Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Transition Metal and Additives Free Intermolecular Hydroarylation of Alkenes with Indoles in Hexafluoroisopropanol

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1. General information

Unless otherwise stated, all reactions were magnetically stirred and conducted in oven-dried (100 °C) or in anhydrous solvents under N_2, applying standard Schlenk techniques. Solvents and liquid reagents, as well as solutions of solid or liquid reagents were added through a weak N_2 counter-flow. Cooling baths were prepared in Dewar vessels, filled with ice/water (0 °C). Heated oil baths were used for reactions requiring elevated temperatures. Solvents were removed under reduced pressure at 40 °C using a rotary evaporator, and unless otherwise stated, the remaining compound was dried in vacuum at ambient temperature. All given yields are isolated yields of chromatographically and NMR spectroscopically pure materials, unless otherwise stated.

Chemicals

Chemicals were purchased from commercial suppliers (including Energy Chemical, Bidepharm, Aladdin, Meryer, Sinopharm) and used without further purification unless otherwise stated.

Solvents

Solvents (CH_2Cl_2, Et_2O, THF) were dried by distillation from an appropriate drying agent. In addition, more solvents were purchased from commercial suppliers.

Gas

Dry N_2 were purchased from Hangzhou Jingong Materials with > 99.9% purity.

Thin Layer chromatography

Thin-layer chromatography (TLC) was performed using silica gel pre-coated glass plates (SIL G-25, with fluorescent indicator UV254; Macherey-Nagel) with fluorescent indicator UV254; Macherey-Nagel), which were visualized by irradiation with UV light (λ = 254 or 366 nm), basic $KMnO_4$, and/or phosphomolybdic acid (PMA).

Column Chromatography

Column chromatography (CC) was carried out using silica gel (60 Å, 230−400 mesh, particle size 0.040−0.063 mm) using technical grade solvents. Elution was accelerated using compressed air. All reported yields, unless otherwise specified, refer to spectroscopically and chromatographically pure compounds.

Nuclear Magnetic Resonance Spectroscopy

^{1}H, ^{13}C, nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV-500, AV-400 spectrometer in a suitable deuterated solvent. The solvent employed and respective measuring frequency are indicated for each experiment. Chemical shifts are reported with tetramethylsilane (TMS) serving as a universal reference of all nuclides

and with two or one digits after the comma. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and bs (broad singlet). All spectra were recorded at 298 K unless otherwise noted, processed with program MestReNova 14.0, and coupling constants are reported as observed. The residual deuterated solvent signal relative to tetramethylsilane (TMS) was used as the internal reference in ^{1}H NMR spectra ($CDCl_3$ δ 7.26, THF δ 1.72, 3.58, C_6D_6 δ 7.16, CD_3OD δ 3.31), and are reported as follows: chemical shift δ in ppm (multiplicity, coupling constant *J* in Hz, number of protons). ^{13}C NMR spectra reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ δ 77.2, THF δ 67.21, 25.31, C_6D_6 δ 128.1, CD_3OD δ 49.0). All spectra are broadband decoupled unless otherwise noted.

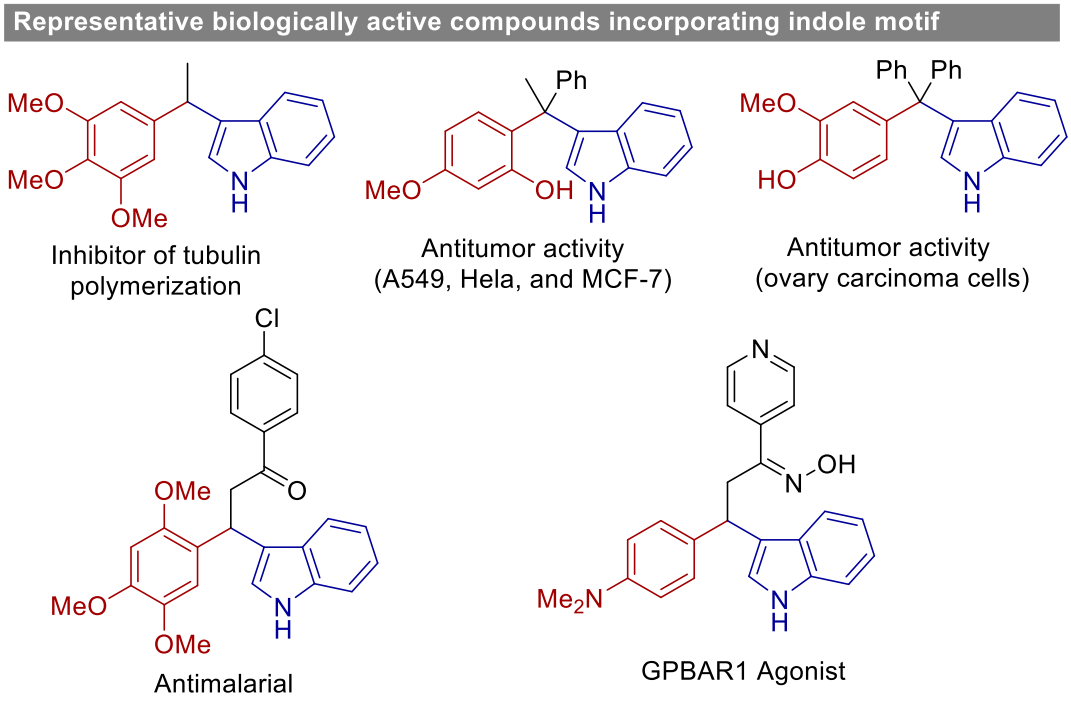
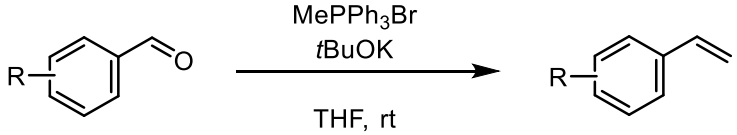


Figure S1. Representative multi-arylalkanes with indole motif

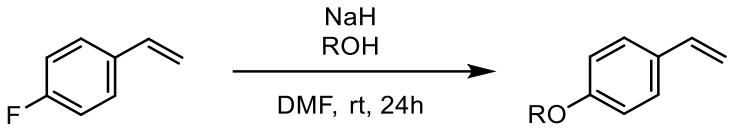
2. General procedures of substrates preparation

Method A:



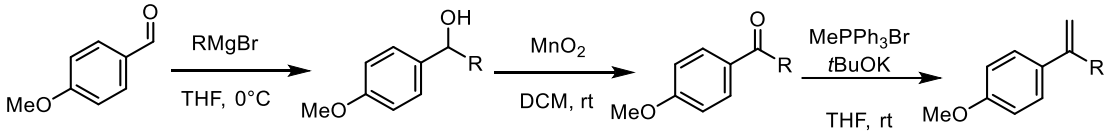
The alkenes **1a**–**1aa** were prepared according to method A.

Method B:



The alkenes **1ab**–**1ad** were prepared according to method B.

Method C:

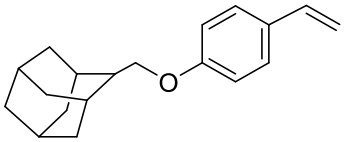


Scheme S1 General procedure of substrates preparation

The alkenes **1ae**–**1ai** were prepared according to method C.

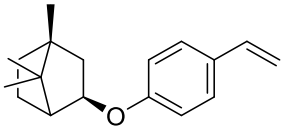
Alkenes **1ab** and **1ad** are not reported in literature: The procedure was adapted from the literature report, **1ab** and **1ad** were afforded with 65% and 55% yields, respectively.

(1R,3S,5r)-2-((4-vinylphenoxy)methyl)adamantane (**1ab**)



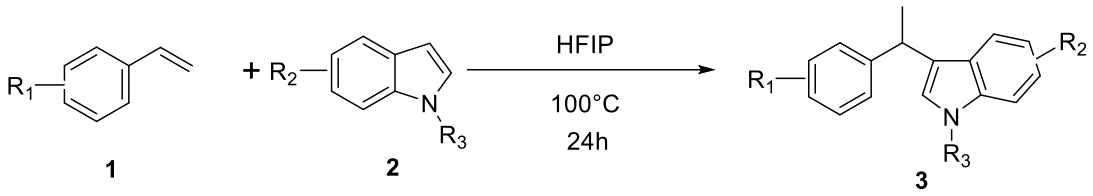
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 2H), 6.56 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.50 (d, *J* = 10.9 Hz, 1H), 5.01 (d, *J* = 10.9 Hz, 1H), 3.39 (s, 2H), 1.92 (s, 3H), 1.73–1.43 (m, 12H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 136.4, 129.9, 127.5, 114.6, 110.9, 78.2, 39.4, 37.4, 33.6, 28.2.
GCMS (m/z): calculated for $C_{19}H_{24}O$ $[M]^+$: 268.18; found 268.1

(1R,3R)-1,7,7-trimethyl-3-(4-vinylphenoxy)bicyclo[2.2.1]heptane (**1ad**)



^{1}H NMR (400 MHz, $CDCl_3$) δ7.34 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 6.67 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.61 (d, *J* = 17.6 Hz, 1H), 5.12 (d, *J* = 10.9 Hz, 1H), 4.47–4.15 (m, 1H), 2.46–2.31 (m, 1H), 2.29–2.22 (m, 1H), 1.86–1.67 (m, 2H), 1.44–1.20 (m, 2H), 1.12 (dd, *J* = 10.3, 5.1 Hz, 1H), 0.97 (s, 3H), 0.94 (d, *J* = 3.4 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 136.3, 129.9, 127.6, 115.4, 111.4, 82.9, 49.7, 47.7, 45.3, 36.9, 28.1, 26.9, 19.8, 19.0, 13.8.
GCMS (m/z): calculated for $C_{18}H_{24}O$ $[M]^+$: 256.18; found 256.1

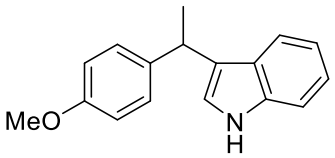
3. General procedure of the hydroarylation



Scheme S2 General procedure of the hydroarylation

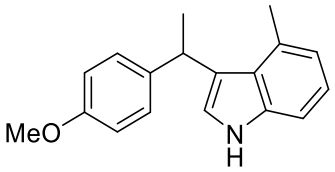
A mixture of indoles (0.2 mmol, 1 equiv.) and alkenes (0.24 mmol, 1.2 equiv.) in HFIP (0.3 mL) were sealed in a Schlenk tube without cautious manipulations to exclusion of air or moisture. Then, the reaction mixture was stirred and heated at 100°C for 24h. After full consumption of the starting material, the HFIP was evaporated and the residue was purified by silica gel column chromatography (petroleum ether: ethyl acetate = 10 : 1) to afford the hydroaryaltion product **3**. The yields were indicated in Table 2 and Table 3.

3-(1-(4-methoxyphenyl)ethyl)-1H-indole (**3a**)



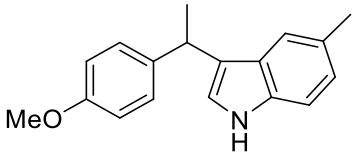
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.15 (t, *J* = 8.8 Hz, 1H), 7.06–6.96 (m, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 4.35 (q, *J* = 7.1 Hz, 1H), 3.85–3.70 (s, 3H), 1.68 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 139.3, 136.7, 128.5, 127.0, 122.1, 121.9, 121.1, 119.9, 119.3, 113.8, 111.1, 55.4, 36.3, 22.7.
HRMS (ESI) (m/z): calculated for $C_{17}H_{18}NO$ $[M+H]^+$: 252.1383; found 252.1489

3-(1-(4-methoxyphenyl)ethyl)-4-methyl-1H-indole (**3b**)



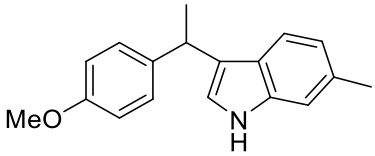
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.19 (d, *J* = 10.3 Hz, 1H), 7.16–6.98 (m, 4H), 6.88–6.69 (m, 3H), 4.67 (q, *J* = 7.1 Hz, 1H), 3.79 (s, 3H), 2.48 (s, 3H), 1.66 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ157.8, 140.6, 137.1, 131.3, 128.5, 125.8, 122.2, 122.0, 121.7, 121.2, 113.8, 109.0, 55.3, 36.9, 24.6, 20.6.
HRMS (ESI) (m/z): calculated for $C_{18}H_{19}NONa$ $[M+Na]^+$: 288.1359; found 288.1408

3-(1-(4-methoxyphenyl)ethyl)-5-methyl-1H-indole (**3c**)



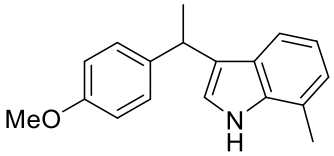
^{1}H NMR (400 MHz, CDCl3) δ 7.82 (s, 1H), 7.25–7.13 (m, 4H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.92 (d, *J* = 1.7 Hz, 1H), 6.80 (t, *J* = 9.9 Hz, 2H), 4.29 (q, *J* = 7.1 Hz, 1H), 3.77 (s, 3H), 2.41 (s, 3H), 1.64 (d, *J* = 7.1 Hz, 3H)
^{13}C NMR (101 MHz, CDCl3) δ 157.8, 139.2, 135.1, 128.7, 127.2, 123.7, 121.4, 119.3, 113.8, 110.6, 55.4, 36.4, 22.9, 21.5.
HRMS (ESI) (m/z): calculated for $C_{18}H_{20}NO$ $[M+H]^+$: 266.1539; found 266.1584

3-(1-(4-methoxyphenyl)ethyl)-6-methyl-1H-indole (**3d**)



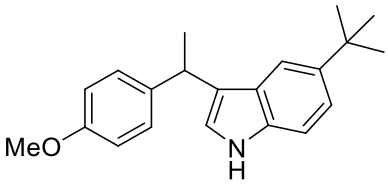
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.25–7.15 (m, 4H), 6.89 (t, *J* = 8.5 Hz, 1H), 6.87–6.71 (m, 3H), 4.29 (q, *J* = 7.0 Hz, 1H), 3.76 (s, 3H), 2.40 (s, 3H), 1.64 (d, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ157.9, 139.2, 137.2, 131.9, 128.3, 124.9, 121.8, 121.1, 120.5, 119.5, 113.8, 111.1, 55.3, 36.4, 22.7, 21.8.
HRMS (ESI) (m/z): calculated for $C_{18}H_{20}NO$ $[M+H]^+$: 266.1467; found 266.1631

3-(1-(4-methoxyphenyl)ethyl)-7-methyl-1H-indole (**3e**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.25–7.15 (m, 4H), 6.98–6.93 (m, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 1H), 3.76 (s, 3H), 2.46 (s, 3H), 1.65 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 139.2, 136.3, 128.4, 126.5, 122.6, 122.5, 120.8, 120.3, 119.5, 117.6, 113.8, 55.4, 36.3, 22.6, 16.7.
HRMS (ESI) (m/z): calculated for $C_{18}H_{20}NO$ $[M+H]^+$: 266.1467; found 266.1558

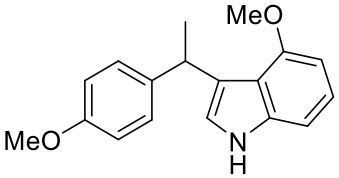
5-(tert-butyl)-3-(1-(4-methoxyphenyl)ethyl)-1H-indole (**3f**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.33 (d, *J* = 1.7 Hz, 1H), 7.26–7.17 (m, 4H), 6.88 (d, *J* = 1.7 Hz, 1H), 6.80 (d, J = 8.7 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 1H), 3.76 (s, 3H), 1.65 (d, *J* = 7.0 Hz, 3H), 1.26 (s, 9H).

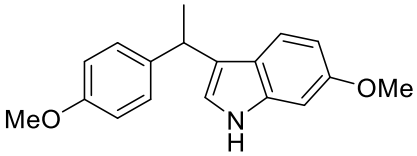
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 142.1, 139.1, 134.9, 128.4, 126.7, 122.2, 121.3, 120.3, 115.6, 113.9, 110.5, 55.4, 36.1, 34.6, 32.0, 22.6.
HRMS (ESI) (m/z): calculated for $C_{21}H_{25}NONa$ $[M+Na]^+$: 330.1828; found 330.1849

4-methoxy-3-(1-(4-methoxyphenyl)ethyl)-1H-indole (**3g**)



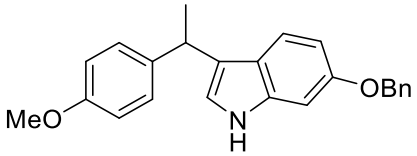
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.18 (d, *J* = 9.0 Hz, 2H), 6.99–6.84 (m, 3H), 6.82–6.74 (m, 2H), 6.59 (d, *J* = 8.0 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 1H), 3.92 (s, 3H), 3.75 (s, 3H), 1.66 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 145.9, 139.2, 128.2, 127.2, 122.3, 120.7, 119.6, 113.7, 112.7, 101.8, 55.3, 36.3, 22.7.
HRMS (ESI) (m/z): calculated for $C_{18}H_{20}NO$ $[M+H]^+$: 282.1489; found 282.1436

6-methoxy-3-(1-(4-methoxyphenyl)ethyl)-1H-indole (**3h**)



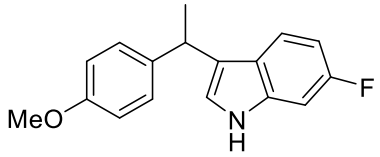
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.18 (dd, *J* = 12.2, 9.0 Hz, 3H), 6.92–6.81 (m, 4H), 6.67 (dd, *J* = 8.7, 2.2 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 1.65 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 156.7, 139.2, 137.4, 128.5, 122.1, 121.4, 120.5, 119.7, 113.8, 109.2, 94.6, 55.8, 55.3, 36.3, 22.6
HRMS (ESI) (m/z): calculated for $C_{18}H_{20}NO_2$ $[M+H]^+$: 282.1489; found 282.1435

6-(benzyloxy)-3-(1-(4-methoxyphenyl)ethyl)-1H-indole (**3i**)



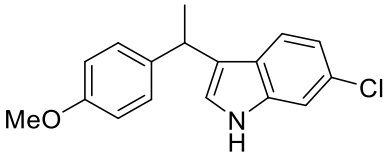
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.43 (d, *J* = 6.7 Hz, 2H), 7.37 (dd, *J* = 9.9, 4.7 Hz, 2H), 7.30 (d, *J* = 4.9 Hz, 1H), 7.22–7.16 (m, 3H), 6.87–6.86 (m, 2H), 6.80 (d, *J* = 7.1 Hz, 2H), 6.74 (dd, *J* = 8.8, 2.1 Hz, 1H), 5.05 (d, *J* = 9.2 Hz, 2H), 4.26 (q, *J* = 7.0 Hz, 1H), 3.76 (s, 3H), 1.63 (d, J = 6.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 155.6, 139.1, 137.5, 137.3, 128.6, 128.3, 127.9, 127.5, 121.8, 121.6, 120.4, 112.0, 113.7, 109.8, 95.9, 70.3, 55.0, 36.3, 23.0.
HRMS (ESI) (m/z): calculated for $C_{24}H_{24}NO_2$ $[M+H]^+$: 358.1802; found 358.1807

6-fluoro-3-(1-(4-methoxyphenyl)ethyl)-1H-indole (**3j**)



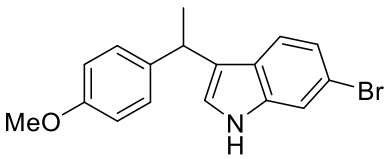
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.31–7.11 (m, 3H), 7.08–6.92 (m, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.7 (td, *J* = 9.2, 2.1Hz, 1H), 4.28 (q, *J* = 7.0 Hz, 1H), 3.78 (s, 3H), 1.65 (d, *J* = 9.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4, 158.9, 157.9, 138.9, 136.7, 136.6, 128.4, 123.6, 122.0, 121.3, 121.3, 120.7, 120.6, 113.8, 108.2, 107.9, 97.6, 97.2, 55.4, 36.2, 22.7.
^{19}F NMR (471 MHz, $CDCl_3$) δ -121.5
HRMS (ESI) (m/z): calculated for $C_{17}H_{16}FNONa$ $[M+Na]^+$: 292.1108; found 292.1327

6-chloro-3-(1-(4-methoxyphenyl)ethyl)-1H-indole (**3k**)



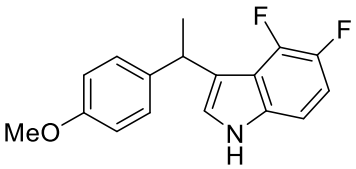
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.34 (d, *J* = 1.7 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 1H), 7.23 – 7.16 (m, 2H), 7.02 (dd, *J* = 2.4, 0.7 Hz, 1H), 7.00 (dd, *J* = 5.4, 1.4 Hz, 1H), 6.88 – 6.82 (m, 2H), 4.31 (q, *J* = 7.1 Hz, 1H), 3.81 (s, 3H), 1.68 (d, *J* = 8.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 138.8, 137.2, 128.5, 128.1, 125.7, 122.2, 121.7, 120.7, 119.9, 113.8, 110.9, 55.4, 36.1, 22.6.
HRMS (ESI) (m/z): calculated for $C_{17}H_{16}ClNOK$ $[M+K]^+$: 324.0552; found 324.0595

6-bromo-3-(1-(4-methoxyphenyl)ethyl)-1H-indole (**3l**)



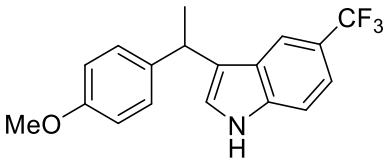
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.49 (d, *J* = 11.4 Hz, 1H), 7.23–7.13 (m, 3H), 7.07 (dd, *J* = 16.2, 6.9 Hz, 1H), 6.98 (d, *J* = 1.2 Hz, 1H), 6.84 (t, *J* = 10.9 Hz, 2H), 4.29 (q, *J* = 7.1 Hz, 1H), 3.78 (s, 3H), 1.66 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 137.6, 136.4, 127.3, 124.8, 121.6, 121.0, 120.6, 120.0, 114.5, 112.9, 112.7, 54.2, 34.9, 21.5.
HRMS (ESI) (m/z): calculated for $C_{17}H_{17}BrNO$ $[M+H]^+$: 330.0488; found 330.0496

4,5-difluoro-3-(1-(4-methoxyphenyl)ethyl)-1H-indole (**3m**)



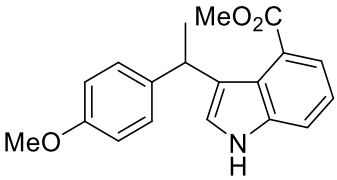
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.22 (d, *J* = 8.6 Hz, 2H), 6.97-6.93 (m, 3H), 6.84 (d, *J* = 8.6 Hz, 2H), 4.51 (q, *J* = 7.1 Hz, 1H), 3.79 (s, 3H), 1.66 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 145.3, 143.1, 138.9, 135.1, 134.8, 128.2, 122.5, 121.8, 116.7, 113.8, 112.1, 111.6, 106.1, 55.2, 36.3, 22.9.
^{19}F NMR (471 MHz, $CDCl_3$) δ -148.2, -158.8.
GCMS (m/z): calculated for $C_{17}H_{15}F_2NO$ $[M]^+$: 287.11; found 287.1

3-(1-(4-methoxyphenyl)ethyl)-5-(trifluoromethyl)-1H-indole (**3n**)



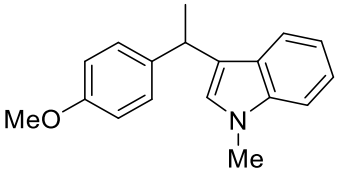
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.62 (s, 1H), 7.40 (d, *J* = 11.1 Hz, 1H), 7.25–7.13 (m, 4H), 6.83 (dd, *J* = 6.8, 4.8 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 1H), 3.78 (s, 3H), 1.67 (d, *J* = 10.5 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 138.6, 135.6, 128.4, 123.7, 122.3, 120.3, 113.9, 55.4, 36.1, 22.6.
^{19}F NMR (471 MHz, $CDCl_3$) δ -60.6
HRMS (ESI) (m/z): calculated for $C_{18}H_{16}F_3NOK$ $[M+K]^+$: 358.0816; found 358.0844

methyl 3-(1-(4-methoxyphenyl)ethyl)-1H-indole-4-carboxylate (**3o**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.17–7.12 (m, 3H), 7.08 (s, 1H), 6.85 (t, *d* = 9.6 Hz, 2H), 4.24 (q, *J* = 7.2 Hz, 1H), 3.99 (s, 3H), 3.78 (s, 3H), 1.73 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 158.6, 146.2, 137.2, 136.2, 128.7, 128.4, 123.5, 120.9, 120.7, 115.4, 114.3, 100.7, 55.6, 51.6, 38.4, 21.2.
HRMS (ESI) (m/z): calculated for $C_{19}H_{20}NO_3$ $[M+H]^+$: 310.1438; found 310.1440

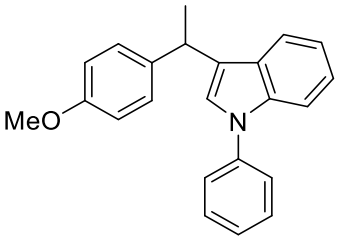
3-(1-(4-methoxyphenyl)ethyl)-1-methyl-1H-indole (**3p**)



^{1}H NMR (400 MHz, $CDCl_3$) δ7.36 (d, *J* = 7.9 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 1H), 7.24–7.11 (m, 3H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.87–6.75 (m, 3H), 4.32 (q, *J* = 7.0 Hz, 1H), 3.74 (d, *J* = 11.9 Hz, 6H), 1.66 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ157.8, 139.4, 137.5, 128.4, 127.3, 125.9, 121.6, 120.4, 119.9, 118.7, 113.8, 109.2, 55.3, 36.3, 32.7, 22.8.

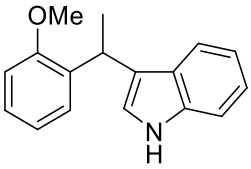
HRMS (ESI) (m/z): calculated for $C_{18}H_{20}NO$ $[M+H]^+$: 266.1539; found 266.1527

3-(1-(4-methoxyphenyl)ethyl)-1-phenyl-1H-indole (**3q**)



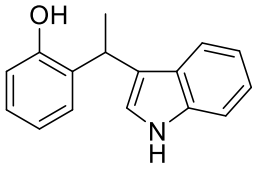
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 6.7 Hz, 1H), 7.52–7.47 (m, 4H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.37–7.29 (m, 1H), 7.28–7.22 (m, 2H), 7.21–7.11 (m, 2H), 7.09–7.01 (t, *J* =6.9 Hz, 1H), 6.86–6.79 (m, 2H), 4.37 (q, *J* = 7.1 Hz, 1H), 3.76 (s, 3H), 1.71 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 139.98, 138.78, 136.4, 129.5, 128.4, 126.0, 125.0, 124.1, 123.0, 122. 5, 120.2, 119.7, 113.7, 110.4, 55.2, 36.2, 22.5.
HRMS (ESI) (m/z): calculated for $C_{23}H_{22}NO$ $[M+H]^+$: 328.1696; found 328.1681.

3-(1-(2-methoxyphenyl)ethyl)-1H-indole (**3r**)



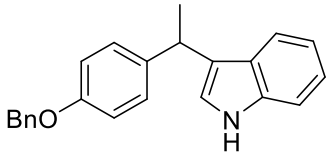
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.35 (dd, *J* = 13.4, 8.1 Hz, 2H), 7.19–7.08 (m, 2H), 7.05–7.02 (m, 2H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 11.1 Hz, 1H), 6.80 (t, *J* = 7.4 Hz, 1H), 4.84 (q, *J* = 6.9 Hz, 1H), 3.90 (s, 3H), 1.63 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 136.7, 135.2, 128.0, 127.2, 126.9, 122.0, 121.6, 121.4, 120.7, 119.9, 119.2, 110.9, 110.5, 55.6, 29.2, 21.1.
HRMS (ESI) (m/z): calculated for $C_{17}H_{18}NO$ $[M+H]^+$: 252.1382; found 252.1241

2-(1-(1H-indol-3-yl)ethyl)phenol (**3s**)



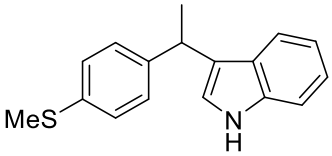
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.39 (d, *J* = 7.0 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 7.3 Hz, 1H), 7.18–7.12 (m, 1H), 7.05–7.02 (m, 2H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 5.27 (s, 1H), 4.54 (q, *J* = 7.1 Hz, 1H), 1.75 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 136.9, 131.4, 128.4, 127.5, 126.6, 122.5, 121.4, 120.9, 119.7, 119.5, 119.4, 116.3, 111.3, 32.3, 20.2.
HRMS (ESI) (m/z): calculated for $C_{16}H_{16}NO$ $[M+H]^+$: 238.1232; found 238.1239

3-(1-(4-(benzyloxy)phenyl)ethyl)-1H-indole (**3t**)



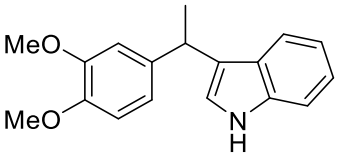
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.49–7.31 (m, 7H), 7.22 (d, *J* = 8.6 Hz, 2H), 7.16 (dt, *J* = 11.6, 2.2 Hz, 1H), 7.06–6.98 (m, 2H), 6.94–6.87 (m, 2H), 5.04 (s, 2H), 4.34 (q, *J* = 7.1 Hz, 1H), 1.67 (dd, *J* = 18.0, 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 139.6, 137.2, 136.7, 128.6, 128.4, 127.9, 127.6, 126.9, 121.9, 121.8, 121.0, 119.8, 119.2, 114.6, 111.0, 70.2, 36.3, 22.5.
GCMS (m/z): calculated for $C_{23}H_{21}NO$ $[M]^+$: 327.16; found 327.1

3-(1-(4-(methylthio)phenyl)ethyl)-1H-indole (**3u**)



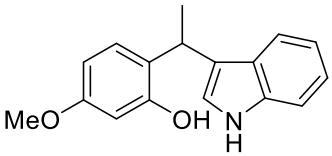
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.34 (dd, *J* = 7.8, 4.5 Hz, 2H), 7.28–7.07 (m, 5H), 7.06–6.91 (m, 2H), 4.33 (q, *J* = 7.1 Hz, 1H), 2.44 (s, 3H), 1.67 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 136.6, 135.2, 128.0, 127.0, 126.7, 122.0, 121.3, 121.0, 119.7, 119.3, 111.1, 36.5, 22.3, 16.2.
GCMS (m/z): calculated for $C_{17}H_{17}NS$ $[M]^+$: 267.11; found 267.1

3-(1-(3,4-dimethoxyphenyl)ethyl)-1H-indole (**3v**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.39 (d, *J* = 9.4 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.02 (t, *J* = 11.8 Hz, 1H), 6.98 (d, *J* = 1.7 Hz, 1H), 6.86-6.85 (m, 2H), 6.80 (d, *J* = 8.8 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 1.71 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 147.2, 139.7, 136.6, 127.0, 122.0, 121.7, 121.1, 119.8, 119.2, 111.1, 111.1, 111.0, 55.9, 36.6, 22.6.
HRMS (ESI) (m/z): calculated for $C_{18}H_{20}NO_2$ $[M+H]^+$: 282.1489; found 282.1469

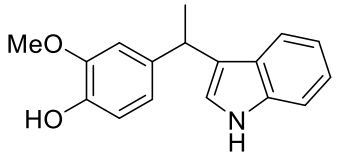
2-(1-(1H-indol-3-yl)ethyl)-5-methoxyphenol (**3w**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.19 (t, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 1.3 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.49 (dt, *J* = 12.7, 6.3 Hz, 1H), 6.36 (d, *J* = 2.5 Hz, 1H), 5.23 (s, 1H), 4.43 (q, *J* = 7.1 Hz, 1H), 3.76 (s, 3H), 1.68 (d, *J* = 6.6 Hz, 3H).

