Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Redox-Triggered Dearomative [5+1] Annulation of Indoles with *O*-Alkyl *ortho*-Oxybenzaldehydes for the Synthesis of Spirochromanes

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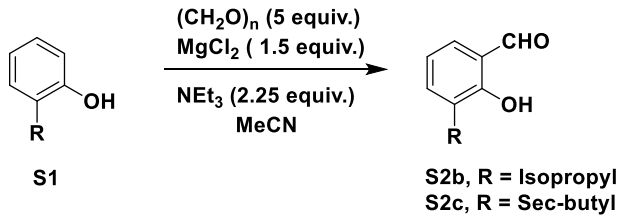
1. General Information

Unless otherwise noted, all reagents and solvents were purchased from the commercial sources and used as received. Thin layer chromatography (TLC) was used to monitor the reaction on Merck 60 F254 precoated silica gel plate (0.2 mm thickness). TLC spots were visualized by UV-light irradiation on Spectroline Model ENF-24061/F 254 nm. The products were purified by flash column chromatography (300-400 mesh silica gel/200-300 mesh basic alumina) eluted with the gradient of petroleum ether, ethyl acetate and dichloromethane. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker 300 MHz NMR spectrometer ($CDCl_3$ or DMSO-d_6 as solvent). The chemical shifts were reported in parts per million (ppm), downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 7.26, singlet). Multiplicities were afforded as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet) or m (multiplets). The number of protons for a given resonance is indicated by nH. Coupling constants were reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) was referenced to the appropriate residual solvent peak. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF.

2. General Procedure

2.1 General Procedure for the Synthesis of S2b and S2c[1]

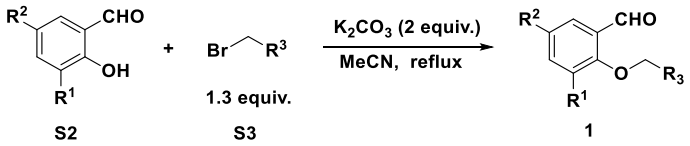


S1

S2b, R = Isopropyl
S2c, R = Sec-butyl

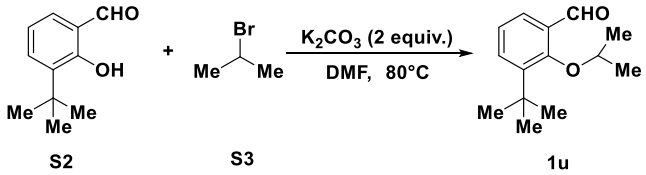
To a solution of phenol derivative **S1** (5 mmol) and magnesium chloride (7.5 mmol) in dry acetonitrile (13 mL) was added triethylamine (11.25 mmol, 2.7 mL). The mixture was stirred at room temperature for 15 min, and then was added dry parafomaldehyde (25 mmol) in one portion. The mixture was heated to reflux in an oil bath until the starting material was consumed (as monitored by TLC), cooled to ambient temperature, and quenched with diluted HCl (3N) until pH = 2. The resulting solution was extracted with EA (3 × 10 mL), and the combined organic layers were washed with brine, dried over sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether, 1:100) to give the desired product **S2b** and **S2c**.

2.2 General Procedure for the Synthesis of 1a'-1t[2]



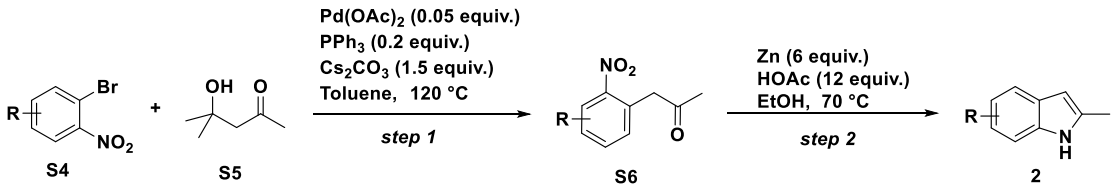
A reaction flask was charged with K_2CO_3 (10 mmol), MeCN (20 mL), salicylaldehyde **S2** (5 mmol), and allyl bromide/benzyl bromide **S3** (6.5 mmol). And the reaction mixture was heated to reflux in an oil bath. Upon the consumption of starting material (as monitored by TLC), the reaction mixture was cooled to room temperature, extracted with EA (3 × 20 mL), and washed with brine (3 × 20 mL). Then combined organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on a silica gel (ethyl acetate: petroleum ether, from 1:100 to 1:10) to give the desired product **1a'-1t**. **1a'**, **1a**, **1b**, **1e**, **1l**, **1r** and **1t** were reported by literatures[3-7].

2.3 Procedure for the Synthesis of 1u[8]



A reaction flask was charged with K_2CO_3 (10 mmol), DMF (20 mL), salicylaldehyde **S2** (5 mmol), and isopropyl bromide **S3** (6.5 mmol). The mixture was heated to 80 ℃ in an oil bath until the starting material was consumed (as monitored by TLC), the reaction mixture was cooled to room temperature, then add the water (15 mL) and extract with EA (3 × 20 mL). The combined organic layer was washed with water (2 × 20 mL) and brine (3 × 20 mL), and dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:50) to give the desired product **1u**.

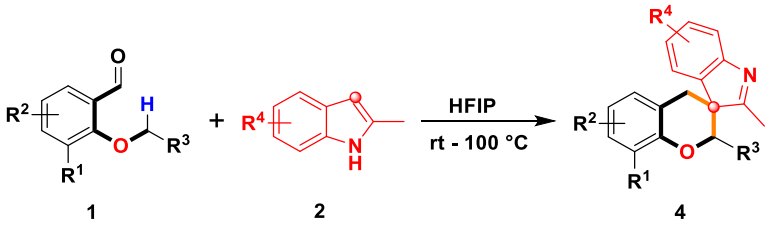
2.4 Procedure for the Synthesis of 2[9]



Step 1: Cs_2CO_3 (4.5 mmol), $Pd(OAc)_2$ (0.15 mmol), PPh_3 (0.6 mmol) and aryl halide **S4** (3 mmol) were added in an oven-dried Schlenk tube. The tube was then sealed, evacuated, and backfilled with nitrogen using standard Schlenk technique. Toluene (18 mL) and diacetone alcohol **S5** (18 mmol) were sequentially added by syringe at ambient temperature. The resulting mixture was heated at 120 ℃ (oil bath) for 5 hours. After the mixture was cooled to room temperature, water (20 mL) was added. The product was extracted with EA (3 × 15 mL). The combined organic layer was then washed with brine, dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by column chromatography on silica gel (ethyl acetate: petroleum ether, 1:10) to give the desired product **S6**.

Step 2: Zinc dust (18 mmol) and glacial acetic acid (36 mmol) were added to a reaction flask. Ethanol (12 mL) and **S6** (6 mmol) were sequentially added by syringe at ambient temperature. The mixture was stirred at 70 ℃ until the starting material consumed (as monitored by TLC). Water (20 mL) was then added to the reaction mixture, and the resulting mixture was extracted with EA (3 × 10 mL). The combined organic layers were then washed with brine (3 × 10 mL), dried over Na_2SO_4, and concentrated in vacuum. The residue was purified by column chromatography on silica gel (ethyl acetate: petroleum ether, 1:10) to give the desired product **2**.

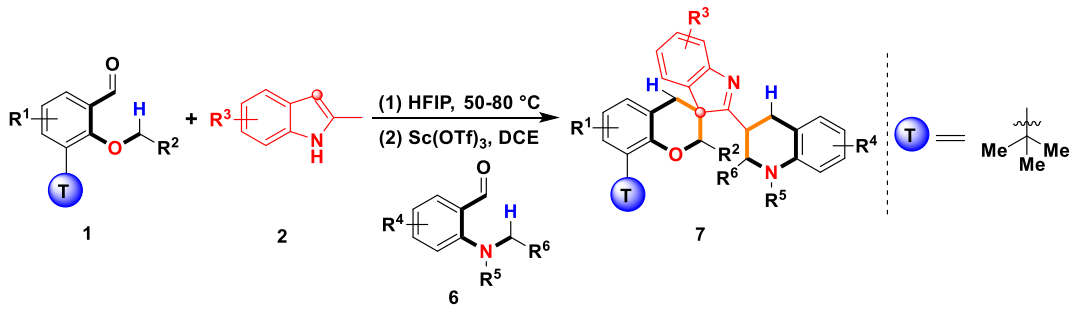
2.5 General Procedure for the Synthesis of Spiroindolenines



1 2 4

A reaction tube was charged with *O*-benzyl *ortho*-oxybenzaldehydes **1** (0.26 mmol) and 2-methylindole **2** (0.2 mmol) in 1.0 mL of HFIP. The mixture was stirred at room temperature to 100 ℃ under an air atmosphere. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50 or ethyl acetate: dichloromethane: petroleum ether, 2:5:50) to afford the desired spiroindolenines **4**.

2.6 General Procedure for the Synthesis of the Twice Redox Neutral [5+1] Annulations

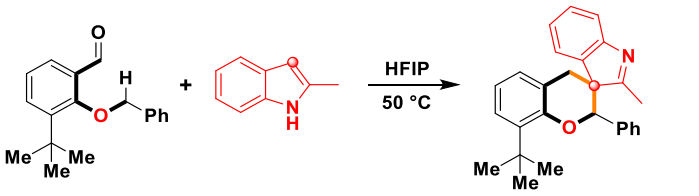


1 2 6 7

A reaction tube was charged with *O*-benzyl *ortho*-oxybenzaldehydes **1** (0.26 mmol) and 2-methylindole **2** (0.2 mmol) in 1.0 mL of HFIP. The mixture was stirred at 50 ℃ to 100 ℃ under an air atmosphere. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum. Next, the residue, *o*-aminobenzaldehyde **6** and $Sc(OTf)_3$ (10 mol %) were stirred in 2 mL of DCE at room temperature to 50 ℃. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50 or ethyl acetate: dichloromethane: petroleum ether, 2:5:50) to afford the desired twice redox neutral [5+1] annulation product **7**.

3. Large Scale Synthesis and Synthetic Transformations

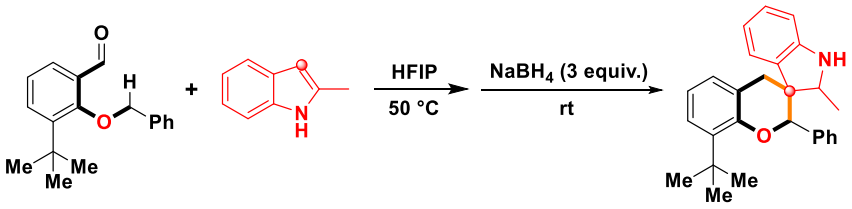
3.1 Large Scale Synthesis of 4a



1a, 2.6 mmol　　**2a**, 2 mmol　　**4a**, 741 mg, 97% yield, dr 3:1

A round-bottom flask was charged with *O*-benzyl *ortho*-oxybenzaldehyde **1a** (2.6 mmol) and 2-methylindole **2a** (2 mmol) in 10.0 mL of HFIP. The mixture was stirred at 50˚C under an air atmosphere. Upon completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50 or ethyl acetate: dichloromethane: petroleum ether, 2:5:50) to afford the desired spiroindolenine **4a** in 97% yield (741 mg, dr 3:1).

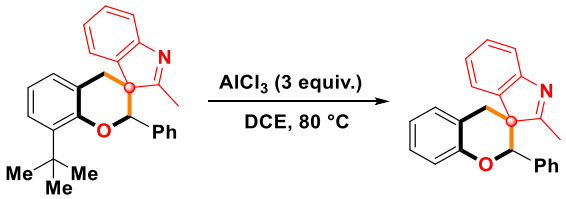
3.2 Procedure for the Synthesis of 8a



1a　　**2a**　　**8a**

A reaction tube was charged with *O*-benzyl *ortho*-oxybenzaldehyde **1a** (0.26 mmol) and 2-methylindole **2a** (0.2 mmol) in 1.0 mL of HFIP. The mixture was stirred at 50 ˚C under an air atmosphere. Upon completion of the reaction as indicated by TLC analysis, then, the $NaBH_4$ (0.6 mmol) was added in the mixture and stirred at room temperature until completion of the reaction as indicated by TLC analysis, the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) to afford the desired spiroindolenine **8a** in 75% yield, dr 2.7:1.

3.3 The Detailed Procedure for the Synthesis of 9a



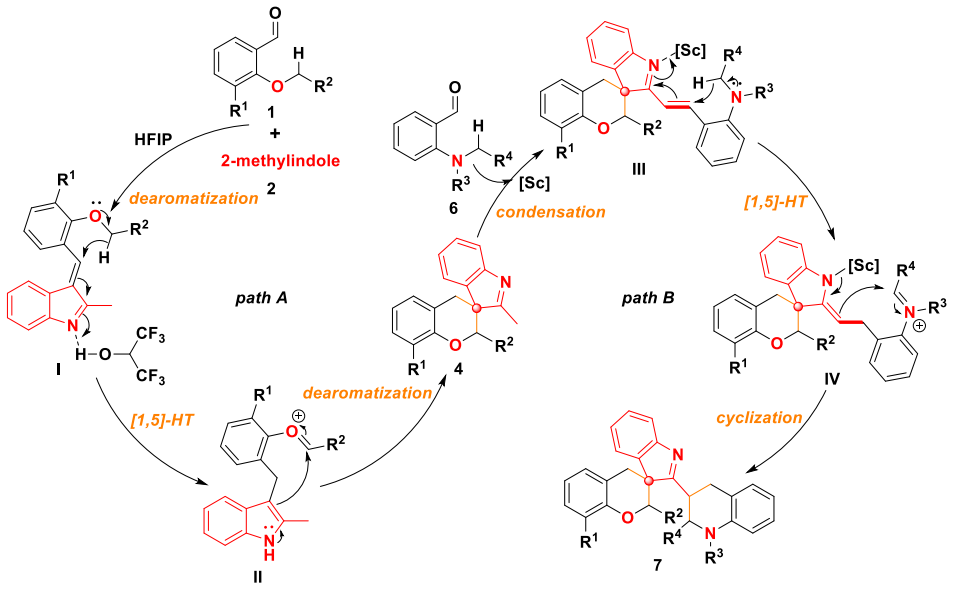
4a　　**9a**

A reaction tube was charged with spiroindolenine **4a** (0.2 mmol) and $AlCl_3$ (0.6 mmol) in 2.0 mL of DCE. The mixture was stirred at 80 ˚C under an air atmosphere. Upon completion of the reaction as indicated by TLC analysis, then add 20 mL ice water and 5 mL 5% NaOH solution to quench the reaction, extract with DCM (3 × 10 mL), combine the organic phases, wash the organic phases with

saturated brine (3 × 10 mL), dry with anhydrous sodium sulfate, and the mixture was concentrated in vacuum and the residue was directly purified by flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) to afford the desired spiroindolenine **9a** in 51% yield.

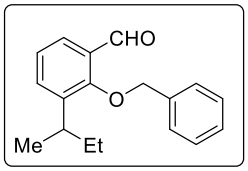
4. Proposed Mechanism

Based on the above experiments and precedent reports, a plausible mechanism was proposed to rationalize the dearomative [5+1] annulation. Initially, HFIP serving as hydrogen bond donor and acceptor plays essential role in the whole process. Initially, the nucleophilic addition/dehydrated dearomatization takes place between 2-methylindole and activated carbonyl group of *O*-alkyl *ortho*-oxybenzaldehyde by HFIP to generate the vinylogous imine **I**. Then HFIP serves as the hydrogen acceptor to active the imine of intermediate **I** for initiating the intramolecular [1,5]-hydride transfer, affording the oxocarbenium intermediate **II**. Subsequently, the dearomative cyclization produces the spirochromane **4** carrying 2-methylindolenine skeleton (path A). In addition, the plausible pathway for the sequential transformation of 2-methylindolenines was proposed as well (path B). At the outset, the Knoevenagel condensation occurs between 2-methylindolenine and *N*-alkyl *ortho*-aminobenzaldehydes in the presence of $Sc(OTf)_3$, furnishing the vinylogous imine **III**. Then the electrophilic vinylogous imine is activated by $Sc(OTf)_3$ to initiate the [1,5]-hydride transfer to generate the zwitterionic intermediate **IV**. Finally, the intermediate **IV** undergoes nucleophilic cyclization to form a new *N*-heterocycle.



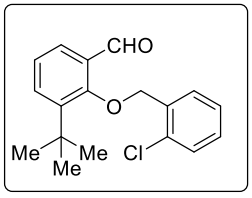
5. Characterization Data of Products

2-(benzyloxy)-3-(sec-butyl)benzaldehyde (1c)



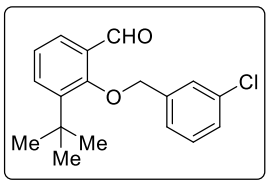
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:100) afforded the product **1c** as a yellow oil (955.3 mg, 71% yield). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 10.31 (s, 1H), 7.73 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.53 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.47 – 7.35 (m, 5H), 7.26 (t, *J* = 7.6 Hz, 1H), 4.97 (s, 2H), 3.20 (h, *J* = 7.1 Hz, 1H), 1.72 – 1.55 (m, 2H), 1.24 (d, *J* = 7.0 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 190.5, 159.6, 142.3, 136.2, 133.6, 129.7, 128.8, 128.6, 128.2, 126.6, 125.0, 79.3, 33.0, 30.8, 26.2, 23.8, 21.7, 12.4. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{18}H_{21}O_2^+$ 269.1536; found: 269.1541.

3-(tert-butyl)-2-((2-chlorobenzyl)oxy)benzaldehyde (1f)



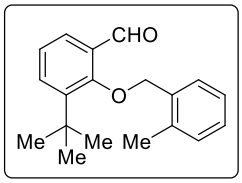
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:50) afforded the product **1f** as a light yellow solid (1.44 g, 95% yield), m.p.: 62.8-63.2 ℃. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 10.28 (s, 1H), 7.84 (d, *J* = 7.2 Hz, 1H), 7.78 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.65 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.39 (t, *J* = 6.9 Hz, 2H), 7.35 – 7.27 (m, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 5.16 (s, 2H), 1.45 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 190.2, 161.7, 144.0, 134.6, 133.8, 131.7, 130.2, 129.4, 129.1, 128.0, 127.9, 127.2, 124.5, 77.4, 35.3, 31.0. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{18}H_{20}ClO_2^+$ 303.1146; found: 303.1151.

3-(tert-butyl)-2-((3-chlorobenzyl)oxy)benzaldehyde (1g)



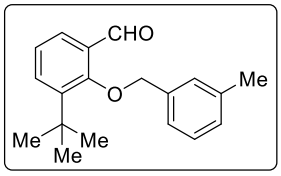
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:50) afforded the product **1g** as a light yellow solid (1.44 g, 95% yield), m.p.: 47.0-47.8 ℃. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 10.30 (s, 1H), 7.75 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.64 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.57 – 7.49 (m, 1H), 7.42 – 7.31 (m, 3H), 7.21 (t, *J* = 7.7 Hz, 1H), 5.03 (s, 2H), 1.45 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 190.3, 161.3, 144.1, 138.6, 134.7, 133.8, 130.14, 130.08, 128.5, 128.4, 127.0, 125.0, 124.5, 79.2, 35.4, 31.0. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{18}H_{20}ClO_2^+$ 303.1146; found: 303.1154.

3-(tert-butyl)-2-((2-methylbenzyl)oxy)benzaldehyde (1h)



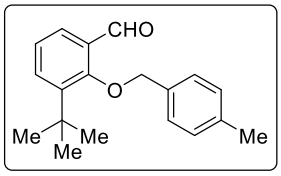
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:50) afforded the product as **1h** a yellow oil (1.33 g, 94% yield). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 10.26 (s, 1H), 7.77 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.66 (td, *J* = 8.6, 7.9, 2.2 Hz, 2H), 7.31 (ddd, *J* = 9.0, 6.7, 2.3 Hz, 2H), 7.21 (dd, *J* = 8.8, 6.7 Hz, 2H), 5.09 (s, 2H), 2.28 (s, 3H), 1.45 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 190.4, 162.3, 144.0, 134.9, 133.6, 130.4, 130.3, 128.0, 127.5, 126.7, 126.3, 124.2, 78.8, 35.3, 30.9, 18.9. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{19}H_{23}O_2^+$ 283.1693; found: 283.1696.

3-(tert-butyl)-2-((3-methylbenzyl)oxy)benzaldehyde (1i)



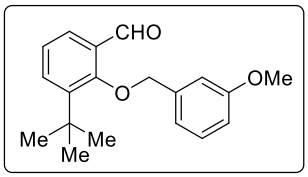
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:50) afforded the product **1i** as a yellow oil (1.36 g, 96% yield). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 10.36 (s, 1H), 7.77 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.64 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.37 – 7.29 (m, 3H), 7.24 – 7.16 (m, 2H), 5.04 (s, 2H), 2.42 (s, 3H), 1.47 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 190.5, 162.0, 144.1, 138.5, 136.4, 133.7, 130.3, 129.1, 128.7, 127.85, 127.80, 124.25, 124.21, 80.7, 35.3, 31.0, 21.6. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{19}H_{23}O_2^+$ 283.1693; found: 283.1695.

3-(tert-butyl)-2-((4-methylbenzyl)oxy)benzaldehyde (1j)



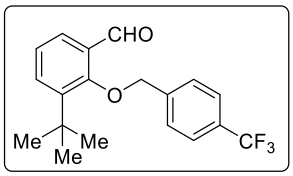
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:50) afforded the product **1j** as a yellow oil (1.32 g, 93% yield). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 10.36 (s, 1H), 7.76 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.64 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.41 (d, *J* = 7.9 Hz, 2H), 7.29 – 7.14 (m, 3H), 5.03 (s, 2H), 2.40 (s, 3H), 1.46 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 190.5, 162.0, 144.1, 138.1, 133.7, 133.5, 130.3, 129.5, 127.8, 127.3, 124.2, 80.7, 35.3, 31.0, 21.3. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{19}H_{23}O_2^+$ 283.1693; found: 283.1695.

3-(tert-butyl)-2-((3-methoxybenzyl)oxy)benzaldehyde (1k)



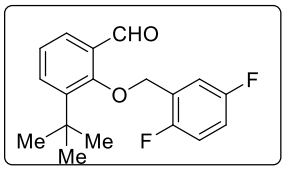
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:15) afforded the product **1k** as a yellow oil (1.37 g, 92% yield). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 10.35 (s, 1H), 7.76 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.64 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.23 – 7.15 (m, 1H), 7.13 – 7.04 (m, 2H), 6.92 (dd, *J* = 8.3, 1.9 Hz, 1H), 5.05 (s, 2H), 3.85 (s, 3H), 1.47 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 190.1, 161.6, 159.8, 143.8, 137.9, 133.5, 130.1, 129.7, 127.8, 124.1, 119.0, 113.5, 112.5, 80.1, 55.1, 35.1, 30.8. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{19}H_{23}O_3^+$ 299.1642; found: 299.1646.

3-(tert-butyl)-2-((4-(trifluoromethyl)benzyl)oxy)benzaldehyde (1m)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:30) afforded the product **1m** as a light yellow solid (1.58 g, 94% yield), m.p.: 88.1-89.3 ℃. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 10.30 (s, 1H), 7.76 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.73 – 7.62 (m, 5H), 7.27 – 7.19 (m, 1H), 5.12 (s, 2H), 1.45 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 190.2, 161.2, 144.1, 140.7, 133.9, 130.25, 130.17, 128.8, 127.0, 126.0 (q, *J* = 234.6 Hz), 125.76 (q, *J* = 3.9 Hz), 124.5, 79.0, 35.4, 31.0. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{19}H_{20}F_3O_2^+$ 337,1410; found: 337.1396.

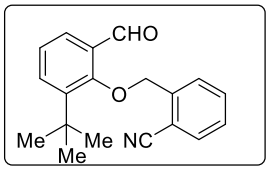
3-(tert-butyl)-2-((2,5-difluorobenzyl)oxy)benzaldehyde (1n)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:40) afforded the product **1n** as a light yellow solid (1.42 g, 93% yield), m.p.: 66.7-68.2 ℃. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 10.29 (s, 1H), 7.80 – 7.71 (m, 1H), 7.69 – 7.61 (m, 1H), 7.51 – 7.41 (m, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.05 (pd, *J* = 8.6, 4.6 Hz, 2H), 5.08 (s, 2H), 1.44 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 190.2, 161.1, 159.0 (dd, *J* = 243.0, 2.0 Hz), 155.8 (dd, *J*

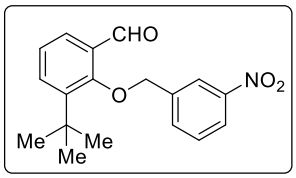
= 242.9, 2.1 Hz), 144.1, 133.9, 130.2, 128.7, 125.8 (dd, *J* = 17.0, 7.9 Hz), 124.6, 116.5 (dd, J = 23.6, 8.8 Hz), 116.1 (dd, *J* = 24.3, 8.6 Hz), 115.5 (dd, *J* = 25.3, 4.4 Hz), 73.3 (d, *J* = 3.3 Hz), 35.4, 31.0.**HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{18}H_{19}F_2O_2^+$ 305.1348; found: 305.1347.

2-((2-(tert-butyl)-6-formylphenoxy)methyl)benzonitrile (1o)



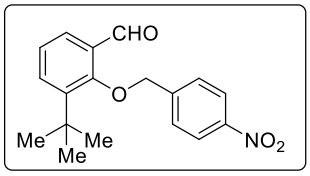
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product **1o** as a white solid (1.35 g, 92% yield), m.p.: 72.6-74.1 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 10.25 (s, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.78 – 7.62 (m, 4H), 7.47 (t, *J* = 7.9 Hz, 1H), 7.30 – 7.19 (m, 1H), 5.27 (s, 2H), 1.43 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 190.0, 160.6, 144.0, 140.5, 134.0, 133.4, 132.8, 130.0, 129.4, 128.5, 127.6, 124.7, 116.9, 110.1, 76.7, 35.3, 31.0. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{19}H_{20}NO_2^+$ 294.1489; found: 294.1480.

3-(tert-butyl)-2-((3-nitrobenzyl)oxy)benzaldehyde (1p)



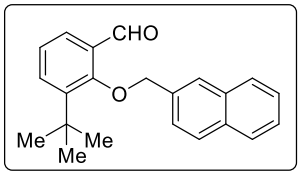
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product **1p** as a yellow solid (1.42 g, 91% yield), m.p.: 51.3-52.8 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 10.25 (s, 1H), 8.40 (s, 1H), 8.22 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.73 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.69 – 7.57 (m, 2H), 7.23 (t, *J* = 7.7 Hz, 1H), 5.14 (s, 2H), 1.43 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 190.1, 160.5, 148.5, 144.0, 138.8, 133.9, 132.7, 129.9, 129.8, 129.5, 124.6, 123.1, 121.7, 77.9, 35.3, 30.9. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{18}H_{20}NO_4^+$ 314.1387; found: 314.1375.

3-(tert-butyl)-2-((4-nitrobenzyl)oxy)benzaldehyde (1q)



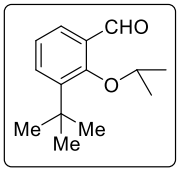
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product **1q** as a yellow solid (1.40 g, 90% yield), m.p.: 90.8-92.6 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 10.25 (s, 1H), 8.29 (d, *J* = 8.6 Hz, 2H), 7.80 – 7.63 (m, 4H), 7.30 – 7.20 (m, 1H), 5.15 (s, 2H), 1.43 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 190.1, 160.6, 147.8, 144.05, 144.01, 134.0, 130.0, 129.5, 127.3, 124.7, 124.0, 78.1, 35.4, 30.9. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{18}H_{20}NO_4^+$ 314.1387; found: 314.1375.

3-(tert-butyl)-2-(naphthalen-2-ylmethoxy)benzaldehyde (1s)



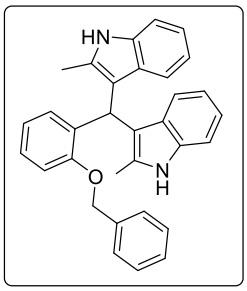
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:50) afforded the product **1s** as a white solid (1.50 g, 94% yield), m.p.: 191.6-192.2 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 10.44 (s, 1H), 8.01 (s, 1H), 7.96 – 7.86 (m, 3H), 7.81 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.68 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.58 – 7.49 (m, 2H), 7.23 (t, *J* = 7.8 Hz, 1H), 5.24 (s, 2H), 1.50 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 190.5, 161.9, 144.1, 134.0, 133.8, 133.4, 133.3, 130.3, 128.6, 128.2, 128.0, 127.9, 126.5, 126.3, 126.0, 124.9, 124.3, 80.6, 35.4, 31.0. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{22}H_{23}O_2^+$ 319.1693; found: 319.1698.

3-(tert-butyl)-2-isopropoxybenzaldehyde (1u)



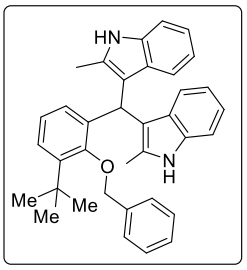
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:50) afforded the product **1u** as a red-brown oil (1.01 g, 92% yield). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 10.25 (s, 1H), 7.64 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.56 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.06 (t, *J* = 7.7 Hz, 1H), 4.45 (hept, *J* = 6.1 Hz, 1H), 1.42 (s, 9H), 1.31 (s, 3H), 1.29 (s, 3H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 190.5, 160.2, 143.7, 133.6, 130.5, 127.5, 122.8, 80.5, 35.3, 31.4, 22.2. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{14}H_{21}O_2^+$ 221.1536; found: 221.1528.

3,3'-((2-(benzyloxy)phenyl)methylene)bis(2-methyl-1H-indole) (3a')



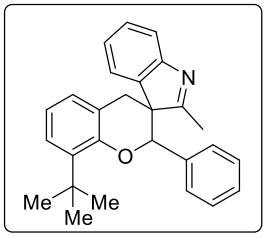
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:7) afforded the product **3a'** as a white solid, m.p.: 168.2-170.5 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.64 (s, 2H), 7.23 (d, *J* = 8.0 Hz, 3H), 7.20 – 7.07 (m, 4H), 7.06 – 6.97 (m, 4H), 6.95 – 6.85 (m, 4H), 6.85 – 6.80 (m, 2H), 6.26 (s, 1H), 4.91 (s, 2H), 2.00 (s, 6H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 156.9, 137.6, 135.2, 132.9, 131.8, 130.3, 129.6, 128.2, 127.4, 127.0, 120.7, 120.6, 119.5, 119.1, 113.4, 111.9, 110.0, 70.0, 33.9, 12.4. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{32}H_{29}N_2O^+$ 457.2274; found: 457.2258.

3,3'-((2-(benzyloxy)-3-(tert-butyl)phenyl)methylene)bis(2-methyl-1H-indole) (3a)



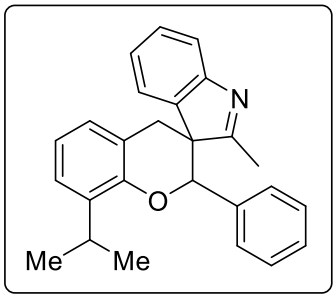
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:10) afforded the product **3a** as a white solid, m.p.: 204.3-205.2 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.60 (s, 2H), 7.34 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.30 – 7.25 (m, 2H), 7.24 – 7.21 (m, 3H), 7.19 (d, *J* = 5.3 Hz, 3H), 7.06 – 6.98 (m, 2H), 6.94 (t, *J* = 7.7 Hz, 3H), 6.87 – 6.78 (m, 2H), 6.17 (s, 1H), 4.96 (s, 2H), 1.88 (s, 6H), 1.46 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 156.8, 143.0, 138.5, 137.8, 135.2, 131.8, 130.8, 129.1, 128.2, 127.3, 126.7, 125.5, 123.4, 120.5, 119.6, 119.2, 114.3, 110.0, 75.3, 35.5, 34.3, 31.5, 12.3. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{36}H_{37}N_2O^+$ 513.2900; found: 513.2867.

8-(tert-butyl)-2'-methyl-2-phenylspiro[chromane-3,3'-indole] (4a)



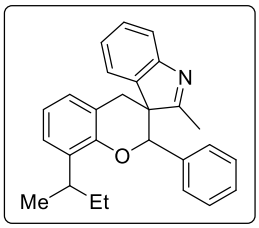
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **4a** as inseparable diastereomers (dr = 3:1) as a yellow solid (75.5 mg, 99% yield), m.p.: 161.6-162.8 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.41 – 7.21 (m, 3H), 7.21 – 7.13 (m, 2H), 7.12 – 6.87 (m, 7H), 5.41 (s, 1H), 3.72 (d, *J* = 16.0 Hz, 1H), 2.62 (d, *J* = 16.2 Hz, 1H), 2.41 (s, 3H), 1.42 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 183.4, 181.3, 155.1, 154.7, 153.7, 153.5, 141.0, 139.2, 138.5, 138.2, 135.9, 135.7, 128.7, 128.49, 128.46, 128.2, 128.1, 127.8, 127.6, 126.82, 126.76, 125.31, 125.27, 125.2, 124.5, 122.1, 121.3, 121.1, 120.1, 120.0, 119.4, 82.4, 80.8, 59.8, 59.7, 34.9, 33.6, 33.4, 29.9, 29.8, 20.2, 17.2. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{27}H_{28}NO^+$ 382.2165; found: 382.2111.

8-isopropyl-2'-methyl-2-phenylspiro[chromane-3,3'-indole] (4b)



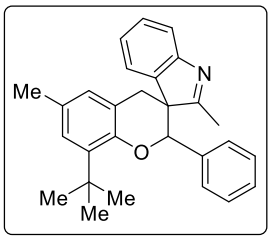
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **4b** as inseparable diastereomers (dr = 2:1) as a yellow solid, m.p.: 85.4-86.1 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.41 – 7.32 (m, 1H), 7.27 (dtt, *J* = 8.6, 4.5, 2.1 Hz, 2H), 7.19 – 7.14 (m, 1H), 7.13 – 7.07 (m, 3H), 7.06 – 6.97 (m, 3H), 6.93 – 6.88 (m, 2H), 5.41 (s, 1H), 3.70 (d, *J* = 16.0 Hz, 1H), 3.45 – 3.32 (m, 1H), 2.59 (d, *J* = 16.1 Hz, 1H), 2.43 (s, 3H), 1.31 (d, *J* = 7.5 Hz, 6H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 183.3, 181.4, 155.0, 154.6, 152.1, 151.7, 141.0, 139.0, 136.9, 136.6, 136.0, 135.9, 128.7, 128.5, 128.4, 128.1, 127.7, 127.6, 127.5, 127.0, 126.7, 126.6, 125.2, 124.9, 124.8, 124.4, 122.2, 121.4, 121.3, 120.1, 120.0, 119.2, 118.6, 81.9, 80.6, 59.9, 59.5, 33.4, 33.2, 27.1, 23.2, 23.0, 22.3, 22.2, 20.3, 17.3. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{26}H_{26}NO^+$ 368.2009; found: 3368.1963.

8-(sec-butyl)-2'-methyl-2-phenylspiro[chromane-3,3'-indole] (4c)



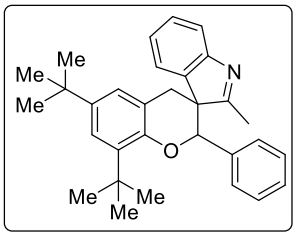
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **4c** as inseparable diastereomers (dr = 2:1) as a yellow solid (56.5 mg, 74% yield), m.p.: 84.0-85.1 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.40 – 7.34 (m, 1H), 7.33 – 7.27 (m, 1H), 7.26 – 7.19 (m, 1H), 7.19 – 7.15 (m, 1H), 7.11 – 7.04 (m, 4H), 7.00 (d, *J* = 5.1 Hz, 2H), 6.91 (d, *J* = 7.2 Hz, 2H), 5.41 (s, 1H), 3.71 (d, *J* = 16.0 Hz, 1H), 3.49 – 3.32 (m, 1H), 2.60 (d, *J* = 16.1 Hz, 1H), 2.44 (s, 3H), 1.79 – 1.62 (m, 1H), 1.31 (s, 3H), 1.28 (s, 1H), 1.04 – 0.88 (m, 3H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 183.3, 181.4, 155.1, 154.7, 152.2, 151.8, 141.1, 139.1, 136.9, 136.6, 136.1, 136.0, 128.71, 128.66, 128.5, 128.4, 128.1, 127.7, 127.6, 127.5, 127.4, 126.7, 126.6, 125.2, 124.9, 124.8, 124.5, 122.2, 121.4, 121.3, 120.1, 120.0, 119.3, 118.6, 81.9, 80.6, 60.0, 59.6, 34.3, 33.7, 33.4, 33.2, 30.1, 29.2, 27.1, 23.1, 23.0, 22.3, 22.2, 21.0, 20.3, 17.3, 12.4, 12.3. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{27}H_{28}NO^+$ 382.2165; found: 382.2153.

8-(tert-butyl)-2',6-dimethyl-2-phenylspiro[chromane-3,3'-indole] (4d)



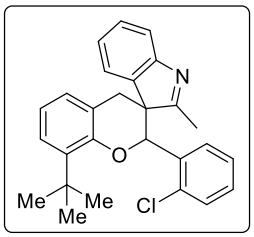
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **4d** as inseparable diastereomers (dr = 4:1) as a yellow solid (60.1 mg, 76% yield), m.p.: 93.9-94.5 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 7.7 Hz, 1H), 7.36 – 7.26 (m, 1H), 7.26 – 7.19 (m, 1H), 7.19 – 7.14 (m, 1H), 7.14 – 7.04 (m, 4H), 6.89 (d, *J* = 7.1 Hz, 2H), 6.84 (s, 1H), 5.36 (s, 1H), 3.68 (d, *J* = 16.0 Hz, 1H), 2.57 (d, *J* = 16.2 Hz, 1H), 2.39 (s, 3H), 2.33 (s, 4H), 1.42 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 183.7, 181.5, 155.0, 154.6, 151.5, 151.3, 141.0, 139.3, 138.2, 137.9, 136.0, 135.8, 130.3, 130.1, 128.7, 128.4, 128.3, 128.0, 127.9, 127.7, 127.5, 126.8, 126.2, 126.1, 125.3, 125.2, 124.6, 122.2, 120.9, 119.9, 119.1, 110.3, 100.4, 82.3, 80.7, 60.0, 59.8, 34.8, 33.6, 33.3, 29.9, 29.8, 21.0, 20.2, 17.3, 13.8. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{28}H_{30}NO^+$ 396.2322; found: 396.2275.

6,8-di-tert-butyl-2'-methyl-2-phenylspiro[chromane-3,3'-indole] (4e)



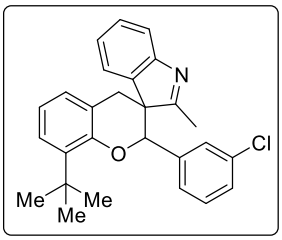
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **4e** as inseparable diastereomers (dr = 2:1) as a yellow solid (62.1 mg, 71% yield), m.p.: 99.8-101.5 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 7.6 Hz, 1H), 7.36 – 7.21 (m, 3H), 7.18 – 7.01 (m, 5H), 6.90 (d, *J* = 7.7 Hz, 2H), 5.39 (s, 1H), 3.75 (d, *J* = 16.6 Hz, 1H), 2.62 (d, *J* = 16.2 Hz, 1H), 2.42 (s, 3H), 1.45 (s, 9H), 1.36 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 183.7, 181.5, 155.0, 154.6, 151.3, 151.1, 143.6, 143.3, 141.1, 139.4, 137.6, 137.3, 136.0, 135.9, 128.6, 128.42, 128.38, 128.0, 127.7, 127.5, 126.8, 126.7, 125.2, 125.1, 124.6, 124.1, 122.5, 122.4, 122.1, 120.0, 119.9, 119.3, 118.4, 82.2, 80.7, 60.1, 59.9, 35.1, 34.4, 33.8, 33.5, 31.7, 30.0, 29.9, 27.0, 22.8, 20.3, 17.3. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{31}H_{36}NO^+$ 438.2791; found: 438.2745.

8-(tert-butyl)-2-(2-chlorophenyl)-2'-methylspiro[chromane-3,3'-indole] (4f)



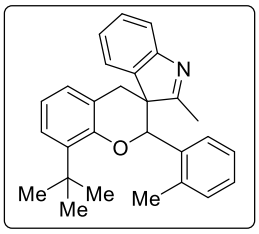
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **4f** as inseparable diastereomers (dr = 2:1) as a yellow solid (78.2 mg, 94% yield), m.p.: 106.8-108.7 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 7.6 Hz, 1H), 7.44 – 7.27 (m, 3H), 7.24 – 7.17 (m, 1H), 7.17 – 7.08 (m, 3H), 7.04 – 6.94 (m, 1H), 6.86 – 6.76 (m, 1H), 6.44 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.08 (s, 1H), 3.75 (d, *J* = 16.6 Hz, 1H), 2.63 (d, *J* = 16.1 Hz, 1H), 2.39 (s, 3H), 1.36 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 183.2, 182.1, 155.1, 154.1, 153.9, 153.8, 139.9, 139.5, 138.3, 138.1, 133.9, 133.6, 133.2, 133.1, 130.1, 129.7, 129.5, 129.4, 128.7, 128.6, 128.3, 127.9, 127.5, 126.9, 126.8, 125.6, 125.35, 125.28, 125.1, 124.5, 122.8, 121.4, 121.3, 120.3, 120.2, 119.7, 119.4, 77.5, 75.7, 59.2, 59.1, 34.9, 34.7, 34.3, 29.7, 29.7, 20.5, 17.3. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{27}H_{27}ClNO^+$ 416.1776; found: 416.1721.

8-(tert-butyl)-2-(3-chlorophenyl)-2'-methylspiro[chromane-3,3'-indole] (4g)



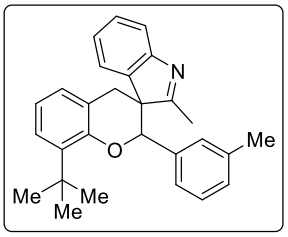
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **4g** as inseparable diastereomers (dr = 3:1) as a yellow solid (75.7 mg, 91% yield), m.p.: 142.6-143.1 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.24 (m, 3H), 7.18 – 6.92 (m, 5H), 6.88 (t, *J* = 2.0 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 5.35 (s, 1H), 3.71 (d, *J* = 16.2 Hz, 1H), 2.63 (d, *J* = 16.3 Hz, 1H), 2.41 (s, 3H), 1.41 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 183.0, 180.9, 155.0, 154.6, 153.4, 153.1, 140.5, 138.7, 138.5, 138.2, 137.8, 137.7, 133.6, 133.3, 129.1, 128.94, 128.89, 128.8, 128.7, 128.3, 128.2, 127.8, 127.14, 127.09, 125.5, 125.4, 125.3, 124.9, 124.7, 124.4, 122.0, 121.6, 121.4, 120.2, 120.1, 119.2, 81.5, 80.1, 59.7, 59.5, 34.9, 33.3, 33.1, 29.9, 29.8, 20.2, 17.3. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{27}H_{27}ClNO^+$ 416.1776; found: 416.1770.

8-(tert-butyl)-2'-methyl-2-(o-tolyl)spiro[chromane-3,3'-indole] (4h)



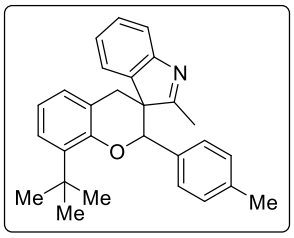
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **4h** as inseparable diastereomers (dr = 2.5:1) as a yellow solid (76.7 mg, 97% yield), m.p.: 94.7-95.6 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 7.7 Hz, 1H), 7.40 – 7.28 (m, 2H), 7.24 – 7.03 (m, 4H), 7.03 – 6.89 (m, 2H), 6.86 – 6.78 (m, 1H), 6.46 (d, *J* = 7.9 Hz, 1H), 3.53 (d, *J* = 16.2 Hz, 1H). 2.72 (d, *J* = 16.2 Hz, 1H), 2.28 (s, 3H), 2.22 (s, 3H), 1.37 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 184.0, 182.7, 154.9, 154.3, 154.1, 153.9, 141.0, 140.2, 138.3, 137.9, 135.8, 135.3, 134.9, 134.8, 130.5, 130.2, 128.8, 128.5, 128.3, 128.2, 127.8, 126.3, 126.2, 126.1, 125.9, 125.5, 125.4, 125.2, 124.9, 124.2, 121.8, 121.1, 120.9, 120.2, 120.0, 119.4, 77.5, 75.6, 59.2, 58.4, 34.9, 34.6, 34.1, 29.9, 29.6, 27.0, 20.3, 20.2, 19.8, 17.3. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{28}H_{30}NO^+$ 396.2322; found: 396.2274.

8-(tert-butyl)-2'-methyl-2-(m-tolyl)spiro[chromane-3,3'-indole] (4i)



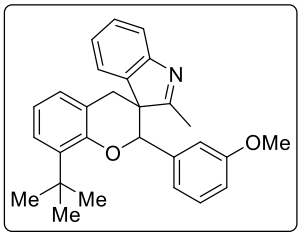
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **4i** as inseparable diastereomers (dr = 3:1) as a yellow solid (77.5 mg, 98% yield), m.p.: 98.7-100.1 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.22 (m, 3H), 7.21 – 7.17 (m, 1H), 7.14 – 7.06 (m, 1H), 7.06 – 6.80 (m, 4H), 6.67 (d, *J* = 8.9 Hz, 1H), 5.36 (s, 1H), 3.72 (d, *J* = 16.1 Hz, 1H), 2.62 (d, *J* = 16.2 Hz, 1H), 2.40 (s, 3H), 2.15 (s, 3H), 1.43 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 183.5, 181.4, 155.0, 154.6, 153.7, 153.4, 141.0, 139.2, 138.4, 138.1, 137.2, 136.9, 135.7, 135.6, 129.5, 128.8, 128.4, 128.2, 127.7, 127.6, 127.4, 125.2, 125.2, 125.1, 124.5, 123.8, 123.6, 122.2, 121.2, 121.0, 120.2, 119.95, 119.88, 119.3, 82.2, 80.8, 59.7, 59.6, 34.9, 33.6, 33.3, 29.9, 29.7, 27.0, 21.4, 20.2, 17.2. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{28}H_{30}NO^+$ 396.2322; found: 396.2268.

8-(tert-butyl)-2'-methyl-2-(p-tolyl)spiro[chromane-3,3'-indole] (4j)



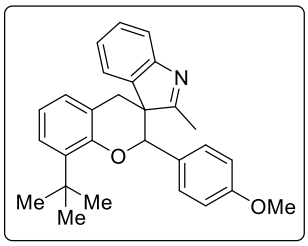
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **4j** as inseparable diastereomers (dr = 2.5:1) as a yellow solid (78.3 mg, 99% yield), m.p.: 193.7-194.6 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 7.5 Hz, 1H), 7.36 – 7.22 (m, 3H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.14 – 7.06 (m, 1H), 7.05 – 6.97 (m, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 2H), 6.77 (d, *J* = 8.1 Hz, 1H), 5.38 (s, 1H), 3.72 (d, *J* = 16.5 Hz, 1H), 2.61 (d, *J* = 16.1 Hz, 1H), 2.40 (s, 3H), 2.22 (s, 3H), 1.42 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 183.6, 181.5, 155.0, 154.5, 153.7, 153.5, 141.0, 139.2, 138.4, 138.0, 137.6, 132.8, 132.7, 128.5, 128.4, 128.3, 128.2, 127.7, 126.6, 126.5, 125.2, 125.1, 124.4, 122.1, 121.2, 121.0, 120.1, 120.0, 119.9, 119.3, 82.0, 80.6, 59.8, 59.6, 34.9, 33.6, 33.3, 29.8, 29.7, 21.2, 21.1, 20.2, 17.2. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{28}H_{30}NO^+$ 396.2322; found: 396.2268.

8-(tert-butyl)-2-(3-methoxyphenyl)-2'-methylspiro[chromane-3,3'-indole] (4k)



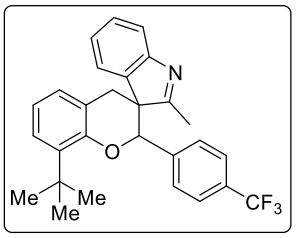
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 2:5:50) afforded the product **4k** as inseparable diastereomers (dr = 6:1) as a yellow solid (79.8 mg, 97% yield), m.p.: 152.0-152.9 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 7.7 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.18 (d, *J* = 6.8 Hz, 1H), 7.14 – 7.04 (m, 1H), 7.04 – 6.92 (m, 3H), 6.76 – 6.68 (m, 1H), 6.62 (dd, *J* = 17.1, 8.0 Hz, 1H), 6.31 – 6.26 (m, 1H), 5.37 (s, 1H), 3.72 (d, *J* = 16.1 Hz, 1H), 3.41 (s, 3H), 2.62 (d, *J* = 16.2 Hz, 1H), 2.39 (s, 3H), 1.41 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 181.4, 158.9, 155.2, 153.7, 139.4, 138.1, 137.2, 128.7, 128.5, 128.2, 125.3, 125.2, 124.5, 121.1, 120.1, 119.4, 115.5, 111.3, 80.6, 59.8, 54.9, 35.0, 33.6, 29.7, 17.3. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{28}H_{30}NO_2^+$ 412.2271; found: 412.2215.

