Electronic Supplementary Information for:

Palladium-catalyzed alkyne hydrocarbonylation at atmospheric pressure of carbon monoxide in the presence of hydrosilane †

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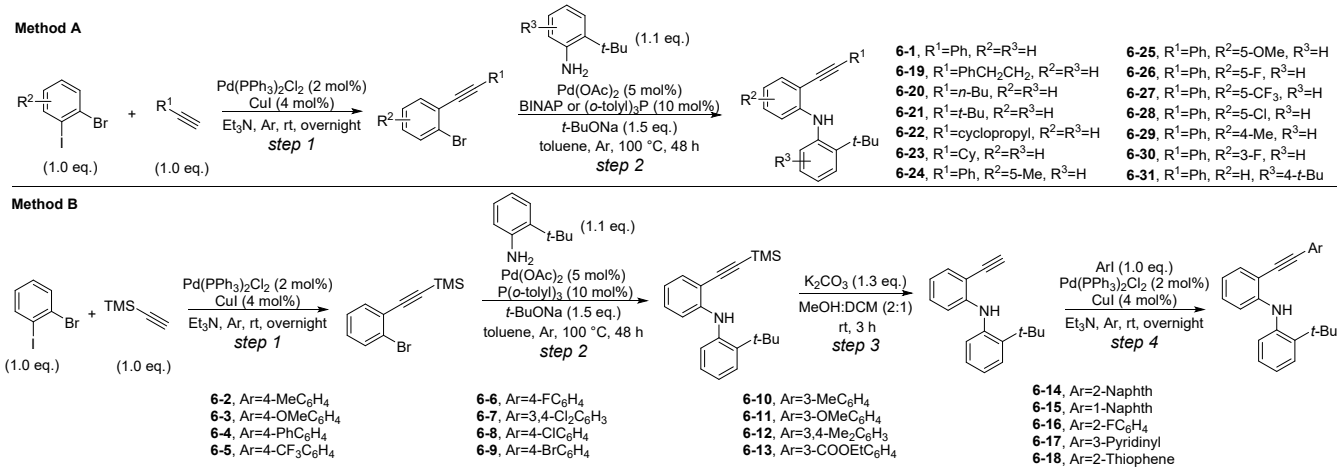
1. General Considerations

Unless otherwise noted, all chemicals were purchased from commercial suppliers and used without further purification. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded at ambient temperature in $CDCl_3$ on 500 MHz Bruker FT-NMR spectrometers. Chemical shifts were given as δ value (ppm), and the data are reported as follows: ^{1}H NMR shifts were referenced to $CDCl_3$ at 7.26 ppm, ^{13}C NMR shifts were referenced to $CDCl_3$ at 77.16 ppm. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. The coupling constants *J* were given in Hertz. Column chromatography was performed using EM silica gel 60 (100−200 mesh). Mass spectroscopy data of the products were collected on ABsciex5600plusQTOF HR mass spectrometer equipped with an ESI source. High pressure liquid chromatography (HPLC condition) analyses were performed on a Shimadzu instrument using a chiral stationary phase column (Daicel Co. CHIRALPAK or FLM Co. MX(2)). The chiral HPLC condition methods were calibrated with the corresponding racemic mixtures.

Caution: CO gas is highly toxic and all operations are performed in a well-ventilated fume hood.

2. Experimental Procedures and Characterization

2.1 Preparation of Substrates 6 and Characterization



Method A:[1]

step 1: To a solution of $Pd(PPh_3)_2Cl_2$ (42 mg, 0.06 mmol, 2 mol%) and CuI (23 mg, 0.12 mmol, 4 mol%) in Et_3N (6 mL) were added 2-bromo-iodobenzene (3 mmol) and phenylacetylene (3 mmol). After being stirred at rt overnight under Ar, the mixture was quenched with NH_4Cl aq and extracted with DCM (20 mL × 3). Then, the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane) to give 1-bromo-2-phenylethynylbenzene.

step 2: To a solution of $Pd(OAc)_2$ (28 mg, 0.125 mmol, 5 mol%), BINAP (155 mg, 0.25 mmol, 10 mol%) or P(*o*-tolyl)$_3$ (76 mg, 0.25 mmol, 10 mol%), *t*-BuONa (360 mg, 3.75 mmol, 1.5 eq.) in dry toluene (8 mL) were added 1-bromo-2-phenylethynylbenzene (2.5 mmol) and 2-*tert*-butylaniline (428 µL, 2.75 mmol, 1.1 eq.). After being stirred at 100 °C for 48 h under Ar, the mixture was quenched with $NaHCO_3$ aq and extracted with EtOAc (20 mL × 3). Then, the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc) to give **6**.

Method B:[1]

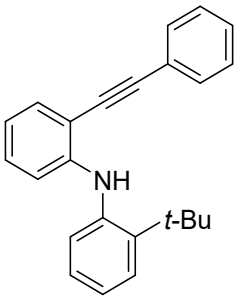
step 1: Same as method A, step 1.

step 2: Same as method A, step 2.

step 3: To a solution of 2-*tert*-butyl-*N*-(2-(trimethylsilylethynyl)phenyl)aniline (2.9 g, 9 mmol) in DCM (3 mL) and CH_3OH (6 mL) was added K_2CO_3 (1.6 g, 11.7 mmol, 1.3 eq.). After being stirred at rt for 3 h, the mixture was quenched with water and extracted with DCM (50 mL × 3). Then, the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane) to give 2-*tert*-butyl-*N*-(2-(ethynyl)phenyl)aniline (1.9 g, 85 % yield).

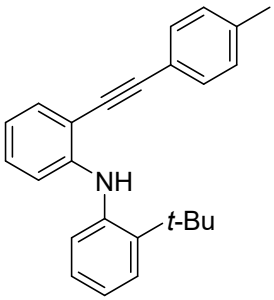
step 4: Same as method A, step 1.

Characterization of Substrates 6



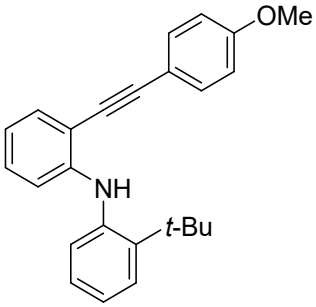
2-(*tert*-butyl)-*N*-(2-(phenylethynyl)phenyl)aniline (**6-1**)

Pale yellow solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.51 – 7.46 (m, 2H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.38 – 7.30 (m, 3H), 7.27 – 7.20 (m, 1H), 7.19 – 7.12 (m, 2H), 6.87 (d, *J* = 8.1 Hz, 1H), 6.80 – 6.71 (m, 1H), 6.55 (s, 1H), 1.48 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.0, 144.4, 139.7, 132.3, 131.3, 129.6, 128.4, 128.3, 127.2, 126.9, 126.8, 124.8, 123.1, 117.7, 111.9, 108.5, 95.2, 86.2, 34.9, 30.6.



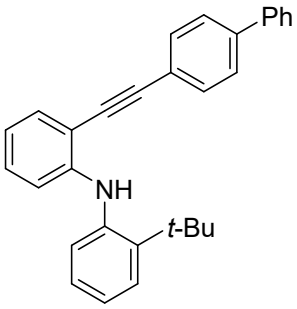
2-(*tert*-butyl)-*N*-(2-(*p*-tolylethynyl)phenyl)aniline (**6-2**)

Pale yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.46 (ddd, *J* = 7.7, 3.3, 1.6 Hz, 2H), 7.42 – 7.36 (m, 3H), 7.22 (td, *J* = 7.5, 1.5 Hz, 1H), 7.18 – 7.09 (m, 4H), 6.83 (d, *J* = 8.3 Hz, 1H), 6.73 (td, *J* = 7.5, 1.1 Hz, 1H), 6.52 (s, 1H), 2.37 (s, 3H), 1.45 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 146.9, 144.4, 139.8, 138.4, 132.2, 131.3, 129.4, 129.2, 127.2, 126.9, 126.8, 124.7, 120.1, 117.7, 111.9, 108.9, 95.4, 85.5, 34.9, 30.6, 21.5.



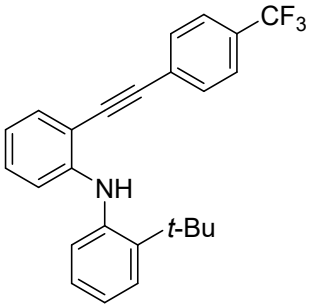
2-(*tert*-butyl)-*N*-(2-((4-methoxyphenyl)ethynyl)phenyl)aniline (**6-3**)

Brown oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.47 (ddd, *J* = 8.8, 6.2, 2.0 Hz, 4H), 7.40 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.26 – 7.20 (m, 1H), 7.14 (qd, *J* = 7.3, 3.2 Hz, 2H), 6.92 – 6.84 (m, 3H), 6.78 – 6.71 (m, 1H), 6.53 (s, 1H), 3.84 (s, 3H), 1.47 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 159.6, 146.8, 144.3, 139.8, 132.8, 132.1, 129.3, 127.2, 126.8, 124.6, 117.7, 115.2, 114.1, 111.9, 109.0, 95.2, 84.8, 55.3, 34.9, 30.6.



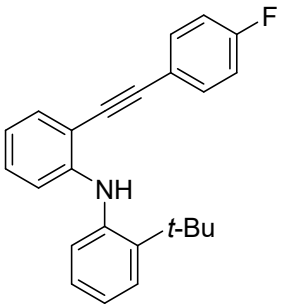
2-([1,1'-biphenyl]-4-ylethynyl)-*N*-(2-(*tert*-butyl)phenyl)aniline (**6-4**)

Yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.68 – 7.59 (m, 6H), 7.53 (td, *J* = 7.5, 1.5 Hz, 2H), 7.49 (t, *J* = 7.6, 2H), 7.45 – 7.37 (m, 2H), 7.28 (dd, *J* = 8.6, 7.1 Hz, 1H), 7.22 – 7.14 (m, 2H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.59 (s, 1H), 1.52 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.0, 144.4, 141.0, 140.2, 139.7, 132.3, 131.7, 129.7, 128.8, 127.6, 127.2, 127.1, 127.0, 127.0, 126.9, 124.8, 122.0, 117.8, 112.0, 108.6, 95.1, 86.9, 34.9, 30.6.



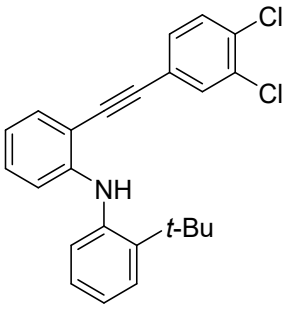
2-(*tert*-butyl)-*N*-(2-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)aniline (**6-5**)

Pale yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.61 (s, 4H), 7.49 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.24 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.21 – 7.12 (m, 2H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.47 (s, 1H), 1.46 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.3, 144.5, 139.5, 132.5, 131.5, 130.3, 129.9 (q, *J* = 32.7 Hz), 127.3, 127.0, 127.0 (q, *J* = 12.6 Hz), 126.9, 125.4 (q, *J* = 3.8 Hz), 124.5, 120.8 (q, *J* = 289.8 Hz), 117.9, 112.2, 107.7, 93.8, 88.8, 34.9, 30.6. **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -62.8.



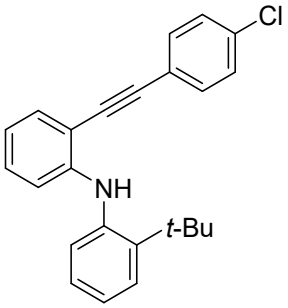
2-(*tert*-butyl)-*N*-(2-((4-fluorophenyl)ethynyl)phenyl)aniline (**6-6**)

Pale yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.55 – 7.46 (m, 4H), 7.41 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.26 (td, *J* = 7.6, 1.6 Hz, 1H), 7.20 – 7.13 (m, 2H), 7.07 (t, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.77 (t, *J* = 7.4 Hz, 1H), 6.51 (s, 1H), 1.48 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 162.5 (d, *J* = 249.7 Hz), 147.0, 144.3, 139.6, 133.2 (d, *J* = 8.2 Hz), 132.2, 129.7, 127.2, 126.9, 124.8, 119.2 (d, *J* = 3.6 Hz), 117.8, 115.8, 115.6, 112.0, 108.4, 94.1, 85.9, 34.9, 30.6. **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -110.7.



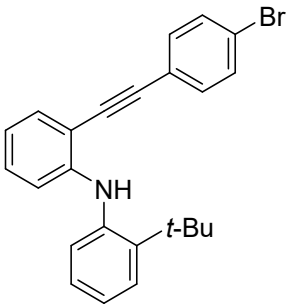
2-(*tert*-butyl)-*N*-(2-((3,4-dichlorophenyl)ethynyl)phenyl)aniline (**6-7**)

Dark yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.60 (t, *J* = 1.5 Hz, 1H), 7.48 (dd, *J* = 13.8, 7.8 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.32 (dt, *J* = 8.3, 1.4 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.17 (td, *J* = 7.8, 3.8 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.44 (s, 1H), 1.48 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 147.2, 144.4, 139.5, 132.9, 132.7, 132.6, 132.4, 130.5, 130.3, 130.2, 127.3, 126.9, 126.9, 125.0, 123.1, 117.9, 112.2, 107.7, 92.8, 88.4, 34.9, 30.6.



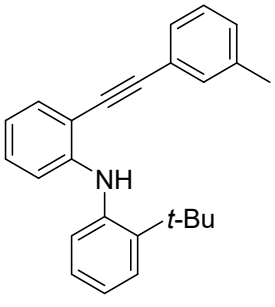
2-(*tert*-butyl)-*N*-(2-((4-chlorophenyl)ethynyl)phenyl)aniline (**6-8**)

Pale yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.50 (ddd, *J* = 7.7, 6.4, 1.6 Hz, 2H), 7.48 – 7.44 (m, 2H), 7.40 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.26 (td, *J* = 7.6, 1.5 Hz, 1H), 7.20 – 7.14 (m, 2H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.77 (td, *J* = 7.5, 1.1 Hz, 1H), 6.50 (s, 1H), 1.48 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 147.0, 144.3, 139.6, 134.3, 132.5, 132.3, 129.9, 128.8, 127.2, 126.9, 126.9, 124.8, 121.6, 117.8, 112.1, 108.2, 94.0, 87.3, 34.9, 30.6.



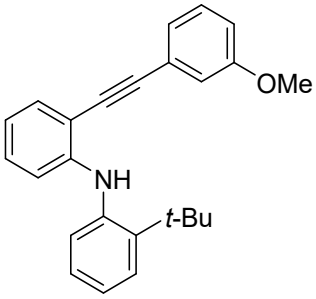
2-((4-bromophenyl)ethynyl)-*N*-(2-(*tert*-butyl)phenyl)aniline (**6-9**)

White solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 4H), 7.37 (t, *J* = 7.5 Hz, 3H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 2H), 6.85 (d, *J* = 8.3 Hz, 1H), 6.75 (t, *J* = 7.5 Hz, 1H), 6.47 (s, 1H), 1.45 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.0, 144.3, 139.5, 132.7, 132.3, 131.7, 129.9, 127.2, 126.9, 124.9, 122.5, 122.0, 117.8, 112.0, 108.1, 94.1, 87.4, 34.9, 30.6.



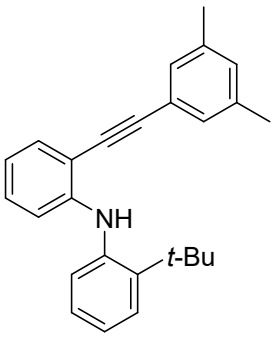
2-(*tert*-butyl)-N-(2-(*m*-tolylethynyl)phenyl)aniline (**6-10**)

Pale yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.47 (ddd, *J* = 7.6, 4.4, 1.5 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.34 (s, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.23 (td, *J* = 7.7, 2.0 Hz, 2H), 7.14 (dd, *J* = 11.6, 7.3 Hz, 3H), 6.83 (d, *J* = 8.3 Hz, 1H), 6.74 (t, *J* = 7.5 Hz, 1H), 6.52 (s, 1H), 2.35 (s, 3H), 1.46 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 147.0, 144.5, 139.8, 138.1, 132.2, 132.0, 129.6, 129.2, 128.4, 128.3, 127.2, 127.0, 126.8, 124.8, 122.9, 117.7, 112.0, 108.7, 95.4, 85.8, 34.9, 30.6, 21.2.



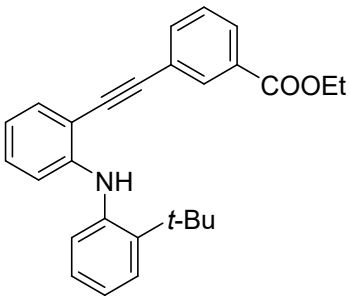
2-(*tert*-butyl)-*N*-(2-((3-methoxyphenyl)ethynyl)phenyl)aniline (**6-11**)

Dark yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.47 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.38 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.28 – 7.20 (m, 2H), 7.17 – 7.09 (m, 3H), 7.04 (dd, *J* = 2.7, 1.4 Hz, 1H), 6.90 (ddd, *J* = 8.4, 2.6, 1.0 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 6.74 (td, *J* = 7.5, 1.2 Hz, 1H), 6.51 (s, 1H), 3.81 (s, 3H), 1.46 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 159.4, 147.0, 144.4, 139.7, 132.3, 129.7, 129.5, 127.2, 127.0, 126.9, 124.8, 124.1, 123.9, 117.8, 116.1, 115.0, 112.0, 108.6, 95.2, 86.0, 55.3, 34.9, 30.6.



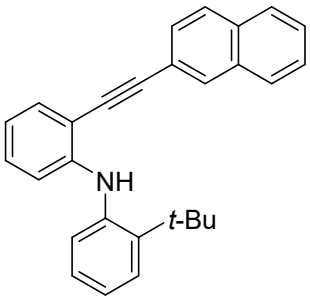
2-(*tert*-butyl)-*N*-(2-((3,5-dimethylphenyl)ethynyl)phenyl)aniline (**6-12**)

Yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 (t, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.25 (t, *J* = 7.4 Hz, 1H), 7.17 (s, 2H), 7.17 – 7.12 (m, 2H), 6.99 (s, 1H), 6.85 (d, *J* = 8.3 Hz, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.54 (s, 1H), 2.33 (s, 6H), 1.49 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 147.0, 144.5, 139.8, 137.9, 132.2, 130.2, 129.5, 129.1, 127.2, 127.0, 126.8, 124.8, 122.8, 117.7, 112.0, 108.9, 95.6, 85.5, 34.9, 30.6, 21.1.



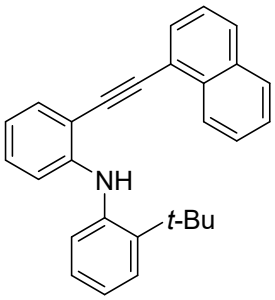
ethyl 3-((2-((2-(*tert*-butyl)phenyl)amino)phenyl)ethynyl)benzoate (**6-13**)

Brown oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.18 (t, *J* = 1.7 Hz, 1H), 8.01 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.67 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.48 (dt, *J* = 8.1, 2.4 Hz, 2H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.38 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.23 (td, *J* = 7.5, 1.6 Hz, 1H), 7.15 (tdd, *J* = 7.3, 4.9, 1.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.75 (t, *J* = 7.5 Hz, 1H), 6.51 (s, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.47 (s, 9H), 1.41 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 165.8, 147.1, 144.4, 139.6, 135.2, 132.4, 132.4, 130.9, 130.0, 129.2, 128.5, 127.2, 126.9, 126.9, 124.8, 123.5, 117.8, 112.1, 108.2, 94.2, 87.2, 61.2, 34.9, 30.6, 14.3.



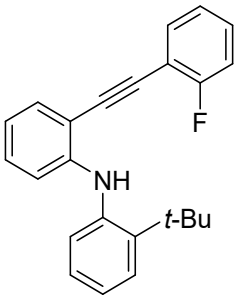
2-(*tert*-butyl)-*N*-(2-(naphthalen-2-ylethynyl)phenyl)aniline (**6-14**)

Brown oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.84 – 7.80 (m, 3H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.55 – 7.48 (m, 4H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 6.2 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.78 (t, *J* = 7.4 Hz, 1H), 6.60 (s, 1H), 1.50 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 147.1, 144.4, 139.7, 133.0, 132.8, 132.3, 131.2, 129.7, 128.2, 128.1, 127.8, 127.8, 127.2, 127.0, 126.9, 126.7, 126.6, 124.8, 120.4, 117.8, 112.1, 108.7, 95.6, 86.6, 34.9, 30.6.



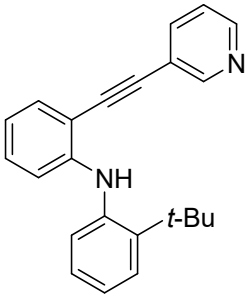
2-(*tert*-butyl)-*N*-(2-(naphthalen-1-ylethynyl)phenyl)aniline (**6-15**)

Yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$δ 8.47 (d, *J* = 7.9 Hz, 1H), 7.89 – 7.85 (m, 2H), 7.75 (d, *J* = 6.9 Hz, 1H), 7.65 – 7.52 (m, 3H), 7.51 – 7.39 (m, 3H), 7.26 (t, *J* = 6.8 Hz, 1H), 7.21 – 7.16 (m, 2H), 6.87 (d, *J* = 8.2 Hz, 1H), 6.81 (t, *J* = 7.2 Hz, 1H), 6.61 (s, 1H), 1.47 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 147.2, 144.7, 139.8, 133.2, 133.0, 132.5, 130.2, 129.8, 128.8, 128.3, 127.4, 127.2, 126.9, 126.8, 126.5, 126.2, 125.3, 125.0, 120.8, 117.8, 112.2, 108.8, 93.2, 91.0, 34.9, 30.7.



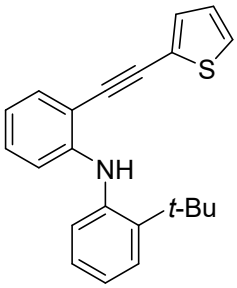
2-(*tert*-butyl)-*N*-(2-((2-fluorophenyl)ethynyl)phenyl)aniline (**6-16**)

White solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 3H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.25 – 7.21 (m, 1H), 7.19 – 7.07 (m, 4H), 6.78 – 6.71 (m, 2H), 6.50 (s, 1H), 1.45 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.3 (d, *J* = 251.6 Hz), 147.5, 145.3, 139.7, 132.9, 132.3, 130.0, 129.9 (d, *J* = 8.2 Hz), 127.9, 127.2, 126.9, 125.2, 124.0 (d, *J* = 3.4 Hz), 117.5, 115.5 (d, *J* = 20.8 Hz), 112.1, 111.9 (d, *J* = 15.9 Hz), 107.9, 91.5 (d, *J* = 3.2 Hz), 88.4, 34.9, 30.6. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -109.5.



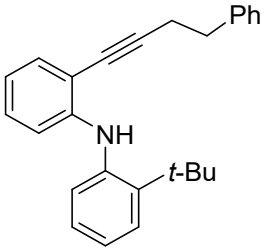
2-(*tert*-butyl)-*N*-(2-(pyridin-3-ylethynyl)phenyl)aniline (**6-17**)

Yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.84 – 8.70 (m, 1H), 8.57 (d, *J* = 4.9 Hz, 1H), 7.86 – 7.77 (m, 1H), 7.55 – 7.44 (m, 2H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.36 – 7.23 (m, 2H), 7.18 (q, *J* = 7.6 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.78 (t, *J* = 7.5 Hz, 1H), 6.48 (s, 1H), 1.48 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 151.9, 148.5, 147.2, 144.4, 139.4, 138.1, 132.4, 130.2, 127.2, 127.0, 126.9, 125.0, 123.1, 120.3, 117.8, 112.2, 107.7, 91.7, 89.7, 34.9, 30.6.



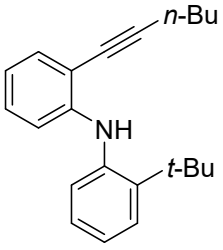
2-(*tert*-butyl)-*N*-(2-(thiophen-2-ylethynyl)phenyl)aniline (**6-18**)

White solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.52 – 7.43 (m, 2H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 5.2 Hz, 1H), 7.28 – 7.21 (m, 2H), 7.15 (t, *J* = 7.6 Hz, 2H), 7.02 (t, *J* = 4.3 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.49 (s, 1H), 1.47 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 146.9, 144.3, 139.6, 132.1, 131.6, 129.8, 127.3, 127.2, 127.1, 126.8, 126.7, 124.7, 123.1, 117.8, 112.0, 108.3, 89.8, 88.3, 34.9, 30.6.



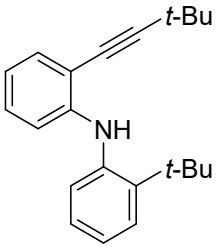
2-(*tert*-butyl)-*N*-(2-(4-phenylbut-1-yn-1-yl)phenyl)aniline (**6-19**)

Pale yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.27 – 7.25 (m, 4H), 7.23 (td, *J* = 7.6, 1.5 Hz, 1H), 7.18 (dt, *J* = 5.2, 4.2 Hz, 1H), 7.14 (td, *J* = 7.9, 1.4 Hz, 1H), 7.10 – 7.06 (m, 1H), 6.80 – 6.74 (m, 1H), 6.69 (td, *J* = 7.5, 1.1 Hz, 1H), 6.33 (s, 1H), 2.95 (t, *J* = 7.5 Hz, 2H), 2.79 (t, *J* = 7.5 Hz, 2H), 1.40 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.0, 144.4, 140.4, 139.9, 132.0, 128.9, 128.4, 127.1, 127.0, 126.8, 126.4, 124.6, 117.5, 111.8, 109.2, 95.2, 78.1, 35.3, 34.8, 30.5, 22.0.



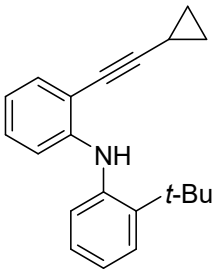
2-(*tert*-butyl)-*N*-(2-(hex-1-yn-1-yl)phenyl)aniline (**6-20**)

Dark yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.22 (td, *J* = 7.6, 1.5 Hz, 1H), 7.15 – 7.11 (m, 1H), 7.10 – 7.05 (m, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 6.68 (td, *J* = 7.5, 1.0 Hz, 1H), 6.43 (s, 1H), 2.50 (t, *J* = 7.1 Hz, 2H), 1.64 – 1.58 (m, 2H), 1.49 (dd, *J* = 15.0, 7.4 Hz, 2H), 1.45 (s, 9H), 0.97 – 0.91 (m, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 146.8, 144.2, 140.0, 132.1, 128.7, 127.1, 126.8, 124.5, 117.5, 111.7, 109.5, 96.2, 34.9, 31.0, 30.5, 22.1, 19.3, 13.6.



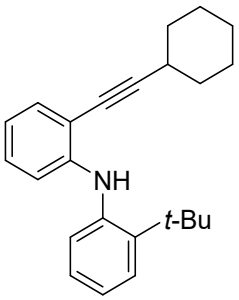
2-(*tert*-butyl)-*N*-(2-(3,3-dimethylbut-1-yn-1-yl)phenyl)aniline (**6-21**)

White solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.53 (d, *J* = 7.9 Hz, 1H), 7.41 (t, *J* = 9.2 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.73 (t, *J* = 7.5 Hz, 1H), 6.40 (s, 1H), 1.52 (s, 9H), 1.41 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 146.7, 144.5, 139.9, 132.2, 128.7, 127.3, 127.1, 126.8, 124.7, 117.5, 111.6, 109.3, 104.3, 75.8, 34.9, 31.2, 30.7, 28.3.



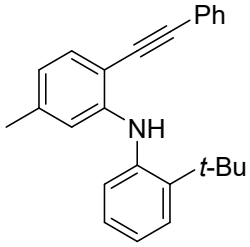
2-(*tert*-butyl)-*N*-(2-(cyclopropylethynyl)phenyl)aniline (**6-22**)

Dark yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.35 (ddd, *J* = 13.4, 7.7, 1.4 Hz, 2H), 7.22 (td, *J* = 7.6, 1.5 Hz, 1H), 7.15 – 7.10 (m, 1H), 7.10 – 7.05 (m, 1H), 6.84 – 6.79 (m, 1H), 6.68 (td, *J* = 7.5, 1.1 Hz, 1H), 6.43 (s, 1H), 1.56 – 1.50 (m, 1H), 1.45 (s, 9H), 0.92 – 0.87 (m, 2H), 0.83 – 0.79 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.0, 144.0, 139.9, 132.2, 128.7, 127.1, 126.8, 126.5, 124.4, 117.6, 111.7, 109.3, 99.3, 72.5, 34.8, 30.5, 8.8, 0.3.



2-(*tert*-butyl)-*N*-(2-(cyclohexylethynyl)phenyl)aniline (**6-23**)

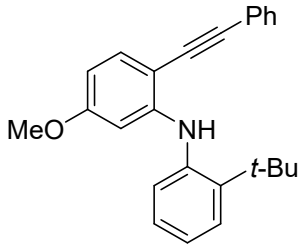
Pale yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.34 (ddd, *J* = 7.5, 4.4, 1.2 Hz, 2H), 7.21 (td, *J* = 7.7, 1.4 Hz, 1H), 7.14 – 7.10 (m, 1H), 7.07 – 7.03 (m, 1H), 6.76 (d, *J* = 8.3 Hz, 1H), 6.67 (td, *J* = 7.5, 0.8 Hz, 1H), 6.37 (s, 1H), 2.66 – 2.63 (m, 1H), 1.95 – 1.89 (m, 2H), 1.79 – 1.71 (m, 2H), 1.56 – 1.48 (m, 3H), 1.43 (s, 9H), 1.36 – 1.30 (m, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 146.8, 144.5, 140.0, 133.0, 132.1, 128.6, 127.1, 126.8, 126.1, 124.6, 117.5, 111.7, 109.5, 100.4, 34.9, 32.9, 30.6, 30.0, 25.8, 25.0.



N-(2-(*tert*-butyl)phenyl)-5-methyl-2-(phenylethynyl)aniline (**6-24**)

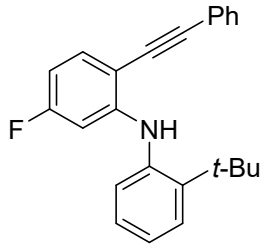
Pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 3H), 7.40 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.36 – 7.30 (m, 3H), 7.26 – 7.23 (m, 1H), 7.17 – 7.12 (m, 1H), 6.68 (s, 1H), 6.58 (dd, *J* = 7.8, 0.8 Hz, 1H), 6.48 (s, 1H), 2.24 (s, 3H), 1.46 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 146.8, 144.2, 140.1, 139.8, 132.1, 131.3, 128.4, 128.1, 127.2, 126.9, 126.8, 124.6, 123.3, 118.9, 112.4, 105.8, 94.7, 86.4, 34.9, 30.6, 22.0.



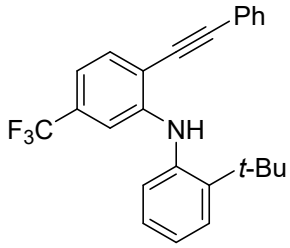
N-(2-(*tert*-butyl)phenyl)-5-methoxy-2-(phenylethynyl)aniline (**6-25**)

Pale yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.48 (dt, *J* = 6.5, 1.6 Hz, 3H), 7.42 – 7.38 (m, 2H), 7.36 – 7.29 (m, 3H), 7.24 (td, *J* = 7.6, 1.5 Hz, 1H), 7.15 (td, *J* = 7.8, 1.4 Hz, 1H), 6.53 (s, 1H), 6.36 (d, *J* = 2.4 Hz, 1H), 6.33 (dd, *J* = 8.5, 2.5 Hz, 1H), 3.72 (s, 3H), 1.45 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.1, 148.5, 144.6, 139.3, 133.4, 131.1, 128.4, 127.9, 127.3, 127.2, 126.9, 125.0, 123.4, 103.6, 101.4, 97.6, 94.2, 86.3, 55.2, 34.9, 30.6.



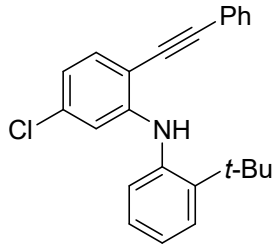
N-(2-(*tert*-butyl)phenyl)-5-fluoro-2-(phenylethynyl)aniline (**6-26**)

Dark yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 3H), 7.42 (dd, *J* = 8.5, 6.4 Hz, 1H), 7.37 – 7.33 (m, 4H), 7.26 (ddd, *J* = 7.7, 6.5, 1.5 Hz, 1H), 7.19 (td, *J* = 7.7, 1.5 Hz, 1H), 6.60 (s, 1H), 6.48 (dd, *J* = 11.6, 2.5 Hz, 1H), 6.43 (td, *J* = 8.4, 2.5 Hz, 1H), 1.44 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 164.0 (d, *J* = 247.1 Hz), 149.0 (d, *J* = 11.8 Hz), 145.1, 138.7, 133.6 (d, *J* = 10.7 Hz), 131.3, 128.4, 128.3, 127.7, 127.4, 127.1, 125.6, 122.9, 104.7 (d, *J* = 22.9 Hz), 104.3 (d, *J* = 2.1 Hz), 98.7 (d, *J* = 27.3 Hz), 94.8 (d, *J* = 1.4 Hz), 85.3, 34.9, 30.6. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -108.4.



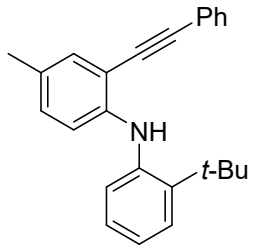
N-(2-(*tert*-butyl)phenyl)-2-(phenylethynyl)-5-(trifluoromethyl)aniline (**6-27**)

Yellow solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 0.28H), 7.65 (d, *J* = 8.2 Hz, 0.3H), 7.56 – 7.48 (m, 4.31H), 7.40 – 7.33 (m, 4.56H), 7.32 – 7.26 (m, 1.72H), 7.22 – 7.19 (m, 2.18H), 7.13 (s, 0.29H), 7.01 (s, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.91 (s, 0.27H), 6.65 (s, 1H), 1.45 (s, 9H), 0.90 (s, 2.6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.4, 147.2, 145.0, 144.1, 139.8, 138.6, 134.7, 132.5, 132.31 (q, *J* = 11.9 Hz), 131.7, 131.5, 131.2, 130.3, 129.9, 129.4, 128.8, 128.5, 128.4, 127.9, 127.5, 127.2 (q, *J* = 8.7 Hz), 127.0, 125.7, 124.9, 123.1, 122.4, 120.6, 116.8 (q, *J* = 3.3 Hz), 113.9 (q, *J* = 3.6 Hz), 111.6, 108.9 (q, *J* = 4.3 Hz), 108.0 (d, *J* = 3.7 Hz), 102.4, 97.0, 84.8, 36.0, 34.9, 31.3, 30.6. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -60.4, -63.0.



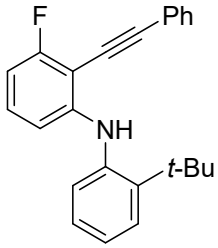
N-(2-(*tert*-butyl)phenyl)-5-chloro-2-(phenylethynyl)aniline (**6-28**)

Yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.49 (td, *J* = 7.0, 2.6 Hz, 3H), 7.38 – 7.32 (m, 5H), 7.28 – 7.24 (m, 1H), 7.18 (td, *J* = 7.5, 1.6 Hz, 1H), 6.75 (d, *J* = 2.0 Hz, 1H), 6.69 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.53 (s, 1H), 1.43 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 148.1, 145.1, 138.7, 135.7, 133.1, 131.4, 128.5, 127.6, 127.4, 127.2, 125.6, 122.8, 117.8, 111.5, 106.9, 102.2, 95.9, 85.2, 34.9, 30.7.



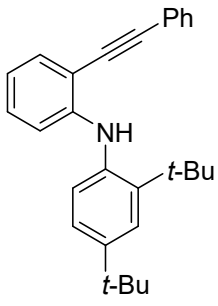
N-(2-(*tert*-butyl)phenyl)-4-methyl-2-(phenylethynyl)aniline (**6-29**)

Pale yellow solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.57 – 7.45 (m, 3H), 7.44 – 7.31 (m, 5H), 7.24 (dd, *J* = 15.5, 8.5 Hz, 1H), 7.18 – 7.10 (m, 1H), 6.98 (d, *J* = 8.6 Hz, 1H), 6.87 – 6.79 (m, 1H), 6.47 – 6.36 (m, 1H), 2.35 – 2.20 (m, 3H), 1.54 – 1.39 (m, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.6, 143.8, 140.2, 132.4, 131.3, 130.4, 128.4, 128.2, 127.1, 127.1, 126.8, 126.2, 124.2, 123.2, 112.3, 108.7, 94.9, 86.4, 34.8, 30.6, 20.3.



N-(2-(*tert*-butyl)phenyl)-3-fluoro-2-(phenylethynyl)aniline (**6-30**)

Pale yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 8.2, 1.1 Hz, 0.17H), 7.57 – 7.51 (m, 1.85H), 7.50 – 7.45 (m, 1.16H), 7.38 – 7.32 (m, 3.82H), 7.32 – 7.28 (m, 0.51H), 7.24 (dd, *J* = 7.6, 1.0 Hz, 1.05H), 7.22 – 7.20 (m, 0.62H), 7.20 – 7.15 (m, 1.06H), 7.05 (dt, *J* = 7.9, 6.8 Hz, 1.17H), 6.94 (s, 0.18H), 6.81 (dd, *J* = 10.1, 7.8 Hz, 0.18H), 6.65 (d, *J* = 8.2 Hz, 0.19H), 6.55 (d, *J* = 8.7 Hz, 1.83H), 6.49 (t, *J* = 8.6 Hz, 1H), 1.44 (s, 9H), 0.91 (s, 1.61H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.5 (d, *J* = 248.8 Hz), 156.0 (d, *J* = 247.2 Hz), 148.7 (d, *J* = 4.3 Hz), 148.4, 145.0, 143.3 (d, *J* = 11.1 Hz), 141.5, 139.1, 135.3, 132.5, 132.4, 131.4, 130.1, 130.1 (d, *J* = 10.2 Hz), 129.1, 128.6, 128.4, 128.3 (d, *J* = 4.6 Hz), 127.7, 127.5, 127.1 (d, *J* = 51.2 Hz), 126.8, 125.5, 122.8, 122.3 (d, *J* = 7.8 Hz), 116.8 (d, *J* = 22.7 Hz), 107.6 (d, *J* = 3.4 Hz), 107.2 (d, *J* = 2.7 Hz), 104.8 (d, *J* = 18.8 Hz), 104.2 (d, *J* = 21.2 Hz), 99.9 (d, *J* = 3.1 Hz), 98.1, 97.6 (d, *J* = 19.0 Hz), 79.9 (d, *J* = 2.2 Hz), 36.0, 34.9, 31.3, 30.6. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -109.4, -122.8.

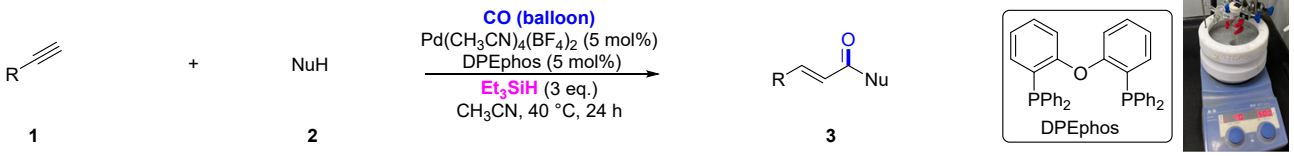


2,4-di-*tert*-butyl-*N*-(2-(phenylethynyl)phenyl)aniline (**6**-**31**)

Pale yellow solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 3.1 Hz, 3H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 5.9 Hz, 3H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.25 (d, *J* = 8.6 Hz, 1H), 7.13 (t, *J* = 7.7 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.43 (s, 1H), 1.46 (s, 9H), 1.36 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.6, 147.4, 144.0, 136.9, 132.1, 131.3, 129.6, 128.4, 128.2, 126.9, 124.1, 123.7, 123.1, 117.3, 111.9, 108.2, 95.1, 86.3, 35.2, 34.7, 31.5, 30.7.

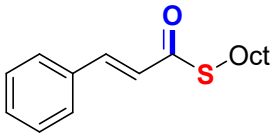
2.2 General Procedure for the Synthesis of Linear Products 3 and Characterization

An oven-dried 10 mL Schlenk tube was charged with $Pd(CH_3CN)_4(BF_4)_2$ (4.4 mg, 0.01 mmol, 5 mol%), DPEphos (5.4 mg, 0.01 mmol, 5 mol%), the above mentioned mixture was degassed and refilled with CO for 3 times. Then, a solution of **1** (0.2 mmol), **2** (0.24 mmol) and Et_3SiH (100 µL, 0.6 mmol, 3.0 eq.) in 4 mL of dry CH_3CN were added to the mixture by syringe. Finally, the mixture was stirred at 40 °C for 24 h under CO balloon. After completion of the reaction, the crude reaction mixture was concentrated in vacuo and the residue was dissolved in $CDCl_3$, then the L/B ratio of the product is determined by ^1H NMR. Finally, these $CDCl_3$ fractions were collected and concentrated again, and the residue was purified by silica gel flash column chromatography to (hexane/EtOAc) to give products **3**.



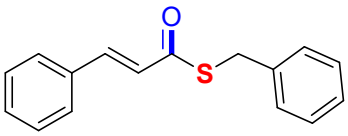
1 **2** **3**

Characterization of Products 3[2]



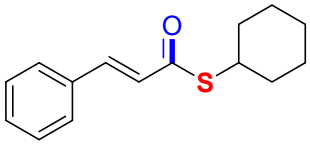
S-octyl (*E*)-3-phenylprop-2-enethioate (**3-1**)

White solid (45.8 mg, 83% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.60 (d, *J* = 15.8 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.41 – 7.36 (m, 3H), 6.71 (d, *J* = 15.8 Hz, 1H), 3.01 (t, *J* = 7.4 Hz, 2H), 1.64 (p, *J* = 7.4 Hz, 2H), 1.40 (q, *J* = 7.0 Hz, 2H), 1.34 – 1.26 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 190.0, 140.1, 134.2, 130.4, 128.9, 128.3, 125.2, 31.8, 29.6, 29.1, 29.1, 29.0, 28.9, 22.6, 14.0.



S-benzyl (*E*)-3-phenylprop-2-enethioate (**3-2**)

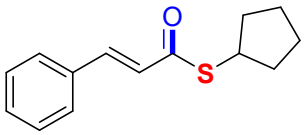
White solid (43.2 mg, 85% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.65 (d, *J* = 15.8 Hz, 1H), 7.54 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.40 (dd, *J* = 5.1, 2.0 Hz, 3H), 7.36 (d, *J* = 7.0 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.29 – 7.24 (m, 1H), 6.73 (d, *J* = 15.8 Hz, 1H), 4.28 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 189.1, 140.9, 137.6, 134.1, 130.6, 128.9, 128.9, 128.6, 128.4, 127.3, 124.6, 33.2.



S-cyclohexyl (*E*)-3-phenylprop-2-enethioate (**3-3**)

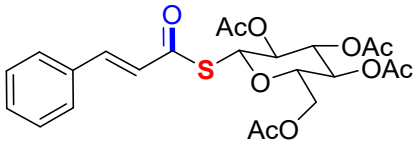
White solid (39.9 mg, 81% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.58 (d, *J* = 15.9 Hz, 1H), 7.53 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.42 – 7.36 (m, 3H), 6.68 (d, *J* = 15.8 Hz, 1H), 3.68 (dd, *J* = 9.4, 4.8 Hz, 1H), 1.99 (dt, *J* = 9.8, 5.8 Hz, 2H), 1.74 (q, *J* = 5.0 Hz, 2H), 1.65 – 1.59 (m,

1H), 1.48 (td, *J* = 9.9, 2.7 Hz, 4H), 1.36 – 1.26 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 189.7, 140.0, 134.3, 130.4, 128.9, 128.3, 125.5, 42.4, 33.1, 25.9, 25.6.



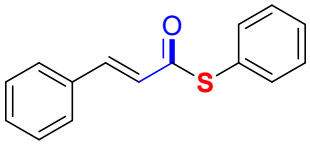
S-cyclopentyl (*E*)-3-phenylprop-2-enethioate (**3-4**)

Yellow oil (38.1 mg, 82% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.58 (d, *J* = 15.8 Hz, 1H), 7.53 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.42 – 7.35 (m, 3H), 6.68 (d, *J* = 15.8 Hz, 1H), 3.87 (p, *J* = 6.9 Hz, 1H), 2.16 (dt, *J* = 12.4, 6.3 Hz, 2H), 1.80 – 1.68 (m, 2H), 1.68 – 1.58 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 190.6, 140.0, 134.3, 130.4, 128.9, 128.3, 125.2, 42.5, 33.3, 24.8.



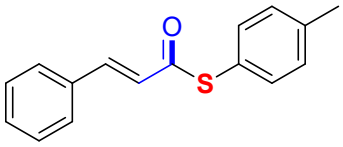
2-(acetoxymethyl)-6-(cinnamoylthio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**3-5**)

White solid (60.3 mg, 61% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.65 (d, *J* = 15.8 Hz, 1H), 7.54 (d, *J* = 7.0 Hz, 2H), 7.41 (d, *J* = 7.3 Hz, 3H), 6.68 (d, *J* = 15.8 Hz, 1H), 5.43 (d, *J* = 10.4 Hz, 1H), 5.32 (t, *J* = 9.3 Hz, 1H), 5.21 (t, *J* = 9.8 Hz, 1H), 5.14 (t, *J* = 9.6 Hz, 1H), 4.29 (dd, *J* = 12.6, 4.4 Hz, 1H), 4.11 (d, *J* = 12.5 Hz, 1H), 3.89 (d, *J* = 7.7 Hz, 1H), 2.08 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 185.9, 170.7, 170.1, 169.5, 169.4, 143.2, 133.6, 131.2, 129.1, 128.6, 124.0, 80.0, 76.4, 74.0, 69.2, 68.0, 61.7, 20.7, 20.6, 20.6. **HRMS (ESI)**: calcd for $C_{23}H_{27}O_{10}S$ $[M+H]^+$ 495.1320; found 495.1313.



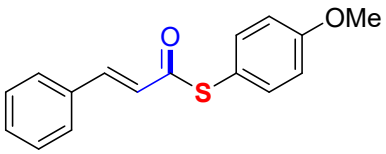
S-phenyl (*E*)-3-phenylprop-2-enethioate (**3-6**)

White solid (42.7 mg, 89% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.69 (d, *J* = 15.8 Hz, 1H), 7.58 – 7.56 (m, 2H), 7.51 – 7.50 (m, 2H), 7.45 – 7.44 (m, 3H), 7.42 – 7.41 (m, 3H), 6.80 (d, *J* = 15.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 187.9, 141.5, 134.6, 134.0, 130.7, 129.4, 129.2, 129.0, 128.5, 127.6, 124.2.



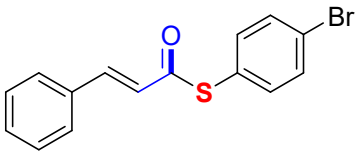
S-(*p*-tolyl) (*E*)-3-phenylprop-2-enethioate (**3-7**)

White solid (42.2 mg, 83% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.68 (d, *J* = 15.8 Hz, 1H), 7.62 – 7.53 (m, 2H), 7.49 – 7.33 (m, 5H), 7.25 (d, *J* = 5.3 Hz, 2H), 6.79 (d, *J* = 15.8 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 188.4, 141.3, 139.7, 134.6, 134.1, 130.7, 130.0, 129.0, 128.5, 124.2, 124.1, 21.3.



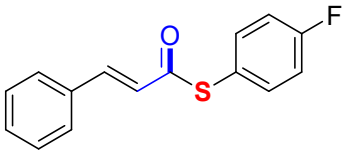
S-(4-methoxyphenyl) (*E*)-3-phenylprop-2-enethioate (**3-8**)

White solid (43.2 mg, 80% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.68 (d, *J* = 15.8 Hz, 1H), 7.57 (dd, *J* = 6.8, 2.9 Hz, 2H), 7.41 (dd, *J* = 8.0, 2.4 Hz, 5H), 7.01 – 6.93 (m, 2H), 6.80 (d, *J* = 15.8 Hz, 1H), 3.84 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 188.9, 160.7, 141.3, 136.2, 134.1, 130.6, 128.9, 128.4, 124.1, 118.2, 114.9, 55.3.



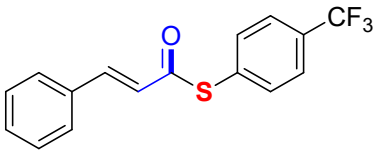
S-(4-bromophenyl) (*E*)-3-phenylprop-2-enethioate (**3-9**)

White solid (21.1 mg, 33% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 15.8 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 4H), 7.42 (d, *J* = 6.4 Hz, 3H), 7.35 (d, *J* = 8.3 Hz, 2H), 6.78 (d, *J* = 15.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 187.2, 142.0, 136.0, 133.9, 132.4, 130.9, 129.0, 128.5, 126.8, 124.1, 123.9.



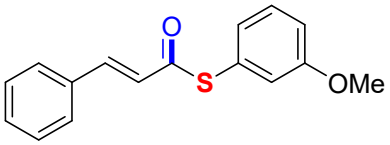
S-(4-fluorophenyl) (*E*)-3-phenylprop-2-enethioate (**3-10**)

White solid (22.2 mg, 43% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.68 (d, *J* = 15.8 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.50 – 7.44 (m, 2H), 7.42 (dd, *J* = 5.2, 1.9 Hz, 3H), 7.14 (t, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 15.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 187.9, 163.5 (d, *J* = 249.9 Hz), 141.8, 136.7 (d, *J* = 8.3 Hz), 133.9, 130.9, 129.0, 128.5, 123.9, 122.9 (d, *J* = 3.4 Hz), 116.5 (d, *J* = 22.5 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -111.1.



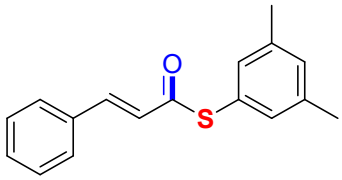
S-(4-(trifluoromethyl)phenyl) (*E*)-3-phenylprop-2-enethioate (**3-11**)

White solid (37.0 mg, 60% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.74 – 7.67 (m, 3H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.61 – 7.56 (m, 2H), 7.43 (d, *J* = 6.2 Hz, 3H), 6.79 (d, *J* = 15.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 186.5, 142.4, 134.6, 133.8, 132.4, 131.3 (q, *J* = 32.7 Hz), 131.0, 129.1, 128.6, 125.9 (q, *J* = 3.7 Hz), 123.8, 123.8 (q, *J* = 274.0 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -62.8.



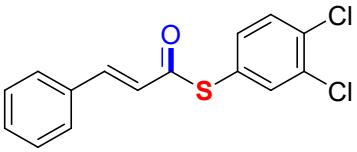
S-(3-methoxyphenyl) (*E*)-3-phenylprop-2-enethioate (**3-12**)

White solid (44.3 mg, 82% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.69 (d, *J* = 15.8 Hz, 1H), 7.57 (dd, *J* = 7.1, 2.7 Hz, 2H), 7.42 (dd, *J* = 5.3, 2.0 Hz, 3H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.10 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.07 (t, *J* = 2.0 Hz, 1H), 6.99 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.80 (d, *J* = 15.8 Hz, 1H), 3.83 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 187.8, 159.9, 141.5, 134.0, 130.7, 129.9, 129.0, 128.5, 128.5, 126.7, 124.1, 119.6, 115.7, 55.3.



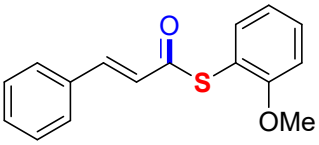
S-(*m*-tolyl) (*E*)-3-phenylprop-2-enethioate (**3-13**)

Pale yellow oil (24.1 mg, 45% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 15.8 Hz, 1H), 7.61 – 7.52 (m, 2H), 7.44 – 7.39 (m, 3H), 7.12 (s, 2H), 7.07 (s, 1H), 6.79 (d, *J* = 15.8 Hz, 1H), 2.35 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 188.5, 141.3, 138.9, 134.1, 132.2, 131.4, 130.7, 129.0, 128.5, 126.8, 124.1, 21.2.



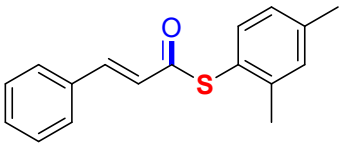
S-(3,4-dichlorophenyl) (*E*)-3-phenylprop-2-enethioate (**3-14**)

White solid (48.0 mg. 78 yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.69 (d, *J* = 15.8 Hz, 1H), 7.62 – 7.55 (m, 3H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.46 – 7.39 (m, 3H), 7.32 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.77 (d, *J* = 15.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 186.6, 142.5, 136.0, 134.1, 133.7, 133.7, 133.1, 131.1, 130.9, 129.1, 128.6, 127.6, 123.6.



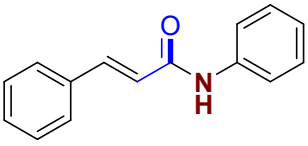
S-(2-methoxyphenyl) (*E*)-3-phenylprop-2-enethioate (**3-15**)

White solid (41.0 mg, 76% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.67 (d, *J* = 15.8 Hz, 1H), 7.56 (dd, *J* = 6.8, 2.9 Hz, 2H), 7.50 – 7.42 (m, 2H), 7.40 (dd, *J* = 5.0, 1.9 Hz, 3H), 7.05 – 7.02 (m, 1H), 7.01 (dd, *J* = 8.5, 1.2 Hz, 1H), 6.82 (d, *J* = 15.8 Hz, 1H), 3.87 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 187.3, 159.4, 141.2, 136.9, 134.2, 131.7, 130.6, 129.0, 128.4, 124.3, 121.1, 115.7, 111.6, 56.1.



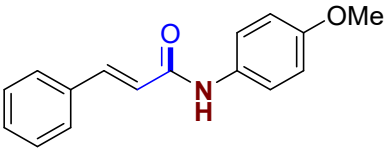
S-(2,4-dimethylphenyl) (*E*)-3-phenylprop-2-enethioate (**3-16**)

White solid (38.1 mg, 71% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.67 (d, *J* = 15.8 Hz, 1H), 7.57 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.44 – 7.37 (m, 3H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.17 (s, 1H), 7.07 (dd, *J* = 7.7, 1.9 Hz, 1H), 6.82 (d, *J* = 15.8 Hz, 1H), 2.36 (s, 3H), 2.36 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 188.1, 142.0, 141.2, 140.4, 135.9, 134.1, 131.7, 130.6, 129.0, 128.4, 127.5, 124.3, 123.6, 21.2, 20.7.



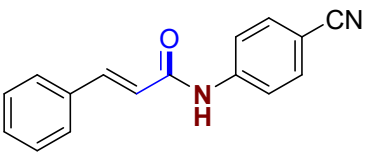
N-phenylcinnamamide (**3-17**)

White solid (35.7 mg, 80% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.83 (s, 1H), 7.75 (d, *J* = 15.5 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.47 (dd, *J* = 6.8, 2.8 Hz, 2H), 7.40 – 7.29 (m, 5H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 15.6 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 164.2, 142.3, 138.1, 134.6, 129.9, 129.0, 128.8, 127.9, 124.4, 120.9, 120.1.



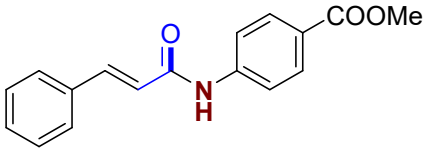
N-(4-methoxyphenyl)cinnamamide (**3-18**)

White solid (27.3 mg, 54% yield). **^{1}H NMR** (500 MHz, Methanol-d_4) δ = 7.62 (d, *J* = 15.7 Hz, 1H), 7.56 (t, *J* = 9.1 Hz, 4H), 7.38 (q, *J* = 7.9 Hz, 3H), 6.88 (d, *J* = 8.5 Hz, 2H), 6.76 (d, *J* = 15.6 Hz, 1H), 3.76 (s, 3H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ = 165.0, 156.6, 141.0, 134.9, 131.6, 129.5, 128.6, 127.5, 121.5, 120.9, 113.6, 54.5.



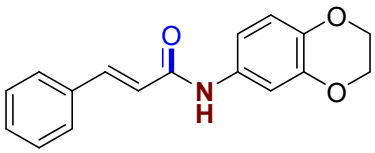
N-(4-cyanophenyl)cinnamamide (**3-19**)

White solid (57.2 mg, 96% yield). **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 10.65 (s, 1H), 7.92 – 7.86 (m, 2H), 7.86 – 7.77 (m, 2H), 7.66 (d, *J* = 4.3 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.51 – 7.38 (m, 3H), 6.83 (d, *J* = 15.7 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ = 164.7, 143.9, 141.9, 134.9, 133.8, 130.6, 129.6, 128.4, 122.0, 119.8, 119.6, 105.5.



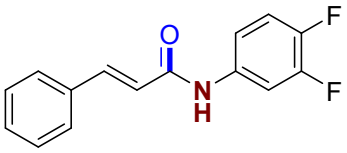
methyl 4-cinnamamidobenzoate (**3-20**)

Yellow solid (48.3 mg, 86% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.07 – 8.01 (m, 2H), 7.79 (d, *J* = 15.5 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.60 (s, 1H), 7.53 (dd, *J* = 6.4, 3.1 Hz, 2H), 7.41 – 7.36 (m, 3H), 6.57 (d, *J* = 15.5 Hz, 1H), 3.91 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 166.6, 164.0, 143.4, 142.2, 134.4, 130.9, 130.3, 129.0, 128.1, 125.7, 120.2, 119.0, 52.0.



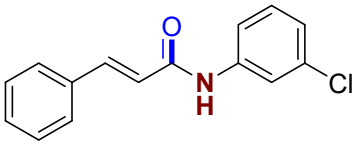
N-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)cinnamamide (**3-21**)

White solid (36.0 mg, 64% yield). **^{1}H NMR** (500 MHz, Methanol-d_4) δ 7.61 (d, *J* = 15.7 Hz, 1H), 7.57 (d, *J* = 6.8 Hz, 2H), 7.41 – 7.35 (m, 3H), 7.29 (d, *J* = 2.0 Hz, 1H), 7.01 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.77 (d, *J* = 8.7 Hz, 1H), 6.73 (d, *J* = 15.7 Hz, 1H), 4.21 (d, *J* = 3.5 Hz, 4H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ = 165.0, 143.4, 141.1, 140.6, 134.9, 132.2, 129.5, 128.6, 127.5, 120.9, 116.6, 113.2, 109.3, 64.3, 64.2.



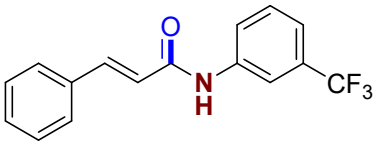
N-(3,4-difluorophenyl)cinnamamide (**3-22**)

White solid (45.6 mg, 88% yield). **^{1}H NMR** (500 MHz, Methanol-d_4) δ 7.80 (ddd, *J* = 12.7, 7.3, 2.3 Hz, 1H), 7.65 (d, *J* = 15.7 Hz, 1H), 7.59 – 7.54 (m, 2H), 7.42 – 7.34 (m, 3H), 7.31 – 7.26 (m, 1H), 7.22 – 7.16 (m, 1H), 6.72 (d, *J* = 15.7 Hz, 1H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ = 165.2, 149.77 (dd, *J* = 244.8, 13.2 Hz), 146.55 (dd, *J* = 243.6, 12.7 Hz), 141.9, 135.6 (dd, *J* = 8.9, 3.2 Hz), 134.7, 129.8, 128.6, 127.6, 120.4, 116.8 (d, *J* = 18.4 Hz), 115.6 (dd, *J* = 8.9, 3.2 Hz), 108.9 (d, *J* = 22.0 Hz). **^{19}F NMR** (471 MHz, Methanol-d_4) δ = -139.0, -145.9.



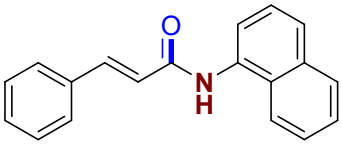
N-(3-chlorophenyl)cinnamamide (**3-23**)

White solid (47.8 mg, 93% yield). **^{1}H NMR** (500 MHz, Methanol-d_4) δ 7.86 (t, *J* = 1.7 Hz, 1H), 7.66 (d, *J* = 15.7 Hz, 1H), 7.59 – 7.57 (m, 2H), 7.49 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.42 – 7.35 (m, 3H), 7.28 (t, *J* = 8.1 Hz, 1H), 7.09 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.75 (d, *J* = 15.7 Hz, 1H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ = 165.3, 141.9, 140.1, 134.7, 134.1, 129.7, 129.7, 128.6, 127.6, 123.6, 120.5, 119.5, 117.7.



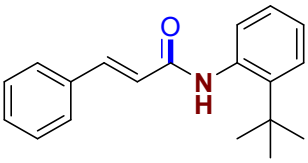
N-(3-(trifluoromethyl)phenyl)cinnamamide (**3-24**)

White solid (55.9 mg, 96% yield). **^{1}H NMR** (500 MHz, Methanol-d_4) δ 8.12 (s, 1H), 7.82 (d, *J* = 7.0 Hz, 1H), 7.67 (dd, *J* = 15.6, 5.8 Hz, 1H), 7.58 (s, 2H), 7.52 – 7.44 (m, 1H), 7.37 (d, *J* = 8.2 Hz, 4H), 6.80 – 6.72 (m, 1H). **^{13}C NMR** (126 MHz, Methanol-d_4) δ = 165.5, 142.1, 139.5, 134.7, 130.8 (q, *J* = 31.9 Hz), 129.8, 129.3, 128.6, 127.6, 124.1 (q, *J* = 271.5 Hz), 122.8, 120.4, 120.0 (q, *J* = 3.8 Hz), 116.1 (q, *J* = 3.9 Hz). **^{19}F NMR** (471 MHz, Methanol-d_4) δ = -64.2.



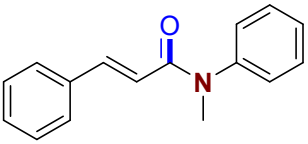
N-(naphthalen-1-yl)cinnamamide (**3-25**)

Grey solid (51.9 mg, 95% yield). **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 10.16 (s, 1H), 8.19 – 8.12 (m, 1H), 7.96 (dd, *J* = 7.4, 1.9 Hz, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.70 – 7.62 (m, 3H), 7.62 – 7.50 (m, 3H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.45 – 7.39 (m, 1H), 7.17 (d, *J* = 15.8 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ = 164.8, 140.8, 135.4, 134.2, 134.0, 130.2, 129.5, 128.7, 128.2, 127.7, 126.5, 126.4, 126.1, 125.6, 123.0, 122.8, 121.4.



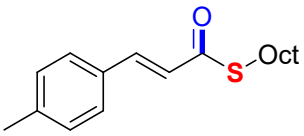
N-(2-(*tert*-butyl)phenyl)cinnamamide (**3-26**)

White solid (53.6 mg, 96% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 15.5 Hz, 1H), 7.69 – 7.56 (m, 2H), 7.42 – 7.38 (m, 5H), 7.27 – 7.20 (m, 3H), 6.61 – 6.40 (m, 1H). 1.44 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 165.8, 142.8, 142.4, 135.2, 134.7, 134.7, 130.4, 128.8, 128.0, 126.9, 126.6, 126.3, 120.9, 34.7, 30.7.



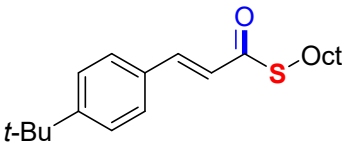
N-methyl-*N*-phenylcinnamamide (**3-27**)

Colorless oil (46.0 mg, 97% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.68 (d, *J* = 15.5 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.39 – 7.34 (m, 1H), 7.32 (dd, *J* = 6.9, 3.1 Hz, 2H), 7.28 (q, *J* = 3.4 Hz, 3H), 7.25 – 7.22 (m, 2H), 6.37 (d, *J* = 15.5 Hz, 1H), 3.41 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 166.2, 143.7, 141.7, 135.2, 129.6, 129.5, 128.7, 127.8, 127.6, 127.3, 118.8, 37.5.



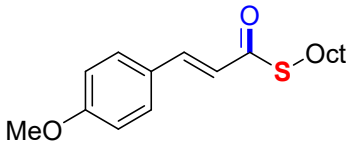
S-octyl (*E*)-3-(*p*-tolyl)prop-2-enethioate (**3-28**)

Pale yellow solid (44.1 mg, 76% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.58 (d, *J* = 15.8 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 6.67 (d, *J* = 15.8 Hz, 1H), 3.00 (t, *J* = 7.4 Hz, 2H), 2.37 (s, 3H), 1.68 – 1.60 (m, 2H), 1.39 (q, *J* = 7.1 Hz, 2H), 1.33 – 1.25 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 190.0, 140.9, 140.2, 131.5, 129.7, 128.3, 124.2, 31.8, 29.6, 29.1, 29.1, 28.9, 28.9, 22.6, 21.5, 14.0.



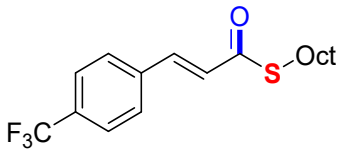
S-octyl (*E*)-3-(4-(*tert*-butyl)phenyl)prop-2-enethioate (**3-29**)

Pale yellow oil (47.1 mg, 71% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.60 (d, *J* = 15.8 Hz, 1H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 6.69 (d, *J* = 15.9 Hz, 1H), 3.00 (t, *J* = 7.3 Hz, 2H), 1.64 (p, *J* = 7.6 Hz, 2H), 1.40 (q, *J* = 7.2 Hz, 2H), 1.33 (s, 9H), 1.32 – 1.24 (m, 8H), 0.88 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 190.0, 154.1, 140.1, 131.4, 128.2, 125.9, 124.4, 34.9, 31.8, 31.1, 29.6, 29.1, 29.1, 28.9, 28.9, 22.6, 14.1.



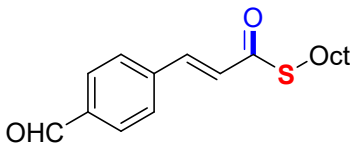
S-octyl (*E*)-3-(4-methoxyphenyl)prop-2-enethioate (**3-30**)

Pale yellow oil (44.7 mg, 73% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.56 (d, *J* = 15.8 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.59 (d, *J* = 15.8 Hz, 1H), 3.83 (s, 3H), 2.99 (t, *J* = 7.4 Hz, 2H), 1.63 (t, *J* = 7.4 Hz, 2H), 1.39 (t, *J* = 7.5 Hz, 2H), 1.33 – 1.24 (m, 8H), 0.88 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, CDC_3) δ = 189.9, 161.6, 139.9, 130.0, 126.9, 122.9, 114.4, 55.4, 31.8, 29.6, 29.1, 29.1, 28.9, 28.9, 22.6, 14.0.



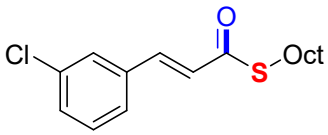
S-octyl (*E*)-3-(4-(trifluoromethyl)phenyl)prop-2-enethioate (**3-31**)

Pale yellow solid (39.2 mg, 57% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.64 (s, 4H), 7.60 (d, *J* = 15.8 Hz, 1H), 6.76 (d, *J* = 15.9 Hz, 1H), 3.02 (t, *J* = 7.3 Hz, 2H), 1.64 (p, *J* = 7.4 Hz, 2H), 1.39 (q, *J* = 7.0 Hz, 2H), 1.33 – 1.24 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 189.7, 138.1, 137.7, 131.9 (q, *J* = 32.7 Hz), 128.4, 127.4, 125.9 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 272.4 Hz), 31.8, 29.5, 29.2, 29.1, 29.1, 28.9, 22.6, 14.1. **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -62.9.



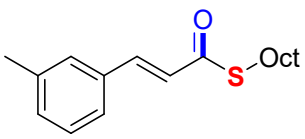
S-octyl (*E*)-3-(4-formylphenyl)prop-2-enethioate (**3-32**)

Pale yellow solid (31.0 mg, 51% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 10.02 (s, 1H), 7.89 (d, *J* = 7.9 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 15.8 Hz, 1H), 6.79 (d, *J* = 15.9 Hz, 1H), 3.01 (t, *J* = 7.4 Hz, 2H), 1.63 (p, *J* = 7.4 Hz, 2H), 1.38 (q, *J* = 7.2 Hz, 2H), 1.27 (dd, *J* = 11.0, 5.2 Hz, 8H), 0.87 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 191.3, 189.6, 139.9, 138.1, 137.2, 130.1, 128.7, 127.9, 31.7, 29.4, 29.1, 29.1, 29.0, 28.8, 22.6, 14.0.



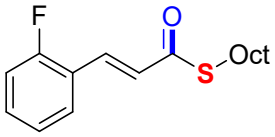
S-octyl (*E*)-3-(3-chlorophenyl)prop-2-enethioate (**3-33**)

Pale yellow solid (42.2 mg, 68% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.56 – 7.47 (m, 2H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.33 (dt, *J* = 15.4, 7.9 Hz, 2H), 6.69 (d, *J* = 16.0 Hz, 1H), 3.01 (t, *J* = 7.3 Hz, 2H), 1.66 – 1.60 (m, 2H), 1.41 – 1.37 (m, 2H), 1.29 – 1.27 (m, 8H), 0.88 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 189.7, 138.3, 136.1, 135.0, 130.3, 130.1, 127.9, 126.5, 126.4, 31.8, 29.5, 29.1, 29.1, 29.1, 28.9, 22.6, 14.0.



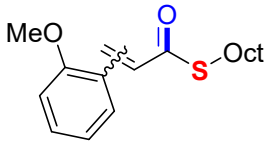
S-octyl (*E*)-3-(*m*-tolyl)prop-2-enethioate (**3-34**)

Pale yellow oil (44.7 mg, 77% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.58 (d, *J* = 15.8 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.25 (m, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 15.8 Hz, 1H), 3.00 (t, *J* = 7.4 Hz, 2H), 2.37 (s, 3H), 1.64 (p, *J* = 7.4 Hz, 2H), 1.40 (p, *J* = 7.0 Hz, 2H), 1.34 – 1.24 (m, 8H), 0.88 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 190.0, 140.3, 138.6, 134.2, 131.3, 128.9, 128.8, 125.6, 125.0, 31.8, 29.6, 29.1, 29.1, 29.0, 28.9, 22.6, 21.3, 14.1.



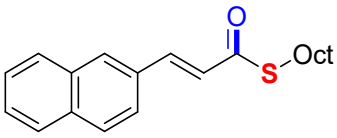
S-octyl (*E*)-3-(2-fluorophenyl)prop-2-enethioate (**3-35**)

Pale yellow oil (25.9 mg, 44% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 16.0 Hz, 1H), 7.54 (td, *J* = 7.6, 1.8 Hz, 1H), 7.36 (tdd, *J* = 7.5, 5.1, 1.7 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.10 (dd, *J* = 10.7, 8.3 Hz, 1H), 6.81 (d, *J* = 16.0 Hz, 1H), 3.01 (t, *J* = 7.4 Hz, 2H), 1.64 (p, *J* = 7.4 Hz, 2H), 1.40 (p, *J* = 7.0 Hz, 2H), 1.32 – 1.25 (m, 8H), 0.88 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 190.1, 161.6 (d, *J* = 254.9 Hz), 132.8 (d, *J* = 2.5 Hz), 131.8 (d, *J* = 8.7 Hz), 129.3 (d, *J* = 2.8 Hz), 127.5 (d, *J* = 6.5 Hz), 124.5 (d, *J* = 3.6 Hz), 122.4 (d, *J* = 11.8 Hz), 116.2 (d, *J* = 21.9 Hz), 31.8, 29.5, 29.1, 29.1, 29.1, 28.9, 22.6, 14.1. **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -113.8.



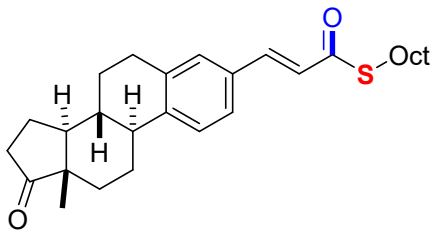
S-octyl (*E*)-3-(2-methoxyphenyl)prop-2-enethioate (**3-36**)

Pale yellow oil (52.6 mg, 86% yield). B/L form: **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.92 (d, *J* = 15.9 Hz, 1H), 7.51 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.35 (m, 1.36H), 7.22 (dd, *J* = 7.4, 1.8 Hz, 0.34H), 6.97 (q, *J* = 8.0 Hz, 1.45H), 6.90 (t, *J* = 8.1 Hz, 1.4H), 6.82 (d, *J* = 16.0 Hz, 1H), 6.20 (s, 0.34 H), 5.60 (s, 0.34 H), 3.89 (s, 3H), 3.78 (s, 1H), 3.00 (t, *J* = 7.4 Hz, 2H), 2.92 (t, *J* = 7.4 Hz, 0.7H), 1.67 – 1.58 (m, 3H), 1.40 (q, *J* = 6.8 Hz, 3H), 1.33 – 1.25 (m, 11H), 0.90 – 0.86 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 193.4, 190.5, 158.7, 157.2, 146.6, 135.8, 131.6, 130.9, 130.2, 129.1, 126.6, 125.8, 123.2, 122.8, 120.7, 120.7, 111.2, 110.9, 55.5, 55.5, 31.8, 29.6, 29.5, 29.2, 29.1, 29.1, 28.9, 28.8, 22.6, 14.0.



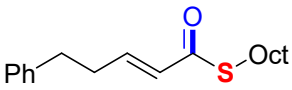
S-octyl (*E*)-3-(naphthalen-2-yl)prop-2-enethioate (**3-37**)

White solid (45.0 mg, 69% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.96 (s, 1H), 7.87 – 7.83 (m, 3H), 7.77 (d, *J* = 15.7 Hz, 1H), 7.67 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.54 – 7.50 (m, 2H), 6.83 (d, *J* = 15.7 Hz, 1H), 3.03 (t, *J* = 7.4 Hz, 2H), 1.66 (dt, *J* = 15.0, 7.4 Hz, 2H), 1.42 (m, 2H), 1.33 – 1.25 (m, 8H), 0.89 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 190.0, 140.2, 134.3, 133.3, 131.7, 130.5, 128.7, 128.6, 127.8, 127.3, 126.8, 125.4, 123.6, 31.8, 29.6, 29.1, 29.1, 29.0, 28.9, 22.6, 14.1.



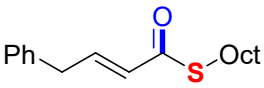
S-octyl (*E*)-3-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)prop-2-enethioate (**3-38**)

Yellow solid (66.0 mg, 73% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 15.8 Hz, 1H), 7.31 (q, *J* = 8.2 Hz, 2H), 7.26 (s, 1H), 6.67 (d, *J* = 15.8 Hz, 1H), 2.99 (t, *J* = 7.2 Hz, 2H), 2.92 (d, *J* = 4.7 Hz, 2H), 2.50 (dd, *J* = 18.9, 8.7 Hz, 1H), 2.42 (d, *J* = 14.3 Hz, 1H), 2.31 (d, *J* = 9.4 Hz, 1H), 2.21 – 2.10 (m, 1H), 2.09 – 2.01 (m, 2H), 1.97 (d, *J* = 11.4 Hz, 1H), 1.68 – 1.57 (m, 5H), 1.56 – 1.45 (m, 3H), 1.43 – 1.39 (m, 2H), 1.28 (s, 8H), 0.91 (s, 3H), 0.87 (t, *J* = 6.5 Hz, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ = 190.0, 142.7, 140.1, 137.2, 131.8, 129.1, 126.0, 125.7, 124.5, 50.5, 47.9, 44.6, 37.9, 35.8, 31.8, 31.5, 29.6, 29.2, 29.1, 29.1, 28.9, 28.9, 26.3, 25.6, 22.6, 21.6, 14.0, 13.8. **HRMS (ESI)**: calcd for $C_{29}H_{41}O_2S$ $[M+H]^+$ 453.2822; found 453.2826.



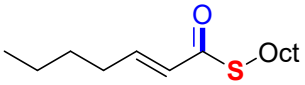
S-octyl (*E*)-5-phenylpent-2-enethioate (**3-39**)

Colorless oil (50.5 mg, 83% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 7.3 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 2H), 6.92 (dt, *J* = 15.4, 6.8 Hz, 1H), 6.13 (d, *J* = 15.5 Hz, 1H), 2.93 (t, *J* = 7.4 Hz, 2H), 2.80 – 2.76 (m, 2H), 2.51 (q, *J* = 7.1 Hz, 2H), 1.63 – 1.54 (m, 2H), 1.38 – 1.34 (m, 2H), 1.31 – 1.22 (m, 8H), 0.88 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 190.1, 143.8, 140.7, 129.2, 128.5, 128.3, 126.2, 34.3, 33.9, 31.8, 29.6, 29.1, 29.1, 28.9, 28.7, 22.6, 14.1.



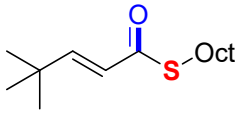
S-octyl (*E*)-4-phenylbut-2-enethioate (**3-40**)

Pale yellow oil (47.0 mg, 81% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.4 Hz, 2H), 7.28 (d, *J* = 7.0 Hz, 1H), 7.20 (d, *J* = 7.4 Hz, 2H), 7.05 (dt, *J* = 15.2, 6.8 Hz, 1H), 6.12 (d, *J* = 15.4 Hz, 1H), 3.54 (d, *J* = 6.7 Hz, 2H), 2.96 (t, *J* = 7.3 Hz, 2H), 1.69 – 1.50 (m, 2H), 1.44 – 1.36 (m, 2H), 1.30 (d, *J* = 4.1 Hz, 8H), 0.91 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 190.1, 143.1, 137.5, 129.6, 128.8, 128.7, 126.7, 38.3, 31.8, 29.5, 29.1, 29.1, 28.8, 28.7, 22.6, 14.1.



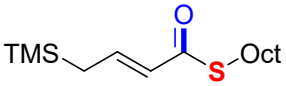
S-octyl (*E*)-hept-2-enethioate (**3-41**)

Pale yellow oil (41.0 mg, 80% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.88 (dt, *J* = 15.2, 7.0 Hz, 1H), 6.09 (d, *J* = 15.5 Hz, 1H), 2.91 (t, *J* = 7.4 Hz, 2H), 2.17 (dt, *J* = 7.7, 4.0 Hz, 2H), 1.64 – 1.54 (m, 2H), 1.48 – 1.40 (m, 2H), 1.39 – 1.30 (m, 4H), 1.30 – 1.21 (m, 8H), 0.90 (t, *J* = 7.3 Hz, 3H), 0.86 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 190.2, 145.3, 128.7, 31.8, 31.8, 30.1, 29.6, 29.1, 29.1, 28.8, 28.6, 22.6, 22.2, 14.0, 13.8.



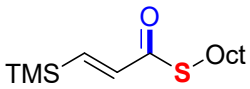
S-octyl (*E*)-4,4-dimethylpent-2-enethioate (**3-42**)

Yellow oil (47.6 mg, 93% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.87 (d, *J* = 15.8 Hz, 1H), 6.00 (d, *J* = 15.7 Hz, 1H), 2.92 (t, *J* = 7.3 Hz, 2H), 1.62 – 1.53 (m, 2H), 1.39 – 1.32 (m, 2H), 1.31 – 1.22 (m, 8H), 1.07 (s, 9H), 0.87 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 190.7, 154.7, 124.1, 33.7, 31.8, 29.6, 29.1, 29.1, 28.9, 28.7, 28.6, 22.6, 14.0.



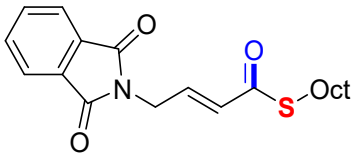
S-octyl (*E*)-4-(trimethylsilyl)but-2-enethioate (**3-43**)

Pale yellow oil (22.9 mg, 40% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.99 (dt, *J* = 15.3, 8.9 Hz, 1H), 5.97 (d, *J* = 15.2 Hz, 1H), 2.91 (t, *J* = 7.4 Hz, 2H), 1.72 (d, *J* = 8.9 Hz, 2H), 1.63 – 1.54 (m, 2H), 1.37 – 1.35 (m, 2H), 1.29 – 1.27 (m, 8H), 0.87 (t, *J* = 6.9 Hz, 3H), 0.06 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 189.7, 144.2, 126.9, 31.8, 29.7, 29.1, 29.1, 28.9, 28.6, 25.0, 22.6, 14.1, -1.8.



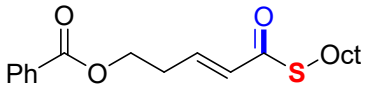
S-octyl (*E*)-3-(trimethylsilyl)prop-2-enethioate (**3-44**)

Dark yellow oil (39.2 mg, 72% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.11 (d, *J* = 18.8 Hz, 1H), 6.45 (d, *J* = 18.7 Hz, 1H), 2.94 (t, *J* = 7.3 Hz, 2H), 1.59 (p, *J* = 7.3 Hz, 2H), 1.36 (dd, *J* = 9.7, 5.6 Hz, 2H), 1.30 – 1.24 (m, 8H), 0.87 (t, *J* = 6.7 Hz, 3H), 0.14 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 190.4, 144.7, 140.4, 31.8, 29.5, 29.1, 29.1, 28.8, 28.8, 22.6, 14.0, -1.9.



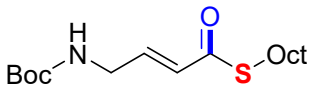
S-octyl (*E*)-4-(1,3-dioxoisoindolin-2-yl)but-2-enethioate (**3-45**)

Pale yellow solid (48.1 mg, 67% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.87 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.74 (dd, *J* = 5.5, 3.1 Hz, 2H), 6.81 (dt, *J* = 15.6, 5.4 Hz, 1H), 6.19 – 6.11 (m, 1H), 4.42 (dd, *J* = 5.5, 1.8 Hz, 2H), 2.91 (t, *J* = 7.3 Hz, 2H), 1.55 (p, *J* = 7.4 Hz, 2H), 1.33 (t, *J* = 7.6 Hz, 2H), 1.25 (dd, *J* = 11.9, 5.1 Hz, 8H), 0.85 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 189.3, 167.5, 136.3, 134.2, 131.9, 130.0, 123.5, 38.1, 31.7, 29.4, 29.1, 29.0, 28.9, 28.8, 22.6, 14.0.



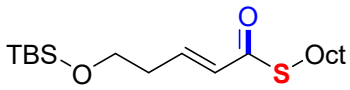
(*E*)-5-(octylthio)-5-oxopent-3-en-1-yl benzoate (**3-46**)

Colorless oil (62.6 mg, 90% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.02 (d, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 6.91 (dt, *J* = 15.6, 6.9 Hz, 1H), 6.24 (d, *J* = 15.5 Hz, 1H), 4.43 (t, *J* = 6.4 Hz, 2H), 2.93 (t, *J* = 7.4 Hz, 2H), 2.66 (qd, *J* = 6.6, 1.5 Hz, 2H), 1.58 (p, *J* = 7.4 Hz, 2H), 1.36 (dd, *J* = 9.6, 5.6 Hz, 2H), 1.27 (dd, *J* = 11.1, 6.0 Hz, 8H), 0.87 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 189.8, 166.3, 139.6, 133.0, 130.7, 129.9, 129.6, 128.3, 62.6, 31.7, 31.4, 29.5, 29.1, 29.0, 28.8, 28.7, 22.6, 14.0.



S-octyl (*E*)-4-((tert-butoxycarbonyl)amino)but-2-enethioate (**3-47**)

Yellow oil (29.6 mg, 45% yield).**^{1}H NMR** (500 MHz, $CDCl_3$) δ = 6.81 (dt, *J* = 15.7, 5.0 Hz, 1H), 6.19 (dt, *J* = 15.4, 1.9 Hz, 1H), 4.70 (s, 1H), 3.91 (s, 2H), 2.93 (t, *J* = 7.3 Hz, 2H), 1.58 (p, *J* = 7.4 Hz, 2H), 1.45 (s, 9H), 1.35 (d, *J* = 7.5 Hz, 2H), 1.27 (q, *J* = 6.9 Hz, 8H), 0.87 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 189.7, 155.5, 140.4, 128.3, 80.0, 41.3, 31.8, 29.5, 29.1, 29.0, 28.8, 28.8, 28.3, 22.6, 14.0. **HRMS (ESI)**: calcd for $C_{17}H_{32}NO_3S$ $[M+H]^+$ 330.2097; found 330.2095.

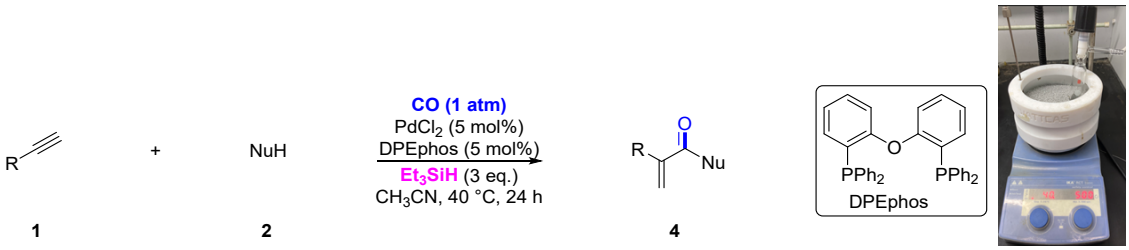


S-octyl (*E*)-5-((tert-butyldimethylsilyl)oxy)pent-2-enethioate (**3-48**)

Yellow oil (45.8 mg, 64% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 6.88 (dt, *J* = 15.8, 7.1 Hz, 1H), 6.15 (dd, *J* = 15.8, 1.8 Hz, 1H), 3.72 (t, *J* = 6.4 Hz, 2H), 2.92 (t, *J* = 7.3 Hz, 2H), 2.39 (q, *J* = 6.6 Hz, 2H), 1.57 (q, *J* = 7.5 Hz, 2H), 1.36 (t, *J* = 7.6 Hz, 2H), 1.27 (dd, *J* = 12.0, 6.1 Hz, 8H), 0.87 (d, *J* = 6.7 Hz, 12H), 0.04 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 190.0, 141.8, 130.3, 61.4, 35.6, 31.8, 29.6, 29.1, 29.1, 28.8, 28.6, 25.8, 22.6, 18.2, 14.0, -5.4. **HRMS (ESI)**: calcd for $C_{19}H_{39}O_2SSi$ $[M+H]^+$ 359.2435; found 359.2431.

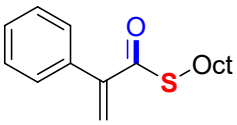
2.3 General Procedure for the Synthesis of Branch Products 4 and Characterization

An oven-dried 35 mL Schlenk tube with a Teflon screwcap was charged with $PdCl_2$ (1.8 mg, 0.01 mmol, 5 mol%), DPEphos (5.4 mg, 0.01 mmol, 5 mol%), the above-mentioned mixture was degassed and refilled with CO for 3 times under the rubber plug. Then, a solution of **1** (0.2 mmol), **2** (0.24 mmol) and Et_3SiH (100 μL, 0.6 mmol, 3.0 eq.) in 4 mL of dry CH_3CN were added to the mixture by syringe. And then, quickly replace to a Teflon screwcap and tighten it in a well-ventilated fume hood. Finally, the mixture was stirred at 40 °C for 24 h. After completion of the reaction, the crude reaction mixture was concentrated in vacuo and the residue was dissolved in $CDCl_3$, then the B/L ratio of the product is determined by ^1H NMR. Finally, these $CDCl_3$ fractions were collected and concentrated again, and the residue was purified by silica gel flash column chromatography (hexane/EtOAc) to give products **4**.



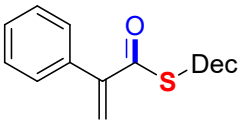
1 **2** **4**

Characterization of Products 4[2]



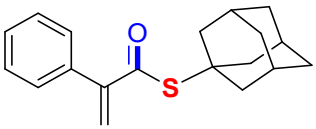
S-octyl 2-phenylprop-2-enethioate (**4-1**)

Clear yellow oil (39.2 mg, 71% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.42 – 7.38 (m, 2H), 7.36 (dt, *J* = 4.4, 2.8 Hz, 3H), 6.18 (s, 1H), 5.77 (s, 1H), 2.97 (t, *J* = 7.4 Hz, 2H), 1.62 (p, *J* = 7.4 Hz, 2H), 1.43 – 1.36 (m, 2H), 1.31 – 1.24 (m, 8H), 0.88 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 193.8, 148.6, 136.2, 128.5, 128.3, 128.2, 122.4, 31.8, 29.6, 29.3, 29.1, 29.1, 28.9, 22.6, 14.0.



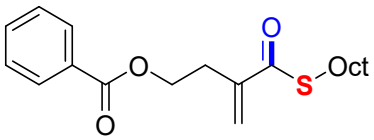
S-decyl 2-phenylprop-2-enethioate (**4-2**)

Dark yellow oil (41.3 mg, 68% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.38 (ddd, *J* = 15.4, 7.3, 3.5 Hz, 5H), 6.18 (s, 1H), 5.77 (s, 1H), 2.96 (t, *J* = 7.4 Hz, 2H), 1.62 (q, *J* = 7.3 Hz, 2H), 1.38 (t, *J* = 7.8 Hz, 2H), 1.27 (d, *J* = 6.4 Hz, 12H), 0.88 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 193.8, 148.5, 136.2, 128.5, 128.3, 128.2, 122.4, 31.9, 29.6, 29.5, 29.5, 29.3, 29.3, 29.1, 28.9, 22.6, 14.1.



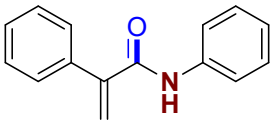
S-(adamantan-1-yl) 2-phenylprop-2-enethioate (**4-3**)

Yellow oil (32.2 mg, 54% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.40 – 7.36 (m, 2H), 7.36 – 7.32 (m, 3H), 6.07 (s, 1H), 5.71 (s, 1H), 2.20 (d, *J* = 3.0 Hz, 6H), 2.09 – 2.05 (m, 3H), 1.78 (dq, *J* = 12.5, 2.2 Hz, 3H), 1.74 – 1.70 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 194.4, 149.3, 136.4, 128.4, 128.2, 128.2, 121.6, 51.4, 41.7, 36.3, 29.8.



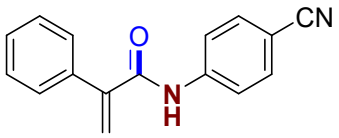
3-((octylthio)carbonyl)but-3-en-1-yl benzoate (**4-4**)

Clear yellow oil (41.1 mg, 59% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.06 – 7.93 (m, 2H), 7.59 – 7.50 (m, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 6.23 (s, 1H), 5.73 (s, 1H), 4.44 (t, *J* = 6.5 Hz, 2H), 2.92 (t, *J* = 7.4 Hz, 2H), 2.85 – 2.79 (m, 2H), 1.61 – 1.54 (m, 2H), 1.37 (t, *J* = 7.5 Hz, 2H), 1.32 – 1.24 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 193.3, 166.4, 144.6, 132.9, 130.2, 129.6, 128.3, 124.4, 63.1, 31.8, 31.3, 29.4, 29.1, 29.1, 29.0, 28.9, 22.6, 14.1.



N,2-diphenylacrylamide (**4-5)**

Colorless solid (27.2 mg, 61% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.52 (d, *J* = 8.0 Hz, 2H), 7.44 (tt, *J* = 8.3, 3.9 Hz, 6H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.29 (s, 1H), 5.73 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 165.2, 145.1, 137.6, 136.7, 129.0, 128.9, 128.8, 128.3, 124.6, 123.3, 119.9.



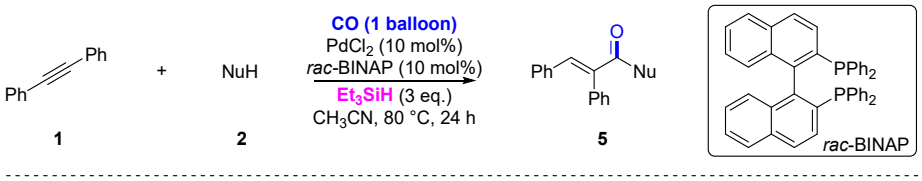
N-(4-cyanophenyl)-2-phenylacrylamide (**4-6**)

Yellow solid (25.3 mg, 51% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.65 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 8.9 Hz, 2H), 7.55 (d, *J* = 4.2 Hz, 1H), 7.44 (dtt, *J* = 6.9, 4.7, 2.0 Hz, 5H), 6.35 (s, 1H), 5.79 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 165.4, 144.5, 141.7, 136.1, 133.2, 129.1, 128.2, 124.5, 119.7, 118.7, 112.0, 107.5.

2.4 General Procedure for the Synthesis of Products 5 and Characterization

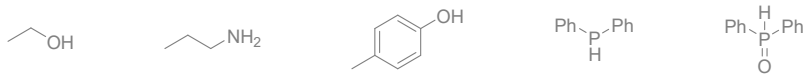
An oven-dried 10 mL Schlenk tube was charged with 1,2-diphenylethyne (17.8 mg, 0.1 mmol), $PdCl_2$ (1.8 mg, 0.01 mmol, 10 mol%), BINAP (6.2 mg, 0.01 mmol, 10 mol%), the above-mentioned mixture was degassed and refilled with CO for 3 times. Then, a solution of **2** (0.12 mmol, 1.2 eq.) and Et_3SiH (50 μL, 0.3 mmol, 3.0 eq.) in 2 mL of dry CH_3CN were added to the mixture by syringe. Finally, the mixture was stirred at 80 °C for 24 h under CO balloon. After completion of the reaction, the crude reaction mixture was concentrated in vacuo and the residue was purified by silica gel flash column chromatography (hexane/EtOAc) to give products **5**.

The authors have tried termination reagents such as aliphatic amine, alcohols and phenols and none of the target products were observed.

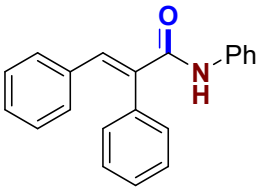


1 2 5

Unsuccessful nucleophilic reagent:

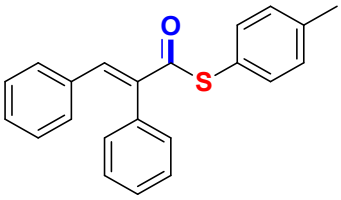


Characterization of Products 5[2]



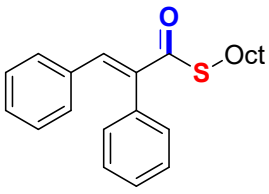
(*E*)-*N*,2,3-triphenylacrylamide (**5-1**)

White solid (22.2 mg, 74% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.98 (s, 1H), 7.51 (d, *J* = 7.0 Hz, 3H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.39 – 7.33 (m, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.20 (t, *J* = 5.0 Hz, 2H), 7.16 (t, *J* = 7.5 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 165.0, 138.2, 137.8, 135.8, 134.8, 134.6, 130.5, 130.0, 129.9, 128.9, 128.9, 128.8, 128.2, 124.4, 119.9.



S-(*p*-tolyl) (*E*)-2,3-diphenylprop-2-enethioate (**5-2**)

White solid (29.7 mg, 90% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.74 (s, 1H), 7.49 – 7.45 (m, 3H), 7.39 (dd, *J* = 6.8, 2.7 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.21 (m, 3H), 7.17 (t, *J* = 7.6 Hz, 2H), 7.07 (d, *J* = 7.5 Hz, 2H), 2.38 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 192.1, 139.4, 138.6, 136.8, 135.1, 134.6, 134.2, 131.1, 130.8, 129.9, 129.4, 128.9, 128.8, 128.3, 125.2, 21.3.



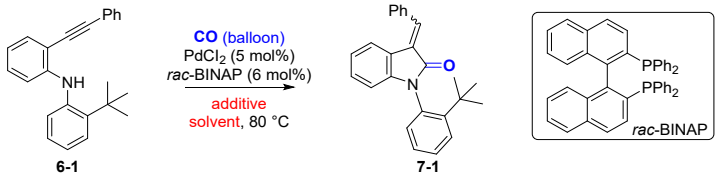
S-octyl (*E*)-2,3-diphenylprop-2-enethioate (**5-3**)

Yellow oil (32.0 mg, 91% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.46 – 7.42 (m, 3H), 7.31 – 7.29 (m, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 2H), 7.05 (d, *J* = 7.6 Hz, 2H), 2.93 (t, *J* = 7.4 Hz, 2H), 1.63 – 1.53 (m, 2H), 1.38 – 1.34 (m, 2H), 1.27 (s, 8H), 0.89 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 193.7, 139.1, 135.9, 135.5, 134.3, 131.0, 130.6, 129.2, 128.8, 128.5, 128.3, 31.8, 30.0, 29.3, 29.1, 29.1, 29.0, 22.6, 14.1.

2.5 Screening of Conditions for the Asymmetric Hydroamidation of 2-(*tert*-butyl)-*N*-(2-(phenylethynyl)phenyl)aniline

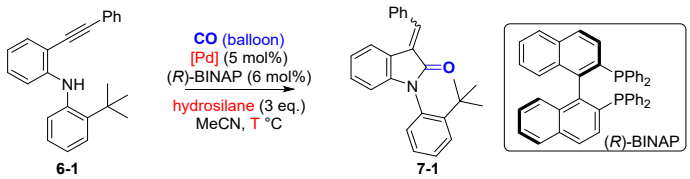
General procedure: An oven-dried 10 mL Schlenk tube was charged with [Pd], **L**, additive and **6-1** (16.3 mg, 0.05 mmol), the above-mentioned mixture was degassed and refilled with CO for 3 times. Then, a solution of Et_3SiH in 4 mL of dry CH_3CN was added to the mixture by syringe. Finally, the mixture was stirred at 60-80 °C for 24 h under CO balloon. After completion of the reaction, the *ee* and *Z*/*E* ratio of the product is determined by HPLC. And then the crude reaction mixture was concentrated in vacuo, and the residue was dissolved in $CDCl_3$, the yield of the product **7-1** is determined by ^1H NMR with 1,3,5-trimethoxybenzene (8.3 mg, 0.05 mmol) as the internal standard.

Table S1. Screening of solvents and additives



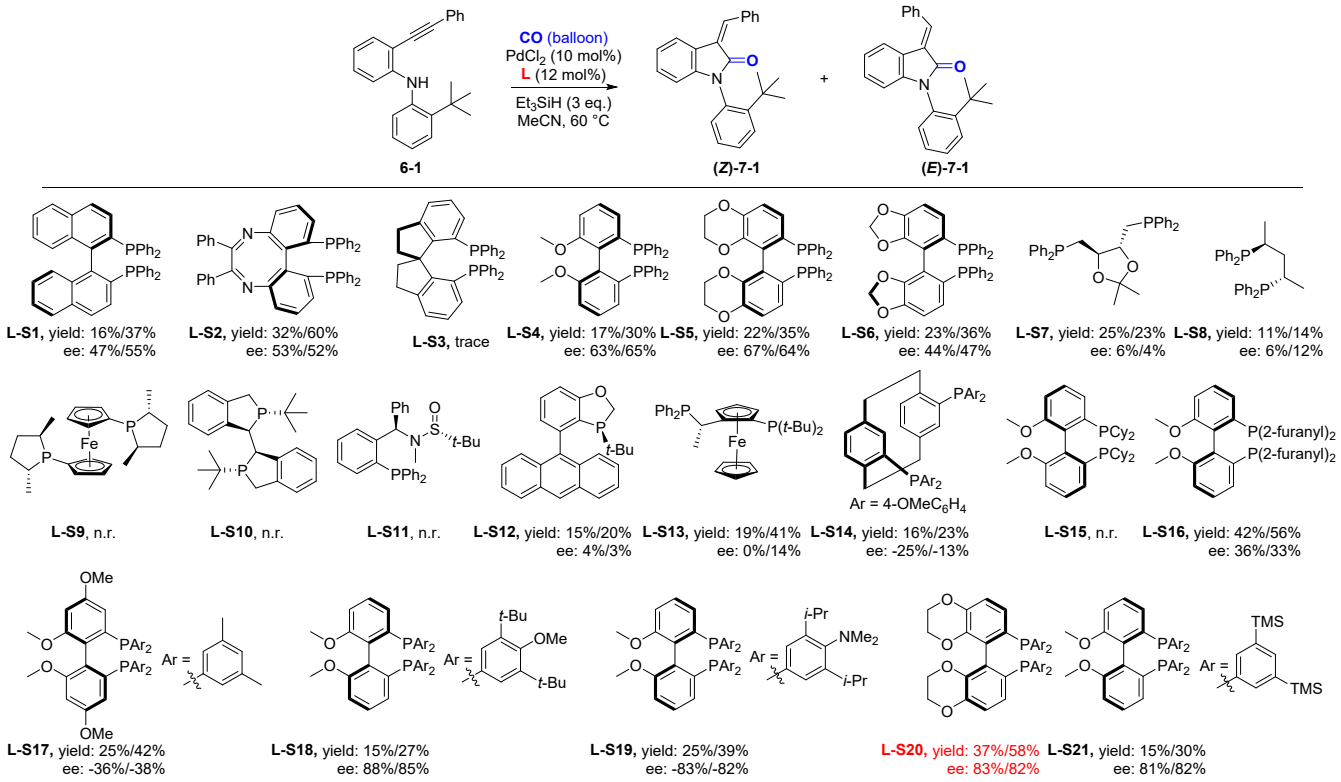
entry	additive	solvent	yield
1	PTSA•H_2O (20 mol%)	MeCN	n.r.
2	PTSA•H_2O (20 mol%)	dioxane	n.r.
3	PTSA•H_2O (20 mol%)	toluene	trace
4	PTSA•H_2O (20 mol%)	anisole	trace
5	$(PhO)_2P(O)OH$ (20 mol%)	anisole	trace
6	HCl (20 mol%)	anisole	n.r.
7	AcOH (20 mol%)	anisole	n.r.
8	PhCOOH (20 mol%)	anisole	n.r.
9	Et_3SiH (3.0 eq.)	anisole	trace
10	Et_3SiH (3.0 eq.)	MeCN	64%

Table S2. Screening of Palladium sources and hydrosilanes



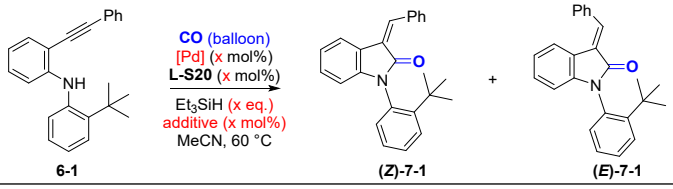
entry	[Pd]	hydrosilane	T (°C)	yield	ee
1	$PdCl_2$	*i*-Pr_3SiH	80	trace	
2	$PdCl_2$	$PhSiH_3$	80	moderate	47%
3	$Pd(TFA)_2$	Et_3SiH	80	high	44%
4	$PdCl_2$	$PhSiH_3$	60	low	52%
5	$PdCl_2$	Et_3SiH	60	moderate	56%
6	PdI_2	Et_3SiH	60	trace	/
7	$Pd(MeCN)_4(BF_4)_2$	Et_3SiH	60	trace	/
8	$Pd(OAc)_2$	Et_3SiH	60	n.r.	/
9	$Pd(acac)_2$	Et_3SiH	60	n.r.	/
10	$[Pd(C_3H_5)Cl]_2$	Et_3SiH	60	n.r.	/

11	$Pd(MeCN)_2Cl_2$	Et_3SiH	60	moderate	51%
12	$Pd(PhCN)_2Cl_2$	Et_3SiH	60	moderate	50%
13	$Pd(COD)_2Cl_2$	Et_3SiH	60	moderate	47%



Scheme S1. Screening of ligands.

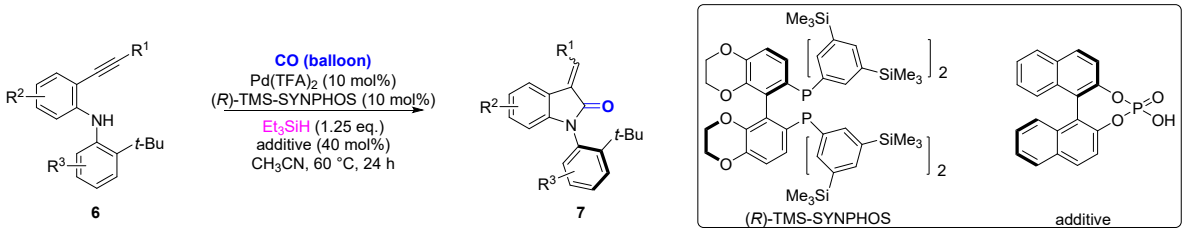
Table S3. Screening of additives and equivalents



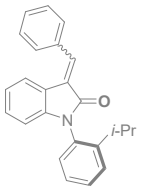
entry	[Pd] (x mol%)	**L-S20** (x mol%)	Et_3SiH (x eq.)	additive (x mol%)	yield *Z*/*E* (%)	ee *Z*/*E* (%)
1	$PdCl_2$ (10)	12	3	$(PhO)_2P(O)OH$ (20)	24/74	88/85
2	$PdCl_2$ (10)	12	1	$(PhO)_2P(O)OH$ (20)	18/59	91/88
3	$PdCl_2$ (10)	12	1	$(PhO)_2P(O)OH$ (60)	16/62	92/91
4	$PdCl_2$ (10)	12	1.25	$(PhO)_2P(O)OH$ (10)	10/46	73/74
5	$PdCl_2$ (10)	12	1.25	$(PhO)_2P(O)OH$ (40)	20/71	91/90
6	$PdCl_2$ (5)	6	1.25	$(PhO)_2P(O)OH$ (40)	16/43	93/92
7	$PdCl_2$ (10)	10	1.25	$(PhO)_2P(O)OH$ (40)	22/70	91/90
8	$PdCl_2$ (10)	10	1.25	benzoic acid (40)	36/60	90/89
9	$PdCl_2$ (10)	10	1.25	(*R*)-(-)-1,1'-binaphthalene-2,2'-diyl hydrogen phosphate (40)	23/71	92/91
10	$Pd(dba)_2$ (10)	10	1.25	(*R*)-(-)-1,1'-binaphthalene-2,2'-diyl hydrogen phosphate (40)	13/21	96/93
11	**$Pd(TFA)_2$ (10)**	**10**	**1.25**	**(*R*)-(-)-1,1'-binaphthalene-2,2'-diyl hydrogen phosphate (40)**	**18/79**	**91/91**

2.6 General Procedure for the Asymmetric Synthesis of Products 7 and Characterization

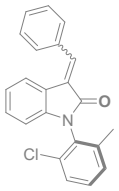
An oven-dried 10 mL Schlenk tube was charged with $Pd(TFA)_2$ (3.3 mg, 0.01 mmol, 10 mol%), (*R*)-TMS-SYNPHOS (12.2 mg, 0.01 mmol, 10 mol%), (*R*)-(-)-1,1'-binaphthalene-2,2'-diyl hydrogen phosphate (14 mg, 0.04 mmol, 40 mol%) and **6** (0.1 mmol), the above-mentioned mixture was degassed and refilled with CO for 3 times. Then, a solution of Et_3SiH (20 μL, 0.125 mmol, 1.25 eq.) in 4 mL of dry CH_3CN was added to the mixture by syringe. Finally, the mixture was stirred at 60 °C for 24 h under CO balloon. After completion of the reaction, the *ee* and *Z*/*E* ratio of the product is determined by HPLC. And then, the crude reaction mixture was concentrated in vacuo, the residue was purified by silica gel flash column chromatography (hexane/EtOAc) to give products **7**. The authors tried groups with less spatial site resistance than *tert*-butyl, such as isopropyl, and only lower enantioselectivity was observed. We found by calculation that this may be due to the lower rotational energy barrier of the product.



Unsuccessful examples:

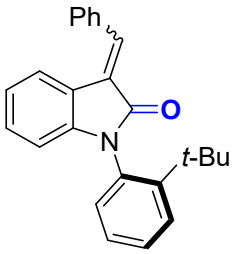


7-32, 91% yield (*Z*/*E* = *1:3.9*)
24% ee, 19% ee
$\Delta G^{\ddagger}$ = 27.02 kcal/mol
(computed at the M062X/def2TZVP // M062X/6 31G(d,p) level)



7-33, 88% yield (*Z*/*E* = *1:3.3*)
14% ee, 11% ee

Characterization of Products 7

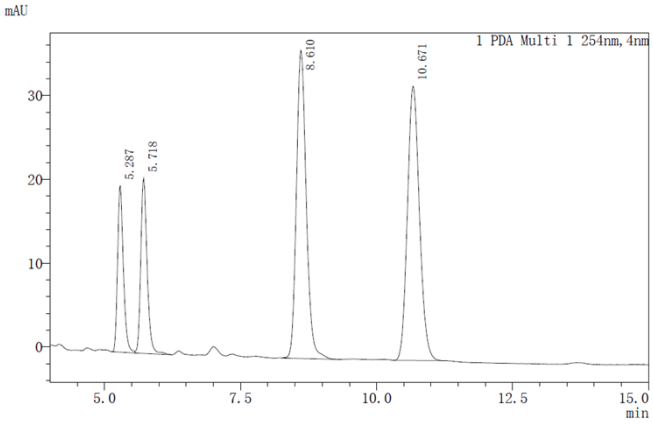


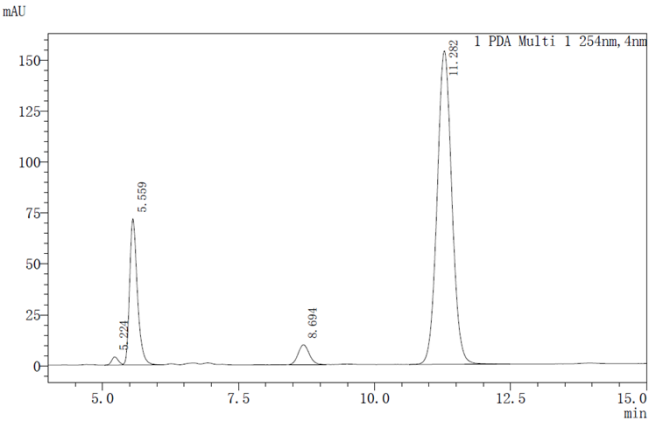
3-benzylidene-1-(2-(*tert*-butyl)phenyl)indolin-2-one (**7-1**)

Yellow solid (33.9 mg, 96% yield, *Z/E* ≈ 1:4, 91% ee, 91% ee). (*Z*) Form: $[\alpha]_D^{25}$ = +38.8 (c = 0.17 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.9 Hz, 2H), 7.68 – 7.58 (m, 3H), 7.45 – 7.39 (m, 4H), 7.33 (td, *J* = 7.6, 1.2 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.11 – 7.01 (m, 2H), 6.37 (d, *J* = 7.7 Hz, 1H), 1.32 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.2, 149.6, 144.6, 137.7, 133.8, 133.2, 132.2, 131.3, 130.6, 129.3, 129.0, 128.9, 128.3, 127.8, 126.1, 124.6, 122.0, 118.9, 110.5, 35.8, 31.7. (*E*) Form: $[\alpha]_D^{25}$ = +14.3 (c = 0.07 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.75 – 7.70 (m, 3H), 7.67 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.50 (t, *J* = 7.3 Hz, 2H), 7.47 – 7.42 (m, 2H), 7.34 (td, *J* = 7.6, 1.1 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.06 (dd, *J* = 7.7, 0.9 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.36 (d, *J* = 7.8 Hz, 1H), 1.35 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.5, 149.6, 146.5, 137.9, 135.0, 133.2, 131.2, 129.8, 129.7, 129.4, 129.0, 128.7, 127.9, 127.3, 122.7, 121.9, 121.2, 110.9, 35.7, 31.7.

HRMS (ESI): calcd for $C_{25}H_{24}NO$ $[M+H]^+$ 354.1852; found 354.1854.

The ee was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), hexane/isopropanol = 90/10, 1.0 mL/min, λ = 254 nm, t_R (minor) = 5.224/8.694 min, t_R (major) = 5.559/11.282 min.



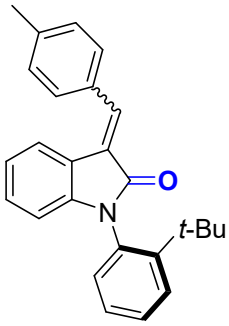


PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	5.287	19841	147014	11.470	--
2	5.718	20902	169341	13.212	1.987
3	8.610	36786	461636	36.016	10.341
4	10.671	32700	503765	39.303	5.505

PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	5.224	3992	34374	0.911	--
2	5.559	71664	711620	18.856	1.310
3	8.694	9698	136250	3.610	9.660
4	11.282	153733	2891645	76.622	5.884

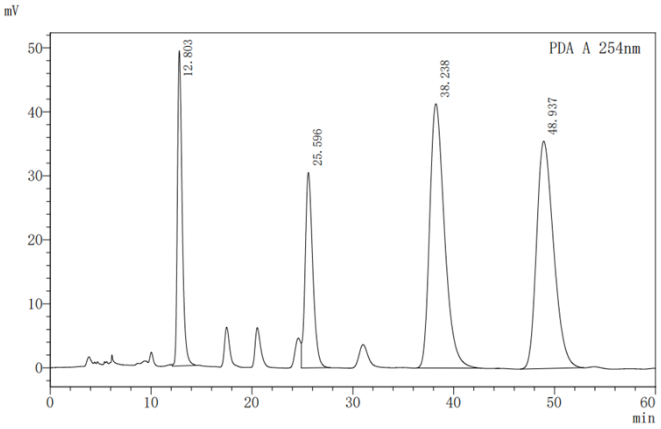


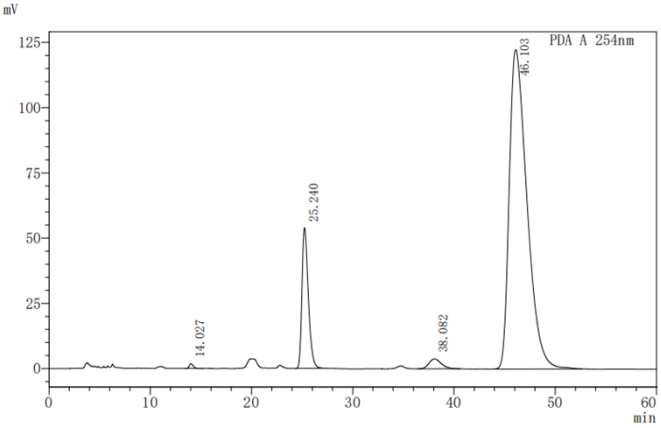
1-(2-(*tert*-butyl)phenyl)-3-(4-methylbenzylidene)indolin-2-one (**7-2**)

Yellow oil (34.1 mg, 93% yield, *Z/E* ≈ 1:6.3, 96% ee, 96% ee). (*Z*)&(*E*) Form: $[\alpha]_D^{25}$ = +10.9 (c = 0.11 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.0 Hz, 0.3H), 7.92 (s, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.69 – 7.58 (m, .3.64H), 7.44 (t, *J* = 7.5 Hz, 1.22H), 7.34 (t, *J* = 7.9 Hz, 1.24H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 0.33H), 7.15 (t, *J* = 7.8 Hz, 1.27H), 7.06 (d, *J* = 7.6 Hz, 1.46H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.35 (d, *J* = 7.8 Hz, 1.18H). 2.45 (s, 3H), 2.40 (s, 0.52H), 1.35 (s, 9H), 1.32 (s, 1.63H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.6, 167.3, 149.7, 149.6, 146.4, 144.4, 141.3, 140.1, 138.2, 137.9, 133.3, 133.3, 132.5, 132.1, 131.3, 131.3, 129.6, 129.5, 129.4, 129.3, 129.2, 129.1, 129.0, 128.9, 128.5, 127.9, 127.8, 126.5, 125.1, 124.8, 122.6, 121.8, 121.4, 118.7, 110.8, 110.4, 35.8, 35.7, 31.8, 31.7, 21.7, 21.6.

HRMS (ESI): calcd for $C_{26}H_{26}NO$ $[M+H]^+$ 368.2009; found 368.2009.

The ee was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), hexane/isopropanol = 99/1, 0.8 mL/min, λ = 254 nm, t_R (minor) = 14.027/38.082 min, t_R (major) = 25.240/46.103 min.



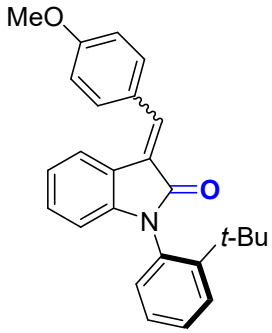


PDA A 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	12.803	49272	1601819	13.834	--
2	25.596	30551	1587502	13.711	11.815
3	38.238	41306	4218638	36.435	6.352
4	48.937	35542	4170707	36.021	3.726

PDA A 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	14.027	1800	47869	0.272	--
2	25.240	53926	2364487	13.412	12.219
3	38.082	3805	320016	1.815	7.696
4	46.103	122399	14897542	84.502	2.969

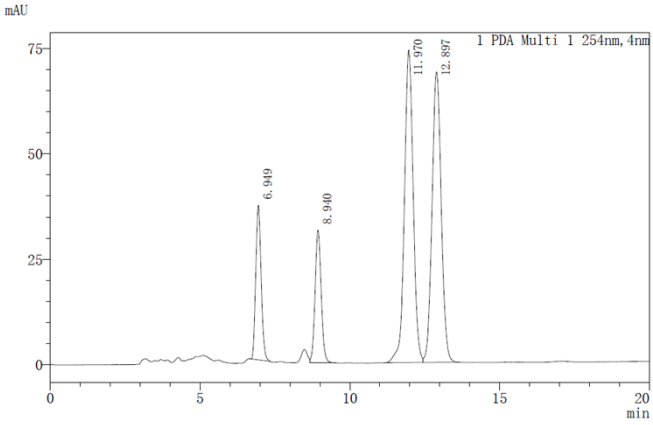


1-(2-(*tert*-butyl)phenyl)-3-(4-methoxybenzylidene)indolin-2-one (**7-3**)

Yellow oil (34.9 mg, 91% yield, *Z*/*E* ≈ 1:3.2, 96% ee, 96% ee). (*Z*)&(*E*) Form: $[\alpha]_D^{25}$ = +2.0 (c = 0.3 in MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.9 Hz, 0.56H), 7.89 (s, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.73 (d, *J* = 8.6 Hz, 2H), 7.66 (ddd, *J* = 8.0, 3.9, 1.2 Hz, 1.29H), 7.59 (t, *J* = 3.6 Hz, 0.55H), 7.46 – 7.39 (m, 1.31H), 7.33 (tdd, *J* = 6.0, 4.7, 1.4 Hz, 1.33H), 7.16 (t, *J* = 7.7 Hz, 1.32H), 7.09 – 7.04 (m, 1.56H), 7.02 (d, *J* = 8.7 Hz, 2H), 6.96 – 6.90 (m, 1.46H), 6.36 (dd, *J* = 7.7, 3.3 Hz, 1.22H), 3.90 (s, 3H), 3.86 (s, 0.76H), 1.34 (s, 9H), 1.31 (s, 2.24H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.77, 167.49, 161.68, 160.89, 149.59, 146.19, 144.03, 138.1, 137.7, 134.7, 133.3, 133.3, 131.5, 131.3, 131.2, 129.3, 129.3, 129.2, 128.9, 128.9, 128.1, 127.9, 127.8, 127.3, 127.0, 125.3, 125.0, 123.4, 122.2, 121.8, 121.5, 118.4, 114.1, 113.8, 110.8, 110.3, 55.4, 55.4, 35.7, 35.7, 31.7, 31.7.

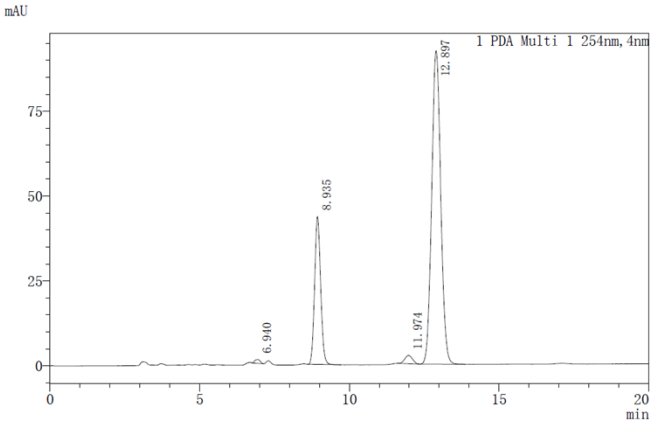
HRMS (ESI): calcd for $C_{26}H_{26}NO_2$ $[M+H]^+$ 384.1958; found 384.1956.

The ee was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), hexane/isopropanol = 90/10, 1 mL/min, λ = 254 nm, t_R (minor) = 6.940/11.974 min, t_R (major) = 8.935/12.897 min.



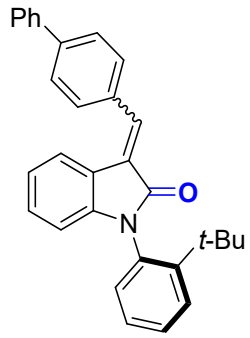
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	6.949	36627	458735	11.797	--
2	8.940	31472	447166	11.499	5.499
3	11.970	74123	1516006	38.985	6.636
4	12.897	68869	1466755	37.719	1.686



PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	6.940	1137	13558	0.521	--
2	8.935	43554	608874	23.385	5.662
3	11.974	2443	43322	1.664	7.035
4	12.897	92366	1937961	74.431	1.764

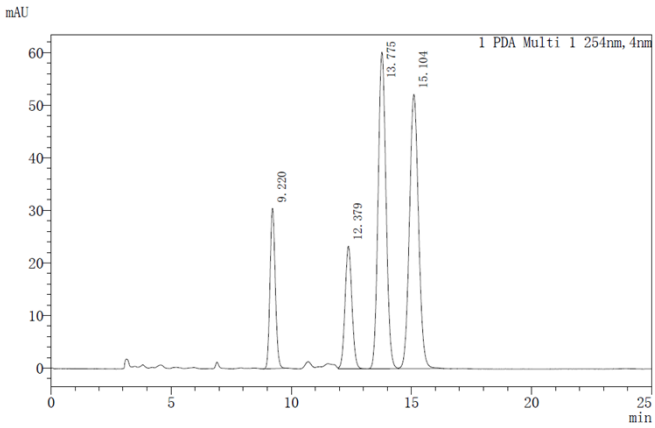


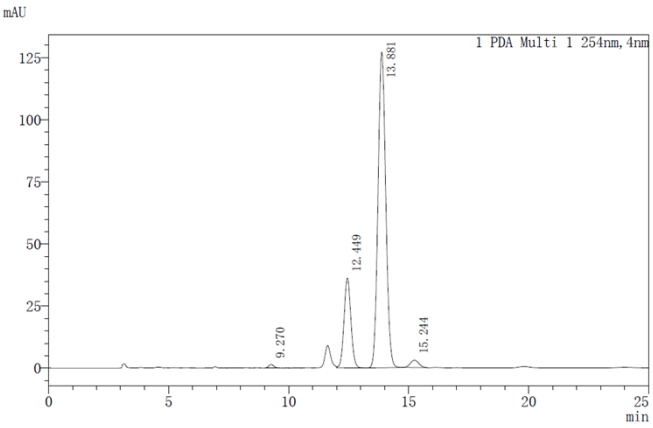
3-([1,1'-biphenyl]-4-ylmethylene)-1-(2-(*tert*-butyl)phenyl)indolin-2-one (**7-4**)

Yellow solid (39.9 mg, 93% yield, *Z/E* ≈ 1:4, 94% ee, 95% ee). (*Z*)&(*E*) Form: $[\alpha]_D^{25}$ = +9.3 (c = 0.15 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.3 Hz, 0.31H), 7.97 (s, 1H), 7.83 (d, *J* = 8.3 Hz, 3H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.69 (t, *J* = 8.9 Hz, 3.56H), 7.66 – 7.62 (m, 0.65H), 7.50 (t, *J* = 7.6 Hz, 2.15H), 7.45 (t, *J* = 7.5 Hz, 1.45H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.37 – 7.32 (m, 1.38H), 7.18 (t, *J* = 7.7 Hz, 1.22H), 7.07 (d, *J* = 6.8 Hz, 1.33H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.37 (d, *J* = 7.8 Hz, 1.17H), 1.36 (s, 9H), 1.33 (s, 1.57H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.5, 167.3, 149.6, 146.5, 144.5, 142.5, 140.4, 140.2, 137.5, 137.2, 133.9, 133.2, 133.0, 132.9, 131.3, 131.2, 130.1, 129.7, 129.4, 129.3, 129.0, 128.9, 128.8, 128.8, 127.9, 127.9, 127.8, 127.2, 127.1, 127.1, 126.9, 125.9, 124.7, 122.7, 121.9, 121.3, 118.9, 110.9, 110.5, 35.8, 35.7, 31.74, 31.69.

HRMS (ESI): calcd for $C_{31}H_{28}NO$ $[M+H]^+$ 430.2165; found 430.2165.

The ee was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), hexane/isopropanol = 95/5, 1 mL/min, λ = 254 nm, t_R (minor) = 9.270/15.244 min, t_R (major) = 12.449/13.881 min.



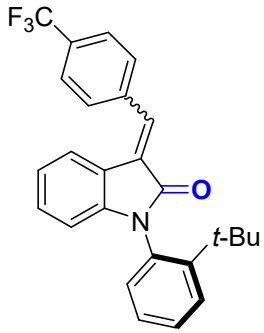


PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	9.220	30470	465948	12.680	--
2	12.379	23327	465200	12.659	6.704
3	13.775	60210	1372688	37.355	2.449
4	15.104	52169	1370906	37.306	2.041

PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	9.270	1440	20613	0.563	--
2	12.449	36166	717479	19.591	6.876
3	13.881	127090	2849101	77.797	2.540
4	15.244	3008	75022	2.049	2.142

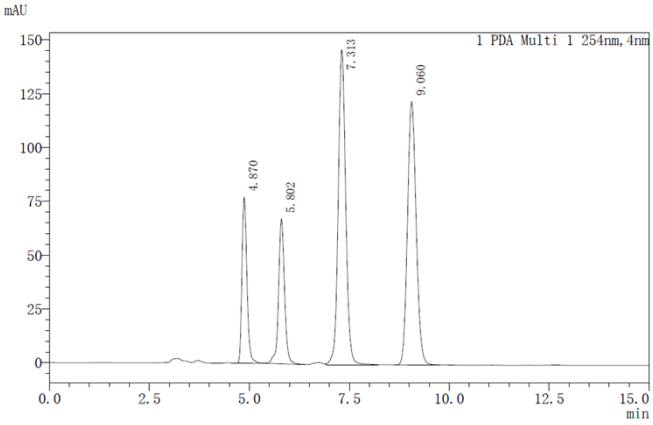


1-(2-(*tert*-butyl)phenyl)-3-(4-(trifluoromethyl)benzylidene)indolin-2-one (**7-5**)

(41.3 mg, 98% yield, *Z/E* ≈ 1:3.5, 78% ee, 82% ee). (*Z*) Form: yellow oil, $[\alpha]_D^{25}$ = +32.0 (c = 0.4 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 3H), 7.62 (d, *J* = 7.5 Hz, 2H), 7.46 – 7.41 (m, 1H), 7.33 (td, *J* = 7.6, 1.2 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.05 (dd, *J* = 7.7, 1.2 Hz, 1H), 6.38 (d, *J* = 7.8 Hz, 1H), 1.31 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.9, 149.5, 145.0, 136.9, 135.2, 132.9, 132.0, 131.5 (q, *J* = 32.4 Hz), 131.1, 129.7, 129.4, 129.0, 128.3, 127.9, 125.1 (q, *J* = 3.8 Hz), 123.9, 122.2, 121.2 (q, *J* = 163.4 Hz), 119.4, 110.7, 35.7, 31.7. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.9. (*E*) Form: yellow solid, $[\alpha]_D^{25}$ = +11.3 (c = 0.3 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.7 Hz, 1H), 7.05 (d, *J* = 7.7 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.37 (d, *J* = 7.9 Hz, 1H), 1.34 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.0, 149.6, 146.9, 138.7, 135.3, 132.9, 131.1 (q, *J* = 32.8 Hz), 131.1, 130.5, 129.5, 129.5, 129.1, 129.0, 128.0, 125.7 (q, *J* = 3.6 Hz), 123.9 (q, *J* = 272.3 Hz), 122.7, 122.1, 120.7, 111.1, 35.7, 31.7. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.7.

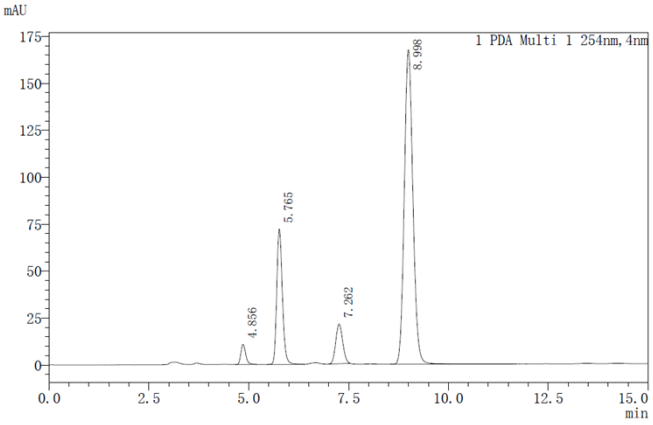
HRMS (ESI): calcd for $C_{26}H_{23}F_3NO$ $[M+H]^+$ 422.1726; found 422.1726.

The ee was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), hexane/isopropanol = 90/10, 1 mL/min, λ = 254 nm, t_R (minor) = 4.856/7.262 min, t_R (major) = 5.765/8.998 min.



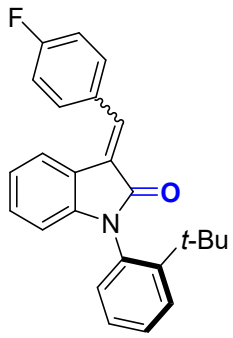
PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	4.870	76966	667470	13.021	--
2	5.802	67241	700589	13.667	3.635
3	7.313	146275	1906659	37.196	4.880
4	9.060	122268	1851275	36.115	4.650



PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	4.856	10721	89924	2.522	--
2	5.765	72030	706386	19.814	3.628
3	7.262	21172	256897	7.206	4.987
4	8.998	167287	2511899	70.458	4.721

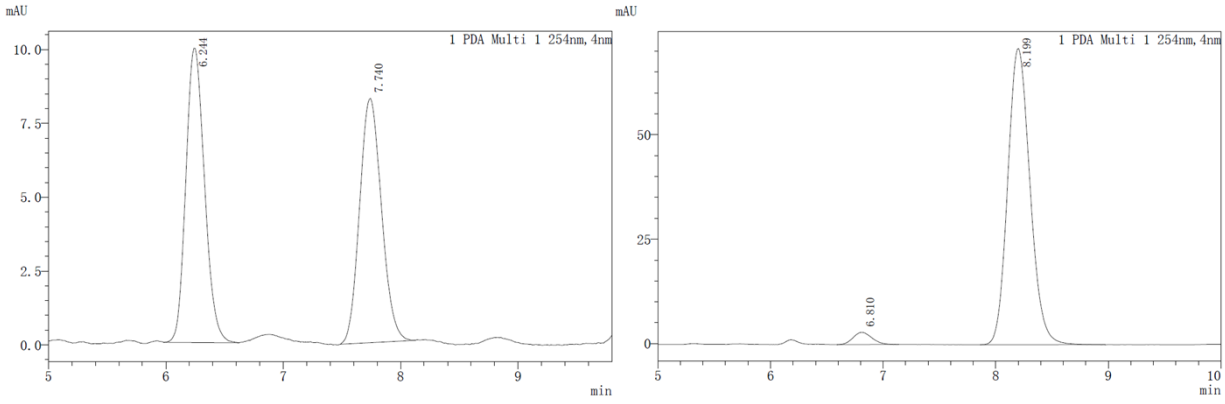


1-(2-(*tert*-butyl)phenyl)-3-(4-fluorobenzylidene)indolin-2-one (**7-6**)

Yellow oil (35.3 mg, 95% yield, *Z*/*E* ≈ 1:2.6, 90% ee, 90% ee). (*Z*) Form: $[\alpha]_D^{25}$ = +36.5 (c = 0.17 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.42 (dd, *J* = 8.8, 5.6 Hz, 2H), 7.66 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.58 (s, 1H), 7.45 – 7.41 (m, 1H), 7.33 (td, *J* = 7.5, 1.4 Hz, 1H), 7.19 (dd, *J* = 11.5, 4.8 Hz, 1H), 7.12 – 7.04 (m, 4H), 6.37 (d, *J* = 7.8 Hz, 1H), 1.31 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.3, 163.9 (d, *J* = 252.9 Hz), 149.5, 144.5, 136.3, 134.6 (d, *J* = 8.8 Hz), 133.1, 131.2, 130.2 (d, *J* = 2.9 Hz), 129.3, 129.0, 128.9, 127.8, 125.6 (d, *J* = 2.4 Hz), 124.5, 122.0, 118.8, 115.4 (d, *J* = 21.7 Hz), 110.5, 35.7, 31.7. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -108.2. (*E*) Form: $[\alpha]_D^{25}$ = +25.2 (c = 0.31 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.72 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.69 – 7.65 (m, 2H), 7.46 – 7.41 (m, 1H), 7.34 (td, *J* = 7.5, 1.4 Hz, 1H), 7.19 (t, *J* = 8.6 Hz, 3H), 7.05 (dd, *J* = 7.7, 1.3 Hz, 1H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.36 (d, *J* = 7.8 Hz, 1H), 1.34 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.3, 163.3 (d, *J* = 251.3 Hz), 149.6, 146.5, 136.6, 133.1, 131.4 (d, *J* = 8.4 HzH), 131.2, 131.0 (d, *J* = 3.5 Hz), 129.9, 129.4, 129.0, 127.9 (d, *J* = 10.7 Hz), 127.2, 122.4, 121.9, 121.0, 115.9 (d, *J* = 21.8 Hz), 111.0, 35.7, 31.67. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -109.9.

HRMS (ESI): calcd for $C_{25}H_{23}FNO$ $[M+H]^+$ 372.1758; found 372.1761.

The ee was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), hexane/isopropanol = 95/5, 1 mL/min, λ = 254 nm, (*Z*) Form: t_R (minor) = 6.810, t_R (major) = 8.199; (*E*) Form: t_R (minor) = 12.944 min, t_R (major) = 15.041 min.

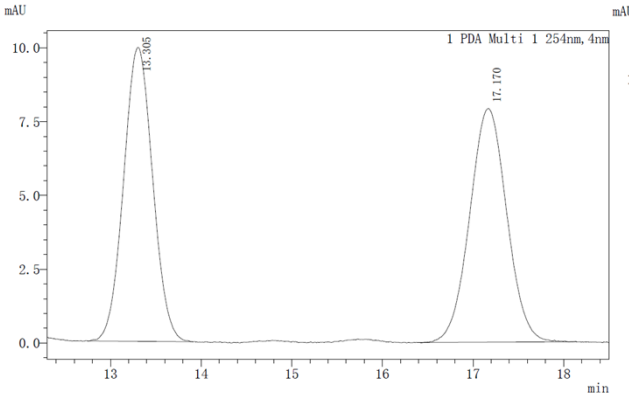


PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	6.244	9970	110365	50.682	--
2	7.740	8269	107393	49.318	4.571

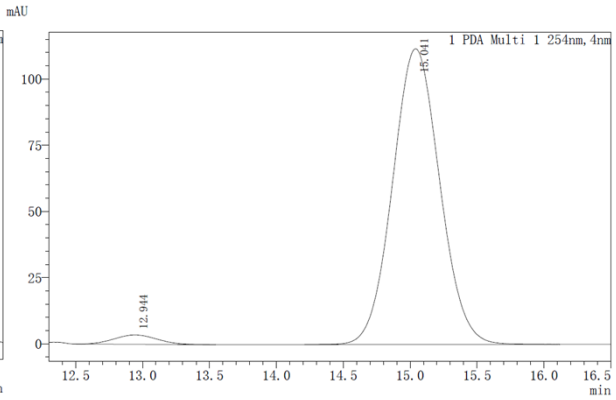
PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	6.810	2906	33504	3.316	--
2	8.199	70913	976884	96.684	4.041



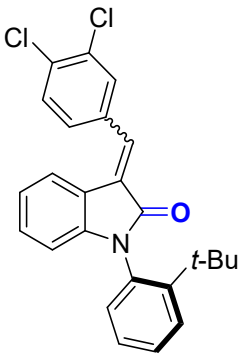
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	13.305	9956	222275	49.645	--
2	17.170	7919	225457	50.355	5.716



PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	12.944	3537	79200	2.814	--
2	15.041	111633	2735398	97.186	3.329

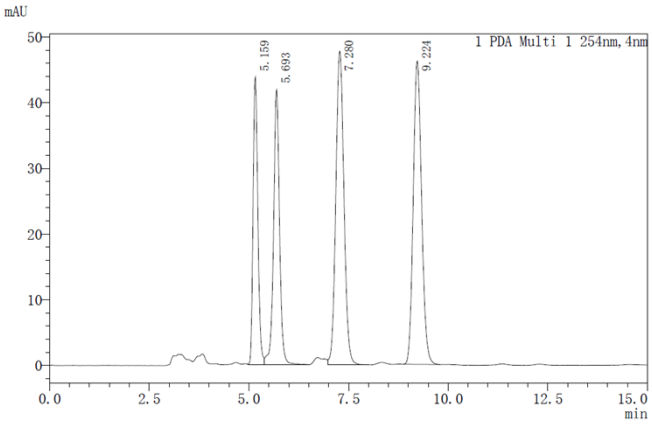


1-(2-(*tert*-butyl)phenyl)-3-(3,4-dichlorobenzylidene)indolin-2-one (**7-7**)

Yellow solid (41.7 mg, 99% yield, *Z/E* ≈ 1:2.1, 82% ee, 84% ee). (*Z*) Form: $[\alpha]_D^{25}$ = +45.7 (c = 0.07 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 1.6 Hz, 1H), 8.20 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 6.6 Hz, 2H), 7.43 (dd, *J* = 11.3, 4.1 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.7 Hz, 1H), 6.37 (d, *J* = 7.8 Hz, 1H), 1.31 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.0, 149.5, 144.9, 134.4, 134.3, 133.7, 133.5, 132.9, 132.5, 131.3, 131.1, 130.2, 129.6, 129.4, 129.1, 127.9, 127.7, 124.0, 122.2, 119.2, 110.7, 35.8, 31.7. (*E*) Form: $[\alpha]_D^{25}$ = +7.1 (c = 0.17 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.77 (s, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.56 (q, *J* = 8.3 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.19 (t, *J* = 7.7 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.36 (d, *J* = 7.9 Hz, 1H), 1.34 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.9, 149.6, 146.8, 135.0, 134.4, 133.5, 133.1, 132.9, 131.1, 130.9, 130.8, 130.4, 129.5, 129.0, 128.7, 128.5, 128.0, 122.7, 122.2, 120.6, 111.1, 35.7, 31.7.

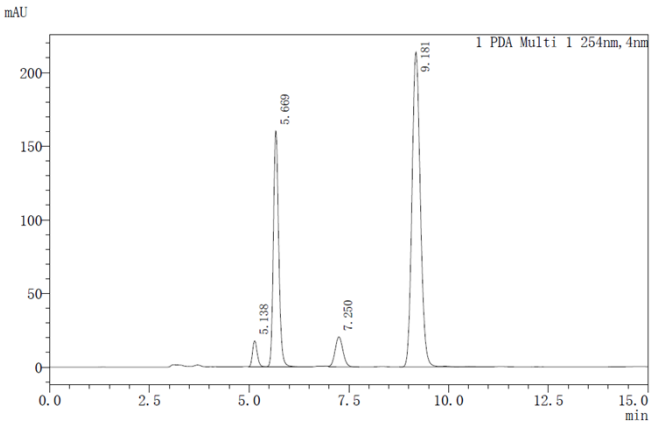
HRMS (ESI): calcd for $C_{25}H_{22}Cl_2NO$ $[M+H]^+$ 422.1073; found 422.1071.

The ee was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), hexane/isopropanol = 90/10, 1 mL/min, λ = 254 nm, t_R (minor) = 5.138/7.250 min, t_R (major) = 5.669/9.181 min.



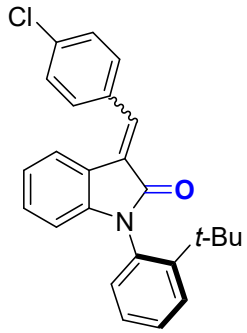
PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	5.159	43761	362393	16.860	--
2	5.693	41871	435857	20.278	2.111
3	7.280	47742	676465	31.472	4.851
4	9.224	46195	674682	31.389	5.025



PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	5.138	17724	146354	2.907	--
2	5.669	160157	1482038	29.437	2.189
3	7.250	20387	279348	5.549	5.066
4	9.181	213833	3126895	62.108	5.068

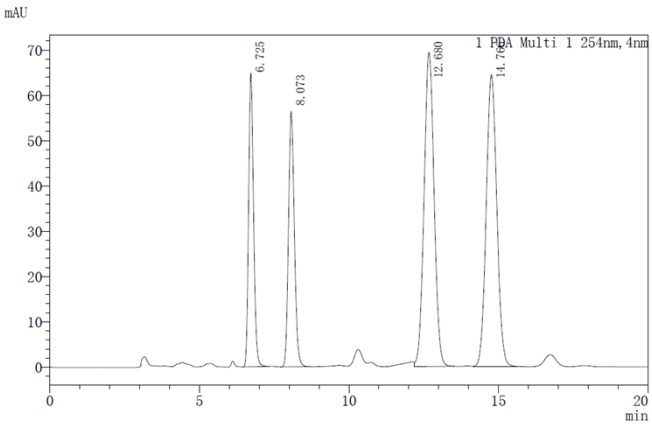


1-(2-(*tert*-butyl)phenyl)-3-(4-chlorobenzylidene)indolin-2-one (**7-8**)

Yellow oil (37.2 mg, 96% yield, *Z/E* ≈ 1:2.8, 96% ee, 96% ee). (*Z*) Form: $[\alpha]_D^{25}$ = +51.1 (c = 0.09 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.6 Hz, 2H), 7.66 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.55 (s, 1H), 7.45 – 7.40 (m, 1H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.33 (td, *J* = 7.5, 1.3 Hz, 1H), 7.19 (dd, *J* = 11.2, 4.1 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.05 (dd, *J* = 7.7, 1.4 Hz, 1H), 6.37 (d, *J* = 7.8 Hz, 1H), 1.31 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.2, 149.5, 144.6, 136.5, 136.0, 133.5, 133.0, 132.3, 131.2, 129.3, 129.1, 129.0, 128.5, 127.9, 126.5, 124.3, 122.1, 119.0, 110.6, 35.7, 31.7. (*E*) Form: $[\alpha]_D^{25}$ = +20.0 (c = 0.18 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.66 (dd, *J* = 7.0, 4.9 Hz, 4H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.46 – 7.42 (m, 1H), 7.34 (td, *J* = 7.5, 1.4 Hz, 1H), 7.17 (td, *J* = 7.8, 0.8 Hz, 1H), 7.04 (dd, *J* = 7.7, 1.4 Hz, 1H), 6.91 (td, *J* = 7.7, 0.8 Hz, 1H), 6.36 (d, *J* = 7.8 Hz, 1H), 1.34 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.2, 149.6, 146.6, 136.2, 135.5, 133.5, 133.4, 133.0, 131.1, 130.7, 130.0, 129.4, 129.0, 127.9, 127.8, 122.6, 122.0, 120.9, 111.0, 35.7, 31.7.

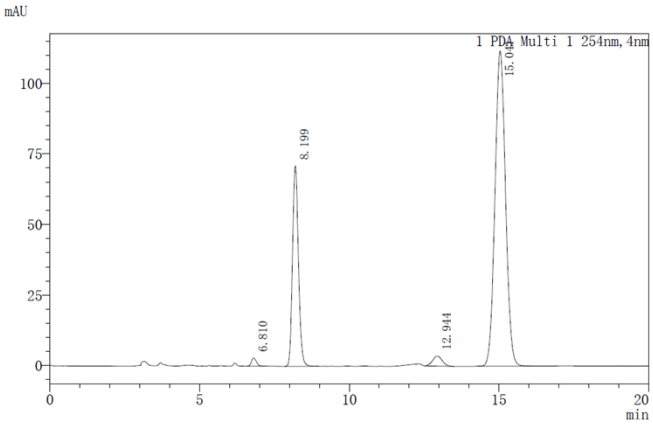
HRMS (ESI): calcd for $C_{25}H_{23}ClNO$ $[M+H]^+$ 388.1463; found 388.1459.

The ee was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), hexane/isopropanol = 95/5, 1 mL/min, λ = 254 nm, t_R (minor) = 6.810/12.944 min, t_R (major) = 8.199/15.041 min.



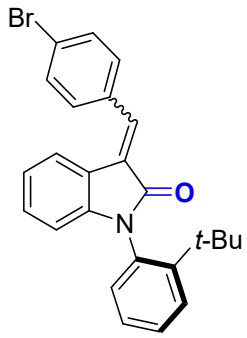
PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	6.725	64795	747226	15.849	--
2	8.073	56295	768234	16.294	3.966
3	12.680	69341	1615767	34.271	9.320
4	14.766	64409	1583503	33.586	3.268



PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	6.810	2906	33504	0.875	--
2	8.199	70913	976884	25.519	4.041
3	12.944	3544	79598	2.079	9.700
4	15.041	111656	2738076	71.526	3.326

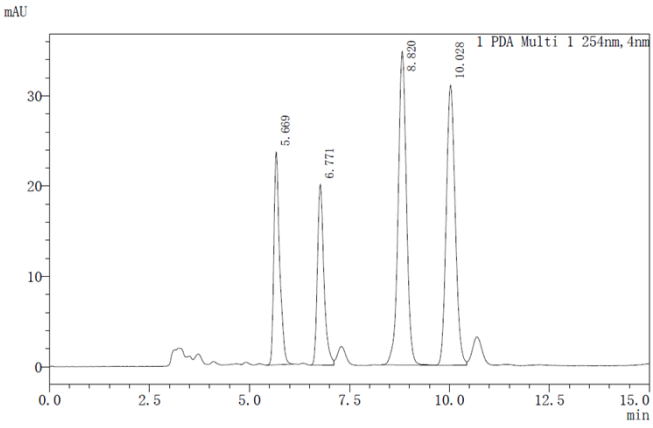


3-(4-bromobenzylidene)-1-(2-(*tert*-butyl)phenyl)indolin-2-one (**7-9**)

Yellow oil (32.8 mg, 76% yield, *Z/E* ≈ 1:3.2, 86% ee, 86% ee). (*E*) Form: $[\alpha]_D^{25}$ = +11.4 (c = 0.07 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.65 (dd, *J* = 16.6, 8.5 Hz, 4H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.36 (d, *J* = 7.8 Hz, 1H), 1.34 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.2, 149.6, 146.6, 136.2, 133.9, 133.0, 132.0, 131.2, 130.9, 130.1, 129.4, 129.0, 127.9, 127.8, 123.9, 122.6, 122.0, 120.9, 111.0, 35.7, 31.7.

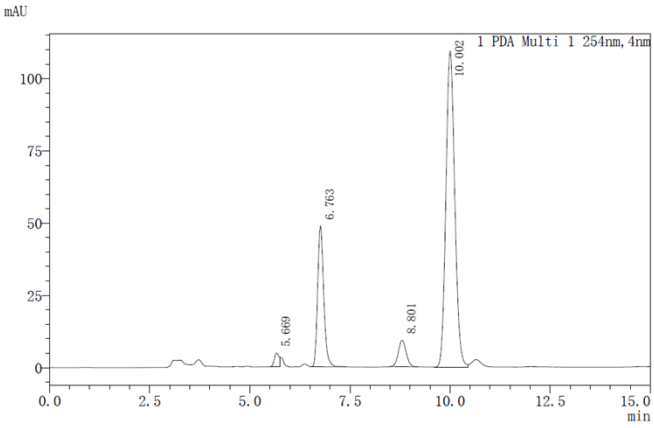
HRMS (ESI): calcd for $C_{25}H_{23}BrNO$ $[M+H]^+$ 432.0958; found 432.0960.

The ee was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), hexane/isopropanol = 90/10, 1 mL/min, λ = 254 nm, t_R (minor) = 5.669/8.801 min, t_R (major) = 6.763/10.002 min.



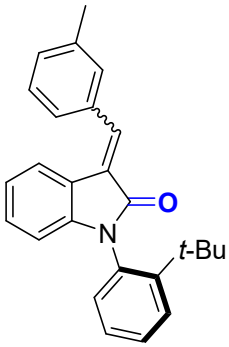
PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	5.669	23540	237717	16.423	--
2	6.771	19986	225561	15.583	3.891
3	8.820	34721	501531	34.649	6.047
4	10.028	31005	482647	33.344	3.028



PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	5.669	4735	39084	1.659	--
2	6.763	48755	515713	21.886	3.542
3	8.801	9170	124183	5.270	6.235
4	10.002	109316	1677431	71.186	3.077

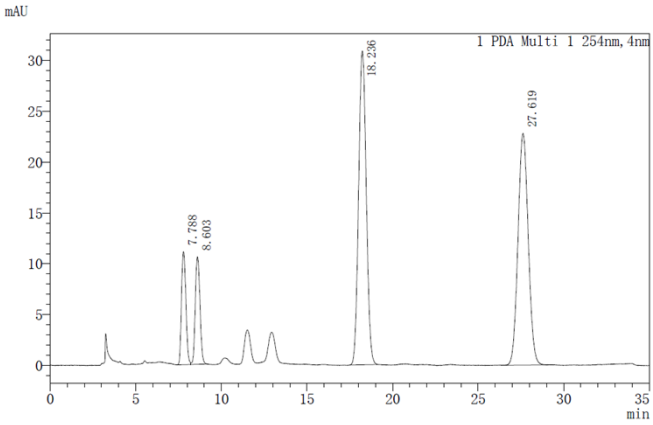


1-(2-(*tert*-butyl)phenyl)-3-(3-methylbenzylidene)indolin-2-one (**7-10**)

Yellow oil (36.0 mg, 98% yield, *Z/E* ≈ 1:4.4, 96% ee, 96% ee). (*Z*)&(*E*) Form: $[\alpha]_D^{25}$ = +18.7 (c = 0.3 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.24 (s, 0.16H), 8.15 (d, *J* = 7.8 Hz, 0.16H), 7.93 (s, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 7.4 Hz, 1.24H), 7.61 (d, *J* = 7.4 Hz, 0.36H), 7.54 (d, *J* = 7.5 Hz, 2H), 7.46 – 7.42 (m, 1.15H), 7.39 (t, *J* = 7.7 Hz, 1.15H), 7.35 (dd, *J* = 10.7, 4.1 Hz, 1.45H), 7.25 (dd, *J* = 14.9, 7.3 Hz, 1.49H), 7.17 (dt, *J* = 15.4, 7.6 Hz, 1.34H), 7.06 (dd, *J* = 5.5, 2.1 Hz, 1.36H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.35 (d, *J* = 7.8 Hz, 1.2H), 2.44 (s, 3H), 2.41 (s, 0.57H), 1.35 (s, 9H), 1.32 (s, 1.86H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.5, 167.2, 149.6, 146.4, 144.5, 138.3, 138.2, 137.9, 137.9, 134.9, 133.8, 133.2, 132.7, 131.5, 131.3, 131.2, 130.4, 130.0, 129.6, 129.6, 129.3, 129.2, 128.9, 128.7, 128.5, 128.2, 127.9, 127.8, 127.1, 126.4, 125.8, 124.7, 122.6, 121.9, 121.3, 118.8, 110.8, 110.4, 35.7, 35.7, 31.7, 31.7, 21.4, 21.4.

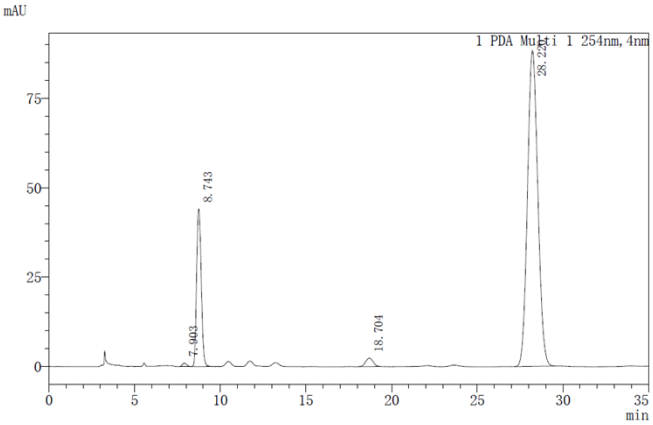
HRMS (ESI): calcd for $C_{26}H_{26}NO$ $[M+H]^+$ 368.2009; found 368.2011.

The ee was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), hexane/isopropanol = 98/2, 1 mL/min, λ = 254 nm, t_R (minor) = 7.903/18.704 min, t_R (major) = 8.743/28.220 min.



