

Supporting Information

Copper-catalyzed Trifluoromethylation of Styrene Derivatives with CF₃SO₂Na

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1. General Information

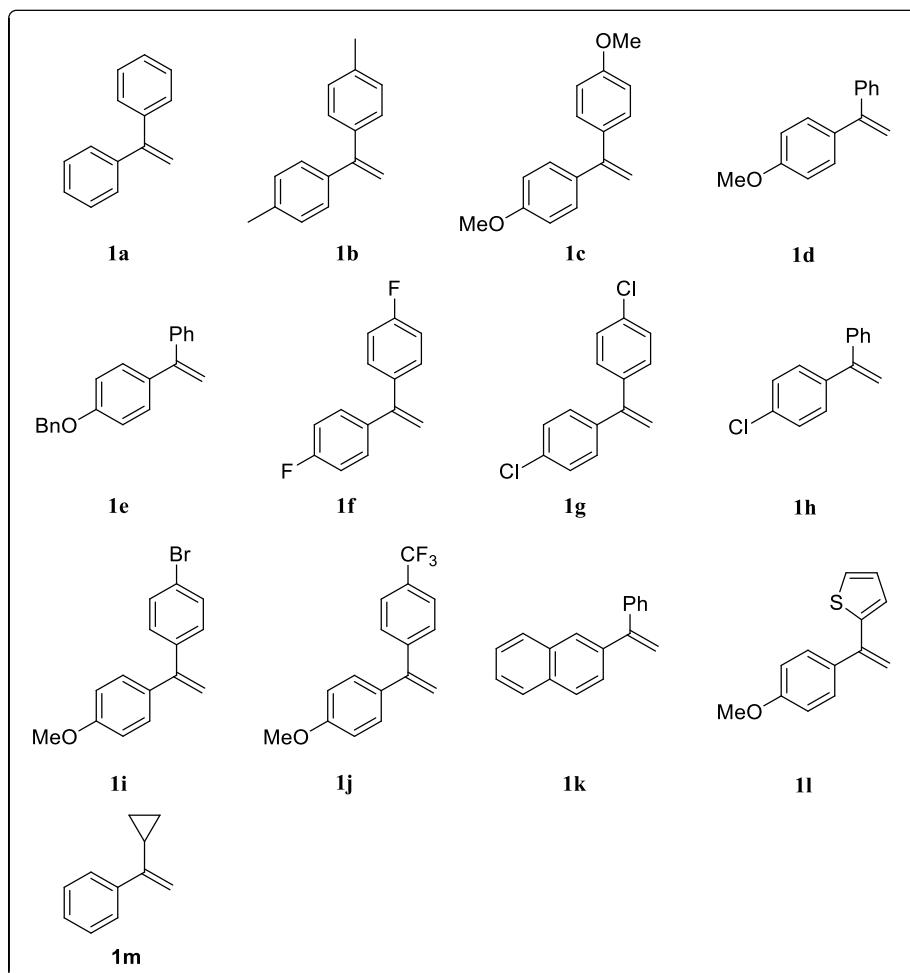
Unless otherwise noted, all reagents and solvents were purchased from the commercial sources and used as received.

The di-*tert*-butyl peroxide (DTBP) and 1-methylimidazole (NMI) were purchased from Alfa-Aesar, copper(I) iodide was purchased from Stream. Thin layer chromatography (TLC) was used to monitor the reaction progress on Merck 60 F254 precoated silica gel plate (0.2 mm thickness). TLC spots were visualized by UV-light irradiation on Spectroline Model ENF-24061/F 254 nm. Other visualization method was staining with a basic solution of potassium permanganate or acidic solution of ceric molybdate, followed by heating.

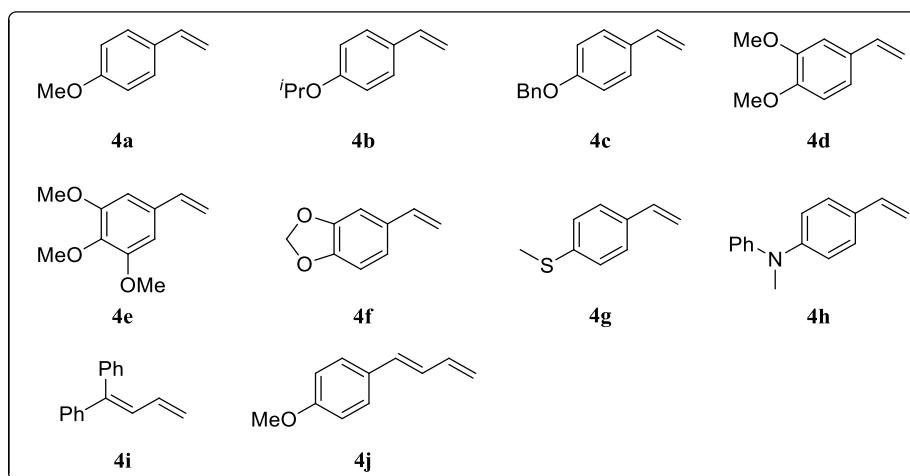
Flash column chromatography was performed using Merck silica gel 60 with analytical grade solvents as eluents.

¹H NMR, ¹³C NMR, ¹⁹F NMR and NOESY spectra were recorded using Bruker Avance 300 MHz spectrometers and Bruker Avance 400 MHz spectrometers. Chemical shifts are reported in ppm downfield relative to TMS and were referenced to the signal of chloroform-d (δ =7.26, singlet). Multiplicities were given as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad singlet, dd=doublets of doublet, dq=doublets of quartet. Values of coupling constant are reported as J in Hz. HRMS spectra were recorded on a Waters Q-Tof Premier Spectrometer

2. General procedures for the synthesis of styrene derivatives.



1a was commercially available, **1b – l**¹ and **1m**² were prepared following the reported procedure.



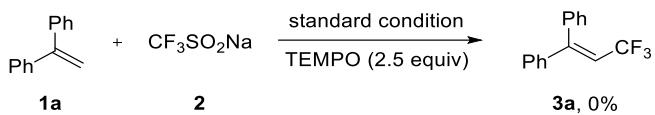
4a – h², **4i**¹ and **4j**² were prepared following the reported procedure.

3. General procedures for the trifluoromethylation of styrene derivatives

To a 8 mL sample vial, charged with CuI (3.8 mg, 0.02 mmol, 10 mol%), $^n\text{Bu}_4\text{NI}$ (14.8 mg, 0.04 mmol, 20 mol%) and $\text{CF}_3\text{SO}_2\text{Na}$ (75.0 mg, 0.48 mmol, 2.4 equiv) in 1,2-dichloroethane (1 mL) was sequentially added 1-methylimidazole (2.5 mg, 0.03 mmol, 15 mol%), di-*tert* butyl peroxide (58.5 mg, 0.4 mmol, 2 equiv) and olefin (0.2 mmol, 1 equiv) under nitrogen atmosphere at room temperature. The vial was sealed with screw cap and stirred at 120 °C for 12 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc (5 mL), filtered through filter paper and concentrated *under vacuum*. Purification by silica gel column chromatograph using EtOAc and hexane as eluent affords the target product.

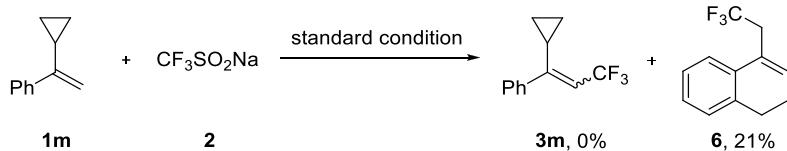
4. Mechanism study

I. Controlled reaction with TEMPO



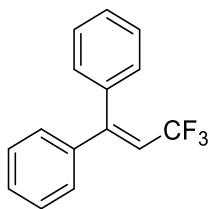
General procedure: the reaction were performed using standard condition with the extra addition of TEMPO (78.1 mg, 0.5 mmol, 2.5 equiv).

II. Controlled reaction with radical clock.



General procedure: the reaction were performed using standard condition.

5. Characterization data for the trifluoromethylated styrene derivatives



(3,3,3-Trifluoroprop-1-ene-1,1-diyl)dibenzene (**3a**)

Colorless oil.

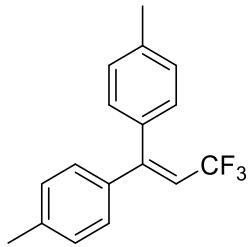
Yield = 73%

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.41 – 7.37 (m, 3H), 7.36 – 7.30 (m, 3H), 7.27 – 7.22 (m, 4H), 6.12 (q, *J* = 8.4 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 152.4 (q, *J* = 6 Hz), 140.1, 137.2, 129.4, 129.1 (q, *J* = 2 Hz), 128.5, 128.4, 128.0, 127.9, 123.1 (q, *J* = 269 Hz), 115.4 (q, *J* = 34 Hz).

¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -55.6 (d, *J* = 8.4 Hz).

HRMS (ESI, m/z): calcd for C₁₅H₁₂F₃⁺ [M+H]⁺ 249.0891, found: 249.0900.



4,4'-(3,3,3-Trifluoroprop-1-ene-1,1-diyl)bis(methylbenzene) (**3b**)

Colorless oil.

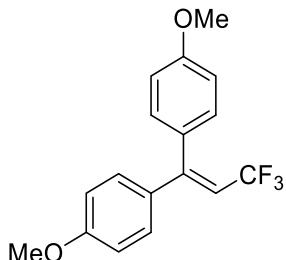
Yield = 83%

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.22 – 7.16 (m, 2H), 7.16 – 7.08 (m, 6H), 6.06 (q, *J* = 8.4 Hz, 1H), 2.39 (s, 3H), 2.35 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 152.4 (q, *J* = 6 Hz), 139.5, 138.3, 137.6, 134.5, 129.1, 129.1 (q, *J* = 2 Hz), 128.7, 127.9, 123.3 (q, *J* = 268 Hz), 114.3 (q, *J* = 34 Hz), 21.3, 21.2.

¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -55.3 (d, *J* = 8.4 Hz).

HRMS (ESI, m/z): calcd for C₁₇H₁₆F₃⁺ [M+H]⁺ 277.1204, found: 277.1194.



4,4'-(3,3,3-Trifluoroprop-1-ene-1,1-diyl)bis(methoxybenzene) (**3c**)

Light yellow oil.

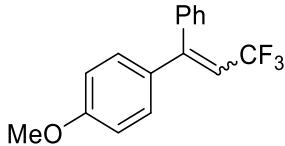
Yield = 77%

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.22 – 7.14 (m, 4H), 6.94 – 6.88 (m, 2H), 6.88 – 6.82 (m, 2H), 5.99 (q, *J* = 8.4 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 160.6, 159.8, 151.8 (q, *J* = 6 Hz), 133.0, 130.6 (q, *J* = 2 Hz), 129.8, 129.5, 123.4 (q, *J* = 268 Hz), 113.7, 113.4, 113.1 (q, *J* = 34 Hz), 56.3, 56.2.

¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -55.0 (d, *J* = 8.4 Hz).

HRMS (ESI, m/z): calcd for C₁₇H₁₆F₃O₂⁺ [M+H]⁺ 309.1102, found: 309.1102.



(*E/Z*)-1-Methoxy-4-(3,3,3-trifluoro-1-phenylprop-1-enyl)benzene (**3d**)

Colorless oil.

Yield = 84%, *E/Z* = 2:1.

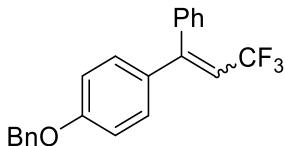
¹H NMR of the E/Z mixture (400 MHz, CDCl₃) δ (ppm): 7.41 – 7.32 (m, 3H, mixture), 7.27 – 7.21 (m, 2H, mixture), 7.20 – 7.15 (m, 2H, mixture), 6.94 – 6.89 (m, 2H, minor), 6.87 – 6.82 (m, 2H, major), 6.06 (q, *J* = 8.4 Hz, 1H, major), 6.04 (q, *J* = 8.4 Hz, 1H, minor), 3.85 (s, 3H, minor), 3.81 (s, 1H, major).

¹³C NMR of the E/Z mixture (100 MHz, CDCl₃) δ (ppm): 160.7, 159.8, 152.4 (q, *J* = 5 Hz), 151.8 (q, *J* = 5 Hz), 140.7, 137.5, 132.4, 130.6 (q, *J* = 2 Hz), 129.6, 129.3, 129.3, 129.1 (q, *J* = 2 Hz), 128.4, 128.3, 128.2, 128.0, 123.3 (q, *J* = 269 Hz), 123.2 (q, *J* = 269 Hz), 114.9 (q, *J* = 33 Hz), 114.0, 113.5 (q, *J* = 33 Hz), 113.4, 55.3, 55.2.

¹⁹F NMR of the E-mixture (376 MHz, CDCl₃) δ (ppm): -55.2 (d, *J* = 8.3 Hz).

¹⁹F NMR of the Z-mixture (376 MHz, CDCl₃) δ (ppm): -55.5 (d, *J* = 8.3 Hz).

HRMS (ESI, m/z): calcd for C₁₆H₁₄F₃O⁺ [M+H]⁺ 279.0997, found: 279.0993.



(*E/Z*)-1-(Benzylxy)-4-(3,3,3-trifluoro-1-phenylprop-1-enyl)benzene (**3e**)

White solid.

Yield = 82%, *E/Z* = 2 : 1.

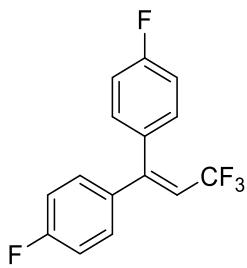
¹H NMR of the E/Z mixture (400 MHz, CDCl₃) δ (ppm): 7.46 – 7.30 (m, 8H, mixture), 7.25 – 7.21 (m, 2H, mixture), 7.19 – 7.15 (m, 2H, mixture), 7.00 – 6.96 (m, 2H, minor), 6.93 – 6.88 (m, 2H, major), 6.05 (q, *J* = 8.4 Hz, 1H, major), 6.04 (q, *J* = 8.4 Hz, 1H, minor), 5.08 (s, 2H, minor), 5.06 (s, 1H, major).

¹³C NMR of the E/Z mixture (100 MHz, CDCl₃) δ (ppm): 159.8, 159.1, 152.3 (q, *J* = 5 Hz), 151.8 (q, *J* = 5 Hz), 140.7, 137.4, 136.7, 136.5, 132.6, 130.7 (q, *J* = 2 Hz), 129.8, 129.3, 129.3, 129.1 (q, *J* = 2 Hz), 128.6, 128.6, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 127.6, 127.4, 123.3 (q, *J* = 268 Hz), 123.2 (q, *J* = 268 Hz), 115.0 (q, *J* = 33 Hz), 114.7, 114.3, 113.6 (q, *J* = 33 Hz), 70.1.

¹⁹F NMR of the E-mixture (376 MHz, CDCl₃) δ (ppm): -55.1 (d, *J* = 7.9 Hz).

¹⁹F NMR of the Z-mixture (376 MHz, CDCl₃) δ (ppm): -55.4 (d, *J* = 8.3 Hz).

HRMS (ESI, m/z): calcd for C₂₂H₁₈F₃O⁺ [M+H]⁺ 355.1310, found: 355.1299.



4,4'-(3,3,3-Trifluoroprop-1-ene-1,1-diyl)bis(fluorobenzene) (**3f**)

Colorless oil.

