Supporting Information

Photoinduced Copper Catalyzed Nitrogen-to-Alkyl Radical Relay Sonogashira-type Coupling of *o*-Alkylbenzamides with Alkynes

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General Information

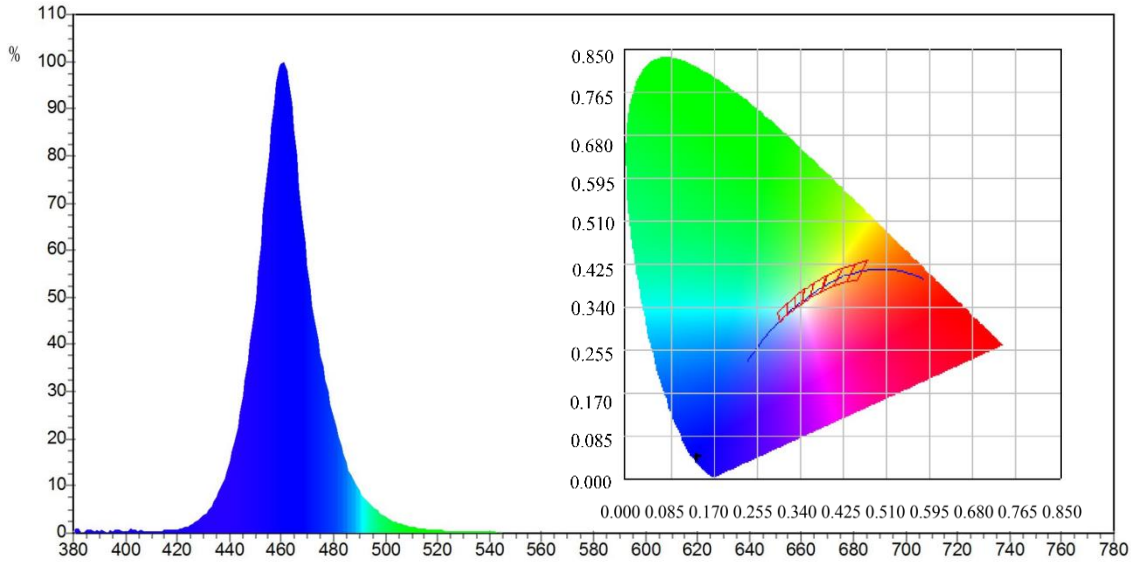
Unless noted otherwise, all the solvents and commercially available reagents were purchased and used directly. Benzene, 1,4-dioxaneand tetrahydrofuranwere distilled freshly over sodium, benzotrifluoride was distilled freshly over P_2O_5, DCM was distilled freshly over CaH_2 andcarefullyfreeze-pump-thawed. Sensitive reagents and solvents were transferred under nitrogen into a nitrogen-filled glovebox with standard techniques. Reactions were monitored with thin layer chromatography (TLC) using silica gel 60 F-254 plates. TLC plates were normally visualized by UV irradiation (254 nm or 365 nm), stained with basic $KMnO_4$. Flash chromatography was performed using silica gel 60 (200−300 mesh). Vials (15 x 45 mm 1 dram (4 mL) / 17 x 60 mm 3 dram (7.5 mL) with PTFE lined cap attached) were purchased from Qorpak and flame-dried or put in an oven overnight and cooled in a desiccator. Mass (HRMS) analysis was obtained using Agilent 6200 Accurate-Mass TOF LC/MS system with Electrospray Ionization (ESI). Nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded with Bruker AVANCE Ⅲ–300 (300 MHz, ^{1}H at 300 MHz, ^{13}C at 75 MHz) or 400 (400 MHz, ^{1}H at 400 MHz, ^{13}C at 101 MHz) or 600 (600 MHz, ^{1}H at 600 MHz, ^{13}C at 151 MHz).^{19}F NMR spectra were recorded on Bruker AVANCE Ⅲ–400.Unless otherwise noted, all spectra were acquired in $CDCl_3$. X-ray data were collected with a Bruker D8 VENTURE diffractometer. Chemical shifts are reported in parts per million (ppm, δ), downfield from tetramethylsilane (TMS, δ = 0.00 ppm) and are referenced to residual solvent ($CDCl_3$, δ = 7.26 ppm (^{1}H) and 77.00 ppm (^{13}C). Coupling constants were reported in Hertz (Hz). Data for ^{1}H NMR spectra were reported as follows: chemical shift (ppm, referenced to protium, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, coupling constant (Hz), and integration). All other materials were obtained from Energy Chemical and were used as received.

The Parameters of the Blue LEDs

Test Report of LED Photoelectric Test System

Test project:	LED spectral analysis	
Test equipment:	Photochromic-electric integrated test system	
The test identification	Product model: 3 W Blue LED	
	Ambient temperature: 27 ℃	Ambient humidity: 65%
	Test organization: spectrotest department	

Spectral relative energy distribution curve



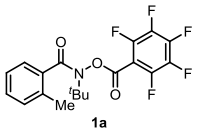
Wavelength/nm

Spectrum parameter		Photoelectric parameter	
peak wavelength:	453.6 nm	lighting current:	3.0 mA
main wavelength:	460.2 nm	preheating time:	500 ms
centroid wavelength:	445.7 nm	test current:	700.0 mA
central wavelength:	446.0 nm	direct voltage:	3.52 V
half-wave width:	22.0 nm	light flow:	40547.6 mlm
colour temperature:	K	light efficiency:	16.456 lm/w
chromaticity coordinate (x, y):	0.1467, 0.0349	optical power:	896.0946 mv
chromaticity coordinate (u, v):	0.1877, 0.0670	backward voltage:	5.00 V
CRI (color rendering index):	0	leakage current:	0.0 μA
colour purity:	0.984		

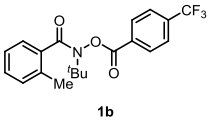
Note:Guanghong 45, 460-462

Synthesis of Starting Materials

The amides **1a**[1], **1b**[2], **1c**[1], **1d**[1] and **1e**[1] are known compounds. The substrates **1f~1x** were prepared according to following precudures.



1a



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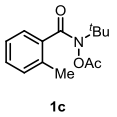
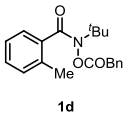
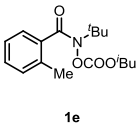


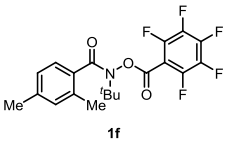
1c



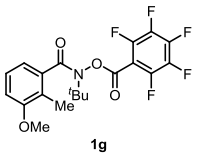
1d



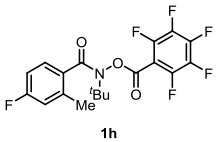
1e



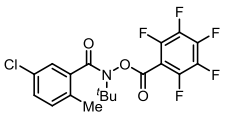
1f



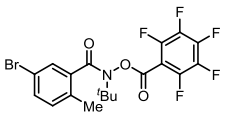
1g



1h



1i



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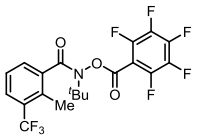

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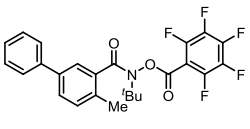
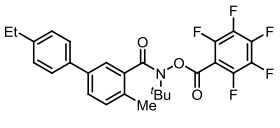


1l



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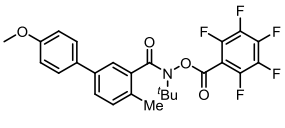

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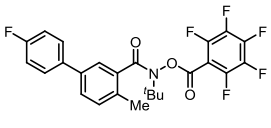
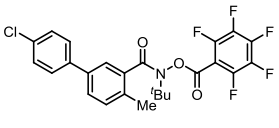


1o



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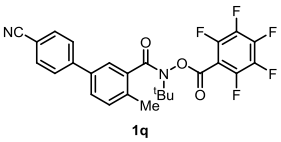
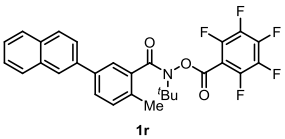


1q



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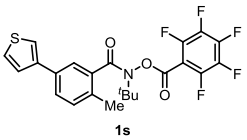

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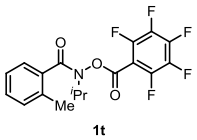
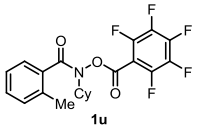
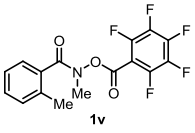


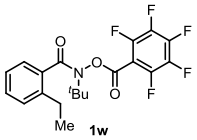
1t



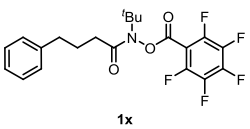
1u



1v

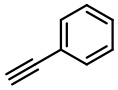


1w

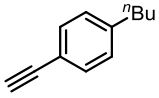


1x

The arylacetylenes **2u**[3] and **2v**[4] were prepared according to the previously reported literature. The substrate **2t** was unknown compound. The others are commercially available and were used as recieved.



2a



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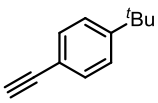

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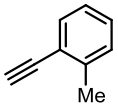

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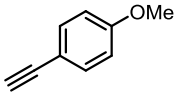

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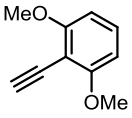

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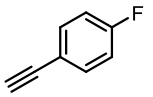

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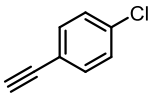
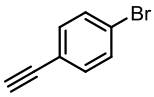


2h



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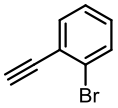

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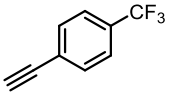

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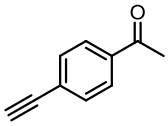

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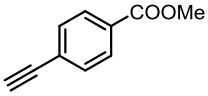

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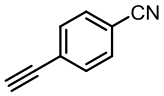

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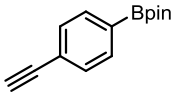

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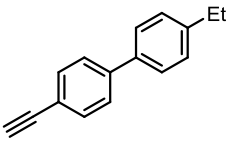
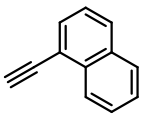


2p



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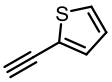

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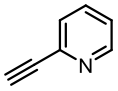

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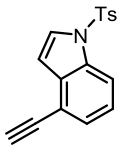

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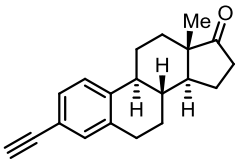
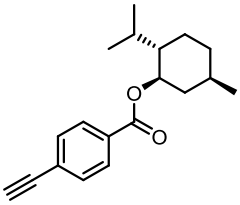
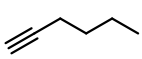


2u



2v

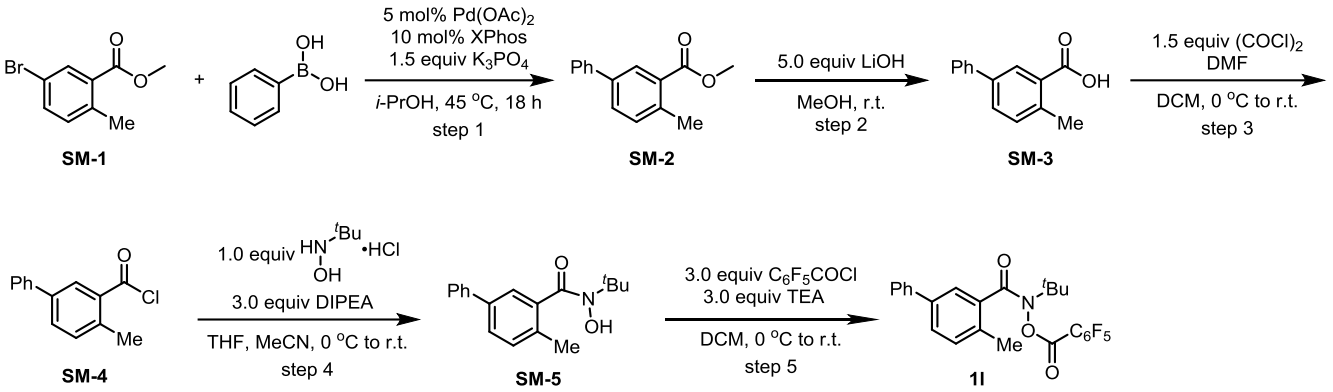


2w

2x

2y

General Procedure A: For the Preparation of Amide Substrates 1l~1s[5,6]



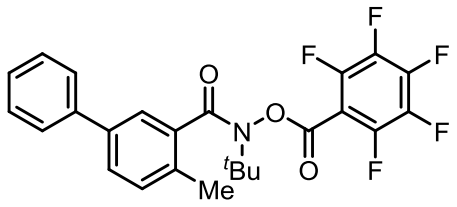
Step 1: To a solution of **SM-1** (458 mg, 2.0 mmol, 1.0 equiv.) in *i*-PrOH (0.1 M) under N_2 atmosphere was added $Pd(OAc)_2$ (22.5 mg, 0.1 mmol, 5 mol%), XPhos (95 mg, 0.2 mmol, 10 mol%), phenylboronic acid (366 mg, 3.0 mmol, 1.5 equiv.) and K_3PO_4 (637 mg, 3.0 mmol, 1.5 equiv.). After stirring for 18 h at 45 □ in a sealed tube, the mixture was directly evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 15:1) to afford the the intermediate **SM-2** in 99% isolated yield (447 mg).

Step 2: To a solution of **SM-2** (447 mg, 2.0 mmol, 1.0 equiv.) in MeOH (0.2 M) was added LiOH (240 mg, 10.0 mmol, 5.0 equiv.). After stirring for 12 h at room temperature in a sealed tube, the mixture was regulated pH to 1~2 by 1 M HCl. Then H_2O (20 mL) was added, then the mixture was extracted with EtOAc. The organic layer was combined, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) to afford the the intermediate **SM-3** in 88% isolated yield (373 mg).

Step 3: To a solution of carboxylic acid **SM-3** (373 mg, 1.76 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (0.3 M) was added 2~3 drops of anhydrous DMF. The solution was cooled to 0 °C and oxalyl chloride (335 mg, 2.64 mmol, 1.5 equiv.) was added dropwise. The reaction was then allowed to warm up to room temperature and vigorously stirred for two hours. The solvent was removed in vacuum. Then the resulting acyl chloride **SM-4** used directly for the next step without further purification.

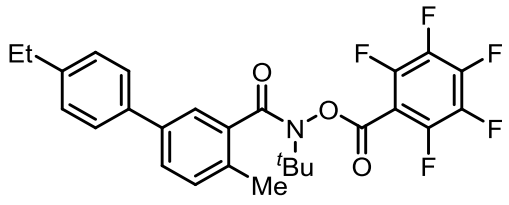
Step 4: To a solution of the *N*-(*tert*-Butyl)hydroxylamine Hydrochloride (373 mg, 1.76 mmol, 1.0 equiv.) in anhydrous THF (0.5 M) was added DIPEA (682 mg, 5.28 mmol, 3.0 equiv.). The solution was cooled to 0 °C and stirred for 15 minutes. The above crude acyl chloride **SM-4** (1.76 mmol, 1.0 equiv.) in anhydrous acetonitrile (0.8 M) was added to the solution dropwise over 15 minutes. Then the mixture was allowed to warm to room temperature, and stirred for 6 hours. The mixture was quenched with saturated $NaHCO_3$ and EtOAc. The aqueous layer was extracted with EtOAc and the combined organic layers were washed with 1 M HCl, saturated $NaHCO_3$ and brine successively. The organic layer was evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) to afford the the intermediate **SM-5** in 70% isolated yield (349 mg).

Step 5: To a solution of hydroxylamine intermediate **SM-5** (349 mg, 1.2 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (0.35 M), was added was added Et_3N (364 mg, 3.6 mmol, 3.0 equiv.) dropwise at 0 °C. Pentafluorobenzoyl chloride (830 mg, 3.6 mmol, 3.0 equiv.) was then added dropwise over 5 minutes. The reaction was vigorously stirred at room temperature for 3 h. The mixture was quenched with saturated $NaHCO_3$ and EtOAc. The aqueous layer was extracted with EtOAc and the combined organic layers were washed with 1 M HCl, saturated $NaHCO_3$ and brine successively. The organic layer was evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to afford **1l** in 76% isolated yield (435 mg).



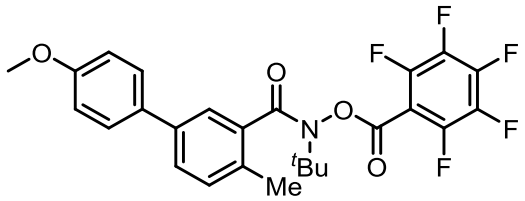
1l

***N*-(*tert*-butyl)-4-methyl-*N*-((perfluorobenzoyl)oxy)-[1,1'-biphenyl]-3-carboxamide (1l).** Isolated yield = 94% on 3 mmol scale; yellow oil. R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 – 7.32 (m, 4H), 7.28 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.22 – 7.17 (m, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 2.28 (s, 3H), 1.53 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.9, 158.1, 146.9 – 146.2 (m), 145.3 – 144.8 (m), 144.3 – 143.6 (m), 142.7 – 142.2 (m), 140.1, 139.1 – 138.5 (m), 138.2, 136.7 – 135.7 (m), 133.7, 130.6, 128.7, 127.8, 127.2, 126.7, 124.5, 104.9 – 104.3 (m), 63.4, 27.6, 18.4. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -136.2, -145.8, -159.3. **HRMS (ESI)** $[M+Na]^+$ Calcd for $C_{25}H_{20}F_5NNaO_3$, 500.1255; Found 500.1252.



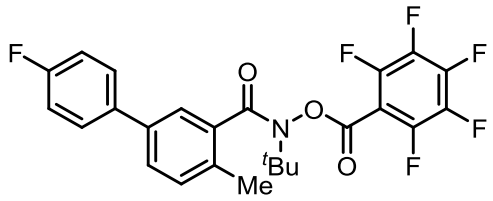
1m

***N*-(*tert*-butyl)-4'-ethyl-4-methyl-*N*-((perfluorobenzoyl)oxy)-[1,1'-biphenyl]-3-carboxamide (1m).** Isolated yield = 60% on 2 mmol scale; yellow oil. R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36 – 7.26 (m, 4H), 7.14 – 6.99 (m, 3H), 2.53 (q, *J* = 7.6 Hz, 2H), 2.26 (s, 3H), 1.50 (s, 9H), 1.12 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.9, 158.0, δ 146.7 – 146.4 (m), 145.2 – 144.7 (m), 144.2 – 143.7 (m), 143.3, 142.7 – 142.0 (m), 139.1 – 138.4 (m), 138.0, 137.4, 136.4 – 136.0 (m), 135.9, 133.3, 130.5, 128.1, 127.6, 126.6, 124.3, 106.1 – 103.3 (m), 63.2, 28.3, 27.5, 18.3, 15.3. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -136.2, -146.0, -159.4. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{27}H_{25}F_5NO_3$, 506.1749; Found 506.1740.



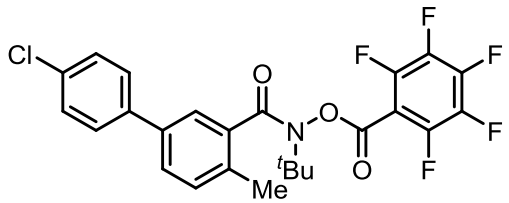
1n

***N*-(*tert*-butyl)-4'-methoxy-4-methyl-*N*-((perfluorobenzoyl)oxy)-[1,1'-biphenyl]-3-carboxamide (1n).** Isolated yield = 80% on 3 mmol scale; white solid; M.p. 62-63 °C. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 – 7.35 (m, 4H), 7.15 (d, *J* = 7.6 Hz, 1H), 6.93 – 6.89 (m, 2H), 3.80 (s, 3H), 2.36 (s, 3H), 1.61 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.0, 159.1, 158.1, 147.0 – 146.2 (m), 145.5 – 144.7 (m), 144.3 – 143.8 (m), 142.8 – 142.2 (m), 139.1 – 138.4 (m), 137.8, 136.6 – 135.6 (m), 135.9, 132.6, 130.5, 127.7, 127.3, 124.0, 114.1, 104.8 – 104.3 (m), 63.3, 55.2, 27.5, 18.3. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -136.2, -145.9, -159.3. **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{26}H_{22}F_5NNaO_4$, 530.1361; Found 530.1351.



1o

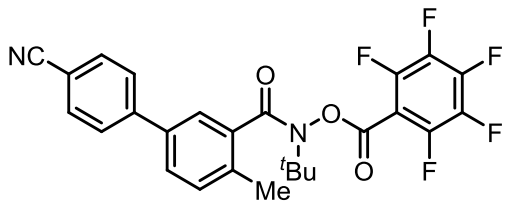
***N*-(*tert*-butyl)-4'-fluoro-4-methyl-*N*-((perfluorobenzoyl)oxy)-[1,1'-biphenyl]-3-carboxamide (1o).** Isolated yield = 82% on 3 mmol scale; yellow oil. R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36 (dd, *J* = 8.8, 5.6 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.02 – 6.94 (m, 2H), 2.28 (s, 3H), 1.53 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.0, 162.4 (d, *J* = 246.5 Hz), 158.1, 146.9 – 146.1 (m), 145.4 – 144.9 (m), 144.3 – 143.7 (m), 142.9 – 142.2 (m), 139.1 – 138.5 (m), 137.2, 136.2 (d, *J* = 3.2 Hz), 136.5 – 135.7 (m), 133.9 – 133.3 (m), 130.6, 128.3 (d, *J* = 8.0 Hz), 127.6, 124.4, 115.6 (d, *J* = 21.5 Hz), 104.9 – 103.8 (m), 63.4, 27.5, 18.4. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -115.6, -136.2, -145.6, -159.1. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{25}H_{20}F_6NO_3$, 496.1342; Found 496.1333.



1p

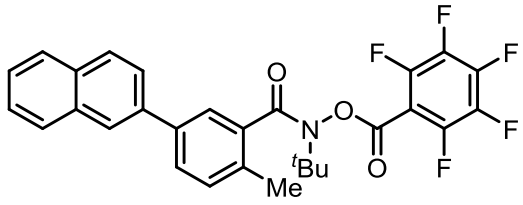
***N*-(*tert*-butyl)-4'-chloro-4-methyl-*N*-((perfluorobenzoyl)oxy)-[1,1'-biphenyl]-3-carboxamide (1p).** Isolated yield =72% on 3 mmol scale; white solid; M.p. 82-83 °C. R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35 – 7.26 (m, 6H), 7.10 (d, *J* = 7.6 Hz, 1H), 2.29 (s, 3H), 1.54 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.8, 158.1, 146.9 – 146.2 (m), 145.4 – 144.8 (m), 144.3 – 143.5 (m),

142.8 – 142.0 (m), 139.1 – 138.6 (m), 138.5, 137.0, 136.5 – 136.0 (m), 134.1 – 133.8 (m), 133.4, 130.7, 128.9, 128.0, 127.6, 124.4, 104.8 – 104.3 (m), 63.5, 27.6, 18.5. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -136.3, -145.6, -159.1. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{25}H_{20}ClF_5NO_3$, 512.1046; Found 512.1045.



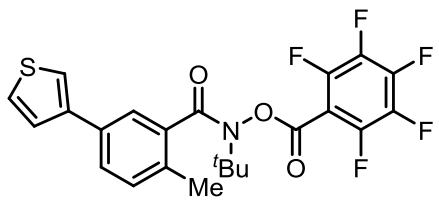
1q

***N*-(*tert*-butyl)-4'-cyano-4-methyl-*N*-((perfluorobenzoyl)oxy)-[1,1'-biphenyl]-3-carboxamide (1q).** Isolated yield = 68% on 3 mmol scale; yellow oil. R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 – 7.60 (m, 2H), 7.58 – 7.52 (m, 2H), 7.41 – 7.31 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 1H), 2.32 (s, 3H), 1.55 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.5, 158.2, 146.7 – 146.4 (m), 145.4 – 145.0 (m), 144.5, 144.1 – 143.6 (m), 142.8 – 142.3 (m), 139.2 – 138.5 (m), 136.7 – 136.3 (m), 136.2, 135.3, 132.6, 130.9, 127.8, 127.4, 124.7, 118.8, 110.9, 104.8 – 103.6 (m), 63.6, 27.5, 18.5. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -136.4, -145.3, -158.9. **HRMS (ESI)** m/z: $[M+NH_4]^+$ Calcd for $C_{26}H_{23}F_5N_3O_3$, 520.1654; Found 520.1661.



1r

***N*-(*tert*-butyl)-2-methyl-5-(naphthalen-2-yl)-*N*-((perfluorobenzoyl)oxy)benzamide (1r).** Isolated yield = 70% on 2 mmol scale; white solid; M.p. 142-143 °C. R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.87 (s, 1H), 7.82 – 7.62 (m, 3H), 7.58 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.44 – 7.37 (m, 2H), 7.16 (d, *J* = 8.4 Hz, 1H), 2.33 (s, 3H), 1.56 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.0, 158.2, 146.7 – 146.3 (m), 145.2 – 144.8 (m), 144.2 – 143.6 (m), 142.7 – 142.0 (m), 140.7, 139.1 – 138.4 (m), 138.1, 137.4, 136.7 – 135.8 (m), 133.8, 133.5, 132.5, 130.7, 128.4, 128.1, 127.5, 126.3, 125.9, 125.4, 125.1, 124.7, 104.9 – 103.9 (m), 63.4, 27.6, 18.5. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -136.1, -145.6, -159.1. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{29}H_{23}F_5NO_3$, 528.1593; Found 528.1589.

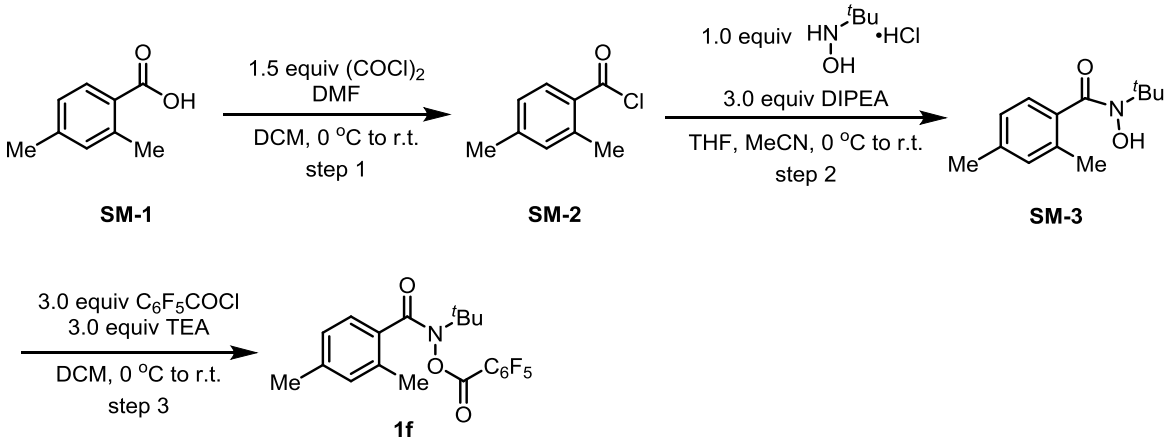


1s

***N*-(*tert*-butyl)-2-methyl-*N*-((perfluorobenzoyl)oxy)-5-(thiophen-3-yl)benzamide (1s).** Isolated yield =

78% on 2 mmol scale; yellow oil. R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39 – 7.31 (m, 2H), 7.30 – 7.27 (m, 1H), 7.26 – 7.20 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 1H), 2.27 (s, 3H), 1.53 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.9, 158.1, 146.9 – 146.3 (m), 145.4 – 144.7 (m), 144.2 – 143.7 (m), 142.8 – 142.1 (m), 141.2, 139.1 – 138.3 (m), 136.6 – 135.5 (m), 133.7 – 133.1 (m), 132.9, 130.6, 127.1, 126.2, 126.0, 123.8, 120.1, 104.9 – 103.7 (m), 63.4, 27.6, 18.5. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -136.1, -145.7, -159.2. **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{23}H_{18}F_5NNaO_3S$, 506.0820; Found 506.0817.

General Procedure B: For the Preparation of Substrates 1f~1k, 1w~1x

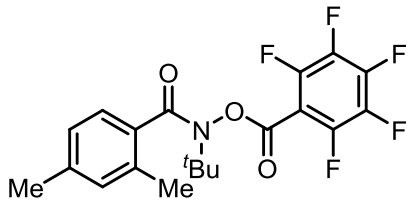


Step 1: To a solution of carboxylic acid **SM-1** (750 mg, 5.0 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (0.3 M) was added 2~3 drops of anhydrous DMF. The solution was cooled to 0 °C and oxalyl chloride (963 mg, 7.5 mmol, 1.5 equiv.) was added dropwise. The reaction was then allowed to warm up to room temperature and vigorously stirred for two hours. The solvent was removed in vacuum. Then the resulting acyl chloride **SM-2** used directly for the next step without further purification.

Step 2: To a solution of the *N*-(*tert*-Butyl)hydroxylamine Hydrochloride (377 mg, 3 mmol, 1.0 equiv.) in anhydrous THF (0.5 M) was added DIPEA (1.1 g, 9.0 mmol, 3.0 equiv.). The solution was cooled to 0 °C and stirred for 15 minutes. The above crude acylchloride **SM-2** (3.0 mmol, 1.0 equiv.) in anhydrous acetonitrile was added to the solution dropwise over 15 minutes and the mixture was allowed to warm to room temperature for 6 hours. Then the mixture was allowed to warm to room temperature, and stirred for 6 hours. The mixture was quenched with saturated $NaHCO_3$ and EtOAc. The aqueous layer was extracted with EtOAc and the combined organic layers were washed with 1 M HCl, saturated $NaHCO_3$ and brine successively. The organic layer was evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) to afford the the intermediate **SM-3** in 63% isolated yield (419 mg).

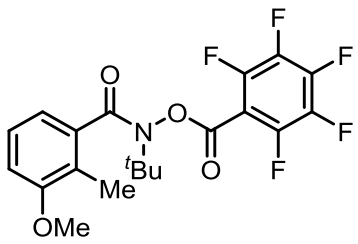
Step 3: To a solution of hydroxylamine intermediate **SM-3** (419 mg, 1.9 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (0.35 M) at 0 °C was added Et_3N (574 mg, 5.7 mmol, 3.0 equiv.) dropwise at 0 °C.

Pentafluorobenzoyl chloride (1.3 g, 5.7 mg, 3.0 equiv.) was then added dropwise over 5 minutes. The reaction was vigorously stirred at room temperature for 3 h. The mixture was quenched with saturated $NaHCO_3$ and EtOAc. The aqueous layer was extracted with EtOAc and the combined organic layers were washed with 1 M HCl, saturated $NaHCO_3$ and brine successively. The organic layer was evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to afford **1f** in 70% isolated yield (553 mg).



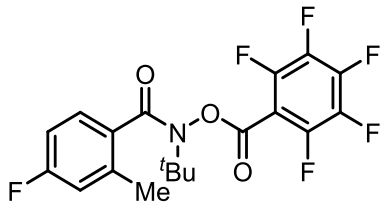
1f

***N*-(*tert*-butyl)-2,4-dimethyl-*N*-((perfluorobenzoyl)oxy)benzamide (1f).** Isolated yield = 70% on 3 mmol scale; colourless oil. R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.02 (d, *J* = 7.6 Hz, 1H), 6.87 – 6.79 (m, 2H), 2.23 (s, 3H), 2.18 (s, 3H), 1.50 (s, 9H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.3, 158.1, 146.9 – 146.2 (m), 145.3 – 144.8 (m), 144.3 – 143.8 (m), 142.8 – 142.2 (m), 139.2, 139.1 – 138.6 (m), 136.7 – 136.0 (m), 135.1 – 134.5 (m), 132.7, 130.8, 126.0, 125.6, 105.2 – 104.2 (m), 63.2, 27.7, 21.1, 18.8. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -136.1, -146.0, -159.5. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{19}F_5NO_3$, 416.1280; Found 416.1276.



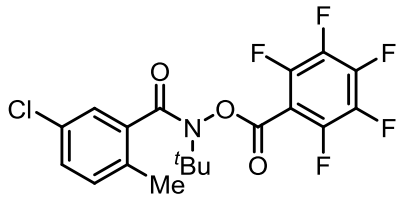
1g

***N*-(*tert*-butyl)-3-methoxy-2-methyl-*N*-((perfluorobenzoyl)oxy)benzamide (1g).** Isolated yield = 94% on 3 mmol scale; colourless oil. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.07 (t, *J* = 7.7 Hz, 1H), 6.85 – 6.72 (m, 2H), 3.79 (s, 3H), 2.18 (s, 3H), 1.60 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.9, 158.0, 157.6 – 157.1 (m), 147.0 – 145.9 (m), 145.5 – 144.6 (m), 144.5 – 143.5 (m), 143.0 – 142.0 (m), 139.2 – 138.3 (m), 137.0 – 135.8 (m), 126.2, 123.2 – 122.4 (m), 117.7, 110.7, 104.9 – 104.0 (m), 63.4, 55.3, 27.4, 12.1. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -136.3, -146.1, -159.5. **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{20}H_{18}F_5NNaO_4$, 454.1048; Found 454.1043.



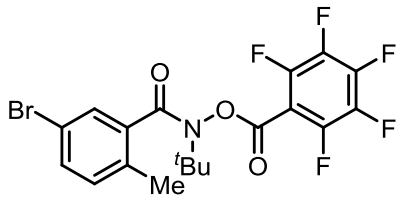
1h

***N*-(*tert*-butyl)-4-fluoro-2-methyl-*N*-((perfluorobenzoyl)oxy)benzaomide (1h).** Isolated yield = 51% on 3 mmol scale; colourless oil. R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.21 (dd, J = 8.4, 5.6 Hz, 1H), 6.95 – 6.63 (m, 2H), 2.36 (s, 3H), 1.59 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.0, 162.9 (d, J_{C-F} = 248.6 Hz), 158.2, 147.1 – 146.3 (m), 145.9 – 144.8 (m), 144.6 – 143.7 (m), 143.1 – 142.1 (m), 139.3 – 138.6 (m), 138.6 – 137.8 (m), 137.0 – 135.4 (m), 131.6, 128.0 (d, J_{C-F} = 8.9 Hz), 117.0 (d, J_{C-F} = 21.5 Hz), 112.1 (d, J_{C-F} = 21.6 Hz), 104.7 – 104.2 (m), 63.4, 27.6, 18.9. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -111.8, -136.3, -145.5, -159.1. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{19}H_{16}F_6NO_3$, 420.1029; Found 420.1021.



1i

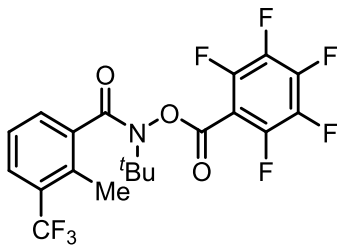
***N*-(*tert*-butyl)-2,4-dimethyl-*N*-((perfluorobenzoyl)oxy)benzamide (1i).** Isolated yield = 91% on 3 mmol scale; colourless solid; M.p. 66-67 ºC. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** 7.21 – 7.16 (m, 2H), 7.10 – 7.05 (m, 1H), 2.32 (s, 3H), 1.60 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.1, 158.1, 146.9 – 146.1 (m), 145.7 – 144.7 (m), 144.2 – 143.4 (m), 143.0 – 142.0 (m), 139.5 – 138.4 (m), 136.8, 136.6 – 135.9 (m), 133.7 – 132.7 (m), 131.6, 130.9, 129.2, 125.8, 104.6 – 104.1 (m), 63.6, 27.5, 18.2. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -136.3, -145.4, -159.0. H**RMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{19}H_{16}ClF_5NO_3$, 436.0734; Found 436.0738.



1j

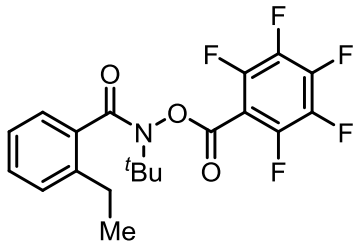
5-bromo-*N*-(*tert*-butyl)-2-methyl-*N*-((perfluorobenzoyl)oxy)benzamide (1j). Isolated yield = 70% on 3 mmol scale; colourless solid; M.p. 89-90 ºC. R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.34 – 7.24 (m, 2H), 7.03 – 6.98 (m, 1H), 2.28 (s, 3H), 1.58 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.9, 158.1, 146.8 – 146.3 (m), 145.6 – 144.9 (m), 144.2 – 143.7 (m), 142.9 – 142.1

(m), 139.3 – 138.5 (m), 137.1, 136.6 – 135.9 (m), 133.9, 132.2, 131.8, 128.6, 118.5, 104.8 – 103.9 (m), 63.5, 27.5, 18.3. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -136.3, -145.5, -159.1. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{19}H_{16}BrF_5NO_3$, 480.0228; Found 480.0225.



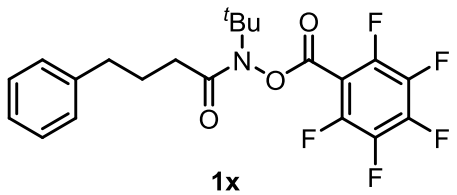
1k

***N*-(*tert*-butyl)-2-methyl-*N*-((perfluorobenzoyl)oxy)-3-(trifluoromethyl)benzamide (1k).** Isolated yield = 61% on 1.2 mmol scale; colourless oil. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.57 (d, J = 7.6 Hz, 1H), 7.45 – 7.36 (m, 1H), 7.24 – 7.18 (m, 1H), 2.42 (s, 3H), 1.61 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** 170.9, 158.1, 146.9 – 146.2 (m), 145.7 – 145.0 (m), 144.2 – 143.7 (m), 143.1 – 142.4 (m), 139.3 – 138.7 (m), 138.3, 136.6 – 136.1 (m), 133.3, 129.2 , 126.7, 126.6 (q, J_{C-F} = 5.3 Hz), 124.1 (q, J_{C-F} = 272.7 Hz), 104.4 – 104.0 (m), 63.7, 27.4, 15.5. **^{19}F NMR (376 MHz, CDCl3)** δ -61.5, -136.6, -145.1, -159.0. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{16}F_8NO_3$, 492.0816; Found 492.0808.



1w

***N*-(*tert*-butyl)-2-ethyl-*N*-((perfluorobenzoyl)oxy)benzamide (1w).** Isolated yield = 64% on 3 mmol scale; colourless oil. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.26 – 7.15 (m, 3H), 7.12 – 7.06 (m, 1H), 2.74 – 2.62 (m, 2H), 1.60 (s, 9H), 1.23 (t, J = 7.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.2, 146.9 – 146.5 (m), 145.3 – 144.9 (m), 144.6, 144.3 – 143.9 (m), 143.2 – 142.3 (m), 141.1 – 140.3 (m), 139.4 – 138.4 (m), 136.6 – 136.0 (m), 135.6 – 134.8 (m), 129.4, 128.4, 125.8, 125.1, 104.9 – 104.6 (m), 63.4, 27.6, 25.8, 15.0. **^{19}F NMR (376 MHz, CDCl3)** δ -136.1, -145.8, -159.3. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{19}F_5NO_3$, 416.1280; Found 416.1273.

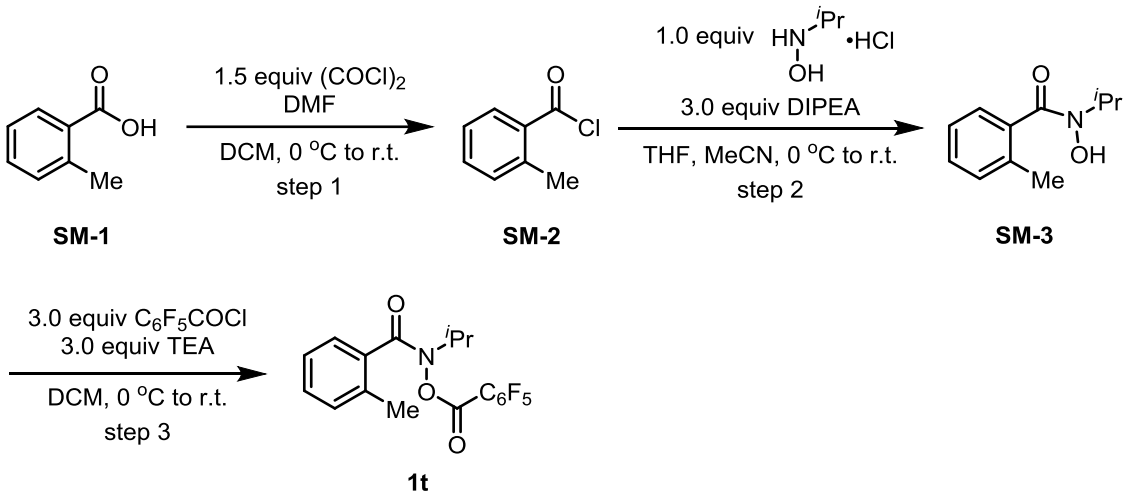


1x

***N*-(*tert*-butyl)-*N*-((perfluorobenzoyl)oxy)-4-phenylbutanamide (1x).** Isolated yield = 67% on 2 mmol scale; colourless solid; M.p. 32-33 ºC. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.17 – 7.11 (m, 2H), 7.10 – 7.00 (m, 3H), 2.64 – 2.46 (m, 2H), 2.24 (dt, J = 15.6, 7.6 Hz, 1H), 2.08 (dt,

J = 16.4, 7.6 Hz, 1H), 1.88– 1.80 (m, 2H), 1.39 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.7, 158.7, 146.9 – 146.5 (m), 145.5 – 145.1 (m), 144.3 – 143.9 (m), 142.9 – 142.5 (m), 141.4, 139.4 – 138.7 (m), 136.8 – 136.2 (m), 128.4, 128.1, 125.7, 105.3 – 104.6 (m), 63.1, 34.9, 33.5, 27.3, 25.5. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -135.9, -145.5, -158.8. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{21}H_{21}F_5NO_3$, 430.1436; Found 430.1434.

General Procedure C: For the Preparation of Amide Substrates 1t~1v

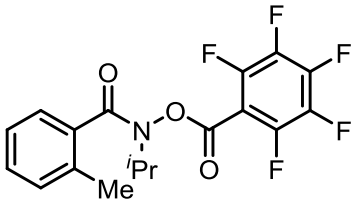


Step 1: To a solution of carboxylic acid **SM-1** (408 mg, 3.0 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (0.3 M) was added 2~3 drops of anhydrous DMF. The solution was cooled to 0 °C and oxalyl chloride (571 mg, 4.5 mmol, 1.5 equiv.) was added dropwise. The reaction was then allowed to warm up to room temperature and vigorously stirred for two hours. The solvent was removed in vacuum. Then the resulting acyl chloride **SM-2** used directly for the next step without further purification.

Step 2: To a solution of the *N*-(*tert*-butyl)hydroxylamine hydrochloride (333 mg, 3.0 mmol, 1.0 equiv.) in anhydrous THF (0.5 M) was added DIPEA (1.1 g, 9.0 mmol, 3.0 equiv.). The solution was cooled to 0 °C and stirred for 15 minutes. The above crude acylchloride **SM-2** (3.0 mmol, 1.0 equiv.) in anhydrous acetonitrile was added to the solution dropwise over 15 minutes and the mixture was allowed to warm to room temperature for 6 hours. Then the mixture was allowed to warm to room temperature, and stirred for 6 hours. The mixture was quenched with saturated $NaHCO_3$ and EtOAc. The aqueous layer was extracted with EtOAc and the combined organic layers were washed with 1 M HCl, saturated $NaHCO_3$ and brine successively. The organic layer was evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) to afford the the intermediate **SM-3** in 63% isolated yield (365 mg).

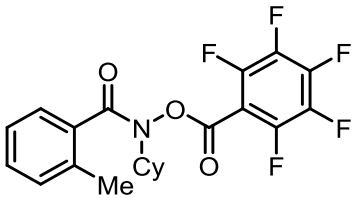
Step 3: To a solution of hydroxylamine intermediate **SM-3** (391 mg, 1.9 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (0.35 M) at 0 °C was added Et_3N (574 mg, 5.7 mmol, 3.0 equiv.) dropwise at 0 °C. Pentafluorobenzoyl chloride (1.3g, 5.7 mg, 3.0 equiv.) was then added dropwise over 5 minutes. The

reaction was vigorously stirred at room temperature for 3 h. The mixture was quenched with saturated $NaHCO_3$ and EtOAc. The aqueous layer was extracted with EtOAc and the combined organic layers were washed with 1 M HCl, saturated $NaHCO_3$ and brine successively. The organic layer was evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to afford **1c** in 70% isolated yield (515 mg).



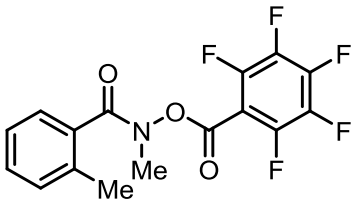
1t

***N*-(*tert*-butyl)-2-methyl-*N*-((perfluorobenzoyl)oxy)benzamide(1t).** Isolated yield =49% on 2.0 mmol scale; yellow oil. R_f = 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** 7.34 – 7.28 (m, 2H), 7.25 – 7.17 (m, 2H), 4.40 (s, 1H), 2.43 (s, 3H), 1.27 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.9, 147.3 – 146.4 (m), 145.6 – 144.9 (m), 144.5 – 143.8 (m), 142.9 – 142.2 (m), 139.3 – 138.6 (m), 136.8 – 136.0 (m), 135.4, 133.6, 130.6, 130.0, 126.4, 125.7, 105.3 – 104.8 (m), 52.4, 19.6, 19.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -135.8, -146.1, -159.4. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{18}H_{15}F_5NO_3$, 388.0967; Found 388.0963.



1u

***N*-cyclohexyl-2-methyl-*N*-((perfluorobenzoyl)oxy)benzamide (1u).** Isolated yield = 67% on 5 mmol scale; white solid; M.p. 50-51 °C. R_f= 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** 7.32 – 7.27 (m, 2H), 7.23 – 7.15 (m, 2H), 4.10 (s, 1H), 2.41 (s, 3H), 1.97 – 1.76 (m, 4H), 1.71 – 1.56 (m, 2H), 1.35 – 0.84 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.0, 147.0 – 146.7 (m), 145.4 – 144.9 (m), 144.6 – 143.9 (m), 142.9 – 142.2 (m), 139.3 – 138.0 (m), 136.9 – 135.6 (m), 135.4, 133.7, 130.5, 129.9, 126.3, 125.6, 105.3 – 104.7 (m), 59.5, 30.0, 25.3, 24.9, 19.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -135.7, -146.1, -159.4. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{21}H_{19}F_5NO_3$, 428.1280; Found 428.1280.

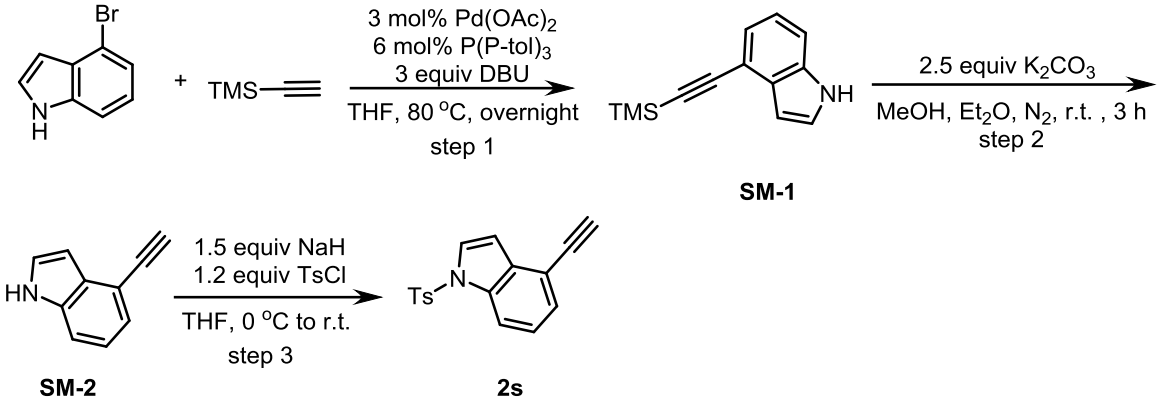


1v

***N*,2-dimethyl-*N*-((perfluorobenzoyl)oxy)benzamide (1v).** Isolated yield = 63% on 3 mmol scale; yellow oil. R_f= 0.5 (Hexane: Ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.25 – 7.19 (m, 2H),

7.16 – 7.08 (m, 2H), 3.37 (s, 3H), 2.33 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.1, 147.3 – 146.6 (m), 145.8 – 145.0 (m), 144.7 – 144.1 (m), 143.2 – 142.5 (m), 139.3 – 138.7 (m), 136.8 – 136.0 (m), 135.7, 132.9, 130.6, 130.1, 126.7, 125.6, 105.0 – 104.0 (m), 37.2, 19.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -135.7, -145.4, -159.3. **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{16}H_{10}F_5NNaO_3$, 382.0473; Found 382.0476.

General Procedure D: For the Preparation of Phenylacetylene 2s[7].

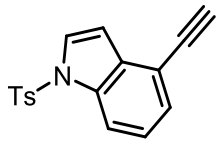


Step 1: An oven-dried screw cap reaction tube was charged with a magnetic stirbar $Pd(OAc)_2$ (27 mg, 0.12 mmol, 3 mol%), Tri(*o*-tolyl)phosphine (73 mg, 0.24 mmol, 6 mol%) and bromo-substrate (784 mg, 4 mmol, 1.0 equiv.). Freshly distil dry THF (10 mL) was added to the reaction tube under nitrogen atmosphere using syringe. DBU (1.8 mL, 12 mmol, 3 equiv.) was injected in it and the reaction was stirred at room temperature. Under 80 °C trimethylsilylacetylene (719 µl, 5.2 mmol, 1.3 equiv.) was added to the reaction mixture slowly. The reaction was stirred continuously for 12 h at room temperature. The mixture was quenched with saturated $NaHCO_3$ and EtOAc. The aqueous layer was extracted with EtOAc and the combined organic layers were washed with 1 M HCl, saturated $NaHCO_3$ and brine successively. The crude residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to afford the the intermediate **SM-1** in 62% isolated yield (525.8 mg).

Step 2: **SM-1** was dissolved in a mixed solution of 4 mL MeOH and Et_2O = 5:1, and 2.5 equivalents of anhydrous K_2CO_3 were added under N_2 atmosphere. The reaction mixture was stirred at room temperature for 3 h. The mixture was quenched with saturated $NaHCO_3$ and EtOAc. The aqueous layer was extracted with EtOAc and the combined organic layers were washed with 1 M HCl, saturated $NaHCO_3$ and brine successively. The crude residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) to afford the the intermediate **SM-2** in 58% isolated yield (199.8 mg).

Step 3: SM-2 (199.8 mg, 1.4 mmol, 1.0 equiv.) was dissolved in 10 mL THF, added with NaH (84 mg, 2.1 mmol, 1.5 equiv.), stirred for 30 min, and then added with TsCl (400 mg, 2.1 mmol, 1.2 equiv.) for 3 h. The mixture was quenched with saturated $NaHCO_3$ and EtOAc. The aqueous layer was extracted with EtOAc and the combined organic layers were washed with 1 M HCl, saturated $NaHCO_3$ and brine

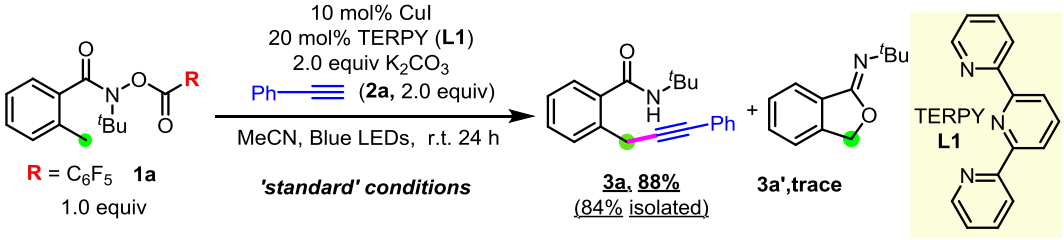
successively. The crude residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1) to afford **2s** in 58% isolated yield (171 mg).



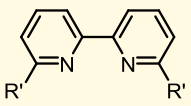
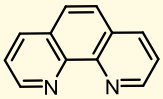
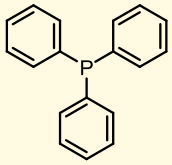
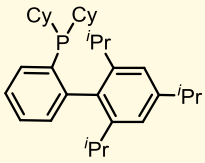
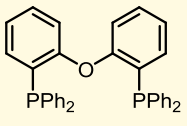
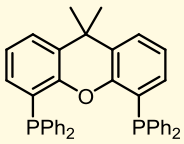
2s

4-ethynyl-1-tosyl-1*H*-indole (**2s**)**.** Isolated yield = 58% on 1.4 mmol scale; black oil; R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 – 7.90 (m, 1H), 7.69 – 7.65 (m, 2H), 7.54 (d, *J* = 3.6 Hz, 1H), 7.32 – 7.29 (m, 1H), 7.25 – 7.05 (m, 3H), 6.77 (dd, *J* = 3.6, 0.8 Hz, 1H), 3.22 (s, 1H), 2.27 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.2, 135.0, 134.4, 132.7, 129.9, 127.3, 127.0, 126.8, 124.3, 114.7, 114.3, 108.3, 81.1, 80.5, 21.6. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{17}H_{14}NO_2S$, 296.0740; Found 296.0746.

Reaction optimization[a,b]

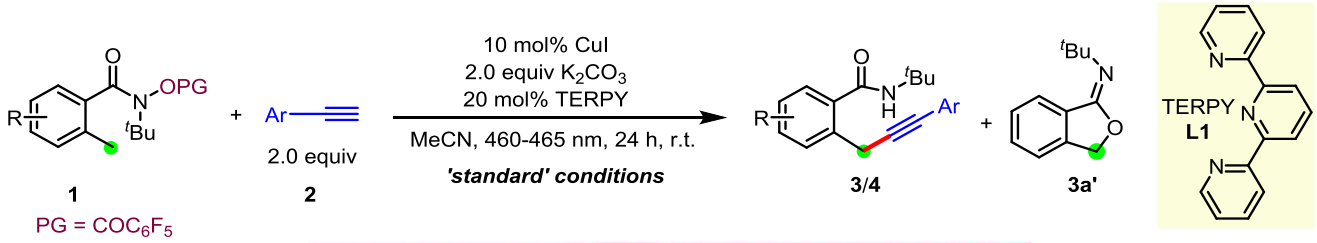


Entry	Variations from the *'standard' conditions*	Yield (%) of **3a** / **3a'**[b]
1	Without **CuI**	0
2	Without **Blue LEDs**	0
3	Without **K_2CO_3 (B1)**	0
4	Without **Ligand(L1)**	0
5	**C2-C9** instead of **CuI**	Listed below
6	**L2-L12** instead of **TERPY**	Listed below
7	**B2-B7** instead of **K_2CO_3**	Listed below
8	carried out in air	15/trace
9	Without Blue LEDs, carried out in 80 °C	0/0
10	solvent = PhH	49/45
11	solvent = $PhCF_3$	21/15
12	solvent = THF	49/22
13	solvent = DMF	44/18
14	1.5 equiv **2a**	67/trace
15	2.5 equiv **2a**	76/trace
16	**R** group investigation	Listed below

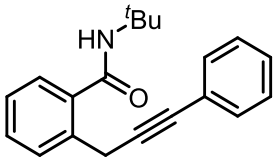
CuCl **C2,** 77%/0%	CuBr **C3,** 70%/6%	CuTc **C4,** 65%/10%	CuO **C5,** trace/14%
$Cu(OAc)_2$ **C6,** 58%/25%	$Cu_2(OH)_2CO_3$ **C7,** 36%/11%	$Cu(acac)_2$ **C8,** 60%/0%	$Pd(OAc)_2$ **C9,** 0%/31%
 **L2,** 3%/trace		**L3,** R' = H, trace/37% **L4,** R' = CH_3, trace/43% **L5,** R' = OMe, 15%/34% **L6,** R' = ^{t}Bu, 0%/24%	 **L7,** trace/0%
 PPh_3 **L8,** 5%/29%	 XPhos **L9,** trace/11%	 DPEphos **L10,** trace/0%	 Xantphos **L11,** trace/15%
Cs_2CO_3 **B2,** 62%/7%	Na_2CO_3 **B3,** 11%/12%	K_3PO_4 **B4,** 48%/47%	$NaOCH_3$ **B5,** 14%/trace
$KHCO_3$ **B6,** 23%/11%	2,4,6-tri-Me-Py **B7,** 56%/7%	Cy_2NMe **B8,** 34%/14%	DBU **B9,** 0%/0%
R Group Investigation:			
1b 4-CF_3-C_6H_4	**3a/3a',** 4%/trace	**1c** Bn	**3a/3a',** 0%/trace
1d H_3C	**3a/3a',** 0%/0%	**1e** ^{i}BuO	**3a/3a',** 0%/0%

[a]Each reaction was run on a 0.1 mmol scale in a sealed 4 mL vial for 24 h; [b]Yields of **3a** were determined by ^{1}H NMR using CH_2Br_2 as the internal standard. Py = pyridine. Cy = cyclohexane.

General Procedure of the Radical Relay Sonogashira Reaction.



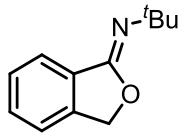
An oven-dried 4.0 mL vial was charged with amide **1** (0.2 mmol, 1.0 equiv.), alkyne **2** (0.4mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:3) to afford **3/4** and **3a'**.



3a

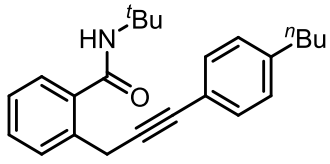
***N*-(*tert*-butyl)-2-(3-phenylprop-2-yn-1-yl)benzamide (3a).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1a** (80.2 mg, 0.2 mmol, 1.0 equiv.), alkyne **2a** (40.4 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED

lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **3a**. Isolated yield = 84% (48.8 mg) as a white solid; M.p. 111-112 °C. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.30 (m, 4H), 7.23 – 7.20 (m, 4H), 5.81 (s, 1H), 3.90 (s, 2H), 1.39 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.9, 137.0, 134.3, 131.5, 130.0, 129.6, 128.2, 127.9, 127.1, 126.9, 123.4, 87.7, 83.0, 51.9, 28.8, 23.7. **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{20}H_{21}NNaO$ 314.1515; Found 314.1512.



3a'

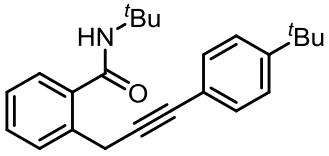
(*E*)-*N*-(*tert*-butyl)isobenzofuran-1(3*H*)-imine (3a′). Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1a** (80.2 mg, 0.2 mmol, 1.0 equiv.), alkyne **2a** (40.4 mg, 0.4 mmol, 2.0 equiv.), $Cu(OAc)_2$ (4.0 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **3a′**. Isolated yield = 25% (9.5 mg) as a white solid. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.44 – 7.35 (m, 1H), 7.36 – 7.28 (m, 1H), 7.28 – 7.23 (m, 1H), 5.24 (s, 2H), 1.33 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.4, 131.8, 130.9, 128.2, 123.8, 121.1, 72.1, 53.6, 30.0. The spectroscopic data match the reported literature[8].



3b

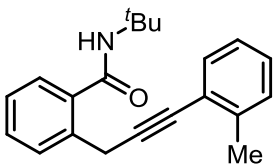
***N*-(*tert*-butyl)-2-(3-(4-butylphenyl)prop-2-yn-1-yl)benzamide (3b).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1a** (80.2 mg, 0.2 mmol, 1.0 equiv.), alkyne **2b** (63.4 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was

tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **3b**. Isolated yield = 54% (39.6 mg) as a yellow oil. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49 (d, *J* = 7.6 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.25 – 7.19 (m, 3H), 7.04 – 7.01 (m, 2H), 5.83 (s, 1H), 3.88 (s, 2H), 2.54 – 2.49 (m, 2H), 1.53 – 1.47 (m, 2H), 1.39 (s, 9H), 1.29 – 1.23 (m, 2H), 0.84 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.0, 143.0, 137.1, 134.4, 131.4, 130.0, 129.6, 128.3, 127.1, 126.9, 120.5, 86.9, 83.2, 51.9, 35.5, 33.4, 28.8, 23.8, 22.3, 13.9. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{24}H_{30}NO$ 348.2322; Found 348.2320.



3c

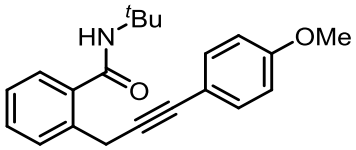
***N*-(*tert*-butyl)-2-(3-(4-(*tert*-butyl)phenyl)prop-2-yn-1-yl)benzamide (3c).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1a** (80.2 mg, 0.2 mmol, 1.0 equiv.), alkyne **2c** (63.4 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **3c**. Isolated yield = 38% (26.4 mg) as a white solid; M.p. 57-58 °C. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51 (d, *J* = 7.6 Hz, 1H), 7.35 – 7.31 (m, 2H), 7.29 – 7.21 (m, 5H), 5.81 (s, 1H), 3.89 (s, 2H), 1.40 (s, 9H), 1.23 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.9, 151.1, 137.1, 134.4, 131.2, 130.0, 129.6, 127.1, 126.9, 125.2, 120.4, 86.9, 83.2, 51.9, 34.7, 31.1, 28.8, 23.8. **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{24}H_{29}NNaO$ 370.2141; Found 370.2144.



3d

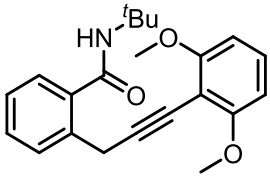
***N*-(*tert*-butyl)-2-(3-(*o*-tolyl)prop-2-yn-1-yl)benzamide (3d).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1a** (80.2 mg, 0.2 mmol, 1.0 equiv.), alkyne **2d** (46.4 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20

mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **3d**. Isolated yield = 89% (54.2 mg) as a white solid; M.p. 82-83 °C. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.34 – 7.17 (m, 4H), 7.12 – 7.01 (m, 3H), 5.78 (s, 1H), 3.96 (s, 2H), 2.34 (s, 3H), 1.38 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.0, 140.0, 136.9, 134.6, 131.8, 130.0, 129.4, 129.3, 127.8, 126.9, 126.8, 125.4, 123.2, 91.4, 82.1, 51.9, 28.8, 23.7, 20.8. **HRMS (ESI)** m/z: $[M+K]^+$ Calcd for $C_{21}H_{23}KNO$ 328.1672; Found 328.1665.



3e

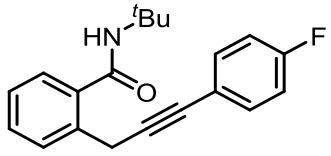
***N*-(*tert*-butyl)-2-(3-(4-methoxyphenyl)prop-2-yn-1-yl)benzamide (3e).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1a** (80.2 mg, 0.2 mmol, 1.0 equiv.), alkyne **2e** (52.8 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **3e**. Isolated yield = 75% (48.2 mg) as a white solid; M.p. 75-76 °C. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.48 (d, *J* = 7.6 Hz, 1H), 7.35 – 7.24 (m, 4H), 7.21 – 7.18 (m, 1H), 6.77 – 6.69 (m, 2H), 5.85 (s, 1H), 3.87 (s, 2H), 3.71 (s, 3H), 1.38 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.9, 159.2, 137.1, 134.4, 132.9, 130.0, 129.6, 127.1, 126.8, 115.5, 113.8, 86.1, 82.8, 55.2, 51.9, 28.8, 23.7. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{21}H_{24}NO_2$ 322.1802; Found 322.1793.



3f

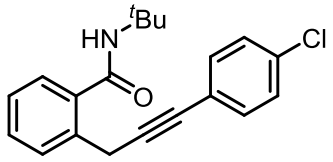
***N*-(*tert*-butyl)-2-(3-(2,6-dimethoxyphenyl)prop-2-yn-1-yl)benzamide (3f).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1a** (80.2 mg, 0.2 mmol,

1.0 equiv.), alkyne **2f** (64.8 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **3f**. Isolated yield = 87% (61.2 mg) as a yellow oil. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.48 (d, *J* = 7.6 Hz, 1H), 7.36 – 7.28 (m, 2H), 7.23 – 7.18 (m, 1H), 6.53 – 6.30 (m, 3H), 5.79 (s, 1H), 3.89 (s, 2H), 3.68 (s, 6H), 1.39 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.9, 160.4, 137.0, 134.2, 130.0, 129.6, 127.1, 126.9, 124.7, 109.4, 101.3, 87.3, 82.9, 55.3, 51.9, 28.8, 23.6. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{22}H_{26}NO_3$ 352.1907; Found 352.1904.



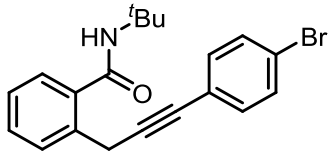
3g

***N*-(*tert*-butyl)-2-(3-(4-fluorophenyl)prop-2-yn-1-yl)benzamide (3g).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1a** (80.2 mg, 0.2 mmol, 1.0 equiv.), alkyne **2g** (48.0 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **3g**. Isolated yield = 70% (38.8 mg) as a white solid; M.p. 142-143 °C. R_f = 0.4 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.48 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.26 (m, 4H), 7.22 – 7.18 (m, 1H), 6.96 – 6.86 (m, 2H), 5.79 (s, 1H), 3.89 (s, 2H), 1.38 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.9, 162.2 (d, $J_{C\text{-}F}$ = 248.7 Hz), 137.0, 134.3, 133.4 (d, $J_{C\text{-}F}$ = 8.3 Hz), 130.0, 129.6, 127.0 (d, $J_{C\text{-}F}$ = 13.2 Hz), 119.5, 119.5, 115.43 (d, $J_{C\text{-}F}$ = 22.1 Hz), 87.3, 81.8, 51.9, 28.8, 23.6. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -111.6. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}FNO$ 310.1602; Found 310.1595.



3h

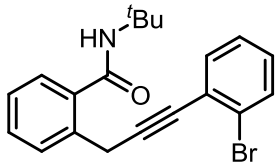
***N*-(*tert*-butyl)-2-(3-(4-chlorophenyl)prop-2-yn-1-yl)benzamide (3h).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1a** (80.2 mg, 0.2 mmol, 1.0 equiv.), alkyne **2h** (54.6 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **3h**. Isolated yield = 71% (46.0 mg) as a white solid; M.p. 142-143 °C. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49 – 7.45 (m, 1H), 7.35 – 7.30 (m, 2H), 7.28 – 7.24 (m, 2H), 7.22 – 7.18 (m, 3H), 5.76 (s, 1H), 3.91 (s, 2H), 1.39 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.9, 137.0, 134.2, 133.8, 132.8, 130.1, 129.6, 128.5, 127.1, 127.0, 121.9, 88.8, 81.8, 51.9, 28.8, 23.7. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}ClNO$ 326.1306; Found 326.1302.



3i

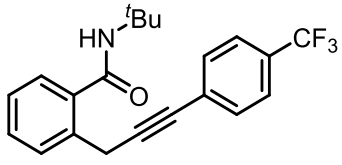
2-(3-(4-bromophenyl)prop-2-yn-1-yl)-*N*-(*tert*-butyl)benzamide (3i). Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1a** (80.2 mg, 0.2 mmol, 1.0 equiv.), alkyne **2i** (72.4 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **3i**. Isolated yield = 58% (43.0 mg) as a white solid; M.p. 108-109 °C. R_f = 0.5 (Hexane: Ethyl acetate = 3:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.31 (m, 4H), 7.21 – 7.18 (m, 3H), 5.75 (s, 1H), 3.90 (s, 2H), 1.39 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.9, 137.0, 134.2, 133.0, 131.5, 130.0, 129.6, 127.0, 127.0,

122.4, 122.0, 89.0, 81.8, 51.9, 28.8, 23.7. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}BrNO$ 370.0801; Found 370.0792.



3j

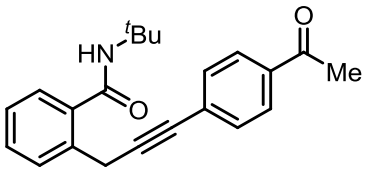
2-(3-(2-bromophenyl)prop-2-yn-1-yl)-*N*-(*tert*-butyl)benzamide (3j). Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1a** (80.2 mg, 0.2 mmol, 1.0 equiv.), alkyne **2j** (72.4 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **3j**. Isolated yield = 66% (46.8 mg) as a yellow oil. R_f = 0.4 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.62 (d, J = 7.6 Hz, 1H), 7.49 (dd, J = 8.0, 1.2 Hz, 1H), 7.41 – 7.29 (m, 3H), 7.23 – 7.16 (m, 2H), 7.10 – 7.03 (m, 1H), 5.77 (s, 1H), 3.98 (s, 2H), 1.39 (s, 9H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 169.0, 137.0, 134.0, 133.3, 132.3, 130.0, 129.7, 129.0, 126.9, 126.9, 126.9, 125.5, 125.4, 92.6, 81.8, 51.9, 28.8, 23.8. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}BrNO$ 370.0801; Found 370.0799.



3k

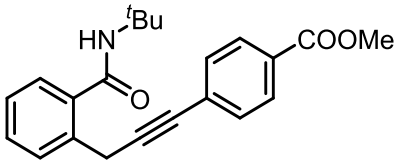
***N*-(*tert*-butyl)-2-(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)benzamide (3k).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1a** (80.2 mg, 0.2 mmol, 1.0 equiv.), alkyne **2k** (68.0 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **3k**. Isolated yield = 81% (58.2 mg) as a yellow oil. R_f = 0.5 (Hexane: Ethyl acetate = 3:1). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.50 – 7.41 (m, 5H), 7.37 – 7.32 (m, 2H), 7.24 – 7.19 (m, 1H), 5.74 (s, 1H), 3.95 (s, 2H), 1.39 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 137.0, 134.1, 131.8, 130.1, 129.6, 129.6 (q, J_{C-F} = 32.8Hz), 127.3, 127.1, 127.0, 125.1 (q, J_{C-F} = 3.9Hz), 123.9 (q, J_{C-F} = 273.1Hz), 90.5, 81.6, 51.9, 28.8, 23.6. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.8. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{21}H_{21}F_3NO$ 360.1570; Found 360.1564.



3l

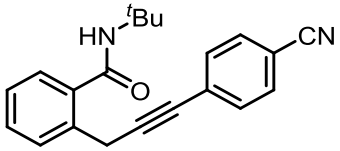
2-(3-(4-acetylphenyl)prop-2-yn-1-yl)-*N*-(*tert*-butyl)benzamide (3l). Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1a** (80.2 mg, 0.2 mmol, 1.0 equiv.), alkyne **2l** (57.6 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **3l**. Isolated yield = 50% (33.0 mg) as a yellow oil. R_f = 0.5 (Hexane: Ethyl acetate = 3:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90 – 7.82 (m, 2H), 7.56 (d, J = 7.2 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.43 – 7.37 (m, 2H), 7.32 – 7.26 (m, 1H), 5.82 (s, 1H), 4.02 (s, 2H), 2.58 (s, 3H), 1.46 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.4, 168.9, 142.9, 137.0, 135.9, 134.1, 131.7, 130.1, 129.6, 128.5, 128.2, 127.0, 92.7, 82.2, 51.9, 28.8, 26.6, 23.7. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{22}H_{24}NO_2$ 334.1802; Found 334.1799.



3m

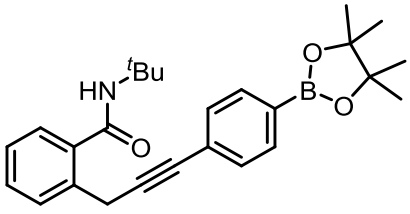
methyl 4-(3-(2-(*tert*-butylcarbamoyl)phenyl)prop-1-yn-1-yl)benzoate (3m). Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1a** (80.2 mg, 0.2 mmol, 1.0 equiv.), alkyne **2m** (52.8 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **3m**. Isolated yield

= 49% (40.4 mg) as a white solid; M.p. 92-93 °C. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.98 – 7.91 (m, 2H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.42 – 7.37 (m, 2H), 7.29 (d, *J* = 7.6 Hz, 1H), 5.82 (s, 1H), 4.02 (s, 2H), 3.90 (s, 3H), 1.45 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.9, 166.6, 137.0, 134.1, 131.5, 130.1, 129.6, 129.4, 129.2, 128.3, 127.0, 91.1, 82.2, 52.2, 51.9, 28.8, 23.7. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{22}H_{24}NO_3$ 350.1751; Found 350.1748.



3n

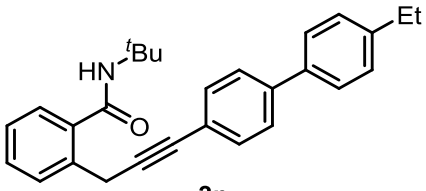
***N*-(*tert*-butyl)-2-(3-(4-cyanophenyl)prop-2-yn-1-yl)benzamide (3n).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1a** (80.2 mg, 0.2 mmol, 1.0 equiv.), alkyne **2n** (50.8 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **3n**. Isolated yield = 66% (41.4 mg) as a white solid; M.p. 98-99 °C. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 – 7.49 (m, 2H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.43 – 7.39 (m, 2H), 7.37 – 7.31 (m, 2H), 7.26 – 7.20 (m, 1H), 5.71 (s, 1H), 3.97 (s, 2H), 1.39 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.8, 136.9, 133.9, 132.1, 131.9, 130.1, 129.6, 128.5, 127.1, 127.0, 118.5, 111.2, 92.8, 81.4, 52.0, 28.8, 23.7. **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{21}H_{20}N_2NaO$ 339.1468; Found 339.1467.



3o

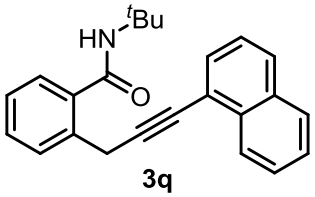
***N*-(*tert*-butyl)-2-(3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)prop-2-yn-1-yl)benzamide (3o).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1a** (80.2 mg, 0.2 mmol, 1.0 equiv.), alkyne **2o** (91.2 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced

pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **3o**. Isolated yield = 52% (43.4 mg) as a yellow oil. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68 – 7.64 (m, 2H), 7.48 (d, *J* = 7.2 Hz, 1H), 7.35 – 7.31 (m, 4H), 7.24 – 7.21 (m, 1H), 5.79 (s, 1H), 3.91 (s, 2H), 1.38 (s, 9H), 1.27 (s, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.9, 137.1, 134.5, 134.2, 130.7, 130.0, 129.7, 129.4, 127.1, 127.0, 126.1, 89.2, 83.9, 83.1, 52.0, 28.8, 24.8, 23.8. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{26}H_{33}BNO_3$ 418.2548; Found 418.2539.



3p

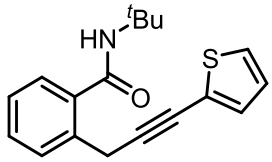
***N*-(*tert*-butyl)-2-(3-(4'-ethyl-[1,1'-biphenyl]-4-yl)prop-2-yn-1-yl)benzamide (3p).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1a** (80.2 mg, 0.2 mmol, 1.0 equiv.), alkyne **2p** (84.6 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **3p**. Isolated yield = 70% (55.4 mg) as a white solid; M.p. 120-121 °C. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.29 (m, 8H), 7.23 – 7.16 (m, 3H), 5.80 (s, 1H), 3.93 (s, 2H), 2.61 (q, *J* = 7.6 Hz, 2H), 1.40 (s, 9H), 1.19 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.9, 143.8, 140.6, 137.7, 137.1, 134.4, 131.9, 130.0, 129.7, 128.3, 127.1, 126.92, 126.86, 126.7, 122.0, 88.2, 83.0, 51.9, 28.8, 28.5, 23.8, 15.6. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{28}H_{30}NO$ 396.2322; Found 396.2316.



3q

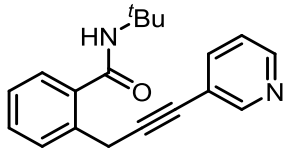
***N*-(*tert*-butyl)-2-(3-(naphthalen-1-yl)prop-2-yn-1-yl)benzamide (3q).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1a** (80.2 mg, 0.2 mmol, 1.0 equiv.), alkyne **2q** (60.8 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue

LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **3q**. Isolated yield = 72% (49.2 mg) as a white solid; M.p. 114-115 °C. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.22 (d, *J* = 8.4 Hz, 1H), 7.75 – 7.69 (m, 2H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.34 – 7.30 (m, 3H), 7.23 – 7.19 (m, 1H), 5.80 (s, 1H), 4.07 (s, 2H), 1.35 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.0, 137.0, 134.5, 133.4, 133.1, 130.1, 130.0, 129.6, 128.3, 128.2, 127.0, 126.9, 126.6, 126.2, 126.1, 125.1, 121.1, 92.6, 81.1, 51.9, 28.7, 23.9. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{24}H_{24}NO$ 342.1853; Found 342.1848.



3r

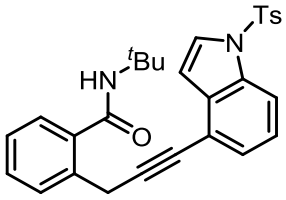
***N*-(*tert*-butyl)-2-(3-(thiophen-2-yl)prop-2-yn-1-yl)benzamide (3r).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1a** (80.2 mg, 0.2 mmol, 1.0 equiv.), alkyne **2r** (43.2 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **3r**. Isolated yield = 64% (38.2 mg) as a white solid; M.p. 123-124 °C. R_f = 0.4 (Hexane: Ethyl acetate = 3:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 – 7.42 (m, 1H), δ 7.35 – 7.27 (m, 2H), 7.25 – 7.19 (m, 1H), 7.12 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.07 (d, *J* = 3.2 Hz, 1H), 6.86 (dd, *J* = 5.2, 3.6 Hz, 1H), 5.78 (s, 1H), 3.92 (s, 2H), 1.39 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.8, 137.1, 134.0, 131.4, 130.0, 129.7, 127.1, 127.0, 126.8, 126.4, 123.4, 91.7, 76.0, 51.9, 28.8, 23.9. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{18}H_{20}NOS$ 298.1260; Found 298.1253.



3s

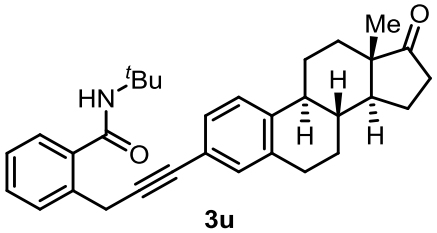
***N*-(*tert*-butyl)-2-(3-(pyridin-3-yl)prop-2-yn-1-yl)benzamide (3s).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1a** (80.2 mg, 0.2 mmol, 1.0 equiv.), alkyne **2s** (41.2 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-

filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **3s**. Isolated yield = 56% (32.8 mg) as a white solid; M.p. 120-121 °C. R_f = 0.5 (Hexane: Ethyl acetate = 3:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.56 (s, 1H), 8.42 (d, *J* = 4.4 Hz, 1H), 7.66 – 7.61 (m, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.25 – 7.12 (m, 2H), 5.75 (s, 1H), 3.96 (s, 2H), 1.39 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.9, 152.0, 148.0, 138.7, 137.0, 134.0, 130.1, 129.6, 127.1, 127.0, 123.0, 120.8, 91.6, 79.4, 51.9, 28.8, 23.6. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{19}H_{20}N_2O$ 293.1649; Found 293.1655.



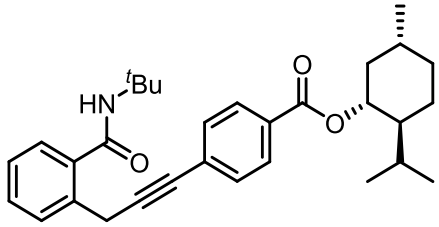
3t

***N*-(*tert*-butyl)-2-(3-(1-tosyl-1*H*-indol-4-yl)prop-2-yn-1-yl)benzamide (3t).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1a** (80.2 mg, 0.2 mmol, 1.0 equiv.), alkyne **2t** (118.0 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **3t**. Isolated yield = 43% (41.6 mg) as a yellow oil. R_f = 0.5 (Hexane: Ethyl acetate = 3:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 8.0 Hz, 1H), 7.74 – 7.72 (m, 2H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 3.6 Hz, 1H), 7.43 – 7.36 (m, 2H), 7.30 – 7.26 (m, 2H), 7.25 – 7.18 (m, 3H), 6.78 (d, *J* = 3.6 Hz, 1H), 5.83 (s, 1H), 4.06 (s, 2H), 2.32 (s, 3H), 1.43 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.9, 145.1, 136.9, 135.0, 134.4, 134.4, 132.4, 130.0, 129.9, 129.4, 126.95, 126.89, 126.7, 126.61, 126.55, 124.4, 116.3, 113.4, 108.5, 91.2, 80.5, 51.9, 28.7, 23.7, 21.5. **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{29}H_{28}N_2NaO_3S$ 507.1713; Found 507.1710.



3u

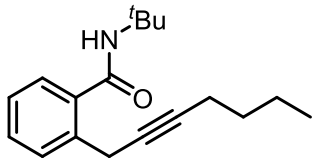
***N*-(*tert*-butyl)-2-(3-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)prop-2-yn-1-yl)benzamide (3u).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1a** (80.2 mg, 0.2 mmol, 1.0 equiv.), alkyne **2u** (111.2 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **3u**. Isolated yield = 52% (48.2 mg) as a yellow oil. R_f = 0.4 (Hexane: Ethyl acetate = 2:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.29 (m, 2H), 7.23 – 7.20 (m, 1H), 7.15 – 7.08 (m, 3H), 5.80 (s, 1H), 3.89 (s, 2H), 2.80 (dd, *J* = 9.2, 4.4 Hz, 2H), 2.44 (dd, *J* = 18.8, 8.8 Hz, 1H), 2.36 – 2.31 (m, 1H), 2.25 – 2.17 (m, 1H), 2.12 – 2.04 (m, 1H), 2.03 – 1.84 (m, 4H), 1.59 – 1.47 (m, 5H), 1.40 (s, 9H), 0.84 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 220.9, 169.0, 139.8, 137.0, 136.4, 134.4, 132.0, 130.0, 129.5, 128.8, 127.1, 126.8, 125.2, 120.7, 86.9, 83.1, 51.9, 50.4, 47.9, 44.3, 37.9, 35.8, 31.4, 29.0, 28.8, 26.3, 25.5, 23.7, 21.5, 13.8. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{32}H_{38}NO_2$ 468.2897; Found 468.2889.



3v

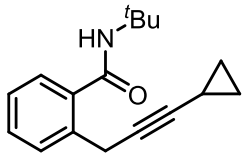
(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclo-hexyl 4-(3-(2-(*tert*-butylcarbamoyl)phenyl)prop-1-yn-1-yl)-benzoate (3v). Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1a** (80.2 mg, 0.2 mmol, 1.0 equiv.), alkyne **2v** (113.8 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **3v**. Isolated yield = 36% (34.1 mg) as a yellow oil. R_f = 0.4 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90 – 7.85 (m, 2H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.41 – 7.36 (m, 2H), 2H), 7.36 – 7.32 (m, 2H), 7.24 – 7.20 (m, 1H), 5.76 (s, 1H), 4.84 (td, *J* = 10.8, 5.6 Hz, 1H), 3.95 (s, 2H), 2.07 – 2.01 (m, 1H), 1.86 (ddt, *J* = 14.0, 7.2, 3.6 Hz, 1H), 1.68 – 1.60 (m, 3H), 1.52 – 1.44 (m,

2H), 1.39 (s, 9H), 1.07 – 0.98 (m, 2H), 0.85 (d, J = 4.0 Hz, 3H), 0.84 (d, J = 4.4 Hz, 3H), 0.71 (d, J = 6.8 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.9, 165.6, 137.0, 134.1, 131.4, 130.1, 129.9, 129.6, 129.4, 128.0, 127.05, 127.02, 90.9, 82.3, 75.0, 51.9, 47.2, 40.9, 34.2, 31.4, 28.8, 26.4, 23.8, 23.5, 22.0, 20.7, 16.5. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{31}H_{40}NO_3$ 474.3003; Found 474.2994.



3w

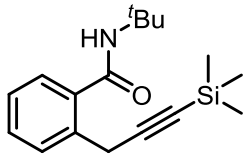
***N*-(*tert*-butyl)-2-(hept-2-yn-1-yl)benzamide (3w).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1a** (80.2 mg, 0.2 mmol, 1.0 equiv.), alkyne **2w** (39.2 mg, 0.4 mmol, 2.0 equiv.), CuI (7.6 mg, 0.04 mmol, 20 mol%), TERPY (18.68 mg, 0.08 mmol, 40 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **3w**. Isolated yield = 47% (25.4 mg) as a white oil. R_f = 0.4 (Hexane: Ethyl acetate = 2:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 (d, J = 7.6 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.19 – 7.15 (m, 1H), 5.87 (s, 1H), 3.61 (t, J = 2.4 Hz, 2H), 2.11 (tt, J = 7.2, 2.4 Hz, 2H), 1.45 – 1.41 (m, 2H), 1.40 (s, 9H), 1.34 – 1.29 (m, 2H), 0.83 (t, J = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.9, 137.0, 134.9, 129.9, 129.5, 127.2, 126.7, 83.3, 77.8, 51.9, 31.0, 28.7, 23.2, 22.0, 18.5, 13.6. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{18}H_{26}NO$ 272.2006; Found 272.2003.