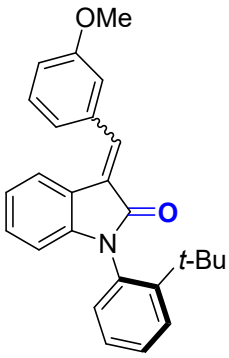
PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	7.788	11119	199241	8.634	--
2	8.603	10581	202224	8.763	1.659
3	18.236	30882	960373	41.616	14.425
4	27.619	22792	945876	40.988	9.715



PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	7.903	989	17669	0.381	--
2	8.743	44063	834549	18.001	1.698
3	18.704	2382	73459	1.585	14.780
4	28.220	88271	3710334	80.033	9.696

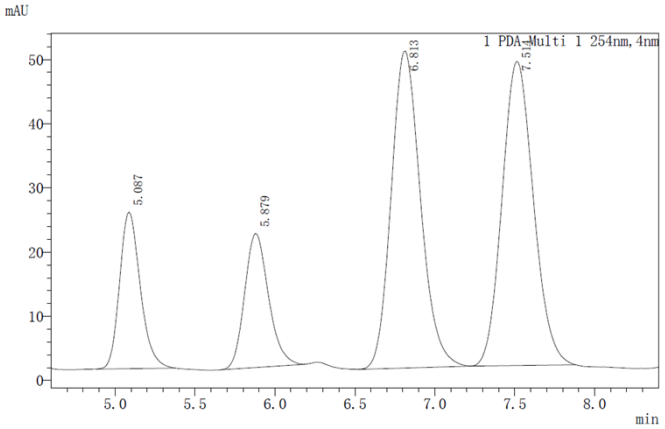


1-(2-(*tert*-butyl)phenyl)-3-(3-methoxybenzylidene)indolin-2-one (**7-11**)

Yellow oil (34.9 mg, 91% yield, *Z/E* ≈ 1:4.2, 90% ee, 90% ee). (*Z*)&(*E*) Form: $[\alpha]_D^{25}$ = +22.5 (c = 0.24 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.38 (s, 0.16H), 7.91 (s, 1H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.68 (t, *J* = 9.5 Hz, 1.40H), 7.61 (t, *J* = 3.6 Hz, 0.36H), 7.42 (dt, *J* = 15.3, 7.6 Hz, 2.28H), 7.33 (dd, *J* = 15.5, 7.7 Hz, 2.47H), 7.24 (s, 1H), 7.17 (dt, *J* = 15.3, 7.8 Hz, 1.26H), 7.07 (dd, *J* = 12.4, 7.7 Hz, 1.38H), 7.00 (dd, *J* = 8.1, 2.2 Hz, 1.21H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.35 (t, *J* = 6.1 Hz, 1.19H), 3.87 (s, 3.65H), 1.35 (s, 9H), 1.32 (s, 1.85H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.4, 167.2, 159.7, 159.5, 149.6, 149.6, 146.5, 144.5), 137.7, 137.7, 136.3, 135.2, 133.2, 133.2, 131.3, 131.2, 129.7, 129.4, 129.3, 129.1, 129.0, 128.8, 127.9, 127.9, 127.4, 126.2, 125.4, 124.6, 122.9, 121.9, 121.9, 121.8, 121.2, 118.9, 117.8, 115.9, 115.6, 114.3, 110.8, 110.4, 55.5, 55.4, 35.7, 31.7.

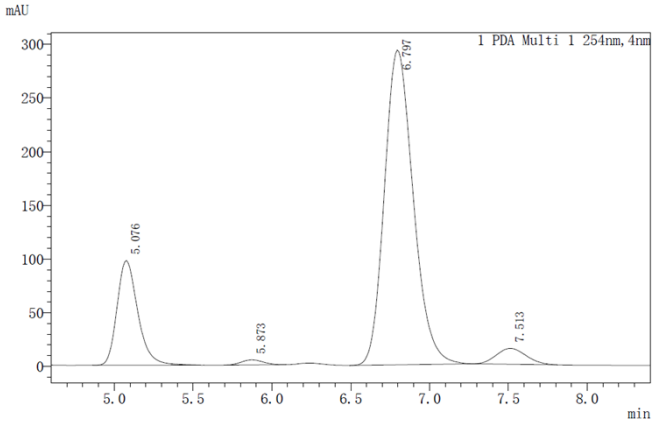
HRMS (ESI): calcd for $C_{26}H_{26}NO_2$ $[M+H]^+$ 384.1958; found 384.1956.

The ee was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexane/isopropanol = 90/10, 1 mL/min, λ = 254 nm, t_R (minor) = 5.873/7.513 min, t_R (major) = 5.076/6.797 min.



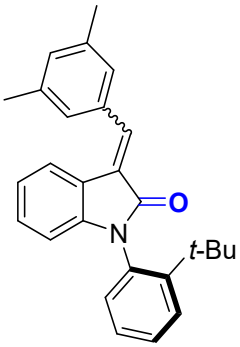
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	5.087	24398	219522	12.803	--
2	5.879	20903	217435	12.681	2.971
3	6.813	49392	630843	36.793	2.966
4	7.514	47352	646795	37.723	1.961



PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	5.076	97542	891526	18.327	--
2	5.873	4763	45761	0.941	3.062
3	6.797	293177	3733407	76.746	3.008
4	7.513	14778	193941	3.987	2.029

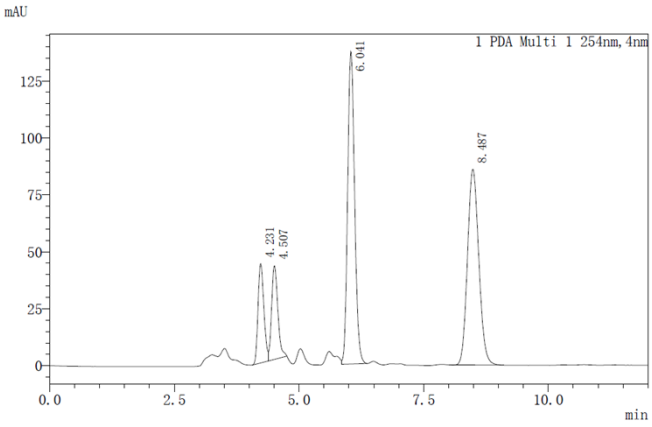


1-(2-(*tert*-butyl)phenyl)-3-(3,5-dimethylbenzylidene)indolin-2-one (**7-12**)

(37.7 mg, 99% yield, *Z*/*E* ≈ 1:5.6, 95% ee, 97% ee). (*Z*) Form: yellow oil, $[\alpha]_D^{25}$ = +50.7 (c = 0.15 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (s, 2H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 6.3 Hz, 3H), 6.34 (d, *J* = 7.8 Hz, 1H), 2.36 (s, 6H), 1.31 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.2, 149.6, 144.4, 138.2, 137.8, 133.8, 133.3, 132.6, 131.4, 130.1, 129.3, 129.0, 128.6, 127.9, 125.6, 124.8, 121.8, 118.7, 110.4, 35.8, 31.7 21.3. (*E*) Form: yellow solid, $[\alpha]_D^{25}$ = +13.3 (c = 0.27 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 11.7 Hz, 3H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.12 – 7.03 (m, 2H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.35 (d, *J* = 7.8 Hz, 1H), 2.40 (s, 6H), 1.35 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.5, 149.6, 146.4, 138.5, 138.2, 134.9, 133.3, 131.3, 131.2, 130.1, 129.5, 129.3, 128.9, 127.9, 127.1, 122.6, 121.8, 121.4, 110.8, 35.7, 31.7, 21.2.

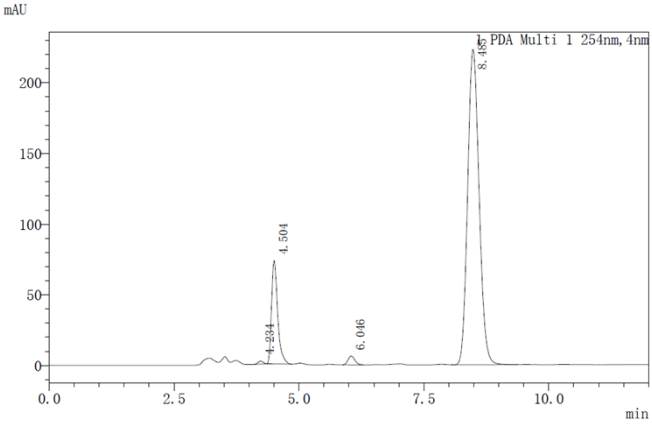
HRMS (ESI): calcd for $C_{27}H_{28}NO$ $[M+H]^+$ 382.2165; found 382.2167.

The ee was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), hexane/isopropanol = 90/10, 1 mL/min, λ = 254 nm, t_R (minor) = 4.234/6.046 min, t_R (major) = 4.504/8.485 min.



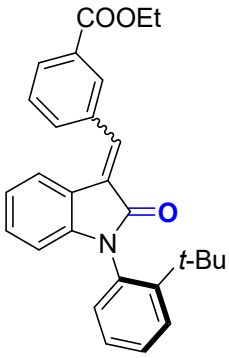
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	4.231	43617	357133	10.510	--
2	4.507	41043	356766	10.499	1.165
3	6.041	137255	1330629	39.160	6.030
4	8.487	85997	1353410	39.830	7.084



PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	4.234	2146	15925	0.375	--
2	4.504	73058	624982	14.720	1.211
3	6.046	6203	58466	1.377	6.211
4	8.485	223171	3546311	83.527	7.072

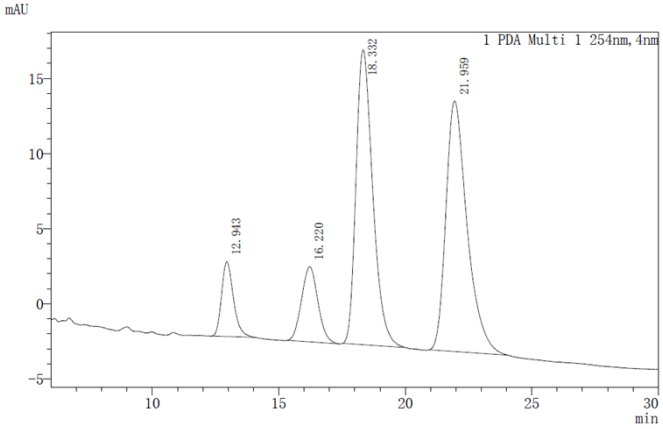


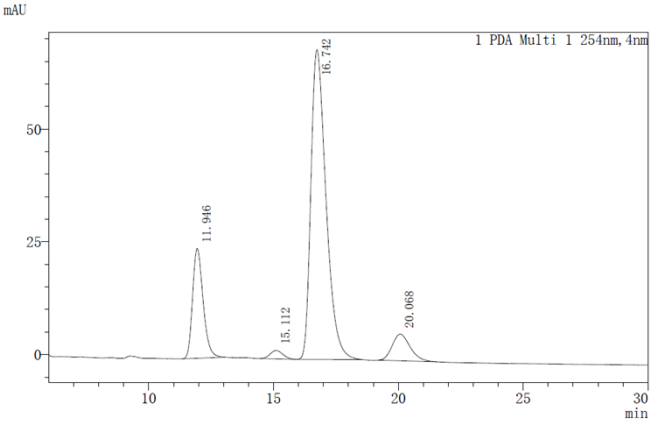
ethyl 3-((1-(2-(*tert*-butyl)phenyl)-2-oxoindolin-3-ylidene)methyl)benzoate (**7-13**)

Yellow oil (27.2 mg, 64% yield, *Z/E* ≈ 1:4.1, 83% ee, 82% ee). (*E*) Form: $[\alpha]_D^{25}$ = +16.0 (c = 0.2 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.43 (s, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 7.93 (s, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.67 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.44 (td, *J* = 7.7, 1.5 Hz, 1H), 7.34 (td, *J* = 7.5, 1.5 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.06 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.36 (d, *J* = 7.9 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.34 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 169.2, 166.0, 149.6, 146.7, 136.3, 135.3, 133.5, 133.1, 131.2, 131.1, 130.5, 130.3, 130.1, 129.4, 129.0, 128.8, 128.2, 127.9, 122.7, 122.1, 120.9, 111.0, 61.3, 35.7, 31.7, 14.3.

HRMS (ESI): calcd for $C_{28}H_{28}NO_3$ $[M+H]^+$ 426.2064; found 426.2062.

The ee was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexane/isopropanol = 98/2, 1 mL/min, λ = 254 nm, t_R (minor) = 15.112/20.068 min, t_R (major) = 11.946/16.742 min.



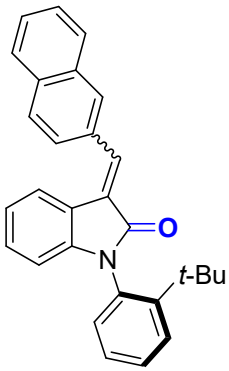


PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	12.943	4981	162028	7.152	--
2	16.220	5007	224714	9.919	3.213
3	18.332	19631	903687	39.888	1.760
4	21.959	16666	975105	43.041	2.690

PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	11.946	24358	715648	18.022	--
2	15.112	1880	66852	1.684	3.703
3	16.742	68712	2893235	72.860	1.601
4	20.068	5899	295235	7.435	2.764

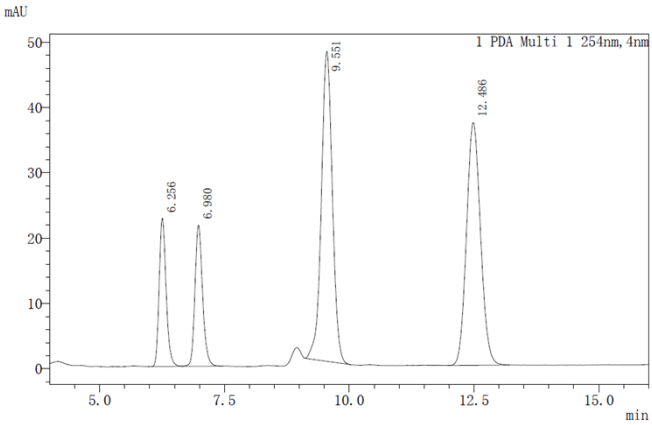


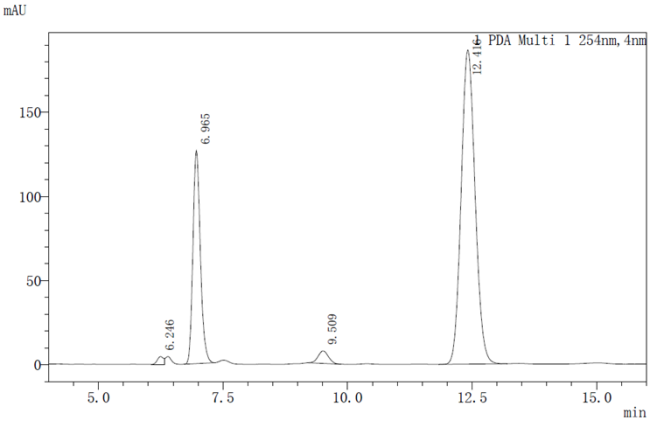
1-(2-(*tert*-butyl)phenyl)-3-(naphthalen-2-ylmethylene)indolin-2-one (**7-14**)

Yellow oil (35.9 mg, 89% yield, *Z/E* ≈ 1:2.8, 94% ee, 94% ee). (*Z*)&(*E*) Form: $[\alpha]_D^{25}$ = +16.0 (c = 0.15 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.92 (s, 0.16H), 8.50 (dd, *J* = 8.6, 1.8 Hz, 0.16H), 8.22 (s, 1H), 8.10 (s, 1H), 7.96 (d, *J* = 8.5 Hz, 1.11H), 7.94 – 7.88 (m, 2.12H), 7.88 – 7.79 (m, 1.58H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.72 – 7.64 (m, 1.35H), 7.57 (dt, *J* = 6.2, 2.5 Hz, 2H), 7.45 (dt, *J* = 8.0, 4.5 Hz, 1.59H), 7.40 – 7.32 (m, 1.21H), 7.17 (t, *J* = 7.7 Hz, 1.21H), 7.11 – 7.06 (m, 1.35H), 6.89 (t, *J* = 7.6 Hz, 1H), 6.38 (d, *J* = 7.8 Hz, 1.15H), 1.37 (s, 9H), 1.34 (s, 1.65H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 168.8, 161.6, 159.6, 149.6, 146.7, 133.1, 132.7, 132.4, 132.3, 131.8, 131.6, 131.5, 131.2, 130.4, 130.4, 130.1, 130.0, 130.0, 129.4, 129.3, 129.3, 129.1, 129.0, 127.9, 127.8, 124.0, 124.0, 123.1, 123.0, 122.9, 122.0, 121.0, 116.2, 116.1, 115.1, 110.8, 35.7, 31.7.

HRMS (ESI): calcd for $C_{29}H_{26}NO$ $[M+H]^+$ 404.2009; found 404.2011.

The ee was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), hexane/isopropanol = 90/10, 1 mL/min, λ = 254 nm, t_R (minor) = 6.246/9.509 min, t_R (major) = 6.965/12.416 min.



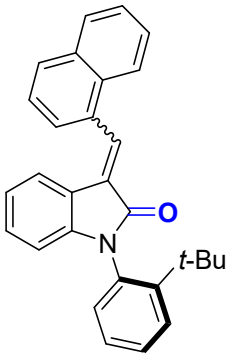


PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	6.256	22668	219524	11.508	--
2	6.980	21632	230471	12.082	2.633
3	9.551	47477	731494	38.347	7.417
4	12.486	37156	726052	38.062	6.321

PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	6.246	4615	40301	0.791	--
2	6.965	126476	1313017	25.783	2.186
3	9.509	7454	108918	2.139	7.503
4	12.416	186675	3630396	71.287	6.348

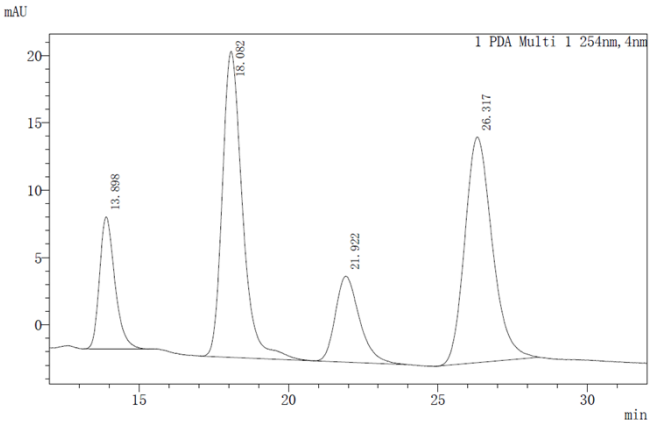


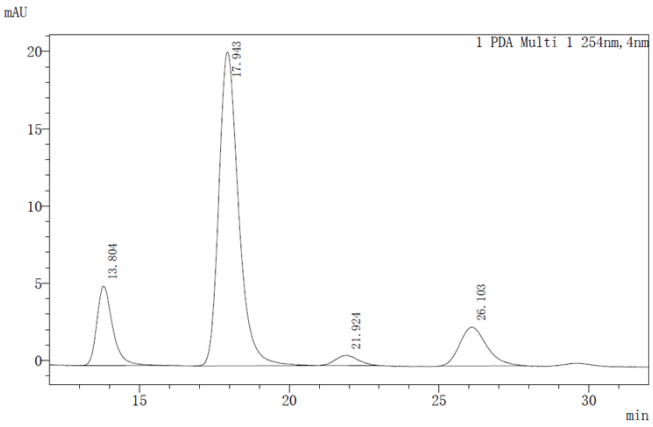
1-(2-(*tert*-butyl)phenyl)-3-(naphthalen-1-ylmethylene)indolin-2-one (**7-15**)

Yellow oil (14.9 mg, 37% yield, *Z/E* ≈ 1:4.9, 70% ee, 71% ee). (*Z*)&(*E*) Form: $[\alpha]_D^{25}$ = +3.7 (c = 0.43 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.4 (d, *J* = 6.2 Hz, 1.42H), 8.4 (s, 0.44H), 8.1 (d, *J* = 8.4 Hz, 0.45H), 8.1 – 8.1 (m, 1H), 8.0 (dd, *J* = 12.9, 8.9 Hz, 2H), 7.9 (t, *J* = 9.1 Hz, 2H), 7.7 (d, *J* = 7.5 Hz, 0.47H), 7.7 (dd, *J* = 8.1 Hz, 1.5, 1H), 7.6 (dd, *J* = 8.2, 1.5 Hz, 0.5H), 7.6 (td, *J* = 6.5, 5.9, 3.3 Hz, 3.36H), 7.5 – 7.5 (m, 1H), 7.5 (td, *J* = 8.2, 7.7, 1.6 Hz, 1.1H), 7.4 (dtd, *J* = 14.9, 7.3, 1.5 Hz, 1.6H), 7.3 (td, *J* = 7.6, 1.5 Hz, 0.53H), 7.2 (dd, *J* = 11.8, 7.7 Hz, 1.7H), 7.2 – 7.1 (m, 2.47H), 7.1 (dd, *J* = 7.8, 1.5 Hz, 0.47H), 6.8 (td, *J* = 7.6, 1.0 Hz, 1H), 6.4 (d, *J* = 7.8 Hz, 0.44H), 6.4 (d, *J* = 7.8 Hz, 1H), 1.4 (s, 9H), 1.3 (s, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 169.0, 167.1, 149.6, 149.6, 146.5, 144.8, 135.8, 134.2, 133.7, 133.5, 133.2, 132.3, 132.0, 131.4, 131.3, 131.2, 130.6, 130.0, 129.7, 129.7, 129.7, 129.4, 129.2, 129.0, 128.9, 128.9, 128.7, 127.9, 127.8, 127.4, 126.9, 126.9, 126.6, 126.5, 125.8, 125.2, 125.2, 124.9, 124.1, 123.9, 123.0, 122.0, 121.9, 121.3, 119.3, 110.8, 110.6, 35.8, 31.7.

HRMS (ESI): calcd for $C_{29}H_{26}NO$ $[M+H]^+$ 404.2009; found 404.2006.

The ee was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexane/isopropanol = 98/2, 1 mL/min, λ = 254 nm, t_R (minor) = 21.924/26.103 min, t_R (major) = 13.804/17.943 min.



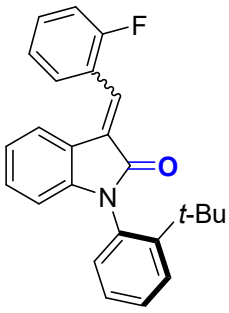


PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	13.898	9807	350465	12.310	--
2	18.082	22723	1064150	37.379	3.978
3	21.922	6391	358799	12.603	2.920
4	26.317	16753	1073514	37.708	2.828

PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	13.804	5141	188125	14.336	--
2	17.943	20319	931390	70.976	3.974
3	21.924	648	34173	2.604	3.159
4	26.103	2515	158563	12.083	2.772

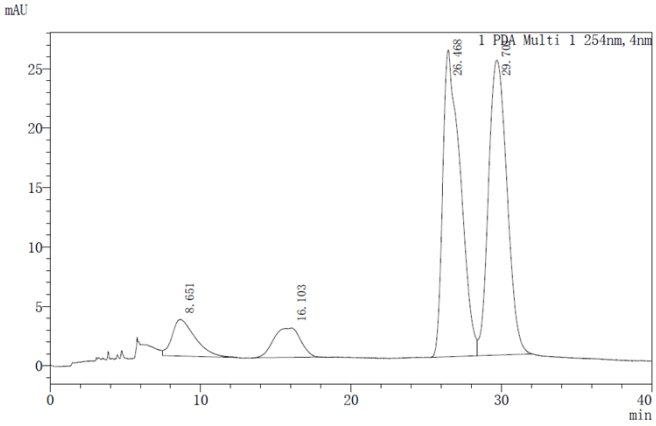


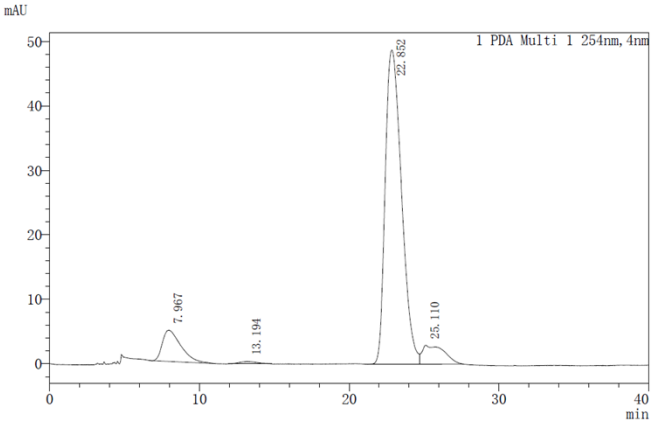
1-(2-(*tert*-butyl)phenyl)-3-(2-fluorobenzylidene)indolin-2-one (**7-16**)

Yellow oil (34.9 mg, 94% yield, *Z/E* ≈ 1:8.9, 86% ee, 85% ee). (*E*) Form: $[\alpha]_D^{25}$ = +13.3 (c = 0.12 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.91 (s, 1H), 7.78 (td, *J* = 7.5 Hz, 1.7, 1H), 7.67 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.44 (ddd, *J* = 12.5, 6.3, 2.0 Hz, 2H), 7.34 (td, *J* = 7.5, 1.5 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.21 (t, *J* = 9.1 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.06 (dd, *J* = 7.7 Hz, 1.6, 1H), 6.89 (t, *J* = 7.6 Hz, 1H), 6.35 (d, *J* = 7.8 Hz, 1H), 1.35 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 169.5, 148.1 (d, *J* = 386.7 Hz), 137.9, 133.8, 133.2 (d, *J* = 13.7 Hz), 132.5, 131.2, 129.8, 129.4, 129.4, 129.0, 128.4, 128.3, 127.9 (d, *J* = 4.6 Hz), 127.4, 127.2, 126.7, 126.5, 122.3 (d, *J* = 84.2 Hz), 121.3, 110.9, 35.7, 31.7. **^{19}F NMR** (471 MHz, $CDCl_3$) δ = -110.5.

HRMS (ESI): calcd for $C_{25}H_{23}FNO$ $[M+H]^+$ 372.1758; found 372.1757.

The ee was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexane/isopropanol = 99.5/0.5, 1 mL/min, λ = 254 nm, t_R (minor) = 13.194/25.110 min, t_R (major) = 7.967/22.852 min.



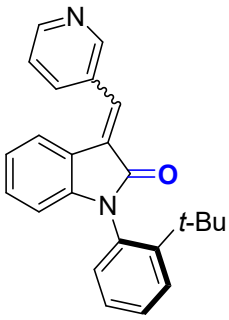


PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	8.651	3084	327718	6.741	--
2	16.103	2476	308163	6.339	2.570
3	26.468	25838	2099645	43.188	3.902
4	29.701	24837	2126099	43.732	1.435

PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	7.967	4853	417120	9.407	--
2	13.194	373	31275	0.705	2.340
3	22.852	48738	3690031	83.220	4.604
4	25.110	2939	295627	6.667	0.983

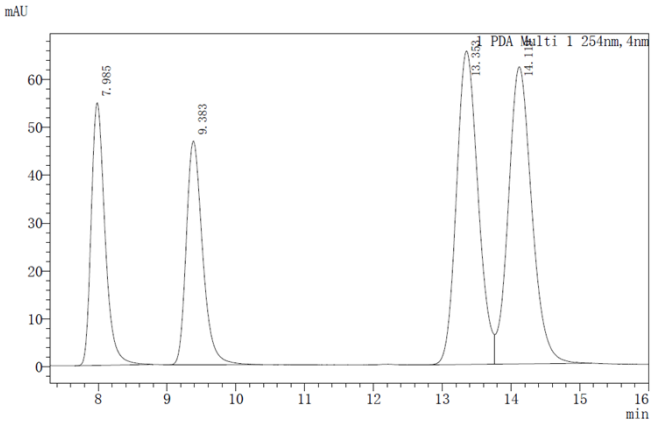


1-(2-*(tert*-butyl)phenyl)-3-(pyridin-3-ylmethylene)indolin-2-one (**7-17**)

Dark yellow solid (34.3 mg, 97% yield, *Z/E* ≈ 1:1.8, 78% ee, 79% ee). (*Z*)&(*E*) Form: $[\alpha]_D^{25}$ = +90.0 (c = 0.22 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 9.22 (dt, *J* = 8.2, 1.9 Hz, 0.44H), 8.98 (s, 1.38H), 8.83 – 8.64 (m, 1H), 8.59 (s, 0.44H), 8.09 – 7.95 (m, 1H), 7.84 (s, 1H), 7.69 – 7.61 (m, 2H), 7.58 (dd, *J* = 9.1, 2.1 Hz, 1.44H), 7.44 (tdd, *J* = 8.1, 6.3, 1.6 Hz, 2.41H), 7.37 – 7.30 (m, 1.90H), 7.24 – 7.14 (m, 1.49H), 7.09 (td, *J* = 7.5, 1.0 Hz, 0.48H), 7.05 (dd, *J* = 7.7, 1.7 Hz, 1.40H), 6.90 (td, *J* = 7.7, 1.1 Hz, 1H), 6.37 (dd, *J* = 7.9, 5.6 Hz, 1.42H), 1.34 (s, 9H), 1.31 (s, 4.54H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 168.8, 167.1, 152.9, 150.6, 150.2, 150.0, 149.6, 149.5, 146.8, 144.9, 138.4, 136.4, 133.2, 133.1, 132.9, 132.8, 131.1, 131.1, 130.5, 129.6, 129.5, 129.4, 129.2, 129.0, 128.5, 128.0, 127.9, 123.9, 123.5, 123.2, 122.5, 122.2, 122.2, 120.7, 119.3, 111.1, 110.7, 35.7, 35.7, 31.7, 31.7.

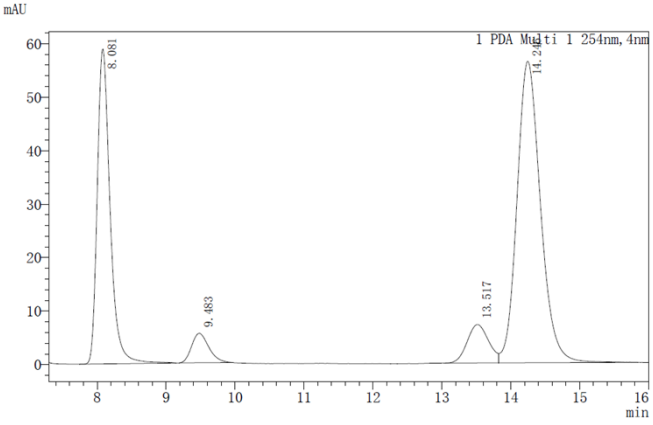
HRMS (ESI): calcd for $C_{24}H_{23}N_2O$ $[M+H]^+$ 355.1805; found 355.1803.

The ee was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), hexane/isopropanol = 90/10, 1 mL/min, λ = 254 nm, t_R (minor) = 9.483/13.517 min, t_R (major) = 8.081/14.246 min.



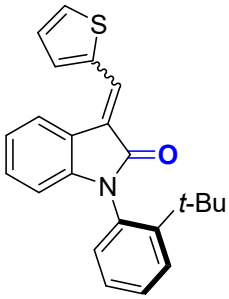
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	7.985	54826	764291	17.248	--
2	9.383	46712	770128	17.380	3.514
3	13.353	65461	1428206	32.231	7.827
4	14.119	62029	1468563	33.142	1.273



PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	8.081	58867	757453	32.333	--
2	9.483	5501	94928	4.052	3.515
3	13.517	7172	155212	6.625	7.631
4	14.246	56343	1335056	56.989	1.203

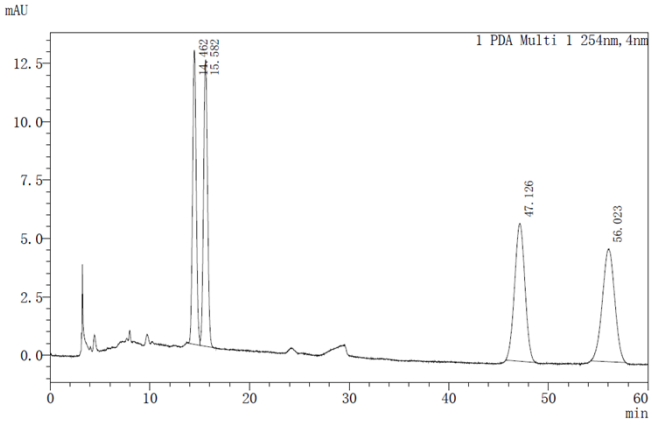


1-(2-(*tert*-butyl)phenyl)-3-(thiophen-2-ylmethylene)indolin-2-one (**7-18**)

Yellow oil (32.0 mg, 89% yield, *Z*/*E* ≈ 1.3/1, 90% ee, 90% ee). (*Z*)&(*E*) Form: $[\alpha]_D^{25}$ = +56.5 (c = 0.23 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.32 (d, *J* = 7.7 Hz, 1H), 8.03 (s, 1H), 7.90 (d, *J* = 4.0 Hz, 0.41H), 7.82 (s, 0.42H), 7.71 – 7.56 (m, 4.27H), 7.43 (tdd, *J* = 7.7, 6.0, 1.5 Hz, 1.46H), 7.38 – 7.29 (m, 1.46H), 7.24 – 7.12 (m, 2.90H), 7.11 – 7.00 (m, 2.89H), 6.48 – 6.31 (m, 1.41H), 1.32 (s, 9H), 1.30 (s, 3.76H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.1, 167.4, 149.7, 149.6, 146.2, 144.3, 138.0, 137.9, 137.0, 134.7, 133.7, 133.2, 133.1, 131.4, 131.2, 130.5, 129.5, 129.4, 129.3, 129.0, 129.0, 128.9, 128.5, 128.4, 128.1, 127.9, 127.8, 127.4, 124.0, 123.6, 123.3, 122.0, 121.8, 121.4, 121.1, 118.6, 110.8, 110.5, 35.7, 35.7, 31.7, 31.6.

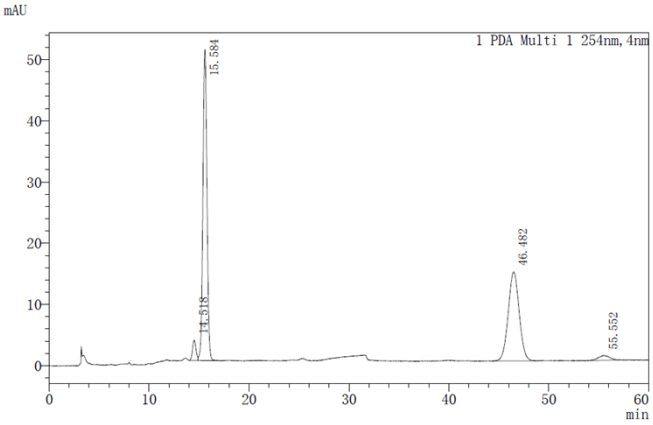
HRMS (ESI): calcd for $C_{23}H_{22}NOS$ $[M+H]^+$ 360.1417; found 360.1413.

The ee was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), hexane/isopropanol = 98/2, 1 mL/min, λ = 254 nm, t_R (minor) = 14.518/55.552 min, t_R (major) = 15.584/46.482 min.



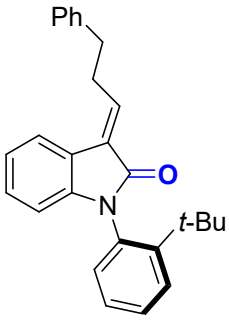
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	14.462	12616	321246	21.361	--
2	15.582	12258	340430	22.636	1.576
3	47.126	5895	425116	28.267	23.735
4	56.023	4836	417113	27.735	4.238



PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	14.518	3299	79906	2.986	--
2	15.584	50713	1430098	53.440	1.531
3	46.482	14539	1105596	41.314	22.526
4	55.552	763	60500	2.261	4.442

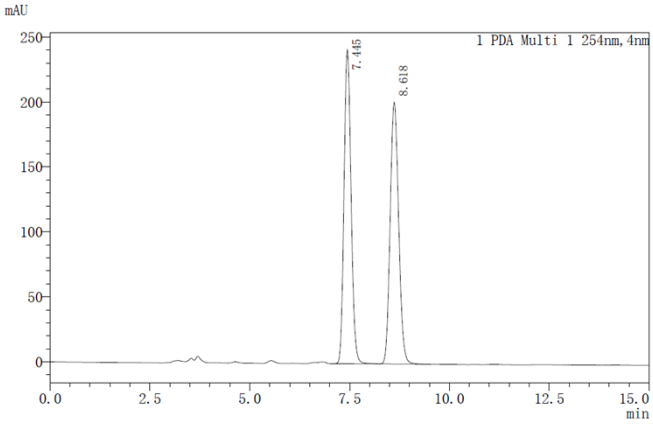


(*E*)-1-(2-(*tert*-butyl)phenyl)-3-(3-phenylpropylidene)indolin-2-one (**7-19**)

Brown oil (25.2 mg, 66% yield, *E/Z* > 10:1, 94% ee). (*E*) Form: $[\alpha]_D^{25}$ = +31.5 (c = 0.26 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.9 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.38 – 7.28 (m, 5H), 7.24 (d, *J* = 7.1 Hz, 1H), 7.17 (td, *J* = 7.3, 4.0 Hz, 2H), 7.03 (dd, *J* = 14.1, 7.1 Hz, 2H), 6.35 (d, *J* = 7.8 Hz, 1H), 3.07 (dd, *J* = 14.6, 7.0 Hz, 2H), 3.04 – 2.94 (m, 2H), 1.31 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.6, 149.6, 145.9, 141.2, 140.7, 133.1, 131.2, 129.3, 128.9, 128.9, 128.6, 128.4, 128.1, 127.8, 126.4, 123.4, 122.2, 122.1, 110.7, 35.7, 34.7, 31.7, 31.3.

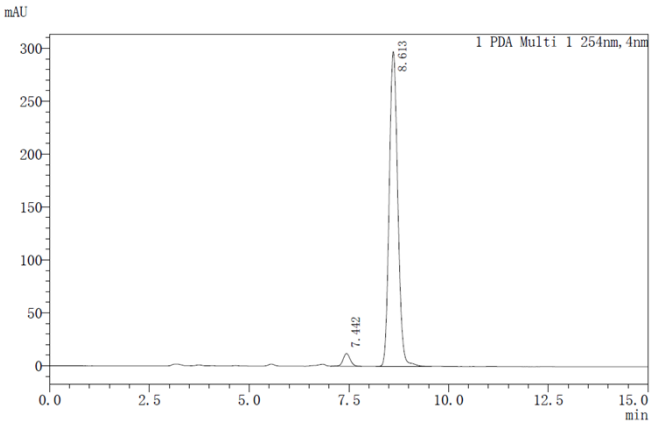
HRMS (ESI): calcd for $C_{27}H_{28}NO$ $[M+H]^+$ 382.2165; found 382.2163.

The ee was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), hexane/isopropanol = 90/10, 1 mL/min, λ = 254 nm, t_R (minor) = 7.442 min, t_R (major) = 8.613 min.



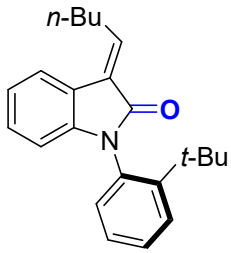
PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	7.445	241464	2972243	50.008	--
2	8.618	201417	2971247	49.992	3.207



PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	7.442	11936	146097	3.199	--
2	8.613	297434	4420852	96.801	3.207

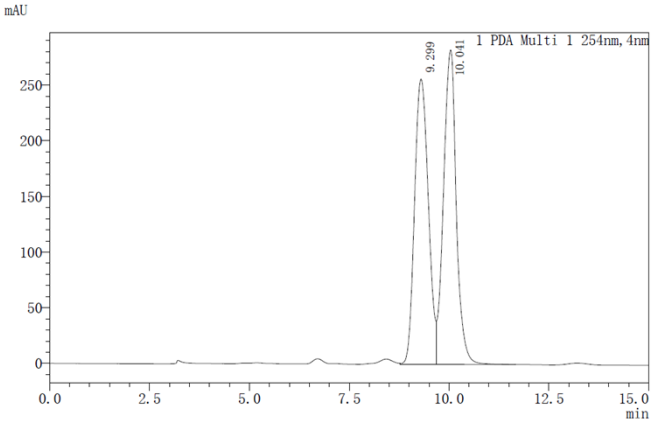


(*E*)-1-(2-(*tert*-butyl)phenyl)-3-pentylideneindolin-2-one (**7-20**)

Pale yellow oil (16.0 mg, 48% yield, *E/Z* > 10:1, 90% ee). (*E*) Form: $[\alpha]_D^{25}$ = +24.7 (c = 0.3 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 – 7.58 (m, 2H), 7.45 – 7.38 (m, 1H), 7.31 (td, *J* = 7.6, 1.3 Hz, 1H), 7.15 (dt, *J* = 13.6, 7.7 Hz, 2H), 7.05 (t, *J* = 7.6 Hz, 1H), 7.01 (dd, *J* = 7.7, 1.3 Hz, 1H), 6.34 (d, *J* = 7.8 Hz, 1H), 2.74 (q, *J* = 7.5 Hz, 2H), 1.71 – 1.63 (m, 2H), 1.50 (dq, *J* = 14.6, 7.3 Hz, 2H), 1.29 (s, 9H), 0.99 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.8, 149.6, 145.8, 143.1, 133.2, 131.3, 129.3, 128.9, 128.6, 127.8, 127.6, 123.3, 122.4, 122.1, 110.6, 35.7, 31.6, 30.7, 29.2, 22.6, 13.9.

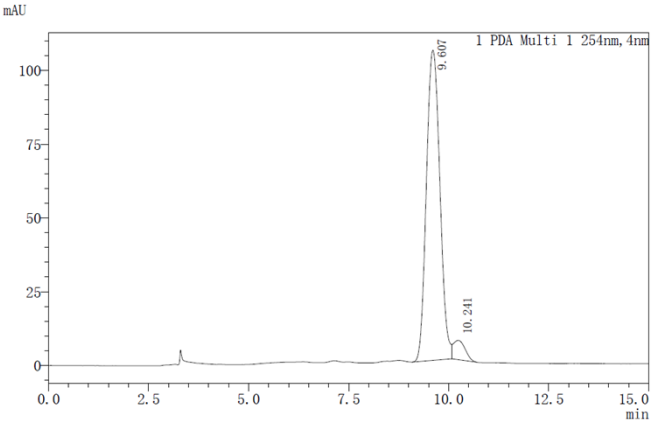
HRMS (ESI): calcd for $C_{23}H_{28}NO$ $[M+H]^+$ 334.2165; found 334.2165.

The ee was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexane/isopropanol = 98/2, 1 mL/min, λ = 254 nm, t_R (minor) = 10.241 min, t_R (major) = 9.607 min.



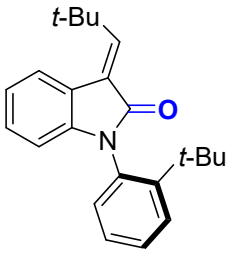
PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	9.299	256438	6168597	49.526	--
2	10.041	282554	6286695	50.474	1.230



PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	9.607	105145	2467511	94.854	--
2	10.241	6565	133867	5.146	0.875

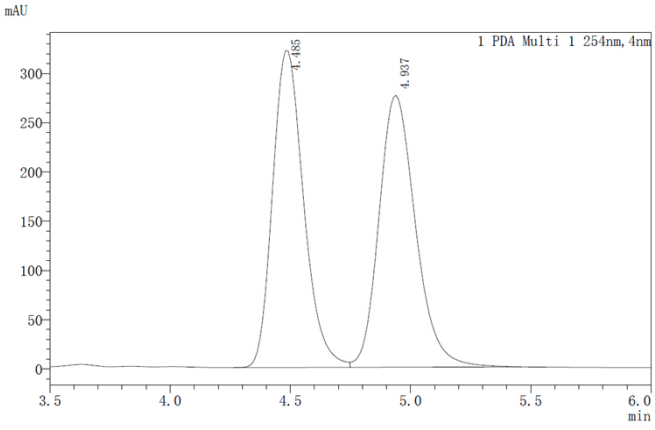


(*E*)-1-(2-(*tert*-butyl)phenyl)-3-(2,2-dimethylpropylidene)indolin-2-one (**7-21**)

Pale yellow oil (12.0 mg, 36% yield, *E/Z* > 15:1, 96% ee). (*E*) Form: $[\alpha]_D^{25}$ = +18.7 (c = 0.46 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 6.34 (d, *J* = 7.8 Hz, 1H), 1.44 (s, 9H), 1.30 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.9, 153.8, 149.5, 146.5, 133.3, 131.2, 129.3, 128.9, 128.7, 127.9, 126.5, 126.2, 121.8, 120.7, 110.9, 35.7, 32.9, 31.6, 29.3.

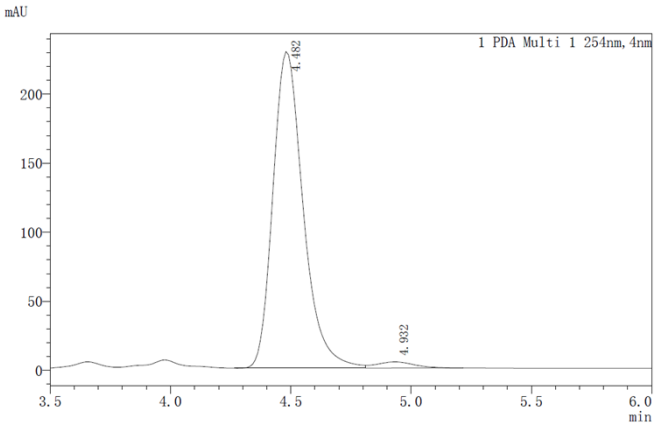
HRMS (ESI): calcd for $C_{23}H_{28}NO$ $[M+H]^+$ 334.2165; found 334.2163.

The ee was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexane/isopropanol = 99/1, 1 mL/min, λ = 254 nm, t_R (minor) = 23.648 min, t_R (major) = 16.541 min.



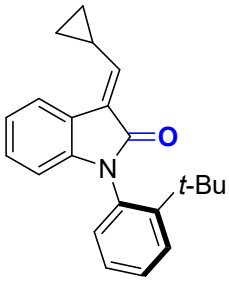
PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	4.485	321953	2891689	49.761	--
2	4.937	276153	2919459	50.239	1.698



PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	4.482	229254	2004412	97.677	--
2	4.932	4447	47662	2.323	1.585

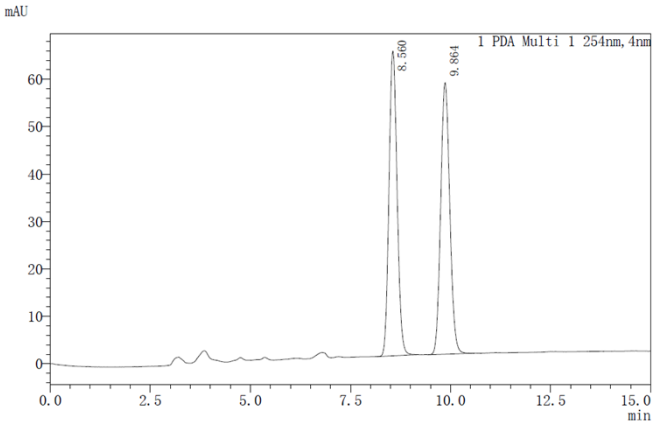


(*E*)-1-(2-(*tert*-butyl)phenyl)-3-(cyclopropylmethylene)indolin-2-one (**7-22**)

Pale yellow oil (16.2 mg, 51% yield, *E/Z* > 10:1, 95% ee). (*E*) Form: $[\alpha]_D^{25}$ = +44.3 (c = 0.23 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.5 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 6.50 (d, *J* = 11.3 Hz, 1H), 6.35 (d, *J* = 7.8 Hz, 1H), 2.36 – 2.29 (m, 1H), 1.30 (s, 9H), 1.26 (d, *J* = 8.2 Hz, 2H), 0.93 (d, *J* = 2.2 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.8, 149.6, 147.9, 145.3, 133.3, 131.3, 129.2, 128.9, 128.2, 127.8, 125.6, 122.6, 122.3, 122.0, 110.6, 35.7, 31.6, 13.4, 10.5, 10.3.

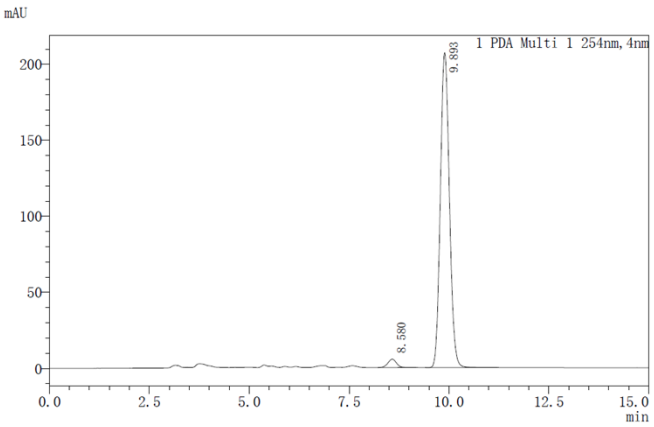
HRMS (ESI): calcd for $C_{22}H_{24}NO$ $[M+H]^+$ 318.1852; found 318.1852.

The ee was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), hexane/isopropanol = 90/10, 1 mL/min, λ = 254 nm, t_R (minor) = 8.580 min, t_R (major) = 9.893 min.



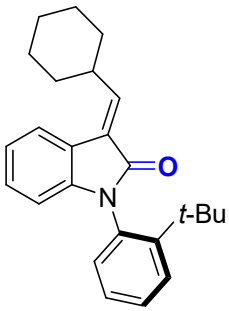
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	8.560	64263	903004	49.950	--
2	9.864	57265	904803	50.050	3.240



PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	8.580	5529	82205	2.458	--
2	9.893	207073	3262717	97.542	3.193

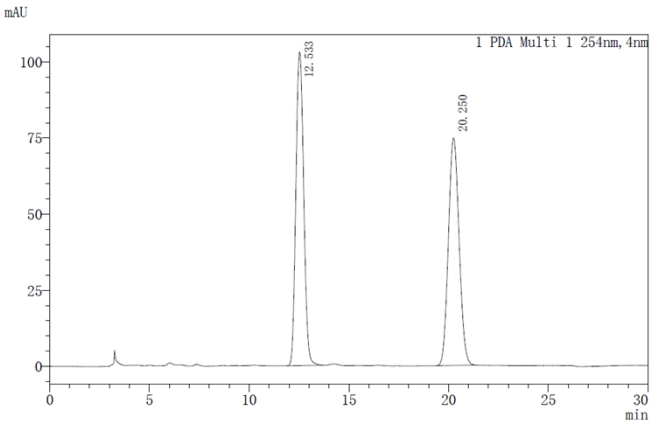


(*E*)-1-(2-(*tert*-butyl)phenyl)-3-(cyclohexylmethylene)indolin-2-one (**7-23**)

Pale yellow solid (20.1 mg, 56% yield, *E/Z* > 15:1, 94% ee). (*E*) Form: $[\alpha]_D^{25}$ = +15.0 (c = 0.32 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.1 Hz, 1H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 9.6 Hz, 2H), 6.34 (d, *J* = 7.8 Hz, 1H), 3.00 (dt, *J* = 13.6, 6.8 Hz, 1H), 1.96 – 1.89 (m, 2H), 1.86 (d, *J* = 12.9 Hz, 2H), 1.77 (d, *J* = 12.8 Hz, 1H), 1.48 – 1.31 (m, 5H), 1.30 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.2, 149.6, 147.7, 145.8, 133.3, 131.2, 129.3, 128.9, 128.6, 127.8, 126.0, 123.2, 122.1, 122.1, 110.7, 38.4, 35.7, 31.9, 31.6, 31.5, 25.8, 25.7, 25.5.

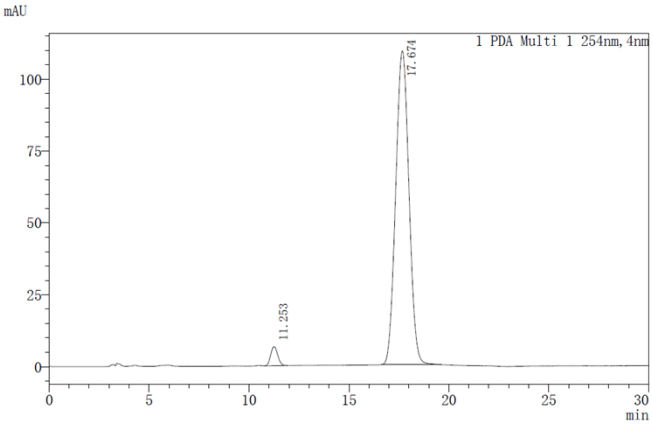
HRMS (ESI): calcd for $C_{25}H_{30}NO$ $[M+H]^+$ 360.2322; found 360.2320.

The ee was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), hexane/isopropanol = 98/2, 1 mL/min, λ = 254 nm, t_R (minor) = 11.253 min, t_R (major) = 17.674 min.



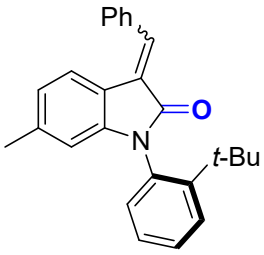
PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	12.533	103095	2811880	50.219	--
2	20.250	74778	2787357	49.781	9.009



PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	11.253	6673	163418	3.135	--
2	17.674	109224	5048855	96.865	6.795

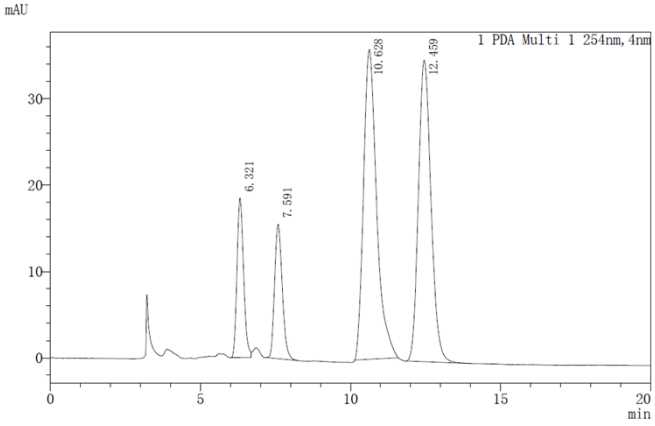


3-benzylidene-1-(2-(*tert*-butyl)phenyl)-6-methylindolin-2-one (**7-24**)

Yellow oil (34.1 mg, 93% yield, *Z/E* ≈ 1:4.4, 96% ee, 96% ee). (*Z*) Form: $[\alpha]_D^{25}$ = +9.6 (c = 0.25 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 6.9 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.56 (s, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.45 – 7.38 (m, 4H), 7.33 (s, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.17 (s, 1H), 2.30 (s, 3H), 1.32 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.5, 149.6, 144.7, 139.4, 136.5, 134.0, 133.3, 132.1, 131.3, 130.3, 129.2, 128.9, 128.2, 127.8, 126.2, 122.7, 122.1, 118.8, 111.1, 35.8, 31.7, 21.9. (*E*) Form: $[\alpha]_D^{25}$ = +8.6 (c = 0.35 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.72 (d, *J* = 7.5 Hz, 2H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.46 – 7.41 (m, 2H), 7.37 – 7.32 (m, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 6.16 (s, 1H), 2.25 (s, 3H), 1.35 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.8, 149.6, 146.7, 140.4, 136.5, 135.2, 133.3, 131.3, 129.4, 129.4, 129.3, 129.0, 128.6, 127.9, 127.3, 122.6, 122.5, 118.7, 111.5, 35.7, 31.7, 21.9.

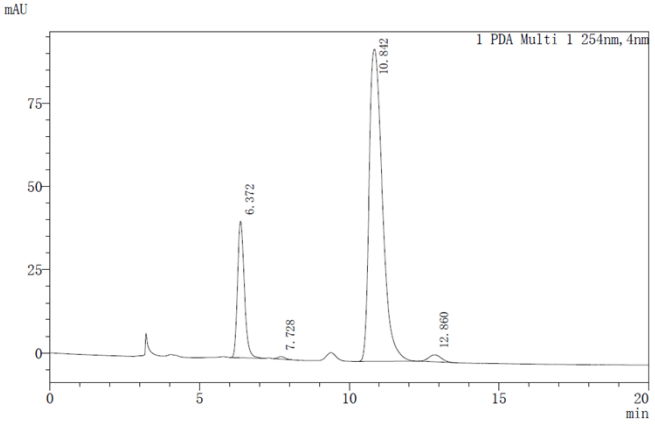
HRMS (ESI): calcd for $C_{26}H_{26}NO$ $[M+H]^+$ 368.2009; found 368.2005.

The ee was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexane/isopropanol = 98/2, 1 mL/min, λ = 254 nm, t_R (minor) = 7.728/12.860 min, t_R (major) = 6.372/10.842 min.



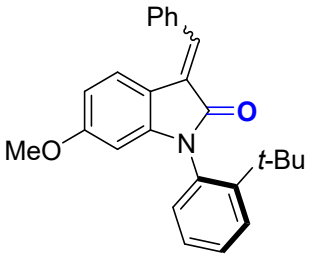
PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	6.321	18461	282022	10.586	--
2	7.591	15551	276519	10.379	2.888
3	10.628	35848	1087043	40.802	4.874
4	12.459	34890	1018612	38.233	2.373



PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	6.372	41065	649655	18.040	--
2	7.728	777	12736	0.354	3.111
3	10.842	93880	2877434	79.901	5.107
4	12.860	2097	61443	1.706	2.600

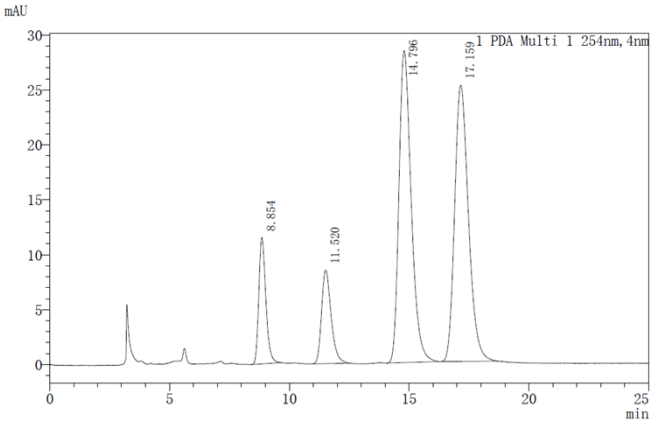


3-benzylidene-1-(2-(*tert*-butyl)phenyl)-6-methoxyindolin-2-one (**7-25**)

Yellow oil (38.0 mg, 99% yield, *Z*/*E* ≈ 1:8, 97% ee, 97% ee). (*Z*) Form: $[\alpha]_D^{25}$ = +32.5 (c = 0.08 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.3 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.46 (s, 1H), 7.40 (dt, *J* = 10.4, 6.9 Hz, 4H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.60 (dd, *J* = 8.4, 2.1 Hz, 1H), 5.92 (d, *J* = 2.1 Hz, 1H), 3.74 (s, 3H), 1.32 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.7, 161.1, 149.6, 146.0, 135.2, 134.1, 133.0, 131.9, 131.3, 130.1, 129.3, 129.0, 128.2, 127.8, 125.8, 120.1, 117.5, 107.0, 97.5, 55.6, 35.8, 31.8. (*E*) Form: $[\alpha]_D^{25}$ = +12.0 (c = 0.1 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.71 (d, *J* = 7.5 Hz, 2H), 7.69 – 7.63 (m, 2H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.45 – 7.40 (m, 2H), 7.33 (dd, *J* = 10.8, 4.1 Hz, 1H), 7.07 – 7.02 (m, 1H), 6.42 (dd, *J* = 8.5, 2.3 Hz, 1H), 5.90 (d, *J* = 2.3 Hz, 1H), 3.70 (s, 3H), 1.35 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.1, 161.4, 149.6, 148.2, 135.3, 134.7, 133.0, 131.2, 129.4, 129.3, 129.2, 129.0, 128.6, 127.9, 126.9, 123.8, 114.3, 106.5, 98.0, 55.5, 35.7, 31.7.

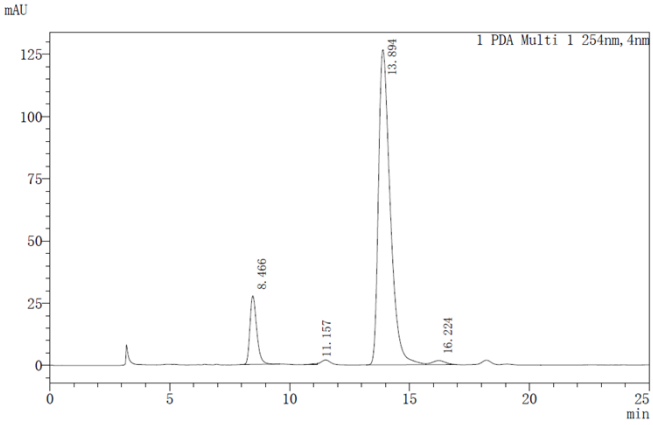
HRMS (ESI): calcd for $C_{26}H_{26}NO_2$ $[M+H]^+$ 384.1958; found 384.1955.

The ee was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexane/isopropanol = 98/2, 1 mL/min, λ = 254 nm, t_R (minor) = 11.157/16.224 min, t_R (major) = 8.466/13.894 min.



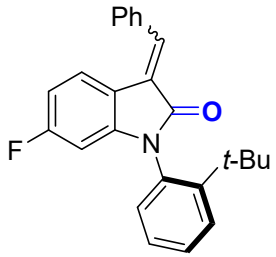
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	8.854	11513	235531	9.469	--
2	11.520	8508	235443	9.465	4.241
3	14.796	28399	1008337	40.537	3.982
4	17.159	25143	1008155	40.529	2.396



PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	8.466	27557	541261	10.974	--
2	11.157	471	8015	0.162	2.745
3	13.894	126689	4318734	87.565	2.355
4	16.224	1671	64022	1.298	2.440

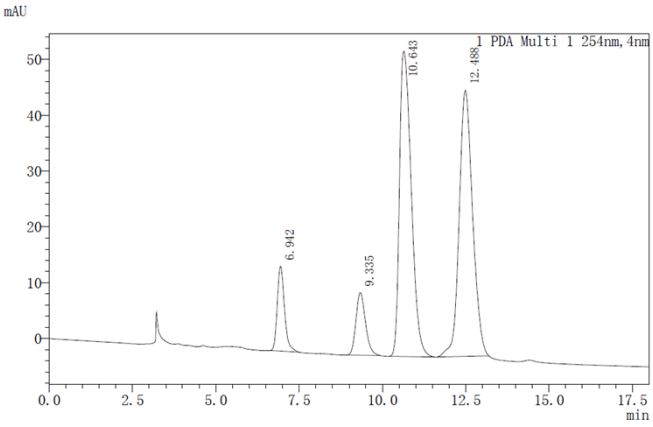


3-benzylidene-1-(2-(*tert*-butyl)phenyl)-6-fluoroindolin-2-one (**7-26**)

Yellow oil (34.9 mg, 94% yield, *Z*/*E* ≈ 1:6.3, 96% ee, 95% ee). (*Z*)&(*E*) Form: $[\alpha]_D^{25}$ = +27.6 (c = 0.5 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.36 – 8.27 (m, 0.35H), 7.90 (s, 1H), 7.73 – 7.62 (m, 4.36H), 7.56 (s, 0.2H), 7.56 – 7.53 (m, 0.18H), 7.50 (t, *J* = 7.3 Hz, 2H), 7.47 – 7.42 (m, 2.75H), 7.34 (q, *J* = 7.1 Hz, 1.29H), 7.04 (d, *J* = 7.7 Hz, 1.2H), 6.80 – 6.72 (m, 0.18H), 6.58 (td, *J* = 9.0, 2.2 Hz, 1H), 6.14 – 6.04 (m, 1.19H), 1.35 (s, 9H), 1.32 (s, 1.83H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.6, 167.3, 163.9 (d, *J* = 249.5 Hz), 163.7 (d, *J* = 248.2 Hz), 149.6, 149.5, 148.2 (d, *J* = 11.2 Hz), 145.8 (d, *J* = 11.4 Hz), 137.4 (d, *J* = 2.9 Hz), 137.3 (d, *J* = 3.0 Hz), 134.8, 133.7, 132.6, 132.1, 131.1, 131.0, 130.6, 129.7 (d, *J* = 5.3 Hz), 129.5, 129.3, 129.1, 129.1, 128.7, 128.3, 128.0, 127.9, 126.3 (d, *J* = 1.6 Hz), 125.0 (d, *J* = 1.6 Hz), 124.1, 124.0, 120.4 (d, *J* = 2.8 Hz), 120.3, 120.2, 117.2 (d, *J* = 2.8 Hz), 108.6 (d, *J* = 21.4 Hz), 108.4 (d, *J* = 22.6 Hz), 99.2 (d, *J* = 27.9 Hz), 98.8 (d, *J* = 27.6 Hz), 35.7, 35.7, 31.7, 31.7. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -108.3, -110.2.

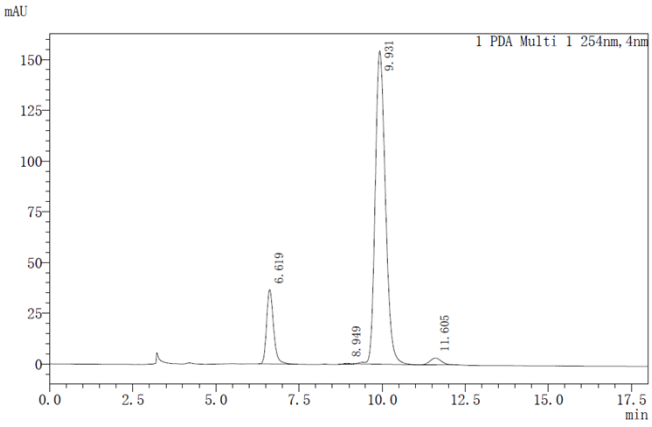
HRMS (ESI): calcd for $C_{25}H_{23}FNO$ $[M+H]^+$ 372.1758; found 372.1761.

The ee was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexane/isopropanol = 98/2, 1 mL/min, λ = 254 nm, t_R (minor) = 8.949/11.605 min, t_R (major) = 6.619/9.931 min.



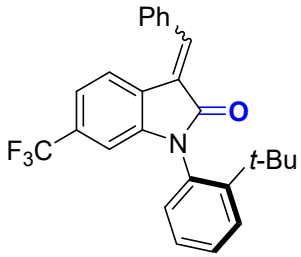
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	6.942	15224	229643	7.318	--
2	9.335	11207	223809	7.132	5.178
3	10.643	54712	1345887	42.888	2.242
4	12.488	47639	1338807	42.662	2.691



PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	6.619	36638	531553	13.525	--
2	8.949	551	9347	0.238	5.190
3	9.931	154374	3313109	84.299	1.813
4	11.605	3281	76188	1.939	2.809

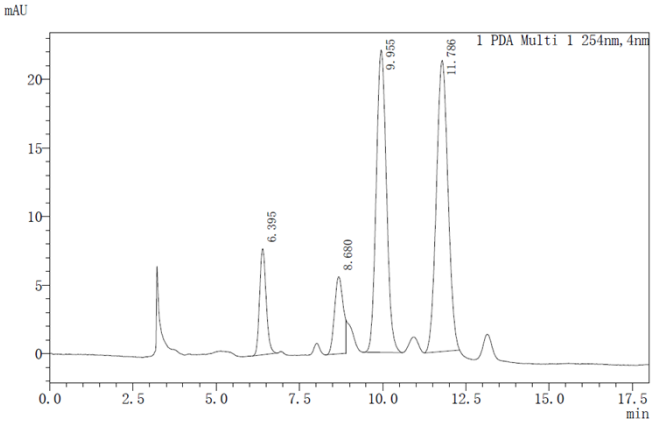


3-benzylidene-1-(2-(*tert*-butyl)phenyl)-6-(trifluoromethyl)indolin-2-one (**7-27**)

Yellow oil (28.2 mg, 67% yield, *Z*/*E* ≈ 1:4.5, 85% ee, 85% ee). (*Z*)&(*E*) Form: $[\alpha]_D^{25}$ = +23.3 (c = 0.3 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.42 – 8.37 (m, 0.29H), 8.07 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.76 – 7.67 (m, 3.65H), 7.57 – 7.43 (m, 4.87H), 7.41 – 7.33 (m, 1.42H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.05 (dd, *J* = 7.7, 1.0 Hz, 1.18H), 6.57 (s, 0.15H), 6.55 (s, 1H), 1.33 (s, 9H), 1.30 (s, 1.48H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.0, 166.9, 149.5, 146.6, 144.5, 140.8, 140.5, 134.4, 132.7, 132.4, 131.6, 131.5, 131.3, 131.1, 131.0, 130.3, 129.8, 129.7, 129.4, 129.3, 129.2, 128., 128.5, 128.2, 128.1, 126.1, 124.8, 124.3, 122.7, 118.9 (q, *J* = 3.8 Hz), 107.34 (q, *J* = 3.8 Hz), 35.8, 35.7, 31.7, 31.7. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.3, -62.8.

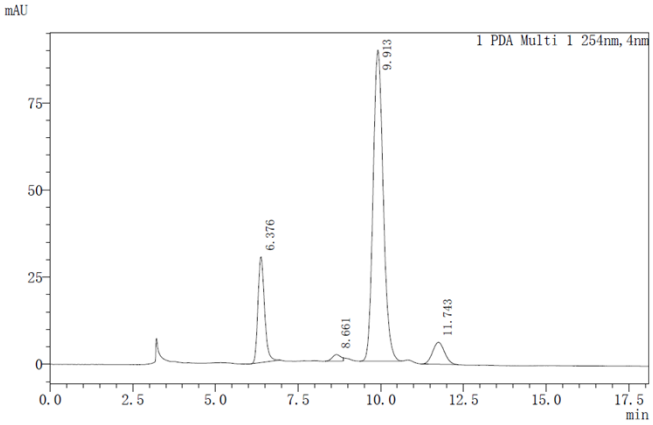
HRMS (ESI): calcd for $C_{26}H_{23}F_3NO$ $[M+H]^+$ 422.1726; found 422.1724.

The ee was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexane/isopropanol = 98/2, 1 mL/min, λ = 254 nm, t_R (minor) = 8.661/11.743 min, t_R (major) = 6.376/9.913 min.



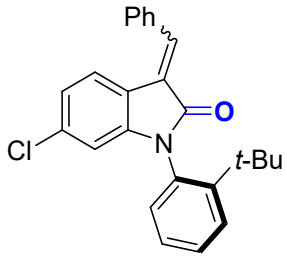
PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	6.395	7725	105790	8.870	--
2	8.680	5633	102332	8.580	5.024
3	9.955	22053	469221	39.342	2.293
4	11.786	21228	515316	43.207	3.000



PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	6.376	30312	420822	16.674	--
2	8.661	1881	34018	1.348	4.918
3	9.913	89211	1910826	75.711	2.229
4	11.743	6292	158189	6.268	2.962

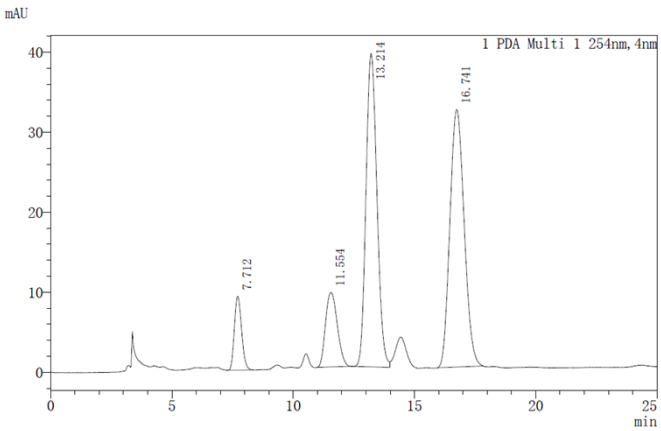


3-benzylidene-1-(2-(*tert*-butyl)phenyl)-6-chloroindolin-2-one (**7-28**)

Yellow oil (36.8 mg, 95% yield, *Z*/*E* ≈ 1:8.1, 95% ee, 95% ee). (*Z*)&(*E*) Form: $[\alpha]_D^{25}$ = +27.6 (c = 0.42 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.37 – 8.29 (m, 0.51H), 7.95 (s, 1H), 7.68 (dd, *J* = 15.2, 7.3 Hz, 3.48H), 7.64 – 7.60 (m, 1.33H), 7.54 – 7.41 (m, 5.63H), 7.35 (q, *J* = 7.6 Hz, 1.36H), 7.04 (t, *J* = 7.5 Hz, 1.56H), 6.87 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.36 (s, 0.22H), 6.34 (d, *J* = 1.3 Hz, 1H), 1.34 (s, 9H), 1.31 (s, 2.56H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.3, 167.0, 149.6, 147.5, 145.3, 138.4, 138.4, 135.5, 134.7, 134.6, 133.6, 132.6, 132.6, 132.3, 131.1, 131.0, 130.9, 129.9, 129.7, 129.5, 129.4, 129.1, 129.1, 128.8, 128.4, 128.0, 127.9, 126.3, 125.0, 123.5, 123.0, 122.0 121.9, 119.9, 119.7, 111.2, 110.8, 35.8, 35.7, 31.7, 31.7.

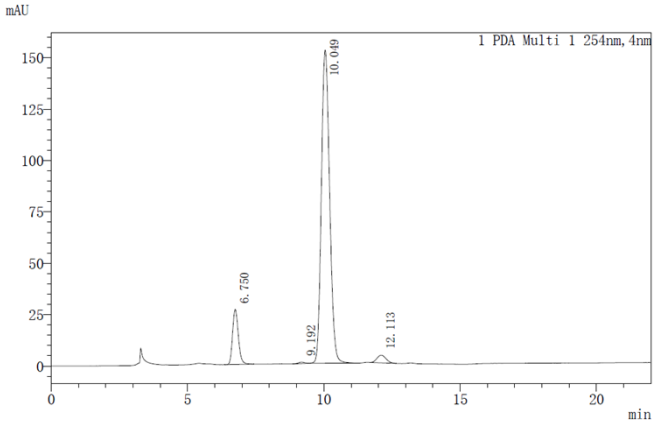
HRMS (ESI): calcd for $C_{25}H_{23}ClNO$ $[M+H]^+$ 388.1463; found 388.1462.

The ee was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexane/isopropanol = 98/2, 1 mL/min, λ = 254 nm, t_R (minor) = 9.192/12.113 min, t_R (major) = 6.750/10.049 min.



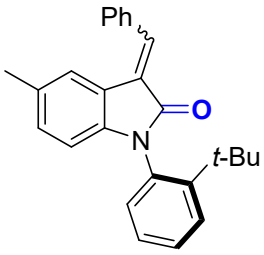
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	7.712	9227	191500	6.275	--
2	11.554	9319	314391	10.301	5.325
3	13.214	39189	1227479	40.218	1.928
4	16.741	32207	1318667	43.206	3.665



PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	6.750	26803	394526	10.672	--
2	9.192	656	10244	0.277	5.945
3	10.049	152343	3205667	86.716	1.731
4	12.113	3739	86291	2.334	3.488

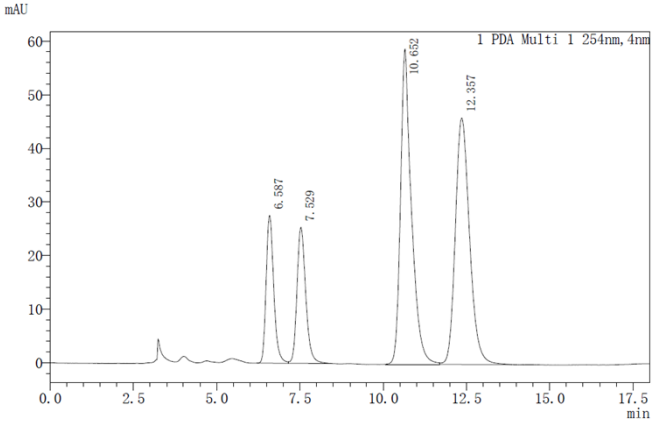


3-benzylidene-1-(2-(*tert*-butyl)phenyl)-5-methylindolin-2-one (**7-29**)

Yellow oil (31.9 mg, 87% yield, *Z*/*E* ≈ 1:4, 92% ee, 92% ee). (*Z*) Form: $[\alpha]_D^{25}$ = +41.5 (c = 0.27 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.36 (d, *J* = 6.5 Hz, 2H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.60 (s, 1H), 7.42 (dd, *J* = 12.9, 5.2 Hz, 5H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.7 Hz, 1H), 7.00 (d, *J* = 7.9 Hz, 1H), 6.26 (d, *J* = 7.9 Hz, 1H), 2.39 (s, 3H), 1.32 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.3, 149.6, 142.5, 137.3, 133.9, 133.4, 132.2, 131.4, 131.3, 130.5, 129.4, 129.2, 128.9, 128.3, 127.8, 126.3, 124.6, 119.6, 110.2, 35.7, 31.7, 21.2. (*E*) Form: $[\alpha]_D^{25}$ = +12.4 (c = 0.37 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.73 (d, *J* = 7.4 Hz, 2H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.54 (s, 1H), 7.50 (t, *J* = 7.4 Hz, 2H), 7.48 – 7.40 (m, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 7.7 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.25 (d, *J* = 8.0 Hz, 1H), 2.23 (s, 3H), 1.34 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.5, 149.6, 144.4, 137.5, 135.1, 133.4, 131.2, 131.2, 130.2, 129.6, 129.4, 129.3, 128.9, 128.6, 127.9, 127.5, 123.3, 121.2, 110.6, 35.7, 31.7, 21.1.

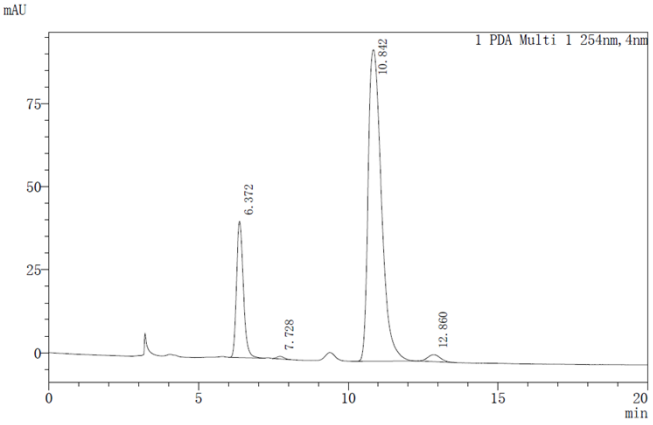
HRMS (ESI): calcd for $C_{26}H_{26}NO$ $[M+H]^+$ 368.2009; found 368.2008.

The ee was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexane/isopropanol = 98/2, 1 mL/min, λ = 254 nm, t_R (minor) = 7.728/12.860 min, t_R (major) = 6.372/10.842 min.



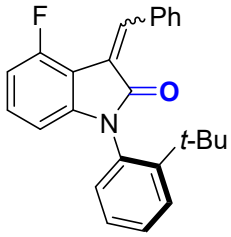
PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	6.587	27566	436972	12.108	--
2	7.529	25363	462979	12.829	2.112
3	10.652	58825	1344342	37.251	5.978
4	12.357	45986	1364627	37.813	2.543



PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	6.372	41065	649655	18.040	--
2	7.728	777	12736	0.354	3.111
3	10.842	93880	2877434	79.901	5.107
4	12.860	2097	61443	1.706	2.600

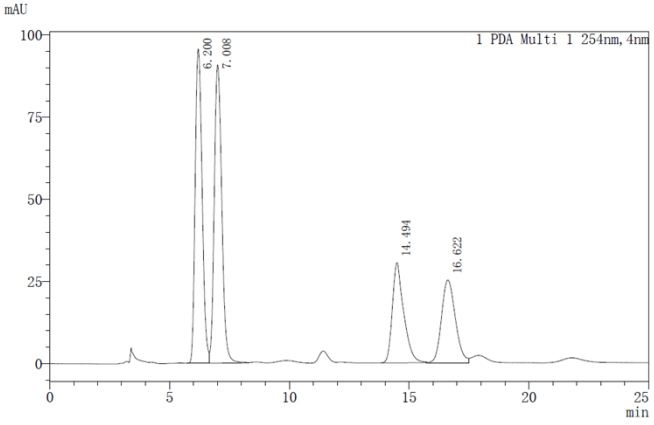


3-benzylidene-1-(2-(*tert*-butyl)phenyl)-4-fluoroindolin-2-one (**7-30**)

Yellow oil (31.9 mg, 86% yield, *Z/E* ≈ 2.1:1, 96% ee, 96% ee). (*Z*)&(*E*) Form: $[\alpha]_D^{25}$ = +7.7 (c = 0.39 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.33 – 8.26 (m, 2H), 8.11 (s, 0.26H), 8.01 (d, *J* = 3.3 Hz, 1H), 7.69 – 7.62 (m, 1.27H), 7.52 (d, *J* = 3.8 Hz, 0.55H), 7.48 – 7.38 (m, 5.14H), 7.34 (dt, *J* = 15.0, 7.6 Hz, 1.33H), 7.12 – 7.05 (m, 1.32H), 7.05 (t, *J* = 6.8 Hz, 1.28H), 6.81 – 6.75 (m, 1H), 6.69 (t, *J* = 9.2 Hz, 0.28H), 6.17 (t, *J* = 8.4 Hz, 1.26H), 1.34 (s, 2.49H), 1.31 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.3, 166.5, 158.3 (d, *J* = 252.0 Hz), 157.7 (d, *J* = 257.0 Hz), 149.5, 149.5, 148.4 (d, *J* = 8.0 Hz), 146.1 (d, *J* = 7.9 Hz), 143.2 (d, *J* = 12.3 Hz), 139.7 (d, *J* = 2.5 Hz), 135.5 (d, *J* = 2.2 Hz), 134.1, 132.9, 132.3, 131.2, 131.2, 130.7 (d, *J* = 8.8 Hz), 130.7, 130.3 (d, *J* = 5.2 Hz), 129.6, 129.5, 129.4, 129.1, 129.1, 128.2, 127.9, 127.8, 127.6, 124.0 (d, *J* = 5.2 Hz), 123.4 (d, *J* = 3.9 Hz), 111.6 (d, *J* = 15.5 Hz), 110.2 (d, *J* = 22.5 Hz), 109.7 (d, *J* = 21.1 Hz), 109.0 (d, *J* = 19.9 Hz), 106.7 (d, *J* = 3.1 Hz), 106.4 (d, *J* = 3.0 Hz), 35.8, 35.8, 31.7, 31.7. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -95.5, -119.5.

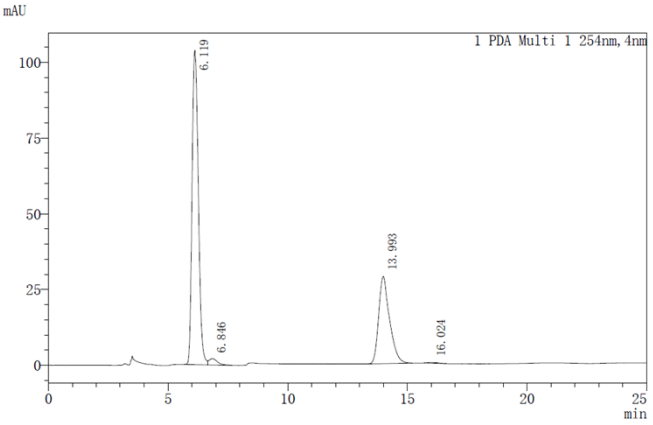
HRMS (ESI): calcd for $C_{25}H_{23}FNO$ $[M+H]^+$ 372.1758; found 372.1755.

The ee was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexane/isopropanol = 98/2, 1 mL/min, λ = 254 nm, t_R (minor) = 6.846/16.024 min, t_R (major) = 6.119/13.993 min.



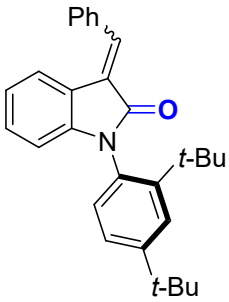
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	6.200	95690	1933844	32.593	--
2	7.008	90797	1982403	33.411	1.464
3	14.494	30480	1006621	16.965	10.693
4	16.622	25204	1010511	17.031	2.260



PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	6.119	103780	1887332	66.080	--
2	6.846	2068	51584	1.806	1.150
3	13.993	28787	909467	31.843	9.045
4	16.024	264	7760	0.272	2.589

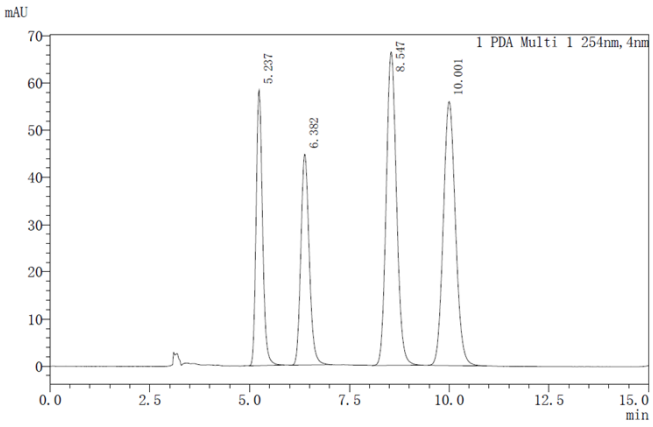


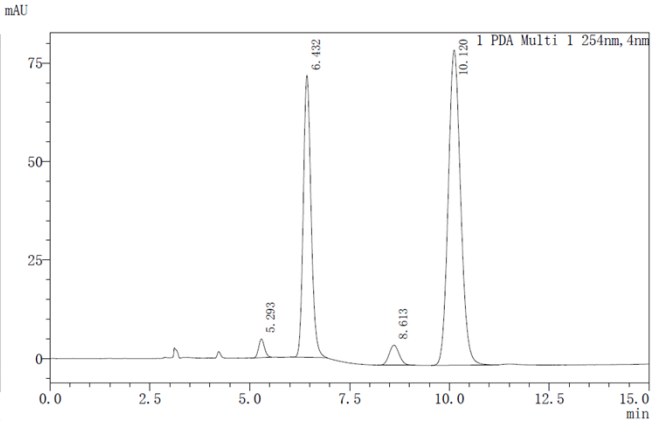
3-benzylidene-1-(2,4-di-*tert*-butylphenyl)indolin-2-one (**7-31**)

Yellow oil (36.0 mg, 88% yield, *Z/E* ≈ 1:1.8, 90% ee, 90% ee). (*Z*) Form: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 7.5, 1.9 Hz, 2H), 7.65 (d, *J* = 2.2 Hz, 1H), 7.62 (s, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.44 – 7.39 (m, 3H), 7.32 (dd, *J* = 8.1, 2.2 Hz, 1H), 7.19 (td, *J* = 7.7, 0.9 Hz, 1H), 7.07 (td, *J* = 7.6, 0.8 Hz, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.42 (d, *J* = 7.8 Hz, 1H), 1.36 (s, 9H), 1.31 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.3, 151.7, 148.5, 144.7, 137.5, 133.9, 132.3, 130.5, 130.5, 130.2, 128.8, 128.3, 126.2, 125.9, 124.8, 124.5, 121.8, 118.8, 110.6, 35.9, 34.8, 31.8, 31.4. (*E*) Form: $[\alpha]_D^{25}$ = +8.5 (c = 0.4 in MeOH), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.72 (d, *J* = 7.4 Hz, 2H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.66 (d, *J* = 2.1 Hz, 1H), 7.49 (t, *J* = 7.3 Hz, 2H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.33 (dd, *J* = 8.1, 2.2 Hz, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.88 (t, *J* = 7.4 Hz, 1H), 6.38 (d, *J* = 7.8 Hz, 1H), 1.37 (s, 9H), 1.34 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.5, 151.8, 148.5, 146.6, 137.7, 135.1, 132.3, 130.5, 130.2, 129.7, 129.6, 129.4, 128.6, 125.9, 125.0, 122.6, 121.8, 121.2, 111.0, 35.9, 34.9, 31.7, 31.4.

HRMS (ESI): calcd for $C_{29}H_{32}NO$ $[M+H]^+$ 410.2478; found 410.2476.

The ee was determined by FLM Co. MX(2) (0.46 cm x 25 cm), hexane/isopropanol = 94/6, 1 mL/min, λ = 254 nm, t_R (minor) = 5.293/8.613 min, t_R (major) = 6.432/10.120 min.



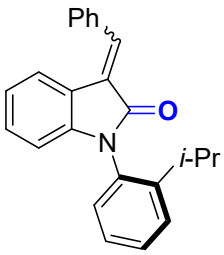


PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	5.237	58401	650864	17.715	--
2	6.382	44646	652242	17.753	3.325
3	8.547	66427	1186580	32.296	5.009
4	10.001	55970	1184336	32.235	2.805

PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	5.293	4742	48264	1.705	--
2	6.432	71579	968667	34.230	3.531
3	8.613	5085	89151	3.150	5.234
4	10.120	80038	1723833	60.915	2.895

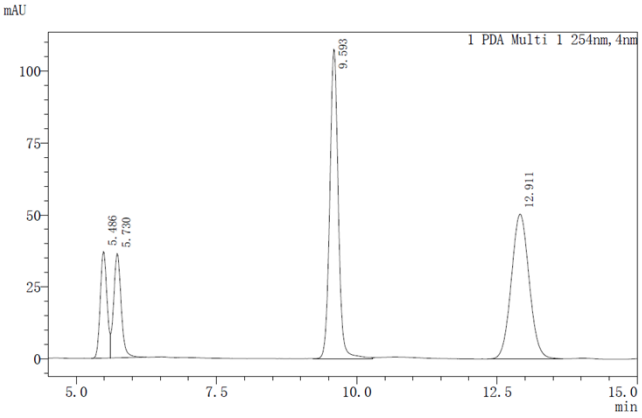


3-benzylidene-1-(2-isopropylphenyl)indolin-2-one (**7-32**)

Yellow oil (30.8 mg, 91% yield, *Z*/*E* ≈ 1:3.9, 24% ee, 19% ee). (*Z*)&(*E*) Form: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.36 (d, *J* = 6.8 Hz, 0.36H), 7.96 (s, 1H), 7.73 – 7.66 (m, 3.42H), 7.63 (d, J = 7.5 Hz, 0.2H), 7.55 – 7.41 (m, 6.34H), 7.35 (t, *J* = 7.3 Hz, 1.44H), 7.22 (d, *J* = 7.7 Hz, 1.28H), 7.19 – 7.14 (m, 1.29H), 7.09 (t, *J* = 7.5 Hz, 0.25H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.44 (d, *J* = 7.8 Hz, 1.23H), 2.97 – 2.91 (m, 1.29H), 1.26 (d, *J* = 6.8 Hz, 3H), 1.21 (d, *J* = 6.8 Hz, 0.66H), 1.14 (d, *J* = 6.7 Hz, 3.98H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.3, 166.0, 147.7, 145.3, 143.5, 137.9, 137.7, 135.1, 133.8, 132.3, 132.2, 132.2, 130.6, 129.8, 129.6, 129.5, 129.3, 128.9, 128.9, 128.7, 128.7, 128.3, 127.3, 127.2, 127.1, 127.1, 126.9, 125.9, 124.4, 122.8, 122.0, 121.1, 119.0, 109.5, 109.2, 28.5, 28.4, 23.9, 23.7, 23.6.

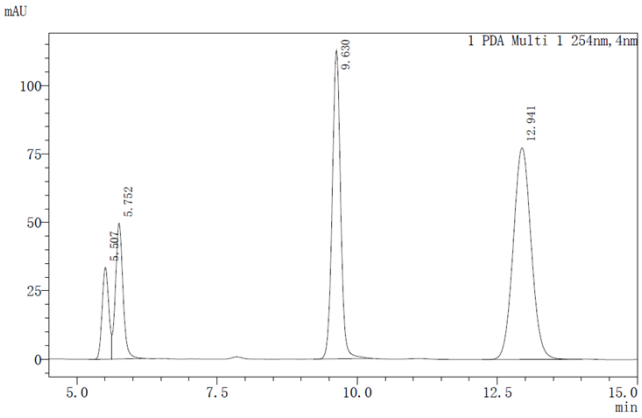
HRMS (ESI): calcd for $C_{24}H_{22}NO$ $[M+H]^+$ 340.1696; found 340.1699.

The ee was determined by FLM Co. MX(2) (0.46 cm x 25 cm), hexane/isopropanol = 90/10, 1 mL/min, λ = 254 nm, t_R (minor) = 5.507/9.630 min, t_R (major) = 5.752/12.941 min.



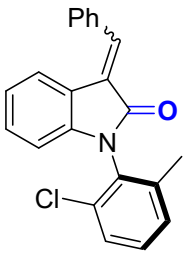
PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	5.486	37042	311866	10.786	--
2	5.730	36258	334383	11.565	0.976
3	9.593	107546	1129844	39.077	14.291
4	12.911	50387	1115212	38.571	7.640



PDA Ch1 254nm

NO.	Ret. Time	Height (uAU)	Area (uAU*min)	Rel. Area %	Resolution (USP)
1	5.507	33578	279771	7.702	--
2	5.752	49651	458480	12.621	0.979
3	9.630	112859	1173077	32.293	14.456
4	12.941	77404	1721305	47.384	7.597

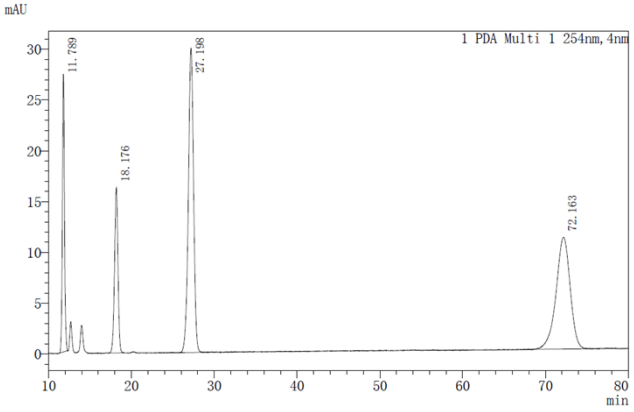


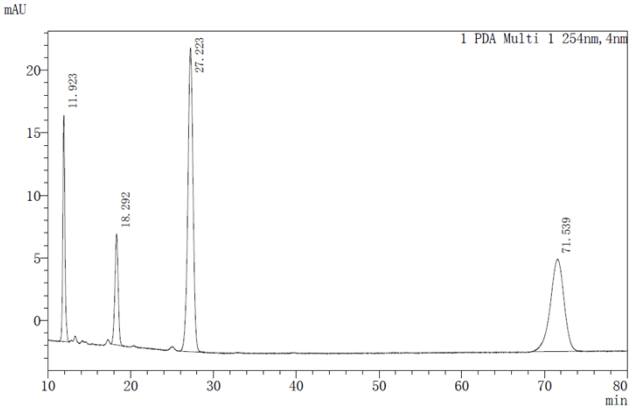
3-benzylidene-1-(2-chloro-6-methylphenyl)indolin-2-one (**7-33**)

Yellow oil (30.4 mg, 88% yield, *Z/E* ≈ 1:3.3, 14% ee, 11% ee). (*Z*)&(*E*) Form: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 6.4 Hz, 0.52H), 7.97 (s, 1H), 7.74 – 7.68 (m, 3.49H), 7.65 (d, *J* = 7.4 Hz, 0.28H), 7.50 (t, *J* = 7.3 Hz, 2H), 7.47 – 7.43 m, 3H), 7.37 – 7.28 (m, 2.84H), 7.21 – 7.16 (m, 1.37H), 7.11 (t, *J* = 7.6 Hz, 0.29H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.38 (t, *J* = 7.2 Hz, 1.28H), 2.24 (s, 3H), 2.22 (s, 0.89H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.3, 143.0, 139.9, 139.9, 138.2, 138.2, 134.9, 134.0, 132.2, 131.1, 130.7, 130.0, 129.9, 129.9, 129.7, 129.5, 129.4, 129.4, 129.0, 128.7, 128.3, 128.1, 128.0, 126.7, 123.1, 122.3, 122.3, 121.2, 119.3, 109.2, 108.9, 18.3.

HRMS (ESI): calcd for $C_{22}H_{17}ClNO^+$ $[M+H]^+$ 346.0993; found 346.0990.

The ee was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), hexane/isopropanol = 95/5, 1 mL/min, λ = 254 nm, t_R (minor) = 18.292/71.539 min, t_R (major) = 11.923/27.223 min.





PDA Ch1 254nm

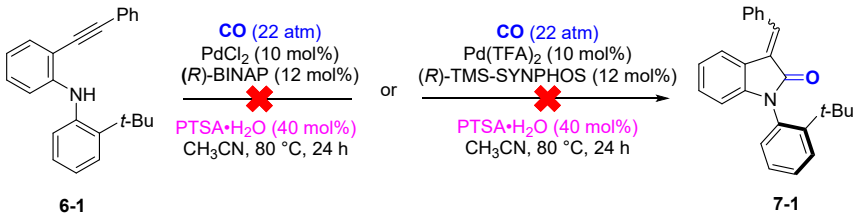
NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	11.789	27369	483406	13.612	--
2	18.176	16294	465780	13.115	10.515
3	27.198	29987	1304183	36.723	9.560
4	72.163	11021	1298074	36.551	21.547

PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	11.923	18110	322420	13.119	--
2	18.292	8851	244820	9.961	10.628
3	27.223	24269	1048365	42.656	9.563
4	71.539	7366	842131	34.265	21.825

2.7 Procedure for Control experiments

A 10 mL tube was charged with $PdCl_2$ or $Pd(TFA)_2$ (0.01 mmol, 10 mol%), (*R*)-BINAP or (*R*)-TMS-SYNPHOS (0.01 mmol, 10 mol%), PTSA•H_2O (7.6 mg, 0.04 mmol, 40 mol%), **6-1** (0.1 mmol), and CH_3CN (1 mL). Then, the reaction tube is placed in the autoclave, and the mixture was refilled with CO for 3 times carefully in a well-ventilated fume hood, and then the CO gas was flushed to 22 atm. Finally, the autoclave was placed at 80 °C for 24 h. After completion of the reaction, according to TLC monitoring, no product was produced and remains as **6-1**.

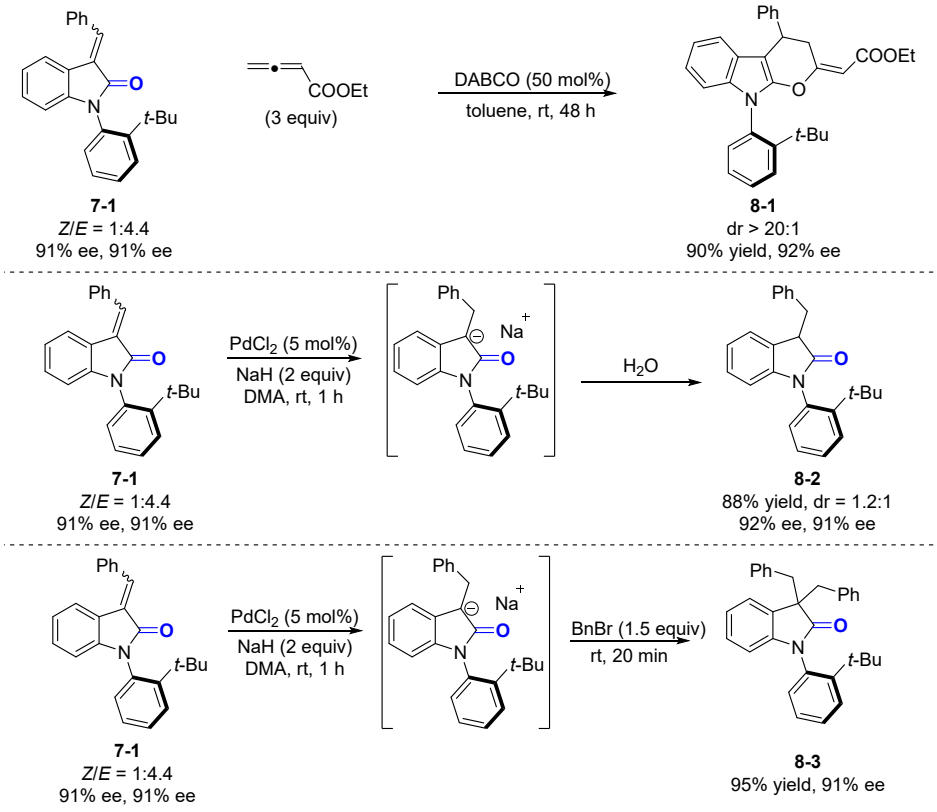


2.8 Procedures for the derivatization of 7-1 and Characterization

*Procedures for **8-1** (Scheme S2):*[3] An oven-dried 10 mL Schlenk tube was charged with **7-1** (35.3 mg, 0.1 mmol), DABCO (5.6 mg, 0.05 mmol, 50 mol%), ethyl 2,3-butadienoate (35 µL, 0.3 mmol, 3.0 eq.), and dry toluene (2 mL). The reaction mixture was stirred at rt for 48 h. And then the crude reaction mixture was concentrated in vacuo, the residue was purified by silica gel flash column chromatography (hexane/EtOAc) to give **8-1**.

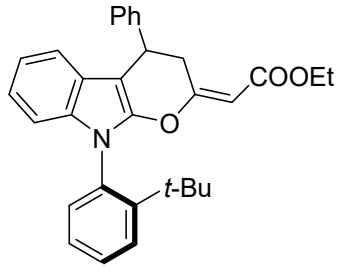
*Procedures for **8-2** (Scheme S2):*[4] A oven-dried 10 mL Schlenk tube was charged with $PdCl_2$ (0.9 mg, 0.005 mmol, 5 mol%), NaH (60% in oil) (8 mg, 0.2 mmol, 2.0 eq.), and DMA (1.0 mL). Then, the reaction mixture was stirred at room temperature for 5 min under Ar until the mixture turned black, **7-1** (35.3 mg, 0.1 mmol) in DMA (0.5 mL) was added through syringe. And then, the reaction was stirred at rt for 1 h. After the reaction was completed monitored by TLC, the mixture was quenched with NH_4Cl aq and extracted with EtOAc (10 mL × 3). Then, the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc) to give **8-2**.

*Procedures for **8-3** (Scheme S2):*[4] A oven-dried 10 mL Schlenk tube was charged with $PdCl_2$ (0.9 mg, 0.005 mmol, 5 mol%), NaH (60% in oil) (8 mg, 0.2 mmol, 2.0 eq.), and DMA (1.0 mL). Then, the reaction mixture was stirred at room temperature for 5 min under Ar until the mixture turned black, **7-1** (35.3 mg, 0.1 mmol) in DMA (0.5 mL) was added through syringe. And then, the reaction was stirred at rt for 1 h. When the starting material was consumed monitored with TLC, BnBr (18 µL, 0.15 mmol, 1.5 eq.) was added through micro syringe and continue to stir for 20 min. Then the mixture was quenched with NH_4Cl aq and extracted with EtOAc (10 mL × 3), and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc) to give **8-3**.



Scheme S2. The derivatization of **7-1**

Characterization of Products 8

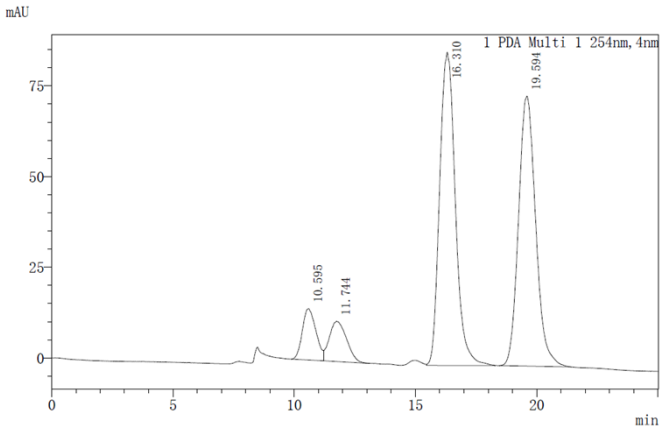


ethyl (*E*)-2-(9-(2-(*tert*-butyl)phenyl)-4-phenyl-4,9-dihydropyrano[2,3-b]indol-2(3*H*)-ylidene)acetate (**8-1**)

Pale yellow solid (41.9 mg, 90% yield, dr > 20:1, 92% ee). $[\alpha]_D^{25}$ = +71.8 (c = 0.17 in MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.70 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.49 (td, *J* = 8.2, 7.8, 1.6 Hz, 1H), 7.38 – 7.30 (m, 5H), 7.29 – 7.25 (m, 1H), 7.07 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.02 (ddd, *J* = 8.1, 6.9, 1.6 Hz, 1H), 6.98 (td, *J* = 7.4, 6.9, 1.3 Hz, 1H), 6.95 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.85 – 6.77 (m, 1H), 5.63 (s, 1H), 4.49 – 4.38 (m, 1H), 4.11 (tq, *J* = 7.1, 3.5 Hz, 2H), 3.79 (dd, *J* = 15.2, 6.0 Hz, 1H), 3.57 (dd, *J* = 15.2, 7.2 Hz, 1H), 1.22 (d, *J* = 3.8 Hz, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 166.6, 165.8, 149.6, 146.7, 142.7, 135.0, 133.0, 132.0, 129.4, 128.7, 128.5, 127.7, 127.0, 126.8, 125.1, 120.4, 120.3, 118.1, 111.0, 102.1, 91.6, 59.9, 35.8, 35.6, 32.7, 31.6, 14.2.

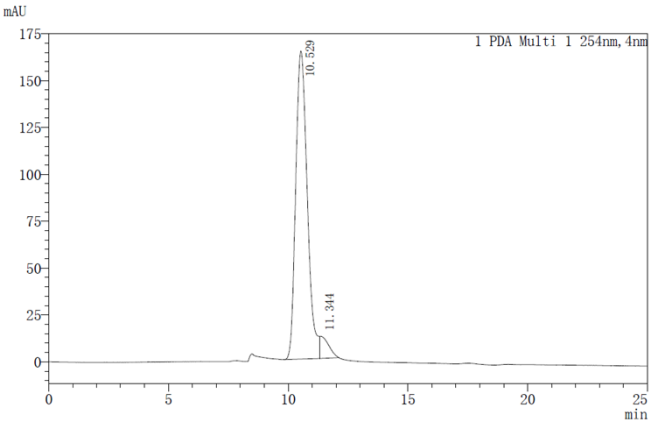
HRMS (ESI): calcd for $C_{31}H_{32}NO_3$ $[M+H]^+$ 466.2378; found 466.2381.

The ee was determined by Daicel Chiralcel OD-H (0.46 cm x 25 cm), hexane/isopropanol = 99/1, 0.5 mL/min, λ = 254 nm, t_R (minor) = 11.334 min, t_R (major) = 10.529 min.



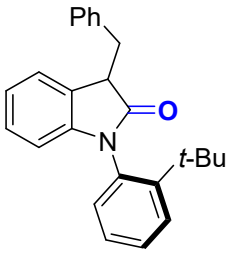
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	10.595	14194	552131	6.388	--
2	11.744	11120	547643	6.337	0.957
3	16.310	86368	3885355	44.956	3.702
4	19.594	74455	3657457	42.319	2.742



PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	10.529	164388	5521055	95.058	--
2	11.344	11754	287025	4.942	--

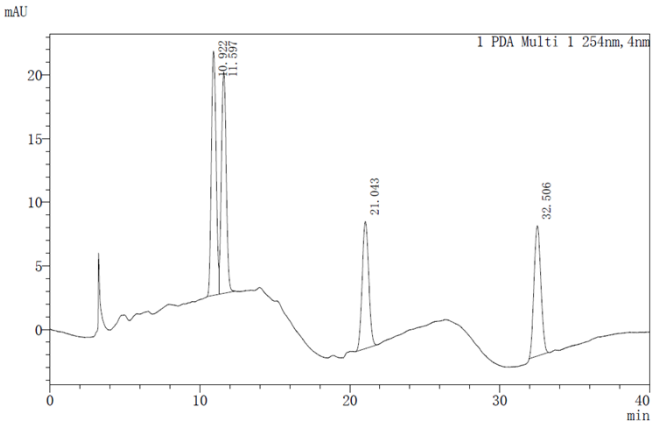


3-benzyl-1-(2-(*tert*-butyl)phenyl)indolin-2-one (**8-2**)

Pale yellow oil (31.2 mg, 88% yield, dr = 1.2:1, 92% ee, 91% ee). *cis* or *trans*: $[\alpha]_D^{25}$ = +20.9 (c = 0.22 in MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.63 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.41 (td, *J* = 7.7, 1.6 Hz, 1H), 7.32 (qd, *J* = 7.4, 2.7 Hz, 3H), 7.28 (dt, *J* = 5.9, 1.5 Hz, 3H), 7.15 – 7.10 (m, 1H), 6.99 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.90 (td, *J* = 7.5, 1.1 Hz, 1H), 6.66 (d, *J* = 7.4 Hz, 1H), 6.30 (d, *J* = 7.8 Hz, 1H), 3.88 (dd, *J* = 10.6, 4.3 Hz, 1H), 3.65 (dd, *J* = 13.6, 4.4 Hz, 1H), 2.87 (dd, *J* = 13.6, 10.5 Hz, 1H), 1.25 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 177.6, 149.4, 146.7, 138.2, 133.5, 131.3, 129.6, 129.3, 128.8, 128.5, 128.4, 128.0, 127.9, 126.8, 124.7, 122.1, 110.7, 47.9, 37.0, 35.6, 31.6. *cis* or *trans*: $[\alpha]_D^{25}$ = +23.2 (c = 0.19 in MeOH). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.58 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.35 (ddd, *J* = 8.3, 7.3, 1.6 Hz, 1H), 7.24 – 7.19 (m, 3H), 7.17 (td, *J* = 7.5, 1.5 Hz, 1H), 7.15 – 7.08 (m, 4H), 6.99 (td, *J* = 7.5, 1.1 Hz, 1H), 6.20 (td, *J* = 6.8, 6.3, 1.4 Hz, 2H), 3.92 (dd, *J* = 7.5, 4.2 Hz, 1H), 3.50 (dd, *J* = 13.6, 4.2 Hz, 1H), 3.27 (dd, *J* = 13.6, 7.5 Hz, 1H), 1.28 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 177.8, 149.3, 146.6, 137.2, 133.0, 130.9, 129.9, 129.2, 128.8, 128.1, 128.0, 127.9, 127.8, 126.6, 124.3, 122.2, 110.5, 47.1, 36.3, 35.6, 31.6.

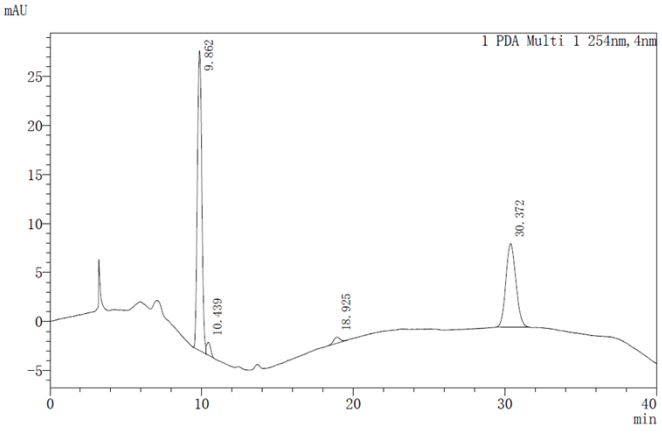
HRMS (ESI): calcd for $C_{25}H_{26}NO$ $[M+H]^+$ 356.2009; found 356.2007.

The ee was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), hexane/isopropanol = 98/2, 1 mL/min, λ = 254 nm, t_R (minor) = 10.439/18.925 min, t_R (major) = 9.862/30.372 min.



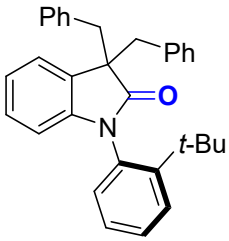
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	10.922	19182	421226	29.237	--
2	11.597	17396	389570	27.039	1.141
3	21.043	9996	303101	21.038	13.430
4	32.506	10231	326848	22.686	13.691



PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	9.862	30614	618394	58.810	--
2	10.439	1320	22836	2.172	0.994
3	18.925	622	18221	1.733	12.270
4	30.372	8528	392055	37.285	11.547

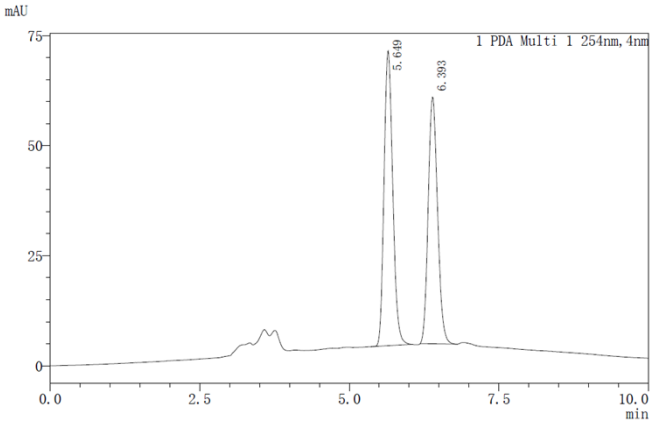


3,3-dibenzyl-1-(2-(*tert*-butyl)phenyl)indolin-2-one (**8-3**)

Pale yellow solid (42.3 mg, 95% yield, 91% ee). $[\alpha]_D^{25}$ = +13.3 (c = 0.09 in MeOH).**^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.44 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.32 (dd, *J* = 7.3, 1.5 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.21 – 7.14 (m, 6H), 7.12 (td, *J* = 7.4, 1.3 Hz, 1H), 7.07 (td, *J* = 7.7, 2.0 Hz, 3H), 6.93 (td, *J* = 7.6, 1.5 Hz, 1H), 6.83 (dd, *J* = 7.8, 1.4 Hz, 2H), 5.95 (dd, *J* = 7.5, 1.2 Hz, 1H), 5.10 (dd, *J* = 7.8, 1.5 Hz, 1H), 3.46 (d, *J* = 13.3 Hz, 1H), 3.41 (d, *J* = 12.7 Hz, 1H), 3.33 (d, *J* = 13.3 Hz, 1H), 3.24 (d, *J* = 12.7 Hz, 1H), 1.00 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 178.7, 149.5, 146.7, 136.1, 135.8, 134.0, 131.2, 131.0, 130.6, 130.2, 128.8, 128.1, 127.9, 127.8, 127.7, 127.6, 126.7, 126.5, 124.4, 121.8, 111.0, 56.3, 44.8, 42.9, 35.0, 31.2.

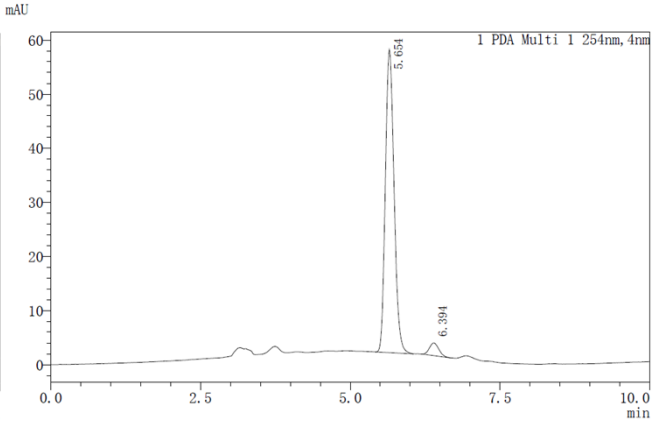
HRMS (ESI): calcd for $C_{32}H_{32}NO$ $[M+H]^+$ 446.2478; found 446.2481.

The ee was determined by Daicel Chiralcel AD-H (0.46 cm x 25 cm), hexane/isopropanol = 90/10, 1 mL/min, λ = 254 nm, t_R (minor) = 6.394 min, t_R (major) = 5.654 min.



PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	5.649	67024	677583	52.618	--
2	6.393	55983	610164	47.382	2.578



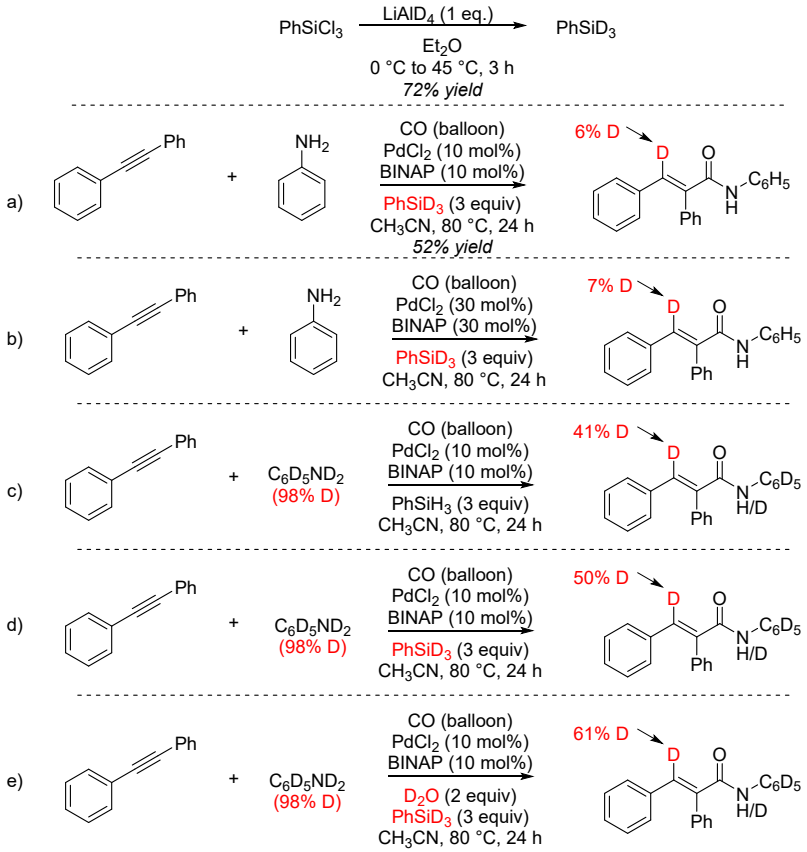
PDA Ch1 254nm

NO.	Ret. Time	Height(uAU)	Area(uAU*min)	Rel. Area %	Resolution(USP)
1	5.654	56077	566347	95.712	--
2	6.394	2344	25375	4.288	2.546

2.9 Procedures for the Deuterium experiments.

Procedures for synthesis of phenylsilane-d3 (Scheme S3):[5] A oven-dried 25 mL Schlenk tube was charged with $LiAlD_4$ (262 mg, 6.24 mmol, 1.0 eq.), the above-mentioned mixture was degassed and refilled with Ar for 3 times, and dry Et_2O (6 mL) was added to the mixture by syringe. Then the reaction was cooled to 0 °C with stirring, and $PhSiCl_3$ (1.0 mL, 6.24 mmol) was added dropwise. And the reaction mixture was warmed to rt and then refluxed for 3 h at 45 °C. The reaction mixture was then cooled to 0 °C again, where it was carefully quenched with ice cold H_2O. The organic layer was separated and held at 0 °C and the aqueous layer extracted with ice-cold Et_2O (10 mL) at 0 °C. The organic layers were combined, washed with ice-cold brine at 0 °C, dried over MgSO4, and concentrated under reduced pressure at 0 °C at 40 mbar to furnish pure $PhSiD_3$ as a colorless oil (880 mg, 57 wt% solution in Et_2O, D: >95%, 72% yield).

General procedures for deuterated experiments a to e (Scheme S3): An oven-dried 10 mL Schlenk tube was charged with 1,2-diphenylethyne (17.8 mg, 0.1 mmol), $PdCl_2$ (1.8 mg, 0.01 mmol, 10 mol%), BINAP (6.2 mg, 0.01 mmol, 10 mol%), the above-mentioned mixture was degassed and refilled with CO for 3 times. Then, a solution of aniline (11 µL, 0.12 mmol, 1.2 eq.) and Et_3SiH (50 µL, 0.3 mmol, 3.0 eq.) in 2 mL of dry CH_3CN were added to the mixture by syringe. Finally, the mixture was stirred at 80 °C for 24 h under CO balloon. After completion of the reaction, the crude reaction mixture was concentrated in vacuo and the residue was purified by silica gel flash column chromatography (hexane/EtOAc) to give products.



Scheme S3. Deuterated experiments.

The deuterated rate based on ^1H NMR identification (Figure S1). When deuterated phenylsilanes was used, only a very low deuteration rate was observed in the product (Figure S1a, 6% D). However, when deuterated aniline substrates were used, higher

deuteration rates were observed in the product (Figure S1c, 41% D). Furthermore, when we used both deuterated phenylsilane and deuterated aniline under the same conditions, it was observed that the product contained 50% D (Figure S1d), which is approximately equal to the sum of the above two terms. These results indicated that most of the hydrogen on the olefins in the product came from the aminolysis process involving aniline, and a small part came from hydrosilane. When we further added deuterated water to the reaction system, the deuteration rate in the product increased (Figure S1e, 61% D). However, the reason why the deuteration rate in the product is always lower than the theoretical value is due to the rapid H/D exchange between the active H (probably water) in the reaction system and the deuterated aniline. It is worth mentioning that when we increase the amount of catalyst and ligand to 30 mol%, the deuteration rate in the product does not increase basically (Figure S1b, 7% D). This indicates that the step of palladium catalyst and hydrosilane to form Pd-H species is slower than the latter step, which may be the rate-determining step for the entire reaction.

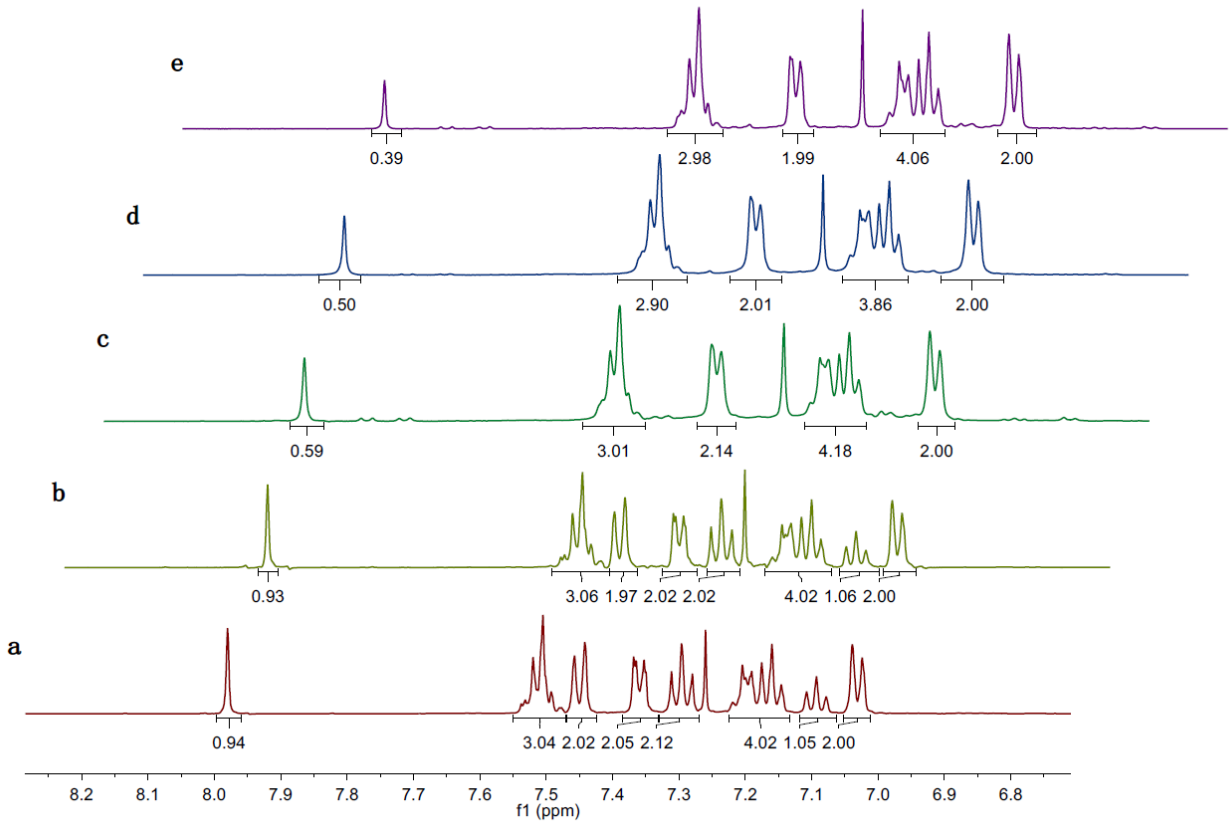
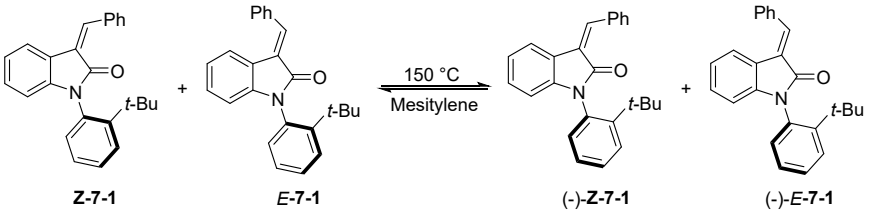


Figure S1. ^{1}H NMR of the product of deuterated experiments**.**

2.10 Racemization Studies of 7-1



Z-7-1 *E*-**7-1** (-)-**Z-7-1** (-)-*E*-**7-1**

*Procedures for thermal racemization of **7-1**:* A solution of **7-1** (10 mg, 49.2% ee, 48.8% ee, Z/E = 1:4.3) in dry mesitylene (2 mL) was heated at 150 °C. At intervals, small samples were taken and the solvent was removed by evaporation. The *ee* and *Z/E* ratio were determined by HPLC (HPLC conditions: CHIRALPAK AD-H, hexane/isopropanol = 90:10, flow: 1.0 mL/min, λ = 254 nm).

In order to explore the enantiomerization process in this study, the activation barriers of the enantiomerization process for typical product (**7-1**) was investigated computationally. The activation barrier ($\Delta G^{\neq}$) for the enantiomerization process was obtained as the Gibbs free energy difference from the ground-state structure to the corresponding transition state. The rate constant for enantiomerization (kent) was calculated based on the following equation, where the transmission coefficient κ is set as 1, Boltzmann constant k_B = 1.3806503 × 10^{-23} J/K, Planck constant h = 6.62606876 × 10^{-34} J·s, idea gas constant R = 8.314472 J/(mol·K), T = 423.15 K.[6]

$$k_{ent} = \kappa \frac{k_B T}{h} exp \frac{-\Delta G^{\ddagger}}{RT}$$

The integrated first order rate law is

$$\ln[R_t] = -k_{ent}t + \ln[R_0]$$

$$\ln(R_0/R_t) = \ln[(1 + ee_0)/(1 + ee_t)]$$

A plot of $\ln(R_0/R_t)$ vs. time t gives a straight line with a slope of k_{ent} (**Figure S2)**

The rates for the isomerization of **7-1** in mesitylene was calculated as shown in **Table S4**

Table S4. Thermal Racemization of **7-1**

time (S)	(*Z*) ee %	(*E*) ee %	*Z/E*	(*Z*) $\ln[(1+ee_0)/(1+ee_t)]$	(*E*) $\ln[(1+ee_0)/(1+ee_t)]$
0	49.2	48.8	1/4.3	0	0
86400	45.7	45.0	1/4.1	0.023737975	0.02586938
172800	41.5	41.5	1/4.1	0.052987971	0.050303405
259200	39.1	38.9	1/4.0	0.070094589	0.068848873
345600	36.5	35.8	1/3.3	0.088963073	0.091419907
432000	32.6	31.4	1/3.7	0.11795061	0.124357016
518400	30.8	28.8	1/3.8	0.131618249	0.144342309

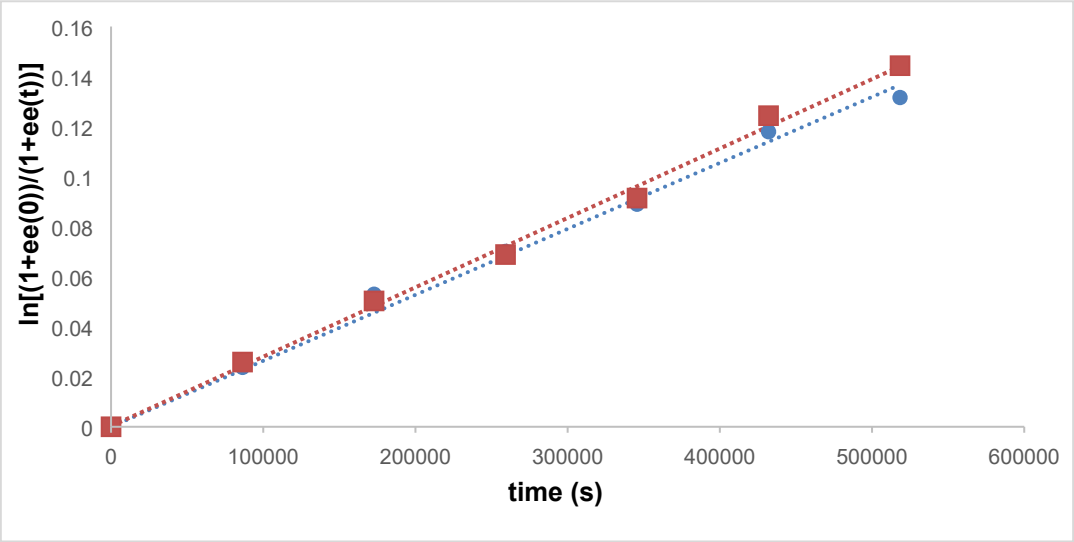


Figure S2. The plot of $\ln(R_0/R_t)$ vesus time t at 423.15 K for **7-1**

Therefore:

$$k_{ent} = 3.0 \times 10^{-7}\ s^{-1}$$

$$k_{rac} = 2k_{ent} = 6.0 \times 10^{-7}\ s^{-1}$$

$$t_{1/2}rac = \frac{ln\,2}{k_{rac}}$$

$$= 1.16 \times 10^{6}\ s = 320.9\ h$$

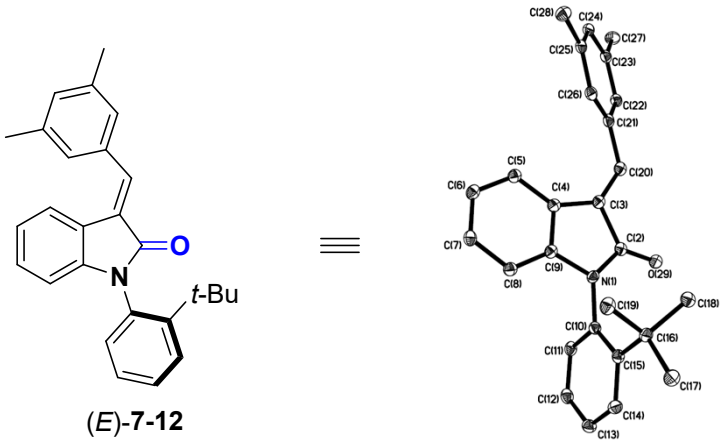
Employing the Eyring equation:

$$\Delta G^{\ddagger} = -RTln(\frac{k_{ent} \times h}{k_B T})$$

$$= 157.7\ kJ/mol = 37.7\ kcal/mol$$

3. X-ray Crystal Structure of (*E*)-7-12 and (*E*)-7-23

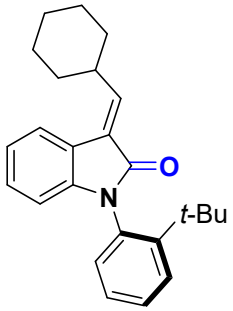
Single crystals of (*E*)-**7-12** were obtained by recrystallization from DCM. The molecular structure and X-ray diffractional data/refinement of (*E*)-**7-12** were shown below.



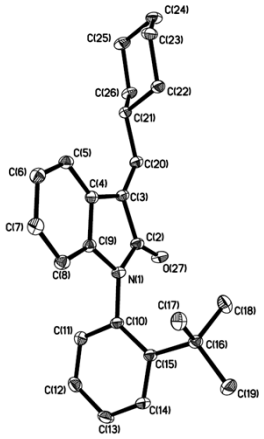
(*E*)-**7-12**

Identification code	chenzhh_A2_220427_auto
Empirical formula	$C_{27}H_{27}NO$
Formula weight	381.49
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.78370(10)
b/Å	31.1021(4)
c/Å	8.64470(10)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2092.79(5)
Z	4
ρ_{calc}g/cm^3	1.211
μ/mm^{-1}	0.558
F(000)	816.0
Crystal size/mm^3	0.450 × 0.400 × 0.300
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.684 to 157.946
Index ranges	-7 ≤ h ≤ 9, -38 ≤ k ≤ 39, -10 ≤ l ≤ 10
Reflections collected	20246
Independent reflections	4366 [R_{int} = 0.0570, R_{sigma} = 0.0323]
Data/restraints/parameters	4366/0/268
Goodness-of-fit on F^2	1.061
Final R indexes [I>= 2σ (I)]	R_1 = 0.0471, wR_2 = 0.1222
Final R indexes [all data]	R_1 = 0.0484, wR_2 = 0.1231
Largest diff. peak/hole / e Å^{-3}	0.26/-0.27
Flack parameter	-0.04 (19)

Single crystals of (*E*)-**7-23** were obtained by recrystallization from DCM. The molecular structure and X-ray diffractional data/refinement of (*E*)-**7-23** were shown below.



(*E*)-**7-23**



Identification code	chenzhh_B1_220427_auto
Empirical formula	$C_{25}H_{29}NO$
Formula weight	359.49
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	11.2000(2)
b/Å	7.87450(10)
c/Å	11.8582(2)
α/°	90
β/°	103.2920(10)
γ/°	90
Volume/Å^3	1017.81(3)
Z	2
ρ_{calc}g/cm^3	1.173
μ/mm^{-1}	0.539
F(000)	388.0
Crystal size/mm^3	0.25 × 0.2 × 0.15
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.66 to 157.59
Index ranges	-14 ≤ h ≤ 14, -9 ≤ k ≤ 8, -14 ≤ l ≤ 15
Reflections collected	20056
Independent reflections	4023 [R_{int} = 0.0323, R_{sigma} = 0.0205]
Data/restraints/parameters	4023/1/278
Goodness-of-fit on F^2	1.083
Final R indexes [I>= 2σ (I)]	R_1 = 0.0312, wR_2 = 0.0800
Final R indexes [all data]	R_1 = 0.0317, wR_2 = 0.0804
Largest diff. peak/hole / e Å^{-3}	0.11/-0.17
Flack parameter	0.08(10)

4. References

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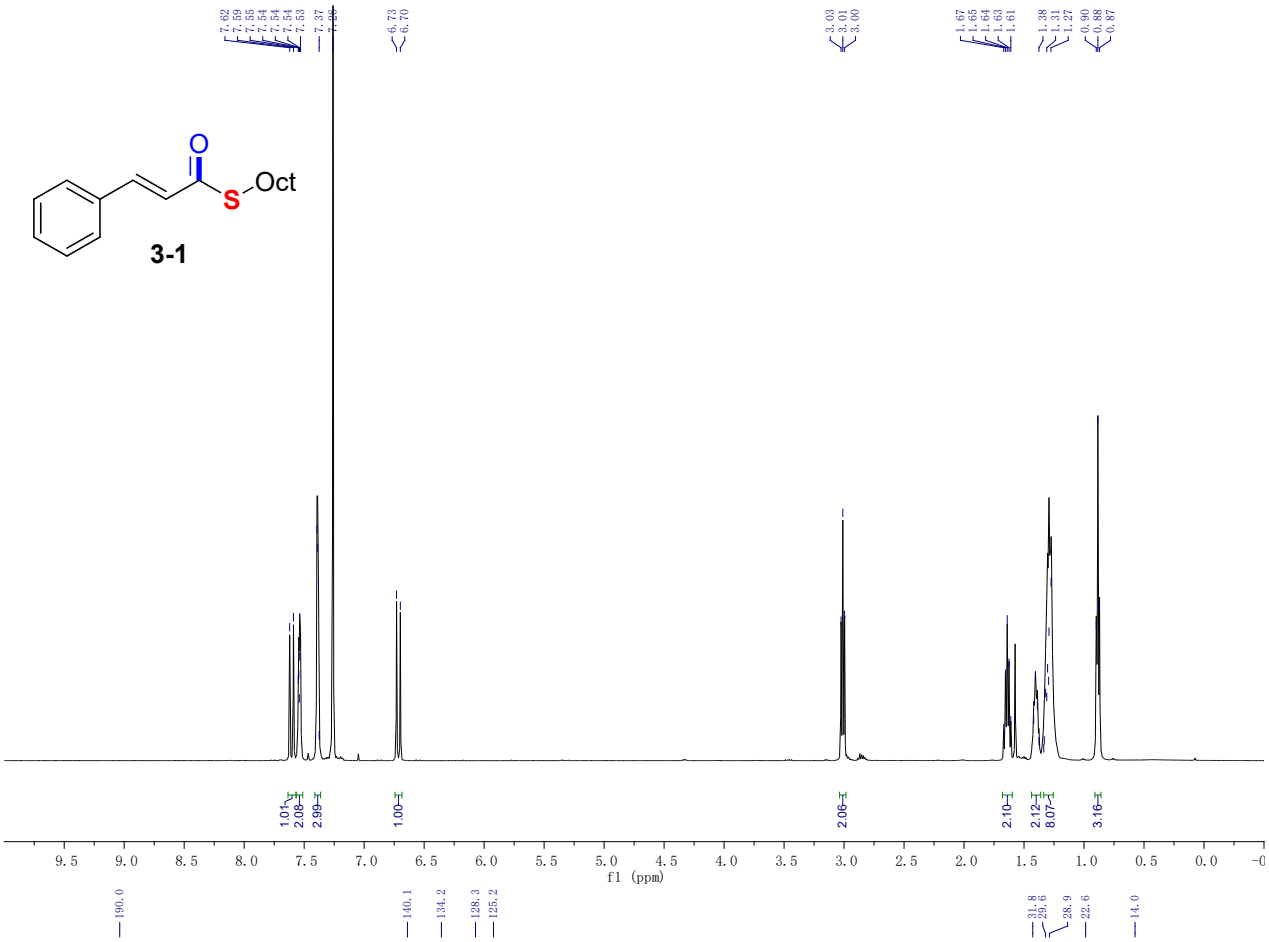
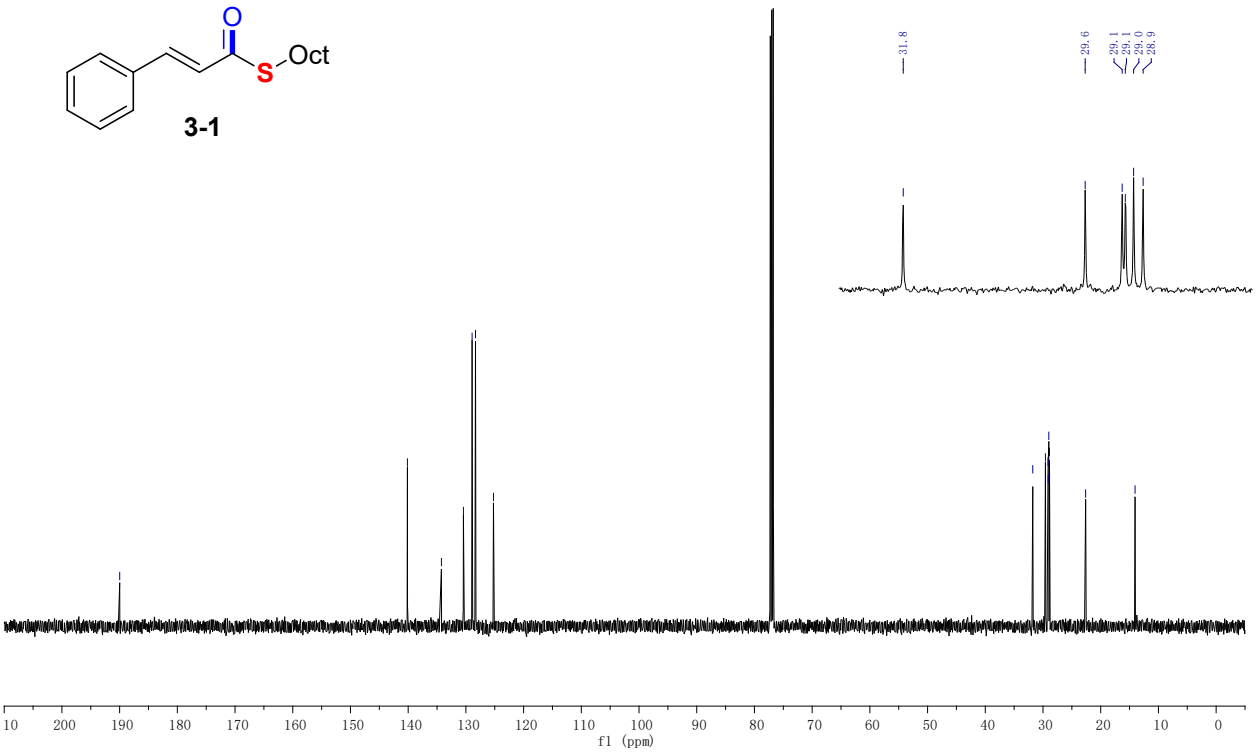
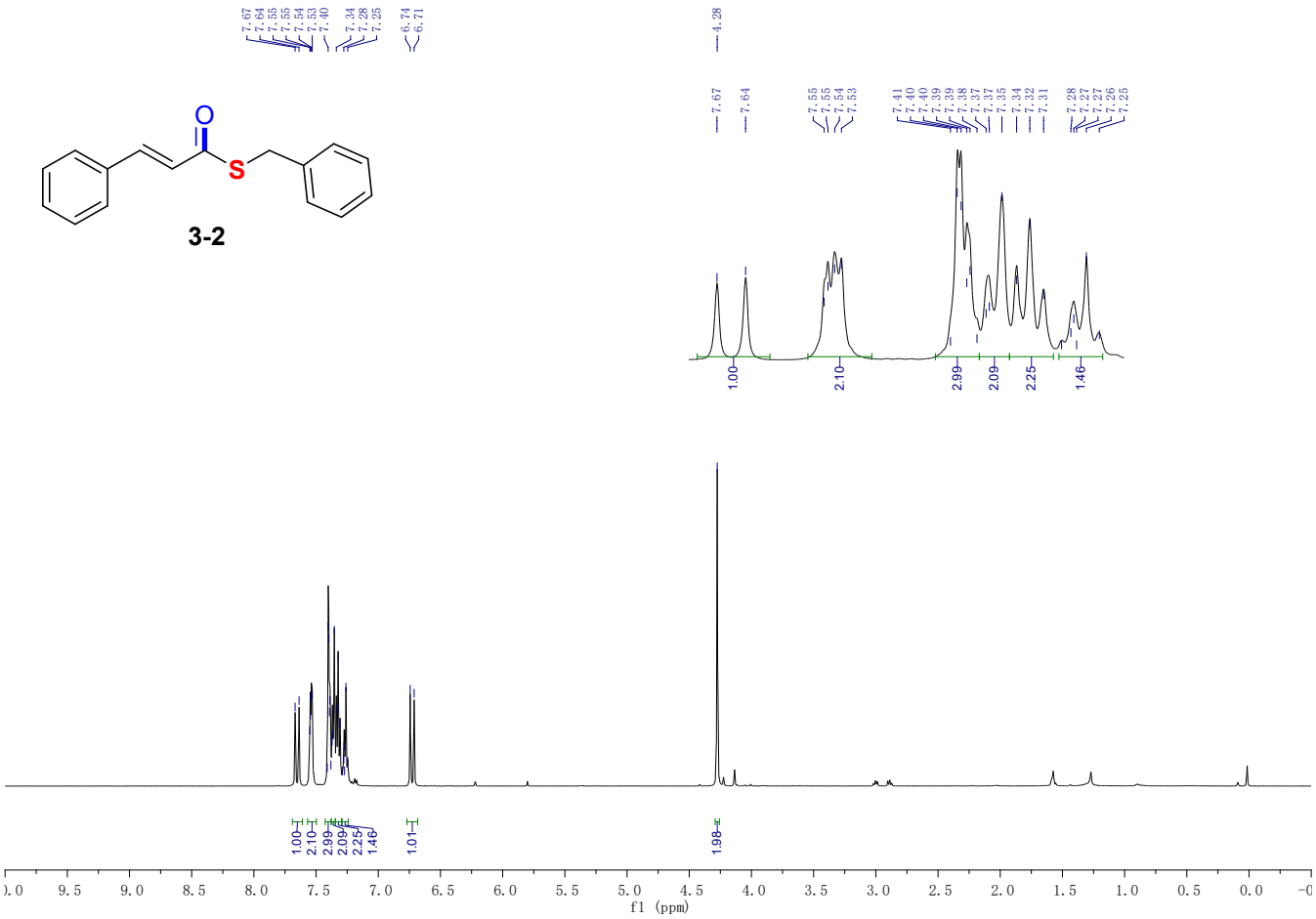
5. NMR Spectra.