8-(tert-butyl)-2-(4-methoxyphenyl)-2'-methylspiro[chromane-3,3'-indole] (4l)



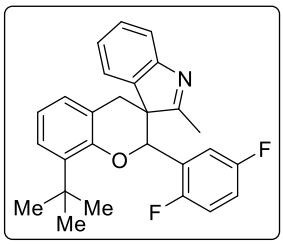
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 2:5:50) afforded the product **4l** as inseparable diastereomers (dr = 2.5:1) as a yellow solid (68.3 mg, 83% yield), m.p.: 128.5-129.2 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 7.6 Hz, 1H), 7.36 – 7.27 (m, 2H), 7.25 – 7.20 (m, 1H), 7.17 (d, *J* = 6.8 Hz, 1H), 7.13 – 7.05 (m, 1H), 7.02 – 6.92 (m, 2H), 6.83 – 6.75 (m, 1H), 6.64 – 6.55 (m, 2H), 5.35 (s, 1H), 3.76 – 3.66 (m, 4H), 2.60 (d, *J* = 16.2 Hz, 1H), 2.38 (s, 3H), 1.41 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 183.6, 181.6, 159.7, 159.1, 155.1, 154.6, 153.8, 153.6, 141.1, 139.3, 138.4, 138.1, 128.4, 128.2, 128.1, 128.0, 127.9, 127.7, 125.2, 125.2, 125.1, 124.5, 122.0, 121.2, 121.0, 120.2, 120.0, 119.4, 113.2, 113.0, 81.9, 80.4, 59.8, 59.7, 55.1, 34.9, 33.7, 33.4, 29.9, 29.7, 20.2, 17.2. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{28}H_{30}NO_2^+$ 412.2271; found: 412.2215.

8-(tert-butyl)-2'-methyl-2-(4-(trifluoromethyl)phenyl)spiro[chromane-3,3'-indole] (4m)



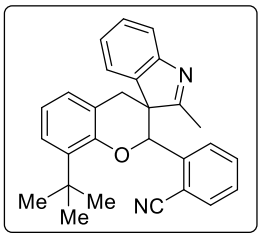
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **4m** as inseparable diastereomers (dr = 2:1) as a yellow solid (78.2 mg, 87% yield), m.p.: 105.3-106.3 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.40 – 7.26 (m, 5H), 7.21 – 7.06 (m, 2H), 7.00 (q, *J* = 7.4, 6.7 Hz, 4H), 5.44 (s, 1H), 3.73 (d, *J* = 16.1 Hz, 1H), 2.64 (d, *J* = 16.3 Hz, 1H), 2.42 (s, 3H), 1.39 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 182.9, 180.7, 155.0, 154.6, 153.4, 153.1, 140.4, 139.7, 138.7, 138.3, 129.0, 128.8, 128.3, 127.8, 127.2, 127.1, 125.54, 125.48, 125.4, 124.9 (q, *J* = 3.7 Hz), 124.6 (q, *J* = 3.7 Hz), 124.5, 124.0 (q, *J* = 272.9 Hz), 122.0, 121.7, 121.5, 120.4, 120.3, 120.2, 119.3, 81.7, 80.2, 59.8, 59.6, 35.0, 33.4, 33.1, 30.0, 29.8, 20.2, 17.3. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{28}H_{27}F_3NO^+$ 450.2039; found: 450.1997.

8-(tert-butyl)-2-(2,5-difluorophenyl)-2'-methylspiro[chromane-3,3'-indole] (4n)



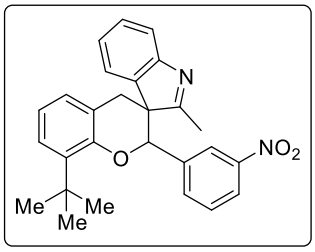
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **4n** as inseparable diastereomers (dr = 1.5:1) as a yellow solid (55.9 mg, 67% yield), m.p.: 136.1-137.0 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 7.5 Hz, 1H), 7.37 – 7.26 (m, 2H), 7.23 – 7.07 (m, 2H), 7.07 – 6.78 (m, 4H), 6.21 – 6.15 (m, 1H), 5.81 (s, 1H), 3.75 (d, *J* = 16.4 Hz, 1H), 2.66 (d, *J* = 16.1 Hz, 1H), 2.39 (s, 3H), 1.38 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 182.7, 181.5, 159.9, 159.7, 156.6, 156.5, 155.5 (dd, J = 241.6, 2.2 Hz), 155.2 (dd, J = 242.9, 2.2), 155.1, 154.2, 153.41, 153.37, 139.4, 138.6, 138.5, 138.3 129.0, 128.7, 128.3 127.9, 125.6, 125.5 125.4 125.3, 124.4, 122.6 (d, *J* = 3.7 Hz), 121.7, 121.6 120.3 120.2 119.8, 119.3, 117.1, 116.84 (dd, *J* = 24.2, 4.7), 116.81, 116.5, 116.0 (dd, *J* = 25.9, 8.6 Hz), 115.0 (dd, *J* = 26.1, 3.5 Hz), 114.0 (dd, *J* = 25.2, 3.1 Hz), 74.5 72.0 (d, *J* = 4.1 Hz), 59.5, 59.2, 34.9, 33.9, 33.41, 29.9, 29.8, 20.4, 16.6, 16.5. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{27}H_{26}F_2NO^+$ 418.1977; found: 418.1943.

2-(8-(tert-butyl)-2'-methylspiro[chromane-3,3'-indol]-2-yl)benzonitrile (4o)



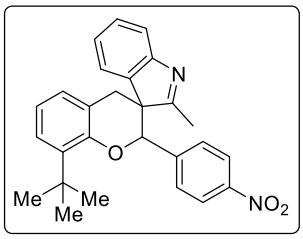
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 3:5:50) afforded the product **4o** separable diastereomers (dr = 3:1) as a yellow solid (44.7 mg, 55% yield), m.p.: 141.9-142.8 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.68 – 7.52 (m, 1H), 7.48 – 7.25 (m, 4H), 7.13 (d, *J* = 7.4 Hz, 3H), 7.08 – 6.92 (m, 2H), 6.52 (d, *J* = 8.1 Hz, 1H), 5.92 (s, 1H), 3.81 (d, *J* = 16.1 Hz, 1H), 2.65 (d, *J* = 16.1 Hz, 1H), 2.46 (s, 3H), 1.35 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 181.5, 155.1, 153.4, 139.2, 138.7, 138.0, 132.8, 132.7, 129.6, 129.0, 128.4, 127.5, 125.7, 125.5, 124.6, 121.7, 120.3, 119.2, 118.0, 111.7, 77.5, 59.5, 34.9, 33.9, 29.7, 17.3. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{28}H_{27}N_2O^+$ 407.2118; found: 407.2085.

8-(tert-butyl)-2'-methyl-2-(3-nitrophenyl)spiro[chromane-3,3'-indole] (4p)



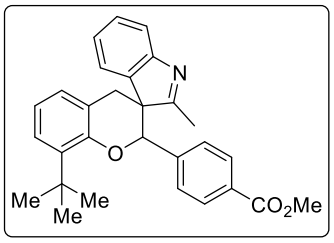
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 3:5:50) afforded the product **4p** as separable diastereomers (dr = 3:1) as a yellow solid (45.2 mg, 53% yield), m.p.: 148.4-149.1 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.08 – 7.99 (m, 1H), 7.84 (t, *J* = 2.0 Hz, 1H), 7.37 – 7.28 (m, 3H), 7.26 – 7.10 (m, 4H), 7.07 – 6.95 (m, 2H), 5.49 (s, 1H), 3.75 (d, *J* = 16.3 Hz, 1H), 2.68 (d, *J* = 16.3 Hz, 1H), 2.45 (s, 3H), 1.40 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 180.5, 154.9, 153.1, 147.6, 138.3, 138.2, 137.8, 132.5, 129.1, 128.8, 128.3, 125.8, 125.6, 124.5, 123.8, 122.0, 121.7, 120.3, 119.2, 79.6, 59.9, 35.0, 32.9, 29.9, 17.4. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{27}H_{27}N_2O_3^+$ 427.2016; found: 427.2000.

8-(tert-butyl)-2'-methyl-2-(4-nitrophenyl)spiro[chromane-3,3'-indole] (4q)



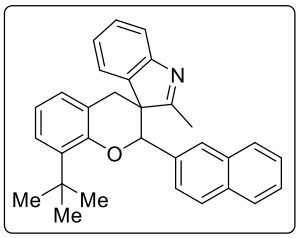
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 3:5:50) afforded the product **4q** as separable diastereomers (dr = 2:1) as a yellow solid (35.8 mg, 42% yield), m.p.: 191.9-193.5 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.8 Hz, 2H), 7.37 – 7.28 (m, 3H), 7.20 – 7.11 (m, 2H), 7.09 – 6.98 (m, 4H), 5.48 (s, 1H), 3.74 (d, *J* = 16.7 Hz, 1H), 2.67 (d, *J* = 16.2 Hz, 1H), 2.44 (s, 3H), 1.39 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 180.4, 154.9, 153.1, 148.1, 142.8, 138.3, 129.1, 128.3, 127.7, 125.74, 125.68, 124.4, 123.1, 121.8, 120.4, 119.2, 79.7, 59.9, 35.0, 33.0, 29.9, 17.4. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{27}H_{27}N_2O_3^+$ 427.2016; found: 427.2000.

methyl 4-(8-(tert-butyl)-2'-methylspiro[chromane-3,3'-indol]-2-yl)benzoate (4r)



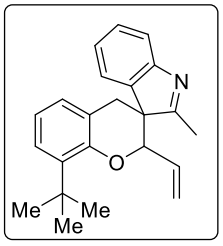
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 2:5:50) afforded the product **4r** as separable diastereomers (dr = 2:1) as a yellow solid (38.7 mg, 44% yield), m.p.: 128.2-129.0 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.37 (dd, *J* = 5.9, 3.3 Hz, 1H), 7.29 (d, *J* = 6.4 Hz, 2H), 7.26 (d, *J* = 2.5 Hz, 2H), 7.16 – 7.07 (m, 3H), 6.99 (t, *J* = 7.6 Hz, 1H), 5.45 (s, 1H), 3.85 (s, 3H), 3.75 (d, *J* = 17.6 Hz, 1H), 2.86 (d, *J* = 17.5 Hz, 1H), 2.36 (s, 3H), 1.42 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 183.0, 166.8, 154.6, 153.2, 140.7, 140.5, 138.6, 129.9, 128.9, 128.8, 127.8, 126.8, 125.42, 125.37, 122.1, 121.6, 120.3, 120.2, 81.9, 59.6, 52.2, 35.0, 33.2, 29.9, 20.2. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{29}H_{30}NO_3^+$ 440.2220; found: 440.2188.

8-(tert-butyl)-2'-methyl-2-(naphthalen-2-yl)spiro[chromane-3,3'-indole] (4s)



Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **4s** as inseparable diastereomers (dr = 3:1) as a yellow solid (85.5 mg, 99% yield), m.p.: 191.6-192.2 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.70 (ddd, *J* = 14.2, 8.2, 4.0 Hz, 2H), 7.62 – 7.27 (m, 8H), 7.22 – 6.98 (m, 3H), 6.92 (dd, *J* = 8.7, 1.7 Hz, 1H), 5.58 (s, 1H), 3.78 (d, *J* = 15.9 Hz, 1H), 2.68 (d, *J* = 16.2 Hz, 1H), 2.45 (s, 3H), 1.46 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 183.4, 181.3, 155.0, 154.6, 153.7, 153.4, 140.9, 139.2, 138.5, 138.1, 133.5, 133.4, 133.0, 132.64, 132.57, 128.5, 128.25, 128.16, 127.8, 127.6, 127.5, 127.2, 126.5, 126.4, 126.3, 126.1, 126.04, 125.96, 125.3, 125.2, 124.5, 124.4, 124.3, 122.1, 121.3, 121.1, 120.1, 119.4, 82.3, 81.0, 59.8, 59.7, 34.9, 33.7, 33.5, 29.9, 29.8, 27.0, 20.3, 17.2. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{31}H_{30}NO^+$ 432.2322; found: 432.2318.

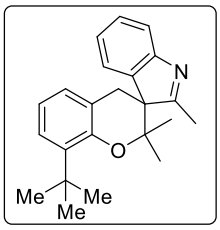
8-(tert-butyl)-2'-methyl-2-vinylspiro[chromane-3,3'-indole] (4t)



Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **4t** as inseparable diastereomers (dr = 2:1) as a yellow solid (57.1 mg, 86% yield), m.p.: 85.7-86.4 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.7 Hz, H), 7.41 – 7.27 (m, 2H), 7.26 – 7.21 (m, 1H), 7.12 – 6.97 (m, 2H), 6.95 – 6.87 (m, 1H), 5.47 – 5.34 (m, 1H), 5.33 – 5.15 (m, 1H), 5.06 (ddd, *J* = 10.4, 7.6, 1.8 Hz, 1H), 4.92 – 4.77 (m, 1H), 3.59 (d, *J* = 16.0 Hz, 1H), 2.52 (d, *J* = 16.2 Hz, 1H), 2.36 (s, 3H), 1.46 (s, 9H). **^{13}C NMR** (75

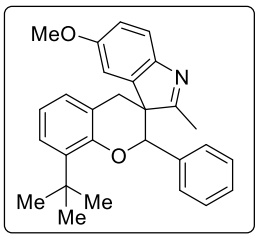
MHz, Chloroform-*d*) δ 184.2, 181.9, 154.9, 154.8, 152.9, 152.7, 145.7, 141.9, 139.4, 138.0, 132.3, 131.9, 131.4, 128.7, 128.4, 128.1, 128.0, 127.7, 126.7, 125.7, 125.5, 125.3, 125.2, 124.1, 123.6, 121.6, 121.2, 120.9, 120.2, 120.0, 119.7, 119.2, 118.5, 78.9, 78.7, 58.6, 58.3, 34.9, 32.8, 32.8, 30.6, 29.8, 29.7, 19.6, 19.1, 16.7. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{23}H_{26}NO^+$ 332.2009; found: 332.1960.

8-(tert-butyl)-2,2,2'-trimethylspiro[chromane-3,3'-indole] (4u)



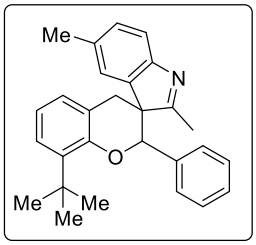
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **4u** as a yellow oil (60.7 mg, 91% yield). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 7.6 Hz, 1H), 7.41 – 7.28 (m, 2H), 7.27 – 7.12 (m, 2H), 6.96 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.88 (t, *J* = 7.6 Hz, 1H), 3.33 (d, *J* = 17.6 Hz, 1H), 2.73 (d, *J* = 17.6 Hz, 1H), 2.23 (s, 3H), 1.48 (s, 5H), 1.44 (s, 9H), 1.12 (s, 3H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 185.6, 155.2, 151.8, 141.1, 138.4, 128.5, 127.5, 125.2, 125.1, 123.4, 120.5, 120.1, 119.5, 76.6, 61.6, 34.9, 30.8, 29.9, 23.8, 23.6, 19.5. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{23}H_{28}NO^+$ 334.2165; found: 334.2108.

8-(tert-butyl)-5'-methoxy-2'-methyl-2-phenylspiro[chromane-3,3'-indole] (4v)



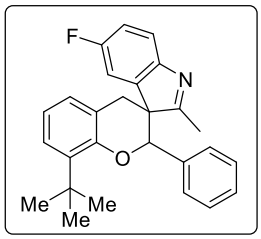
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 2:5:50) afforded the product **4v** as inseparable diastereomers (dr = 3:1) as a yellow solid (79.8 mg, 97% yield), m.p.: 89.2-90.3 ℃. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.34 – 7.28 (m, 2H), 7.23 – 7.17 (m, 1H), 7.16 – 7.02 (m, 3H), 6.99 (d, *J* = 7.3 Hz, 2H), 6.95 – 6.93 (m, 1H), 6.87 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.80 (d, *J* = 2.4 Hz, 1H), 5.41 (s, 1H), 3.78 (d, *J* = 16.1 Hz, 1H), 3.69 (s, 3H), 2.64 (d, *J* = 16.2 Hz, 1H), 2.39 (s, 3H), 1.44 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 181.2, 179.1, 157.9, 157.7, 153.6, 153.4, 148.8, 148.3, 142.5, 140.7, 138.4, 138.1, 135.9, 135.8, 129.5, 128.8, 128.3, 128.1, 127.8, 127.7, 127.6, 126.9, 126.8, 125.3, 125.2, 121.3, 121.2, 120.3, 120.2, 119.2, 113.6, 112.6, 110.6, 109.2, 82.3, 80.7, 59.8, 59.7, 55.9, 55.6, 34.9, 33.7, 33.6, 29.9, 29.8, 27.0, 20.1, 17.1. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{28}H_{30}NO_2^+$ 412.2271; found: 412.2264.

8-(tert-butyl)-2',5'-dimethyl-2-phenylspiro[chromane-3,3'-indole] (4w)



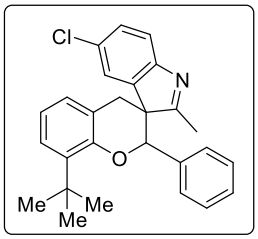
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **4w** as inseparable diastereomers (dr = 3:1) as a yellow solid (72.8 mg, 92% yield), m.p.: 98.4-99.5 ℃. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 8.1 Hz, 2H), 7.25 – 7.09 (m, 5H), 7.06 (d, *J* = 10.6 Hz, 2H), 6.93 (d, *J* = 7.3 Hz, 2H), 5.41 (s, 1H), 3.76 (d, *J* = 16.2 Hz, 1H), 2.67 (d, *J* = 16.2 Hz, 1H), 2.43 (s, 3H), 2.33 (s, 3H), 1.47 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 182.4, 180.2, 153.8, 153.5, 152.9, 152.5, 141.1, 139.3, 138.5, 138.1, 136.0, 135.9, 135.0, 134.9, 129.05, 128.99, 128.7, 128.2, 128.1, 127.8, 127.7, 127.6, 126.9, 126.8, 125.4, 125.2, 125.2, 122.9, 121.3, 121.1, 120.4, 119.6, 119.5, 82.3, 80.9, 59.6, 59.5, 34.9, 33.7, 33.5, 29.9, 29.7, 21.7, 21.6, 20.2, 17.2. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{28}H_{30}NO^+$ 396.2322; found: 396.2268.

8-(tert-butyl)-5'-fluoro-2'-methyl-2-phenylspiro[chromane-3,3'-indole] (4x)



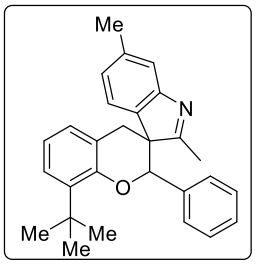
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **4x** as separable diastereomers (dr = 3:1) as a yellow solid (68.7 mg, 86% yield), m.p.: 159.8-160.6 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.32 – 7.26 (m, 2H), 7.22 – 7.16 (m, 2H), 7.15 – 7.09 (m, 3H), 7.09 – 7.02 (m, 3H), 6.97 (t, *J* = 7.6 Hz, 1H), 5.34 (s, 1H), 3.67 (d, *J* = 17.4 Hz, 1H), 2.84 (d, *J* = 17.3 Hz, 1H), 2.33 (s, 3H), 1.40 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 184.0, 153.4 (d, *J* = 12.0 Hz), 142.9, 137.1 (d, *J* = 241.3 Hz), 131.0, 128.5 (d, *J* = 22.8 Hz), 127.84, 127.80 (d, *J* = 8 Hz), 126.8, 125.4, 122.7, 121.5, 121.0, 119.8, 82.2, 60.3, 35.0, 33.3, 29.9, 20.2. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{27}H_{27}FNO^+$ 400.2071; found: 400.2054.

8-(tert-butyl)-5'-chloro-2'-methyl-2-phenylspiro[chromane-3,3'-indole] (4y)



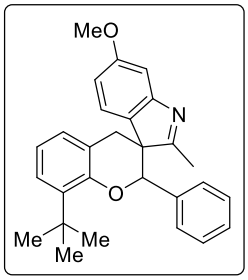
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **4y** as separable diastereomers (dr = 2.5:1) as a yellow solid (69.1 mg, 83% yield), m.p.: 161.2-162.3 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.30 – 7.26 (m, 1H), 7.21 – 7.15 (m, 1H), 7.15 – 7.08 (m, 3H), 7.07 – 7.03 (m, 3H), 7.02 – 6.93 (m, 2H), 6.92 – 6.86 (m, 1H), 5.33 (s, 1H), 3.65 (d, *J* = 17.4 Hz, 1H), 2.85 (d, *J* = 17.4 Hz, 1H), 2.33 (s, 3H), 1.40 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 183.4, 153.4, 150.7, 143.0, 138.6, 135.5, 128.4, 127.8, 127.7, 126.8, 125.4, 121.5, 120.9, 120.8, 119.9, 115.2, 114.9, 110.1, 109.8, 82.3, 60.3, 35.0, 33.4, 29.9, 20.3. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{27}H_{27}ClNO^+$ 416.1776; found: 416.1760.

8-(tert-butyl)-2',6'-dimethyl-2-phenylspiro[chromane-3,3'-indole] (4z)



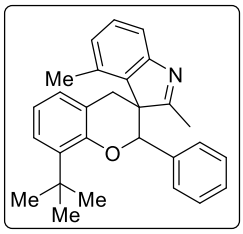
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **4z** as inseparable diastereomers (dr = 5:1) as a yellow solid (74.4 mg, 94% yield), m.p.: 154.2-155.6 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 7.4 Hz, 1H), 7.23 – 7.14 (m, 2H), 7.13 – 6.98 (m, 5H), 6.93 – 6.87 (m, 3H), 5.38 (s, 1H), 3.70 (d, *J* = 16.1 Hz, 1H), 2.58 (d, *J* = 16.1 Hz, 1H), 2.38 (s, 3H), 2.36 (s, 3H), 1.41 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 183.5, 181.5, 155.3, 154.8, 153.7, 153.5, 138.4, 138.1, 138.0, 136.2, 136.0, 135.9, 128.7, 128.2, 128.0, 127.8, 127.6, 126.9, 126.8, 126.0, 125.9, 125.2, 124.0, 121.7, 121.2, 121.0, 120.75, 120.69, 120.3, 119.5, 82.3, 80.8, 59.5, 59.3, 34.9, 33.9, 33.6, 29.9, 29.8, 21.6, 20.2, 17.3. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{28}H_{30}NO^+$ 396.2322; found: 396.2281.

8-(tert-butyl)-6'-methoxy-2'-methyl-2-phenylspiro[chromane-3,3'-indole] (4za)



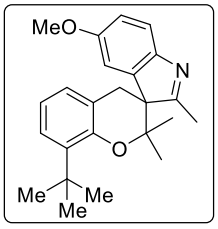
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 2:5:50) afforded the product **4za** as inseparable diastereomers (dr = 3:1) as a yellow solid (73.3 mg, 89% yield), m.p.: 129.6-131.1 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.35 – 7.26 (m, 1H), 7.22 – 7.14 (m, 1H), 7.14 – 7.00 (m, 4H), 7.00 – 6.82 (m, 4H), 6.64 (dd, *J* = 8.3, 2.4 Hz, 1H), 5.36 (s, 1H), 3.78 (s, 2H), 3.69 (d, *J* = 16.1 Hz, 1H), 2.58 (d, *J* = 16.1 Hz, 1H), 2.38 (s, 3H), 1.40 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 184.8, 182.7, 160.5, 156.5, 156.0, 153.7, 153.5, 138.5, 138.2, 136.05, 135.97, 133.0, 131.2, 128.8, 128.2, 128.1, 127.8, 127.7, 127.6, 126.9, 126.8, 125.3, 125.2, 124.7, 122.3, 121.3, 121.1, 120.4, 119.5, 111.3, 111.2, 105.9, 82.4, 81.0, 59.4, 59.2, 55.6, 34.9, 34.1, 33.6, 29.9, 29.8, 20.3, 17.3. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{28}H_{30}NO_2^+$ 412.2271; found: 412.2264.

8-(tert-butyl)-2',4'-dimethyl-2-phenylspiro[chromane-3,3'-indole] (4zb)



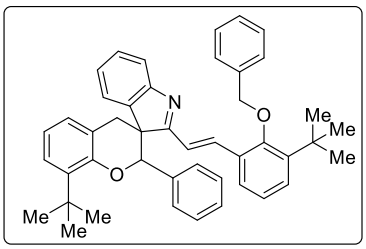
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **4zb** as inseparable diastereomers (dr >20:1) as a yellow solid (39.6 mg, 50% yield), m.p.: 117.6-119.8 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 6.7 Hz, 1H), 7.17 – 7.04 (m, 8H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.98 – 6.93 (m, 1H), 5.72 (s, 1H), 4.02 (d, *J* = 17.9 Hz, 1H), 2.77 (d, *J* = 17.9 Hz, 1H), 2.63 (s, 3H), 2.37 (s, 3H), 1.43 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 183.4, 155.0, 153.8, 138.8, 138.1, 136.0, 132.6, 128.6, 128.2, 128.0, 127.8, 127.7, 126.1, 125.1, 121.5, 120.2, 118.0, 79.0, 61.4, 34.9, 29.9, 29.8, 20.3, 18.8. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{28}H_{30}NO^+$ 396.2322; found: 396.2281.

8-(tert-butyl)-5'-methoxy-2,2,2'-trimethylspiro[chromane-3,3'-indole] (4zc)



Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 2:5:50) afforded the product **4zc** as a yellow solid (65.4 mg, 90% yield), m.p.: 152.7-153.3 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 9.1 Hz, 1H), 7.21 (dd, *J* = 7.5, 1.8 Hz, 1H), 6.99 – 6.91 (m, 1H), 6.92 – 6.81 (m, 3H), 3.78 (s, 3H), 3.23 (d, *J* = 17.4 Hz, 1H), 2.77 (d, *J* = 17.6 Hz, 1H), 2.20 (s, 3H), 1.44 (s, 12H), 1.16 (s, 3H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 183.1, 157.8, 151.8, 148.9, 142.8, 138.4, 127.6, 125.1, 120.5, 120.3, 119.5, 112.6, 110.8, 76.6, 61.7, 55.8, 35.0, 31.0, 29.9, 23.9, 23.4, 19.4. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{24}H_{30}NO_2^+$ 364.2271; found: 364.2239.

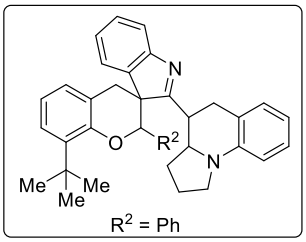
(E)-2'-(2-(benzyloxy)-3-(tert-butyl)styryl)-8-(tert-butyl)-2-phenylspiro[chromane-3,3'-indole] (5a)



Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **5a** as separable diastereomers (dr = 2.5:1) as a yellow oil. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 16.5 Hz, 1H), 7.61 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.51 – 7.41 (m, 4H), 7.37 – 7.24 (m, 6H), 7.20 (dd, *J* = 8.9, 6.9 Hz, 2H), 7.15 – 7.03 (m, 2H), 6.97 (td, *J* = 7.7, 2.4 Hz, 3H), 6.92 – 6.85 (m, 3H), 5.43 (s, 1H), 5.06 (s, 2H), 3.78 (d, *J* = 16.5 Hz, 1H), 2.62 (d, *J* = 16.7 Hz, 1H), 1.51 (s, 9H), 1.44 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*)

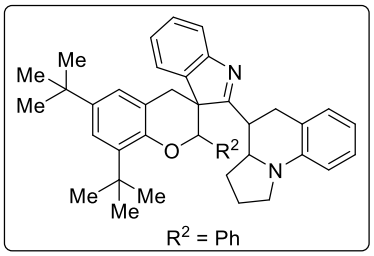
δ 177.4, 157.7, 155.4, 153.7, 143.9, 140.1, 138.1, 137.1, 135.8, 134.8, 130.6, 128.9, 128.7, 128.6, 128.4, 128.3, 127.9, 127.3, 127.1, 126.9, 125.6, 125.1, 124.5, 124.3, 121.7, 121.0, 120.7, 119.5, 80.6, 76.6, 59.3, 35.4, 34.9, 33.6, 31.2, 29.9, 27.0. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{45}H_{46}NO_2^+$ 632.3523; found: 632.3508.

8-(tert-butyl)-2'-(1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)-2-phenylspiro[chromane-3,3'-indole] (7a)



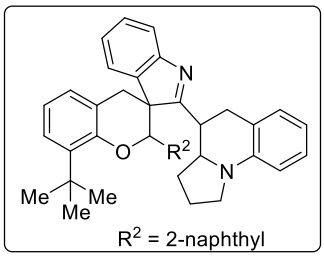
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **7a** as separable diastereomers (dr = 3:1) as a yellow solid (81.9 mg, 76% yield), m.p.: 218.6-220.9 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.7 Hz, 1H), 7.48 – 7.36 (m, 1H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.33 – 7.23 (m, 2H), 7.20 (t, *J* = 7.7 Hz, 3H), 7.18 – 7.08 (m, 3H), 7.00 (d, *J* = 6.3 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 2H), 6.82 (t, *J* = 8.2 Hz, 3H), 6.58 (t, *J* = 7.3 Hz, 1H), 6.47 (d, *J* = 8.0 Hz, 1H), 5.40 (s, 1H), 3.85 (td, *J* = 11.1, 10.3, 5.0 Hz, 2H), 3.46 (t, *J* = 8.8 Hz, 1H), 3.28 (td, *J* = 9.5, 6.9 Hz, 1H), 2.79 (dd, *J* = 15.7, 11.9 Hz, 1H), 2.60 – 2.44 (m, 2H), 2.23 (dd, *J* = 15.9, 3.1 Hz, 1H), 2.17 – 2.06 (m, 2H), 2.07 – 1.85 (m, 1H), 1.65 – 1.48 (m, 1H), 1.35 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 187.3, 154.9, 153.8, 143.9, 139.3, 138.0, 136.8, 129.6, 128.7, 128.4, 128.3, 128.1, 128.0, 127.7, 125.9, 125.4, 124.7, 121.4, 121.1, 120.6, 119.2, 115.0, 109.7, 81.2, 64.1, 59.4, 47.1, 38.3, 35.8, 34.9, 34.8, 32.6, 29.6, 24.1. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{38}H_{39}N_2O^+$ 539.3057; found: 539.3035.

6,8-di-tert-butyl-2'-(1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)-2-phenylspiro[chromane-3,3'-indole] (7b)



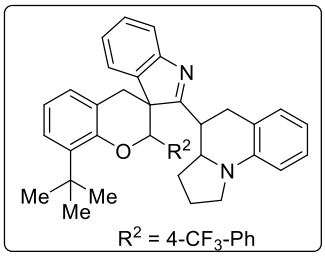
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **7b** as separable diastereomers (dr = 2:1) as a yellow solid (89.2 mg, 75% yield), m.p.: 115.3-116.4 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 7.6 Hz, 1H), 7.42 (td, *J* = 7.8, 7.3, 1.9 Hz, 1H), 7.38 – 7.26 (m, 2H), 7.24 – 7.08 (m, 5H), 6.96 (d, *J* = 2.2 Hz, 1H), 6.85 – 6.75 (m, 3H), 6.57 (t, *J* = 7.1 Hz, 1H), 6.47 (d, *J* = 8.0 Hz, 1H), 5.37 (s, 1H), 3.85 (td, *J* = 11.9, 10.9, 5.5 Hz, 2H), 3.46 (t, *J* = 8.8 Hz, 1H), 3.29 (td, *J* = 9.4, 7.3 Hz, 1H), 2.79 (dd, *J* = 15.8, 11.9 Hz, 1H), 2.58 – 2.43 (m, 2H), 2.27 – 2.07 (m, 3H), 2.08 – 1.88 (m, 1H), 1.66 – 1.51 (m, 1H), 1.36 (s, 9H), 1.33 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 187.5, 155.1, 151.5, 144.0, 143.3, 139.5, 137.1, 129.5, 128.6, 128.4, 128.12, 128.08, 127.7, 125.8, 124.9, 124.8, 122.6, 121.5, 120.6, 118.3, 115.0, 109.7, 81.3, 64.1, 59.7, 47.1, 38.4, 35.8, 35.14, 35.08, 34.5, 32.6, 31.7, 29.7, 24.2. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{42}H_{47}N_2O^+$ 595.3683; found: 595.3653.

8-(tert-butyl)-2'-(1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)-2-(naphthalen-2-yl)spiro [chromane-3,3'-indole] (7c)



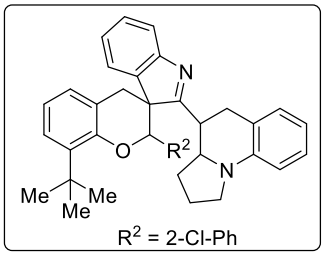
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **7c** as separable diastereomers (dr = 3.5:1) as a yellow solid (96.6 mg, 82% yield), m.p.: 167.6-169.2 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.83 – 7.75 (m, 1H), 7.73 – 7.65 (m, 1H), 7.62 – 7.54 (m, 2H), 7.54 – 7.47 (m, 2H), 7.46 – 7.40 (m, 2H), 7.32 – 7.27 (m, 1H), 7.24 – 7.08 (m, 3H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.77 (dd, *J* = 8.7, 1.4 Hz, 1H), 6.67 (d, *J* = 7.0 Hz, 1H), 6.57 (t, *J* = 7.2 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 1H), 5.57 (s, 1H), 3.94 (d, *J* = 15.5 Hz, 1H), 3.80 (td, *J* = 10.2, 4.8 Hz, 1H), 3.44 (t, *J* = 8.8 Hz, 1H), 3.28 (td, *J* = 9.9, 7.6 Hz, 1H), 2.78 – 2.66 (m, 1H), 2.62 (dd, *J* = 9.3, 2.5 Hz, 1H), 2.55 (d, *J* = 15.6 Hz, 1H), 2.28 (dd, *J* = 15.1, 2.0 Hz, 1H), 2.12 (dq, *J* = 11.3, 5.7 Hz, 2H), 2.04 – 1.85 (m, 1H), 1.59 – 1.48 (m, 1H), 1.33 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 187.1, 155.1, 153.8, 143.9, 139.2, 138.1, 134.4, 133.9, 132.8, 128.8, 128.33, 128.27, 128.2, 128.1, 127.9, 127.7, 126.8, 126.4, 125.9, 125.5, 124.9, 124.8, 121.4, 121.1, 120.7, 119.2, 115.1, 109.7, 81.5, 64.3, 59.8, 47.1, 38.4, 36.0, 34.9, 34.7, 32.7, 29.7, 24.2. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{42}H_{41}N_2O^+$ 589.3213; found: 589.3188.

8-(tert-butyl)-2'-(1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)-2-(4-(trifluoromethyl)phenyl) spiro[chromane-3,3'-indole] (7d)



Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **7d** as separable diastereomers (dr = 2:1) as a yellow solid (61.9 mg, 51% yield), m.p.: 229.3-230.4 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 7.8 Hz, 1H), 7.50 – 7.40 (m, 3H), 7.31 – 7.26 (m, 1H), 7.19 – 7.10 (m, 3H), 7.02 – 6.91 (m, 4H), 6.79 (d, *J* = 7.2 Hz, 1H), 6.59 (t, *J* = 7.4 Hz, 1H), 6.47 (d, *J* = 8.0 Hz, 1H), 5.44 (s, 1H), 3.92 – 3.77 (m, 2H), 3.45 (t, *J* = 8.8 Hz, 1H), 3.28 (q, *J* = 8.7 Hz, 1H), 2.86 (dd, *J* = 15.7, 11.9 Hz, 1H), 2.59 – 2.47 (m, 2H), 2.27 – 2.19 (m, 1H), 2.17 – 2.06 (m, 2H), 2.03 – 1.88 (m, 1H), 1.57 – 1.49 (m, 1H), 1.33 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 186.7, 155.0, 153.4, 143.9, 140.7, 138.8, 138.1, 131.7 (q, *J* = 32.6 Hz), 129.0, 128.6, 128.3, 128.0, 127.8, 126.1, 125.6, 125.4 (q, *J* = 3.8 Hz), 124.7, 124.0 (q, *J* = 270.2 Hz), 121.5, 121.1, 120.9, 119.1, 115.2, 109.8, 80.5, 64.1, 59.3, 47.1, 38.4, 36.1, 34.9, 34.5, 32.6, 29.7, 24.1. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{39}H_{38}F_3N_2O^+$ 607.2931; found: 607.2884.

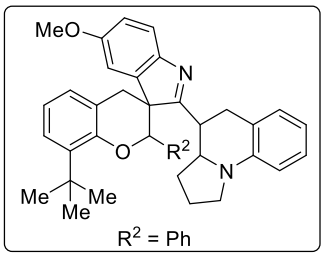
8-(tert-butyl)-2-(2-chlorophenyl)-2'-(1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)spiro [chromane-3,3'-indole] (7e)



Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **7e** as inseparable diastereomers (dr = 1:1) as a yellow solid (84.8 mg, 74% yield), m.p.: 192.3-193.5 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.51 – 7.38 (m, 2H), 7.33 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.30 (dd, *J* = 3.8, 1.5 Hz, 3H), 7.29 – 7.20 (m, 1H), 7.15 (dd, *J* = 7.9, 1.6 Hz, 3H), 7.11 (dd, *J* = 9.1, 2.5 Hz, 5H), 7.06 – 6.95 (m, 3H), 6.95 (d, *J* = 7.3 Hz, 1H), 6.96 – 6.85 (m, 2H), 6.87 – 6.77 (m, 2H), 6.56 (t, *J* = 7.2 Hz, 1H), 6.47 (t, *J* = 7.4 Hz, 2H), 6.42 – 6.30 (m, 2H), 6.12 (s, 1H), 6.01 (s, 1H), 3.90 (dtd, *J* = 15.2, 10.1, 5.2 Hz, 3H), 3.61 (d, *J* = 16.8 Hz, 1H), 3.45 (t, *J* = 8.8 Hz, 1H), 3.39 – 3.21 (m, 2H), 3.22 – 3.00

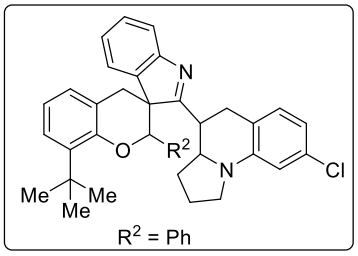
(m, 4H), 2.74 (dd, *J* = 15.5, 12.1 Hz, 1H), 2.63 – 2.37 (m, 3H), 2.21 – 1.87 (m, 7H), 1.63 – 1.45 (m, 2H), 1.34 (s, 9H), 1.20 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 189.6, 187.4, 155.1, 155.0, 154.1, 153.9, 143.82, 143.76, 141.2, 139.4, 138.9, 138.1, 134.7, 134.6, 134.4, 134.2, 130.7, 130.1, 129.9, 129.7, 128.8, 128.7, 128.5, 128.3, 128.2, 127.8, 127.6, 127.4, 127.2, 127.0, 126.0, 125.9, 125.54, 125.46, 124.5, 121.8, 121.5, 121.4, 121.2, 120.8, 120.5, 119.2, 115.1, 114.7, 109.6, 79.3, 75.6, 63.8, 62.8, 59.4, 59.0, 47.2, 46.9, 40.5, 38.2, 36.2, 35.8, 35.3, 35.1, 34.9, 34.7, 32.4, 31.9, 29.8, 29.6, 24.1, 23.7. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{38}H_{38}ClN_2O^+$ 573.2667; found: 573.2634.

8-(tert-butyl)-2'-(1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)-5'-methoxy-2-phenylspiro [chromane-3,3'-indole] (7f)



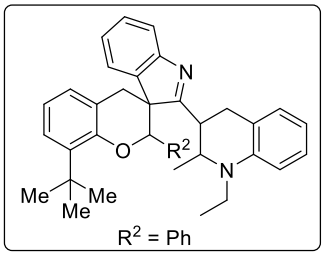
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 2:5:50) afforded the product **7f** as separable diastereomers (dr = 4:1) as a yellow solid (80.8 mg, 71% yield), m.p.: 204.6-205.9 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 8.5 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.27 – 7.16 (m, 3H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.02 – 6.91 (m, 2H), 6.90 (dd, *J* = 11.6, 3.4 Hz, 2H), 6.85 (s, 1H), 6.76 (d, *J* = 7.2 Hz, 1H), 6.72 (d, *J* = 2.5 Hz, 1H), 6.55 (t, *J* = 7.4 Hz, 1H), 6.45 (d, *J* = 8.0 Hz, 1H), 5.37 (s, 1H), 3.82 (td, *J* = 10.6, 10.0, 4.6 Hz, 2H), 3.64 (s, 3H), 3.44 (t, *J* = 8.5 Hz, 1H), 3.27 (td, *J* = 9.6, 7.0 Hz, 1H), 2.74 (dd, *J* = 15.5, 12.1 Hz, 1H), 2.55 – 2.38 (m, 2H), 2.23 – 2.04 (m, 3H), 2.06 – 1.84 (m, 1H), 1.60 – 1.42 (m, 1H), 1.34 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 185.0, 158.2, 153.7, 148.8, 144.0, 140.9, 137.9, 136.9, 129.5, 128.5, 128.4, 128.2, 128.1, 127.6, 125.4, 121.5, 121.2, 120.9, 119.1, 115.0, 114.1, 110.7, 109.6, 81.2, 64.0, 59.3, 55.6, 47.2, 38.2, 35.8, 35.0, 34.9, 32.6, 29.7, 24.2. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{39}H_{41}N_2O_2^+$ 569.3163; found: 569.3130.

8-(tert-butyl)-2'-(8-chloro-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)-2-phenylspiro [chromane-3,3'-indole] (7g)



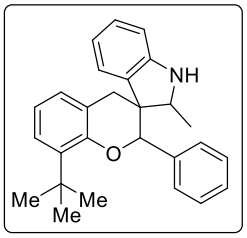
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **7g** as separable diastereomers (dr = 2:1) as a yellow solid (78 mg, 68% yield), m.p.: 180.8-182.7 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 7.7 Hz, 1H), 7.41 (td, *J* = 7.6, 1.3 Hz, 1H), 7.38 – 7.27 (m, 1H), 7.27 (d, *J* = 4.6 Hz, 1H), 7.24 – 7.09 (m, 3H), 7.09 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.03 (d, *J* = 1.8 Hz, 1H), 7.03 – 6.88 (m, 2H), 6.85 – 6.76 (m, 2H), 6.66 (q, *J* = 4.0 Hz, 2H), 5.37 (s, 1H), 4.17 (dt, *J* = 10.0, 7.9 Hz, 1H), 3.87 – 3.74 (m, 1H), 3.66 (d, *J* = 15.8 Hz, 1H), 3.17 – 3.02 (m, 1H), 2.90 – 2.67 (m, 2H), 2.56 (ddd, *J* = 12.0, 10.3, 4.2 Hz, 1H), 2.40 (dd, *J* = 16.2, 3.7 Hz, 1H), 2.26 – 2.07 (m, 1H), 2.06 – 1.86 (m, 1H), 1.90 – 1.66 (m, 2H), 1.30 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 188.2, 155.0, 153.7, 143.3, 139.2, 138.1, 137.2, 129.5, 129.1, 128.8, 128.4, 128.2, 127.5, 127.3, 125.8, 125.6, 124.7, 123.6, 121.2, 120.7, 119.9, 119.1, 80.9, 64.0, 59.2, 52.8, 36.6, 34.9, 34.5, 33.8, 29.8, 29.6, 23.5. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{38}H_{38}ClN_2O^+$ 573.2667; found: 573.2634.

8-(tert-butyl)-2'-(1-ethyl-2-methyl-1,2,3,4-tetrahydroquinolin-3-yl)-2-phenylspiro[chromane-3,3'-indole] (7h)



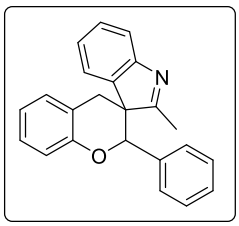
Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **7h** as separable diastereomers (dr = 2:1) as a yellow solid (66 mg, 61% yield) ,m.p.: 127.2-129.1 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.13 (dddd, *J* = 20.8, 14.4, 8.1, 3.7 Hz, 7H), 6.99 – 6.88 (m, 2H), 6.84 (d, *J* = 7.9 Hz, 2H), 6.62 (dd, *J* = 8.2, 5.5 Hz, 2H), 5.49 (s, 1H), 3.85 (d, *J* = 15.6 Hz, 1H), 3.48 – 3.29 (m, 2H), 3.26 – 3.08 (m, 3H), 2.95 – 2.79 (m, 1H), 2.49 (d, *J* = 15.8 Hz, 1H), 1.36 (s, 9H), 1.22 (t, *J* = 6.9 Hz, 3H), 1.00 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 185.5, 155.0, 153.9, 143.2, 139.5, 138.0, 136.9, 129.5, 129.4, 128.6, 128.4, 128.3, 127.8, 127.7, 126.0, 125.3, 124.6, 121.2, 120.9, 120.5, 119.5, 115.6, 111.4, 81.0, 60.3, 54.6, 44.8, 38.3, 35.5, 34.9, 30.3, 29.7, 13.8, 13.3. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{38}H_{41}N_2O^+$ 541.3213; found: 541.3187.

8-(tert-butyl)-2'-methyl-2-phenylspiro[chromane-3,3'-indoline] (8a)



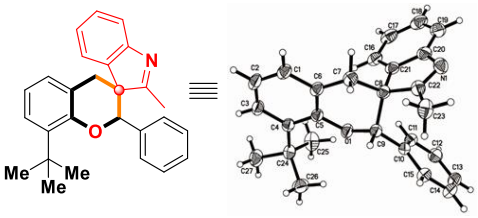
Flash column chromatography on a silica gel (ethyl acetate: dichloromethane: petroleum ether, 1:5:50) afforded the product **8a** as separable diastereomers (dr = 2.7:1) as a yellow solid (56 mg, 75% yield), m.p.: 73.8-74.2 ˚C. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.30 – 7.16 (m, 2H), 7.20 – 7.00 (m, 5H), 6.90 (td, *J* = 7.6, 2.5 Hz, 1H), 6.85 – 6.77 (m, 2H), 6.60 (d, *J* = 7.7 Hz, 1H), 6.61 – 6.46 (m, 1H), 6.32 (dd, *J* = 7.5, 1.3 Hz, 1H), 5.30 (s, 1H), 3.83 – 3.68 (m, 1H), 3.24 (d, *J* = 16.6 Hz, 1H), 2.96 (d, *J* = 16.7 Hz, 1H), 1.37 (d, *J* = 6.8 Hz, 3H), 1.32 (s, 9H). **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 153.5, 153.3, 150.9, 150.8, 139.5, 138.5, 138.0, 137.3, 134.3, 132.5, 128.6, 128.5, 128.4, 127.9, 127.8, 127.7, 127.5, 127.3, 127.1, 126.0, 124.9, 124.7, 123.9, 121.8, 120.9, 120.5, 119.9, 119.4, 118.9, 110.7, 109.7, 82.5, 79.1, 67.1, 65.7, 48.2, 47.8, 39.0, 34.8, 30.0, 29.7, 16.3, 15.6. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{27}H_{30}NO^+$ 384.2322; found: 384.2263.

2'-methyl-2-phenylspiro[chromane-3,3'-indole] (9a)



Flash column chromatography on a basic alumina (ethyl acetate: dichloromethane: petroleum ether, 2:5:50) afforded the product **9a** as a light yellow solid (27.3 mg, 42% yield), m.p.:164.3-165.8 ˚C. **^{1}H NMR** (300 MHz, DMSO-d_6) δ 7.76 – 7.61 (m, 1H), 7.31 – 6.94 (m, 12H), 5.72 (s, 1H), 3.76 (d, *J* = 17.2 Hz, 1H), 2.71 (d, *J* = 17.4 Hz, 1H), 2.16 (s, 3H). **^{13}C NMR** (75 MHz, DMSO-d_6) δ 182.3, 154.4, 154.2, 141.2, 136.1, 129.9, 128.2, 128.0, 127.9, 127.4, 126.9, 125.1, 123.2, 121.5, 120.4, 119.2, 116.5, 81.0, 58.8, 32.4, 20.0. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{23}H_{20}NO^+$ 326.1539; found: 326.1488.

5. Crystal Structures and Data



4a (CCDC 2112671)

ORTEP diagram of compound **4a**, thermal ellipsoids are drawn on 50% probability level Crystal data and structure refinement for **4a**.

