

Supporting Information

Synthesis of 4-(Trifluoromethyl)cyclopentenones and 2-(Trifluoromethyl)furans by Reductive Trifluoroacetylation of Ynones

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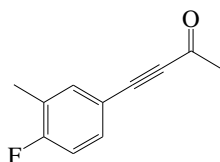
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General information

All chemicals (Tokyo chemical industry, Aldrich, Nacalai tesque, Wako, Kanto Chemical and SynQuest) were commercially available and used without further purification. Starting materials were synthesized according to the reported procedure,¹ therein, all starting materials **1** and **7** are known compounds except **1j** and **7g**. Thin-layer chromatography (TLC) was performed on Merck pre-coated plates (silica gel 60 F₂₅₄, Art 5715, 0.25 mm). Products were purified by column chromatography on neutral silica gel (60N, spherical, 63-210 mesh) using standard techniques. NMR spectra (¹H, ¹³C, ¹⁹F) were recorded on a JEOL JNM AL-400 and EX-400 (400 MHz) spectrometers. Chemical shifts (δ) in parts per million (ppm) are reported relative to the residual signal of chloroform (7.26 ppm), and coupling constants are reported in hertz (Hz). Carbon chemical shifts were referenced to the carbon signal of CDCl₃ at 77.00 ppm or DMSO-*d*₆ at 39.50 ppm. Fluorine chemical shifts were referenced to the signal of CF₃COOH at -76.5 ppm. Signal multiplicity is as follows: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), m (multiplet). IR spectra were obtained on a JASCO 470Plus FTIR spectrometer, and peaks are reported in wavenumber (cm⁻¹). Mass spectra and high-resolution mass spectra were recorded on a JEOL JMS-600H spectrometer. Melting points (mp) were performed on a Yanaco MP-500D instrument and are uncorrected. Cyclic voltammograms were measured by ALS-600, and were carried out with a three-electrode system using a platinum working electrode, a platinum counter electrode, and Ag/AgCl as a reference electrode with sweeping rate of 200 mVs⁻¹ in 1% tetrabutylammonium perchlorate/DMF.

Reference

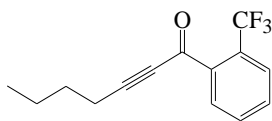
- (1) (a) Schuler, M.; Silva, F.; Bobbio, C.; Tessier, A.; Gouverneur, V. *Angew. Chem. Int. Ed.* **2008**, *47*, 7927.
(b) Livingston, R.; Cox, L. R.; Odermatt, S.; Diederich, F. *Helv. Chim. Acta.* **2002**, *85*, 3052.



4-(4-Fluoro-3-methylphenyl)but-3-yn-2-one (**1j**)^{1a}

57% isolated yield (750 mg), pale yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 2.25 (s, 3H), 2.42 (s, 3H), 6.99 (t, *J*=8.9 Hz, 1H), 7.35-7.42 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 14.23 (d, ³*J*_{CF}=3.3 Hz), 32.57, 87.89 (d, ⁵*J*_{CF}=1.6 Hz), 89.61, 115.53 (d, ⁴*J*_{CF}=6.4 Hz), 115.64 (d, ²*J*_{CF}=24.0 Hz), 125.83 (d, ²*J*_{CF}=18.0 Hz), 132.63 (d, ³*J*_{CF}=9.1 Hz), 136.42 (d, ³*J*_{CF}=5.8 Hz), 162.62 (d, ¹*J*_{CF}=252.4 Hz), 184.36 ppm; ¹⁹F NMR (376