3x

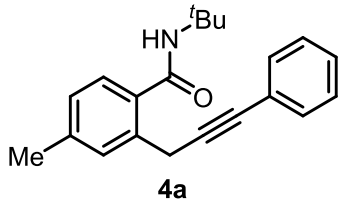
***N*-(*tert*-butyl)-2-(3-cyclopropylprop-2-yn-1-yl)benzamide(3x).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1a** (80.2 mg, 0.2 mmol, 1.0 equiv.), alkyne **2x** (26.6 mg, 0.4 mmol, 2.0 equiv.), CuI (7.6 mg, 0.04 mmol, 20 mol%), TERPY (18.68 mg, 0.08 mmol, 40 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column

chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **3x**. Isolated yield = 33% (16.4 mg) as a yellow oil. R_f = 0.4 (Hexane: Ethyl acetate = 2:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 (d, *J* = 7.2 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.13 – 7.08 (m, 1H), 5.85 (s, 1H), 3.58 (d, *J* = 2.0 Hz, 2H), 1.40 (s, 9H), 1.20 – 1.17 (m, 1H), 0.69 – 0.63 (m, 2H), 0.60 – 0.53 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.9, 137.1, 134.8, 129.9, 129.5, 127.2, 126.7, 86.1, 73.3, 51.9, 28.8, 23.2, 7.9, -0.4. (The product contains a small amount of (N- (tert-butyl) -2-methylbenzamide.) **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{17}H_{21}NO$ 256.1696; Found 256.1703.



3y

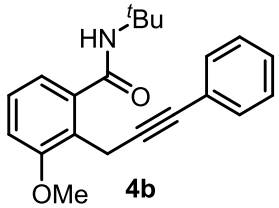
***N*-(*tert*-butyl)-2-(3-(trimethylsilyl)prop-2-yn-1-yl)benzamid*e* (3y).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1a** (80.2 mg, 0.2 mmol, 1.0 equiv.), alkyne **2y** (39.2 mg, 0.4 mmol, 2.0 equiv.), CuI (7.6 mg, 0.04 mmol, 20 mol%), TERPY (18.68 mg, 0.08 mmol, 40 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **3y**. Isolated yield = 49% (28.0 mg) as a white solid; M.p. 76-77 ºC. R_f = 0.4 (Hexane: Ethyl acetate = 2:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.34 (d, *J* = 7.8 Hz, 1H), 7.23 – 7.19 (m, 2H), 7.10 – 7.06 (m, 1H), 5.72 (s, 1H), 3.61 (s, 2H), 1.30 (s, 9H), -0.00 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.8, 137.0, 133.8, 129.9, 129.4, 127.1, 126.8, 104.3, 87.3, 51.9, 28.7, 24.1, 0.0. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{17}H_{26}NOSi$ 288.1778; Found 288.1774.



4a

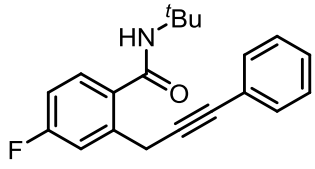
***N*-(*tert*-butyl)-4-methyl-2-(3-phenylprop-2-yn-1-yl)benzamide (4a).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1f** (83.0 mg, 0.2 mmol, 1.0 equiv.), alkyne **2a** (40.2 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue

LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **4a**. Isolated yield = 62% (53.6 mg) as a white solid; M.p. 85-86 °C. R_f = 0.4 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36 – 7.31 (m, 2H), 7.27 (s, 1H), 7.25 – 7.17 (m, 4H), 7.01 (d, *J* = 7.6 Hz, 1H), 5.80 (s, 1H), 3.87 (s, 2H), 2.30 (s, 3H), 1.38 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.0, 140.1, 134.3, 131.6, 130.4, 128.2, 127.8, 127.5, 127.3, 123.5, 87.9, 82.9, 51.8, 28.8, 23.7, 21.3. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{21}H_{24}NO$ 306.1853; Found 306.1846.



4b

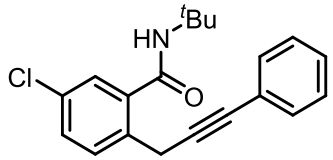
***N*-(*tert*-butyl)-3-methoxy-2-(3-phenylprop-2-yn-1-yl)benzamide (4b).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1g** (86.2 mg, 0.2 mmol, 1.0 equiv.), alkyne **2a** (40.4 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.35 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **4b**. Isolated yield = 79% (50.6 mg) as a white solid; M.p. 99-100 °C. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.28 – 7.25 (m, 2H), 7.19 – 7.15 (m, 4H), 7.00 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.85 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.01 (s, 1H), 3.80 (s, 2H), 3.80 (s, 3H), 1.38 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.6, 157.2, 139.2, 131.5, 128.2, 128.1, 127.7, 123.5, 122.3, 119.8, 111.9, 88.6, 80.6, 55.9, 52.0, 28.7, 17.2. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{21}H_{24}NO_2$ 322.1802; Found 322.1803.



4c

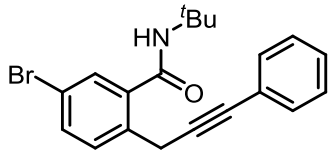
***N*-(*tert*-butyl)-4-fluoro-2-(3-phenylprop-2-yn-1-yl)benzamide (4c).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1h** (83.8 mg, 0.2 mmol, 1.0 equiv.), alkyne **2a** (40.4 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was

tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **4c**. Isolated yield = 64% (45.0 mg) as a white solid; M.p. 113-114 °C. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 – 7.30 (m, 3H), 7.26 – 7.20 (m, 4H), 6.88 (td, *J* = 8.4, 2.8 Hz, 1H), 5.78 (s, 1H), 3.90 (s, 2H), 1.38 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.0, δ 163.3 (d, *J* = 249.5 Hz), 137.6 (d, *J* = 8.0 Hz), 133.1 (d, *J* = 3.3 Hz), 131.6, 129.1 (d, *J* = 8.5 Hz), 128.3, 128.1, 123.1, 116.6 (d, *J* = 22.7 Hz), 113.7 (d, *J* = 21.5 Hz), 86.6, 83.6, 52.0, 28.8, 23.7. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -110.2. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}FNO$ 310.1602; Found 310.1595.



4d

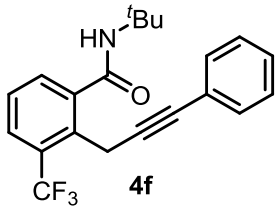
***N*-(*tert*-butyl)-5-chloro-2-(3-phenylprop-2-yn-1-yl)benzamide (4d).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1i** (87.2 mg, 0.2 mmol, 1.0 equiv.), alkyne **2a** (40.4 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.35 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **4d**. Isolated yield = 60% (48.2 mg) as a yellow oil. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.27 (m, 4H), 7.25 – 7.20 (m, 3H), 5.78 (s, 1H), 3.85 (s, 2H), 1.39 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.4, 138.4, 132.9, 132.7, 131.5, 131.1, 129.9, 128.3, 128.0, 127.1, 123.2, 87.0, 83.3, 52.2, 28.7, 23.2. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}ClNO$ 326.1306; Found 326.1301.



4e

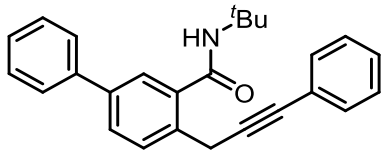
5-bromo-*N*-(*tert*-butyl)-2-(3-phenylprop-2-yn-1-yl)benzamide (4e). Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1j** (96.0 mg, 0.2 mmol, 1.0 equiv.), alkyne **2a** (40.4 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04

mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **4e**. Isolated yield = 76% (76.0 mg) as a yellow oil. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45 – 7.42 (m, 2H), 7.39 – 7.36 (m, 1H), 7.34 – 7.30 (m, 2H), 7.23 – 7.19 (m, 3H), 5.80 (s, 1H), 3.83 (s, 2H), 1.38 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.3, 138.7, 133.4, 132.9, 131.5, 131.3, 129.9, 128.3, 128.0, 123.1, 120.5, 86.9, 83.3, 52.2, 28.7, 23.3. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}BrNO$ 370.0801; Found 370.0797.



4f

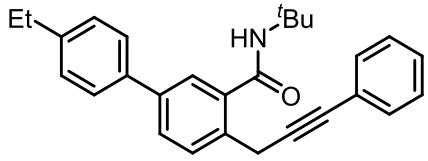
***N*-(*tert*-butyl)-2-(3-phenylprop-2-yn-1-yl)-3-(trifluoromethyl)benzamide (4f).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1k** (93.8 mg, 0.2 mmol, 1.0 equiv.), alkyne **2a** (40.4 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.35 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **4f**. Isolated yield = 84% (57.6 mg) as a yellow oil. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.29 – 7.22 (m, 2H), 7.20 – 7.17 (m, 3H), 6.00 (s, 1H), 3.97 (s, 2H), 1.40 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.9, 140.6, 132.3, 131.5, 129.3(q, $J_{C\text{-}F}$=31.3Hz) 128.2, 128.1, 127.43, 127.42(q, $J_{C\text{-}F}$ = 5.7Hz) 125.4, 124.0(q, $J_{C\text{-}F}$ = 274.7Hz),123.1, 87.4, 82.4, 52.4, 28.6, 20.3(q, $^4J_{C\text{-}F}$ =1.4Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -59.4. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{21}H_{21}F_3NO$ 360.1570; Found 360.1569.



4g

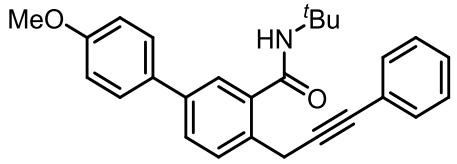
***N*-(*tert*-butyl)-4-(3-phenylprop-2-yn-1-yl)-[1,1'-biphenyl]-3-carboxamide (4g).** Following the typical

procedure described above, an oven-dried 4.0 mL vial was charged with amide **1l** (95.4 mg, 0.2 mmol, 1.0 equiv.), alkyne **2a** (40.4 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.35 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **4g**. Isolated yield = 71% (52.4 mg) as a white solid; M.p. 114-115 °C. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 – 7.49 (m, 5H), 7.39 – 7.33 (m, 5H), 7.22 – 7.19 (m, 3H), 5.88 (s, 1H), 3.92 (s, 2H), 1.40 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.9, 140.0, 137.5, 133.2, 131.5, 130.1, 128.8, 128.5, 128.2, 127.9, 127.6, 127.0, 125.8, 123.4, 87.6, 83.1, 52.0, 28.8, 23.4. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{26}H_{26}NO$ 368.2009; Found 368.2003.



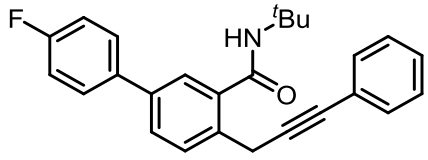
4h

***N-(tert*-butyl)-4'-ethyl-4-(3-phenylprop-2-yn-1-yl)-[1,1'-biphenyl]-3-carboxamide (4h).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1m** (101.0 mg, 0.2 mmol, 1.0 equiv.), alkyne **2a** (40.4 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.35 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **4h**. Isolated yield = 89% (71.4 mg) as a white solid; M.p. 58-59 °C. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.52 – 7.49 (m, 3H), 7.43 – 7.39 (m, 2H), 7.36 – 7.29 (m, 2H), 7.20 – 7.17 (m, 5H), 5.89 (s, 1H), 3.89 (s, 2H), 2.60 (q, J = 7.6 Hz, 2H), 1.38 (s, 9H), 1.18 (t, J = 7.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.0, 143.8, 140.0, 137.4, 137.4, 132.9, 131.5, 130.1, 128.4, 128.3, 128.2, 127.9, 126.9, 125.7, 123.4, 87.7, 83.0, 52.0, 28.8, 28.5, 23.4, 15.6. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{28}H_{30}NO$ 396.2322; Found 396.2326.



4i

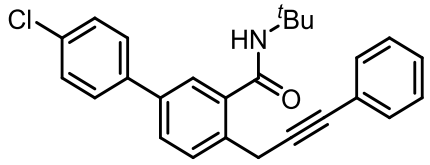
***N*-(*tert*-butyl)-4'-methoxy-4-(3-phenylprop-2-yn-1-yl)-[1,1'-biphenyl]-3-carboxamide (4i).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1n** (97.6 mg, 0.2 mmol, 1.0 equiv.), alkyne **2a** (40.4 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.35 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **4i**. Isolated yield = 56% (44.2 mg) as a yellow oil. R_f = 0.5 (Hexane: Ethyl acetate = 4:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 – 7.49 (m, 3H), 7.45 – 7.42 (m, 2H), 7.36 – 7.32 (m, 2H), 7.22 – 7.19 (m, 3H), 6.91 – 6.89 (m, 2H), 5.87 (s, 1H), 3.90 (s, 2H), 3.77 (s, 3H), 1.40 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.9, 159.3, 139.6, 137.5, 132.5, 132.50, 131.48, 130.1, 128.2, 128.07, 128.05, 127.9, 125.4, 123.4, 114.3, 87.7, 83.0, 55.3, 52.0, 28.8, 23.4. **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{27}H_{27}NNaO_2$ 420.1934; Found 420.1926.



4j

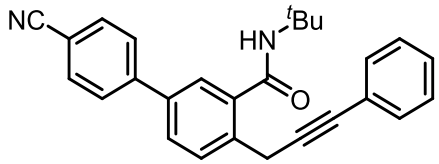
***N*-(*tert*-butyl)-4'-fluoro-4-(3-phenylprop-2-yn-1-yl)-[1,1'-biphenyl]-3-carboxamide (4j).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1o** (99.0 mg, 0.2 mmol, 1.0 equiv.), alkyne **2a** (40.4 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.35 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **4j**. Isolated yield = 70% (53.2 mg) as a yellow oil. R_f = 0.6 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 – 7.52 (m, 1H), 7.50 – 7.44 (m, 4H), 7.36 – 7.32 (m, 2H), 7.23 – 7.21 (m, 3H), 7.07 – 7.03 (m, 2H), 5.88 (s, 1H), 3.91 (s, 2H), 1.40 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.7, 162.6 (d,

$J_{C\text{-}F}$ = 247.1 Hz), 139.0, 137.7,136.1 (d, $J_{C\text{-}F}$ = 3.2 Hz), 133.2, 131.5, 130.2, 128.6 (d, $J_{C\text{-}F}$ = 8.0 Hz), 128.4, 128.2, 128.0, 125.7, 123.3, 115.7 (d, $J_{C\text{-}F}$ = 21.4 Hz), 87.5, 83.1, 52.1, 28.8, 23.4. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -115.2. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{26}H_{26}FNO$ 386.1915; Found 386.1911.



4k

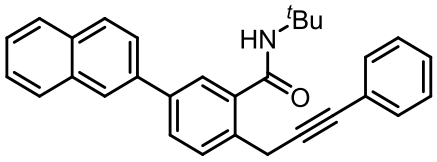
***N*-(*tert*-butyl)-4'-chloro-4-(3-phenylprop-2-yn-1-yl)-[1,1'-biphenyl]-3-carboxamide (4k).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1p** (102.4 mg, 0.2 mmol, 1.0 equiv.), alkyne **2a** (40.4 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.35 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **4k**. Isolated yield = 69% (55.4 mg) as a yellow oil. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 – 7.52 (m, 1H), 7.52 – 7.44 (m, 2H), 7.46 – 7.39 (m, 2H), 7.37 – 7.29 (m, 4H), 7.24 – 7.18 (m, 3H), 5.89 (s, 1H), 3.90 (s, 2H), 1.40 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.6, 138.7, 138.4, 137.7, 133.7, 133.5, 131.5, 130.3, 129.0, 128.3, 128.2, 128.0, 125.7, 123.3, 87.4, 83.2, 52.1, 28.8, 23.5. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{26}H_{25}ClNO$ 402.1619; Found 402.1615.



4l

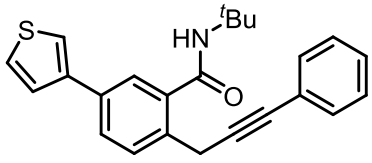
***N*-(*tert*-butyl)-4'-cyano-4-(3-phenylprop-2-yn-1-yl)-[1,1'-biphenyl]-3-carboxamide (4l).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1q** (100.4 mg, 0.2 mmol, 1.0 equiv.), alkyne **2a** (40.4 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **4l**. Isolated yield = 68% (53.4 mg) as a yellow oil. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400**

MHz, $CDCl_3$) δ 7.66 – 7.58 (m, 6H), 7.58 – 7.52 (m, 1H), 7.36 – 7.32 (m, 2H), 7.24 – 7.21 (m, 3H), 5.92 (s, 1H), 3.92 (s, 2H), 1.41 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.3, 144.4, 138.0, 137.9, 134.7, 132.6, 131.5, 130.5, 128.5, 128.3, 128.1, 127.6, 126.0, 123.1, 118.8, 111.2, 87.1, 83.4, 52.2, 28.8, 23.6. **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{27}H_{24}N_2NaO$ 415.1781; Found 415.1780.



4m

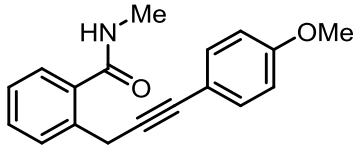
***N*-(*tert*-butyl)-5-(naphthalen-2-yl)-2-(3-phenylprop-2-yn-1-yl)benzamide (4m).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1r** (105.4 mg, 0.2 mmol, 1.0 equiv.), alkyne **2a** (40.4 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 22.4 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **4m**. Isolated yield = 62% (45.8 mg) as a yellow oil. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.97 – 7.95 (m, 1H), 7.85 – 7.77 (m, 3H), 7.68 – 7.63 (m, 3H), 7.58 (d, J = 8.0 Hz, 1H), 7.44 – 7.40 (m, 2H), 7.37 – 7.33 (m, 2H), 7.23 – 7.19 (m, 3H), 5.92 (s, 1H), 3.93 (s, 2H), 1.41 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.9, 139.9, 137.7, 137.3, 133.6, 133.2, 132.7, 131.6, 130.3, 128.8, 128.6, 128.2, 128.2, 127.9, 127.6, 126.4, 126.1, 125.8, 125.2, 123.4, 87.6, 83.1, 52.1, 28.8, 23.5. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{30}H_{28}NO$ 418.2166; Found 418.2158.



4n

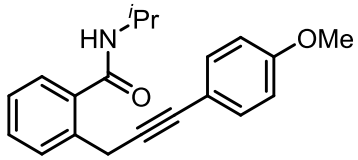
***N*-(*tert*-butyl)-2-(3-phenylprop-2-yn-1-yl)-5-(thiophen-3-yl)benzamide (4n).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1s** (96.6 mg, 0.2 mmol, 1.0 equiv.), alkyne **2a** (40.4 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by

column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **4n**. Isolated yield = 74% (55.6 mg) as a yellow oil. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 – 7.52 (m, 1H), 7.51 – 7.48 (m, 2H), 7.38 – 7.37 (m, 1H), 7.34 – 7.32 (m, 2H), 7.30 – 7.29 (m, 2H), 7.21 – 7.19 (m, 3H), 5.90 (s, 1H), 3.87 (s, 2H), 1.39 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.7, 141.1, 137.6, 134.6, 132.8, 131.5, 130.1, 128.2, 127.9, 127.8, 126.4, 126.1, 125.1, 123.3, 120.7, 87.6, 83.1, 52.0, 28.8, 23.4. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{24}H_{24}NOS$ $[M+H]^+$: 374.1573; Found 374.1571.



4o

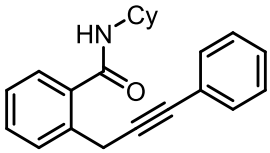
2-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-*N*-methylbenzamide (**4o**)**.** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1v** (71.8 mg, 0.2 mmol, 1.0 equiv.), alkyne **2a** (40.2 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **4o**. Isolated yield = 51% (28.4 mg) as a white solid; M.p. 123-124 °C. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 (d, *J* = 7.8 Hz, 1H), 7.34 (m, 2H), 7.30 – 7.26 (m, 2H), 7.24 – 7.21 (m, 1H), 6.77 – 6.73 (m, 2H), 5.99 (s, 1H), 3.91 (s, 2H), 3.73 (s, 3H), 2.93 (d, *J* = 4.8 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.2, 159.2, 135.7, 135.1, 132.9, 130.3, 129.7, 127.1, 126.9, 115.5, 113.8, 85.9, 82.7, 55.2, 26.7, 23.8. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}NO_2$ 280.1333; Found 280.1340.



4p

N-isopropyl-2-(3-phenylprop-2-yn-1-yl)benzamide (**4p**)**.** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1t** (77.4 mg, 0.2 mmol, 1.0 equiv.), alkyne **2e** (52.8mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5

mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **4p**. Isolated yield = 46% (28.2 mg) as a white solid; M.p. 131-132 ºC. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 (d, *J* = 7.5 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.29 – 7.26 (m, 2H), 7.24 – 7.20 (m, 1H), 6.77 – 6.73 (m, 2H), 5.87 (d, *J* = 7.9 Hz, 1H), 4.27 – 4.16 (m, 1H), 3.89 (s, 2H), 3.73 (s, 3H), 1.18 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.6, 159.3, 136.2, 134.8, 132.9, 130.3, 129.8, 127.3, 126.9, 115.5, 113.8, 86.1, 82.9, 55.2, 41.9, 23.9, 22.8. **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{20}H_{21}NNaO_2$ 330.1464; Found 330.1468.

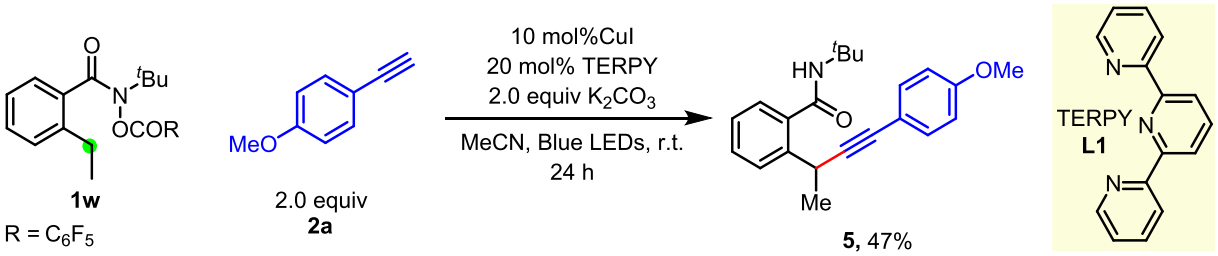


4q

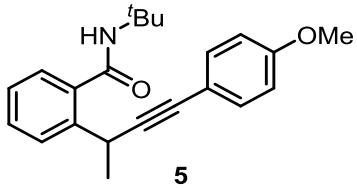
***N*-cyclohexyl-2-(3-phenylprop-2-yn-1-yl)benzamide (4q).** Following the typical procedure described above, an oven-dried 4.0 mL vial was charged with amide **1u** (85.4 mg, 0.2 mmol, 1.0 equiv.), alkyne **2a** (40.4 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:5) to afford **4q**. Isolated yield = 62% (39.0 mg) as a white solid; M.p. 142-143 ºC. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.52 (d, *J* = 7.6 Hz, 1H), 7.36 – 7.33 (m, 3H), 7.25 – 7.18 (m, 5H), 5.86 (d, *J* = 8.0 Hz, 1H), 3.94 – 3.82 (m, 3H), 1.99 – 1.94 (m, 2H), 1.71 – 1.52 (m, 4H), 1.38 – 1.30 (m, 2H), 1.17 – 1.12 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.5, 136.2, 134.7, 131.6, 130.2, 129.7, 128.2, 127.9, 127.2, 126.9, 123.4, 87.7, 83.1, 48.7, 33.1, 25.5, 24.8, 23.8. **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{22}H_{23}NNaO$ 340.1672; Found 340.1669.

Control Experiment and Synthetic Application

Procedure for the synthesis of product 5.

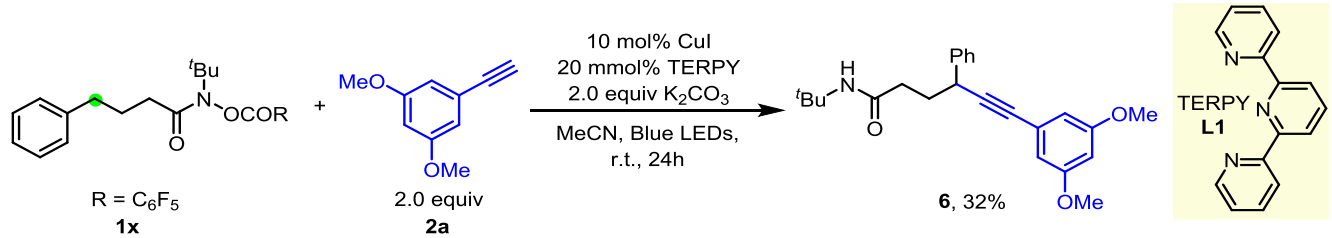


An oven-dried 4.0 mL vial was charged with amide **1w** (83.0 mg, 0.2 mmol, 1.0 equiv.), alkene **2a** (40.4 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.34 mg, 0.04 mmol, 20 mol%) and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:3) to afford **5** in 47% isolated yield (31.4 mg).



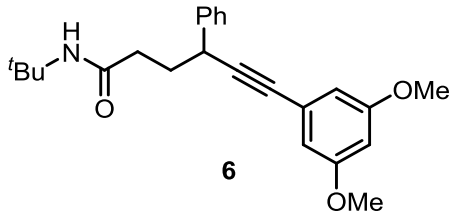
***N*-(*tert*-butyl)-2-(4-(4-methoxyphenyl)but-3-yn-2-yl)benzamide (5).** Isolated yield = 47% on 0.2 mmol scale; as a colourless oil. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 (d, *J* = 7.6 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.29 – 7.24 (m, 3H), 7.21 – 7.15 (m, 1H), 6.77 – 6.71 (m, 2H), 5.72 (s, 1H), 4.37 (q, *J* = 7.2 Hz, 1H), 3.72 (s, 3H), 1.53 (d, *J* = 7.2 Hz, 3H), 1.39 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.2, 159.1, 141.1, 136.5, 132.9, 130.0, 127.8, 126.8, 126.6, 115.6, 113.7, 91.5, 81.7, 55.2, 51.9, 28.9, 28.7, 24.0. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{22}H_{25}NO_2$ 336.1959; Found 336.1961.

Procedure for the synthesis of product 6.



An oven-dried 4.0 mL vial was charged with amide **1x** (86.0 mg, 0.2 mmol, 1.0 equiv.), alkene **2a** (40.4 mg, 0.4 mmol, 2.0 equiv.), CuI (3.8 mg, 0.02 mmol, 10 mol%), TERPY (9.35 mg, 0.04 mmol, 20 mmol%)

and K_2CO_3 (55.2 mg, 0.4 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 2 mL of degassed 1,4-dioxane were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:3) to afford **6** in 32% isolated yield (24.3 mg).



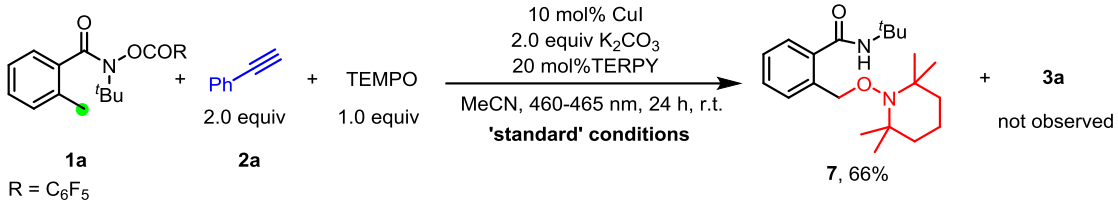
6

***N*-(*tert*-butyl)-6-(3,5-dimethoxyphenyl)-4-phenylhex-5-ynamide (6).** Isolated yield = 32% on 0.2 mmol scale; as a colourless oil. R_f = 0.5 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 – 7.34 (m, 2H), 7.30 – 7.25 (m, 2H), 7.22 – 7.15 (m, 1H), 6.53 (d, *J* = 2.4 Hz, 2H), 6.36 (t, *J* = 2.4 Hz, 1H), 5.22 (s, 1H), 3.88 – 3.83 (m, 1H), 3.71 (s, 6H), 2.25 – 1.99 (m, 4H), 1.26 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.5, 160.4, 141.1, 128.5, 127.5, 126.9, 124.7, 109.4, 101.3, 90.2, 83.8, 55.4, 51.2, 37.5, 34.9, 33.9, 28.8. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{24}H_{30}NO_3$ 380.2220; Found 380.2230.

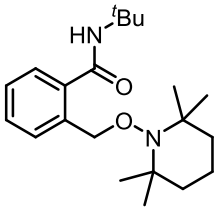
Grams Scale Synthesis.

An oven-dried 250 mL reaction flask was charged with amide **1a** (2.41 g, 6.0 mmol, 1.0 equiv.), alkene **2a** (1.23 g, 12.0 mmol, 2.0 equiv.), CuI (114.3 mg, 0.6 mmol, 10 mol%), TERPY (279.9 mg, 1.2 mmol, 20 mol%) and K_2CO_3 (1.66 g, 12 mmol, 2.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 60 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 48 hours. After completion of the reaction, the resulting mixture was diluted with acetone (100 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:5) to afford **3a** in 75% isolated yield (1.31 g).

The Radical Trapping Experiment with TEMPO



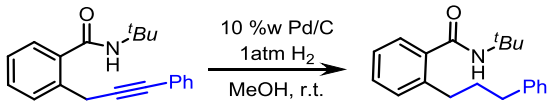
An oven-dried 4.0 mL vial was charged with amide amide **1a** (40.1 mg, 0.1 mmol, 1.0 equiv.), alkyne **2a** (20.2 mg, 0.2 mmol, 2.0 equiv.), CuI (1.9 mg, 0.01 mmol, 10 mol%), TERPY (4.67 mg, 0.2 mmol, 20 mol%) and K_2CO_3 (27.6 mg, 0.2 mmol, 2.0 equiv.) and TEMPO (15.7 mg, 0.1 mmol, 1.0 equiv.). It was directly transferred in a nitrogen-filled glovebox with caps. In the glovebox, 1 mL of degassed MeCN were added to the vial. The vial was tightly sealed, transferred out of glovebox and stirred at room temperature under the irradiation of blue LED lamps for 24 hours. After completion of the reaction, the resulting mixture was diluted with acetone (5 mL), filtered (Celite), and concentrated under a reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10 to 1:3) to afford **7** in 66% isolated yield (22.8 mg).



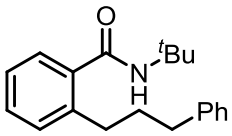
7

***N*-(*tert*-butyl)-2-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)benzamide (7).** Isolated yield = 66% on 0.1 mmol scale; colourless oil; R_f = 0.6 (Hexane: Ethyl acetate = 5:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 (d, *J* = 7.6 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.22 – 7.19 (m, 1H), 5.71 (s, 1H), 4.92 (s, 2H), 1.38 (s, 15H), 1.09 (d, *J* = 17.6 Hz, 12H). The spectroscopic data match the reported literature[1].

Derivatizations of product 3a.

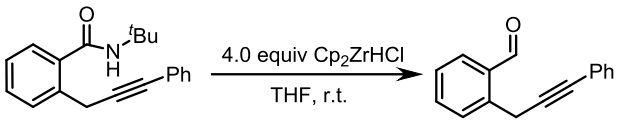


An oven-dried 4 mL vial was charged with amide **3a** (29.1mg, 0.1 mmol, 1.0 equiv.) and palladium on carbon (5.8 mg, 10%w). The vial was evacuated and refilled with hydrogen through a hydrogen balloon. After addition of 0.5 mL of methanol, the mixture was stirred at r.t. for 24 h under hydrogen. The reaction mixture was filtered through celite and washed with EtOAc. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum ether = 1:10) to afford **8** in 95% isolated yield (28 mg).



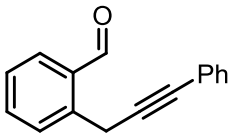
8

***N*-(*tert*-butyl)-2-(3-phenylpropyl)benzamide (8). ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.24 – 7.18 (m, 5H), 7.12 – 7.07 (m, 4H), 5.47 (s, 1H), 2.77 – 2.72 (m, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 1.91 – 1.82 (m, 2H), 1.36 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.7, 142.2, 139.9, 137.7, 129.9, 129.4, 128.4, 128.2, 126.6, 125.8, 125.7, 51.7, 35.9, 33.1, 32.8, 28.7. The spectroscopic data match the reported literature[10].



3a **9**

In a glovebox, the Schwartz reagent (103.2 mg, 0.4 mmol, 4.0 equiv.) and a stir bar were added to a Schlenk tube, which was then sealed with a rubber septum and removed from the box. Next, amide **3a** (29.1 mg, 0.1 mmol, 1.0 equiv.) in anhydrous THF (2.0 mL) was added into the tube via syringe and the heterogeneous mixture was stirred vigorously at rt for 4 h. The resulting reaction mixture was then transferred to a separatory funnel and diluted with 20 mL water. The resulting mixture was extracted with DCM and the combined organic layers were dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel to give the corresponding aldehyde **9** (12.1 mg, 55%) as a colorless oil.



9

***N*-(*tert*-butyl)-2-(3-phenylpropyl)benzamide (9). ^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.20 (s, 1H), 7.79 – 7.69 (m, 2H), 7.57 – 7.50 (m, 1H), 7.43 – 7.34 (m, 3H), 7.26 – 7.19 (m, 3H), 4.23 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 192.8, 138.7, 134.0, 133.6, 133.2, 131.6, 129.9, 128.2, 128.0, 127.3, 123.4, 86.6, 83.9, 23.5. The spectroscopic data match the reported literature[10].

Reference

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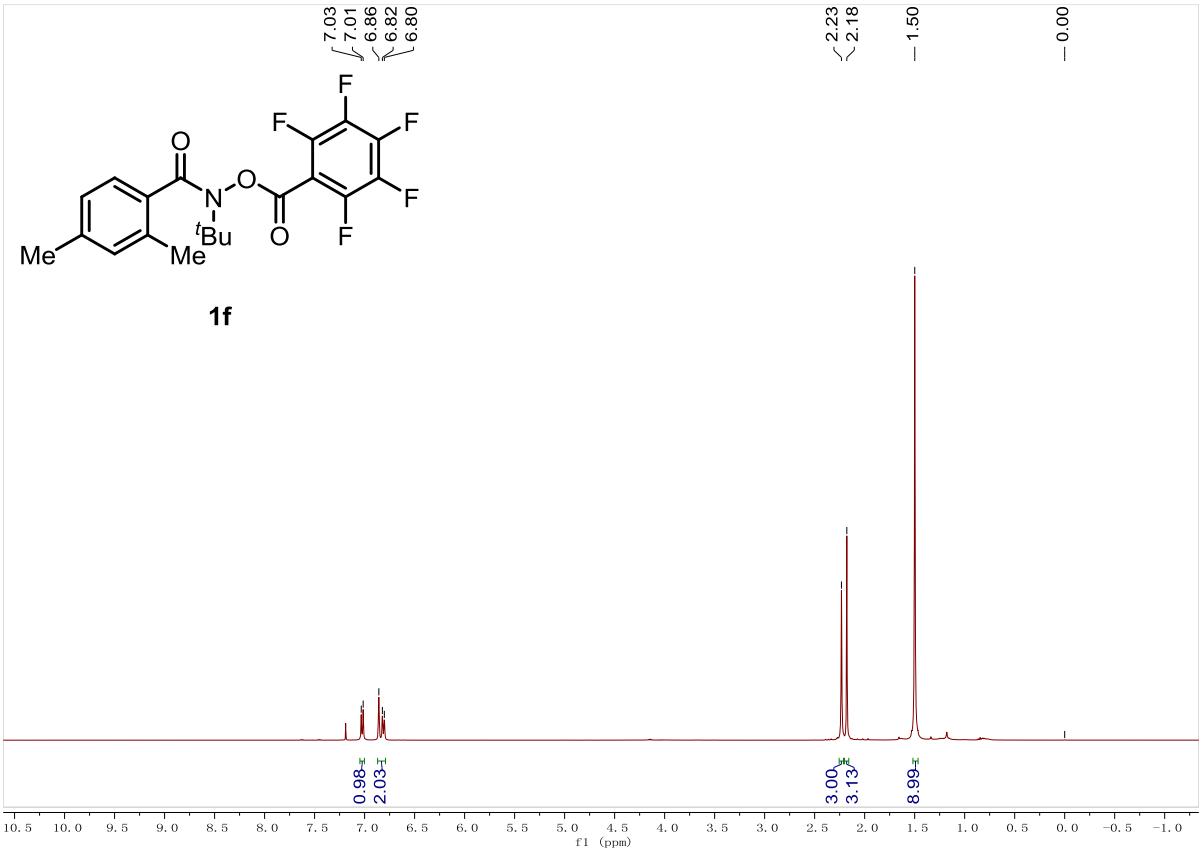
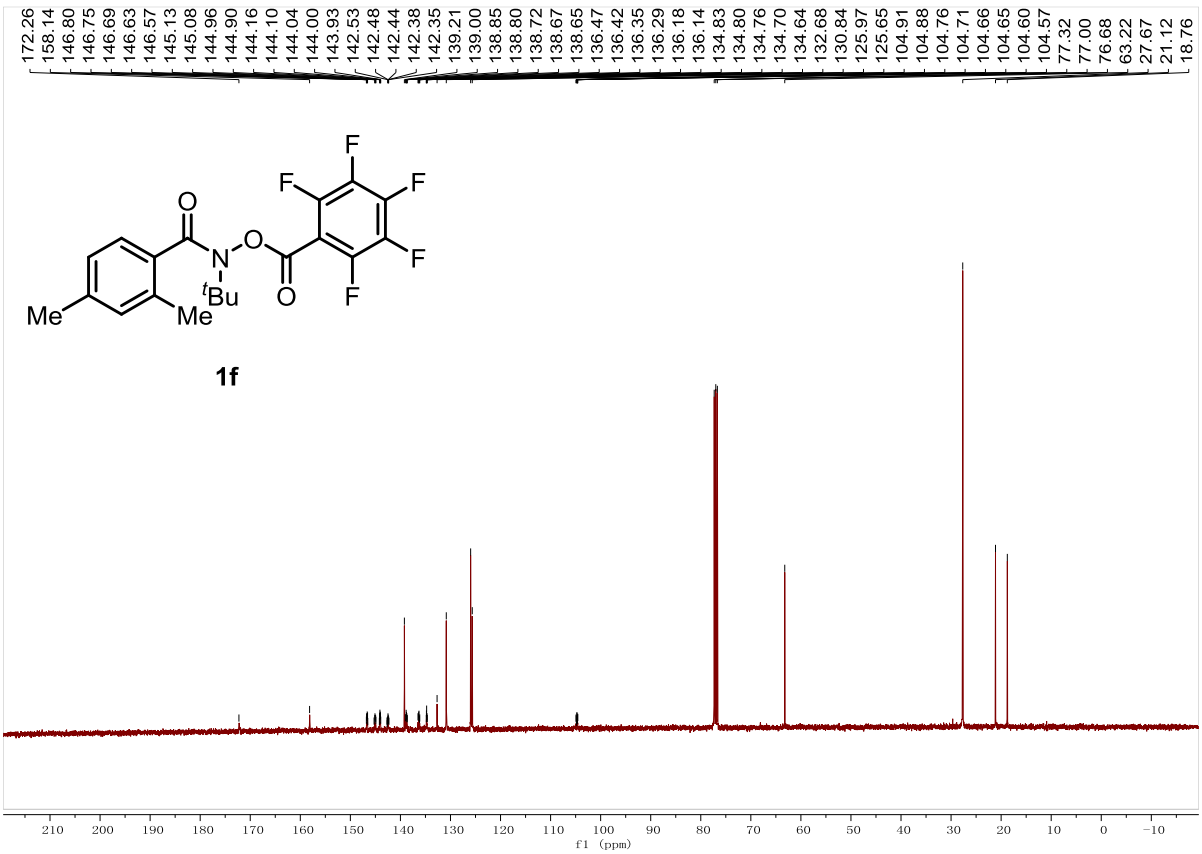
NMR Spectra

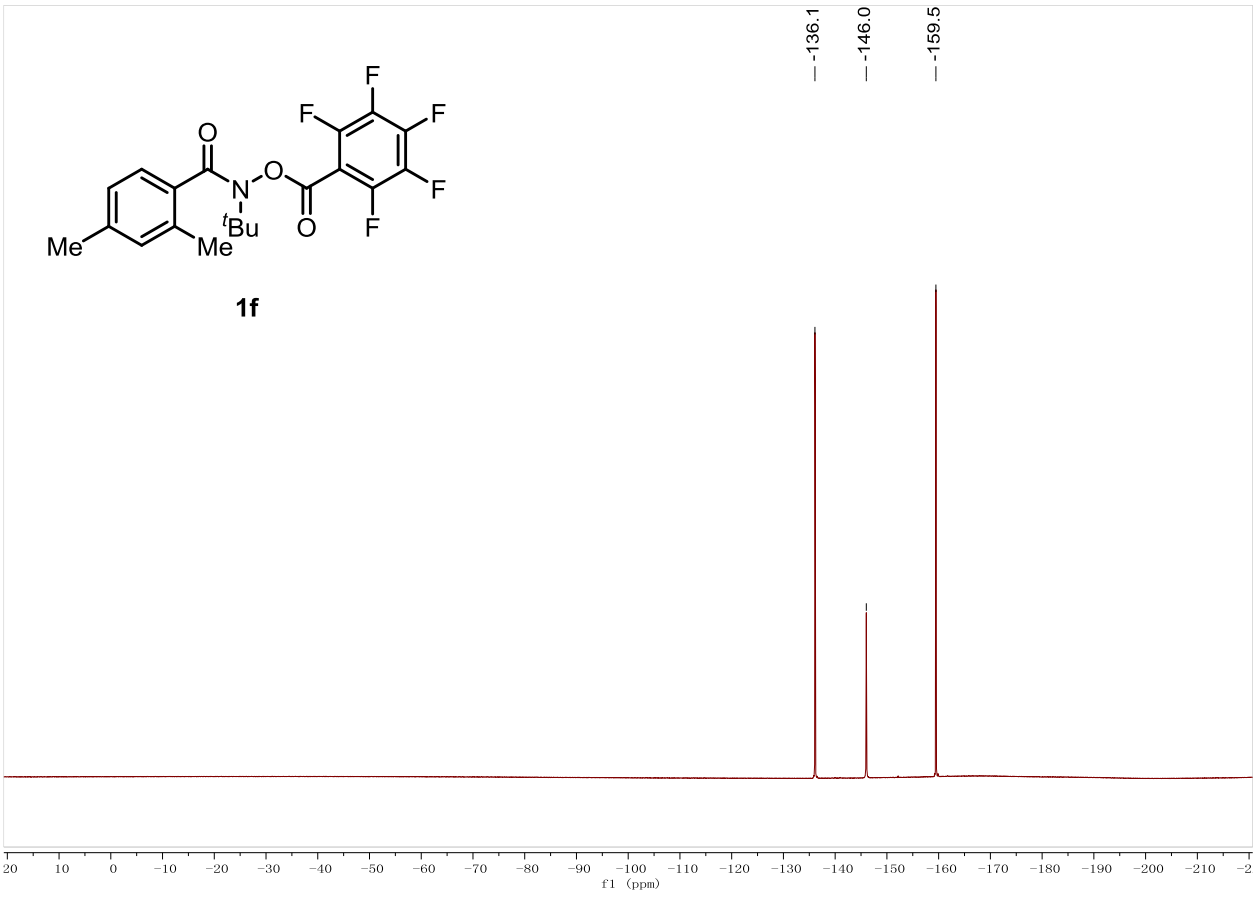
1f, ^{1}H NMR (400 MHz, $CDCl_3$)



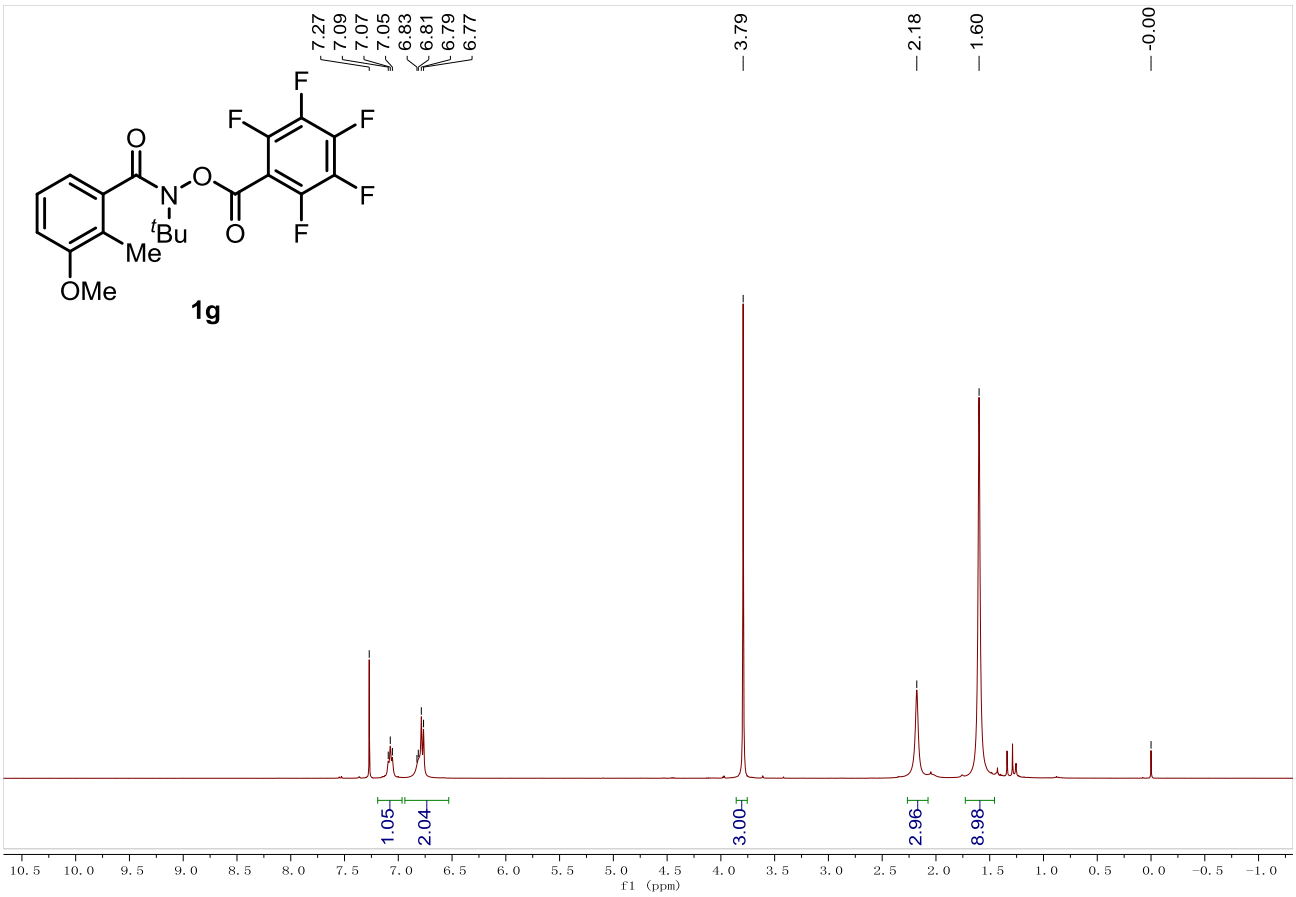
1f, ^{13}C NMR (101 MHz, $CDCl_3$)



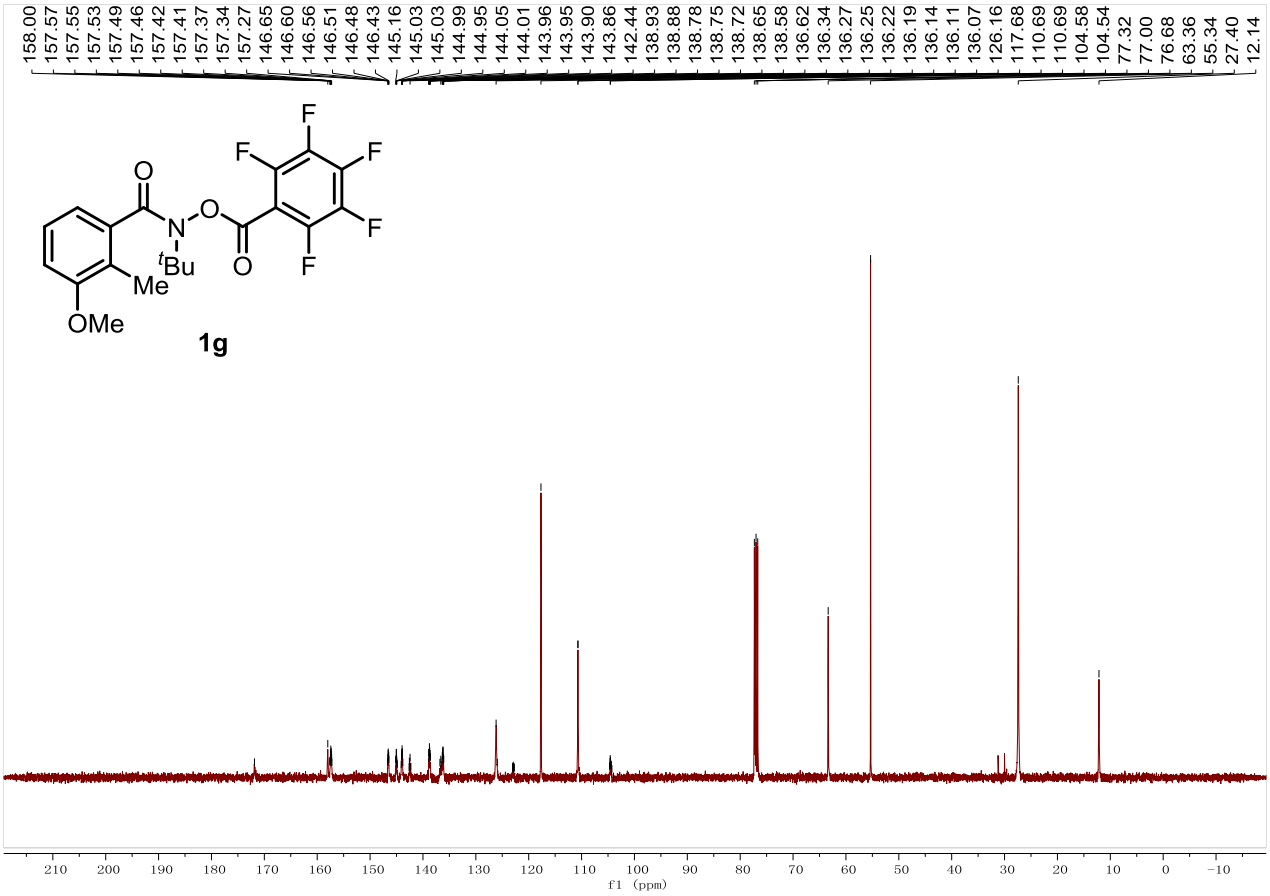
1f, ^{19}F NMR (376 MHz, $CDCl_3$)



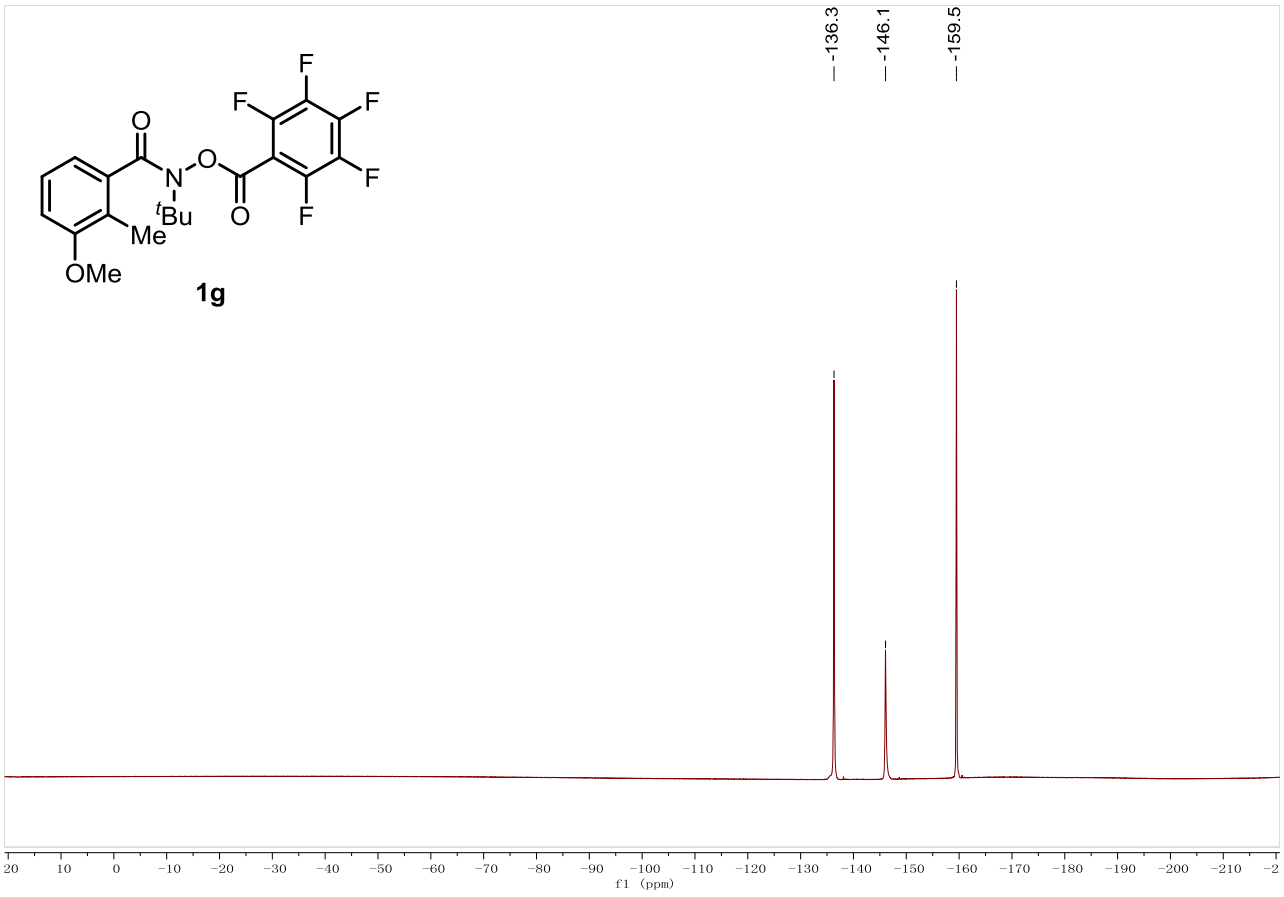
1g, ^{1}H NMR (400 MHz, $CDCl_3$)



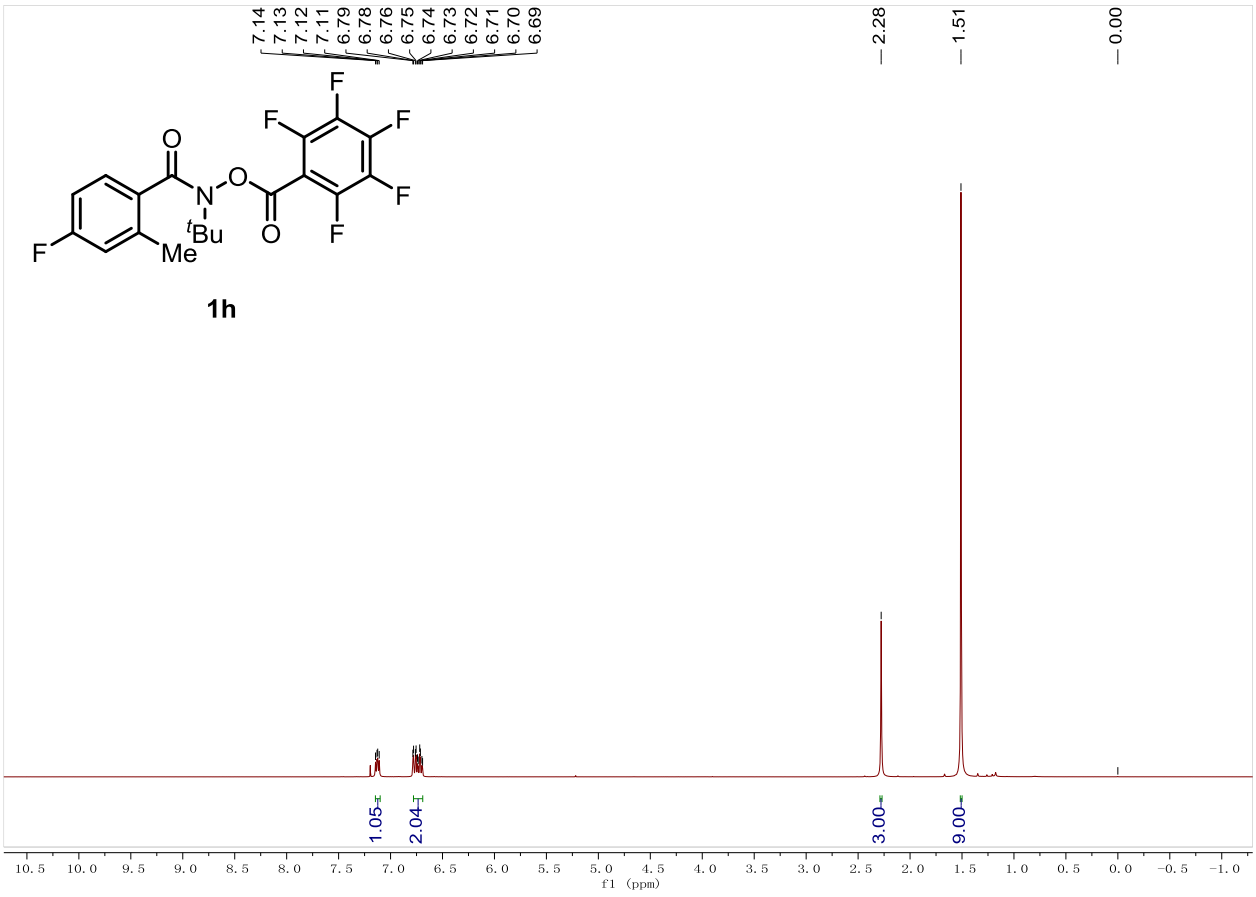
1g, ^{13}C NMR (101 MHz, $CDCl_3$)



1g, ^{19}F NMR (376 MHz, $CDCl_3$)

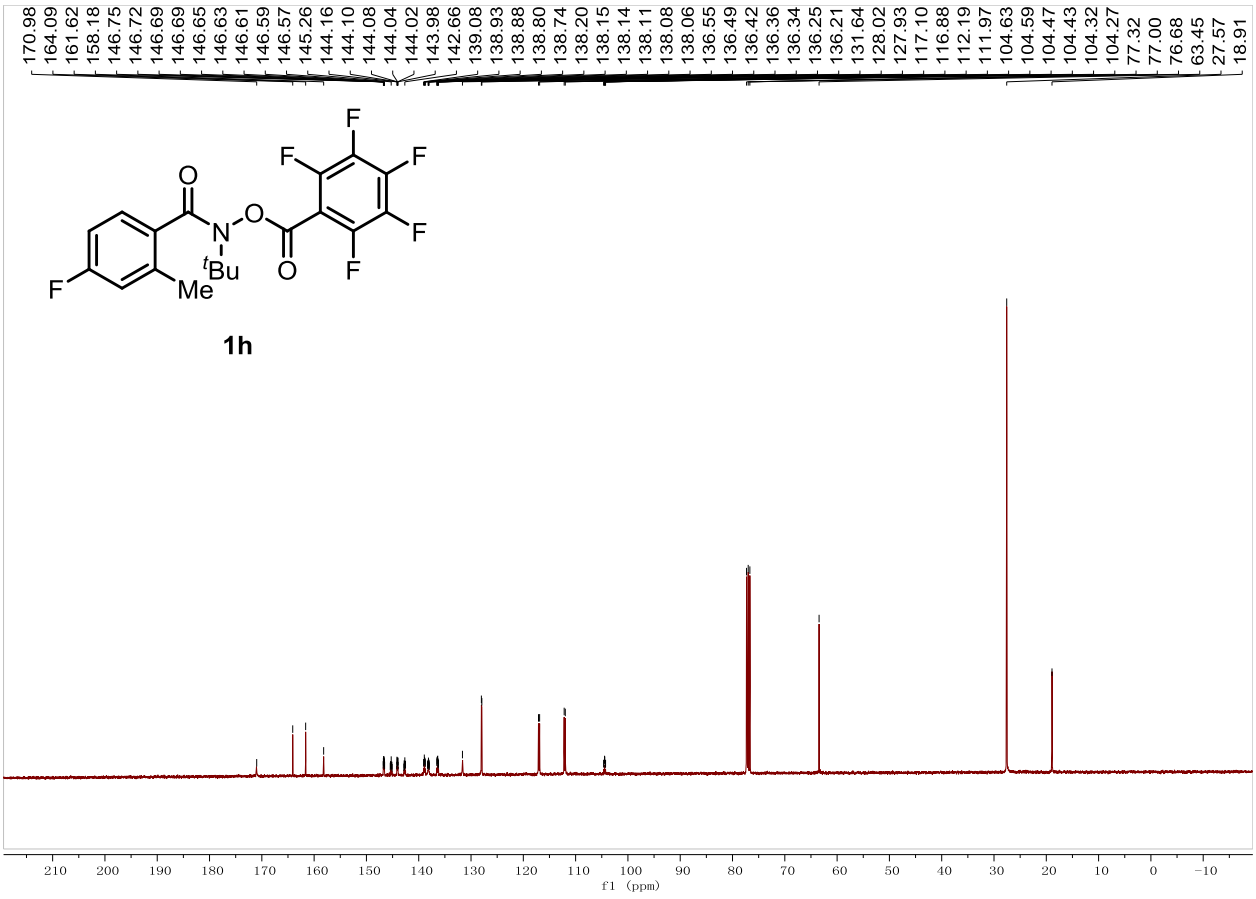


1h, ^{1}H NMR (400 MHz, $CDCl_3$)



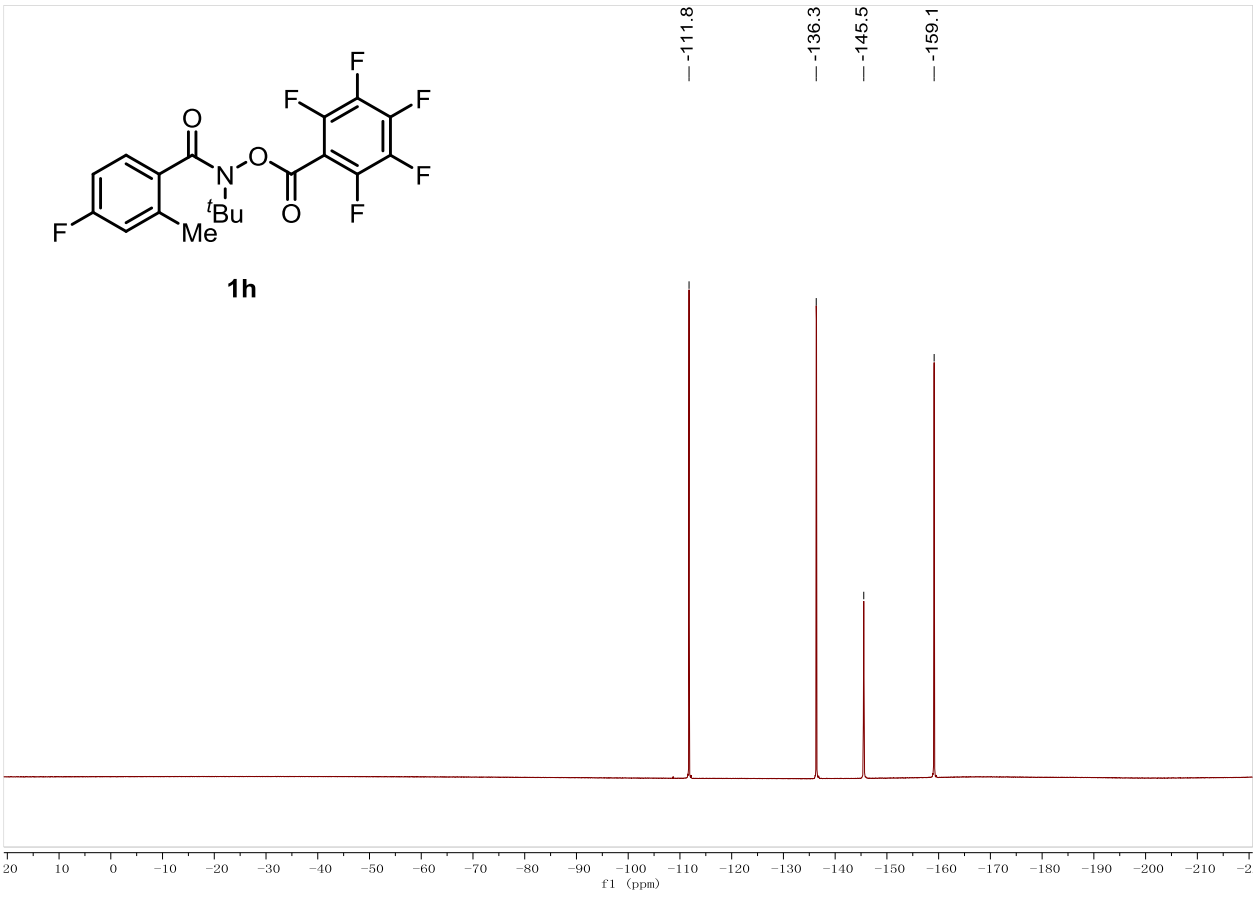
1h

1h, ^{13}C NMR (101 MHz, $CDCl_3$)

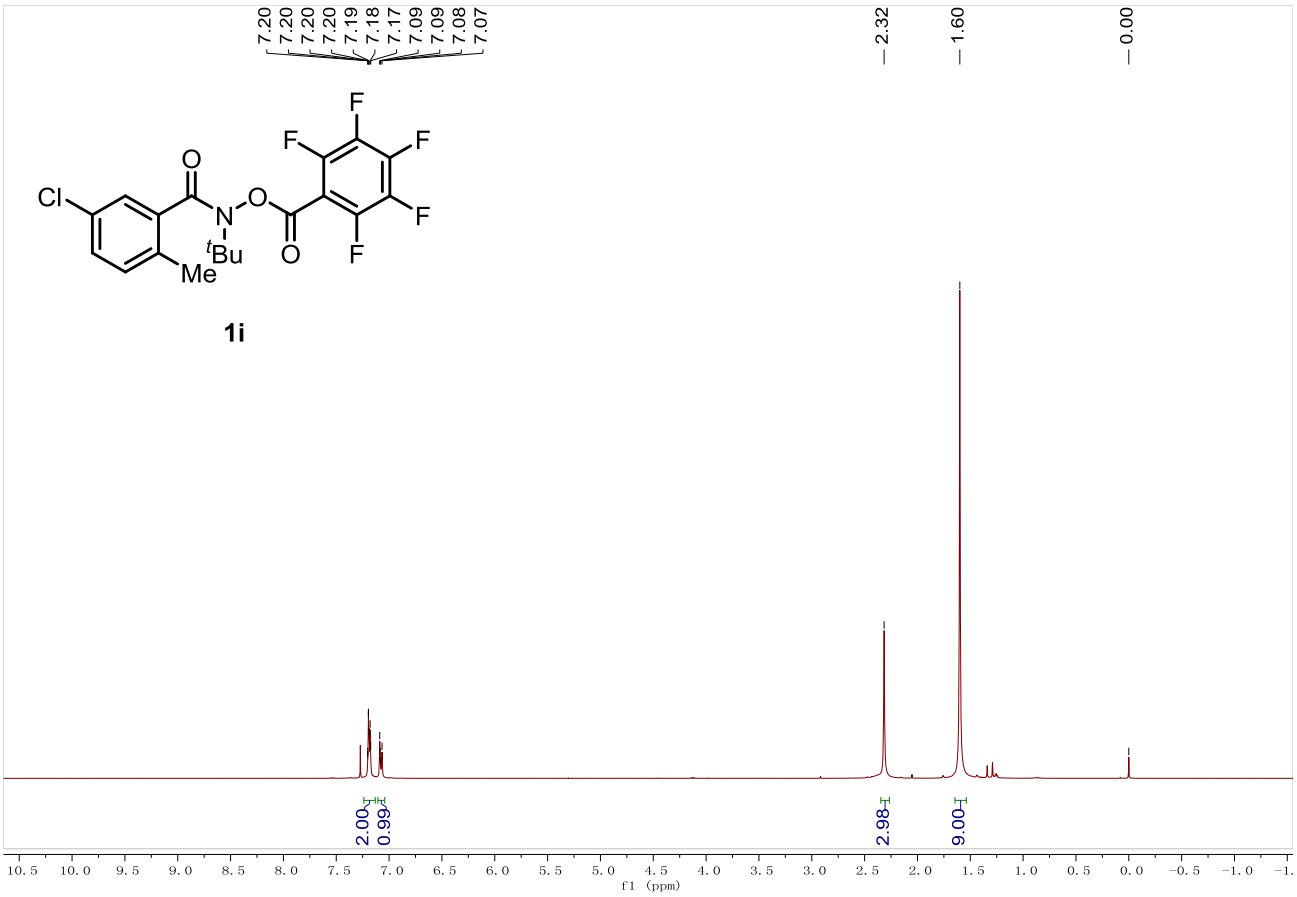


1h

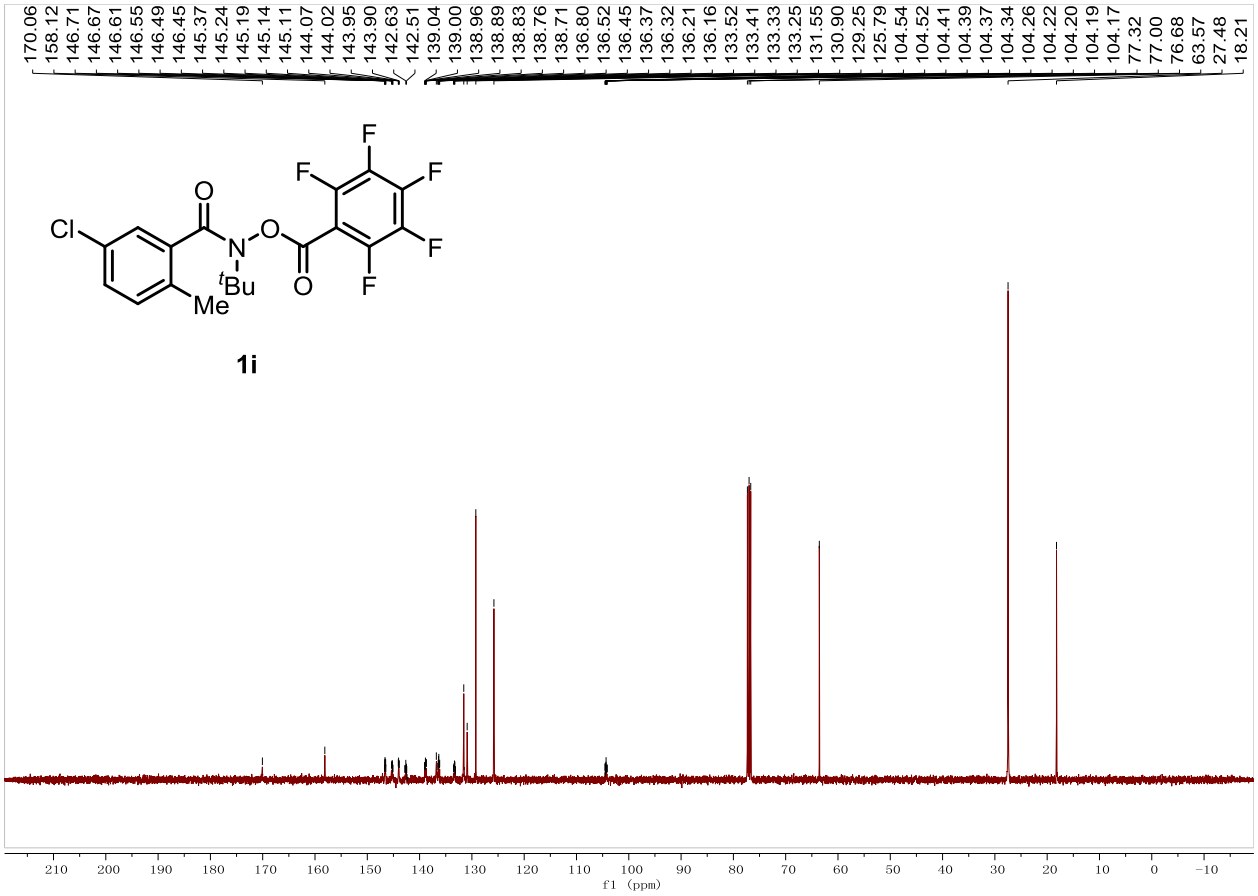
1h, ^{19}F NMR (376 MHz, $CDCl_3$)



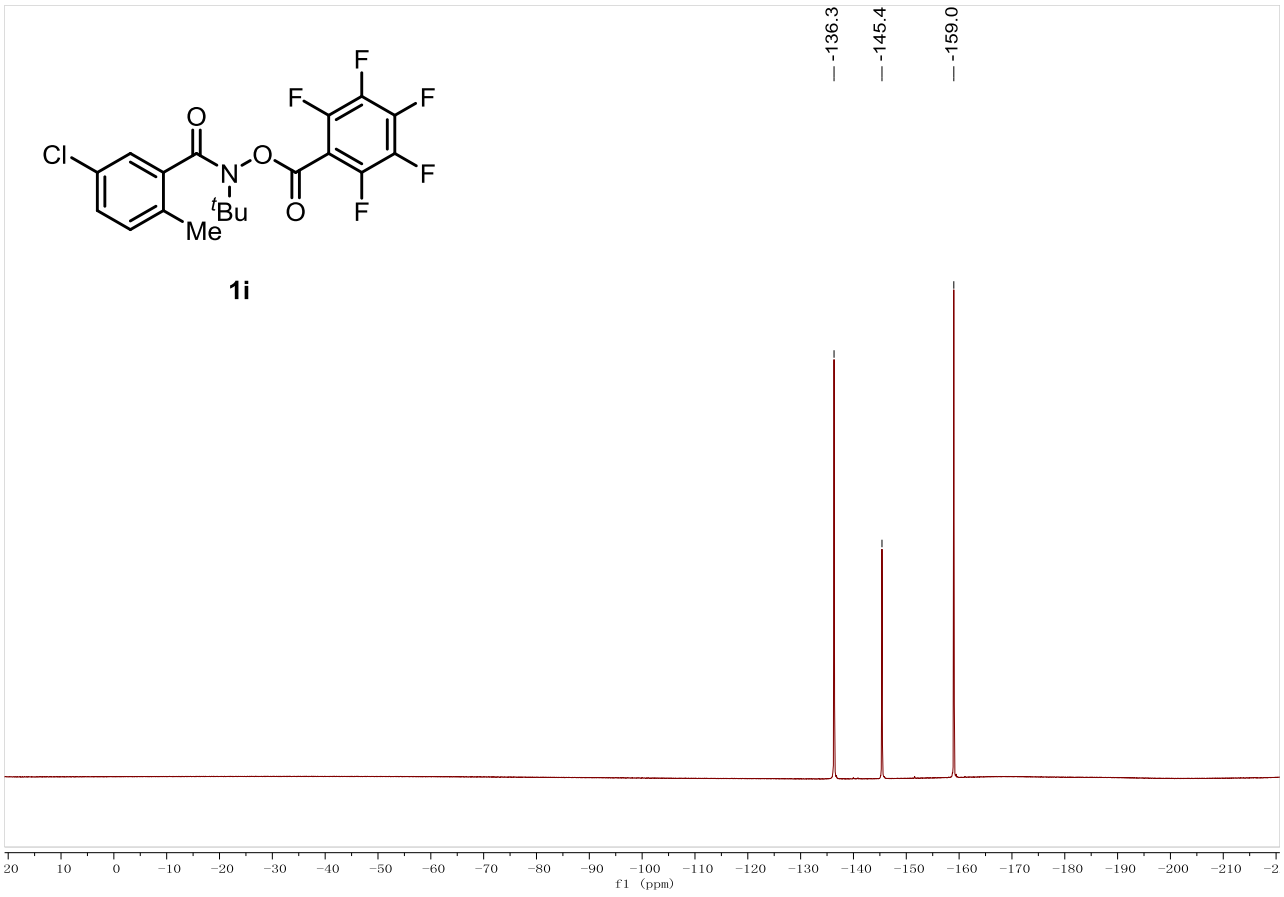
1i, ^{1}H NMR (400 MHz, $CDCl_3$)



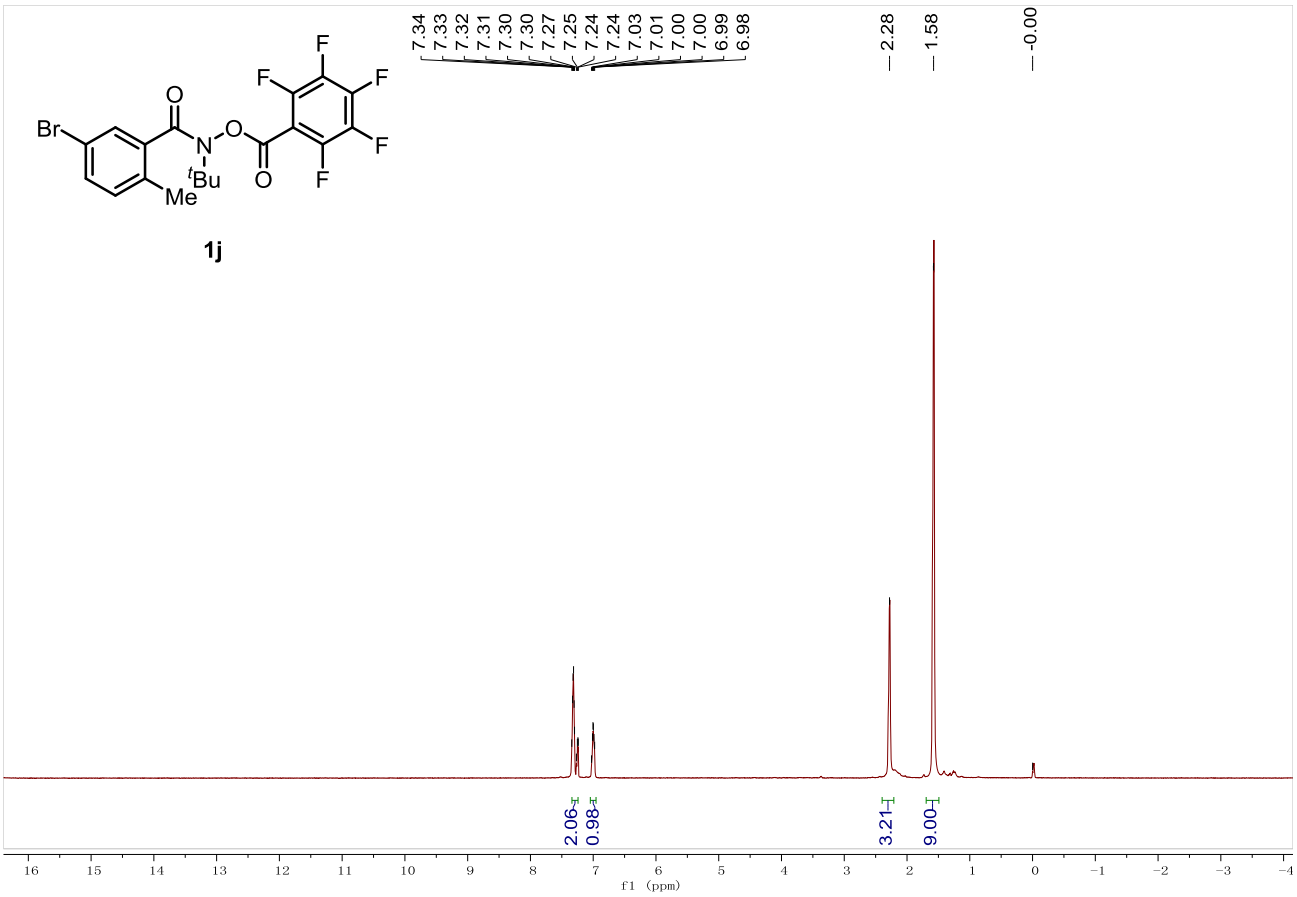
1i, ^{13}C NMR (101 MHz, $CDCl_3$)



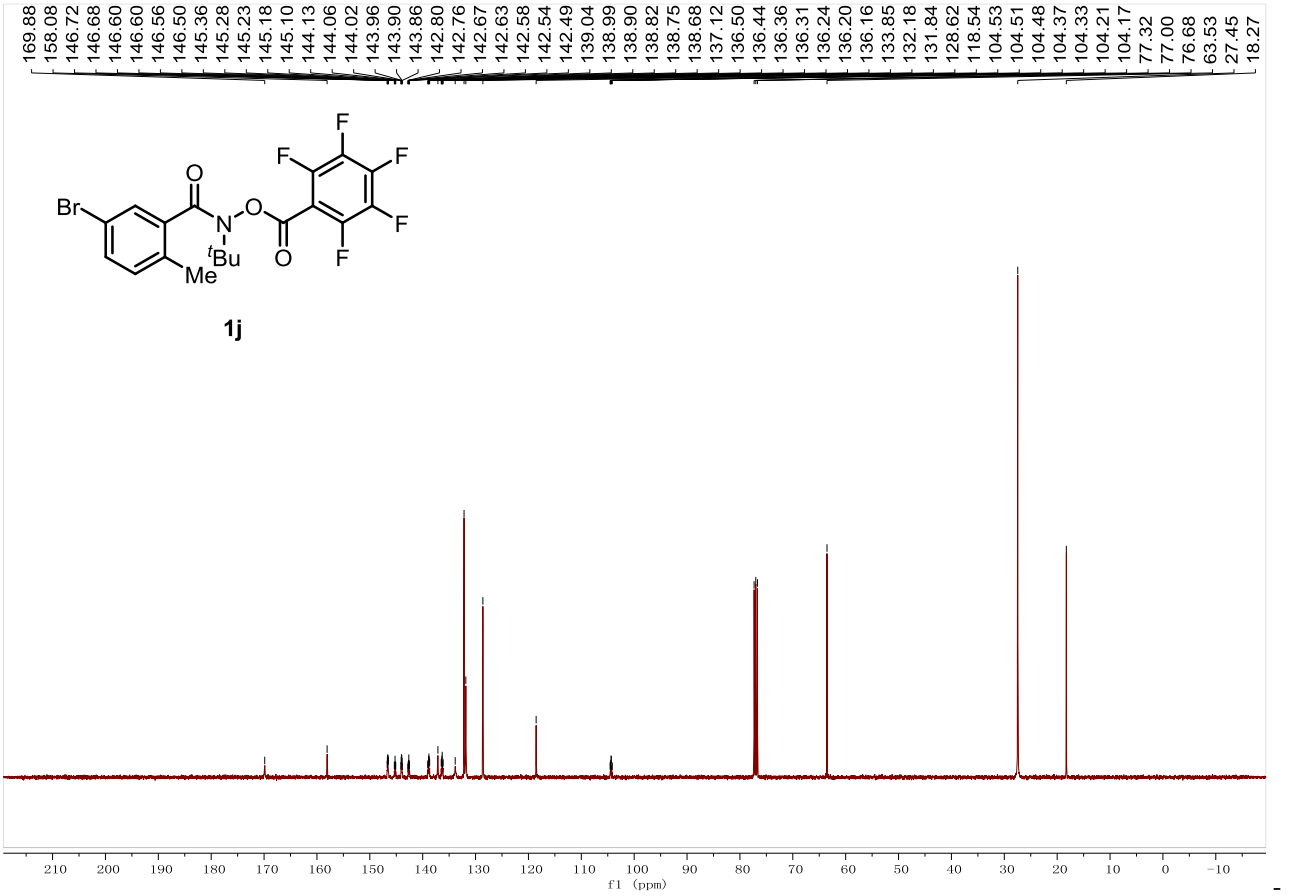
1i, ^{19}F NMR (376 MHz, $CDCl_3$)



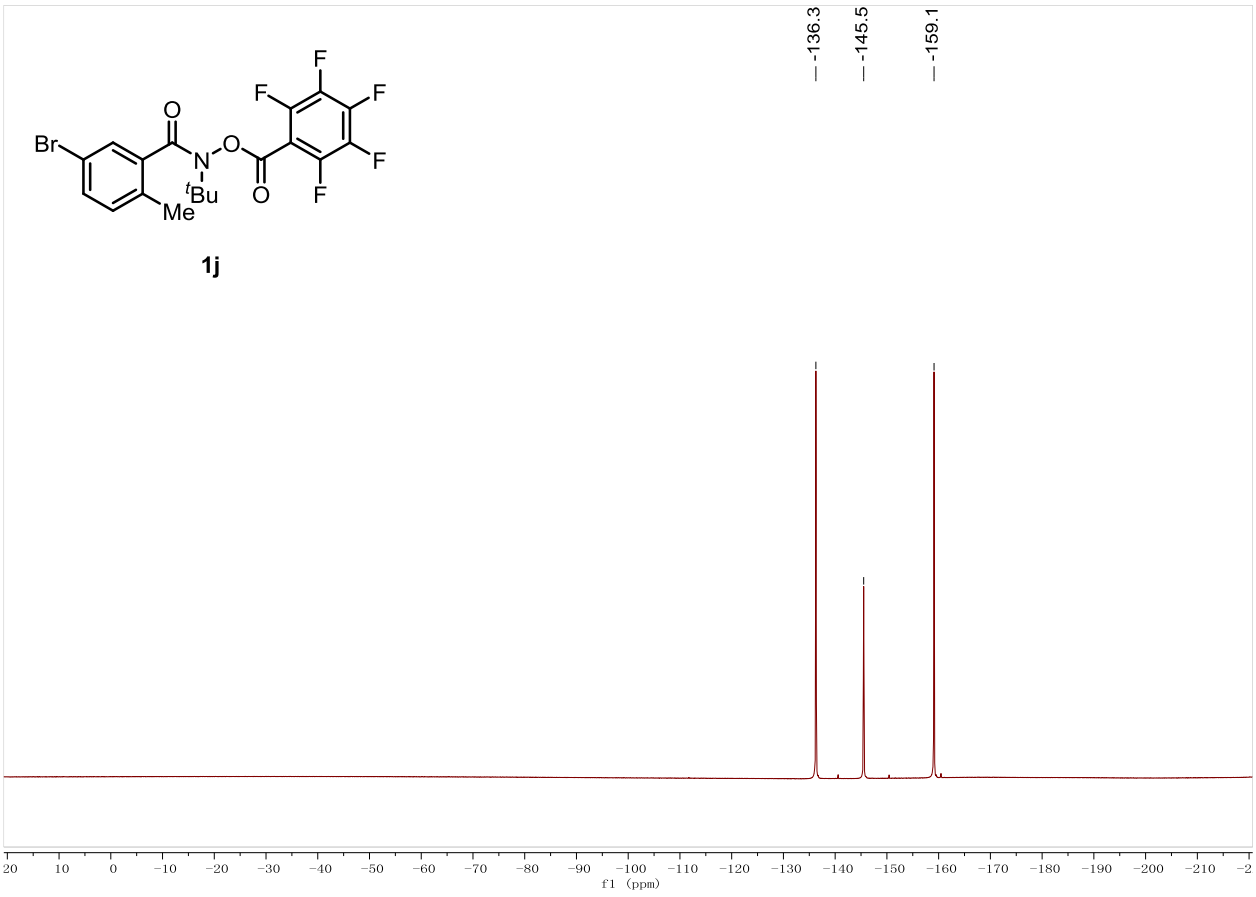
1j, ^{1}H NMR (400 MHz, $CDCl_3$)



