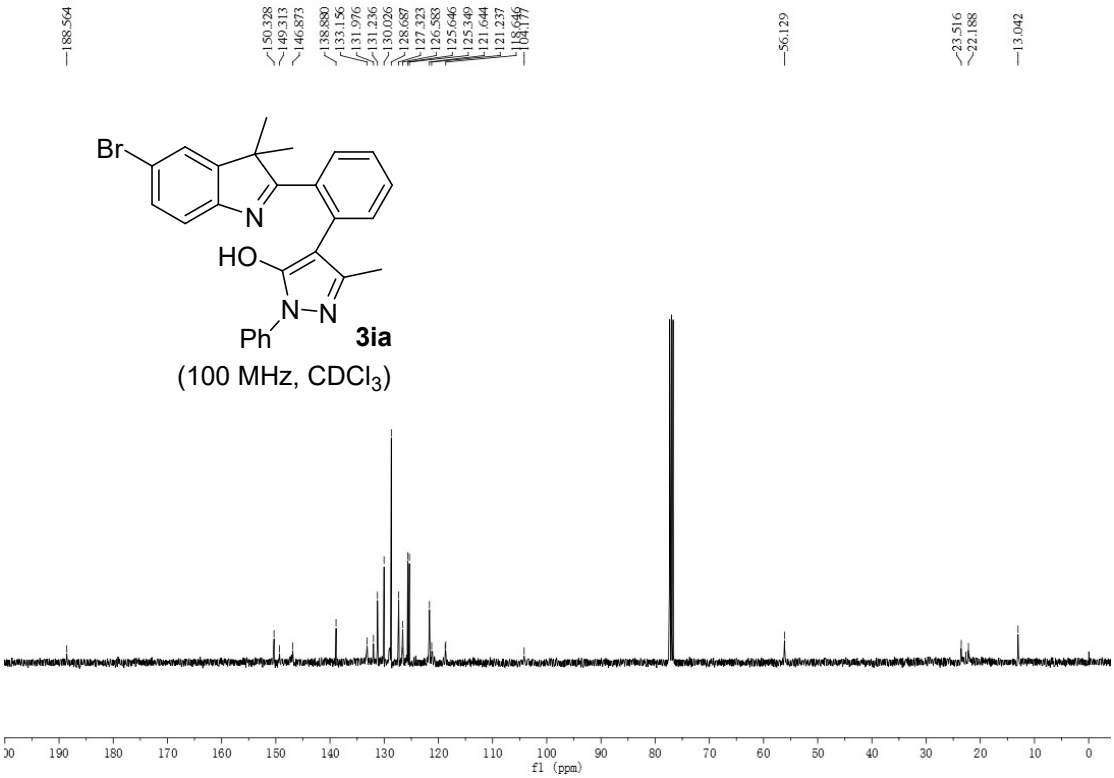
3ha

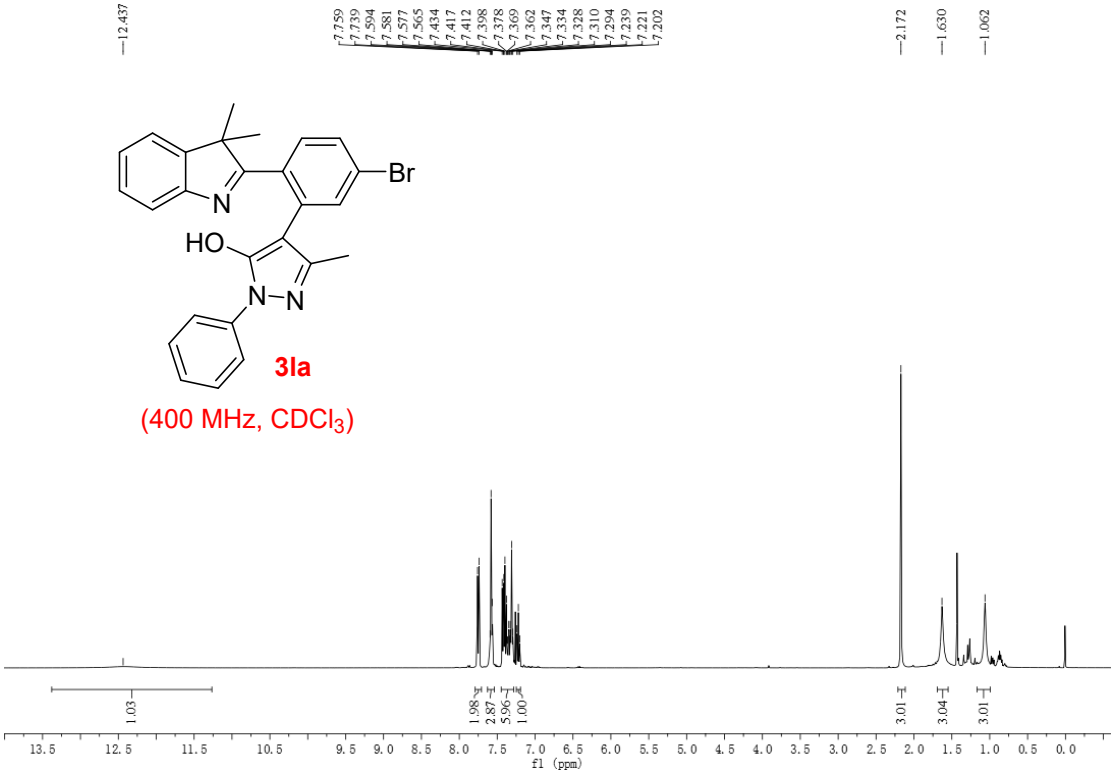
(400 MHz, $CDCl_3$)

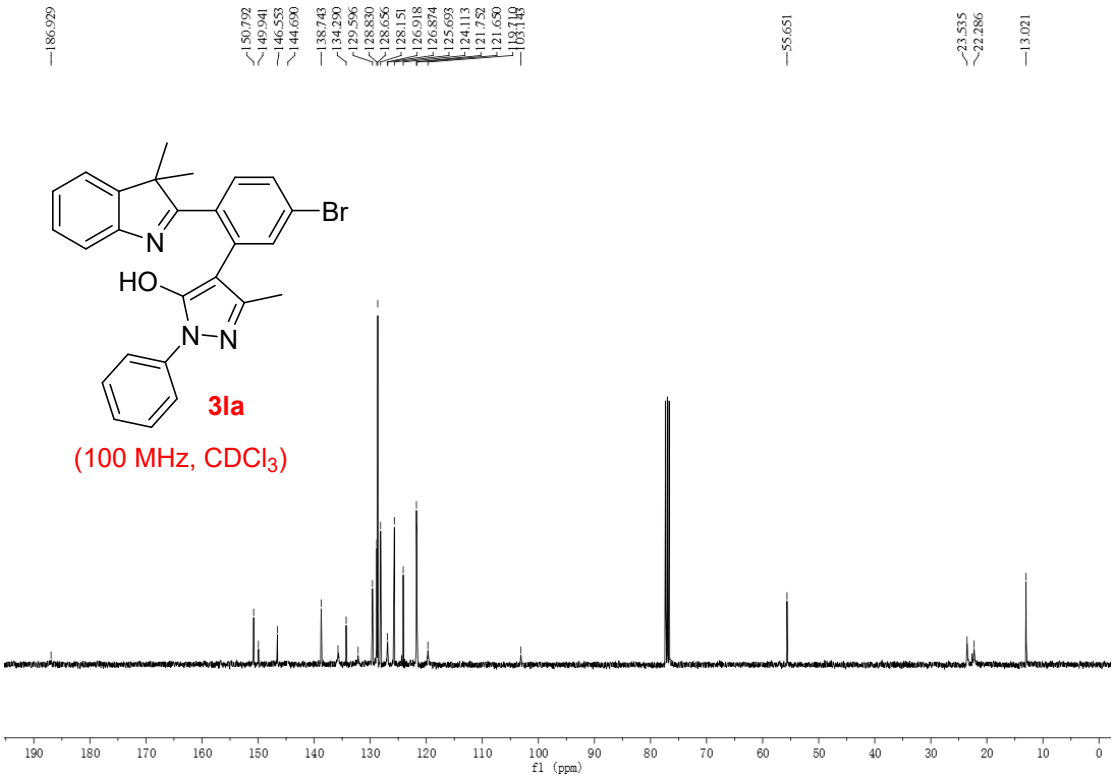


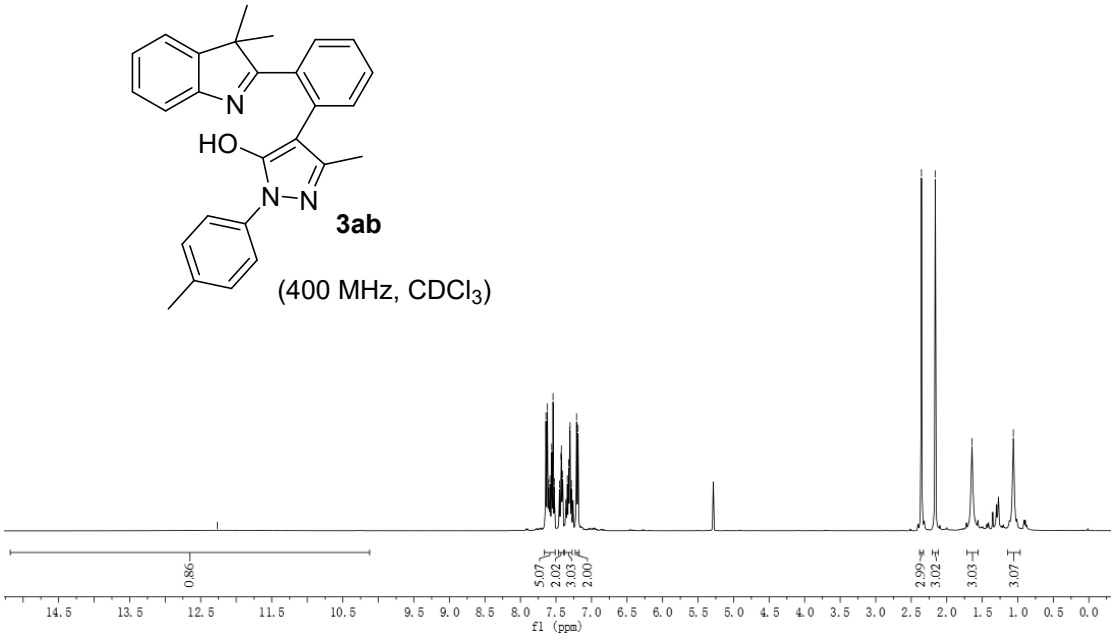

188.598
150.399
148.807
146.877
138.911
133.157
132.020
130.024
128.696
128.331
127.361
126.591
125.648
122.455
121.651
120.718
104.132
56.114
23.545
22.216
13.046
Cl
N
HO
N–N
Ph
3ha
(100 MHz, CDCl3)
f1 (ppm)

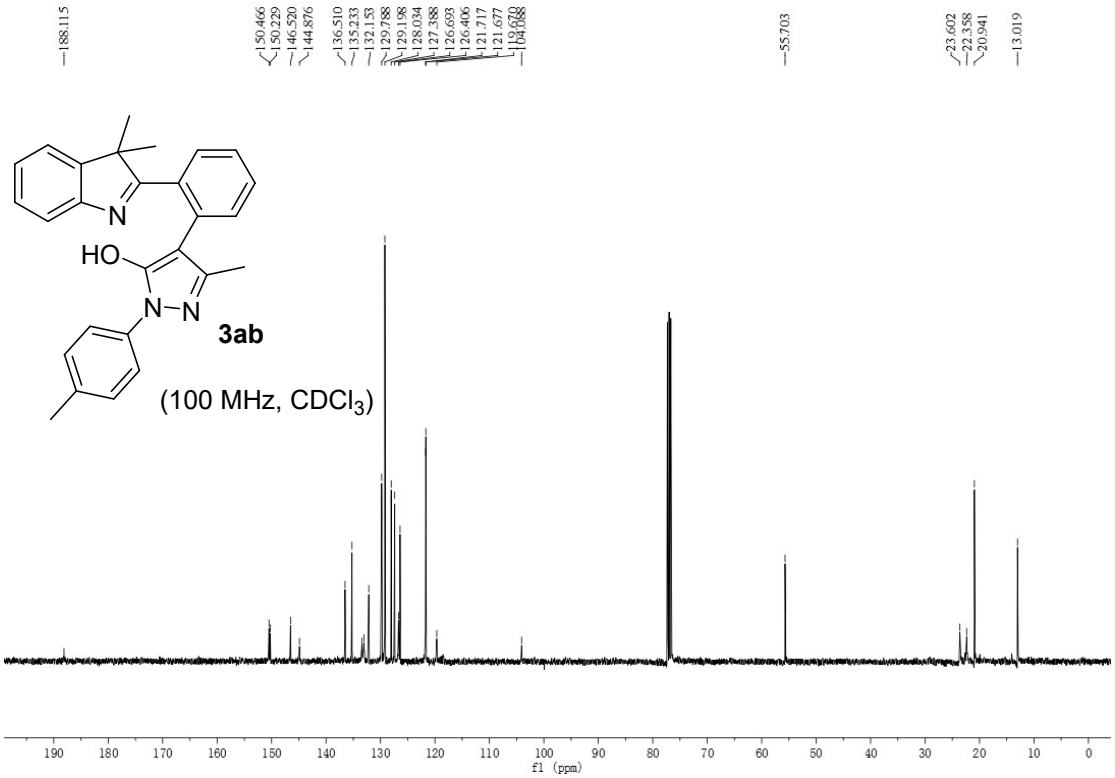

11.924
7.751
7.731
7.573
7.554
7.533
7.513
7.462
7.437
7.419
7.411
7.391
7.371
7.232
7.213
7.195
2.148
1.639
1.053
Br
N
HO
N–N
Ph
3ia
(400 MHz, CDCl3)
1.00
1.98
2.17
6.96
1.00
2.98
3.17
3.01
f1 (ppm)