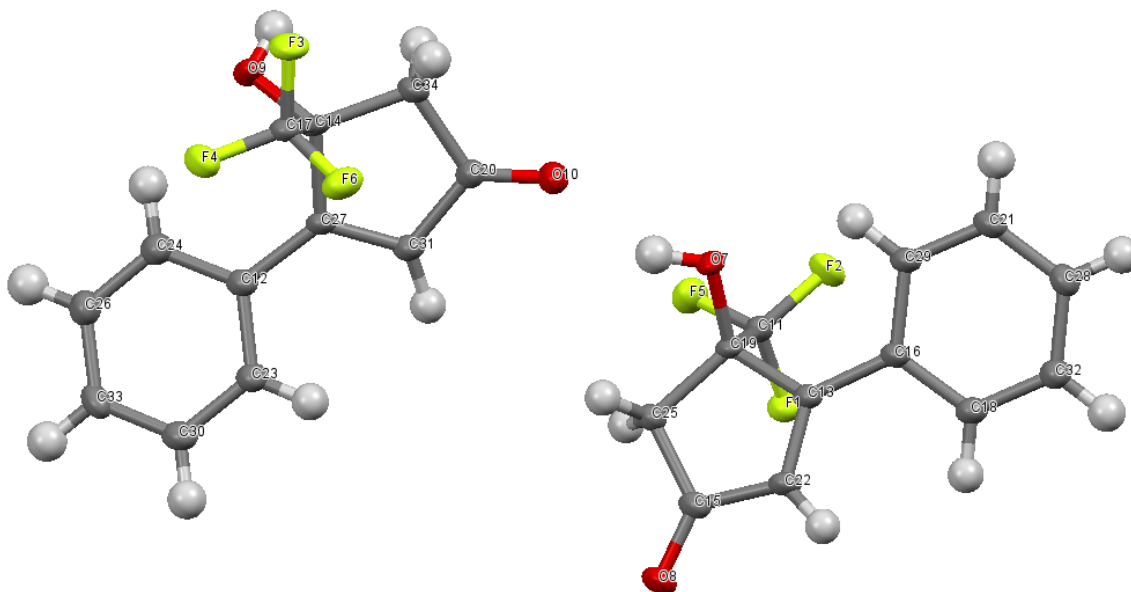
MHz, CDCl₃): δ -110.80 (m) ppm; IR (neat): 3074, 3002, 2962, 2928, 2195, 1674 cm⁻¹; MS (EI) m/z: 176 [M⁺]; HRMS (EI) calcd for C₁₁H₉FO: 176.0637, found 176.0638.



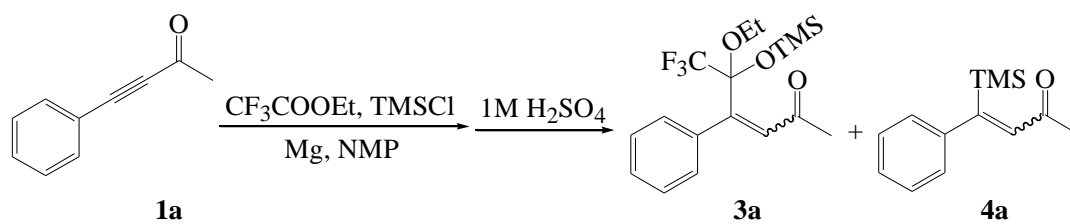
1-(2-Trifluoromethylphenyl)hept-2-yn-1-one (**7g**)^{1a,1b}

44% isolated yield (1126 mg), pale yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 0.93 (t, J =7.3 Hz, 3H), 1.45 (sext, J =7.3 Hz, 2H), 1.61 (quint, J =7.3 Hz, 2H), 2.45 (t, J =7.3 Hz, 2H), 7.60-7.67 (m, 2H), 7.76 (d, J =7.3 Hz, 1H), 8.00 (d, J =7.3 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 13.40, 18.87, 21.96, 29.55, 80.87, 98.40, 123.24 (q, ¹ J_{CF} =273.5 Hz), 127.09 (q, ³ J_{CF} =5.8 Hz), 128.22 (q, ² J_{CF} =32.8 Hz), 131.06, 131.64, 131.69, 137.62 (q, ³ J_{CF} =1.6 Hz), 177.96 ppm; ¹⁹F NMR (376 MHz, CDCl₃): δ -58.60 ppm; IR (neat): 3074, 2962, 2936, 2875, 2206, 1602 cm⁻¹; MS (EI) m/z: 254 [M⁺]; HRMS (EI) calcd for C₁₄H₁₃F₃O: 254.0918, found 254.0964.

