

Supporting Information

Rh(III)-catalyzed regioselective C4 alkylation of indoles with allylic alcohols: direct access to β -indolyl ketones

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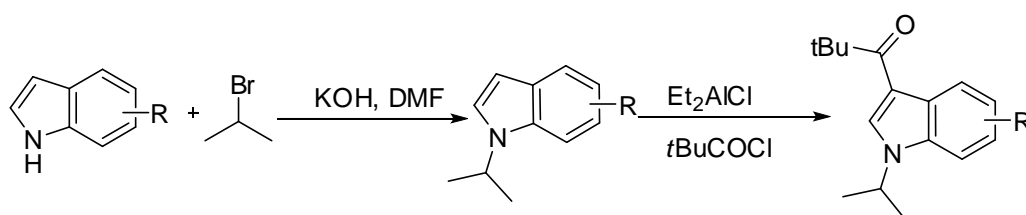
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| 1. General experimental details..... | S2 |
| 2. Characterization data of the compounds 1..... | S8 |
| 3. Characterization data of the products..... | S12 |
| 4. Copies of ^1H NMR and ^{13}C NMR spectra of the compounds 1..... | S23 |
| 5. Copies of ^1H NMR and ^{13}C NMR spectra of the products..... | S39 |

1. General experimental details

General Information: All chemicals were used as received without further purification unless stated otherwise. NMR spectra were recorded at ambient temperature on a 300 or 400 MHz NMR spectrometer. Chemical shifts (δ) are given in ppm relative to TMS, the coupling constants J are given in Hz. HRMS were recorded on a TOF LC/MS equipped with electrospray ionization (ESI) probe operating in positive or negative ion mode.

The synthesis of 1-(1-isopropyl-1H-indol-3-yl)-2,2-dimethylpropan-1-one **1**:



A mixture of indoles (5.0 mmol), 2-bromopropane (0.92 g, 7.5 mmol), and KOH (0.42 g, 7.5 mmol) in DMF (10 mL) was vigorously stirred at room temperature for 2 h. The reaction mixture was diluted with EtOAc and washed with H₂O. The aqueous phase was extracted with EtOAc, and the combined organic phases were dried over Na₂SO₄. After filtration and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel to give 1-isopropyl-1H-indoles.¹

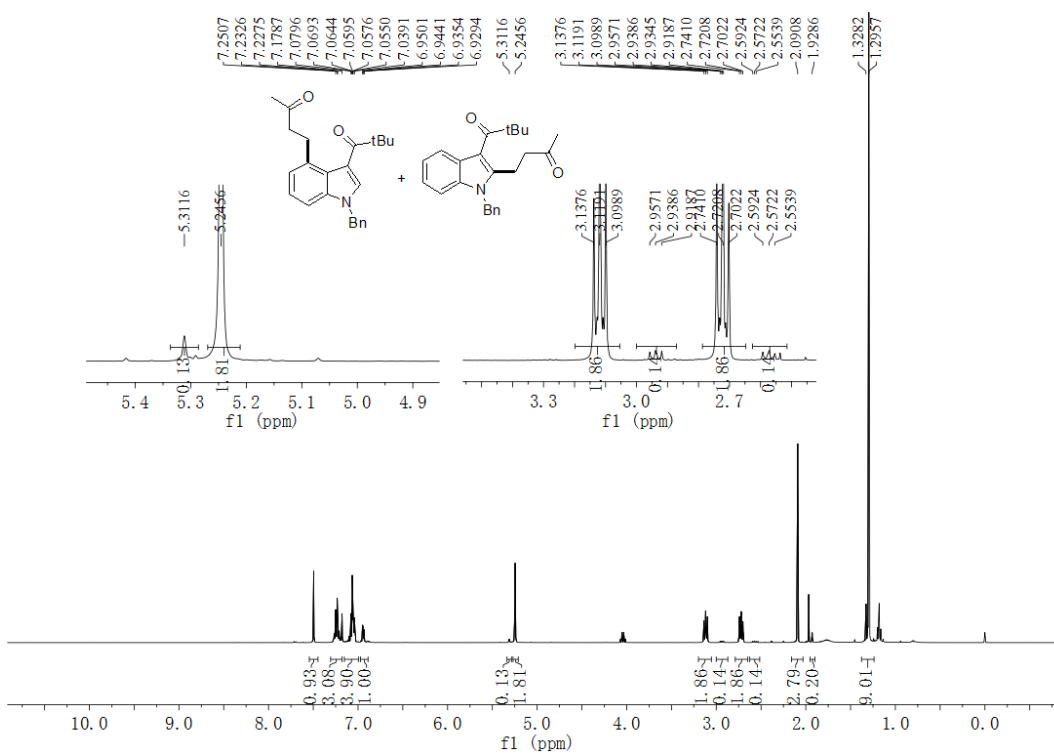
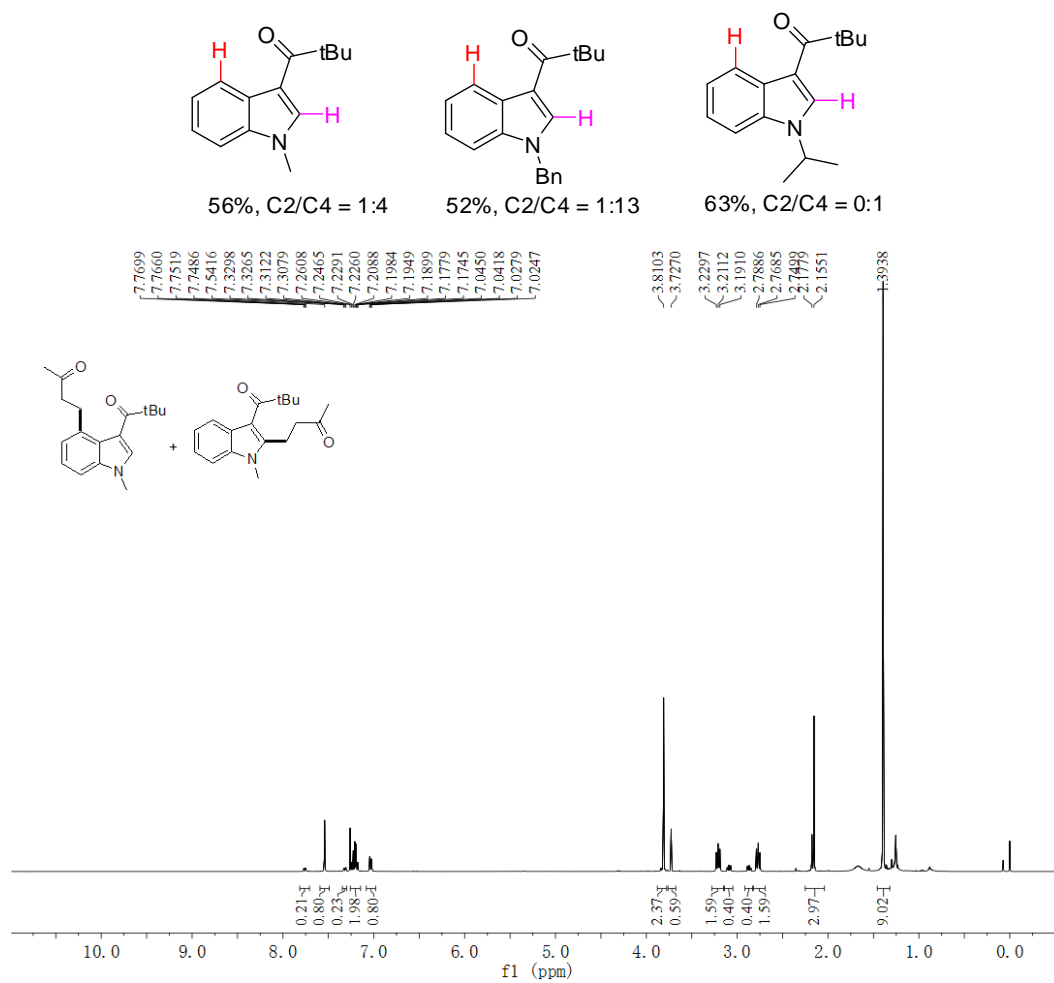
To a CH₂Cl₂ solution of 1-isopropyl-1H-indole (3 mmol) was added Et₂AlCl (1.6 equiv, 1.0 M in hexane) at 0 °C. The mixture was stirred at 0 °C for 30 min. To this solution was added dropwise a CH₂Cl₂ solution of tBuCOCl (1.5 equiv) at 0 °C. The resulting solution was stirred at 0 °C for 12 h, and H₂O was added to quench the reaction. Then the mixture was extracted with ethyl acetate and dried over Na₂SO₄. The crude product was purified by chromatography on silica gel to afford the 1-(1-isopropyl-1H-indol-3-yl)-2,2-dimethylpropan-1-one **1**.²

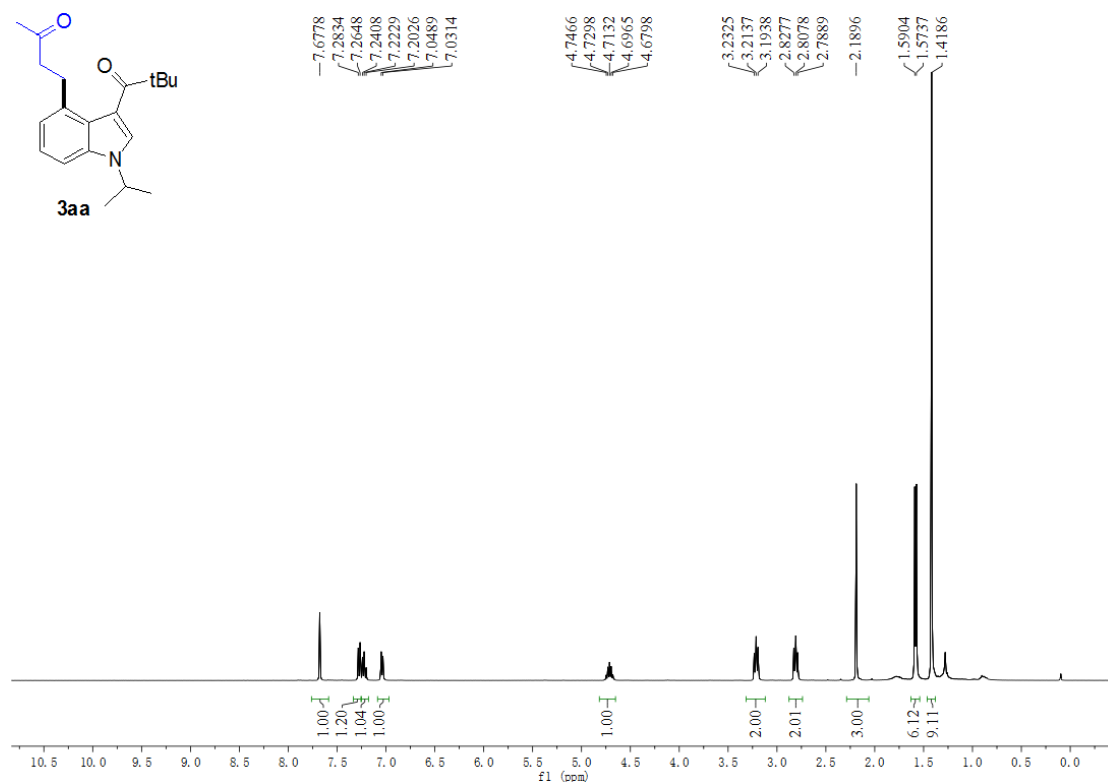
The procedure for the synthesis of the product 3: Under air, the mixture of **1a** (0.2 mmol), **2a** (0.8 mmol), [Cp**Rh*Cl₂]₂ (5 mol%, 6.2 mg), AgSbF₆ (20 mol%, 6.8 mg), Cu(OAc)₂ (0.06 mmol, 10.9 mg) and DCE (2 mL) were added into the tube and sealed. After the mixture was stirred at 40 °C for 48 h, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel gave the product.

¹ X. Hong, Q. Tan, B. Liu and B. Xu, *Angew. Chem. Int. Ed.*, 2017, **56**, 3961.

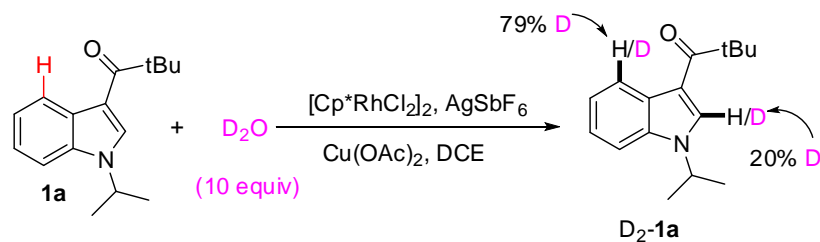
² Y. Yang, P. Gao, Y. Zhao and Z. Shi, *Angew. Chem. Int. Ed.*, 2017, **56**, 3966.

The effect of substituent on N atom of indole for the regioselectivity of C2/C4

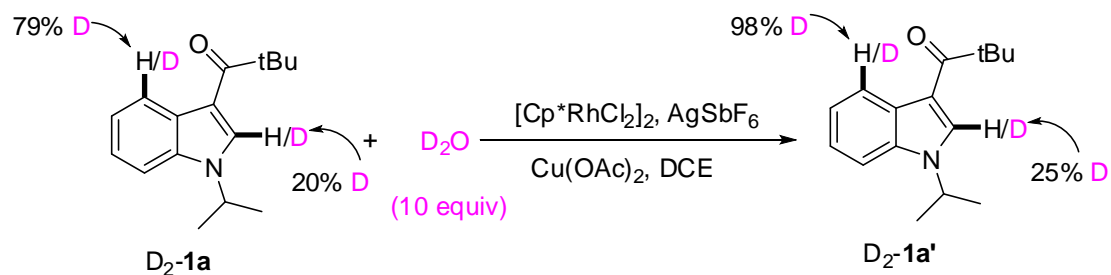
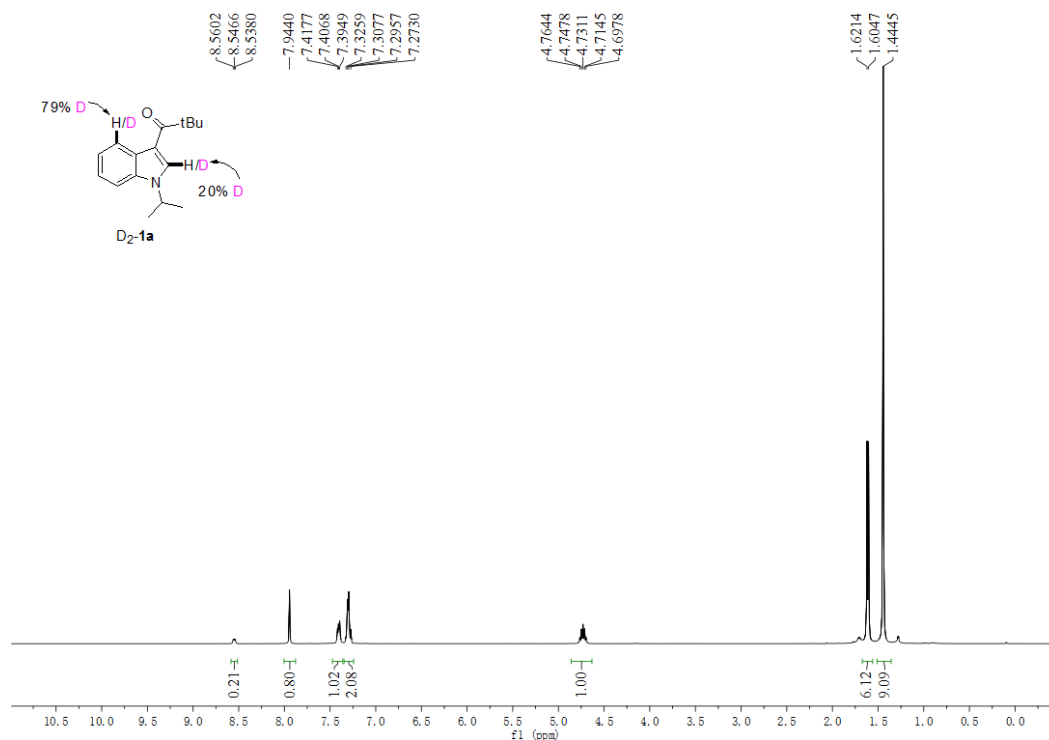




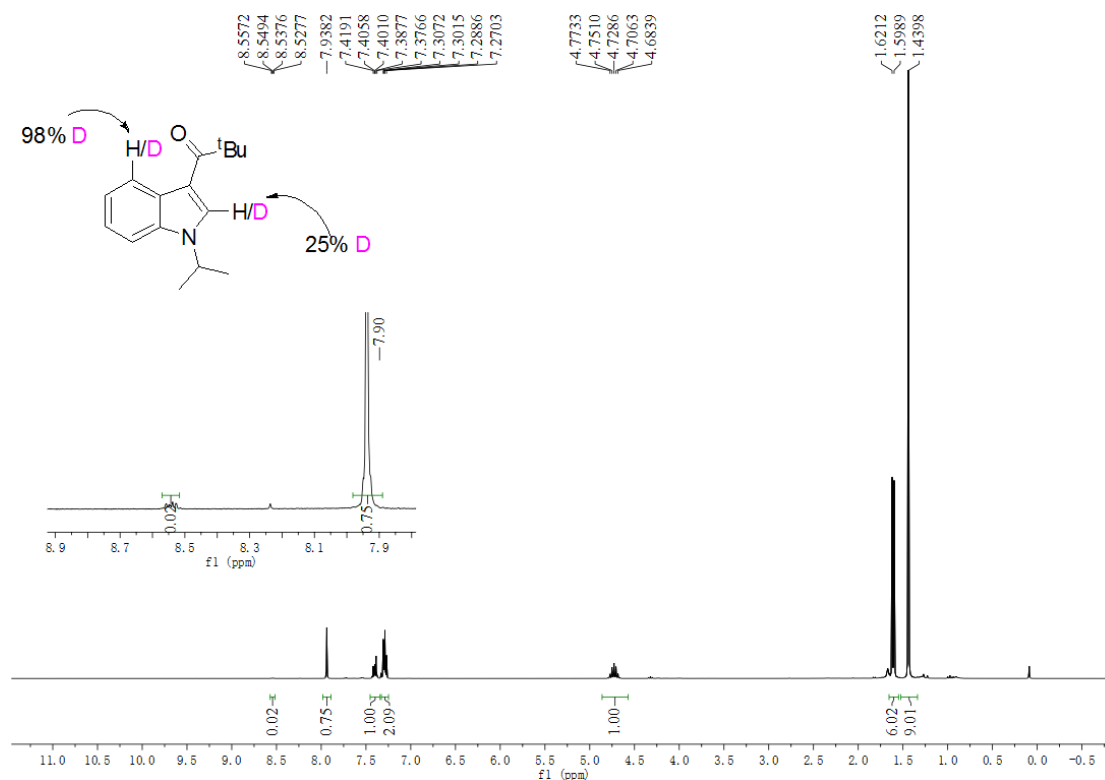
H/D-exchange experiment



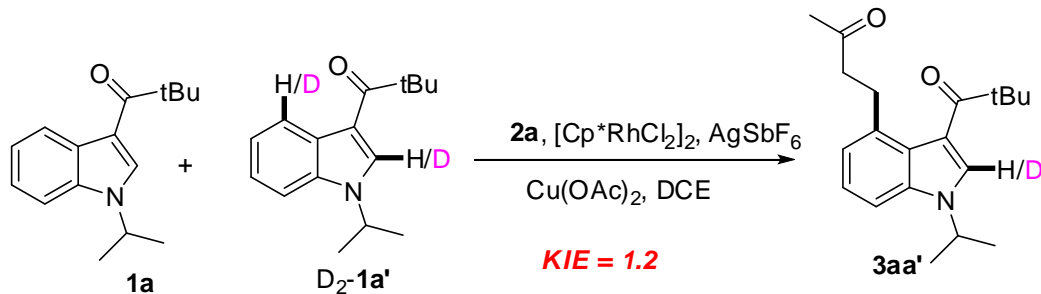
The mixture of 1-(1-isopropyl-1*H*-indol-3-yl)-2,2-dimethylpropan-1-one **1a** (0.1 mmol, 24.3 mg), $[Cp^*RhCl_2]_2$ (5 mol%, 3.1 mg), $AgSbF_6$ (20 mol%, 3.4 mg), $Cu(OAc)_2$ (0.03 mmol, 5.4 mg), DCE (1 mL) and D_2O (1 mmol, 20 mg) were added into the tube and sealed. The reaction mixture was vigorously stirred at 40 °C for 24 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to give the **D₂-1a** in 97% yield. ¹H NMR ($CDCl_3$, 400 MHz): δ 8.56-8.54 (m, 0.21H), 7.94 (s, 0.8H), 7.42-7.39 (m, 1H), 7.32-7.29 (m, 2H), 4.76-4.69 (m, 1H), 1.62 (d, $J = 6.7$ Hz, 6H), 1.44 (s, 9H).