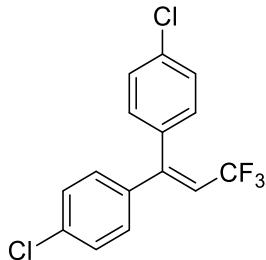
Yield = 72%

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.25 – 7.18 (m, 4H), 7.12 – 7.00 (m, 4H), 6.08 (q, *J* = 8.4 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 164.5 (d, *J* = 62 Hz), 162.0 (d, *J* = 62 Hz), 150.4 (q, *J* = 6 Hz), 136.1 (d, *J* = 3 Hz), 133.0 (d, *J* = 4 Hz), 131.0 (dq, *J*₁ = 9 Hz, *J*₂ = 2 Hz), 129.8 (d, *J* = 8 Hz), 122.9 (q, *J* = 269 Hz), 115.6 (q, *J* = 33 Hz), 115.6 (d, *J* = 22 Hz), 115.3 (d, *J* = 22 Hz).

¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -55.6 (d, *J* = 8.4 Hz), -111.4 (m), -112.6 (m).

HRMS (ESI, m/z): calcd for C₁₅H₁₀F₃⁺ [M+H]⁺ 285.0703, found: 285.0689.



4,4'-(3,3,3-Trifluoroprop-1-ene-1,1-diyl)bis(chlorobenzene) (**3g**)

Colorless oil.

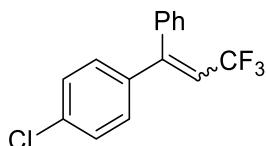
Yield = 65%

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.41 – 7.35 (m, 2H), 7.35 – 7.28 (m, 2H), 7.21 – 7.11 (m, 4H), 6.12 (q, *J* = 8.4 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 150.2 (q, *J* = 6 Hz), 138.1, 135.9, 135.2, 135.0, 130.4 (q, *J* = 2 Hz), 129.2, 128.8, 128.5, 122.7 (q, *J* = 269 Hz), 116.3 (q, *J* = 34 Hz).

¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -55.7 (d, *J* = 7.9 Hz).

HRMS (ESI, m/z): calcd for C₁₅H₁₀Cl₂F₃⁺ [M+H]⁺ 317.0112, found: 317.0096.



(*E/Z*)-1-Chloro-4-(3,3,3-trifluoro-1-phenylprop-1-enyl)benzene (**3h**)

Light yellow oil.

Yield = 68%, *E/Z* = 1 : 1.

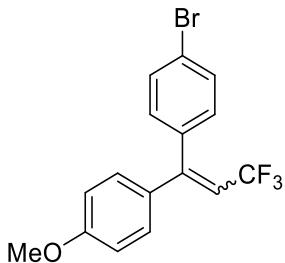
¹H NMR of the E/Z mixture (400 MHz, CDCl₃) δ (ppm): 7.42 – 7.28 (m, 5H, mixture), 7.25 –

7.15 (m, 4H, mixture), 6.14 (q, $J = 8.4$ Hz, 1H), 6.11 (q, $J = 8.4$ Hz, 1H).

^{13}C NMR of the E/Z mixture (100 MHz, CDCl_3) δ (ppm): 151.3 (q, $J = 5$ Hz), 151.3 (q, $J = 5$ Hz), 139.6, 138.6, 136.8, 135.7, 135.6, 134.7, 130.5 (q, $J = 2$ Hz), 129.6, 129.2, 129.0 (q, $J = 2$ Hz), 128.7, 128.7, 128.6, 128.4, 128.2, 127.9, 122.9 (q, $J = 269$ Hz), 122.9 (q, $J = 269$ Hz), 116.3 (q, $J = 33$ Hz), 116.1 (q, $J = 33$ Hz).

^{19}F NMR of the E/Z mixture (376 MHz, CDCl_3) δ (ppm): -55.6 (d, $J = 8.4$ Hz), -55.7 (d, $J = 8.4$ Hz).

HRMS (ESI, m/z): calcd for $\text{C}_{15}\text{H}_{11}\text{ClF}_3^+ [\text{M}+\text{H}]^+$ 283.0501, found: 283.0492.



(*E/Z*)-1-Bromo-4-(3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-enyl)benzene (**3i**)

Colorless oil.

Yield = 83%, $E/Z = 1 : 3$.

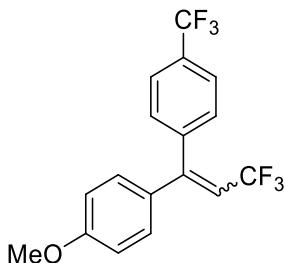
^1H NMR of the E/Z mixture (400 MHz, CDCl_3) δ (ppm): 7.55 – 7.50 (m, 2H, major), 7.48 – 7.44 (m, 2H, minor), 7.18 – 7.09 (m, 4H, mixture), 6.94 – 6.89 (m, 2H, minor), 6.87 – 6.82 (m, 2H, major), 6.07 (q, $J = 8.4$ Hz, 1H, major), 6.02 (q, $J = 8.4$ Hz, 1H, minor), 3.85 (s, 3H, minor), 3.82 (s, 1H, major).

^{13}C NMR of the E/Z mixture (100 MHz, CDCl_3) δ (ppm): 160.8, 160.1, 151.3 (q, $J = 5$ Hz), 150.6 (q, $J = 5$ Hz), 139.7, 136.4, 131.8, 131.6, 130.8 (q, $J = 2$ Hz), 130.6 (q, $J = 2$ Hz), 129.7, 129.3, 129.0, 123.8, 122.8 (q, $J = 269$ Hz), 123.0 (q, $J = 269$ Hz), 122.7, 115.2 (q, $J = 34$ Hz), 113.9, 113.9 (q, $J = 34$ Hz), 113.6, 55.4, 55.2.

^{19}F NMR of the E-mixture (376 MHz, CDCl_3) δ (ppm): -55.7(d, $J = 8.3$ Hz).

^{19}F NMR of the Z-mixture (376 MHz, CDCl_3) δ (ppm): -55.1 (d, $J = 8.3$ Hz).

HRMS (ESI, m/z): calcd for $\text{C}_{16}\text{H}_{13}\text{BrF}_3\text{O}^+ [\text{M}+\text{H}]^+$ 357.0102, found: 357.0091.



(*E/Z*)-1-Methoxy-4-(3,3,3-trifluoro-1-(4-(trifluoromethyl)phenyl)prop-1-enyl)benzene (**3j**)

Colorless oil.

Yield = 75%, $E/Z = 6 : 1$.

^1H NMR of the E/Z mixture (400 MHz, CDCl_3) δ (ppm): 7.69 – 7.63 (m, 2H, major), 7.61 – 7.57 (m, 2H, minor), 7.39 – 7.27 (m, 2H, mixture), 7.18 – 7.05 (m, 2H, mixture), 6.95 – 6.90 (m, 2H, minor), 6.89 – 6.83 (m, 2H, major), 6.14 (q, $J = 8.4$ Hz, 1H, major), 6.07 (q, $J = 8.4$ Hz, 1H, minor),

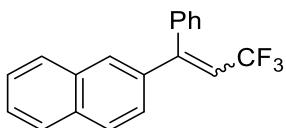
3.85 (s, 3H, minor), 3.82 (s, 1H, major).

¹³C NMR of the E-isomer (100 MHz, CDCl₃) δ (ppm): 160.9, 150.4 (q, *J* = 5 Hz), 141.2, 131.4, 130.6 (q, *J* = 32 Hz), 129.5 (q, *J* = 2 Hz), 129.2, 125.0 (q, *J* = 4 Hz), 124.0 (q, *J* = 271 Hz), 123.0 (q, *J* = 268 Hz), 114.4 (q, *J* = 34 Hz), 114.0, 55.4.

¹⁹F NMR of the E-mixture (376 MHz, CDCl₃) δ (ppm): -55.2 (d, *J* = 8.3 Hz), -62.6.

¹⁹F NMR of the Z-mixture (376 MHz, CDCl₃) δ (ppm): -55.9 (d, *J* = 8.3 Hz), -62.8.

HRMS (ESI, m/z): calcd for C₁₇H₁₃F₆O⁺ [M+H]⁺ 347.0871, found: 347.0876.



(*E/Z*)-2-(3,3,3-Trifluoro-1-phenylprop-1-enyl)naphthalene (**3k**)

White solid.

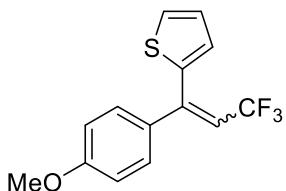
Yield = 74%, *E/Z* = 1 : 1.

¹H NMR of the E/Z mixture (400 MHz, CDCl₃) δ (ppm): 7.90 – 7.62 (m, 4H, mixture), 7.57 – 7.47 (m, 2H, mixture), 7.57 – 7.47 (m, 2H, mixture), 7.39 – 7.27 (m, 4H, mixture), 6.27 (q, *J* = 8.4 Hz, 1H), 6.22 (q, *J* = 8.4 Hz, 1H).

¹³C NMR of the E/Z mixture (100 MHz, CDCl₃) δ (ppm): 152.4, 152.3, 140.1, 137.4, 137.2, 134.7, 133.6, 133.1, 132.9, 132.8, 129.4, 129.2 (q, *J* = 2 Hz), 128.6, 128.5, 128.3, 128.2, 128.1, 128.1, 127.7, 127.7, 127.6, 127.0, 126.8, 126.8, 126.6, 126.6, 126.4, 124.8, 123.1 (q, *J* = 269 Hz), 123.1 (q, *J* = 269 Hz), 122.9 (q, *J* = 269 Hz), 115.8 (q, *J* = 33 Hz).

¹⁹F NMR of the E/Z mixture (376 MHz, CDCl₃) δ (ppm): -55.4 (d, *J* = 8.3 Hz), -55.5 (d, *J* = 8.3 Hz).

HRMS (ESI, m/z): calcd for C₁₉H₁₄F₃⁺ [M+H]⁺ 299.1048, found: 299.1053.



(*E/Z*)-2-(3,3,3-Trifluoro-1-(4-methoxyphenyl)prop-1-enyl)thiophene (**3l**)

Yellow solid.

Yield = 76%, *E/Z* = 3 : 1.

¹H NMR of the E-isomer (400 MHz, CDCl₃) δ (ppm): 7.33 (dd, *J*₁ = 5.2 Hz, *J*₂ = 1.2 Hz, 1H), 7.26 – 7.23 (m, 2H), 6.98 – 6.95 (m, 1H), 6.95 – 6.90 (m, 2H), 6.85 – 6.82 (m, 1H), 6.13 (q, *J* = 8.4 Hz, 1H), 3.85 (s, 3H).

¹H NMR of the Z-isomer (400 MHz, CDCl₃) δ (ppm): 7.45 (dd, *J*₁ = 5.2 Hz, *J*₂ = 1.2 Hz, 1H), 7.28 – 7.26 (m, 2H), 7.22 – 7.20 (m, 1H), 7.09 – 7.06 (m, 1H), 6.88 – 6.85 (m, 2H), 5.95 (q, *J* = 8.4 Hz, 1H), 3.82 (s, 3H).

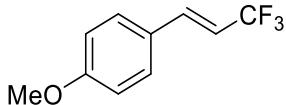
¹³C NMR of the E-isomer (100 MHz, CDCl₃) δ (ppm): 160.9, 145.4 (q, *J* = 5 Hz), 144.3, 130.2 (q, *J* = 2 Hz), 129.6, 129.2, 127.8, 127.7, 123.1 (q, *J* = 269 Hz), 113.4, 112.7 (q, *J* = 34 Hz), 55.2.

¹³C NMR of the Z-isomer (100 MHz, CDCl₃) δ (ppm): 160.0, 145.1 (q, *J* = 5 Hz), 138.1, 132.9, 129.8 (q, *J* = 2 Hz), 128.6, 128.0, 126.8, 123.0 (q, *J* = 269 Hz), 114.9 (q, *J* = 33 Hz), 113.7, 55.4.

¹⁹F NMR of the E-mixture (376 MHz, CDCl₃) δ (ppm): -55.0 (d, *J* = 8.6 Hz).

¹⁹F NMR of the Z-mixture (376 MHz, CDCl₃) δ (ppm): -55.6 (d, *J* = 7.9 Hz).

HRMS (ESI, m/z): calcd for C₁₄H₁₂F₃OS⁺ [M+H]⁺ 285.0561, found: 285.0566.



(*E*)-1-Methoxy-4-(3,3,3-trifluoroprop-1-enyl)benzene (**5a**)

Colorless oil.

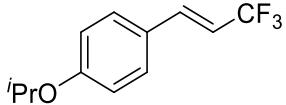
Yield = 69%

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.44 – 7.35 (m, 2H), 7.09 (dq, *J*₁ = 16.0 Hz, *J*₂ = 2.4 Hz, 1H), 6.95 – 6.86 (m, 1H), 6.06 (dq, *J*₁ = 16.0 Hz, *J*₂ = 6.4 Hz, 1H), 3.84 (s, 1H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 161.0, 137.1 (q, *J* = 7 Hz), 129.0, 126.1, 123.9 (q, *J* = 267 Hz), 114.3, 113.4 (q, *J* = 34 Hz), 55.3.

¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -62.8 (dd, *J*₁ = 6.4 Hz, *J*₂ = 2.4 Hz).

HRMS (ESI, m/z): calcd for C₁₀H₁₀F₃O⁺ [M+H]⁺ 203.0684, found: 203.0687.



(*E*)-1-Isopropoxy-4-(3,3,3-trifluoroprop-1-enyl)benzene (**5b**)

Colorless oil.

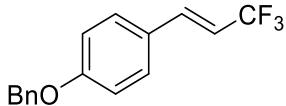
Yield = 53%

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.38 (d, *J* = 8.4 Hz, 1H) 7.08 (dq, *J*₁ = 16.0 Hz, *J*₂ = 2.4 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.05 (dq, *J*₁ = 16.0 Hz, *J*₂ = 6.4 Hz, 1H), 4.64 – 4.53 (m, 1H), 1.36 (d, *J* = 6.0 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 159.5, 137.1 (q, *J* = 6 Hz), 129.0, 125.7, 124.0 (q, *J* = 267 Hz), 116.0, 113.2 (q, *J* = 34 Hz), 70.0, 22.0.

¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -62.8 (dd, *J*₁ = 6.4 Hz, *J*₂ = 2.4 Hz).

HRMS (ESI, m/z): calcd for C₁₂H₁₄F₃O⁺ [M+H]⁺ 231.0997, found: 231.1003.



(*E*)-1-(Benzylxy)-4-(3,3,3-trifluoroprop-1-enyl)benzene (**5c**)

White solid (m.p. = 59 – 63 °C)

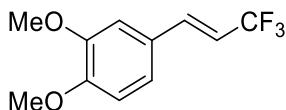
Yield = 62%

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.46 – 7.37 (m, 6H) 7.37 – 7.32 (m, 1H), 7.08 (dq, *J*₁ = 16.0 Hz, *J*₂ = 2.4 Hz, 1H), 7.01 – 6.94 (m, 2H), 6.07 (dq, *J*₁ = 16.0 Hz, *J*₂ = 6.4 Hz, 1H), 5.10 (s, 2H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 160.2, 137.0 (q, *J* = 7 Hz), 136.4, 129.0, 128.6, 128.1, 127.4, 126.3, 123.9 (q, *J* = 267 Hz), 115.2, 113.5 (q, *J* = 33 Hz), 70.0.

¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -62.8 (dd, *J*₁ = 6.4 Hz, *J*₂ = 2.4 Hz).

HRMS (ESI, m/z): calcd for C₁₆H₁₄F₃O⁺ [M+H]⁺ 279.0997, found: 279.0988.



(*E*)-1,2-Dimethoxy-4-(3,3,3-trifluoroprop-1-enyl)benzene (**5d**)

Light yellow oil.

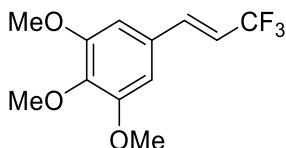
Yield = 74%

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.08 (dq, *J*₁ = 16.0 Hz, *J*₂ = 2.4 Hz, 1H), 7.02 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.4 Hz, 1H), 6.99 – 6.95 (m, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.07 (dq, *J*₁ = 16.0 Hz, *J*₂ = 6.4 Hz, 1H), 3.92 (s, 3H), 3.91 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 150.7, 149.2, 137.4 (q, *J* = 7 Hz), 126.3, 123.8 (q, *J* = 267 Hz), 121.6, 113.6 (q, *J* = 34 Hz), 111.1, 109.3, 55.9, 55.9.

¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -62.8 (dd, *J*₁ = 6.4 Hz, *J*₂ = 2.4 Hz).

HRMS (ESI, m/z): calcd for C₁₁H₁₂F₃O₂⁺ [M+H]⁺ 233.0789, found: 233.0791.



(*E*)-1,2,3-Trimethoxy-5-(3,3,3-trifluoroprop-1-enyl)benzene (**5e**)

White solid (m.p. = 104 – 106 °C).

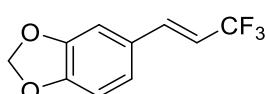
Yield = 67%

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.07 (dq, *J*₁ = 16.0 Hz, *J*₂ = 2.4 Hz, 1H), 6.67 (s, 1H), 6.11 (dq, *J*₁ = 16.0 Hz, *J*₂ = 6.4 Hz, 1H), 3.88 (s, 6H), 3.82 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 153.5, 139.8, 137.6 (q, *J* = 7 Hz), 128.9, 123.6 (q, *J* = 267 Hz), 115.2 (q, *J* = 34 Hz), 104.7, 60.9, 56.1.

¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -63.1 (dd, *J*₁ = 6.4 Hz, *J*₂ = 2.4 Hz).

HRMS (ESI, m/z): calcd for C₁₂H₁₄F₃O₃⁺ [M+H]⁺ 263.0895, found: 263.0903.



(*E*)-5-(3,3,3-Trifluoroprop-1-enyl)benzo[d][1,3]dioxole (**5f**)

Colorless oil

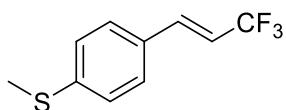
Yield = 65%

¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.04 (dq, *J*₁ = 16.0 Hz, *J*₂ = 2.4 Hz, 1H), 6.97 – 6.89 (m, 2H), 6.84 – 6.77 (m, 1H), 6.08 – 5.95 (m, 1H), 6.01 (s, 2H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 149.2, 148.4, 137.2 (q, *J* = 7 Hz), 127.7, 123.8 (q, *J* = 267 Hz), 123.4, 113.9 (q, *J* = 33 Hz), 108.5, 106.2, 101.5.

¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -62.9 (d, *J* = 6.4 Hz).

HRMS (ESI, m/z): calcd for C₁₀H₈F₃O₂⁺ [M+H]⁺ 217.0476, found: 217.0466.



(E)-Methyl(4-(3,3,3-trifluoroprop-1-enyl)phenyl)sulfane (**5g**)

White solid (59 – 60 °C).

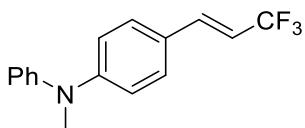
Yield = 62%

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.39 – 7.34 (m, 2H), 7.26 – 7.21 (m, 2H), 7.09 (dq, *J*₁ = 16.0 Hz, *J*₂ = 2.4 Hz, 1H), 6.15 (dq, *J*₁ = 16.0 Hz, *J*₂ = 6.4 Hz, 1H), 2.50 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 141.4, 137.0 (q, *J* = 7 Hz), 129.9, 127.8, 126.1, 123.7 (q, *J* = 267 Hz), 114.8 (q, *J* = 34 Hz), 15.2.

¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -63.1 (dd, *J*₁ = 6.4 Hz, *J*₂ = 2.4 Hz).

HRMS (ESI, m/z): calcd for C₁₀H₁₀F₃S⁺ [M+H]⁺ 219.0455, found: 219.0459.



(E)-N-Methyl-N-phenyl-4-(3,3,3-trifluoroprop-1-enyl)aniline (**5h**)

Light yellow solid (m.p. = 65 – 68 °C).

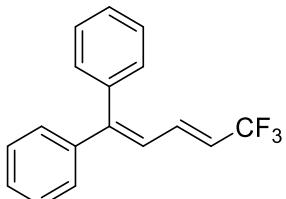
Yield = 51%

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.40 – 7.33 (m, 2H), 7.33 – 7.28 (m, 2H), 7.20 – 7.11 (m, 3H), 7.05 (dq, *J*₁ = 16.0 Hz, *J*₂ = 2.4 Hz, 1H), 6.88 – 6.81 (m, 2H), 6.00 (dq, *J*₁ = 16.0 Hz, *J*₂ = 2=6.4 Hz, 1H), 3.35 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 150.4, 148.0, 137.3 (q, *J* = 7 Hz), 129.6, 128.6, 124.5, 124.3, 124.2 (q, *J* = 267 Hz), 123.9, 116.2, 111.9 (q, *J* = 34 Hz), 40.2.

¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -62.4 (dd, *J*₁ = 6.4 Hz, *J*₂ = 2.4 Hz).

HRMS (ESI, m/z): calcd for C₁₆H₁₅F₃N⁺ [M+H]⁺ 278.1157, found: 278.1164.



(E)-(5,5,5-Trifluoropenta-1,3-diene-1,1-diyl)dibenzene (**5i**)

Colorless oil

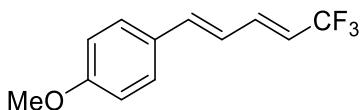
Yield = 59%

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.46 – 7.40 (m, 3H), 7.35 – 7.28 (m, 5H), 7.23 – 7.18 (m, 2H), 5.92 – 5.80 (m, 1H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 149.9, 141.2, 138.4, 135.1 (q, *J* = 7 Hz), 130.2, 128.6, 128.4, 128.3, 128.2, 128.0, 123.8, 123.5 (q, *J* = 267 Hz), 119.2 (q, *J* = 34 Hz).

¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -63.0 (d, *J* = 6.4 Hz).

HRMS (ESI, m/z): calcd for C₁₇H₁₄F₃⁺ [M+H]⁺ 275.1048, found: 275.1053.



1-Methoxy-4-((1*E*,3*E*)-5,5,5-trifluoropenta-1,3-dienyl)benzene (**5j**)

Light yellow solid (m.p. = 72 – 74 °C).

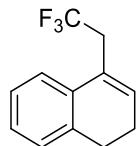
Yield = 33%

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.42 – 7.35 (m, 2H), 6.93 – 6.83 (m, 3H), 6.80 – 6.72 (m, 1H), 6.68 – 6.60 (m, 1H), 5.80 – 5.68 (m, 1H), 3.83 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 160.3, 138.9, 137.8 (q, *J* = 7 Hz), 128.6, 128.4, 123.6 (q, *J* = 267 Hz), 122.8, 117.1 (q, *J* = 33 Hz), 114.3, 55.3.

¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -62.9 (d, *J* = 6.4 Hz).

HRMS (ESI, m/z): calcd for C₁₂H₁₂F₃O⁺ [M+H]⁺ 229.0840, found: 229.0834.



4-(2,2,2-Trifluoroethyl)-1,2-dihydronaphthalene (**6**)

Colorless oil

Yield = 21%

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.25 – 7.10 (m, 4H) 7.26 – 7.21 (m, 2H), 6.14 (t, *J* = 4.8 Hz, 1H), 3.24 (qd, *J*₁ = 10.8 Hz, *J*₂ = 1.2 Hz, 2H), 2.79 (t, *J* = 8.0 Hz, 2H), 2.37 – 2.29 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 136.3, 133.7, 132.0, 127.8, 127.3, 126.7 (q, *J* = 3 Hz), 126.4, 126.0 (q, *J* = 275 Hz), 122.7, 36.8 (q, *J* = 29 Hz), 27.9, 23.2.

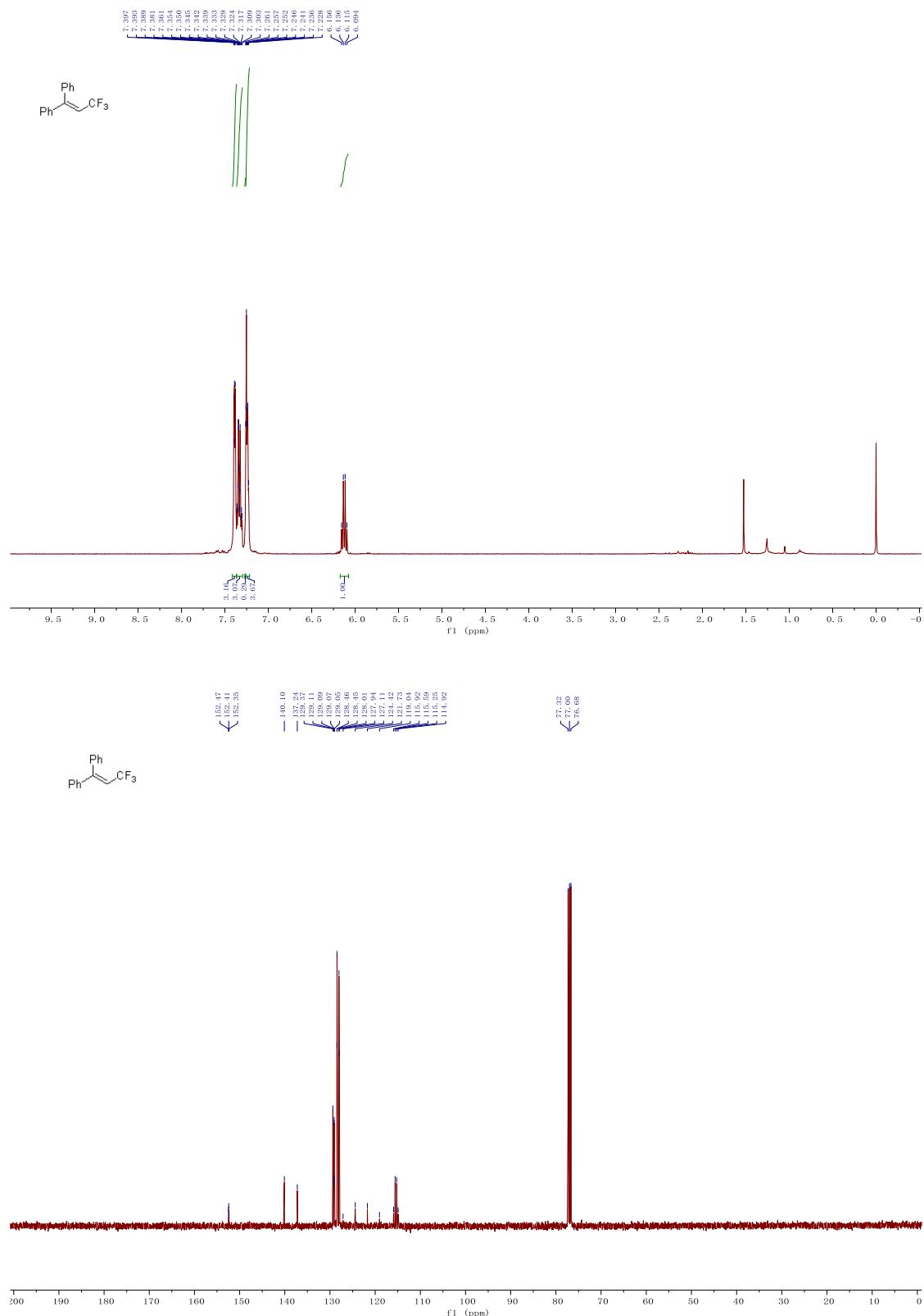
¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -64.5 (t, *J* = 11.3 Hz).

HRMS (ESI, m/z): calcd for C₁₂H₁₁F₃⁺ [M+H]⁺ 213.0891, found: 213.0894.

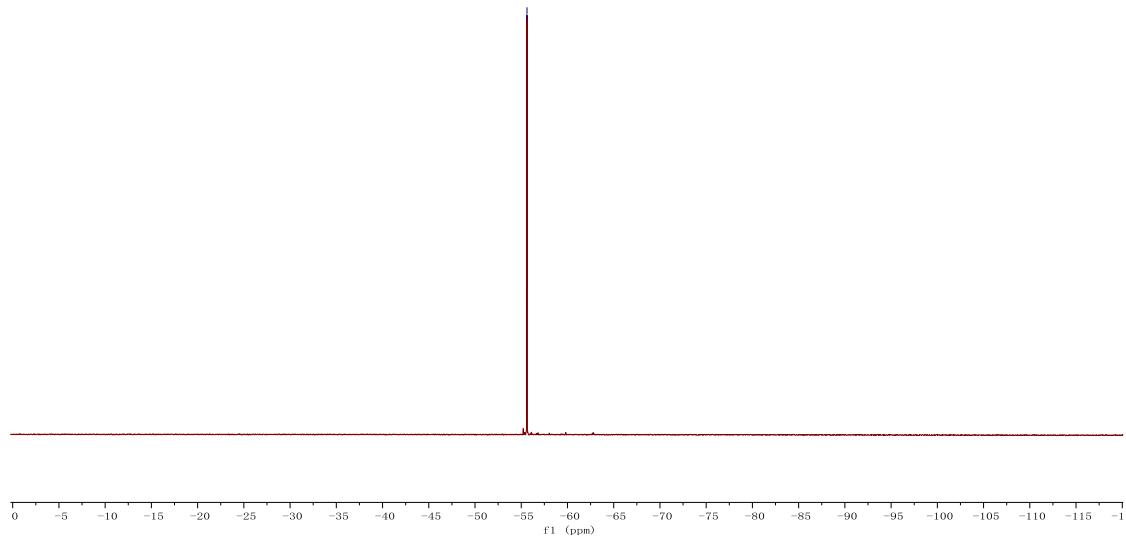
6. Reference

1. T. Wang, Y. Hu, S. Zhang, *Org. Biomol. Chem.* **2010**, *8*, 2312.
2. A. J. Perkowski, W. You, D. A. Nicewicz, *J. Am. Chem. Soc.* **2015**, *137*, 7580.