X-Ray crystallography structures of compound **6a**



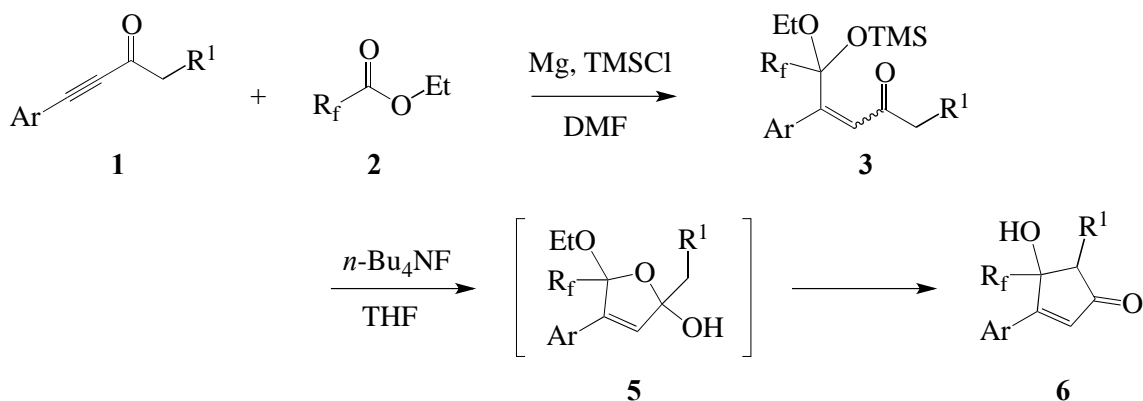
Crystal data for **6a**: C₁₂H₉O₂F₃, Mw = 242.06, triclinic, a = 9.1479(6) Å, b = 10.7709(8) Å, c = 11.3143(5) Å, α = 106.270(5)°, β = 92.281(5)°, γ = 106.304(6)°, V = 1018.60(12) Å³, T = 93 K, space group *P*-1 (#2), Z = 4, 8760 reflections collected, 3652 independent reflections [R(int) = 0.0441] which were used in all calculation. Crystallographic data for the structural analyses of **6a** in this paper has been deposited with the Cambridge Crystallographic Data Center as supplementary publication NO. CCDC-1489242.

Table S1. Investigation on equivalents of reagents

entry	CF_3COOEt (equiv)	TMSCl (equiv)	Mg (equiv)	GC yield (%)	
				3a	4a
1	12	4	3	42	11
2	11	4	3	73	13
3	10	4	3	58	7
4	9	4	3	40	7
5	8	4	3	32	28
6	11	5	3	36	13
7	11	3	3	66	5
8	11	2	3	36	6
9	11	4	4	24	7
10	11	4	2	37	14

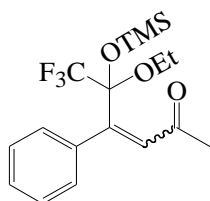
Reaction Conditions: **1a** (2 mmol), Mg (2-4 equiv), TMSCl (2-5 equiv), CF_3COOEt (8-12 equiv), 2 h, $-10\text{ }^\circ\text{C}$, NMP (20 mL), N_2 atmosphere.