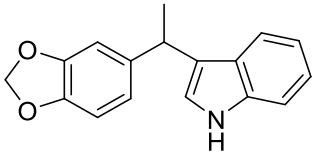
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 154.9, 136.9, 128.7, 126.4, 123.6, 122.4, 121.0, 119.4, 110.9, 106.1, 102.4, 54.9, 31.4, 20.4.
GCMS (m/z): calculated for $C_{17}H_{17}NO_2$ $[M]^+$: 267.13; found 267.1

4-(1-(1H-indol-3-yl)ethyl)-2-methoxyphenol (**3x**)



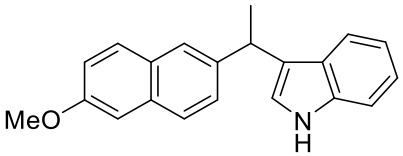
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.40 (d, *J* = 10.4 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 2.5 Hz, 1H), 6.88–6.76 (m, 3H), 5.40 (s, 1H), 4.32 (q, *J* = 7.0 Hz, 1H), 3.81 (s, 3H), 1.70 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 143.7, 138.9, 136.7, 126.8, 121.9, 121.8, 121.0, 120.0, 119.7, 119.2, 114.1, 111.0, 110.0, 55.9, 36.7, 22.5.
The structure was confirmed by comparison of the NMR spectra with the literature.[1]

3-(1-(benzo[d][1,3]dioxol-5-yl)ethyl)-1H-indole (**3y**)



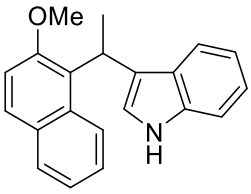
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.08–6.94 (m, 2H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.74–6.71 (m, 2H), 5.88 (d, *J* = 7.8 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 1H), 1.66 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 145.7, 141.2, 136.7, 127.0, 122.1, 121.6, 121.0, 120.3, 119.7, 119.3, 111.1, 108.1, 100.7, 36.8, 22.8.
GCMS (ESI) (m/z): calculated for $C_{17}H_{15}NO_2$ $[M]^+$: 265.11; found 265.1

3-(1-(6-methoxynaphthalen-2-yl)ethyl)-1H-indole (**3z**)



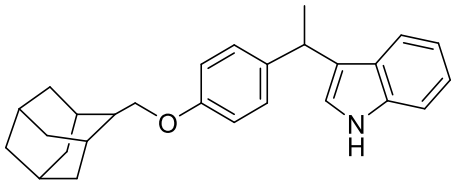
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.71–7.58 (m, 3H), 7.35 (dd, *J* = 18.7, 8.1 Hz, 3H), 7.37–7.33 (m, 3H), 7.01 (d, *J* = 1.6 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 4.50 (q, *J* = 7.1 Hz, 1H), 3.89 (s, 3H), 1.72 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 142.2, 136.7, 133.1, 129.3, 129.3, 127.2, 127.0, 126.9, 125.3, 122.1, 121.6, 121.3, 119.8, 119.3, 118.6, 111.1, 105.7, 55.4, 36.8, 22.3.
The structure was confirmed by comparison of the NMR spectra with the literature.[1]

3-(1-(2-methoxynaphthalen-1-yl)ethyl)-1H-indole (**3aa**)



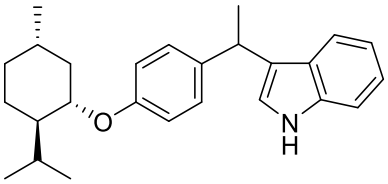
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 9.0 Hz, 1H), 7.93 (s, 1H), 7.75 (d, *J* = 9.1 Hz, 2H), 7.35–7.21 (m, 4H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.14–7.10 (m, 1H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.84 (t, *J* = 7.2 Hz, 1H), 5.48 (q, *J* = 6.7 Hz, 1H), 3.92 (s, 3H), 1.93 (d, *J* = 13.4, 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 146.1, 139.1, 128.5, 128.0, 127.2, 122.3, 120.6, 119.6, 113.8, 112.5, 101.8, 55.4, 36.3, 22.6.
HRMS (ESI) (m/z): calculated for $C_{21}H_{20}NO$ $[M+H]^+$: 302.1539; found 302.1529

3-(1-(4-(((1R,3S,5r)-adamantan-2-yl)methoxy)phenyl)ethyl)-1H-indole (**3ab**)



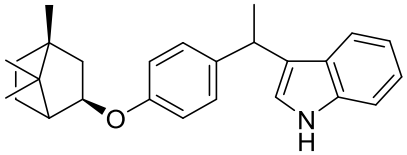
^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 9.3 Hz, 1H), 7.22–7.11 (m, 3H), 6.99–6.96 (m, 2H), 6.81 (d, *J* = 9.5 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 1H), 3.44 (s, 2H), 2.07–1.93 (m, 4H), 1.80–1.61 (m, 14H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 138.5, 136.7, 128.4, 126.9, 121.9, 121.0, 119.8, 119.2, 114.2, 110.9, 78.3, 39.5, 37.2, 28.3.
HRMS (ESI) (m/z): calculated for $C_{27}H_{31}NNaO$ $[M+Na]^+$: 408.2298; found 408.2279

3-(1-(4-(((1S,2R,5S)-2-isopropyl-5-methylcyclohexyl)oxy)phenyl)ethyl)-1H-indole (**3ac**)



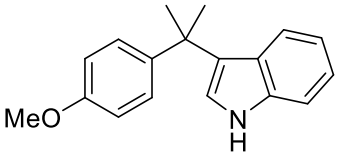
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.23–7.11 (m, 3H), 7.05–6.95 (m, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 4.31 (q, *J* = 7.0 Hz, 1H), 3.96 (td, *J* = 10.5, 4.0 Hz, 1H), 2.23–2.13 (m, 2H), 1.71–1.66 (m, 4H), 1.53–0.82 (m, 12H), 0.75 (dd, *J* = 7.8, 2.0 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 138.8, 136.8, 128.3, 122.0, 121.1, 119.9, 119.0, 115.8, 111.1, 48.2, 40.6, 36.1, 34.7, 31.6, 26.0, 23.9, 22.7, 22.1, 20.9, 16.6.
HRMS (ESI) (m/z): calculated for $C_{26}H_{33}NONa$ $[M+Na]^+$: 398.2454; found 398.2471

3-(1-(4-(((2R,4R)-4,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)phenyl)ethyl)-1H-indole (**3ad**)



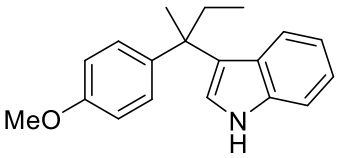
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.17–7.14 (m, 3H), 7.04–6.97 (m, 2H), 6.74 (d, *J* = 8.6 Hz, 2H), 4.42–4.13 (m, 2H), 2.35–2.19 (m, 2H), 1.79–1.70 (m, 2H), 1.67 (d, *J* = 7.1 Hz, 3H), 1.35–1.32 (m, 2H), 1.15–1.05 (m, 1H), 0.90 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 138.5, 136.7, 128.2, 127.0, 122.0, 121.0, 119.9, 119.1, 115.4, 111.1, 82.9, 49.3, 47.4, 45.0, 36.8, 36.0, 27.9, 26.7, 22.9, 19.8, 19.0, 13.6.
HRMS (ESI) (m/z): calculated for $C_{20}H_{31}NNaO_2$ $[M+Na]^+$: 396.2370; found 396.2367

3-(2-(4-methoxyphenyl)propan-2-yl)-1H-indole (**3ae**)



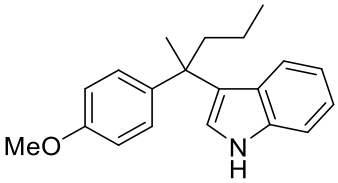
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.28–7.20 (m, 2H), 7.11–7.06 (m, 3H), 6.88 (td, *J* = 8.2, 3.5 Hz, 1H), 6.82–6.73 (m, 2H), 3.76 (s, 3H), 1.74 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 142.3, 137.2, 127.5, 126.5, 126.0, 121.7, 121.5, 120.6, 118.9, 113.4, 111.2, 55.2, 38.3, 30.8.
HRMS (ESI) (m/z): calculated for $C_{18}H_{19}NONa$ $[M+Na]^+$: 288.1583; found 255.1581
The structure was confirmed by comparison of the NMR spectra with the literature.[1]

3-(2-(4-methoxyphenyl)butan-2-yl)-1H-indole (**3af**)



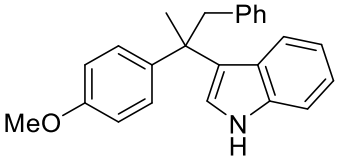
^{1}H NMR (400 MHz, $CDCl_3$) δ7.89 (s, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.10–7.05 (m, 2H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.85 (dd, *J* = 7.9, 7.2 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 2H), 3.75 (s, 3H), 2.33–2.18 (m, 1H), 2.18–2.05 (m, 1H), 1.64 (s, 3H), 0.72 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 139.3, 136.7, 128.5, 127.0, 122.1, 121.9, 121.1, 119.9, 119.3, 113.8, 111.1, 55.4, 36.3, 22.7.
HRMS (ESI) (m/z): calculated for $C_{19}H_{21}NO$ $[M+H]^+$: 280.1701; found 280.1671

3-(2-(4-methoxyphenyl)pentan-2-yl)-1H-indole (**3ag**)



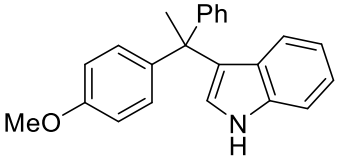
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.24–7.16 (m, 2H), 7.09–7.07 (m, 2H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.85 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 2H), 3.76 (s, 3H), 2.24–2.11 (m, 1H), 2.11–1.97 (m, 1H), 1.67 (s, 3H), 1.20–1.00 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 141.4, 137.0, 127.9, 126.1, 125.3, 121.6, 121.5, 121.2, 118.8, 113.1, 111.0, 55.2, 44.2, 41.7, 27.8, 18.0, 14.9.
HRMS (ESI) (m/z): calculated for $C_{20}H_{24}NO$ $[M+H]^+$: 294.1952; found 294.1951

3-(2-(4-methoxyphenyl)-1-phenylpropan-2-yl)-1H-indole (**3ah**)



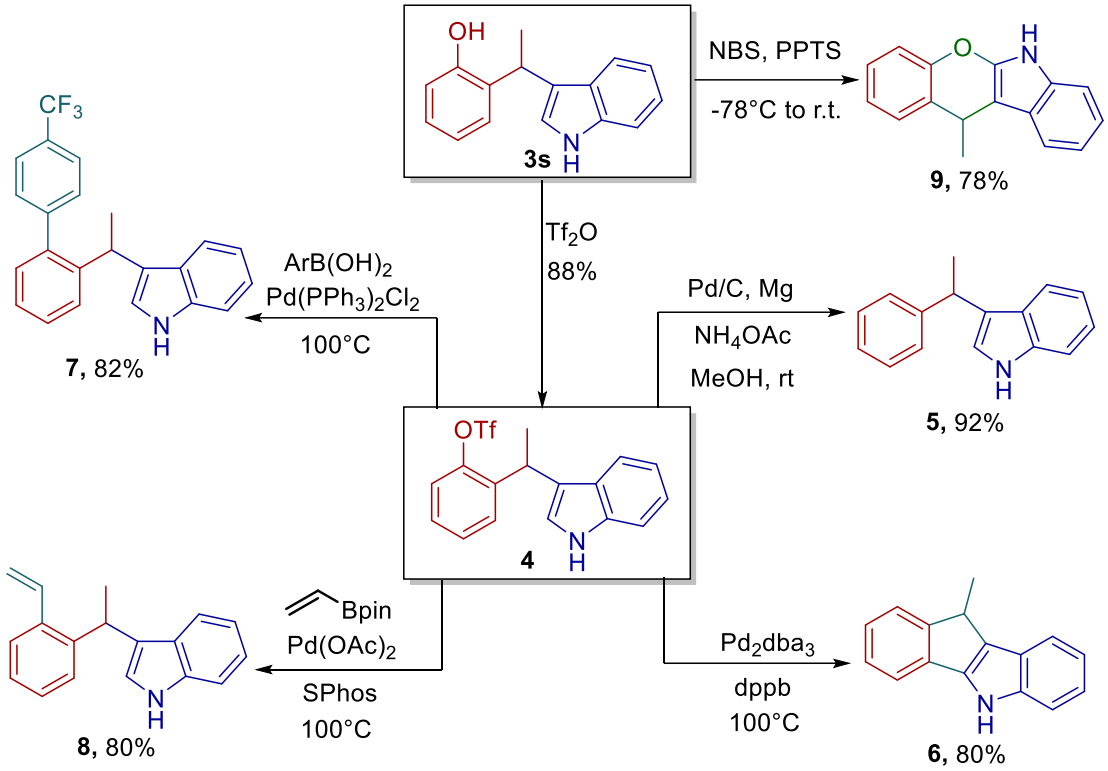
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.23–7.00 (m, 7H), 6.96 (d, *J* = 2.2 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 8.7 Hz, 2H), 6.60 (d, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 3.47 (d, *J* = 12.4 Hz, 1H), 3.41 (d, *J* = 12.4 Hz, 1H), 1.58 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 140.1, 138.3, 137.0, 130.8, 128.2, 127.1, 126.2, 125.8, 124.3, 121.6, 121.5, 121.3, 119.0, 113.1, 111.1, 55.1, 46.9, 42.6, 27.2.
HRMS (ESI) (m/z): calculated for $C_{24}H_{24}NO$ $[M+H]^+$: 342.1852; found 342.1848

3-(1-(4-methoxyphenyl)-1-phenylethyl)-1H-indole (**3ai**)



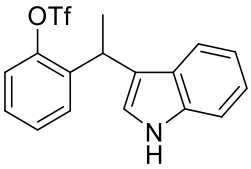
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.22 (d, *J* = 10.8 Hz, 1H), 7.18–7.14 (m, 3H), 7.14–7.02 (m, 4H), 6.85 (t, *J* = 7.5 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 2H), 6.33 (d, *J* = 2.4 Hz, 2H), 3.69 (s, 3H), 2.15 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 148.8, 140.8, 137.2, 129.4, 128.4, 127.9, 126.4, 125.8, 123.7, 122.2, 121.8, 119.1, 113.2, 111.2, 55.1, 47.4, 29.4.
GC-MS (m/z): calculated for $C_{23}H_{21}NO$ $[M]^+$: 327.16; found 327.1

4. Synthetic transformations



Scheme S3 Synthetic transformations

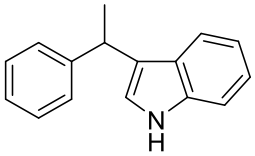
2-(1-(1H-indol-3-yl)ethyl)phenyl trifluoromethanesulfonate (**4**)



In a dry two neck flask 239 mg (1 mmol, 1.0 equiv) of **3s** was dissolved in 15 mL DCM. 560 µL of Et_3N (4 mmol, 4.0 equiv) was added to the reaction mixture at -20 °C. At this temperature 200 µL (1.2 mmol, 1.2 equiv) of Tf_2O was added drop wise. The reaction mixture was allowed to stir for 30 min at -20 °C and slowly warmed to room temperature. The reaction was followed by TLC. After full consumption of starting material, it was quenched with saturated NH_4Cl aq. and extracted with DCM for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (PE:EtOAc = 10:1) to afford the product **4** (324 mg) in 88% yield .

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.24–7.20 (m, 3H), 7.18–7.03 (m, 4H), 6.99 (d, *J* = 1.8 Hz, 1H), 6.96–6.86 (m, 1H), 4.66 (q, *J* = 7.0 Hz, 1H), 1.61 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 139.6, 136.7, 129.9, 128.6, 127.8, 126.6, 122.4, 121.8, 121.2, 119.6, 119.5, 119.3, 111.2, 30.6, 20.7.
^{19}F NMR (471 MHz, $CDCl_3$) δ -73.8
HRMS (ESI) (m/z): calculated for $C_{17}H_{14}F_3NNaO_3S$ $[M+Na]^+$: 392.0539; found 392.0545

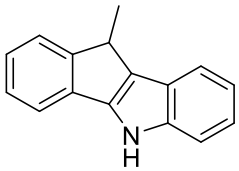
3-(1-phenylethyl)-1H-indole (**5**)



The reaction procedure was adapted from the previous literature[2]: Methanol (2 mL) was added to the mixture of compound **4** (37 mg, 0.1 mmol, 1 equiv.), magnesium powder (24 mg, 1 mmol, 10 equiv.), 10 % Pd/C (3.7 mg) and ammonium acetate (246 mg, 3.2 mmol, 32 equiv.). The reaction mixture was stirred at room temperature overnight. After evaporation of the methanol, the residue was purified by silica column chromatography (PE:EtOAc = 10:1) to afford the product **5** (20.3 mg) in 92% yield .

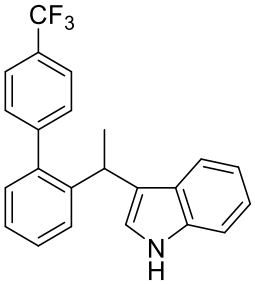
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.27 (d, *J* = 8.2 Hz, 1H), 7.24–7.19 (m, 2H), 7.19–7.05 (m, 5H), 7.04 (d, *J* = 1.4 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 4.67 (q, *J* = 7.1 Hz, 1H), 1.63 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ147.4, 139.6, 136.7, 129.8, 128.7, 127.8, 126.5, 122.3, 121.7, 121.1, 119.6, 119.5, 119.3, 111.1, 30.4, 21.0.
HRMS (ESI) (m/z): calculated for $C_{16}H_{15}N$ $[M]^+$: 221.1205; found 222.1214

10-methyl-5,10-dihydroindeno[1,2-b]indole (**6**)



The reaction procedure was adapted from the previous literature: In a flame-dried Schlenk flask under N_2 and equipped with a magnetic stir bar, compound **4** (65 mg, 0.18 mmol, 1 equiv.), potassium carbonate (100 mg, 1.12 mmol, 4 equiv.), $Pd_2(dba)_3$ (16 mg, 0.018 mmol, 0.1 equiv.) and dppb (15mg, 0.036 mmol, 0.2 equiv.) were dissolved in DMA (1.0 mL). Then the reaction mixture was heated at 100 °C. 15 h later, the mixture was cooled to r.t., it was quenched with saturated NH_4Cl and extracted with DCM for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane:EtOAc = 10:1) to afford desired product **6** (34 mg) in 86 % yield.
The structure was confirmed by comparison of the NMR spectra with the literature.[3]

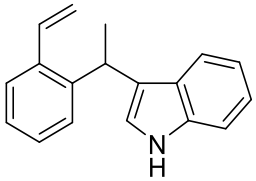
3-(1-(4'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)ethyl)-1H-indole (**7**)



In a flame-dried Schlenk flask under N_2 and equipped with a magnetic stir bar, compound **4** (104 mg, 0.28 mmol, 1 equiv.), 4-trifluoromethylphenylboronic acid (65 mg, 0.34 mmol, 1.2 equiv.), potassium carbonate (156 mg, 1.12 mmol, 4 equiv.), $Pd(PPh_3)_2Cl_2$ (10 mg, 0.014 mmol, 0.05 equiv.) were dissolved in a mixture solvent of 1,4-dioxane (0.8 mL) and degassed water (0.2 mL). Then the reaction mixture was heated at 100 °C. 15 h later, the mixture was cooled to r.t., it was quenched with saturated NH_4Cl and extracted with DCM for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane:EtOAc = 10:1) to afford desired product **7** (85mg) in 82 % yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.38–7.18 (m, 5H), 7.13 (dd, *J* = 14.0, 7.3 Hz, 2H), 6.96 (t, *J* = 7.4 Hz, 2H), 4.39 (q, *J* = 6.9 Hz, 1H), 1.59 (t, *J* = 8.8 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 144.0, 139.7, 136.7, 129.8, 128.4, 127.8, 126.5, 125.9, 125.0, 121.9, 121.6, 121.5, 119.5, 119.2, 111.2, 32.9, 22.7.
^{19}F NMR (471 MHz, $CDCl_3$) δ -62.3
HRMS (ESI) (m/z): calculated for $C_{23}H_{19}F_3N$ $[M+H]^+$: 366.1464; found 366.1458

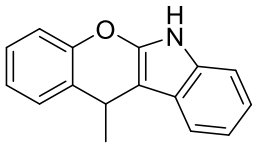
3-(1-(2-vinylphenyl)ethyl)-1H-indole (**8**)



In a flame-dried Schlenk flask under N_2 and equipped with a magnetic stir bar, compound **4** (86 mg, 0.233 mmol, 1 equiv.), pinacol vinylboronate (79 µL, 0.466 mmol, 2 equiv.), potassium carbonate (128 mg, 0.932 mmol, 4 equiv.), $Pd(OAc)_2$ (3 mg, 0.011 mmol, 0.05 equiv.) and Sphos (9.6 mg, 0.0233 mmol, 0.1 equiv.) were dissolved in a mixture solvent of THF (0.8 mL) and degassed water (0.2 mL). Then the reaction mixture was heated at 100 °C. 15 h later, the mixture was cooled to r.t., it was quenched with saturated NH_4Cl and extracted with DCM for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (hexane:EtOAc = 10:1) to afford desired product **8** (46 mg) in 80 % yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.35 (dd, *J* = 15.9, 8.1 Hz, 2H), 7.28–7.13 (m, 5H), 7.03 (t, *J* = 8.1 Hz, 1H), 6.97 (d, *J* = 1.4 Hz, 1H), 5.70 (dd, *J* = 17.3, 1.5 Hz, 1H), 5.34 (dd, *J* = 10.9, 1.5 Hz, 1H), 4.72 (q, *J* = 7.0 Hz, 1H), 1.70 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 136.8, 136.3, 135.1, 128.0, 127.2, 126.9, 126.2, 122.2, 121.5, 121.5, 119.7, 119.4, 116.2, 111.1, 32.6, 21.9.
HRMS (ESI) (m/z): calculated for $C_{18}H_{18}N$ $[M+H]^+$: 248.1434; found 248.1432

11-methyl-6,11-dihydrochromeno[2,3-b]indole (**9**)



The reaction procedure was adapted from the previous literature: In a dry two neck flask 37 mg (0.1 mmol, 1.0 equiv) of **3s** was dissolved in 3 mL DCM. PPTS (28mg, 0.11 mmol, 1.1 equiv) was added to the reaction mixture was cooled to -78 °C. At this temperature NBS (20 mg, 0.11 mmol, 1.1 equiv) in THF (2 mL) was added drop wise. The reaction mixture was allowed to stir for 1h at -78 °C. The reaction was followed by TLC. After full consumption of starting material, it was quenched with saturated NH_4Cl aq. and extracted with DCM for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (PE:EtOAc = 10:1) to afford the product **9** (18 mg) in 80% yield .

The structure was confirmed by comparison of the NMR spectra with the literature.[3]

5. Gram scale reaction

A mixture of indoles (10 mmol, 1 equiv.) and alkenes **1a** and **1s** (12 mmol, 1.2 equiv.) in HFIP (15 mL) were sealed in a Schlenk tube without cautious manipulations to exclusion of air or moisture. Then, the reaction mixture was stirred and heated at 100°C for 24h. After full consumption of the starting material, the HFIP was evaporated and the residue was purified by silica gel column chromatography (petroleum ether: ethyl acetate = 10 : 1) to afford the hydroaryaltion products **3a** 1.79g and **3s** 1.89g in 71% and 80% yields, respectively.

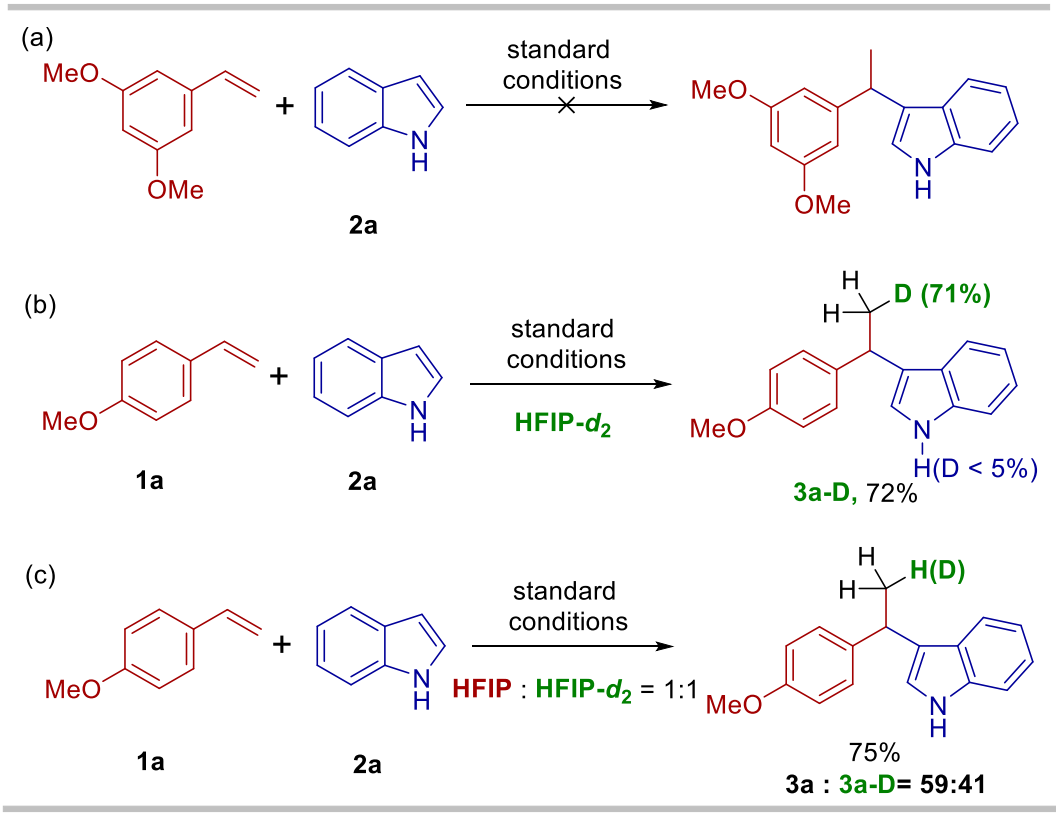
6. In vitro cell cytotoxicity

Method and materials:

The following reagents were obtained from commercial sources as indicated: DMEM or DMEM/F12 containing 2.5 mM L-glutamine and 15 mM HEPES buffer (HyClone); fetal bovine serum (FBS) was heat inactivated (HyClone); 100x penicillin-streptomycin-glutamine (PS) (Gibco); Molecular biology grade DMSO (Sigma); 0.05% Trypsin-EDTA (Gibco); Initial Evaluation of Compounds 3ai, 3v, 3w and 3x-: MCF-7, MDA-MB-231 or GL-261 cells were seeded at 4,000 cells per well in a 96 well flat bottom plate with DMEM or DMEM/F12 media supplemented with 10% FBS, and incubated with 5% CO_2 at 37 °C overnight. The compounds, were dissolved in molecular biology grade DMSO to achieve a 40 mM stock and then subsequently diluted by a factor of four using DMEM or DMEM/F12 media supplemented with 10 % FBS. The media was aspirated from the 96 well plate containing the MCF-7, MDA-MB-231, and GL-261cells and the media containing the compounds or DMSO vehicle controls were added. After culturing for 24-72 h, cell proliferation was measured by metabolic reduction of MTT/Thiazolyl Blue Tetrazolium Bromideor CCK8 assay. All cells were confirmed to be *Mycoplasma*-free and were maintained at 37 °C and 5% CO_2.

	IC50 (μ M)		
	MCF-7	**MDA-MB-231**	**GL-261**
3ai	31.3	5	3.9
3v	36.3	8.7	nd
3w	2.5	11.3	2.8
3x	10.8	16.8	8.1

7.Control experiments



Scheme S4. Control experiments

With the aim of better understanding the role of HFIP, several control experiments were performed to shed light onto this reaction. First, the hydroarylation of 1,3-dimethoxy-5-vinylbenzene with indole in HFIP did not deliver any of the desired products (Scheme **S4a**), implying the quinone methides structure might be involved as the key intermediate in this transformation. Second, when deuterated HFIP-d_2 was used as the promoter in the model reaction, it afforded the corresponding product **3a-D** with 71% incorporation of the deuterium on the terminal position of olefinic bond, clearly indicating the protonation of double bond by HFIP (Scheme **S4b** and Figure S2). Notably, N-H of the indole did not show significant incorporation of the deuterium, while the proton at C-2 position of indole exhibit deuterium incorporation by dissolving indole in HFIP-d_2 under standard conditions (Figure S5-S6). Intermolecular competition experiment between HFIP and HFIP-d_2 was also carried out (Scheme **S4c**), a ratio of 59:41 between **3a** and **3a-D** was afforded with an estimated KIE of 1.4 (Supporting information Figure S3-S4), indicating the protonation step might not be the rate-determining step, which was not fully consistent with the previous report involving additional Lewis acids catalysts.

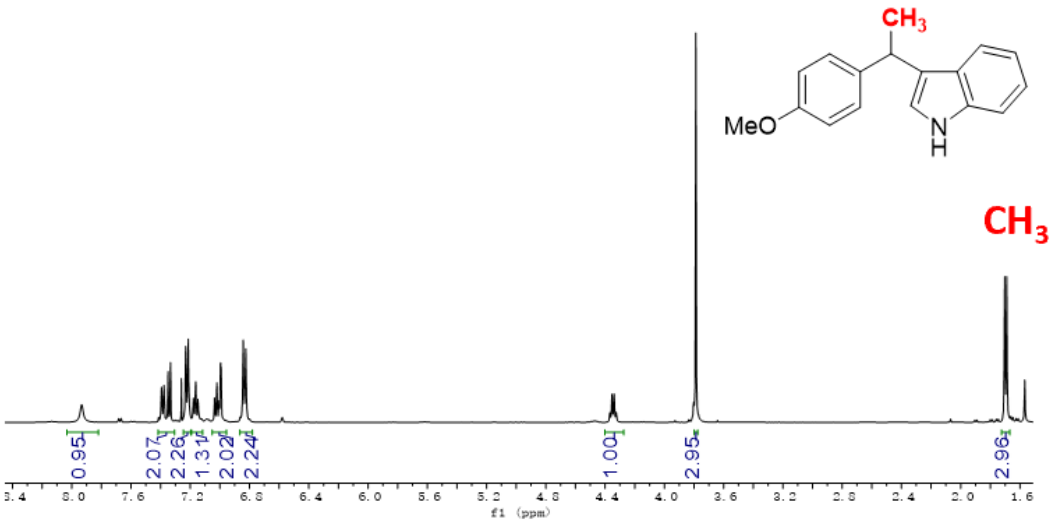
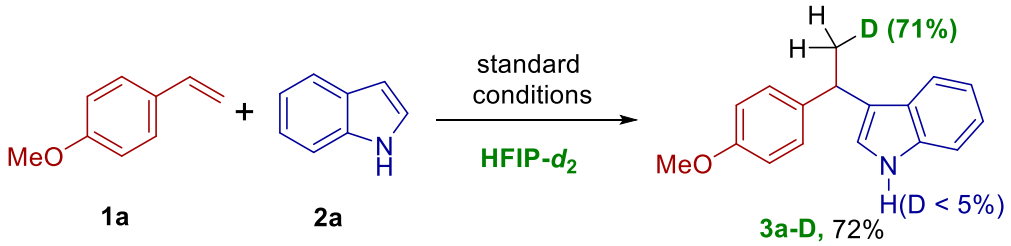


Figure S1 ^{1}H NMR of **3a**, $CDCl_3$, 298K



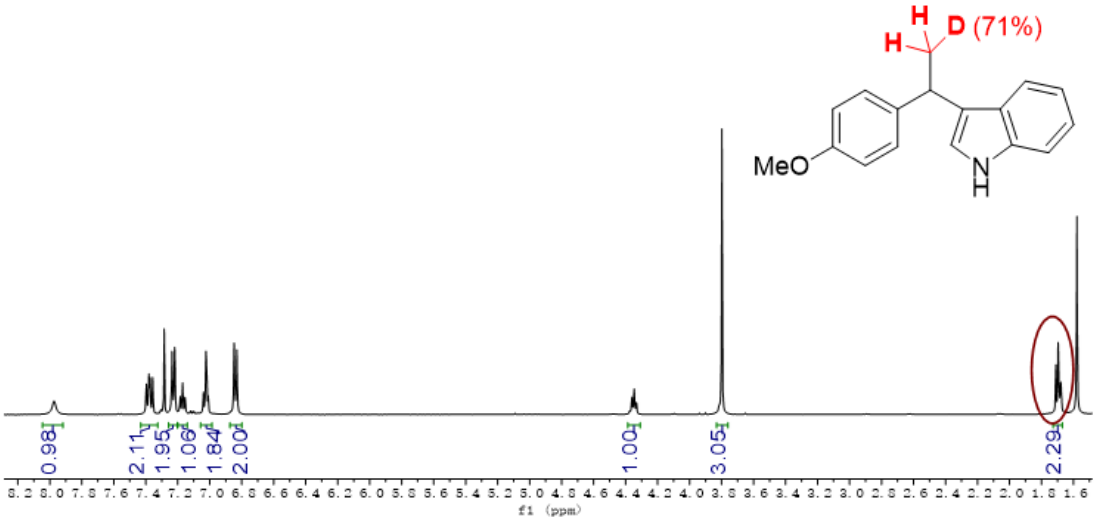


Figure S2 ^{1}H NMR of **3a-D**, $CDCl_3$, 298K

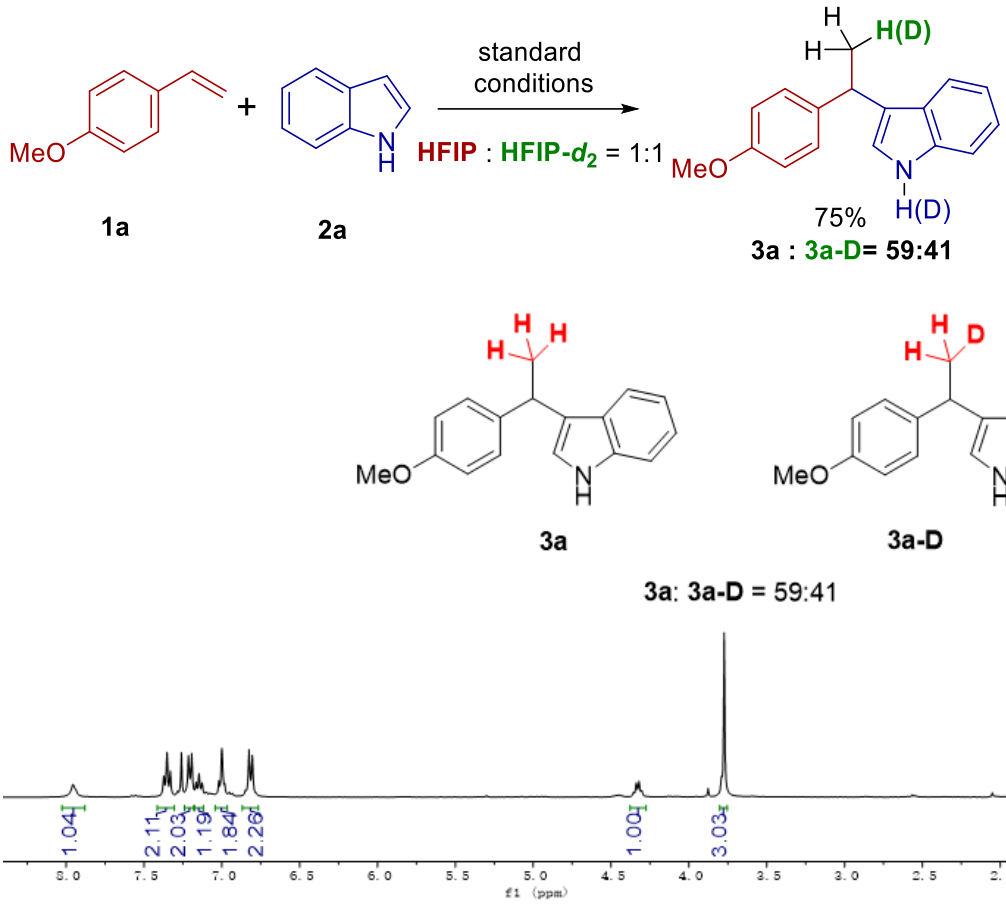


Figure S3 ^{1}H NMR of **3a** and **3a-D**, $CDCl_3$, 298K

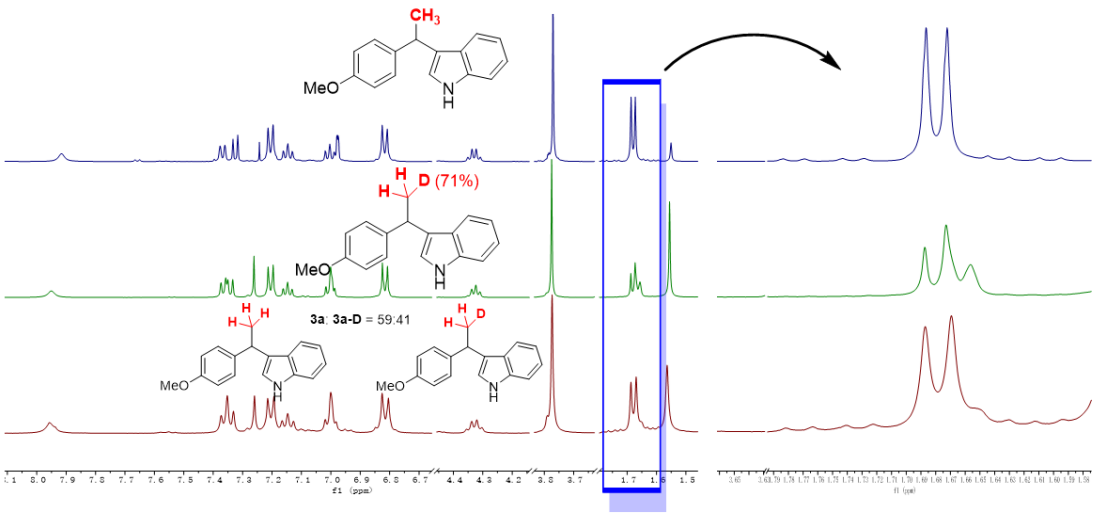


Figure S4 Stacked ^{1}H NMR of **3a** and **3a-D**, $CDCl_3$, 298K

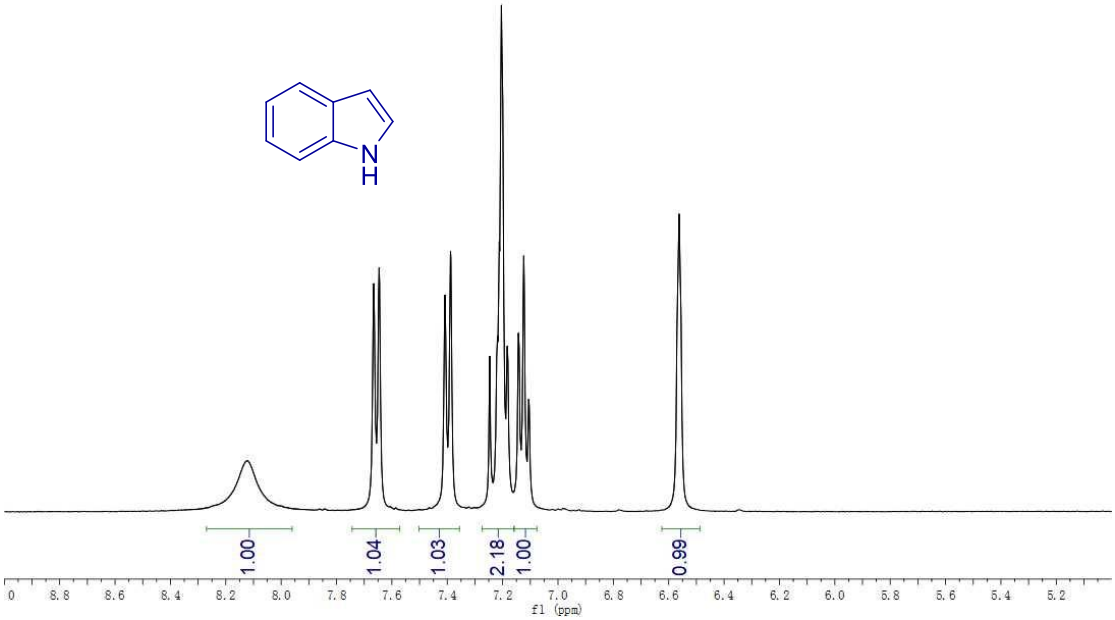
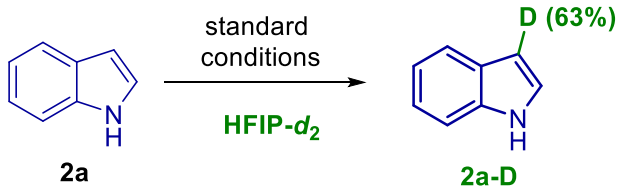