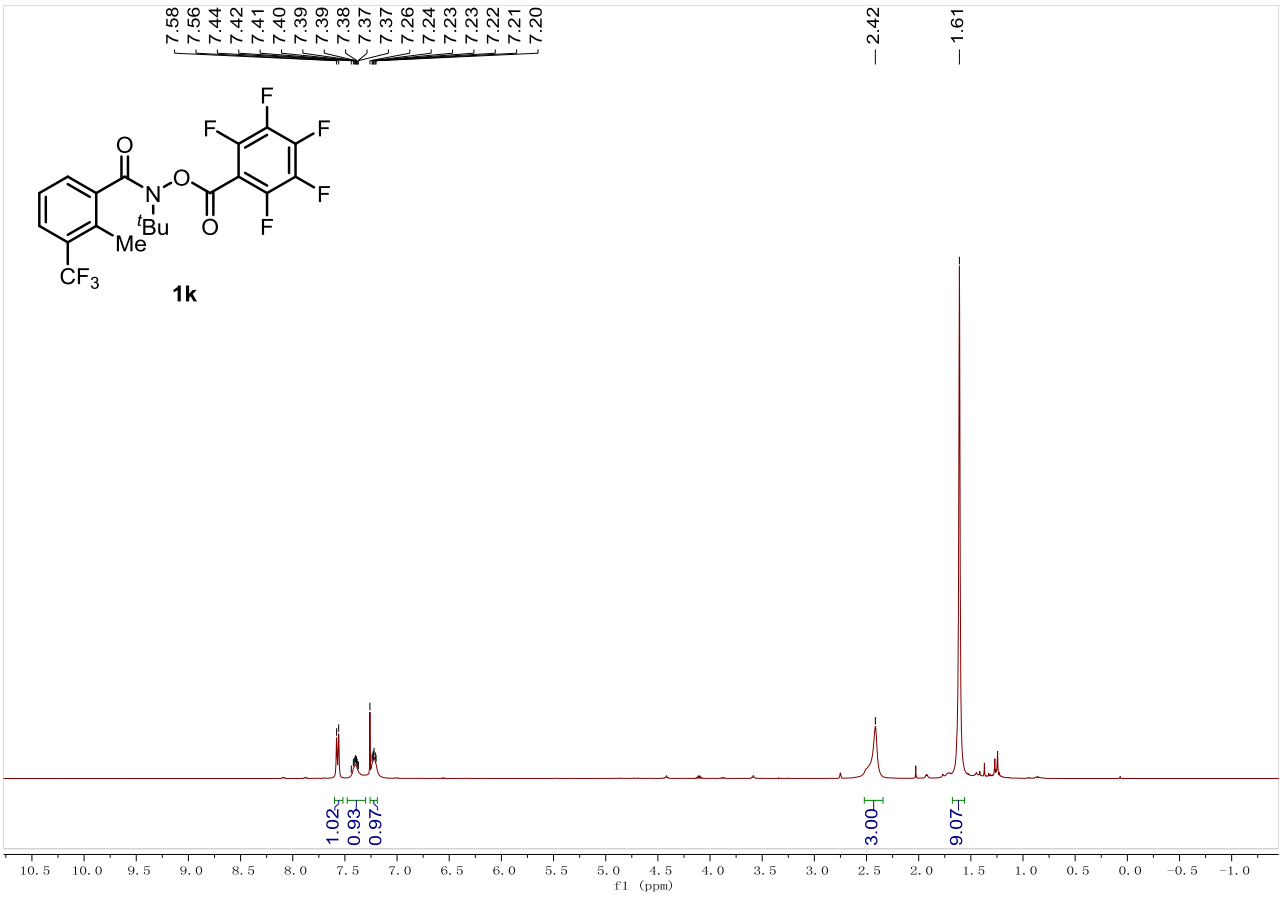
1j, ^{13}C NMR (101 MHz, $CDCl_3$)



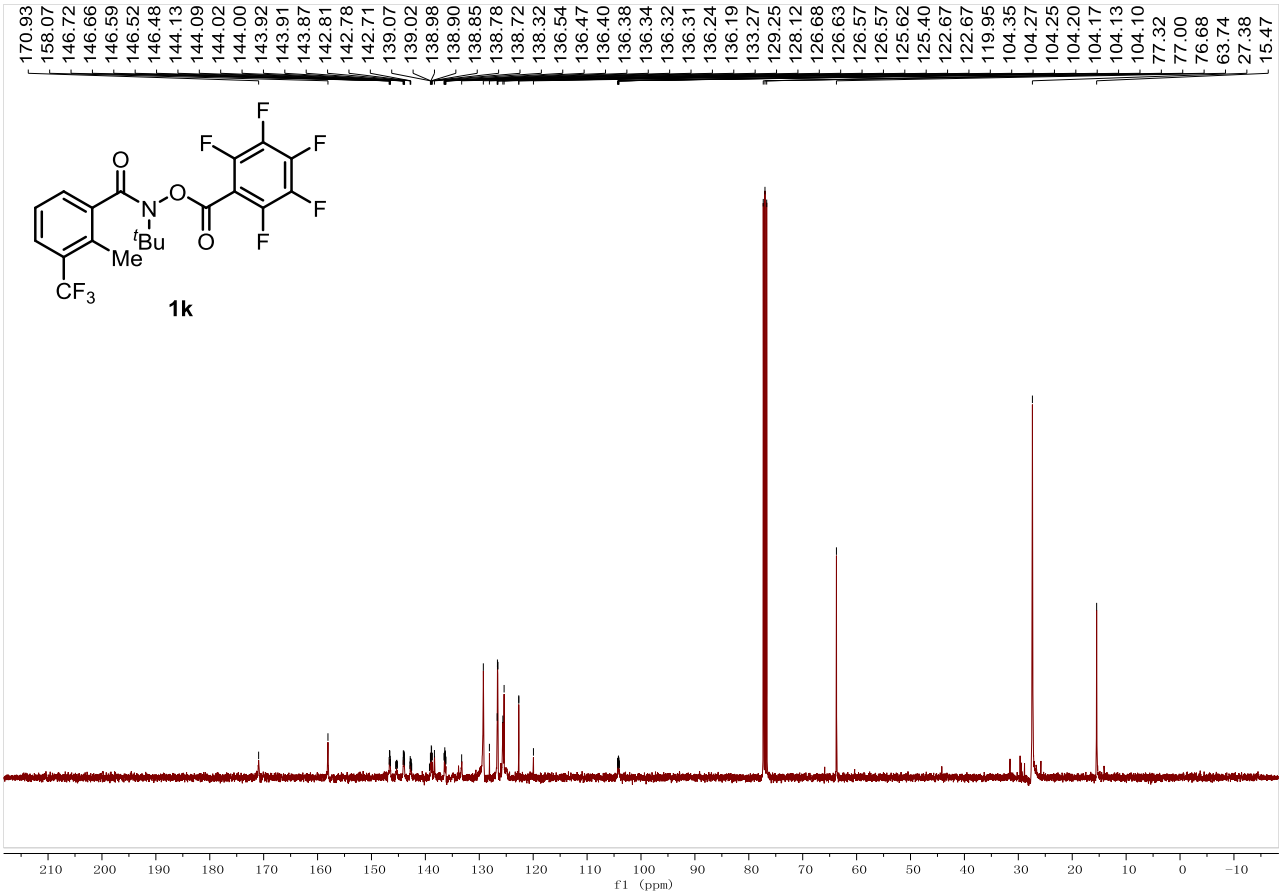
1j, ^{19}F NMR (376 MHz, $CDCl_3$)



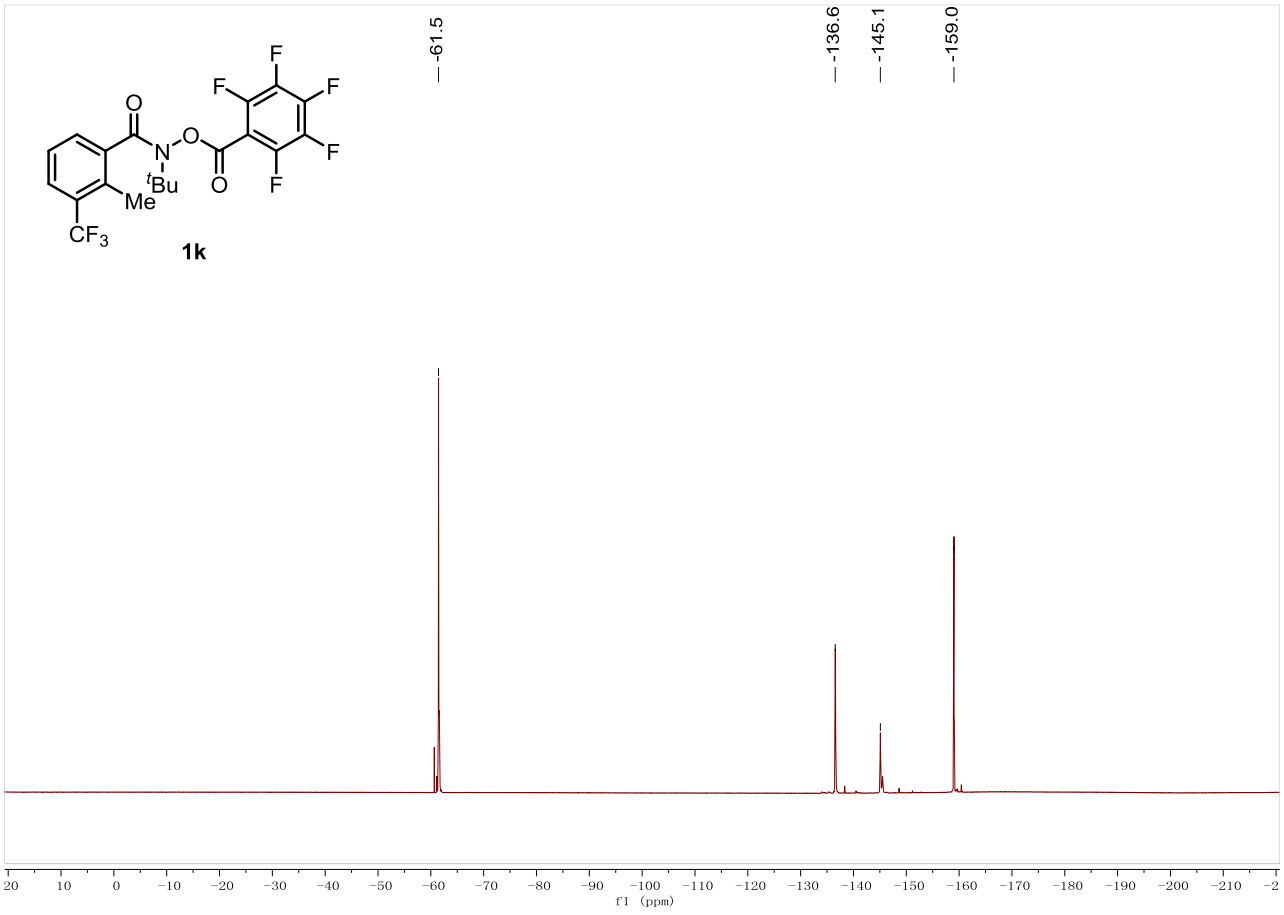
1k, ^{1}H NMR (400 MHz, $CDCl_3$)



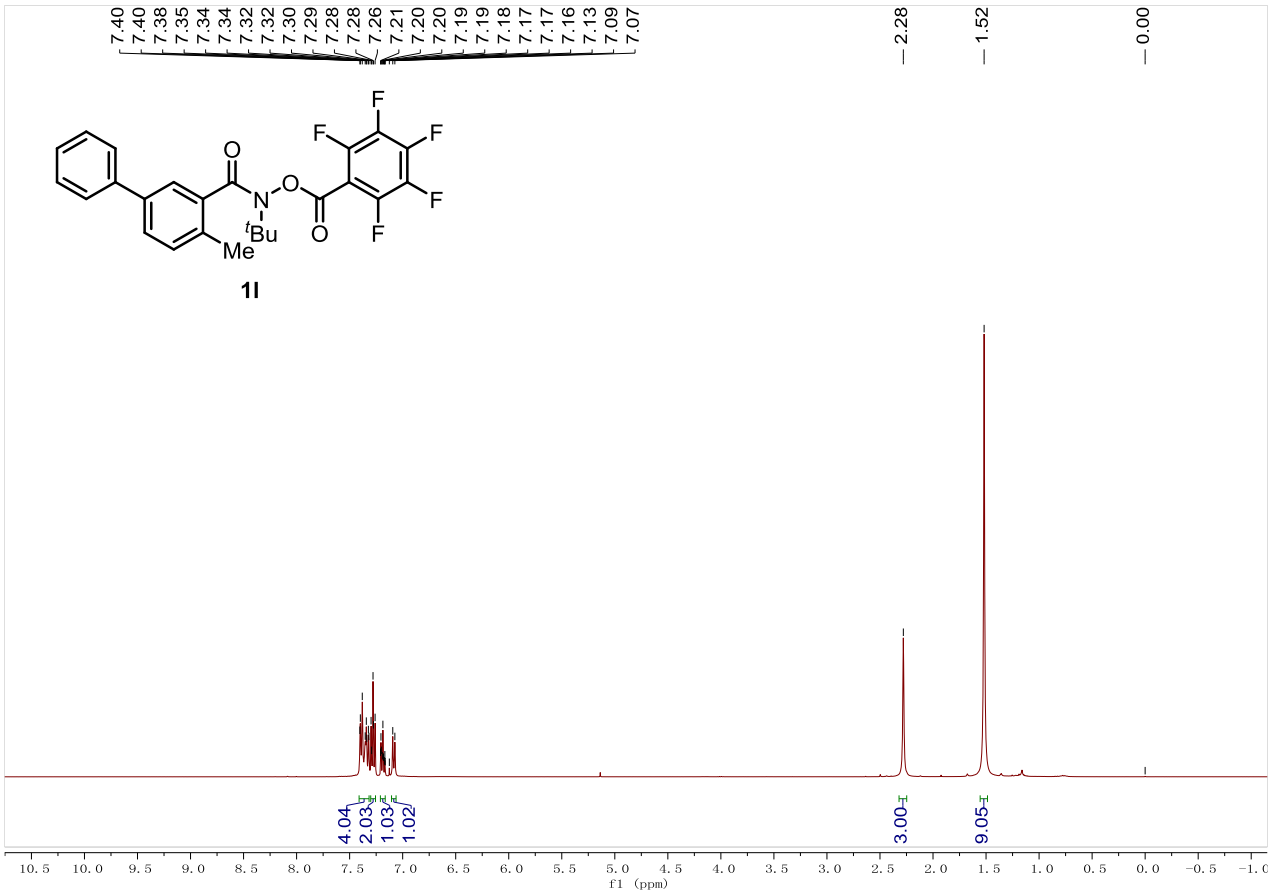
1k, ^{13}C NMR (101 MHz, $CDCl_3$)



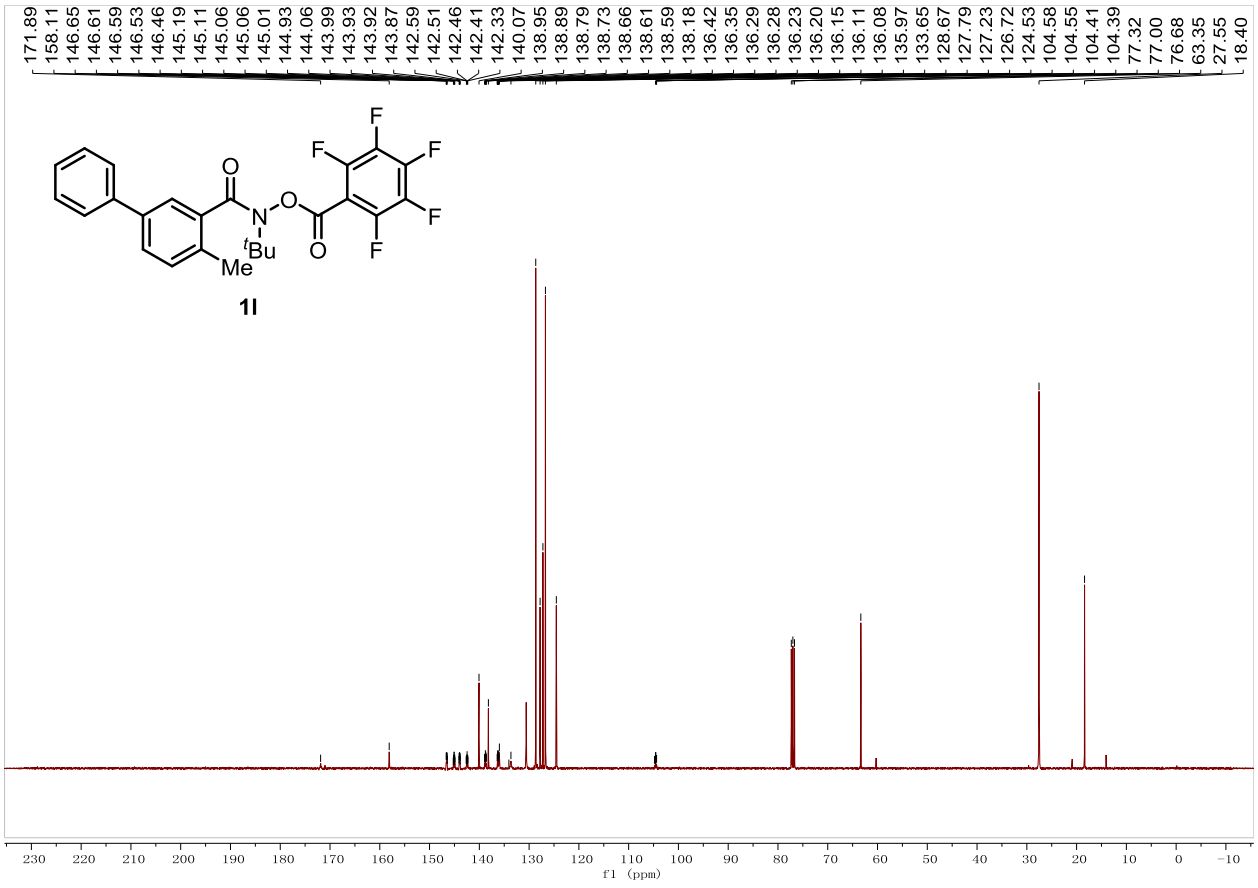
1k, ^{19}F NMR (376 MHz, $CDCl_3$)



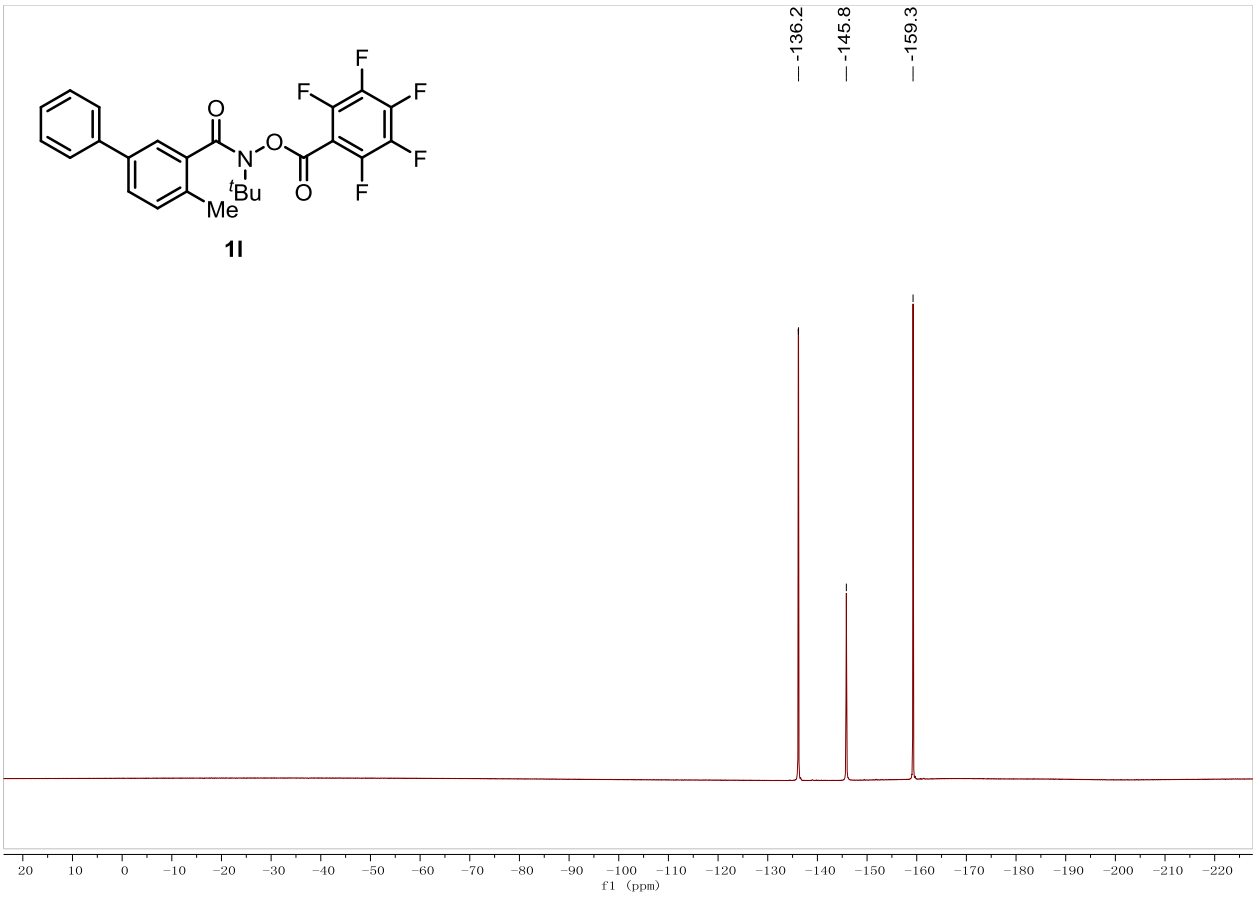
1l, ^{1}H NMR (400 MHz, $CDCl_3$)



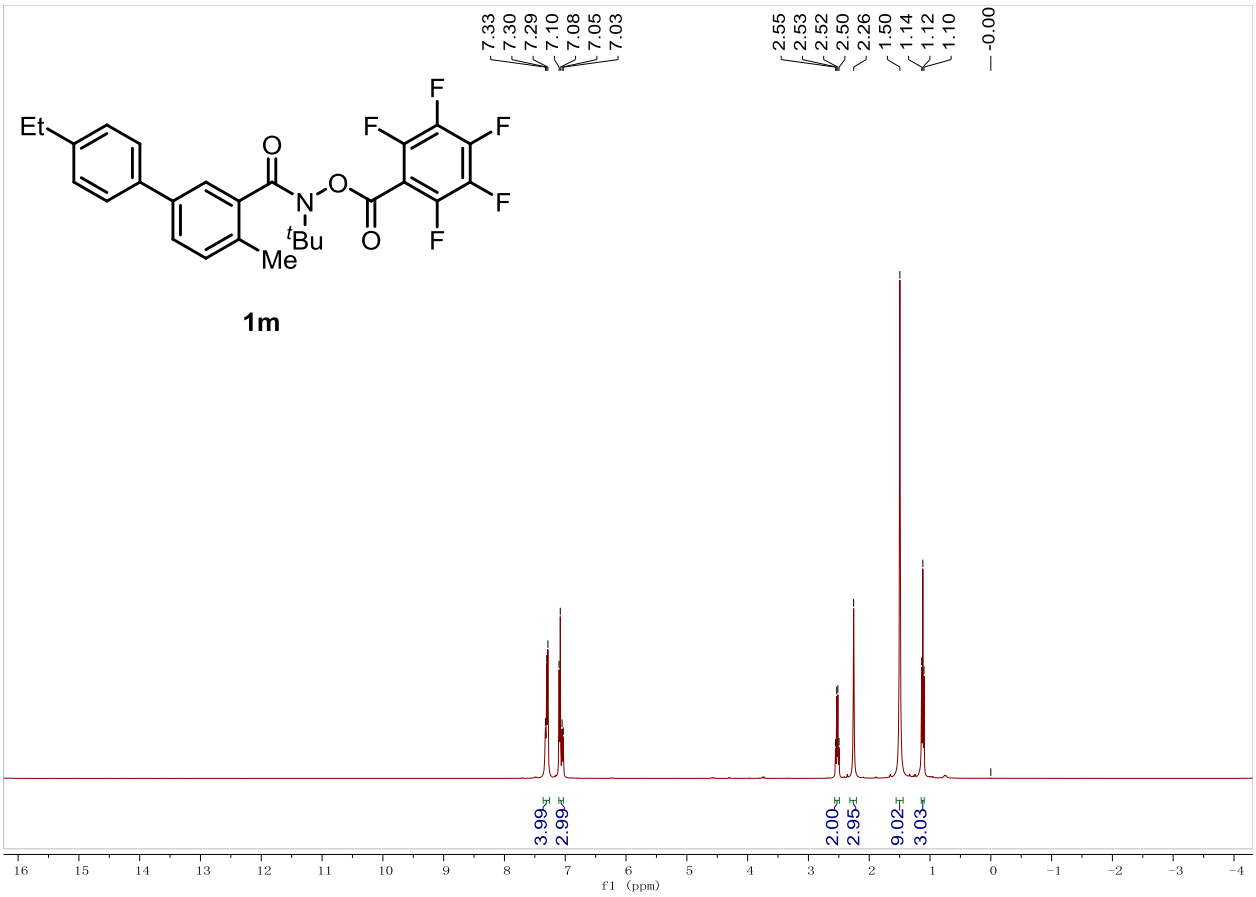
1l, ^{13}C NMR (101 MHz, $CDCl_3$)



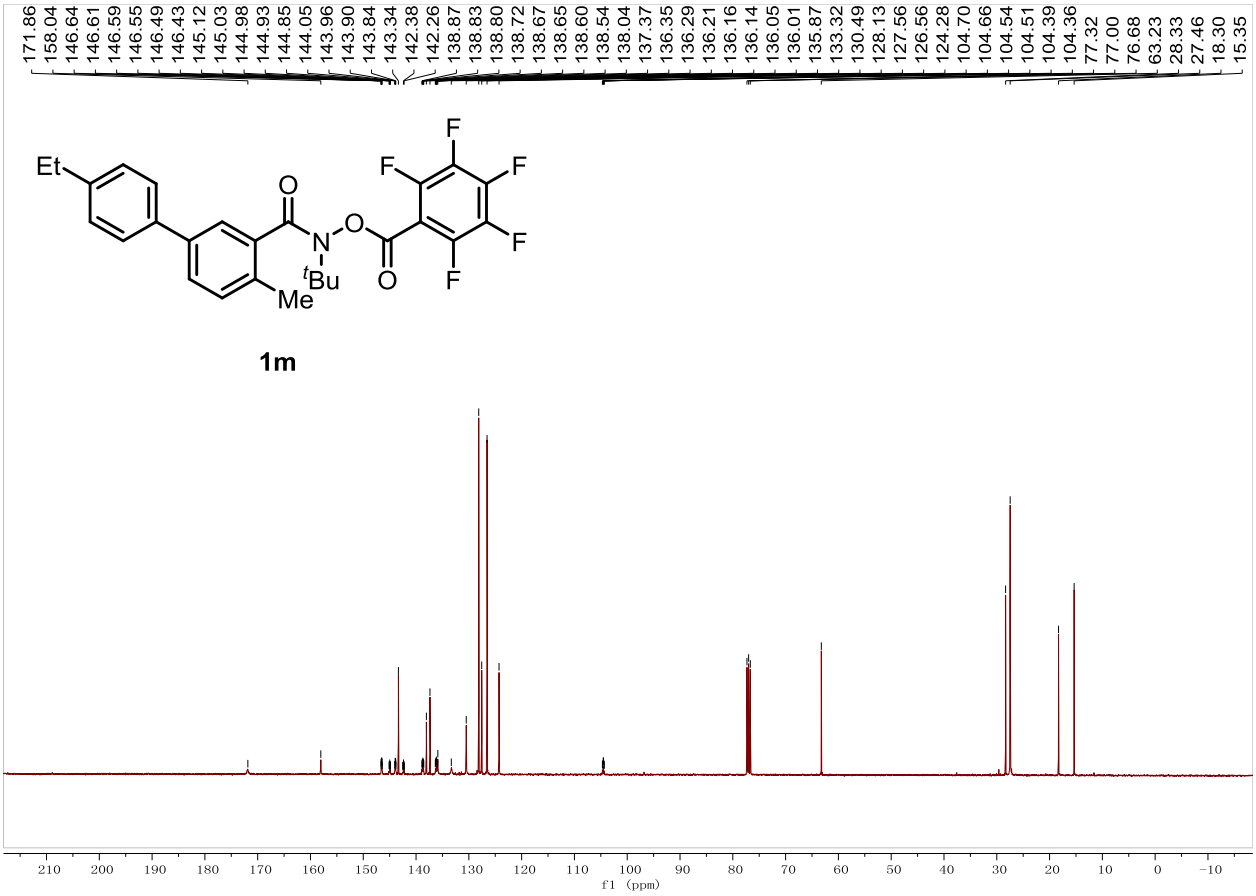
1l, ^{19}F NMR (376 MHz, $CDCl_3$)



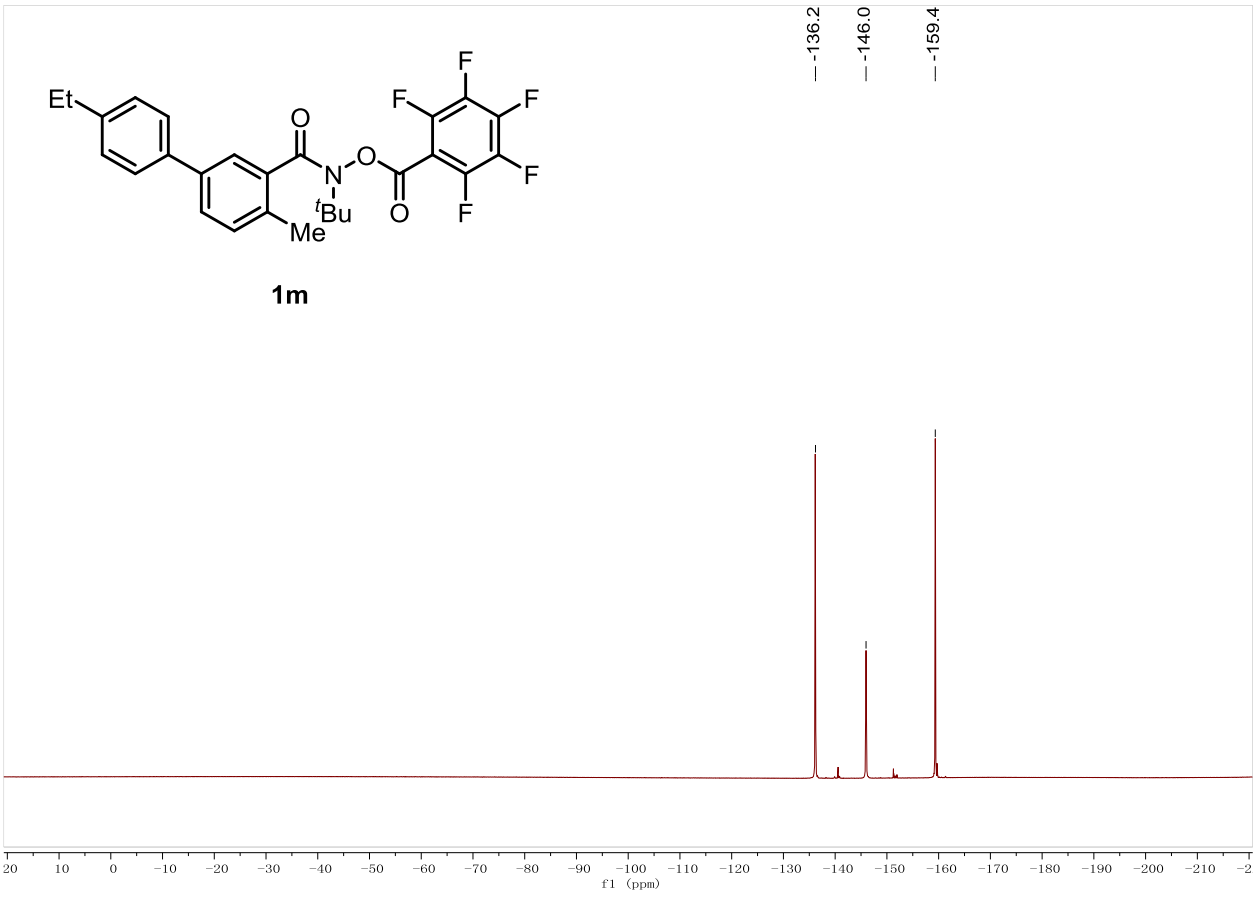
1m, ^{1}H NMR (400 MHz, $CDCl_3$)



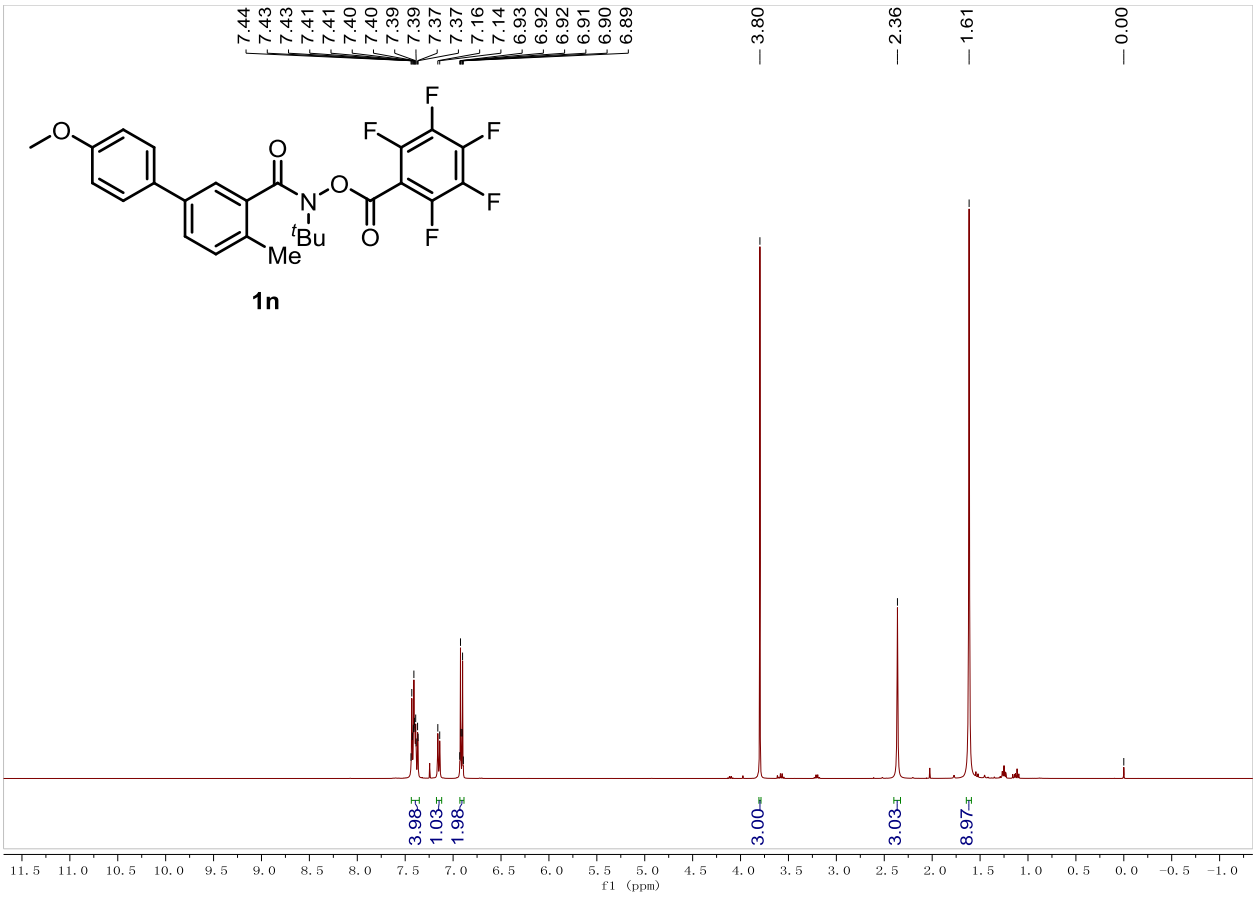
1m, ^{13}C NMR (101 MHz, $CDCl_3$)



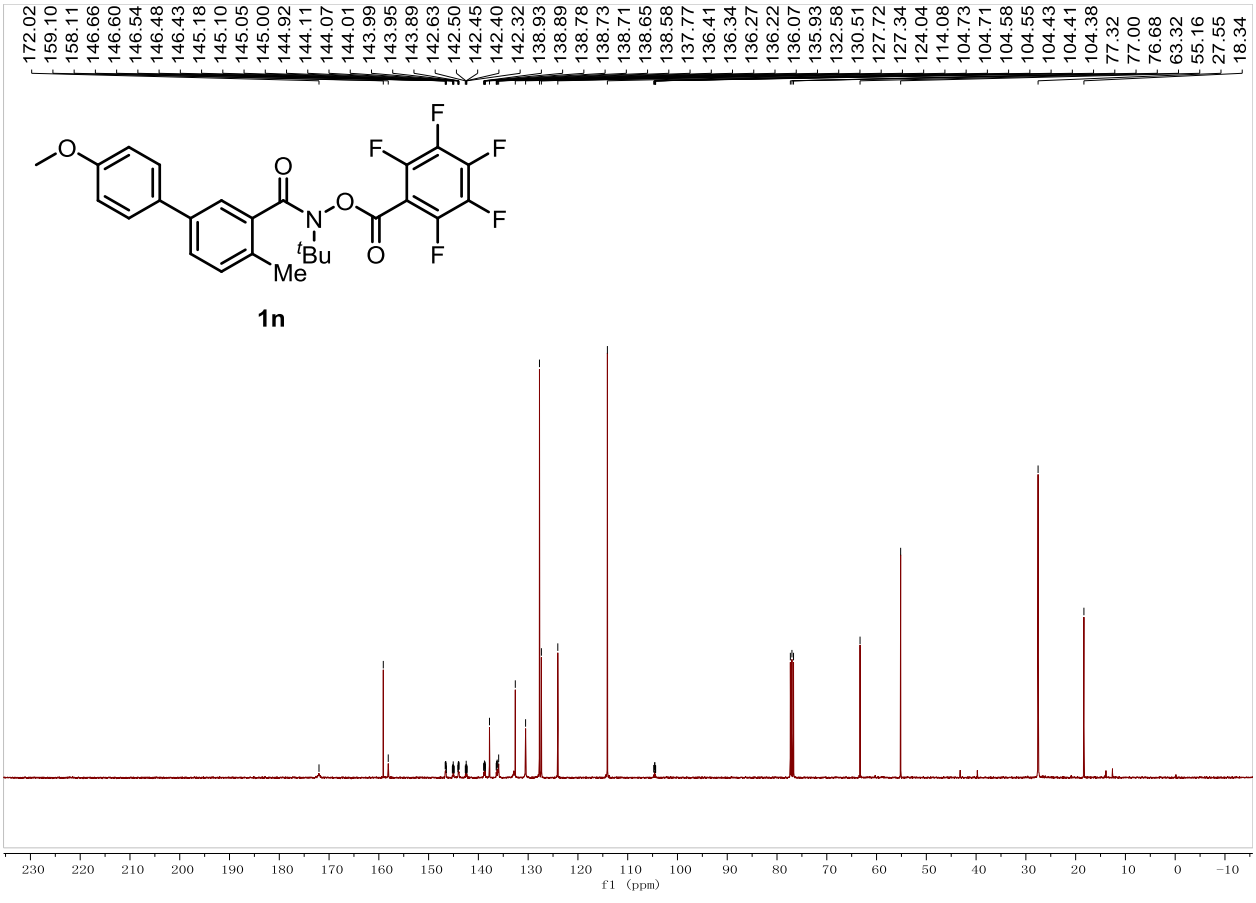
1m, ^{19}F NMR (376 MHz, $CDCl_3$)



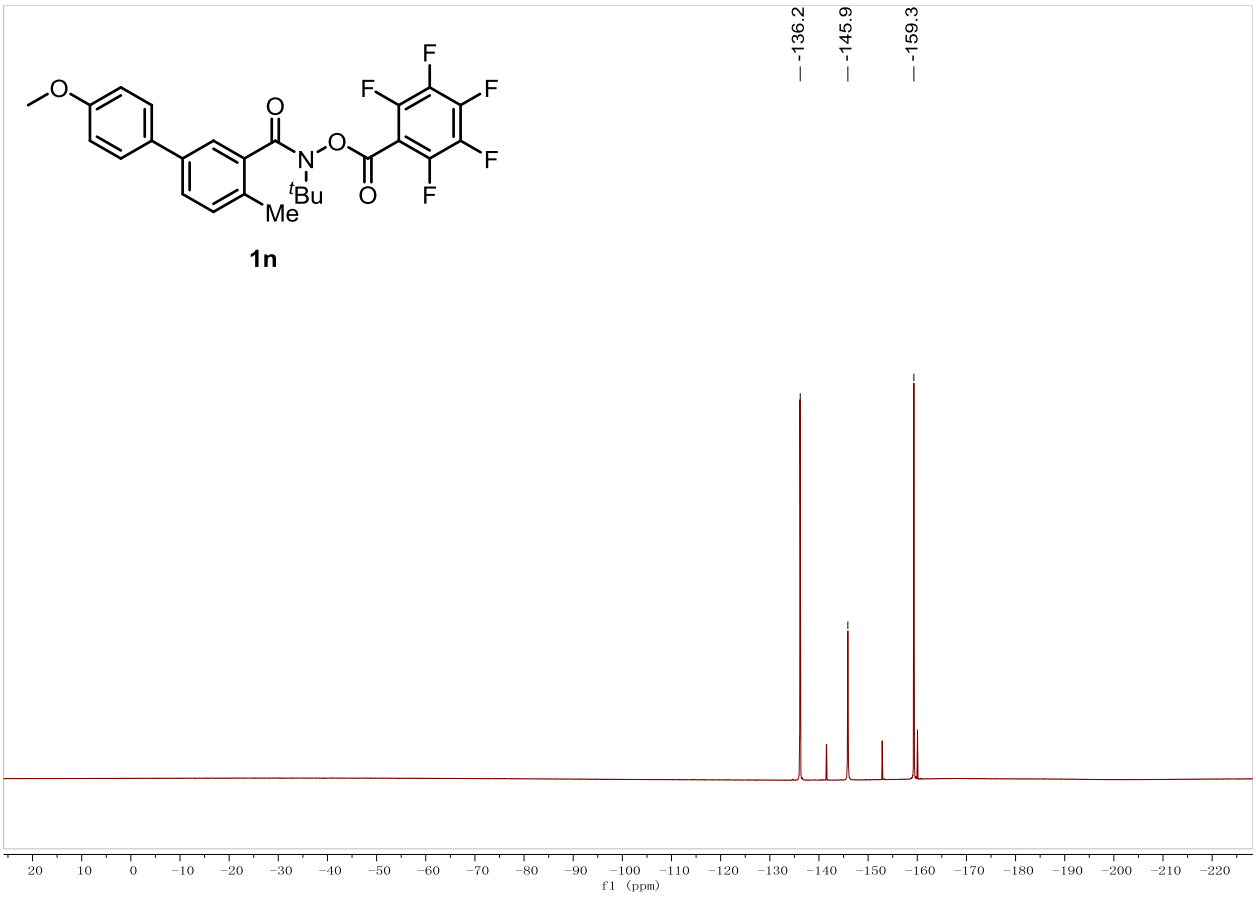
1n, ^{1}H NMR (400 MHz, $CDCl_3$)



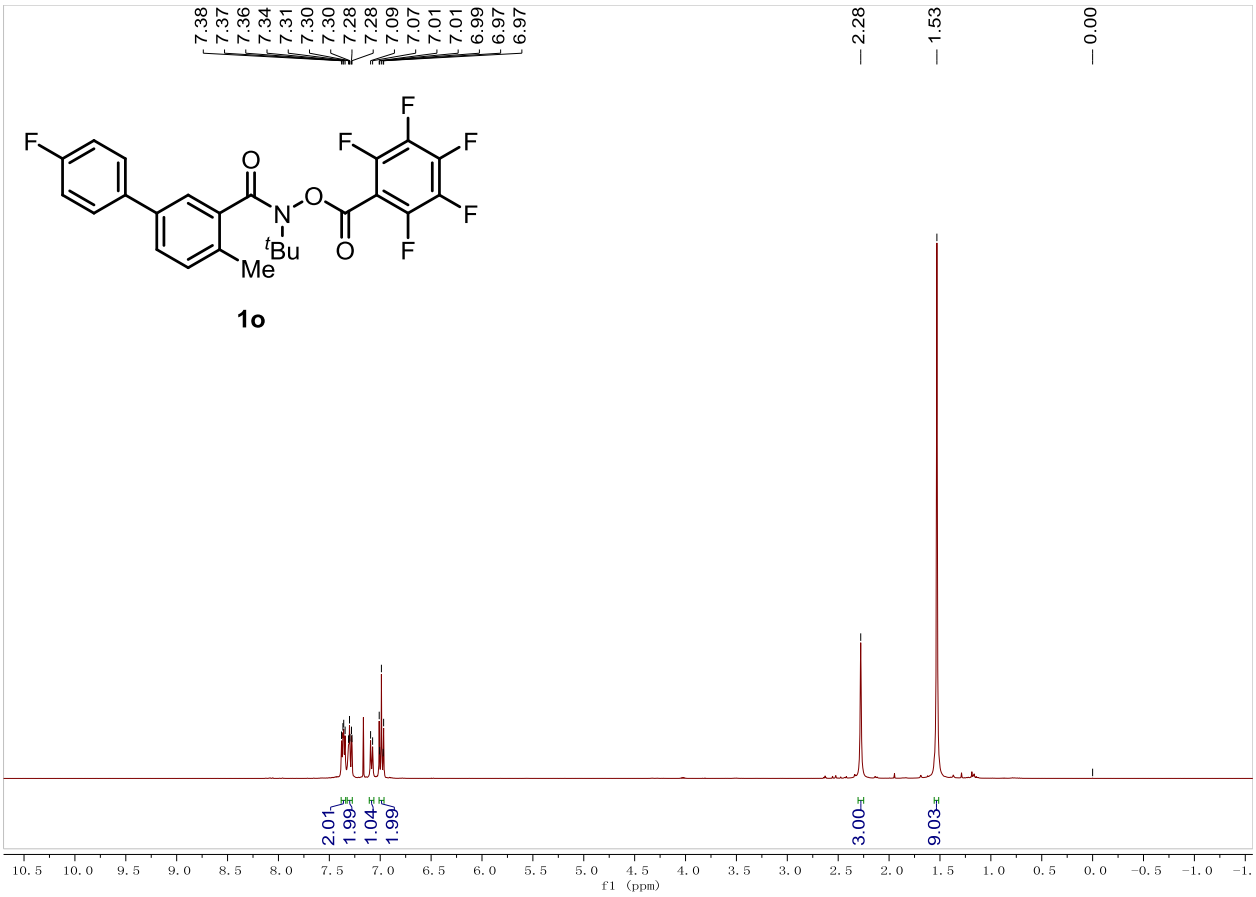
1n, ^{13}C NMR (101 MHz, $CDCl_3$)



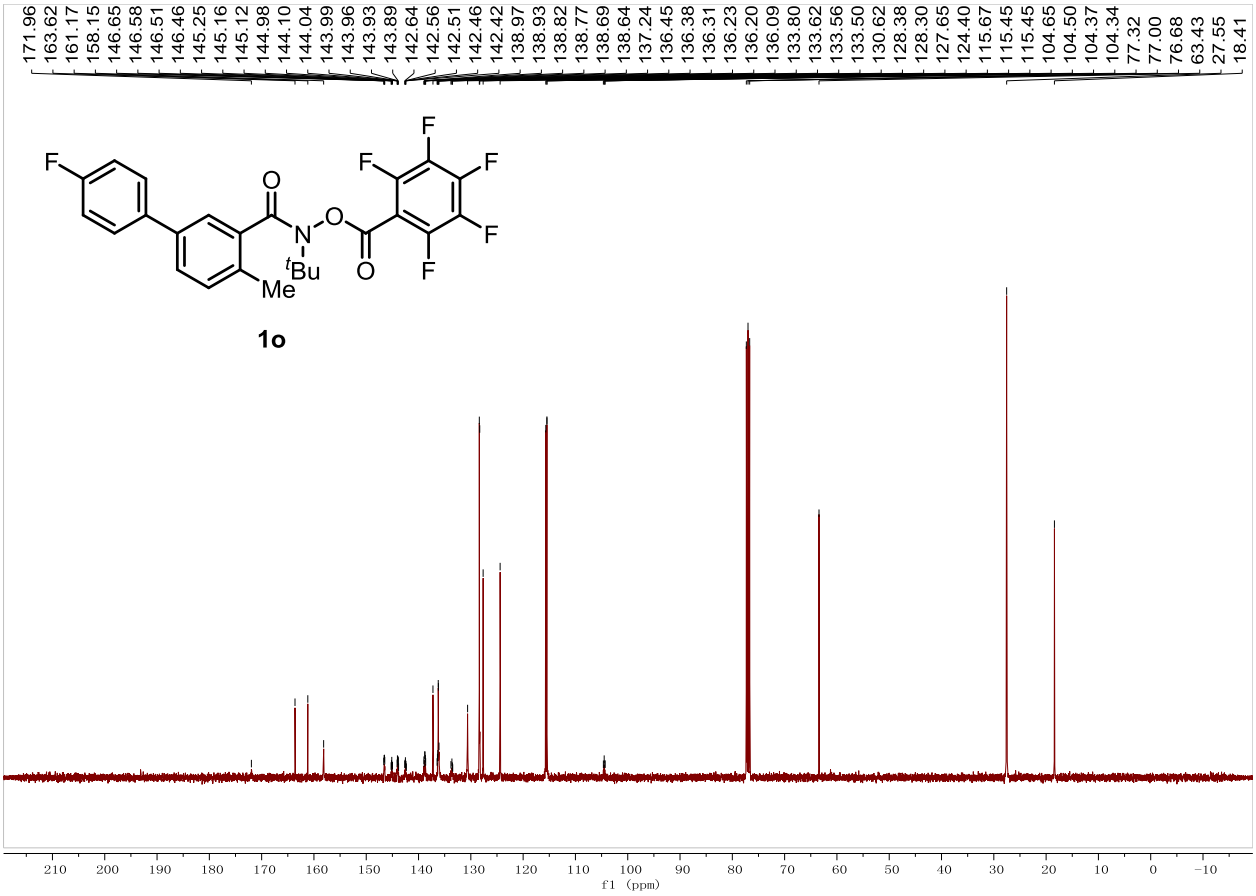
1n, ^{19}F NMR (376 MHz, $CDCl_3$)



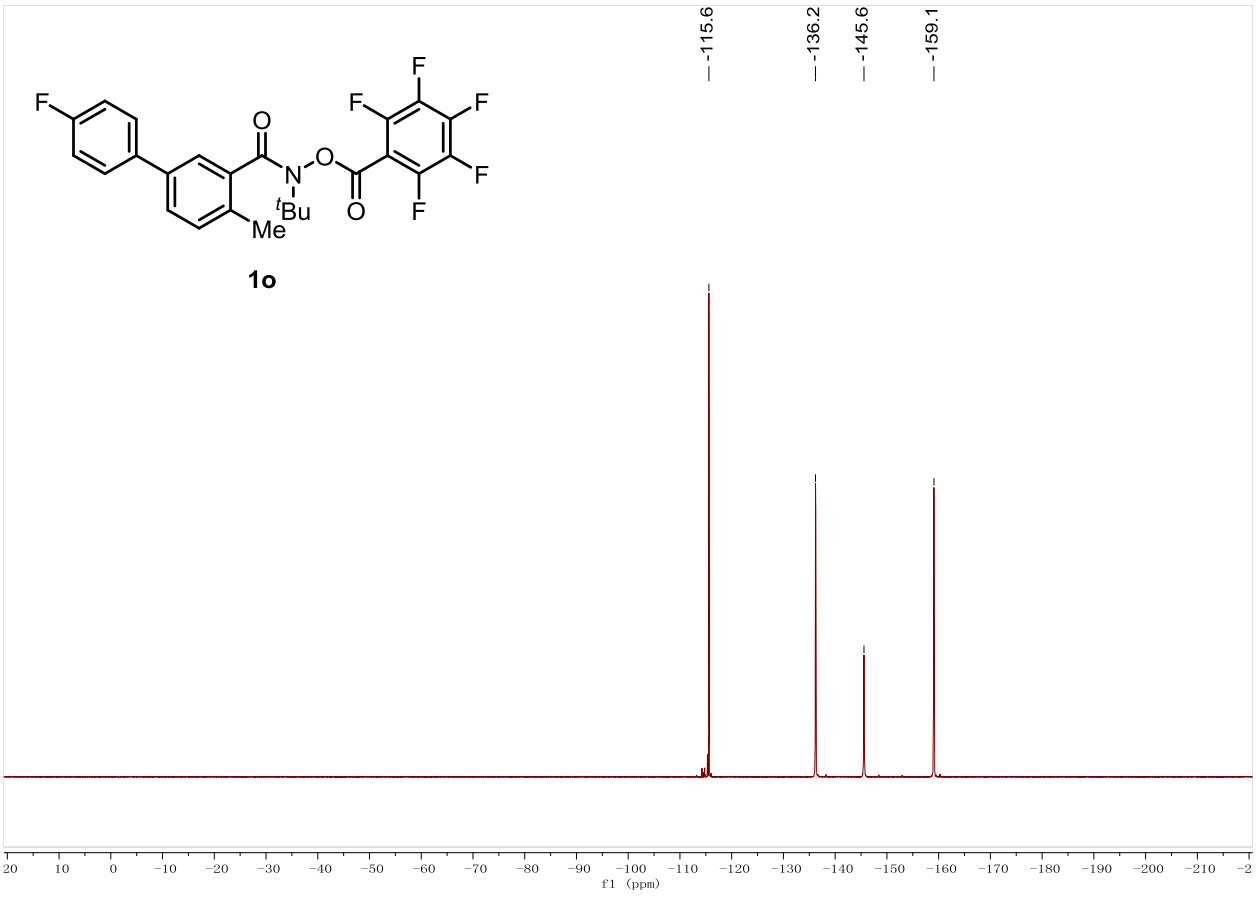
1o, ^{1}H NMR (400 MHz, CDCl$_3$)



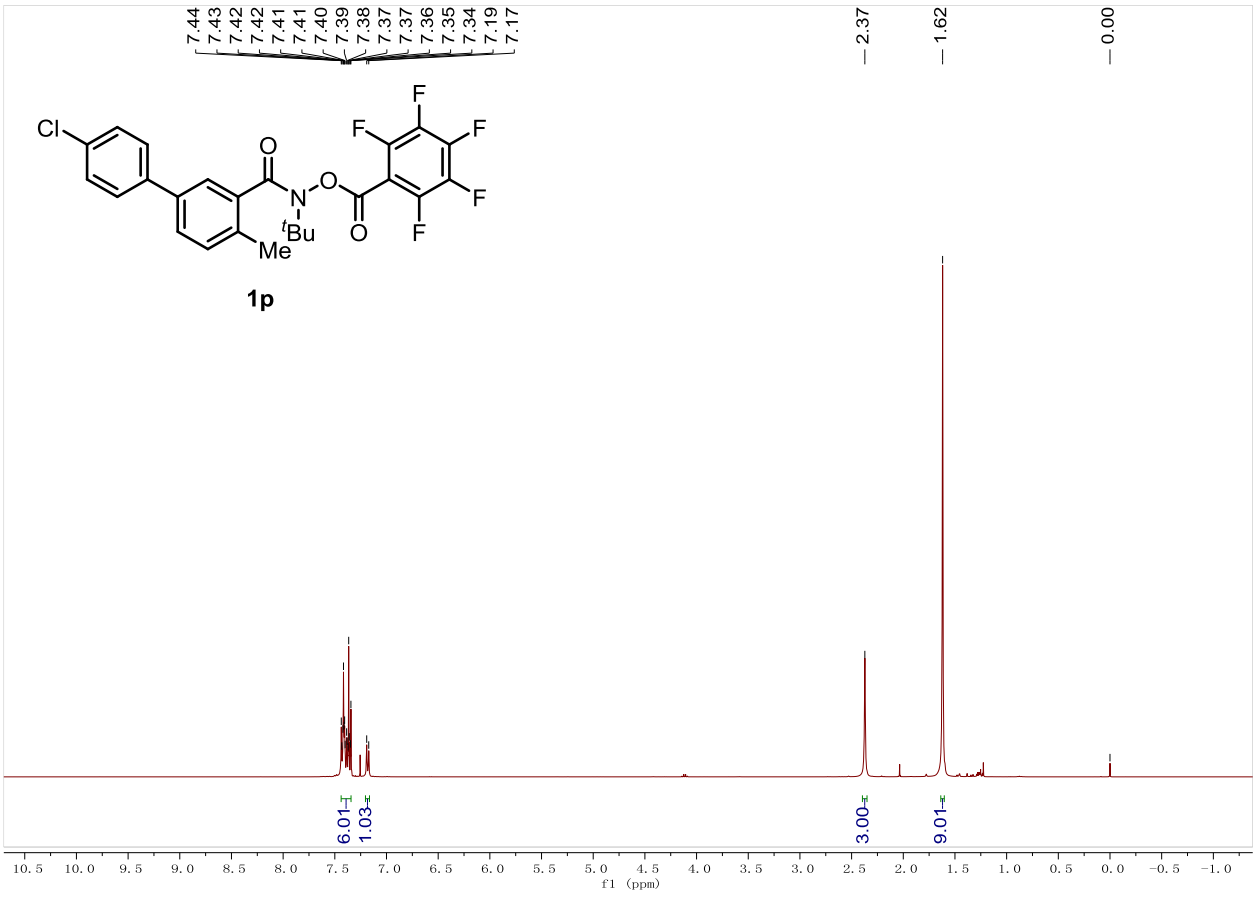
1o, ^{13}C NMR (101 MHz, CDCl$_3$)



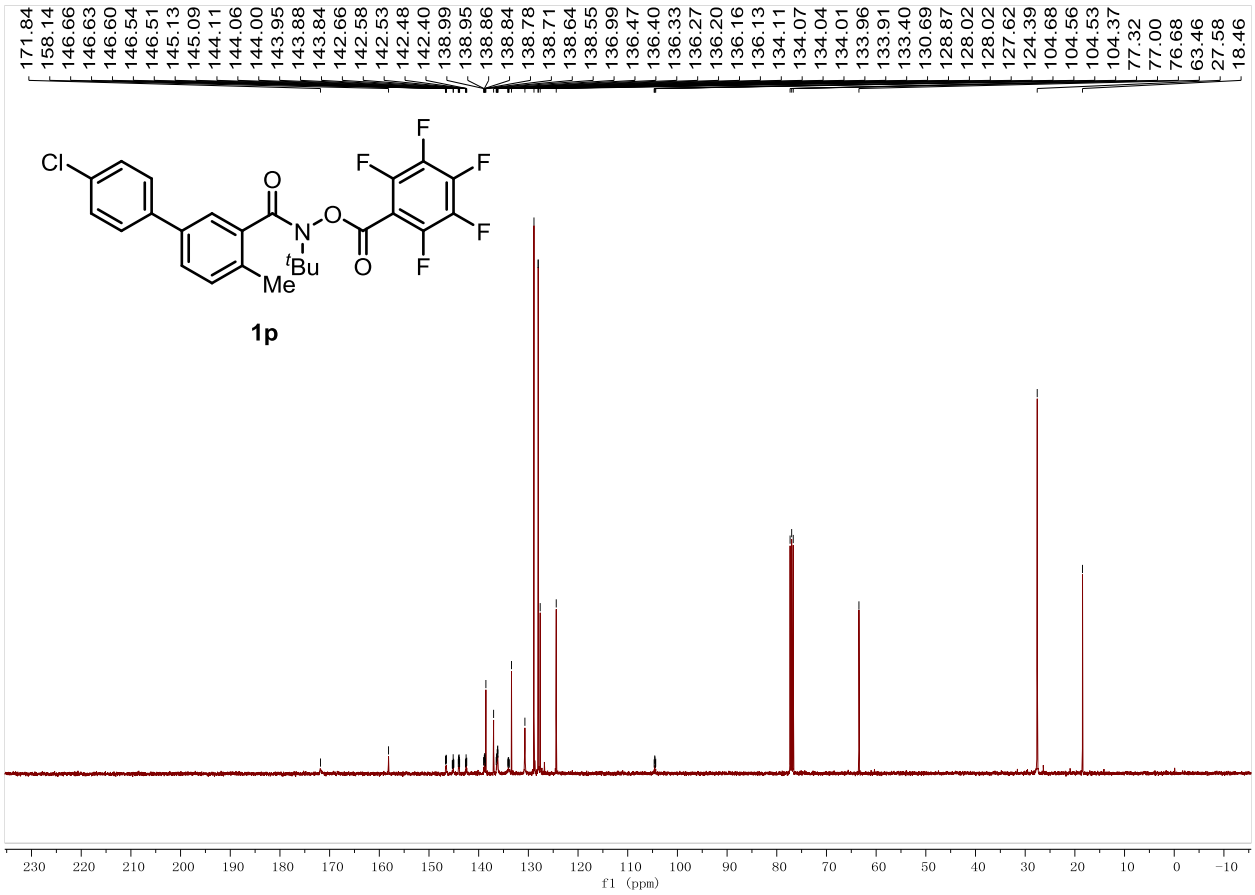
1o, ^{19}F NMR (376 MHz, $CDCl_3$)



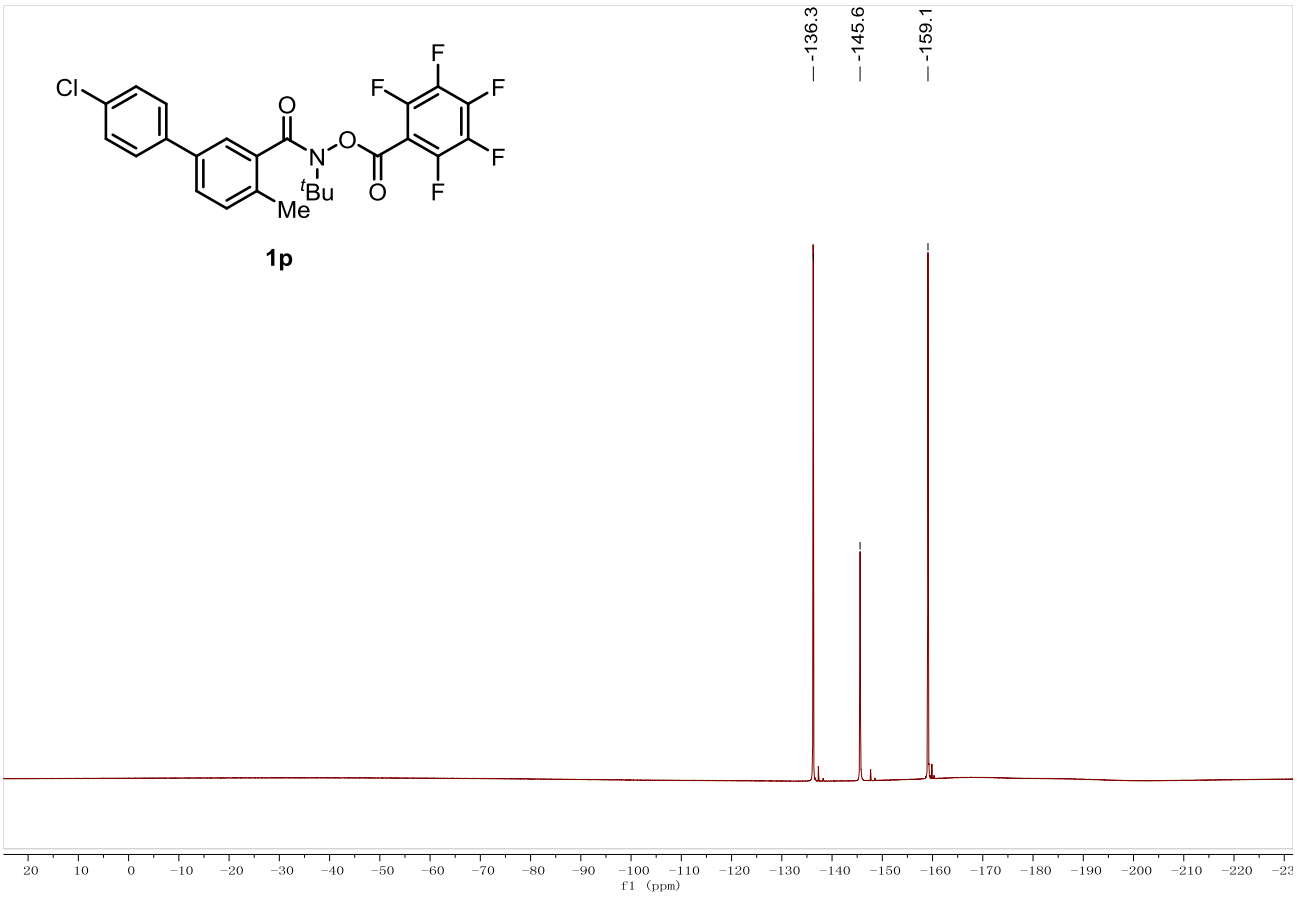
1p, ^{1}H NMR (400 MHz, CDCl$_3$)



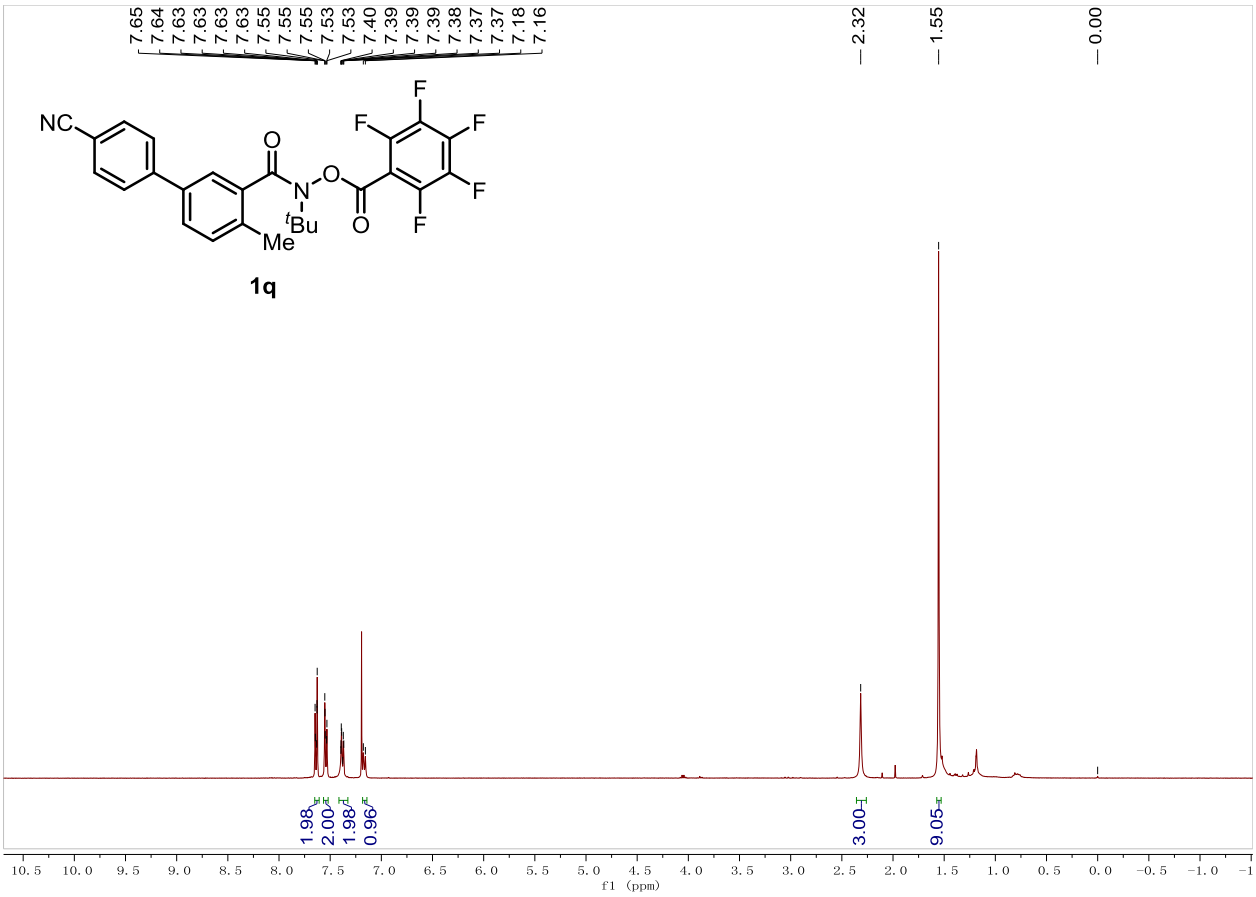
1p, ^{13}C NMR (101 MHz, CDCl$_3$)



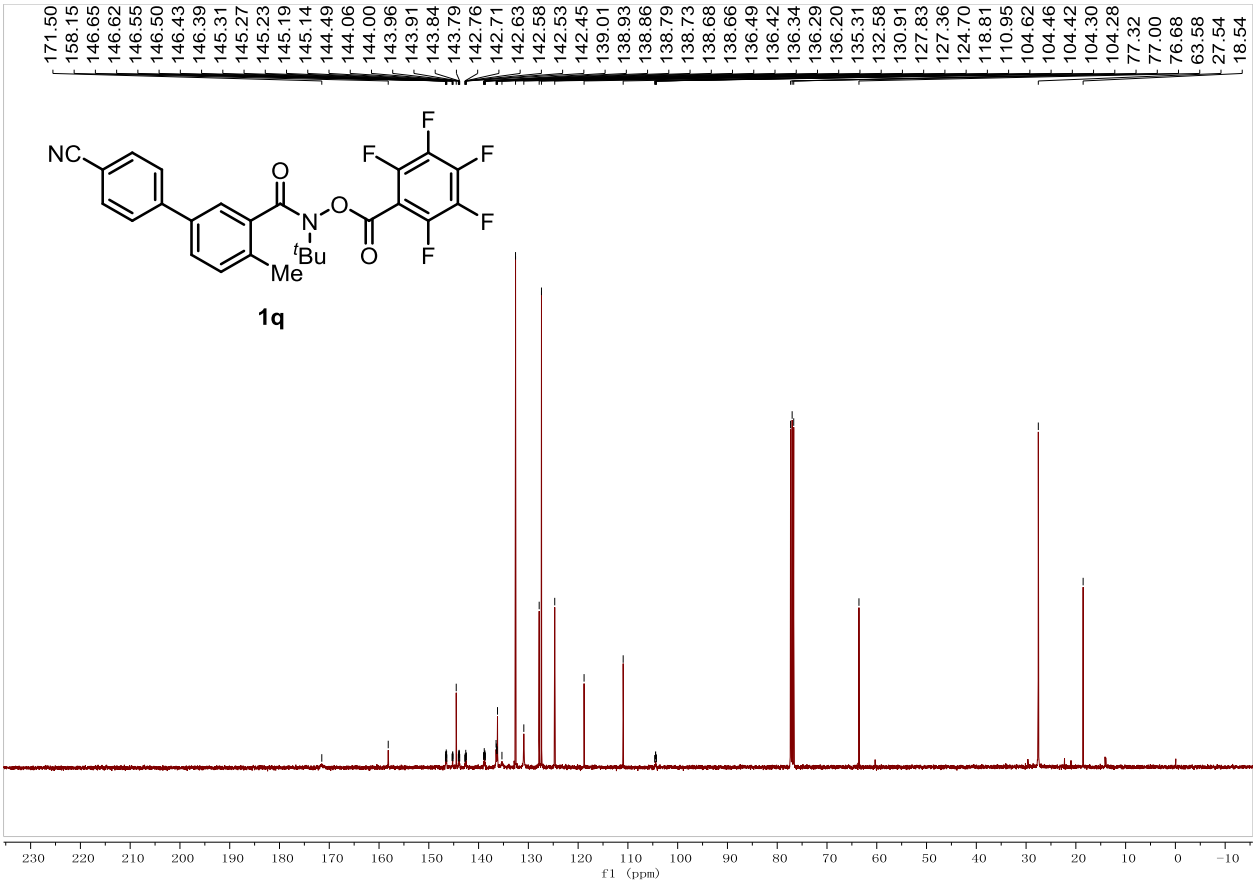
1p, ^{19}F NMR (376 MHz, $CDCl_3$)



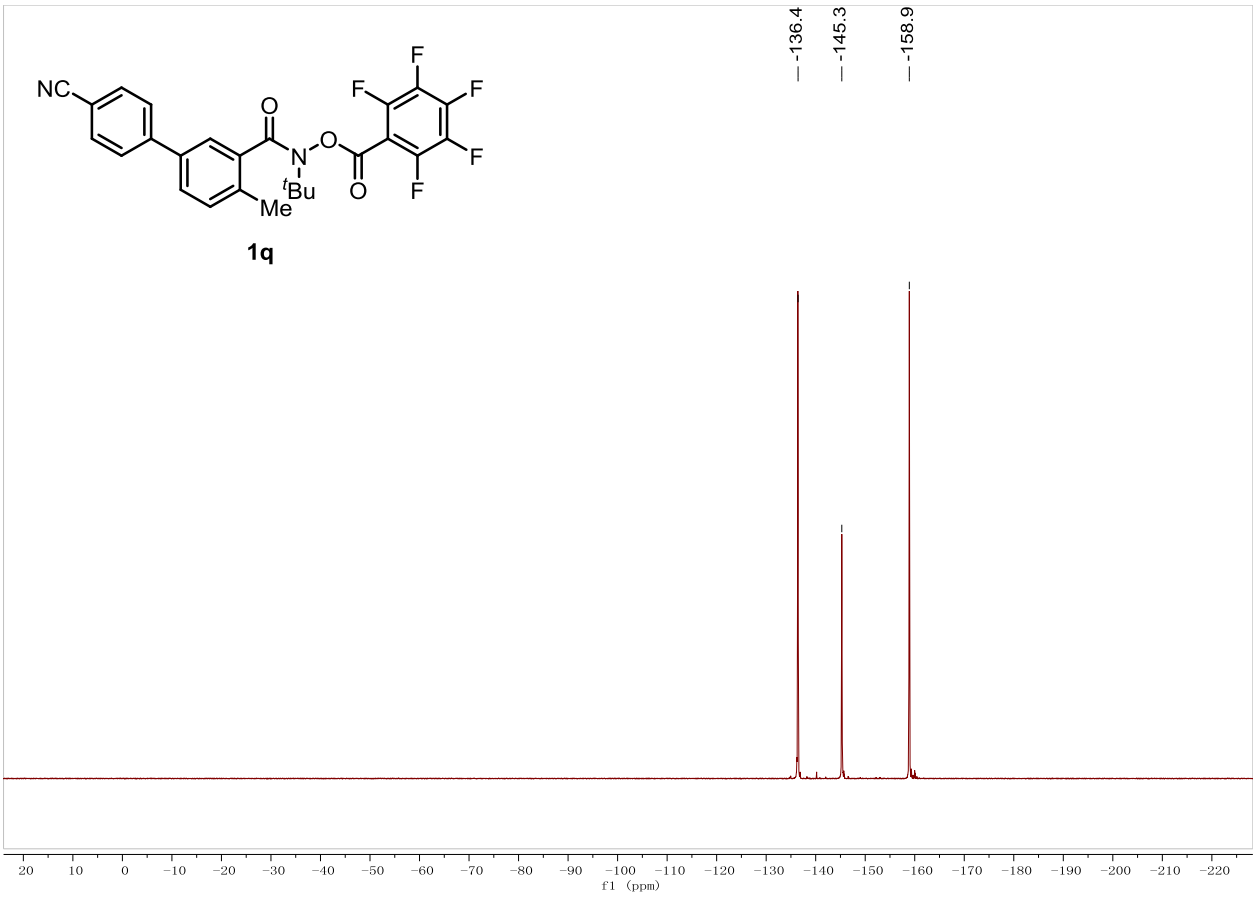
1q, ^{1}H NMR (400 MHz, CDCl$_3$)



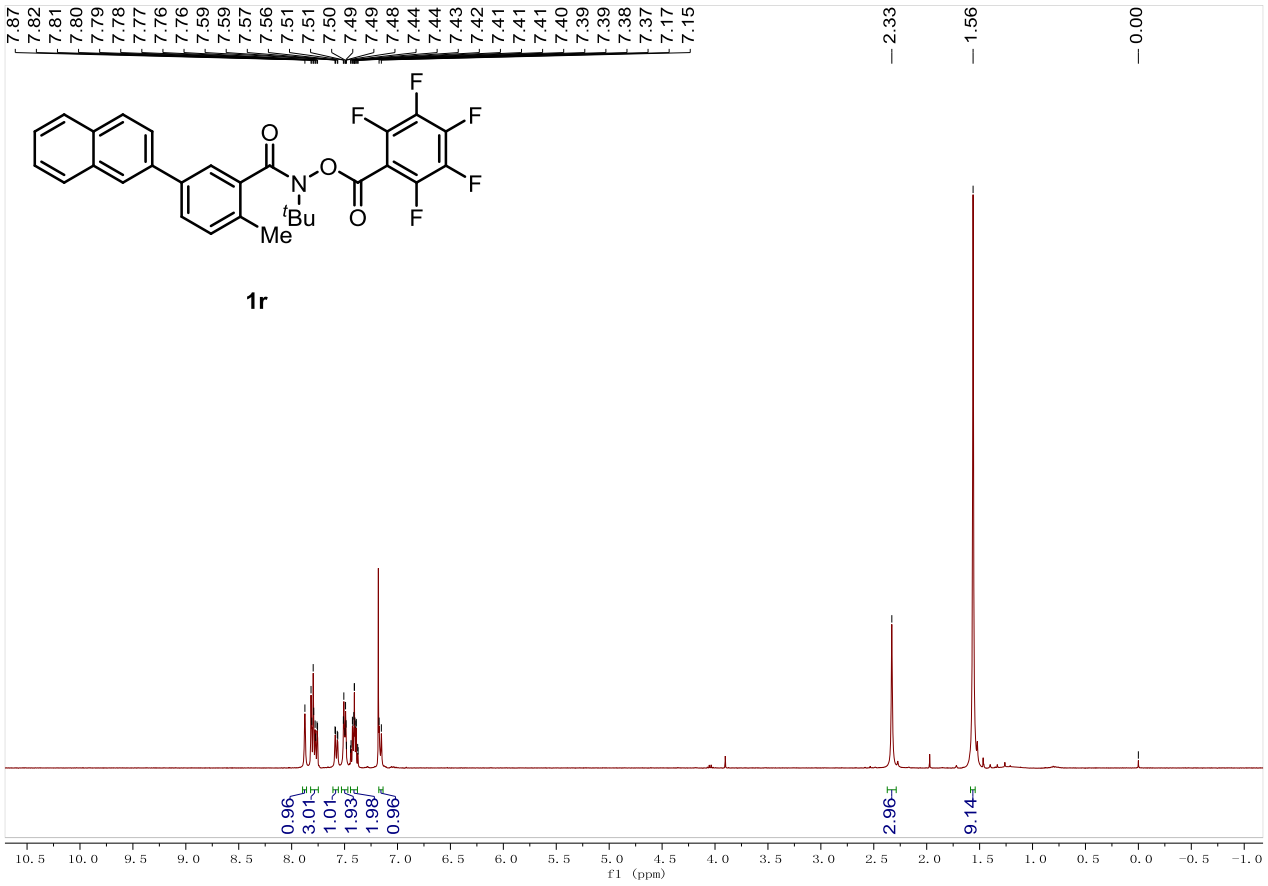
1q, ^{13}C NMR (101 MHz, CDCl$_3$)



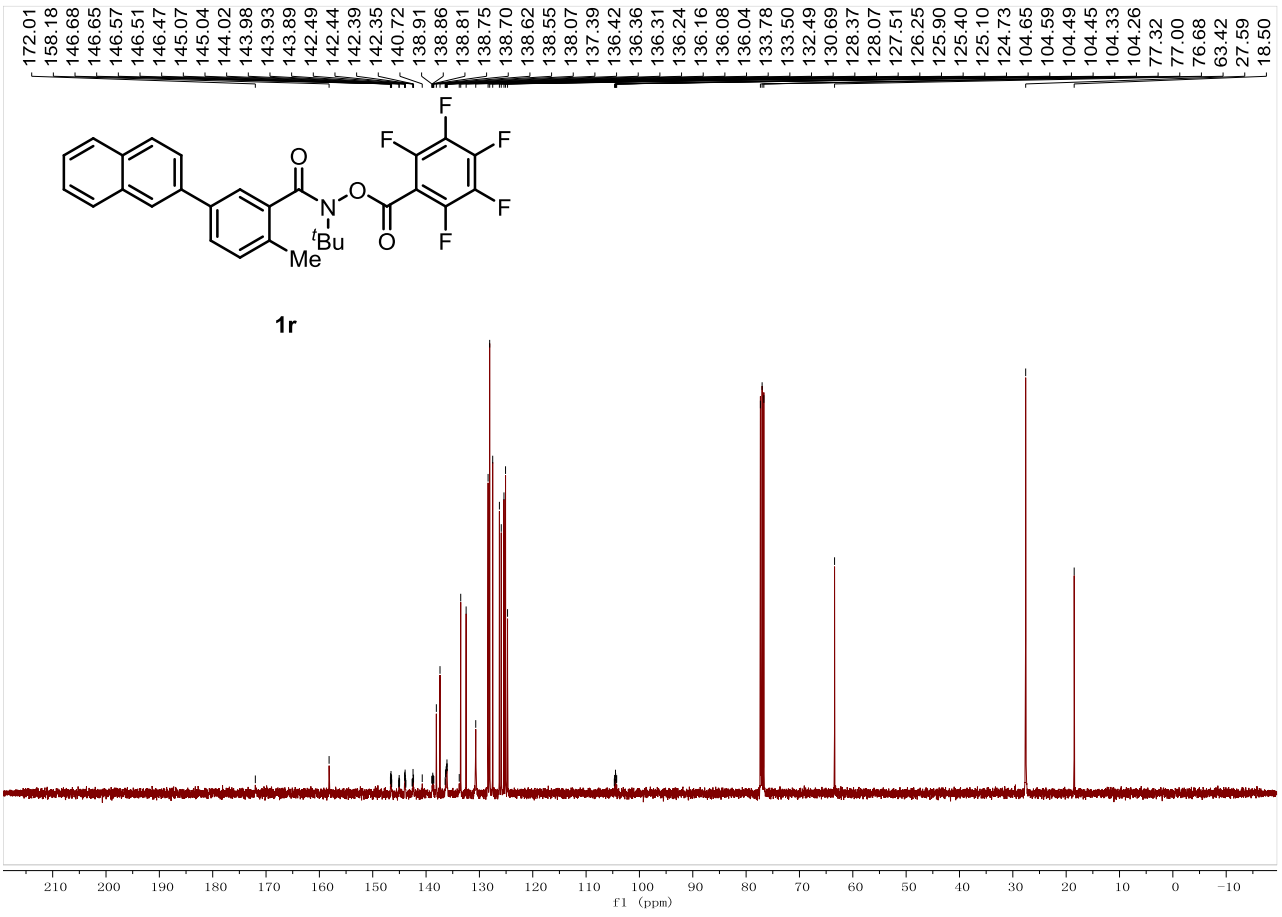
1q, ^{19}F NMR (376 MHz, $CDCl_3$)