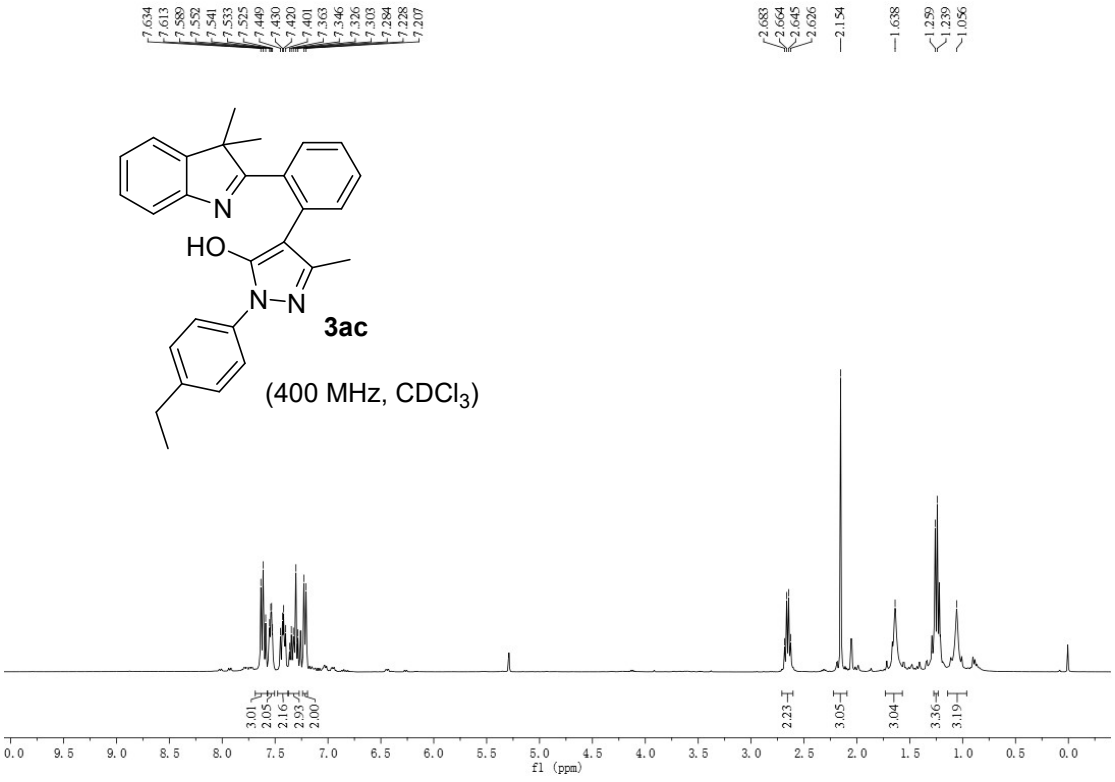

Br
N
HO
N–N
Ph
3ia
(100 MHz, CDCl3)
f1 (ppm)

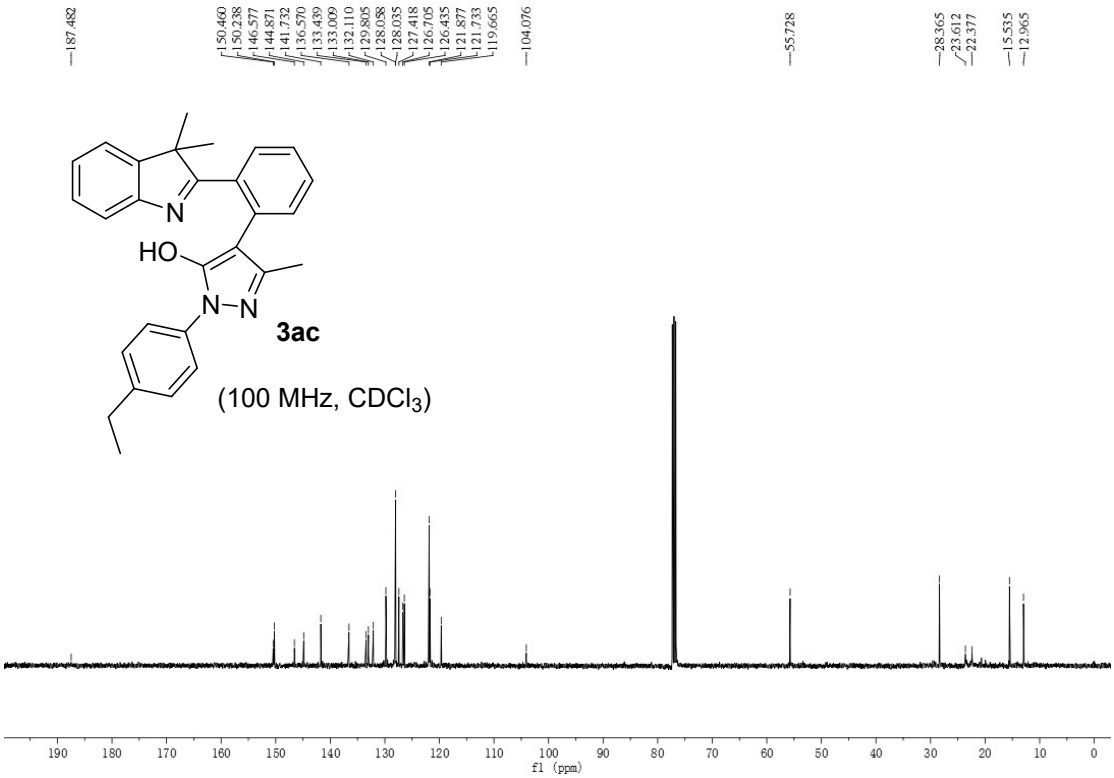

Br
N
HO
N–N
3la
(400 MHz, CDCl3)
f1 (ppm)

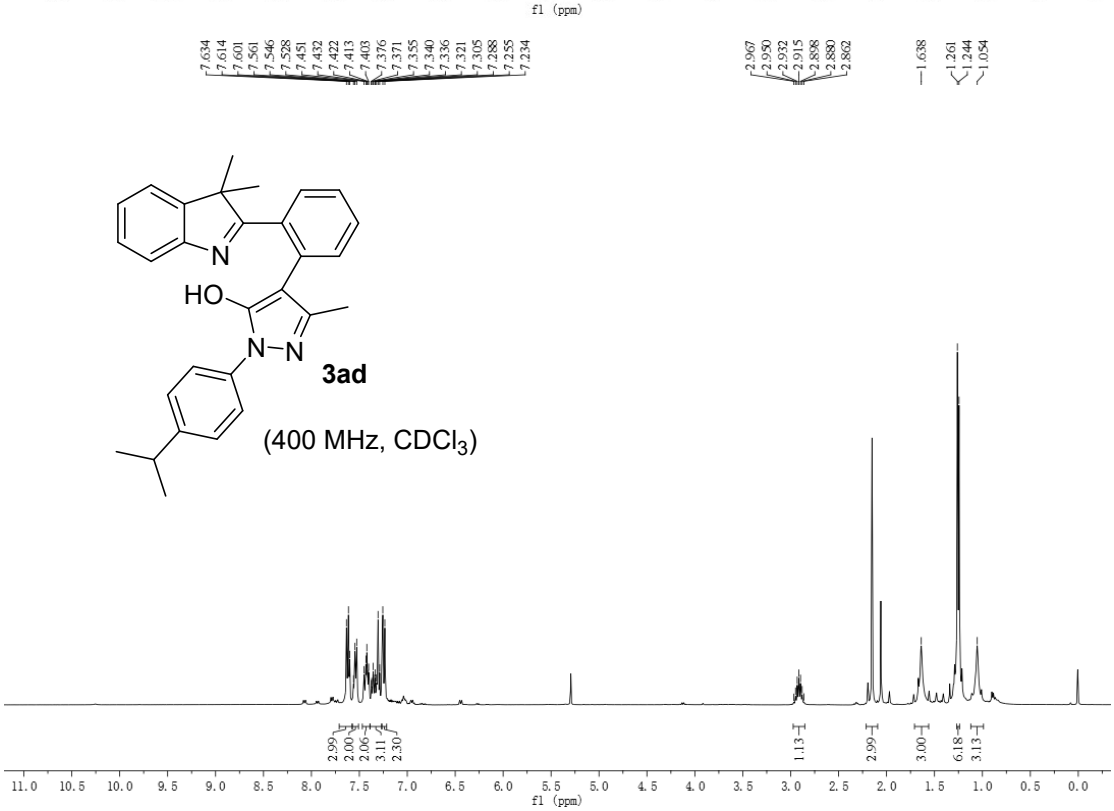

Br
HO
N
N–N
3la
(100 MHz, CDCl3)
f1 (ppm)

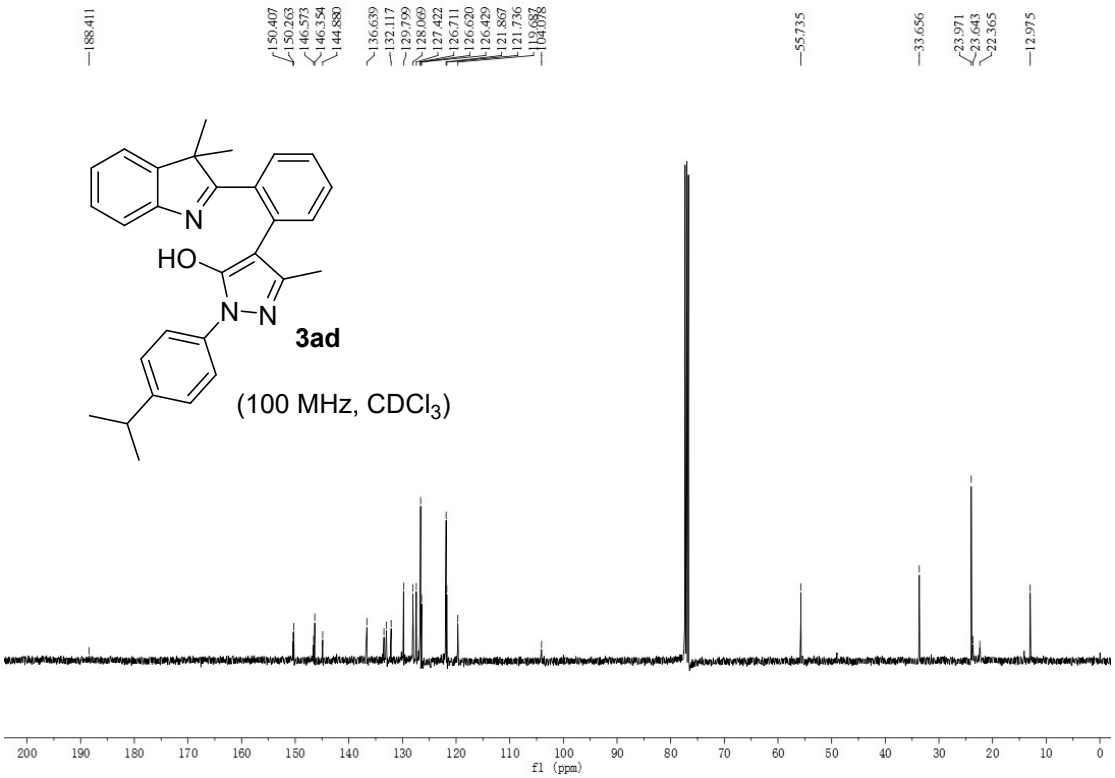

HO
N
N–N
3ab
(400 MHz, CDCl3)
f1 (ppm)