Figure S5 ^{1}H NMR of **3a** and **3a-D**, $CDCl_3$, 298K



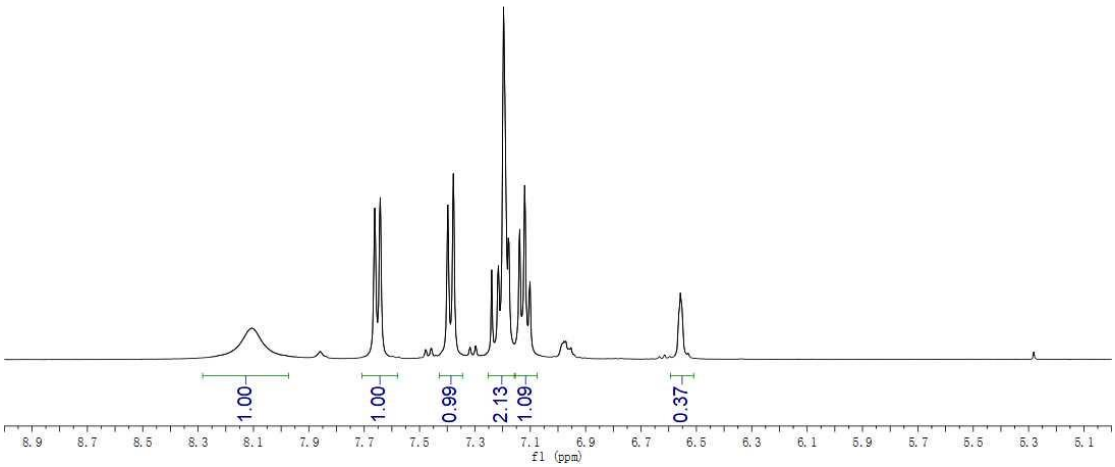


Figure S6 ^{1}H NMR of **3a** and **3a-D**, $CDCl_3$, 298K

8. X-Ray analysis

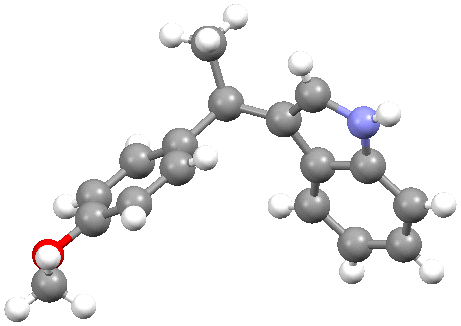


Figure S Single-crystal X-Ray diffraction of **3a**

Table S1 Crystal data and structure refinement

Identification code	mo230428a
Empirical formula	$C_{17}H_{17}NO$
Formula weight	251.31
Temperature/K	296.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.9302(9)
b/Å	10.5748(14)
c/Å	19.067(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1397.4(3)
Z	4
ρ_{calc}g/cm^3	1.195
μ/mm^{-1}	0.074
F(000)	536.0
Crystal size/mm^3	0.15 × 0.15 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.272 to 61
Index ranges	-9 ≤ h ≤ 9, -14 ≤ k ≤ 15, -26 ≤ l ≤ 26
Reflections collected	20151
Independent reflections	3983 [R_{int} = 0.0436, R_{sigma} = 0.0356]
Data/restraints/parameters	3983/0/174
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0434, wR_2 = 0.0987
Final R indexes [all data]	R_1 = 0.0649, wR_2 = 0.1102
Largest diff. peak/hole / e Å^{-3}	0.15/-0.16
Flack parameter	0.4(6)

Table S2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for mo230428a. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O(1)	5046(2)	9214.0(13)	3371.0(8)	54.4(4)
N(1)	6534(3)	1701.5(16)	3861.0(11)	58.3(5)
C(2)	6138(3)	2594.8(18)	4367.5(13)	52.8(5)
C(3)	7438(3)	3552.2(16)	4330.0(9)	39.6(4)
C(4)	8730(3)	3242.2(17)	3769.9(10)	40.6(4)
C(5)	10358(3)	3822(2)	3482.9(13)	56.4(6)
C(6)	11296(4)	3237(3)	2932.1(15)	75.6(8)
C(7)	10650(5)	2090(3)	2661.2(14)	78.1(9)
C(8)	9083(4)	1489(2)	2936.0(12)	64.4(7)
C(9)	8123(3)	2074.9(19)	3490.4(11)	47.4(5)
C(10)	7526(3)	4733.7(17)	4770.2(10)	42.8(4)
C(11)	6865(3)	5907.8(17)	4370.1(9)	39.6(4)
C(12)	7780(3)	7057(2)	4460.3(11)	50.3(5)
C(13)	7139(3)	8135.3(19)	4125.0(12)	52.4(5)
C(14)	5559(3)	8086.6(17)	3687.3(10)	41.5(4)
C(15)	4604(3)	6957.6(19)	3590.9(12)	50.3(5)
C(16)	5272(3)	5884.4(19)	3933.2(12)	50.3(5)
C(17)	6377(4)	4605(2)	5450.1(11)	63.6(6)
C(18)	3597(4)	9171(2)	2843.3(14)	67.5(7)

Table S3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for mo230428a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\cdots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	65.8(9)	30.5(7)	67.0(9)	2.3(6)	-17.4(8)	0.1(7)
N(1)	62.5(12)	32.8(8)	79.7(13)	-2.5(8)	-4.5(10)	-8.8(8)
C(2)	52.6(12)	39.0(10)	66.7(14)	5.8(10)	7.7(11)	-2.6(9)
C(3)	43.6(10)	31.2(8)	44.0(9)	6.0(7)	-0.9(8)	2.1(8)
C(4)	46.5(10)	32.1(9)	43.3(9)	7.6(8)	-2.5(8)	4.6(8)
C(5)	53.4(12)	47.2(12)	68.6(14)	9.7(10)	9.3(11)	3.0(10)
C(6)	74.3(18)	72.6(17)	79.8(17)	20.9(14)	32.0(15)	18.9(15)
C(7)	109(2)	67.2(17)	58.3(14)	8.7(13)	21.2(16)	42.7(17)
C(8)	98(2)	44.1(12)	51.3(12)	-3.6(10)	-7.3(13)	25.3(13)
C(9)	60.1(13)	32.7(9)	49.4(10)	4.1(8)	-8.1(10)	9.3(9)
C(10)	45.1(10)	38.9(10)	44.2(9)	1.4(8)	-3.4(9)	2.6(9)
C(11)	44.1(10)	33.9(8)	40.7(9)	-3.8(8)	-2.1(8)	1.1(8)
C(12)	51.6(12)	42.2(10)	57.2(12)	-2.0(9)	-19.1(10)	-4.0(9)
C(13)	58.0(13)	32.7(9)	66.6(12)	-1.6(9)	-15.5(10)	-10.4(9)
C(14)	48.8(11)	30.1(9)	45.7(9)	-2.4(8)	-4.1(8)	0.3(8)
C(15)	52.3(12)	36.9(10)	61.7(12)	-1.3(9)	-19.3(10)	-4.1(9)
C(16)	55.2(12)	30.1(9)	65.7(13)	-1.3(9)	-15.3(11)	-9.5(9)

Table S3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for mo230428a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\cdots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(17)	83.7(17)	59.4(13)	47.8(11)	4.1(10)	9.9(12)	15.8(13)
C(18)	77.3(17)	48.9(12)	76.2(16)	8.9(12)	-27.6(14)	5.6(13)

Table S4 Bond Lengths for mo230428a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O(1)	C(14)	1.383(2)	C(7)	C(8)	1.363(4)
O(1)	C(18)	1.422(3)	C(8)	C(9)	1.394(3)
N(1)	C(2)	1.379(3)	C(10)	C(11)	1.528(3)
N(1)	C(9)	1.367(3)	C(10)	C(17)	1.528(3)
C(2)	C(3)	1.357(3)	C(11)	C(12)	1.382(3)
C(3)	C(4)	1.432(3)	C(11)	C(16)	1.383(3)
C(3)	C(10)	1.506(3)	C(12)	C(13)	1.381(3)
C(4)	C(5)	1.396(3)	C(13)	C(14)	1.378(3)
C(4)	C(9)	1.409(3)	C(14)	C(15)	1.377(3)
C(5)	C(6)	1.381(4)	C(15)	C(16)	1.389(3)
C(6)	C(7)	1.393(4)			

Table S5 Bond Angles for mo230428a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(14)	O(1)	C(18)	117.55(16)	C(8)	C(9)	C(4)	122.2(2)
C(9)	N(1)	C(2)	108.95(18)	C(3)	C(10)	C(11)	112.56(15)
C(3)	C(2)	N(1)	110.0(2)	C(3)	C(10)	C(17)	112.20(17)
C(2)	C(3)	C(4)	106.48(17)	C(17)	C(10)	C(11)	109.84(17)
C(2)	C(3)	C(10)	128.06(19)	C(12)	C(11)	C(10)	120.99(17)
C(4)	C(3)	C(10)	125.45(17)	C(12)	C(11)	C(16)	117.20(17)
C(5)	C(4)	C(3)	134.22(19)	C(16)	C(11)	C(10)	121.72(17)
C(5)	C(4)	C(9)	118.6(2)	C(13)	C(12)	C(11)	121.39(18)
C(9)	C(4)	C(3)	107.21(18)	C(14)	C(13)	C(12)	120.37(18)
C(6)	C(5)	C(4)	118.8(2)	C(13)	C(14)	O(1)	115.87(17)
C(5)	C(6)	C(7)	121.4(3)	C(15)	C(14)	O(1)	124.45(17)
C(8)	C(7)	C(6)	121.3(2)	C(15)	C(14)	C(13)	119.68(18)
C(7)	C(8)	C(9)	117.7(2)	C(14)	C(15)	C(16)	119.04(18)
N(1)	C(9)	C(4)	107.36(18)	C(11)	C(16)	C(15)	122.31(18)
N(1)	C(9)	C(8)	130.4(2)				

Table S6 Torsion Angles for mo230428a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O(1)	C(14)	C(15)	C(16)	179.4(2)	C(6)	C(7)	C(8)	C(9)	1.2(4)
N(1)	C(2)	C(3)	C(4)	-0.2(2)	C(7)	C(8)	C(9)	N(1)	179.8(2)
N(1)	C(2)	C(3)	C(10)	178.60(19)	C(7)	C(8)	C(9)	C(4)	-0.4(3)

Table S6 Torsion Angles for mo230428a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C(2)	N(1)	C(9)	C(4)	-0.5(2)	C(9)	N(1)	C(2)	C(3)	0.4(2)
C(2)	N(1)	C(9)	C(8)	179.3(2)	C(9)	C(4)	C(5)	C(6)	0.7(3)
C(2)	C(3)	C(4)	C(5)	-178.8(2)	C(10)	C(3)	C(4)	C(5)	2.3(3)
C(2)	C(3)	C(4)	C(9)	-0.1(2)	C(10)	C(3)	C(4)	C(9)	-178.93(17)
C(2)	C(3)	C(10)	C(11)	-105.7(2)	C(10)	C(11)	C(12)	C(13)	-177.1(2)
C(2)	C(3)	C(10)	C(17)	18.8(3)	C(10)	C(11)	C(16)	C(15)	177.1(2)
C(3)	C(4)	C(5)	C(6)	179.4(2)	C(11)	C(12)	C(13)	C(14)	-0.2(3)
C(3)	C(4)	C(9)	N(1)	0.3(2)	C(12)	C(11)	C(16)	C(15)	0.4(3)
C(3)	C(4)	C(9)	C(8)	-179.49(19)	C(12)	C(13)	C(14)	O(1)	-179.3(2)
C(3)	C(10)	C(11)	C(12)	-141.6(2)	C(12)	C(13)	C(14)	C(15)	0.7(3)
C(3)	C(10)	C(11)	C(16)	41.9(3)	C(13)	C(14)	C(15)	C(16)	-0.7(3)
C(4)	C(3)	C(10)	C(11)	72.9(2)	C(14)	C(15)	C(16)	C(11)	0.1(4)
C(4)	C(3)	C(10)	C(17)	-162.59(19)	C(16)	C(11)	C(12)	C(13)	-0.4(3)
C(4)	C(5)	C(6)	C(7)	0.0(4)	C(17)	C(10)	C(11)	C(12)	92.6(2)
C(5)	C(4)	C(9)	N(1)	179.32(18)	C(17)	C(10)	C(11)	C(16)	-83.9(2)
C(5)	C(4)	C(9)	C(8)	-0.5(3)	C(18)	O(1)	C(14)	C(13)	171.5(2)
C(5)	C(6)	C(7)	C(8)	-1.0(4)	C(18)	O(1)	C(14)	C(15)	-8.5(3)

Table S7 Hydrogen Atom Coordinates (Å × 10^4) and Isotropic Displacement Parameters (Å^2×10^3) for mo230428a.

Atom	*x*	*y*	*z*	U(eq)
H(1)	5886.56	1019.73	3789.78	70
H(2)	5128.13	2548.18	4687.72	63
H(5)	10803.51	4588.39	3659.37	68
H(6)	12382.21	3617.86	2738.01	91
H(7)	11301.19	1726.34	2285.42	94
H(8)	8668	715.75	2759.71	77
H(10)	8879.94	4865.66	4899.93	51
H(12)	8851.02	7105.64	4753.11	60
H(13)	7776.97	8898.65	4195.03	63
H(15)	3527.11	6914.7	3300.73	60
H(16)	4625.58	5123.16	3866.37	60
H(17A)	5050.09	4433.01	5341.53	95
H(17B)	6462.77	5378.75	5711.98	95
H(17C)	6895.4	3923.82	5724.14	95
H(18A)	3988.53	8600.81	2478.32	101
H(18B)	3417.02	10001.2	2650.46	101
H(18C)	2406.66	8881.75	3045.01	101

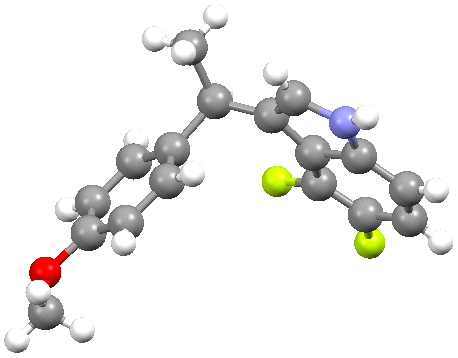


Figure S Single-crystal X-Ray diffraction of **3m**

Table S8 Crystal data and structure refinement.

Identification code	mo230505b
Empirical formula	$C_{17}H_{15}F_2NO$
Formula weight	287.311
Temperature/K	296.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.4260(14)
b/Å	10.475(2)
c/Å	18.684(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1453.4(5)
Z	4
ρ_{calc}g/cm^3	1.313
μ/mm^{-1}	0.099
F(000)	600.4
Crystal size/mm^3	0.13 × 0.13 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.36 to 60.96
Index ranges	-8 ≤ h ≤ 10, -14 ≤ k ≤ 14, -19 ≤ l ≤ 25
Reflections collected	10744
Independent reflections	4011 [R_{int} = 0.0710, R_{sigma} = 0.1065]
Data/restraints/parameters	4011/0/192
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0543, wR_2 = 0.1127
Final R indexes [all data]	R_1 = 0.1470, wR_2 = 0.1556
Largest diff. peak/hole / e Å^{-3}	0.30/-0.34
Flack parameter	0.3(11)

Table S9 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for mo230505b. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F(1)	4263(2)	5083.3(18)	3835.5(11)	80.8(6)
O(1)	10150(3)	667.4(16)	3432.1(11)	57.7(6)
F(2)	2417(3)	6220(2)	2792.7(14)	115.0(9)
N(1)	8583(4)	8234(2)	3835.2(18)	76.5(8)
C(13)	9602(4)	1813(2)	3730.1(14)	46.0(7)
C(3)	6494(4)	6713(2)	3809.3(15)	47.8(7)
C(2)	7756(4)	6394(2)	4357.9(15)	49.7(7)
C(10)	8350(4)	4026(2)	4401.6(14)	45.1(7)
C(11)	9787(4)	4050(2)	3936.4(16)	54.5(8)
C(12)	10421(4)	2959(3)	3598.2(16)	55.5(8)
C(9)	7740(5)	5209(3)	4812.0(14)	52.9(7)
C(15)	7552(4)	2856(3)	4520.2(17)	59.3(8)
C(8)	7038(5)	7875(3)	3494.1(18)	60.7(9)
C(4)	4892(5)	6182(3)	3551.6(16)	57.1(8)
C(14)	8170(4)	1762(3)	4188.6(17)	61.0(9)
C(1)	8992(5)	7352(3)	4351(2)	67.6(9)
C(5)	3985(5)	6764(4)	3021(2)	73.1(10)
C(7)	6105(6)	8457(3)	2943(2)	80.3(11)
C(17)	11410(5)	705(3)	2859.9(18)	72.6(10)
C(16)	8877(5)	5361(3)	5482.1(17)	79.0(11)
C(6)	4574(7)	7882(4)	2700(2)	89.2(14)

Table S10 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for mo230505b. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\cdots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
F(1)	73.3(14)	67.7(12)	101.4(14)	-21.1(10)	-12.3(11)	3.2(11)
O(1)	67.9(14)	35.9(10)	69.2(12)	-1.2(10)	17.6(12)	0.8(8)
F(2)	97.1(19)	126(2)	121.9(19)	25.6(15)	-46.3(16)	-23.8(15)
N(1)	82(2)	36.8(13)	111(2)	-9.6(14)	21.6(19)	-1.3(15)
C(13)	53.7(19)	34.4(13)	49.7(15)	-2.3(13)	1.9(15)	0.7(11)
C(3)	56.6(19)	34.7(13)	52.0(16)	4.5(13)	12.6(15)	-6.2(12)
C(2)	54.1(19)	36.9(14)	58.1(17)	-3.4(13)	0.4(16)	-6.5(12)
C(10)	50.2(18)	41.3(14)	43.8(15)	0.7(13)	0.5(15)	2.6(11)
C(11)	64(2)	32.8(13)	66.5(18)	-11.1(14)	14.2(17)	3.3(12)
C(12)	57(2)	41.8(16)	67.3(19)	-6.1(14)	18.6(16)	2.8(13)
C(9)	59(2)	47.7(16)	52.3(16)	-0.3(15)	1.0(15)	-4.4(13)
C(15)	62(2)	46.5(16)	70(2)	-10.8(16)	22.7(17)	-5.2(14)
C(8)	74(2)	36.1(14)	72(2)	9.6(16)	22.0(19)	-1.2(14)
C(4)	61(2)	46.7(16)	63.9(19)	0.6(15)	-2.9(18)	-4.7(14)
C(14)	62(2)	41.6(15)	79(2)	-14.1(15)	21.4(17)	0.1(14)

Table S10 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for mo230505b. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\cdots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	67(2)	45.9(16)	90(2)	-6.5(16)	0(2)	-13.2(17)
C(5)	68(3)	76(2)	76(2)	25(2)	-15(2)	-17(2)
C(7)	113(3)	53(2)	75(2)	28(2)	27(2)	12.3(18)
C(17)	81(3)	55.7(19)	81(2)	9.6(18)	30(2)	-9.2(17)
C(16)	96(3)	81(2)	60(2)	15(2)	-15(2)	-12.1(17)
C(6)	123(4)	81(3)	64(2)	52(3)	6(3)	2(2)

Table S11 Bond Lengths for mo230505b.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F(1)	C(4)	1.351(3)	C(2)	C(1)	1.360(4)
O(1)	C(13)	1.384(3)	C(10)	C(11)	1.377(4)
O(1)	C(17)	1.421(3)	C(10)	C(9)	1.526(4)
F(2)	C(5)	1.365(4)	C(10)	C(15)	1.379(4)
N(1)	C(8)	1.365(4)	C(11)	C(12)	1.388(4)
N(1)	C(1)	1.369(4)	C(9)	C(16)	1.518(4)
C(13)	C(12)	1.368(4)	C(15)	C(14)	1.381(4)
C(13)	C(14)	1.367(4)	C(8)	C(7)	1.383(5)
C(3)	C(2)	1.429(4)	C(4)	C(5)	1.345(4)
C(3)	C(8)	1.411(4)	C(5)	C(6)	1.386(5)
C(3)	C(4)	1.398(4)	C(7)	C(6)	1.365(5)
C(2)	C(9)	1.504(4)			

Table S12 Bond Angles for mo230505b.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(17)	O(1)	C(13)	118.2(2)	C(16)	C(9)	C(2)	112.0(3)
C(1)	N(1)	C(8)	109.2(3)	C(16)	C(9)	C(10)	109.5(2)
C(12)	C(13)	O(1)	123.9(2)	C(14)	C(15)	C(10)	121.5(3)
C(14)	C(13)	O(1)	116.6(2)	C(3)	C(8)	N(1)	106.5(3)
C(14)	C(13)	C(12)	119.5(2)	C(7)	C(8)	N(1)	130.3(3)
C(8)	C(3)	C(2)	108.3(3)	C(7)	C(8)	C(3)	123.2(4)
C(4)	C(3)	C(2)	135.4(3)	C(3)	C(4)	F(1)	119.9(3)
C(4)	C(3)	C(8)	116.3(3)	C(5)	C(4)	F(1)	120.1(3)
C(9)	C(2)	C(3)	126.4(2)	C(5)	C(4)	C(3)	120.0(3)
C(1)	C(2)	C(3)	105.2(3)	C(15)	C(14)	C(13)	120.5(3)
C(1)	C(2)	C(9)	128.3(3)	C(2)	C(1)	N(1)	110.8(3)
C(9)	C(10)	C(11)	122.2(2)	C(4)	C(5)	F(2)	118.0(4)
C(15)	C(10)	C(11)	116.8(2)	C(6)	C(5)	F(2)	119.1(4)
C(15)	C(10)	C(9)	120.9(2)	C(6)	C(5)	C(4)	122.9(4)
C(12)	C(11)	C(10)	122.4(2)	C(6)	C(7)	C(8)	118.1(4)
C(11)	C(12)	C(13)	119.3(3)	C(7)	C(6)	C(5)	119.5(4)
C(10)	C(9)	C(2)	112.6(2)				

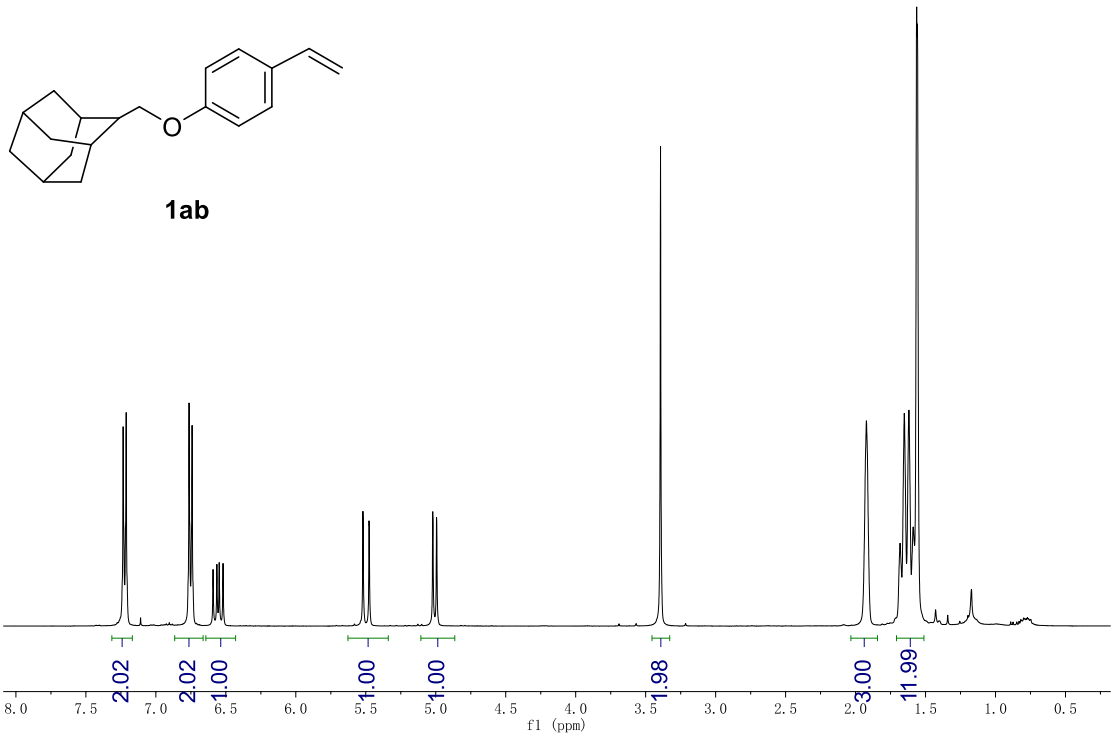
Table S13 Torsion Angles for mo230505b.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
F(1)	C(4)	C(3)	C(2)	-1.9(4)	N(1)	C(1)	C(2)	C(9)	176.8(2)
F(1)	C(4)	C(3)	C(8)	-178.7(3)	C(13)	C(12)	C(11)	C(10)	-0.3(3)
F(1)	C(4)	C(5)	F(2)	1.0(3)	C(13)	C(14)	C(15)	C(10)	-0.0(4)
F(1)	C(4)	C(5)	C(6)	-179.0(3)	C(3)	C(2)	C(9)	C(10)	74.1(3)
O(1)	C(13)	C(12)	C(11)	-178.7(3)	C(3)	C(2)	C(9)	C(16)	-161.9(3)
O(1)	C(13)	C(14)	C(15)	178.9(3)	C(3)	C(8)	C(7)	C(6)	0.8(3)
F(2)	C(5)	C(4)	C(3)	-179.2(3)	C(3)	C(4)	C(5)	C(6)	0.8(4)
F(2)	C(5)	C(6)	C(7)	177.6(3)	C(2)	C(9)	C(10)	C(11)	41.8(3)
N(1)	C(8)	C(3)	C(2)	0.7(3)	C(2)	C(9)	C(10)	C(15)	-142.7(3)
N(1)	C(8)	C(3)	C(4)	178.3(2)	C(8)	C(7)	C(6)	C(5)	1.5(4)
N(1)	C(8)	C(7)	C(6)	-180.0(4)	C(4)	C(5)	C(6)	C(7)	-2.4(4)
N(1)	C(1)	C(2)	C(3)	-0.3(3)					

Table S14 Hydrogen Atom Coordinates (Å × 10^4) and Isotropic Displacement Parameters (Å^2×10^3) for mo230505b.

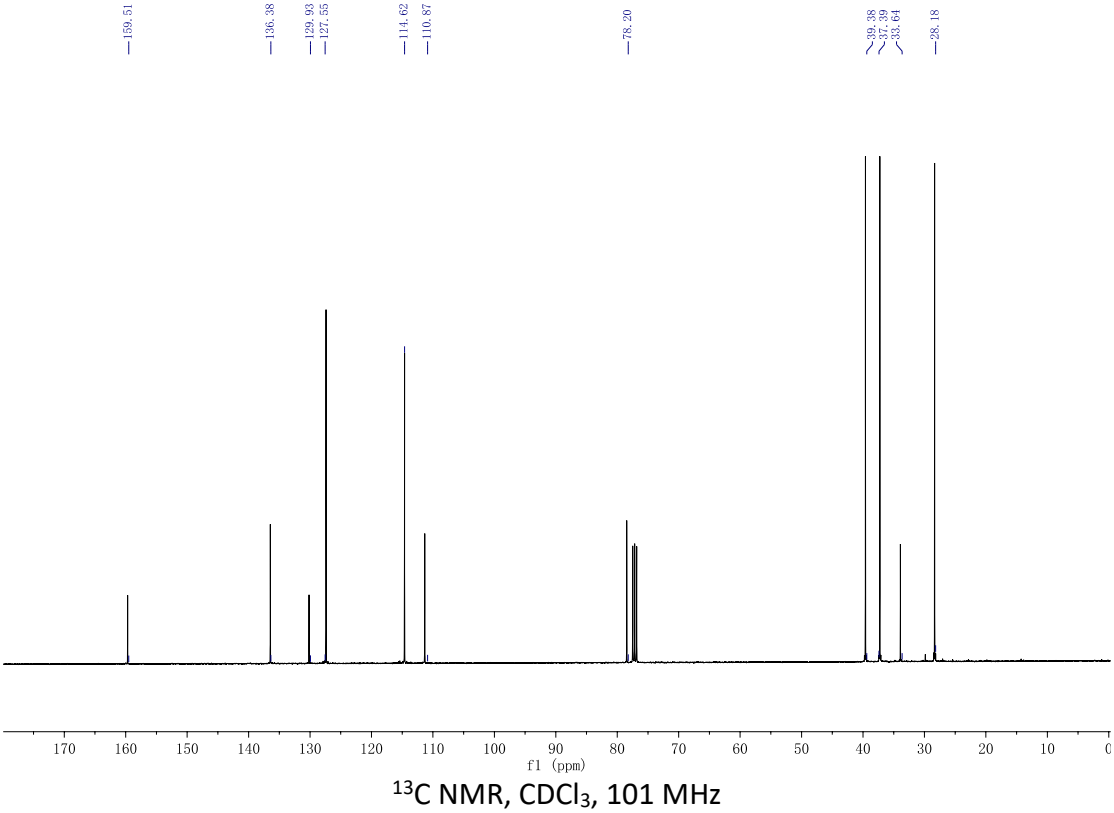
Atom	*x*	*y*	*z*	U(eq)
H(1)	9201(4)	8907(2)	3740.9(18)	91.8(10)
H(11)	10354(4)	4825(2)	3845.5(16)	65.4(9)
H(12)	11392(4)	3007(3)	3285.0(16)	66.6(10)
H(9)	6495(5)	5063(3)	4965.0(14)	63.5(9)
H(15)	6576(4)	2802(3)	4830.4(17)	71.1(10)
H(14)	7608(4)	985(3)	4278.1(17)	73.2(10)
H(1a)	9980(5)	7402(3)	4655(2)	81.2(11)
H(7)	6510(6)	9218(3)	2743(2)	96.4(14)
H(17a)	10988(16)	1282(18)	2497(6)	108.9(15)
H(17b)	12554(9)	990(20)	3036(3)	108.9(15)
H(17c)	11540(20)	-134(6)	2659(9)	108.9(15)
H(16a)	10110(8)	5500(20)	5349.3(17)	118.5(16)
H(16b)	8450(20)	6077(15)	5754(7)	118.5(16)
H(16c)	8790(30)	4600(10)	5767(7)	118.5(16)
H(6)	3930(7)	8237(4)	2322(2)	107.0(16)