General procedure for trifluoroacetylation of aromatic ynone **1**



Under nitrogen atmosphere, to a 100 mL four-necked flask, Mg turnings (3 equiv), DMF (5 mL), chlorotrimethylsilane (4 equiv) and **2** (11 equiv) were added in order, and then the mixture was stirred for 30 min at 25 °C. To this mixture, aromatic ynone **1** (2 mmol) in DMF (15 mL) was added dropwise within 30 min at 0 °C. After the addition, the reaction mixture was cooled to -10 °C and stirred for additional 2 hours. After the reaction, 1M sulfuric acid (50 mL) was added carefully, and this mixture was stirred for 30 minutes. The products were extracted with diethyl ether, and organic layers were combined, washed with saturated sodium bicarbonate solution and brine in sequence, and dried over anhydrous sodium sulfate. At this step, intermediate **3** could be isolated by flash column chromatography (hexane/ethyl acetate = 10:1). For the second step, under the N₂ atmosphere, to the crude product **3** in THF (15 mL), 1M tetrabutylammonium fluoride (1.1 equiv) in THF was added at -15 °C. Intermediate **5** could be isolated by flash column chromatography (hexane/ethyl acetate = 4:1) after 2 hours stirring and subsequent usual workup as shown above. For the product **6**, the reaction mixture was allowed to warm to room temperature gradually and after 18 hours stirring, water (50 mL) was added. The product was extracted with diethyl ether for three times, and organic layers were combined, washed with brine and dried over anhydrous sodium sulfate. The product **6** was purified by column chromatography on neutral silica gel (hexane/ethyl acetate = 3:1).

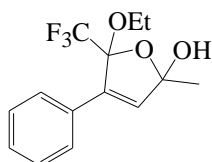
5-Ethoxy-6,6,6-trifluoro-4-phenyl-5-trimethylsiloxy-hex-3-en-2-one (**3a**, Z/E = 13:1)



70% isolated yield (504 mg), pale yellow oil. *Z*-isomer. ¹H NMR (400 MHz, CDCl₃): δ 0.25 (s, 9H), 1.35 (t, *J*=7.1 Hz, 3H), 2.36 (s, 3H), 3.68-3.80 (m, 2H), 6.19 (s, 1H), 7.30-7.35 (m, 5H) ppm; ¹³C NMR (100 MHz,

CDCl₃): δ 0.88, 14.08, 31.10, 58.97, 99.01 (q, $^2J_{CF}=32.0$ Hz), 122.14 (q, $^1J_{CF}=289.9$ Hz), 127.97, 128.14, 128.54, 137.25, 137.54, 138.14, 201.85 ppm; ^{19}F NMR (376 MHz, CDCl₃): δ -77.32 ppm; IR (neat): 3088, 3058, 2980, 2903, 1708, 1642 cm⁻¹; MS (EI) m/z: 360 [M⁺]; HRMS (EI) calcd for C₁₇H₂₃O₃F₃Si: 360.1369, found 360.1329.

5-Ethoxy-2-methyl-4-phenyl-5-trifluoromethyl-2,5-dihydrofuran-2-ol (5a, isomeric ratio = 5:1)

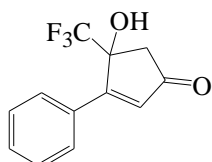


68% total isolated yield from **1a** (391 mg), white solid. Isomeric mixture of diastereomers.

Major isomer

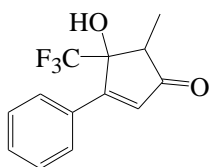
Melting point: 105.2-109.8 °C; ^1H NMR (400 MHz, CDCl₃): δ 1.35 (t, $J=7.1$ Hz, 3H), 1.73 (s, 3H), 3.13 (s, 1H), 3.54 (quint, $J=7.1$ Hz, 1H), 3.90 (quint, $J=7.1$ Hz, 1H), 6.48 (s, 1H), 7.37-7.38 (m, 3H), 7.61-7.63 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl₃): δ 14.75, 26.38, 59.18, 106.91, 108.42 (q, $^2J_{CF}=33.7$ Hz), 121.91 (q, $^1J_{CF}=286.7$ Hz), 127.05, 128.53, 129.33, 130.23, 134.21, 137.22 ppm; ^{19}F NMR (376 MHz, CDCl₃): δ -80.47 ppm; IR (KBr): 3469, 3089, 3028, 2989, 2918, 1647 cm⁻¹; MS (EI) m/z: 288 [M⁺]; HRMS (EI) calcd for C₁₄H₁₅O₃F₃: 288.0973, found 288.0929.