7. ^1H , ^{13}C , ^{19}F NMR spectra



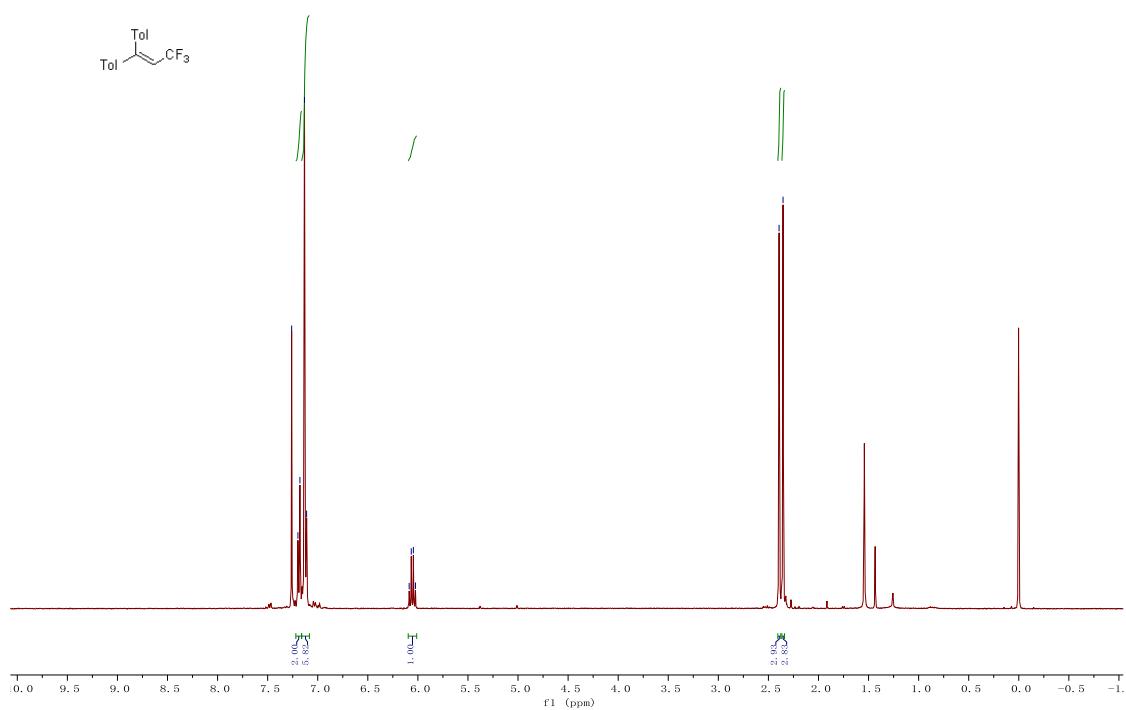
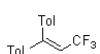
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-55.62

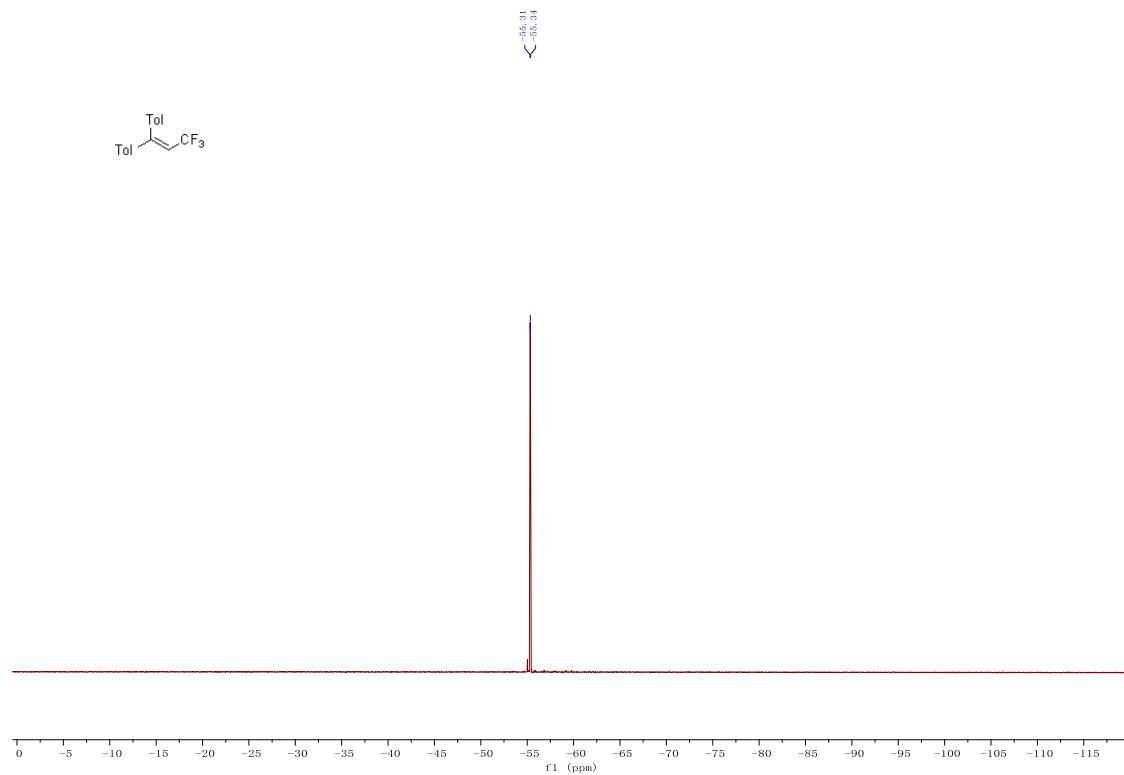
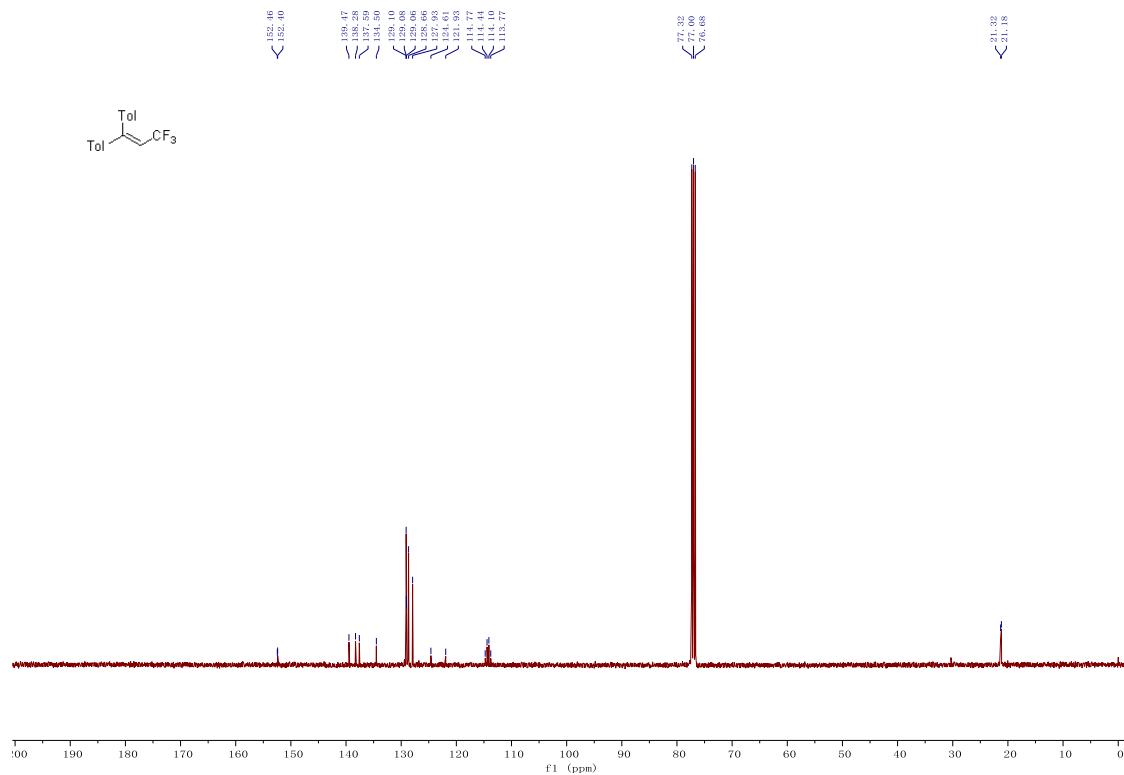