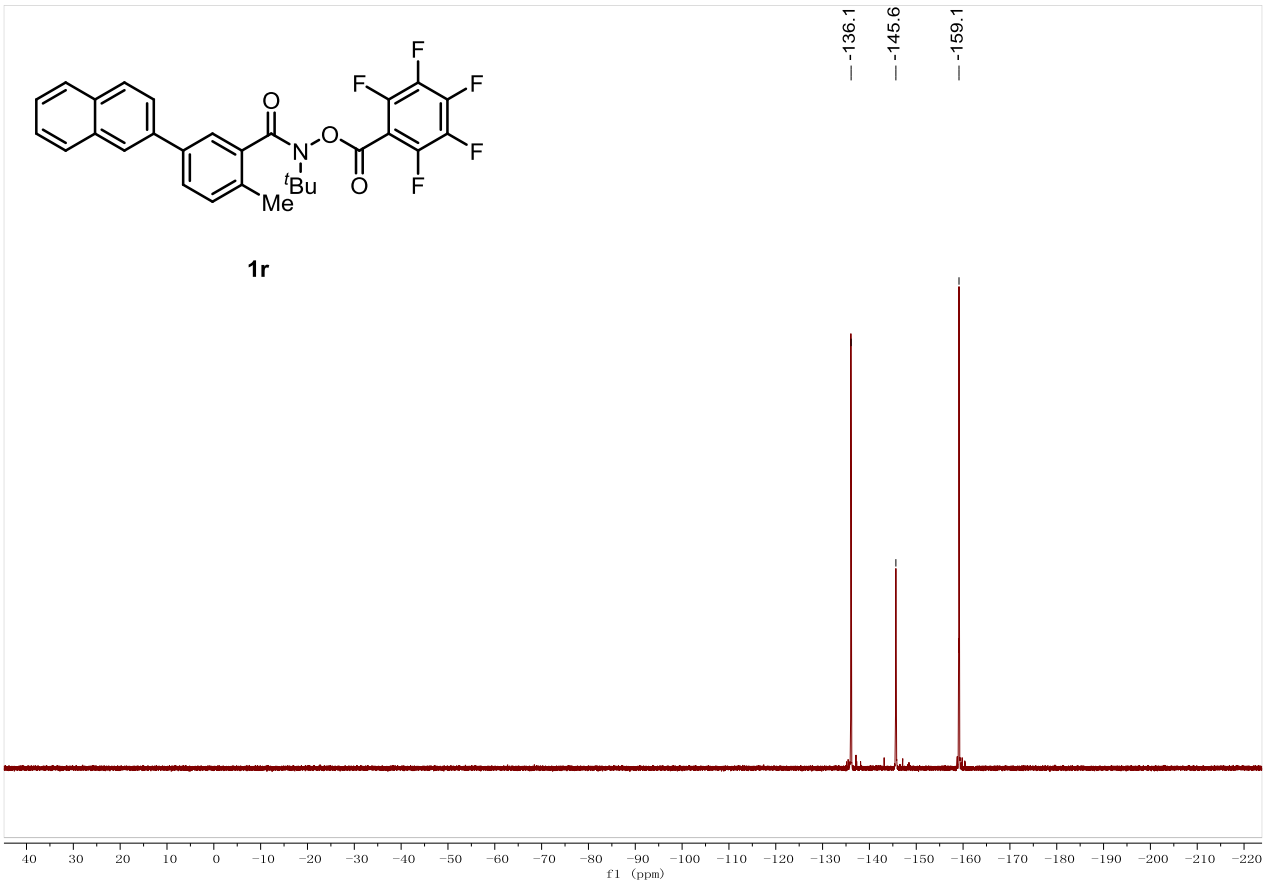
1r, ^{1}H NMR (400 MHz, $CDCl_3$)



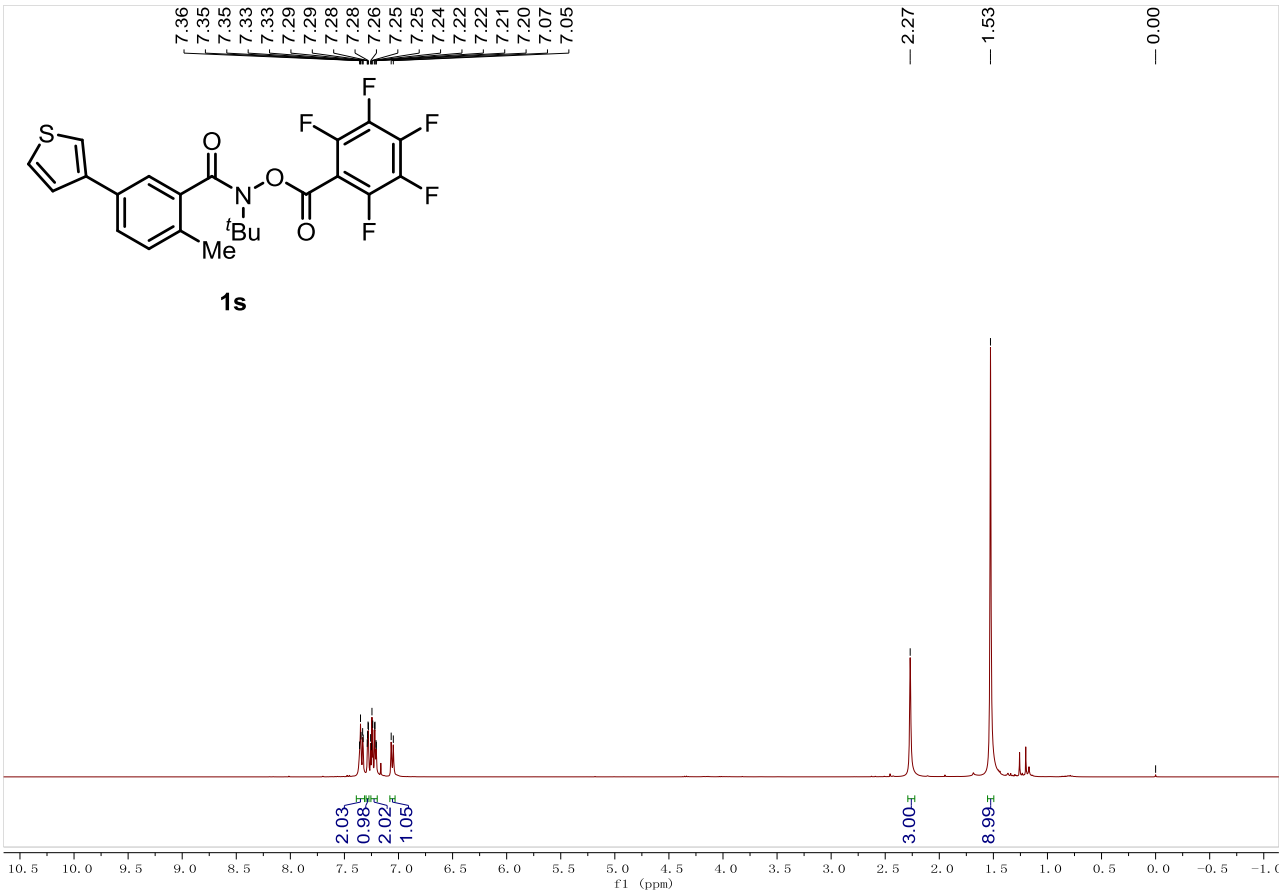
1r, ^{13}C NMR (101 MHz, $CDCl_3$)



1r, ^{19}F NMR (376 MHz, $CDCl_3$)

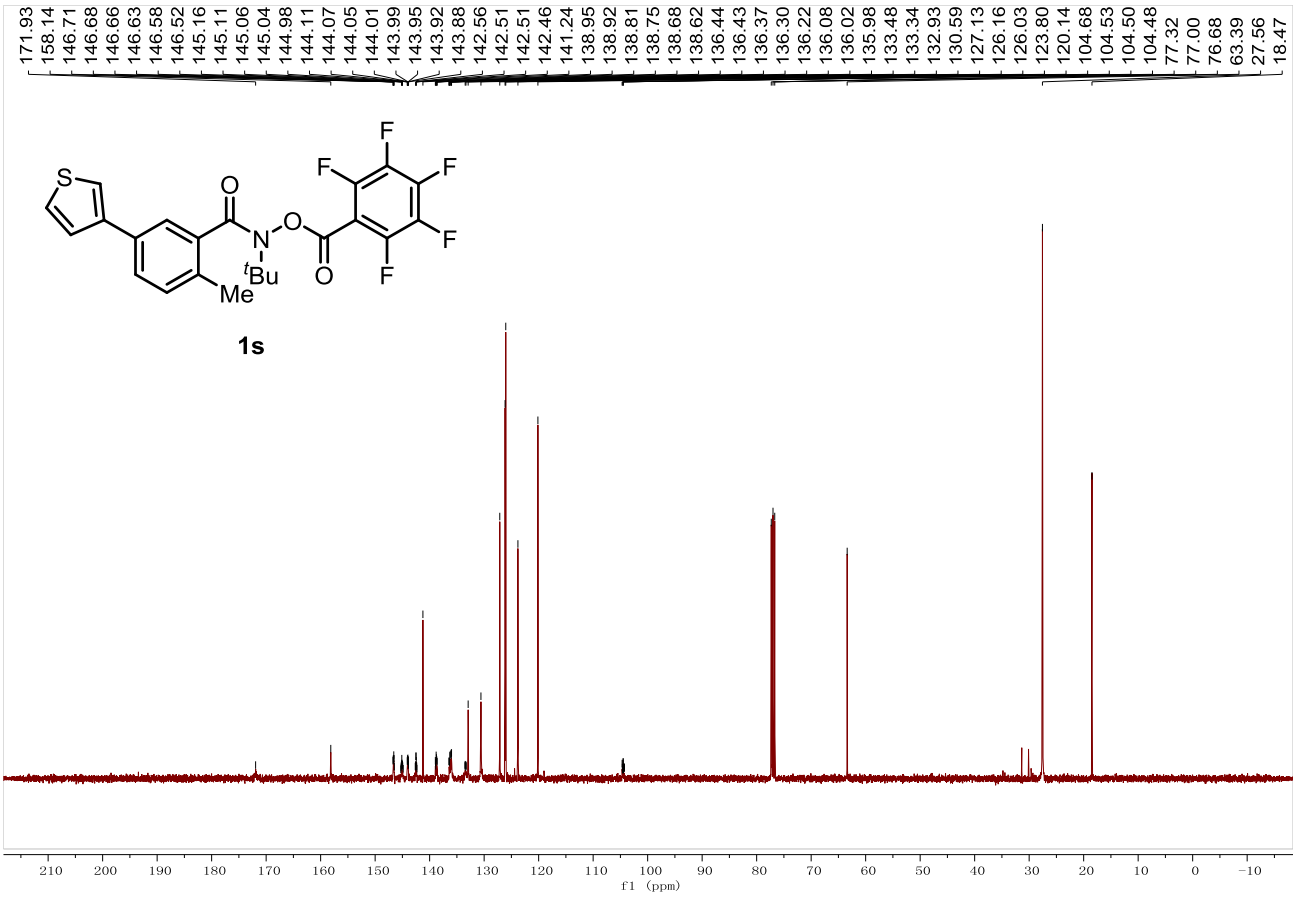


1s, ^{1}H NMR (400 MHz, $CDCl_3$)



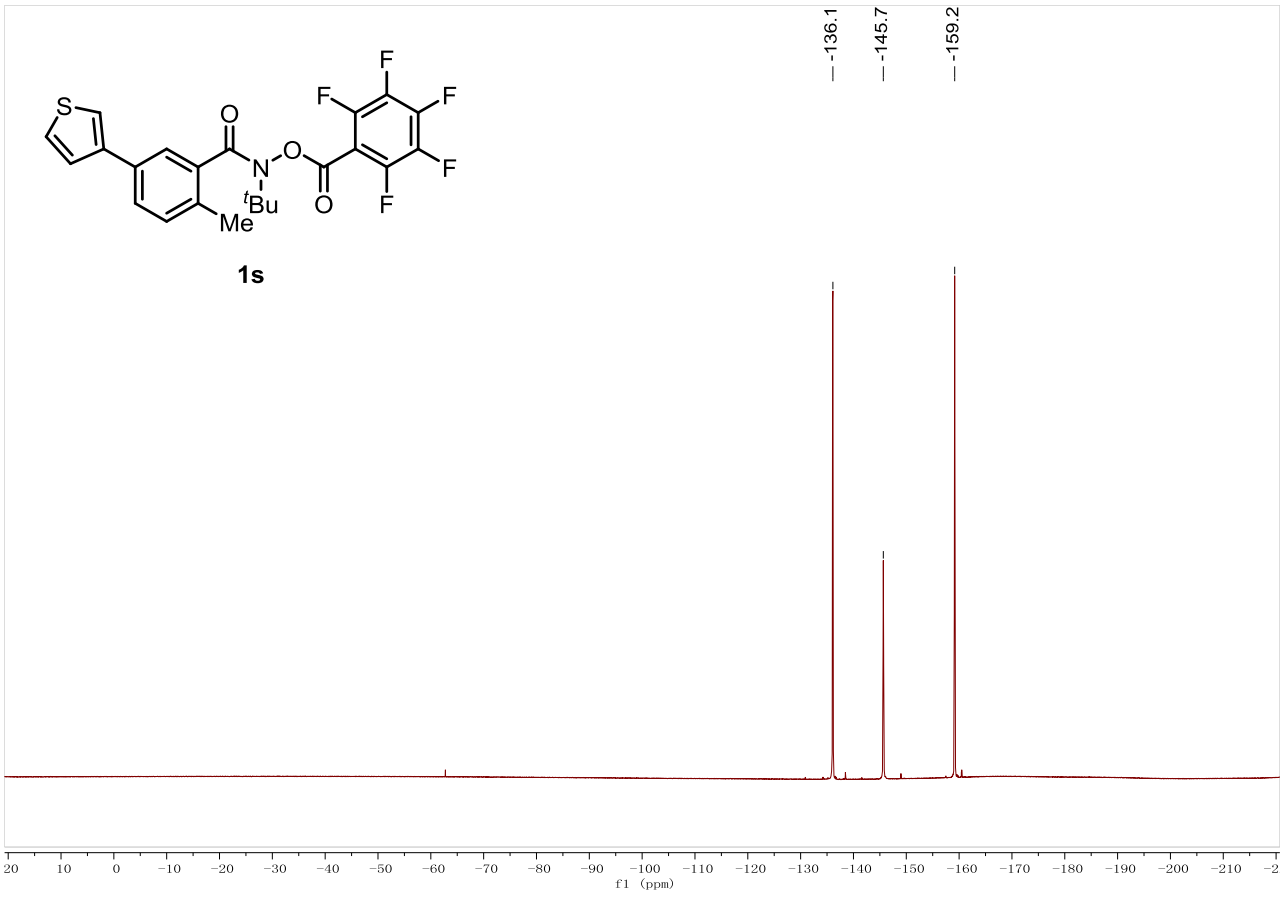
1s

1s, ^{13}C NMR (101 MHz, $CDCl_3$)

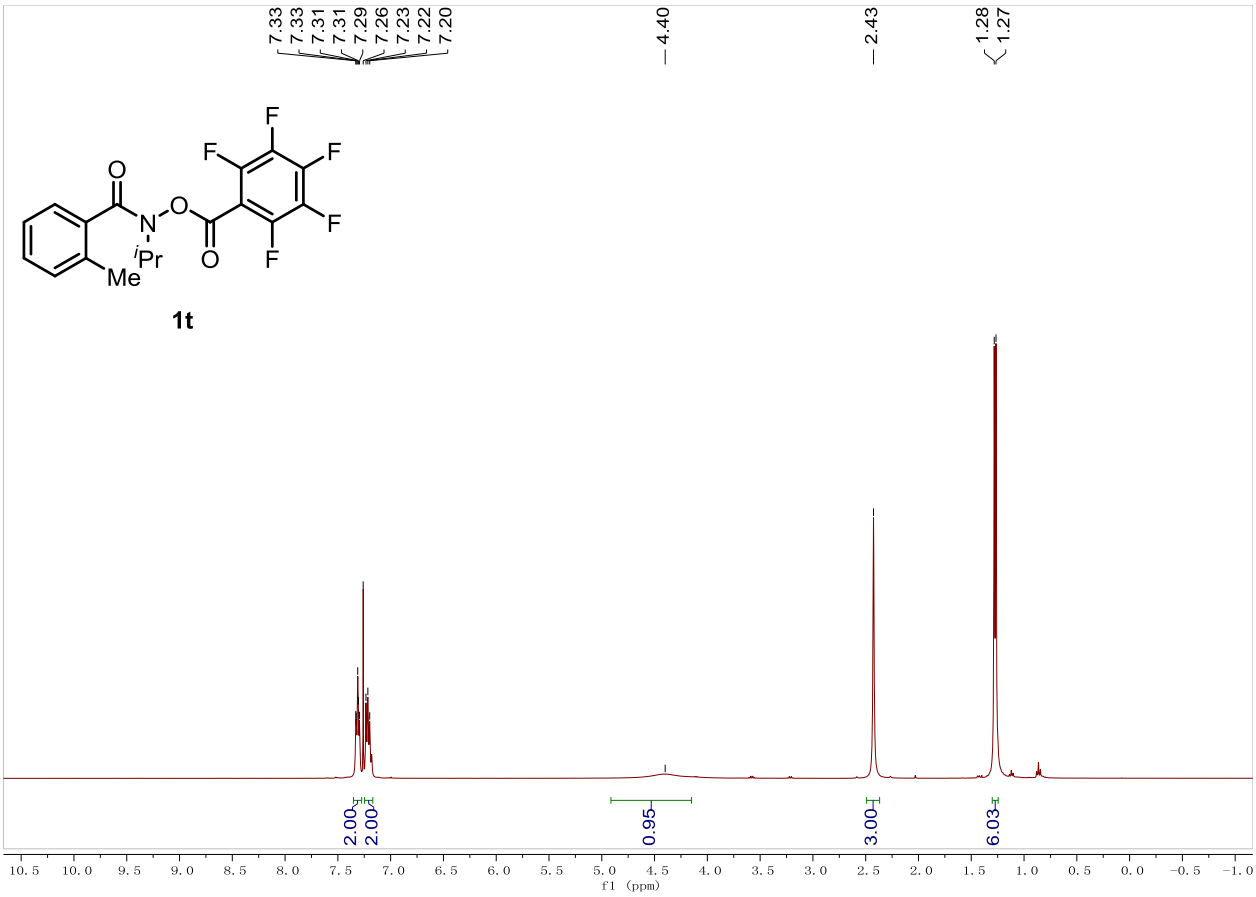


1s

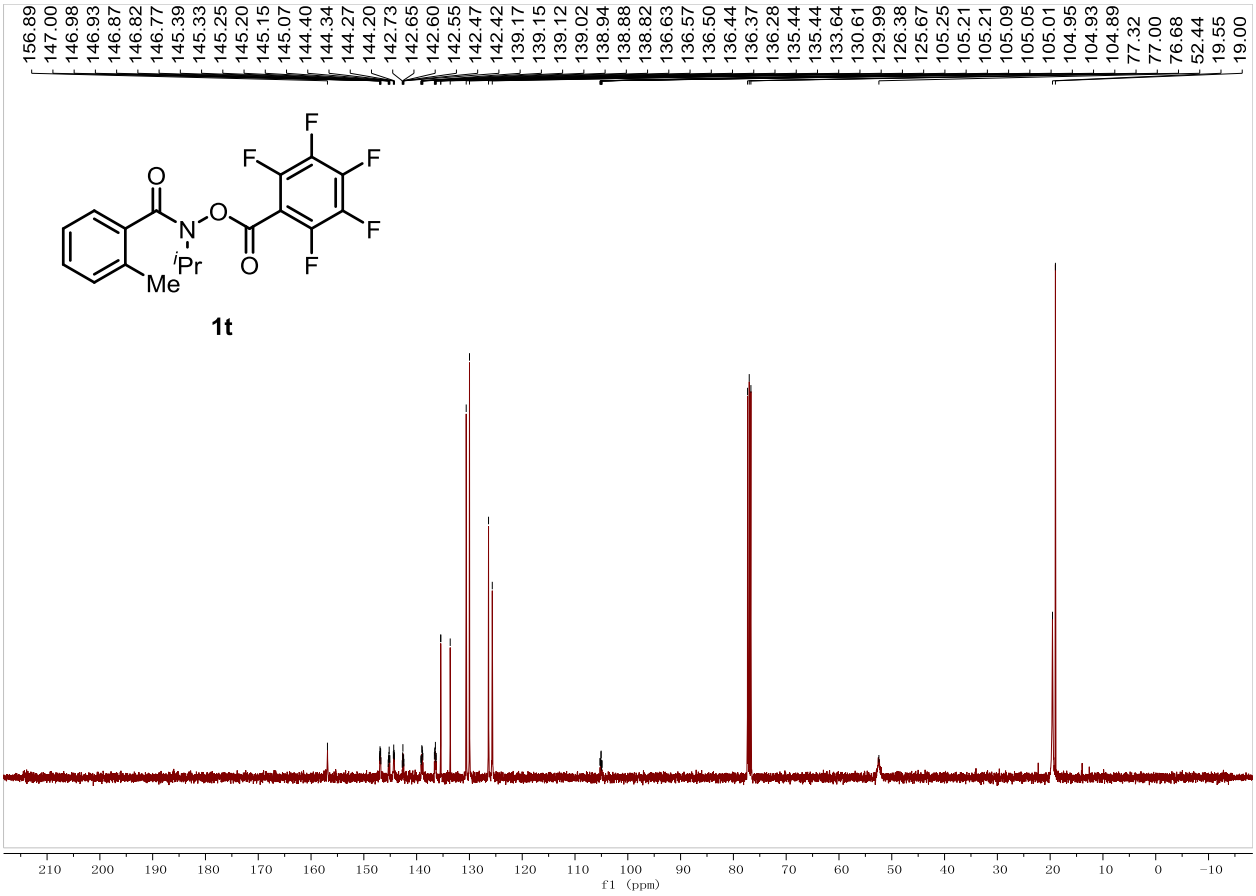
1s, ^{19}F NMR (376 MHz, $CDCl_3$)



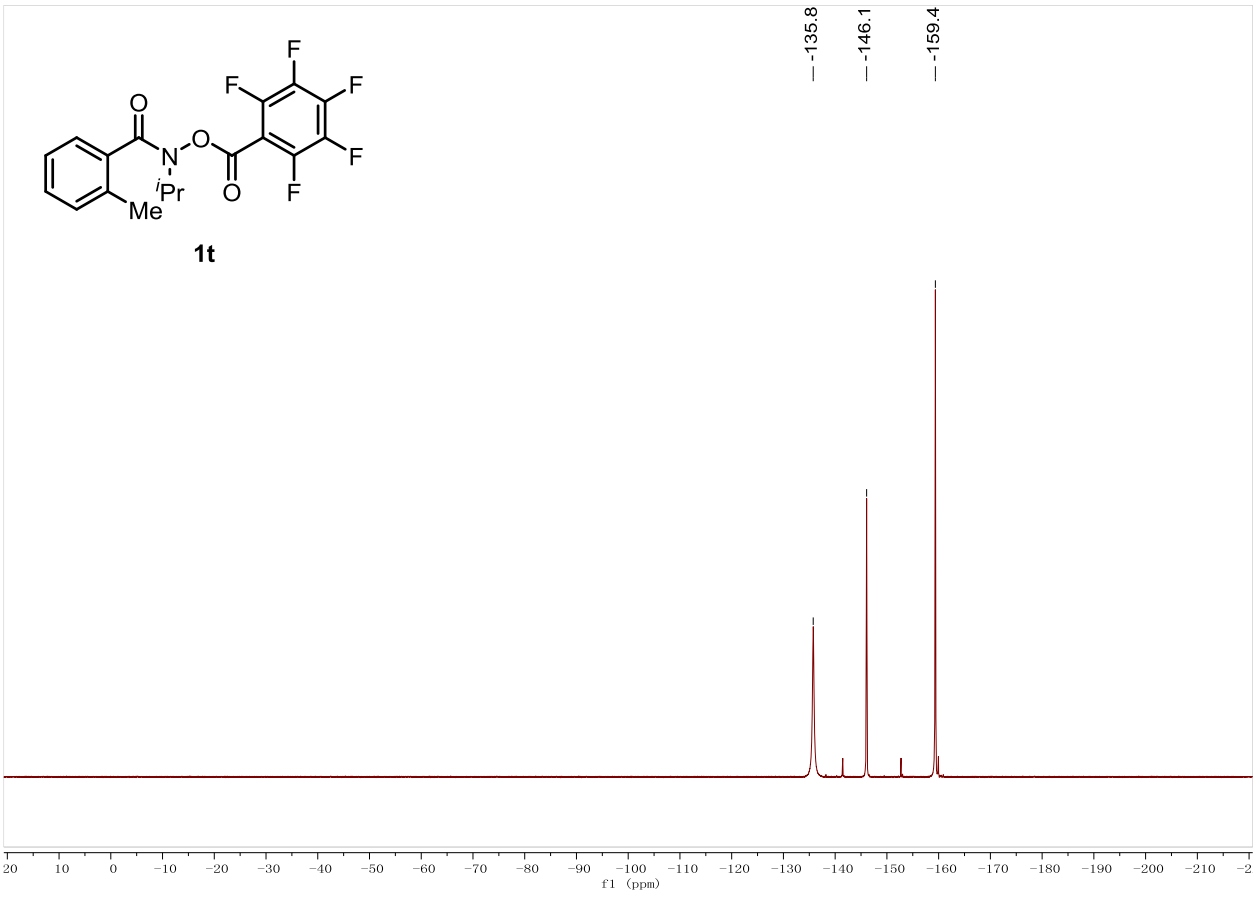
1t, ^{1}H NMR (400 MHz, $CDCl_3$)



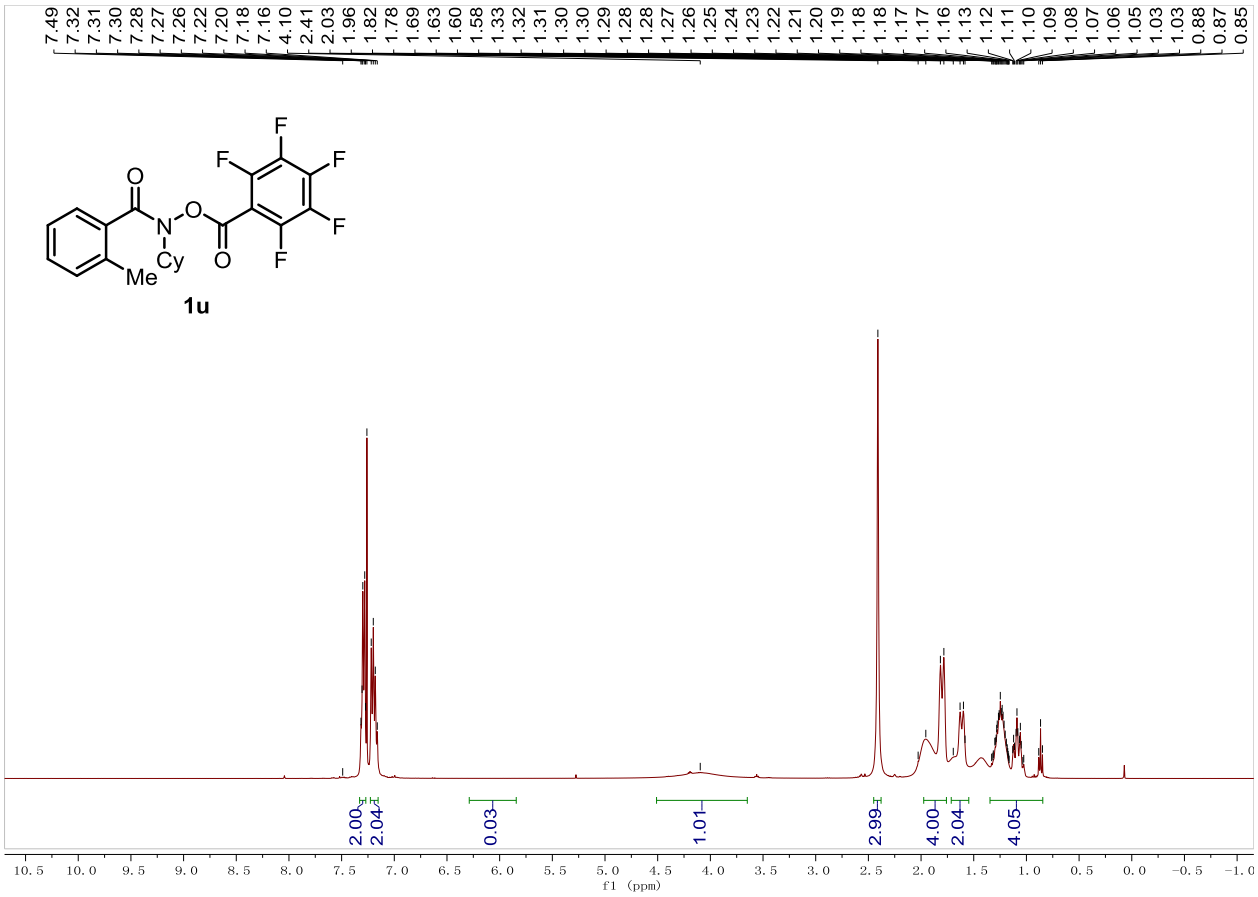
1t, ^{13}C NMR (101 MHz, $CDCl_3$)



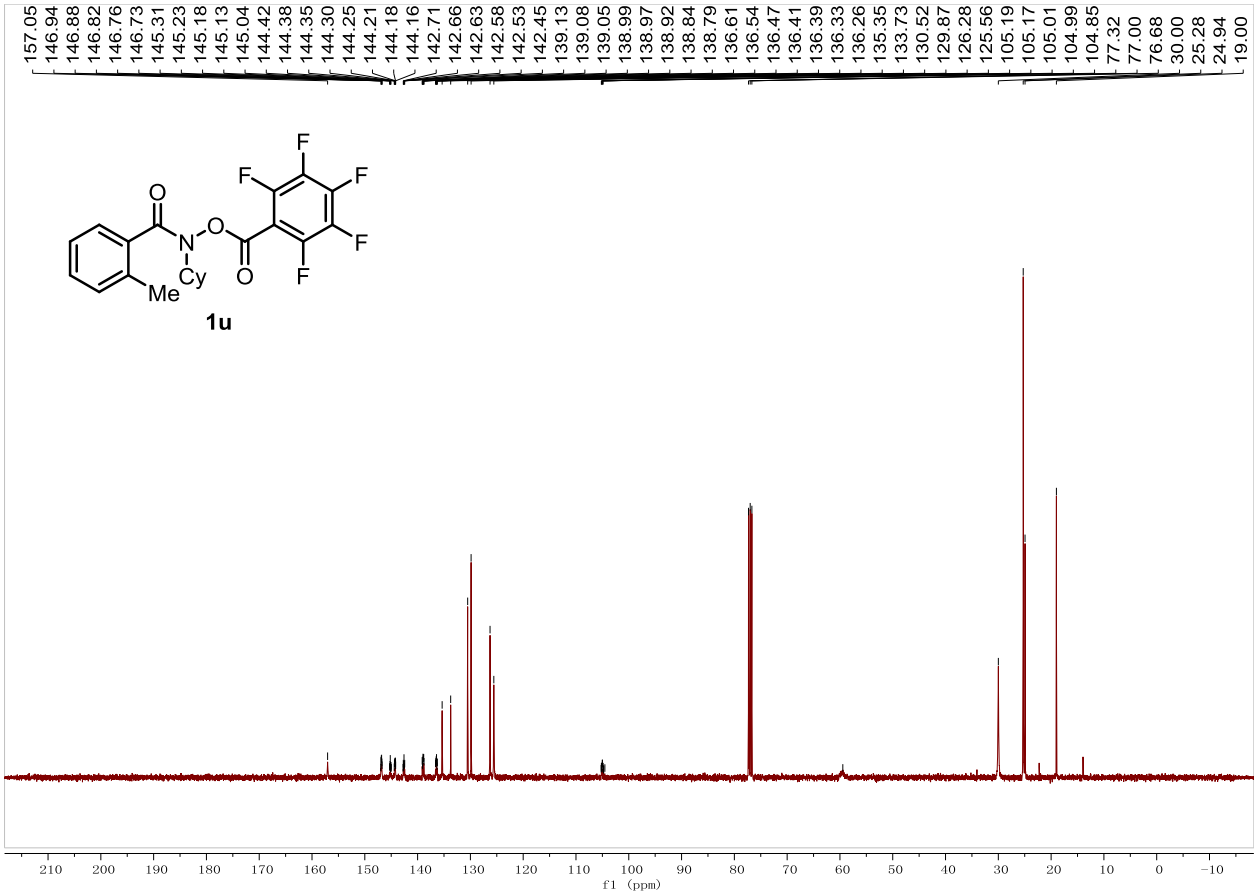
1t, ^{19}F NMR (376 MHz, $CDCl_3$)



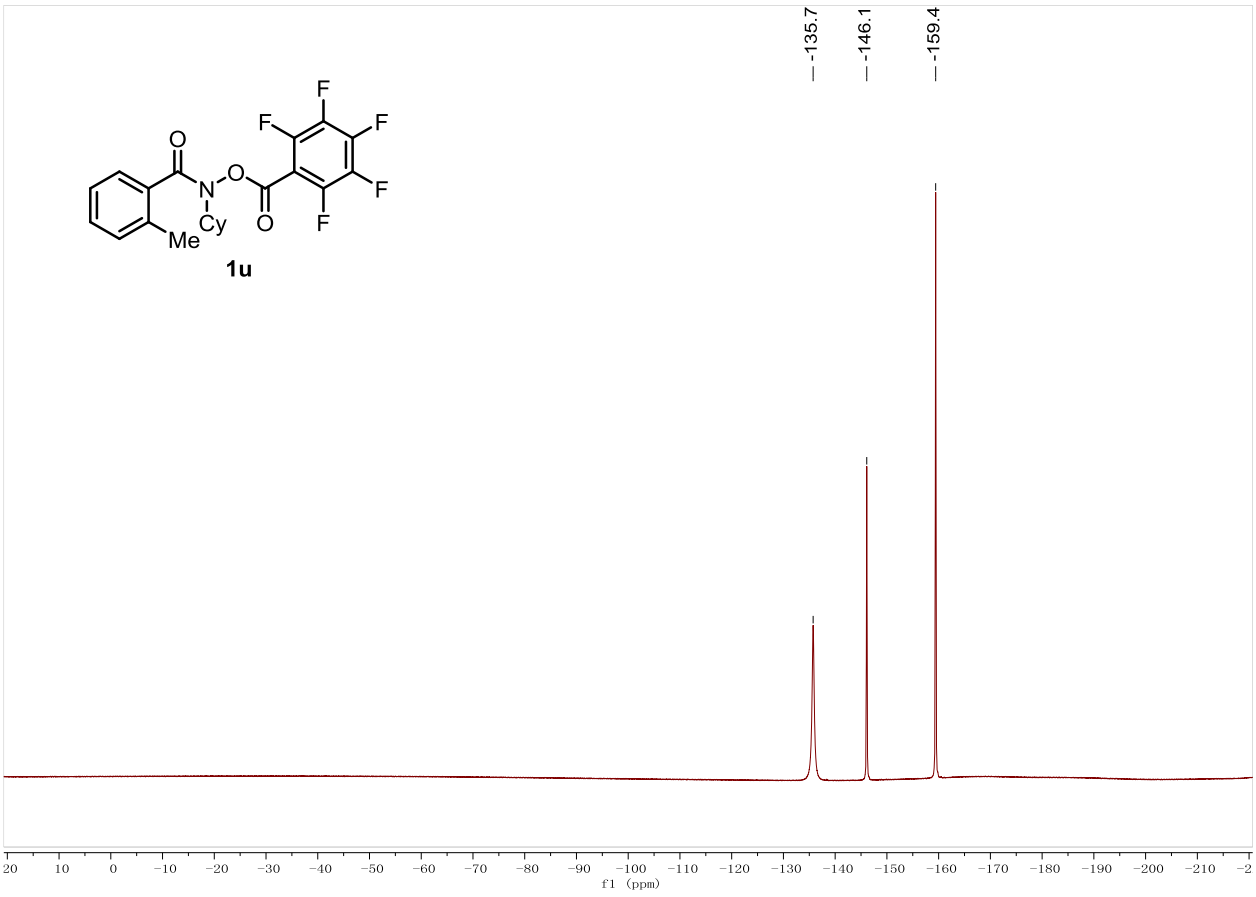
1u, ^{1}H NMR (400 MHz, $CDCl_3$)



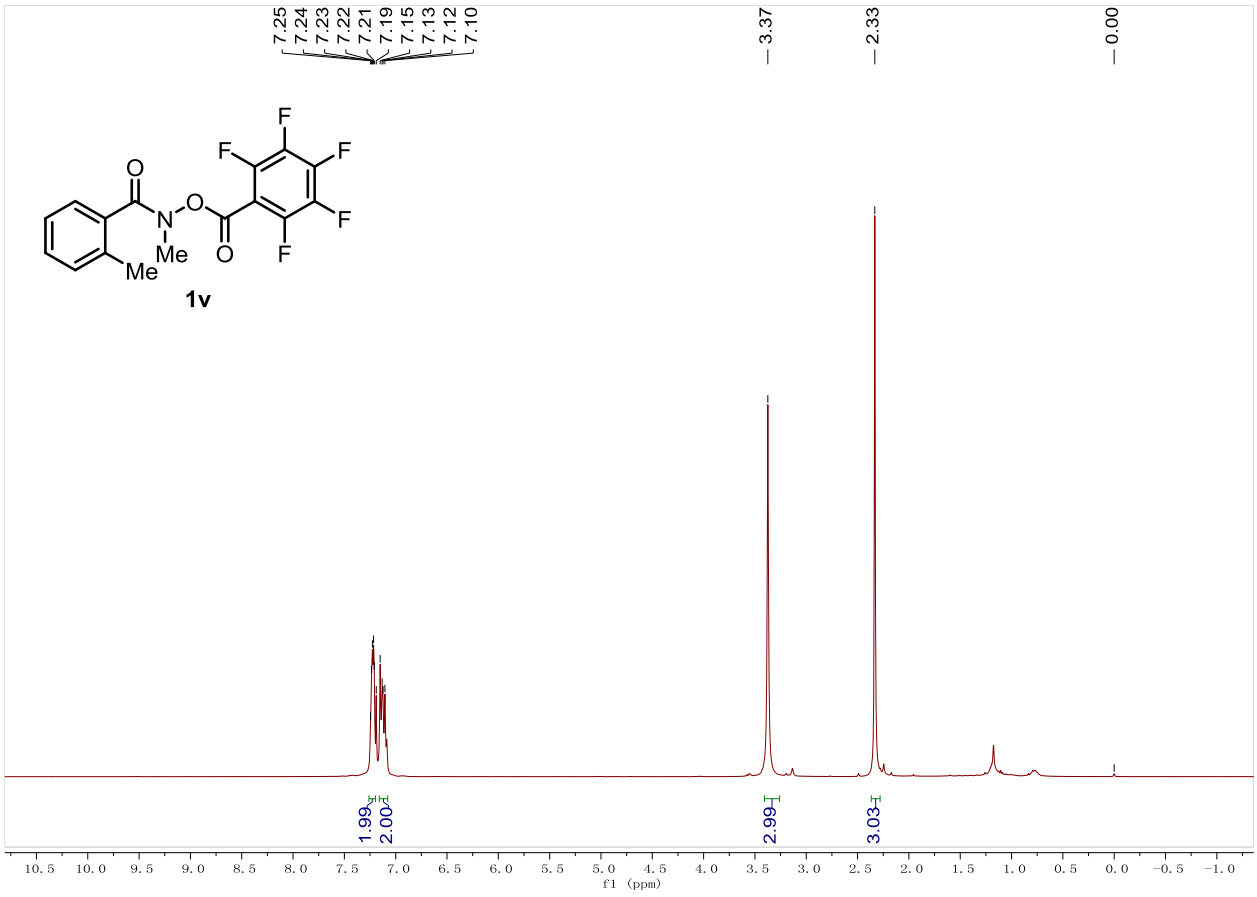
1u, ^{13}C NMR (101 MHz, $CDCl_3$)



1u, ^{19}F NMR (376 MHz, $CDCl_3$)

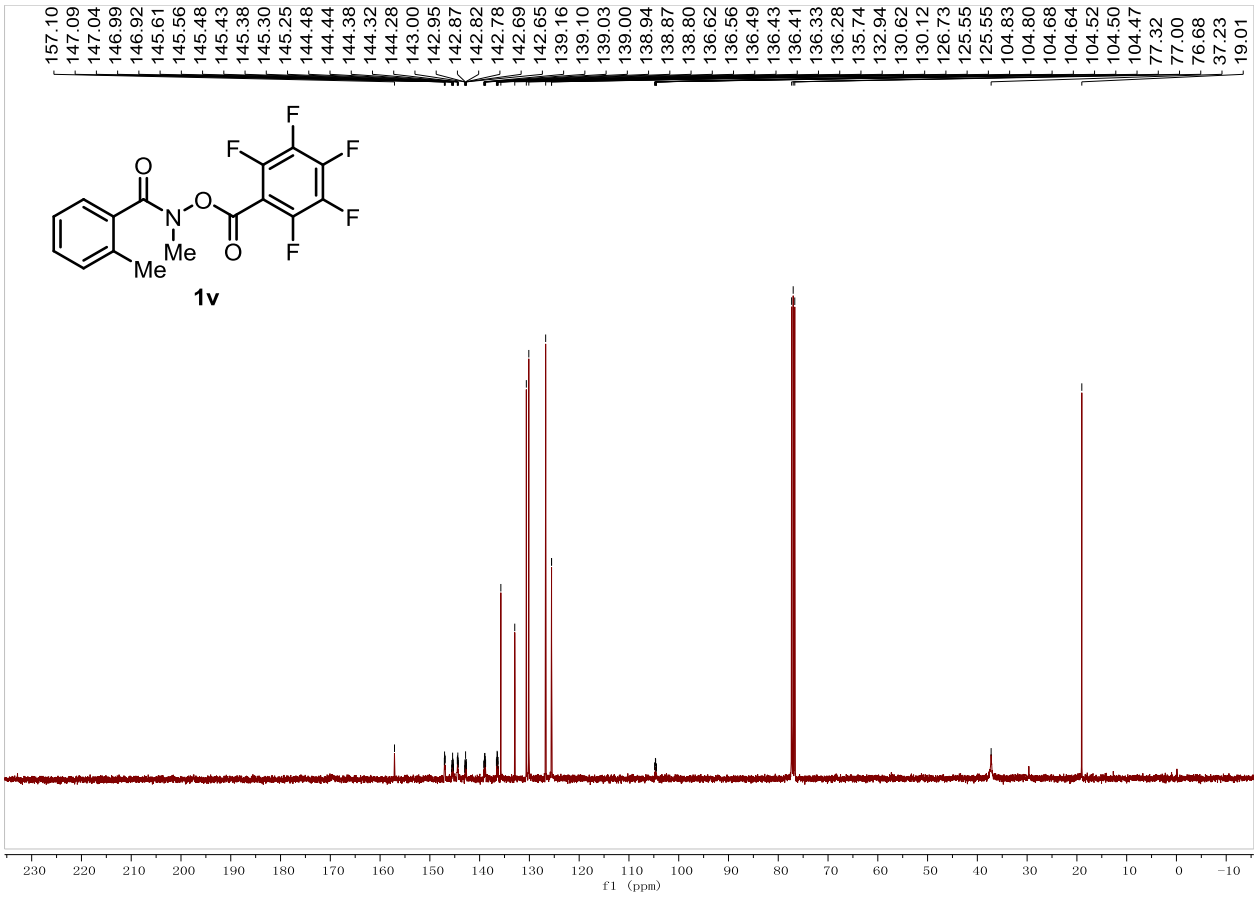


1v, ^{1}H NMR (400 MHz, $CDCl_3$)



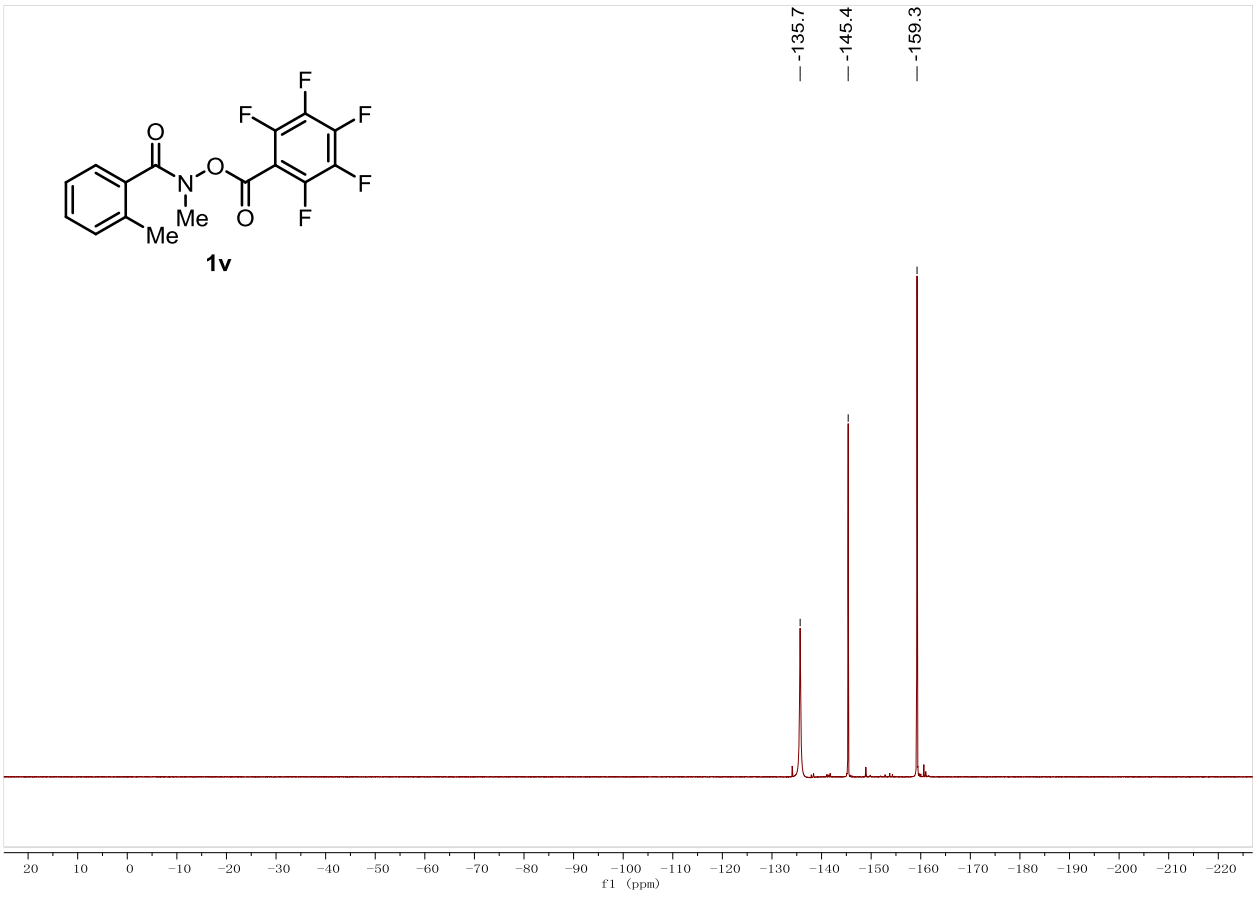
1v

1v, ^{13}C NMR (101 MHz, $CDCl_3$)

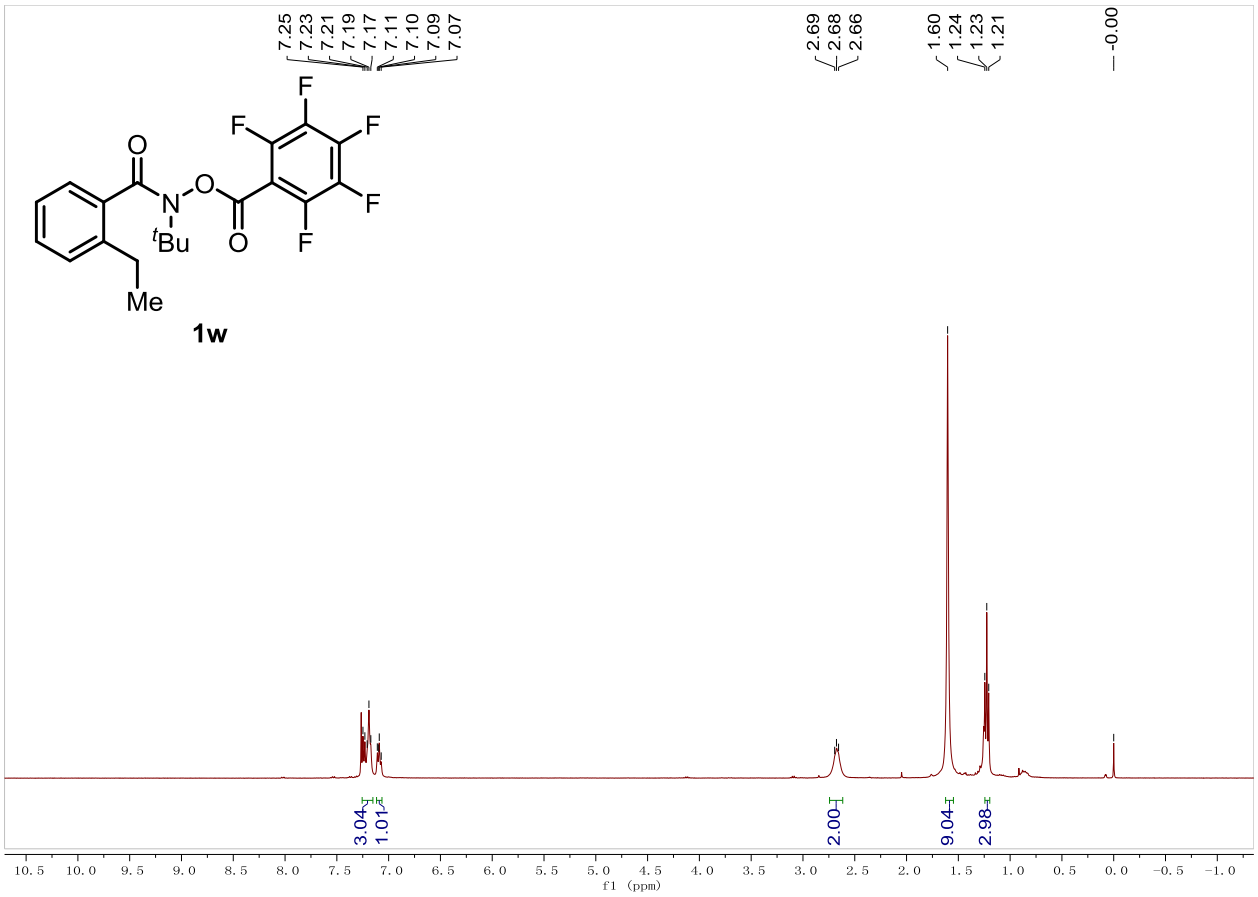


1v

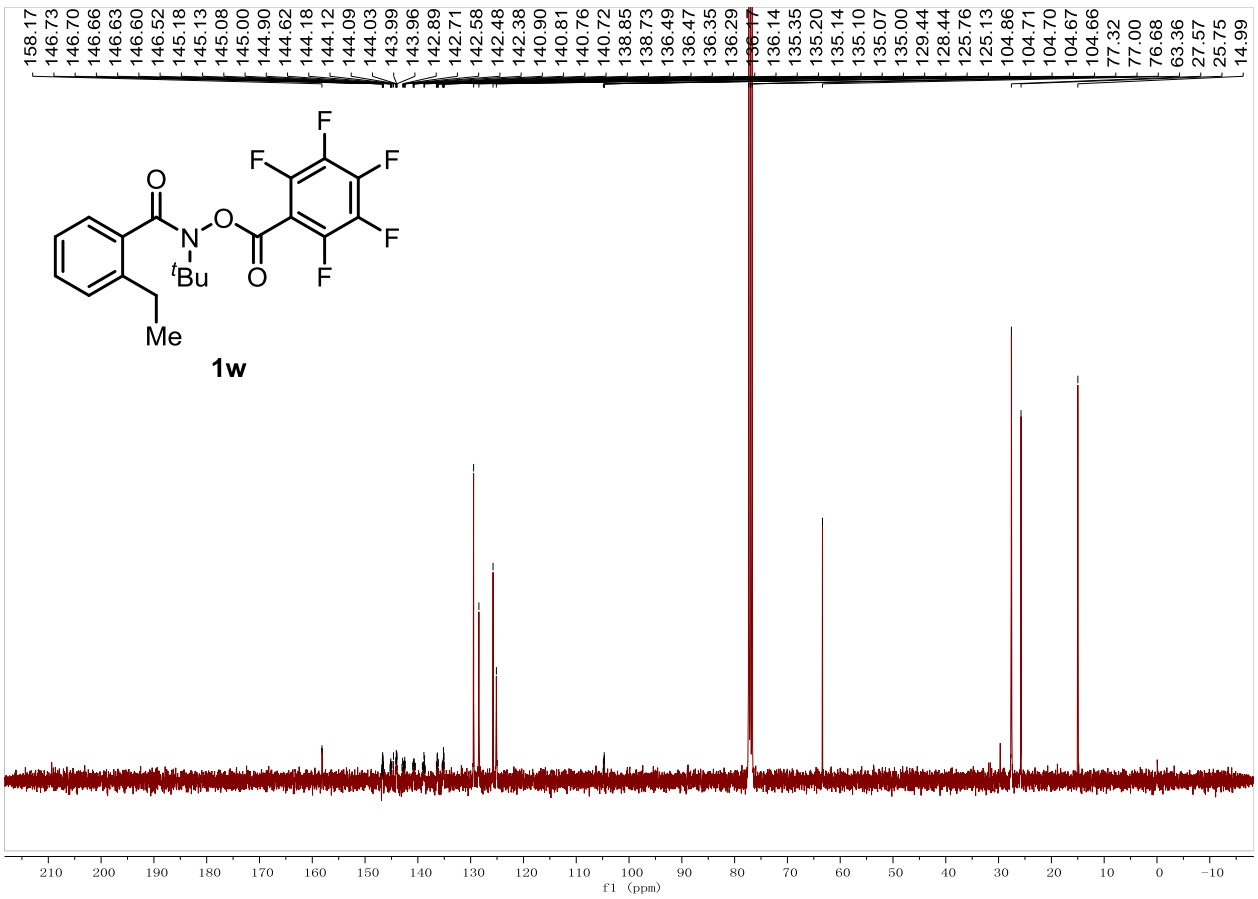
1v, ^{19}F NMR (376 MHz, $CDCl_3$)



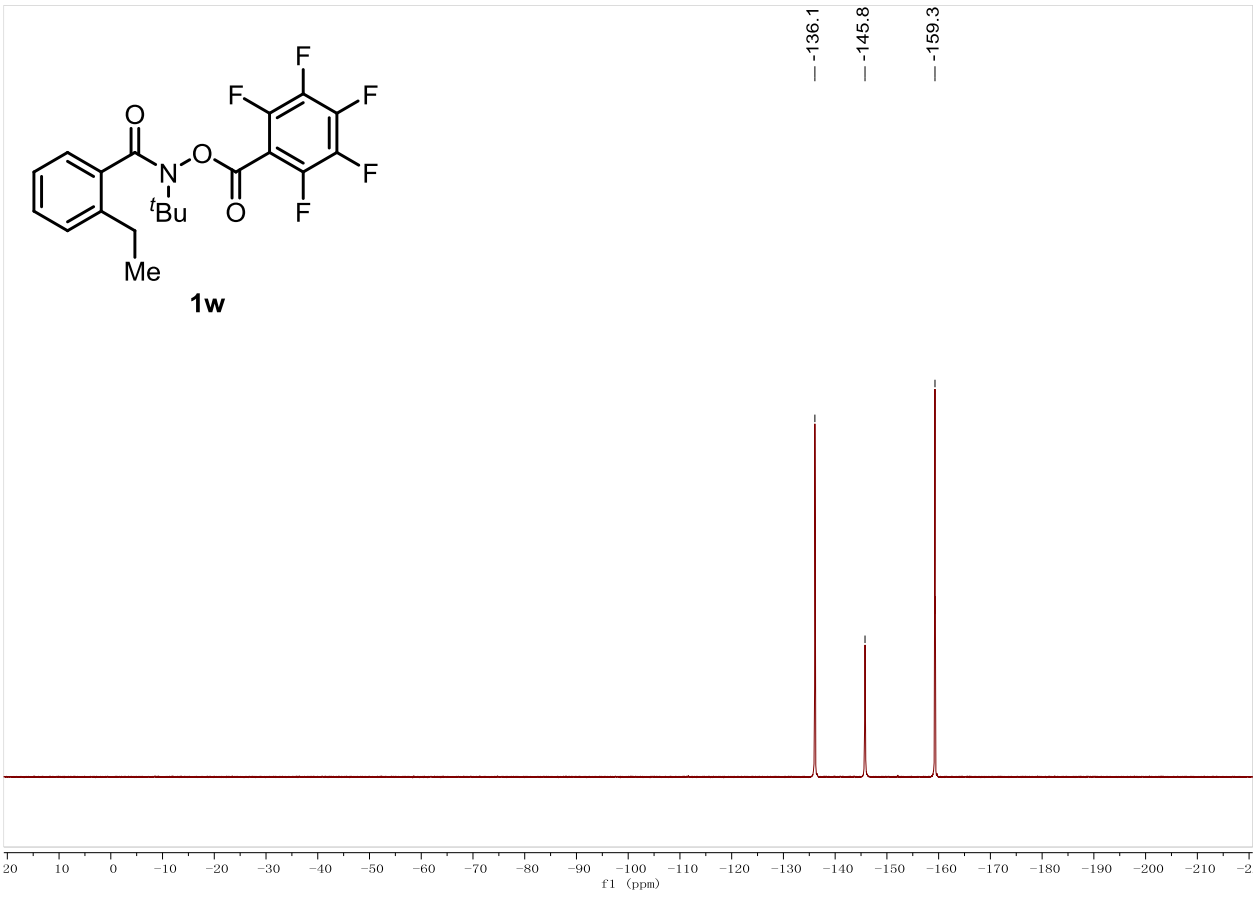
1w, ^{1}H NMR (400 MHz, $CDCl_3$)



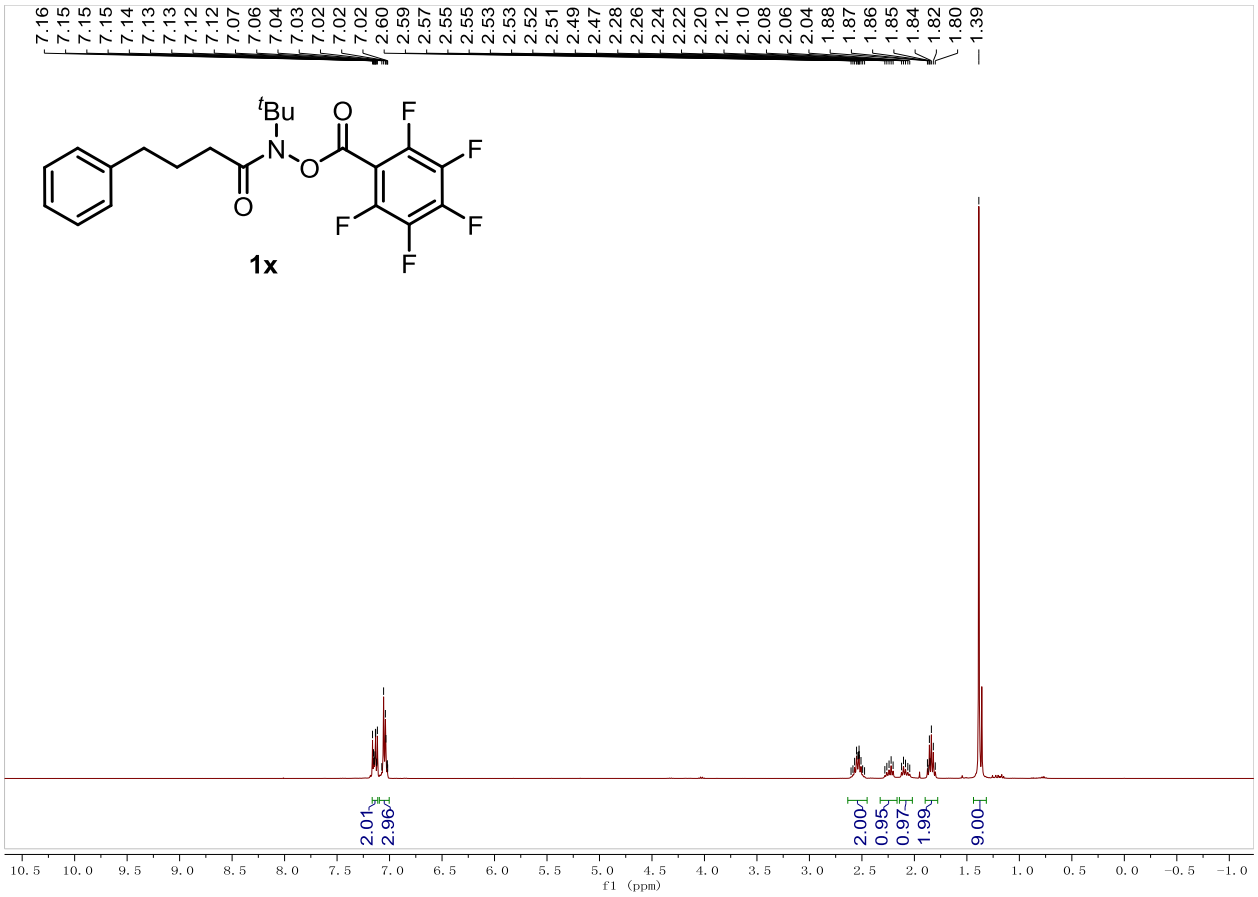
1w, ^{13}C NMR (101 MHz, $CDCl_3$)



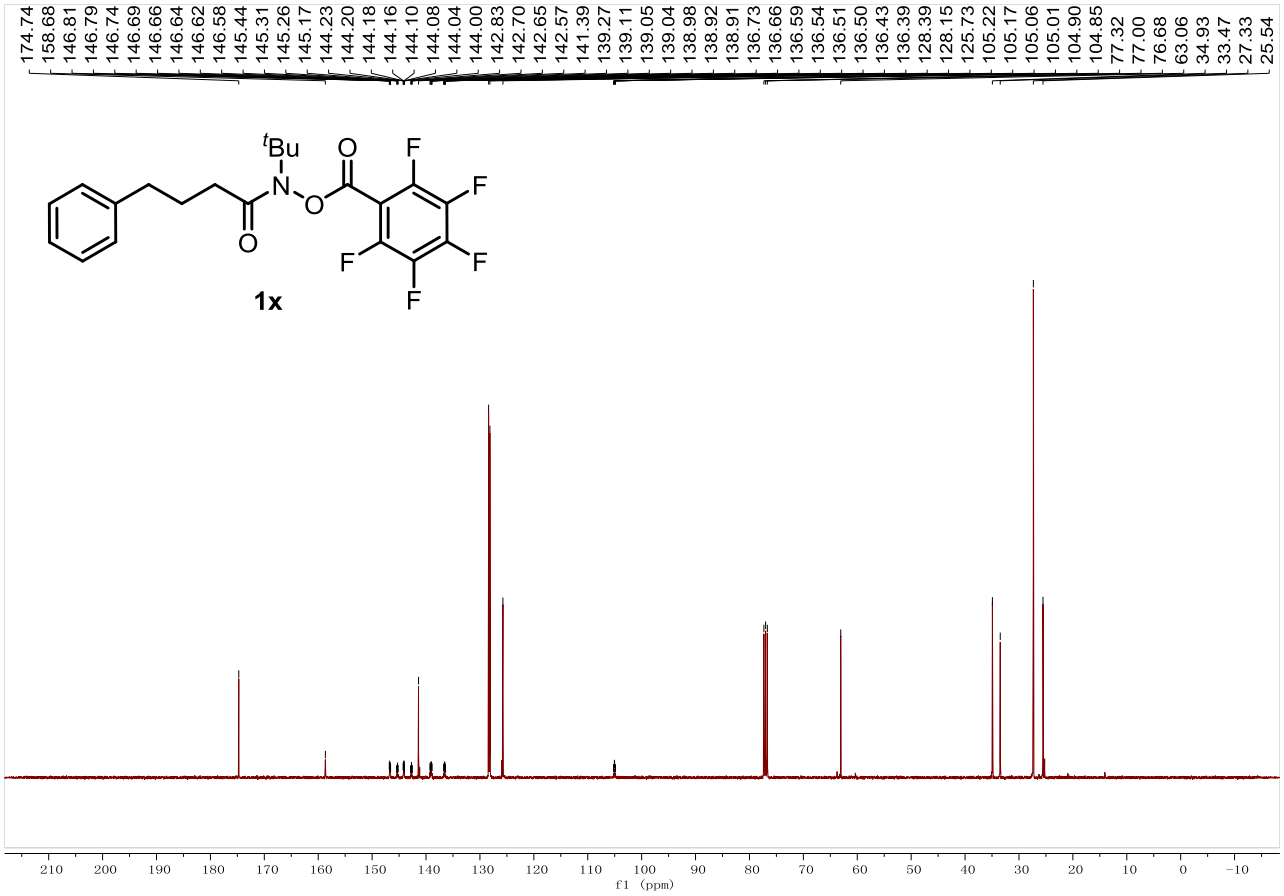
1w, ^{19}F NMR (376 MHz, $CDCl_3$)



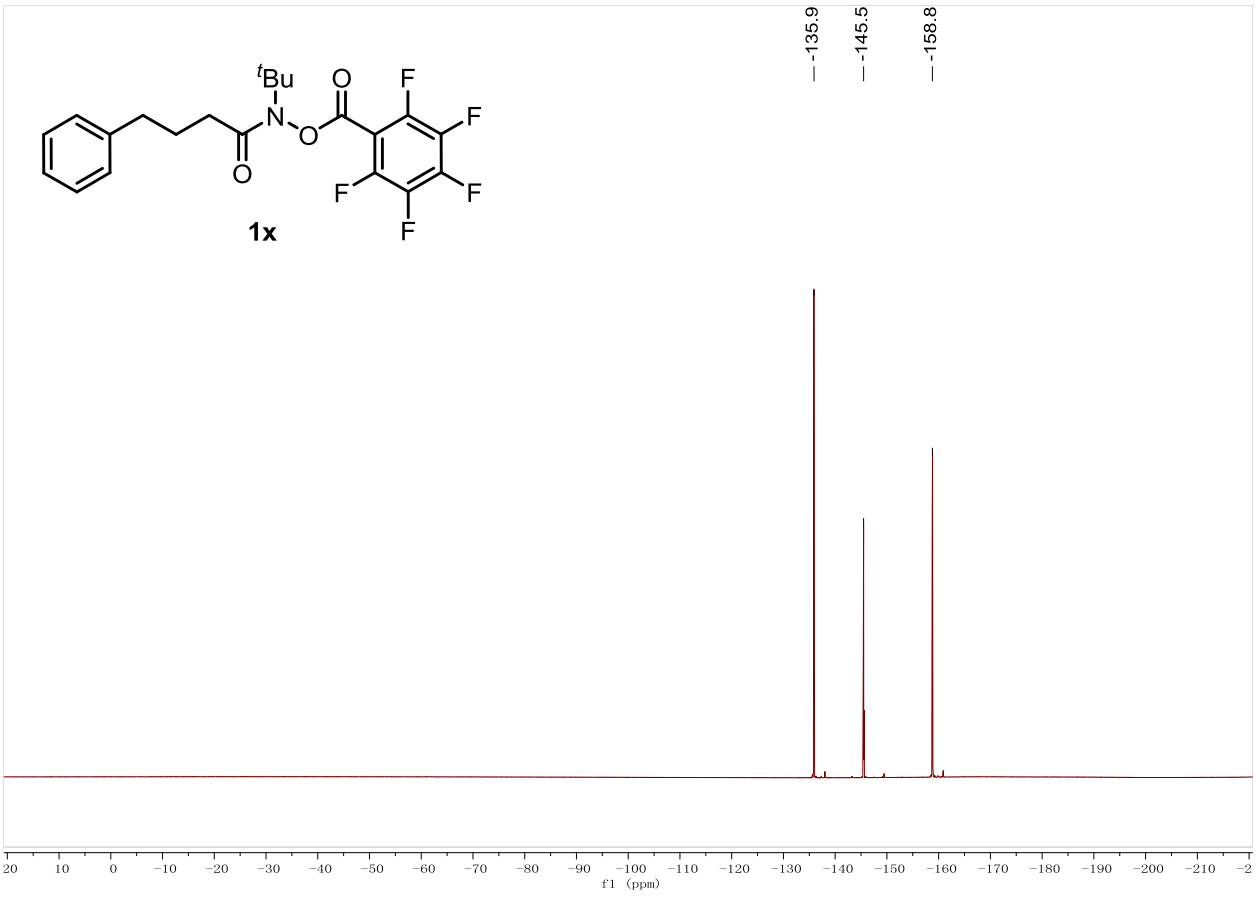
1x, ^{1}H NMR (400 MHz, $CDCl_3$)



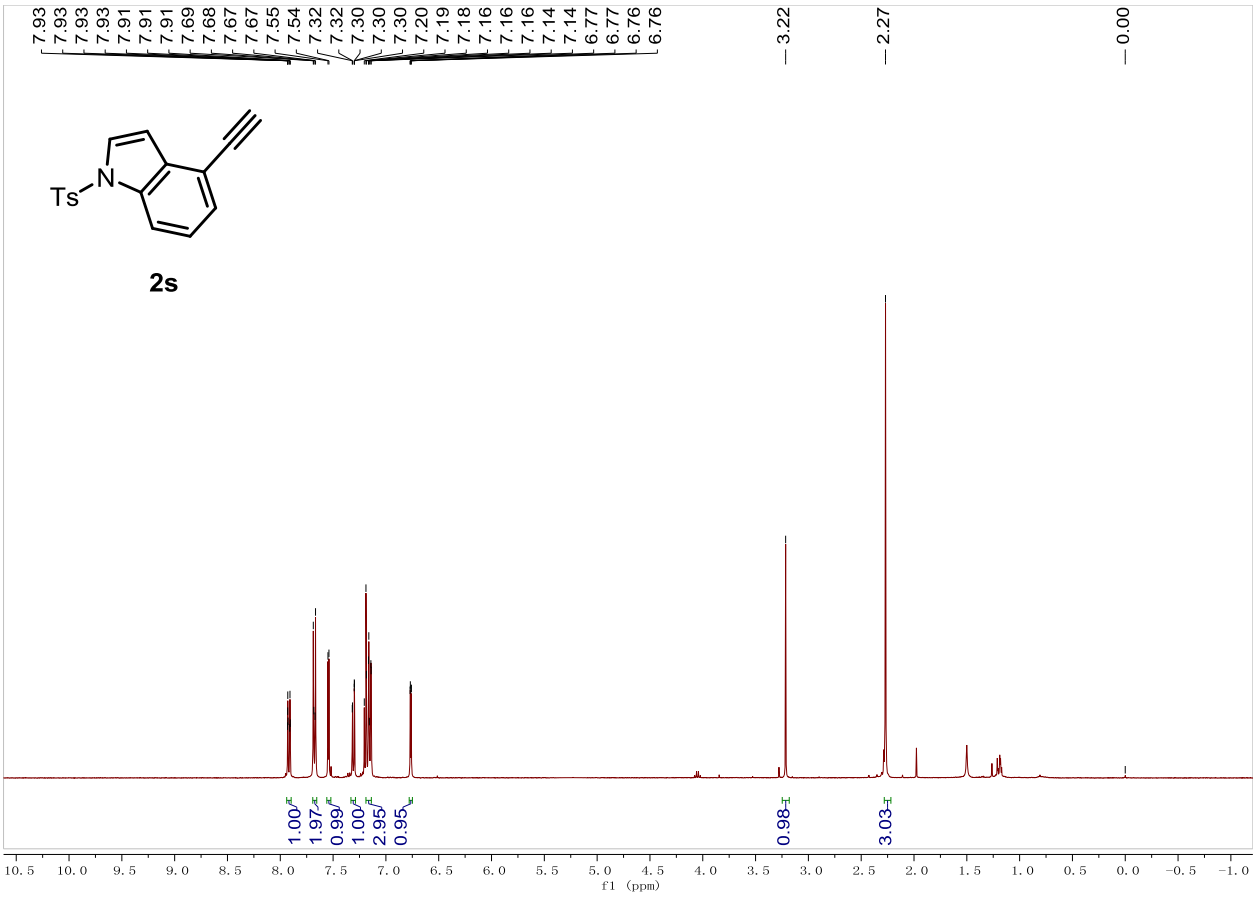
1x, ^{13}C NMR (101 MHz, $CDCl_3$)



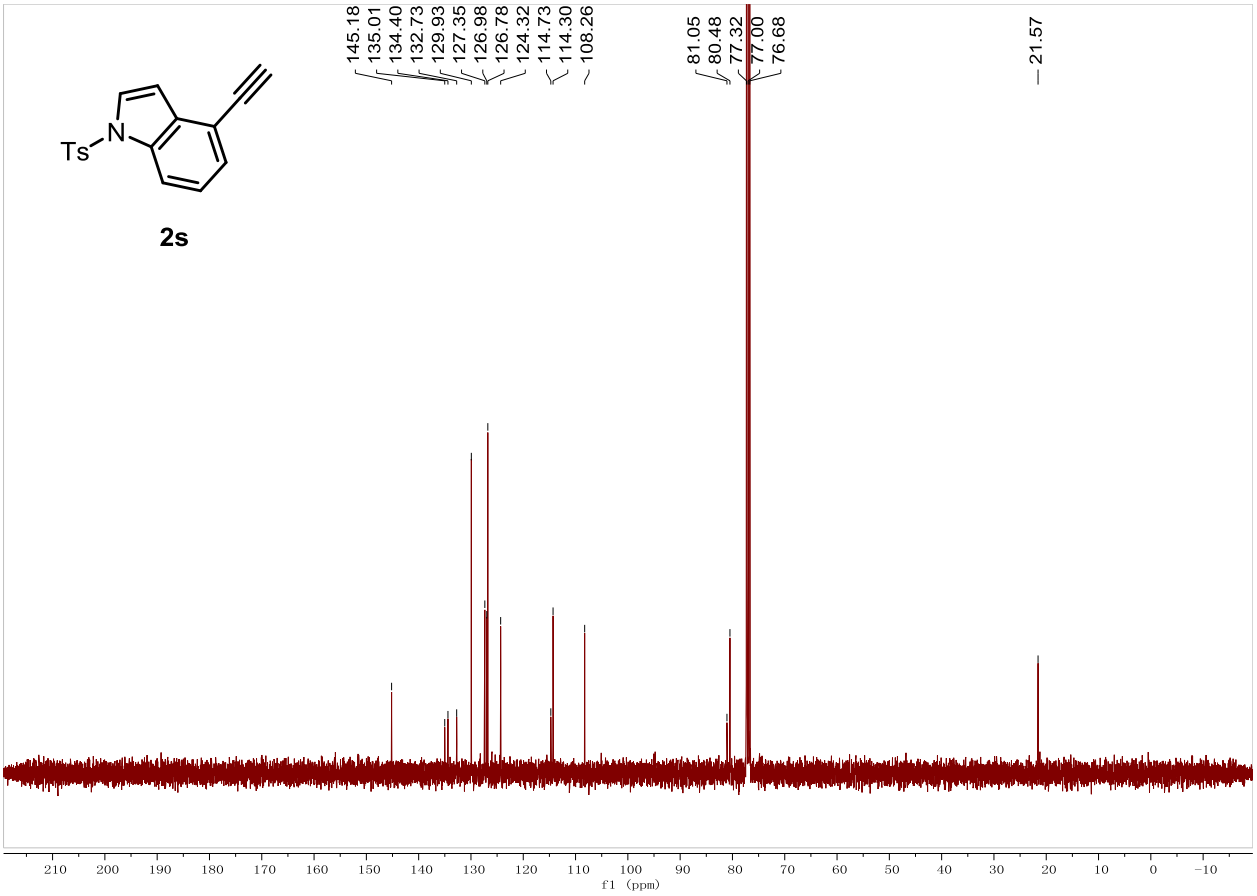
1x, ^{19}F NMR (376 MHz, $CDCl_3$)



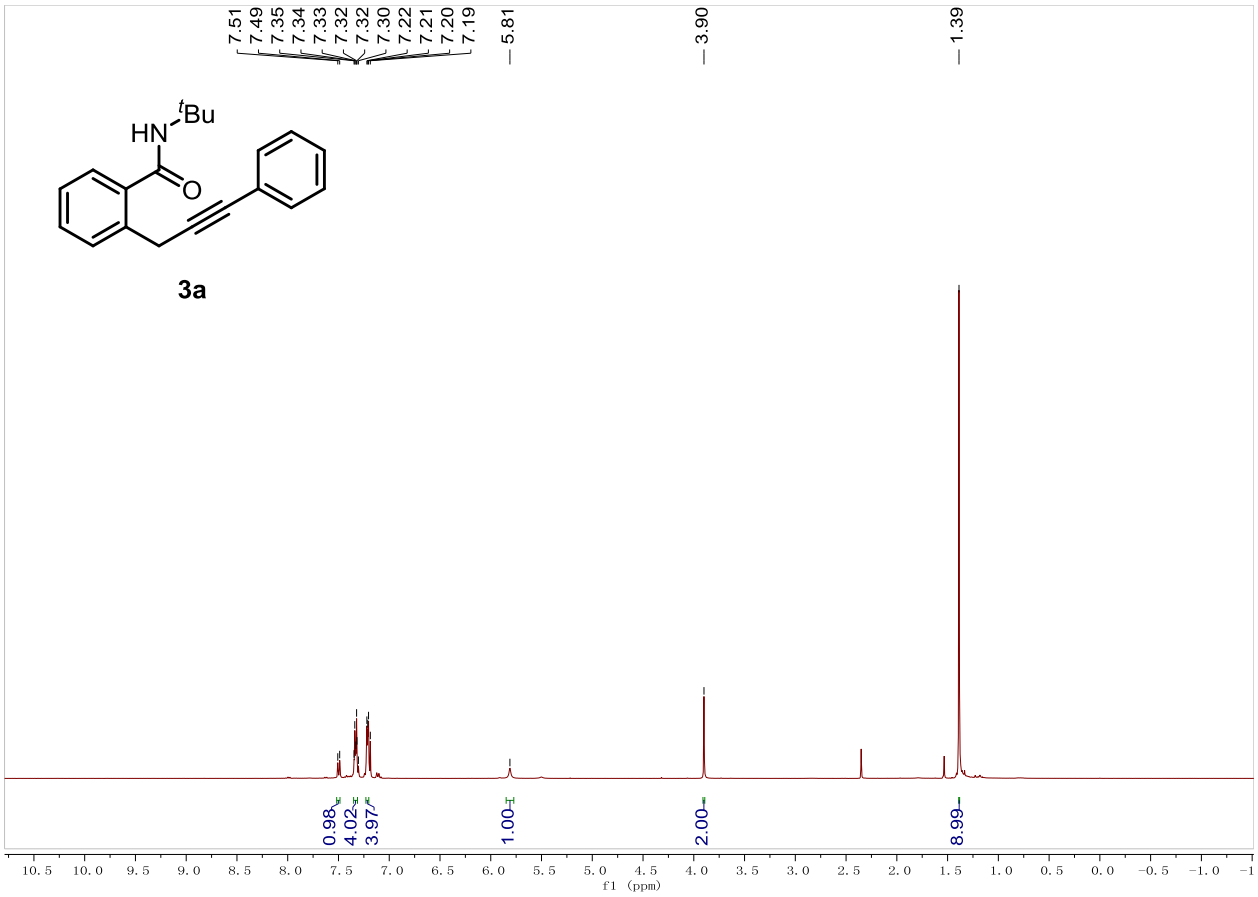
2s, ^{1}H NMR (400 MHz, $CDCl_3$)



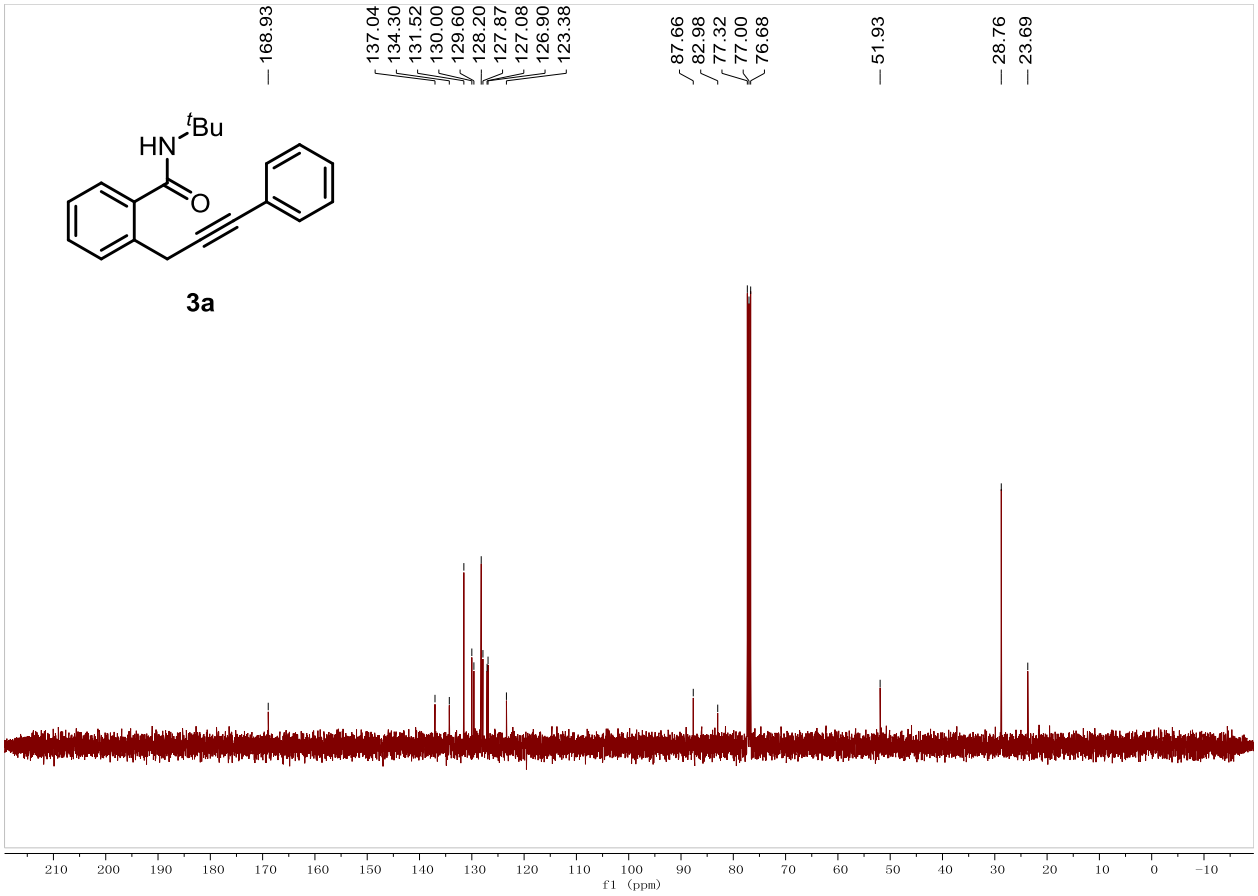
2s, ^{13}C NMR (101 MHz, $CDCl_3$)



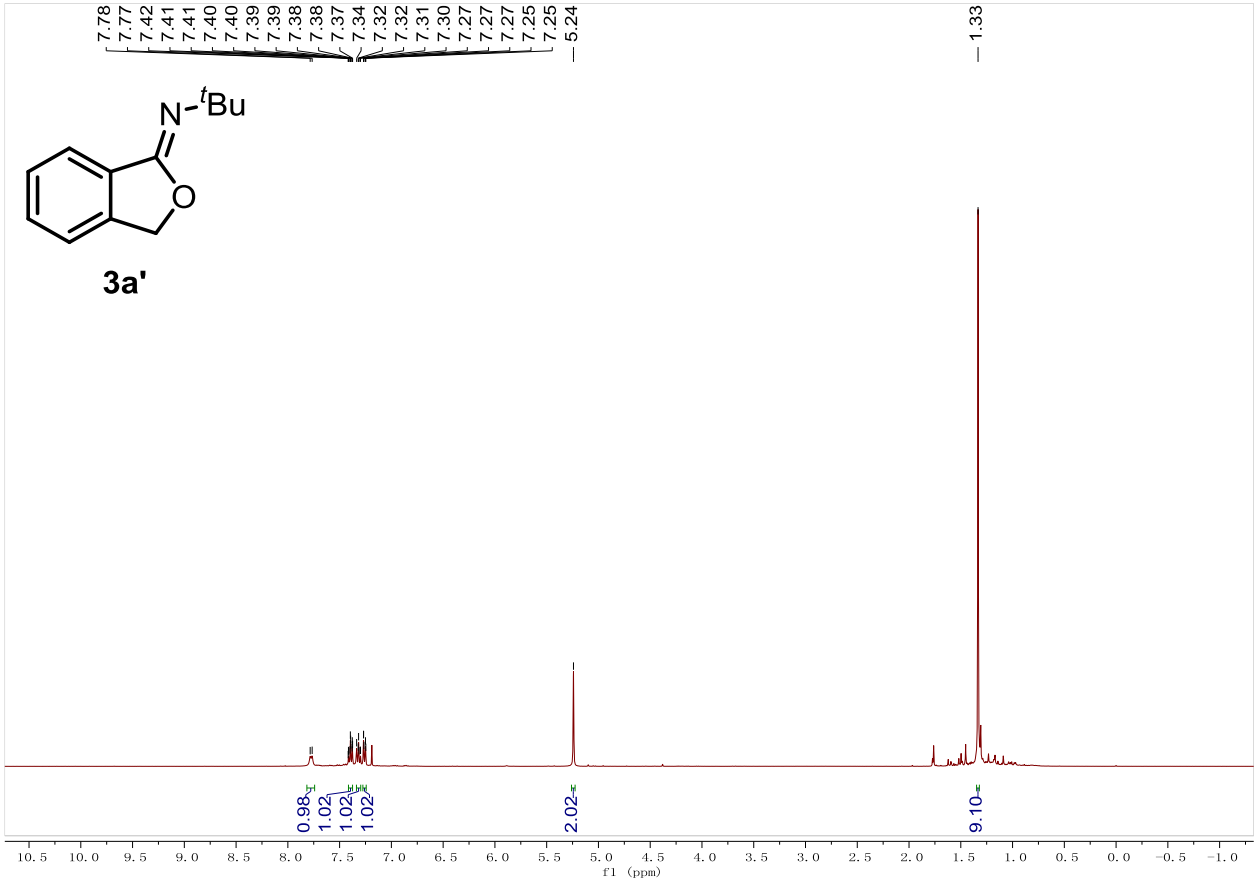
3a, ^{1}H NMR (400 MHz, $CDCl_3$)