9.NMR spectra

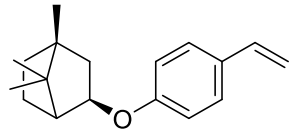


1ab

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

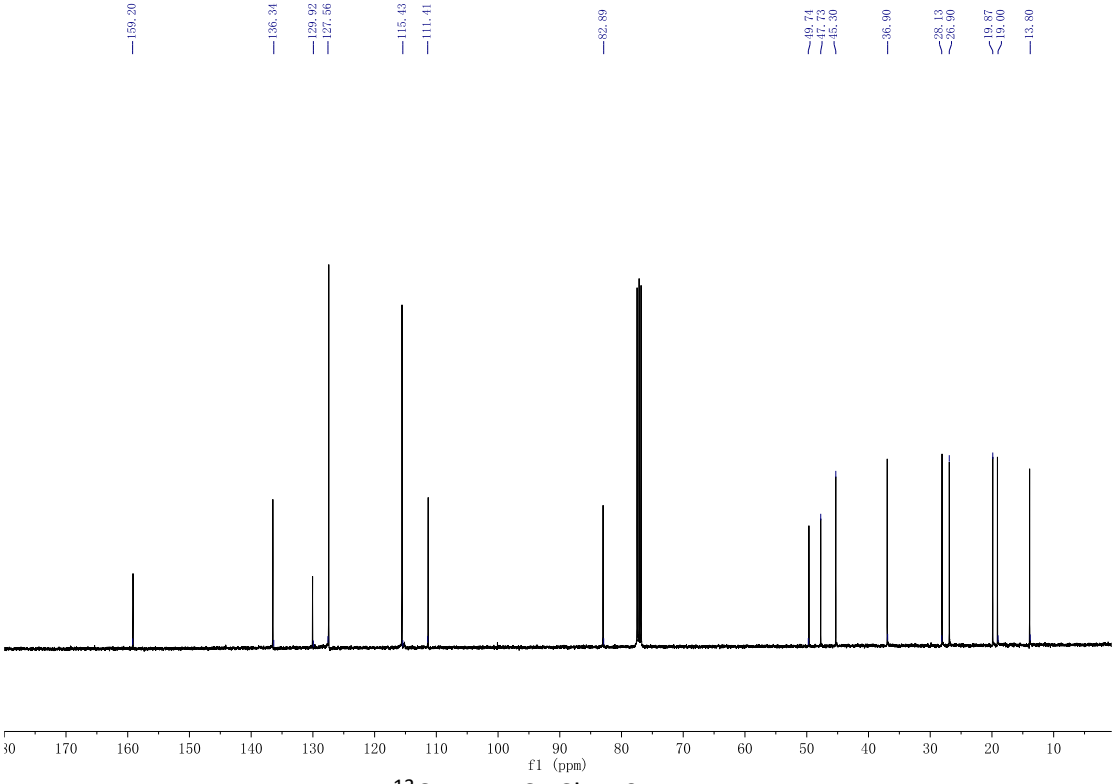


^{13}C NMR, $CDCl_3$, 101 MHz

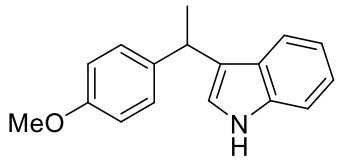


1ad

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



^{13}C NMR, $CDCl_3$, 101 MHz



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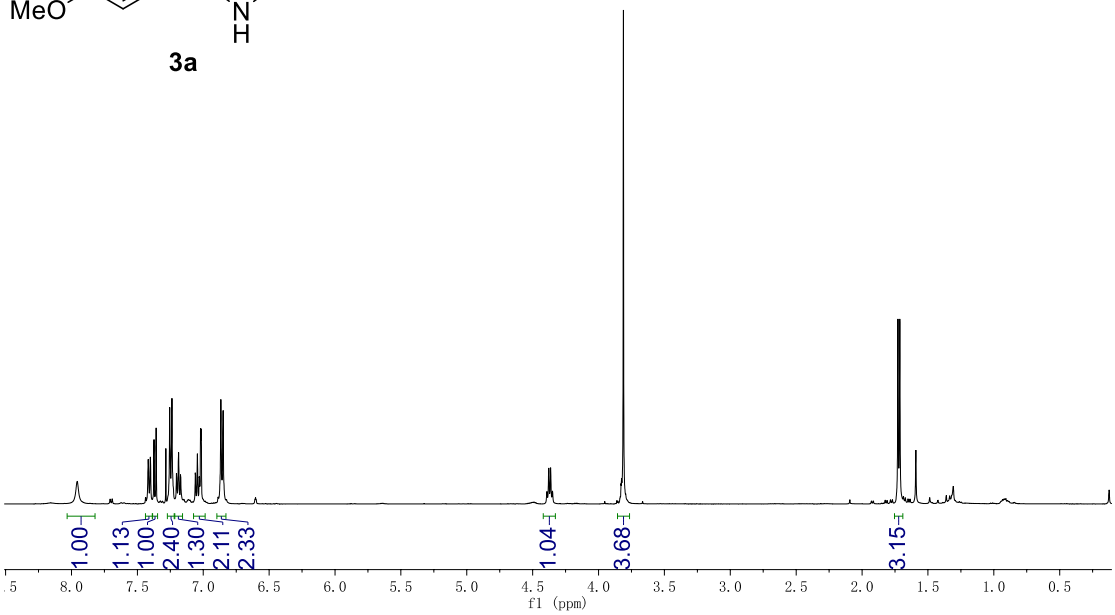
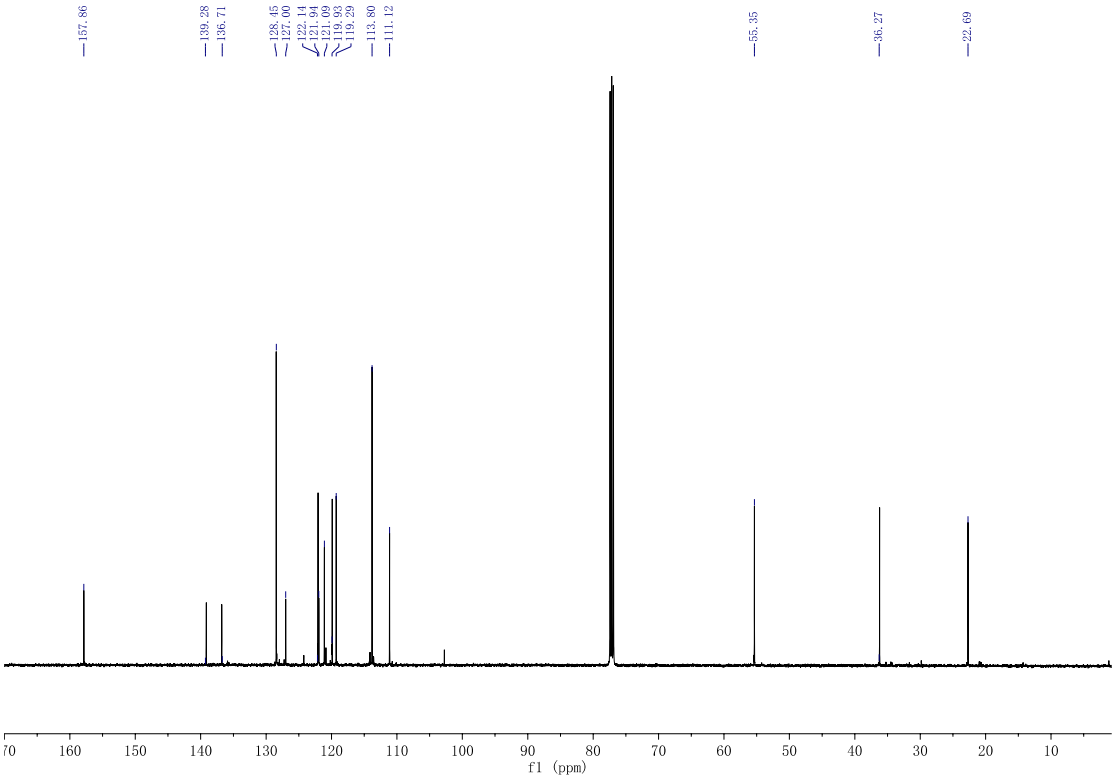
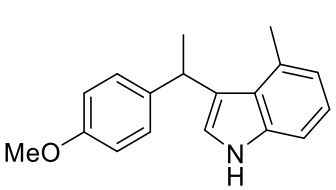


^{1}H NMR, $CDCl_3$, 400 MHz

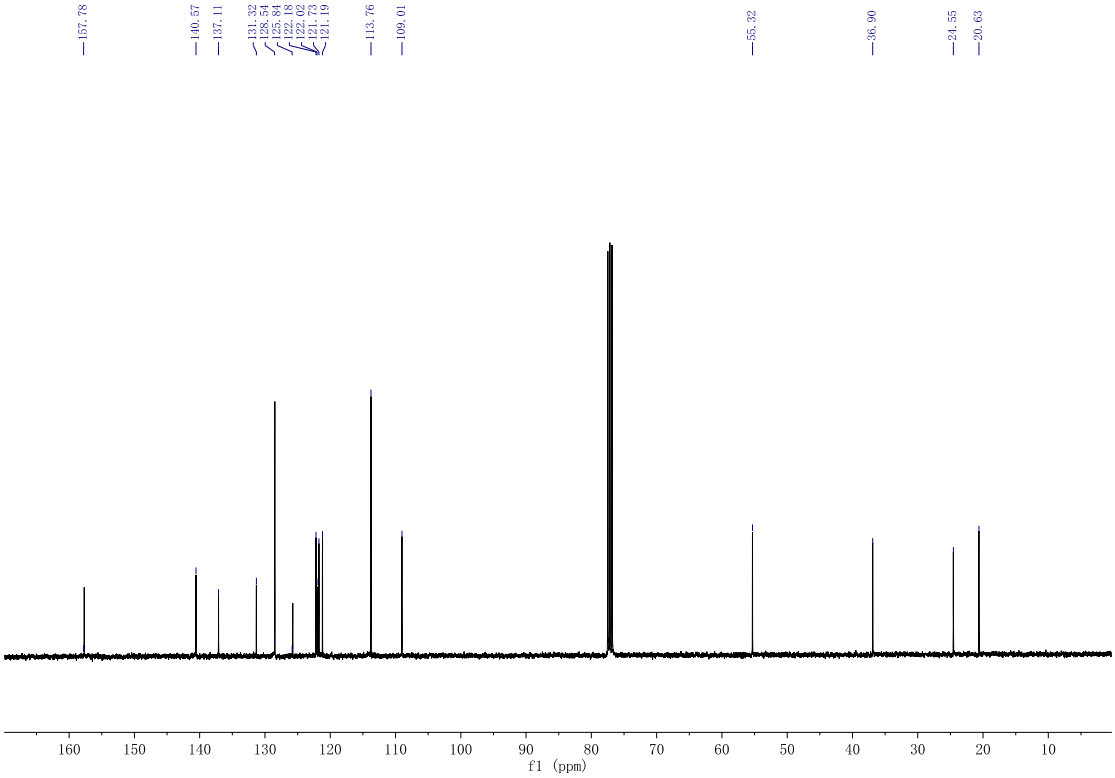


^{13}C NMR, $CDCl_3$, 101 MHz

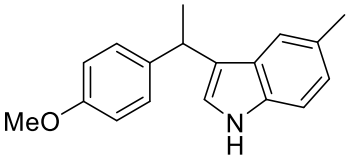


3b

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

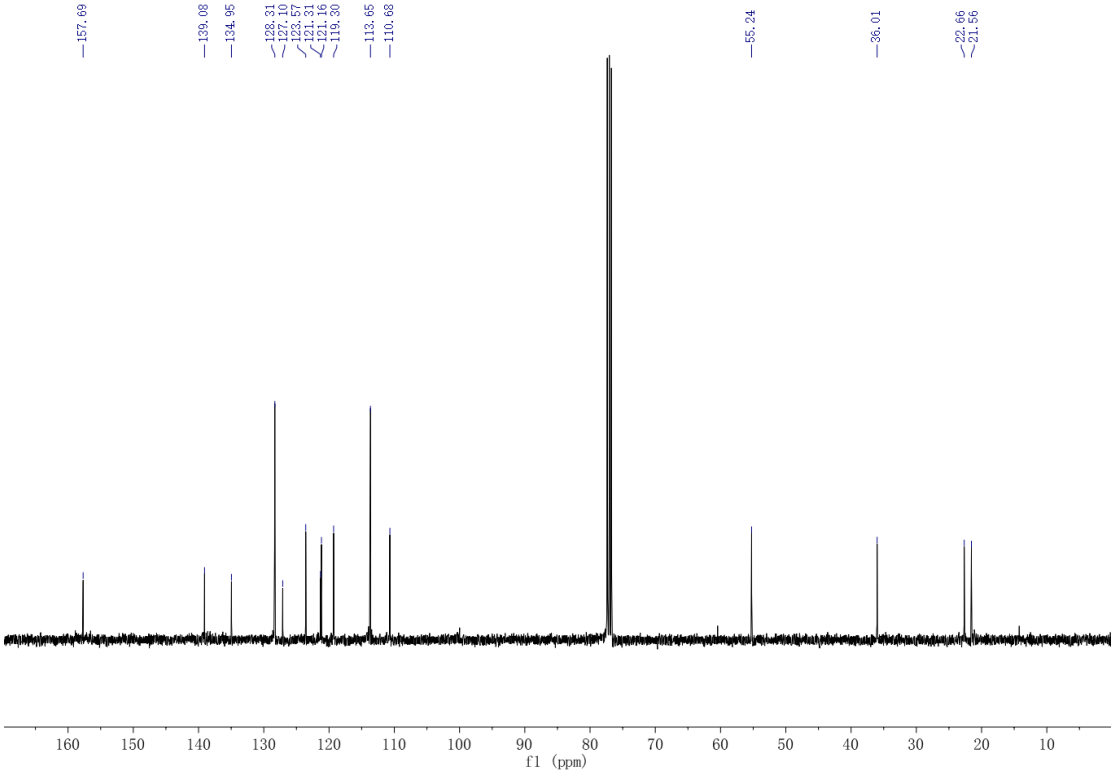


^{13}C NMR, $CDCl_3$, 101 MHz

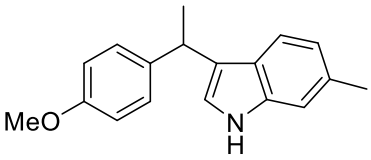


3c

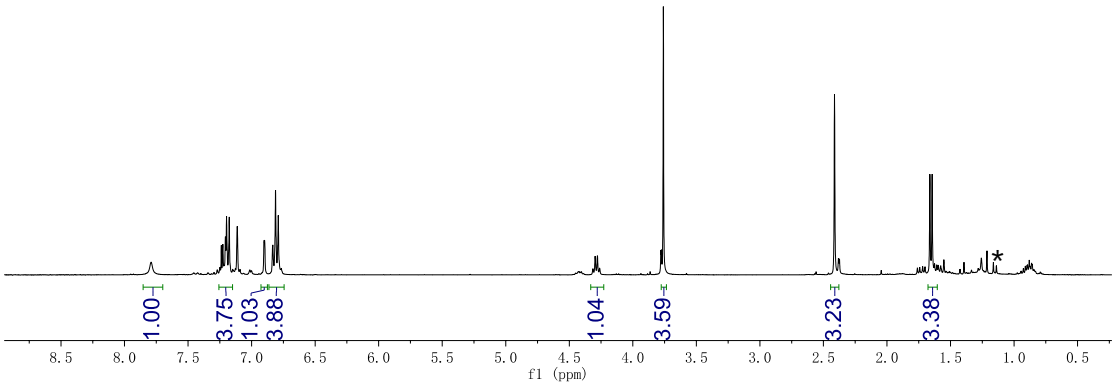
^{1}H NMR, $CDCl_3$, 400 MHz (* EtOAc)



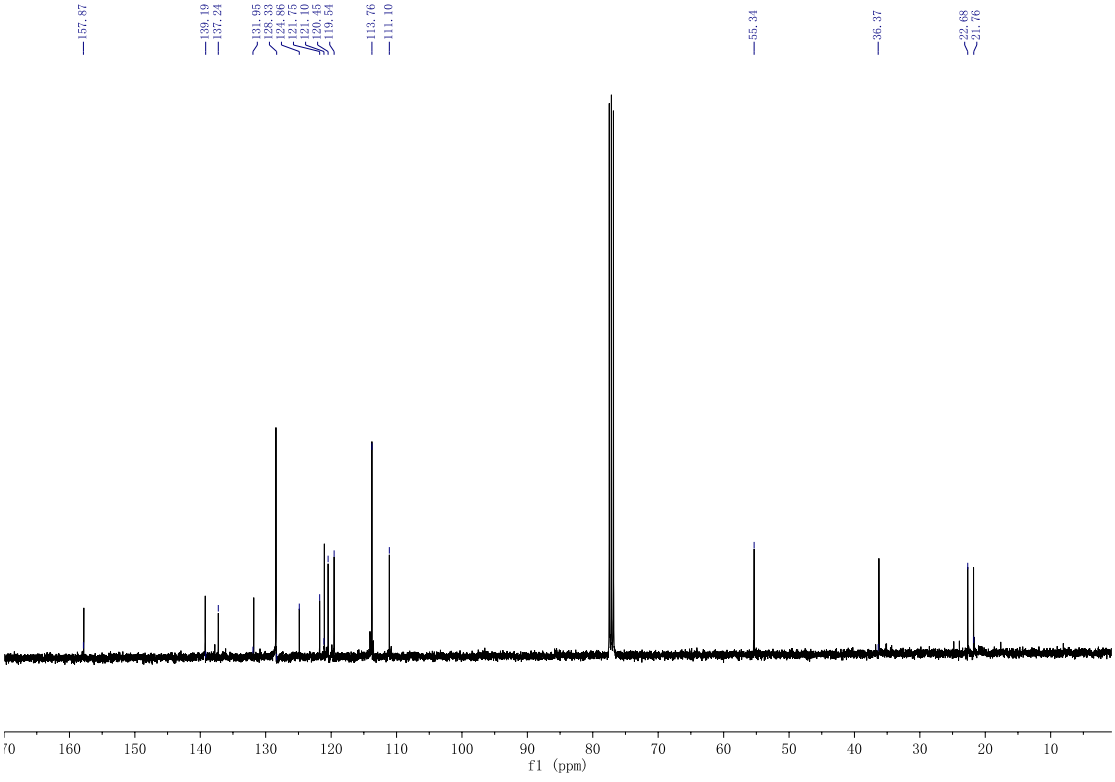
^{13}C NMR, $CDCl_3$, 101 MHz



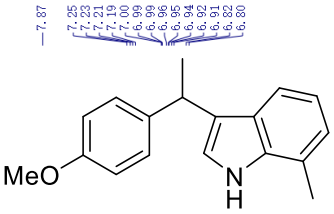
3d



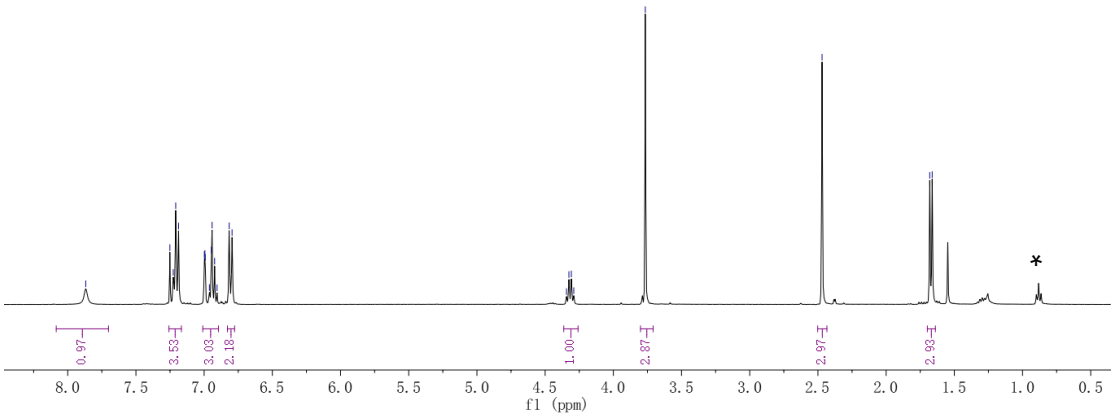
^{1}H NMR, $CDCl_3$, 400 MHz (* grease)



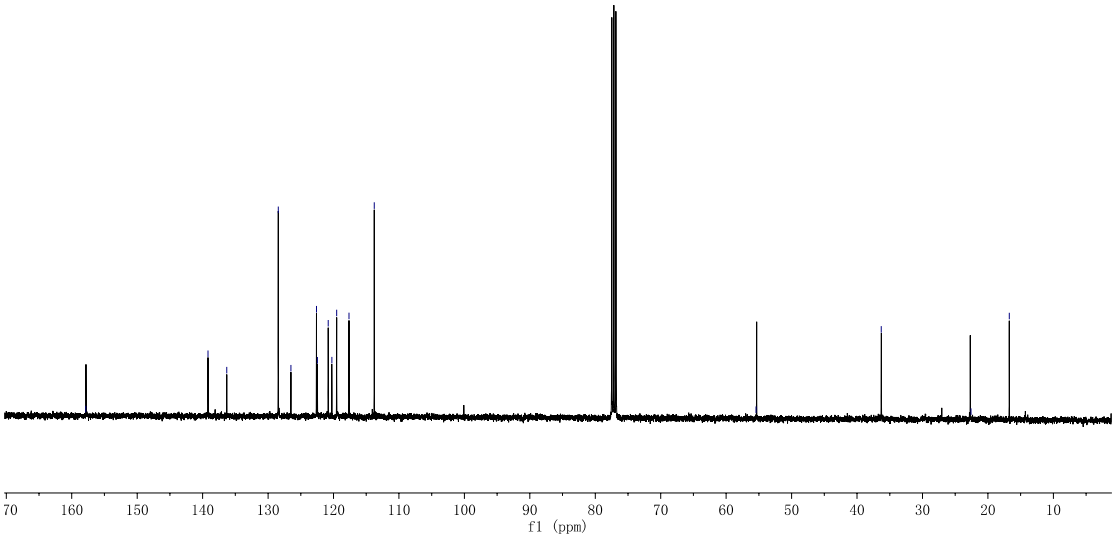
^{13}C NMR, $CDCl_3$, 101 MHz



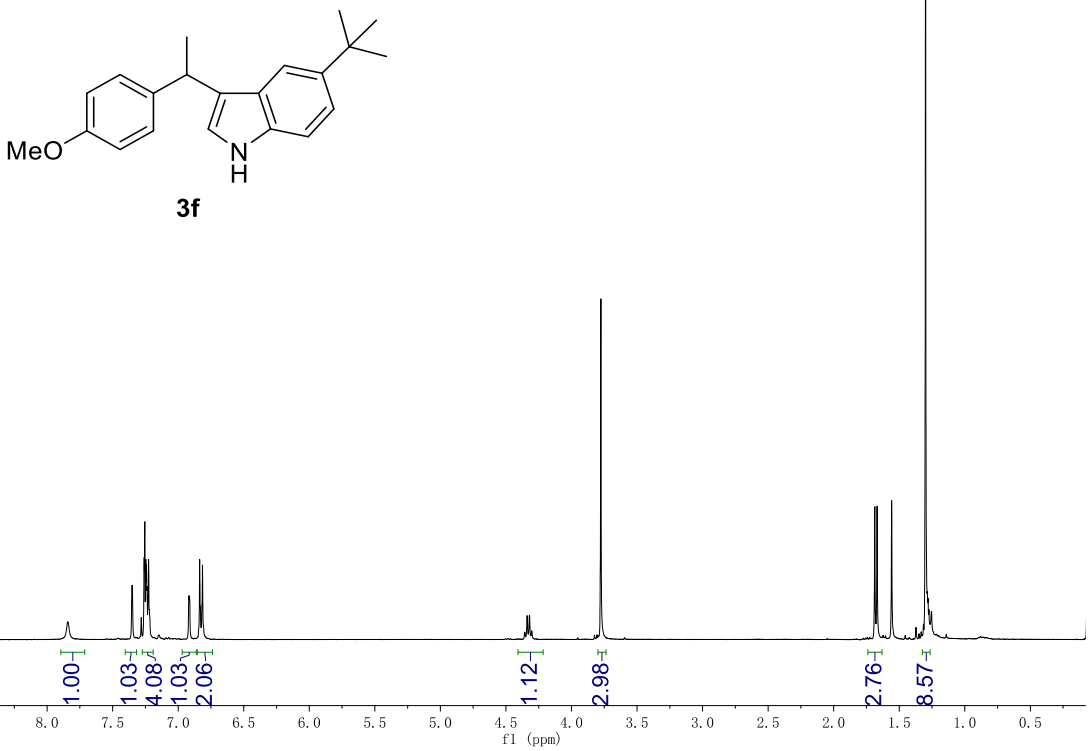
3e



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

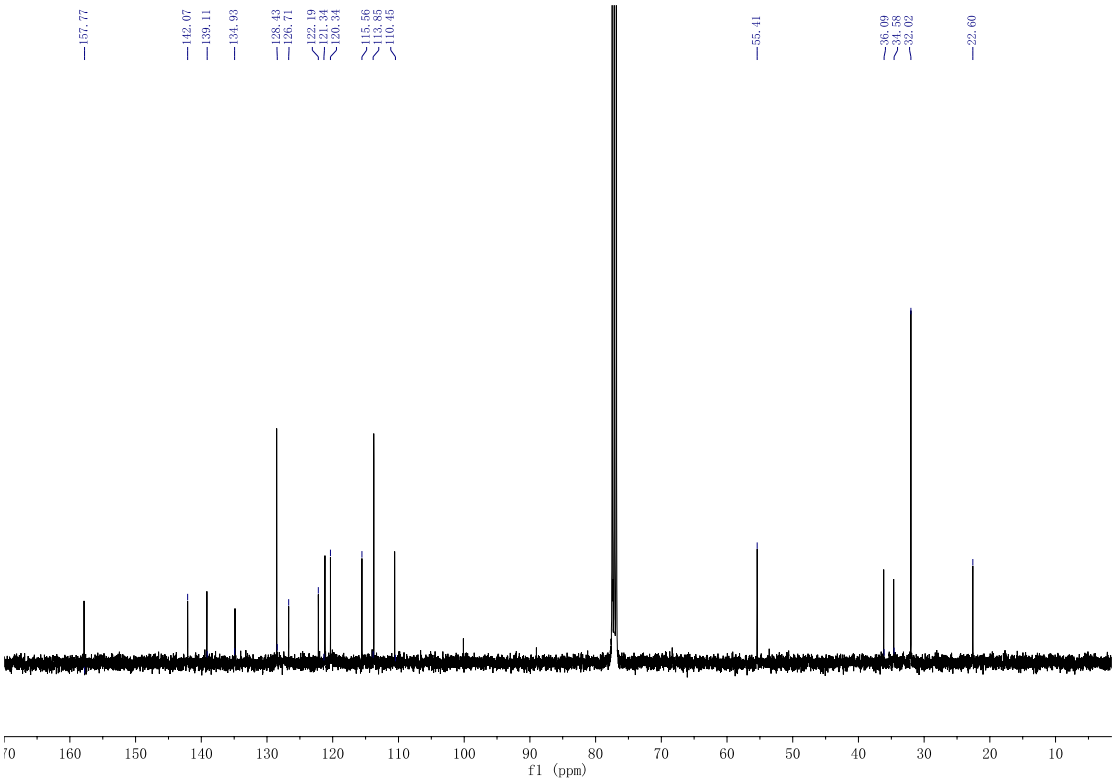


^{13}C NMR, $CDCl_3$, 101 MHz

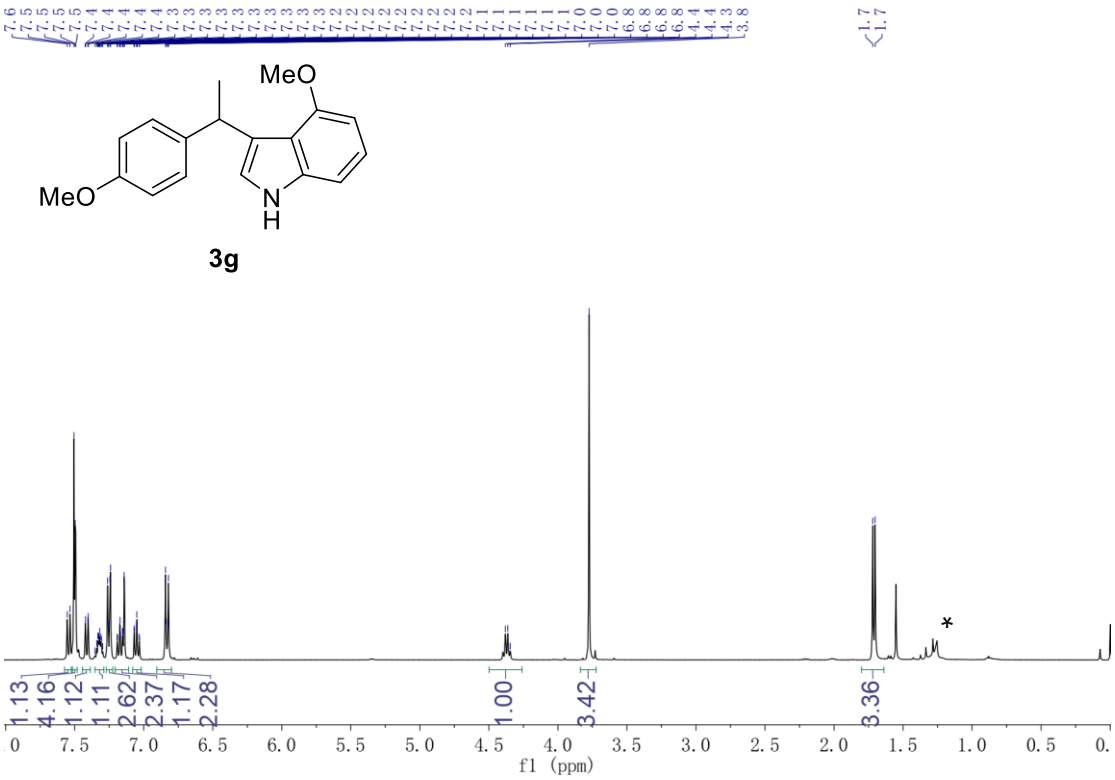


3f

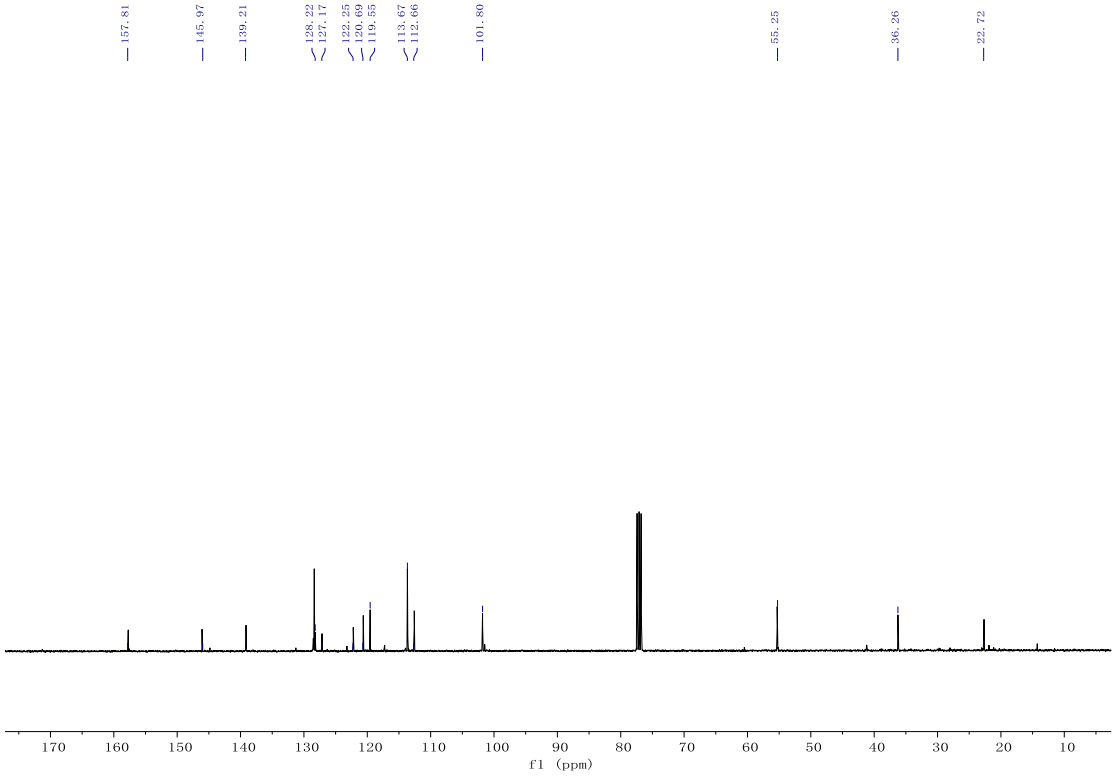
^{1}H NMR, $CDCl_3$, 400 MHz



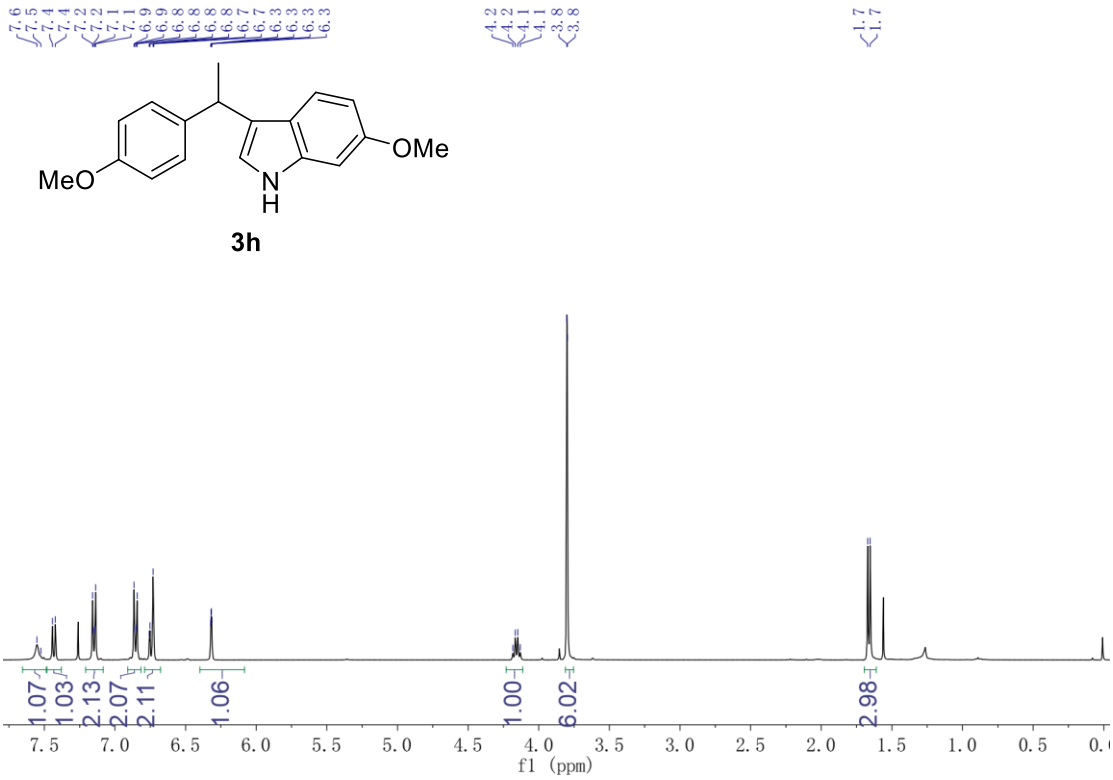
^{13}C NMR, $CDCl_3$, 101 MHz



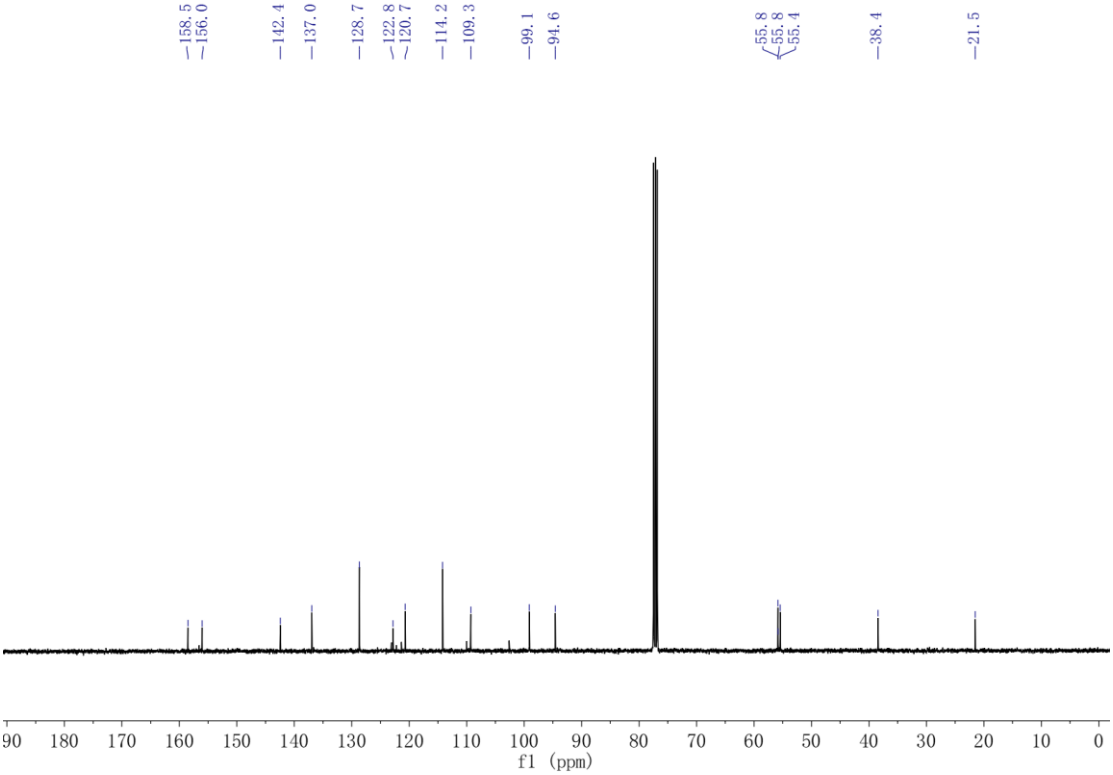
^{1}H NMR, $CDCl_3$, 400 MHz (* grease)