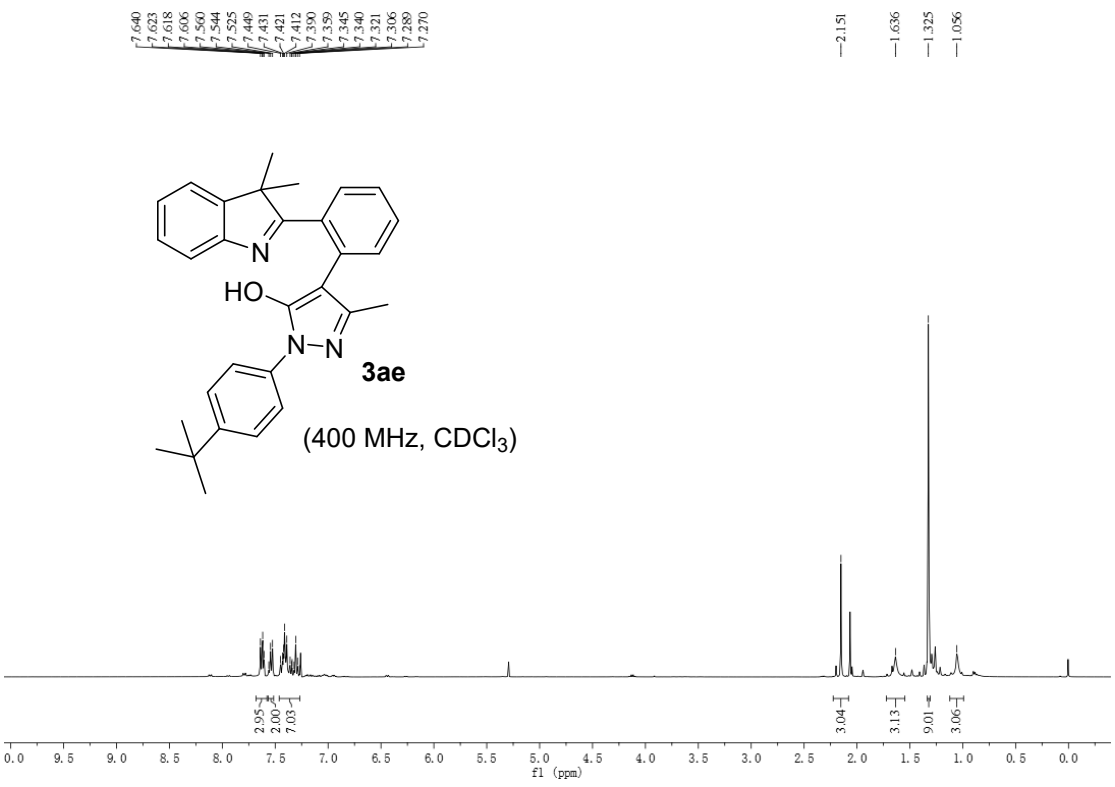

188.115
150.466
150.229
146.520
144.876
136.510
135.233
132.153
129.788
129.198
128.034
127.388
126.693
126.406
121.717
121.677
119.670
114.088
55.703
23.602
22.358
20.941
13.019
HO
N
N–N
3ab
(100 MHz, CDCl3)
f1 (ppm)

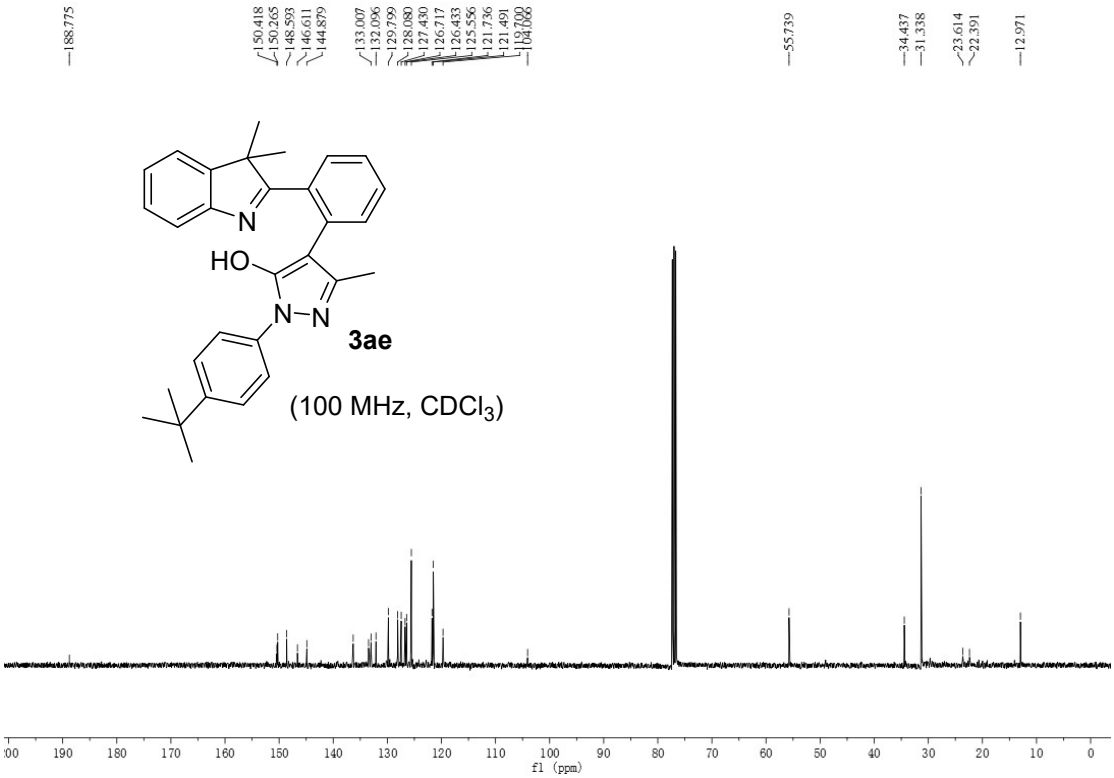

7.634
7.613
7.589
7.552
7.541
7.533
7.525
7.449
7.430
7.420
7.401
7.363
7.346
7.326
7.303
7.284
7.228
7.207
2.683
2.664
2.645
2.626
2.154
1.638
1.259
1.239
1.056
HO
N
N–N
3ac
(400 MHz, CDCl3)
3.01
2.05
2.16
2.93
2.00
2.23
3.05
3.04
3.36
3.19
f1 (ppm)

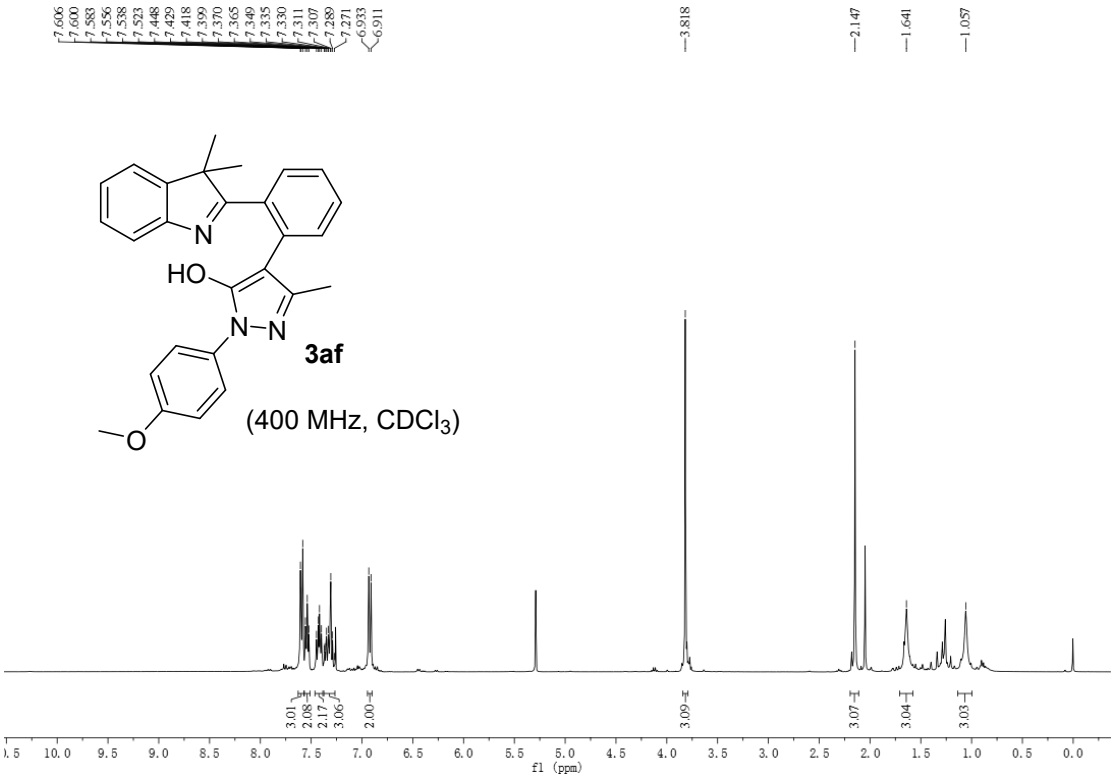

187.482
150.460
150.238
146.577
144.871
141.732
136.570
133.439
133.009
132.110
129.805
128.038
128.035
127.418
126.705
126.435
121.877
121.733
119.665
104.076
55.728
28.365
23.612
22.377
15.535
12.965
HO
N
N–N
3ac
(100 MHz, CDCl3)
f1 (ppm)

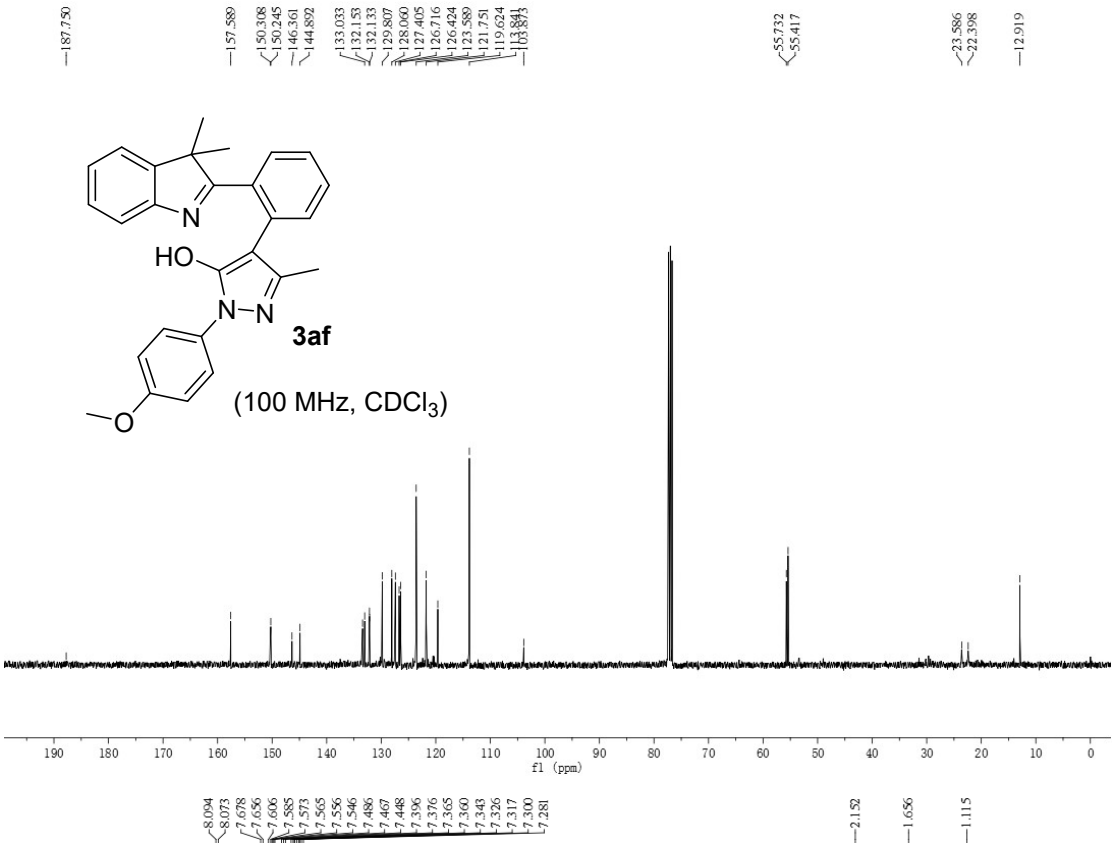

7.634
7.614
7.601
7.561
7.546
7.528
7.451
7.432
7.422
7.413
7.403
7.376
7.371
7.355
7.340
7.336
7.321
7.305
7.288
7.255
7.234
2.967
2.950
2.932
2.915
2.898
2.880
2.862
1.638
1.261
1.244
1.054
HO
N
N–N
3ad
(400 MHz, CDCl3)
2.99
2.00
2.06
3.11
2.30
1.13
2.99
3.00
6.18
3.13
f1 (ppm)