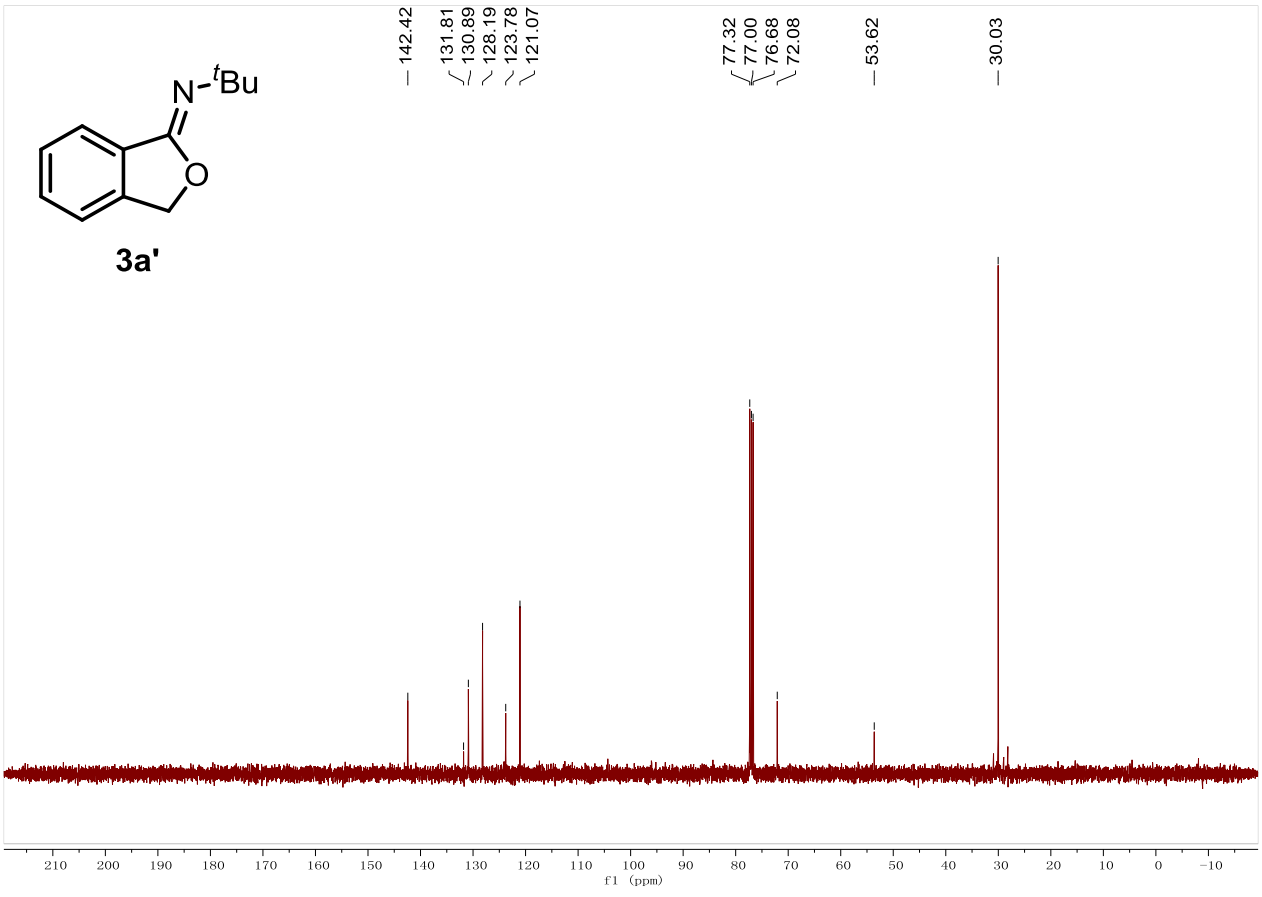
3a, ^{13}C NMR (101 MHz, $CDCl_3$)



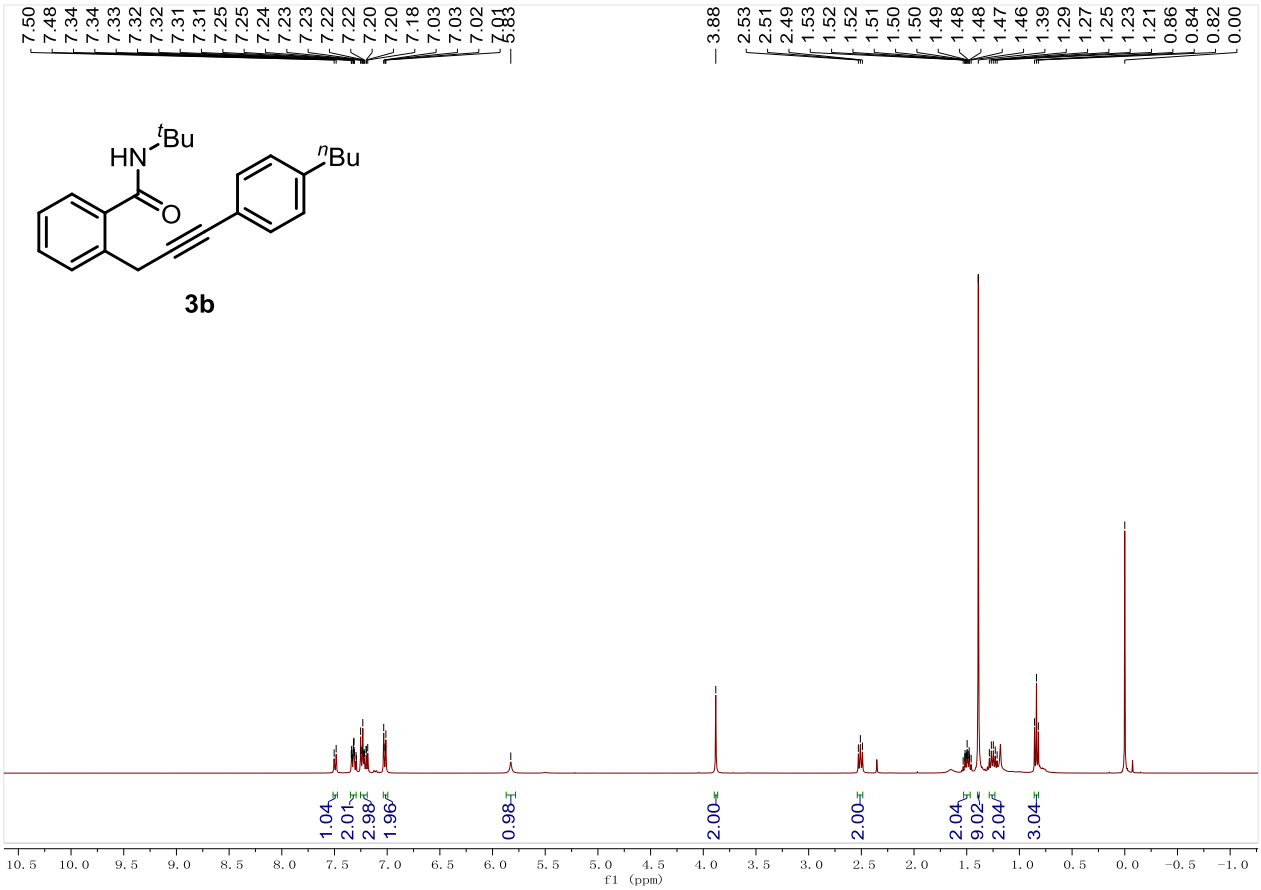
3a′, ^{1}H NMR (400 MHz, $CDCl_3$)



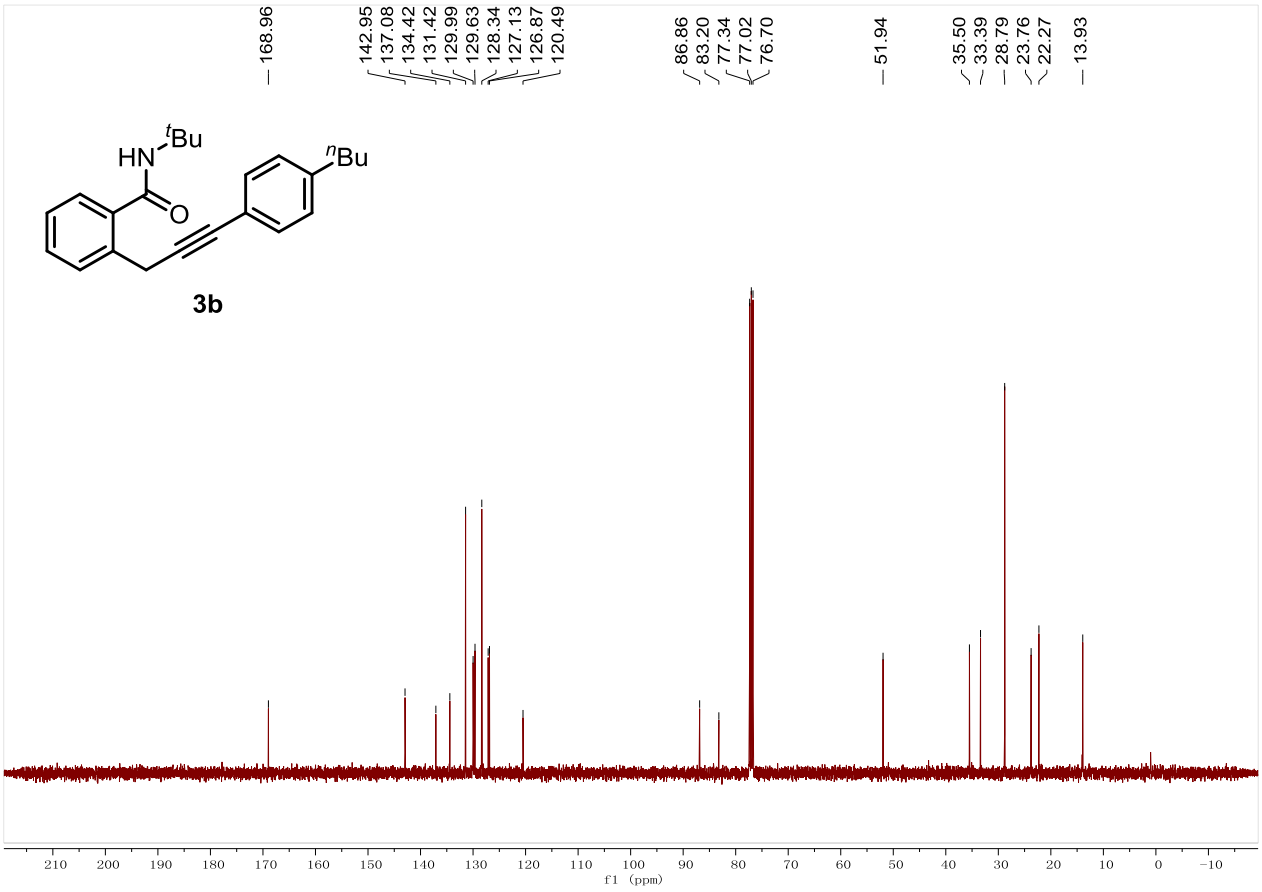
3a′, ^{13}C NMR (101 MHz, $CDCl_3$)



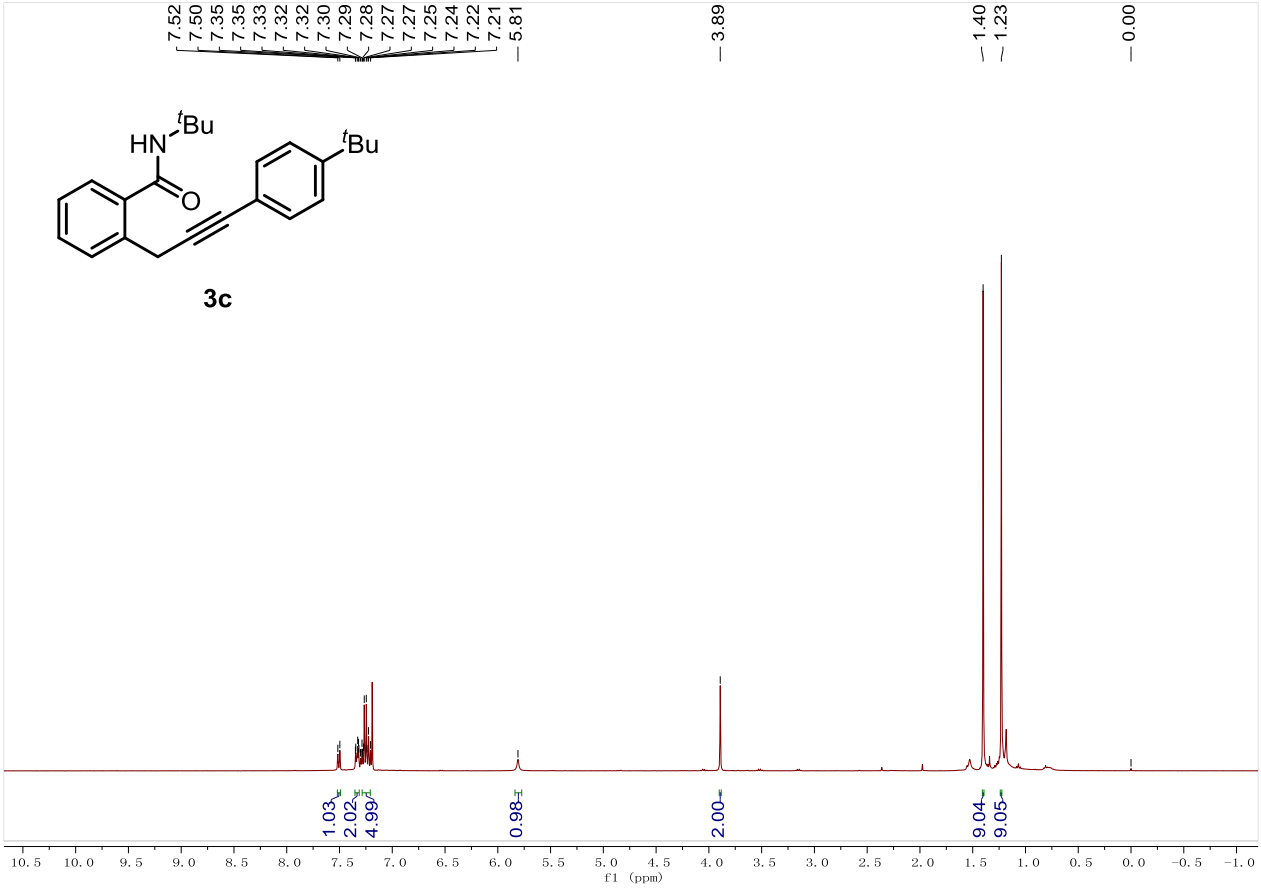
3b, ^{1}H NMR (400 MHz, $CDCl_3$)



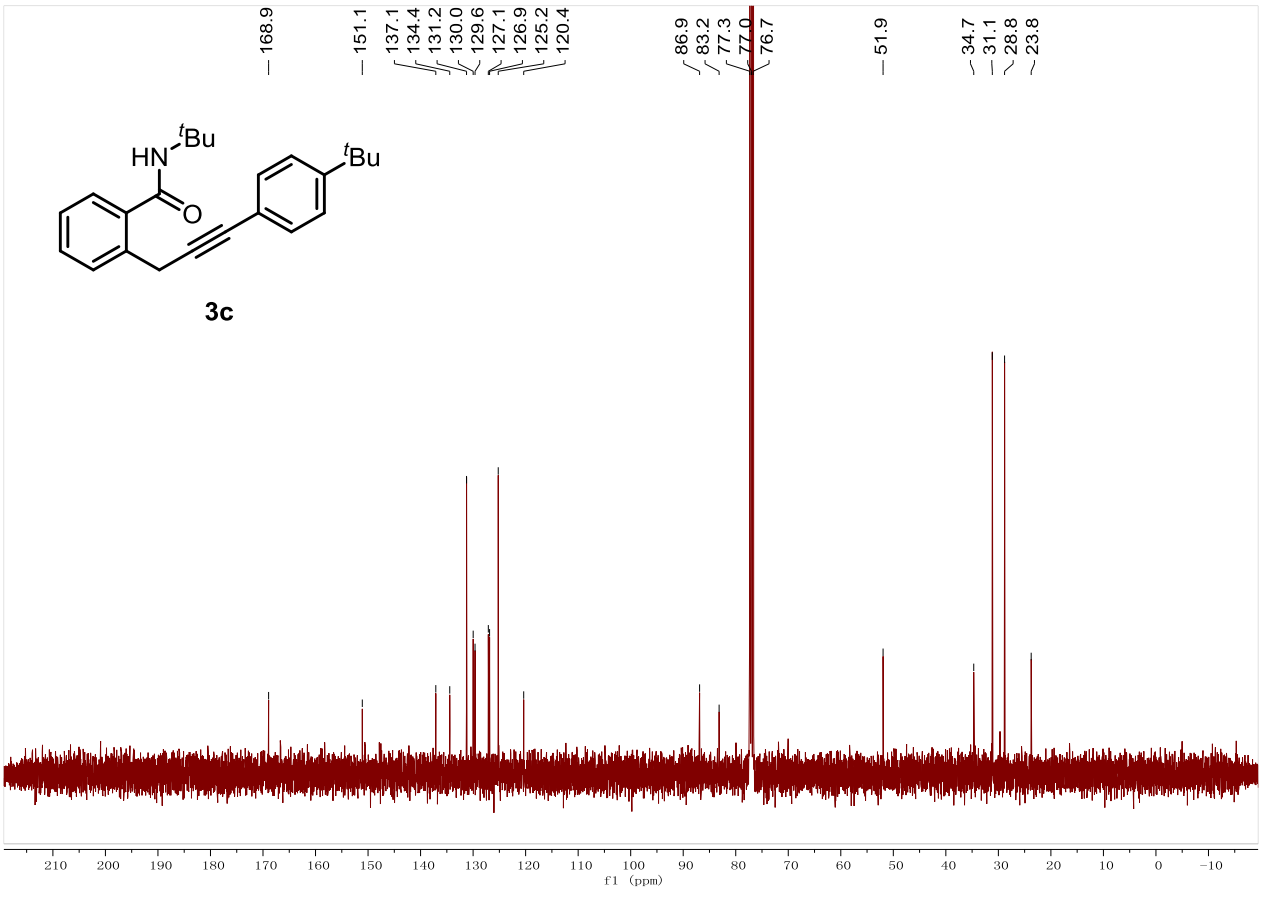
3b, ^{13}C NMR (101 MHz, $CDCl_3$)



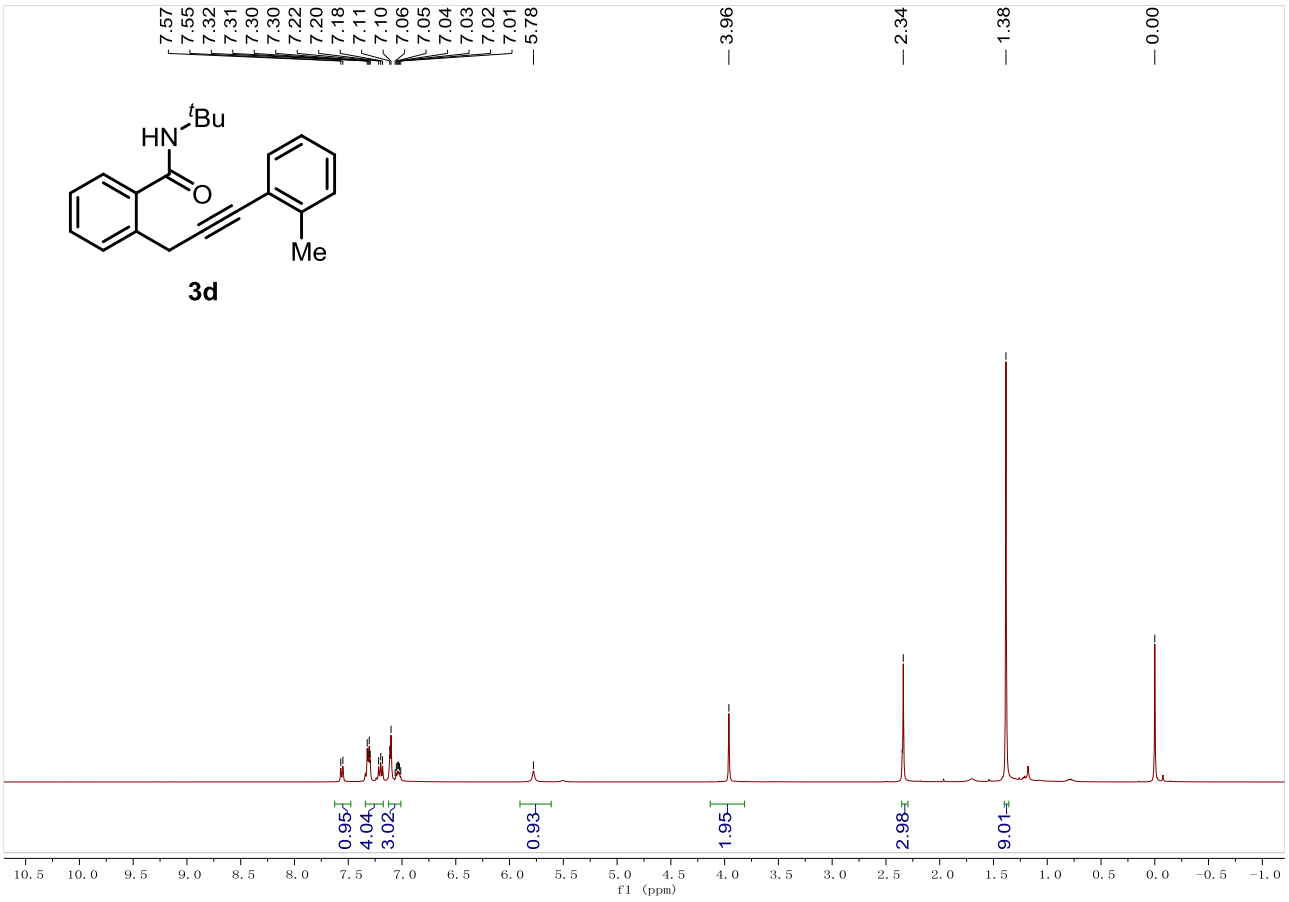
3c, ^{1}H NMR (400 MHz, $CDCl_3$)



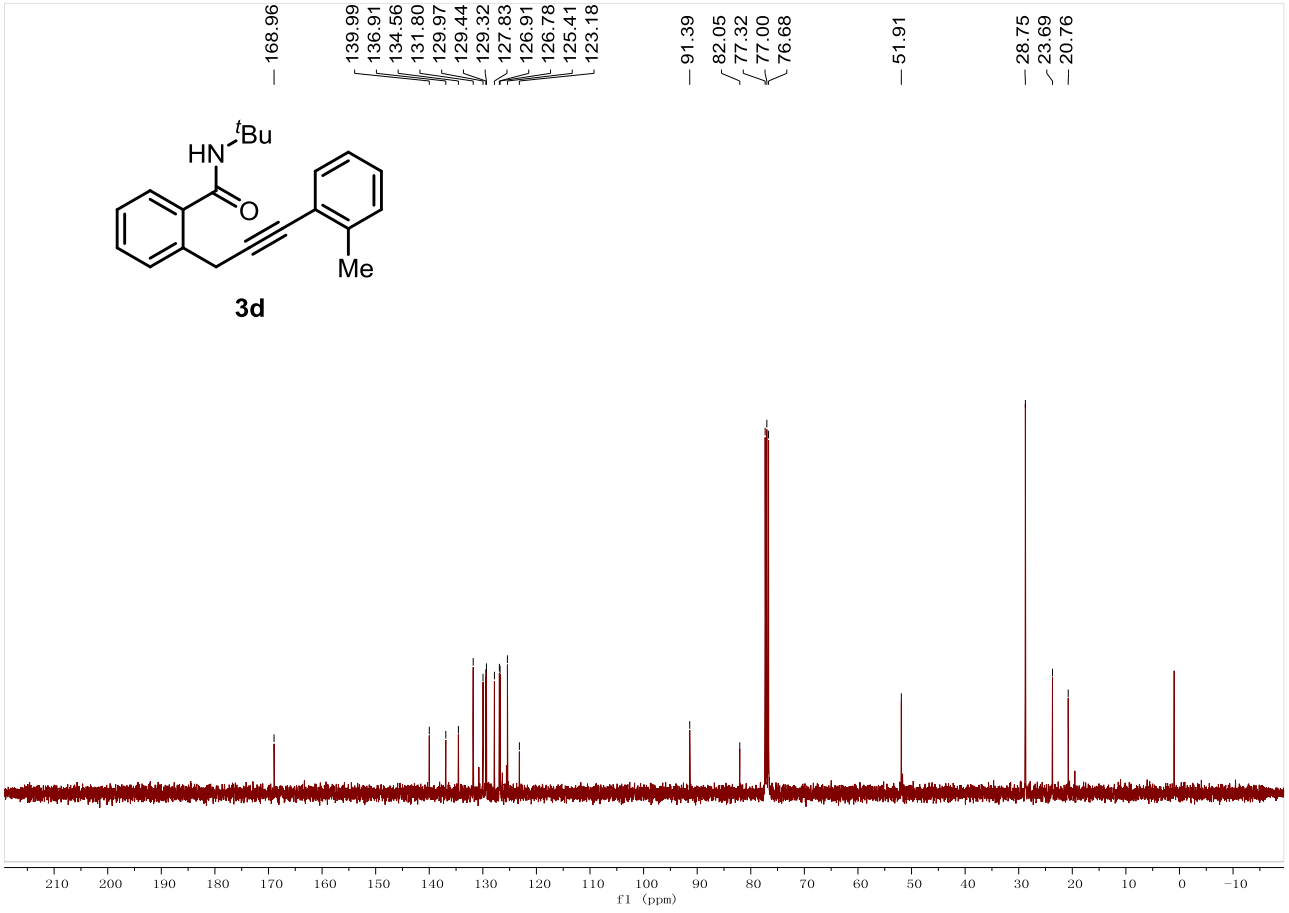
3c, ^{13}C NMR (101 MHz, $CDCl_3$)



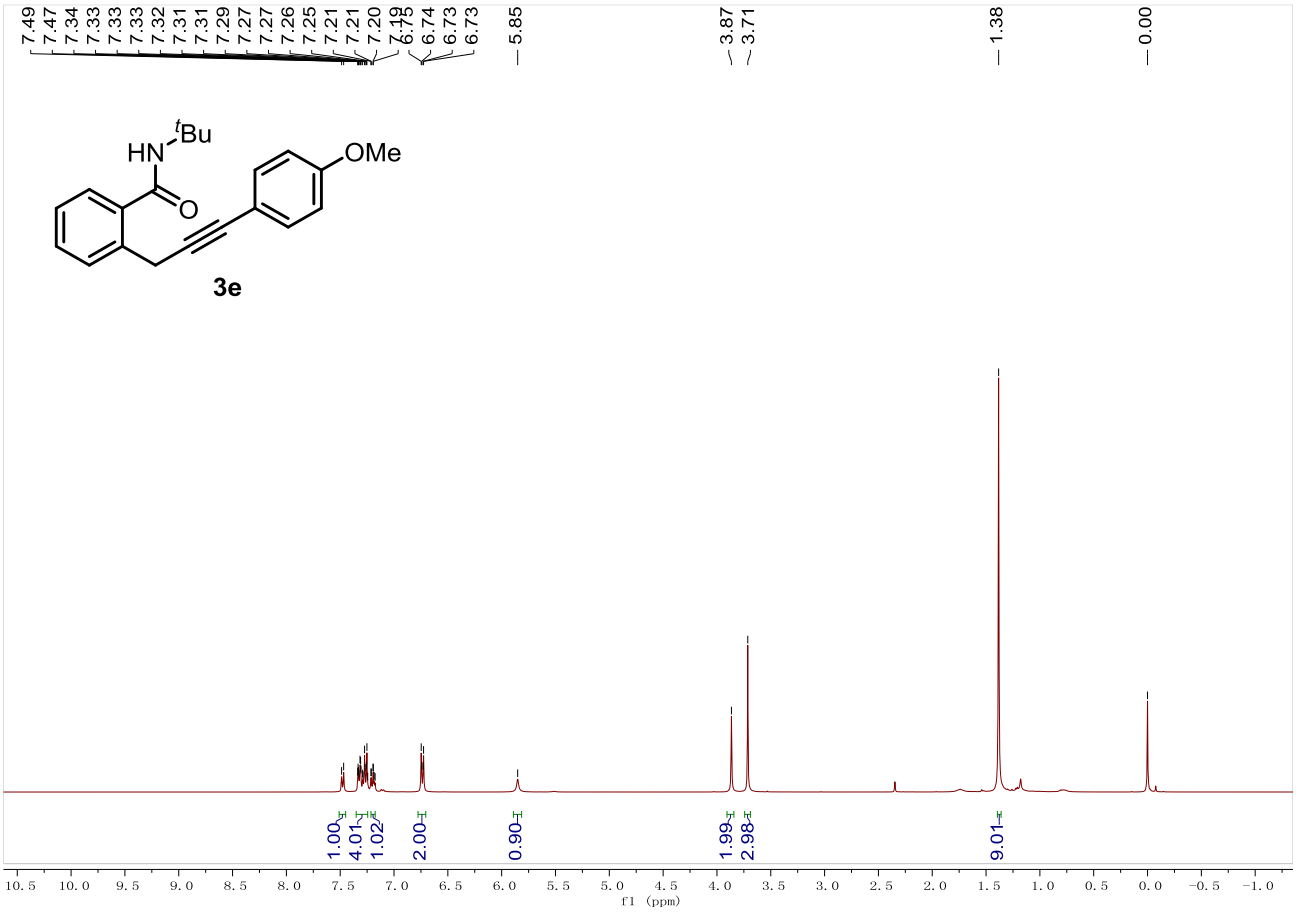
3d, ^{1}H NMR (300 MHz, $CDCl_3$)



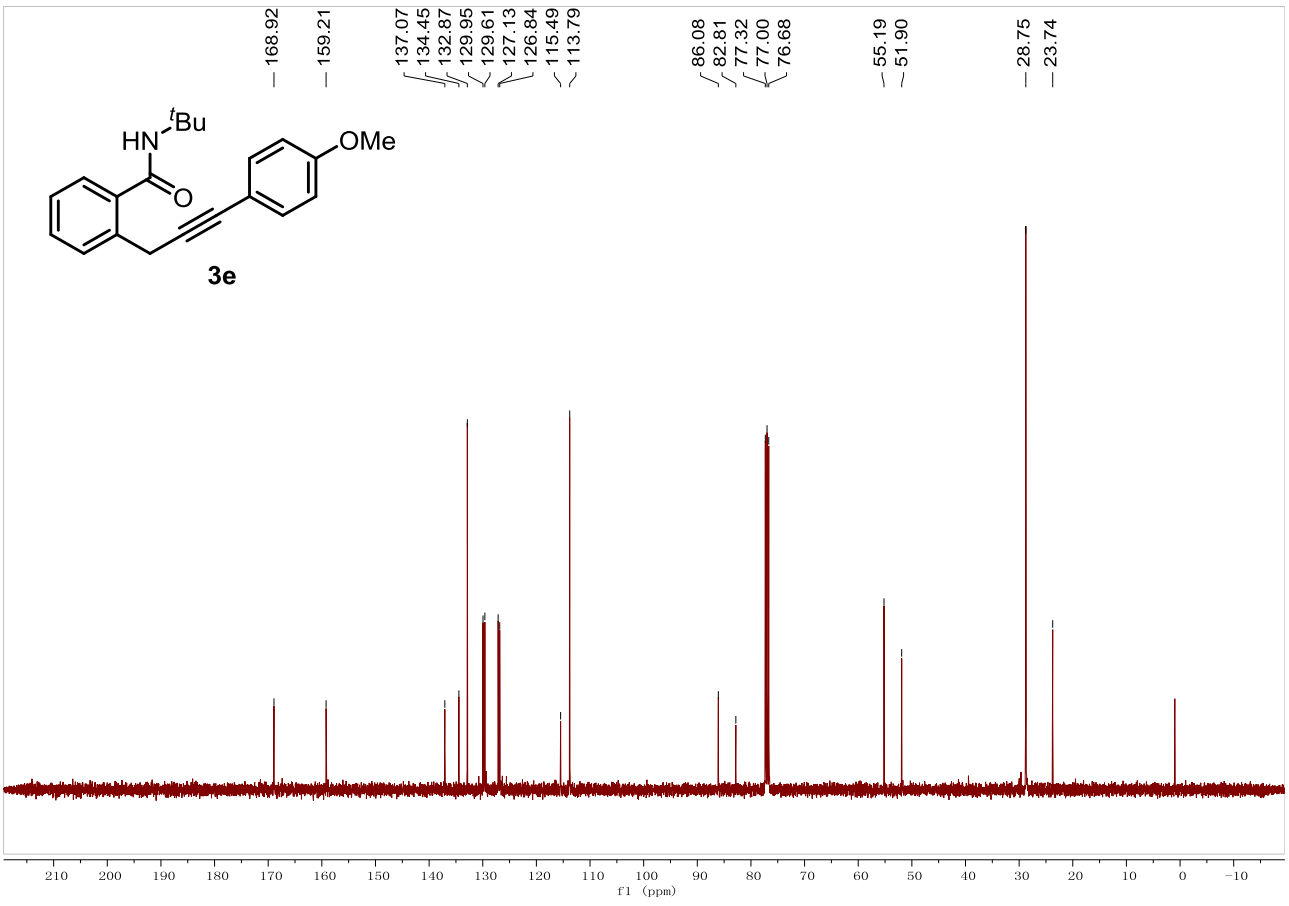
3d, ^{13}C NMR (101 MHz, $CDCl_3$)



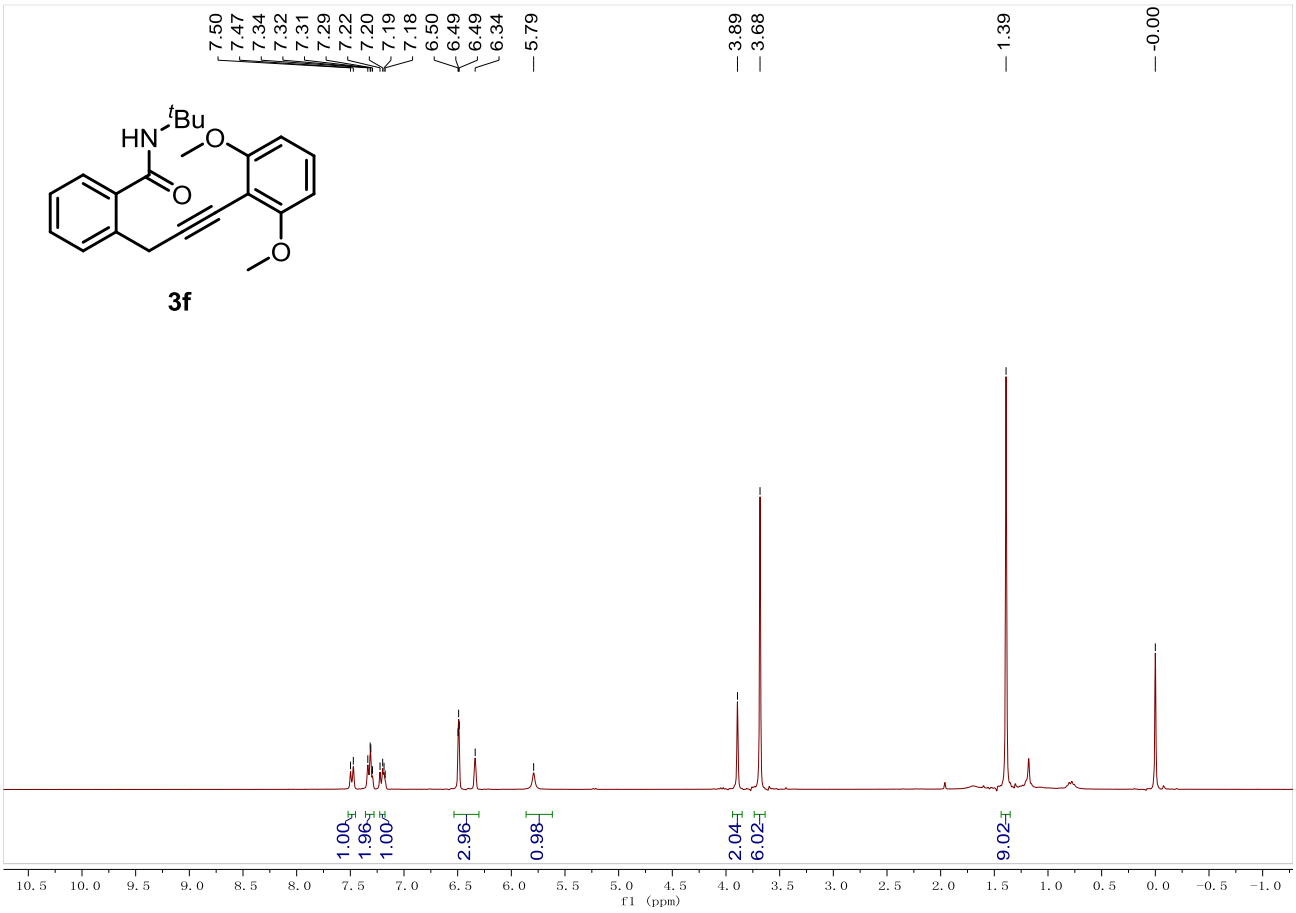
3e, ^{1}H NMR (400 MHz, $CDCl_3$)



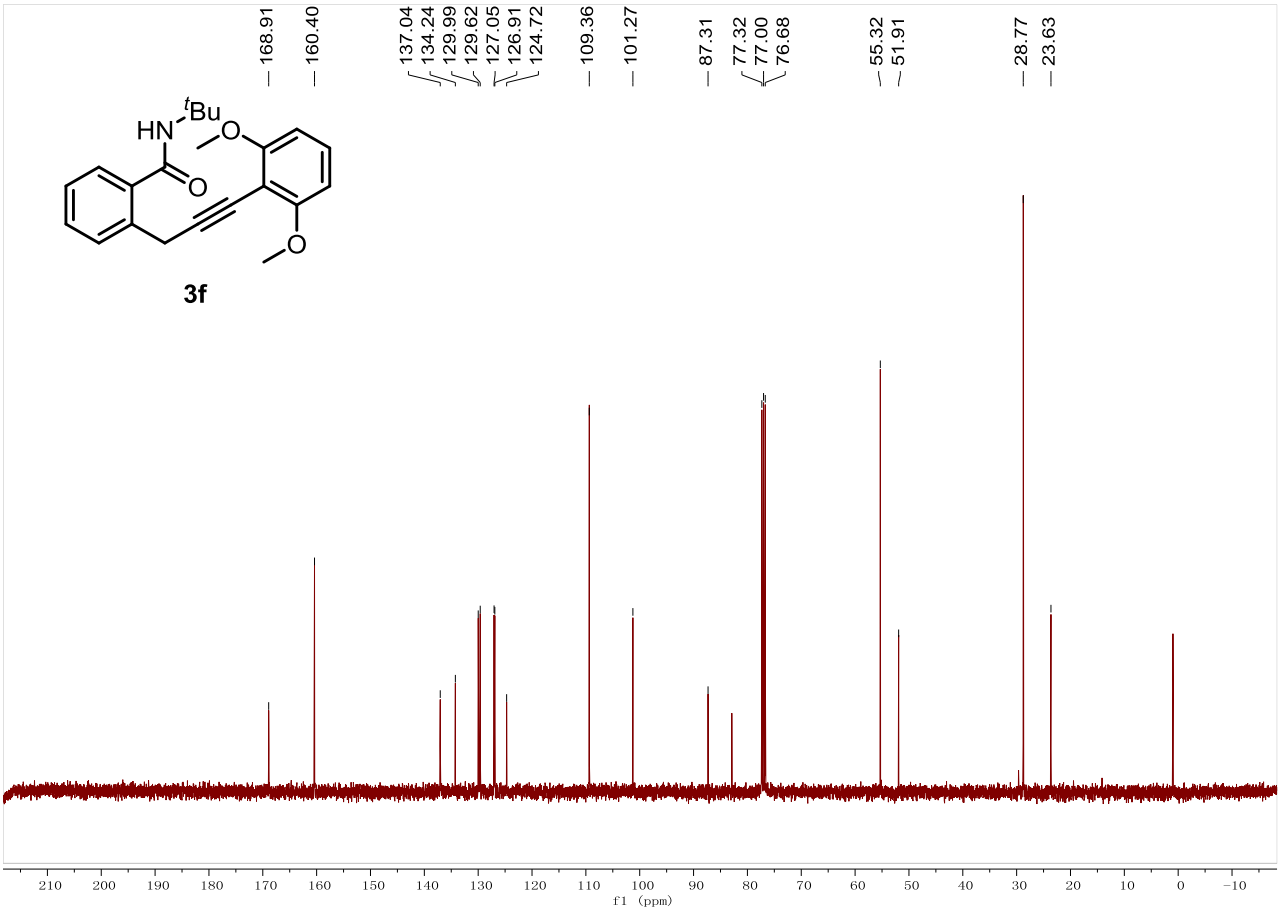
3e, ^{13}C NMR (101 MHz, $CDCl_3$)



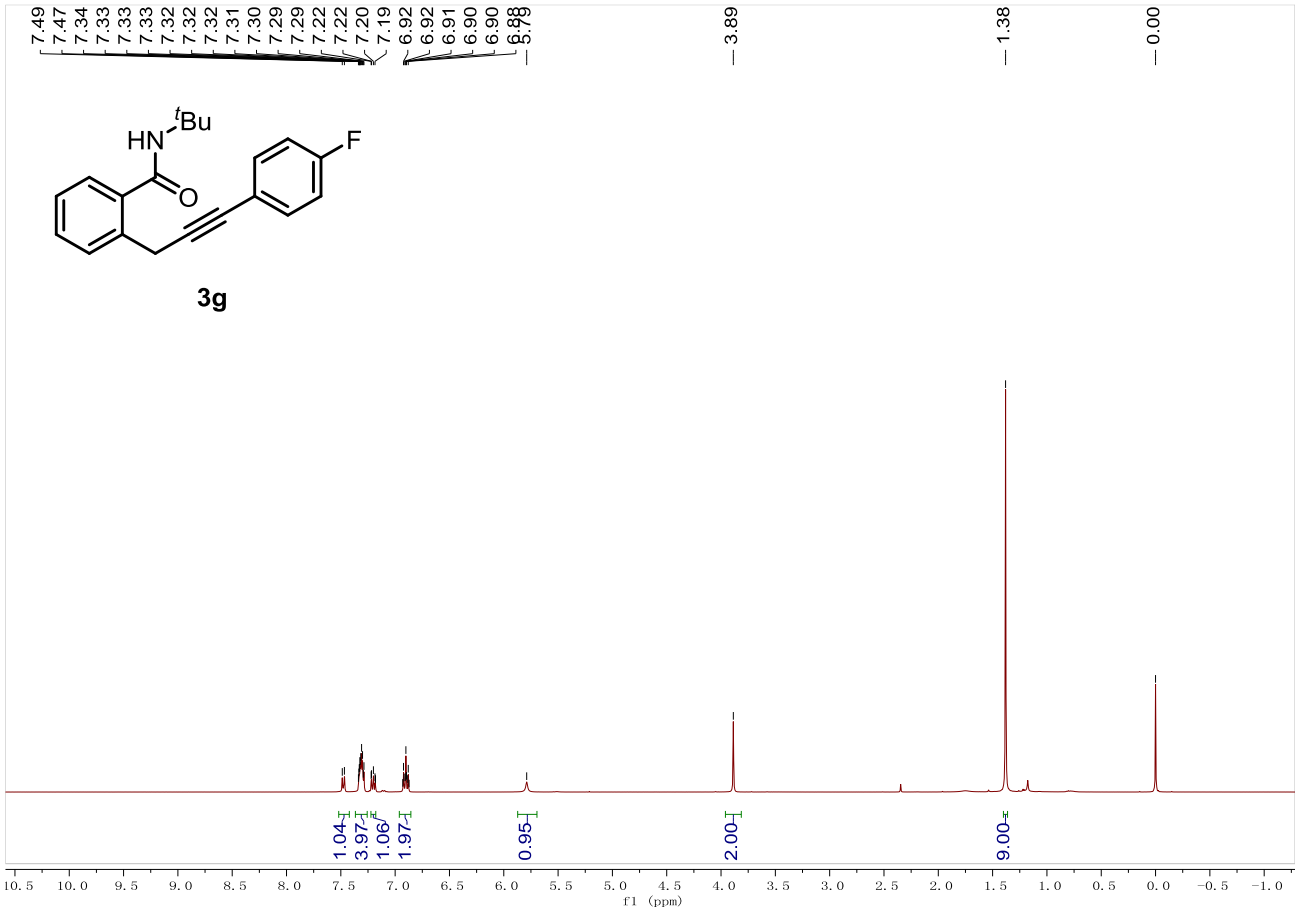
3f, ^{1}H NMR (300 MHz, $CDCl_3$)



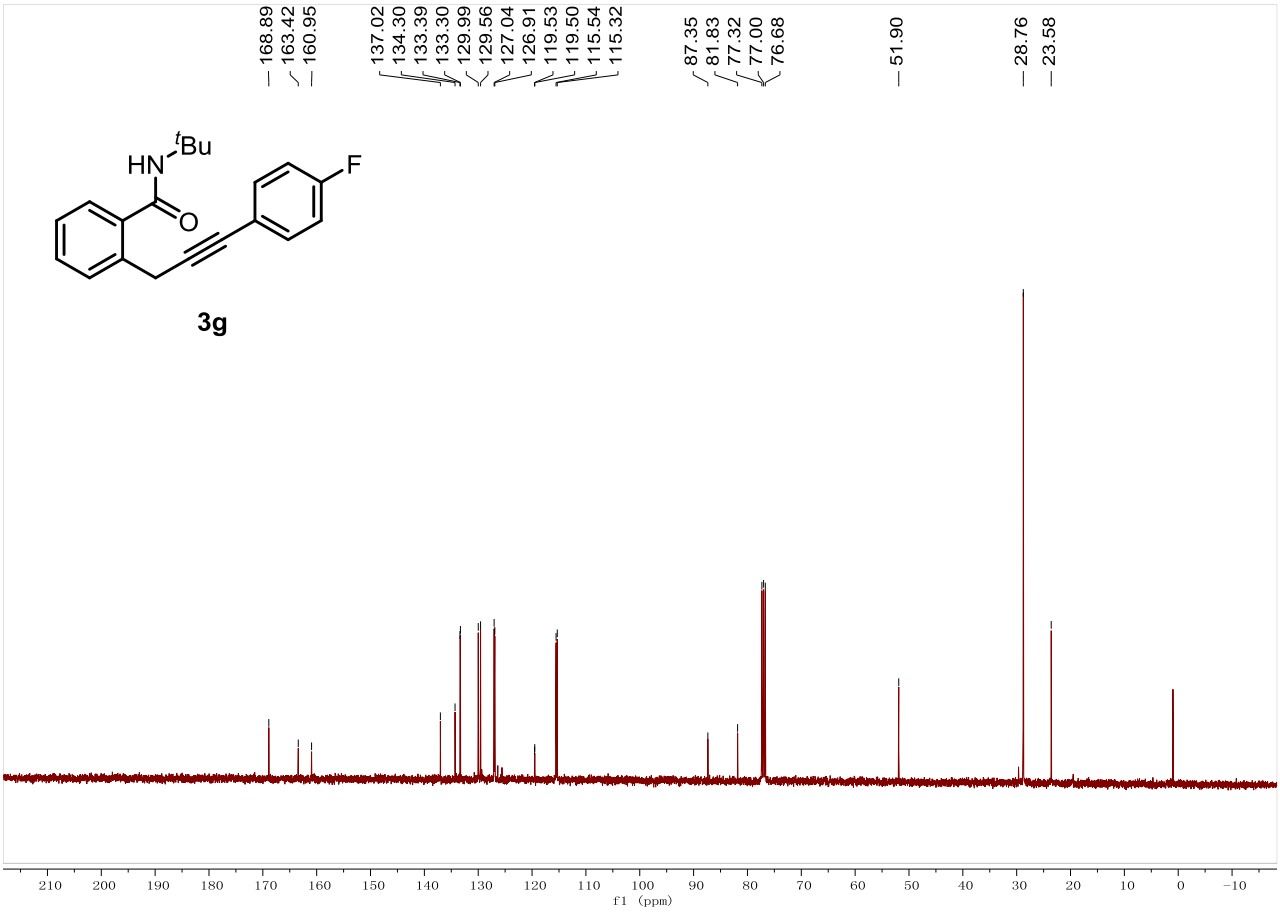
3f, ^{13}C NMR (101 MHz, $CDCl_3$)



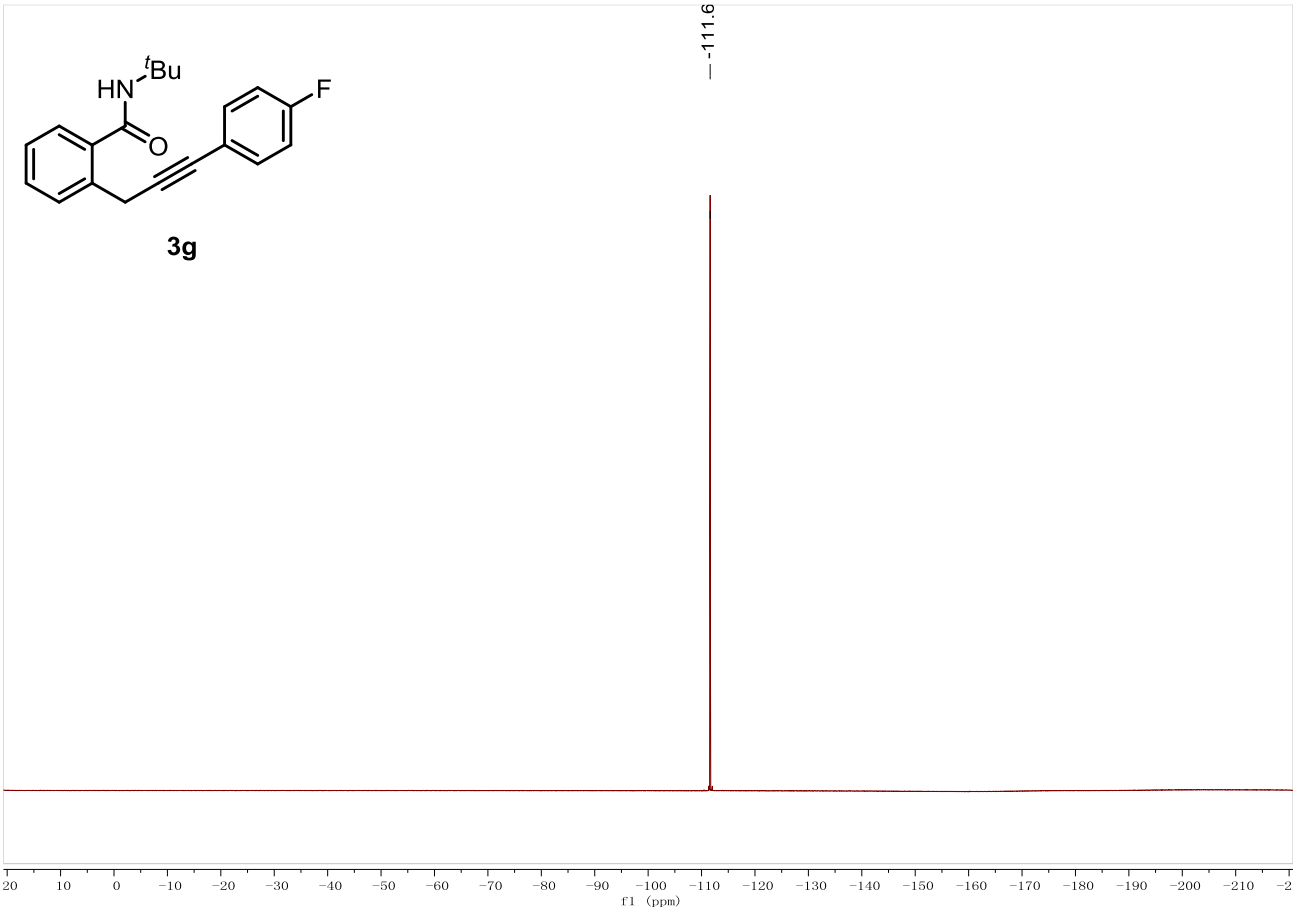
3g, ^{1}H NMR (400 MHz, $CDCl_3$)



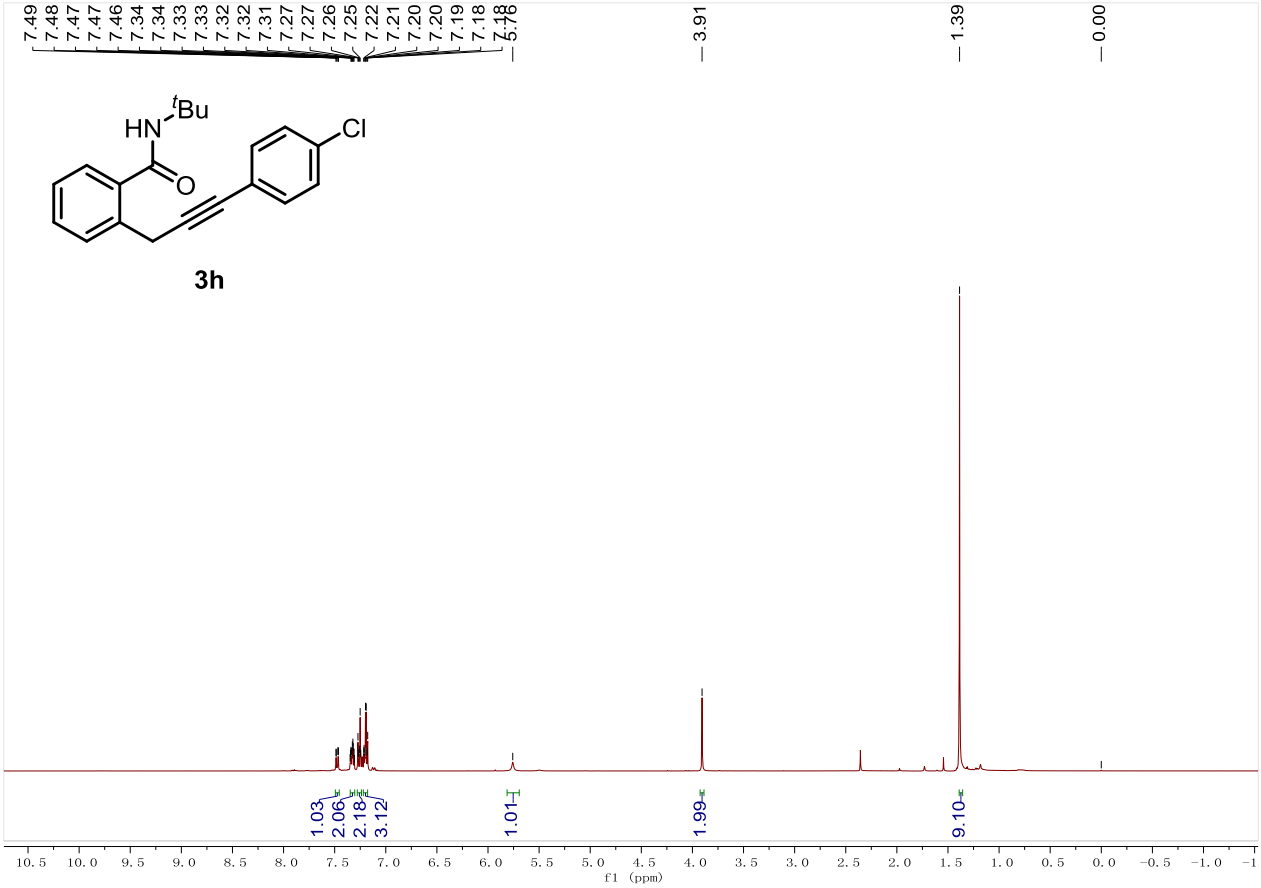
3g, ^{13}C NMR (101 MHz, $CDCl_3$)



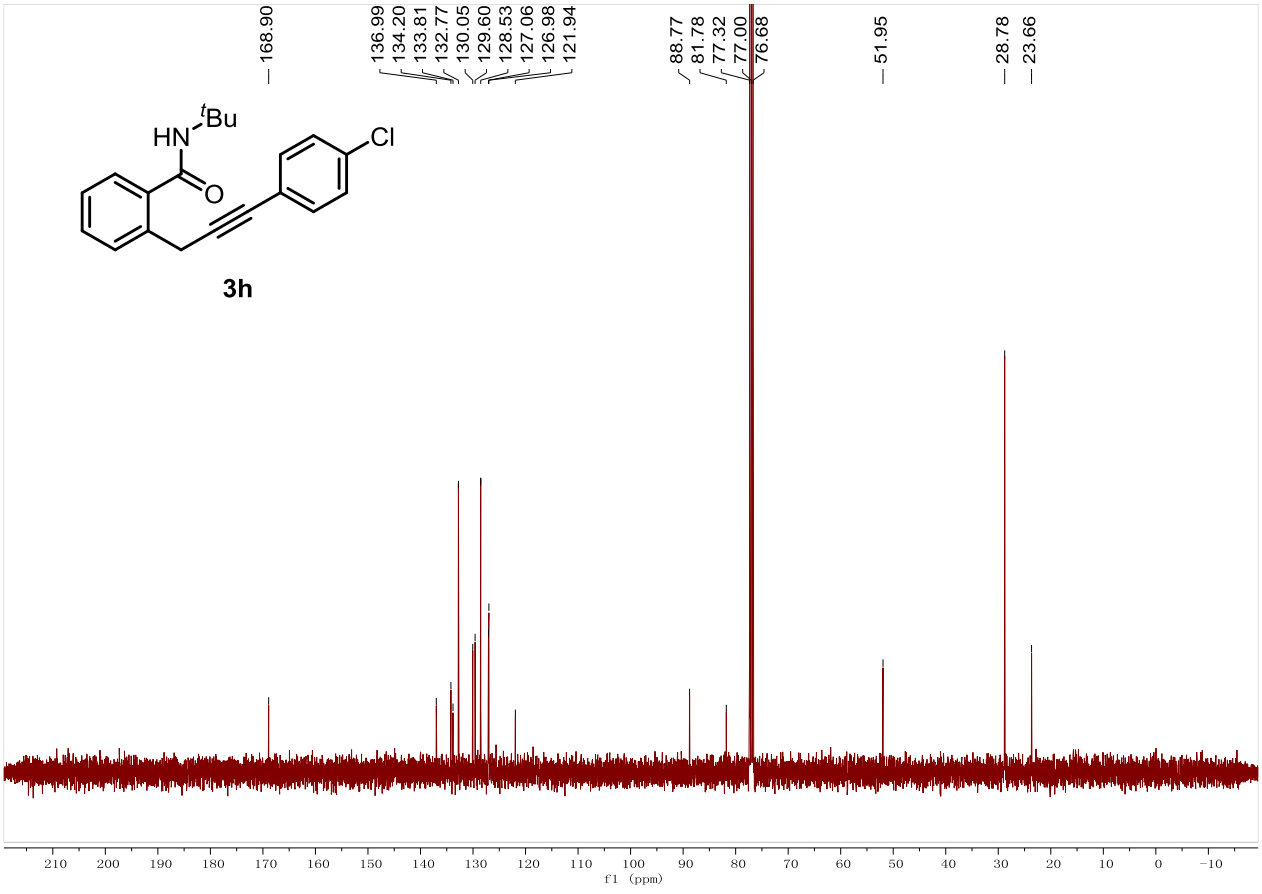
3g, ^{19}F NMR (376 MHz, $CDCl_3$)



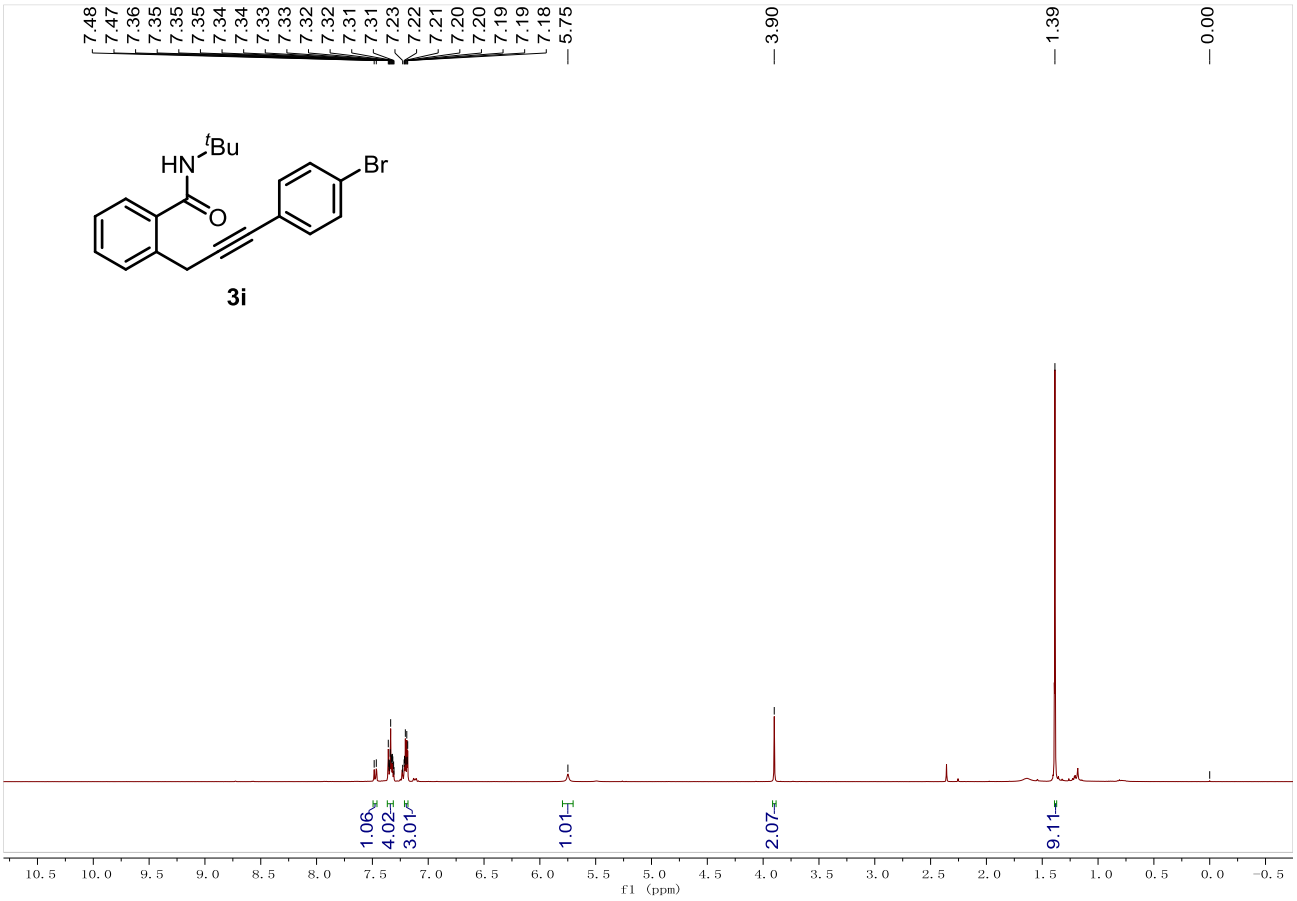
3h, ^{1}H NMR (400 MHz, $CDCl_3$)



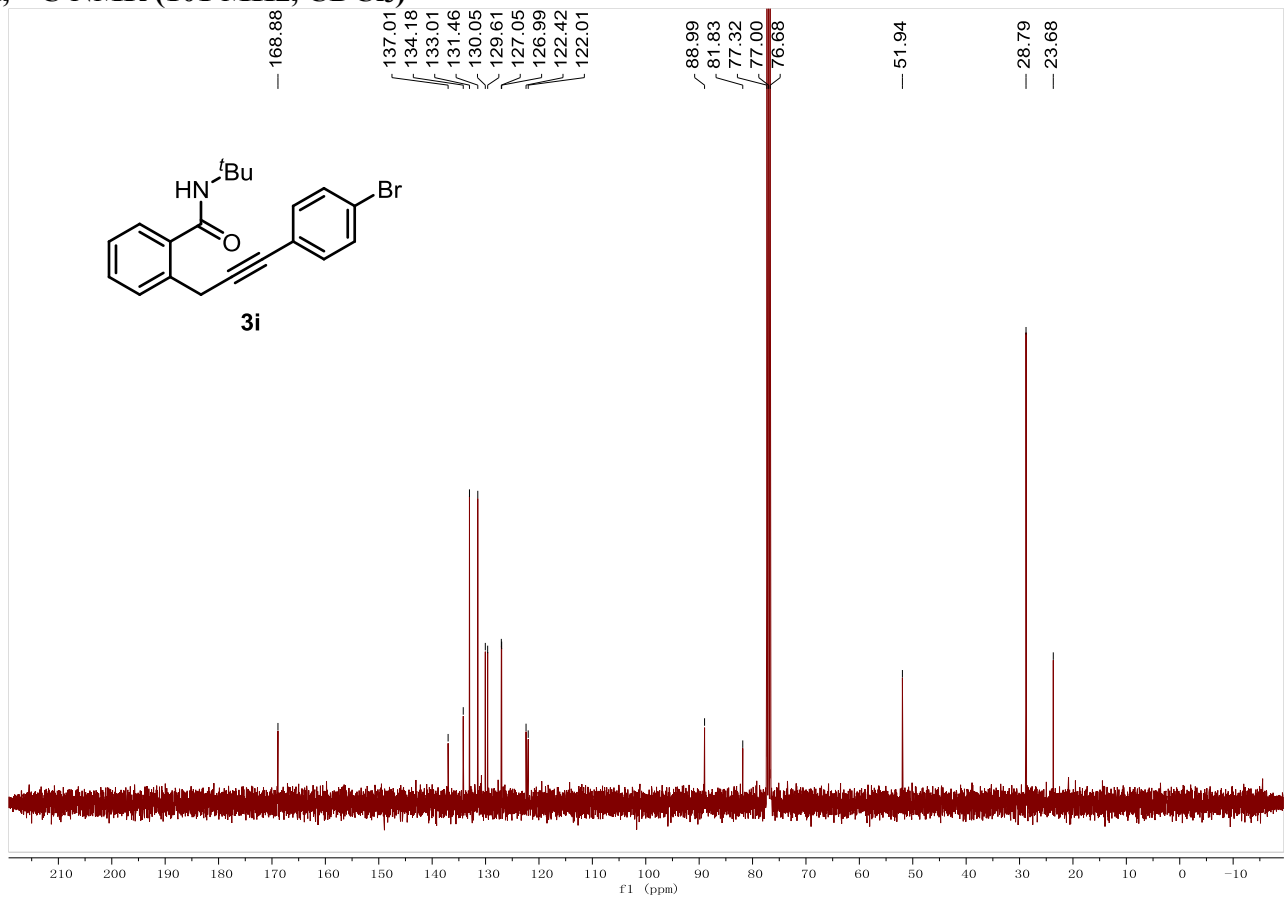
3h, ^{13}C NMR (101 MHz, $CDCl_3$)



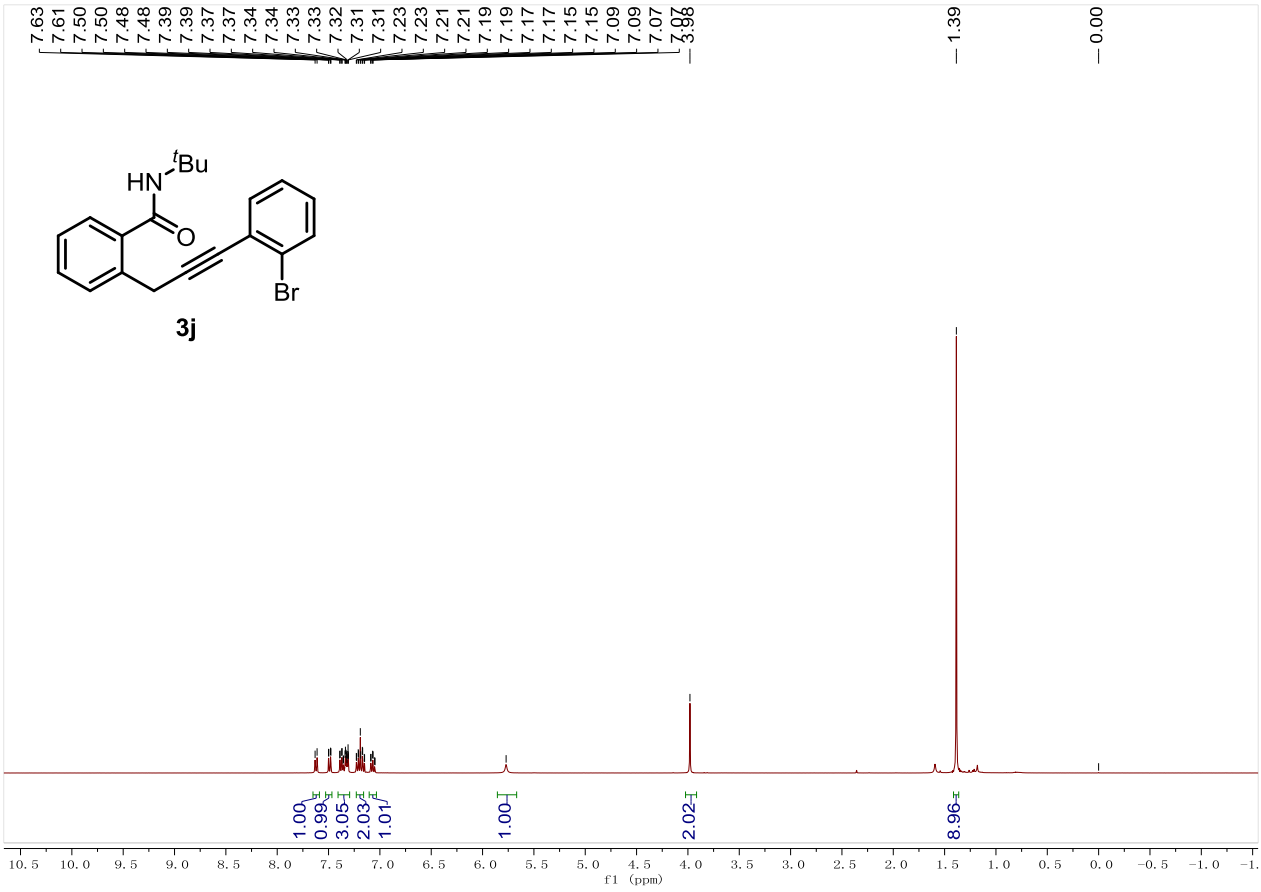
3i, ^{1}H NMR (400 MHz, $CDCl_3$)



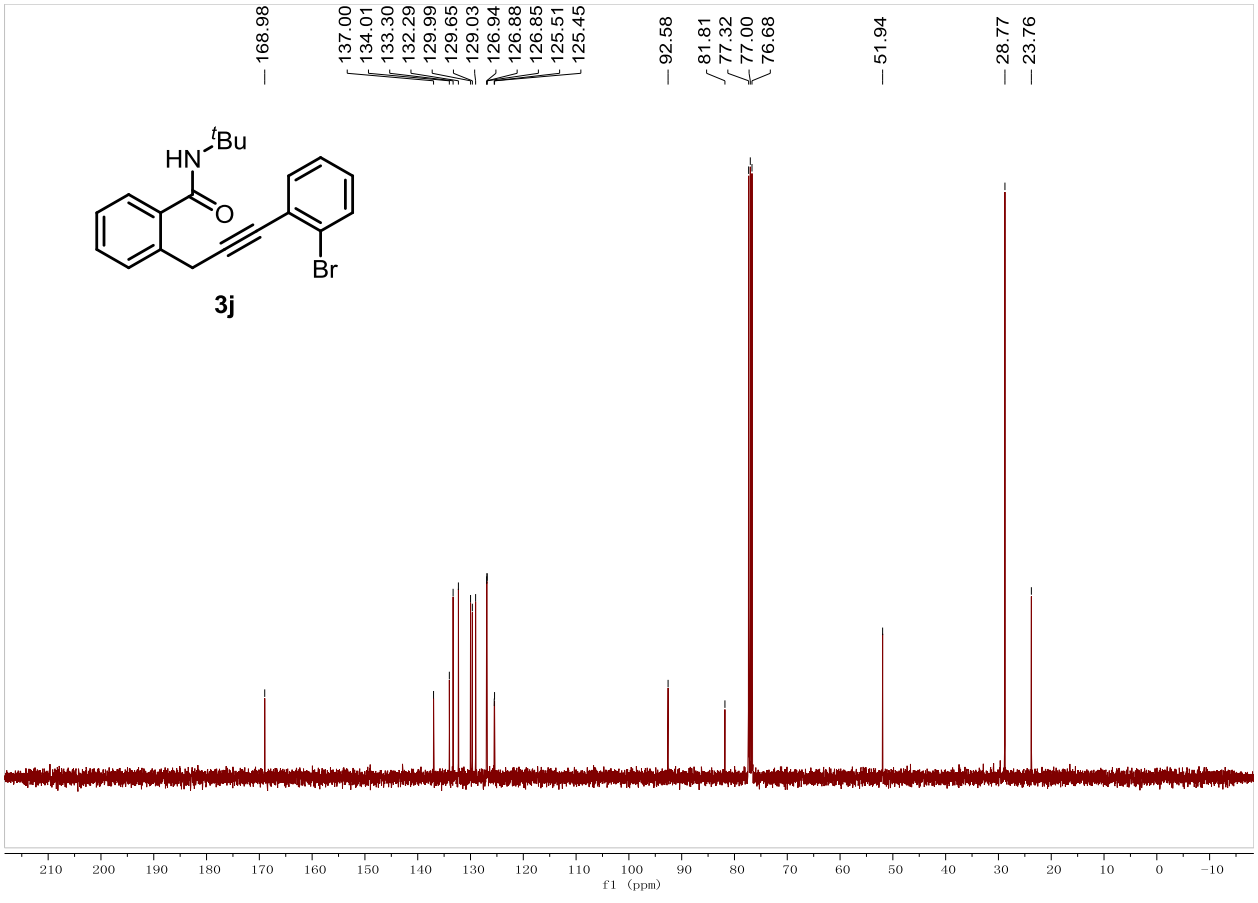
3i, ^{13}C NMR (101 MHz, $CDCl_3$)



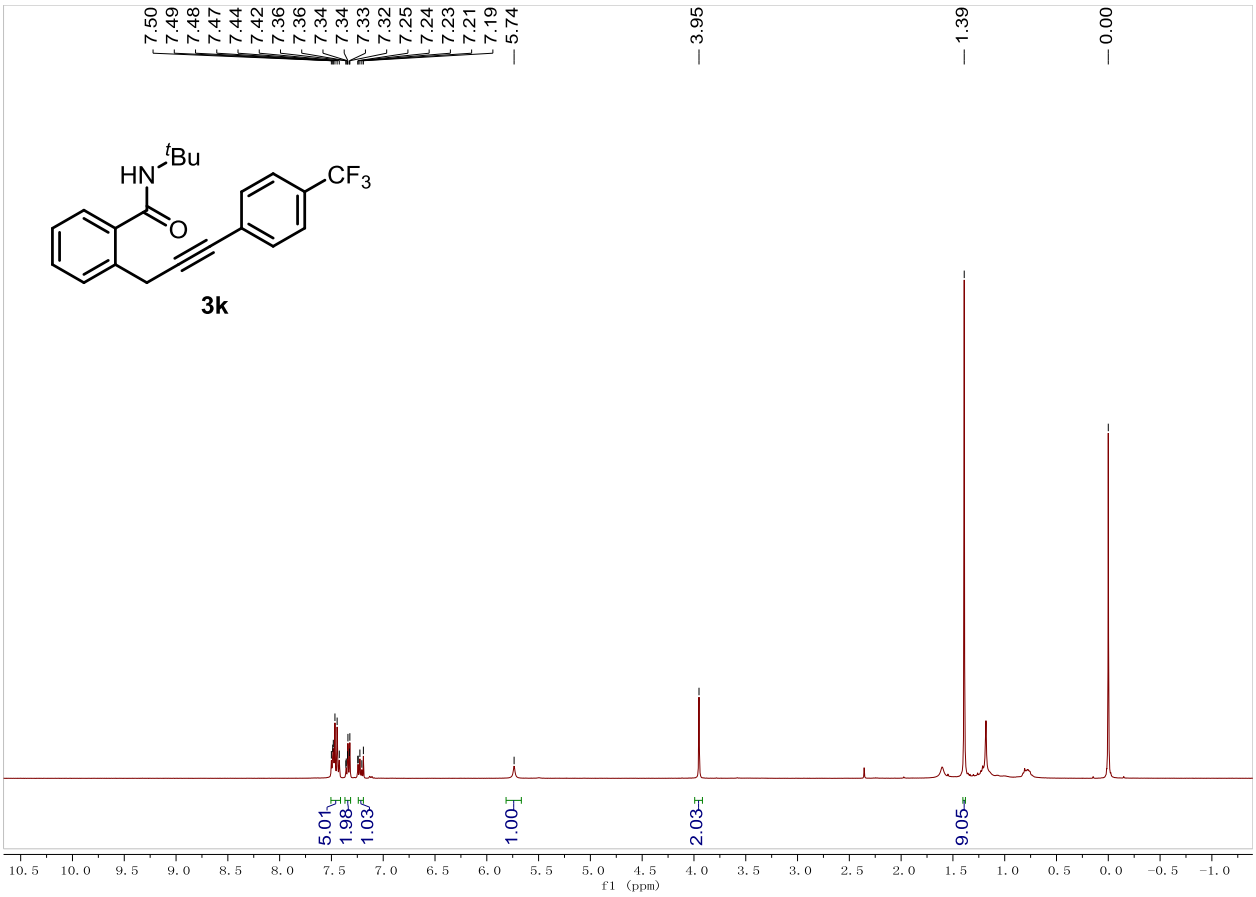
3j, ^{1}H NMR (400 MHz, $CDCl_3$)



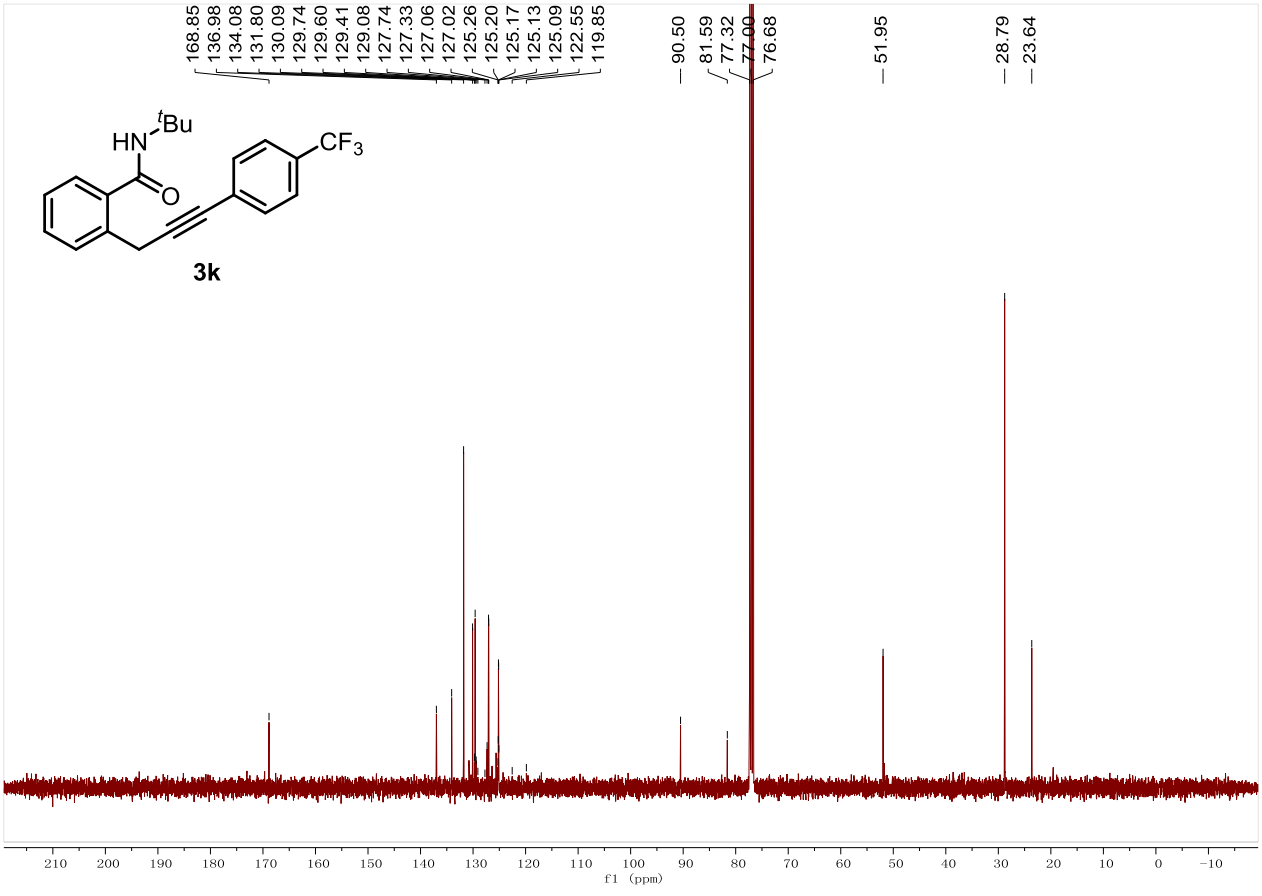
3j, ^{13}C NMR (101 MHz, $CDCl_3$)



3k, ^{1}H NMR (400 MHz, $CDCl_3$)

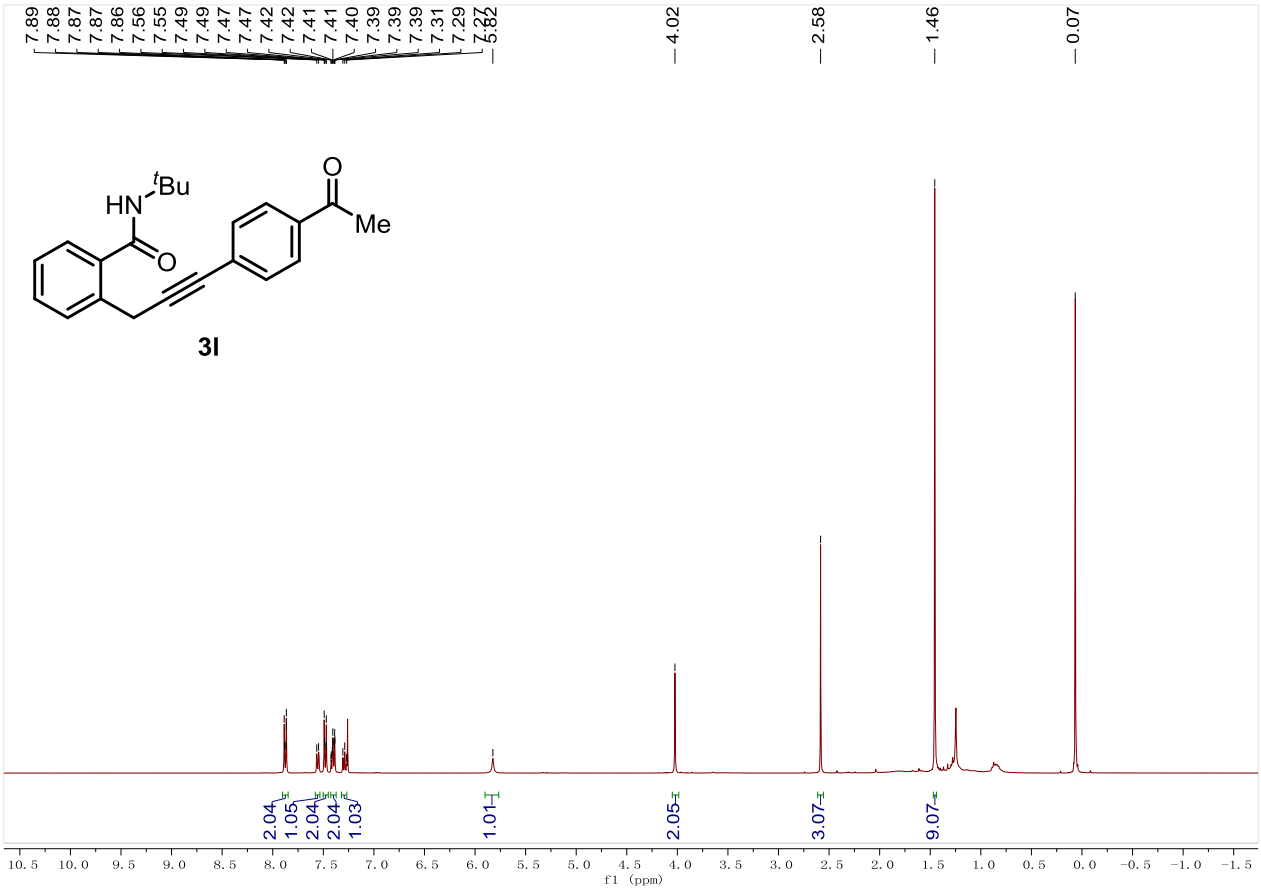


3k, ^{13}C NMR (101 MHz, $CDCl_3$)

