Supplementary Information (SI) for Organic Chemistry Frontiers.


# Bromotrifluoromethoxylation of Allenes: An Expedient Access to Allylic Trifluoromethoxy Derivatives

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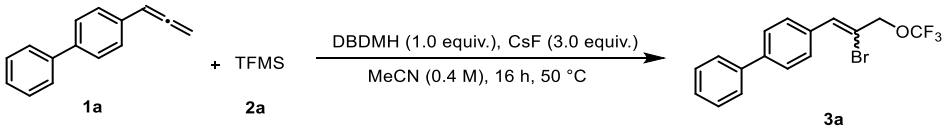
# 1 General Information

**Materials:** All purchased reagents were used without further purification unless otherwise stated., THF and toluene were distilled from sodium/benzophenone prior to use, DCE, $C_2H_5OC_2H_5$, DMC, $Et_2O$, $CH_3CN$, $CH_2Cl_2$ was distilled from $CaH_2$. Analytical thin layer chromatography was performed on 0.20 mm Qingdao Haiyang silica gel plates. Silica gel (200-300 mesh) (from Qingdao Haiyang Chem. Company, Ltd.) was used for flash chromatography.

**Methods:** $^1H$, $^{13}C$ and $^{19}F$ NMR spectra were recorded on Bruker AV 400 MHz instrument at 400 MHz ($^1H$ NMR), 100 MHz ($^{13}C$ NMR), and 376 MHz ($^{19}F$ NMR), or Bruker AV 600 MHz instrument at 600 MHz ($^1H$ NMR), 151 MHz ($^{13}C$ NMR). Chemical shifts were reported in ppm down field from internal $Me_4Si$ and external $CCl_3D$, respectively. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br (broad). Coupling constants were reported in Hertz (Hz). MS were recorded on a VG ZABHS spectrometer with the ESI resource. High resolution mass spectrometry (HRMS) spectra were obtained on a Bruker miorOTOF-QII instrument. Optical rotations were determined using an Autopol IV-T.

# 2 Condition Optimization

### Table S1. Initial Attempt[a]

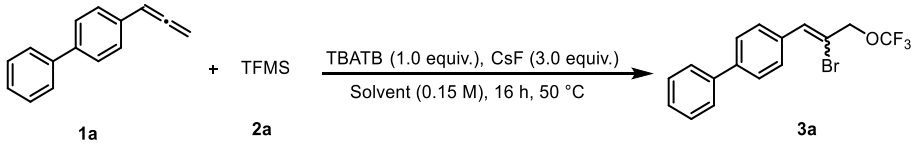



In a glove box, to a 2 mL of vial tube were added CsF (0.15 mmol, 3.0 equiv.), DBDMH (14.3 mg, 0.05 mmol, 1.0 equiv.), **1a** (9.62 mg, 0.05 mmol, 1.0 equiv.) in 0.125 mL $CH_3CN$, then TFMS (27.0 μL, 0.15 mmol, 3.0 equiv.) were added. The reaction mixture was stirred for 16 h at 50 °C. After cooling to room temperature, acetonitrile (1.0 mL) and benzotrifluoride (6.0 μL, 0.049 mmol) were added to the reaction mixture. The yield of **3a** was determined by comparing the integration of the $^{19}F$ NMR resonance (-60.0 ppm, -60.2 ppm) with that of benzotrifluoride (-62.8 ppm).

| Entry | Addition | Yield (%) (*E*/*Z*) [b] |
|---|---|---|
| 1 | $(DHQD)_2PHAL$ (10%)<br>AgF (0.3 equiv) | 24 (58:42) |
| 2 | AgF (0.3 equiv) | 23 (56:44) |
| 3 | / | 11 (63:37) |

[a] **1a** (0.05 mmol), TFMS (3.0 equiv.), DBDMH (1.0 equiv.), CsF (3.0 equiv.), $CH_3CN$ (0.125 ml), 50 °C, 16 h. [b]Determined by $^{19}F$ NMR spectrum with benzotrifluoride as internal standards. The *E*/*Z* value is provided in parenthesis.

### Table S2. Screening of the Solvent[a]



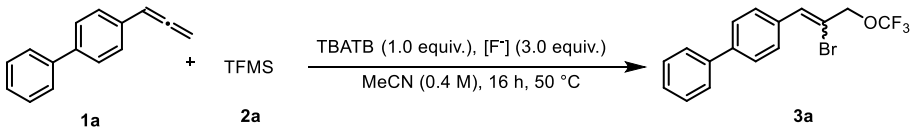

In a glove box, to a 2 mL of vial tube were added CsF (0.15 mmol, 3.0 equiv.), TBATB (24.1 mg, 0.05 mmol, 1.0 equiv.) and **1a** (9.62 mg, 0.05 mmol, 1.0 equiv.) in 0.125 mL solvent, then TFMS (27.0 μL, 0.150 mmol, 3.0 equiv) were added. The reaction mixture was stirred for 16 h at 50 °C. After cooling to

room temperature, acetonitrile (1.0 mL) and benzotrifluoride (6.0 μL, 0.049 mmol) were added to the reaction mixture. The yield of **3a** was determined by comparing the integration of the $^{19}F$ NMR resonance (-60.0 ppm, -60.2 ppm) with that of benzotrifluoride (-62.8 ppm).

| Entry | Solvent | Yield (%) (*E/Z*) [b] |
|---|---|---|
| 1 | MeCN | 86 (84:16) |
| 2 | DME | 12 (67: 33) |
| 3 | DCM | 31 (50:50) |
| 4 | DEA | N.D. |
| 5 | EtOAc | 12 (67:33) |
| 6 | DMC | 19 (63:37) |
| 7 | THF | 36 (63: 37) |
| 8 | 1,4-Dioxane | 29 (72:28) |
| 9 | Anisole | 29 (69:31) |
| 10 | Hexane | N.D. |
| 11 | Toluene | 30 (76:24) |

[a] **1a** (0.05 mmol), TFMS (3.0 equiv.), TBATB (1.0 equiv.), CsF (3.0 equiv.), $CH_3CN$ (0.125 ml), 50 ºC, 16 h. [b]Determined by $^{19}F$ NMR spectrum with benzotrifluoride as internal standards. The *E/Z* value is provided in parenthesis. N.D. = not detected.

## Table S3. Screening of the fluorine salts[a]

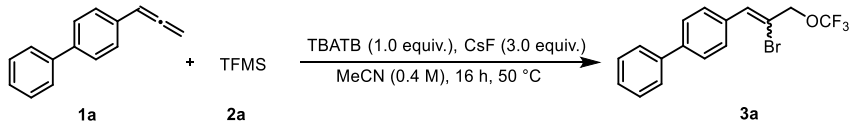



In a glove box, to a 2 mL of vial tube were added fluorine salts (0.15 mmol, 3.0 equiv.), TBATB (24.1 mg, 0.05 mmol, 1.0 equiv.), and **1a** (9.62 mg, 0.05 mmol, 1.0 equiv.) in 0.125 mL $CH_3CN$, then TFMS (27.0 μL, 0.15 mmol, 3.0 equiv.) were added. The reaction mixture was stirred for 16 h at 50 °C. After cooling to room temperature, acetonitrile (1.0 mL) and benzotrifluoride (6.00 μL, 0.049 mmol) were added to the reaction mixture. The yield of **3a** was determined by comparing the integration of the $^{19}F$ NMR resonance (-60.0 ppm, -60.2 ppm) with that of benzotrifluoride (-62.8 ppm).

| Entry | Fluorine salt | Yield (%) (*E/Z*) [b] |
|---|---|---|
| 1 | NaF | N.D. |
| 2 | KF | 63 (78:22) |
| 3 | CsF | 86 (84:16) |
| 4 | AgF | 27 (52:48) |
| 5 | $CaF_2$ | N.D. |
| 6 | ZnF2 | N.D. |
| 7 | CsF (2.0 equiv) | 60 (75:25) |
| 8 | CsF (4.0 equiv) | 77 (82:18) |
| 9 | CsF (5.0 equiv) | 52 (68:32) |

[a] **1a** (0.05 mmol), TFMS (3.0 equiv.), TBATB (1.0 equiv.), $CH_3CN$ (0.125 ml), 50 ºC, 16 h. [b]Determined by $^{19}F$ NMR spectrum with benzotrifluoride as internal standards. The *E/Z* value is provided in parenthesis. N.D. = not detected.

## Table S4. Screening of the "$OCF_3$" equivalent[a]

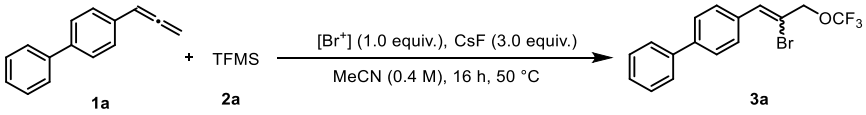



In a glove box, to a 2 mL of vial tube were added CsF (0.15 mmol, 3.0 equiv.), TBATB (24.1 mg, 0.05 mmol, 1.0 equiv.) and **1a** (9.62 mg, 0.05 mmol, 1.0 equiv.) in 0.125 mL $CH_3CN$, then TFMS were added. The reaction mixture was stirred for 16 h at 50 °C. After cooling to room temperature, acetonitrile (1.0 mL) and benzotrifluoride (6.0 μL, 0.049 mmol) were added to the reaction mixture. The yield of **3a** was determined by comparing the integration of the $^{19}F$ NMR resonance (-60.0 ppm, -60.2 ppm) with that of benzotrifluoride (-62.8 ppm).

| Entry | [TFMS] | Yield (%) (*E*/*Z*) [b] |
|---|---|---|
| 1 | 1.0 | 7 (85:15) |
| 2 | 2.0 | 58 (77:23) |
| 3 | 3.0 | 86 (84:16) |
| 4 | 4.0 | 84 (76:24) |
| 5 | 5.0 | 87 (73:27) |
| 6 | 6.0 | 76 (76:24) |

[a] **1a** (0.05 mmol), TFMS (3.0 equiv.), TBATB (1.0 equiv.), $CH_3CN$ (0.125 ml), 50 °C, 16 h. [b]Determined by $^{19}F$ NMR spectrum with benzotrifluoride as internal standards. The *E/Z* value is provided in parenthesis. N.D. = not detected.

## Table S5. Screening of the Bromine reagent[a]



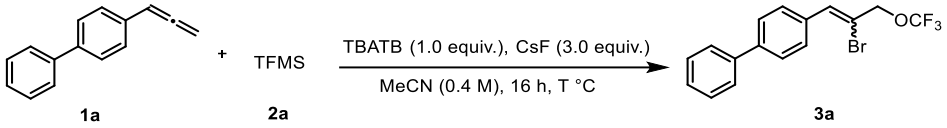

In a glove box, to a 2 mL of vial tube were added CsF (0.15 mmol, 3.0 equiv.), bromine reagent (0.05 mmol, 1.0 equiv.) and **1a** (9.62 mg, 0.05 mmol, 1.0 equiv.) in 0.125 mL $CH_3CN$, then TFMS (27.0 μL, 0.15 mmol, 3.0 equiv.) were added. The reaction mixture was stirred for 16 h at 50 °C. After cooling to room temperature, acetonitrile (1.0 mL) and benzotrifluoride (6.0 μL, 0.049 mmol) were added to the reaction mixture. The yield of **3a** was determined by comparing the integration of the $^{19}F$ NMR resonance (-60.0 ppm, -60.2 ppm) with that of benzotrifluoride (-62.8 ppm).

| Entry | $Br^+$ reagent | Yield (%) (*E*/*Z*) [b] |
|---|---|---|
| 1 | NBS | 16 (56:44) |
| 2 | DBDMH | 11 (63:37) |
| 3 | TBCA | 1 |
| 4 | PHBP | N.D. |
| 5 | TBATB (1.0 eq) | 86 (84:16) |
| 6 | TBCO | N.D. |
| 7 | N-Bromosaccharin | 2 (50:50) |
| 8 | 5,5-Dibromo-2,2-dimethyl-4,6-dioxo-1,3-dioxane | 5 (60:40) |
| 9 | TBATB (1.5 eq) | 82 (80:20) |
| 10 | TBATB (2.0 eq) | 80 (76:24) |

[a] **1a** (0.05 mmol), TFMS (3.0 equiv.), [$Br^+$] (1.0 equiv.), $CH_3CN$ (0.125 ml), 50 °C, 16 h. [b]Determined by $^{19}F$ NMR spectrum with benzotrifluoride as internal standards. The *E/Z* value is provided in parenthesis.

N.D. = not detected.

**Table S6. Screening of the temperature**



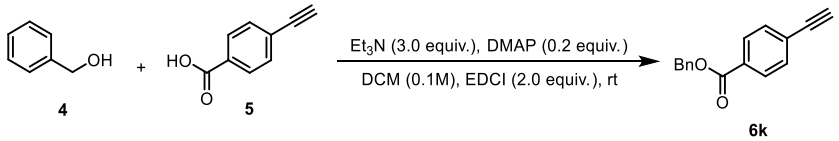

In a glove box, to a 2 mL of vial tube were added CsF (0.15 mmol, 3.0 equiv.), TBATB (24.1 mg, 0.05 mmol, 1.0 equiv.) and **1a** (9.62 mg, 0.05 mmol, 1.0 equiv.) in 0.125 mL $CH_3CN$, then TFMS (27.0 μL, 0.15 mmol, 3.0 equiv.) were added. The reaction mixture was stirred for 16 h at different temperature. After cooling to room temperature, acetonitrile (1.0 mL) and benzotrifluoride (6.0 μL, 0.049 mmol) were added to the reaction mixture. The yield of **3a** was determined by comparing the integration of the $^{19}F$ NMR resonance (-60.0 ppm, -60.2 ppm) with that of benzotrifluoride (-62.8 ppm).

| Entry | Temperature | Yield (%) (*E*/*Z*) [b] |
|---|---|---|
| 1 | rt | 66 (84:16) |
| 2 | 40 | 74 (80:20) |
| 3 | 50 | 84 (82:18) |
| 4 | 60 | 78 (77:23) |
| 5 | 70 | 72 (58: 42) |

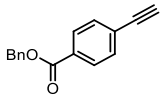
[a] **1a** (0.05 mmol), TFMS (3.0 equiv.), [$Br^+$] (1.0 equiv.), $CH_3CN$ (0.125 ml), 50 °C, 16 h. [b]Determined by $^{19}F$ NMR spectrum with benzotrifluoride as internal standards. The *E*/*Z* value is provided in parenthesis. N.D. = not detected.

# 3 Synthesis of Substrates

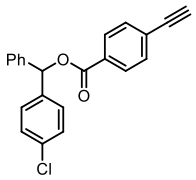
## 3.1 Typical Procedure for the Preparation of compound 6k-6s [1]:



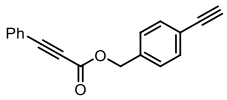

To a solution of **5** (10.0 mmol, 1.0 equiv.), DMAP (2.0 mmol, 0.2 equiv.), $Et_3N$ (30.0 mmol, 3.0 equiv.), and $CH_2Cl_2$ (100.0 mL) at room temperature were added EDCI (1-ethyl-(3-(3-dimethylamino) propyl)-carbodiimide hydrochloride) (20.0 mmol, 2.0 equiv.) and **4** (12.0 mmol, 1.2 equiv.). The reaction mixture was stirred at room temperature for 6 h before quenched with $H_2O$ (30.0 mL) and extracted 3 times with $CH_2Cl_2$ (30.0 mL). The combined organic layer was dried over $Na_2SO_4$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel to give the target compound **6k**.



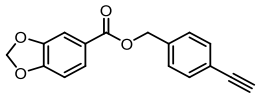

**benzyl 4-ethynylbenzoate (6k):** The reaction was carried out on 10 mmol scale. The compound **6k** was obtained in 70% yield (1.7 g) as a yellow oil after flash column chromatography (hexane/EtOAc = 30/1); **$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 7.9 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 5.37 (s, 2H), 3.23 (s, 1H); **$^{13}$C NMR** (151 MHz, Chloroform-*d*) δ 165.9, 135.9, 132.2, 130.3, 129.7, 128.8, 128.5, 128.4, 127.0, 82.9, 80.3, 67.1; **HRMS-**ESI (m/z): Calc'd for $C_{16}H_{13}O_2$ $[M+H]^+$ 237.0910, found 237.0913.



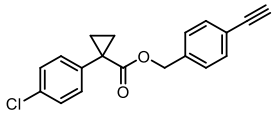
**(4-chlorophenyl) (phenyl)methyl 4-ethynylbenzoate (6l):** The reaction was carried out on 10 mmol scale. The compound **6l** was obtained in 72% yield (2.5 g) as a white solid after flash column chromatography (hexane/EtOAc = 10/1); m.p.: 69.8 °C; **$^1$H NMR** (400 MHz, Chloroform-d) δ 8.08 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.43 – 7.30 (m, 9H), 7.07 (s, 1H), 3.25 (s, 1H); **$^{13}$C NMR** (101 MHz, Chloroform-d) δ 165.0, 139.7, 138.8, 134.1, 132.3, 130.1, 129.8, 129.0, 128.9, 128.7, 128.4, 127.3, 127.2, 82.9, 80.5, 77.2; **HRMS-**ESI (m/z): Calc'd for $C_{22}H_{15}ClNaO_2$ $[M+Na]^+$ 369.0653, found 369.0657.



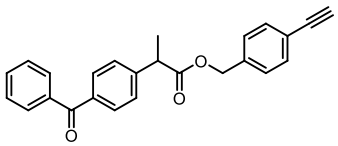
**4-ethynylbenzyl 3-phenylpropiolate (6m):** The reaction was carried out on 15 mmol scale. The compound **6m** was obtained in 72% yield (2.8 g) as a yellow oil after flash column chromatography (hexane/EtOAc = 10/1) ; **$^1$H NMR** (600 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.7 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.1 Hz, 4H), 5.25 (s, 2H), 3.10 (s, 1H); **$^{13}$C NMR** (151 MHz, Chloroform-*d*) δ 153.9, 135.7, 133.2, 132.5, 130.9, 128.7, 128.5, 122.5, 119.6, 87.2, 83.3, 80.4, 78.0, 67.2; **HRMS-**ESI (m/z): Calc'd for $C_{18}H_{12}O_2Na$ $[M+Na]^+$ 283.0730, found 283.0732.



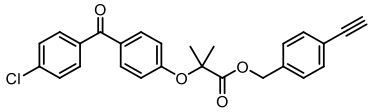
**4-ethynylbenzyl benzo[d] [1,3] dioxole-5-carboxylate (6o):** The reaction was carried out on 20 mmol scale. The compound **6o** was obtained in 80% yield (4.5 g) as a yellow solid after flash column chromatography (hexane/EtOAc = 10/1); m.p.: 59.6 °C; **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.68 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 3H), 7.38 (d, *J* = 7.9 Hz, 2H), 6.83 (dd, *J* = 8.2, 1.0 Hz, 1H), 6.03 (d, *J* = 1.3 Hz, 2H), 5.31 (s, 2H), 3.09 (s, 1H); **$^{13}$C NMR** (101 MHz, Chloroform-d) δ 165.8, 151.9, 147.9, 137.0, 132.4, 128.0, 125.7, 124.0, 122.1, 109.7, 108.1, 102.0, 83.4, 77.8, 66.2; **HRMS-**ESI (m/z): Calc'd for $C_{17}H_{13}O_4$ $[M+H]^+$ 281.0808, found 281.0807.



**4-ethynylbenzyl 1-(4-chlorophenyl) cyclopropane-1-carboxylate (6q):** The reaction was carried out on 14 mmol scale. The compound **6q** was obtained in 45% yield (2.0 g) as a yellow solid after flash column chromatography (hexane/EtOAc = 10/1); m.p.: 67.2 °C; **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.27 (s, 4H), 7.13 (d, *J* = 8.8 Hz, 2H), 5.05 (s, 2H), 3.06 (s, 1H), 1.69 – 1.56 (m, 2H), 1.24 – 1.10 (m, 2H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 173.8, 137.9, 136.8, 133.1, 132.3, 132.0, 128.4, 127.4, 121.8, 83.3, 77.7, 66.1, 28.6, 16.9; **HRMS-**ESI (m/z): Calc'd for $C_{19}H_{16}ClO_2$ $[M+H]^+$ 311.0833, found 311.0838.

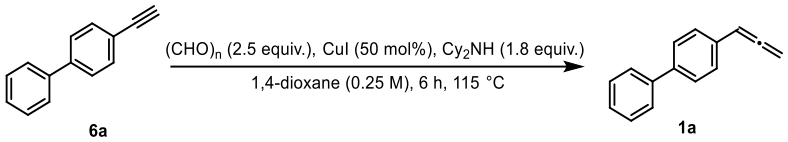


**4-ethynylbenzyl 2-(4-benzoylphenyl) propanoate (6r):** The reaction was carried out on 20 mmol scale. The compound **6r** was obtained in 92% yield (6.8 g) as a yellow oil after flash column chromatography (hexane/EtOAc = 10/1) ; **$^1$H NMR** (400 MHz, Chloroform-d) δ 7.81 – 7.73 (m, 3H), 7.68 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.54 – 7.50 (m, 1H), 7.49 – 7.39 (m, 5H), 7.18 (d, *J* = 8.1 Hz, 2H), 5.10 (s, 2H), 3.85 (q, *J* = 7.2 Hz, 1H), 3.07 (s, 1H), 1.55 (d, *J* = 7.2 Hz, 3H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 196.5, 173.8, 140.7, 138.1, 137.6, 136.6, 132.6, 132.4, 131.6, 130.1, 129.3, 129.2, 128.7, 128.4, 127.8, 122.1, 83.3, 77.8, 66.1, 45.5, 18.4; **HRMS-**ESI (m/z): Calc'd for $C_{25}H_{20}NaO_3$ $[M+Na]^+$ 391.1305, found 391.1310.

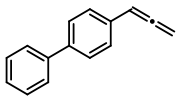


**4-ethynylbenzyl 2-(4-(4-chlorobenzoyl) phenoxy)-2-methylpropanoate (6s):** The reaction was carried out on 12 mmol scale. The compound **6s** was obtained in 83% yield (4.3 g) as a white solid after flash column chromatography (hexane/EtOAc = 10/1); m.p.: 72.5 °C; **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.64 (t, *J* = 8.3 Hz, 4H), 7.45 – 7.35 (m, 4H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 8.8 Hz, 2H), 5.16 (s, 2H), 3.08 (s, 1H), 1.66 (s, 6H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 194.0, 173.3, 159.4, 138.3, 136.3, 135.7, 132.2, 132.0, 131.1, 130.4, 128.5, 128.3, 122.3, 117.2, 83.0, 79.4, 78.1, 66.7, 25.4; **HRMS-**ESI (m/z): Calc'd for $C_{26}H_{22}ClO_4$ $[M+H]^+$ 433.1201, found 433.1199.

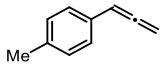
## 3.2 Typical Procedure for the Preparation of Allene synthesis 1a-1t [2,3]:



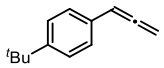

According to a modified literature procedure, to a pressure tube was added CuI (50 mol%), $(CH_2O)_n$ (2.5 equiv.), dioxane (0.50 M), alkyne (1.0 equiv.), and amine (1.8 equiv.) sequentially under Ar. The reaction mixture was heated to 115 °C and stirred 6 h. The reaction was quenched with $H_2O$ and extracted with DCM. The separated organic layers were dried over $Na_2SO_4$, and the solvents were removed in vacuo. The crude product was purified by column chromatography on silica gel to provide the target compounds **1a-1v**.



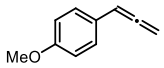
**4-(propa-1,2-dien-1-yl)-1,1'-biphenyl (1a):** The reaction was carried out on 10 mmol scale. The compound **1a** was obtained in 81% yield (1.6 g) as a white solid after flash column chromatography (hexane); m.p.: 59.6 °C; **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.70 – 7.58 (m, 4H), 7.54 – 7.36 (m, 5H), 6.28 (t, *J* = 6.8 Hz, 1H), 5.25 (d, *J* = 6.8 Hz, 2H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 210.1, 140.9, 139.8, 133.1, 128.9, 127.4, 127.3, 127.2, 127.0, 93.8, 79.0.



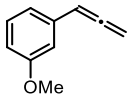
**1-methyl-4-(propa-1,2-dien-1-yl) benzene (1b):** The reaction was carried out on 10 mmol scale. The compound **1c** was obtained in 87% yield (1.1 g) as a colorless liquid after flash column chromatography (hexane); **$^1$H NMR** (400 MHz, Chloroform-d) δ 7.14 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 8.7 Hz, 2H), 6.04 (t, *J* = 6.8 Hz, 1H), 5.04 (d, *J* = 6.8 Hz, 2H), 3.71 (s, 3H).



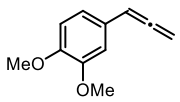
**1-(tert-butyl)-4-(propa-1,2-dien-1-yl) benzene (1c):** The reaction was carried out on 8.9 mmol scale. The compound **1c** was obtained in 92% yield (1.4 g) as a yellow oil after flash column chromatography (hexane); **$^1$H NMR** (400 MHz, Chloroform-d) δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 6.19 (t, *J* = 6.8 Hz, 1H), 5.16 (d, *J* = 6.8 Hz, 2H), 1.35 (s, 9H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 209.9, 150.1, 131.1, 126.5, 125.7, 93.7, 78.7, 34.7, 31.5.



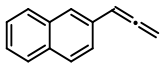
**1-methoxy-4-(propa-1,2-dien-1-yl) benzene (1d):** The reaction was carried out on 20 mmol scale. The compound **1d** was obtained in 58% yield (1.7 g) as a yellow liquid after flash column chromatography (hexane); **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.23 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.14 (t, *J* = 6.8 Hz, 1H), 5.13 (d, *J* = 6.8 Hz, 2H), 3.81 (s, 3H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 209.5, 158.8, 127.9, 126.2, 114.3, 93.5, 78.9, 55.4.



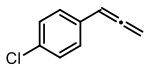
**1-methoxy-3-(propa-1,2-dien-1-yl) benzene (1e):** The reaction was carried out on 20 mmol scale. The compound **1e** was obtained in 78% yield (2.3 g) as a yellow liquid after flash column chromatography (hexane/EtOAc = 50/1); **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.18 – 7.10 (m, 1H), 6.84 – 6.74 (m, 2H), 6.67 (d, *J* = 8.1 Hz, 1H), 6.06 (t, *J* = 7.8 Hz, 1H), 5.07 (d, *J* = 6.8 Hz, 2H), 3.72 (s, 3H); **$^{13}$C NMR** (101 MHz, Chloroform-d) δ 210.0, 160.0, 135.5, 129.7, 119.5, 112.9, 112.0, 94.1, 79.0, 55.3.



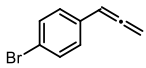
**1,2-dimethoxy-4-(propa-1,2-dien-1-yl) benzene (1f):** The reaction was carried out on 10 mmol scale. The compound **1f** was obtained in 68% yield (1.2 g) as a yellow oil after flash column chromatography (hexane/EtOAc = 60/1); **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 6.86 (s, 1H), 6.81 (d, *J* = 1.1 Hz, 2H), 6.12 (t, *J* = 6.8 Hz, 1H), 5.14 (d, *J* = 6.8 Hz, 2H), 3.88 (d, *J* = 4.5 Hz, 6H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 209.5, 149.3, 148.4, 126.6, 119.4, 111.4, 109.4, 93.9, 79.1, 56.1, 55.9.



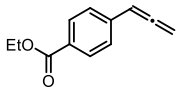
**2-(propa-1,2-dien-1-yl) naphthalene (1g):** The reaction was carried out on 6 mmol scale. The compound **1g** was obtained in 79% yield (777.8 mg) as a yellow solid after flash column chromatography (hexane/EtOAc = 30/1); m.p.: 60.2 ℃; **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.83 – 7.74 (m, 3H), 7.66 (s, 1H), 7.54 – 7.38 (m, 3H), 6.34 (t, *J* = 6.7 Hz, 1H), 5.23 (d, *J* = 7.1 Hz, 2H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 210.5, 133.8, 132.7, 131.6, 128.4, 127.9, 127.8, 126.4, 125.8, 125.5, 124.8, 94.5, 79.3.



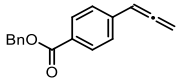
**1-chloro-4-(propa-1,2-dien-1-yl) benzene (1h):** The reaction was carried out on 20 mmol scale. The compound **1h** was obtained in 50% yield (1.5 g) as a yellow liquid after flash column chromatography (hexane); **$^1$H NMR** (400 MHz, Chloroform-d) δ 7.28 (d, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 2H), 6.13 (t, *J* = 6.8 Hz, 1H), 5.17 (d, *J* = 6.8 Hz, 2H); **$^{13}$C NMR** (75 MHz, CDCl3) δ 209.7, 132.4, 132.4, 128.6, 127.8, 93.0, 79.1.



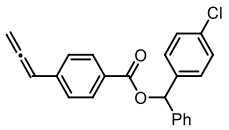
**1-bromo-4-(propa-1,2-dien-1-yl) benzene (1i):** The reaction was carried out on 11.1 mmol scale. The compound **1i** was obtained in 68% yield (1.5 g) as a yellow liquid after flash column chromatography (hexane); **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 2H), 6.11 (t, *J* = 6.8 Hz, 1H), 5.15 (d, *J* = 6.8 Hz, 2H); $^{13}$C NMR (126 MHz, CDCl3) δ 210.5, 133.7, 132.4, 128.9, 121.2, 93.9, 80.0.



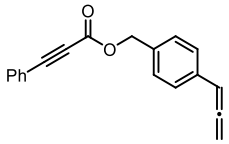
**ethyl 4-(propa-1,2-dien-1-yl) benzoate (1j):** The reaction was carried out on 6.3 mmol scale. The compound **1j** was obtained in 67% yield (794.8 mg) as a yellow oil after flash column chromatography (hexane/EtOAc = 100/1); **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 6.17 (t, *J* = 6.7 Hz, 1H), 5.18 (d, *J* = 6.8 Hz, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H); **$^{13}$C NMR** (101 MHz, Chloroform-d) δ 210.6, 166.4, 138.9, 129.9, 128.8, 126.5, 93.7, 79.2, 60.9, 14.4.



**benzyl 4-(propa-1,2-dien-1-yl) benzoate (1k):** The reaction was carried out on 7.2 mmol scale. The compound **1k** was obtained in 68% yield (1.2 mg) as a yellow oil after flash column chromatography (hexane/EtOAc = 30/1); **$^1$H NMR** (600 MHz, Chloroform-d) δ 7.91 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 3H), 6.09 (t, *J* = 6.8 Hz, 1H), 5.26 (s, 2H), 5.10 (d, *J* = 6.8 Hz, 2H); **$^{13}$C NMR** (151 MHz, Chloroform-*d*) δ 210.8, 166.3, 139.3, 136.2, 130.2, 128.7, 128.5, 128.3, 128.2, 126.6, 93.7, 79.3, 66.7; **HRMS-**ESI (m/z): Calc'd for $C_{17}H_{15}O_2$ $[M+H]^+$ 251.1067, found 251.1071.

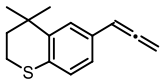


**(4-chlorophenyl) (phenyl)methyl 4-(propa-1,2-dien-1-yl) benzoate (1l):** The reaction was carried out on 7.2 mmol scale. The compound **1l** was obtained in 85% yield (2.2 g) as a white solid after flash column chromatography (hexane/EtOAc = 40/1); m.p.: 65.3 ℃; **$^1$H NMR** (400 MHz, Chloroform-d) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.38 – 7.32 (m, 6H), 7.32 – 7.27 (m, 3H), 7.10 (s, 1H), 6.17 (t, *J* = 6.8 Hz, 1H), 5.17 (d, *J* = 6.8 Hz, 2H); **$^{13}$C NMR** (101 MHz, Chloroform-d) δ 210.7, 165.2, 139.9, 139.5, 138.9, 133.8, 130.1, 128.7, 128.7, 128.5, 128.2, 128.1, 127.1, 126.7, 93.6, 79.3, 76.6; **HRMS-**ESI (m/z): Calc'd for $C_{23}H_{17}ClNaO_2$ $[M+Na]^+$ 383.0809, found 383.0815.

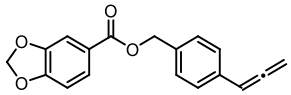


**4-(propa-1,2-dien-1-yl) benzyl 3-phenylpropiolate (1m):** The reaction was carried out on 10.8 mmol scale. The compound **1m** was obtained in 84% yield (2.5 g) as a yellow oil after flash column chromatography (hexane/EtOAc = 30/1); **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.39 – 7.30 (m, 6H), 6.18 (t, *J* = 6.8 Hz, 1H), 5.24 (s, 2H), 5.17 (d, *J* = 6.7 Hz,

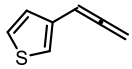
2H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 210.1, 153.9, 134.6, 133.5, 133.1, 130.8, 129.1, 128.6, 127.0, 119.6, 93.6, 86.8, 80.6, 79.0, 67.6; **HRMS-**ESI (m/z): Calc'd for $C_{19}H_{14}O_2Na$ $[M+Na]^+$ 297.0886, found 297.0895.



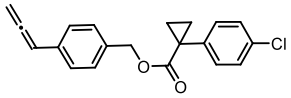
**4,4-dimethyl-6-(propa-1,2-dien-1-yl) thiochromane (1n):** The reaction was carried out on 10 mmol scale. The compound **1n** was obtained in 87% yield (1.9 g) as a yellow oil after flash column chromatography (hexane); **$^1$H NMR** (400 MHz, Chloroform-d) δ 7.25 (s, 1H), 7.06 – 6.93 (m, 2H), 6.09 (t, *J* = 6.8 Hz, 1H), 5.12 (d, *J* = 6.8 Hz, 2H), 3.07 – 2.95 (m, 2H), 1.97 – 1.90 (m, 2H), 1.32 (s, 6H); **$^{13}$C NMR** (151 MHz, Chloroform-*d*) δ 209.6, 142.2, 130.5, 129.6, 126.9, 124.9, 124.5, 94.0, 79.0, 37.7, 33.1, 30.2, 23.2; **HRMS-**ESI (m/z): Calc'd for $C_{14}H_{17}S$ $[M+H]^+$ 217.1045, found 217.1047.



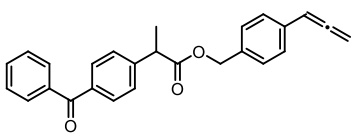
**4-(propa-1,2-dien-1-yl) benzyl benzo[d] [1,3] dioxole-5-carboxylate (1o):** The reaction was carried out on 16.1 mmol scale. The compound **1o** was obtained in 65% yield (3.1 g) as a yellow solid after flash column chromatography (hexane/EtOAc = 30/1); m.p.: 59.7 ℃; **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.59 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.40 (d, *J* = 1.7 Hz, 1H), 7.31 – 7.20 (m, 4H), 6.74 (d, *J* = 8.2 Hz, 1H), 6.09 (t, *J* = 6.8 Hz, 1H), 5.94 (s, 2H), 5.21 (s, 2H), 5.07 (d, *J* = 6.8 Hz, 2H); **$^{13}$C NMR** (151 MHz, Chloroform-*d*) δ 210.1, 165.9, 151.8, 147.8, 134.8, 134.2, 128.7, 127.0, 125.6, 124.2, 109.7, 108.1, 101.9, 93.7, 79.1, 66.6; **HRMS-**ESI (m/z): Calc'd for $C_{18}H_{14}NaO_4$ $[M+Na]^+$ 317.0784, found 317.0786.



**3-(propa-1,2-dien-1-yl) thiophene (1p):** The reaction was carried out on 20 mmol scale. The compound **1x** was obtained in 87% yield (2.2 g) as a yellow liquid after flash column chromatography (hexane); **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.29 – 7.29 (m, 1H), 7.13 – 7.06 (m, 2H), 6.25 (t, *J* = 6.8 Hz, 1H), 5.10 (d, *J* = 6.5 Hz, 2H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*)) δ 210.4, 135.2, 126.4, 126.0, 120.9, 88.7, 78.2; **HRMS-**ESI (m/z): Calc'd for $C_7H_7S^+$ $[M+H]^+$ 123.0263, found 123.0267.

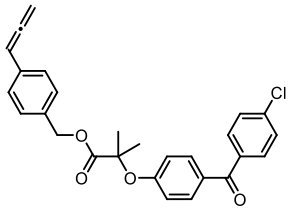


**4-(propa-1,2-dien-1-yl) benzyl 1-(4-chlorophenyl) cyclopropane-1-carboxylate (1q):** The reaction was carried out on 6.4 mmol scale. The compound **1q** was obtained in 73% yield (1.5 g) as a yellow oil after flash column chromatography (hexane/EtOAc = 40/1); **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.13 (s, 4H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.00 (t, *J* = 6.8 Hz, 1H), 5.00 (d, *J* = 6.8 Hz, 2H), 4.92 (s, 2H), 1.50 (q, *J* = 4.0 Hz, 2H), 1.02 (q, *J* = 4.0 Hz, 2H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 209.9, 173.7, 137.9, 134.6, 133.8, 133.0, 131.9, 128.3, 128.0, 126.7, 93.6, 78.9, 66.4, 28.6, 16.7; **HRMS-**ESI (m/z): Calc'd for $C_{20}H_{17}ClNaO_2$ $[M+Na]^+$ 347.0809, found 347.0808.

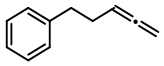


**4-(propa-1,2-dien-1-yl) benzyl 2-(4-benzoylphenyl) propanoate (1r):** The reaction was carried out on 18.5 mmol scale. The compound **1r** was obtained in 55% yield (3.9 g) as a yellow oil after flash

column chromatography (hexane/EtOAc = 30/1); **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.80 – 7.72 (m, 3H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.50 – 7.39 (m, 3H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 6.13 (t, *J* = 6.8 Hz, 1H), 5.14 (d, *J* = 6.8 Hz, 2H), 5.08 (d, *J* = 3.7 Hz, 2H), 3.84 (q, *J* = 7.2 Hz, 1H), 1.57 – 1.51 (m, 3H); **$^{13}$C NMR** (101 MHz, Chloroform-d) δ 210.1, 196.6, 173.9, 140.8, 138.0, 137.6, 134.5, 134.1, 132.6, 131.7, 130.2, 129.4, 129.1, 128.7, 128.5, 128.4, 126.9, 93.7, 79.1, 66.6, 45.5, 18.5; **HRMS-**ESI (m/z): Calc'd for $C_{26}H_{22}NaO_3$ $[M+Na]^+$ 405.1461, found 405.1464.



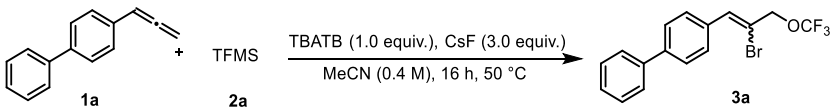

**4-(propa-1,2-dien-1-yl) benzyl 2-(4-(4-chlorobenzoyl) phenoxy)-2-methylpropanoate (1s):** The reaction was carried out on 9.9 mmol scale. The compound **1s** was obtained in 72% yield (3.2 g) as a yellow solid after flash column chromatography (hexane/EtOAc = 10/1); m.p.: 76.7 °C; **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.62 – 7.58 (m, 2H), 7.57 – 7.53 (m, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.15 – 7.08 (m, 4H), 6.68 (d, *J* = 8.9 Hz, 2H), 6.02 (t, *J* = 6.8 Hz, 1H), 5.09 (s, 2H), 5.04 (d, *J* = 6.8 Hz, 2H), 1.59 (s, 6H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 210.1, 194.3, 173.6, 159.6, 138.5, 136.5, 134.5, 133.7, 132.1, 131.3, 130.4, 129.0, 128.6, 126.9, 117.3, 93.6, 79.5, 79.1, 67.3, 29.8, 25.5; **HRMS-**ESI (m/z): Calc'd for $C_{27}H_{24}ClO_4$ $[M+H]^+$ 447.1358, found 447.1359.



**penta-3,4-dien-1-ylbenzene (1t):** The reaction was carried out on 15 mmol scale. The compound **1t** was obtained in 92% yield (2.0 g) as a colorless liquid after flash column chromatography (hexane); **$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.29 - 7.26 (m, 2H), 7.22 - 7.16 (m, 3H), 5.18 – 5.11 (m 1H), 4.72 – 4.62 (m, 2H), 2.78 – 2.68 (m, 2H), 2.37 – 2.25 (m, 2H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 208.7, 141.9, 128.6, 128.4, 126.0, 89.6, 75.3, 35.5, 30.1; **HRMS-**ESI (m/z): Calc'd for $C_{11}H_{12}Na$ $[M+Na]^+$ 167.0831, found 167.0833.

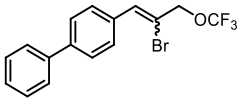
**1u** [4], **1v** [5], **1w** [5], **1x** [2,3] were synthesized according to the relevant literature.

## 3.3 Typical Procedure for the Preparation of Allenylic Trifluoromethoxylation 3a-3t



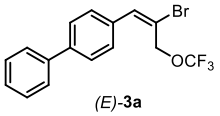

In a glove box, to a 2.0 mL sealed tube were added in sequence CsF (91.1 mg, 0.6 mmol, 3.0 equiv.), TBATB (96.4 mg, 0.2 mmol, 1.0 equiv.), 0.5 mL $CH_3CN$, **1a** (38.5 mg, 0.2 mmol, 1.0 equiv.) and TFMS (108 μl, 0.6 mmol, 3.0 equiv.). The mixture was stirred at 50 ºC for 16 h. After cooling to room temperature, the reaction mixture was concentrated in vacuo. The residue was then added 3 mL $CH_2Cl_2$ and filtered. The organic layer was concentrated in vacuo. The residue was purified by preparative TLC. (**Note**: It's difficult to obtain pure spectra, we only get pure NMR spectrum of one configuration including *Z*-**3e**, *E*-**3j**, *E*-**3l**, *E*-**3p,** *E*-**3s**. We can obtain both pure NMR spectra of two configurations of

the other compounds.)



**3a**, 86%
*E/Z* = 84:16

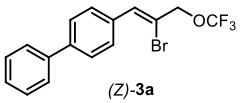
**4-(2-bromo-3-(trifluoromethoxy) prop-1-en-1-yl)-1,1'-biphenyl (3a):** The reaction was carried out on 0.2 mmol scale. The compound ***E*-3a** was obtained in 72% yield (47.2 mg) as yellow oil and ***Z*-3a** (9.5 mg, 14%) as yellow oil after purified by preparative TLC (*n*-hexane).



*(E)*-**3a**

$\mathbf{R}_f$ = 0.6 (*n*-hexane)

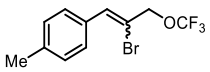
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.63 (t, *J* = 8.1 Hz, 4H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 6.5 Hz, 2H), 7.34 (s, 1H), 7.32 (s, 1H), 4.85 (s, 2H); **$^{13}$C NMR** (151 MHz, Chloroform-*d*) δ 141.6, 140.2, 139.5, 133.8, 129.1, 128.8, 127.9, 127.6, 127.2, 121.7 (q, *J* = 256.7 Hz),118.3, 68.3 (q, *J* = 3.6 Hz); **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -60.2 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{16}H_{12}BrNaF_3O$ $[M+Na]^+$ 378.9916, found 378.9909.



*(Z)*-**3a**

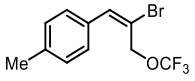
$\mathbf{R}_f$ = 0.6 (*n*-hexane)

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.66 – 7.59 (m, 4H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.17 (s, 1H), 4.77 (s, 2H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 141.8, 140.5, 133.3, 131.7, 129.8, 129.0, 127.8, 127.2, 127.1, 121.7 (q, *J* = 258.6 Hz), 116.6, 72.8 (q, *J* = 3.0 Hz); **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -60.2 (s, 3F) ; **HRMS-ESI (m/z):** Calc'd for $C_{16}H_{12}BrNaF_3O$ $[M+Na]^+$ 378.9916, found 378.9924.



**3b**, 79%
*E/Z* = 81:19

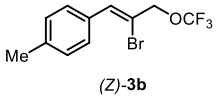
**1-(2-bromo-3-(trifluoromethoxy) prop-1-en-1-yl)-4-methylbenzene (3b):** The reaction was carried out on 0.2 mmol scale. The compound ***E*-3b** was obtained in 65% yield (38.4 mg) as yellow oil and ***Z*-3b** (8.3 mg, 14%) as yellow oil after purified by preparative TLC (*n*-hexane).



*(E)*-**3b**

$\mathbf{R}_f$ = 0.5 (*n*-hexane)

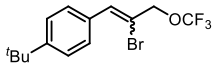
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.32 (s, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 4.78 (s, 2H), 2.36 (s, 3H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 139.9, 138.9, 132.1, 129.7, 128.2, 121.6 (q, *J* = 256.7 Hz), 117.7, 68.3 (q, *J* = 3.6 Hz), 21.4; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -60.3 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{11}H_{11}BrF_3O$ $[M+H]^+$ 294.9940, found 294.9945.



*(Z)*-**3b**

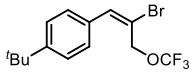
$\mathbf{R}_f$ = 0.5 (*n*-hexane)

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.09 (s, 1H), 4.74 (s, 2H), 2.37 (s, 3H); **$^{13}$C NMR** (151 MHz, Chloroform-*d*) δ 139.2, 132.2, 131.5, 129.2, 129.2, 121.6 (q, *J* = 256.7 Hz), 115.7, 72.9 (q, *J* = 3.7 Hz), 21.5; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -60.2 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{11}H_{11}BrF_3O$ $[M+H]^+$ 294.9940, found 294.9932..




**3c**, 79%
*E*/*Z* = 75:25

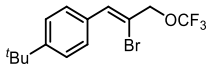
**1-(2-bromo-3-(trifluoromethoxy) prop-1-en-1-yl)-4-(tert-butyl) benzene (3c):** The reaction was carried out on 0.2 mmol scale. The compound ***E*-3c** was obtained in 60% yield (40.5 mg) as yellow oil and ***Z*-3c** (12.8 mg, 19%) as yellow oil after purified by preparative TLC (*n*-hexane).




*(E)*-**3c**

$\mathbf{R}_f$ = 0.5 (*n*-hexane)

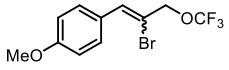
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.33 (s, 1H), 7.18 (d, *J* = 8.3 Hz, 2H), 4.81 (s, 2H), 1.34 (s, 9H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 152.1, 139.8, 132.1, 128.1,121.7(q, *J* = 258.6 Hz), 117.7, 68.4 (q, *J* = 3.7 Hz), 34.9, 31.3; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -60.2 (s, 3F) ; **HRMS-**ESI (m/z): Calc'd for $C_{14}H_{17}BrF_3O$ $[M+H]^+$ 337.0409, found 337.0412.




*(Z)*-**3c**

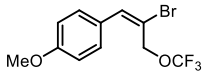
$\mathbf{R}_f$ = 0.5 (*n*-hexane)

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.44 – 7.39 (m, 2H), 7.10 (s, 1H), 4.74 (s, 2H), 1.33 (s, 9H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 152.3, 132.1, 131.4, 129.1, 125.4, 121.6 (q, *J* = 257.6 Hz), 115.7, 73.0 (q, *J* = 3.6 Hz), 34.9, 31.3; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -60.2 (s, 3F) ; **HRMS-**ESI (m/z): Calc'd for $C_{14}H_{17}BrF_3O$ $[M+H]^+$ 337.0409, found 337.0412.




**3d**, 79%
*Z*/*E* = 80:20

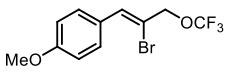
**1-(2-bromo-3-(trifluoromethoxy) prop-1-en-1-yl)-4-methoxybenzene (3d):** The reaction was carried out on 0.2 mmol scale. The compound ***Z*-3d** was obtained in 64% yield (40.4 mg) as colorless oil and ***E*-3d** (9.3 mg, 15%) as colorless oil after purified by preparative TLC (*n*-hexane).




*(E)*-**3d**

$\mathbf{R}_f$ = 0.6 (*n*-hexane)

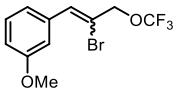
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.29 (s, 1H), 7.17 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 4.78 (s, 2H), 3.83 (s, 3H); **$^{13}$C NMR** (151 MHz, Chloroform-*d*) δ 160.0, 139.6, 135.3, 129.7, 127.4, 121.6 (q, *J* = 258.2 Hz), 120.8, 116.6, 114.4, 68.4 (q, *J* = 3.8 Hz), 55.5. **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -60.3 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{11}H_{10}BrF_3NaO_2$ $[M+H]^+$ 332.9708, found 332.9703.



*(Z)*-**3d**

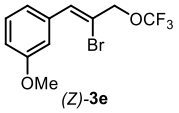
$\mathbf{R}_f$ = 0.6 (*n*-hexane)

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.8 Hz, 2H), 7.05 (s, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 4.74 (s, 2H), 3.84 (s, 3H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 160.2, 132.0, 130.9, 126.7, 121.6 (q, *J* = 256.8 Hz), 114.4, 113.9, 73.3 (q, *J* = 3.5 Hz), 55.4; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -60.1 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{11}H_{10}BrF_3NaO_2$ $[M+H]^+$ 332.9708, found 332.9703.



**3e**, 62%
*Z*/*E* = 88:12

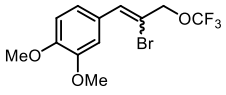
**1-(2-bromo-3-(trifluoromethoxy) prop-1-en-1-yl)-3-methoxybenzene (3e):** The reaction was carried out on 0.2 mmol scale. The compound ***Z*-3e** was obtained in 62% yield (38.6 mg) as yellow oil after purified by preparative TLC (*n*-hexane/EtOAc 100:1 (v/v)).



*(Z)*-**3e**

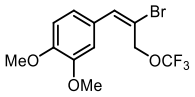
$\mathbf{R}_f$ = 0.6 (*n*-hexane/EtOAc 100:1 (v/v))

**$^1$H NMR** (400 MHz, Chloroform-d) δ 7.31 (d, *J* = 7.9 Hz, 1H), 7.24 (t, *J* = 2.1 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.11 (s, 1H), 6.93 – 6.89 (m, 1H), 4.74 (d, *J* = 1.1 Hz, 2H), 3.83 (s, 3H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 159.5, 135.6, 131.9, 129.5, 121.9, 121.6 (q, *J* = 256.9 Hz),116.9, 114.8, 114.4, 72.6 (q, *J* = 3.4 Hz), 55.4; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -60.3 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{11}H_{10}BrF_3NaO_2$ $[M+H]^+$ 332.9708, found 332.9703.



**3f**, 82%
*Z*/*E* = 80:20

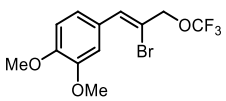
**4-(2-bromo-3-(trifluoromethoxy) prop-1-en-1-yl)-1,2-dimethoxybenzene (3f):** The reaction was carried out on 0.2 mmol scale. The compound ***Z*-3f** was obtained in 66% yield (45.0 mg) as yellow solid and ***E*-3f** (10.9 mg, 16%) as yellow solid after purified by preparative TLC (*n*-hexane/EtOAc 50:1 (v/v)).



*(E)*-**3f**

$\mathbf{R}_f$ = 0.5 (*n*-hexane/EtOAc 50:1 (v/v))

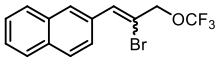
**$^1$H NMR** (400 MHz, Chloroform-d) δ 7.30 (s, 1H), 6.89-6.87 (m, 1H), 6.82-6.80 (m, 1H), 6.78-6.77 (m, 1H), 4.81 (s, 2H), 3.90 (s, 3H), 3.87 (s, 3H); **$^{13}$C NMR** (151 MHz, Chloroform-*d*) δ 149.6, 149.2, 140.0, 127.7, 121.6 (q, *J* = 257.2 Hz), 121.2, 116.7, 111.3, 111.1, 68.7 (q, *J* = 4.2 Hz), 56.1, 55.9; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -60.3 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{12}H_{13}BrF_3O_3$ $[M+H]^+$ 340.9995, found 340.9996; m.p.: 71.2 ℃.



*(Z)*-**3f**

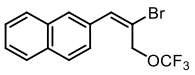
$\mathbf{R}_f$ = 0.5 (*n*-hexane/EtOAc 50:1 (v/v))

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 2.1 Hz, 1H), 7.23-7.20 (m, 1H), 7.04 (s, 1H), 6.89-6.86 (m, 1H), 4.73 (s, 2H), 3.90 (m, 6H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 149.8, 148.7, 132.1, 126.9, 123.0, 121.6 (q, *J* = 256.5 Hz), 114.4, 112.0, 110.9, 73.2 (q, *J* = 3.5 Hz), 56.0, 56.0; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -59.4 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{12}H_{13}BrF_3O_3$ $[M+H]^+$ 340.9995, found 340.9996; m.p.: 70.8 ℃.




**3g**, 82%
*E*/*Z* =83:17

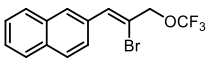
**2-(2-bromo-3-(trifluoromethoxy) prop-1-en-1-yl) naphthalene (3g):** The reaction was carried out on 0.2 mmol scale. The compound ***E*-3g** was obtained in 68% yield (45.0 mg) as white solid and ***Z*-3g** (9.3 mg, 14%) as yellow oil after purified by preparative TLC (*n*-hexane/EtOAc 100:1 (v/v)).




*(E)*-**3g**

$\mathbf{R}_f$ = 0.6 (*n*-hexane/EtOAc 50:1 (v/v))

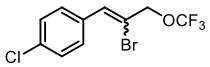
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.90 – 7.82 (m, 3H), 7.72 (s, 1H), 7.58 – 7.49 (m, 3H), 7.34-7.32 (m, 1H), 4.85 (s, 2H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 139.9, 133.3, 133.1, 132.3, 128.8, 128.4, 127.9, 127.7, 127.1, 127.0, 125.7, 121.7 (q, *J* = 257.1 Hz), 118.6, 68.4 (q, *J* = 3.5 Hz); **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -59.8 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{14}H_{10}BrF_3NaO$ $[M+Na]^+$ 352.9759, found 352.9754; m.p.: 78.3 ℃.




*(Z)*-**3g**

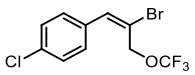
$\mathbf{R}_f$ = 0.6 (*n*-hexane/EtOAc 50:1 (v/v))

**$^1$H NMR** (400 MHz, Chloroform-d) δ 8.14 (s, 1H), 7.88 – 7.83 (m, 3H), 7.77-7.75 (m, 1H), 7.54 – 7.49 (m, 2H), 7.29 (s, 1H), 4.80 (s, 2H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 133.4, 133.1, 132.1, 131.8, 129.1, 128.5, 128.0, 127.8, 127.0, 126.6, 126.4, 121.6 (q, *J* = 256.8 Hz), 116.9, 72.7 (q, *J* = 3.3 Hz); **$^{19}$F NMR** (376 MHz, DMSO-$d_6$) δ -60.3 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{14}H_{10}BrF_3NaO$ $[M+Na]^+$ 352.9759, found 352.9754.




**3h**, 80%
*E*/*Z* = 90:10

**1-(2-bromo-3-(trifluoromethoxy) prop-1-en-1-yl)-4-chlorobenzene (3h):** The reaction was carried out on 0.2 mmol scale. The compound ***E*-3h** was obtained in 72% yield (45.4 mg) as colorless oil and ***Z*-3h** (5.1 mg, 8%) as colorless oil after purified by preparative TLC (*n*-hexane).

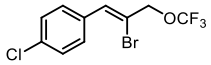



*(E)*-**3h**

$\mathbf{R}_f$ = 0.5 (*n*-hexane)

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.30 (s, 1H), 7.17 (d, *J* = 8.1 Hz, 2H), 4.73 (s, 2H); **$^{13}$C NMR** (151 MHz, Chloroform-*d*) δ 138.6, 134.9, 133.3, 129.6, 129.3, 121.6 (q, *J* = 257.1 Hz), 119.0, 68.0 (q, *J* = 3.8 Hz); **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -60.4 (s, 3F); **HRMS-**ESI (m/z):

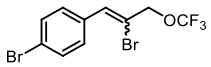
Calc'd for $C_{10}H_8ClF_3O$ $[M+H]^+$ 314.9394, found 314.9386.



*(Z)*-**3h**

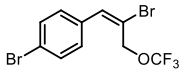
$\mathbf{R}_f$ = 0.5 (*n*-hexane)

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.08 (s, 1H), 4.73 (s, 2H); **$^{13}$C NMR** (151 MHz, Chloroform-*d*) δ 134.8, 132.8, 130.6, 130.5, 128.7, 121.6 (q, *J* = 256.6 Hz), 117.5, 72.3 (q, *J* = 3.7 Hz); **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -60.6 (s, 3F); **HRMS**-ESI (m/z): Calc'd for $C_{10}H_8ClF_3O$ $[M+H]^+$ 314.9394, found 314.9386.



**3i**, 82%
*E*/*Z* = 89:11

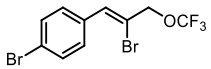
1-bromo-4-(2-bromo-3-(trifluoromethoxy) prop-1-en-1-yl) benzene **(3i):** The reaction was carried out on 0.2 mmol scale. The compound ***E*-3i** was obtained in 73% yield (52.6 mg) as colorless oil and ***Z*-3i** (6.5mg, 9%) as colorless oil after purified by preparative TLC (*n*-hexane).



(*E*)-**3i**

$\mathbf{R}_f$ = 0.5 (*n*-hexane)

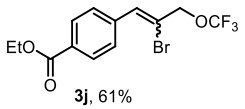
$^1$**H NMR** (400 MHz, Chloroform-d) δ 7.53 (d, J = 8.4 Hz, 1H), 7.27 (s, 1H), 7.10 (d, J = 8.2 Hz, 1H), 4.74 (s, 1H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 138.6, 133.7, 132.2, 129.8, 123.1, 121.6 (d, *J* = 257.0 Hz), 119.0, 68.0 (q, *J* = 3.6 Hz); **$^{19}$F NMR** (376 MHz, Chloroform-d) δ -59.2 (s, 3F); **HRMS**-ESI (m/z): Calc'd for $C_{10}H_7Br_2F_3NaO$ $[M+Na]^+$ 380.8708, found380.8706.



*(Z)*-**3i**

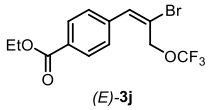
$\mathbf{R}_f$ = 0.5 (*n*-hexane)

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 7.51 (s, 4H), 7.07 (s, 1H), 4.73 (s, 2H); **$^{13}$C NMR** (151 MHz, Chloroform-*d*) δ 133.2, 131.7, 130.7, 130.7, 123.1, 121.6 (q, *J* = 256.7 Hz), 117.6, 72.3 (q, *J* = 3.6 Hz); **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -59.1 (s, 3F); **HRMS**-ESI (m/z): Calc'd for $C_{10}H_7Br_2F_3NaO$ $[M+Na]^+$ 380.8708, found380.8706.



**3j**, 61%
*E*/*Z* = 90:10

**ethyl 4-(2-bromo-3-(trifluoromethoxy) prop-1-en-1-yl) benzoate (3j):** The reaction was carried out on 0.2 mmol scale. The compound ***E*-3j** was obtained in 61% yield (43.1 mg) as yellow solid after purified by preparative TLC (*n*-hexane/EtOAc 30:1 (v/v)).

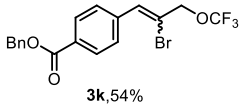


*(E)*-**3j**

$\mathbf{R}_f$ = 0.5 (*n*-hexane/EtOAc 30:1 (v/v))

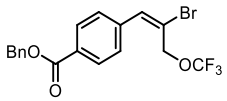
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.19 – 8.11 (m, 2H), 7.45 (s, 1H), 7.41 – 7.35 (m, 2H), 4.83 (s,

2H), 4.51 – 4.42 (m, 3H), 1.48 (t, *J* = 6.6 Hz, 3H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 166.0, 139.0, 138.8, 130.6, 130.2, 128.2, 121.5 (q, *J* = 257.6 Hz), 120.1, 67.8 (q, *J* = 3.8 Hz), 61.3, 14.4; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -60.4 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{13}H_{13}BrF_3O_3$ $[M+H]^+$ 352.9995, found 352.9997; m.p.: 79.4 ℃.




**3k**,54%
*E*/*Z* =91:9

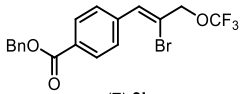
**benzyl 4-(2-bromo-3-(trifluoromethoxy) prop-1-en-1-yl) benzoate (3k):** The reaction was carried out on 0.2 mmol scale. The compound ***E*-3k** was obtained in 49% yield (40.7 mg) as white solid and ***Z*-3k** (4.2 mg, 5%) as white solid after purified by preparative TLC (*n*-hexane/EtOAc 30:1 (v/v)).




*(E)*-**3k**

$\mathbf{R}_f$ = 0.5 (*n*-hexane/EtOAc 30:1 (v/v))

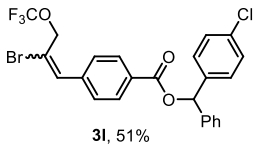
**$^1$H NMR** (400 MHz, Chloroform-d) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.36 (m, 2H), 7.34 – 7.27 (m, 4H), 7.22 (s, 1H), 7.20 (s, 1H), 5.29 (s, 2H), 4.66 (s, 2H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 165.9, 139.3, 138.7, 135.9, 130.4, 128.8, 128.5, 128.4, 128.3, 120.2, 67.9 (q, *J* = 3.7 Hz), 67.1; **$^{19}$F NMR** (376 MHz, DMSO-$d_6$) δ -60.3 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{21}H_{17}BrClF_3NaO_3$ $[M+Na]^+$ 510.9894, found 510.9886; m.p.: 81.8 ℃.




*(Z)*-**3k**

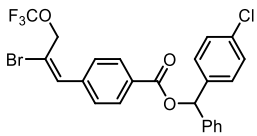
$\mathbf{R}_f$ = 0.6 (*n*-hexane/EtOAc 30:1 (v/v))

**$^1$H NMR** (400 MHz, Chloroform-d) δ 8.09 (d, J = 8.4 Hz, 2H), 7.69-7.67 (m, 2H), 7.46 – 7.44 (m, 2H), 7.42 – 7.33 (m, 3H), 7.18 (s, 1H), 5.37 (s, 2H), 4.75 (s, 2H); **$^{13}$C NMR** (101 MHz, Chloroform-d) δ 166.1, 139.0, 136.0, 130.6, 130.2, 129.8, 129.1, 128.8, 128.5, 128.4, 121.5 (q, *J* = 257.6 Hz), 119.0, 72.0 (q, *J* = 3.6 Hz), 67.0; **$^{19}$F NMR** (376 MHz, DMSO-$d_6$) δ -60.2 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{21}H_{17}BrClF_3NaO_3$ $[M+Na]^+$ 510.9894, found 510.9886; m.p.: 80.3 ℃.




**3l**, 51%
*E*/*Z* =91:9

**(4-chlorophenyl) (phenyl)methyl 4-(2-bromo-3-(trifluoromethoxy) prop-1-en-1-yl) benzoate (3l):** The reaction was carried out on 0.2 mmol scale. The compound ***E*-3l** was obtained in 51% yield (52.3 mg) as yellow oil after purified by preparative TLC (*n*-hexane/EtOAc 20:1 (v/v)).

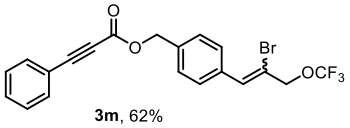



*(E)*-**3l**

$\mathbf{R}_f$ = 0.5 (*n*-hexane/EtOAc 20:1 (v/v))

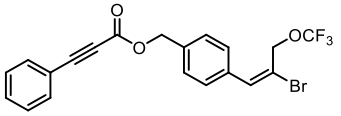
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.27 (m, 12H), 7.03 (s, 1H), 4.69

(s, 2H); **$^{13}$C NMR** (151 MHz, Acetonitrile-$d_3$) δ 165.6, 141.2, 140.5, 139.5, 136.6, 134.3, 131.0, 129.8, 129.7, 129.6, 129.4, 129.2, 127.7, 122.5 (q, $J$ = 256.7 Hz), 121.1, 78.0, 69.0 (d, $J$ = 3.7 Hz); **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -60.3 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{24}H_{17}BrClF_3NaO_3$ $[M+Na]^+$ 546.9894, found 546.9885.




**3m**, 62%
*E*/*Z*= 89:11

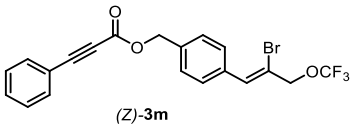
**4-(2-bromo-3-(trifluoromethoxy) prop-1-en-1-yl) benzyl 3-phenylpropiolate (3m):** The reaction was carried out on 0.2 mmol scale. The compound ***E*-3m** was obtained in 55% yield (48.3 mg) as colorless oil and ***Z*-3m** (6.1 mg, 7%) as colorless oil after purified by preparative TLC (*n*-hexane/EtOAc 20:1 (v/v)).




*(E)*-**3m**

$\mathbf{R}_f$ = 0.5 (*n*-hexane/EtOAc 5:1 (v/v))

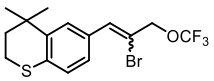
**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 7.73 (d, $J$ = 7.7 Hz, 2H), 7.60 (d, $J$ = 7.9 Hz, 3H), 7.53-7.49 (m, 3H), 7.40 (d, $J$ = 7.7 Hz, 2H), 5.41 (s, 2H), 4.91 (s, 2H); **$^{13}$C NMR** (151 MHz, Chloroform-*d*) δ 153.9, 139.2, 135.6, 135.1, 133.1, 130.9, 129.0, 128.7, 128.5, 121.6 (q, $J$ = 257.0 Hz), 119.5, 118.9, 87.2, 80.4, 68.0 (q, $J$ = 3.9 Hz), 67.1; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -60.3 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{20}H_{15}BrF_3O_3$ $[M+H]^+$ 439.0151, found 439.0147.




*(Z)*-**3m**

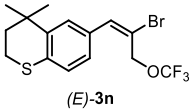
$\mathbf{R}_f$ = 0.5 (*n*-hexane/EtOAc 5:1 (v/v))

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 7.66 (d, $J$ = 7.9 Hz, 2H), 7.59 (d, $J$ = 7.7 Hz, 2H), 7.47-7.42 (m, 3H), 7.39-7.36 (m, 2H), 7.14 (s, 1H), 5.27 (s, 2H), 4.75 (s, 2H); **$^{13}$C NMR** (151 MHz, Chloroform-*d*) δ 154.0, 135.6, 134.7, 133.2, 131.3, 130.9, 129.5, 128.7, 128.6, 121.6 (q, $J$ = 256.8 Hz), 119.6, 117.4, 87.1, 80.5, 72.4 (q, $J$ = 3.7 Hz), 67.3; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -60.3 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{20}H_{15}BrF_3O_3$ $[M+H]^+$ 439.0151, found 439.0147.




**3n**, 65%
*E*/*Z* = 75:25

**6-(2-bromo-3-(trifluoromethoxy) prop-1-en-1-yl)-4,4-dimethylthiochromane (3n):** The reaction was carried out on 0.2 mmol scale. The compound ***E*-3n** was obtained in 49% yield (37.4 mg) as yellow oil and ***Z*-3n** (12.2 mg, 16%) as yellow oil after purified by preparative TLC (*n*-hexane/EtOAc 50:1 (v/v)).

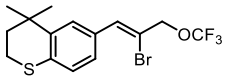



*(E)*-**3n**

$\mathbf{R}_f$ = 0.6 (*n*-hexane/EtOAc 50:1 (v/v))

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.30 (s, 1H), 7.29 (s, 1H), 7.12 (d, $J$ = 8.0 Hz, 1H), 6.92 (dd, $J$ =

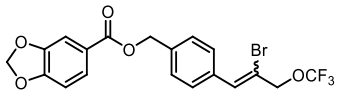
8.1, 2.0 Hz, 1H), 4.80 (s, 2H), 3.09 – 3.05 (m, 2H), 2.01 – 1.97 (m, 2H), 1.35 (s, 6H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 142.6, 140.1, 133.5, 130.6, 127.0, 126.4, 125.8, 121.6 (q, *J* = 257.0 Hz), 116.9, 68.7 (q, *J* = 3.7 Hz), 37.3, 33.1, 30.1, 23.3; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -60.3 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{15}H_{17}BrOS$ $[M+H]^+$ 381.0130, found 381.0132.