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2.25
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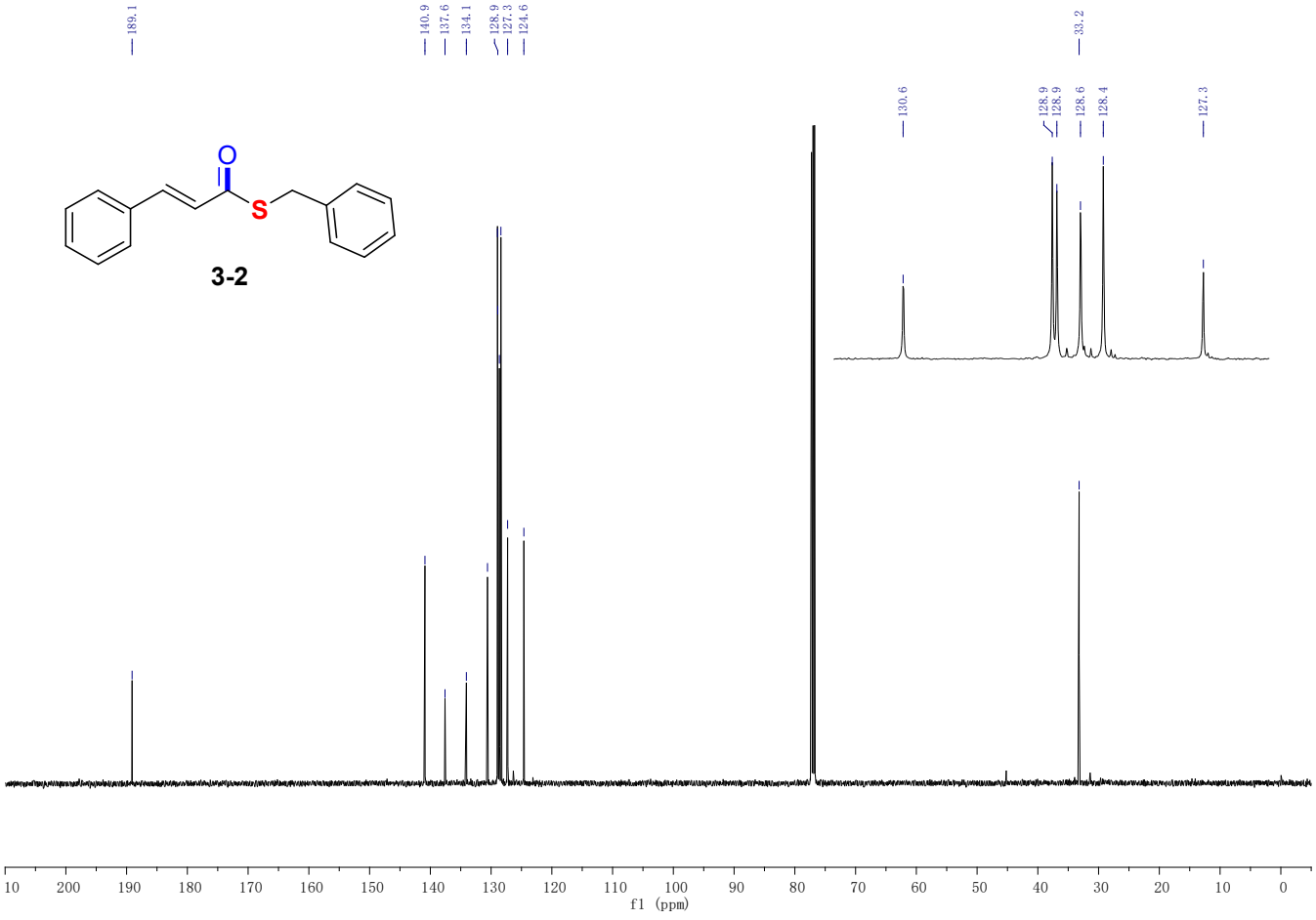
1.01
1.98
f1 (ppm)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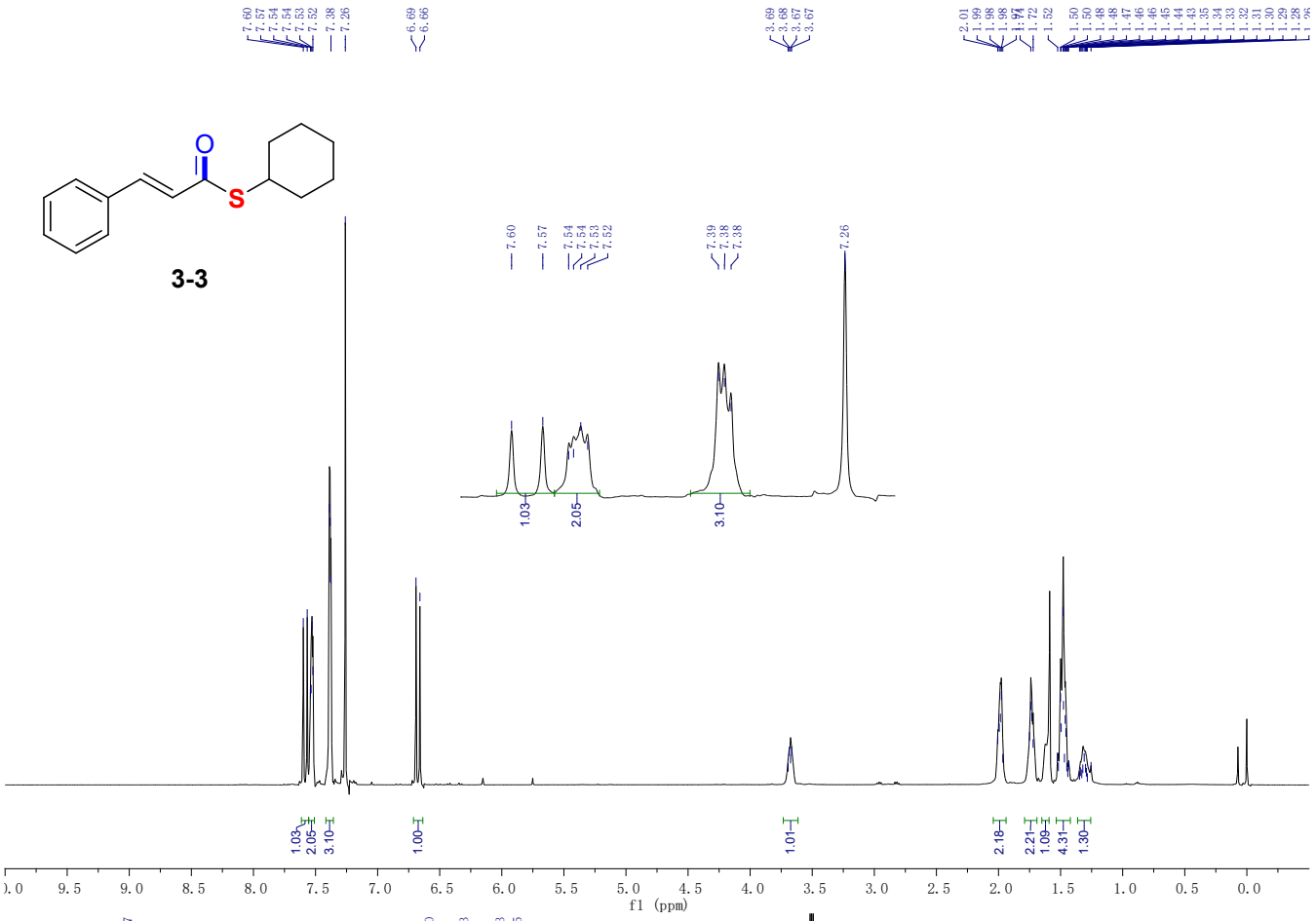
O
S
3-2
f1 (ppm)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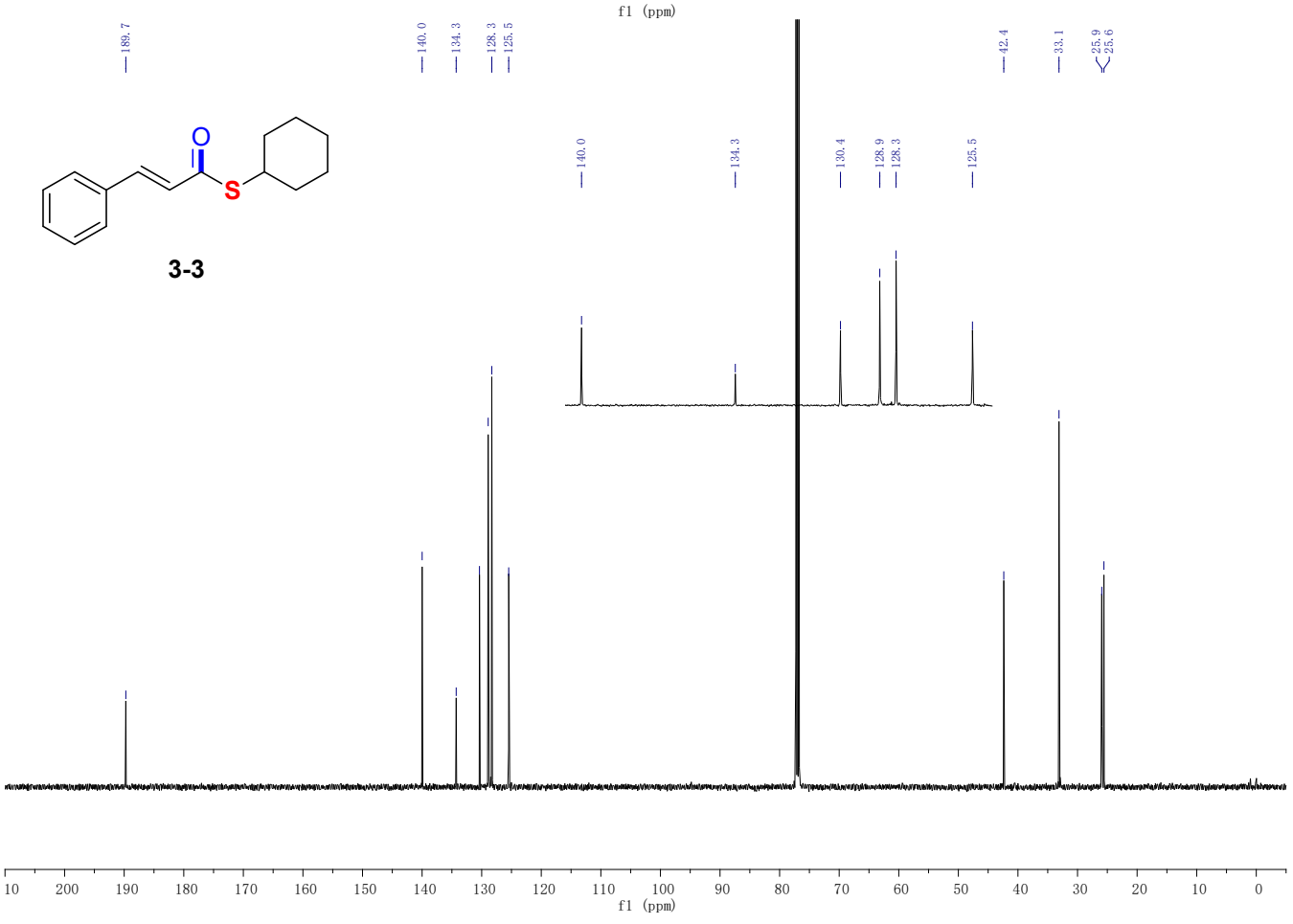
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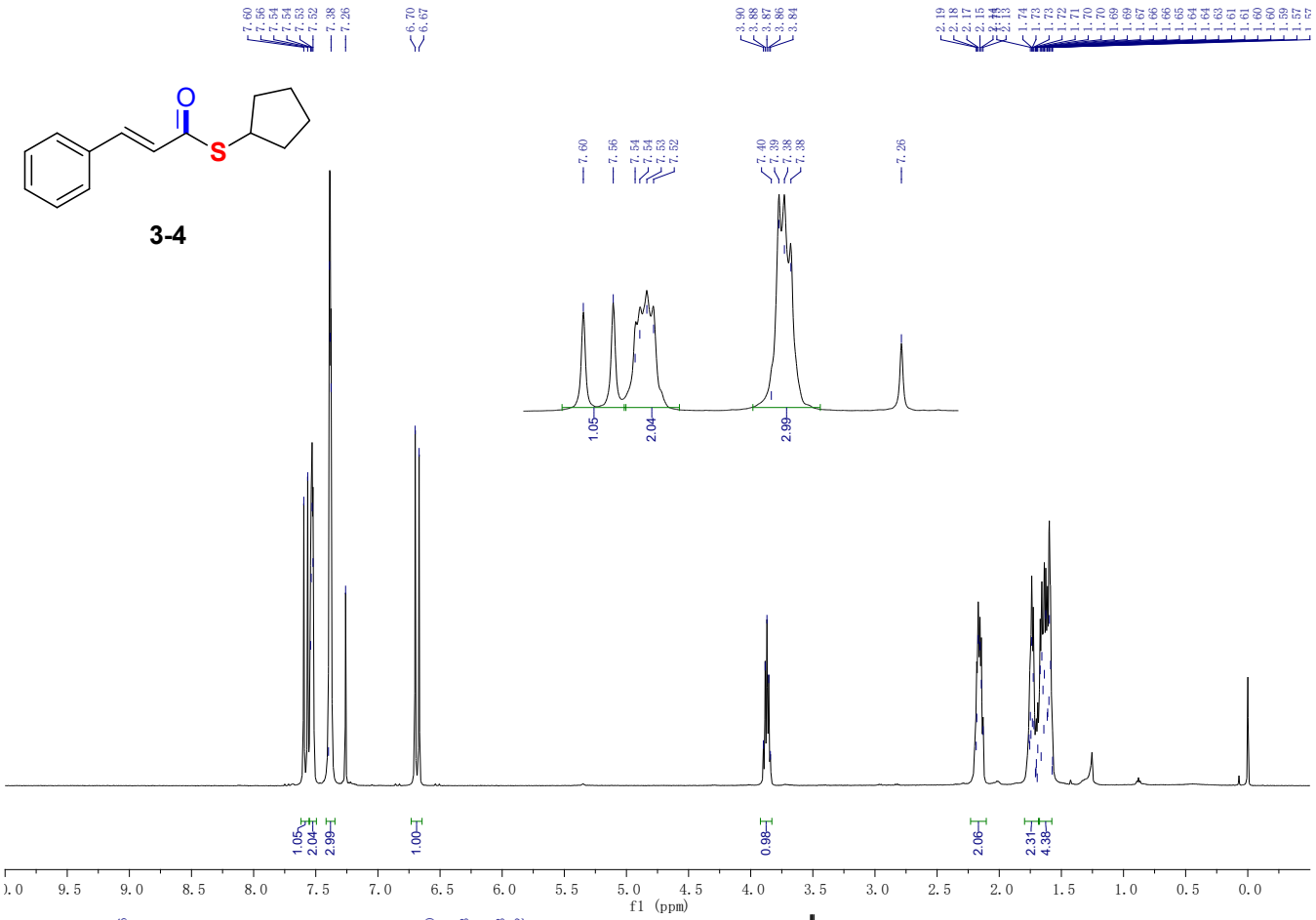
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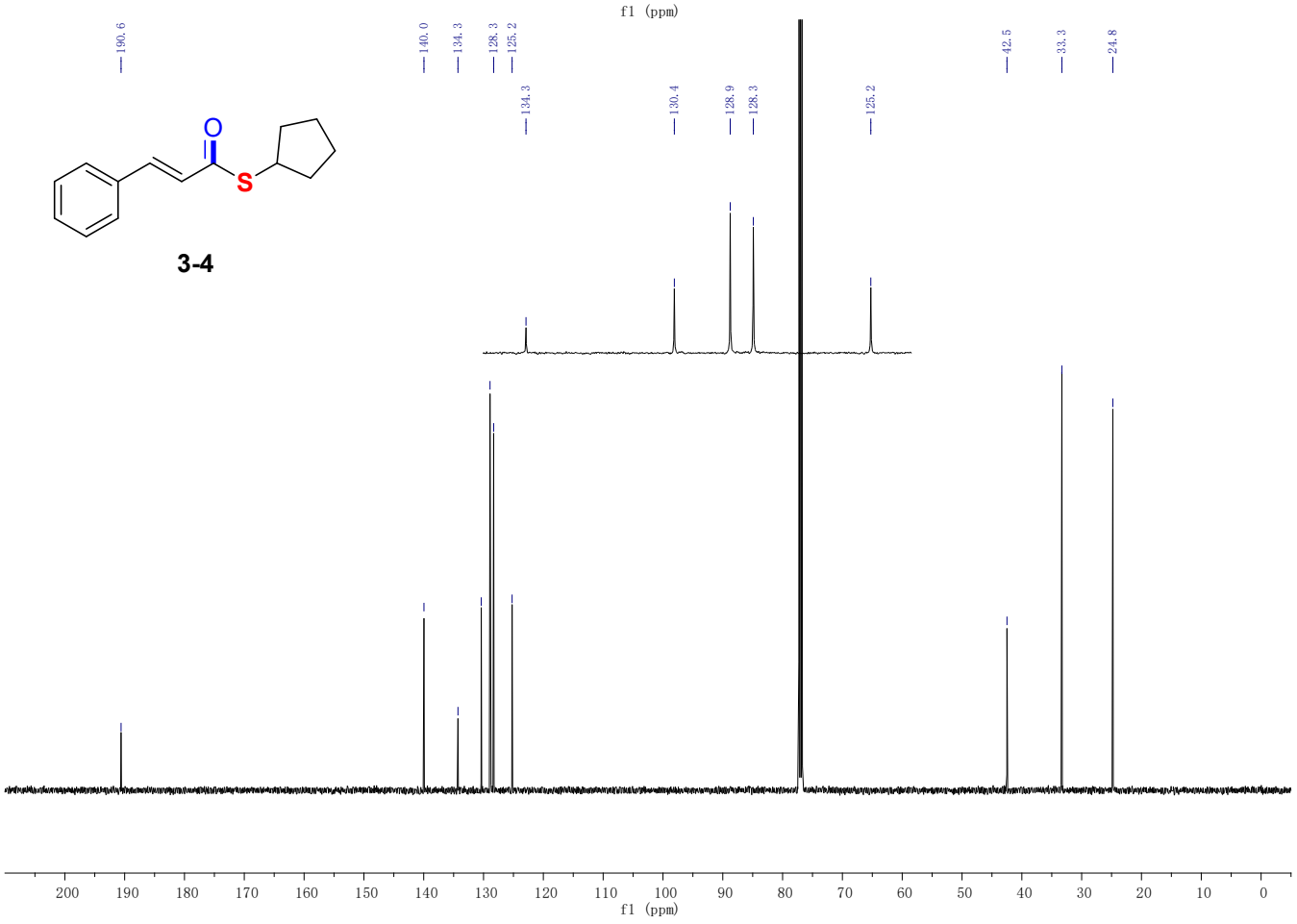
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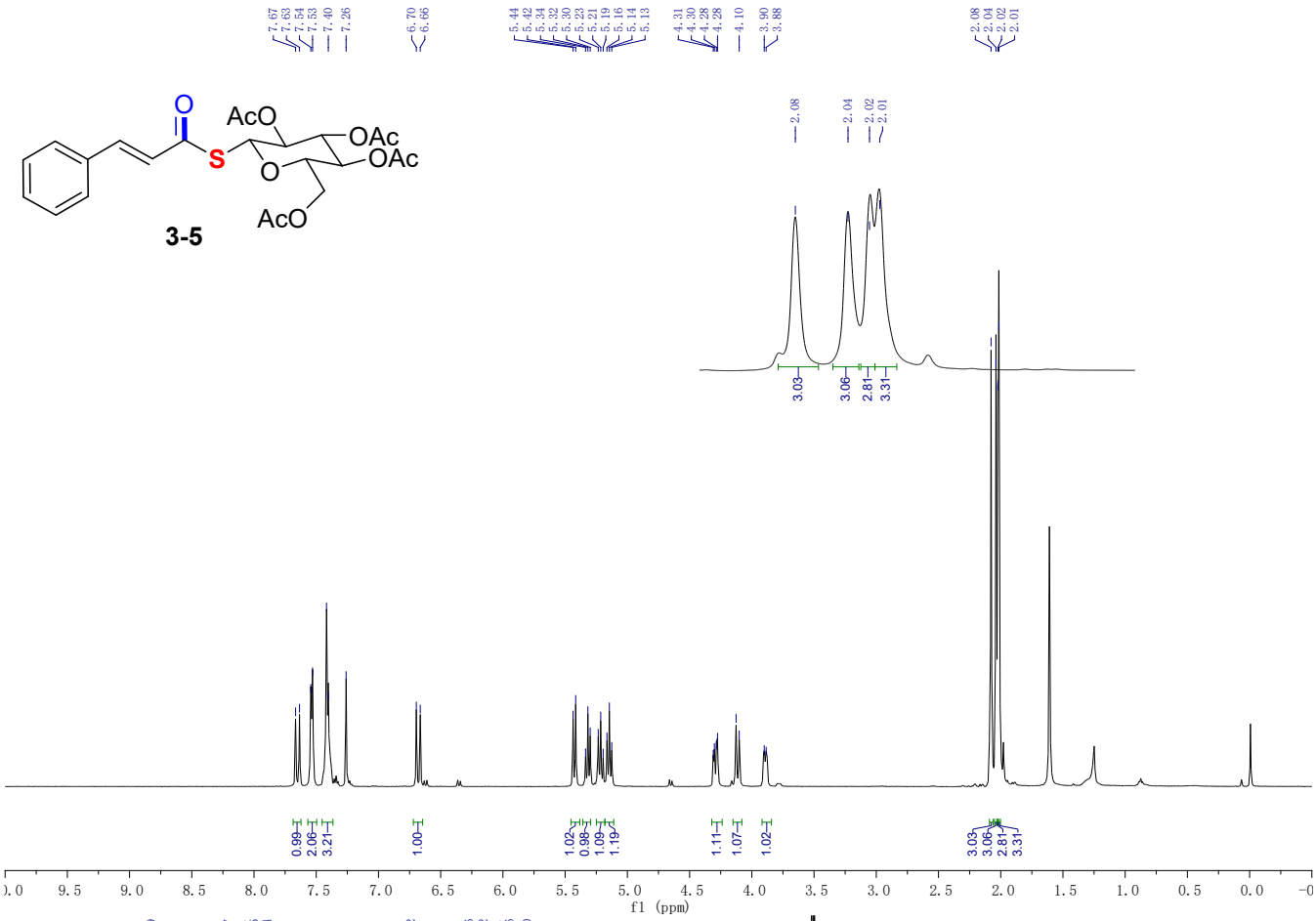
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2.01
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OAc
AcO
O
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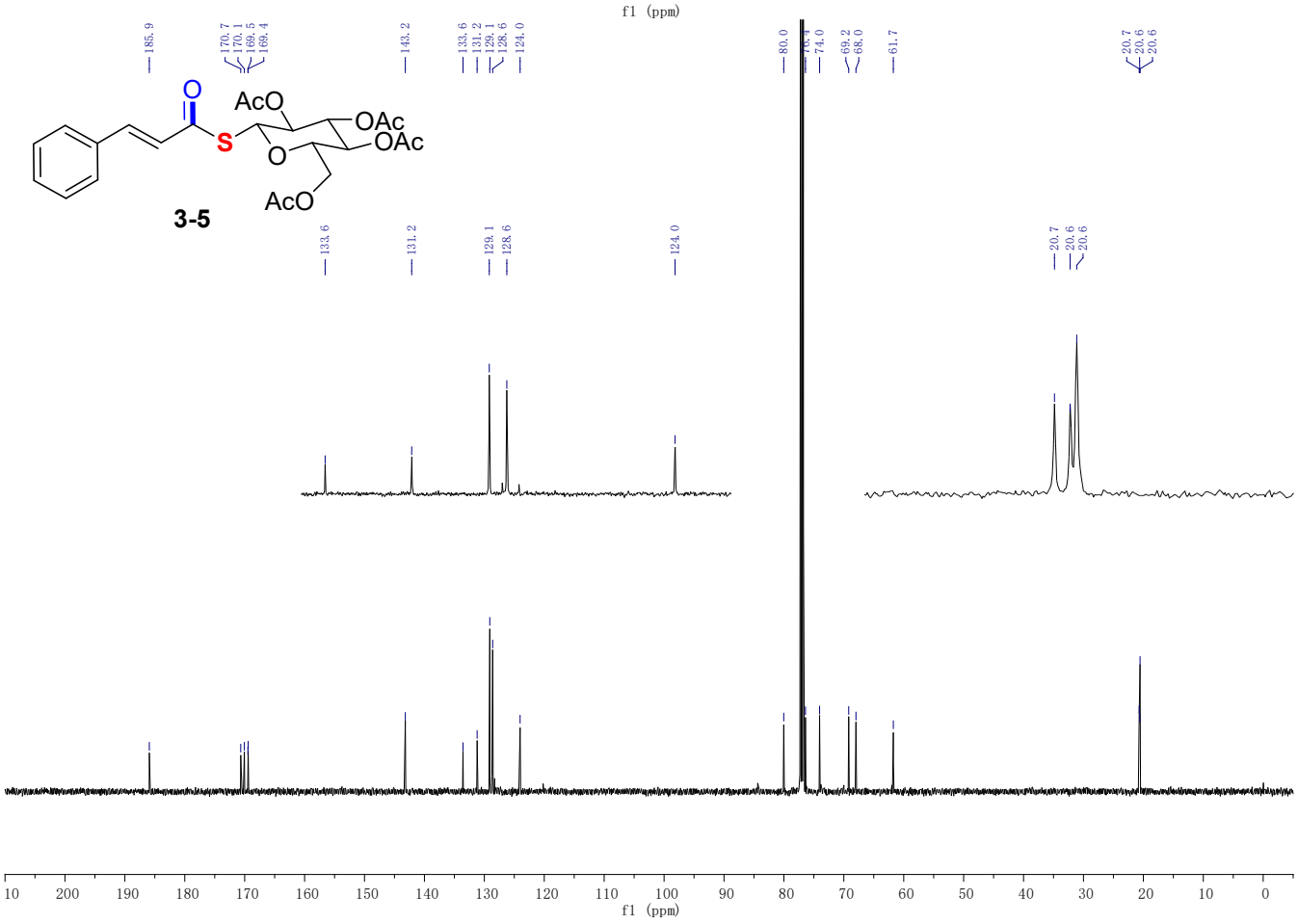
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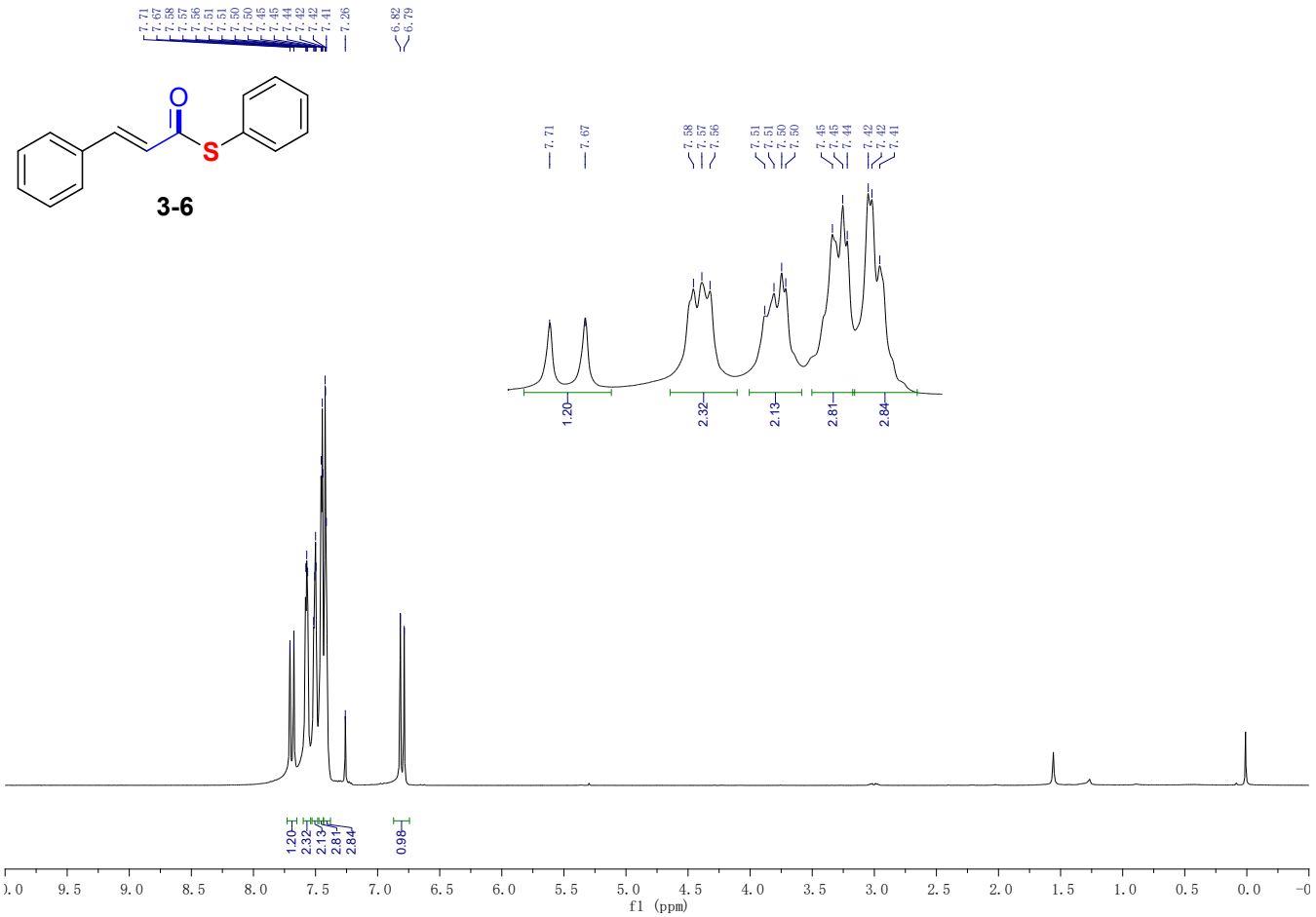
3-5
f1 (ppm)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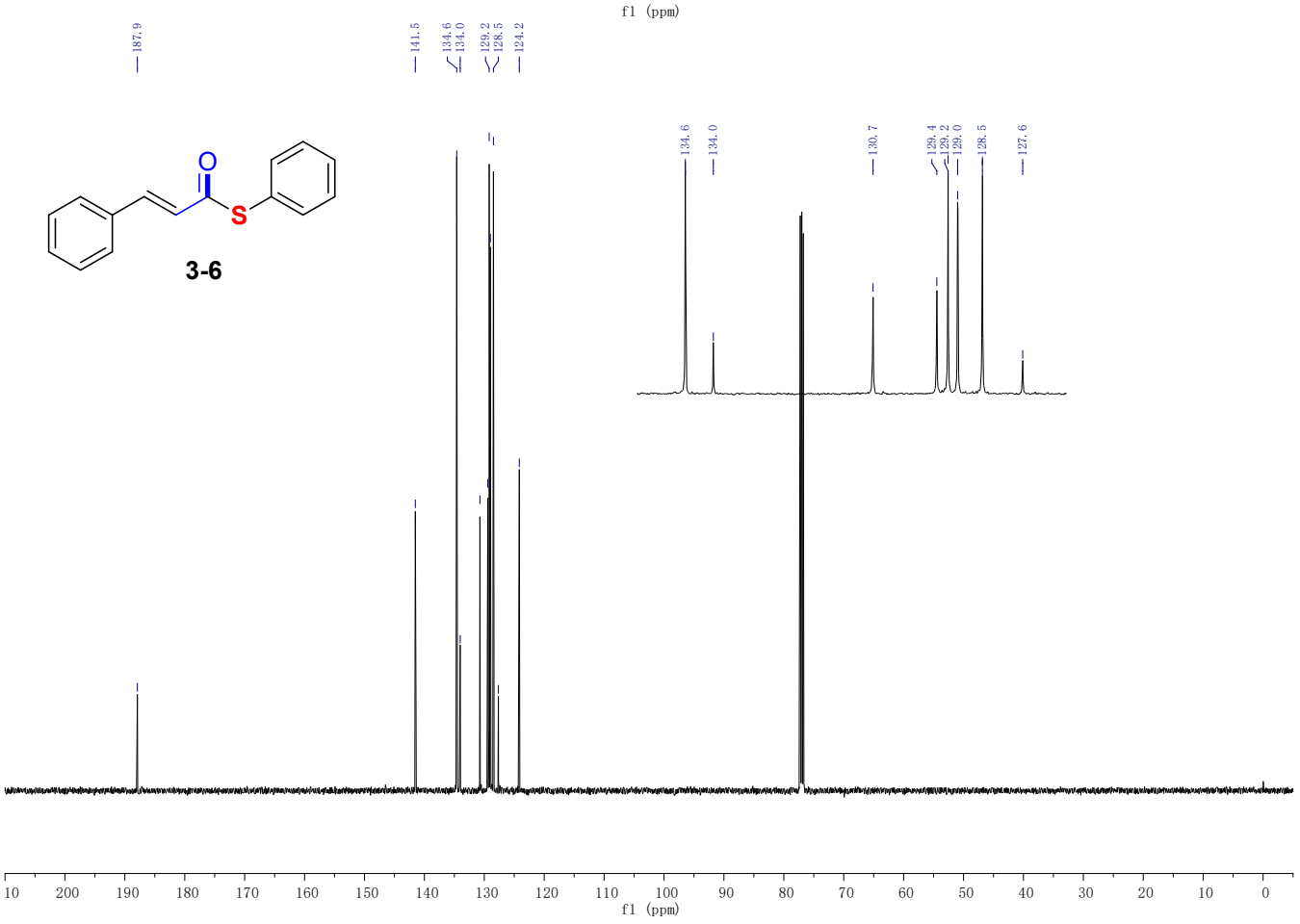
f1 (ppm)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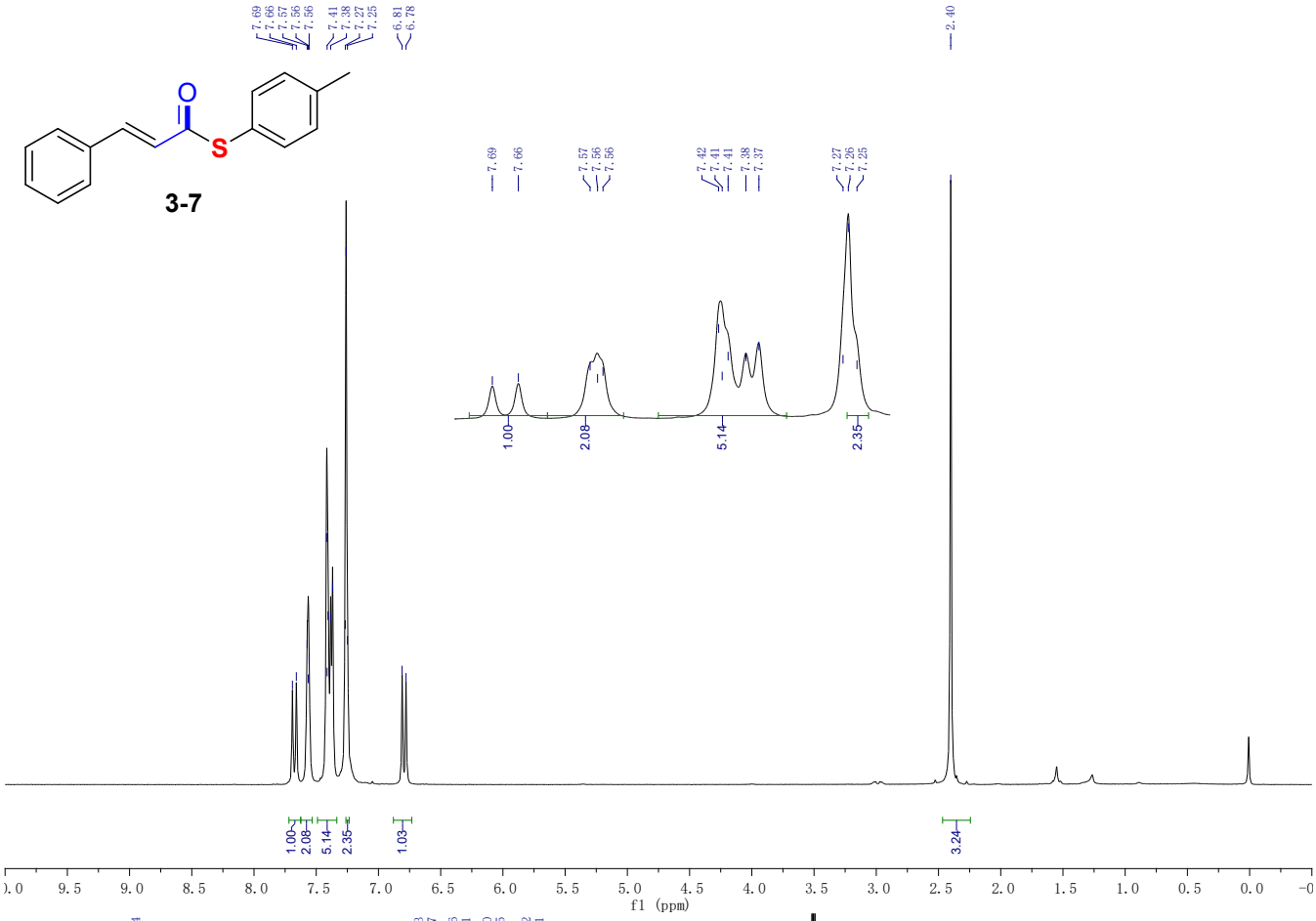
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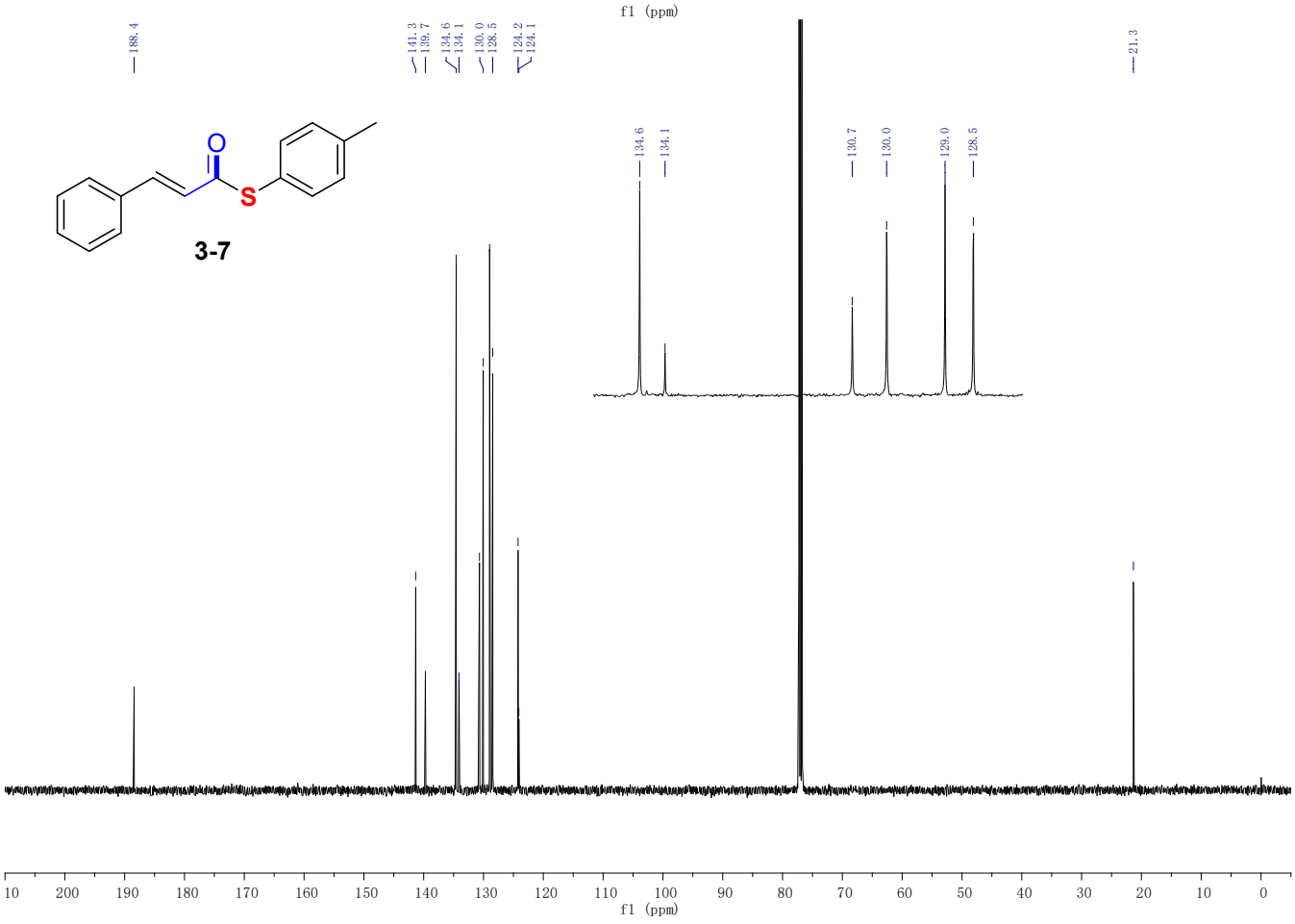
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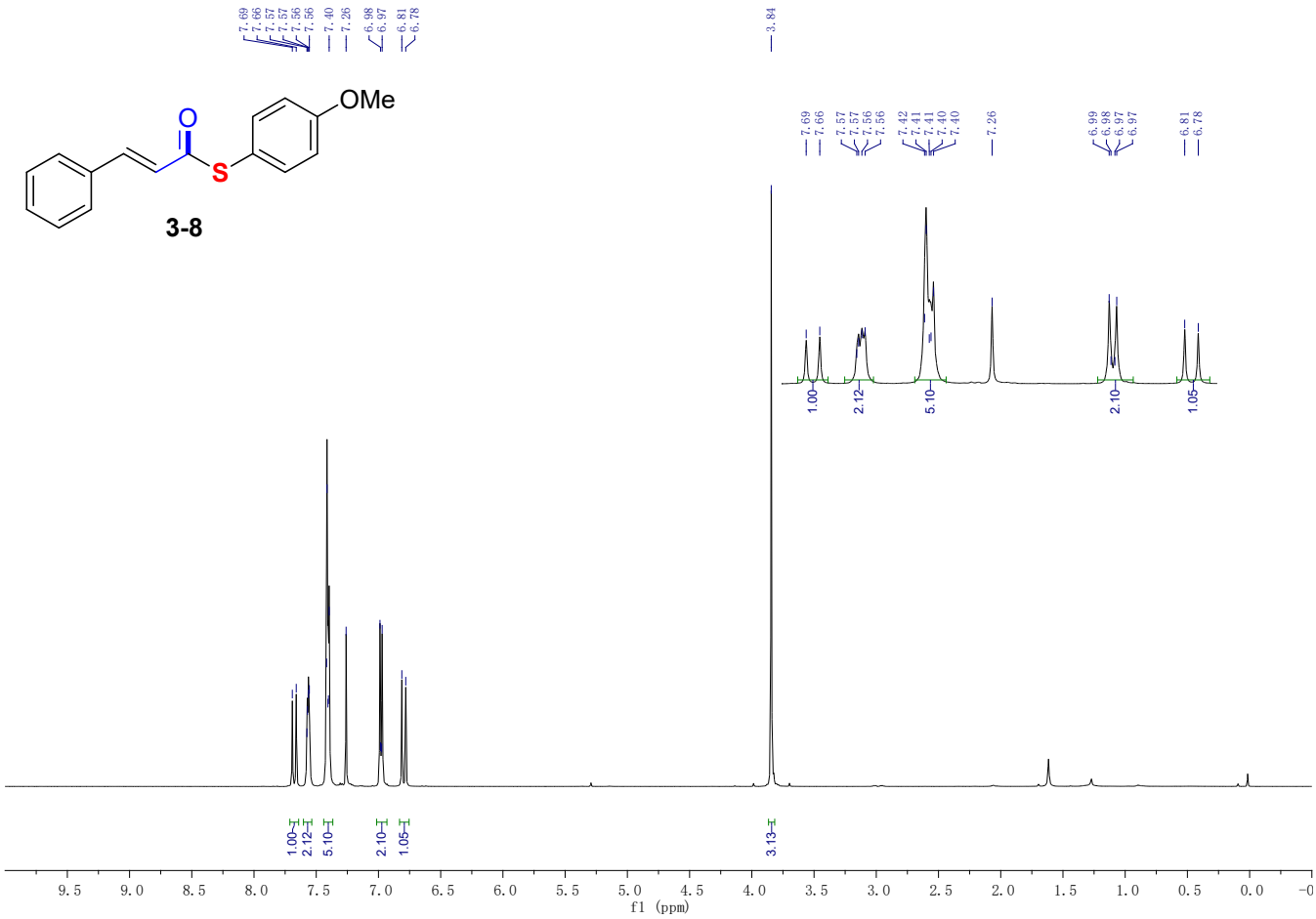
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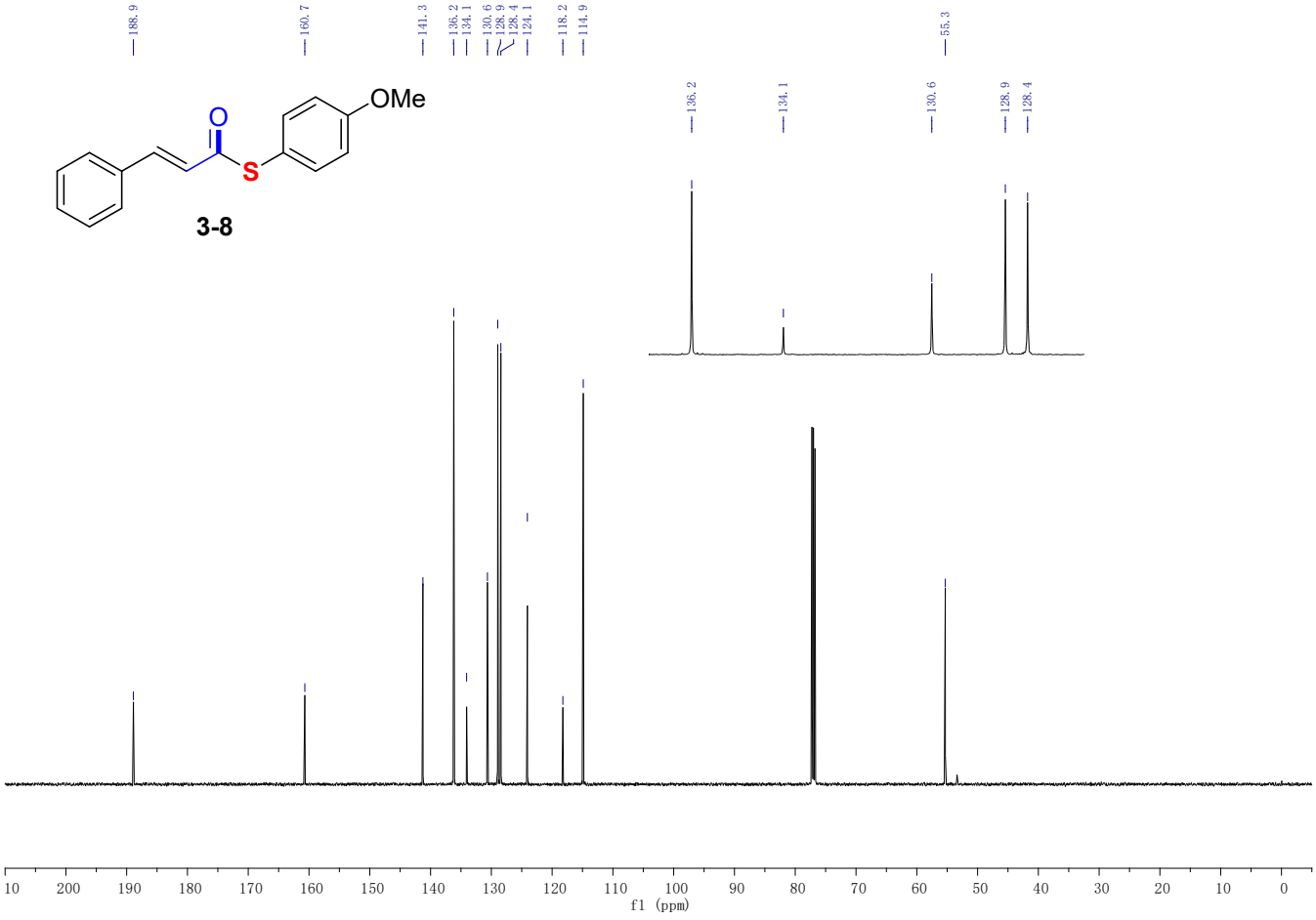
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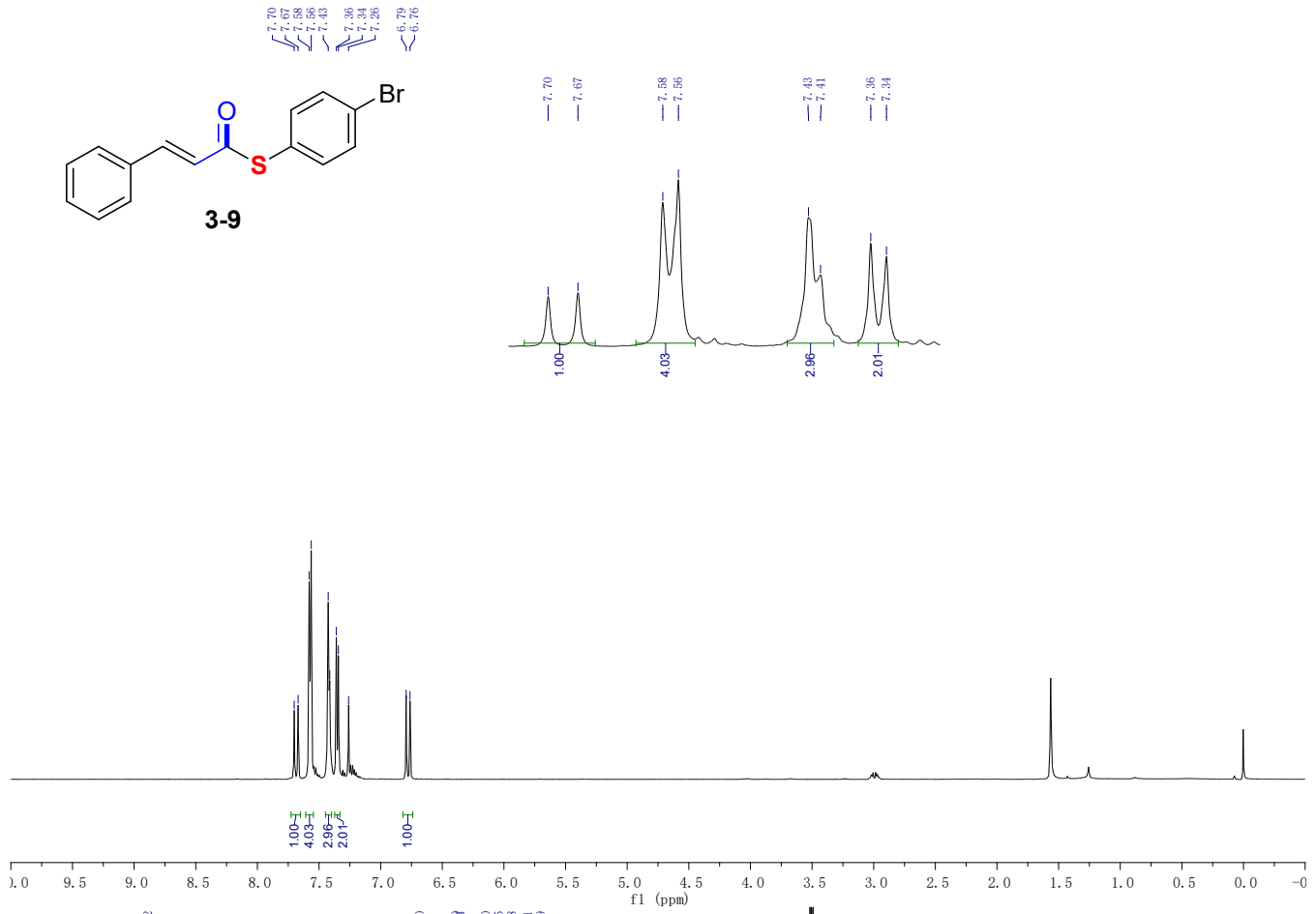
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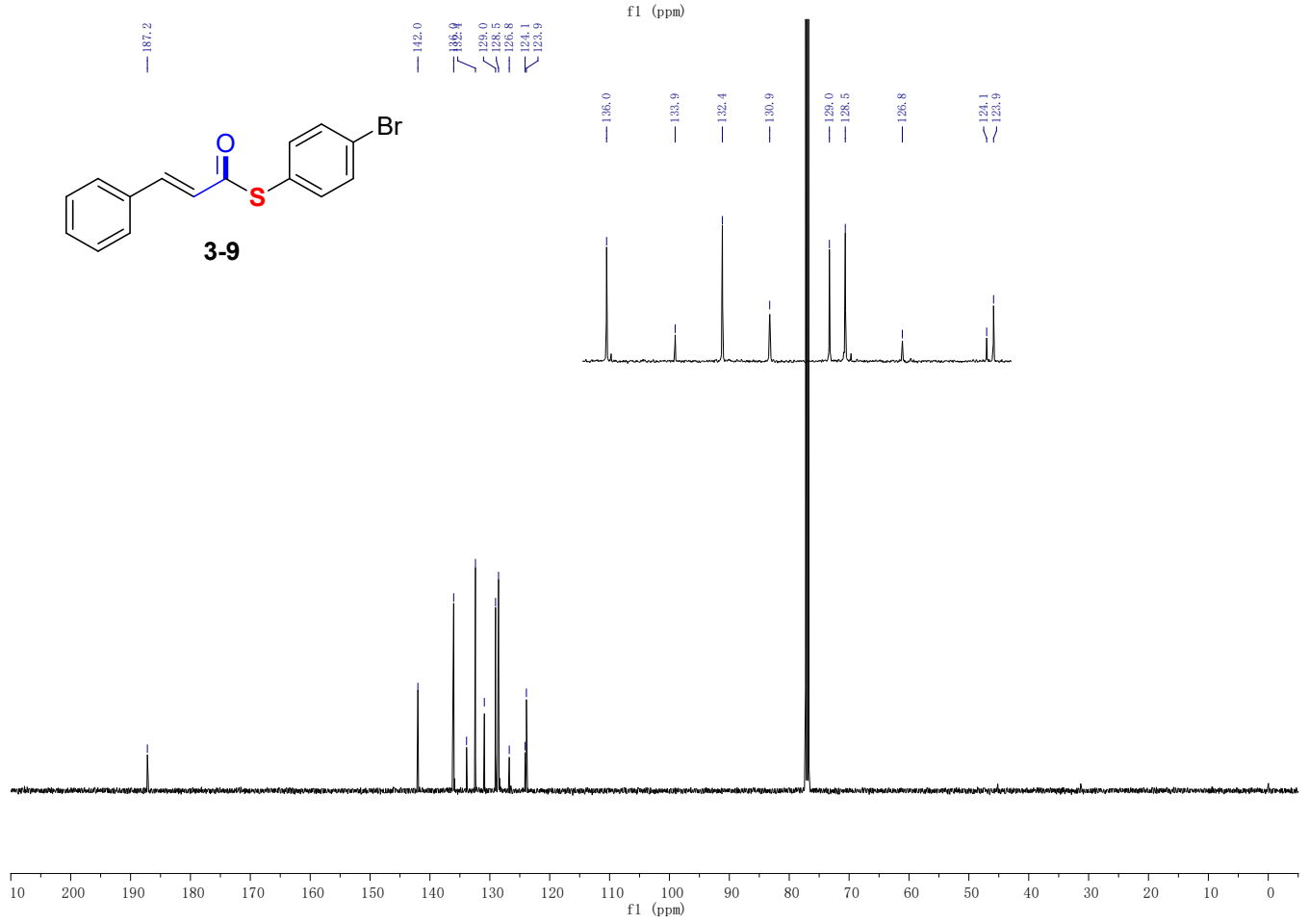
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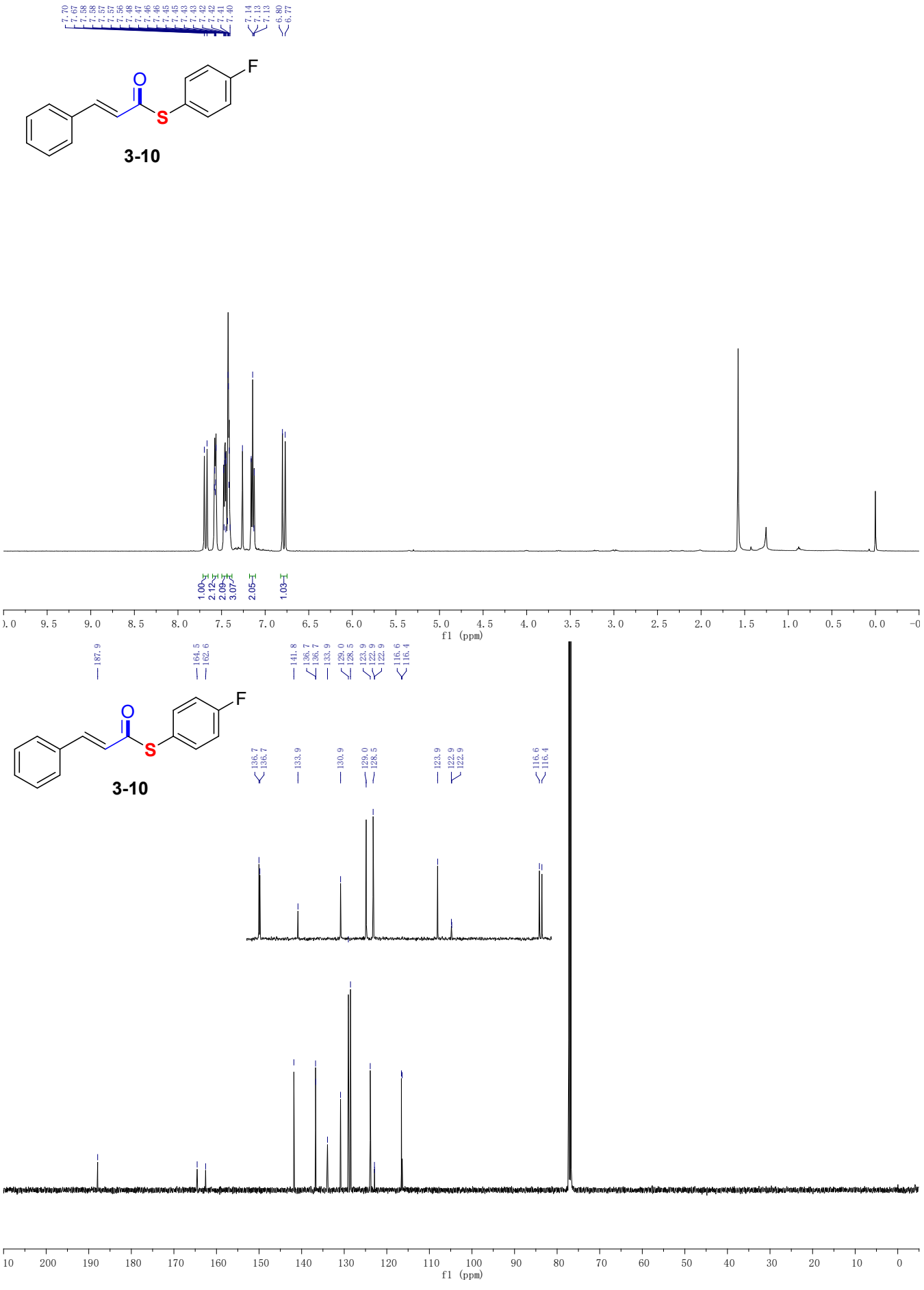
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O
S
F
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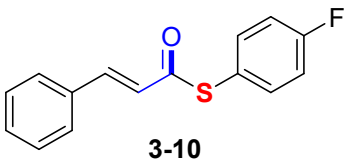
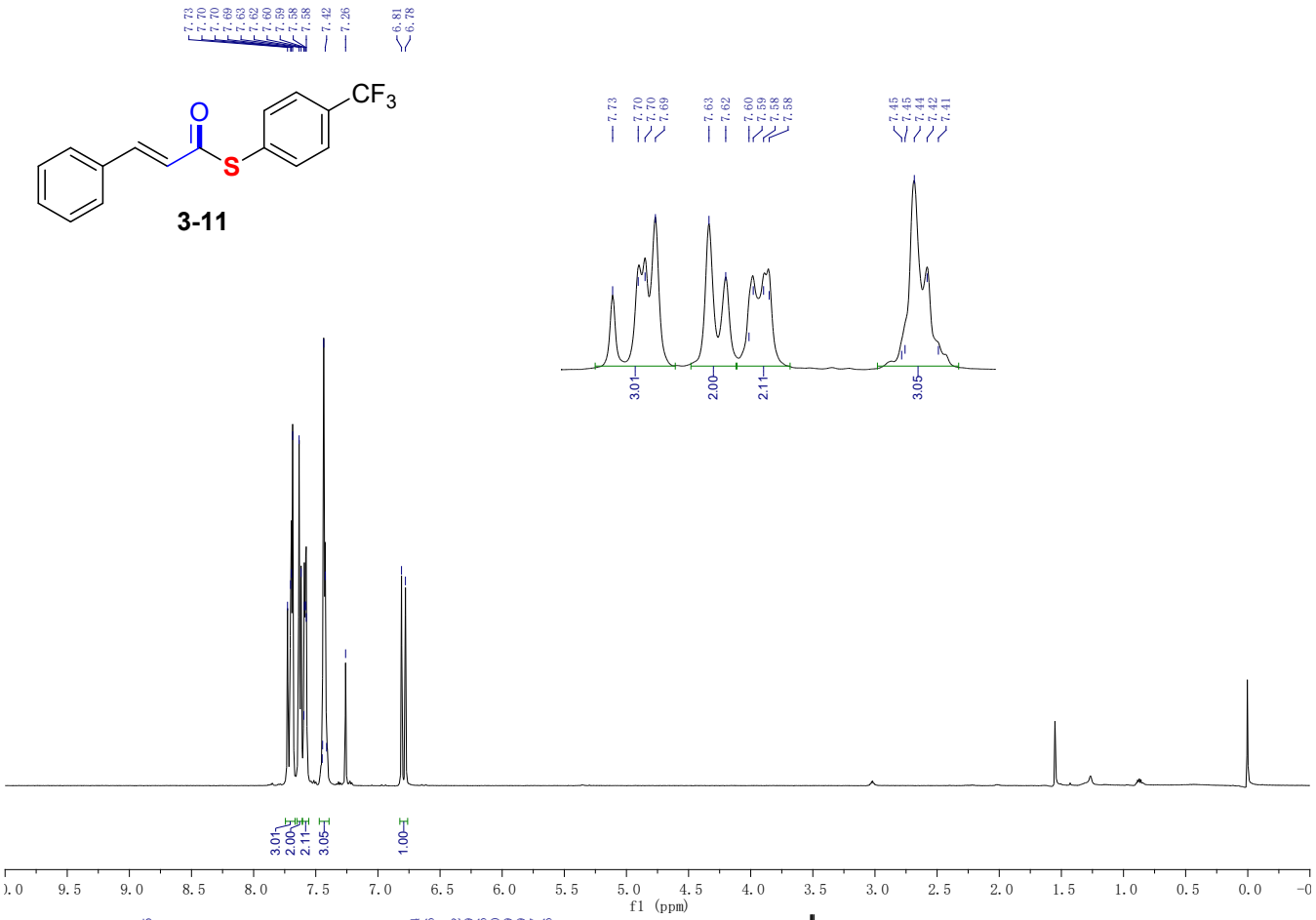
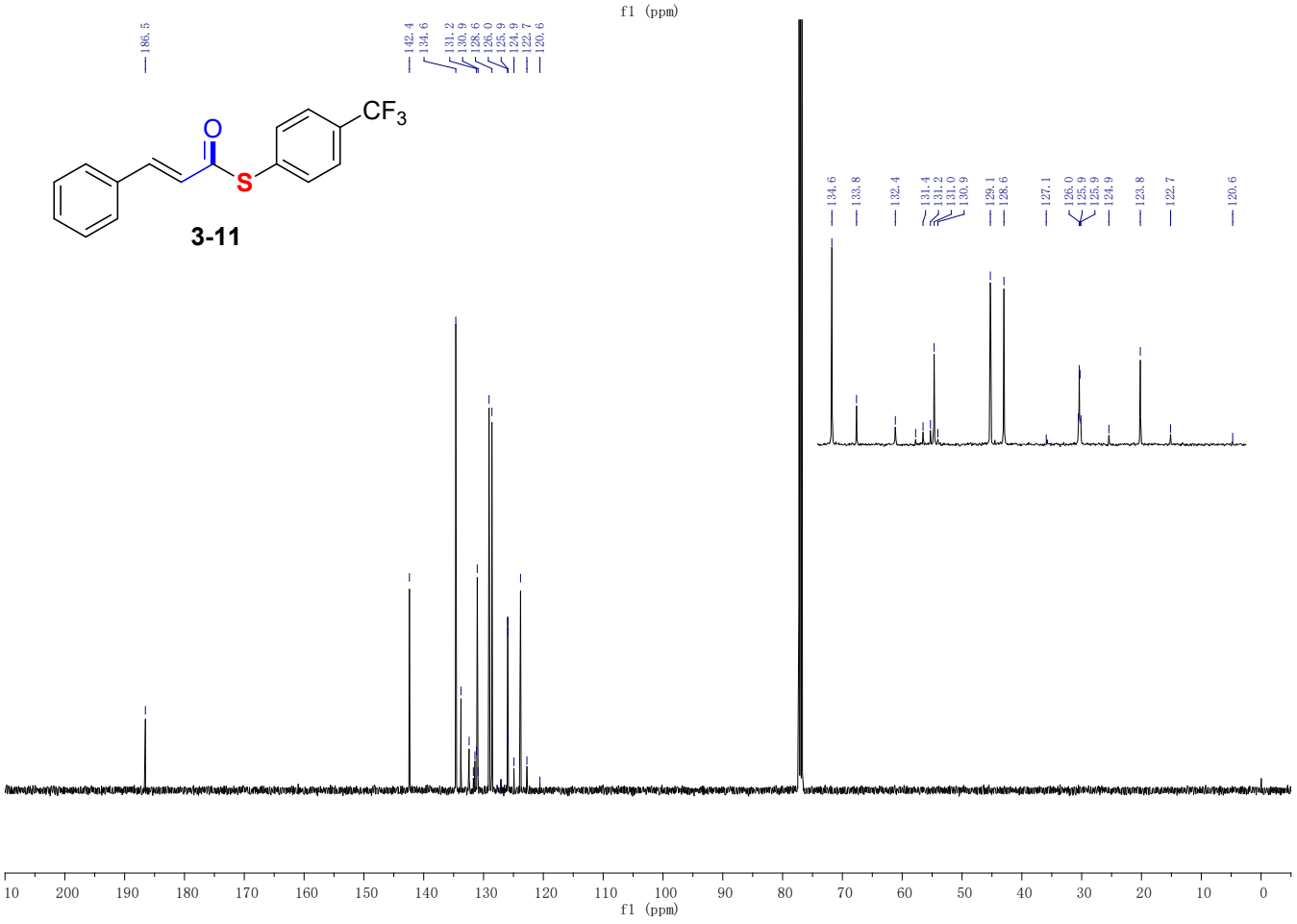
116.6
116.4
f1 (ppm)

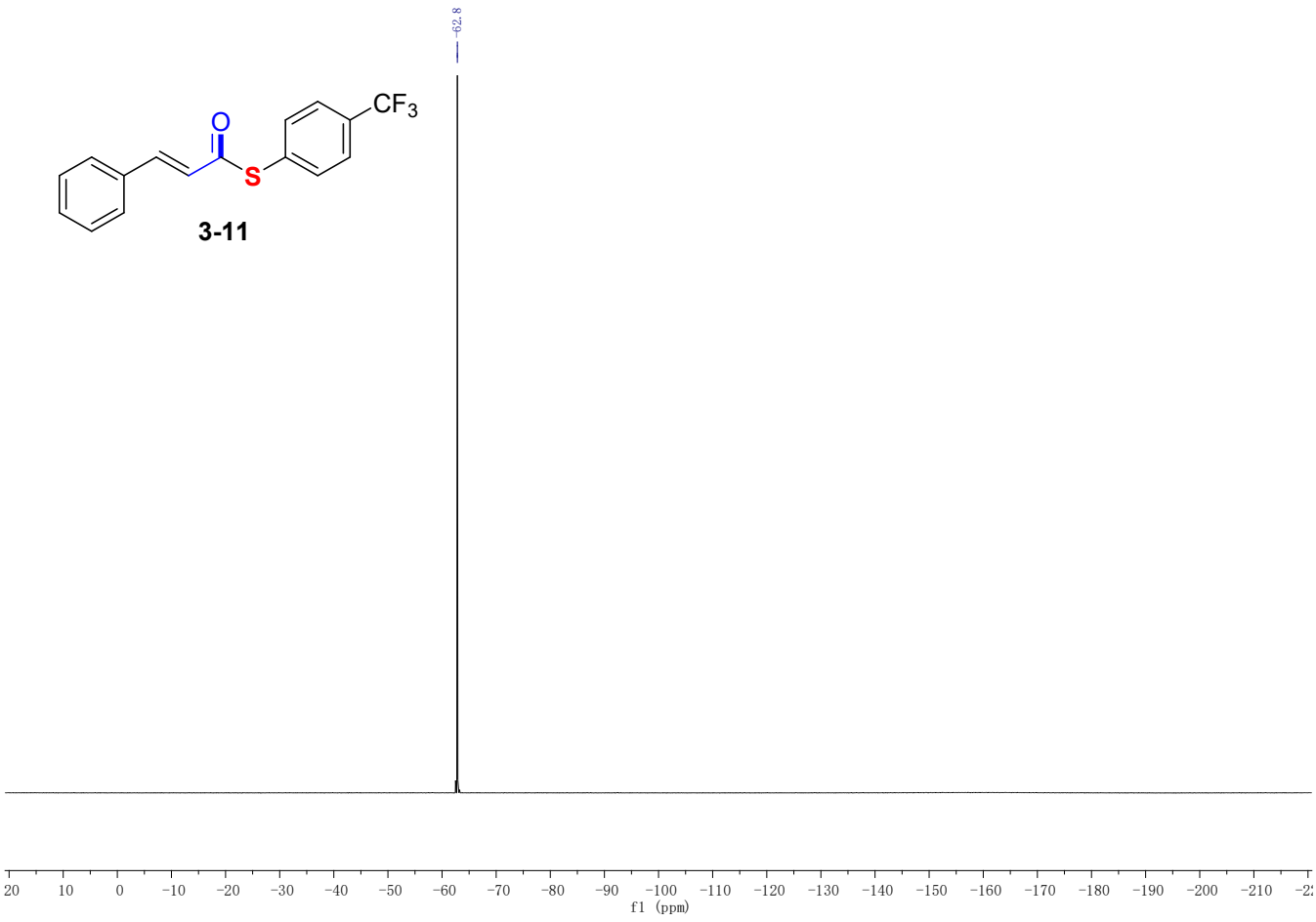

O
S
F

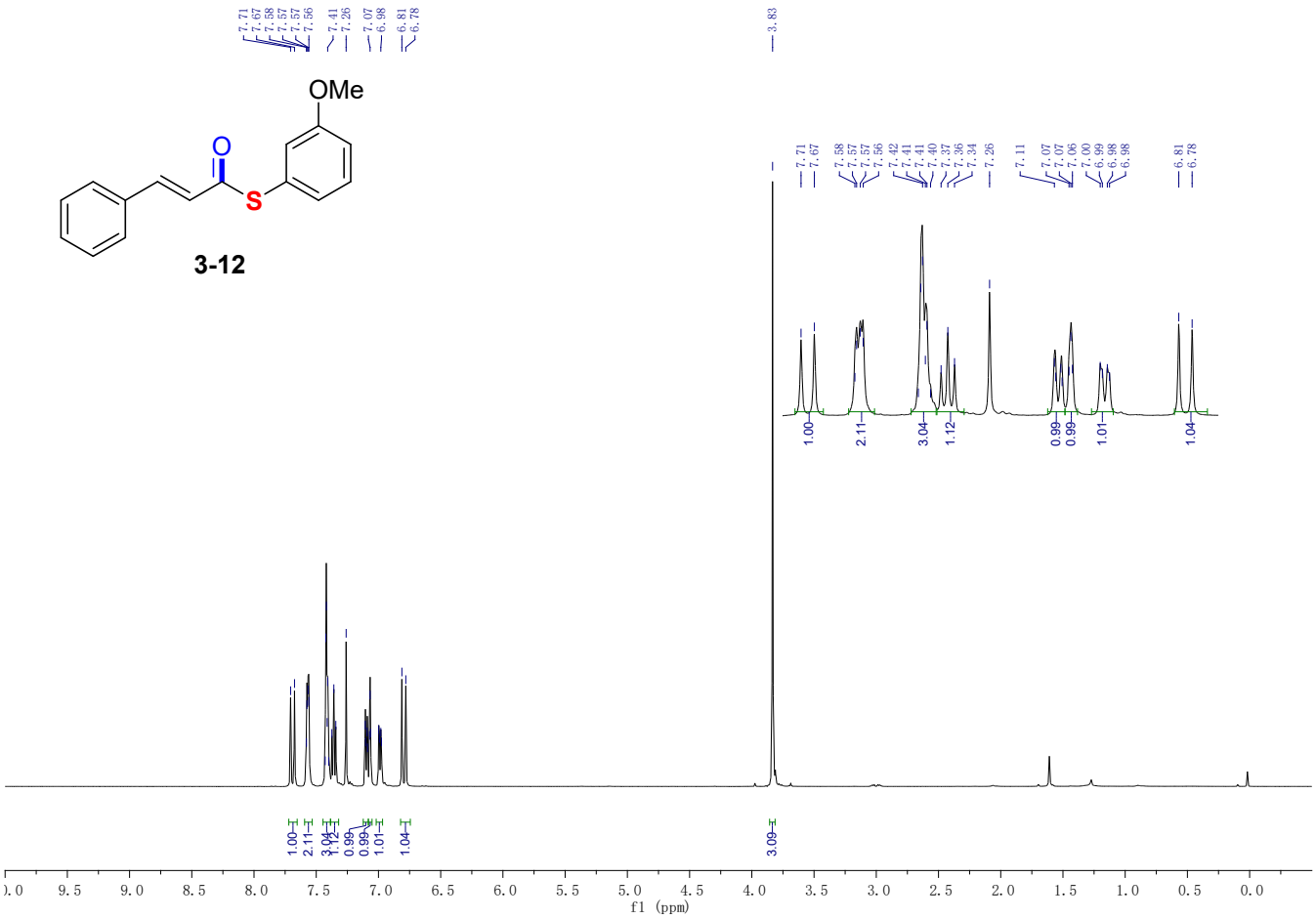
3-10

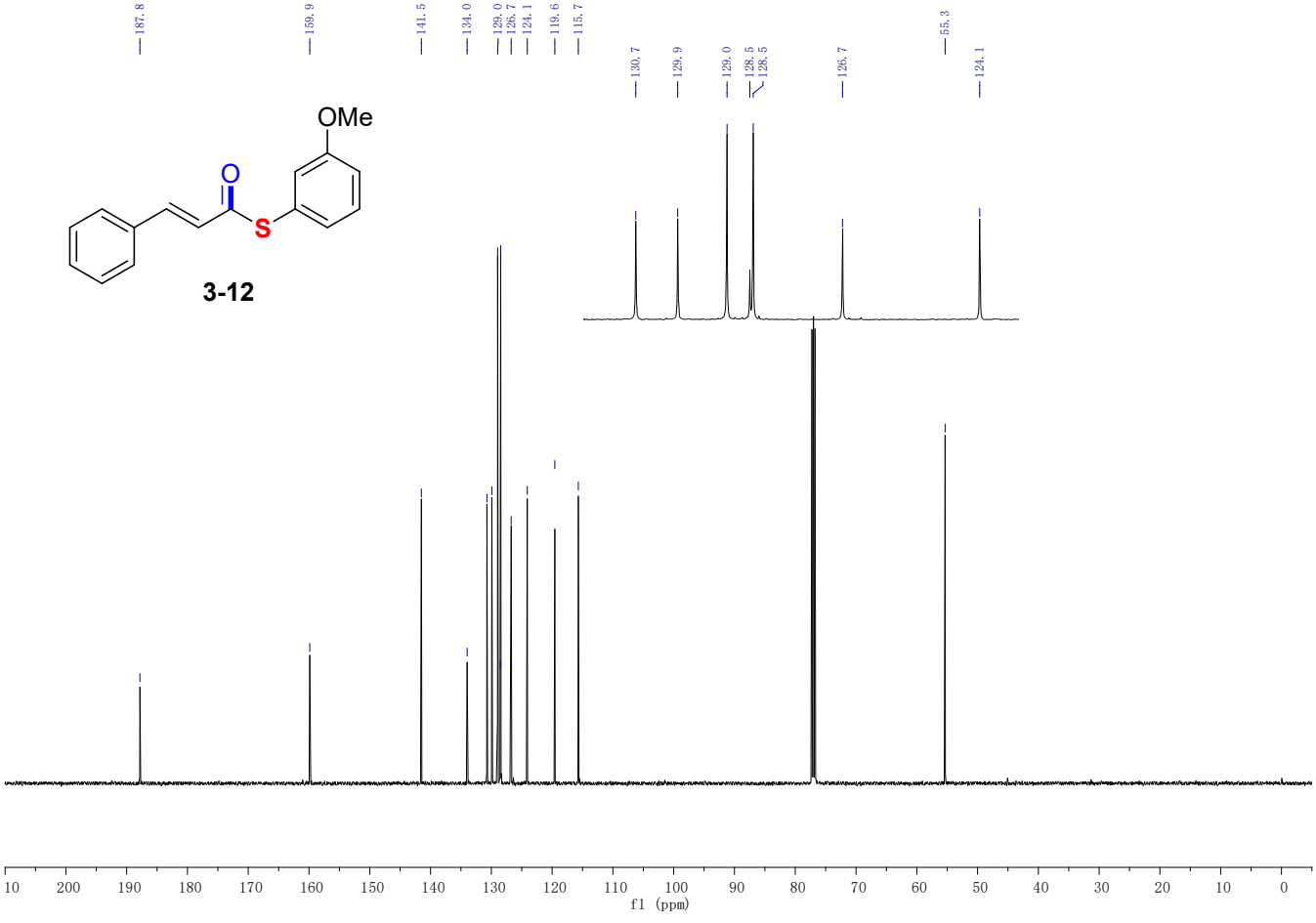
-111.1
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

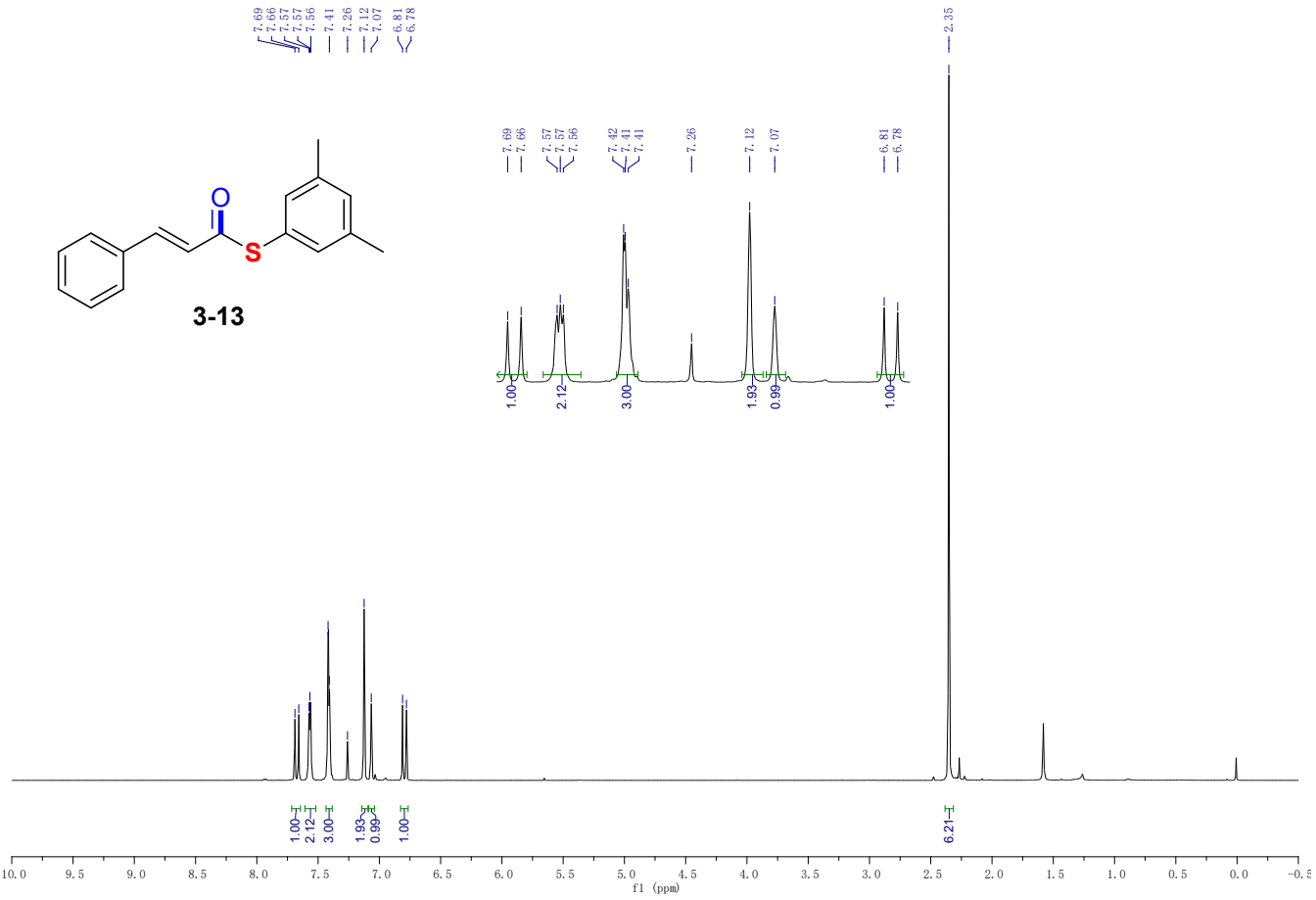

7.73
7.70
7.70
7.69
7.63
7.62
7.60
7.59
7.58
7.58
7.42
7.26
6.81
6.78
CF3
O
S
3-11
3.01
2.00
2.11
3.05
1.00
f1 (ppm)

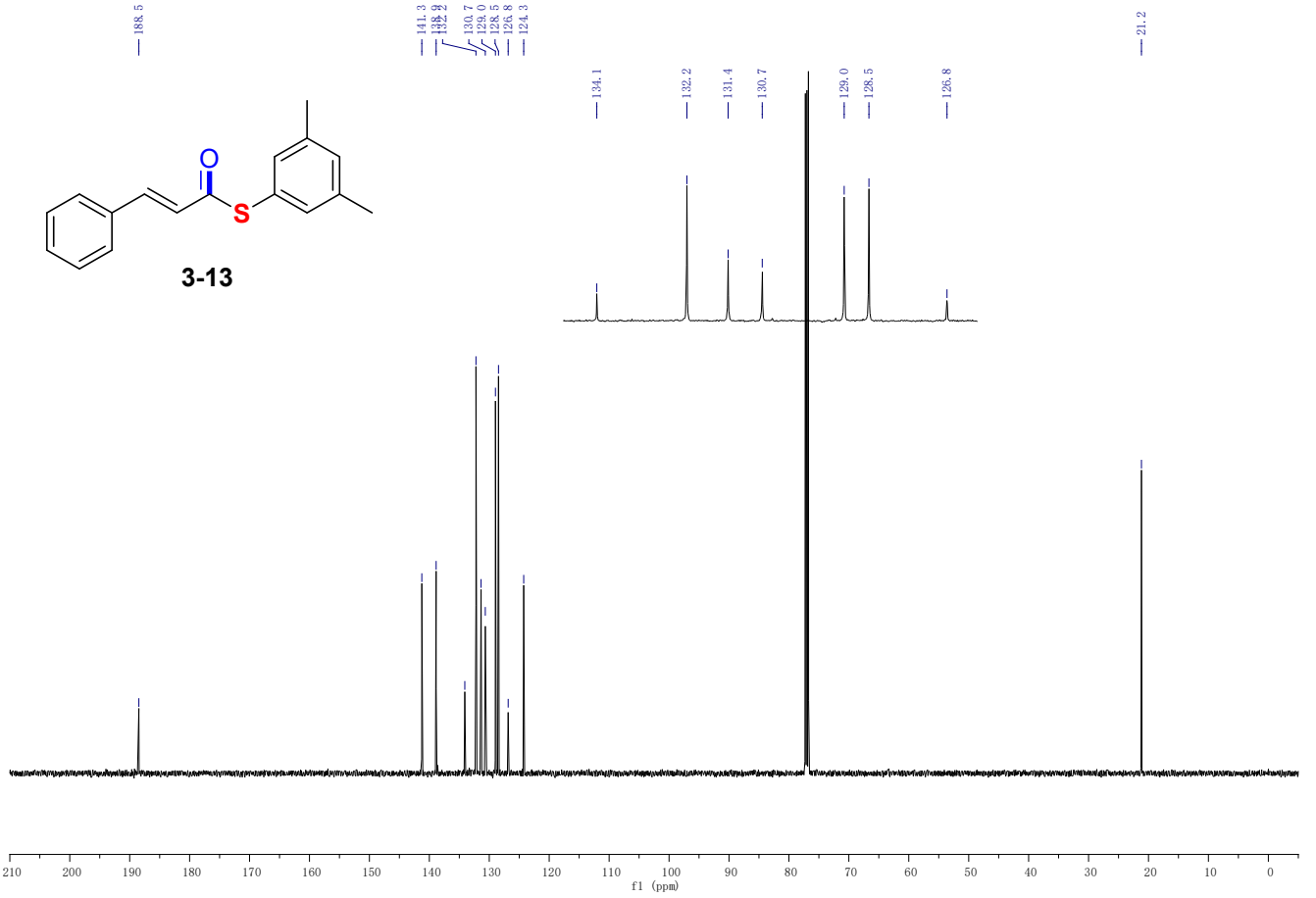

186.5
142.4
134.6
131.2
130.8
128.6
126.0
125.9
124.9
122.7
120.6
CF3
O
S
3-11
f1 (ppm)

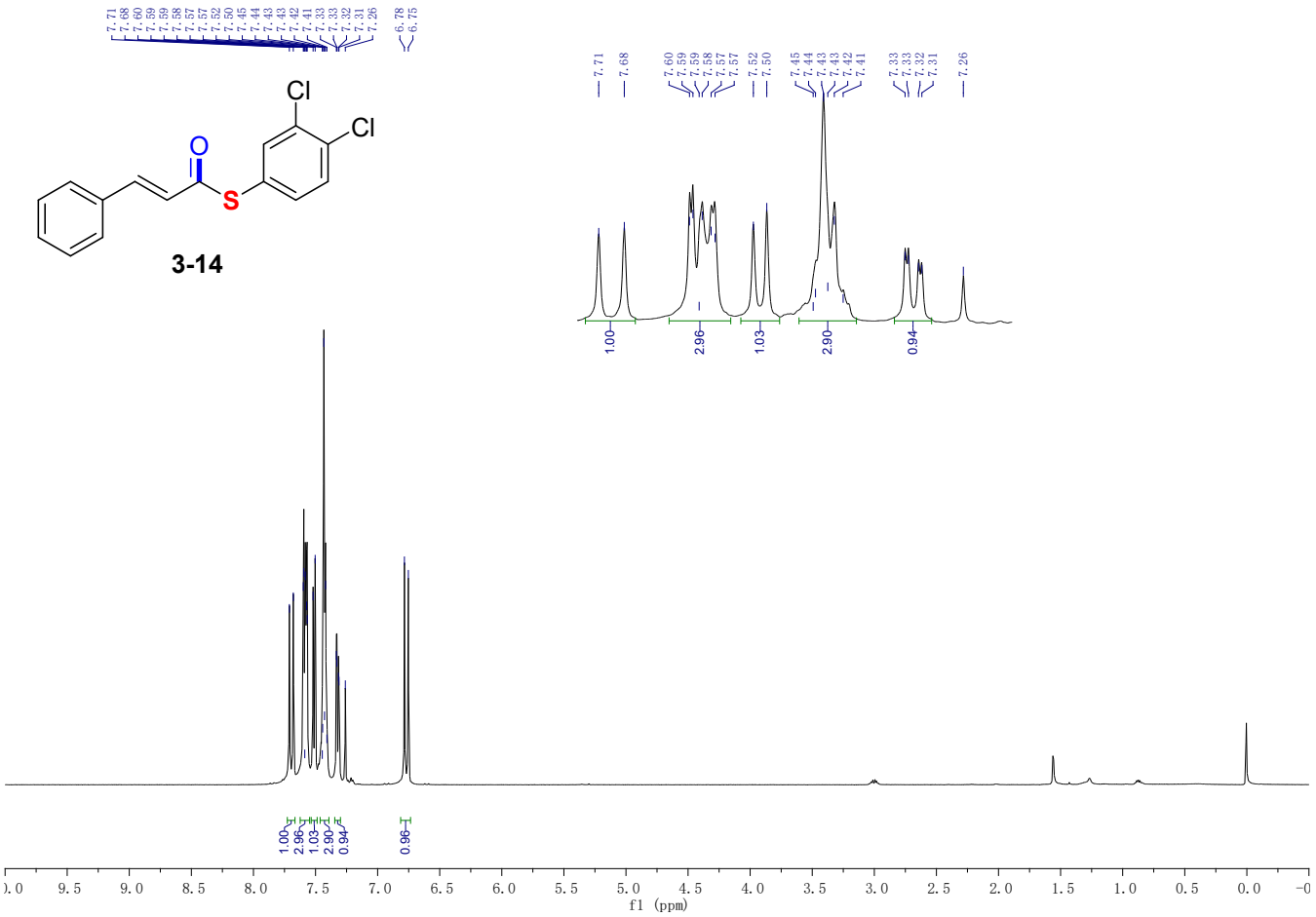

-62.8
O
S
CF3
3-11
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

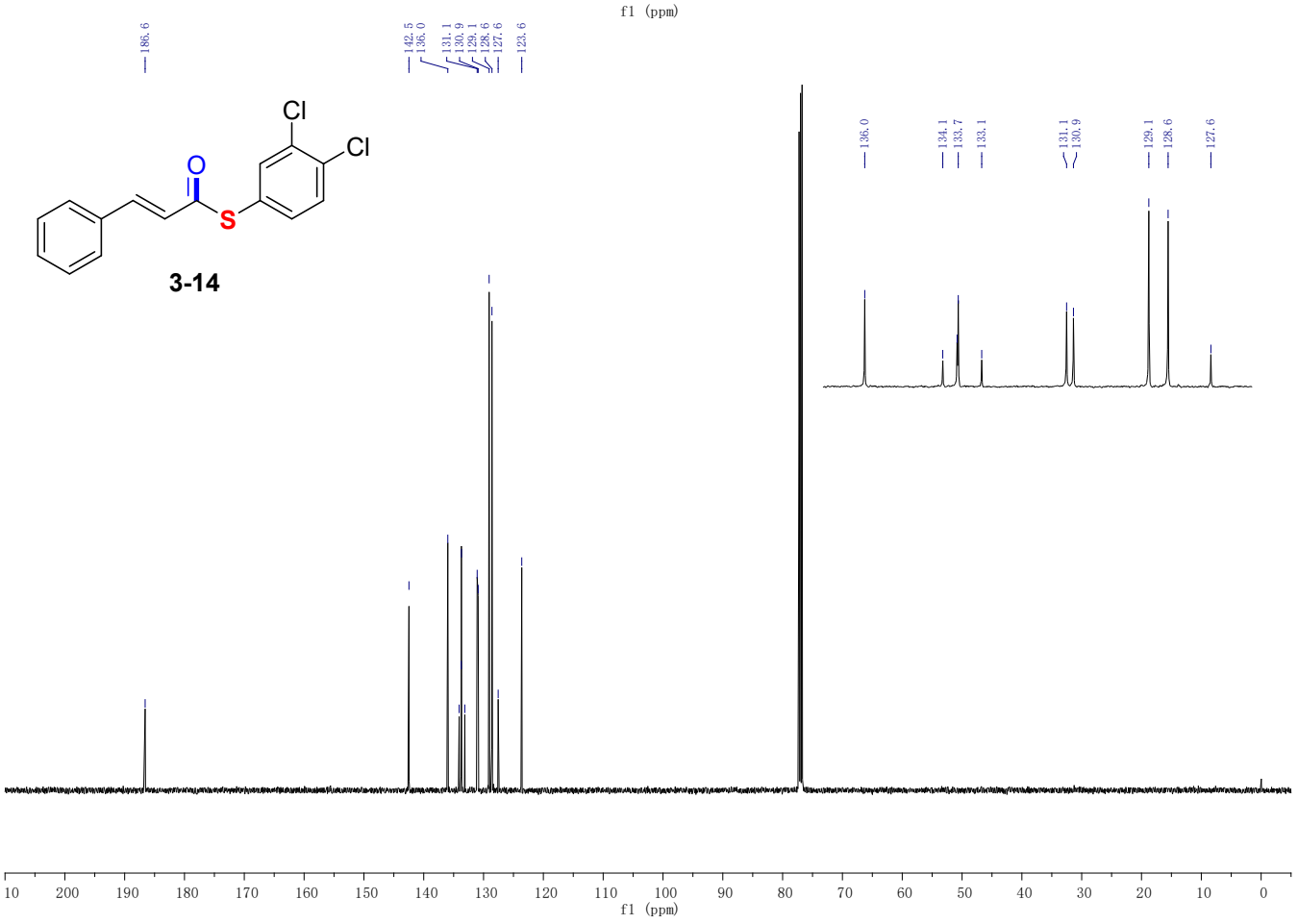

OMe
O
S
3-12
f1 (ppm)

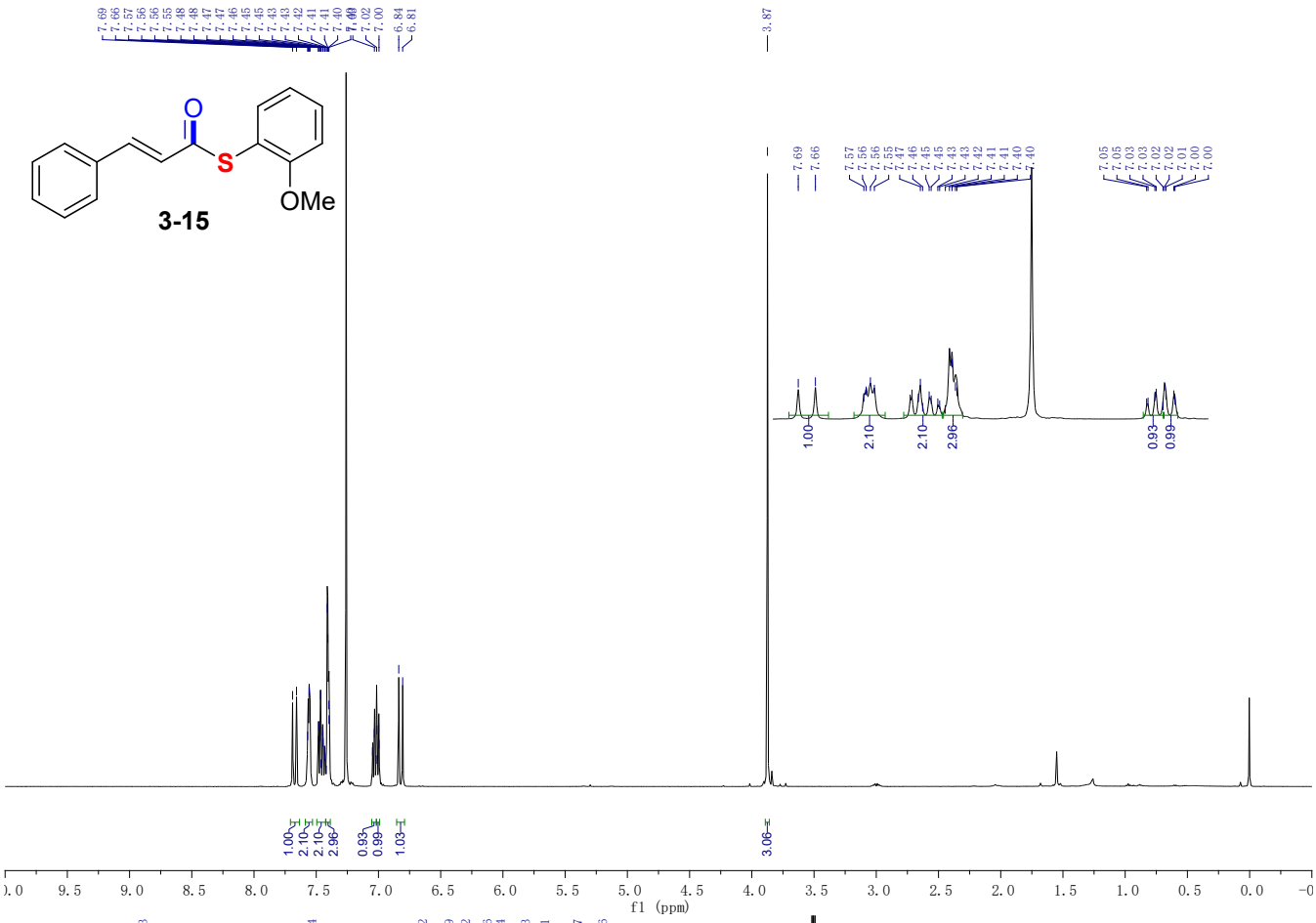

OMe
O
S
3-12
f1 (ppm)

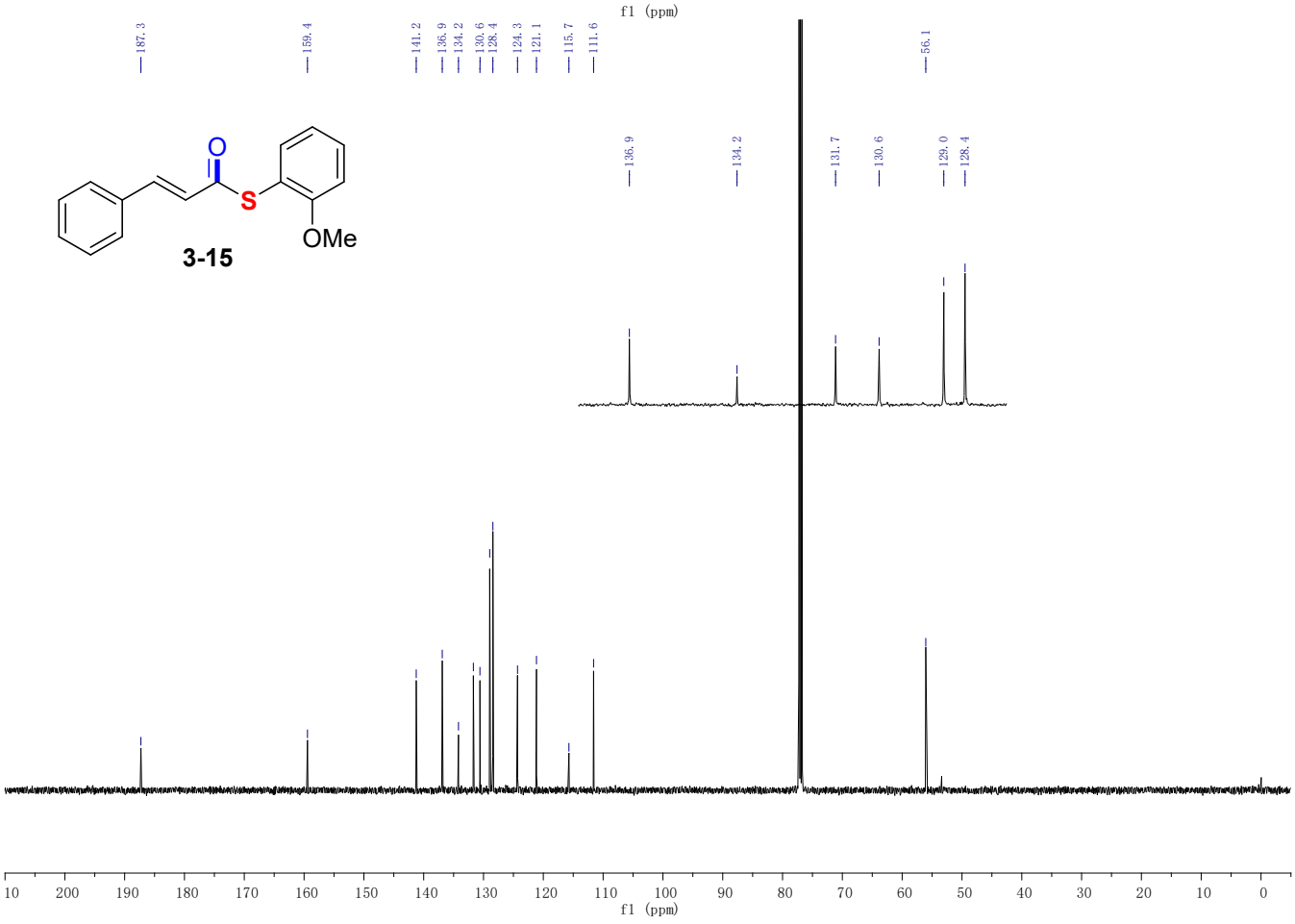

7.69
7.66
7.57
7.57
7.56
7.41
7.26
7.12
7.07
6.81
6.78
2.35
O
S
3-13
1.00
2.12
3.00
1.93
0.99
1.00
6.21
f1 (ppm)

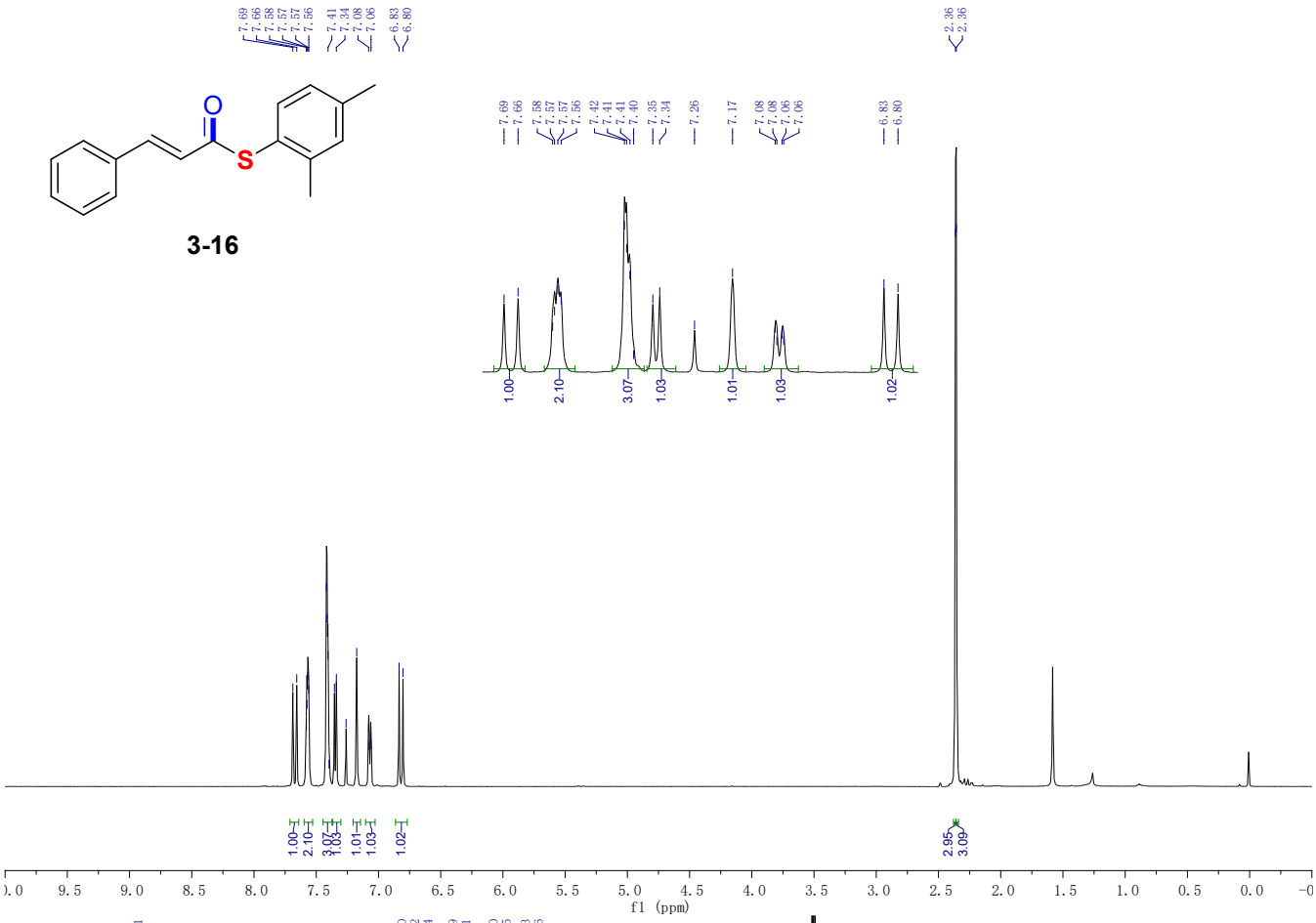

188.5
141.3
138.9
132.2
130.7
129.0
128.5
126.8
124.3
134.1
132.2
131.4
130.7
129.0
128.5
126.8
21.2
O
S
3-13
f1 (ppm)

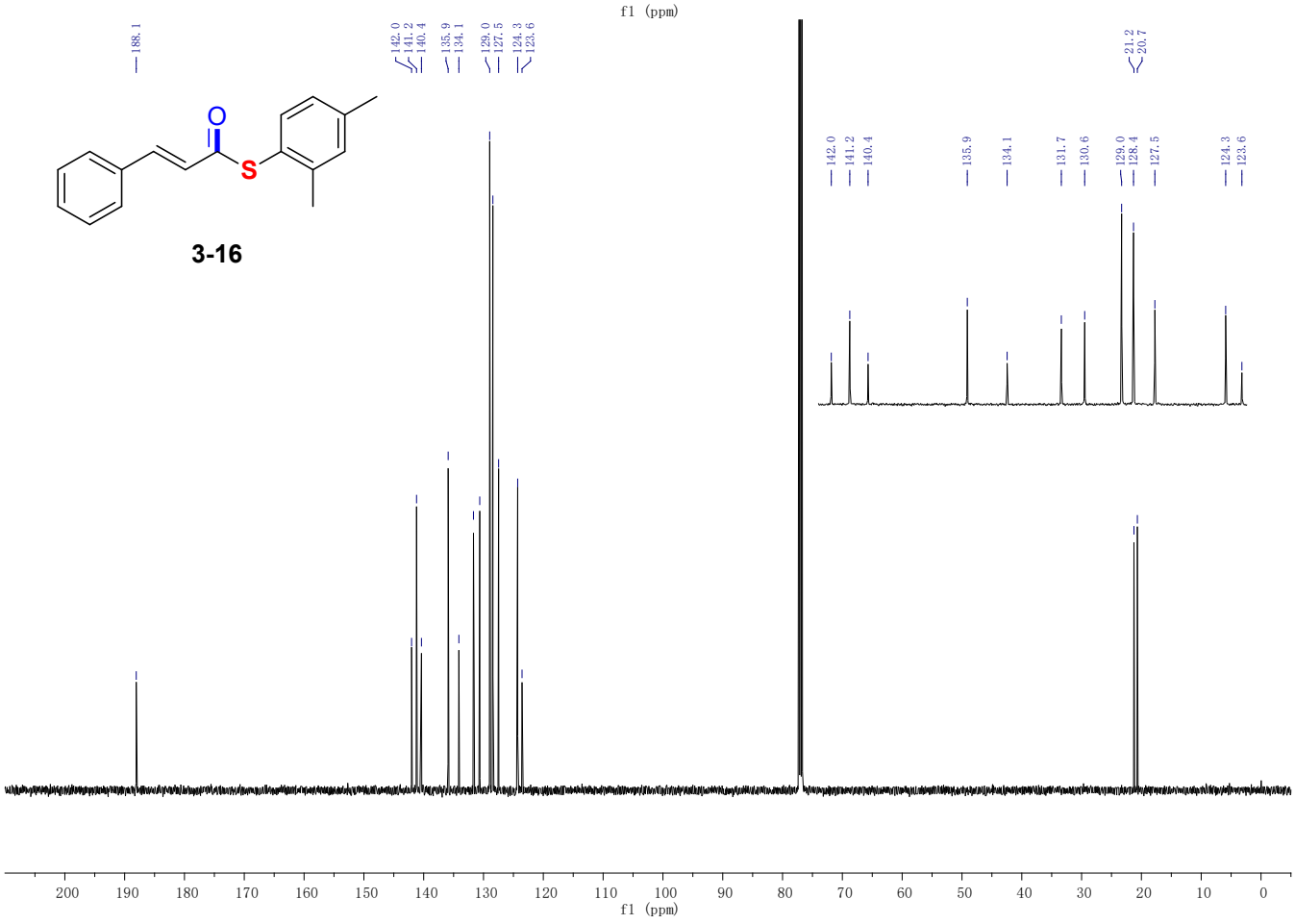

7.71
7.68
7.60
7.59
7.59
7.58
7.57
7.57
7.52
7.50
7.45
7.44
7.43
7.42
7.41
7.33
7.33
7.32
7.31
7.26
6.78
6.75
Cl
Cl
O
S
3-14
1.00
2.96
1.03
2.90
0.94
0.96
f1 (ppm)

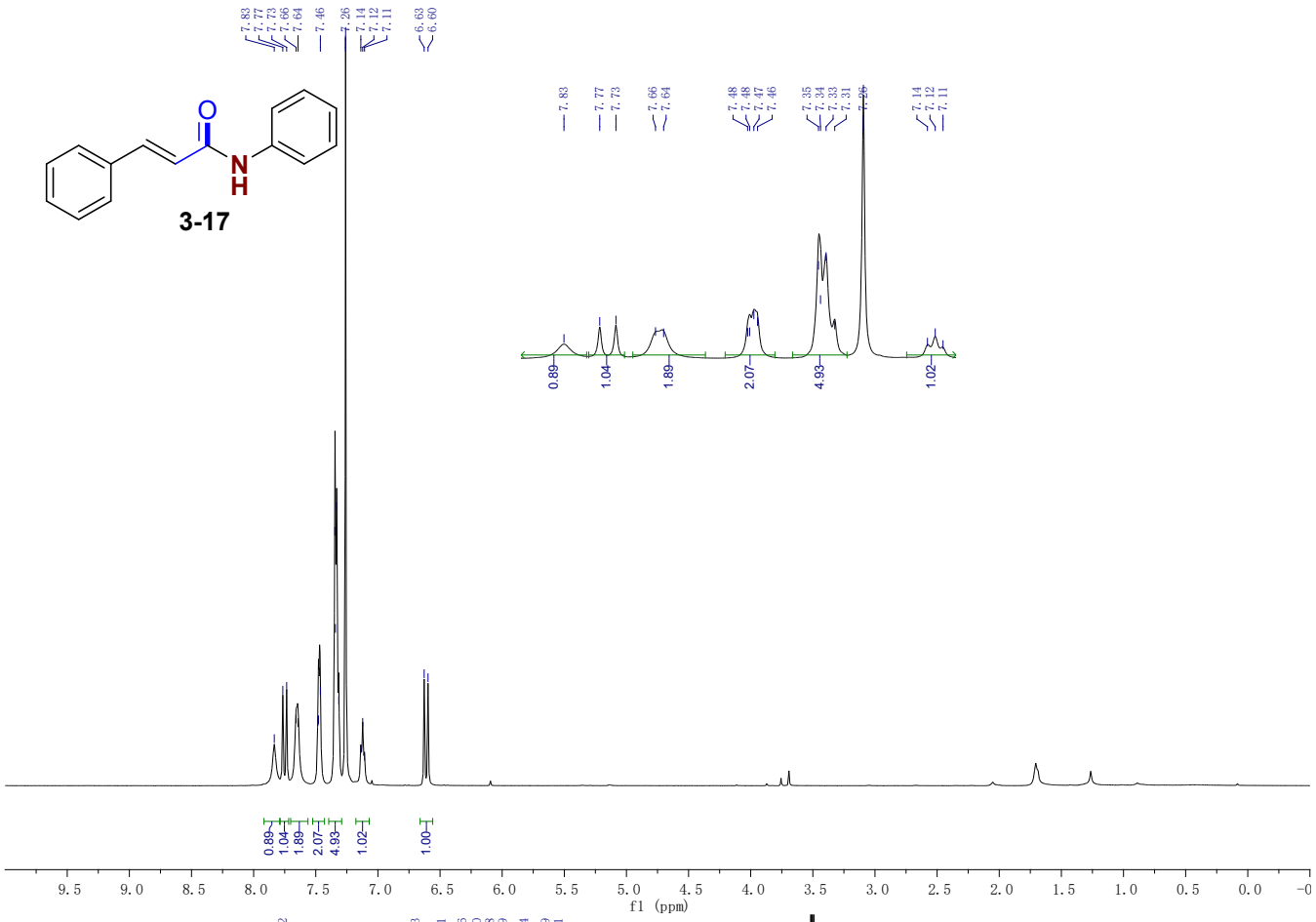

186.6
142.5
136.0
131.1
130.9
129.1
128.6
127.6
123.6
Cl
Cl
O
S
3-14
136.0
134.1
133.7
133.1
131.1
130.9
129.1
128.6
127.6
f1 (ppm)

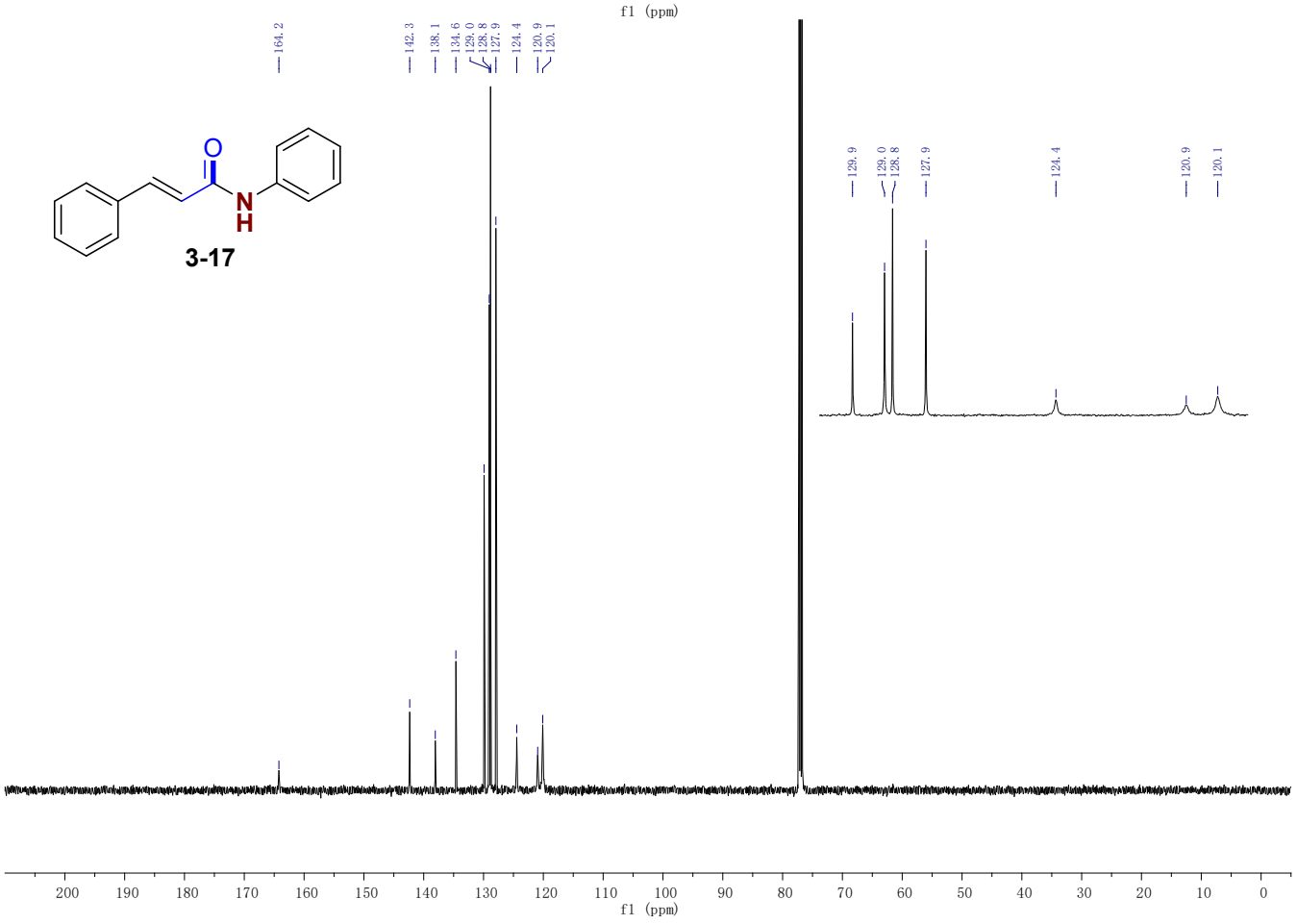

3-15
OMe
f1 (ppm)

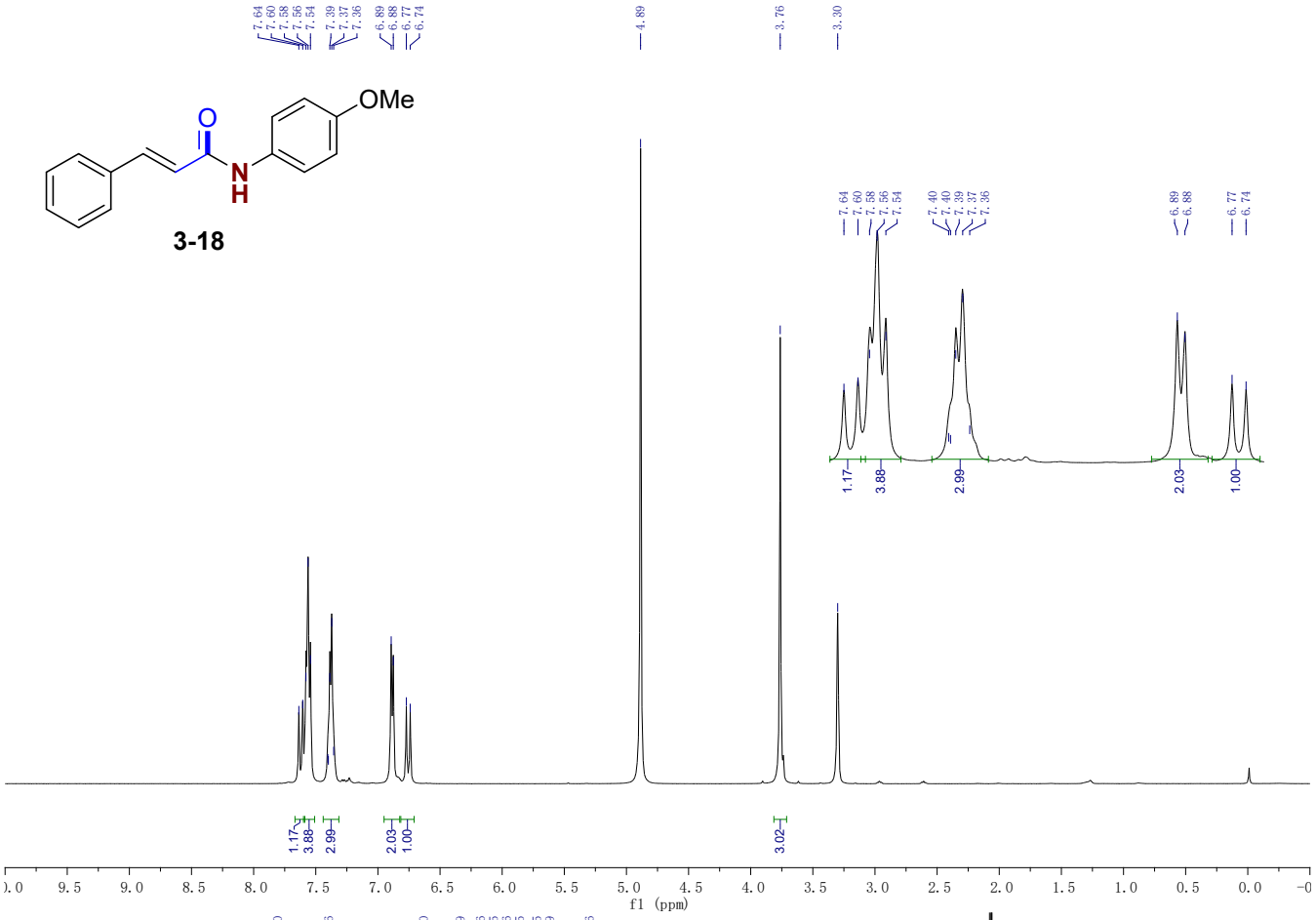

3-15
OMe
f1 (ppm)

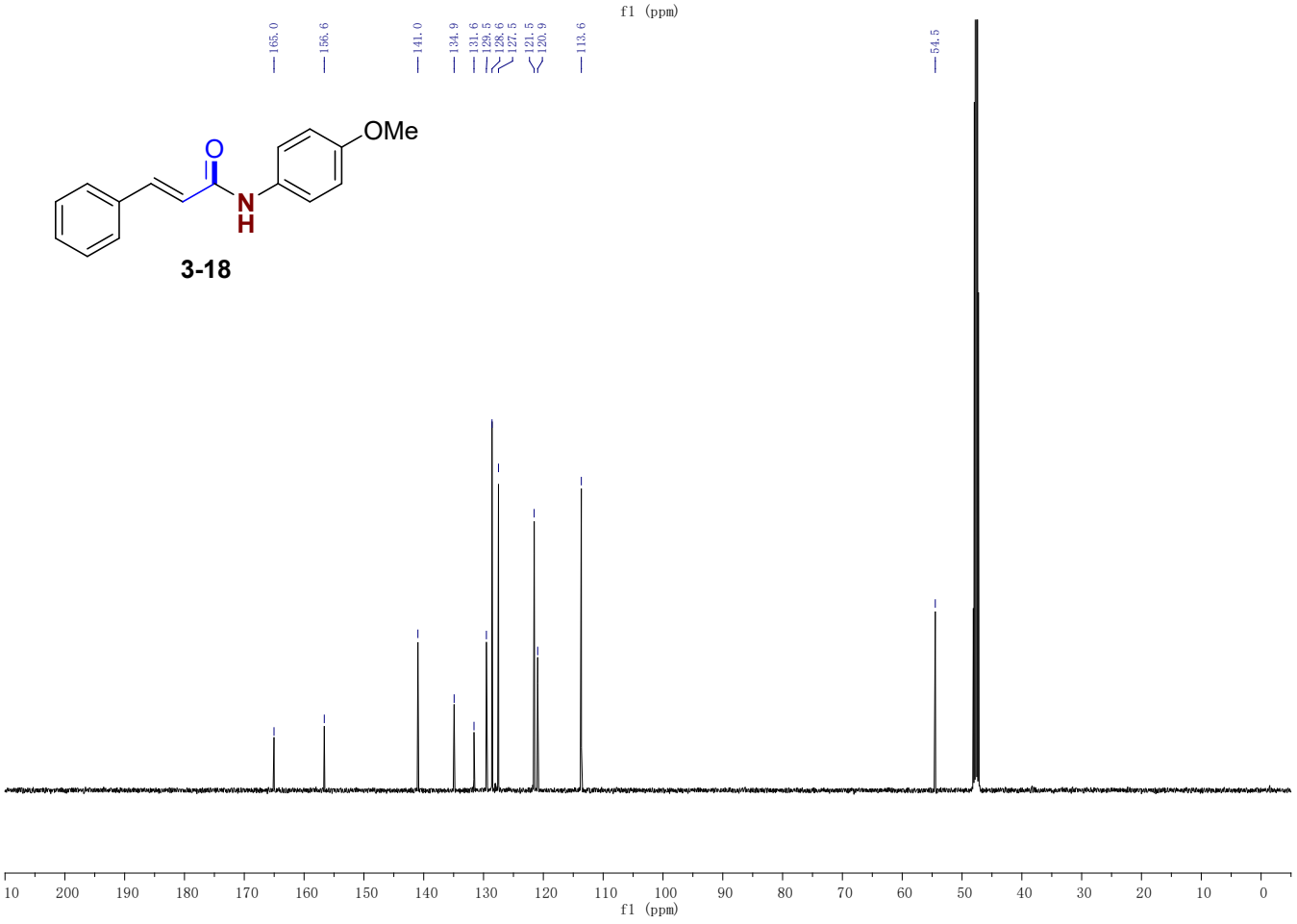

3-16
f1 (ppm)

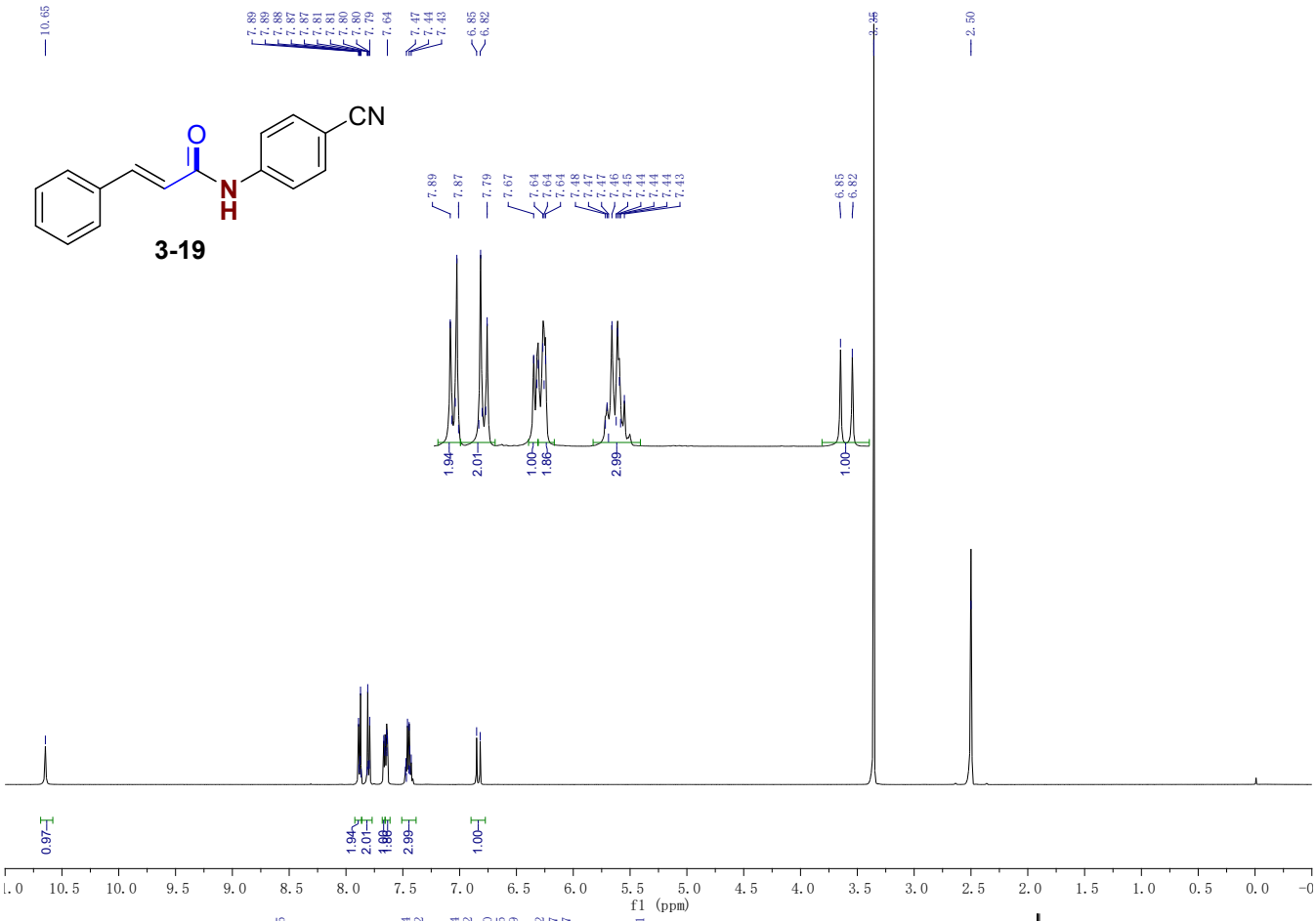

3-16
f1 (ppm)

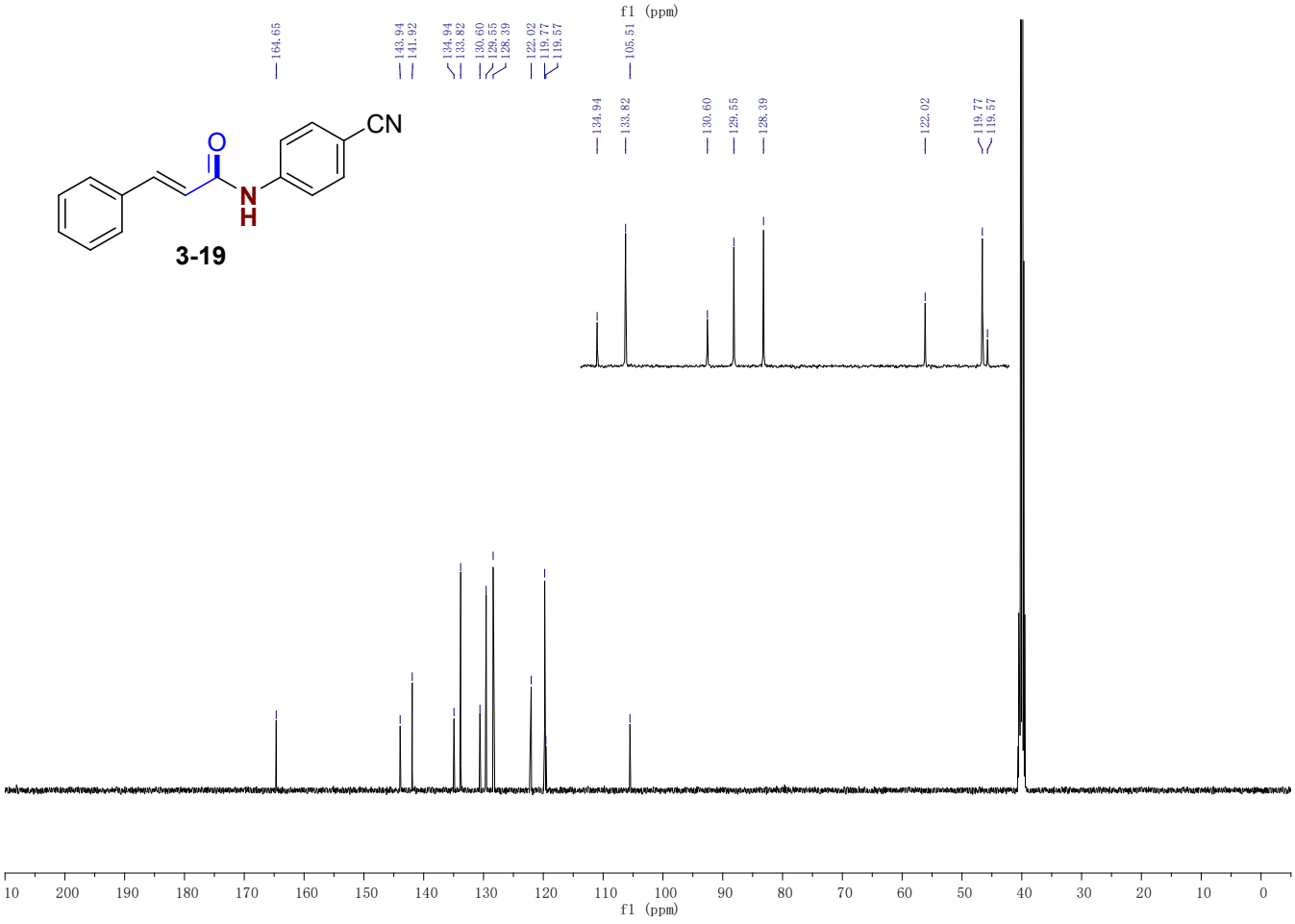

7.83
7.77
7.73
7.66
7.64
7.46
7.26
7.14
7.12
7.11
6.63
6.60
O
N
H
3-17
0.89
1.04
1.89
2.07
4.93
1.02
1.00
f1 (ppm)

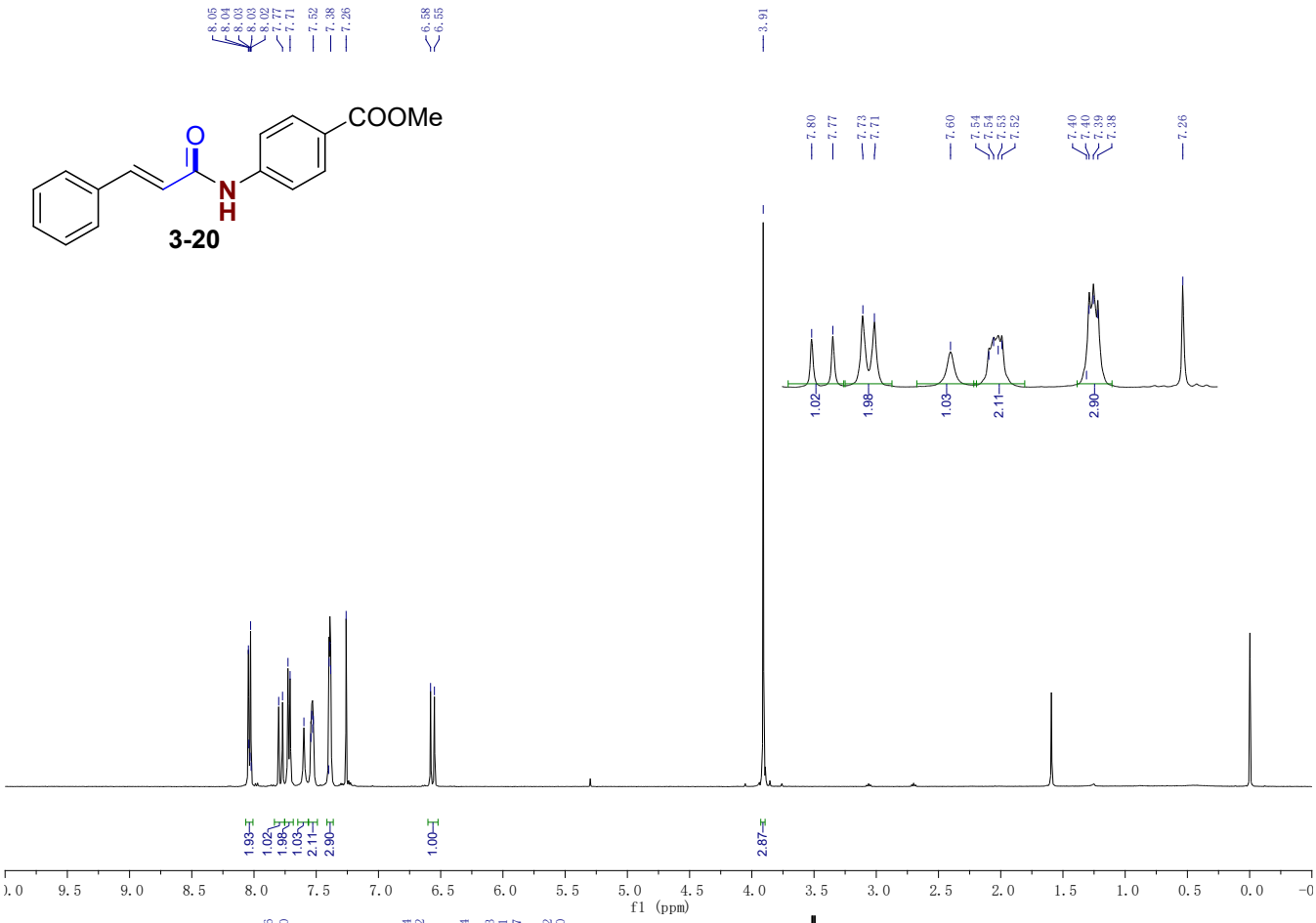

164.2
142.3
138.1
134.6
129.0
128.8
127.9
124.4
120.9
120.1
O
N
H
3-17
f1 (ppm)

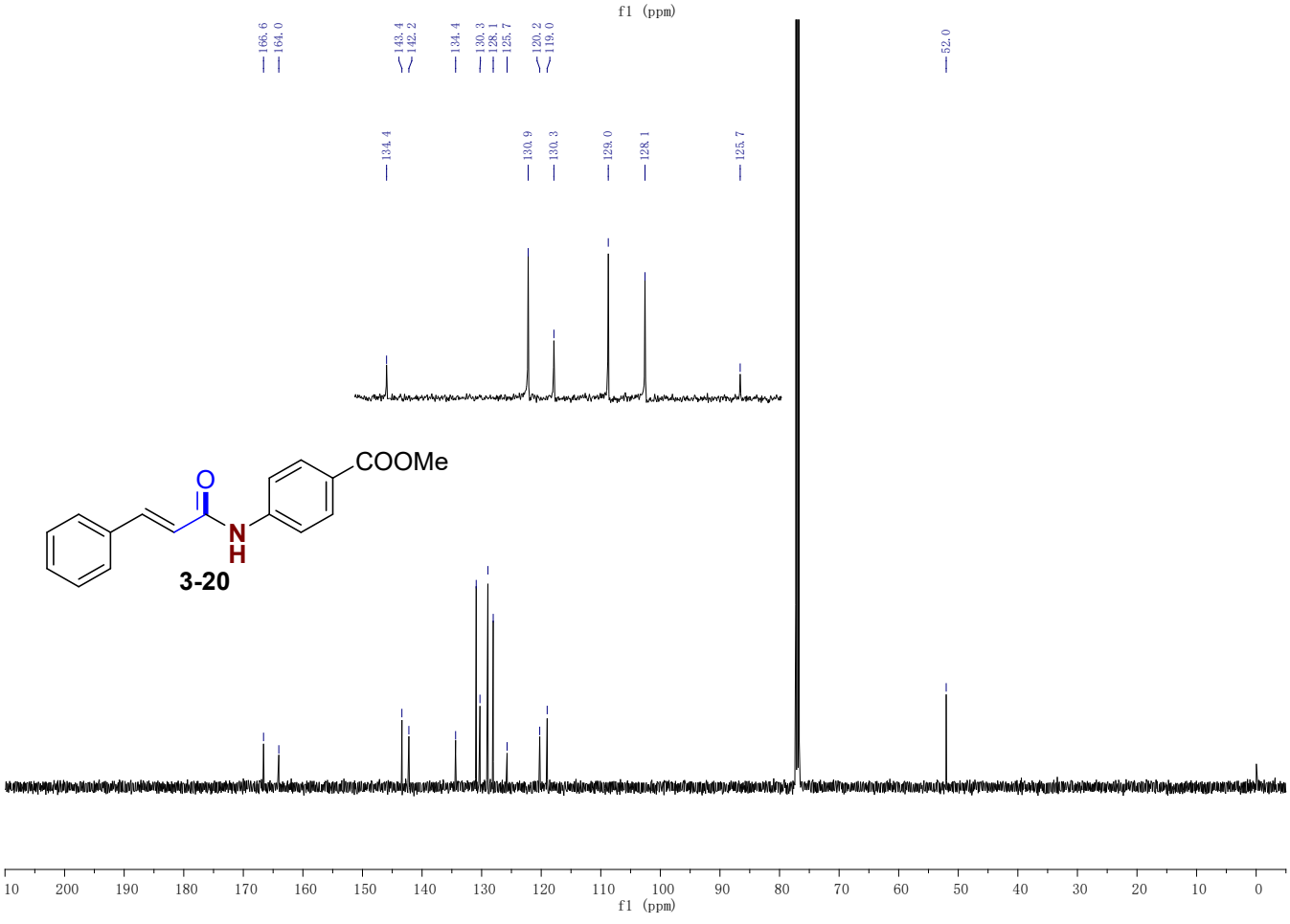

7.64
7.60
7.58
7.56
7.54
7.39
7.37
7.36
6.89
6.88
6.77
6.74
4.89
3.76
3.30
OMe
O
N
H
3-18
1.17
3.88
2.99
2.03
1.00
3.02
f1 (ppm)

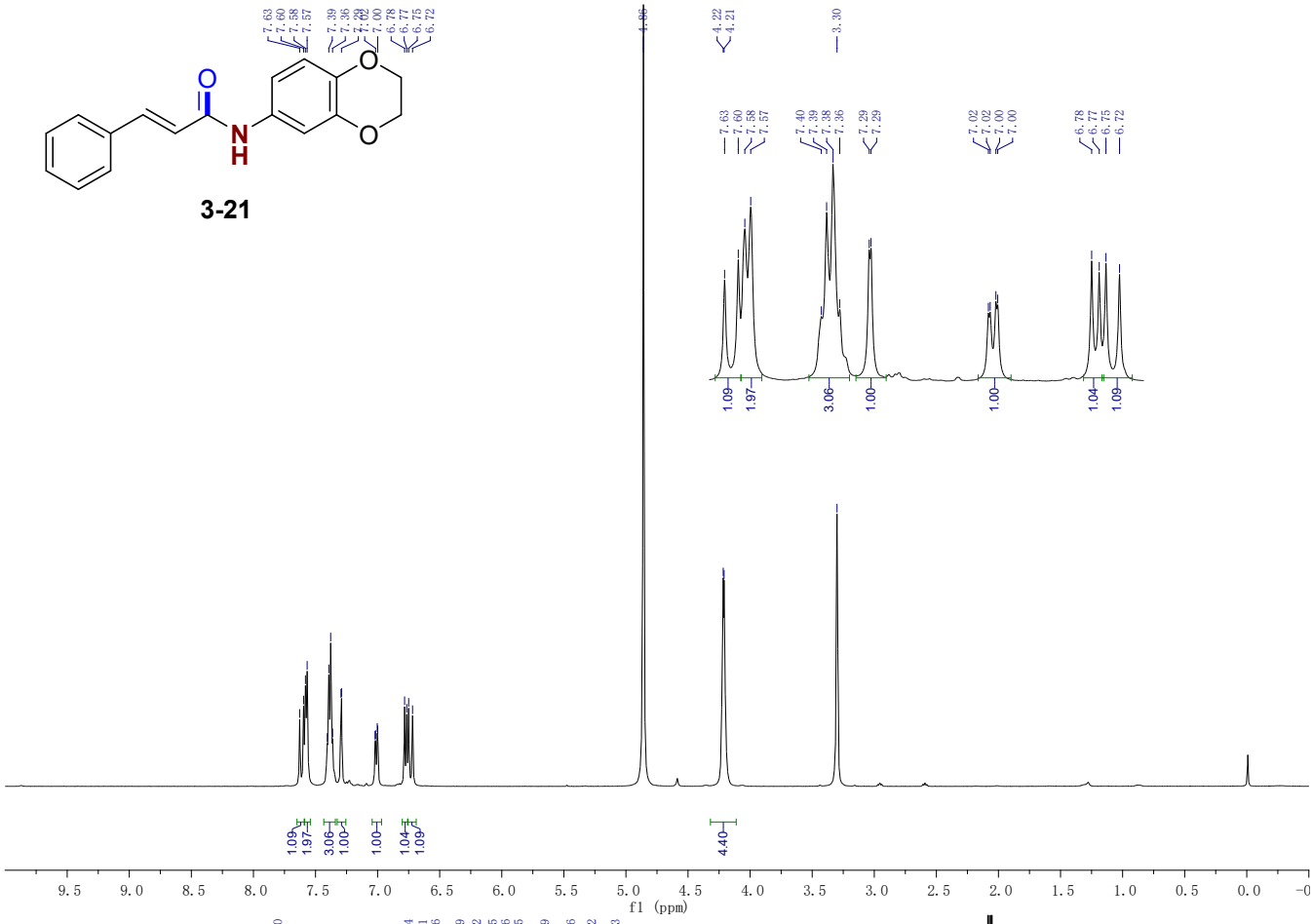

165.0
156.6
141.0
134.9
131.6
129.5
128.6
127.5
121.5
120.9
113.6
54.5
OMe
O
N
H
3-18
f1 (ppm)

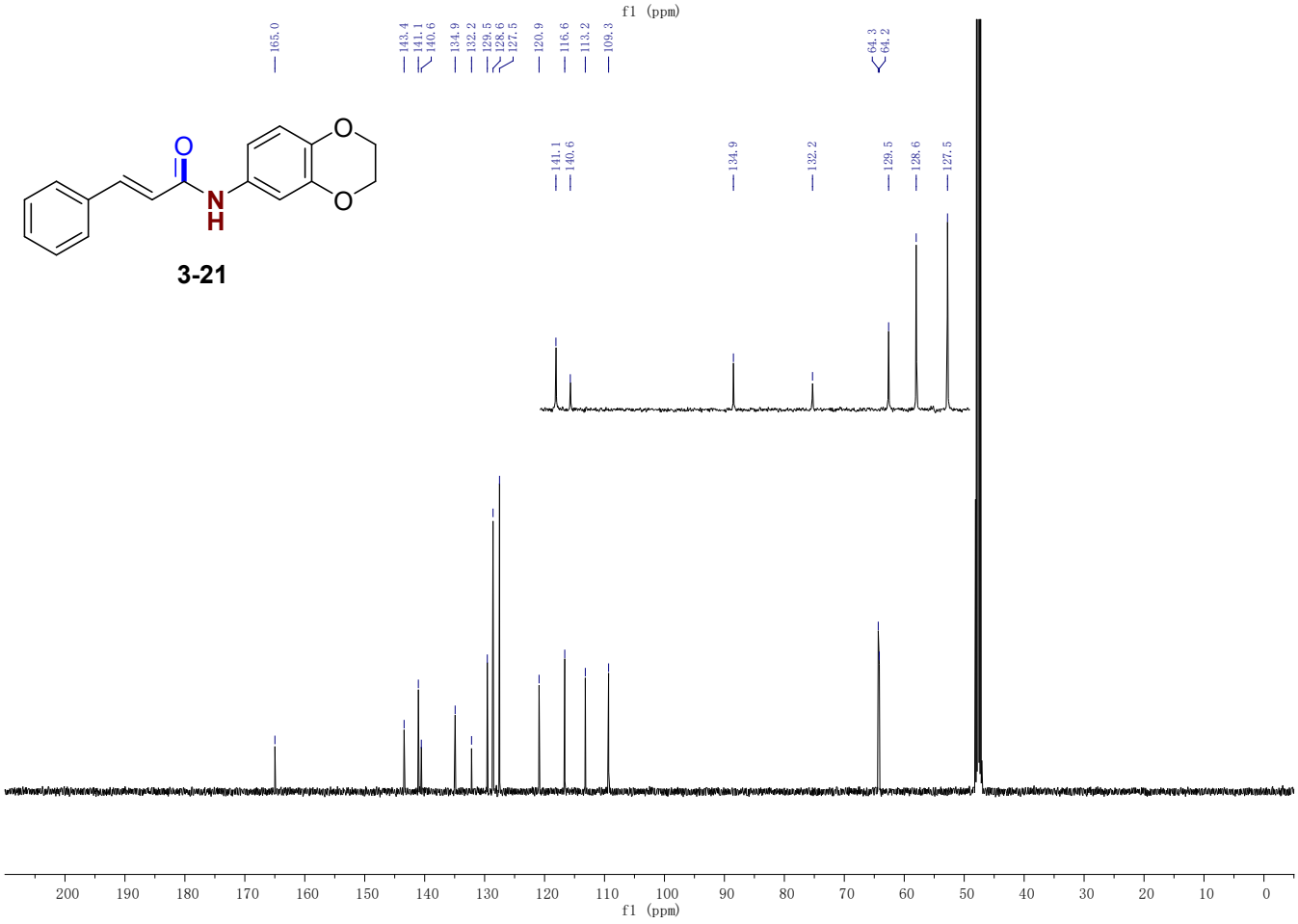

10.65
7.89
7.88
7.87
7.81
7.80
7.79
7.64
7.47
7.44
7.43
6.85
6.82
3.35
2.50
CN
O
N
H
3-19
1.94
2.01
1.00
1.86
2.99
1.00
0.97
f1 (ppm)

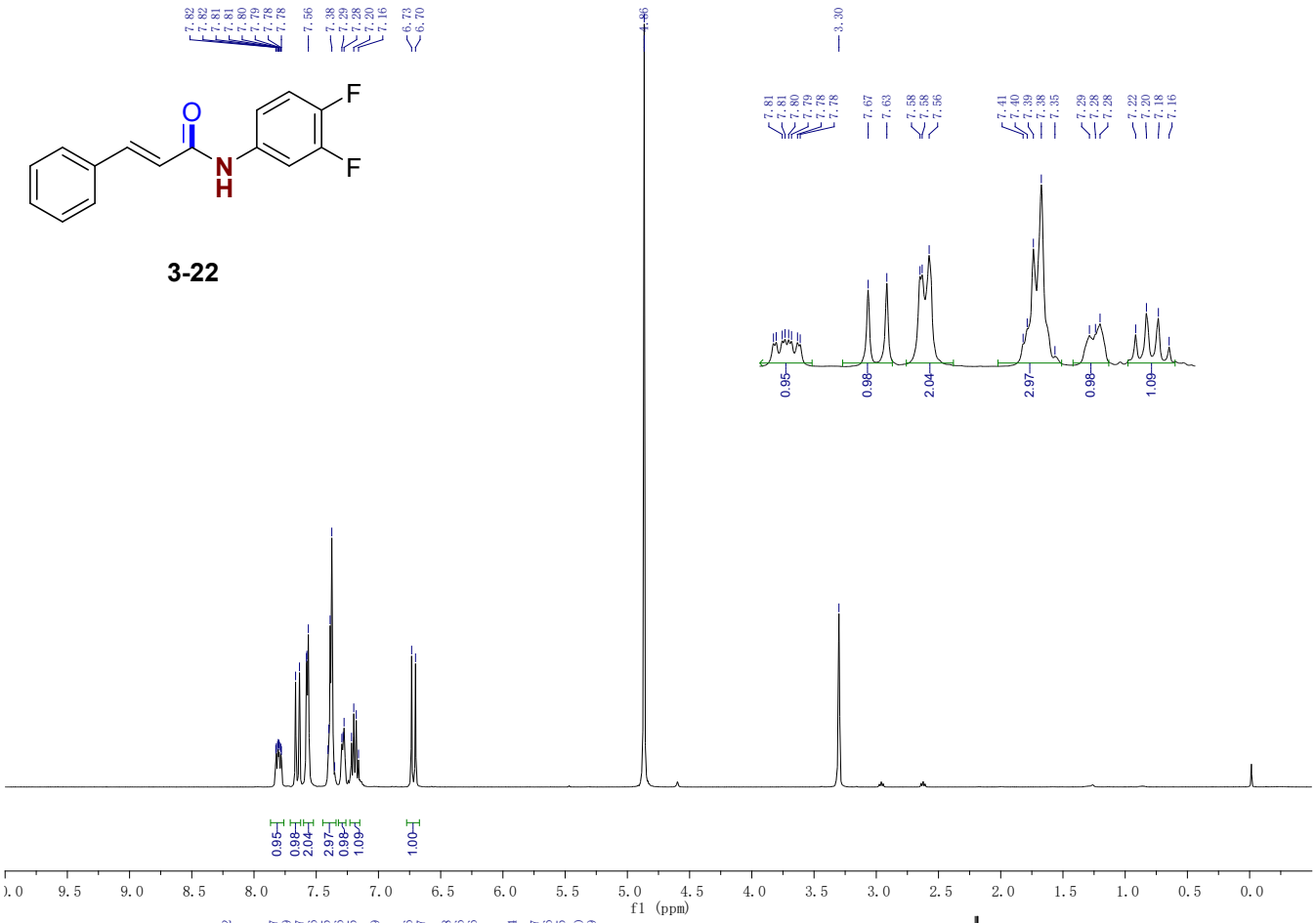

164.65
143.94
141.92
134.94
133.82
130.60
129.55
128.39
122.02
119.77
119.57
105.51
CN
O
N
H
3-19
f1 (ppm)


8.05
8.04
8.03
8.03
8.02
7.77
7.71
7.52
7.38
7.26
6.58
6.55
3.91
COOMe
O
N
H
3-20
7.80
7.77
7.73
7.71
7.60
7.54
7.54
7.53
7.52
7.40
7.40
7.39
7.38
7.26
1.02
1.98
1.03
2.11
2.90
1.93
1.02
1.98
1.03
2.11
2.90
1.00
2.87
f1 (ppm)

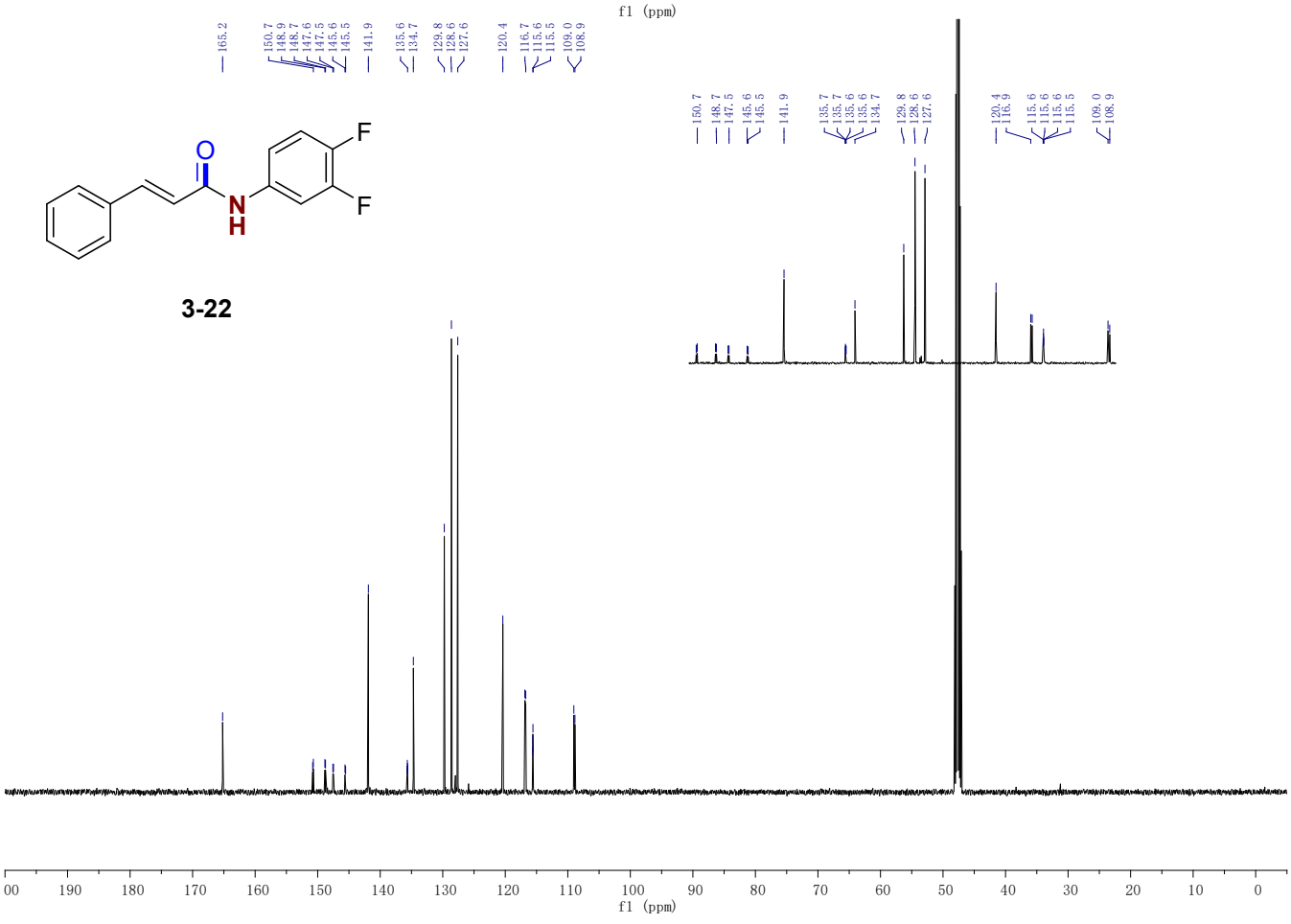

166.6
164.0
143.4
142.2
134.4
130.3
128.1
125.7
120.2
119.0
52.0
134.4
130.9
130.3
128.0
128.1
125.7
COOMe
O
N
H
3-20
f1 (ppm)


3-21
f1 (ppm)

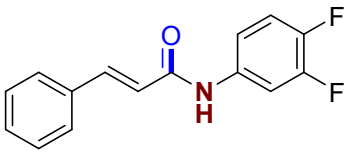

3-21
f1 (ppm)


7.82
7.82
7.81
7.81
7.80
7.79
7.78
7.78
7.56
7.38
7.29
7.28
7.20
7.16
6.73
6.70
4.86
3.30
F
F
O
N
H
0.95
0.98
2.04
2.97
0.98
1.09
1.00
f1 (ppm)

3-22

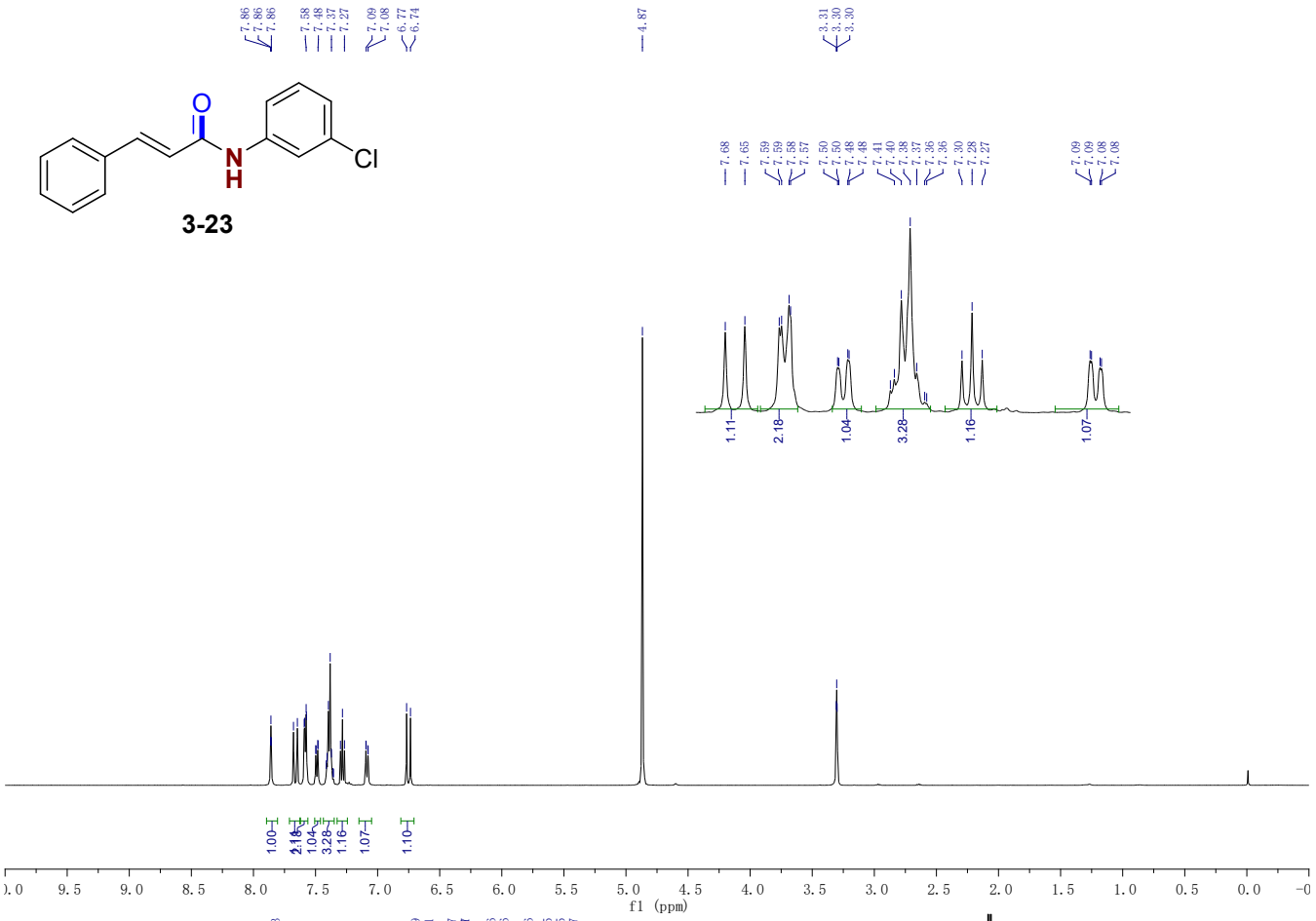

165.2
150.7
148.9
148.7
147.6
147.5
145.6
145.5
141.9
135.6
134.7
129.8
128.6
127.6
120.4
116.7
115.6
115.5
109.0
108.9
F
F
O
N
H
f1 (ppm)