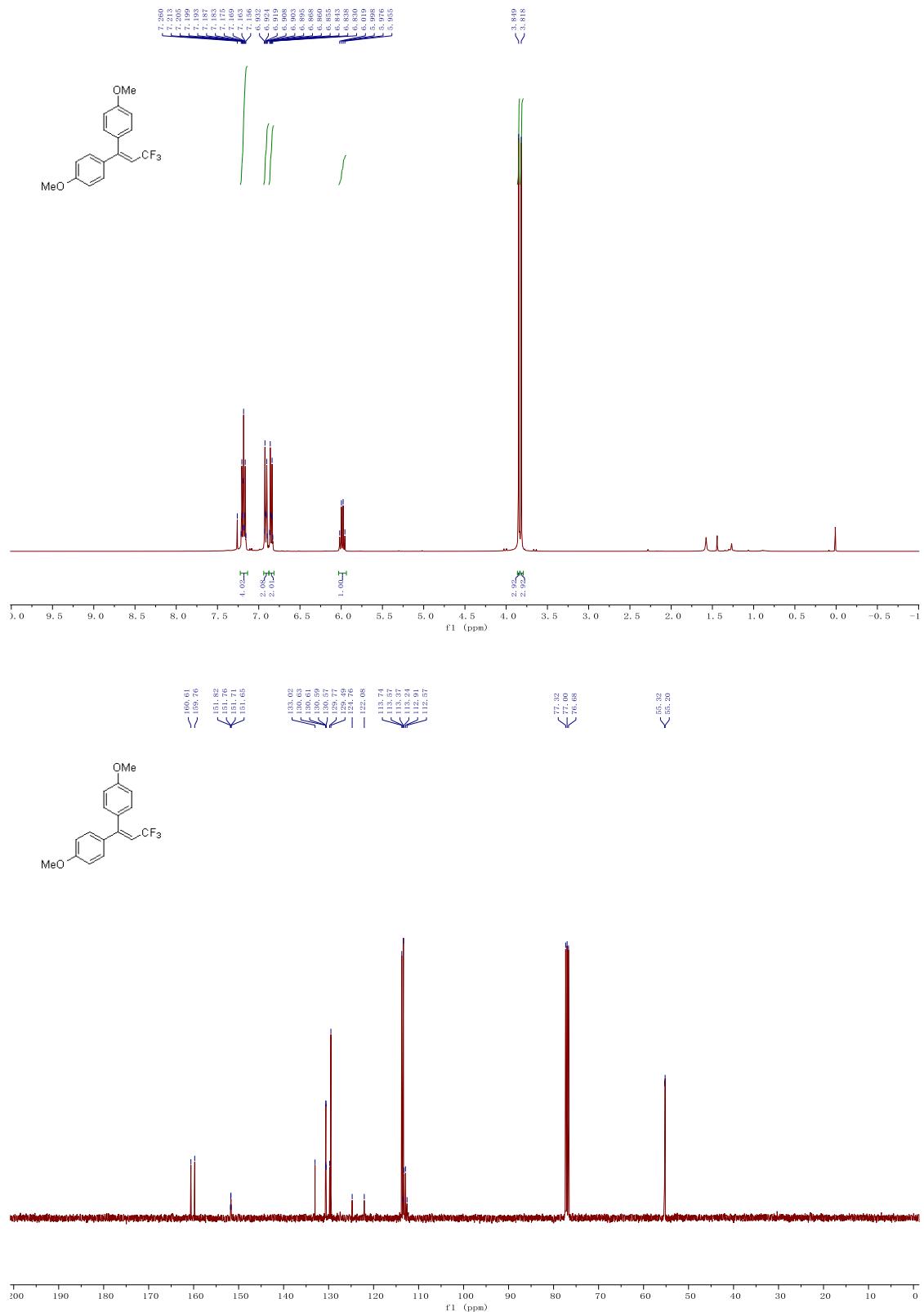
7.200
7.198
7.175
7.132
7.111

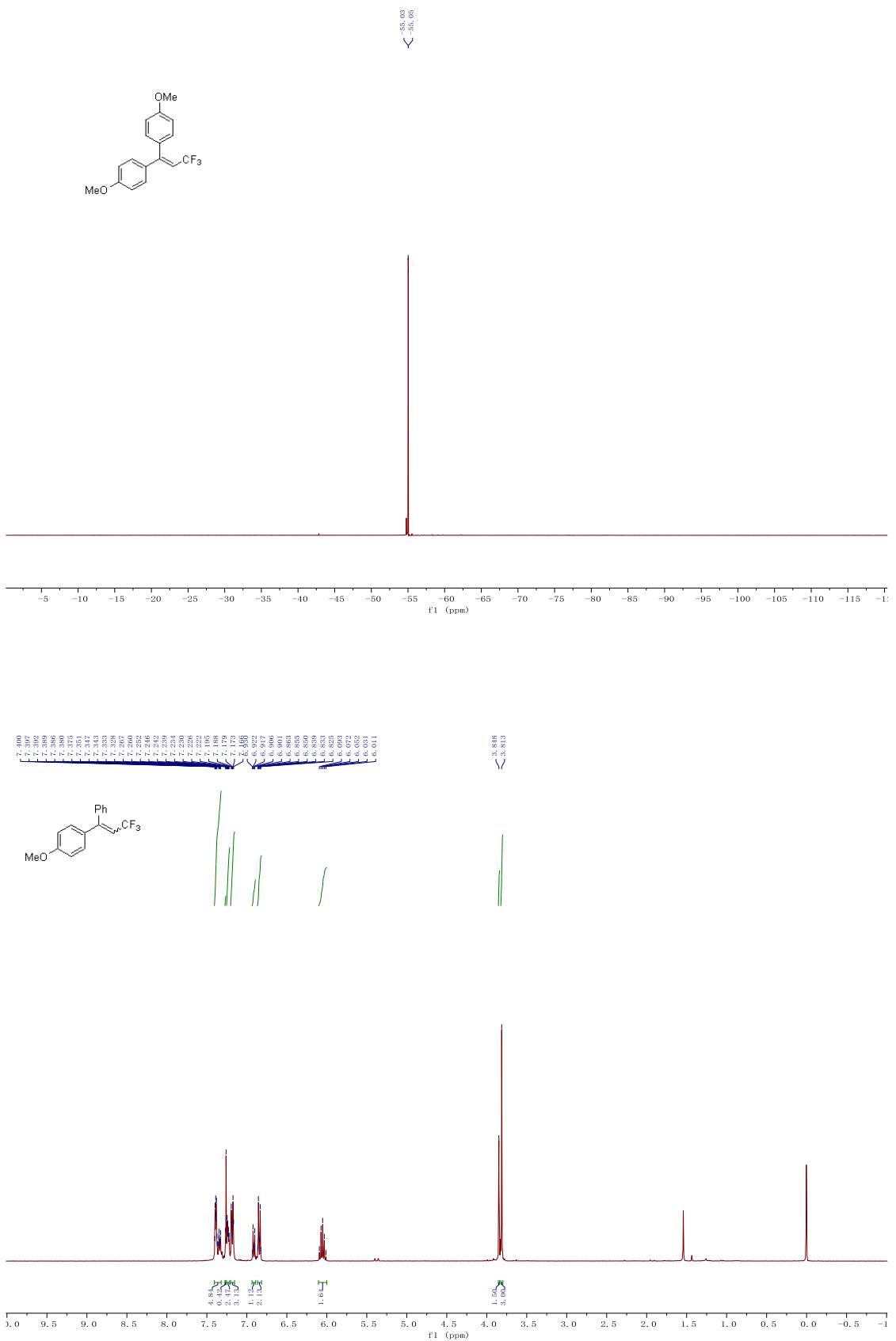
6.087
6.066
6.046
6.026

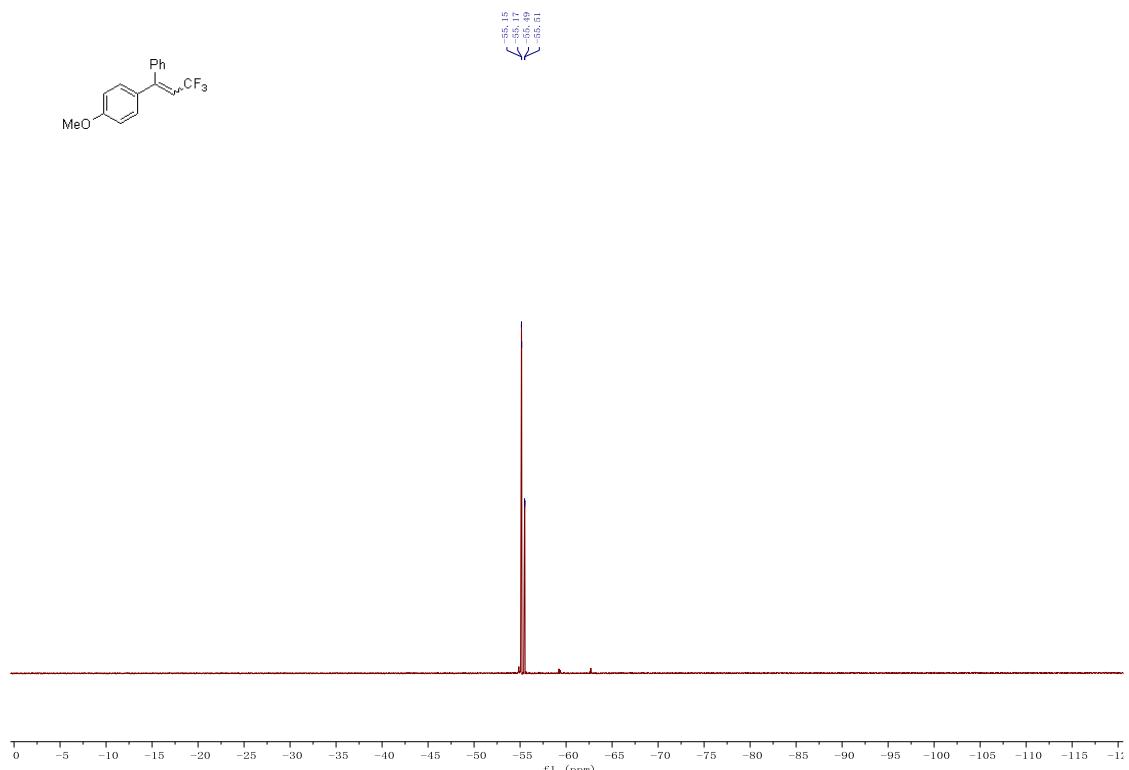
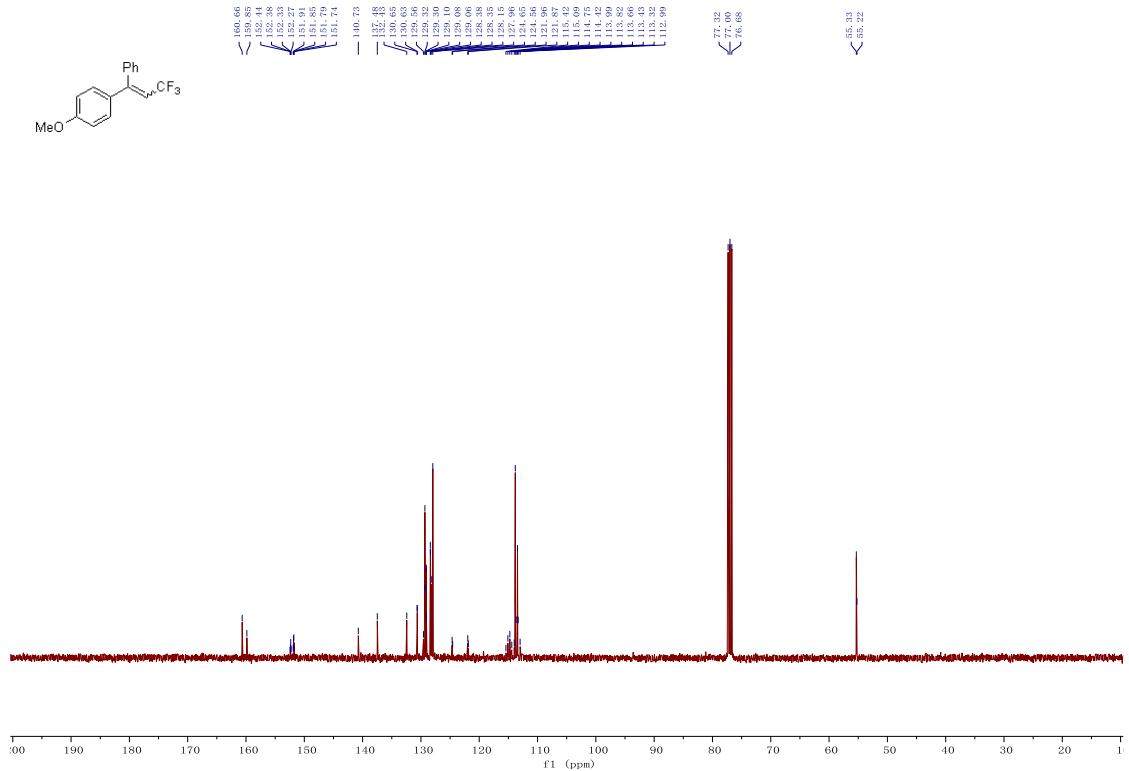
2.393
2.354

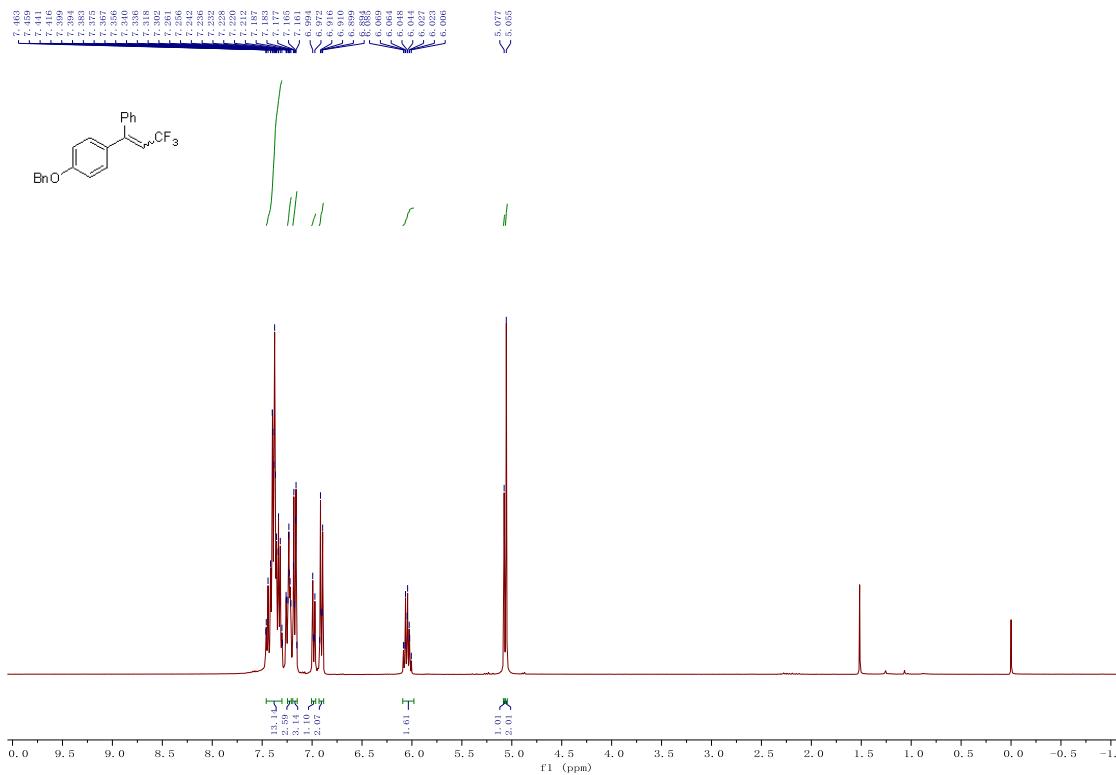
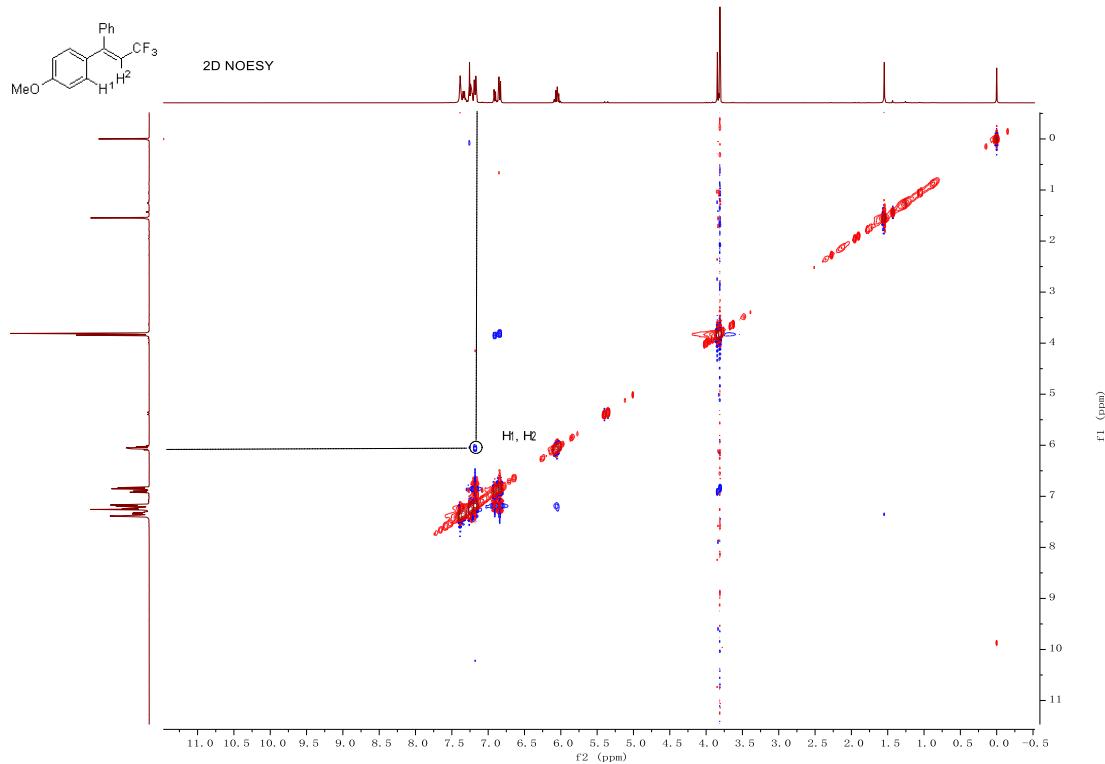


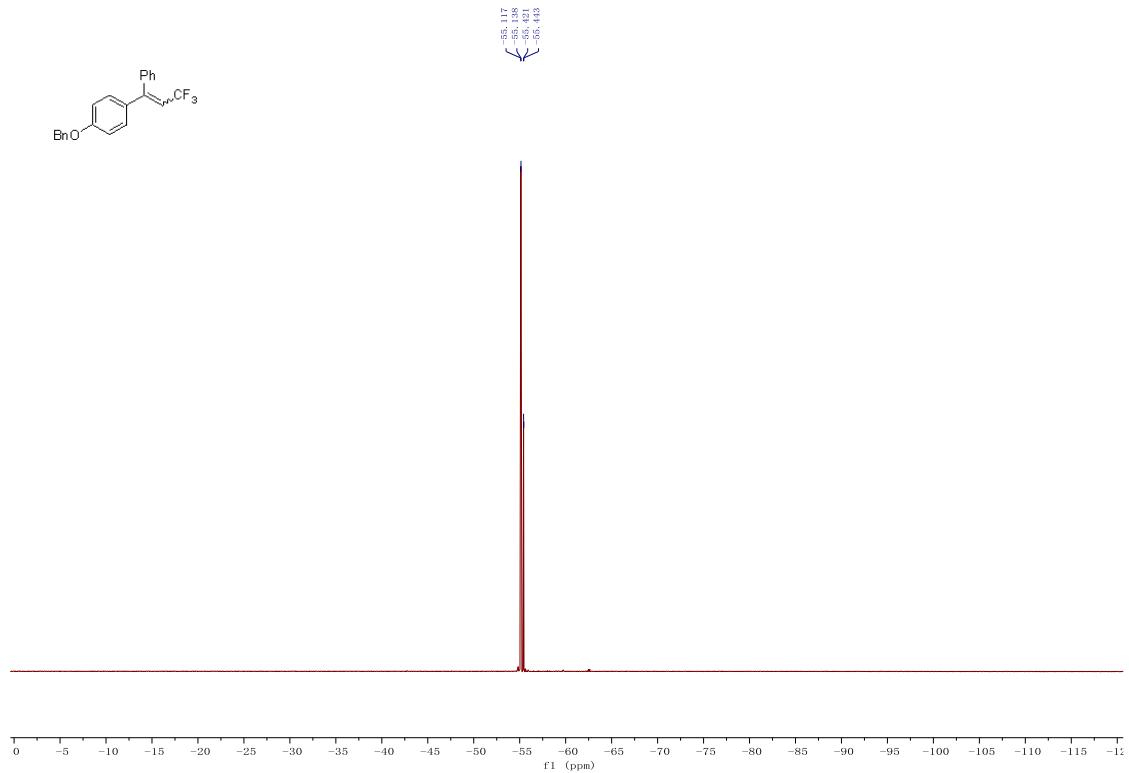
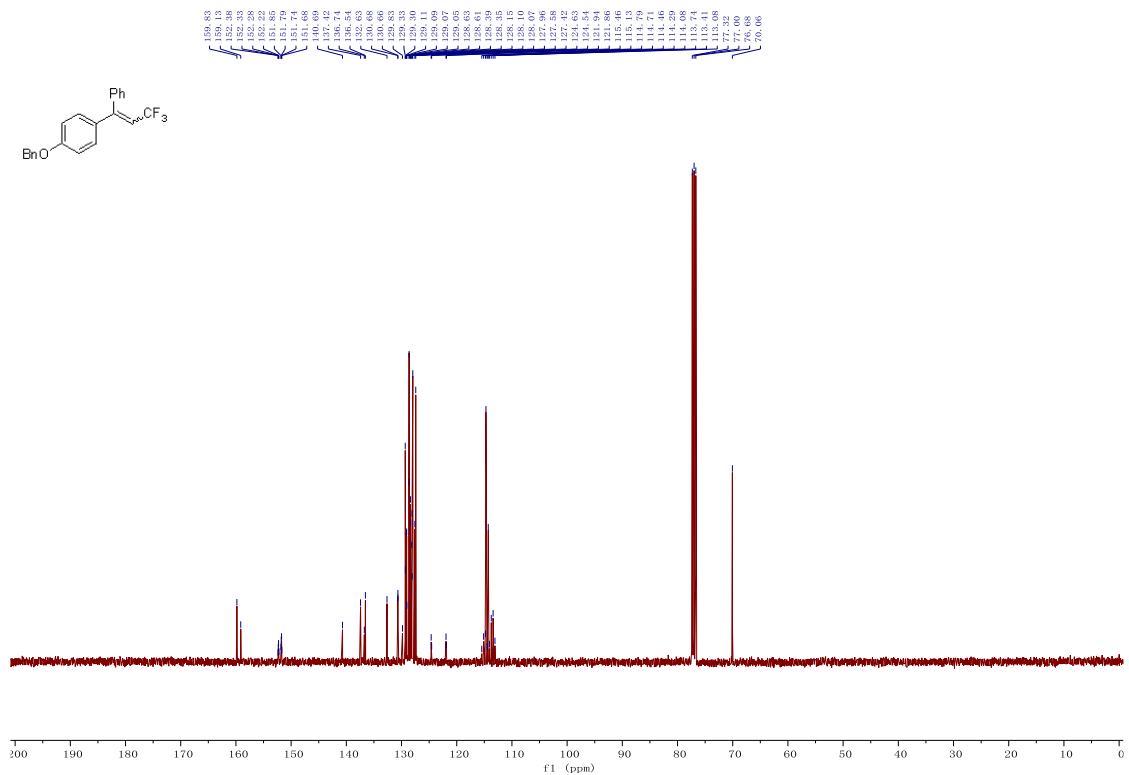