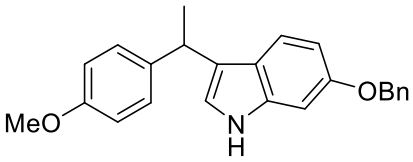
^{13}C NMR, $CDCl_3$, 101 MHz



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



^{13}C NMR, $CDCl_3$, 101 MHz



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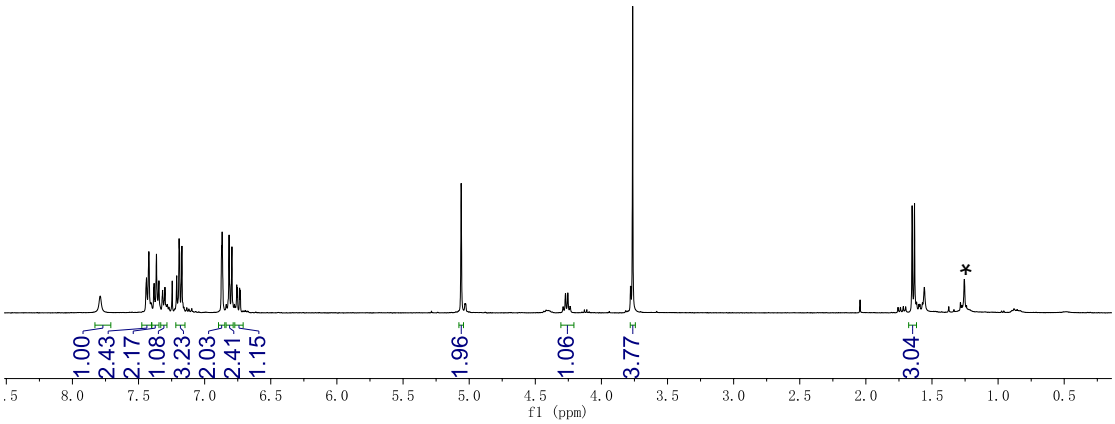
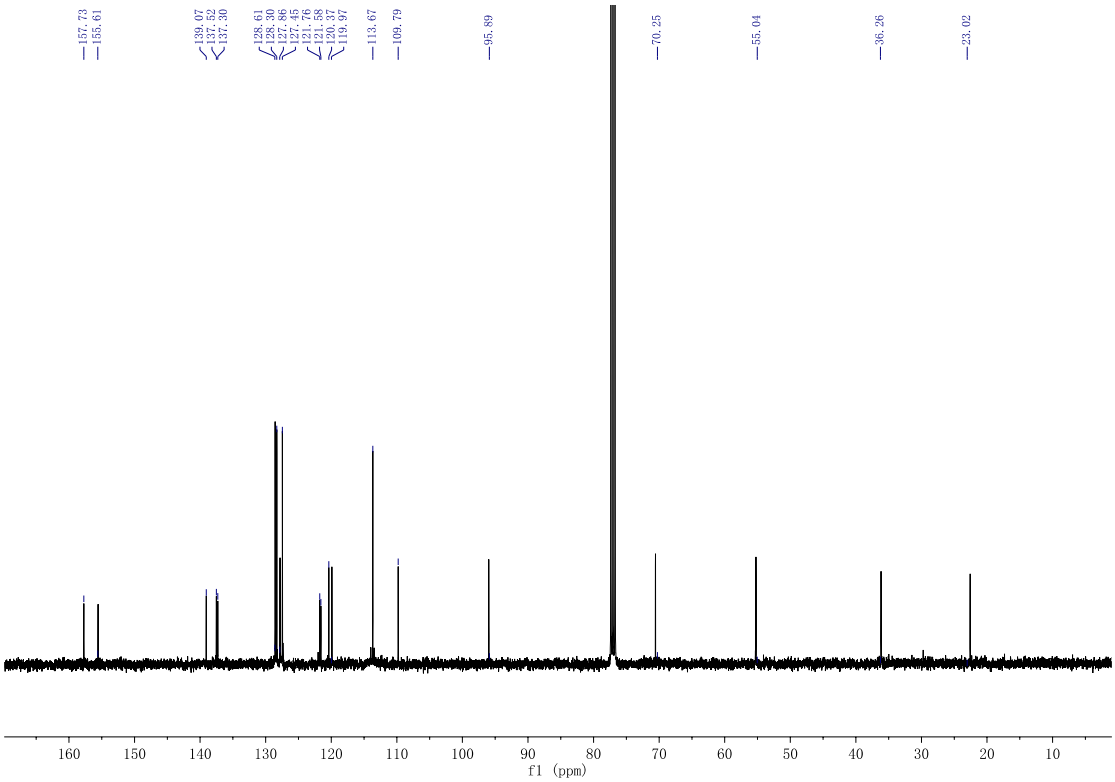
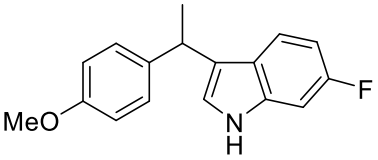


^{1}H NMR, $CDCl_3$, 400 MHz (* grease)



^{13}C NMR, $CDCl_3$, 101 MHz



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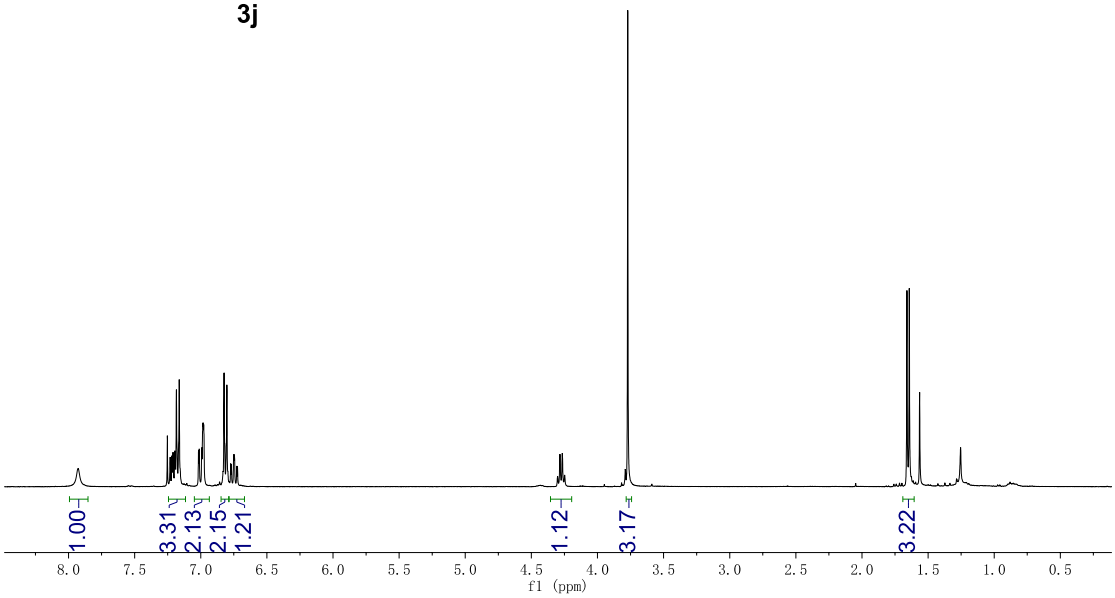
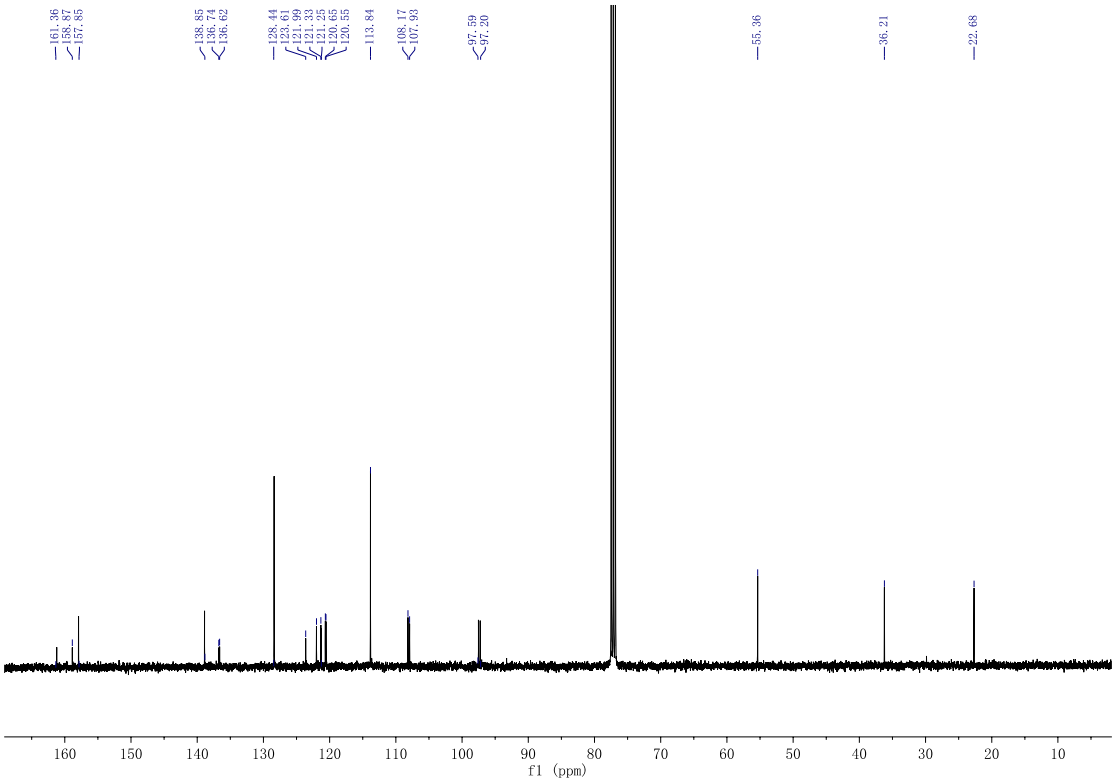
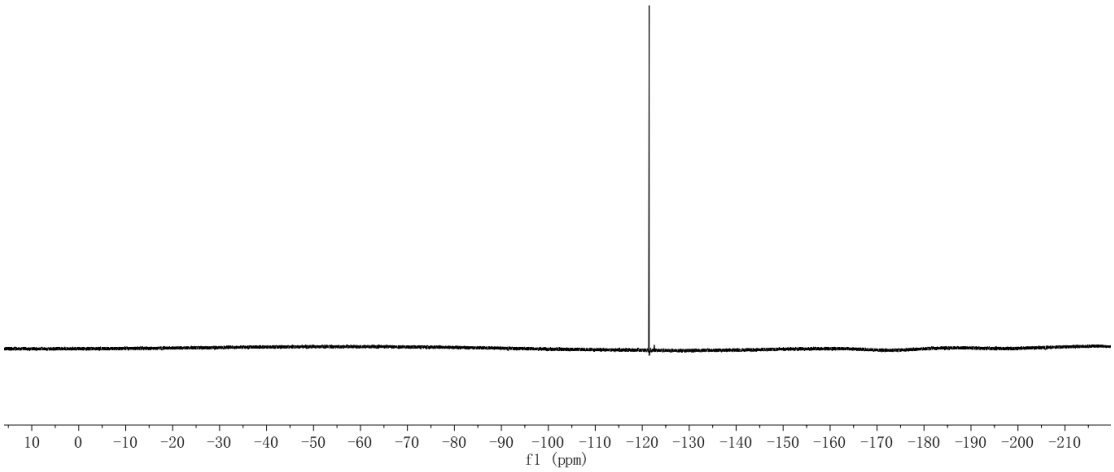


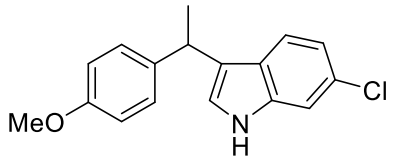
^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz



^{19}F NMR, $CDCl_3$, 471 MHz



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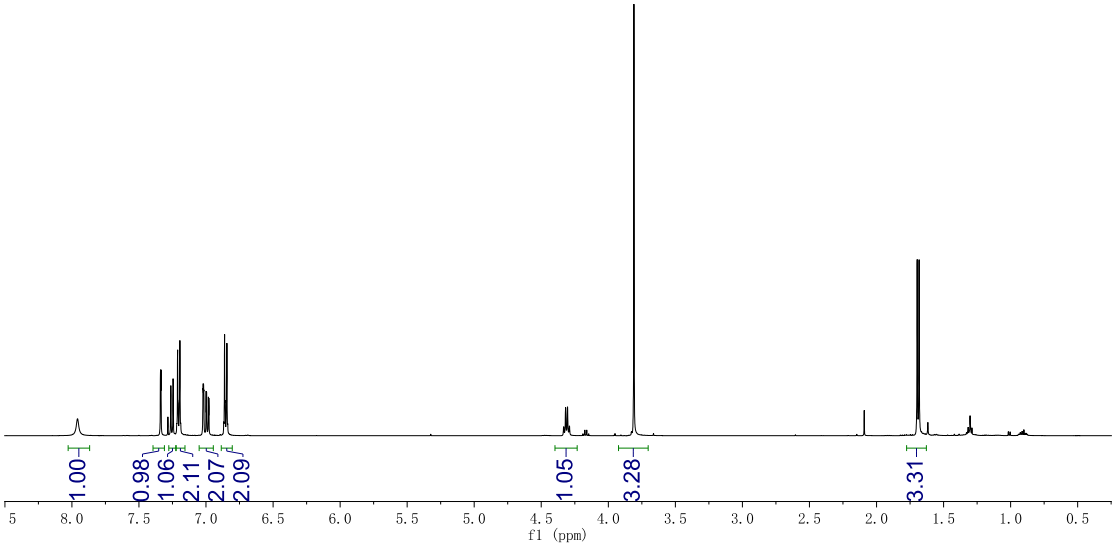
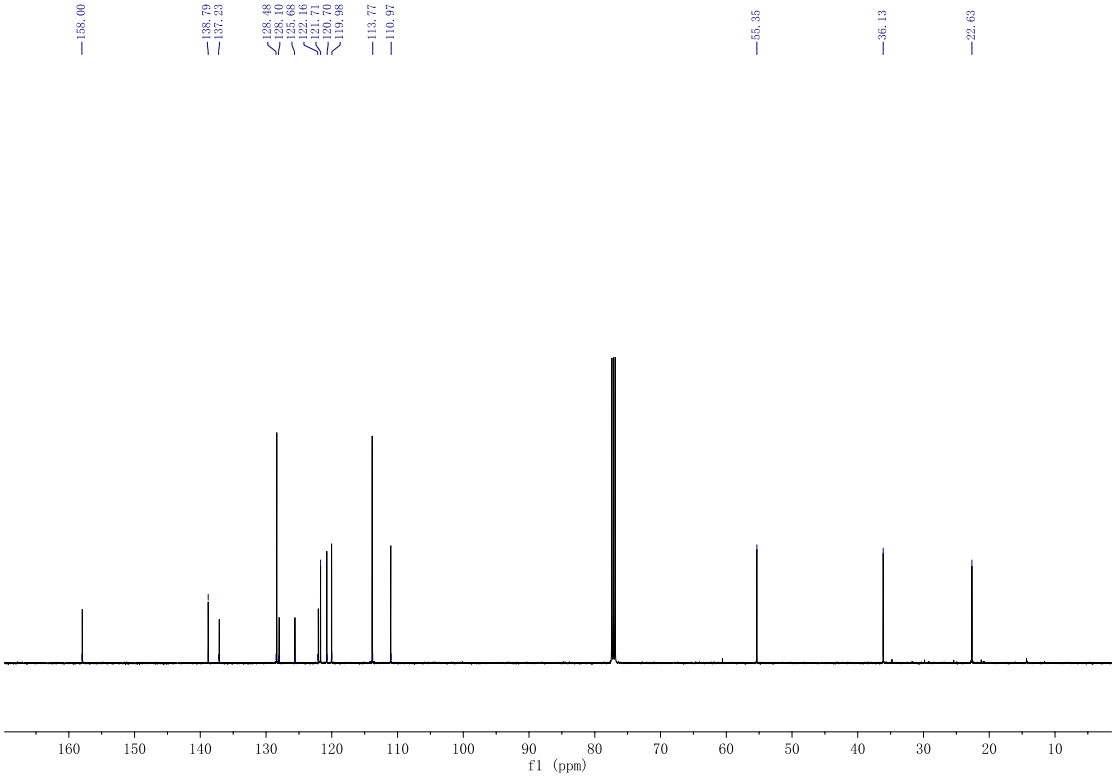
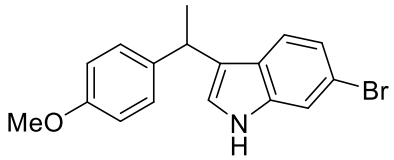


^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz



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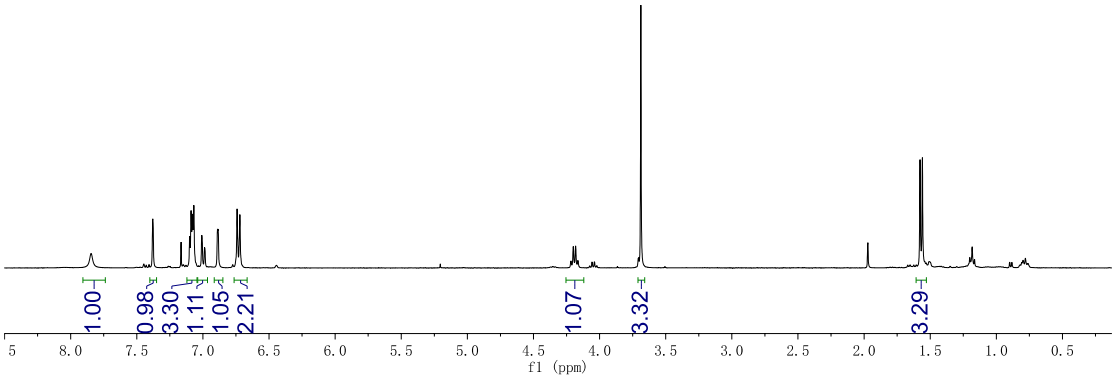
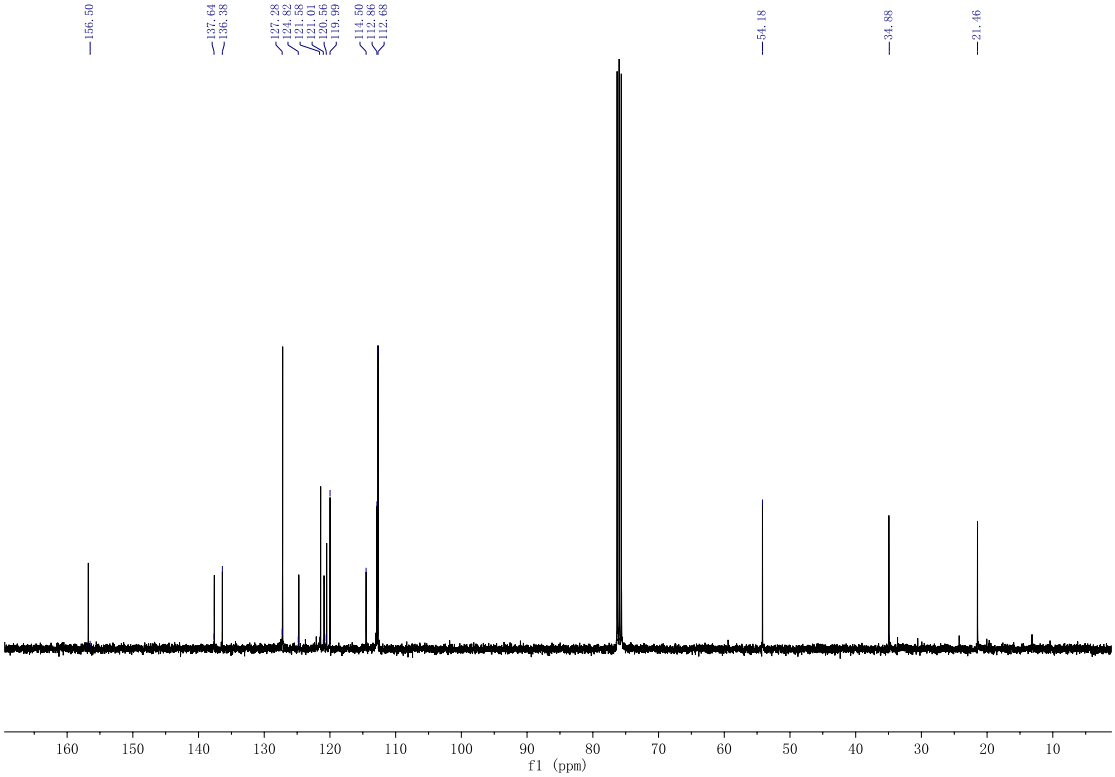
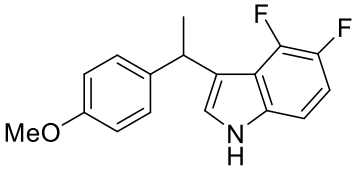


^{1}H NMR, $CDCl_3$, 400 MHz

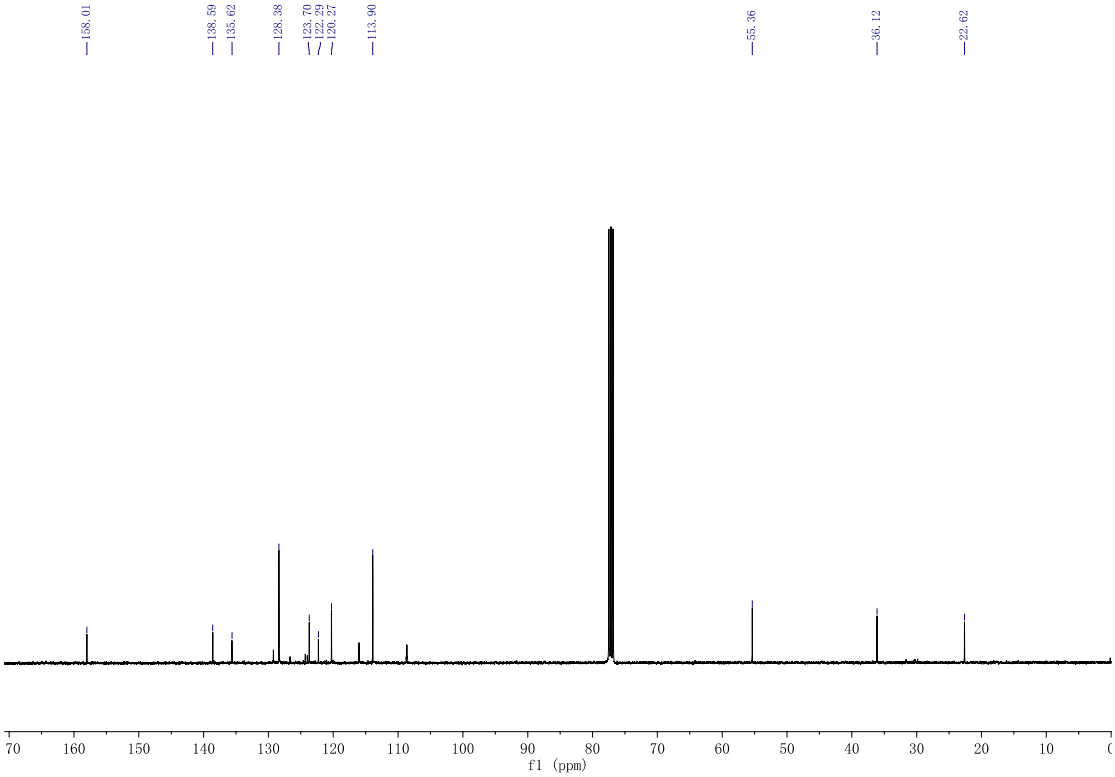


^{13}C NMR, $CDCl_3$, 101 MHz

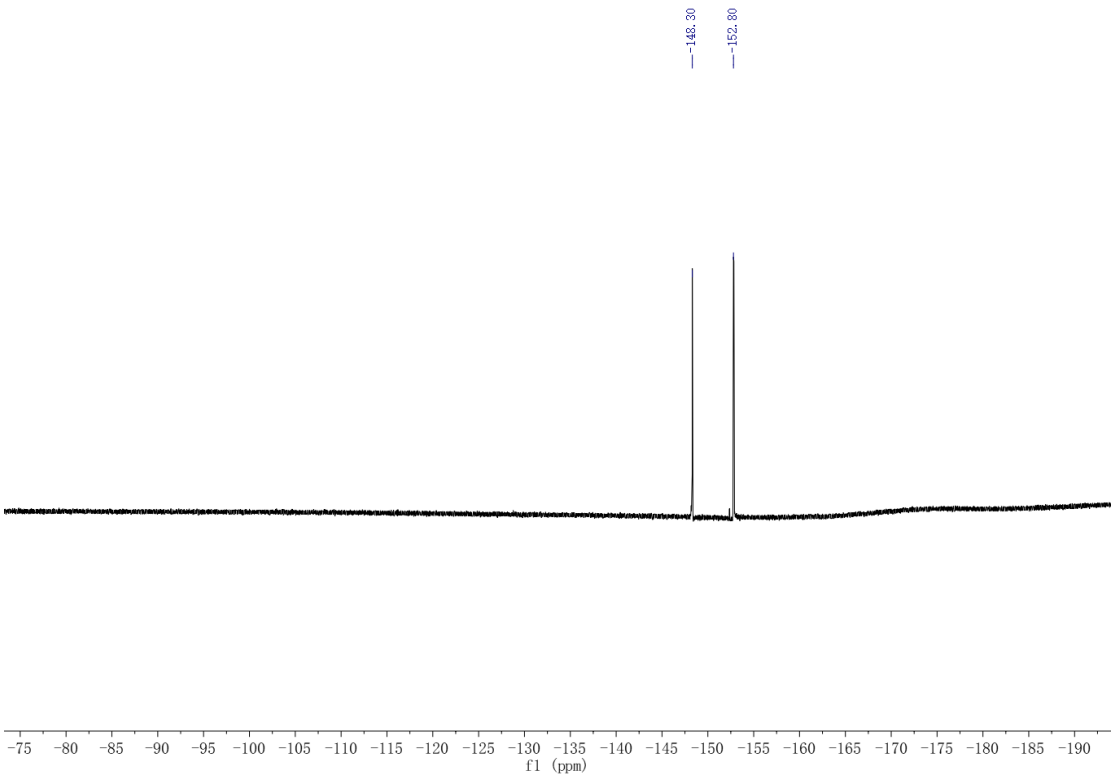


3m

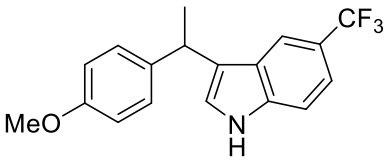
^{1}H NMR, $CDCl_3$, 400 MHz(* grease)



^{13}C NMR, $CDCl_3$, 101 MHz

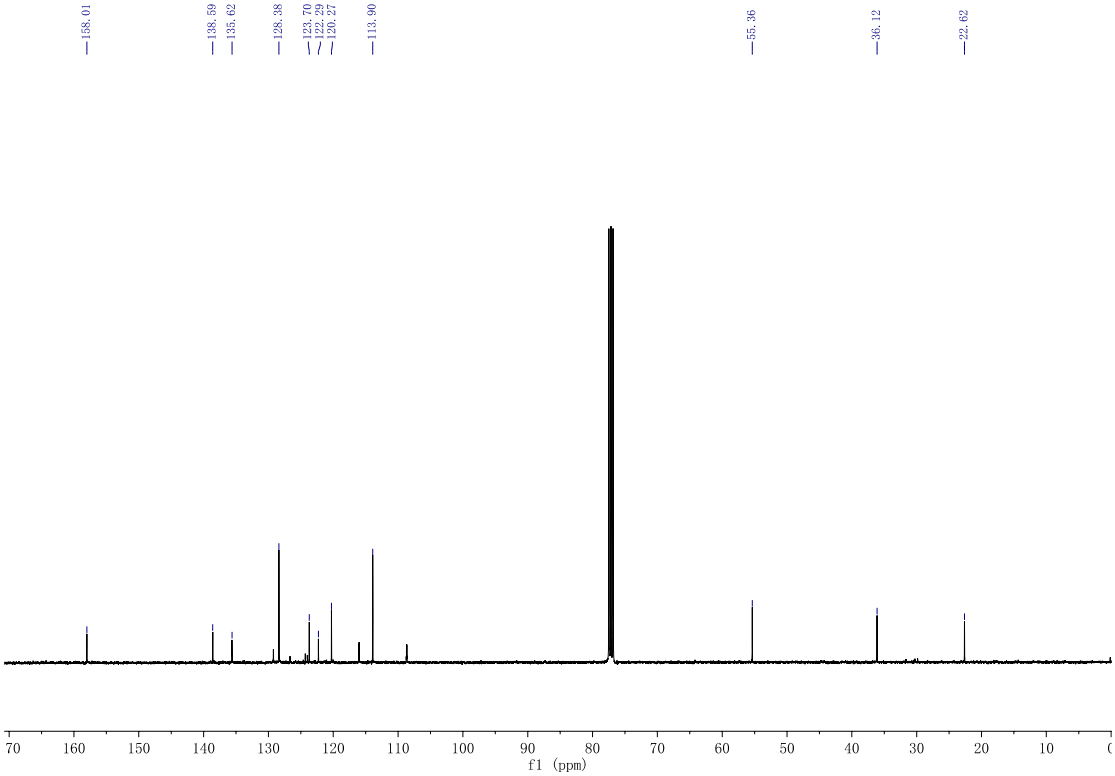


^{19}F NMR, $CDCl_3$, 471 MHz

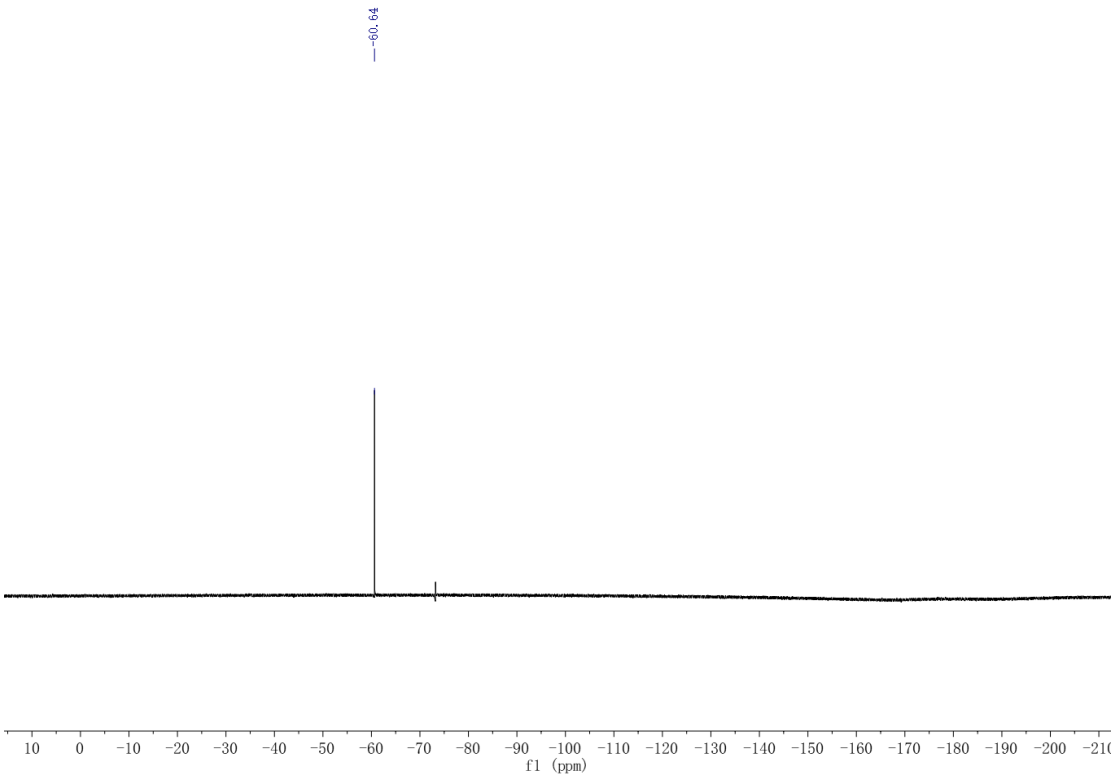


3n

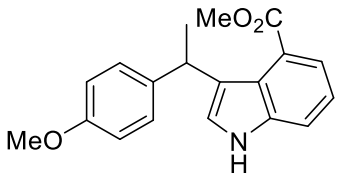
^{1}H NMR, $CDCl_3$, 400 MHz (* grease)



^{13}C NMR, $CDCl_3$, 101 MHz



^{19}F NMR, $CDCl_3$, 471 MHz



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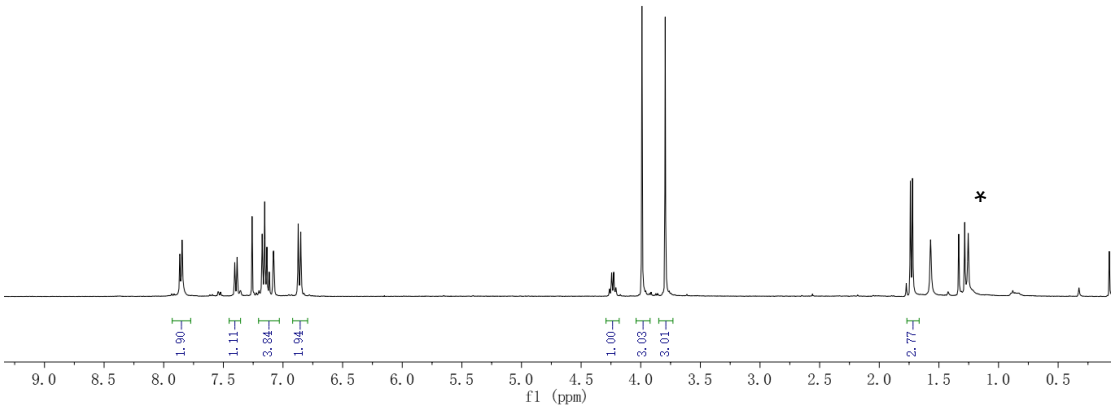
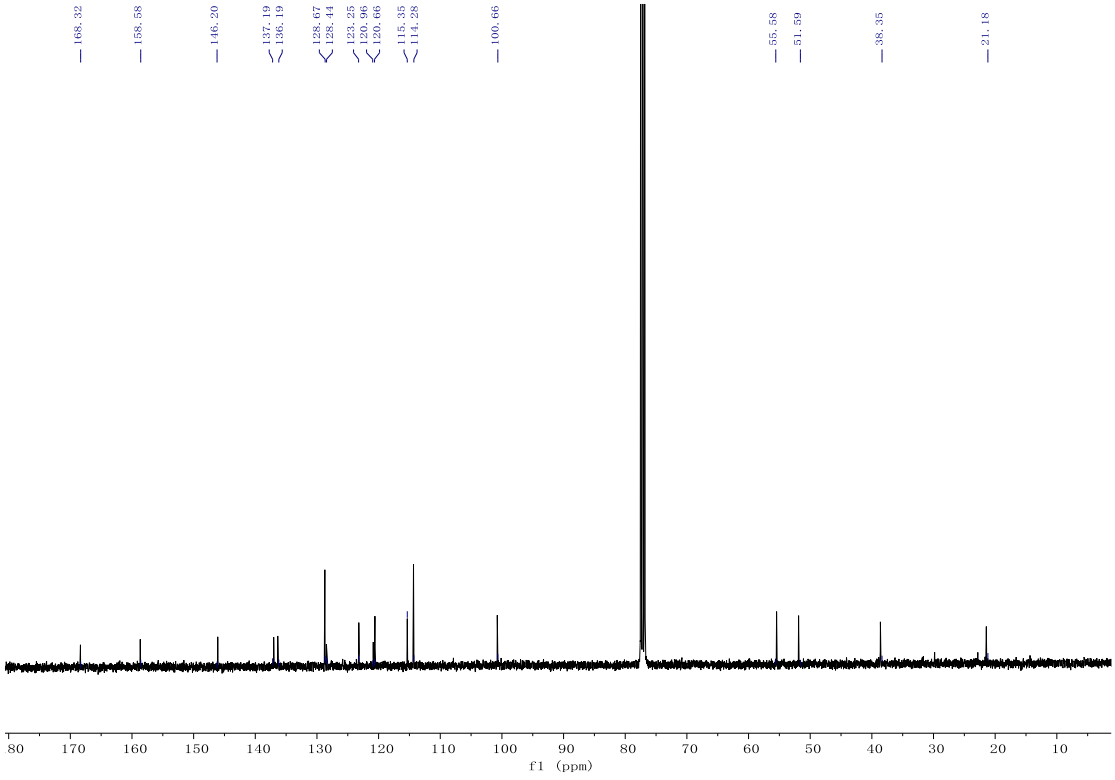
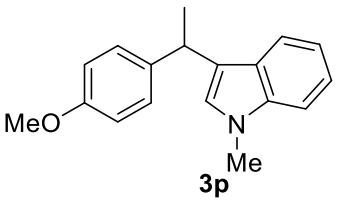