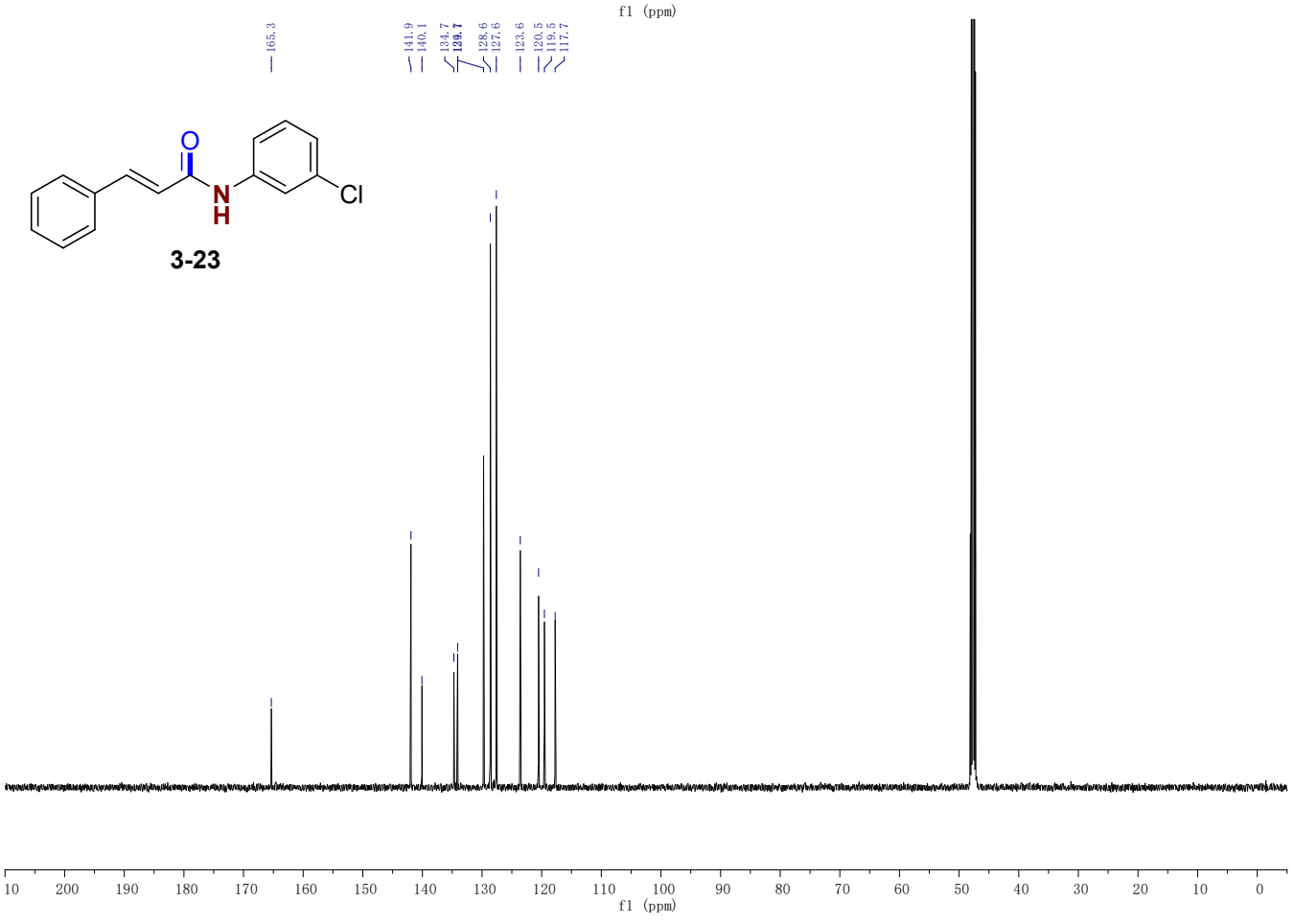
3-22

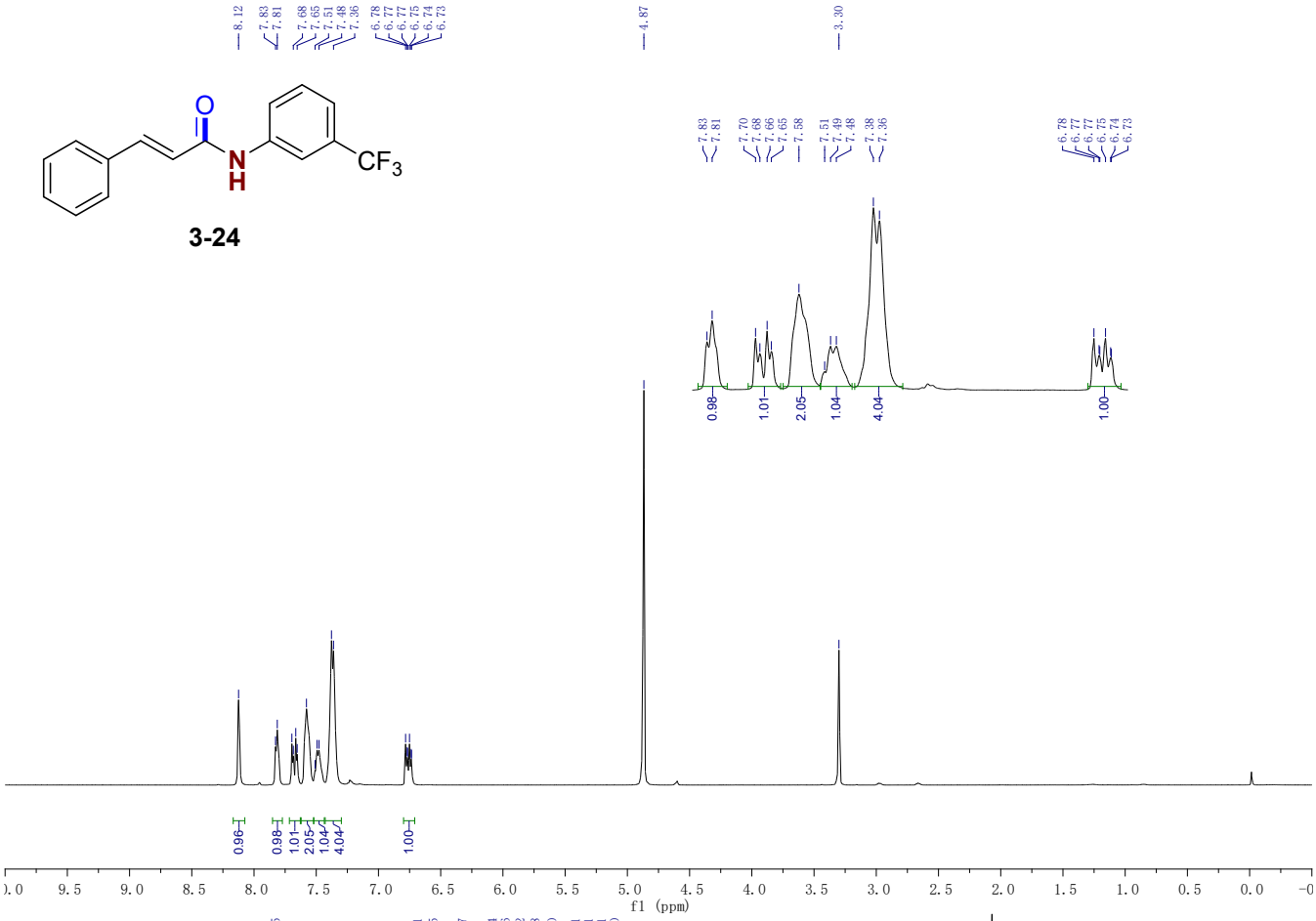

O
N
H
F
F

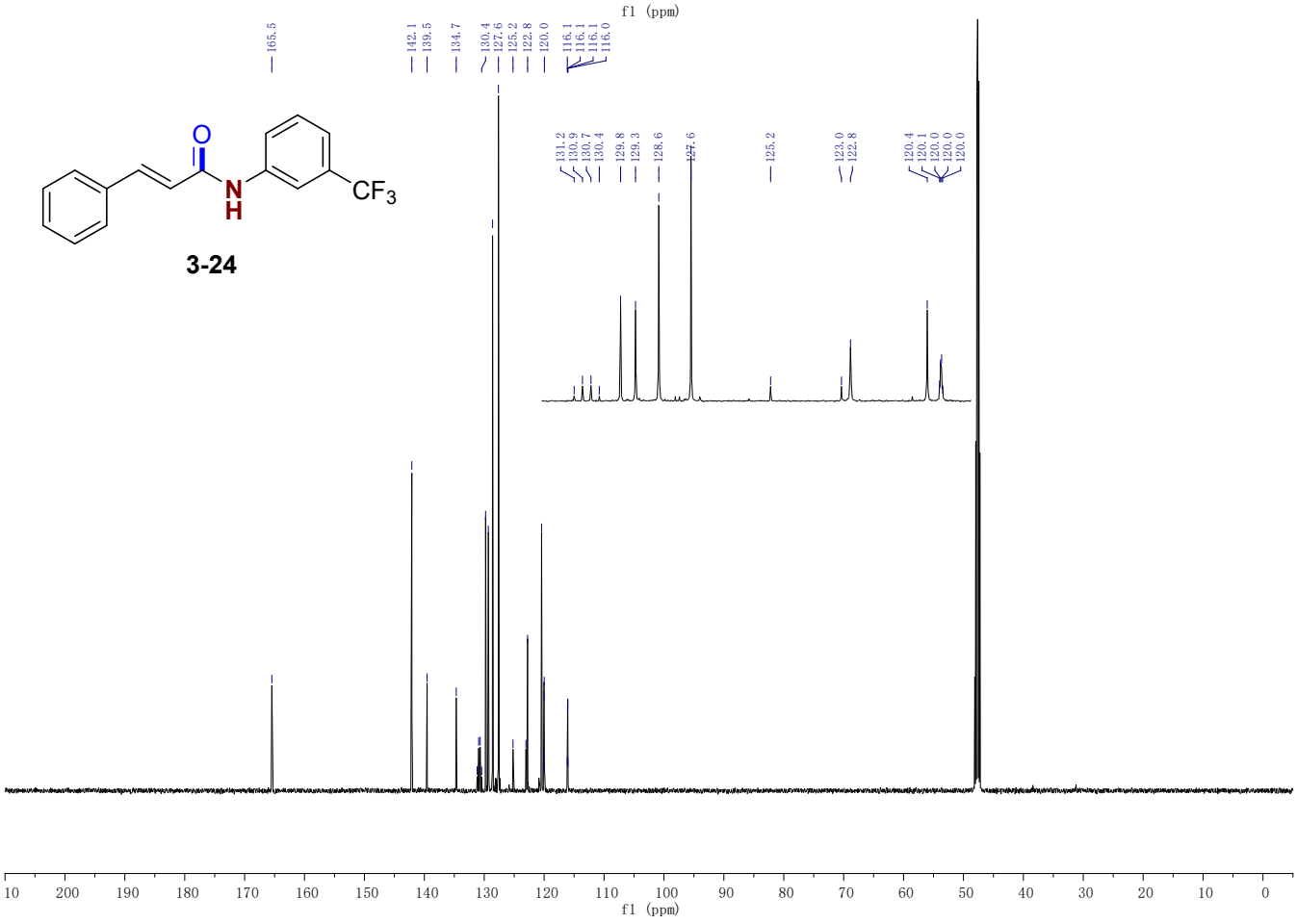
3-22

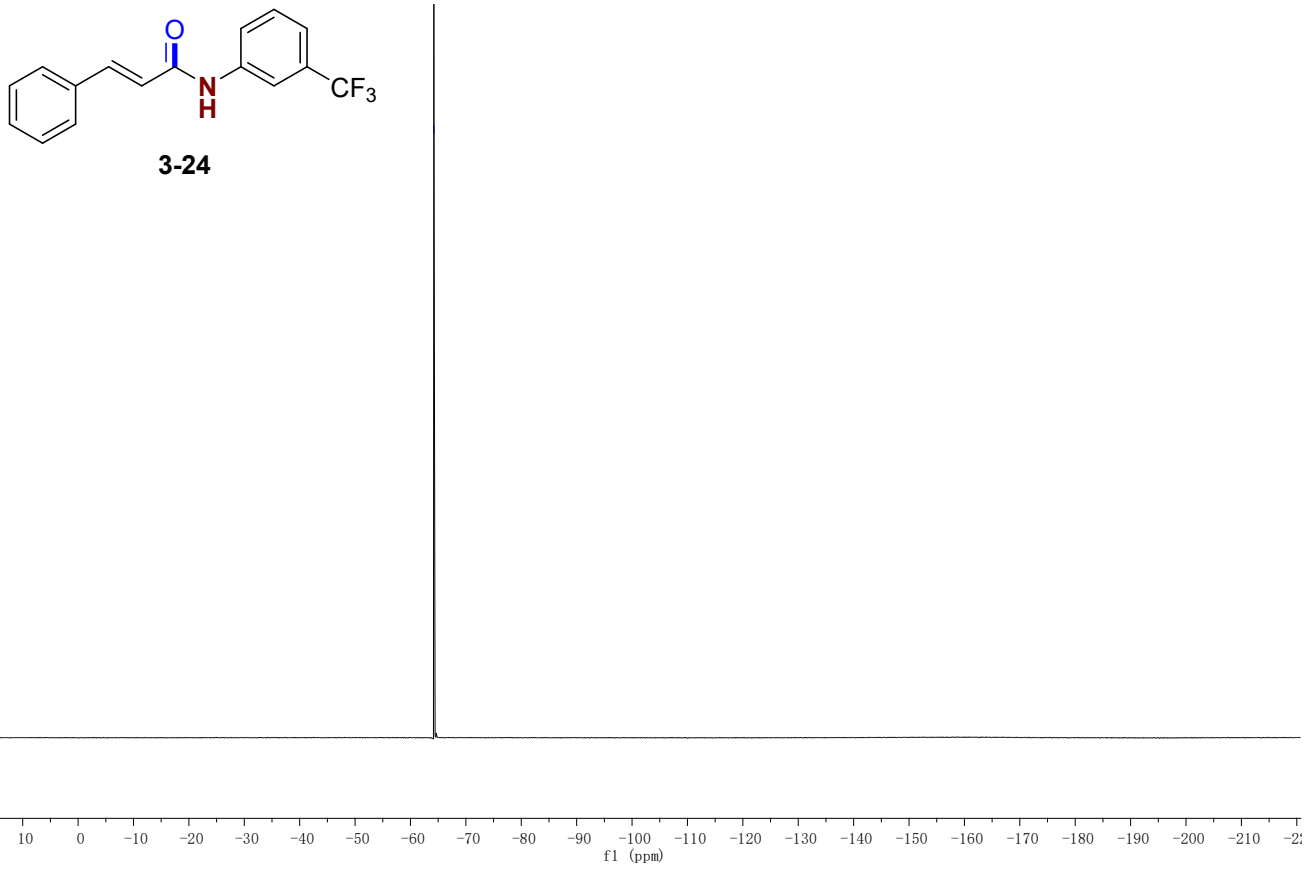
139.0
145.9
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)


7.86
7.86
7.86
7.58
7.48
7.37
7.27
7.09
7.08
6.77
6.74
4.87
3.31
3.30
3.30
O
N
H
Cl
3-23
7.68
7.65
7.59
7.59
7.58
7.57
7.50
7.50
7.48
7.48
7.41
7.40
7.38
7.37
7.36
7.36
7.30
7.28
7.27
7.09
7.09
7.08
7.08
1.11
2.18
1.04
3.28
1.16
1.07
1.00
2.18
1.04
3.28
1.16
1.07
1.10
f1 (ppm)

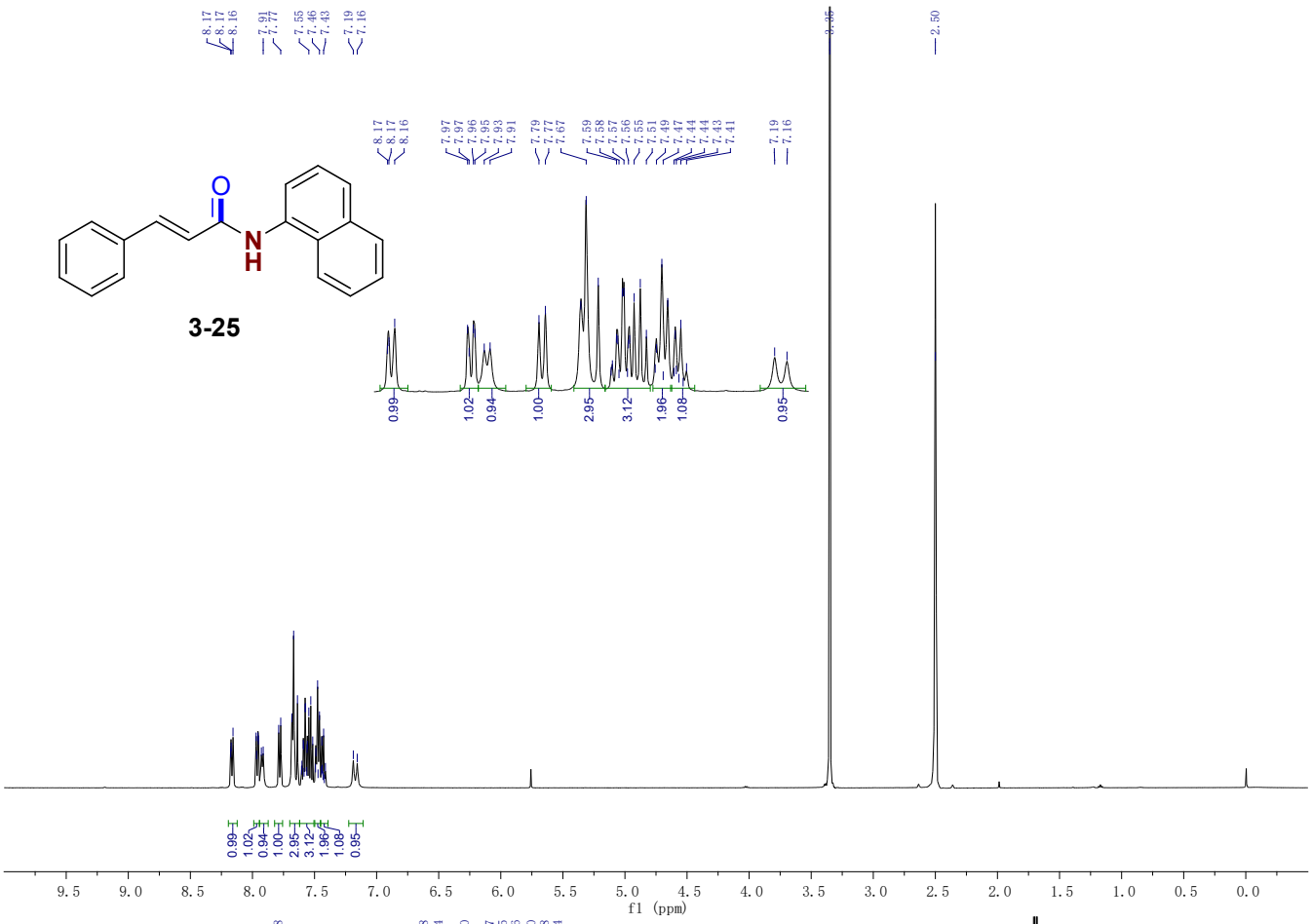

165.3
141.9
140.1
134.7
129.7
128.6
127.6
123.6
120.5
119.5
117.7
O
N
H
Cl
3-23
f1 (ppm)

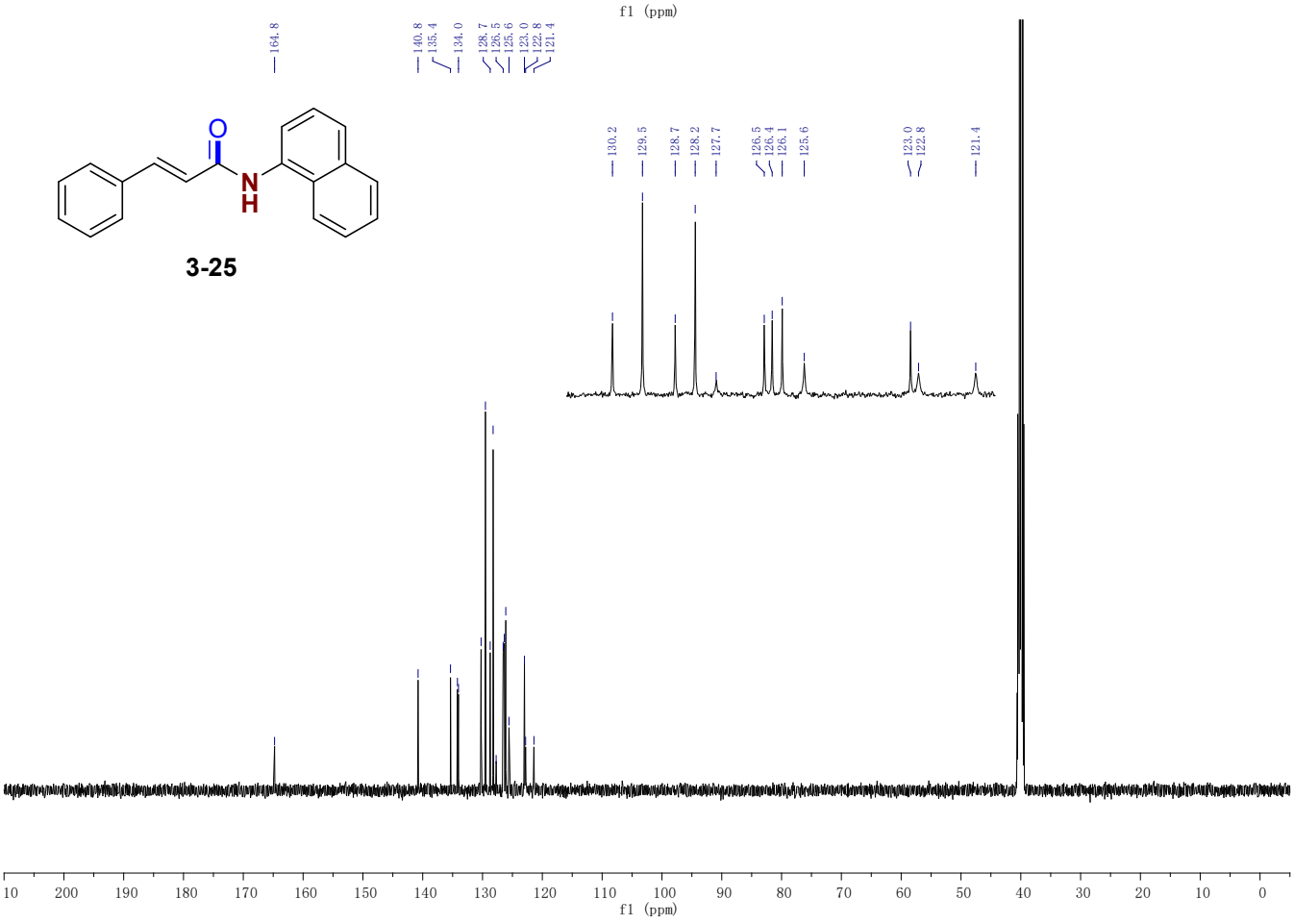

8.12
7.83
7.81
7.68
7.65
7.51
7.48
7.36
6.78
6.77
6.77
6.75
6.74
6.73
4.87
3.30
O
N
H
CF3
3-24
0.96
0.98
1.01
2.05
1.04
4.04
1.00
f1 (ppm)

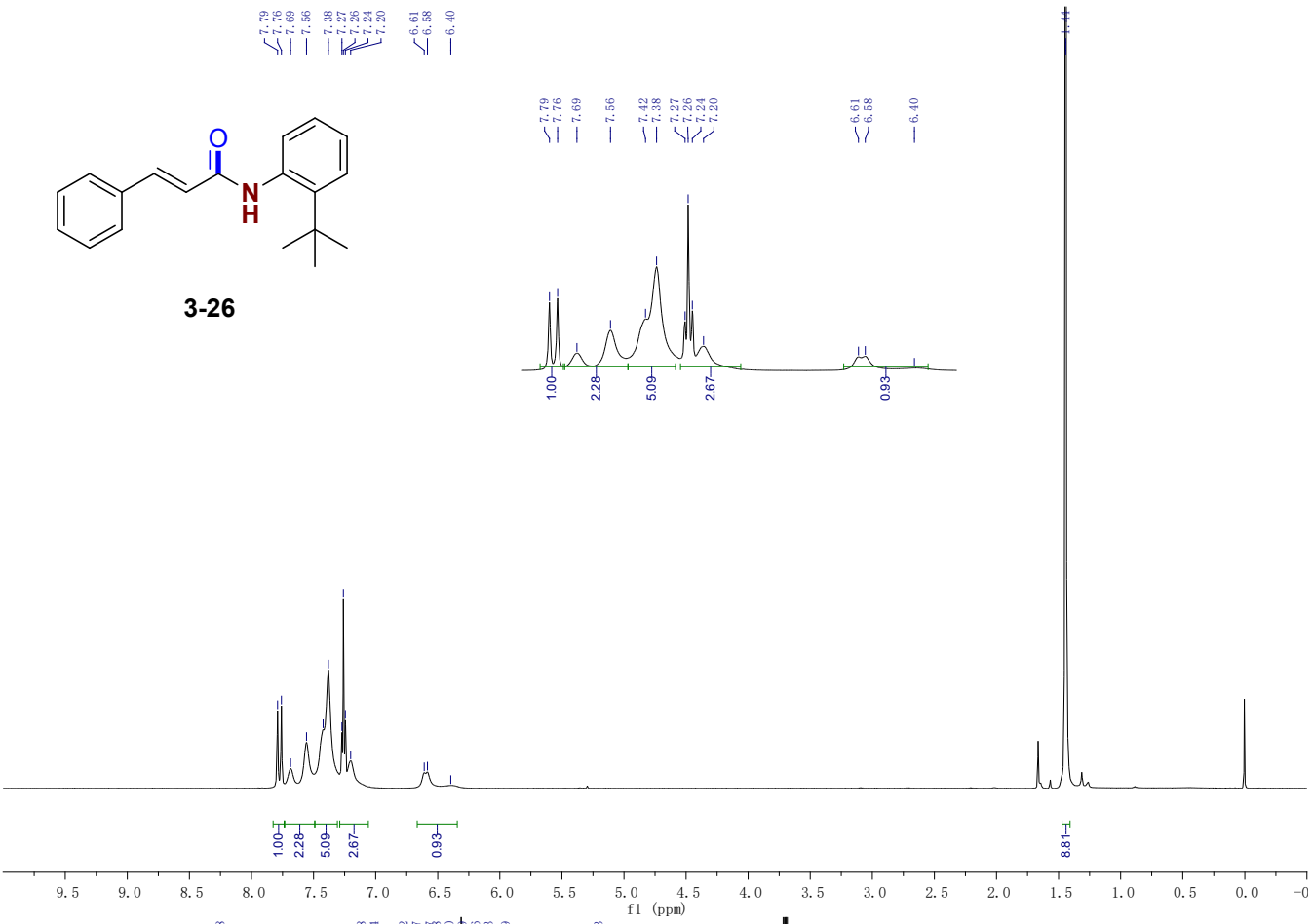

165.5
142.1
139.5
134.7
130.4
127.6
125.2
122.8
120.0
116.1
116.1
116.1
116.0
131.2
130.9
130.7
130.4
129.8
129.3
128.6
127.6
125.2
123.0
122.8
120.4
120.1
120.0
120.0
120.0
O
N
H
CF3
3-24
f1 (ppm)


O
N
H
CF3
-64.2
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

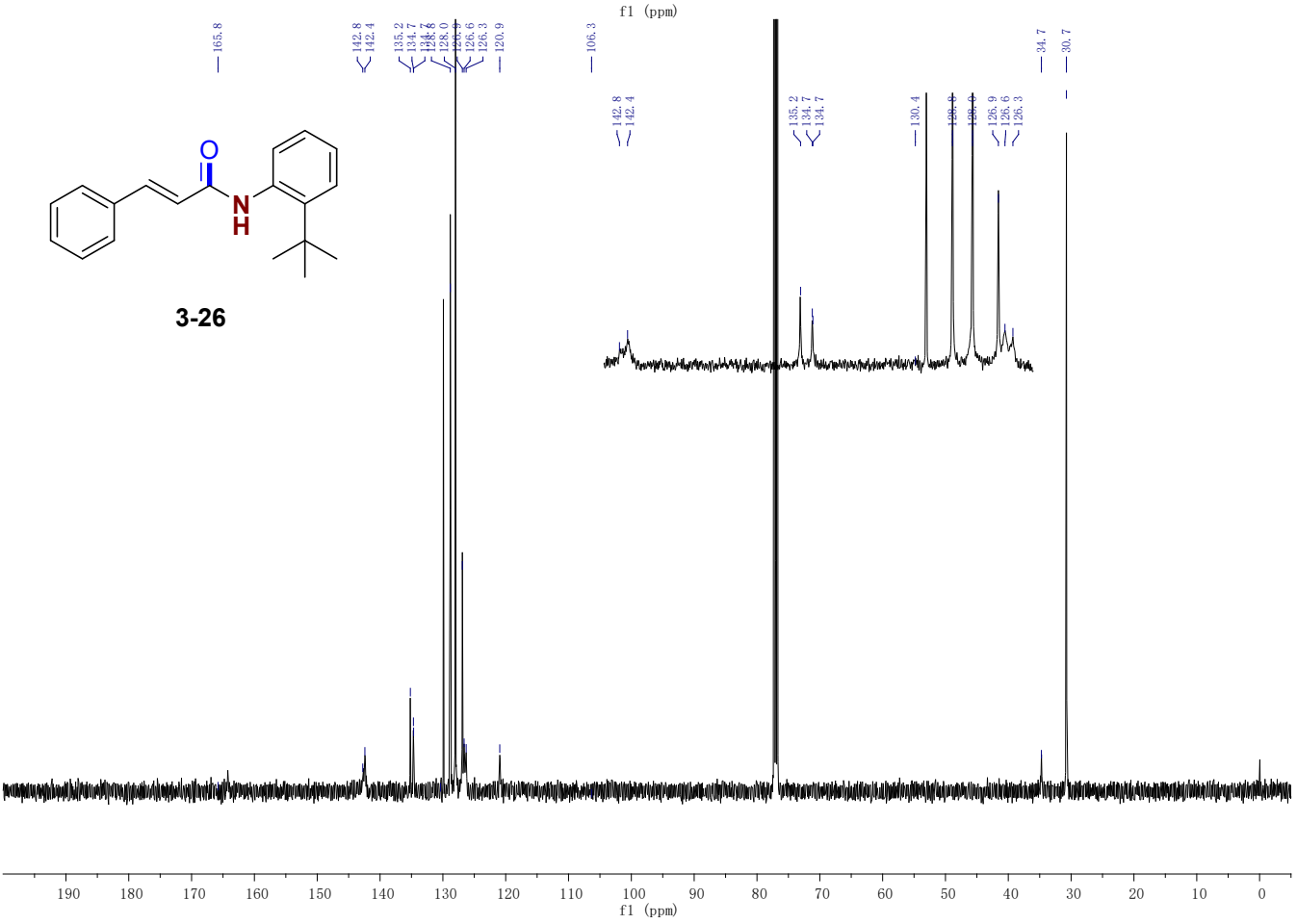
3-24


8.17
8.17
8.16
7.91
7.77
7.55
7.46
7.43
7.19
7.16
8.05
2.50
7.97
7.97
7.96
7.95
7.93
7.91
7.79
7.77
7.67
7.59
7.58
7.57
7.56
7.55
7.51
7.49
7.47
7.44
7.44
7.43
7.41
0.99
1.02
0.94
1.00
2.95
3.12
1.96
1.08
0.95
O
N
H
3-25
f1 (ppm)


164.8
140.8
135.4
134.0
128.7
126.5
125.6
123.0
122.8
121.4
130.2
129.5
128.7
128.2
127.7
126.5
126.4
126.1
125.6
123.0
122.8
121.4
O
N
H
3-25
f1 (ppm)


7.79
7.76
7.69
7.56
7.38
7.27
7.26
7.24
7.20
6.61
6.58
6.40
1.44
O
N
H
1.00
2.28
5.09
2.67
0.93
8.81
f1 (ppm)

3-26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142.8
142.4
135.2
134.7
134.7
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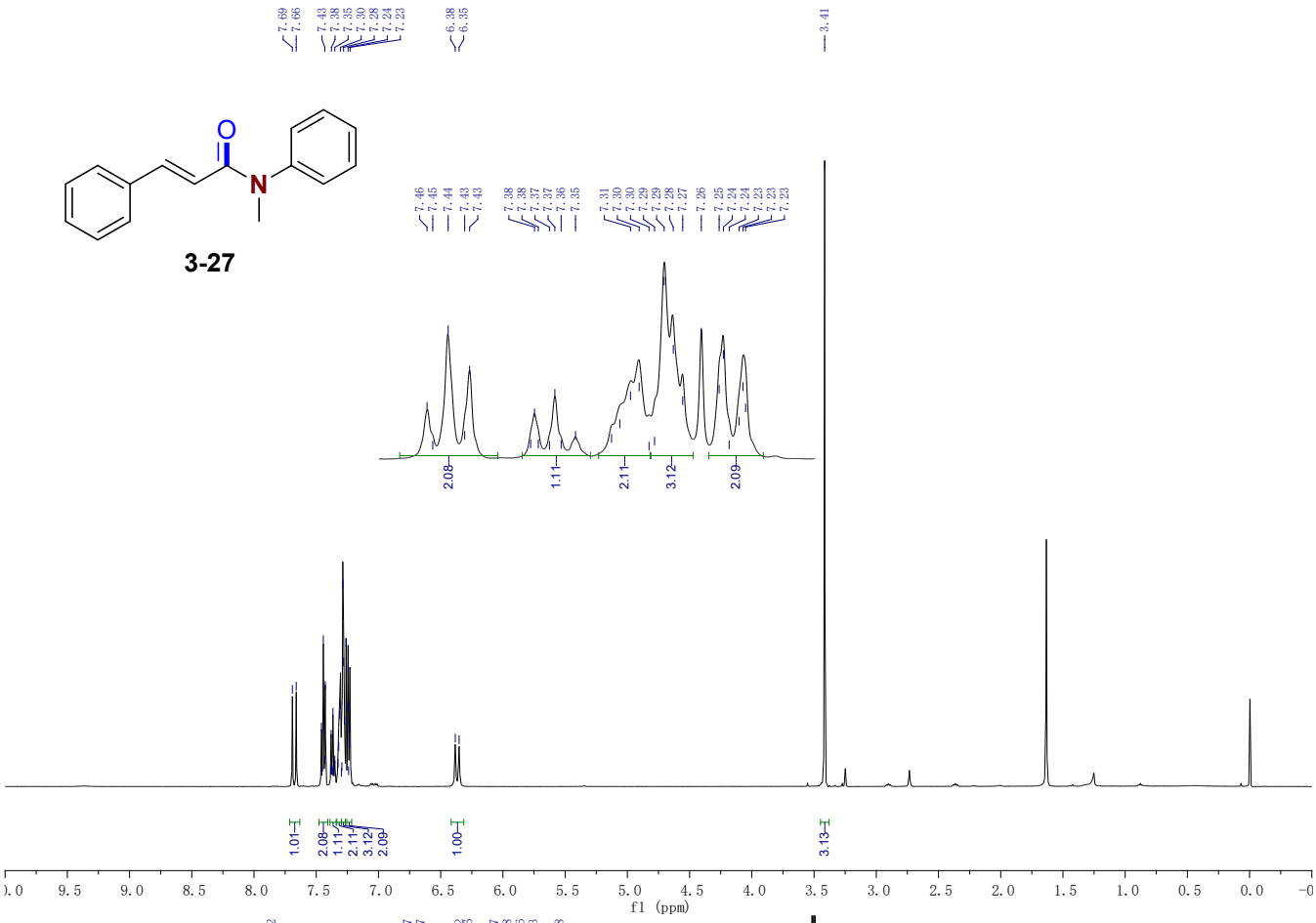
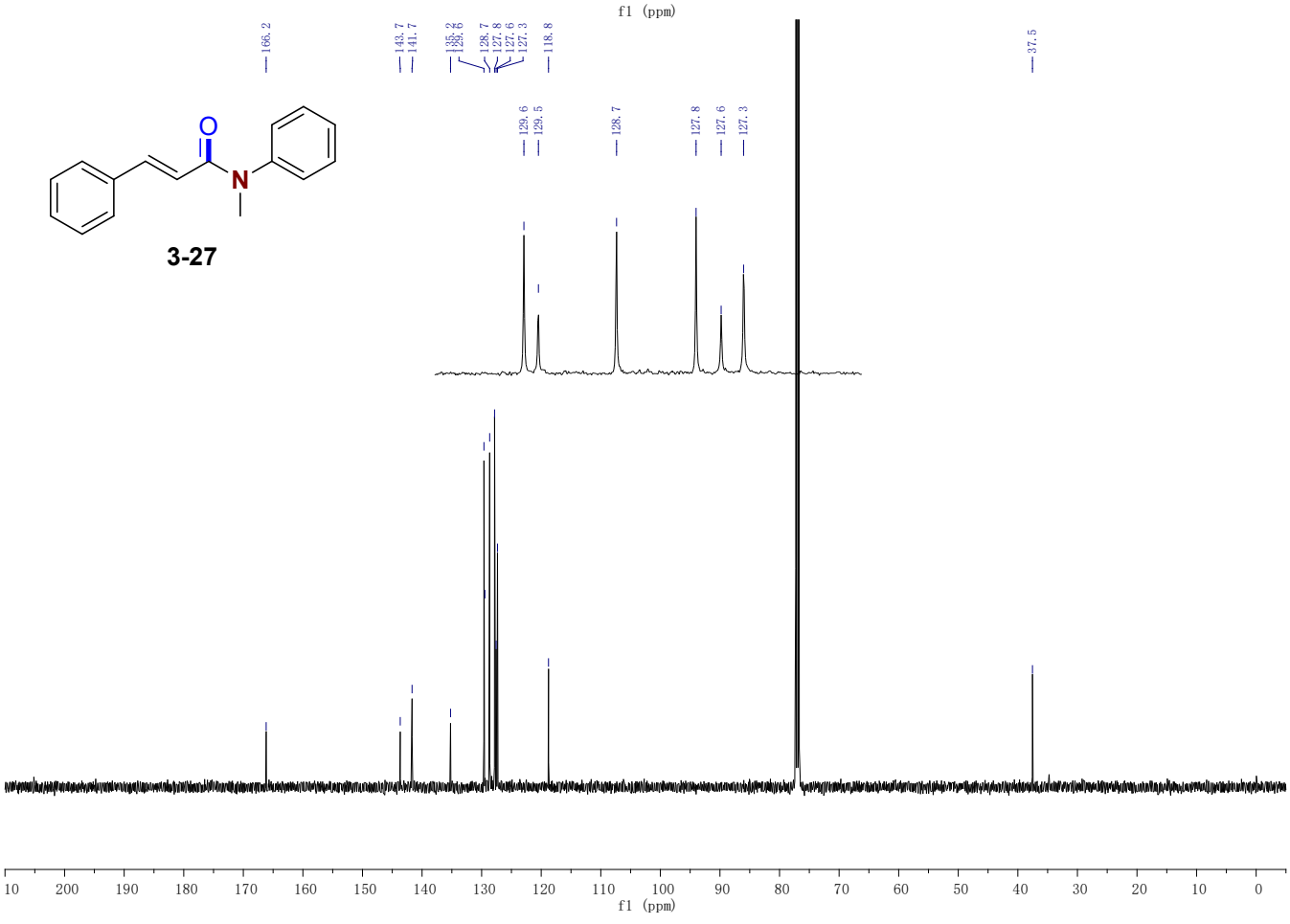
126.6
126.3
120.9
106.3
34.7
30.7
O
N
H
f1 (ppm)

3-26


7.69
7.66
7.43
7.38
7.35
7.30
7.28
7.24
7.23
6.38
6.35
3.41
O
N
3-27
7.46
7.45
7.44
7.43
7.43
7.38
7.38
7.37
7.37
7.36
7.35
7.31
7.30
7.30
7.29
7.29
7.28
7.27
7.26
7.25
7.24
7.24
7.23
7.23
7.23
2.08
1.11
2.11
3.12
2.09
1.01
2.08
1.11
2.11
3.12
2.09
1.00
3.13
f1 (ppm)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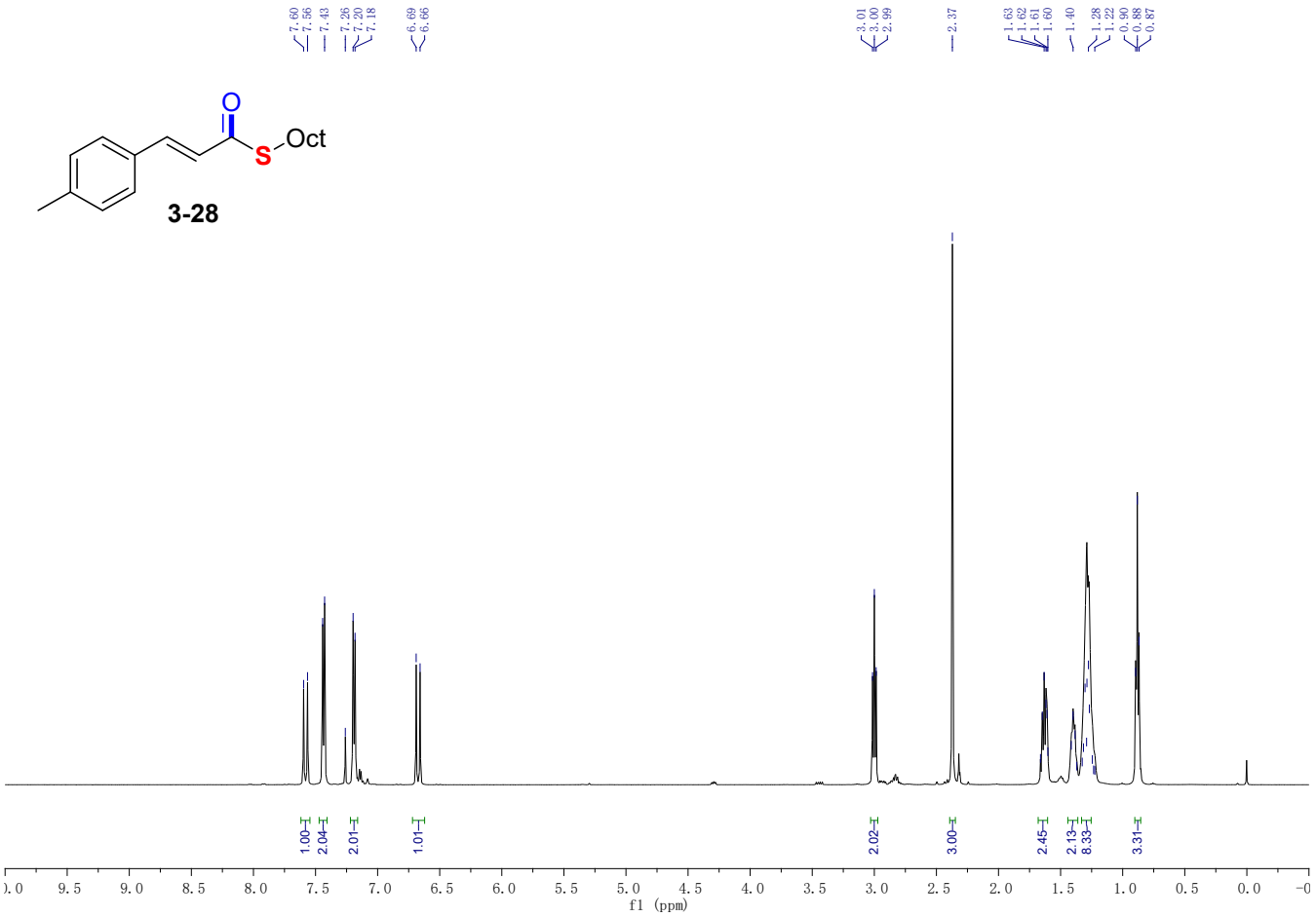
143.7
141.7
135.2
128.6
128.7
127.8
127.6
127.3
118.8
37.5
129.6
129.5
128.7
127.8
127.6
127.3
O
N
3-27
f1 (ppm)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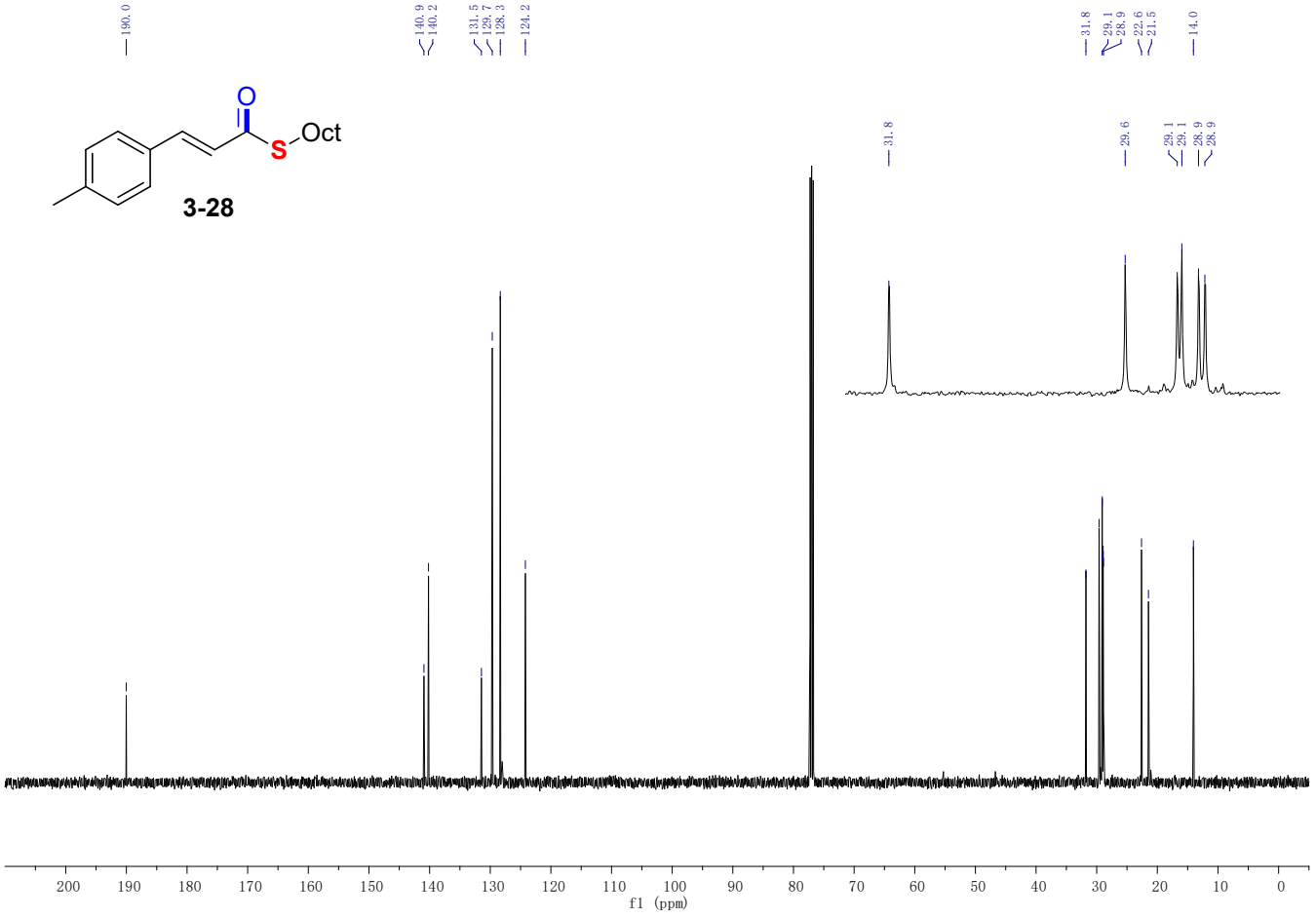
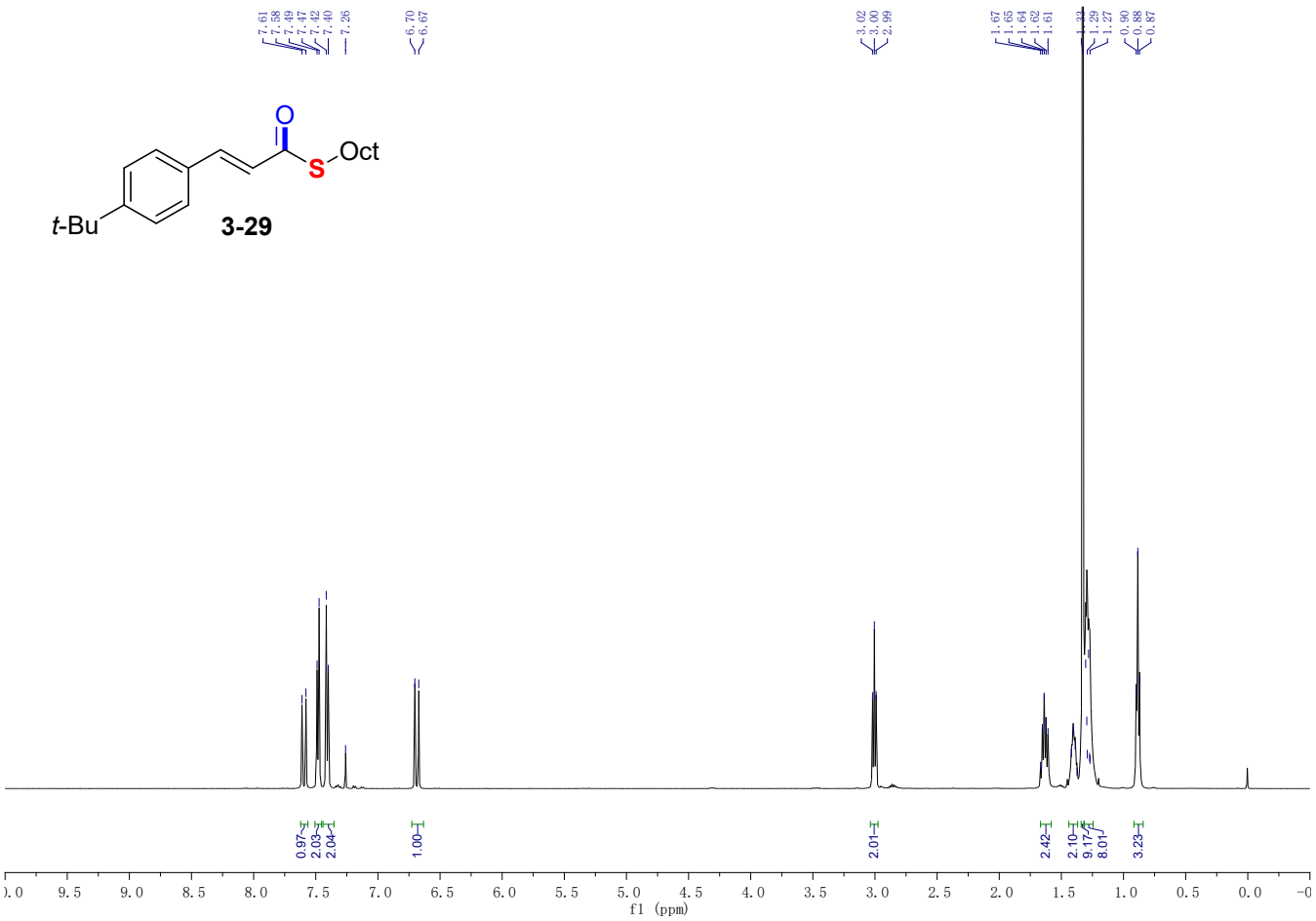
7.43
7.26
7.20
7.18
6.69
6.66
3.01
3.00
2.99
2.37
1.63
1.62
1.61
1.60
1.40
1.28
1.22
0.90
0.88
0.87
O
S
Oct
3-28
1.00
2.04
2.01
1.01
2.02
3.00
2.45
2.13
8.33
3.31
f1 (ppm)


190.0
140.9
140.2
131.5
129.7
128.3
124.2
31.8
29.1
28.9
22.6
21.5
14.0
O
S
Oct
3-28
31.8
29.6
29.1
29.1
28.9
28.9
f1 (ppm)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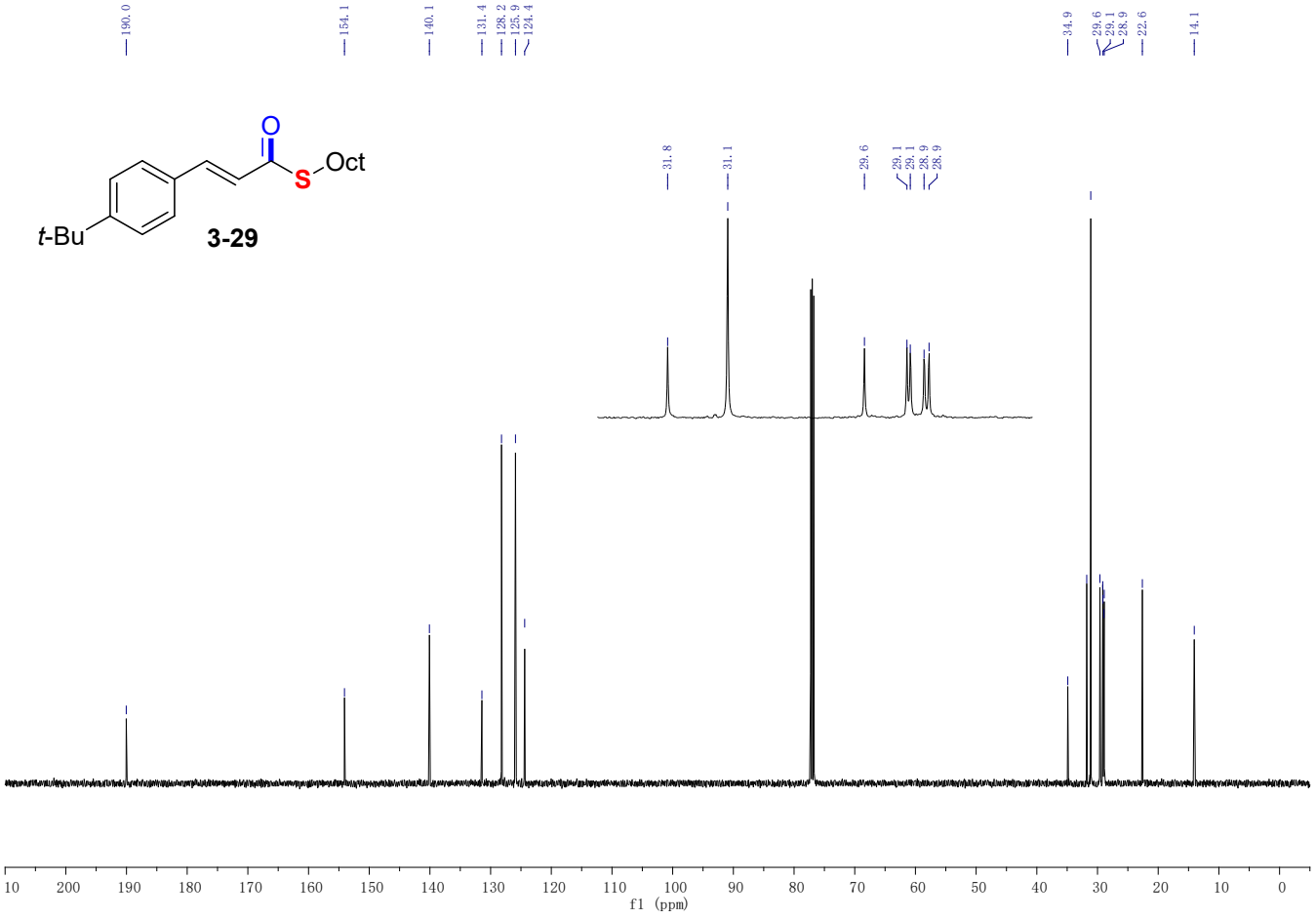
7.58
7.49
7.47
7.42
7.40
7.26
6.70
6.67
3.02
3.00
2.99
1.67
1.65
1.64
1.62
1.61
1.33
1.29
1.27
0.90
0.88
0.87
O
S
Oct
t-Bu
3-29
0.97
2.03
2.04
1.00
2.01
2.42
2.10
9.17
8.01
3.23
f1 (ppm)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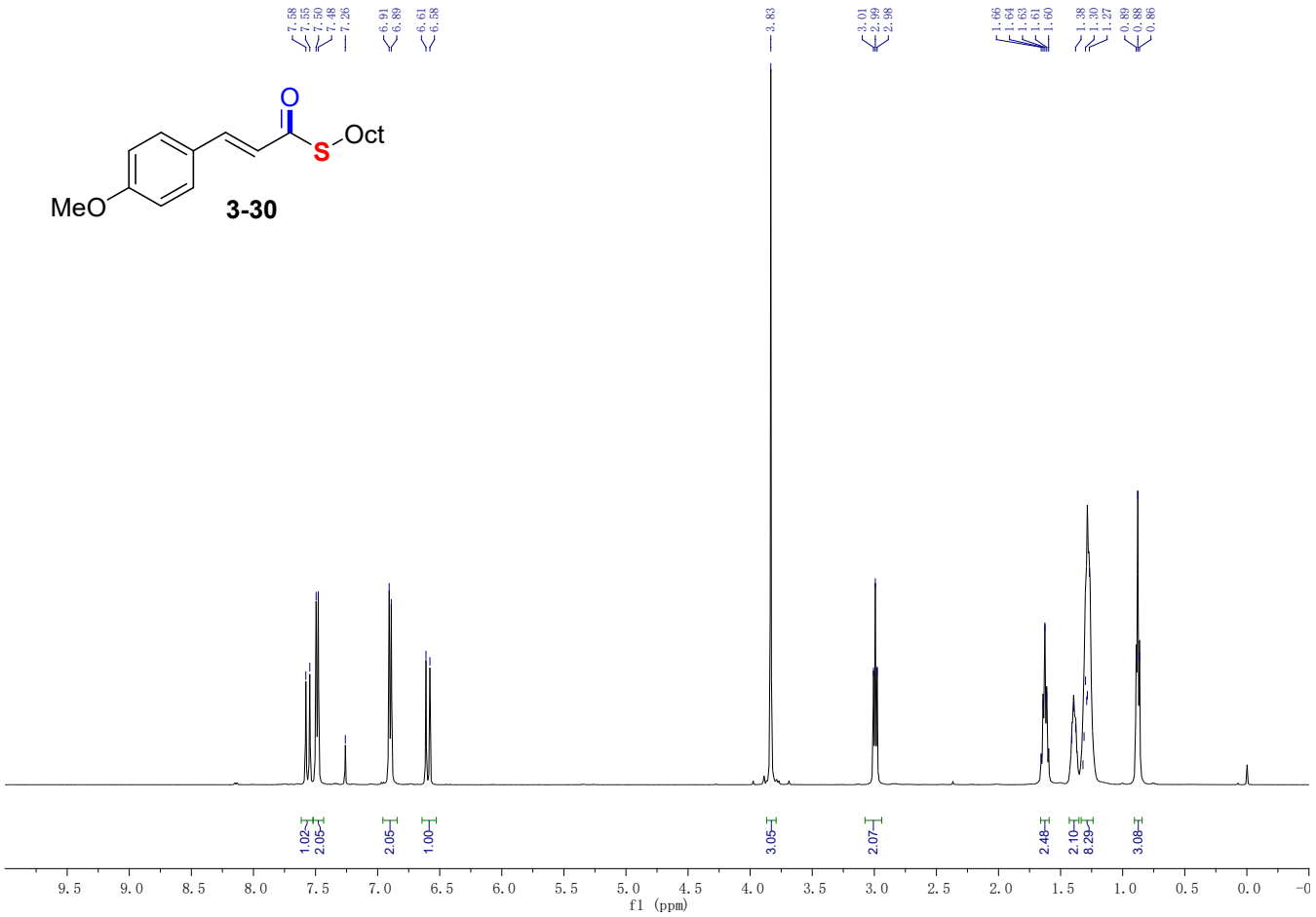
154.1
140.1
131.4
128.2
125.9
124.4
34.9
29.6
29.1
28.9
22.6
14.1
O
S
Oct
t-Bu
3-29
31.8
31.1
29.6
29.1
29.1
28.9
28.9
f1 (ppm)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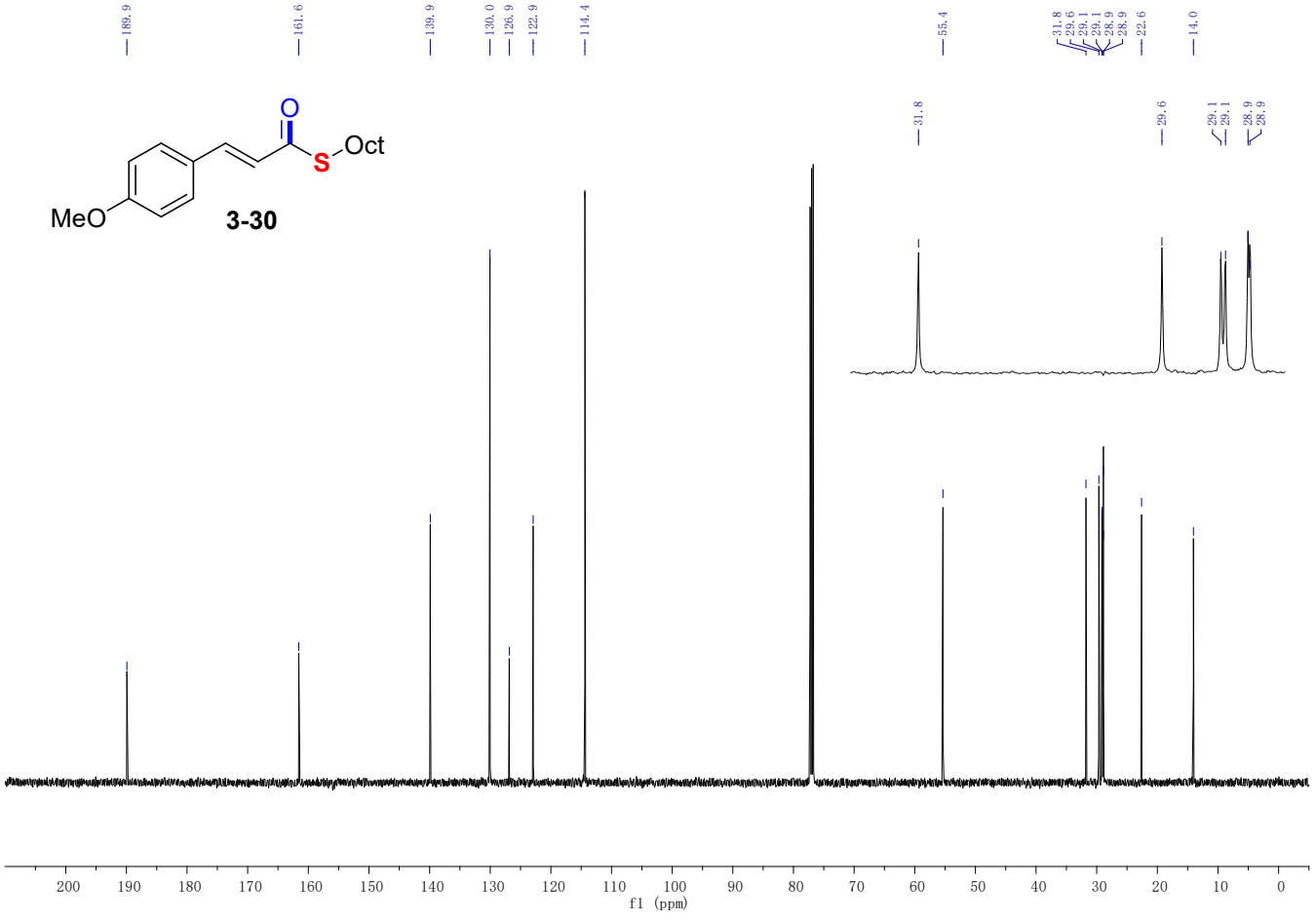
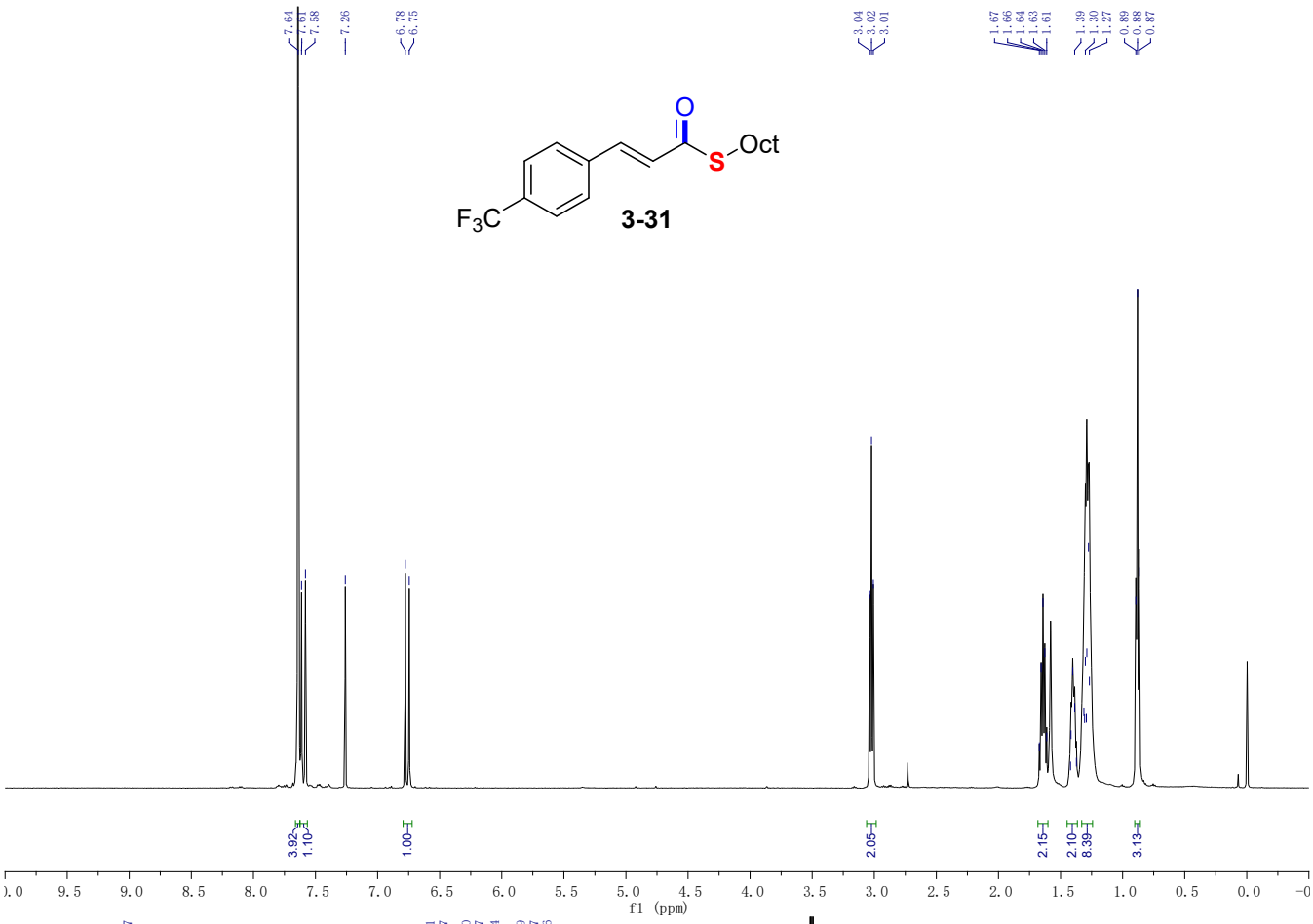
7.55
7.50
7.48
7.26
6.91
6.89
6.61
6.58
3.83
3.01
2.99
2.98
1.66
1.64
1.63
1.61
1.60
1.38
1.30
1.27
0.89
0.88
0.86
O
S
Oct
MeO
3-30
1.02
2.05
2.05
1.00
3.05
2.07
2.48
2.10
8.29
3.08
f1 (ppm)


189.9
161.6
139.9
130.0
126.9
122.9
114.4
55.4
31.8
29.6
29.1
29.1
28.9
28.9
22.6
14.0
O
S
Oct
MeO
3-30
f1 (ppm)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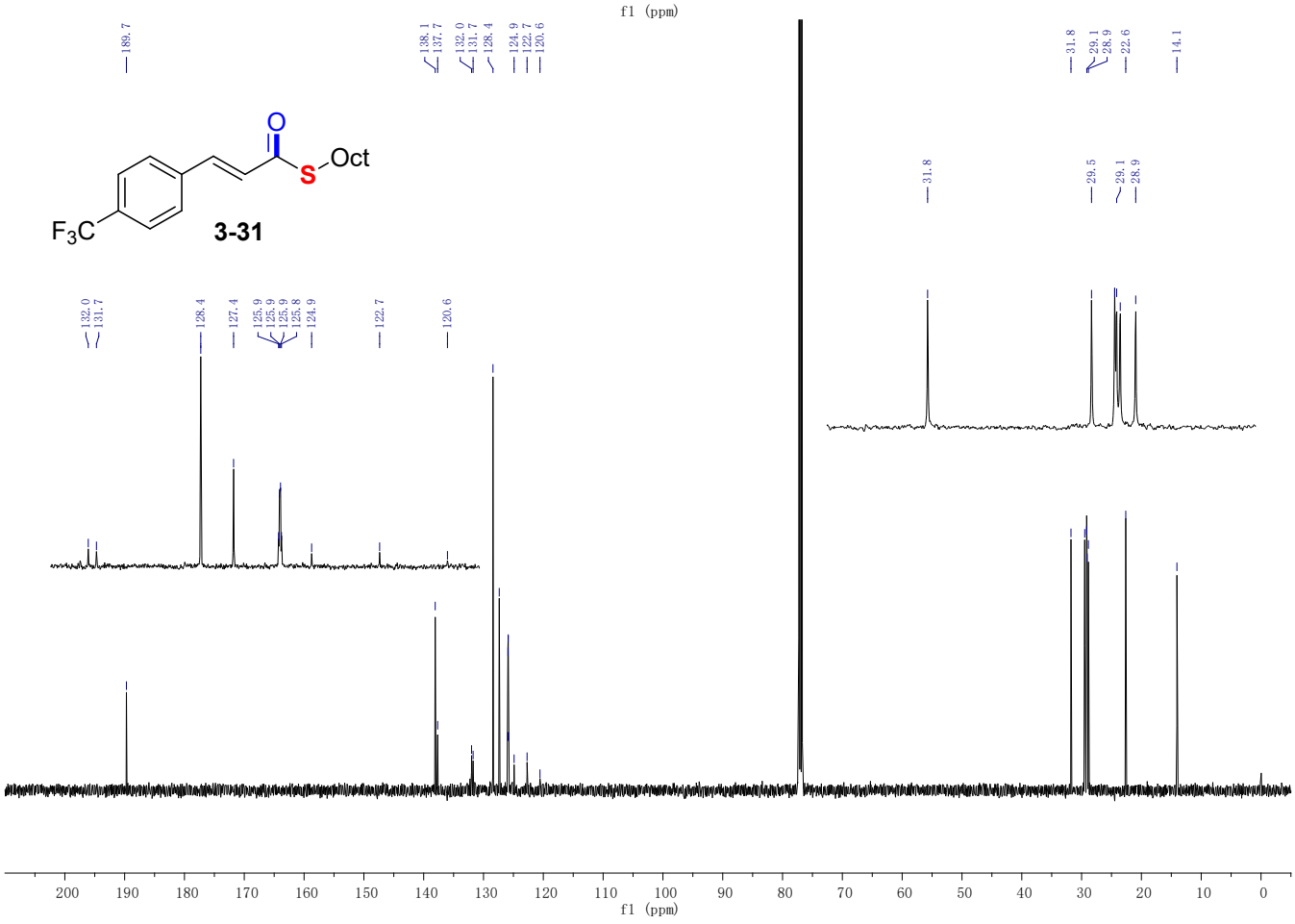
7.61
7.58
7.26
6.78
6.75
3.04
3.02
3.01
1.67
1.66
1.64
1.63
1.61
1.39
1.30
1.27
0.89
0.88
0.87
O
S
Oct
F3C
3-31
3.92
1.10
1.00
2.05
2.15
2.10
8.39
3.13
f1 (ppm)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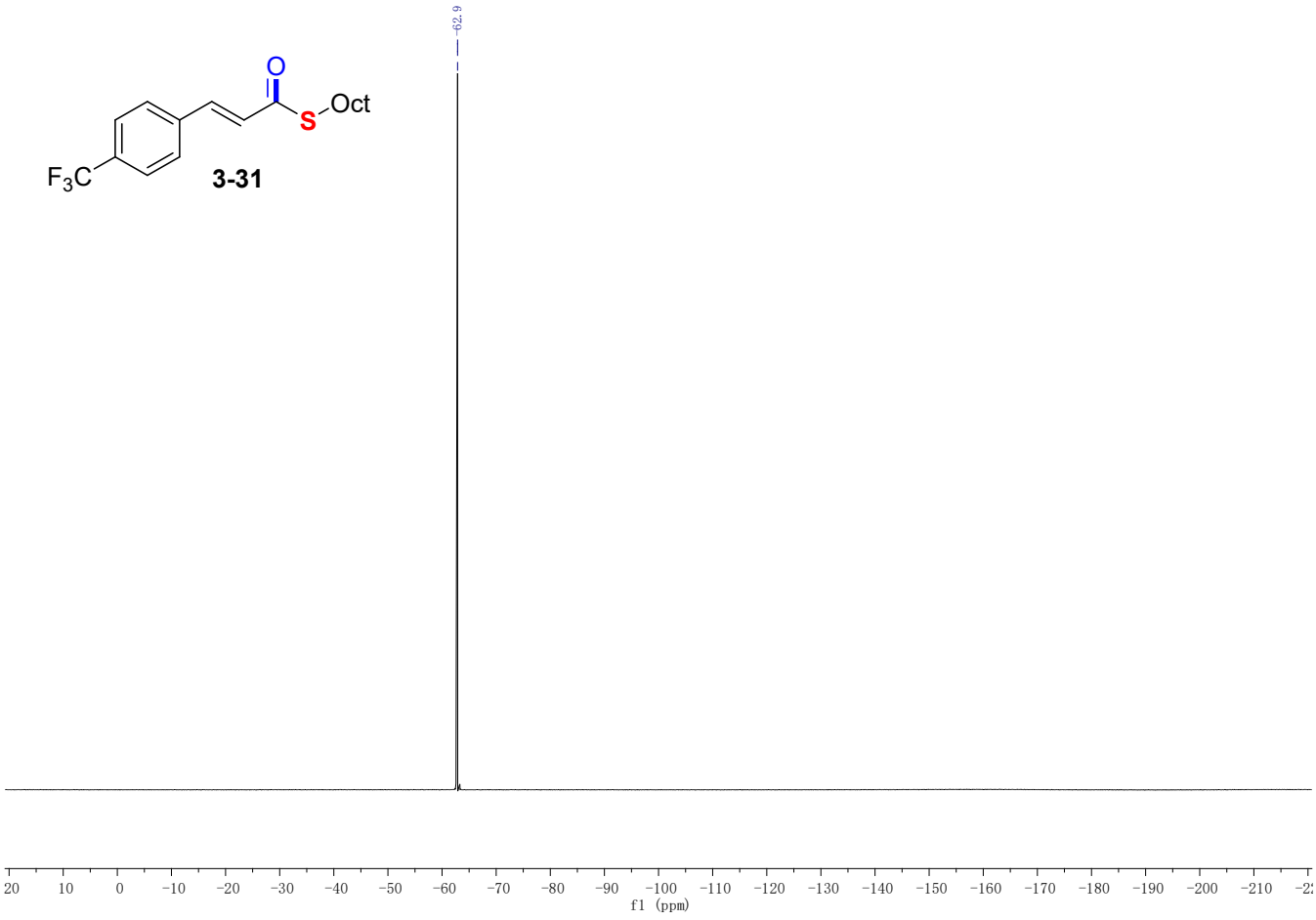
138.1
137.7
132.0
131.7
128.4
124.9
122.7
120.6
31.8
29.1
28.9
22.6
14.1
O
S
Oct
F3C
3-31
31.8
29.5
29.1
28.9
132.0
131.7
128.4
127.4
125.9
125.9
125.9
125.8
124.9
122.7
120.6
f1 (ppm)


-62.9
O
S
Oct
F3C
3-31
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
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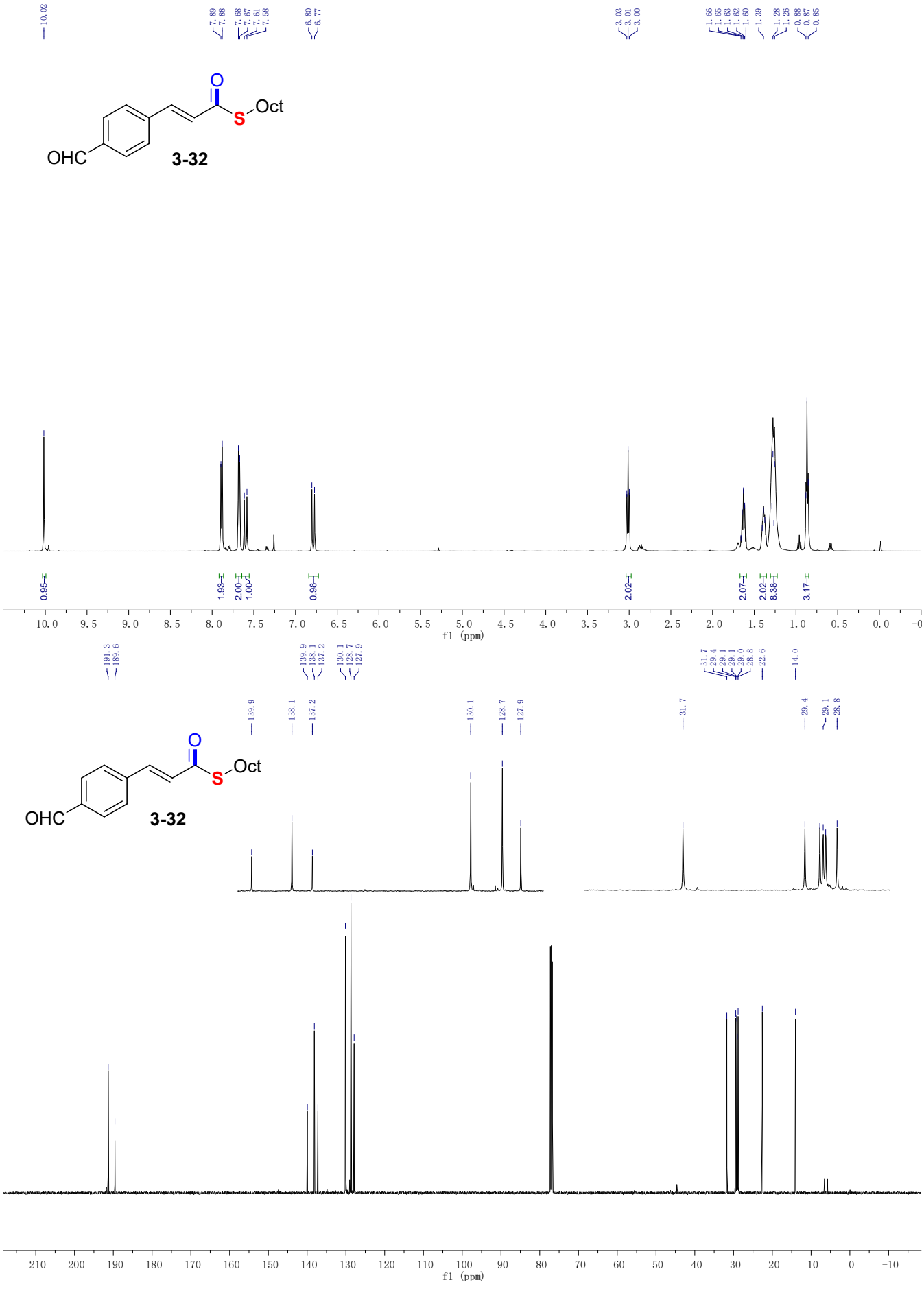
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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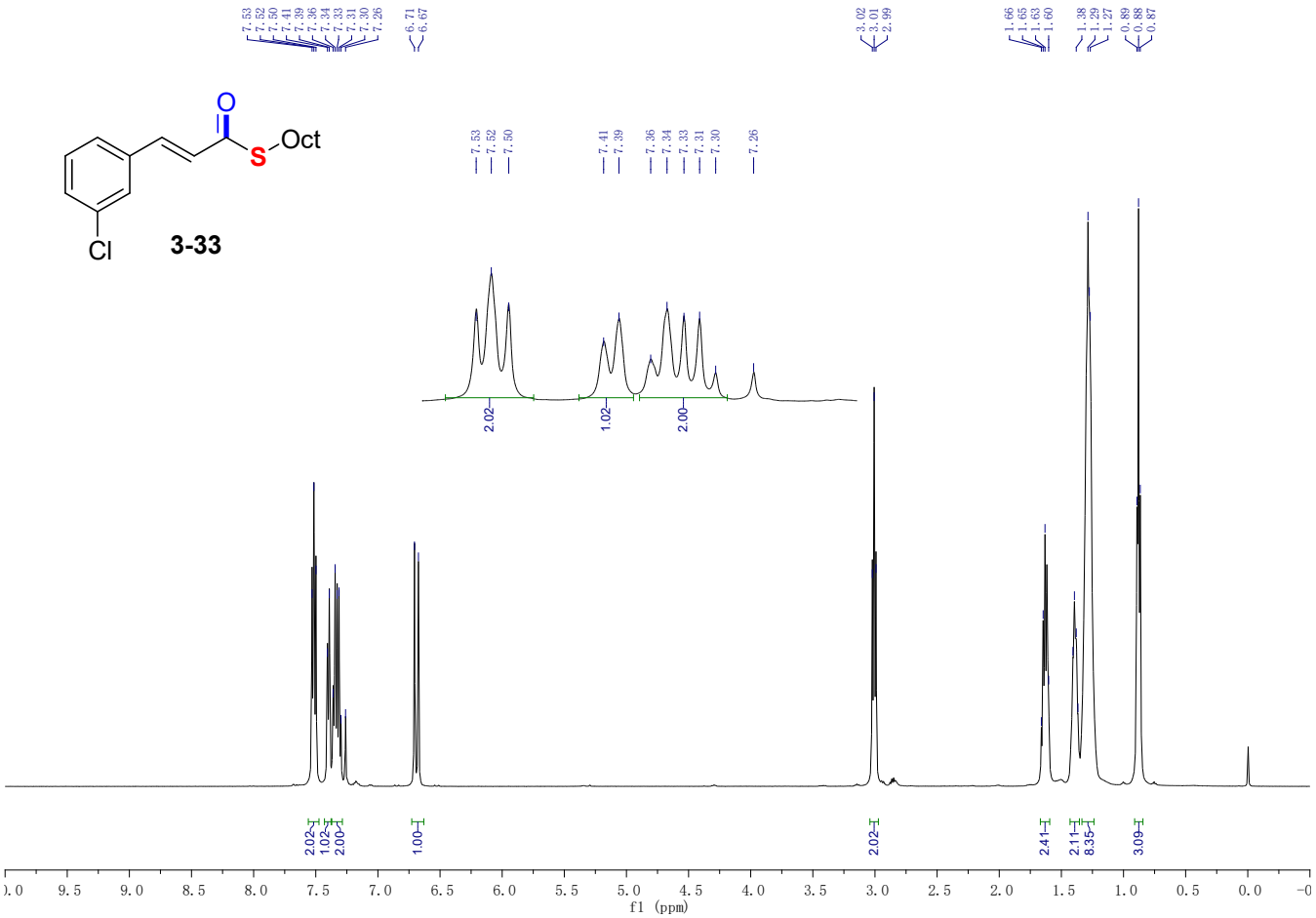
7.89
7.88
7.68
7.67
7.61
7.58
6.80
6.77
3.03
3.01
3.00
1.66
1.65
1.63
1.62
1.60
1.39
1.28
1.26
0.88
0.87
0.85
O
S
Oct
OHC
3-32
0.95
1.93
2.00
1.00
0.98
2.02
2.07
2.02
8.38
3.17
f1 (ppm)
191.3
189.6
139.9
138.1
137.2
130.1
128.7
127.9
31.7
29.4
29.1
29.0
28.8
22.6
14.0
f1 (ppm)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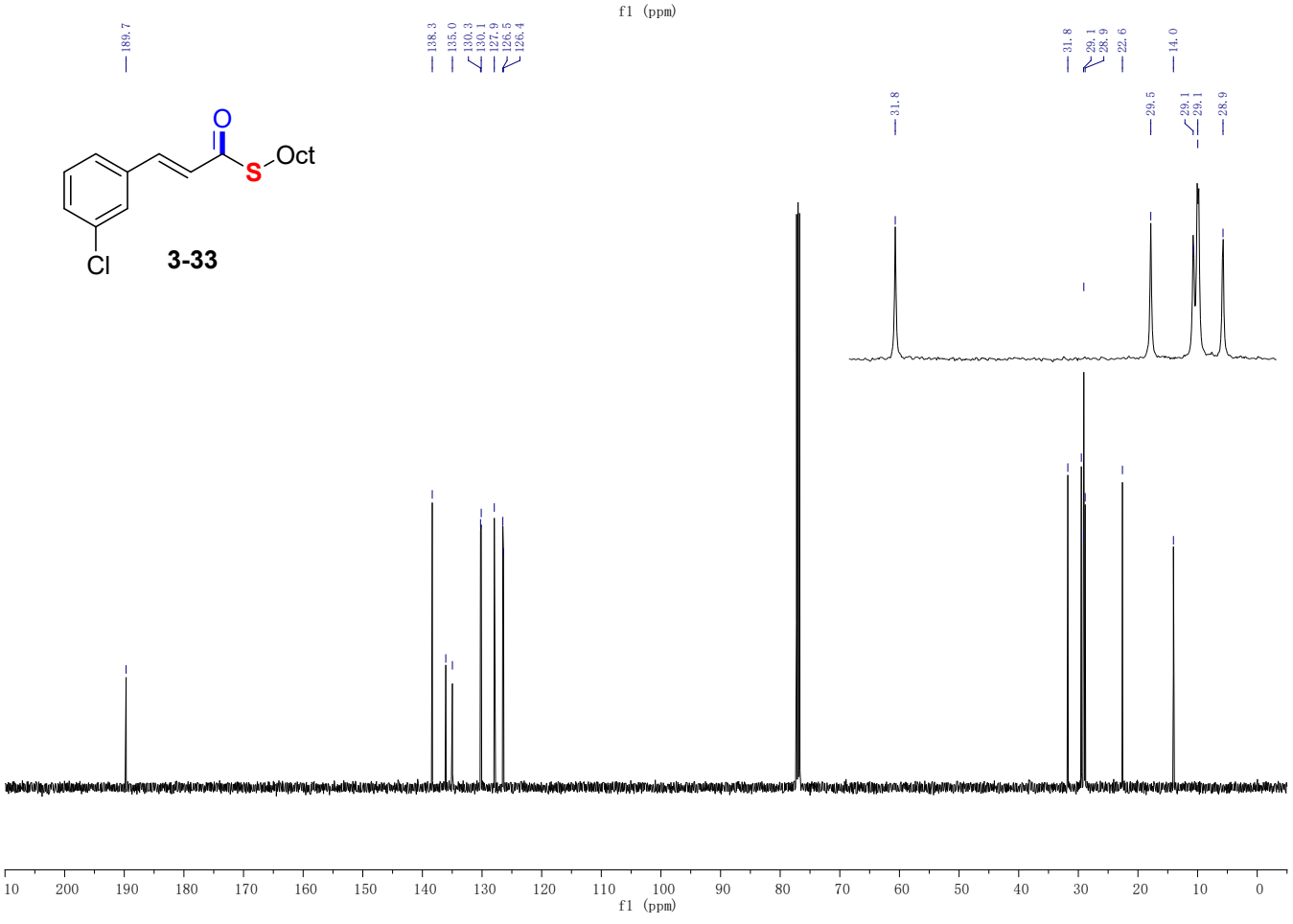
7.52
7.50
7.41
7.39
7.36
7.34
7.33
7.31
7.30
7.26
6.71
6.67
3.02
3.01
2.99
1.66
1.65
1.63
1.60
1.38
1.29
1.27
0.89
0.88
0.87
O
S
Oct
Cl
3-33
2.02
1.02
2.00
1.00
2.02
2.41
2.11
8.35
3.09
f1 (ppm)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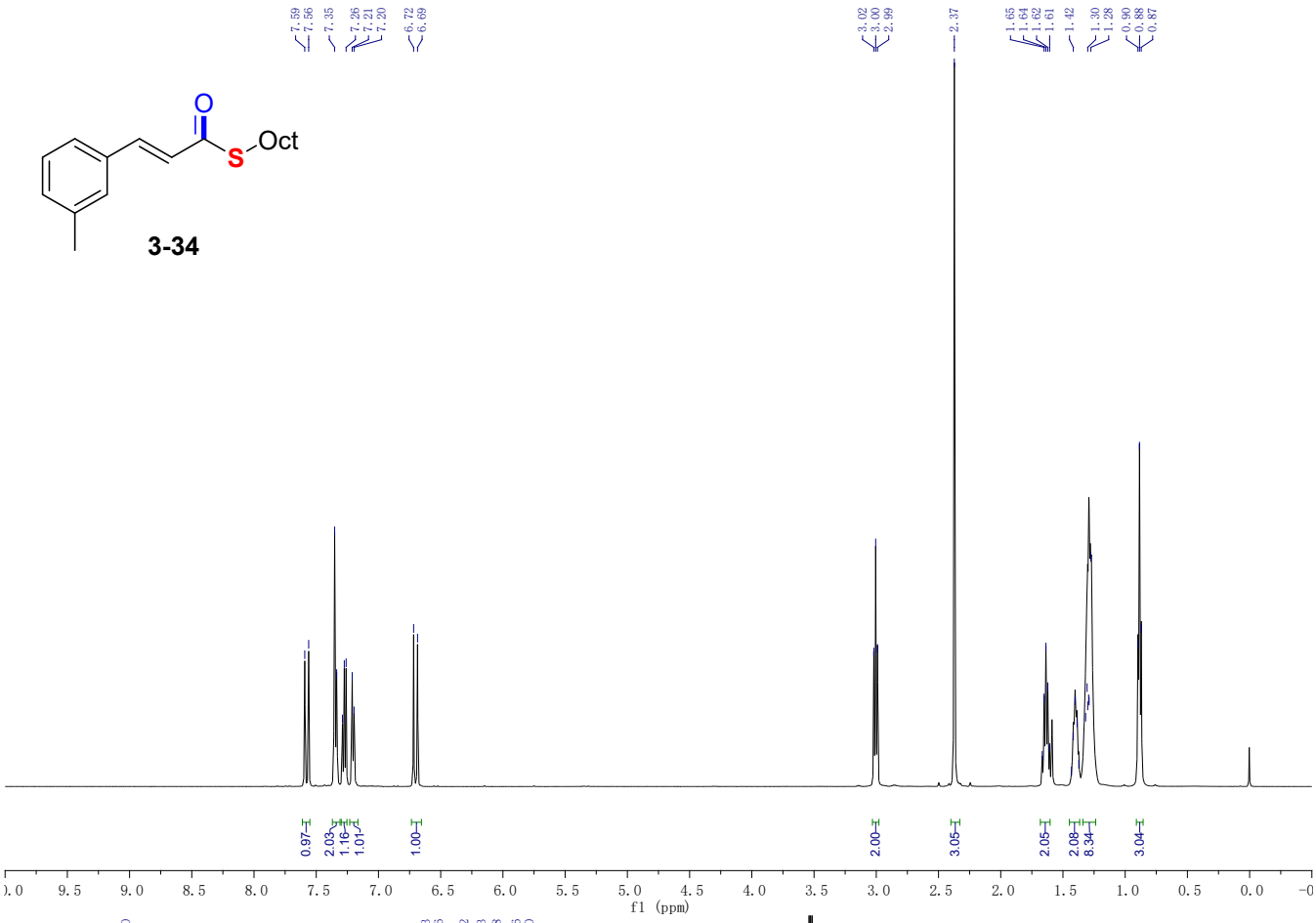
138.3
135.0
130.3
130.1
127.9
126.5
126.4
31.8
29.1
28.9
22.6
14.0
29.5
O
S
Oct
Cl
3-33
f1 (ppm)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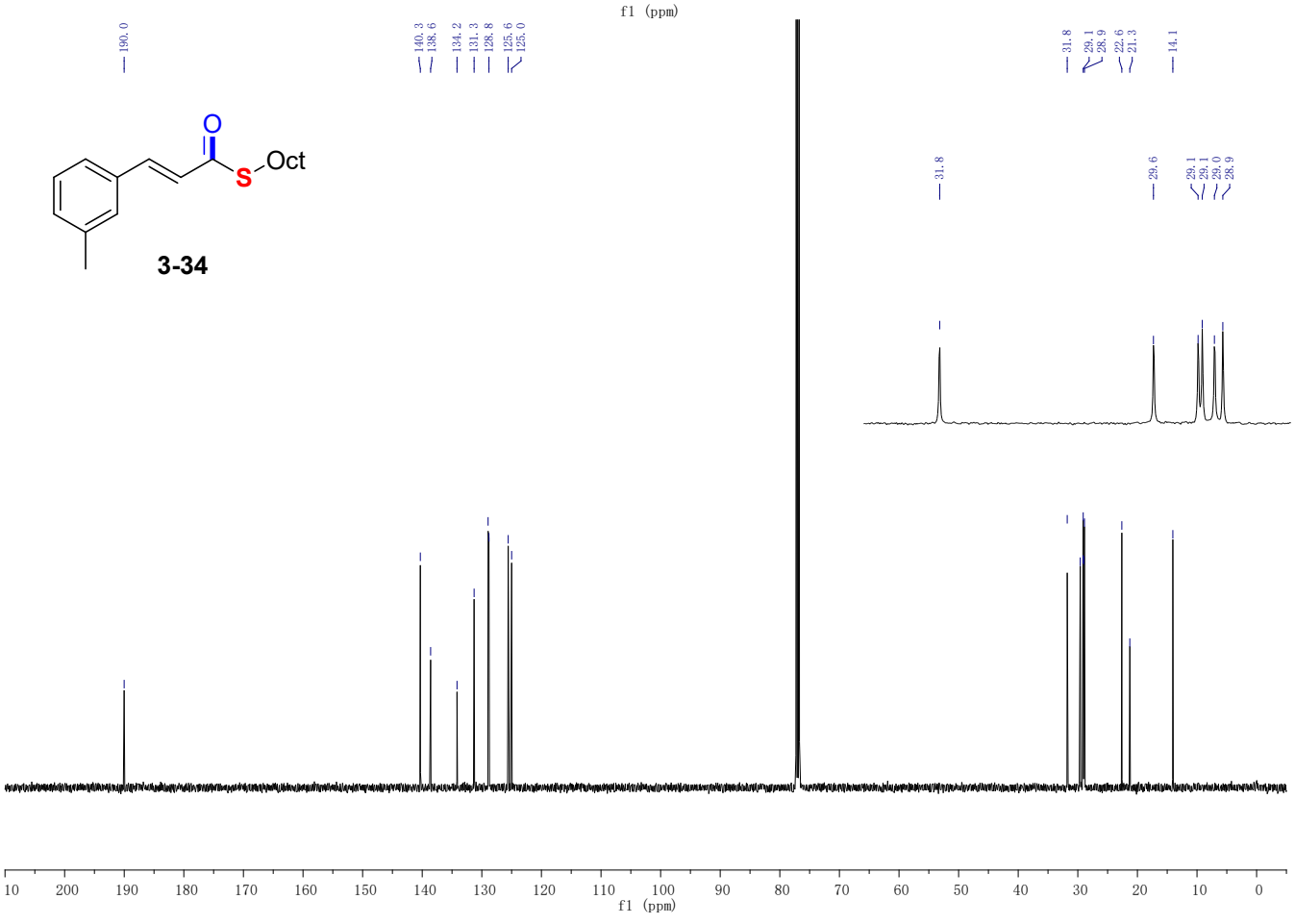
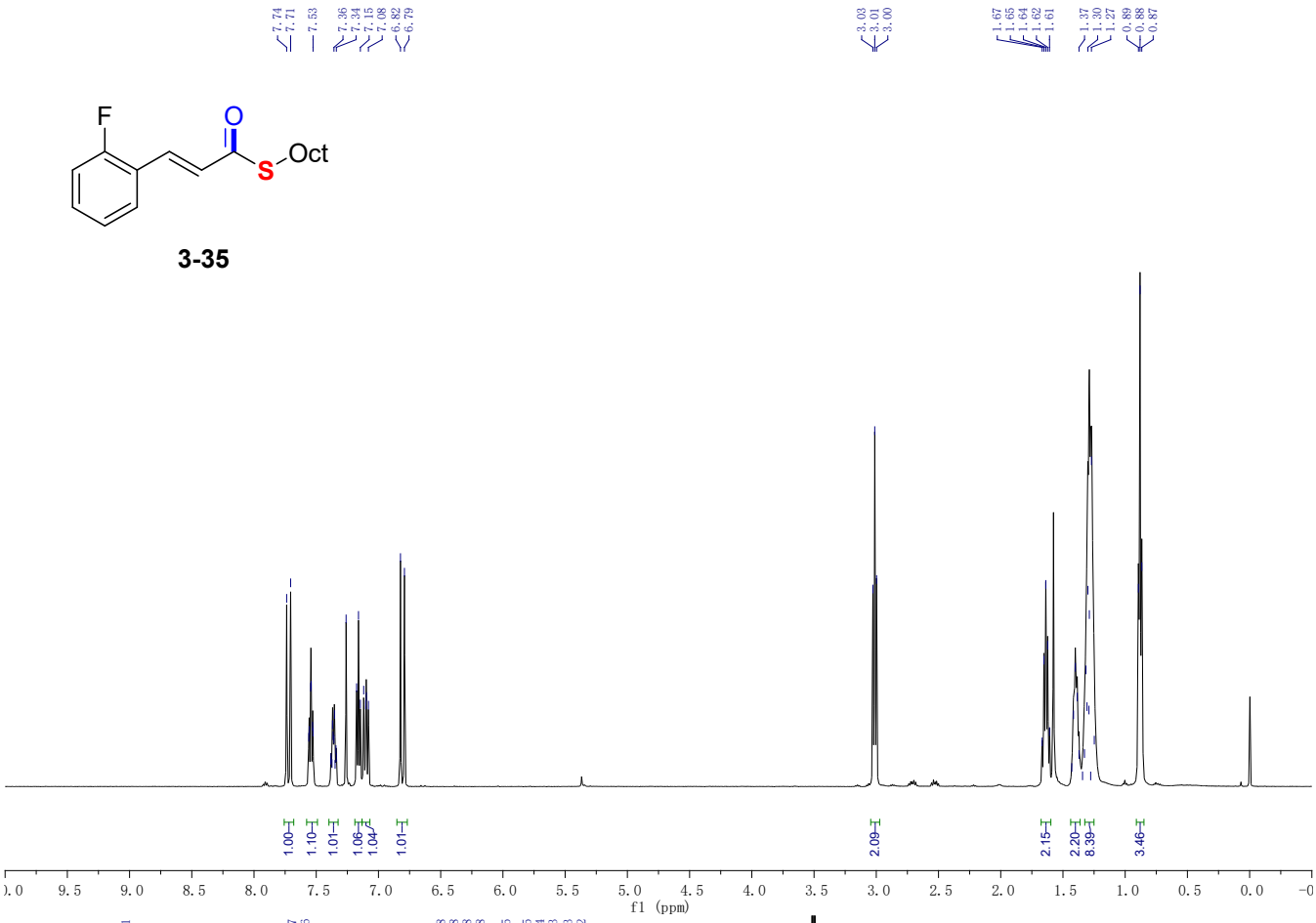
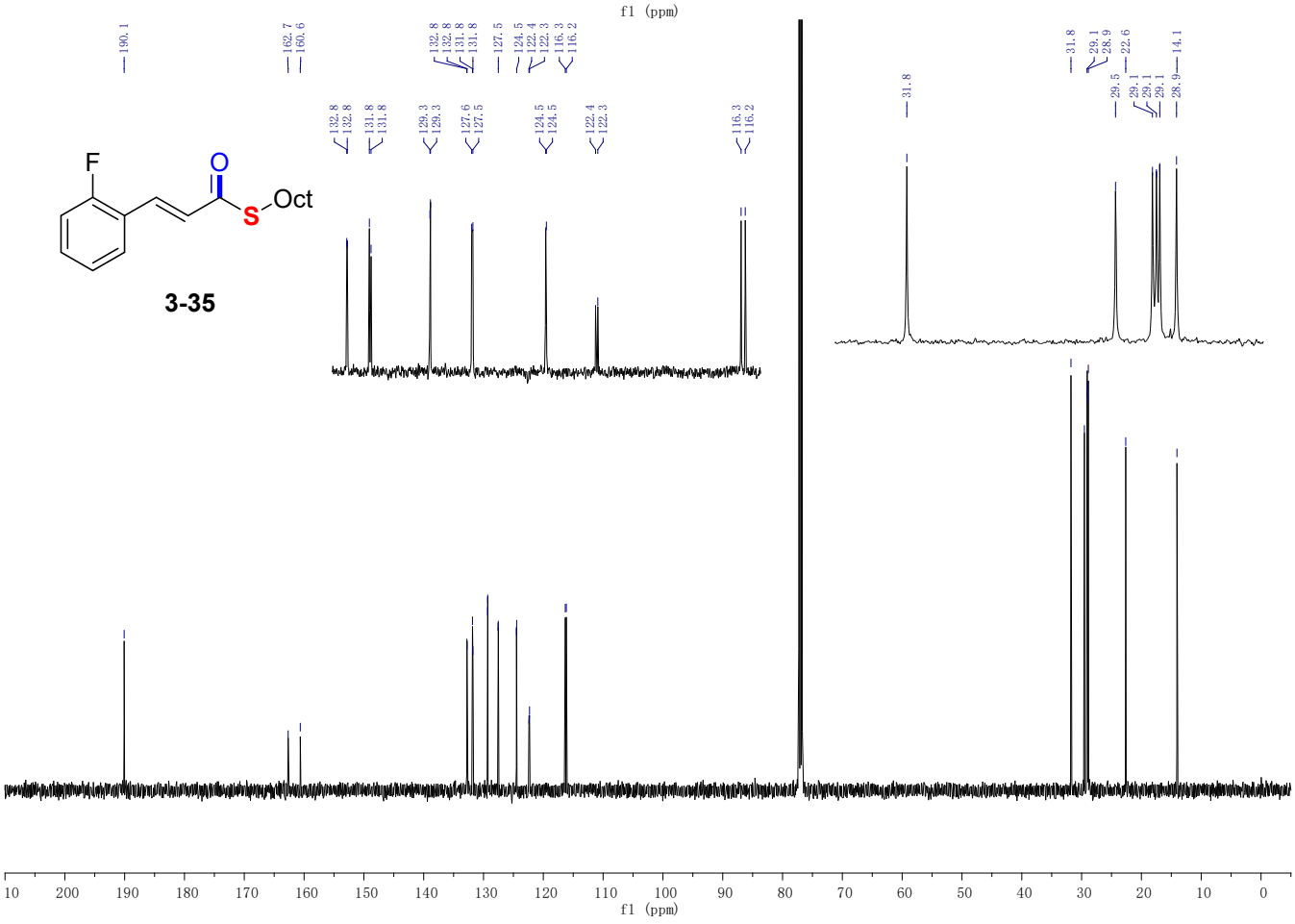
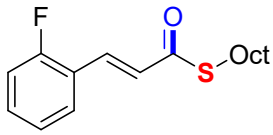
7.26
7.21
7.20
6.72
6.69
3.02
3.00
2.99
2.37
1.65
1.64
1.62
1.61
1.42
1.30
1.28
0.90
0.88
0.87
O
S
Oct
3-34
0.97
2.03
1.16
1.01
1.00
2.00
3.05
2.05
2.08
8.34
3.04
f1 (ppm)


190.0
140.3
138.6
134.2
131.3
128.8
125.6
125.0
31.8
29.1
28.9
22.6
21.3
14.1
O
S
Oct
3-34
f1 (ppm)

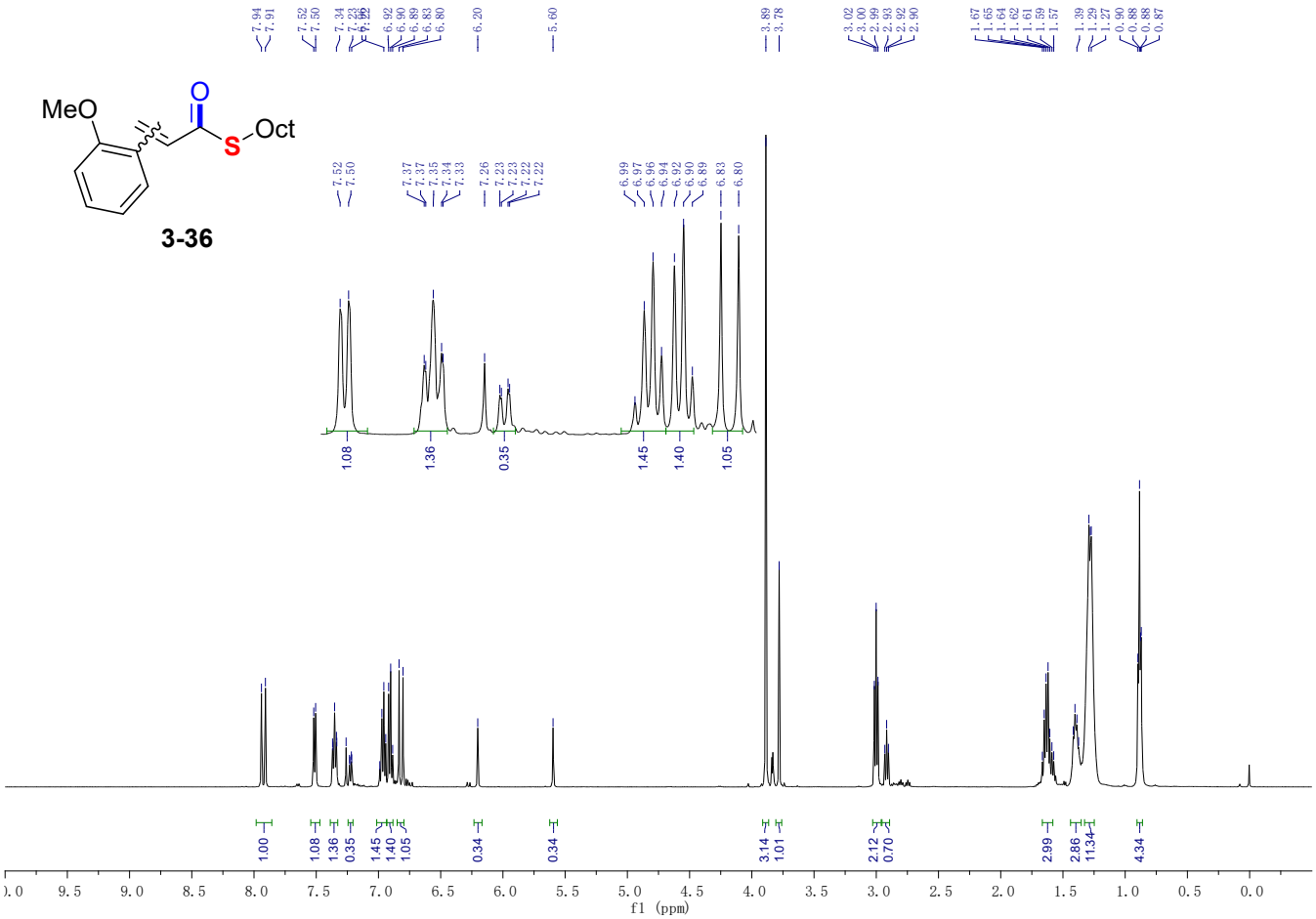

F
O
S
Oct
3-35
f1 (ppm)

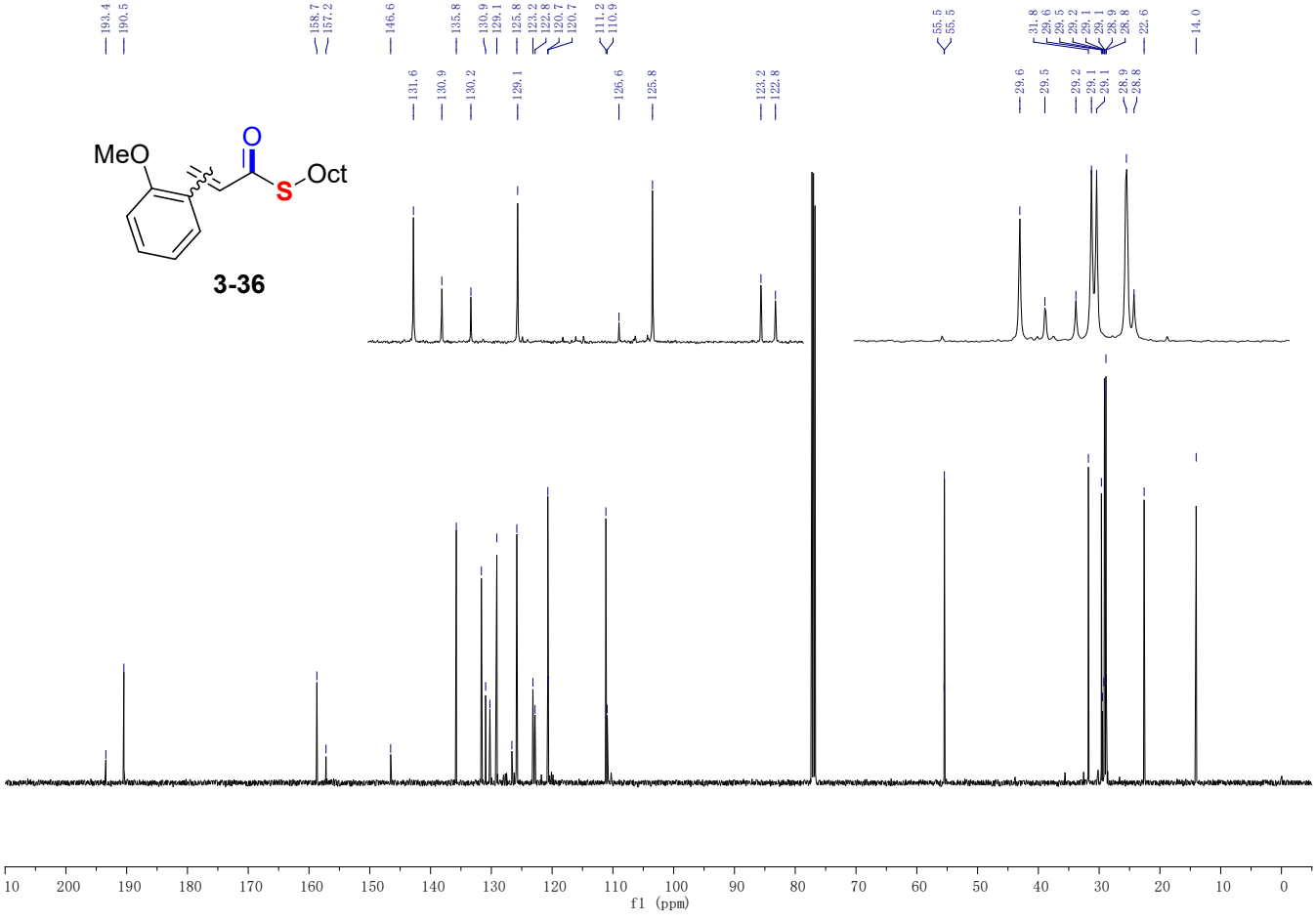

F
O
S
Oct
3-35
f1 (ppm)

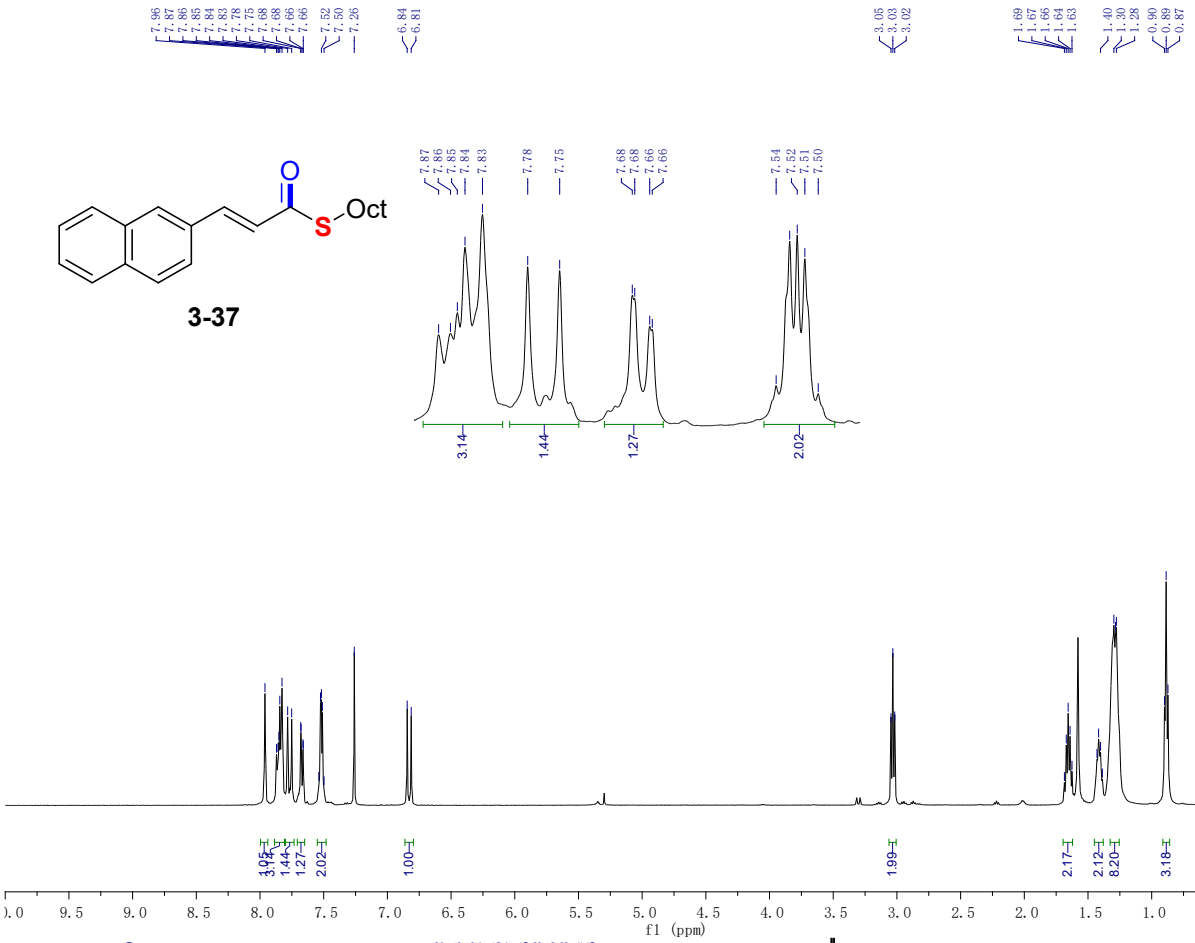

F
O
S
Oct

3-35

-113.8
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


MeO
O
S
Oct
3-36
f1 (ppm)


MeO
O
S
Oct
3-36
f1 (ppm)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7.75
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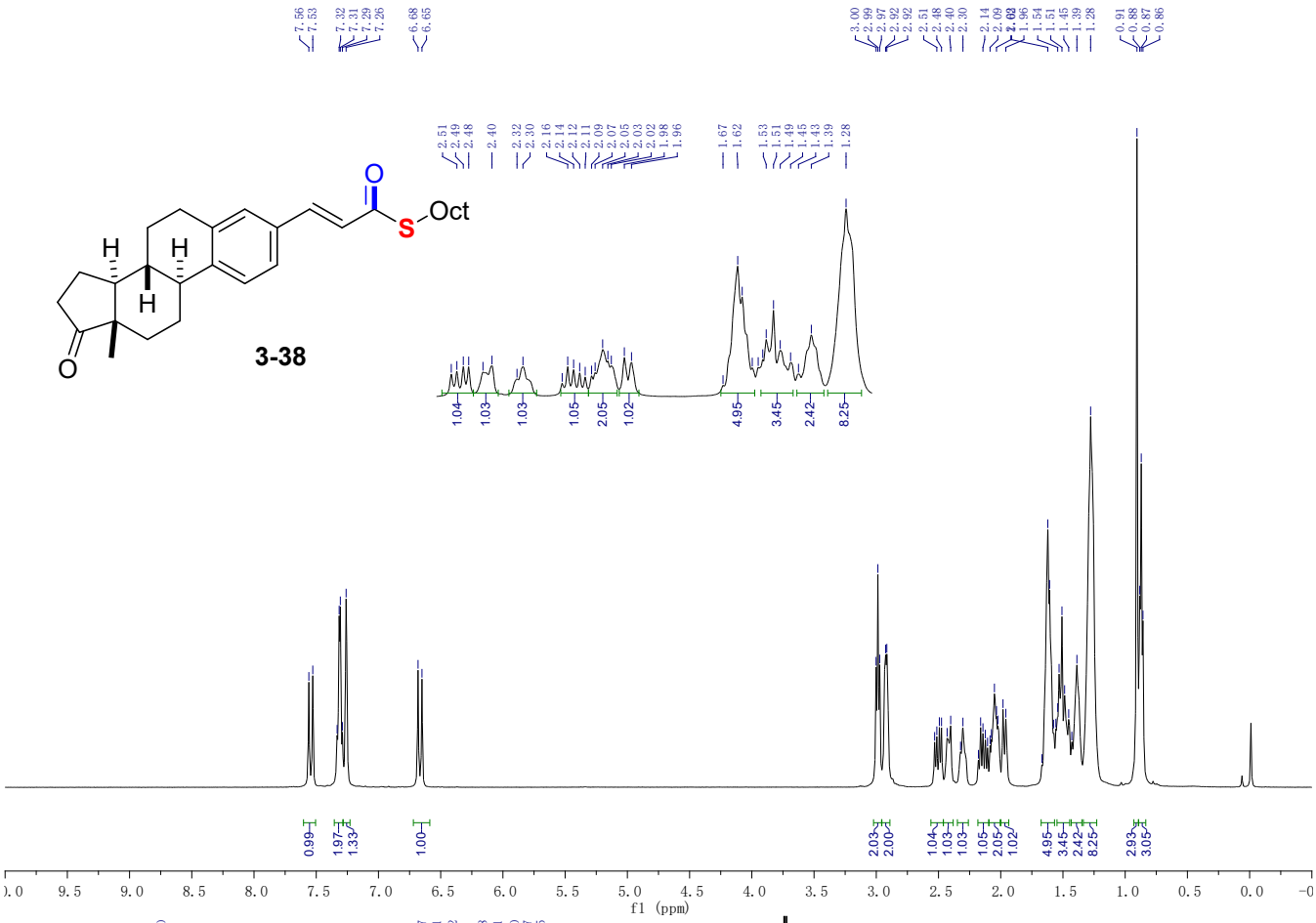
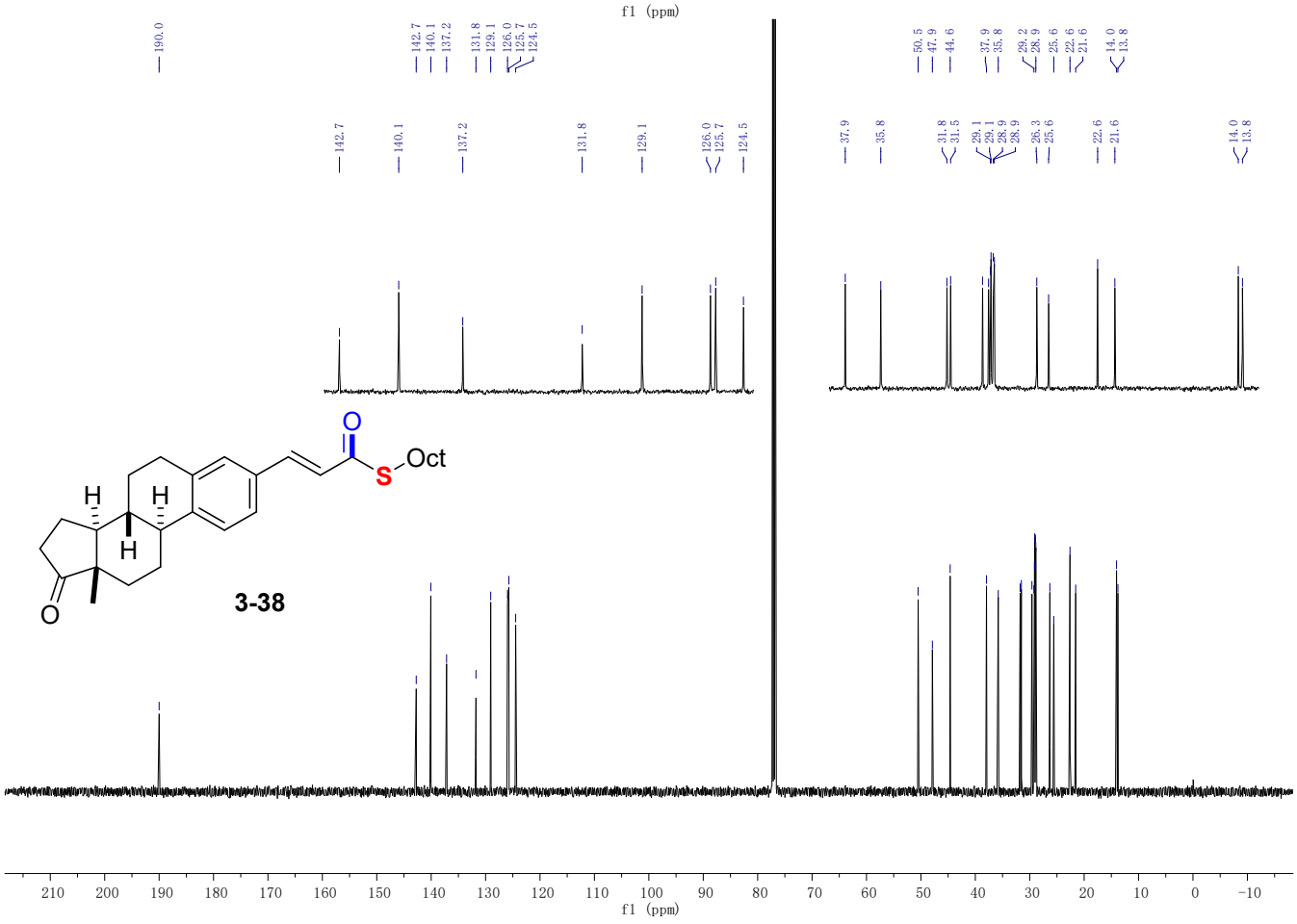
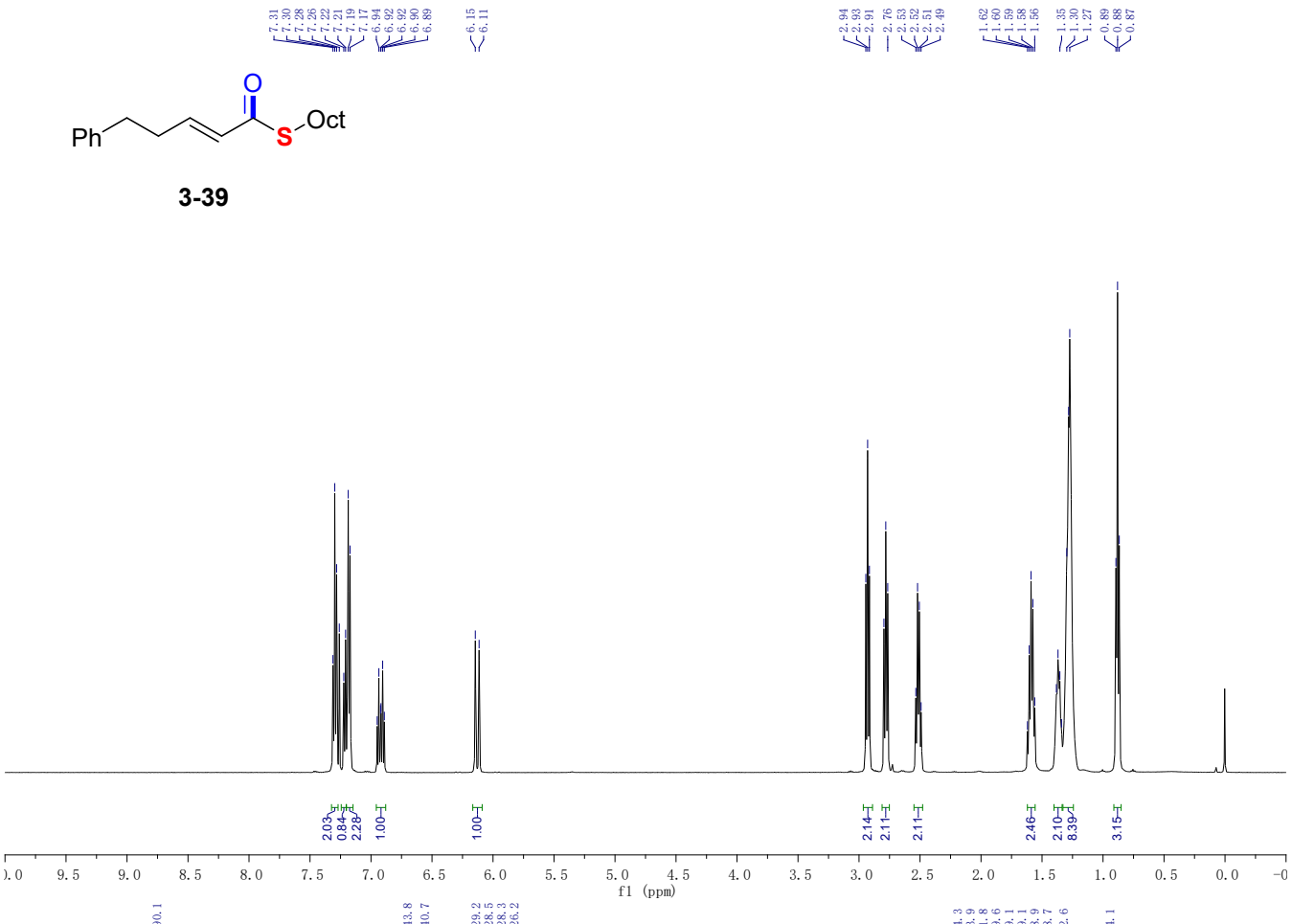
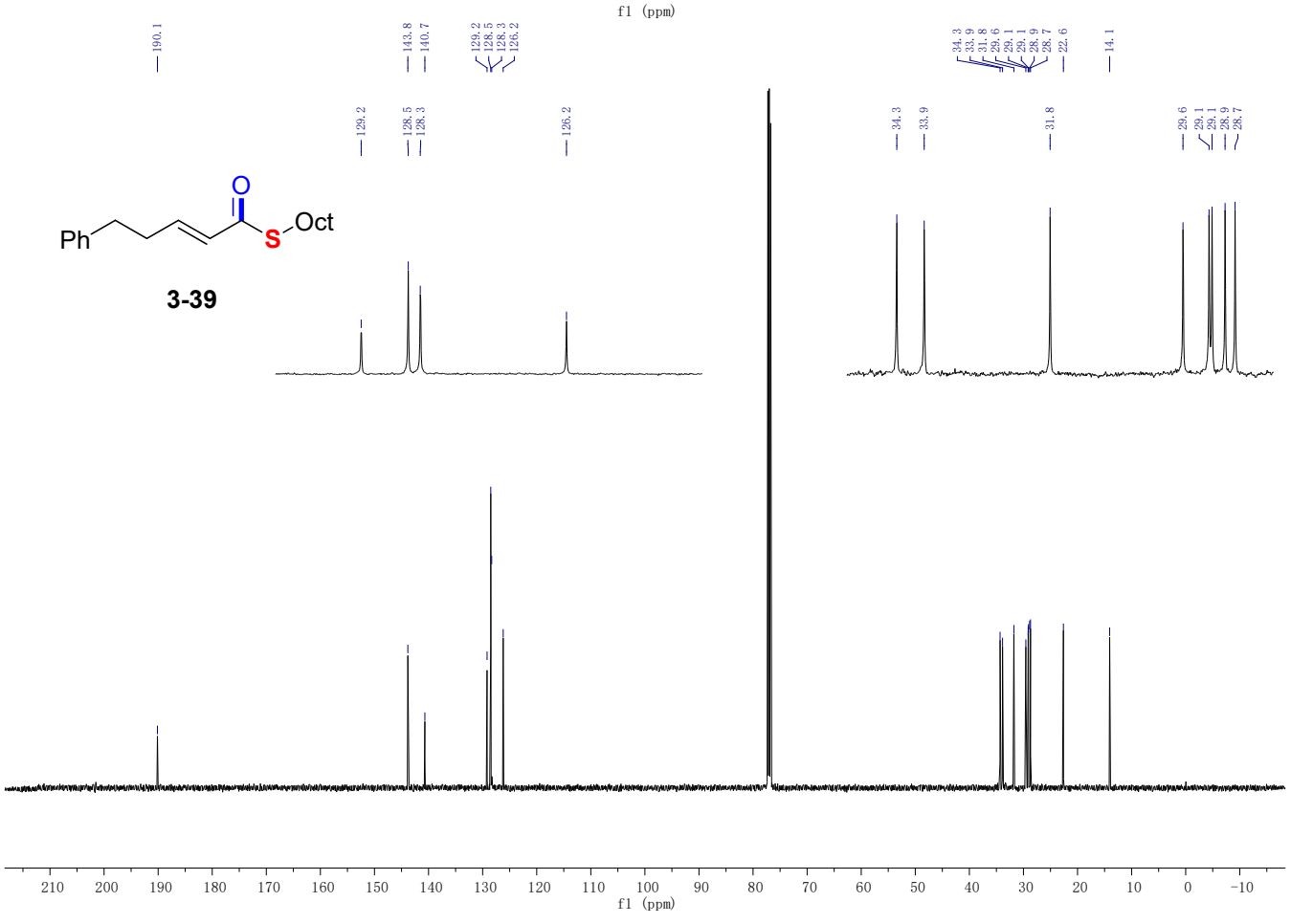
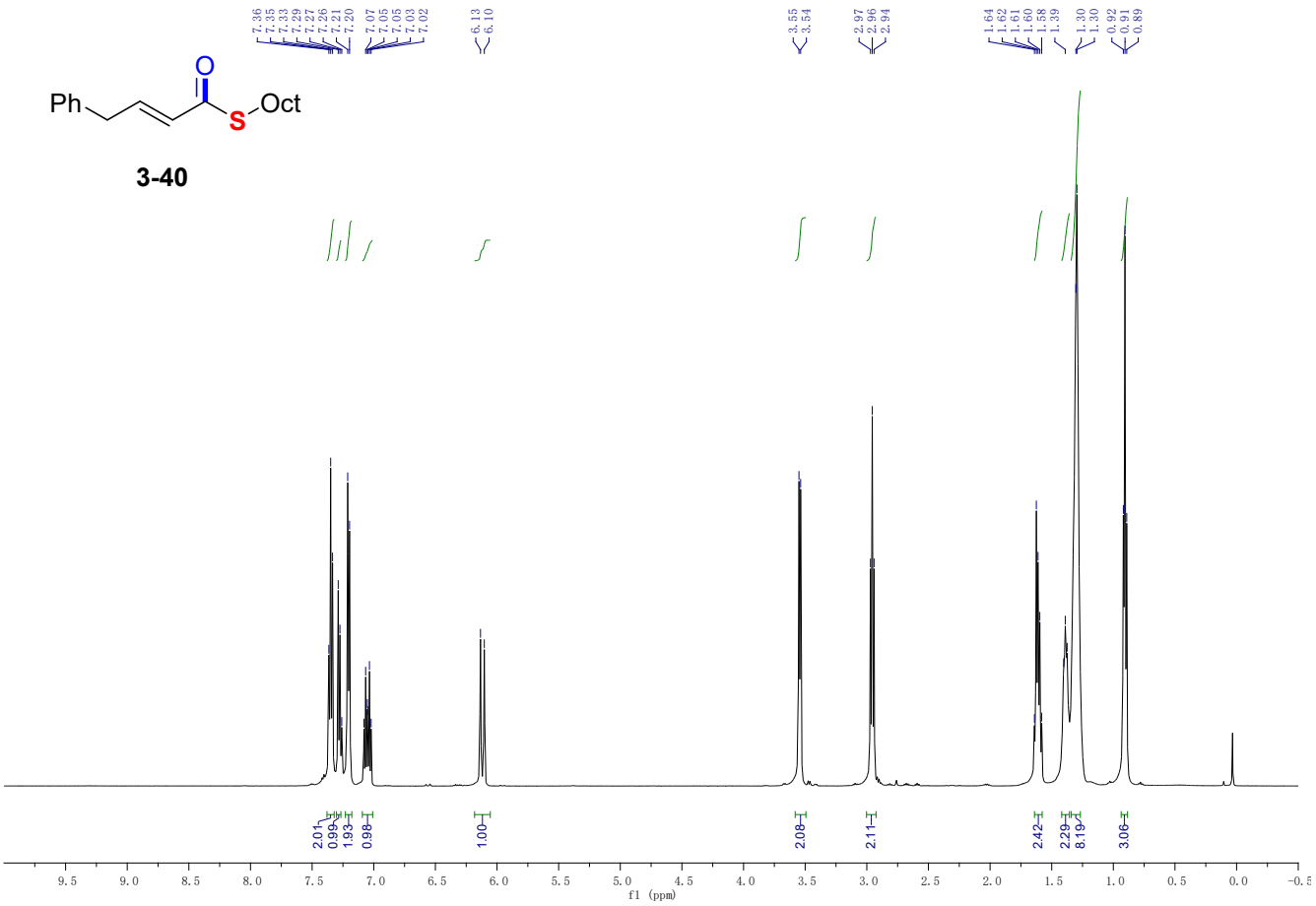
7.68
7.66
7.66
7.52
7.50
7.26
6.84
6.81
3.05
3.03
3.02
1.69
1.67
1.66
1.64
1.63
1.40
1.30
1.28
0.90
0.89
0.87
O
S
Oct
3-37
3.14
1.44
1.27
2.02
1.00
1.99
2.17
2.12
8.20
3.18
f1 (ppm)
190.0
140.2
134.3
133.3
131.7
130.5
128.7
128.6
127.8
127.3
126.8
125.4
123.6
31.8
29.1
28.9
22.6
14.1
29.6
29.1
29.1
29.0
28.9
O
S
Oct
3-37
f1 (ppm)


3-38
f1 (ppm)


3-38
f1 (ppm)


Ph
O
S
Oct
3-39
f1 (ppm)


Ph
O
S
Oct
3-39
f1 (ppm)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7.35
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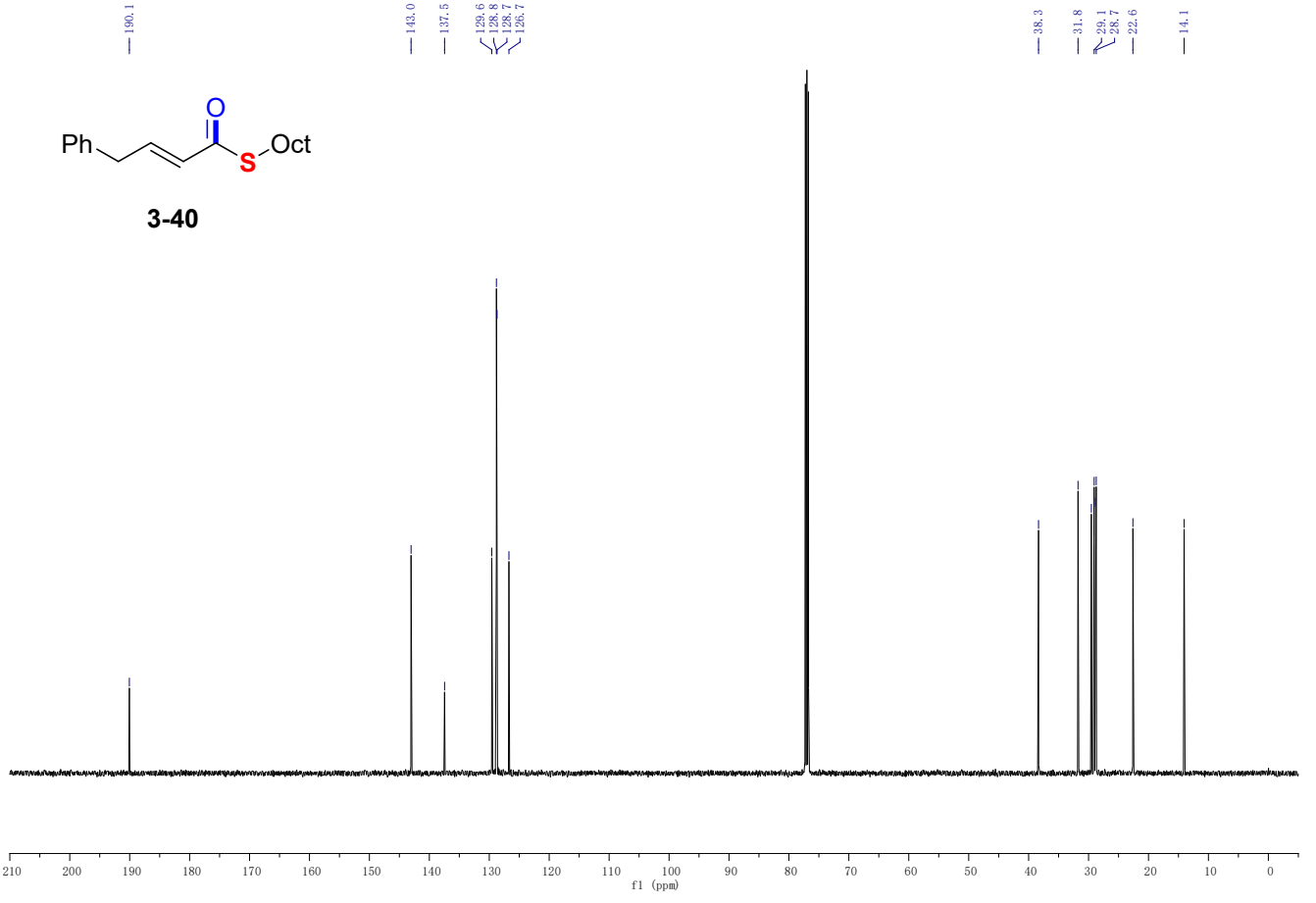
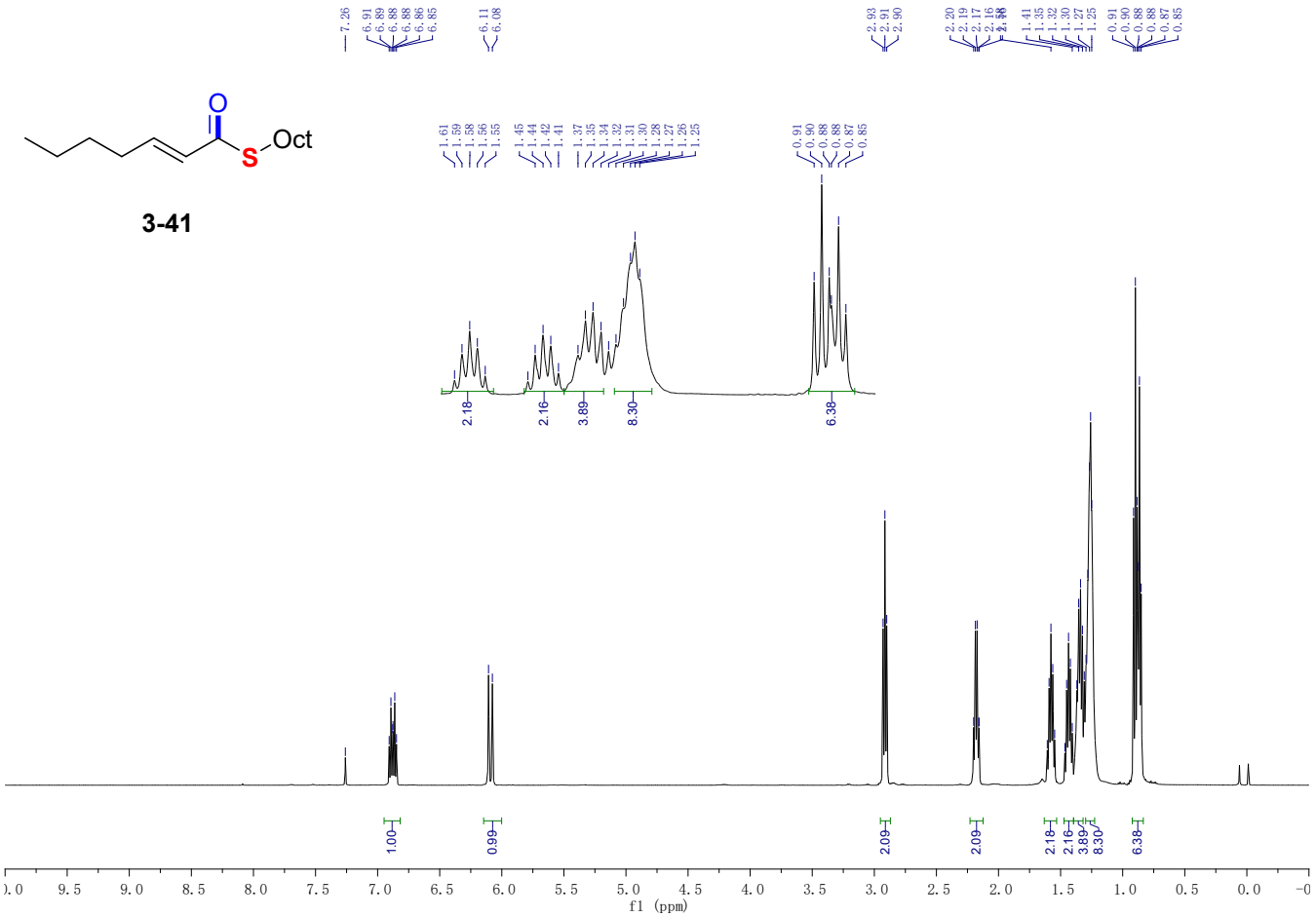
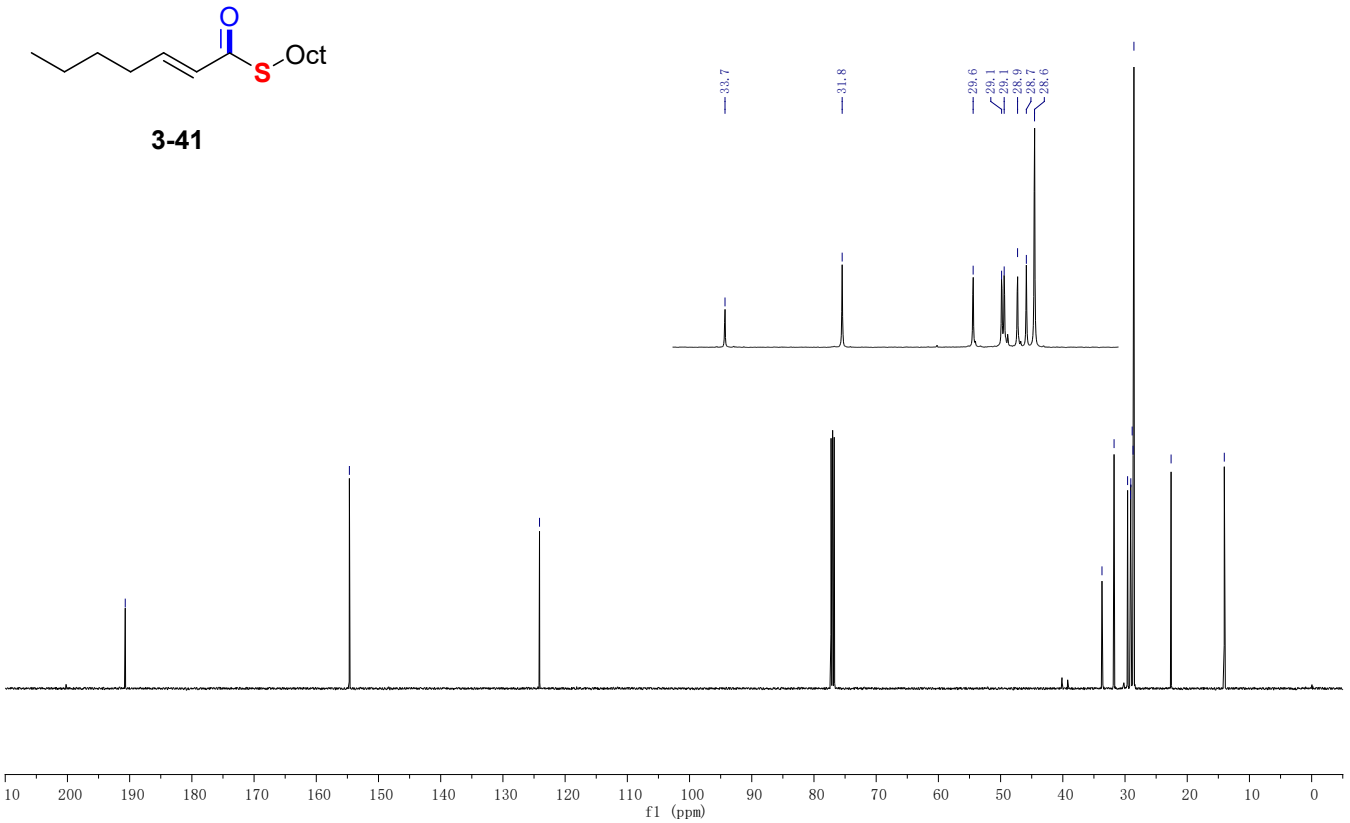
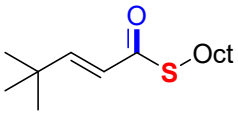
7.29
7.27
7.26
7.21
7.20
7.07
7.05
7.05
7.03
7.02
6.13
6.10
3.55
3.54
2.97
2.96
2.94
1.64
1.62
1.61
1.60
1.58
1.39
1.30
1.30
0.92
0.91
0.89
Ph
O
S
Oct
3-40
2.01
0.99
1.93
0.98
1.00
2.08
2.11
2.42
2.29
8.19
3.06
f1 (ppm)


190.1
143.0
137.5
129.6
128.8
128.7
126.7
38.3
31.8
29.1
28.7
22.6
14.1
Ph
O
S
Oct
3-40
f1 (ppm)

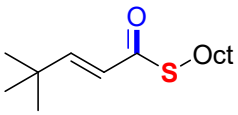

O
S
Oct
3-41
f1 (ppm)


O
S
Oct
3-41
f1 (ppm)


O
S
Oct

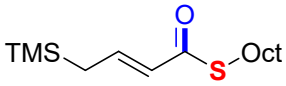
3-42

7.26
6.89
6.86
6.02
5.99
2.94
2.92
2.91
1.60
1.58
1.57
1.35
1.26
1.07
0.88
0.87
0.85
1.00
1.01
2.11
2.14
2.27
8.48
9.47
3.16
f1 (ppm)

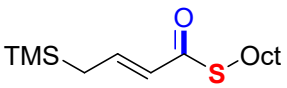

O
S
Oct

3-42

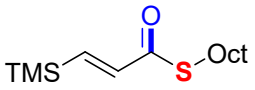
190.7
154.7
124.1
33.7
31.8
29.1
28.6
22.6
14.0
29.6
29.1
29.1
28.9
28.7
28.6
f1 (ppm)



3-43

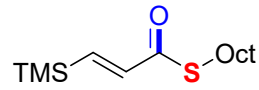


3-43


TMS
O
S
Oct

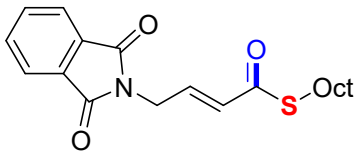
3-44

7.26
7.13
7.09
6.47
6.43
2.95
2.94
2.92
1.62
1.60
1.59
1.57
1.56
1.37
1.27
1.25
0.88
0.87
0.85
0.14
0.11
1.00
1.01
2.28
2.23
2.32
8.30
3.47
9.12
f1 (ppm)

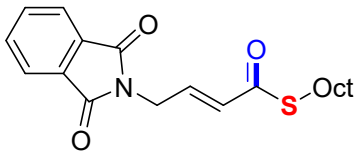

TMS
O
S
Oct

3-44

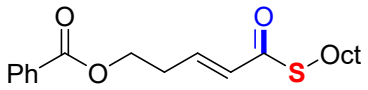
190.4
144.7
140.4
31.8
29.5
29.1
28.8
22.6
14.0
-1.9
f1 (ppm)



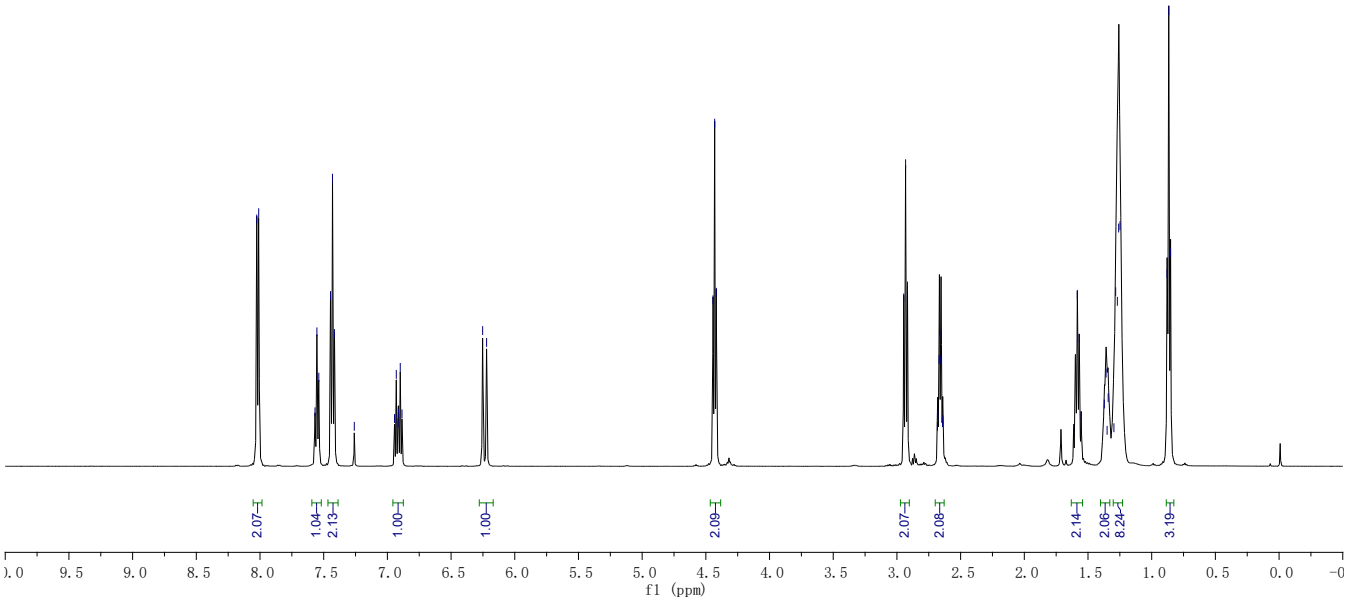
3-45

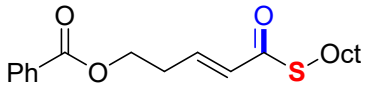


3-45

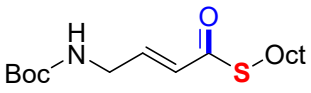


3-46



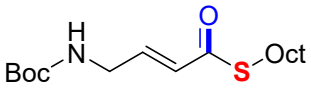


3-46


H
N
O
Boc
S
Oct

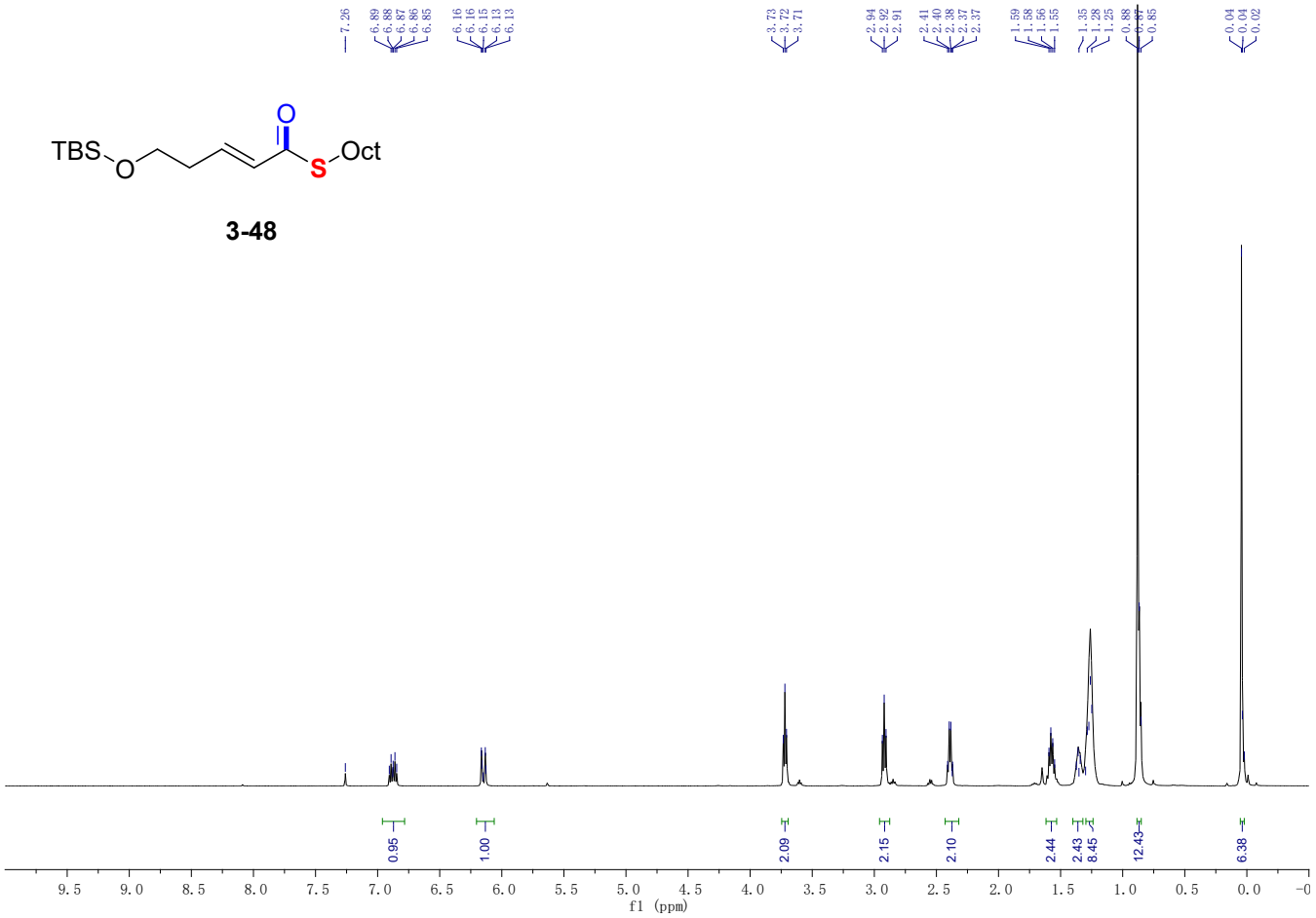
3-47

7.26
6.82
6.82
6.80
6.79
6.78
6.21
6.21
6.20
6.18
6.18
6.17
4.70
3.91
2.95
2.93
2.92
1.61
1.60
1.58
1.57
1.55
1.36
1.27
1.25
0.88
0.87
0.85
1.01
1.00
0.90
2.10
2.15
2.39
9.07
2.27
8.46
3.16
f1 (ppm)