*(Z)*-**3n**

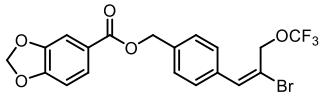
**R**$_f$ = 0.6 (*n*-hexane/EtOAc 50:1 (v/v))

**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.71 (s, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 7.04 (s, 1H), 4.73 (s, 2H), 3.08 – 3.01 (m, 2H), 2.01 – 1.93 (m, 2H), 1.34 (s, 6H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 141.9, 133.7, 132.2, 129.9, 127.6, 126.8, 121.6 (q, *J* = 257.6 Hz), 114.9, 73.1 (q, *J* = 3.4 Hz), 37.5, 33.2, 30.3, 23.3; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -60.1 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{15}H_{17}BrOS$ $[M+H]^+$ 381.0130, found 381.0132.




**3o**, 58%
E/Z = 86:14

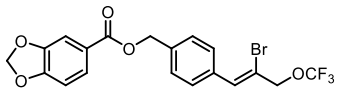
**4-(2-bromo-3-(trifluoromethoxy) prop-1-en-1-yl) benzyl benzo[d] [1,3] dioxole-5-carboxylate (3o):** The reaction was carried out on 0.2 mmol scale. The compound ***E*-3o** was obtained in 50% yield (45.9 mg) as yellow solid and ***Z*-3o** (7.3 mg, 8%) as yellow solid after purified by preparative TLC (*n*-hexane/EtOAc 20:1 (v/v)).




*(E)*-**3o**

**R**$_f$ = 0.6 (*n*-hexane/EtOAc 20:1 (v/v))

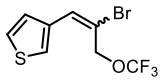
**$^{1}$H NMR** (400 MHz, Chloroform-d) δ 7.63 – 7.61(m, 1H), 7.42 (d, J = 1.7 Hz, 1H), 7.39 – 7.37 (m, 2H), 7.27 (s, 1H), 7.18 – 7.16 (m, 2H), 6.76 (d, *J* = 8.2 Hz, 1H), 5.96 (s, 2H), 5.25 (s, 2H), 4.69 (s, 2H); **$^{13}$C NMR** (101 MHz, Chloroform-d) δ 165.8, 152.0, 147.9, 139.3, 136.9, 134.7, 128.6, 128.5, 125.7, 124.0, 121.6 (d, *J* = 257.1 Hz), 118.8, 109.7, 108.2, 102.0, 68.1 (q, *J* = 3.5 Hz), 66.1; **$^{19}$F NMR** (376 MHz, Chloroform-d) δ -60.3 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{19}H_{14}BrF_3NaO_5$ $[M+Na]^+$ 480.9869, found 480.9878; m.p.: 79.3 ℃.




*(Z)*-**3o**

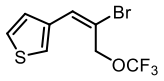
**R**$_f$ = 0.6 (*n*-hexane/EtOAc 20:1 (v/v))

**$^{1}$H NMR** (400 MHz, Chloroform-d) δ 7.71 – 7.69 (m, 1H), 7.67 – 7.65 (m, 2H), 7.51 (d, *J* = 1.7 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.13 (s, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 6.04 (s, 2H), 5.33 (s, 2H), 4.75 (s, 2H); **$^{13}$C NMR** (101 MHz, Chloroform-d) δ 165.8, 151.9, 147.9, 136.9, 134.2, 131.5, 129.5, 128.0, 125.7, 124.1, 121.6 (q, *J* = 256.6 Hz), 117.1, 109.7, 108.2, 102.0, 72.5 (q, *J* = 3.6 Hz), 66.3; **$^{19}$F NMR** (376 MHz, Chloroform-d) δ -59.8 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{19}H_{14}BrF_3NaO_5$ $[M+Na]^+$ 480.9869, found 480.9878; m.p.: 81.9 ℃.



**3p**, 56%
*E*/*Z*= 70:30

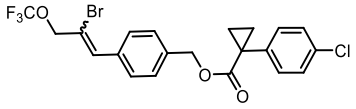
**3-(2-bromo-3-(trifluoromethoxy) prop-1-en-1-yl) thiophene (3p):** The reaction was carried out on 0.2 mmol scale. The compound ***E*-3p** was obtained in 56% yield (32.2 mg) as colorless liquid after purified by preparative TLC (*n*-hexane).



*(E)*-**3p**

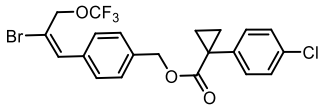
$\mathbf{R}_f$ = 0.5 (*n*-hexane)

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 7.49 (d, *J* = 5.0 Hz, 1H), 7.38 – 7.30 (m, 1H), 7.15 (s, 1H), 4.74 (s, 2H); **$^{13}$C NMR** (151 MHz, Chloroform-*d*) δ 135.3, 128.5, 126.9, 126.8, 125.4, 121.6 (q, *J* = 256.8 Hz), 115.3, 72.9 (q, *J* = 3.9 Hz); **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -59.1 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_8H_7BrF_3OS$ $[M+H]^+$ 286.9348, found 286.9350.



**3q**, 65%
*E*/*Z* = 86:14

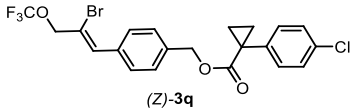
**4-(2-bromo-3-(trifluoromethoxy) prop-1-en-1-yl) benzyl 1-(4-chlorophenyl) cyclopropane-1-carboxylate (3q):** The reaction was carried out on 0.2 mmol scale. The compound ***E*-3q** was obtained in 56% yield (54.8 mg) as yellow oil and ***Z*-3p** (8.8 mg, 9%) as yellow oil after purified by preparative TLC (*n*-hexane/EtOAc 20:1 (v/v)).



*(E)*-**3q**

$\mathbf{R}_f$ = 0.6 (*n*-hexane/EtOAc 20:1 (v/v))

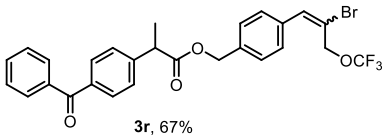
**$^1$H NMR** (400 MHz, Chloroform-d) δ 7.24 (s, 2H), 7.21 (s, 5H), 7.16 – 7.08 (m, 4H), 5.00 (s, 2H), 4.67 (s, 2H), 1.57 (q, *J* = 4.0 Hz, 2H), 1.13 (q, *J* = 4.0 Hz, 2H); **$^{13}$C NMR** (101 MHz, Chloroform-d) δ 174.0, 139.3, 137.9, 136.8, 134.5, 133.2, 132.0, 128.5, 128.4, 127.9, 121.6 (q, *J* = 257.1 Hz), 118.7, 68.1 (q, *J* = 3.5 Hz), 66.1, 28.7, 16.9; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -60.0 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{21}H_{17}BrClF_3NaO_3$ $[M+Na]^+$ 510.9894, found 510.9902.



*(Z)*-**3q**

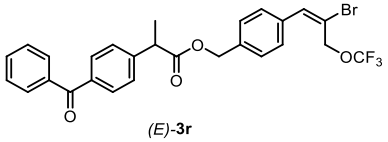
$\mathbf{R}_f$ = 0.6 (*n*-hexane/EtOAc 20:1 (v/v))

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.29 (s, 4H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.10 (s, 1H), 5.09 (s, 2H), 4.74 (s, 2H), 1.65 (q, *J* = 4.1 Hz, 2H), 1.20 (q, *J* = 4.1 Hz, 2H); **$^{13}$C NMR** (101 MHz, Chloroform-d) δ 174.0, 138.0, 136.8, 134.0, 133.2, 132.0, 131.5, 129.4, 128.5, 127.4, 121.6 (q, *J* = 256.8 Hz), 117.0, 72.5 (q, *J* = 3.4 Hz), 66.3, 28.8, 16.9; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -59.8 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{21}H_{17}BrClF_3NaO_3$ $[M+Na]^+$ 510.9894, found 510.9891.



**3r**, 67%
*E/Z* = 85:15

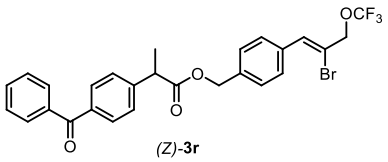
**4-(2-bromo-3-(trifluoromethoxy) prop-1-en-1-yl) benzyl 2-(4-benzoylphenyl) propanoate (3r):** The reaction was carried out on 0.2 mmol scale. The compound ***E*-3r** was obtained in 57% yield (62.4 mg) as a colorless liquid and ***Z*-3r** (11.9 mg, 10%) as colorless liquid after purified by preparative TLC (*n*-hexane/EtOAc 10:1 (v/v)).



*(E)*-**3r**

$\mathbf{R}_f$ = 0.5 (*n*-hexane/EtOAc 5:1 (v/v))

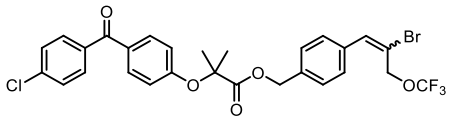
**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 7.80 – 7.74 (m, 3H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.50 – 7.40 (m, 3H), 7.31 – 7.23 (m, 3H), 7.16 (d, *J* = 7.7 Hz, 2H), 5.12 (s, 2H), 4.73 (s, 2H), 3.87 (q, *J* = 7.2 Hz, 1H), 1.57 (d, *J* = 7.2 Hz, 3H); **$^{13}$C NMR** (151 MHz, Chloroform-*d*) δ 196.5, 173.9, 140.7, 139.2, 138.1, 137.5, 136.5, 136.3, 134.7, 132.7, 131.6, 130.2, 129.3, 129.2, 128.7, 128.4, 128.4, 128.4, 128.3, 121.6 (q, *J* = 257.6 Hz), 118.7, 68.0 (q, *J* = 3.5 Hz), 66.1, 45.5, 18.5; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -59.9 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{27}H_{22}BrF_3NaO_4$ $[M+Na]^+$ 569.0546, found 569.0553.



*(Z)*-**3r**

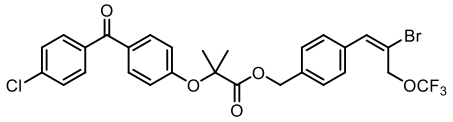
$\mathbf{R}_f$ = 0.5 (*n*-hexane/EtOAc 5:1 (v/v))

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 7.81 – 7.73 (m, 3H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 3H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.45 (dt, *J* = 16.7, 7.6 Hz, 3H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.09 (s, 1H), 5.12 (s, 2H), 4.73 (s, 2H), 3.87 (q, *J* = 7.2 Hz, 1H), 1.56 (d, *J* = 7.3 Hz, 3H); **$^{13}$C NMR** (151 MHz, Chloroform-*d*) δ 196.6, 173.9, 140.7, 138.1, 137.6, 136.6, 134.2, 132.7, 131.7, 131.4, 130.2, 129.4, 129.2, 128.7, 128.5, 127.9, 121.6 (q, *J* = 256.7 Hz), 117.1, 72.5 (q, *J* = 3.8 Hz), 66.3, 45.5, 18.5; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -59.9 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{27}H_{22}BrF_3NaO_4$ $[M+Na]^+$ 569.0546, found 569.0553.



**3s**, 65%
*E/Z* = 88:12

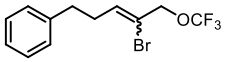
**4-(2-bromo-3-(trifluoromethoxy) prop-1-en-1-yl) benzyl 2-(4-(4-chlorobenzoyl) phenoxy)-2-methylpropanoate (3s):** The reaction was carried out on 0.2 mmol scale. The compound ***E*-3s** was obtained in 65% yield (79.5 mg) as a white solid after purified by preparative TLC (*n*-hexane/EtOAc 10:1 (v/v)).



*(E)*-**3s**

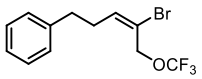
$\mathbf{R}_f$ = 0.6 (*n*-hexane/EtOAc 10:1 (v/v))

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.67 (dd, *J* = 15.8, 8.7 Hz, 4H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.30 – 7.27 (m, 2H), 7.25 (s, 1H), 7.16 (d, *J* = 7.8 Hz, 2H), 6.80 (d, *J* = 8.9 Hz, 2H), 5.19 (s, 2H), 4.72 (s, 2H), 1.69 (s, 6H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 194.1, 173.5, 159.6, 139.0, 138.6, 136.4, 136.1, 135.8, 135.0, 132.0, 131.2, 128.8, 128.7, 128.4, 121.5 (q, *J* = 257.2 Hz), 119.0, 117.4, 79.6, 68.0 (q, *J* = 3.6 Hz), 66.8, 25.6; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -59.7 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{28}H_{23}BrClF_3O_5$ $[M+H]^+$ 611.0442, found 611.0438; m.p.: 84.2 ℃.



**3t**, 56%
*E*/*Z*= 57:43

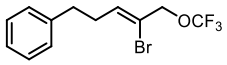
**(4-bromo-5-(trifluoromethoxy) pent-3-en-1-yl) benzene (3t):** The reaction was carried out on 0.2 mmol scale. The compound ***E*-3t** was obtained in 32% yield (19.8 mg) as yellow oil and ***Z*-3t** (14.8 mg, 24%) as yellow oil after purified by preparative TLC (*n*-hexane).



*(E)*-**3t**

$\mathbf{R}_f$ = 0.6 (*n*-hexane)

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.23 – 7.20 (m, 2H), 7.12 – 7.08 (m, 3H), 7.07 (s, 1H), 6.16 (t, *J* = 8.0 Hz, 1H), 4.39 (s, 2H), 2.38 – 2.32 (m, 2H), 2.26 – 2.20 (m, 2H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 140.3, 134.3, 128.8, 128.7, 121.6 (q, *J* = 257.6 Hz), 120.1, 66.6 (q, *J* = 4.0 Hz), 33.5, 31.9; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -59.6 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{12}H_{12}BrF_3NaO$ $[M+Na]^+$ 330.9916, found 330.9910.

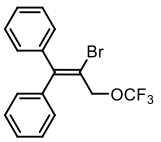


*(Z)*-**3t**

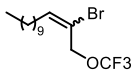
$\mathbf{R}_f$ = 0.6 (*n*-hexane)

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 7.31 -7.29 (m, 2H), 7.23 - 7.19 (m, 3H), 6.17 - 6.15(m, 1H), 4.56 (s, 2H), 2.76 - 2.74 (m, 2H), 2.57 - 2.54 (m, 2H); **$^{13}$C NMR** (151 MHz, Chloroform-*d*) δ 140.9, 134.3, 128.6, 128.5, 126.4, 121.5 (q, *J* = 256.6 Hz), 119.0, 71.8 (q, *J* = 4.0 Hz), 34.1, 32.8; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -60.3 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{12}H_{12}BrF_3NaO$ $[M+Na]^+$ 330.9916, found 330.9910.

# 4 Other Substrates



**3w**, 0%.

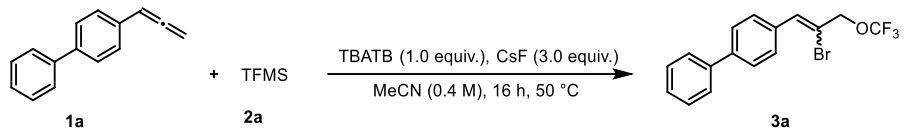


**3x**, 20%[b] (*E*:*Z* 60:40)

[b]Determined by $^{19}$F NMR spectrum with benzotrifluoride as internal standards

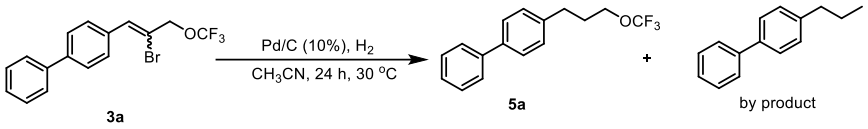
**Scheme S1** Other substrates

# 5 Gram Scale Reaction



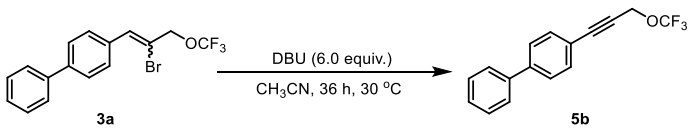

In a glove box, to a 40.0 mL vial tube were added CsF (2.3 g, 15.0 mmol, 3.0 equiv.), TBATB (2.4 g, 5.0 mmol, 1.0 equiv.) and **1a** (961.5 mg, 5.0 mmol, 1.0 equiv.) in 12.5 mL $CH_3CN$, then TFMS (2.7 mL, 15 mmol, 3.0 equiv.) were added. The mixture was stirred at 50 ºC for 16 h. After cooling to room temperature, the reaction mixture was then added 50 mL $CH_2Cl_2$. The yield was determined by $^{19}F$ NMR using benzotrifluoride as an internal standard. The filtrate was concentrated, and the residue was purified by chromatography on silica gel, eluting with hexanes to afford 232.2 mg (*Z*)-4-(2-bromo-3-(trifluoromethoxy) prop-1-en-1-yl)-1,1'-biphenyl (**(*Z*)-3a**, 13% yield) and 1.1 g (*E*)-4-(2-bromo-3-(trifluoromethoxy) prop-1-en-1-yl)-1,1'-biphenyl (**(*E*)-3a**, 60% yield).

# 6 Transformations of Compounds 3a




To a flask was added compound **3a** (41.2 mg, 0.10 mmol), Pd/C (4.2 mg) and dry $CH_3CN$ (0.4 mL). After the reaction was stirred at 30 ℃ under 1 atm $H_2$ for 24 h, the resulting mixture was filtered. The compound **5a** was obtained in 61% yield (19.6 mg) as yellow oil after purified by preparative TLC (*n*-hexane). $\mathbf{R}_f$ = 0.5 (*n*-hexanes).

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.59-7.53 (m, 4H), 7.45 – 7.41 (m, 2H), 7.35-7.32 (m, 1H), 7.27-7.25 (m, 2H), 4.00 (t, *J* = 6.3 Hz, 2H), 2.80-2.76 (m, 2H), 2.08-2.01 (m, 2H); **$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 141.1, 139.8, 139.4, 129.0, 128.9, 127.4, 127.3, 127.2, 121.9 (q, *J* = 254.1 Hz), 66.6 (q, *J* = 3.2 Hz), 31.3, 30.5; **$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ -60.6 (s, 3F); **HRMS-**ESI (m/z): Calc'd for $C_{16}H_{16}F_3O^+$ $[M+H]^+$ 281.1148, found 281.1147.

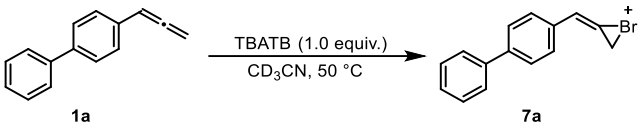



To a solution of 4-(2-bromo-3-(trifluoromethoxy) prop-1-en-1-yl)-1,1'-biphenyl (**3a**) (35.7 mg, 0.1 mmol, 1.0 equiv.) in dry $CH_3CN$ (2.0 mL) at 30 °C (oil bath) under $N_2$ were added DBU (1,8-diazabicyclo [5.4.0] undec-7-ene) (90.0 μL, 6.0 mmol, 6.0 equiv.). The reaction mixture was stirred for 36 h. When completed, the reaction was diluted with $CH_2Cl_2$ (10.0 mL) and washed with saturated aqueous solution of $NH_4Cl$ (5.00 mL). The aqueous fraction was separated and extracted three times with $CH_2Cl_2$ (10.0 mL). The combined organic layers were dried over $Na_2SO_4$. The filtrate was concentrated in vacuo, and the residue was purified by preparative TLC, eluting with *n*-hexanes to afford 12.7 mg 4-(3-(trifluoromethoxy) prop-1-yn-1-yl)-1,1'-biphenyl (**5b**) as a colorless liquid (46% yield). $R_f$ = 0.4 (*n*-hexanes).

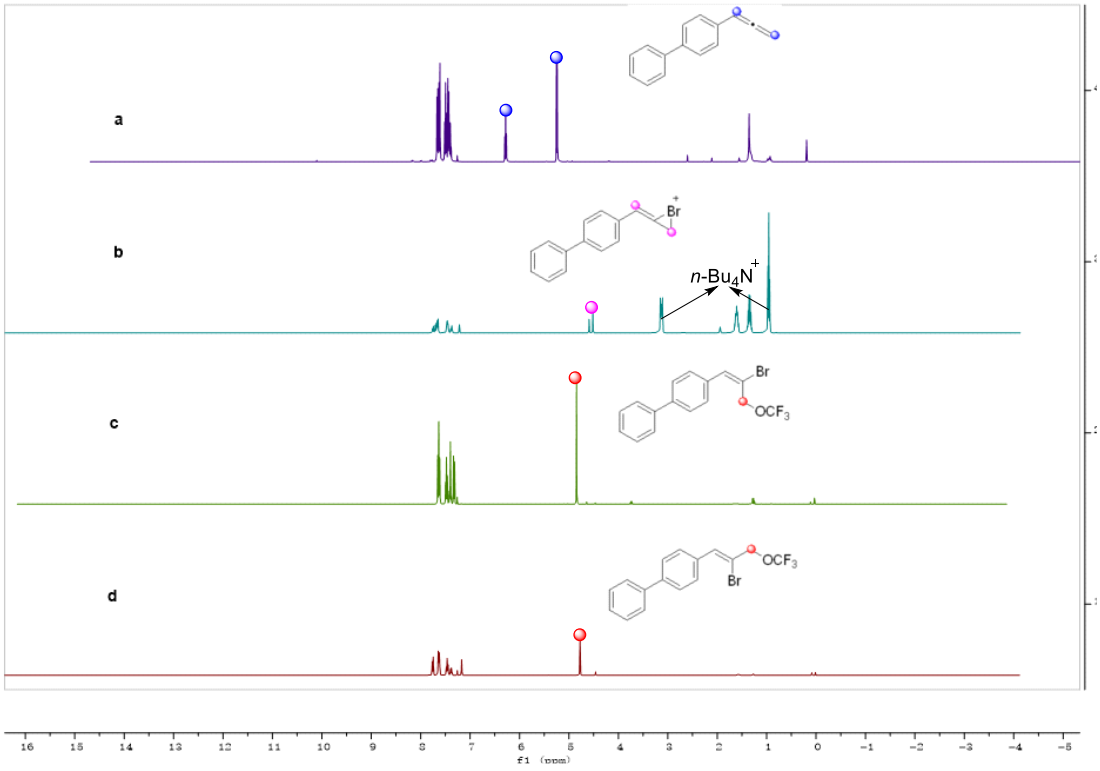
$^1$H NMR (600 MHz, Chloroform-*d*) δ 7.61 – 7.56 (m, 4H), 7.55-7.54 (m, 2H), 7.47-7.45 (m, 2H), 7.39-7.37 (m, 1H), 4.86 (s, 2H); $^{13}$C NMR (151 MHz, Chloroform-*d*) δ 142.1, 140.3, 132.5, 129.0, 128.0, 127.2, 121.8 (q, *J* = 257.4 Hz), 120.6, 88.2, 81.5, 56.2 (q, *J* = 4.6 Hz); **$^{19}$F NMR** (376 MHz, Chloroform-

*d*) δ -60.6 (s, 3F) ; **HRMS**-ESI (m/z): Calc'd for $C_{16}H_{12}F_3O^+$ $[M+H]^+$ 277.0835, found 277.0841.

# 7 Mechanistic Experiment




In a glove box, to a 2.0 mL vial tube were added TBATB (96.4 mg, 0.2 mmol, 1.0 equiv.), and **1a** (38.4 mg, 0.2 mmol, 1.0 equiv.) in 0.5 mL deuterated acetonitrile. The reaction mixture was stirred for 1 h at 50 °C. After cooling to room temperature, the complex system was characterized by **$^1$H NMR** spectrum.




a $^1$H NMR spectrum of **1a**;

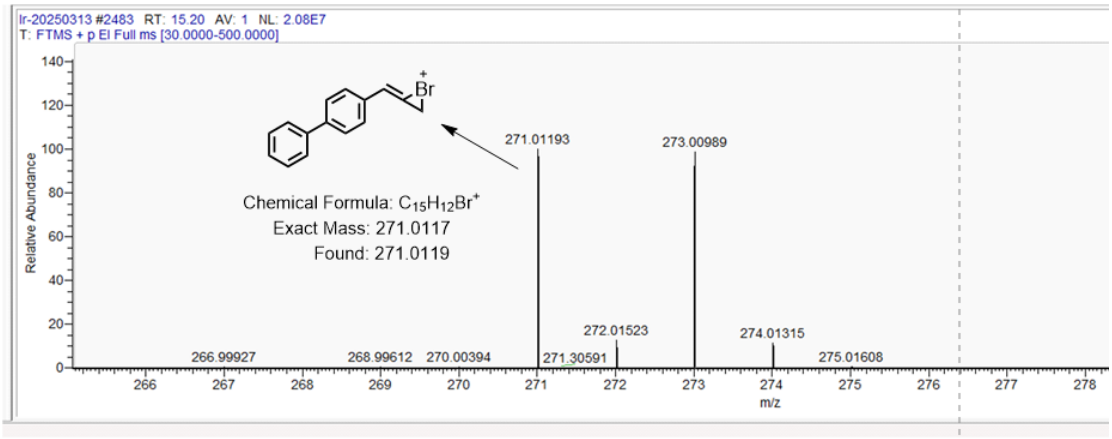
b $^1$H NMR spectrum of the bromonium active intermediates;

c $^1$H NMR spectrum of the ***E*-3a**;

d $^1$H NMR spectrum of the ***Z*-3a**.

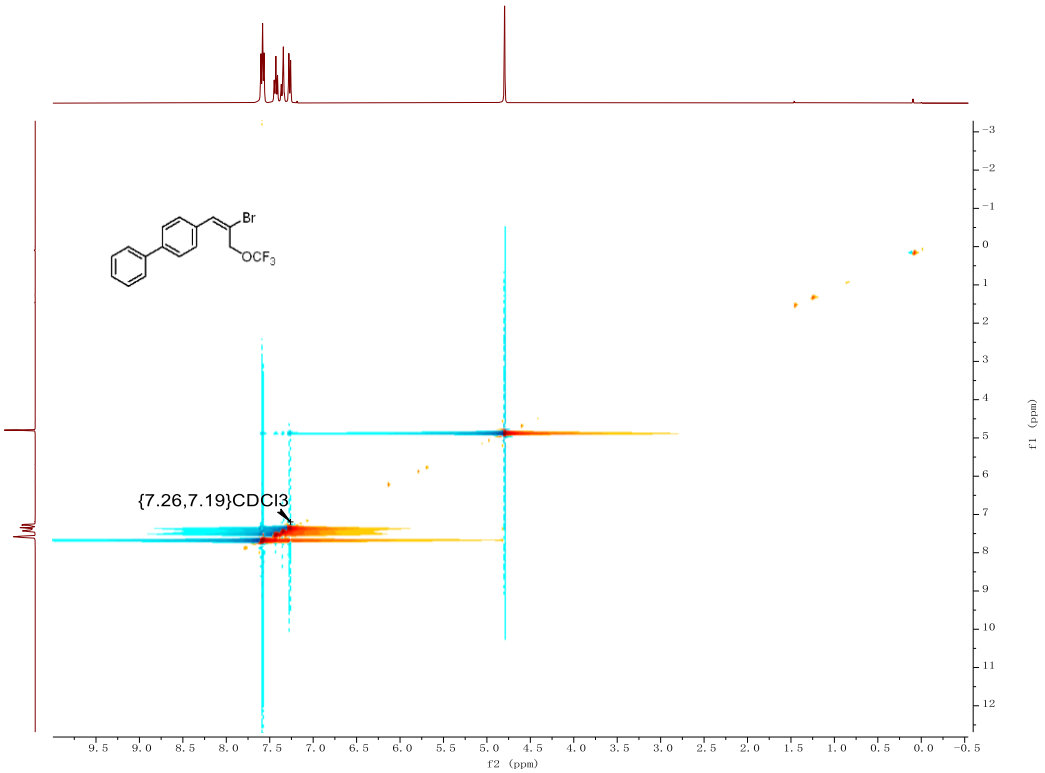
**Scheme S2** The $^1$H NMR spectrum of the control experiments

In a glove box, to a 2.0 mL vial tube were added TBATB (24.1 mg, 0.05 mmol, 1.0 equiv.), and **1a** (9.62 mg, 0.05 mmol, 1.0 equiv.) in 0.125 mL $CH_3CN$.The reaction mixture was stirred for 1 h at 50 °C. After cooling to room temperature, the complex system was characterized by HRMS (Scheme S3). **HRMS**-ESI (m/z): Calc'd for $C_{15}H_{12}Br$ $[M+]^+$ 271.0117, found 271.0119.

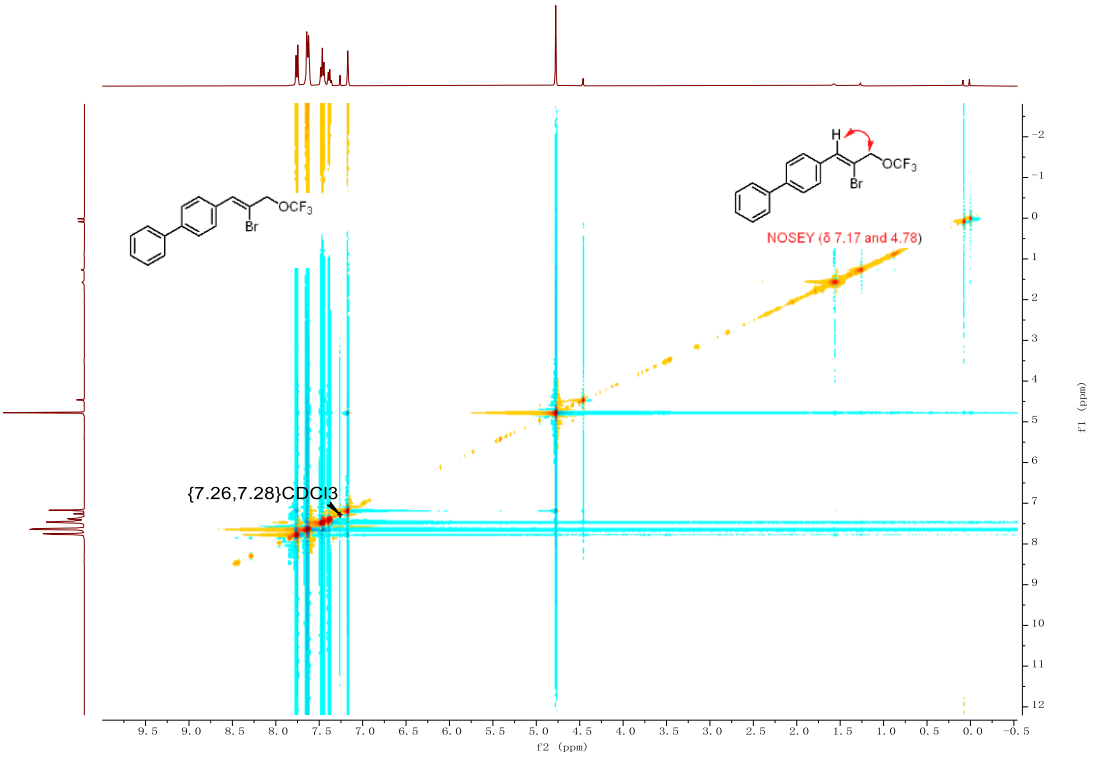



**Scheme S3** The HRMS of the **7a**

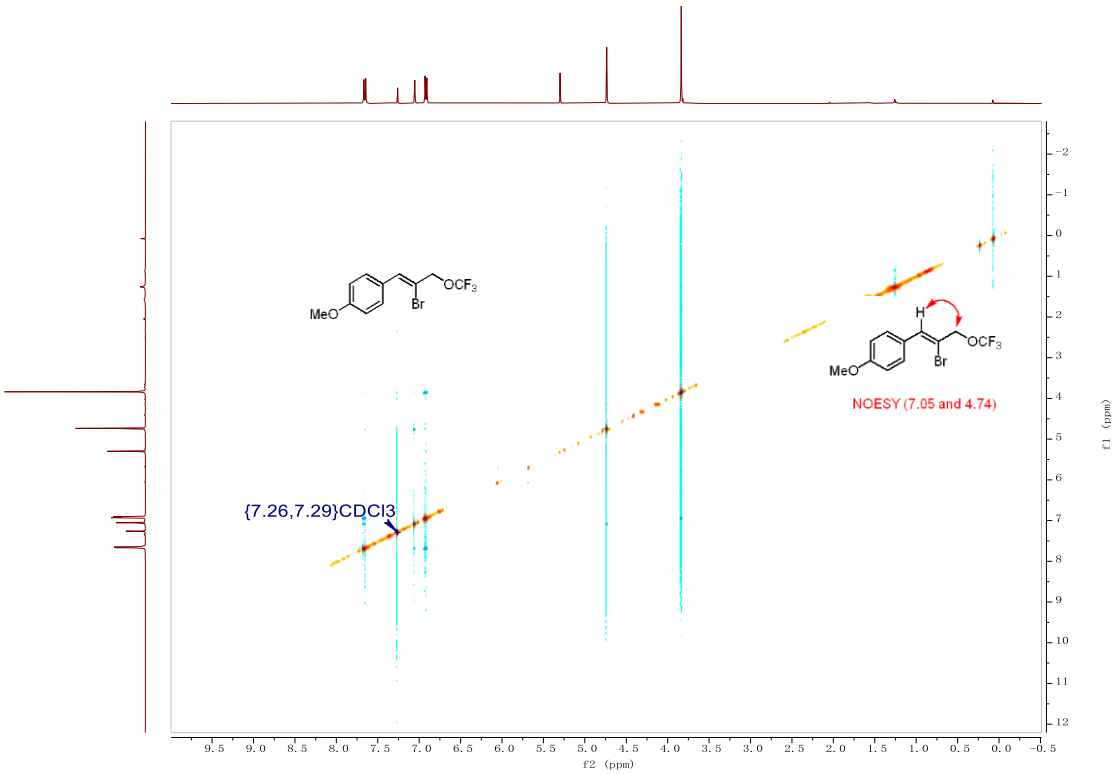
# 8 D-NOESY NMR spectrum (400 MHz, $CDCl_3$) of (*E*)-3a, (*Z*)-3a and *(Z)*-3d




**Scheme S4** 2D-NOESY NMR spectrum (400 MHz, $CDCl_3$) of **(*E*)-3a.**




**Scheme S5** 2D-NOESY NMR spectrum (400 MHz, $CDCl_3$) of ***(Z)*-3a.**




**Scheme S6** 2D- H-$^1$H NOESY NMR spectrum (400 MHz, $CDCl_3$) of ***(Z)*-3d**

# Reference


[1] Wang, L. Y.; Jiang, X. H.; Tang, P. P. Silver-mediated fluorination of alkyl iodides with $TMSCF_3$ as the fluorinating agent. *Org. Chem. Front.* **2017**, *4*, 1958-1961.

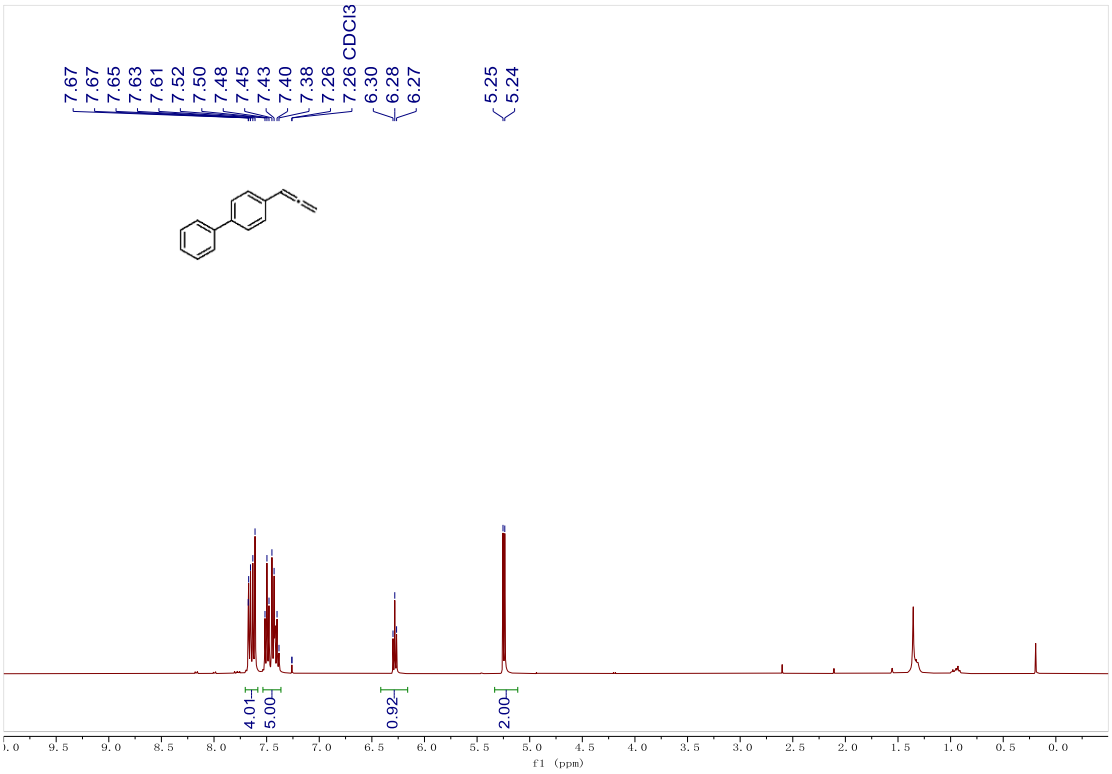
[2] Zhao, Z. S.; Racicot, L.; Murphy, G. K. Fluorinative Rearrangements of Substituted Phenylallenes Mediated by (Difluoroiodo)toluene: Synthesis of α-(Difluoromethyl) styrenes. *Angew. Chem. Int. Ed.* **2017**, *56*, 11620-11623.

[3] Liu, J. W.; Han, Z. B.; Wang, X. M.; Wang, Z.; Ding, K. L. Highly Regio- and Enantioselective Alkoxycarbonylative Amination of Terminal Allenes Catalyzed by a Spiroketal-Based Diphosphine/Pd (II) Complex. *J. Am. Chem. Soc.* **2015**, *137*, 15346-15349.

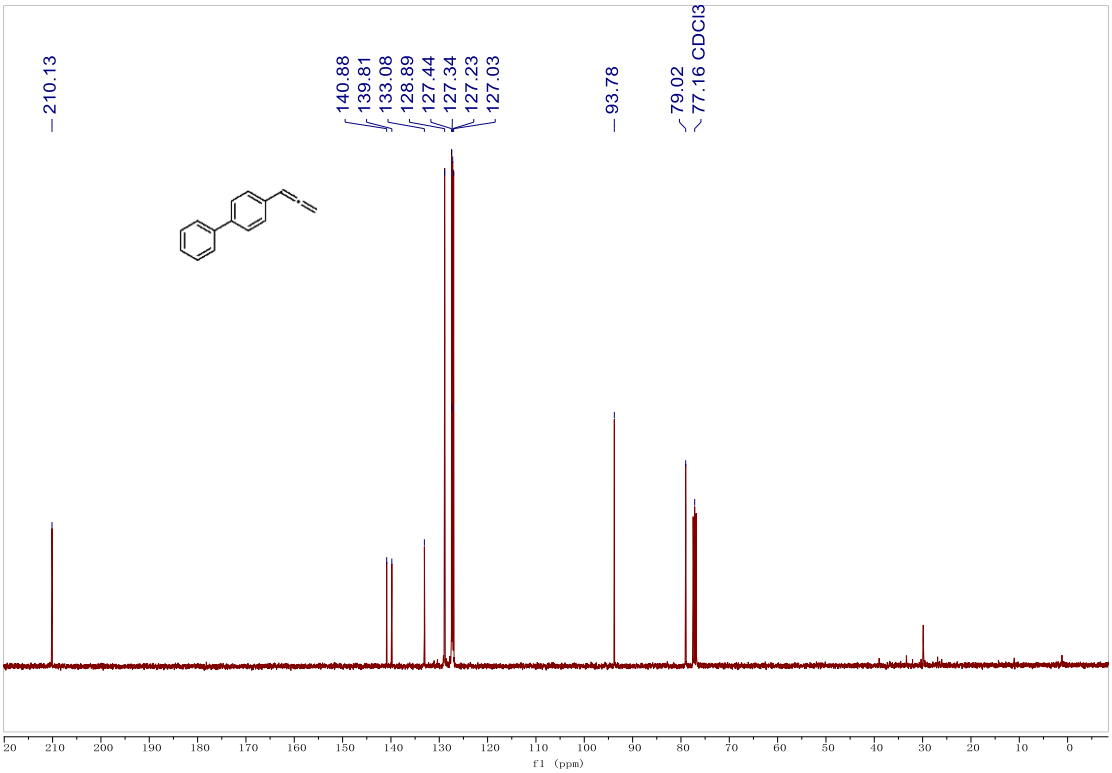
[4] Hu, T. J.; Beluze, C.; Fagué, V.; Kambire, O. E.; Bouyssi, D.; Monteiro, N.; Amgoune, A. Nickle-Catalyzed Photoredox Allenylation of Alkyl Halides. *Org. Lett.* **2024**, *26*, 9519-9524.

[5] Xia, X. F.; Wang, Y. Q.; Zhang, L. L.; Song, X. R.; Liu, X. Y.; Liang, Y. M. Palladium-Catalyzed C-H Activation and Intermolecular Annulation with Allenes. *Chem. Eur. J.* **2014**, *20*, 5087-5091.

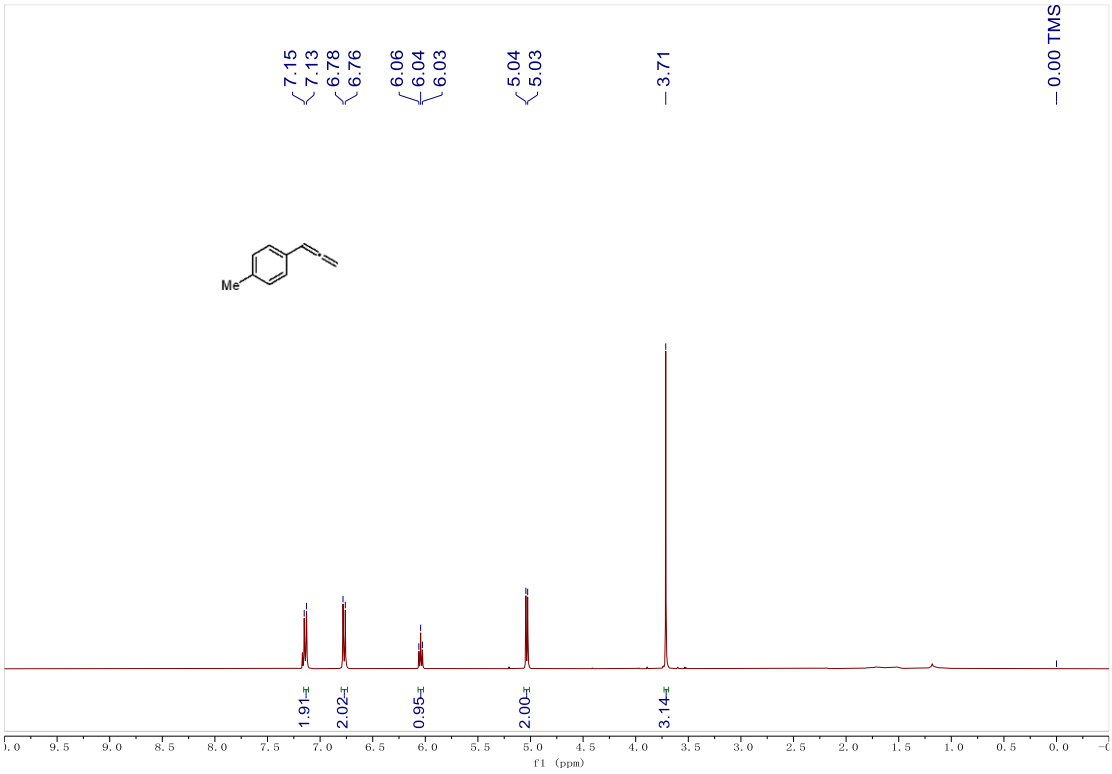
# NMR Spectra of Substrates



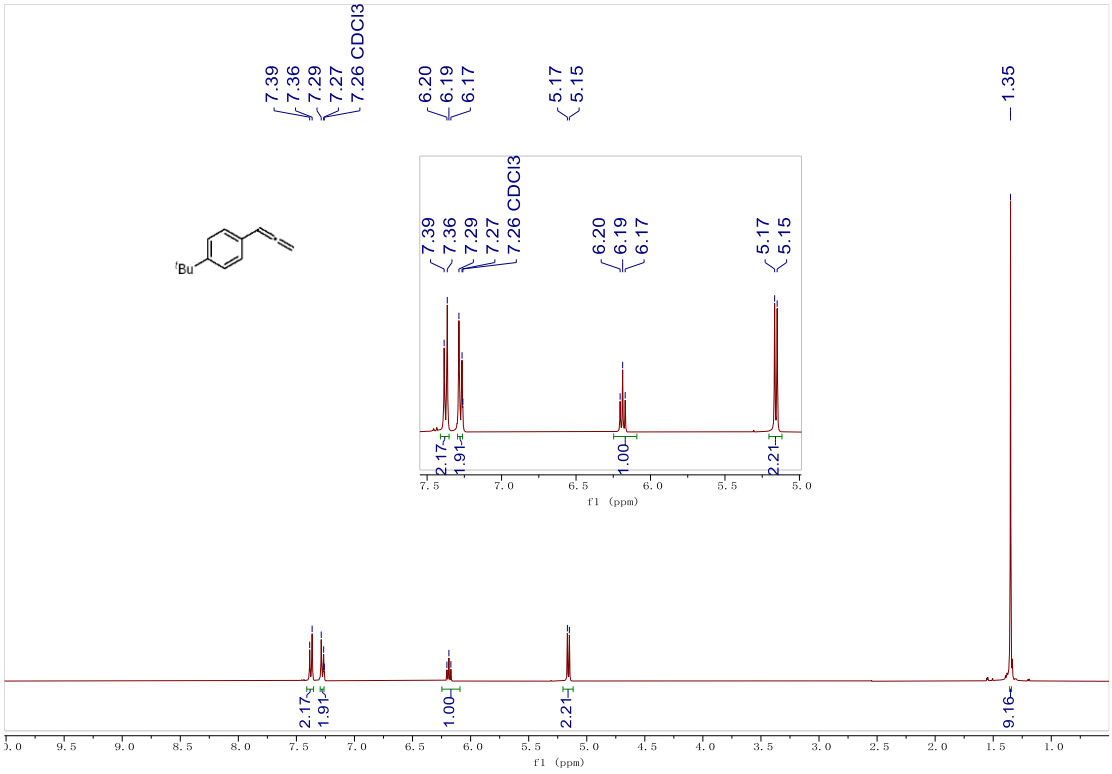

$^{1}$H NMR spectrum ((400 MHz, $CDCl_3$) of **1a**



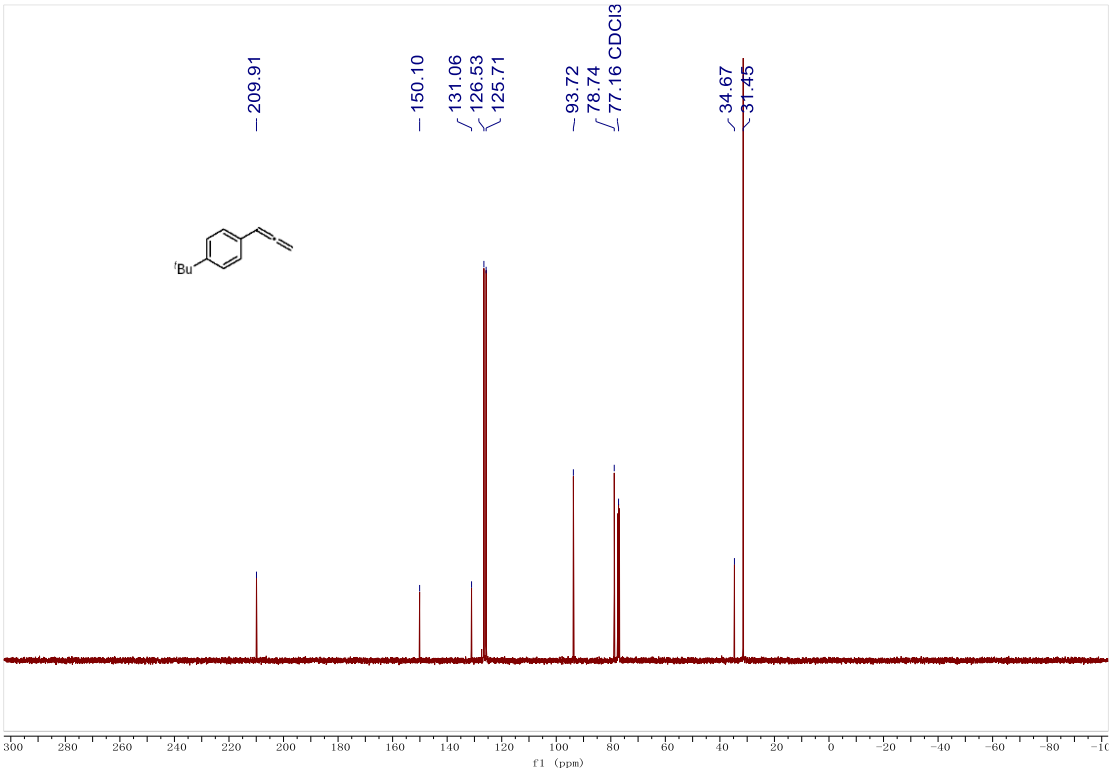

$^{13}$C NMR spectrum ((101 MHz, $CDCl_3$)) of **1a**



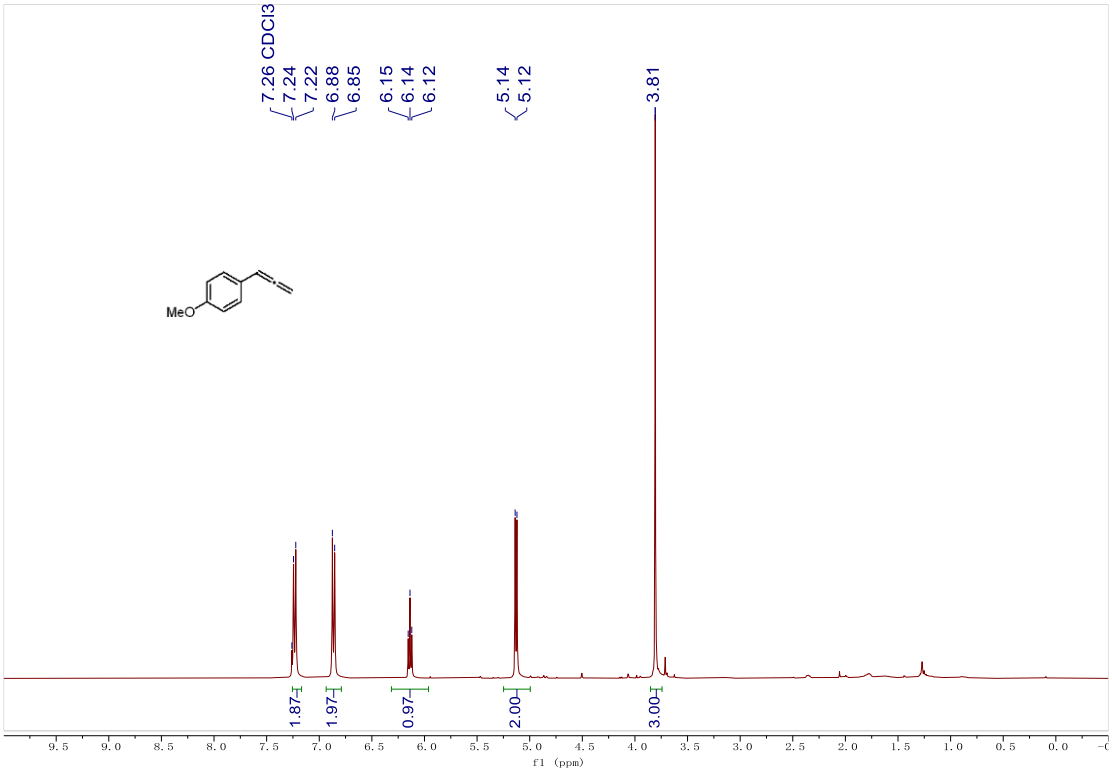

$^1$H NMR spectrum (400 MHz, $CDCl_3$) of **1b**



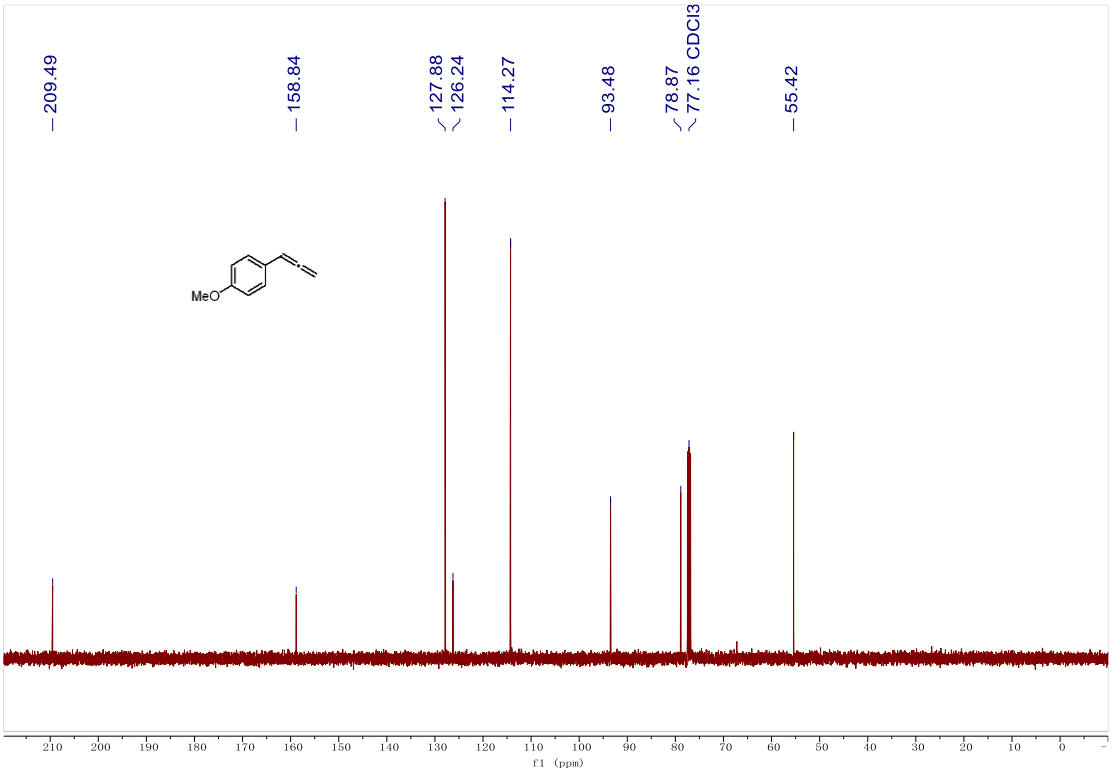

$^1$H NMR spectrum ((400 MHz, $CDCl_3$)) of **1c**



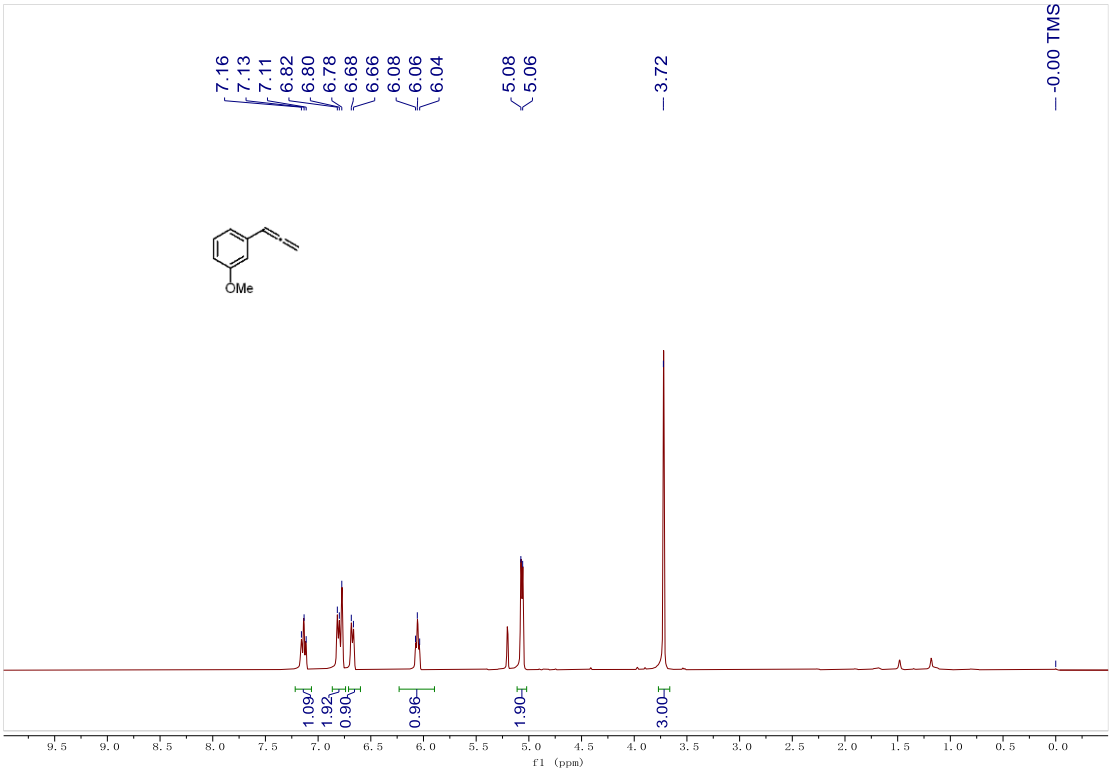

$^{13}$C NMR spectrum ((101 MHz, $CDCl_3$) of **1c**



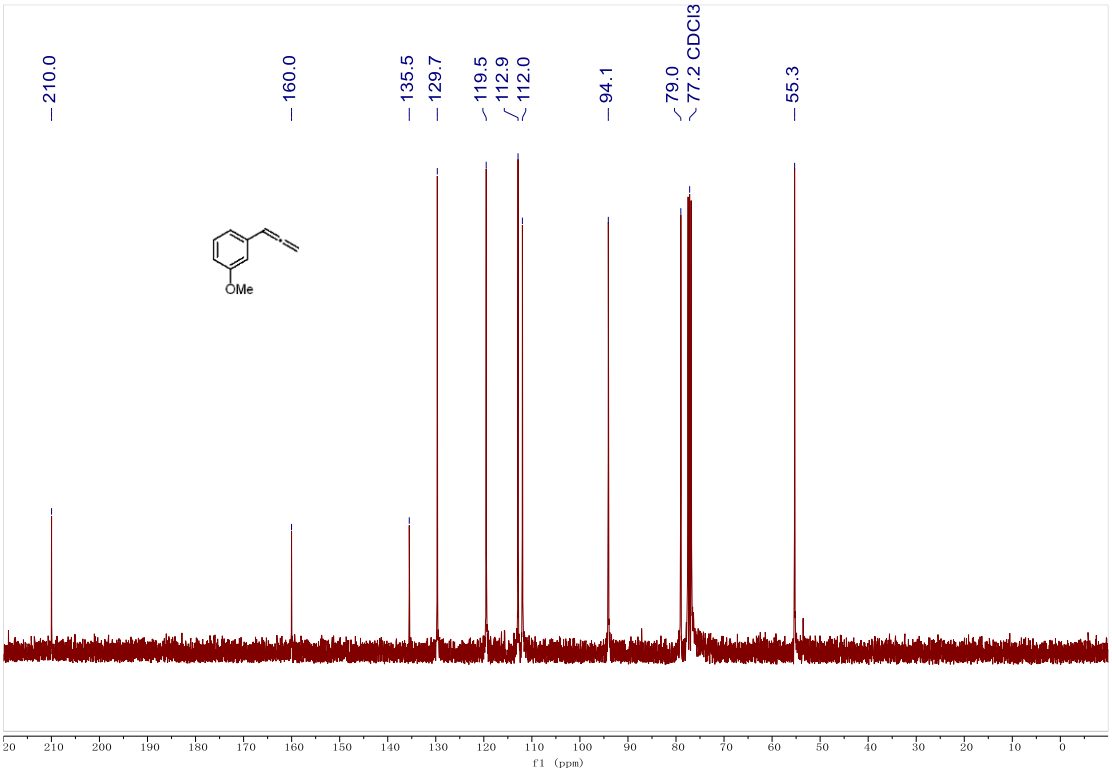

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **1d**




$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **1d**




$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **1e**

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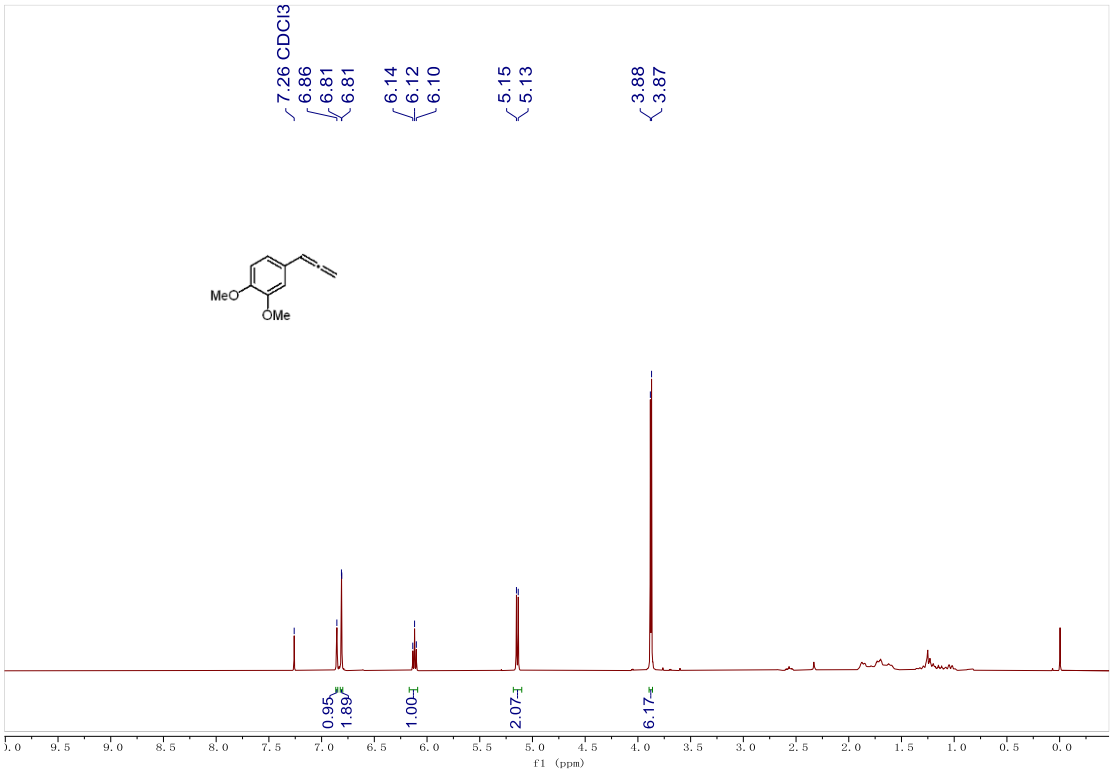
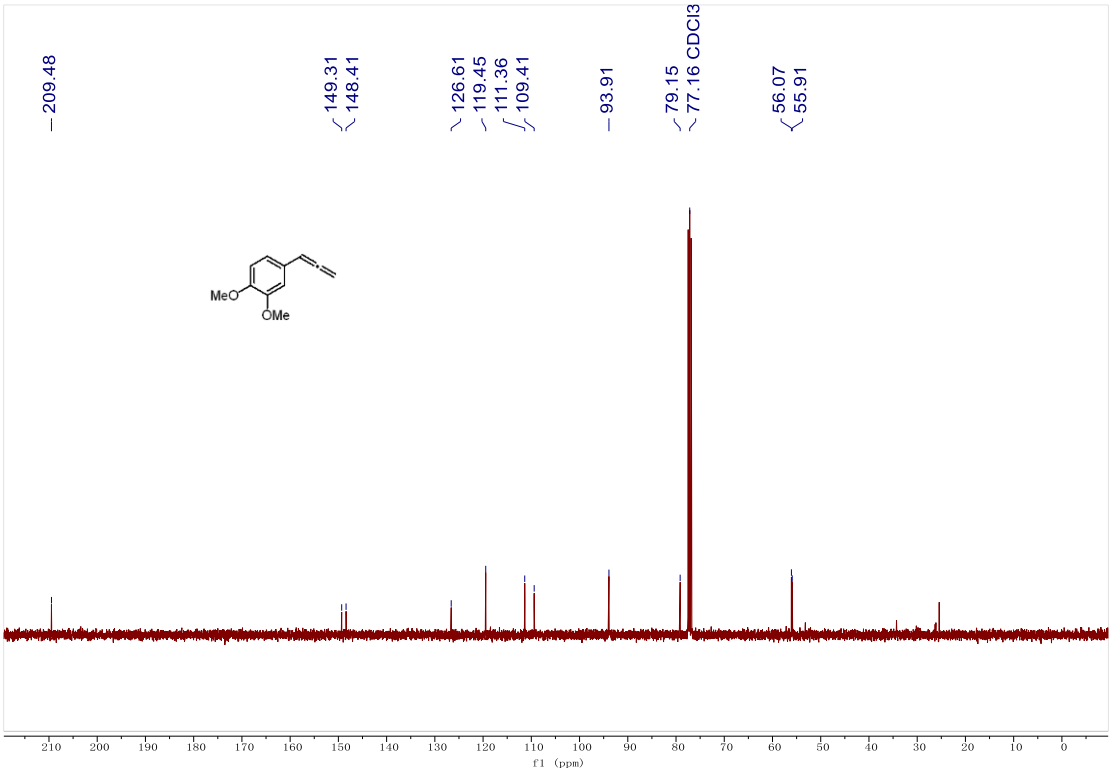
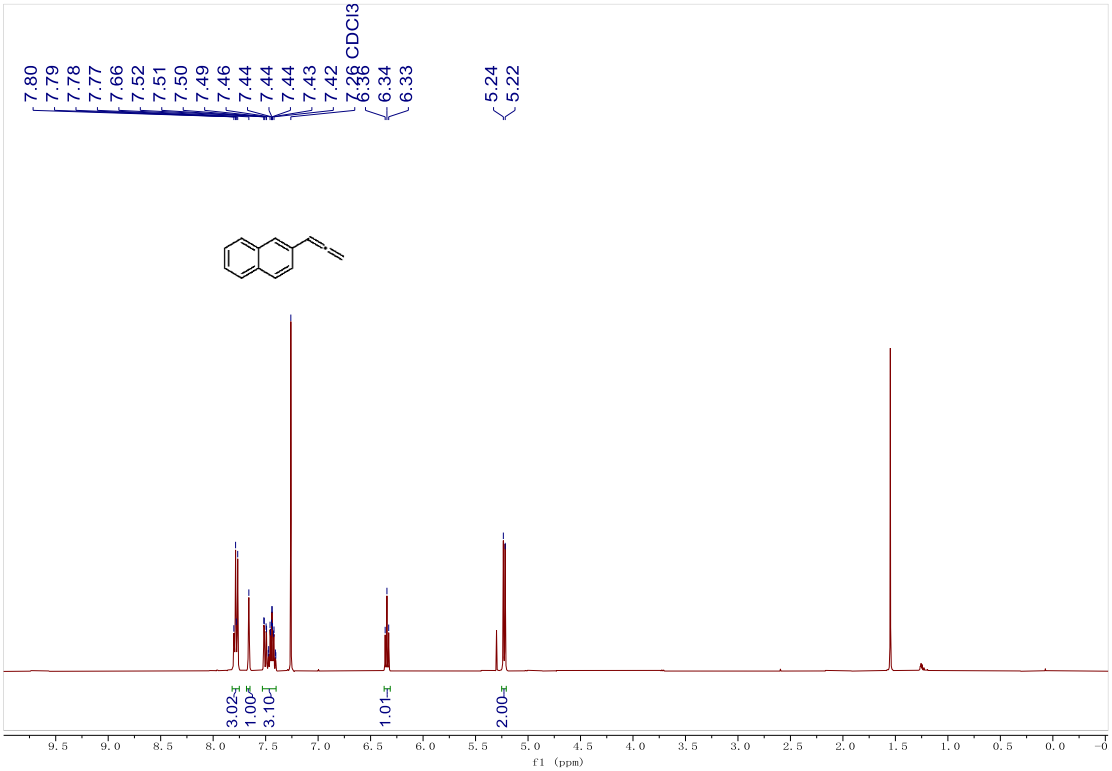