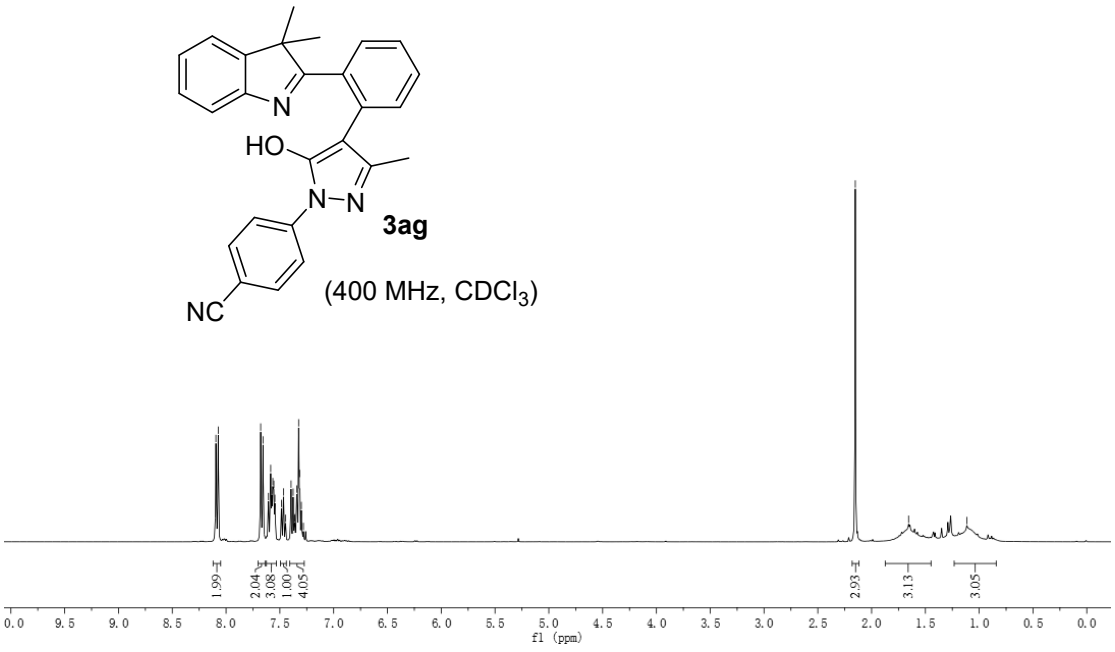

188.411
150.407
150.263
146.573
146.354
144.880
136.639
132.117
129.799
128.069
127.422
126.711
126.620
126.429
121.867
121.736
119.687
104.098
55.735
33.656
23.971
23.643
22.365
12.975
HO
N
N–N
3ad
(100 MHz, CDCl3)
f1 (ppm)

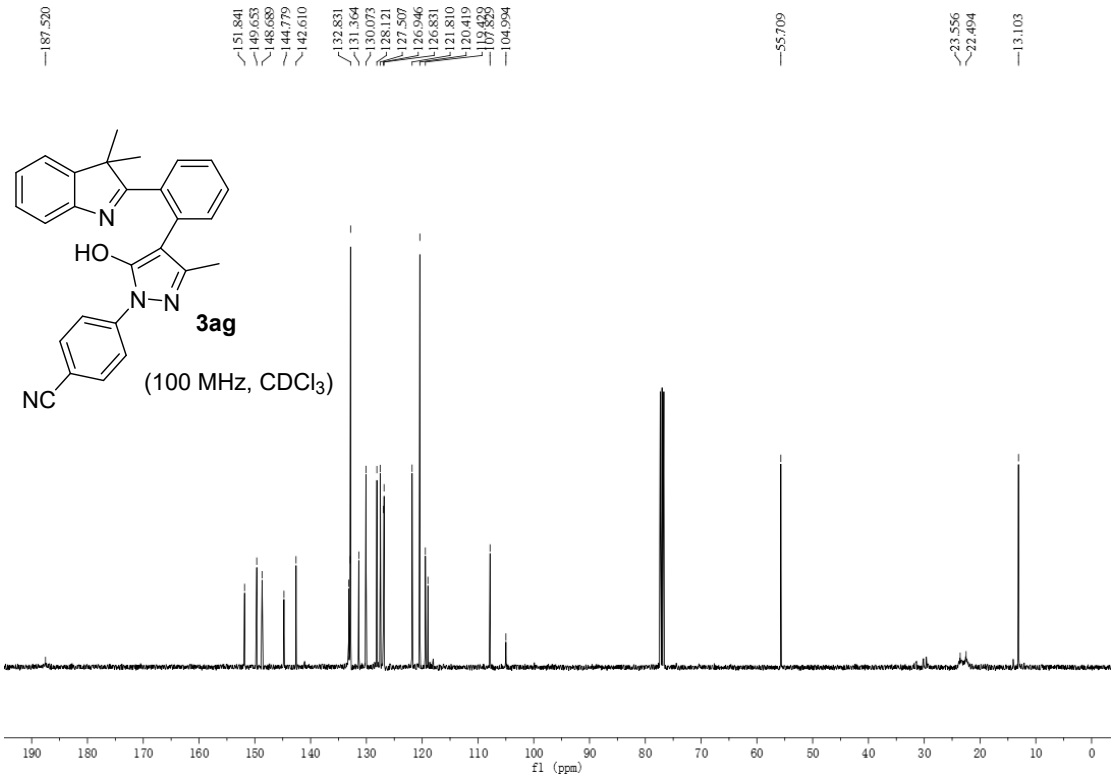

7.640
7.623
7.618
7.606
7.560
7.544
7.525
7.449
7.431
7.421
7.412
7.390
7.359
7.345
7.340
7.321
7.306
7.289
7.270
2.151
1.636
1.325
1.056
HO
N
N–N
3ae
(400 MHz, CDCl3)
2.95
2.00
7.03
3.04
3.13
9.01
3.06
f1 (ppm)

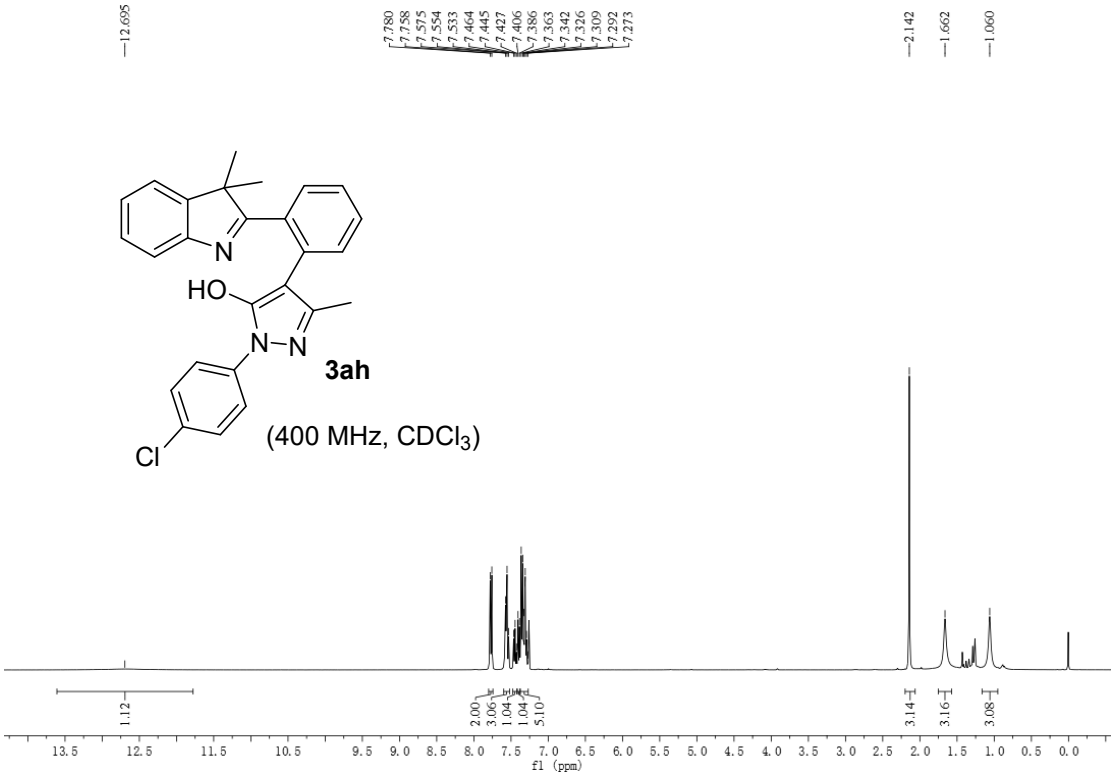

188.775
150.418
150.265
148.593
146.611
144.879
133.007
132.096
129.799
128.080
127.430
126.717
126.433
125.556
121.736
121.491
119.700
104.000
55.739
34.437
31.338
23.614
22.391
12.971
HO
N
N–N
3ae
(100 MHz, CDCl3)
f1 (ppm)

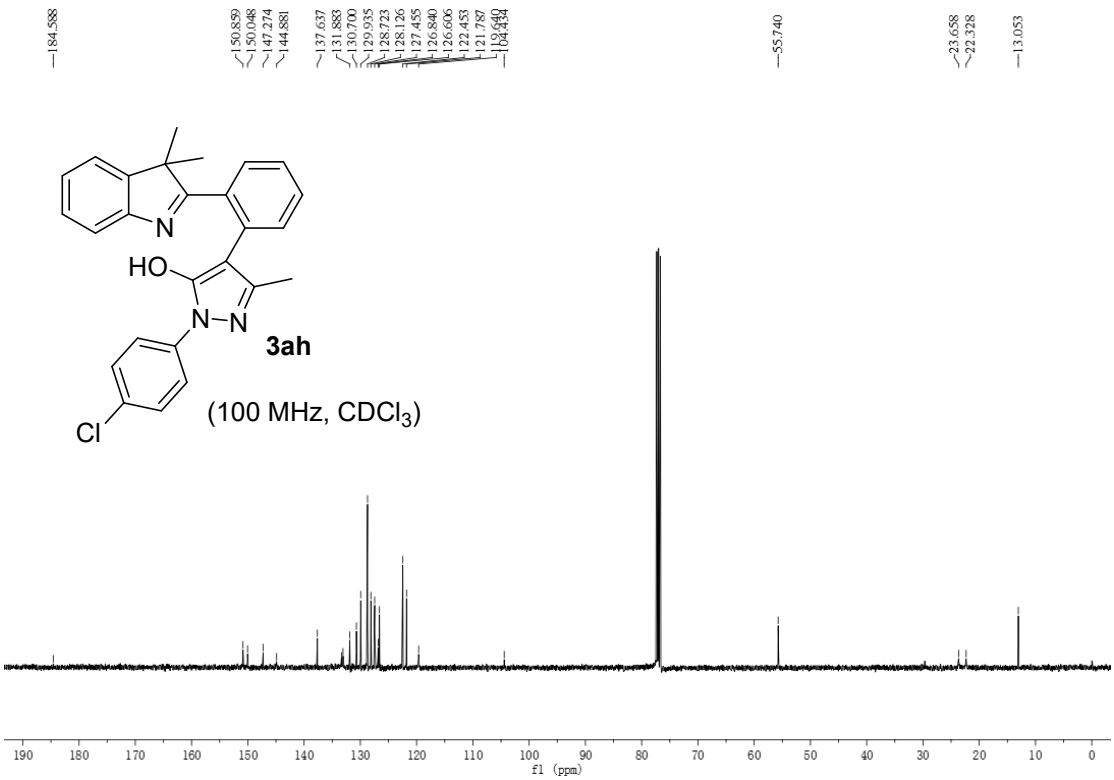

7.606
7.600
7.583
7.556
7.538
7.523
7.448
7.429
7.418
7.399
7.370
7.365
7.349
7.335
7.330
7.311
7.307
7.289
7.271
6.933
6.911
3.818
2.147
1.641
1.057
HO
N
N–N
O
3af
(400 MHz, CDCl3)
3.01
2.08
2.17
3.06
2.00
3.09
3.07
3.04
3.03
f1 (ppm)