^{1}H NMR, $CDCl_3$, 400 MHz(* grease)



^{13}C NMR, $CDCl_3$, 101 MHz



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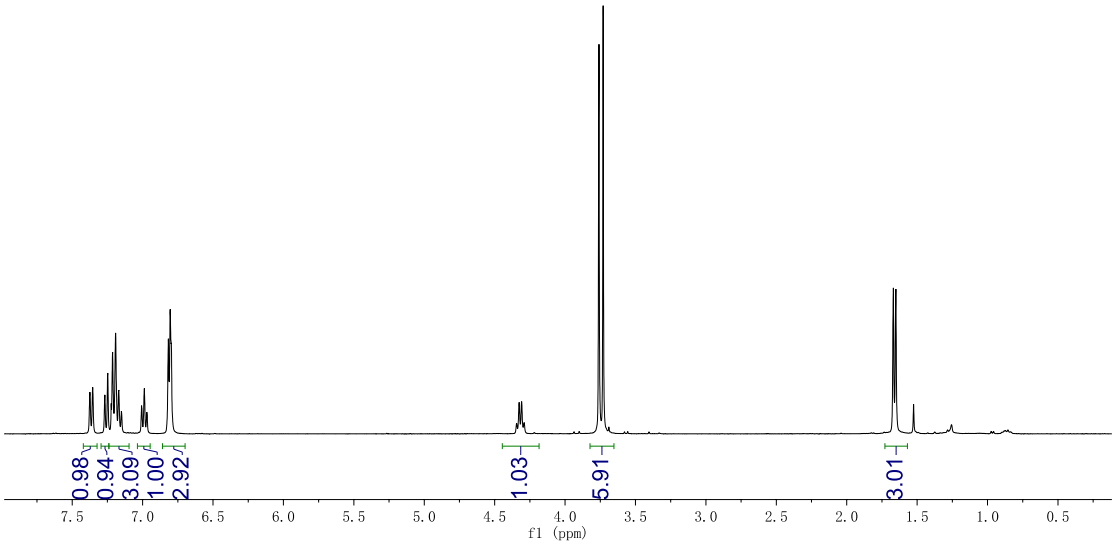
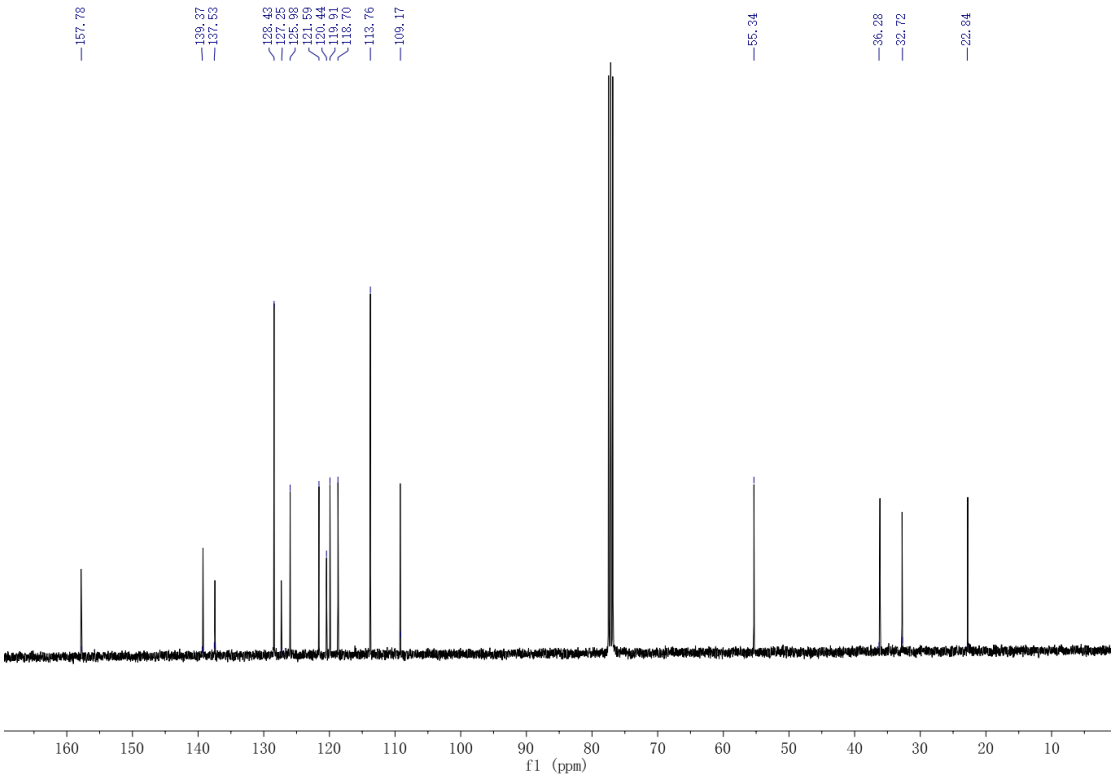
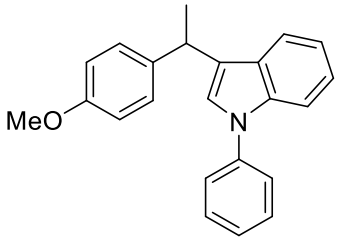


^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz



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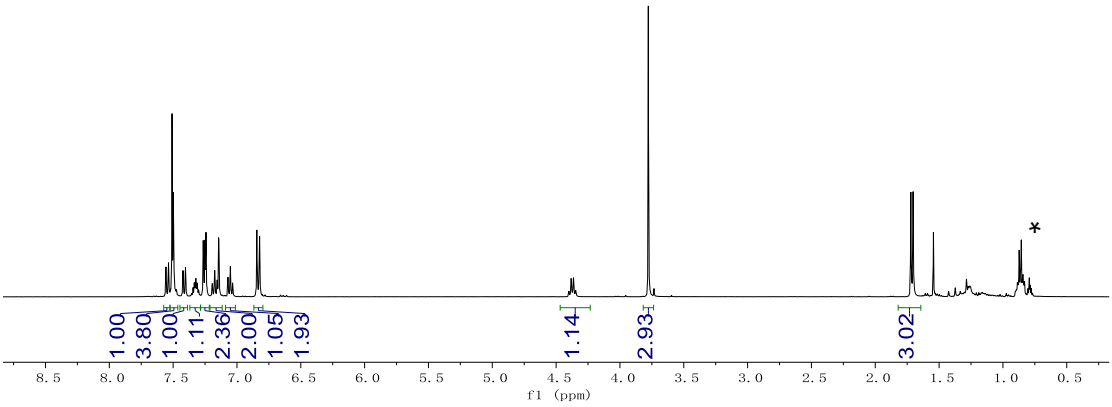
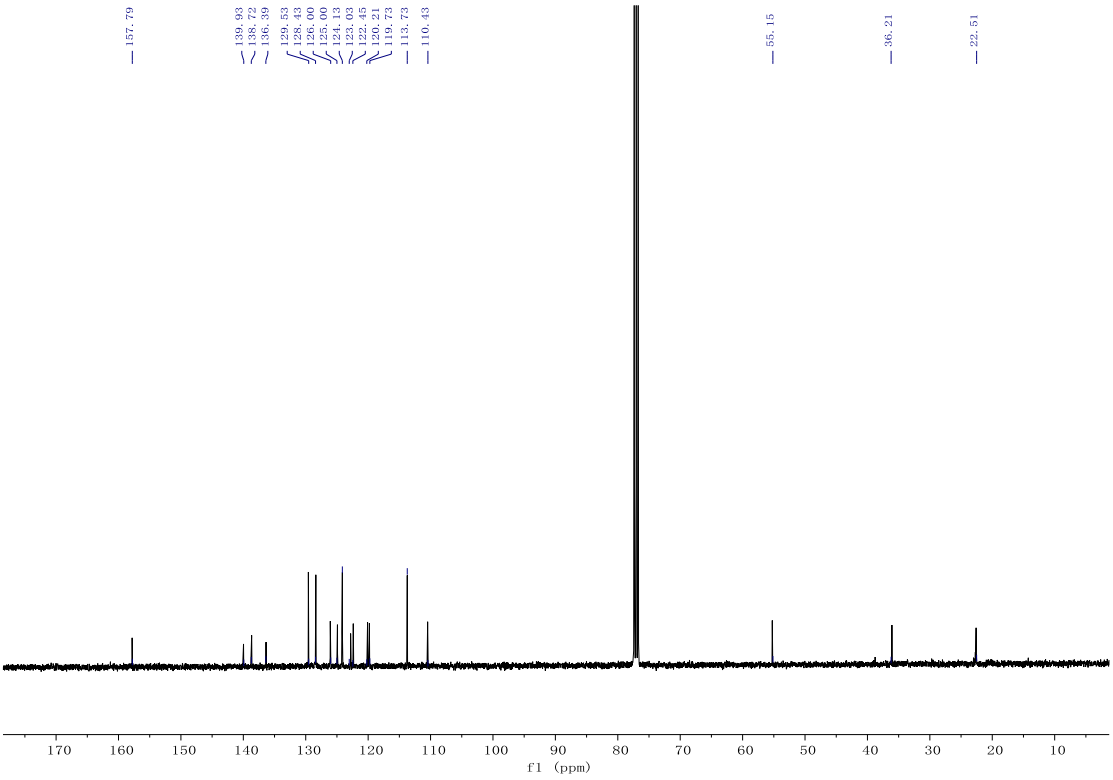
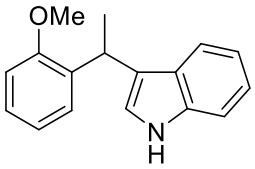


^{1}H NMR, $CDCl_3$, 400 MHz(* grease)



^{13}C NMR, $CDCl_3$, 101 MHz



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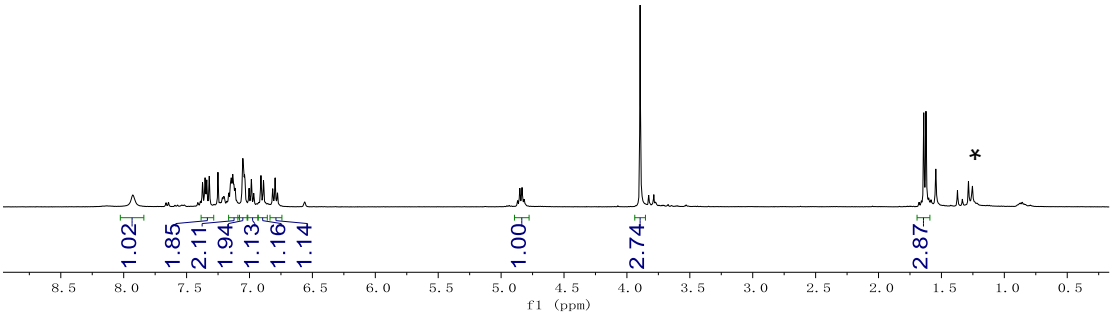
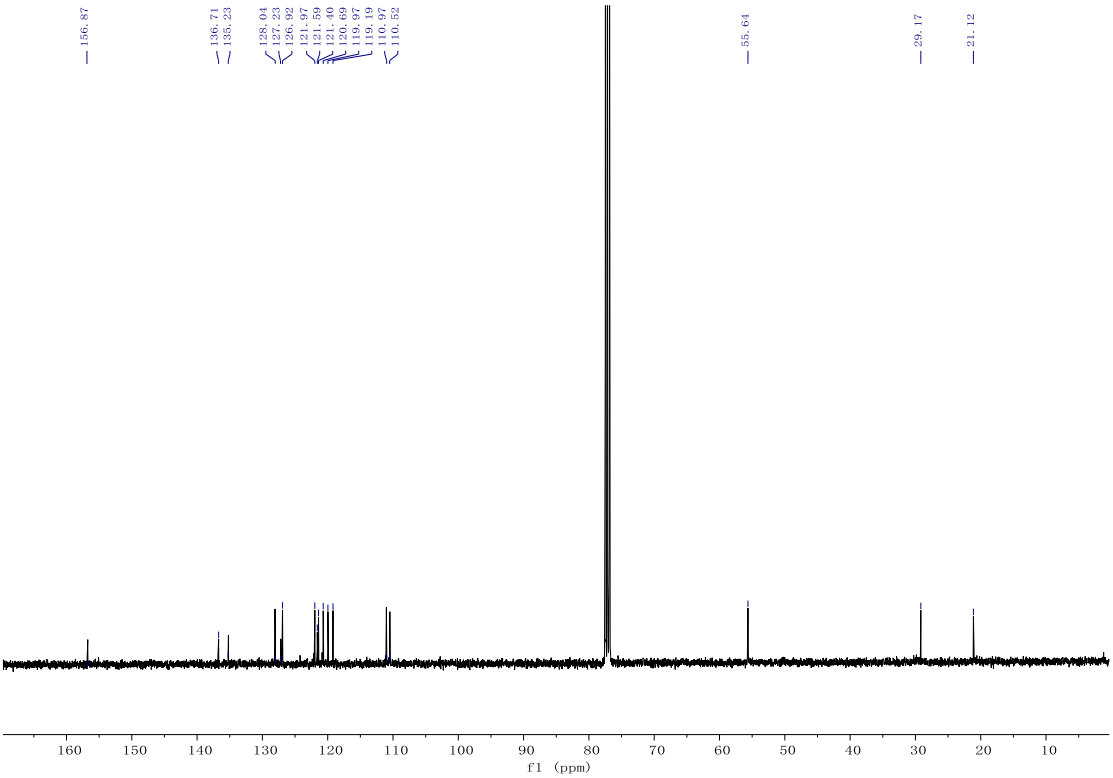
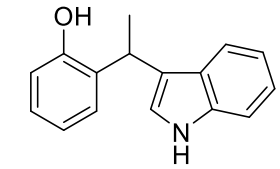


^{1}H NMR, $CDCl_3$, 400 MHz(* grease)

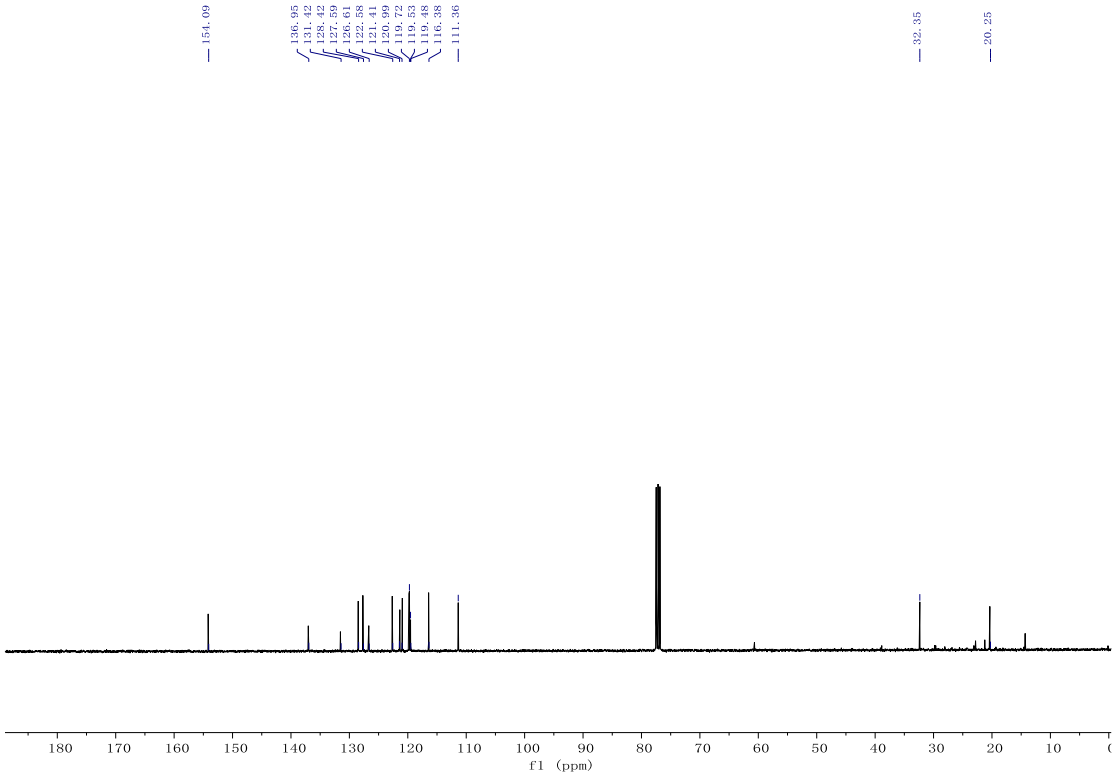


^{13}C NMR, $CDCl_3$, 101 MHz

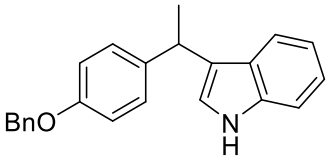


3s

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



^{13}C NMR, $CDCl_3$, 101 MHz



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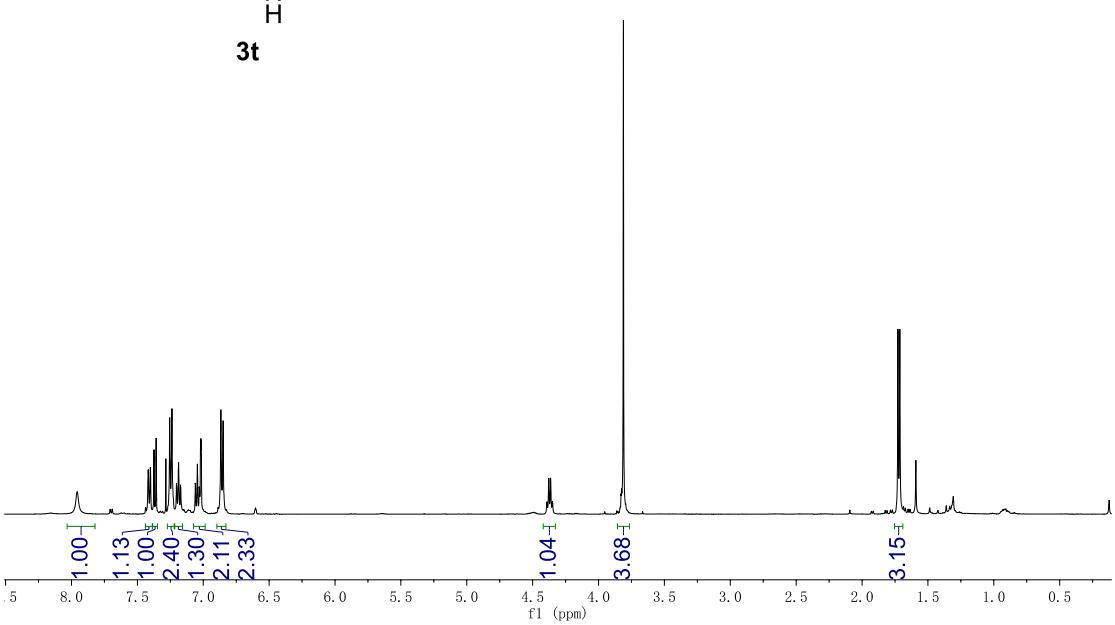
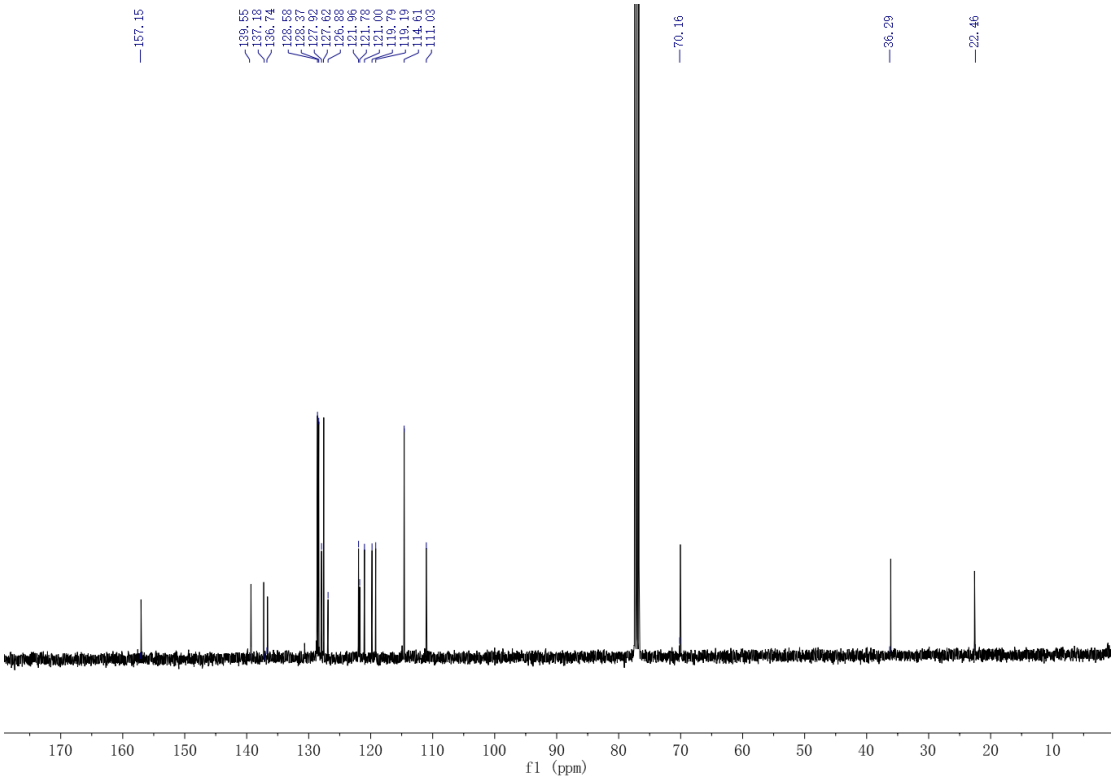
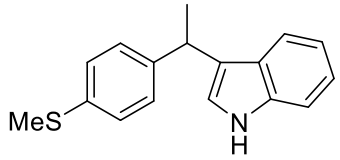


^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz



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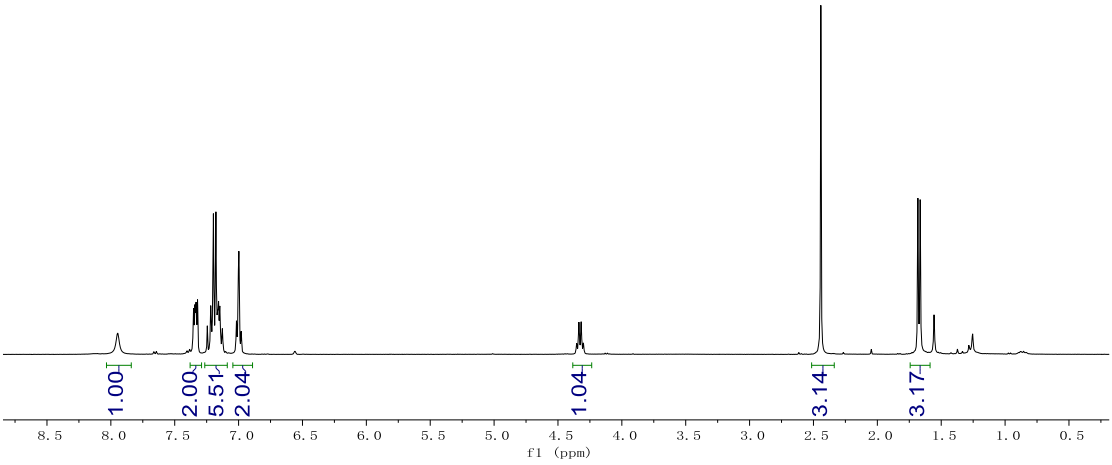
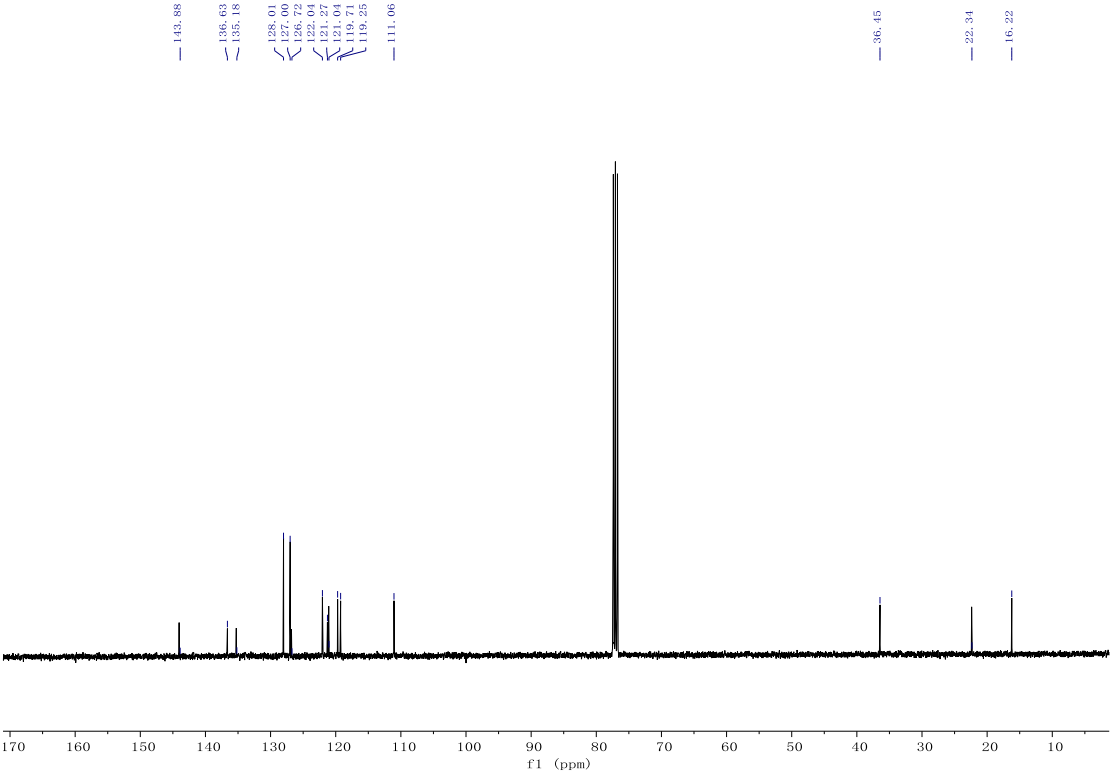
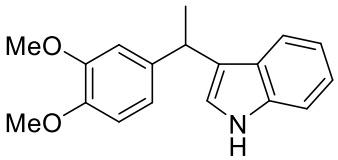


^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz



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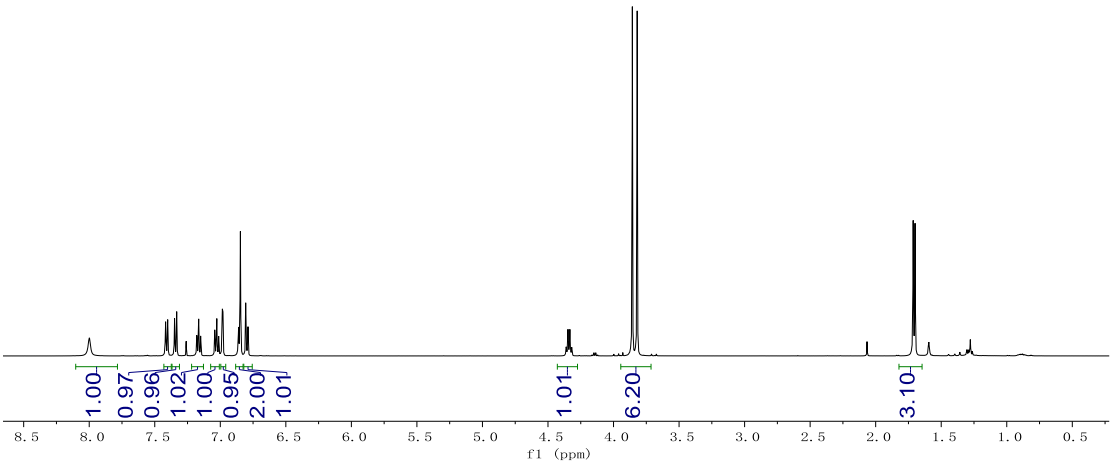
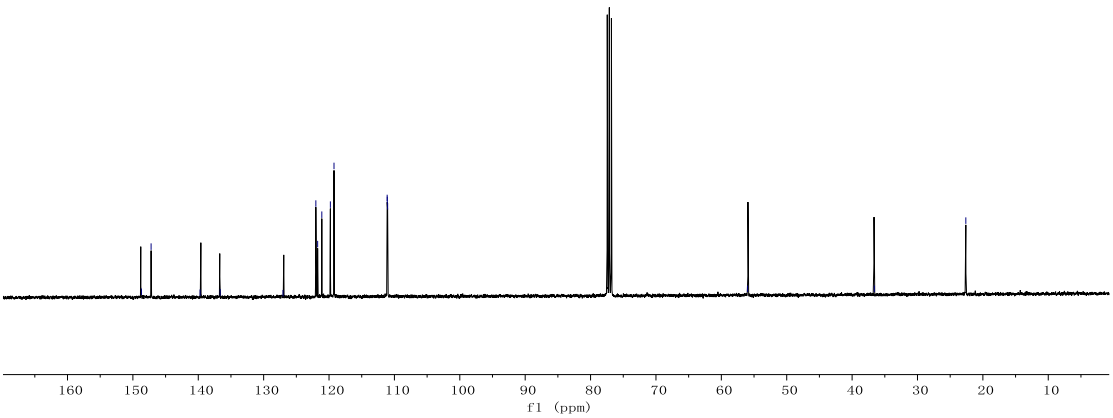
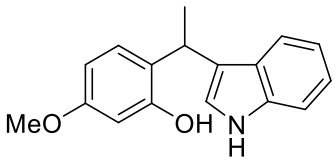


^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz



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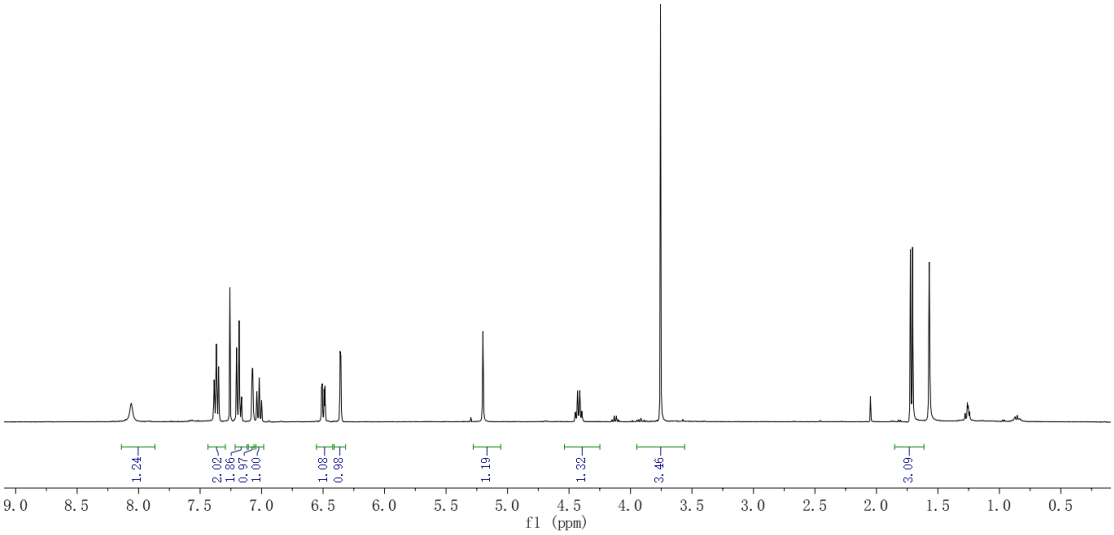
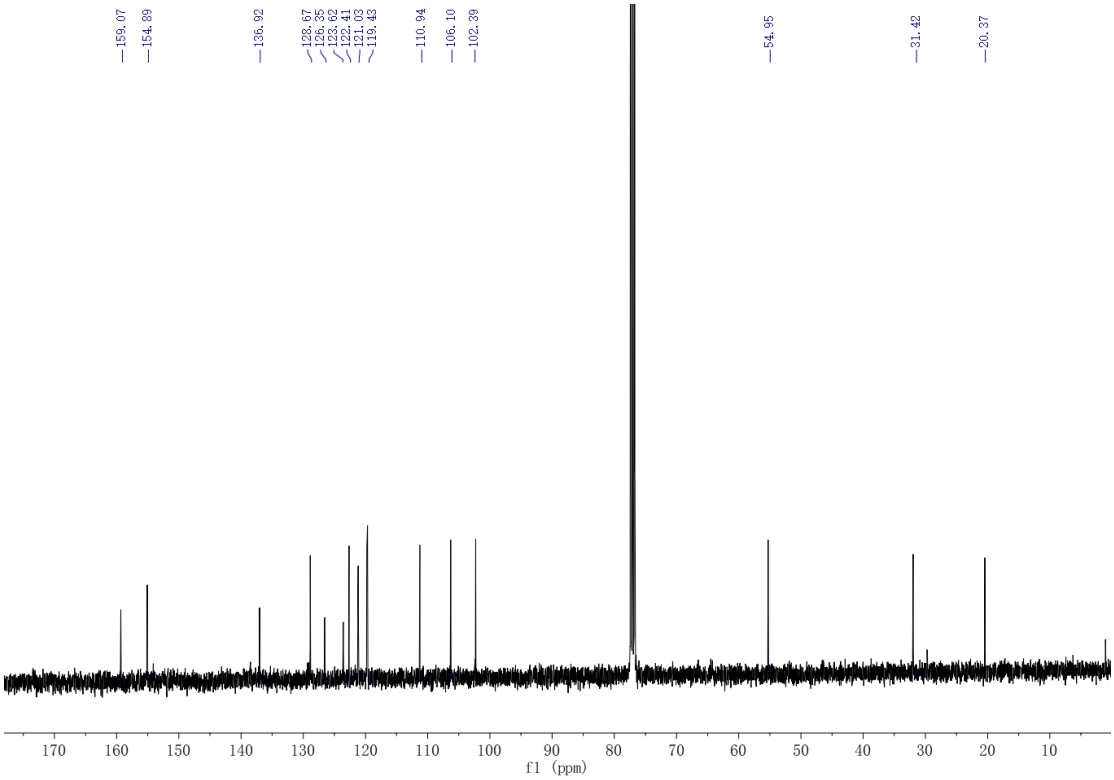
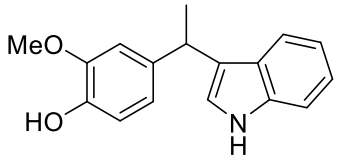