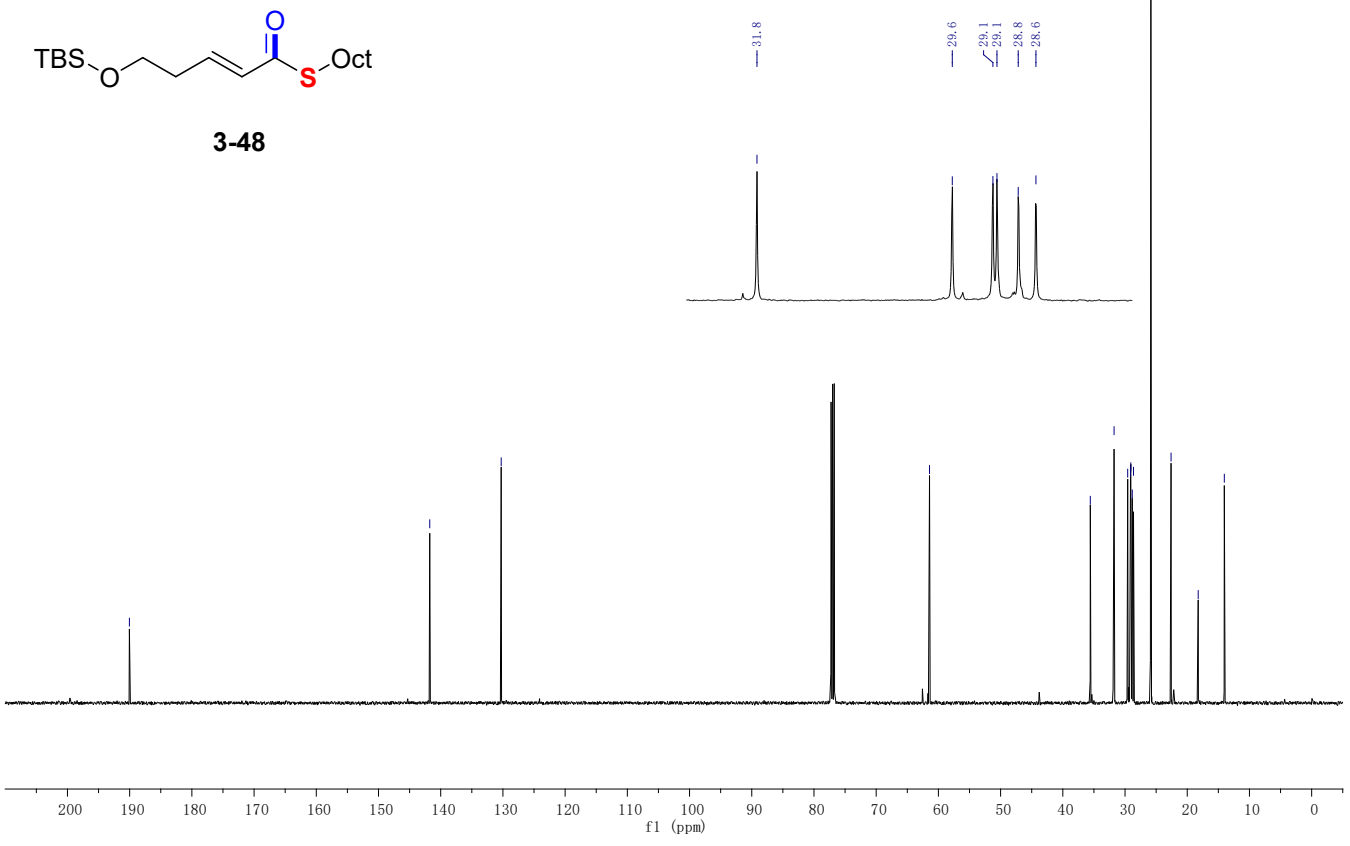

H
N
O
Boc
S
Oct

3-47

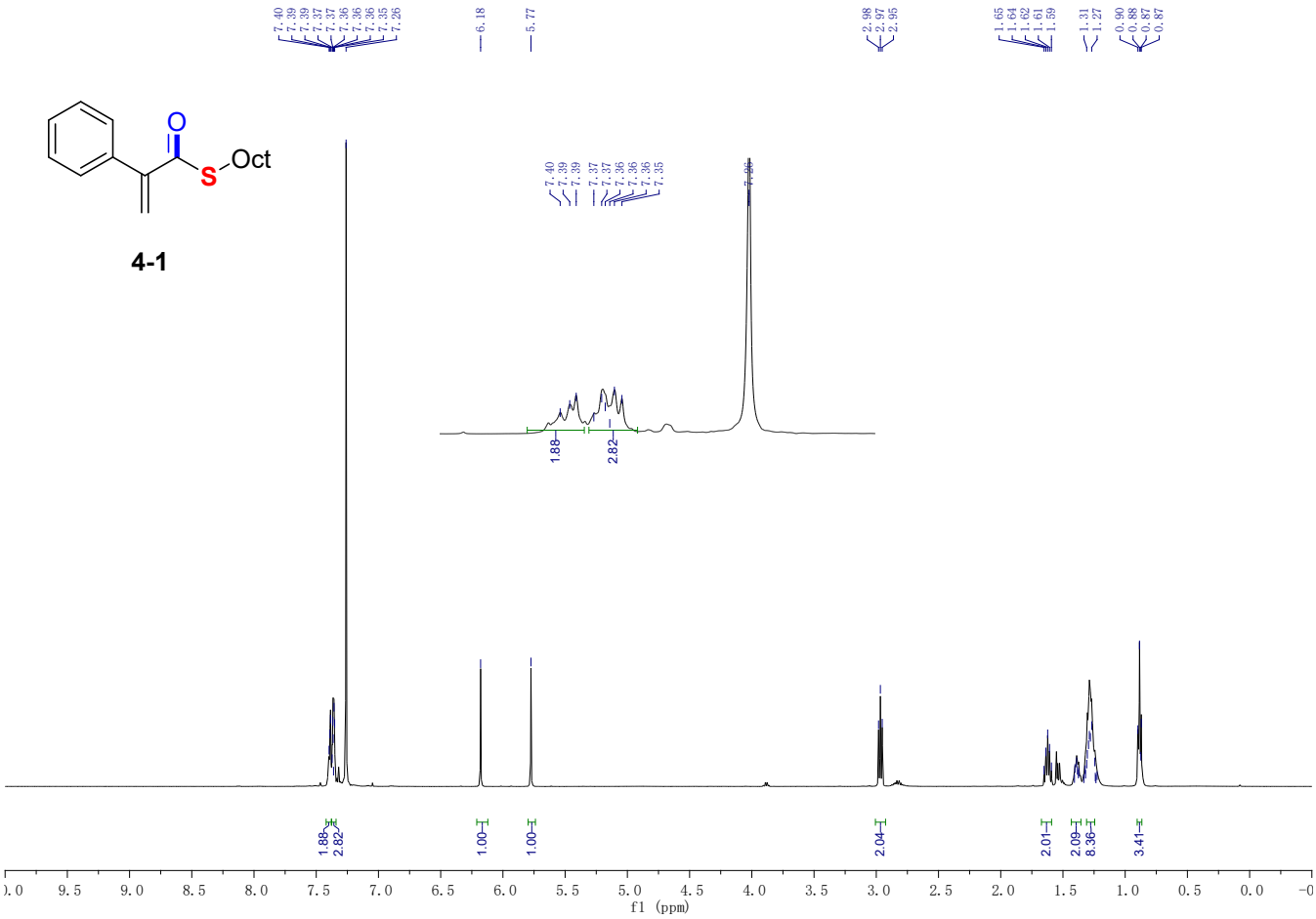
189.7
155.5
140.4
128.3
80.0
41.3
31.8
29.0
28.3
22.6
14.0
31.8
29.5
29.1
29.0
28.8
28.8
28.3
f1 (ppm)

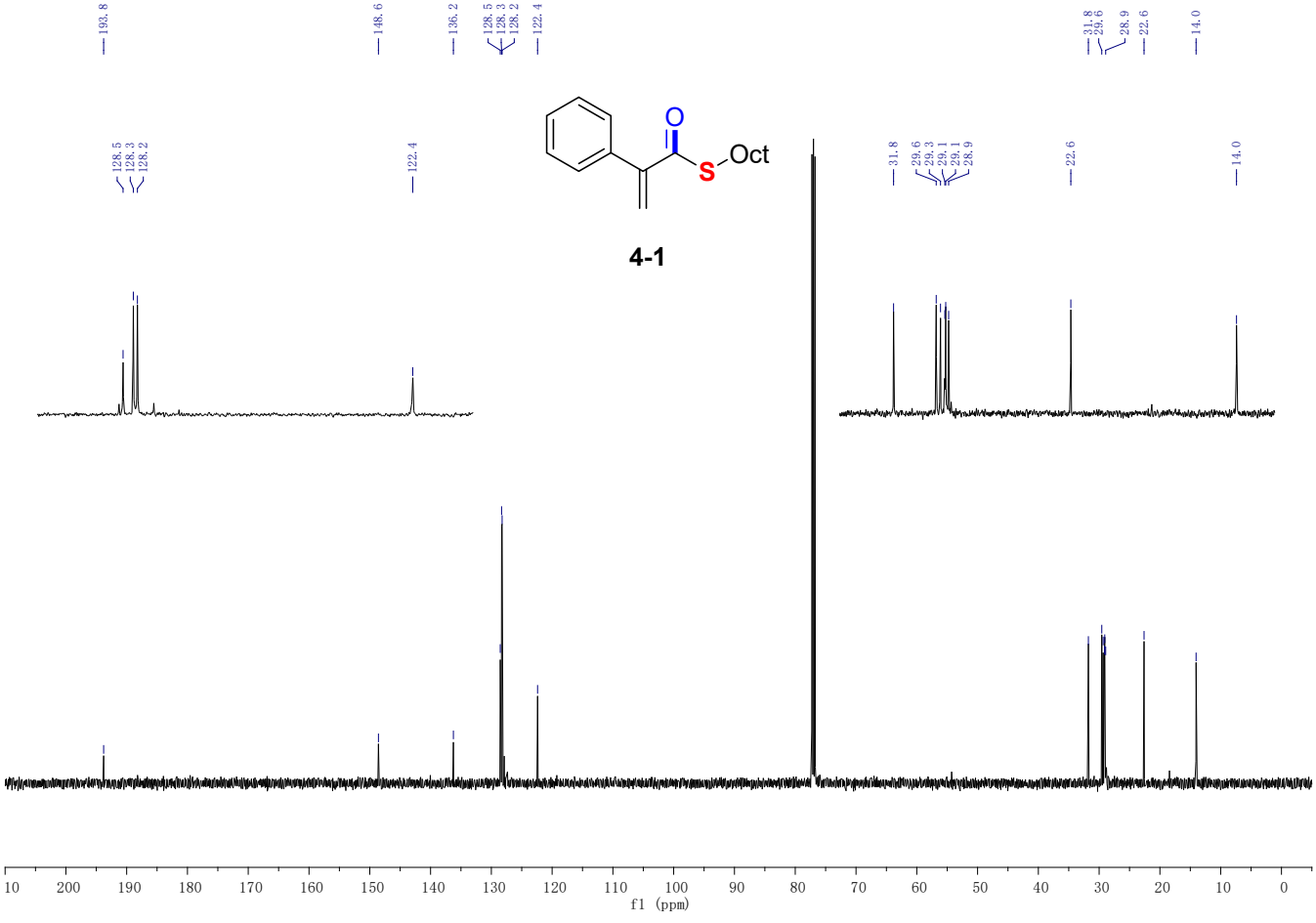


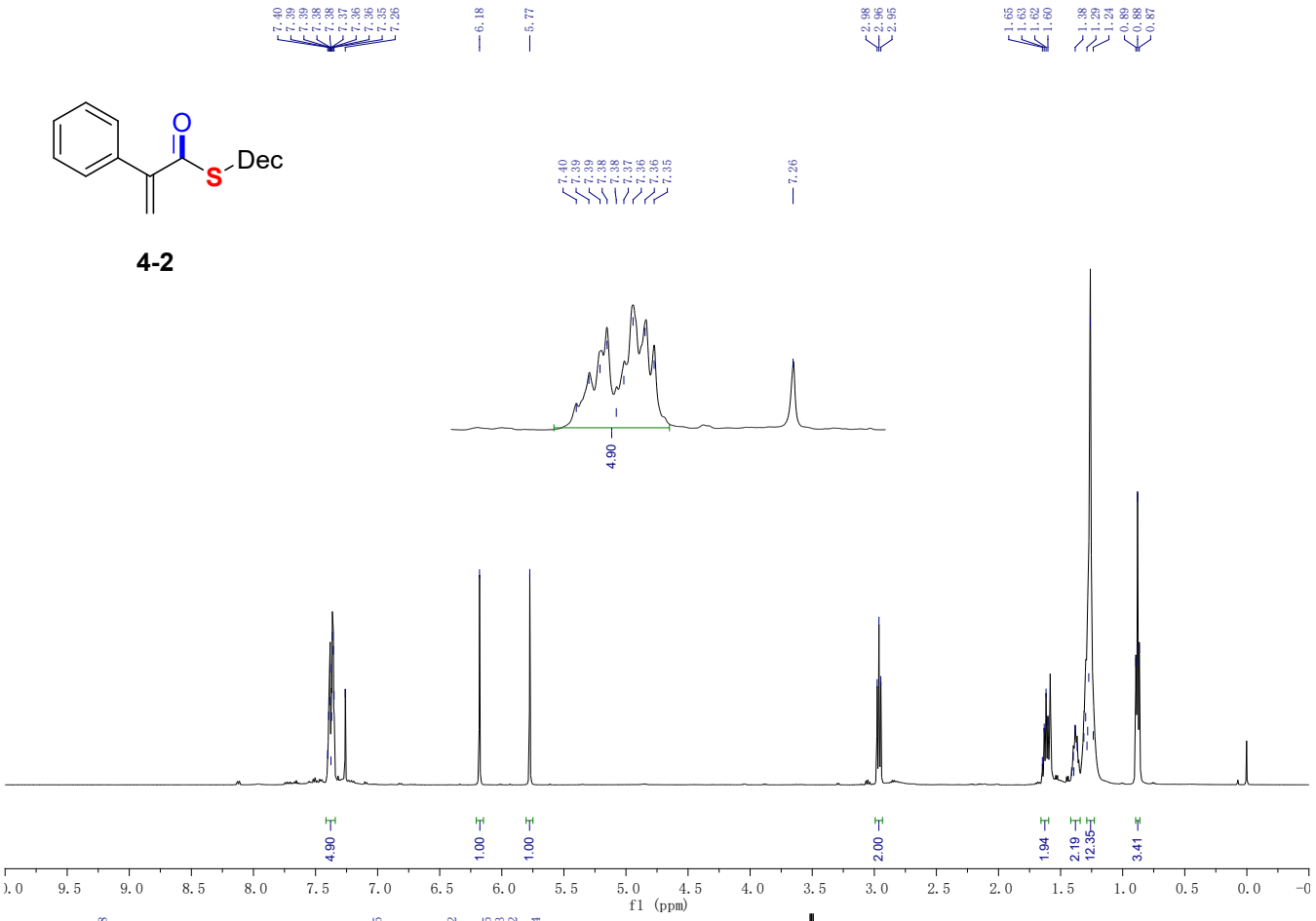
3-48

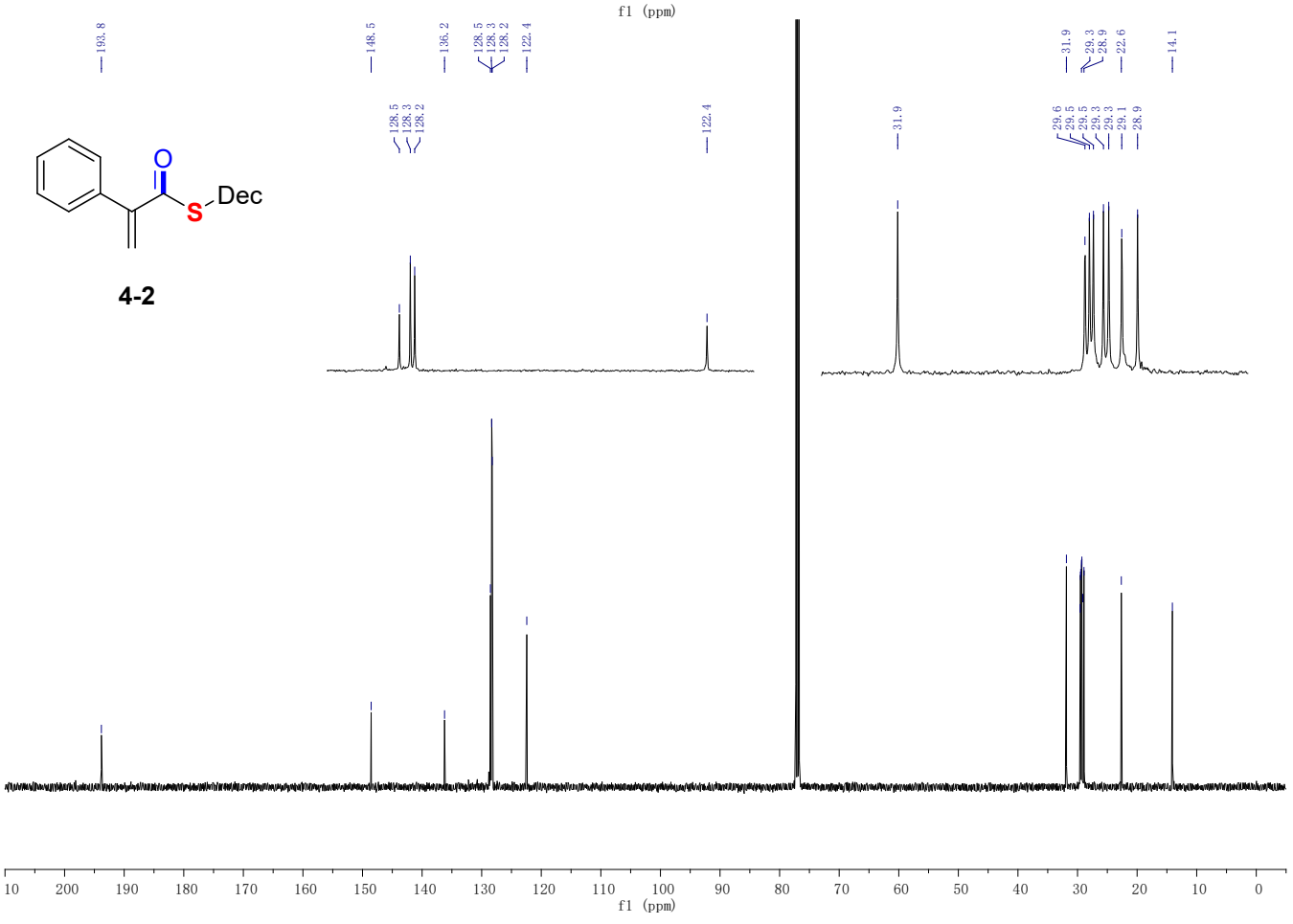


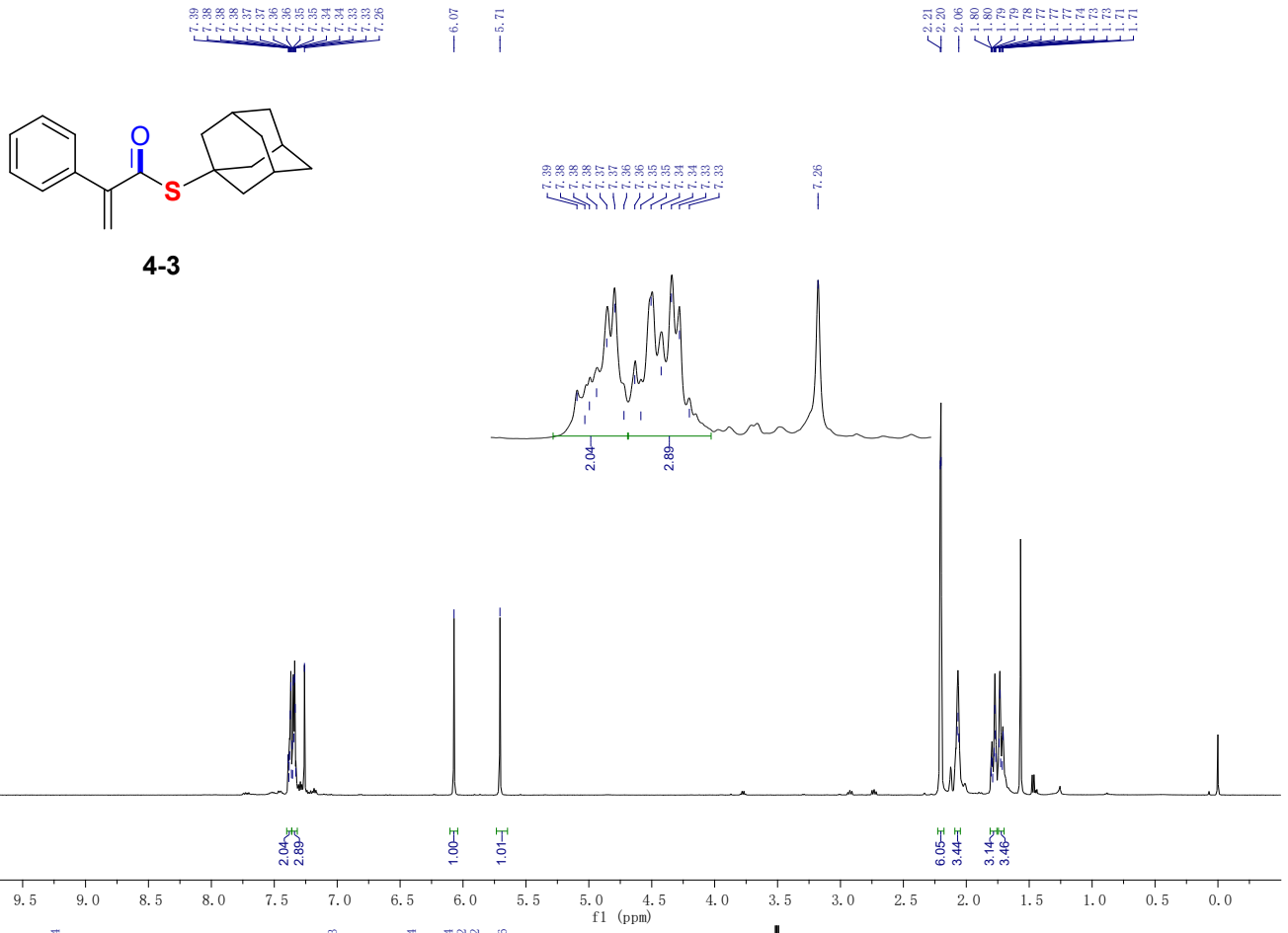
3-48

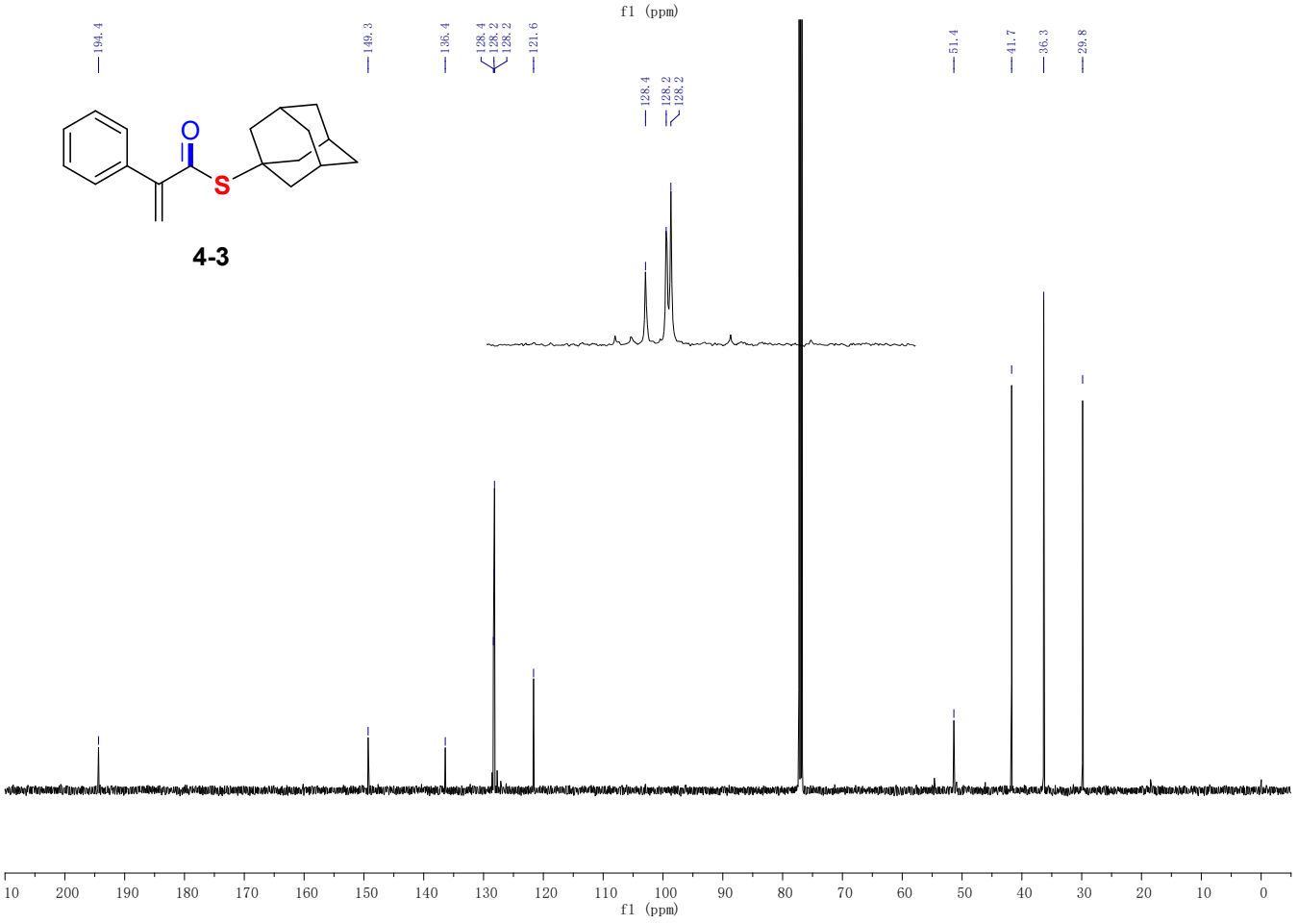

4-1
f1 (ppm)

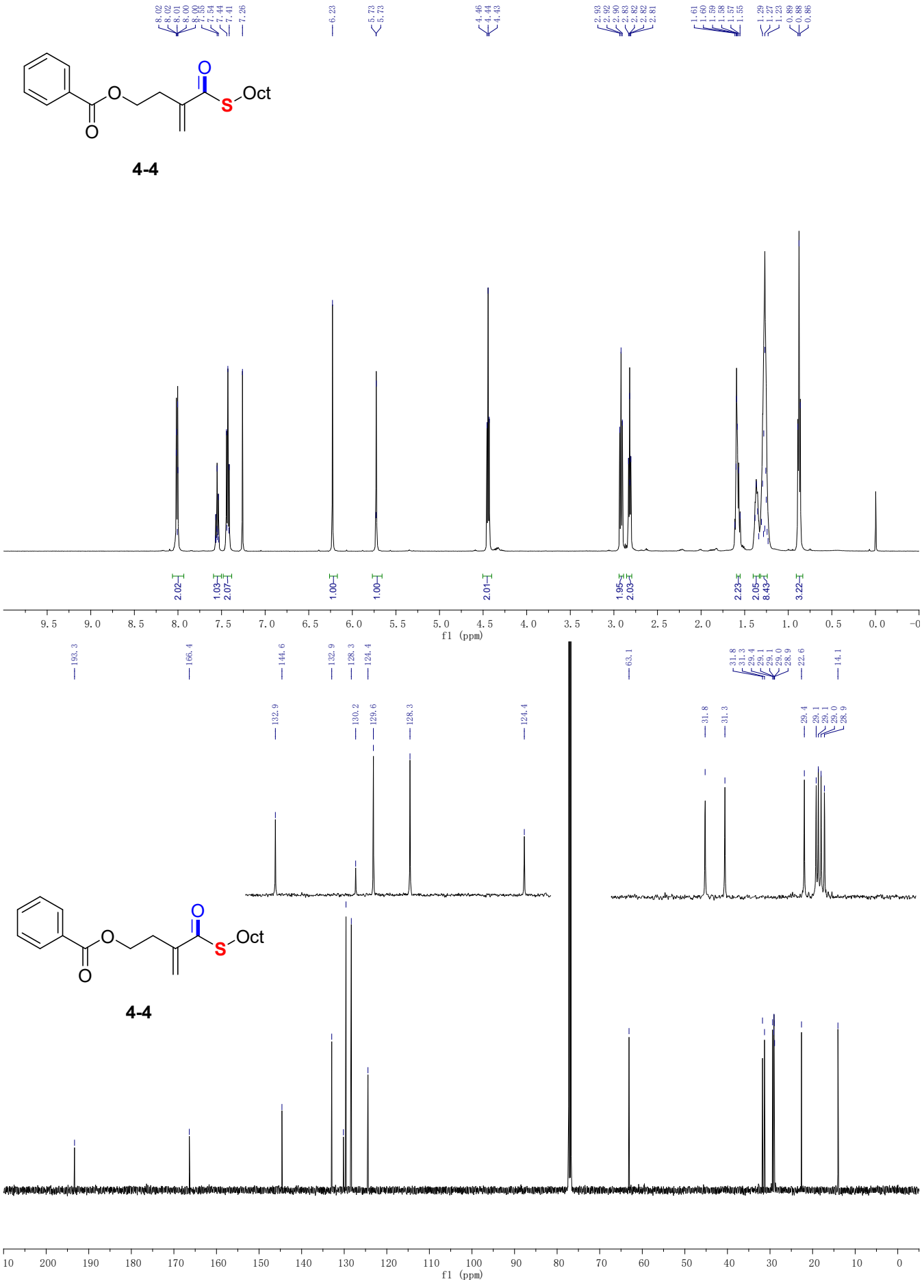

4-1
f1 (ppm)

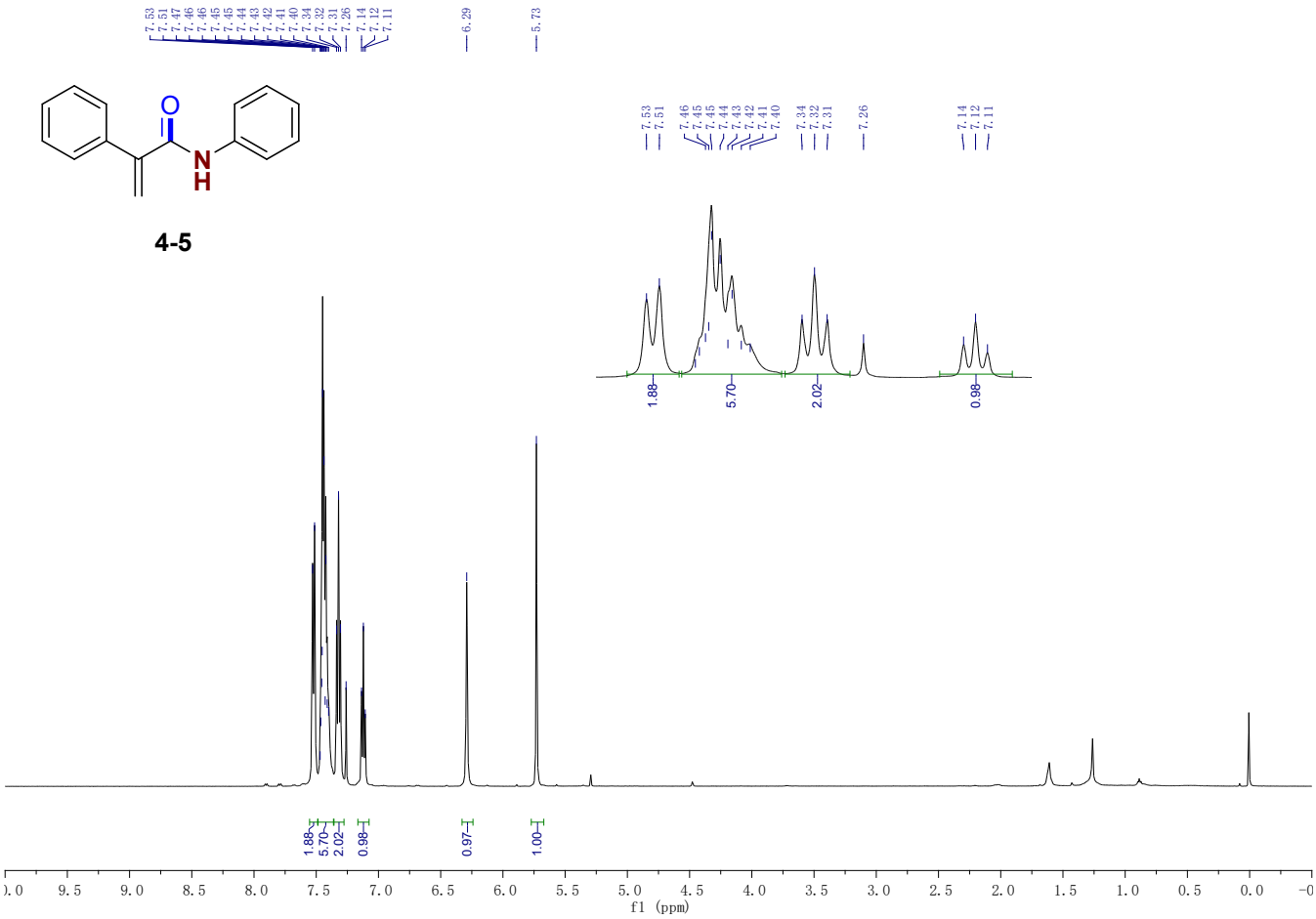

7.40
7.39
7.39
7.38
7.38
7.37
7.36
7.36
7.35
7.26
6.18
5.77
2.98
2.96
2.95
1.65
1.63
1.62
1.60
1.38
1.29
1.24
0.89
0.88
0.87
O
S
Dec
4-2
4.90
4.90
1.00
1.00
2.00
1.94
2.19
12.35
3.41
f1 (ppm)


193.8
148.5
136.2
128.5
128.3
128.2
122.4
31.9
29.3
28.9
22.6
14.1
29.6
29.5
29.1
O
S
Dec
4-2
f1 (ppm)

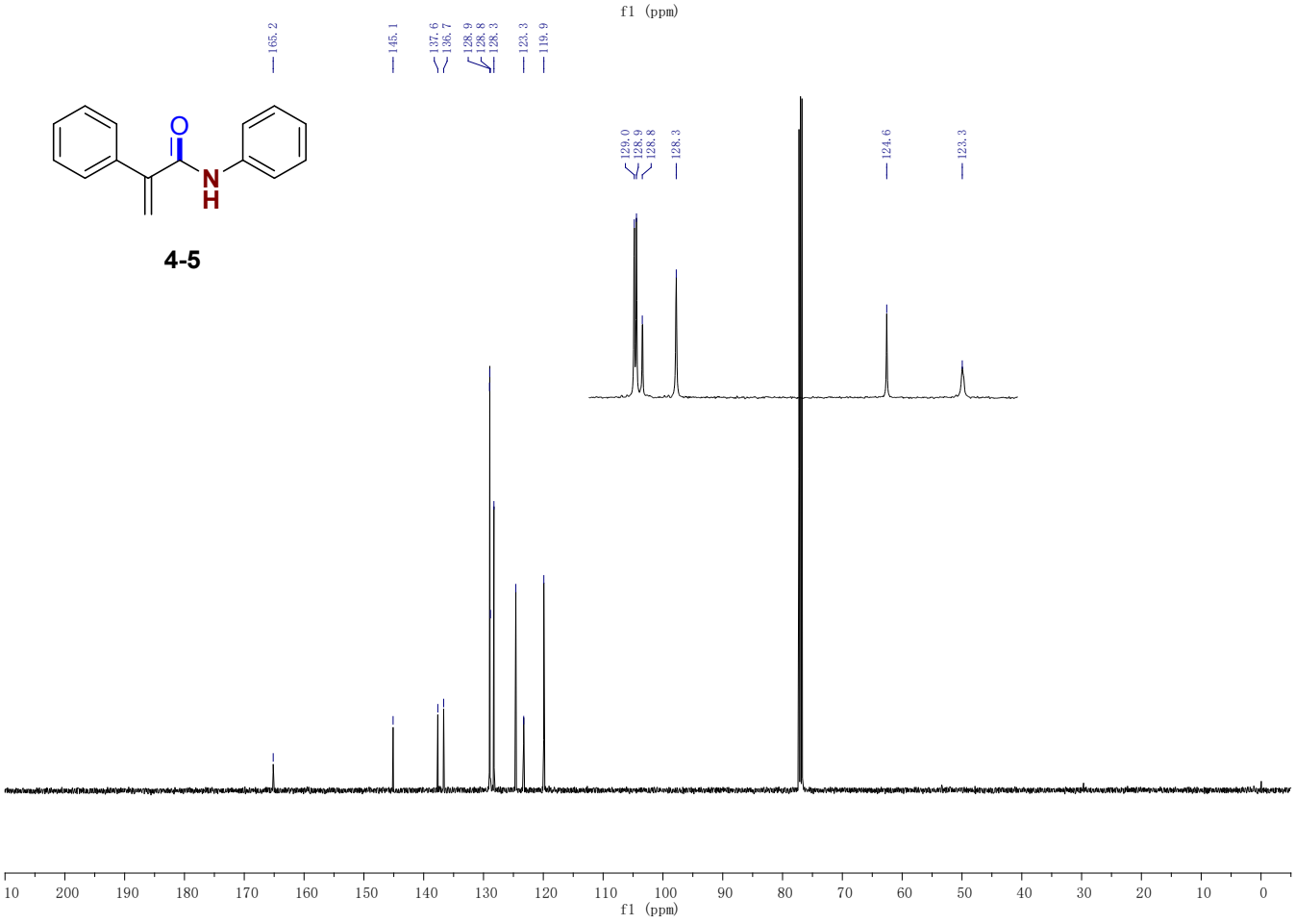

4-3
f1 (ppm)


4-3
f1 (ppm)

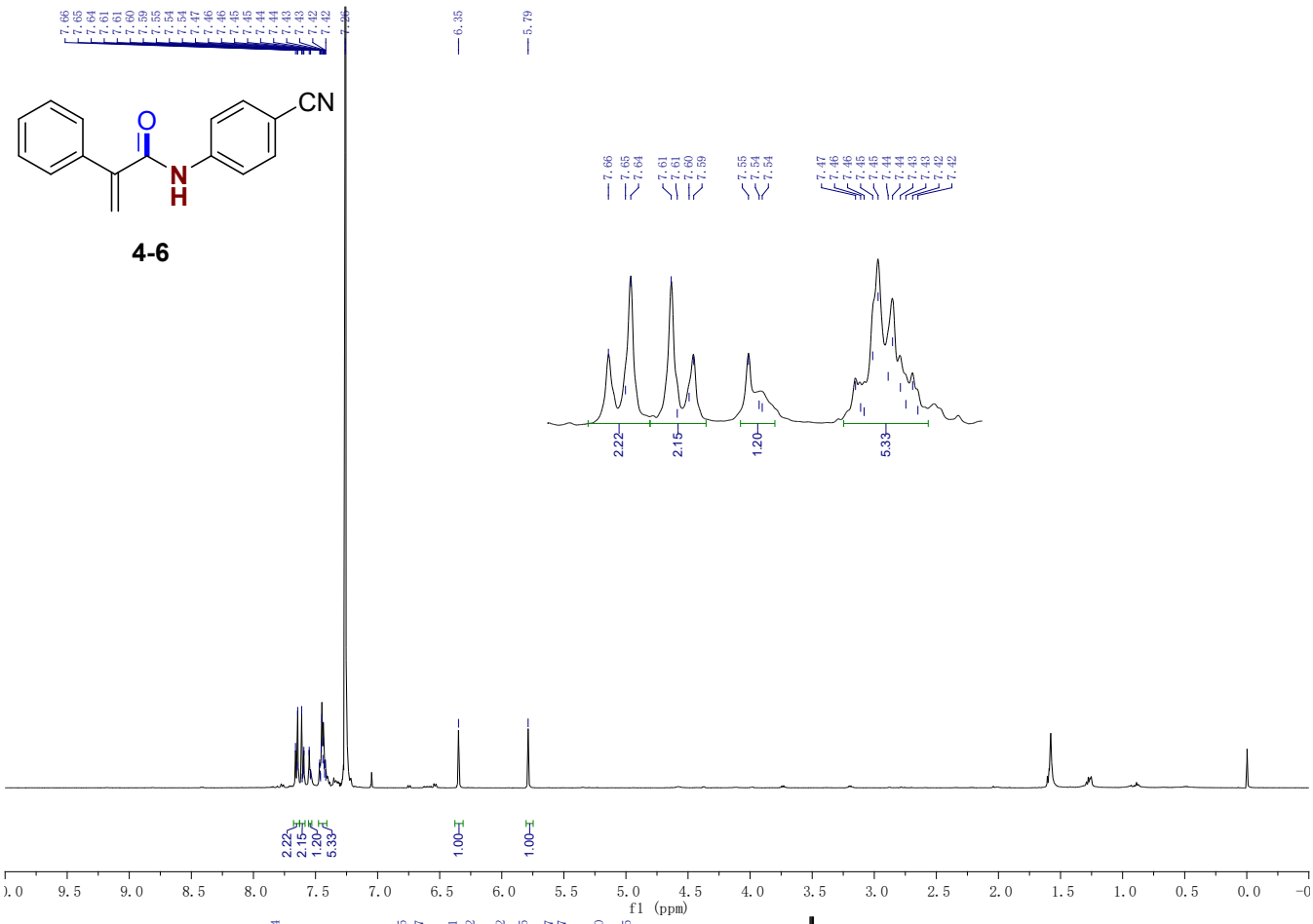

8.02
8.02
8.01
8.00
7.99
7.55
7.54
7.44
7.41
7.26
6.23
5.73
5.73
4.46
4.44
4.43
2.93
2.92
2.90
2.83
2.82
2.82
2.81
1.61
1.60
1.59
1.58
1.57
1.55
1.29
1.27
1.23
0.89
0.88
0.86
O
O
O
S
Oct
4-4
2.02
1.03
2.07
1.00
1.00
2.01
1.95
2.03
2.23
2.05
8.43
3.22
f1 (ppm)
193.3
166.4
144.6
132.9
128.3
124.4
63.1
31.8
31.3
29.4
29.1
29.0
28.9
22.6
14.1
132.9
130.2
129.6
128.3
124.4
31.8
31.3
29.4
29.1
29.0
28.9
O
O
O
S
Oct
4-4
f1 (ppm)

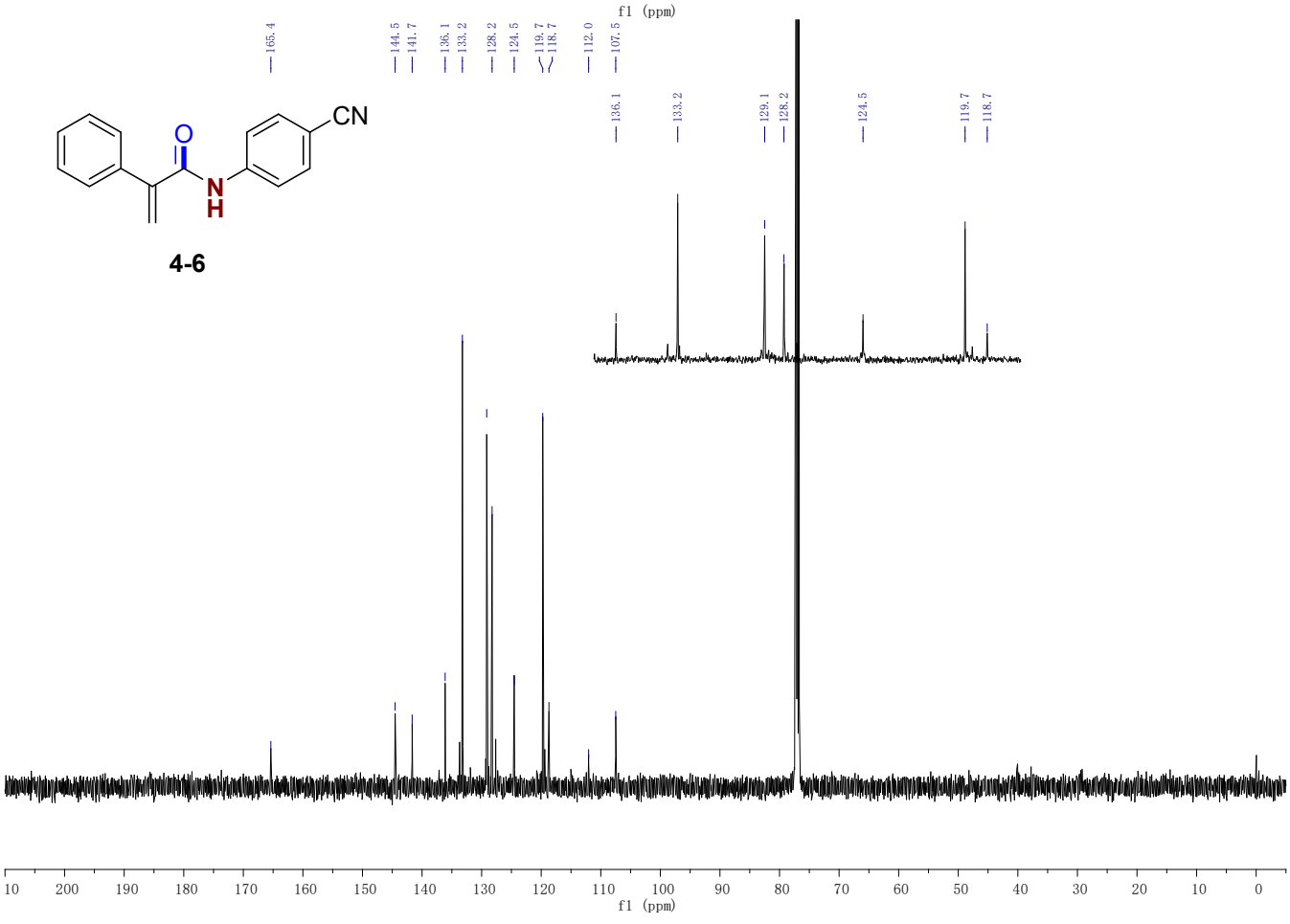

7.53
7.51
7.47
7.46
7.46
7.45
7.45
7.44
7.43
7.42
7.41
7.40
7.34
7.32
7.31
7.26
7.14
7.12
7.11
6.29
5.73
O
N
H
1.88
5.70
2.02
0.98
0.97
1.00
f1 (ppm)

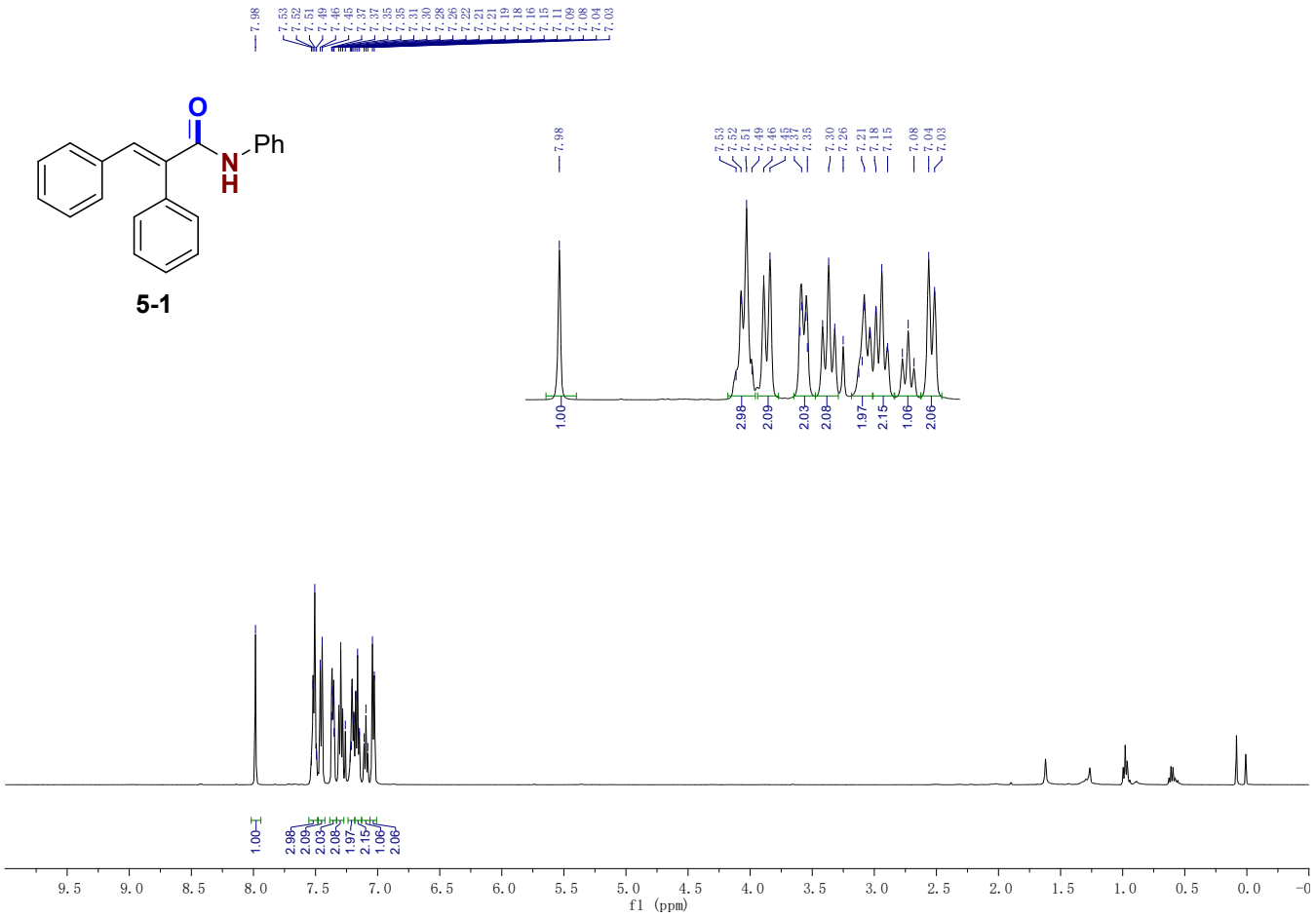
4-5

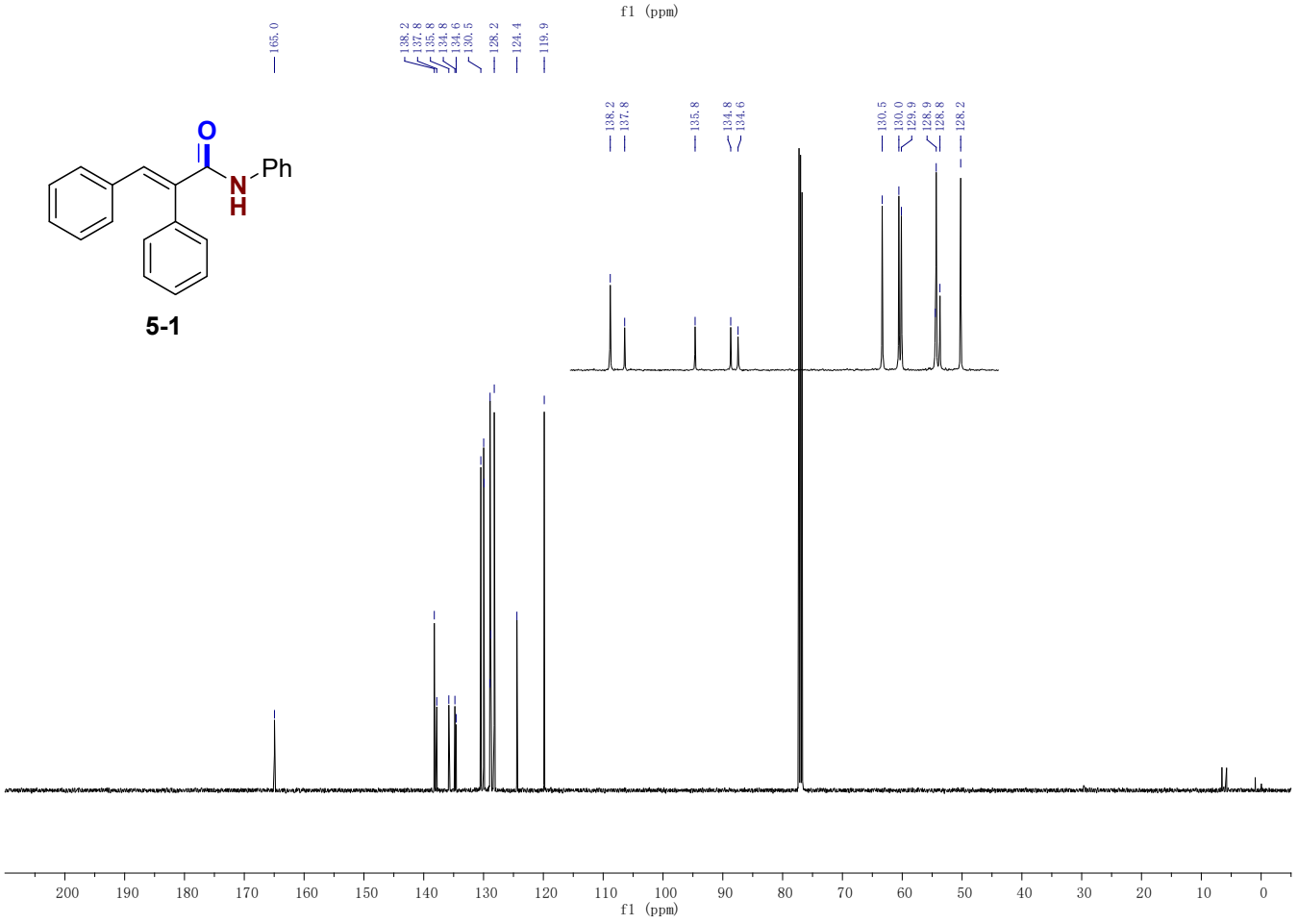

165.2
145.1
137.6
136.7
128.9
128.8
128.3
123.3
119.9
129.0
128.9
128.8
128.3
124.6
123.3
O
N
H
f1 (ppm)

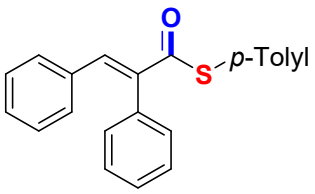
4-5


7.66
7.65
7.64
7.61
7.61
7.60
7.59
7.55
7.54
7.54
7.47
7.46
7.46
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.42
7.26
6.35
5.79
CN
O
N
H
4-6
2.22
2.15
1.20
5.33
1.00
1.00
f1 (ppm)


165.4
144.5
141.7
136.1
133.2
128.2
124.5
119.7
118.7
112.0
107.5
CN
O
N
H
4-6
f1 (ppm)

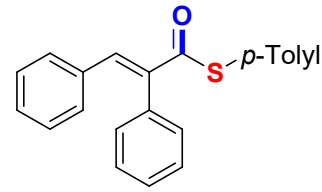

O
N
H
Ph
5-1
7.98
7.53
7.52
7.51
7.49
7.46
7.45
7.37
7.35
7.30
7.26
7.21
7.18
7.15
7.08
7.04
7.03
1.00
2.98
2.09
2.03
2.08
1.97
2.15
1.06
2.06
f1 (ppm)


O
N
H
Ph
5-1
165.0
138.2
137.8
135.8
134.8
134.6
130.5
130.0
129.9
128.9
128.8
128.2
124.4
119.9
f1 (ppm)


O
S
p-Tolyl

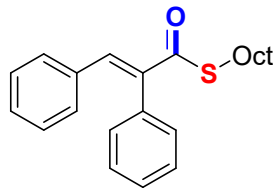
5-2

7.74
7.48
7.47
7.46
7.46
7.40
7.40
7.39
7.38
7.32
7.30
7.26
7.23
7.23
7.22
7.19
7.17
7.16
7.08
7.06
2.38
2.86
2.36
2.07
3.46
2.04
2.37
1.00
3.24
f1 (ppm)

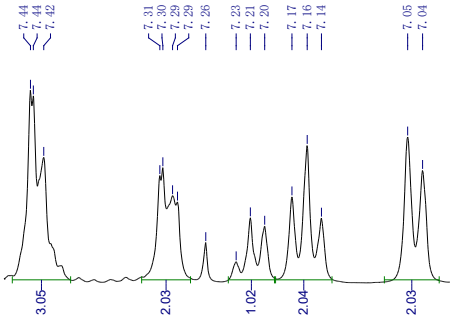

O
S
p-Tolyl

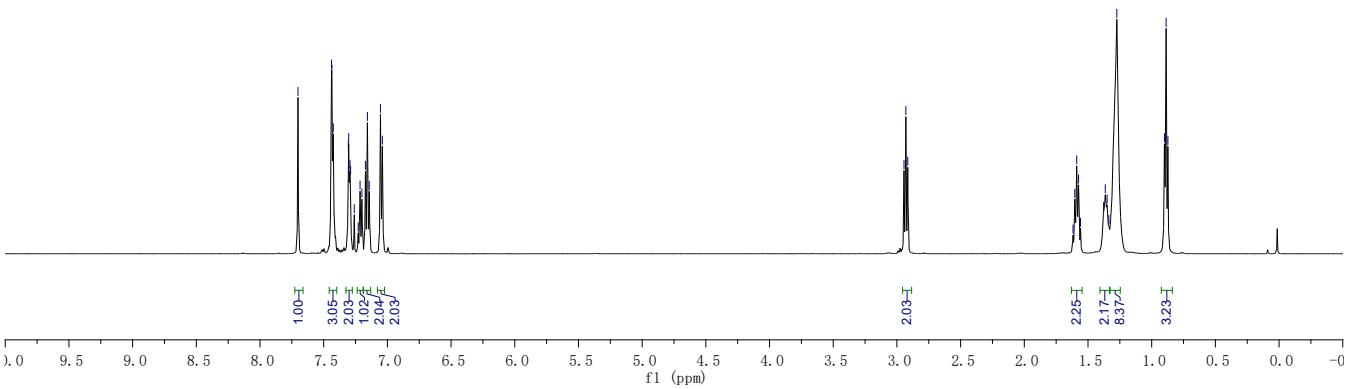
5-2

192.1
139.4
138.6
136.8
135.1
134.6
134.2
131.1
128.3
125.2
21.3
f1 (ppm)

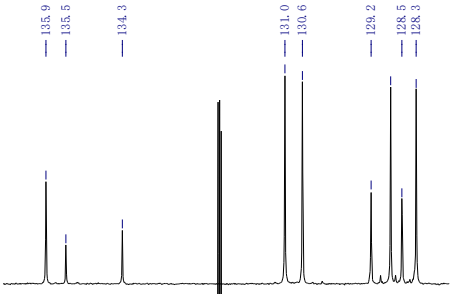


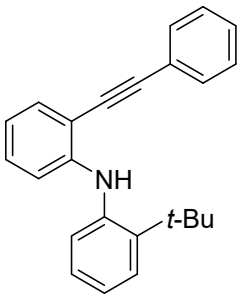
5-3



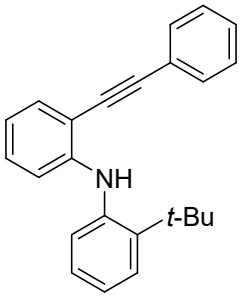


5-3

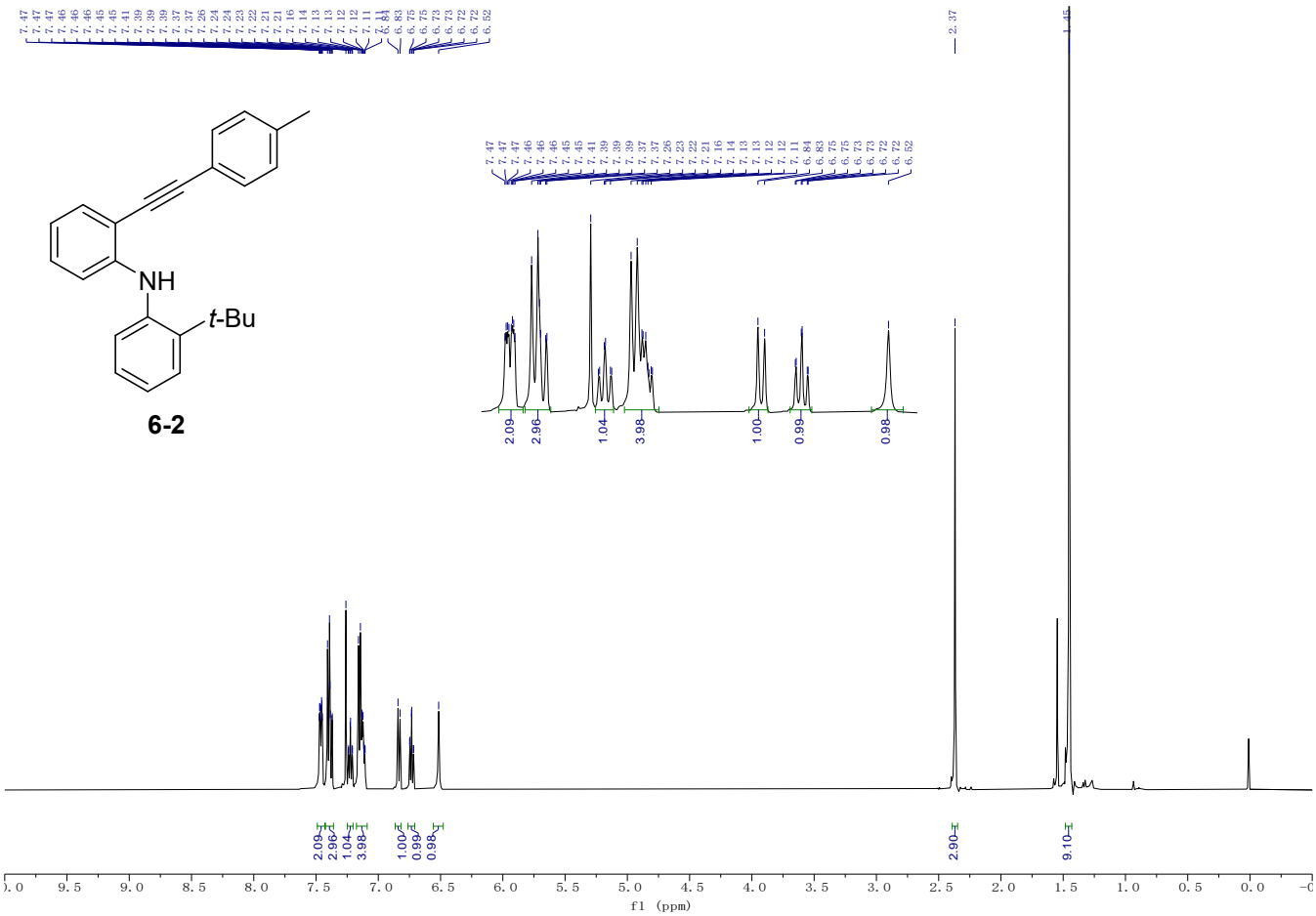


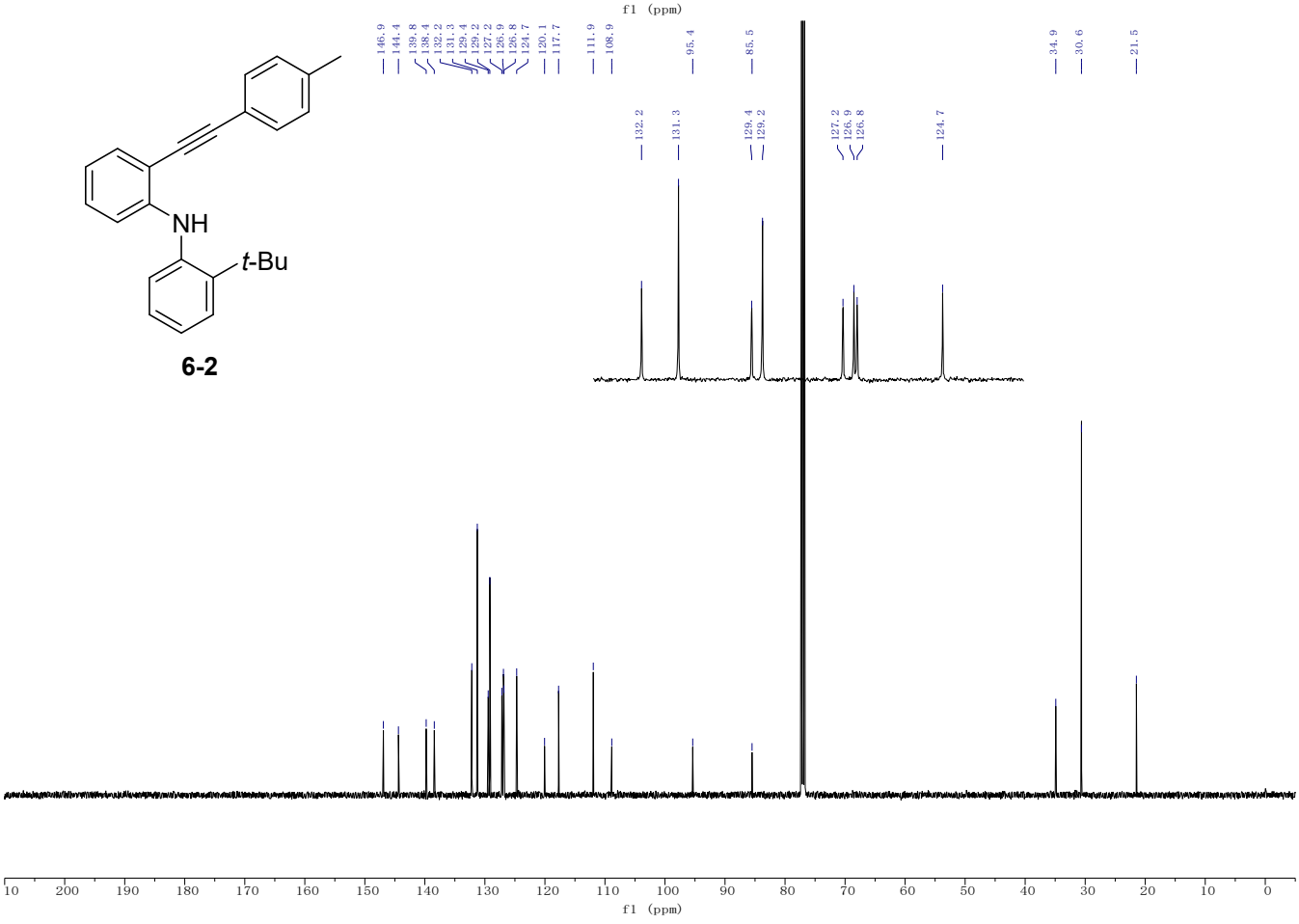


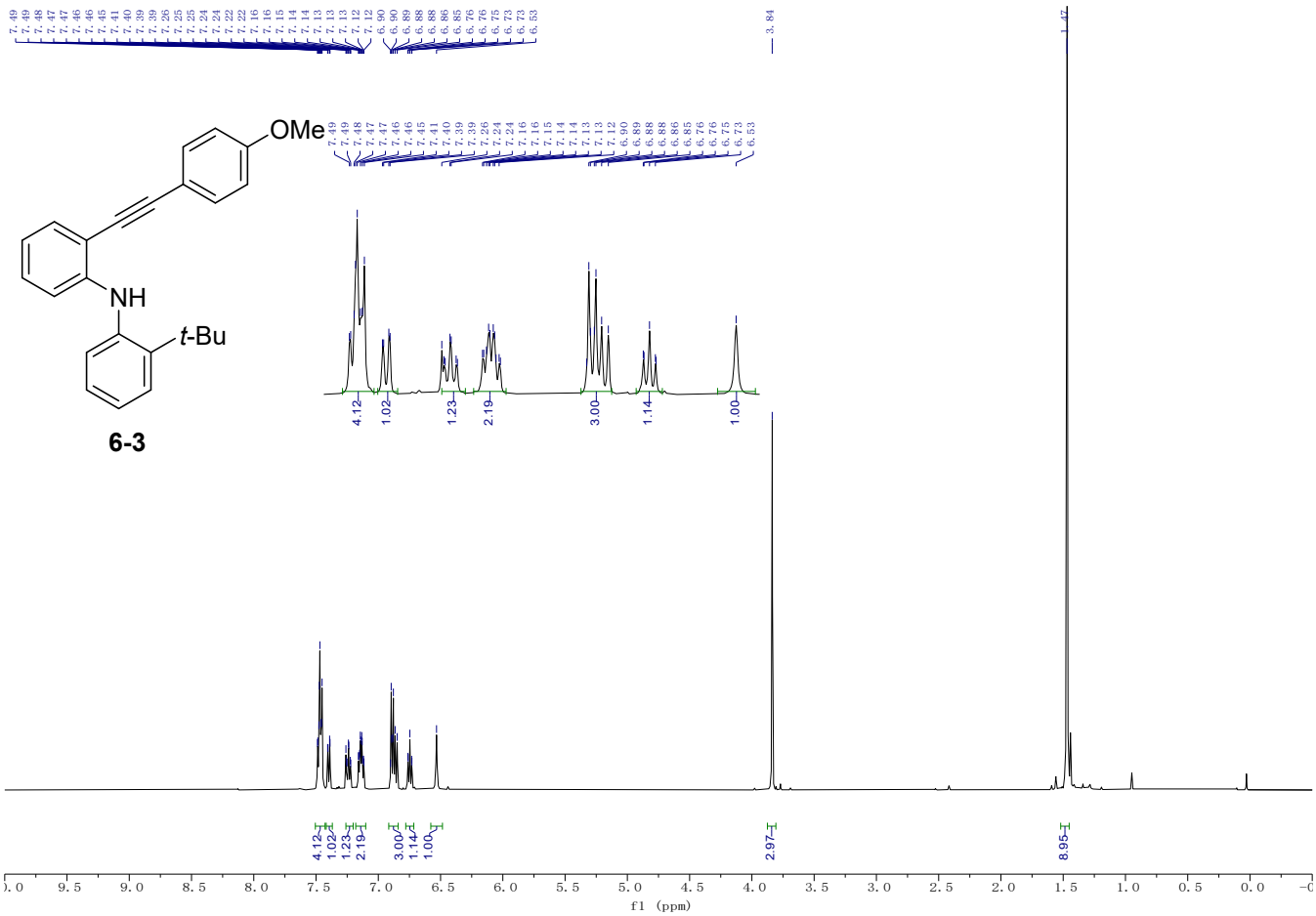
6-1

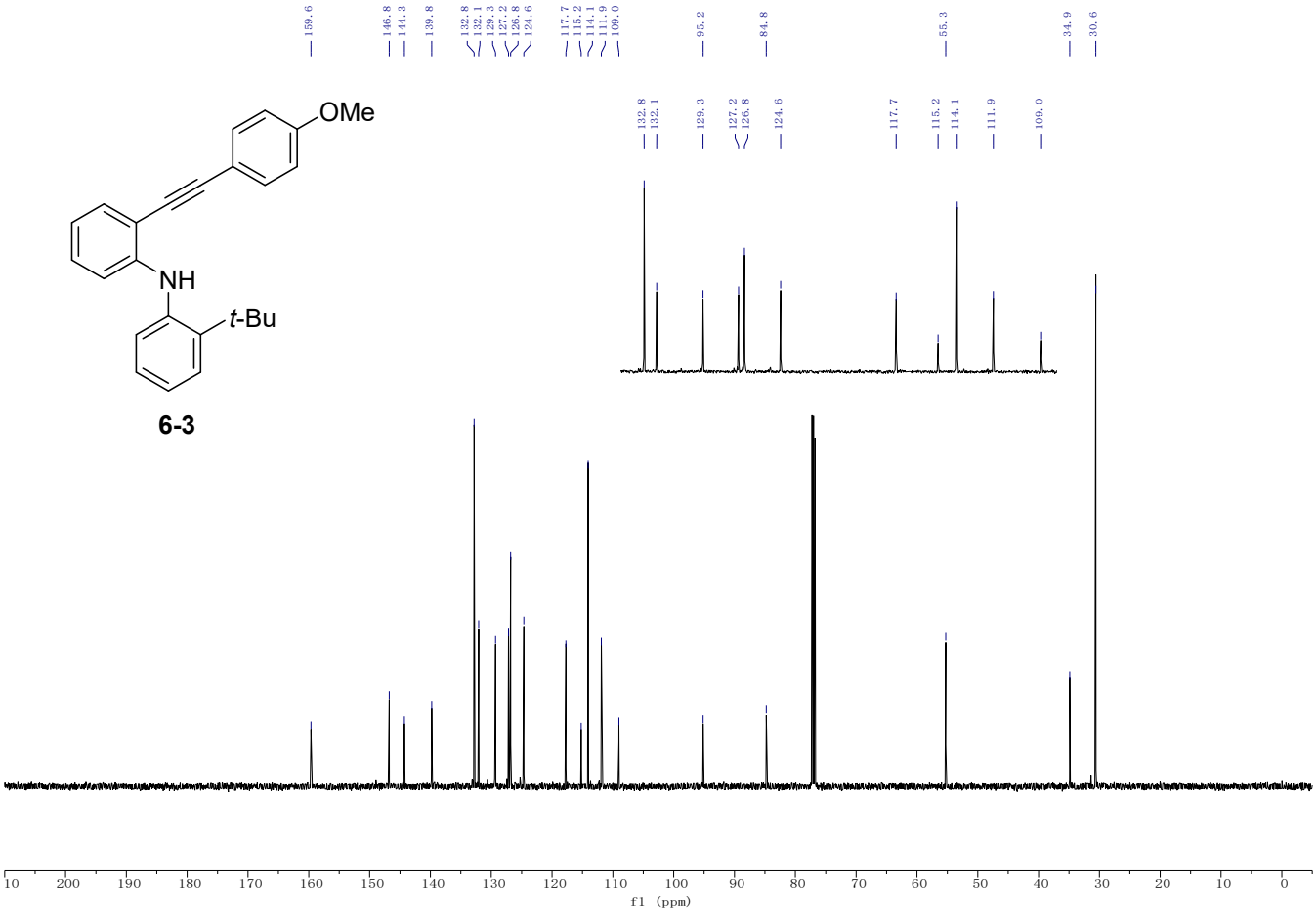


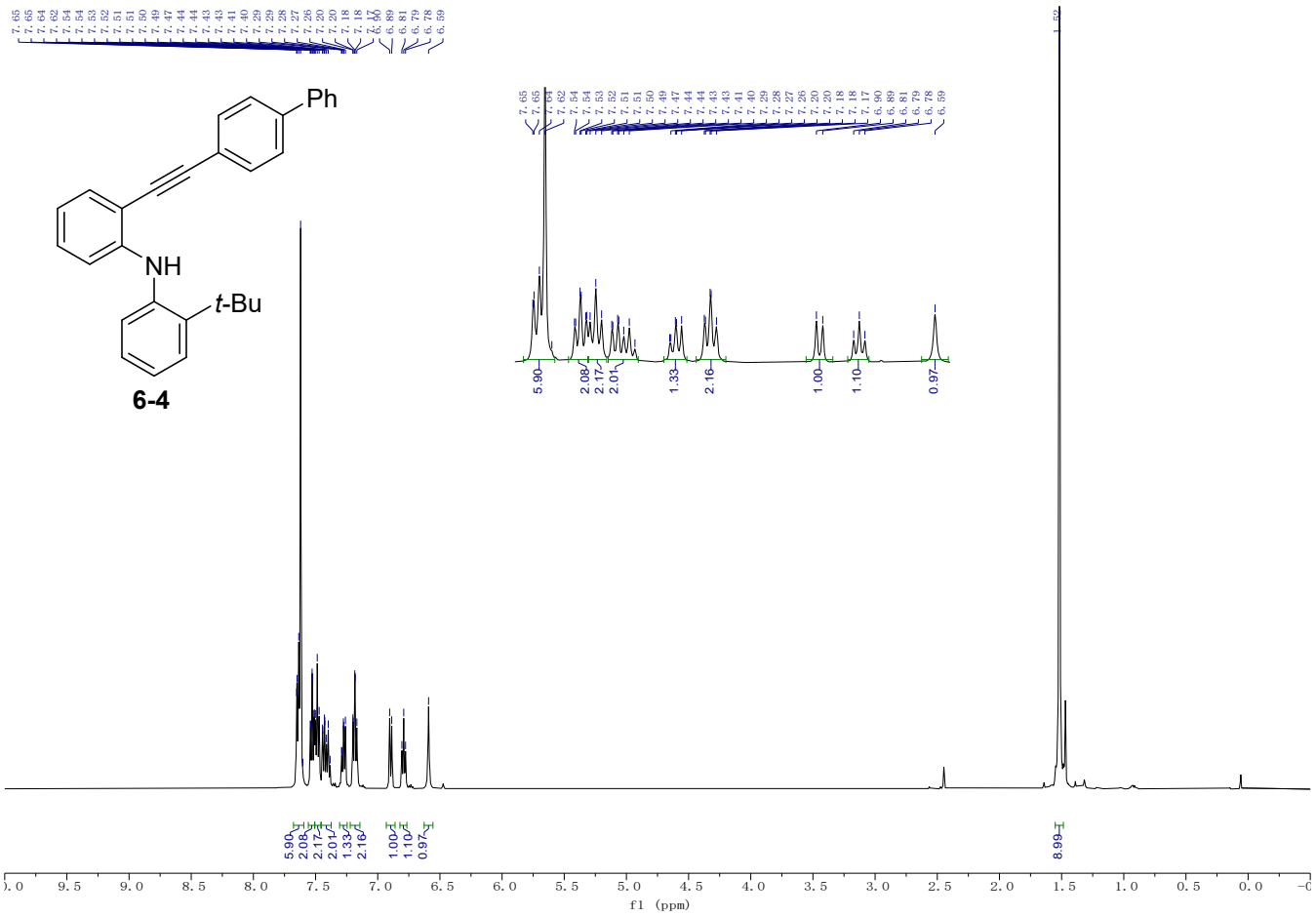
6-1

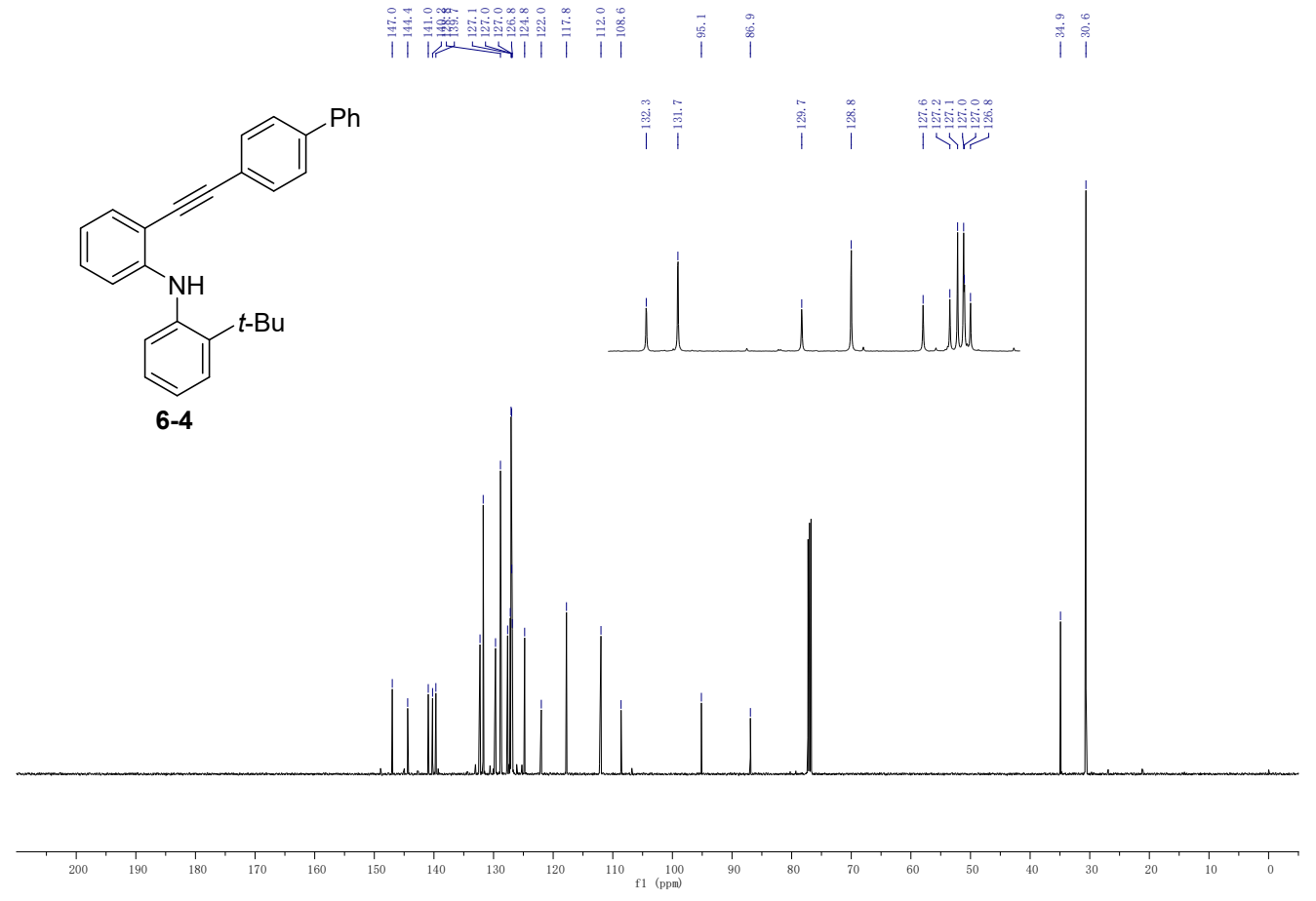

NH
t-Bu
6-2
f1 (ppm)

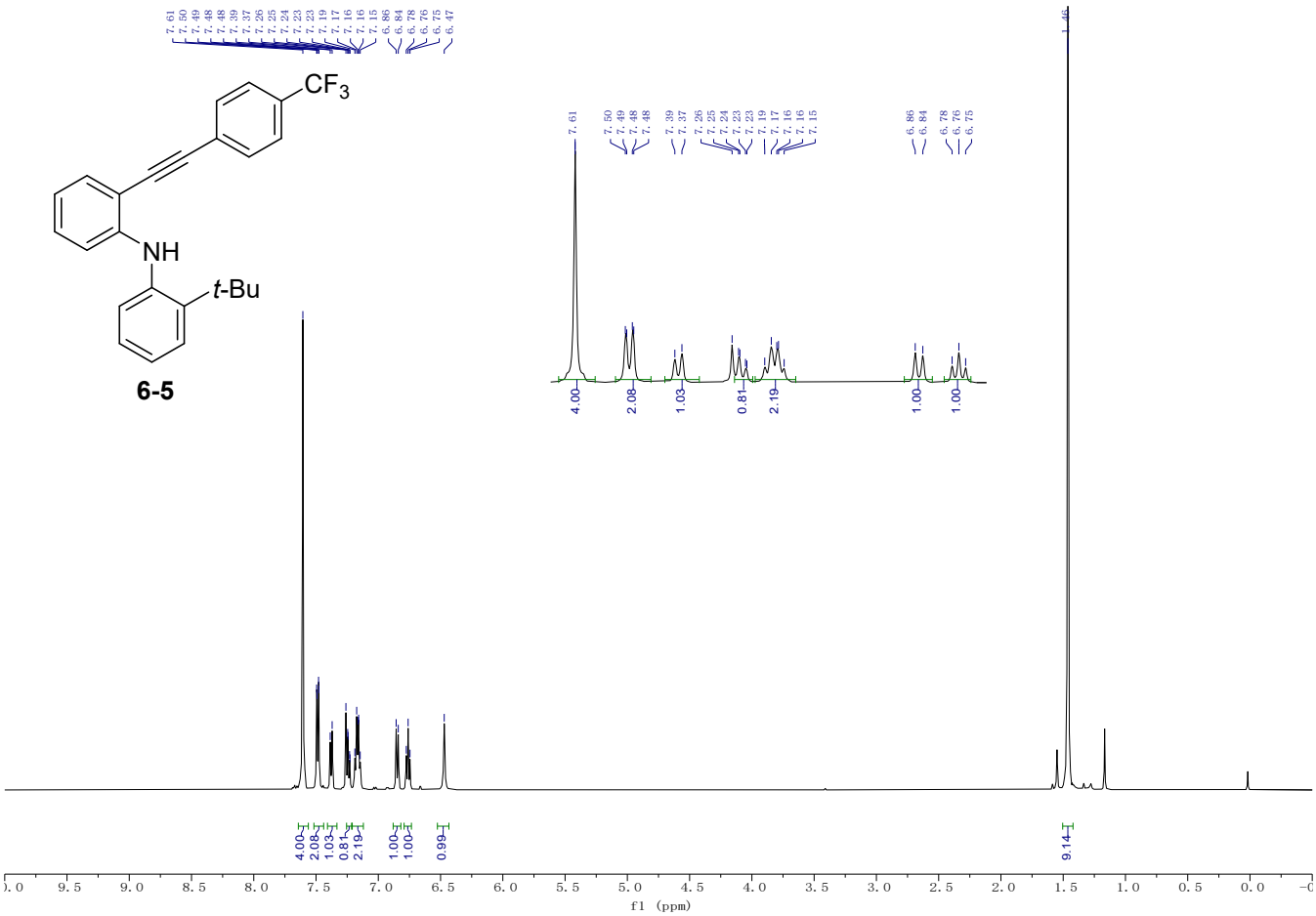

NH
t-Bu
6-2
f1 (ppm)

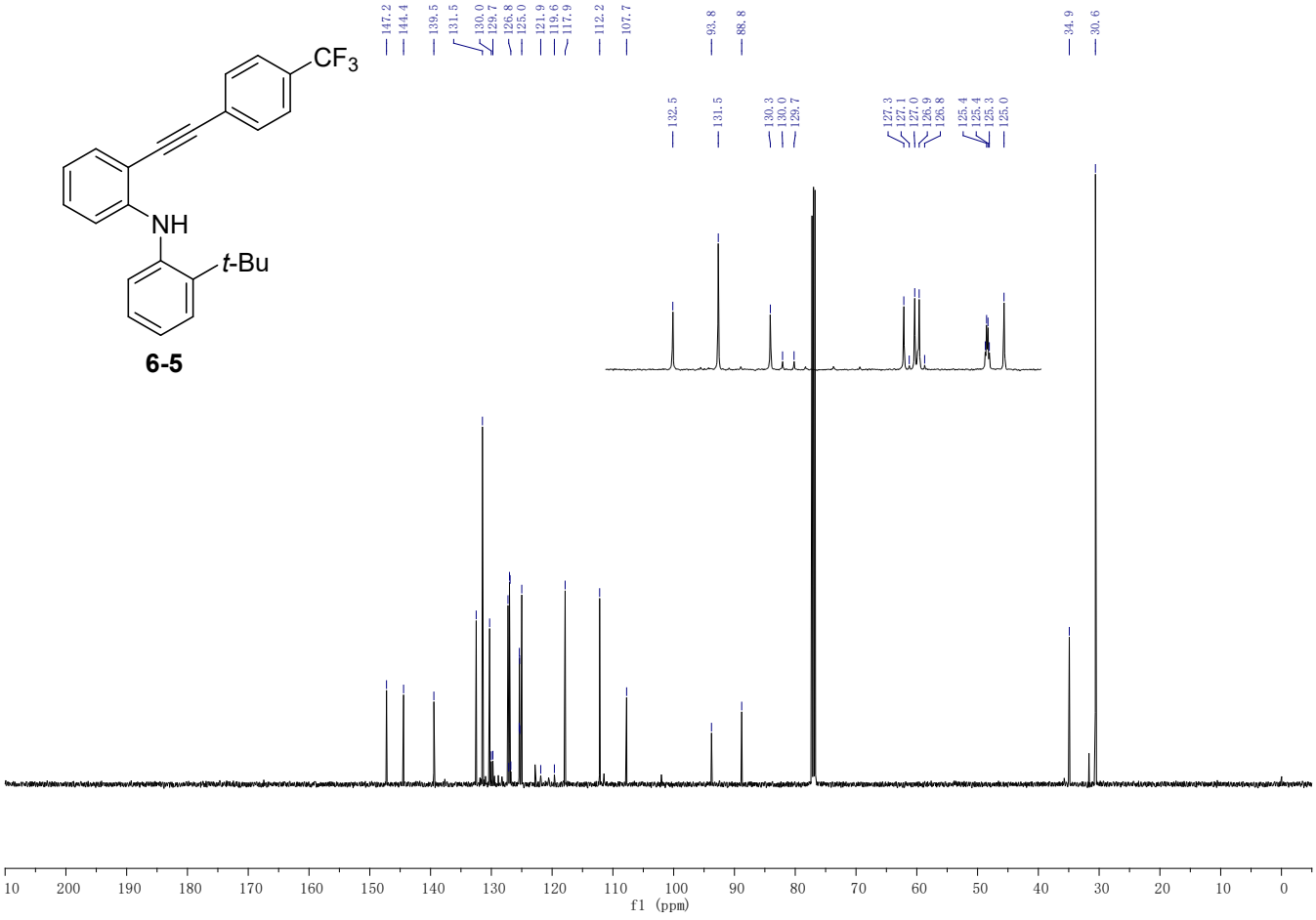

OMe
NH
t-Bu
6-3
f1 (ppm)

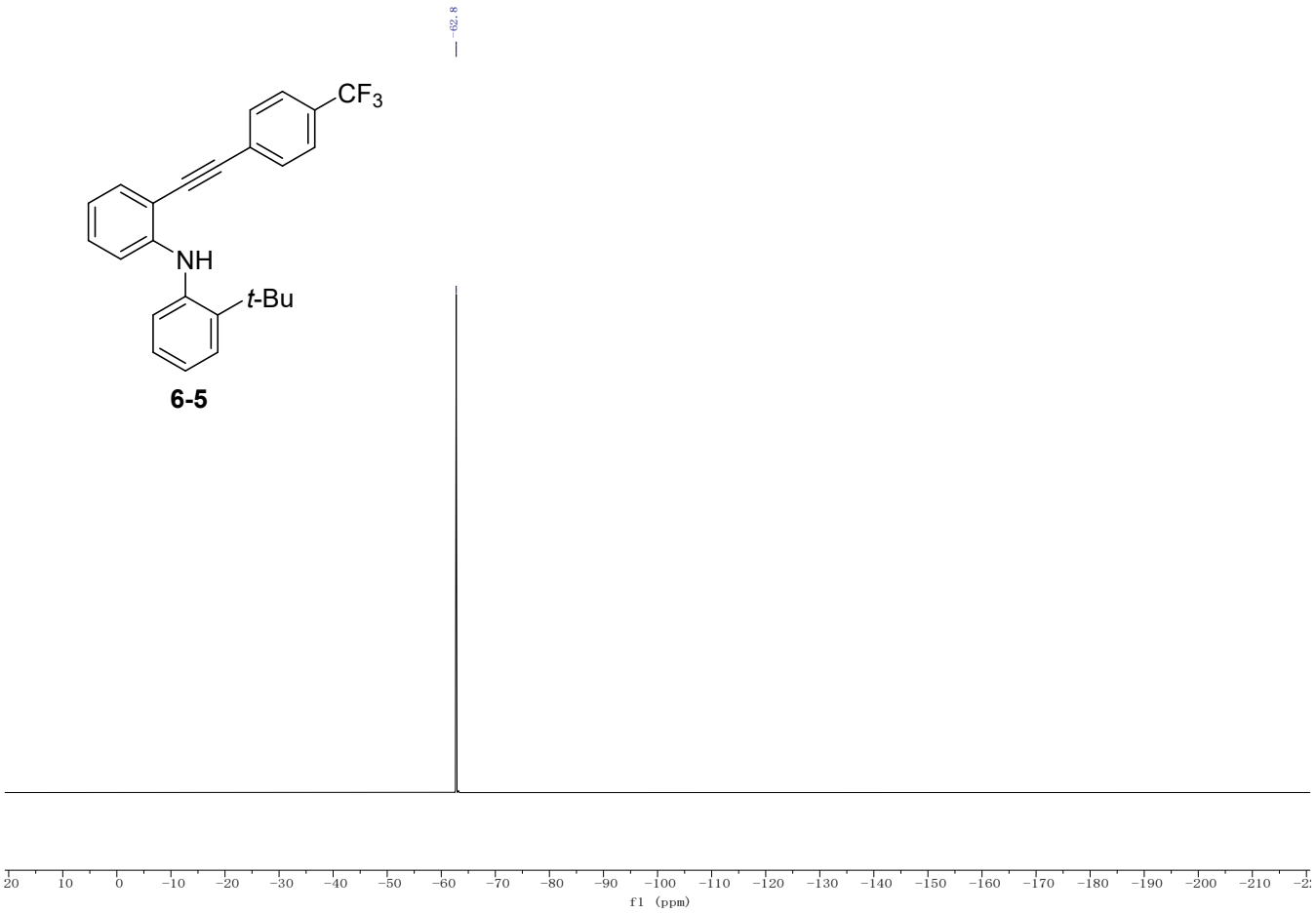

OMe
NH
t-Bu
6-3
f1 (ppm)


Ph
NH
t-Bu
6-4
f1 (ppm)

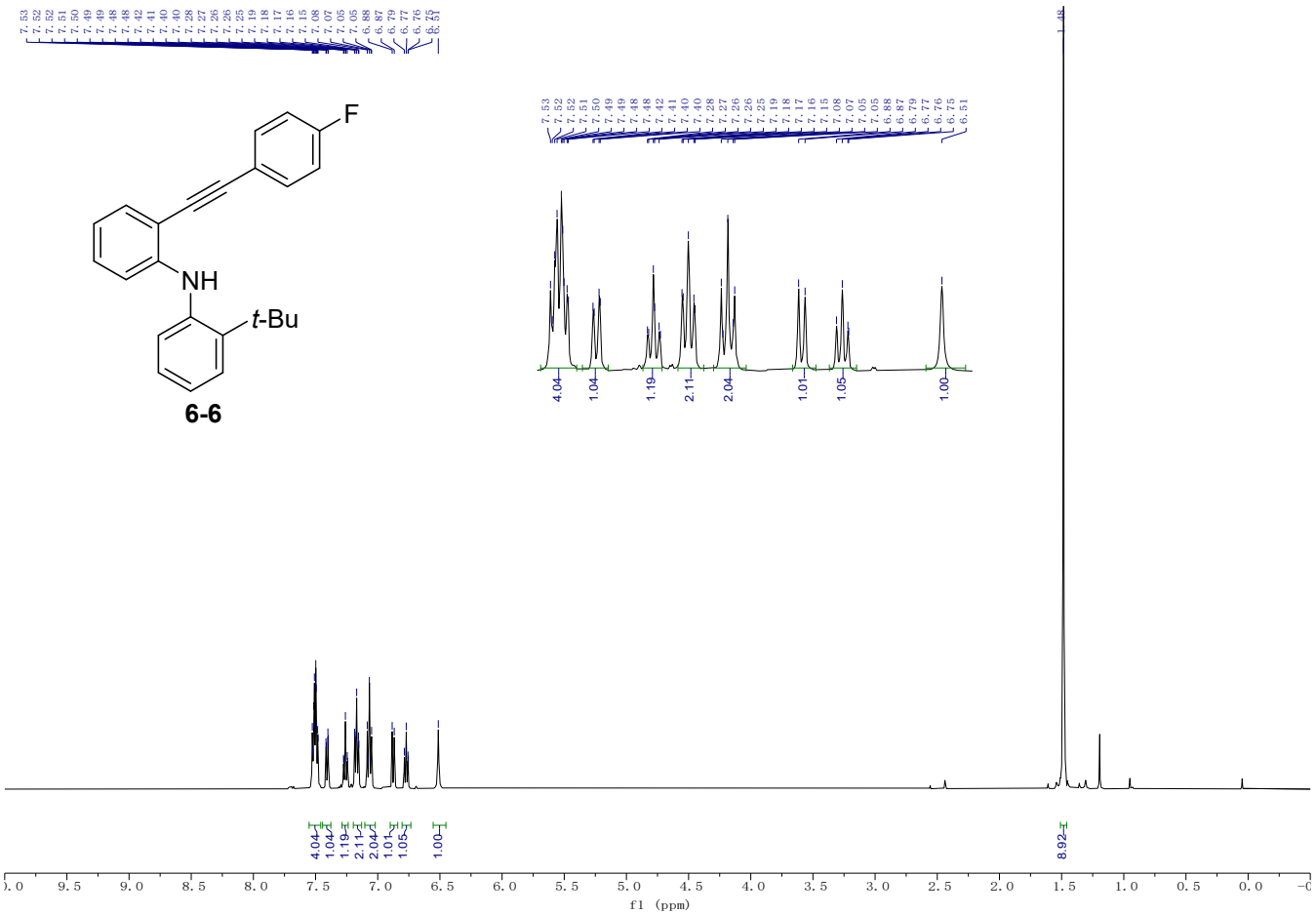

Ph
NH
t-Bu
6-4
f1 (ppm)

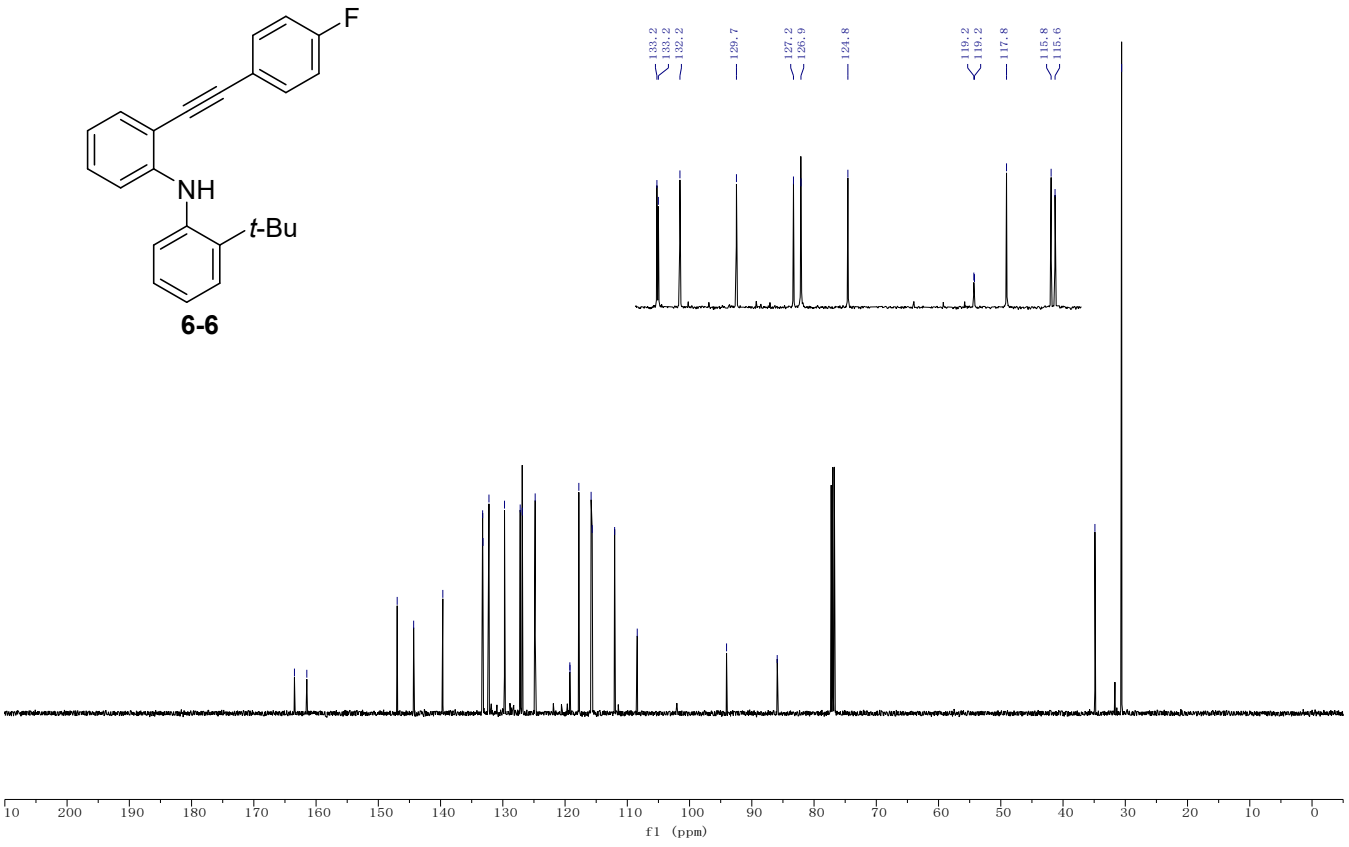

7.61
7.50
7.49
7.48
7.48
7.39
7.37
7.26
7.25
7.24
7.23
7.23
7.19
7.17
7.16
7.16
7.15
6.86
6.84
6.78
6.76
6.75
6.47
1.46
CF3
NH
t-Bu
6-5
4.00
2.08
1.03
0.81
2.19
1.00
1.00
0.99
9.14
f1 (ppm)

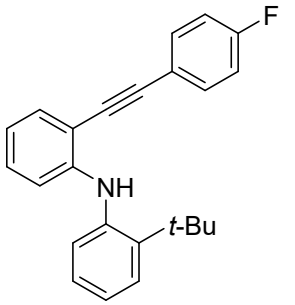

147.2
144.4
139.5
131.5
130.0
129.7
126.8
125.0
121.9
119.6
117.9
112.2
107.7
93.8
88.8
34.9
30.6
132.5
131.5
130.3
130.0
129.7
127.3
127.1
127.0
126.9
126.8
125.4
125.4
125.3
125.0
CF3
NH
t-Bu
6-5
f1 (ppm)


-62.8
CF3
NH
t-Bu
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

6-5

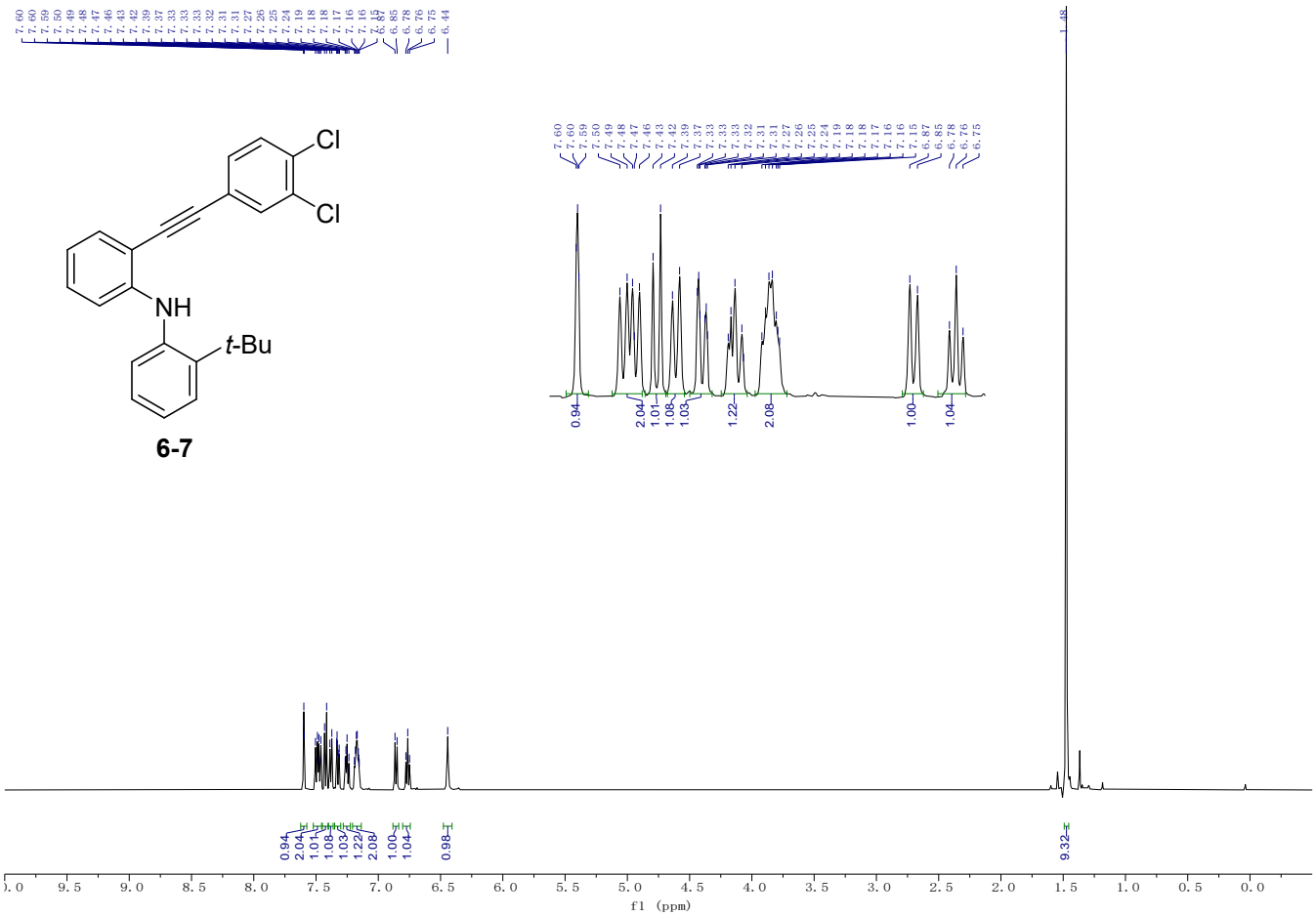

F
NH
t-Bu
6-6
f1 (ppm)

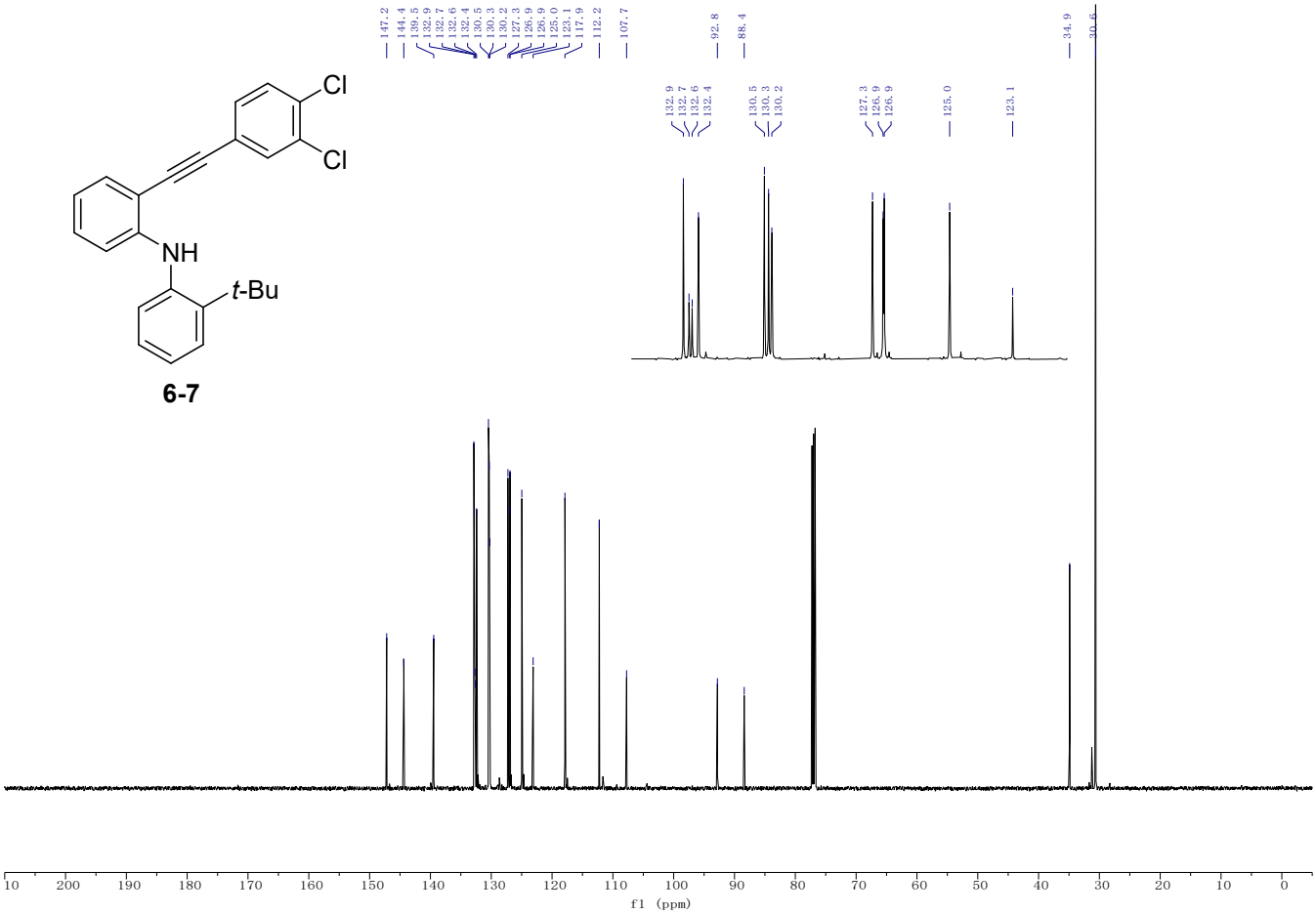

F
NH
t-Bu
6-6
f1 (ppm)

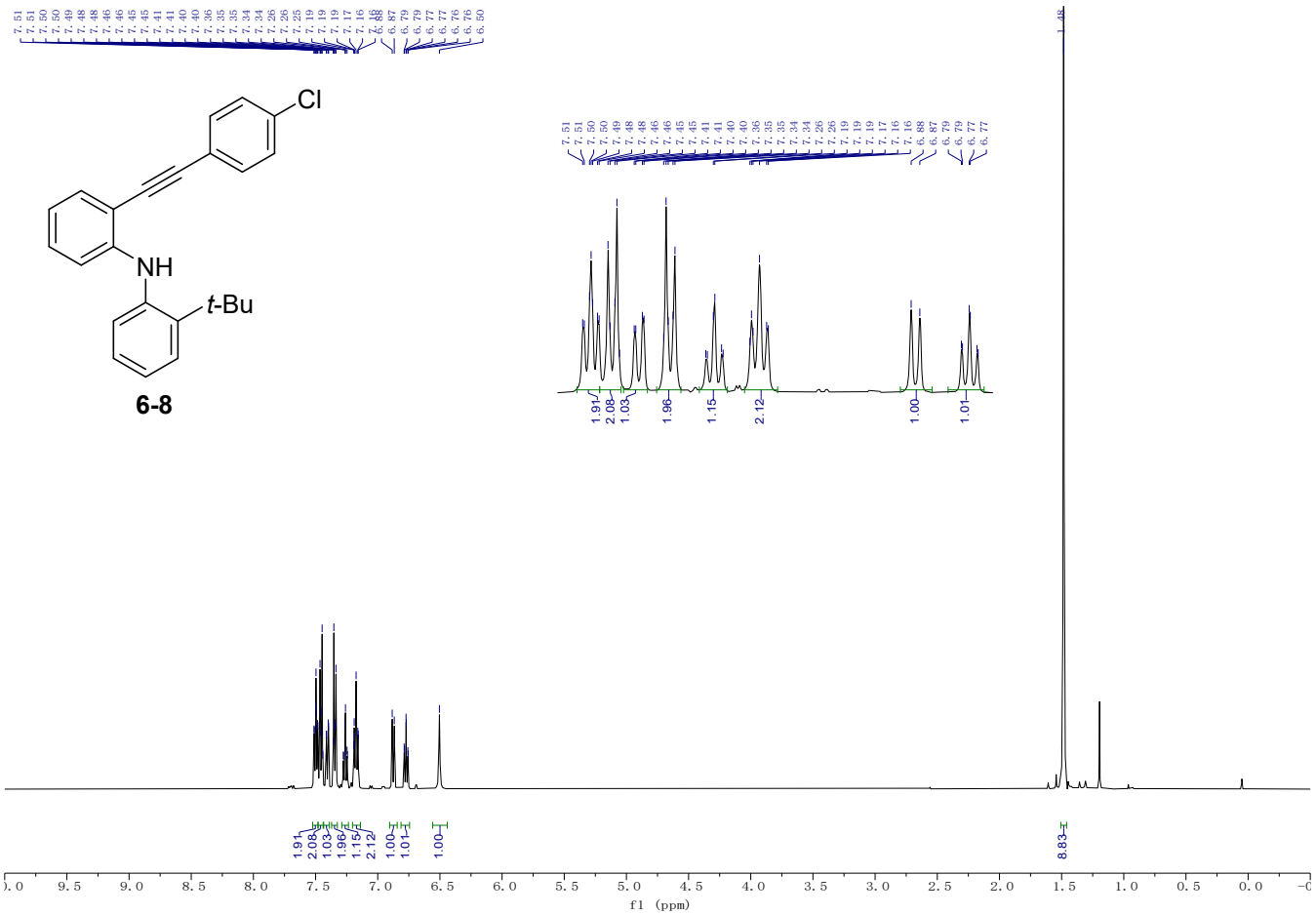

F
NH
t-Bu

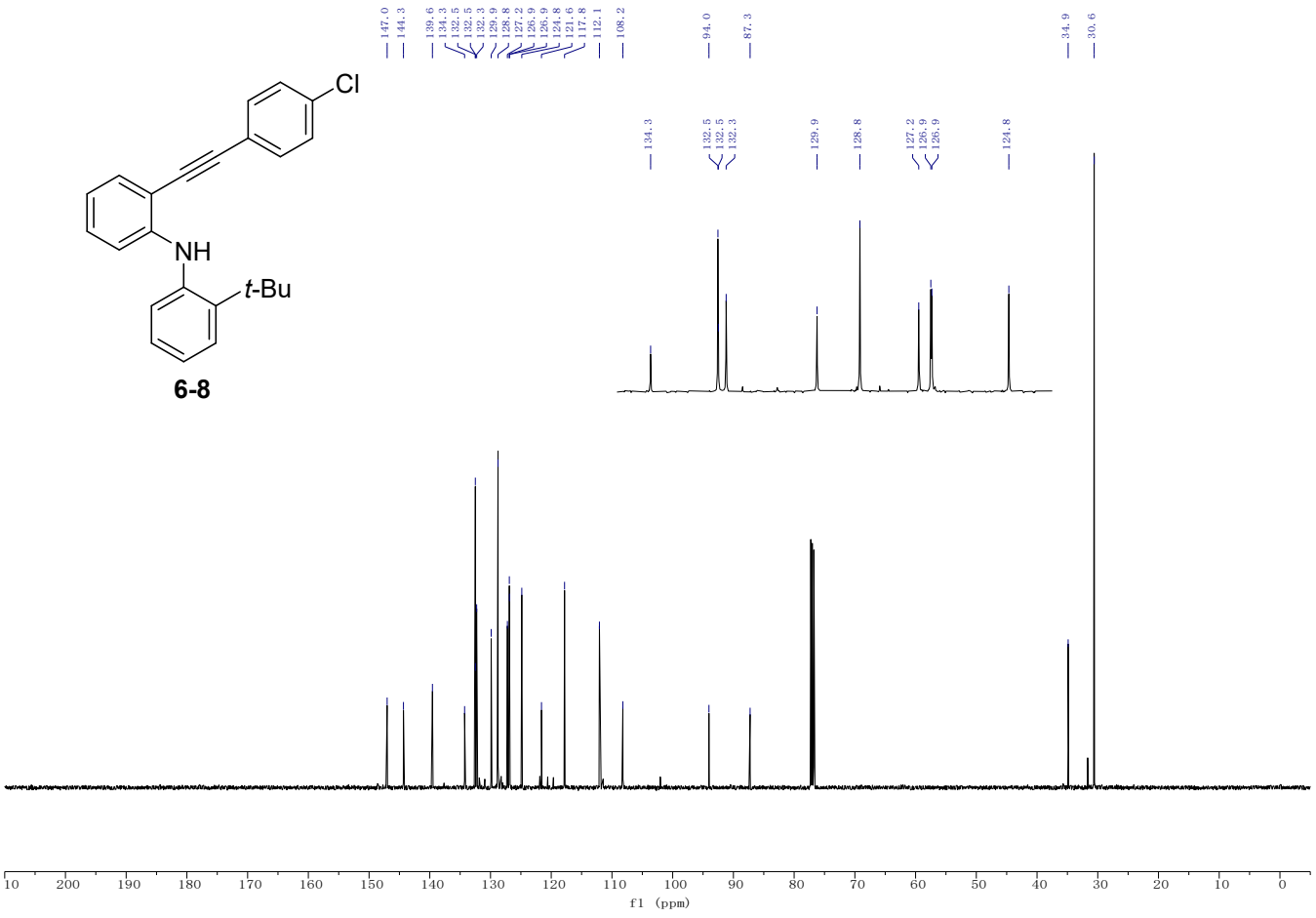
6-6

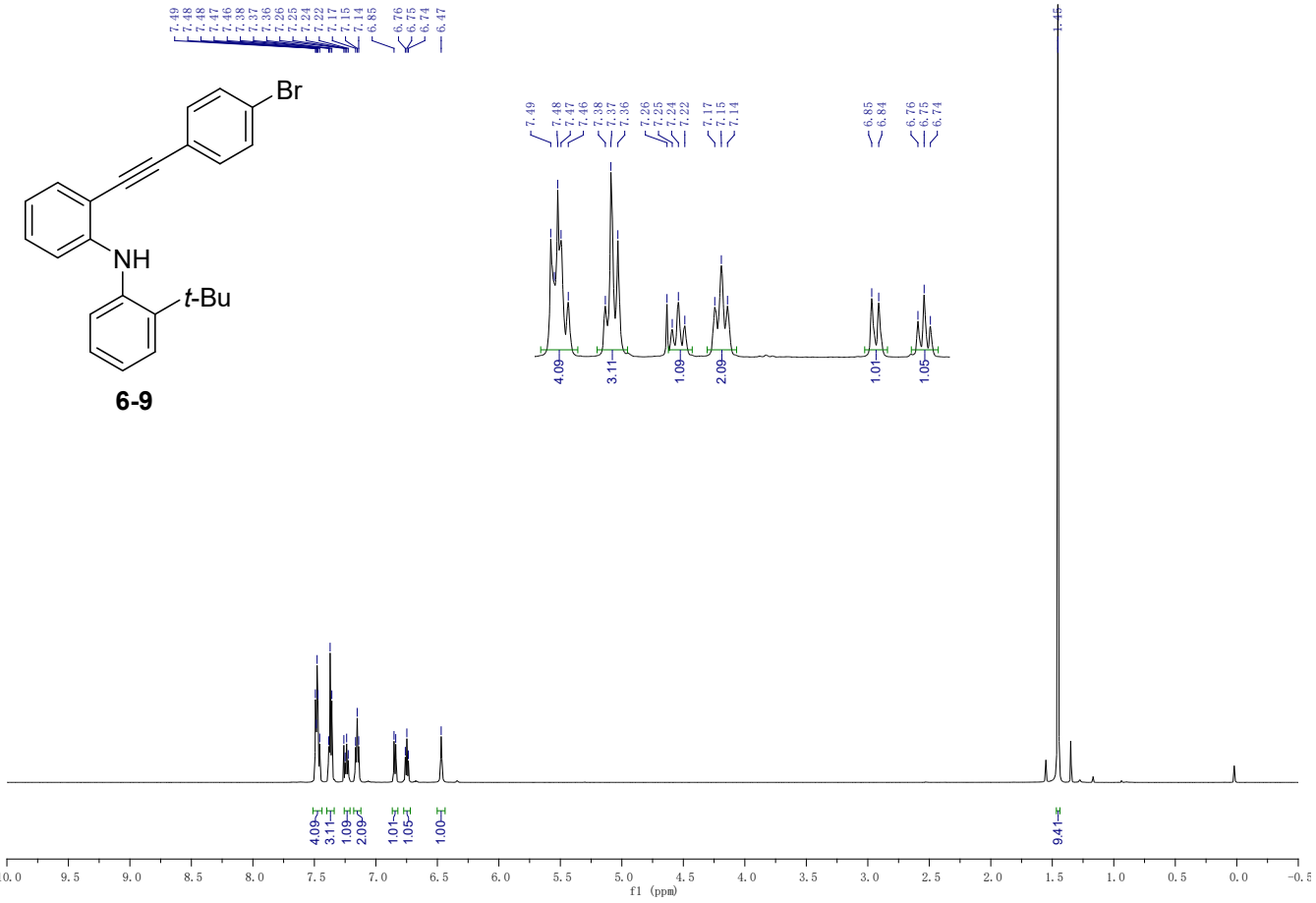
-110.7
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

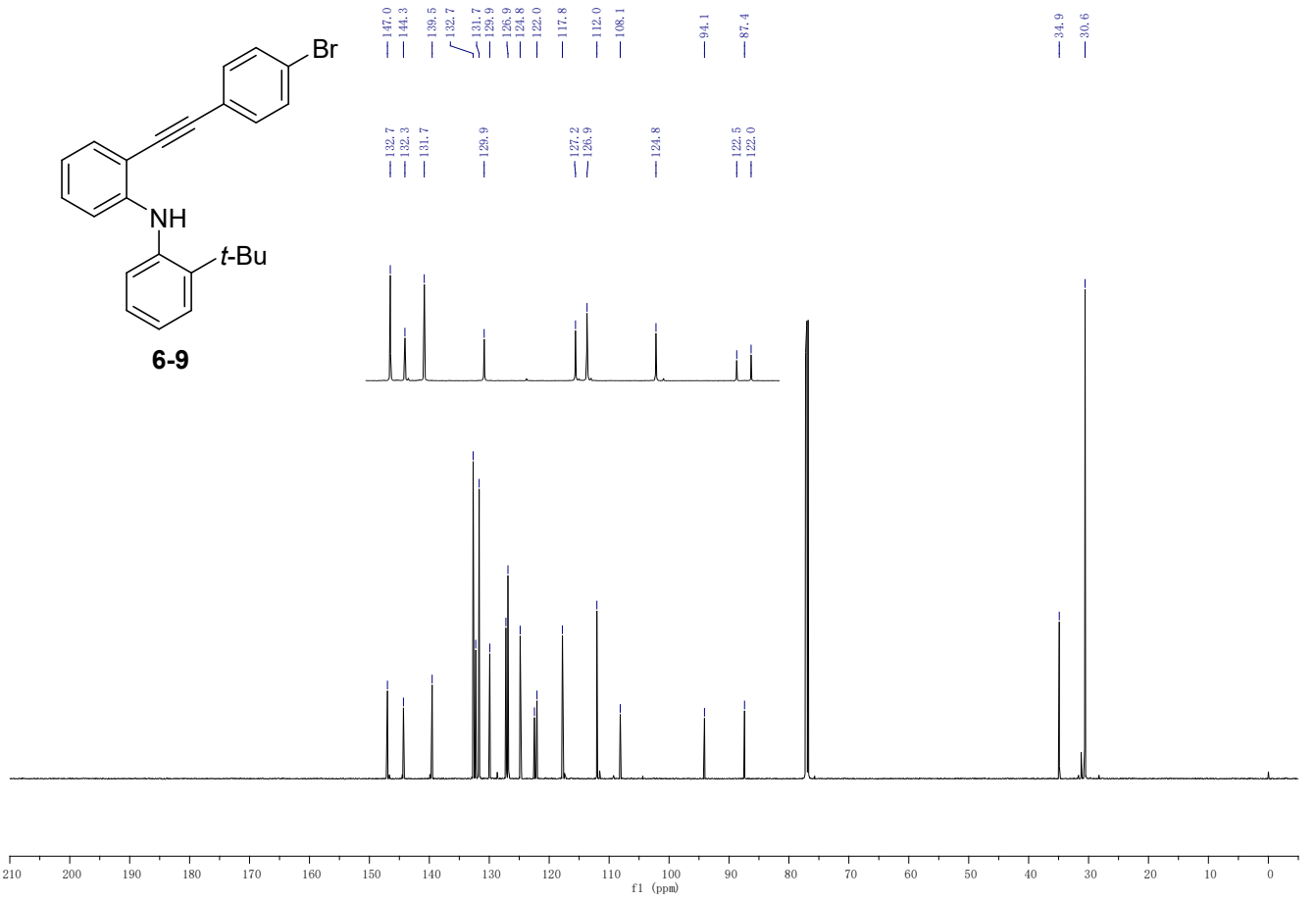

Cl
Cl
NH
t-Bu
6-7
f1 (ppm)

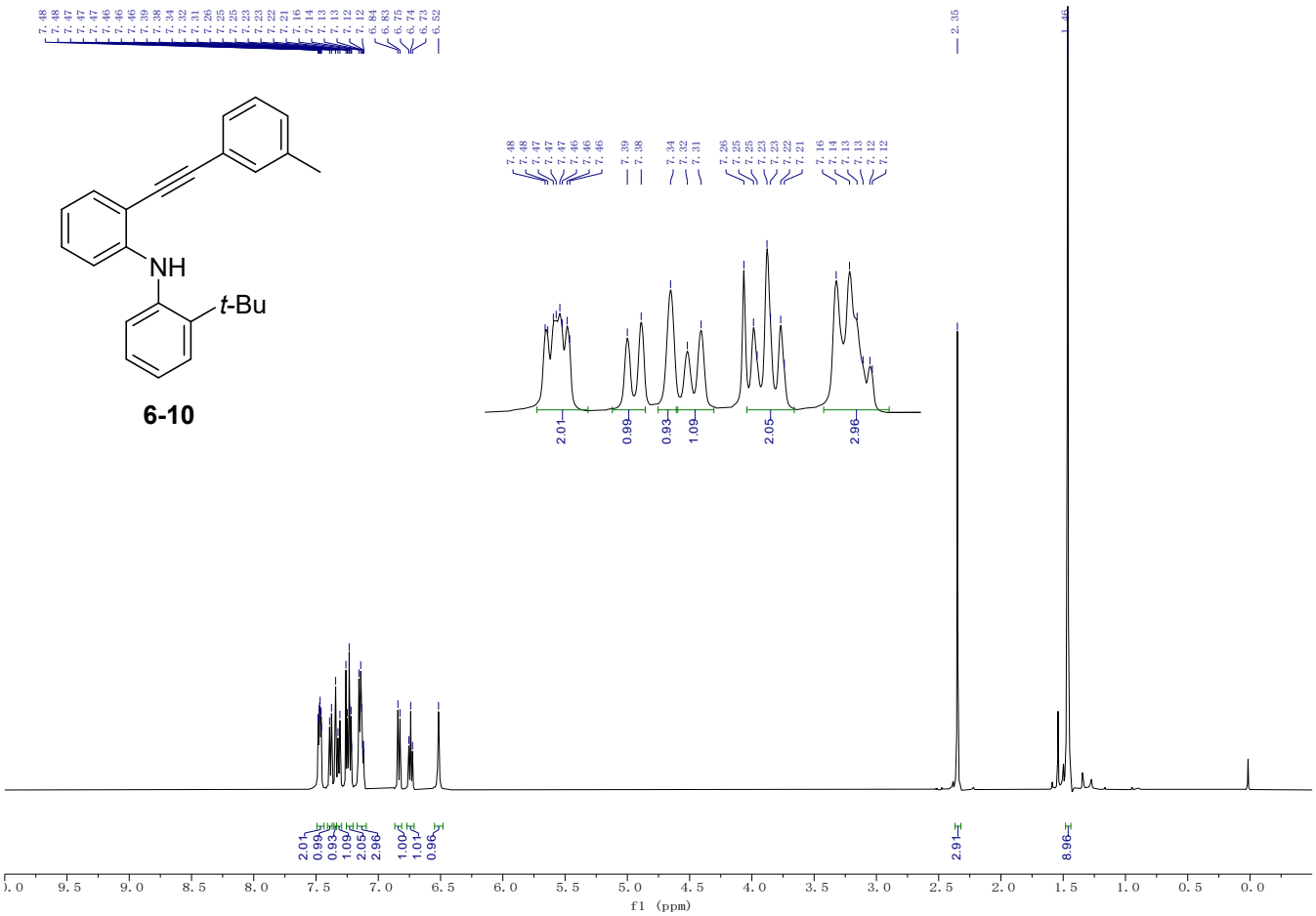

Cl
Cl
NH
t-Bu
6-7
f1 (ppm)

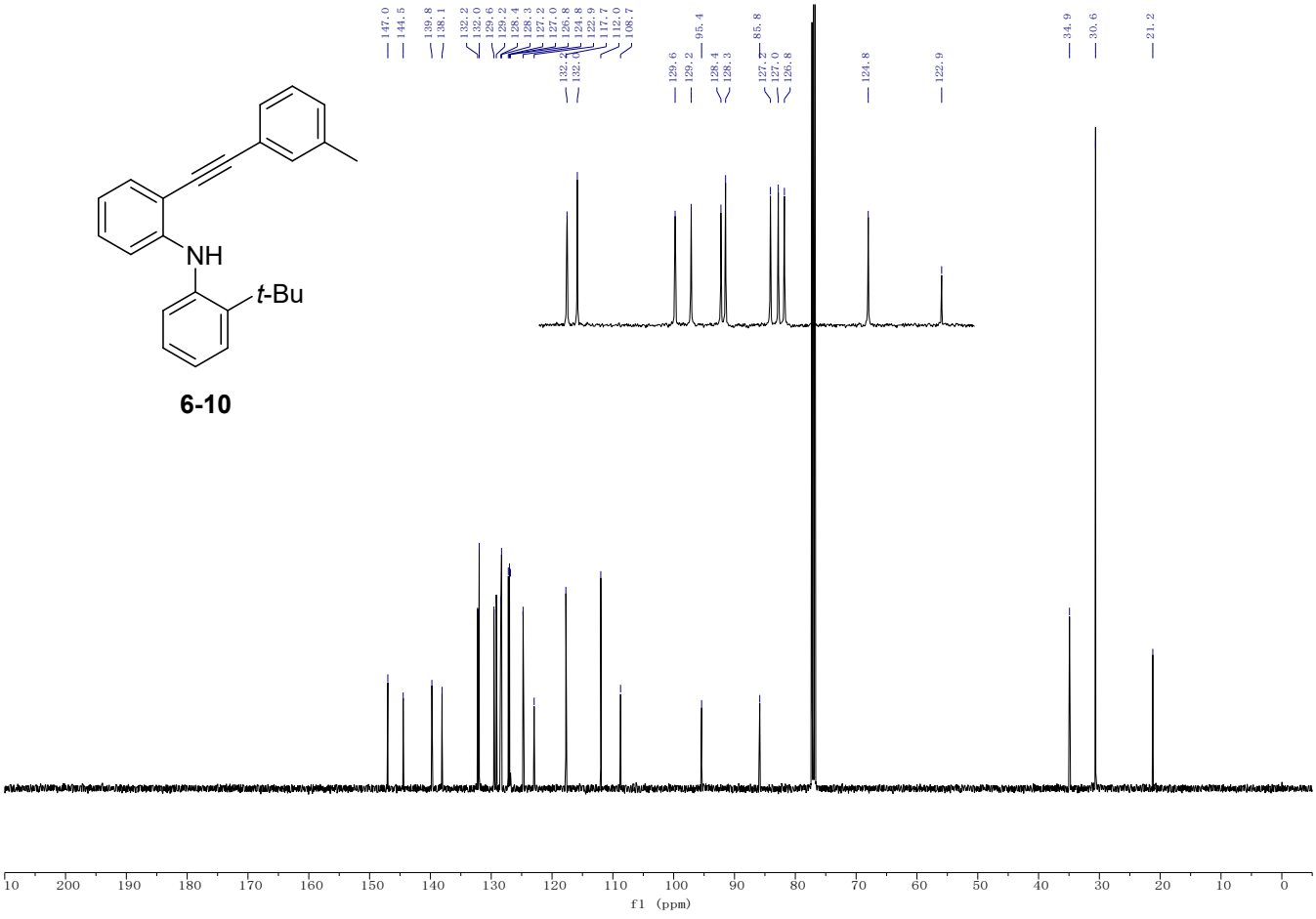

Cl
NH
t-Bu
6-8
f1 (ppm)

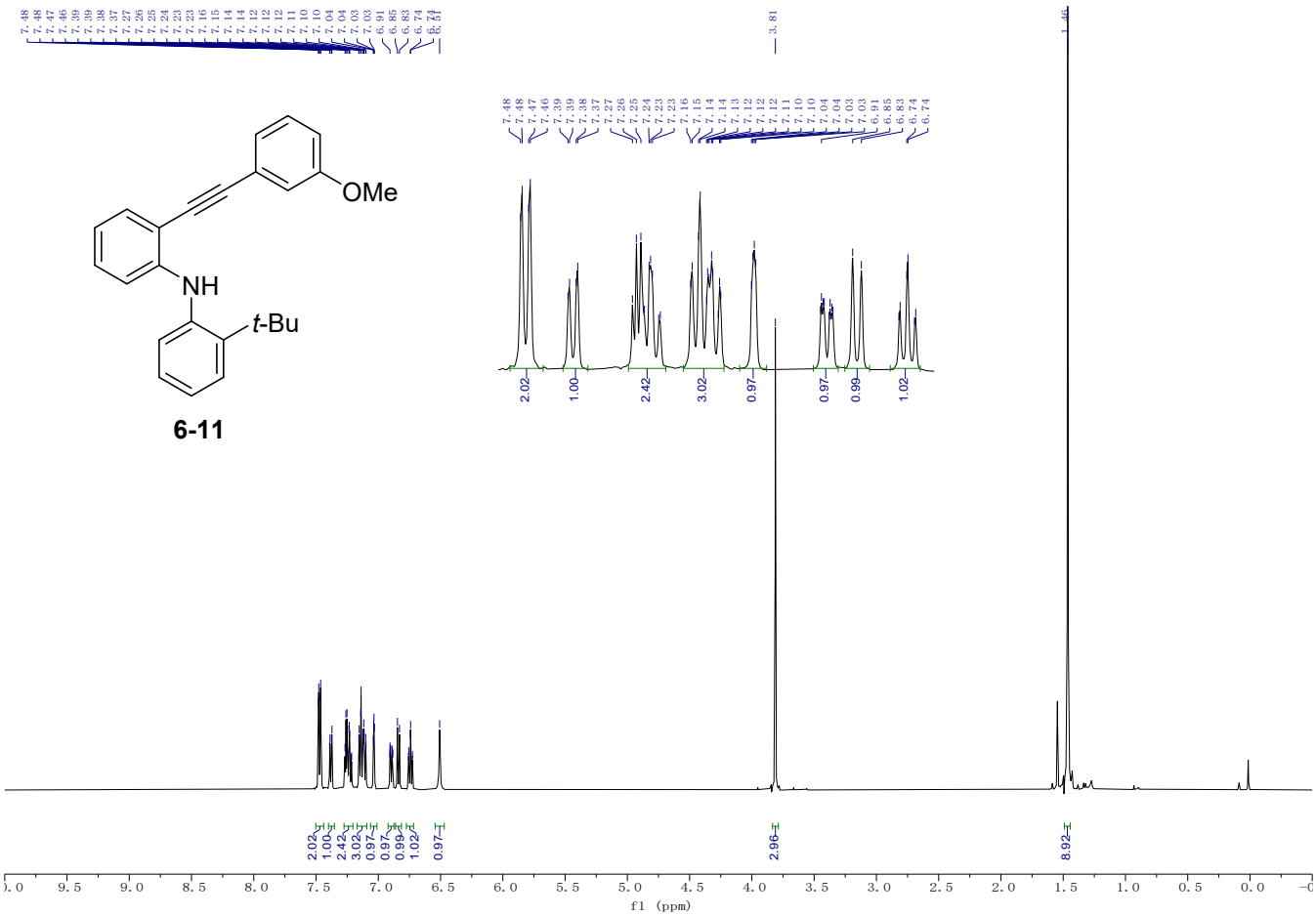

Cl
NH
t-Bu
6-8
f1 (ppm)

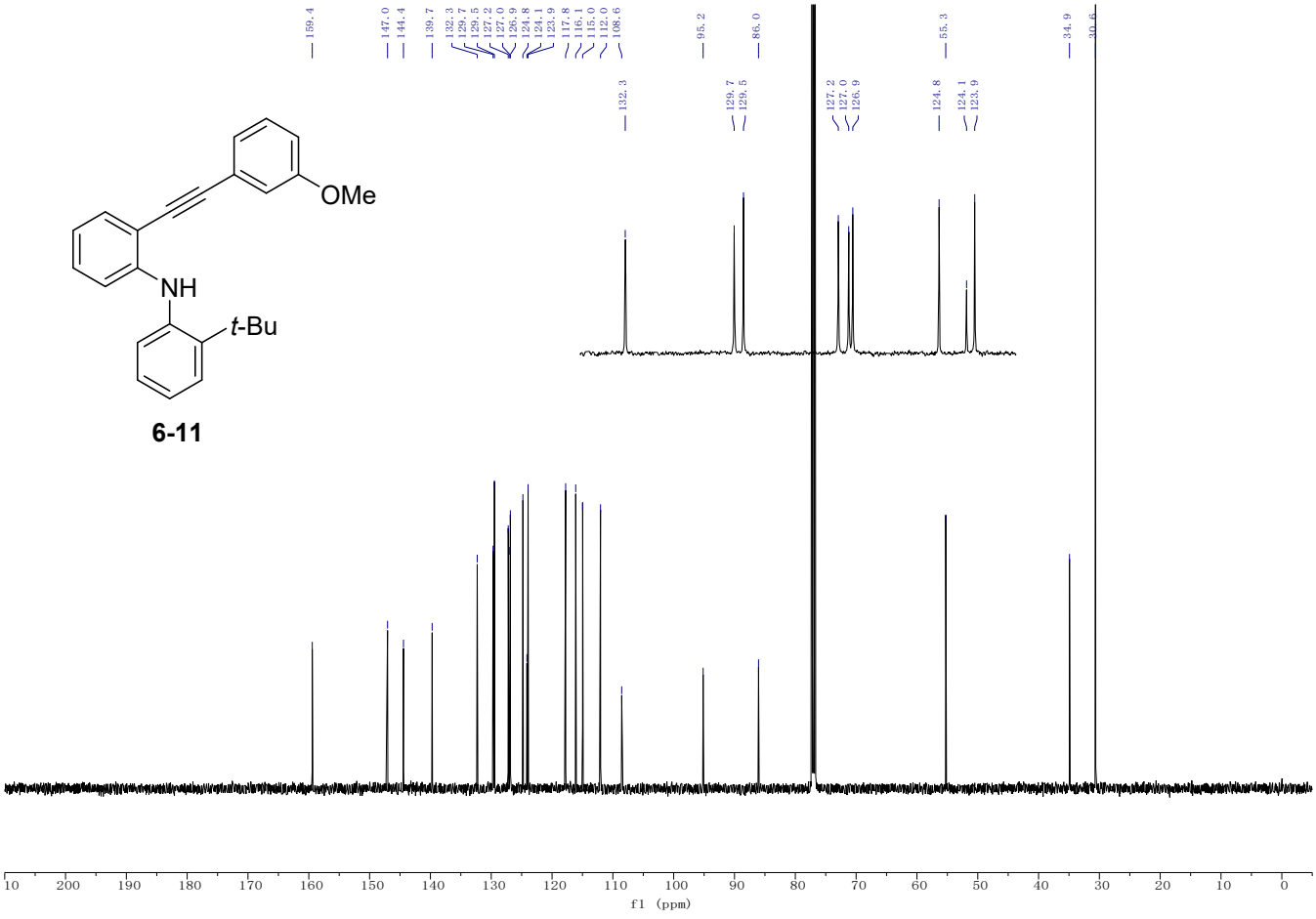

Br
NH
t-Bu
6-9
f1 (ppm)

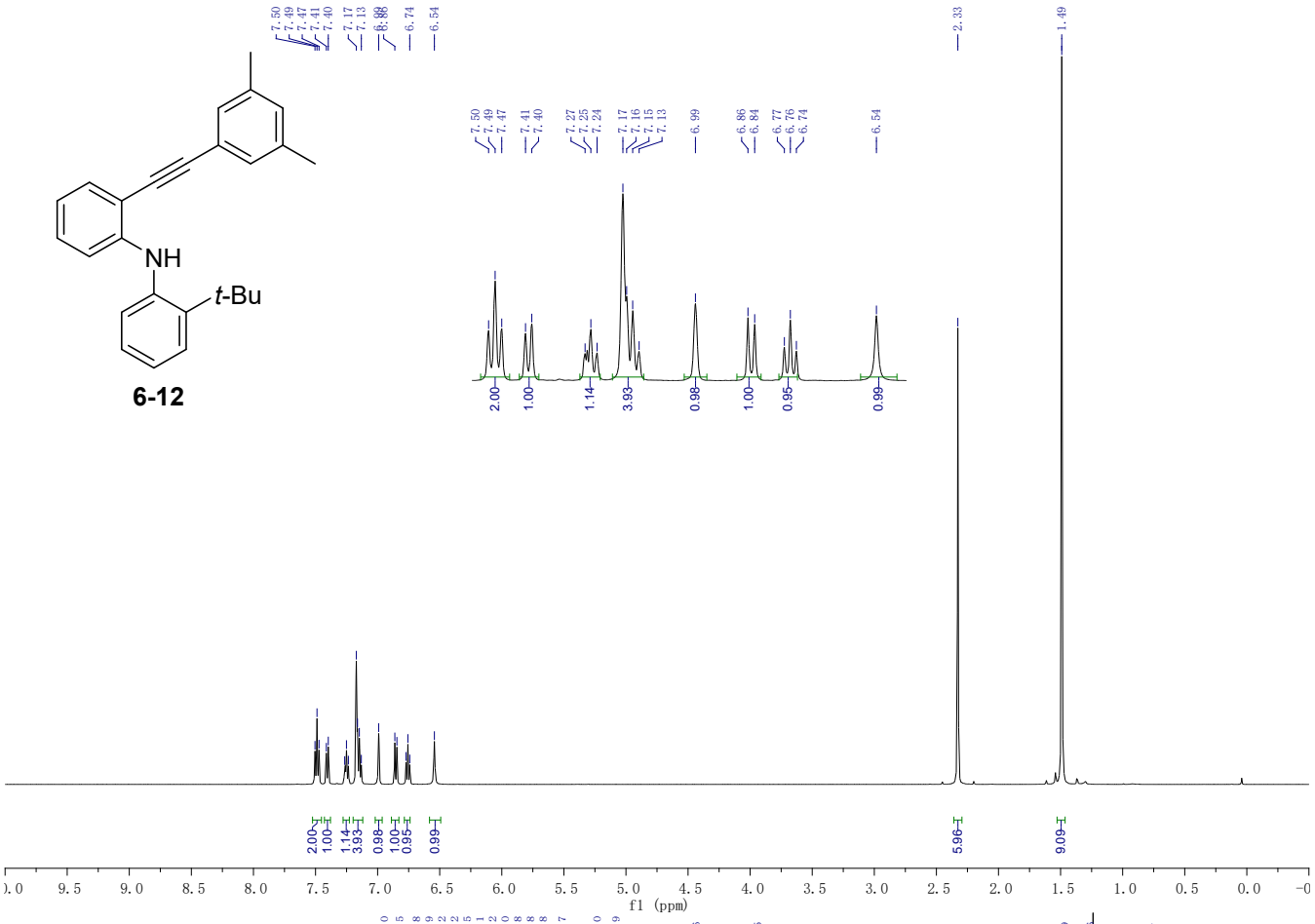

Br
NH
t-Bu
6-9
f1 (ppm)

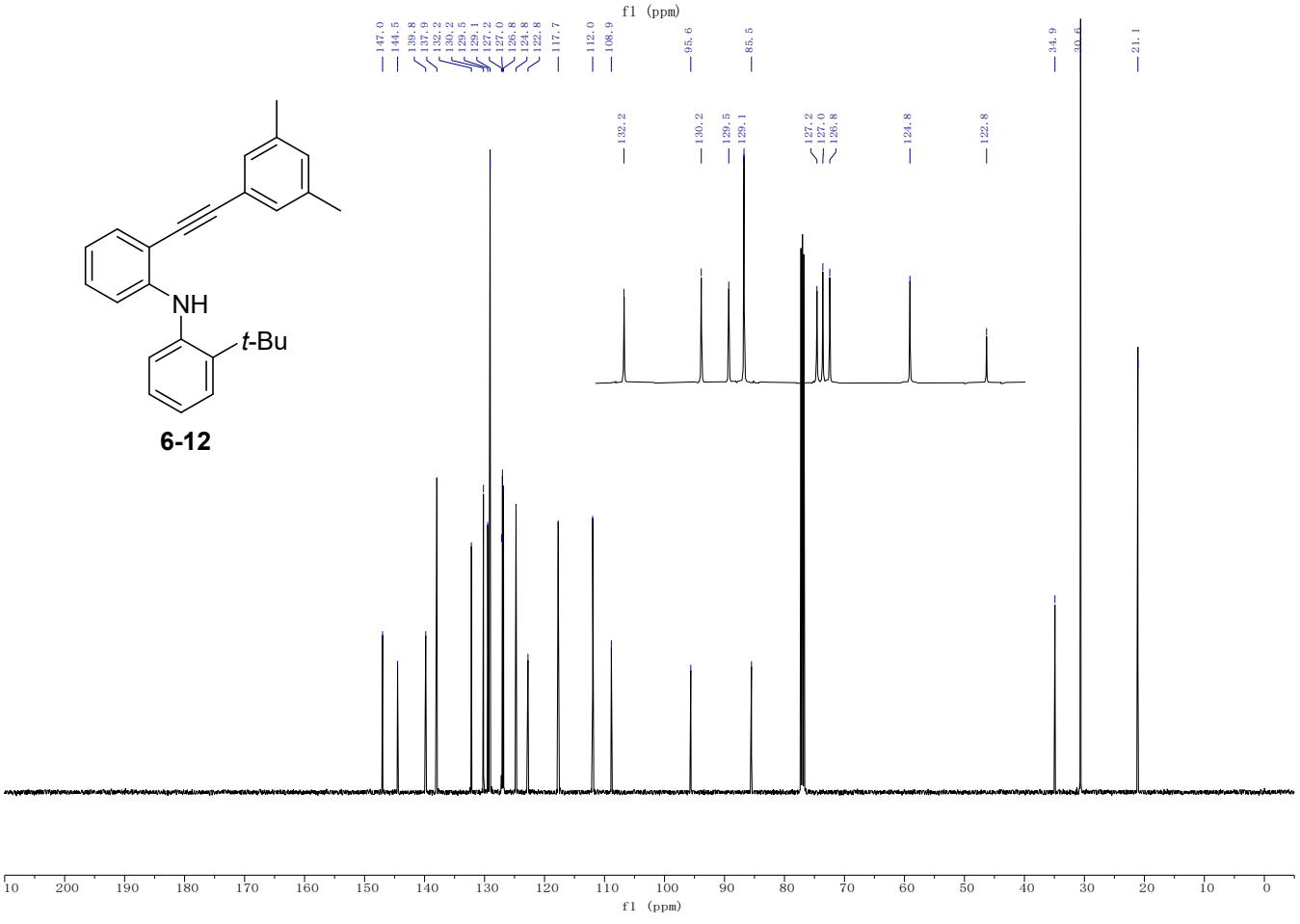

NH
t-Bu
6-10
f1 (ppm)

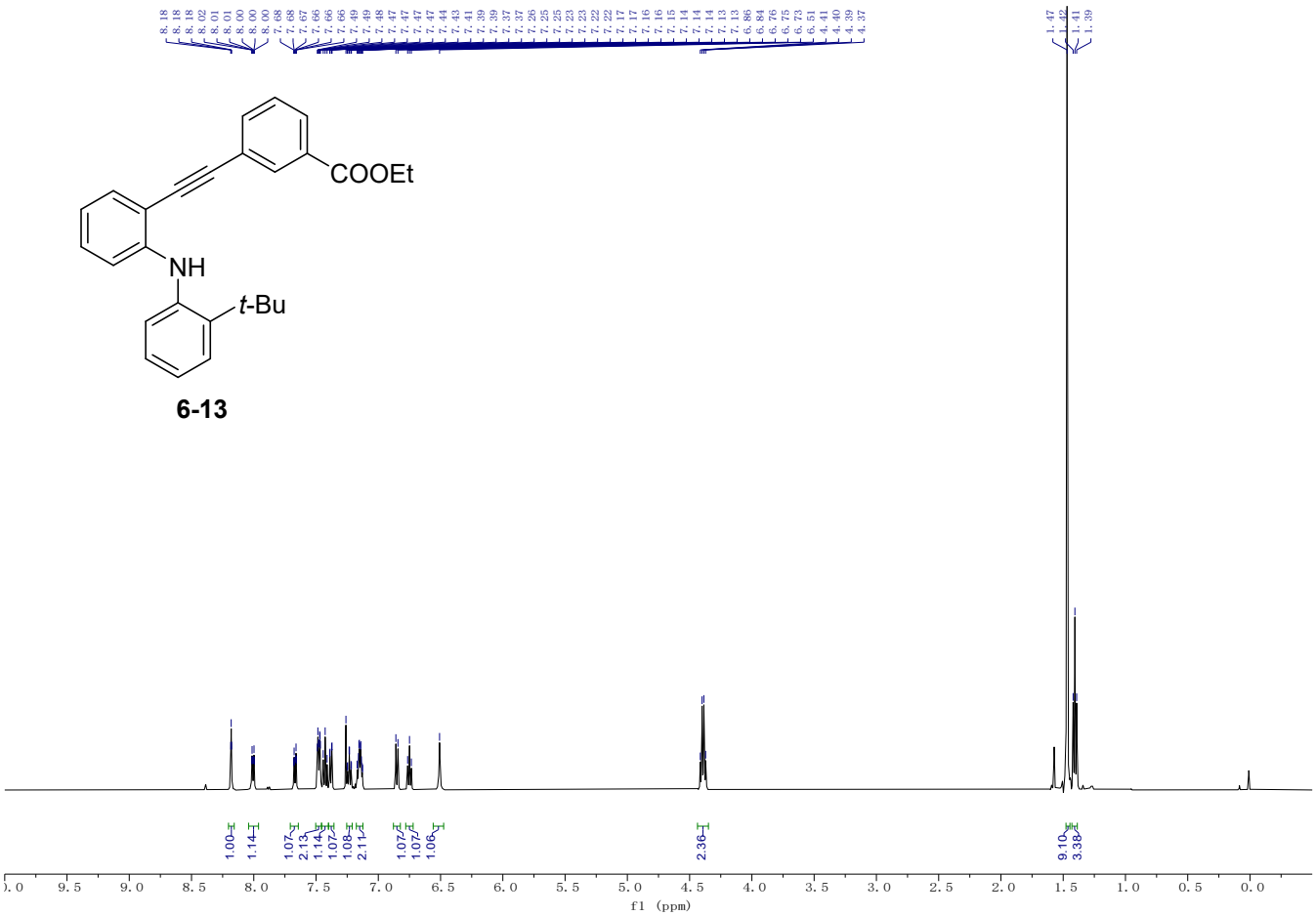

NH
t-Bu
6-10
f1 (ppm)

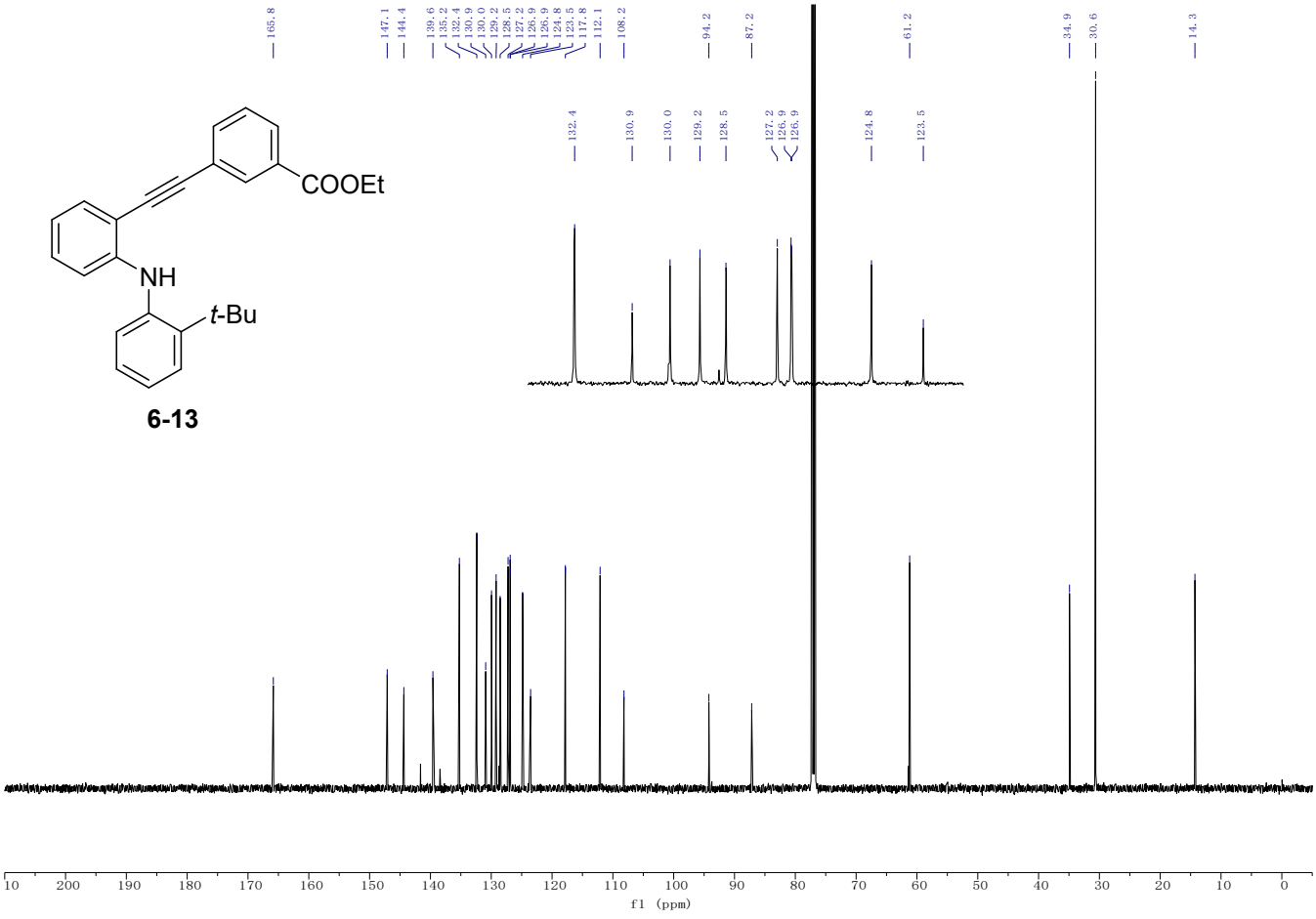

OMe
NH
t-Bu
6-11
f1 (ppm)