4-Hydroxy-3-phenyl-4-trifluoromethylcyclopent-2-en-1-one (6a)



65% total isolated yield (314 mg), white solid. Melting point: 117.6-119.1 °C; ^1H NMR (400 MHz, CDCl₃): δ 2.75 (d, $J=18.3$ Hz, 1H), 3.15 (d, $J=18.3$ Hz, 1H), 3.41 (s, 1H), 6.54 (s, 1H), 7.41-7.50 (m, 3H), 7.77 (d, $J=6.8$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl₃): δ 47.04, 81.35 (q, $^2J_{CF}=31.2$ Hz), 124.75 (q, $^1J_{CF}=285.5$ Hz), 128.54, 128.61, 130.96, 132.23, 134.05, 168.37, 201.22 ppm; ^{19}F NMR (376 MHz, CDCl₃): δ -77.68 ppm; IR (KBr): 3393, 3081, 2982, 2923, 1697, 1654 cm⁻¹; MS (EI) m/z: 242 [M⁺]; HRMS (EI) calcd for C₁₂H₉O₂F₃: 242.0555, found 242.0560.

4-Hydroxy-5-methyl-3-phenyl-4-trifluoromethylcyclopent-2-en-1-one (6b, isomeric ratio = 1:1)



54% total isolated yield (277 mg), pale yellow solid. Isomeric mixture of diastereomers.

Isomer (**6b-1**)

Melting point: 87.6-94.4 °C; ¹H NMR (400 MHz, CDCl₃): δ 1.37 (d, *J*=7.3 Hz, 3H), 2.98 (q, *J*=7.3 Hz, 1H), 3.70 (s, 1H), 6.61 (s, 1H), 7.43-7.48 (m, 3H), 7.80 (d, *J*=7.3 Hz, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 8.44, 54.88, 84.19 (q, ²*J*_{CF}=28.4 Hz), 124.49 (q, ¹*J*_{CF}=287.7 Hz), 128.47, 128.79, 130.68, 132.52, 132.76, 166.38, 202.05 ppm; ¹⁹F NMR (376 MHz, CDCl₃): δ -73.89 ppm;

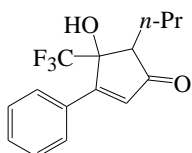
Isomer (**6b-2**)

Melting point: 143.0-147.4 °C; ¹H NMR (400 MHz, CDCl₃): δ 1.32 (d, *J*=7.3 Hz, 3H), 2.92 (q, *J*=7.3 Hz, 1H), 2.97 (s, 1H), 6.49 (s, 1H), 7.41-7.47 (m, 3H), 7.76 (d, *J*=7.3 Hz, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 10.73, 47.19, 82.54 (q, ²*J*_{CF}=30.1 Hz), 125.00 (q, ¹*J*_{CF}=285.2 Hz), 128.52, 128.57, 130.79, 132.54, 133.28, 167.37, 204.68 ppm; ¹⁹F NMR (376 MHz, CDCl₃): δ -77.85 ppm;

Isomers mixture (**6b**)

IR (KBr): 3215, 3000, 2951, 2901, 1691, 1648 cm⁻¹; MS (EI) *m/z*: 256 [M⁺]; HRMS (EI) calcd for C₁₃H₁₁O₂F₃: 256.0711, found 256.0747.

4-Hydroxy-3-phenyl-5-propyl-4-trifluoromethylcyclopent-2-en-1-one (**6c**, isomeric ratio = 5.5:1)

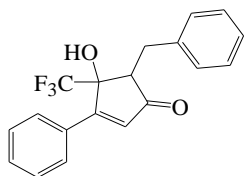


26% total isolated yield (147 mg), yellow solid. Isomeric mixture of diastereomers.