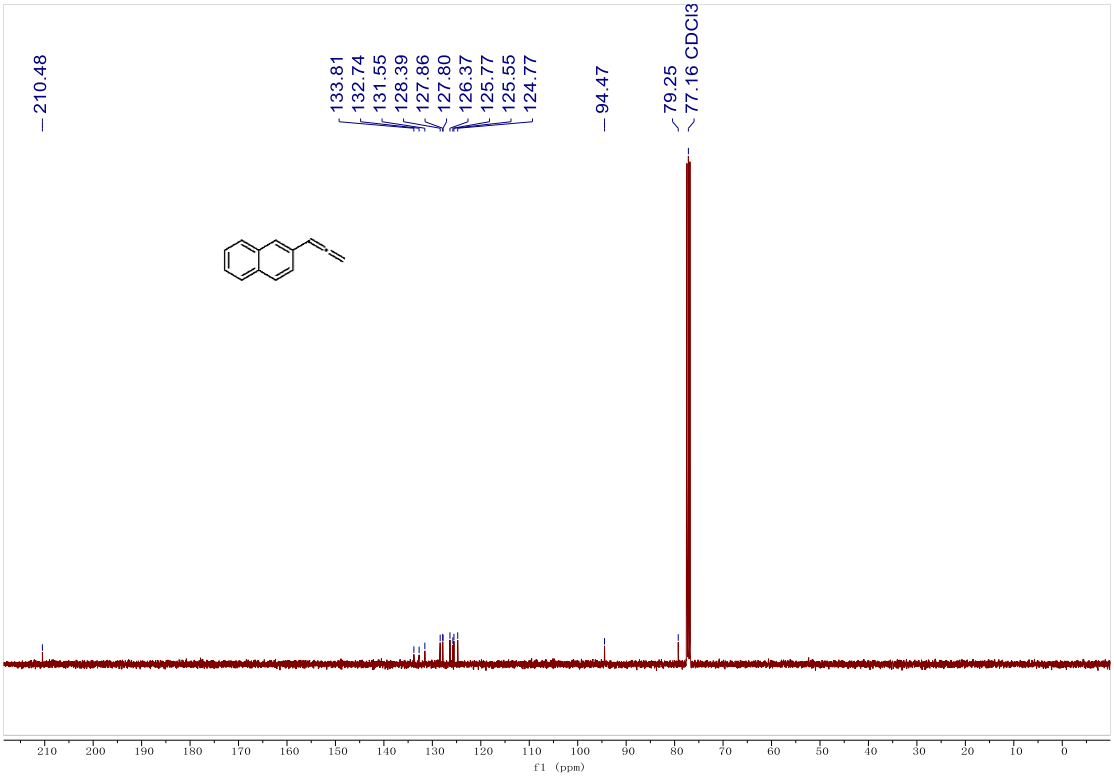

$^{1}$H NMR spectrum ((400 MHz, $CDCl_3$) of **1f**



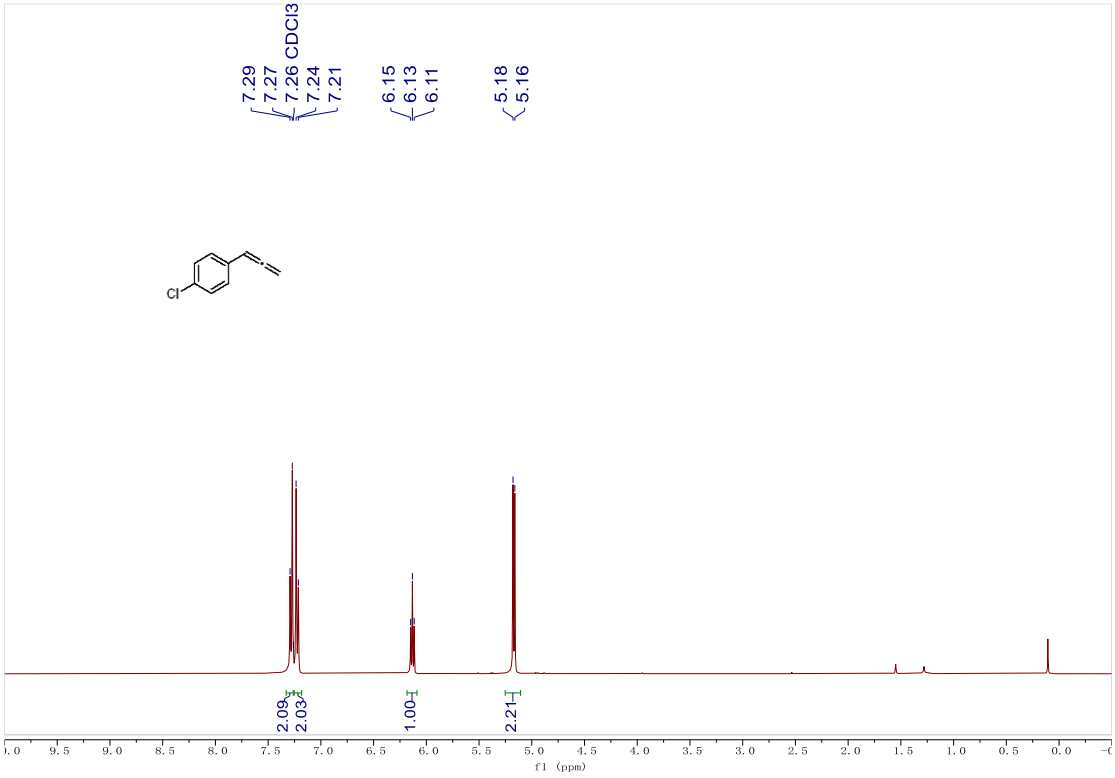

$^{13}C$ NMR spectrum (101 MHz, $CDCl_3$) of **1f**



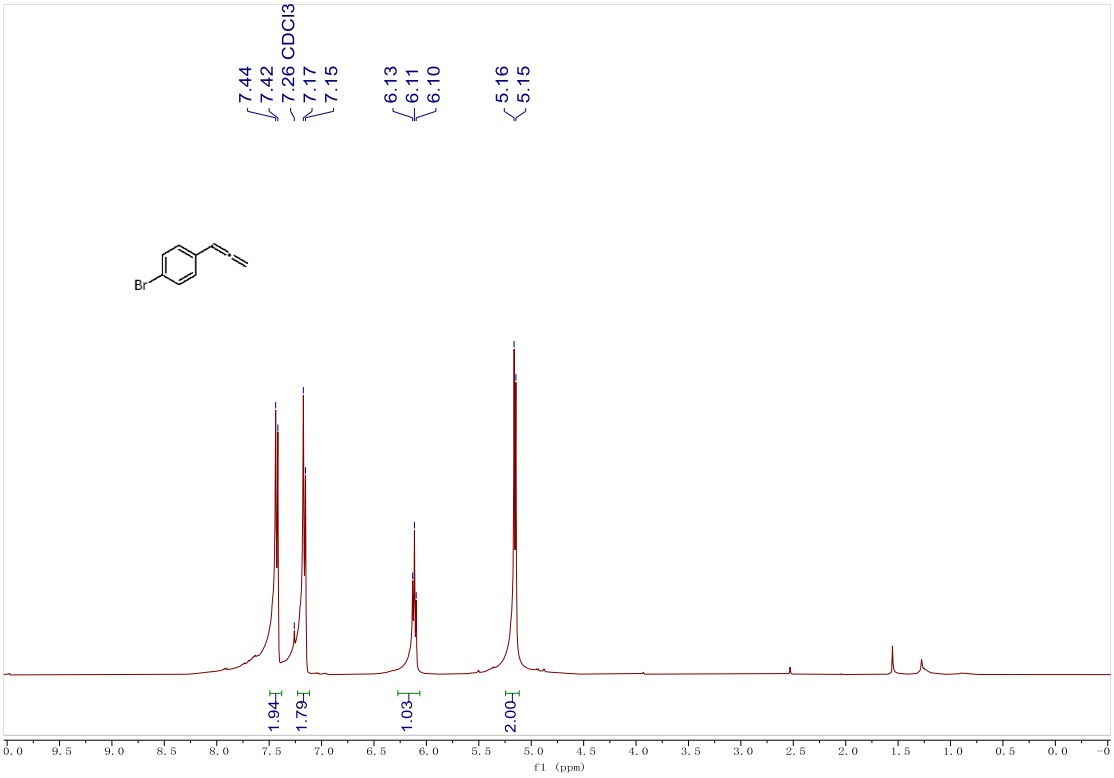

$^{1}H$ NMR spectrum (400 MHz, $CDCl_3$) of **1g**



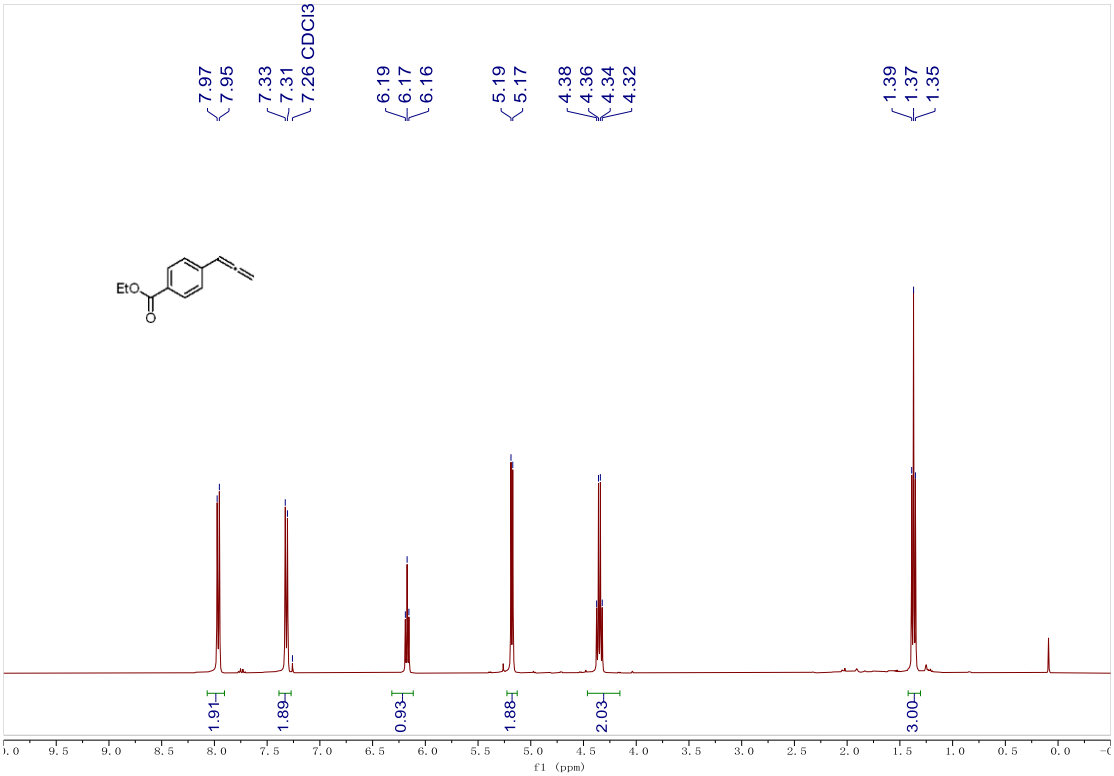

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **1g**



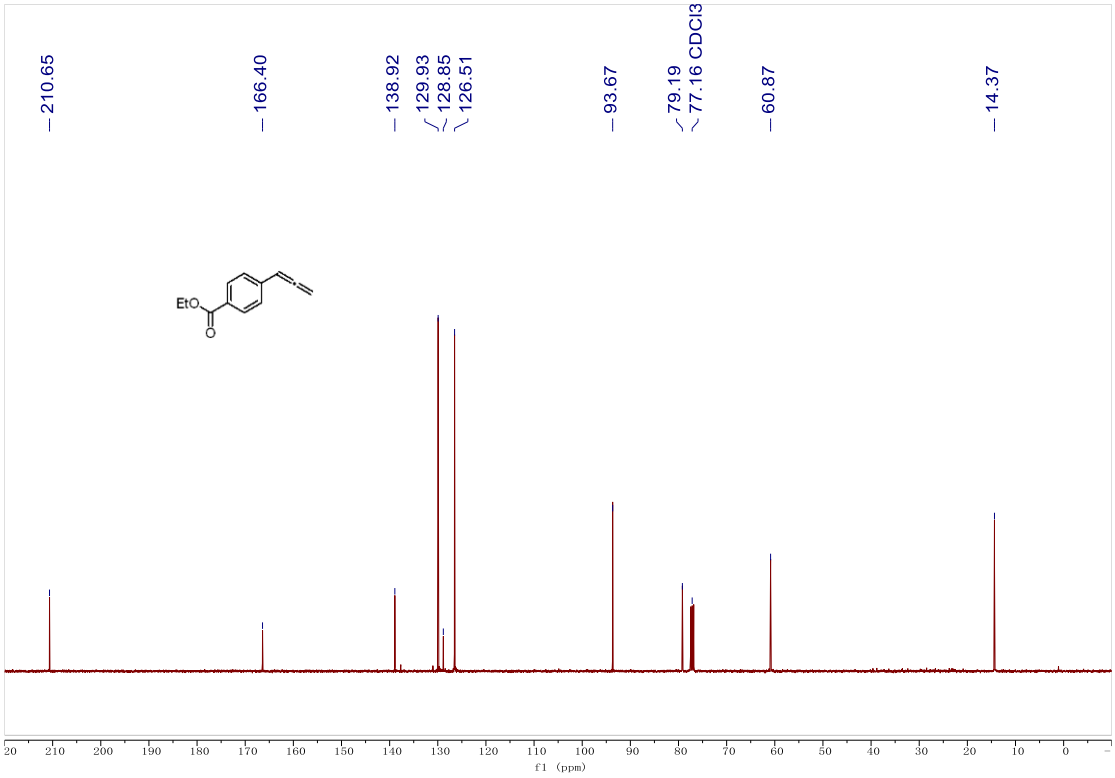

$^{1}$H NMR spectrum ((400 MHz, $CDCl_3$)) of **1h**




$^1$H NMR spectrum (400 MHz, $CDCl_3$) of **1i**




$^1$H NMR spectrum ((400 MHz, $CDCl_3$)) of **1j**

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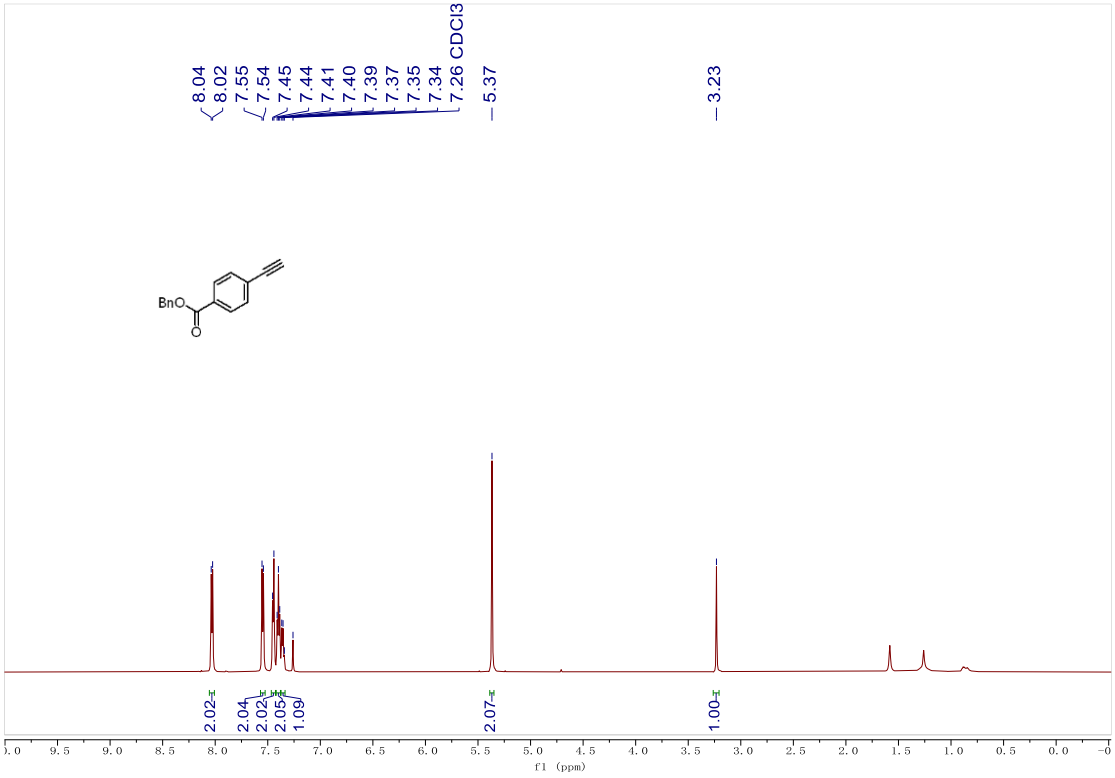
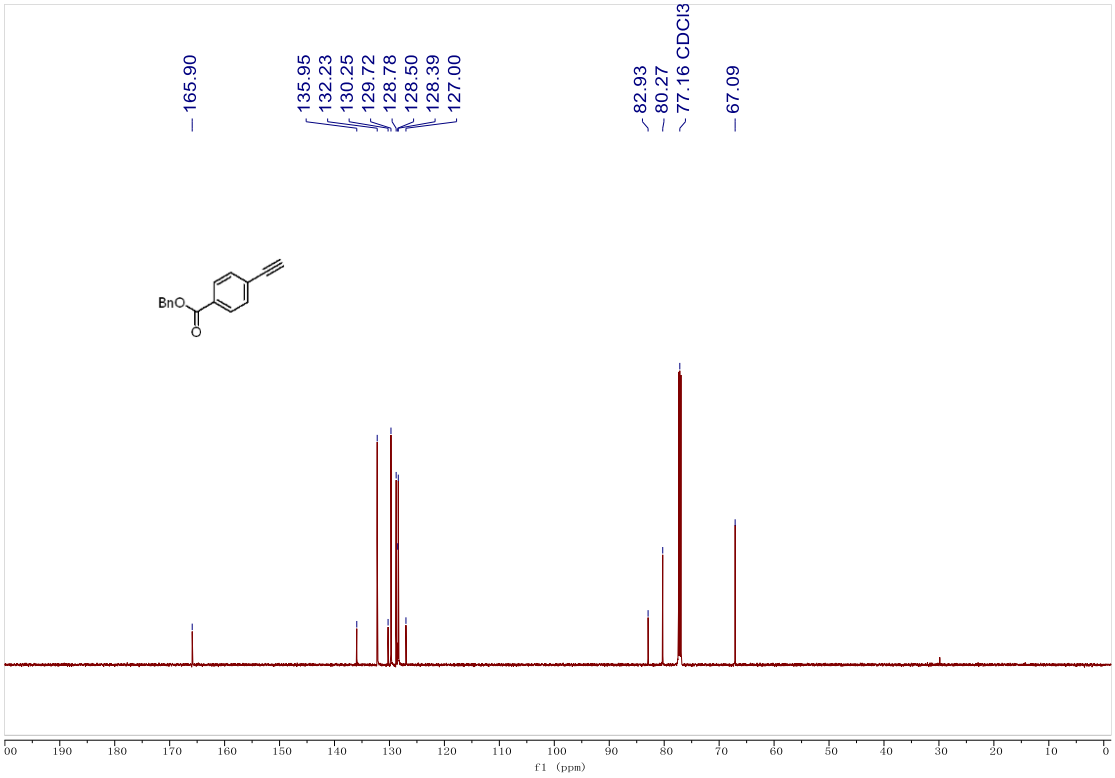
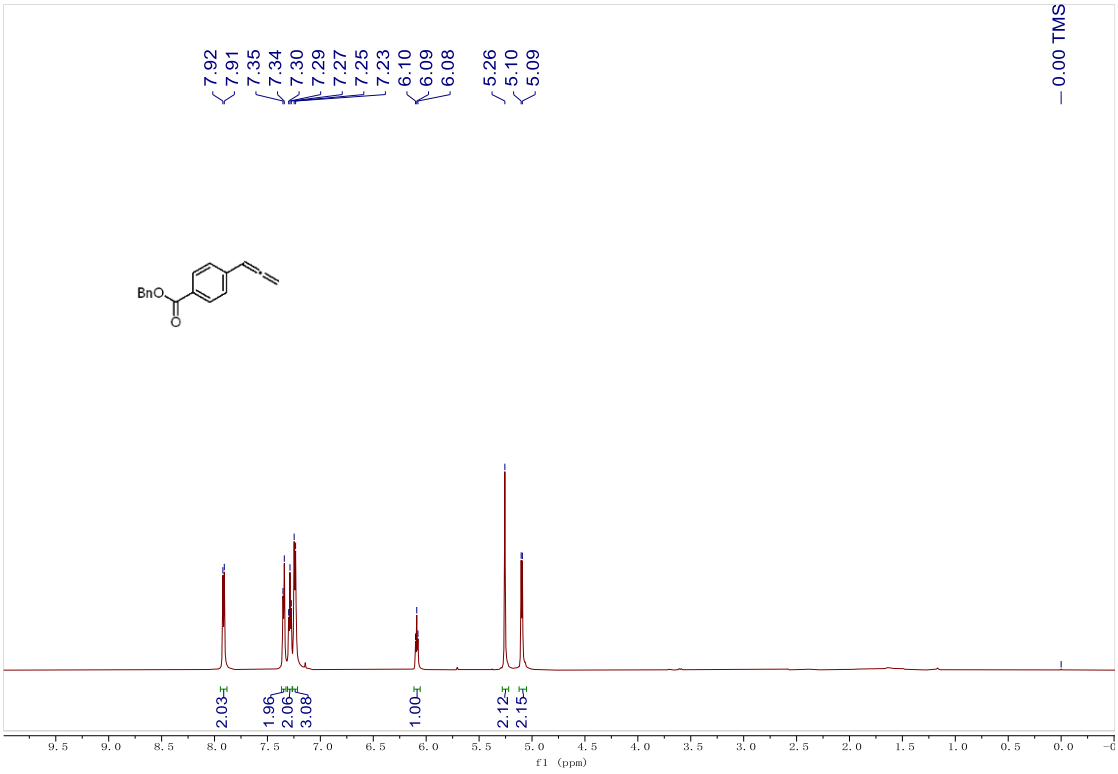


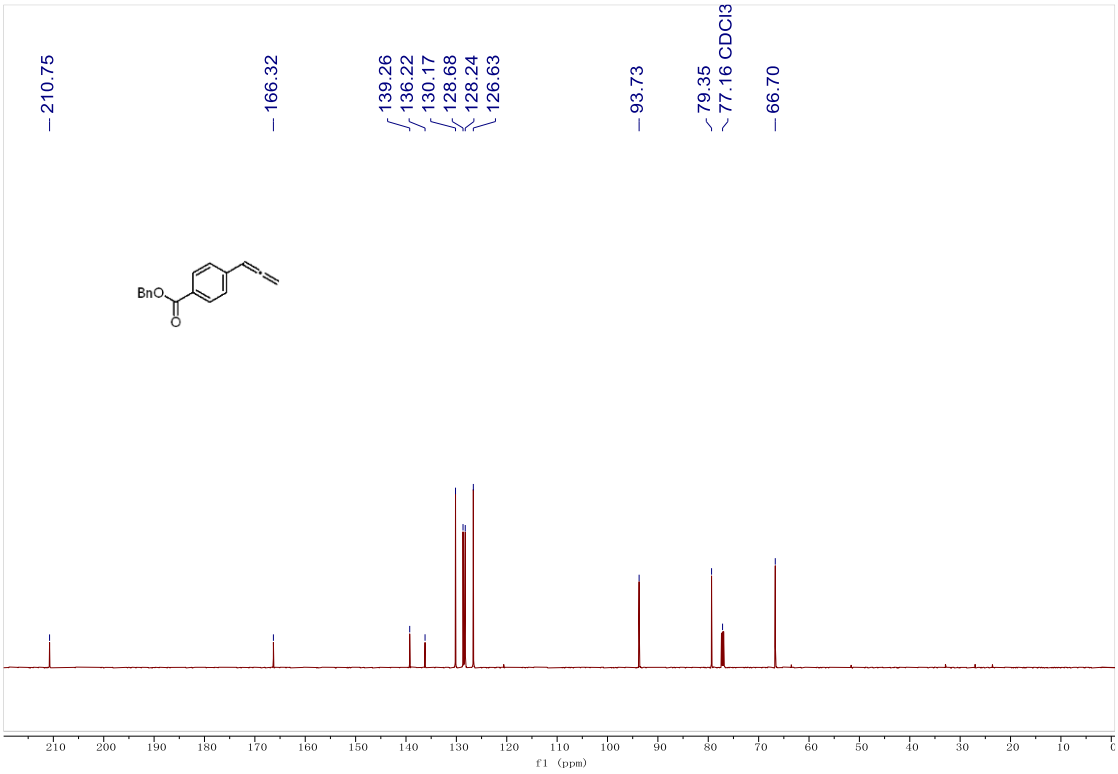

$^{1}$H NMR spectrum (600 MHz, $CDCl_3$) of **6k**



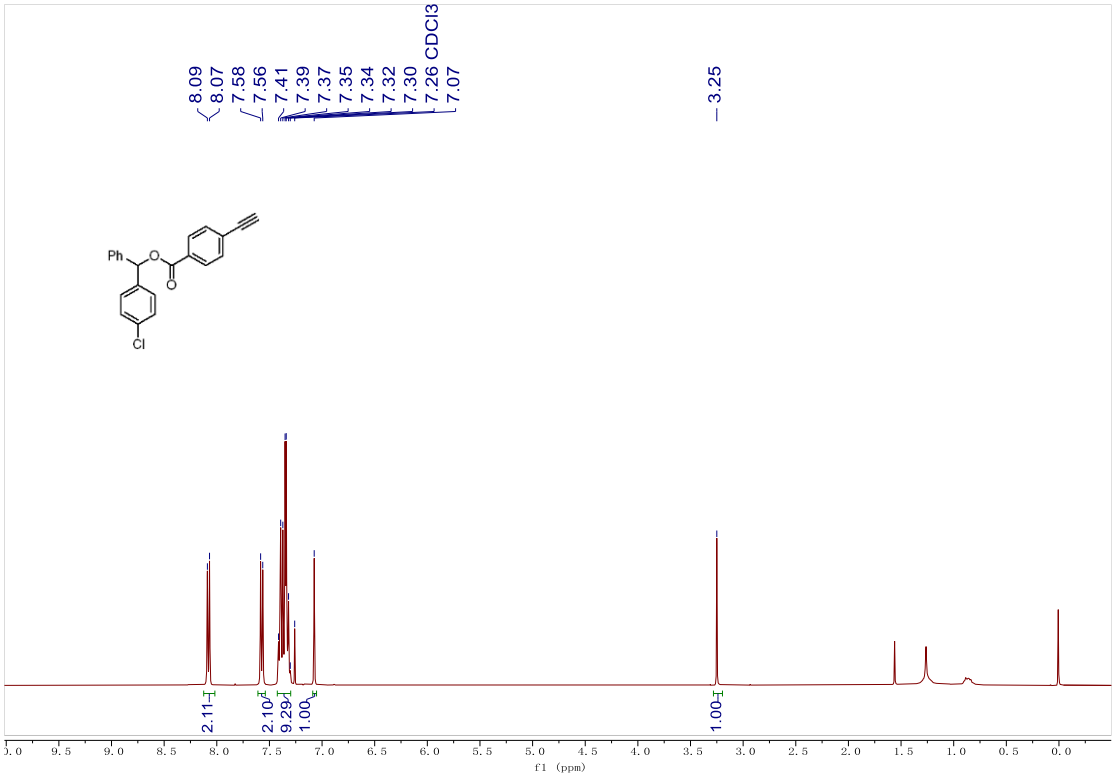

$^{13}$C NMR spectrum (151 MHz, $CDCl_3$) of **6k**



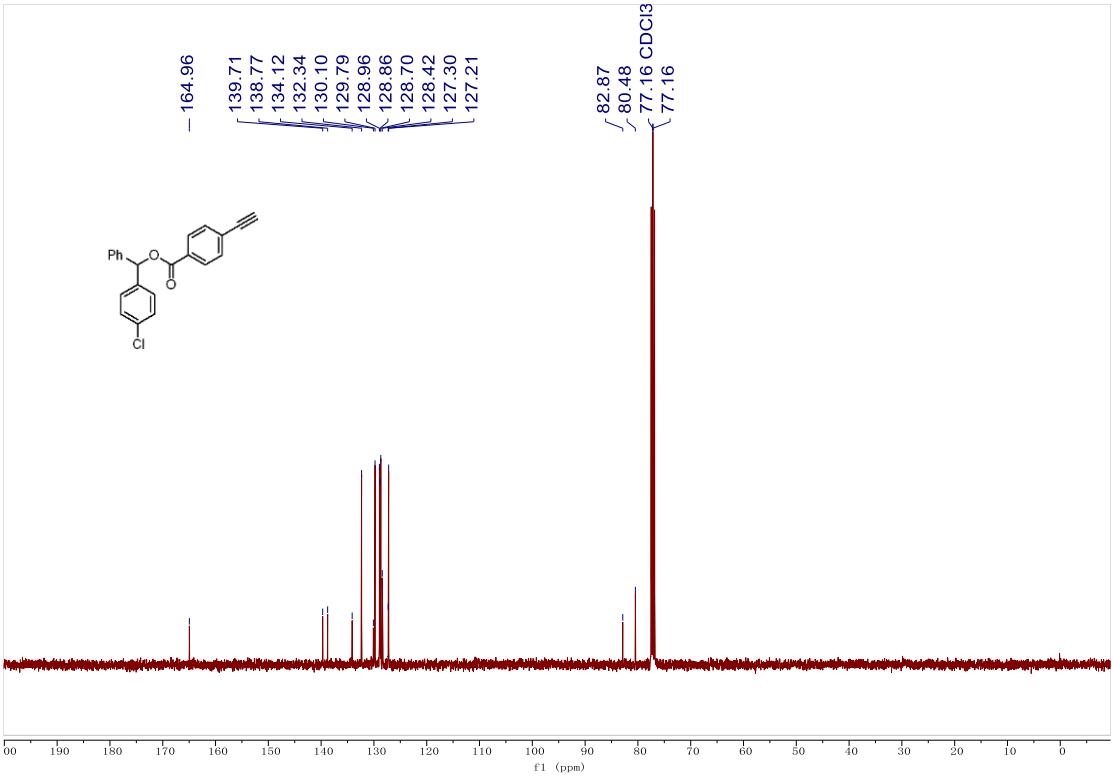

$^{1}$H NMR spectrum (600 MHz, CDCl3) of **1k**




$^{13}$C NMR spectrum (151 MHz, CDCl3) of **1k**




$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **6l**

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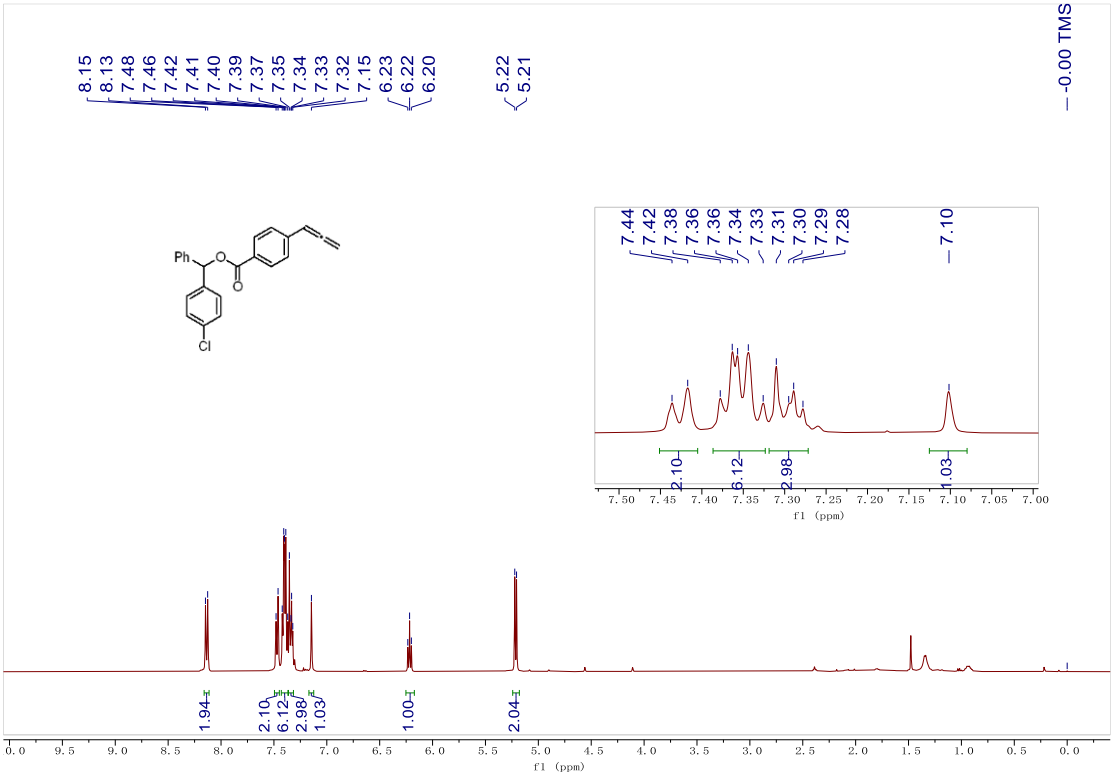
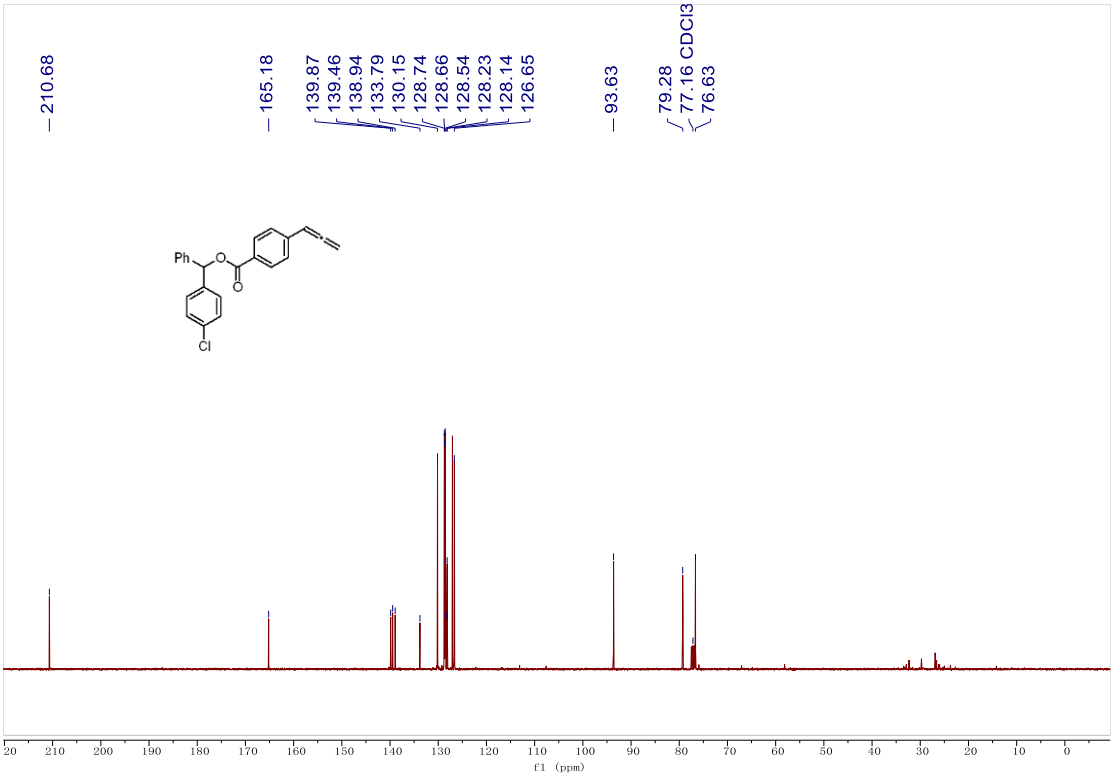



$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **1l**

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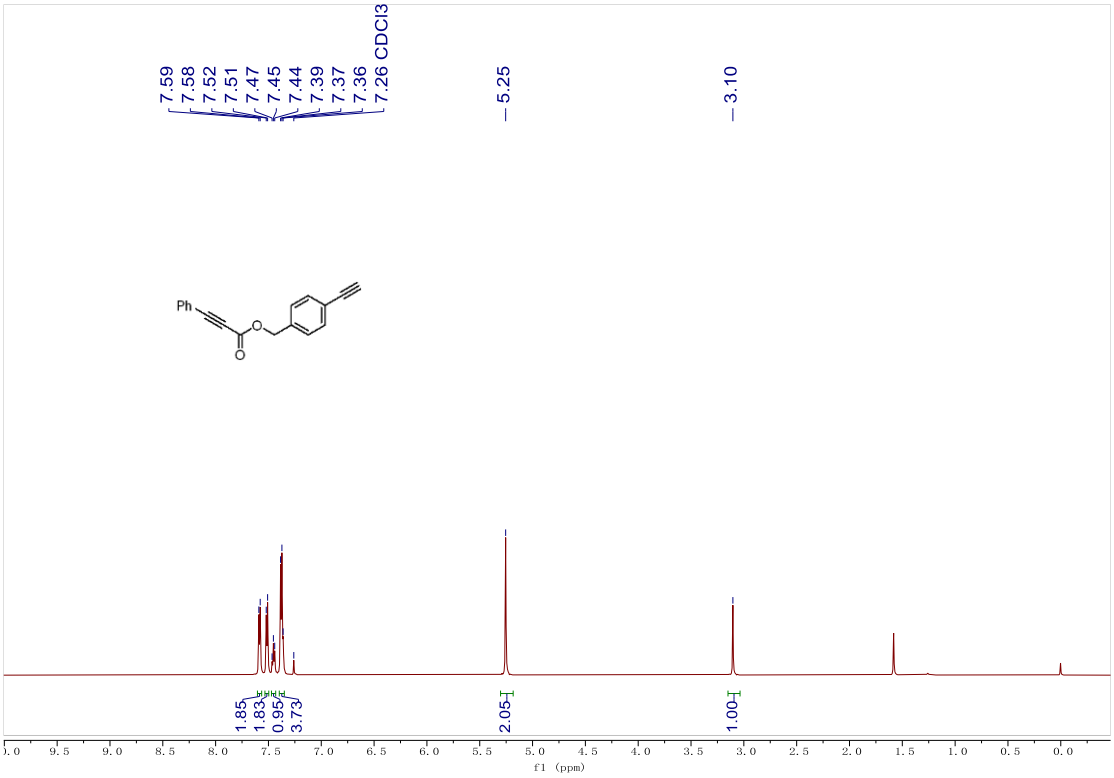
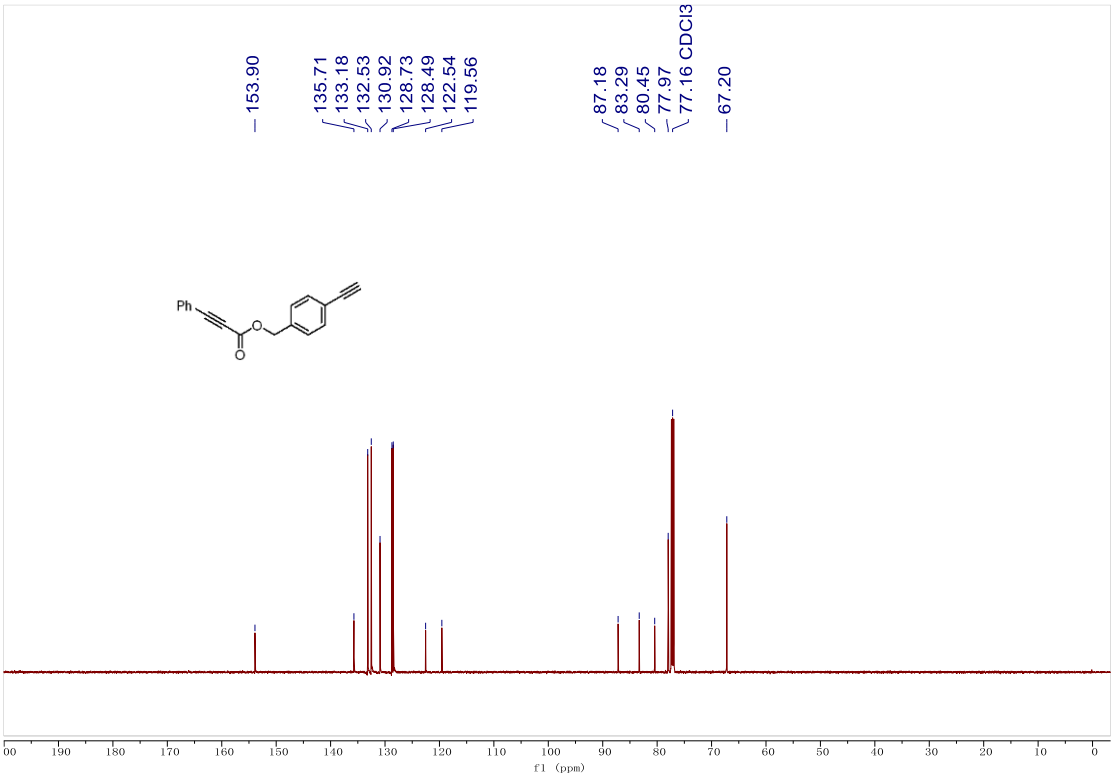
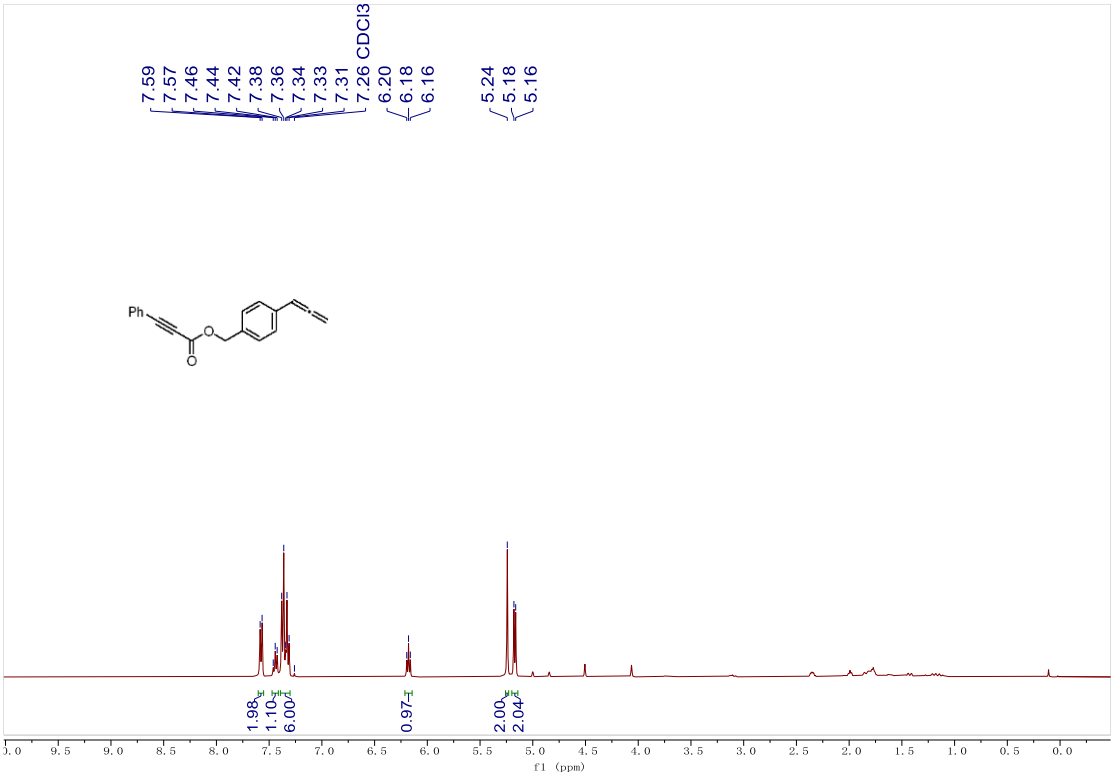


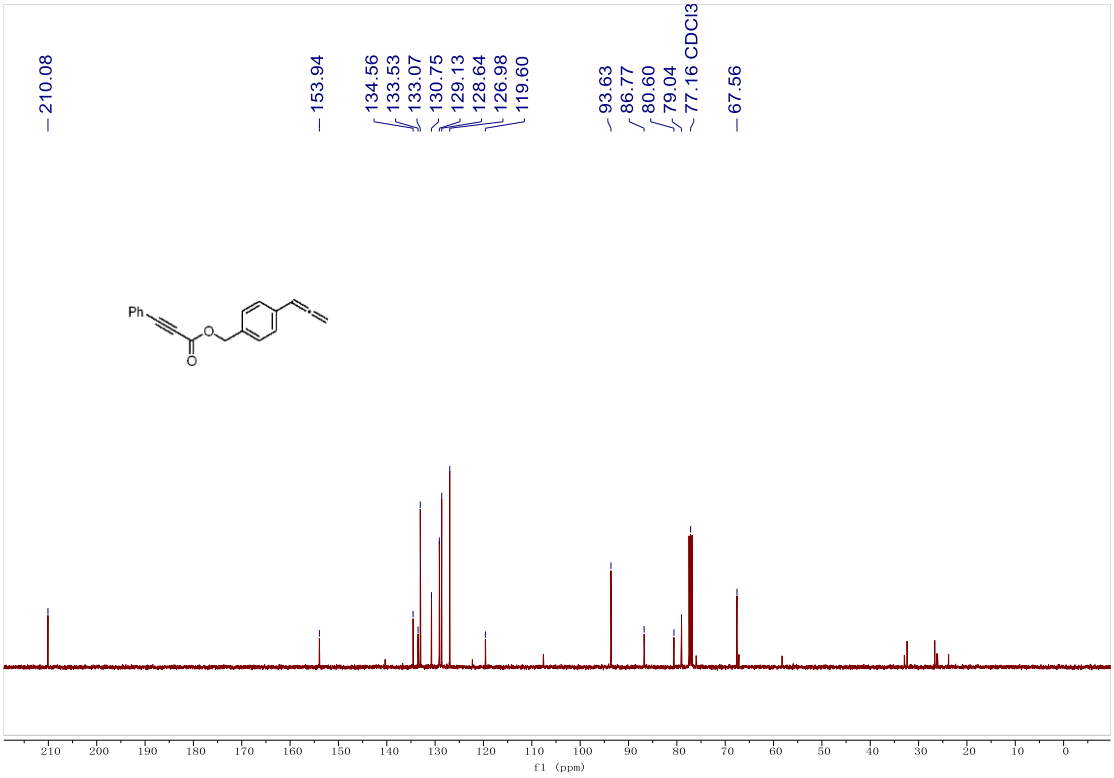

$^{1}$H NMR spectrum (600 MHz, $CDCl_3$) of **6m**




$^{13}$C NMR spectrum (151 MHz, $CDCl_3$) of **6m**




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

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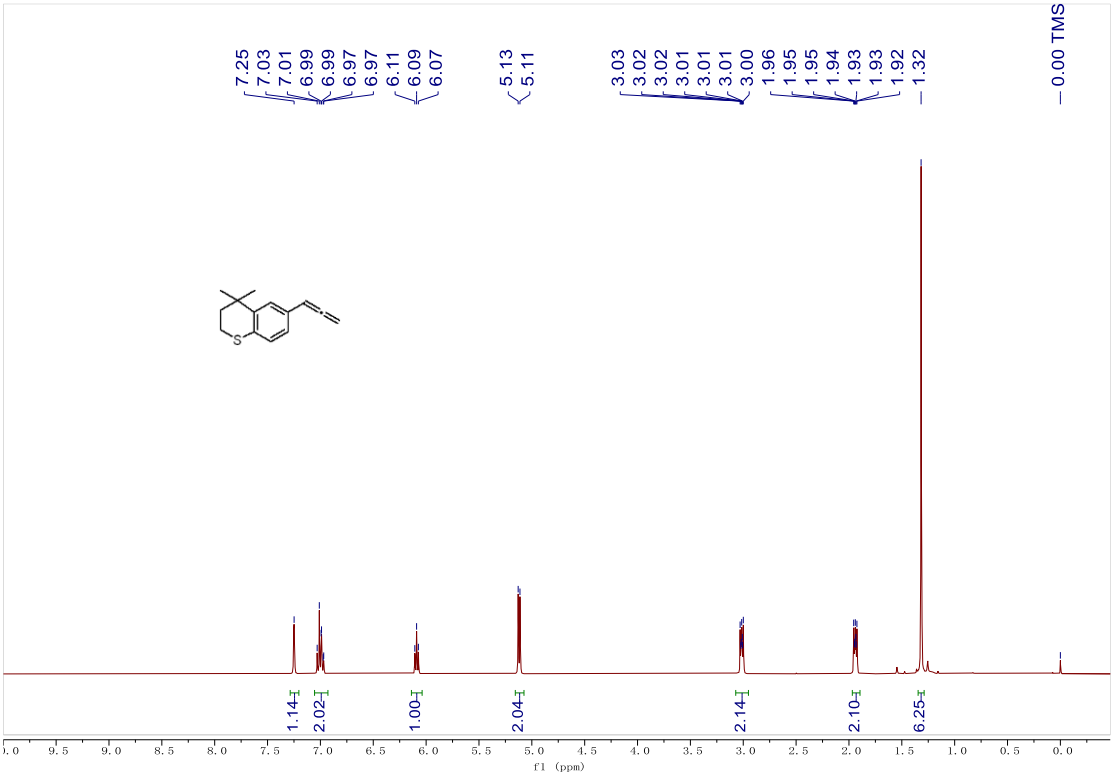
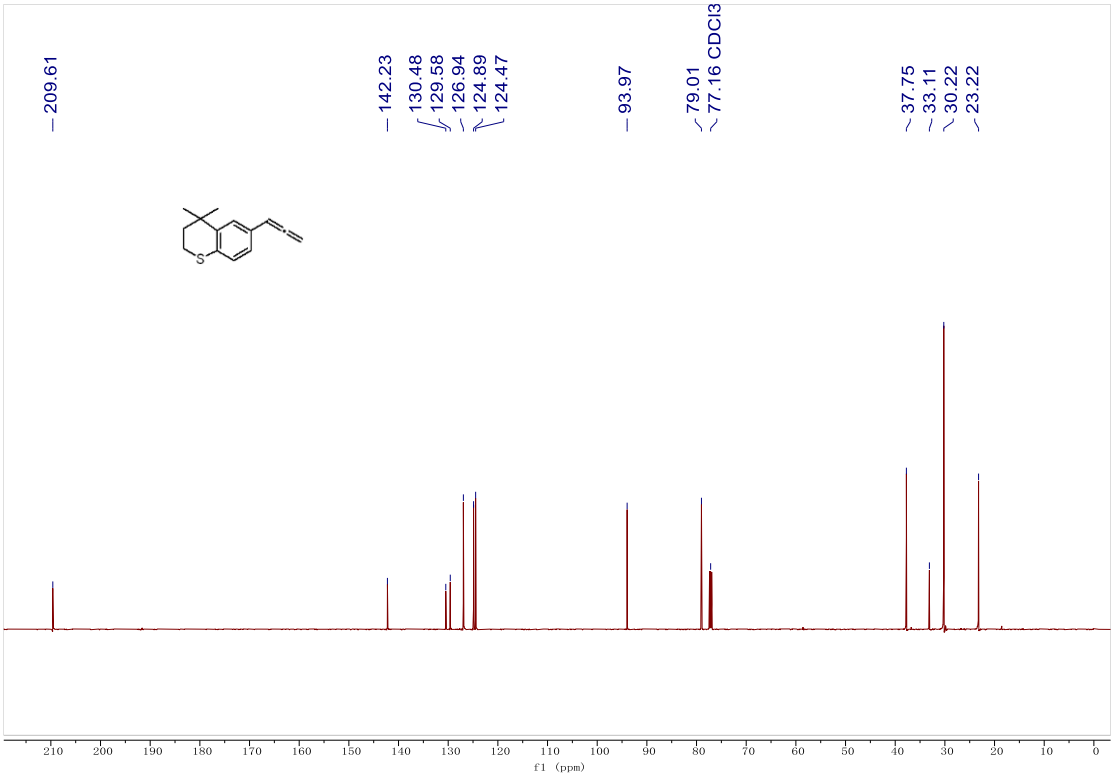
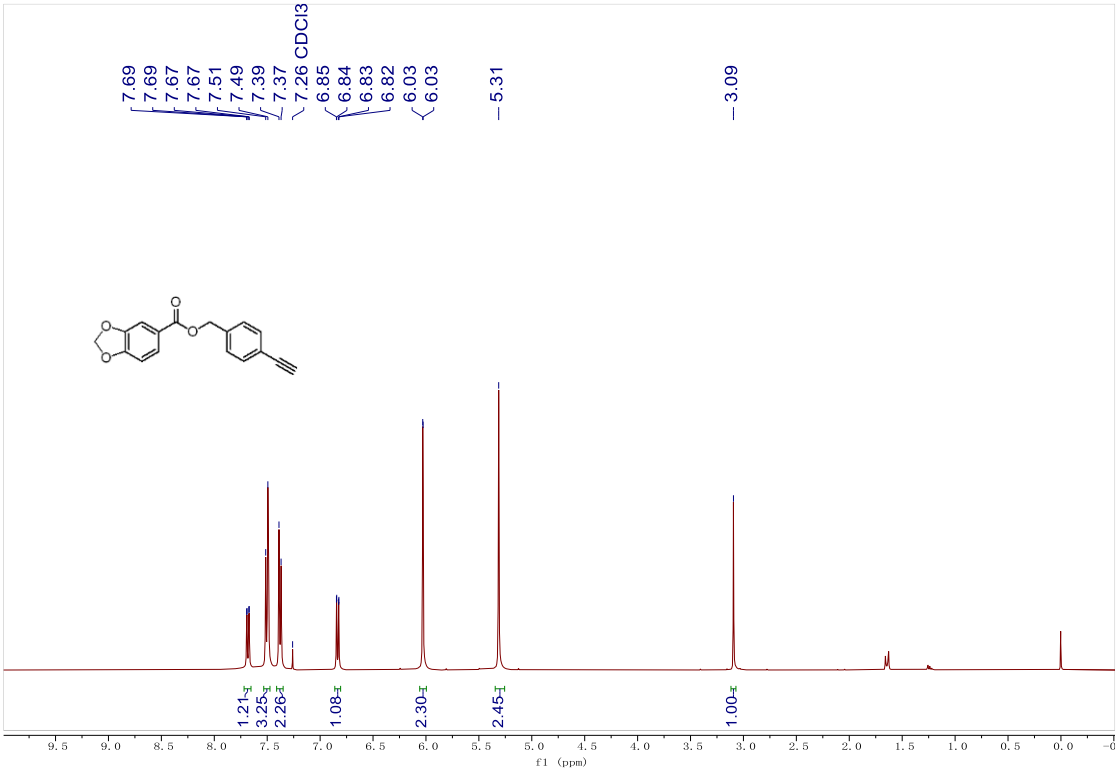


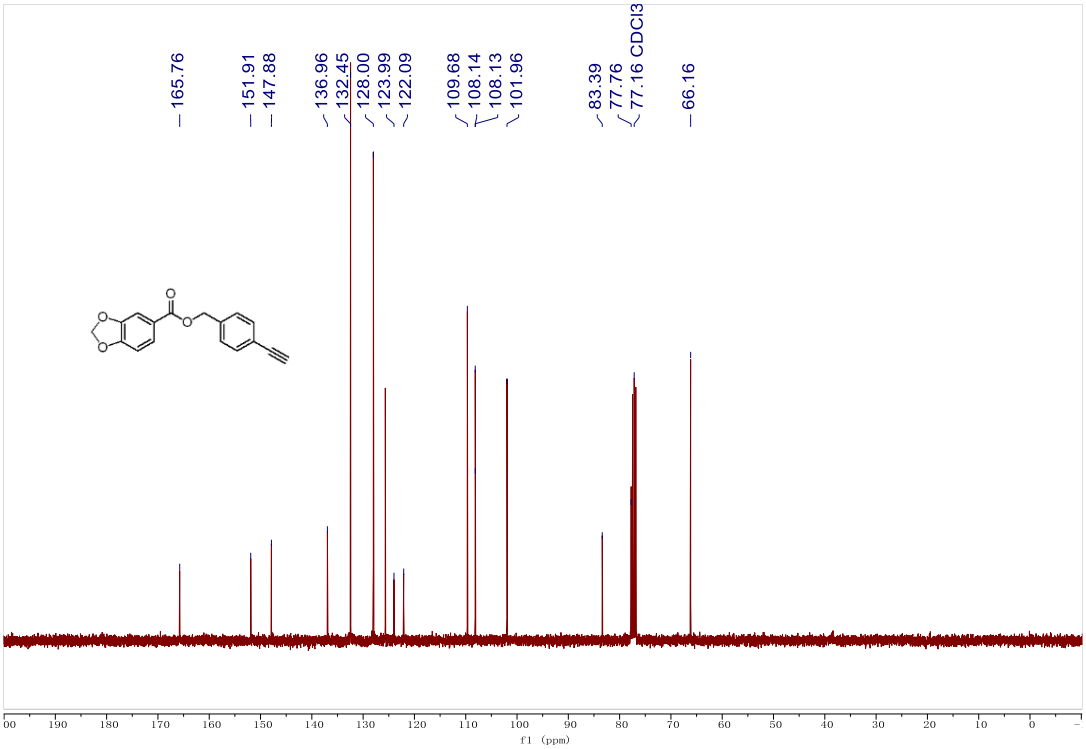

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **1n**




$^{13}$C NMR spectrum (151 MHz, $CDCl_3$) of **1n**




$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **6o**

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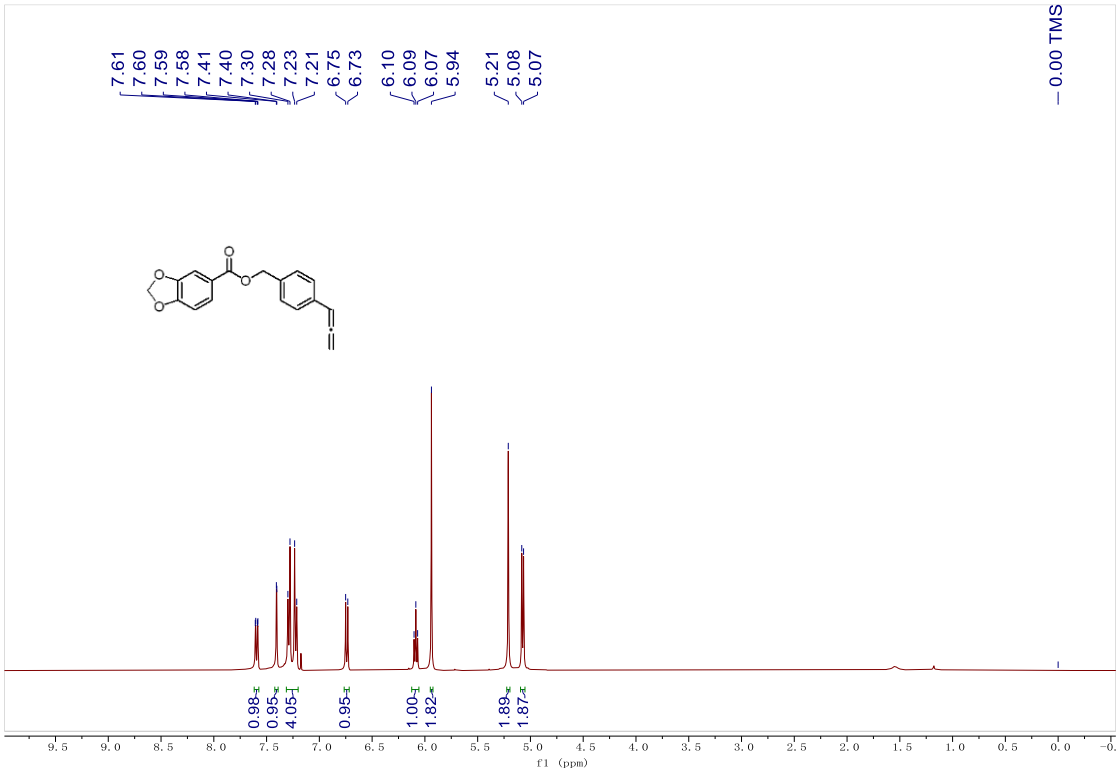


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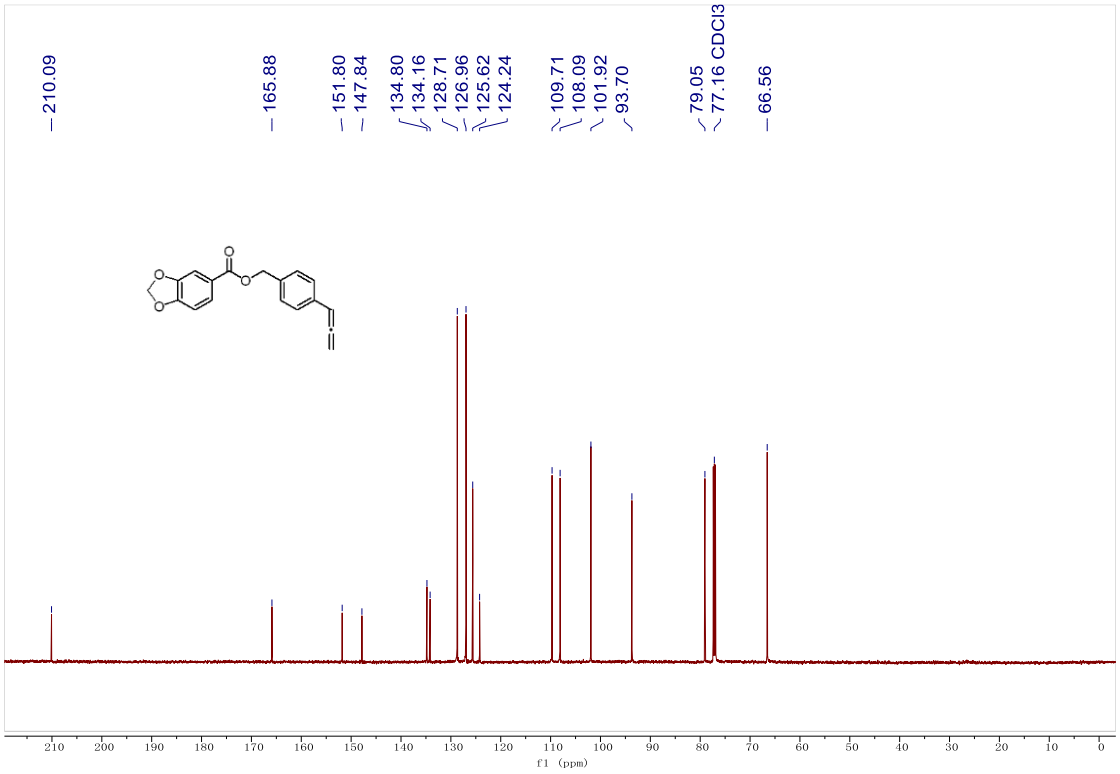
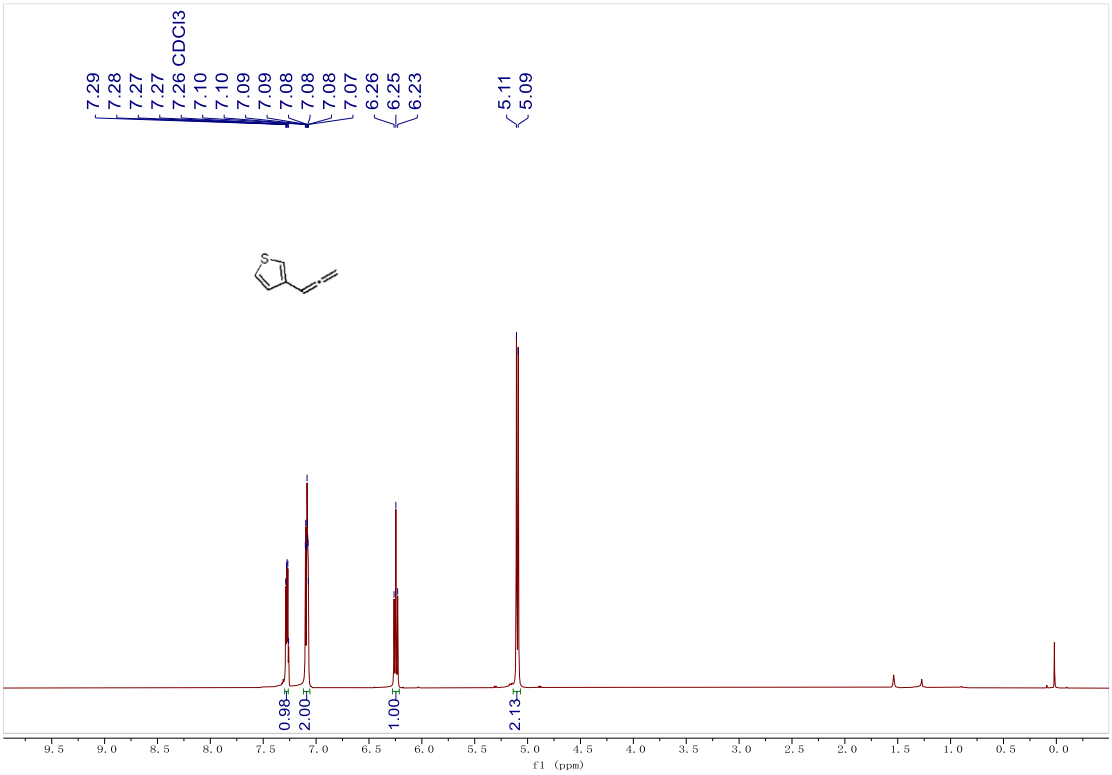
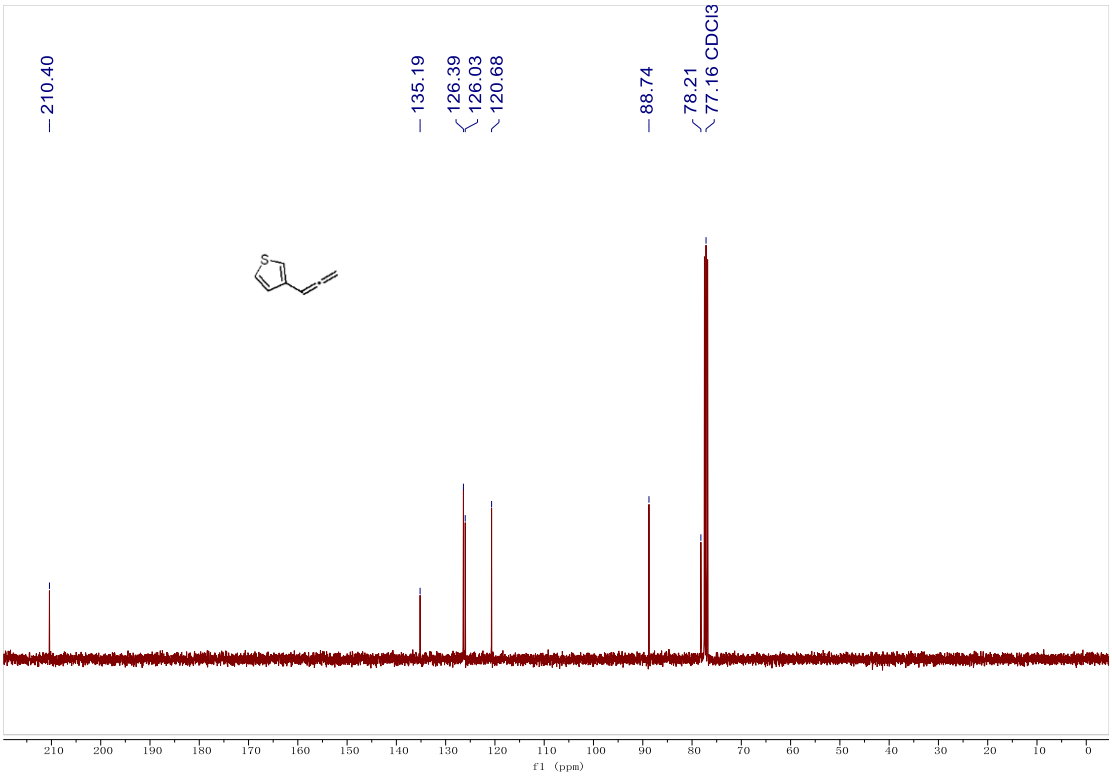