Identification code	**4a**
Empirical formula	$C_{27}H_{27}NO$
Formula weight	381.49
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.2106(3)
b/Å	14.2230(5)
c/Å	16.4314(6)
α /°	90
β /°	90
γ /°	90
Volume/Å^3	2152.54(13)
Z	4
ρ_{calc}g/cm^3	1.177
μ /mm^{-1}	0.543
F(000)	816.0
Crystal size/mm^3	0.16 × 0.1 × 0.09
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.222 to 141.546
Index ranges	-11 ≤ h ≤ 10, -17 ≤ k ≤ 17, -19 ≤ l ≤ 20
Reflections collected	8129
Independent reflections	4068 [R_{int} = 0.0351, R_{sigma} = 0.0465]
Data/restraints/parameters	4068/0/266
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0475, wR_2 = 0.1119
Final R indexes [all data]	R_1 = 0.0584, wR_2 = 0.1209
Largest diff. peak/hole / e Å^{-3}	0.21/-0.21
Flack parameter	-0.2(3)

6. References

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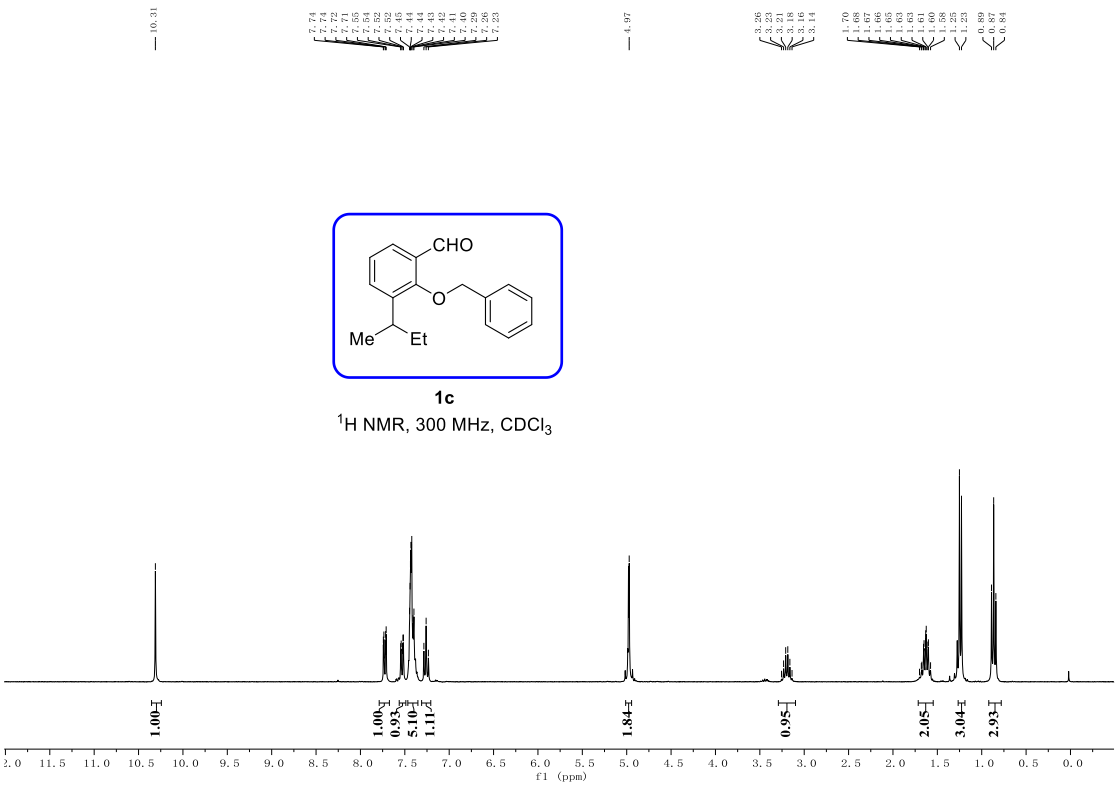
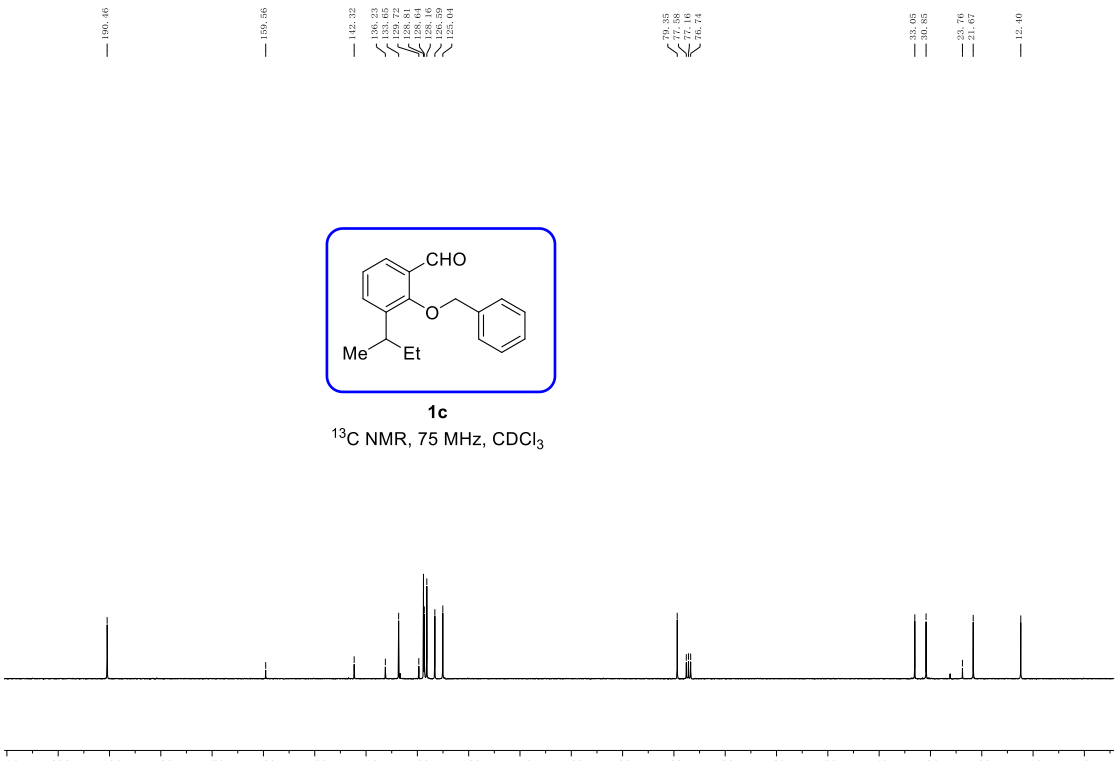
7. ^{1}H and ^{13}C NMR Spectra

2-(benzyloxy)-3-(sec-butyl)benzaldehyde (1c)



1c

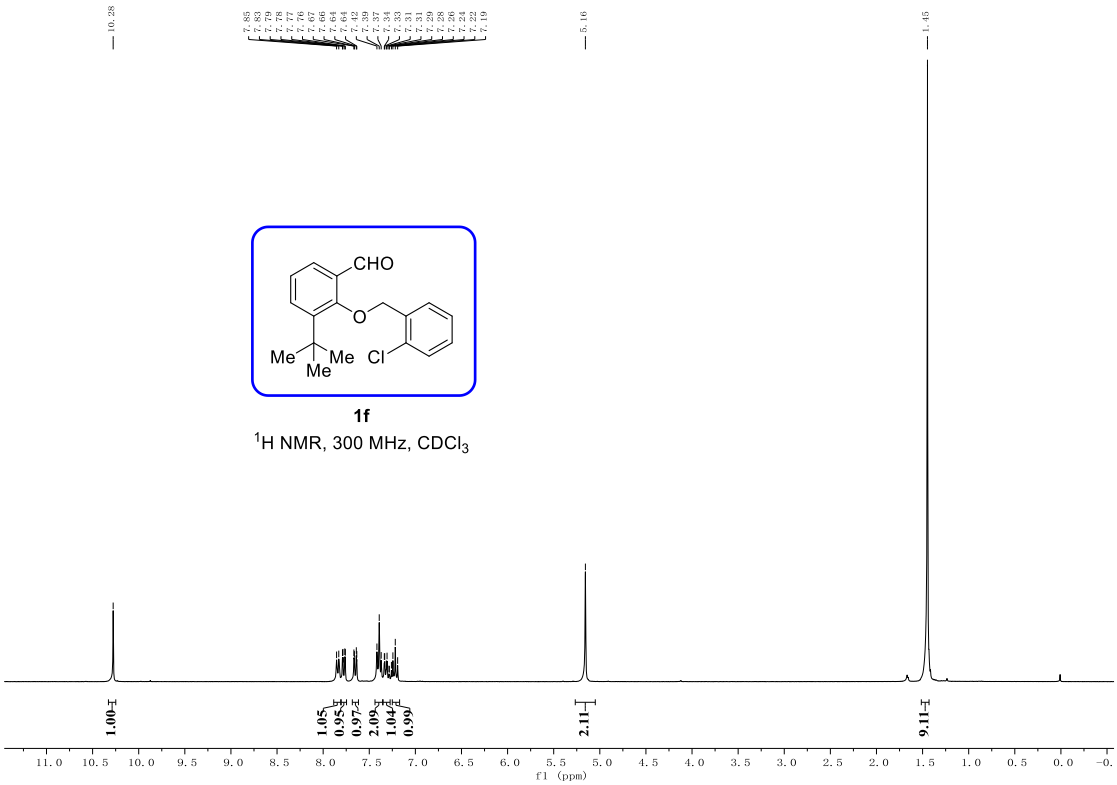
^{1}H NMR, 300 MHz, $CDCl_3$



1c

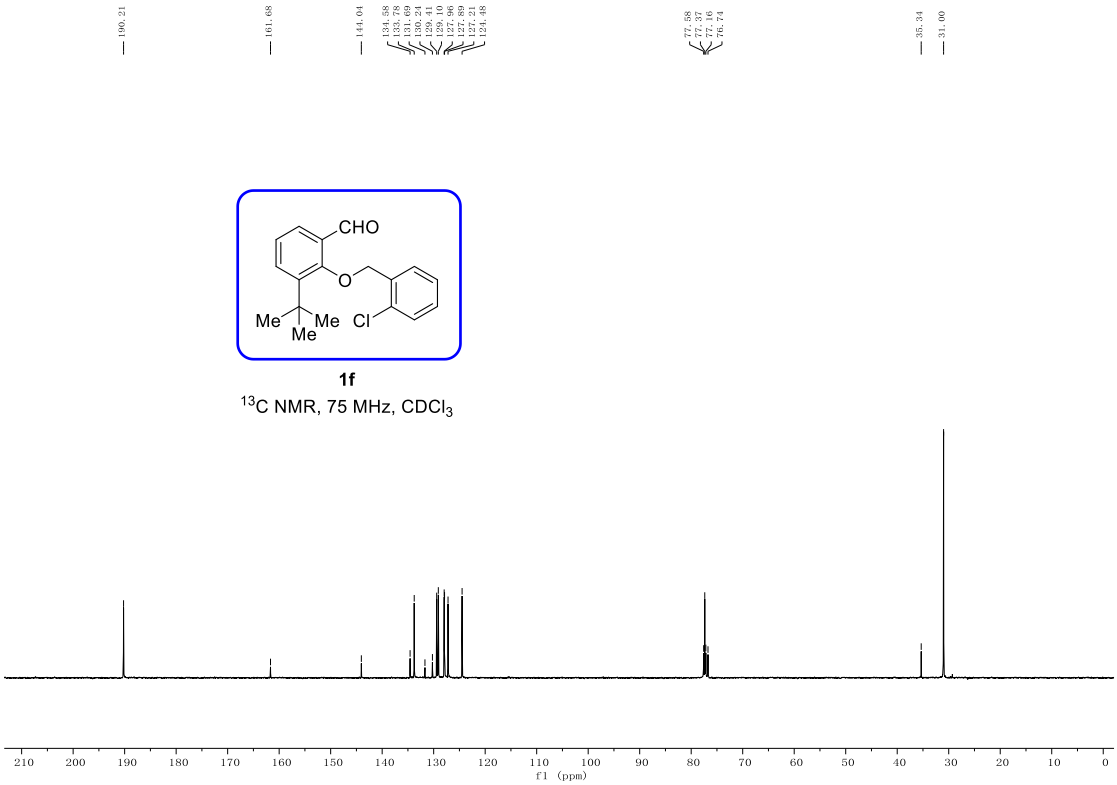
^{13}C NMR, 75 MHz, $CDCl_3$

3-(tert-butyl)-2-((2-chlorobenzyl)oxy)benzaldehyde (1f)



1f

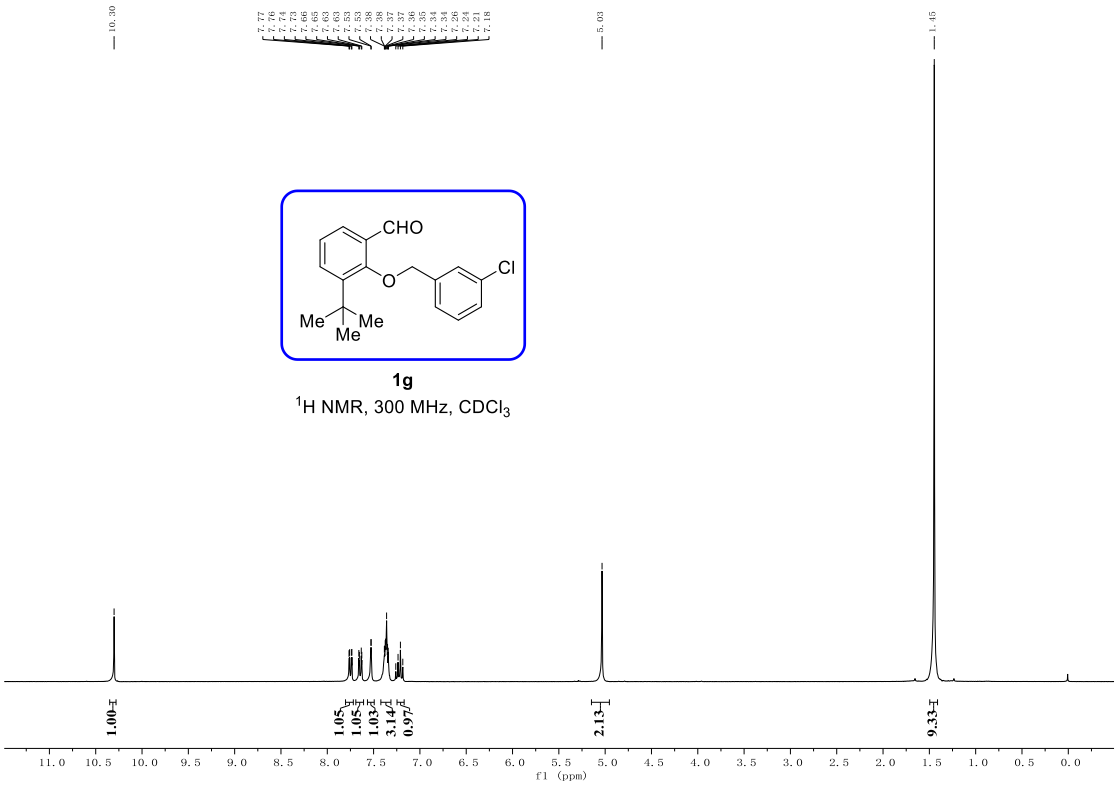
^{1}H NMR, 300 MHz, $CDCl_3$



1f

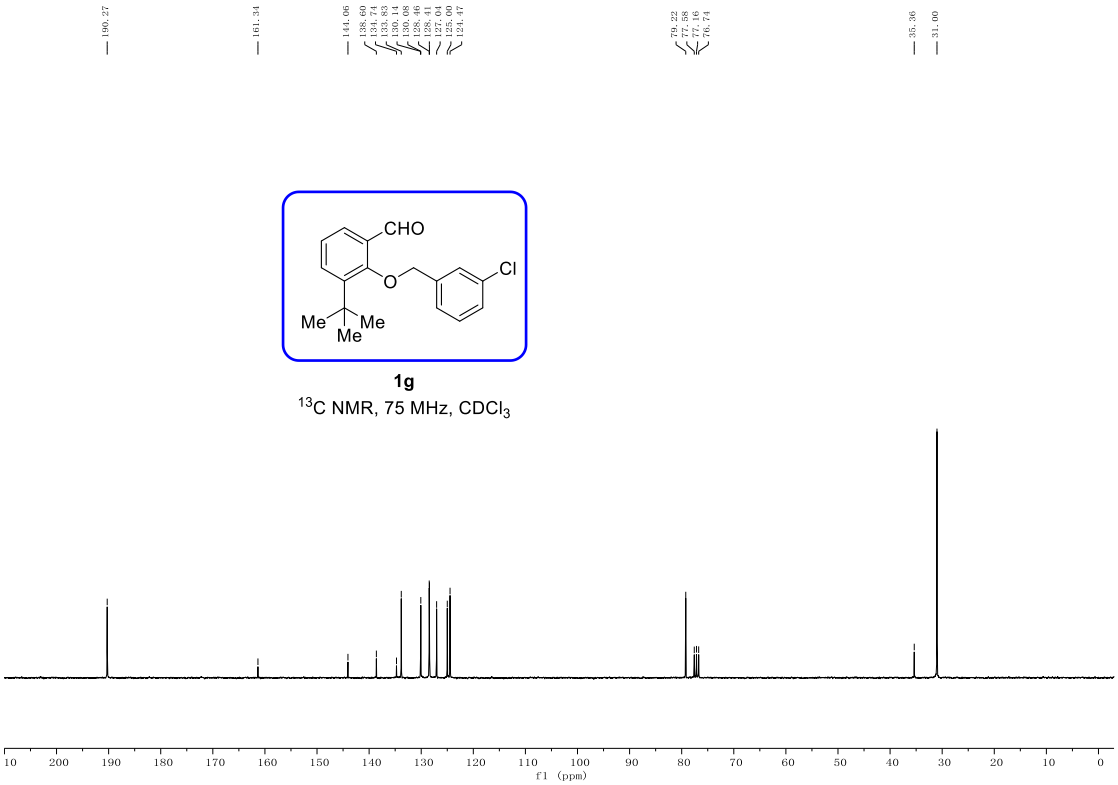
^{13}C NMR, 75 MHz, $CDCl_3$

3-(tert-butyl)-2-((3-chlorobenzyl)oxy)benzaldehyde (1g)



1g

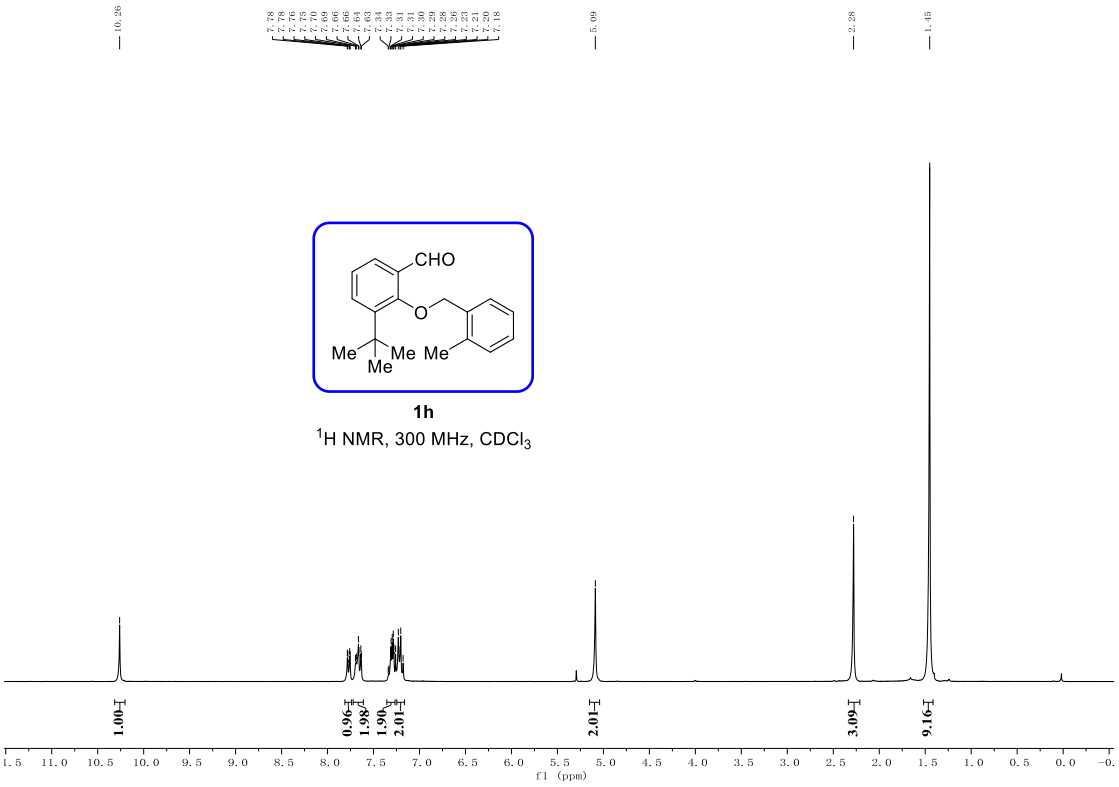
^{1}H NMR, 300 MHz, $CDCl_3$

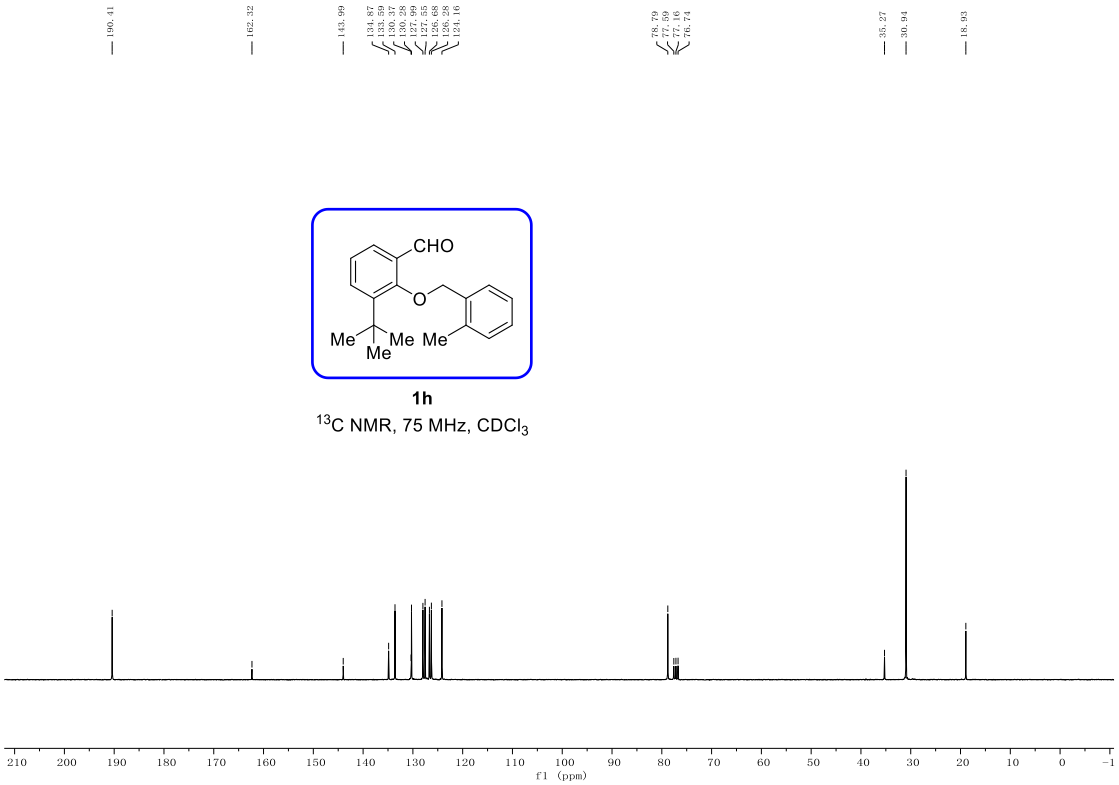


1g

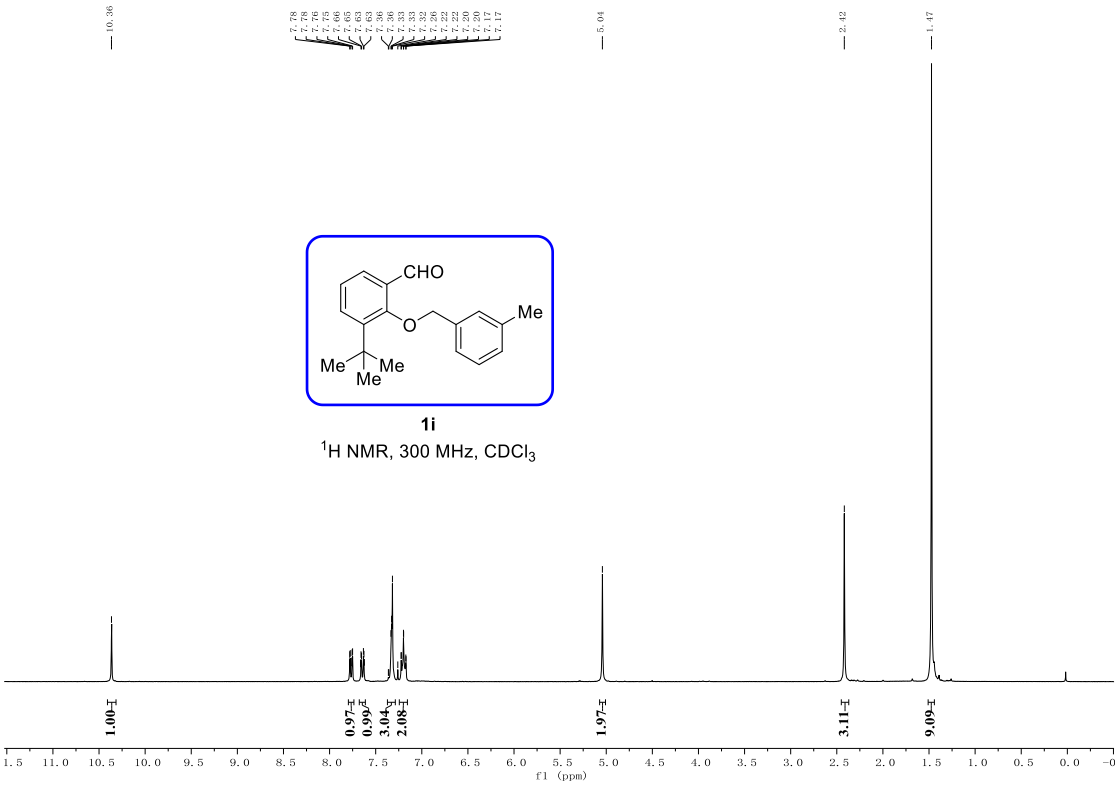
^{13}C NMR, 75 MHz, $CDCl_3$

3-(tert-butyl)-2-((2-methylbenzyl)oxy)benzaldehyde (1h)



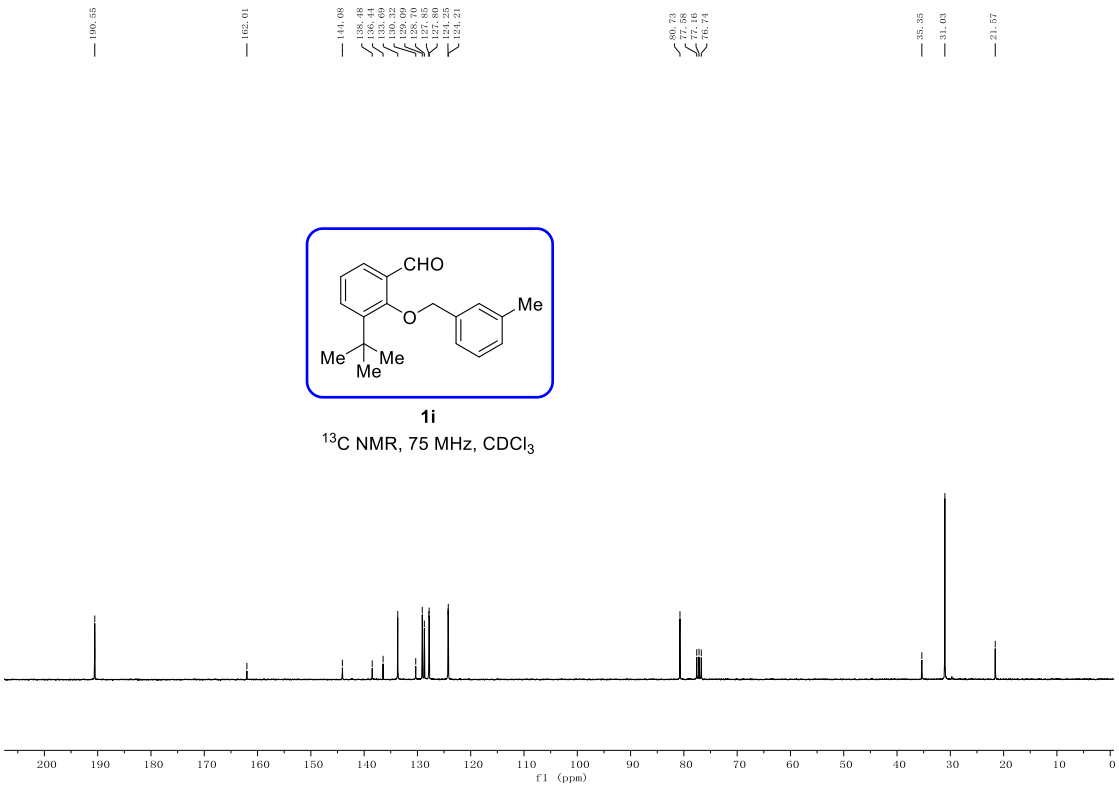


3-(tert-butyl)-2-((3-methylbenzyl)oxy)benzaldehyde (1i)



1i

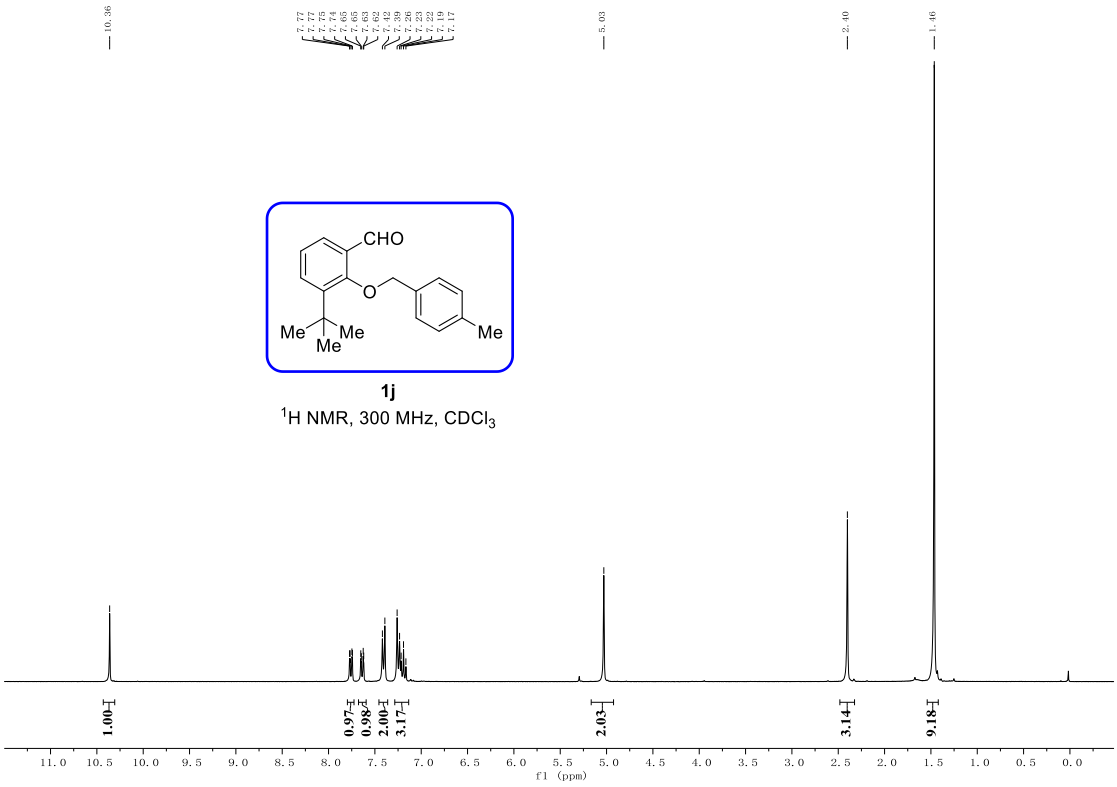
^{1}H NMR, 300 MHz, $CDCl_3$



1i

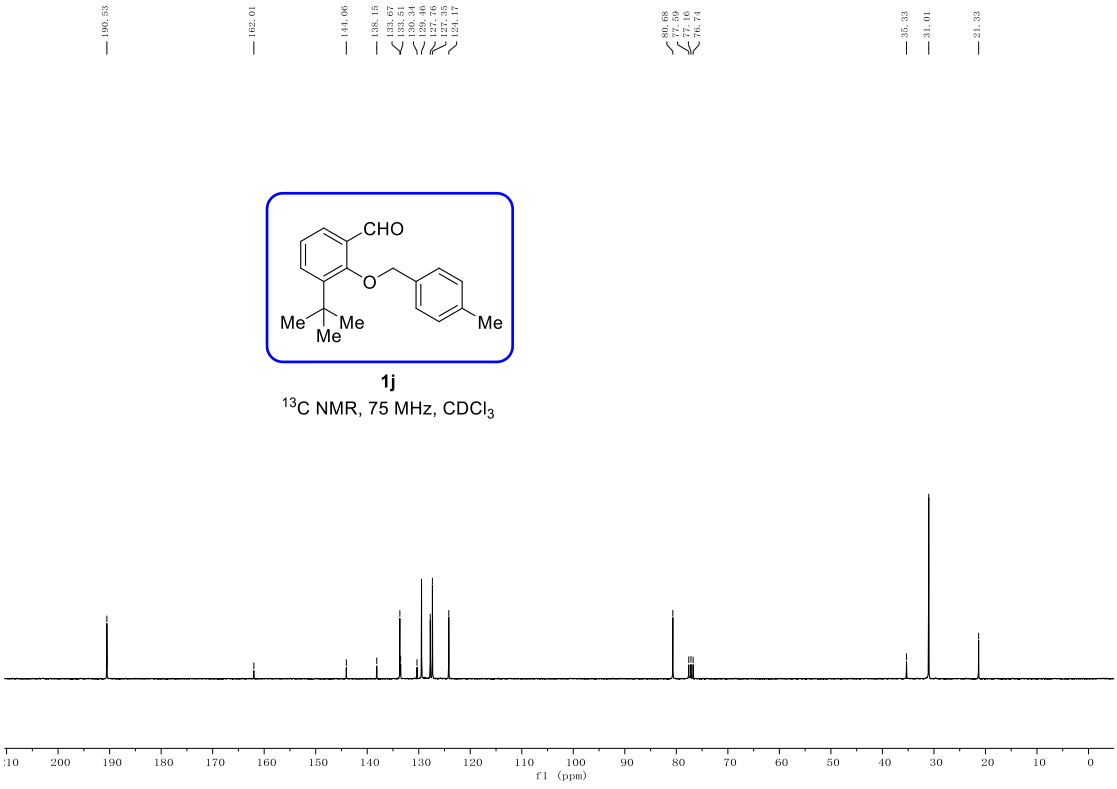
^{13}C NMR, 75 MHz, $CDCl_3$

3-(tert-butyl)-2-((4-methylbenzyl)oxy)benzaldehyde (1j)



1j

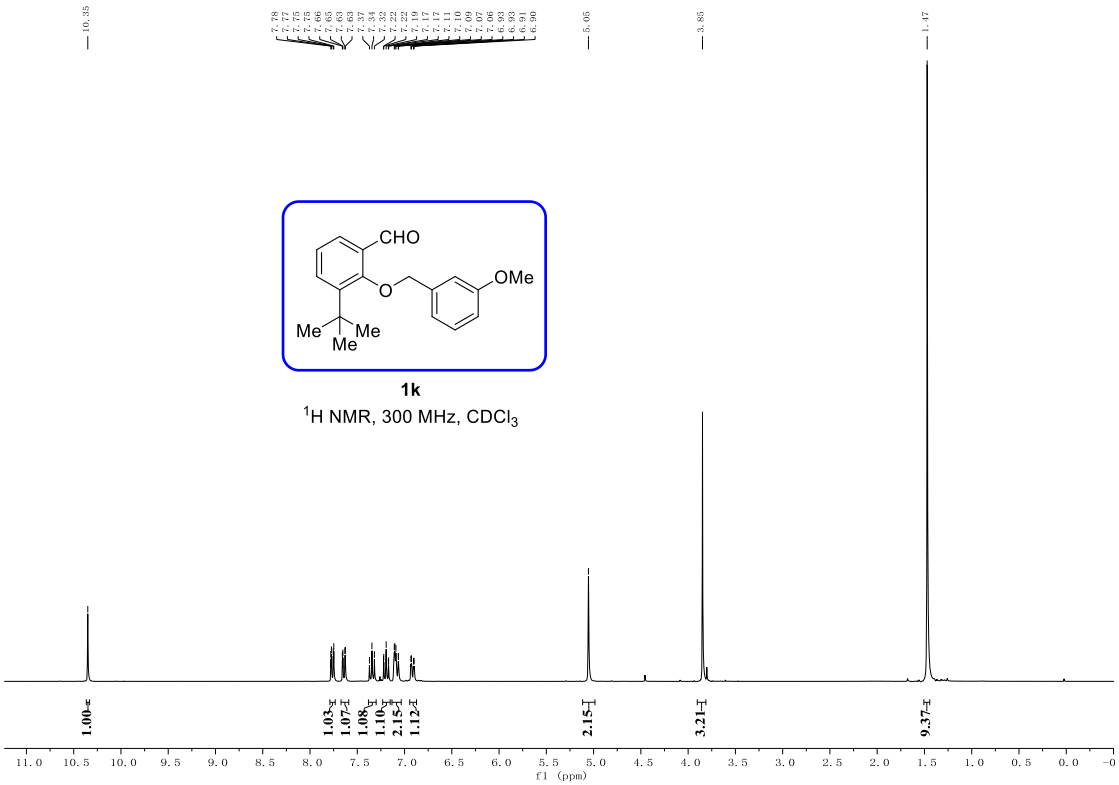
^{1}H NMR, 300 MHz, $CDCl_3$



1j

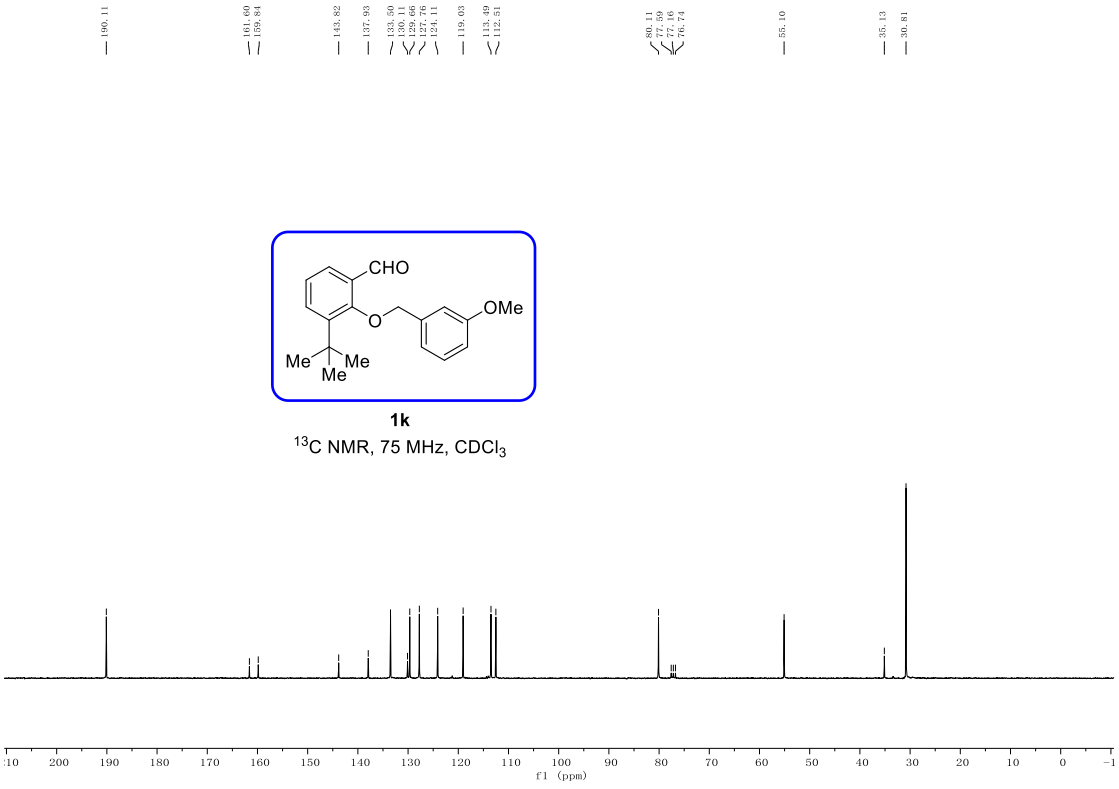
^{13}C NMR, 75 MHz, $CDCl_3$

3-(tert-butyl)-2-((3-methoxybenzyl)oxy)benzaldehyde (1k)



1k

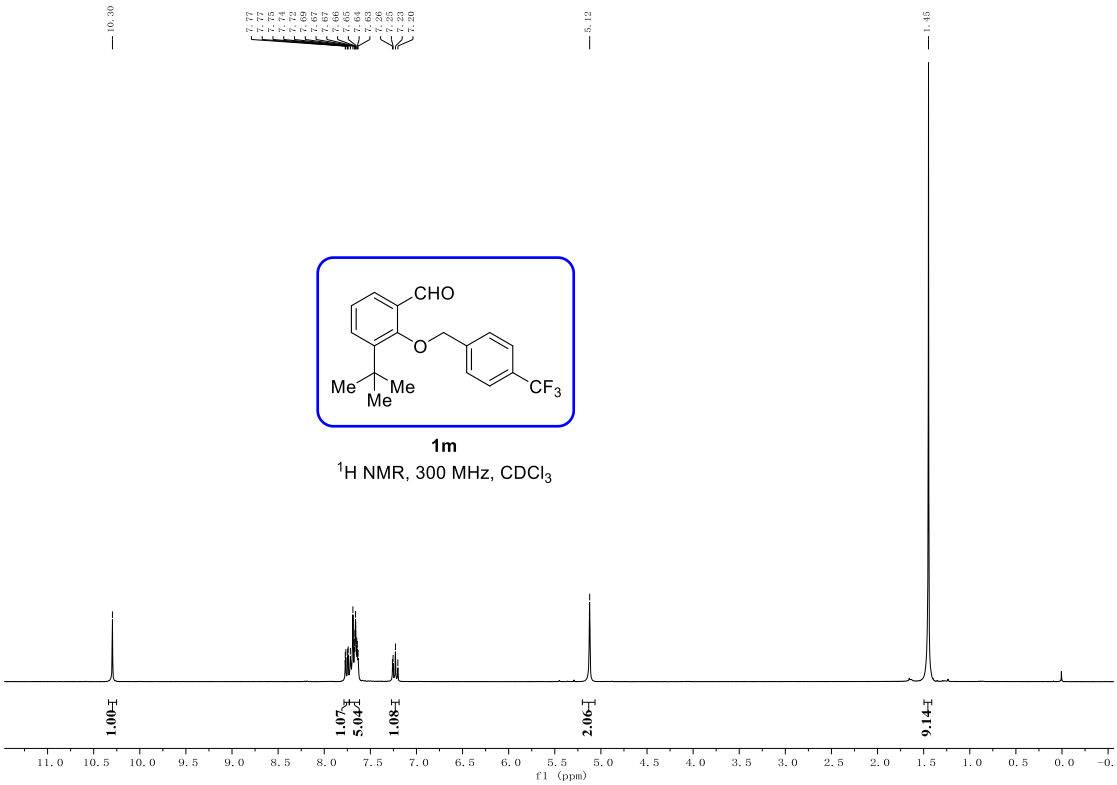
^{1}H NMR, 300 MHz, $CDCl_3$



1k

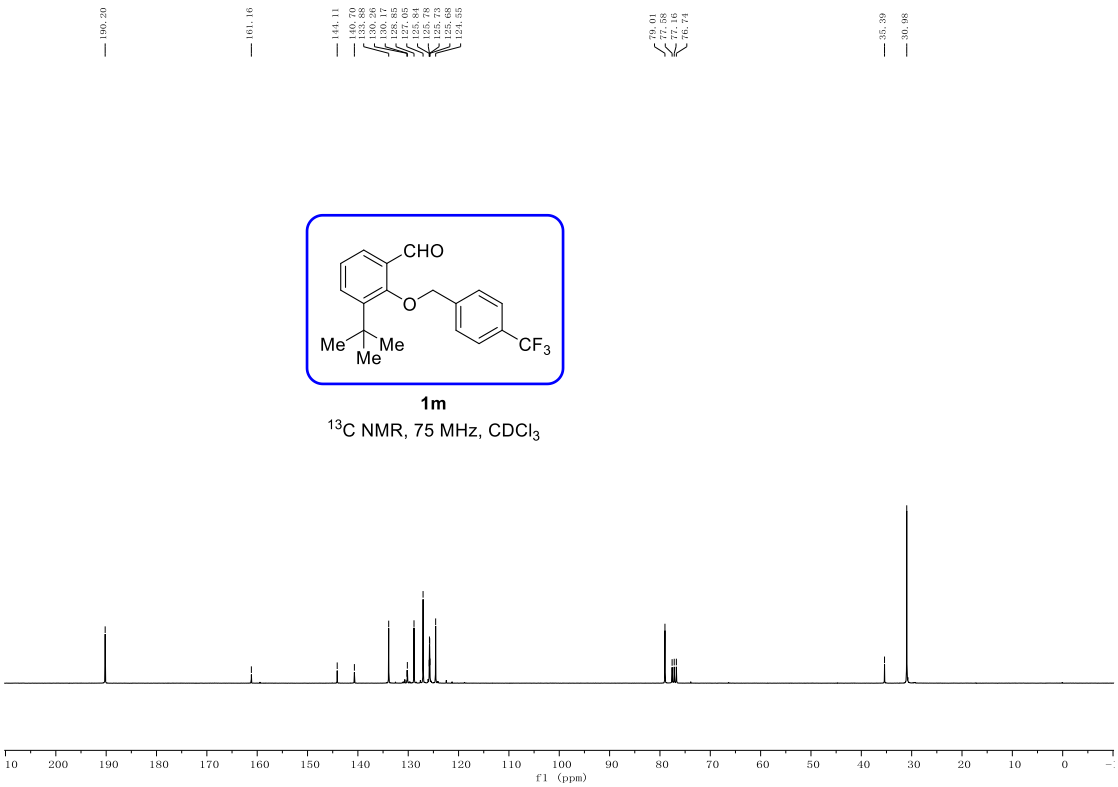
^{13}C NMR, 75 MHz, $CDCl_3$

3-(tert-butyl)-2-((4-(trifluoromethyl)benzyl)oxy)benzaldehyde (1m)