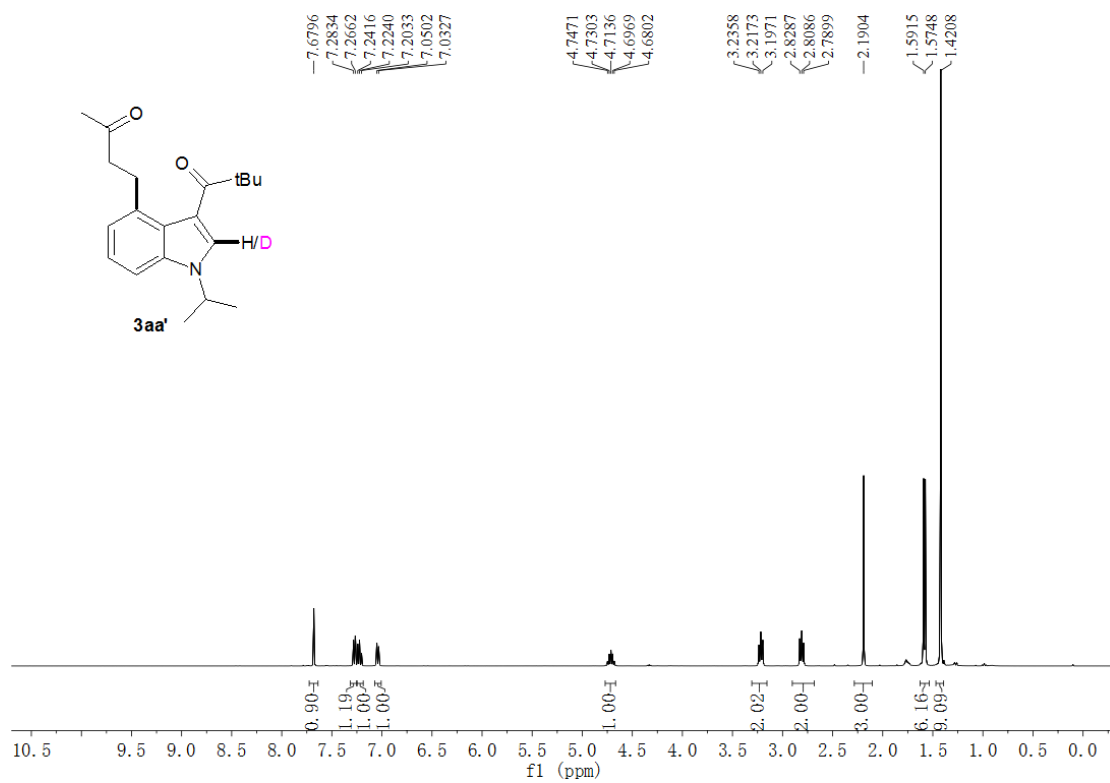
The mixture of **D₂-1a** (0.1 mmol, 24.4 mg), $[\text{Cp}^*\text{RhCl}_2]_2$ (5 mol%, 3.1 mg), AgSbF_6 (20 mol%, 3.4 mg), $\text{Cu}(\text{OAc})_2$ (0.03 mmol, 5.4 mg), DCE (1 mL) and D_2O (1 mmol, 20 mg) were added into the tube and sealed. The reaction mixture was vigorously stirred at 40 °C for 24 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to give the **D₂-1a'** in 98% yield. ¹H NMR (CDCl₃, 400 MHz): δ 8.56-8.53 (m, 0.02H), 7.94 (s, 0.75H), 7.42-7.38 (m, 1H), 7.31-7.28 (m, 2H), 4.77-4.68 (m, 1H), 1.61 (d, $J = 6.7$ Hz, 6H), 1.44 (s, 9H).



Intermolecular competition experiment with isotopically labeled D_2 -**1a'**

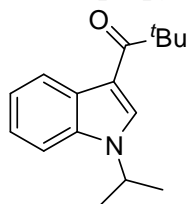


The mixture of **1a** (0.05 mmol, 12.1 mg), **D₂-1a'** (0.05 mmol, 12.2 mg), [Cp*RhCl₂]₂ (5 mol%, 3.1 mg), AgSbF₆ (20 mol%, 3.4 mg), Cu(OAc)₂ (0.03 mmol, 5.4 mg) and DCE (1 mL) were added into the tube and sealed. The reaction mixture was vigorously stirred at 40 °C for 24 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to give the **3aa'** in 56% yield. ¹H NMR (CDCl₃, 400 MHz): δ 7.68 (s, 0.9H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.22 (t, *J* = 7.0 Hz, 1H), 7.04 (d, *J* = 7.0 Hz, 1H), 4.75-4.68 (m, 1H), 3.22 (t, *J* = 7.4 Hz, 2H), 2.81 (t, *J* = 7.5 Hz, 2H), 2.19 (s, 3H), 1.58 (d, *J* = 6.7 Hz, 6H), 1.42 (s, 9H).



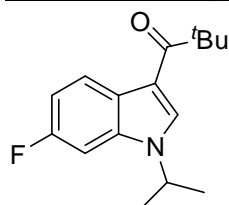
2. Characterization data of the compounds 1

1-(1-isopropyl-1H-indol-3-yl)-2,2-dimethylpropan-1-one (1a)



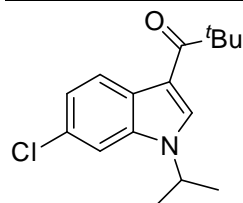
^1H NMR (CDCl_3 , 400 MHz): δ 8.45-8.43 (m, 1H), 7.82 (s, 1H), 7.26-7.24 (m, 1H), 7.17-7.14 (m, 2H), 4.59-4.52 (m, 1H), 1.45 (d, $J = 6.7$ Hz, 6H), 1.31 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 202.0, 135.5, 129.6, 128.5, 123.5, 123.0, 122.4, 112.9, 109.7, 47.8, 44.1, 29.1, 22.7. HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{21}\text{NNaO}$ ($\text{M}+\text{Na}$) $^+$ 266.1515, found 266.1517.

1-(6-fluoro-1-isopropyl-1H-indol-3-yl)-2,2-dimethylpropan-1-one (1b)



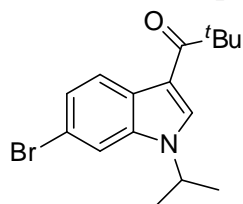
^1H NMR (CDCl_3 , 400 MHz): δ 8.49-8.46 (m, 1H), 7.92 (s, 1H), 7.07-7.01 (m, 2H), 4.64-4.57 (m, 1H), 1.59 (d, $J = 6.7$ Hz, 6H), 1.43 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 202.0, 160.1 (d, $J = 238.3$ Hz), 135.5 (d, $J = 11.6$ Hz), 129.7, 124.7, 124.6 (d, $J = 9.7$ Hz), 113.1, 110.8 (d, $J = 23.4$ Hz), 96.1 (d, $J = 26.3$ Hz), 48.1, 44.1, 29.0, 22.5. HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{20}\text{FNNaO}$ ($\text{M}+\text{Na}$) $^+$ 284.1421, found 284.1425.

1-(6-chloro-1-isopropyl-1H-indol-3-yl)-2,2-dimethylpropan-1-one (1c)



^1H NMR (CDCl_3 , 400 MHz): δ 8.45 (d, $J = 8.6$ Hz, 1H), 7.91 (s, 1H), 7.39 (s, 1H), 7.26-7.23 (m, 1H), 4.67-4.61 (m, 1H), 1.59 (d, $J = 6.7$ Hz, 6H), 1.42 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 201.9, 135.9, 129.8, 128.9, 126.9, 124.5, 122.9, 113.1, 109.7, 48.1, 44.1, 28.9, 22.6. HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{20}\text{ClNNaO}$ ($\text{M}+\text{Na}$) $^+$ 300.1126, found 300.1123.

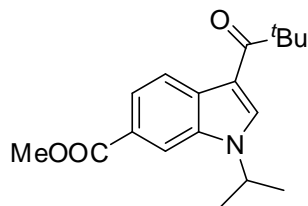
1-(6-bromo-1-isopropyl-1H-indol-3-yl)-2,2-dimethylpropan-1-one (1d)



^1H NMR (CDCl_3 , 400 MHz): δ 8.39 (d, $J = 8.6$ Hz, 1H), 7.88 (s, 1H), 7.54 (s, 1H), 7.39-7.36 (m, 1H), 4.68-4.61 (m, 1H), 1.59 (d, $J = 6.7$ Hz, 6H), 1.42 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ

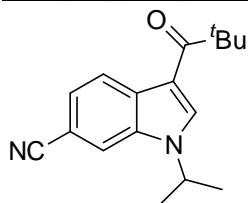
201.9, 136.2, 129.6, 127.3, 125.6, 124.8, 116.7, 113.1, 112.6, 48.0, 44.1, 28.9, 22.7. HRMS (ESI) m/z calcd for $C_{16}H_{20}BrNNaO$ ($M+Na$)⁺ 344.0620, found 344.0628.

methyl 1-isopropyl-3-pivaloyl-1H-indole-6-carboxylate (1e)



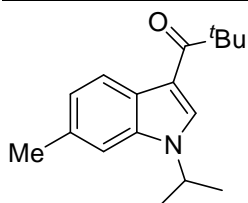
¹H NMR (CDCl₃, 400 MHz): δ 8.54 (d, J = 8.5 Hz, 1H), 8.15 (s, 1H), 8.05 (s, 1H), 7.97-7.94 (m, 1H), 4.83-4.78 (m, 1H), 3.94 (s, 3H), 1.62 (d, J = 6.6 Hz, 6H), 1.41 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ 201.8, 167.8, 134.9, 132.1, 131.8, 124.6, 123.3, 123.0, 113.2, 111.8, 52.1, 48.1, 44.1, 28.8, 22.8. HRMS (ESI) m/z calcd for $C_{18}H_{23}NNaO_3$ ($M+Na$)⁺ 324.1570, found 324.1567.

1-isopropyl-3-pivaloyl-1H-indole-6-carbonitrile (1f)



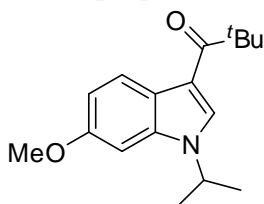
¹H NMR (CDCl₃, 400 MHz): δ 8.87 (s, 1H), 8.02 (s, 1H), 7.45 (s, 2H), 4.78-4.71 (m, 1H), 1.62 (d, J = 6.7 Hz, 6H), 1.40 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ 201.8, 136.9, 131.1, 129.1, 128.2, 125.6, 120.3, 113.4, 110.6, 105.4, 48.4, 44.2, 28.7, 22.7. HRMS (ESI) m/z calcd for $C_{17}H_{20}N_2NaO$ ($M+Na$)⁺ 291.1468, found 291.1470.

1-(1-isopropyl-6-methyl-1H-indol-3-yl)-2,2-dimethylpropan-1-one (1g)



¹H NMR (CDCl₃, 400 MHz): δ 8.46 (d, J = 8.0 Hz, 1H), 7.92 (s, 1H), 7.23 (s, 1H), 7.16 (d, J = 8.2 Hz, 1H), 4.74-4.67 (m, 1H), 2.53 (s, 3H), 1.59 (d, J = 6.7 Hz, 6H), 1.47 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ 202.0, 135.9, 132.8, 129.1, 126.2, 124.2, 123.1, 112.9, 109.6, 47.7, 44.0, 29.1, 22.7, 21.9. HRMS (ESI) m/z calcd for $C_{17}H_{23}NNaO$ ($M+Na$)⁺ 280.1672, found 280.1671.

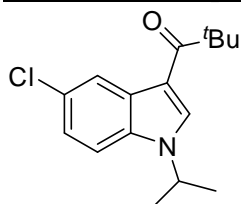
1-(1-isopropyl-6-methoxy-1H-indol-3-yl)-2,2-dimethylpropan-1-one (1h)



¹H NMR (CDCl₃, 400 MHz): δ 8.41 (d, J = 8.8 Hz, 1H), 7.84 (s, 1H), 6.97-6.94 (m, 1H), 6.85 (s, 1H), 4.68-4.61 (m, 1H), 3.89 (s, 3H), 1.60 (d, J = 6.7 Hz, 6H), 1.43 (s, 9H). ¹³C NMR (CDCl₃, 100

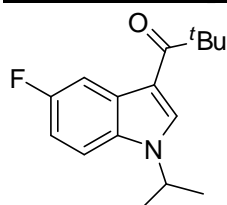
MHz): δ 202.0, 156.9, 136.3, 128.6, 124.2, 122.5, 113.1, 111.4, 93.7, 55.8, 47.6, 44.0, 29.1, 22.6.
HRMS (ESI) m/z calcd for $C_{17}H_{23}NNaO_2$ ($M+Na$)⁺ 296.1621, found 296.1627.

1-(5-chloro-1-isopropyl-1H-indol-3-yl)-2,2-dimethylpropan-1-one (1i)



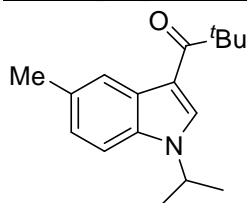
¹H NMR ($CDCl_3$, 400 MHz): δ 8.57 (s, 1H), 7.93 (s, 1H), 7.28 (d, J = 8.8 Hz, 1H), 7.23-7.21 (m, 1H), 4.70-4.64 (m, 1H), 1.59 (d, J = 6.7 Hz, 6H), 1.42 (s, 9H). ¹³C NMR ($CDCl_3$, 100 MHz): δ 201.8, 133.8, 130.2, 129.4, 128.3, 123.3, 123.0, 112.6, 110.6, 48.2, 44.0, 28.9, 22.6. HRMS (ESI) m/z calcd for $C_{16}H_{20}ClNNaO$ ($M+Na$)⁺ 300.1126, found 300.1123.

1-(5-fluoro-1-isopropyl-1H-indol-3-yl)-2,2-dimethylpropan-1-one (1j)



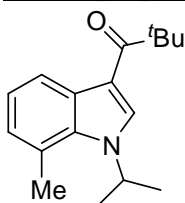
¹H NMR ($CDCl_3$, 400 MHz): δ 8.24 (d, J = 7.7 Hz, 1H), 7.97 (s, 1H), 7.27-7.24 (m, 1H), 6.98-6.93 (m, 1H), 4.65-4.58 (m, 1H), 1.54 (d, J = 6.8 Hz, 6H), 1.39 (s, 9H). ¹³C NMR ($CDCl_3$, 100 MHz): δ 201.9, 159.6 (d, J = 235.1 Hz), 132.0, 130.8, 159.6 (d, J = 11.0 Hz), 112.8 (d, J = 4.7 Hz), 111.2 (d, J = 26.3 Hz), 110.5 (d, J = 9.8 Hz), 108.5 (d, J = 24.9 Hz), 48.3, 43.9, 28.9, 22.5. HRMS (ESI) m/z calcd for $C_{16}H_{20}FNNaO$ ($M+Na$)⁺ 284.1421, found 284.1424.

1-(1-isopropyl-5-methyl-1H-indol-3-yl)-2,2-dimethylpropan-1-one (1k)



¹H NMR ($CDCl_3$, 400 MHz): δ 8.39 (s, 1H), 7.91 (s, 1H), 7.29 (d, J = 8.4 Hz, 1H), 7.13 (d, J = 8.4 Hz, 1H), 4.72-4.65 (m, 1H), 2.50 (s, 3H), 1.60 (d, J = 6.7 Hz, 6H), 1.45 (s, 9H). ¹³C NMR ($CDCl_3$, 100 MHz): δ 202.1, 133.8, 132.2, 129.5, 128.7, 124.4, 123.2, 112.5, 109.3, 47.9, 44.0, 29.1, 22.7, 21.5. HRMS (ESI) m/z calcd for $C_{17}H_{23}NNaO$ ($M+Na$)⁺ 280.1672, found 280.1669.

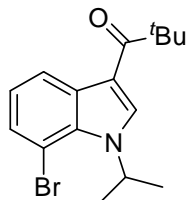
1-(1-isopropyl-7-methyl-1H-indol-3-yl)-2,2-dimethylpropan-1-one (1l)



¹H NMR ($CDCl_3$, 400 MHz): δ 8.47 (d, J = 8.0 Hz, 1H), 8.00 (s, 1H), 7.18 (t, J = 7.8 Hz, 1H),

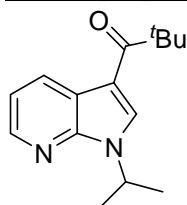
7.03 (d, $J = 7.1$ Hz, 1H), 5.26-5.19 (m, 1H), 2.76 (s, 3H), 1.60 (d, $J = 6.6$ Hz, 6H), 1.45 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 202.0, 134.6, 129.8, 129.1, 126.6, 122.4, 121.3, 120.5, 113.1, 48.6, 44.1, 29.1, 24.2, 20.7. HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{23}\text{NNaO}$ ($\text{M}+\text{Na}$) $^+$ 280.1672, found 280.1669.

1-(7-bromo-1-isopropyl-1H-indol-3-yl)-2,2-dimethylpropan-1-one (1m)



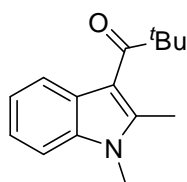
^1H NMR (CDCl_3 , 400 MHz): δ 8.55 (d, $J = 8.0$ Hz, 1H), 8.02 (s, 1H), 7.45 (d, $J = 7.6$ Hz, 1H), 7.09 (d, $J = 7.8$ Hz, 1H), 5.94-5.88 (m, 1H), 1.59 (d, $J = 6.6$ Hz, 6H), 1.42 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 201.7, 132.2, 131.7, 130.8, 128.9, 123.3, 122.6, 112.9, 103.5, 48.1, 44.2, 28.9, 23.9. HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{20}\text{BrNNaO}$ ($\text{M}+\text{Na}$) $^+$ 344.0620, found 344.0628.

1-(1-isopropyl-1H-pyrrolo[2,3-b]pyridin-3-yl)-2,2-dimethylpropan-1-one (1n)



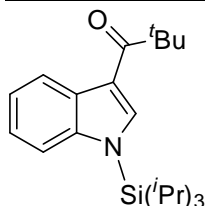
^1H NMR (CDCl_3 , 400 MHz): δ 8.72 (d, $J = 7.9$ Hz, 1H), 8.36-8.34 (m, 1H), 7.99 (s, 1H), 7.22-7.19 (m, 1H), 5.25-5.18 (m, 1H), 1.57 (d, $J = 6.8$ Hz, 6H), 1.41 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 201.9, 146.8, 143.9, 131.8, 129.6, 120.9, 118.6, 111.6, 46.2, 44.0, 28.8, 22.8. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{20}\text{N}_2\text{NaO}$ ($\text{M}+\text{Na}$) $^+$ 267.1468, found 267.1469.

1-(1,2-dimethyl-1H-indol-3-yl)-2,2-dimethylpropan-1-one (1o)



^1H NMR (CDCl_3 , 400 MHz): δ 7.68 (d, $J = 7.6$ Hz, 1H), 7.30 (d, $J = 7.7$ Hz, 1H), 7.23-7.15 (m, 2H), 3.69 (s, 3H), 2.49 (s, 3H), 1.39 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 209.4, 140.0, 136.2, 125.3, 121.3, 121.1, 120.4, 115.1, 109.2, 44.5, 29.6, 27.4, 12.4. HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{19}\text{NNaO}$ ($\text{M}+\text{Na}$) $^+$ 252.1359, found 252.1362.

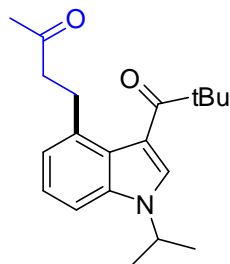
2,2-dimethyl-1-(1-(triisopropylsilyl)-1H-indol-3-yl)propan-1-one (1p)



^1H NMR (CDCl_3 , 400 MHz): δ 8.53 (d, $J = 8.0$ Hz, 1H), 8.03 (s, 1H), 7.51 (d, $J = 8.0$ Hz, 1H), 7.31-7.22 (m, 2H), 1.79-1.68 (s, 3H), 1.45 (s, 3H), 1.20 (d, $J = 7.6$ Hz, 18H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 202.4, 140.4, 137.7, 130.4, 123.0, 122.9, 122.4, 116.0, 113.6, 44.2, 29.0, 18.1, 12.7. HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{35}\text{NNaOSi}$ ($\text{M}+\text{Na}$) $^+$ 380.2380, found 380.2392.