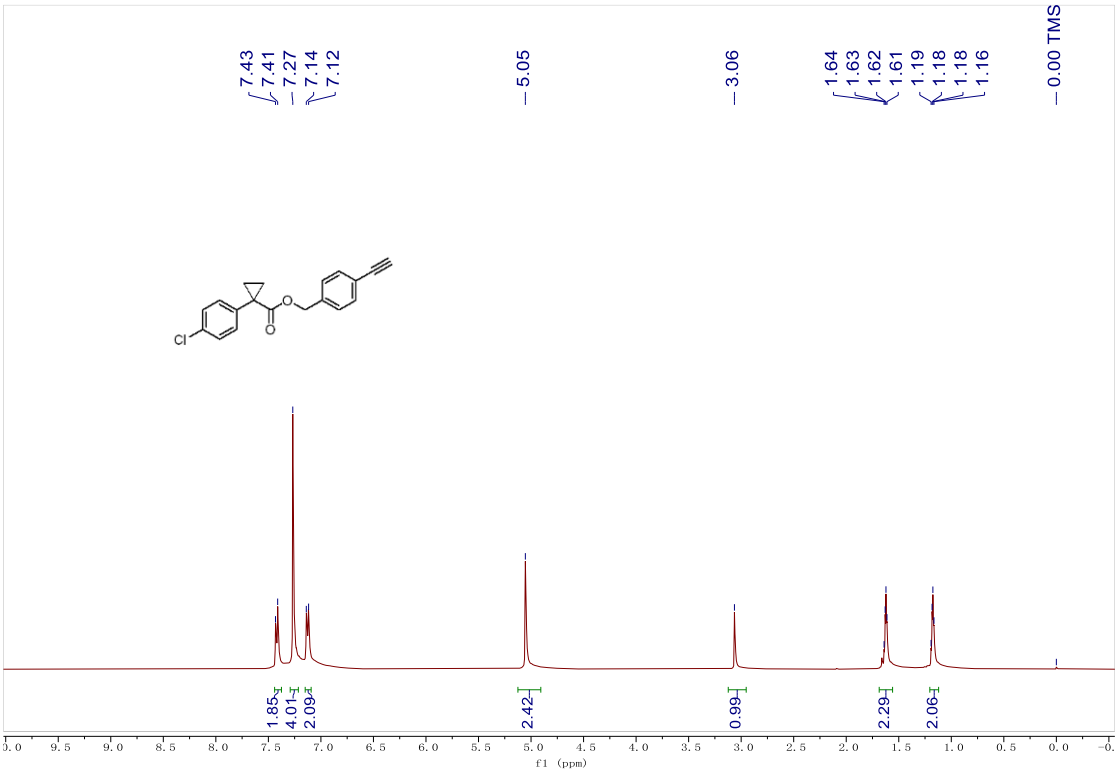

$^{13}$C NMR spectrum (151 MHz, $CDCl_3$) of **1o**



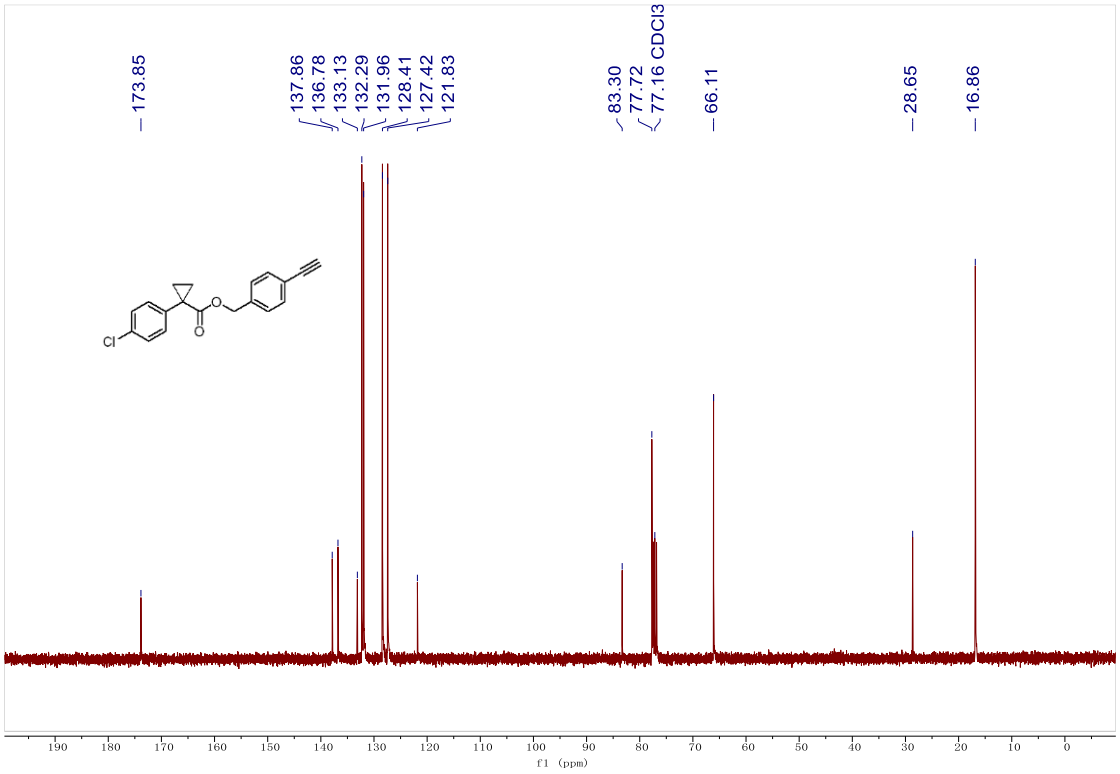

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **1p**



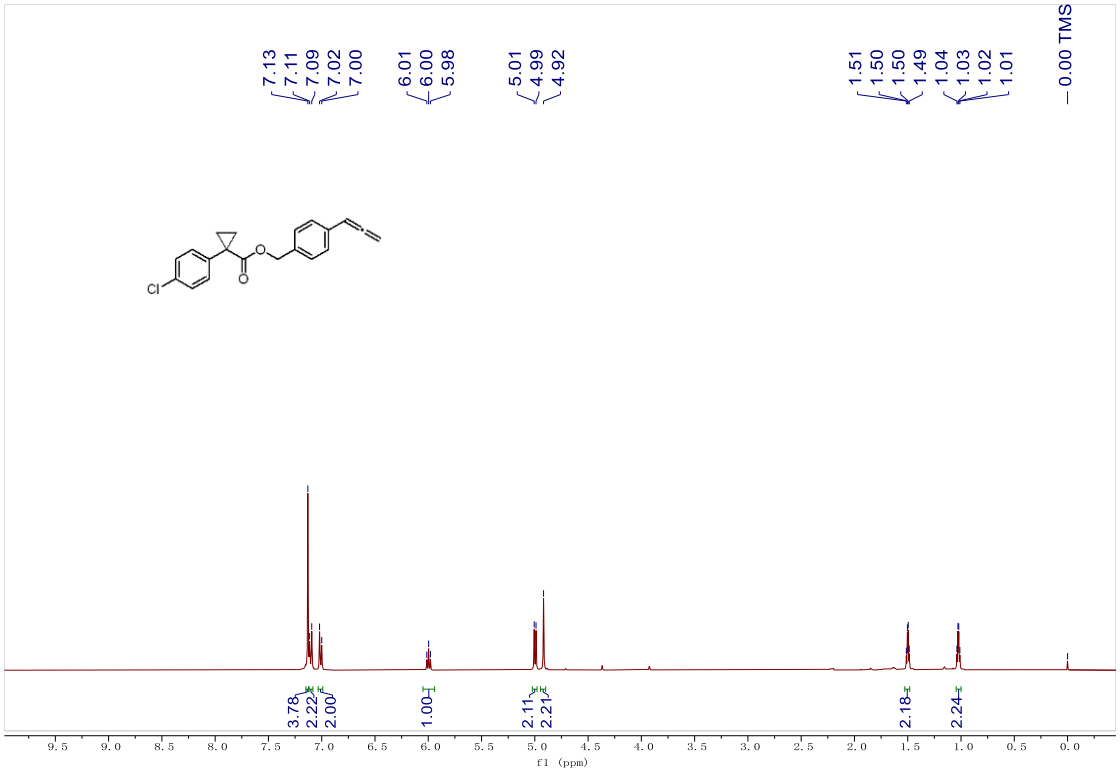

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **1p**



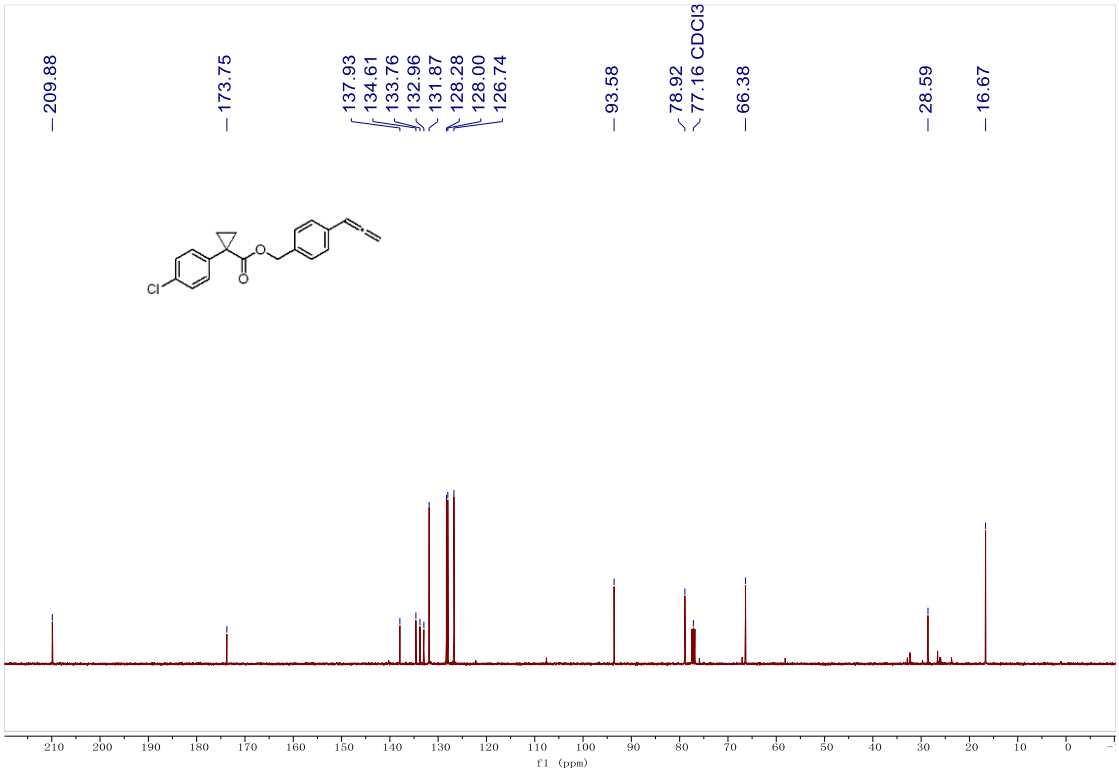

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **6q**



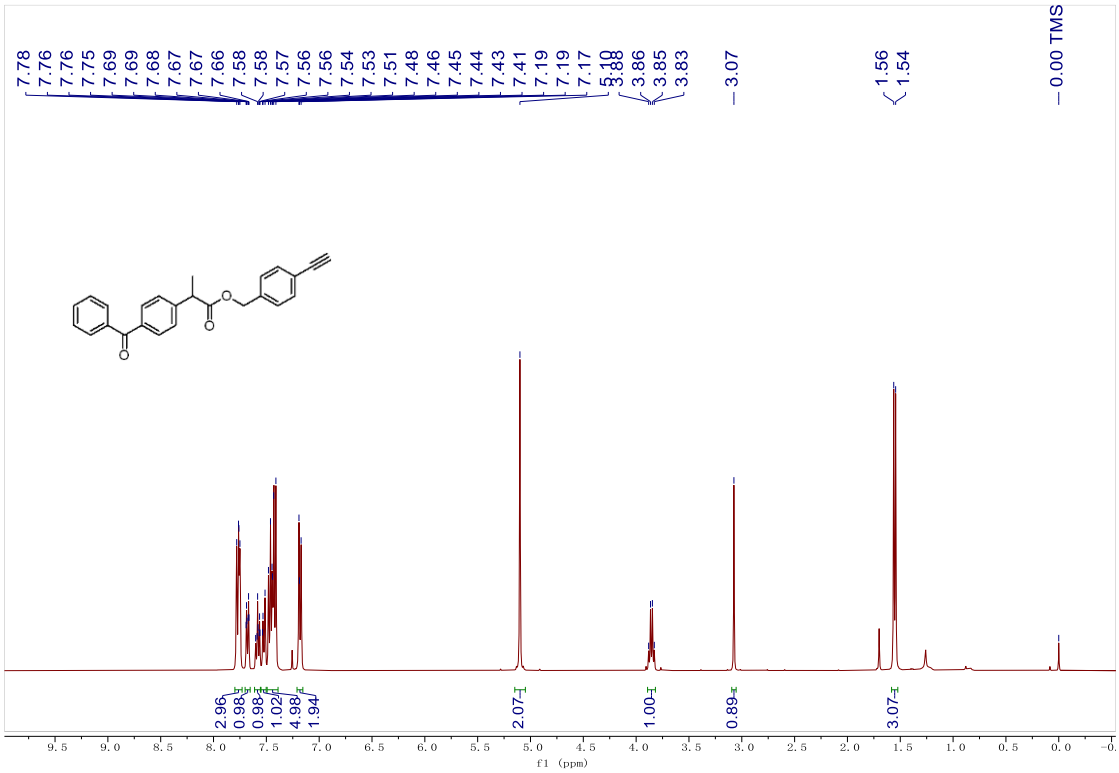

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **6q**



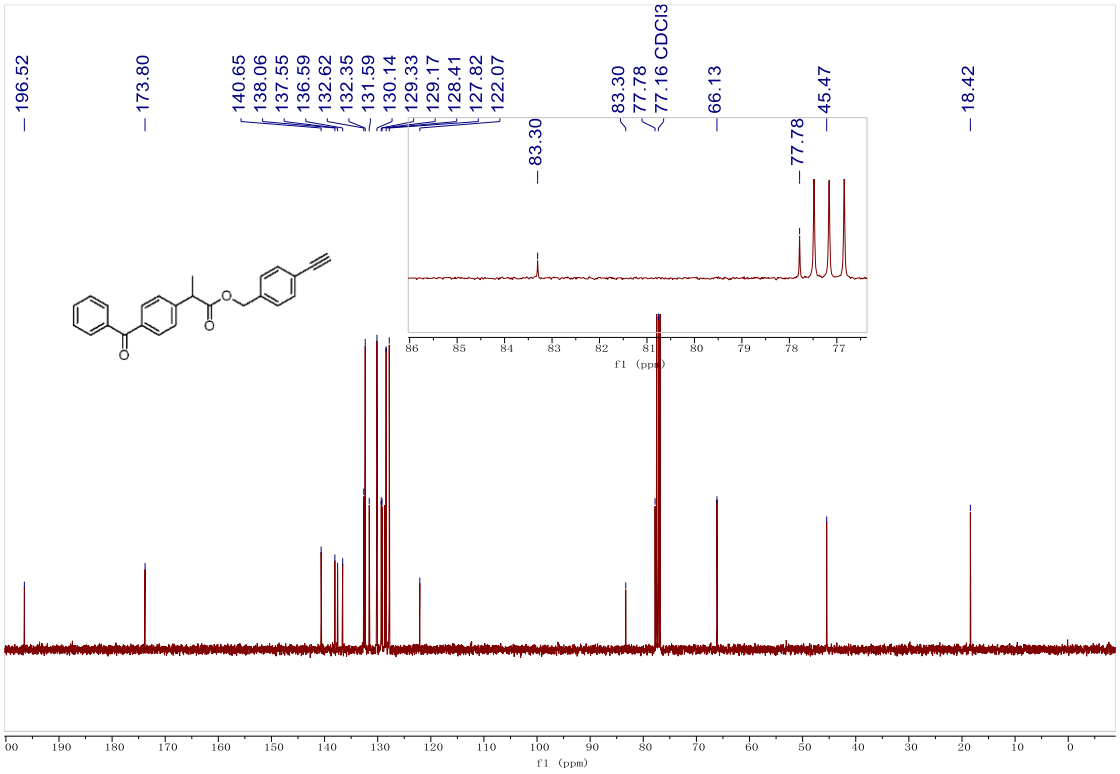

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **1q**



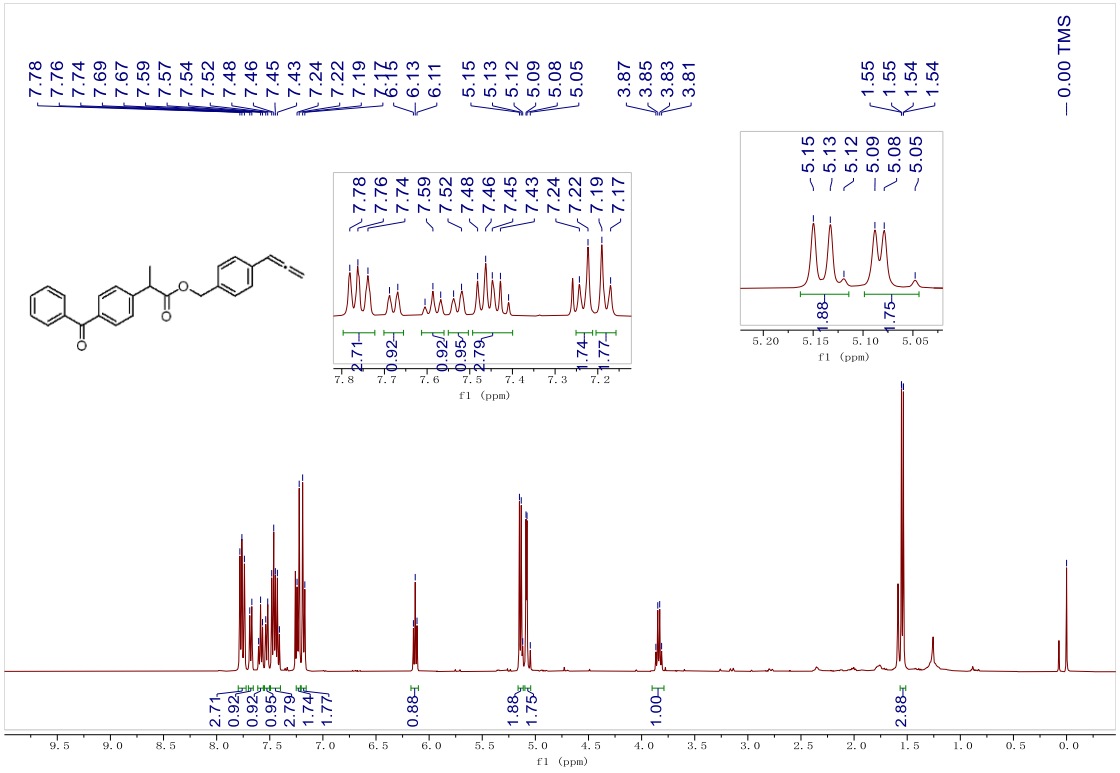

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **1q**



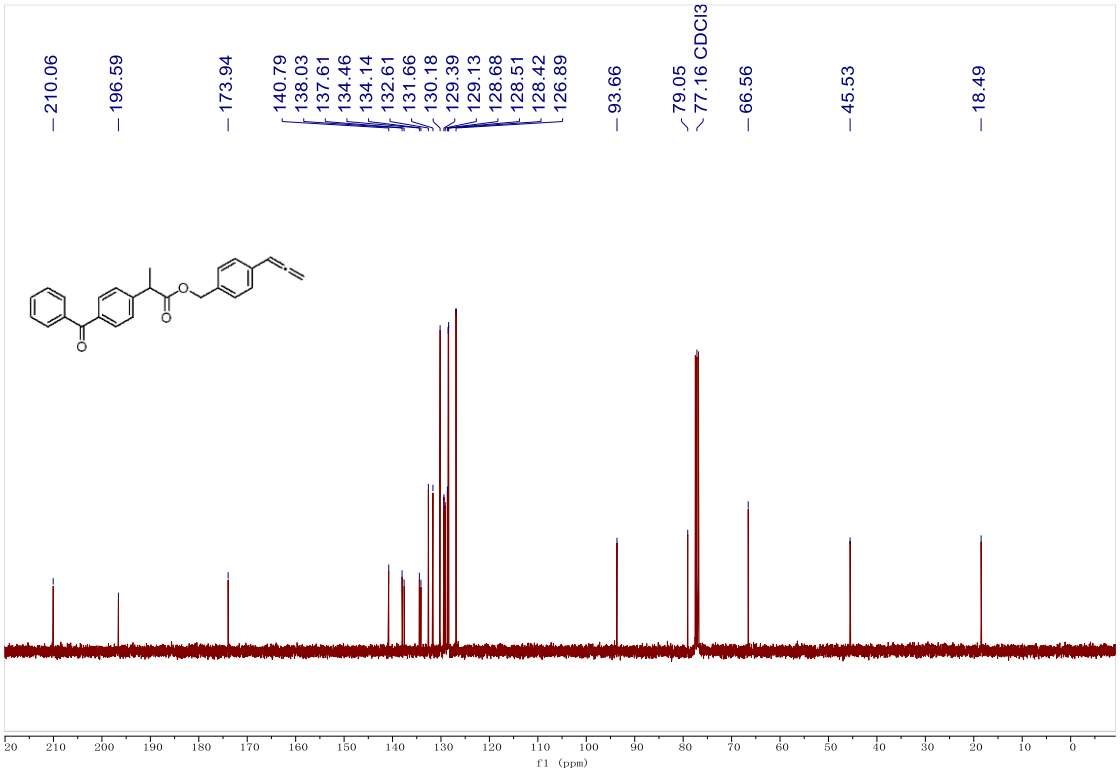

$^{1}$H NMR spectrum ((400 MHz, $CDCl_3$)) of **6r**



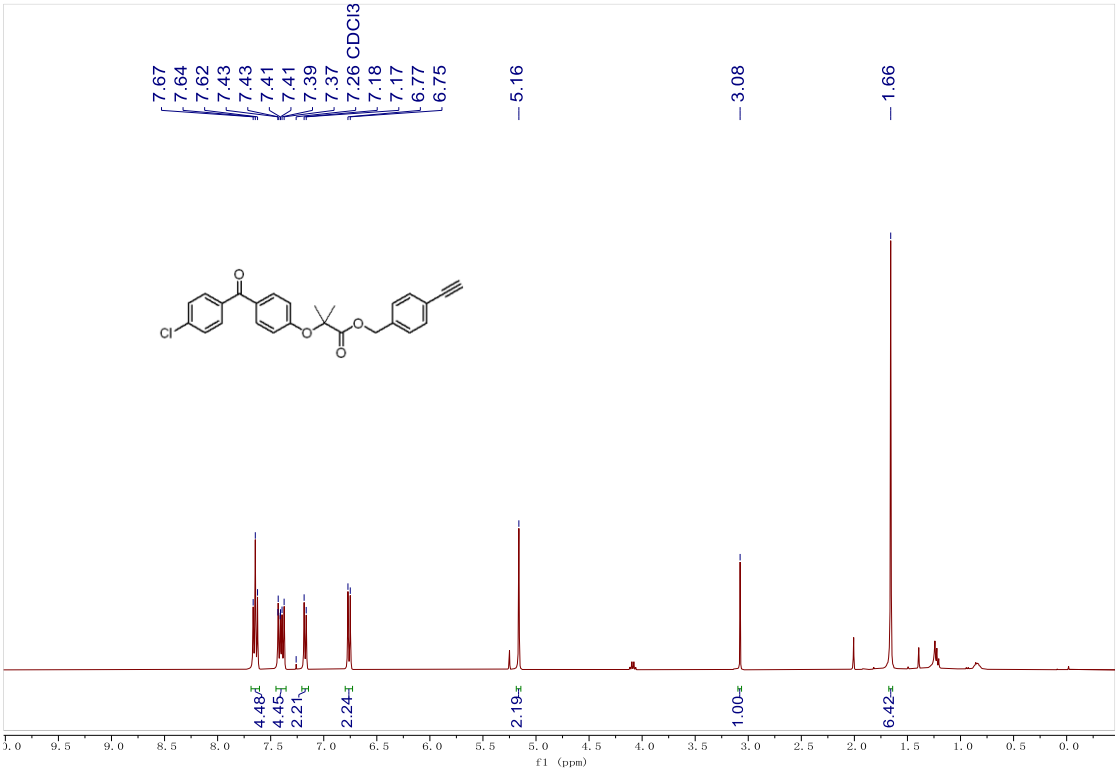

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **6r**



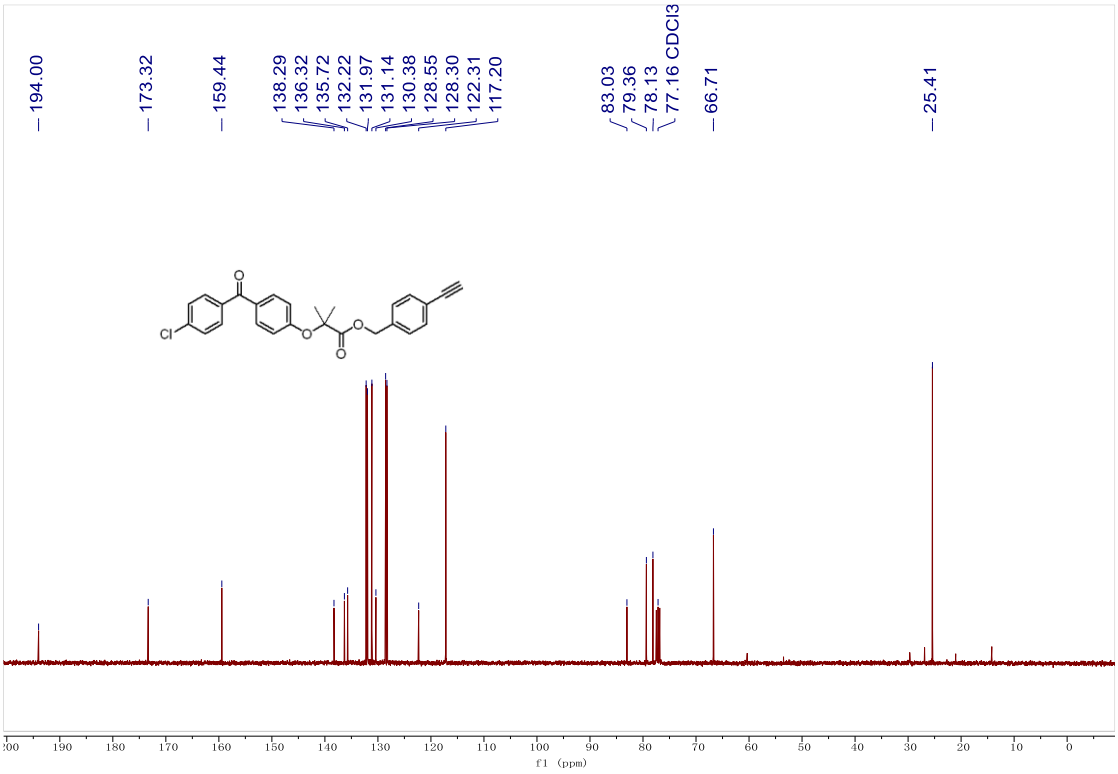

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **1r**



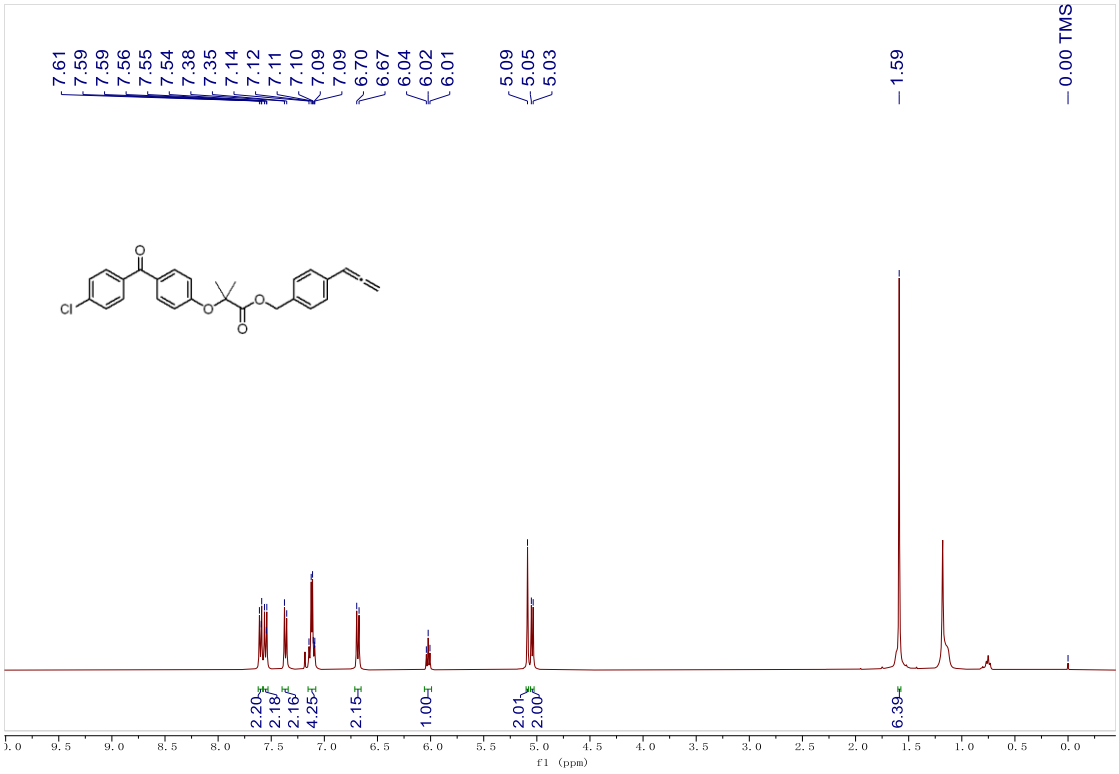

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **1r**



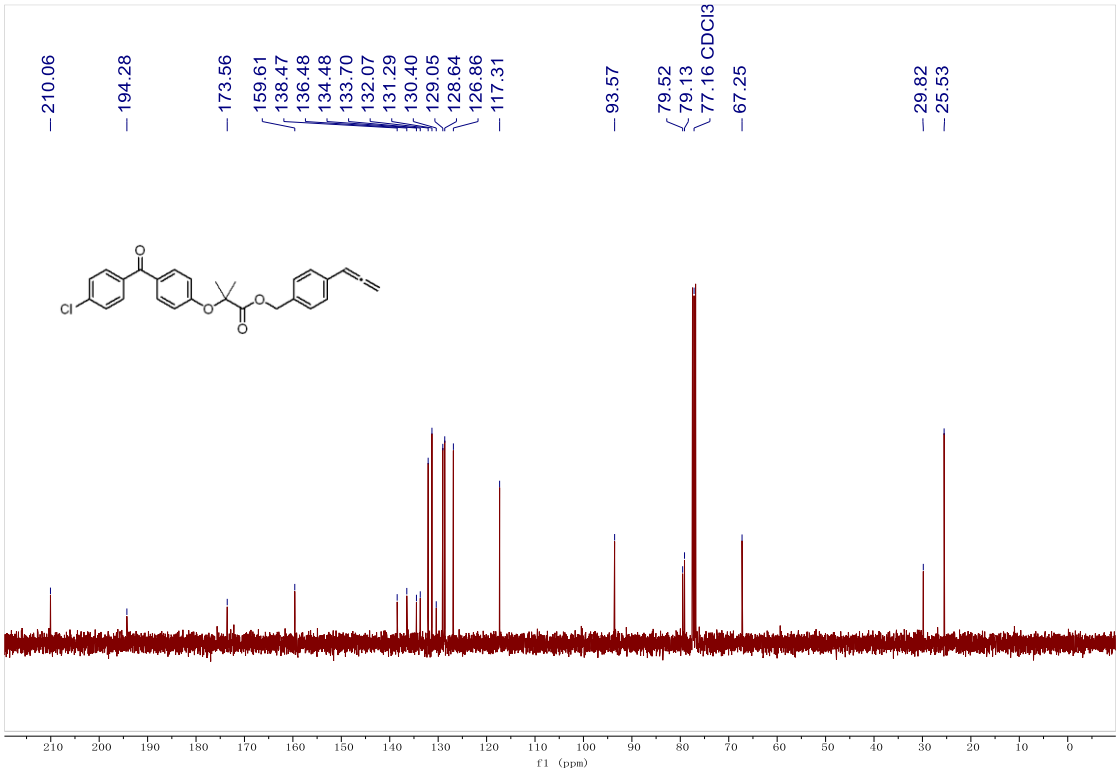

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **6s**



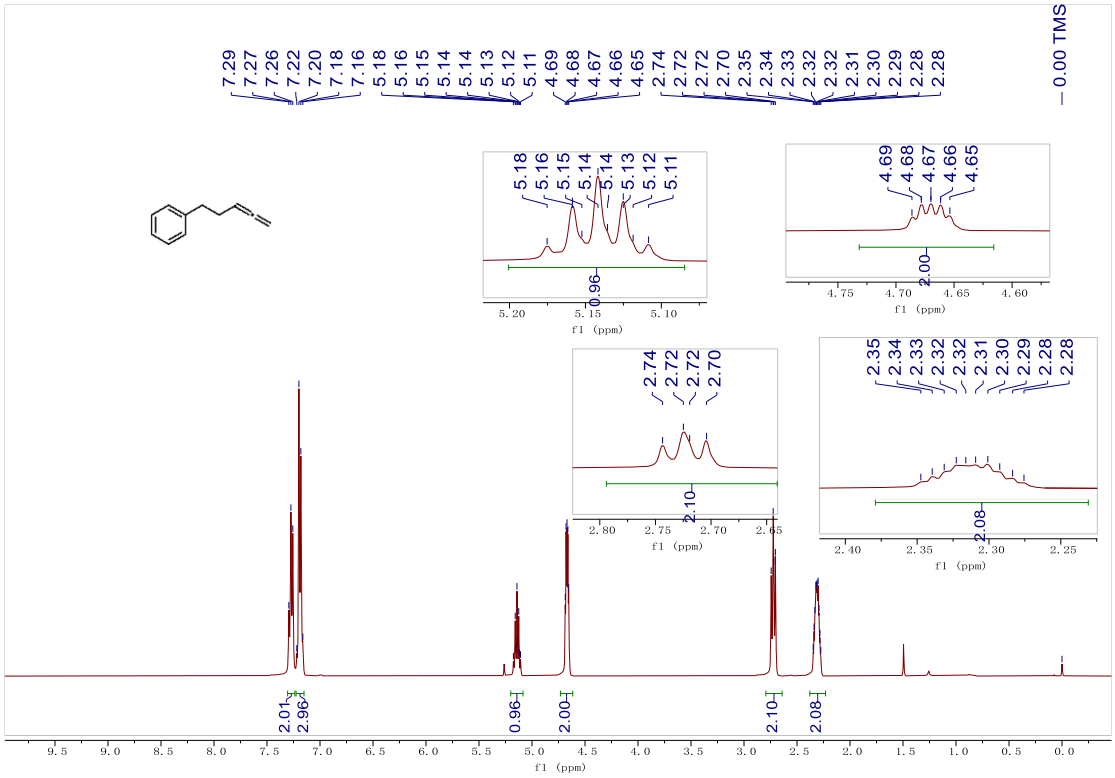

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **6s**



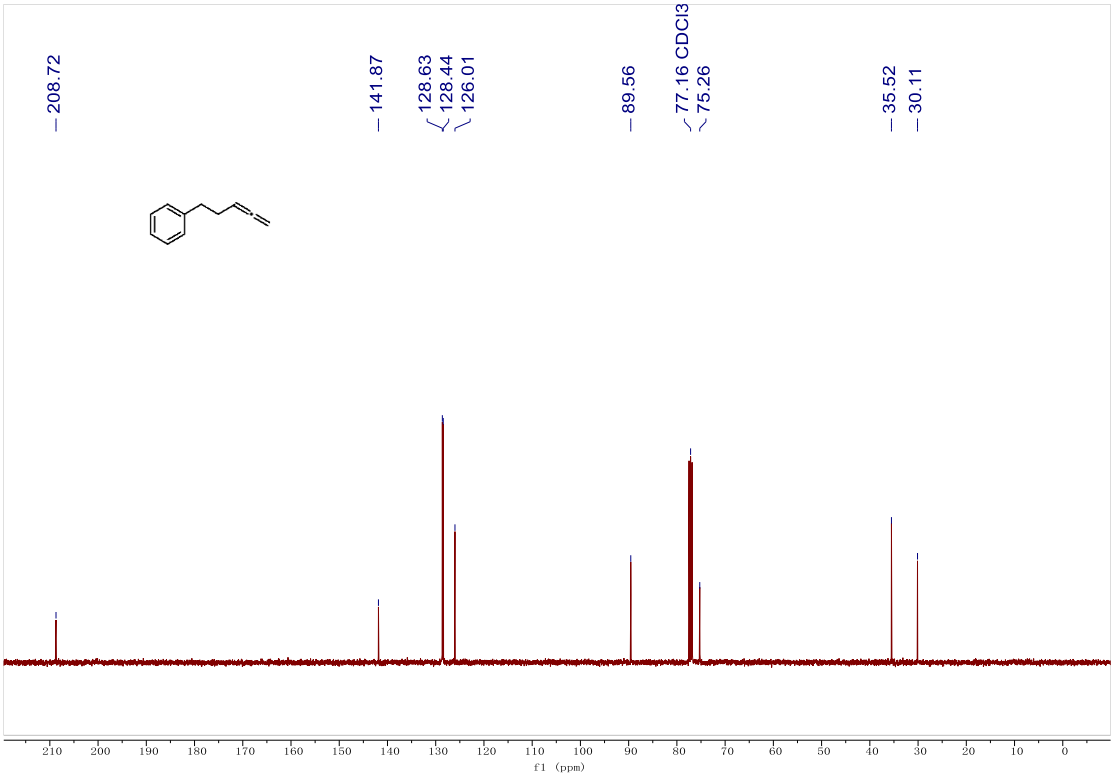

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **1s**



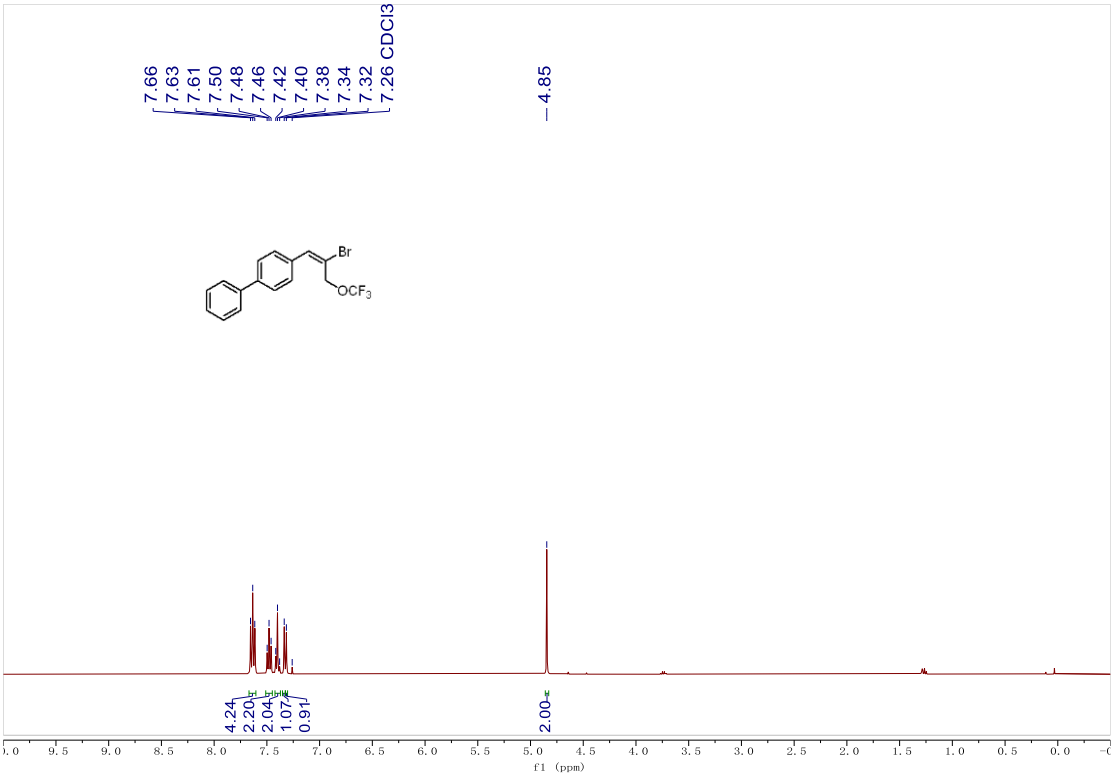

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **1s**



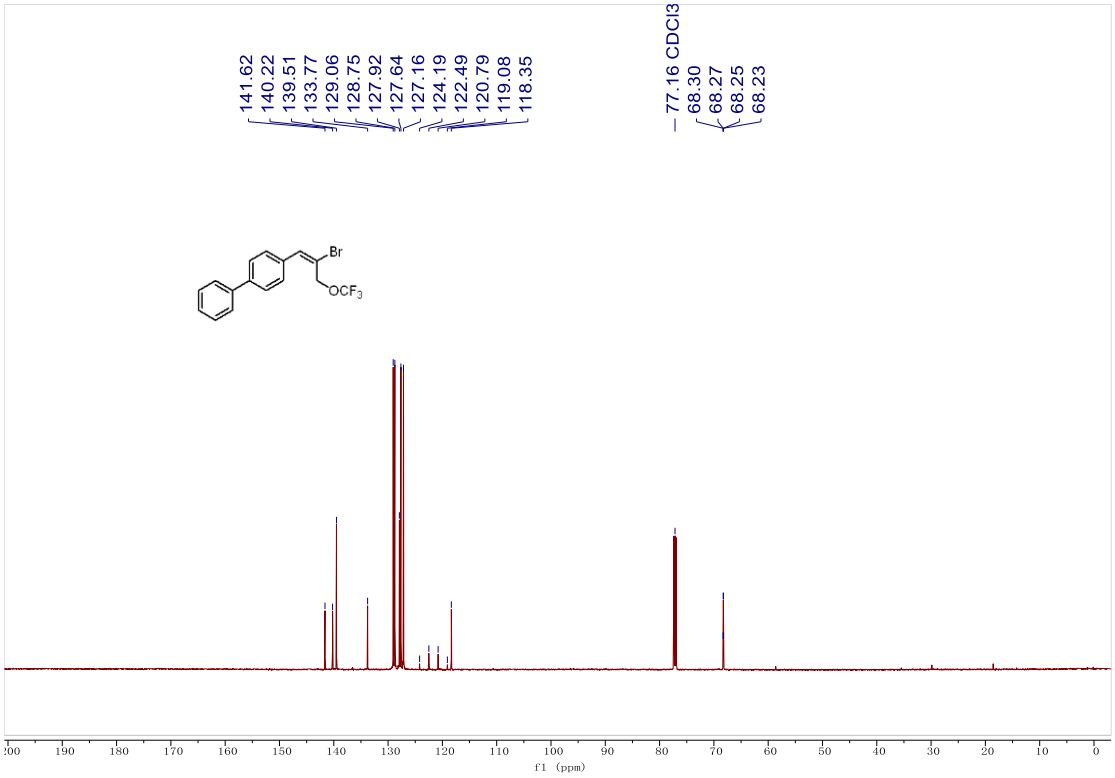

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **1t**



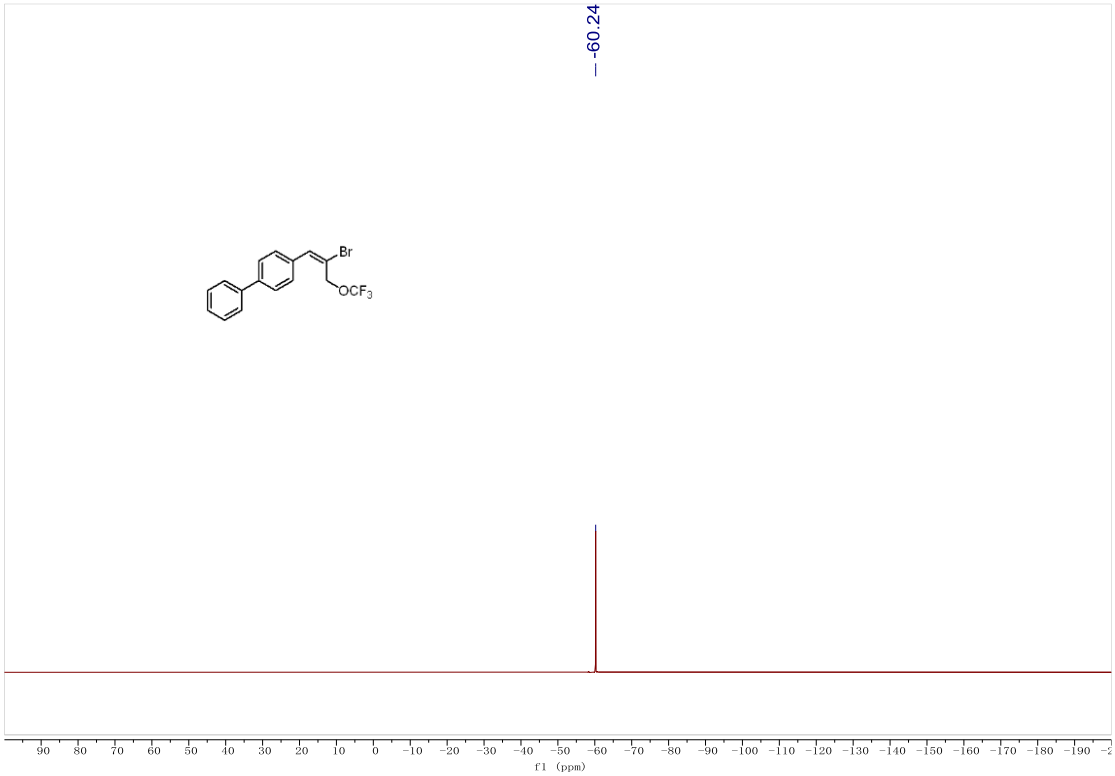

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **1t**



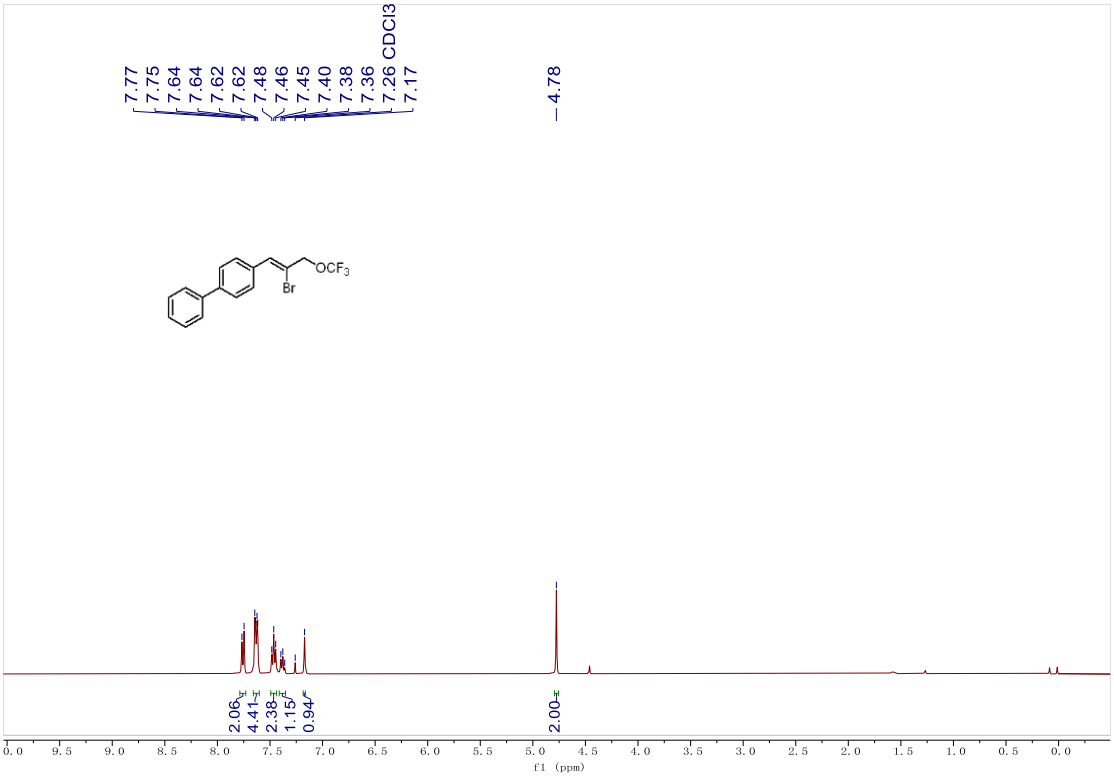

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **(*E*)-3a**



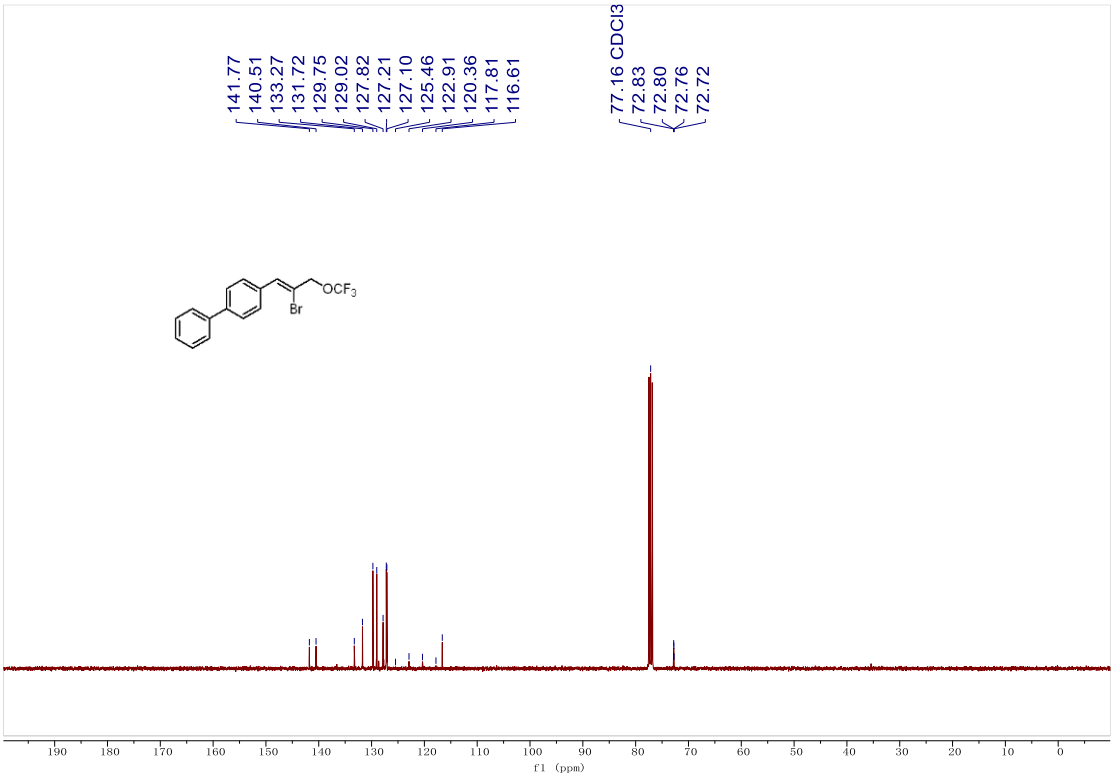

$^{13}$C NMR spectrum (151 MHz, $CDCl_3$) of **(*E*)-3a**



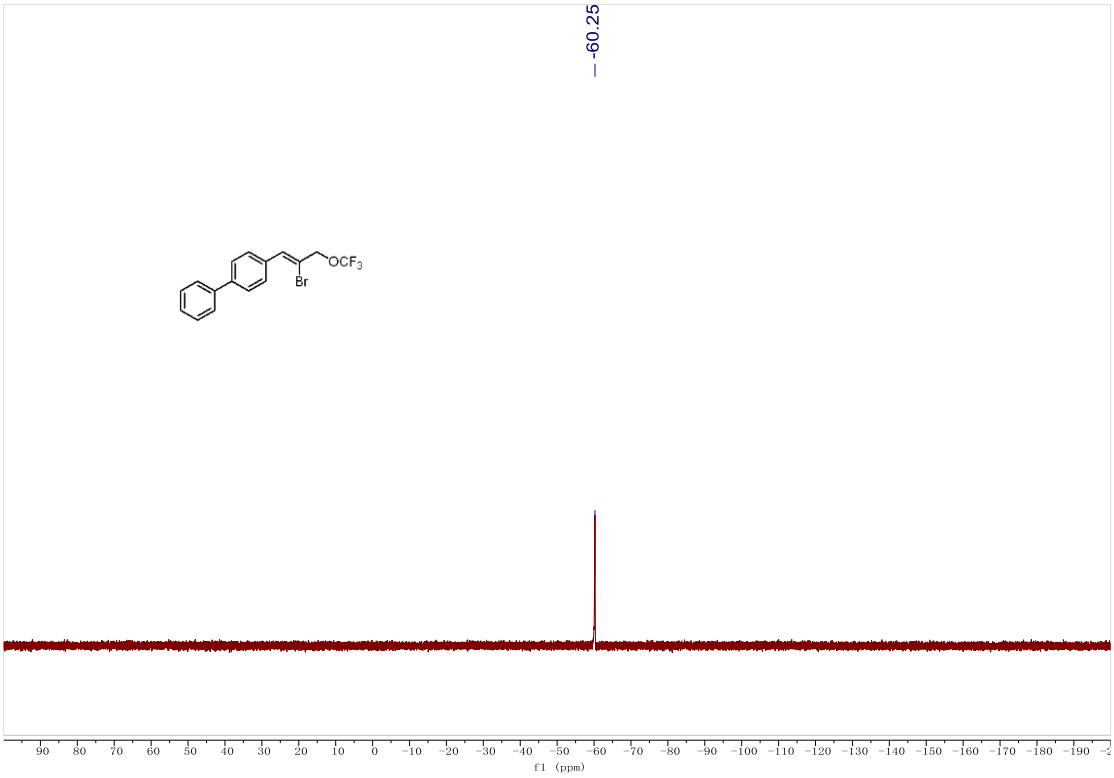

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*E*)-3a**



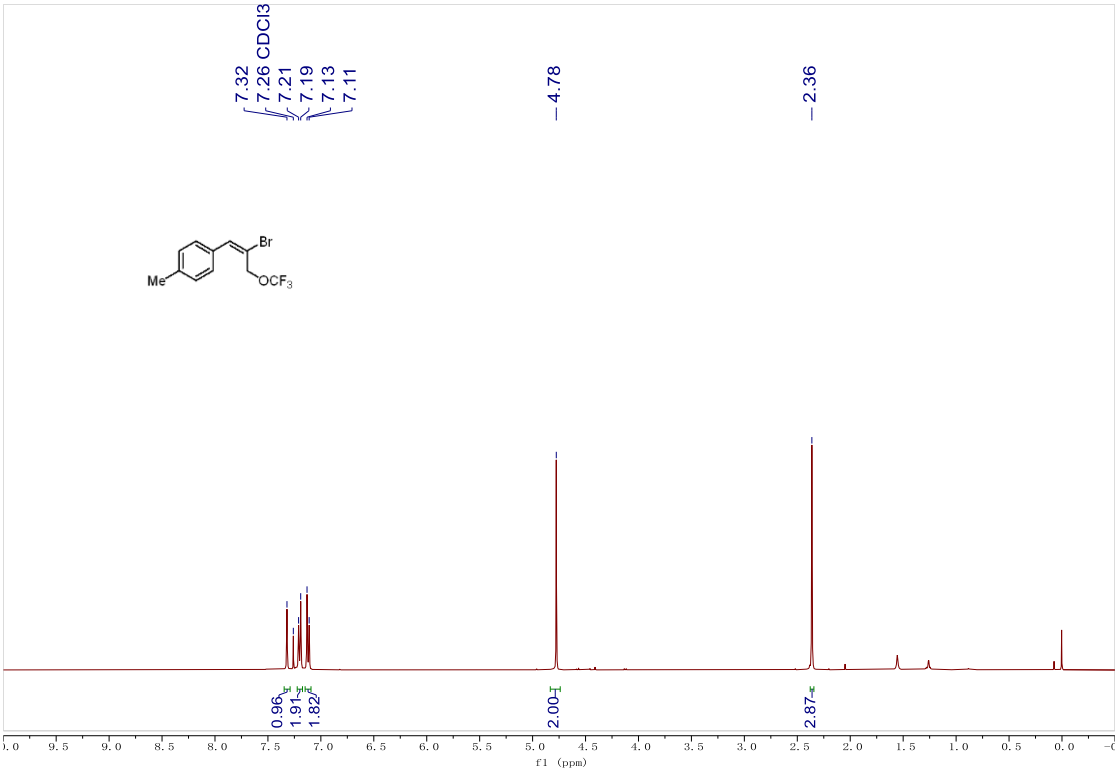

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **(*Z*)-3a**



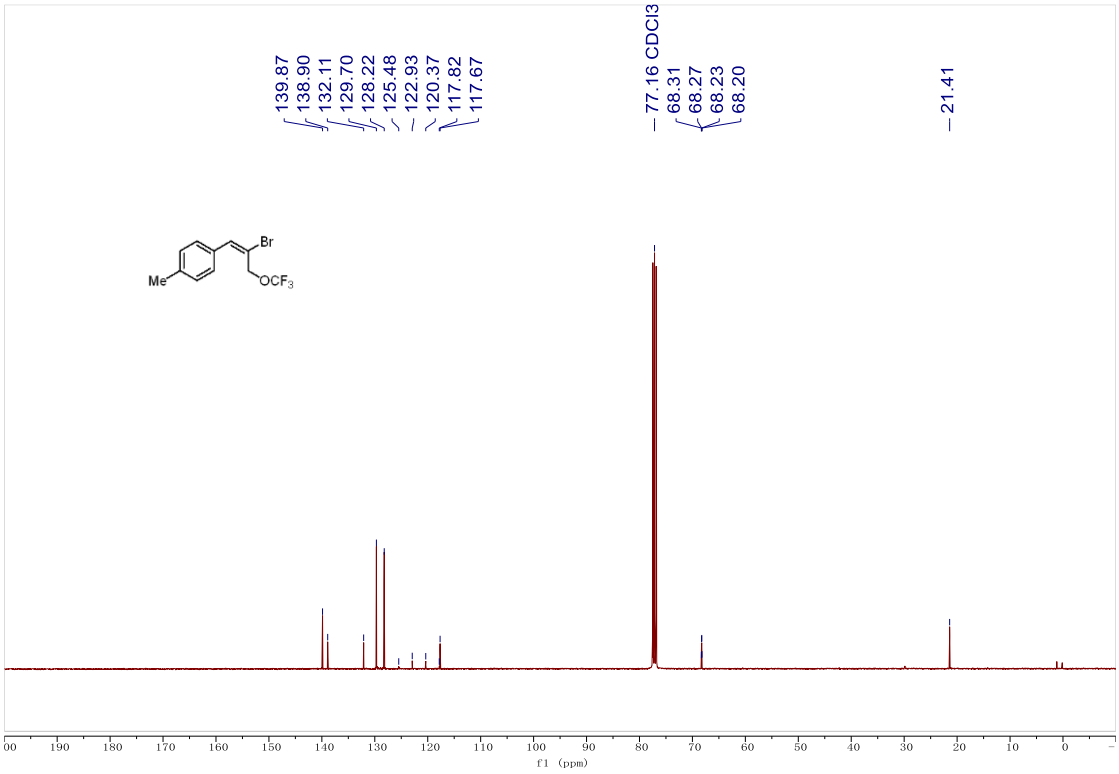

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **(*Z*)-3a**



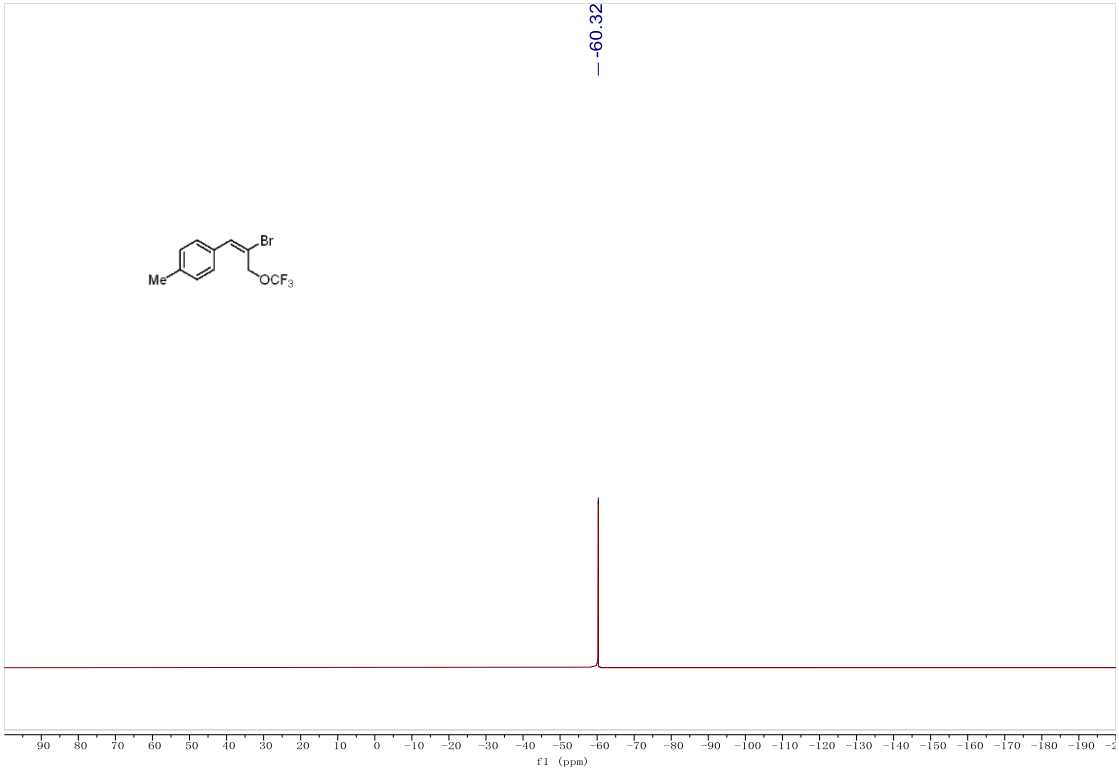

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*Z*)-3a**



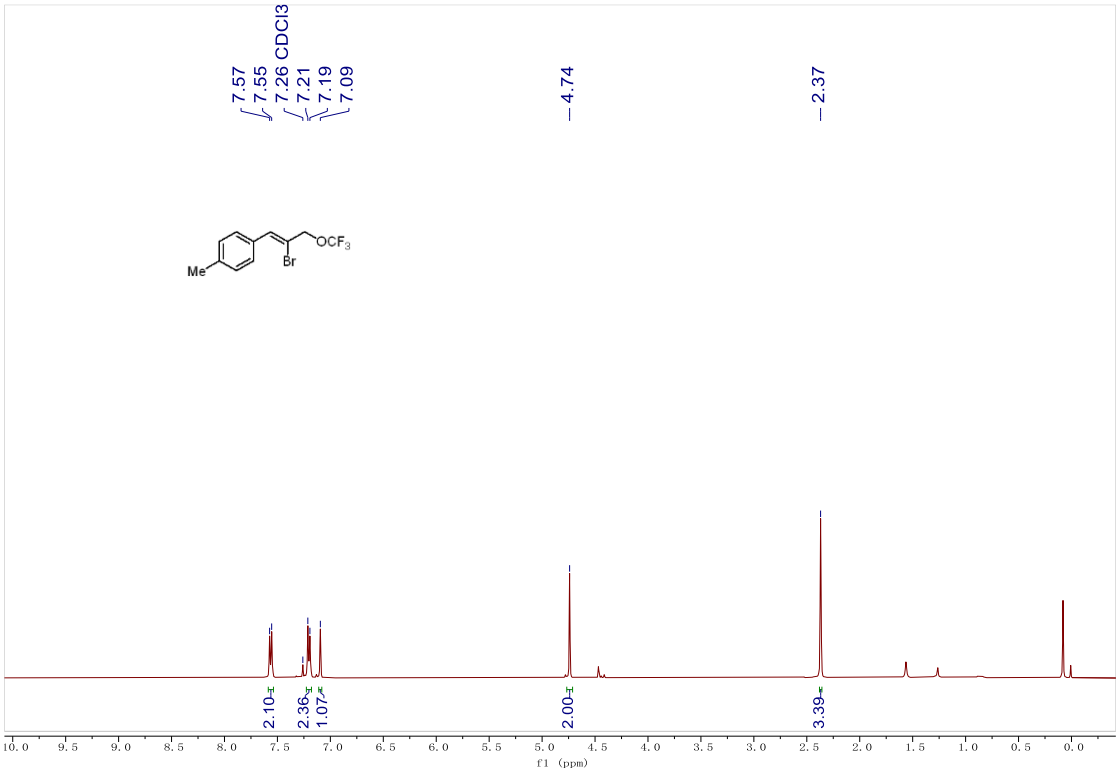

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **(*E*)-3b**



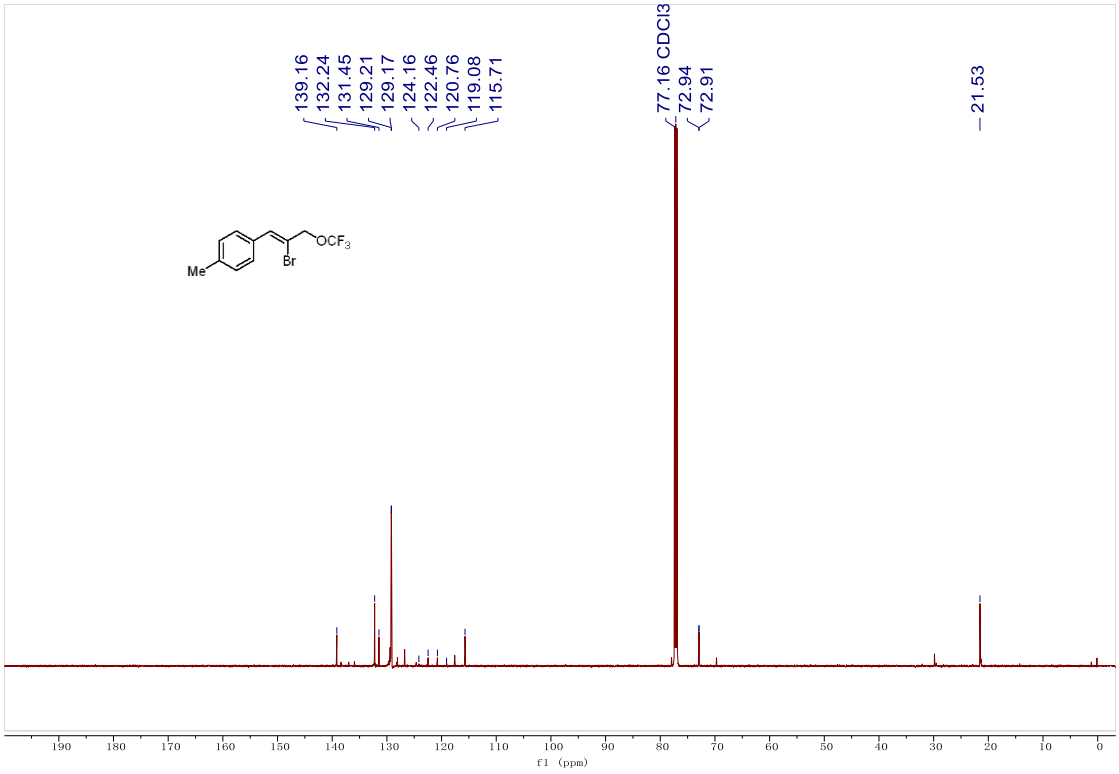

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **(*E*)-3b**



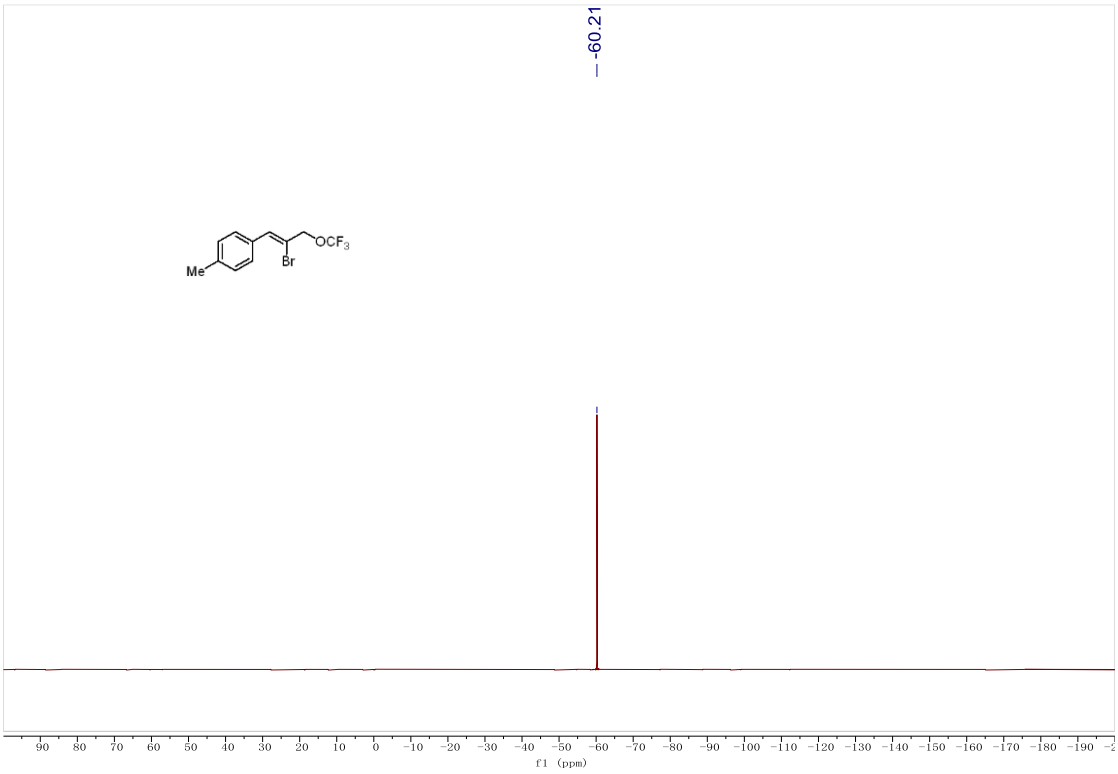