1m

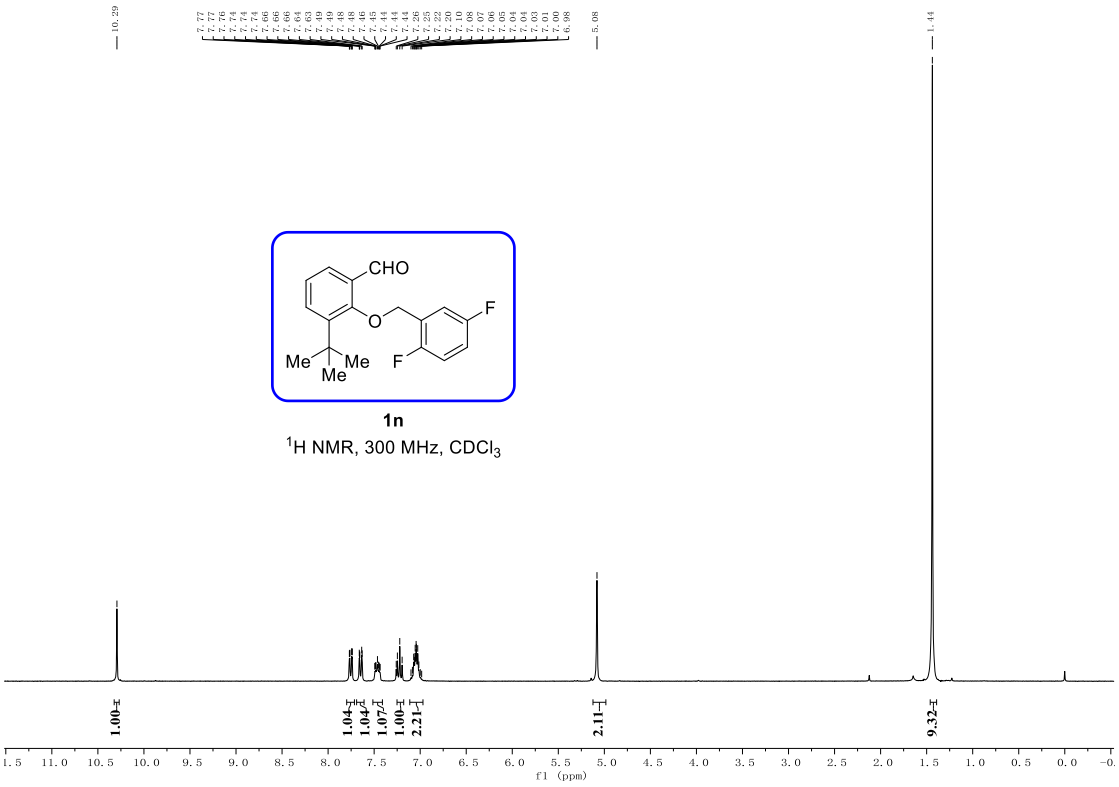
^{1}H NMR, 300 MHz, $CDCl_3$

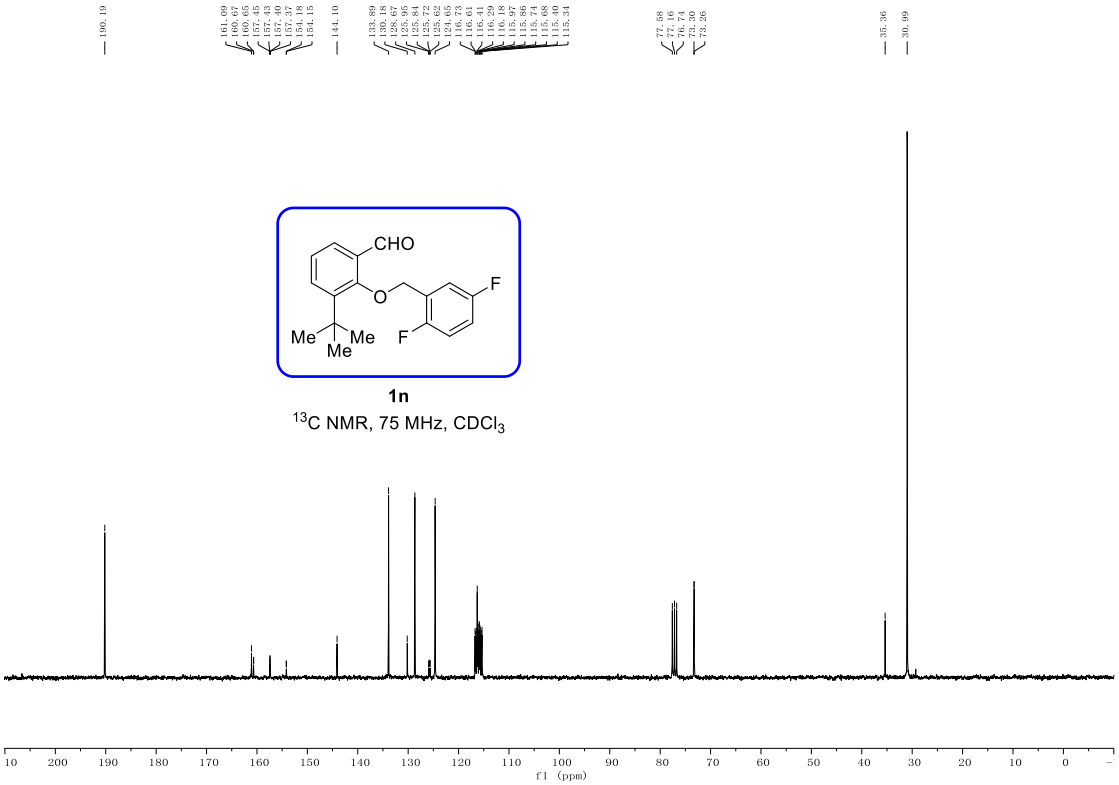


1m

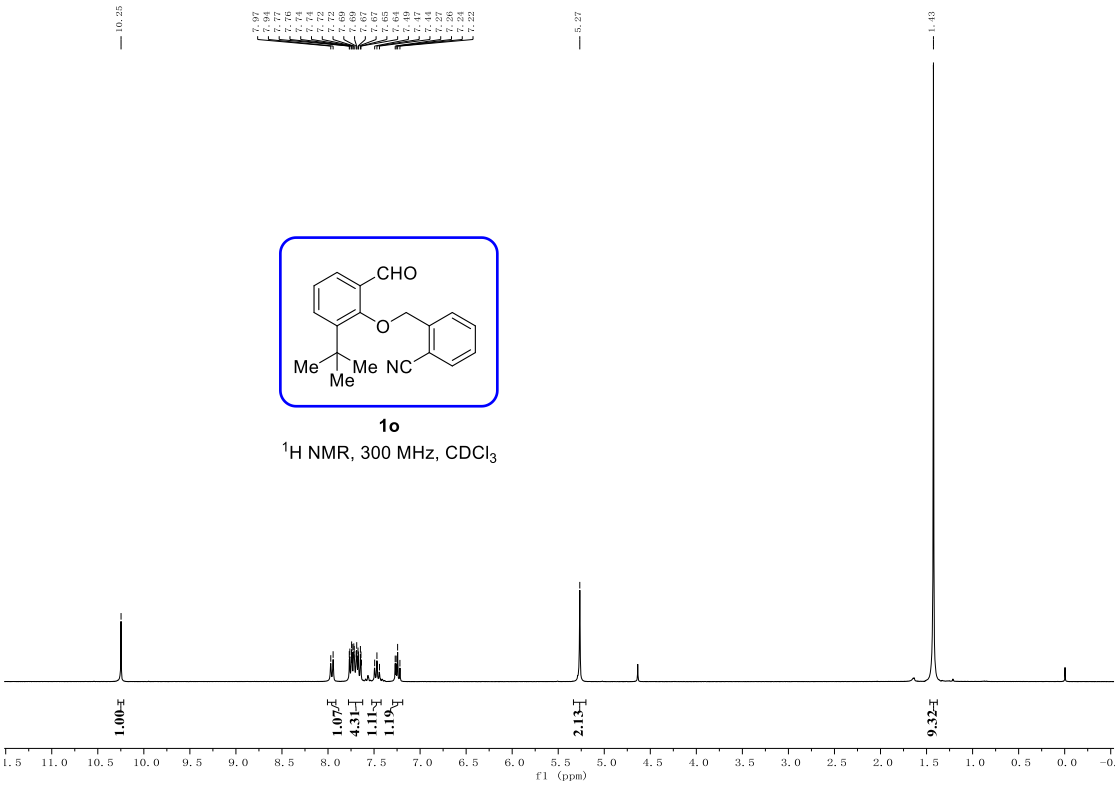
^{13}C NMR, 75 MHz, $CDCl_3$

3-(tert-butyl)-2-((2,5-difluorobenzyl)oxy)benzaldehyde (1n)



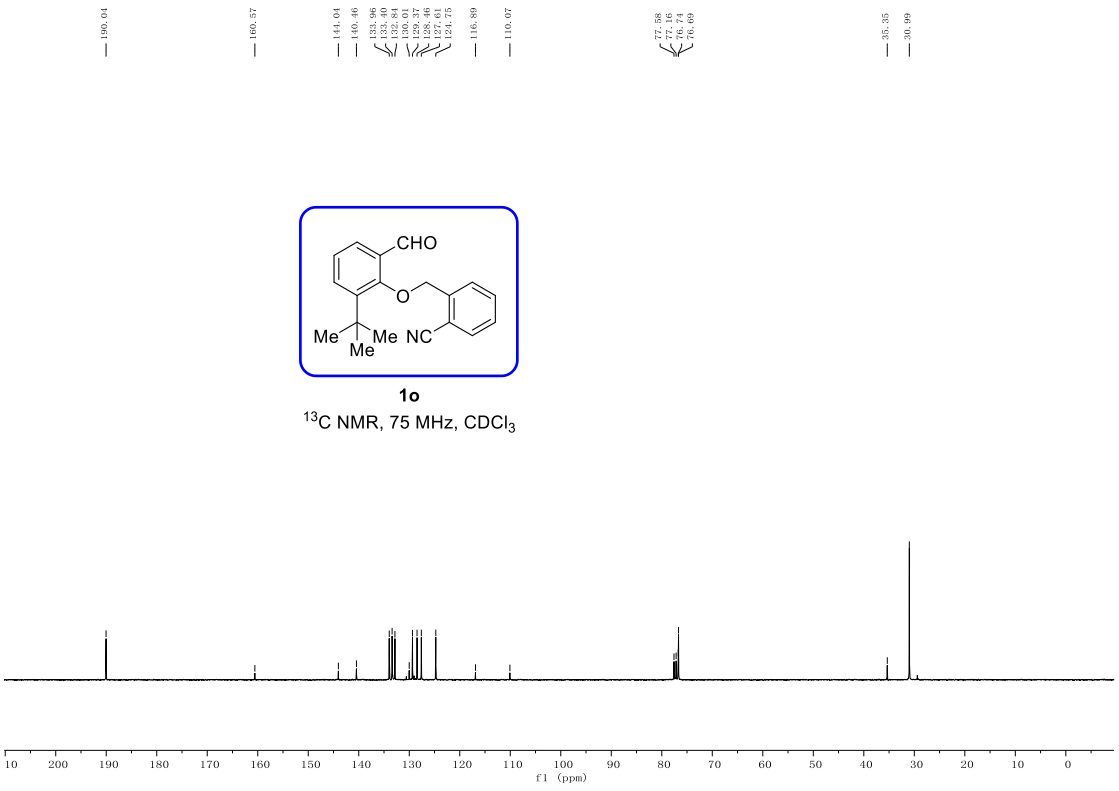


2-((2-(tert-butyl)-6-formylphenoxy)methyl)benzonitrile (1o)



1o

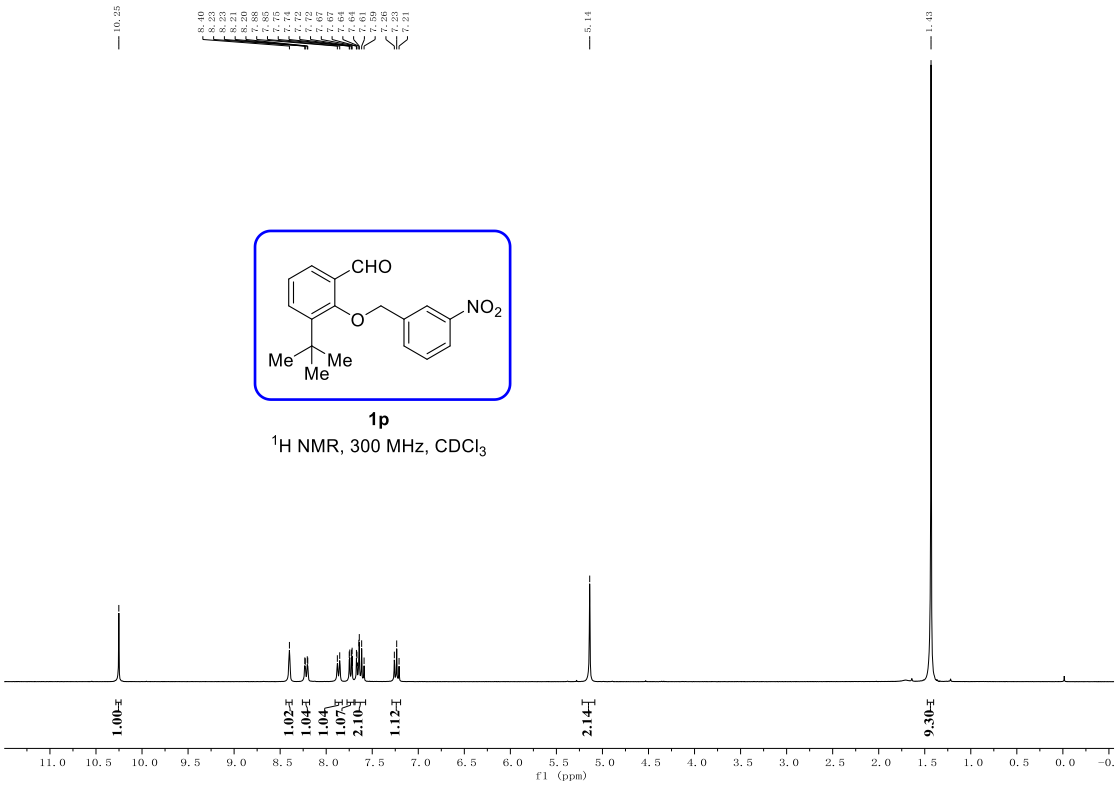
^{1}H NMR, 300 MHz, $CDCl_3$



1o

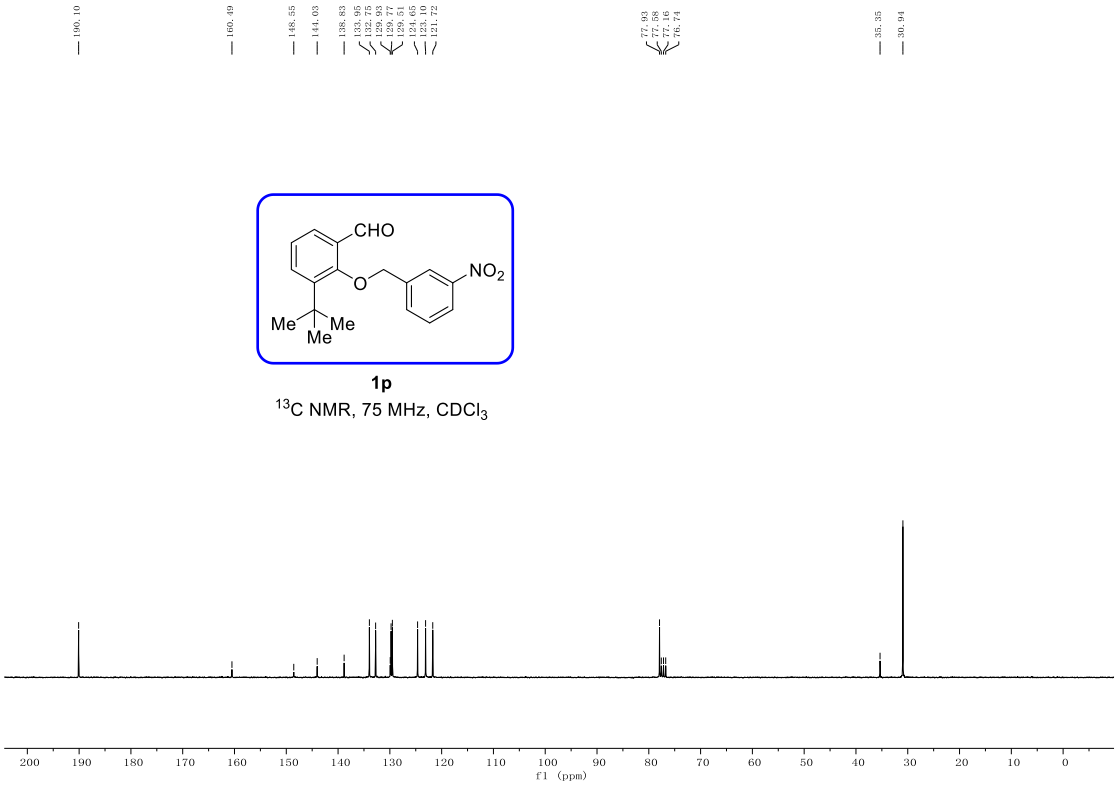
^{13}C NMR, 75 MHz, $CDCl_3$

3-(tert-butyl)-2-((3-nitrobenzyl)oxy)benzaldehyde (1p)



1p

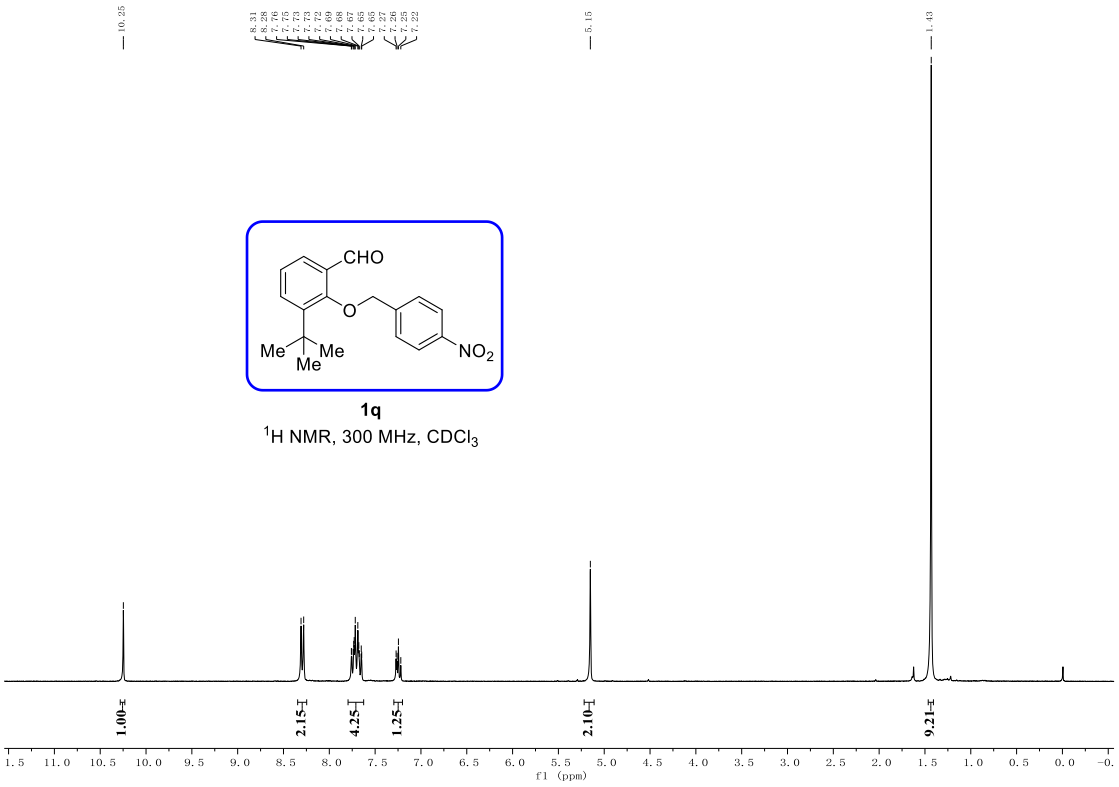
^{1}H NMR, 300 MHz, $CDCl_3$



1p

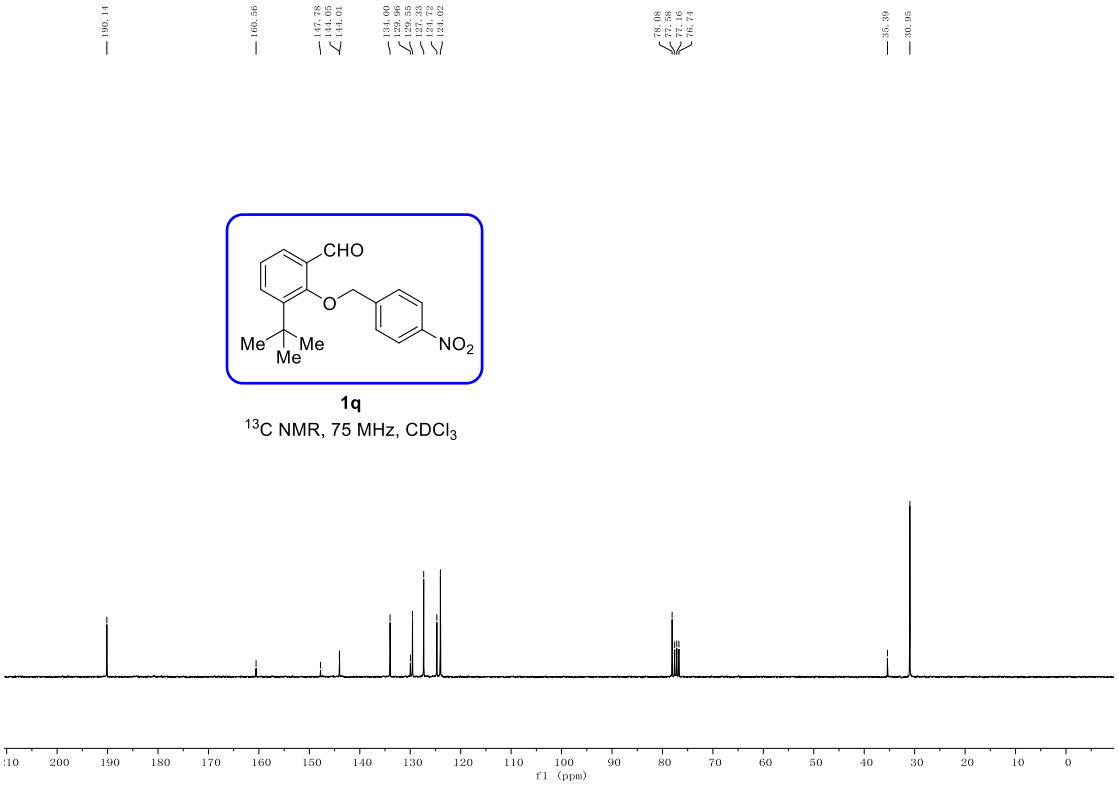
^{13}C NMR, 75 MHz, $CDCl_3$

3-(tert-butyl)-2-((4-nitrobenzyl)oxy)benzaldehyde (1q)



1q

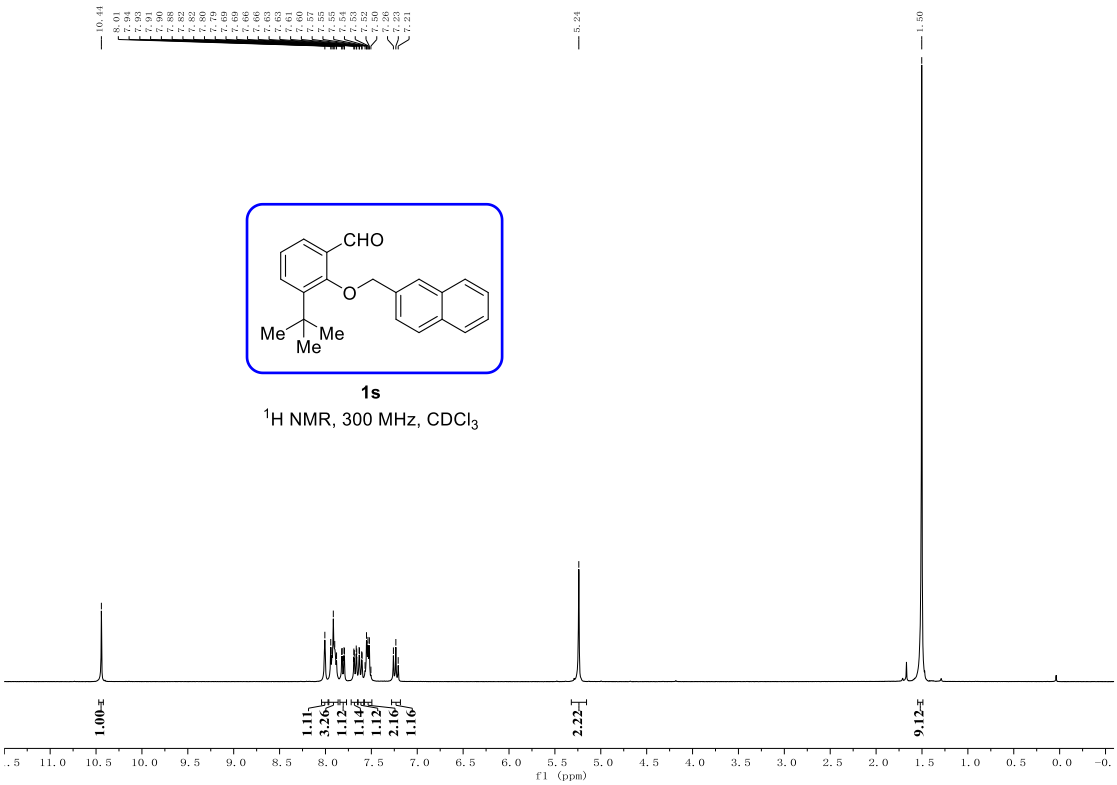
^{1}H NMR, 300 MHz, $CDCl_3$



1q

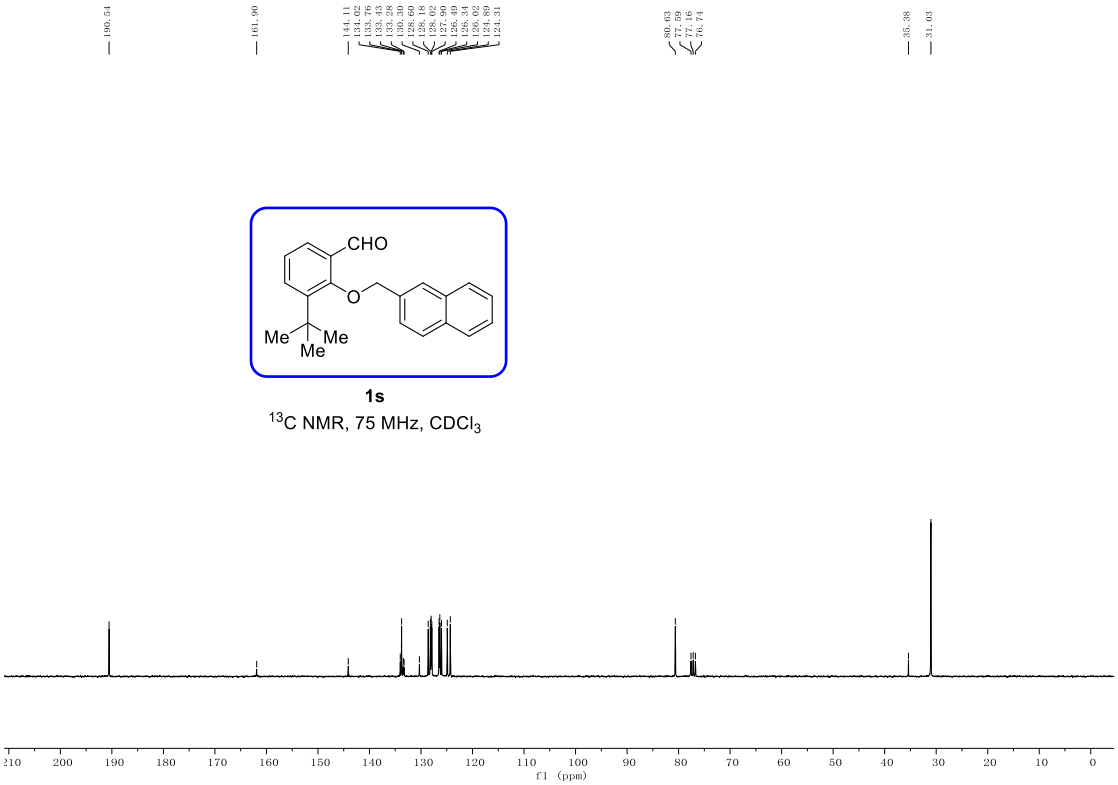
^{13}C NMR, 75 MHz, $CDCl_3$

3-(tert-butyl)-2-(naphthalen-2-ylmethoxy)benzaldehyde (1s)



1s

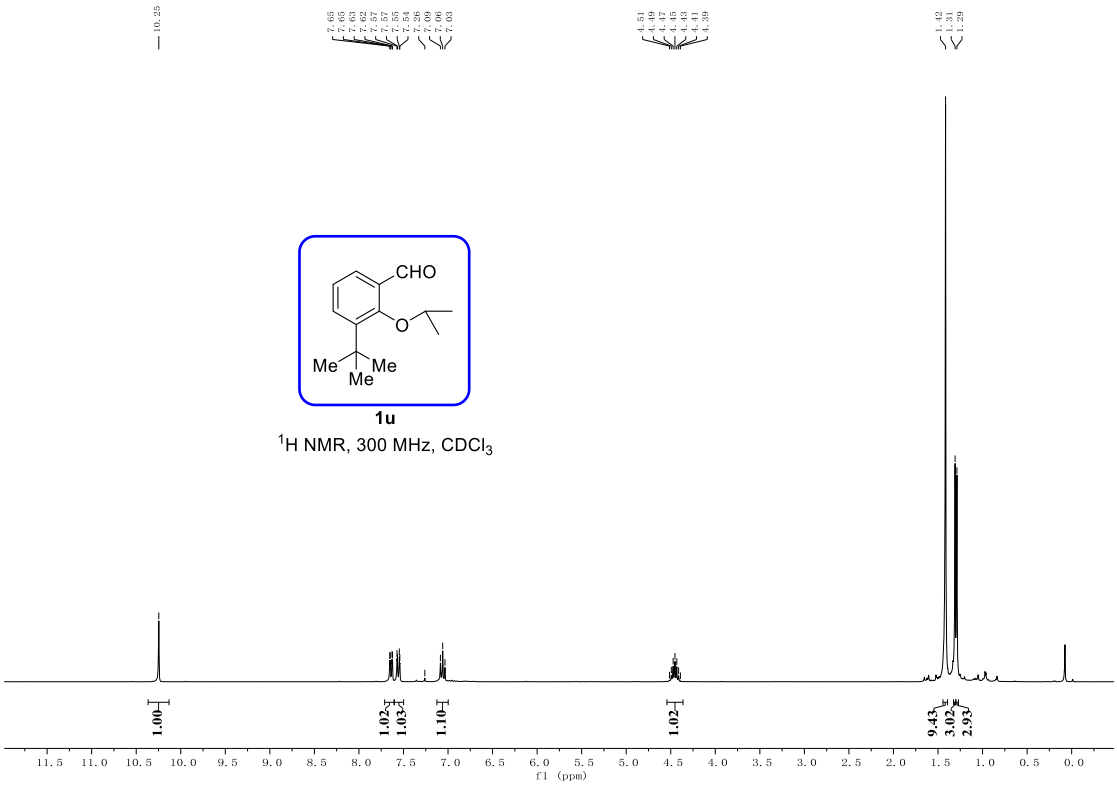
^{1}H NMR, 300 MHz, $CDCl_3$



1s

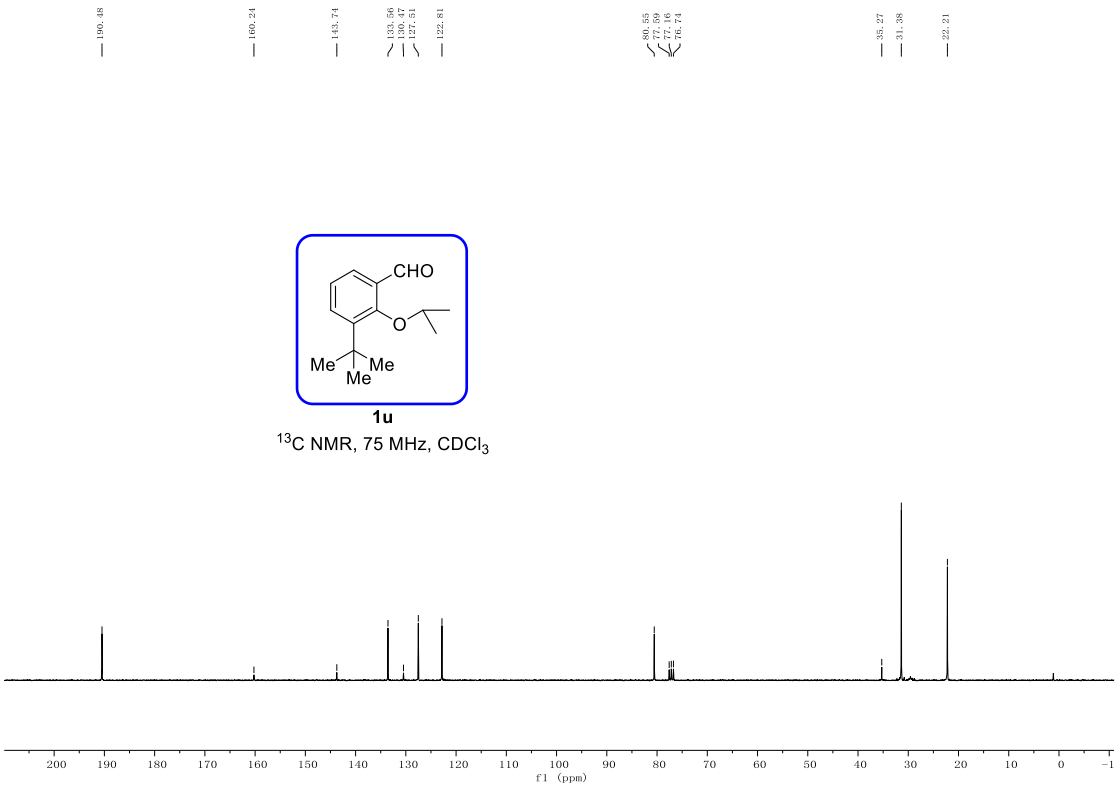
^{13}C NMR, 75 MHz, $CDCl_3$

3-(tert-butyl)-2-isopropoxybenzaldehyde (1u)



1u

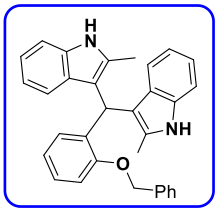
^{1}H NMR, 300 MHz, $CDCl_3$



1u

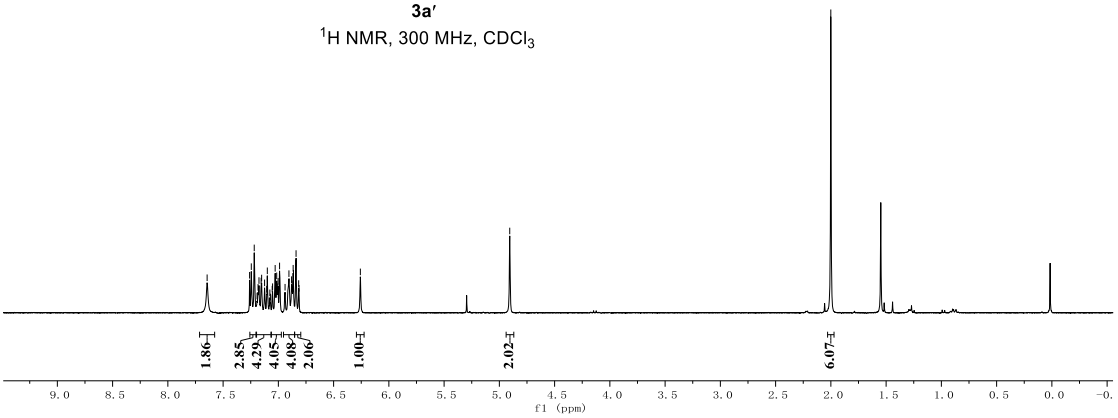
^{13}C NMR, 75 MHz, $CDCl_3$

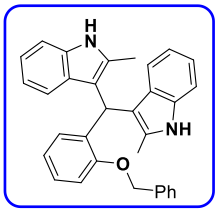
3,3'-((2-(benzyloxy)phenyl)methylene)bis(2-methyl-1H-indole) (3a')



3a′

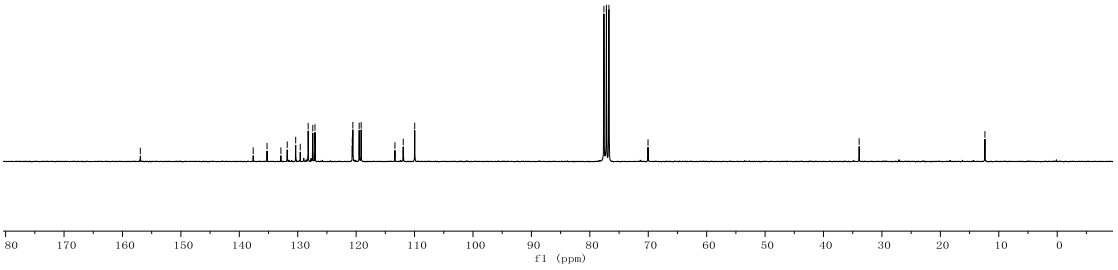
^{1}H NMR, 300 MHz, $CDCl_3$



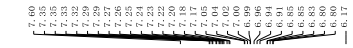


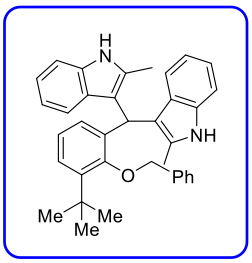
3a′

^{13}C NMR, 75 MHz, $CDCl_3$



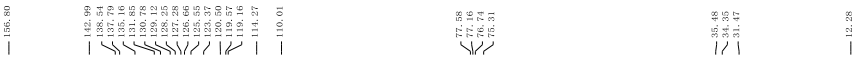
3,3'-((2-(benzyloxy)-3-(tert-butyl)phenyl)methylene)bis(2-methyl-1H-indole) (3a)

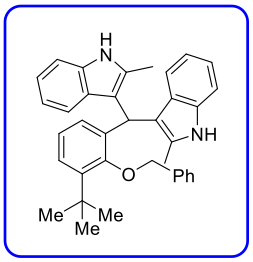




3a

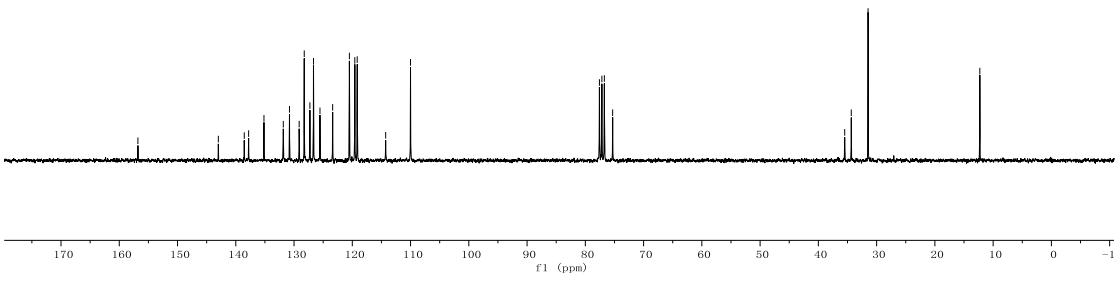
^{1}H NMR, 300 MHz, $CDCl_3$



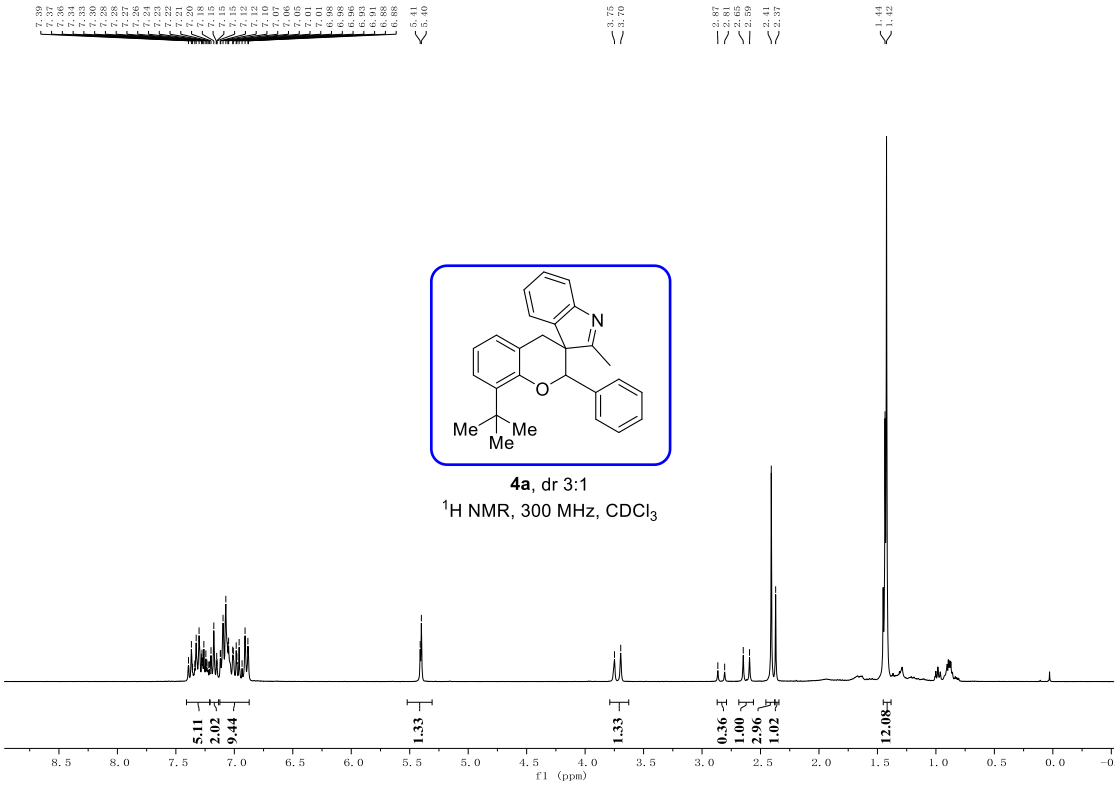


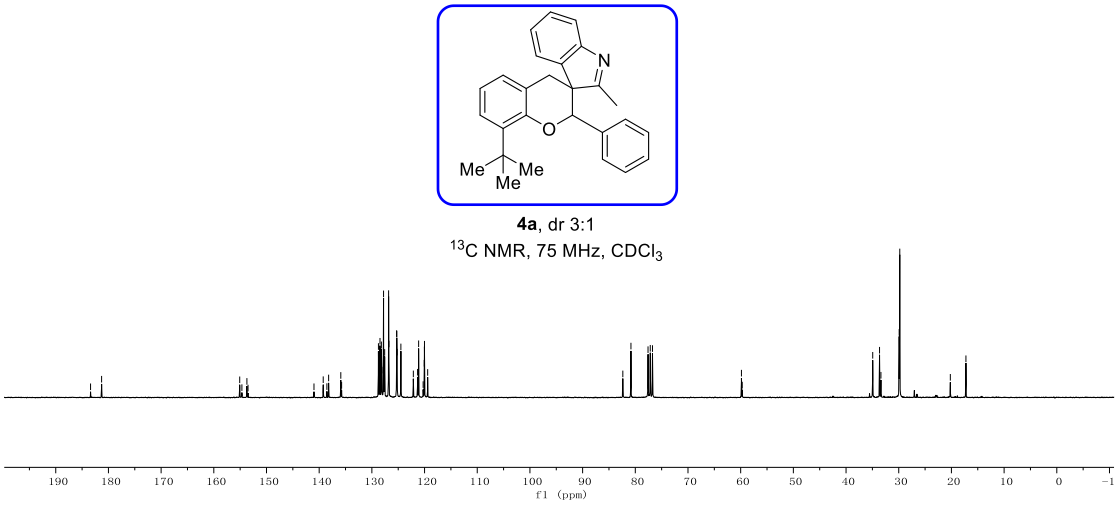
3a

^{13}C NMR, 75 MHz, $CDCl_3$

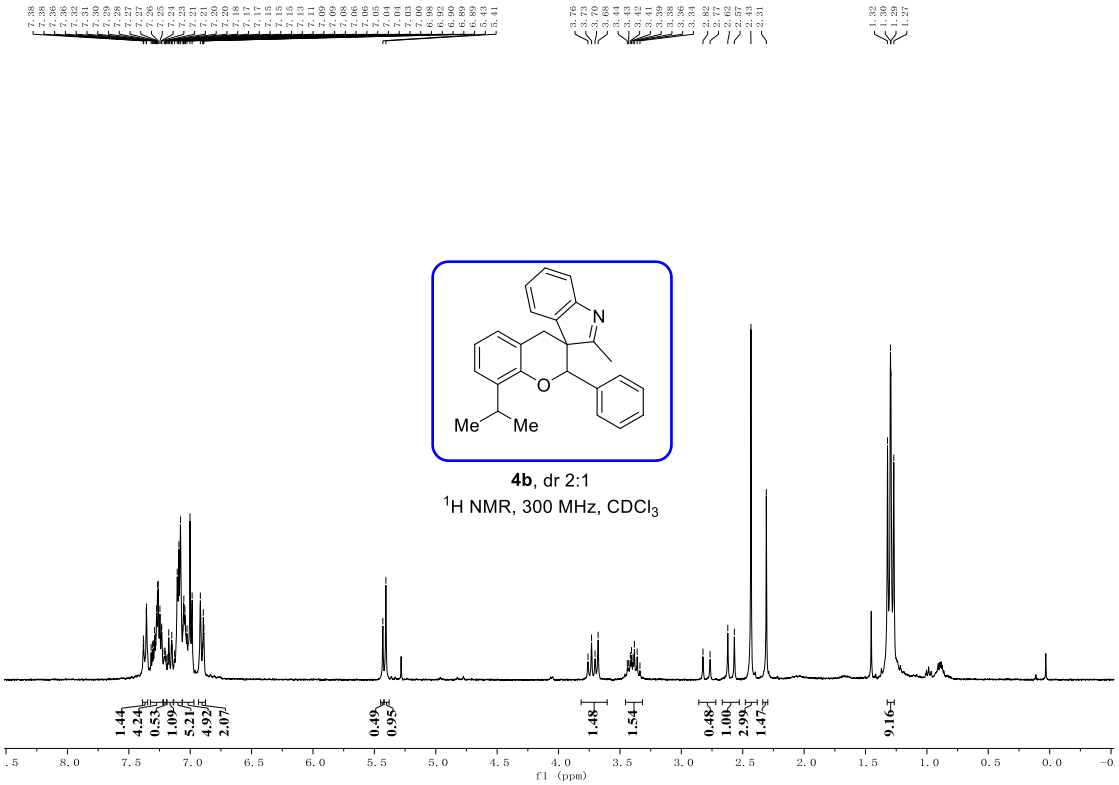


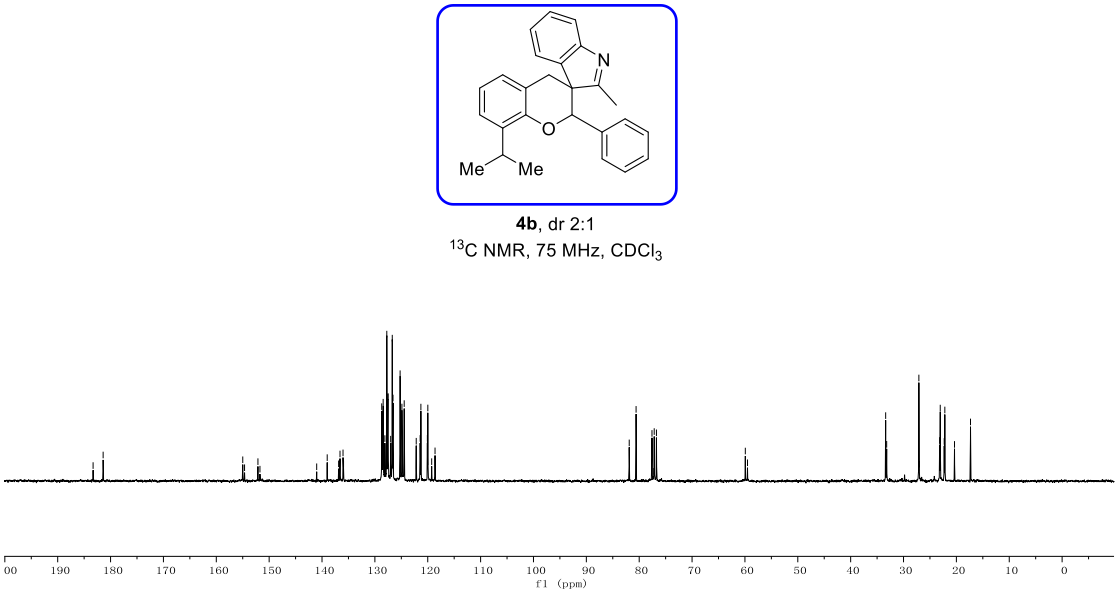
8-(tert-butyl)-2'-methyl-2-phenylspiro[chromane-3,3'-indole] (4a)



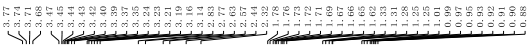


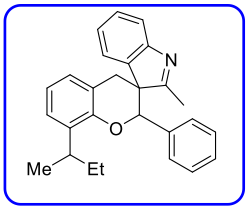
8-isopropyl-2'-methyl-2-phenylspiro[chromane-3,3'-indole] (4b)



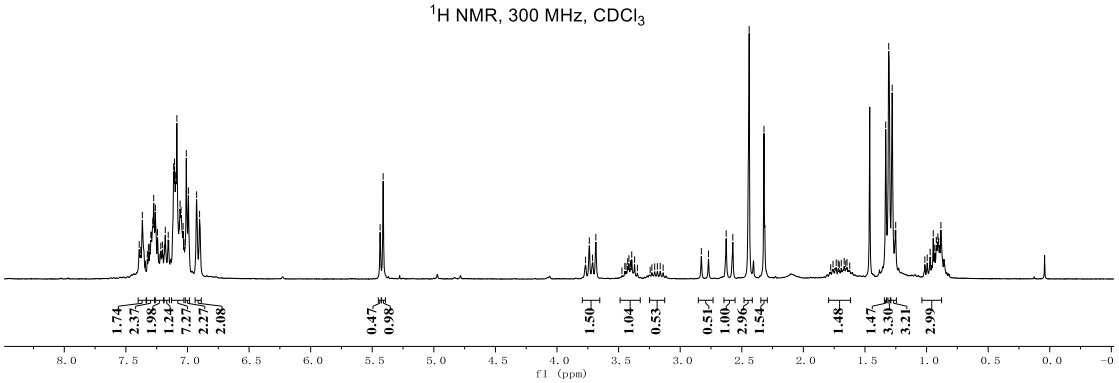


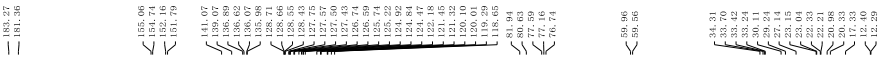
8-(sec-butyl)-2'-methyl-2-phenylspiro[chromane-3,3'-indole] (4c)