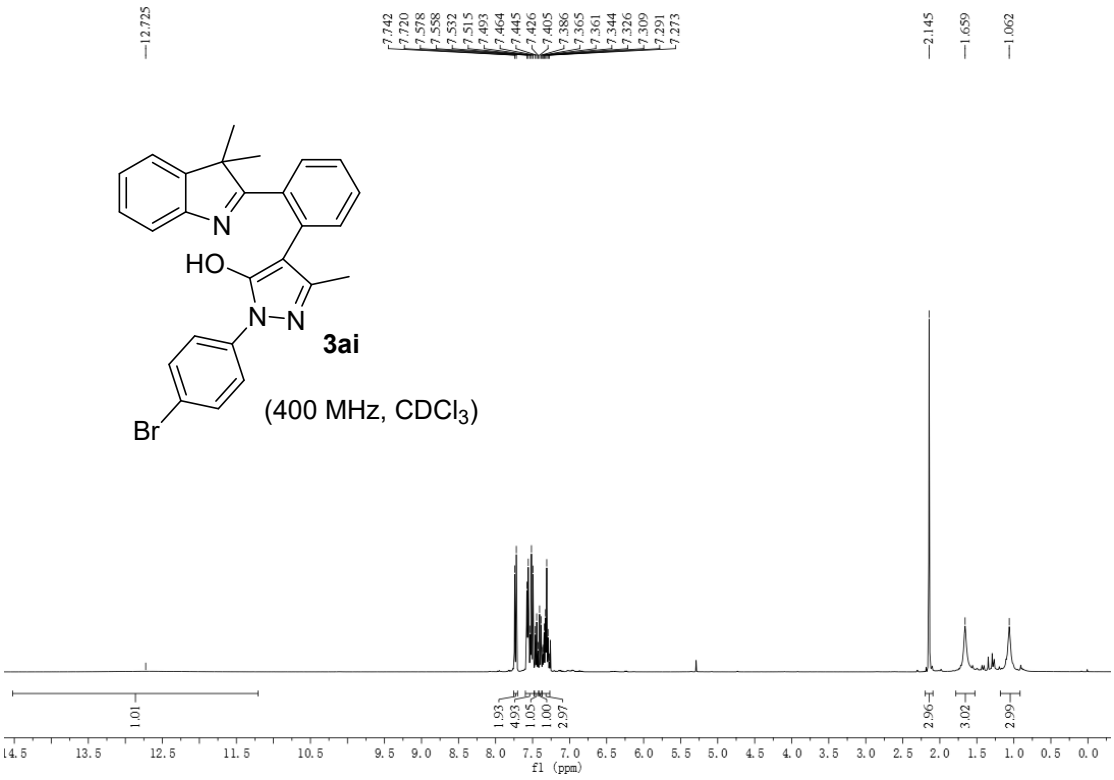

187.750
157.589
150.308
150.245
146.361
144.892
133.033
132.153
132.133
129.807
128.090
127.405
126.716
126.424
123.589
121.751
119.624
55.732
55.417
23.586
22.398
12.919
HO
N
N–N
O
3af
(100 MHz, CDCl3)
f1 (ppm)
8.094
8.073
7.678
7.656
7.606
7.585
7.573
7.565
7.556
7.546
7.486
7.467
7.448
7.396
7.376
7.365
7.360
7.343
7.326
7.317
7.300
7.281
2.152
1.656
1.115

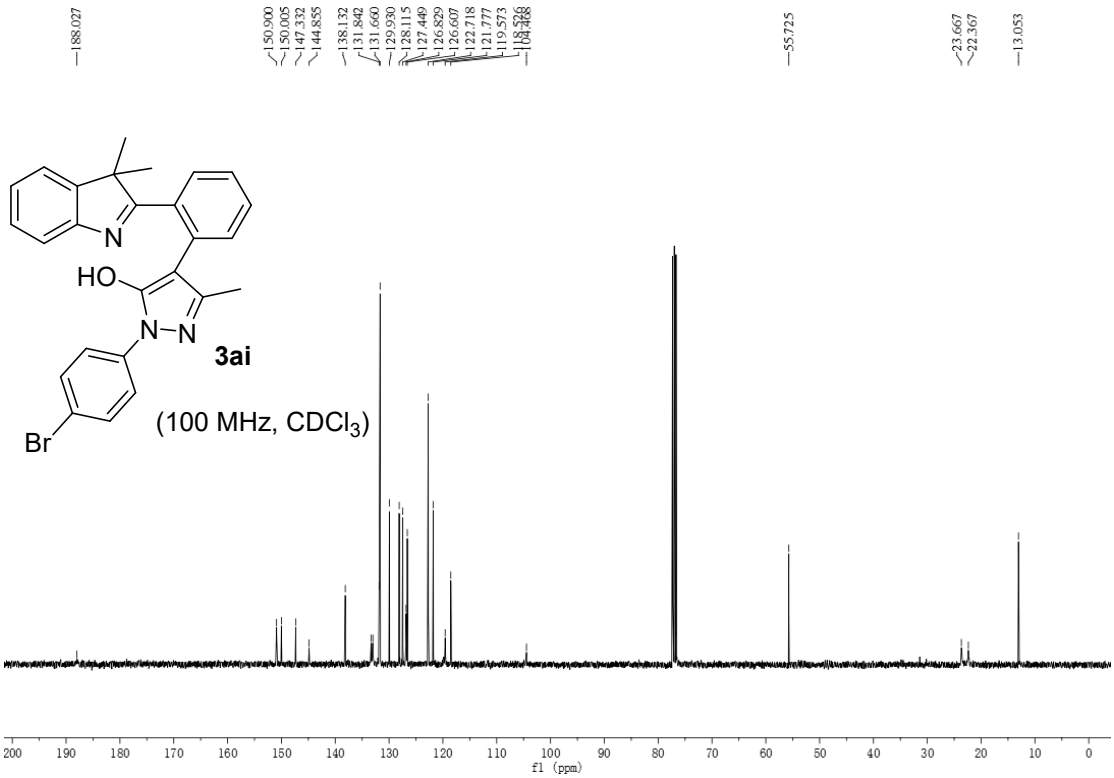

HO
N
N–N
NC
3ag
(400 MHz, CDCl3)
1.99
2.04
3.08
1.00
4.05
2.93
3.13
3.05
f1 (ppm)

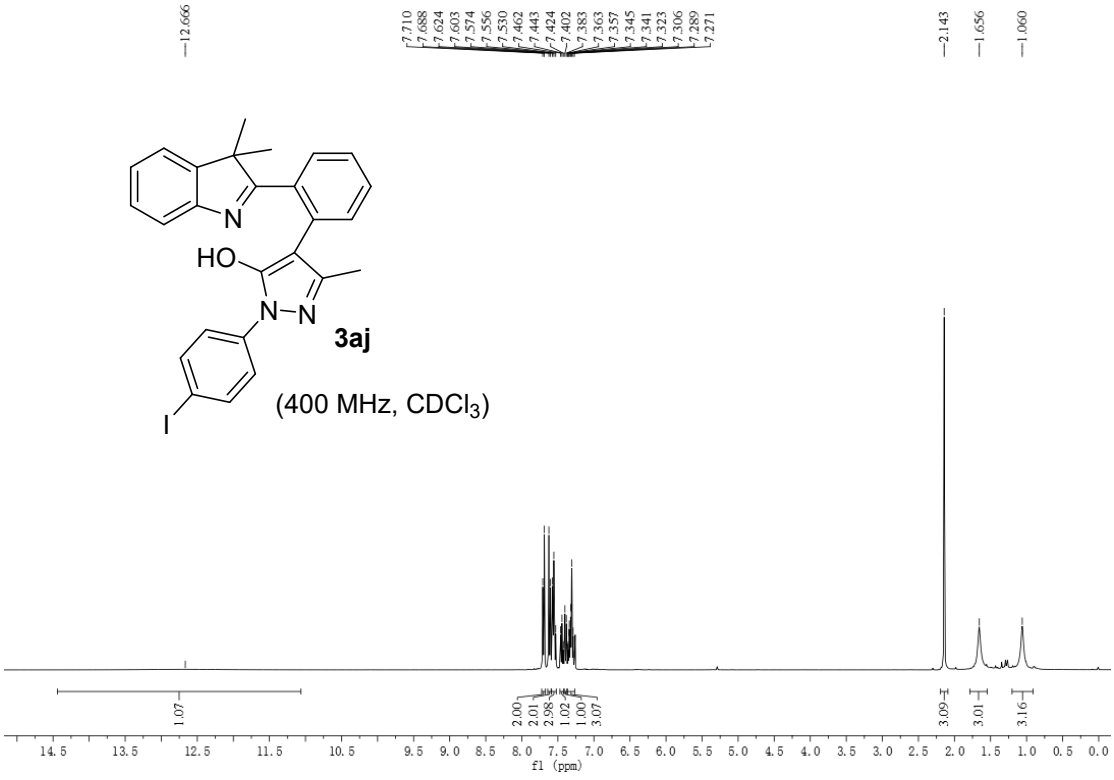

187.520
151.841
149.653
148.689
144.779
142.610
132.831
131.364
130.073
128.121
127.507
126.946
126.831
121.810
120.419
107.522
104.994
55.709
23.556
22.494
13.103
HO
N
N–N
NC
3ag
(100 MHz, CDCl3)
f1 (ppm)

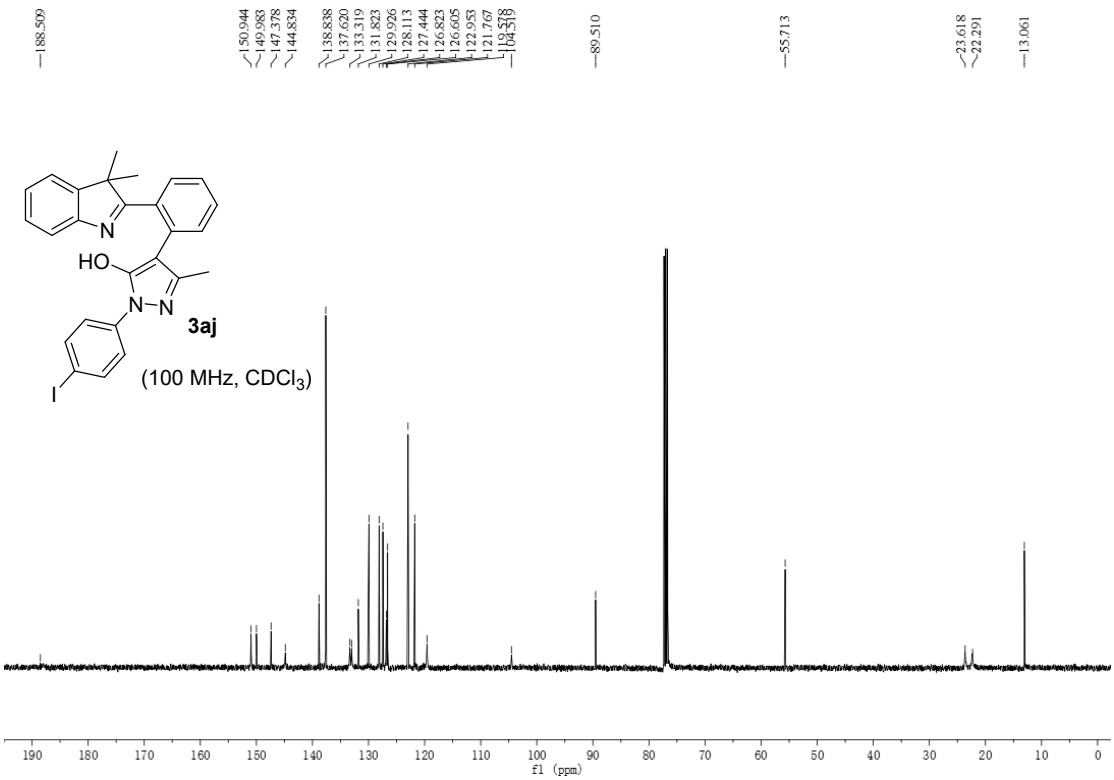

12.695
7.780
7.758
7.575
7.554
7.533
7.464
7.445
7.427
7.406
7.386
7.363
7.342
7.326
7.309
7.292
7.273
2.142
1.662
1.060
HO
N
N–N
Cl
3ah
(400 MHz, CDCl3)
1.12
2.00
3.06
1.04
1.04
5.10
3.14
3.16
3.08
f1 (ppm)