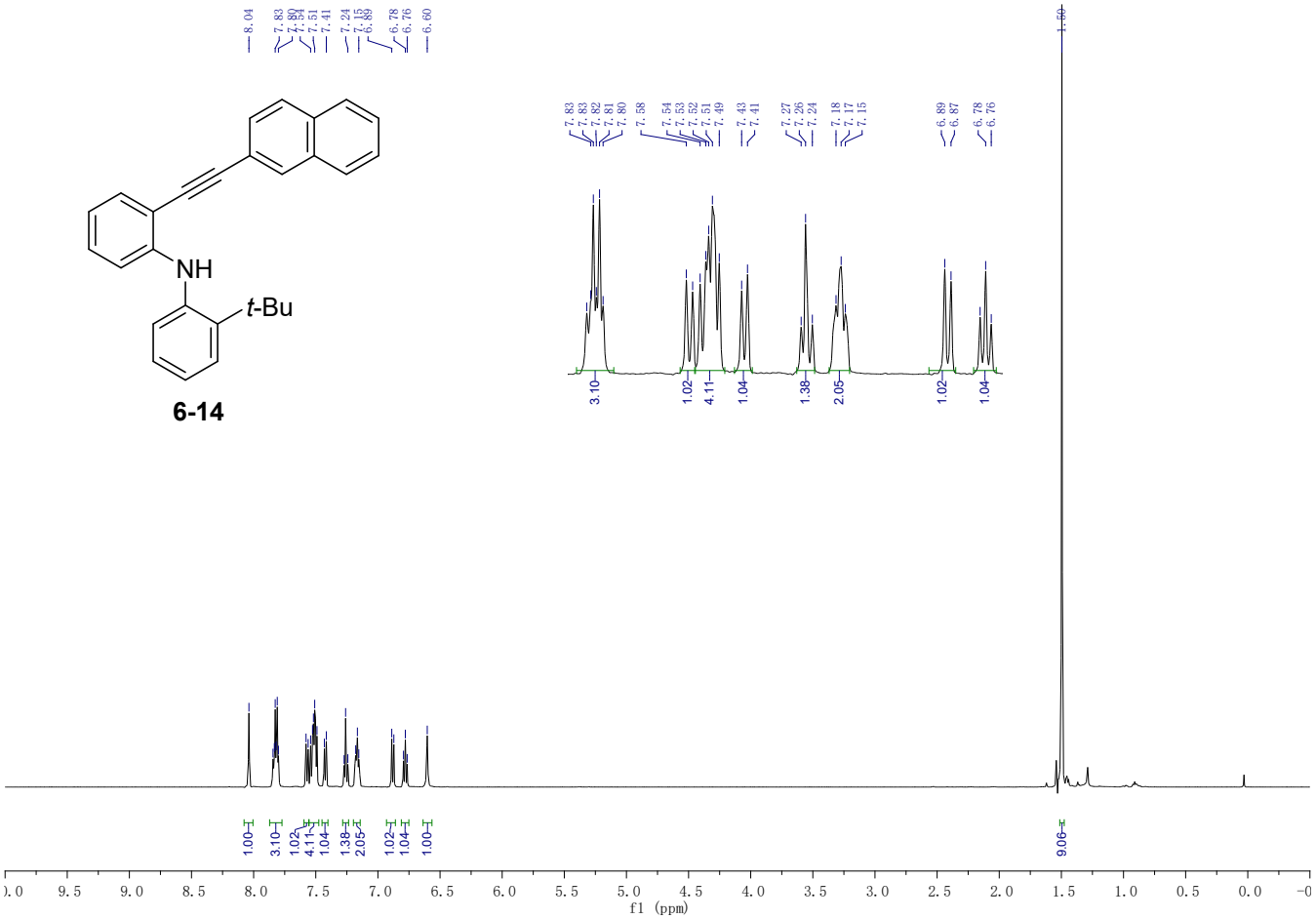

OMe
NH
t-Bu
6-11
f1 (ppm)

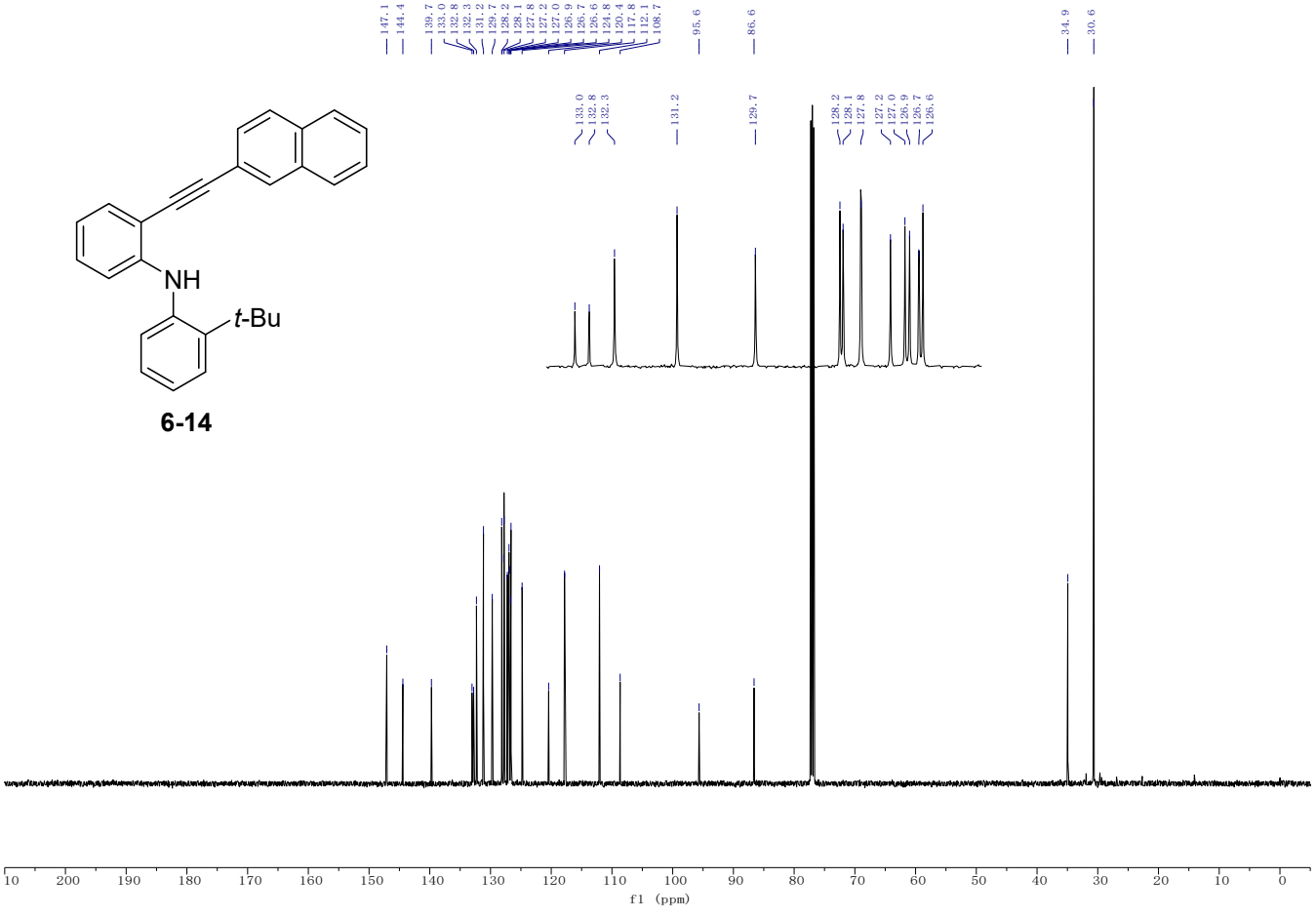

NH
t-Bu
6-12
f1 (ppm)

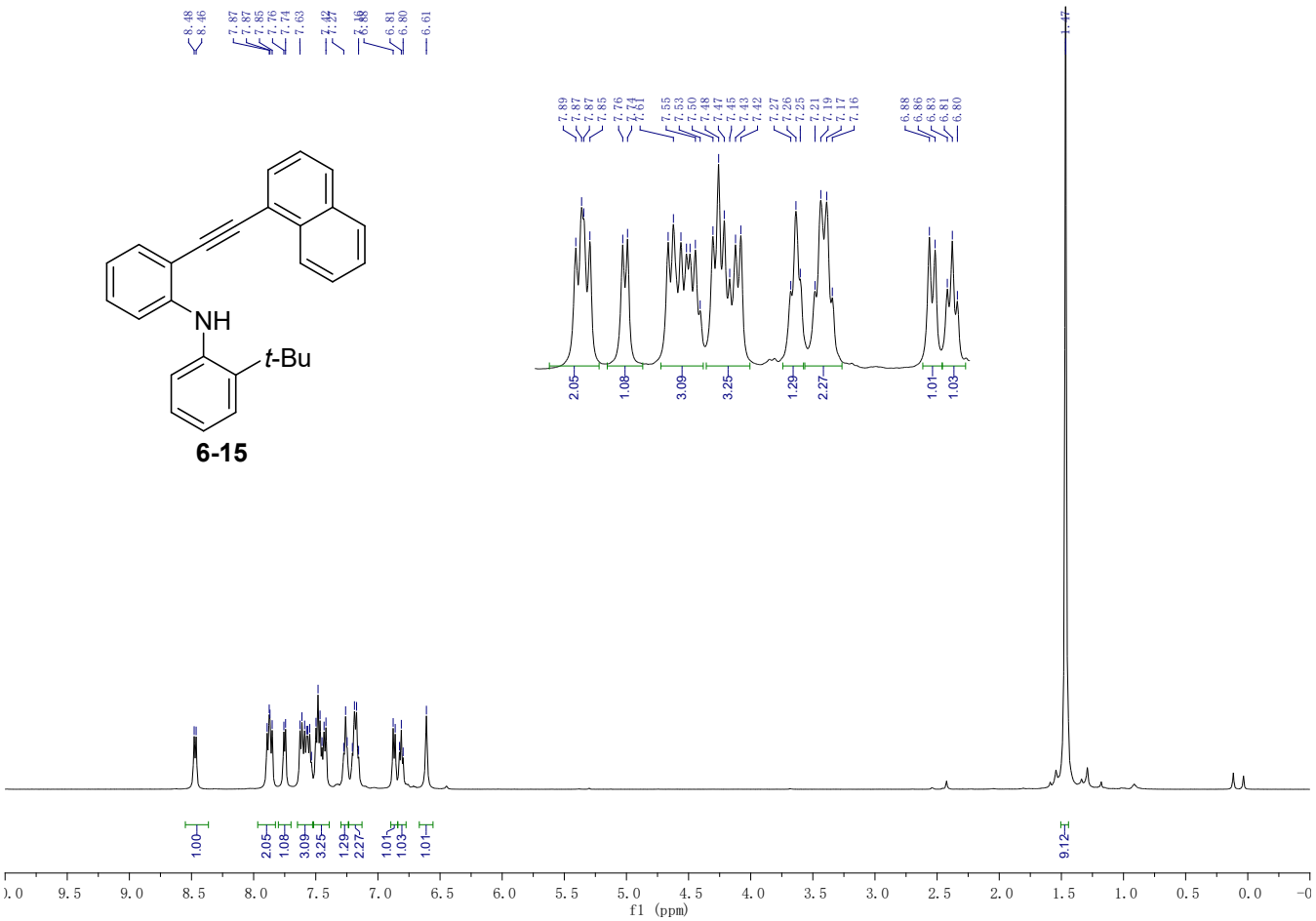

NH
t-Bu
6-12
f1 (ppm)

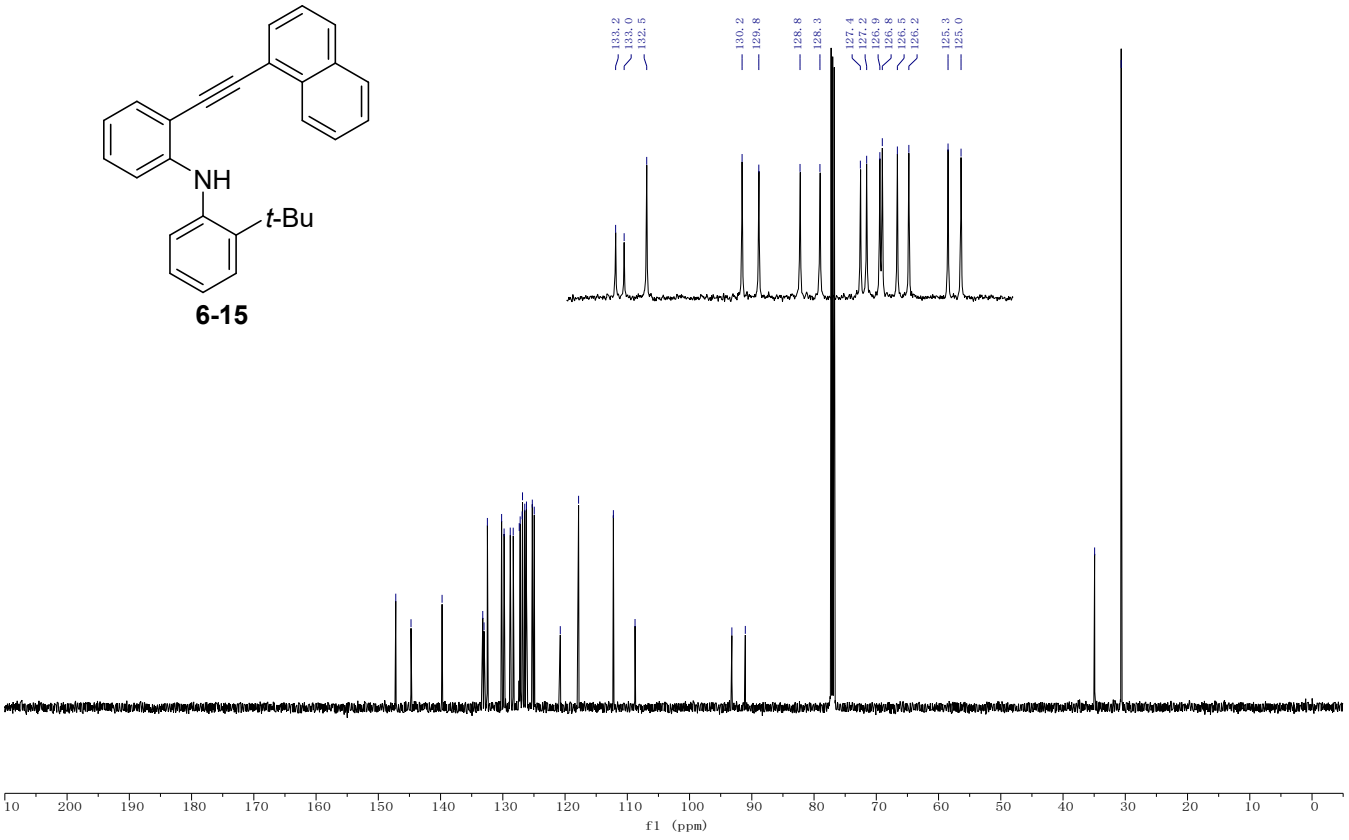

COOEt
NH
t-Bu
6-13
f1 (ppm)

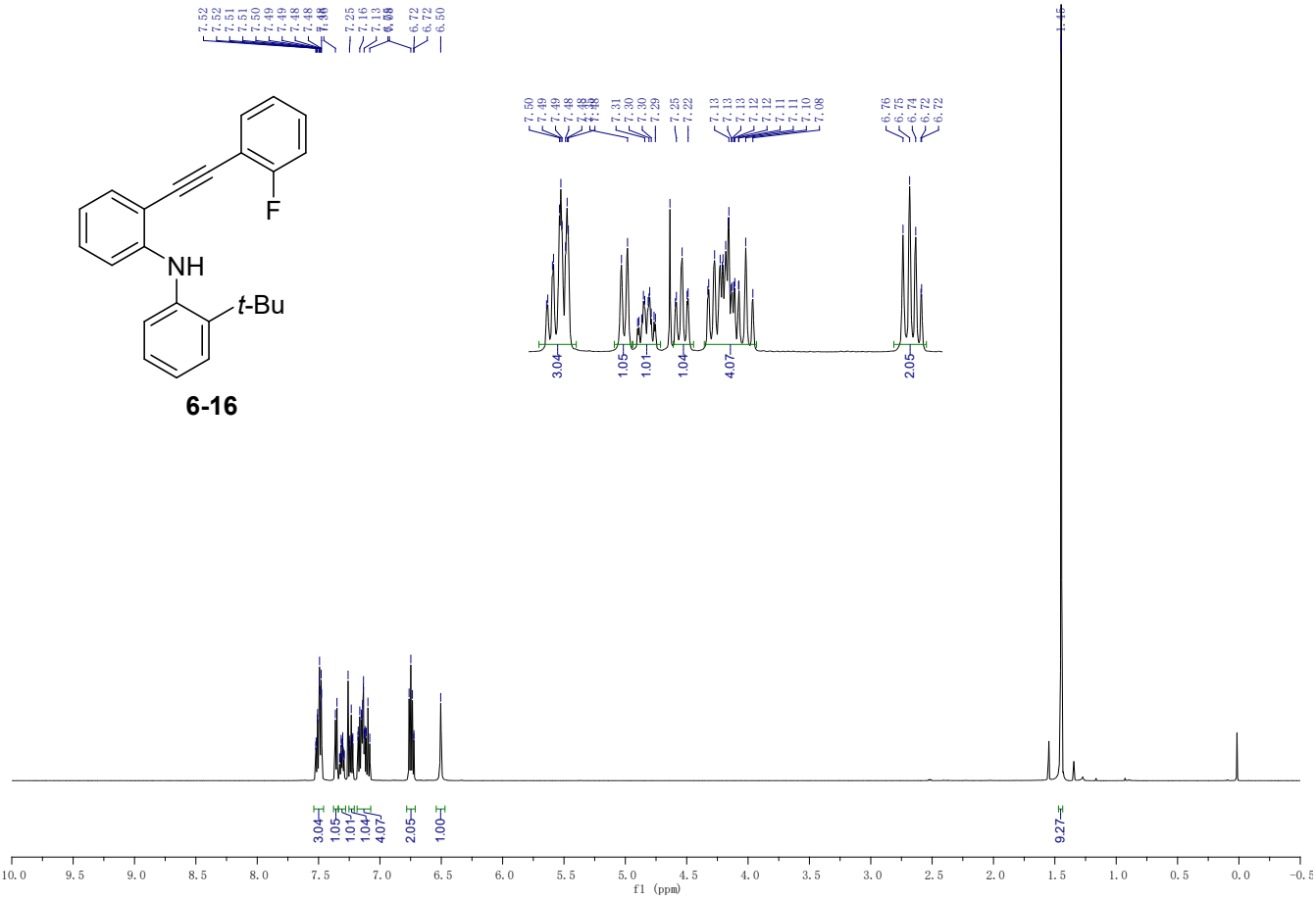

COOEt
NH
t-Bu
6-13
f1 (ppm)

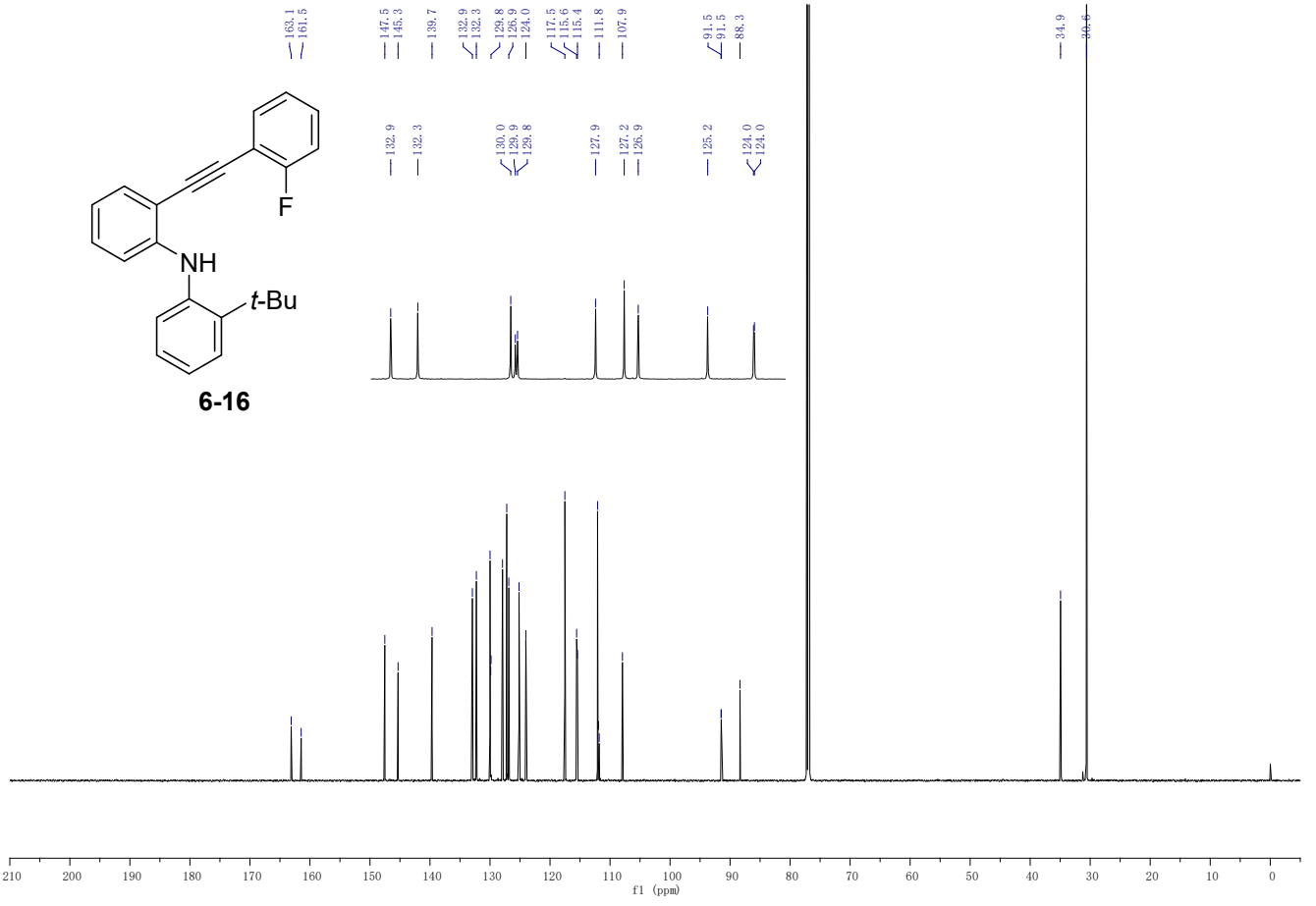

8.04
7.83
7.80
7.54
7.51
7.41
7.24
7.15
6.89
6.78
6.76
6.60
1.60
NH
t-Bu
6-14
f1 (ppm)

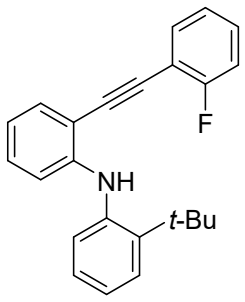

147.1
144.4
139.7
133.0
132.8
132.3
131.2
129.7
128.2
128.1
127.8
127.2
127.0
126.9
126.7
126.6
124.8
120.4
117.8
112.1
108.7
95.6
86.6
34.9
30.6
NH
t-Bu
6-14
f1 (ppm)


NH
t-Bu
6-15
f1 (ppm)


NH
t-Bu
6-15
f1 (ppm)


F
NH
t-Bu
6-16
3.04
1.05
1.01
1.04
4.07
2.05
1.00
9.27
f1 (ppm)


F
NH
t-Bu
6-16
f1 (ppm)


F
NH
t-Bu

6-16

-109.5
10
0
-10
-20
-30
-40
-50
-60
-70
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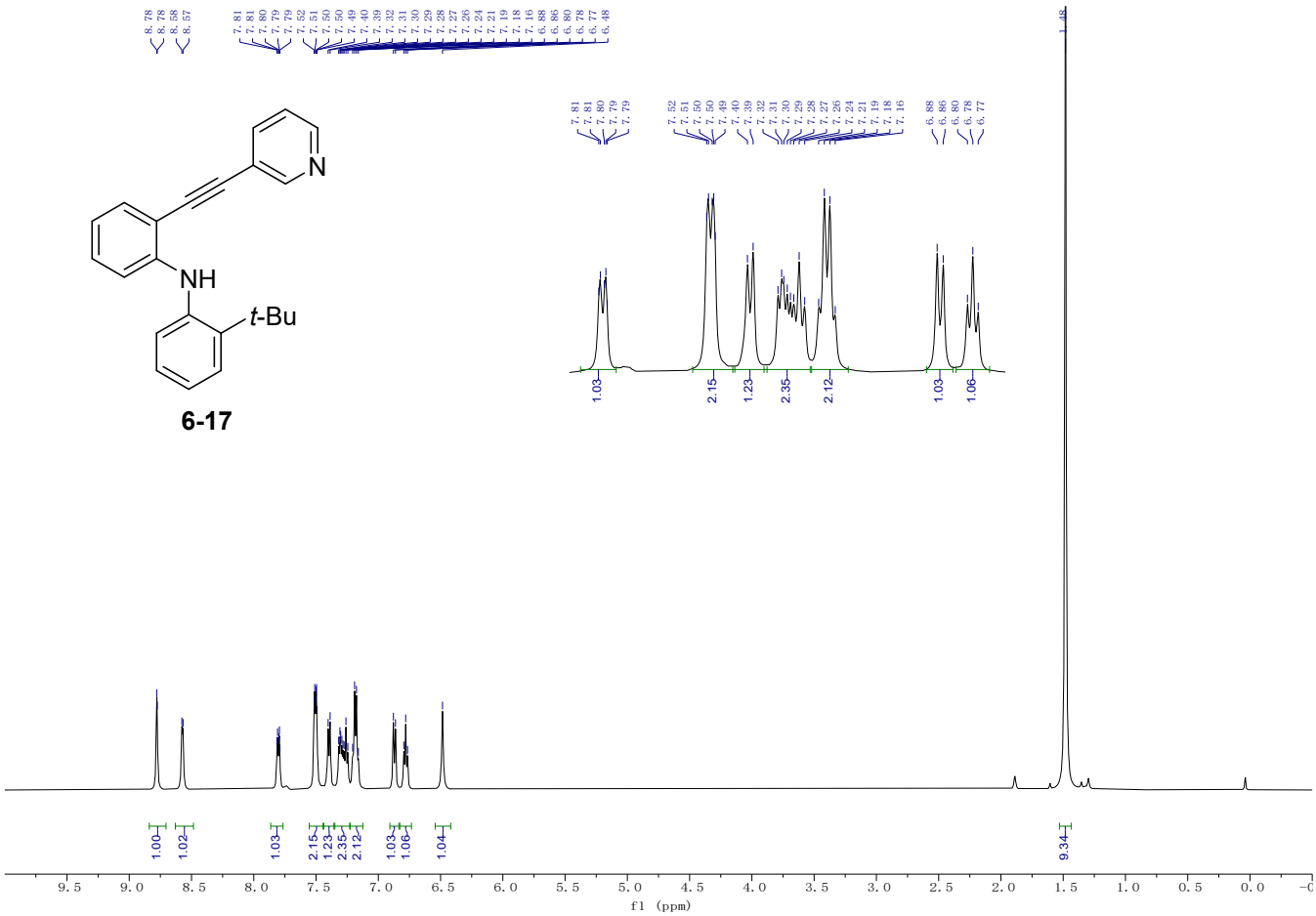
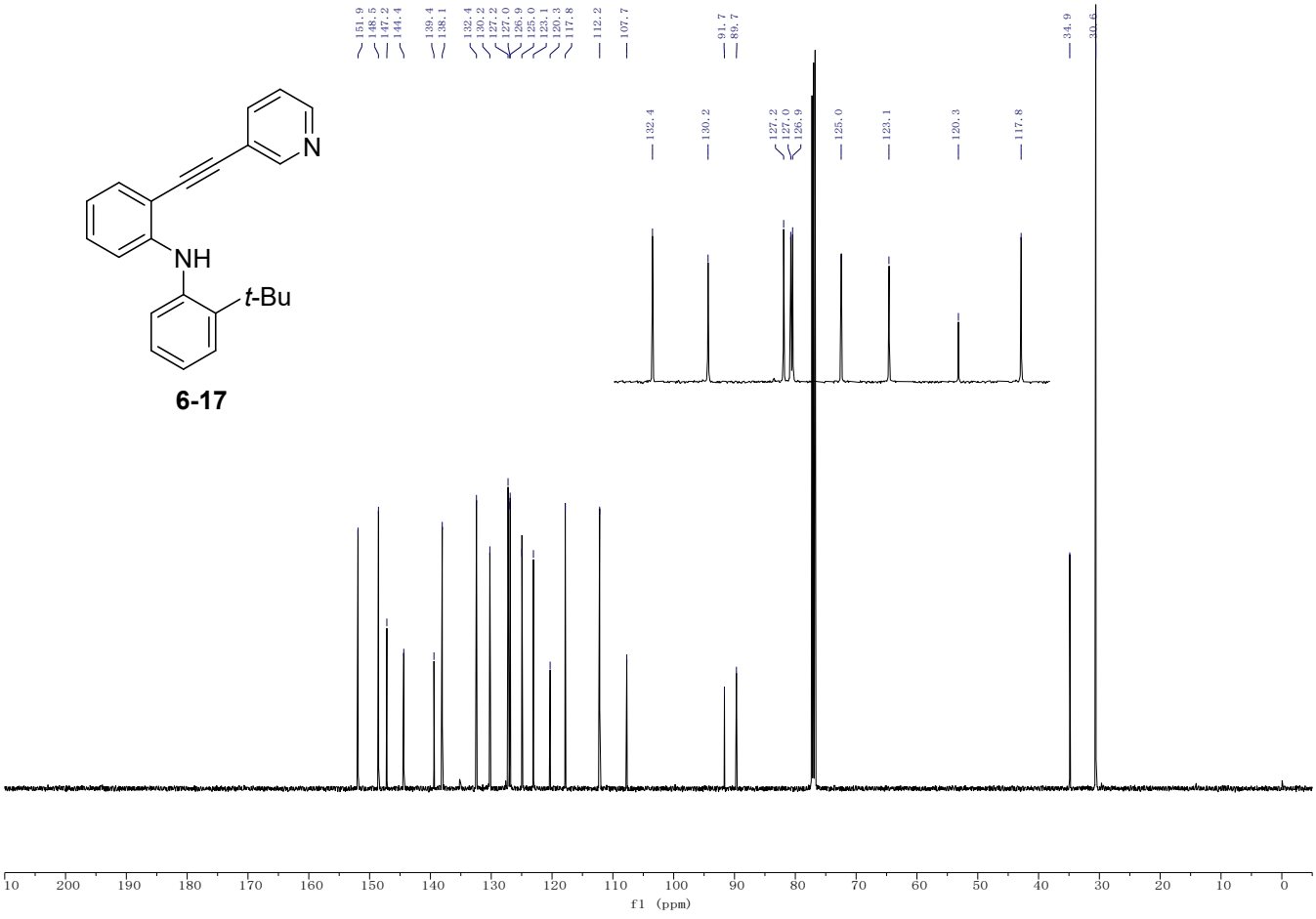
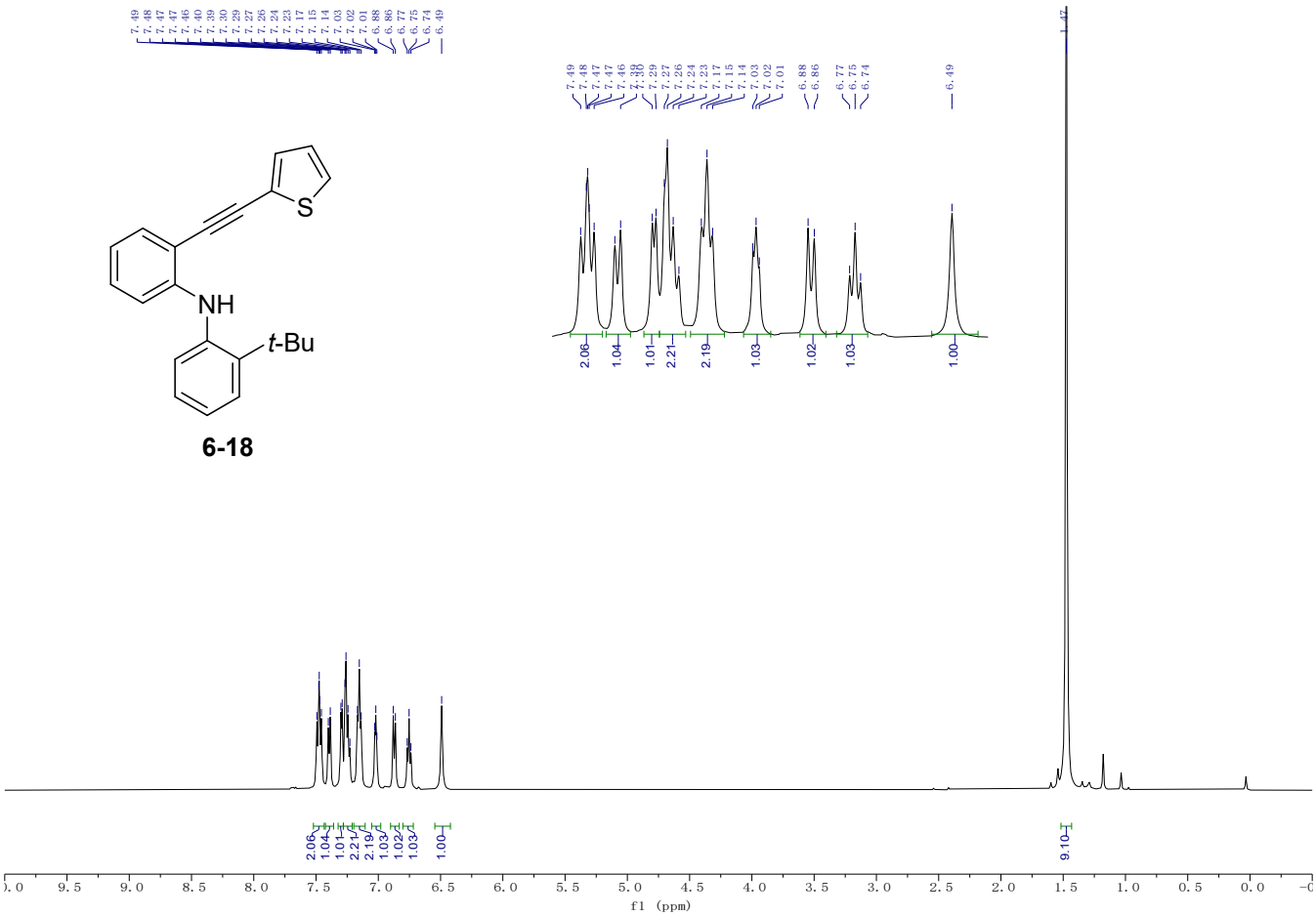
-170
-180
-190
-200
-210
f1 (ppm)


N
NH
t-Bu
6-17
f1 (ppm)


N
NH
t-Bu
6-17
f1 (ppm)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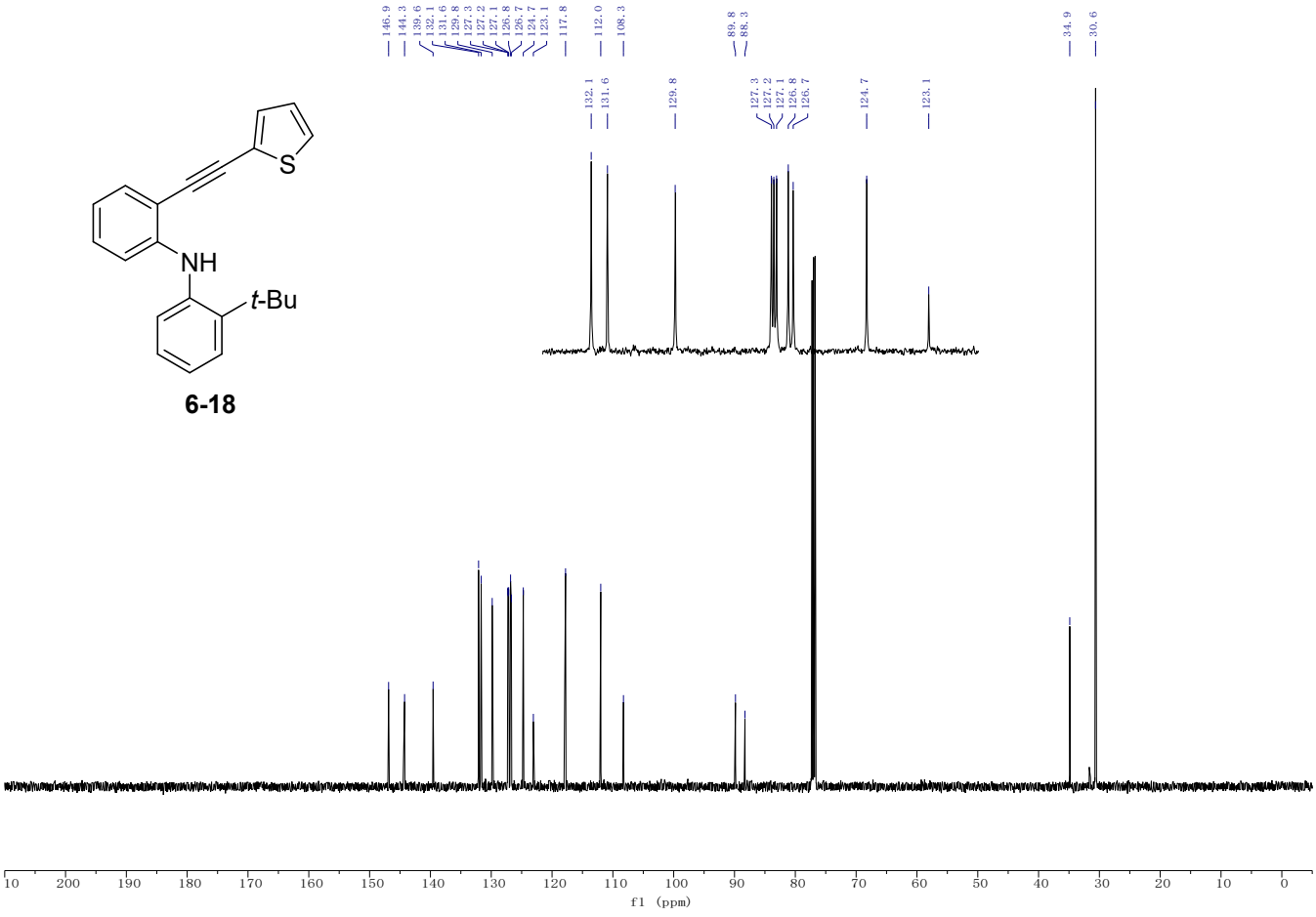
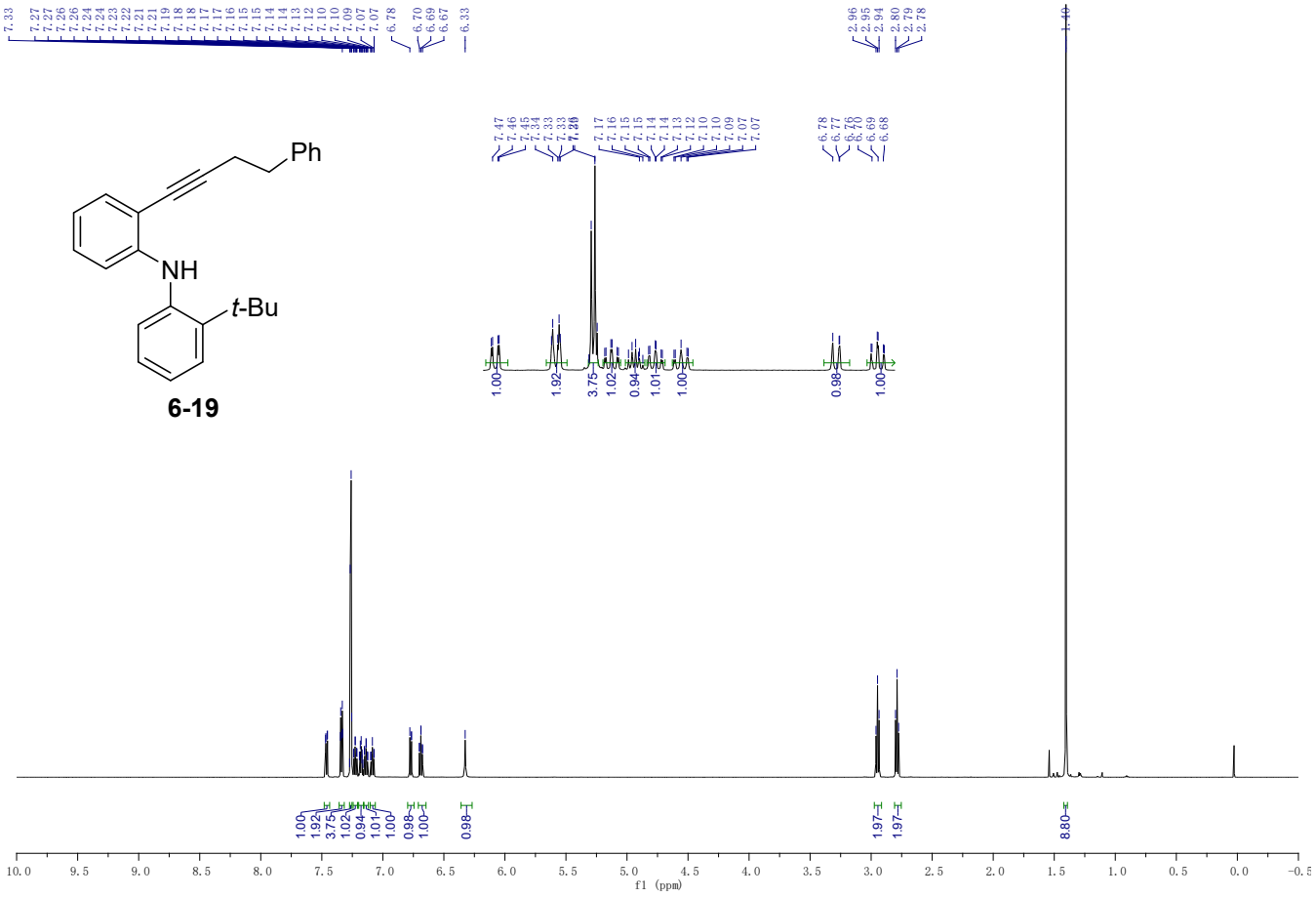
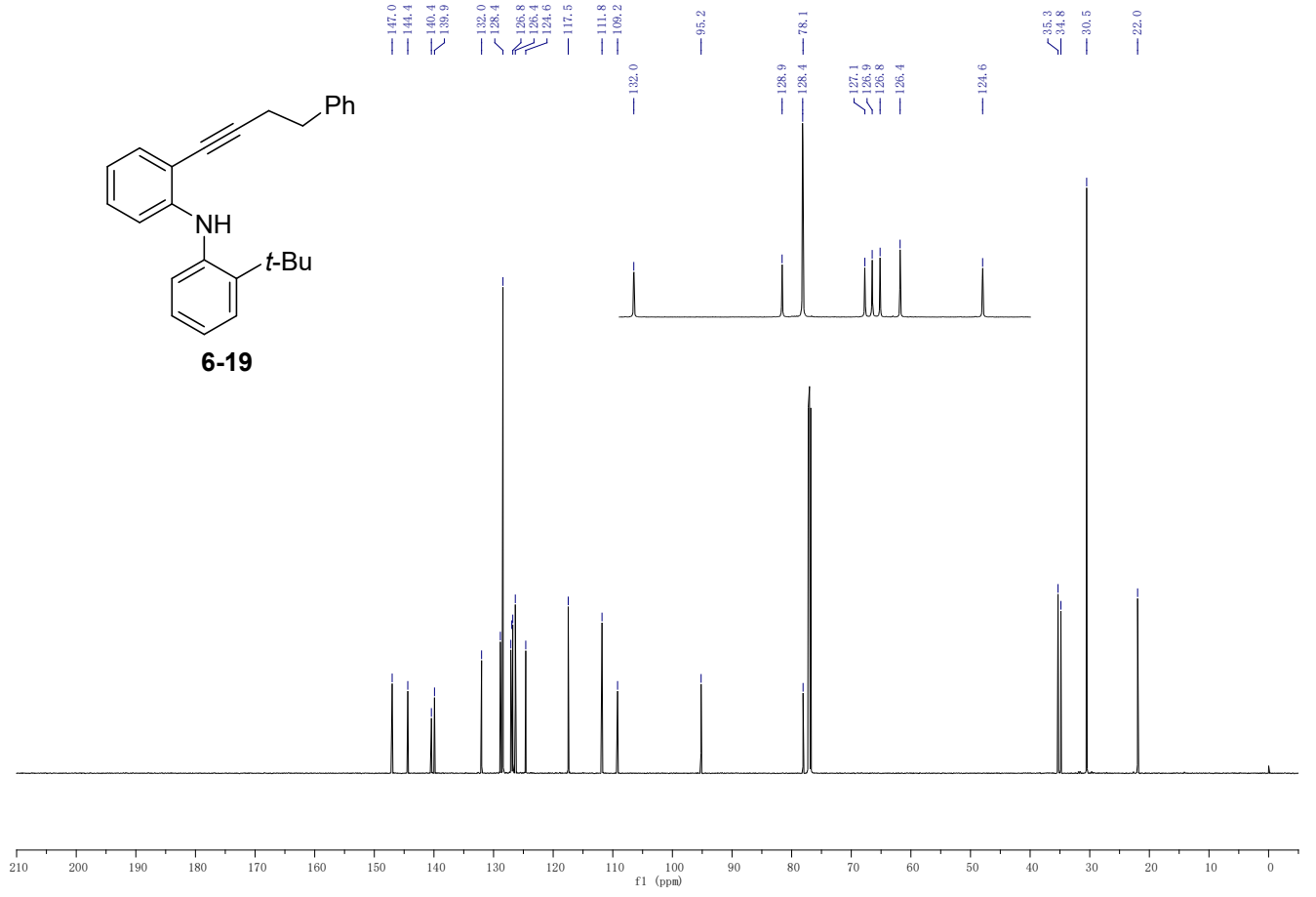
7.48
7.47
7.47
7.46
7.40
7.39
7.30
7.29
7.27
7.26
7.24
7.23
7.17
7.15
7.14
7.03
7.02
7.01
6.88
6.86
6.77
6.75
6.74
6.49
1.42
S
NH
t-Bu
2.06
1.04
1.01
2.21
2.19
1.03
1.02
1.03
1.00
9.10
f1 (ppm)

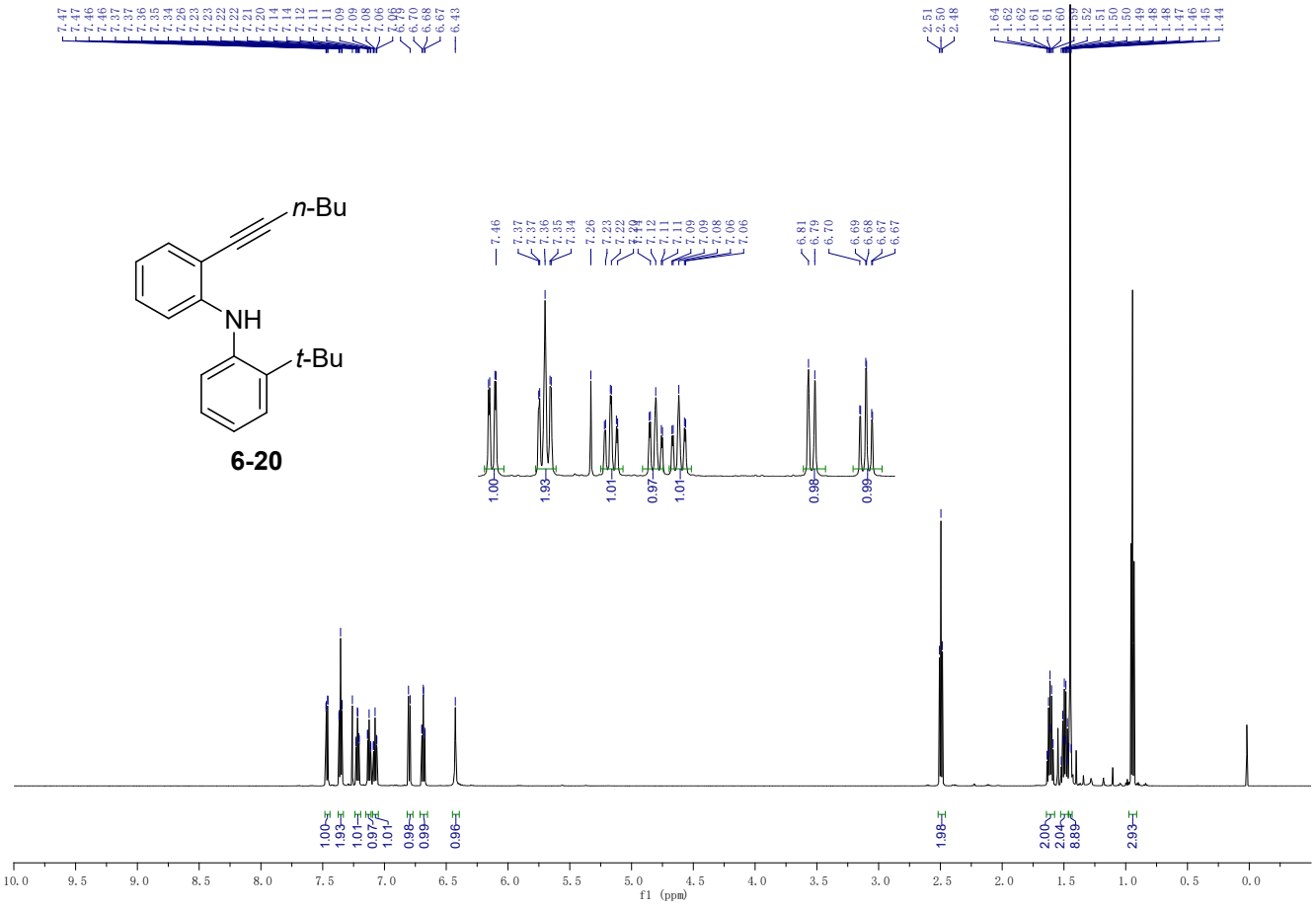
6-18


146.9
144.3
139.6
132.1
131.6
129.8
127.3
127.2
127.1
126.8
126.7
124.7
123.1
117.8
112.0
108.3
89.8
88.3
34.9
30.6
S
NH
t-Bu
f1 (ppm)

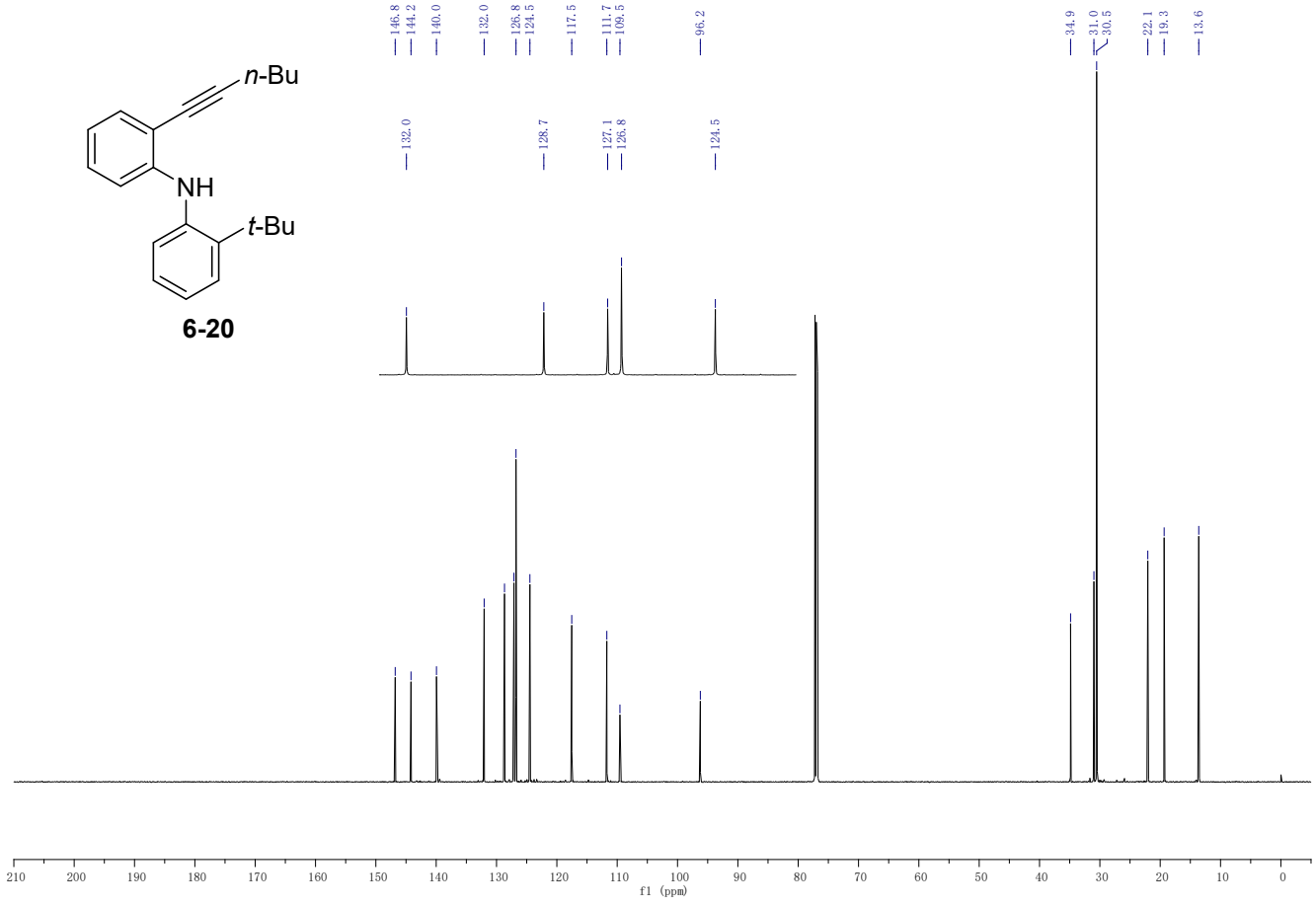
6-18


Ph
NH
t-Bu
6-19
f1 (ppm)

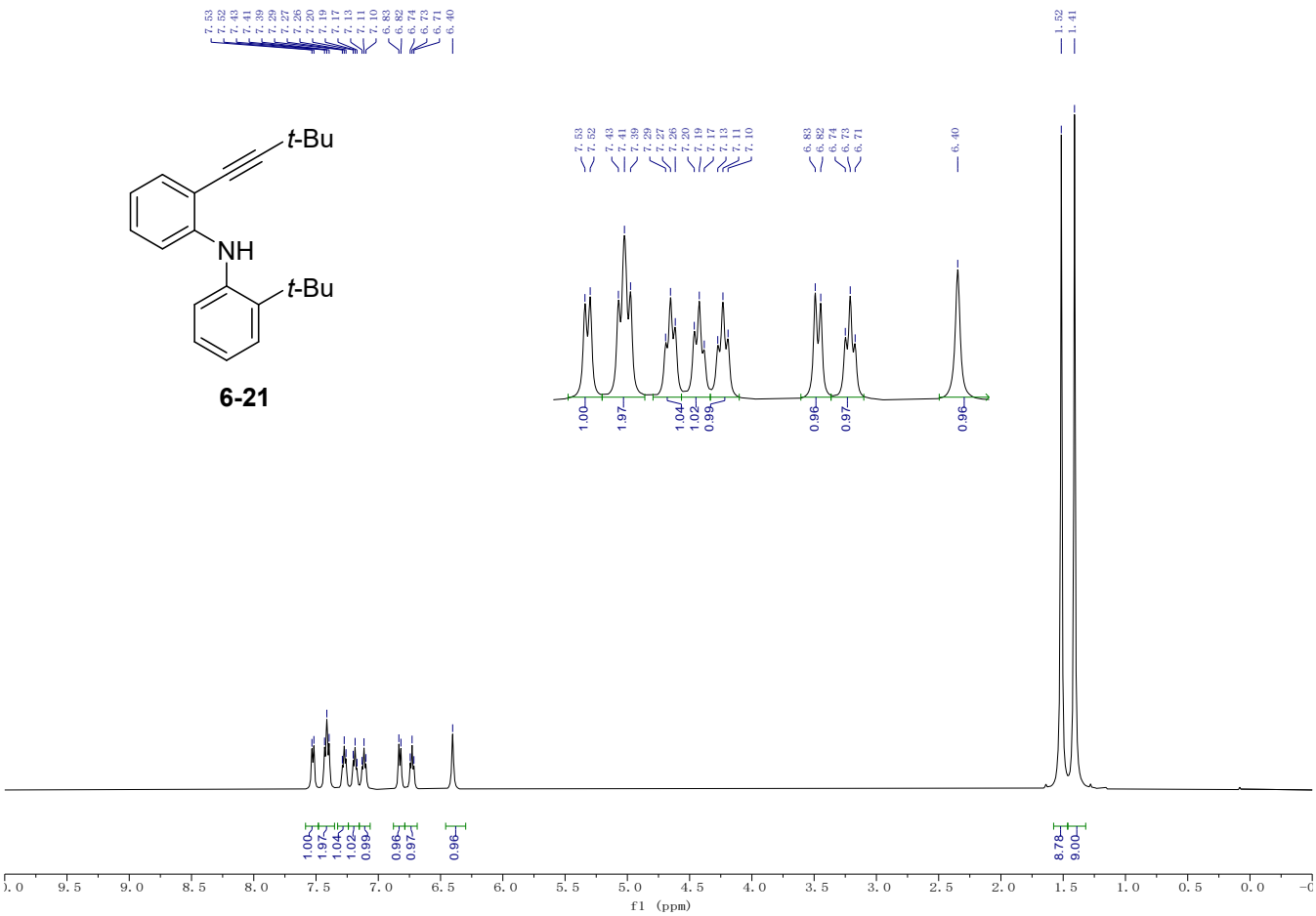

Ph
NH
t-Bu
6-19
f1 (ppm)

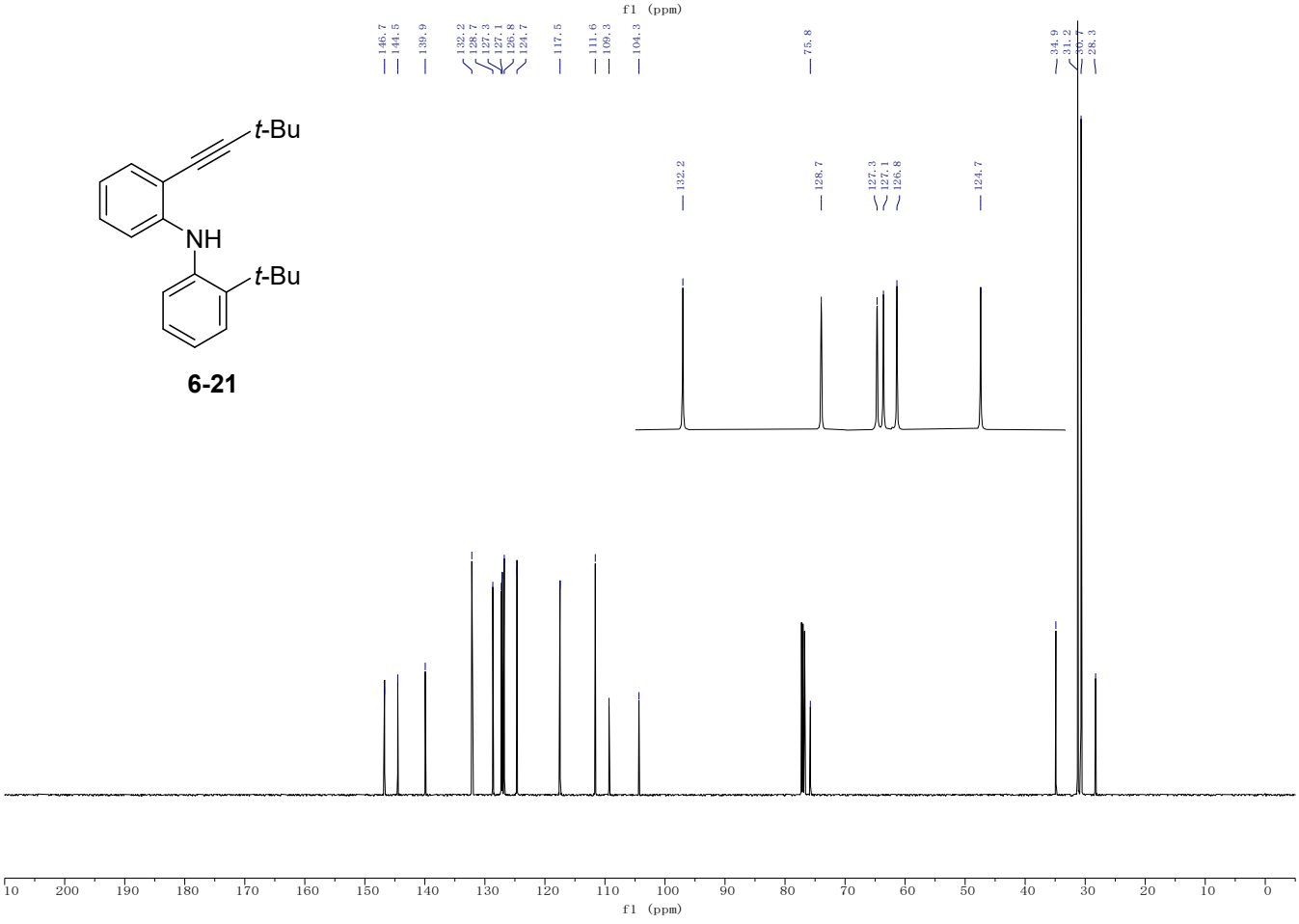


6-20



6-20


7.53
7.52
7.43
7.41
7.39
7.29
7.27
7.26
7.20
7.19
7.17
7.13
7.11
7.10
6.83
6.82
6.74
6.73
6.71
6.40
1.52
1.41
t-Bu
NH
t-Bu
6-21
1.00
1.97
1.04
1.02
0.99
0.96
0.97
0.96
8.78
9.00
f1 (ppm)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144.5
139.9
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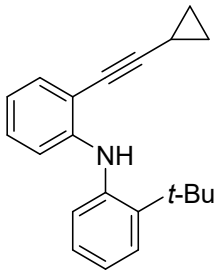
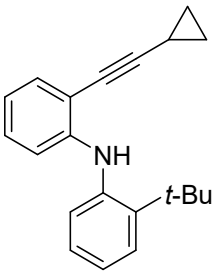
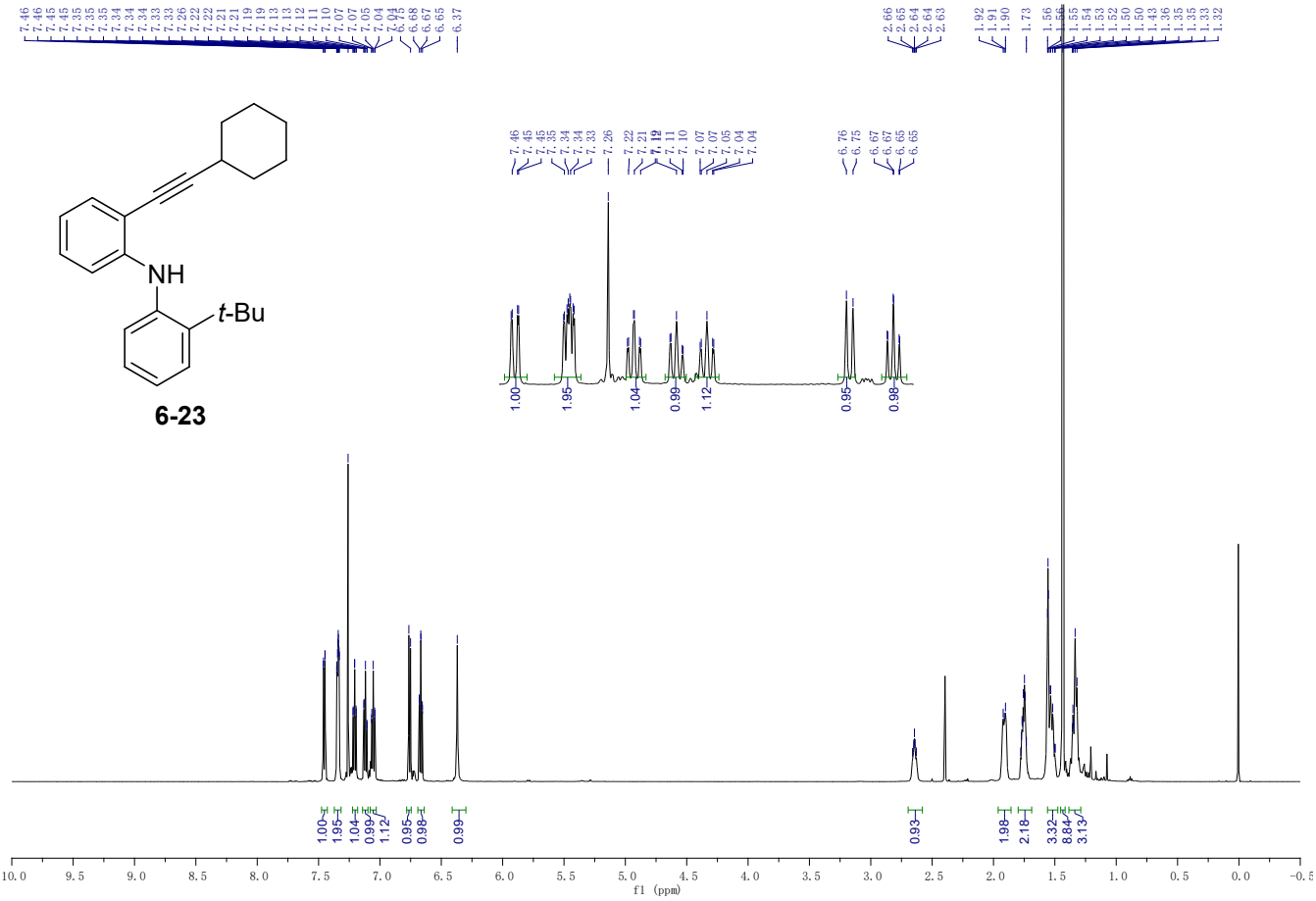
128.7
127.3
127.1
126.8
124.7
117.5
111.6
109.3
104.3
75.8
34.9
31.2
30.4
28.3
t-Bu
NH
t-Bu
6-21
f1 (ppm)

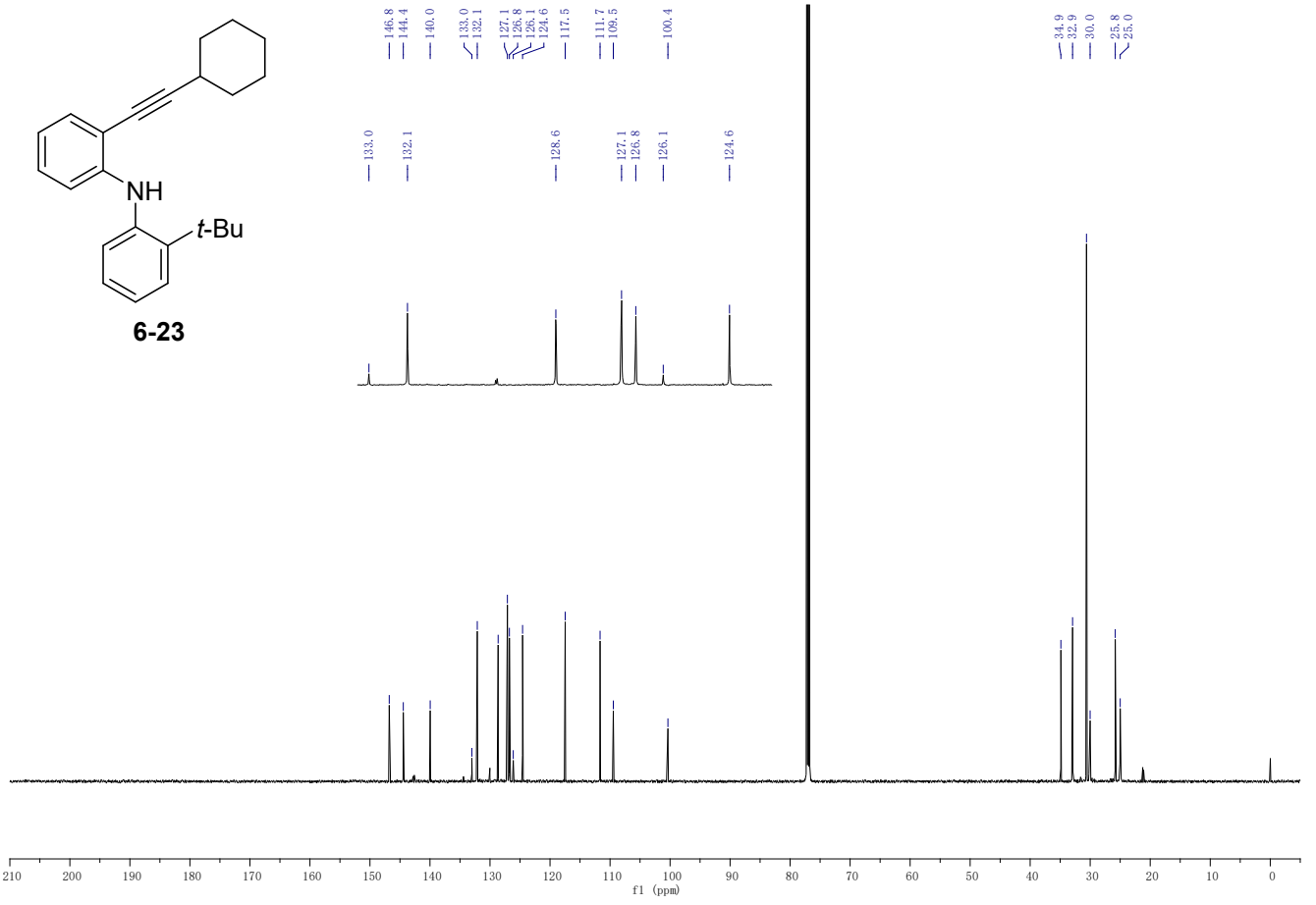


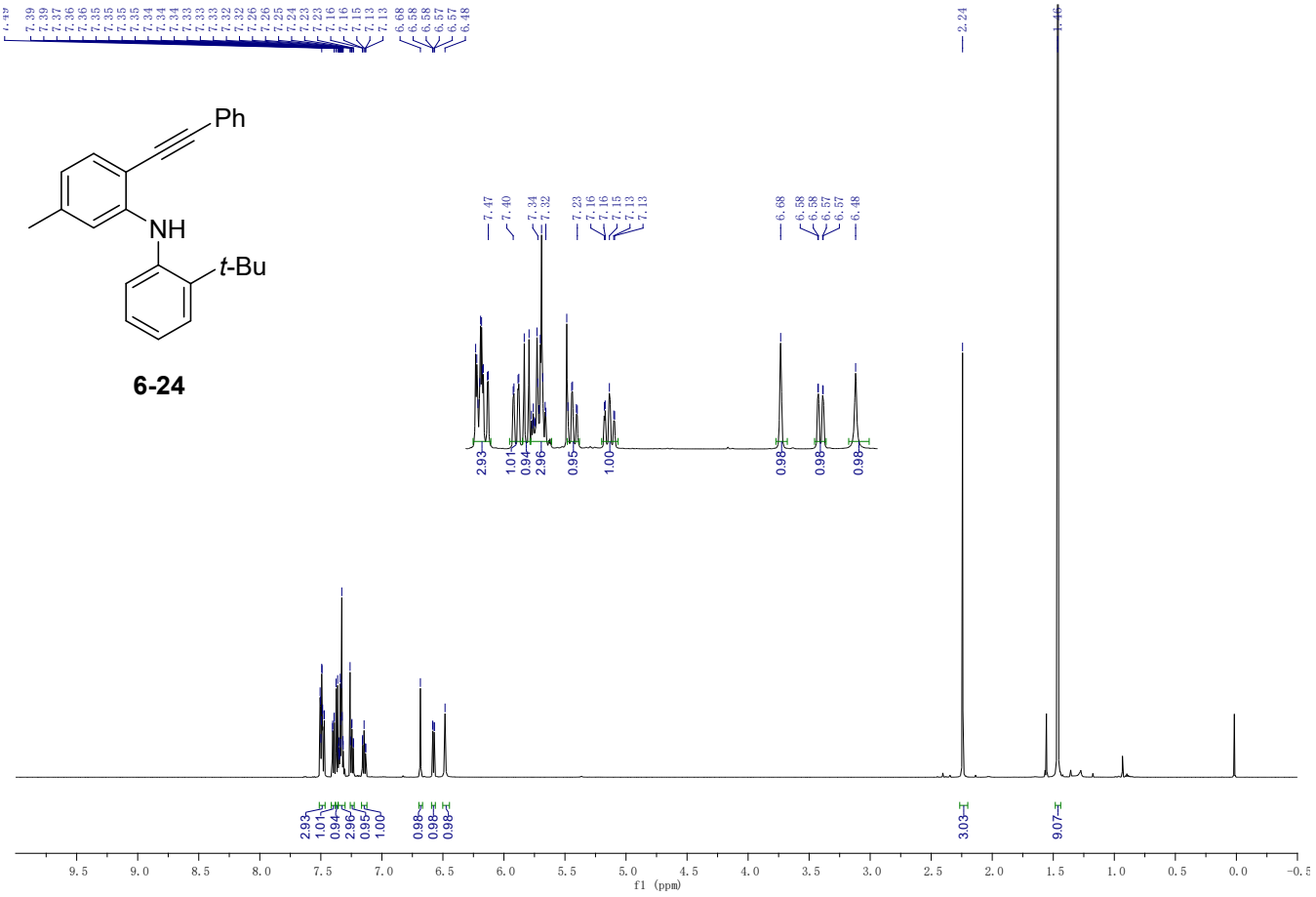
6-22



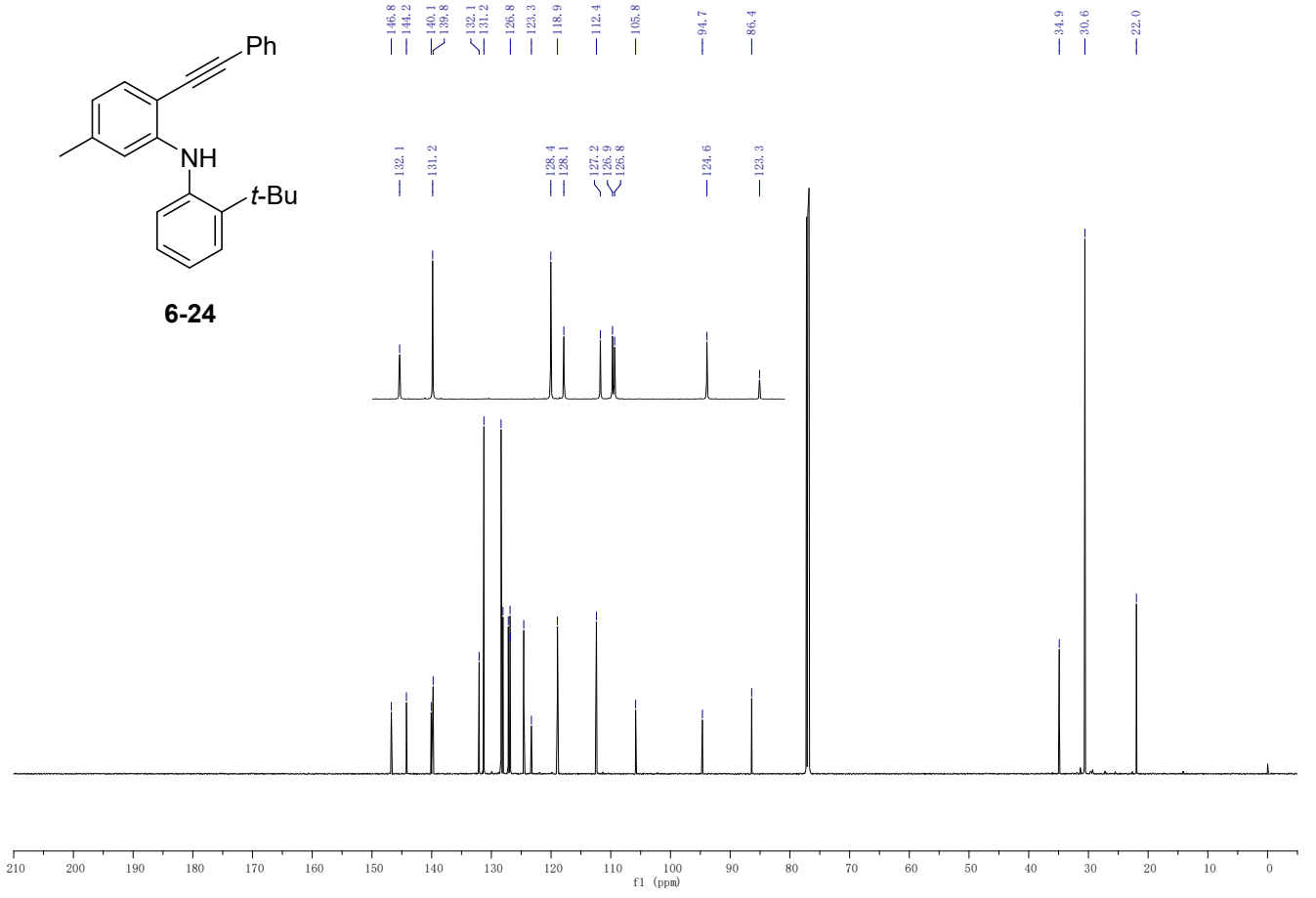
6-22


NH
t-Bu
6-23
f1 (ppm)

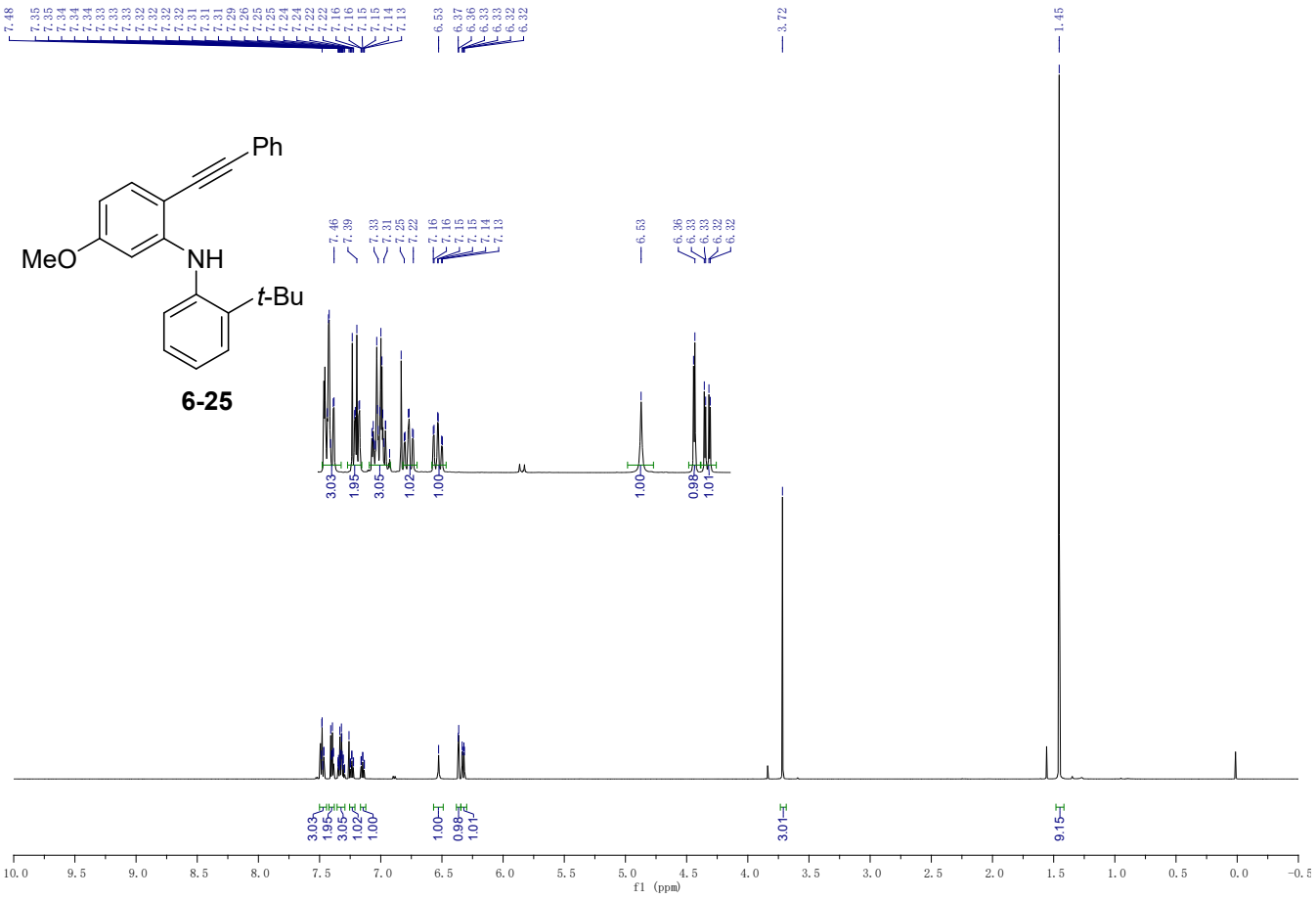

NH
t-Bu
6-23
f1 (ppm)

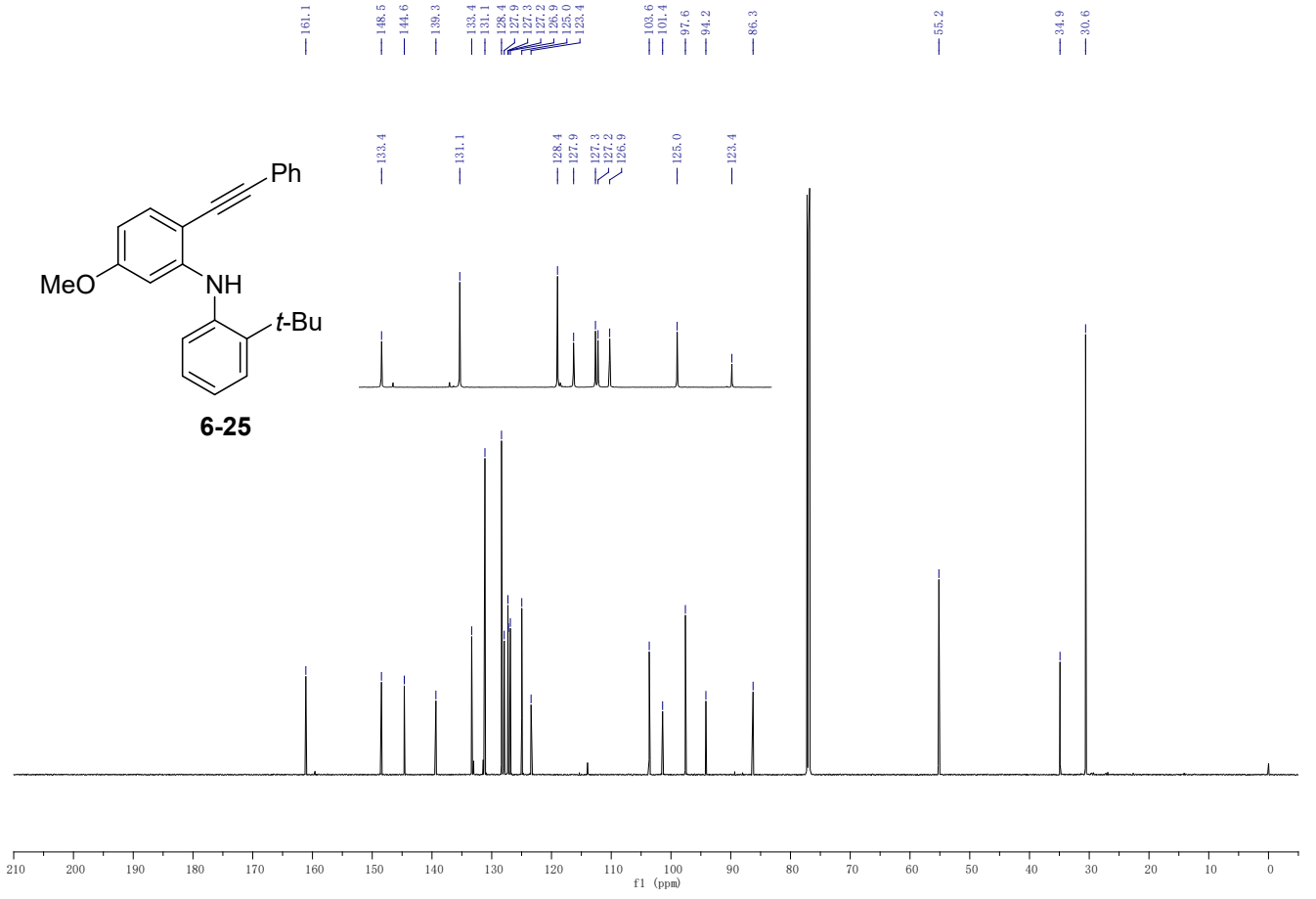


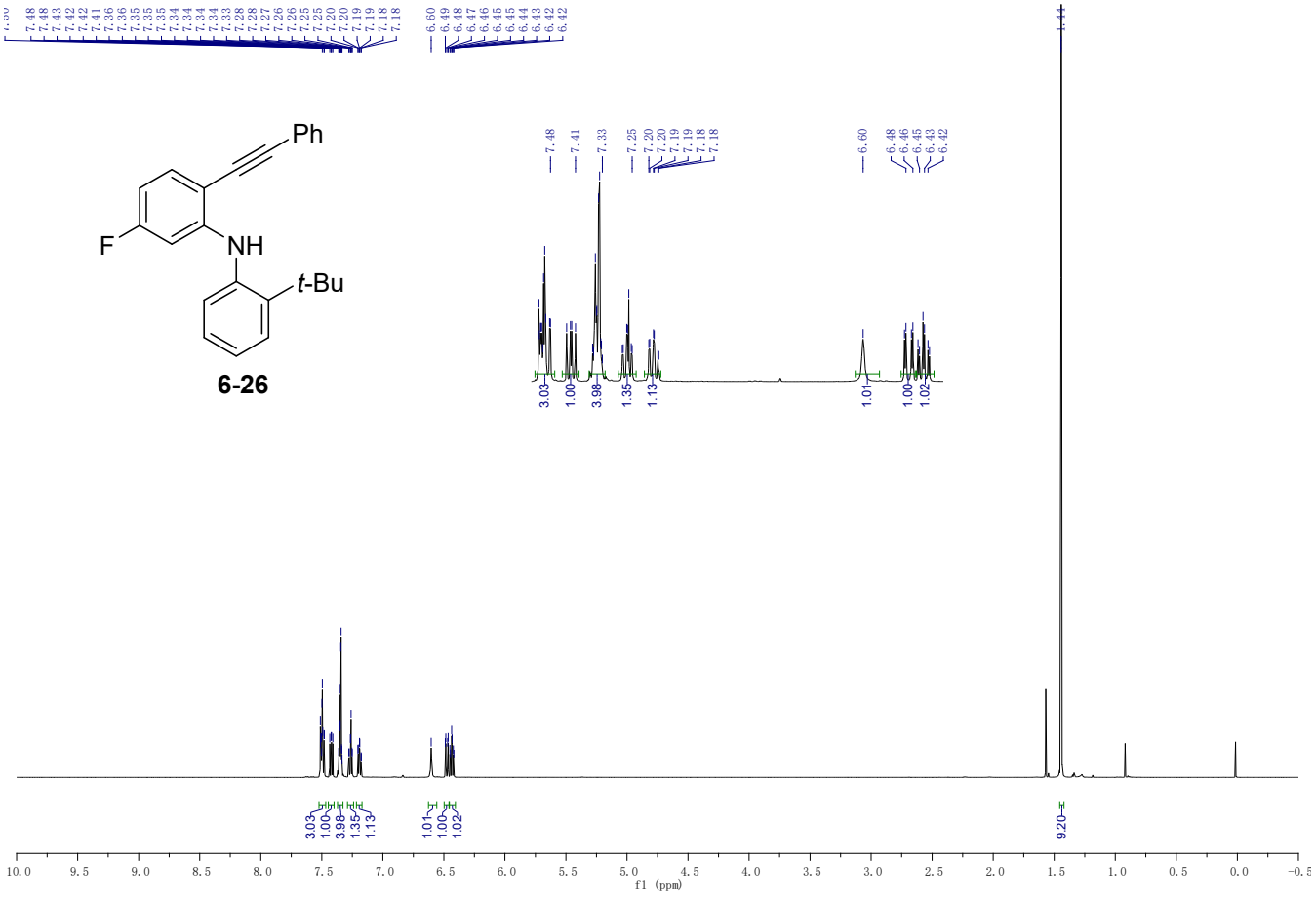
6-24

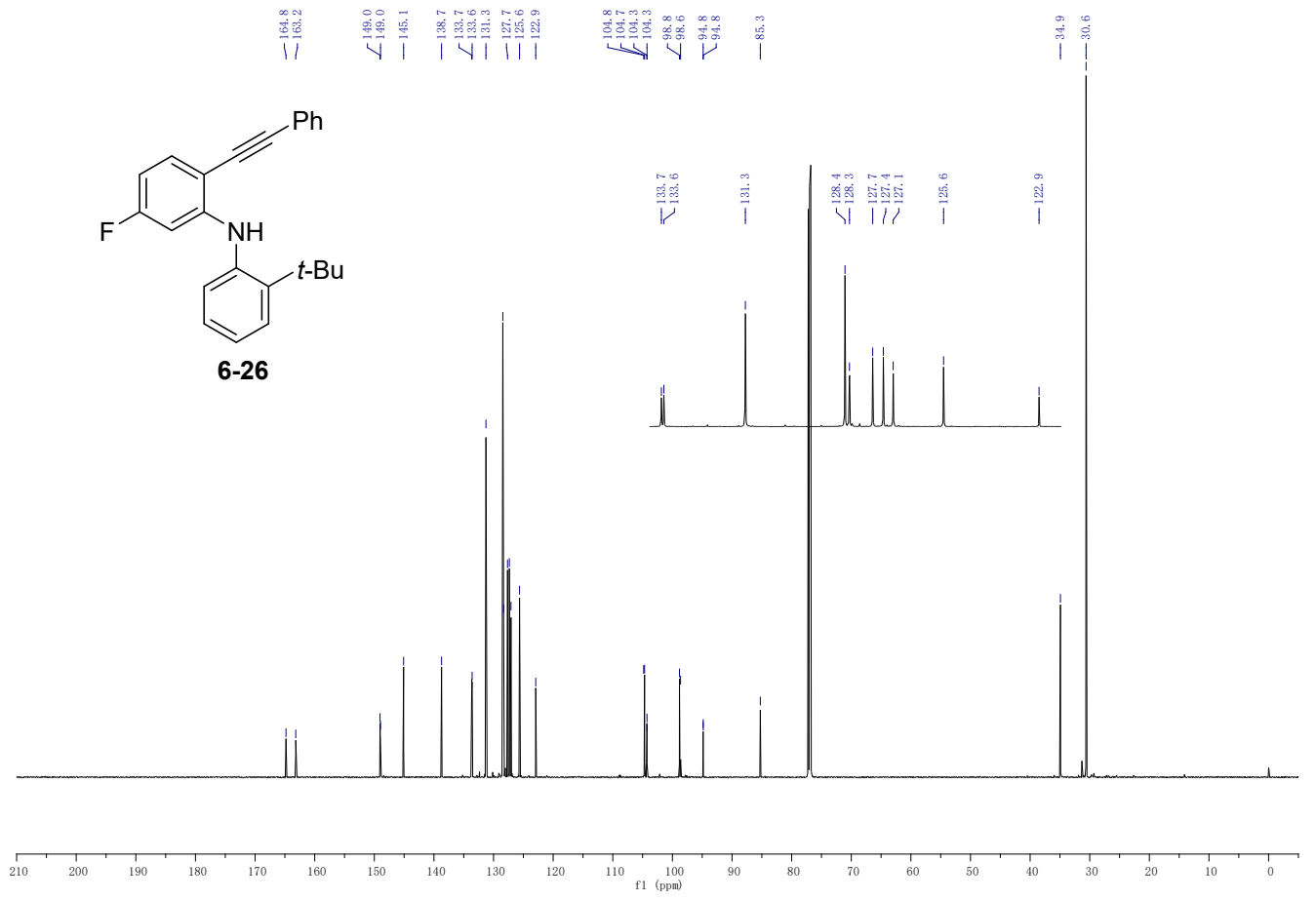


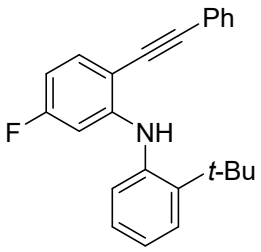
6-24


Ph
MeO
NH
t-Bu
6-25
f1 (ppm)


Ph
MeO
NH
t-Bu
6-25
f1 (ppm)

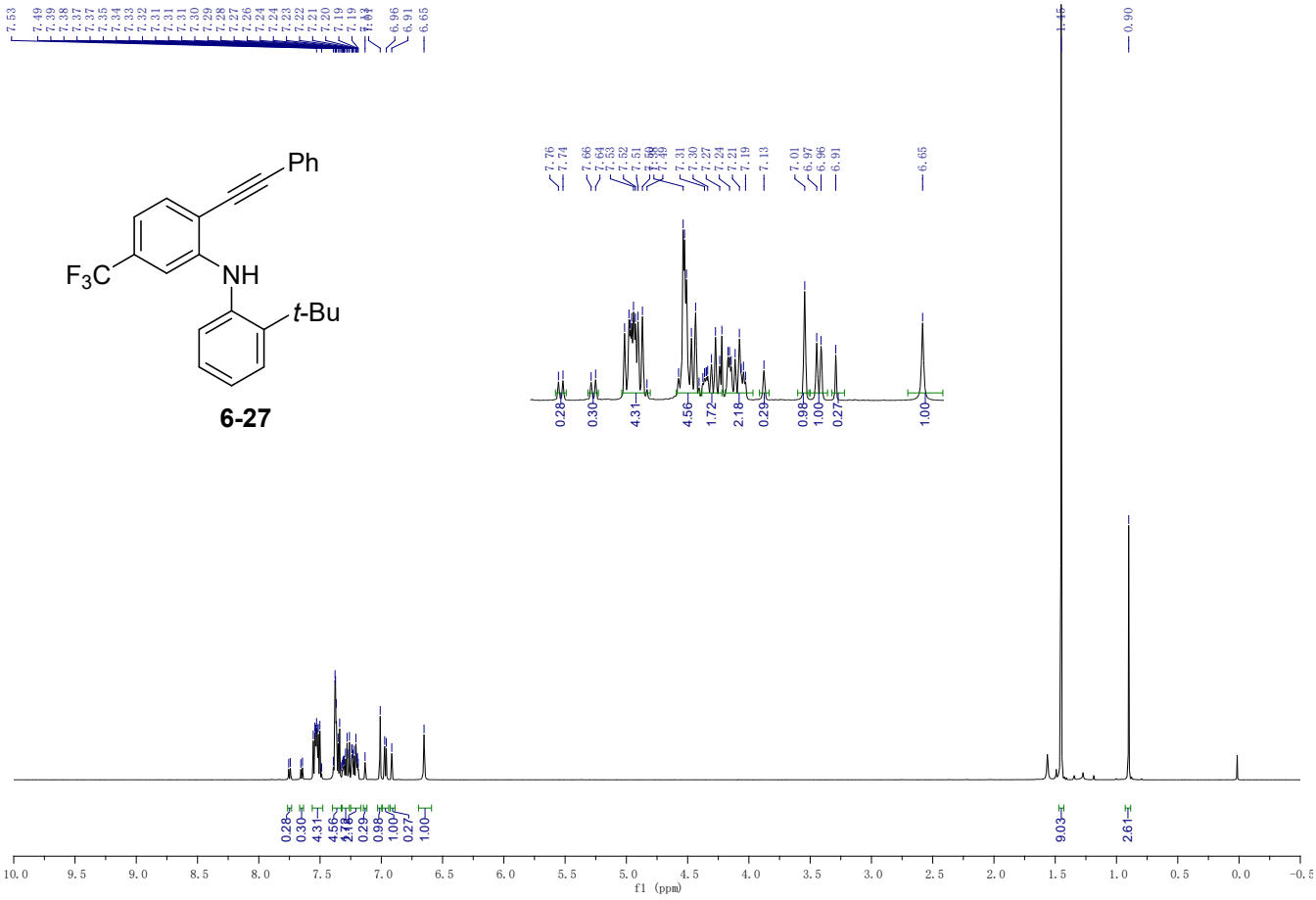

Ph
F
NH
t-Bu
6-26
f1 (ppm)

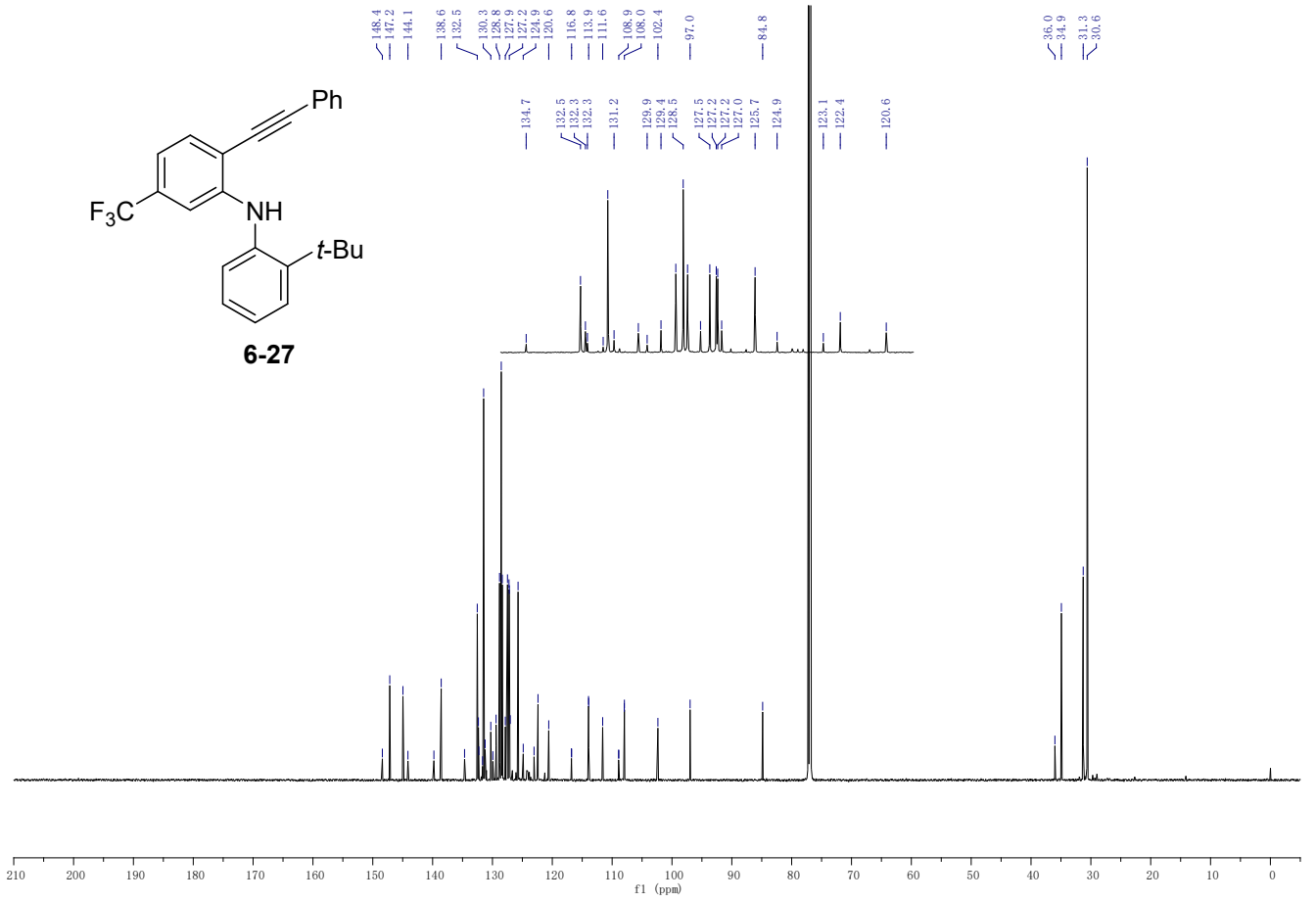

Ph
F
NH
t-Bu
6-26
f1 (ppm)

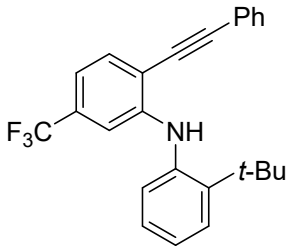

Ph
F
NH
t-Bu

6-26

-108.4
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

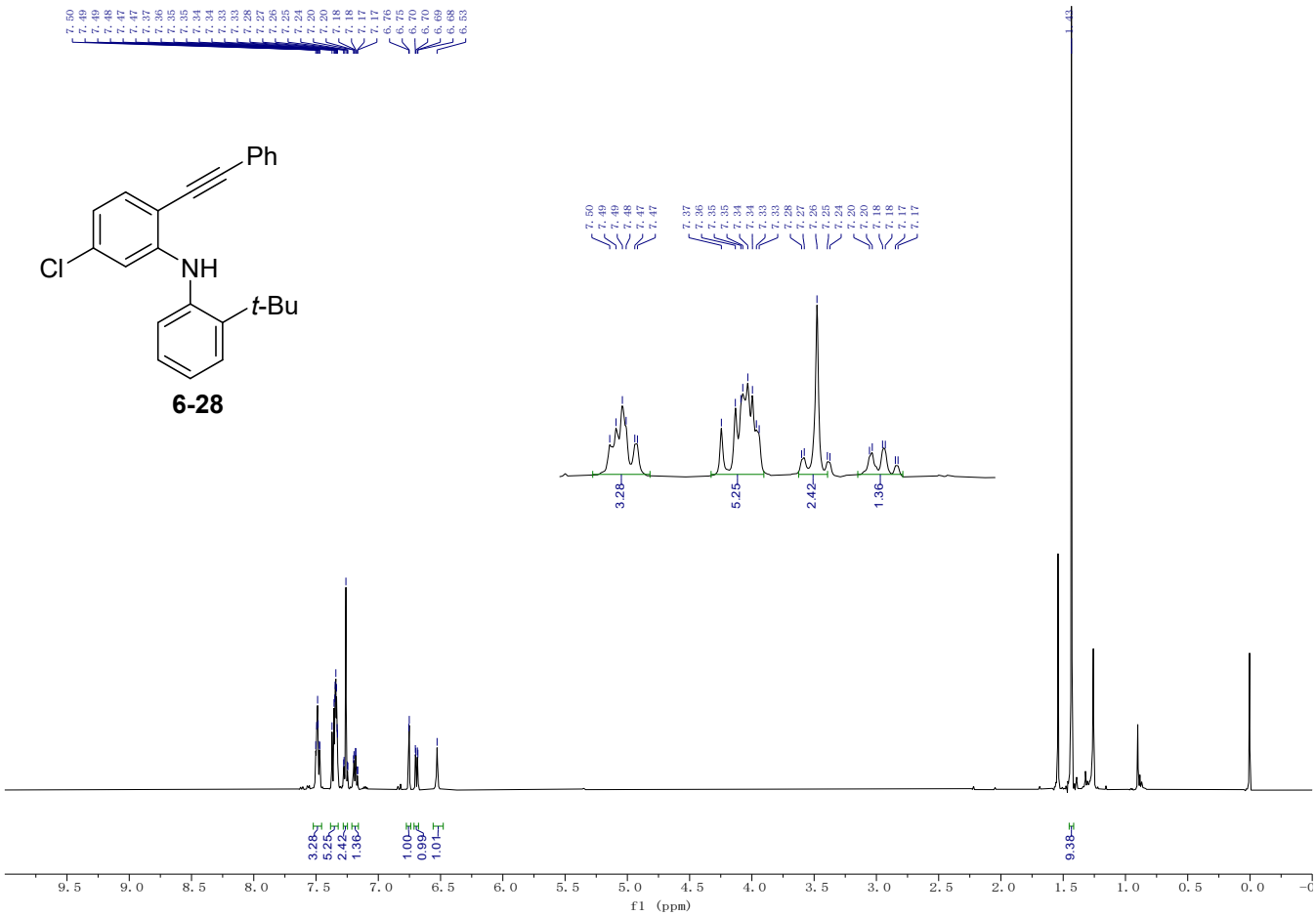

Ph
F3C
NH
t-Bu
6-27
f1 (ppm)

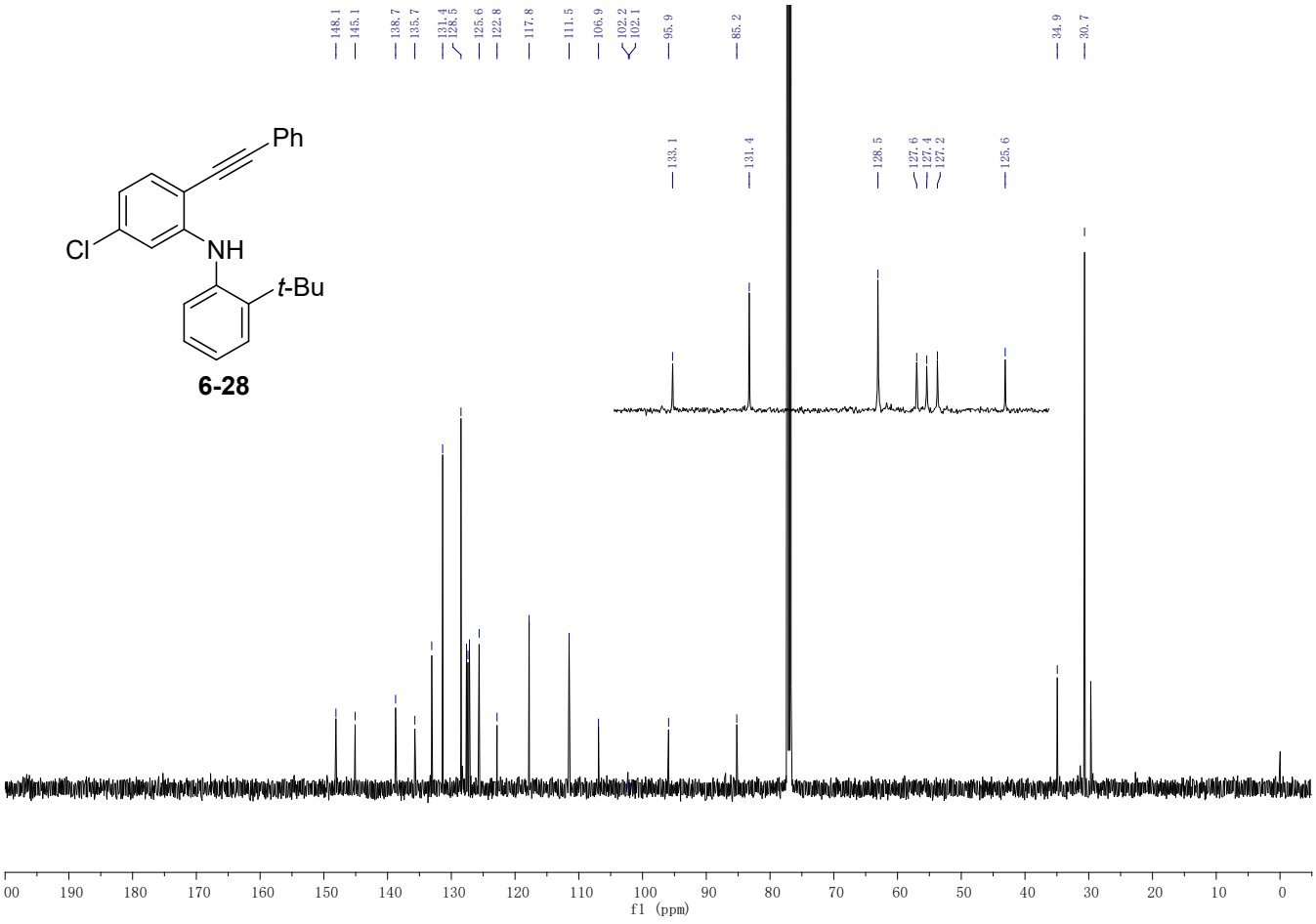

Ph
F3C
NH
t-Bu
6-27
f1 (ppm)

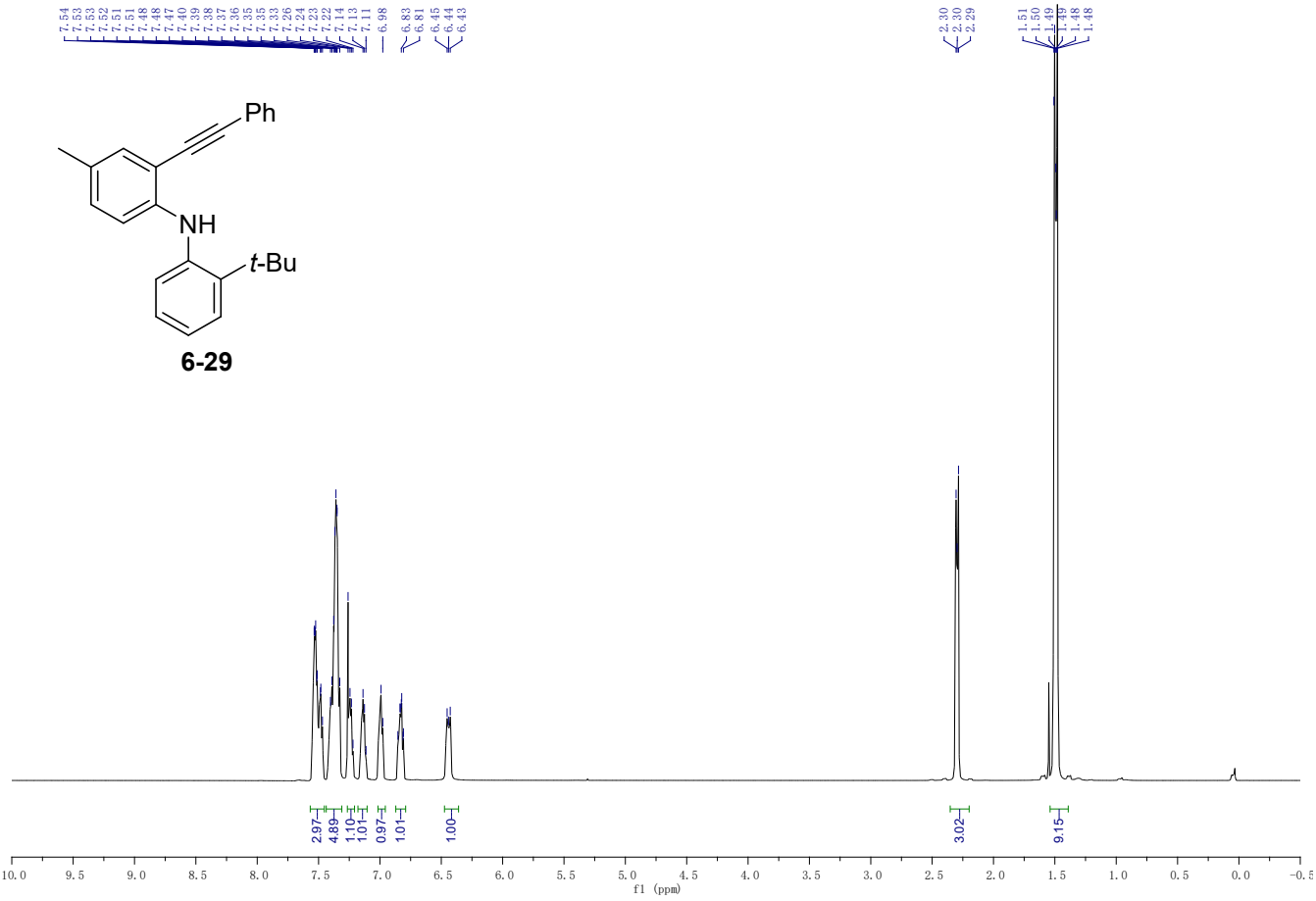

Ph
F3C
NH
t-Bu

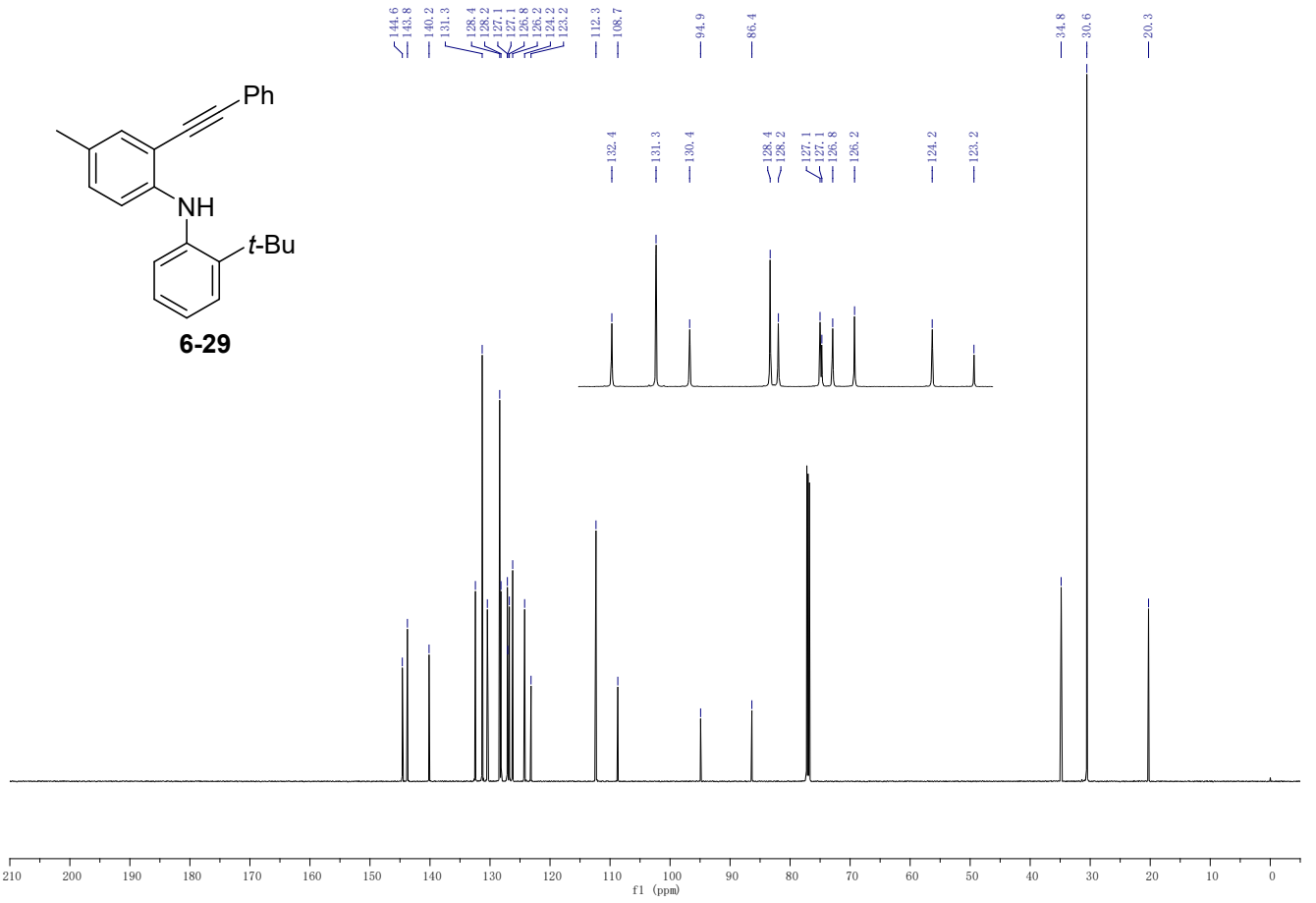
6-27

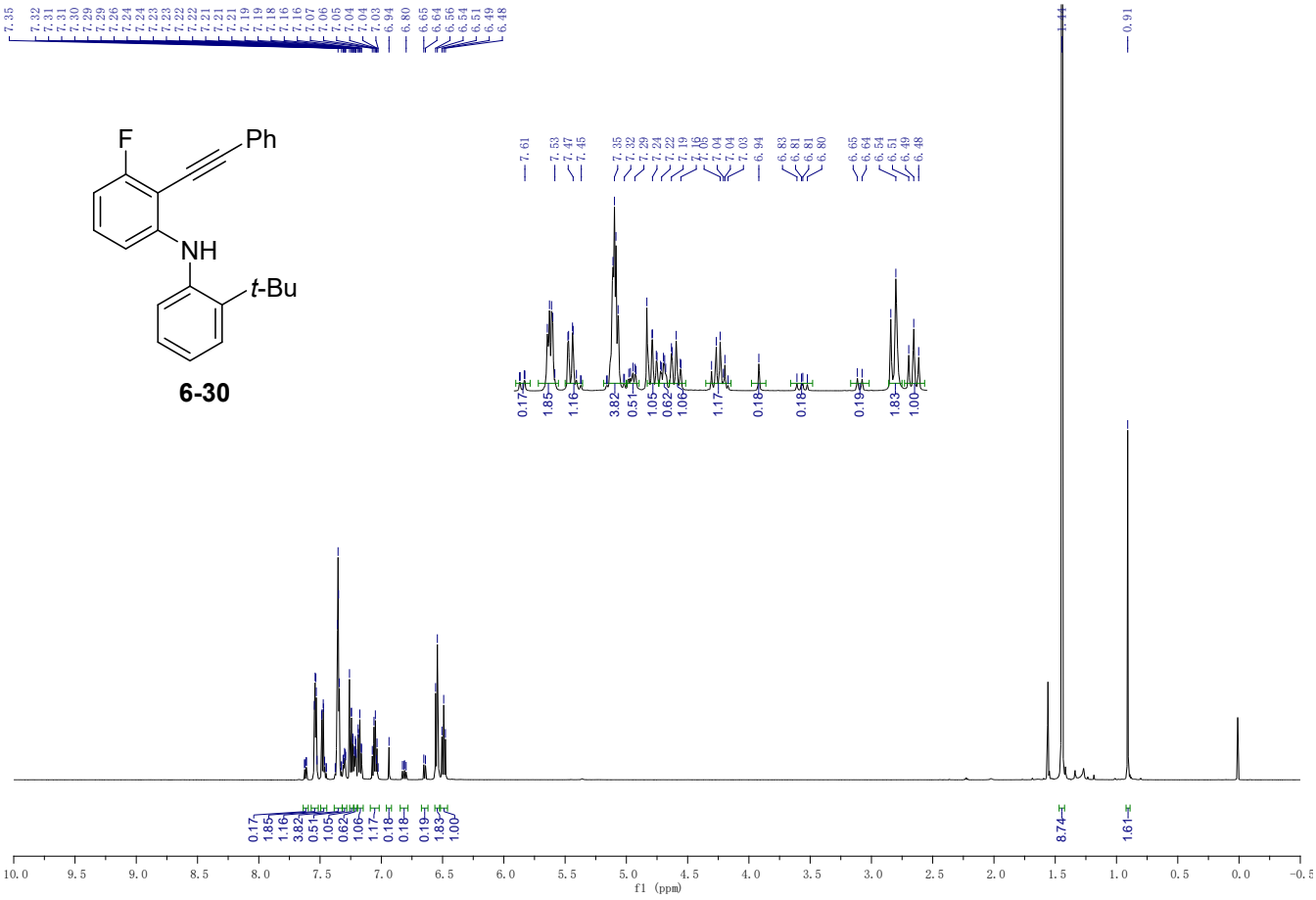
-60.4
-63.0
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

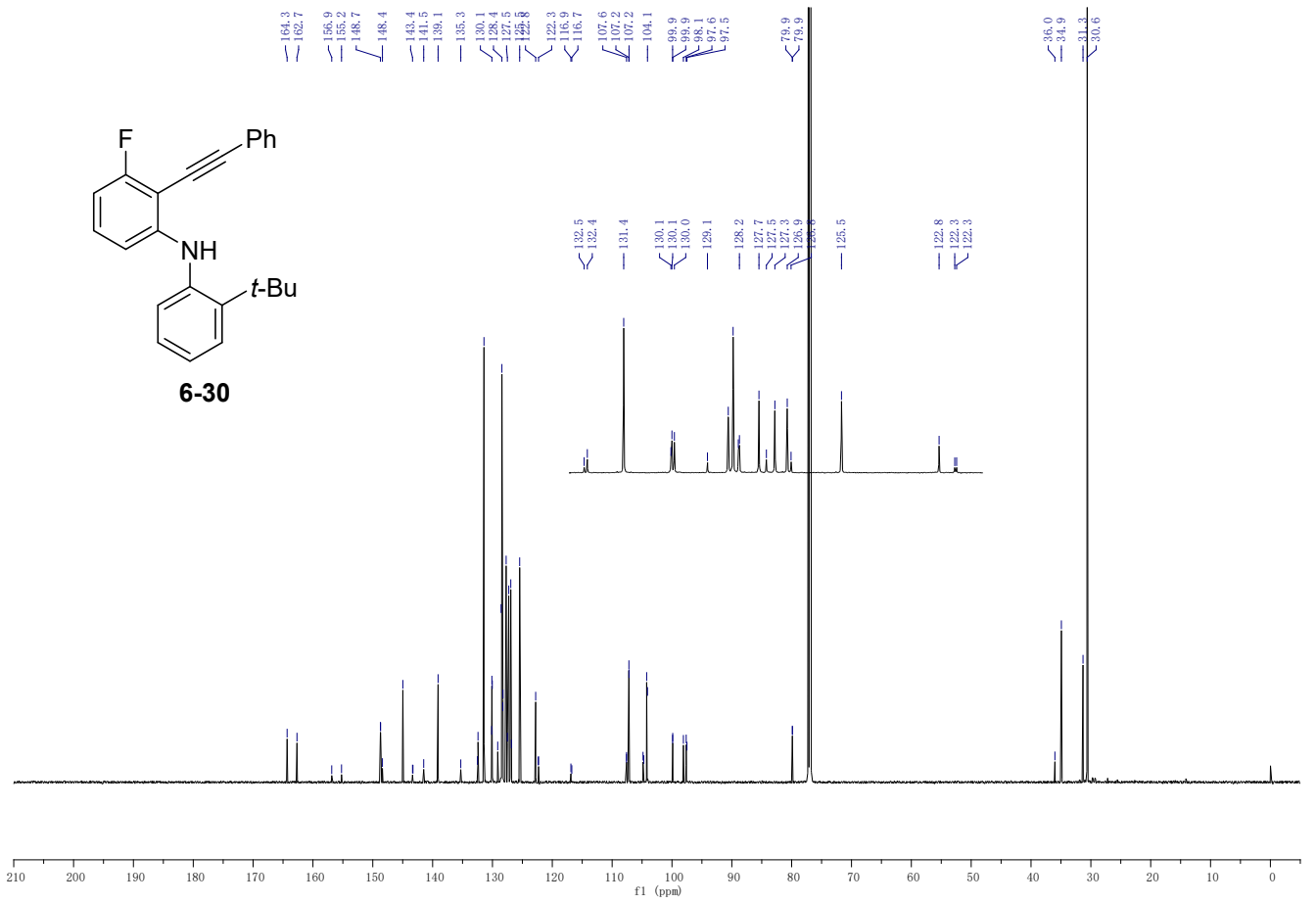

Ph
Cl
NH
t-Bu
6-28
3.28
5.25
2.42
1.36
1.00
0.99
1.01
9.38
f1 (ppm)

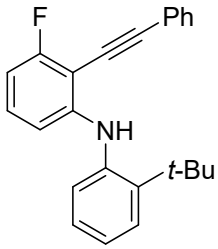

Ph
Cl
NH
t-Bu
6-28
f1 (ppm)


Ph
NH
t-Bu
6-29
f1 (ppm)


Ph
NH
t-Bu
6-29
f1 (ppm)

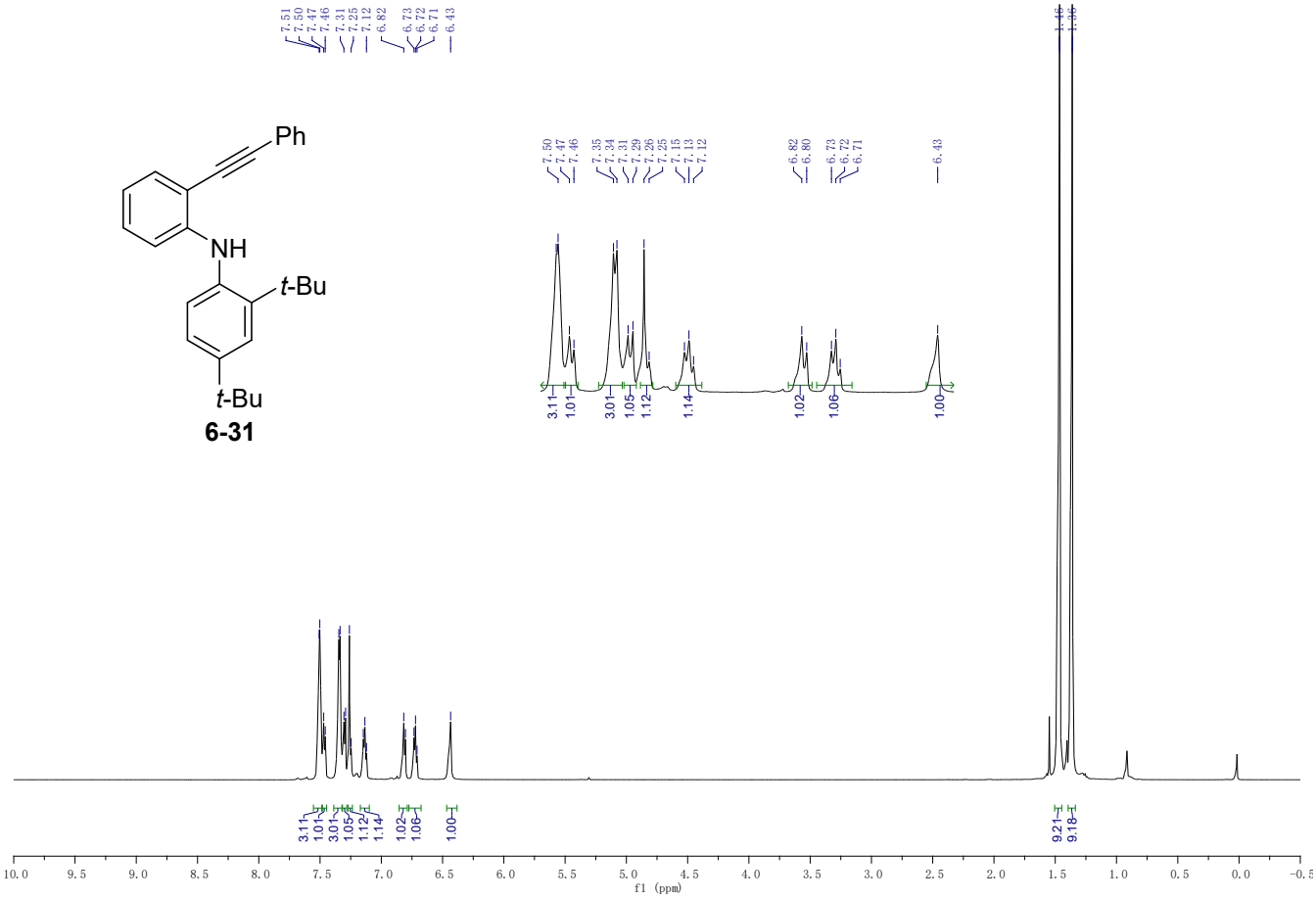

F
Ph
NH
t-Bu
6-30
f1 (ppm)

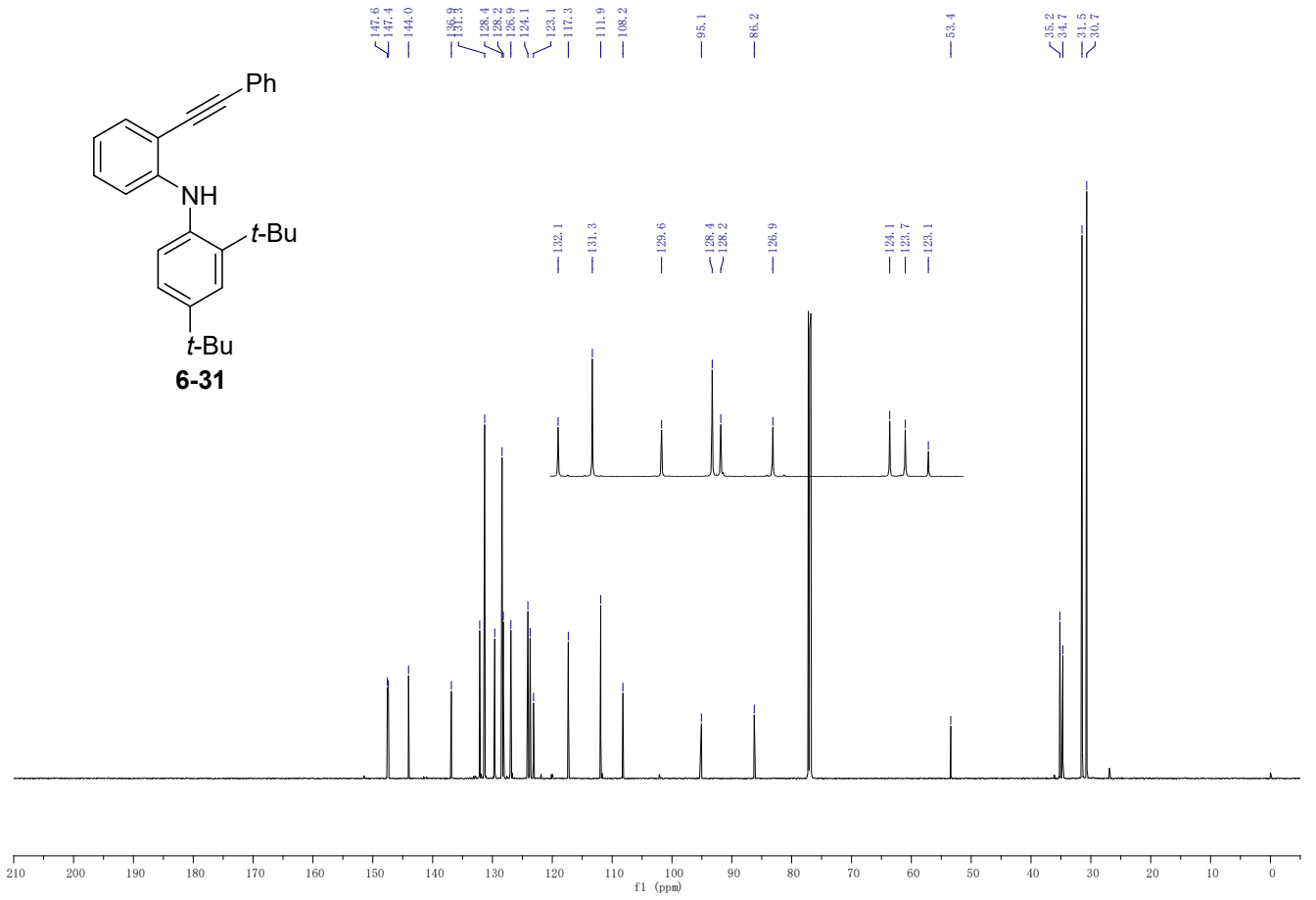

F
Ph
NH
t-Bu
6-30
f1 (ppm)

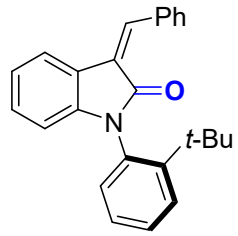

F
Ph
NH
t-Bu

6-30

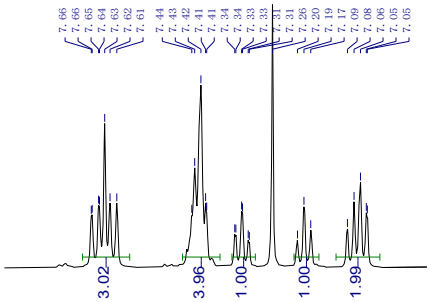
-109.4
-122.8
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

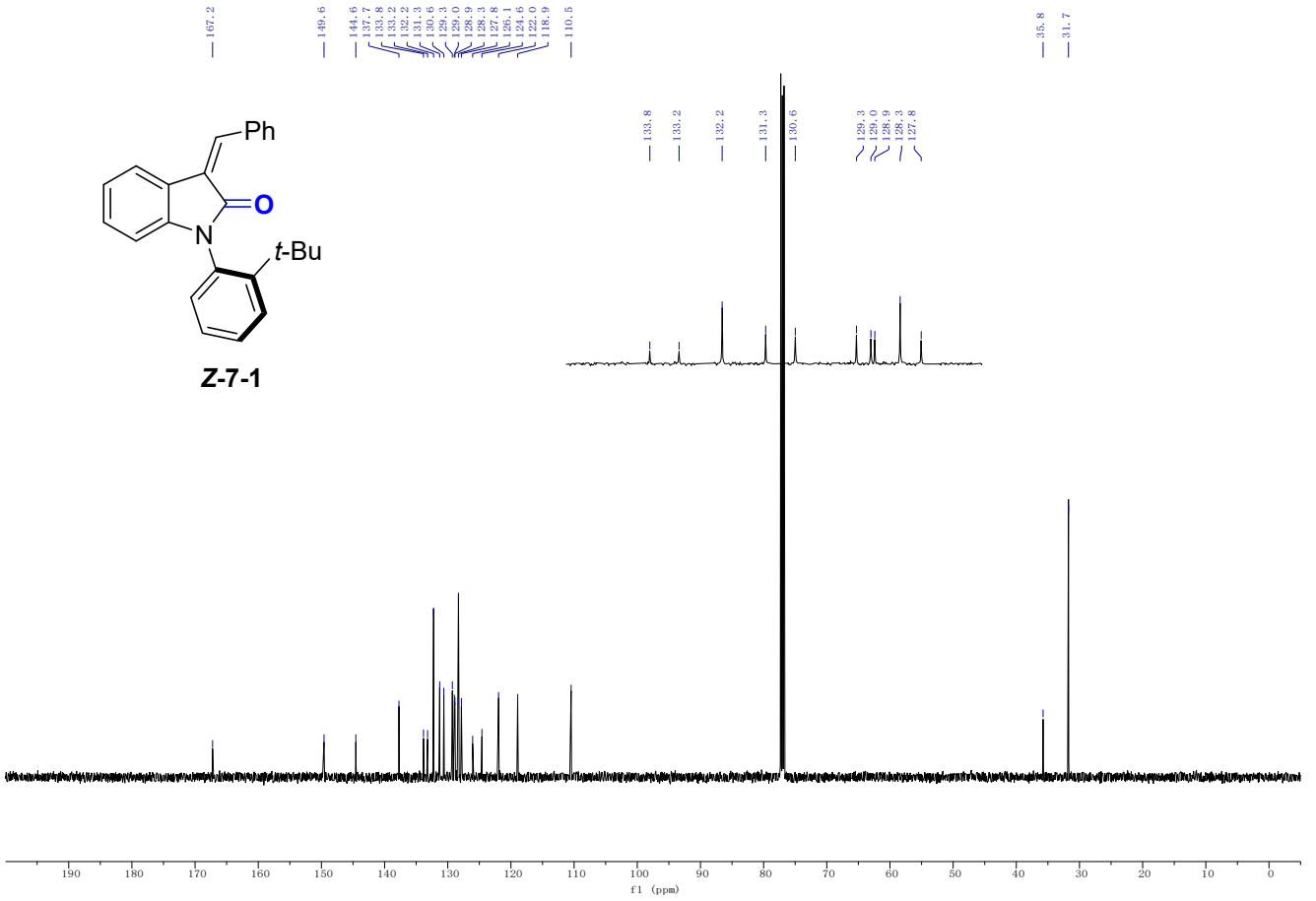

Ph
NH
t-Bu
t-Bu
6-31
f1 (ppm)


Ph
NH
t-Bu
t-Bu
6-31
f1 (ppm)

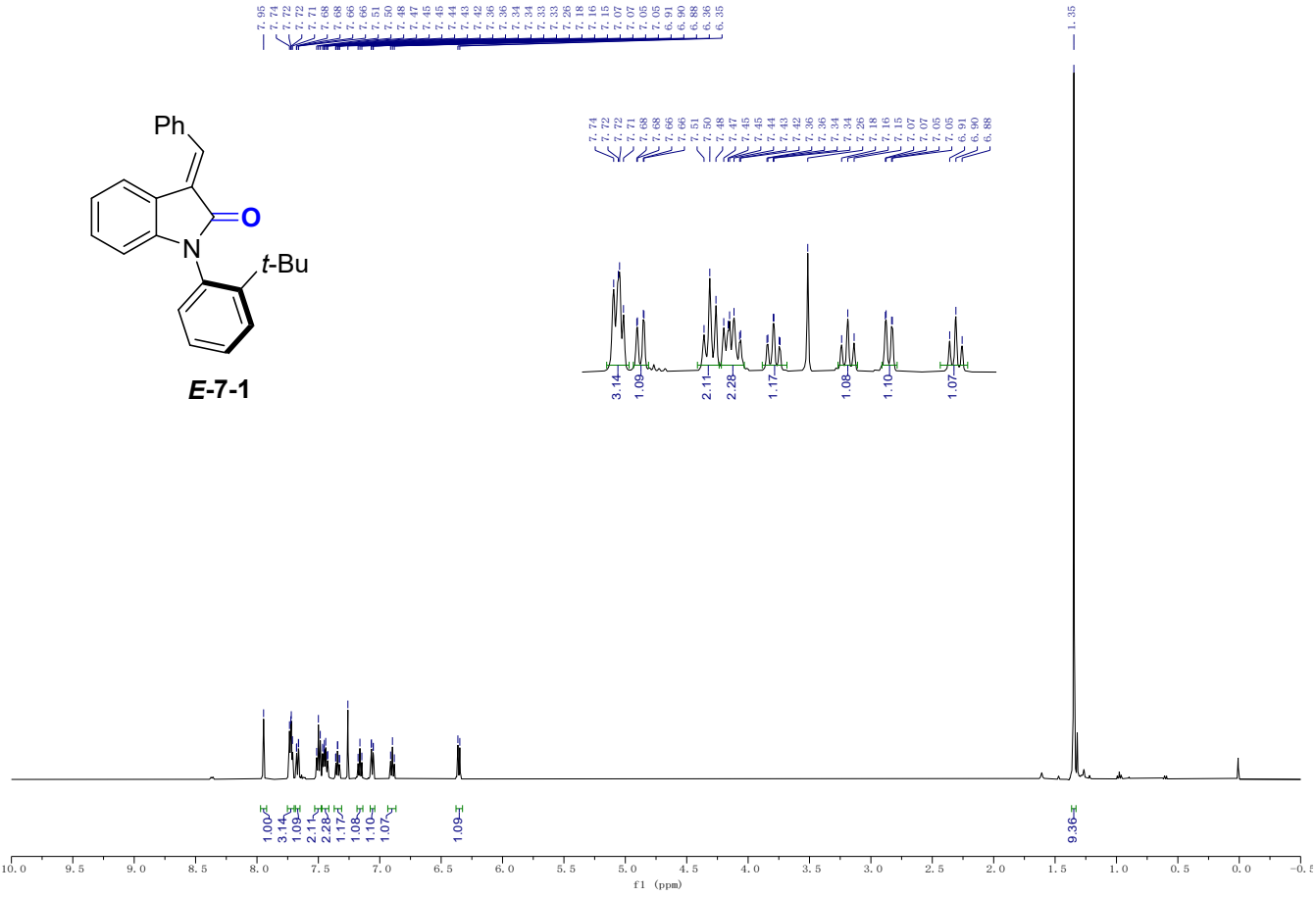


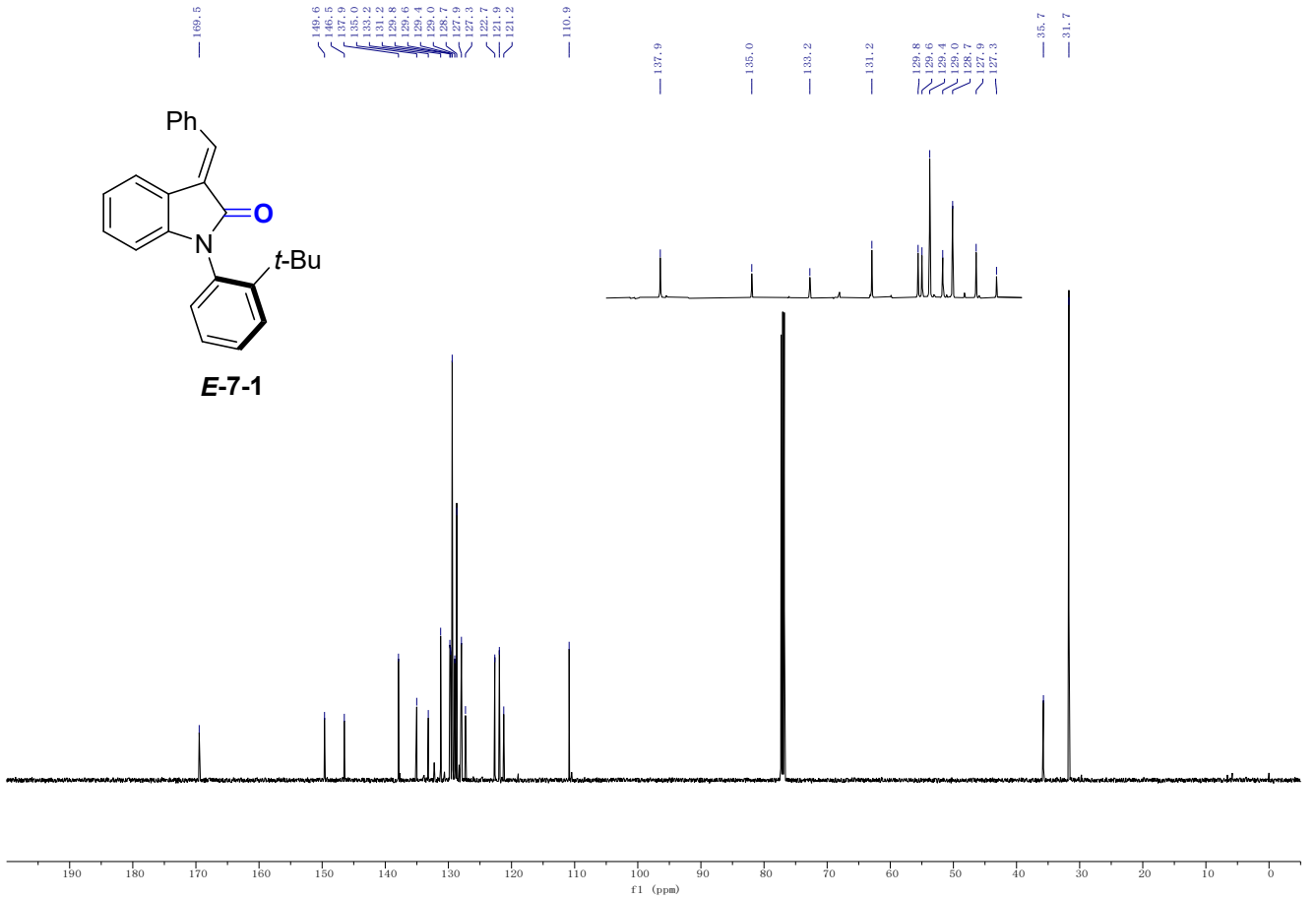
***Z*-7-1**

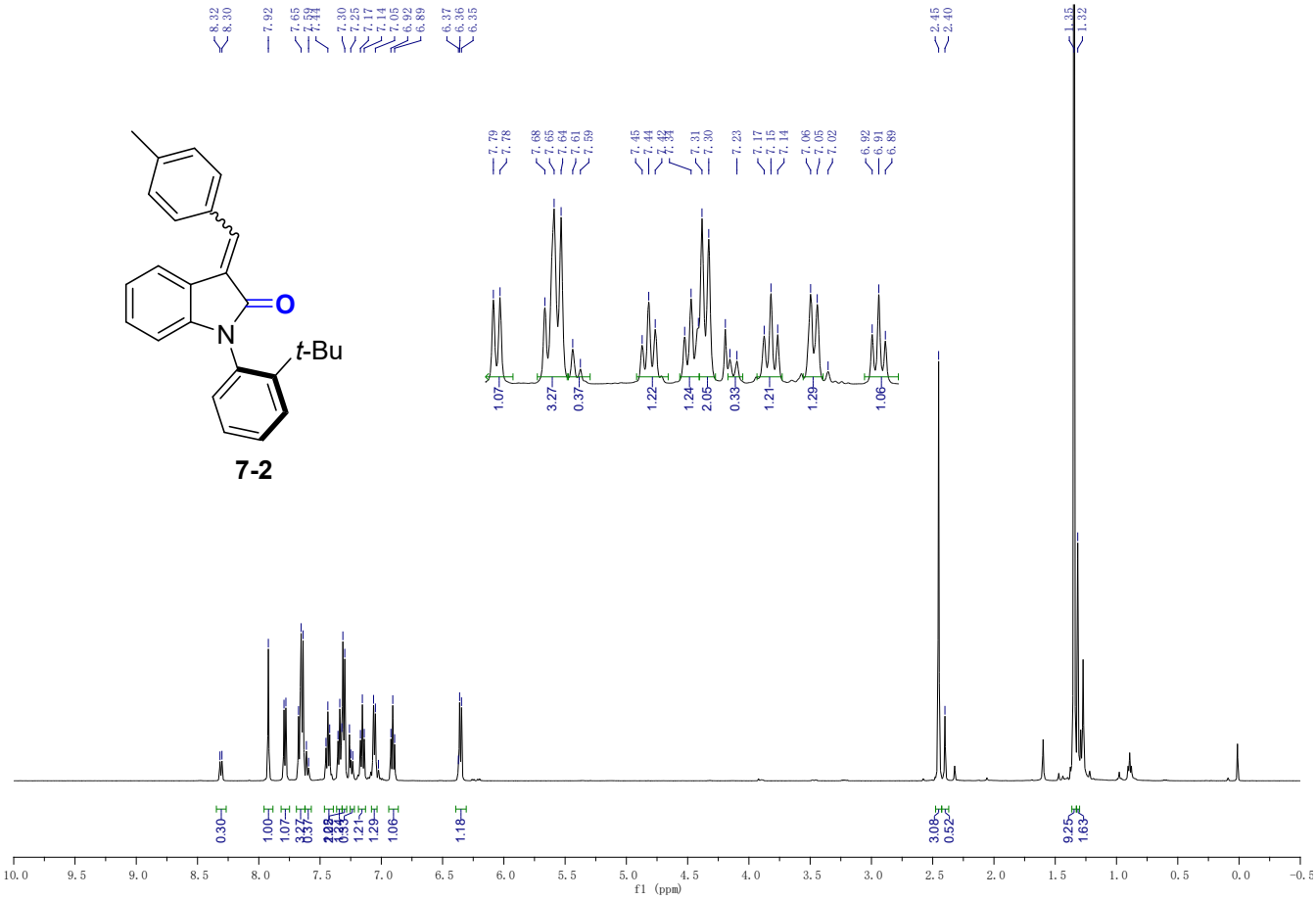


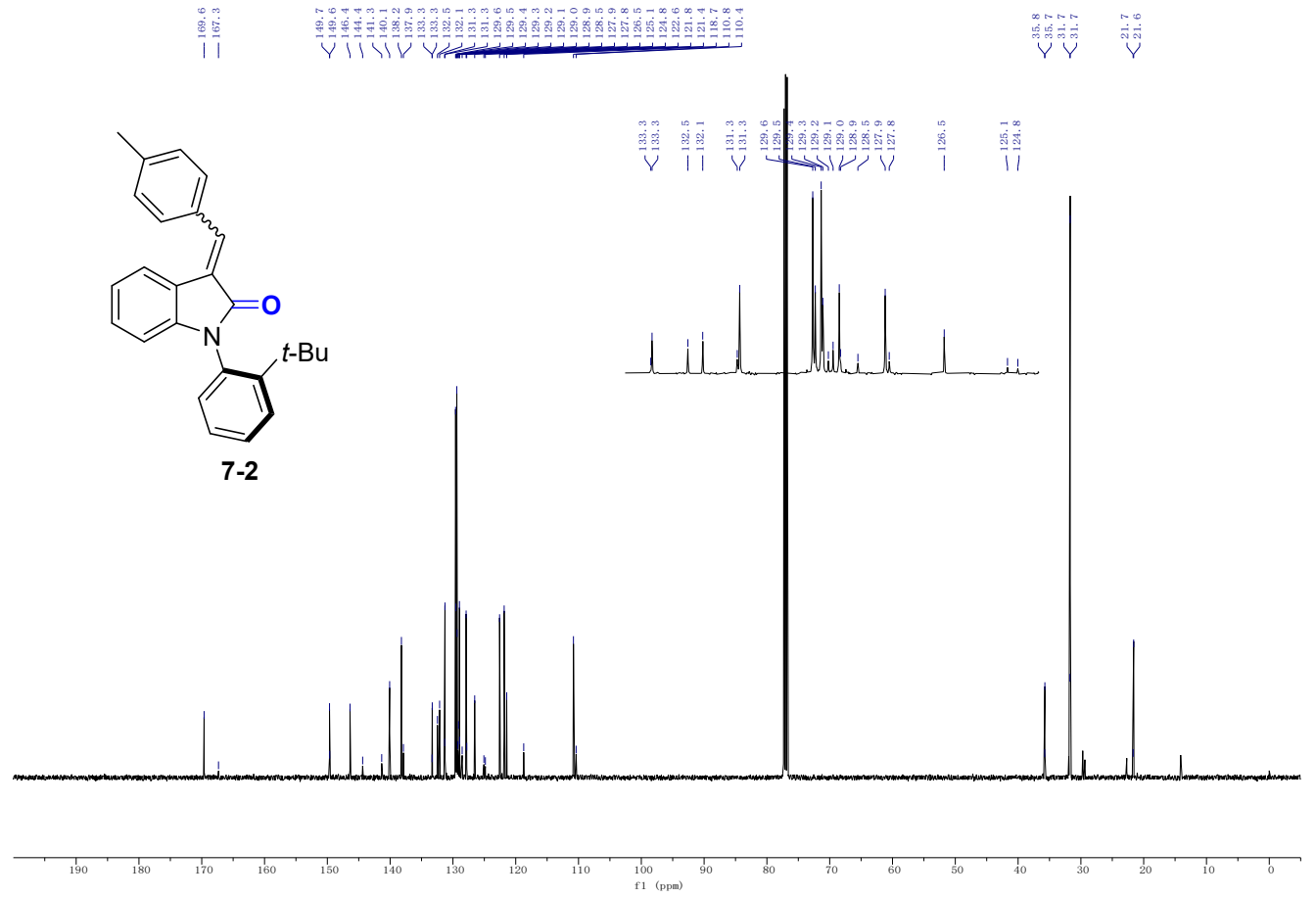


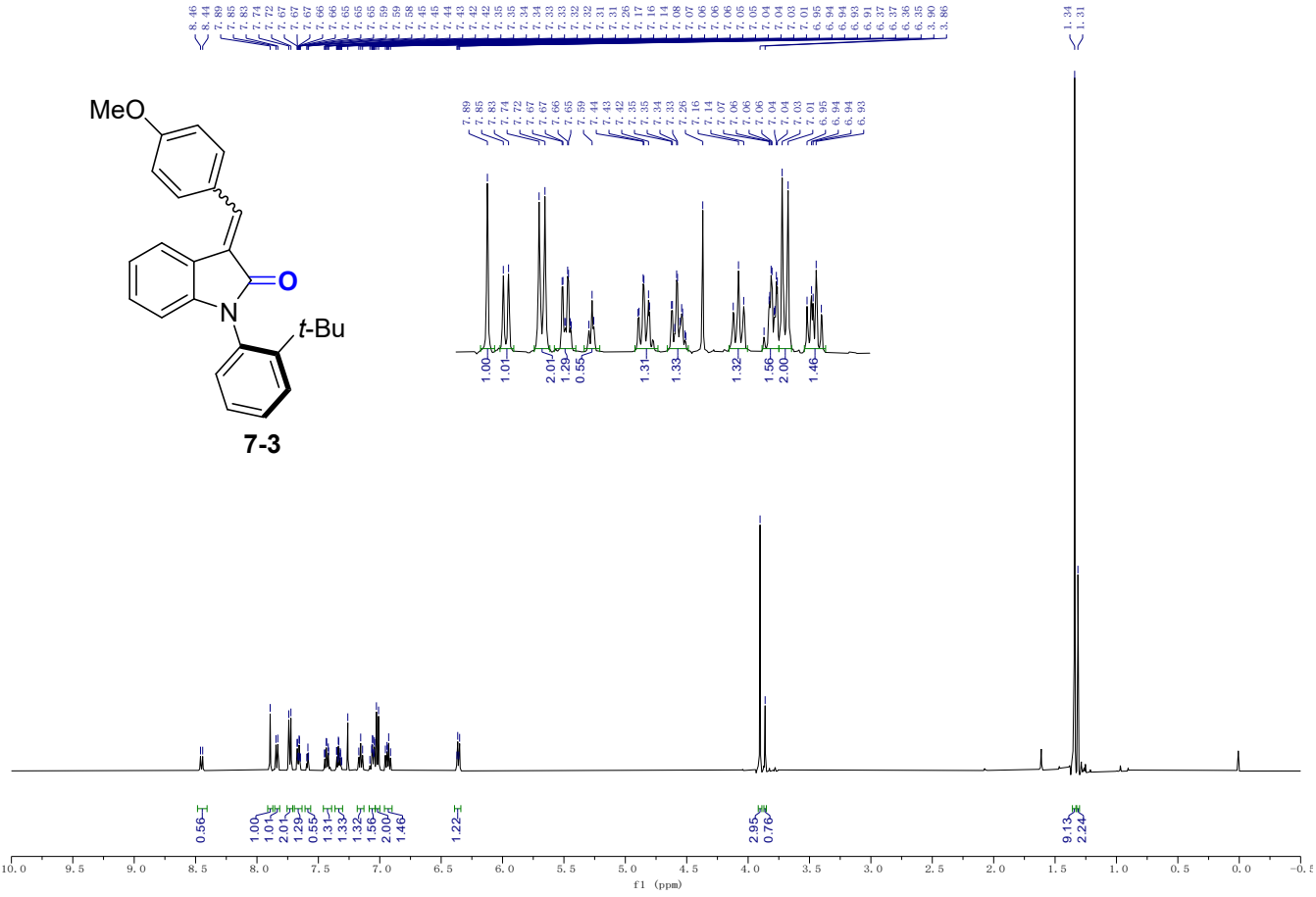
***Z*-7-1**

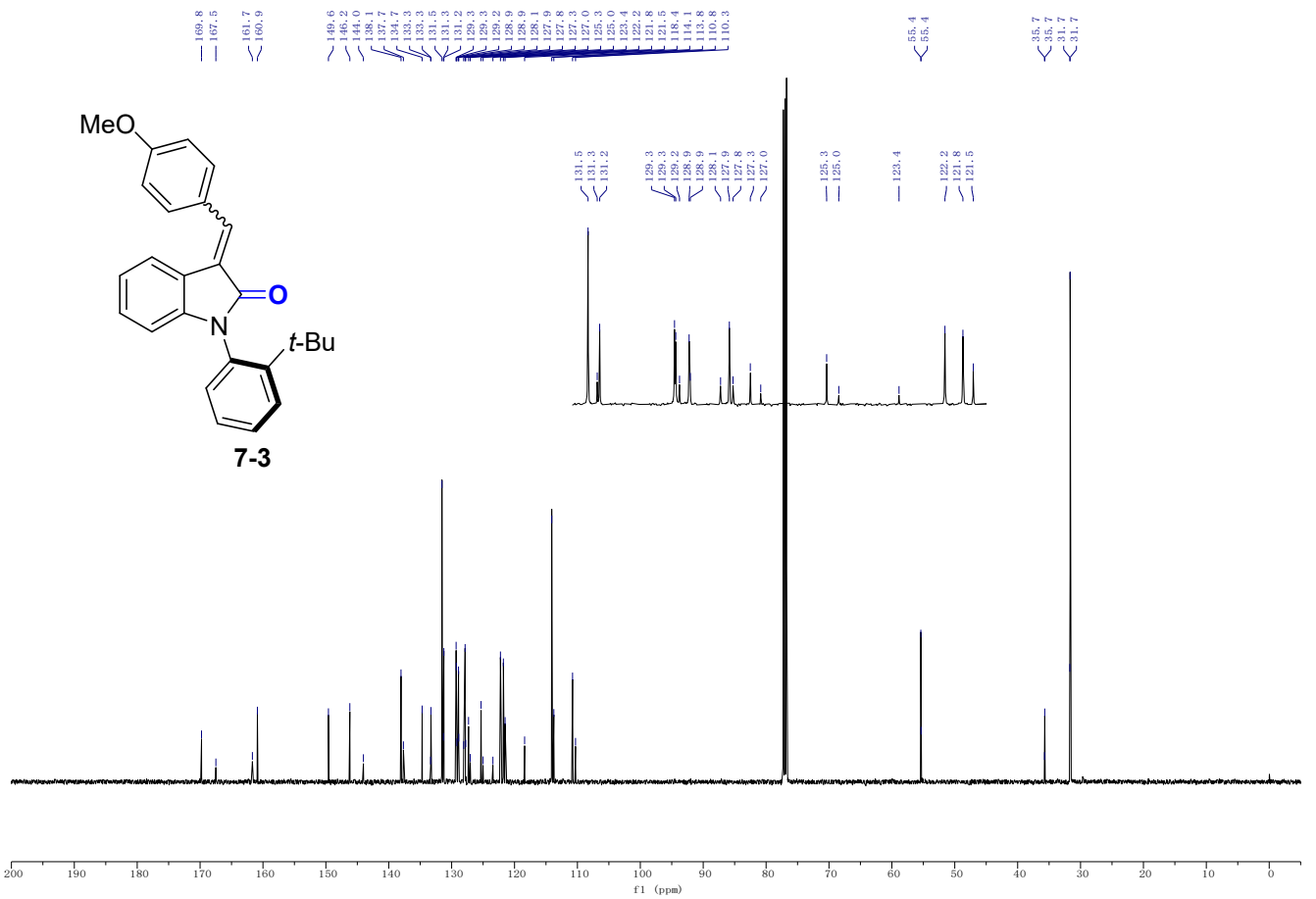

Ph
O
N
t-Bu
E-7-1
f1 (ppm)