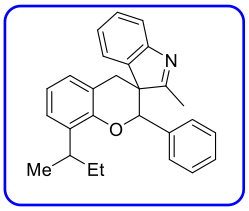




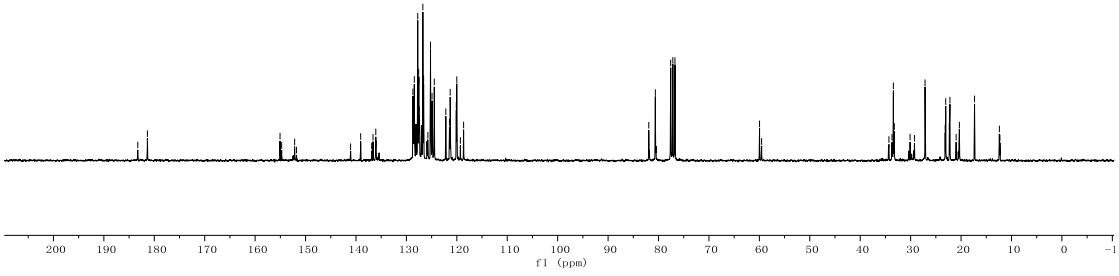
4c, dr 2:1
^{1}H NMR, 300 MHz, $CDCl_3$



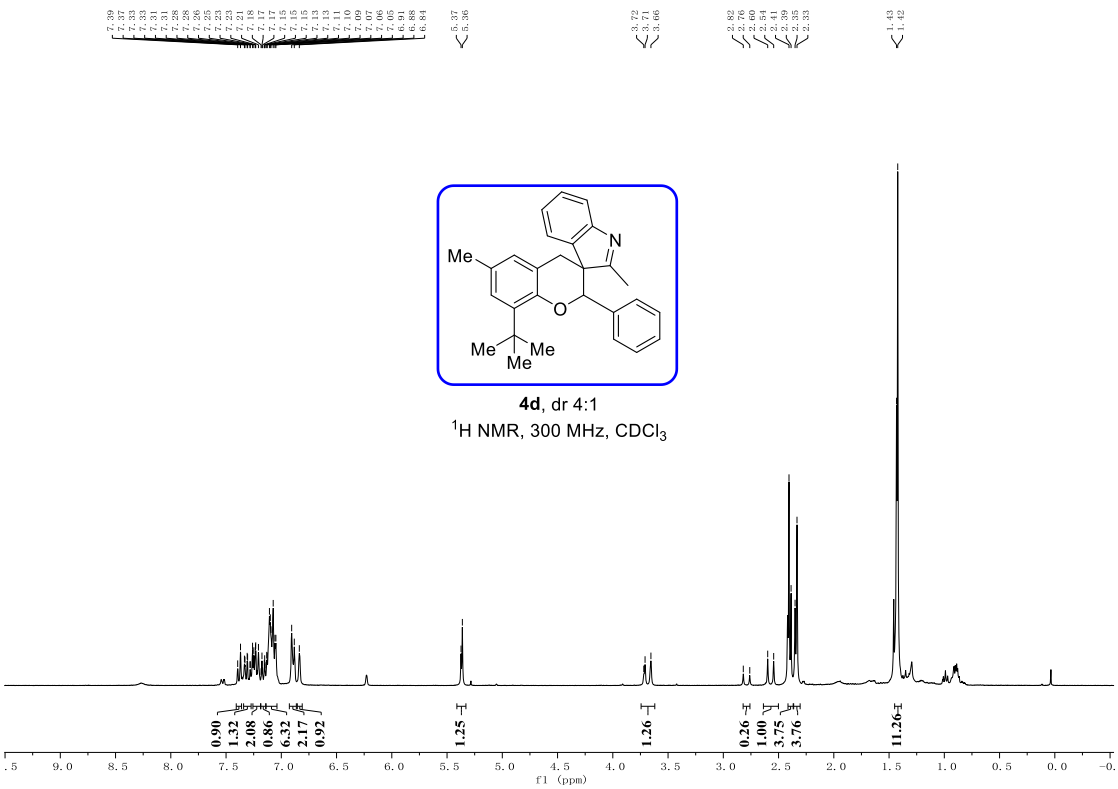


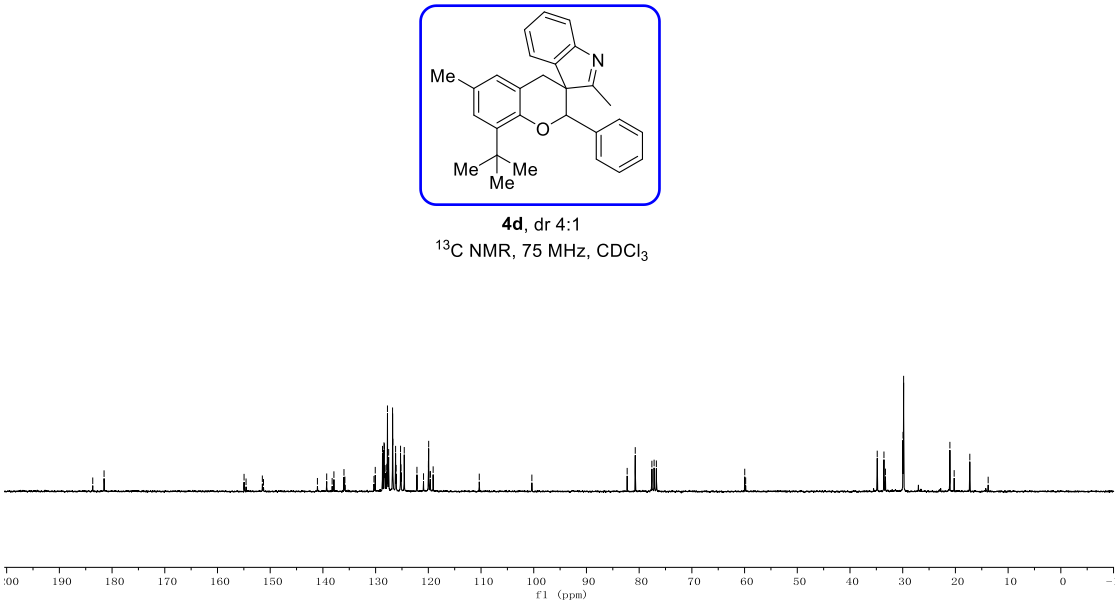


4c, dr 2:1
^{13}C NMR, 75 MHz, $CDCl_3$

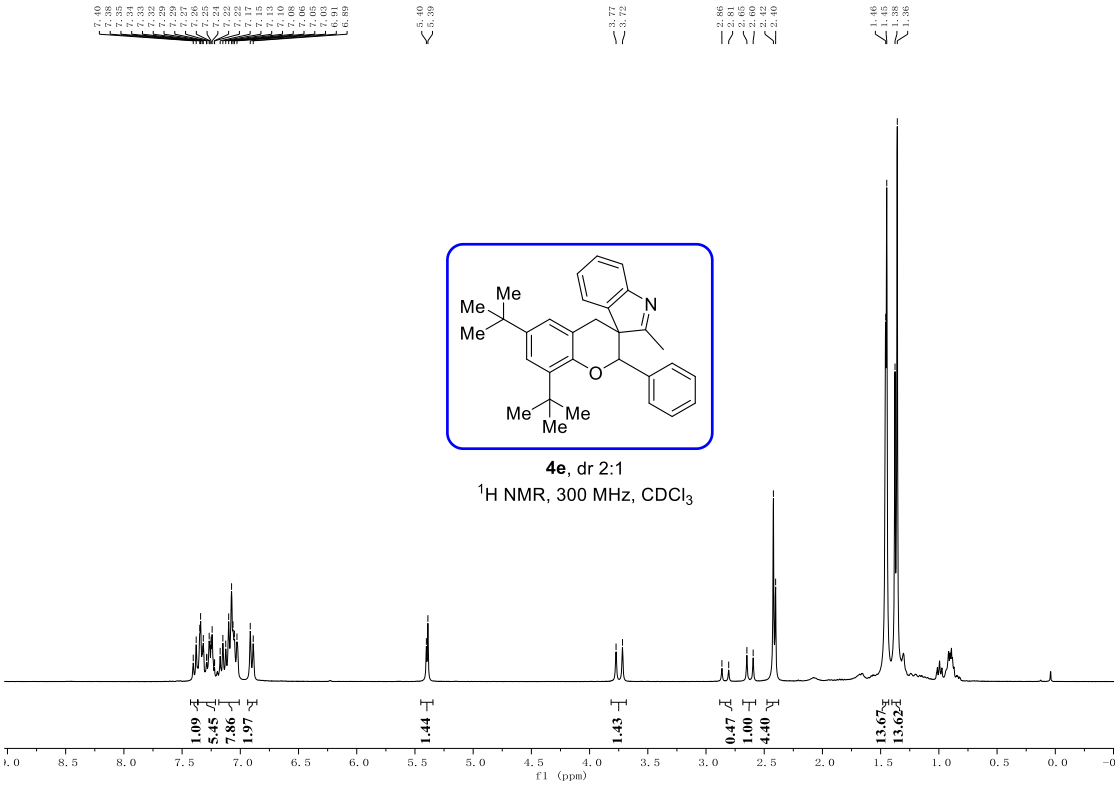


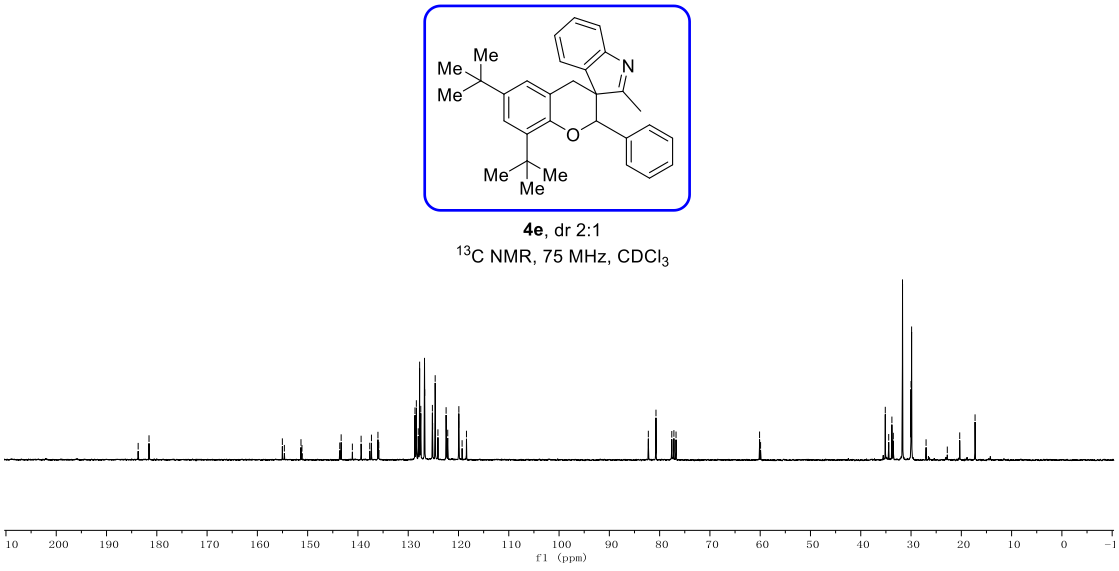
8-(tert-butyl)-2',6-dimethyl-2-phenylspiro[chromane-3,3'-indole] (4d)



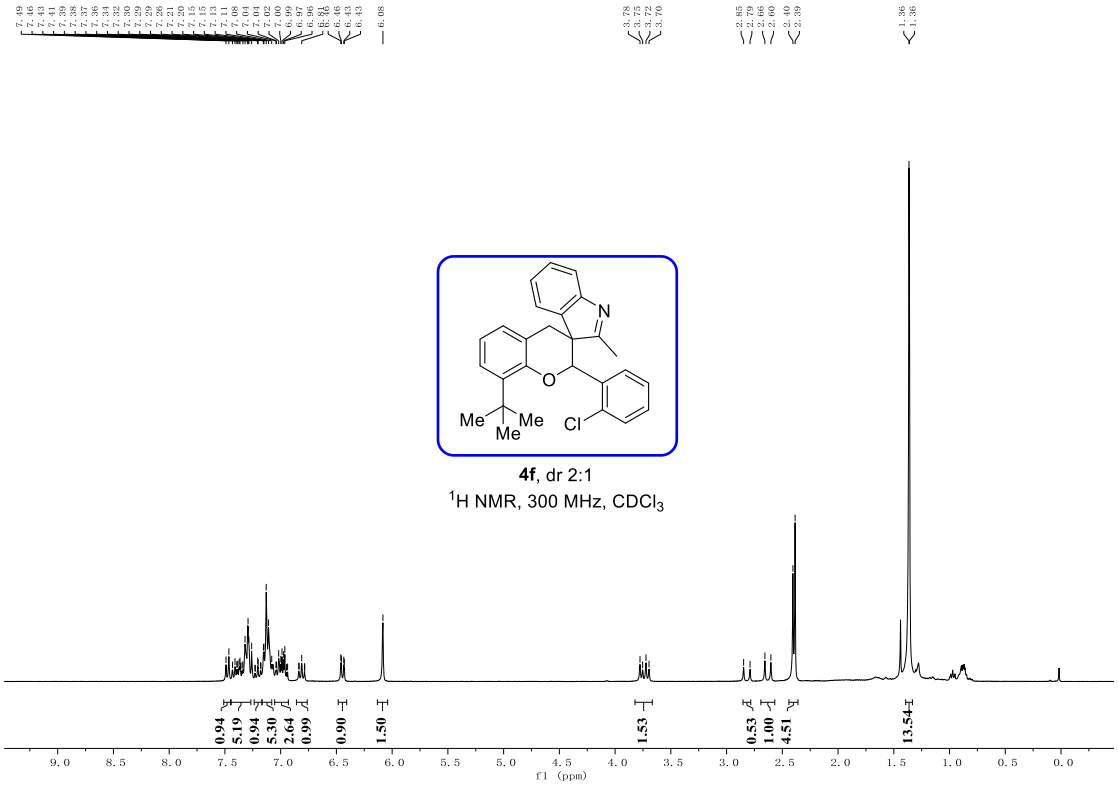


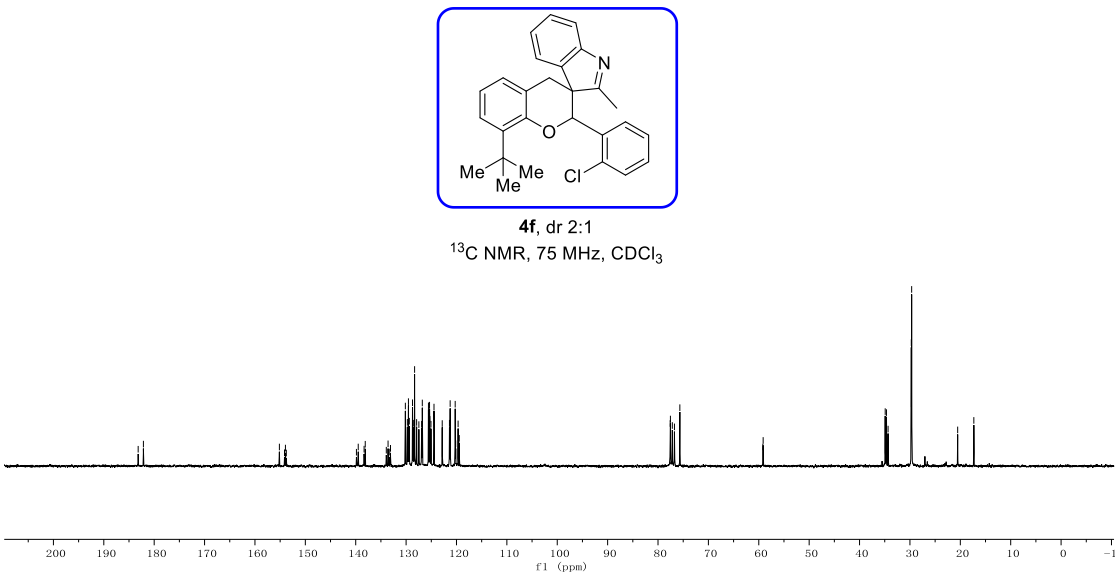
6,8-di-tert-butyl-2'-methyl-2-phenylspiro[chromane-3,3'-indole] (4e)



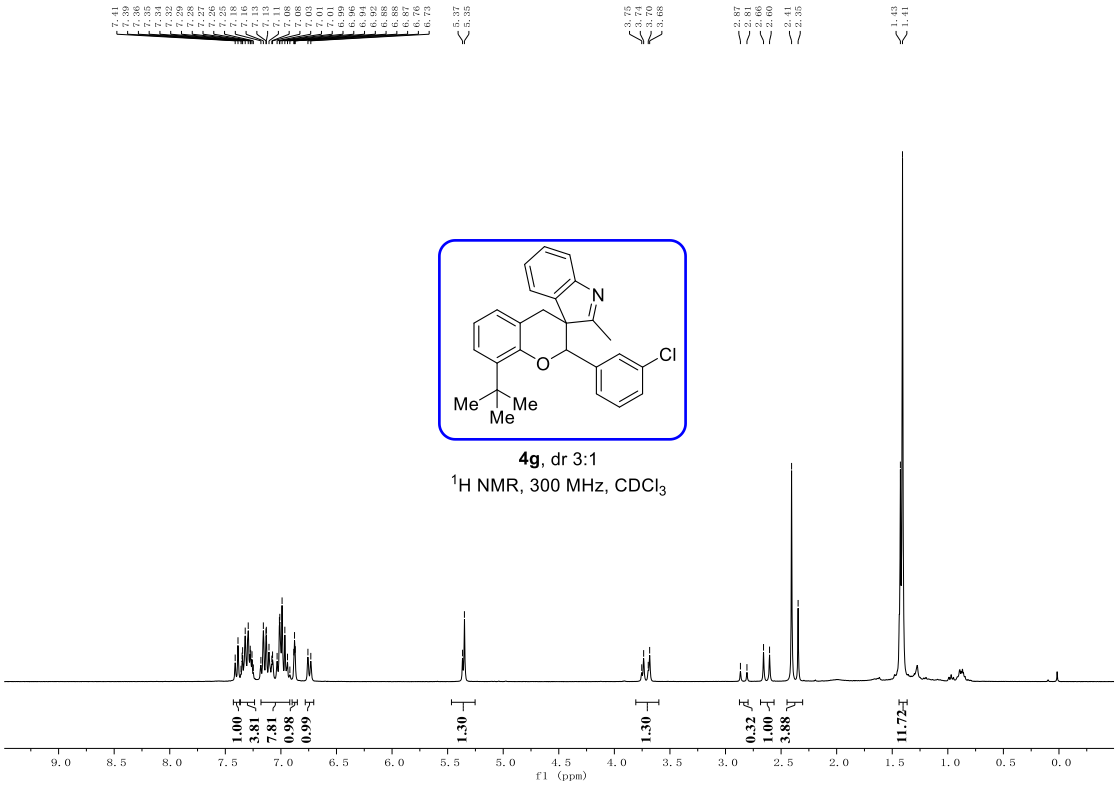


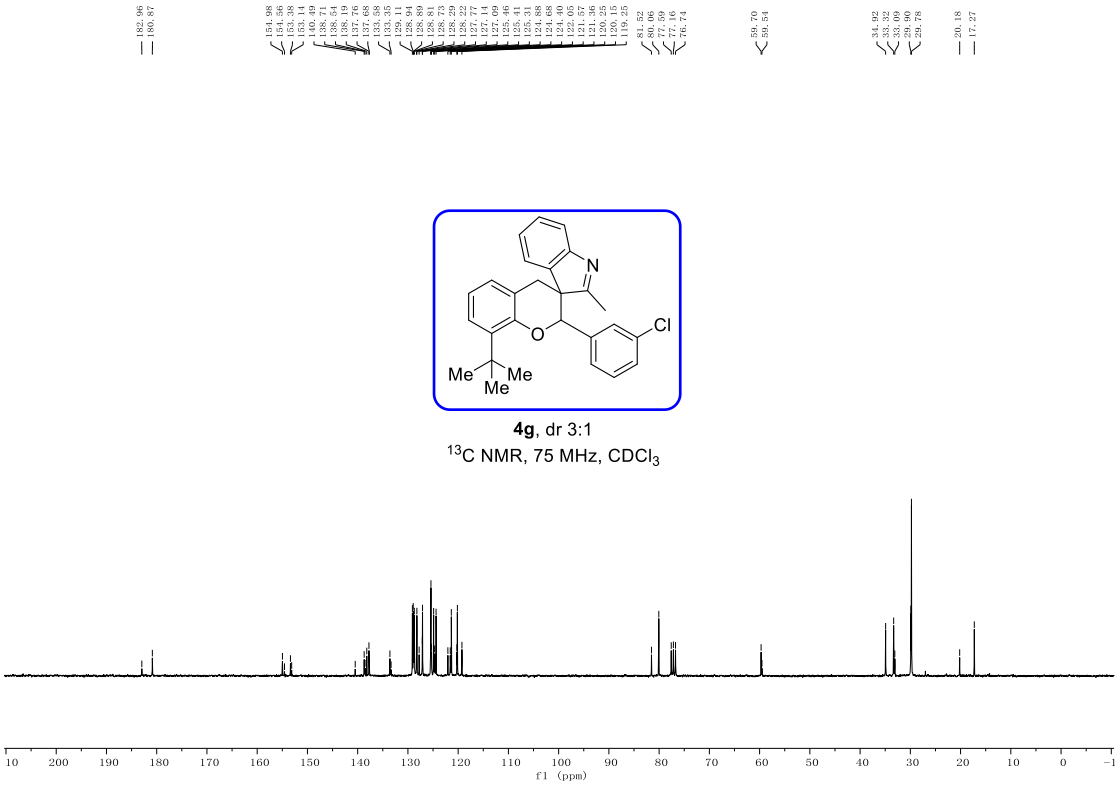
8-(tert-butyl)-2-(2-chlorophenyl)-2'-methylspiro[chromane-3,3'-indole] (4f)



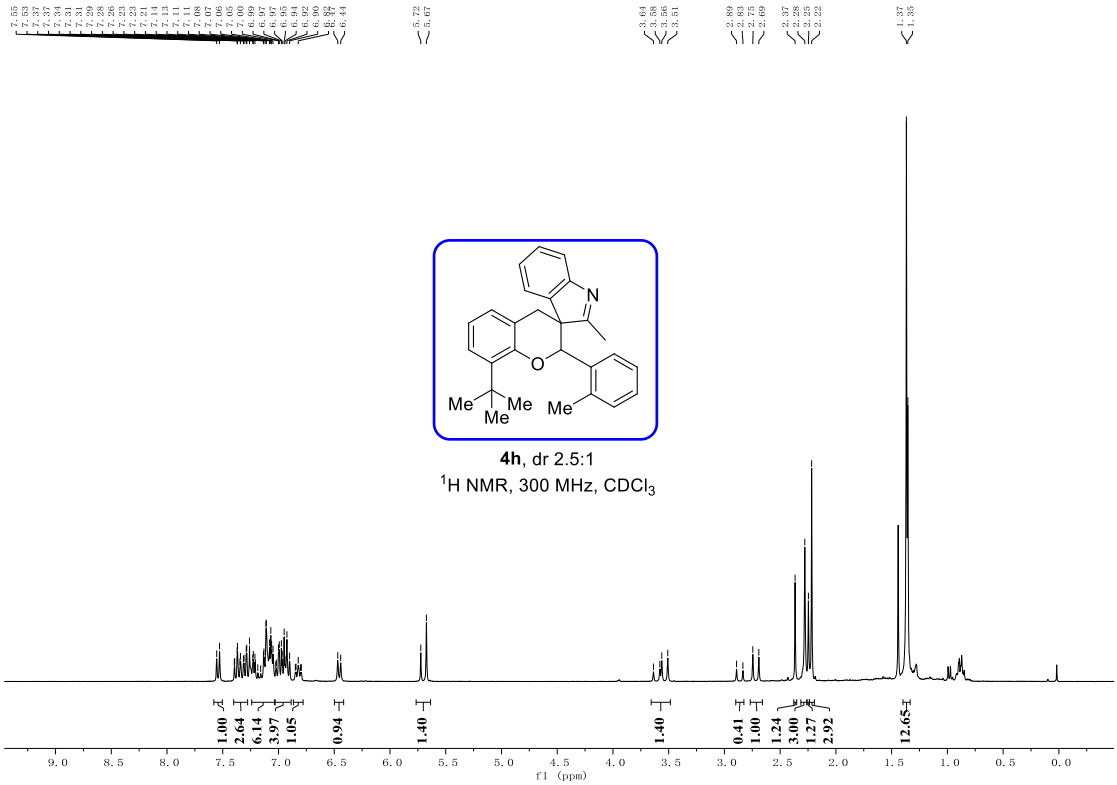


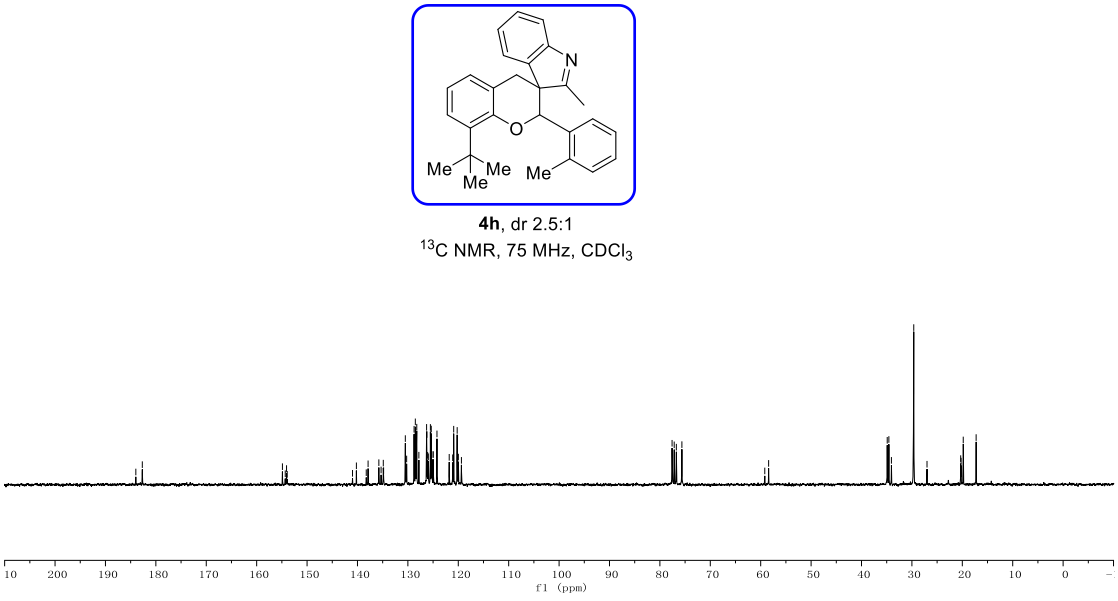
8-(tert-butyl)-2-(3-chlorophenyl)-2'-methylspiro[chromane-3,3'-indole] (4g)



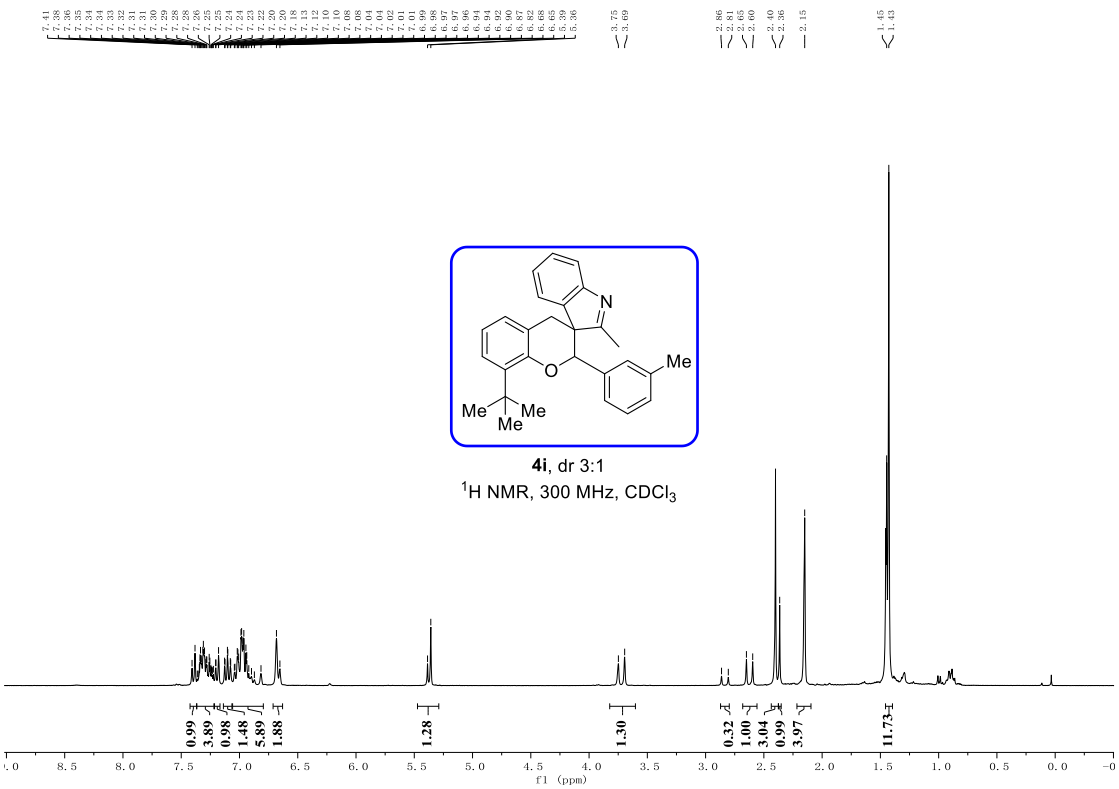


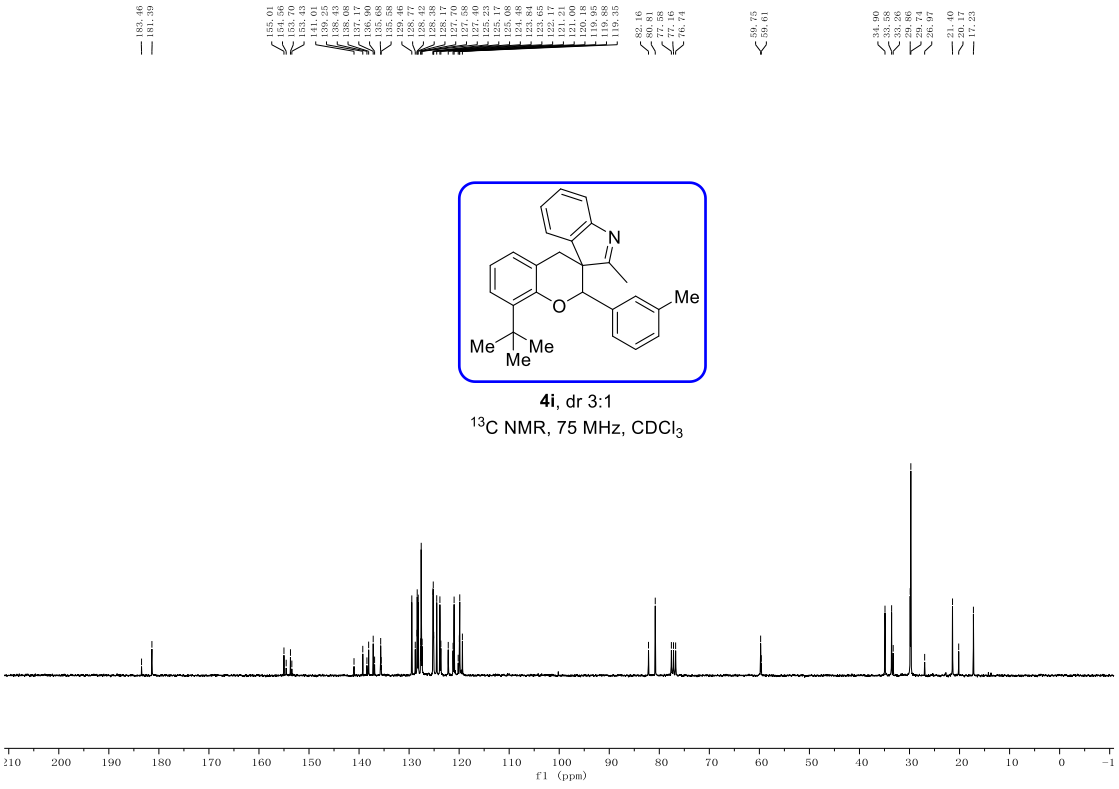
8-(tert-butyl)-2'-methyl-2-(o-tolyl)spiro[chromane-3,3'-indole] (4h)



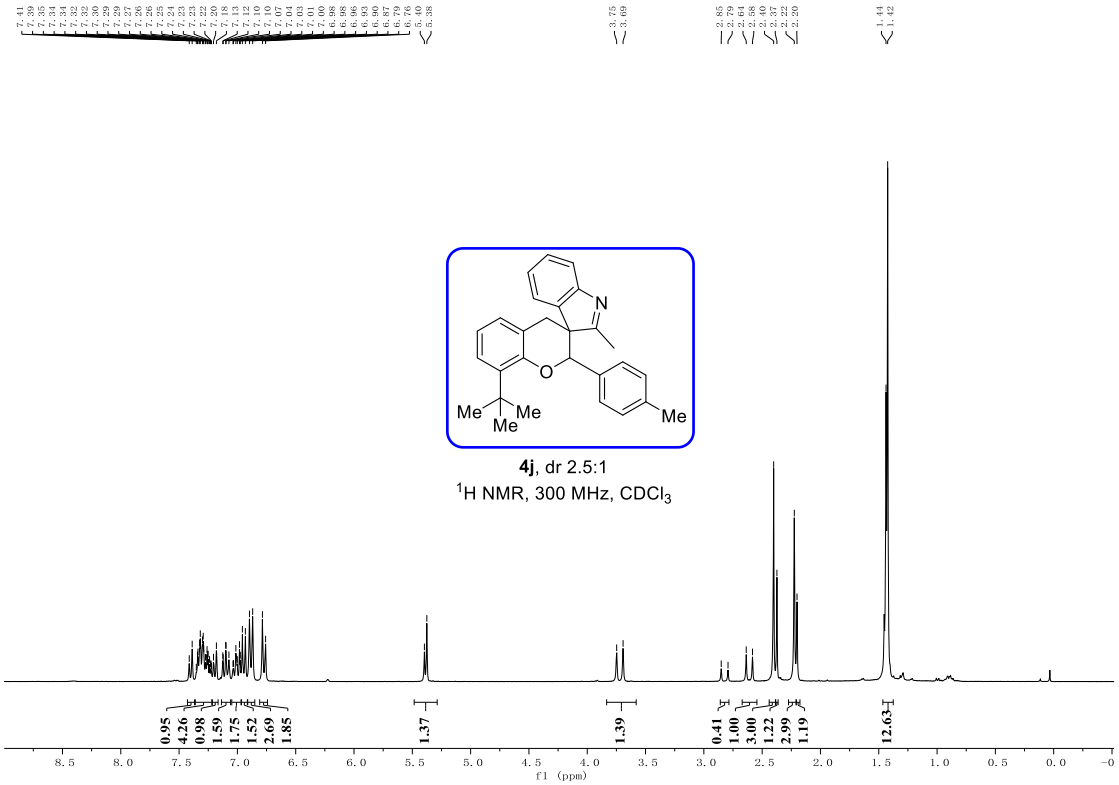


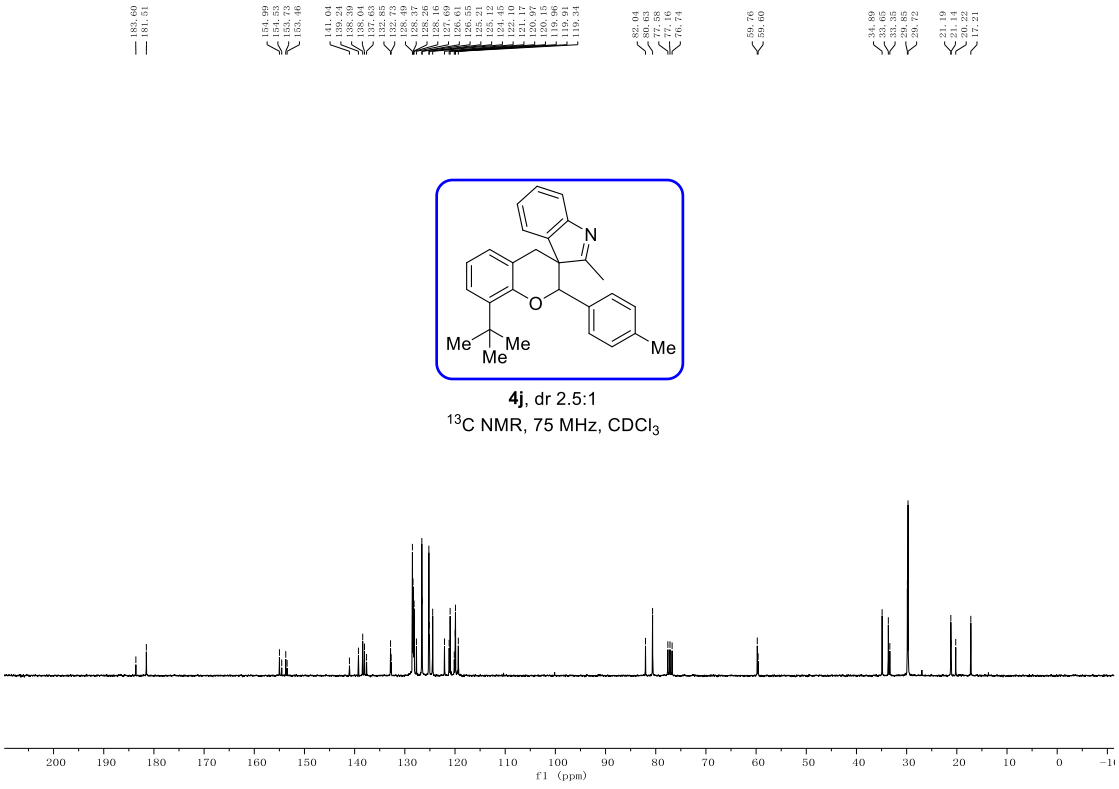
8-(tert-butyl)-2'-methyl-2-(m-tolyl)spiro[chromane-3,3'-indole] (4i)



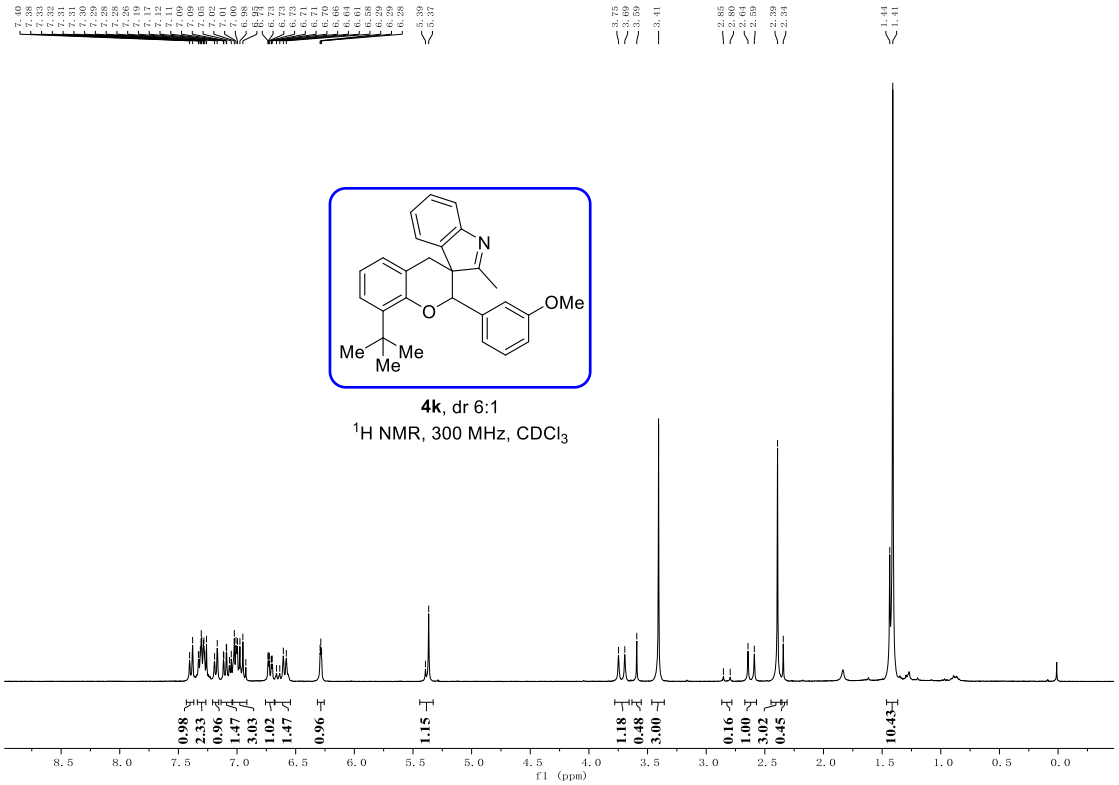


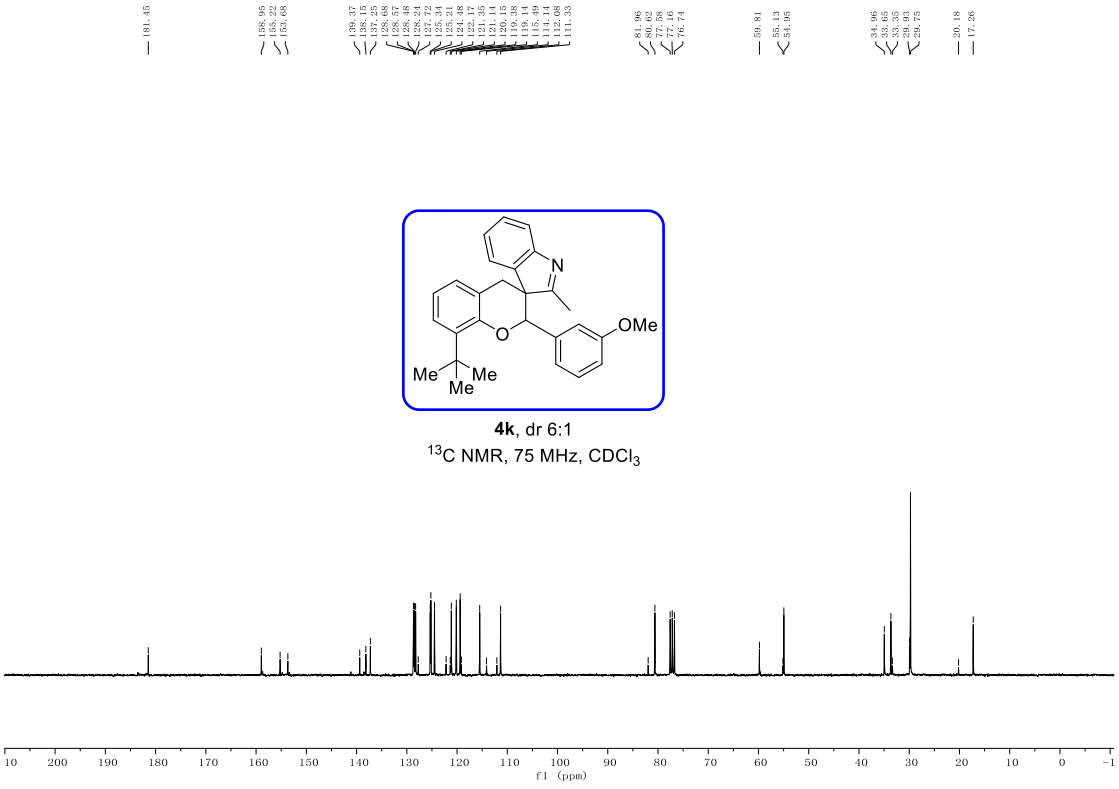
8-(tert-butyl)-2'-methyl-2-(p-tolyl)spiro[chromane-3,3'-indole] (4j)



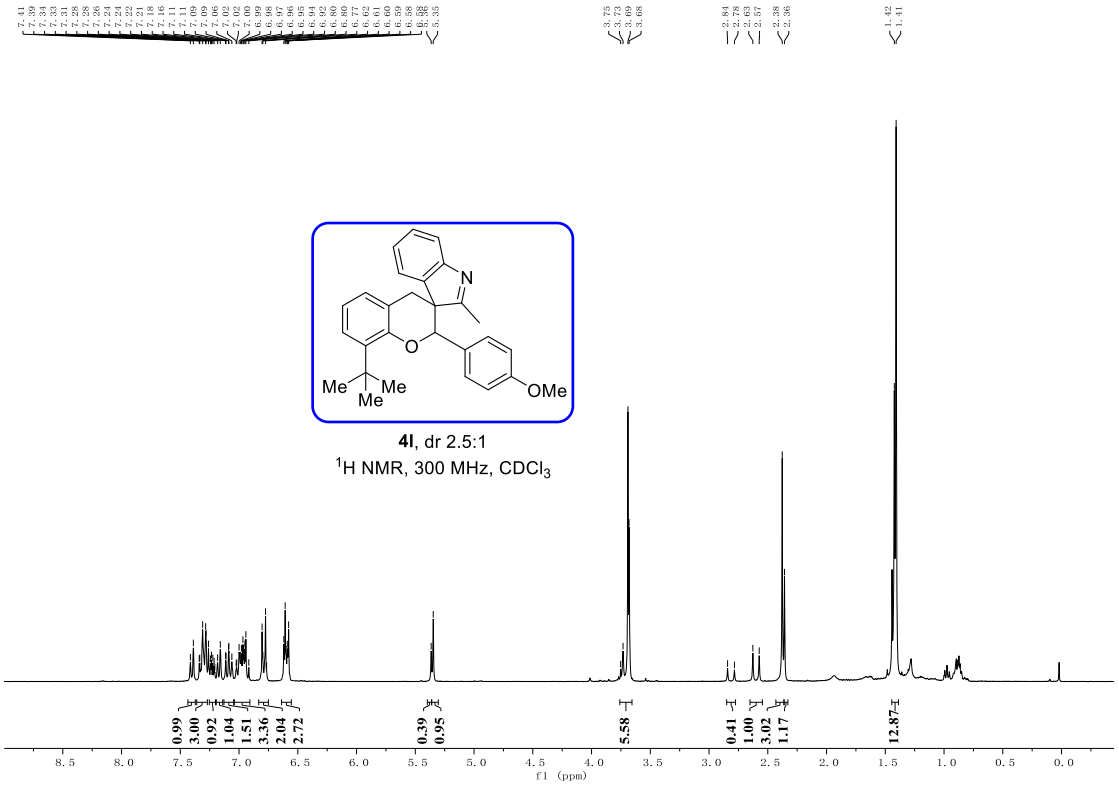


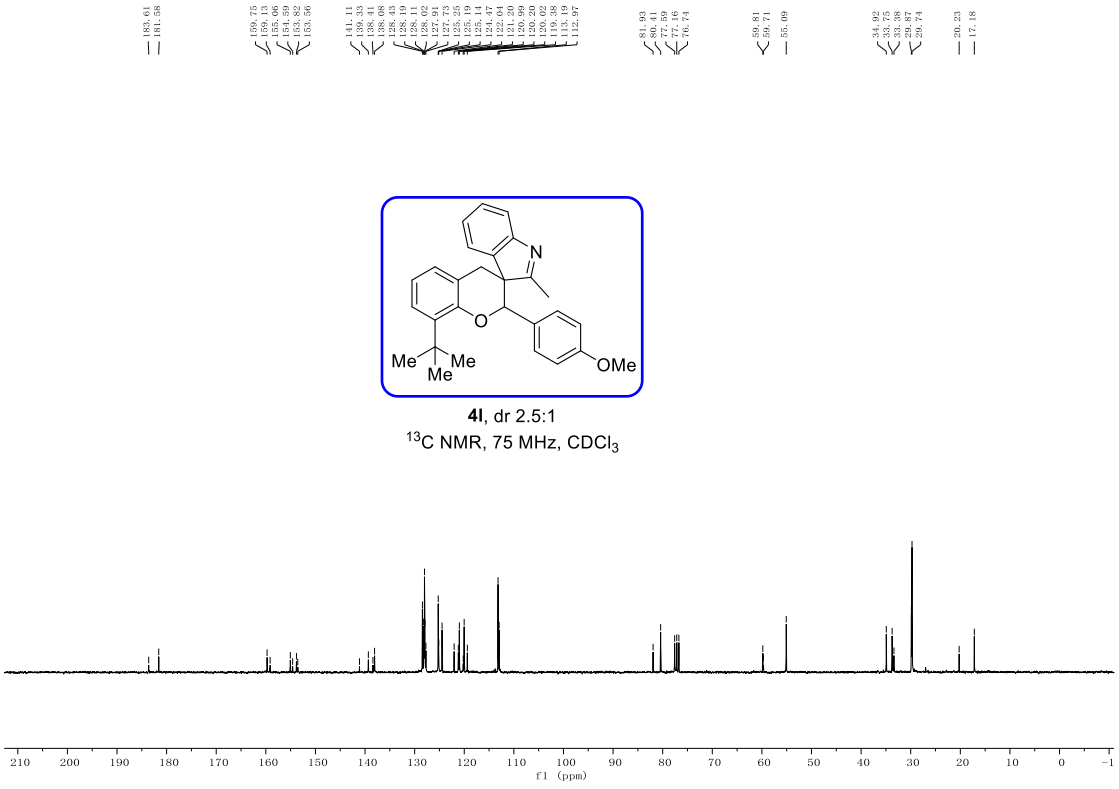
8-(tert-butyl)-2-(3-methoxyphenyl)-2'-methylspiro[chromane-3,3'-indole] (4k)