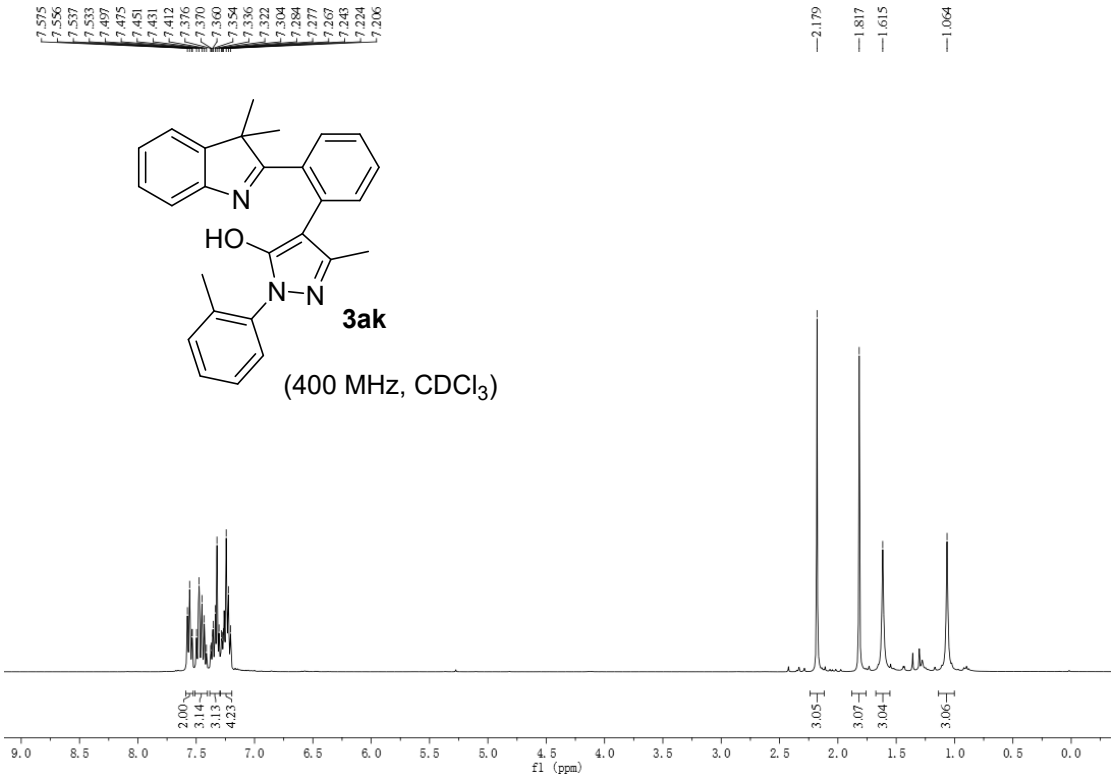

184.588
150.859
150.048
147.274
144.881
137.637
131.883
130.700
129.935
128.723
128.126
127.455
126.840
126.606
122.453
121.787
55.740
23.658
22.328
13.053
HO
N
N–N
Cl
3ah
(100 MHz, CDCl3)
f1 (ppm)

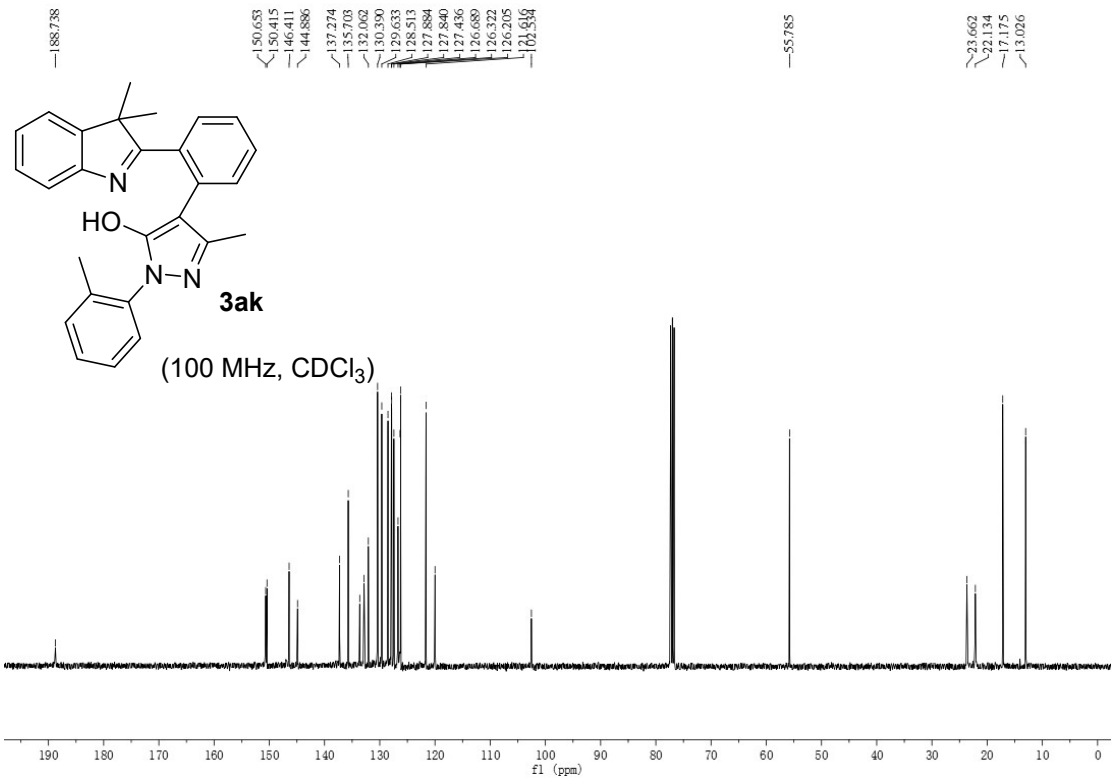

12.725
7.742
7.720
7.578
7.558
7.532
7.515
7.493
7.464
7.445
7.426
7.405
7.386
7.365
7.361
7.344
7.326
7.309
7.291
7.273
2.145
1.659
1.062
HO
N
N–N
Br
3ai
(400 MHz, CDCl3)
1.01
1.93
4.93
1.05
1.00
2.97
2.96
3.02
2.99
f1 (ppm)

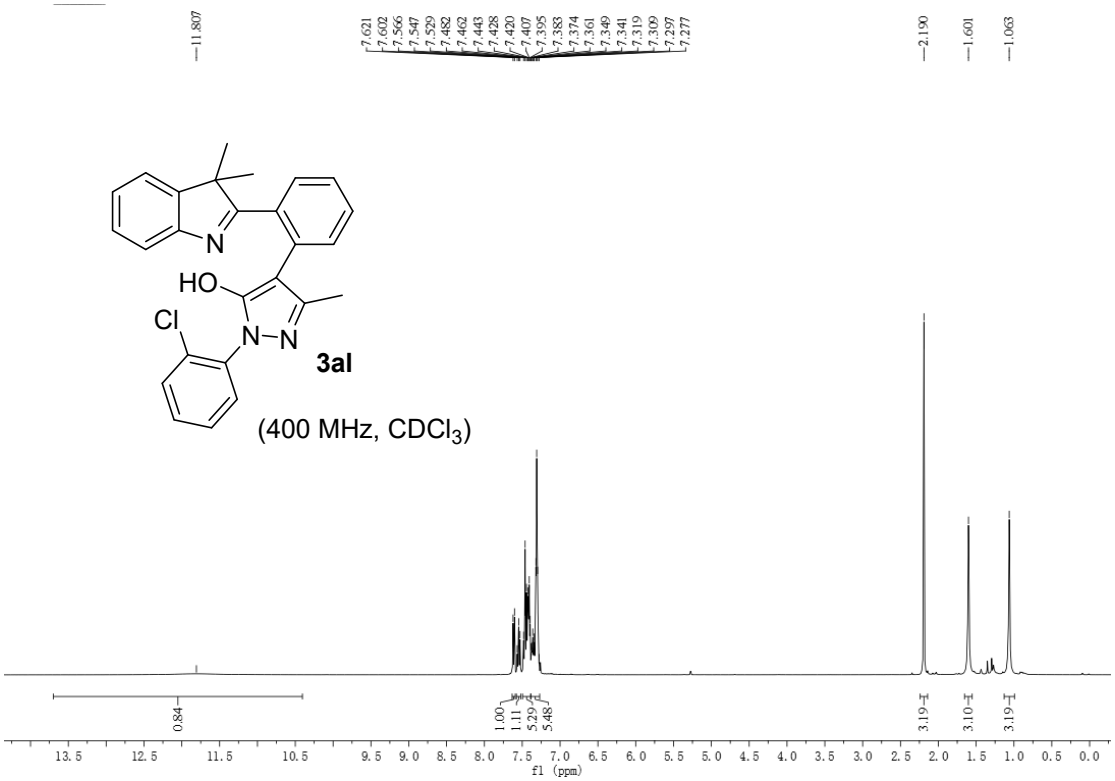

188.027
150.900
150.005
147.332
144.855
138.132
131.842
131.660
129.930
128.115
127.449
126.829
126.607
122.718
121.777
119.573
55.725
23.667
22.367
13.053
HO
N
N–N
Br
3ai
(100 MHz, CDCl3)
f1 (ppm)

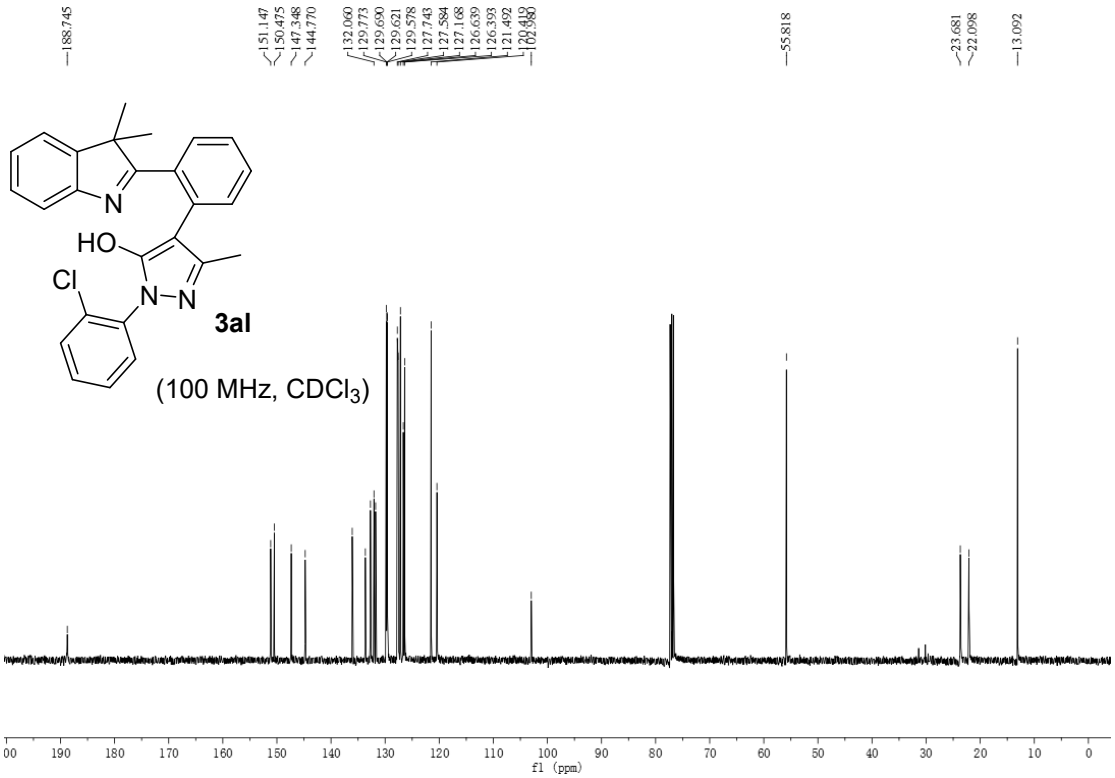

12.666
7.710
7.688
7.624
7.603
7.574
7.556
7.530
7.462
7.443
7.424
7.402
7.383
7.363
7.357
7.345
7.341
7.323
7.306
7.289
7.271
2.143
1.656
1.060
HO
N
N–N
I
3aj
(400 MHz, CDCl3)
1.07
2.00
2.01
2.98
1.02
1.00
3.07
3.09
3.01
3.16
f1 (ppm)

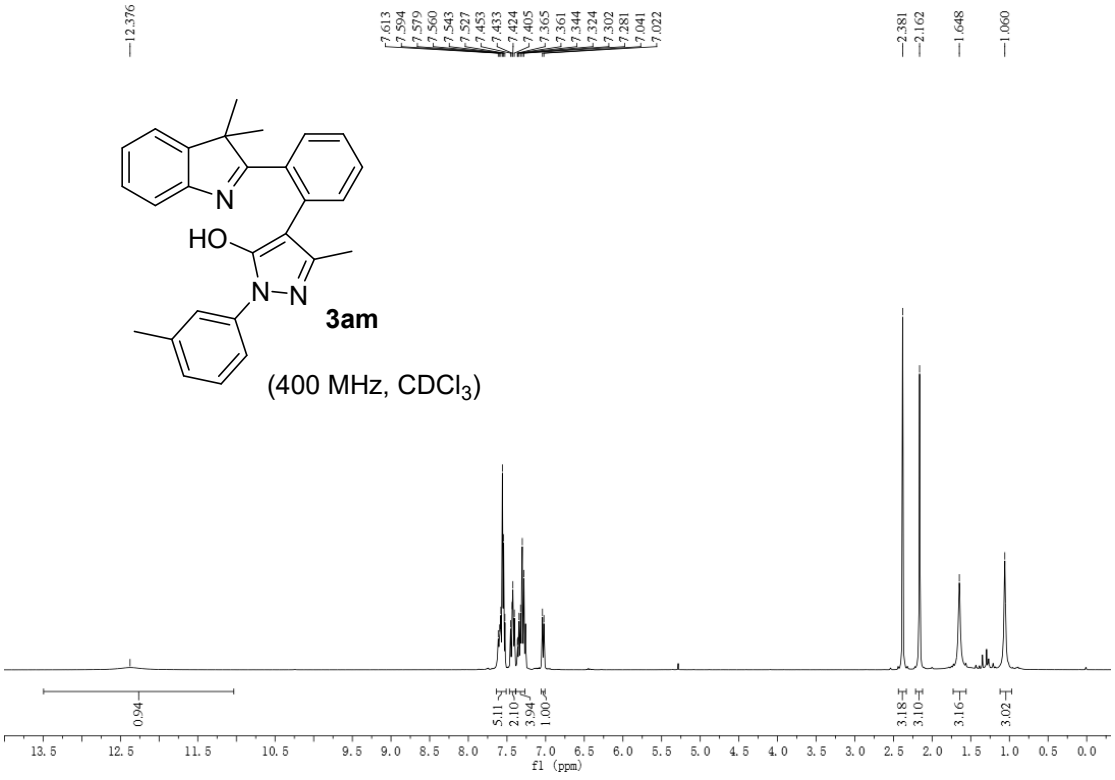

188.509
150.944
149.983
147.378
144.834
138.838
137.620
133.319
131.823
129.926
128.113
127.444
126.823
126.605
122.953
121.767
119.578
104.519
89.510
55.713
23.618
22.291
13.061
HO
N
N–N
I
3aj
(100 MHz, CDCl3)
f1 (ppm)