^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz



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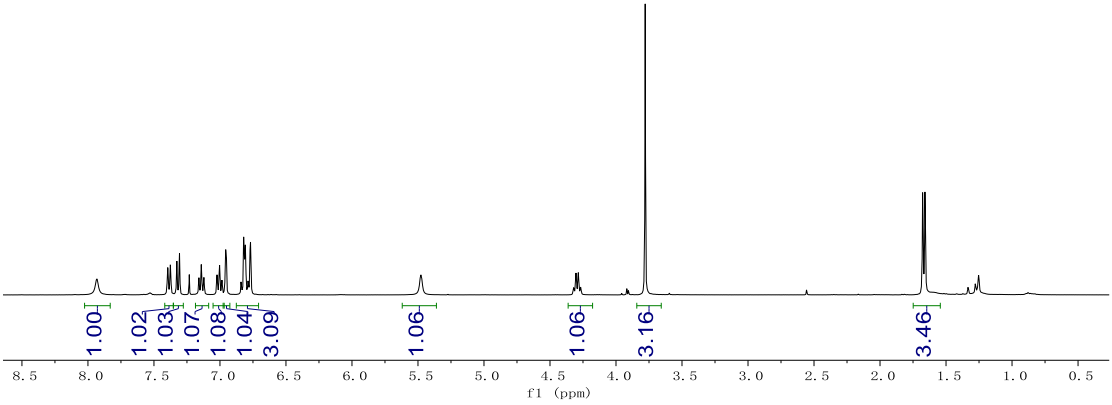
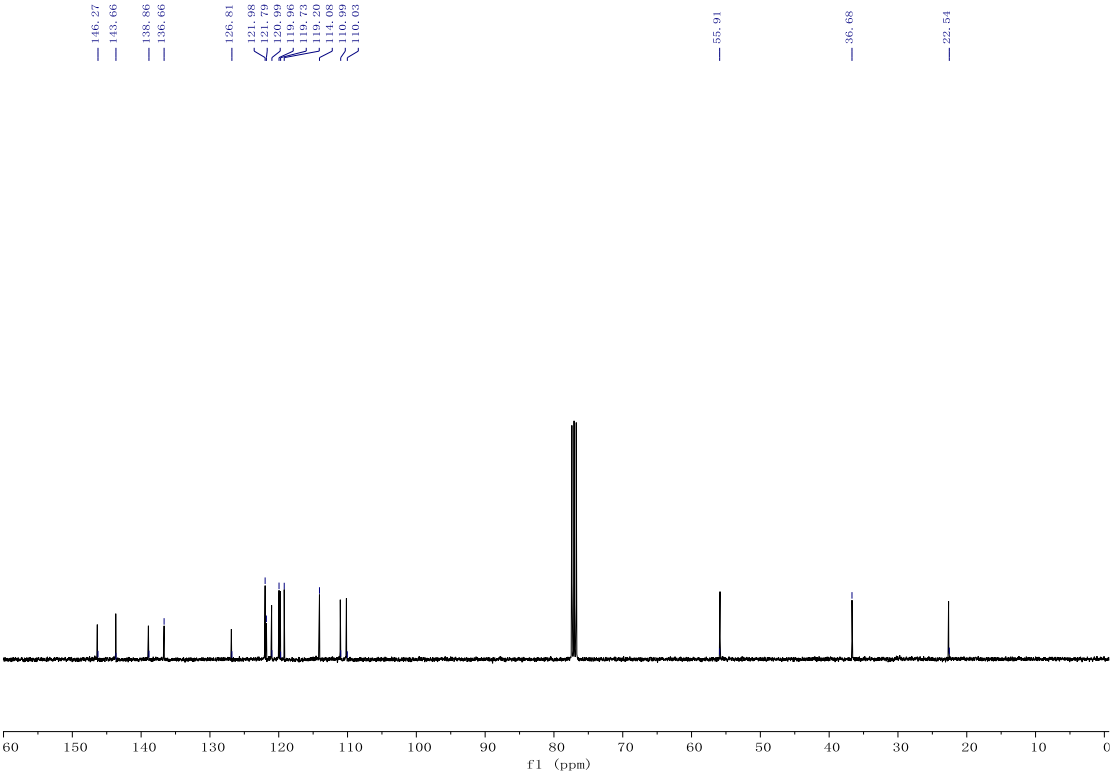
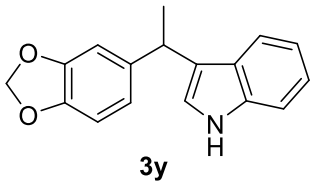


^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz



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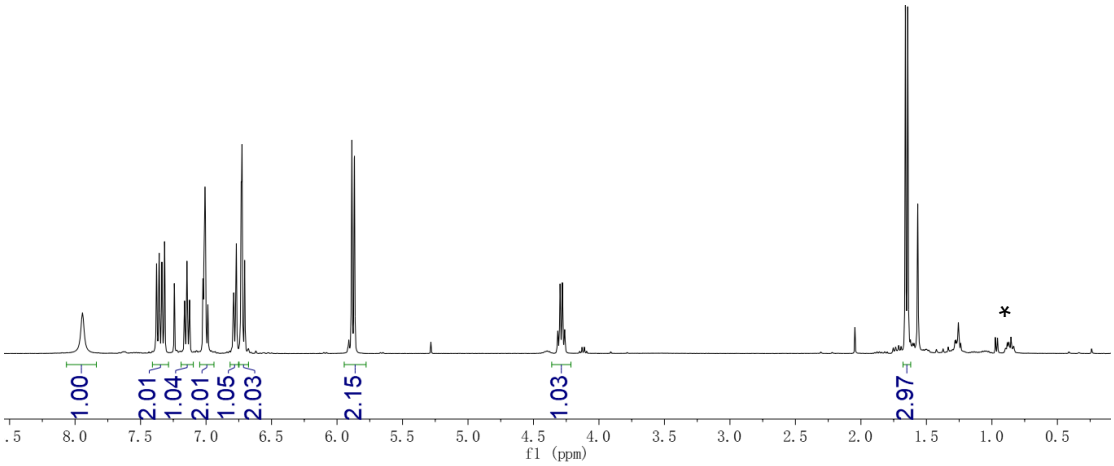
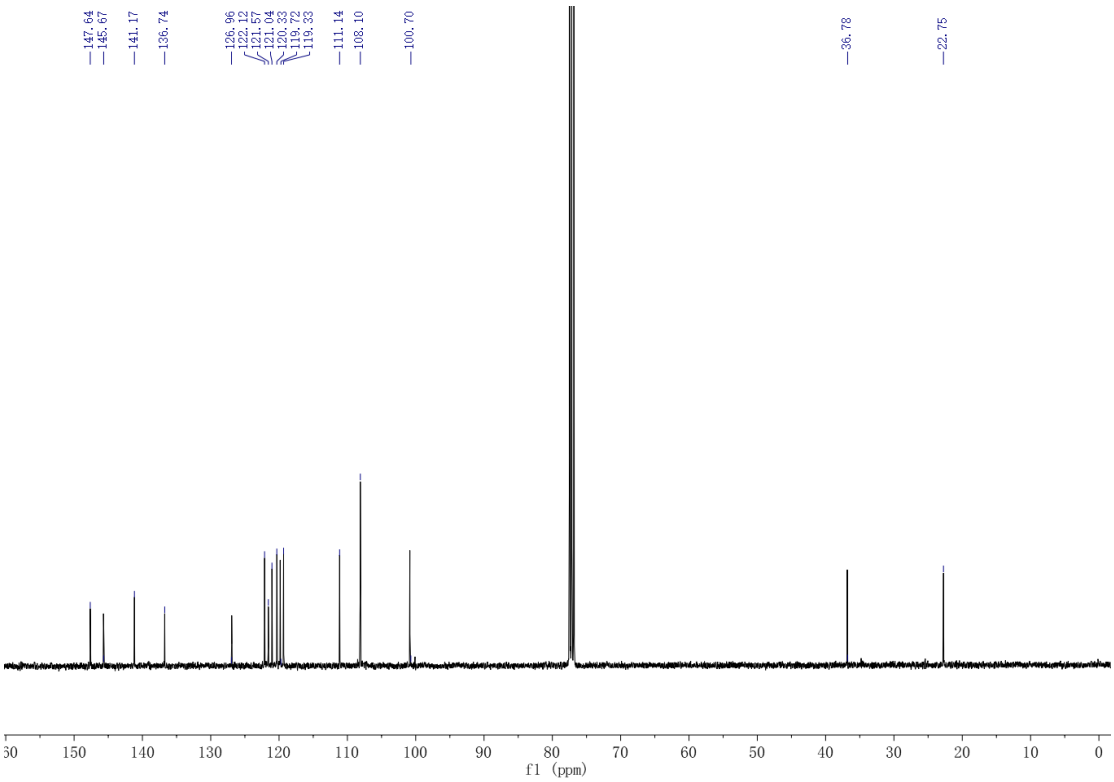
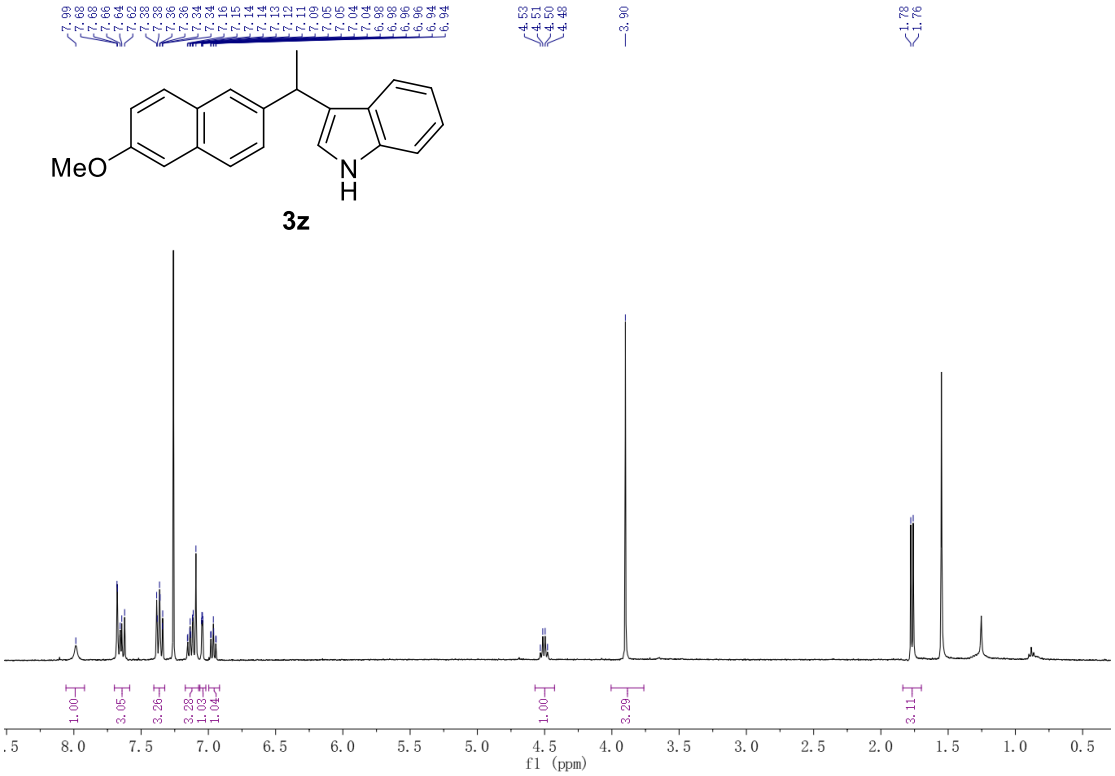


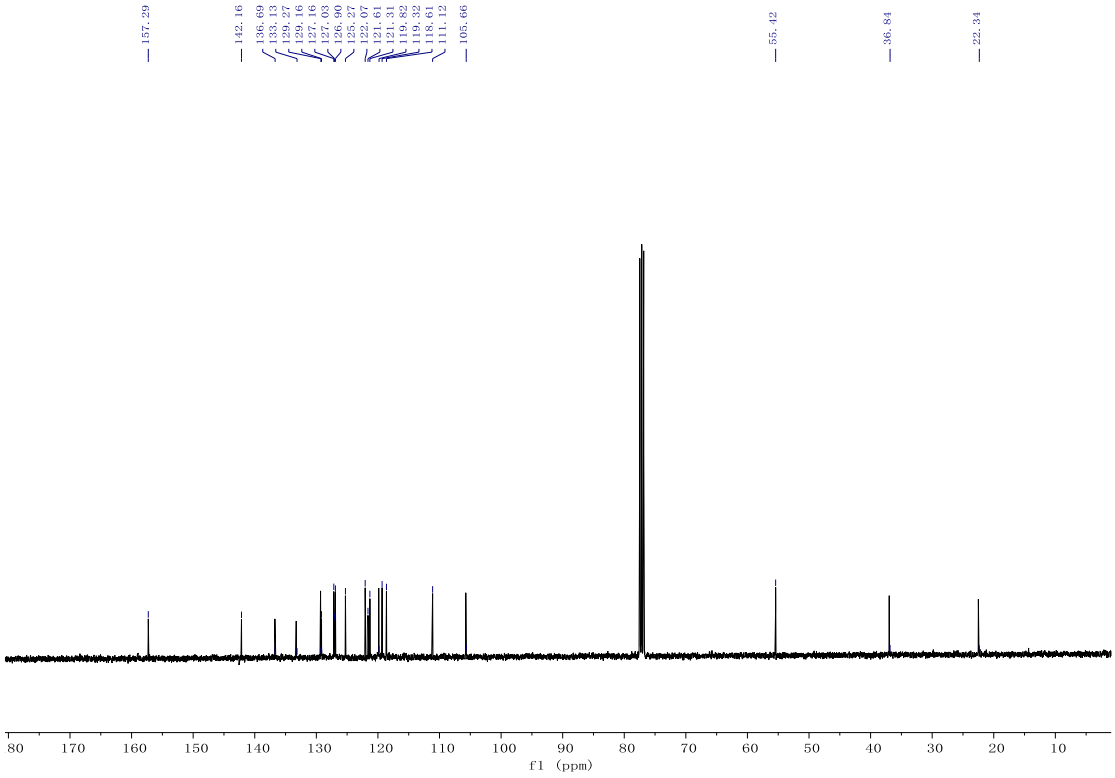
^{1}H NMR, $CDCl_3$, 400 MHz(* grease)



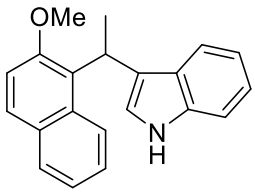
^{13}C NMR, $CDCl_3$, 101 MHz



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



^{13}C NMR, $CDCl_3$, 101 MHz



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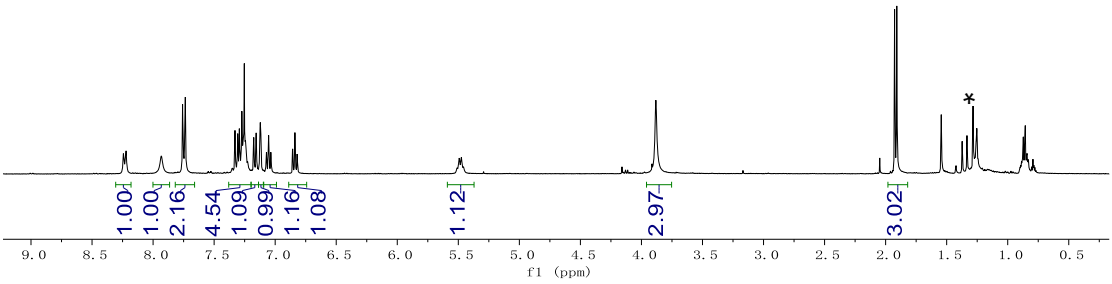
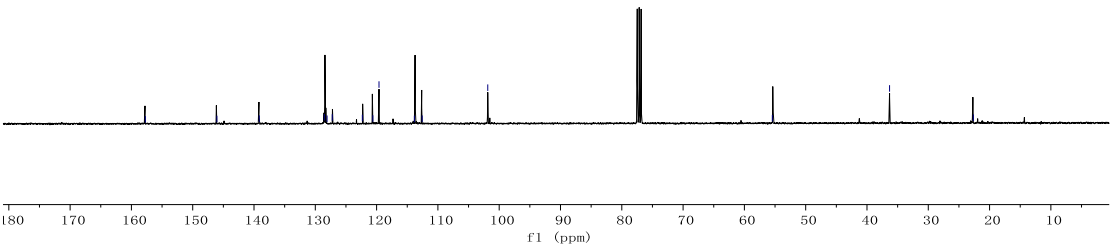
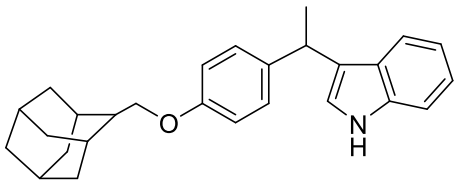


^{1}H NMR, $CDCl_3$, 400 MHz (*grease)



^{13}C NMR, $CDCl_3$, 101 MHz



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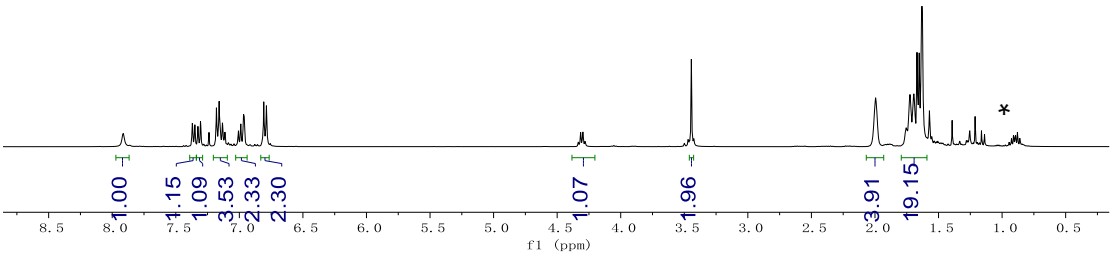
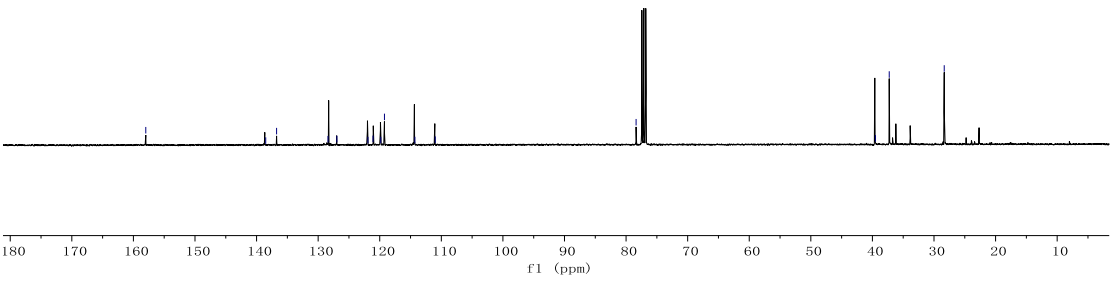
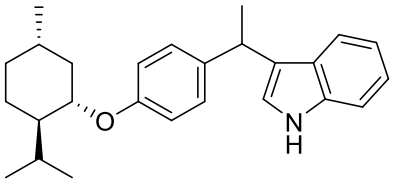


^{1}H NMR, $CDCl_3$, 400 MHz (*grease)



^{13}C NMR, $CDCl_3$, 101 MHz



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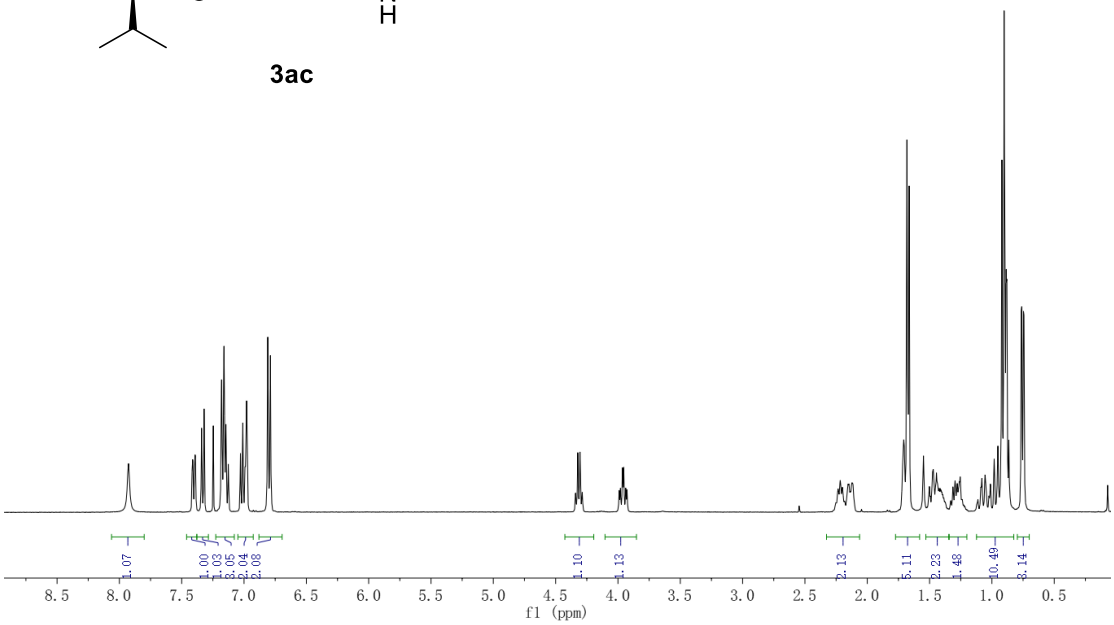
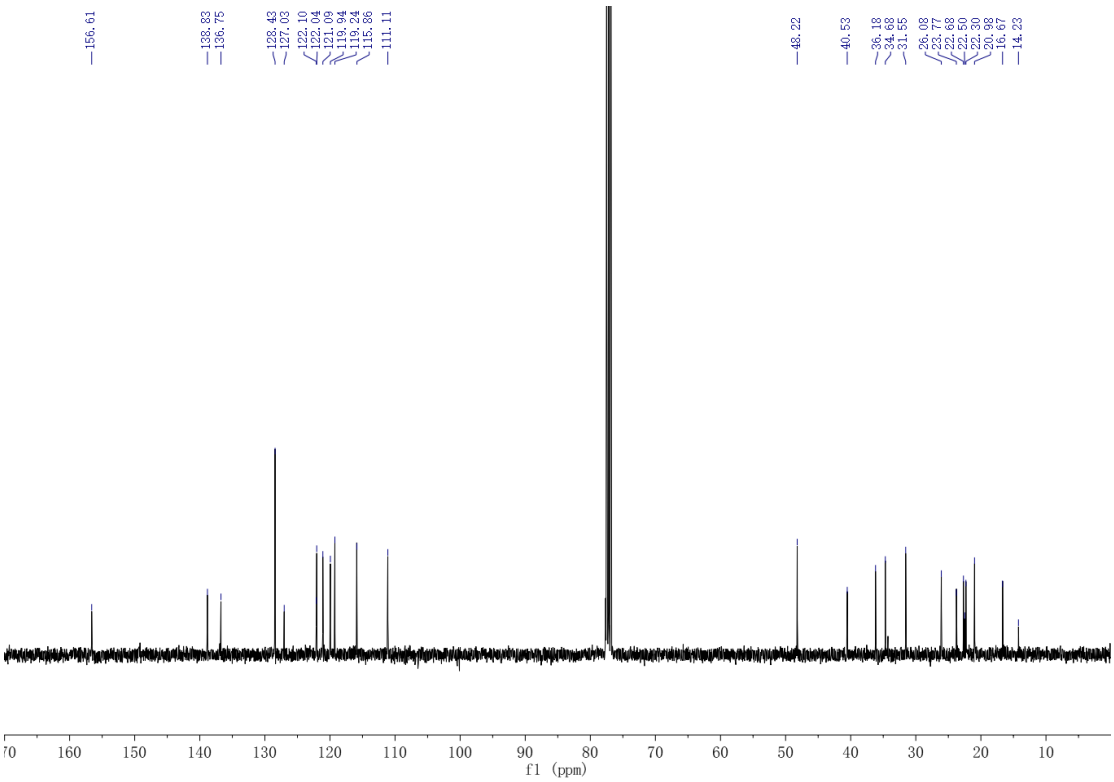
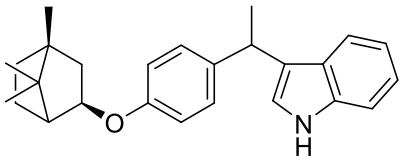


^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz



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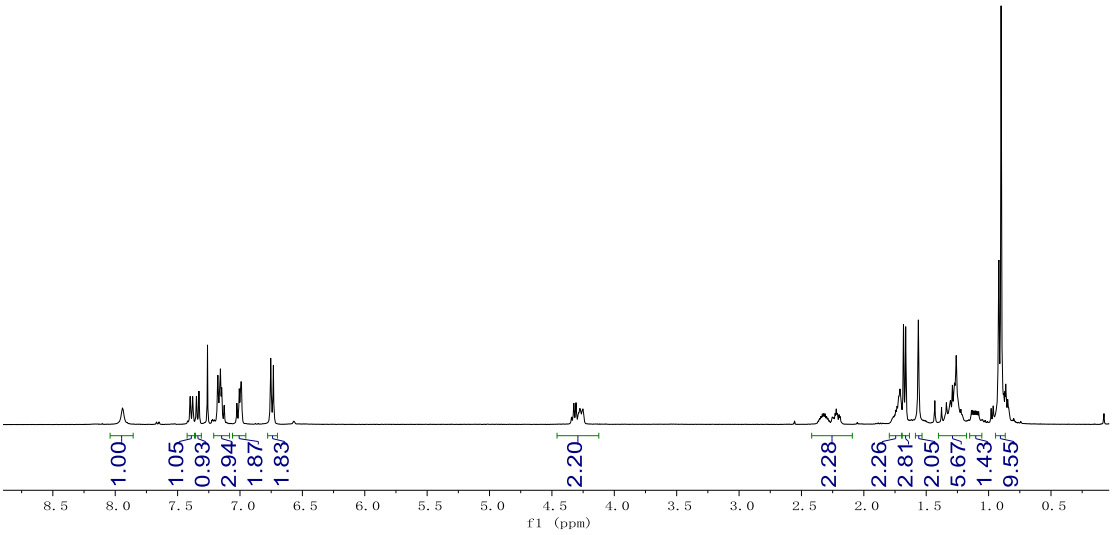
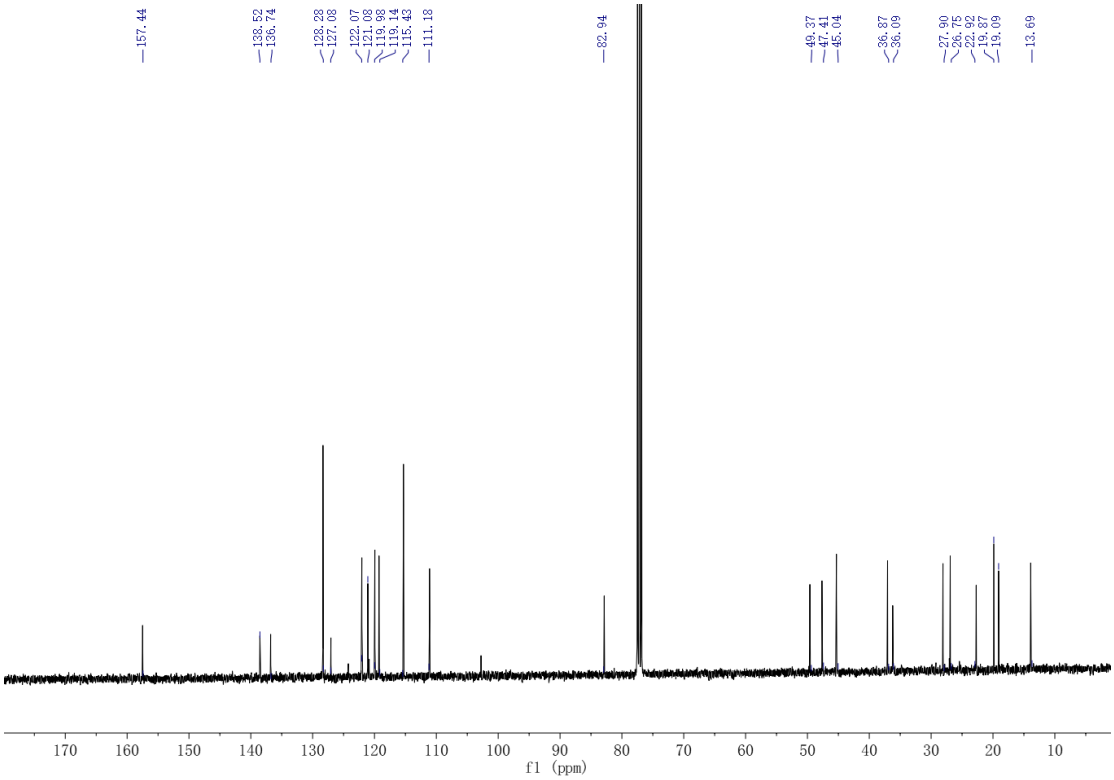
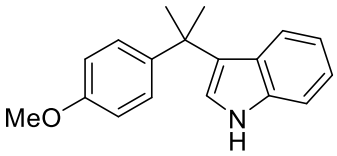


^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz



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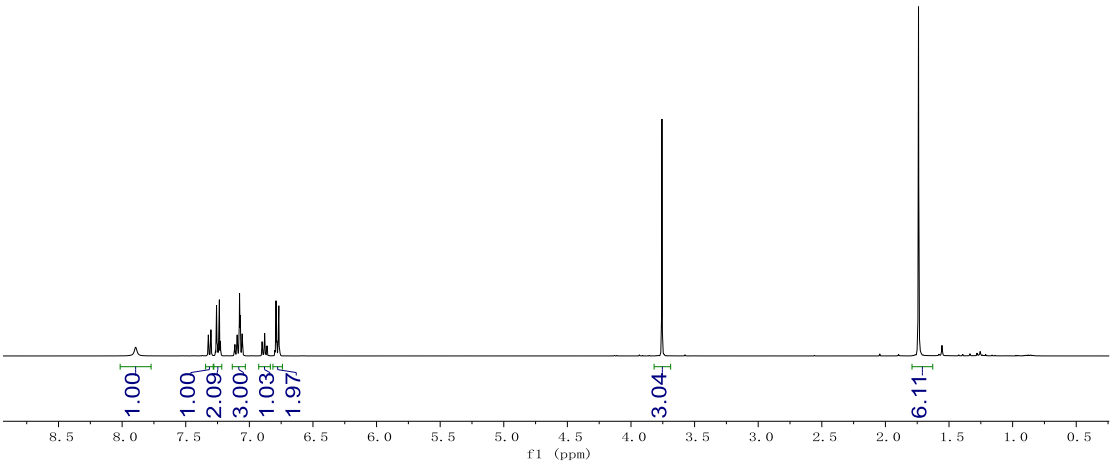
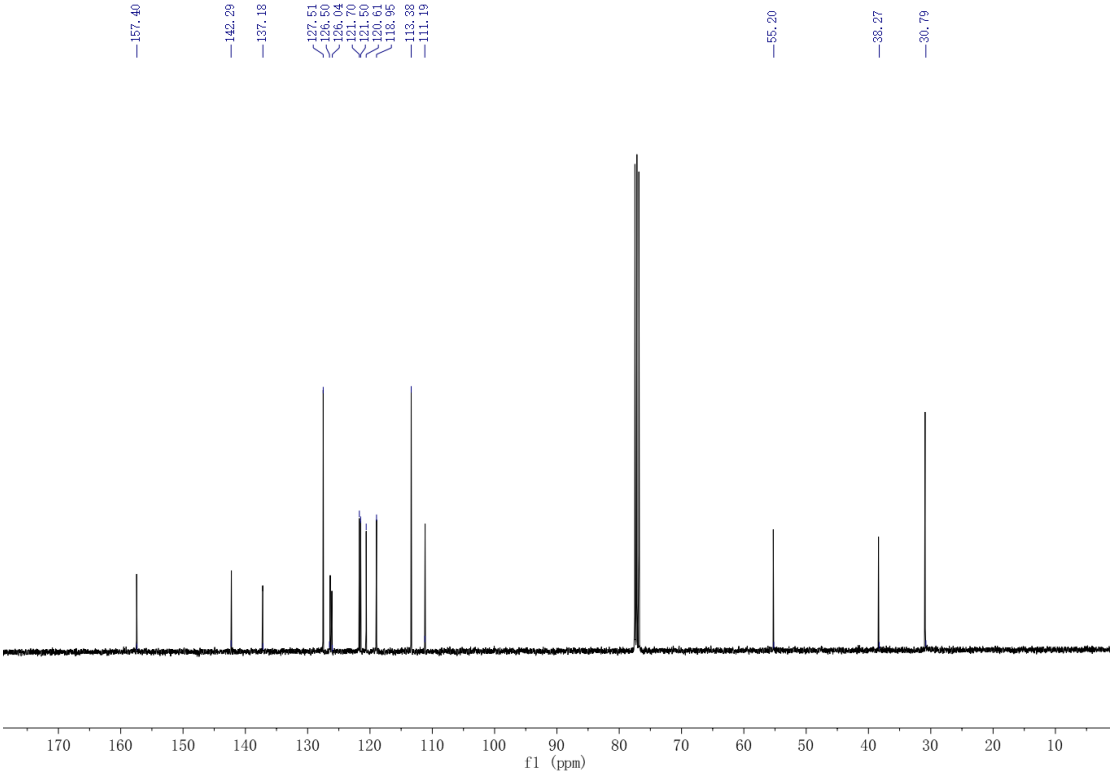
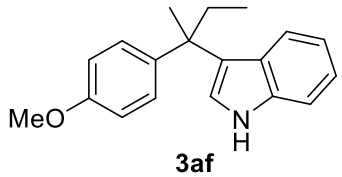


^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz



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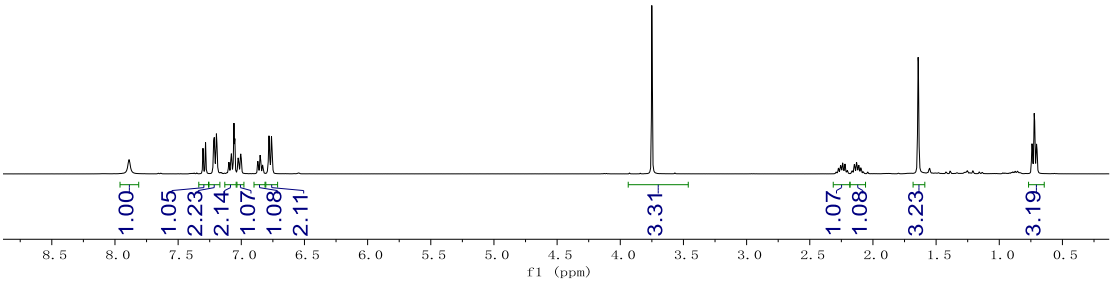
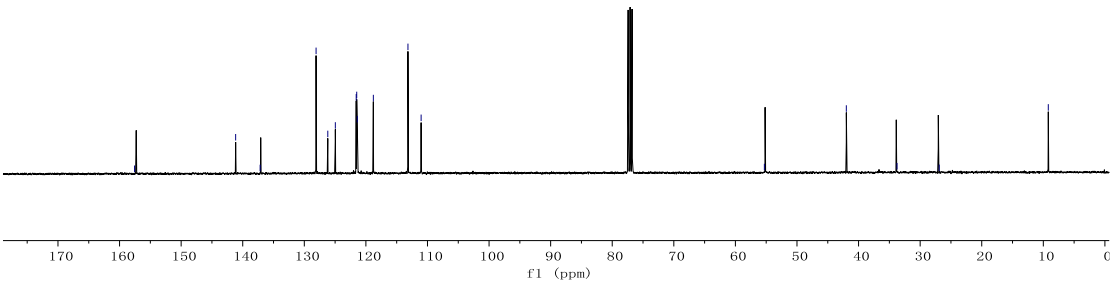
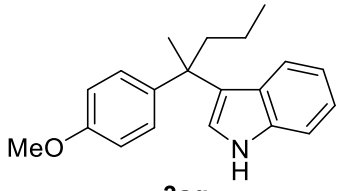