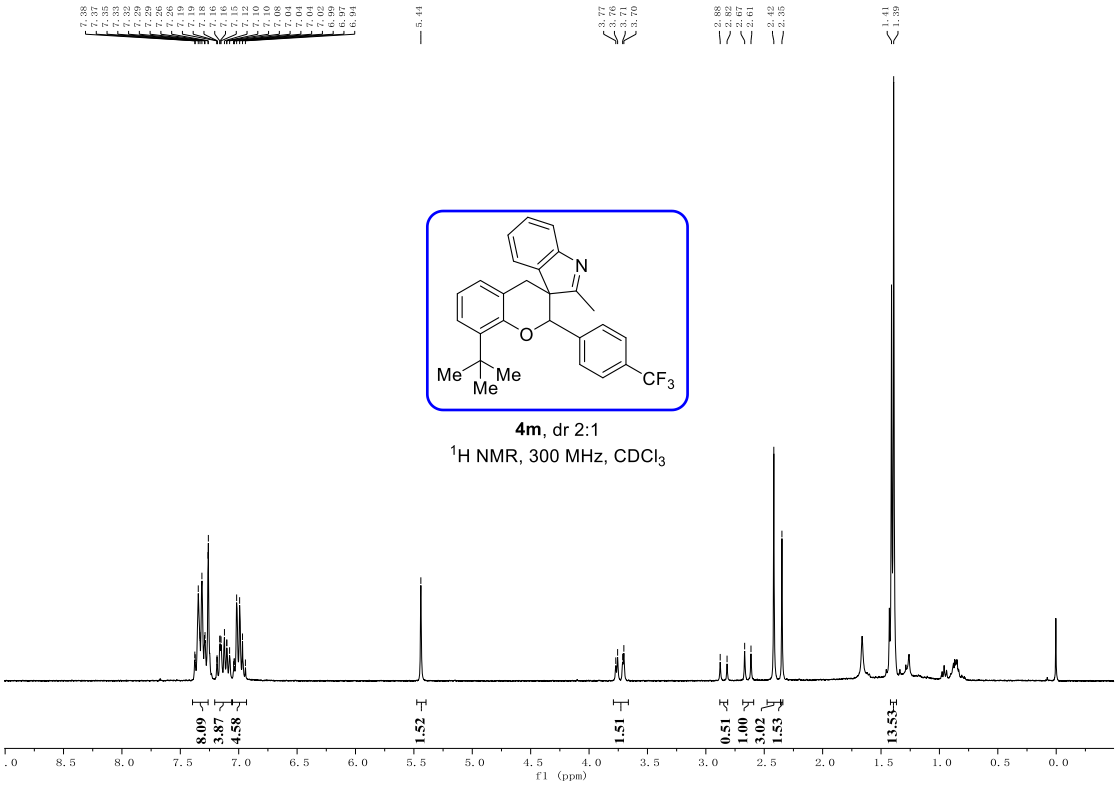


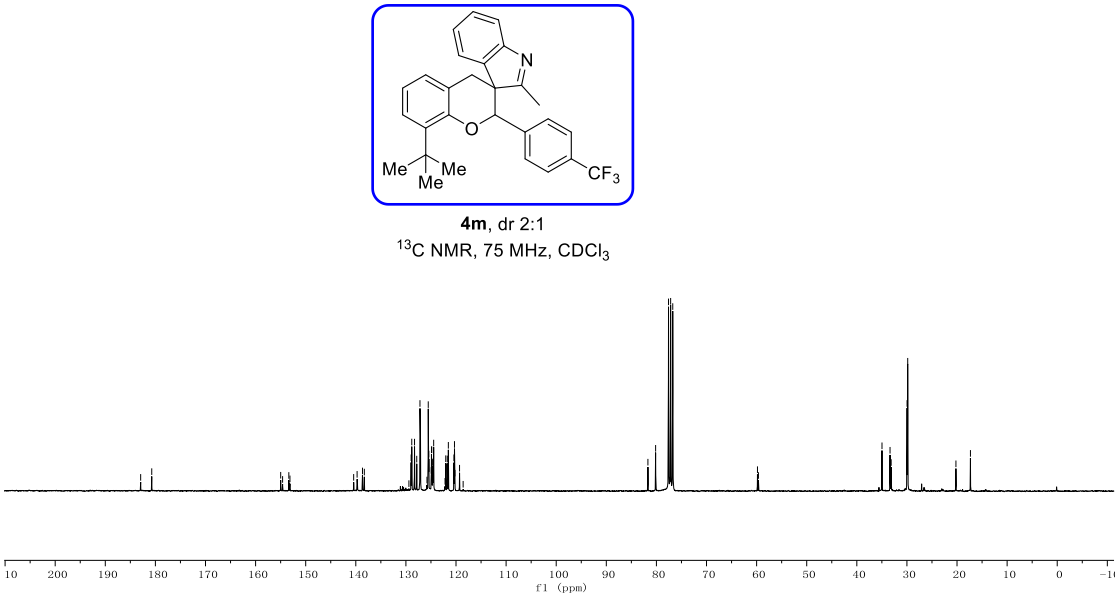
8-(tert-butyl)-2-(4-methoxyphenyl)-2'-methylspiro[chromane-3,3'-indole] (4l)



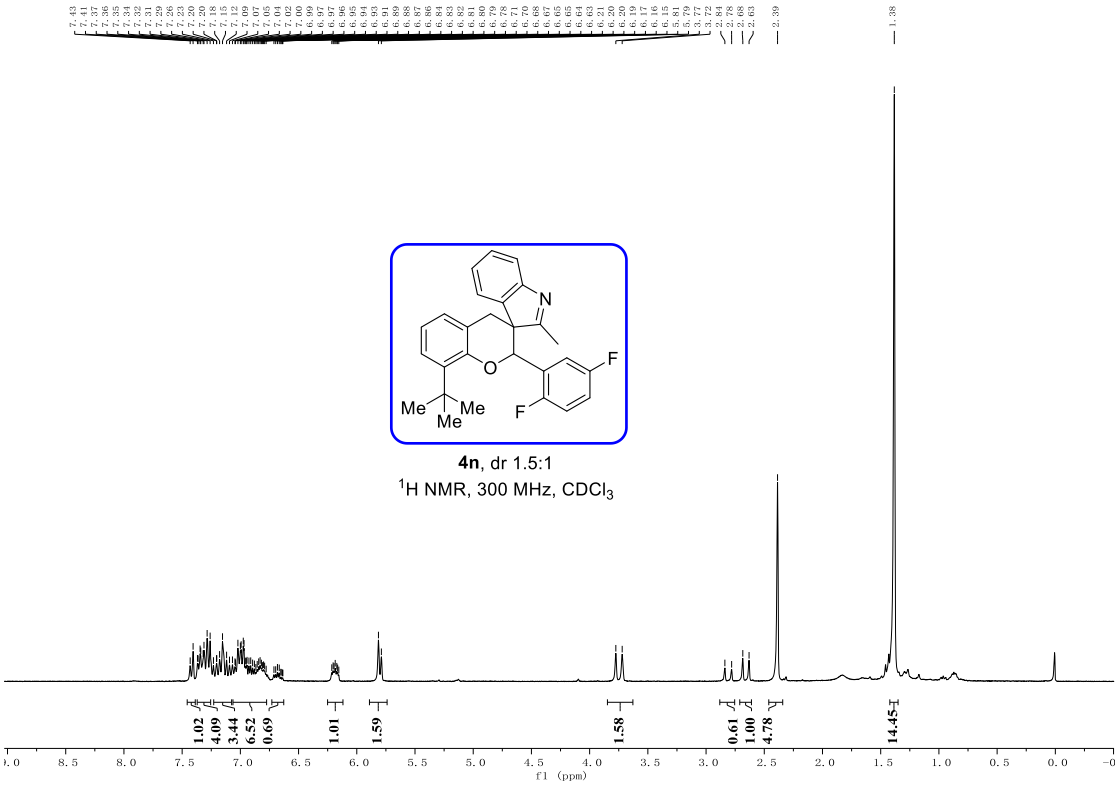


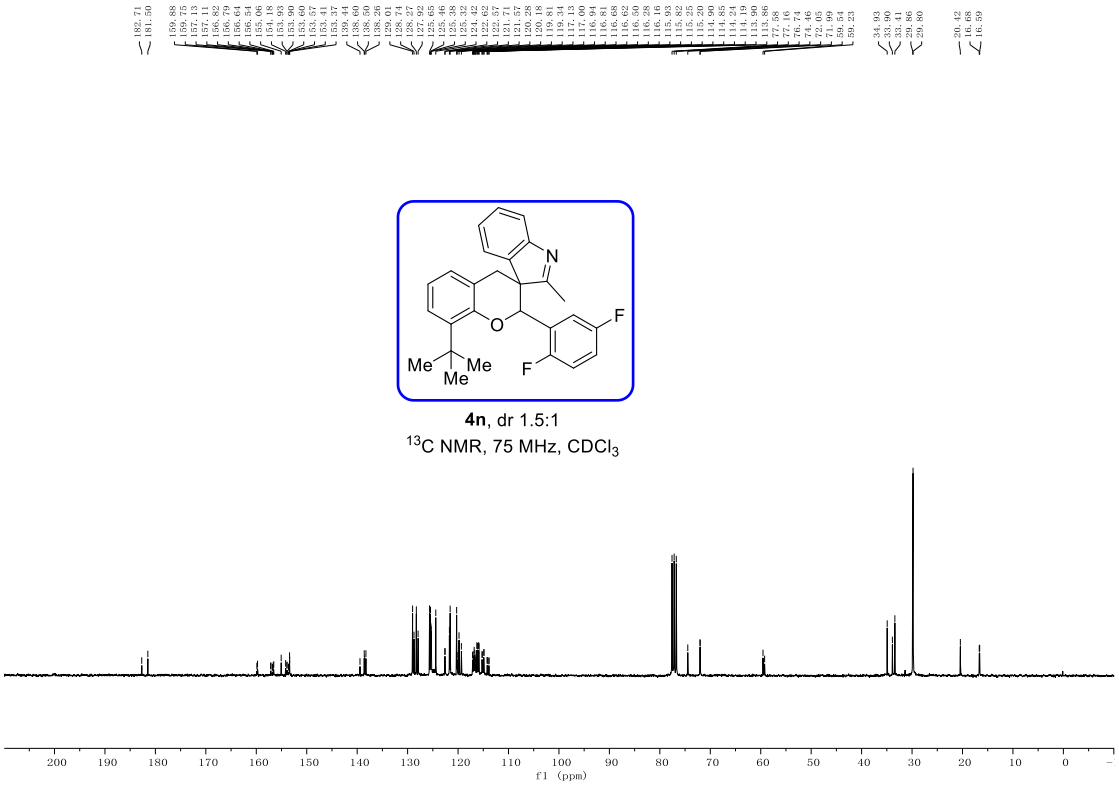
8-(tert-butyl)-2'-methyl-2-(4-(trifluoromethyl)phenyl)spiro[chromane-3,3'-indole] (4m)



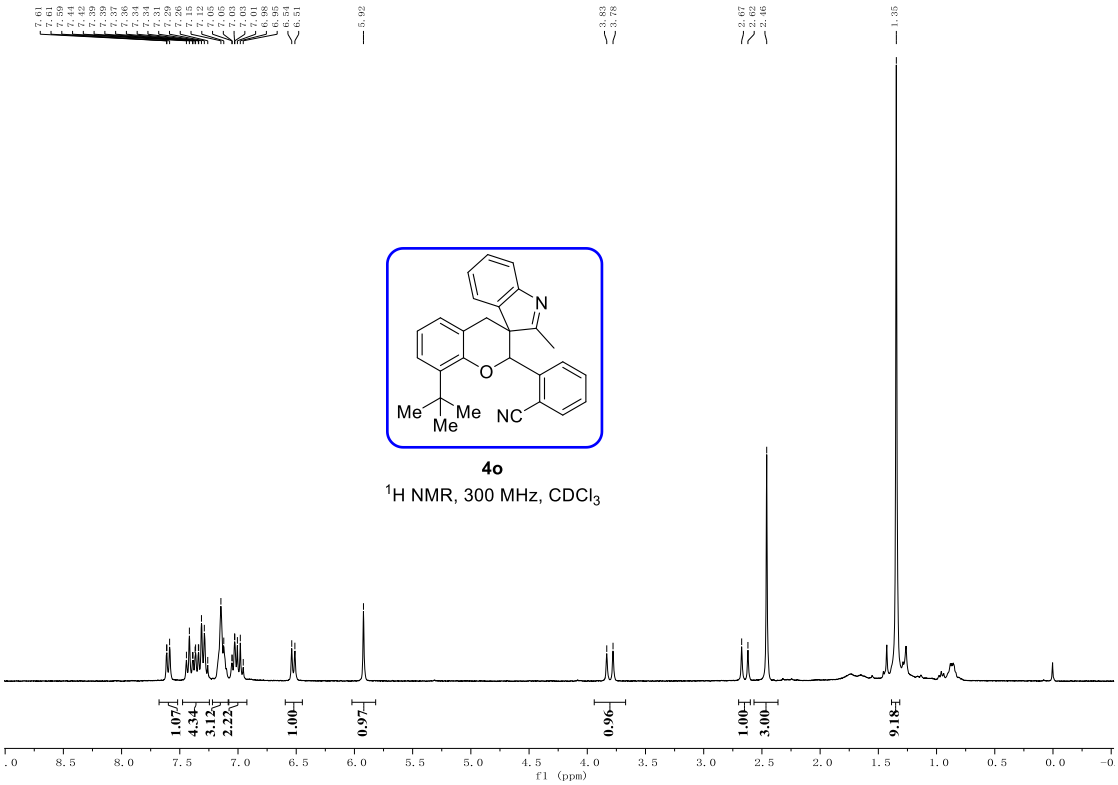


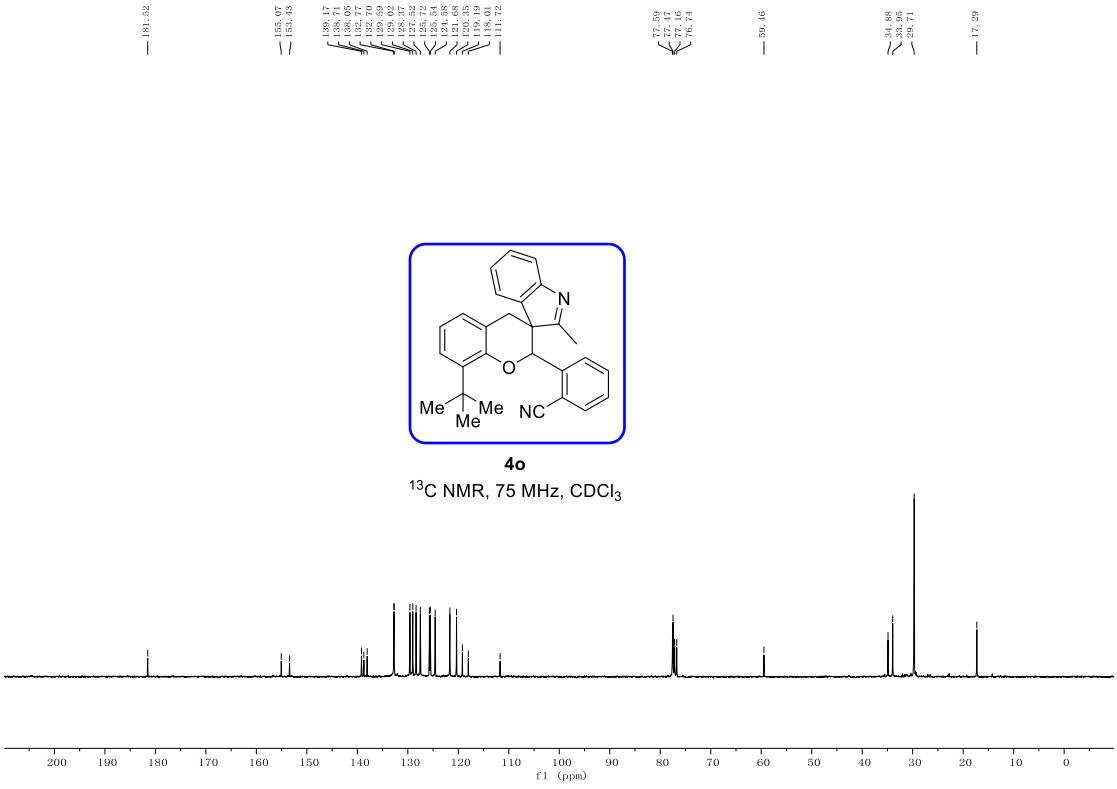
8-(tert-butyl)-2-(2,5-difluorophenyl)-2'-methylspiro[chromane-3,3'-indole] (4n)



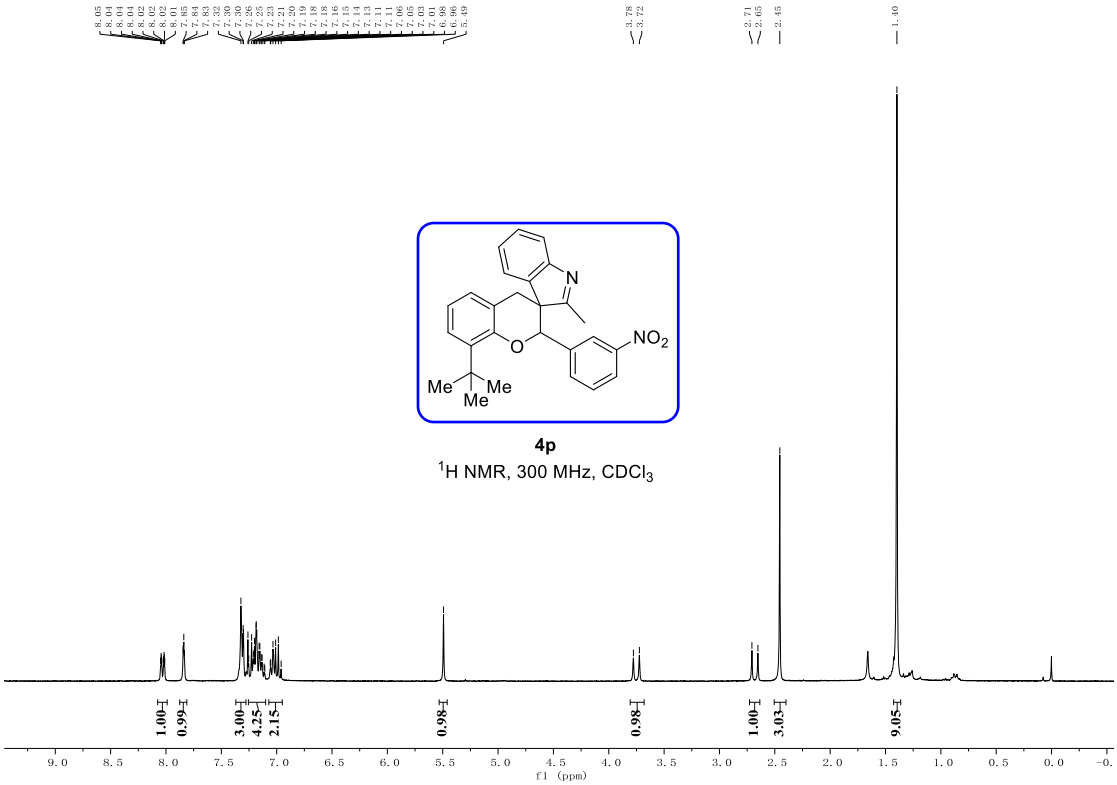


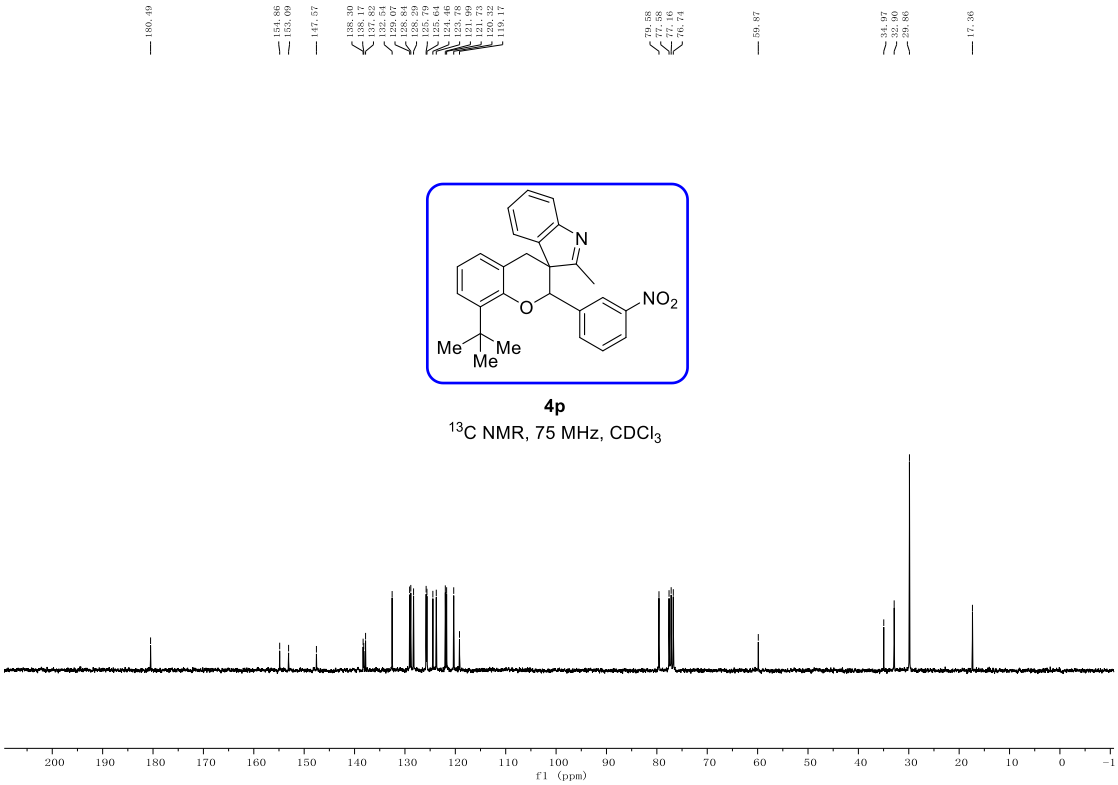
2-(8-(tert-butyl)-2'-methylspiro[chromane-3,3'-indol]-2-yl)benzonitrile (4o)



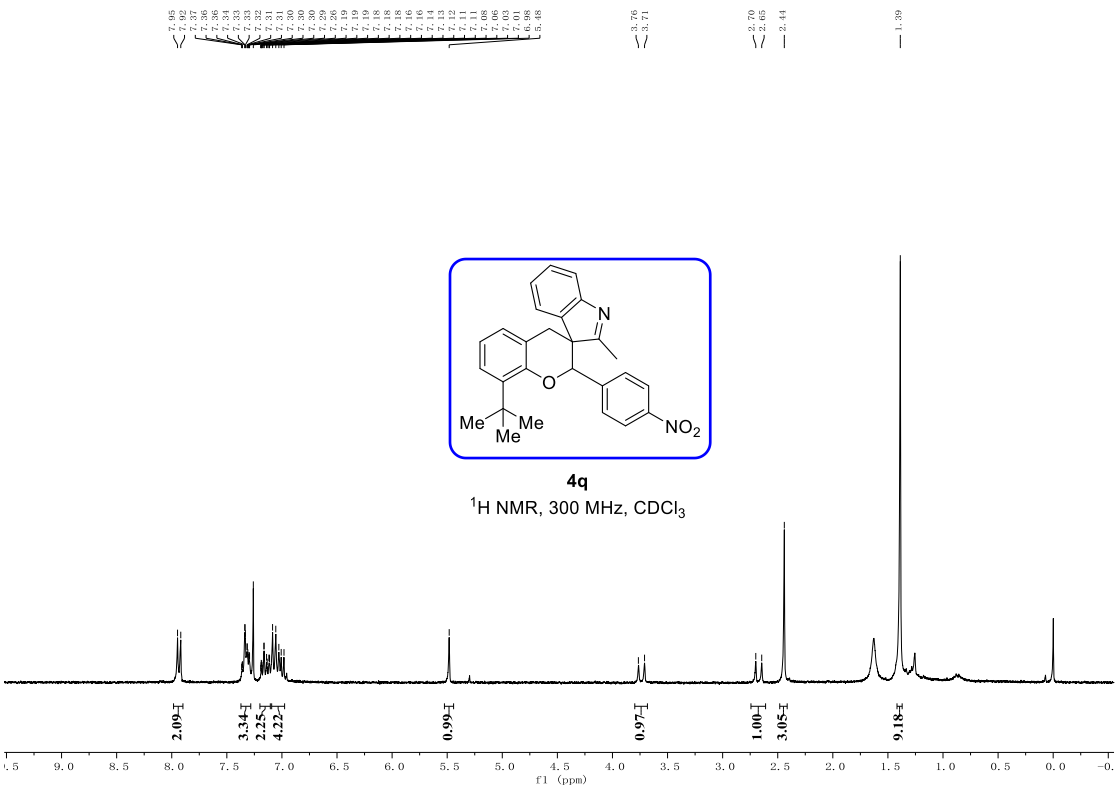


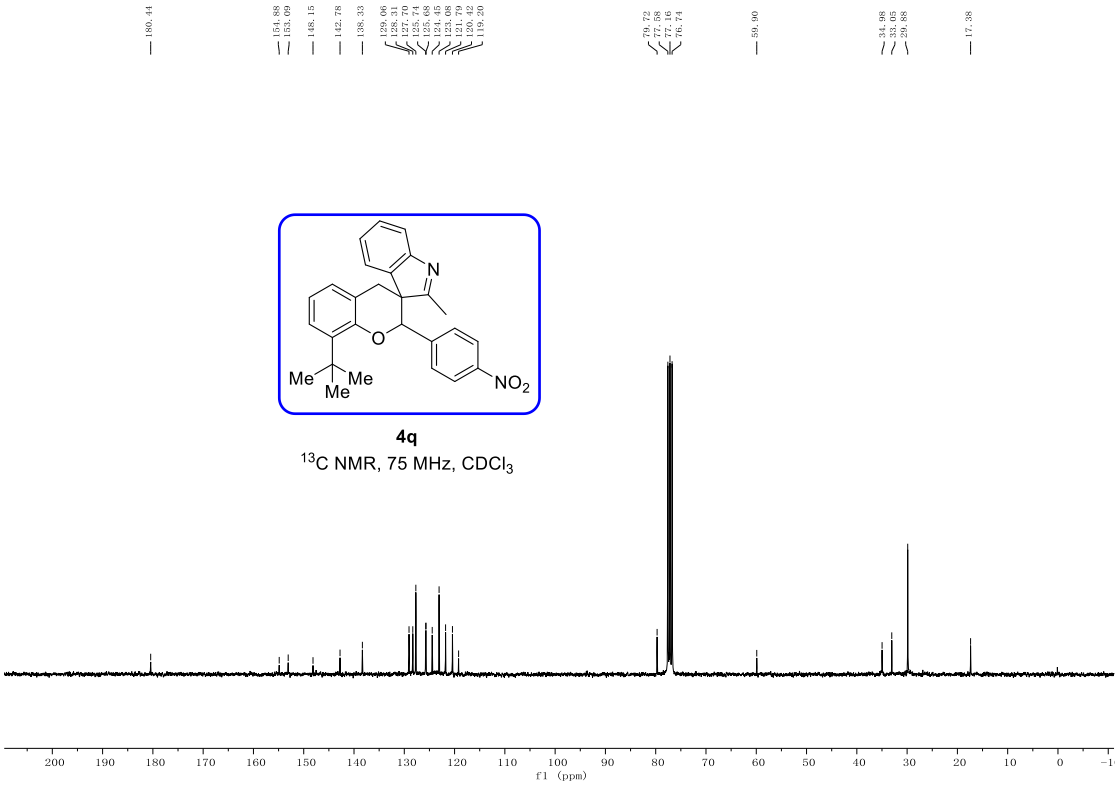
8-(tert-butyl)-2'-methyl-2-(3-nitrophenyl)spiro[chromane-3,3'-indole] (4p)



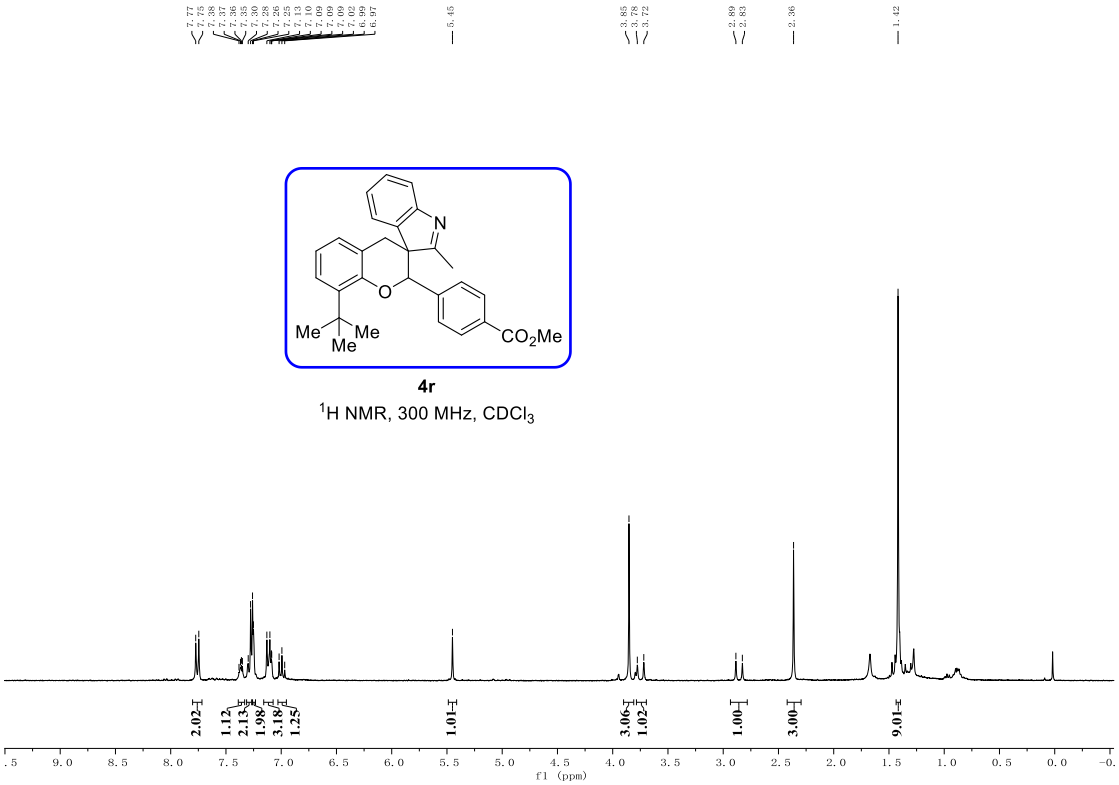


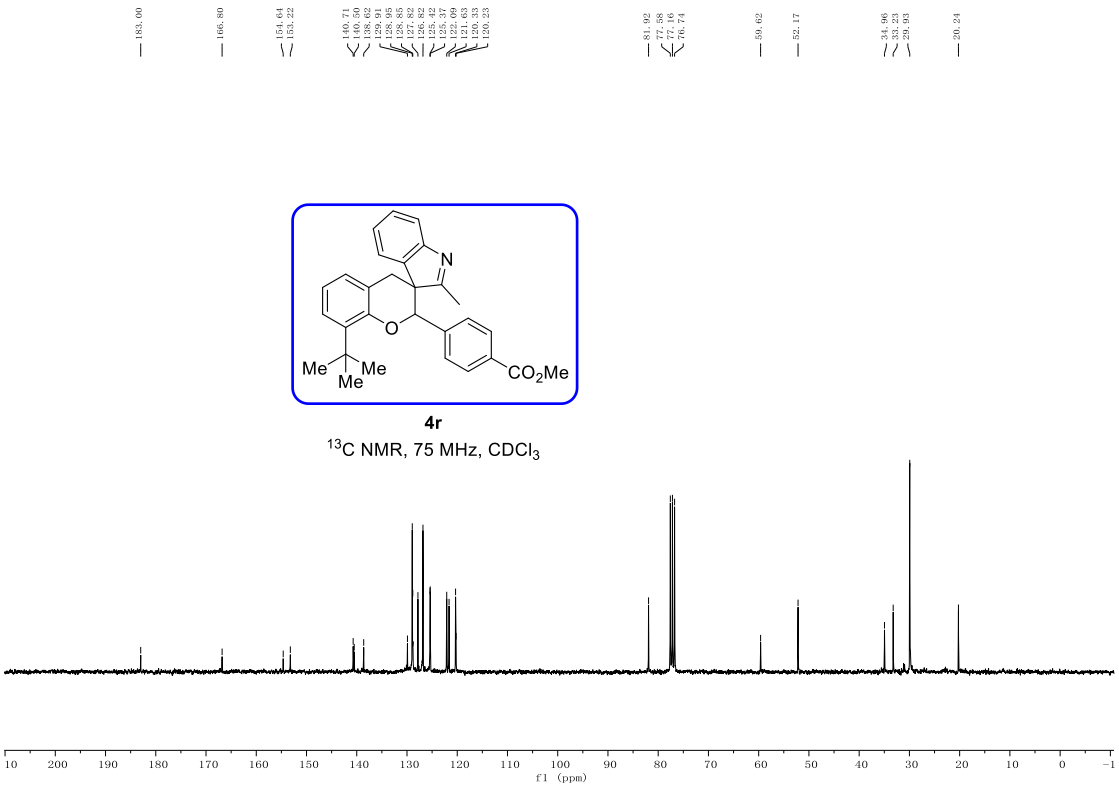
8-(tert-butyl)-2'-methyl-2-(4-nitrophenyl)spiro[chromane-3,3'-indole] (4q)



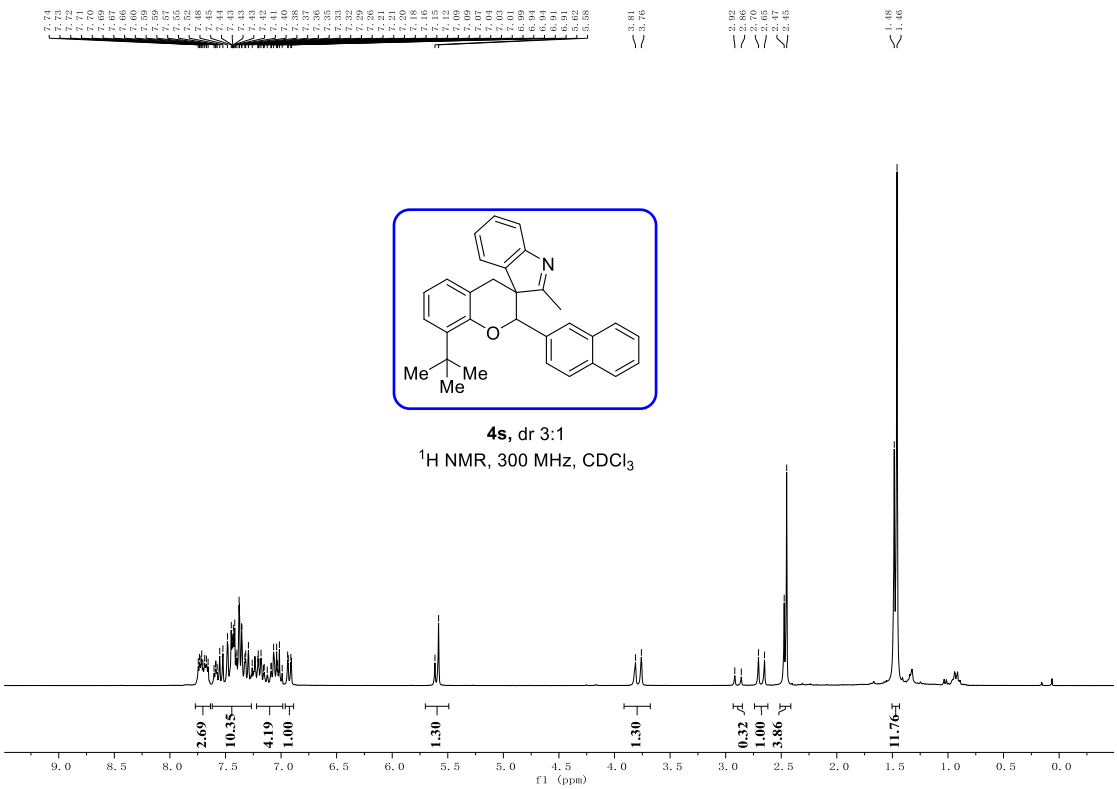


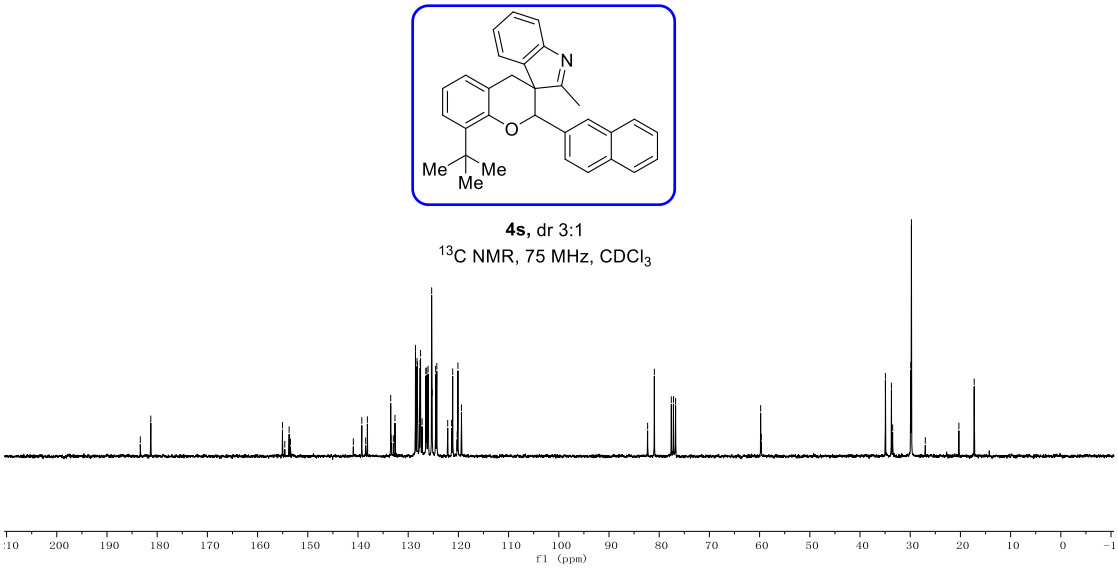
methyl 4-(8-(tert-butyl)-2'-methylspiro[chromane-3,3'-indol]-2-yl)benzoate (4r)



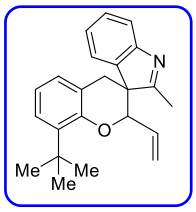


8-(tert-butyl)-2'-methyl-2-(naphthalen-2-yl)spiro[chromane-3,3'-indole] (4s)



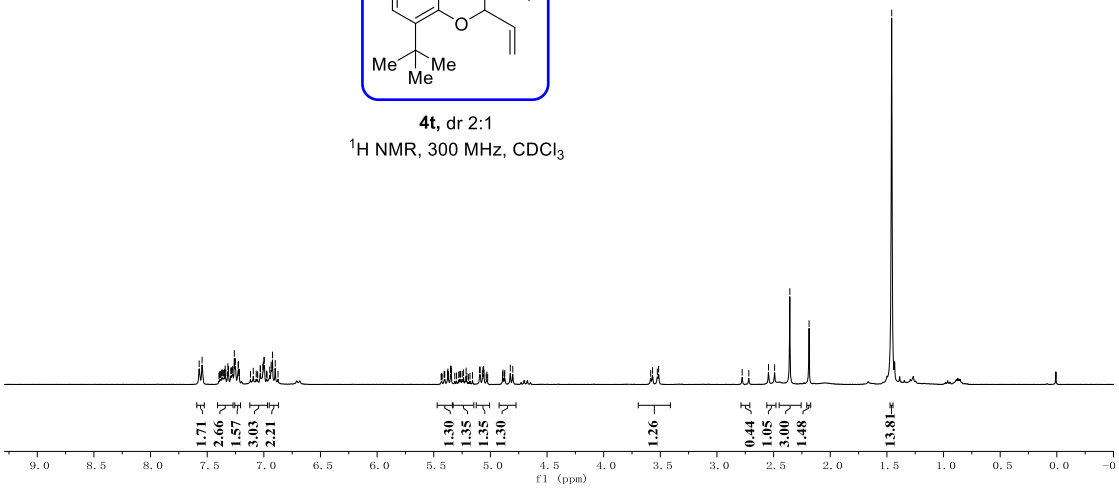


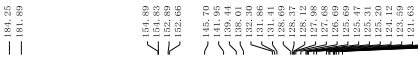
8-(tert-butyl)-2'-methyl-2-vinylspiro[chromane-3,3'-indole] (4t)

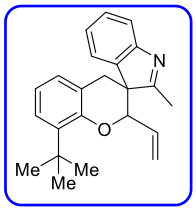


4t, dr 2:1

^{1}H NMR, 300 MHz, $CDCl_3$

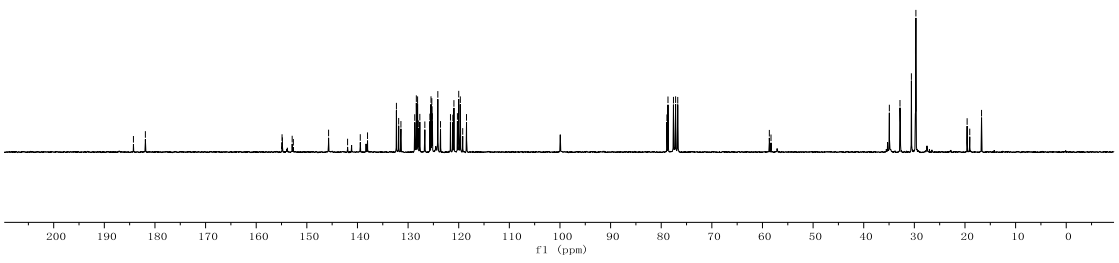




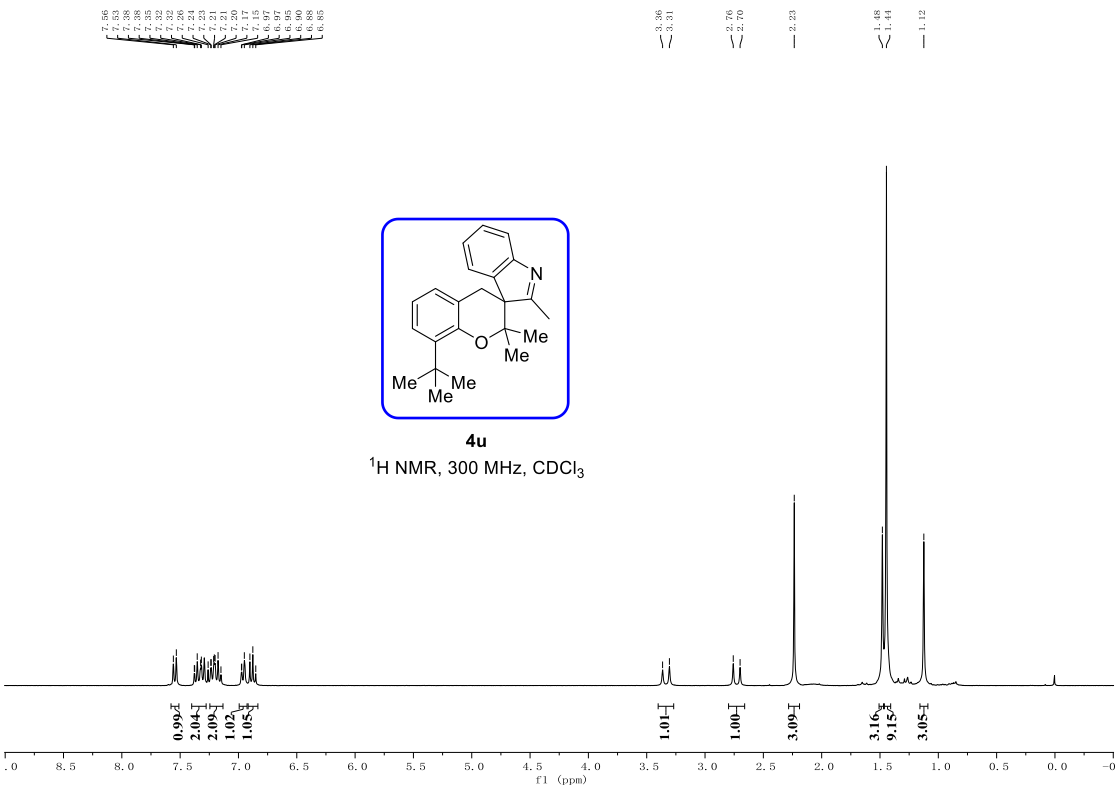


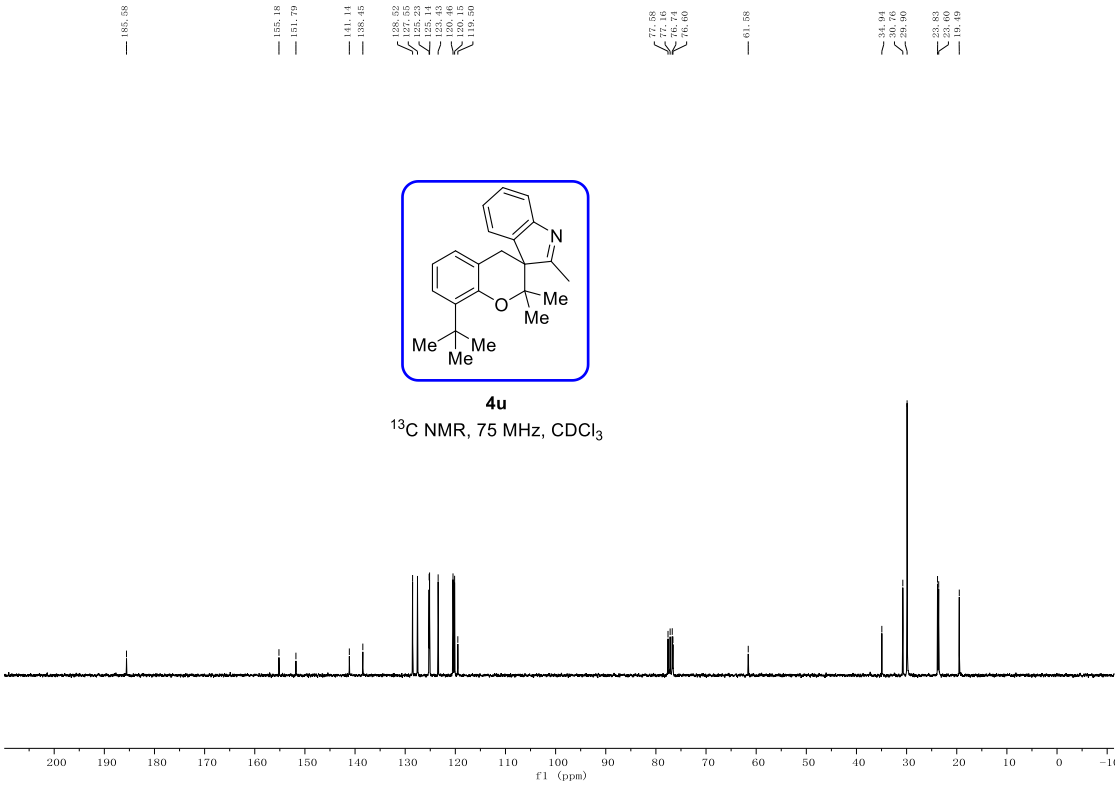
4t, dr 2:1

^{13}C NMR, 75 MHz, $CDCl_3$

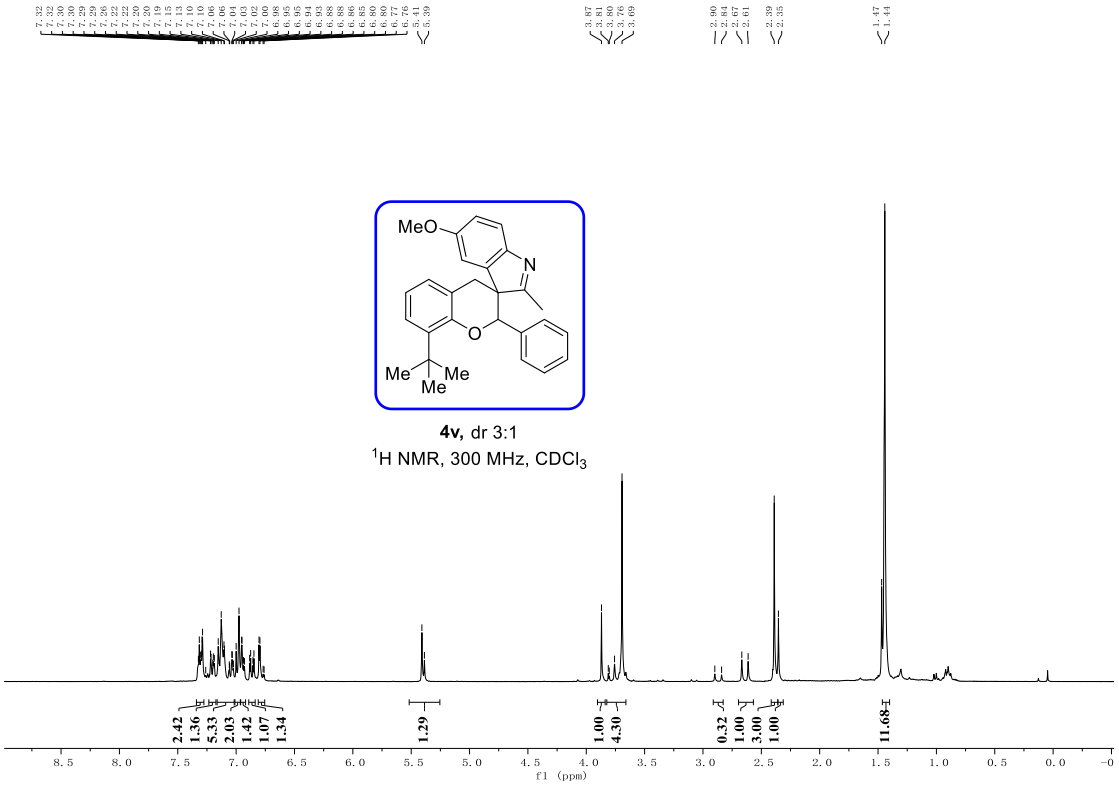


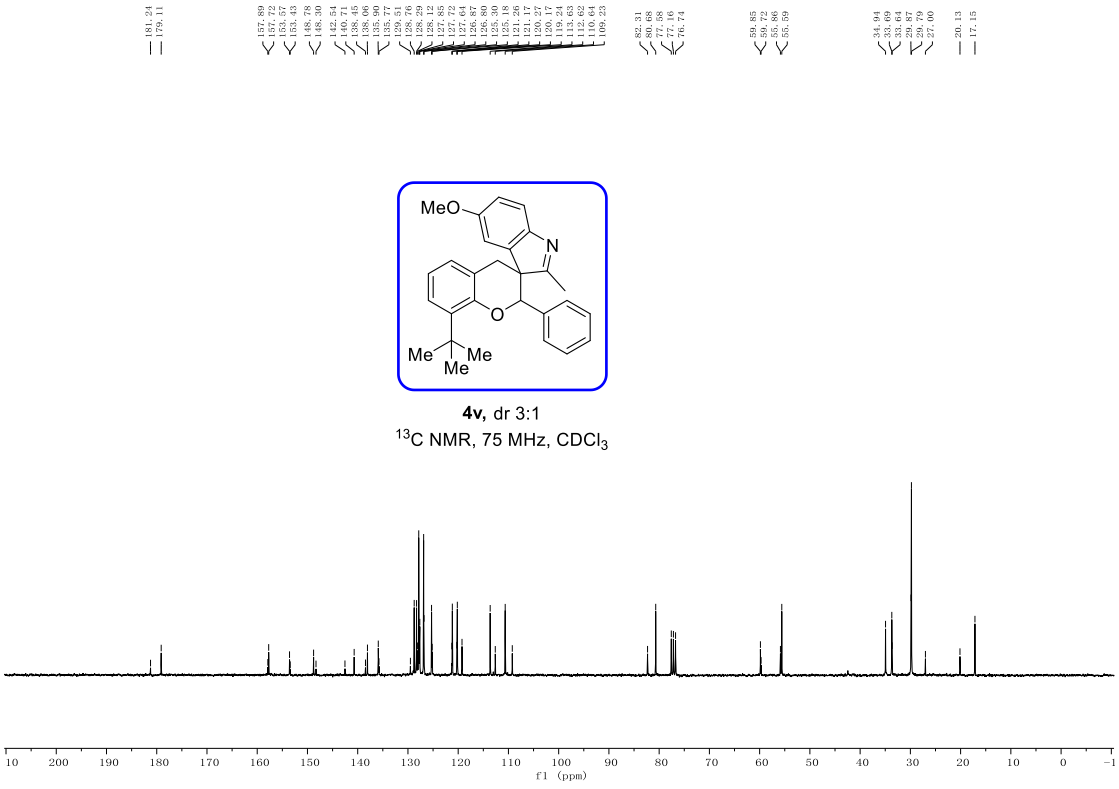
8-(tert-butyl)-2,2,2'-trimethylspiro[chromane-3,3'-indole] (4u)