Isomers mixture (**6c**)

Melting point: 83.6-85.4 °C; ¹H NMR (400 MHz, CDCl₃): δ 0.97 (t, *J*=7.2 Hz, 0.46H), 0.99 (t, *J*=7.2 Hz, 2.54H), 1.52-1.94 (m, 4H), 2.79 (t, *J*=7.2 Hz, 0.15H), 2.89 (t, *J*=7.2 Hz, 0.85H), 3.50 (s, 0.15H), 3.93 (s, 0.85H), 6.48 (s, 0.15H), 6.57 (s, 0.85H), 7.39-7.46 (m, 3H), 7.75-7.80 (m, 2H) ppm; ¹⁹F NMR (376 MHz, CDCl₃): δ (Major) -73.95 ppm, (Minor) -77.71 ppm; IR (KBr): 3382, 3074, 2964, 2937, 2875, 1700, 1594 cm⁻¹; MS (EI) *m/z*: 284 [M⁺]; HRMS (EI) calcd for C₁₅H₁₅O₂F₃: 284.1024, found 284.0983.

5-Benzyl-4-hydroxy-3-phenyl-4-trifluoromethylcyclopent-2-en-1-one (**6d**, isomeric ratio = 2.3:1)

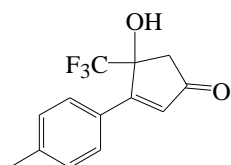


57% total isolated yield (378 mg), yellow viscous oil. Isomeric mixture of diastereomers.

Isomers mixture (ratio 4:1, after column chromatography) (**6d**)

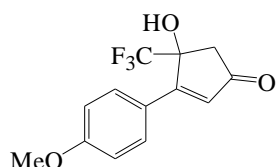
^1H NMR (400 MHz, CDCl_3): δ 2.82 (s, 0.80H), 2.84 (s, 0.20H), 2.87-2.93 (m, 0.20H), 2.98 (dd, $J=15.6$ Hz, $J=11.5$ Hz, 0.80H), 3.29-3.34 (m, 1.60H), 3.46-3.55 (m, 0.40H), 6.62 (s, 0.80H), 6.71 (s, 0.20H), 7.27-7.48 (m, 8H), 7.78-7.81 (m, 2H) ppm; ^{19}F NMR (376 MHz, CDCl_3): δ (Major) -77.87 ppm, (Minor) -73.49 ppm; IR (neat): 3258, 3067, 3032, 2945, 2878, 1689, 1648 cm^{-1} ; MS (EI) m/z : 332 [M^+]; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{15}\text{O}_2\text{F}_3$: 332.1024, found 332.0922.

4-Hydroxy-3-(4-methylphenyl)-4-trifluoromethylcyclopent-2-en-1-one (**6e**)



61% total isolated yield (312 mg), pale yellow solid. Melting point: 117.8-121.3 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 2.40 (s, 3H), 2.73 (d, $J=18.3$ Hz, 1H), 3.03 (s, 1H), 3.14 (d, $J=18.3$ Hz, 1H), 6.53 (s, 1H), 7.24 (d, $J=8.0$ Hz, 2H), 7.68 (d, $J=8.0$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 21.45, 47.19, 81.35 (q, $^2J_{\text{CF}}=31.2$ Hz), 124.81 (q, $^1J_{\text{CF}}=285.8$ Hz), 128.73, 129.29, 129.34, 132.80, 141.76, 168.65, 201.67 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -77.97 ppm; IR (KBr): 3257, 3036, 2993, 2935, 1683, 1613 cm^{-1} ; MS (EI) m/z : 256 [M^+]; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{11}\text{O}_2\text{F}_3$: 256.0711, found 256.0669.