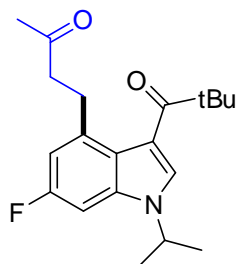
3. Characterization data of the products

4-(1-isopropyl-3-pivaloyl-1H-indol-4-yl)butan-2-one (3aa)



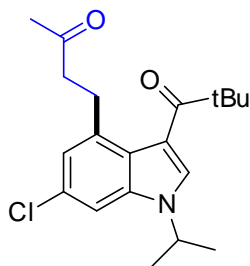
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1) give **3aa** as a colorless liquid (54.5 mg, 87% yield). ^1H NMR (CDCl_3 , 400 MHz): δ 7.68 (s, 1H), 7.27 (d, $J = 7.4$ Hz, 1H), 7.22 (t, $J = 7.2$ Hz, 1H), 7.04 (d, $J = 7.0$ Hz, 1H), 4.75-4.68 (m, 1H), 3.21 (t, $J = 7.6$ Hz, 2H), 2.81 (t, $J = 7.6$ Hz, 2H), 2.19 (s, 3H), 1.58 (d, $J = 6.7$ Hz, 6H), 1.42 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 209.3, 205.7, 136.3, 135.5, 126.4, 125.5, 122.9, 122.7, 115.6, 107.9, 47.4, 45.2, 44.7, 29.8, 29.0, 28.7, 22.7. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{27}\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$ 336.1934, found 336.1937.

4-(6-fluoro-1-isopropyl-3-pivaloyl-1H-indol-4-yl)butan-2-one (3ba)



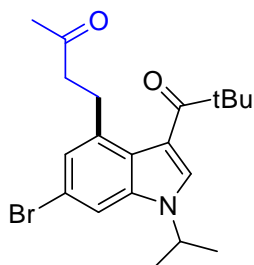
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1) give **3ba** as a brown liquid (50.3 mg, 76% yield). ^1H NMR (CDCl_3 , 400 MHz): δ 7.64 (s, 1H), 6.94-6.91 (m, 1H), 6.82-6.79 (m, 1H), 4.60-4.54 (m, 1H), 3.16 (t, $J = 7.5$ Hz, 2H), 2.79 (t, $J = 7.5$ Hz, 2H), 2.18 (s, 3H), 1.55 (d, $J = 6.7$ Hz, 6H), 1.39 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 208.4, 205.6, 159.9 (d, $J = 238.0$ Hz), 137.3 (d, $J = 9.1$ Hz), 136.4 (d, $J = 12.2$ Hz), 126.5 (d, $J = 2.6$ Hz), 121.9, 115.8, 111.0 (d, $J = 23.7$ Hz), 94.2 (d, $J = 25.9$ Hz), 47.7, 44.73, 44.71, 29.8, 28.7 (d, $J = 1.2$ Hz), 28.6, 22.5. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{26}\text{FNNaO}_2$ ($\text{M}+\text{Na}$) $^+$ 354.1840, found 354.1842.

4-(6-chloro-1-isopropyl-3-pivaloyl-1H-indol-4-yl)butan-2-one (3ca)



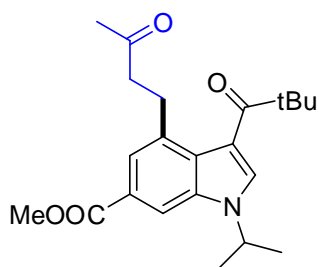
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1) give **3ca** as a brown liquid (57.6 mg, 83% yield). ^1H NMR (CDCl_3 , 400 MHz): δ 7.64 (s, 1H), 7.25 (s, 1H), 7.01 (s, 1H), 4.65-4.58 (m, 1H), 3.14 (t, $J = 7.5$ Hz, 2H), 2.79 (t, $J = 7.7$ Hz, 2H), 2.18 (s, 3H), 1.55 (d, $J = 6.7$ Hz, 6H), 1.39 (s, 9H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 208.4, 205.6, 136.9, 136.7, 128.8, 126.6, 124.1, 122.9, 115.8, 107.8, 47.7, 44.79, 44.78, 29.8, 28.6, 28.6, 22.6. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{26}\text{ClNNaO}_2$ ($\text{M}+\text{Na}$) $^+$ 370.1544, found 370.1548.

4-(6-bromo-1-isopropyl-3-pivaloyl-1H-indol-4-yl)butan-2-one (3da)



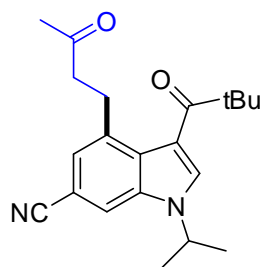
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1) give **3da** as a black liquid (67.6 mg, 86% yield). ^1H NMR (CDCl_3 , 400 MHz): δ 7.64 (s, 1H), 7.41 (s, 1H), 7.13 (s, 1H), 4.63-4.57 (m, 1H), 3.15 (t, $J = 7.5$ Hz, 2H), 2.76 (t, $J = 7.5$ Hz, 2H), 2.15 (s, 3H), 1.53 (d, $J = 6.2$ Hz, 6H), 1.37 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 208.4, 205.6, 137.4, 137.2, 126.8, 125.7, 124.6, 116.6, 115.9, 111.1, 47.9, 44.9, 44.8, 29.9, 28.72, 28.70, 22.7. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{26}\text{BrNNaO}_2$ ($\text{M}+\text{Na}$) $^+$ 414.1039, found 414.1025.

methyl 1-isopropyl-4-(3-oxobutyl)-3-pivaloyl-1H-indole-6-carboxylate (3ea)



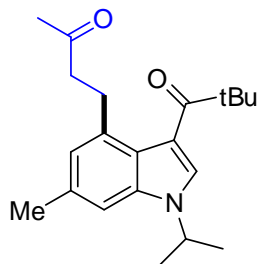
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 3:1) give **3ea** as a brown liquid (48.2 mg, 65% yield). ^1H NMR (CDCl_3 , 400 MHz): δ 8.02 (s, 1H), 7.76 (s, 1H), 7.69 (s, 1H), 4.83-4.76 (m, 1H), 3.94 (s, 3H), 3.18 (t, $J = 7.5$ Hz, 2H), 2.81 (t, $J = 7.6$ Hz, 2H), 2.18 (s, 3H), 1.58 (d, $J = 6.7$ Hz, 6H), 1.39 (s, 9H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 208.5, 205.8, 167.7, 135.8, 135.2, 129.1, 128.5, 124.5, 123.1, 115.9, 110.2, 52.1, 47.7, 44.8, 29.9, 28.7, 28.5, 22.8. HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{29}\text{NNaO}_4$ ($\text{M}+\text{Na}$) $^+$ 394.1989, found 394.1997.

1-isopropyl-4-(3-oxobutyl)-3-pivaloyl-1H-indole-6-carbonitrile (3fa)



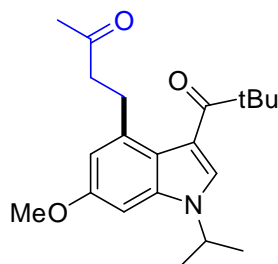
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 3:1) give **3fa** as a colorless liquid (38.5 mg, 57% yield). ^1H NMR (CDCl_3 , 400 MHz): δ 7.076 (s, 1H), 7.61 (s, 1H), 7.25 (s, 1H), 4.74-4.67 (m, 1H), 3.14 (t, $J = 7.4$ Hz, 2H), 2.81 (t, $J = 7.4$ Hz, 2H), 2.19 (s, 3H), 1.58 (d, $J = 6.6$ Hz, 6H), 1.39 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 207.8, 205.9, 136.8, 135.1, 128.8, 128.4, 124.6, 120.1, 116.4, 112.7, 105.6, 48.1, 44.9, 44.3, 29.9, 28.3, 28.1, 22.7. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{26}\text{N}_2\text{NaO}_2$ ($\text{M}+\text{Na}$) $^+$ 361.1886, found 361.1879.

4-(1-isopropyl-6-methyl-3-pivaloyl-1H-indol-4-yl)butan-2-one (3ga)



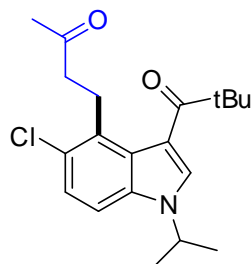
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1) give **3ga** as a brown liquid (38.9 mg, 61% yield). ^1H NMR (CDCl_3 , 400 MHz): δ 7.64 (s, 1H), 7.07 (s, 1H), 6.89 (s, 1H), 4.71-4.65 (m, 1H), 3.19 (t, $J = 7.5$ Hz, 2H), 2.79 (t, $J = 7.5$ Hz, 2H), 2.47 (s, 3H), 2.19 (s, 3H), 1.58 (d, $J = 6.7$ Hz, 6H), 1.41 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 209.5, 205.6, 136.9, 135.3, 132.9, 126.2, 124.8, 123.5, 115.6, 108.0, 47.4, 45.5, 44.8, 29.9, 29.2, 28.9, 22.8, 21.8. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{29}\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$ 350.2091, found 350.2089.

4-(1-isopropyl-6-methoxy-3-pivaloyl-1H-indol-4-yl)butan-2-one (3ha)



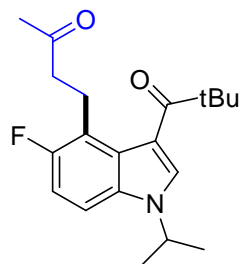
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 3:1) give **3ha** as a white solid (45.9 mg, 67% yield), m.p 104-106 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 7.59 (s, 1H), 6.71 (s, 1H), 4.65-4.58 (m, 1H), 3.87 (s, 3H), 3.18 (t, $J = 7.8$ Hz, 2H), 2.79 (t, $J = 7.7$ Hz, 2H), 2.19 (s, 3H), 1.56 (d, $J = 6.7$ Hz, 6H), 1.40 (s, 9H). ^{13}C NMR (CDCl_3 , 75MHz): δ 209.1, 205.4, 156.7, 137.2, 136.6, 125.7, 119.8, 115.6, 112.1, 91.4, 55.6, 47.3, 45.1, 44.6, 29.8, 29.2, 28.8, 22.5. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{29}\text{NNaO}_3$ ($\text{M}+\text{Na}$) $^+$ 350. 366.2040, found 366.2045.

4-(5-chloro-1-isopropyl-3-pivaloyl-1H-indol-4-yl)butan-2-one (3ia)



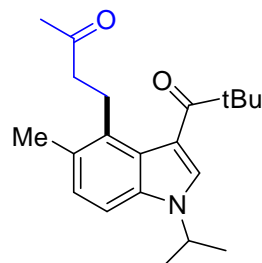
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1) give **3ia** as a brown liquid (54.1 mg, 78% yield). $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.56 (s, 1H), 7.26 (d, $J = 8.8$ Hz, 1H), 7.19 (d, $J = 8.8$ Hz, 1H), 4.68-4.61 (m, 1H), 3.11 (t, $J = 7.1$ Hz, 2H), 2.93 (t, $J = 7.2$ Hz, 2H), 2.25 (s, 3H), 1.55 (d, $J = 6.7$ Hz, 6H), 1.37 (s, 9H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 208.9, 207.1, 134.7, 132.2, 127.4, 127.1, 125.9, 124.3, 116.1, 108.9, 47.8, 45.1, 42.5, 29.9, 28.3, 25.9, 22.8. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{26}\text{ClNNaO}_2$ ($\text{M}+\text{Na}$) $^+$ 370.1544, found 370.1548.

4-(5-fluoro-1-isopropyl-3-pivaloyl-1H-indol-4-yl)butan-2-one (3ja)



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1) give **3ja** as a brown liquid (49.6 mg, 76% yield). $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.68 (s, 1H), 7.21-7.17 (m, 1H), 7.04-6.99 (m, 1H), 4.69-4.62 (m, 1H), 3.13 (t, $J = 7.4$ Hz, 2H), 2.84 (t, $J = 7.5$ Hz, 2H), 2.22 (s, 3H), 1.55 (d, $J = 6.7$ Hz, 6H), 1.39 (s, 9H). $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 208.8, 205.4, 156.9 (d, $J = 232.9$ Hz), 132.6, 127.3, 126.6 (d, $J = 6.3$ Hz), 120.6 (d, $J = 18.1$ Hz), 115.9 (d, $J = 4.7$ Hz), 111.3 (d, $J = 28$ Hz), 108.3 (d, $J = 10.3$ Hz), 47.7, 44.6, 43.7, 29.6, 28.6, 22.6, 21.1 (d, $J = 4.5$ Hz). HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{26}\text{FNNaO}_2$ ($\text{M}+\text{Na}$) $^+$ 354.1840, found 354.1842.

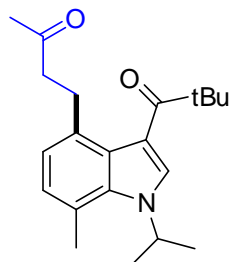
4-(1-isopropyl-5-methyl-3-pivaloyl-1H-indol-4-yl)butan-2-one (3ka)



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1) give **3ka** as a colorless liquid (15 mg, 23% yield). $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.51 (s, 1H), 7.16 (d, $J = 8.4$ Hz, 1H), 7.10 (d, $J = 8.4$ Hz, 1H), 4.68-4.62 (m, 1H), 3.02 (t, $J = 7.3$ Hz, 2H), 2.79 (t, $J = 7.3$ Hz, 2H), 2.39 (s, 3H), 2.24 (s, 3H), 1.54 (d, $J = 6.6$ Hz, 6H), 1.37 (s, 9H). $^{13}\text{C NMR}$ (CDCl_3 , 75 MHz):

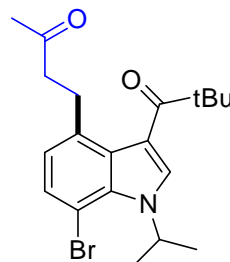
δ 209.5, 207.4, 134.9, 132.6, 128.8, 126.3, 125.9, 125.2, 115.6, 107.5, 47.3, 44.9, 43.0, 29.8, 28.4, 25.2, 22.6, 19.2. HRMS (ESI) m/z calcd for $C_{21}H_{29}NNaO_2$ ($M+Na$)⁺ 350.2091, found 350.2089.

4-(1-isopropyl-7-methyl-3-pivaloyl-1H-indol-4-yl)butan-2-one (3la)



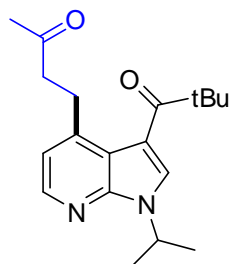
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1) give **3la** as a colorless liquid (43.2 mg, 66% yield). ¹H NMR (CDCl₃, 400 MHz): δ 7.61 (s, 1H), 6.93 (d, J = 7.6 Hz, 1H), 6.88 (d, J = 7.4 Hz, 1H), 5.25-5.18 (m, 1H), 3.07 (t, J = 7.3 Hz, 2H), 2.79 (t, J = 7.3 Hz, 2H), 2.72 (s, 3H), 2.17 (s, 3H), 1.58 (d, J = 6.6 Hz, 6H), 1.39 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ 209.3, 206.9, 135.2, 132.8, 126.6, 126.1, 125.8, 122.2, 118.7, 116.1, 48.3, 44.9, 44.8, 29.8, 28.5, 28.4, 24.2, 20.8. HRMS (ESI) m/z calcd for $C_{21}H_{29}NNaO_2$ ($M+Na$)⁺ 350.2091, found 350.2089.

4-(7-bromo-1-isopropyl-3-pivaloyl-1H-indol-4-yl)butan-2-one (3ma)



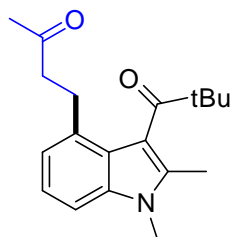
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1) give **3ma** as a white solid (64.9 mg, 83% yield), m.p. 136-138 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.62 (s, 1H), 7.35 (d, J = 7.9 Hz, 1H), 7.13 (d, J = 7.8 Hz, 1H), 5.95-5.89 (m, 1H), 3.02 (t, J = 7.5 Hz, 2H), 2.79 (t, J = 7.5 Hz, 2H), 2.16 (s, 3H), 1.54 (d, J = 6.6 Hz, 6H), 1.37 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ 208.3, 206.7, 134.3, 132.4, 128.7, 128.5, 126.4, 123.1, 116.0, 101.4, 47.7, 44.9, 44.4, 29.7, 28.1, 27.9, 23.7. HRMS (ESI) m/z calcd for $C_{20}H_{26}BrNNaO_2$ ($M+Na$)⁺ 414.1039, found 414.1025.

4-(1-isopropyl-3-pivaloyl-1H-pyrrolo[2,3-b]pyridin-4-yl)butan-2-one (3na)



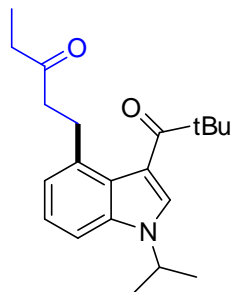
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 3:1) give **3na** as a white solid (42.7 mg, 68% yield), m.p. 128-129 °C. ¹H NMR (CDCl₃, 400 MHz): δ 8.24 (d, *J* = 4.8 Hz, 1H), 7.83 (s, 1H), 6.98 (d, *J* = 4.8 Hz, 1H), 5.27-5.20 (m, 1H), 3.26 (t, *J* = 7.4 Hz, 2H), 2.79 (t, *J* = 7.5 Hz, 2H), 2.17 (s, 3H), 1.55 (d, *J* = 6.7 Hz, 6H), 1.40 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ 208.3, 204.3, 147.4, 145.7, 144.0, 127.7, 119.3, 118.6, 113.9, 46.1, 44.7, 44.6, 29.9, 28.9, 28.8, 22.9. HRMS (ESI) *m/z* calcd for C₁₉H₂₆N₂NaO₂ (M+Na)⁺ 337.1886, found 337.1890.

4-(1,2-dimethyl-3-pivaloyl-1H-indol-4-yl)butan-2-one (3oa)



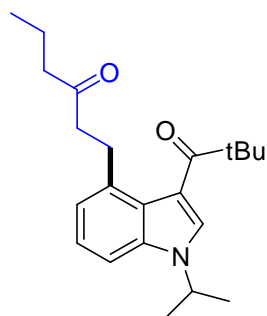
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1) give **3oa** as a white solid (43.7 mg, 73% yield), m.p 107-109 °C. ¹H NMR (CDCl₃, 400 MHz): δ 7.15-7.09 (m, 2H), 6.90-6.86 (m, 1H), 3.65 (s, 3H), 2.93 (t, *J* = 7.4 Hz, 2H), 2.72 (t, *J* = 7.3 Hz, 2H), 2.37 (s, 3H), 2.13 (s, 3H), 1.27 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ 215.9, 208.3, 136.7, 132.3, 132.1, 124.7, 121.8, 120.2, 114.1, 107.1, 46.4, 44.8, 29.9, 29.6, 28.1, 27.9, 12.5. HRMS (ESI) *m/z* calcd for C₁₉H₂₅NNaO₂ (M+Na)⁺ 322.1778, found 322.1775.

1-(1-isopropyl-3-pivaloyl-1H-indol-4-yl)pentan-3-one (3ab)



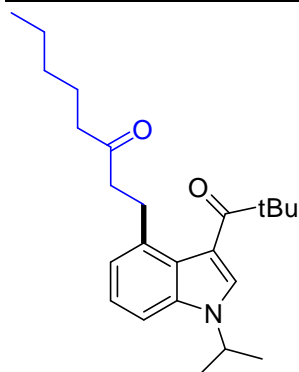
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1) give **3ab** as a brown liquid (60.2 mg, 92% yield). ¹H NMR (CDCl₃, 400 MHz): δ 7.69 (s, 1H), 7.27 (d, *J* = 7.9 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.04 (t, *J* = 7.0 Hz, 1H), 4.74-4.68 (m, 1H), 3.23 (t, *J* = 7.6 Hz, 2H), 2.81 (t, *J* = 7.6 Hz, 2H), 2.47 (q, *J* = 7.3 Hz, 2H), 1.58 (d, *J* = 6.6 Hz, 6H), 1.42 (s, 9H), 1.07 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ 211.5, 205.5, 136.2, 135.5, 126.2, 125.4, 122.8, 122.6, 115.5, 107.7, 47.3, 44.6, 43.7, 35.6, 28.9, 28.6, 22.5, 7.7. HRMS (ESI) *m/z* calcd for C₂₁H₂₉NNaO₂ (M+Na)⁺ 350.2091, found 350.2092.