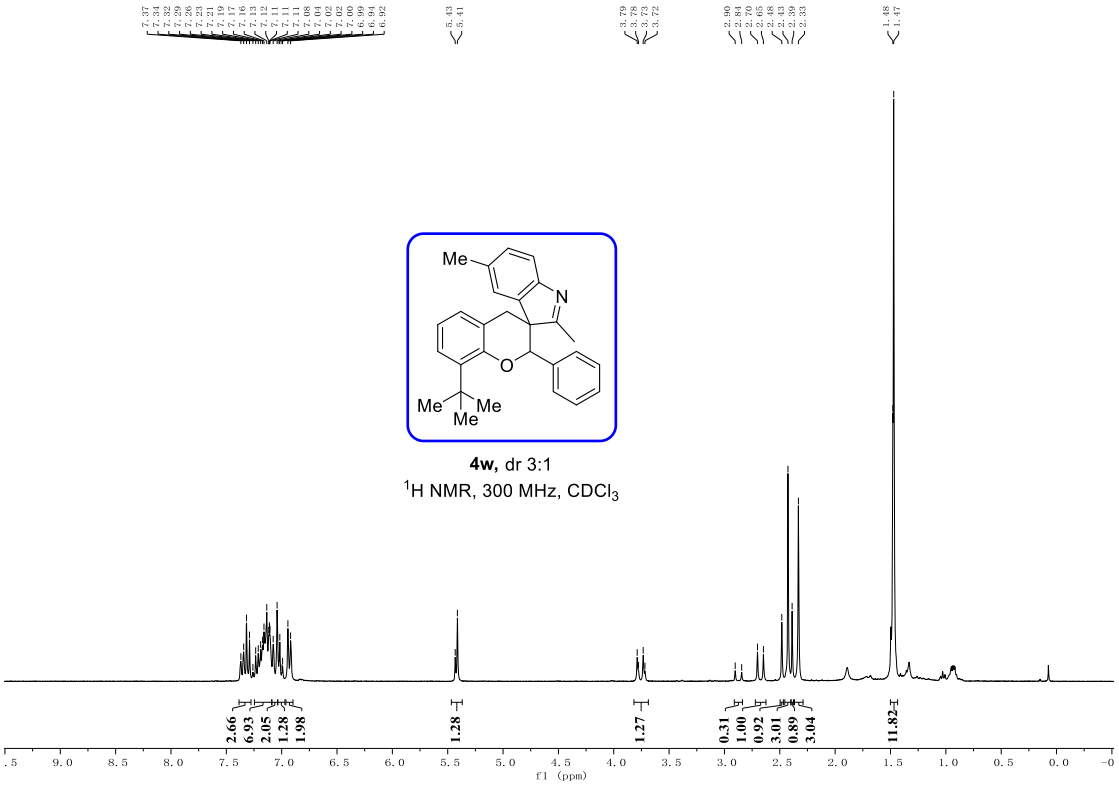


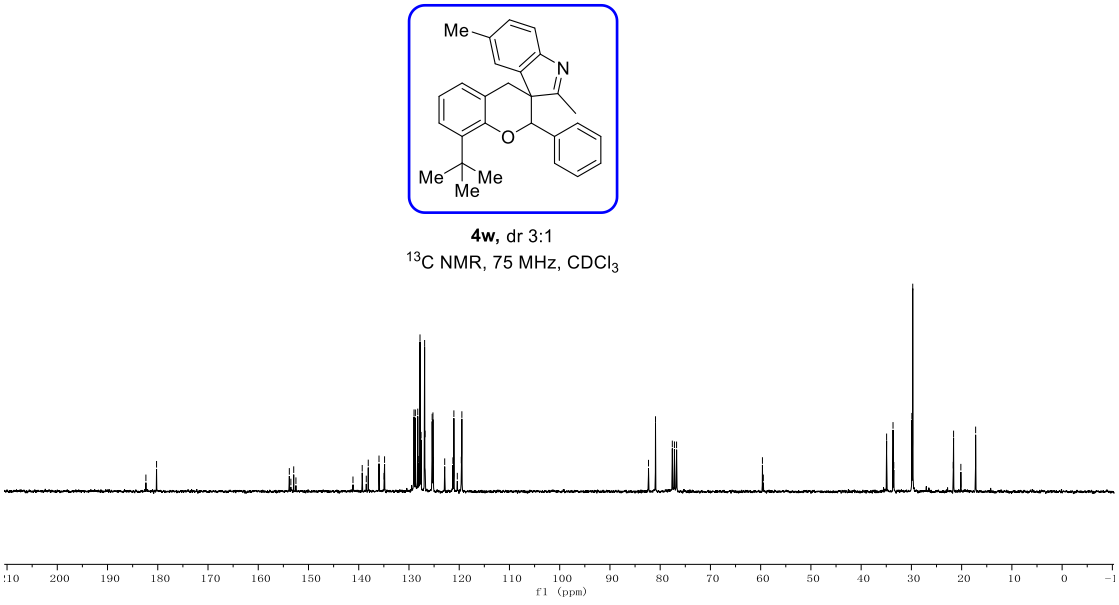
8-(tert-butyl)-5'-methoxy-2'-methyl-2-phenylspiro[chromane-3,3'-indole] (4v)



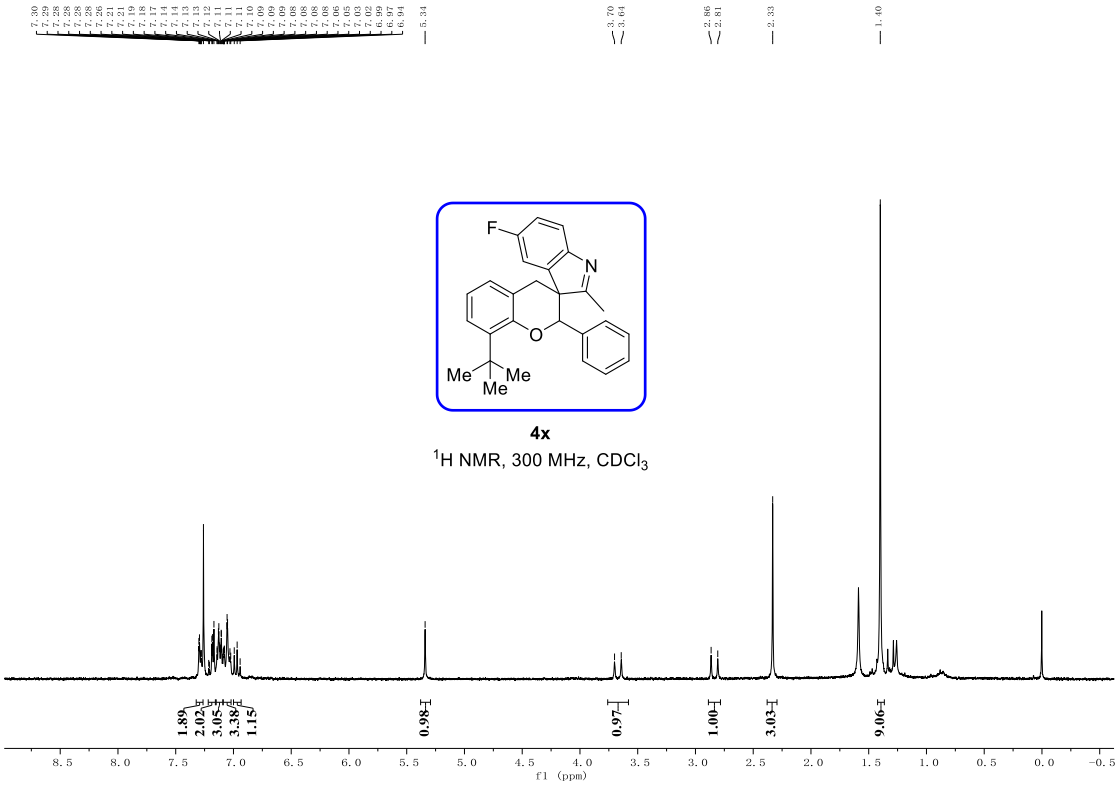


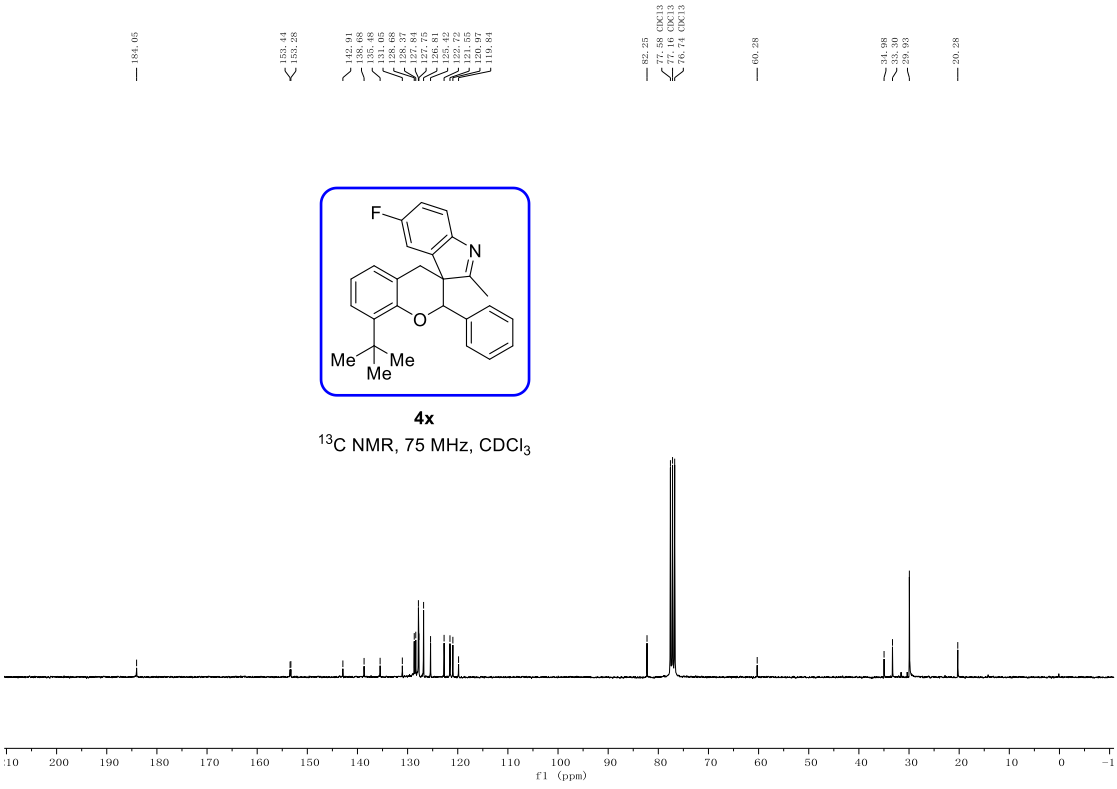
8-(tert-butyl)-2',5'-dimethyl-2-phenylspiro[chromane-3,3'-indole] (4w)



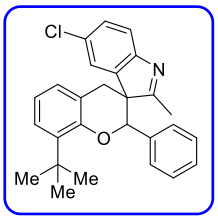


8-(tert-butyl)-5'-fluoro-2'-methyl-2-phenylspiro[chromane-3,3'-indole] (4x)



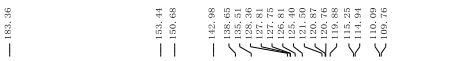


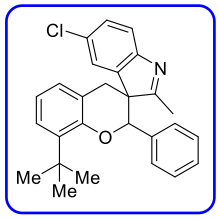
8-(tert-butyl)-5'-chloro-2'-methyl-2-phenylspiro[chromane-3,3'-indole] (4y)



4y

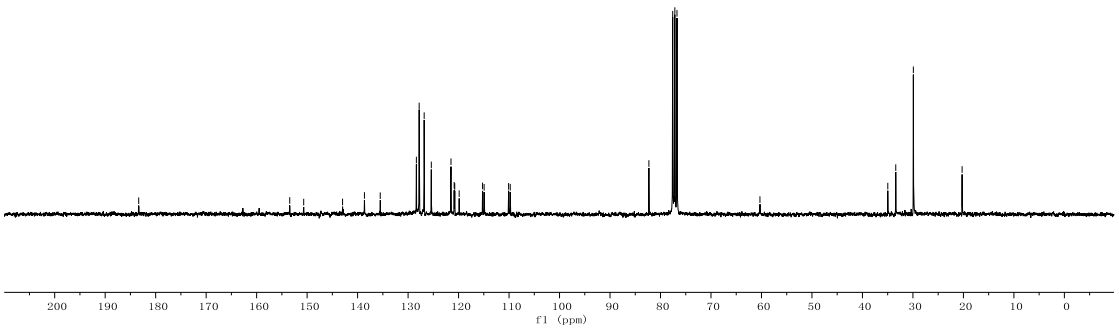
^{1}H NMR, 300 MHz, $CDCl_3$



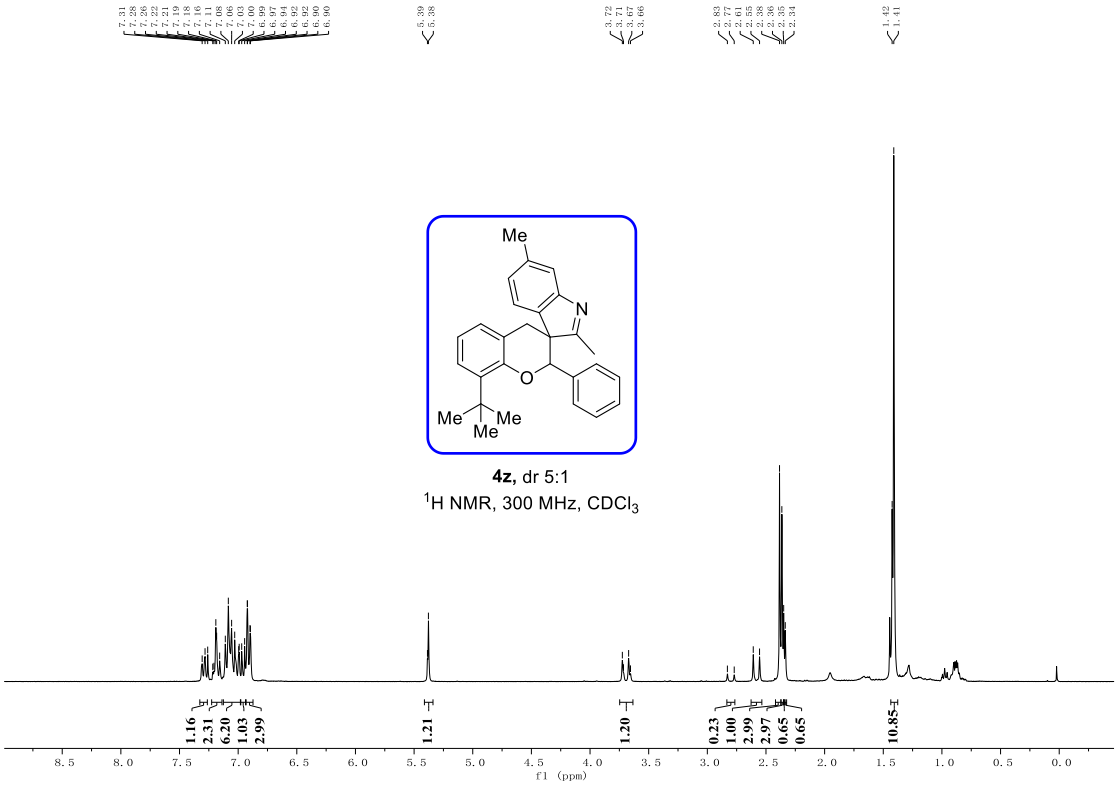


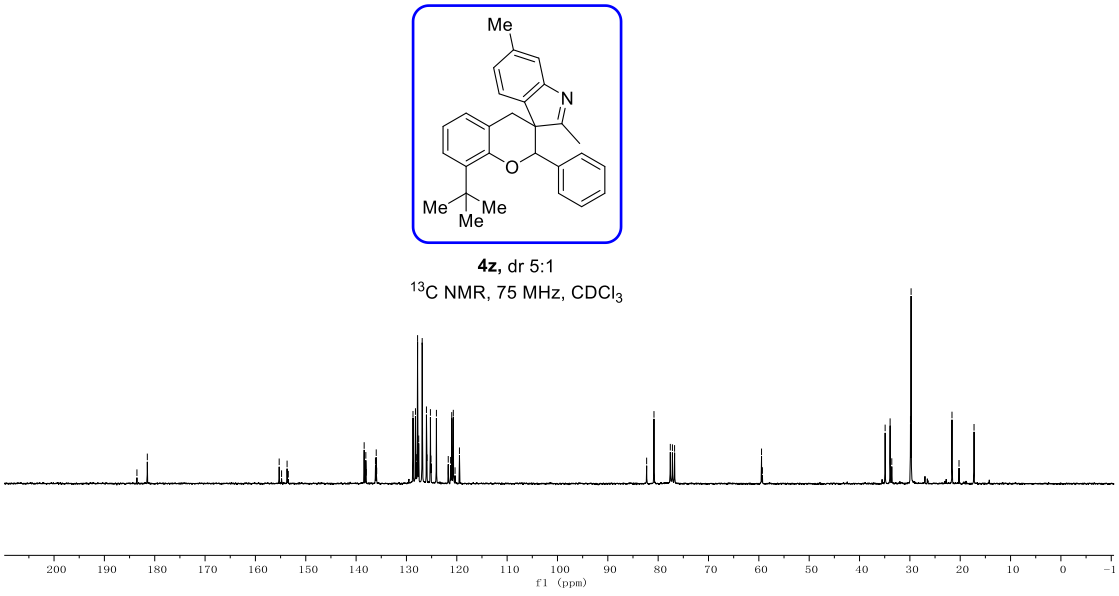
4y

^{13}C NMR, 75 MHz, $CDCl_3$

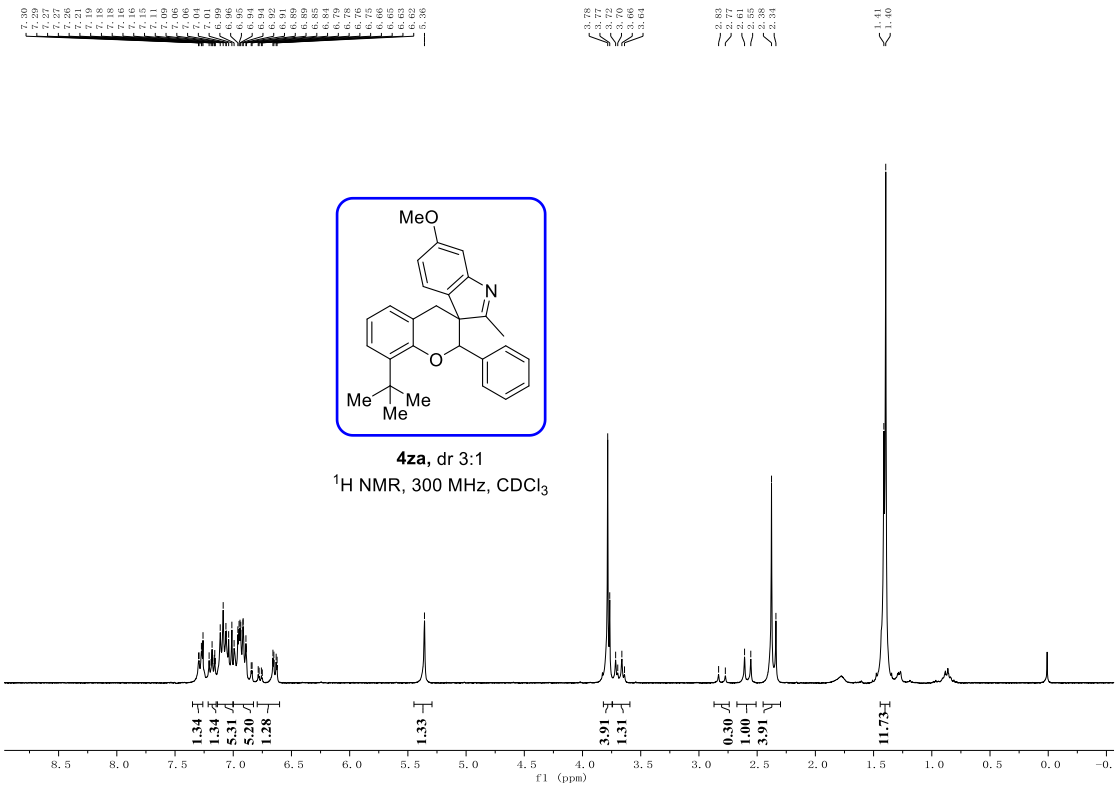


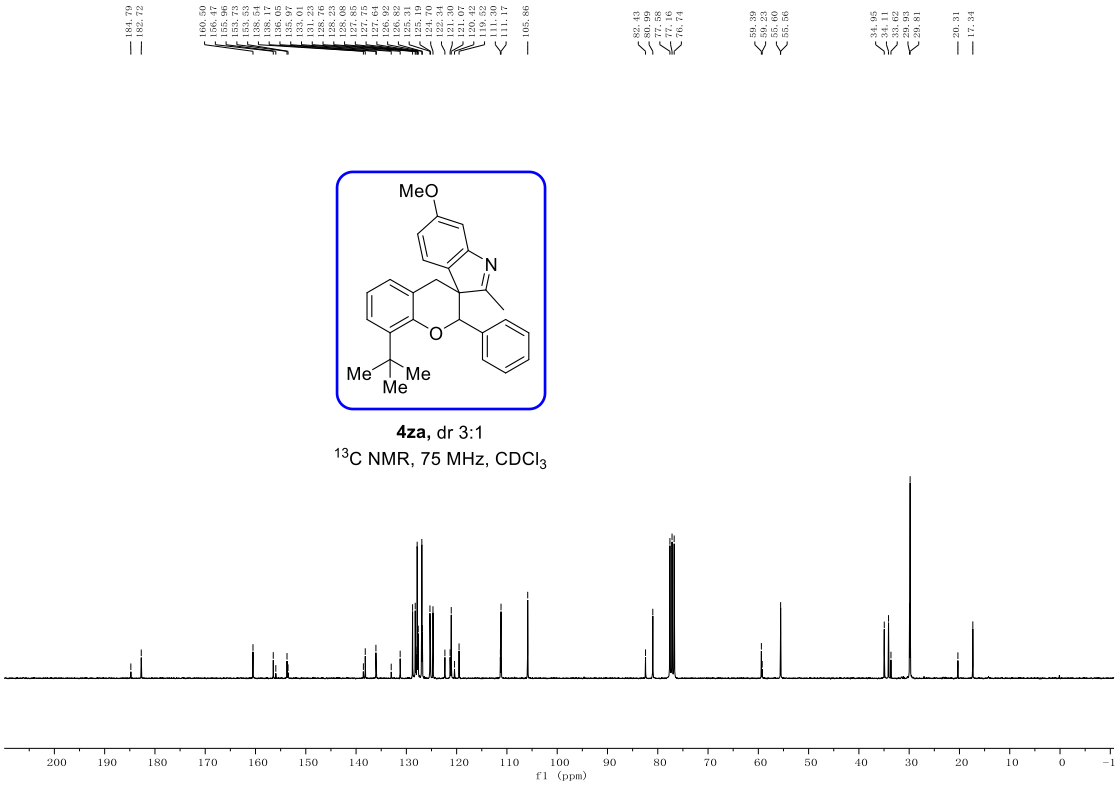
8-(tert-butyl)-2',6'-dimethyl-2-phenylspiro[chromane-3,3'-indole] (4z)



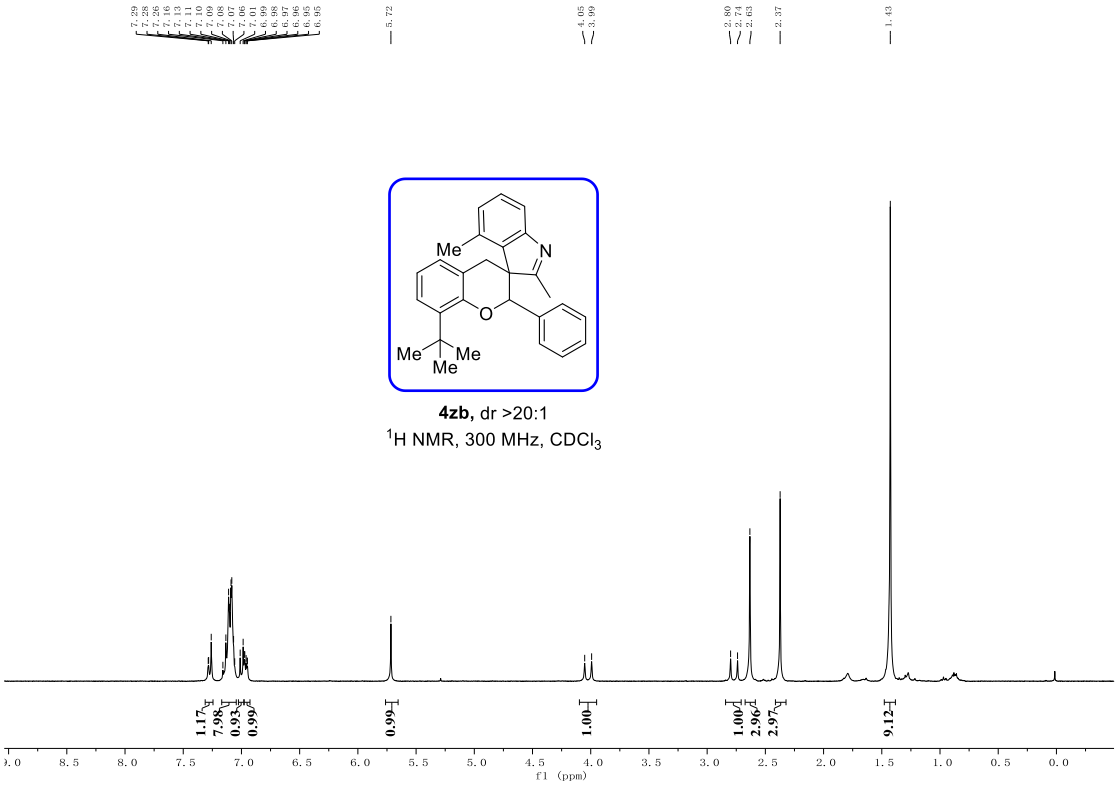


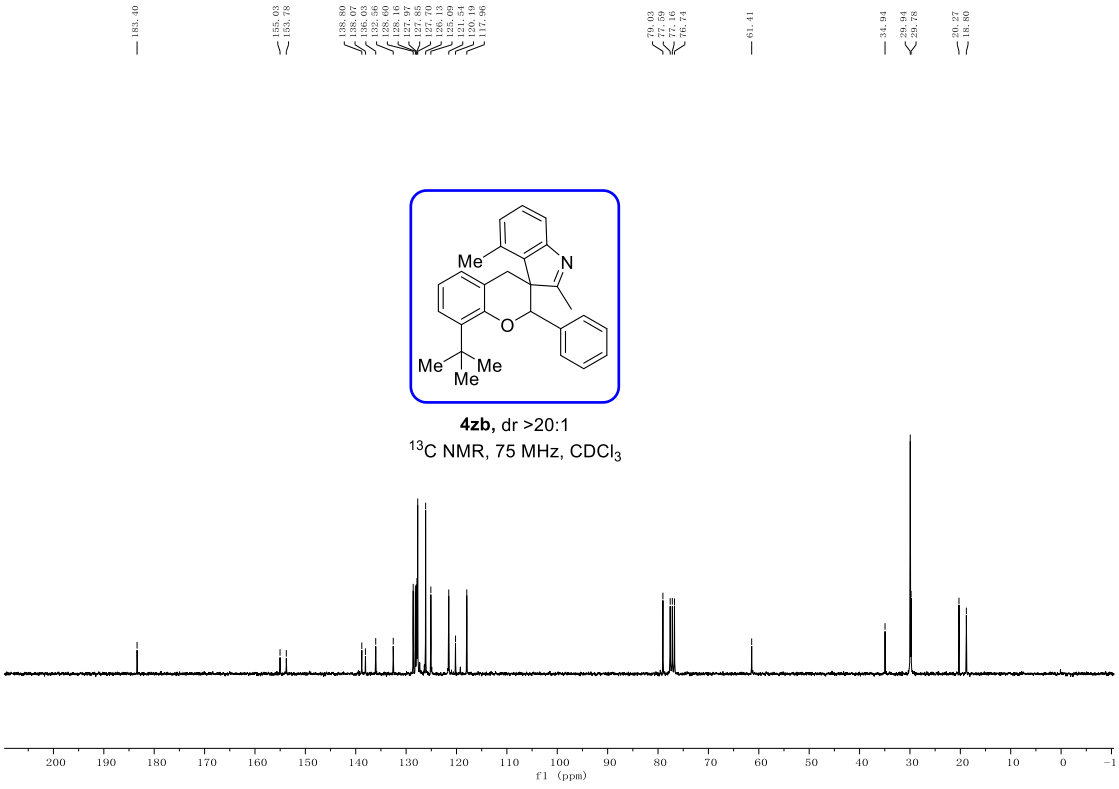
8-(tert-butyl)-6'-methoxy-2'-methyl-2-phenylspiro[chromane-3,3'-indole] (4za)



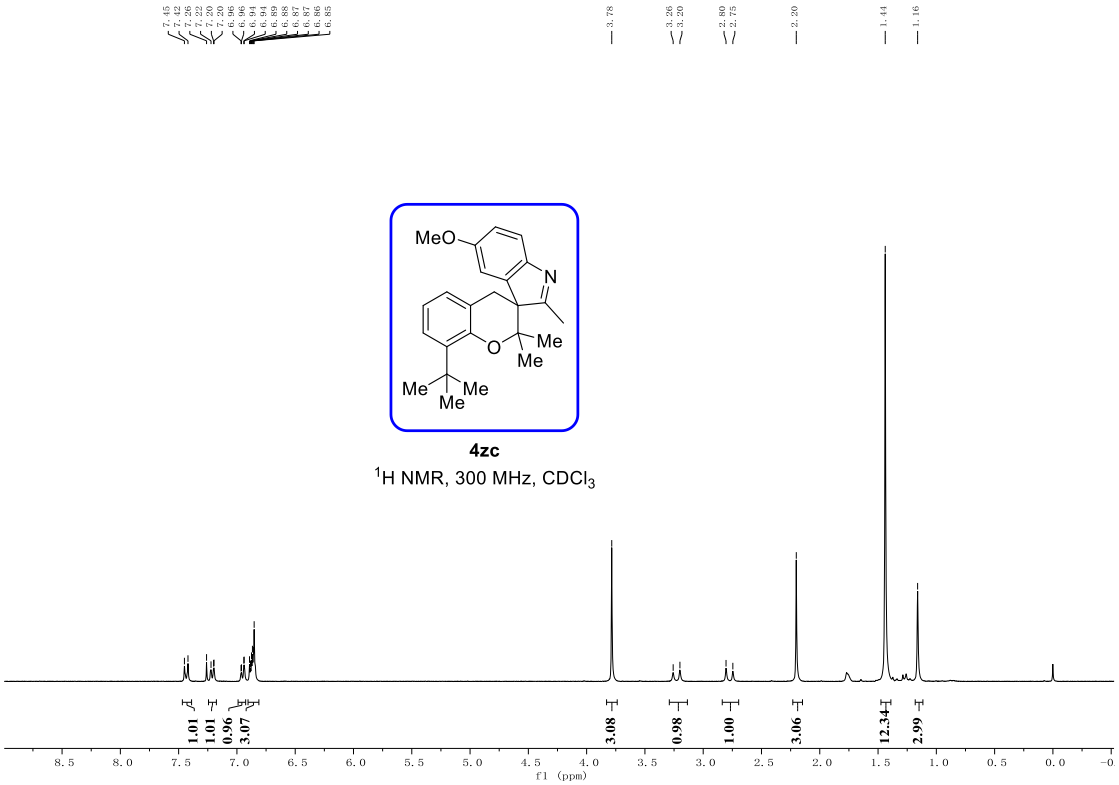


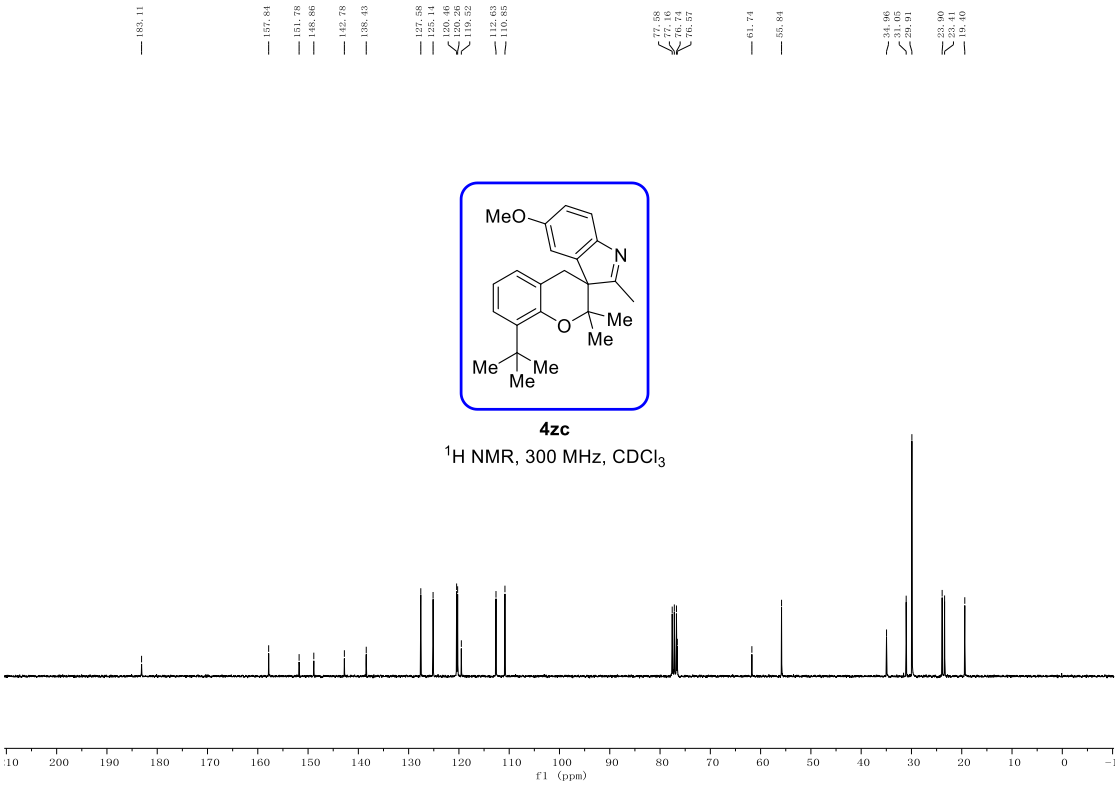
8-(tert-butyl)-2',4'-dimethyl-2-phenylspiro[chromane-3,3'-indole] (4zb)



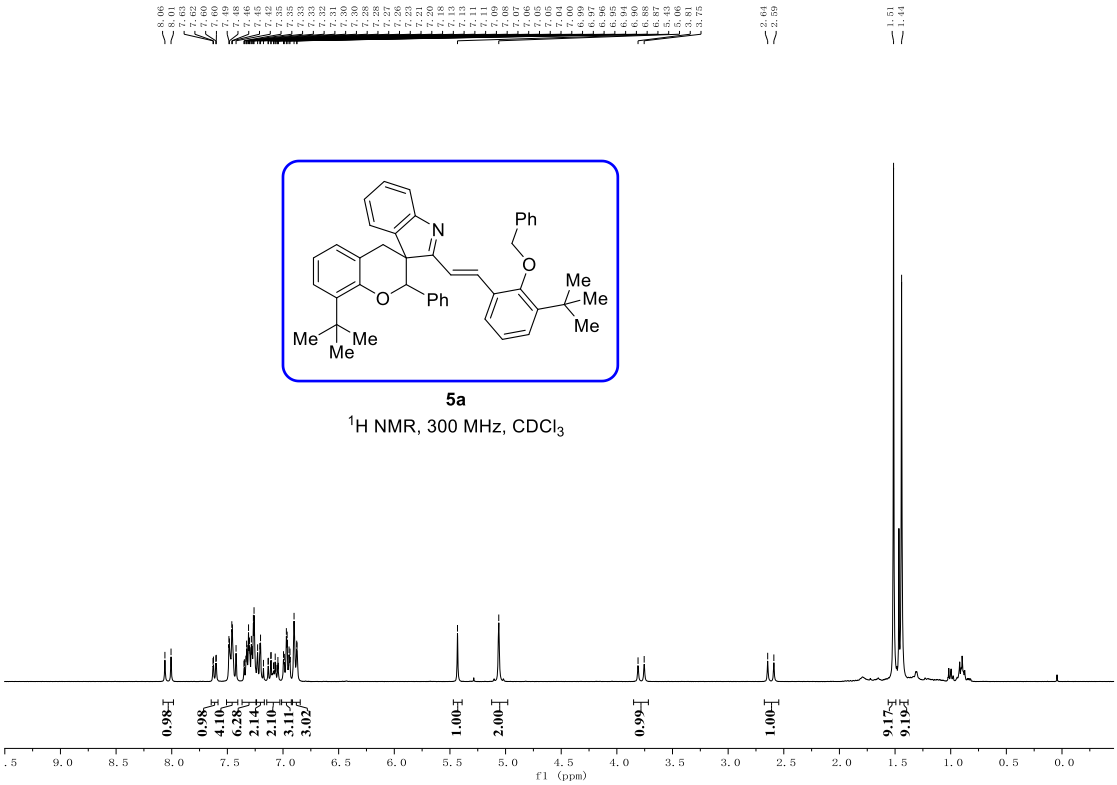


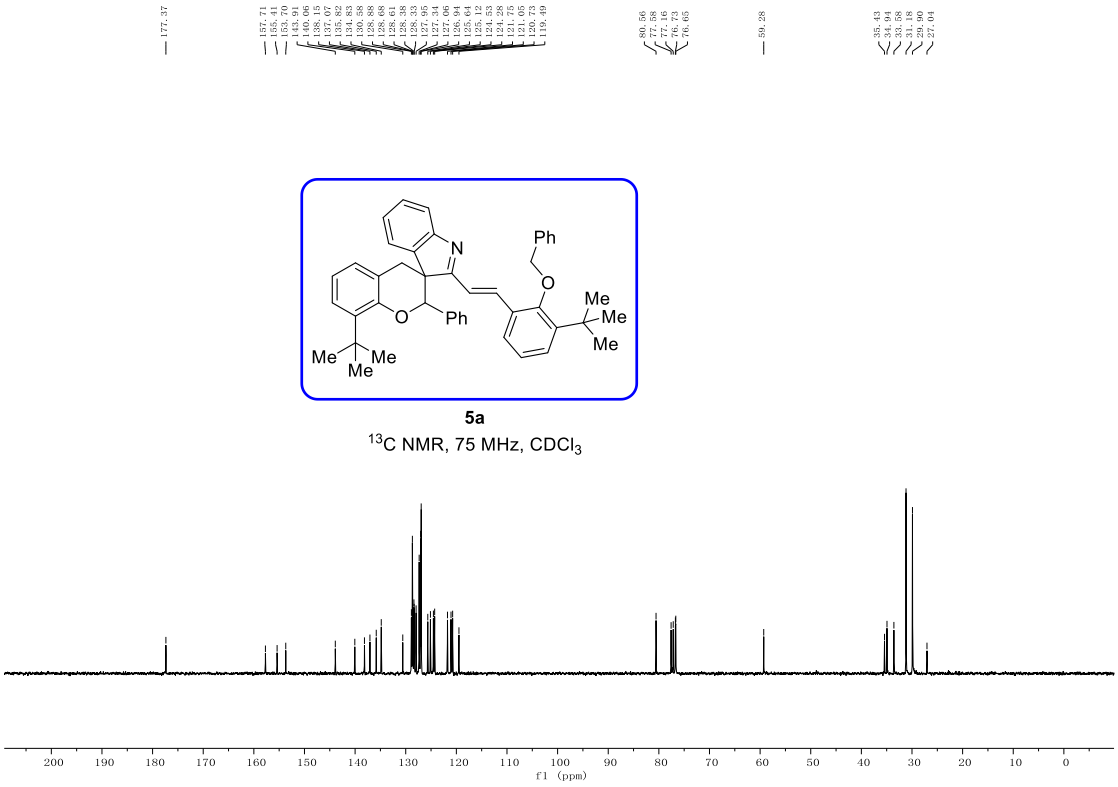
8-(tert-butyl)-5'-methoxy-2,2,2'-trimethylspiro[chromane-3,3'-indole](4zc)



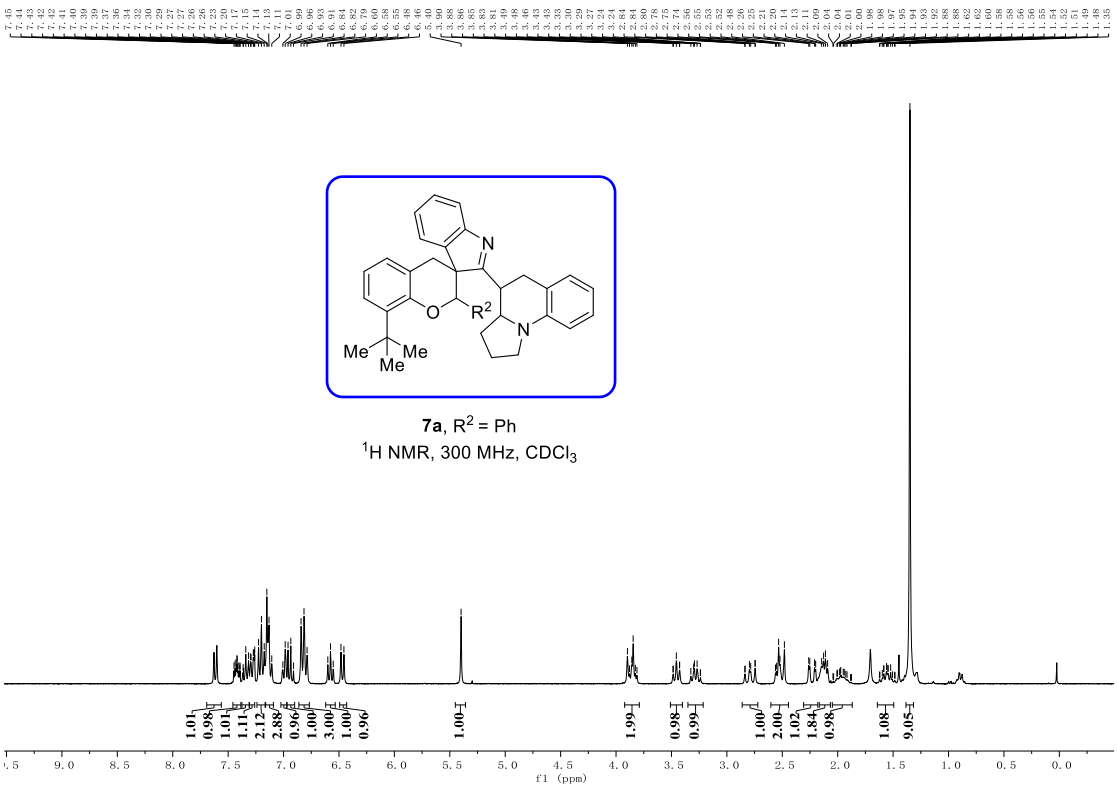


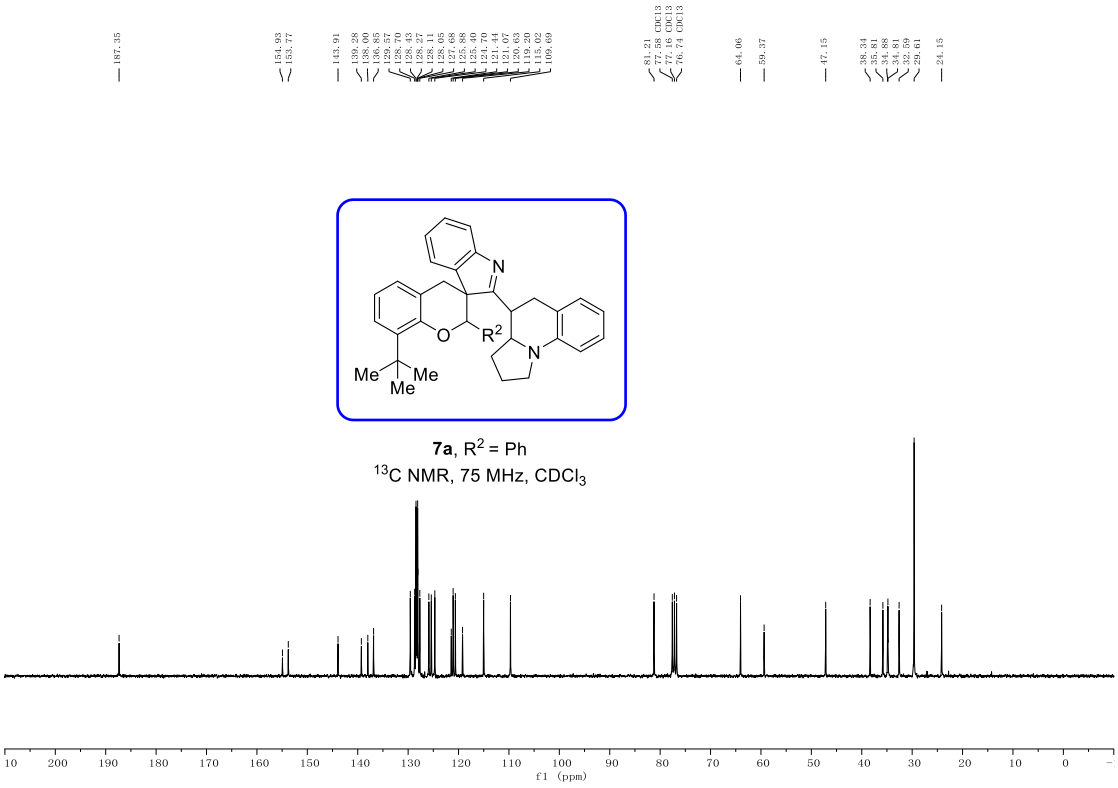
(E)-2'-(2-(benzyloxy)-3-(tert-butyl)styryl)-8-(tert-butyl)-2-phenylspiro[chromane-3,3'-indole] (5a)