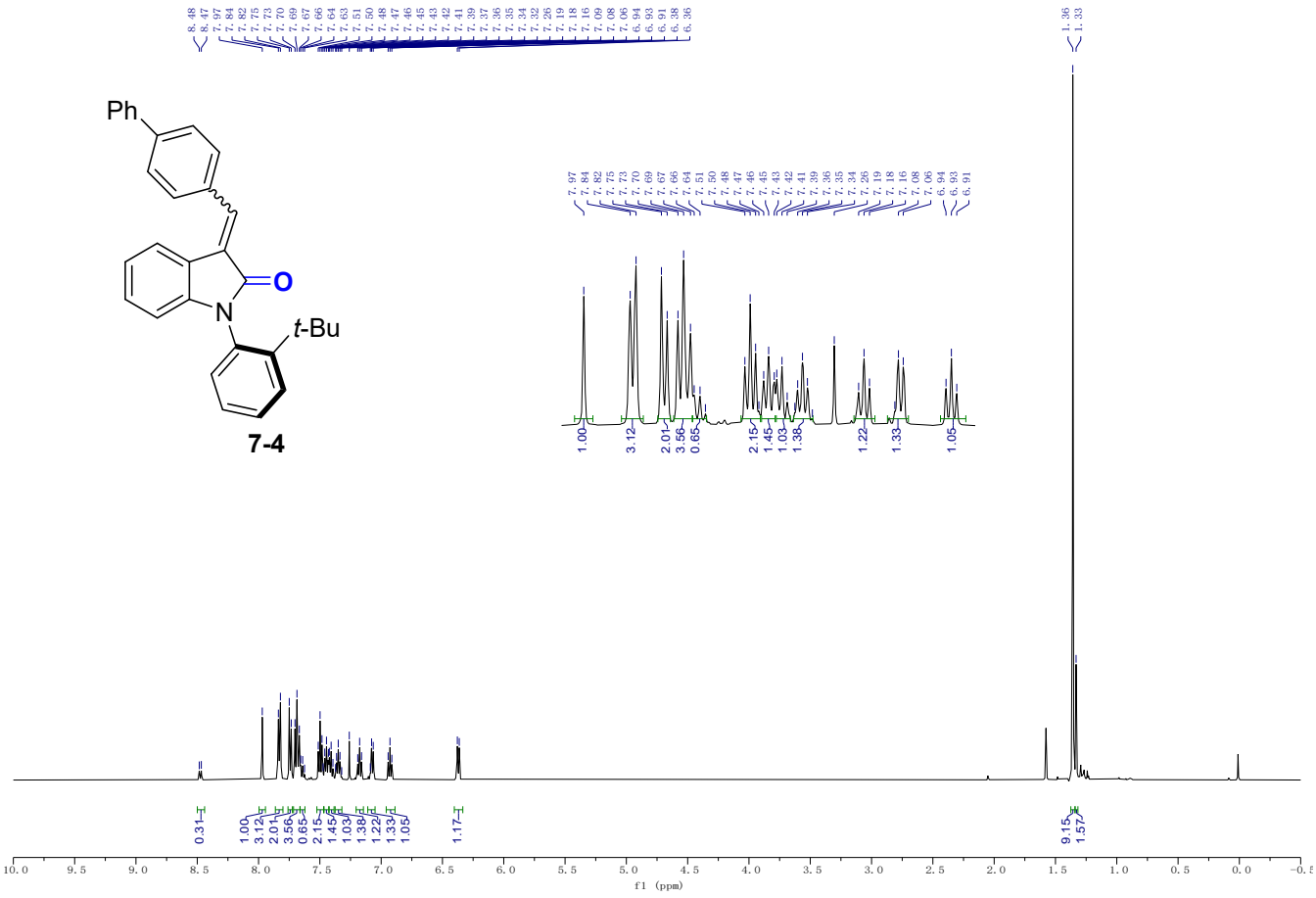

Ph
O
N
t-Bu
E-7-1
f1 (ppm)

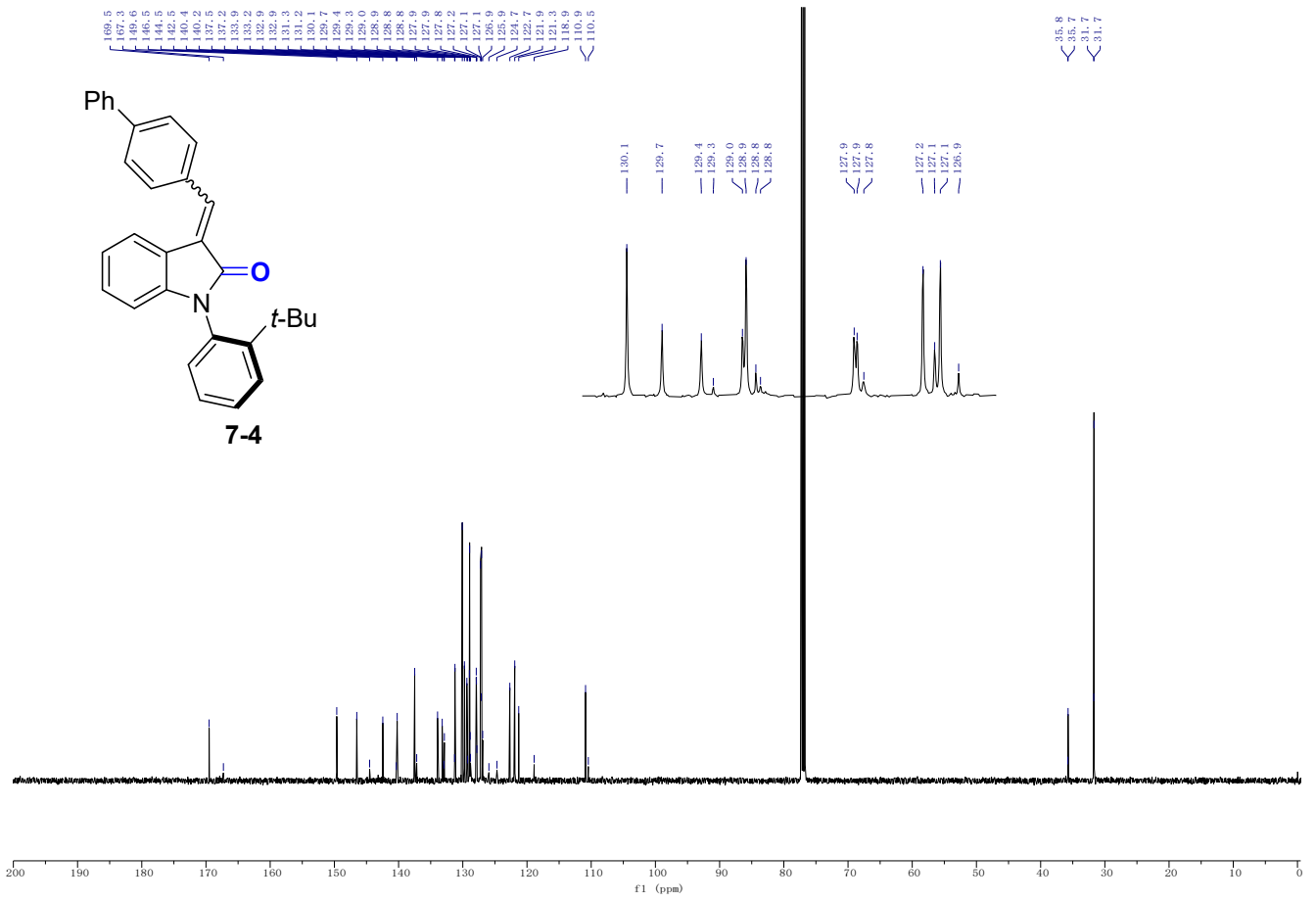

O
N
t-Bu
7-2
f1 (ppm)

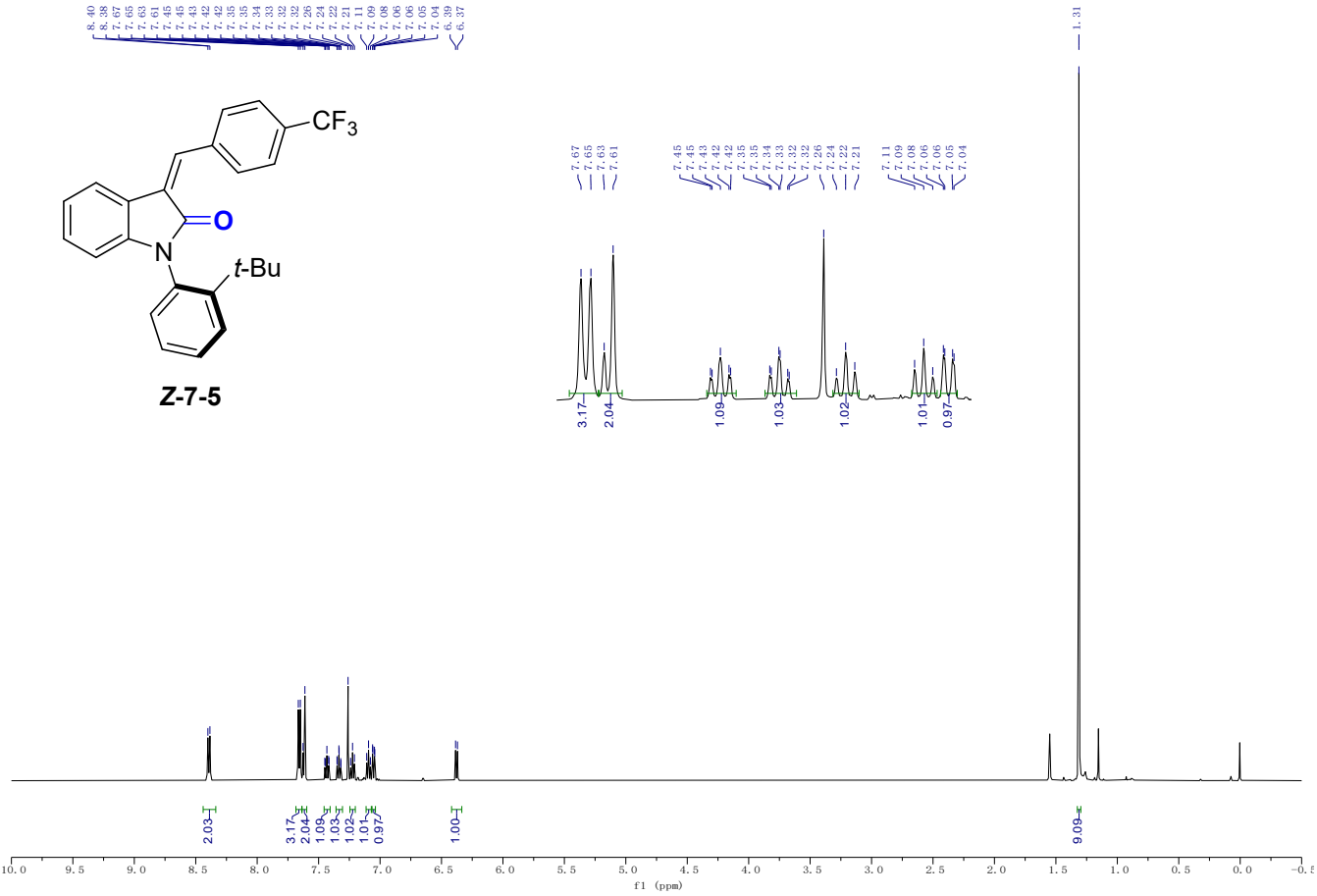

O
N
t-Bu
7-2
f1 (ppm)

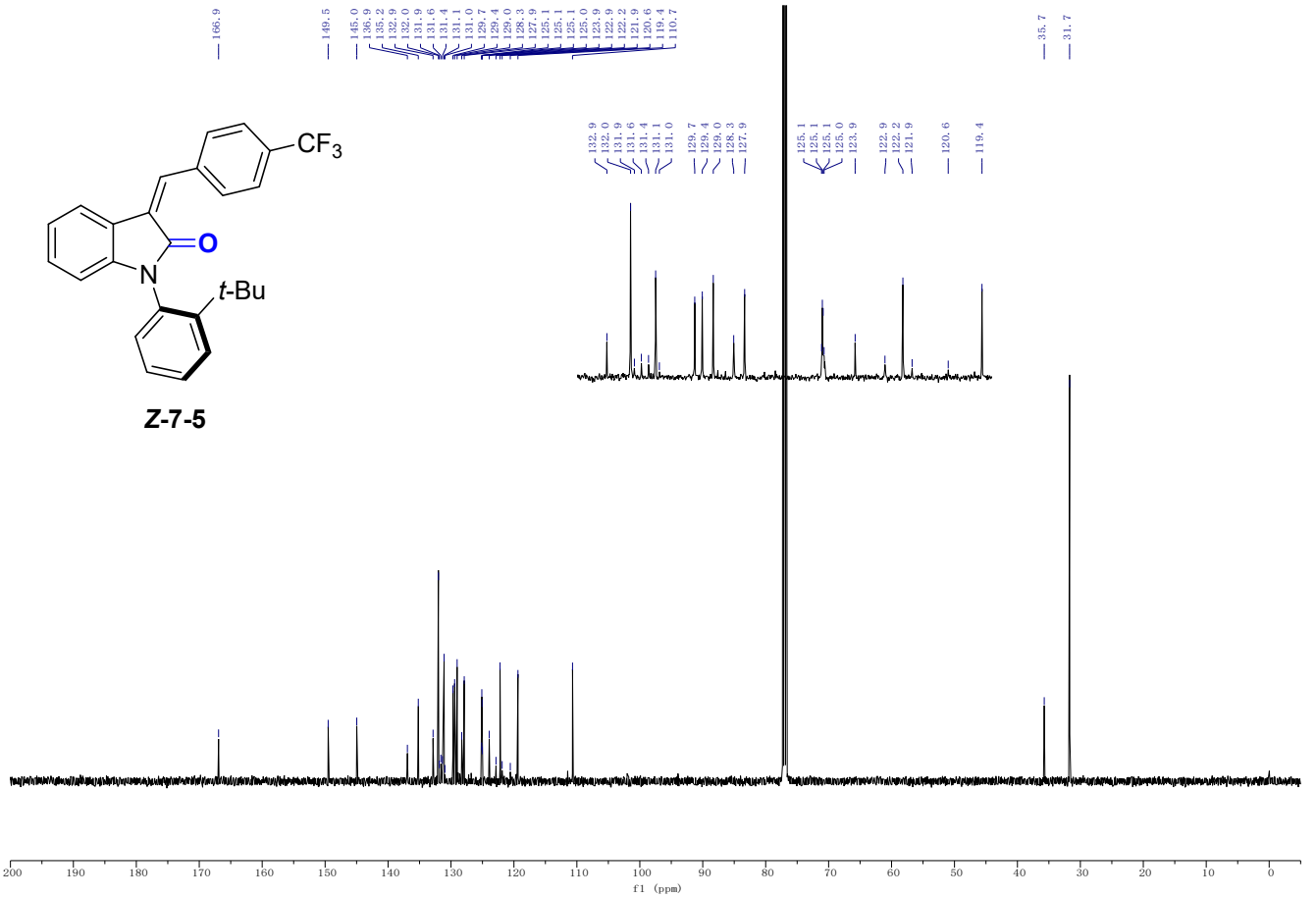

MeO
O
N
t-Bu
7-3
f1 (ppm)

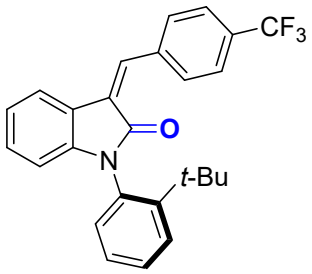

MeO
O
N
t-Bu
7-3
f1 (ppm)


Ph
O
N
t-Bu
7-4
f1 (ppm)


Ph
O
N
t-Bu
7-4
f1 (ppm)

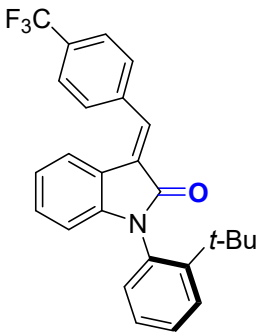

CF3
O
N
t-Bu
Z-7-5
f1 (ppm)


CF3
O
N
t-Bu
Z-7-5
f1 (ppm)


CF3
O
N
t-Bu

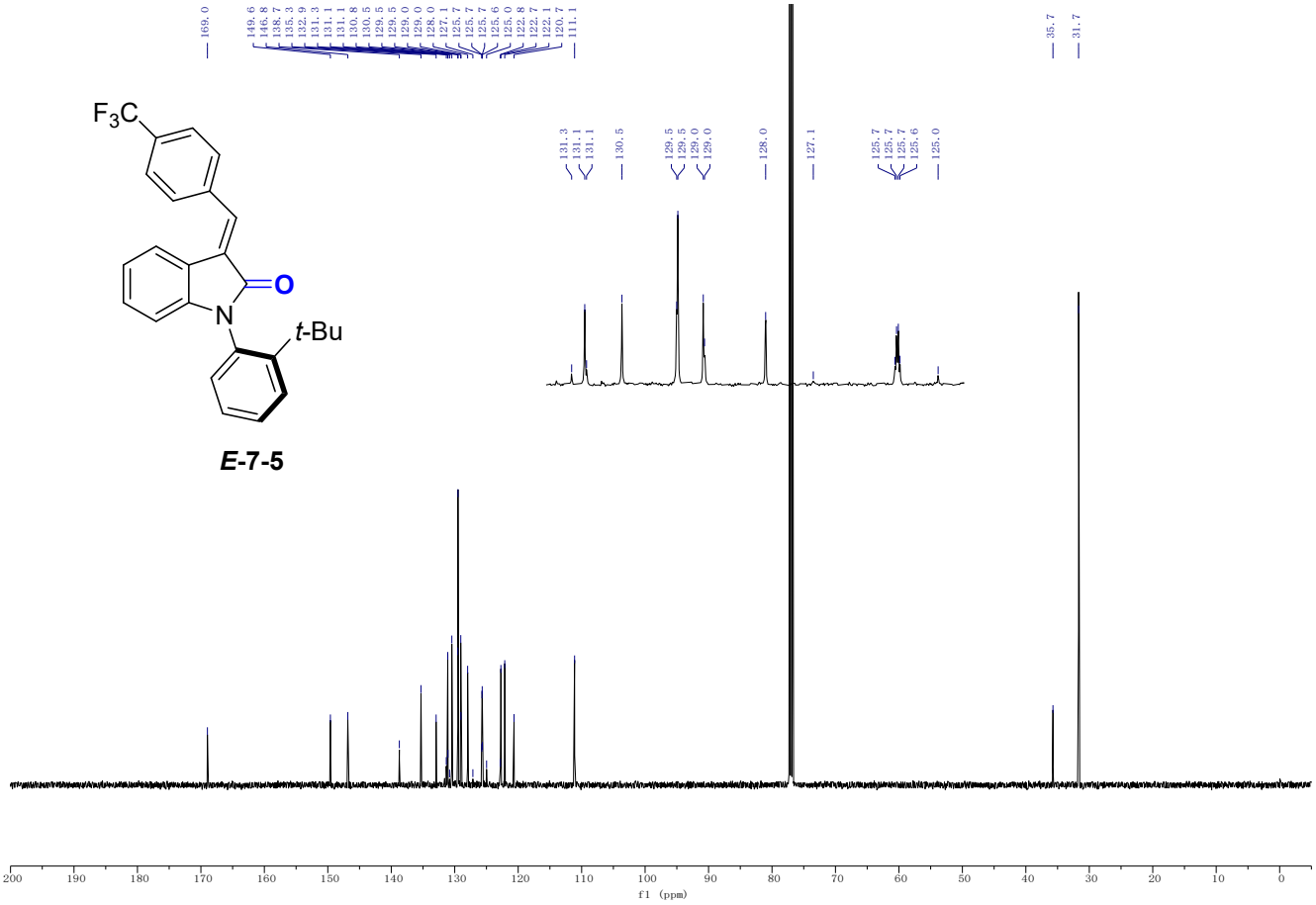
***Z*-7-5**

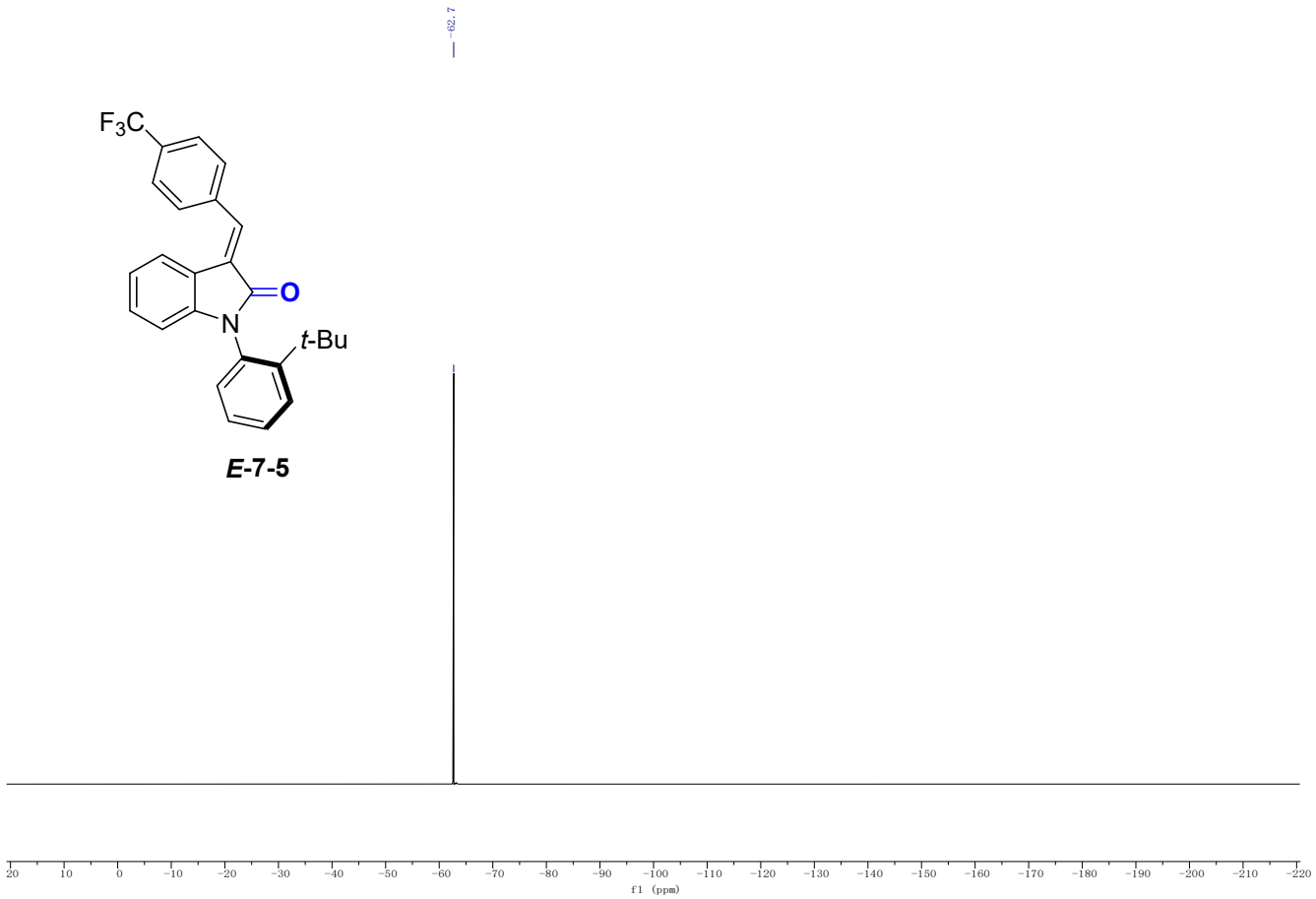
-62.9
f1 (ppm)

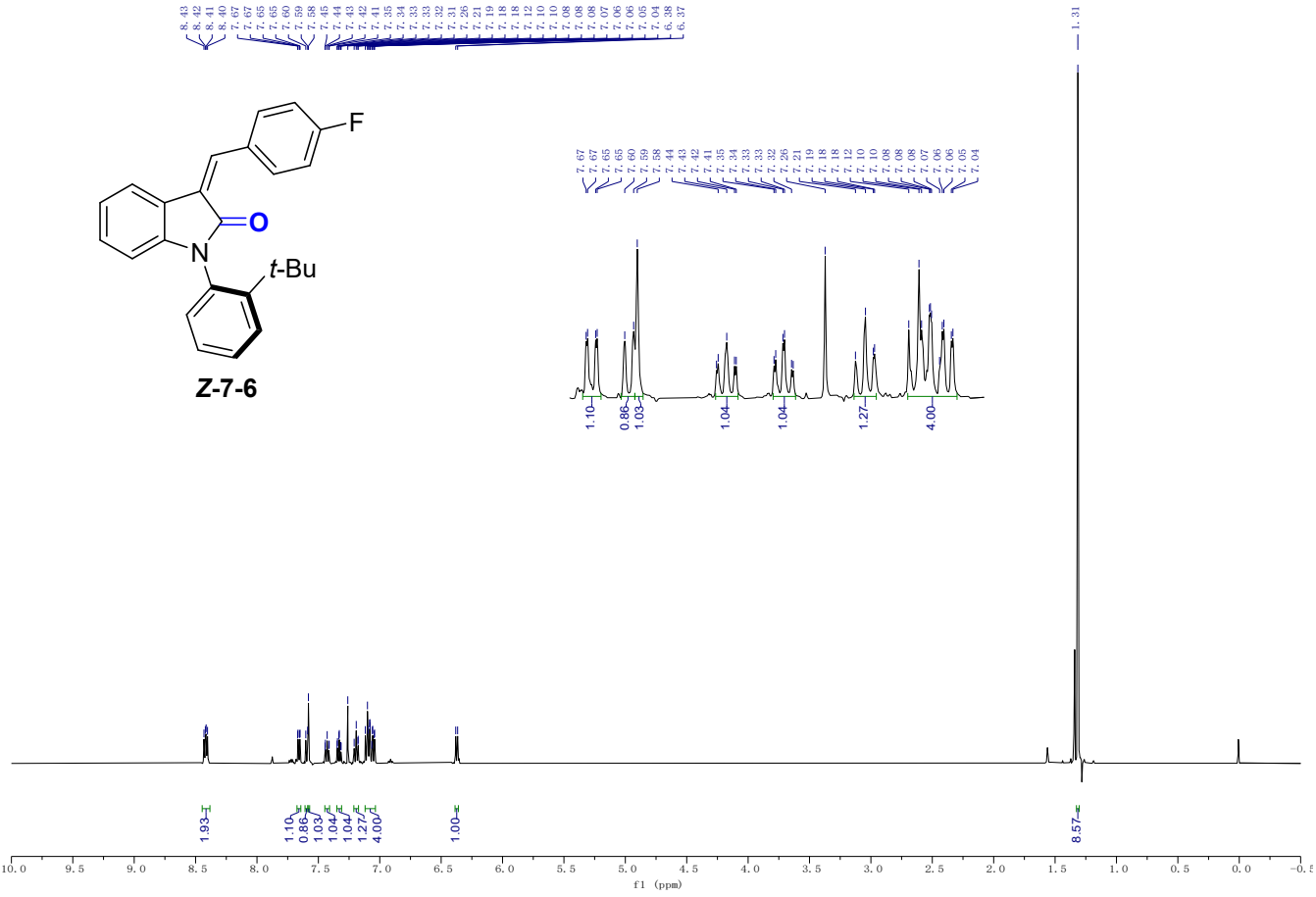

F3C
O
N
t-Bu

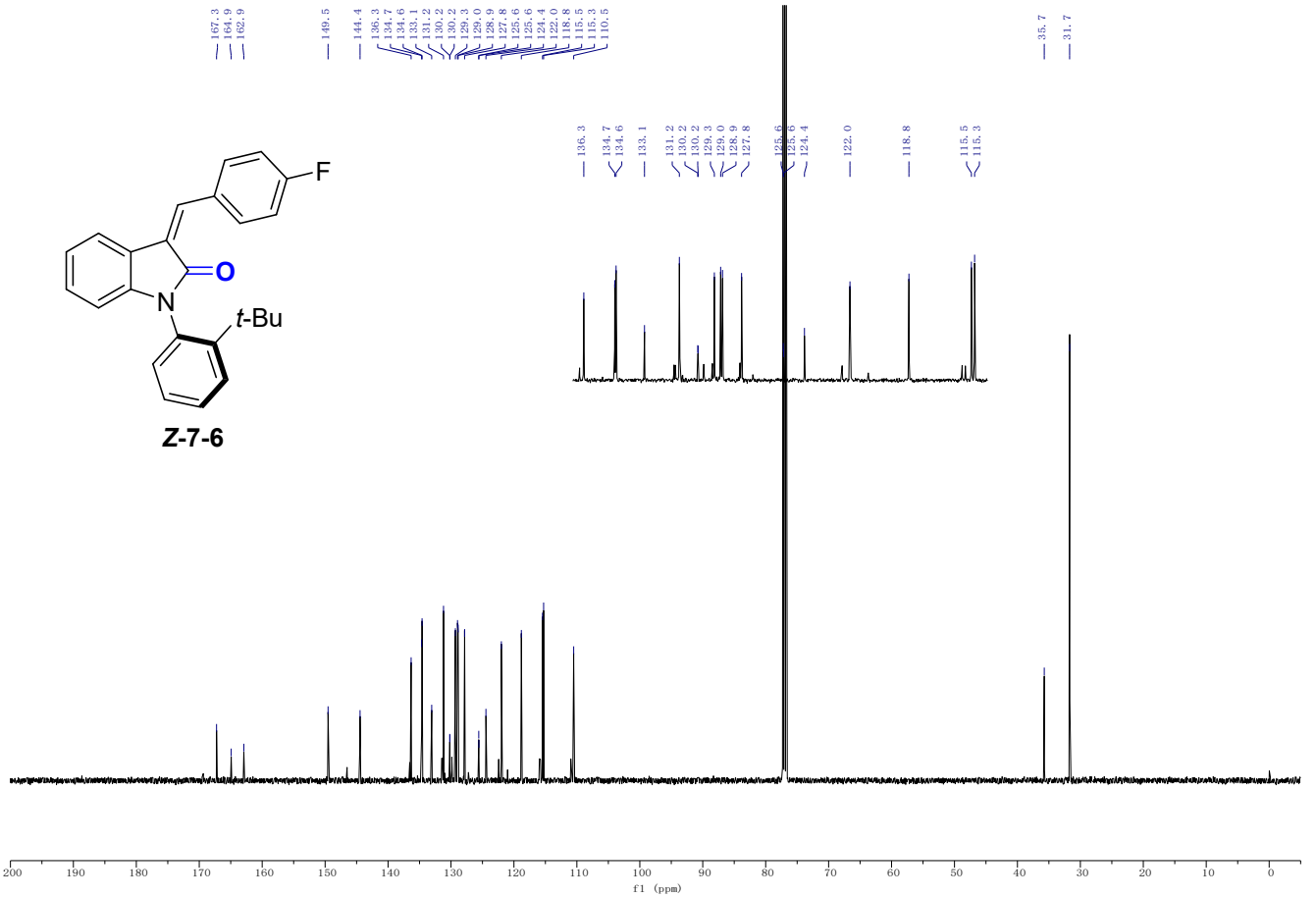
***E*-7-5**

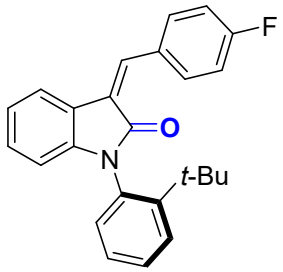
7.89
7.83
7.81
7.76
7.75
7.68
7.66
7.57
7.55
7.46
7.45
7.43
7.36
7.35
7.33
7.26
7.20
7.19
7.17
7.06
7.04
6.92
6.90
6.89
6.37
6.36
1.34
1.00
2.08
2.05
1.06
1.03
1.04
1.04
1.04
1.03
1.03
1.01
9.23
f1 (ppm)


169.0
149.6
146.8
138.7
135.3
132.9
131.3
131.1
131.1
130.8
130.5
129.5
129.5
129.0
129.0
128.0
127.1
125.7
125.7
125.6
125.0
122.8
122.7
122.1
120.7
111.1
35.7
31.7
131.3
131.1
131.1
130.5
129.5
129.5
129.0
129.0
128.0
127.1
125.7
125.7
125.7
125.6
125.0
F3C
O
N
t-Bu
E-7-5
f1 (ppm)


-62.7
F3C
O
N
t-Bu
E-7-5
f1 (ppm)

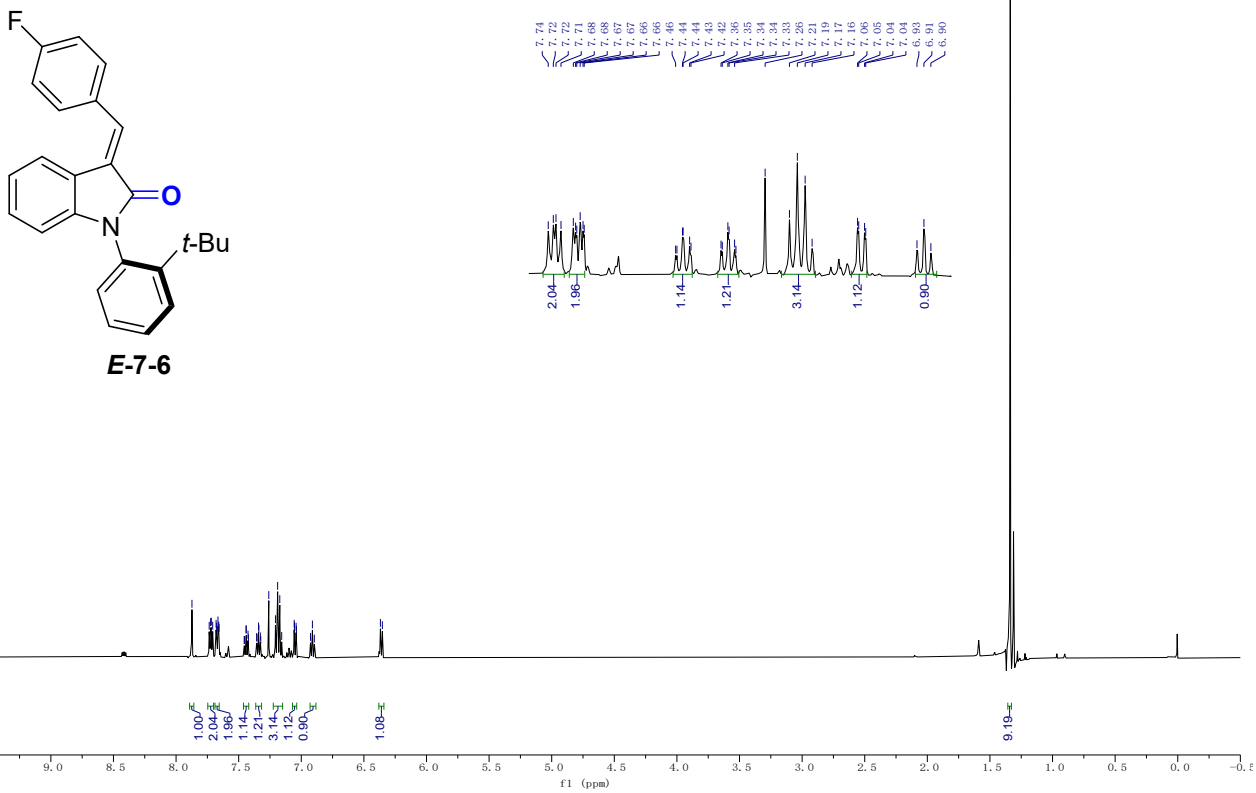

F
O
N
t-Bu
Z-7-6
f1 (ppm)


F
O
N
t-Bu
Z-7-6
f1 (ppm)


F
O
N
t-Bu

***Z*-7-6**

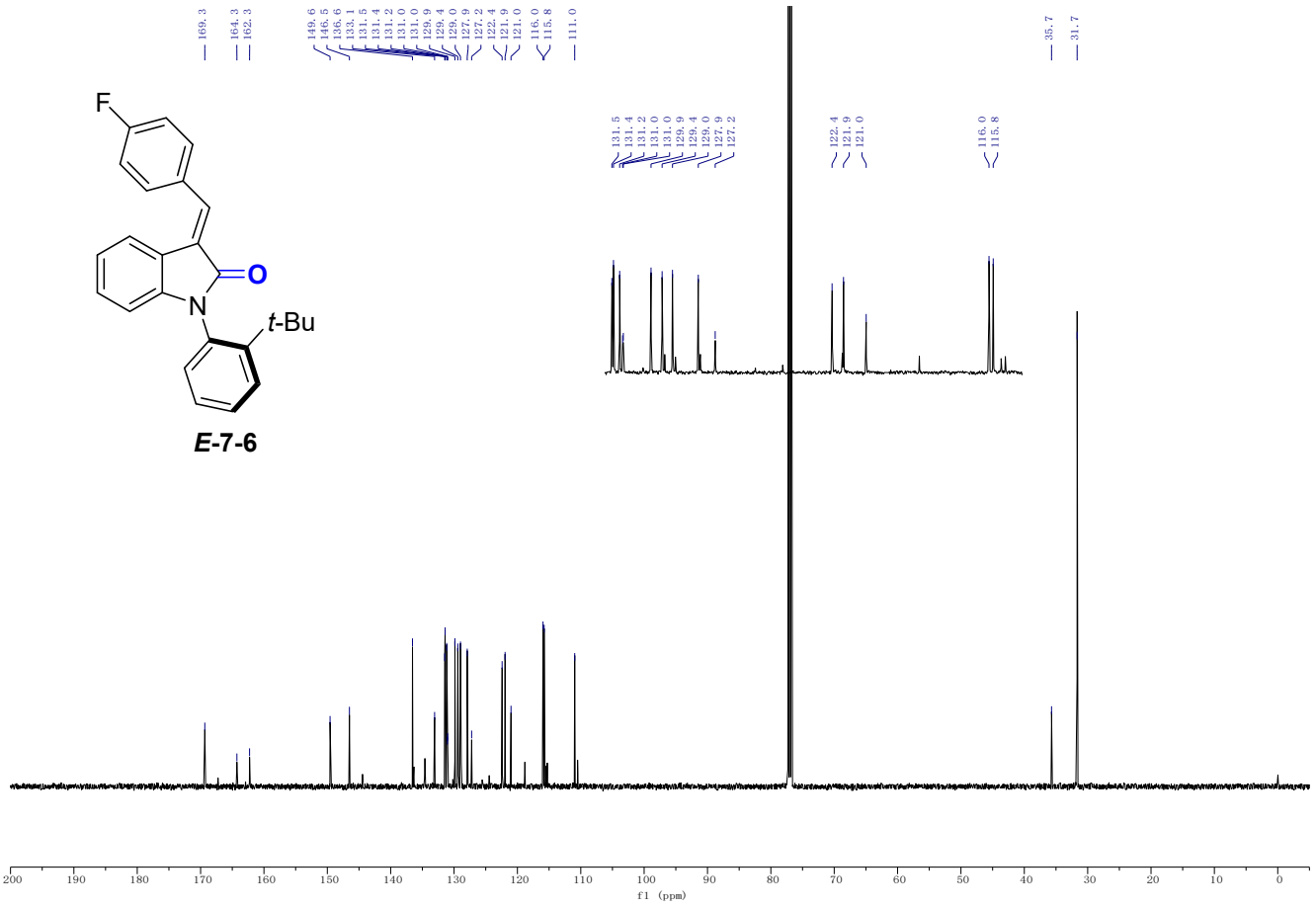
-108.2
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)


7.87 7.74 7.72 7.72 7.71 7.68 7.68 7.67 7.67 7.66 7.66 7.46 7.45 7.44 7.44 7.43 7.42 7.36 7.35 7.34 7.34 7.33 7.26 7.21 7.19 7.17 7.16 7.06 7.05 7.04 7.04 6.93 6.91 6.90 6.35
1.34
1.00 2.04 1.96 1.14 1.21 3.14 1.12 0.90 1.08 9.19
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

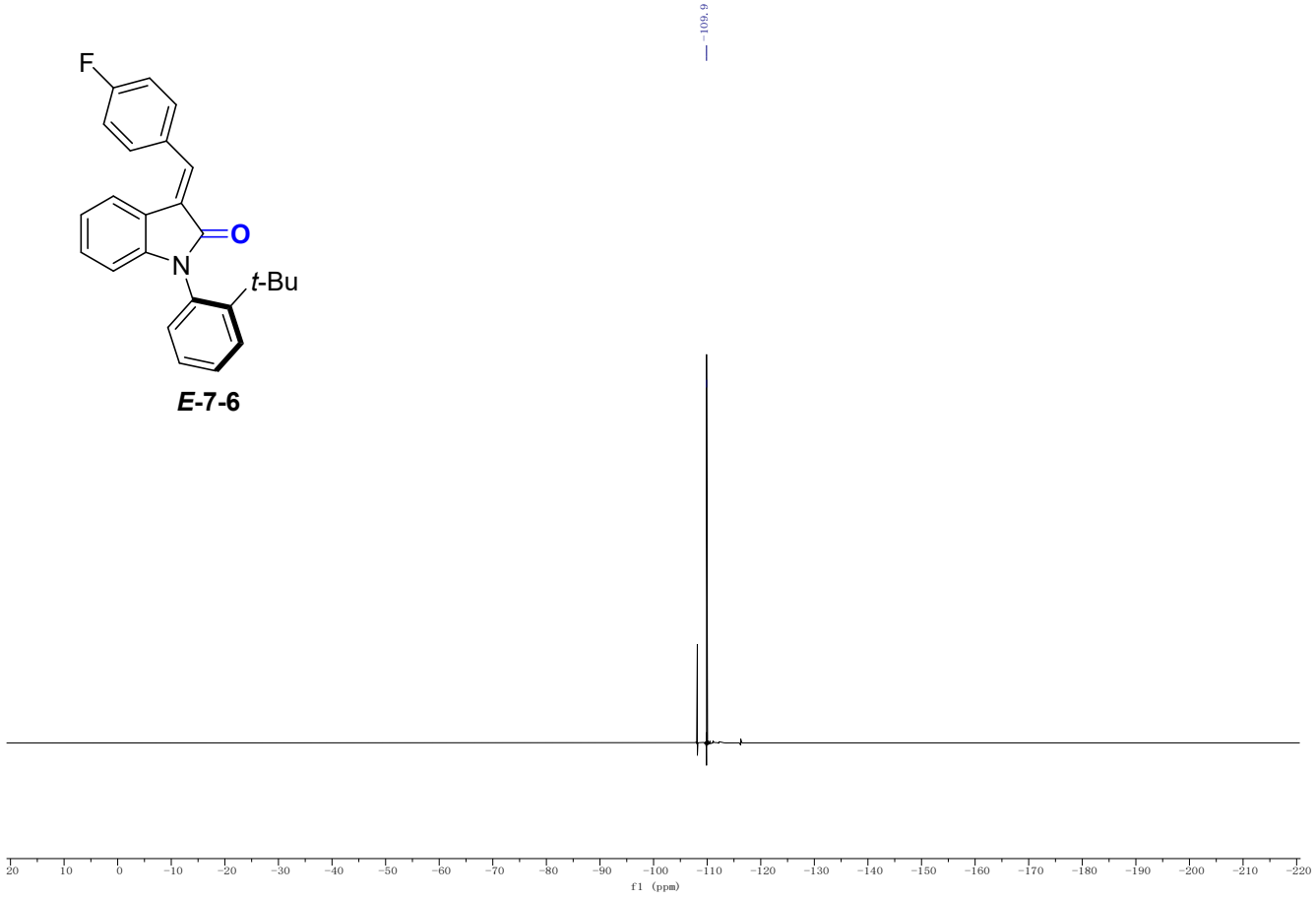
F
O
N
t-Bu

***E*-7-6**

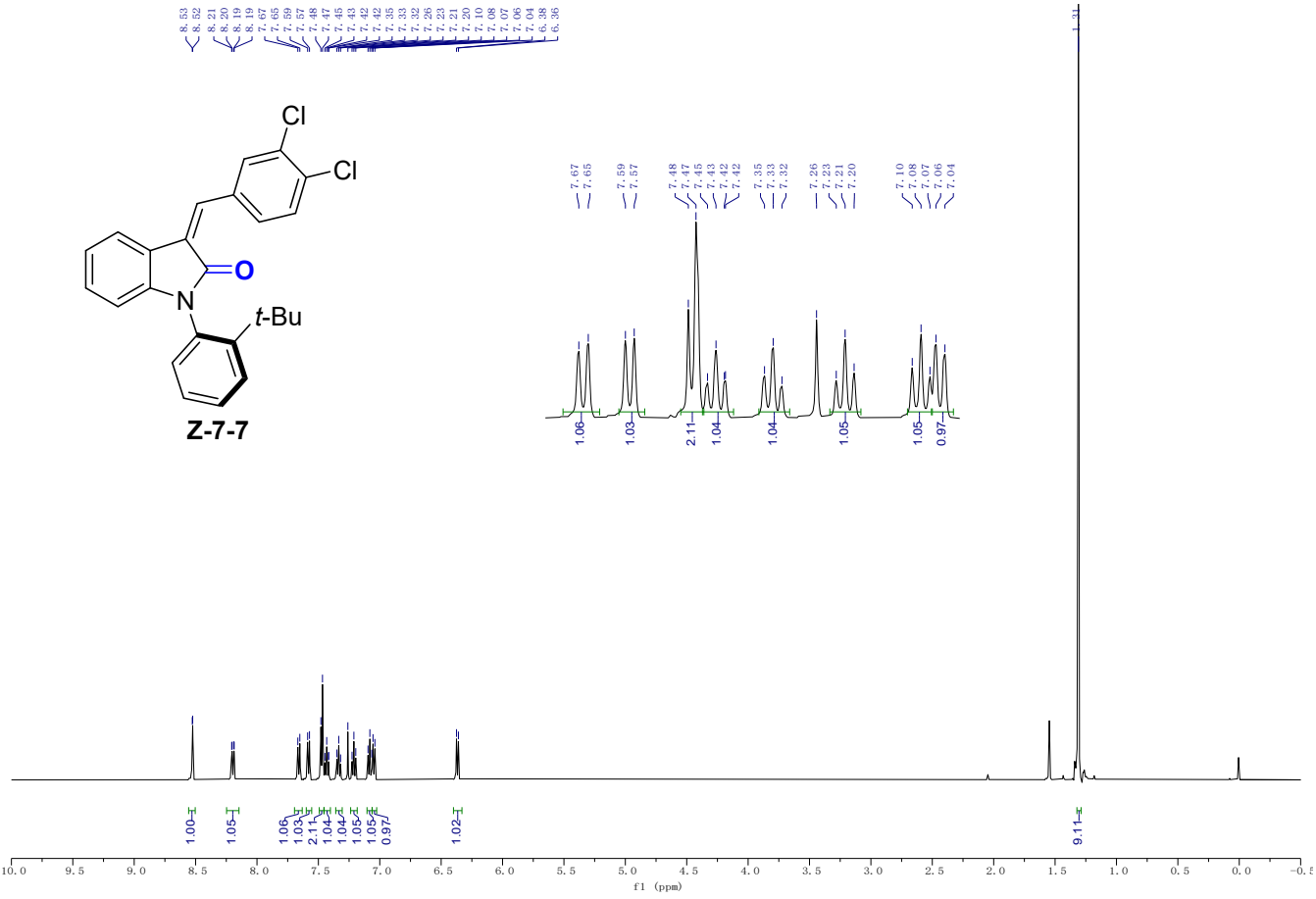
7.74 7.72 7.72 7.71 7.68 7.68 7.67 7.67 7.66 7.66 7.46 7.44 7.44 7.43 7.42 7.36 7.35 7.34 7.34 7.33 7.26 7.21 7.19 7.17 7.16 7.06 7.05 7.04 7.04 6.93 6.91 6.90
2.04 1.96 1.14 1.21 3.14 1.12 0.90

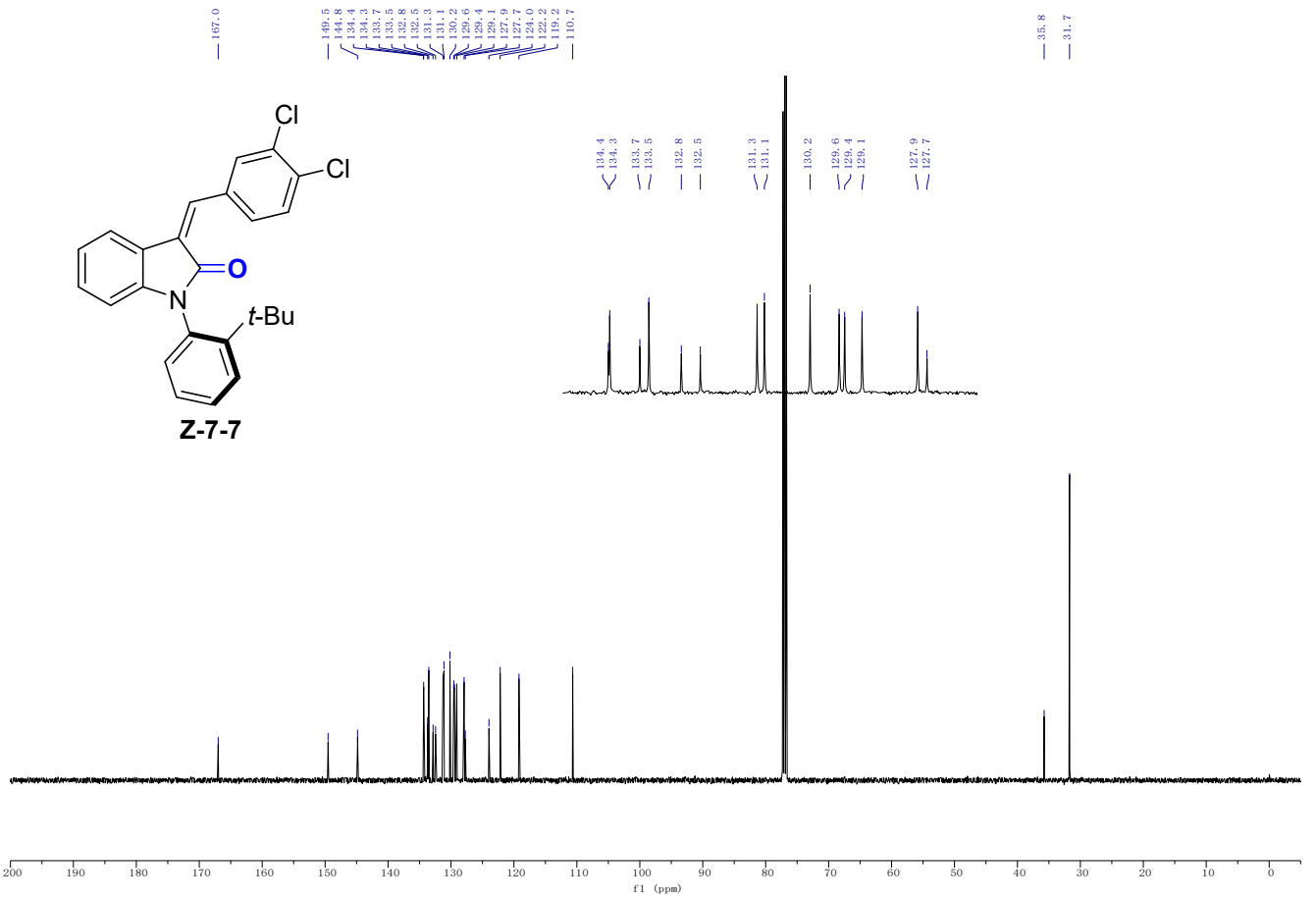

169.3
164.3
162.3
149.6
146.5
136.6
133.1
131.5
131.4
131.2
131.0
131.0
129.9
129.4
129.0
127.9
127.2
122.4
121.9
121.0
116.0
115.8
111.0
35.7
31.7
F
O
N
t-Bu
f1 (ppm)

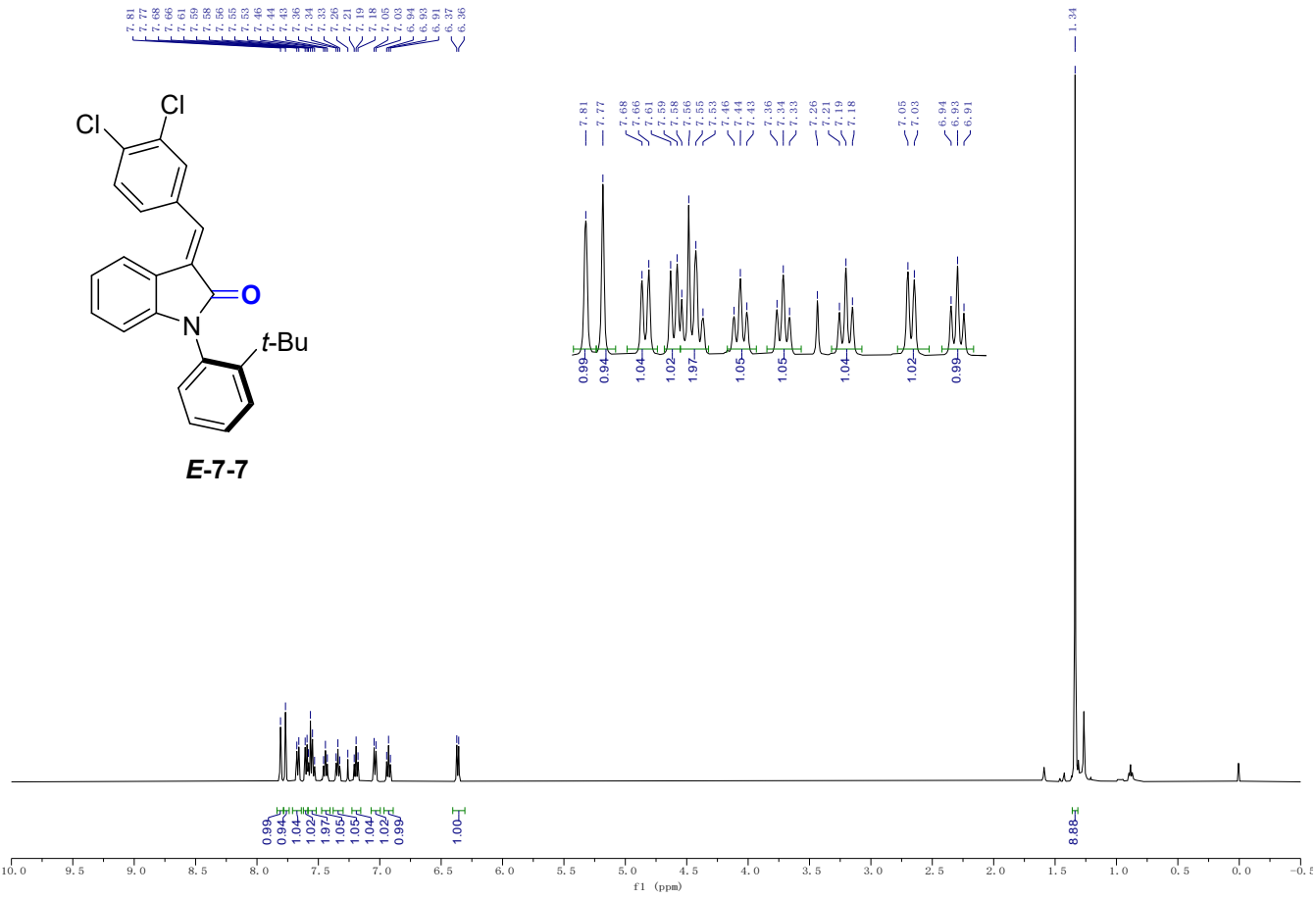
***E*-7-6**

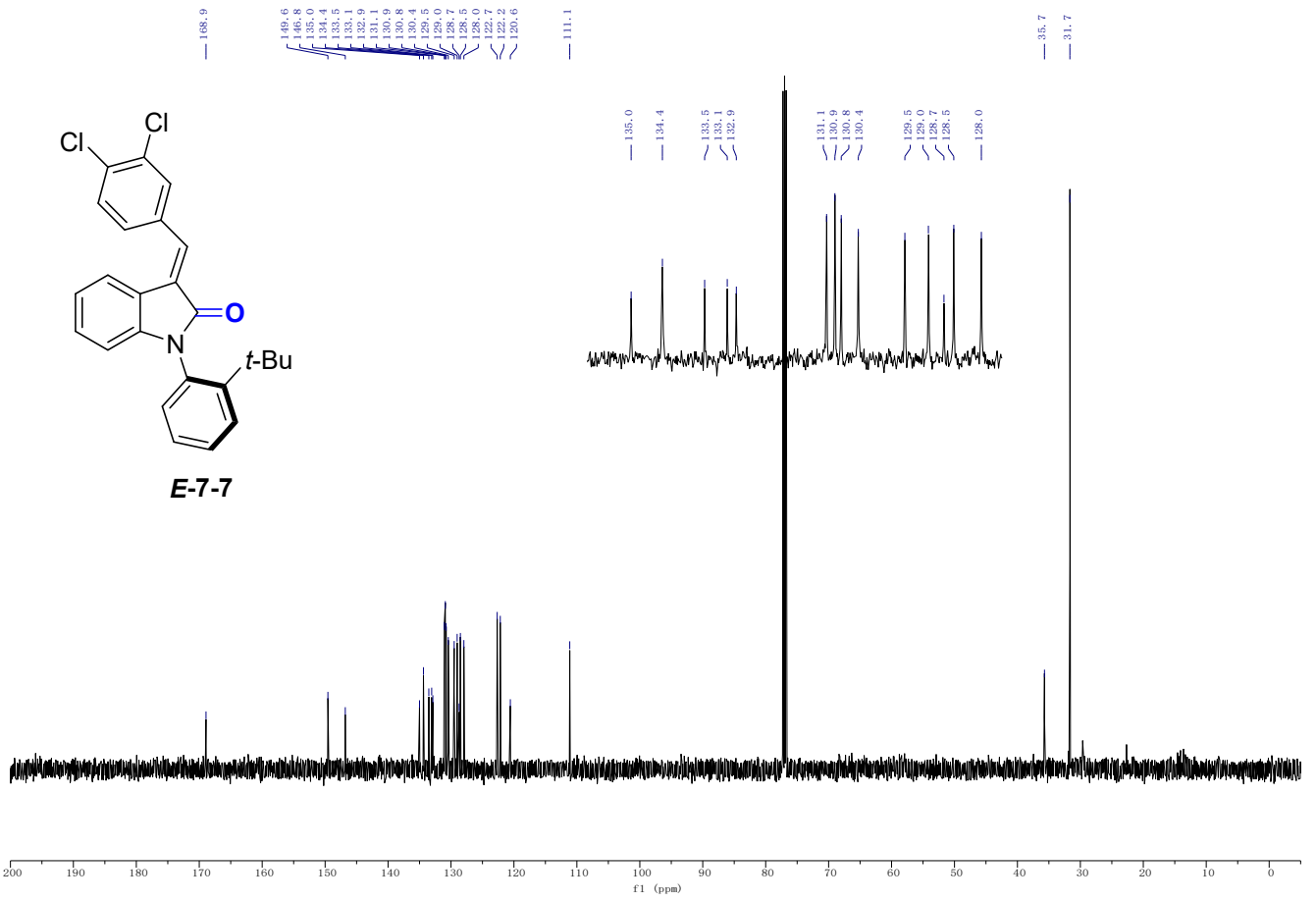

-109.9
F
O
N
t-Bu
f1 (ppm)

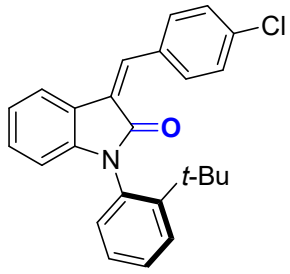
***E*-7-6**


Cl
Cl
O
N
t-Bu
Z-7-7
f1 (ppm)


Cl
Cl
O
N
t-Bu
Z-7-7
f1 (ppm)

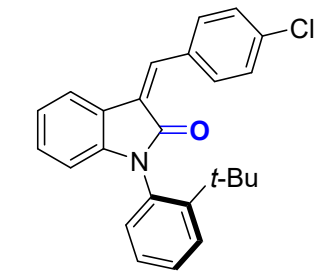

Cl
Cl
O
N
t-Bu
E-7-7
f1 (ppm)


Cl
Cl
O
N
t-Bu
E-7-7
f1 (ppm)


Cl
O
N
t-Bu

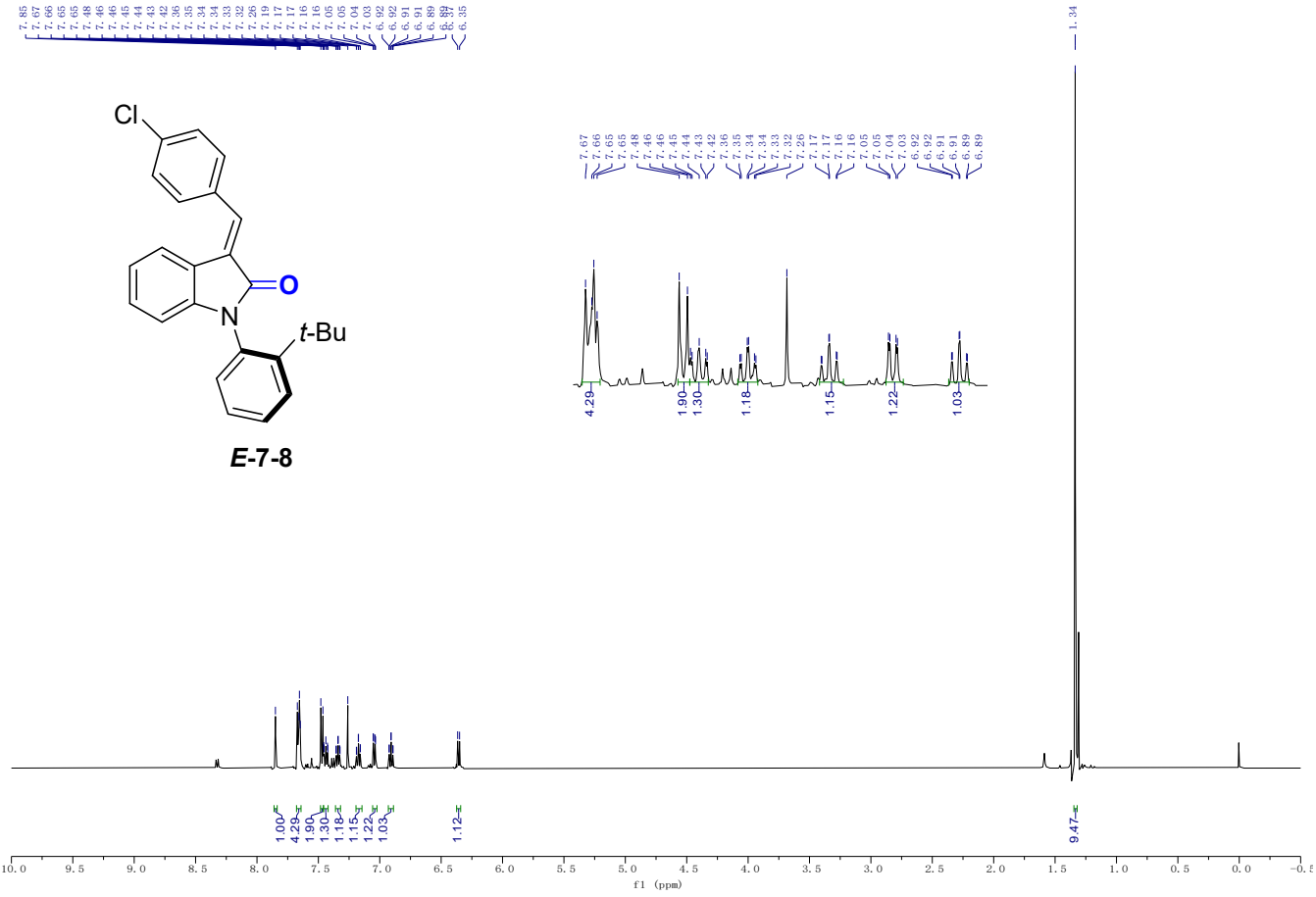
Z-7-8

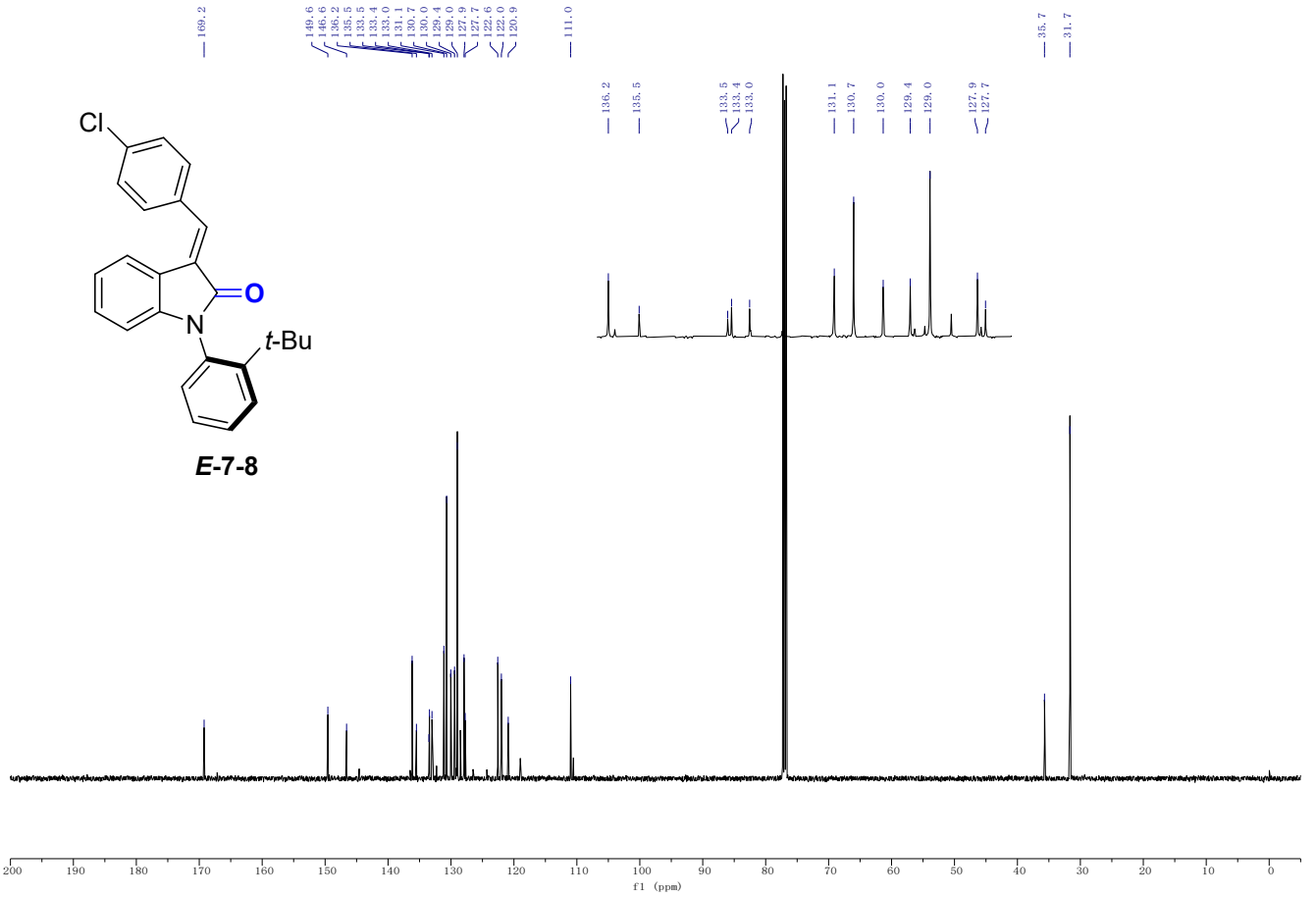
1.95
1.32
1.01
1.00
1.09
1.94
1.03
1.00
0.99
1.10
0.99
9.02
f1 (ppm)

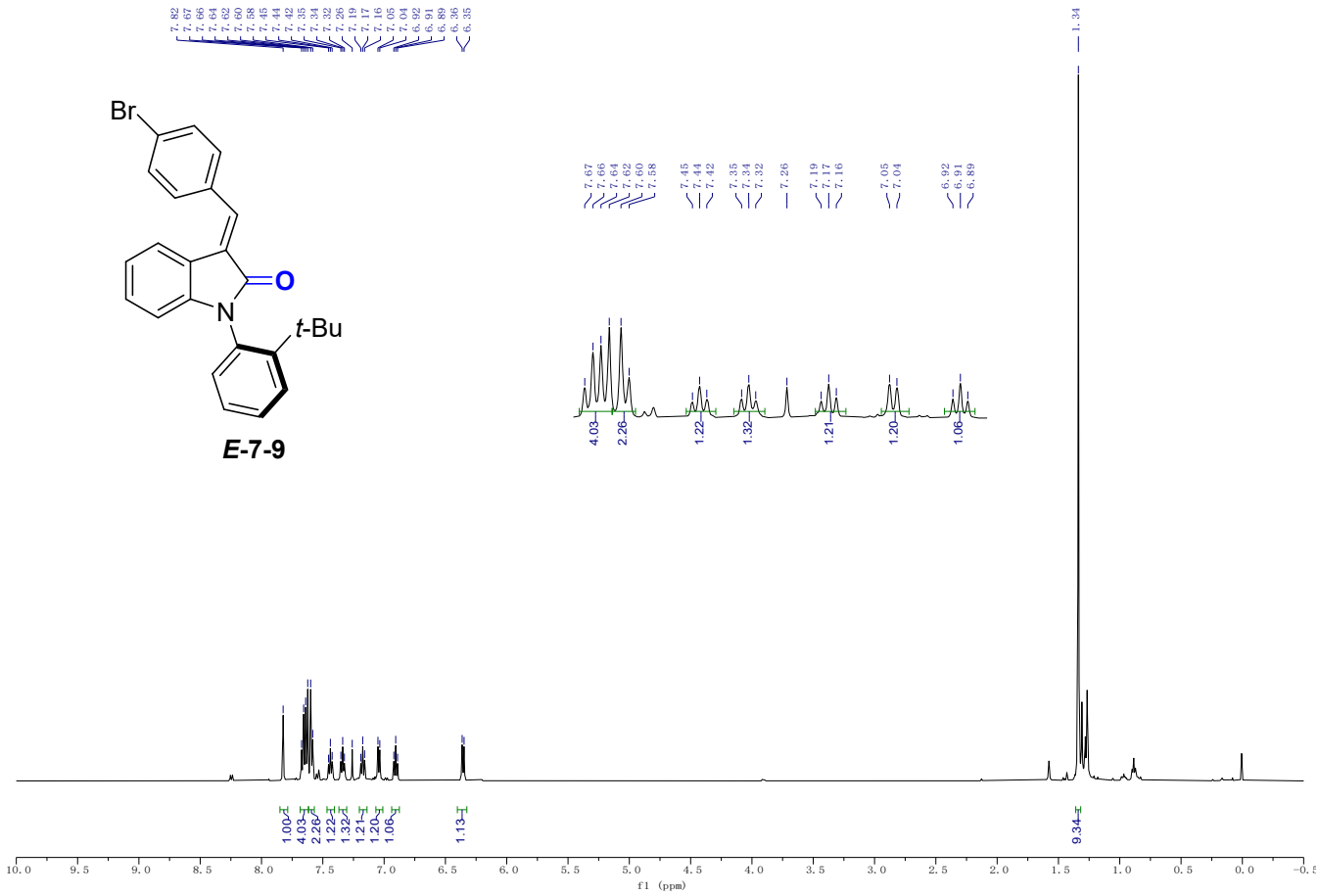

Cl
O
N
t-Bu

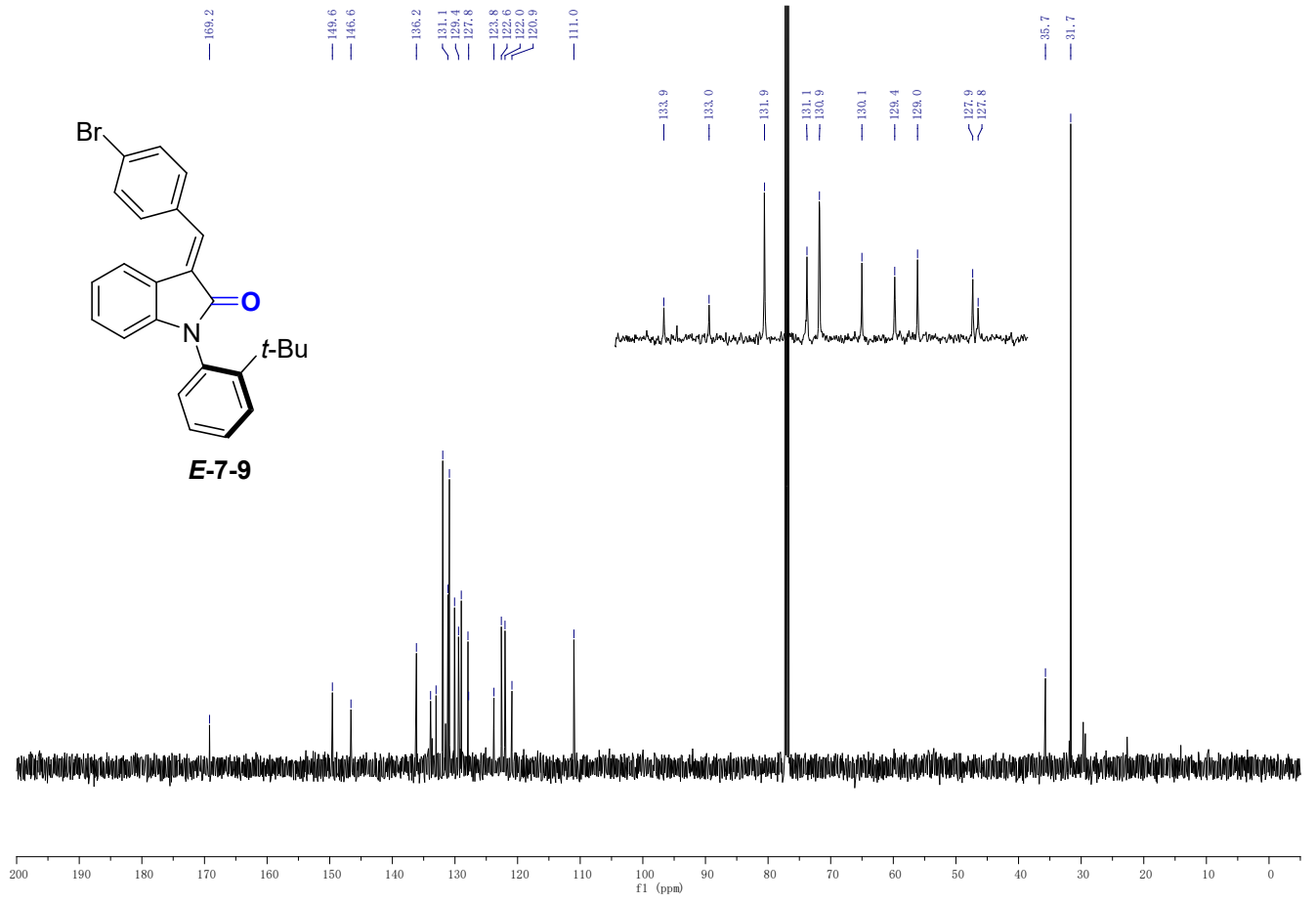
Z-7-8

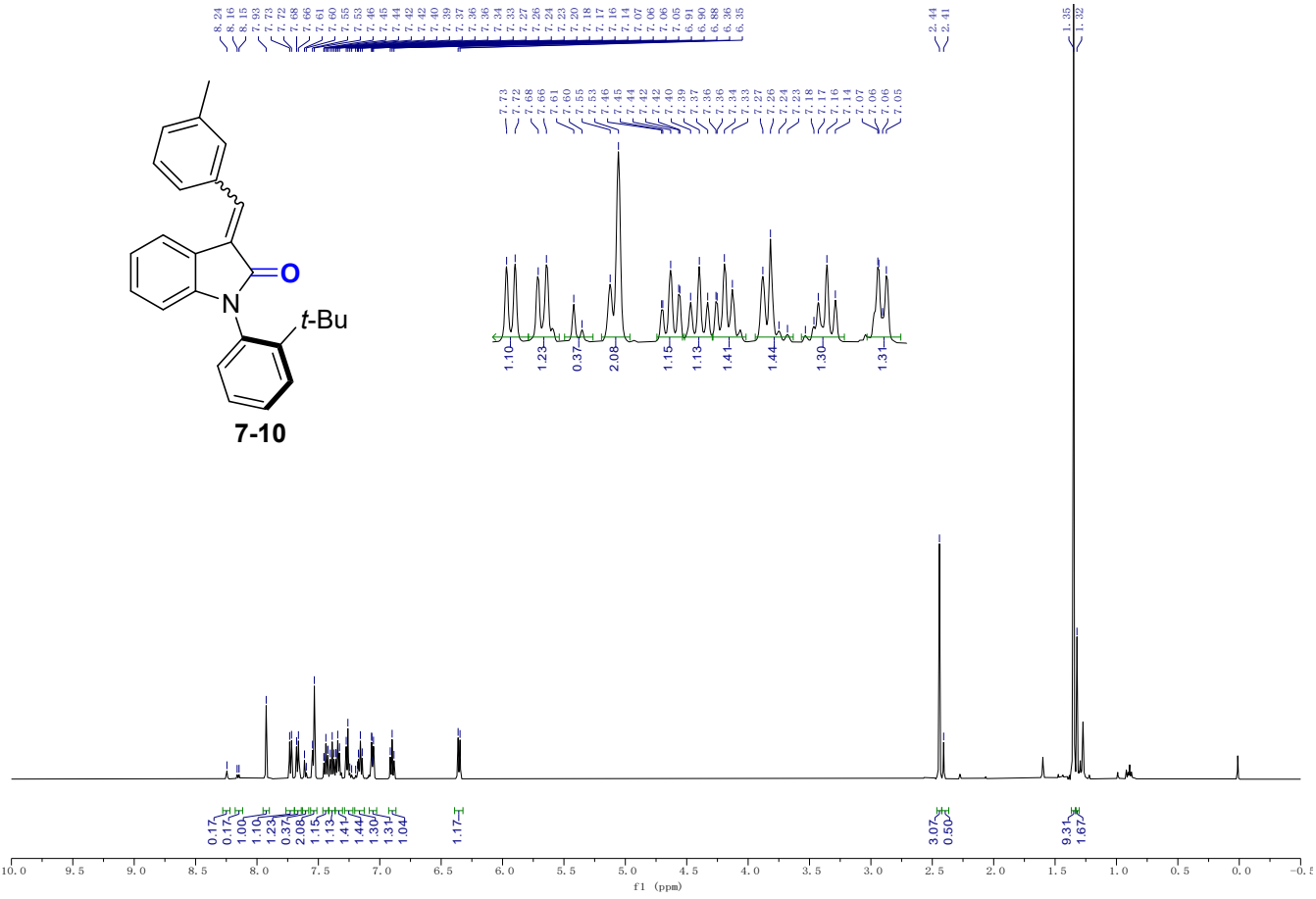
167.2
149.5
144.6
136.5
136.0
133.5
133.0
132.3
131.2
129.3
129.1
129.0
128.5
127.9
126.5
124.3
122.1
119.0
110.6
35.7
31.7
f1 (ppm)


Cl
O
N
t-Bu
E-7-8
f1 (ppm)

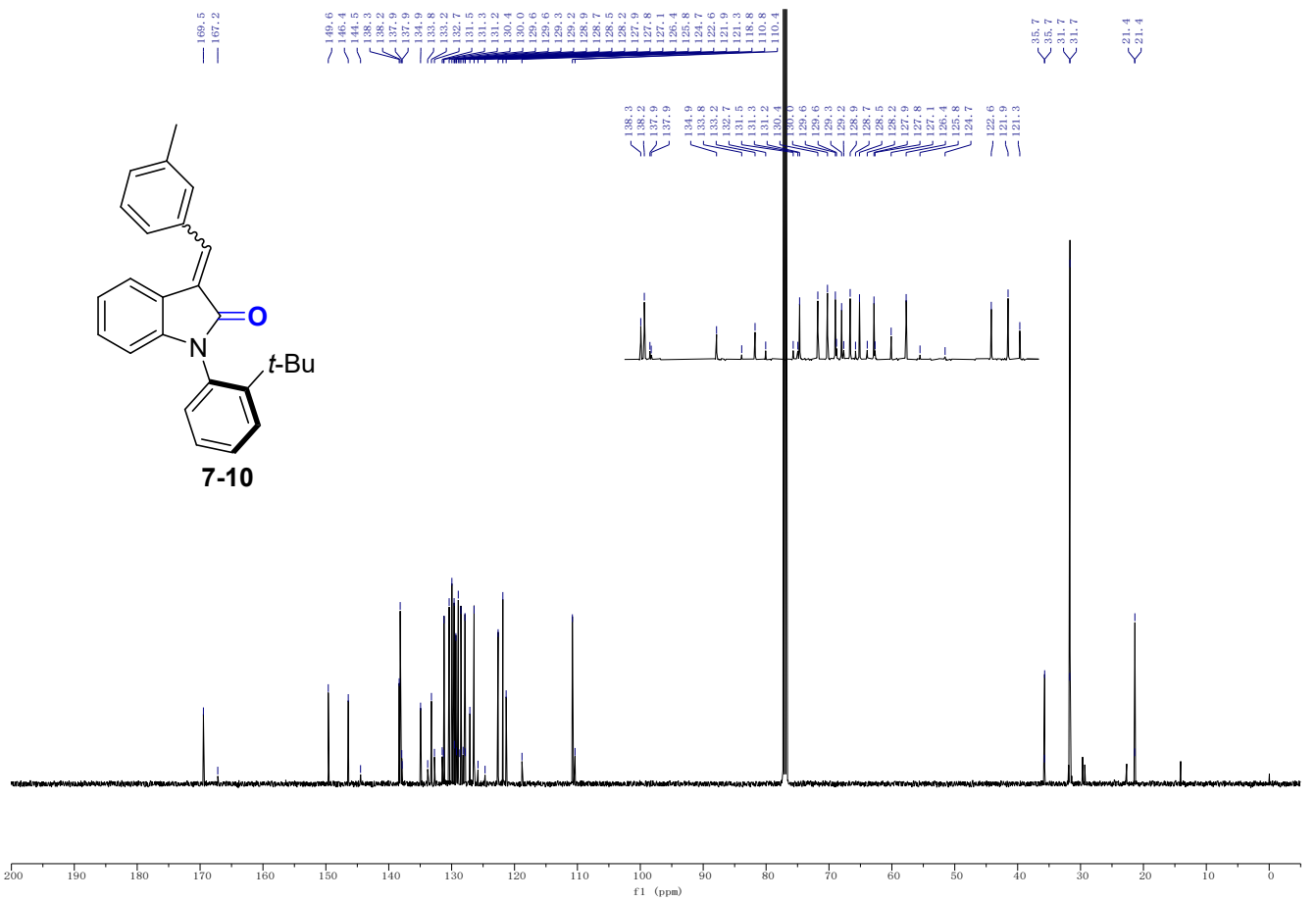

Cl
O
N
t-Bu
E-7-8
f1 (ppm)


Br
O
N
t-Bu
E-7-9
f1 (ppm)

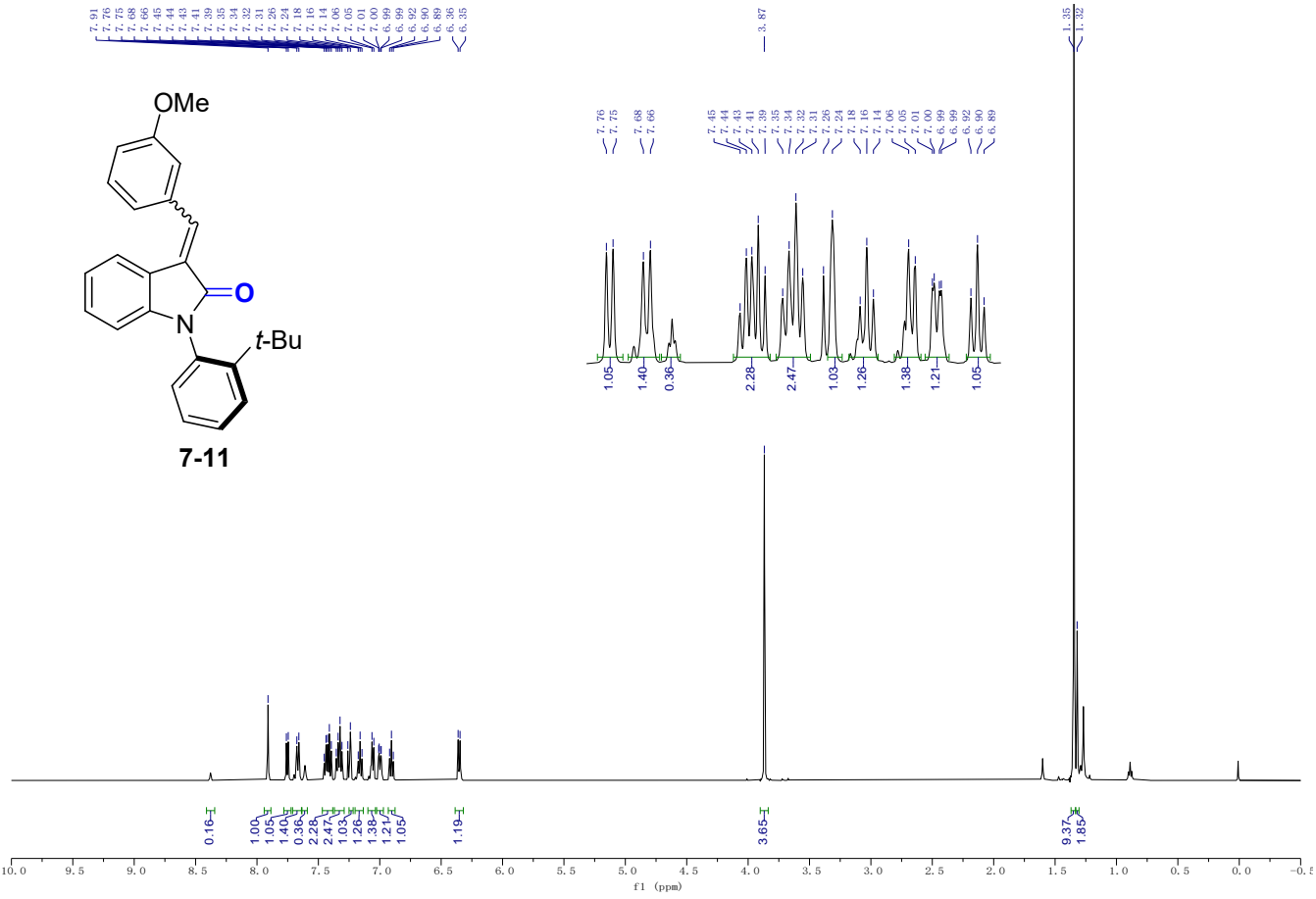

Br
O
N
t-Bu
E-7-9
f1 (ppm)

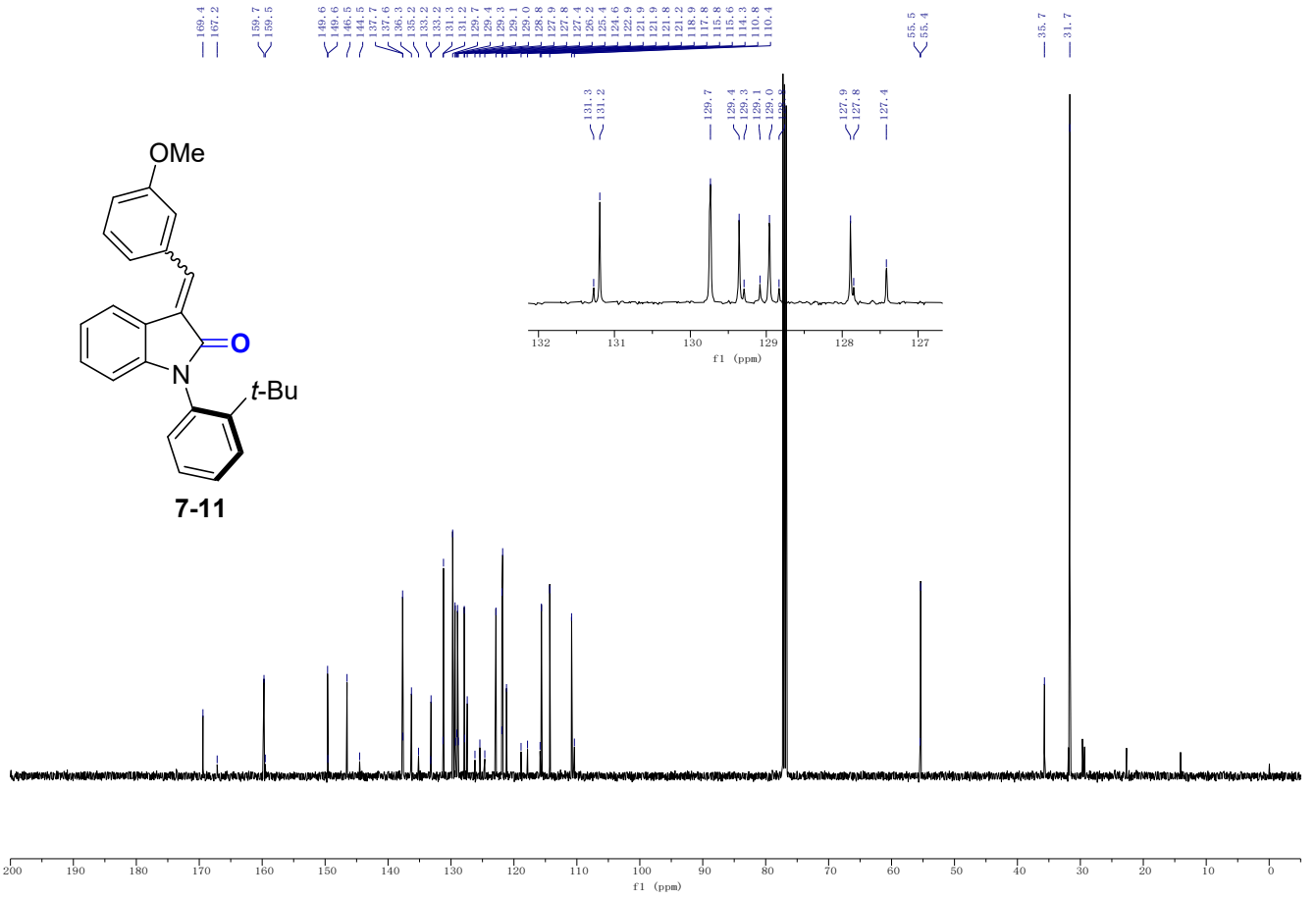


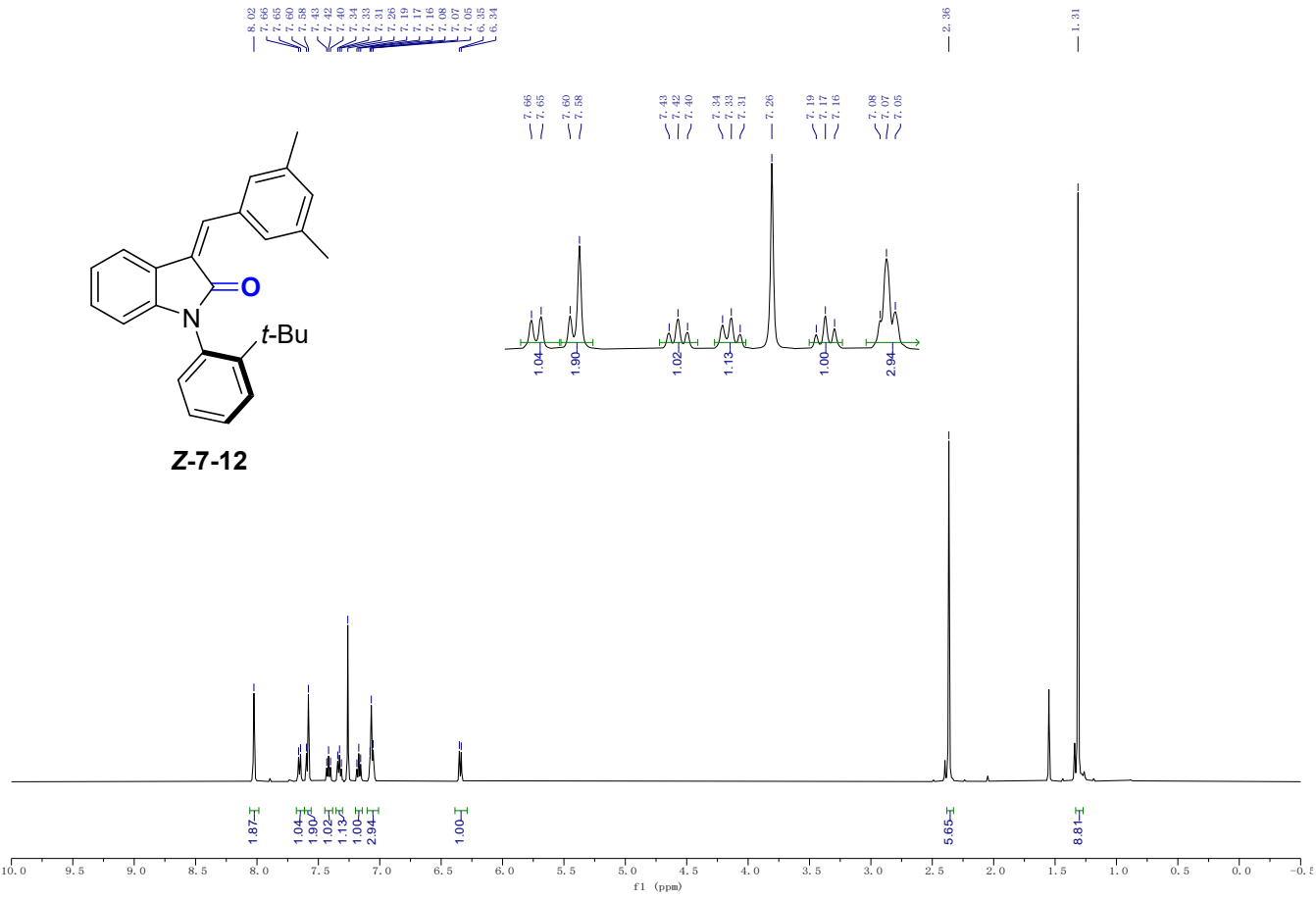
7-10



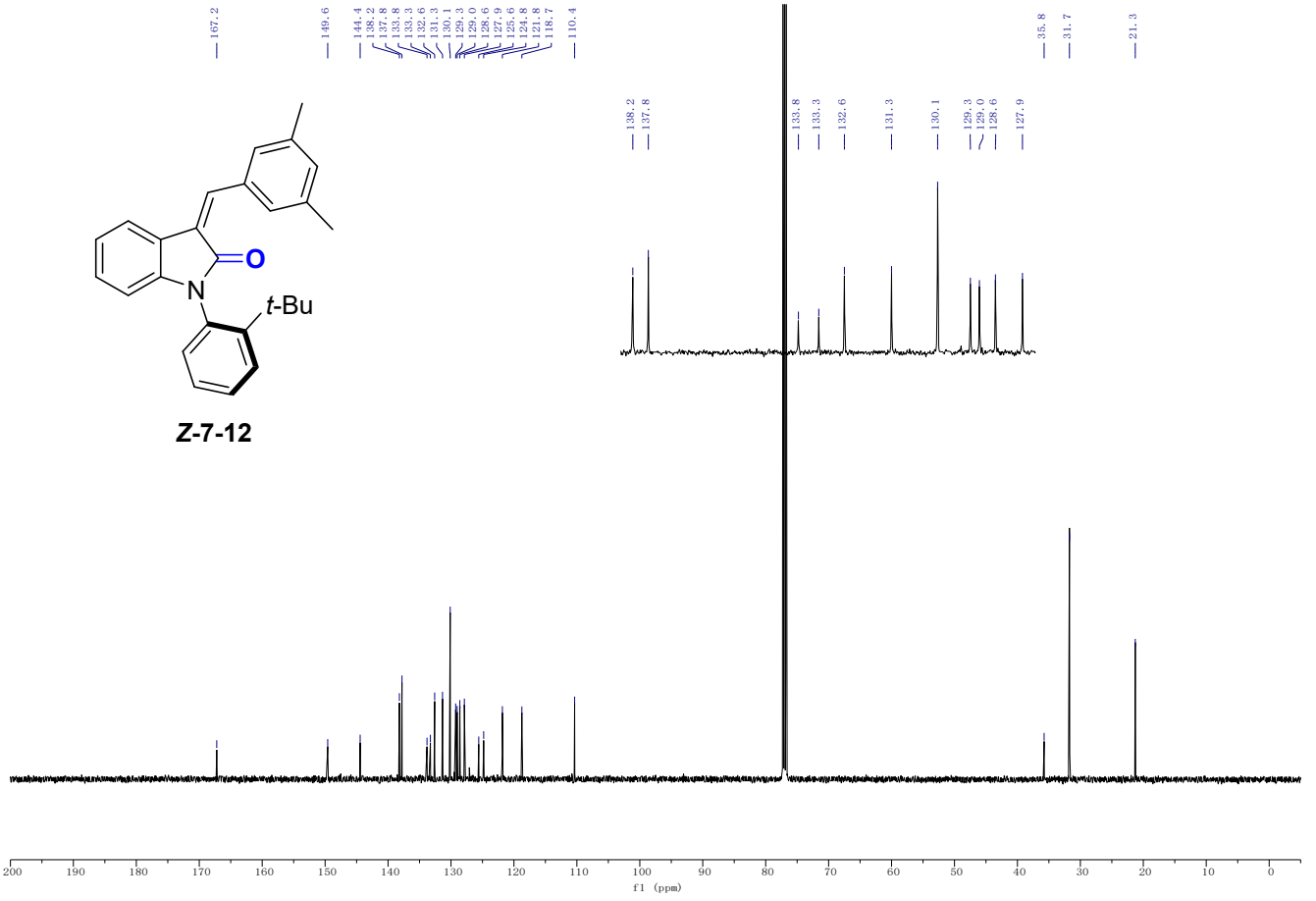
7-10


OMe
O
N
t-Bu
7-11
f1 (ppm)

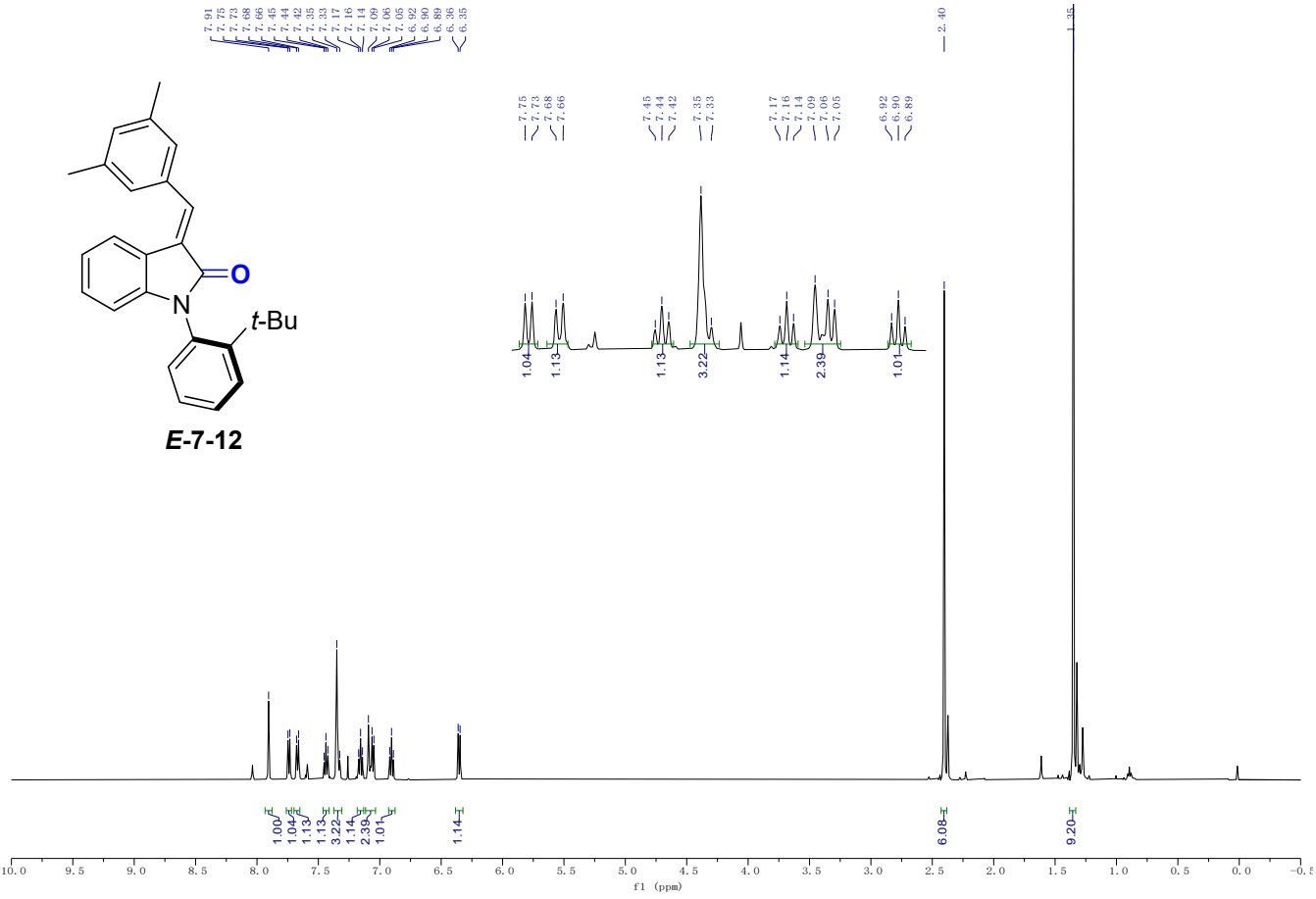

OMe
O
N
t-Bu
7-11
f1 (ppm)

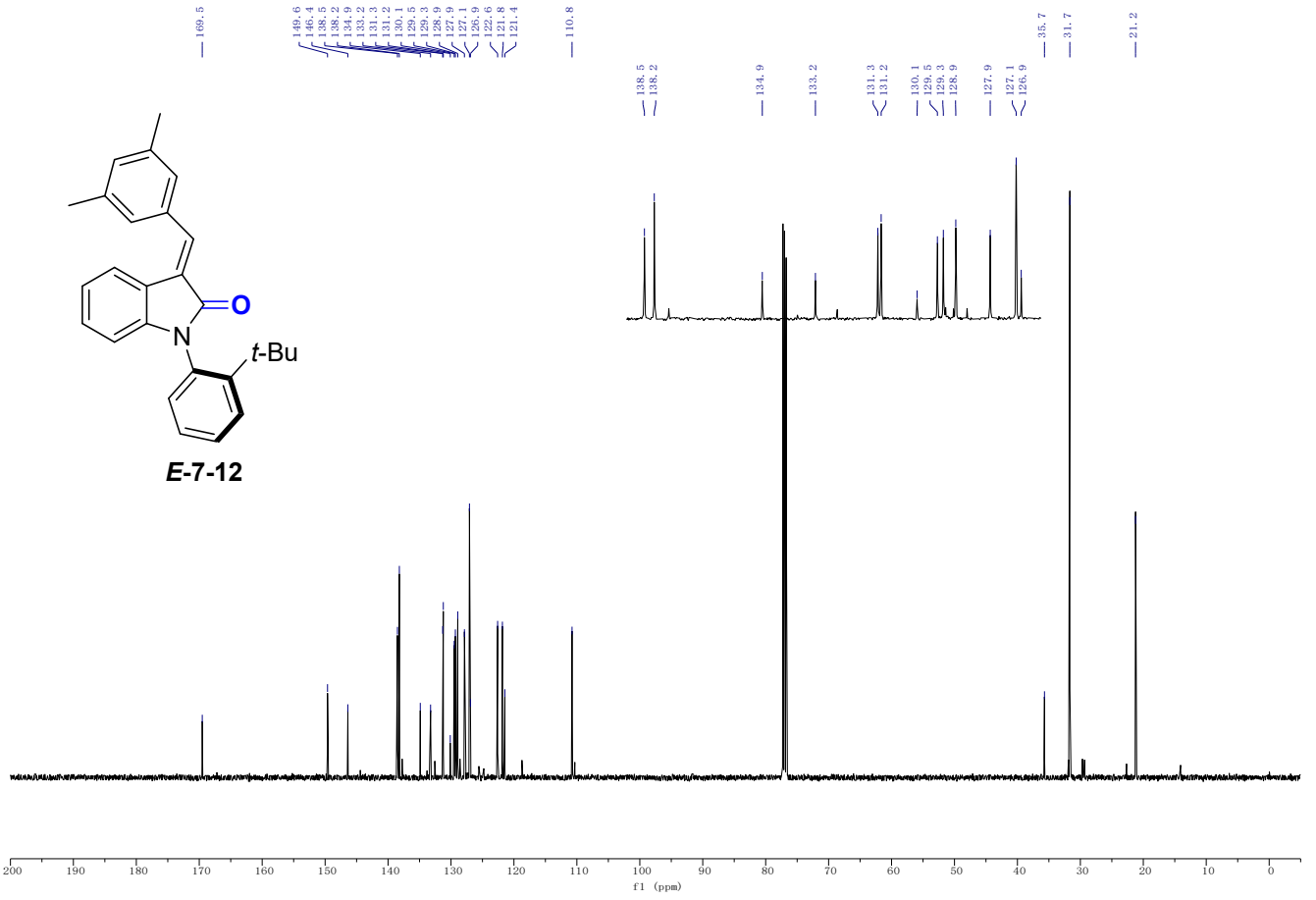

8.02
7.66
7.65
7.60
7.58
7.43
7.42
7.40
7.34
7.33
7.31
7.26
7.19
7.17
7.16
7.08
7.07
7.05
6.55
6.34
2.36
1.31
O
N
t-Bu
1.87
1.04
1.90
1.02
1.13
1.00
2.94
1.00
5.65
8.81
f1 (ppm)

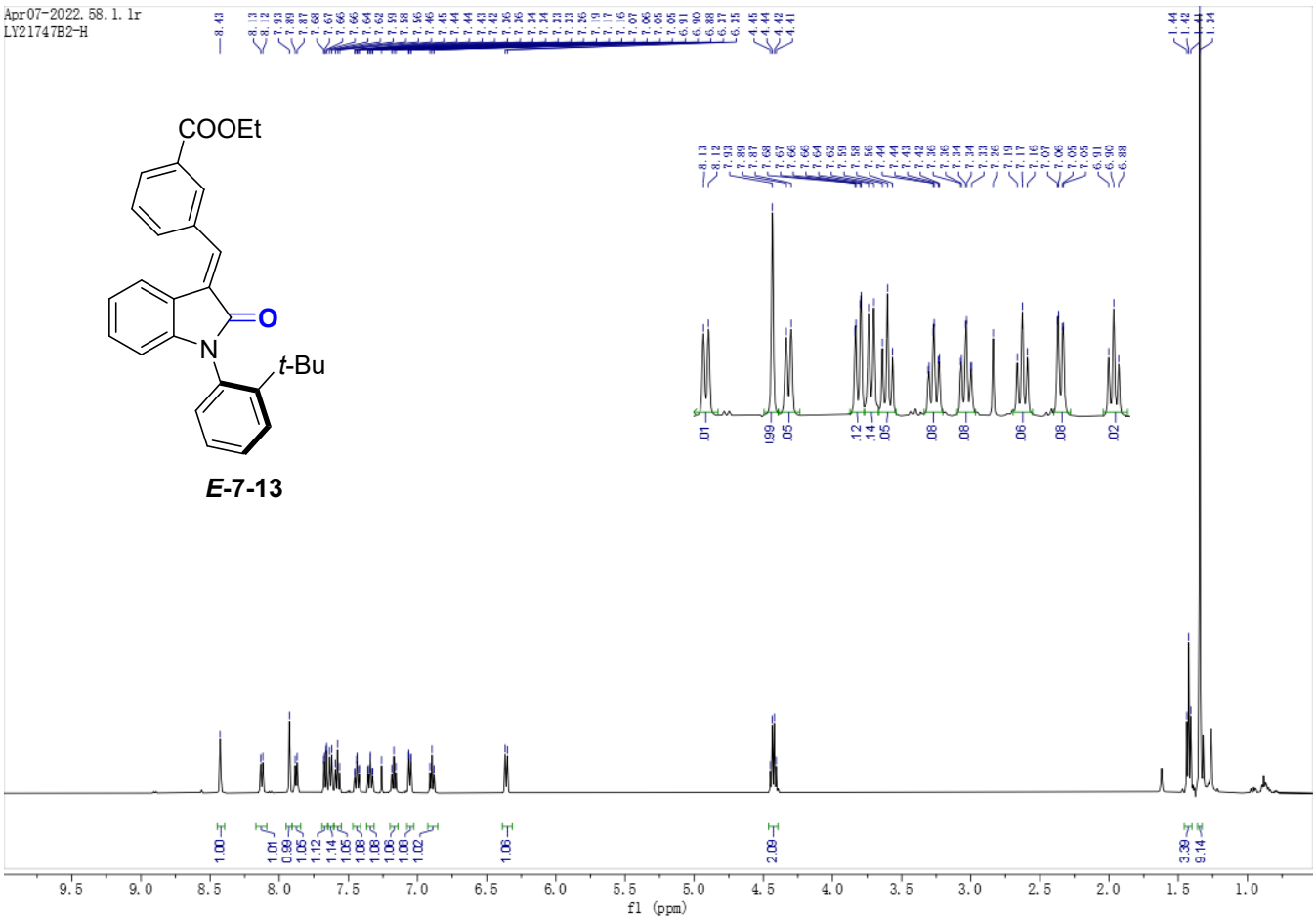
***Z*-7-12**


167.2
149.6
144.4
138.2
137.8
133.8
133.3
132.6
131.3
130.1
129.3
129.0
128.6
127.9
125.6
124.8
121.8
118.7
110.4
35.8
31.7
21.3
O
N
t-Bu
f1 (ppm)

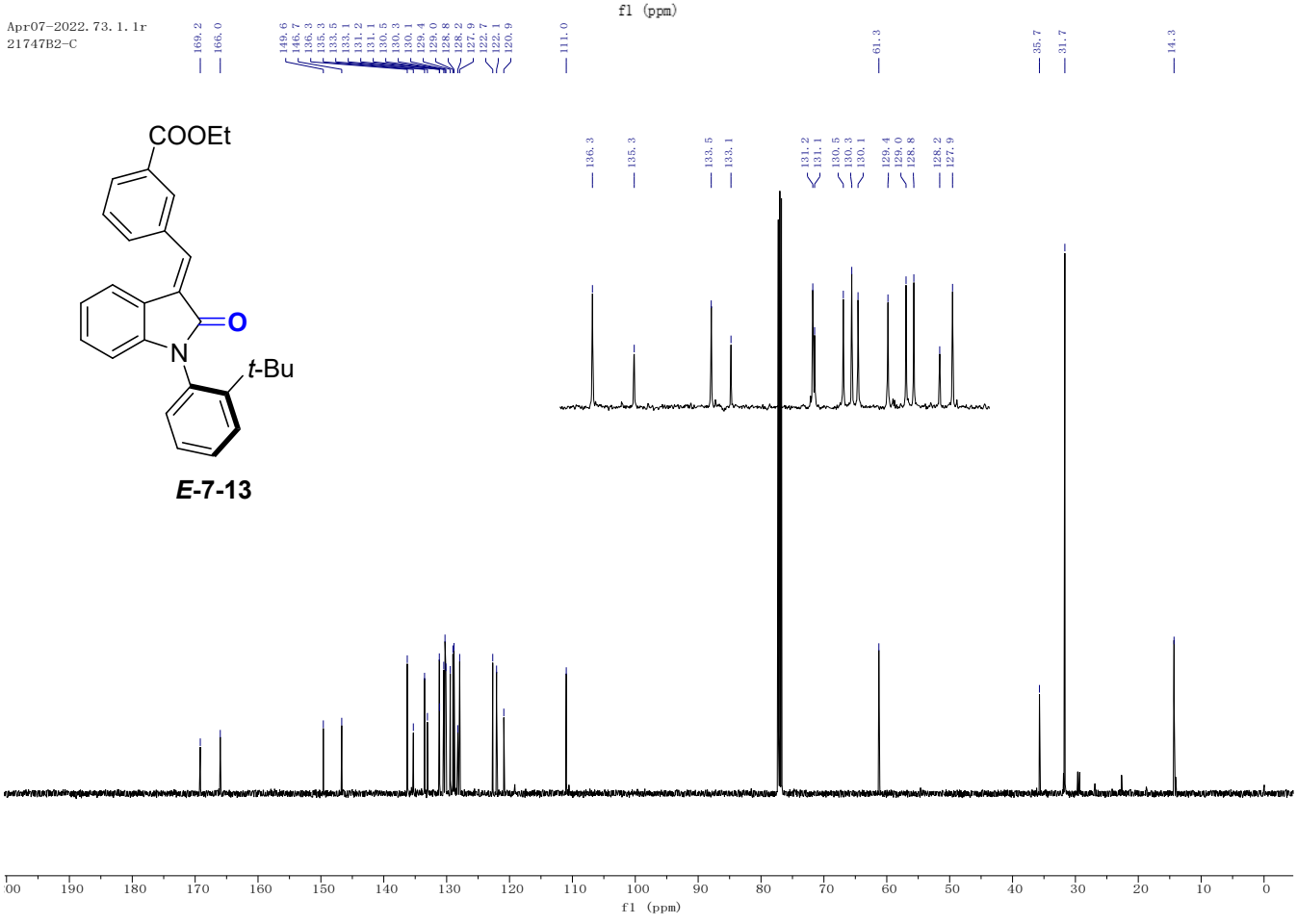
***Z*-7-12**


O
N
t-Bu
E-7-12
f1 (ppm)

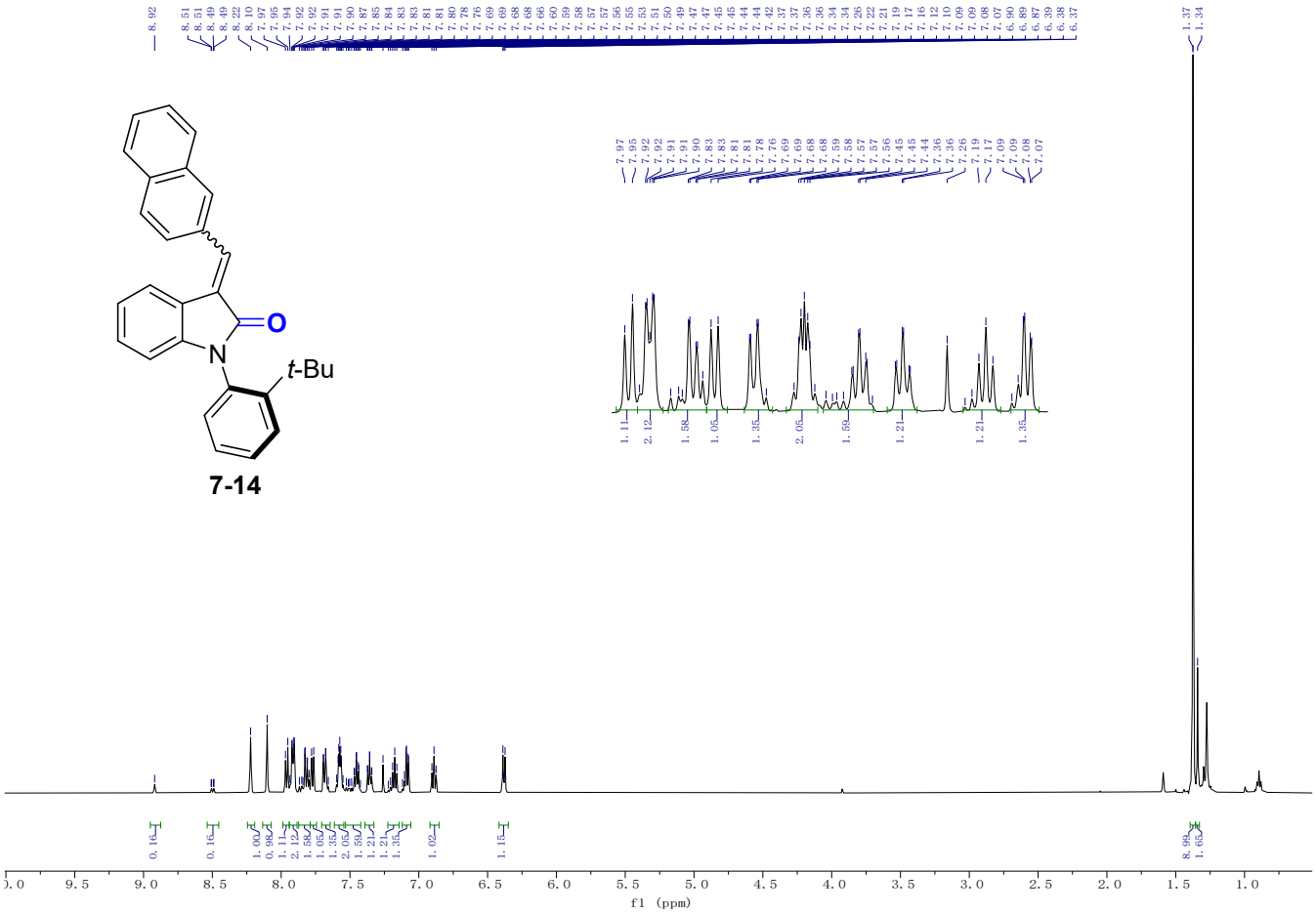

O
N
t-Bu
E-7-12
f1 (ppm)

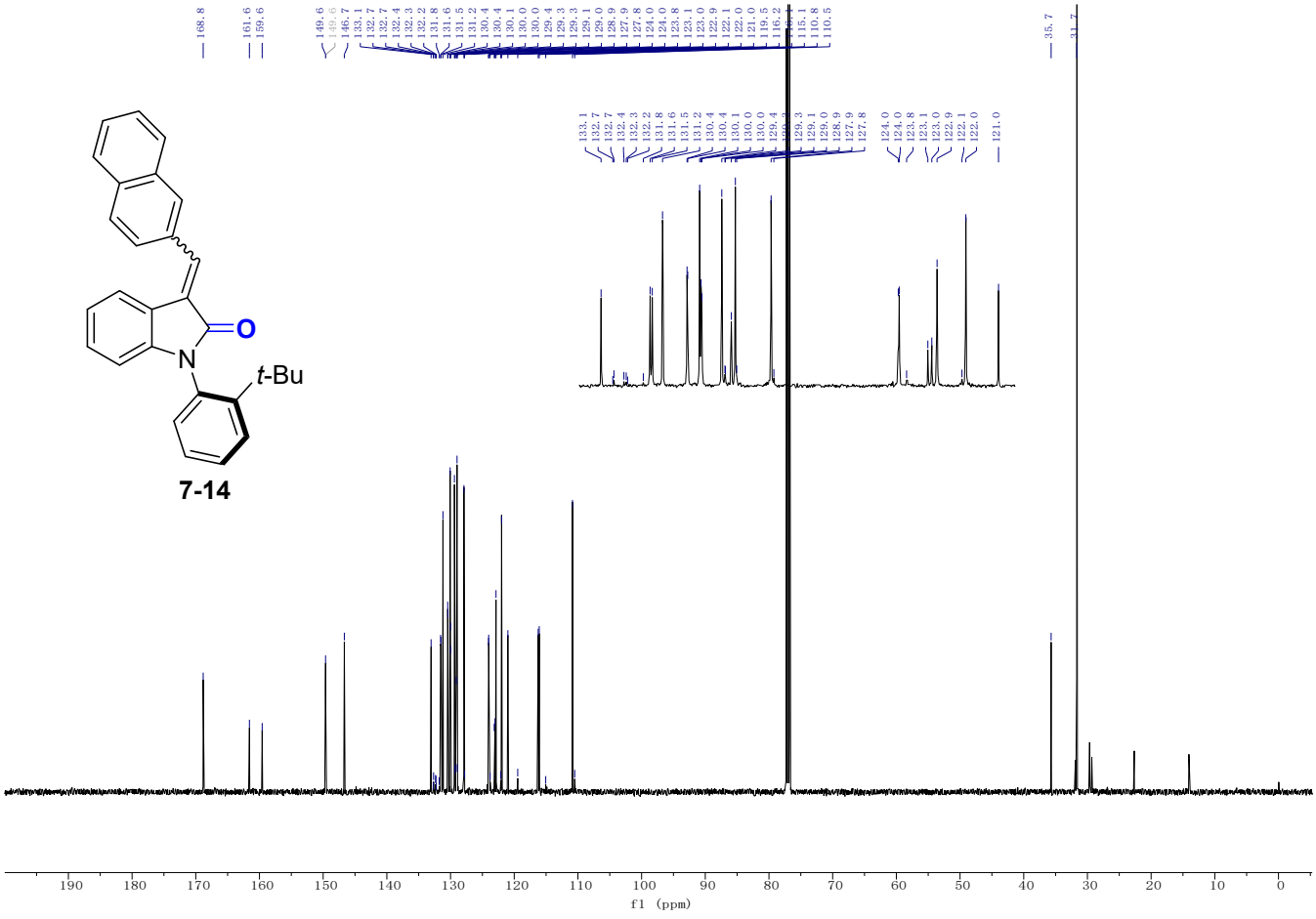

Apr07-2022.58.1.1r
LY21747B2-H
COOEt
O
N
t-Bu
f1 (ppm)

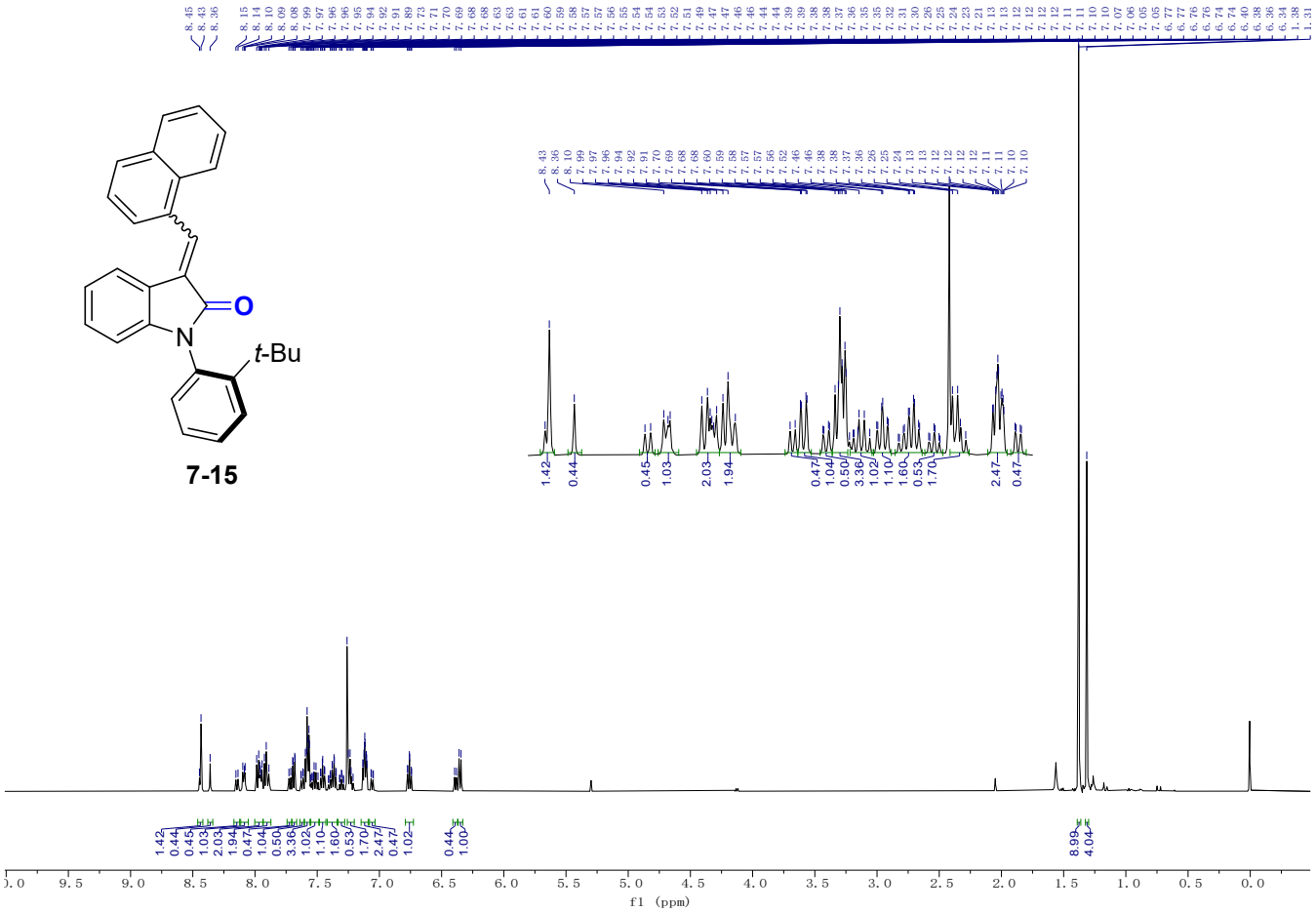
E-7-13

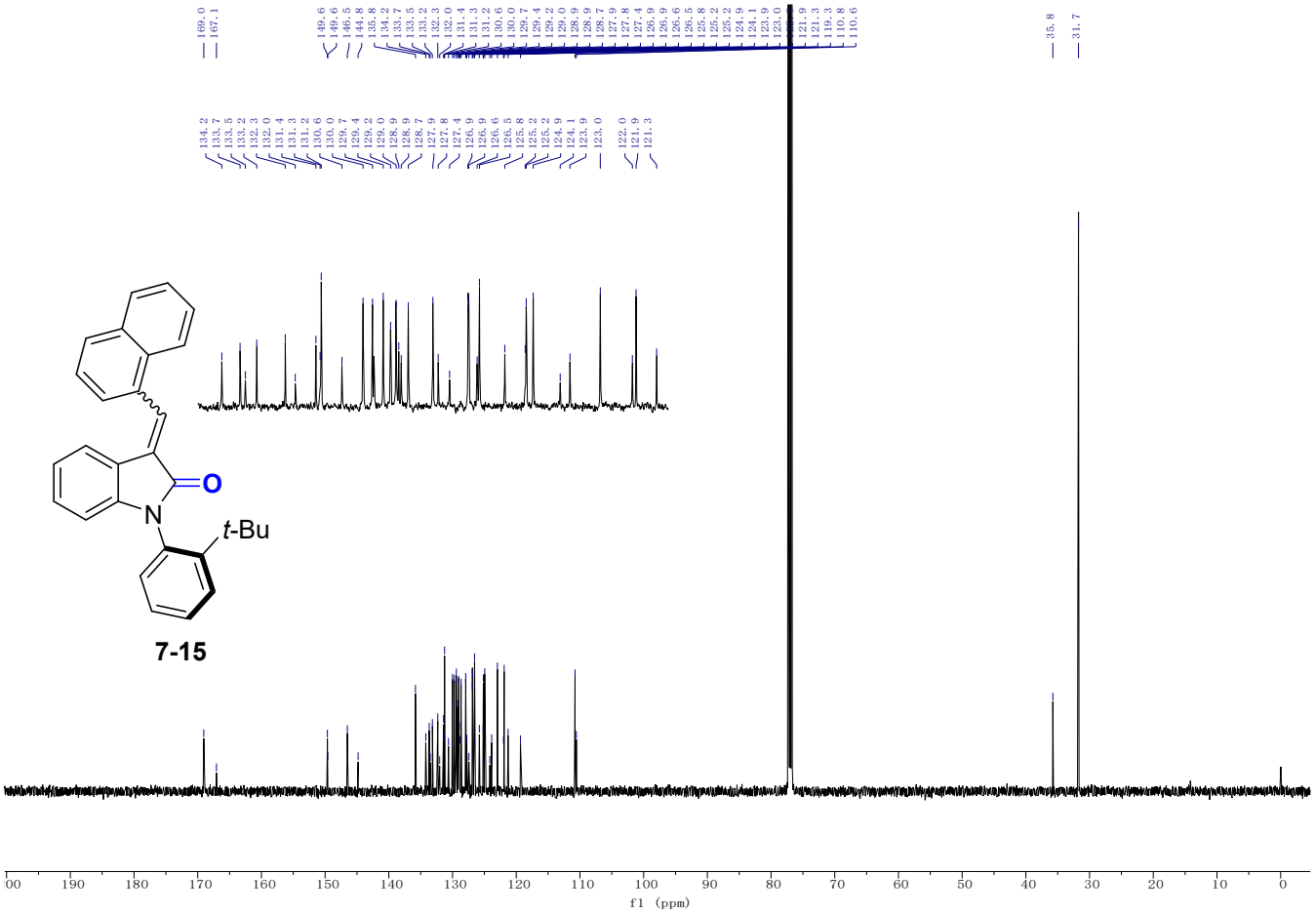

Apr07-2022.73.1.1r
21747B2-C
COOEt
O
N
t-Bu
f1 (ppm)

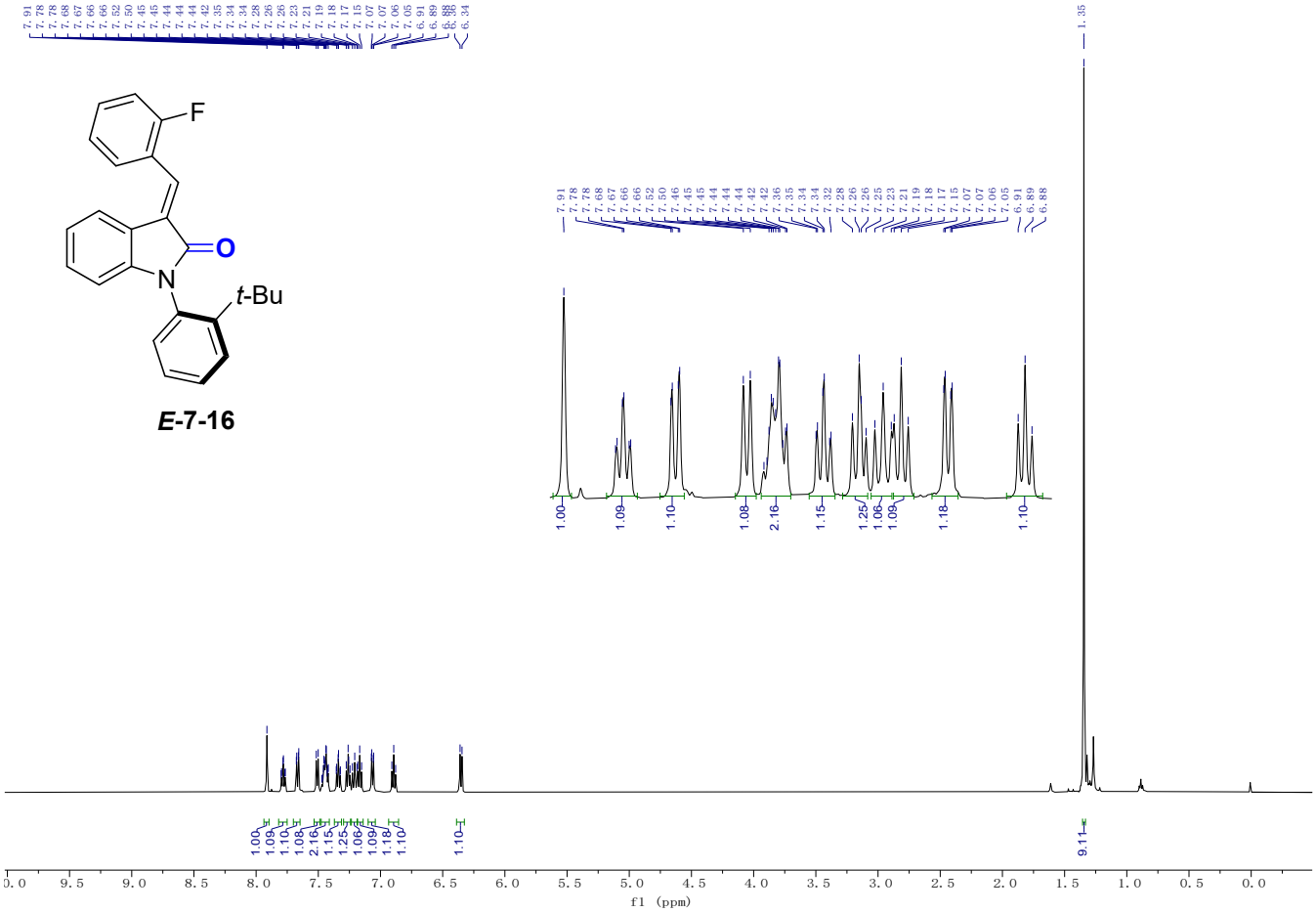
E-7-13

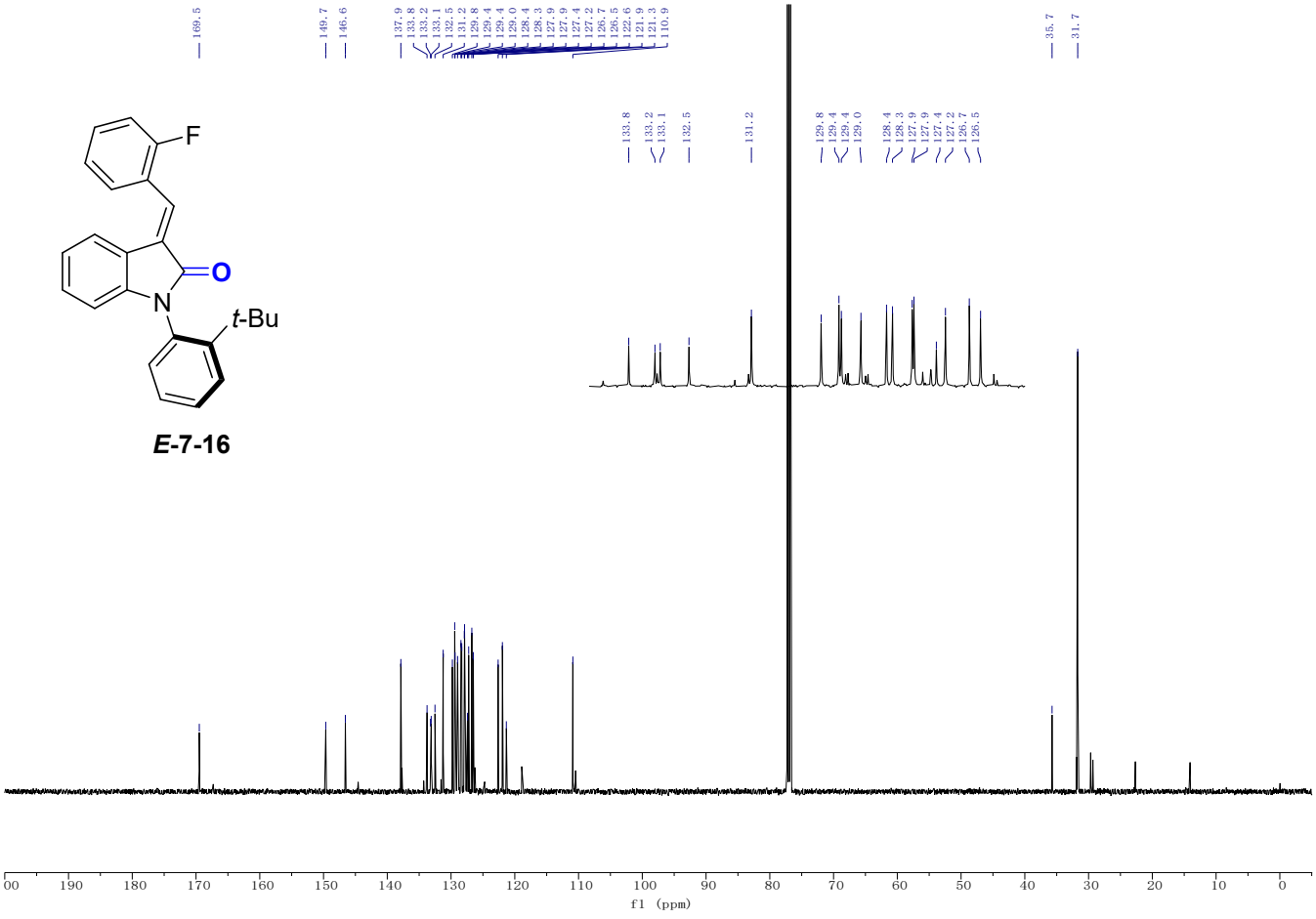

O
N
t-Bu
7-14
f1 (ppm)

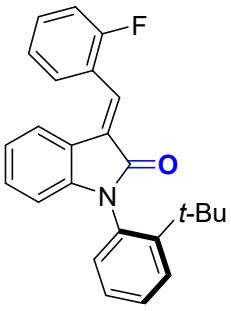

O
N
t-Bu
7-14
f1 (ppm)


O
N
t-Bu
7-15
f1 (ppm)


O
N
t-Bu
7-15
f1 (ppm)

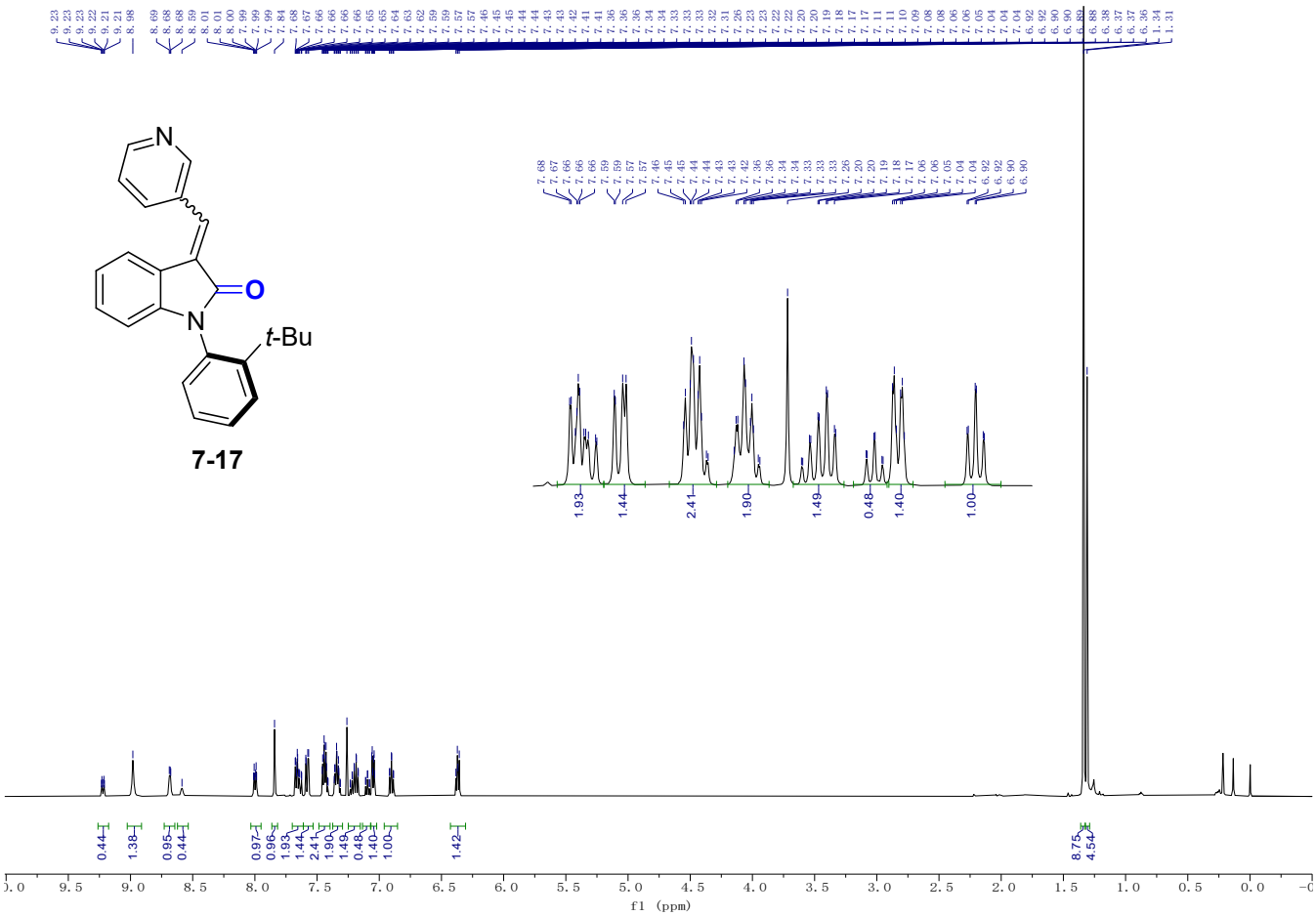

F
O
N
t-Bu
E-7-16
f1 (ppm)


F
O
N
t-Bu
E-7-16
f1 (ppm)

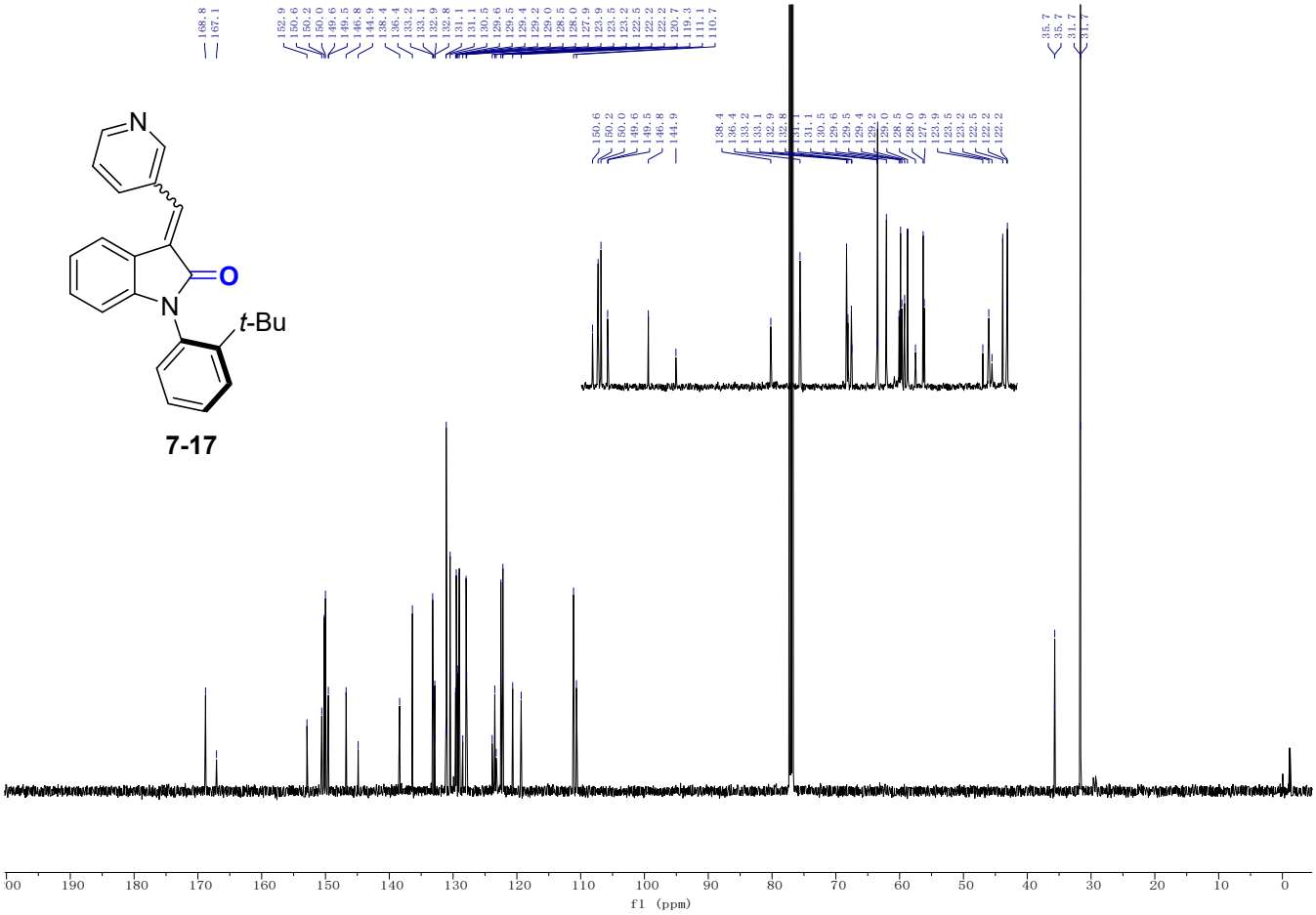

F
O
N
t-Bu

***E*-7-16**

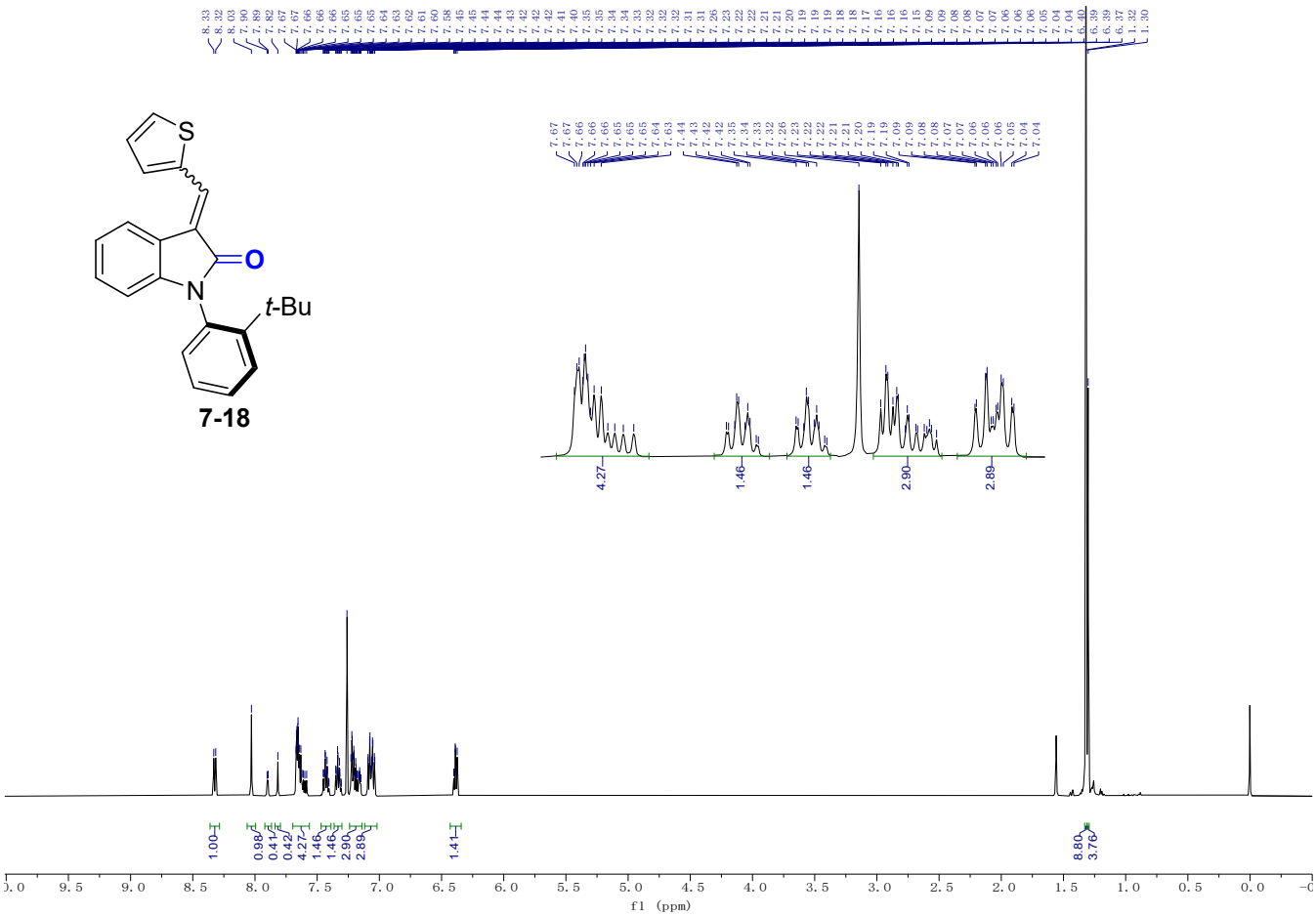
-110.5
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