1-(1-isopropyl-3-pivaloyl-1H-indol-4-yl)hexan-3-one (3ac)



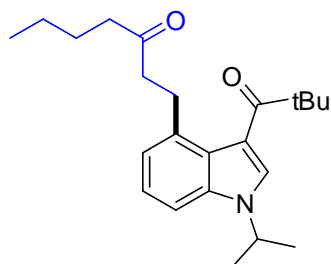
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1) give **3ac** as a brown liquid (51.8 mg, 76% yield). ^1H NMR (CDCl_3 , 400 MHz): δ 7.68 (s, 1H), 7.27 (d, $J = 8.2$ Hz, 1H), 7.22 (t, $J = 8.1$ Hz, 1H), 7.04 (t, $J = 7.0$ Hz, 1H), 4.74-4.68 (m, 1H), 3.22 (t, $J = 7.6$ Hz, 2H), 2.78 (t, $J = 7.5$ Hz, 2H), 2.43 (t, $J = 7.3$ Hz, 2H), 2.62 (t, $J = 7.4$ Hz, 2H), 1.58 (d, $J = 6.7$ Hz, 6H), 1.42 (s, 9H), 0.92 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 211.2, 205.6, 136.2, 135.6, 126.2, 125.5, 122.9, 122.7, 115.6, 107.8, 47.4, 44.7, 44.6, 44.2, 28.9, 28.7, 22.6, 17.2, 13.8. HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{31}\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$ 364.2247, found 364.2252.

1-(1-isopropyl-3-pivaloyl-1H-indol-4-yl)octan-3-one (3ad)



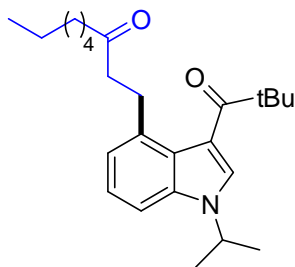
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1) give **3ad** as a brown liquid (51.7 mg, 70% yield). ^1H NMR (CDCl_3 , 400 MHz): δ 7.68 (s, 1H), 7.27 (d, $J = 8.2$ Hz, 1H), 7.22 (t, $J = 8.2$ Hz, 1H), 7.04 (t, $J = 7.0$ Hz, 1H), 4.74-4.68 (m, 1H), 3.22 (t, $J = 7.8$ Hz, 2H), 2.78 (t, $J = 7.5$ Hz, 2H), 2.44 (t, $J = 7.4$ Hz, 2H), 1.59 (q, $J = 7.4$ Hz, 2H), 1.58 (d, $J = 6.7$ Hz, 6H), 1.43 (s, 9H), 1.33-1.25 (m, 4H), 0.89 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 211.6, 205.8, 136.4, 135.8, 126.4, 125.7, 123.1, 122.9, 115.8, 107.9, 47.5, 44.8, 44.3, 42.8, 31.6, 29.2, 28.9, 23.7, 22.8, 22.6, 14.1. HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{35}\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$ 392.2560, found 392.2556.

1-(1-isopropyl-3-pivaloyl-1H-indol-4-yl)heptan-3-one (3ae)



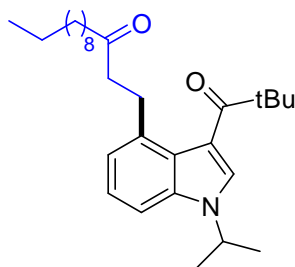
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1) give **3ae** as a brown liquid (51.8 mg, 73% yield). ^1H NMR (CDCl_3 , 400 MHz): δ 7.66 (s, 1H), 7.27-7.18 (m, 2H), 7.02 (d, $J = 7.0$ Hz, 1H), 4.73-4.66 (m, 1H), 3.19 (t, $J = 7.4$ Hz, 2H), 2.77 (t, $J = 7.4$ Hz, 2H), 2.43 (t, $J = 7.4$ Hz, 2H), 1.59 -1.52 (m, 8H), 1.41 (s, 9H), 1.33-1.27 (m, 2H), 0.89 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 211.4, 205.6, 136.3, 135.7, 126.2, 125.5, 122.9, 122.7, 115.6, 107.8, 47.4, 44.7, 44.2, 42.4, 29.0, 28.7, 25.9, 22.6, 22.4, 13.9. HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{33}\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$ 378.2404, found 378.2405.

1-(1-isopropyl-3-pivaloyl-1H-indol-4-yl)nonan-3-one (3af)



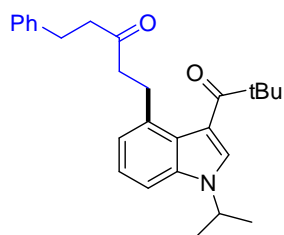
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1) give **3af** as a brown liquid (52.1 mg, 68% yield). ^1H NMR (CDCl_3 , 400 MHz): δ 7.66 (s, 1H), 7.27-7.18 (m, 2H), 7.02 (d, $J = 7.0$ Hz, 1H), 4.73-4.66 (m, 1H), 3.19 (t, $J = 7.4$ Hz, 2H), 2.76 (t, $J = 7.4$ Hz, 2H), 2.43 (t, $J = 7.4$ Hz, 2H), 1.58 -1.52 (m, 8H), 1.41 (s, 9H), 1.32-1.25 (m, 6H), 0.88 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 211.4, 205.6, 136.3, 135.7, 126.2, 125.5, 122.9, 122.7, 115.6, 107.8, 47.4, 44.7, 44.2, 42.7, 31.6, 29.0, 28.9, 28.7, 23.8, 22.6, 22.5, 14.1. HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{37}\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$ 406.2717, found 406.2725.

1-(1-isopropyl-3-pivaloyl-1H-indol-4-yl)tridecan-3-one (3ag)



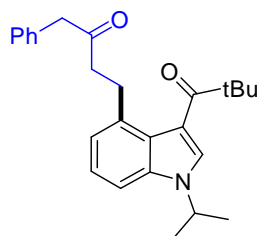
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1) give **3ag** as a brown liquid (57.9 mg, 66% yield). ^1H NMR (CDCl_3 , 400 MHz): δ 7.66 (s, 1H), 7.28-7.19 (m, 2H), 7.03 (d, $J = 6.9$ Hz, 1H), 4.74-4.68 (m, 1H), 3.20 (t, $J = 7.6$ Hz, 2H), 2.77 (t, $J = 7.7$ Hz, 2H), 2.43 (t, $J = 7.4$ Hz, 2H), 1.58 -1.57 (m, 8H), 1.42 (s, 9H), 1.27 (s, 14H), 0.90 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 211.4, 205.6, 136.3, 135.7, 126.1, 125.5, 122.9, 122.7, 115.6, 107.8, 47.4, 44.7, 44.2, 42.7, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 28.9, 28.7, 23.8, 22.7, 22.6, 14.1. HRMS (ESI) m/z calcd for $\text{C}_{29}\text{H}_{45}\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$ 462.3343, found 462.3327.

1-(1-isopropyl-3-pivaloyl-1H-indol-4-yl)-5-phenylpentan-3-one (3ah)



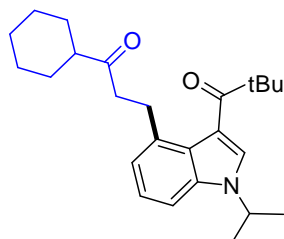
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1) give **3ah** as a brown liquid (70.1 mg, 87% yield). ^1H NMR (CDCl_3 , 400 MHz): δ 7.71 (s, 1H), 7.33-7.28 (m, 3H), 7.24-7.21 (m, 4H), 7.05 (d, $J = 7.0$ Hz, 1H), 4.76-4.69 (m, 1H), 3.26 (t, $J = 7.6$ Hz, 2H), 2.95 (t, $J = 7.5$ Hz, 2H), 2.85-2.78 (m, 4H), 1.60 (d, $J = 6.6$ Hz, 6H), 1.44 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 210.0, 205.5, 141.2, 136.2, 135.4, 128.3, 128.2, 126.3, 125.8, 125.4, 122.9, 122.7, 115.5, 107.8, 47.3, 44.6, 44.2, 44.1, 29.6, 28.9, 28.6, 22.5. HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{33}\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$ 426.2404, found 426.2417.

4-(1-isopropyl-3-pivaloyl-1H-indol-4-yl)-1-phenylbutan-2-one (3ai)



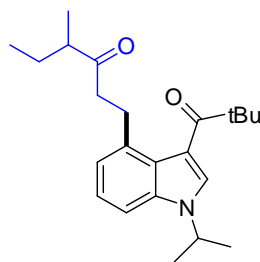
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1) give **3ai** as a brown liquid (59.1 mg, 76% yield). ^1H NMR (CDCl_3 , 400 MHz): δ 7.68 (s, 1H), 7.32-7.18 (m, 7H), 7.01 (d, $J = 7.0$ Hz, 1H), 4.75-4.68 (m, 1H), 3.73 (s, 2H), 3.24 (t, $J = 7.6$ Hz, 2H), 2.84 (t, $J = 7.6$ Hz, 2H), 1.58 (d, $J = 6.6$ Hz, 6H), 1.39 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 208.3, 205.5, 136.3, 135.5, 134.5, 129.5, 128.5, 126.7, 126.3, 125.5, 122.9, 122.8, 115.6, 107.9, 49.9, 47.4, 44.7, 43.5, 29.0, 28.7, 22.7. HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{31}\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$ 412.2247, found 412.2253.

1-(4-(3-cyclohexyl-3-oxopropyl)-1-isopropyl-1H-indol-3-yl)-2,2-dimethylpropan-1-one(3aj)



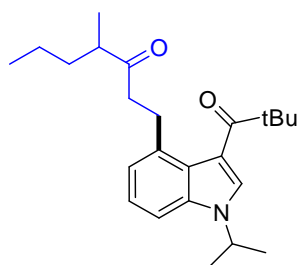
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 6:1) give **3aj** as a colorless liquid (42.7 mg, 56% yield). ^1H NMR (CDCl_3 , 400 MHz): δ 7.65 (s, 1H), 7.28-7.19 (m, 2H), 7.03 (d, $J = 7.0$ Hz, 1H), 4.74-4.67 (m, 1H), 3.17 (t, $J = 7.6$ Hz, 2H), 2.83 (t, $J = 7.8$ Hz, 2H), 2.41-2.35 (m, 1H), 1.86-1.83 (m, 2H), 1.78-1.75 (m, 2H), 1.67-1.61 (m, 1H), 1.58 (d, $J = 6.6$ Hz, 6H), 1.42 (s, 9H), 1.36-1.17 (m, 5H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 214.2, 205.9, 136.4, 136.0, 126.1, 125.7, 123.1, 122.8, 115.8, 107.9, 50.8, 47.5, 44.9, 44.3, 42.3, 28.9, 28.8, 28.6, 26.1, 25.9, 22.8. HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{35}\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$ 404.2560, found 404.2552.

1-(1-isopropyl-3-pivaloyl-1H-indol-4-yl)-4-methylhexan-3-one (3ak)



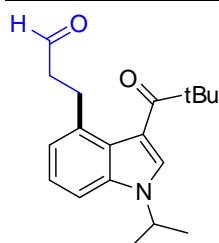
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 6:1) give **3ak** as a brown liquid (36.9 mg, 52% yield). ^1H NMR (CDCl_3 , 400 MHz): δ 7.65 (s, 1H), 7.28-7.19 (m, 2H), 7.04 (d, $J = 6.9$ Hz, 1H), 4.74-4.67 (m, 1H), 3.18 (t, $J = 7.4$ Hz, 2H), 2.83 (t, $J = 8.4$ Hz, 2H), 2.53-2.47 (m, 1H), 1.75-1.65 (m, 1H), 1.58 (d, $J = 6.6$ Hz, 6H), 1.41-1.35 (s, 10H), 1.06 (d, $J = 6.9$ Hz, 3H), 0.87 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 214.8, 205.9, 136.4, 136.0, 126.1, 125.8, 123.1, 122.9, 115.8, 107.9, 47.9, 47.5, 44.8, 42.8, 28.9, 28.7, 26.1, 22.8, 16.0, 11.8. HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{33}\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$ 378.2404, found 378.2407.

1-(1-isopropyl-3-pivaloyl-1H-indol-4-yl)-4-methylheptan-3-one (3al)



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 6:1) give **3al** as a brown liquid (40.6 mg, 55% yield). ^1H NMR (CDCl_3 , 400 MHz): δ 7.65 (s, 1H), 7.28-7.19 (m, 2H), 7.04 (d, $J = 6.9$ Hz, 1H), 4.74-4.67 (m, 1H), 3.18 (t, $J = 7.4$ Hz, 2H), 2.83 (t, $J = 8.4$ Hz, 2H), 2.60-2.52 (m, 1H), 1.58 (d, $J = 6.7$ Hz, 6H), 1.41 (s, 9H), 1.32-1.22 (m, 4H), 1.05 (d, $J = 6.9$ Hz, 3H), 0.88 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 214.8, 205.7, 136.3, 135.9, 125.9, 125.6, 122.9, 122.8, 115.7, 107.7, 47.4, 46.1, 44.7, 42.6, 35.1, 28.8, 28.6, 22.7, 20.4, 16.2, 14.1. HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{35}\text{NNaO}_2$ ($\text{M}+\text{Na}$) $^+$ 392.2560, found 392.2558.

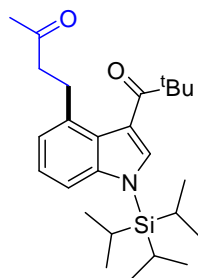
3-(1-isopropyl-3-pivaloyl-1H-indol-4-yl)propanal (3am)



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1) give **3am** as a colorless liquid (36.5 mg, 61% yield). ^1H NMR (CDCl_3 , 400 MHz): δ 9.81 (s, 1H), 7.71 (s, 1H), 7.27 (d, $J = 7.5$ Hz, 1H), 7.22 (t, $J = 7.1$ Hz, 1H), 7.03 (t, $J = 7.0$ Hz, 1H), 4.73-4.67 (m, 1H), 3.31 (t, $J = 7.5$ Hz, 2H), 2.75 (t, $J = 7.4$ Hz, 2H), 1.56 (d, $J = 6.7$ Hz, 6H), 1.40 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 205.2, 203.1, 136.4, 134.9, 126.9, 125.4, 123.0, 122.8, 115.5, 108.2, 47.5,

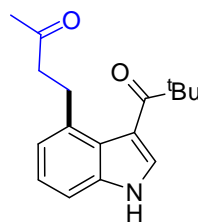
44.9, 44.7, 28.8, 27.4, 22.7. HRMS (ESI) m/z calcd for $C_{19}H_{25}NNaO_2$ ($M+Na$)⁺ 322.1778, found 322.1774.

4-(3-pivaloyl-1-(triisopropylsilyl)-1H-indol-4-yl)butan-2-one (3pa)



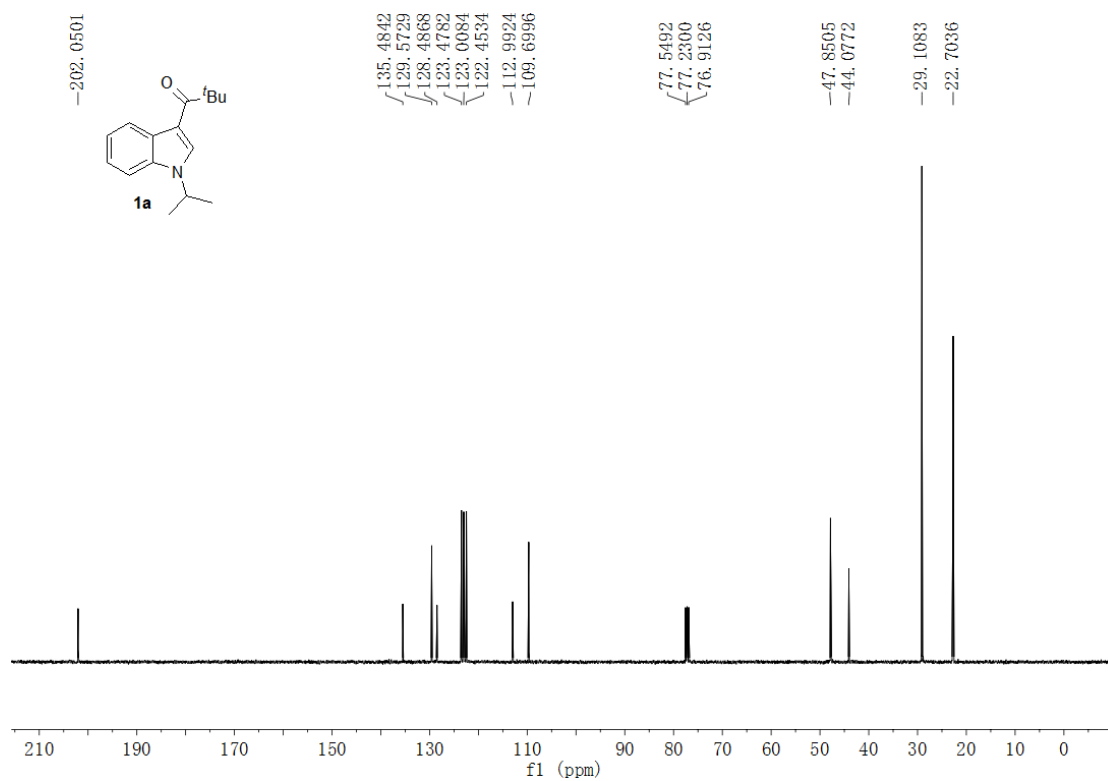
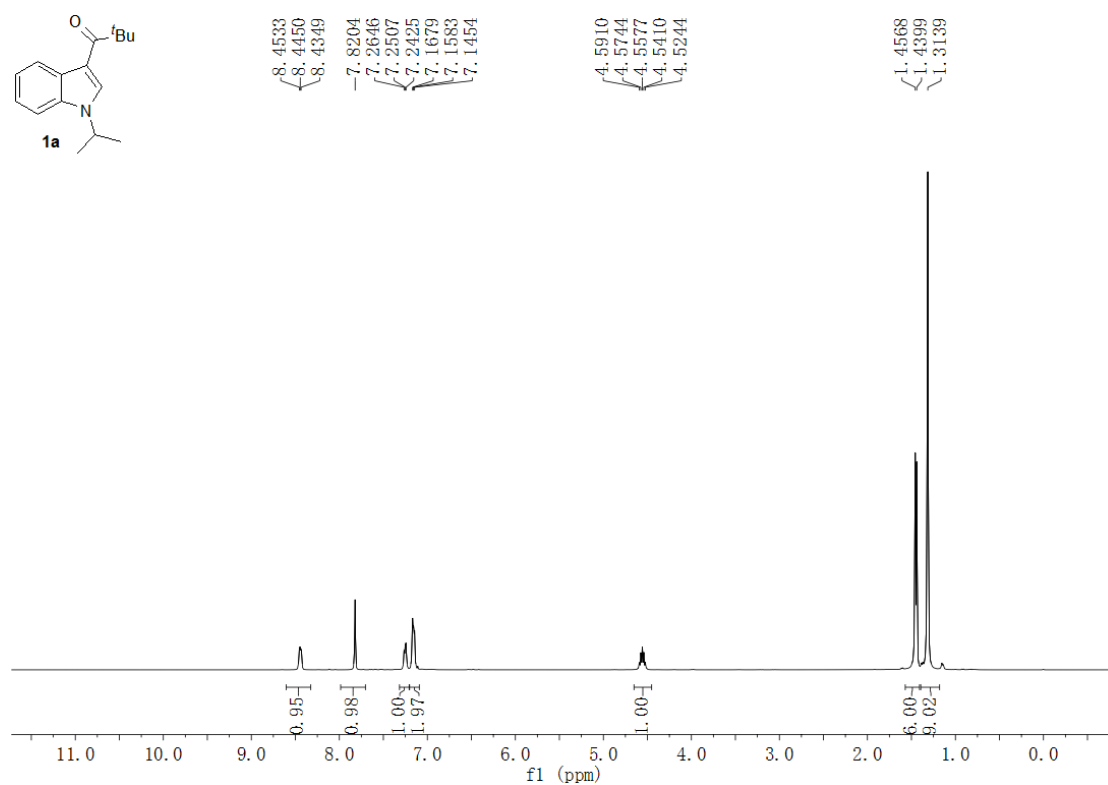
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 10:1) give **3oa** as a colorless liquid (29.9 mg, 35% yield). ¹H NMR (CDCl₃, 400 MHz): δ 7.66 (s, 1H), 7.36 (d, J = 8.3 Hz, 1H), 7.13 (d, J = 8.1 Hz, 1H), 6.99 (d, J = 7.2 Hz, 1H), 3.14 (t, J = 7.4 Hz, 2H), 2.82 (t, J = 7.4 Hz, 2H), 2.18 (s, 3H), 1.74-1.67 (m, 3H), 1.39 (s, 9H), 1.17 (d, J = 7.5 Hz, 18H). ¹³C NMR (CDCl₃, 100 MHz): δ 209.2, 206.7, 141.3, 134.8, 133.6, 127.8, 122.8, 122.5, 118.7, 112.0, 45.1, 44.9, 29.8, 28.9, 28.5, 18.1, 12.8. HRMS (ESI) m/z calcd for $C_{26}H_{41}NNaO_2Si$ ($M+Na$)⁺ 450.2799, found 450.2812.