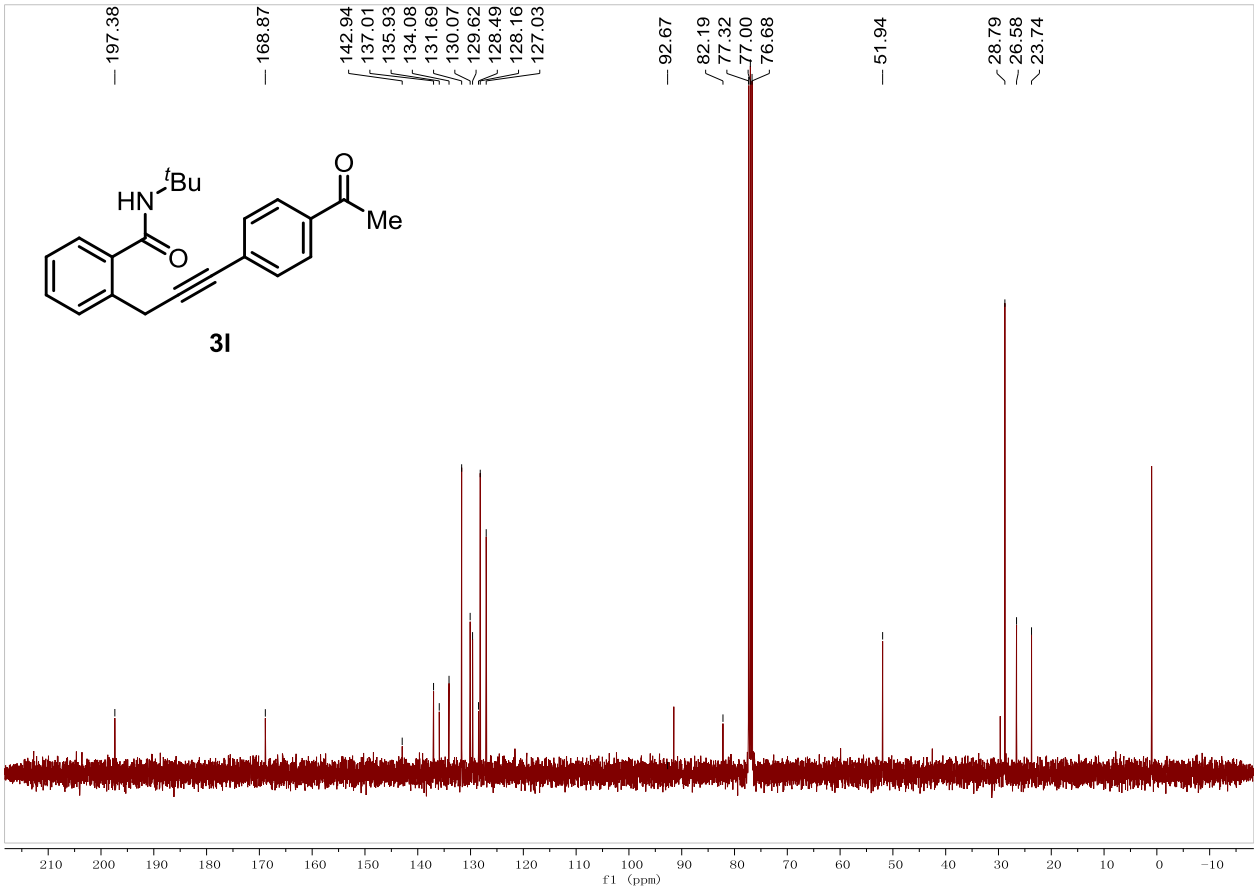


3k,^{19}F NMR (376 MHz, $CDCl_3$)

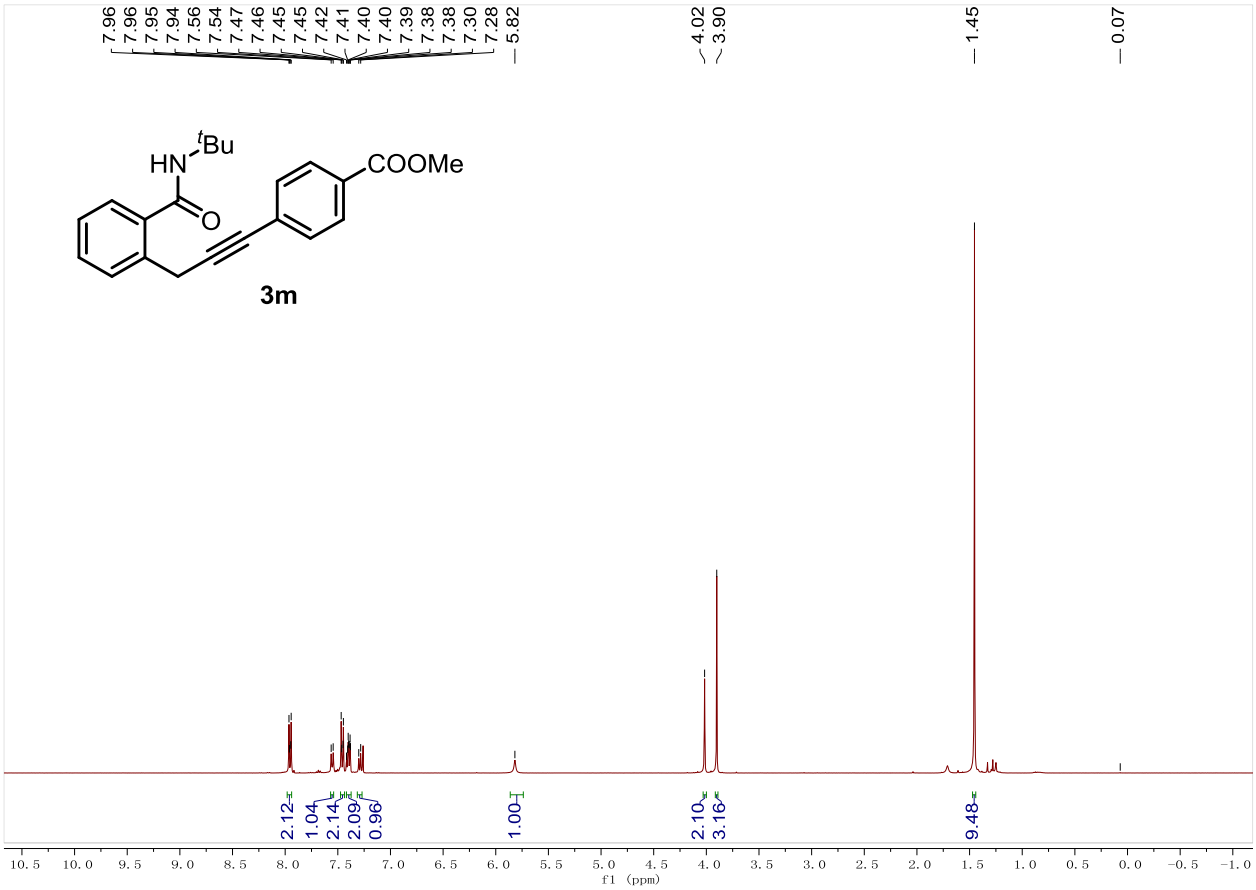
3l, ^{1}H NMR (400 MHz, $CDCl_3$)



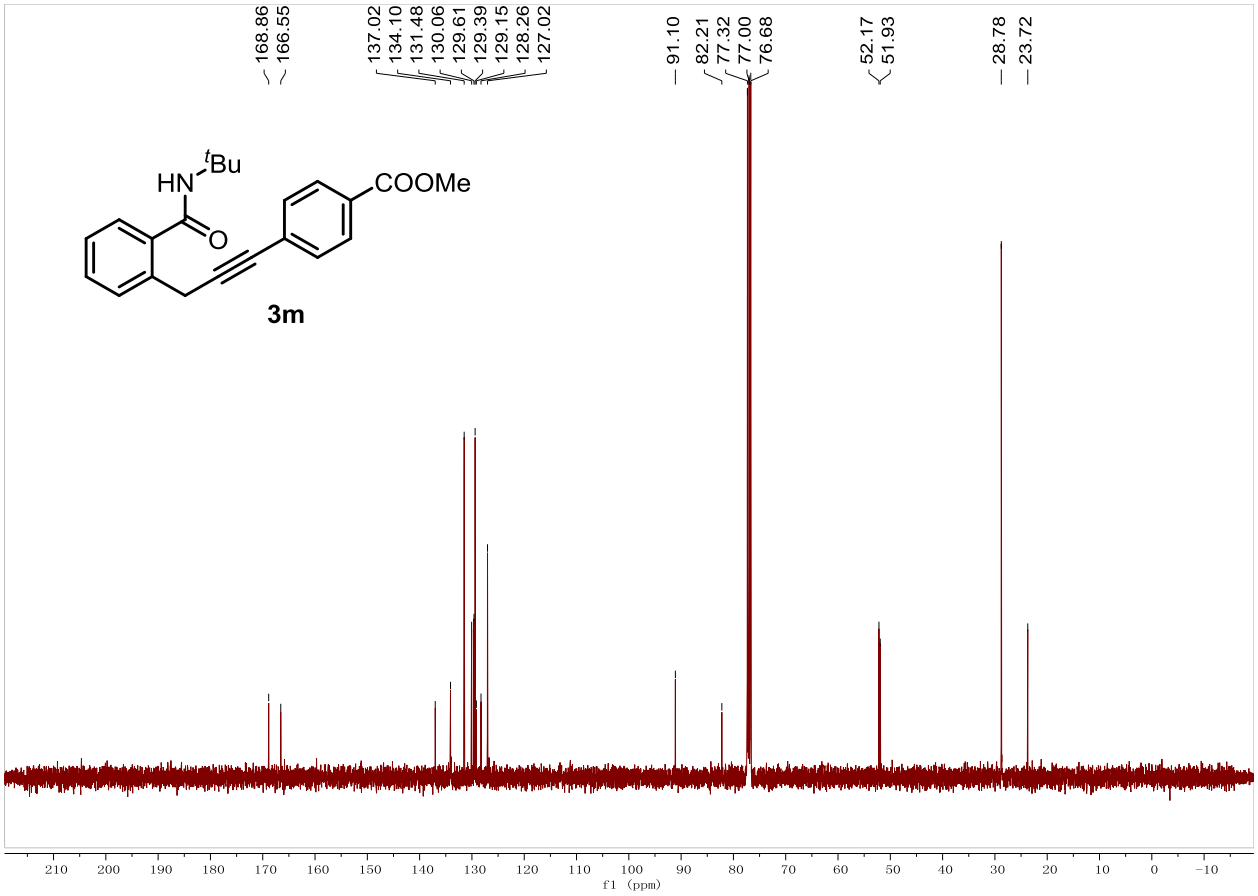
3l, ^{13}C NMR (101 MHz, $CDCl_3$)



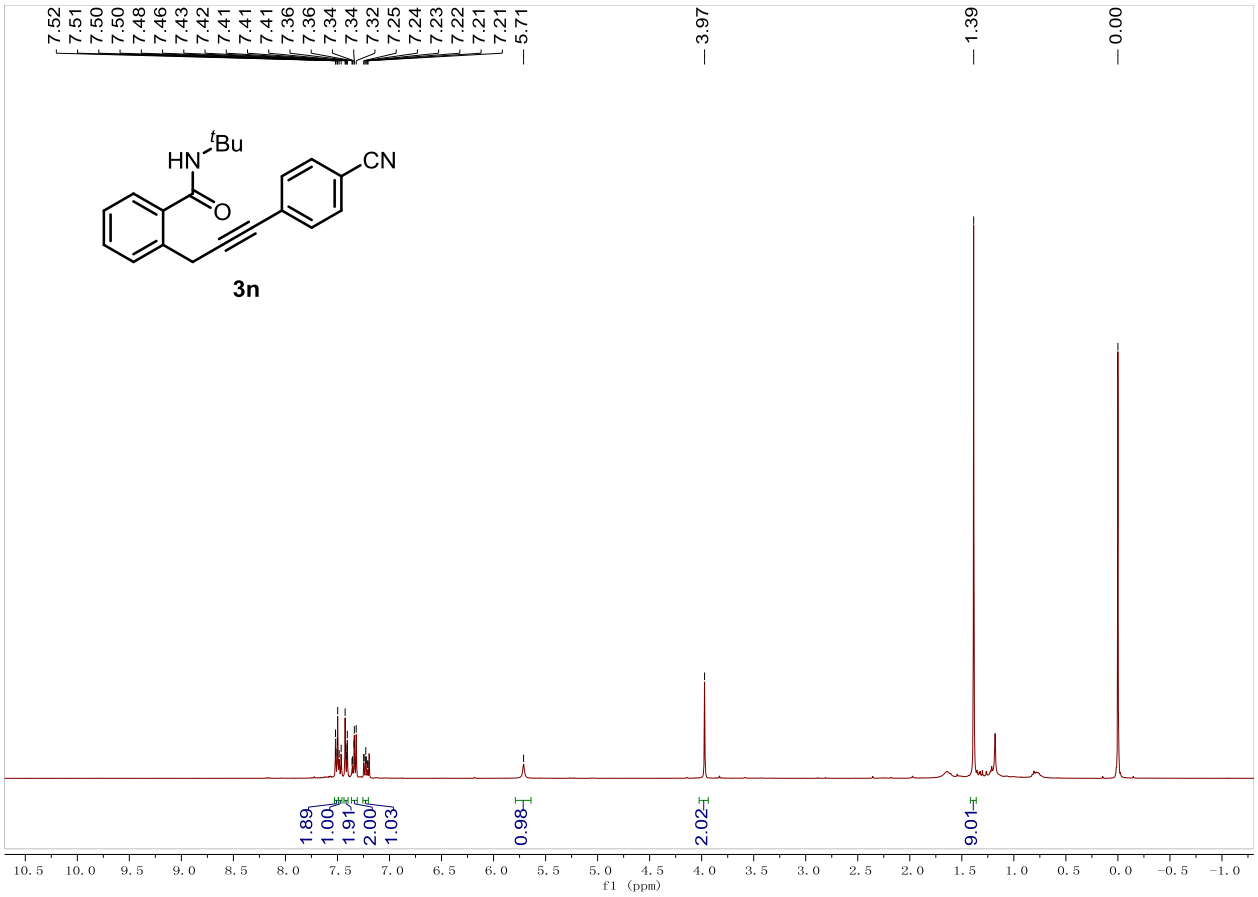
3m, ^{1}H NMR (400 MHz, $CDCl_3$)



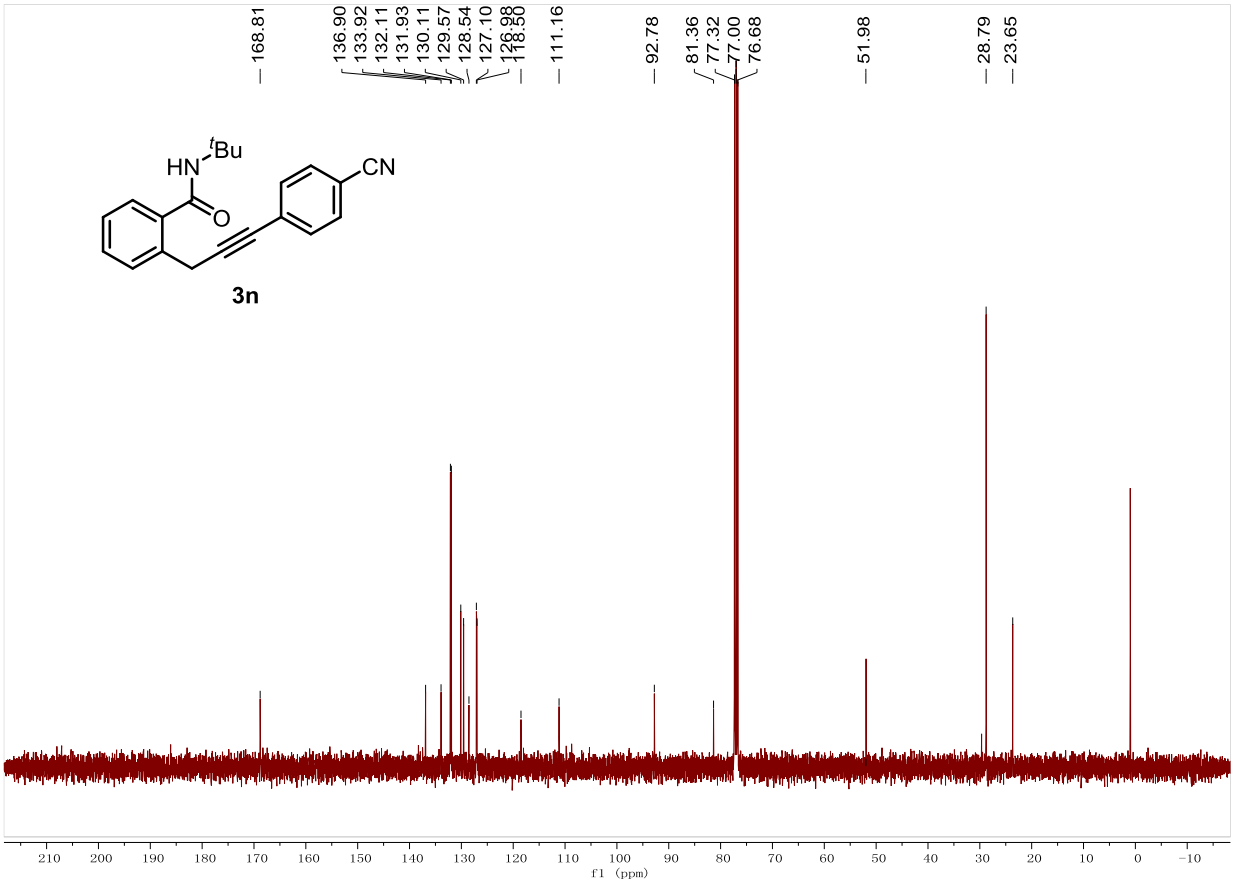
3m, ^{13}C NMR (101 MHz, $CDCl_3$)



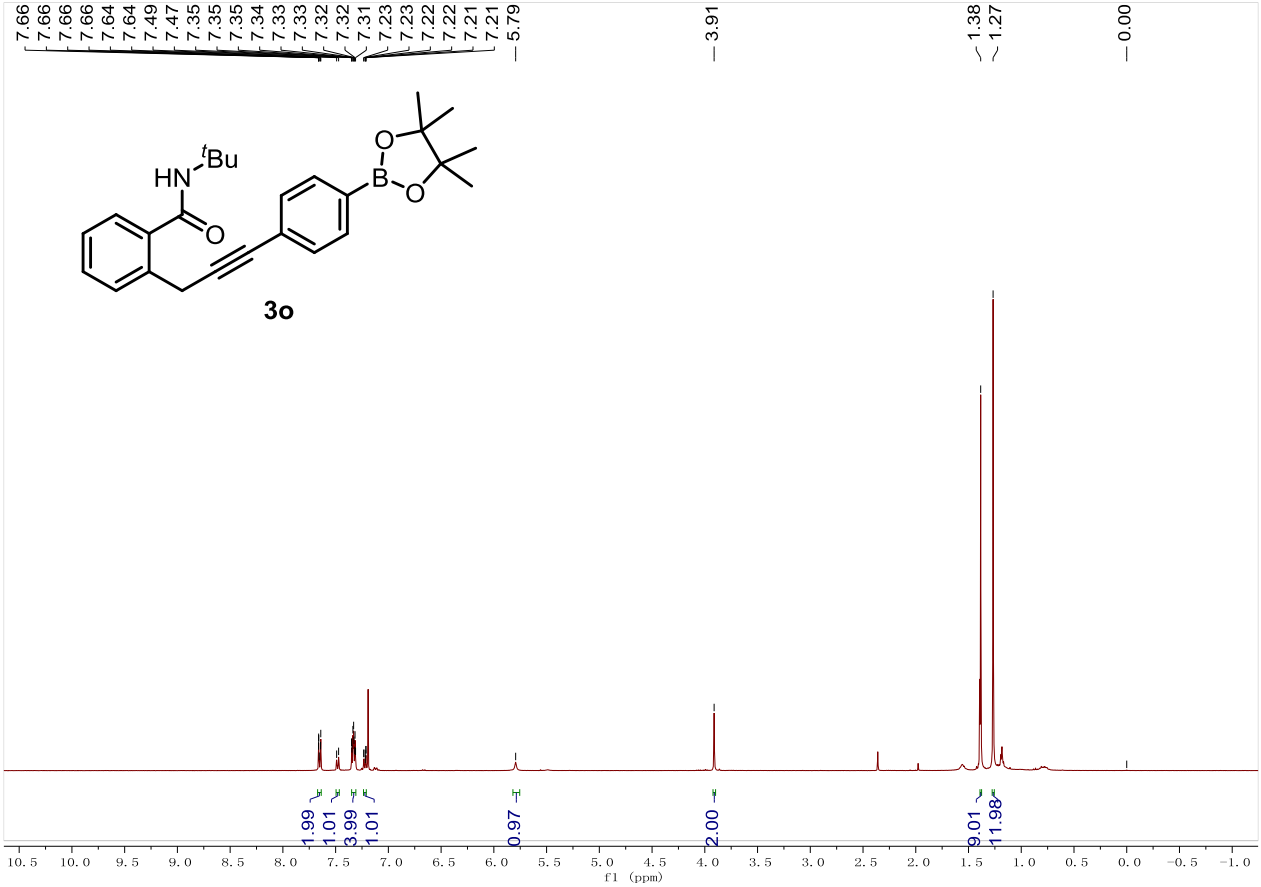
3n, ^{1}H NMR (400 MHz, $CDCl_3$)



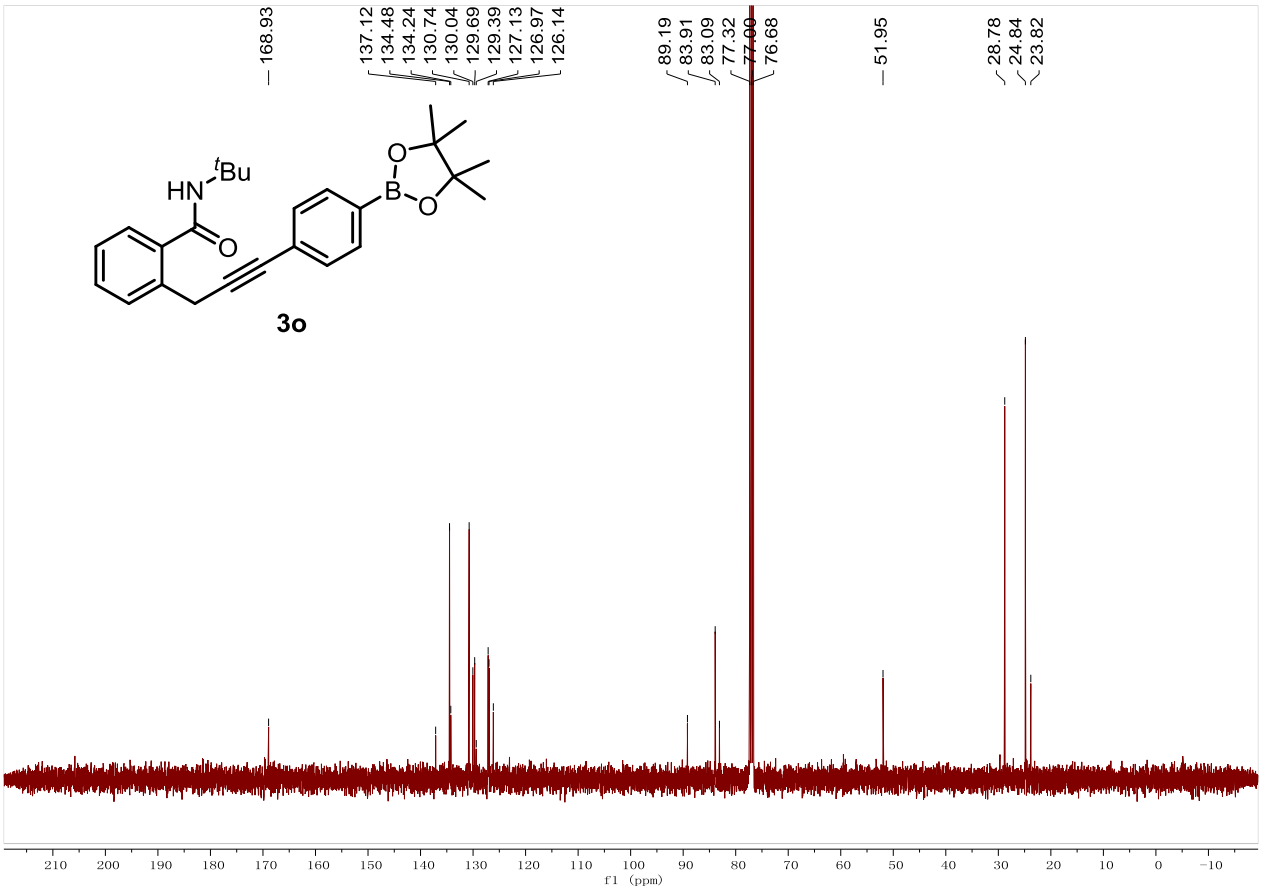
3n, ^{13}C NMR (101 MHz, $CDCl_3$)



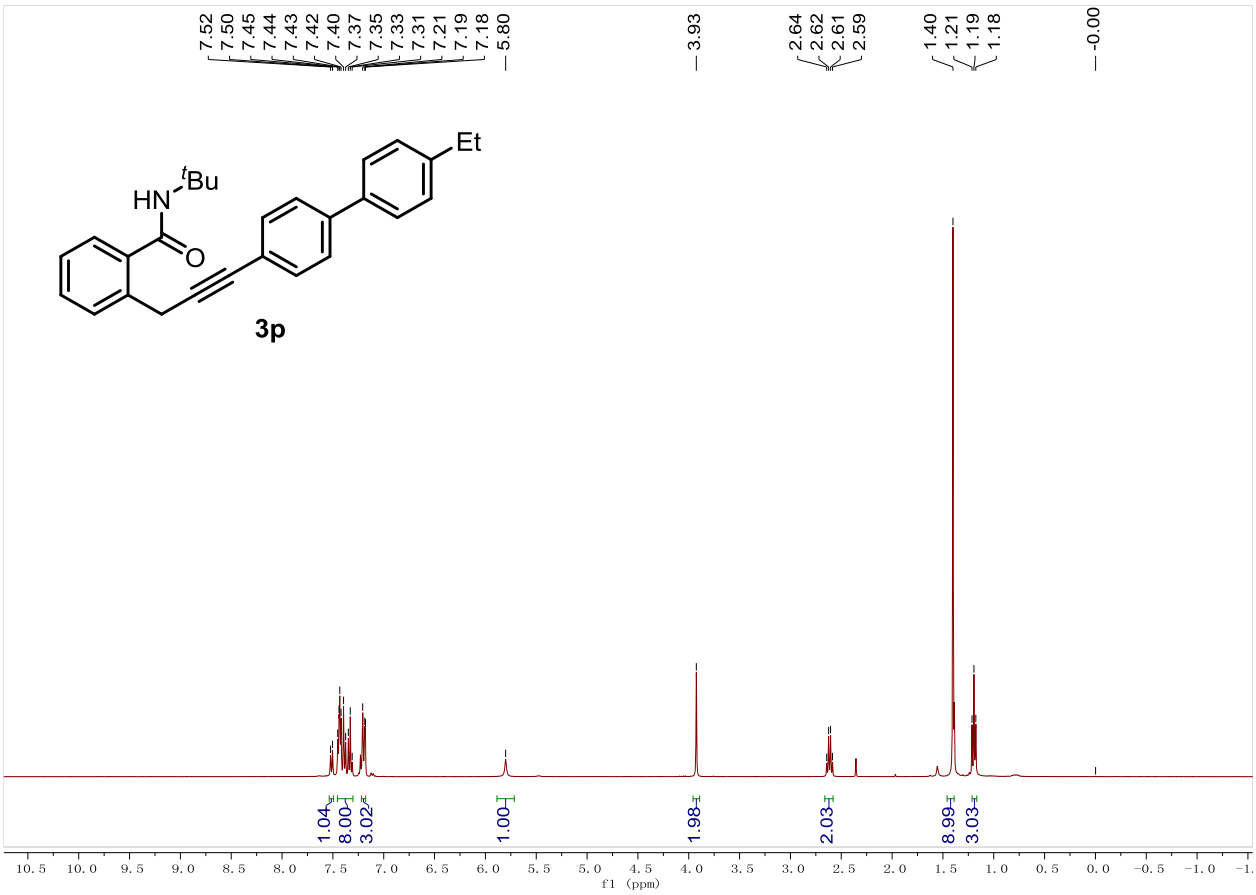
3o, ^{1}H NMR (400 MHz, $CDCl_3$)



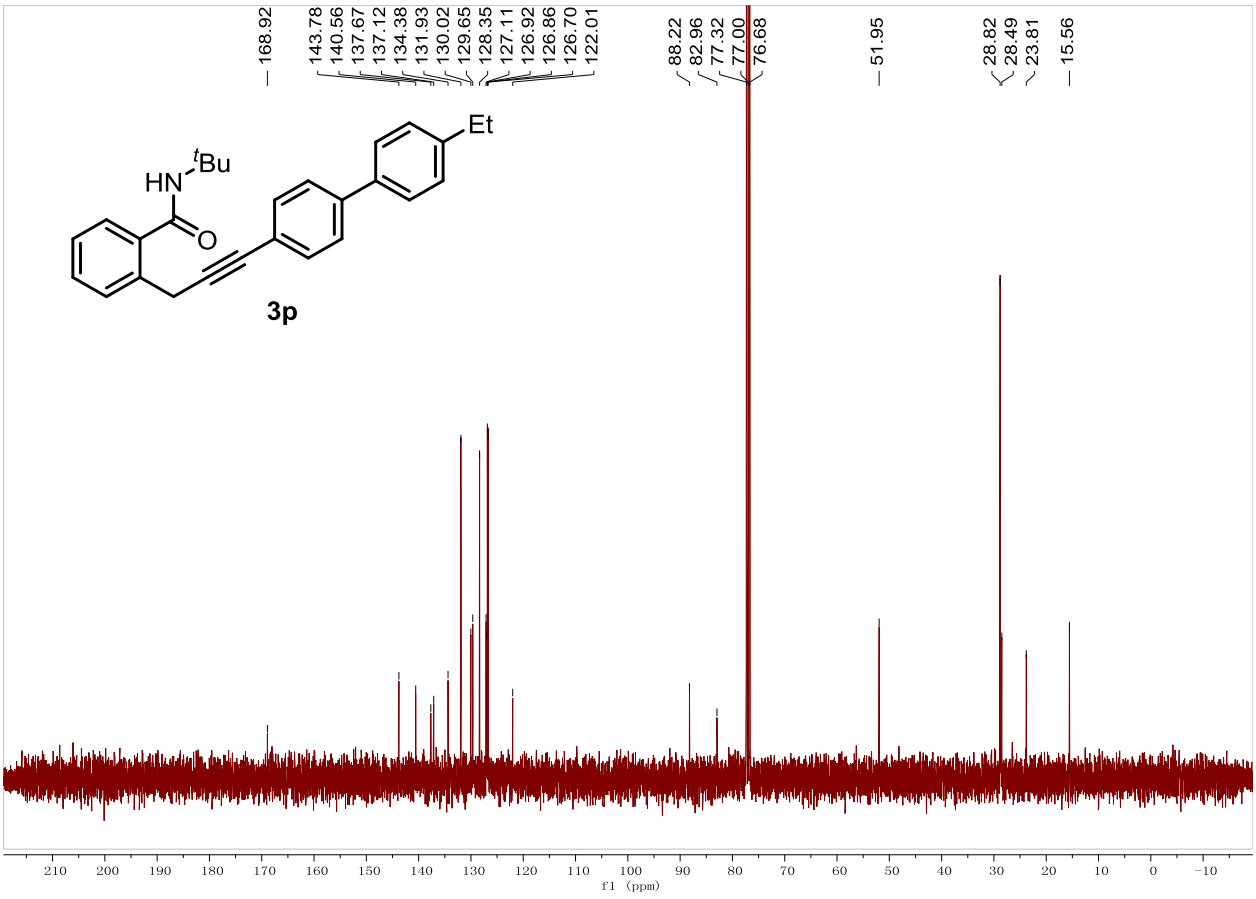
3o, ^{13}C NMR (101 MHz, $CDCl_3$)



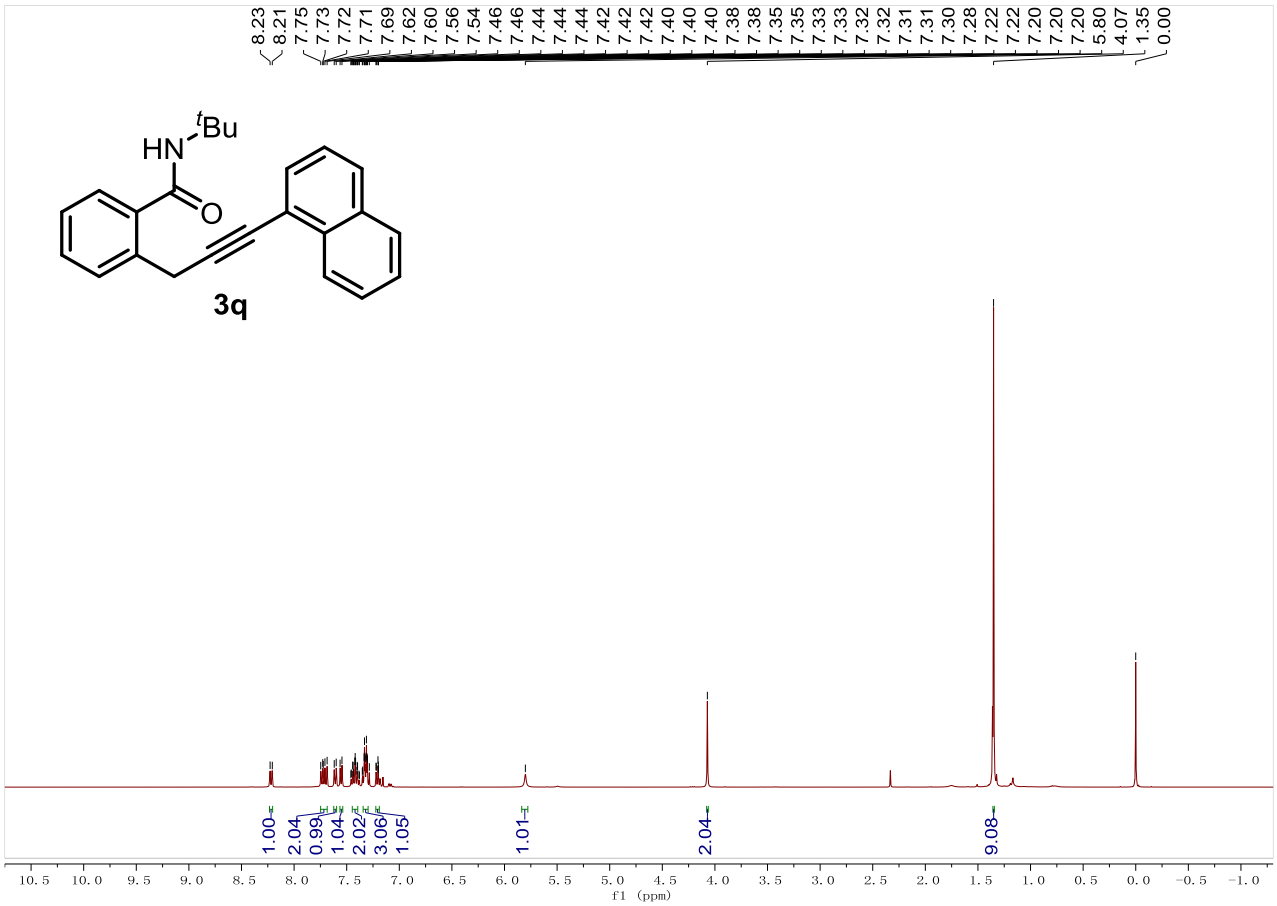
3p, ^{1}H NMR (400 MHz, $CDCl_3$)



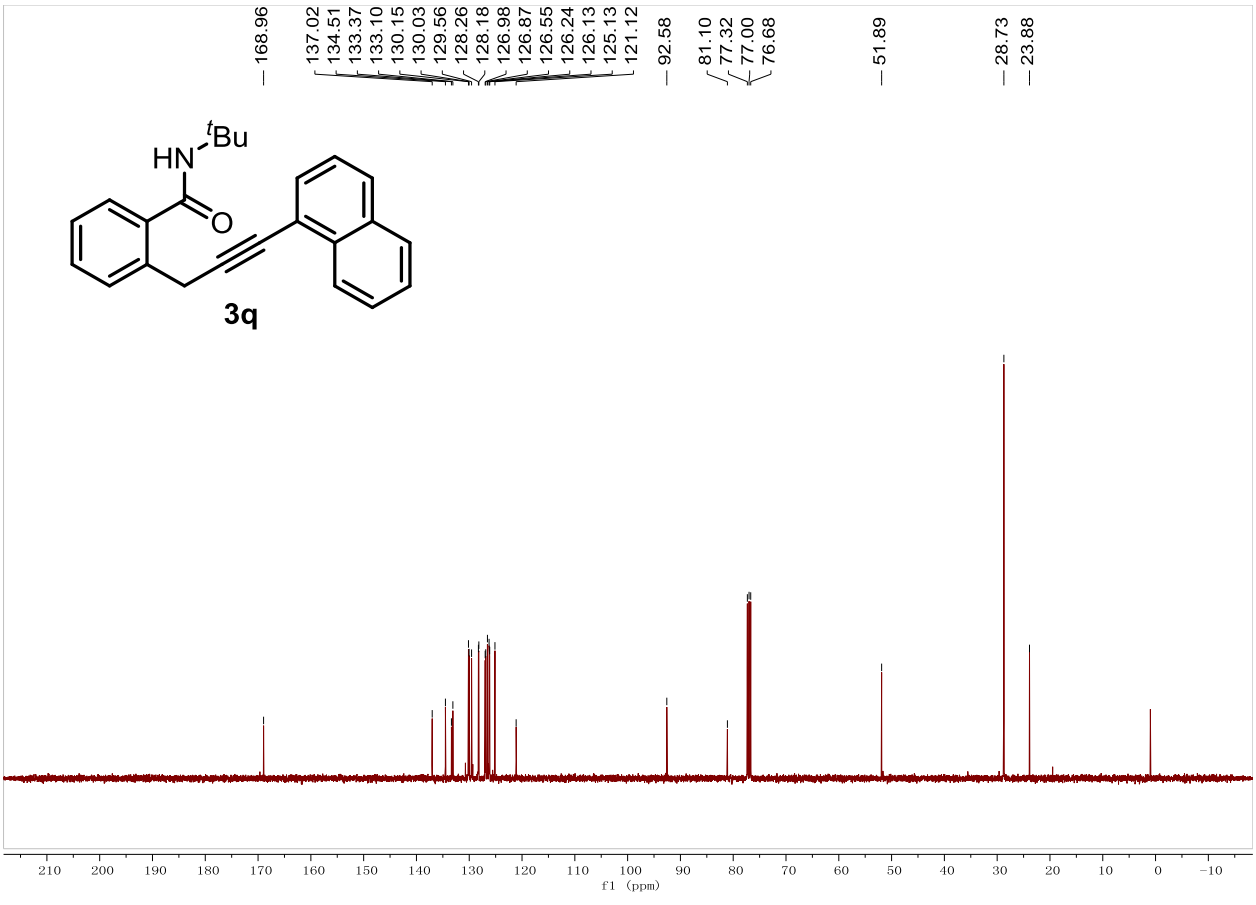
3p, ^{13}C NMR (101 MHz, $CDCl_3$)



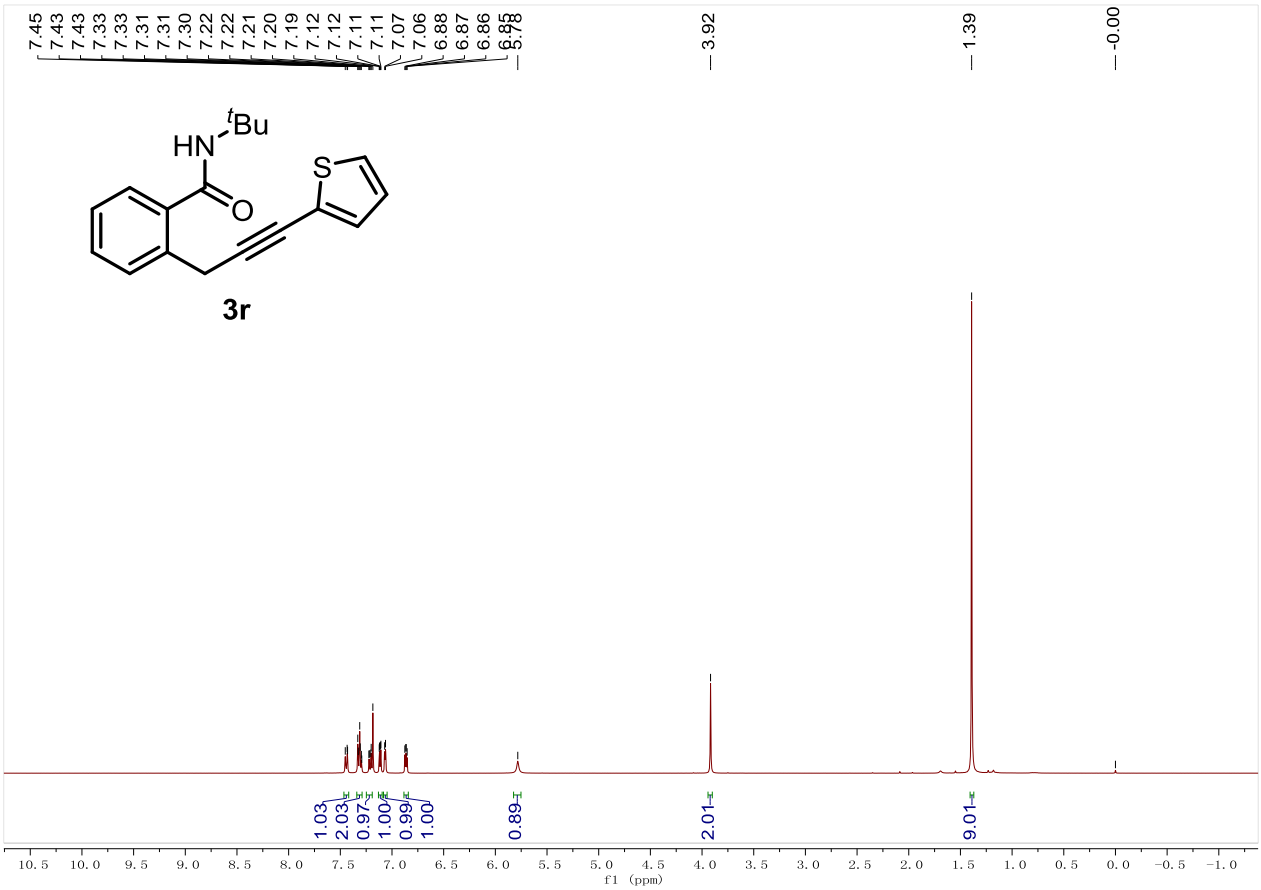
3q, ^{1}H NMR (400 MHz, $CDCl_3$)



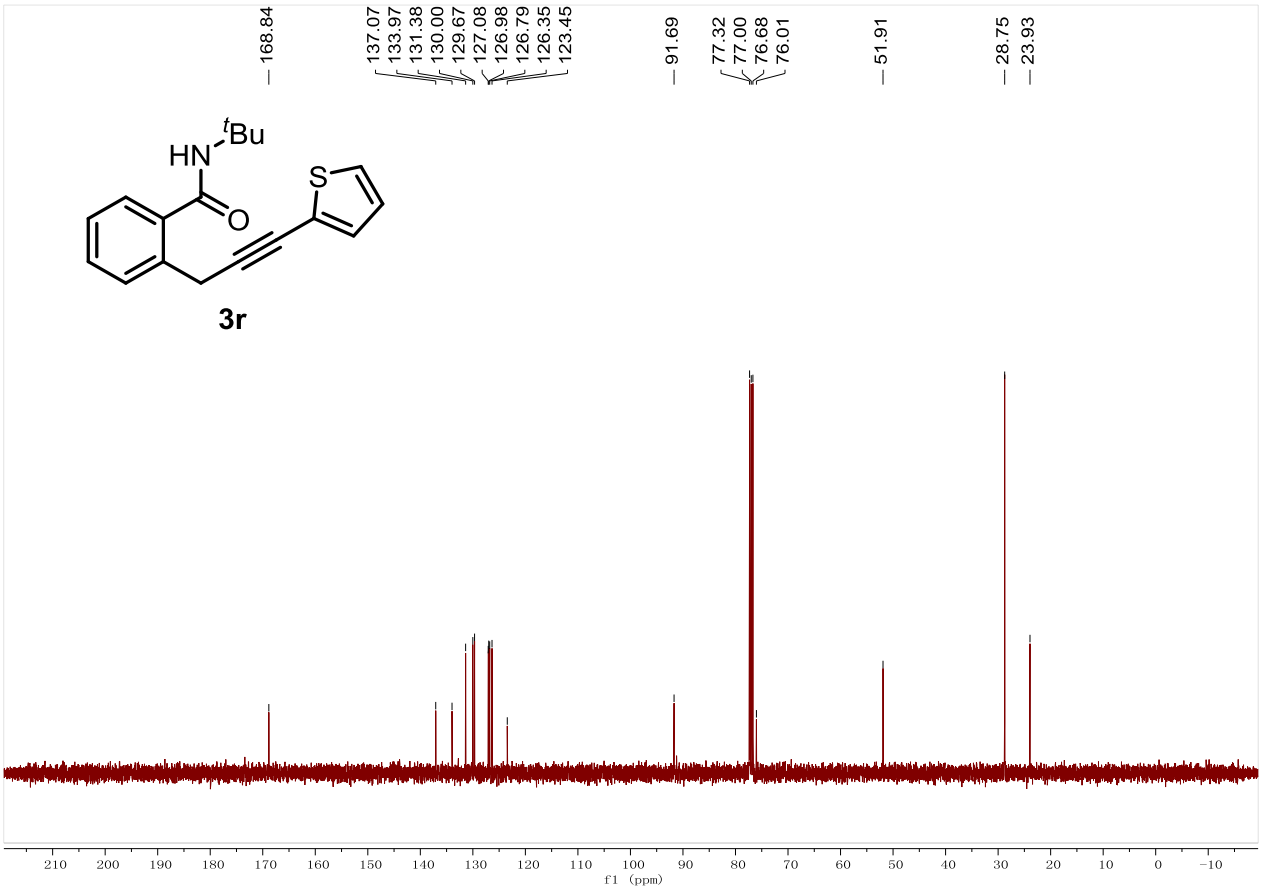
3q, ^{13}C NMR (101 MHz, $CDCl_3$)



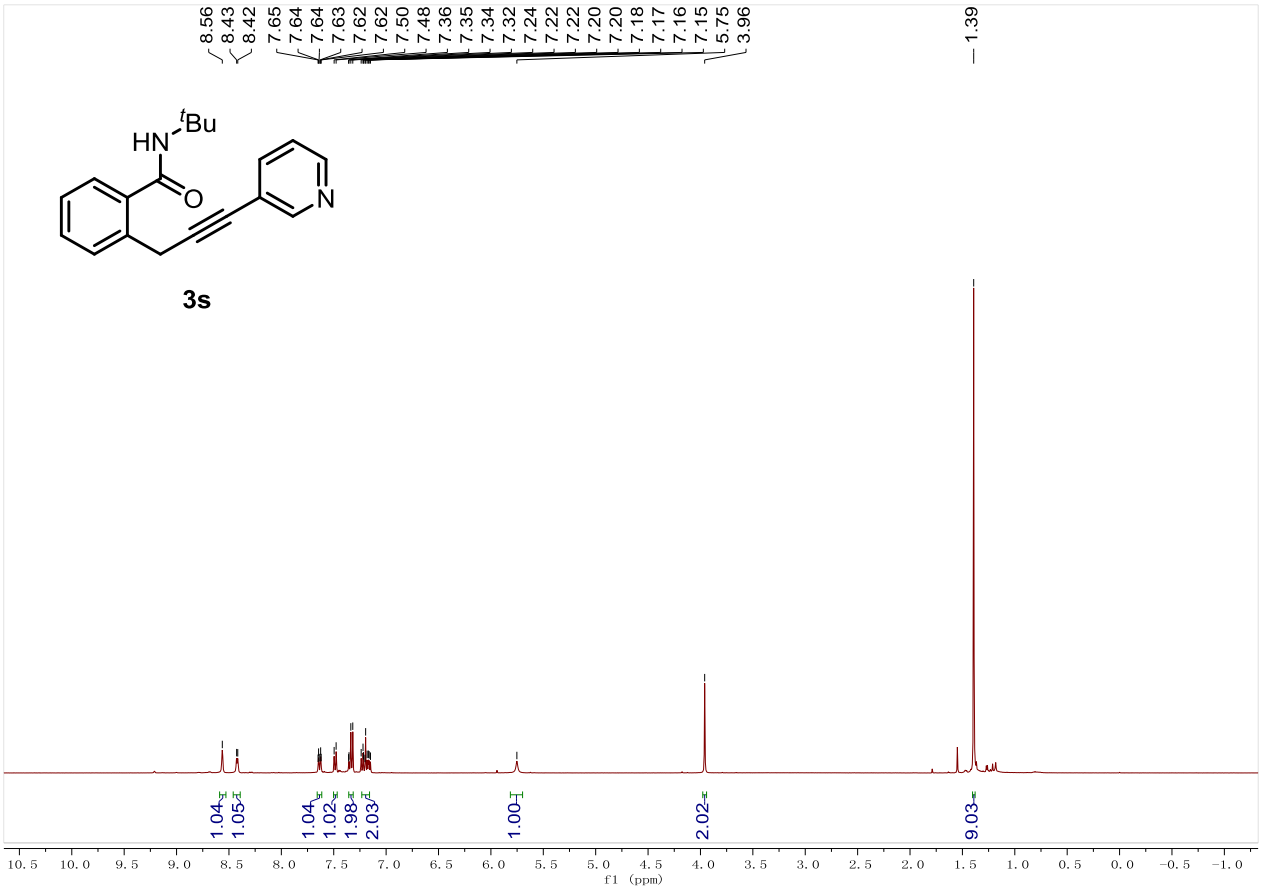
3r, ^{1}H NMR (400 MHz, $CDCl_3$)



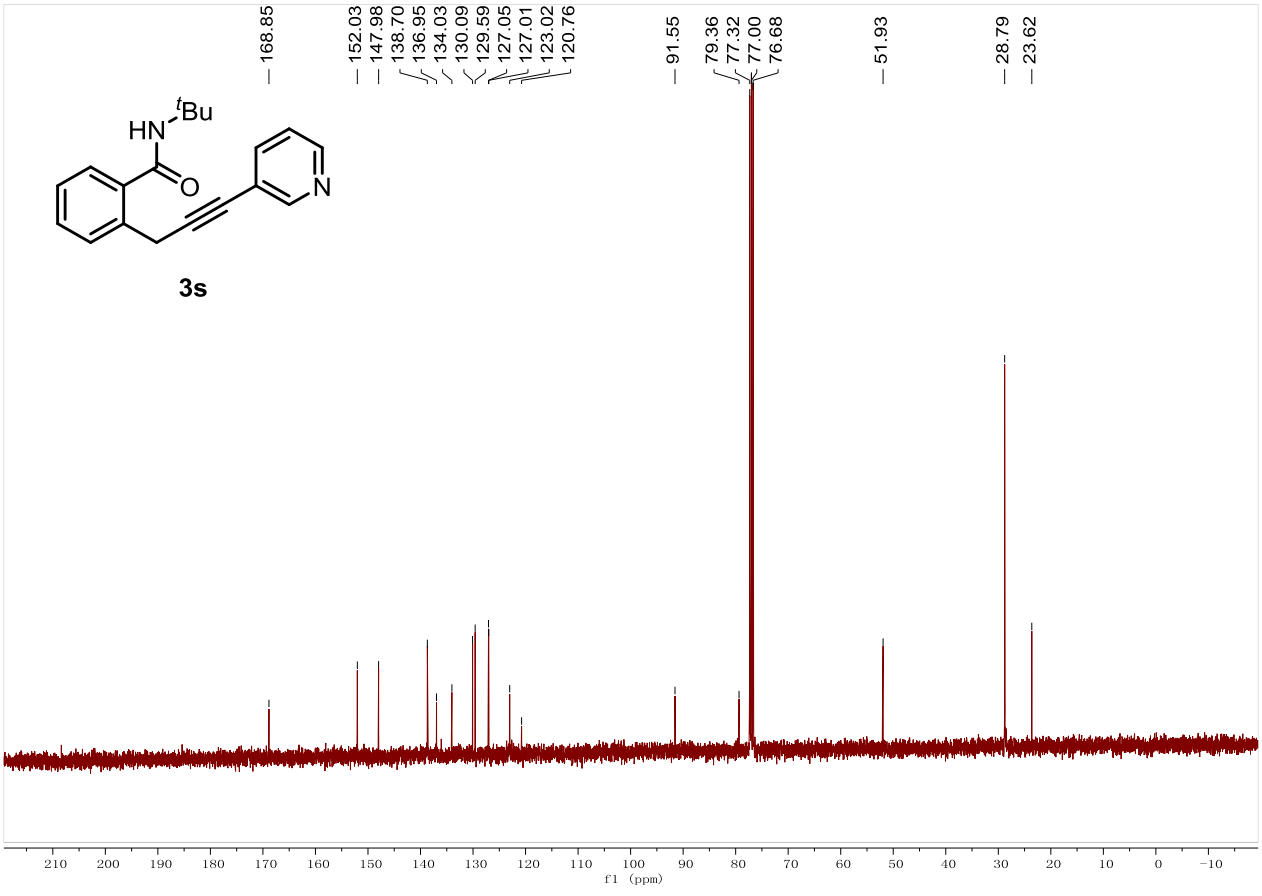
3r, ^{13}C NMR (101 MHz, $CDCl_3$)



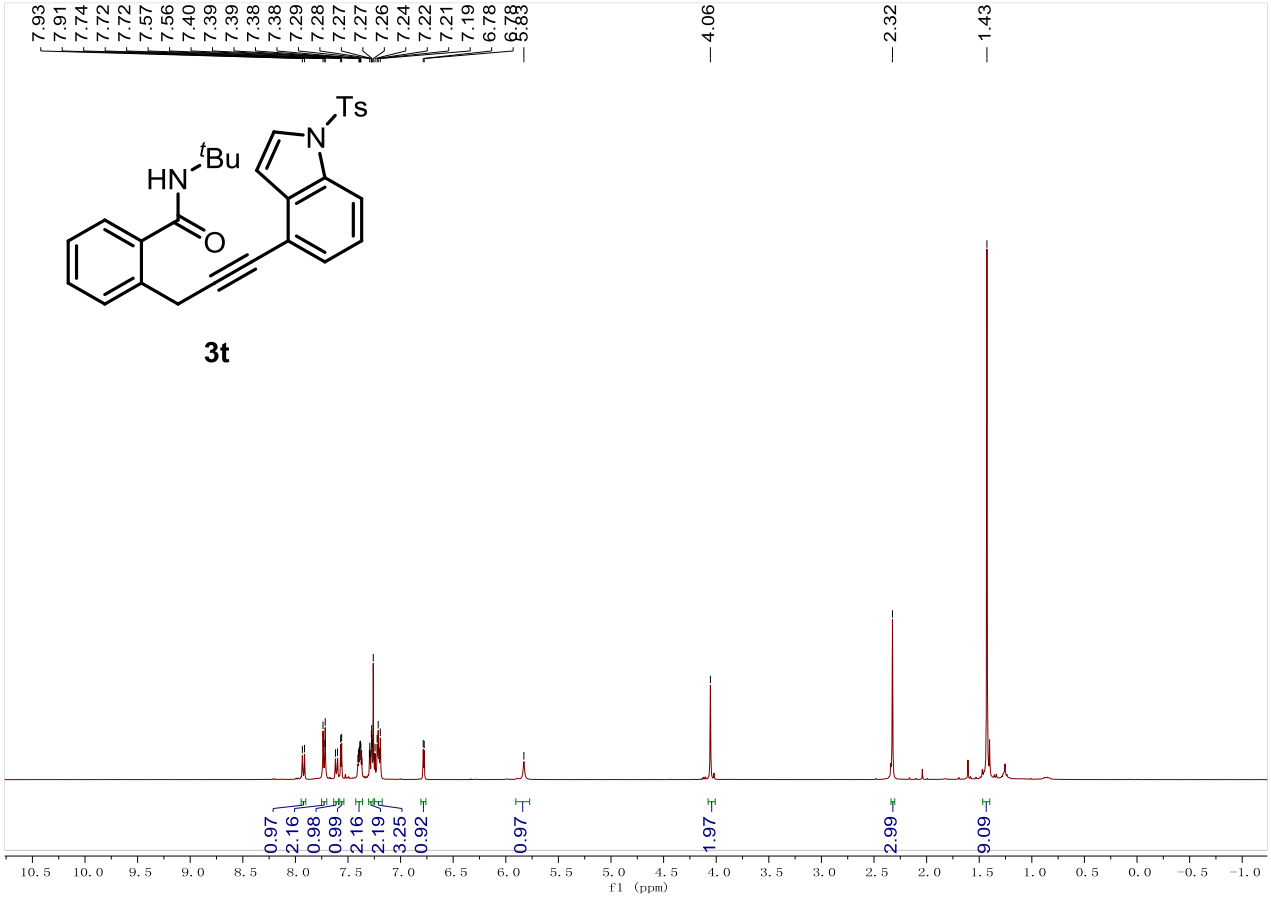
3s, ^{1}H NMR (400 MHz, $CDCl_3$)



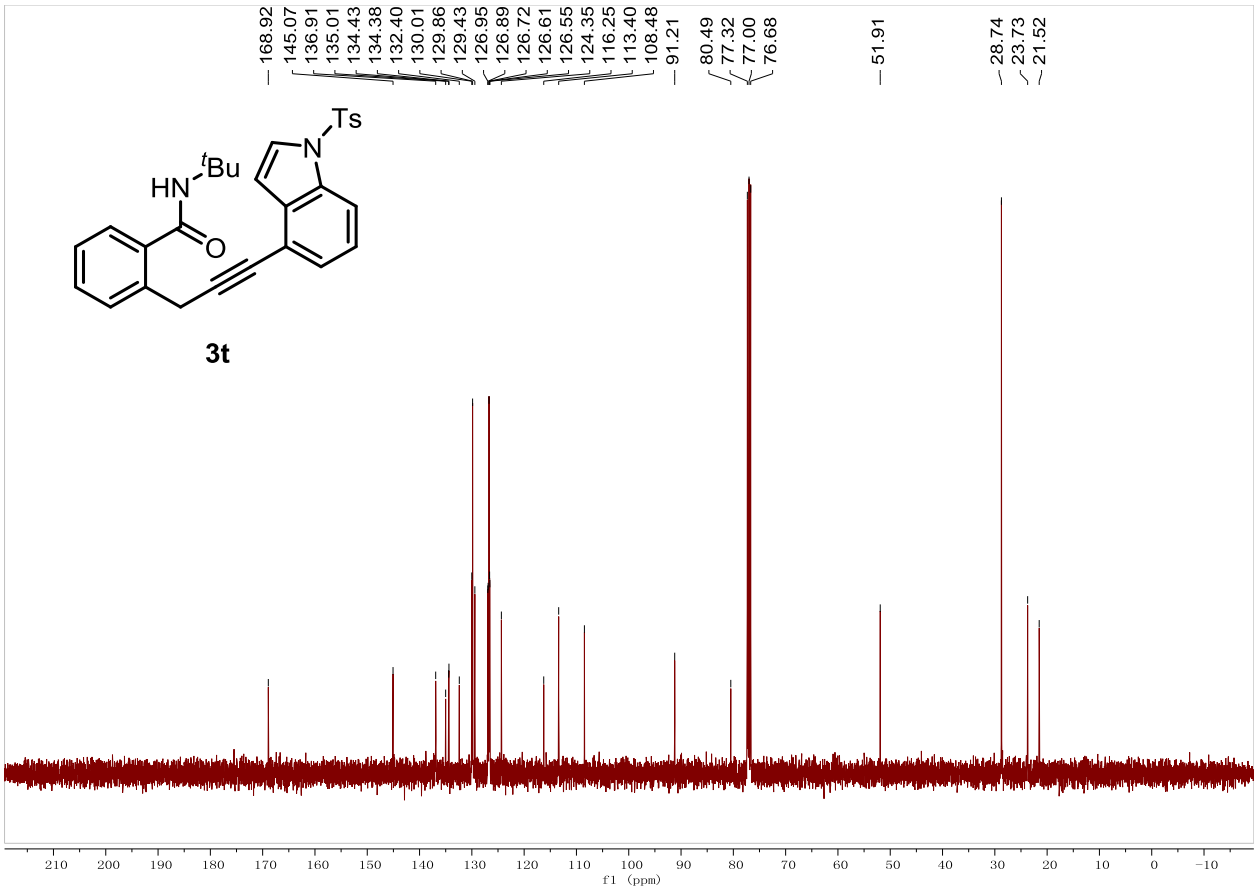
3s, ^{13}C NMR (101 MHz, $CDCl_3$)



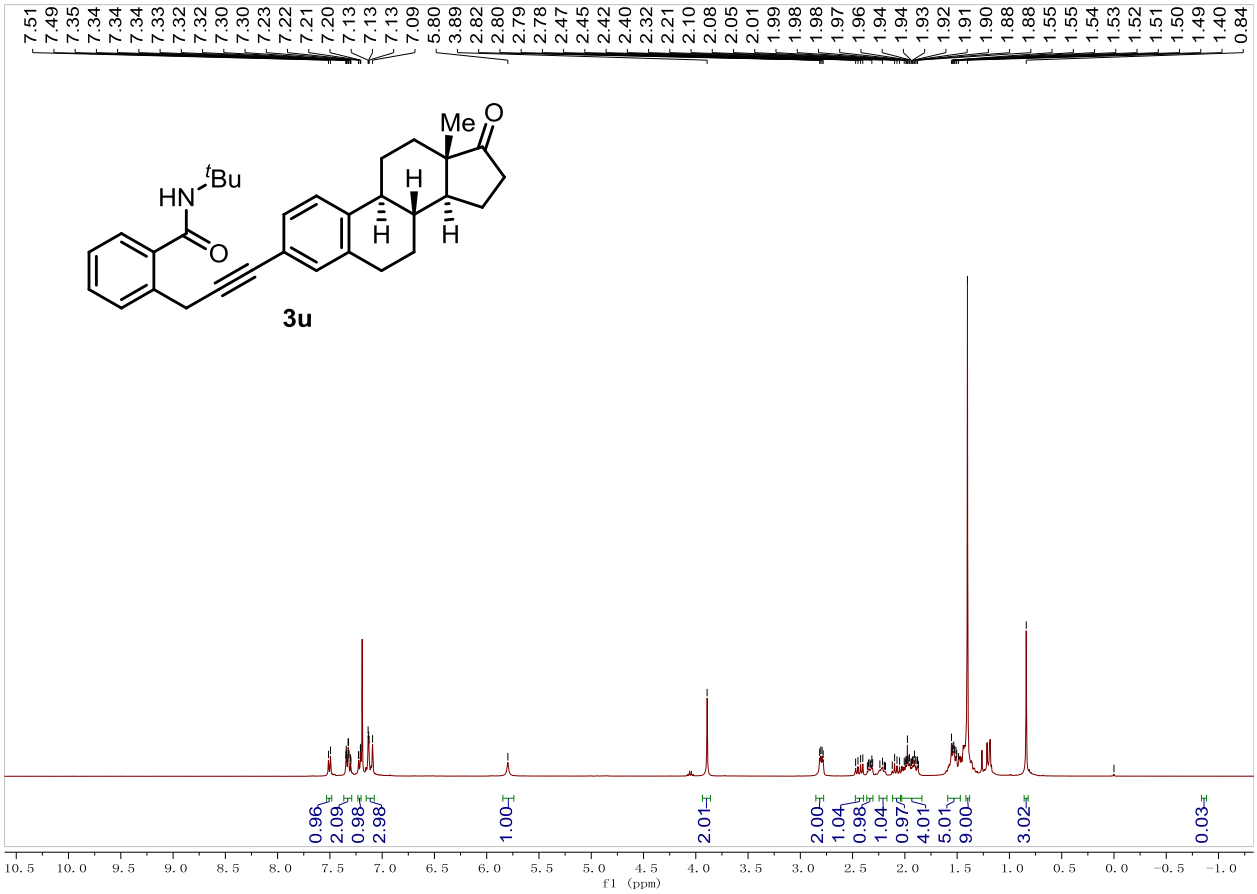
3t, ^{1}H NMR (400 MHz, $CDCl_3$)



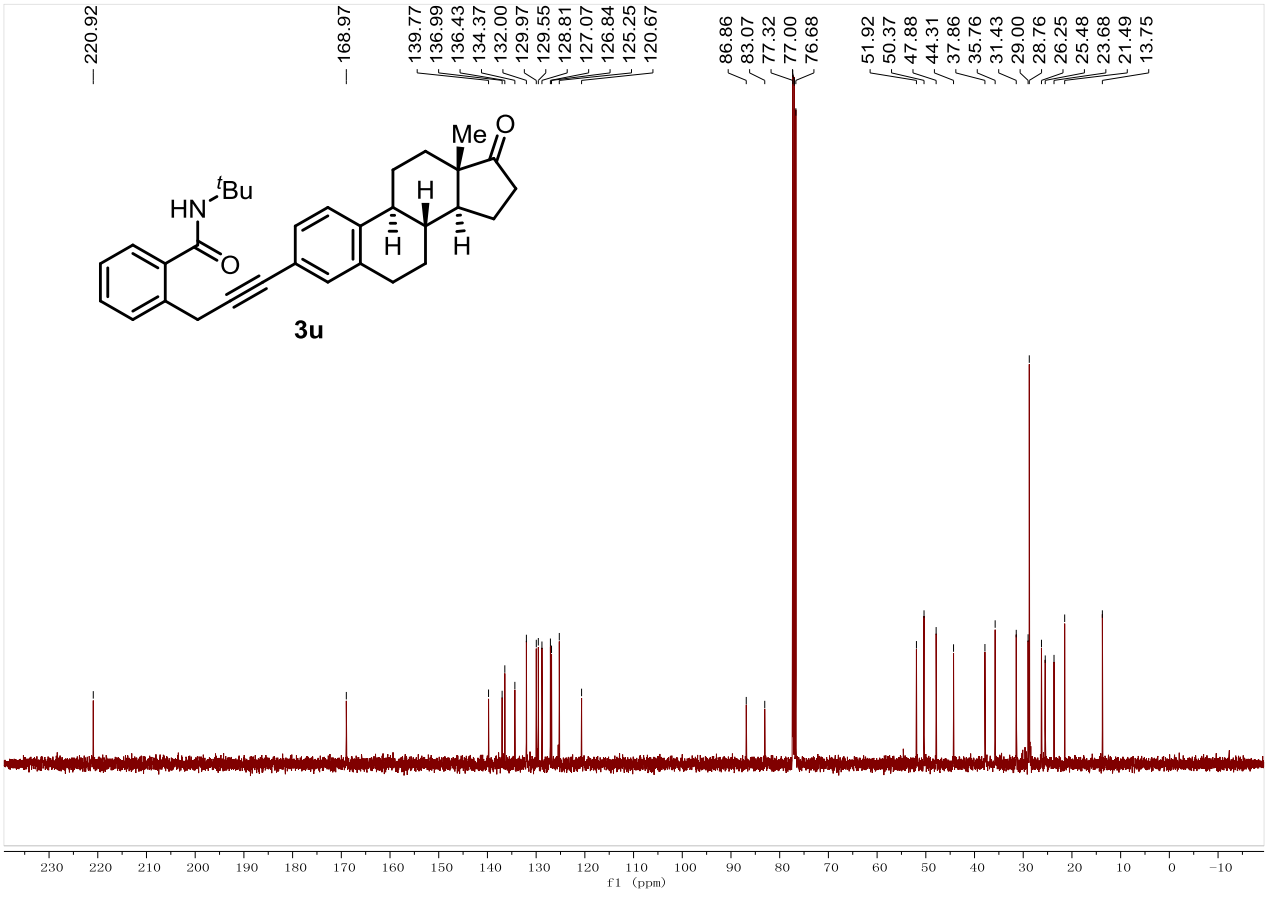
3t, ^{13}C NMR (101 MHz, $CDCl_3$)



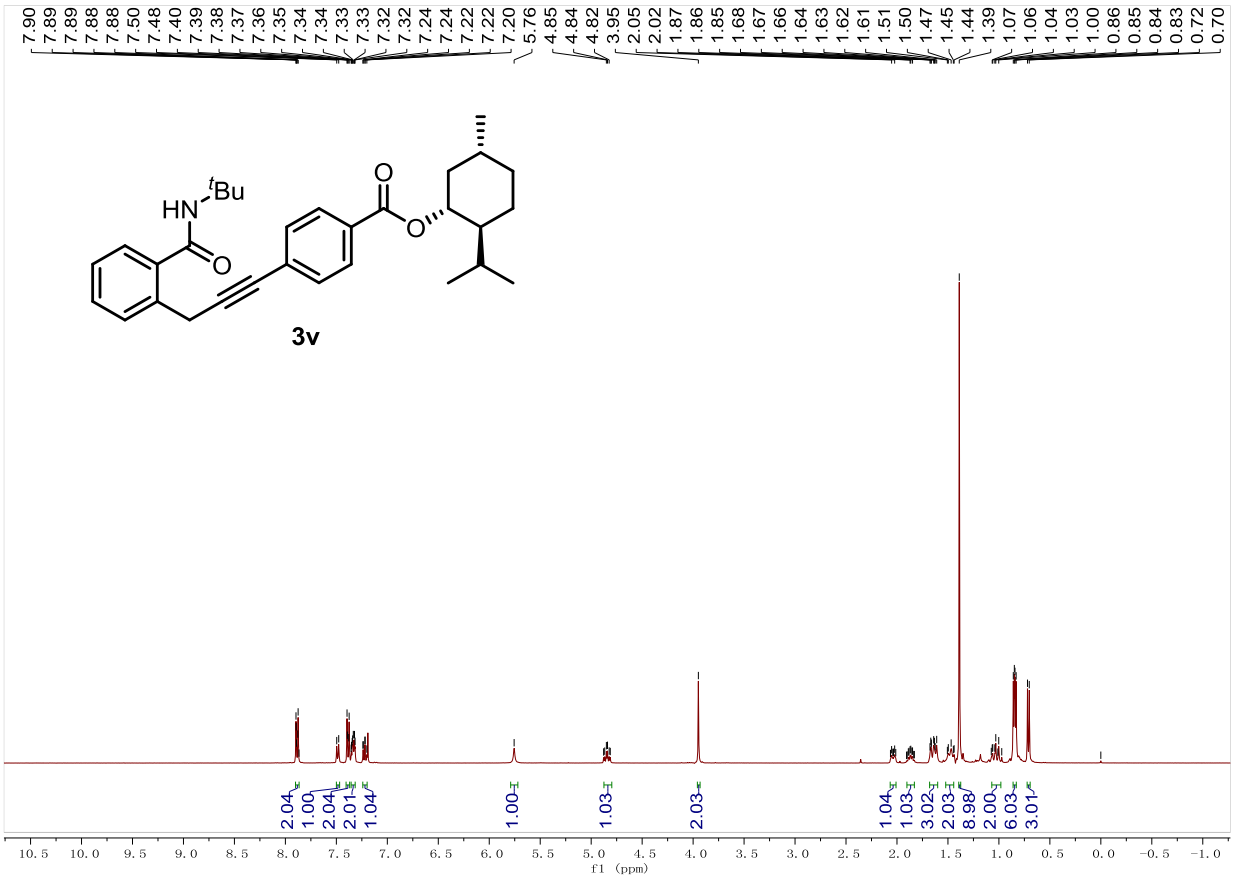
3u, ^{1}H NMR (400MHz, $CDCl_3$)



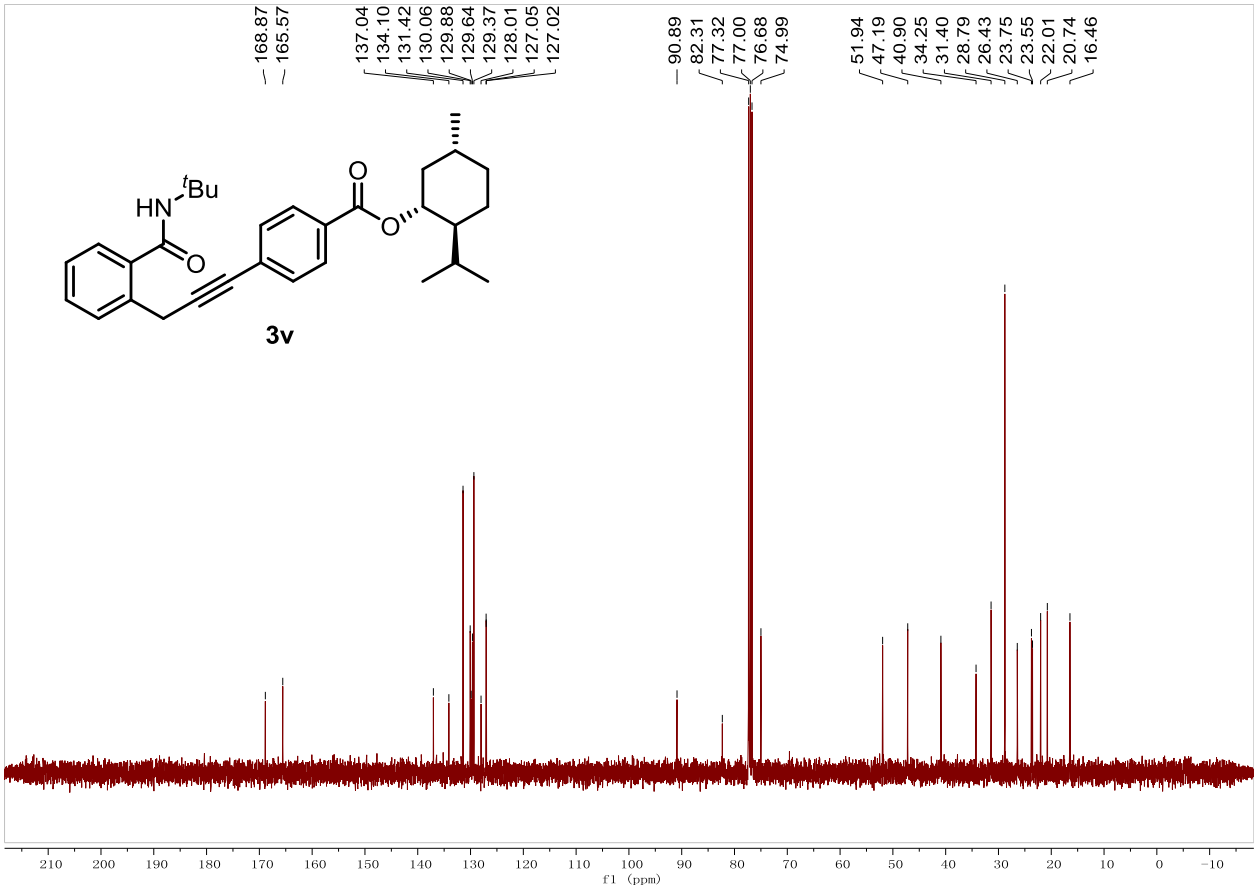
3u, ^{13}C NMR (101 MHz, $CDCl_3$)



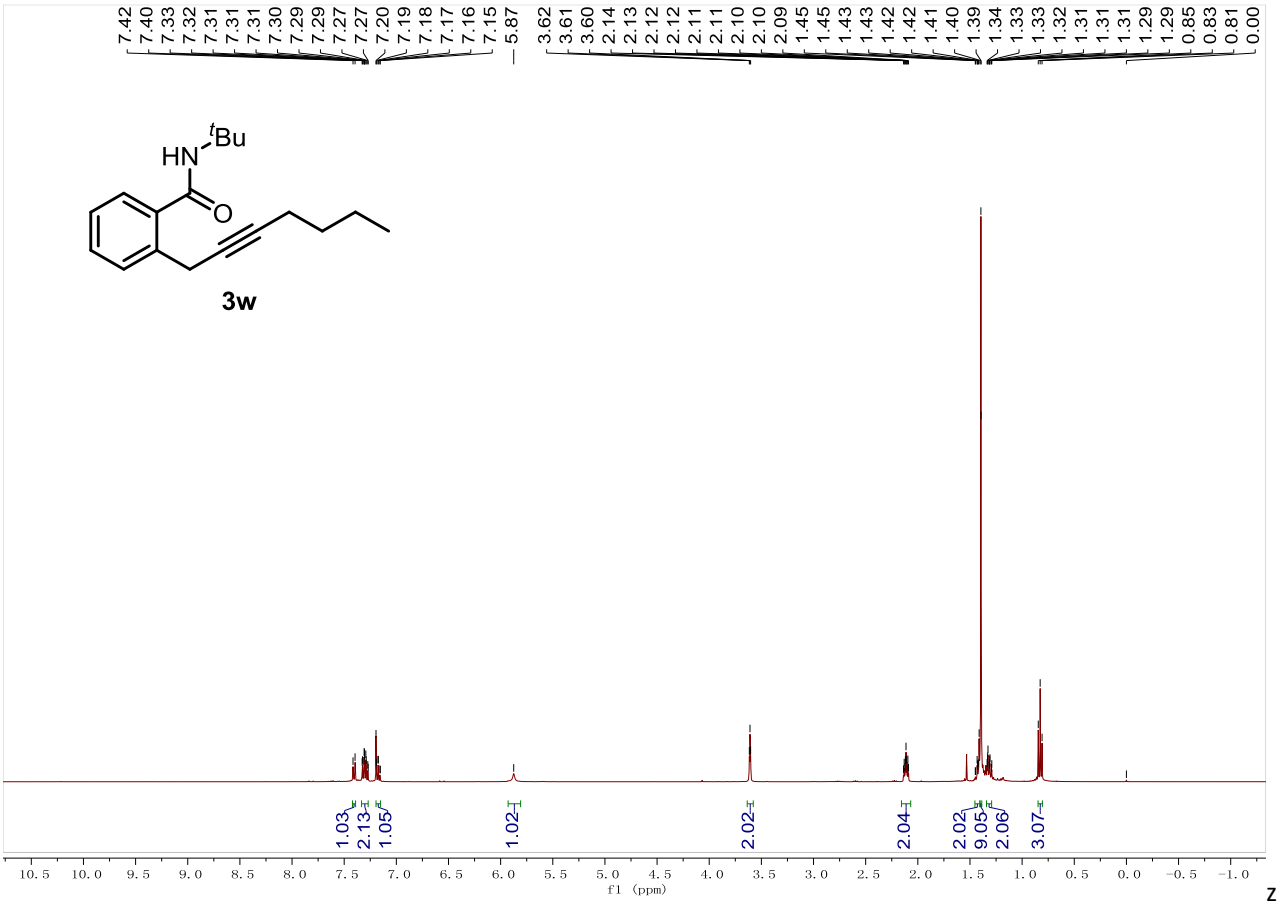
3v, ^{1}H NMR (400 MHz, $CDCl_3$)



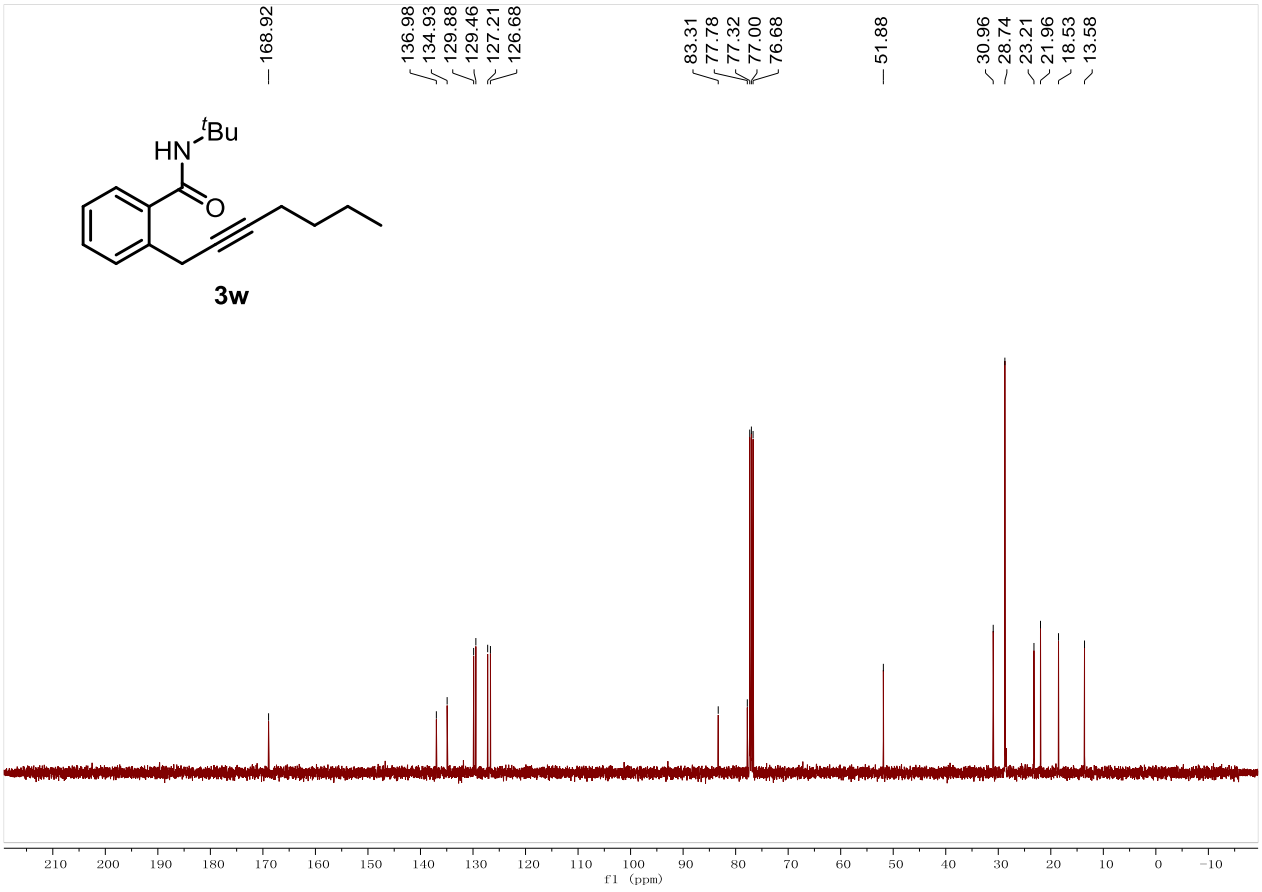
3v, ^{13}C NMR (101 MHz, $CDCl_3$)



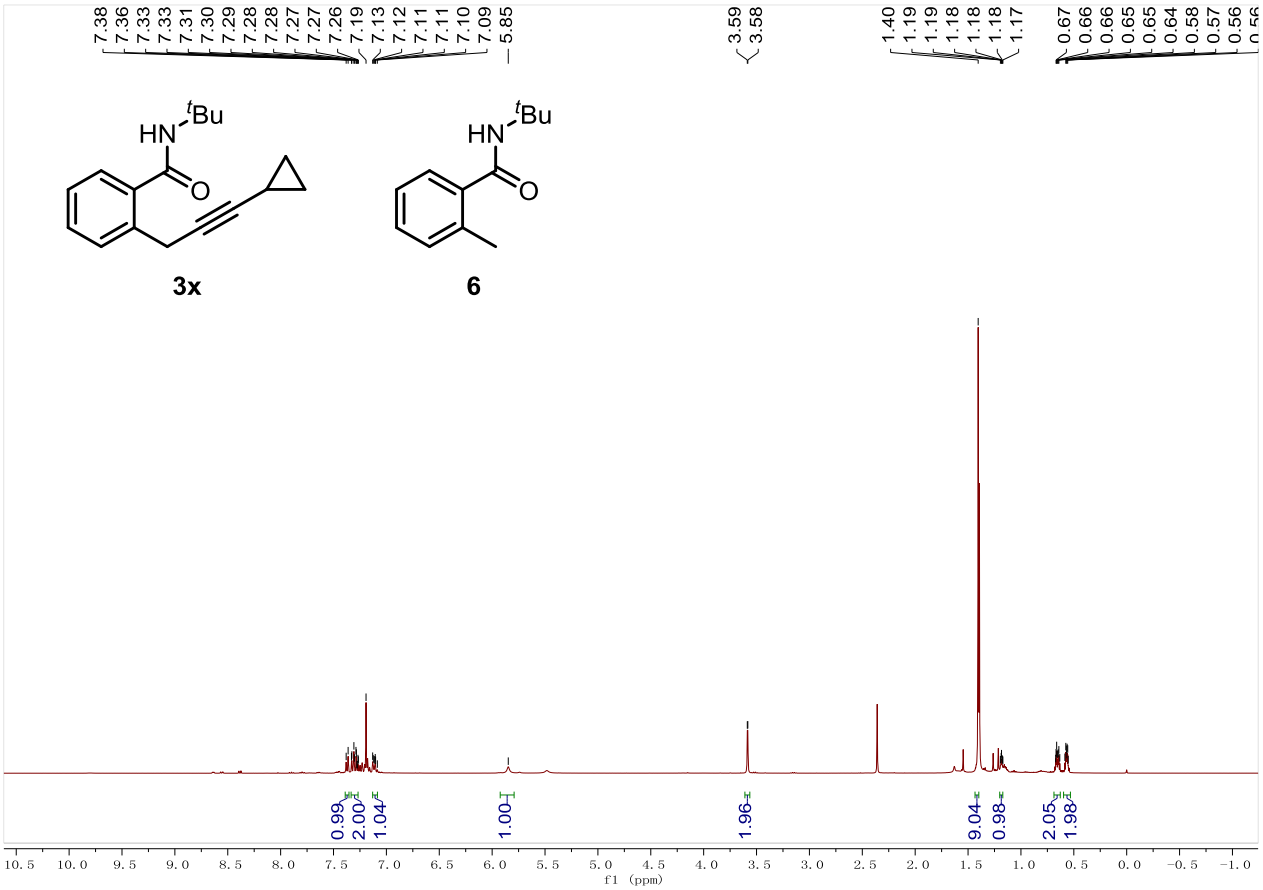
3w, ^{1}H NMR (400 MHz, $CDCl_3$)