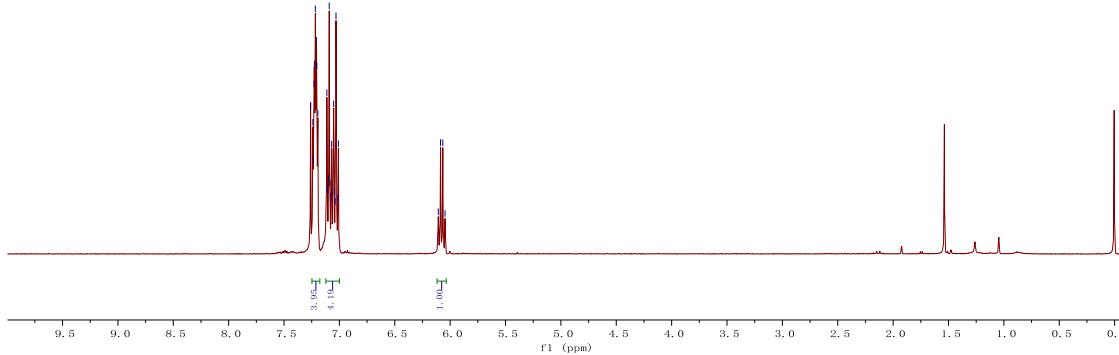
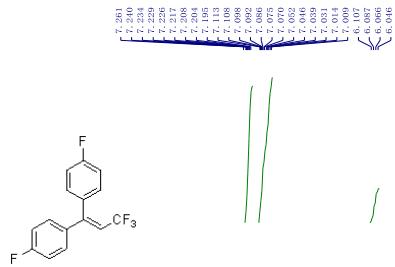
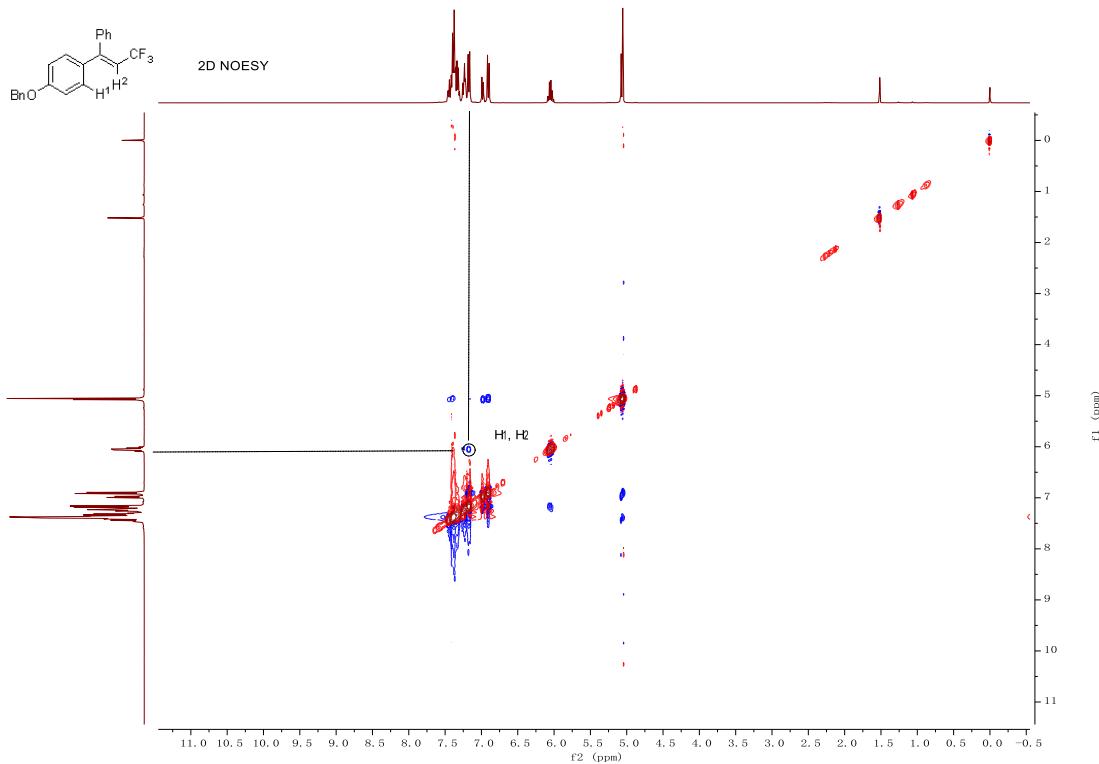


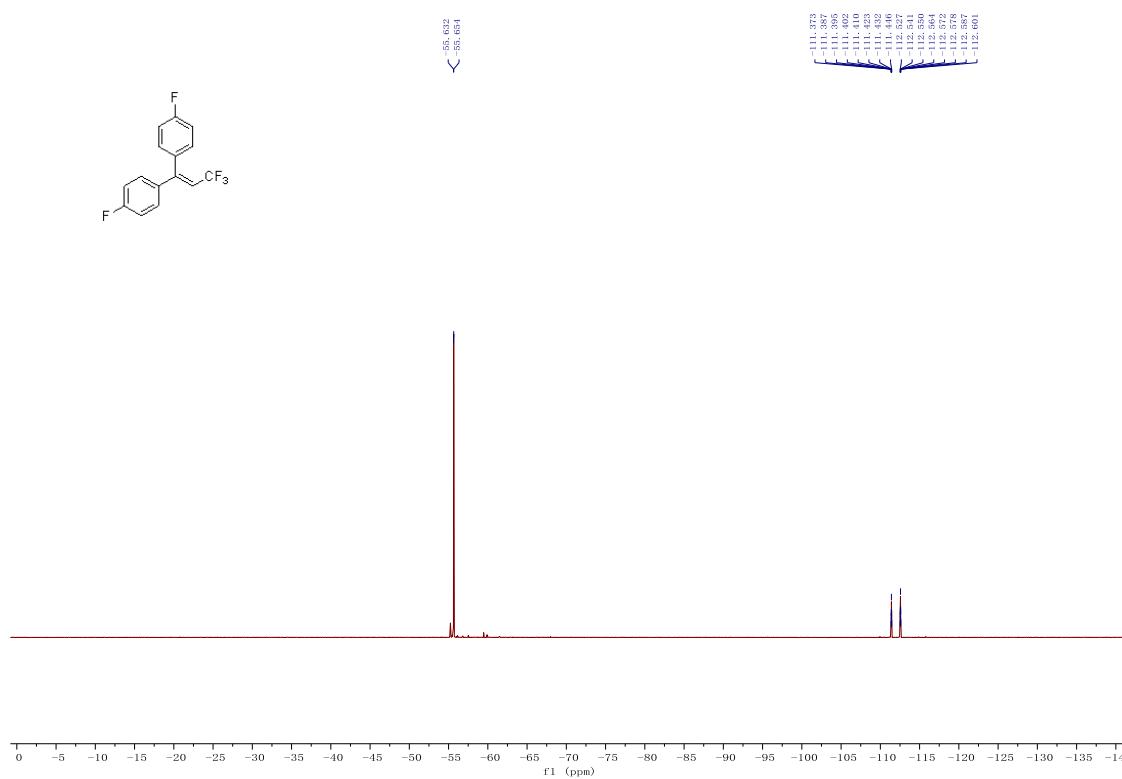
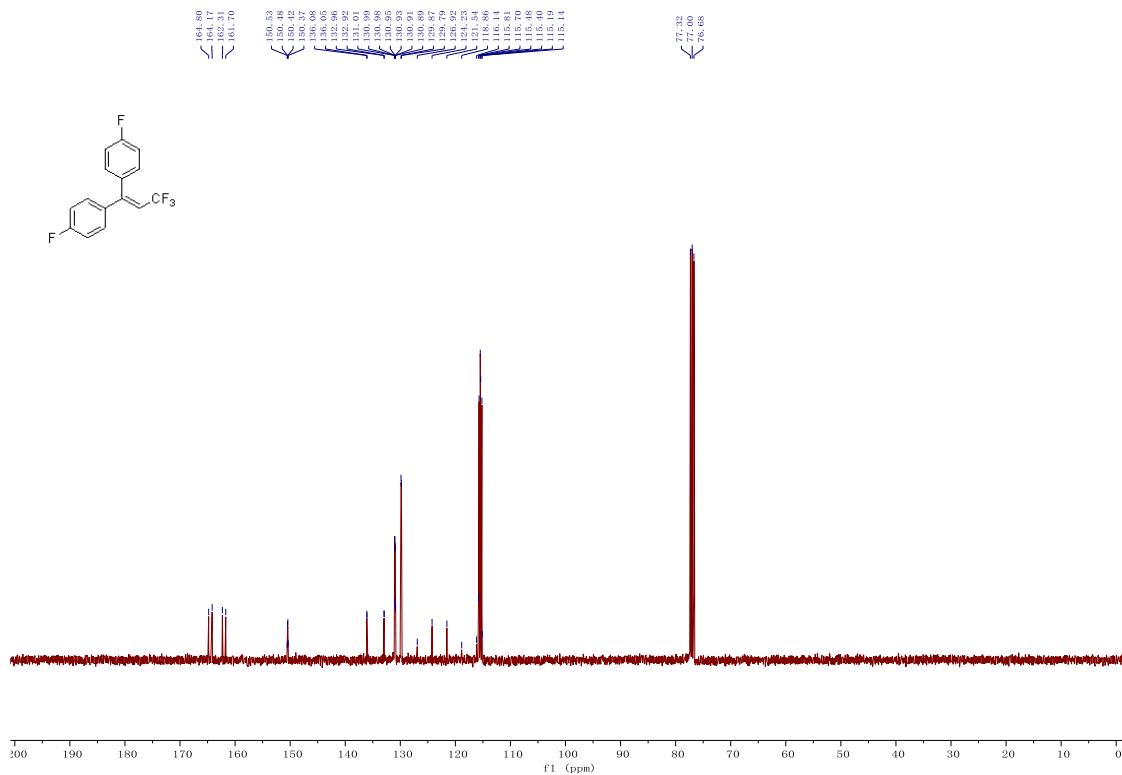


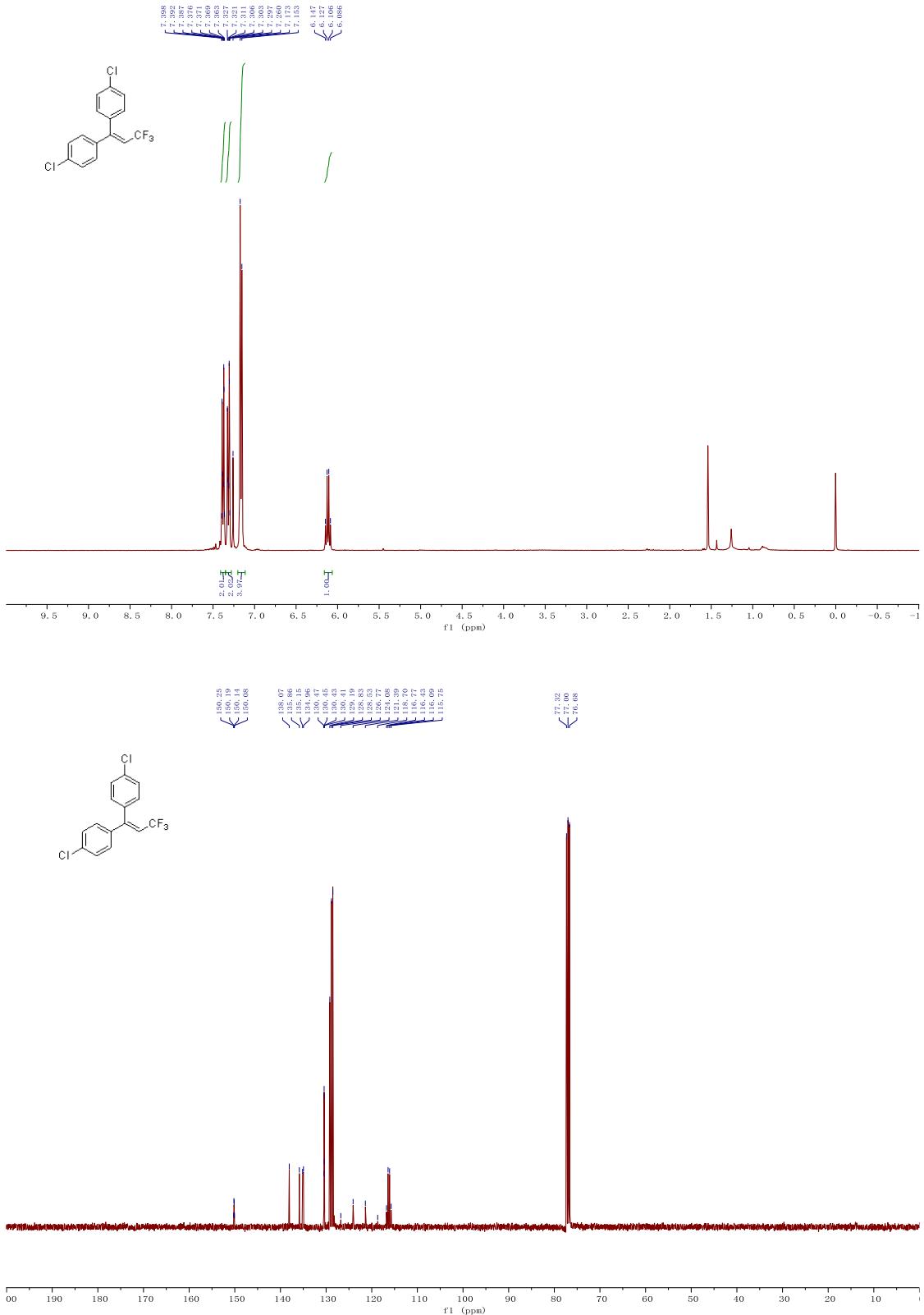


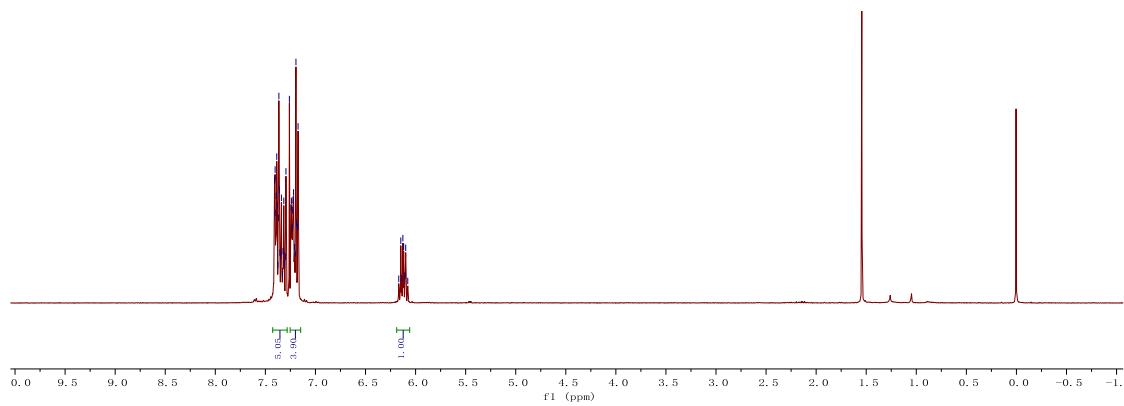
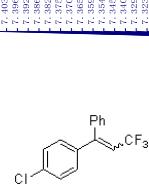
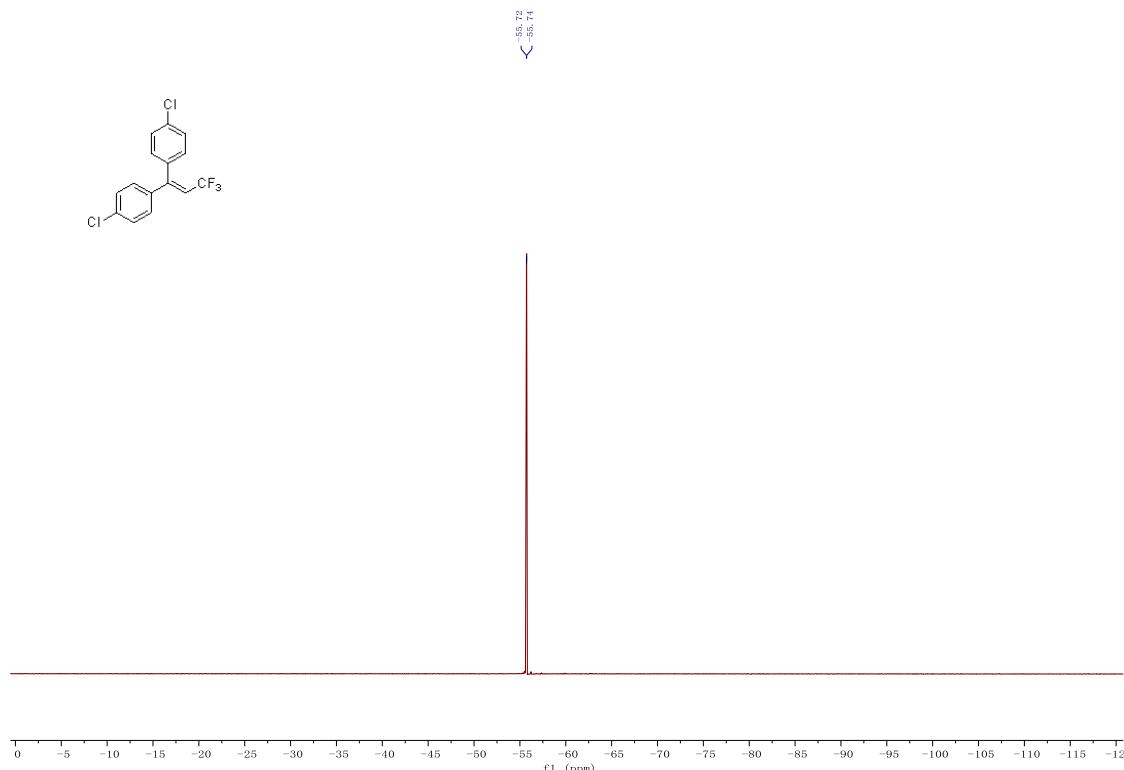
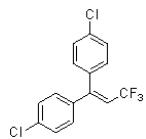