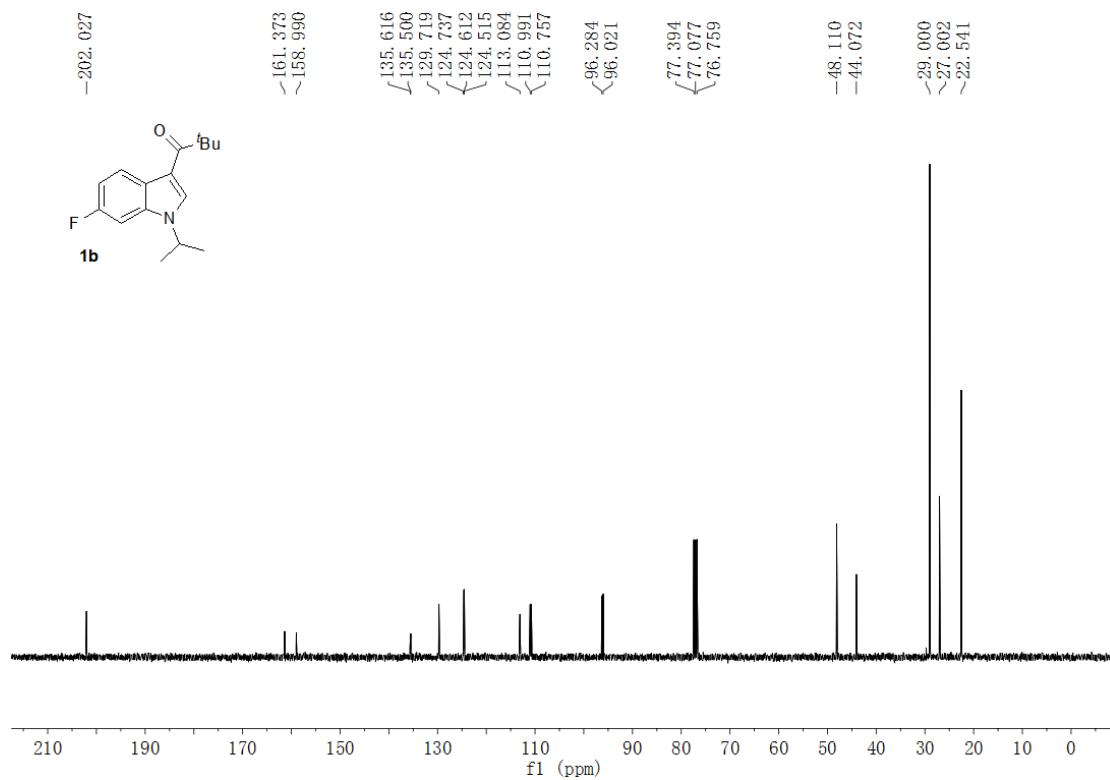
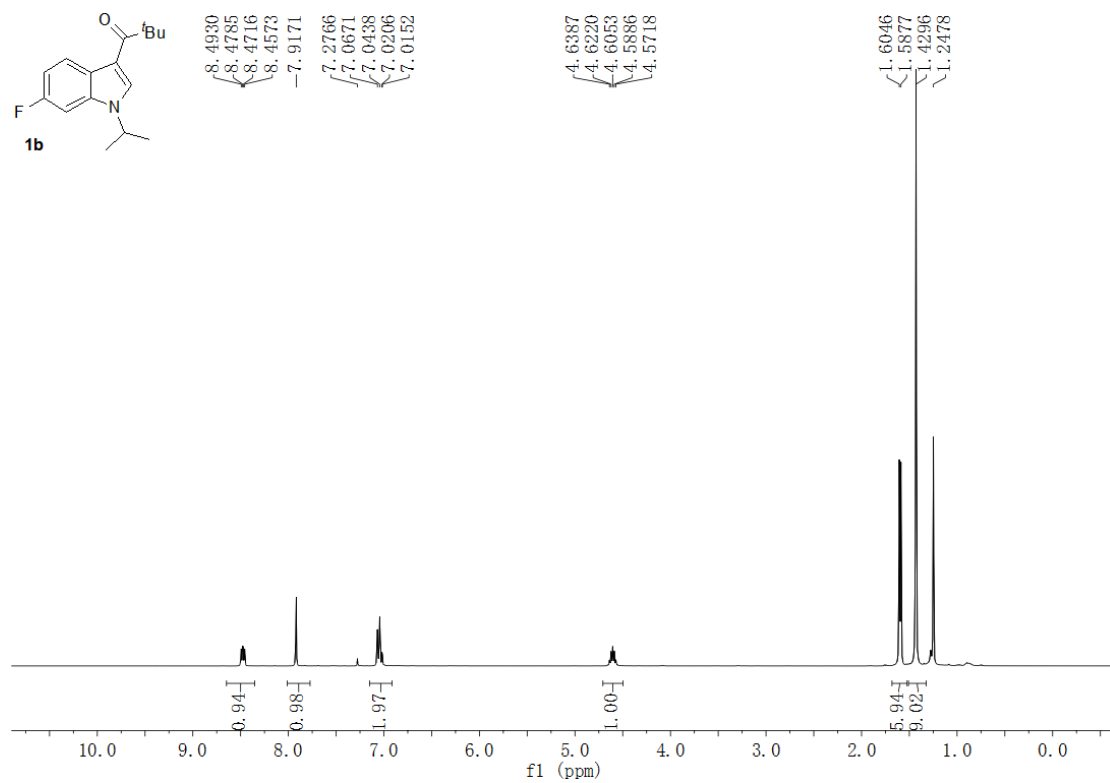
4-(3-pivaloyl-1H-indol-4-yl)butan-2-one (3qa)

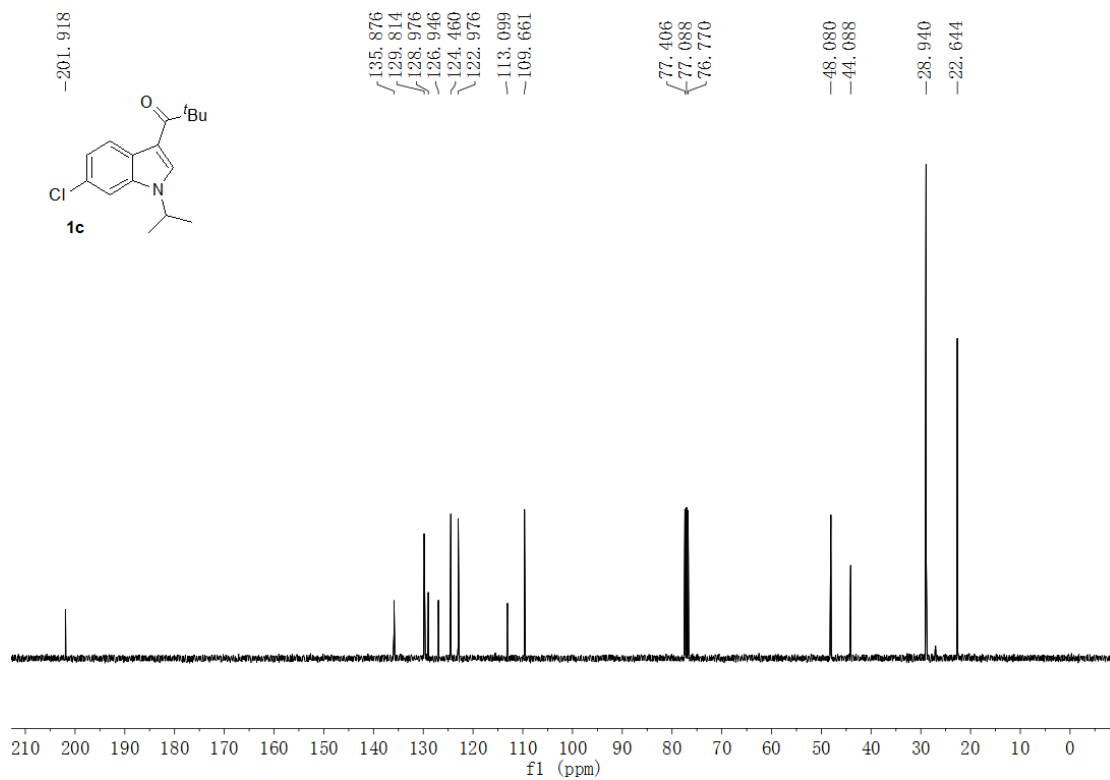
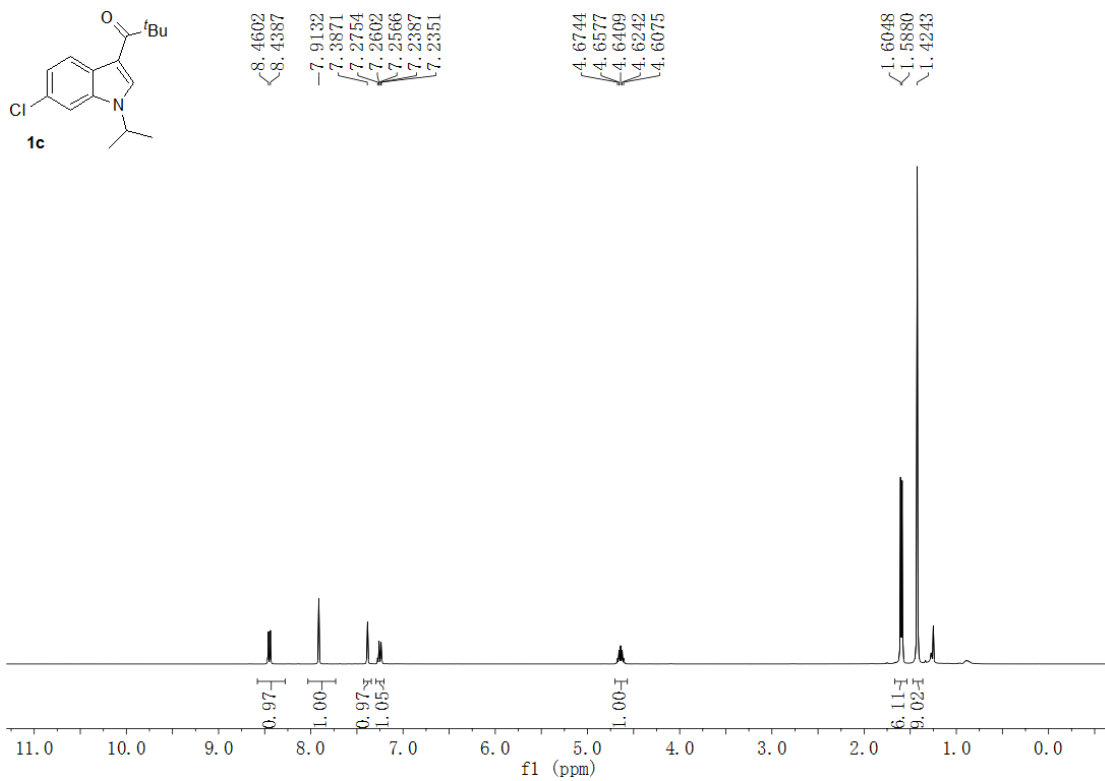


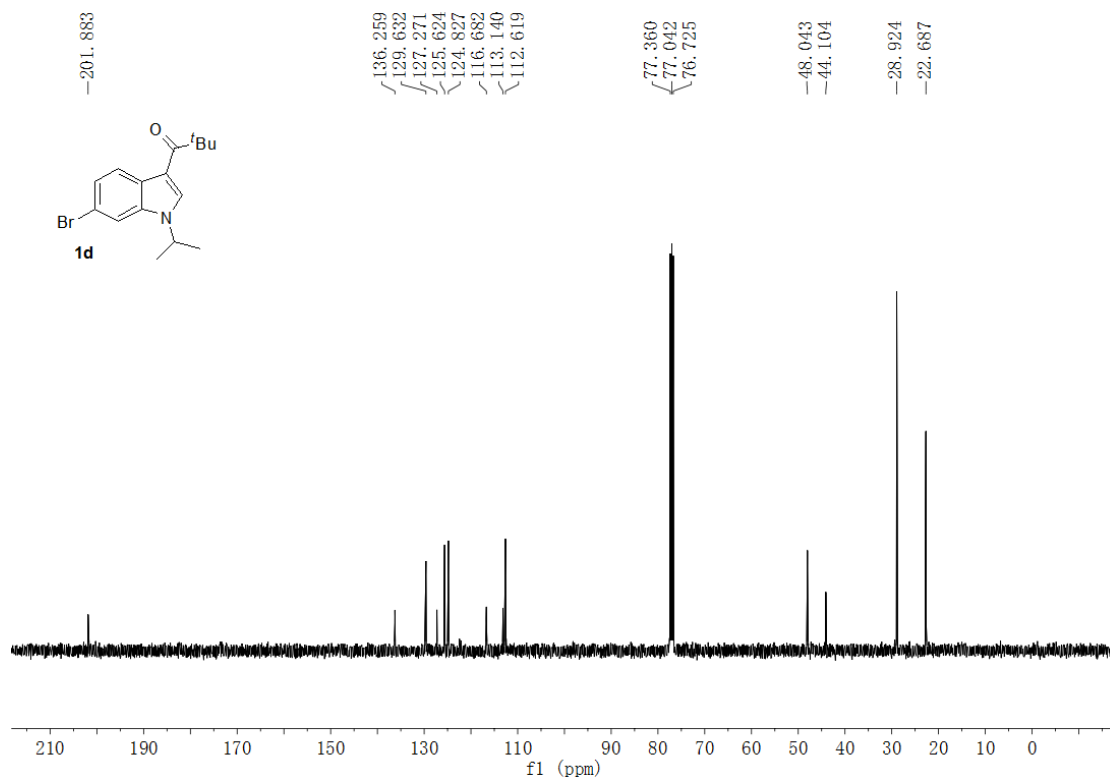
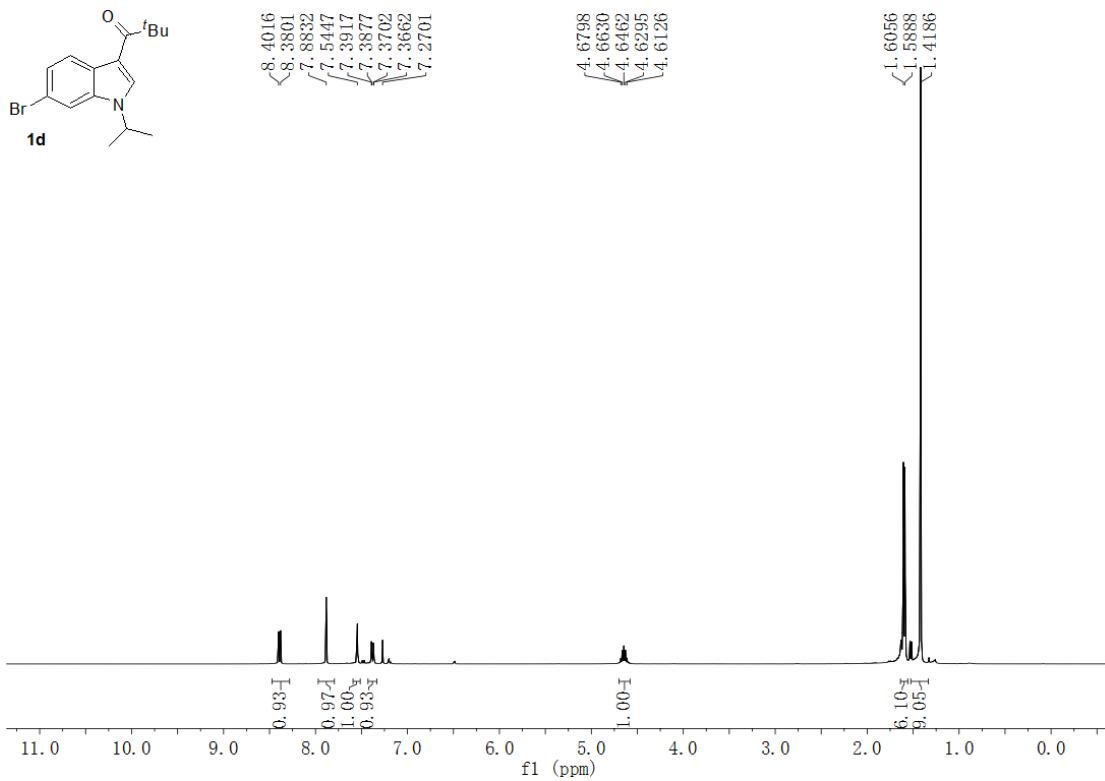
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1) give **3oa** as a colorless liquid (24.9 mg, 92% yield). ¹H NMR (CDCl₃, 300 MHz): δ 8.97 (s, 1H), 7.51 (s, 1H), 7.22-7.13 (m, 2H), 7.00 (dd, J = 6.6, 1.6 Hz, 1H), 3.21 (t, J = 7.4 Hz, 2H), 2.77 (t, J = 7.4 Hz, 2H), 2.15 (s, 3H), 1.38 (s, 9H). ¹³C NMR (CDCl₃, 75 MHz): δ 209.4, 206.5, 136.4, 134.9, 127.2, 124.5, 123.5, 122.7, 116.6, 109.7, 45.0, 44.8, 29.9, 28.9, 28.6. HRMS (ESI) m/z calcd for $C_{17}H_{21}NNaO_2$ ($M+Na$)⁺ 294.1465, found 294.1462.

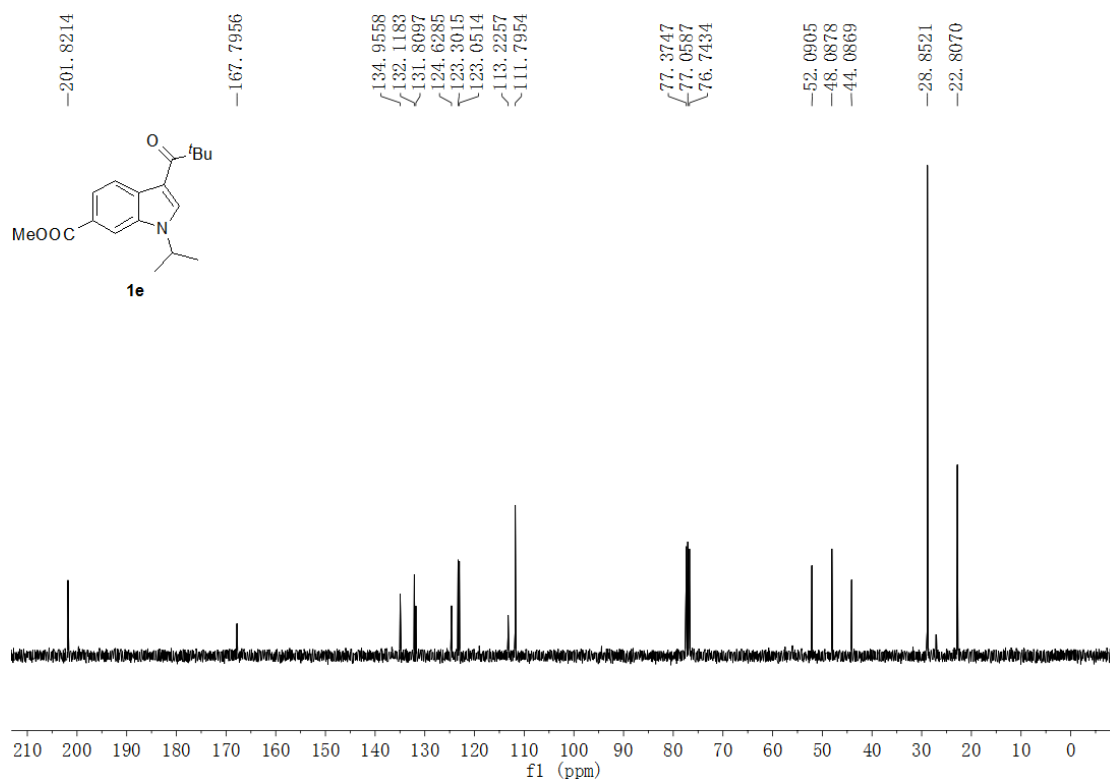
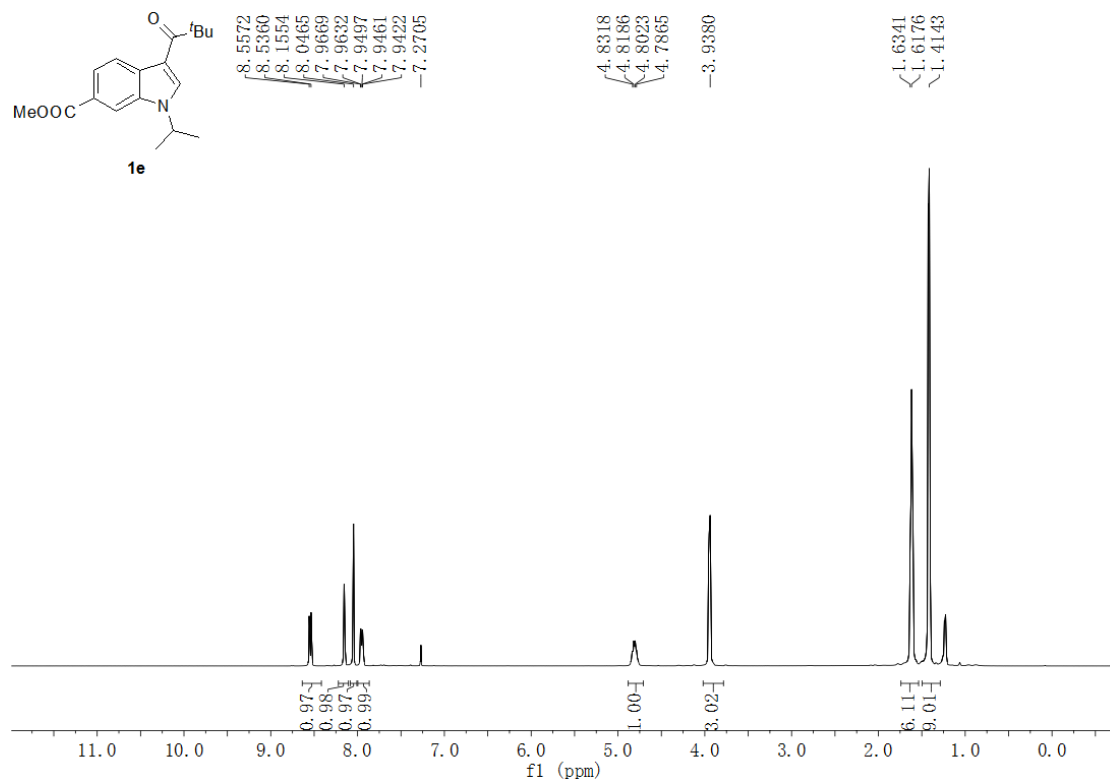
4. Copies of ^1H NMR and ^{13}C NMR spectra of the compounds 1