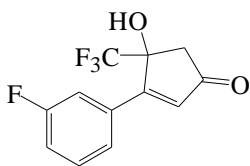
4-Hydroxy-3-(4-methoxyphenyl)-4-trifluoromethylcyclopent-2-en-1-one (**6f**)



55% total isolated yield (301 mg), pale yellow solid. Melting point: 137.0-142.7 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 2.73 (d, $J=18.3$ Hz, 1H), 3.11 (d, $J=18.3$ Hz, 1H), 3.86 (s, 3H), 3.97 (broad s, 1H), 6.47 (s, 1H), 6.93 (d, $J=8.9$ Hz, 2H), 7.83 (d, $J=8.9$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 46.74, 55.38, 81.35 (q, $^2J_{\text{CF}}=29.8$ Hz), 113.90, 124.69, 125.49 (q, $^1J_{\text{CF}}=285.8$ Hz), 130.72, 131.02, 161.41, 167.16, 200.77 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -77.98 ppm; IR (KBr): 3321, 3022, 2967, 2937, 2842, 1696, 1607 cm^{-1} ; MS

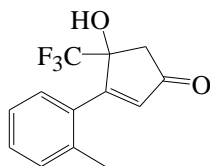
(EI) m/z: 272 [M⁺]; HRMS (EI) calcd for C₁₃H₁₁O₃F₃: 272.0660, found 272.0666.

3-(3-Fluorophenyl)-4-hydroxy-4-trifluoromethylcyclopent-2-en-1-one (6g)



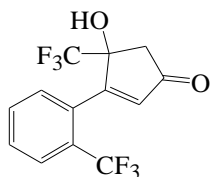
63% total isolated yield (329 mg), pale yellow solid. Melting point: 105.0-107.4 °C; ¹H NMR (400 MHz, CDCl₃): δ 2.77 (d, *J*=18.5 Hz, 1H), 3.14 (d, *J*=18.5 Hz, 1H), 3.88 (s, 1H), 6.54 (s, 1H), 7.15-7.20 (m, 1H), 7.40 (td, *J*=8.0 Hz, *J*=5.8 Hz, 1H), 7.54 (d, *J*=8.0 Hz, 1H), 7.56-7.59 (m, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 47.03, 81.26 (q, ²*J*_{CF}=31.2 Hz), 115.72 (d, ²*J*_{CF}=23.2 Hz), 117.87 (d, ²*J*_{CF}=21.5 Hz), 124.30 (d, ⁴*J*_{CF}=2.5 Hz), 124.64 (q, ¹*J*_{CF}=285.5 Hz), 130.21 (d, ³*J*_{CF}=8.3 Hz), 134.13 (d, ³*J*_{CF}=8.3 Hz), 134.73, 162.47 (d, ¹*J*_{CF}=247.5 Hz), 166.93, 201.00 ppm; ¹⁹F NMR (376 MHz, CDCl₃): δ -78.15, -111.97 (m) ppm; IR (KBr): 3335, 3124, 3096, 2980, 1699, 1576 cm⁻¹; MS (EI) m/z: 260 [M⁺]; HRMS (EI) calcd for C₁₂H₈O₂F₄: 260.0460, found 260.0423.

4-Hydroxy-3-(2-methylphenyl)-4-trifluoromethylcyclopent-2-en-1-one (6h)



70% total isolated yield (357 mg), pale yellow solid. Melting point: 112.0-113.5 °C; ¹H NMR (400 MHz, CDCl₃): δ 2.24 (s, 3H), 2.72 (d, *J*=18.5 Hz, 1H), 3.01 (d, *J*=18.5 Hz, 1H), 3.16 (s, 1H), 6.25 (s, 1H), 7.18-7.31 (m, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 19.83, 44.96, 81.33 (q, ²*J*_{CF}=30.3 Hz), 124.72 (q, ¹*J*_{CF}=285.6 Hz), 125.56, 127.45, 129.47, 130.90, 131.59, 135.40, 137.65, 168.41, 201.26 ppm; ¹⁹F NMR (376 MHz, CDCl₃): δ -78.29 ppm; IR (KBr): 3335, 3124, 3096, 2980, 1699, 1576 cm⁻¹; MS (EI) m/z: 256 [M⁺]; HRMS (EI) calcd for C₁₃H₁₁O₂F₃: 256.0711, found 256.0688.