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*E*)-3b**



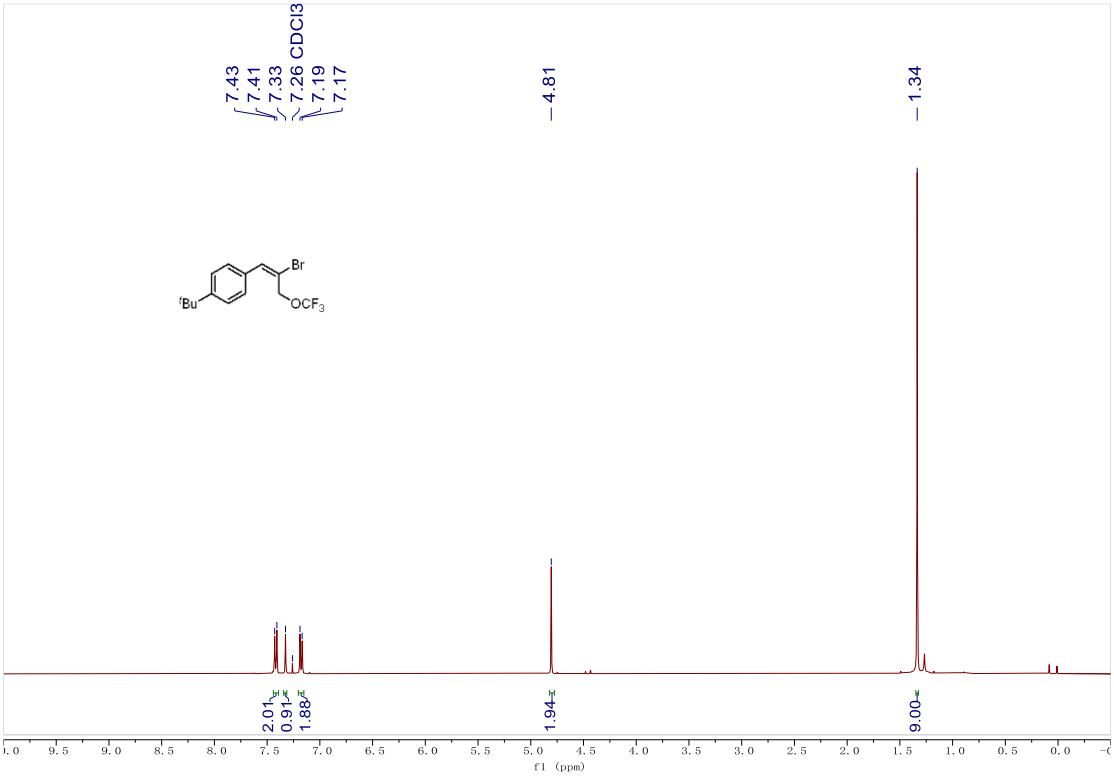

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **(*Z*)-3b**



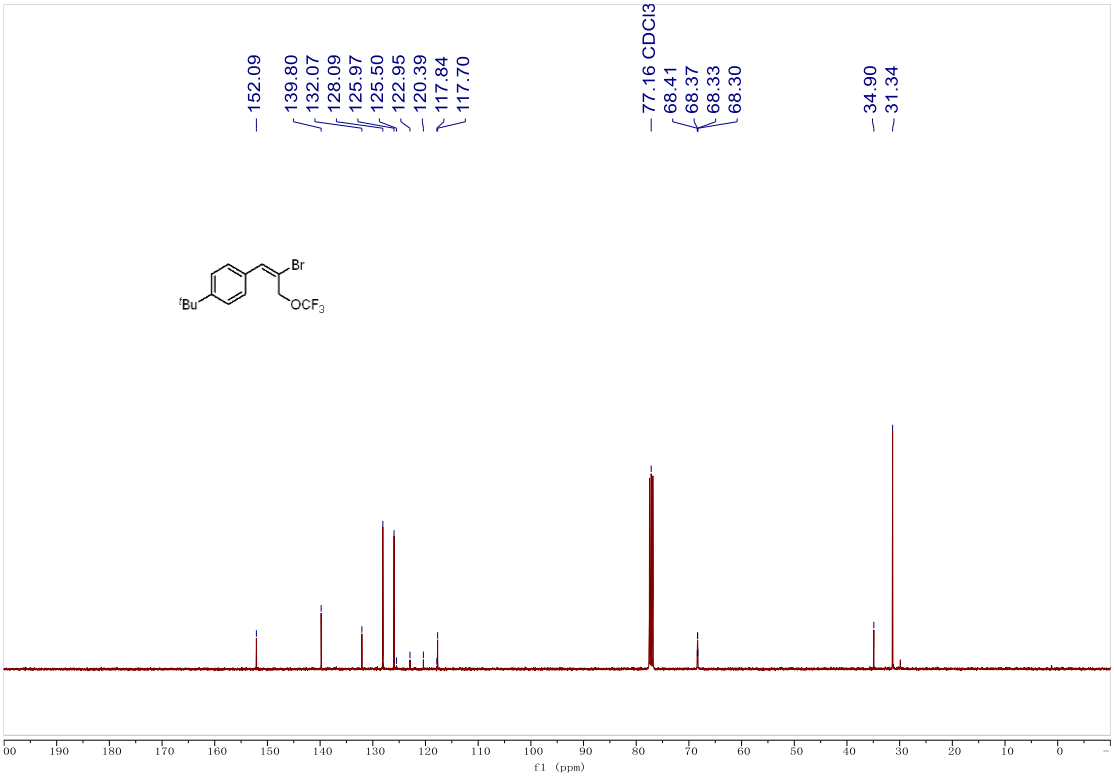

$^{13}$C NMR spectrum (151 MHz, $CDCl_3$) of **(*Z*)-3b**



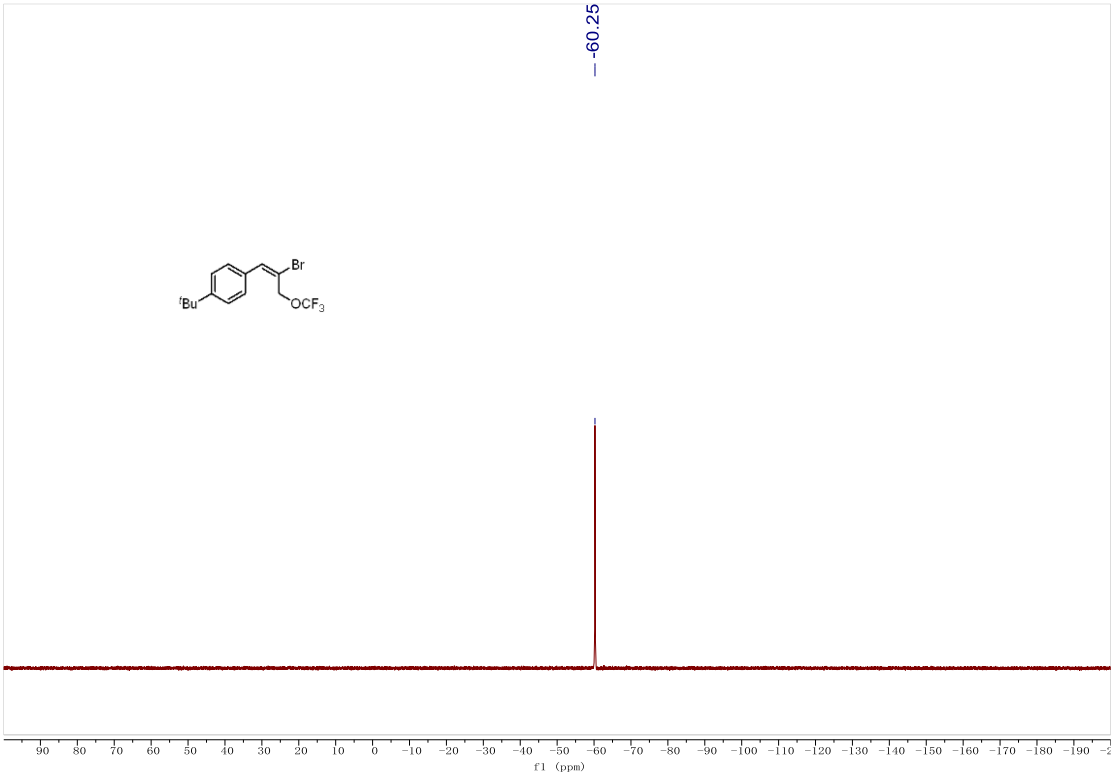

$^{19}F$ NMR spectrum (376 MHz, $CDCl_3$) of **(*Z*)-3b**



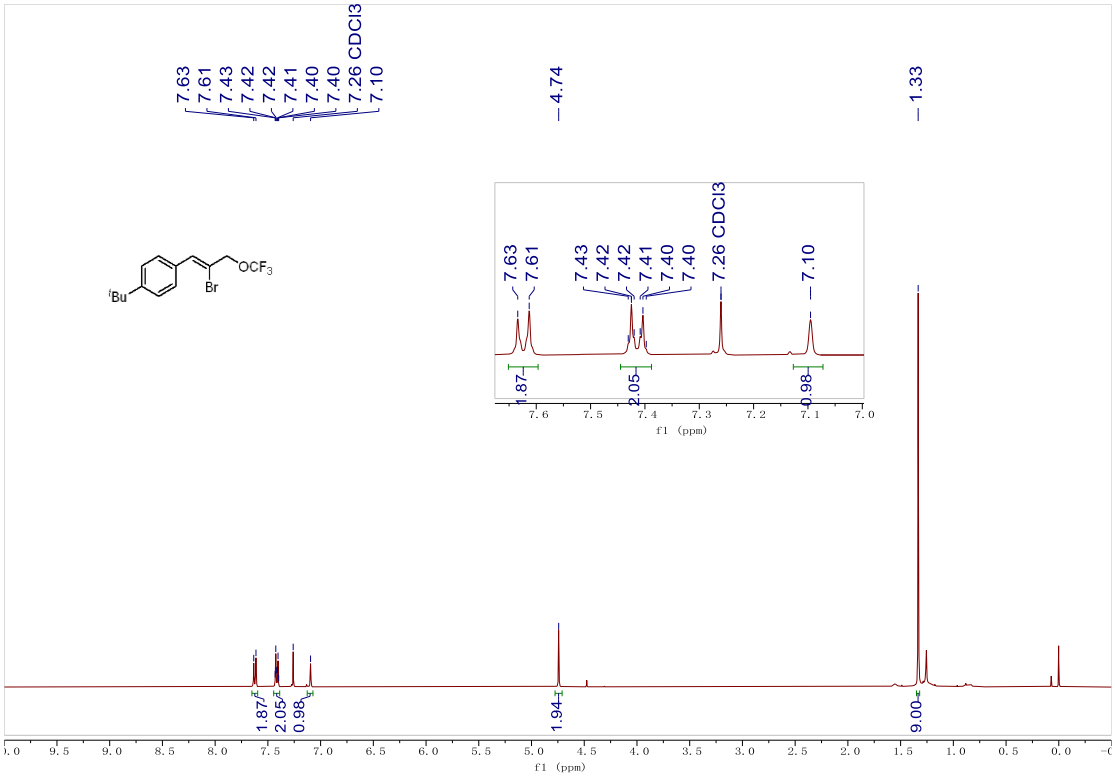

$^{1}H$ NMR spectrum (400 MHz, $CDCl_3$) of **(*E*)-3c**



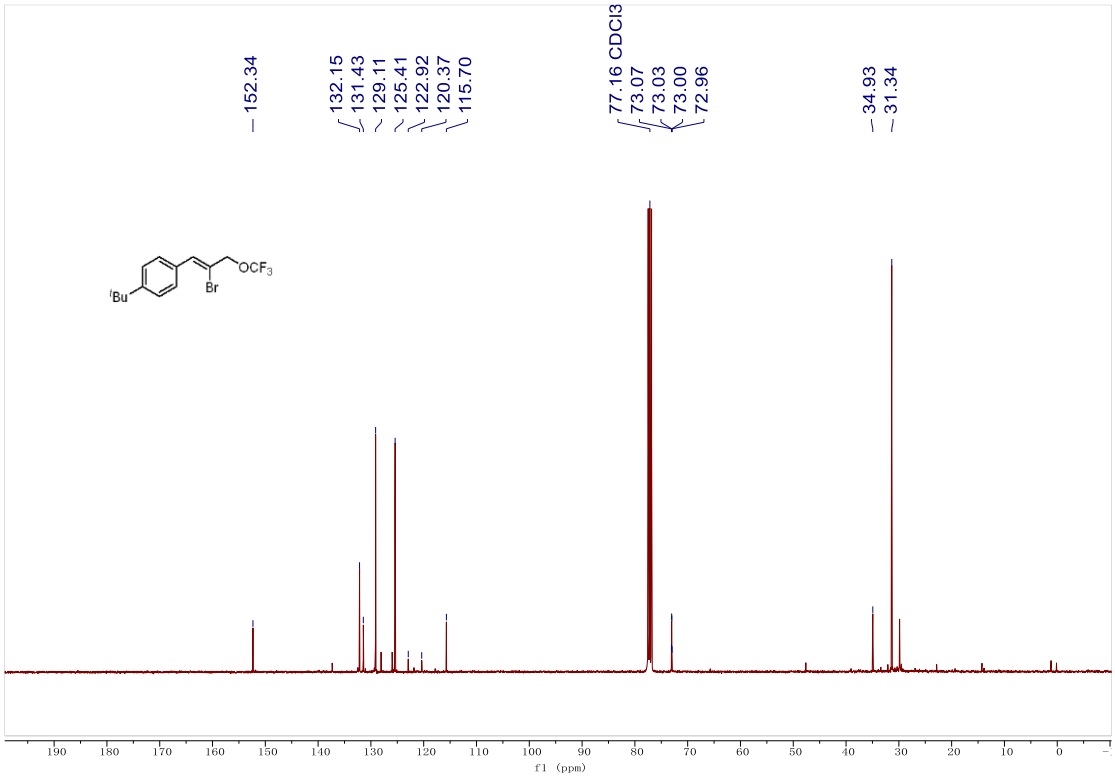

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **(*E*)-3c**



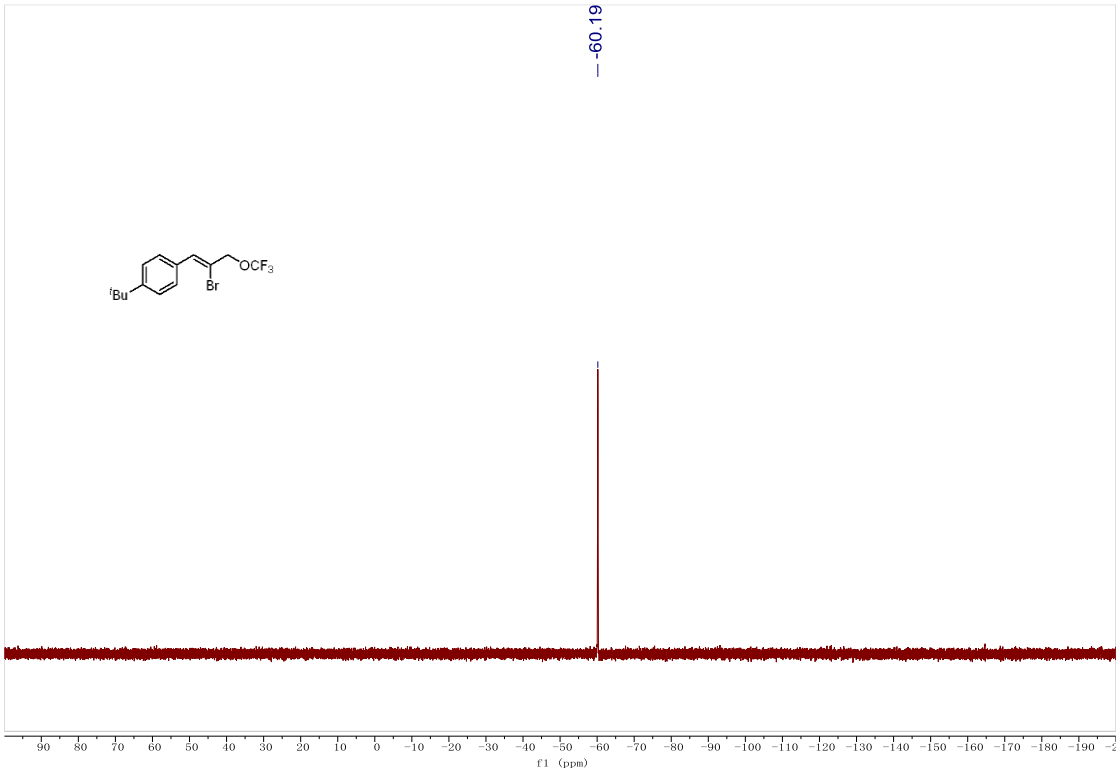

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*E*)-3c**



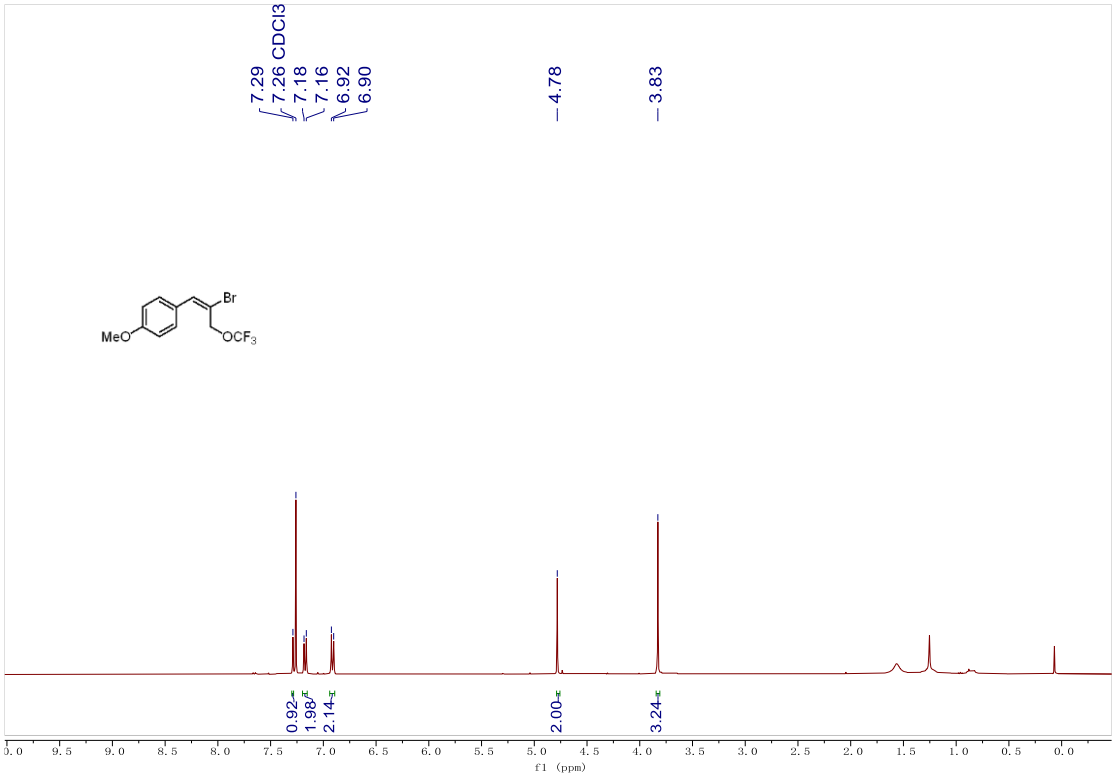

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **(*Z*)-3c**



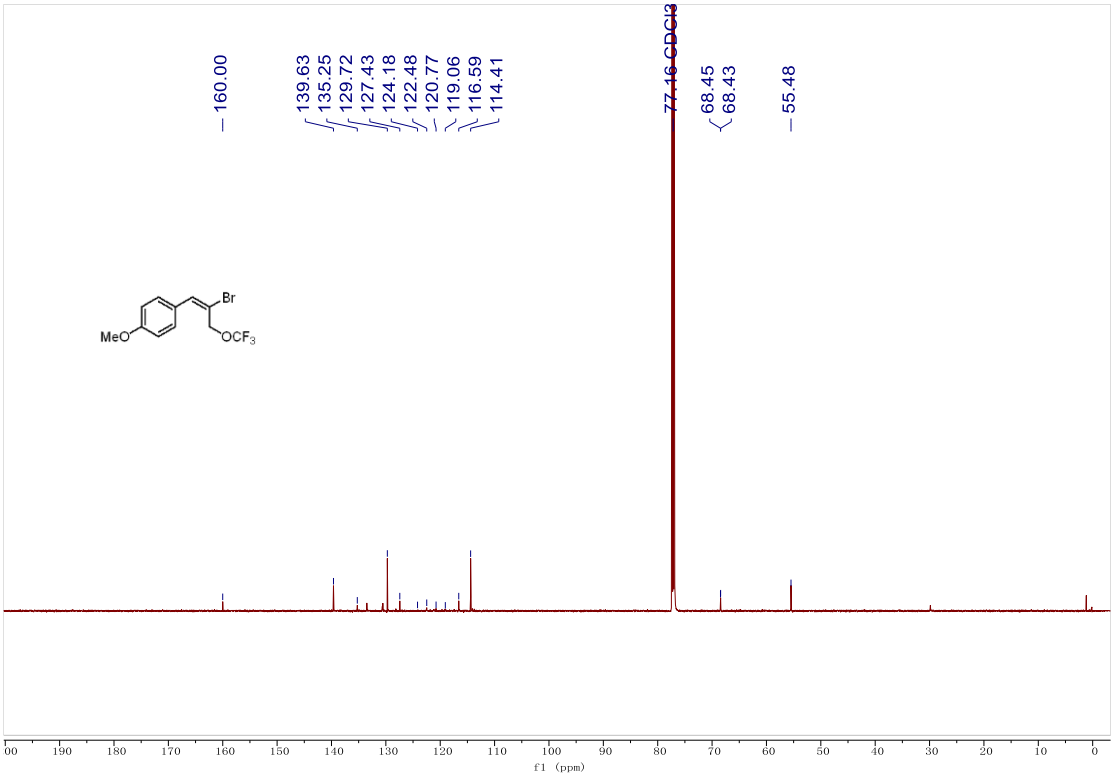

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **(*Z*)-3c**



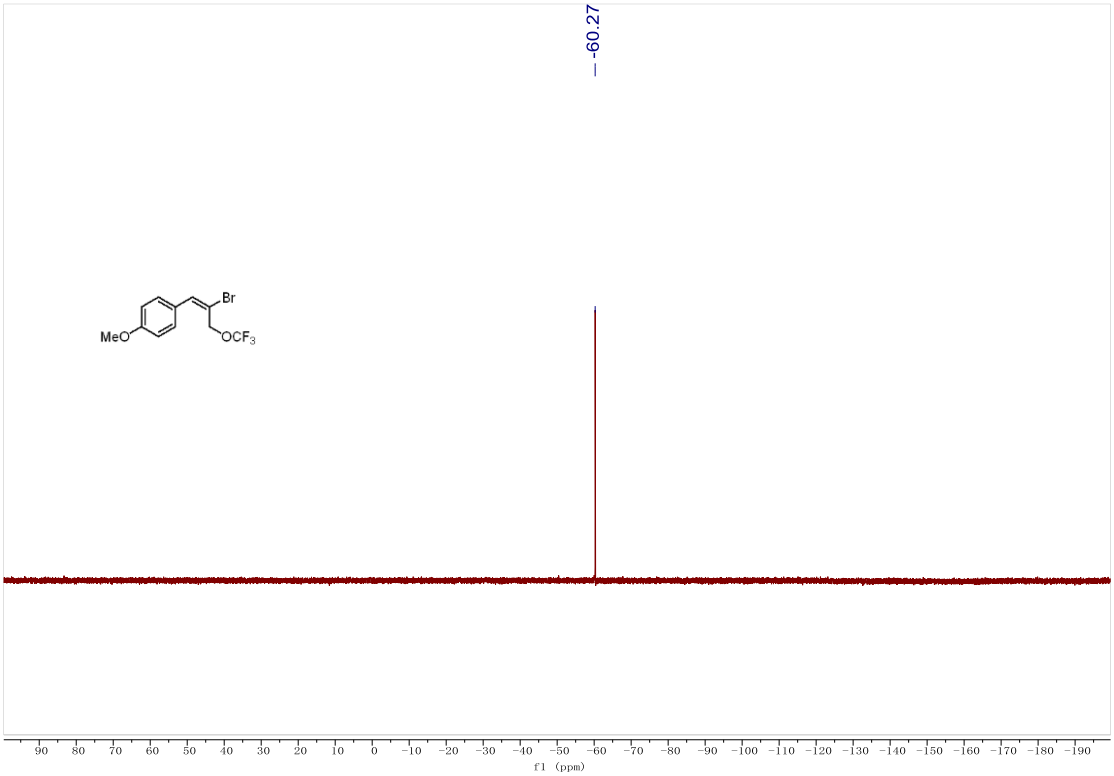

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*Z*)-3c**



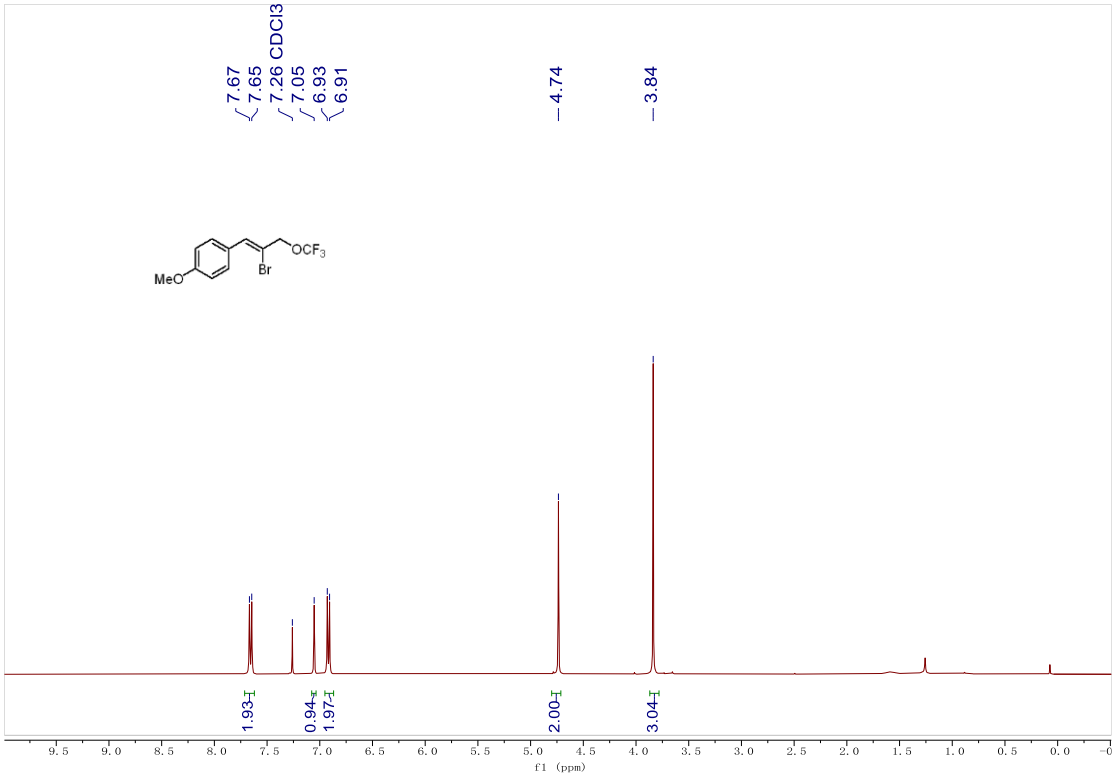

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **(*E*)-3d**



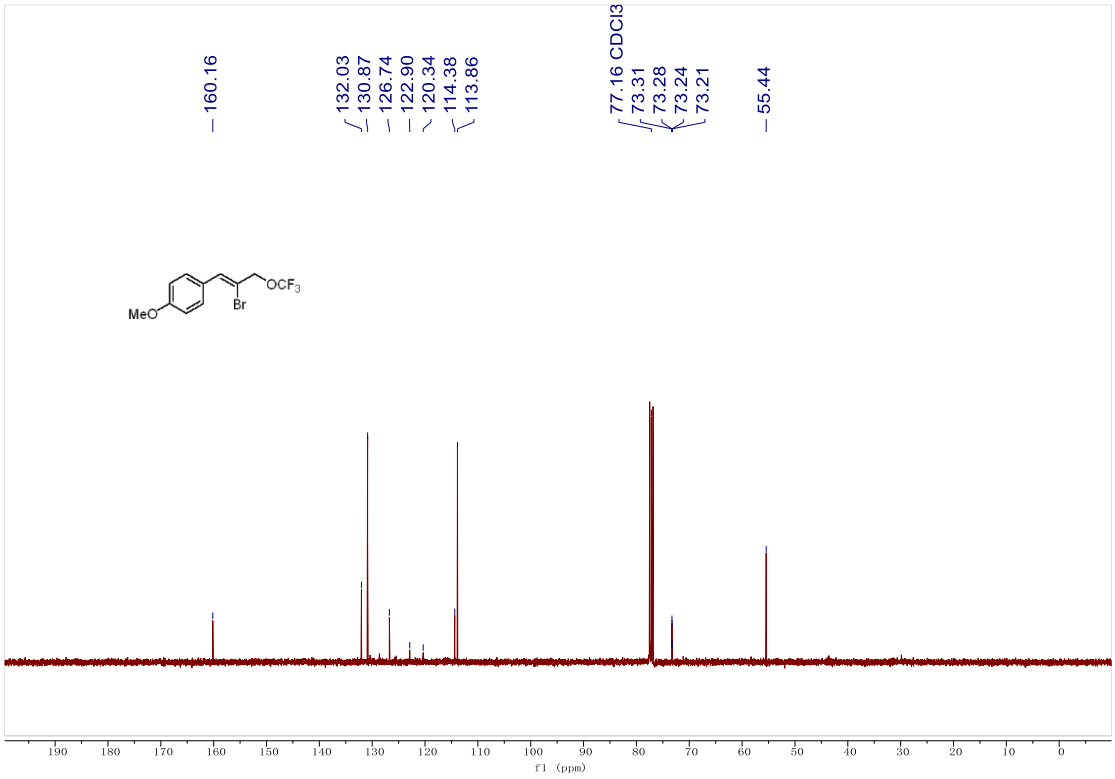

$^{13}$C NMR spectrum (151 MHz, $CDCl_3$) of **(*E*)-3d**



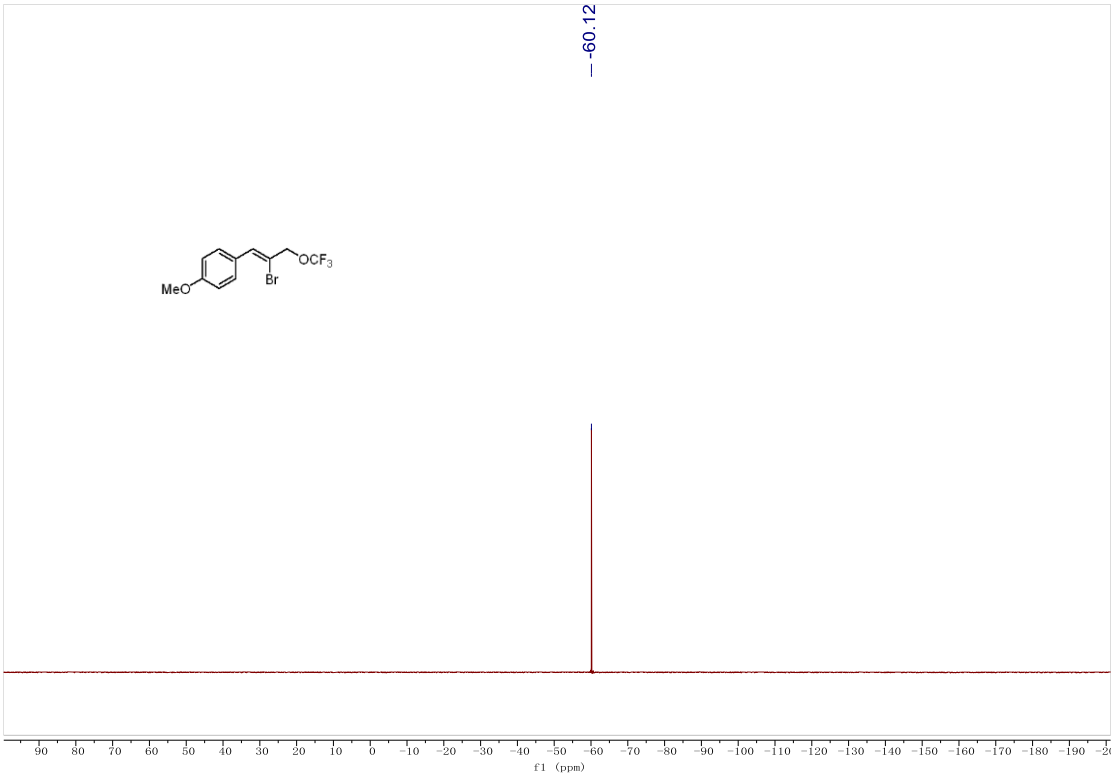

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*E*)-3d**



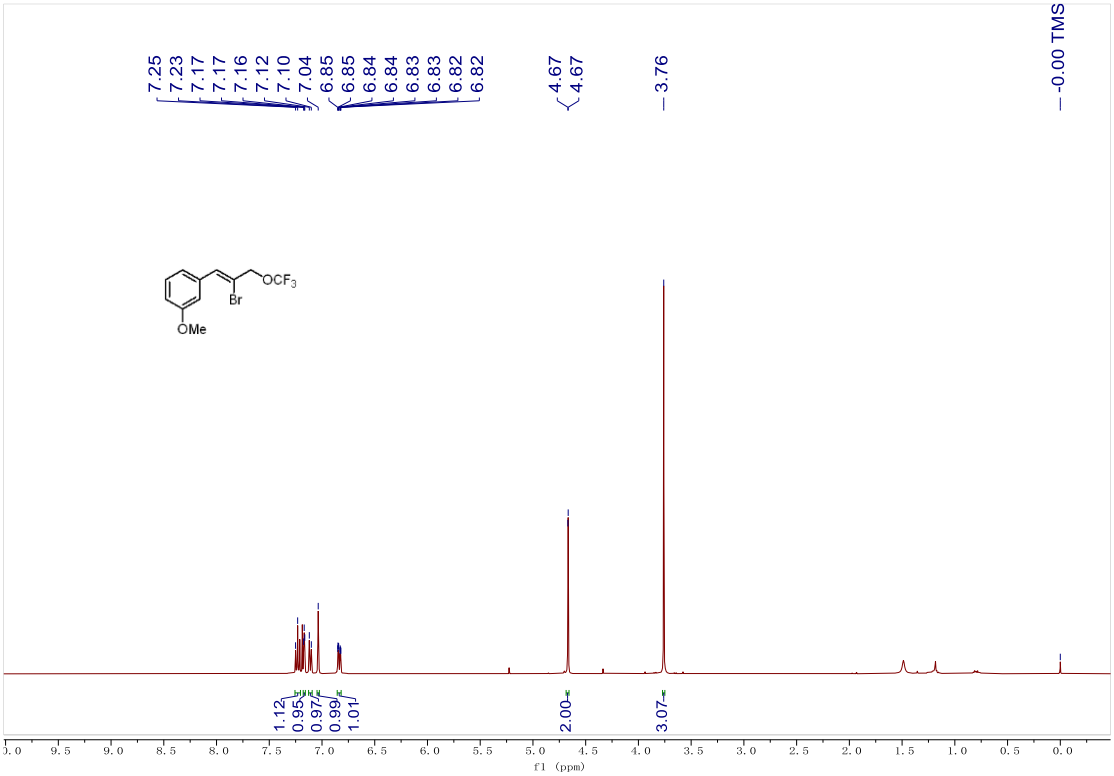

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **(*Z*)-3d**



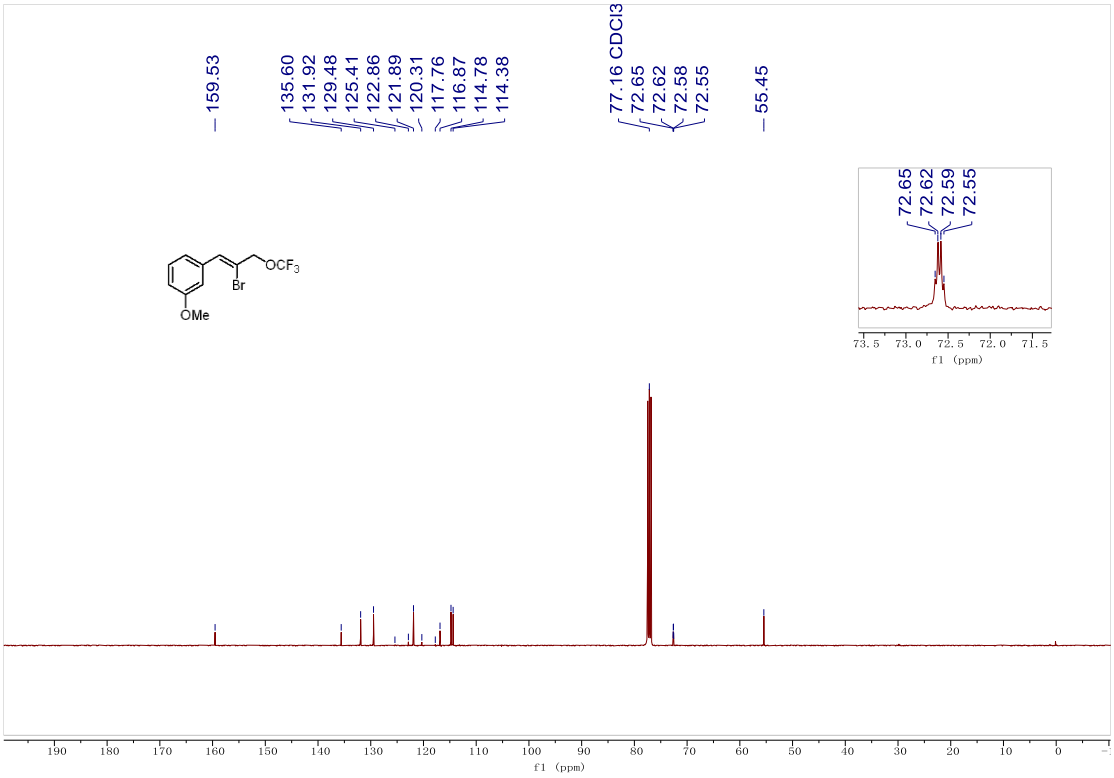

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **(*Z*)-3d**



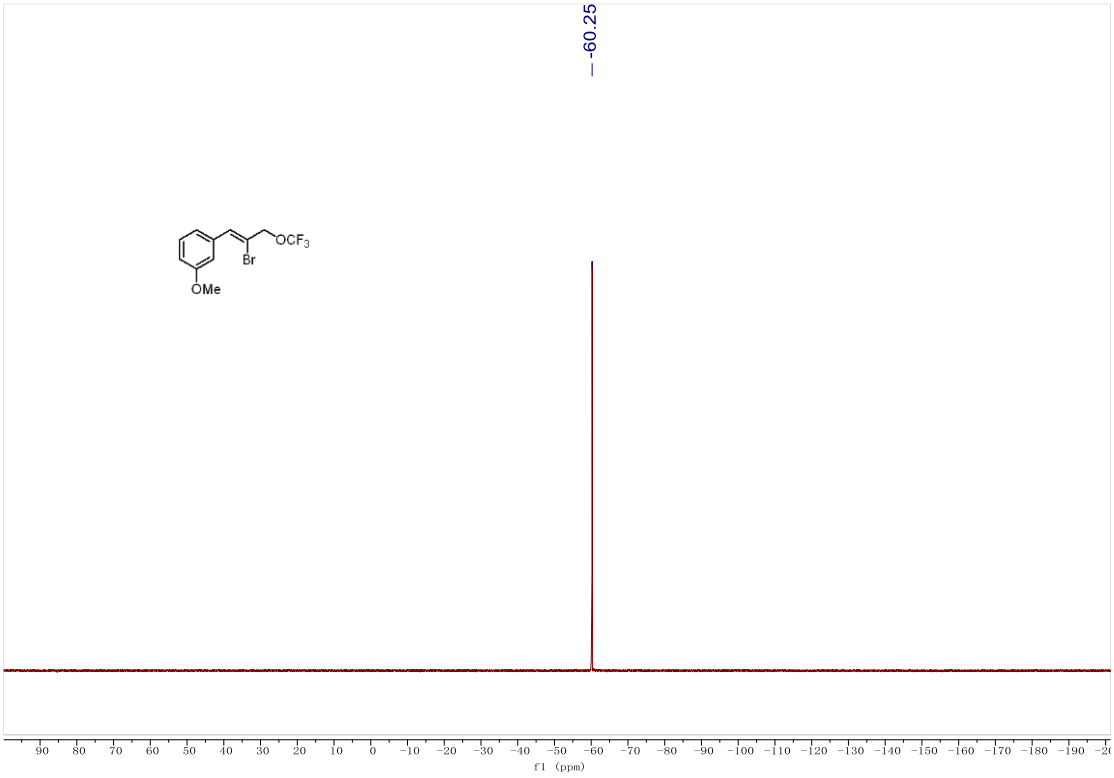

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*Z*)-3d**



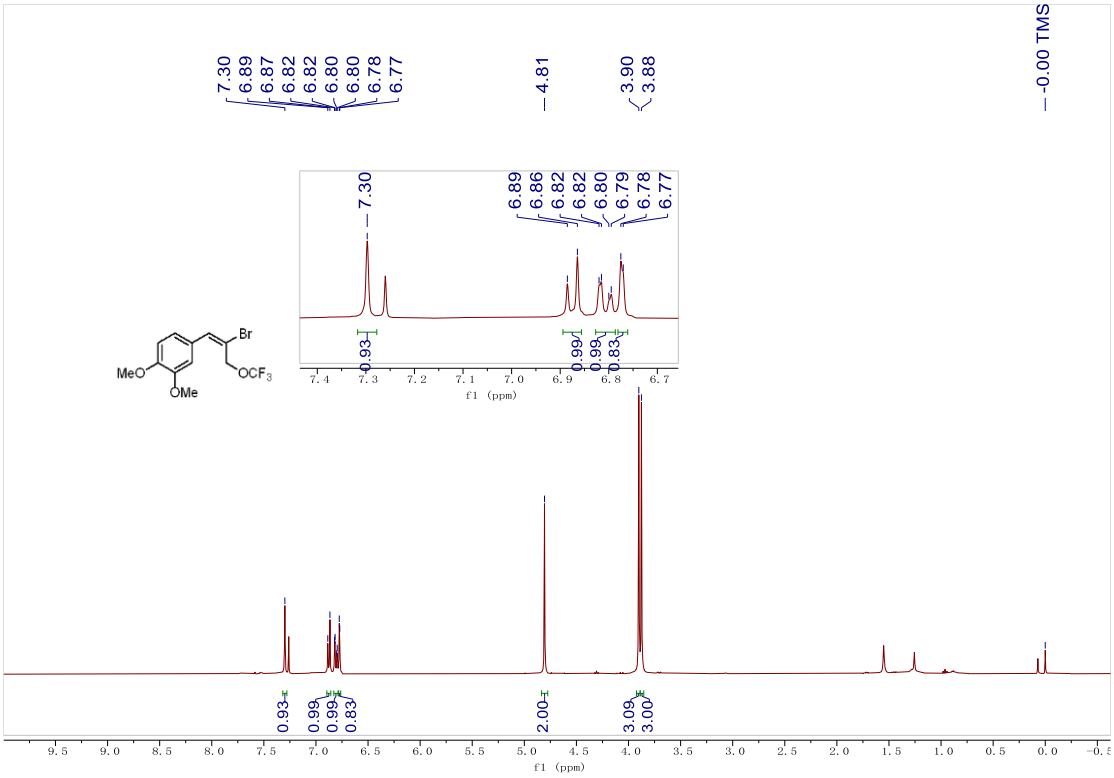

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **(*Z*)-3e**



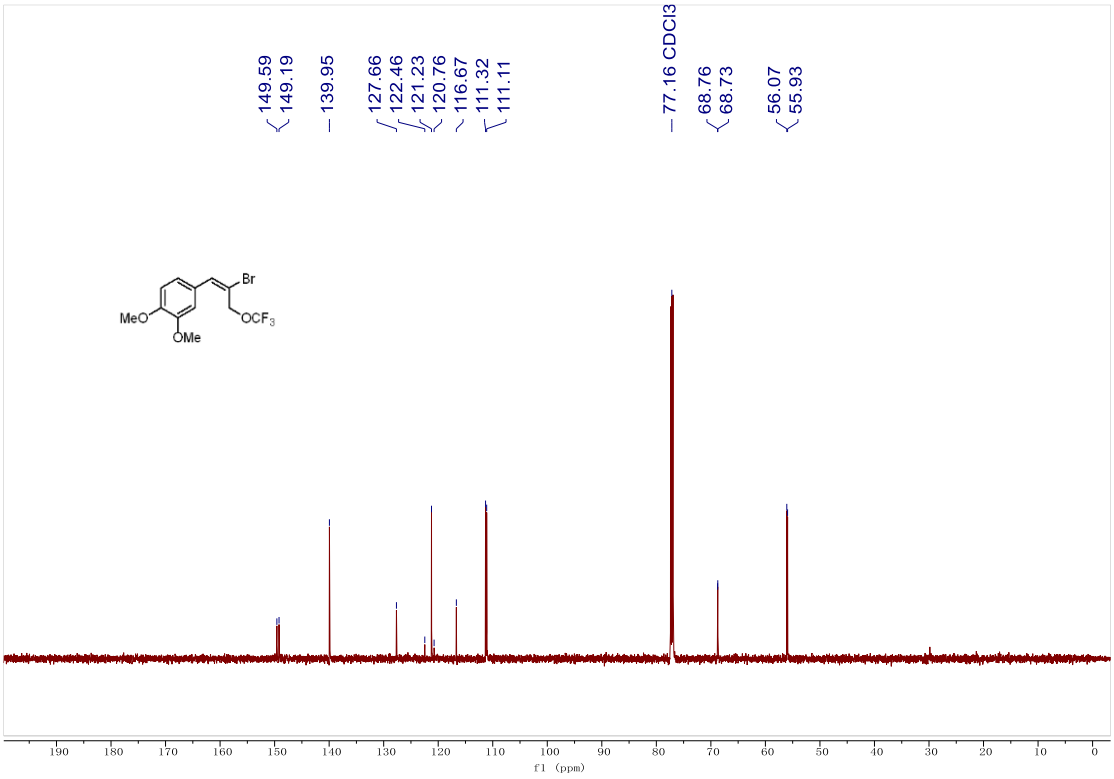

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **(*Z*)-3e**



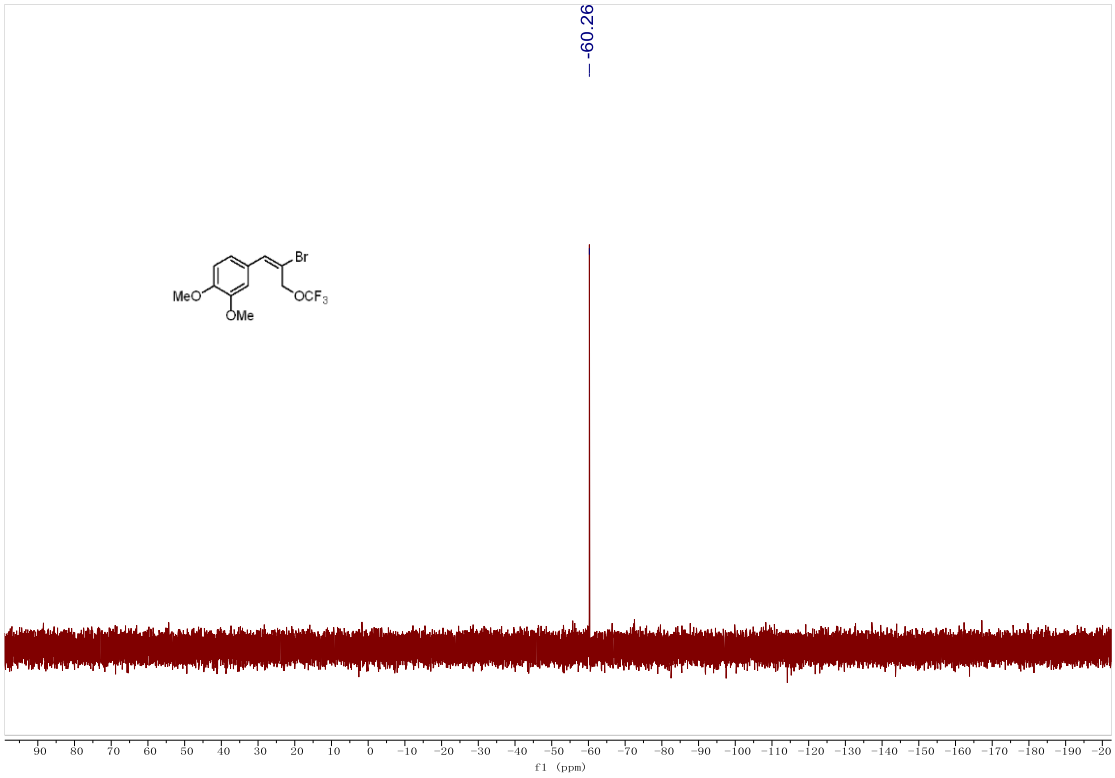

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*Z*)-3e**



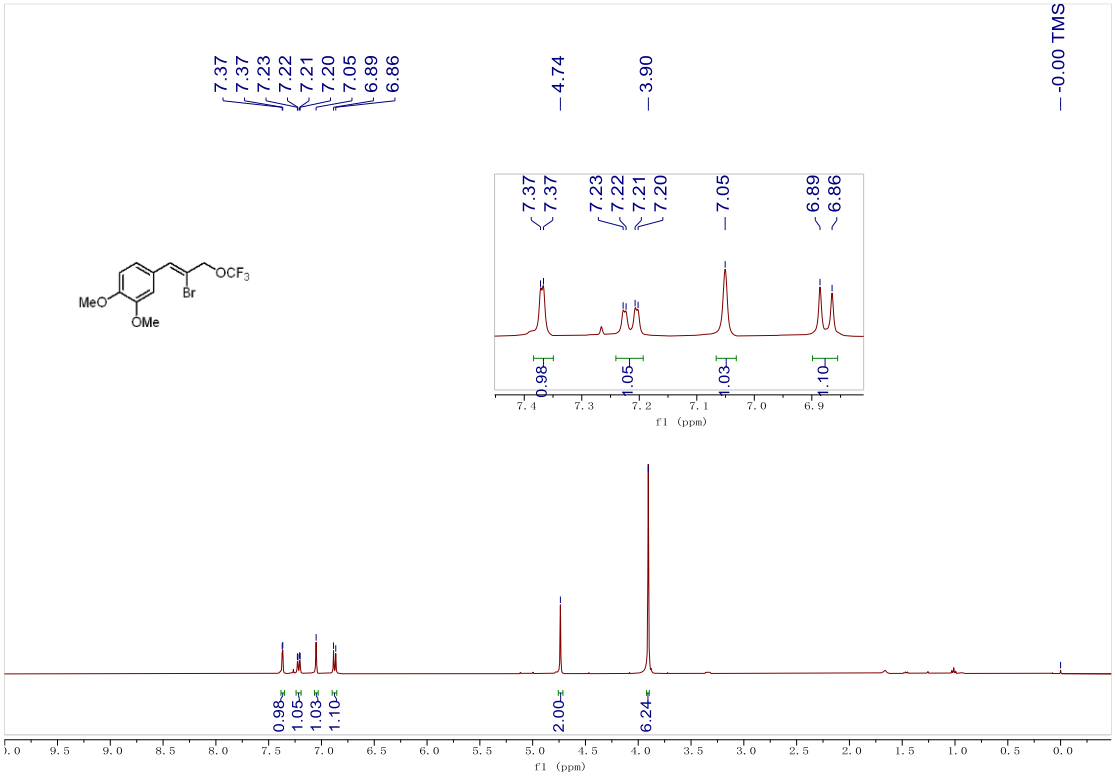

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **(*E*)-3f**



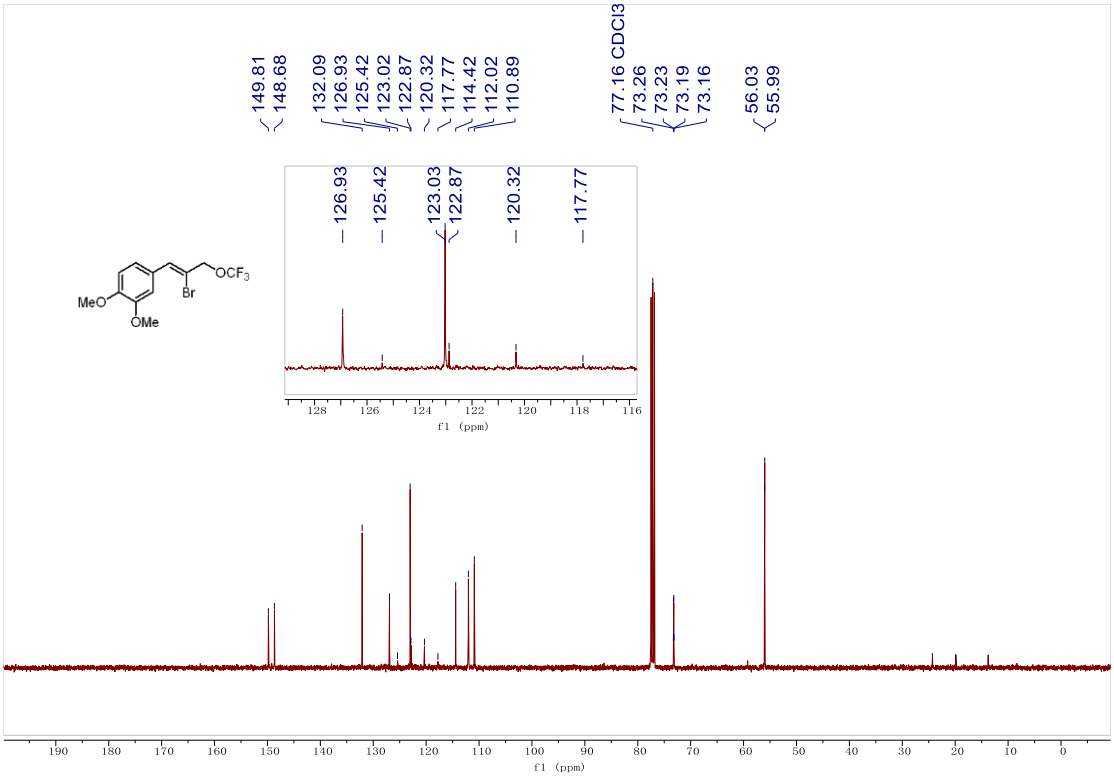

$^{13}$C NMR spectrum (151 MHz, $CDCl_3$) of **(*E*)-3f**



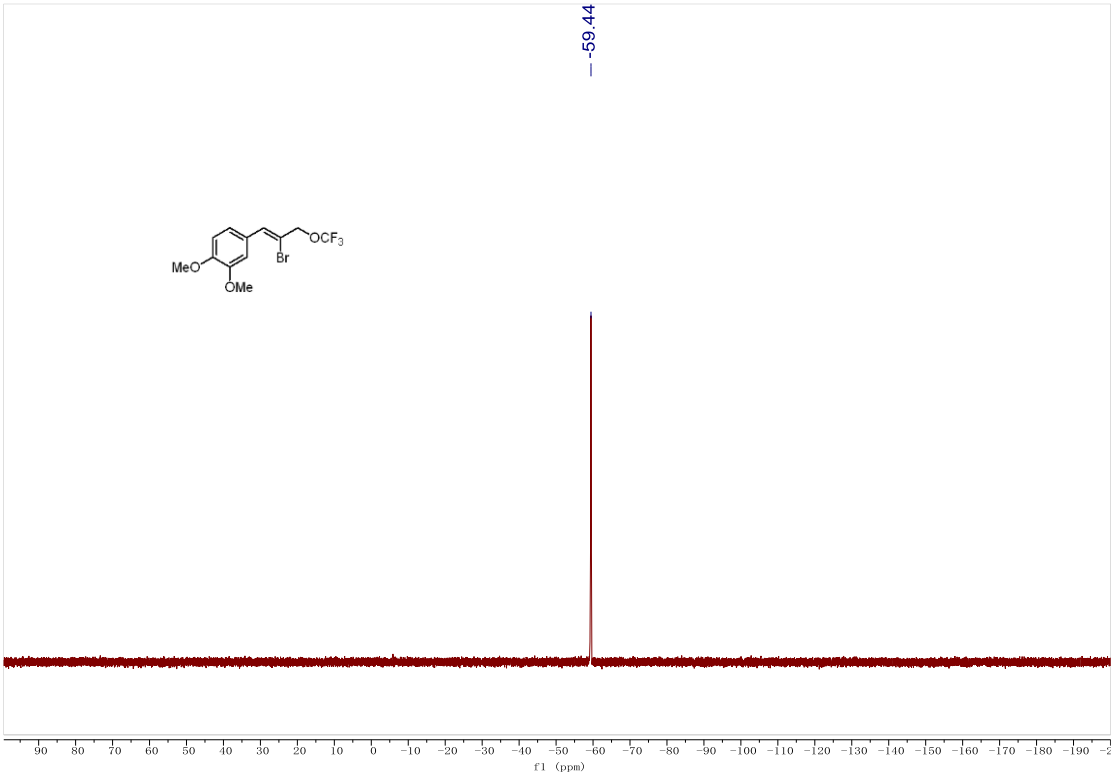

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*E*)-3f**



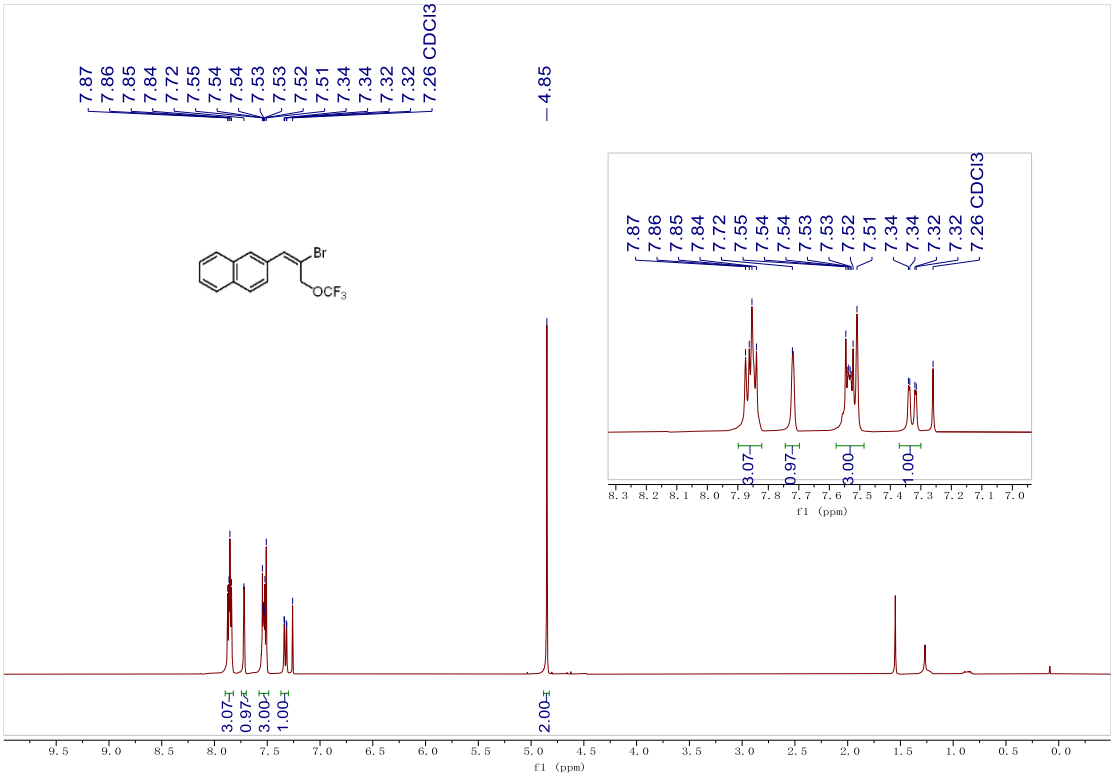

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **(*Z*)-3f**



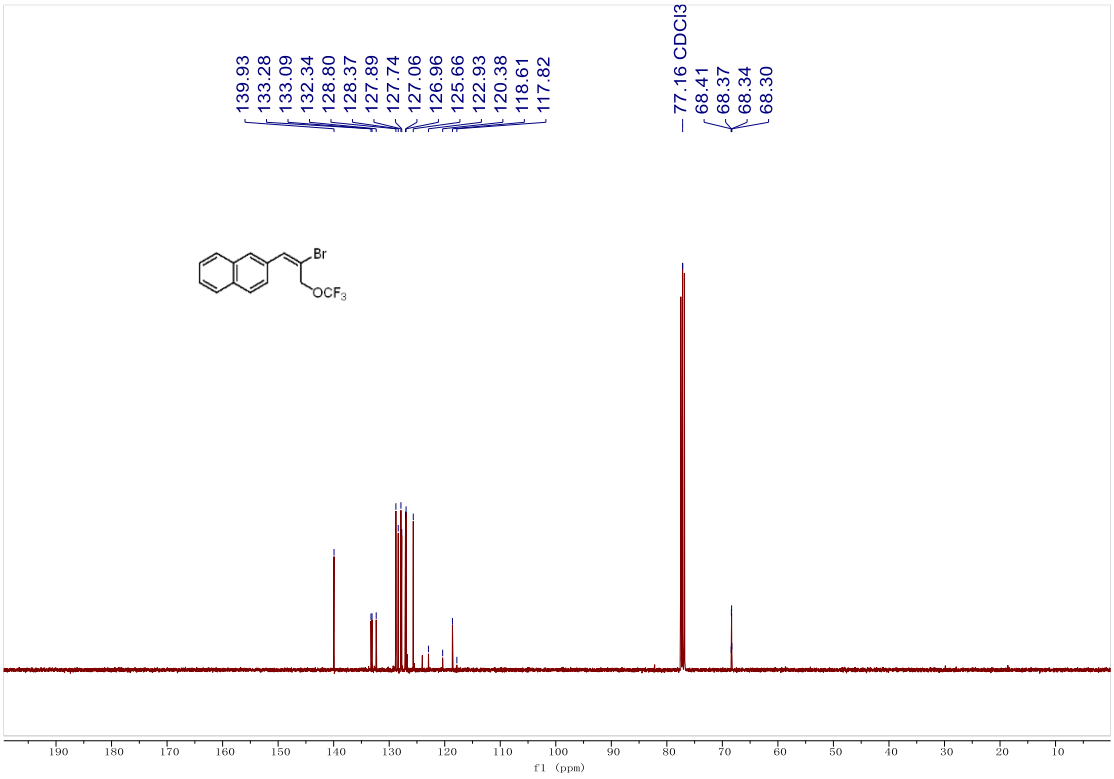

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **(*Z*)-3f**



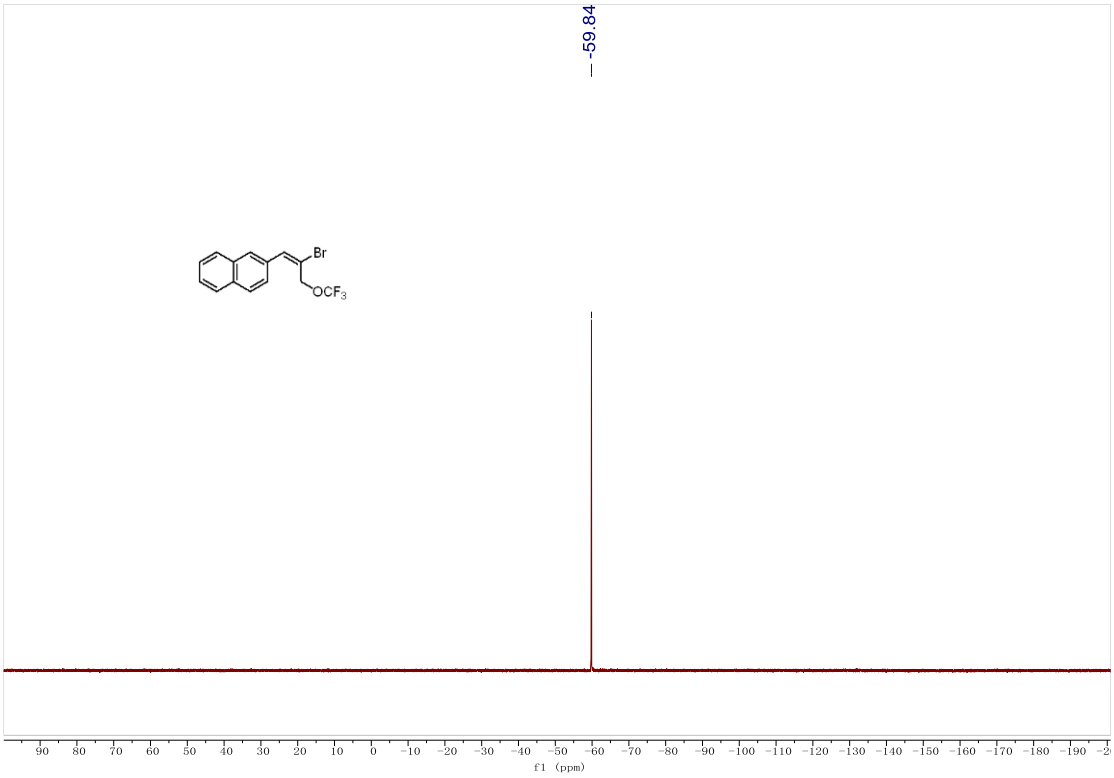

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*Z*)-3f**



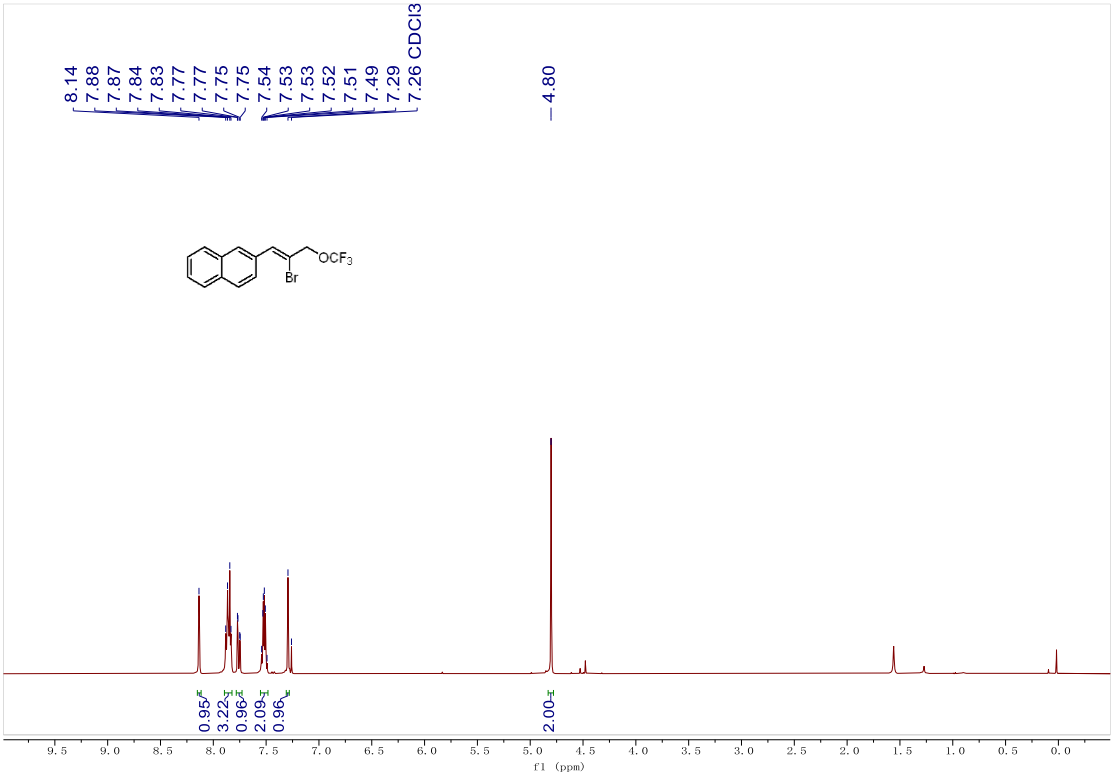