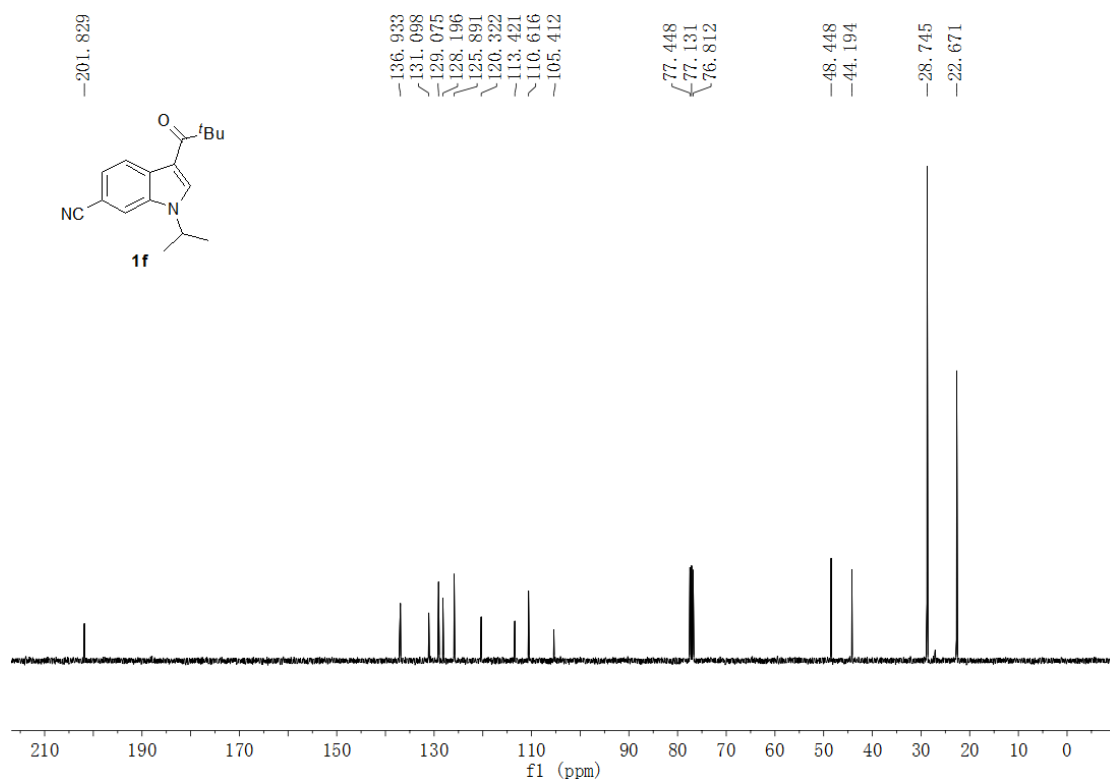
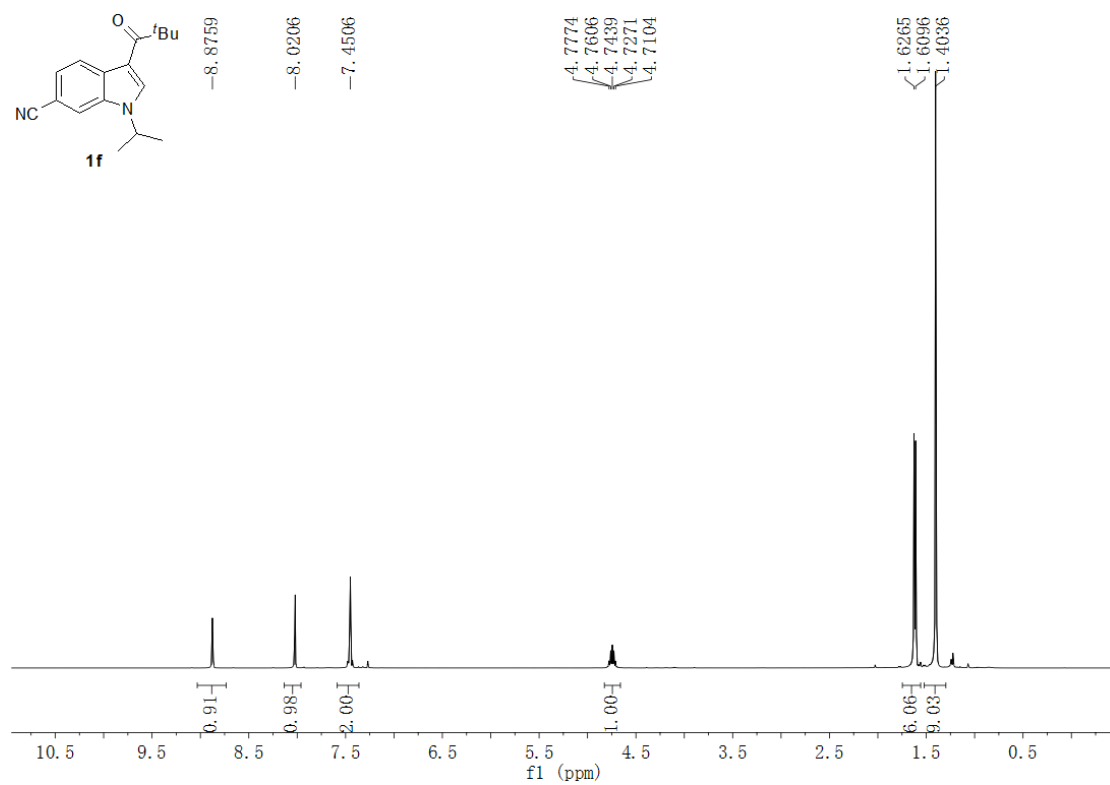


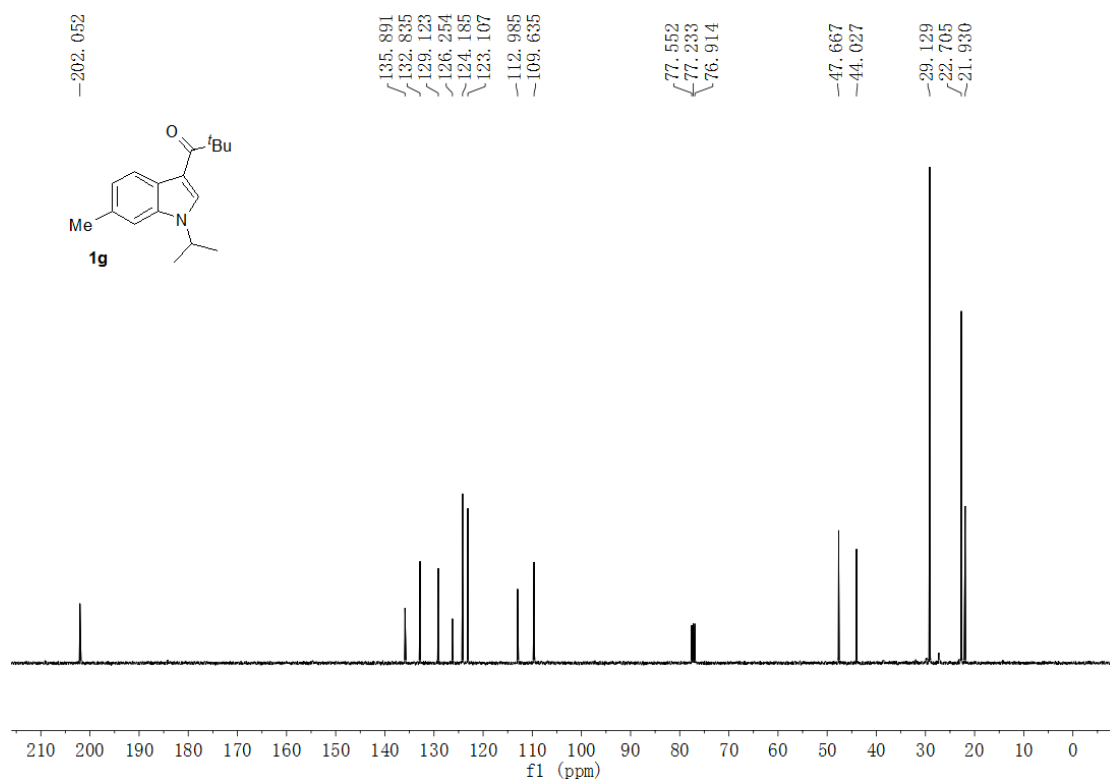
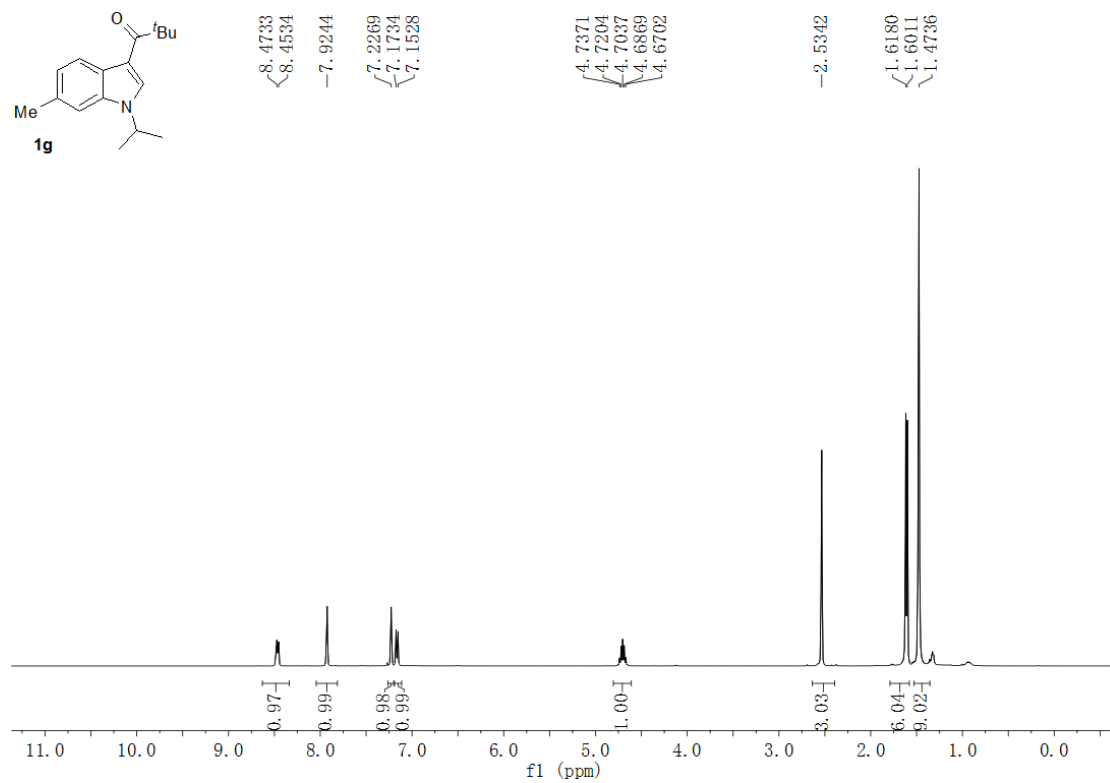


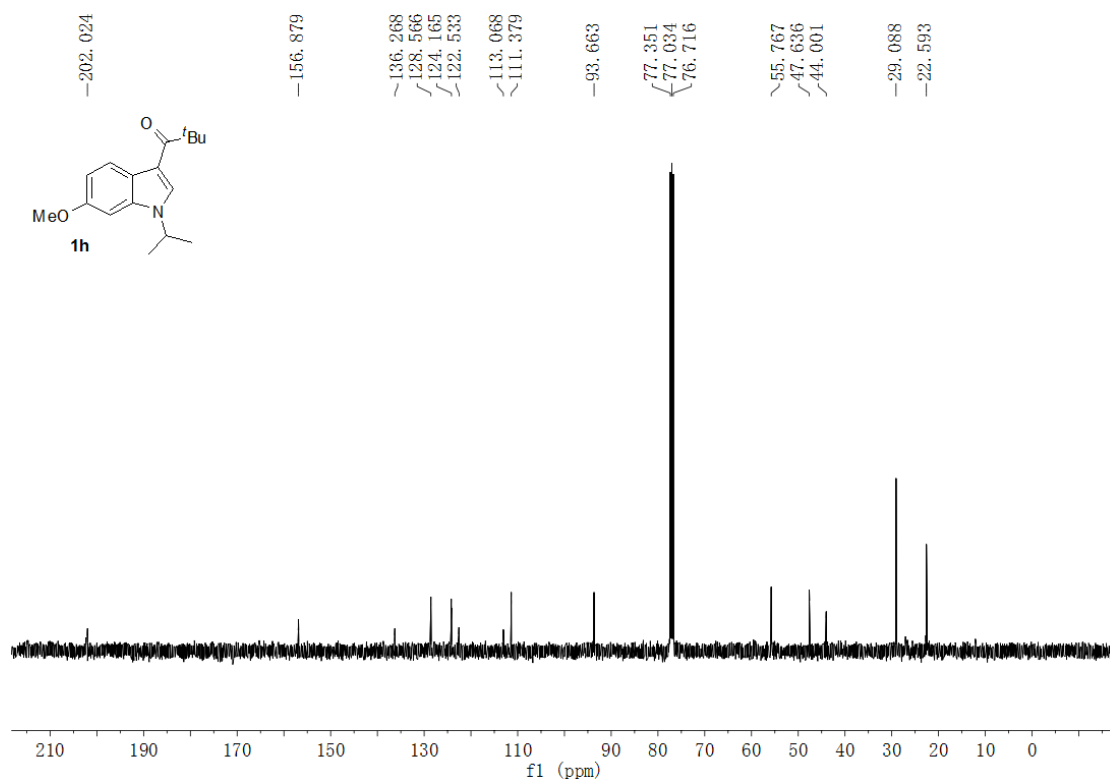
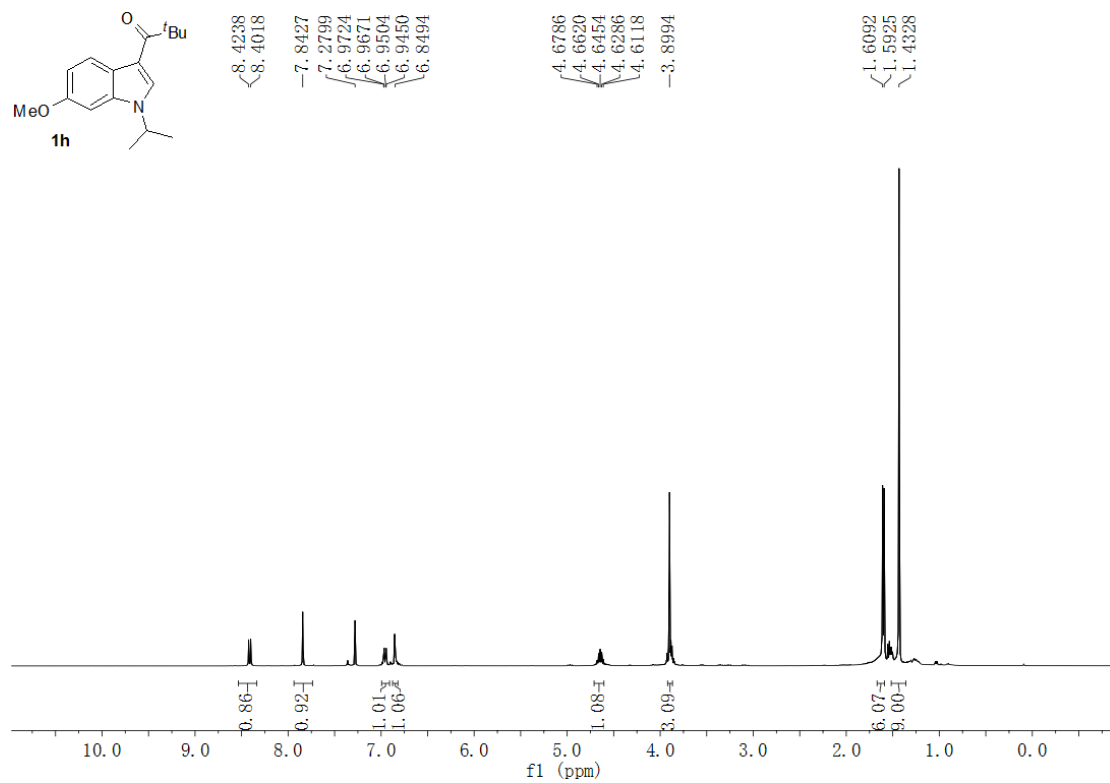