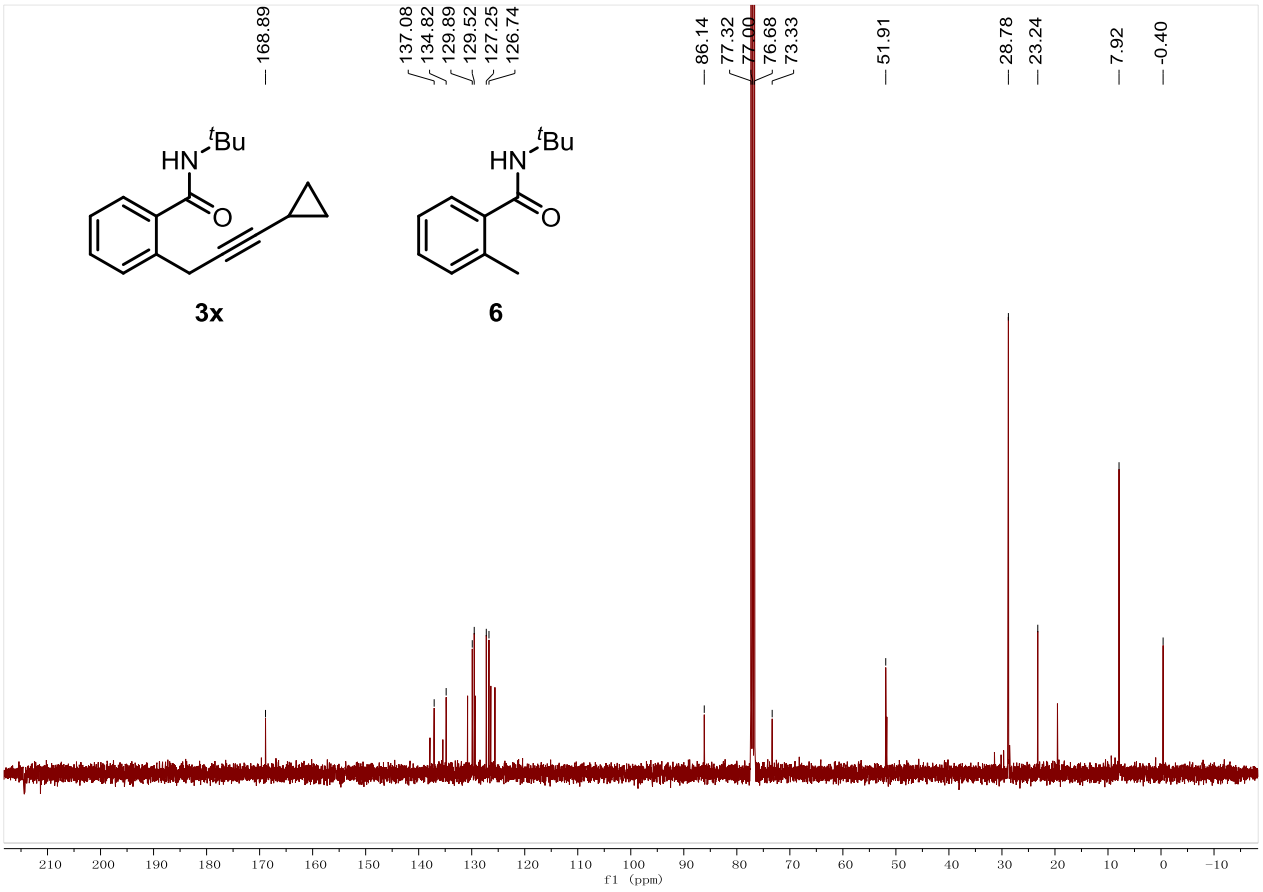
3w, ^{13}C NMR (101 MHz, $CDCl_3$)



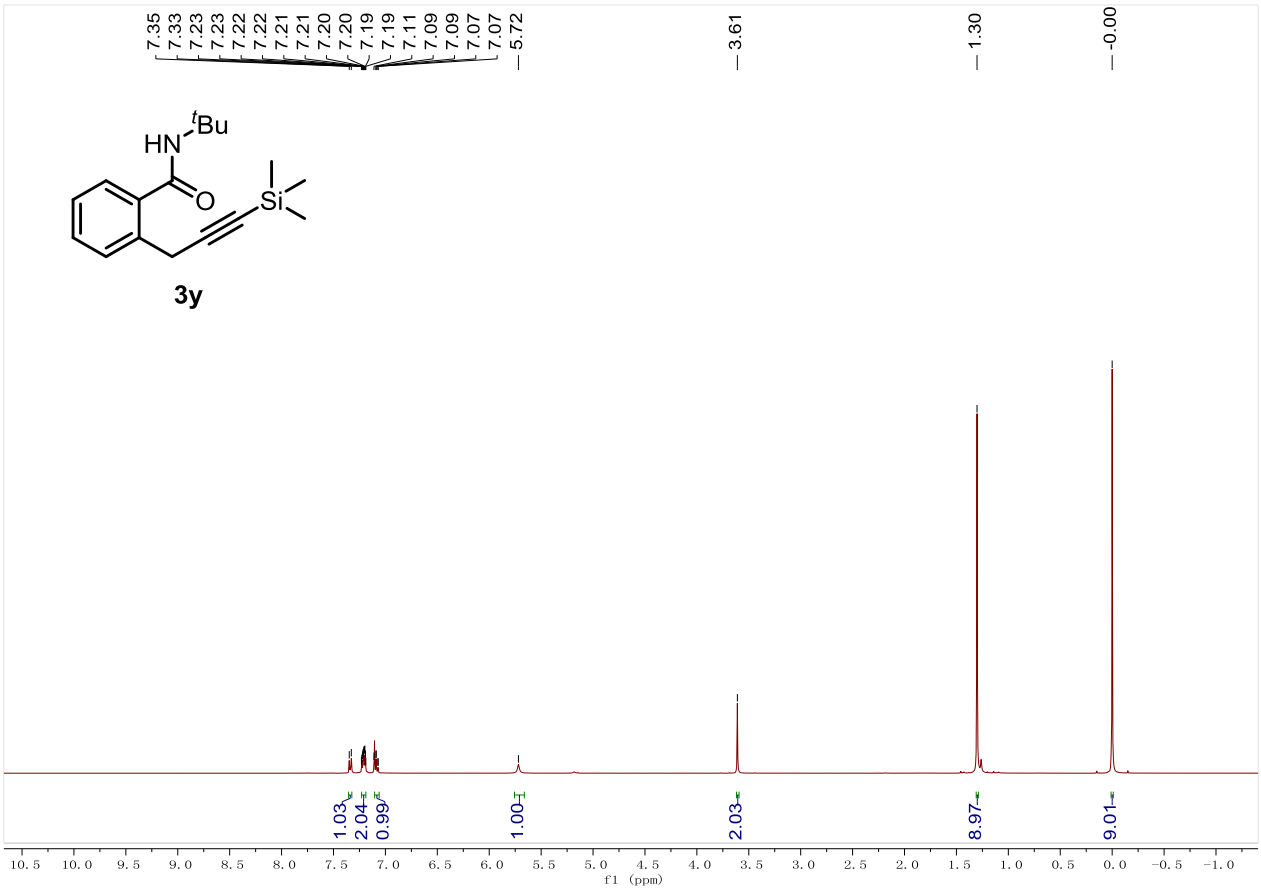
3x, ^{1}H NMR (400 MHz, $CDCl_3$)



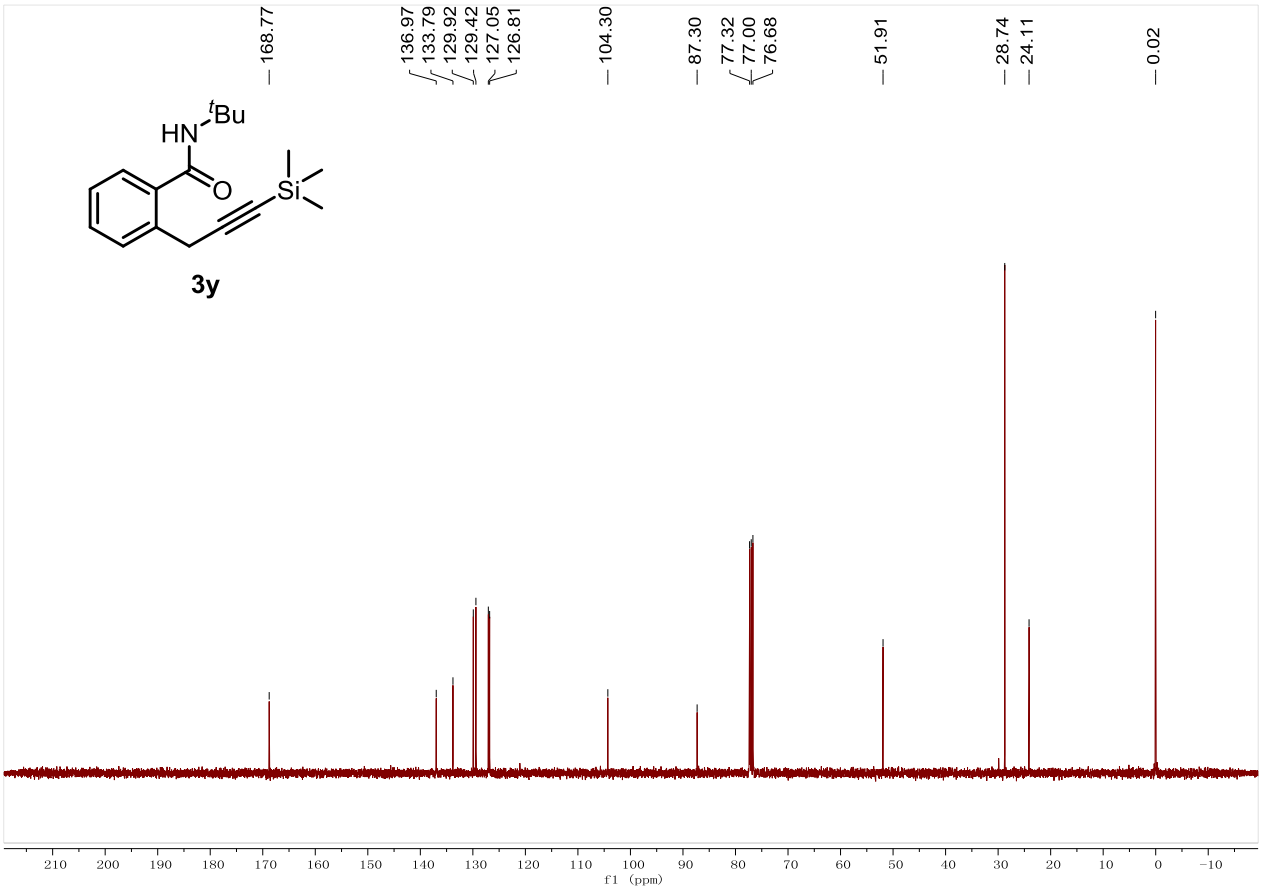
3x, ^{13}C NMR (101 MHz, $CDCl_3$)



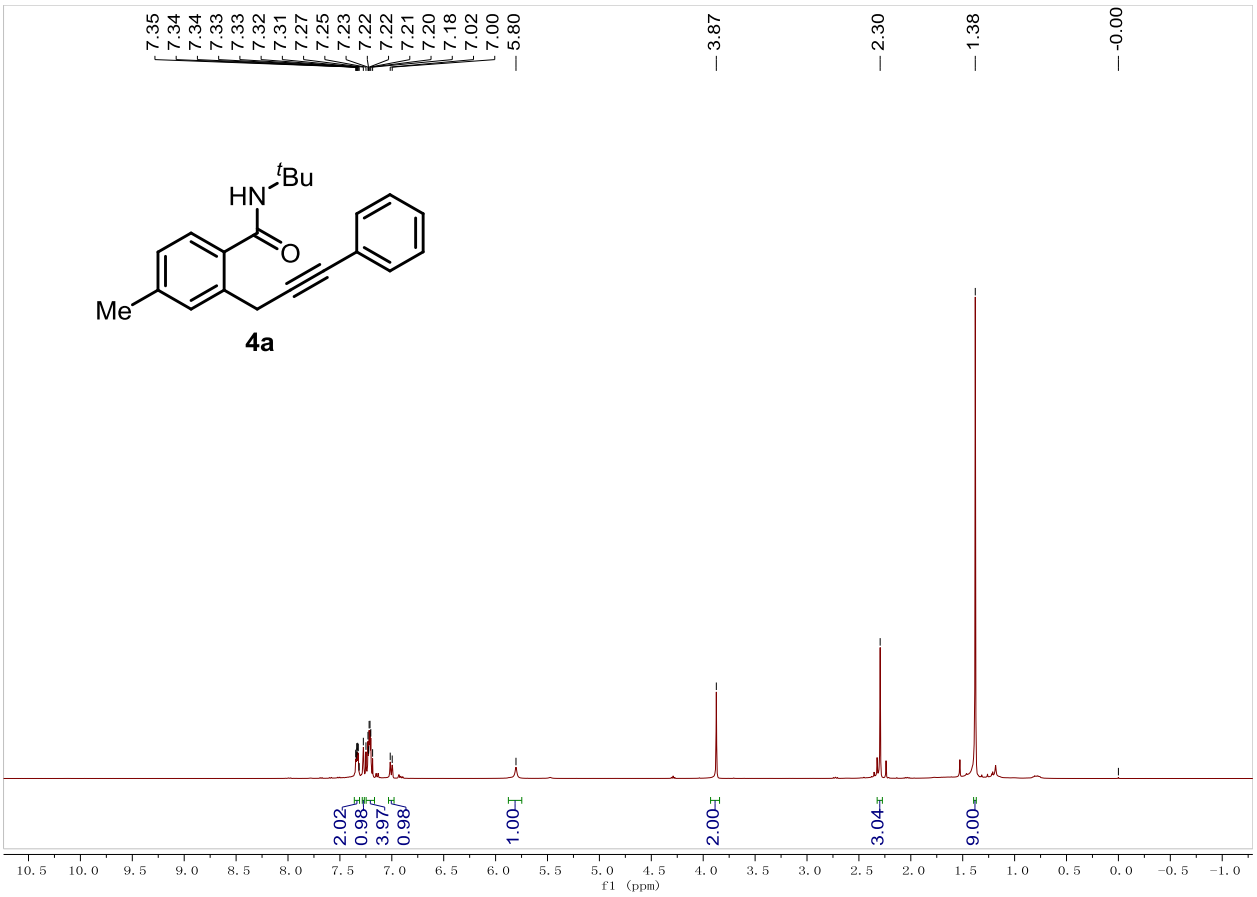
3y, ^{1}H NMR (400 MHz, $CDCl_3$)



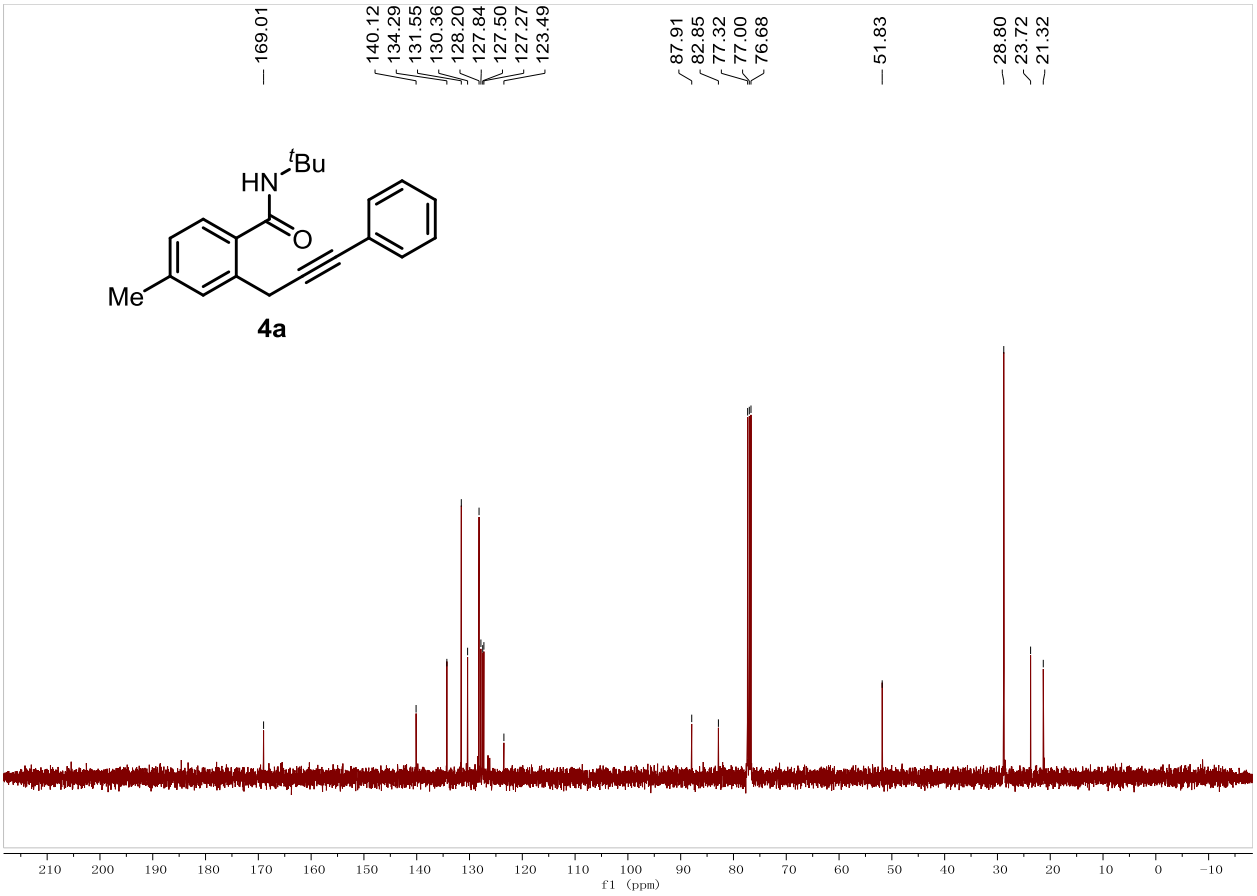
3y, ^{13}C NMR (101 MHz, $CDCl_3$)



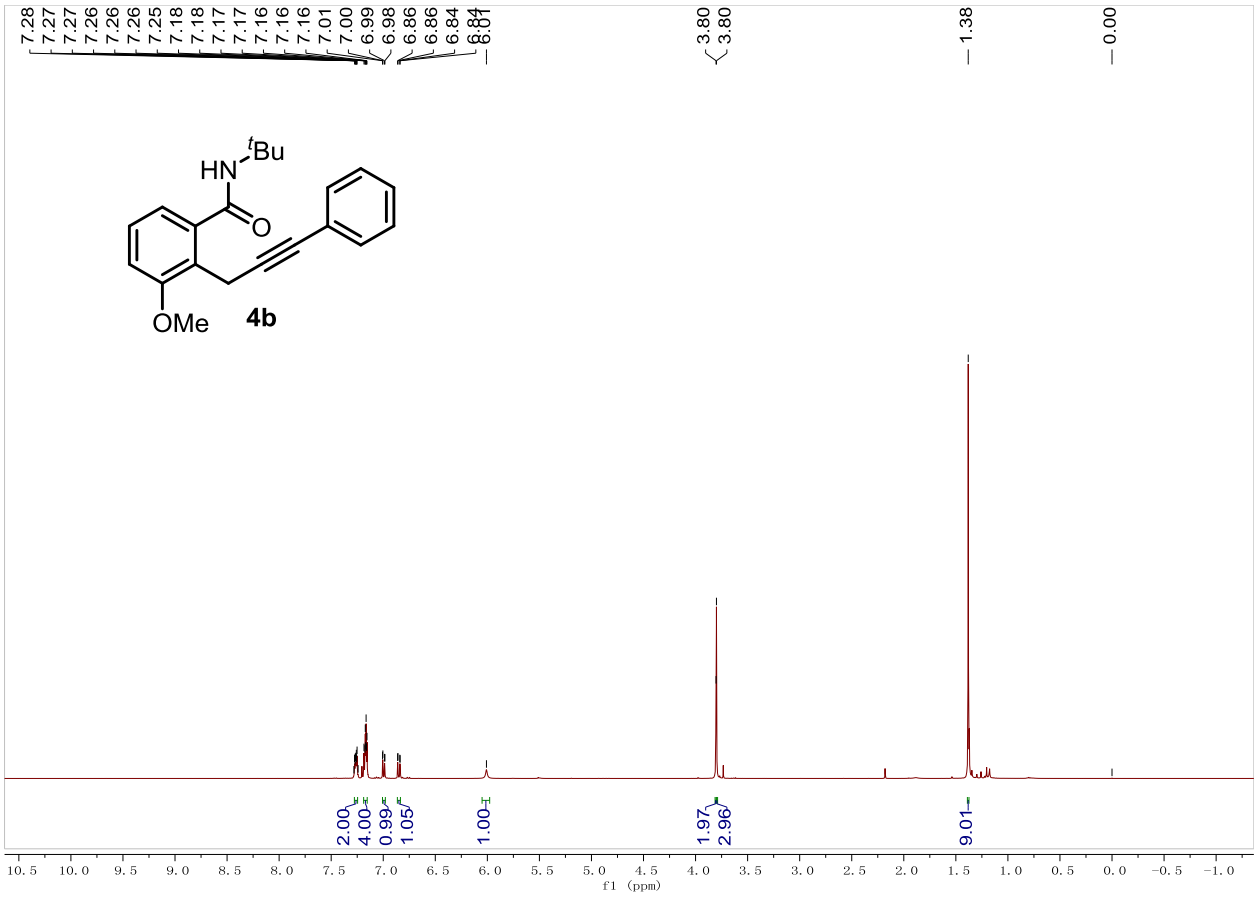
4a, ^{1}H NMR (400 MHz, $CDCl_3$)



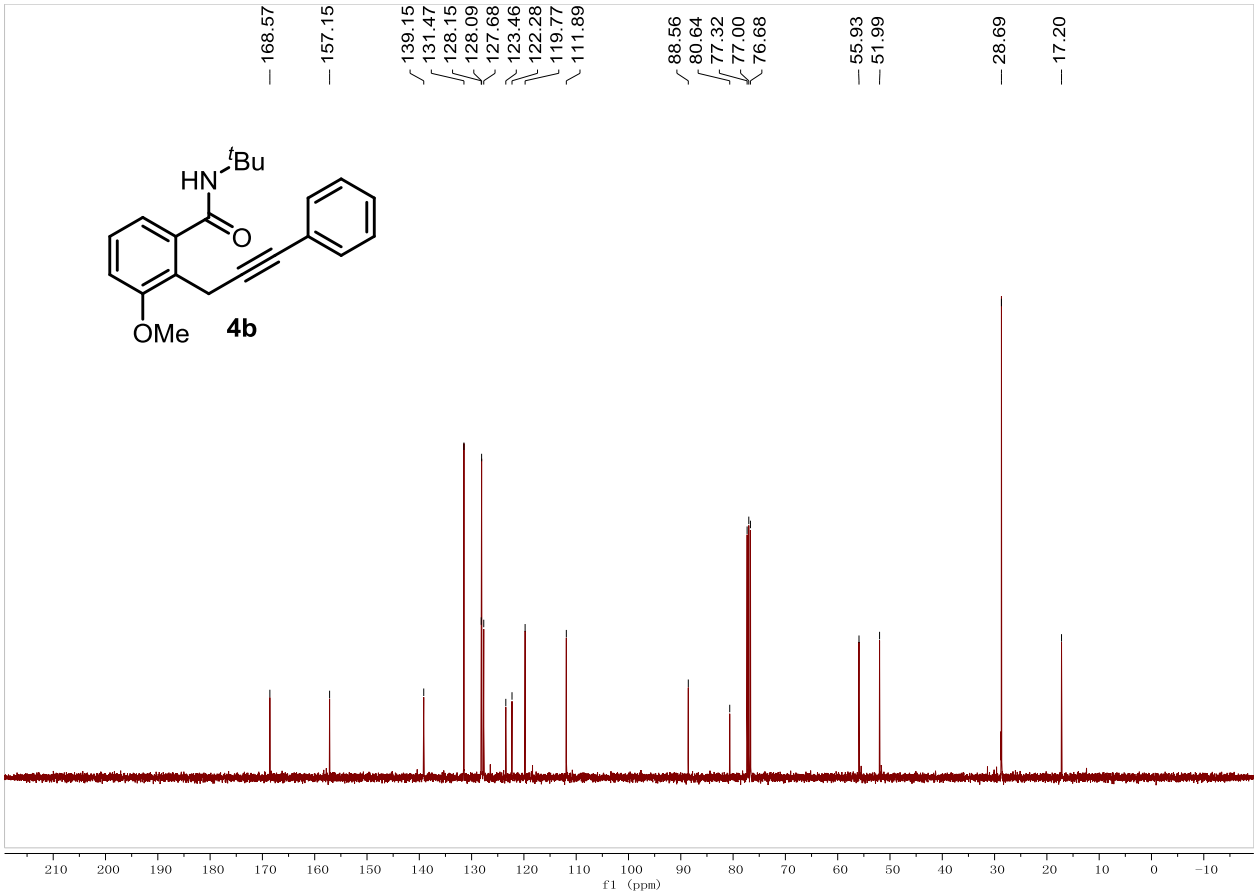
4a, ^{13}C NMR (101 MHz, $CDCl_3$)



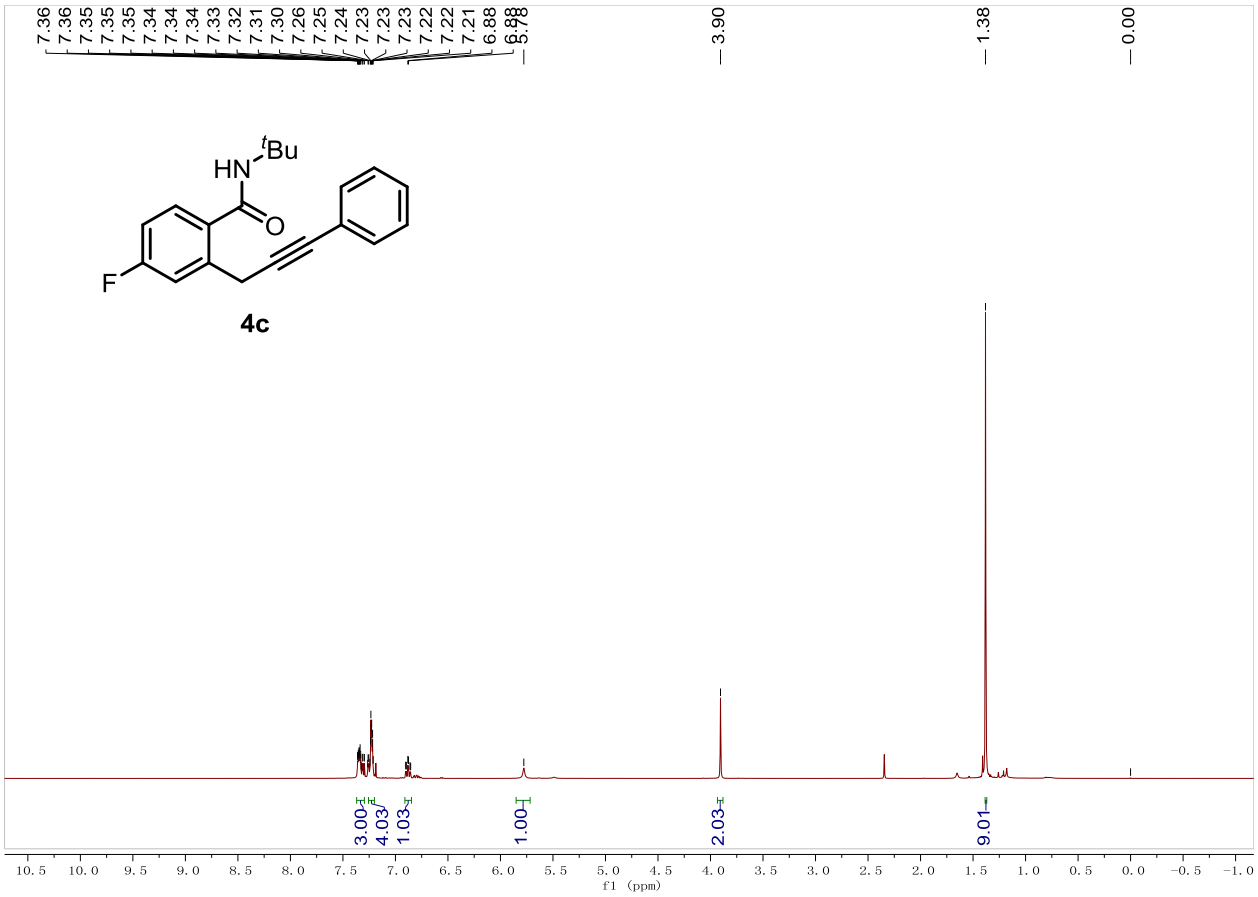
4b, ^{1}H NMR (400 MHz, $CDCl_3$)



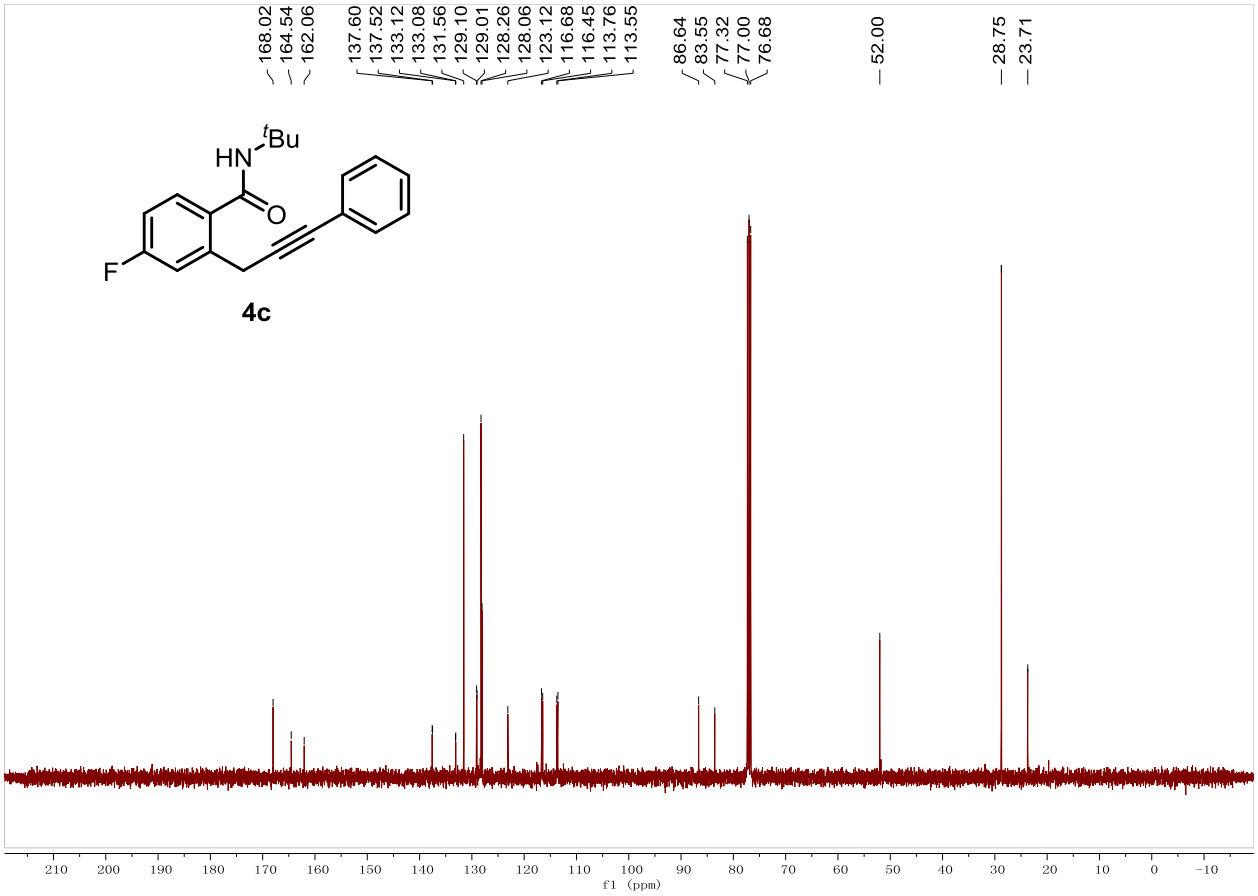
4b, ^{13}C NMR (101 MHz, $CDCl_3$)



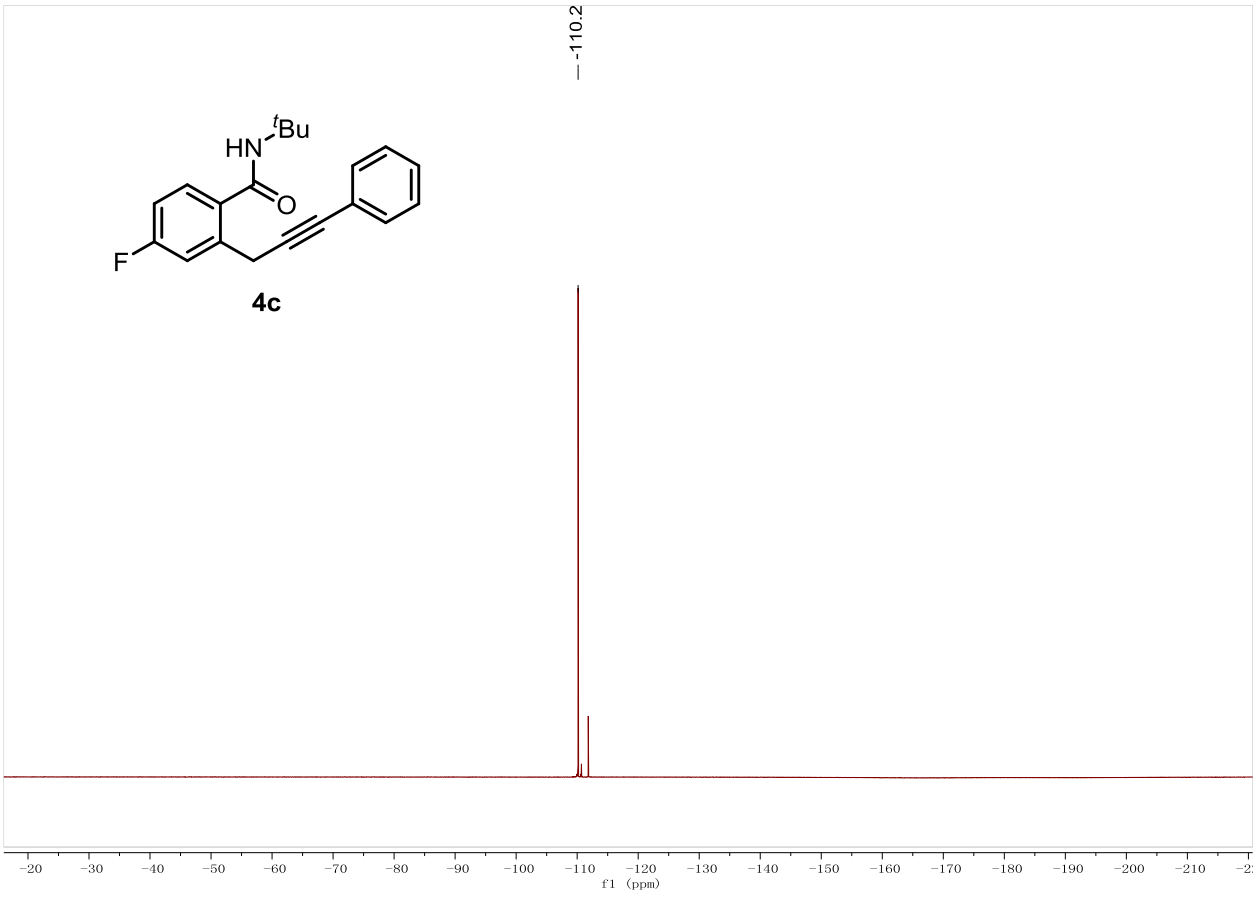
4c, ^{1}H NMR (400 MHz, $CDCl_3$)



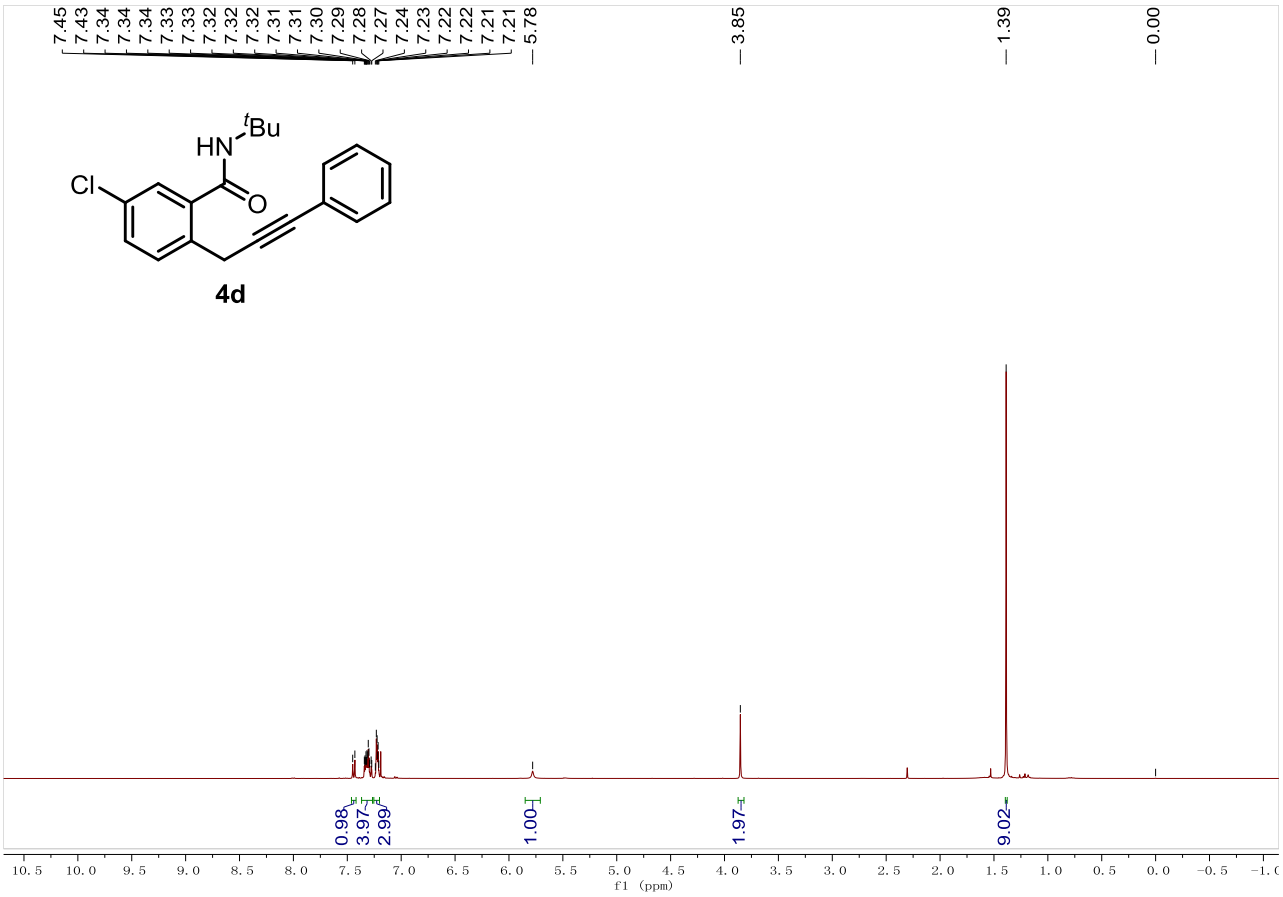
4c, ^{13}C NMR (101 MHz, $CDCl_3$)



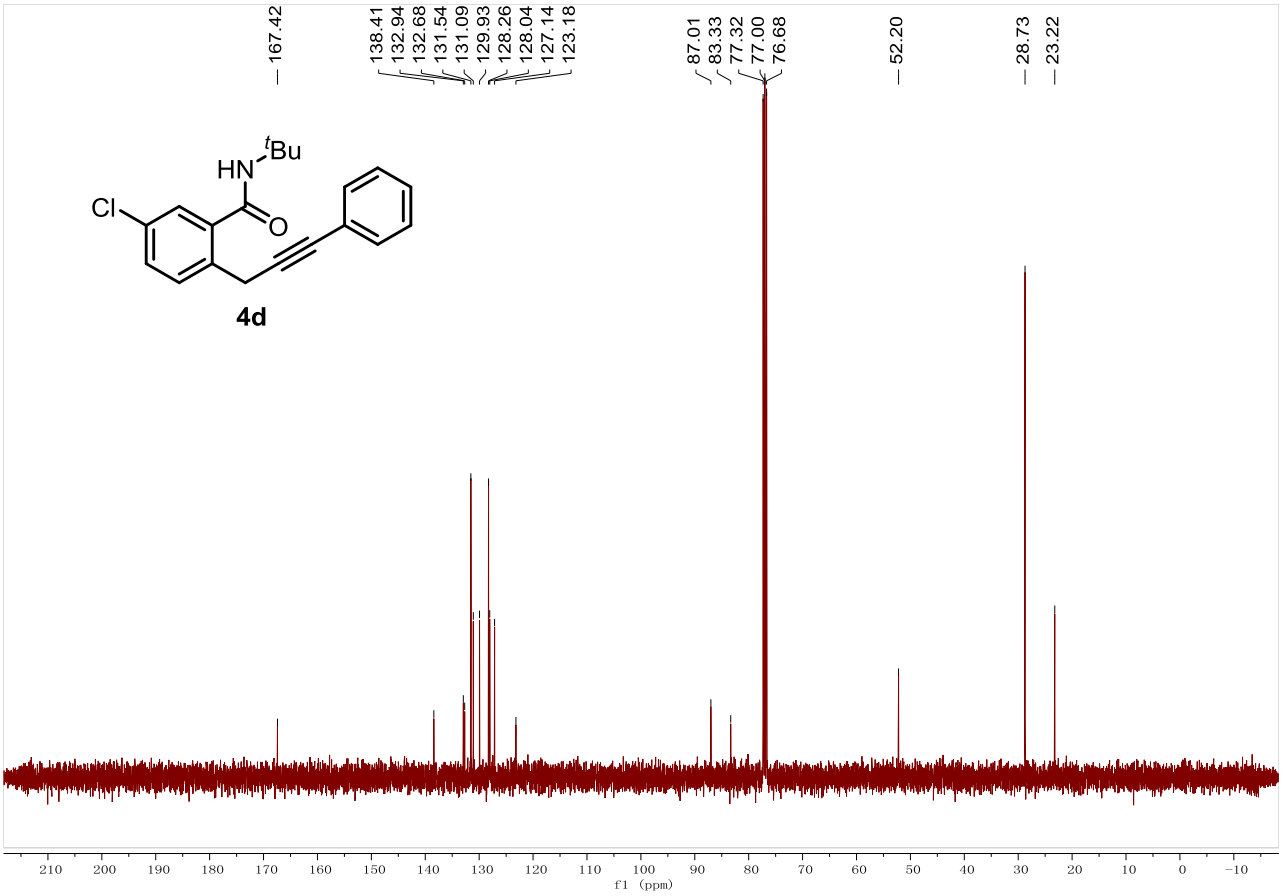
4c, ^{19}F NMR (376 MHz, $CDCl_3$)



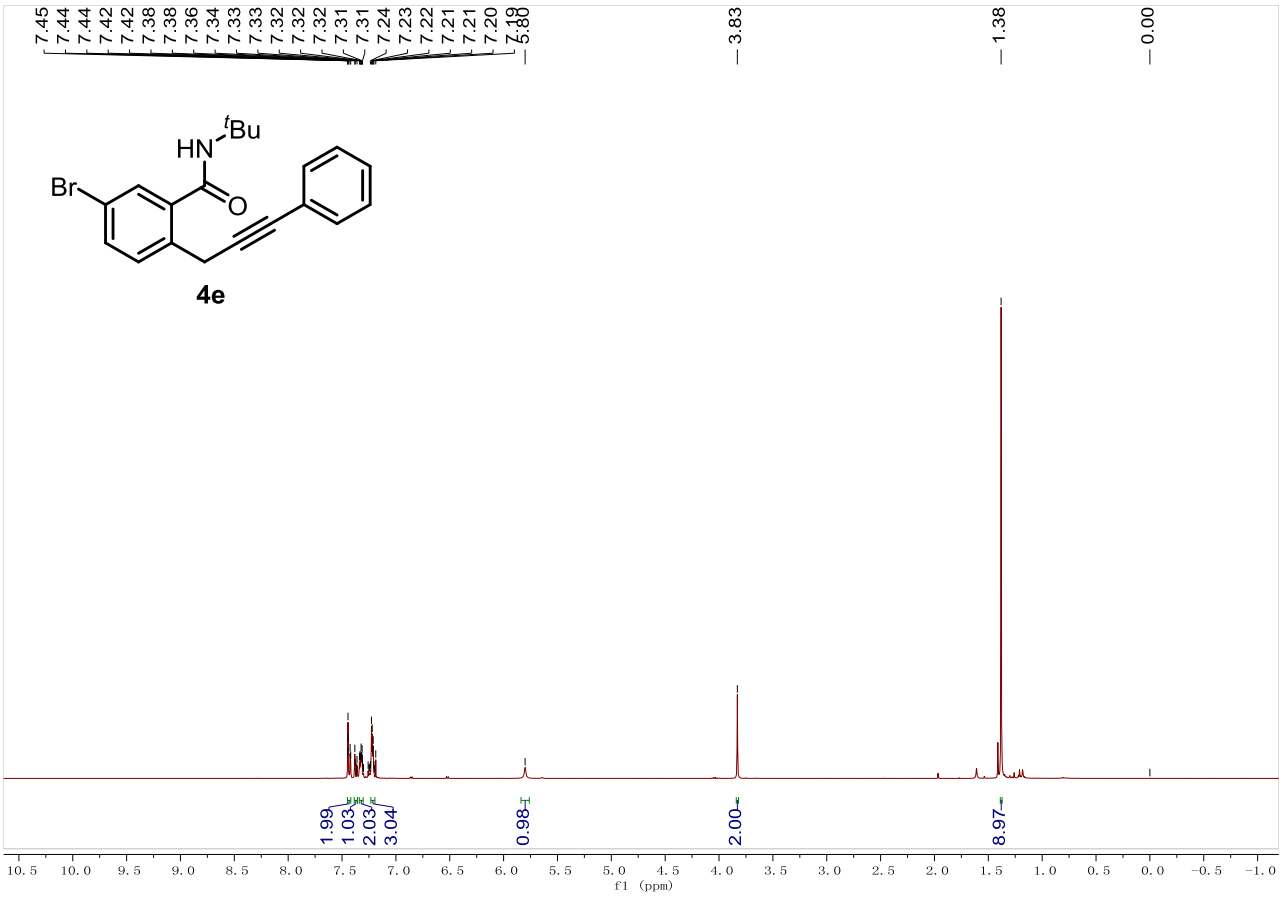
4d, ^{1}H NMR (400 MHz, $CDCl_3$)



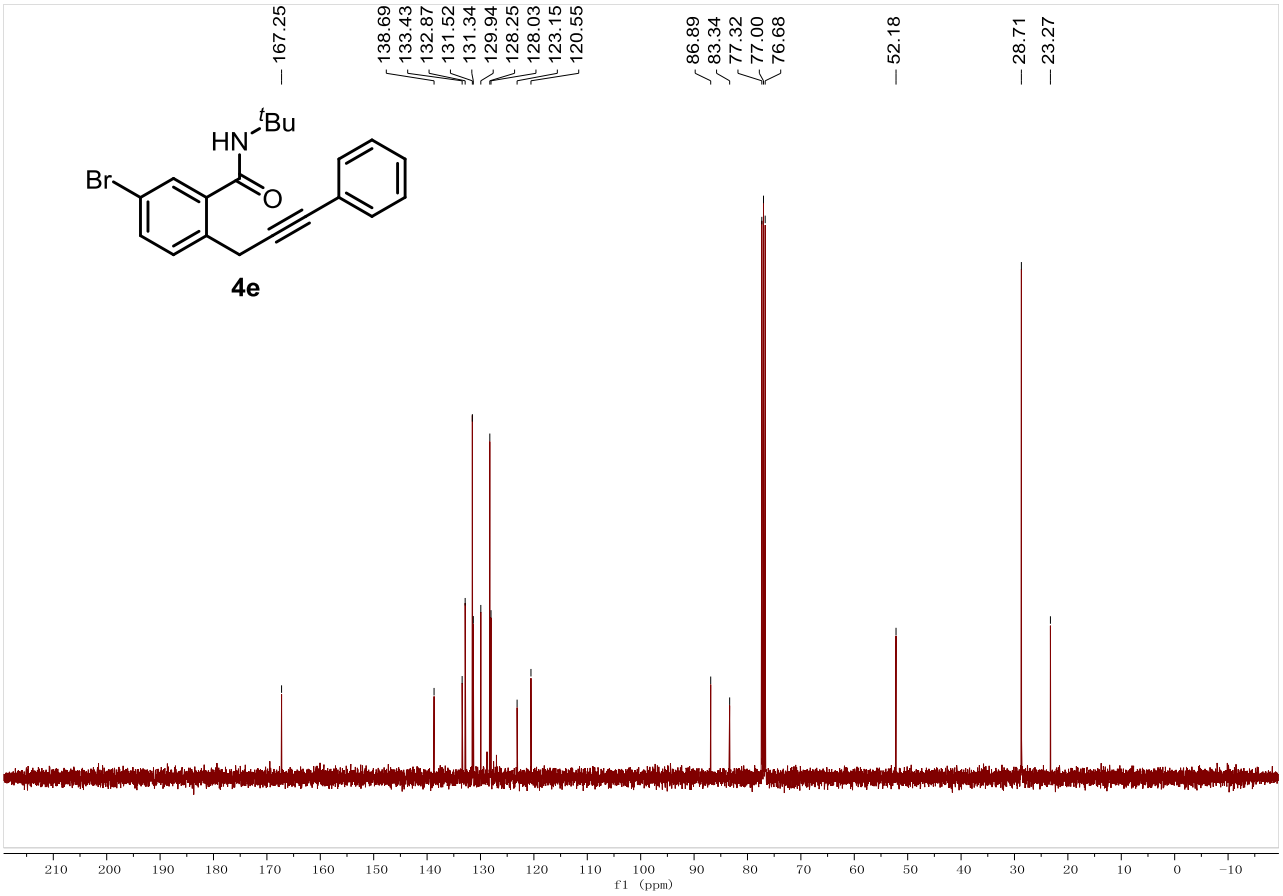
4d, ^{13}C NMR (101 MHz, $CDCl_3$)



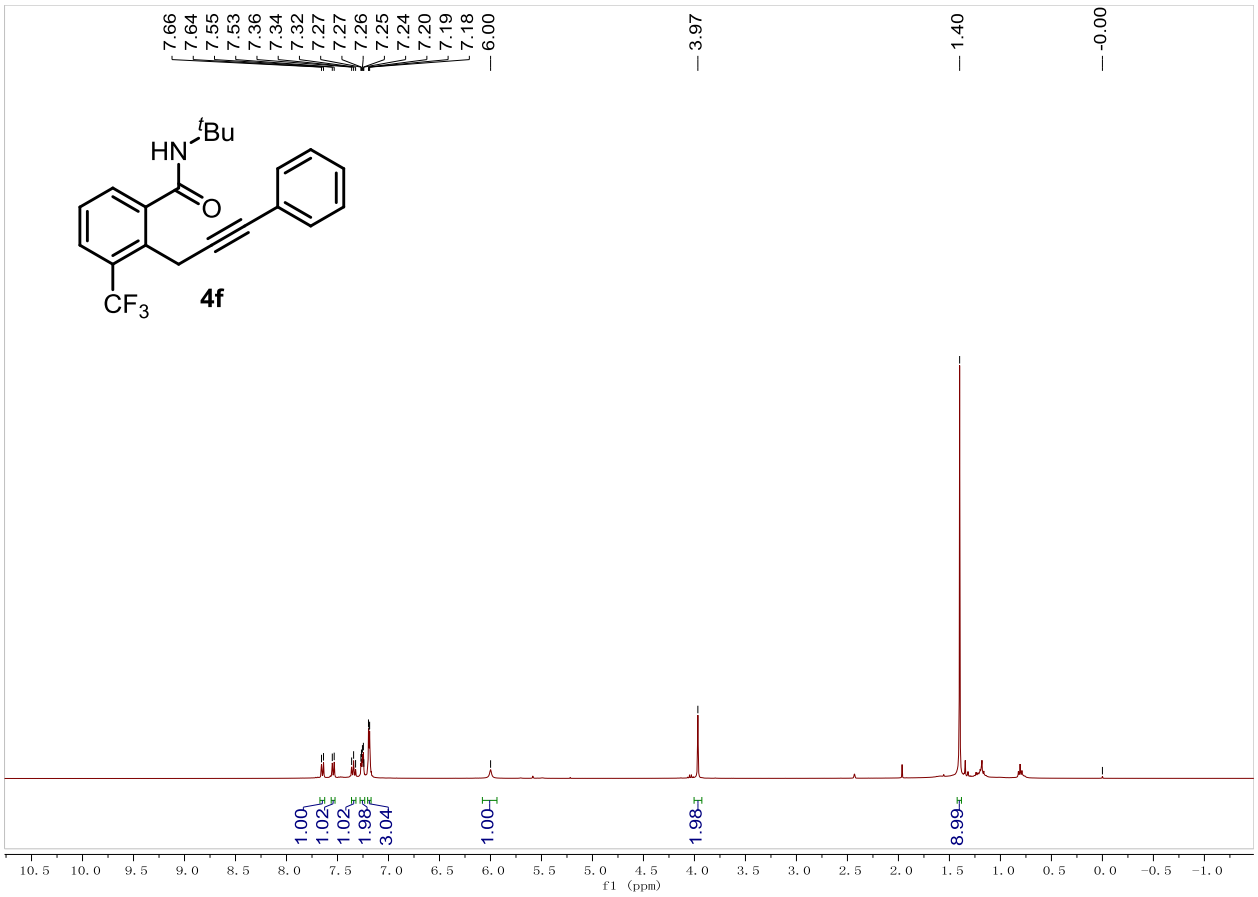
4e, ^{1}H NMR (400 MHz, $CDCl_3$)



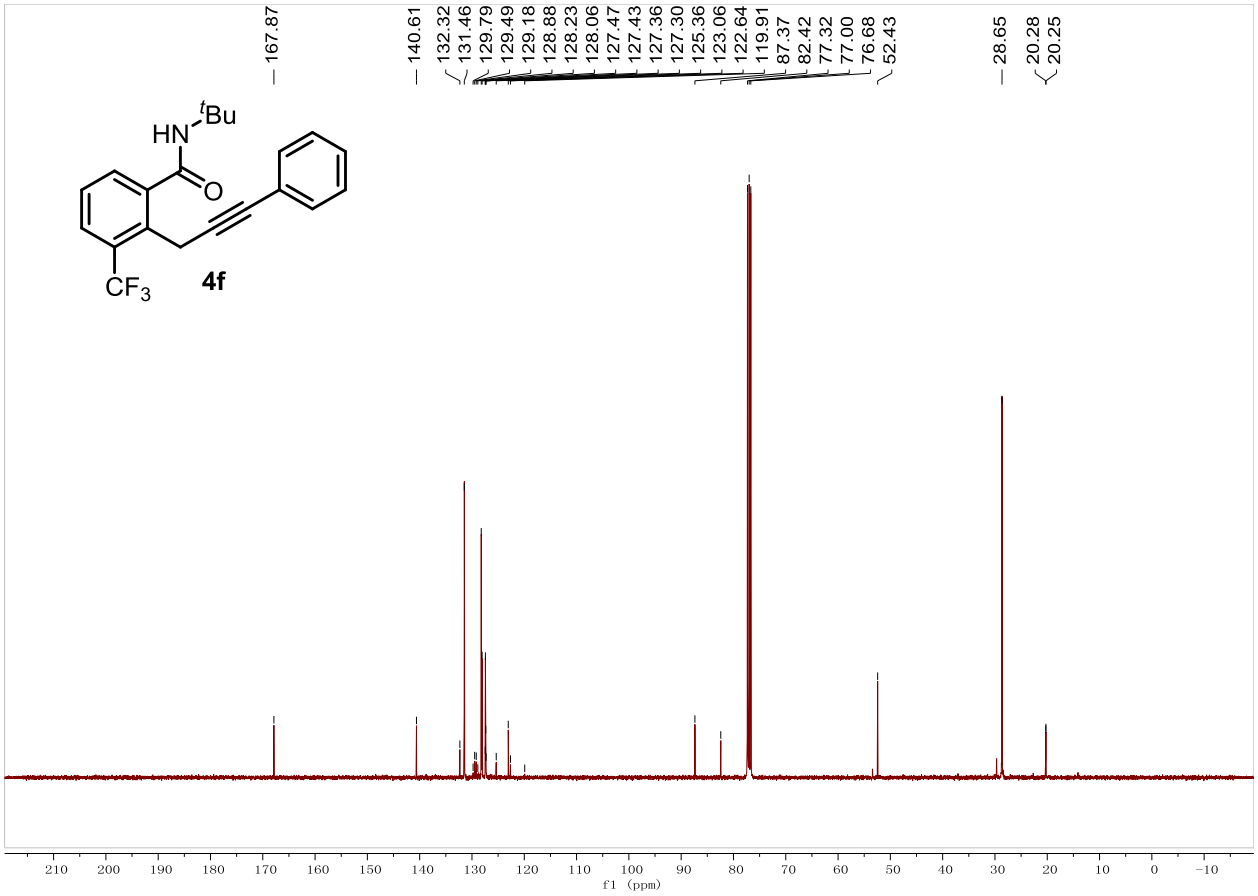
4e, ^{13}C NMR (101 MHz, $CDCl_3$)



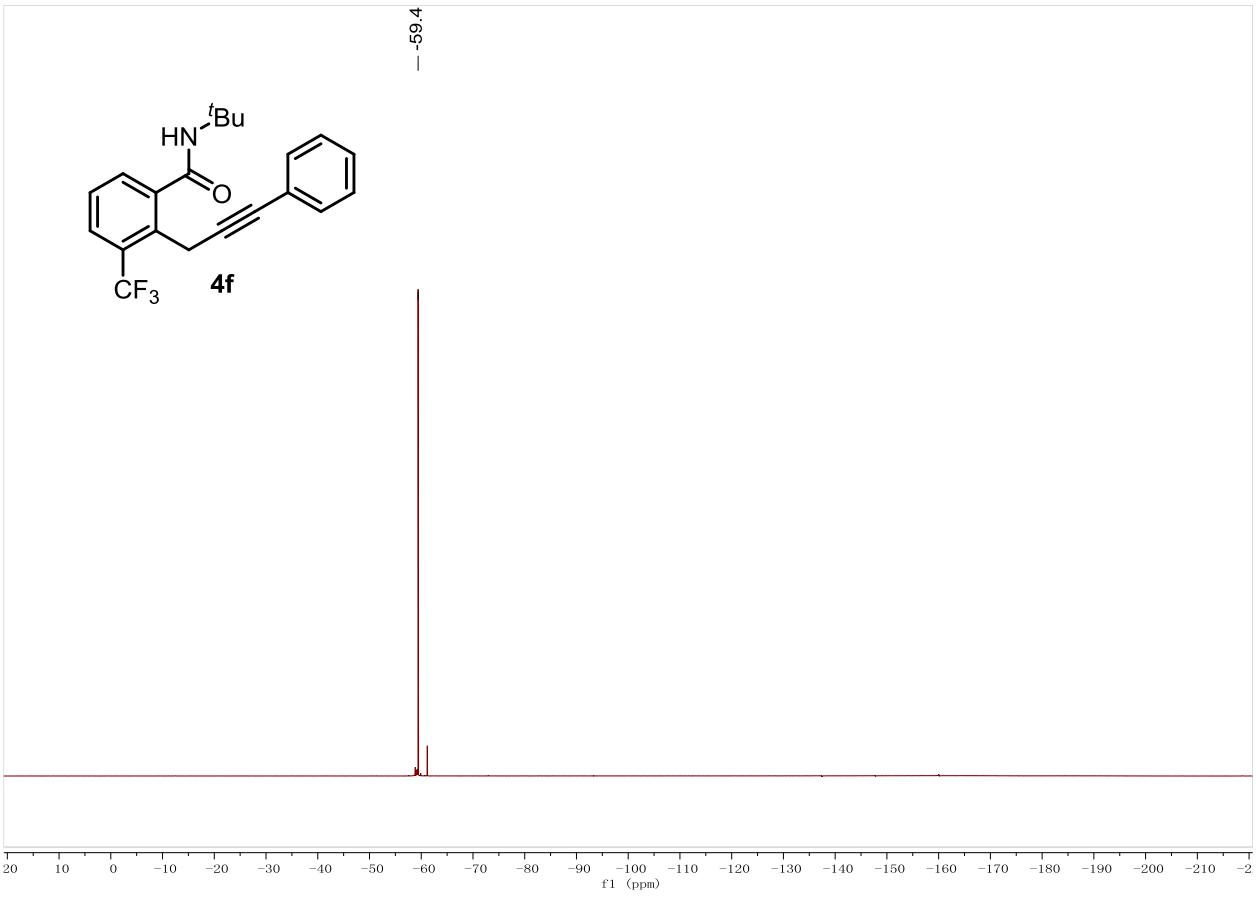
4f, ^{1}H NMR (400 MHz, $CDCl_3$)



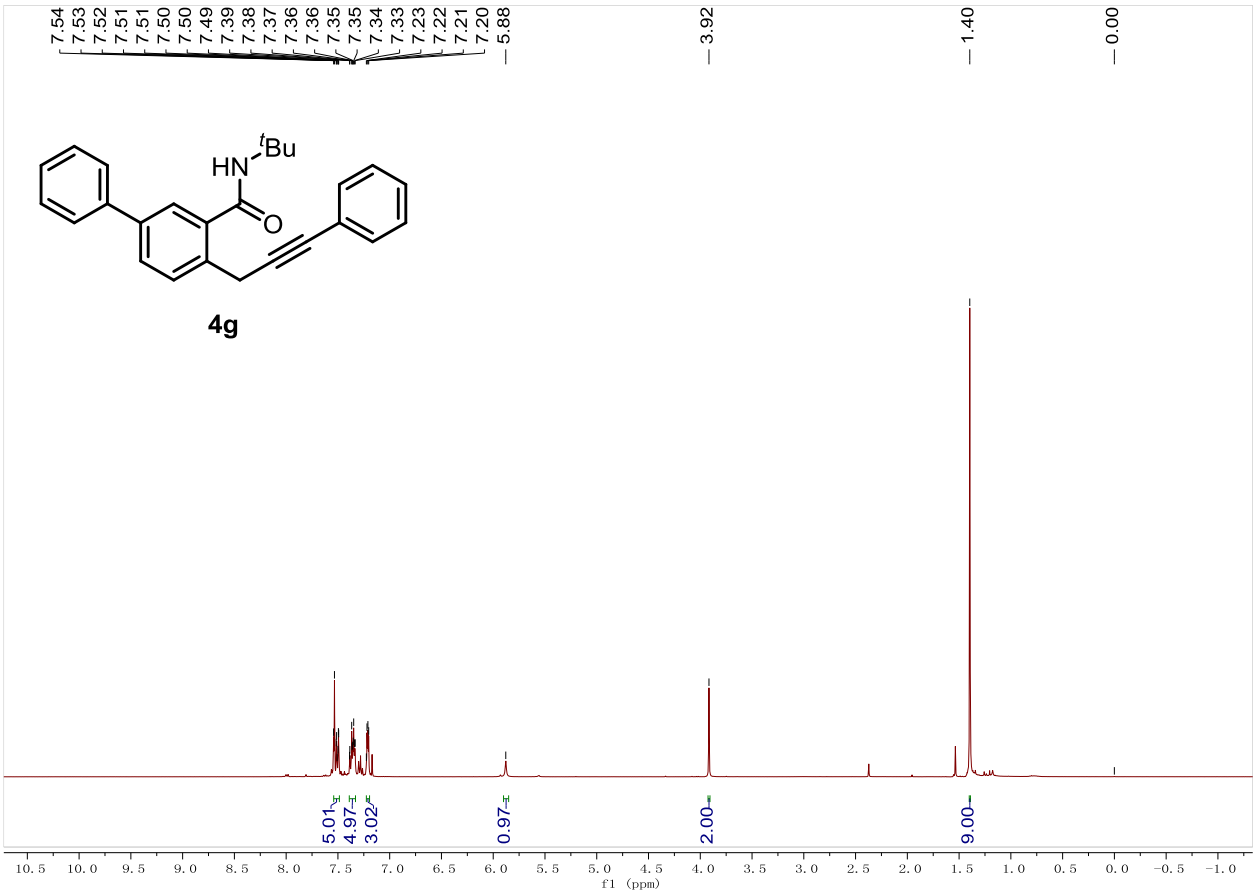
4f, ^{13}C NMR (101 MHz, $CDCl_3$)



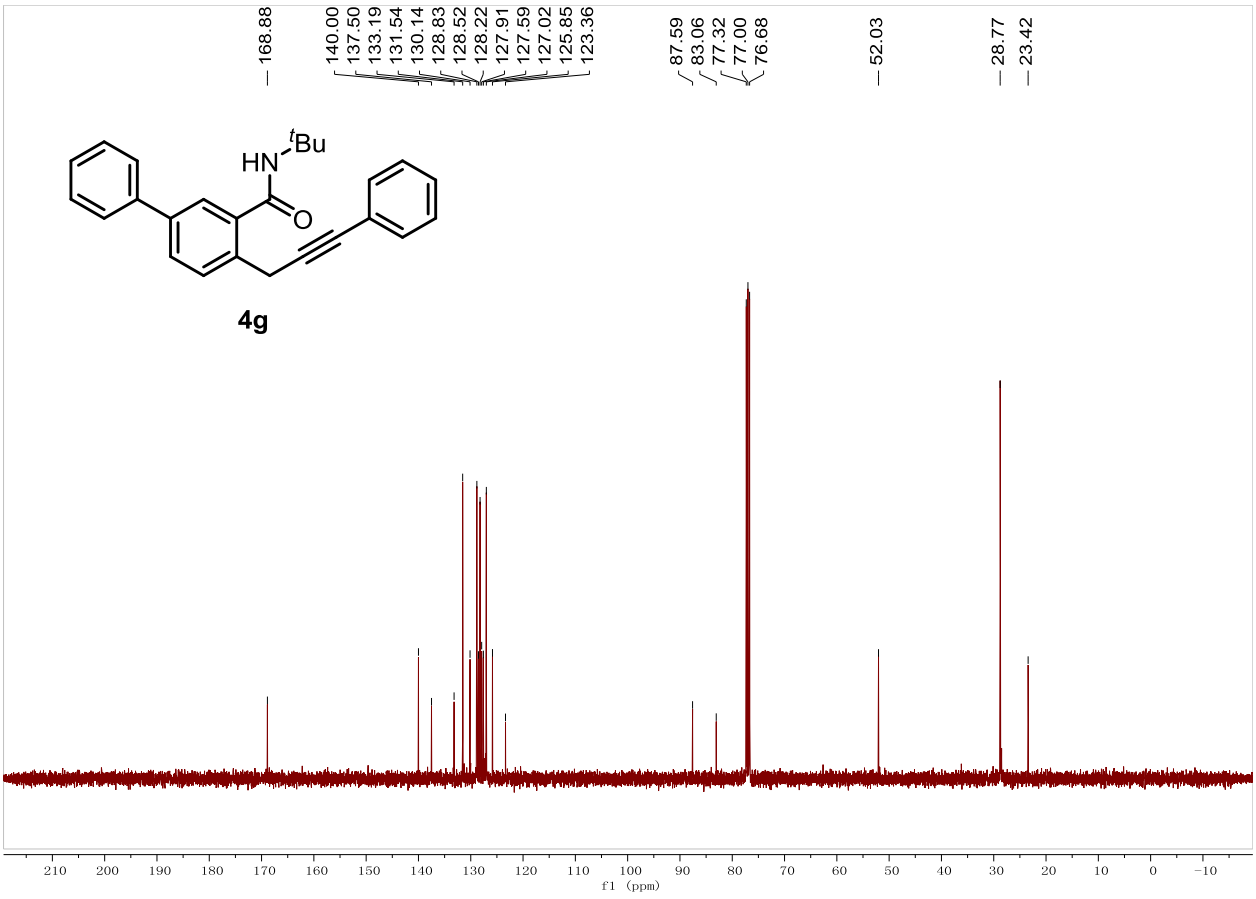
4f, ^{19}F NMR (376 MHz, $CDCl_3$)



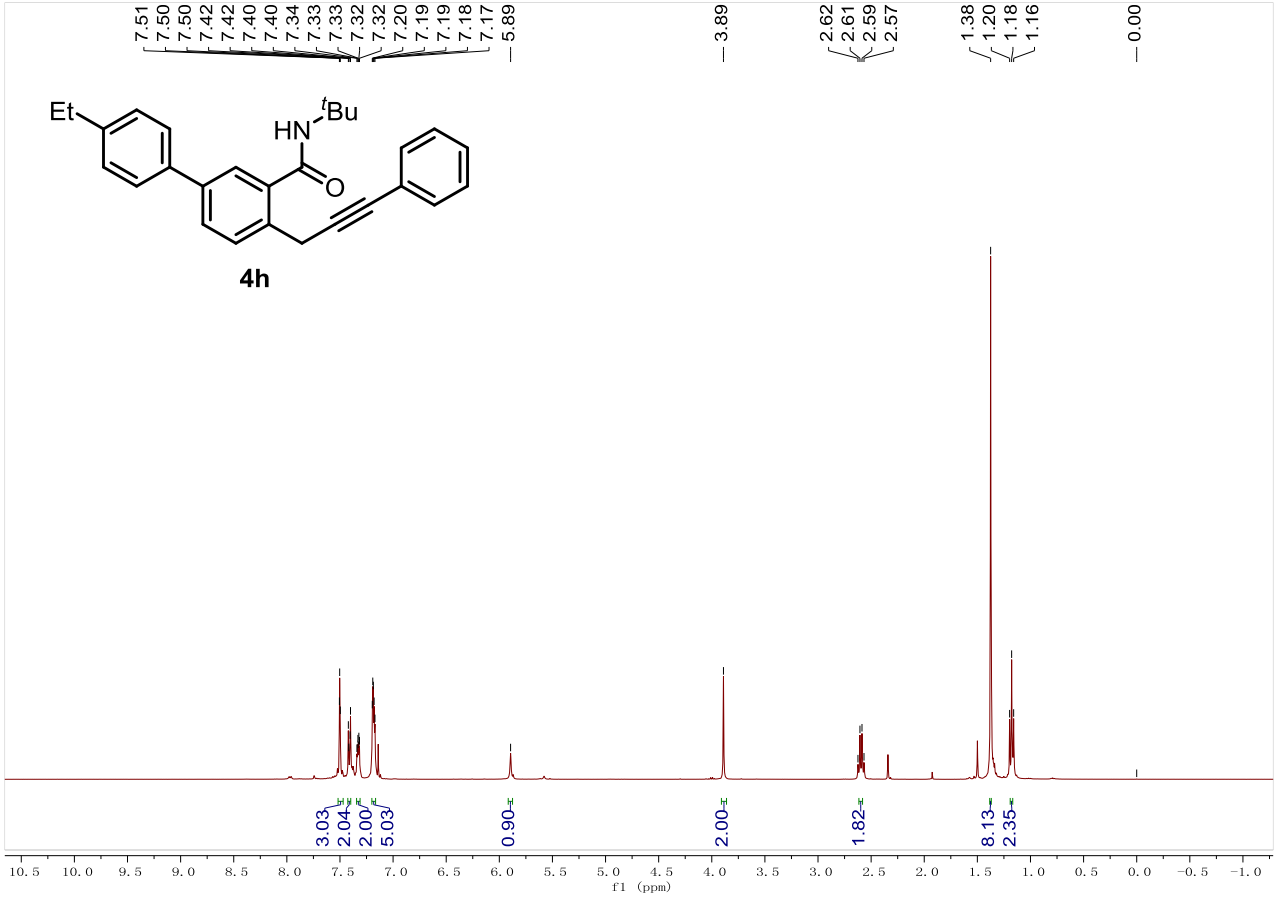
4g, ^{1}H NMR (400 MHz, $CDCl_3$)



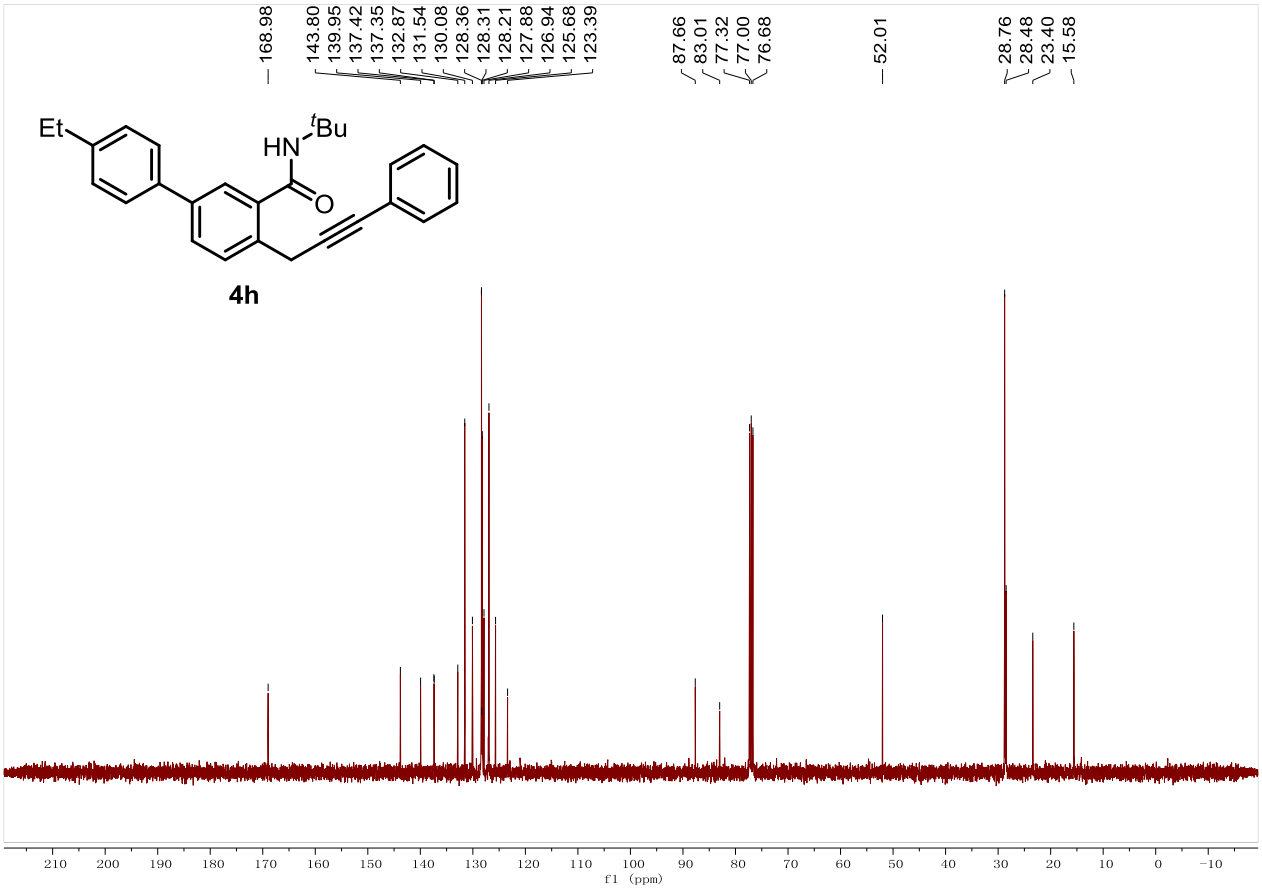
4g, ^{13}C NMR (101 MHz, $CDCl_3$)



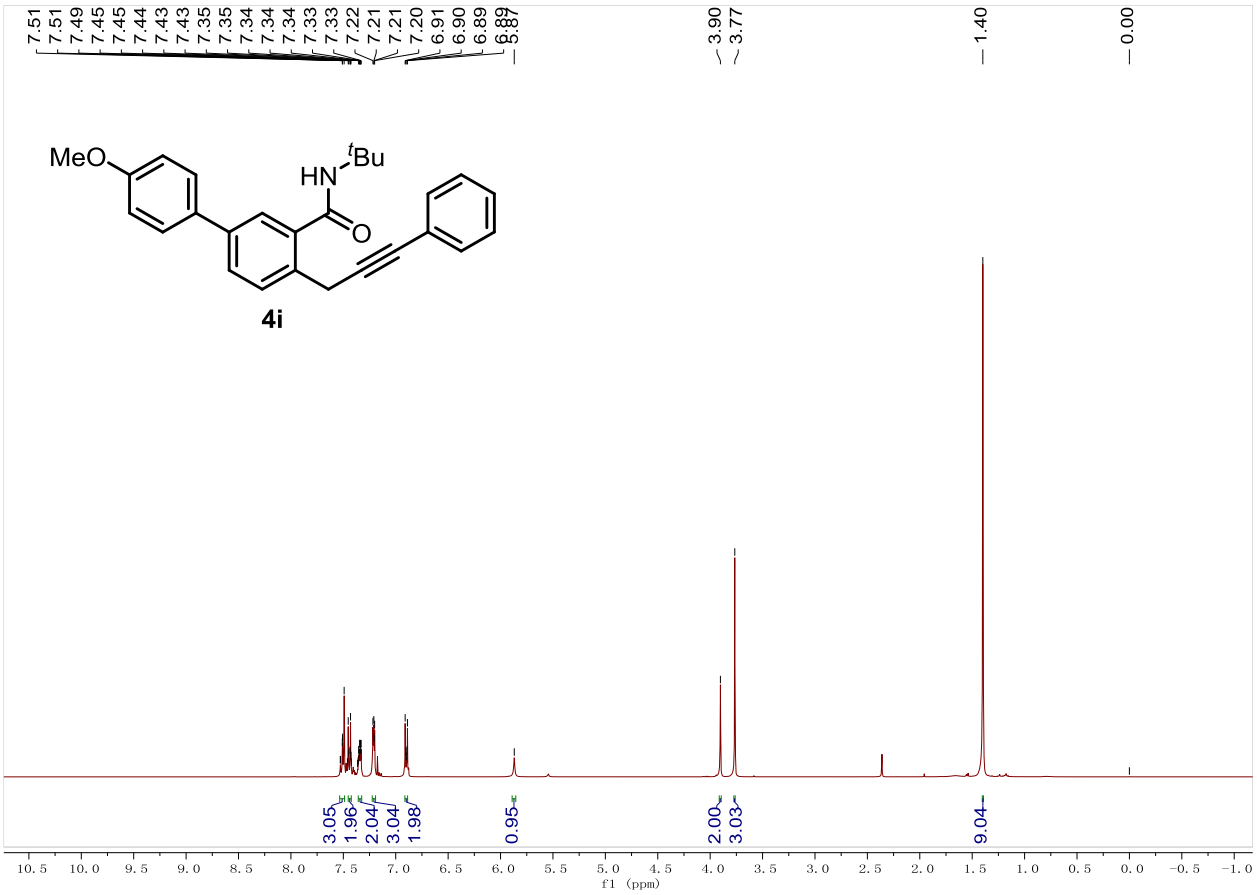
4h, ^{1}H NMR (400 MHz, $CDCl_3$)



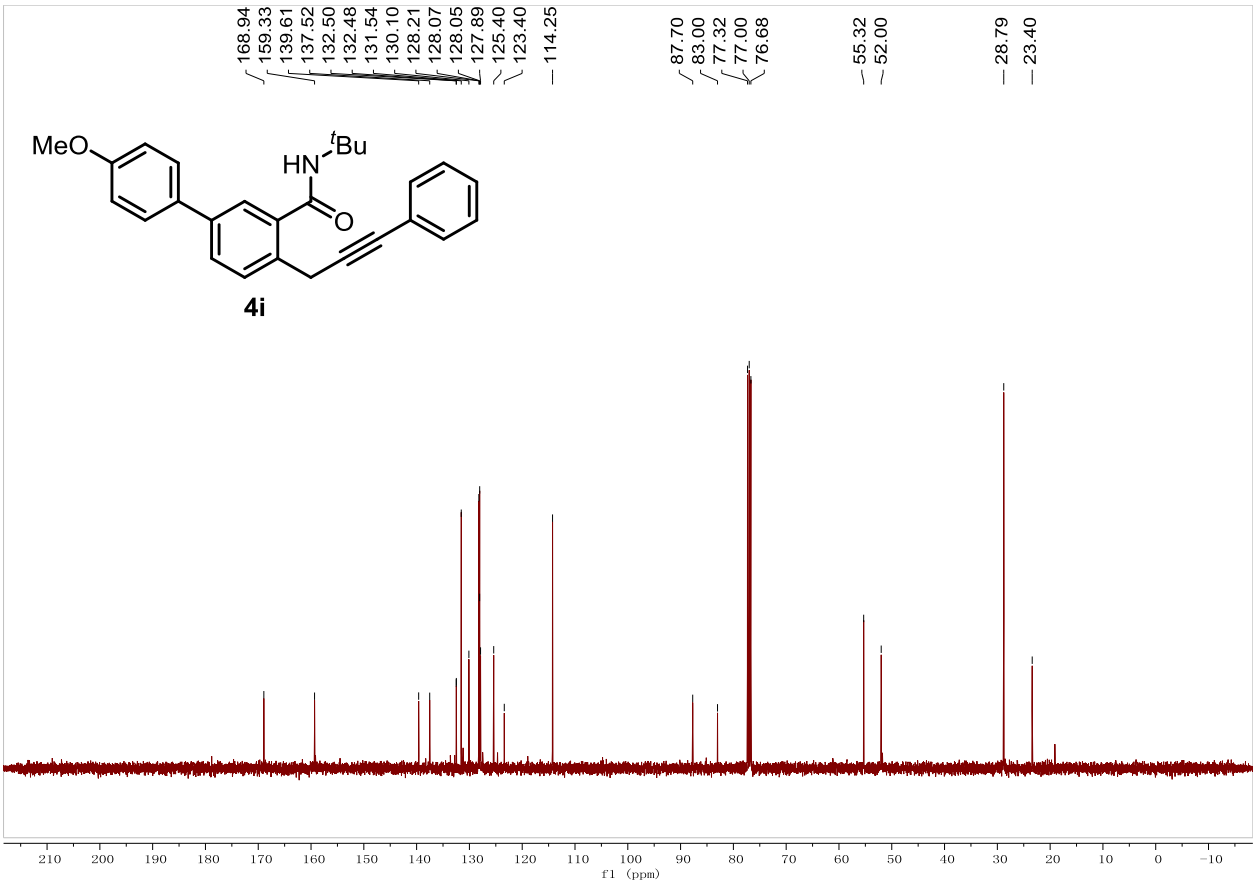
4h, ^{13}C NMR (101 MHz, $CDCl_3$)