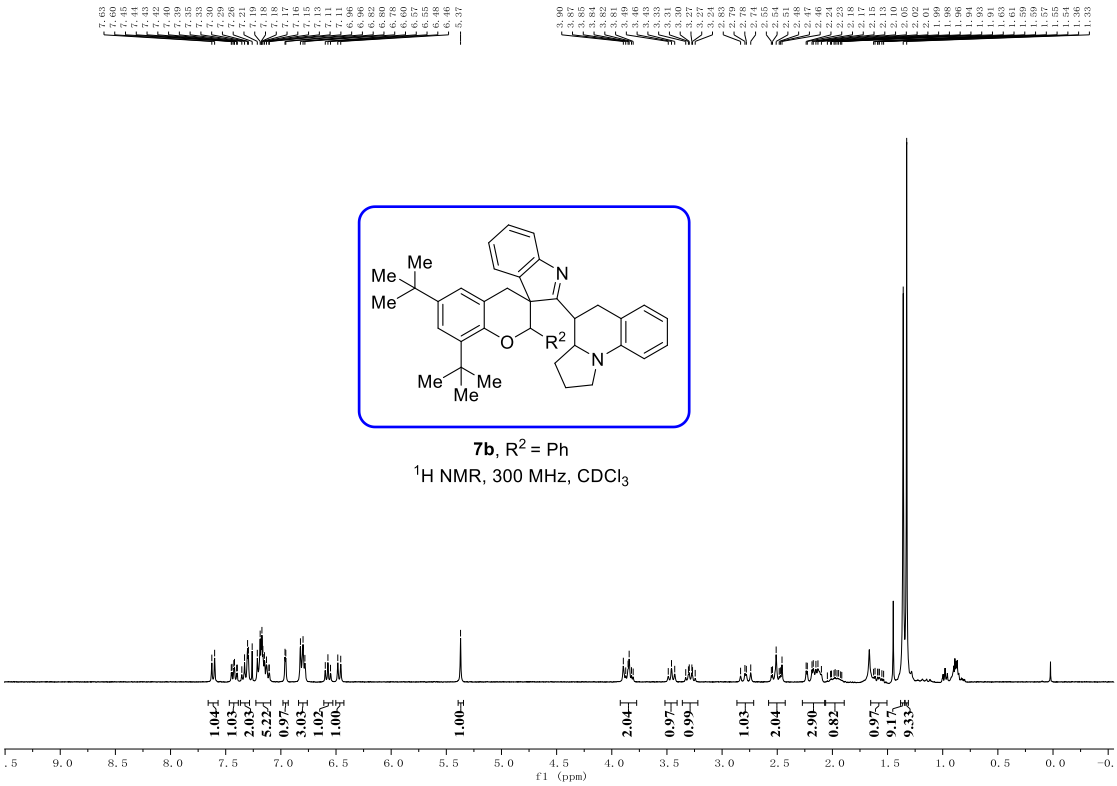


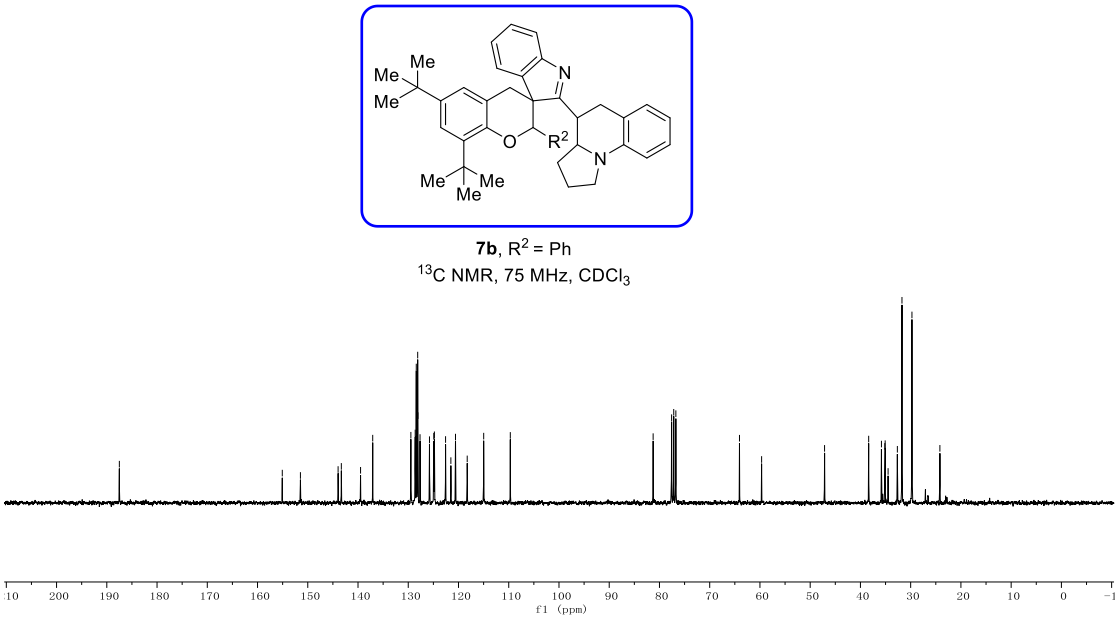
8-(tert-butyl)-2'-(1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)-2-phenylspiro[chromane-3,3'-indole] (7a)



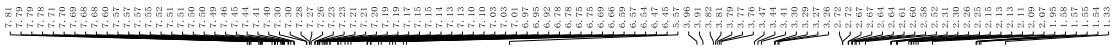


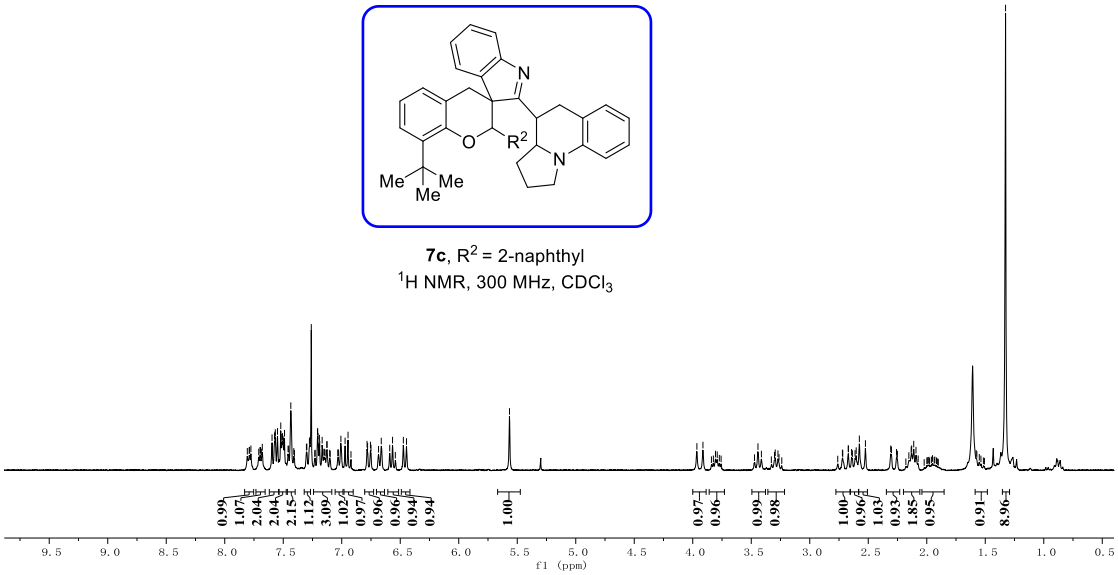
6,8-di-tert-butyl-2'-(1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)-2-phenylspiro[chromane-3,3'-indole] (7b)



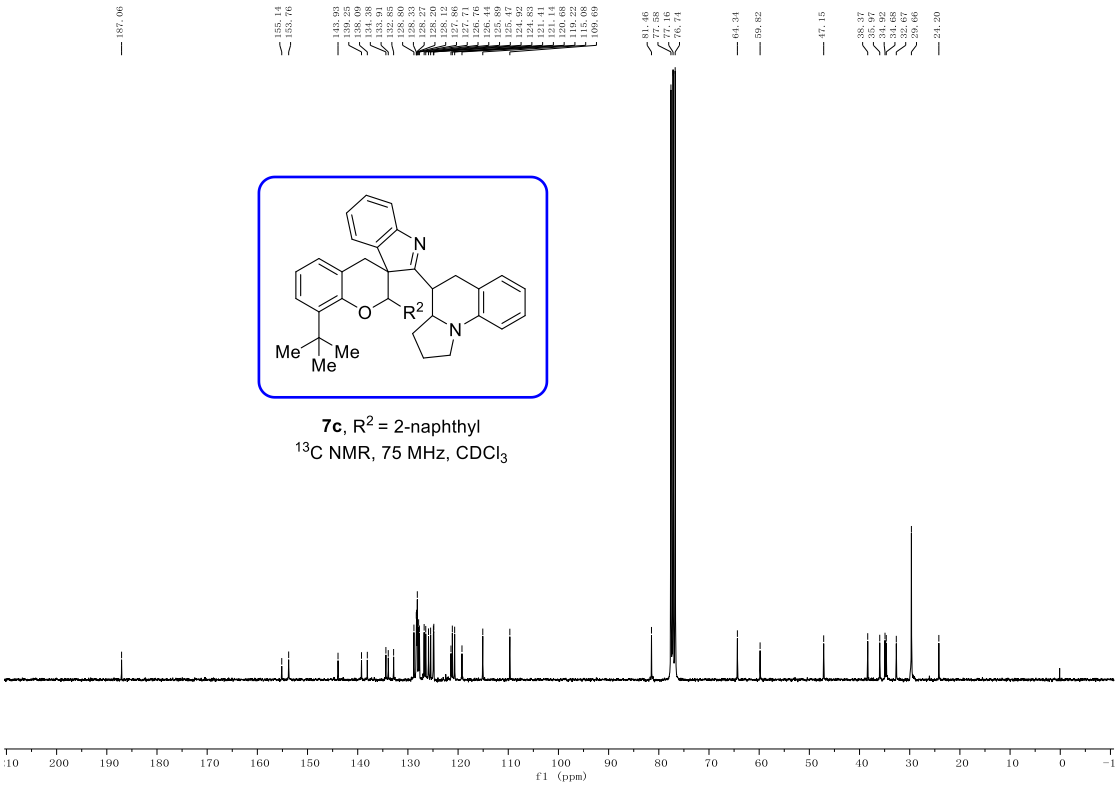


8-(tert-butyl)-2'-(1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)-2-(naphthalen-2-yl)spiro [chromane-3,3'-indole] (7c)



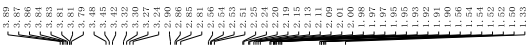


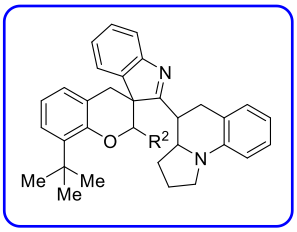
7c, R^2 = 2-naphthyl
^{1}H NMR, 300 MHz, $CDCl_3$



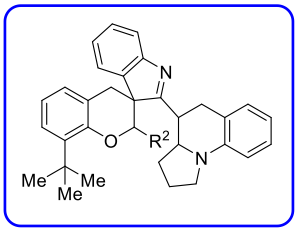
7c, R^2 = 2-naphthyl
^{13}C NMR, 75 MHz, $CDCl_3$

8-(tert-butyl)-2'-(1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)-2-(4-(trifluoromethyl)phenyl) spiro[chromane-3,3'-indole] (7d)

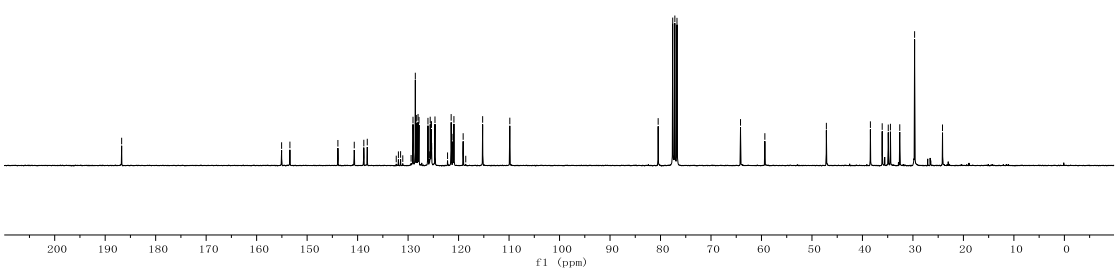




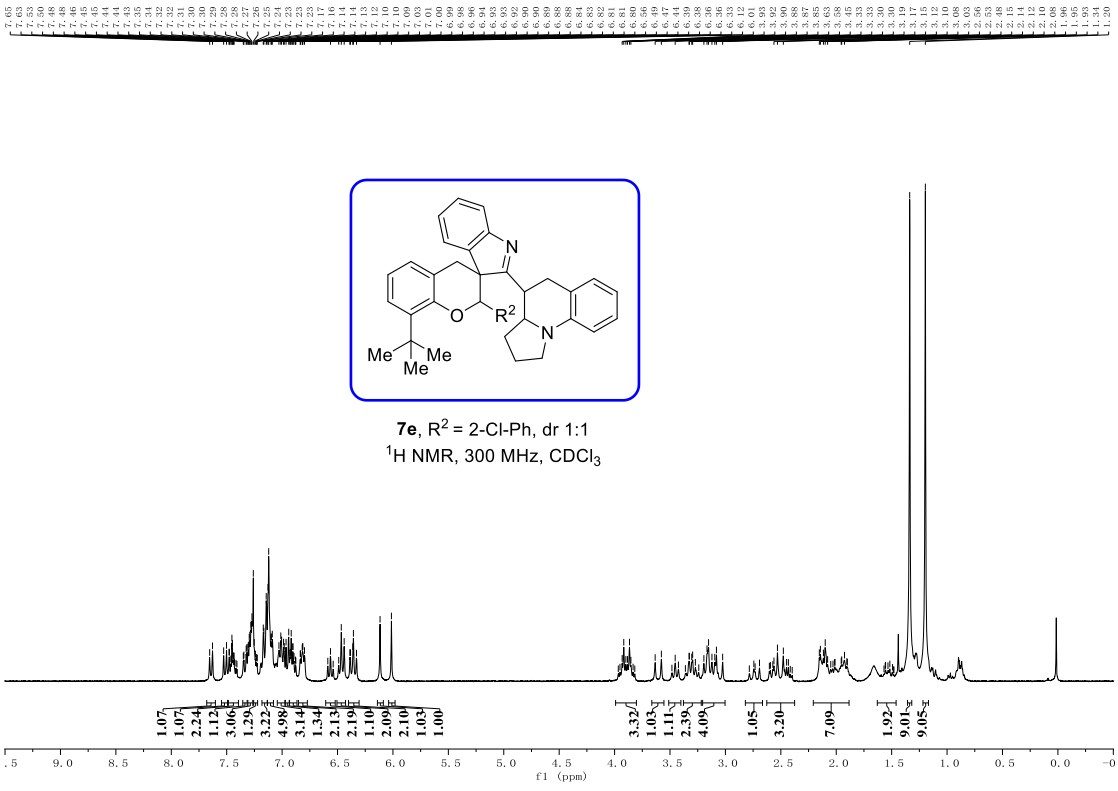
7d, R^2 = 4-CF_3-Ph
^{1}H NMR, 300 MHz, $CDCl_3$

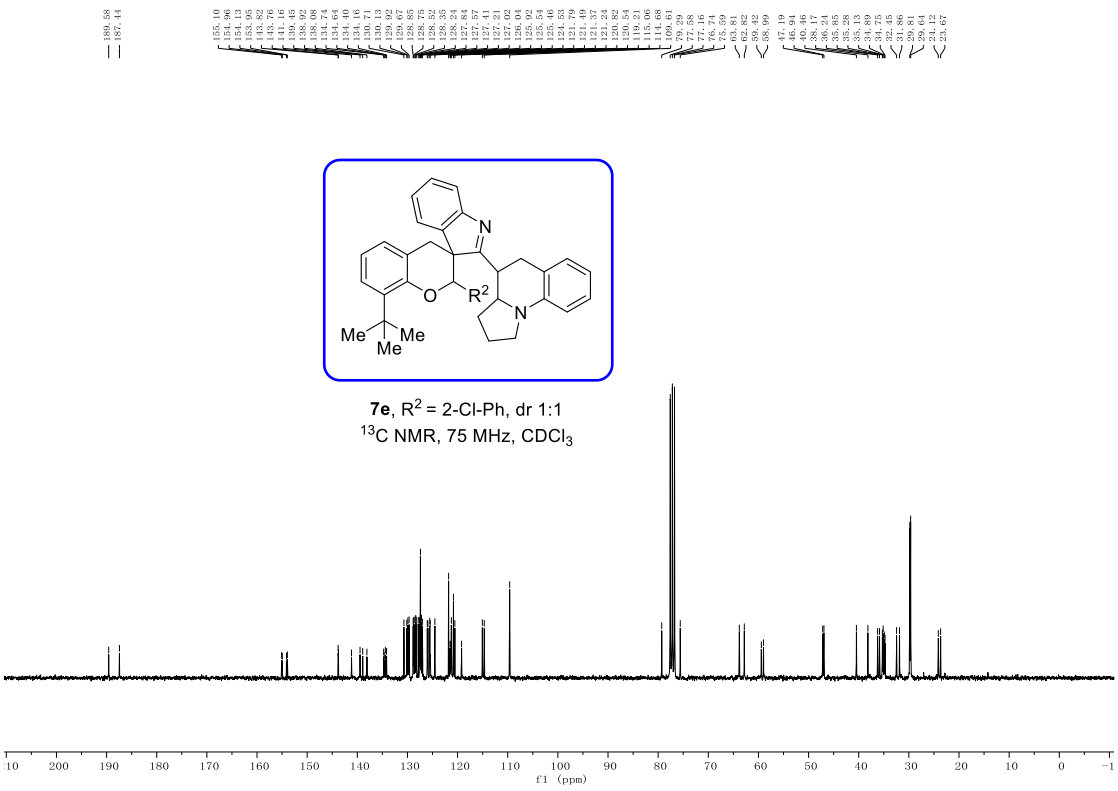


7d, R^2 = 4-CF_3-Ph
^{13}C NMR, 75 MHz, $CDCl_3$

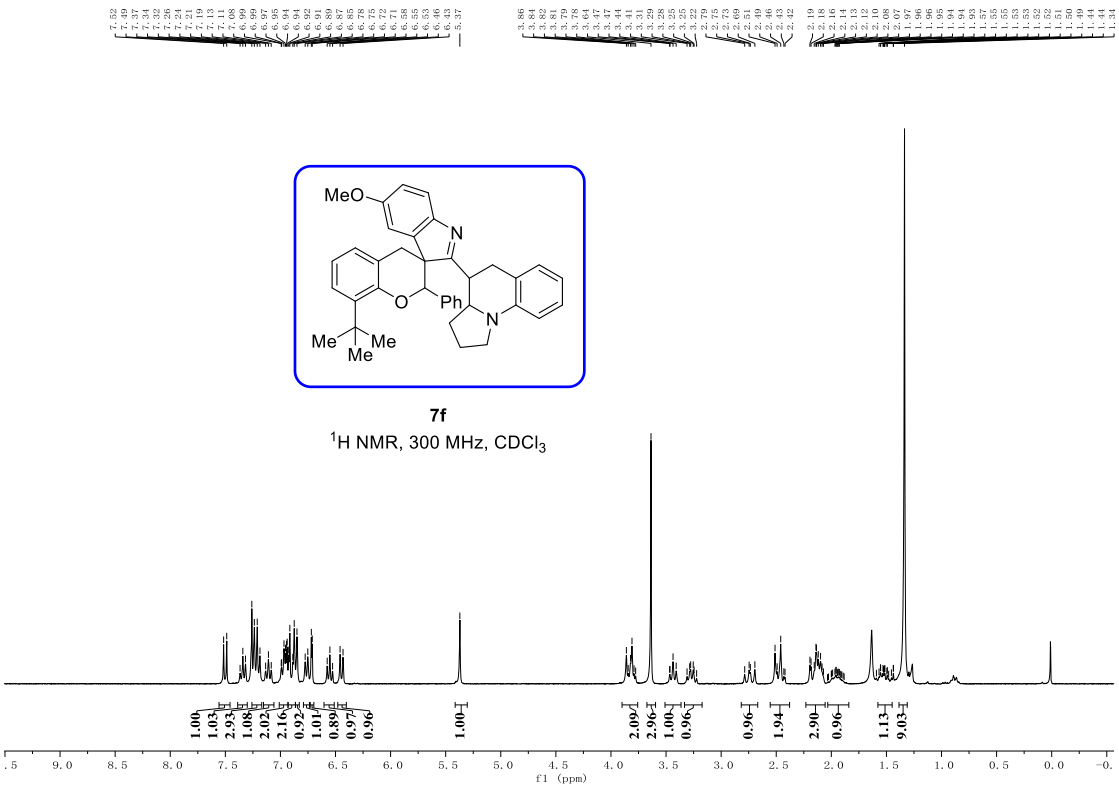


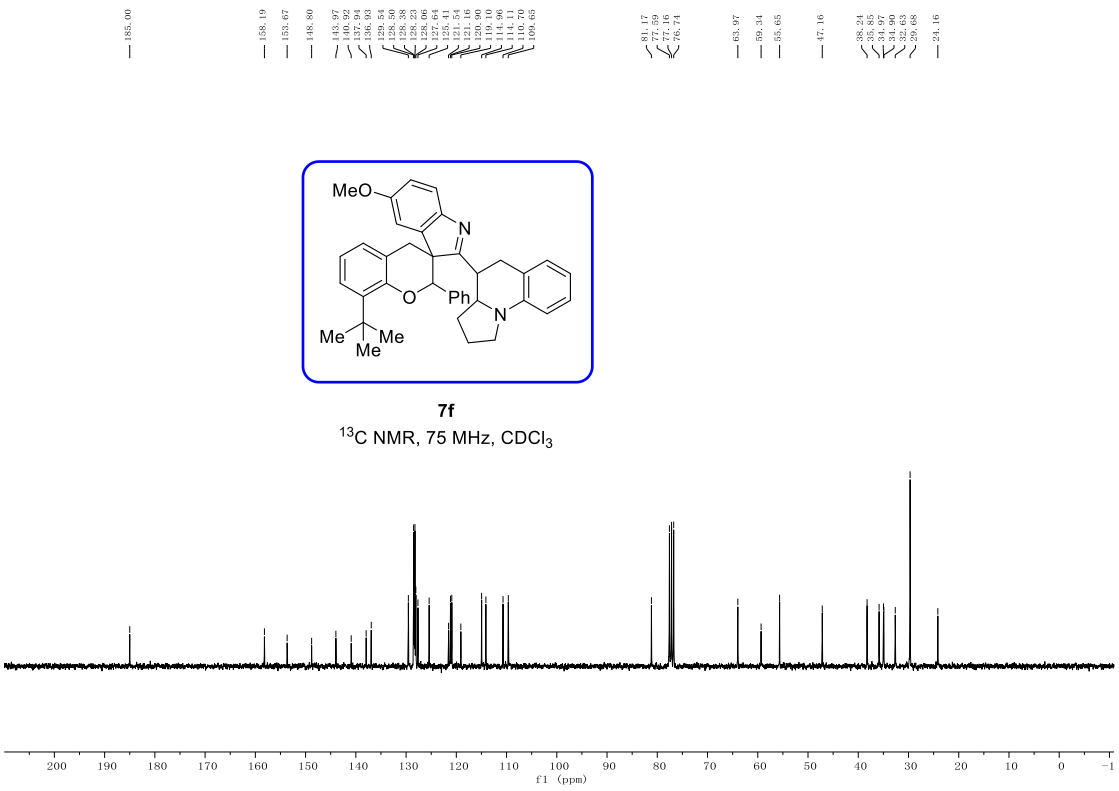
8-(tert-butyl)-2-(2-chlorophenyl)-2'-(1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)spiro [chromane-3,3'-indole] (7e)



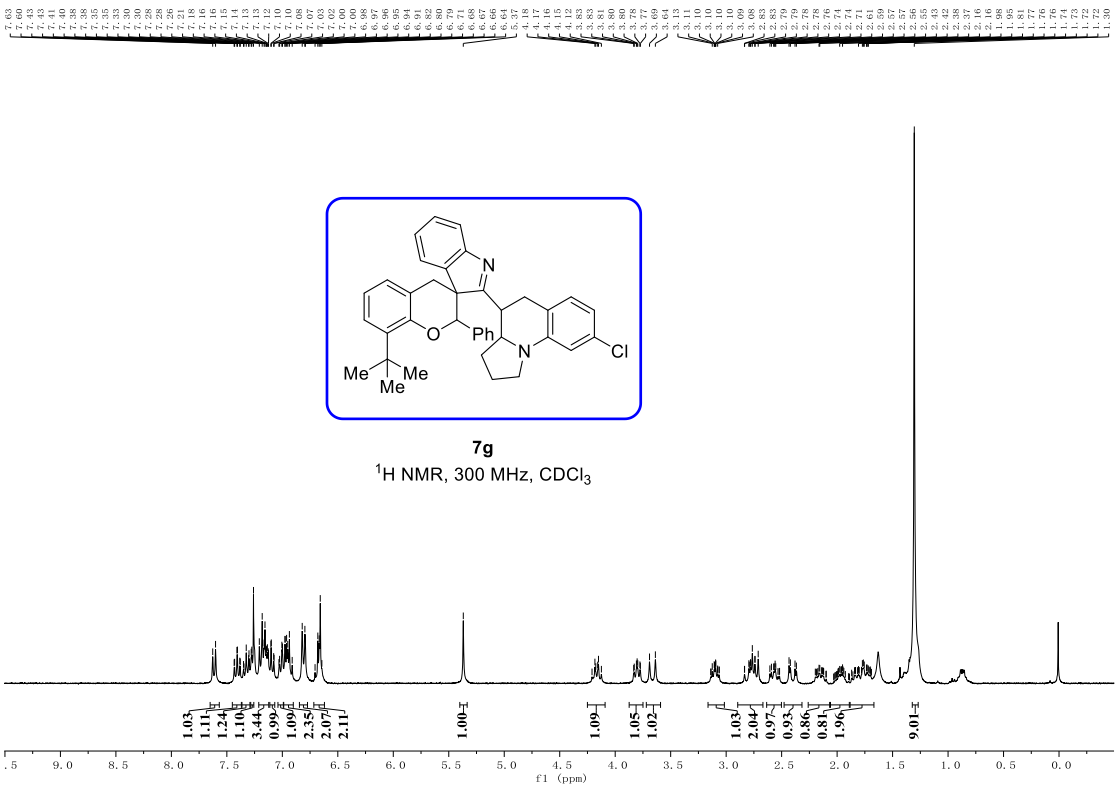


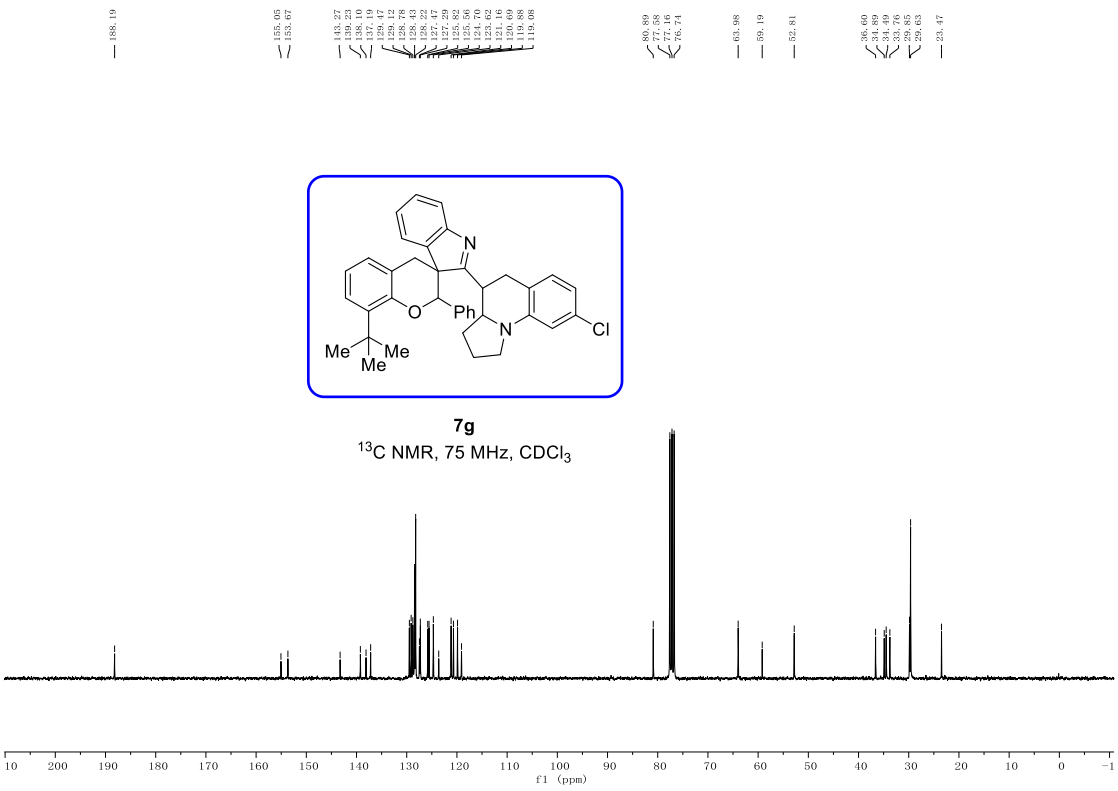
8-(tert-butyl)-2'-(1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)-5'-methoxy-2-phenylspiro [chromane-3,3'-indole] (7f)



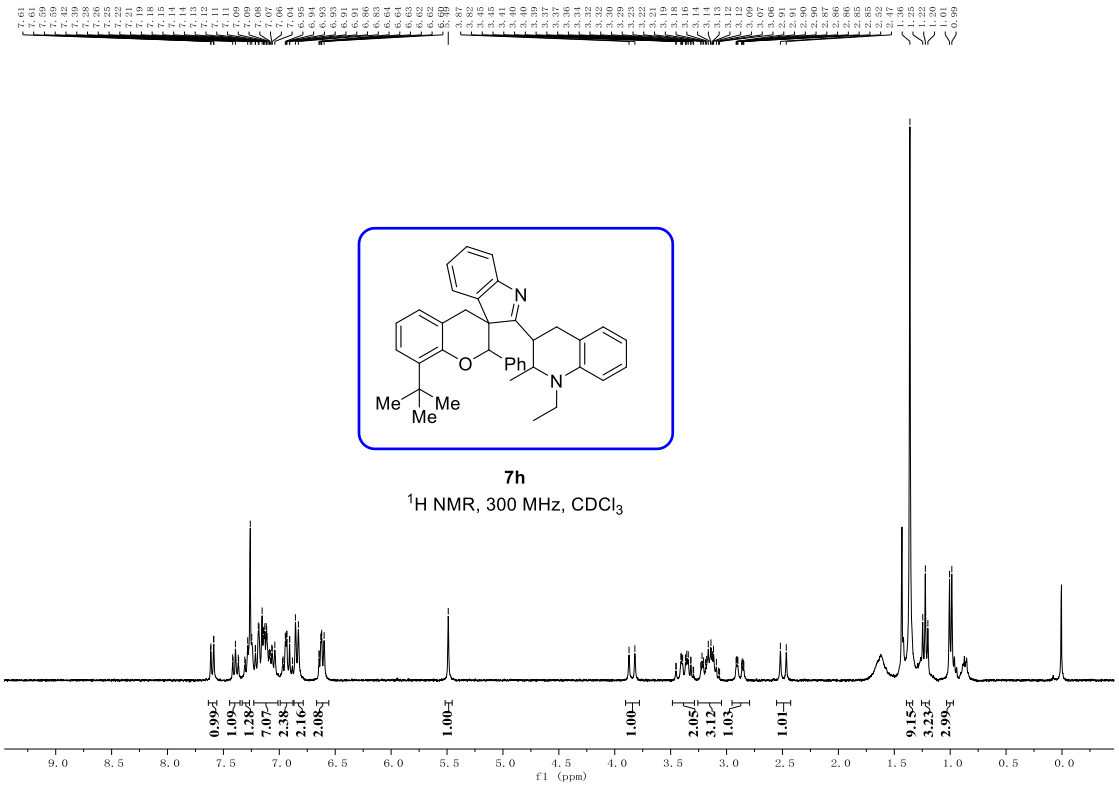


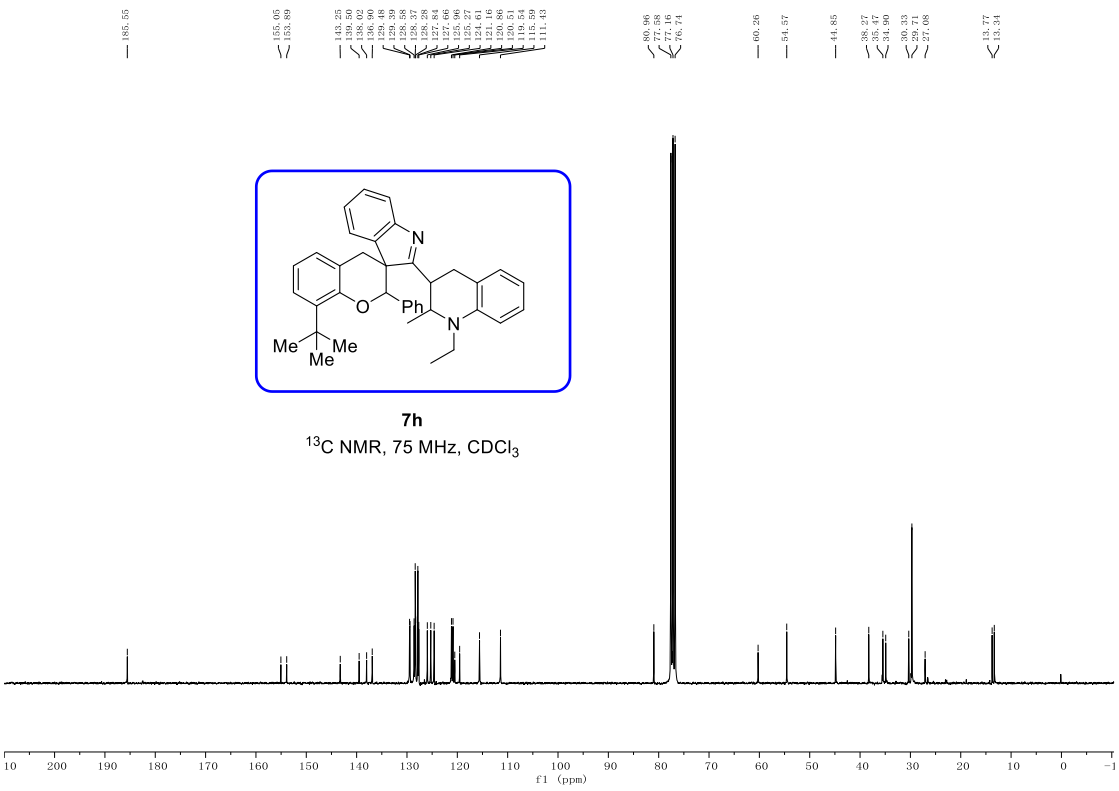
8-(tert-butyl)-2'-(8-chloro-1,2,3,3a,4,5-hexahydropyrrolo[1,2-a]quinolin-4-yl)-2-phenylspiro [chromane-3,3'-indole] (7g)



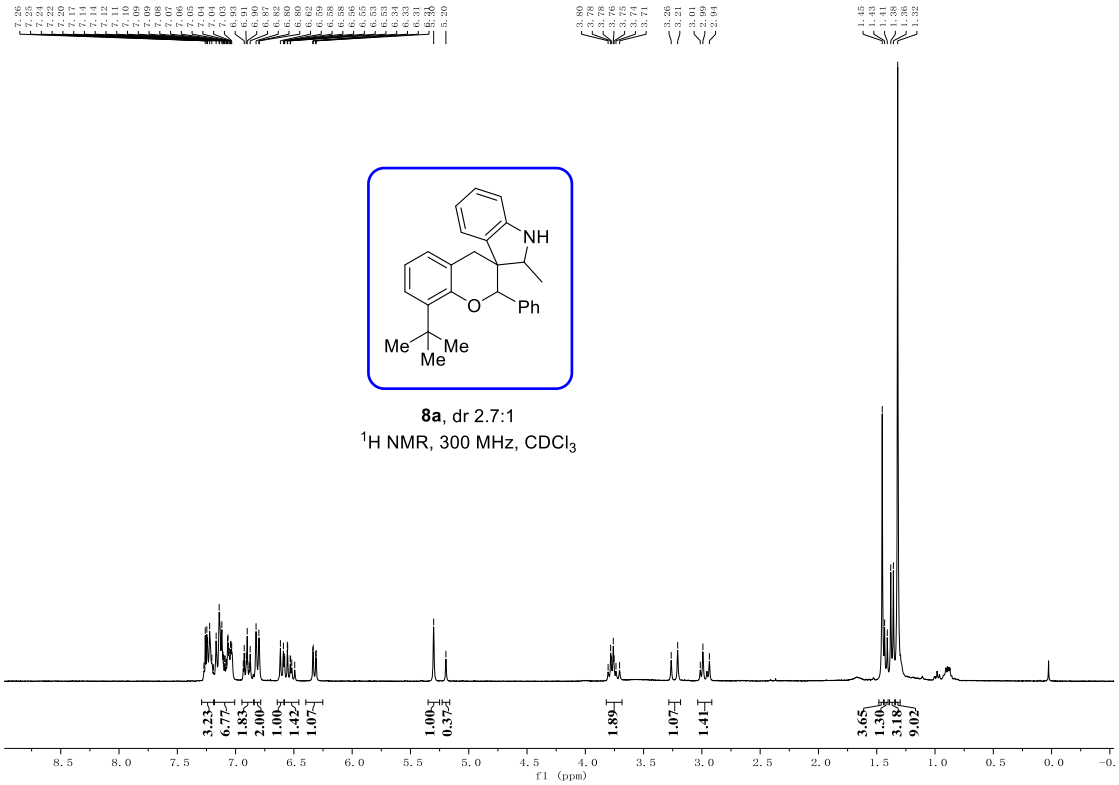


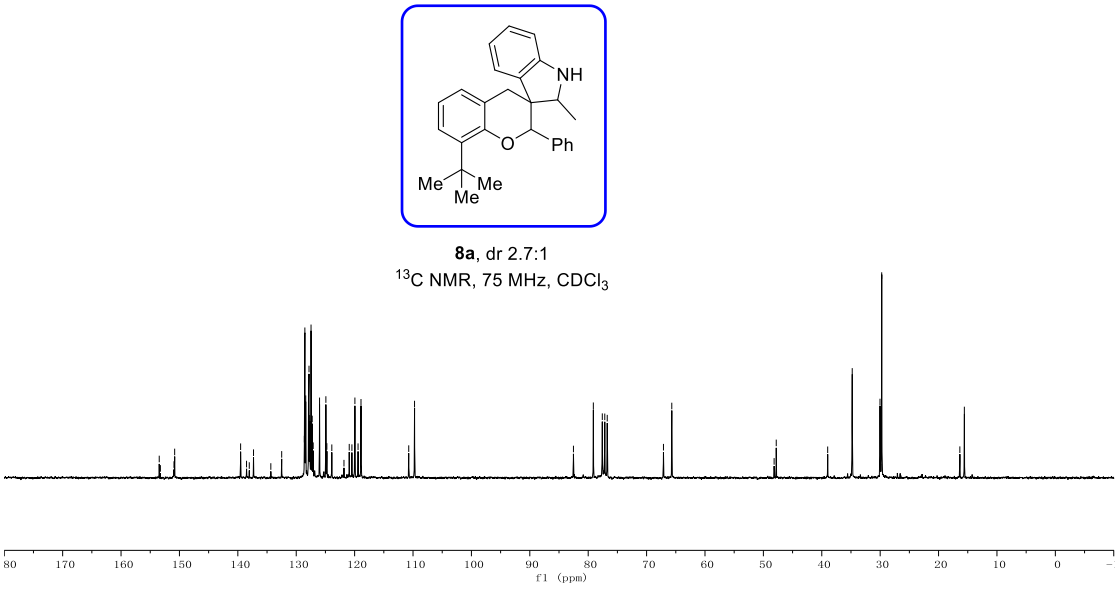
8-(tert-butyl)-2'-(1-ethyl-2-methyl-1,2,3,4-tetrahydroquinolin-3-yl)-2-phenylspiro[chromane-3,3'-indole] (7h)



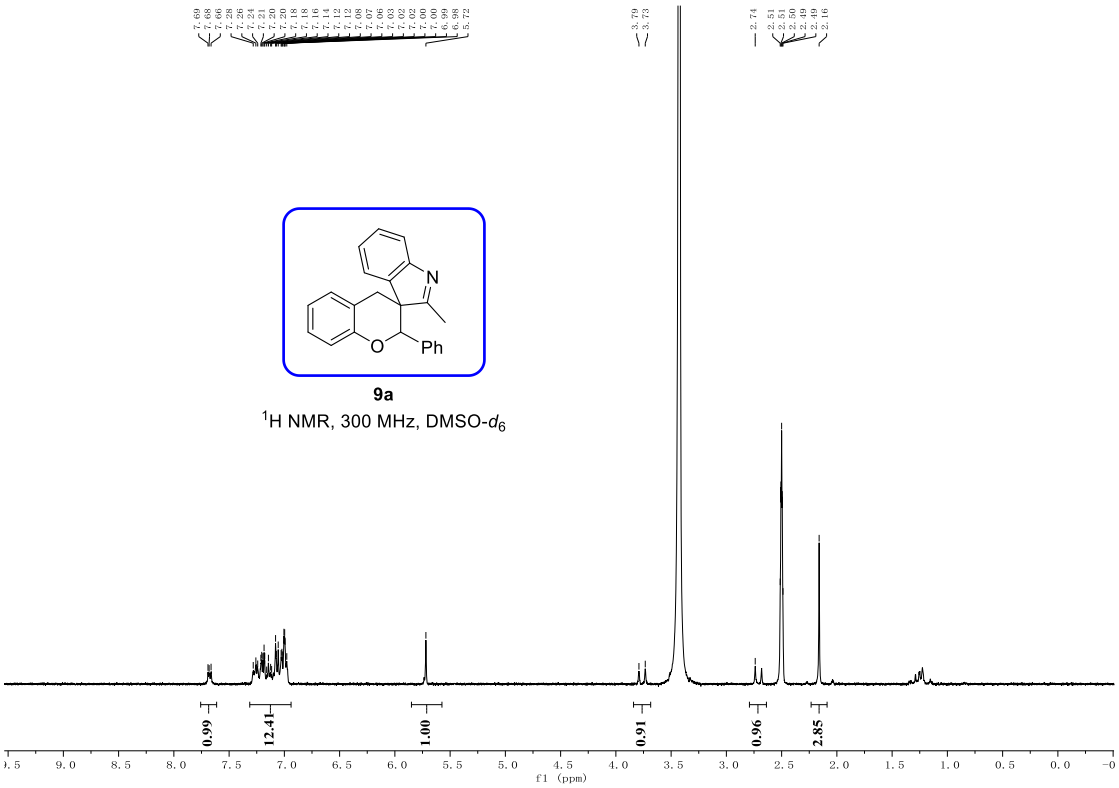


8-(tert-butyl)-2'-methyl-2-phenylspiro[chromane-3,3'-indoline] (8a)



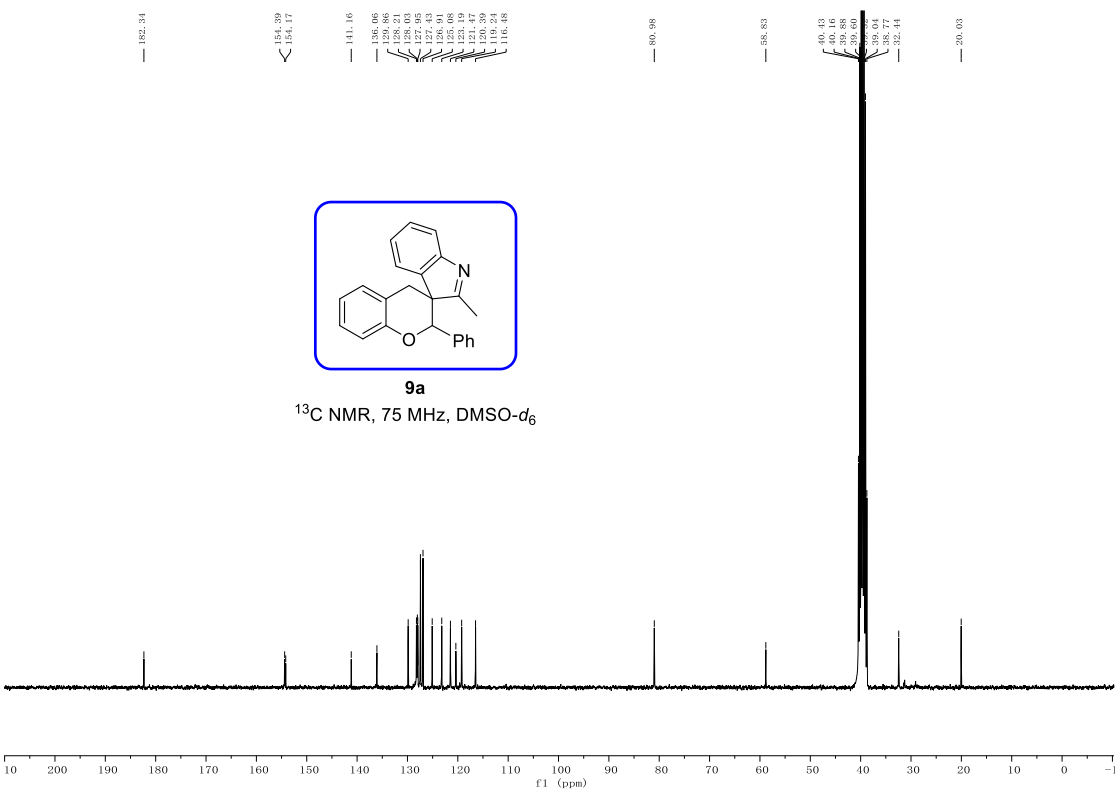


2'-methyl-2-phenylspiro[chromane-3,3'-indole] (9a)



9a

^{1}H NMR, 300 MHz, DMSO-d_6



9a

^{13}C NMR, 75 MHz, DMSO-d_6