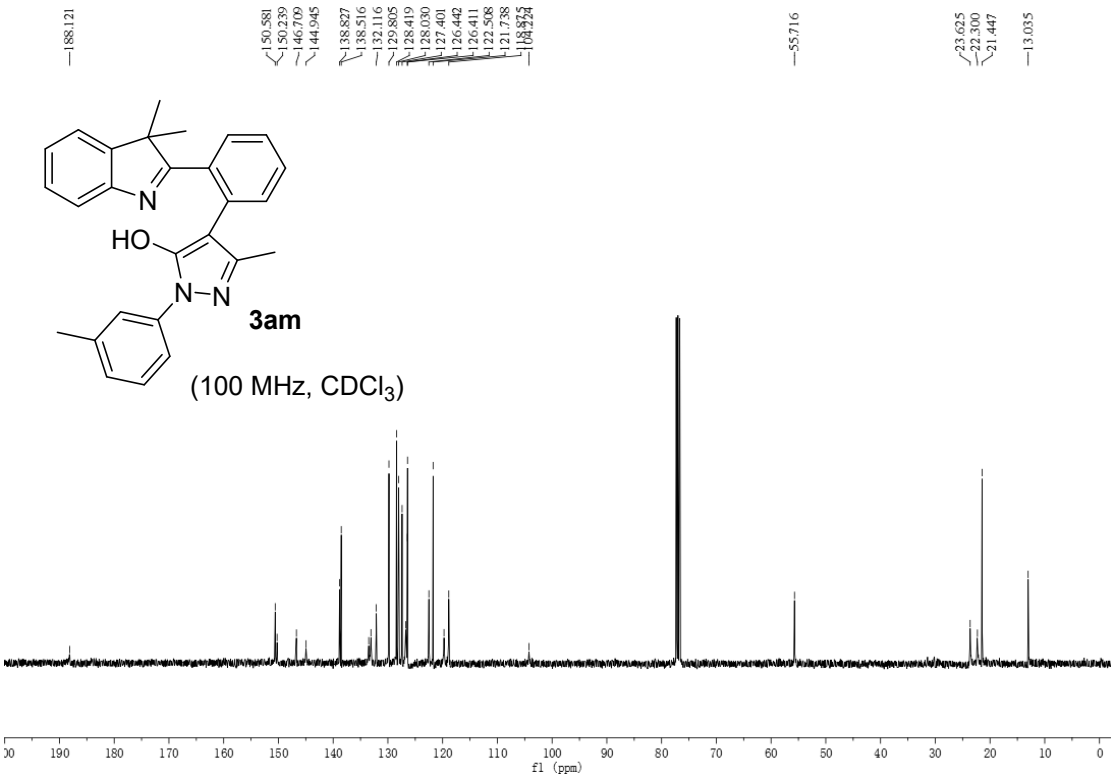

7.575
7.556
7.537
7.533
7.497
7.475
7.451
7.431
7.412
7.376
7.370
7.360
7.354
7.336
7.322
7.304
7.284
7.277
7.267
7.243
7.224
7.206
2.179
1.817
1.615
1.064
HO
N
N–N
3ak
(400 MHz, CDCl3)
2.00
3.14
3.13
4.23
3.05
3.07
3.04
3.06
f1 (ppm)

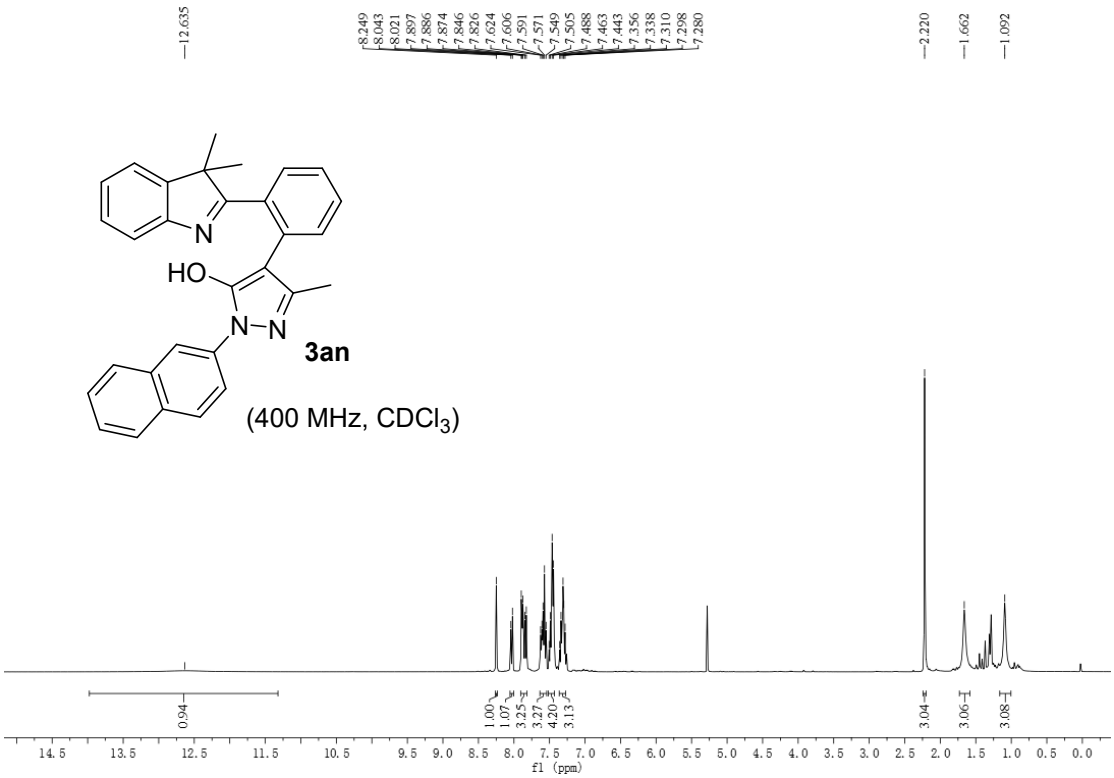

188.738
150.653
150.415
146.411
144.886
137.274
135.703
132.062
130.390
129.633
128.513
127.884
127.840
127.436
126.689
126.322
126.205
102.554
55.785
23.662
22.134
17.175
13.026
HO
N–N
3ak
(100 MHz, CDCl3)
f1 (ppm)

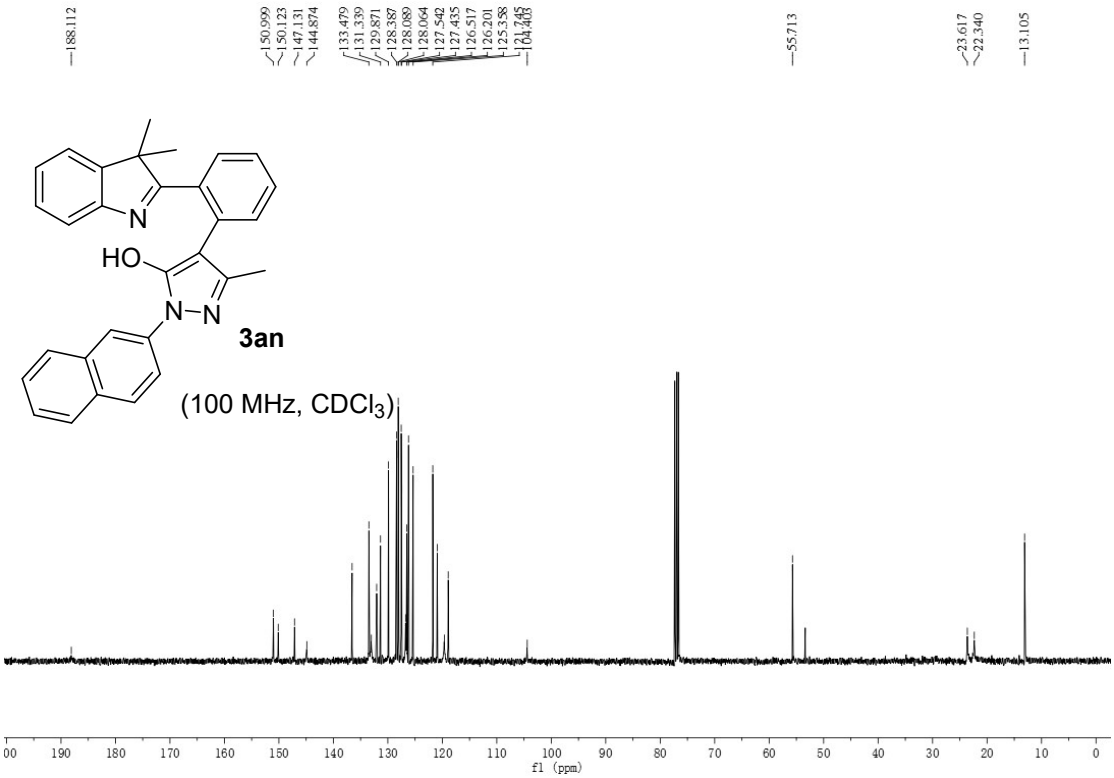

11.807
7.621
7.602
7.566
7.547
7.529
7.482
7.462
7.443
7.428
7.420
7.407
7.395
7.383
7.374
7.361
7.349
7.341
7.319
7.309
7.297
7.277
2.190
1.601
1.063
HO
Cl
N–N
3al
(400 MHz, CDCl3)
0.84
1.00
1.11
5.29
5.48
3.19
3.10
3.19
f1 (ppm)

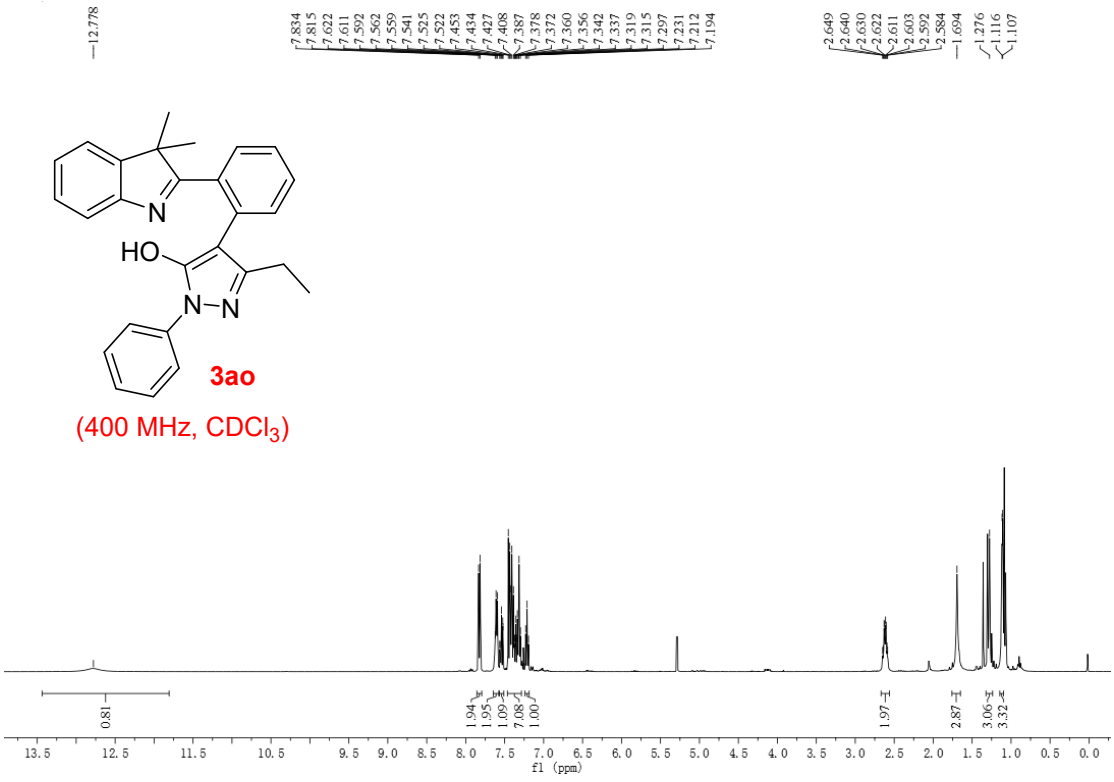

188.745
151.147
150.475
147.348
144.770
132.060
129.773
129.690
129.621
129.578
127.743
127.584
127.168
126.639
126.393
121.492
120.410
102.380
55.818
23.681
22.098
13.092
HO
Cl
N–N
3al
(100 MHz, CDCl3)
f1 (ppm)