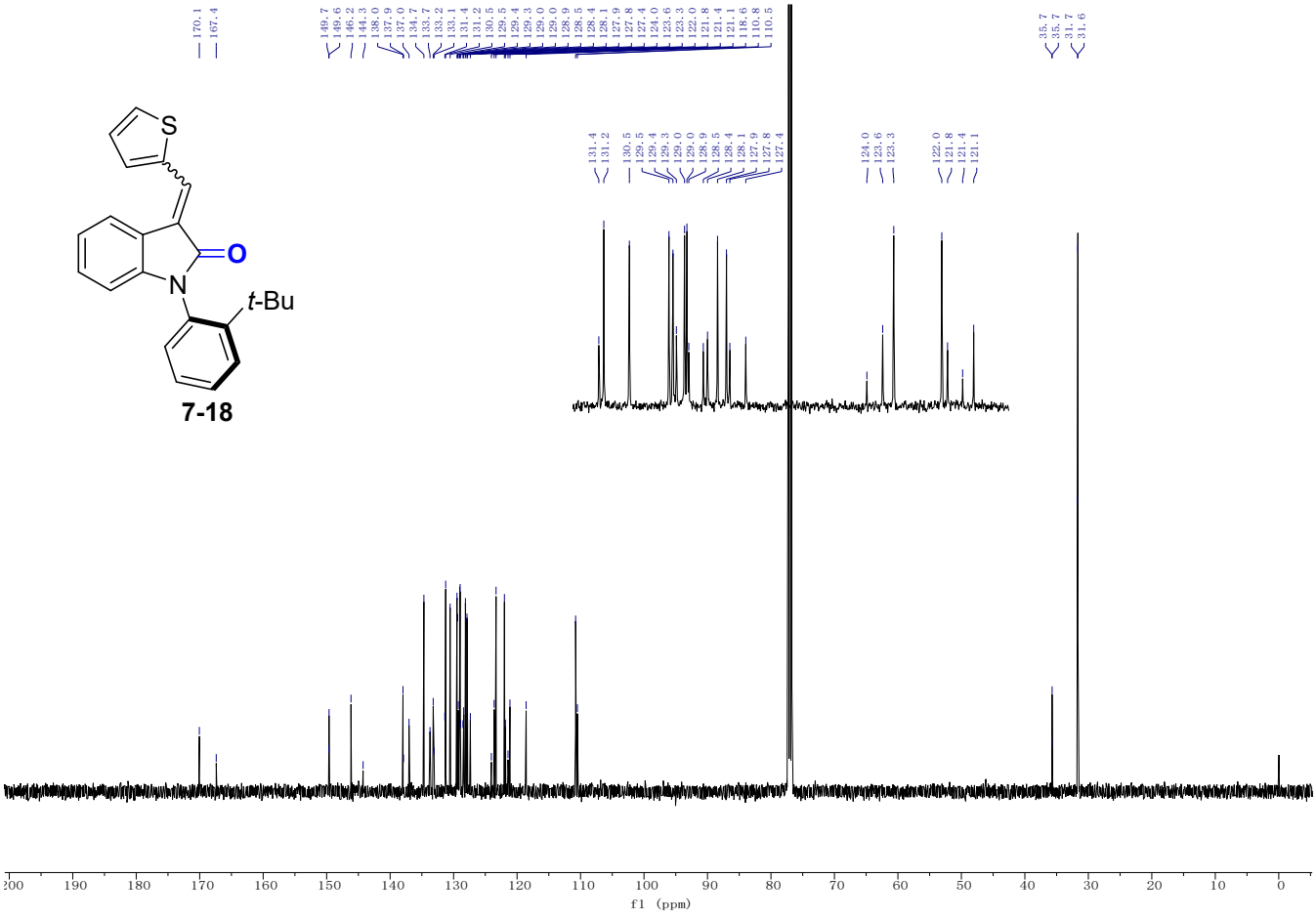


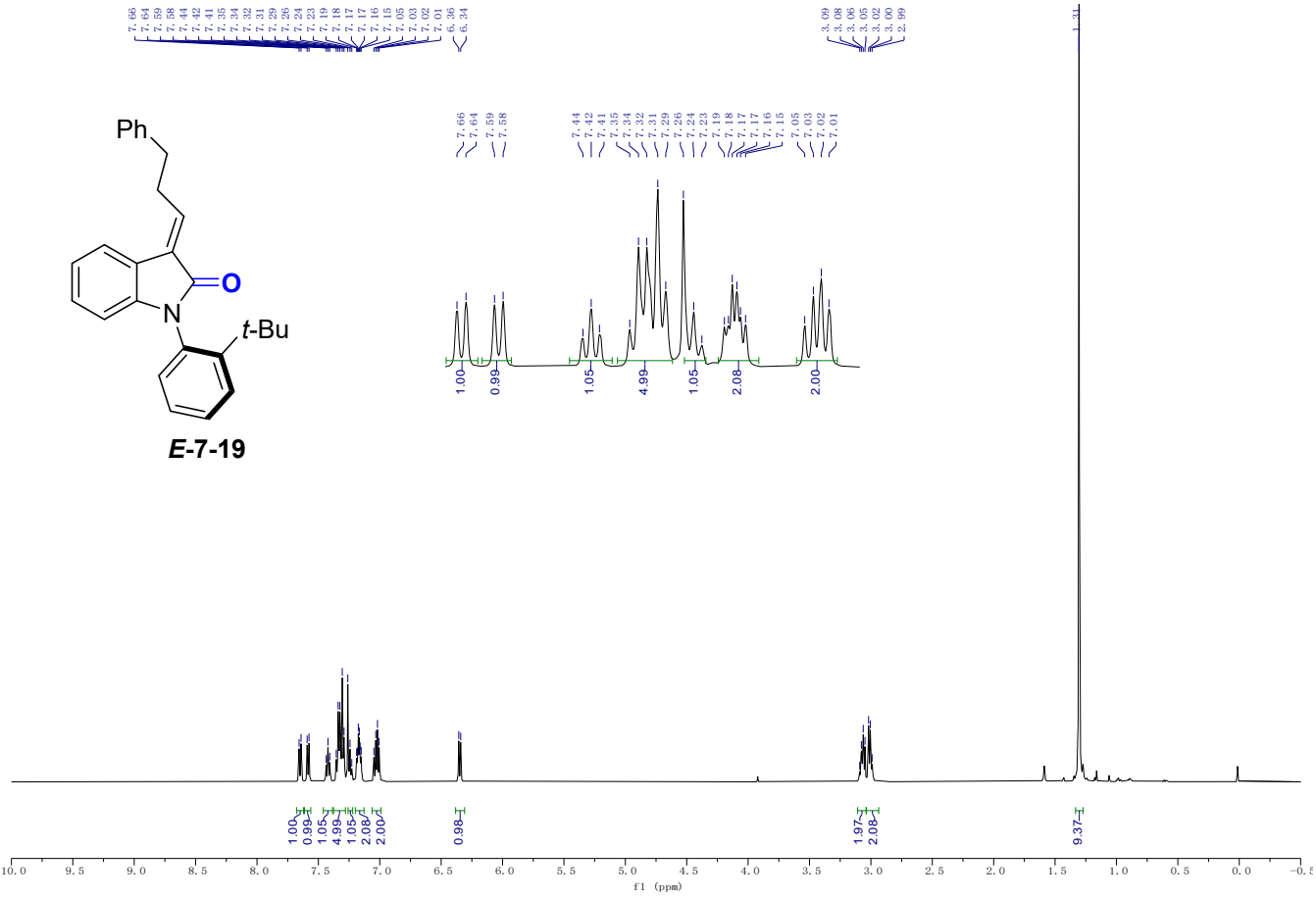
7-17



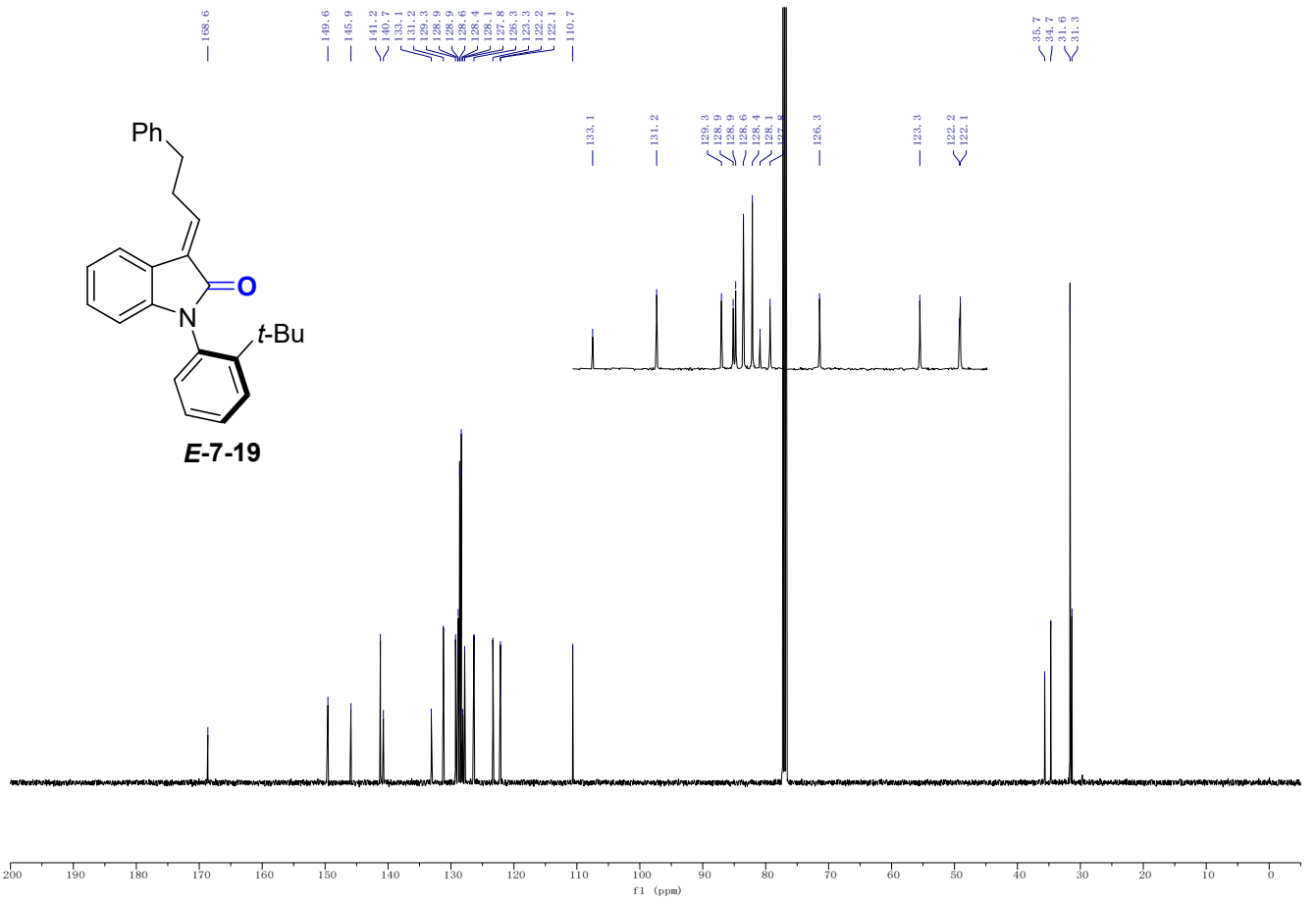
7-17


S
O
N
t-Bu
7-18
f1 (ppm)

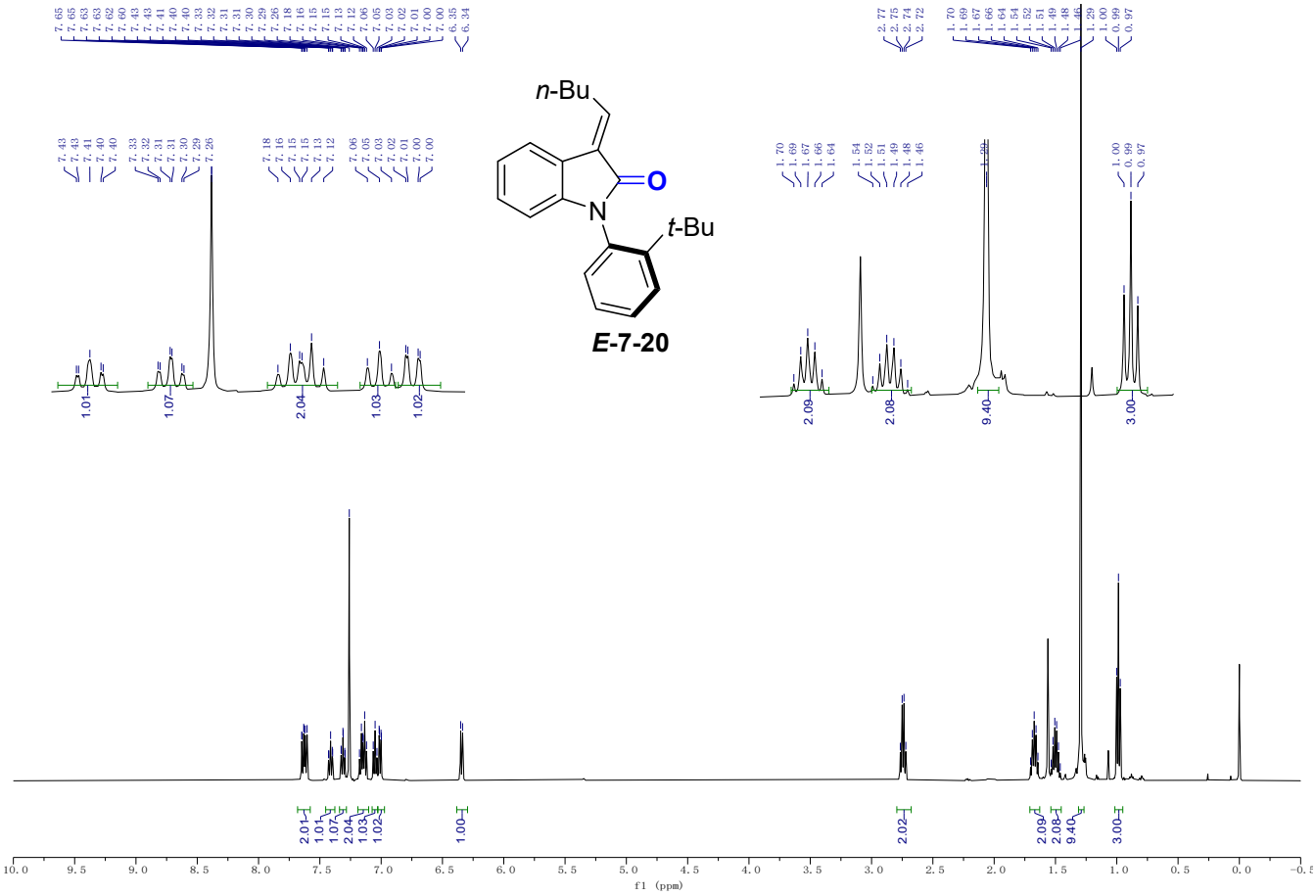

S
O
N
t-Bu
7-18
f1 (ppm)

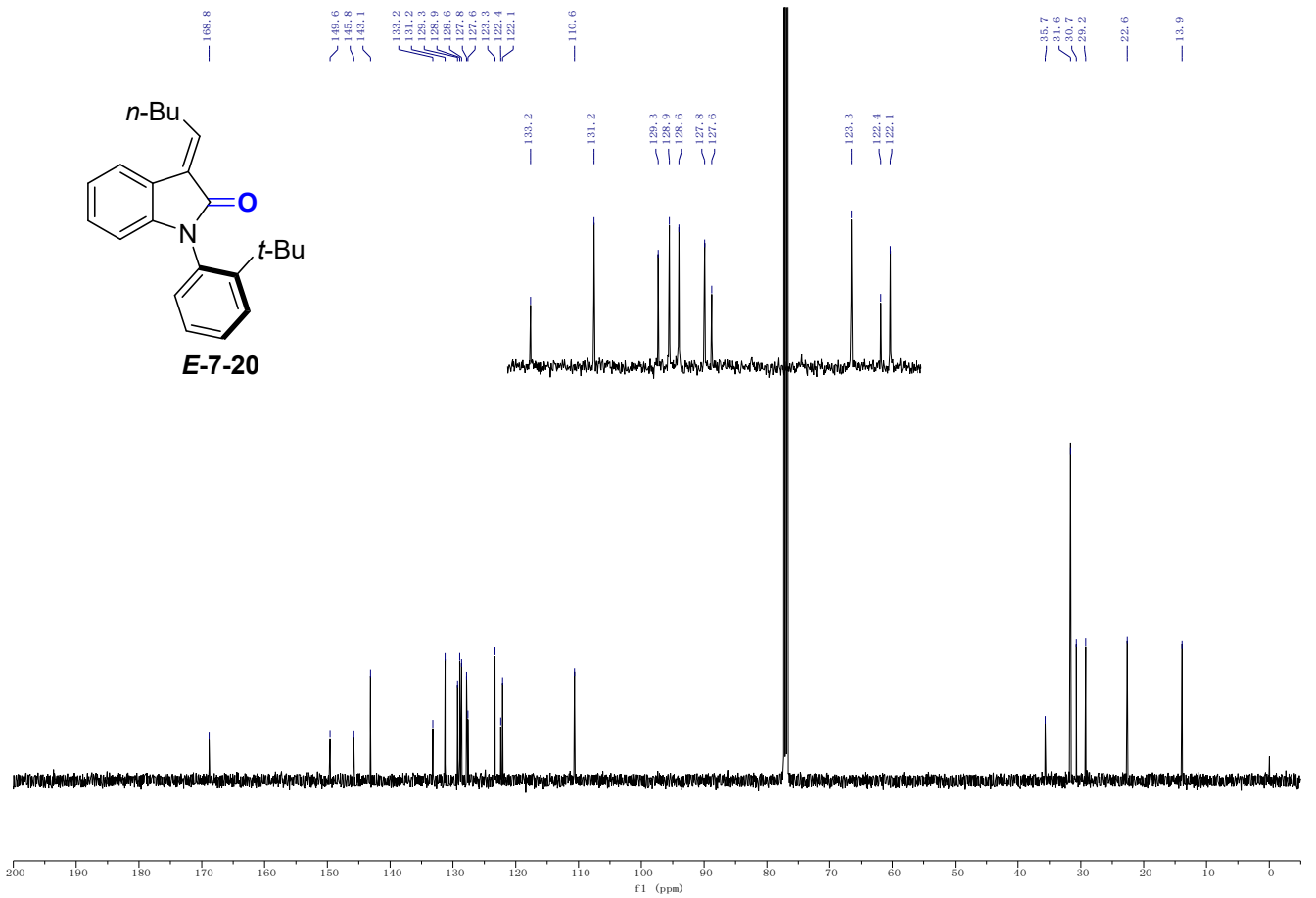


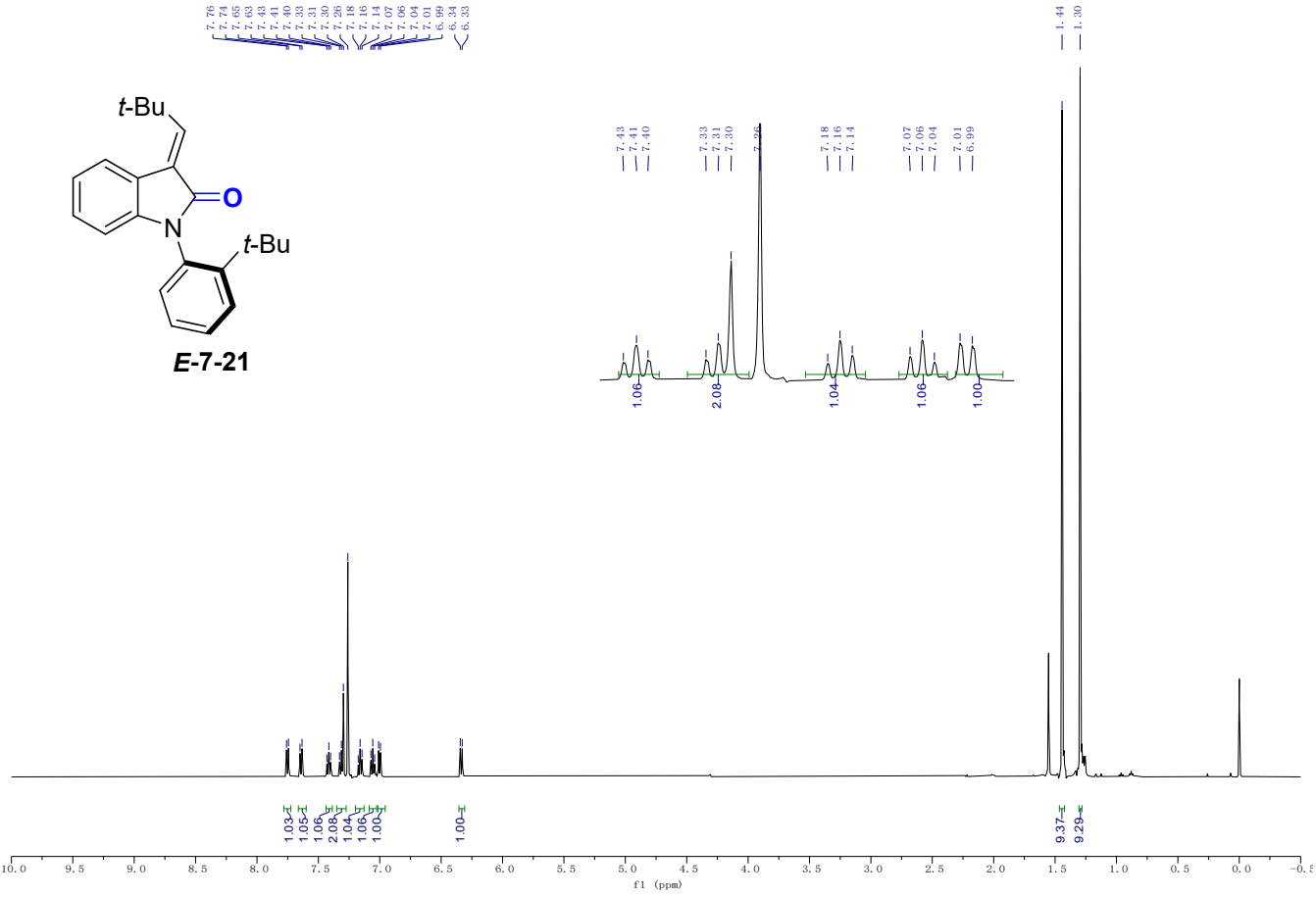
***E*-7-19**

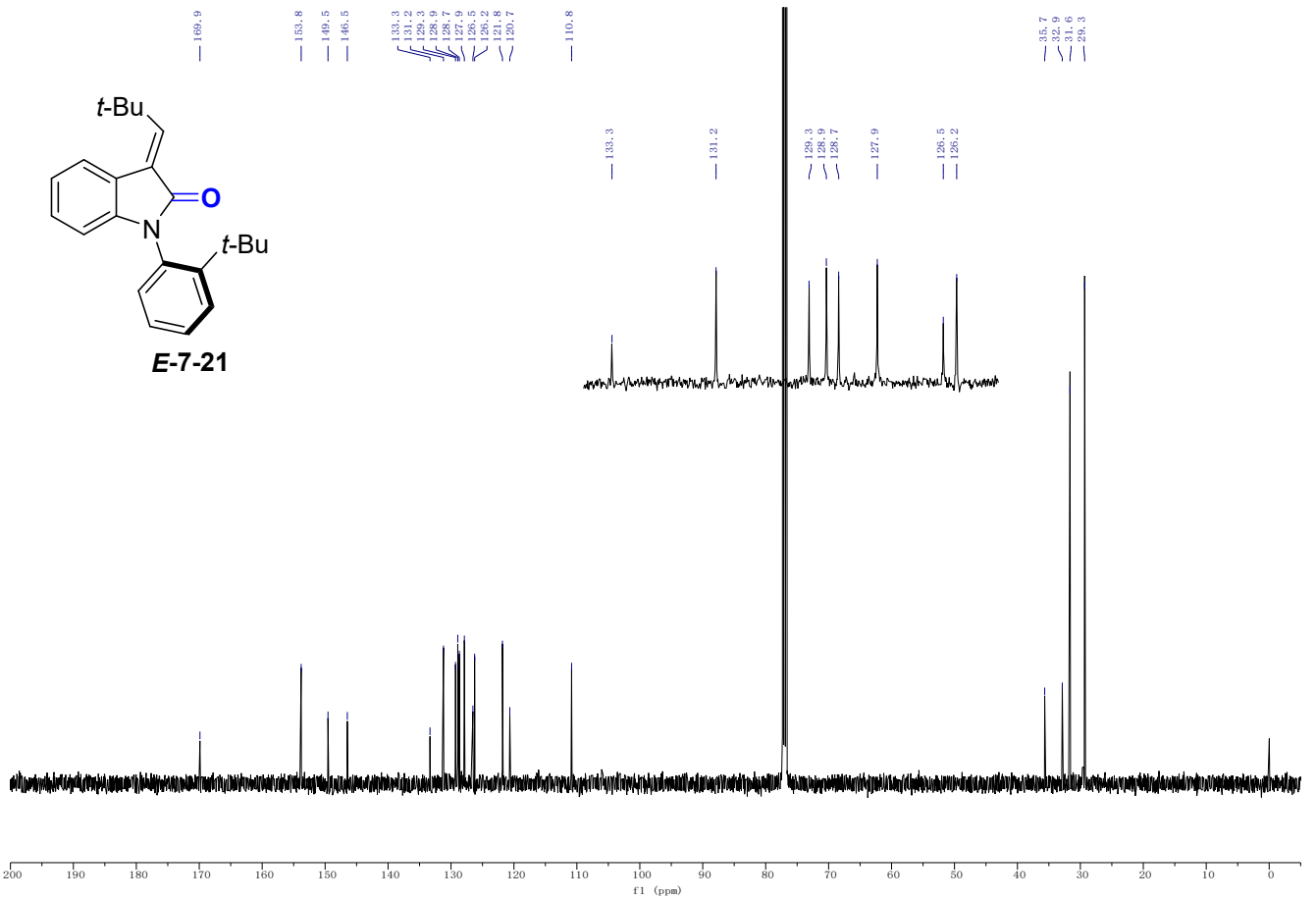


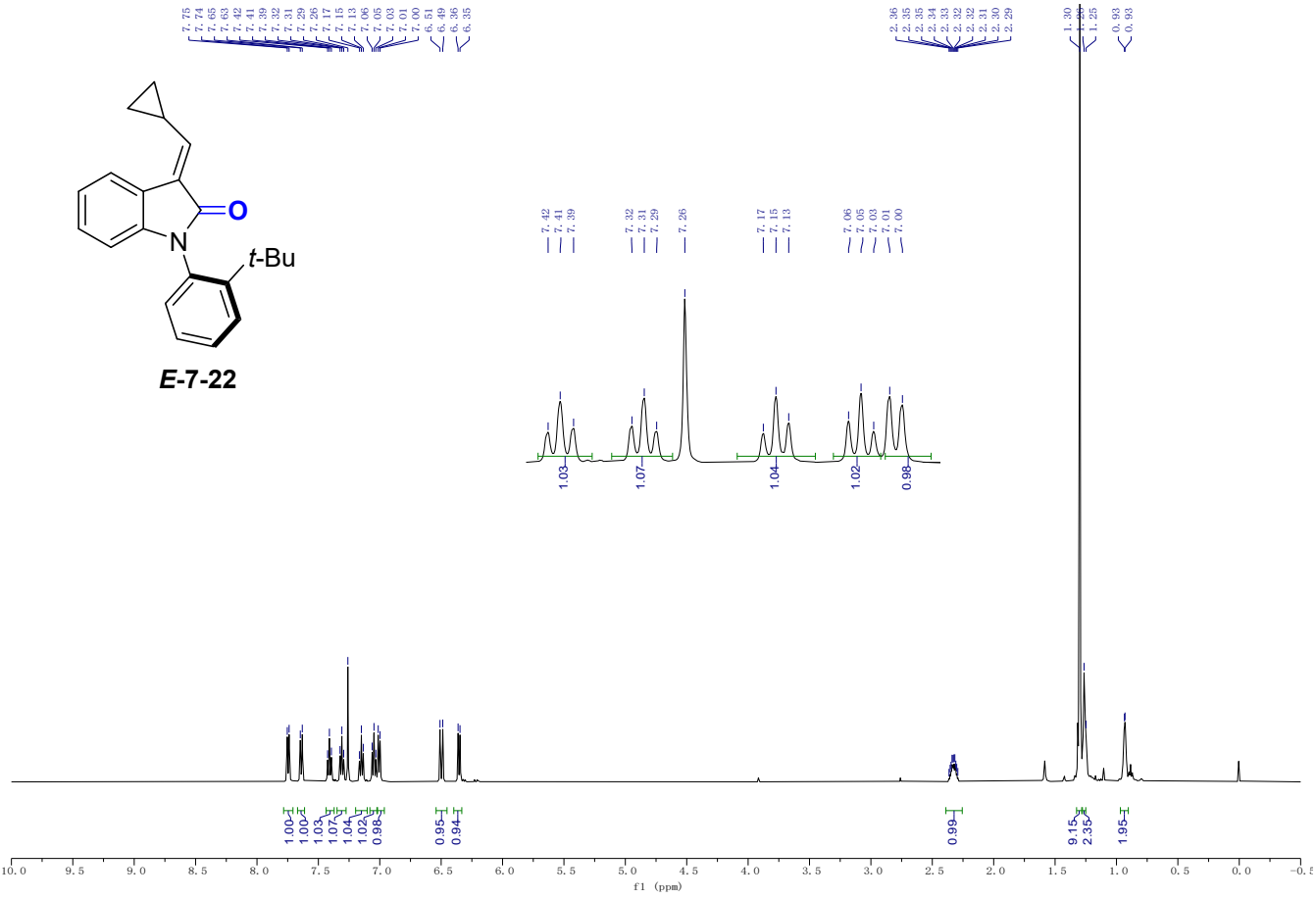
***E*-7-19**

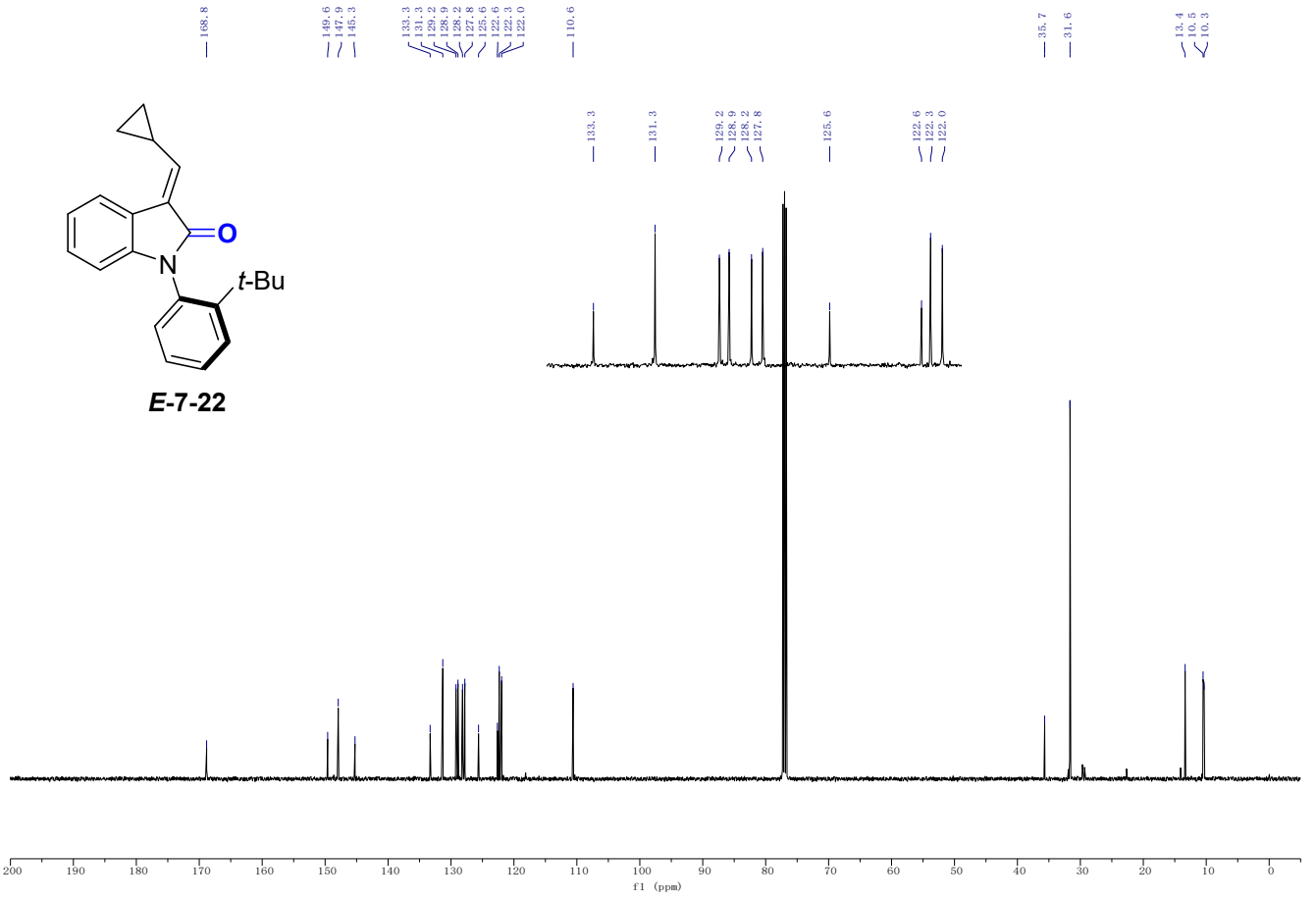

n-Bu
O
N
t-Bu
E-7-20
f1 (ppm)

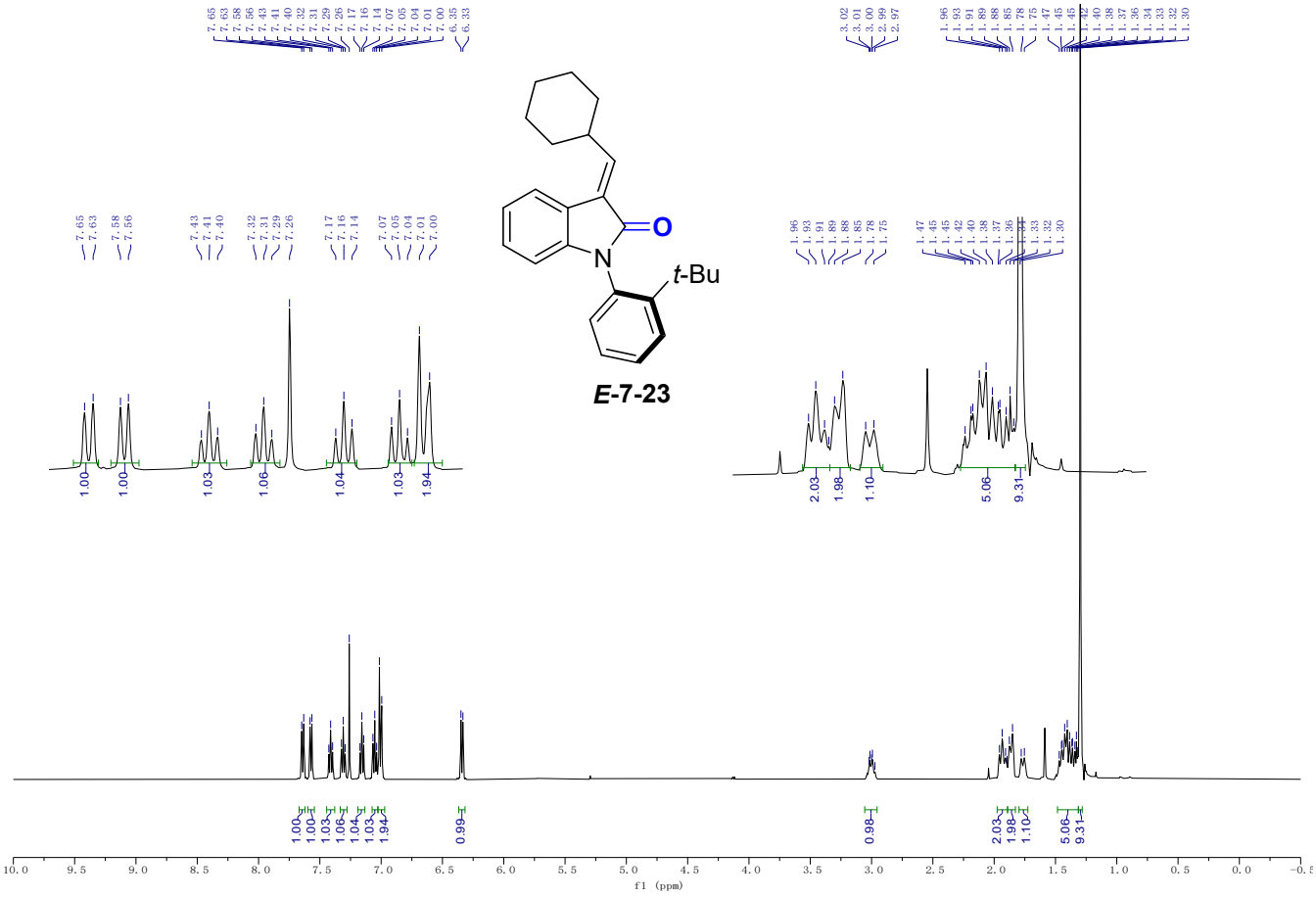

n-Bu
O
N
t-Bu
E-7-20
f1 (ppm)

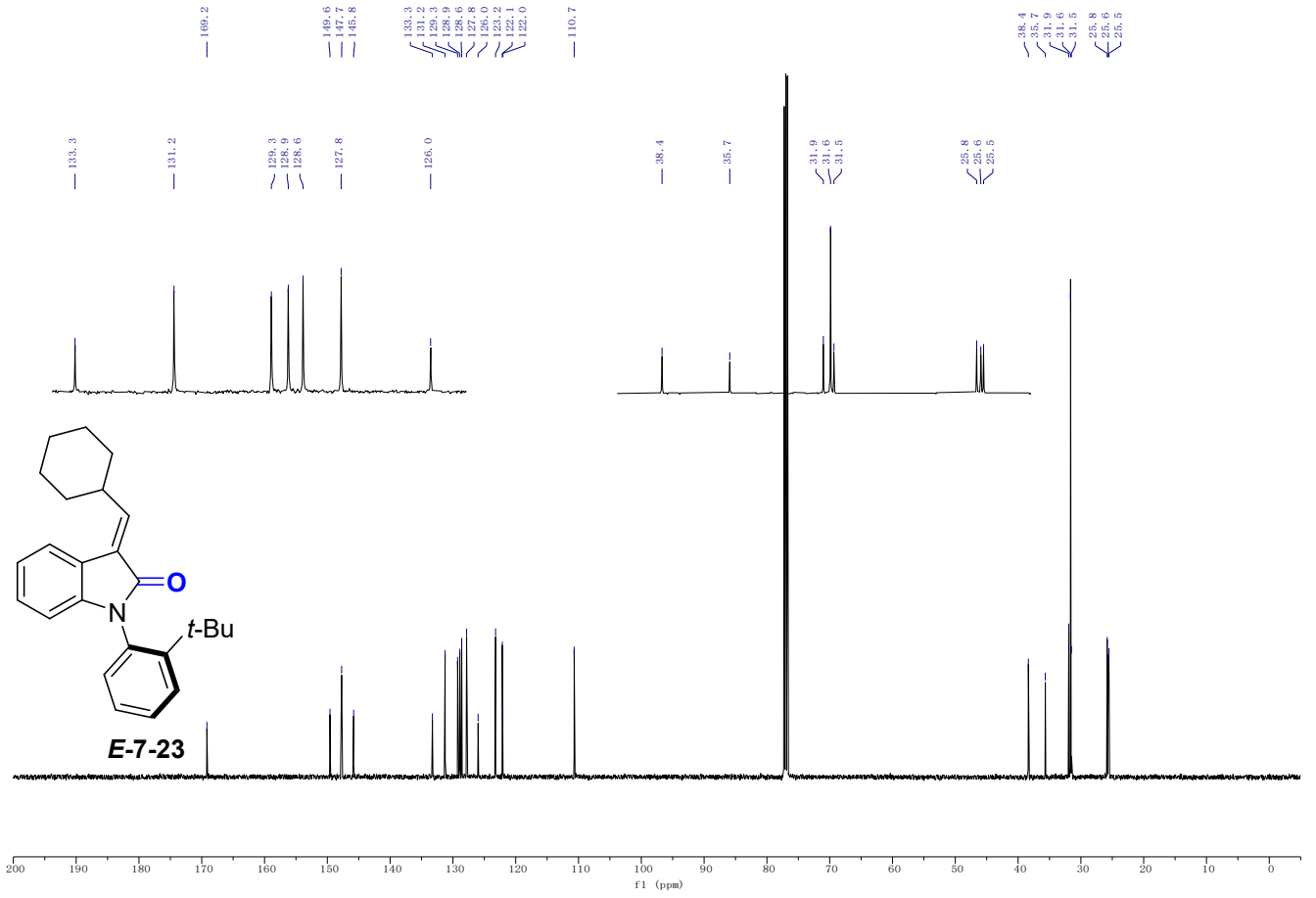

t-Bu
O
N
t-Bu
E-7-21
f1 (ppm)

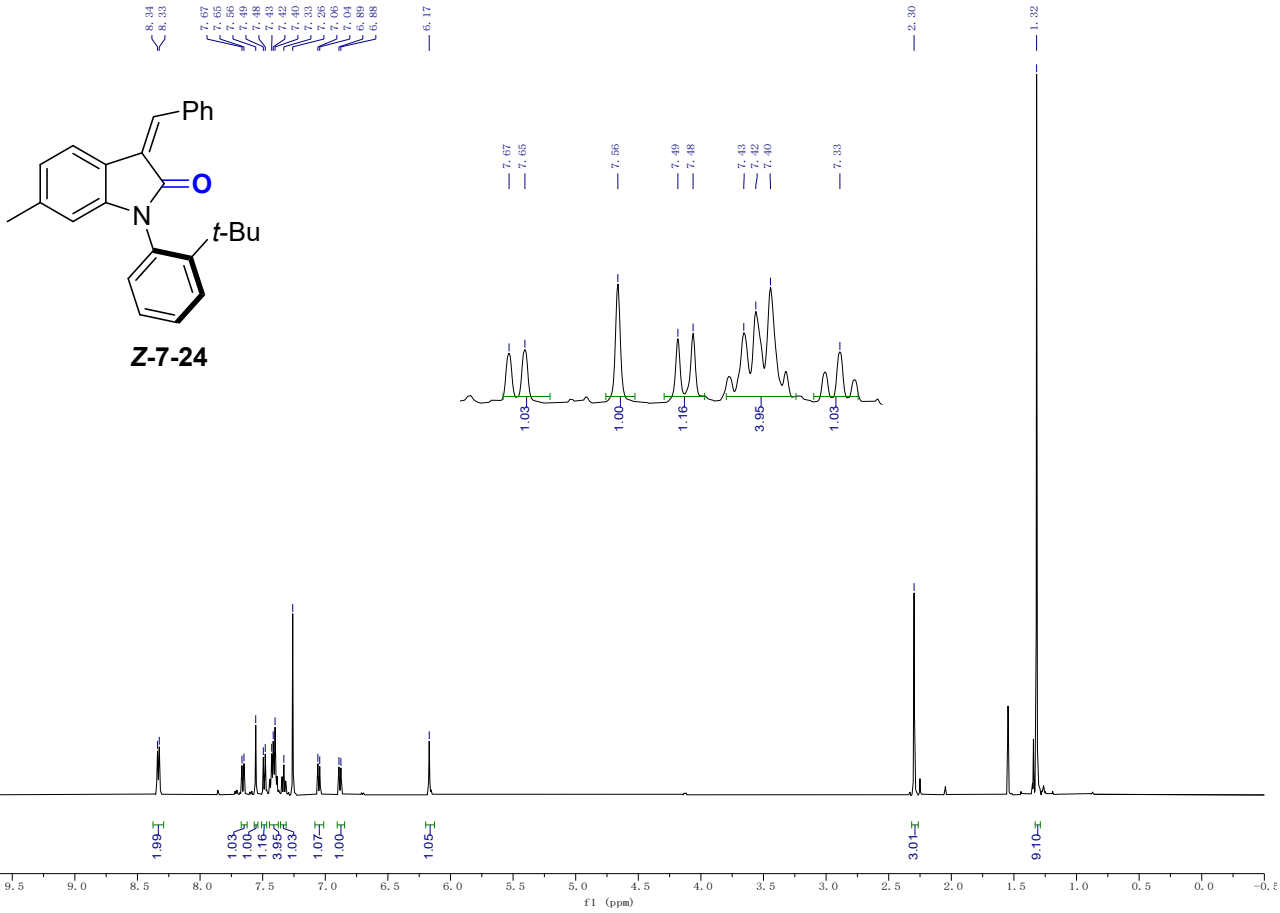

t-Bu
O
N
t-Bu
E-7-21
f1 (ppm)


O
N
t-Bu
E-7-22
f1 (ppm)

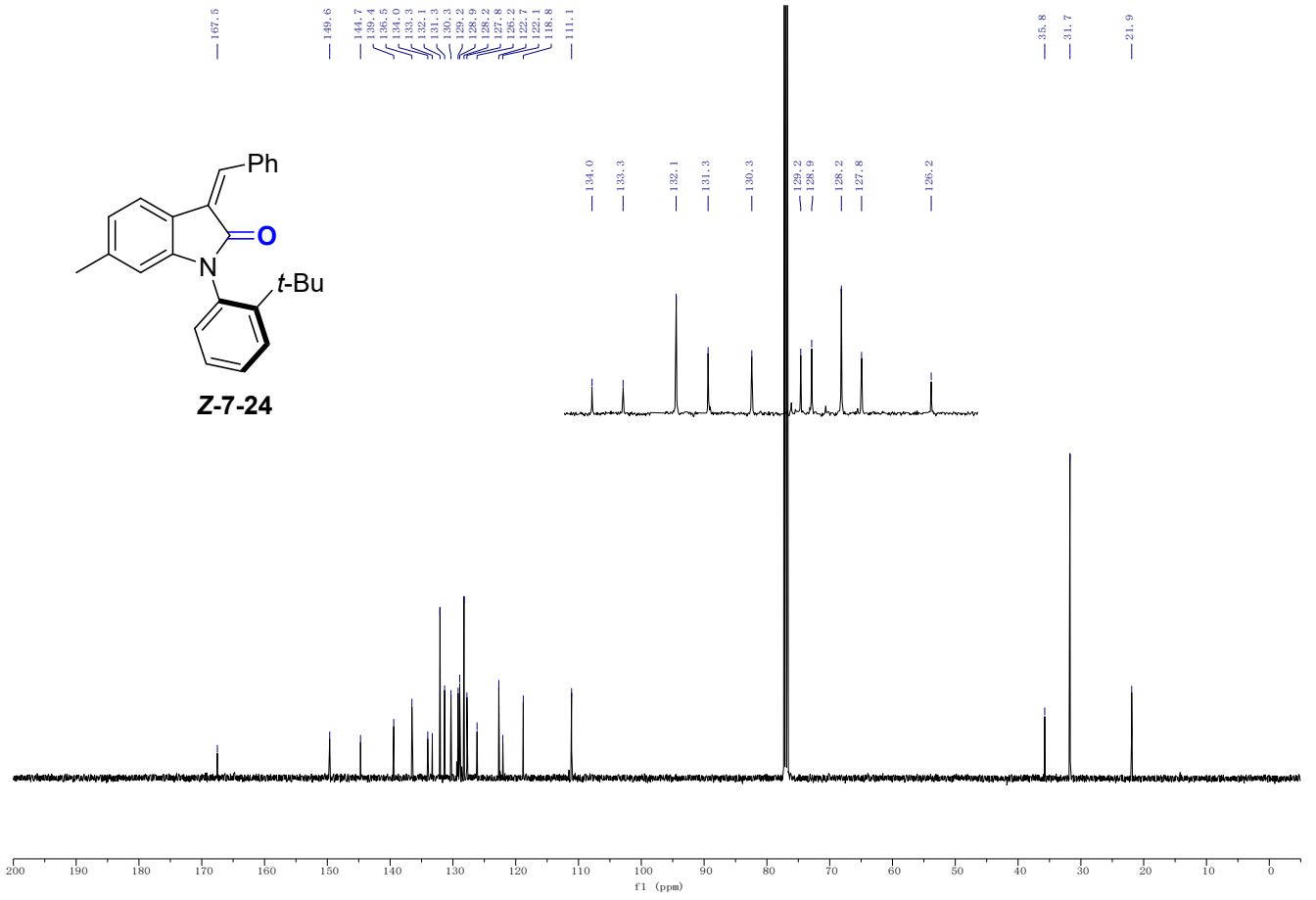

O
N
t-Bu
E-7-22
f1 (ppm)


O
N
t-Bu
E-7-23

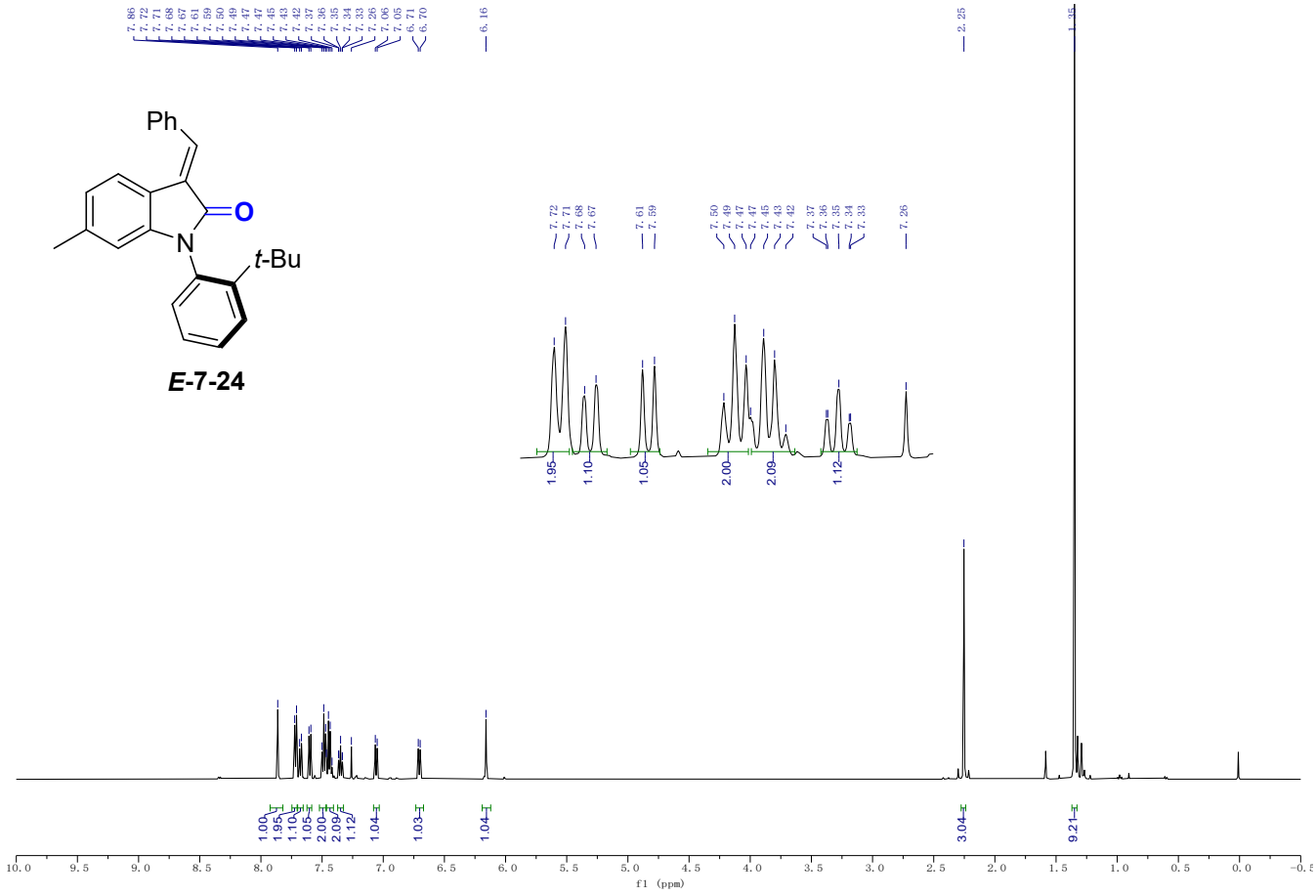

O
N
t-Bu
E-7-23

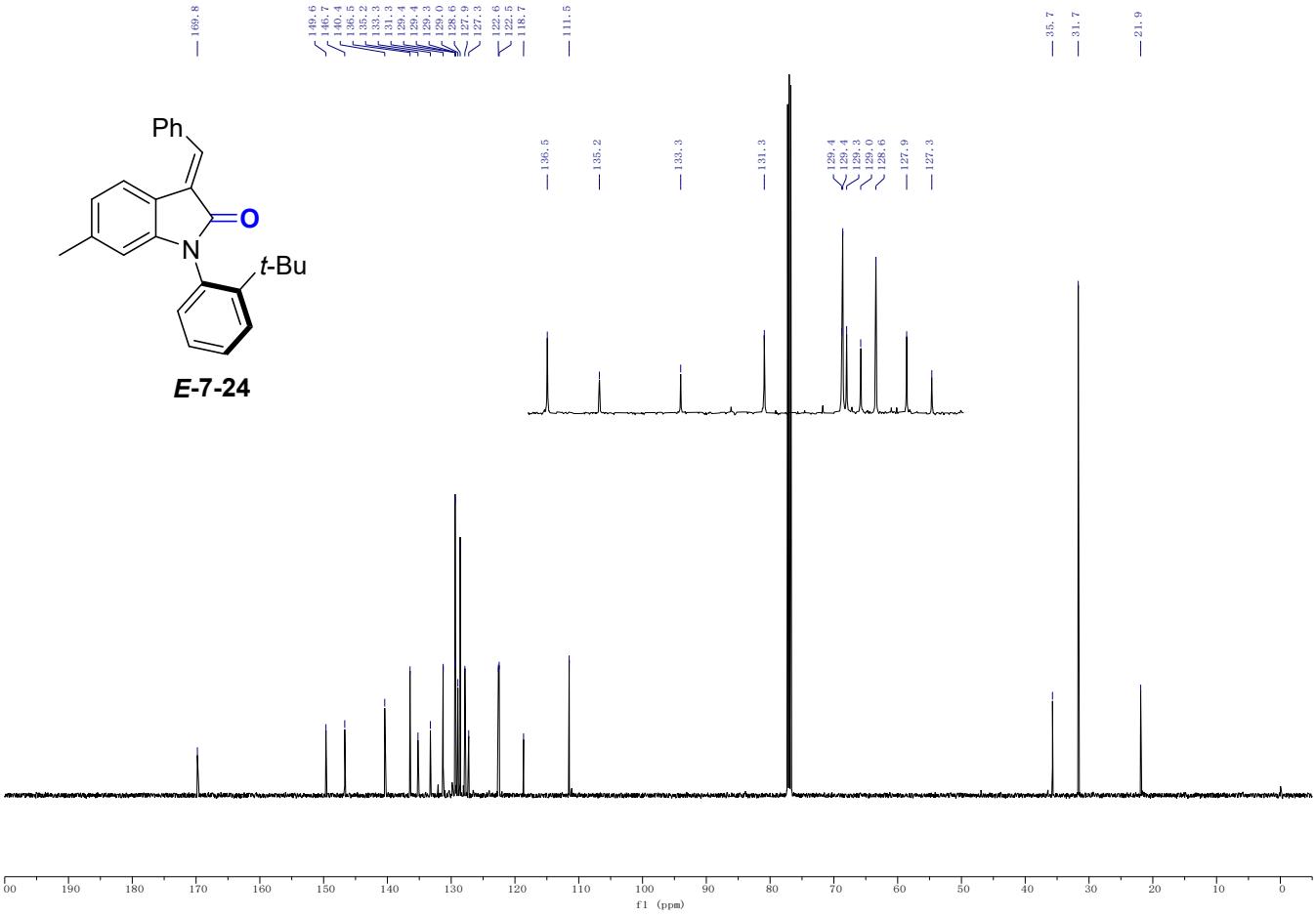


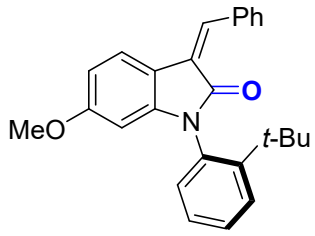
***Z*-7-24**



***Z*-7-24**

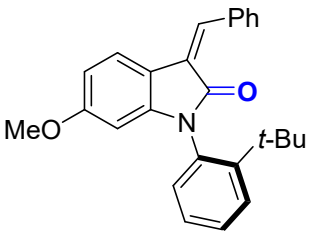

Ph
O
N
t-Bu
E-7-24


Ph
O
N
t-Bu
E-7-24


Ph
O
MeO
N
t-Bu

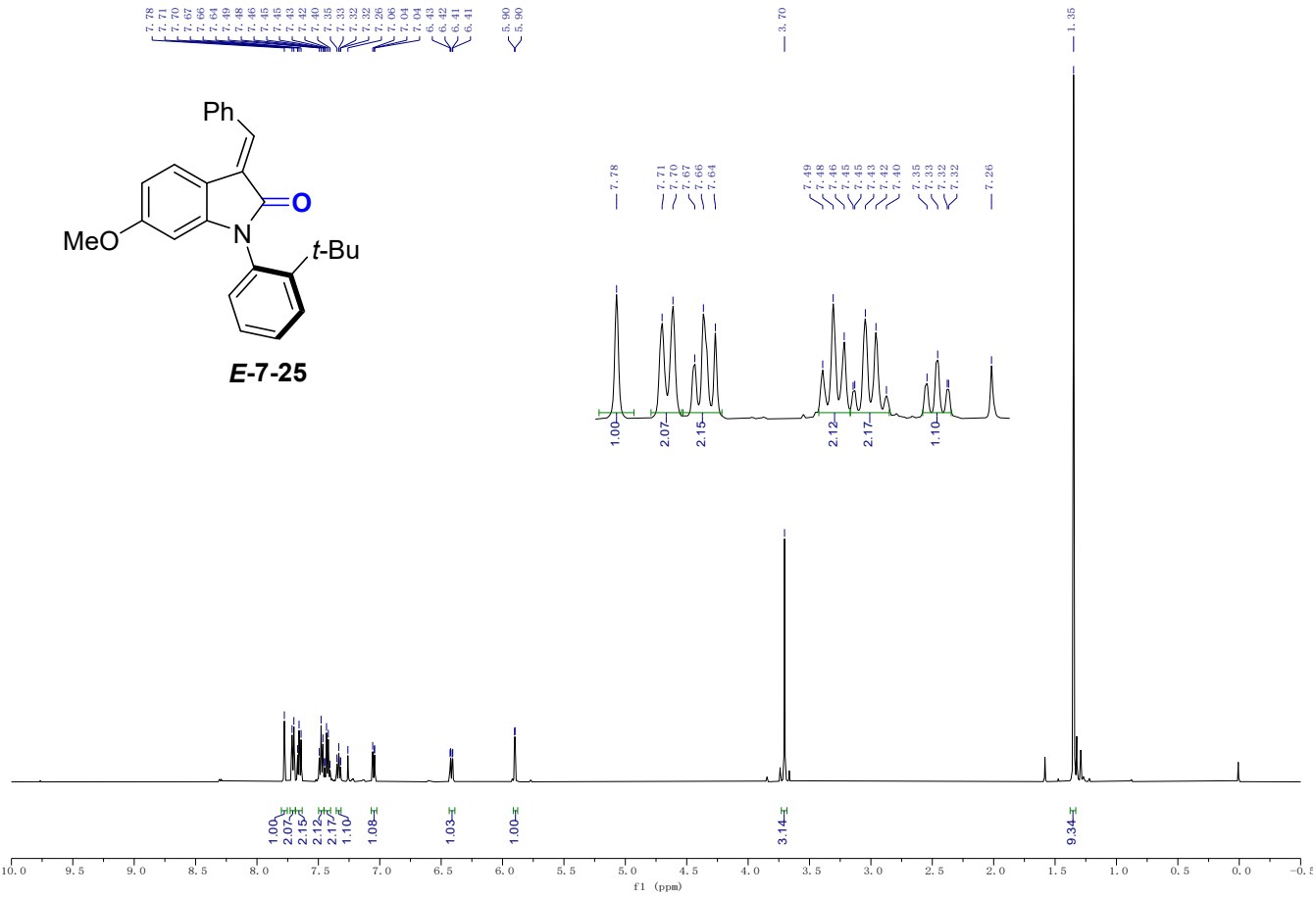
***Z*-7-25**

8.30
8.29
7.65
7.64
7.52
7.50
7.46
7.43
7.42
7.40
7.39
7.38
7.37
7.33
7.32
7.30
7.26
7.05
7.04
6.61
6.60
6.59
6.59
5.92
5.91
3.74
1.32
1.96
1.18
1.06
1.07
4.03
1.09
1.14
1.00
1.00
3.06
9.09
f1 (ppm)

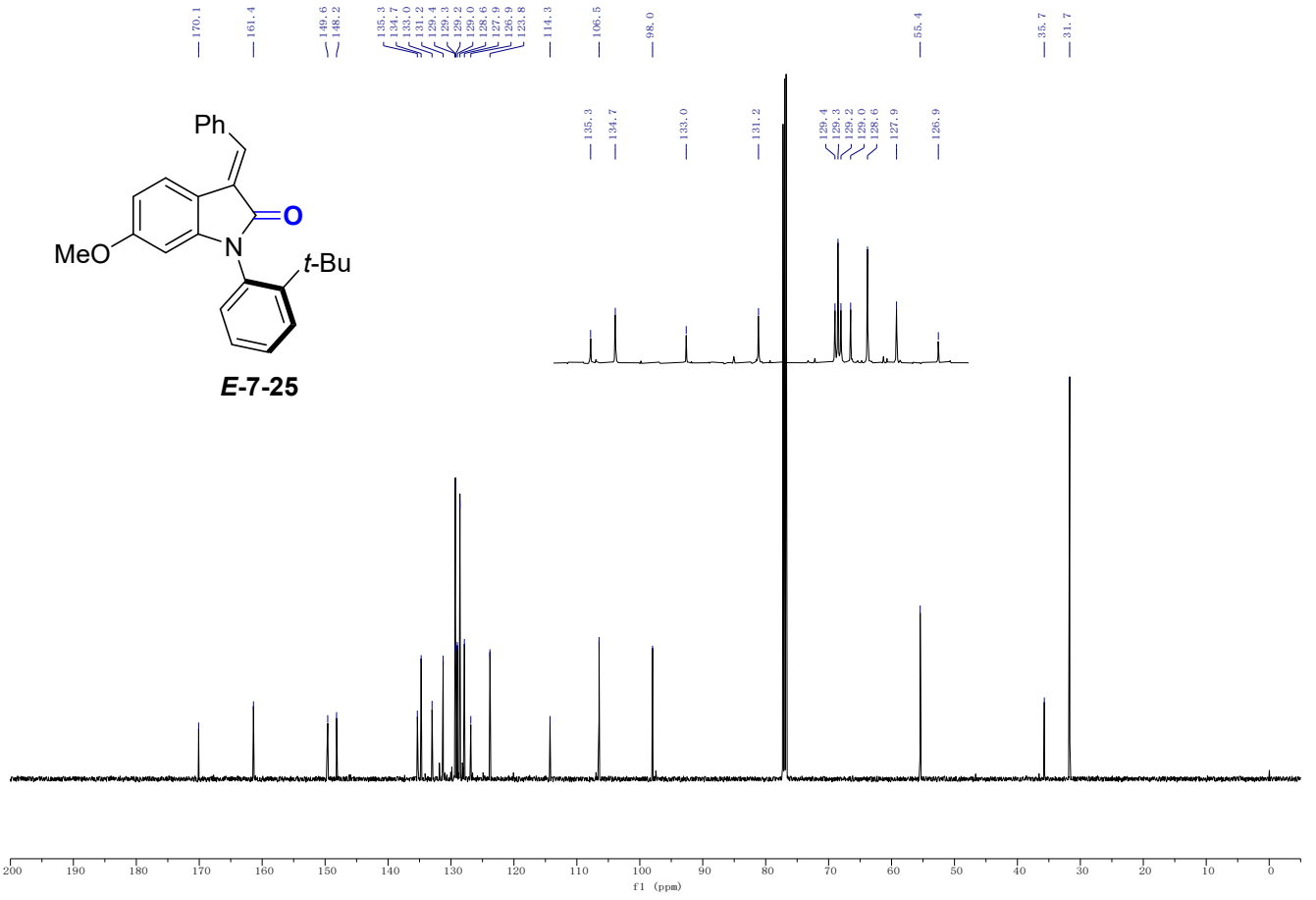

Ph
O
MeO
N
t-Bu

***Z*-7-25**

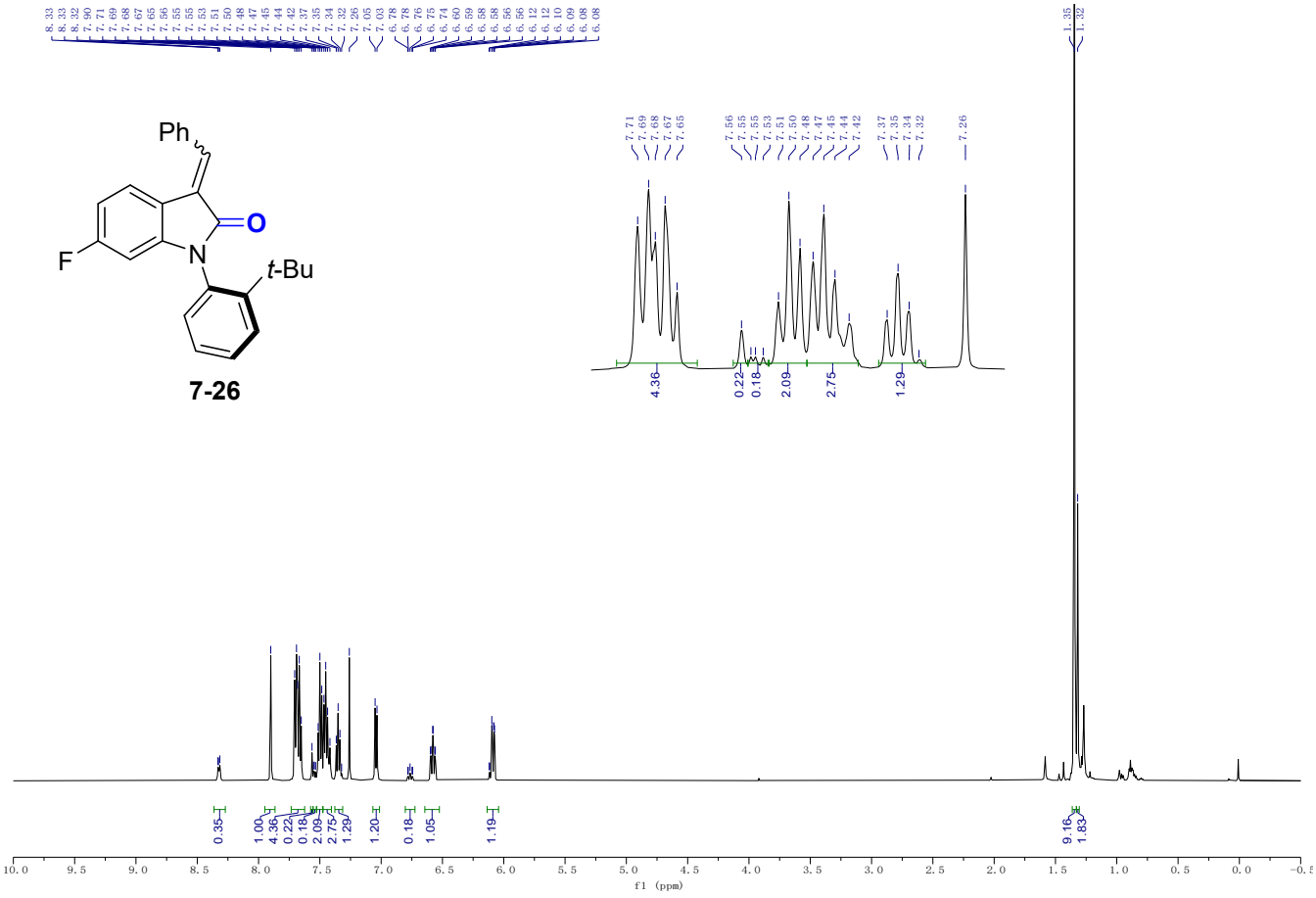
167.7
161.1
149.6
146.0
135.2
134.1
133.0
131.9
131.3
130.0
129.3
129.0
128.2
127.8
125.8
120.1
117.5
107.0
97.5
55.6
35.8
31.8
f1 (ppm)



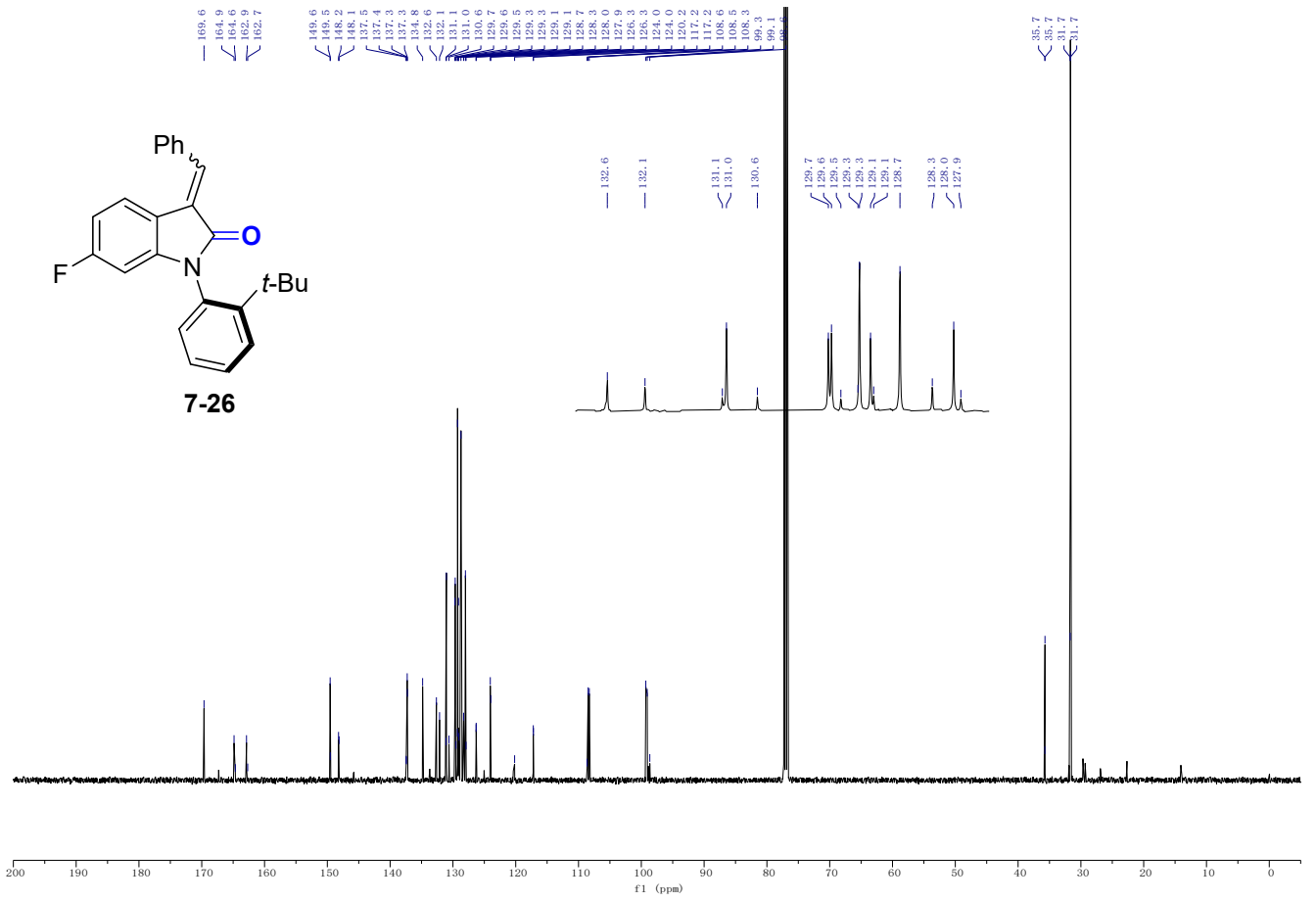
***E*-7-25**



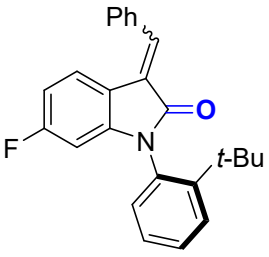
***E*-7-25**



7-26

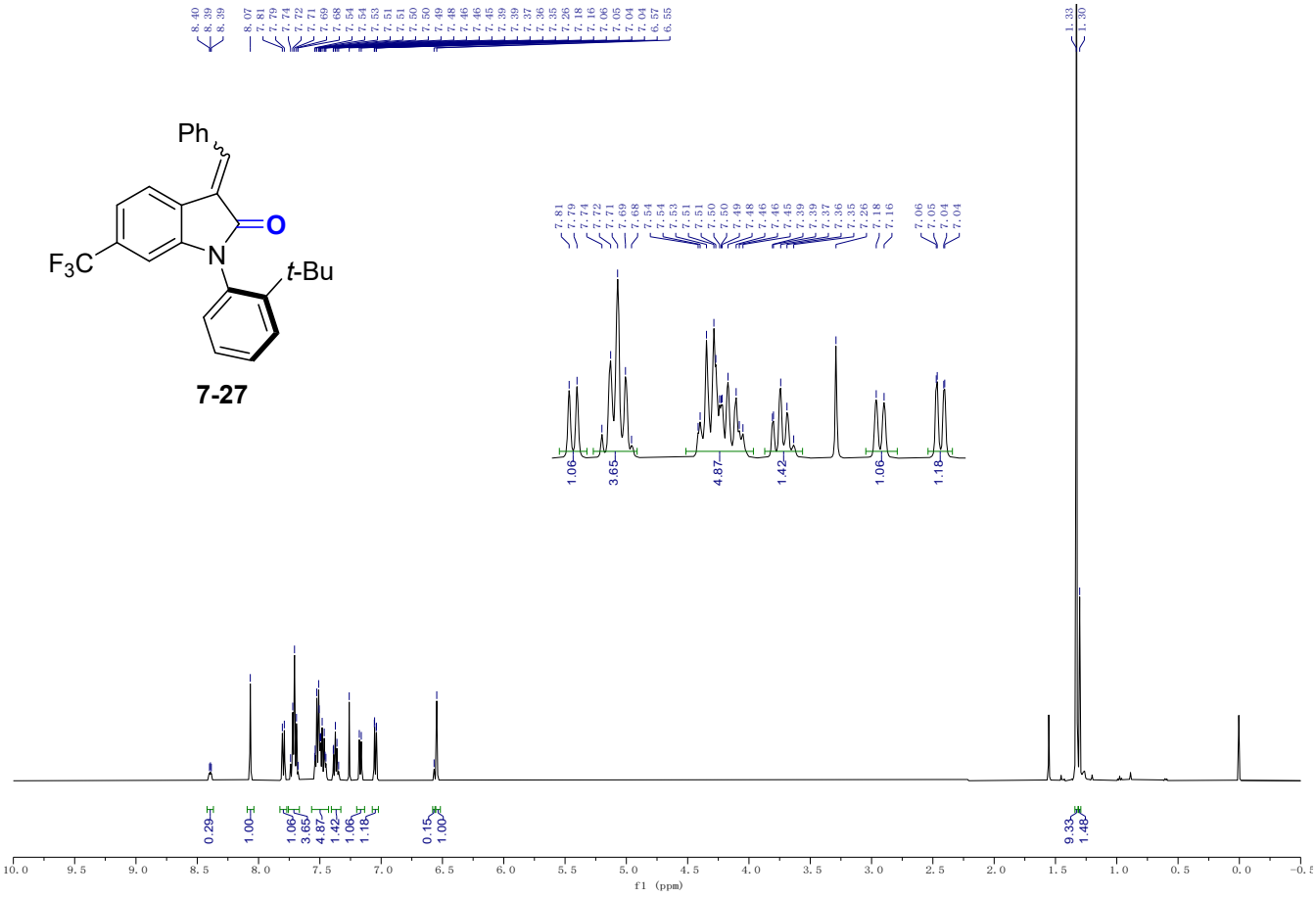


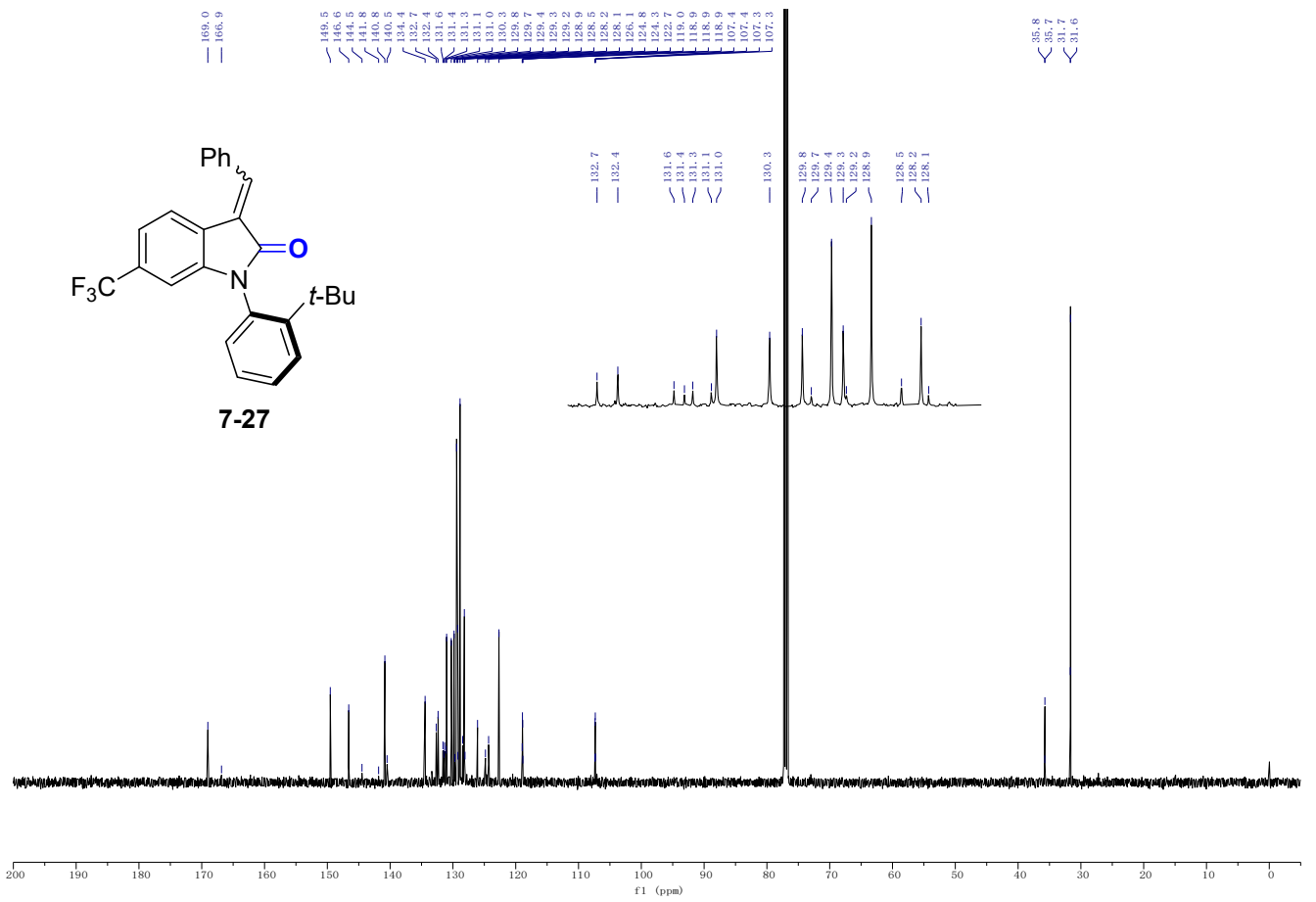
7-26

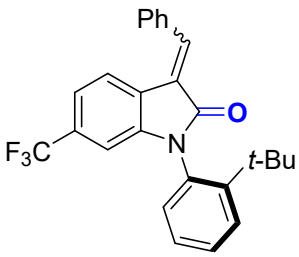

Ph
O
F
N
t-Bu

7-26

108.3
110.2
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)

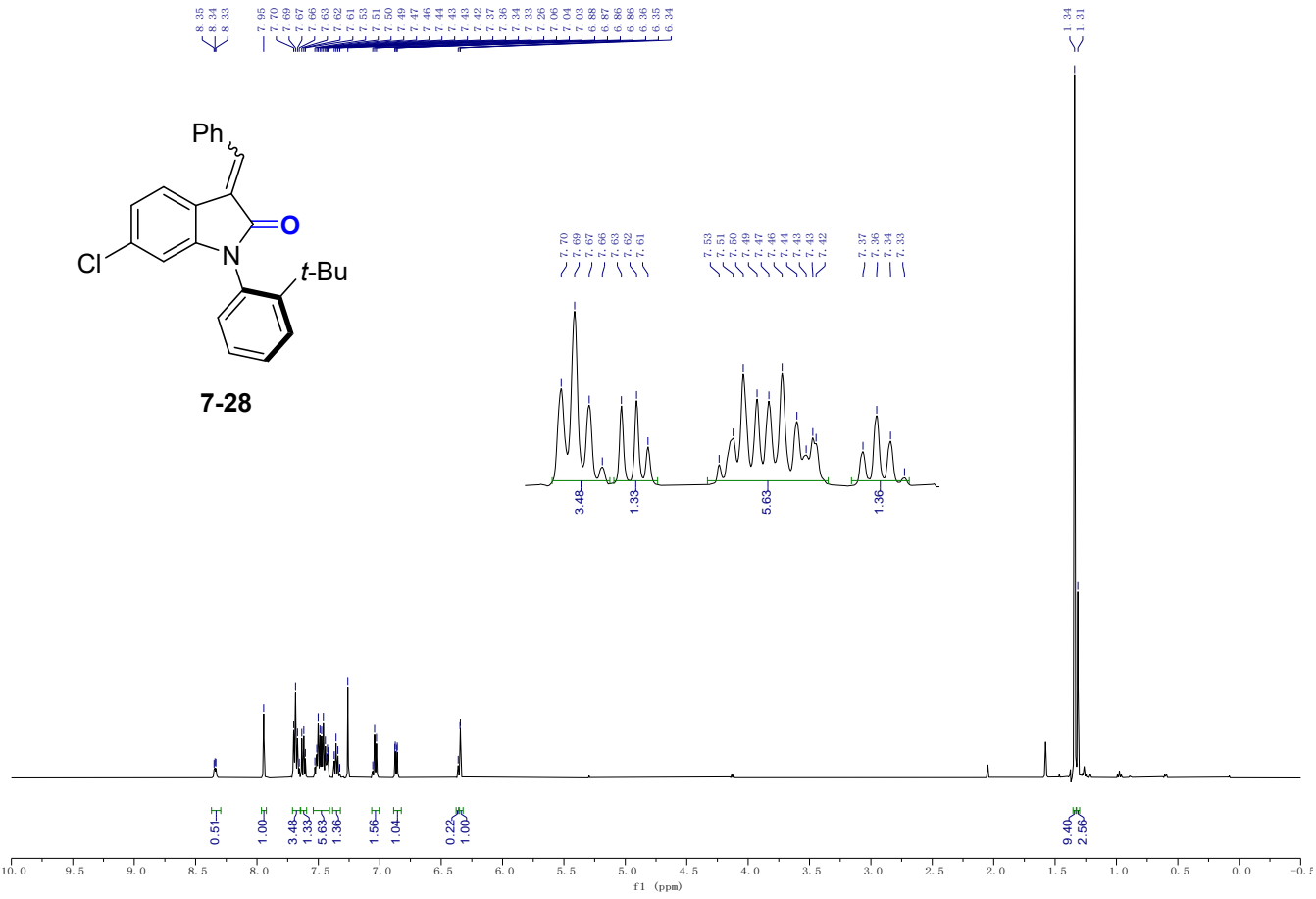

Ph
O
N
F3C
t-Bu
7-27


Ph
O
N
F3C
t-Bu
7-27
f1 (ppm)

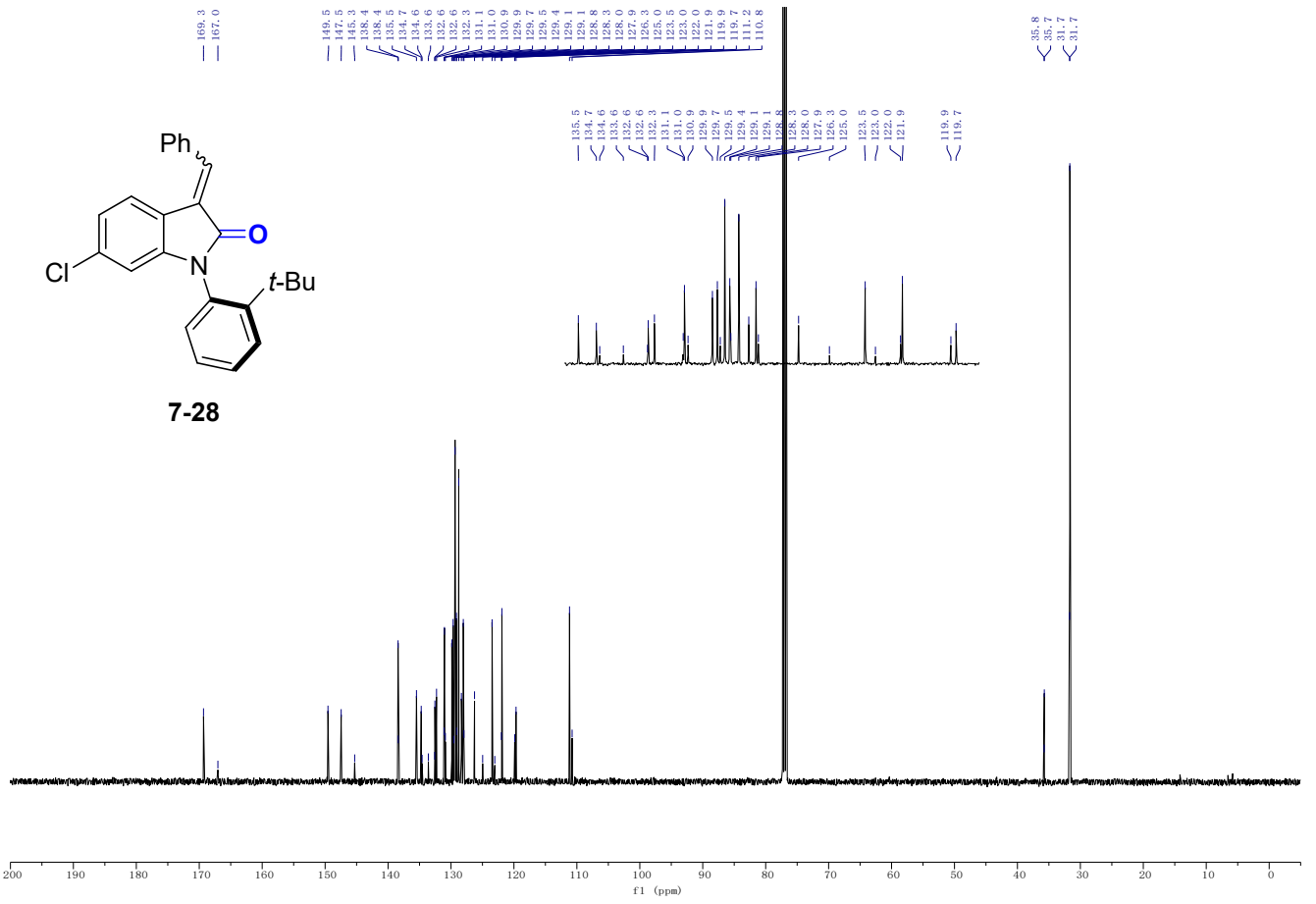

Ph
O
N
F3C
t-Bu

7-27

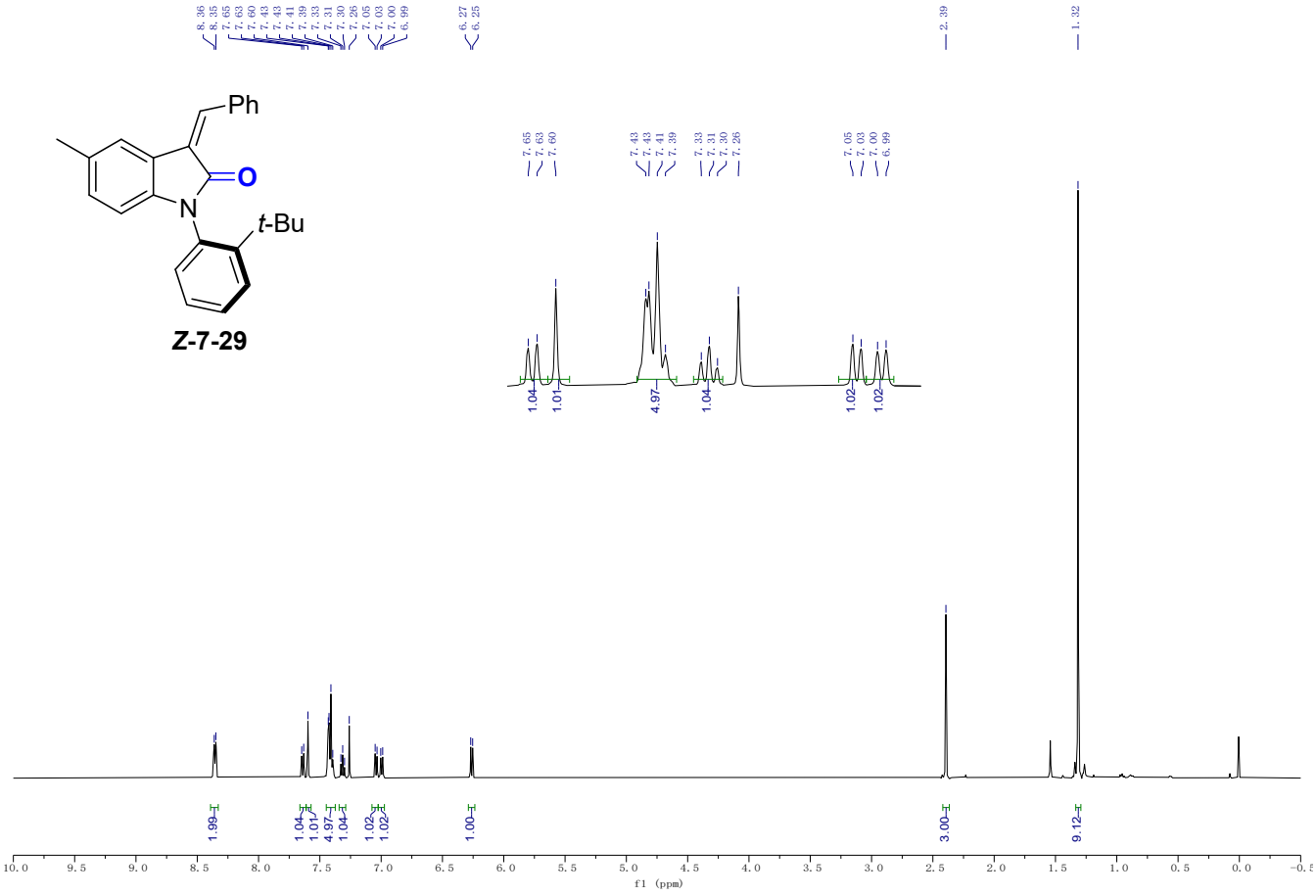
-62.3
-62.8
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)



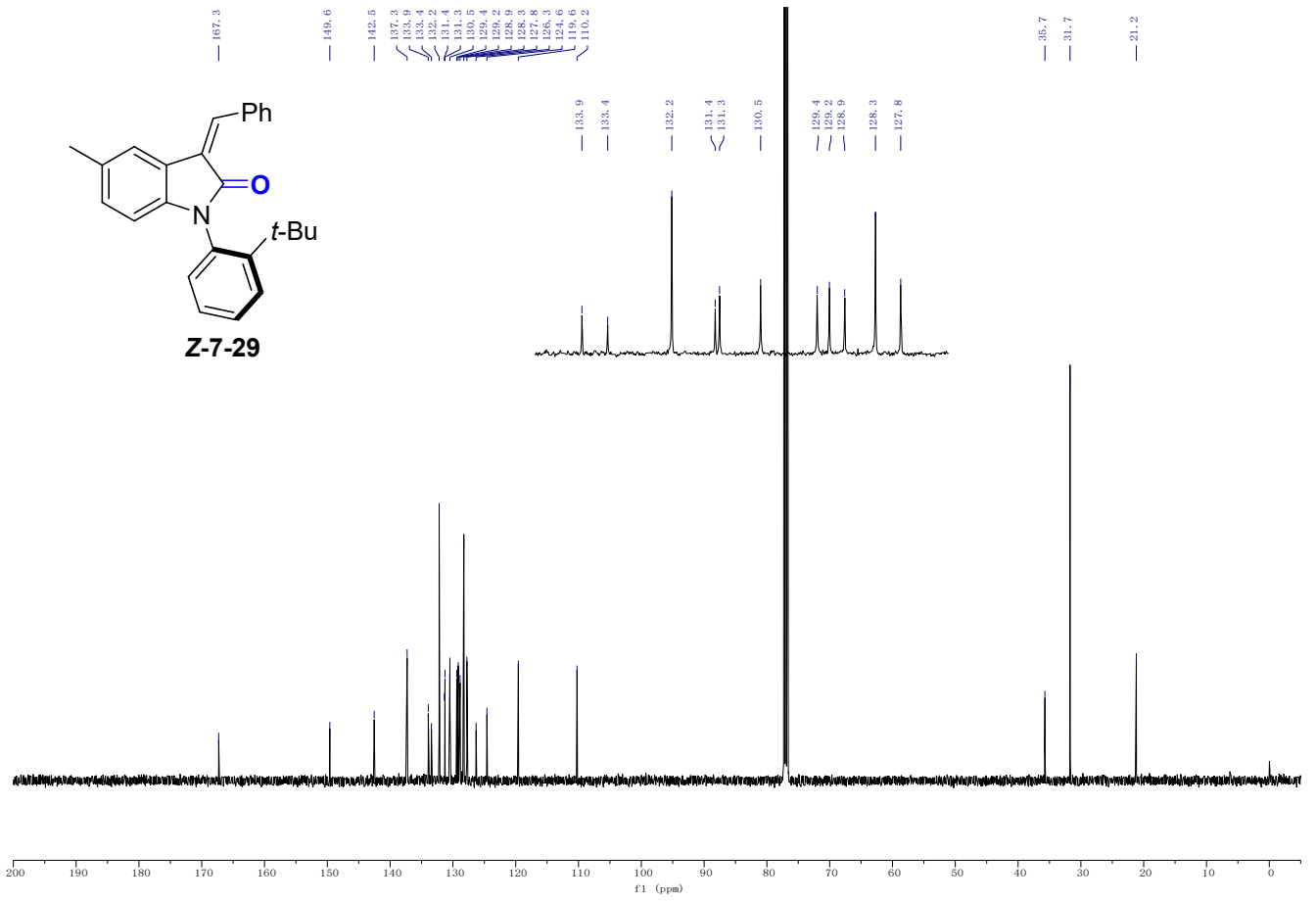
7-28



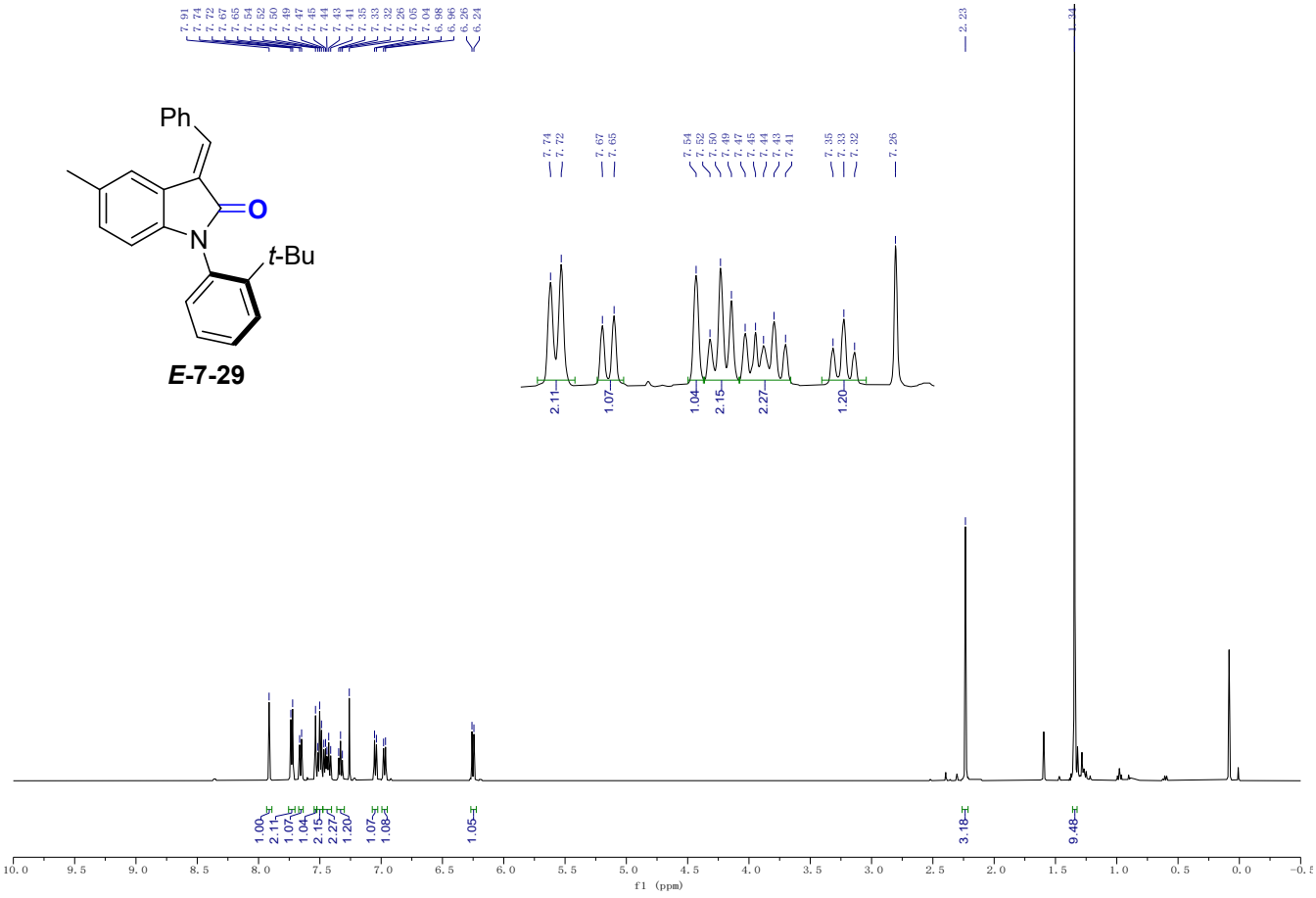
7-28



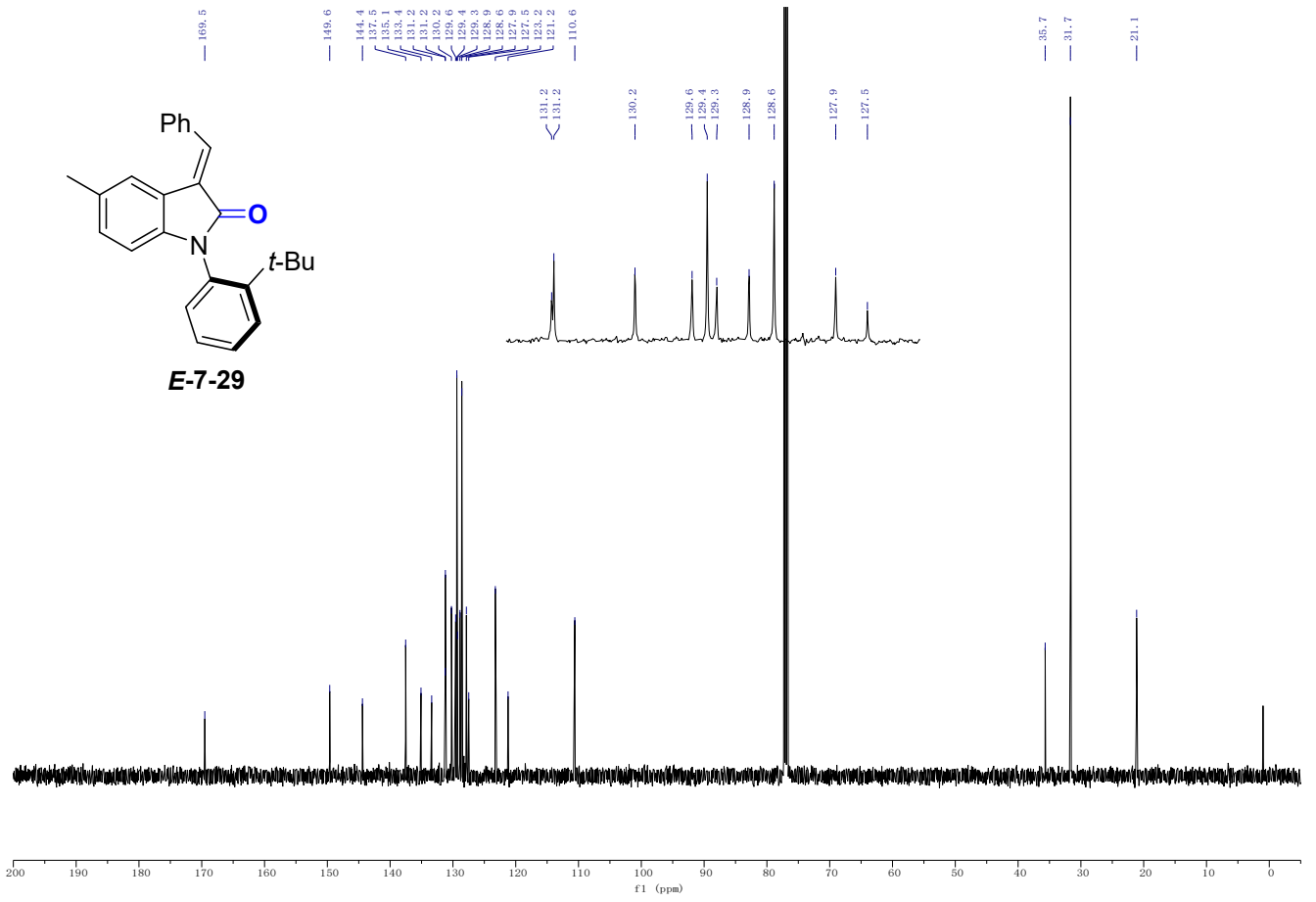
***Z*-7-29**



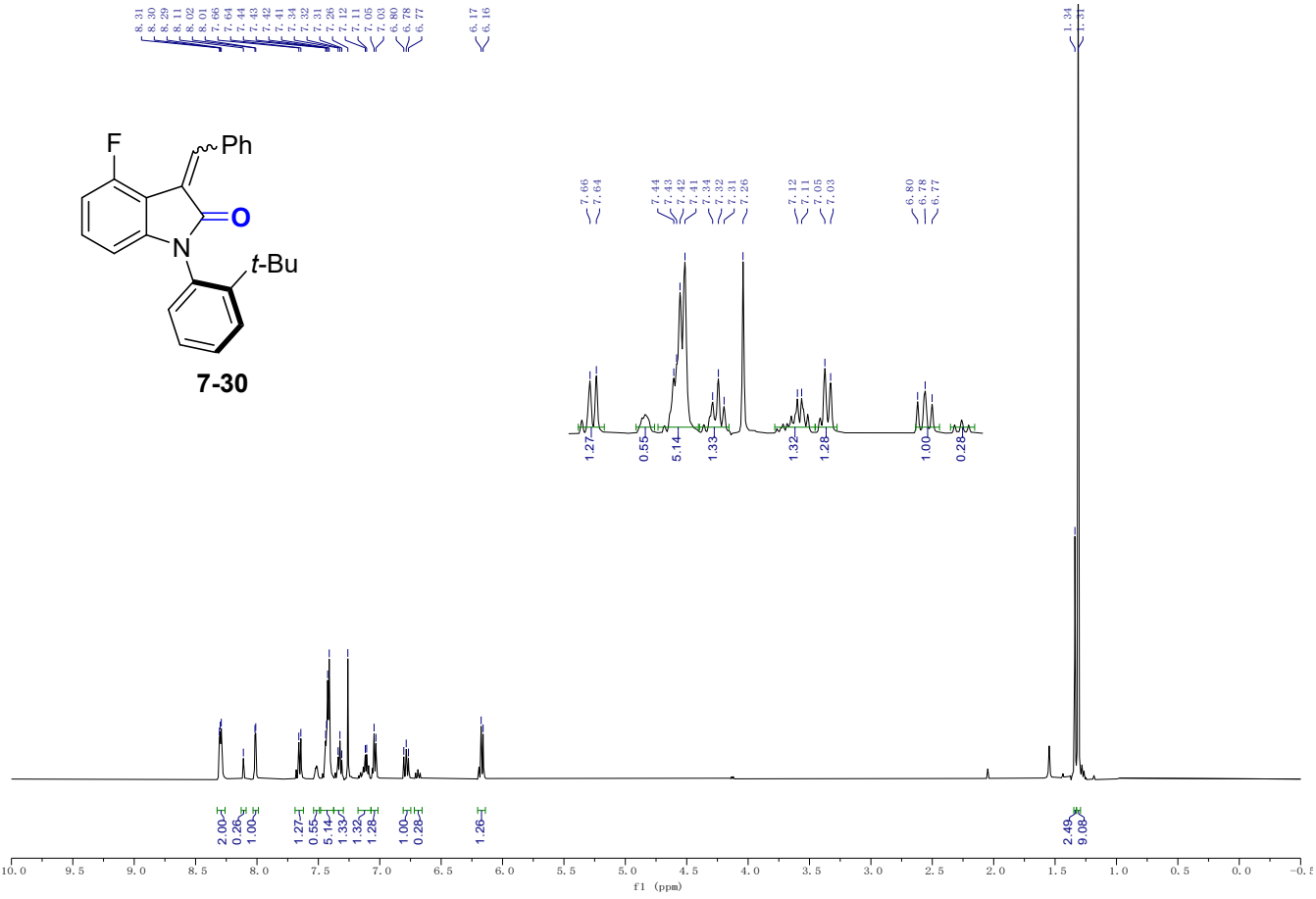
***Z*-7-29**



***E*-7-29**



***E*-7-29**



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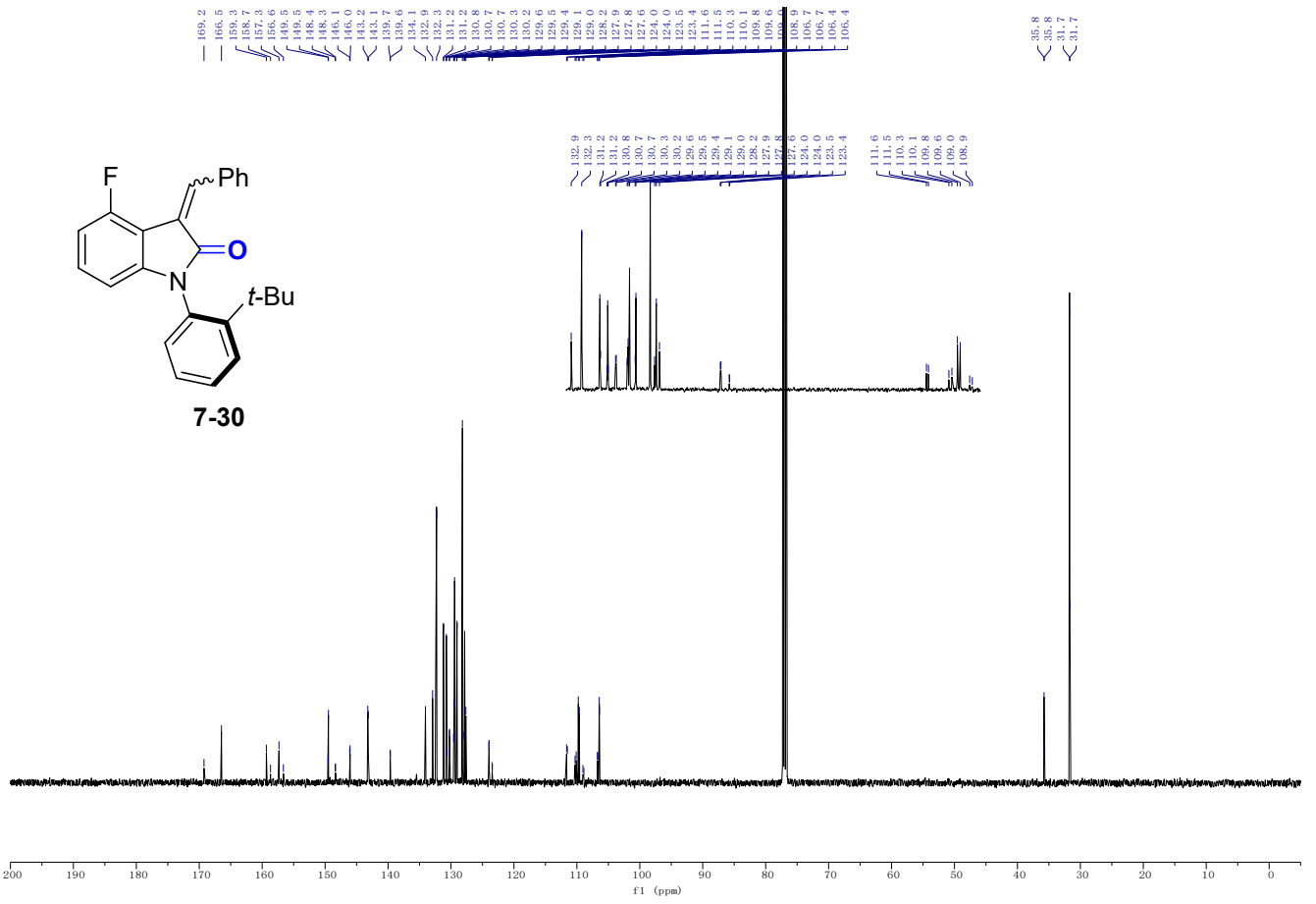
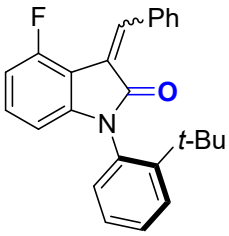


7-30


F
Ph
O
N
t-Bu

7-30

-95.5
-119.5
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
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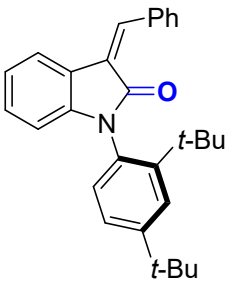
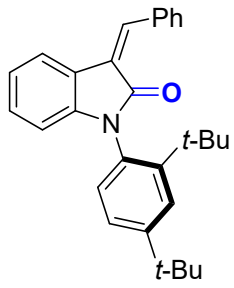
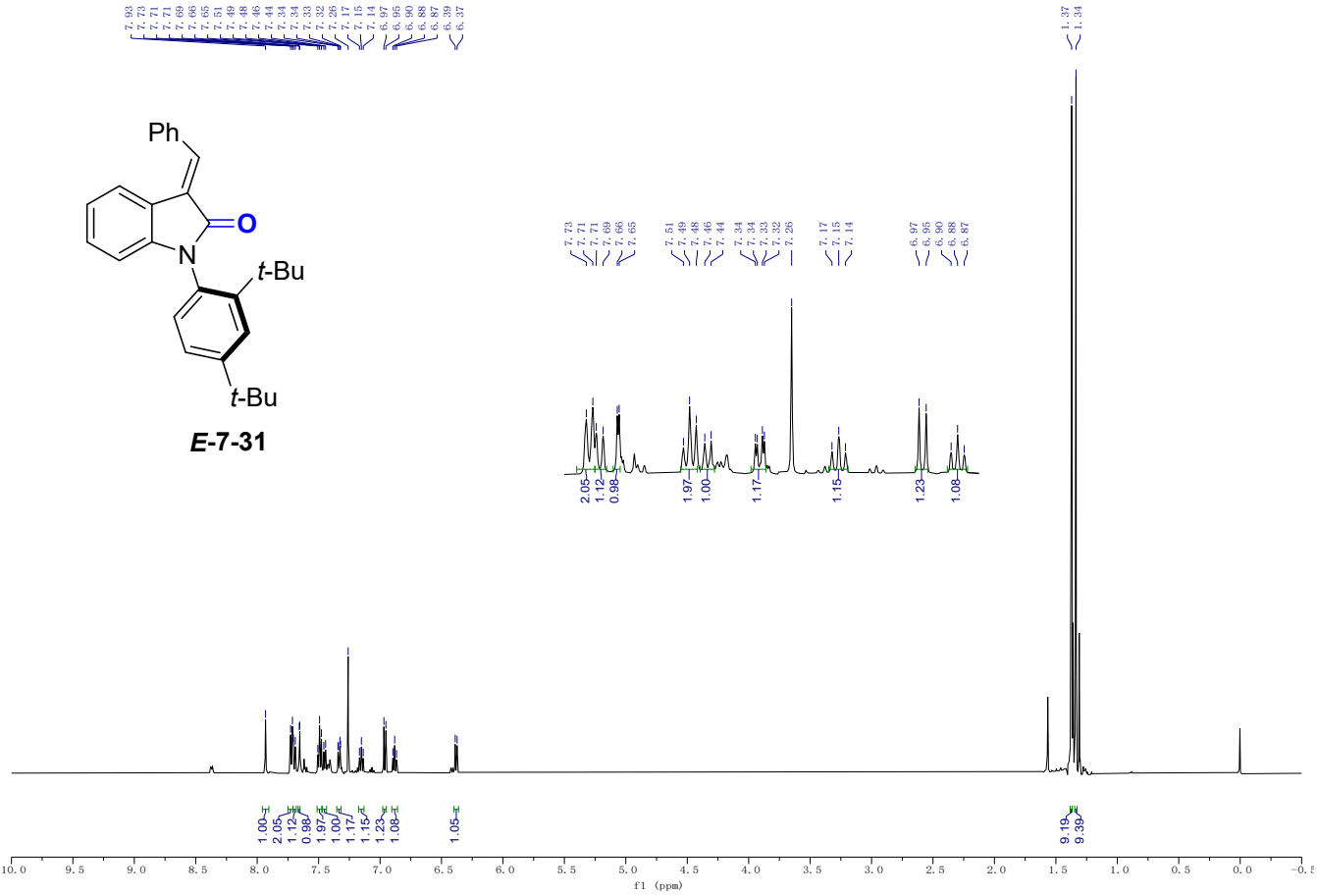
-180
-190
-200
-210
-220
f1 (ppm)

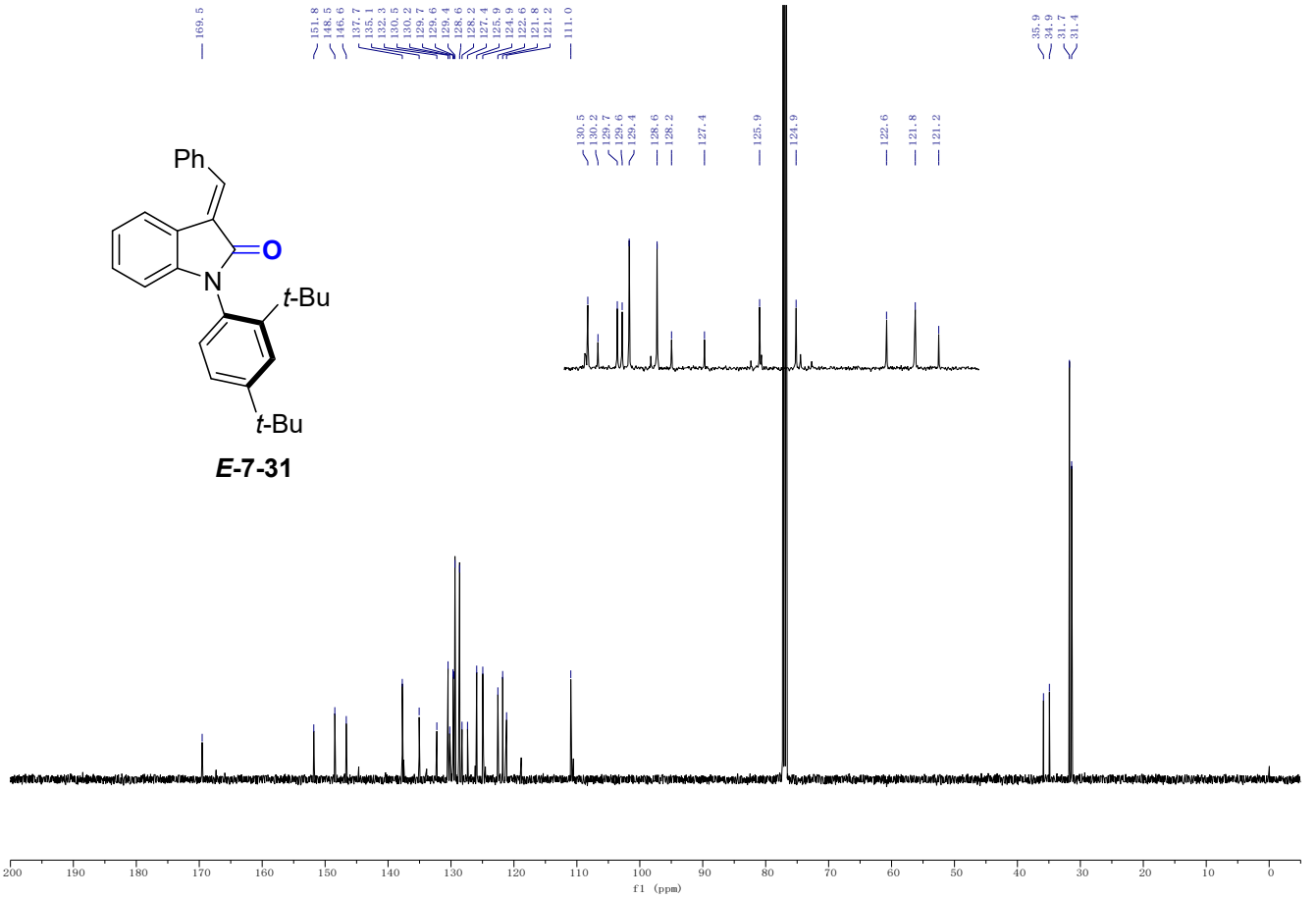


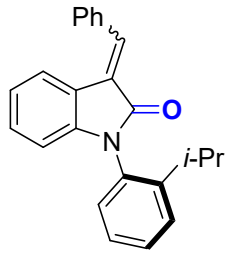
***Z*-7-31**



***Z*-7-31**


Ph
O
N
t-Bu
t-Bu
E-7-31
f1 (ppm)


Ph
O
N
t-Bu
t-Bu
E-7-31
f1 (ppm)



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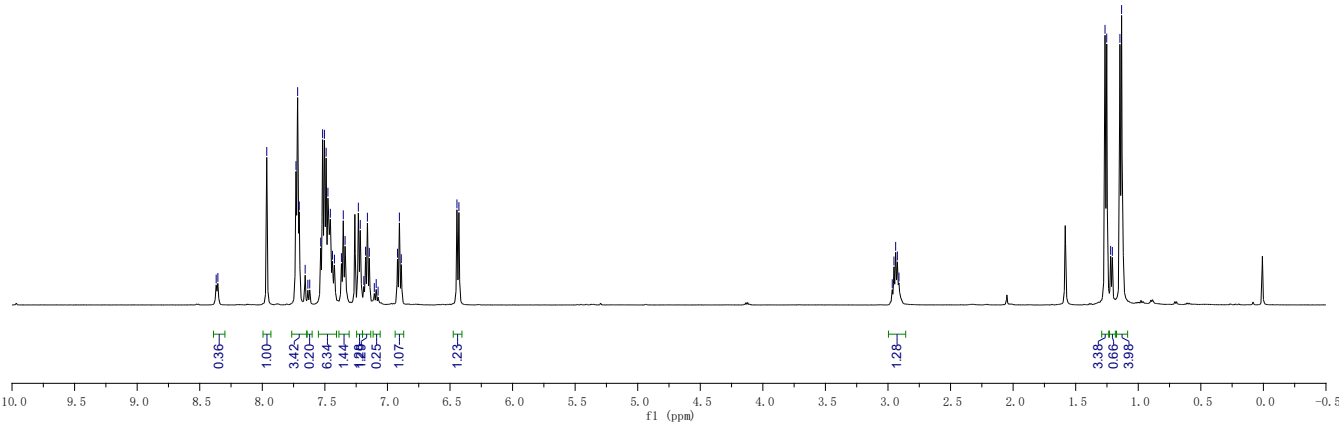

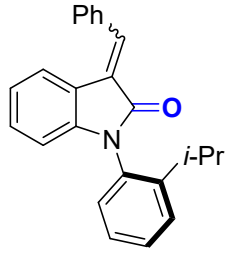

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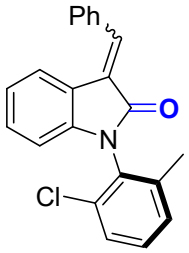

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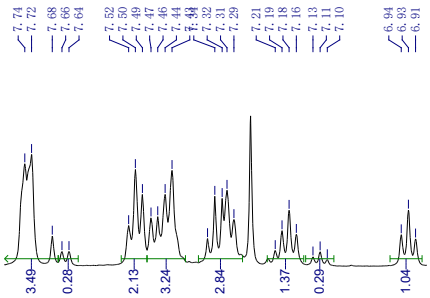
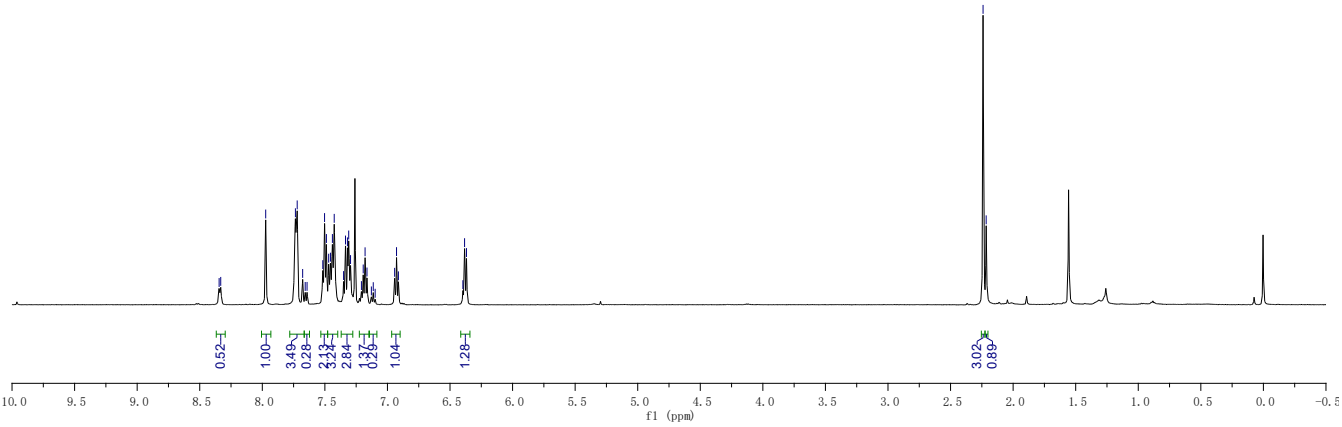
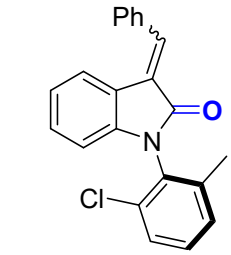
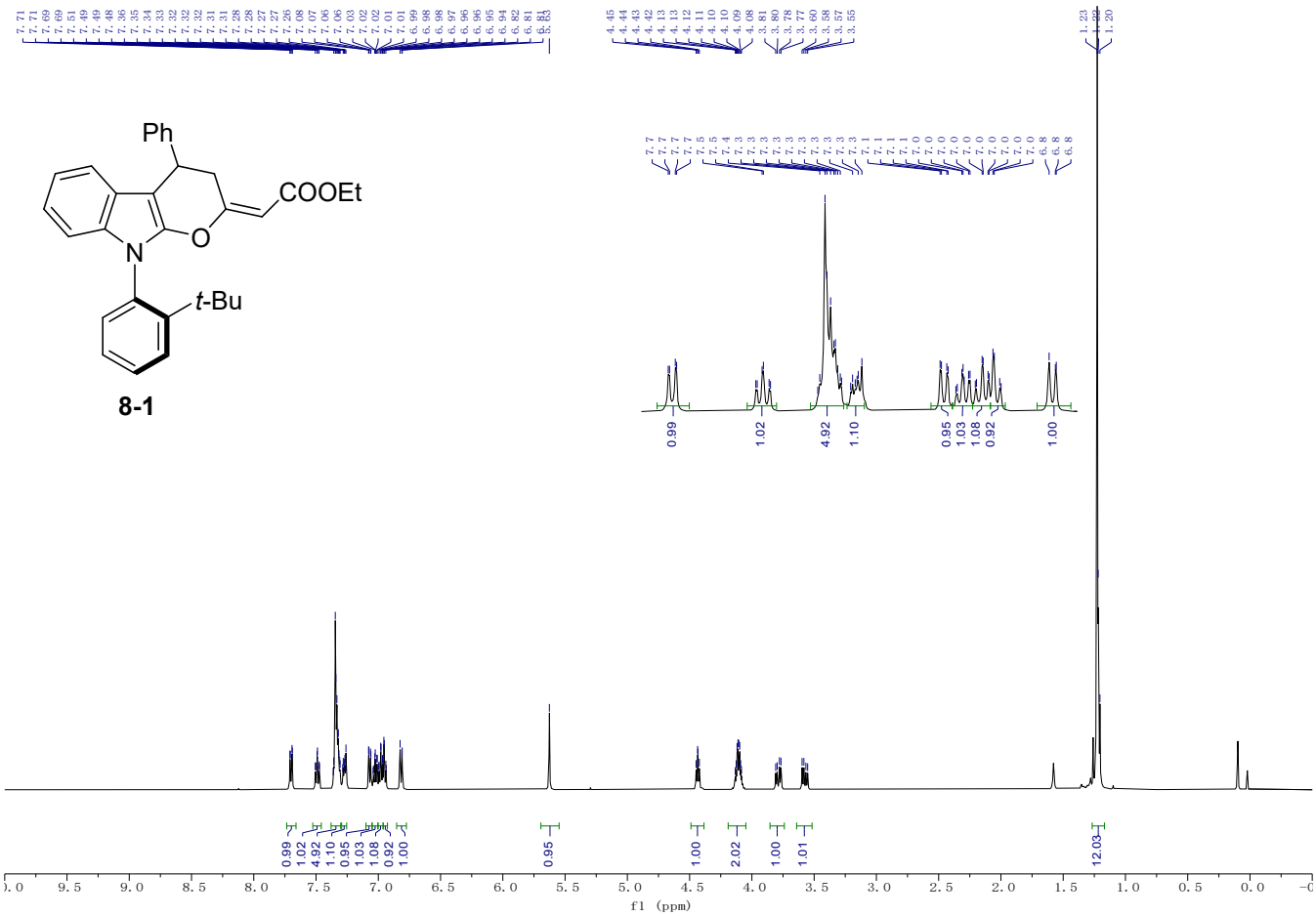
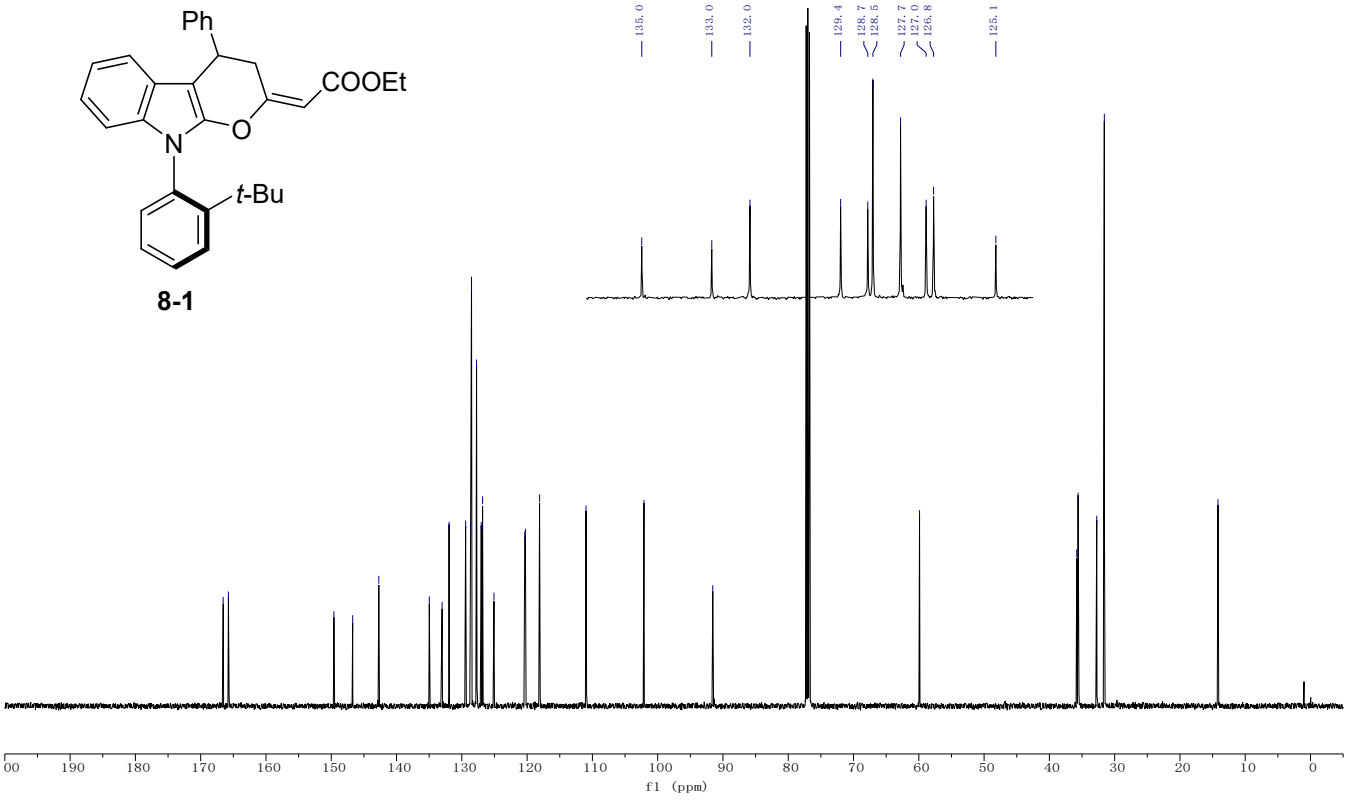


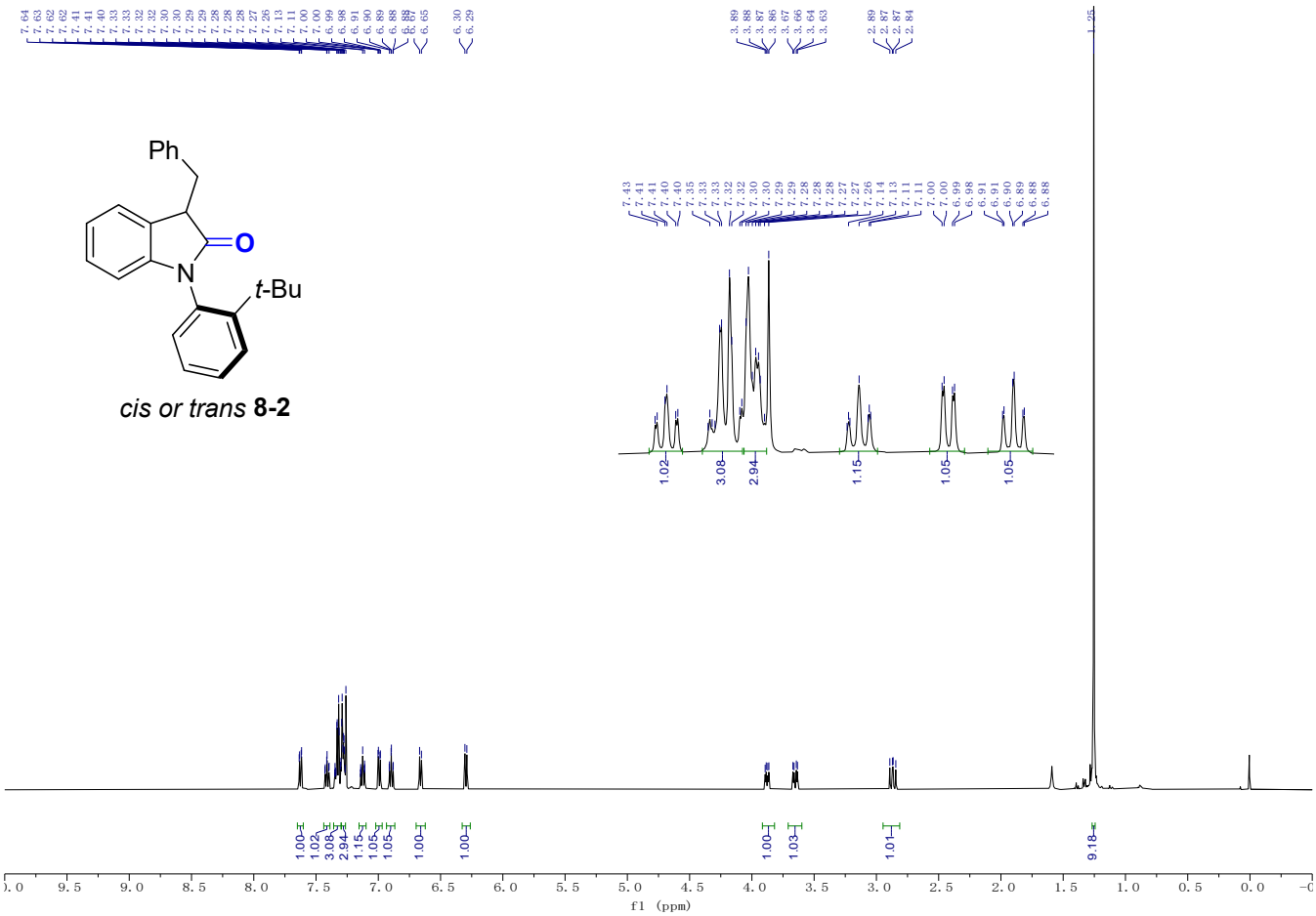




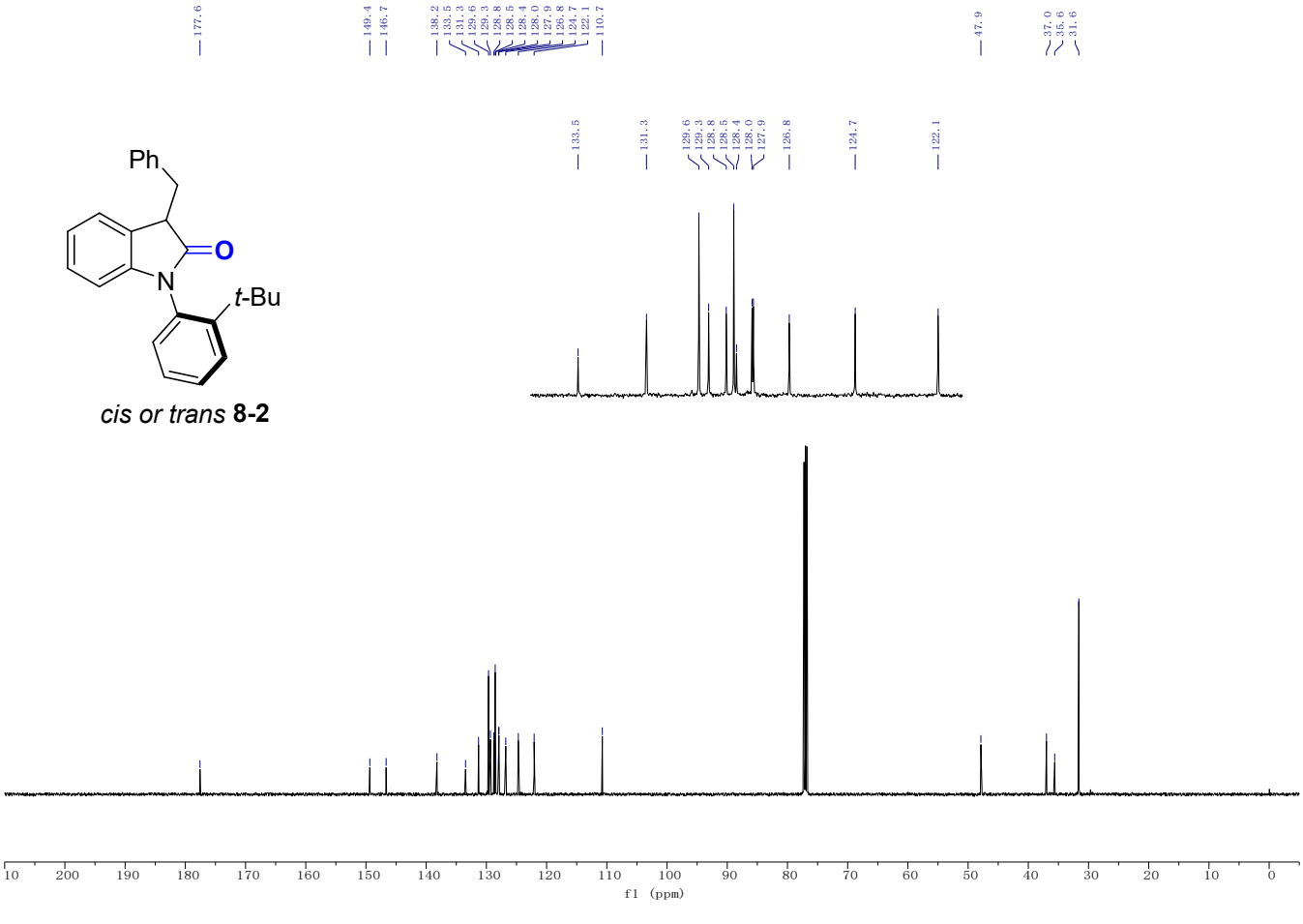
7-33


Ph
COOEt
O
N
t-Bu
8-1
f1 (ppm)

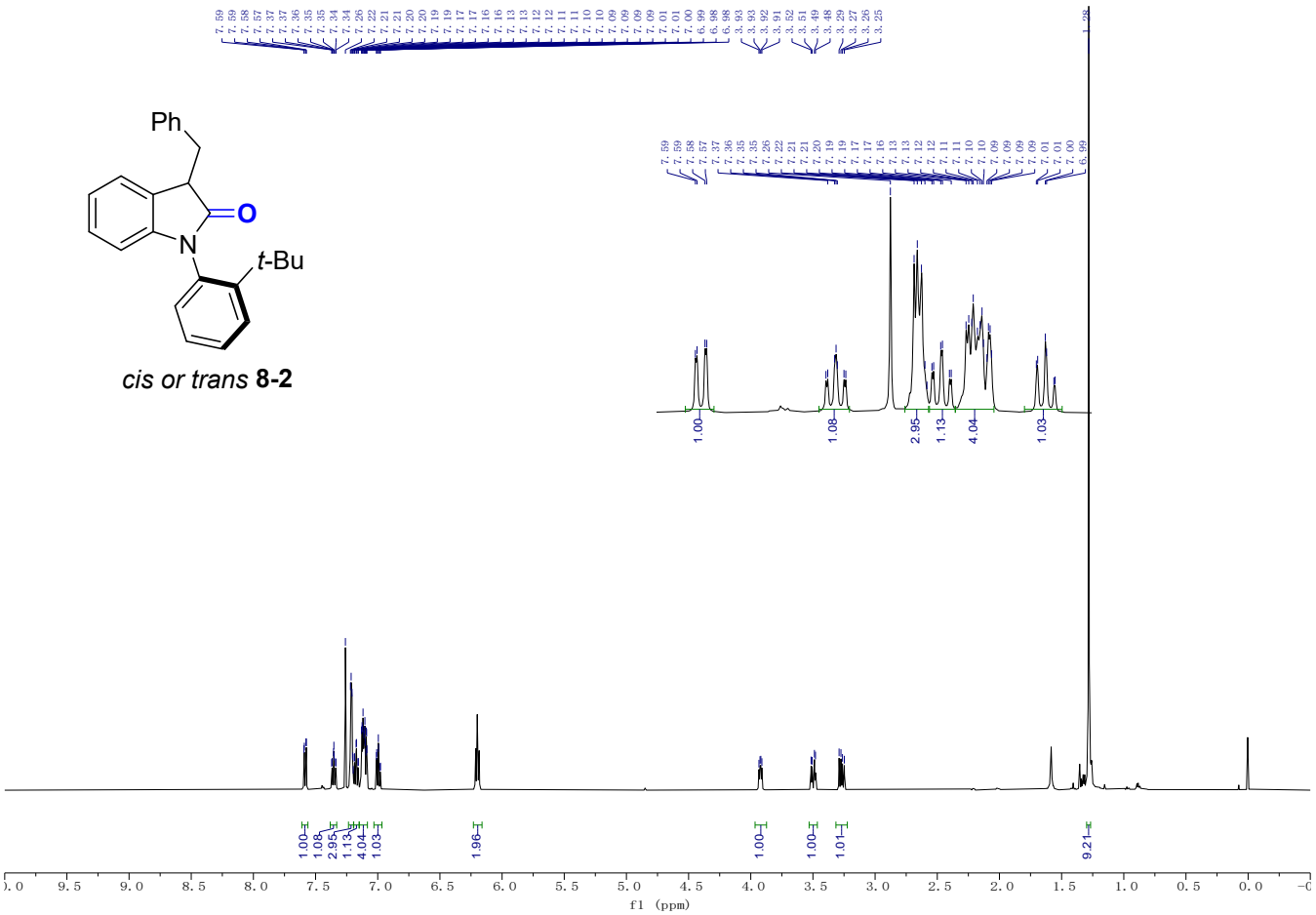

Ph
COOEt
O
N
t-Bu
8-1
f1 (ppm)



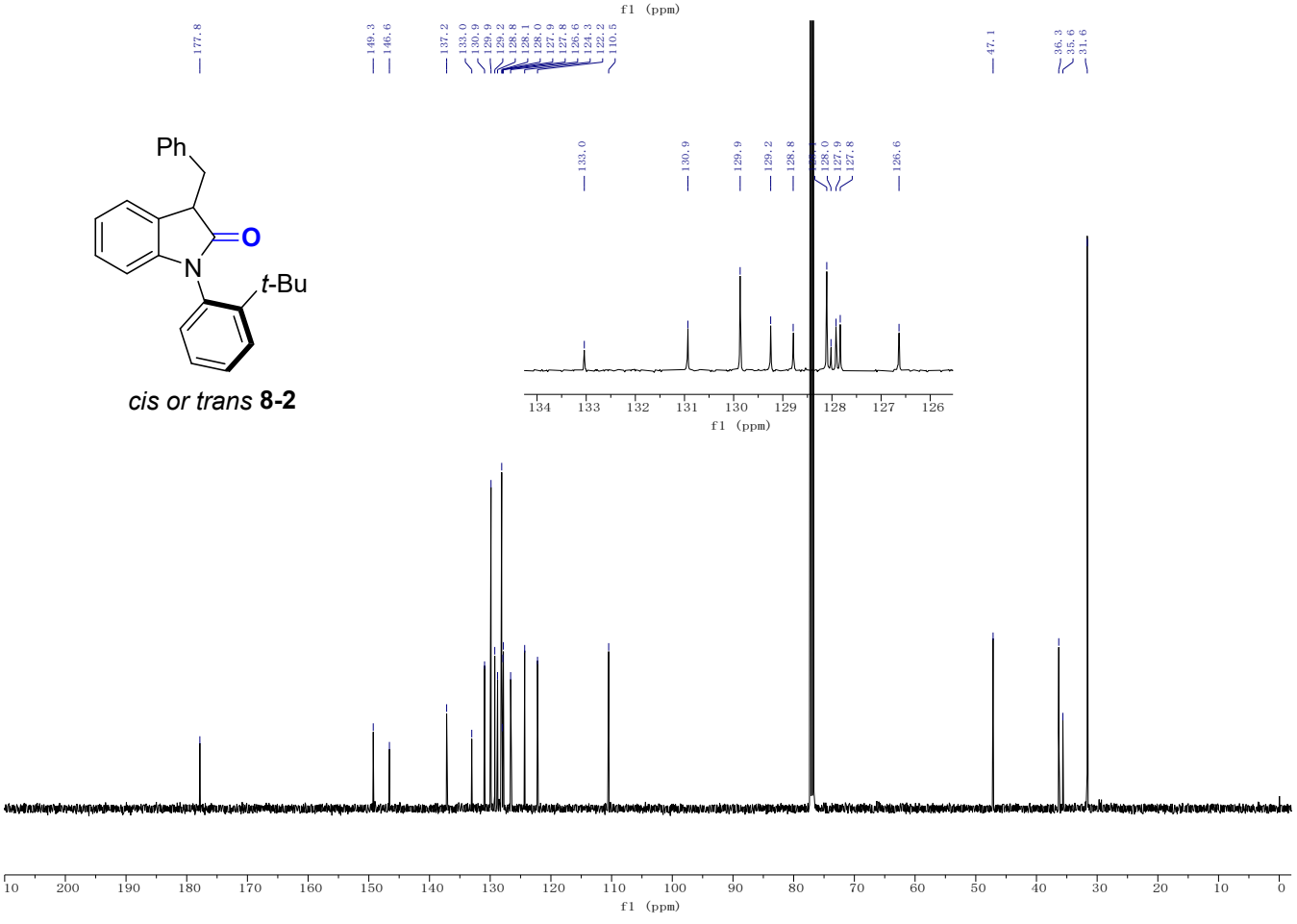
cis or trans **8-2**



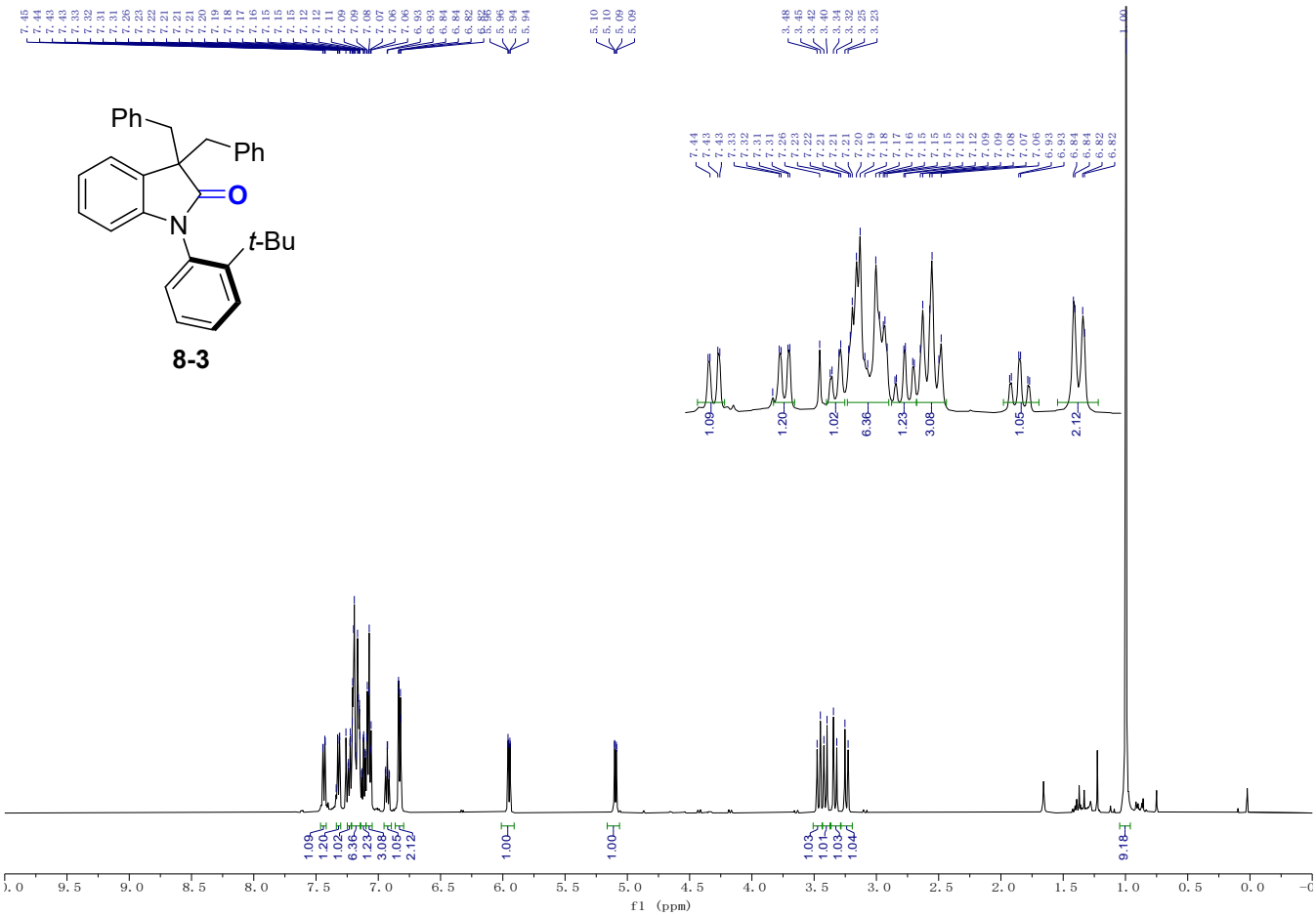
cis or trans **8-2**

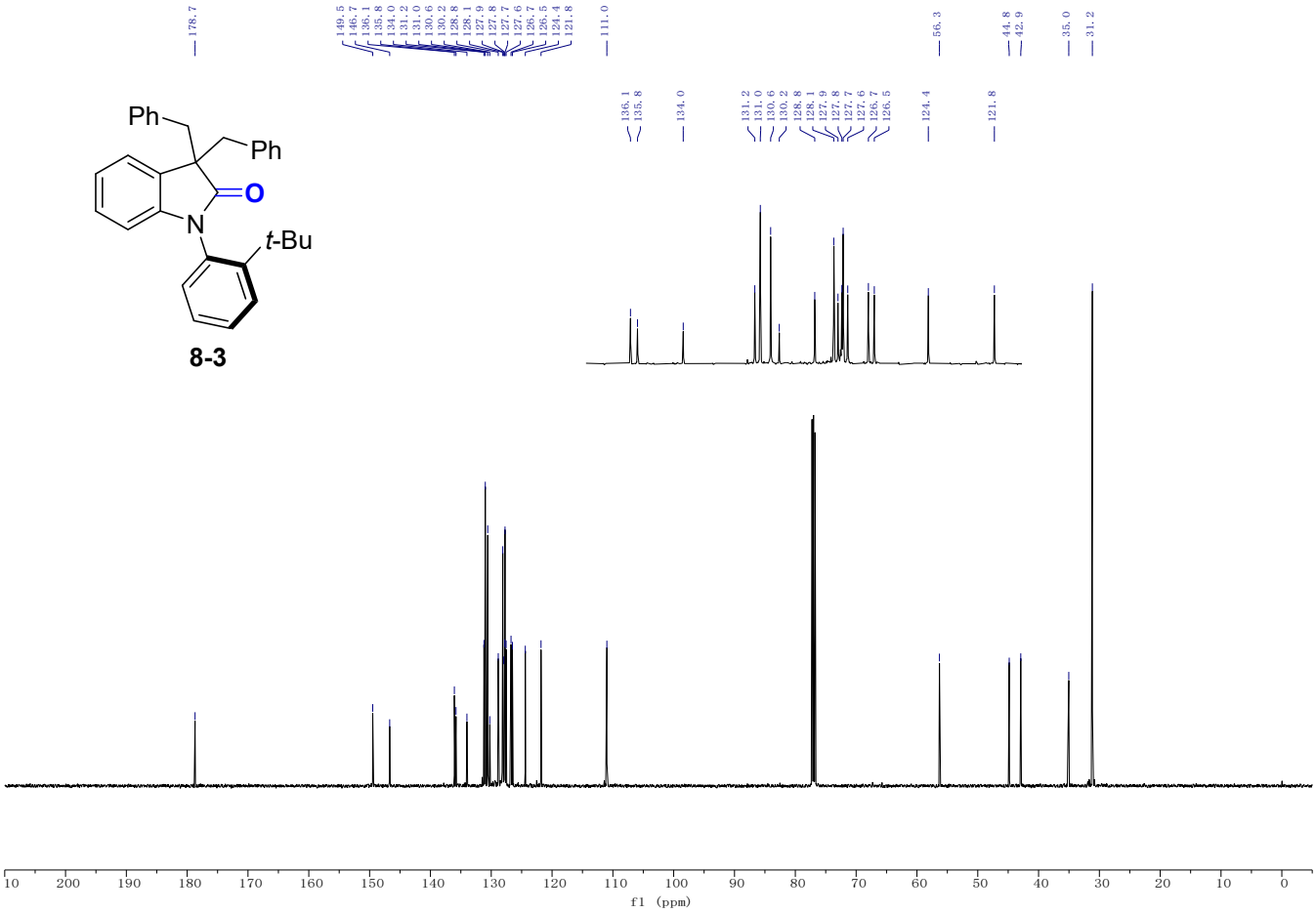


cis or trans **8-2**



cis or trans **8-2**


Ph
Ph
O
N
t-Bu
8-3
f1 (ppm)


Ph
Ph
O
N
t-Bu
8-3
f1 (ppm)