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **(*E*)-3g**



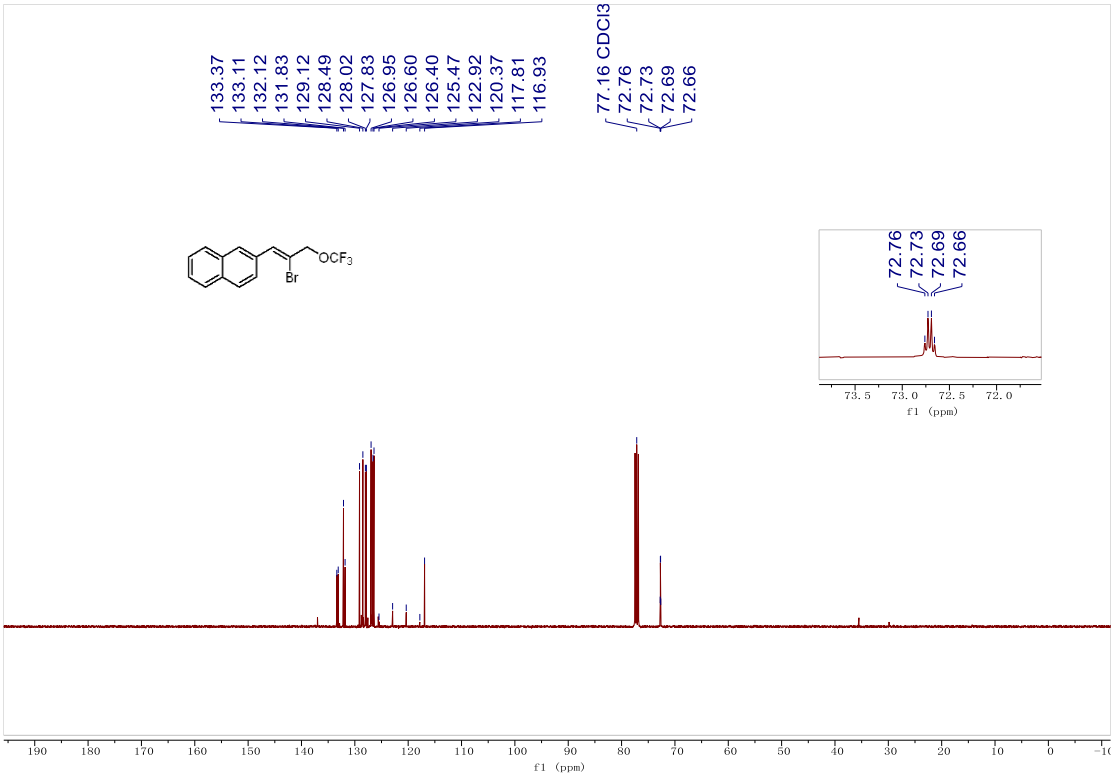

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **(*E*)-3g**



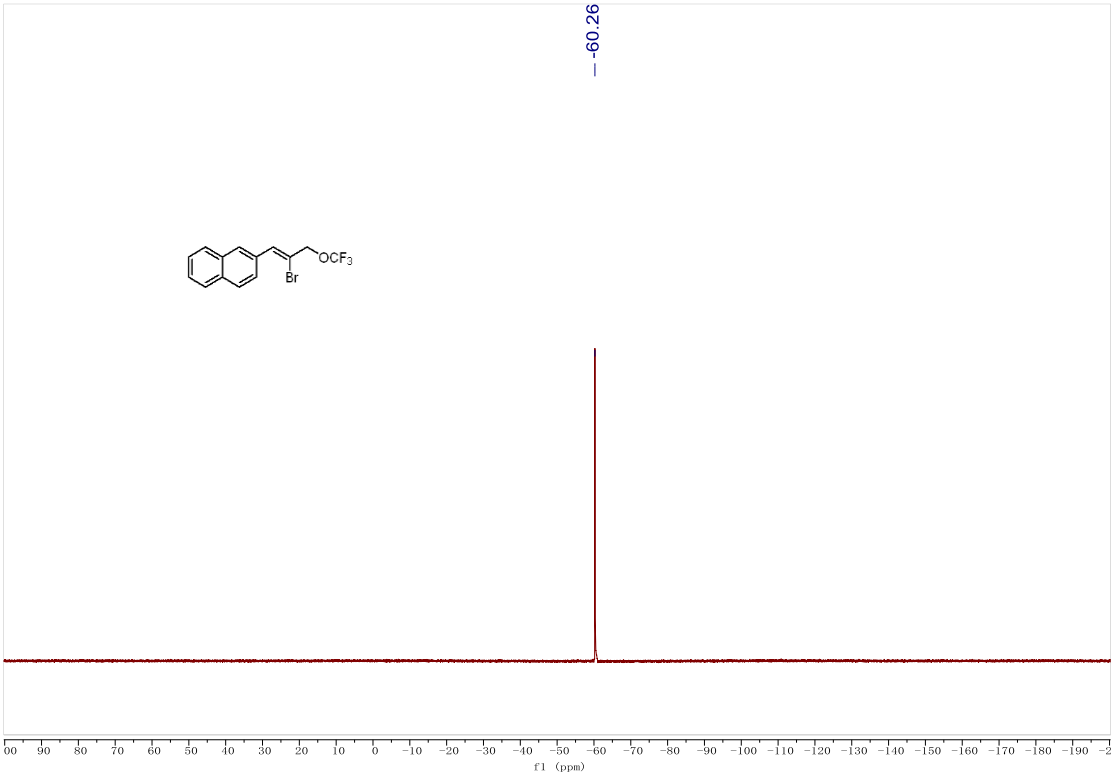

$^{19}F$ NMR spectrum (376 MHz, $CDCl_3$) of **(*E*)-3g**



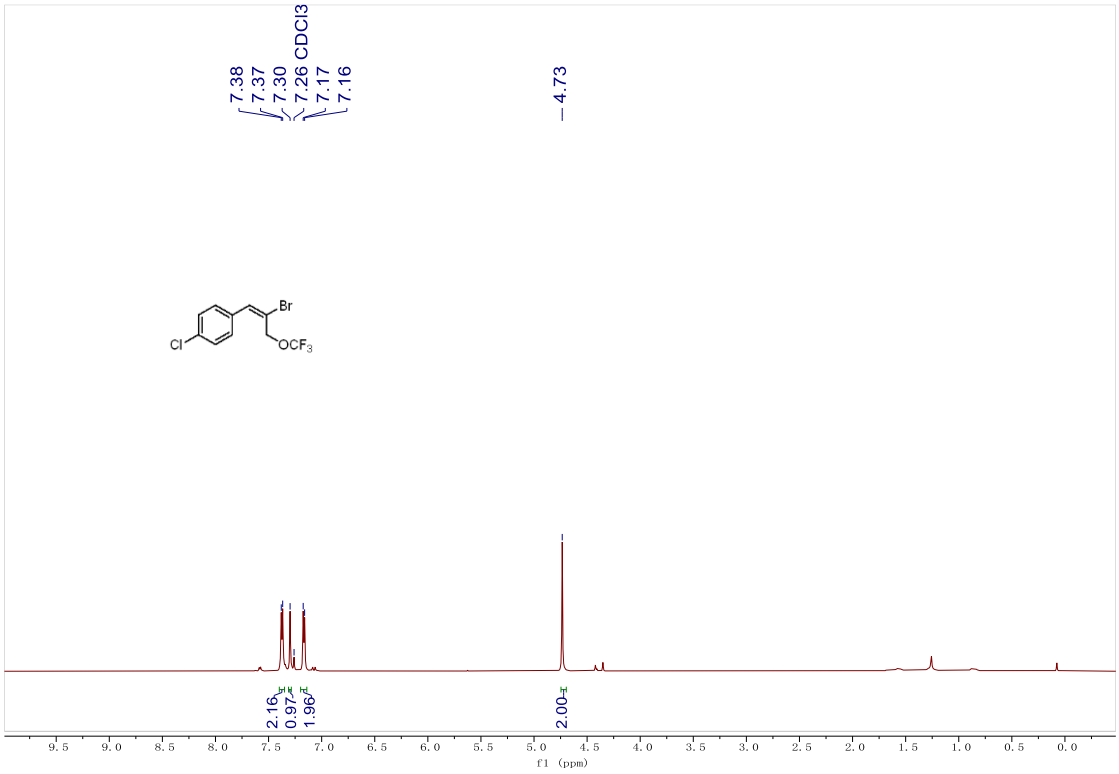

$^{1}H$ NMR spectrum (400 MHz, $CDCl_3$) of **(*Z*)-3g**



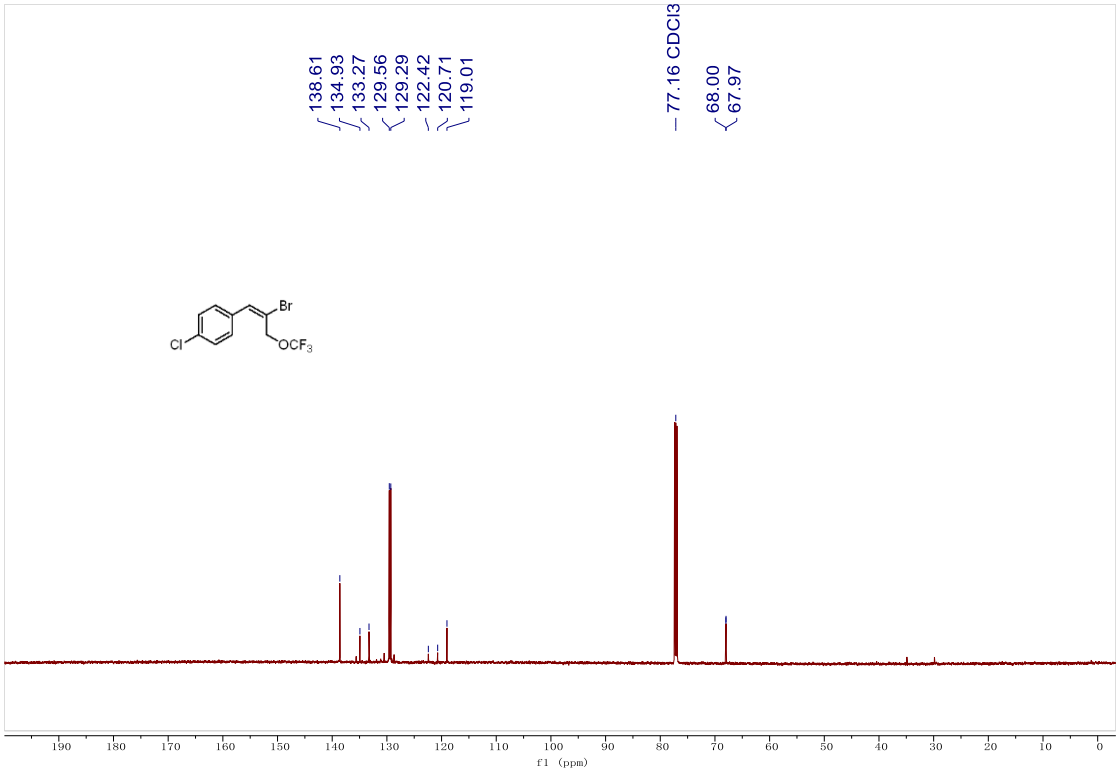

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **(*Z*)-3g**



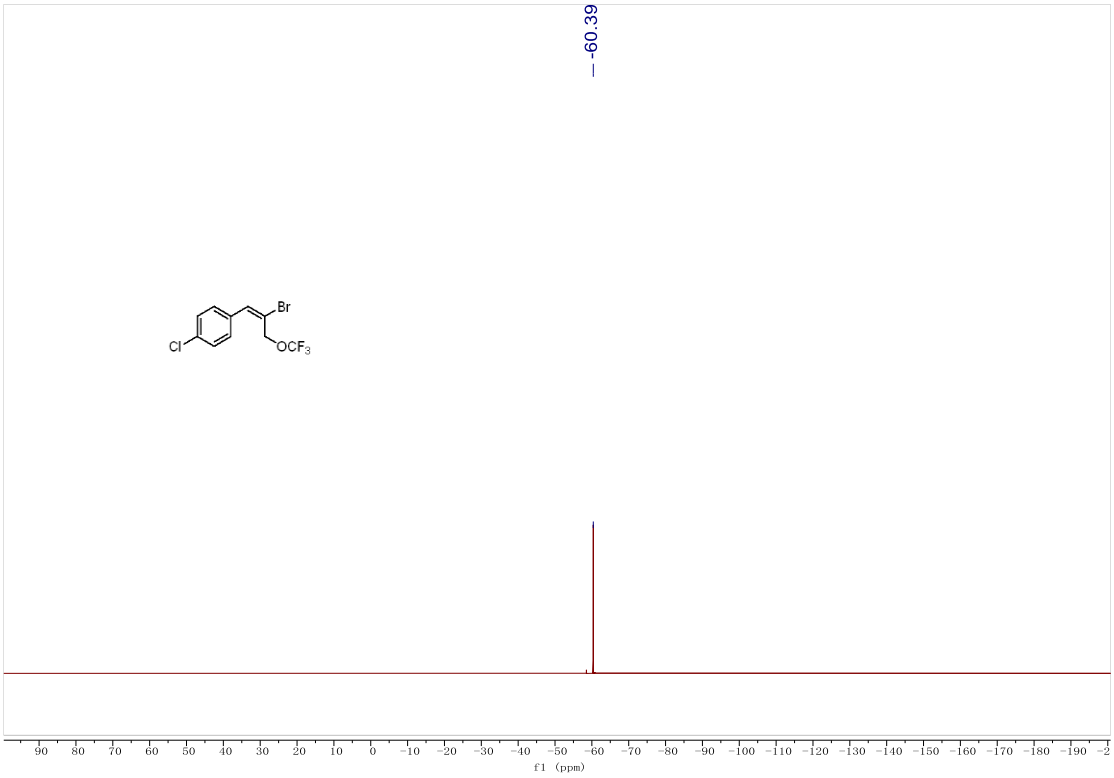

$^{19}$F NMR spectrum (376 MHz, DMSO-$d_6$) of **(*Z*)-3g**



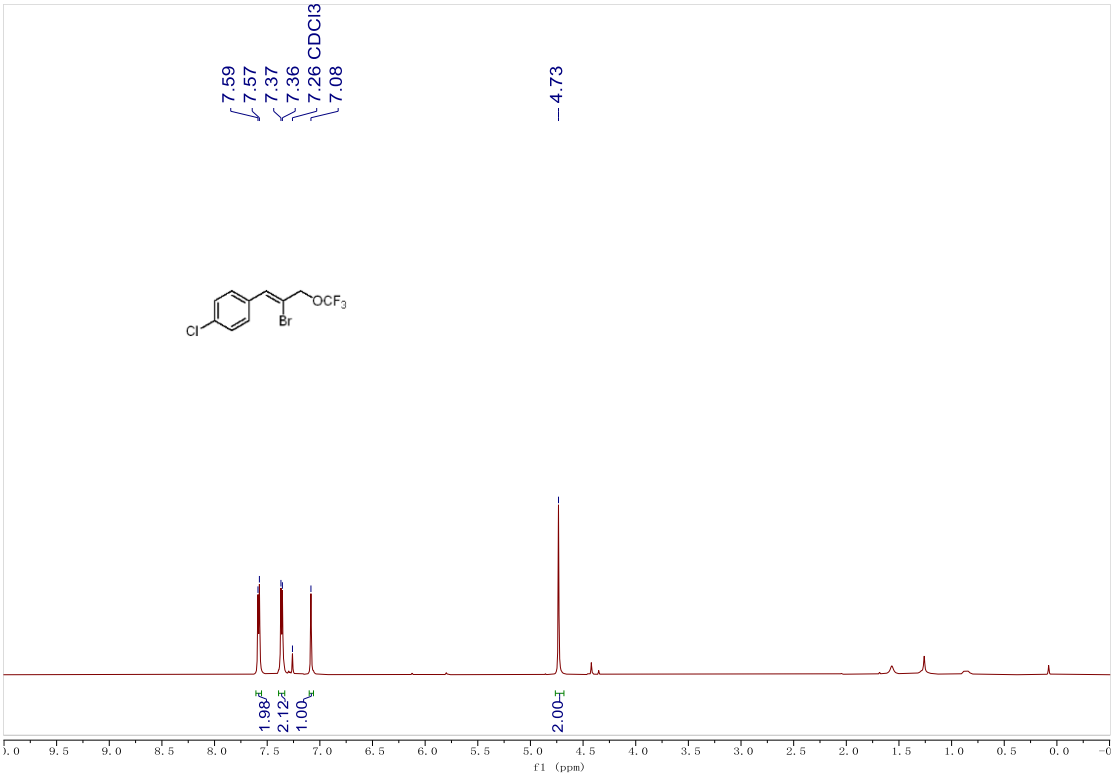

$^{1}$H NMR spectrum (600 MHz, $CDCl_3$) of **(*E*)-3h**



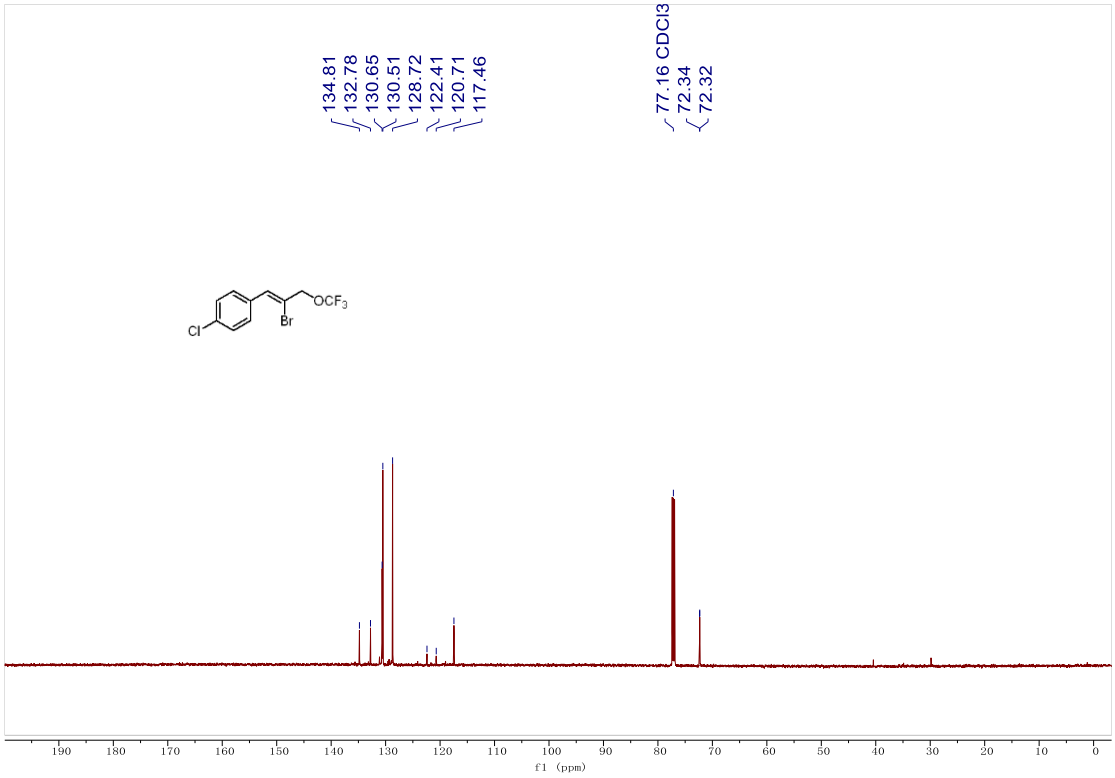

$^{13}$C NMR spectrum (151 MHz, $CDCl_3$) of **(*E*)-3h**



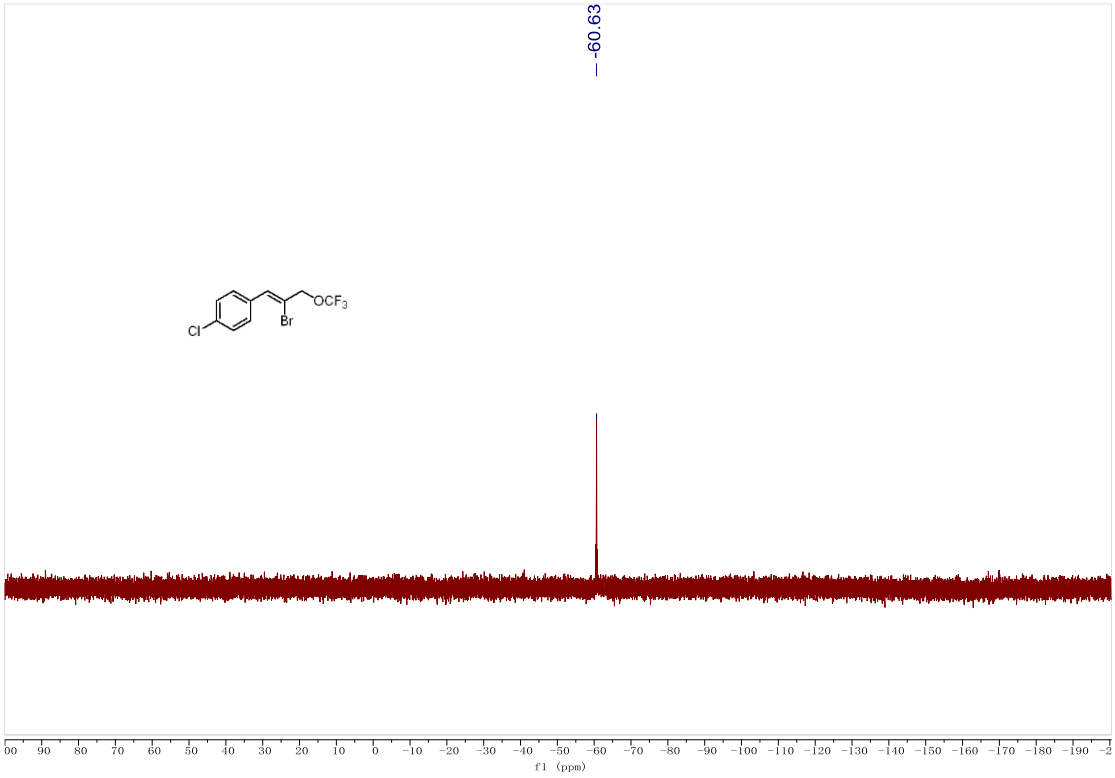

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*E*)-3h**




$^{1}$H NMR spectrum (600 MHz, $CDCl_3$) of **(*Z*)-3h**

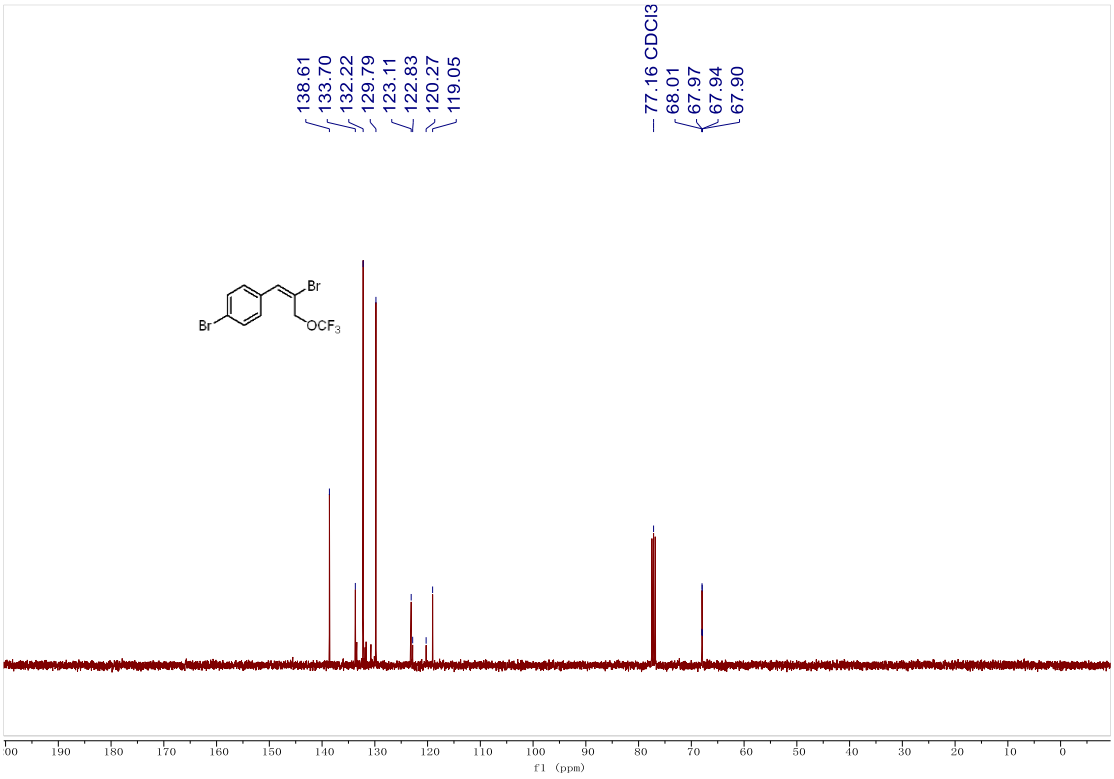



$^{13}$C NMR spectrum (151 MHz, $CDCl_3$) of **(*Z*)-3h**

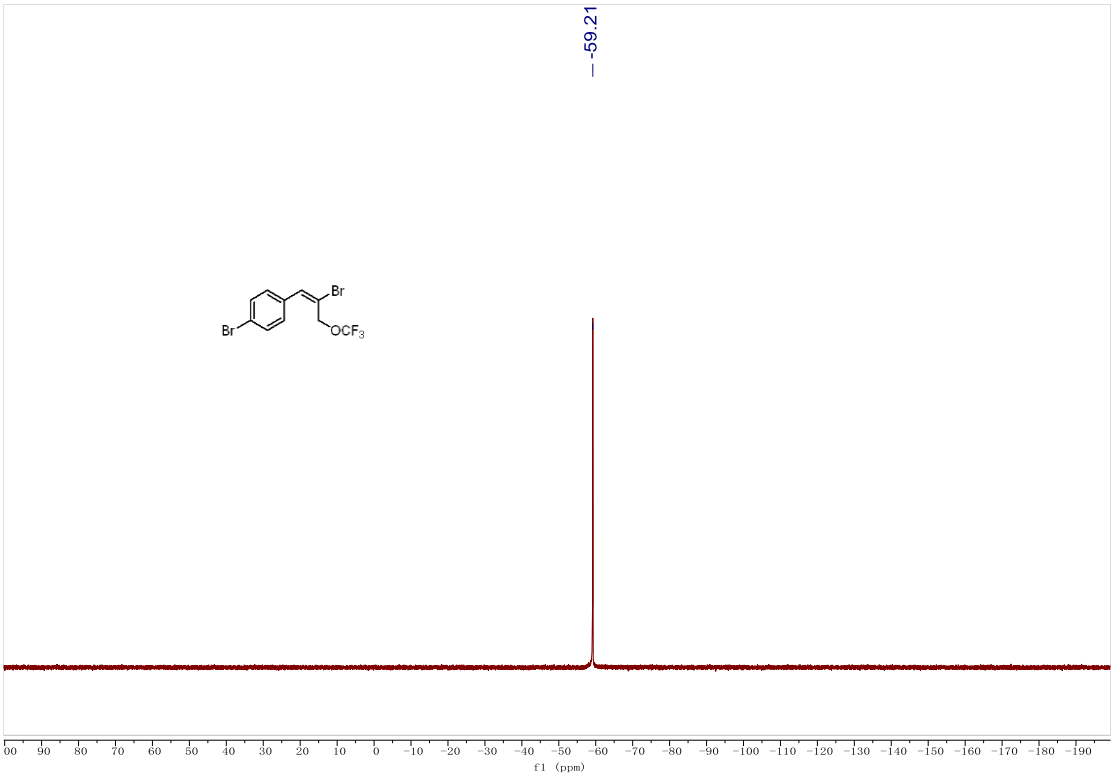



$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*Z*)-3h**

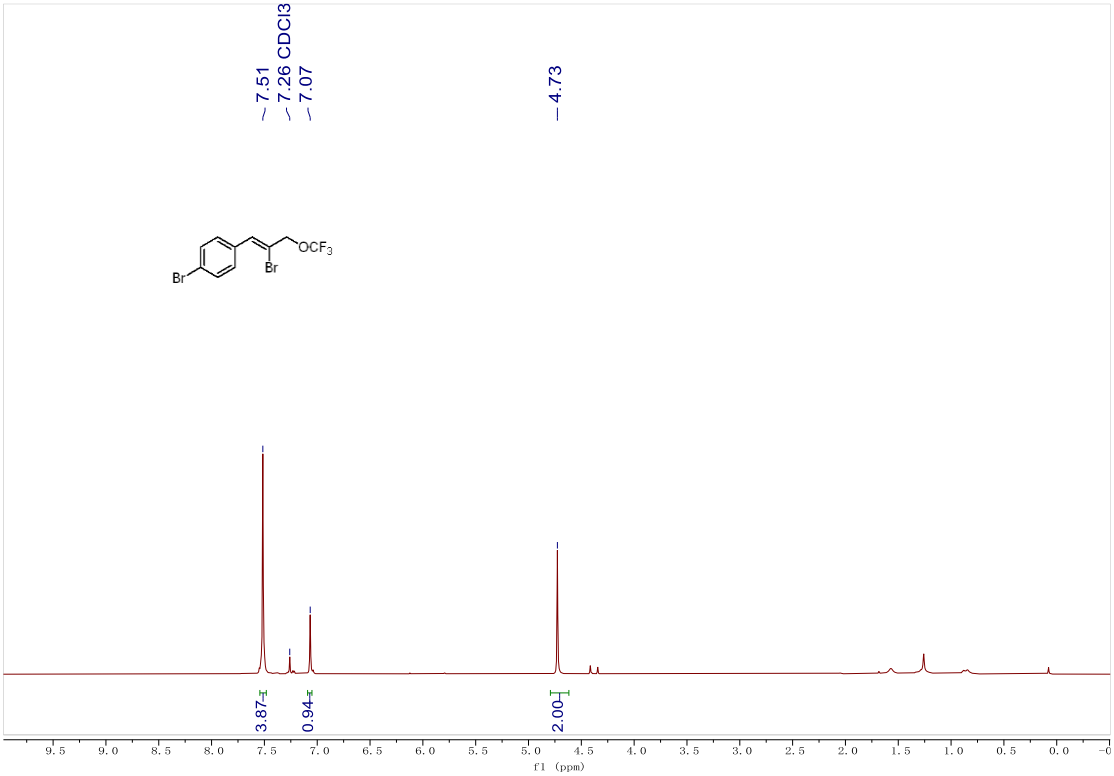

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **(*E*)-3i**



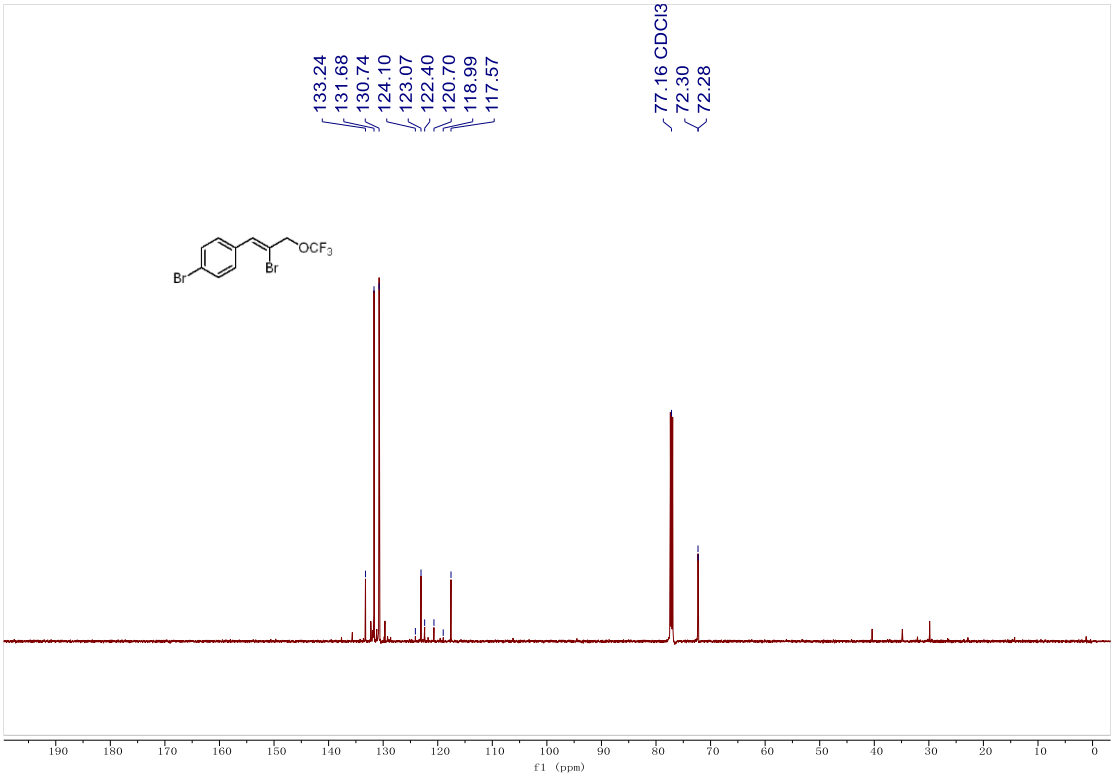

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **(*E*)-3i**



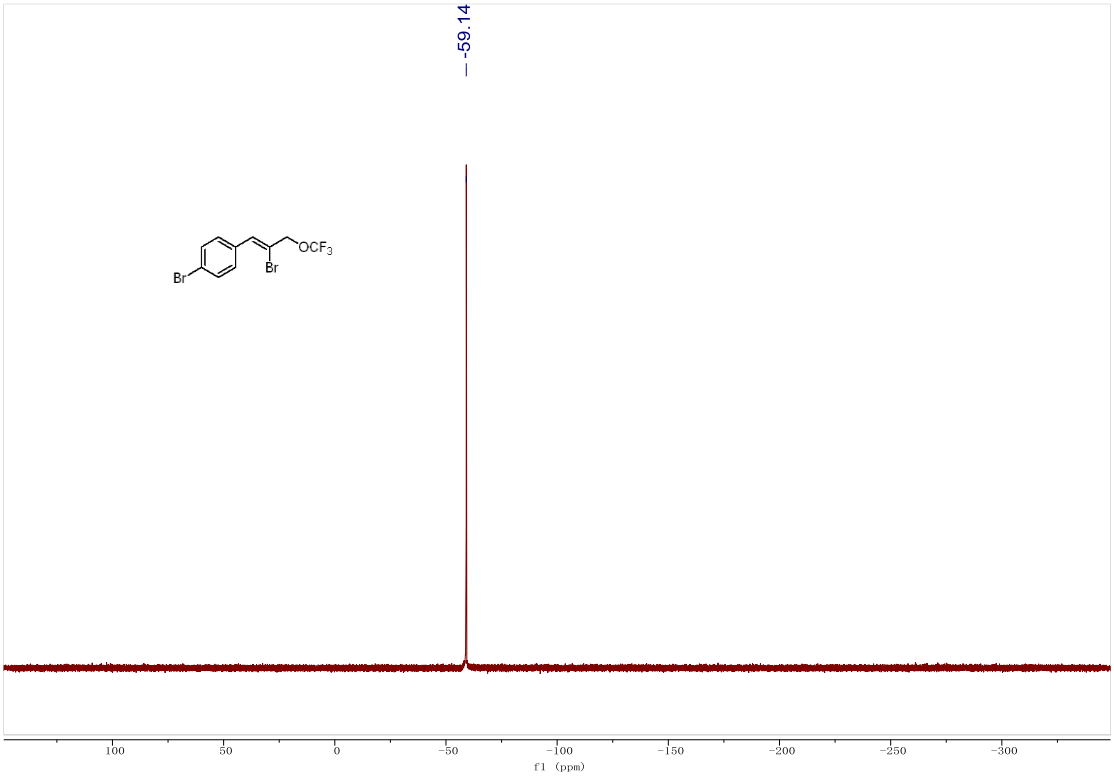

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*E*)-3i**



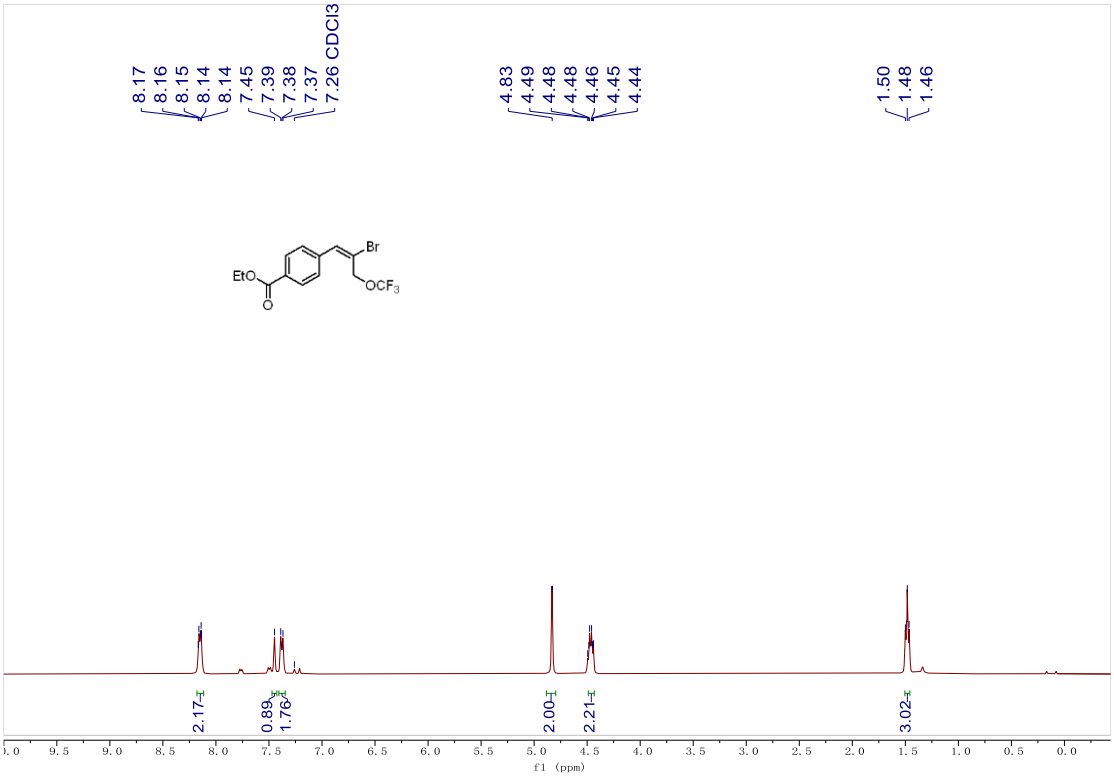

$^{1}$H NMR spectrum (600 MHz, $CDCl_3$) of **(*Z*)-3i**



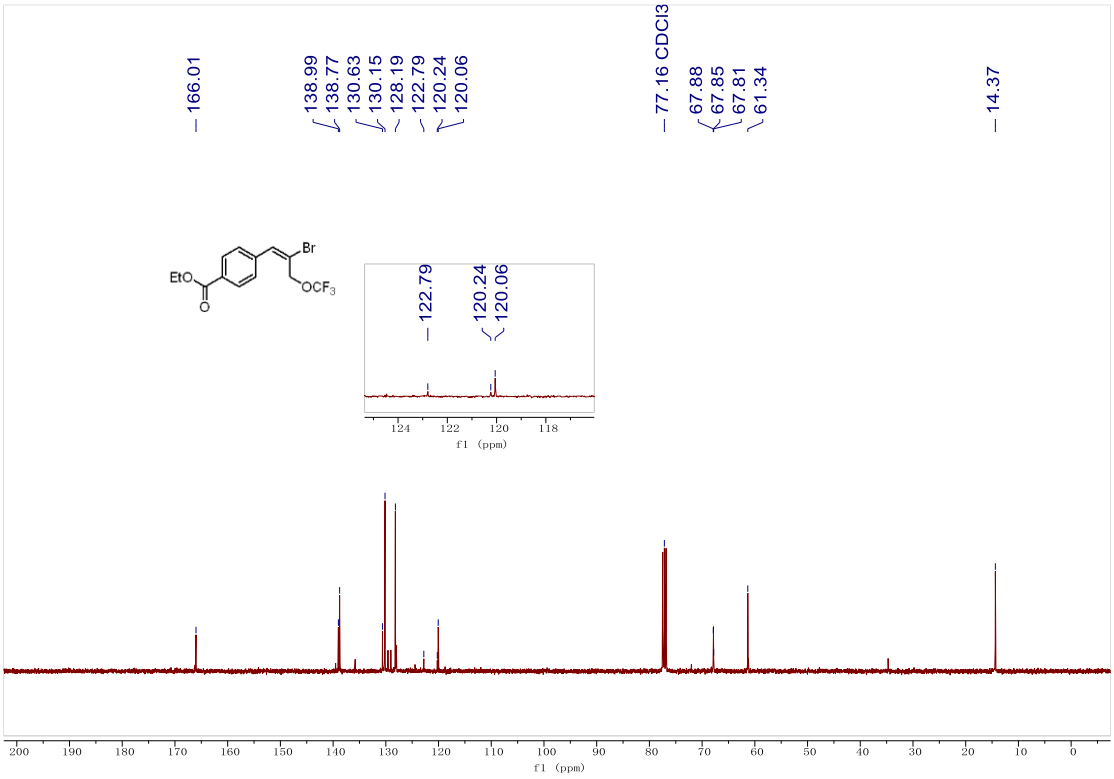

$^{13}$C NMR spectrum (151 MHz, $CDCl_3$) of **(*Z*)-3i**



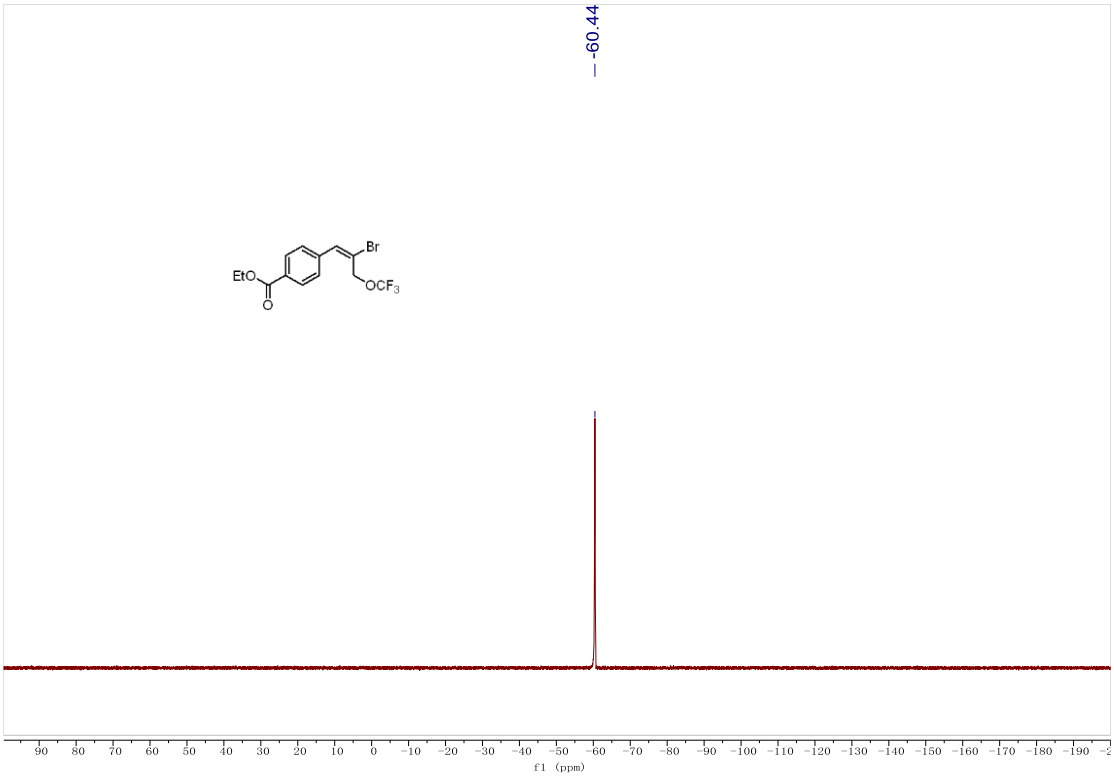

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*Z*)-3i**



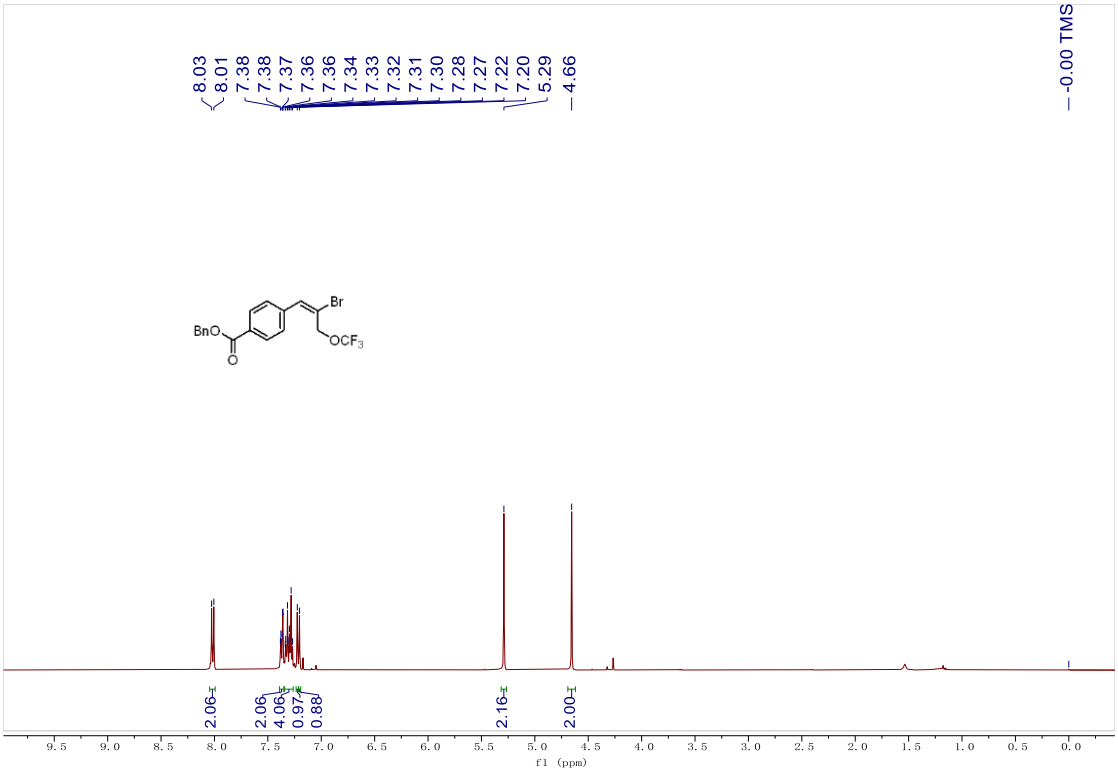

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **(*E*)-3j**



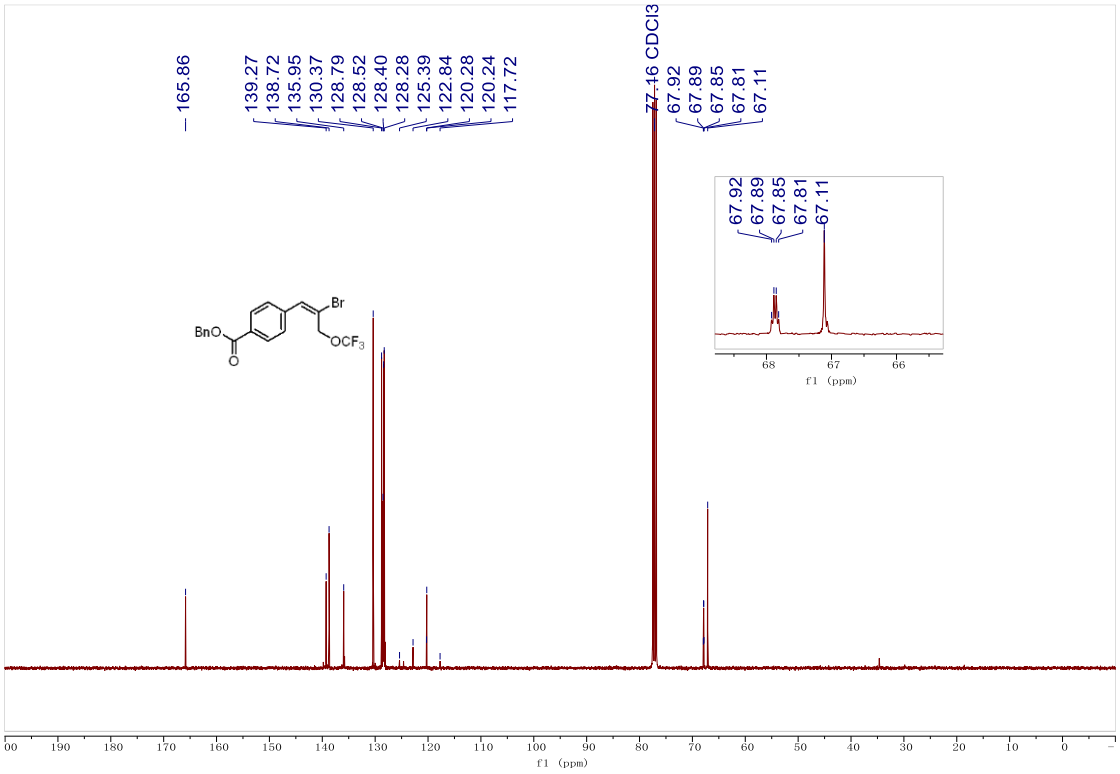

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **(*E*)-3j**



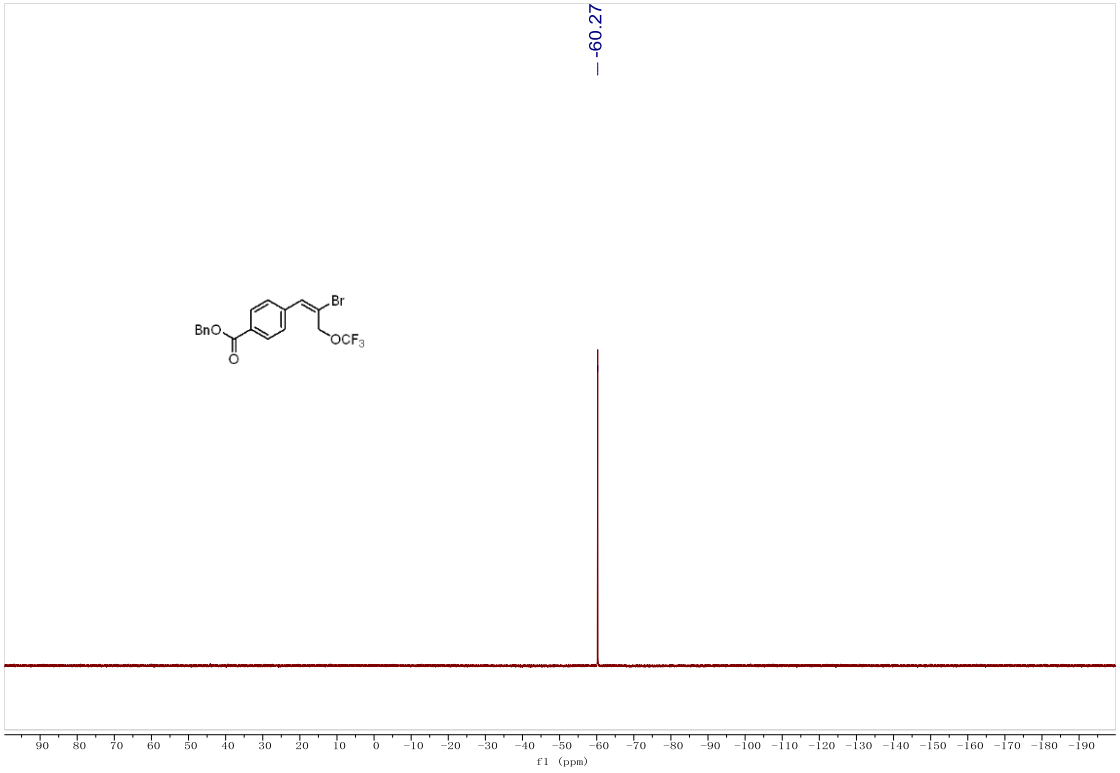

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*E*)-3j**



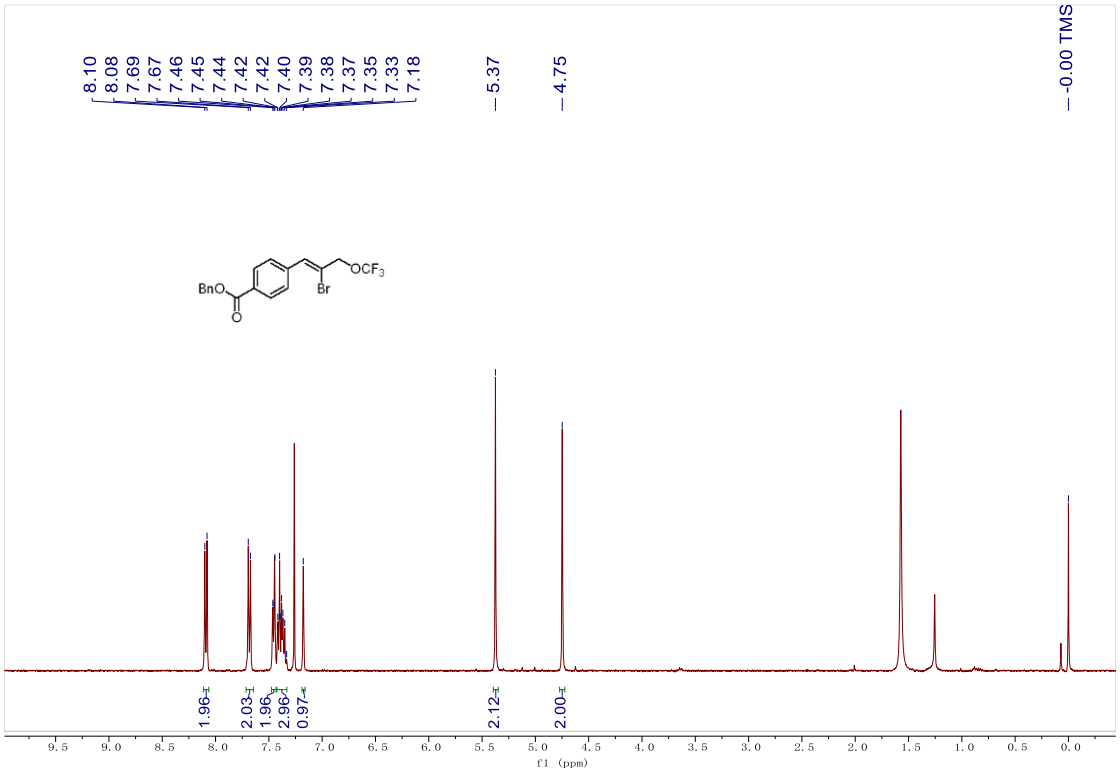

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **(*E*)-3k**



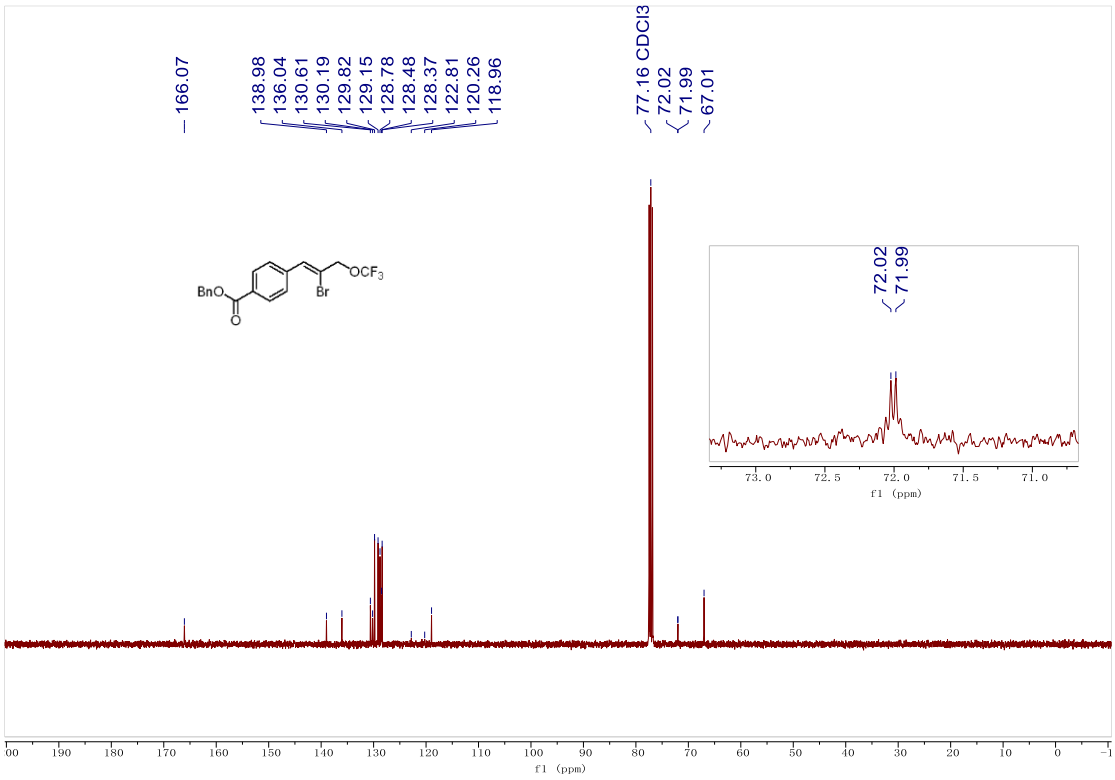

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **(*E*)-3k**



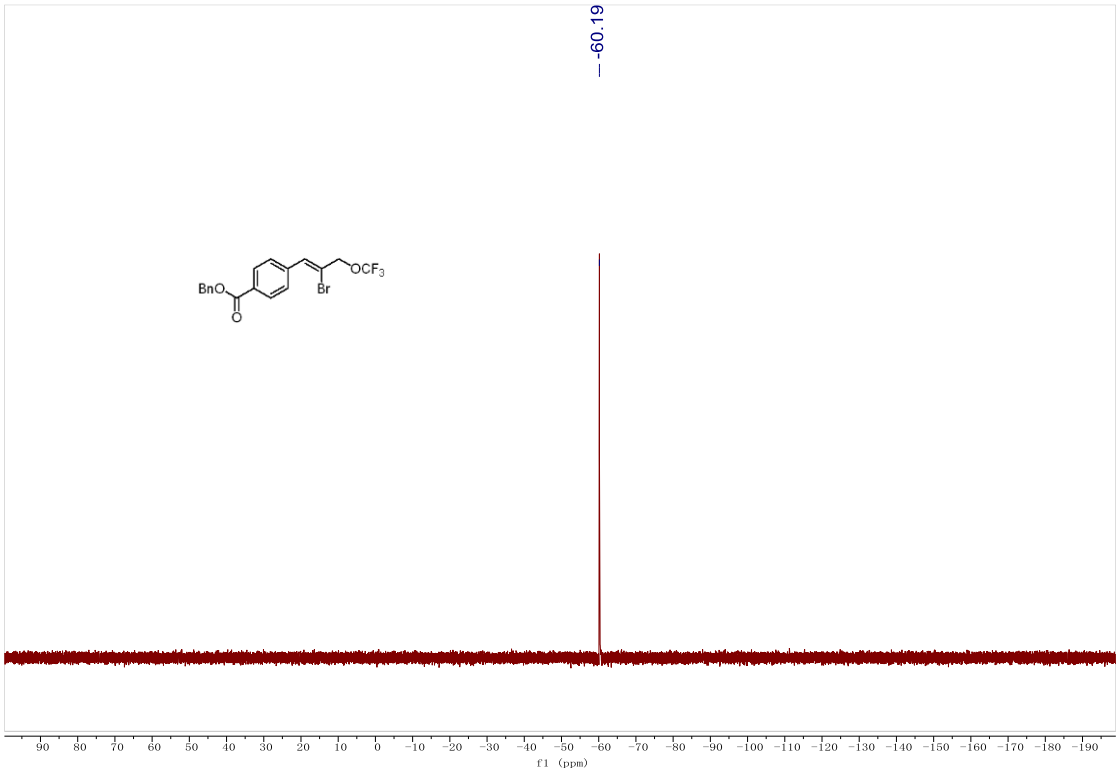

$^{19}$F NMR spectrum (376 MHz, DMSO-$d_6$) of **(*E*)-3k**



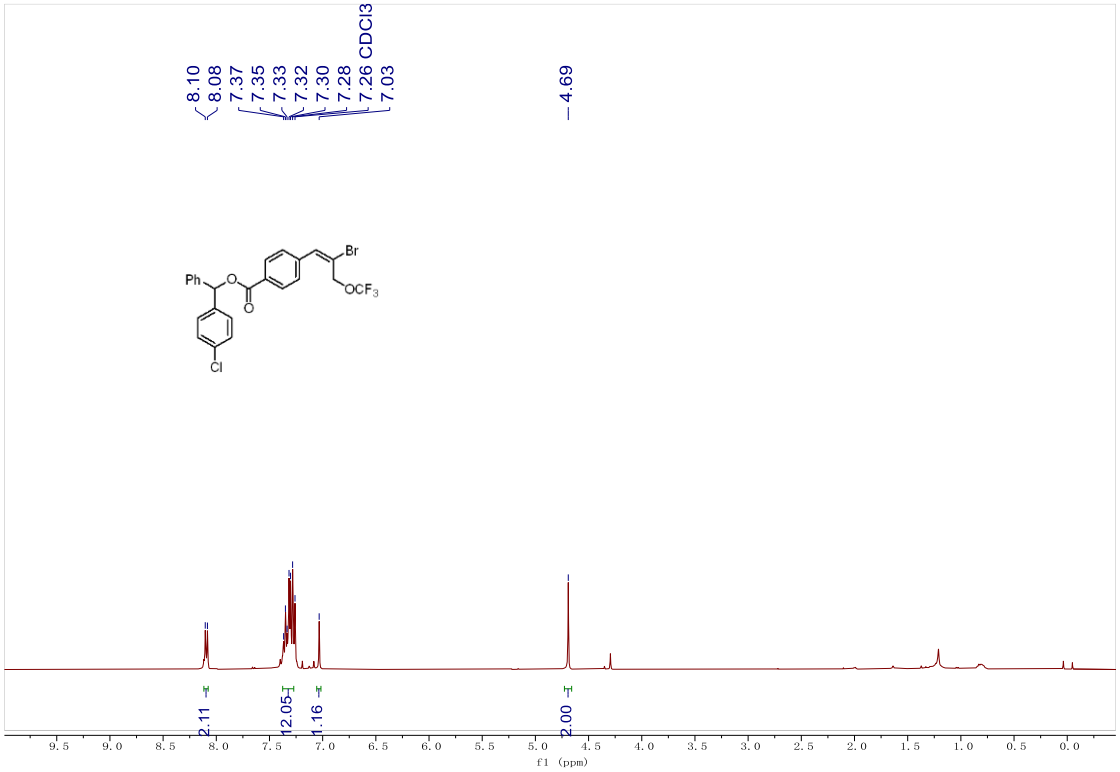

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **(*Z*)-3k**



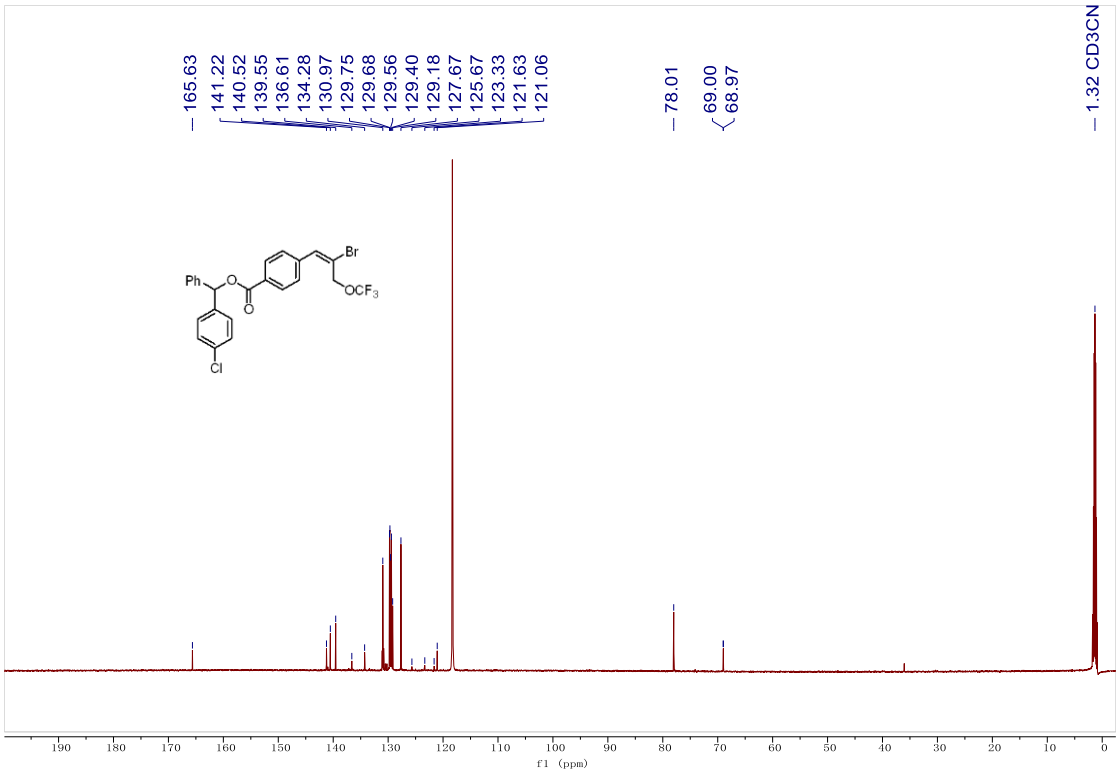

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **(*Z*)-3k**



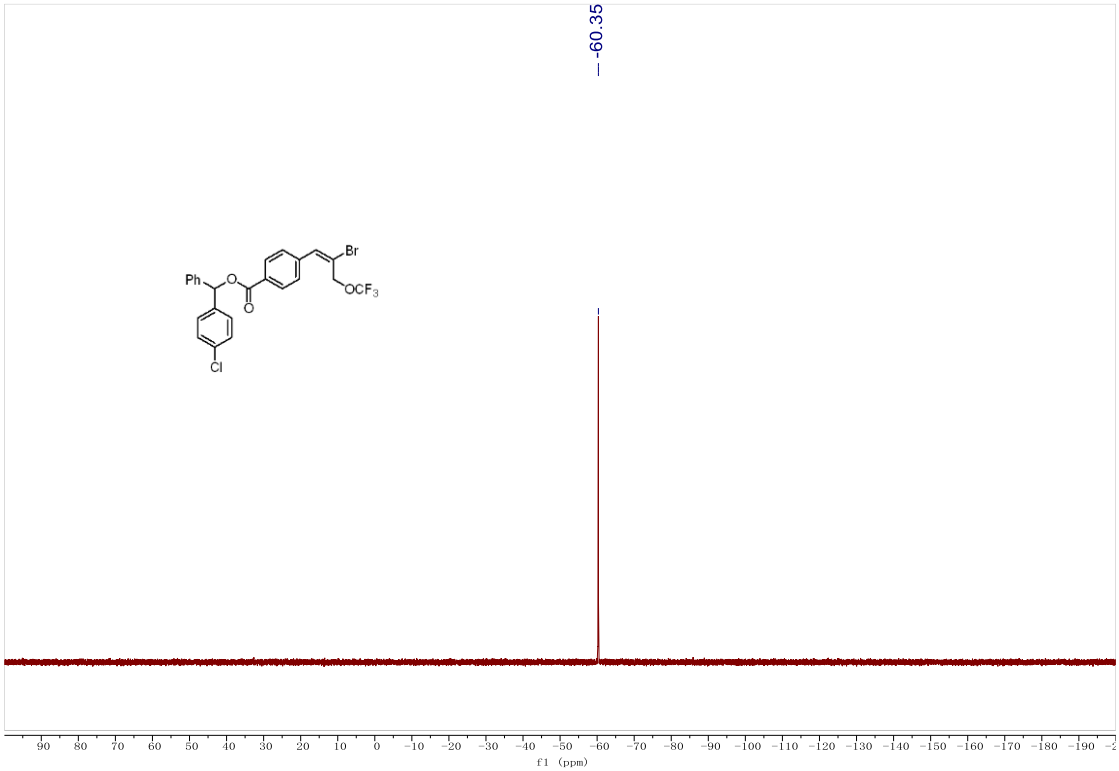