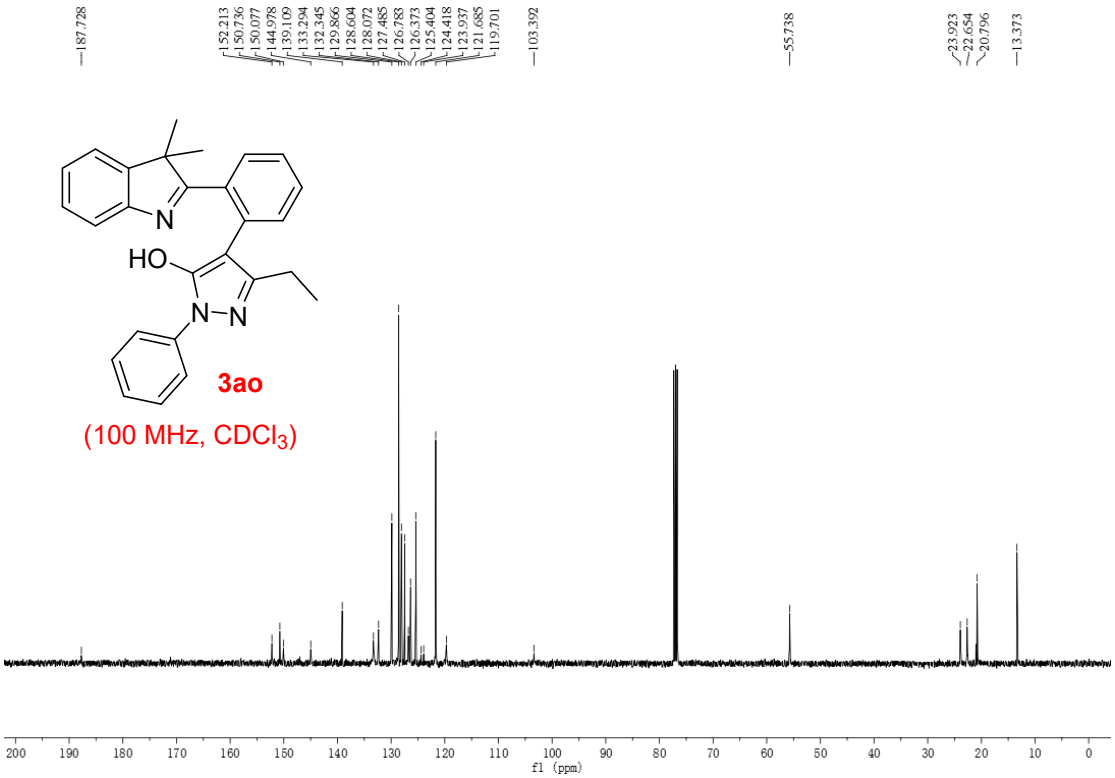

12.376
7.613
7.594
7.579
7.560
7.543
7.527
7.453
7.433
7.424
7.405
7.365
7.361
7.344
7.324
7.302
7.281
7.041
7.022
2.381
2.162
1.648
1.060
HO
N–N
3am
(400 MHz, CDCl3)
0.94
5.11
2.10
3.94
1.00
3.18
3.10
3.16
3.02
f1 (ppm)

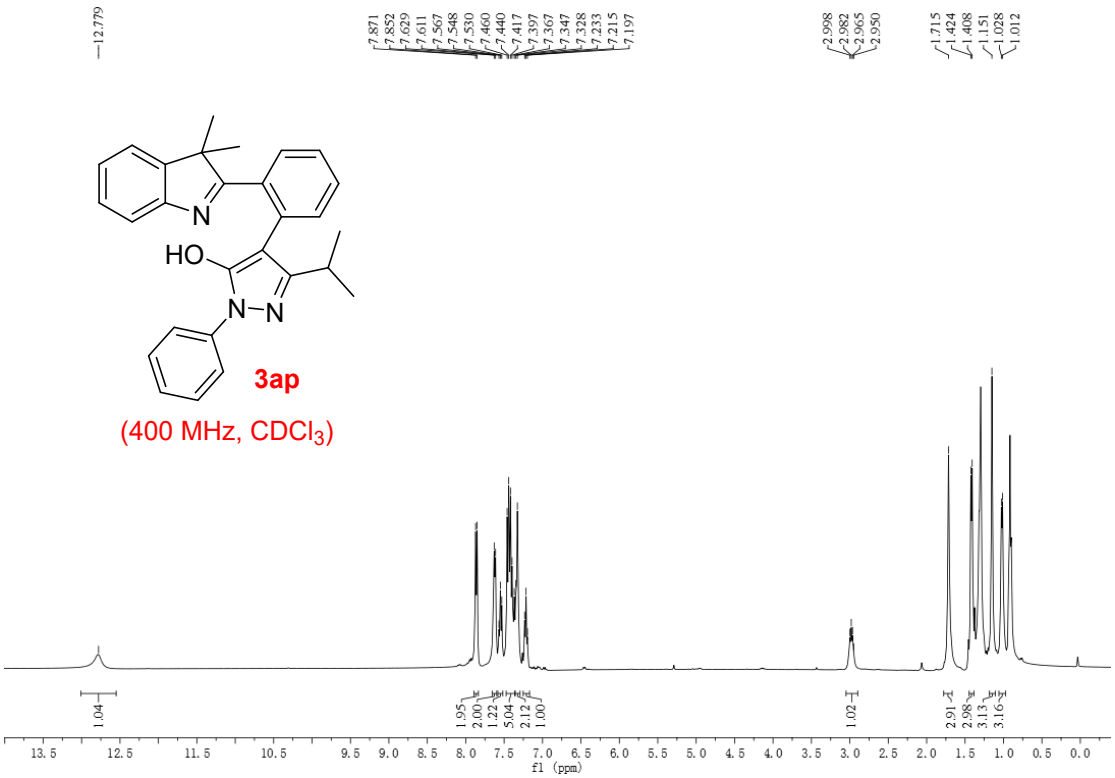

188.121
150.581
150.239
146.709
144.945
138.827
138.516
132.116
129.805
128.419
128.030
127.401
126.442
126.411
122.508
121.738
55.716
23.625
22.300
21.447
13.035
HO
N
N–N
3am
(100 MHz, CDCl3)
f1 (ppm)

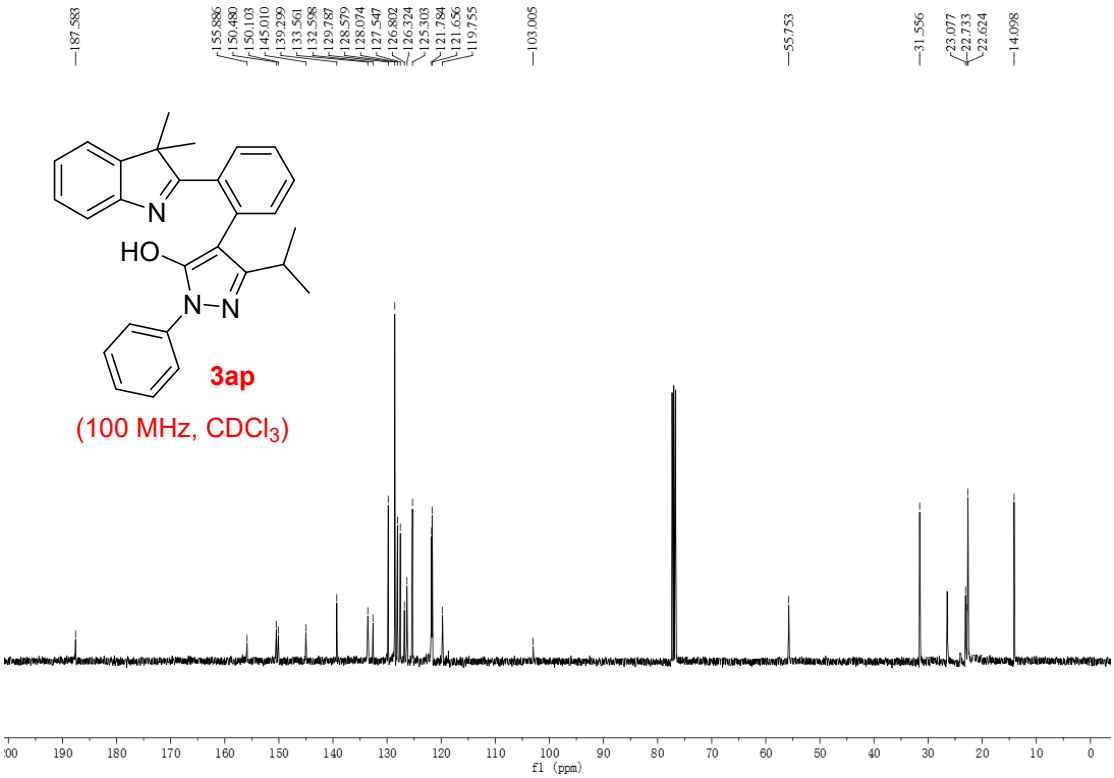

12.635
8.249
8.043
8.021
7.897
7.886
7.874
7.846
7.826
7.624
7.606
7.591
7.571
7.549
7.505
7.488
7.463
7.443
7.356
7.338
7.310
7.298
7.280
2.220
1.662
1.092
HO
N
N–N
3an
(400 MHz, CDCl3)
0.94
1.00
1.07
3.25
3.27
4.20
3.13
3.04
3.06
3.08
f1 (ppm)


188.112
150.999
150.123
147.131
144.874
133.479
131.339
129.871
128.387
128.089
128.064
127.542
127.435
126.517
126.201
125.398
121.745
114.403
55.713
23.617
22.340
13.105
HO
N
N–N
3an
(100 MHz, CDCl3)
f1 (ppm)


12.778
7.834
7.815
7.622
7.611
7.592
7.562
7.559
7.541
7.525
7.522
7.453
7.434
7.427
7.408
7.387
7.378
7.372
7.360
7.356
7.342
7.337
7.319
7.315
7.297
7.231
7.212
7.194
2.649
2.640
2.630
2.622
2.611
2.603
2.592
2.584
1.694
1.276
1.116
1.107
HO
N
N–N
3ao
(400 MHz, CDCl3)
0.81
1.94
1.95
1.09
7.08
1.00
1.97
2.87
3.06
3.32
f1 (ppm)


187.728
152.213
150.736
150.077
144.978
139.109
133.294
132.345
129.866
128.604
128.072
127.485
126.783
126.373
125.404
124.418
123.937
121.685
119.701
103.392
55.738
23.923
22.654
20.796
13.373
HO
N
N–N
3ao
(100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


12.779
7.871
7.852
7.629
7.611
7.567
7.548
7.530
7.460
7.440
7.417
7.397
7.367
7.347
7.328
7.233
7.215
7.197
2.998
2.982
2.965
2.950
1.715
1.424
1.408
1.151
1.028
1.012
HO
N
N–N
3ap
(400 MHz, CDCl3)
1.04
1.95
2.00
1.22
5.04
2.12
1.00
1.02
2.91
2.98
3.13
3.16
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



8. Cell antiproliferative activity assay

The cell antiproliferative activities of our compounds against HeLa cell were evaluated by the MTT method. HeLa cell suspensions were diluted in growth medium to desired density, and 200 μL diluted suspensions were taken to 96-well plates (4×10^3 cells/well). The test compounds with different concentration gradients were prepared. Add 180 μL culture medium containing compounds into 96-well plate according to the plate map. Final DMSO concentration in each well was below 1%. Then the cell was incubated at 37 ℃, 5% CO_2 for 48 h. Equilibrate the assay plate to room temperature before measurement. Add 20 μL of MTT into each well. Mix contents for 2 minutes on an orbital shaker to induce cell lysis. Incubate at 37 ℃ and 5% CO_2 for 4 hours, the cell medium was discarded and DMSO (150 μL) was added. The absorbance of the wells was measured at 570 nm (BioTeK Synergy H1), and the viability of the untreated cells was set to 100% as a reference. The IC50 values were calculated using GraphPad Prism 6.0 software and determined by the concentration causing a half-maximal percent activity. All assays were conducted with two parallel samples and two repetitions, and 5-fluorouracil was used as the positive control.