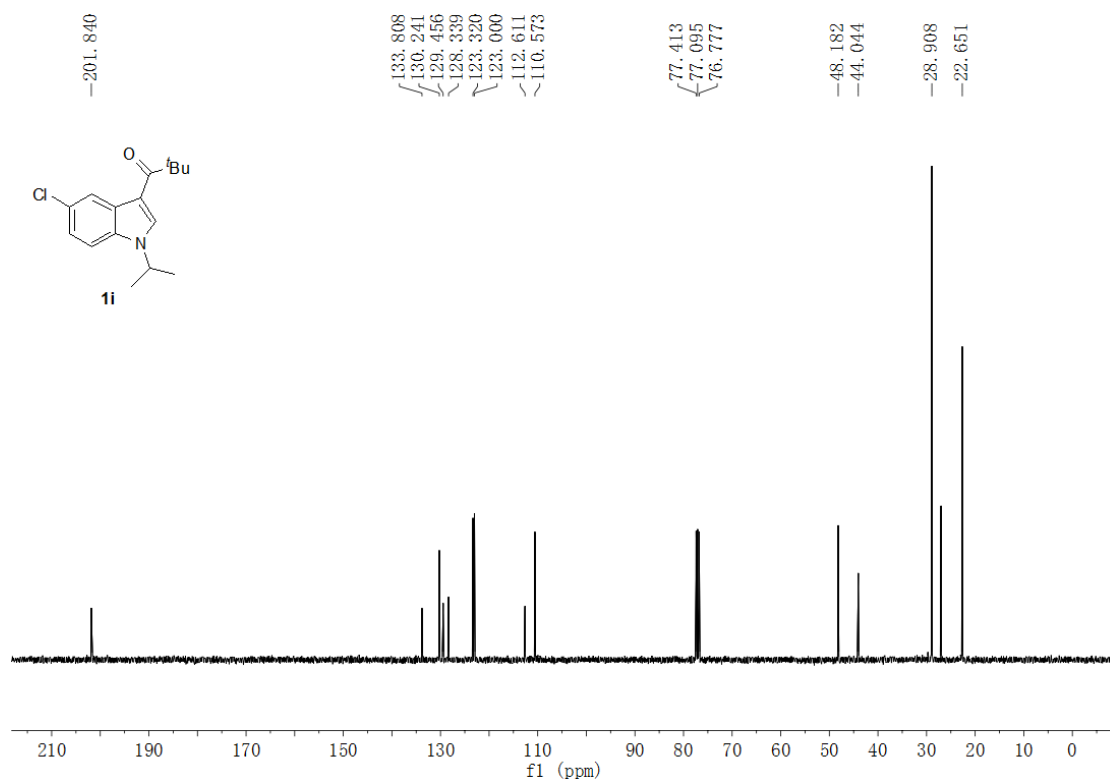
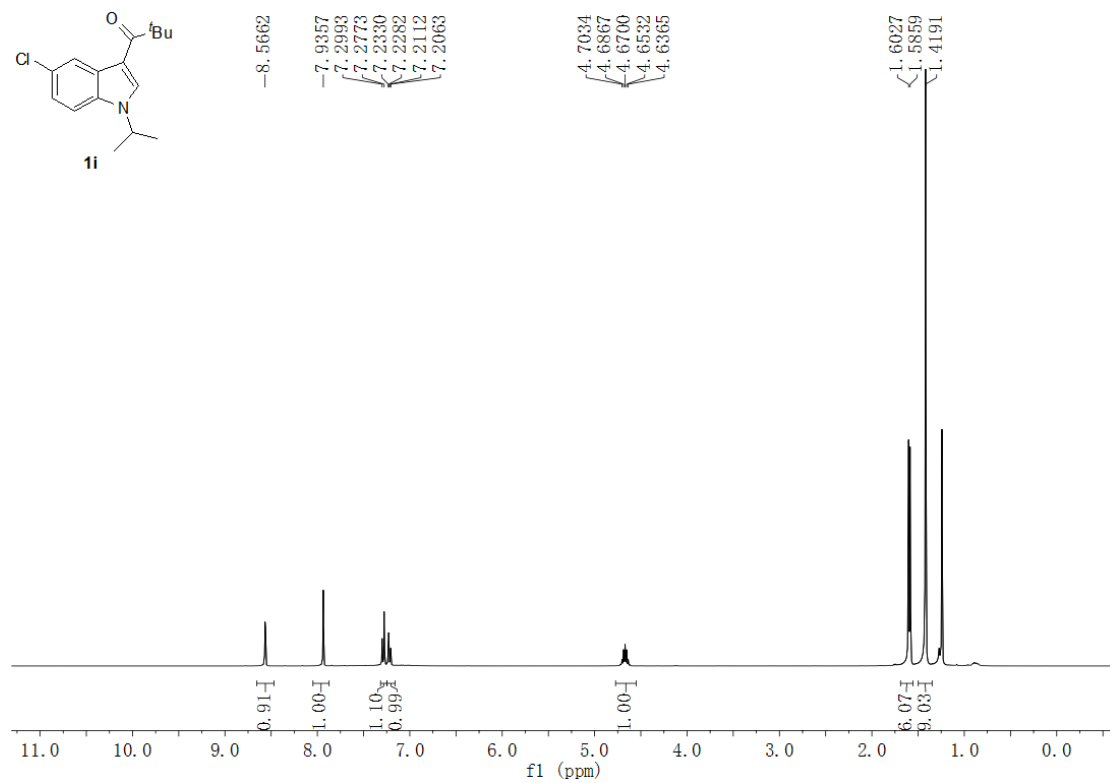


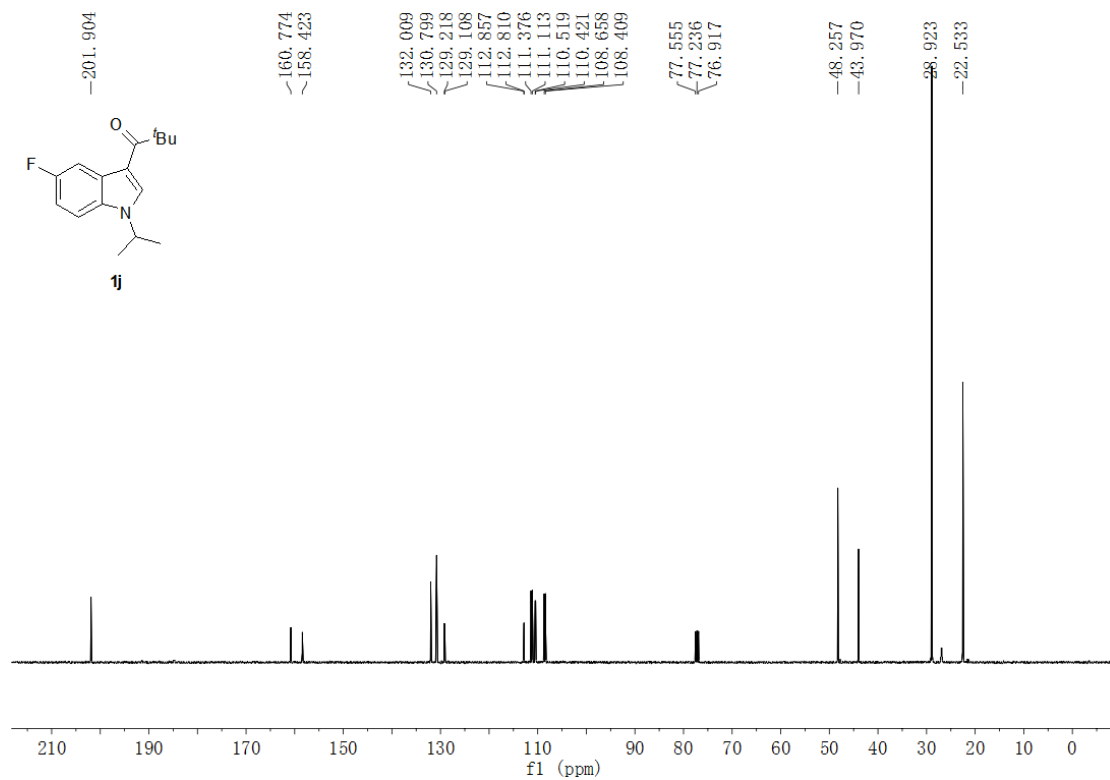
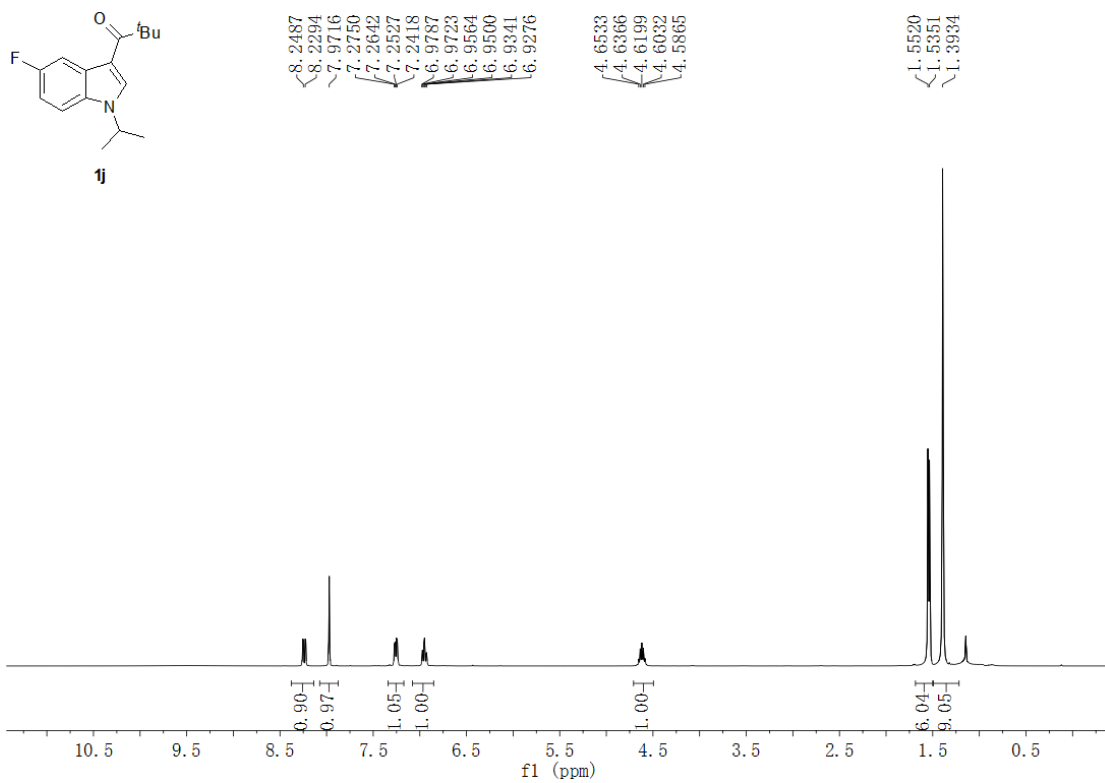


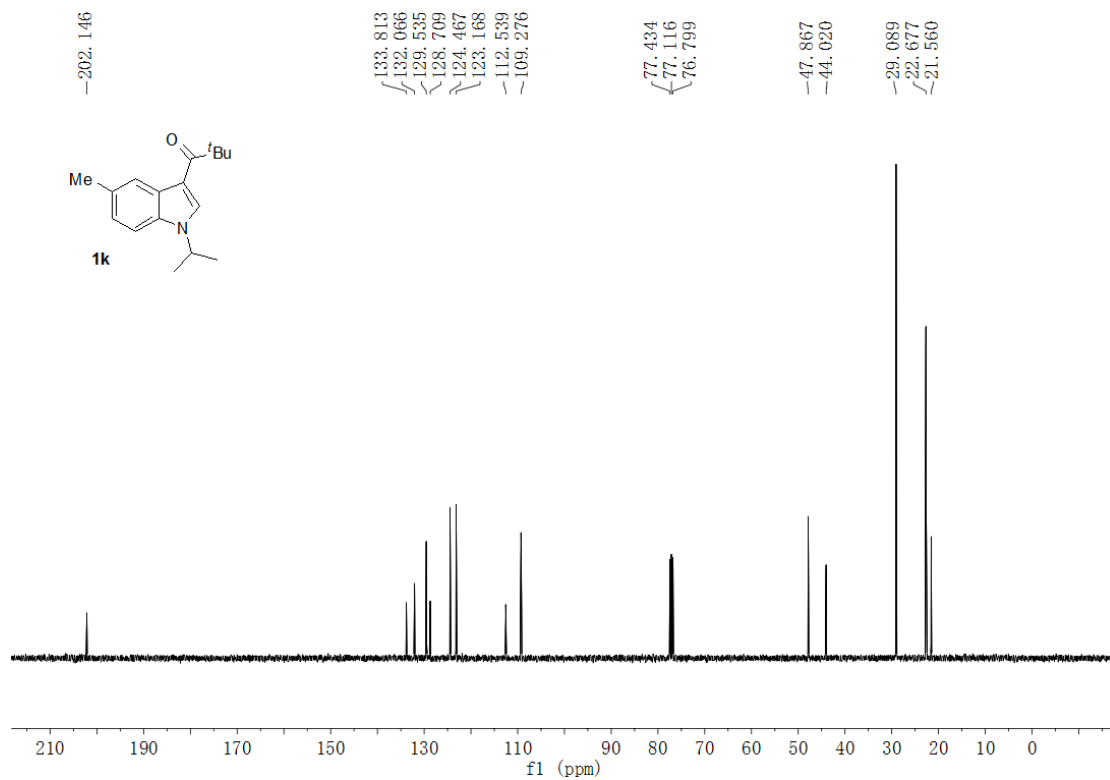
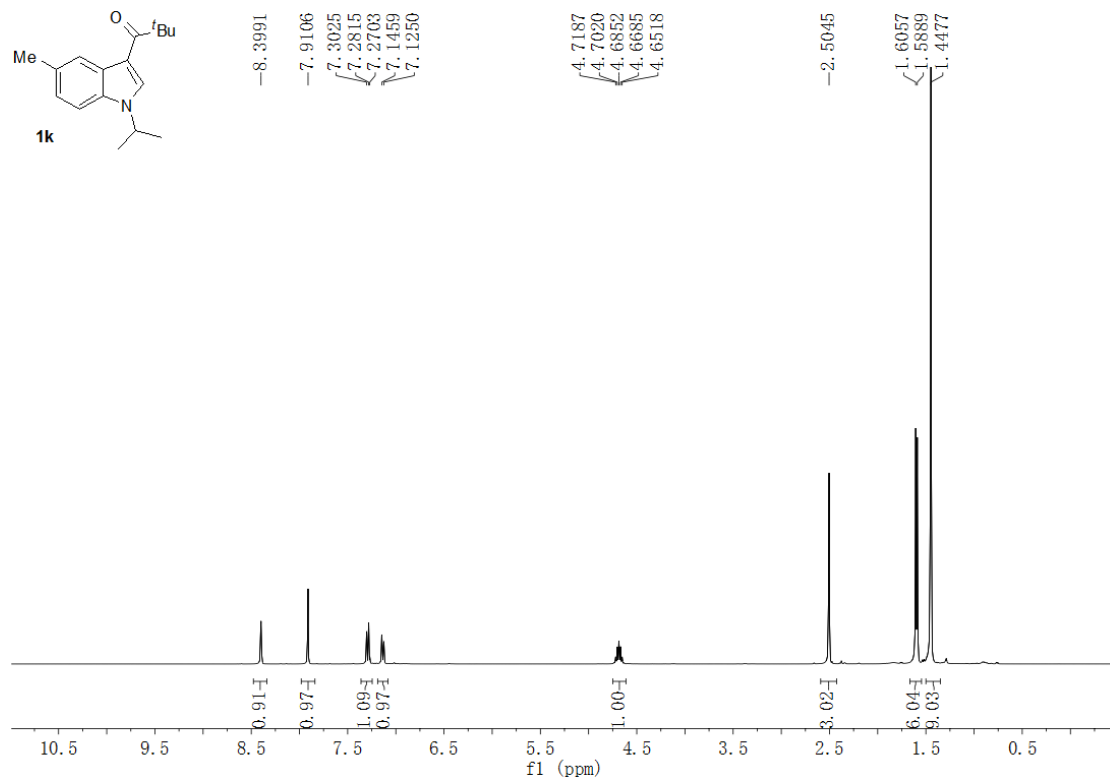


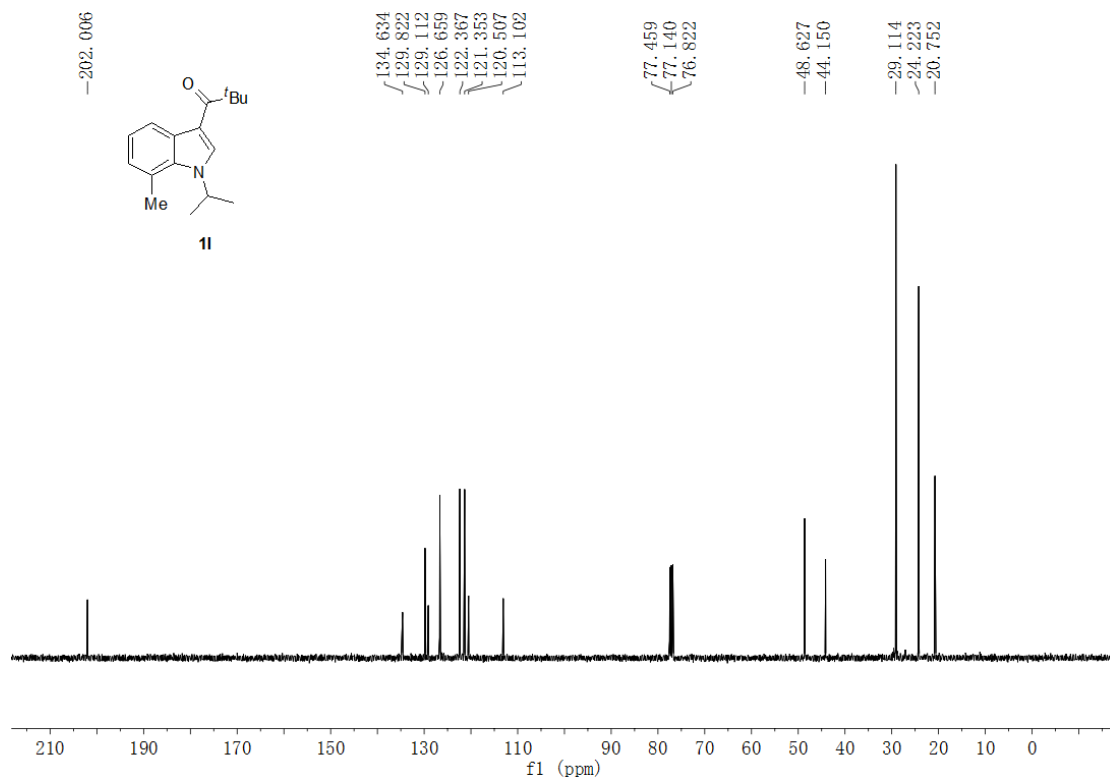
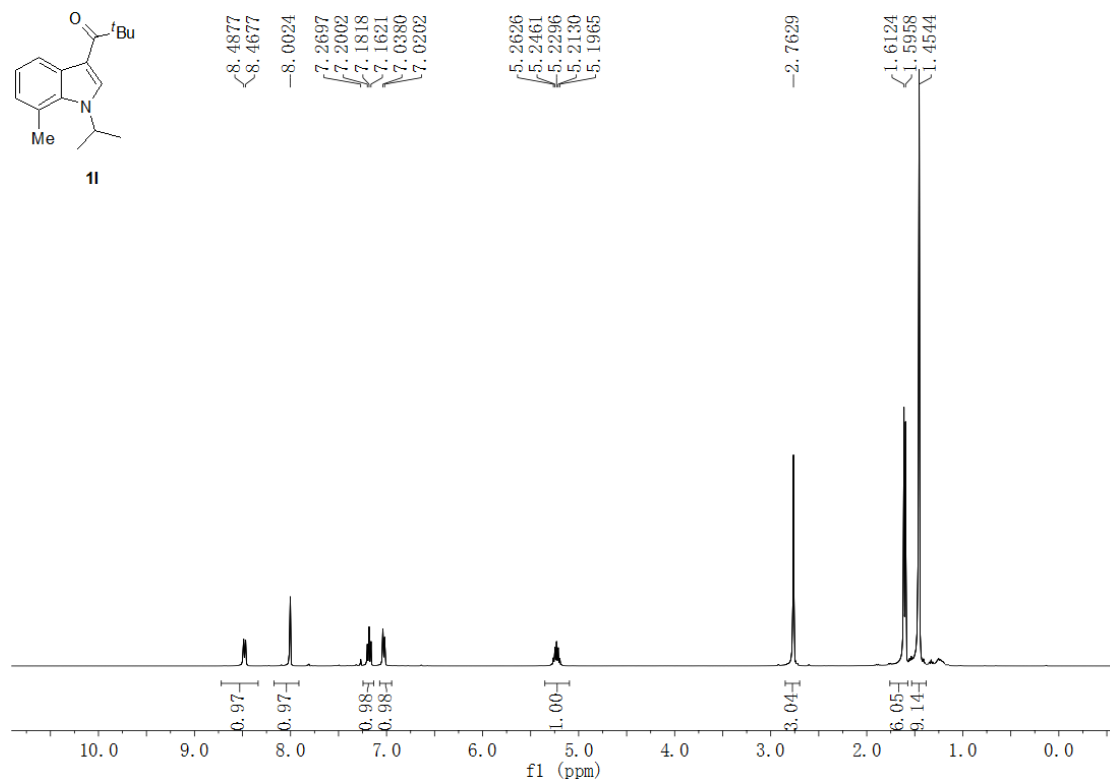