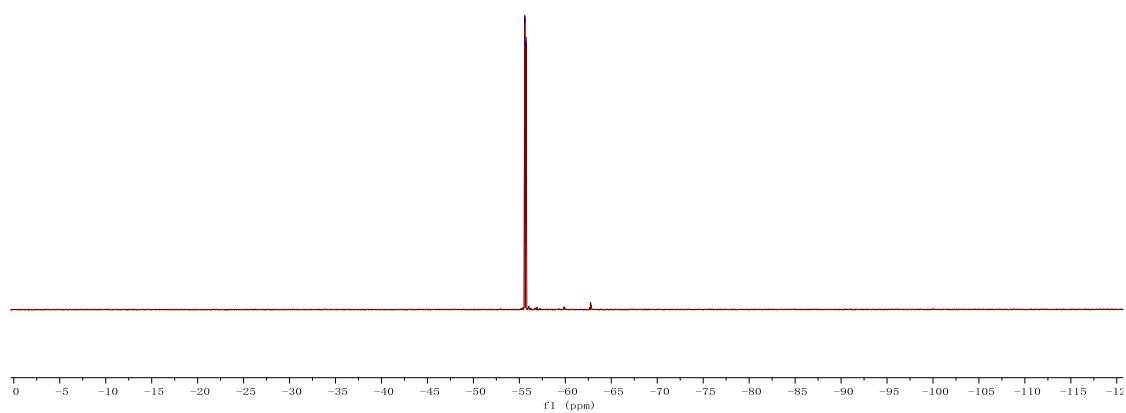
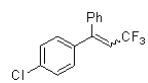
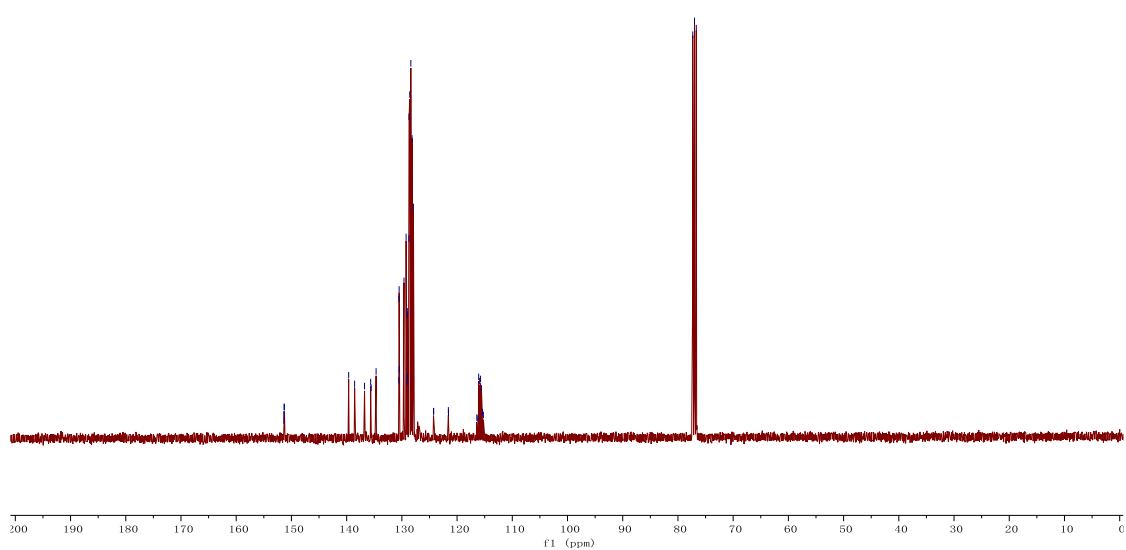
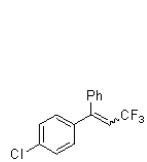


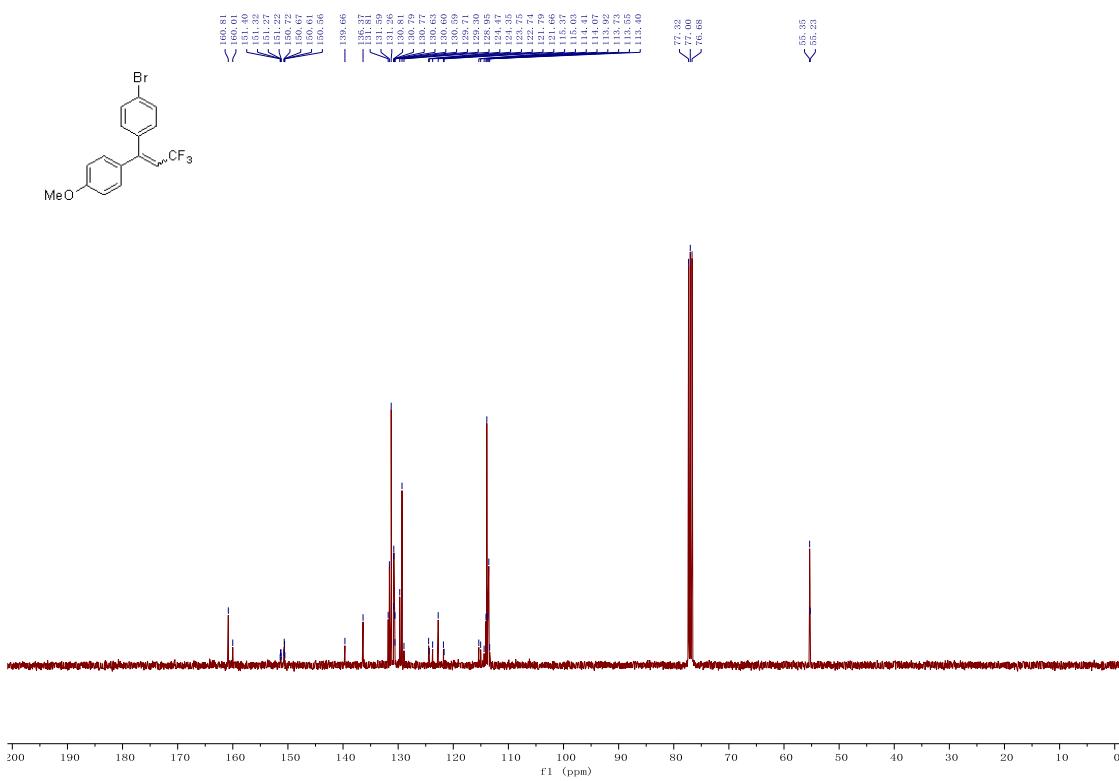
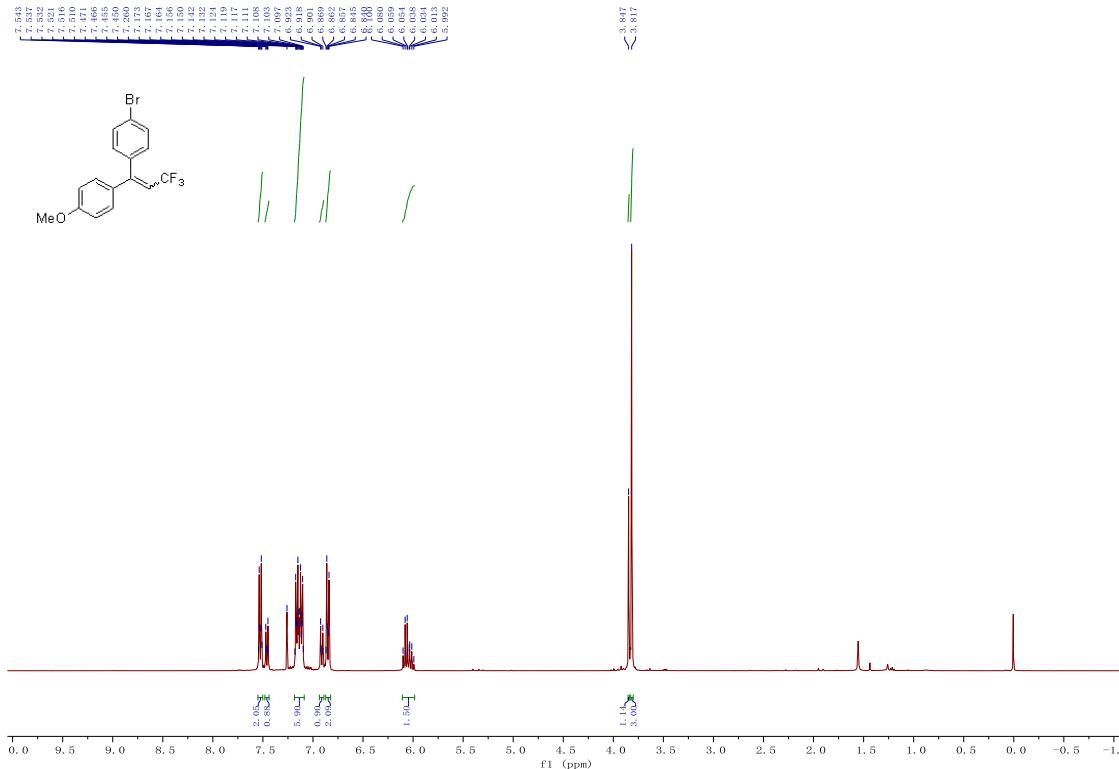


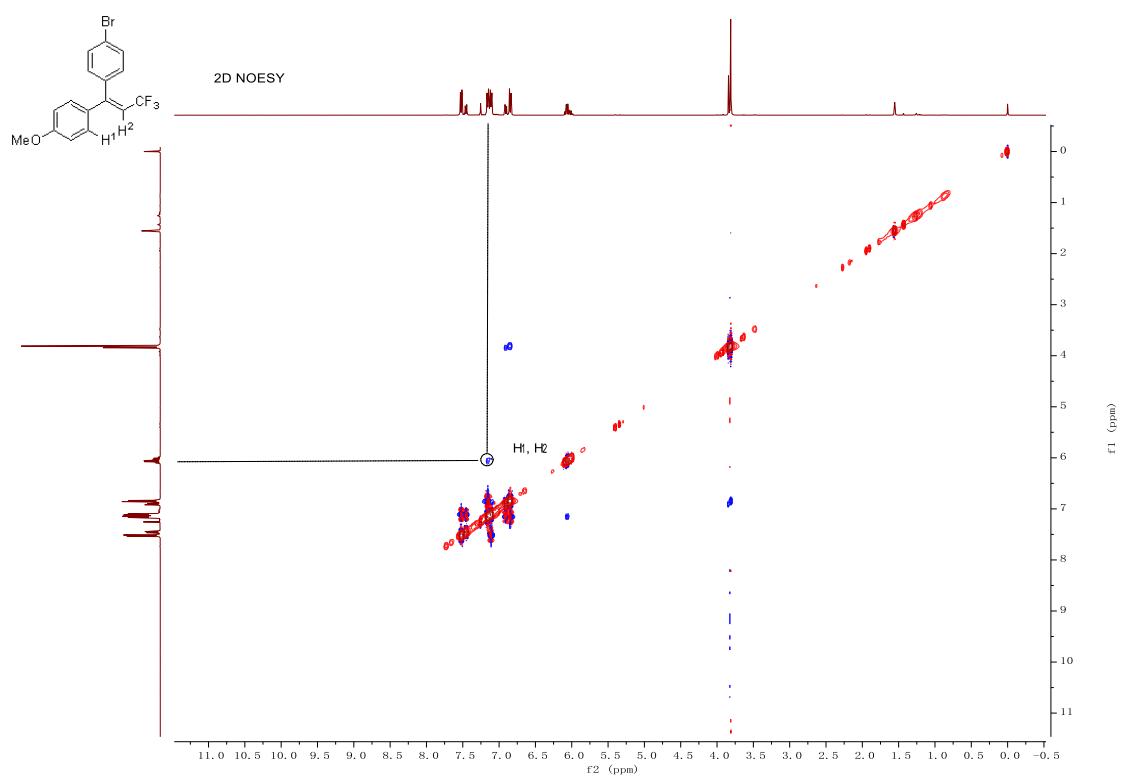
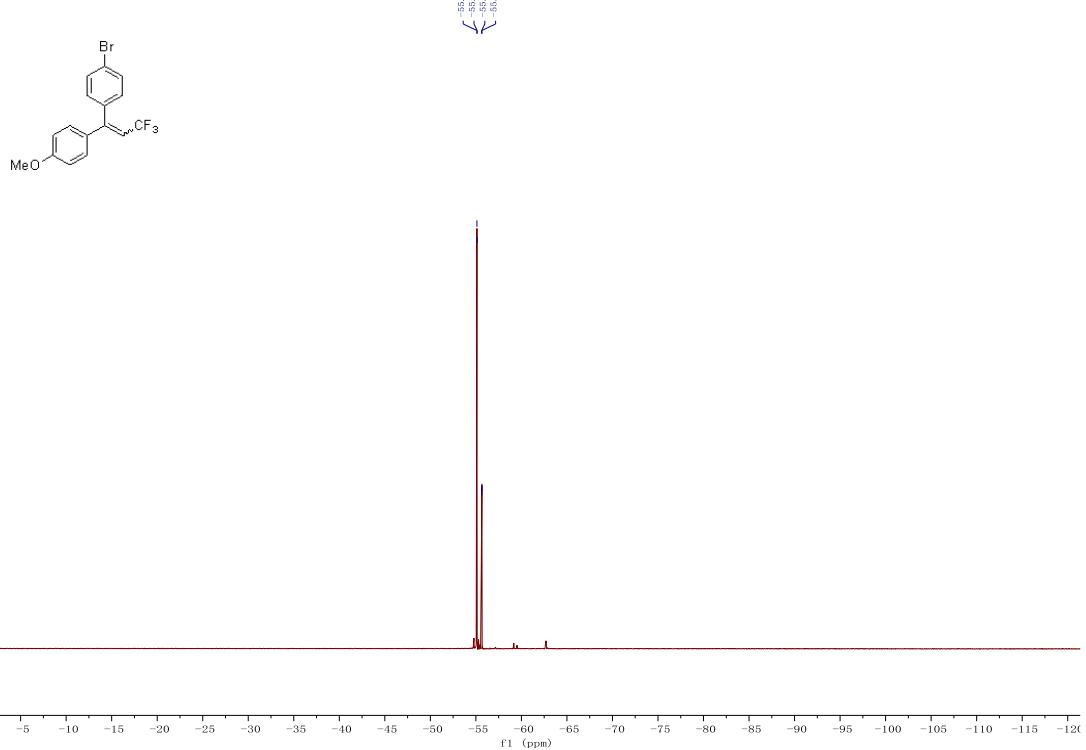