^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz



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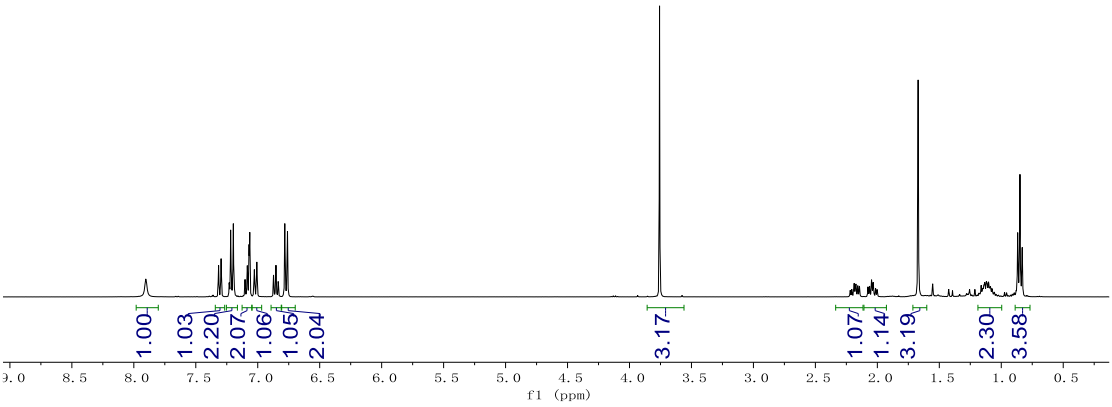
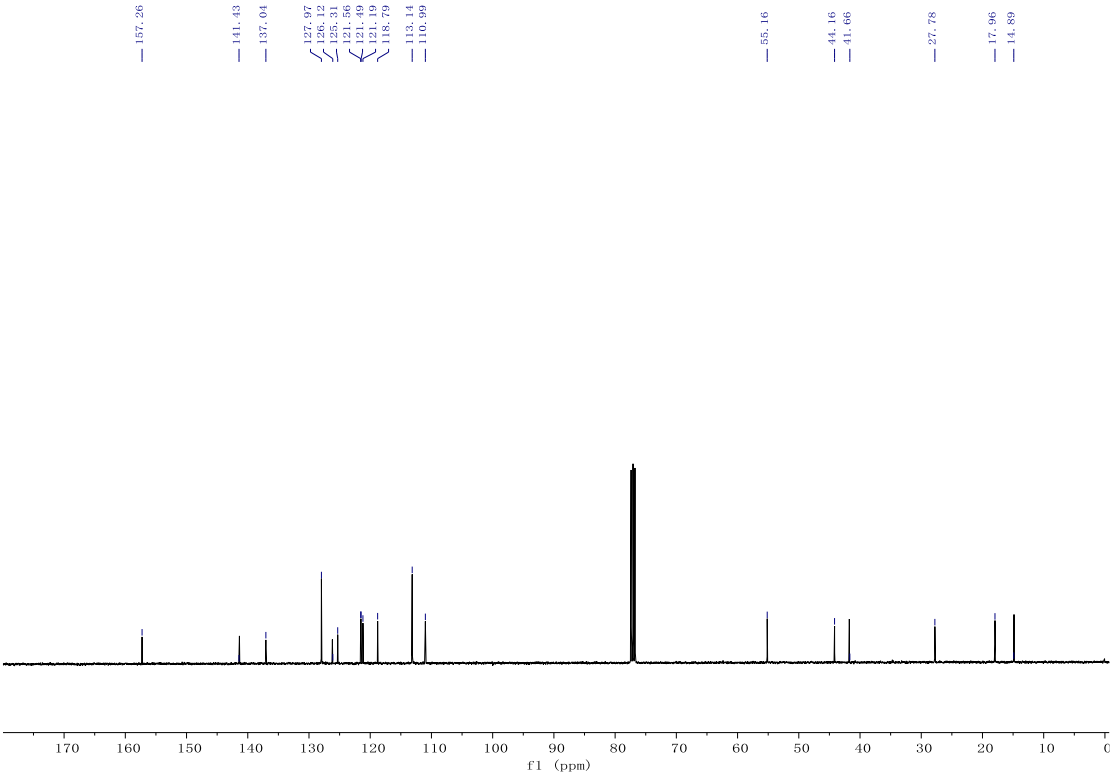
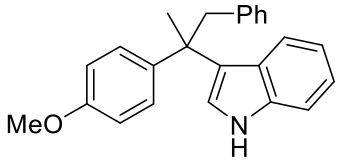


^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz



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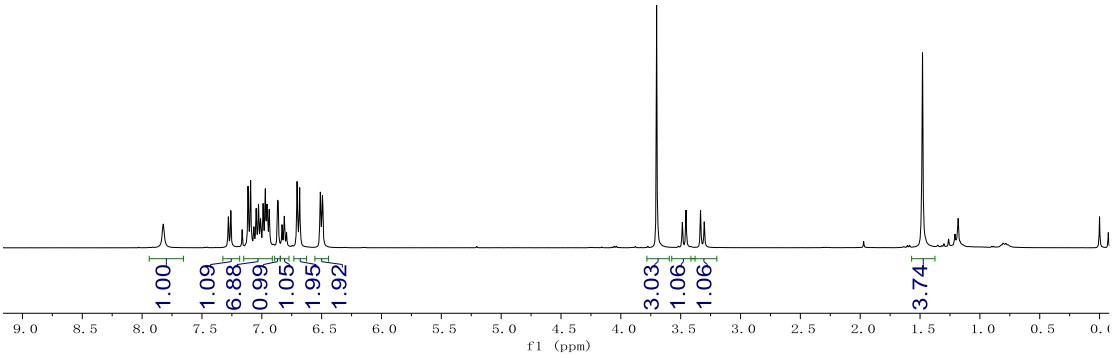
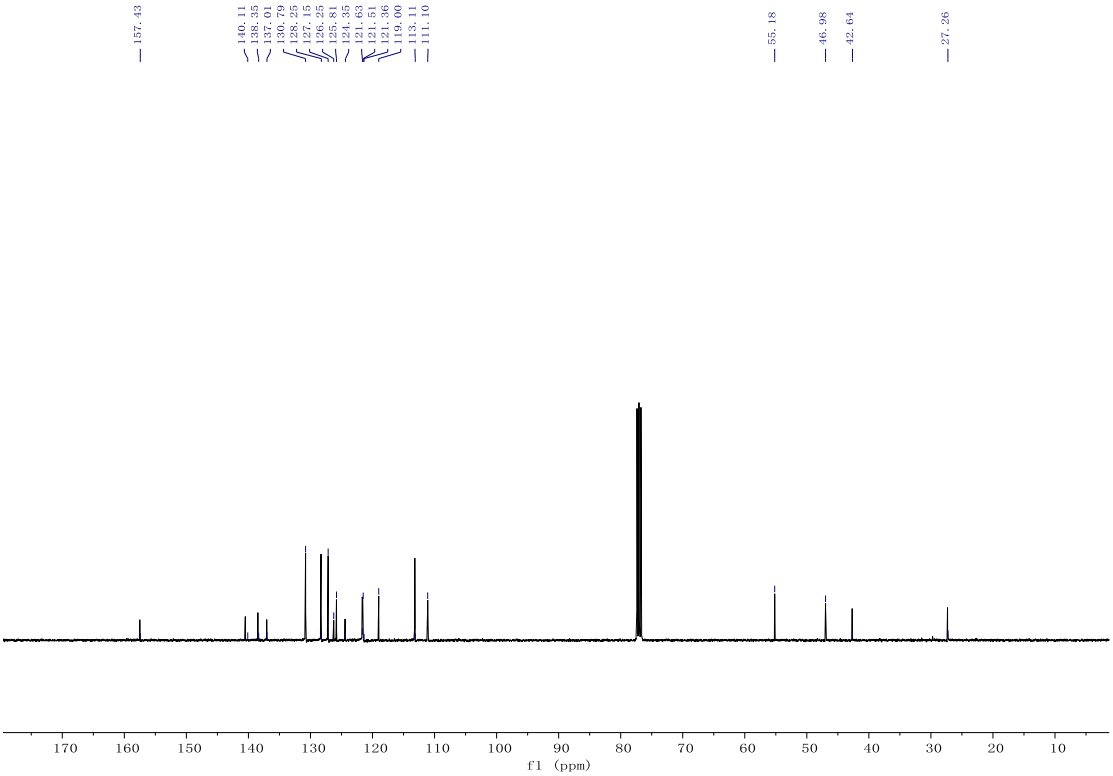
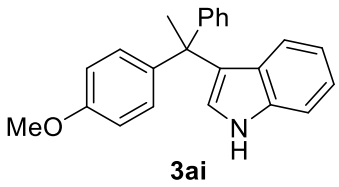


^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz



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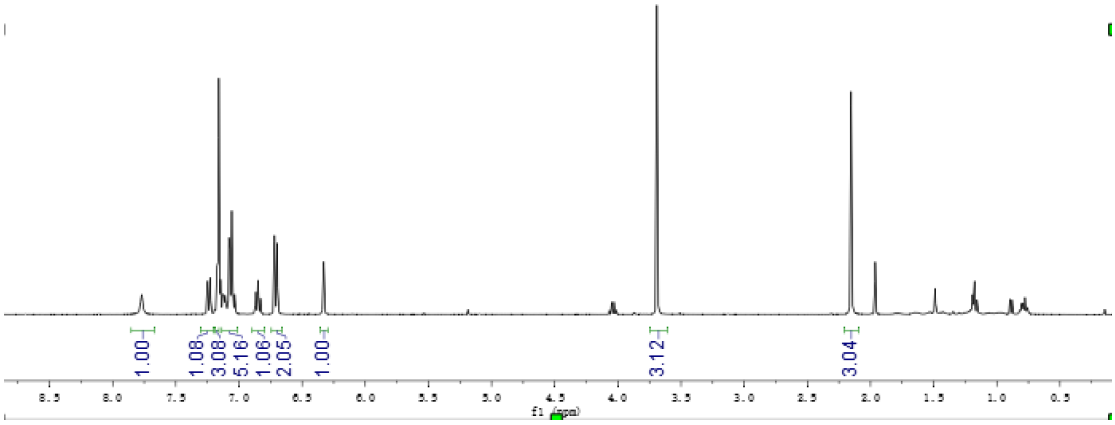
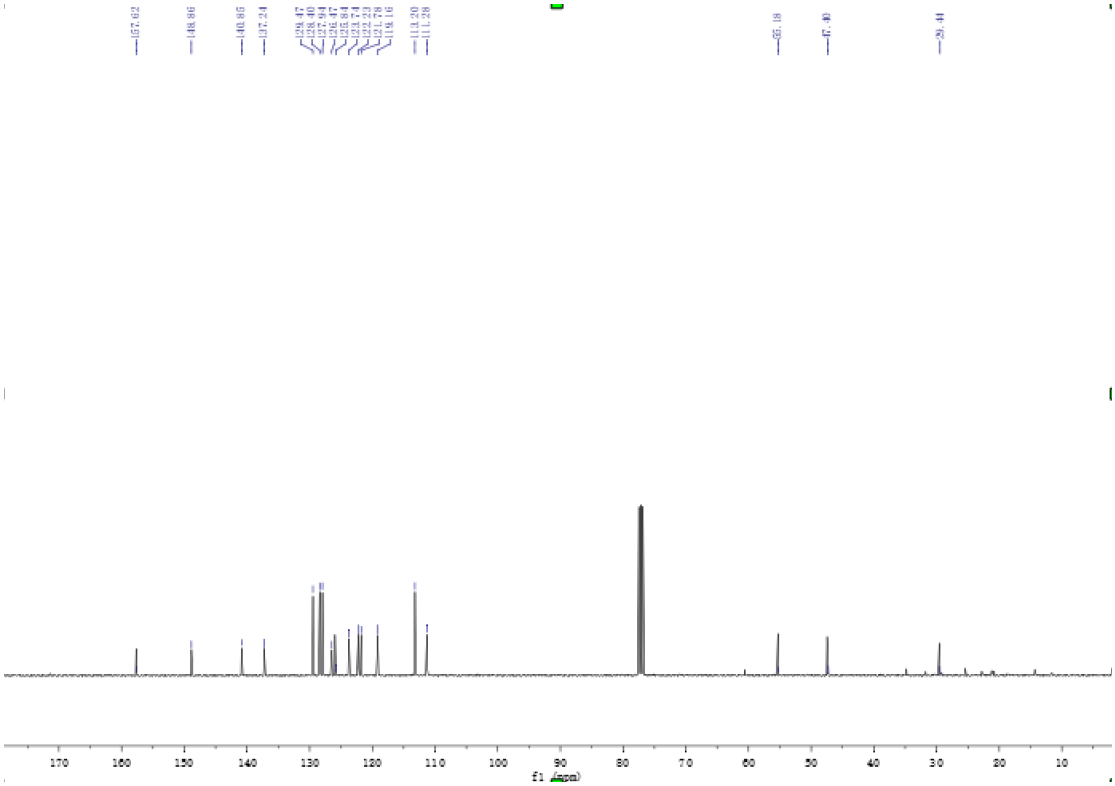
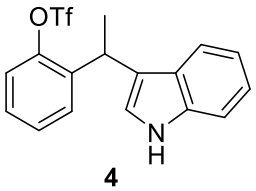


^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz



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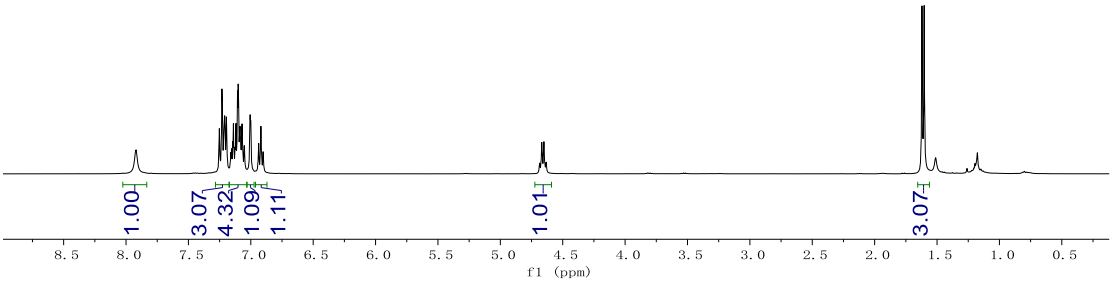
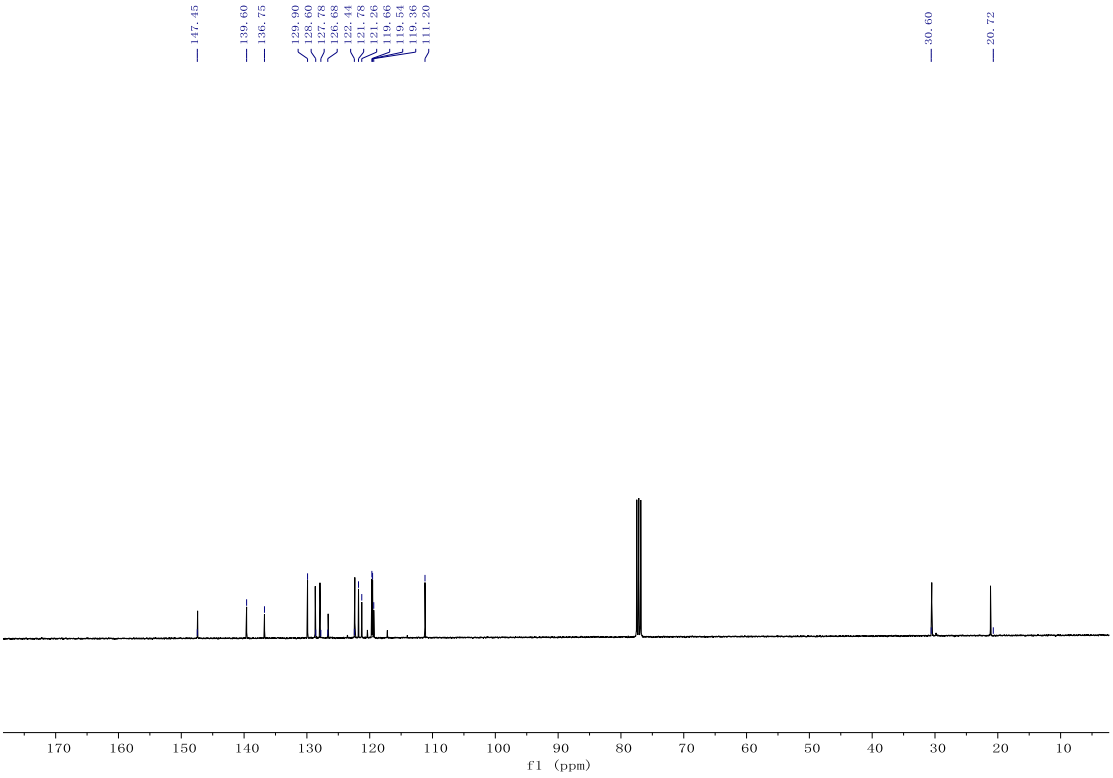
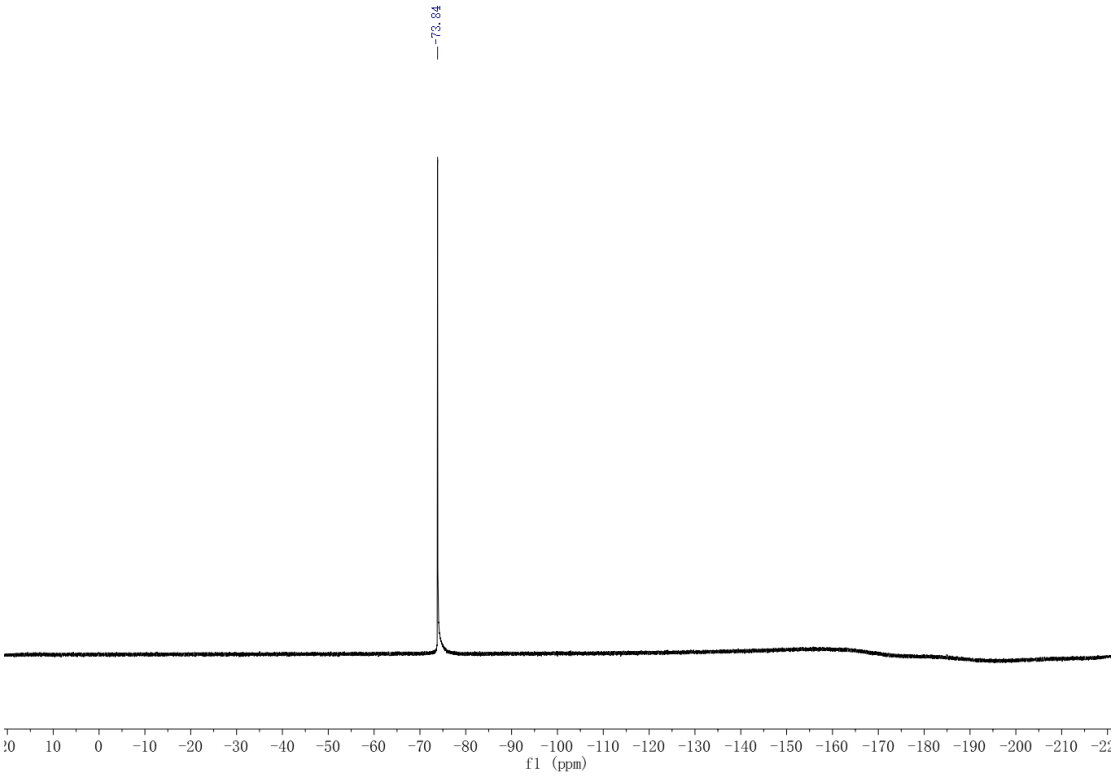


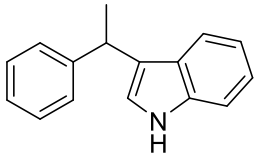
^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz



^{19}F NMR, $CDCl_3$, 471 MHz



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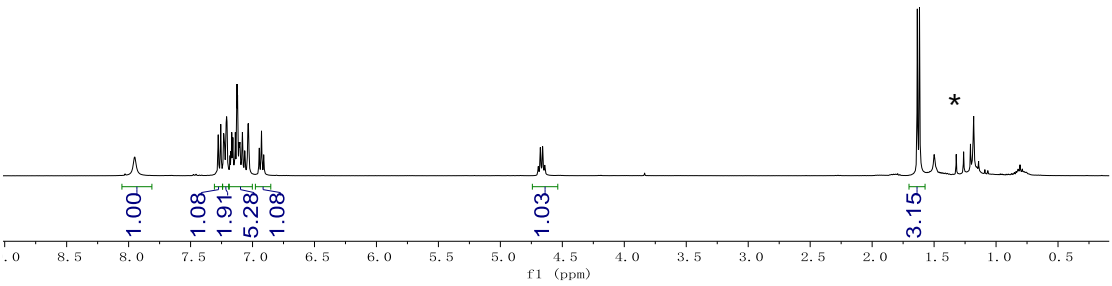
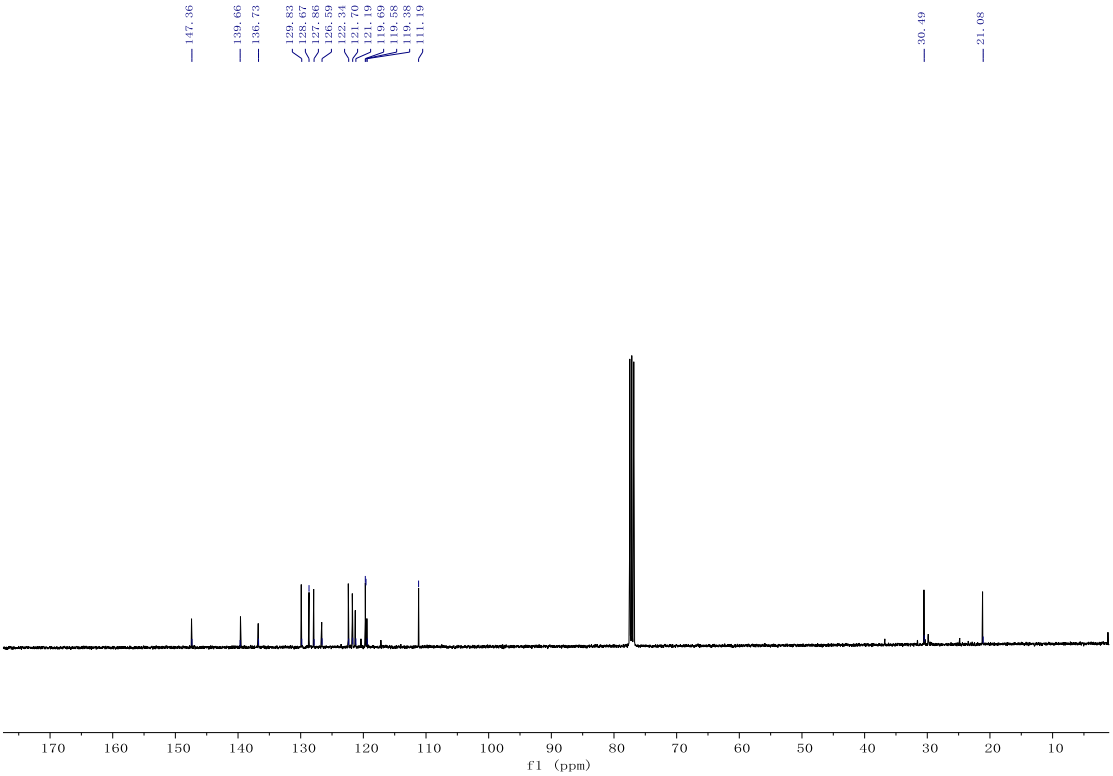
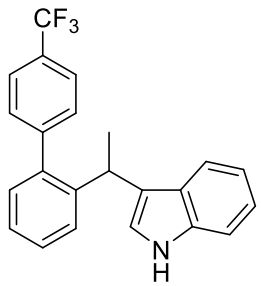


^{1}H NMR, $CDCl_3$, 400 MHz (* grease)



^{13}C NMR, $CDCl_3$, 101 MHz



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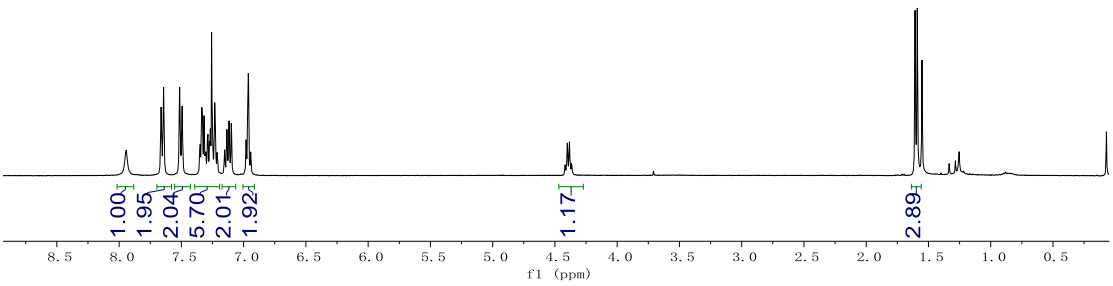
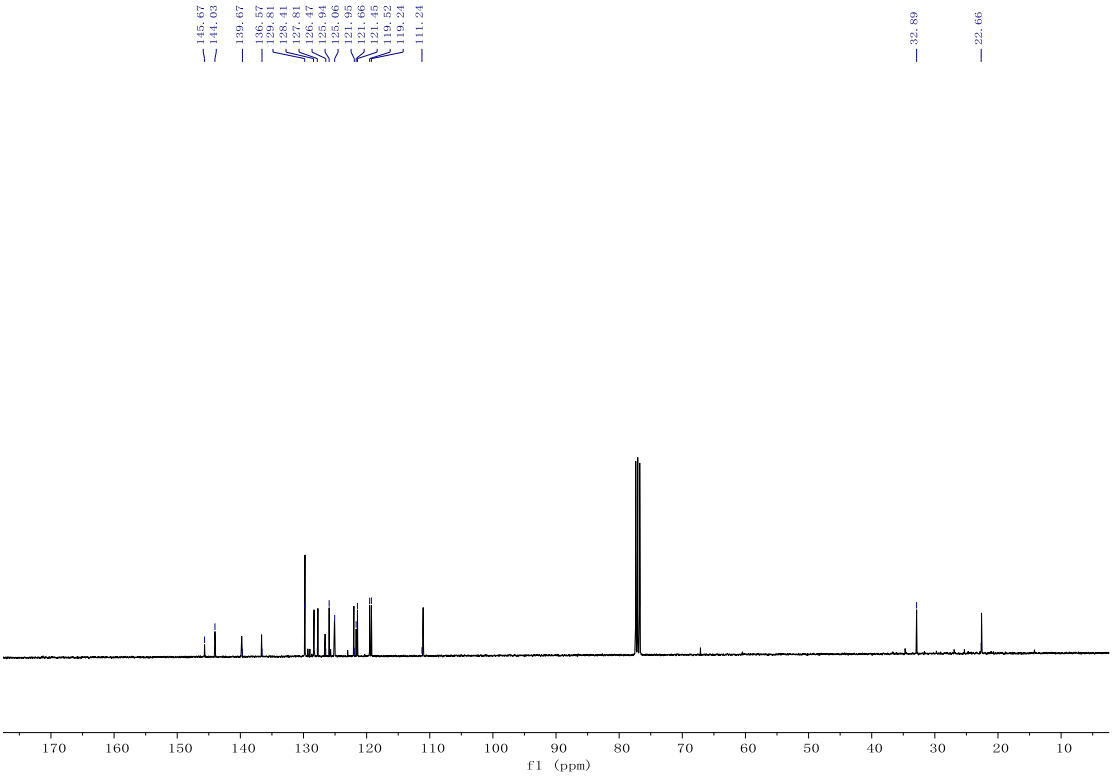
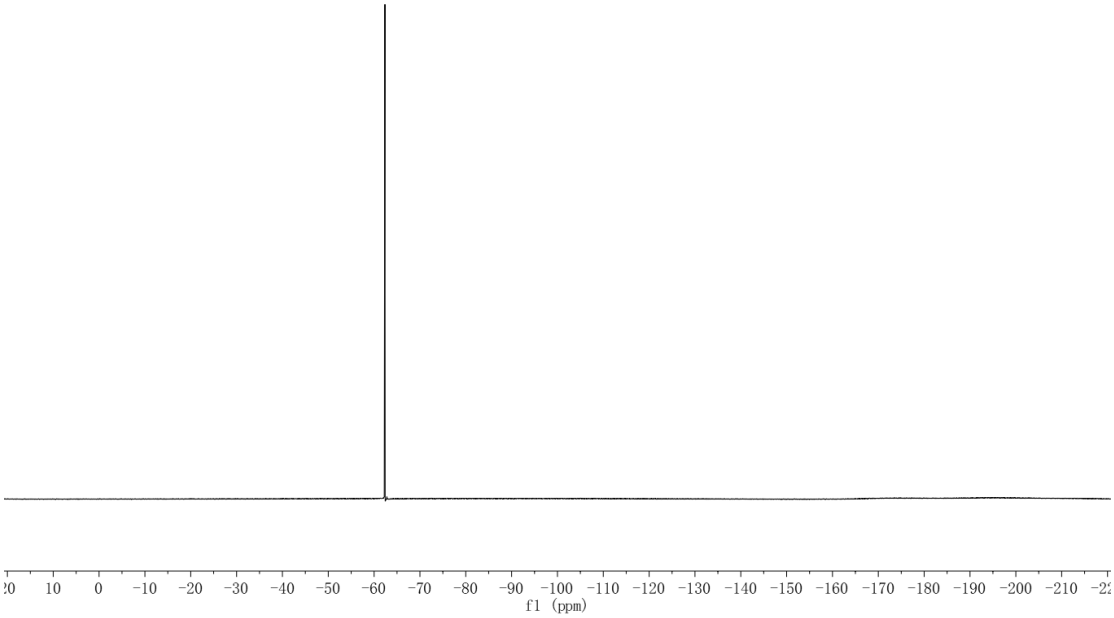


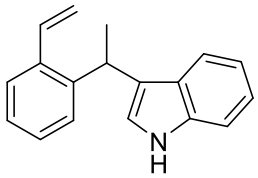
^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz



^{19}F NMR, $CDCl_3$, 471 MHz



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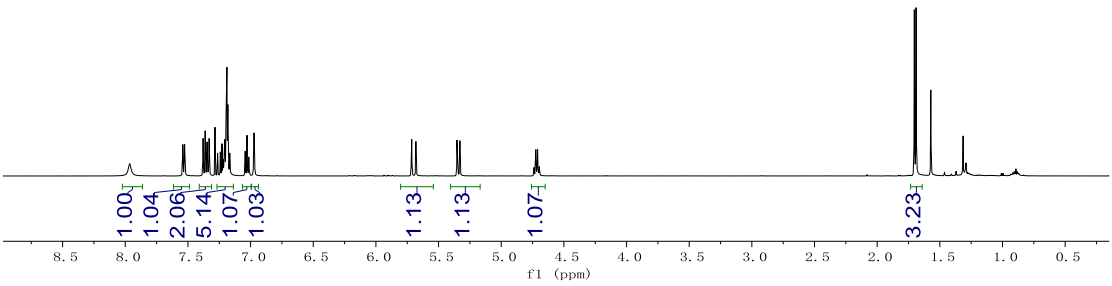
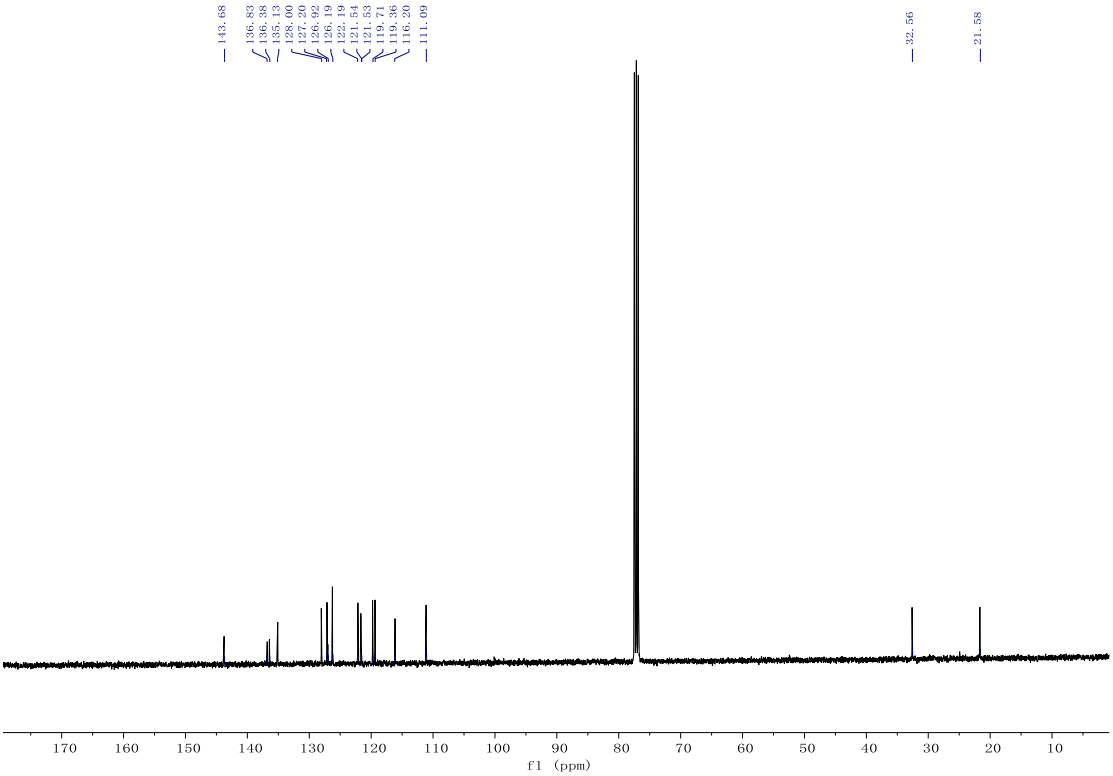


^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz

10.Reference and notes

(1) Esezobor, O. Z.; Zeng, W.; Niederegger, L.; Grübel, M.; Hess, C. R. *J. Am. Chem. Soc.* **2022**, *144*, 2994–3004.
(2) Jiang, F.; Zhang, Y-C.; Sun, S-B.; Zhou, L-J.; Shi, F. *Adv. Synth. Catal.* **2015**, *357*, 1283–1292.
(3) Pathak, T. P.; Sigman, M. S. *Org Lett.* **2011**, *13*, 2774-2777.