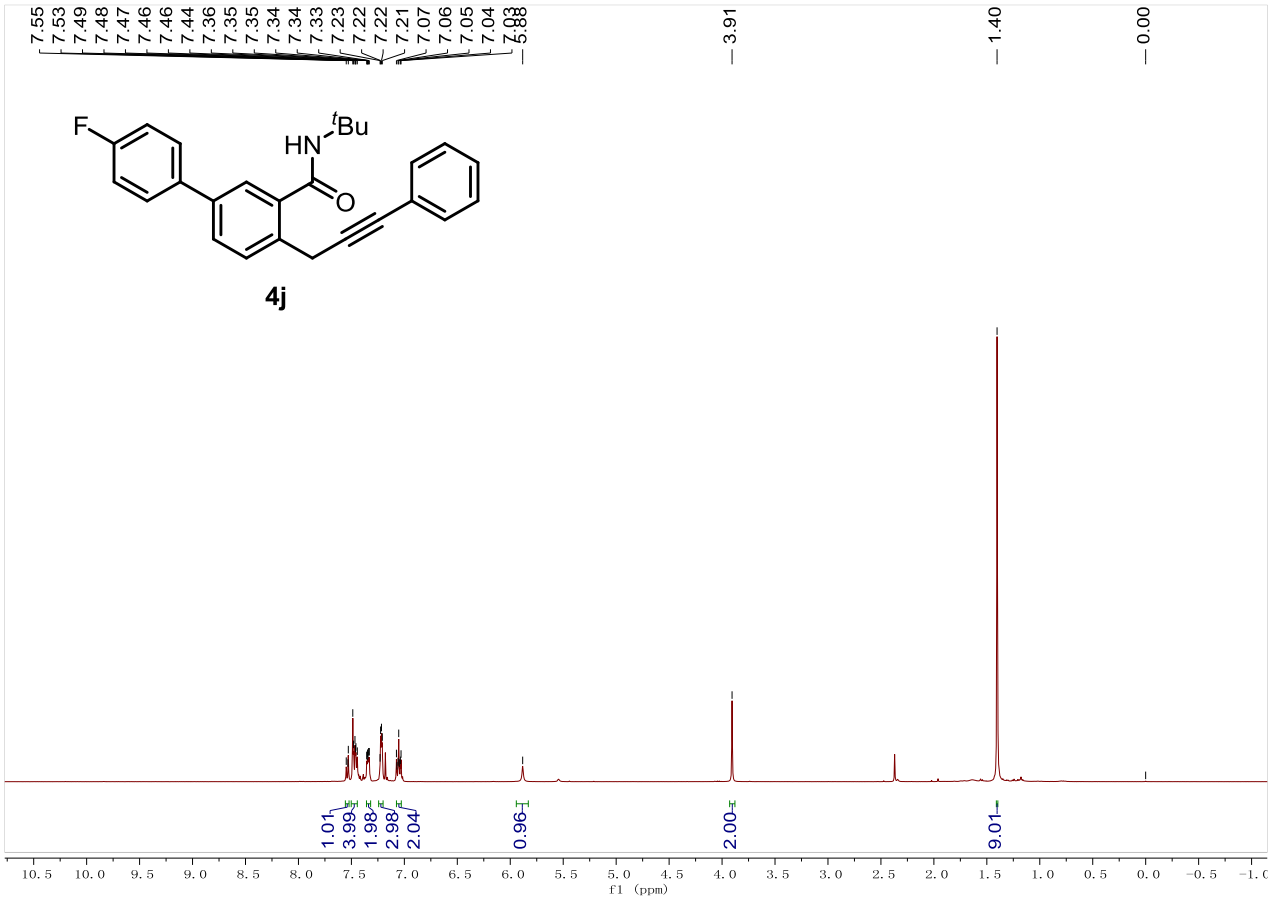
4i, ^{1}H NMR (400 MHz, $CDCl_3$)



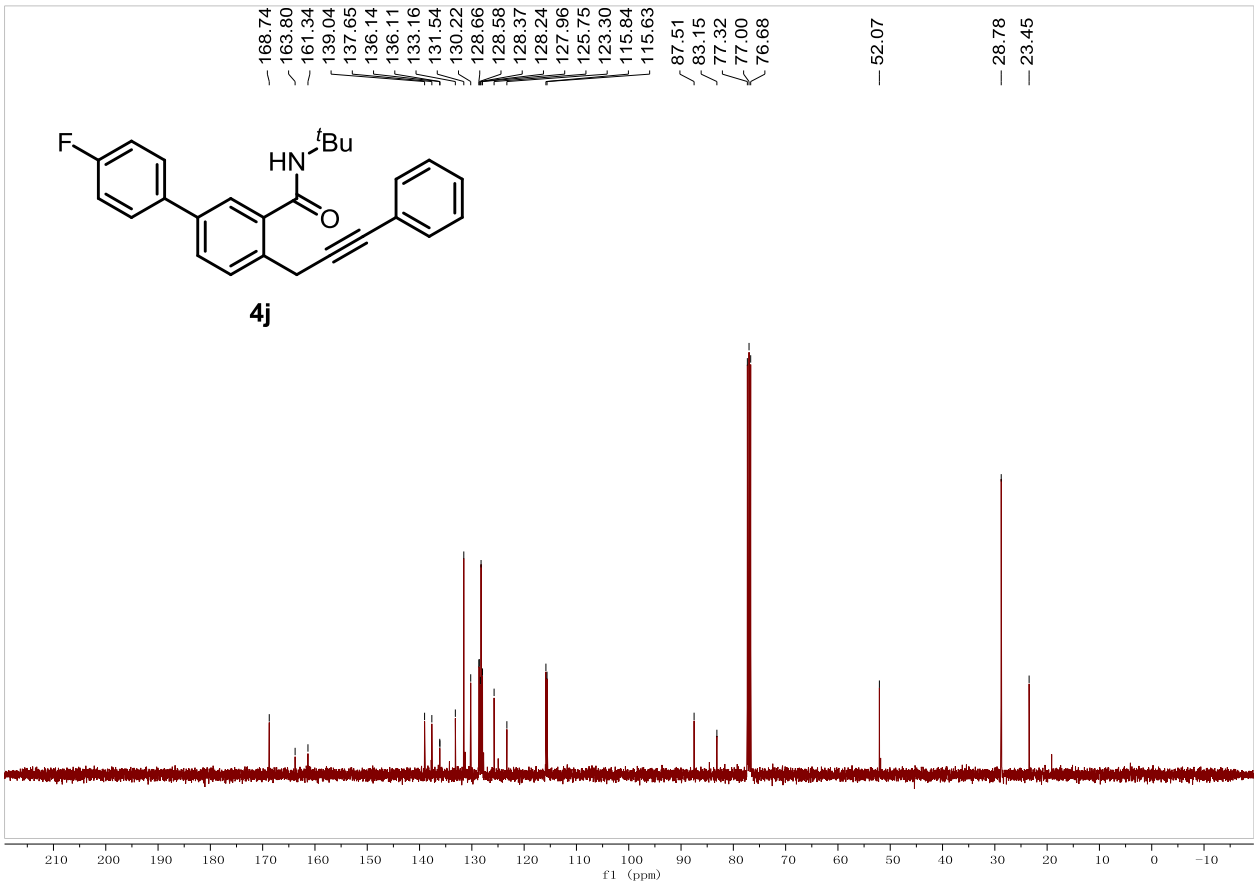
4i, ^{13}C NMR (101 MHz, $CDCl_3$)



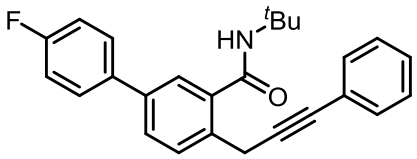
4j, ^{1}H NMR (400 MHz, $CDCl_3$)



4j, ^{13}C NMR (101 MHz, $CDCl_3$)

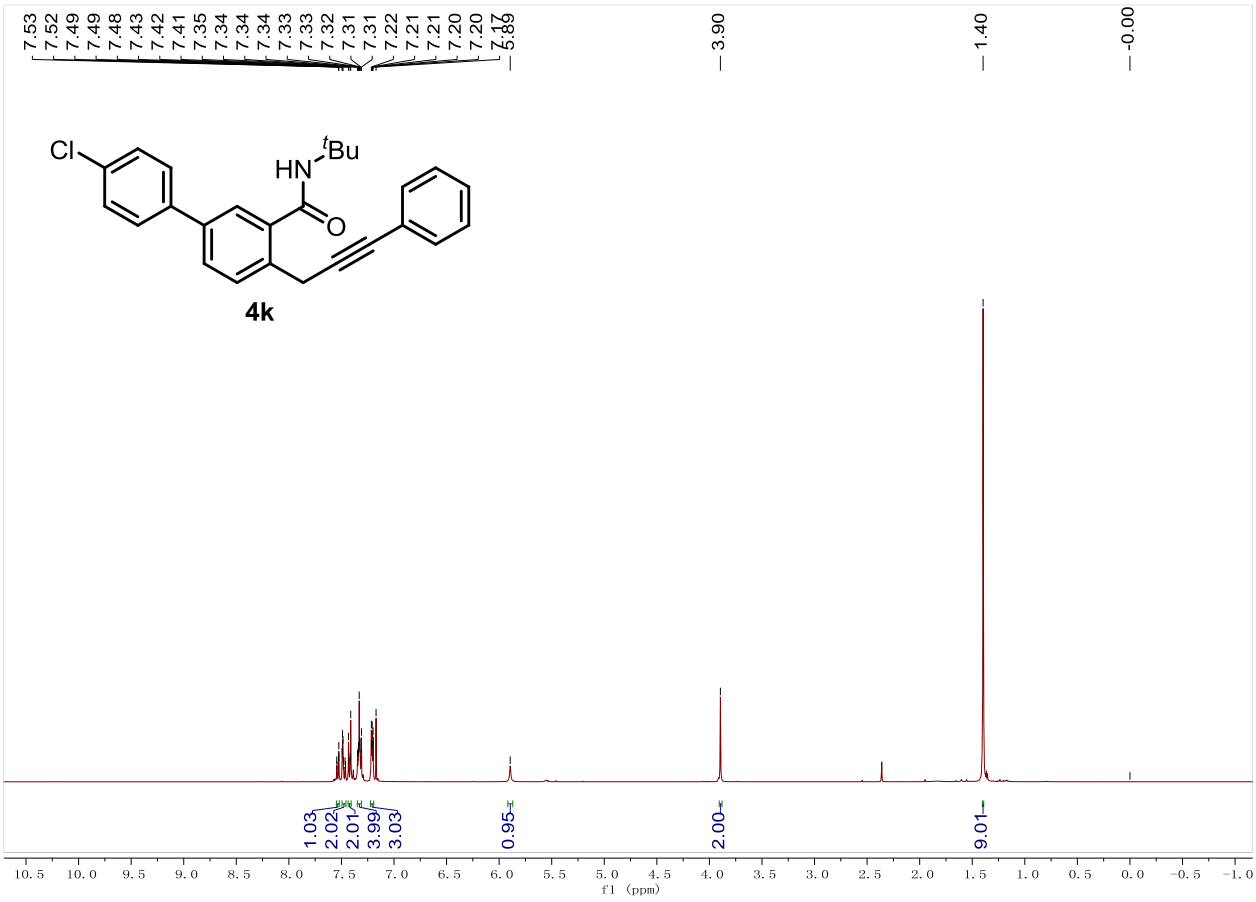


4j, ^{19}F NMR (376 MHz, $CDCl_3$)

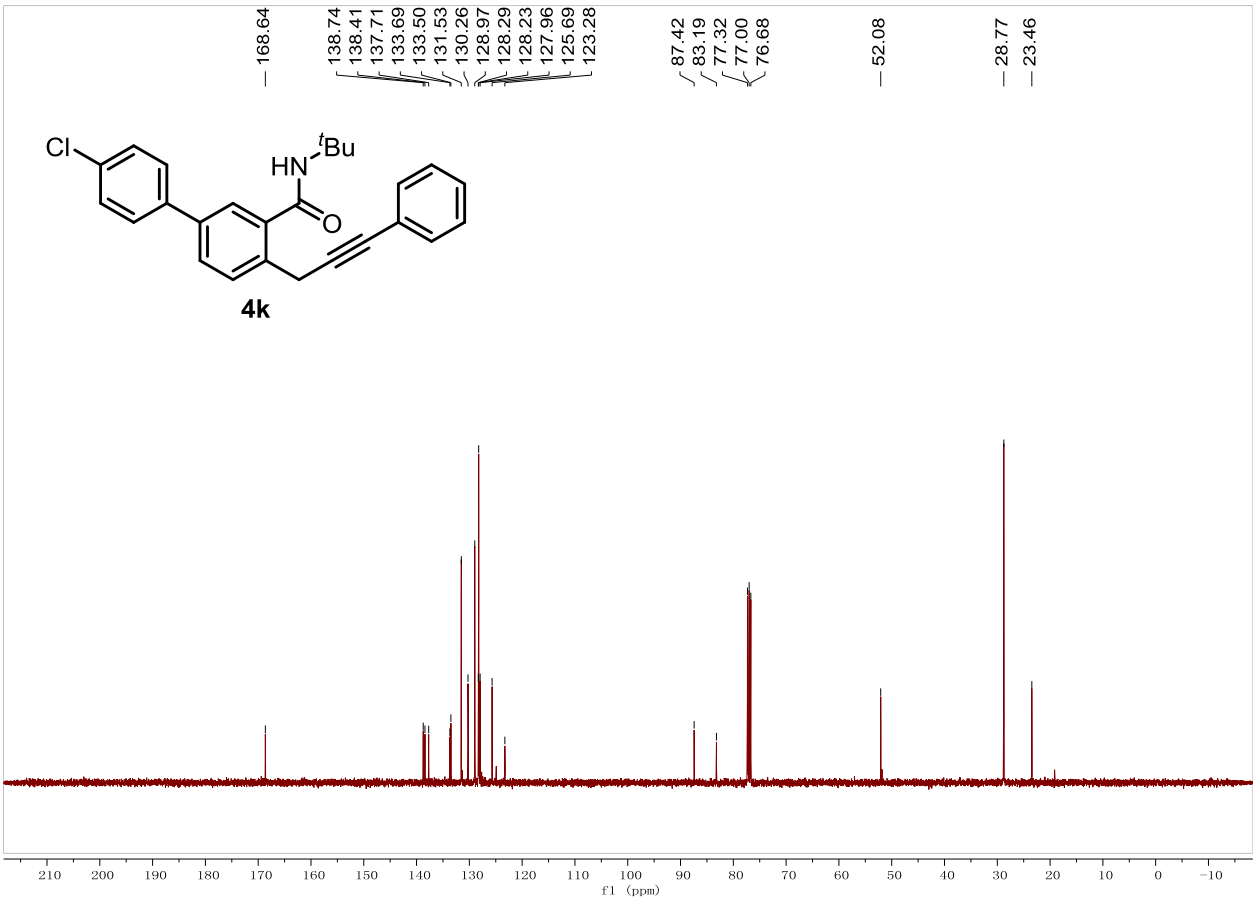


4j

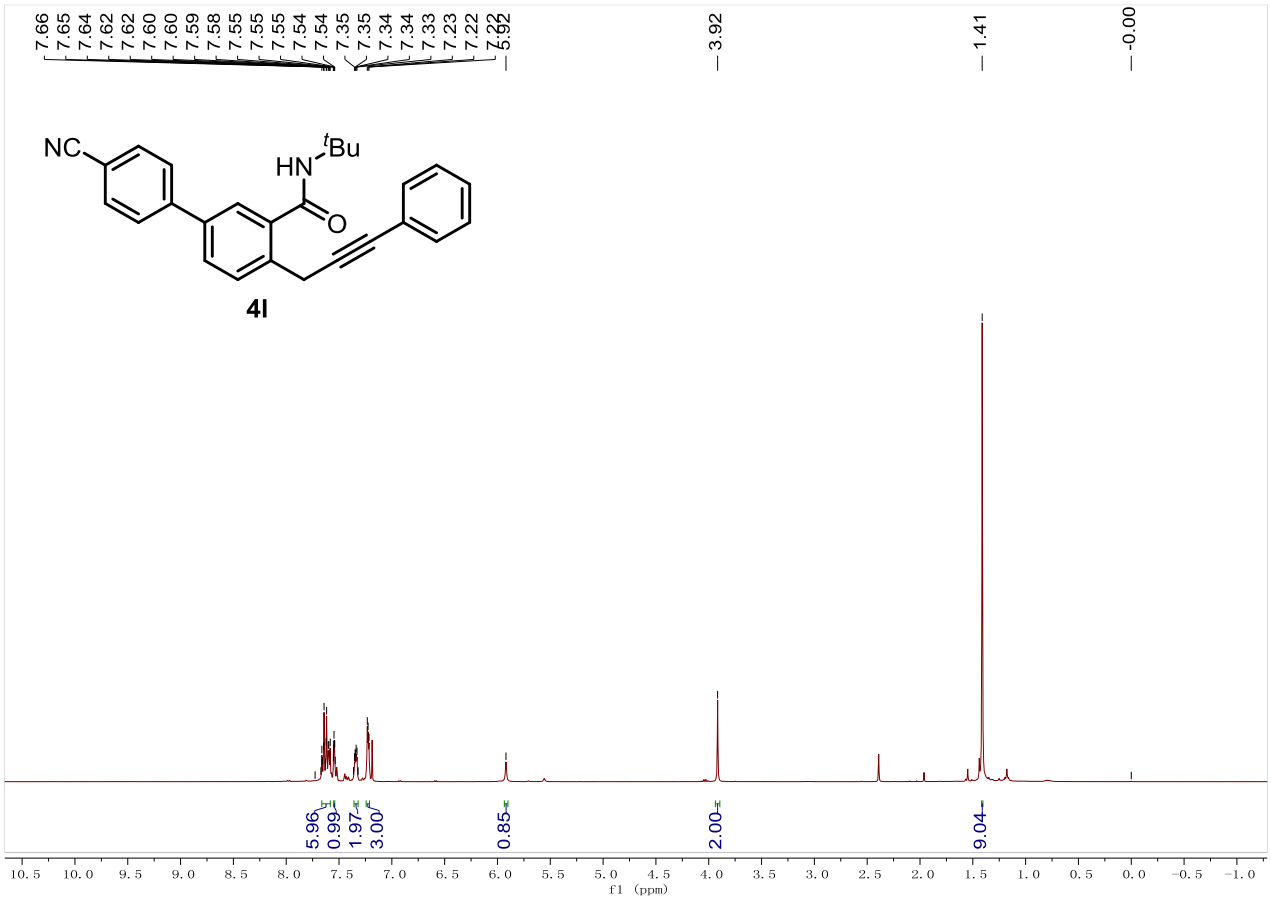
4k, ^{1}H NMR (400 MHz, $CDCl_3$)



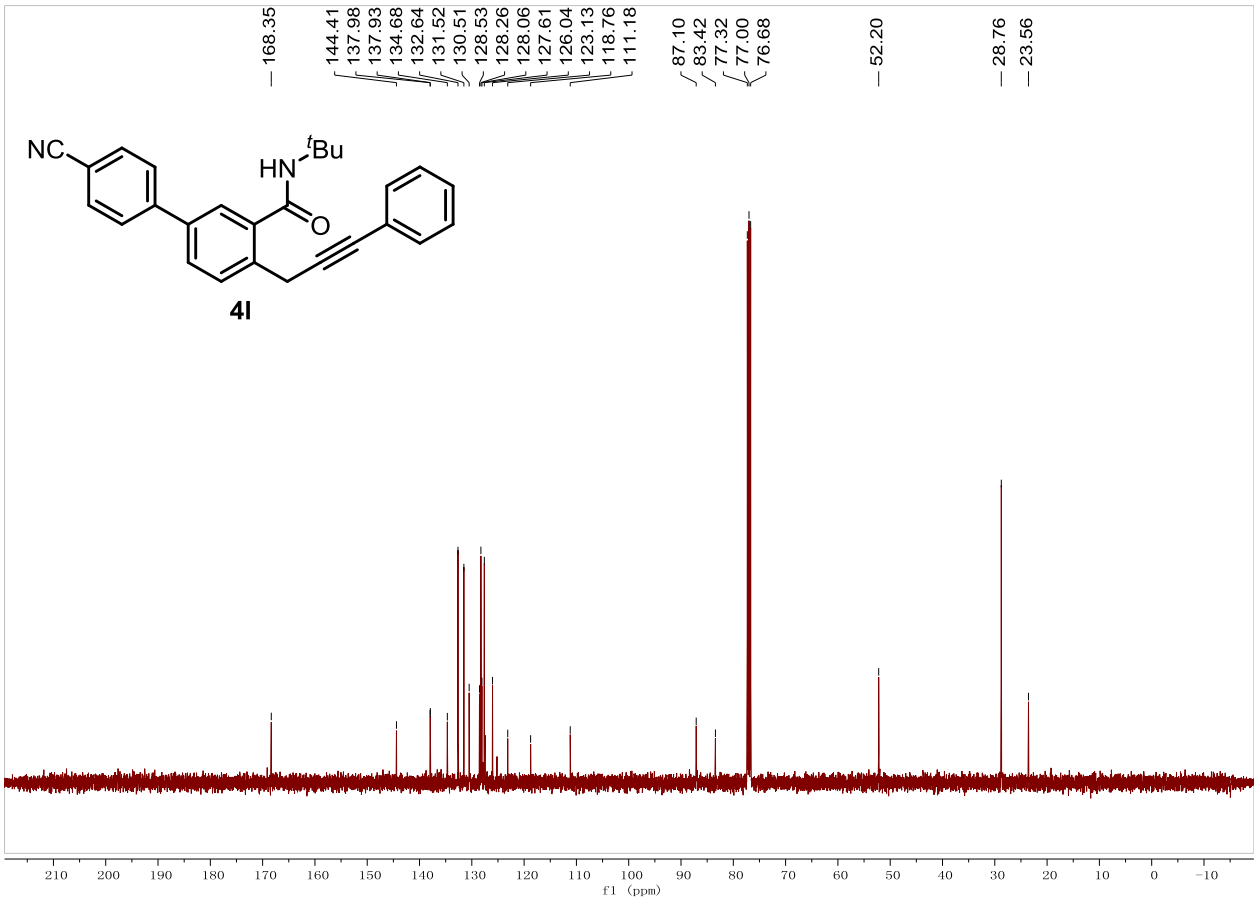
4k, ^{13}C NMR (101 MHz, $CDCl_3$)



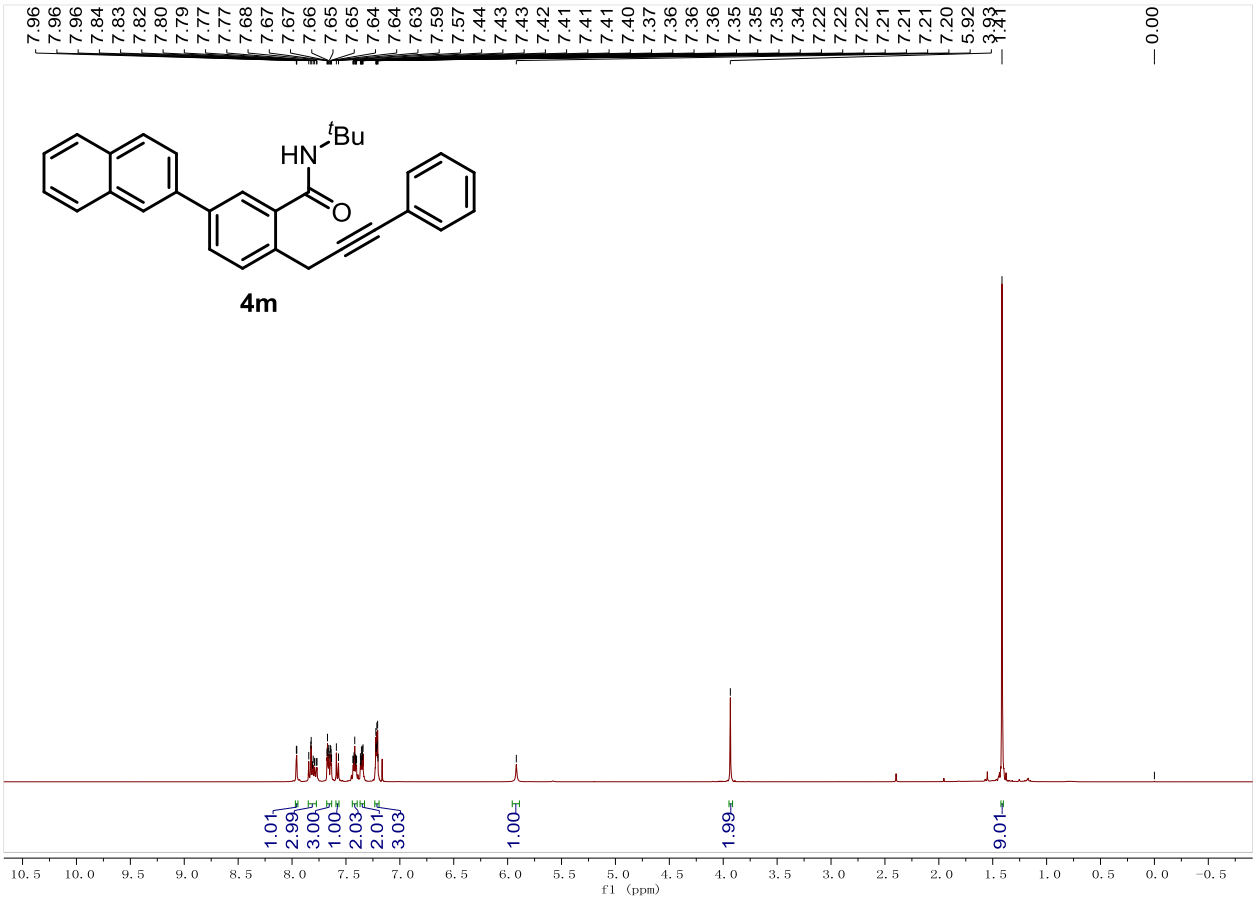
4l, ^{1}H NMR (400 MHz, $CDCl_3$)



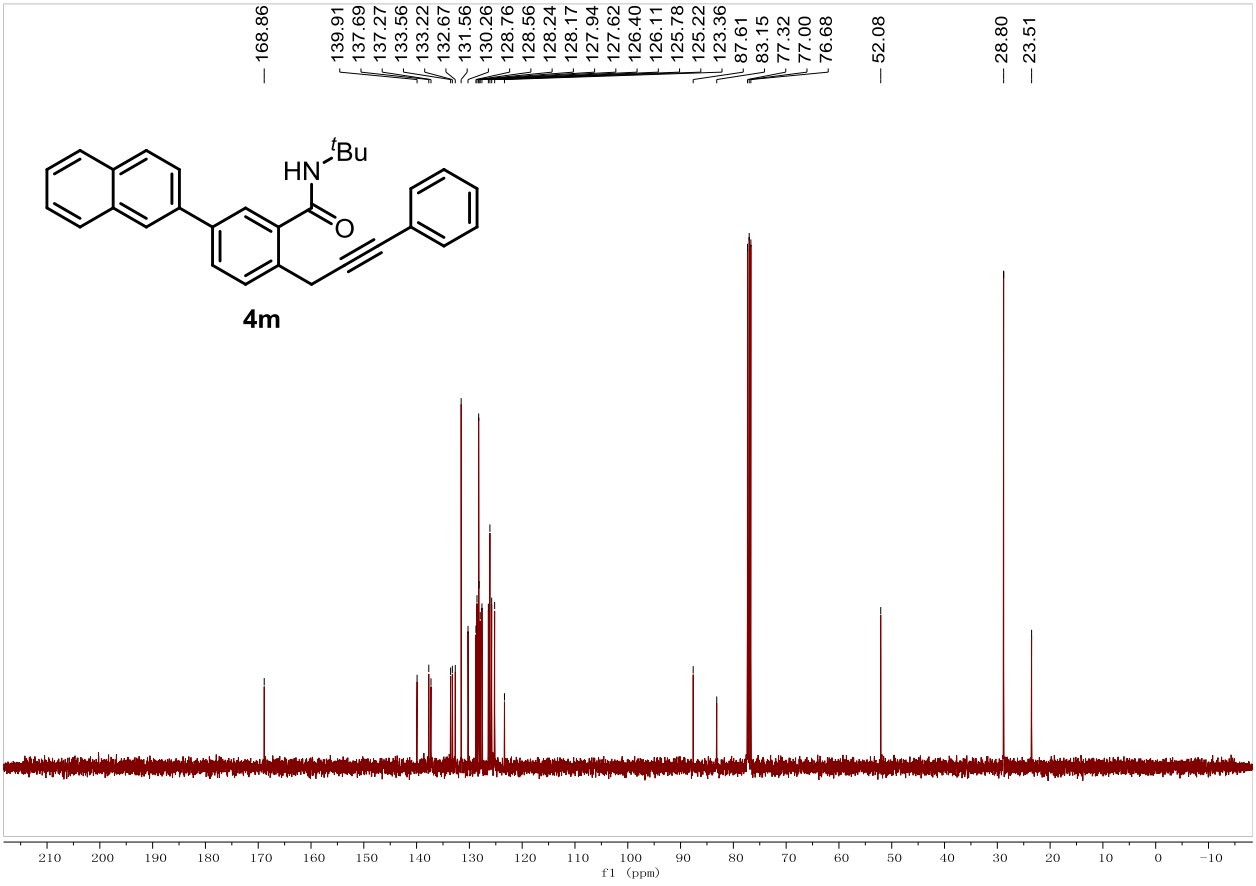
4l, ^{13}C NMR (101 MHz, $CDCl_3$)



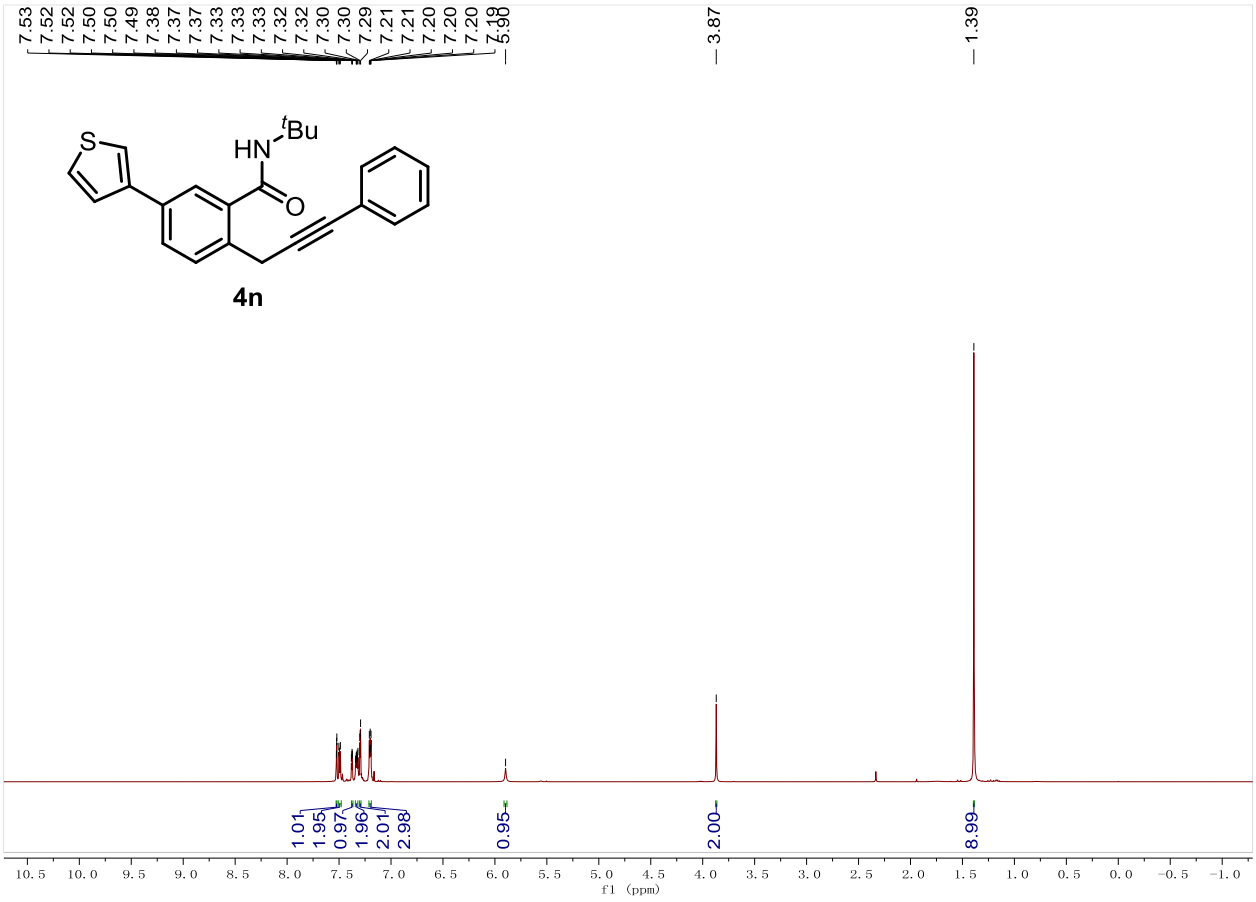
4m, ^{1}H NMR (400 MHz, $CDCl_3$)



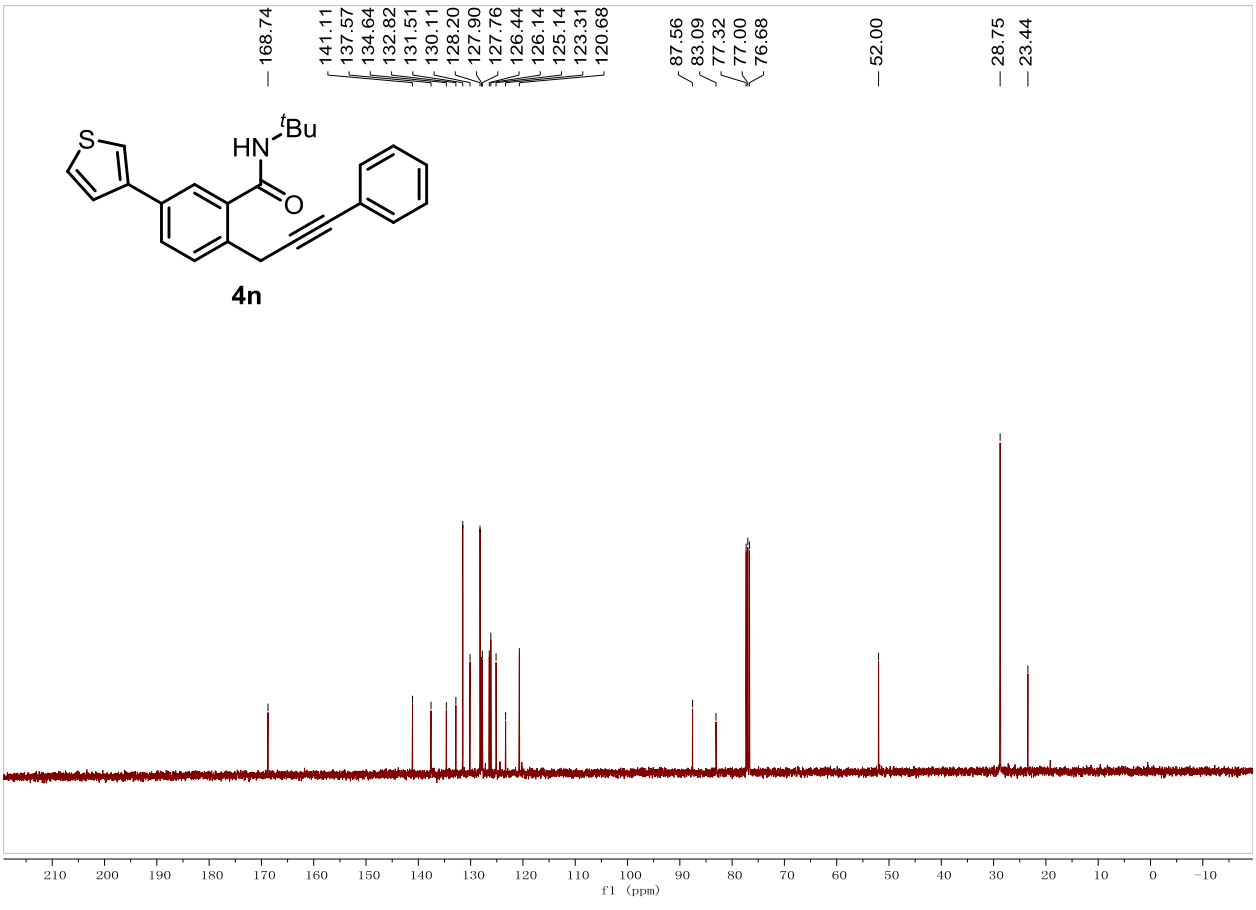
4m, ^{13}C NMR (101 MHz, $CDCl_3$)



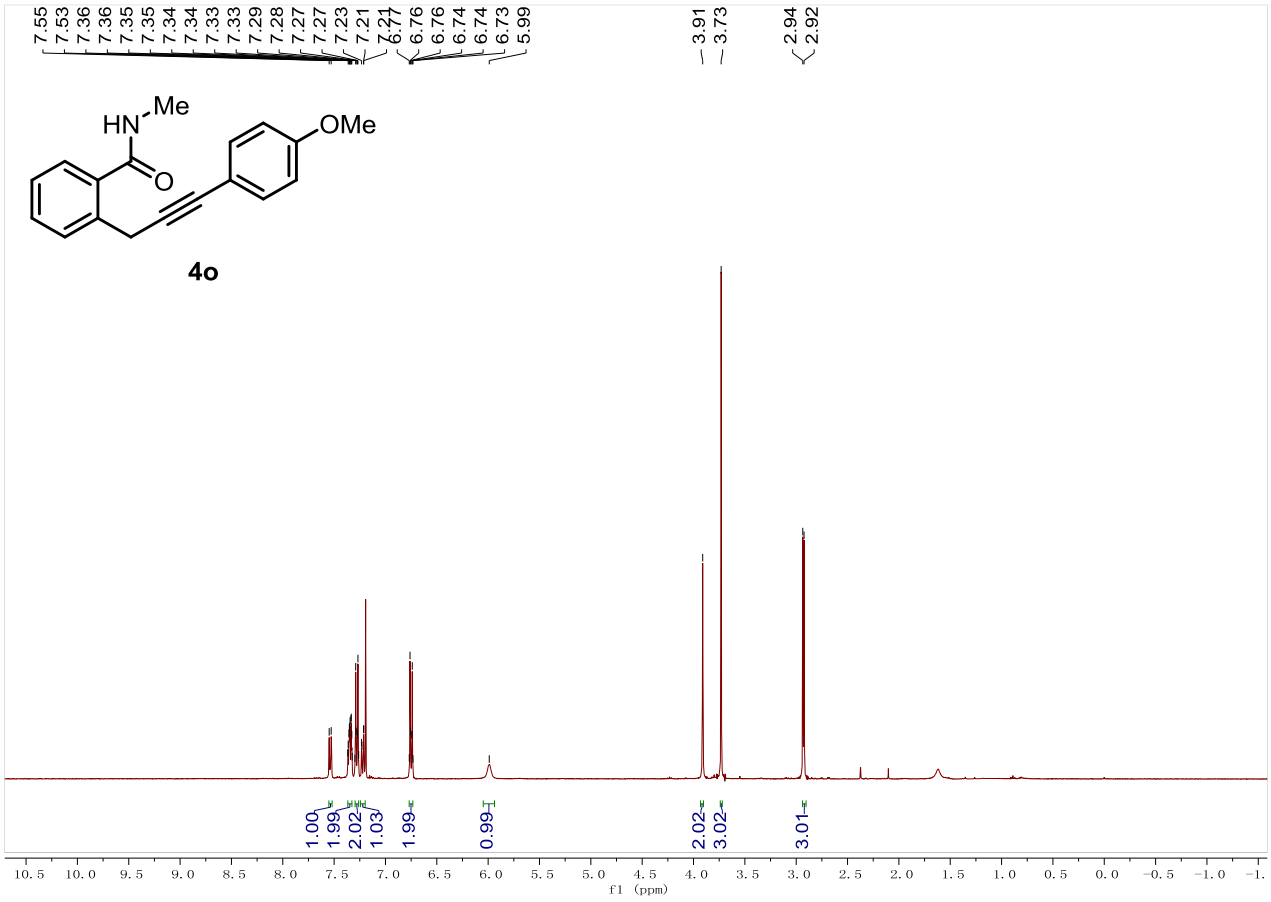
4n, ^{1}H NMR (400 MHz, $CDCl_3$)



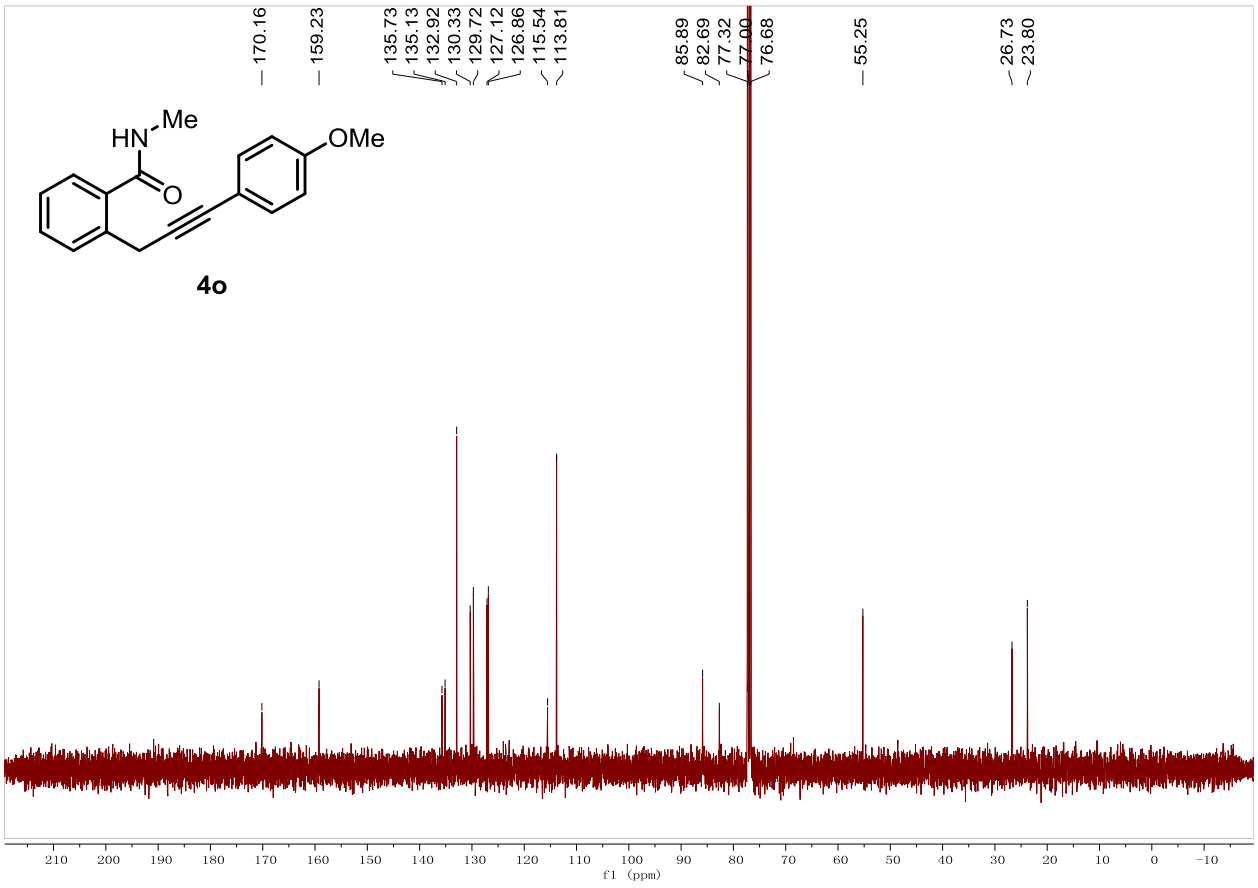
4n, ^{13}C NMR (101 MHz, $CDCl_3$)



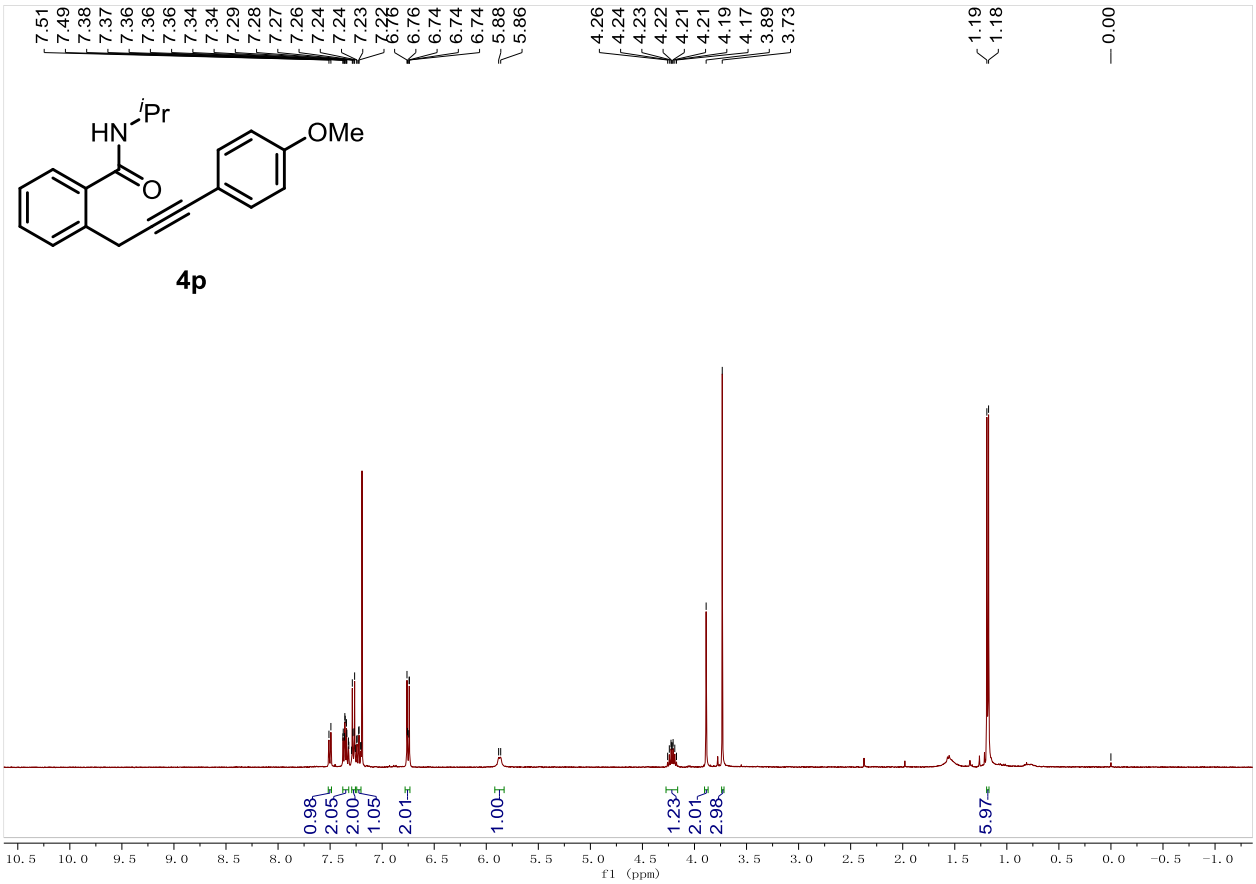
4o, ^{1}H NMR (400 MHz, $CDCl_3$)



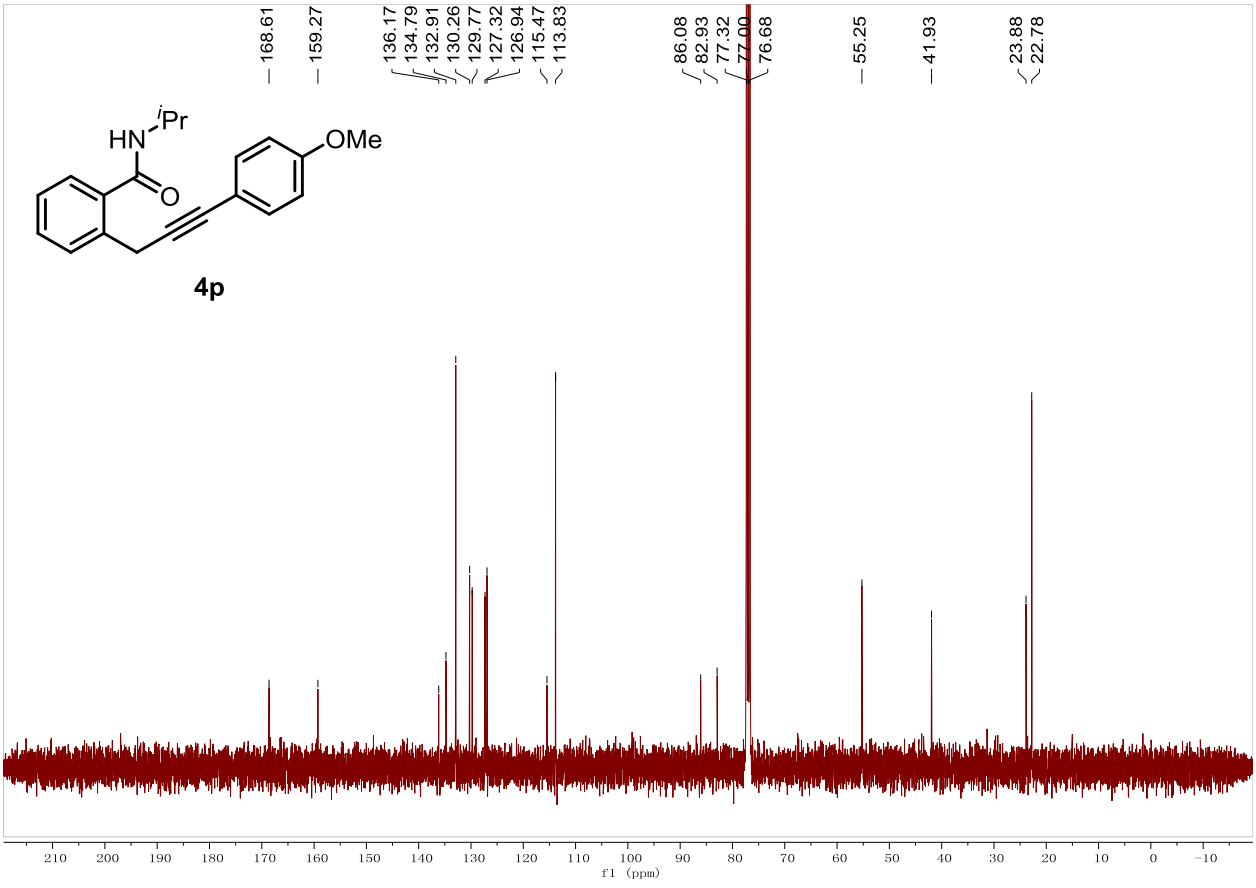
4o, ^{13}C NMR (101 MHz, $CDCl_3$)



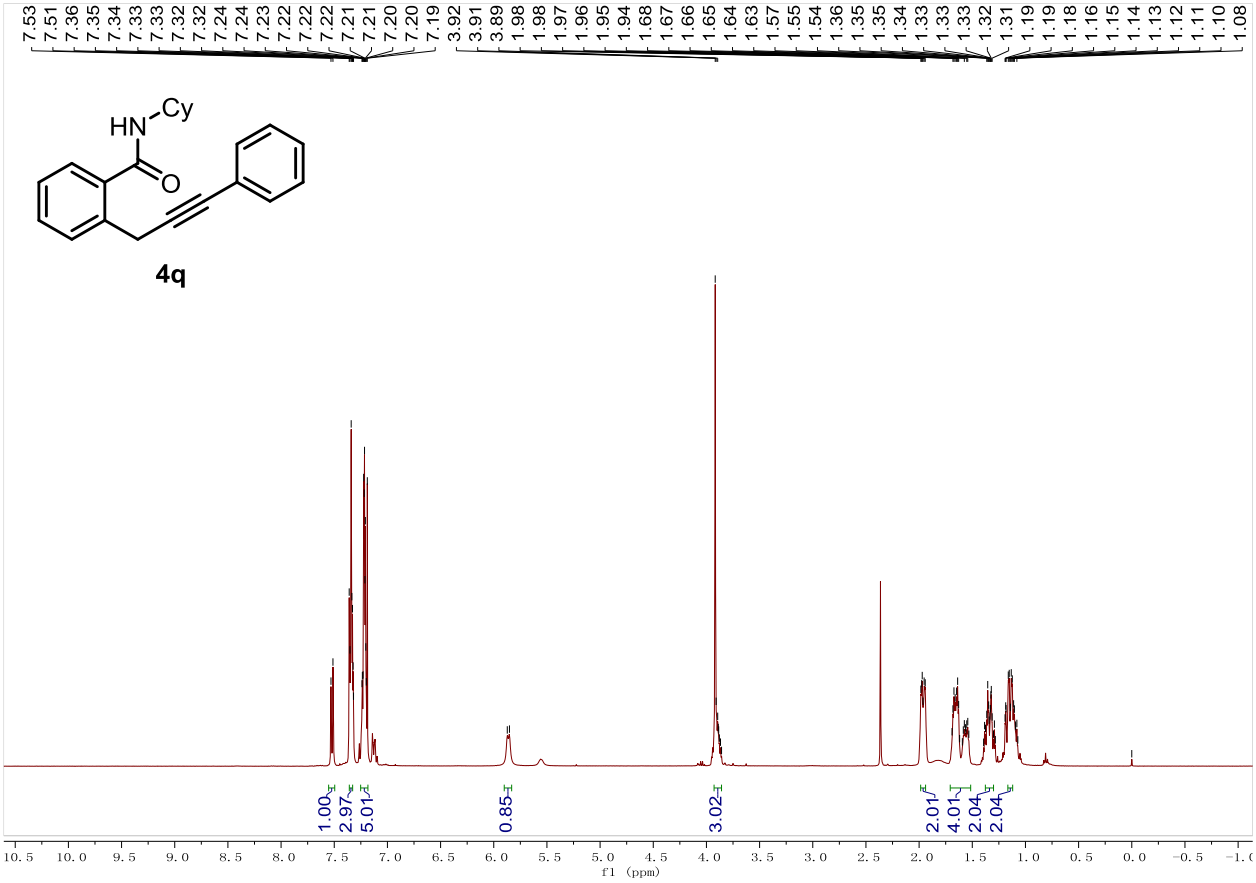
4p, ^{1}H NMR (400 MHz, CDCl$_3$)



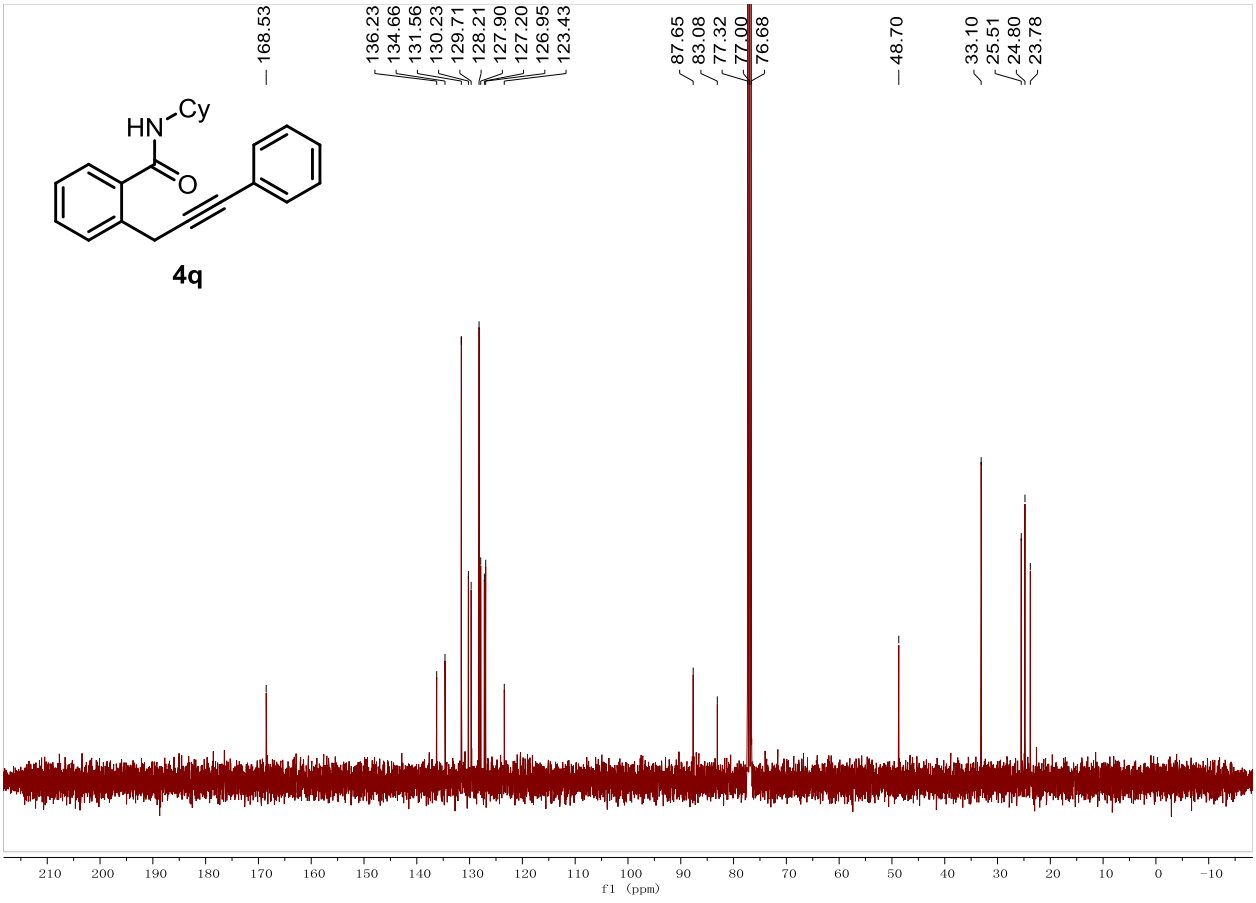
4p, ^{13}C NMR (101 MHz, CDCl$_3$)



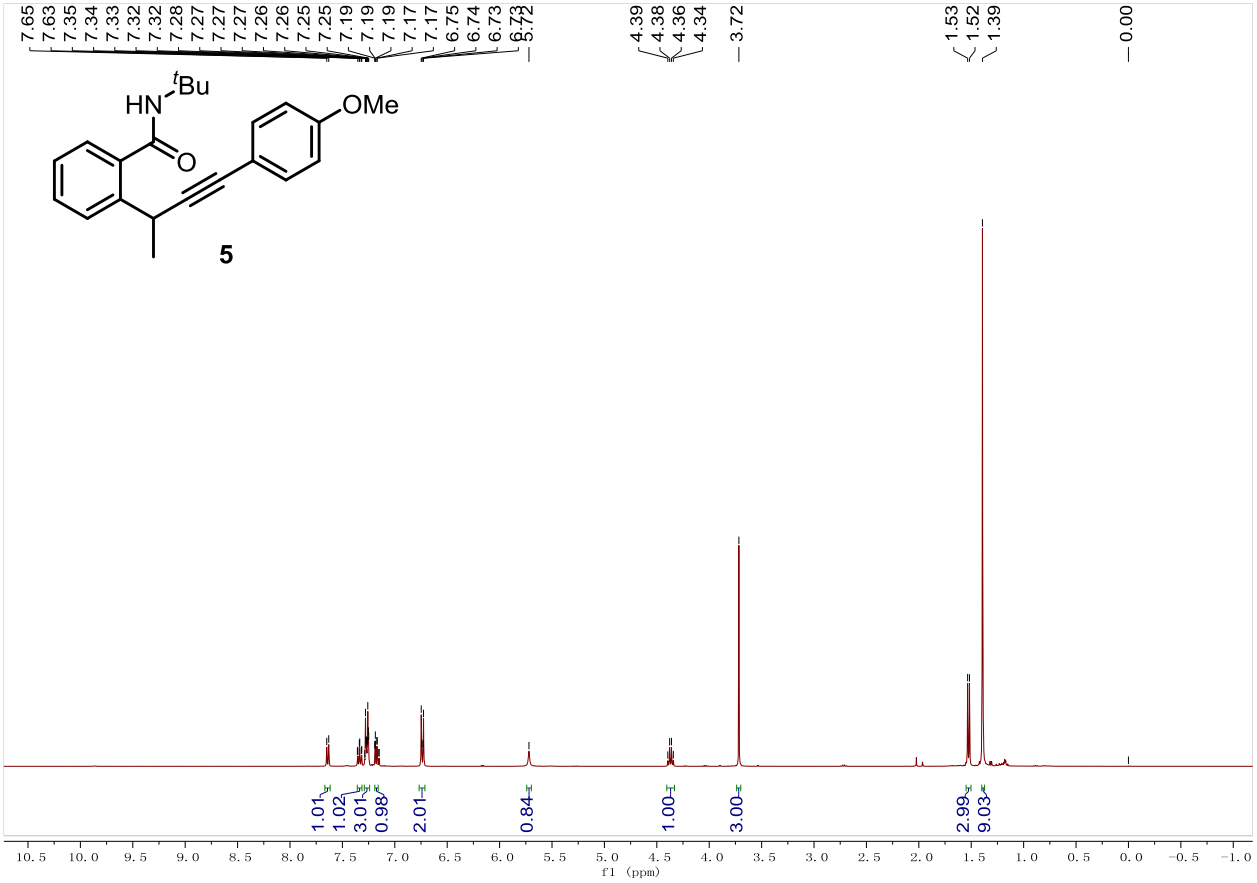
4q, ^{1}H NMR (400 MHz, CDCl$_3$)



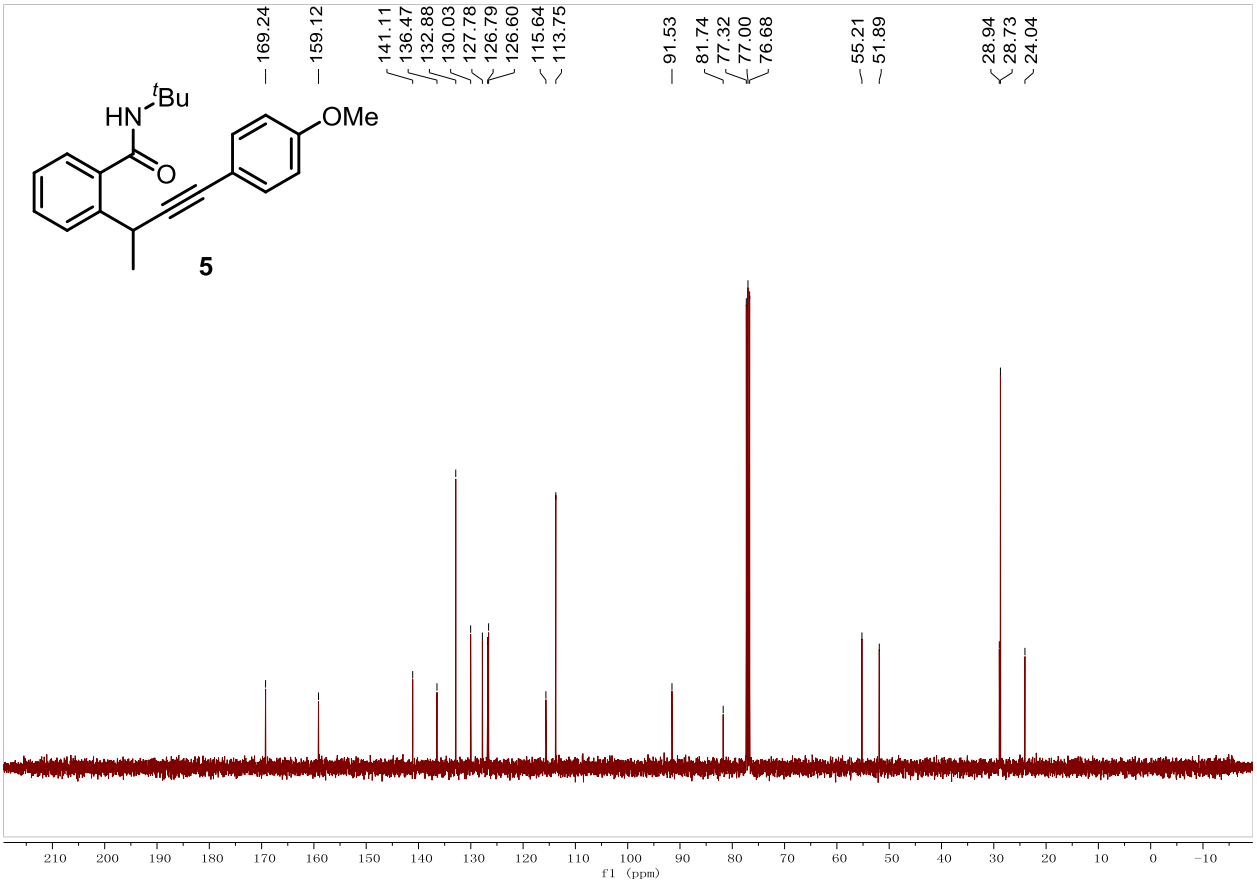
4q, ^{13}C NMR (101 MHz, $CDCl_3$)



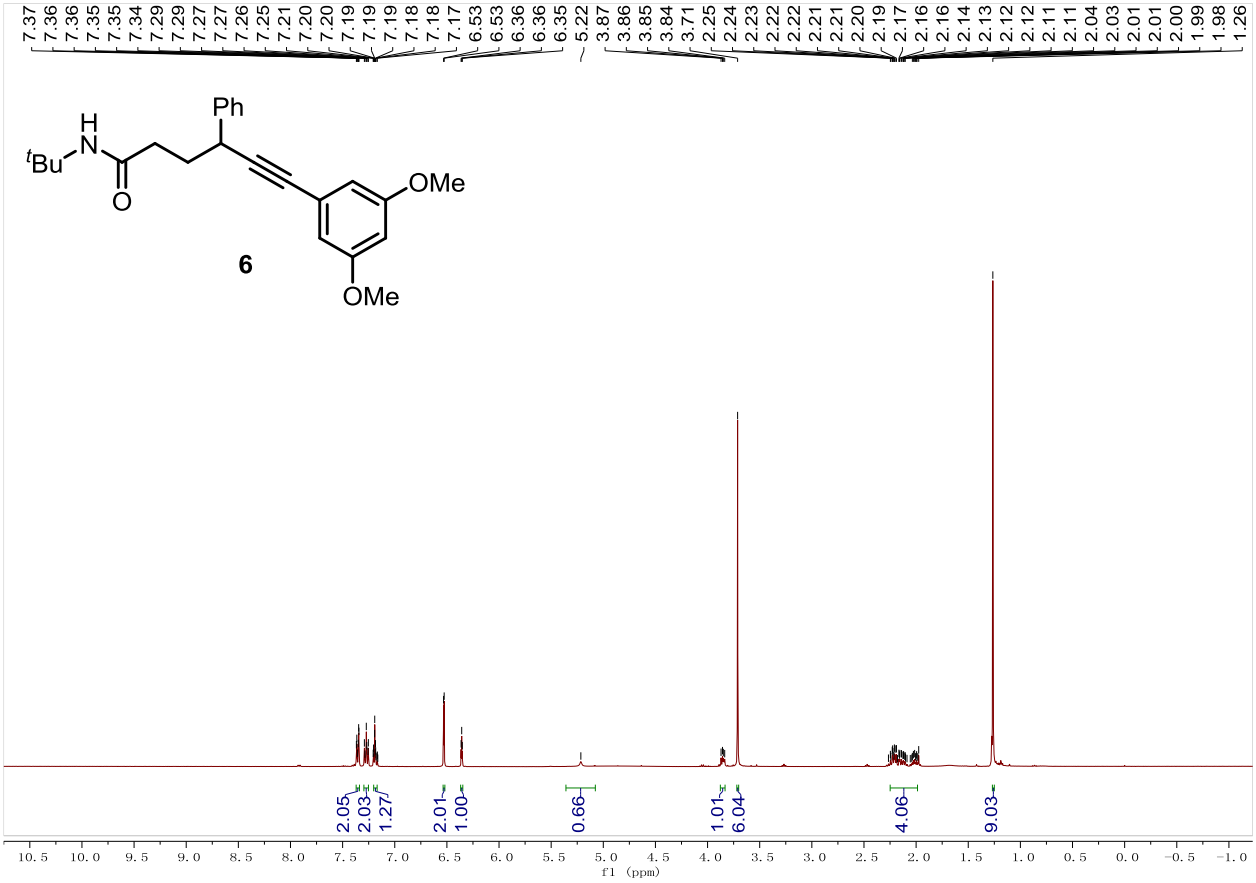
5, ^{1}H NMR (400 MHz, $CDCl_3$)



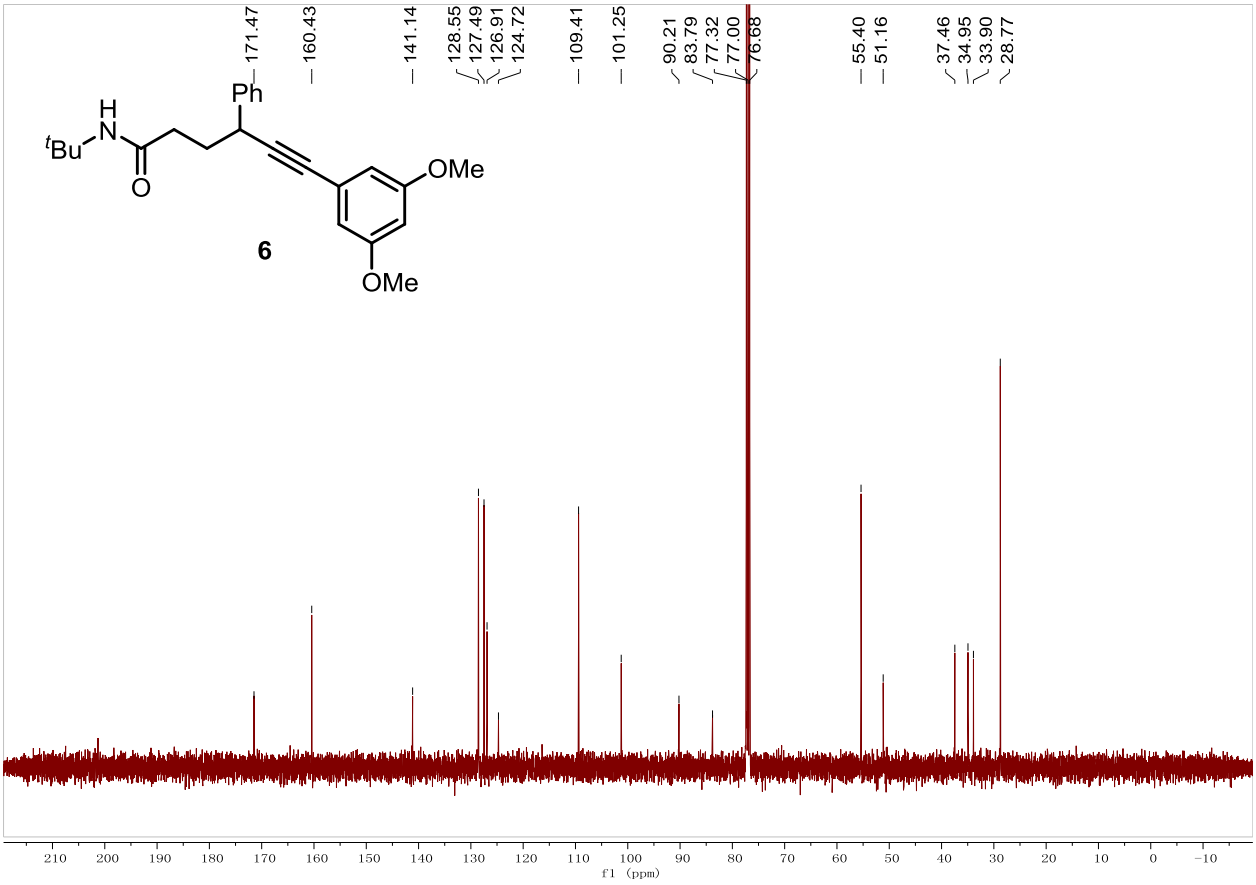
5, ^{13}C NMR (101 MHz, $CDCl_3$)



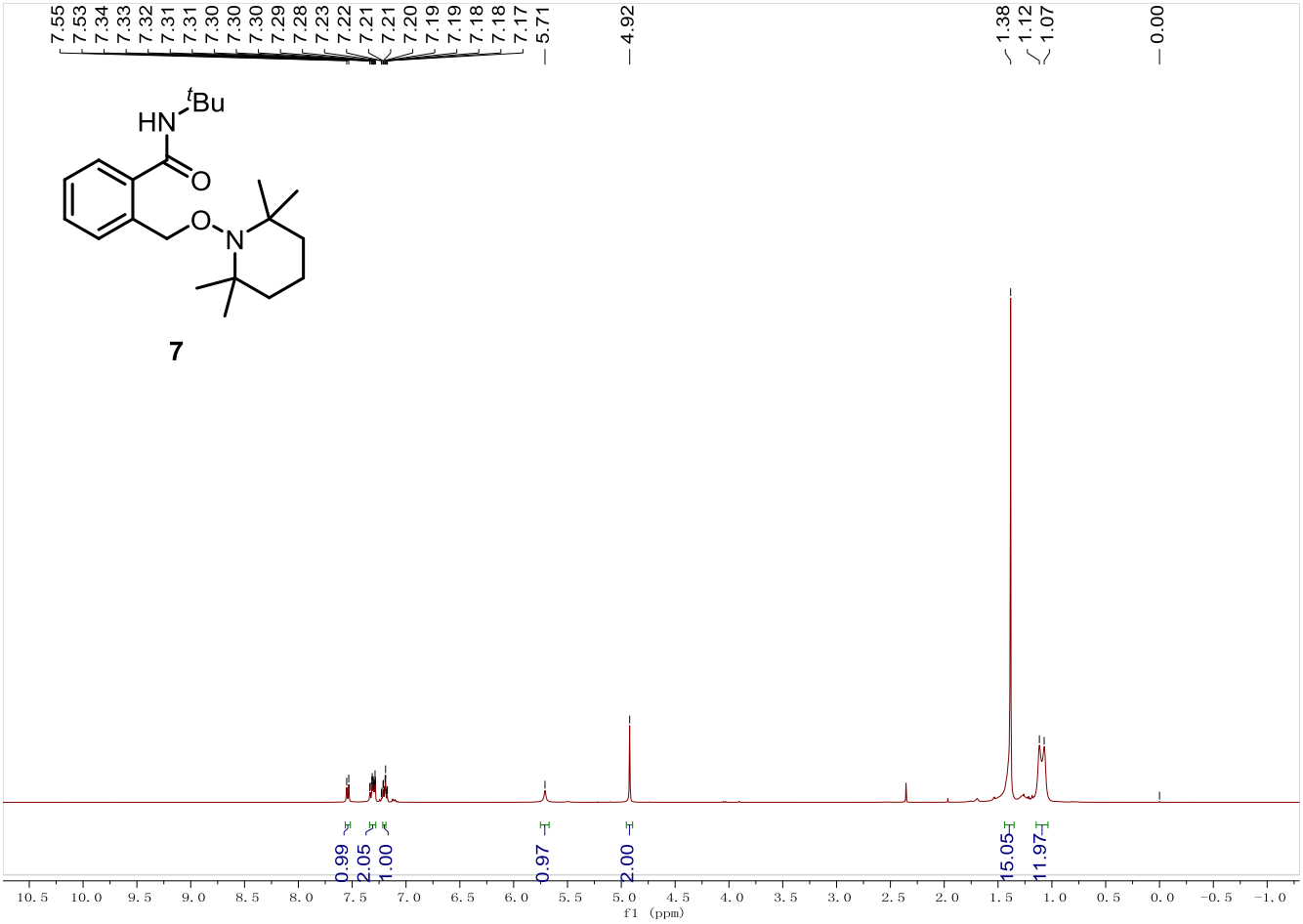
6, ^{1}H NMR (400 MHz, $CDCl_3$)



6, ^{13}C NMR (101 MHz, $CDCl_3$)

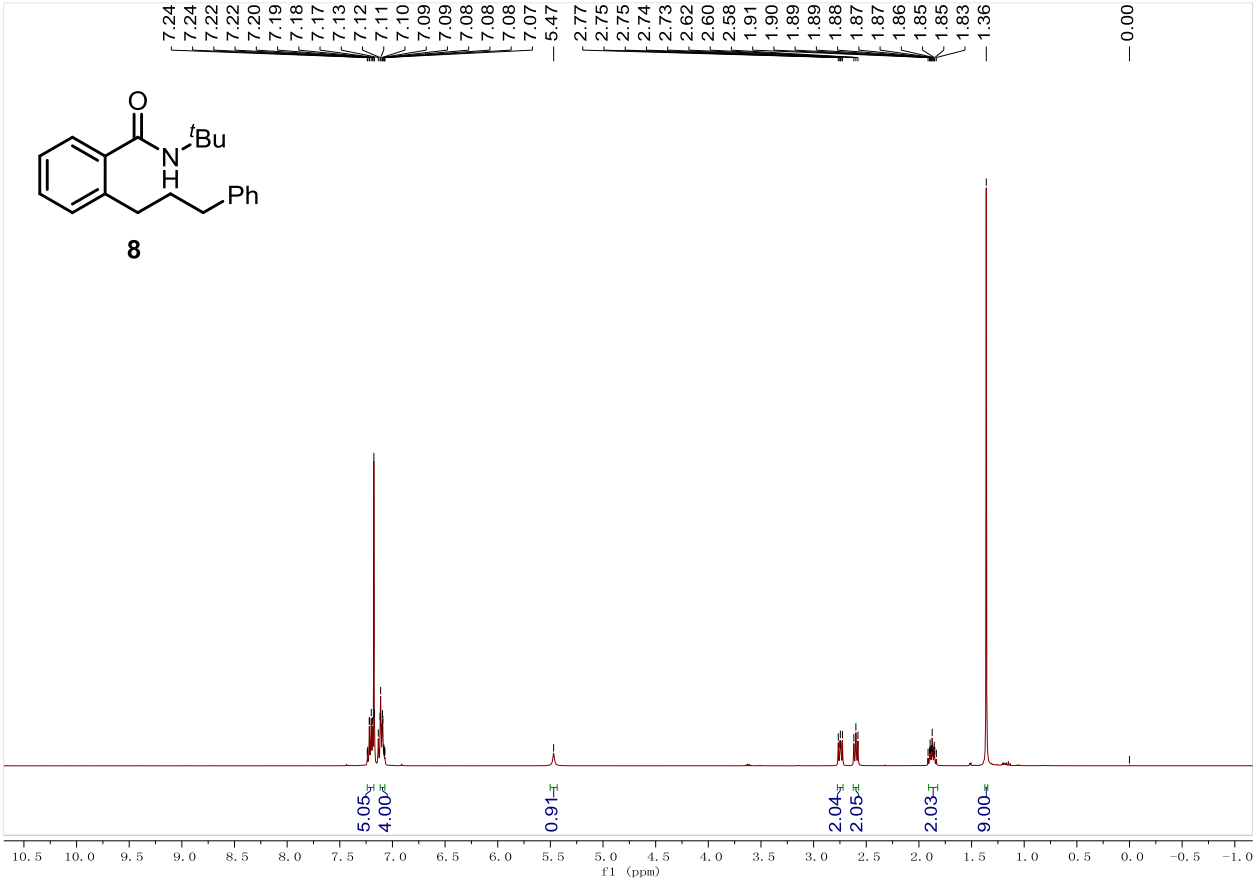


7, ^{1}H NMR (400 MHz, $CDCl_3$)

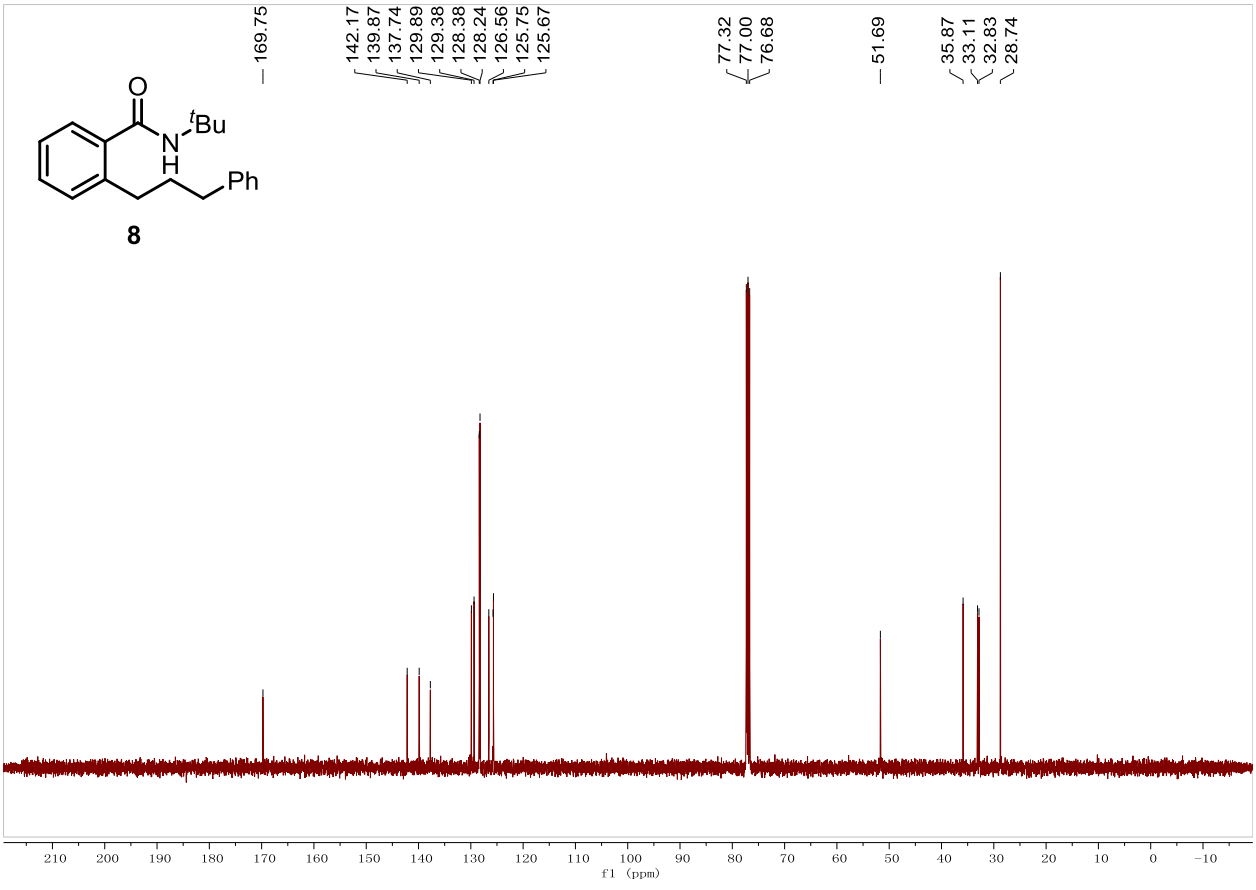

7.55
7.53
7.34
7.33
7.32
7.31
7.31
7.30
7.30
7.30
7.29
7.28
7.23
7.22
7.21
7.21
7.20
7.19
7.19
7.18
7.18
7.17
5.71
4.92
1.38
1.12
1.07
0.00
HN
tBu
O
O
N
0.99
2.05
1.00
0.97
2.00
15.05
11.97
f1 (ppm)

7

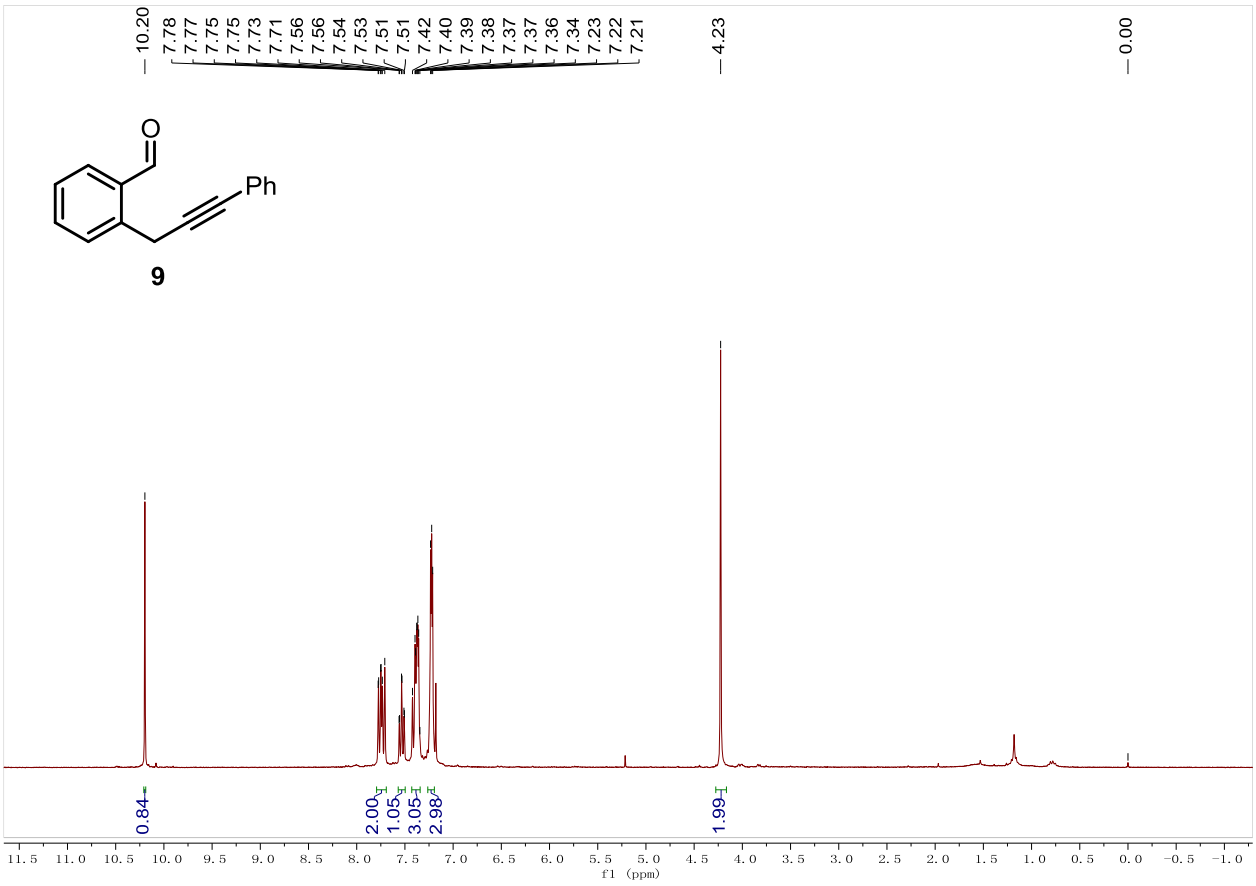
8, ^{1}H NMR (400 MHz, $CDCl_3$)



8, ^{13}C NMR (101 MHz, $CDCl_3$)



9, ^{1}H NMR (400 MHz, $CDCl_3$)



9, ^{13}C NMR (101 MHz, $CDCl_3$)