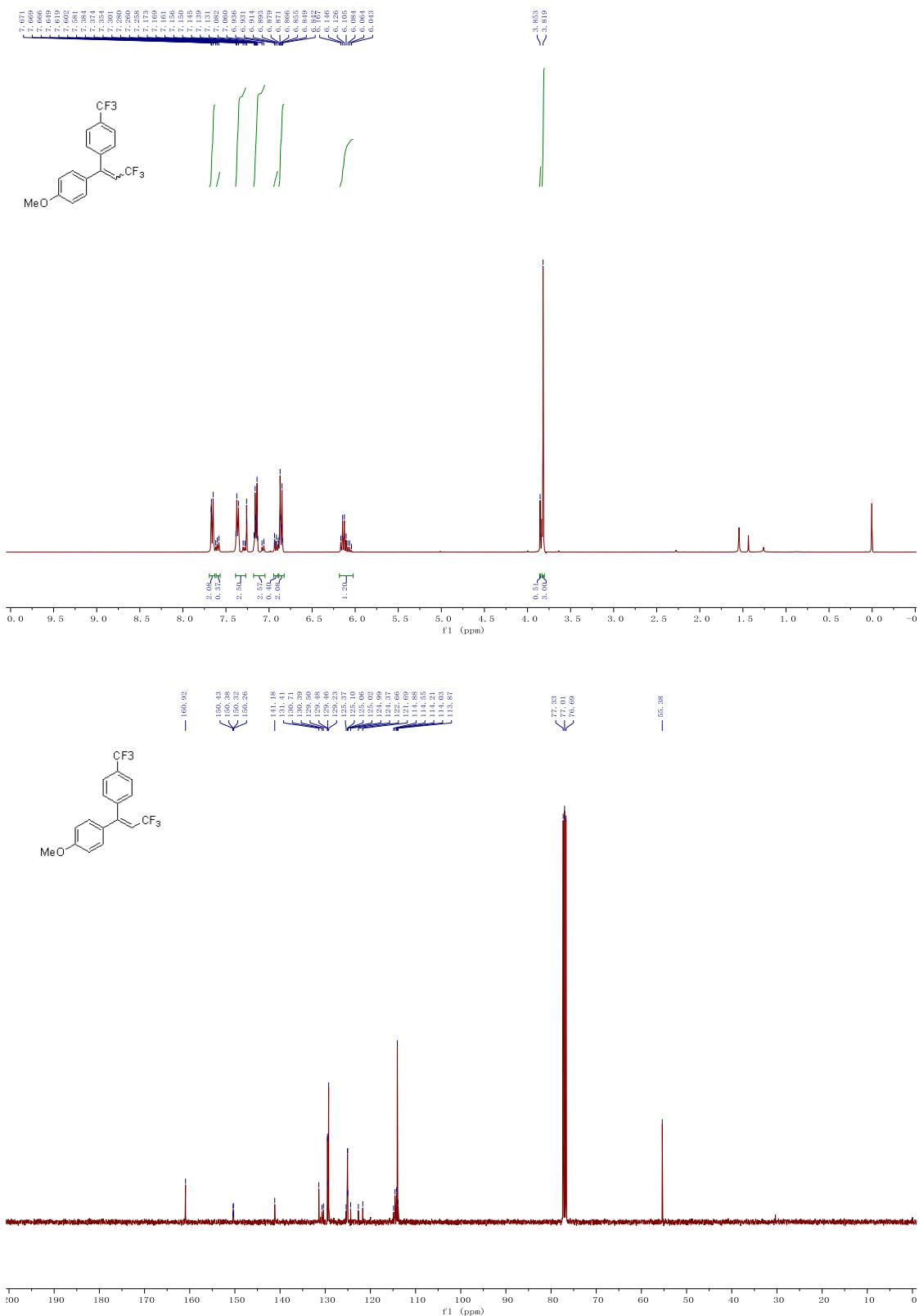


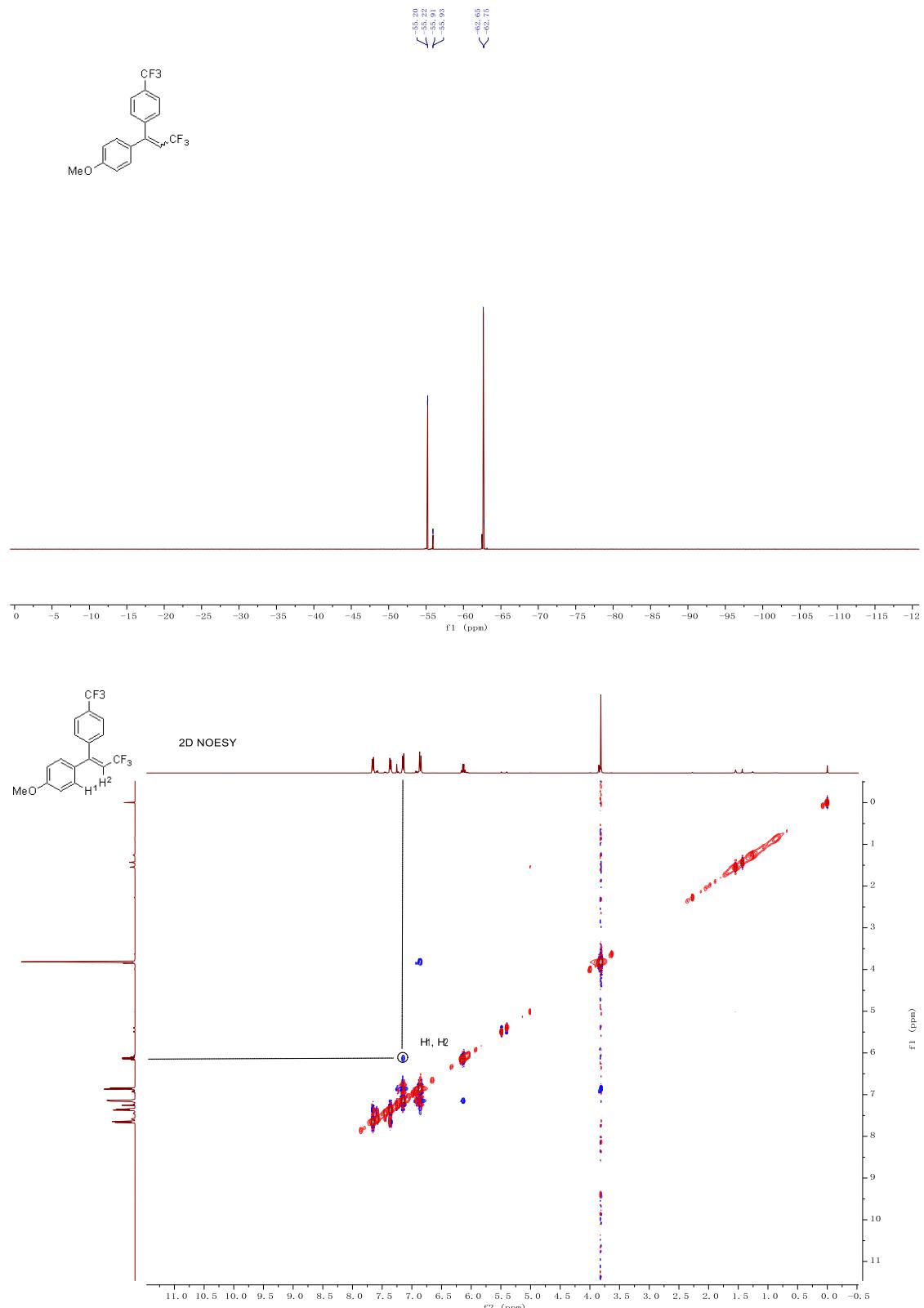


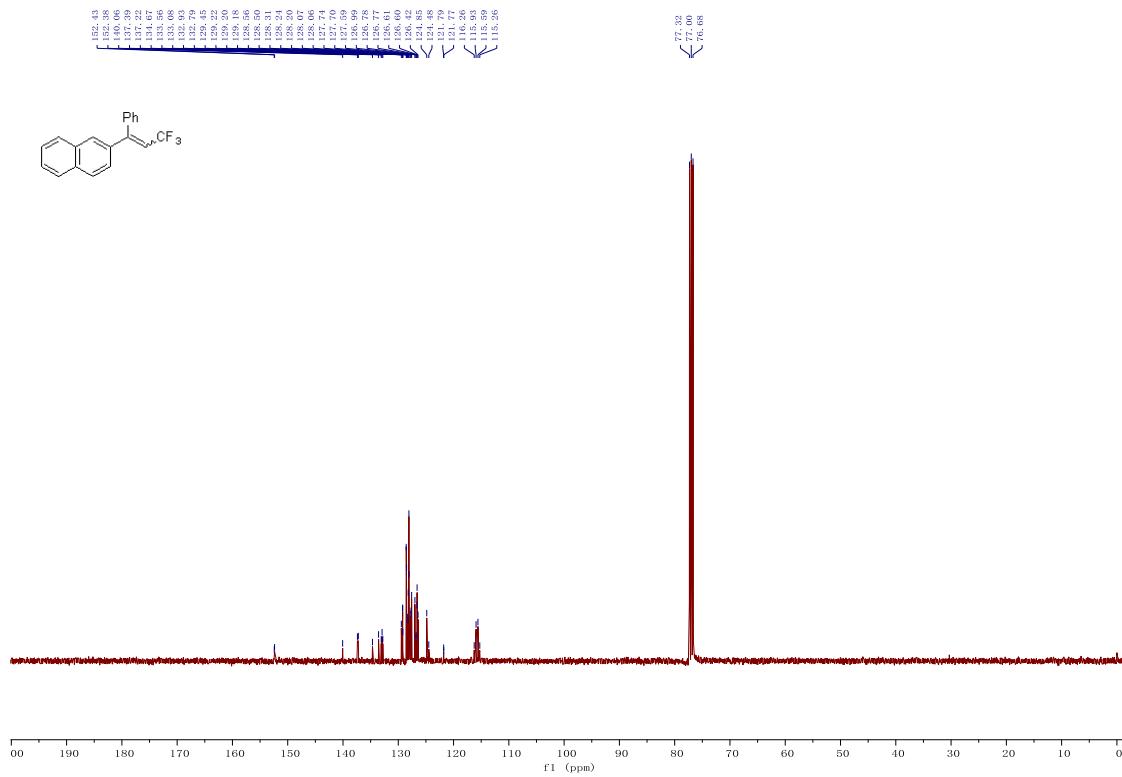
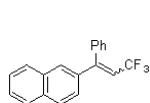
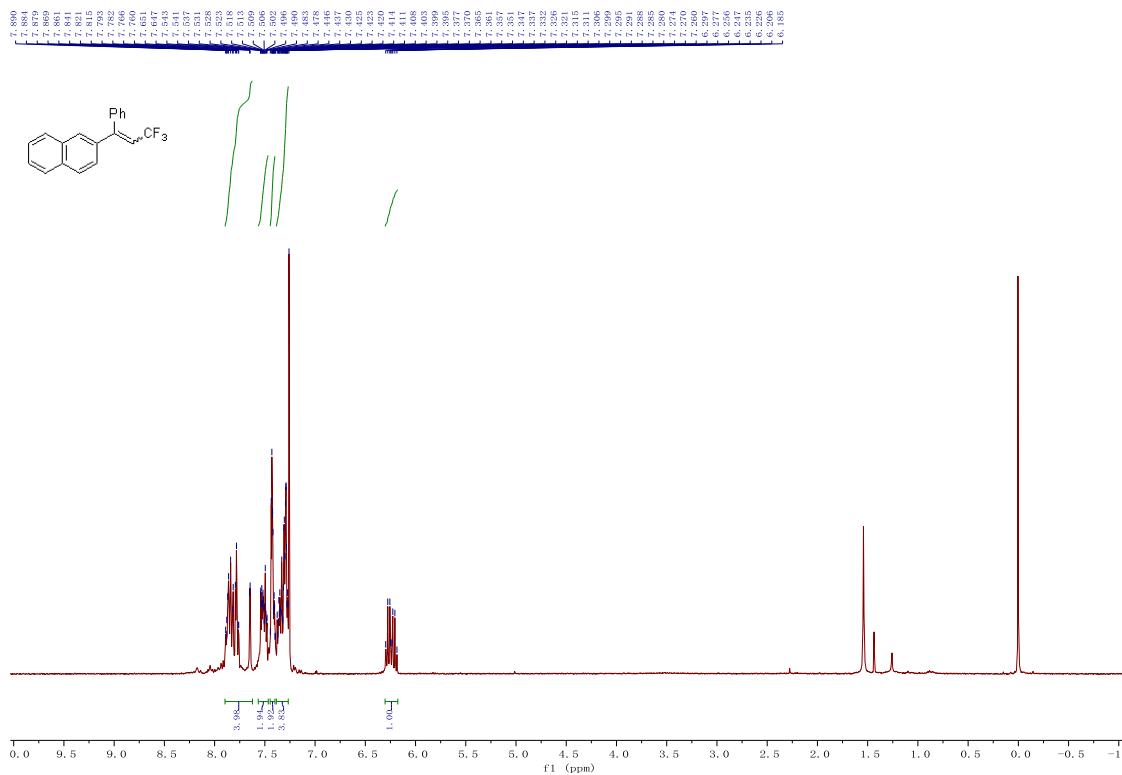


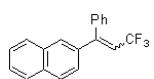












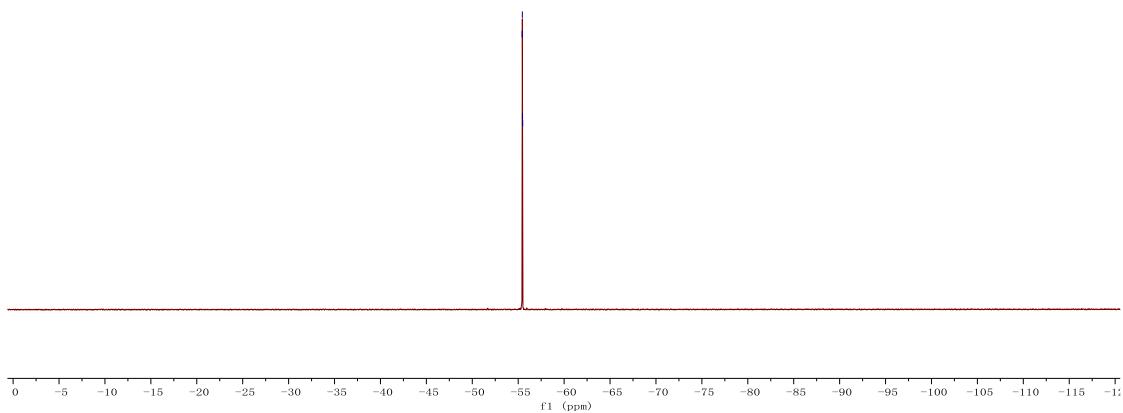
$\delta =$

-55.43

-55.45

-55.46

-55.49



7.163
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7.129
7.128
7.126
7.125
7.123
7.121
7.119
7.117
7.115
7.107
6.976
6.967
6.964
6.963
6.944
6.937
6.933
6.929
6.919
6.876
6.854
6.844
6.834
6.824
6.155
6.098
5.985
5.962
5.920

3.810
3.824