$^{19}$F NMR spectrum (376 MHz, DMSO-$d_6$) of **(*Z*)-3k**



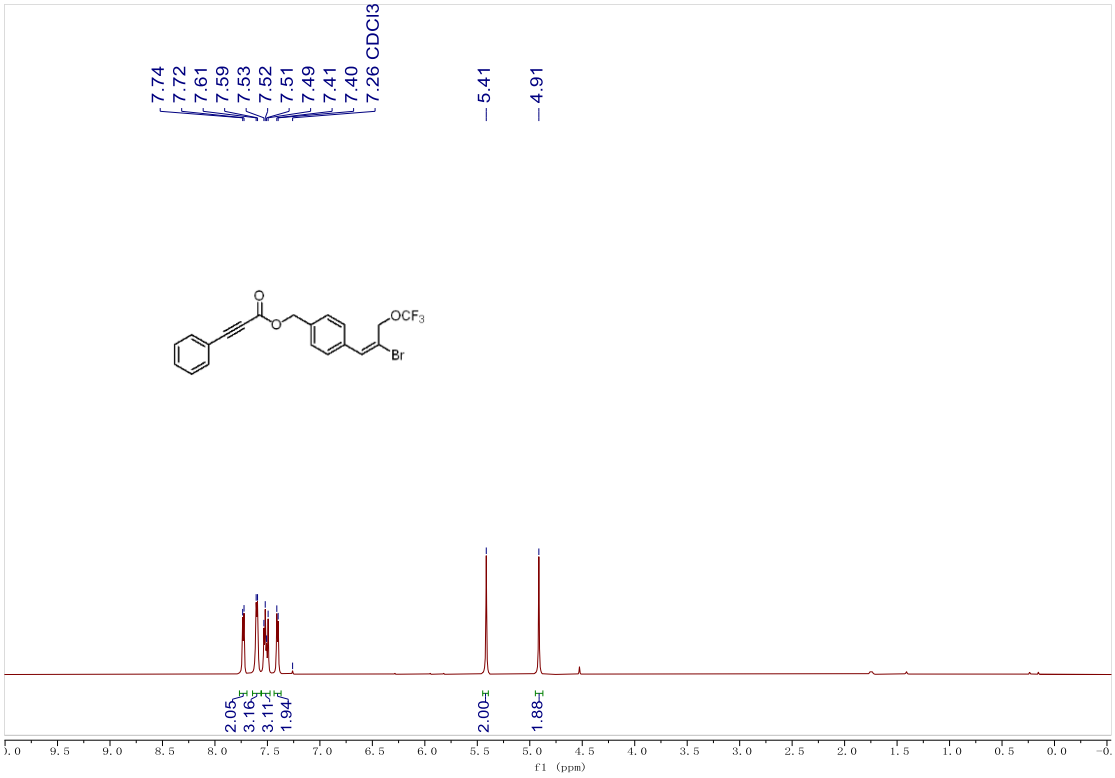

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **(*E*)-3l**



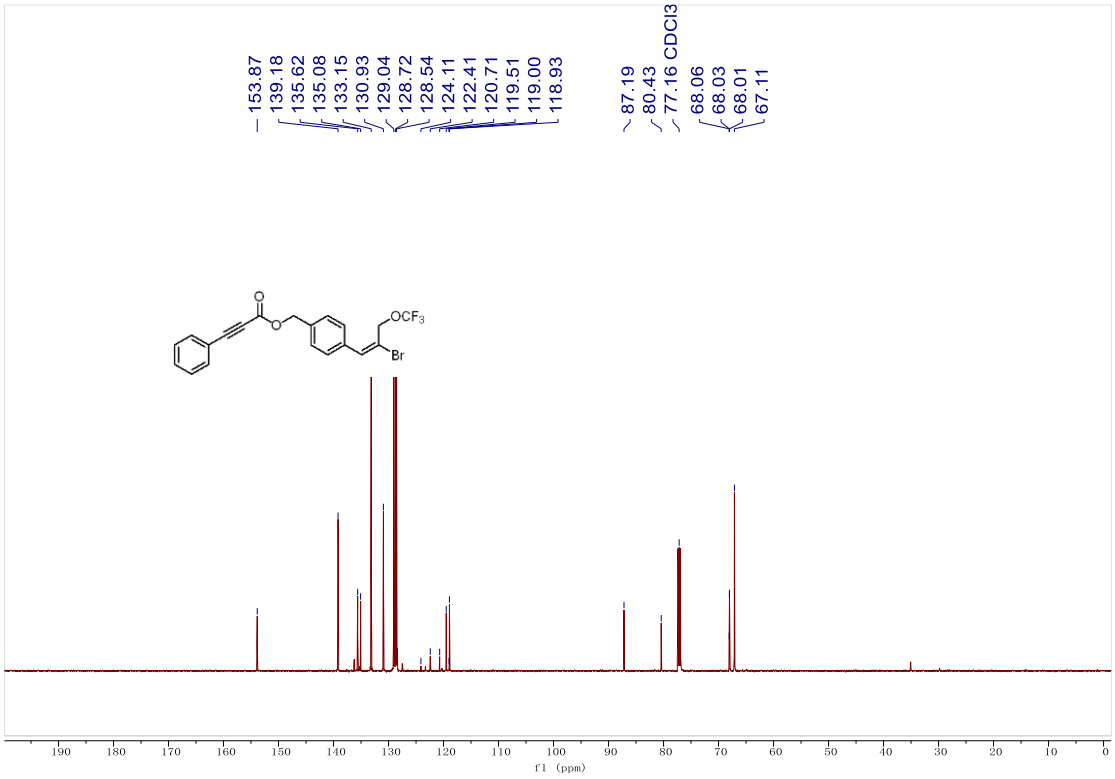

$^{13}$C NMR spectrum (151 MHz, Acetonitrile-$d_3$) of **(*E*)-3l**



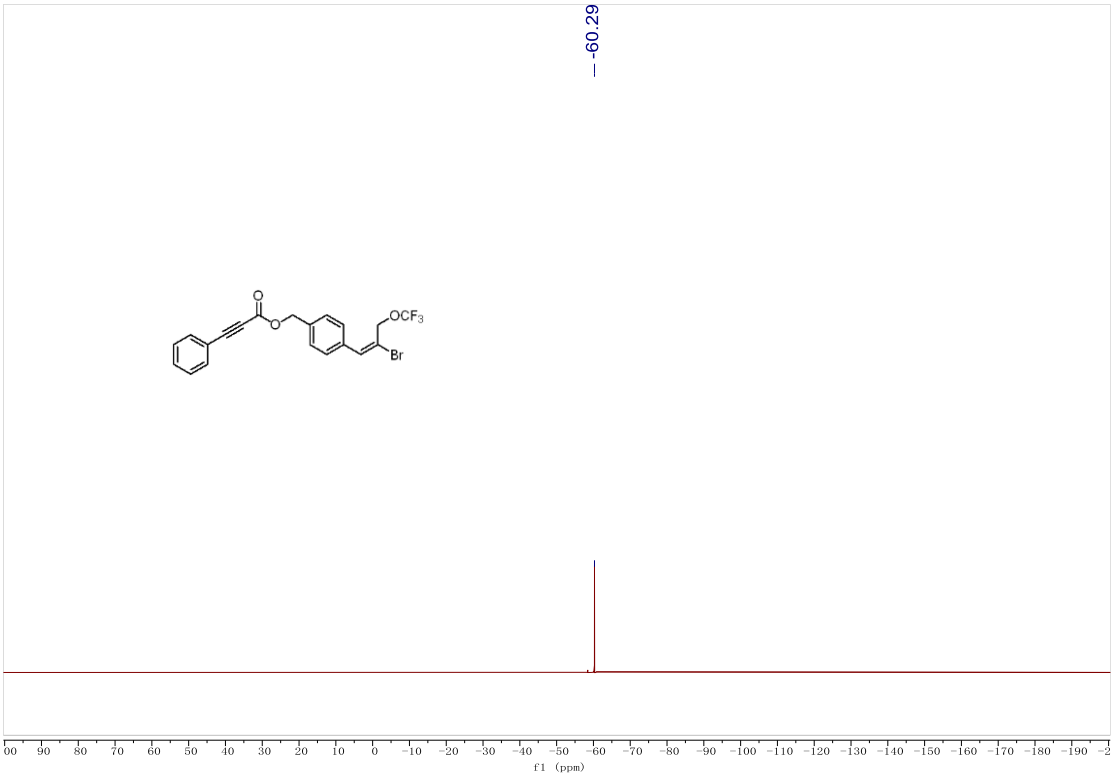

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*E*)-3l**



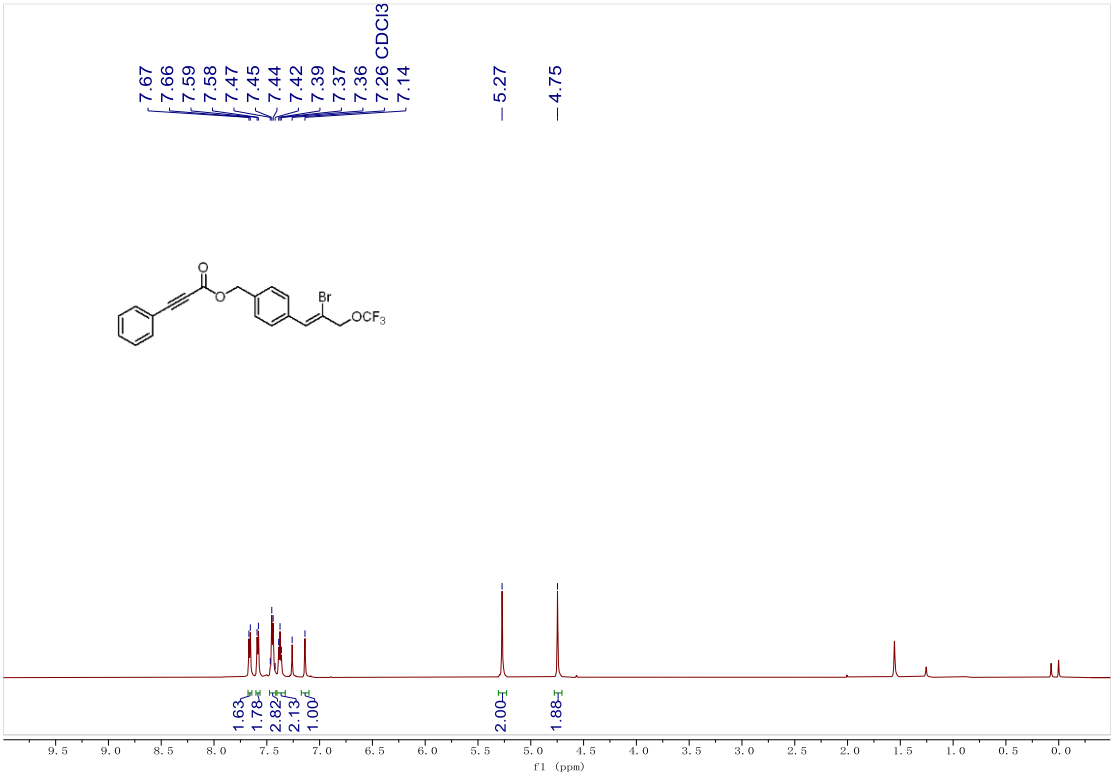

$^{1}$H NMR spectrum (600 MHz, $CDCl_3$) of **(*E*)-3m**



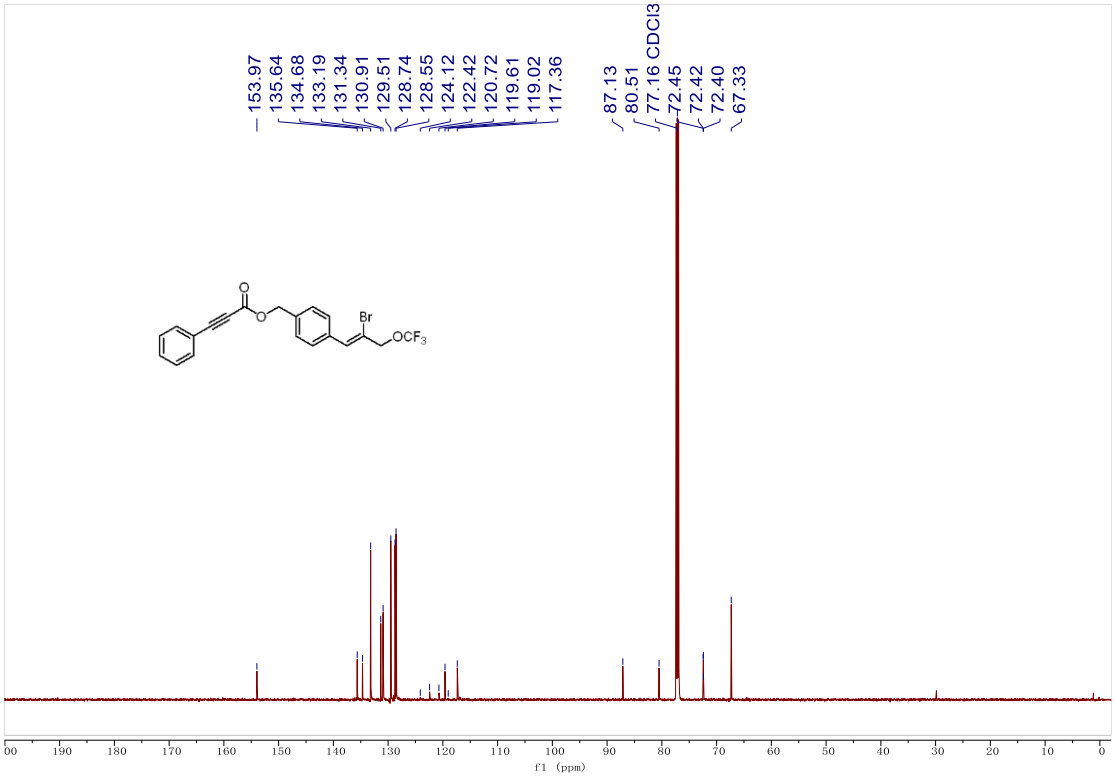

$^{13}$C NMR spectrum (151 MHz, $CDCl_3$) of **(*E*)-3m**



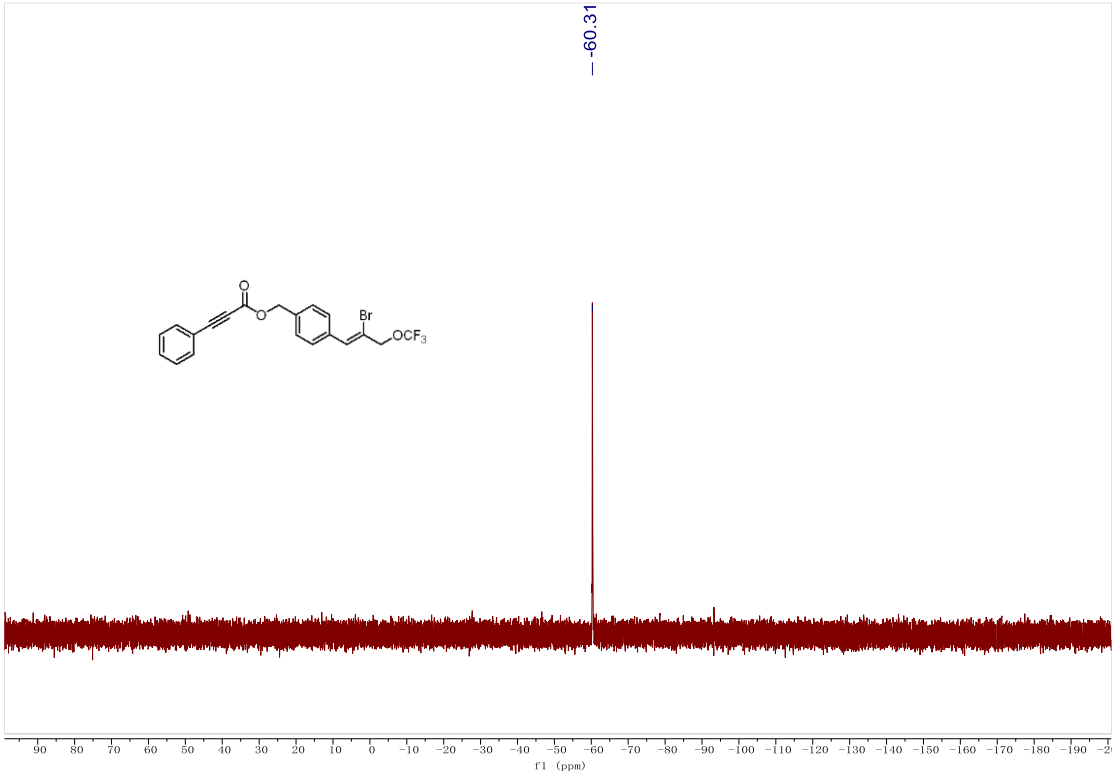

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*E*)-3m**



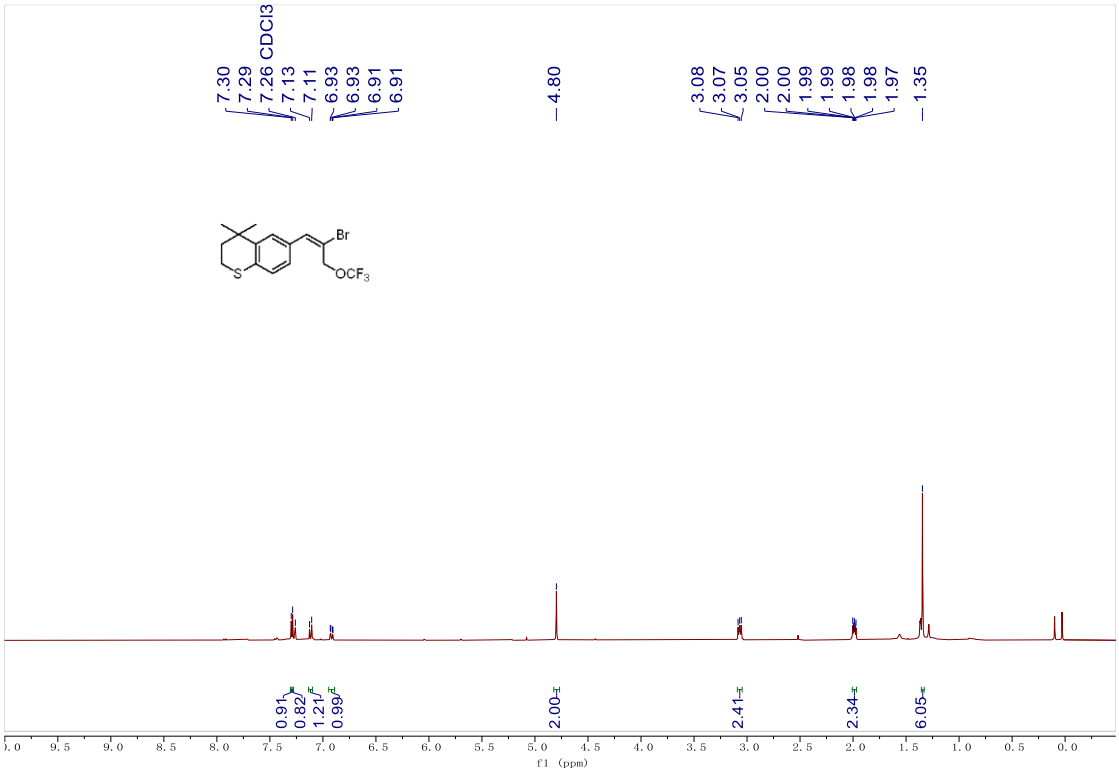

$^{1}$H NMR spectrum (600 MHz, $CDCl_3$) of **(*Z*)-3m**



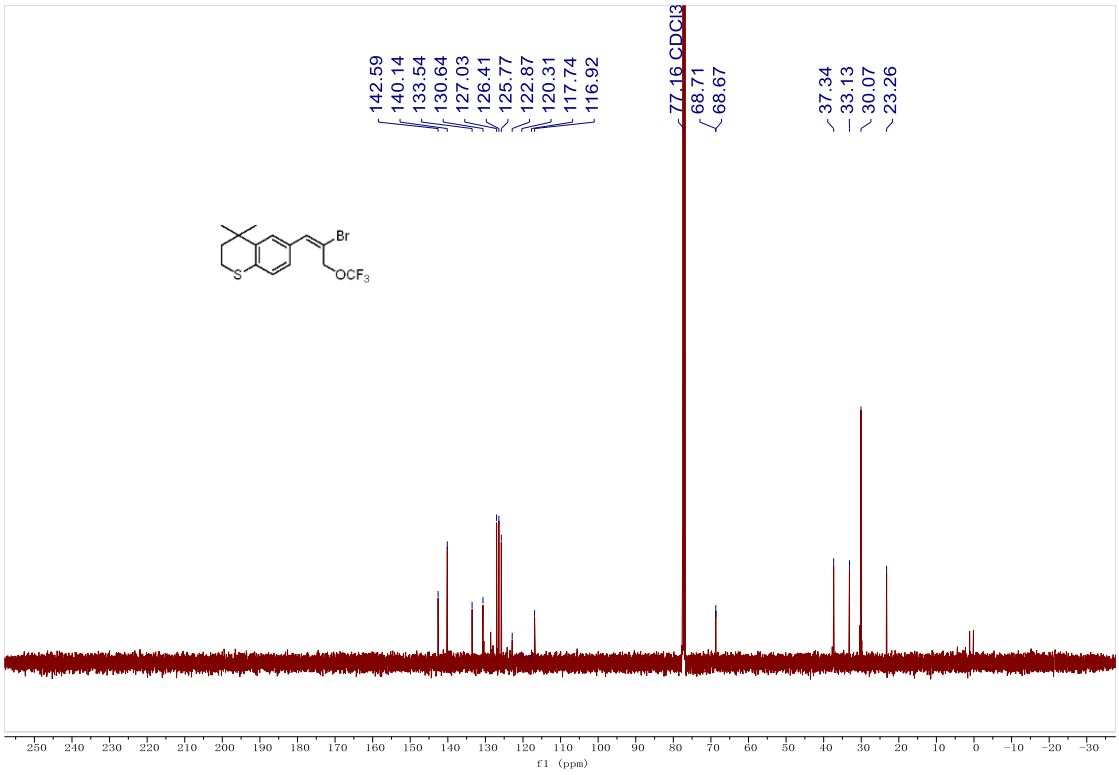

$^{13}$C NMR spectrum (151 MHz, $CDCl_3$) of **(*Z*)-3m**



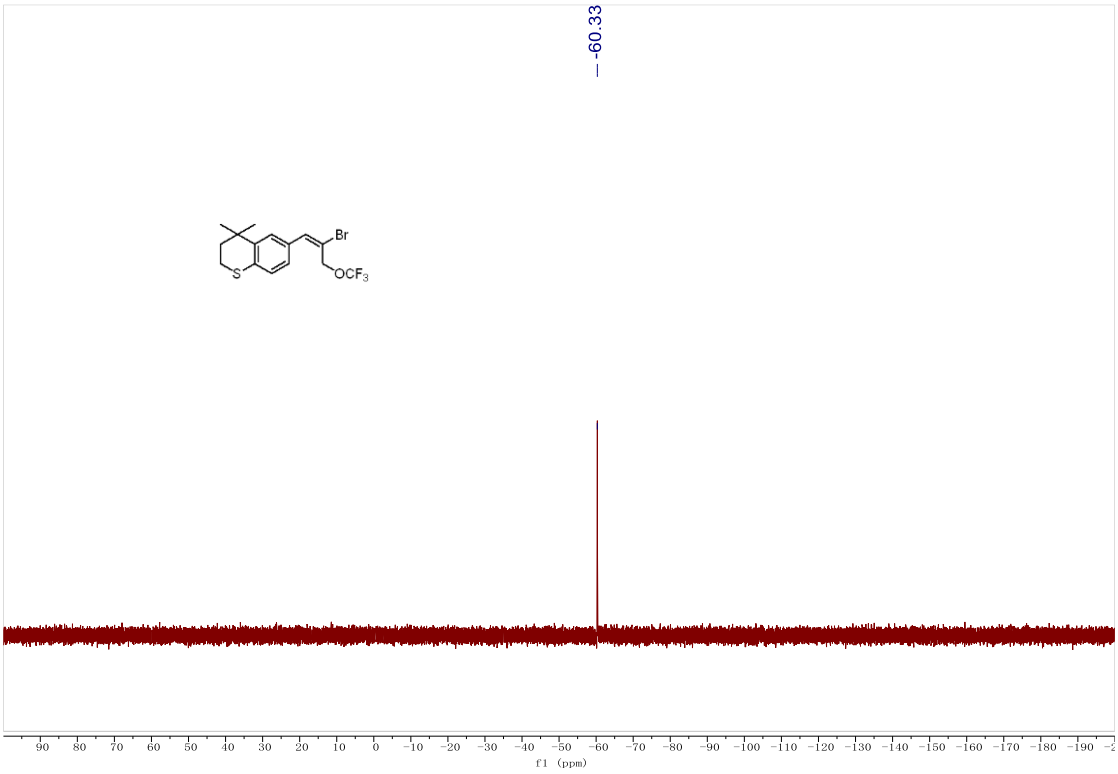

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*Z*)-3m**



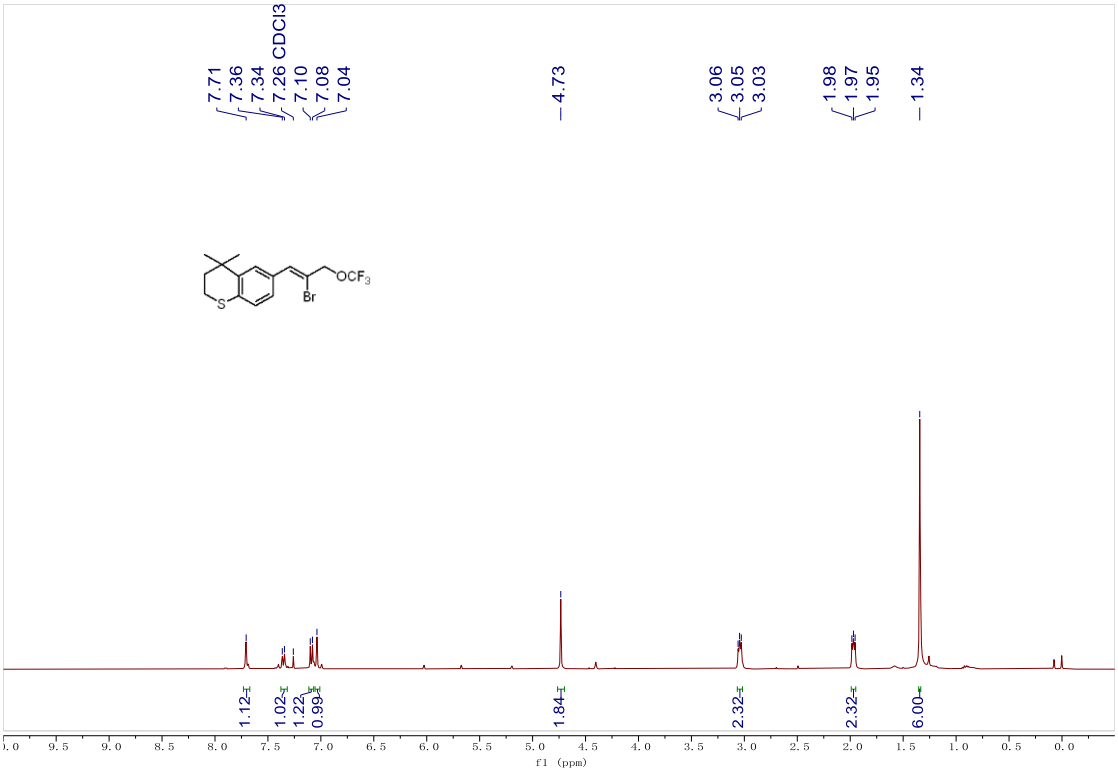

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **(*E*)-3n**



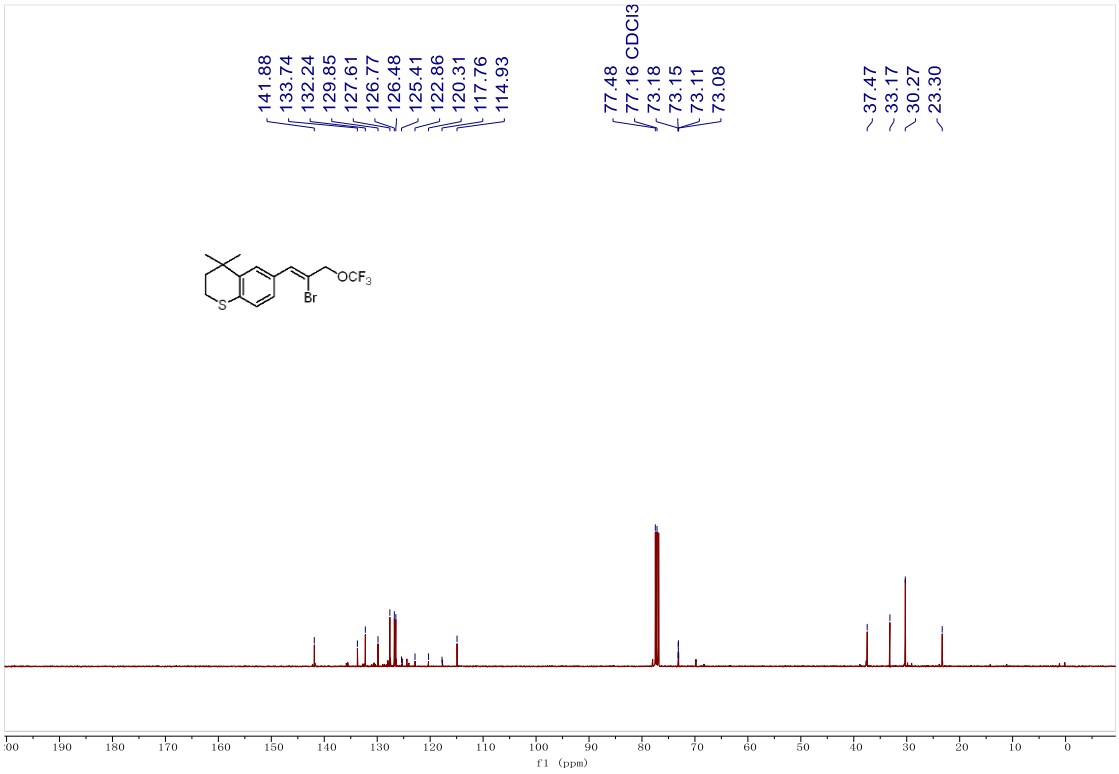

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **(*E*)-3n**



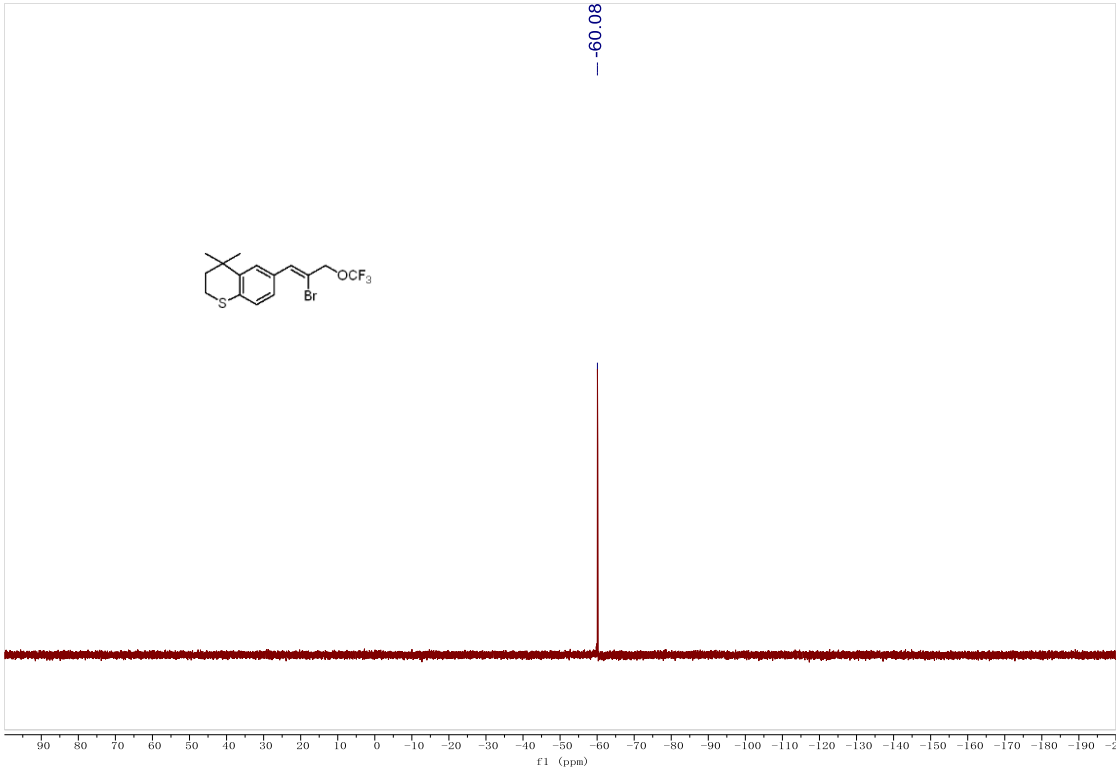

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*E*)-3n**



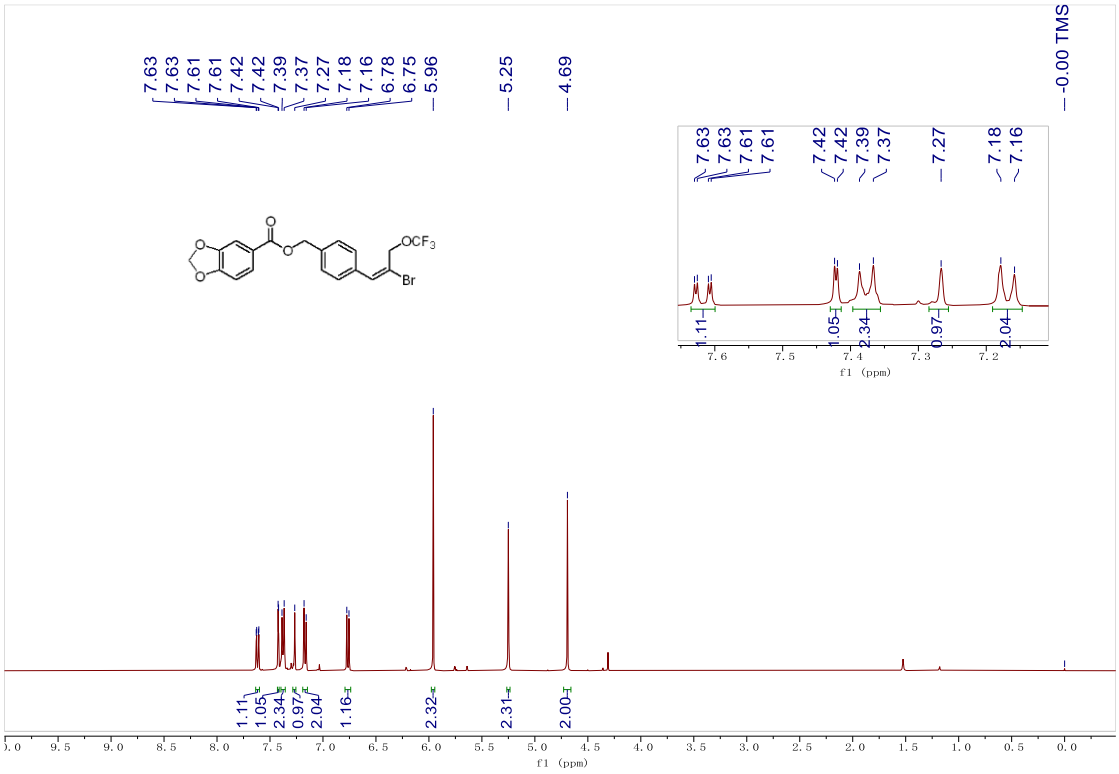

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **(*Z*)-3n**



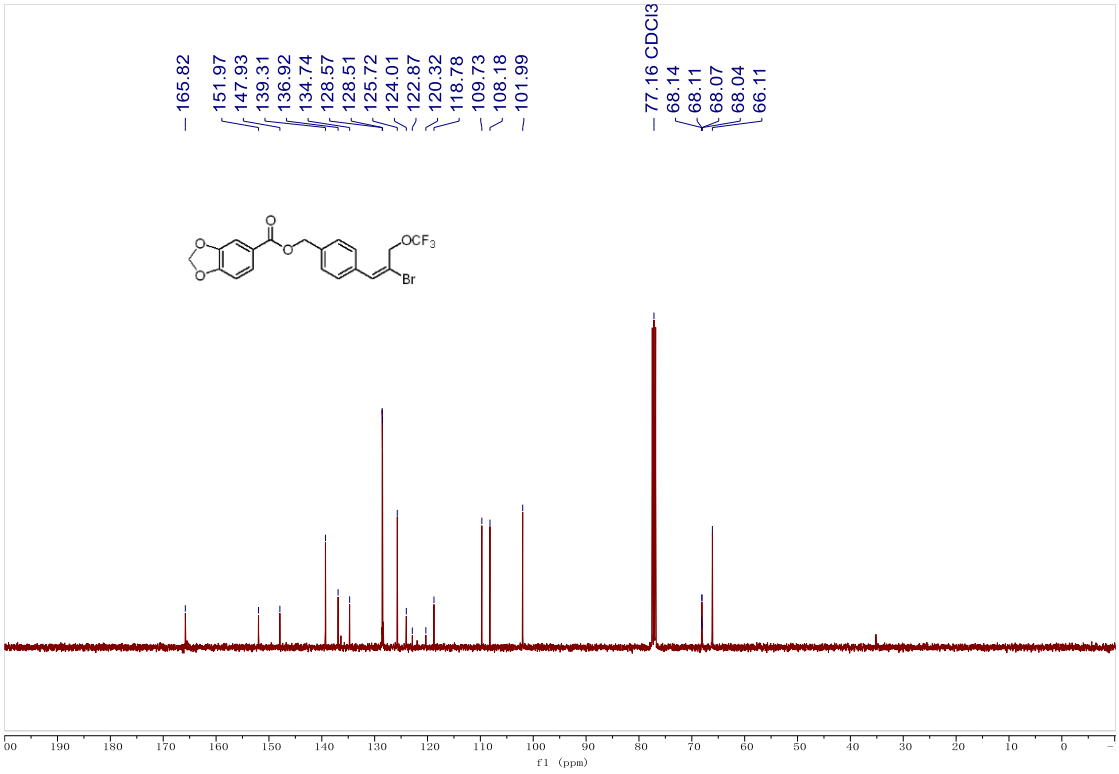

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **(*Z*)-3n**



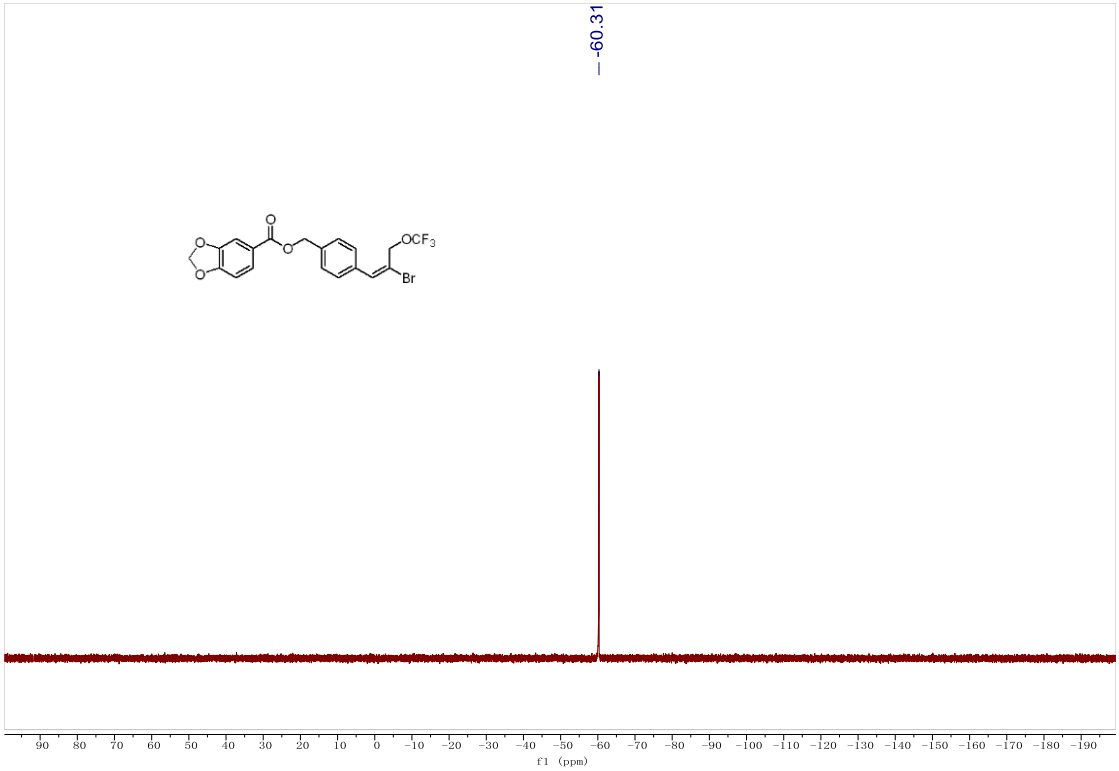

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*Z*)-3n**



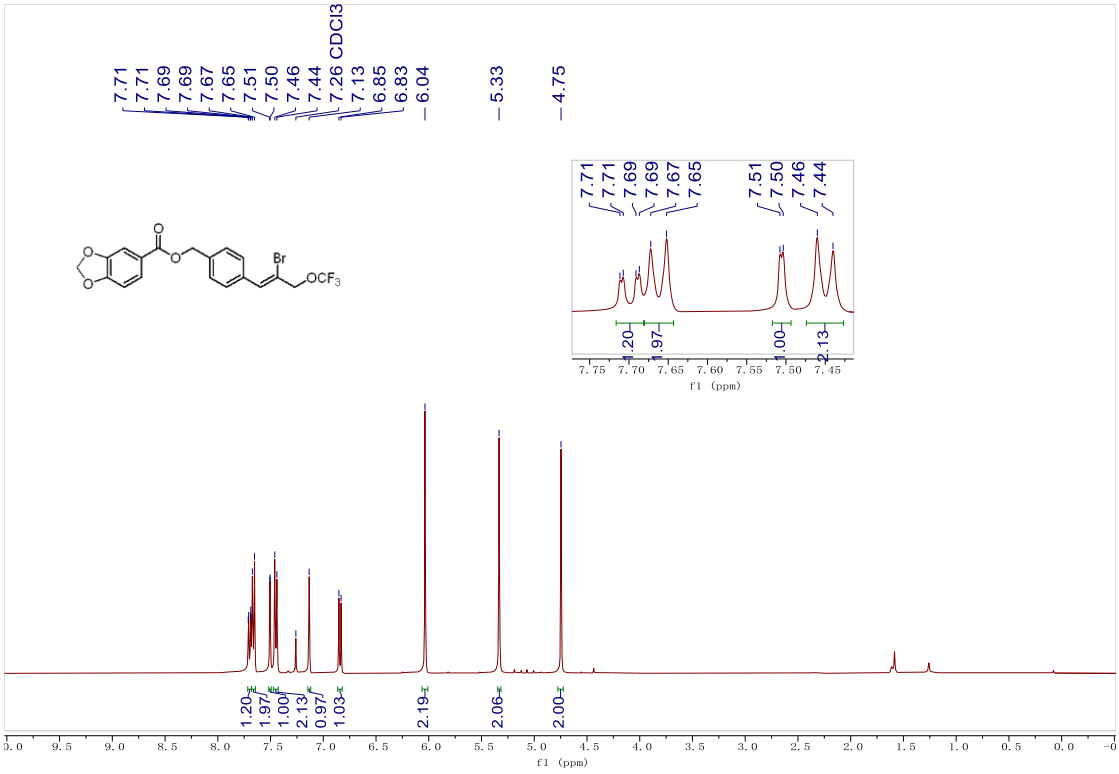

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **(*E*)-3o**



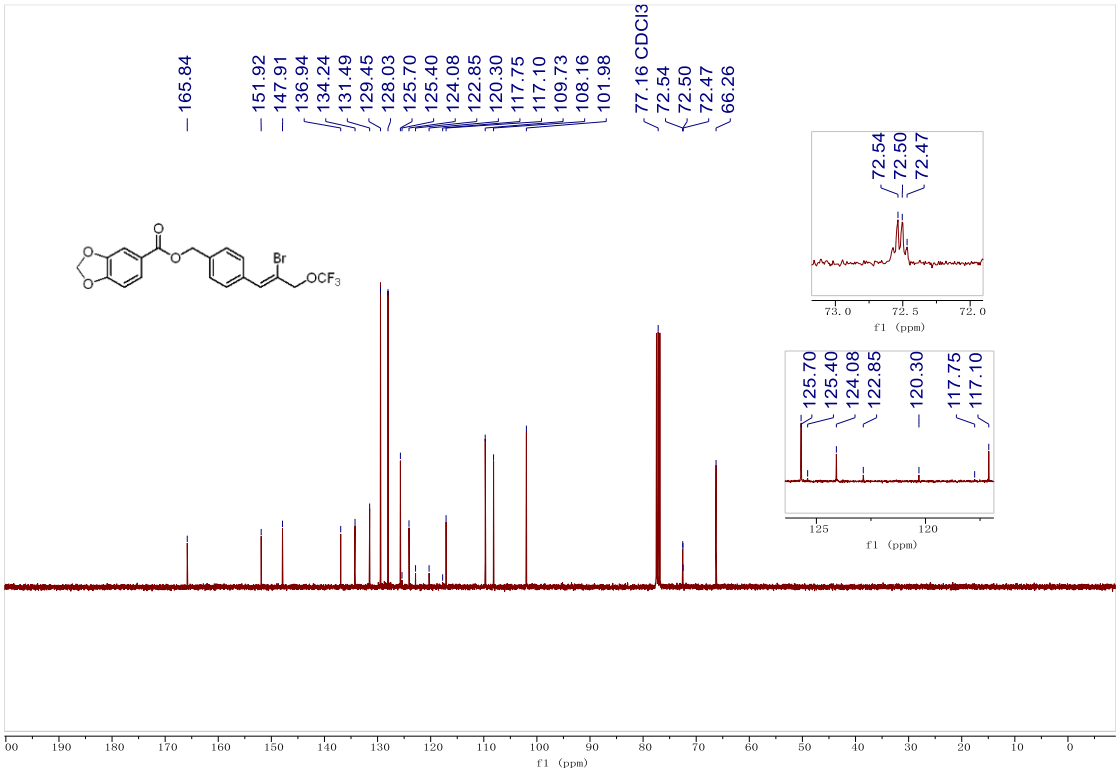

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **(*E*)-3o**



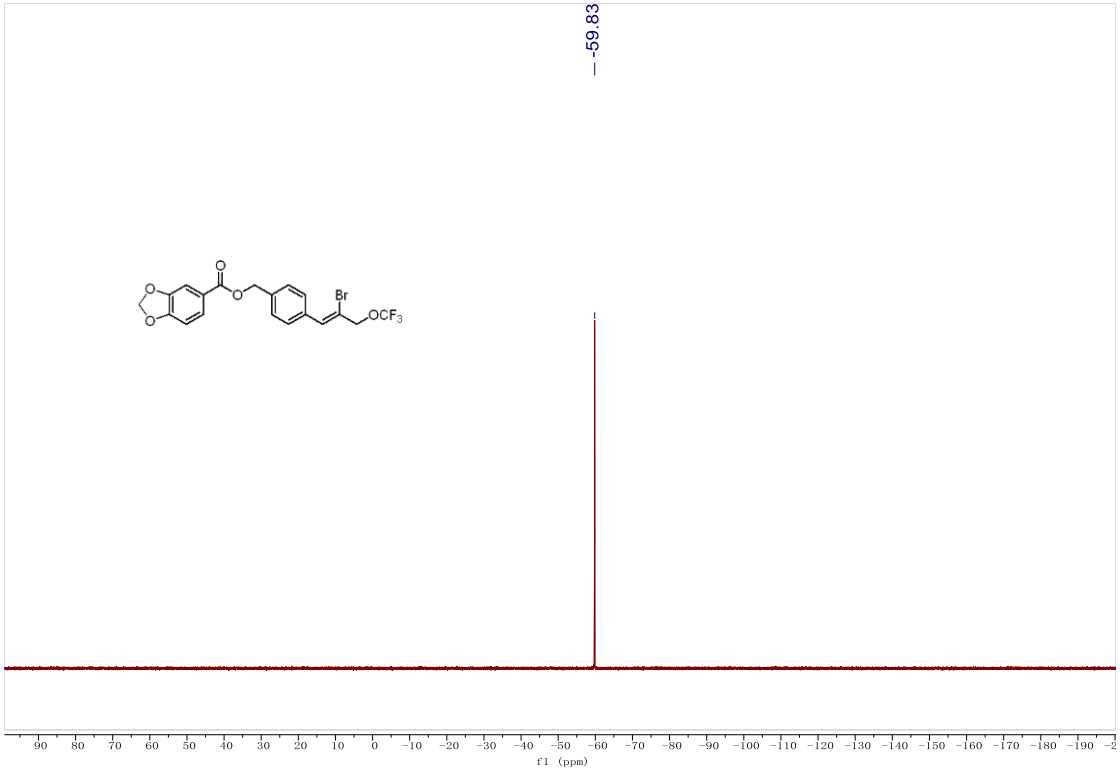

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*E*)-3o**



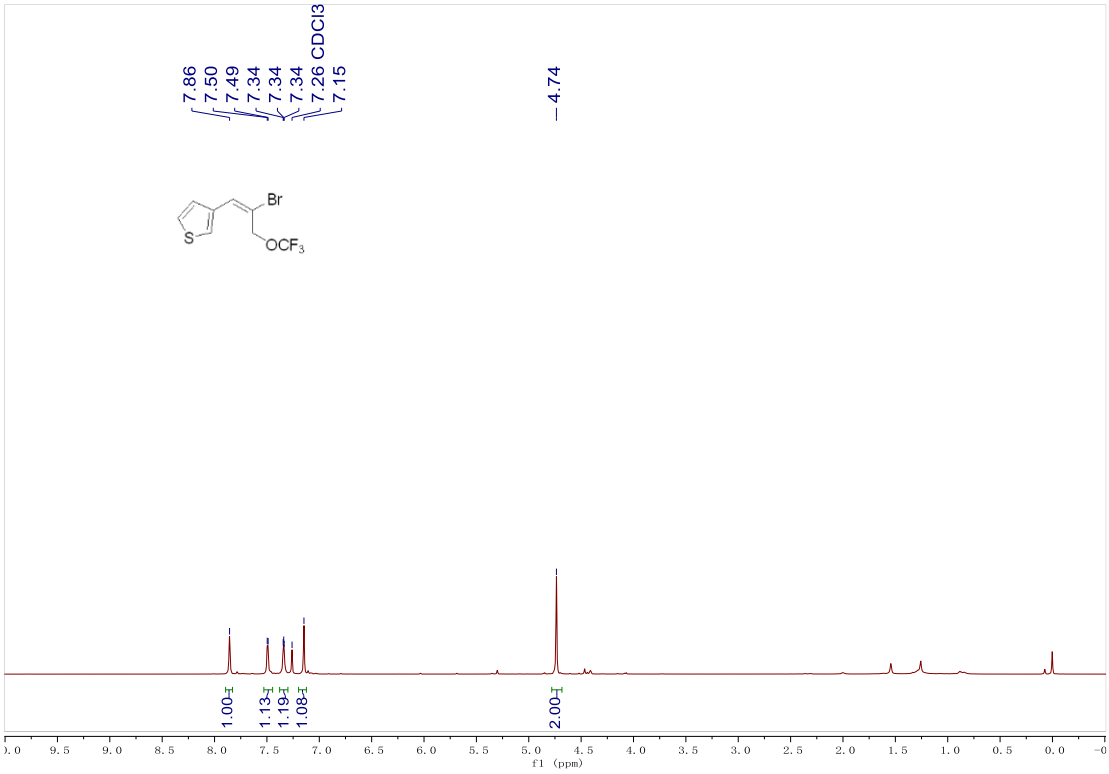

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **(*Z*)-3o**



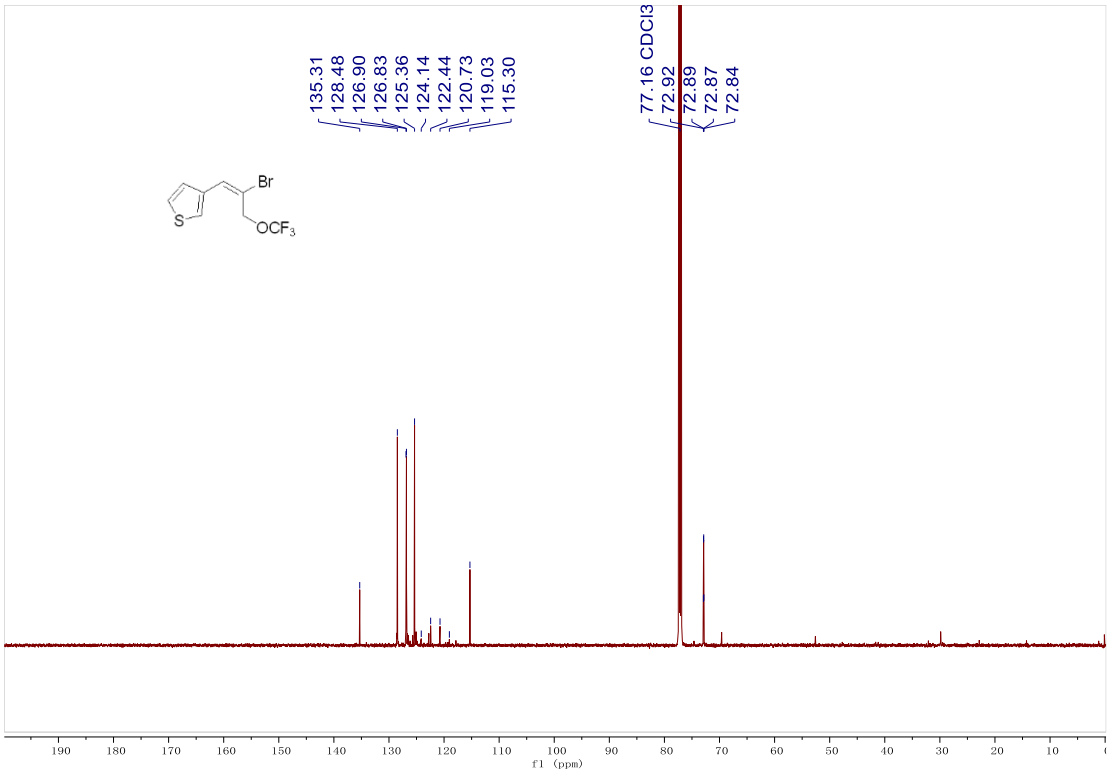

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **(*Z*)-3o**



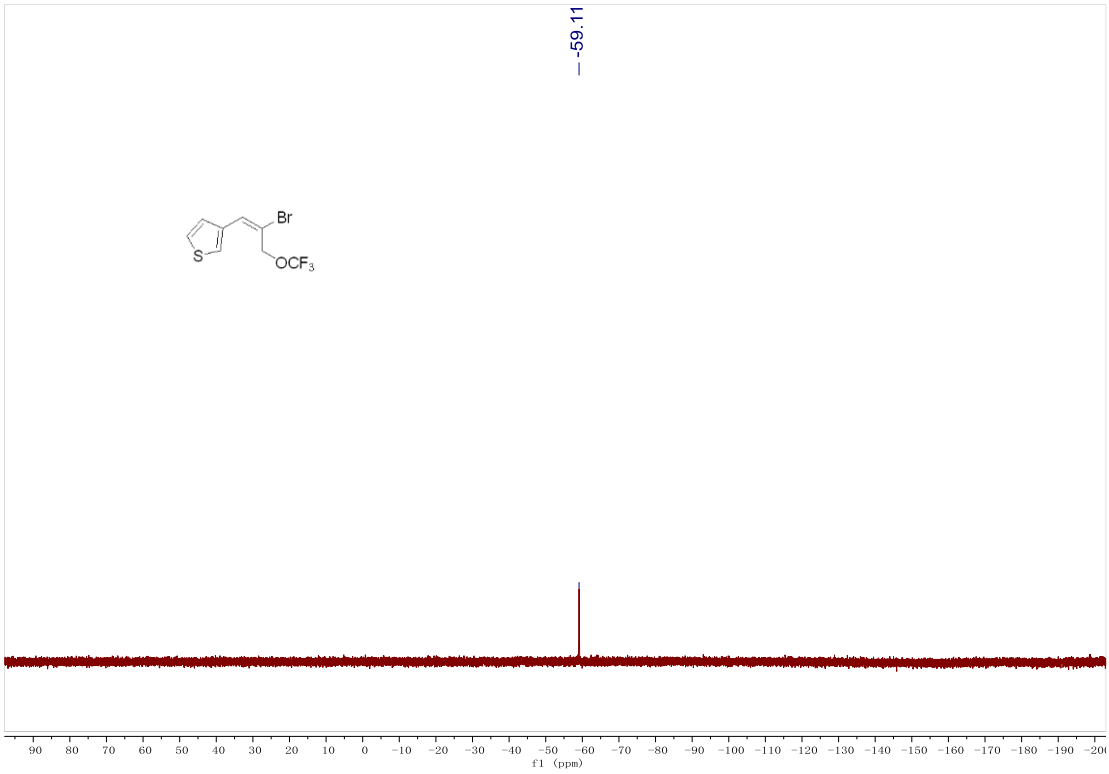

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*Z*)-3o**



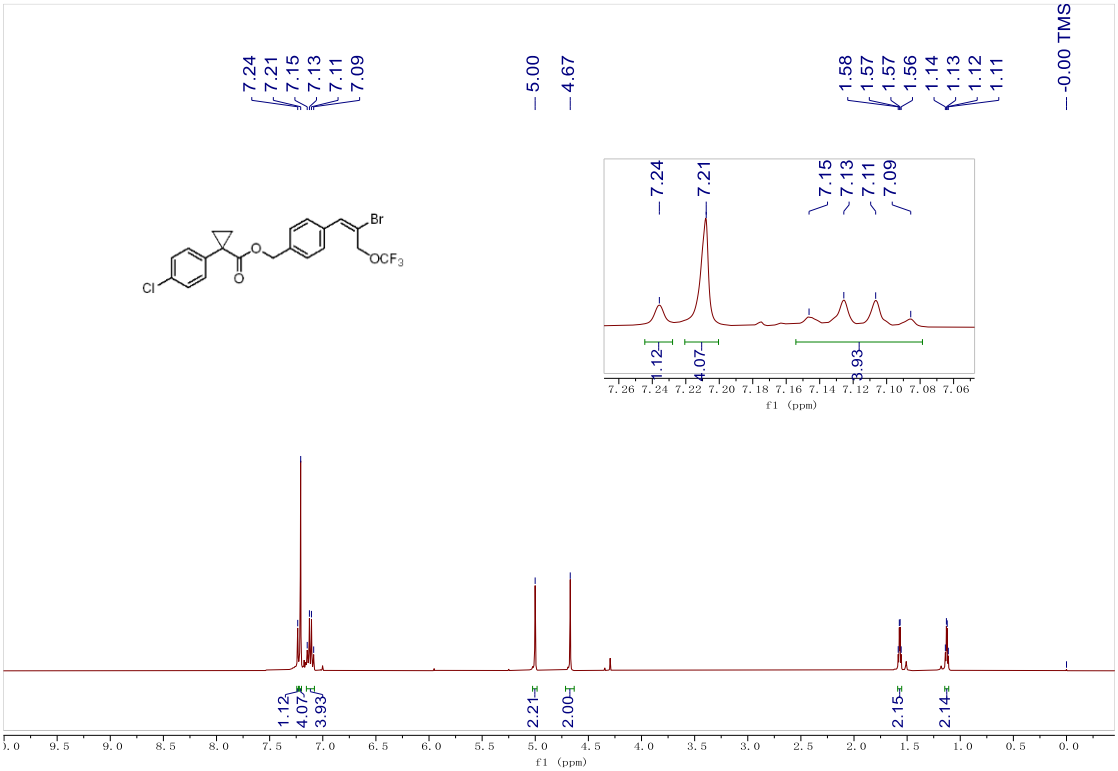

$^{1}$H NMR spectrum (600 MHz, $CDCl_3$) of **(*E*)-3p**



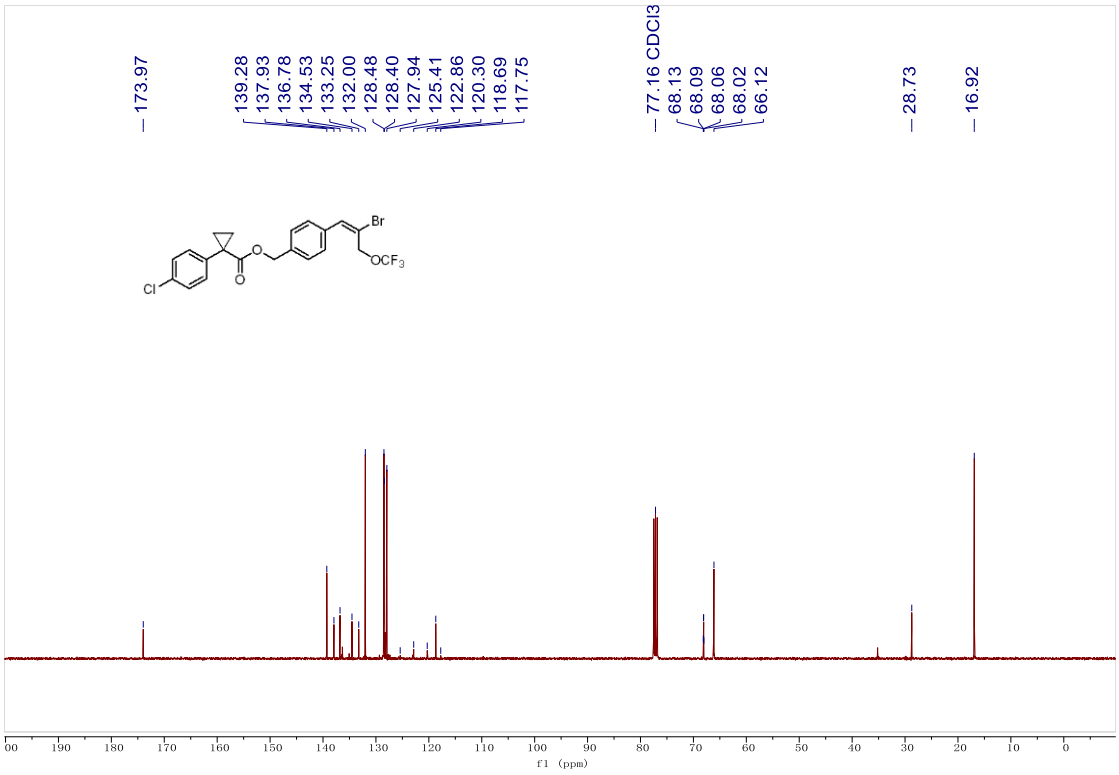

$^{13}$C NMR spectrum (151 MHz, $CDCl_3$) of **(*E*)-3p**



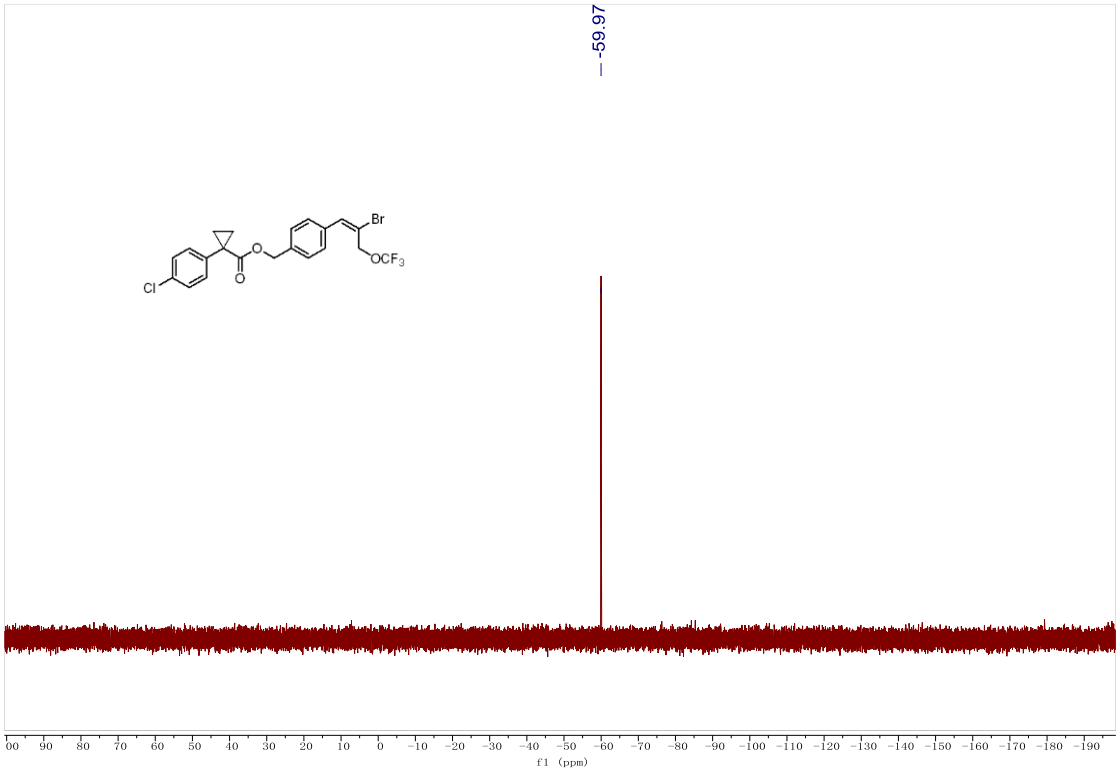

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*E*)-3p**



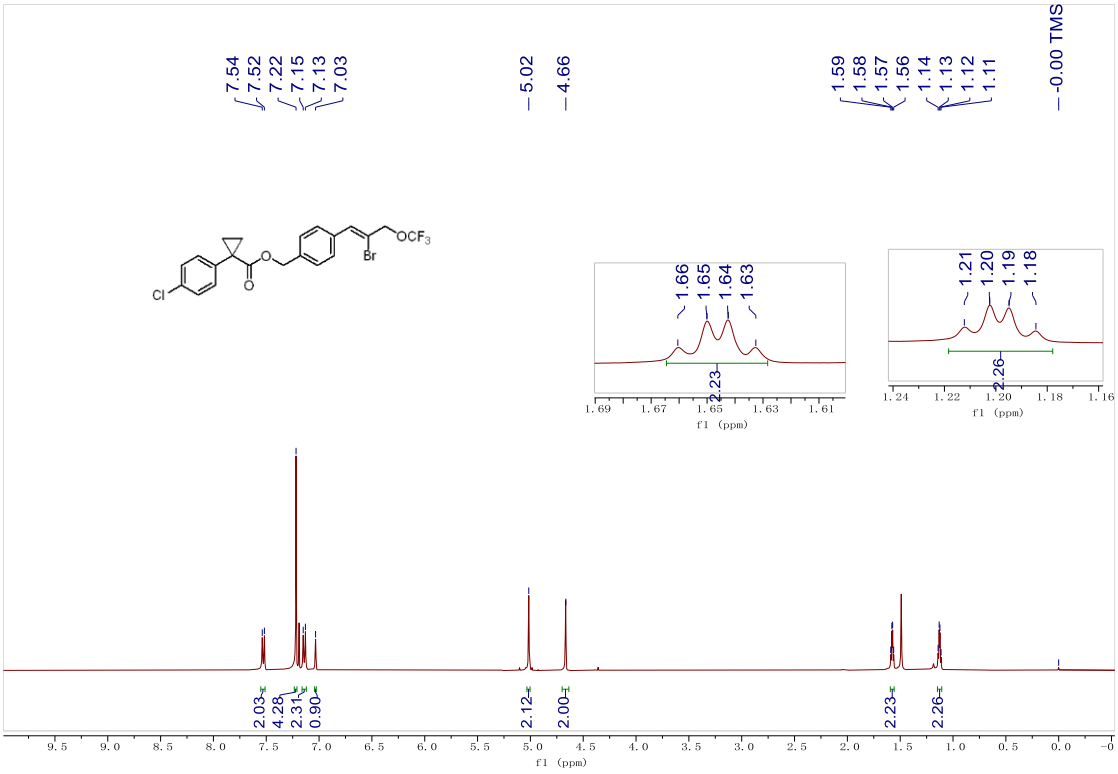