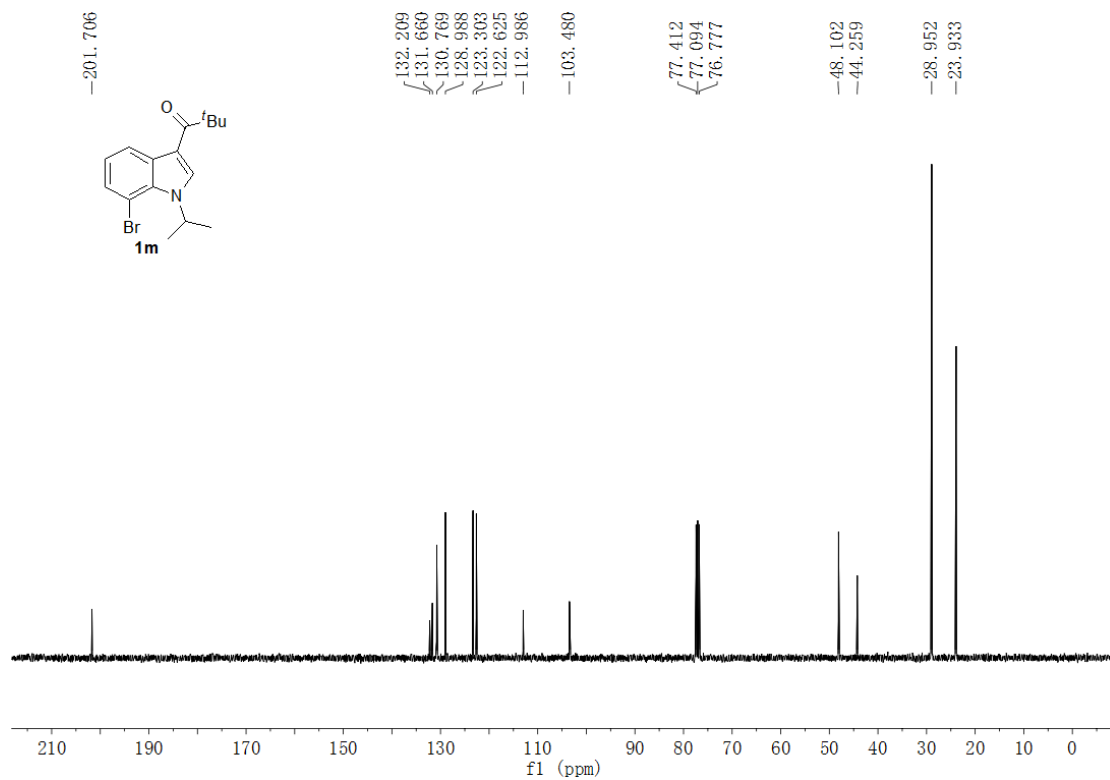
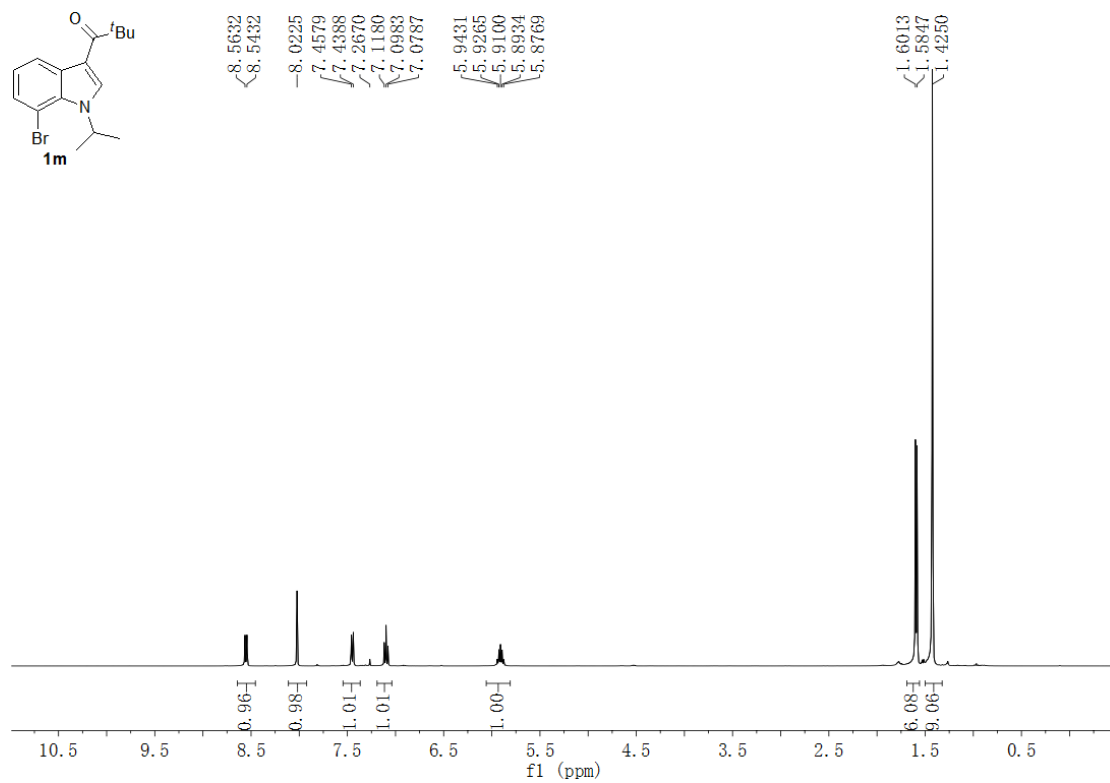


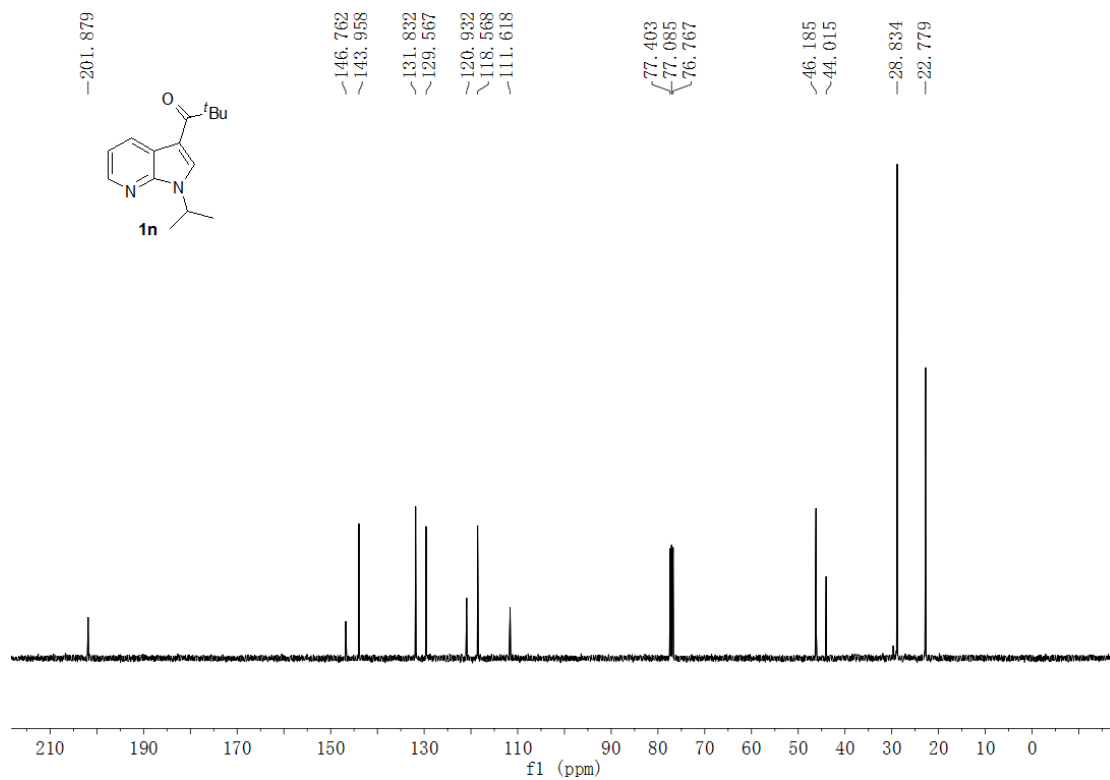
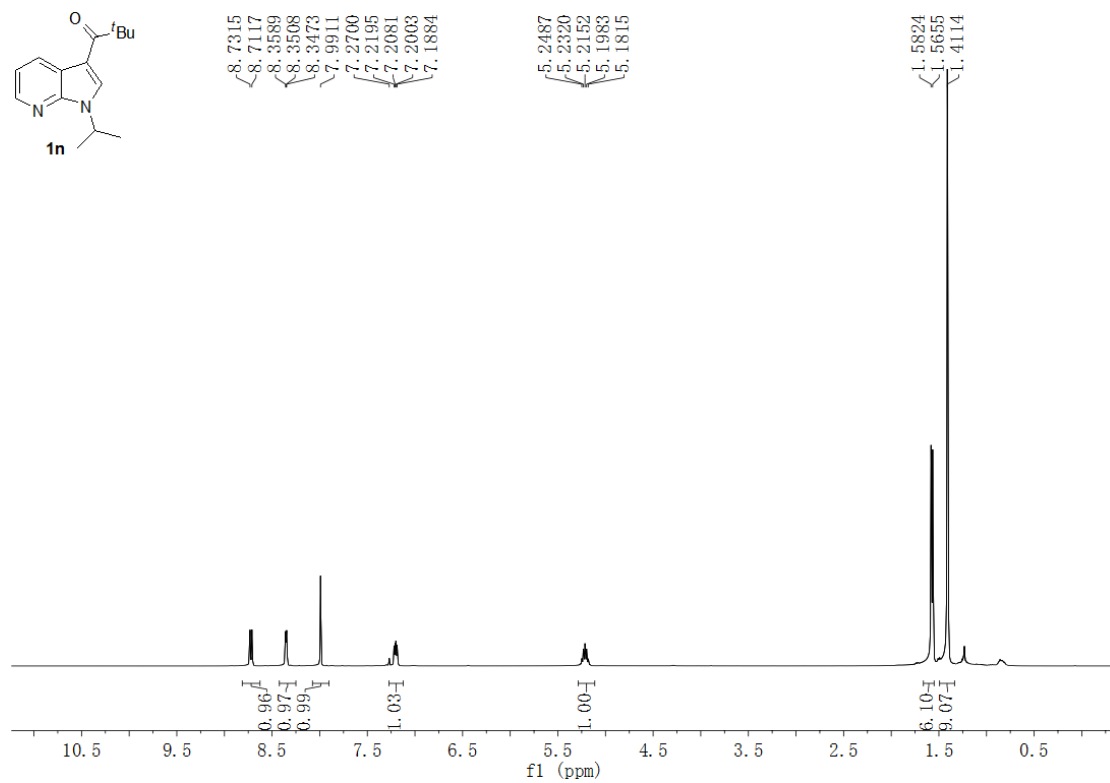


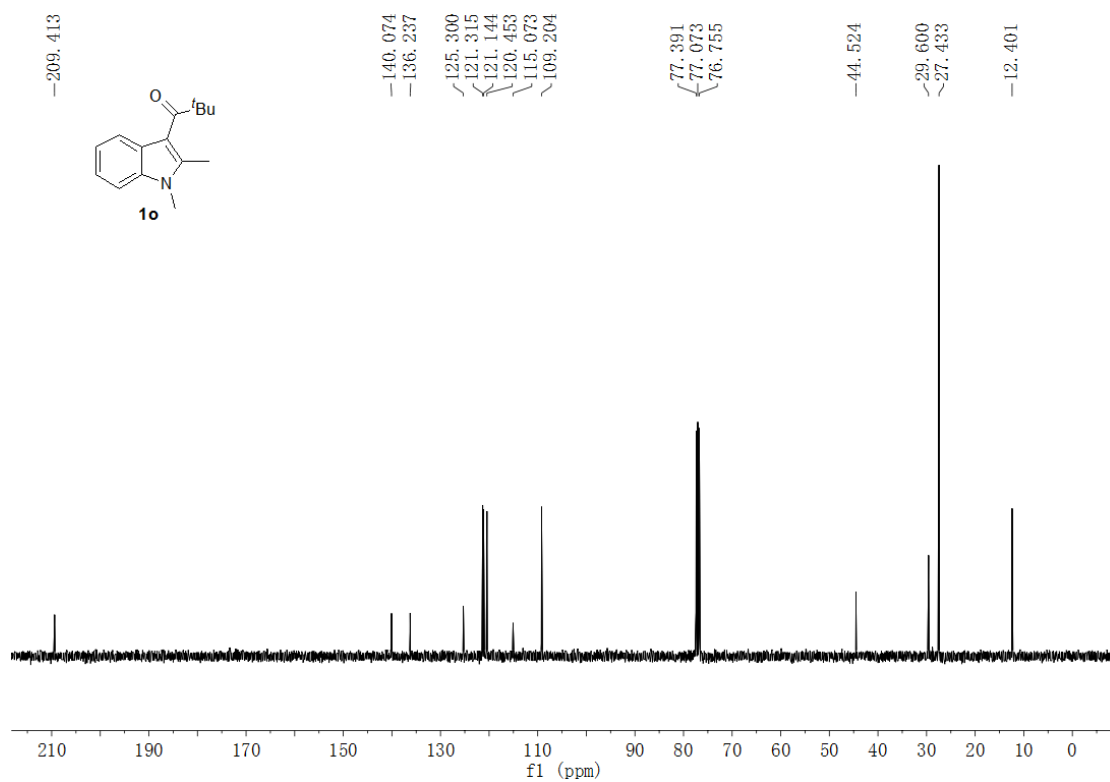
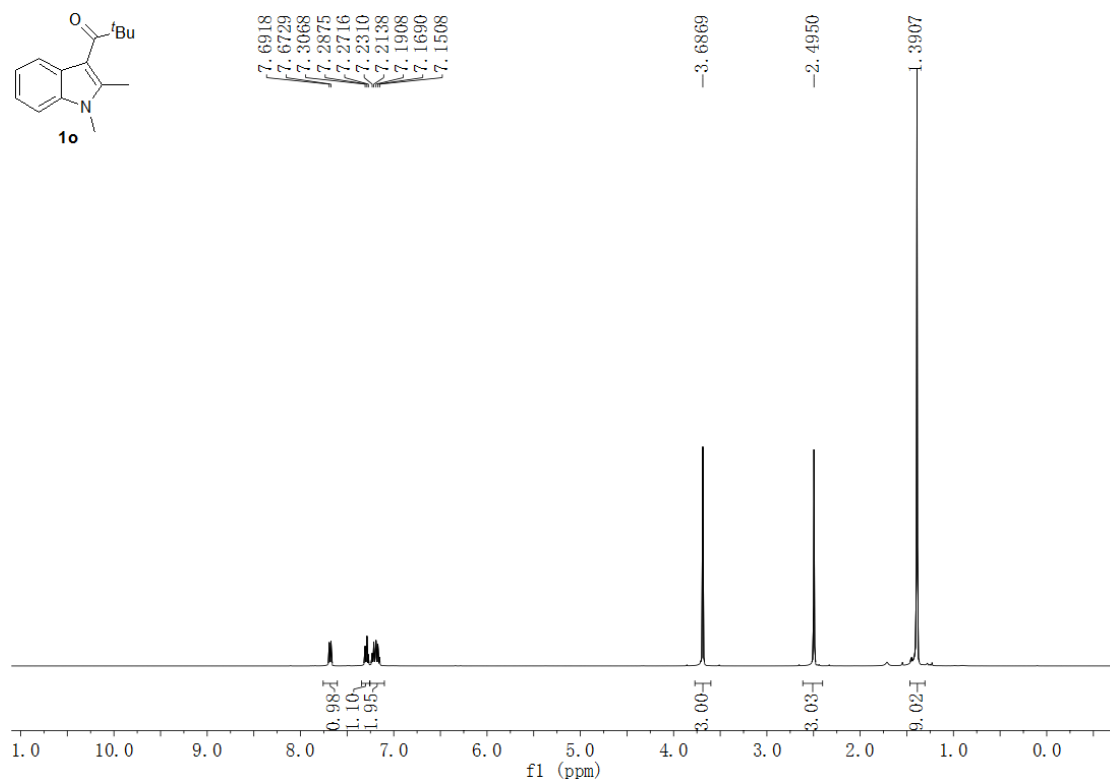


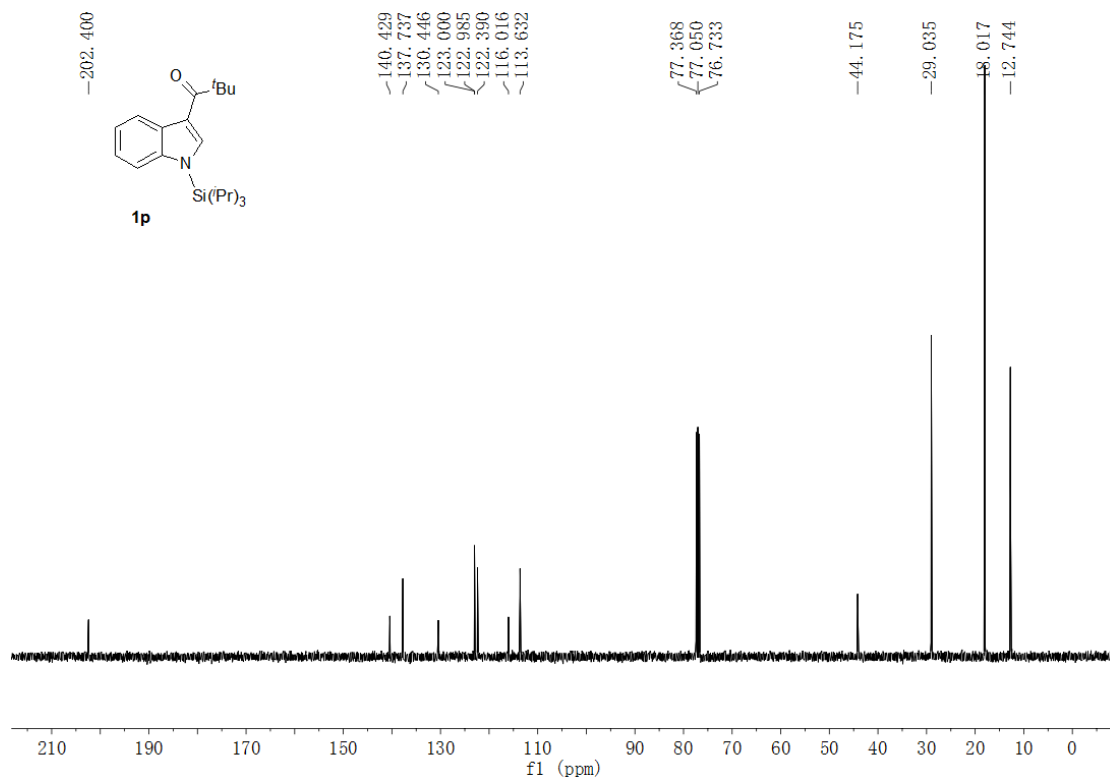
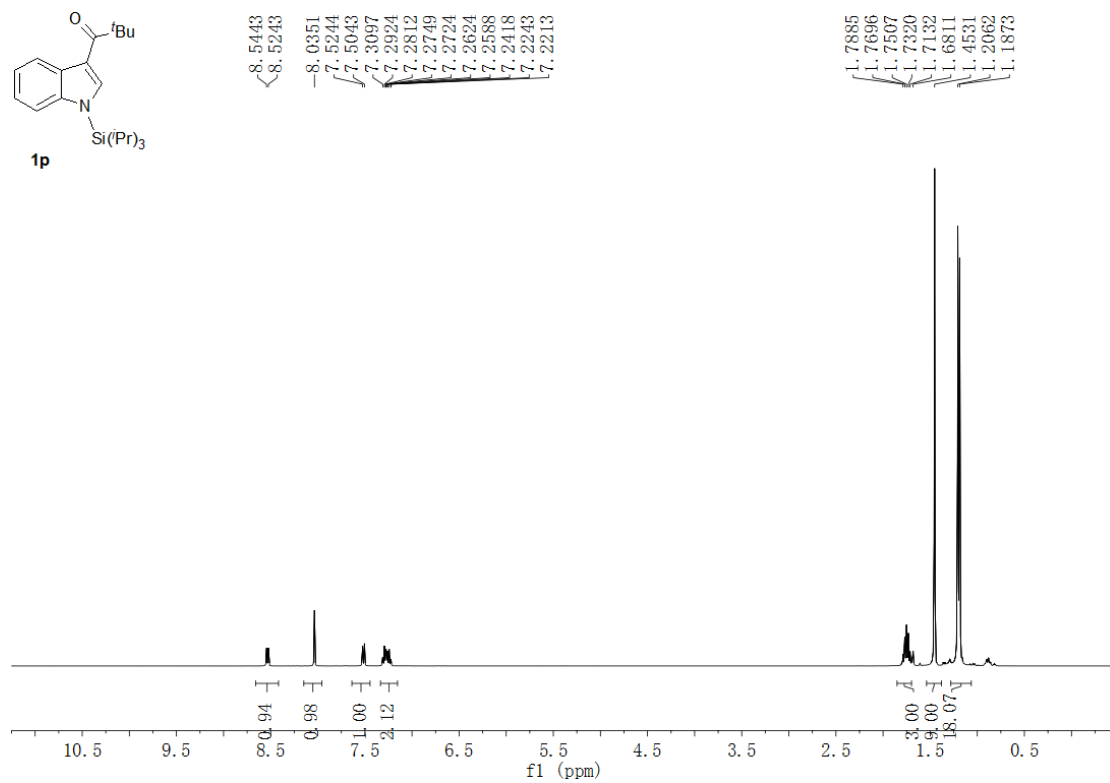












5. Copies of ^1H NMR and ^{13}C NMR spectra of the products