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **(*E*)-3q**



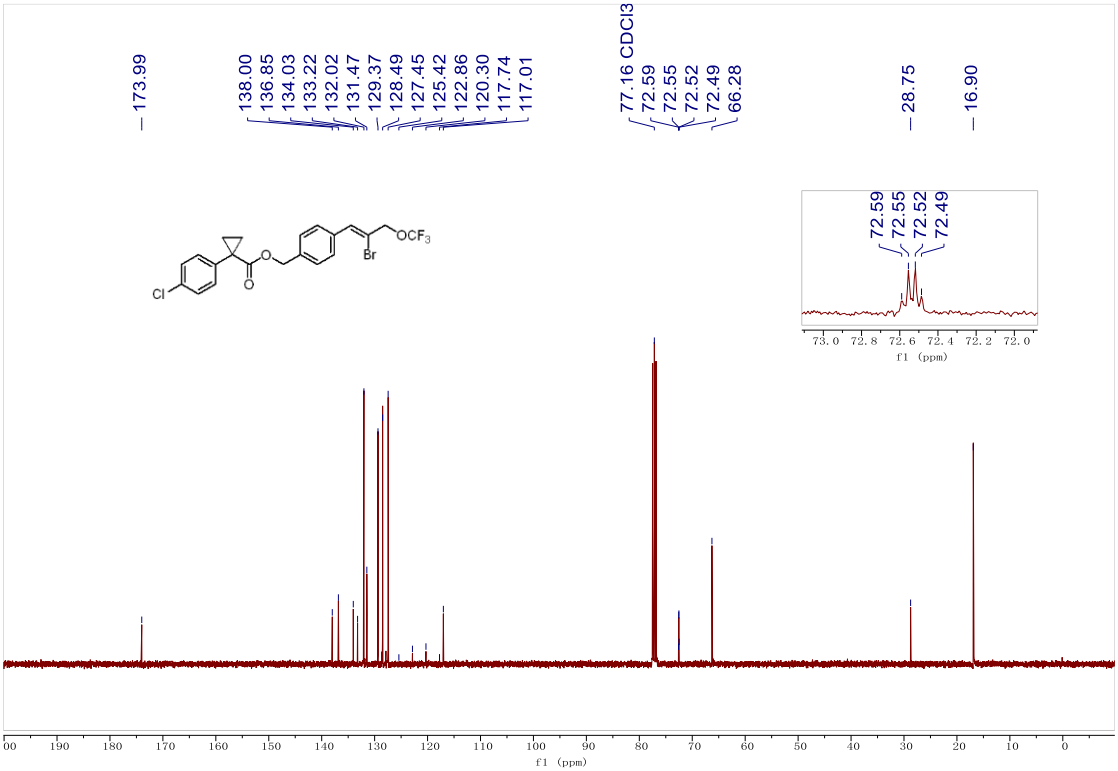

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **(*E*)-3q**



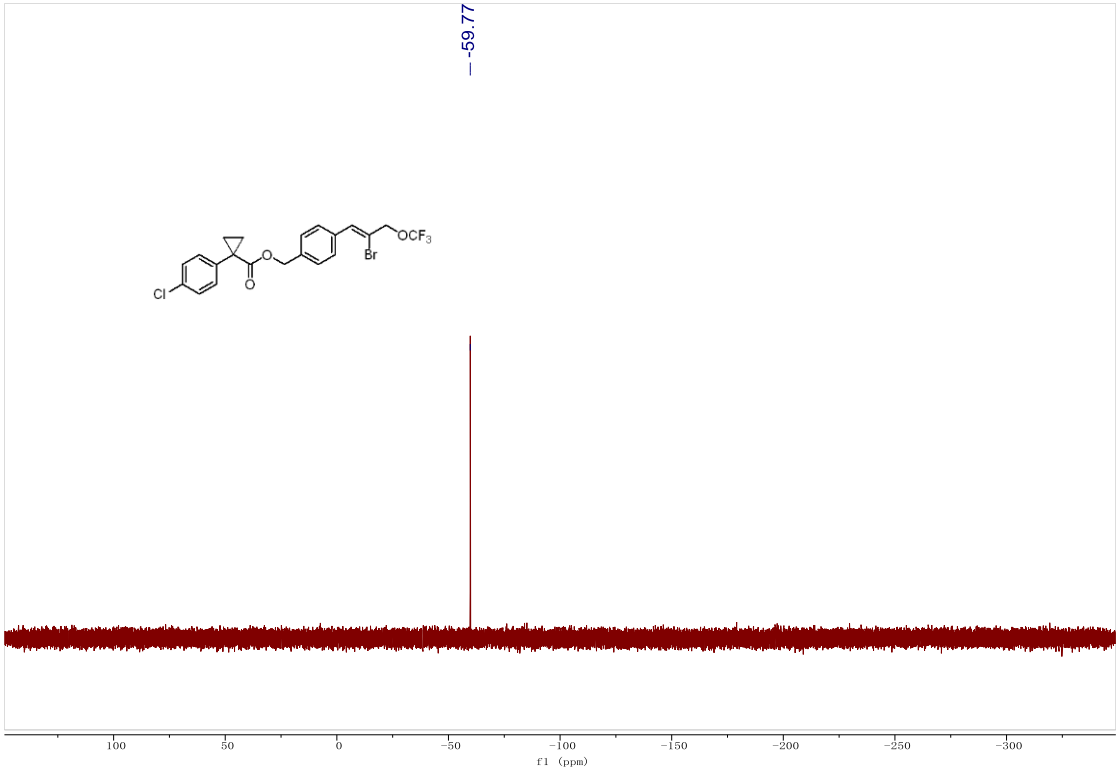

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*E*)-3q**



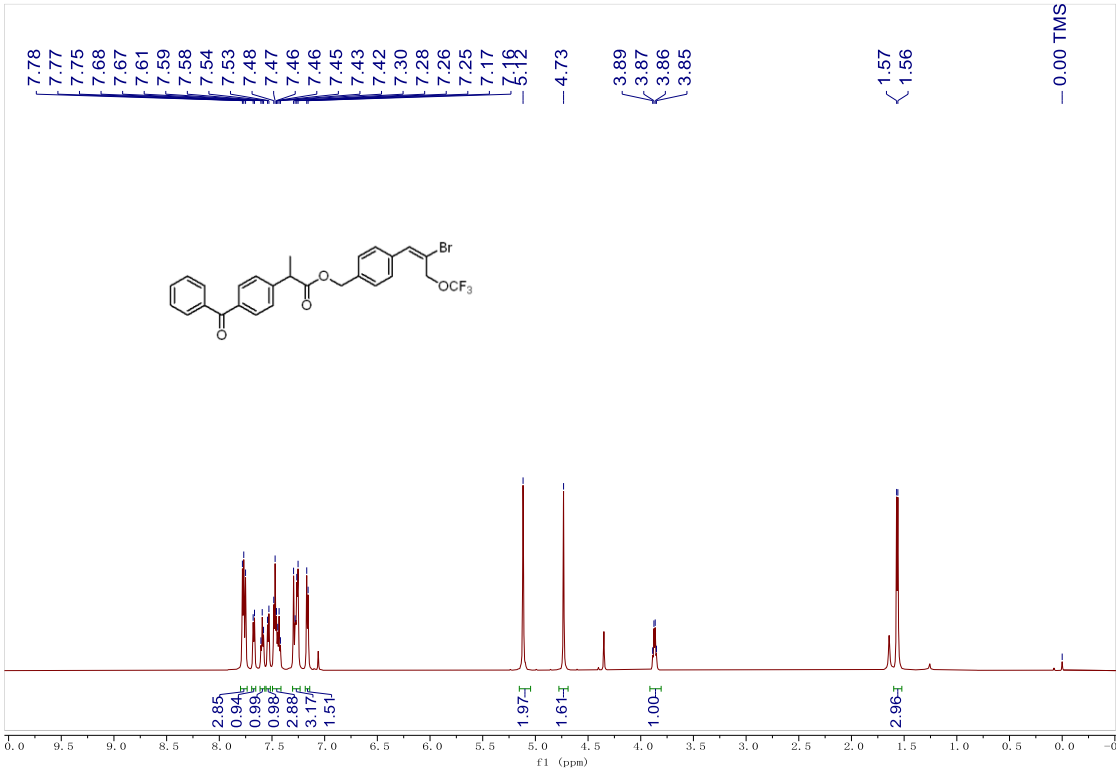

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **(*Z*)-3q**



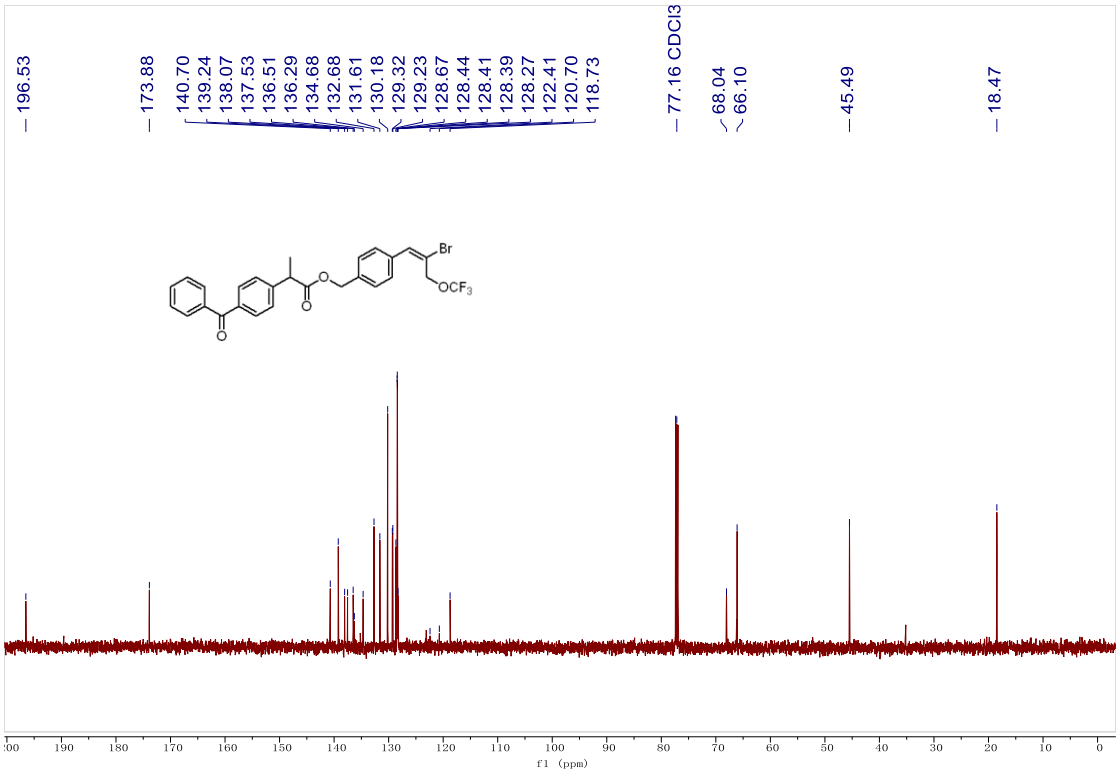

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **(*Z*)-3q**



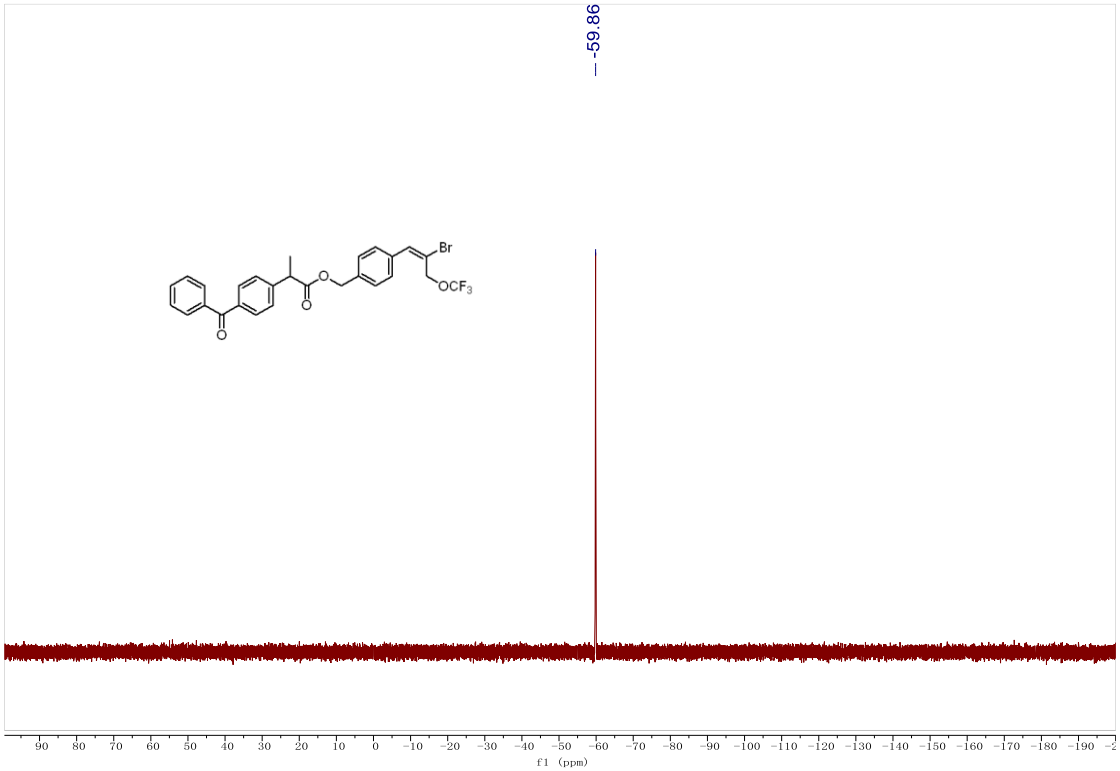

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*Z*)-3q**



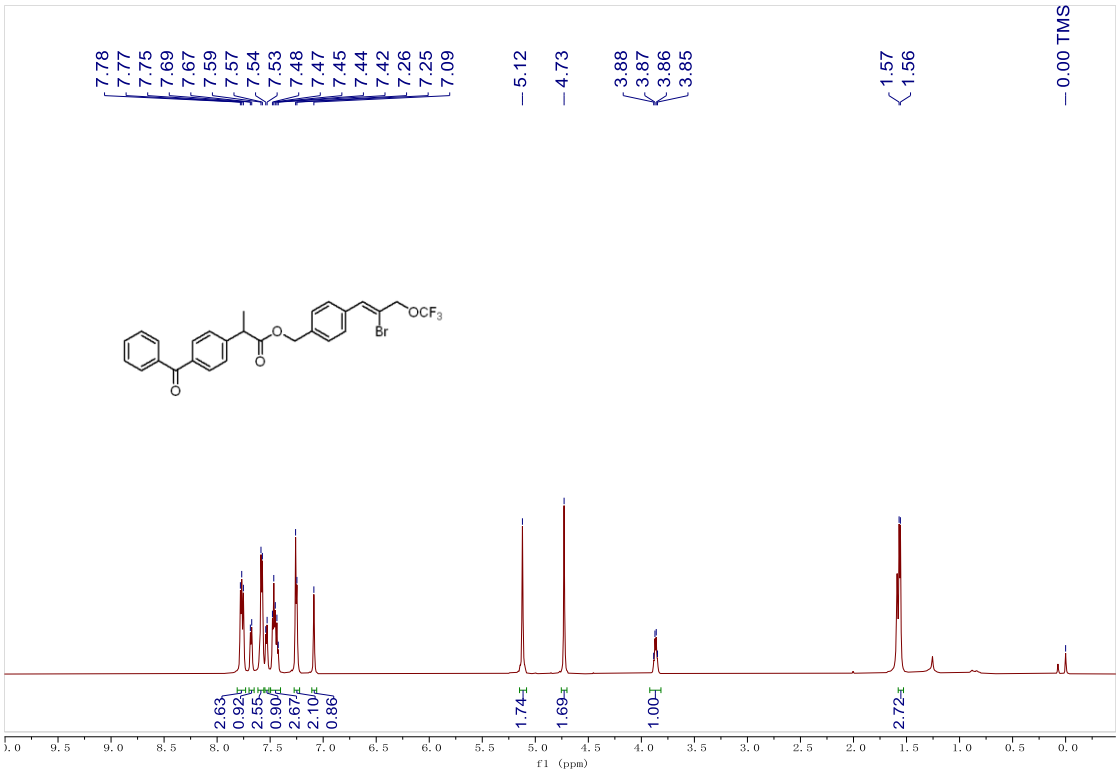

$^{1}$H NMR spectrum (600 MHz, $CDCl_3$) of **(*E*)-3r**



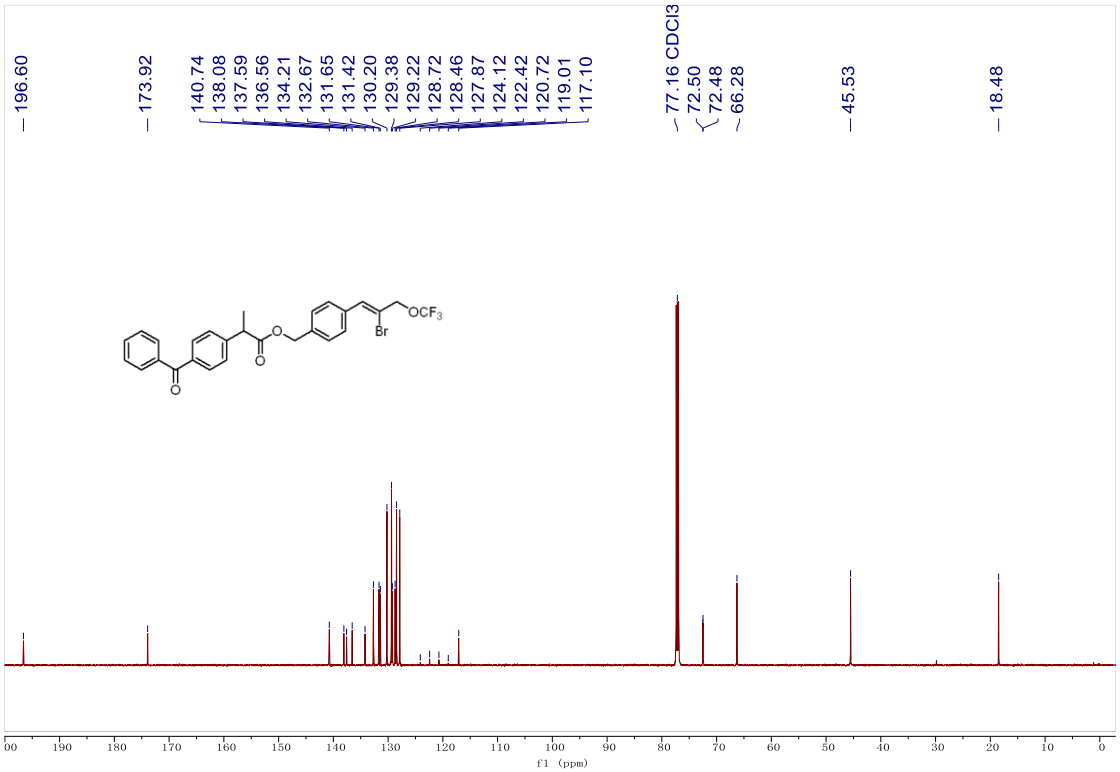

$^{13}$C NMR spectrum (151 MHz, $CDCl_3$) of **(*E*)-3r**



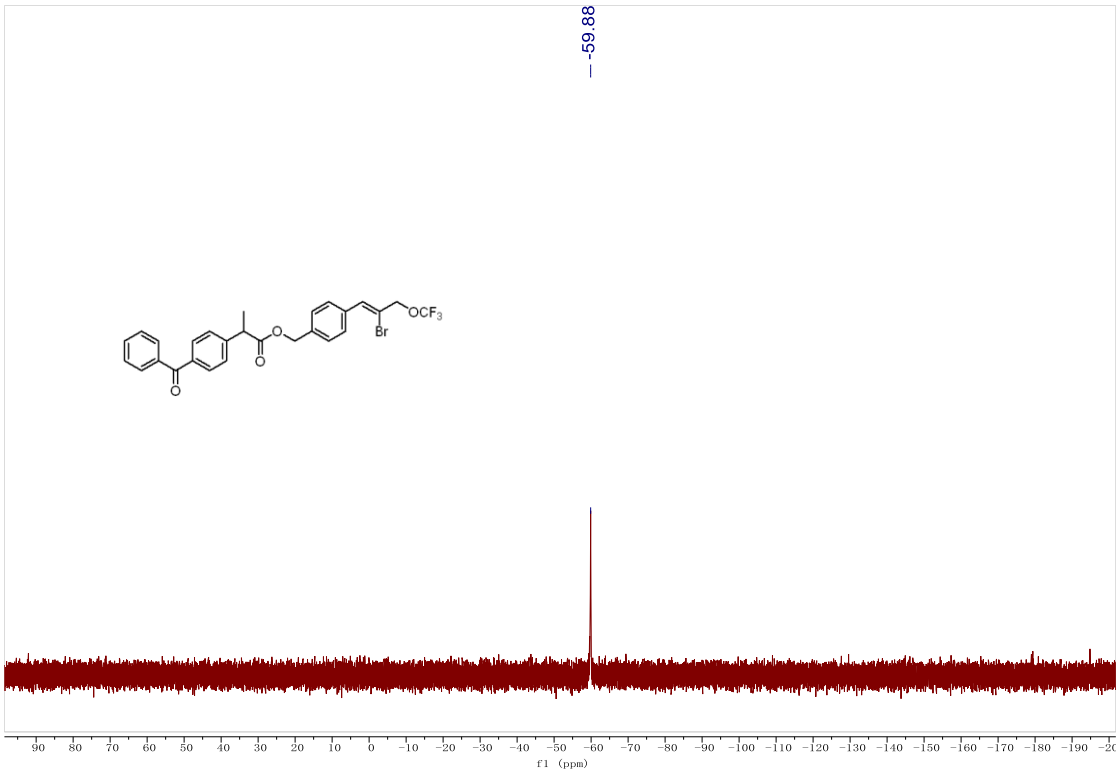

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*E*)-3r**



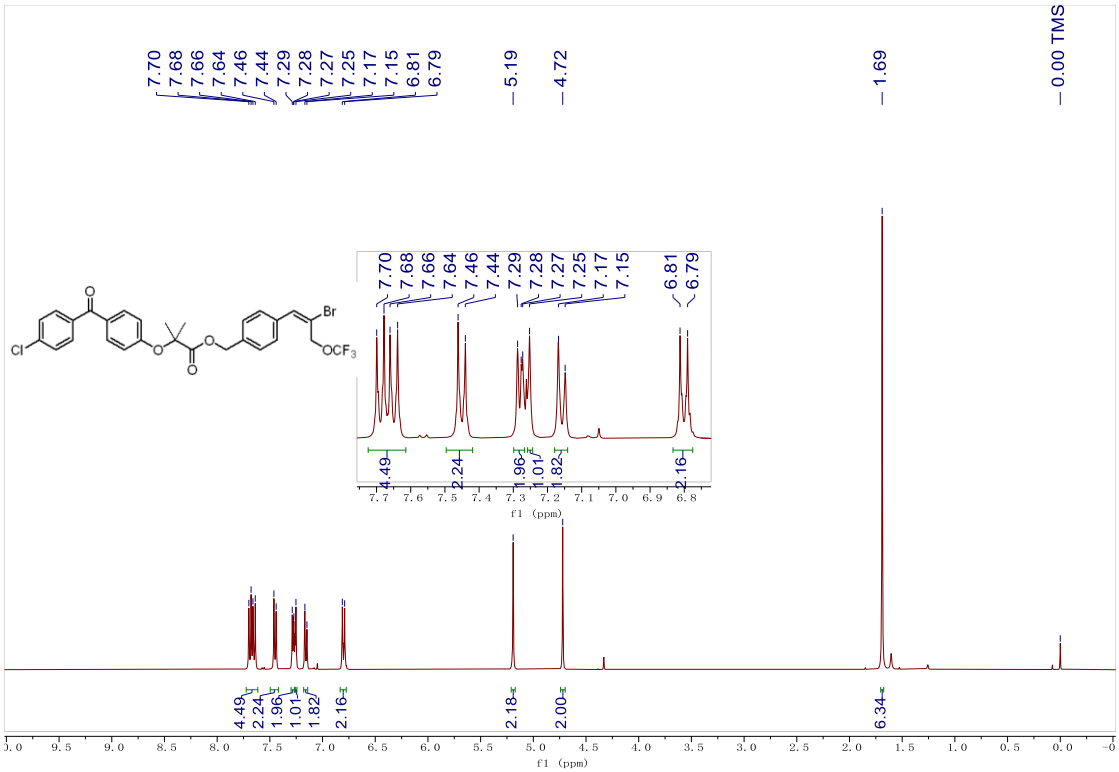

$^{1}$H NMR spectrum (600 MHz, $CDCl_3$) of **(*Z*)-3r**



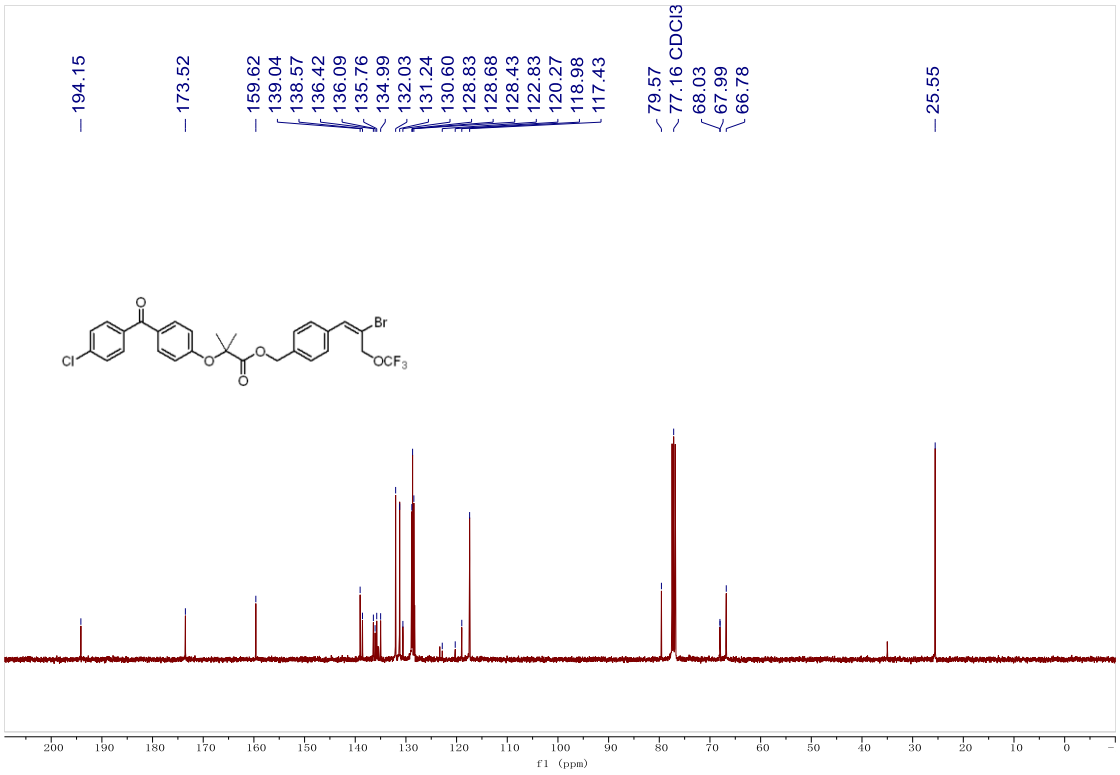

$^{13}$C NMR spectrum (151 MHz, $CDCl_3$) of **(*Z*)-3r**



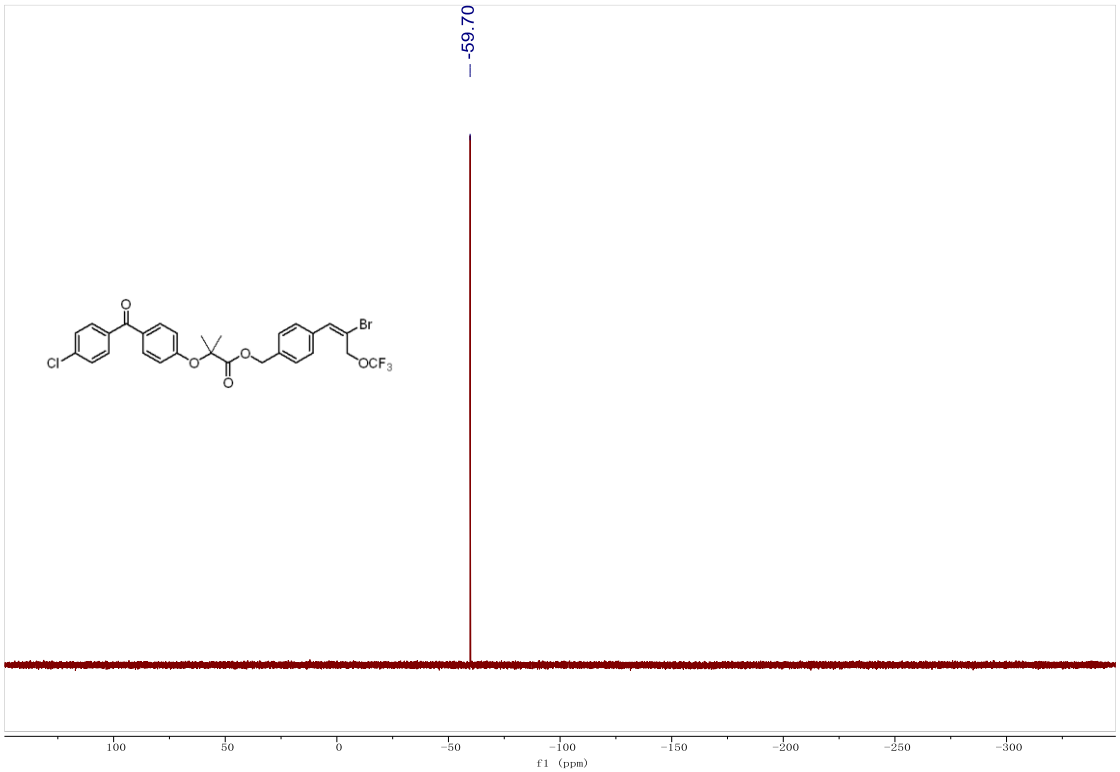

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*E*)-3r**



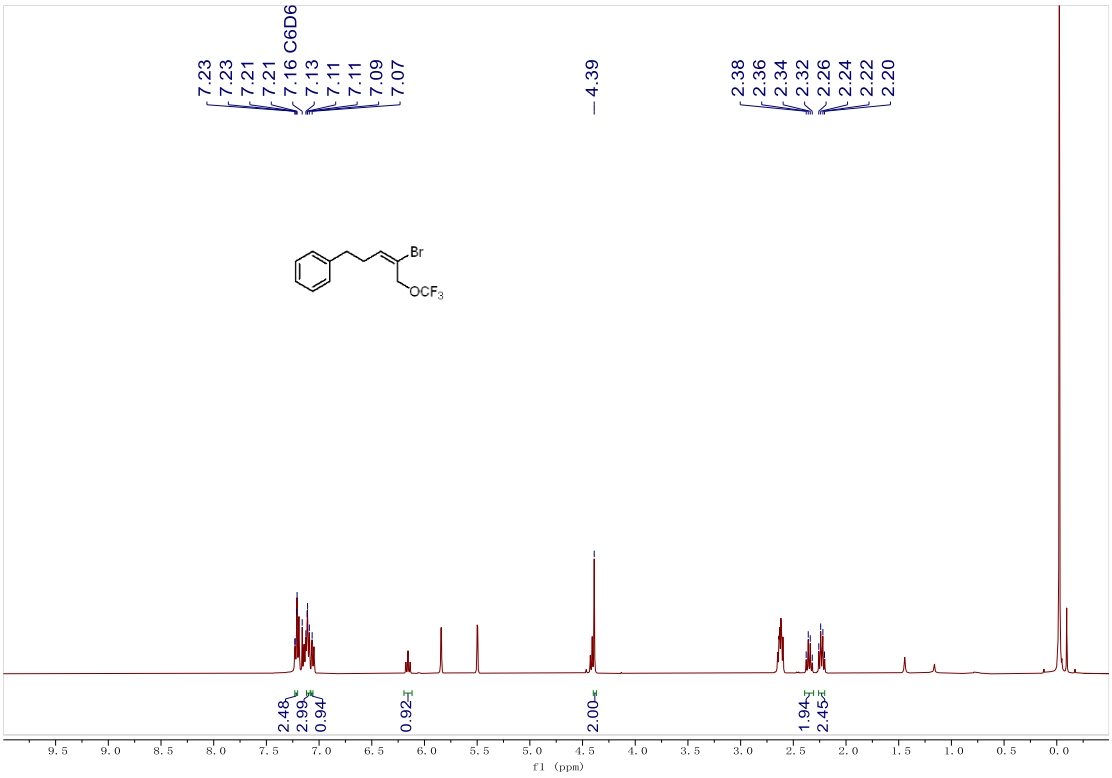

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **(*E*)-3s**



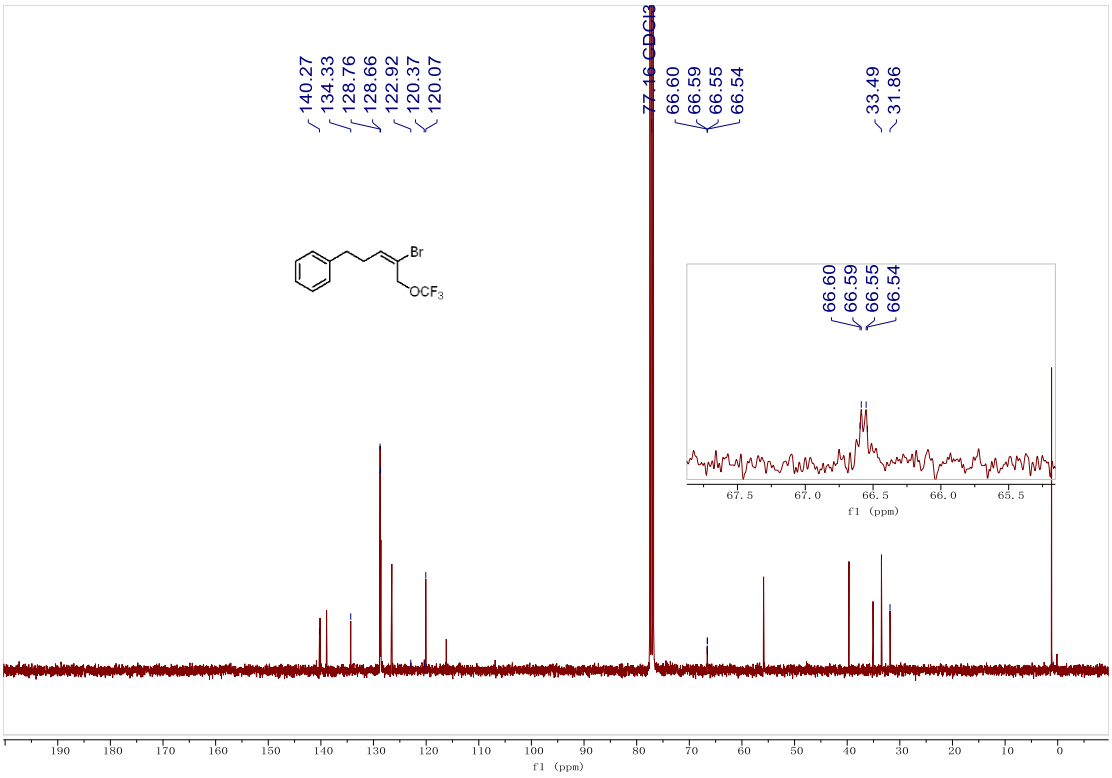

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **(*E*)-3s**



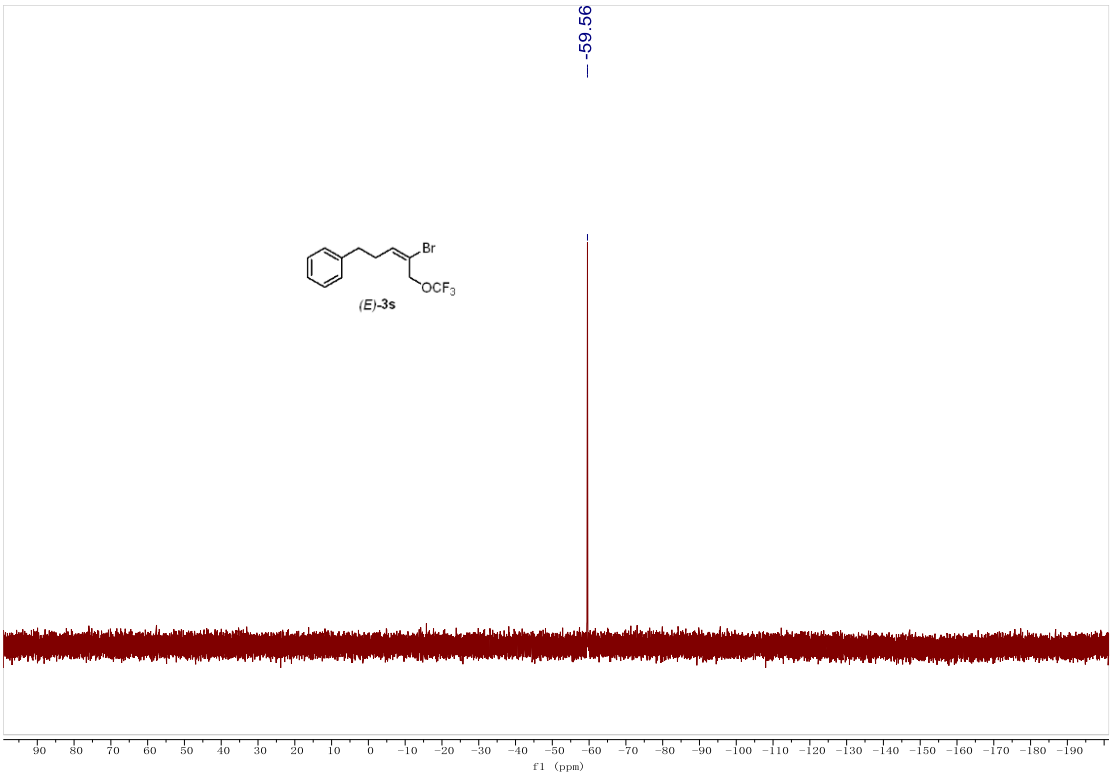

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*E*)-3s**



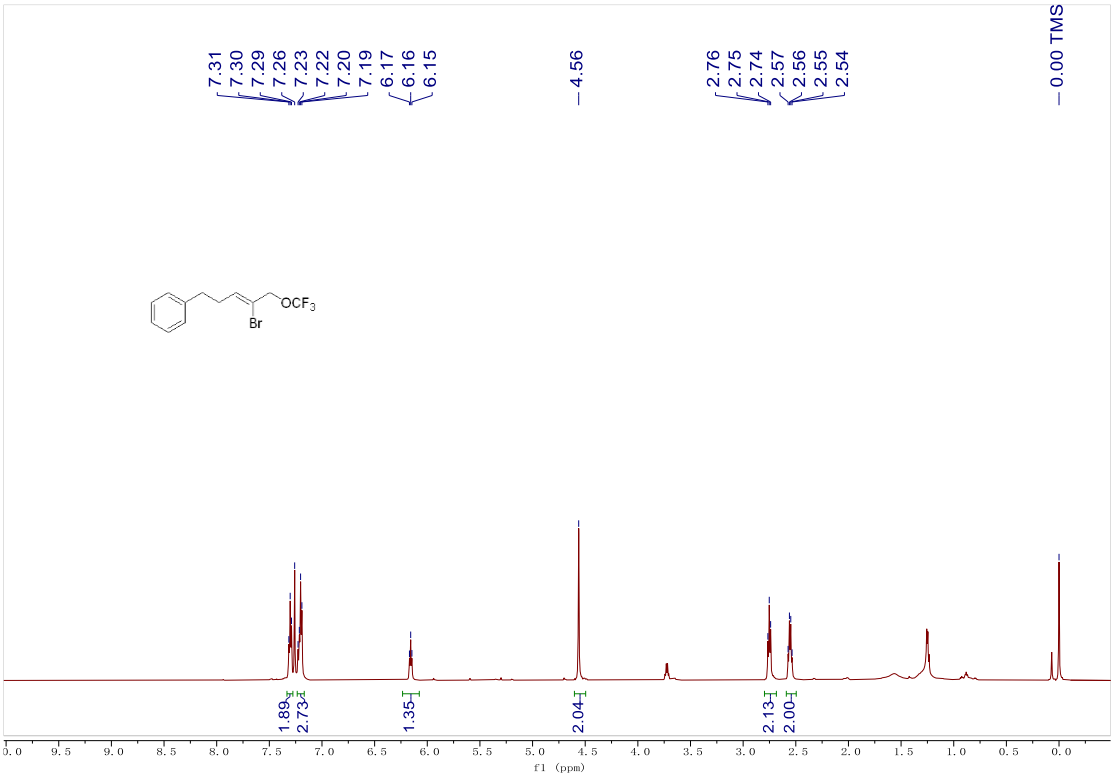

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **(*E*)-3t**



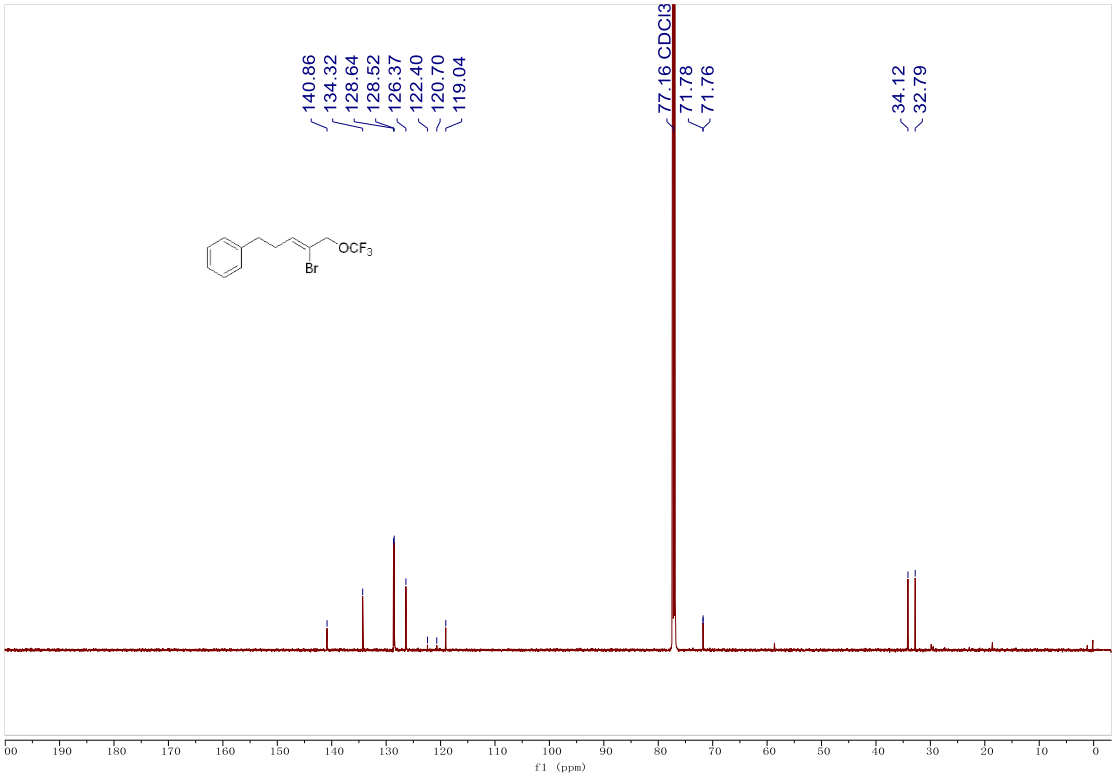

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **(*E*)-3t**



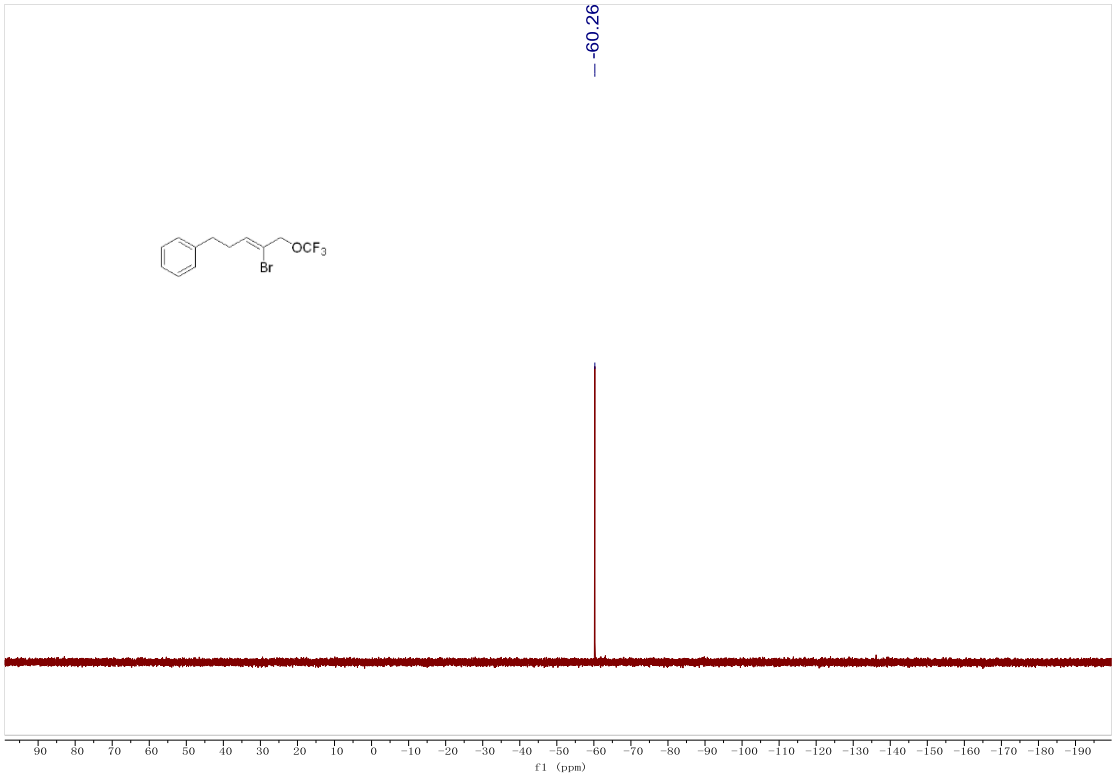

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*E*)-3t**



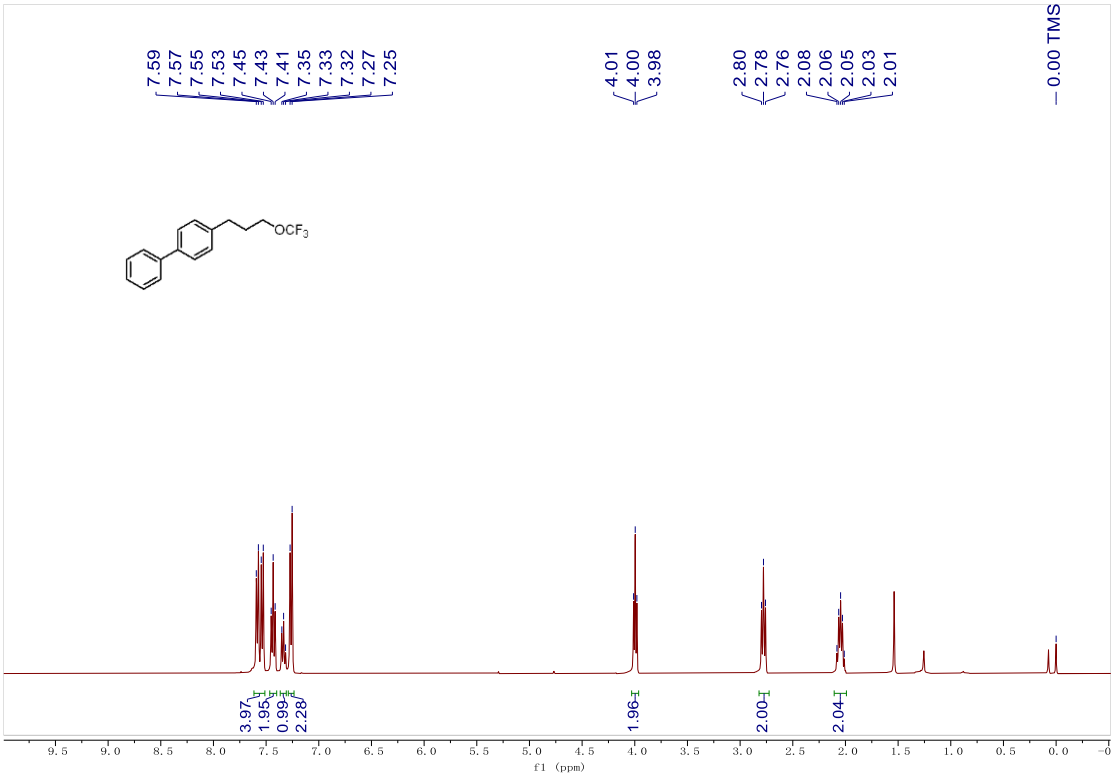

$^{1}$H NMR spectrum (600 MHz, $CDCl_3$) of **(*Z*)-3t**



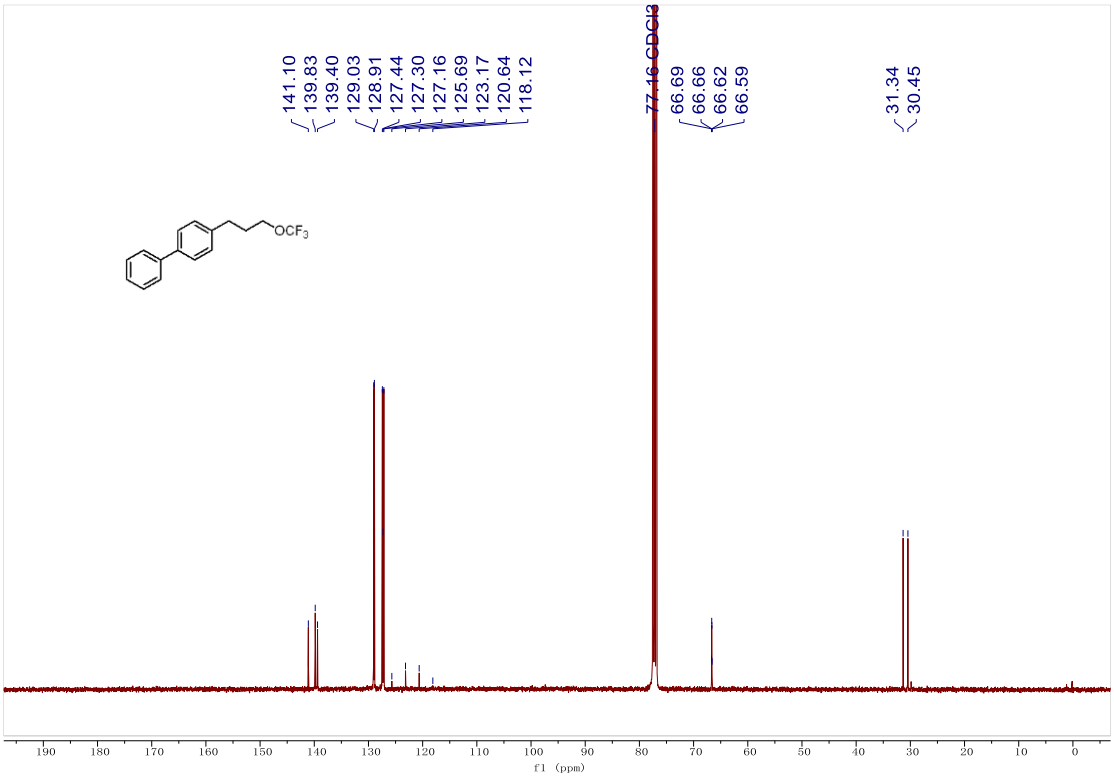

$^{13}$C NMR spectrum (151 MHz, $CDCl_3$) of **(*Z*)-3t**



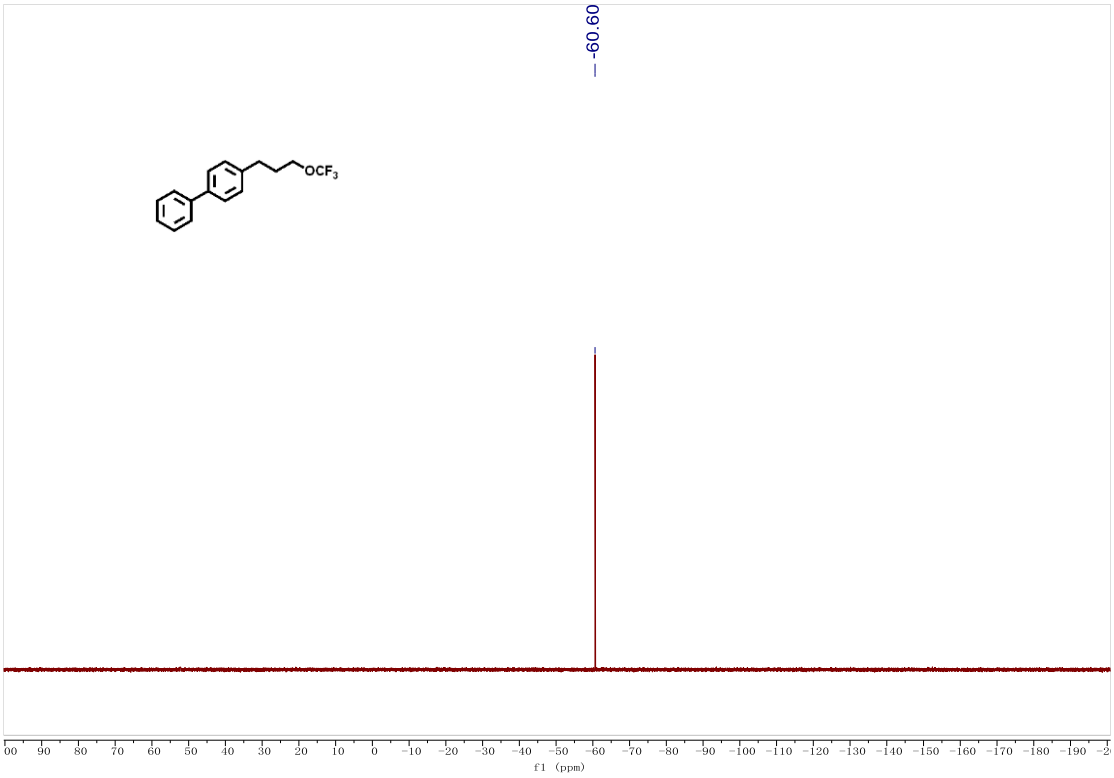

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **(*Z*)-3t**



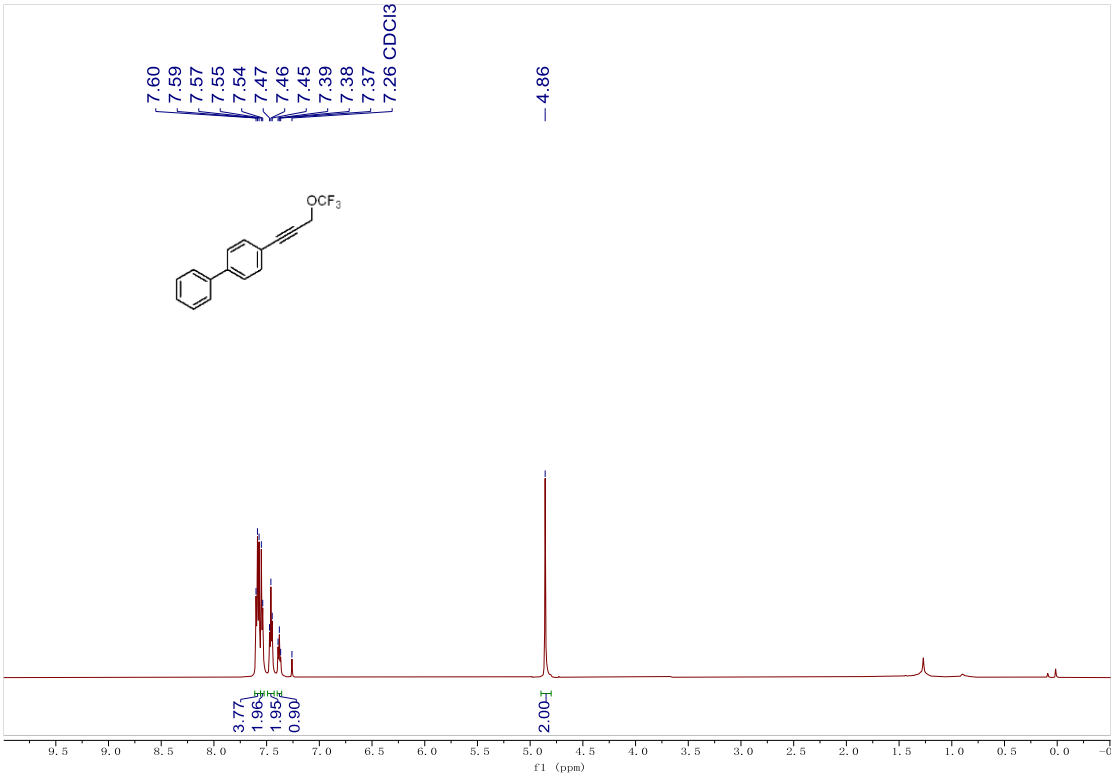

$^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **5a**



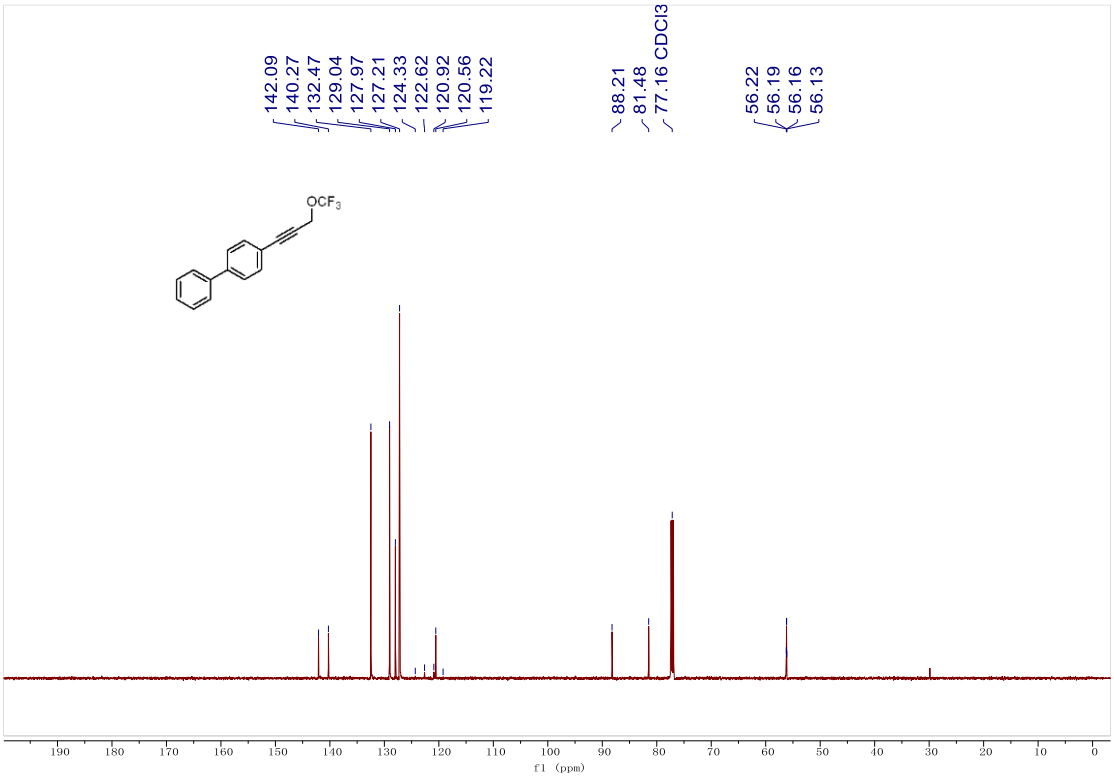

$^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **5a**



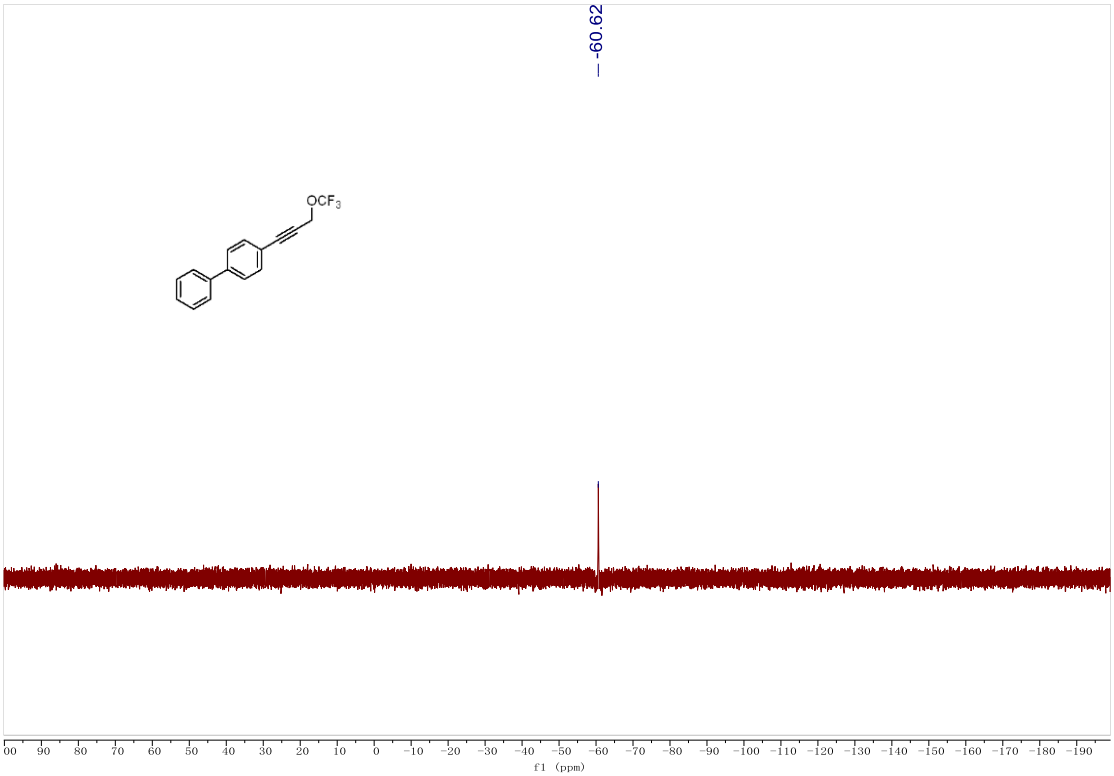

$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **5a**




$^{1}$H NMR spectrum (600 MHz, $CDCl_3$) of **5b**




$^{13}$C NMR spectrum (151 MHz, $CDCl_3$) of **5b**




$^{19}$F NMR spectrum (376 MHz, $CDCl_3$) of **5b**