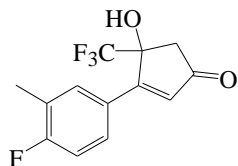
4-Hydroxy-4-trifluoromethyl-3-(2-trifluoromethylphenyl)cyclopent-2-en-1-one (6i)



76% total isolated yield (469 mg), pale yellow solid. Melting point: 94.8-97.0 °C; ¹H NMR (400 MHz, CDCl₃): δ 2.76 (d, *J*=18.5 Hz, 1H), 3.10 (d, *J*=18.5 Hz, 1H), 3.90 (s, 1H), 6.40 (s, 1H), 7.53-7.62 (m, 2H),

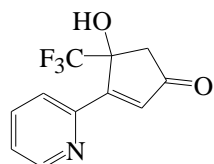
7.72 (d, $J=7.8$ Hz, 1H), 7.78 (d, $J=7.8$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 45.67, 81.45 (q, $^2J_{\text{CF}}=31.2$ Hz), 123.56 (q, $^1J_{\text{CF}}=273.7$ Hz), 124.45 (q, $^1J_{\text{CF}}=285.0$ Hz), 126.83 (q, $^3J_{\text{CF}}=5.2$ Hz), 128.26 (q, $^2J_{\text{CF}}=30.1$ Hz), 129.59, 129.70, 130.39 (m), 131.26, 138.70 (m), 165.39, 201.46 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -56.76, -78.19 ppm; IR (KBr): 3336, 3093, 2994, 2948, 1699, 1616 cm^{-1} ; MS (EI) m/z : 310 [M^+]; HRMS (EI) calcd for $\text{C}_{13}\text{H}_8\text{O}_2\text{F}_6$: 310.0428, found 310.0478.

3-(4-Fluoro-3-methylphenyl)-4-hydroxy-4-trifluoromethylcyclopent-2-en-1-one (6j)



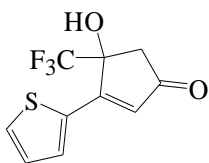
62% total isolated yield (339 mg), pale yellow solid. Melting point: 103.6-105.1 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 2.31 (s, 3H), 2.75 (d, $J=18.3$ Hz, 1H), 3.12 (d, $J=18.3$ Hz, 1H), 4.02 (s, 1H), 6.48 (s, 1H), 7.05 (t, $J=8.8$ Hz, 1H), 7.65-7.69 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 14.57 (d, $^3J_{\text{CF}}=3.3$ Hz), 47.13, 81.29 (q, $^2J_{\text{CF}}=31.2$ Hz), 115.39 (d, $^2J_{\text{CF}}=23.2$ Hz), 124.72 (q, $^1J_{\text{CF}}=285.5$ Hz), 125.47 (d, $^2J_{\text{CF}}=17.4$ Hz), 128.05 (d, $^4J_{\text{CF}}=4.1$ Hz), 128.37 (d, $^3J_{\text{CF}}=7.5$ Hz), 132.18 (d, $^3J_{\text{CF}}=5.8$ Hz), 133.30, 163.02 (d, $^1J_{\text{CF}}=251.6$ Hz), 167.66, 201.34 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -78.04, -112.29 (m) ppm; IR (KBr): 3371, 3084, 2988, 2933, 1700, 1612 cm^{-1} ; MS (EI) m/z : 274 [M^+]; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{10}\text{O}_2\text{F}_4$: 274.0617, found 274.0572.

4-Hydroxy-3-(2-pyridyl)-4-trifluoromethylcyclopent-2-en-1-one (6k)



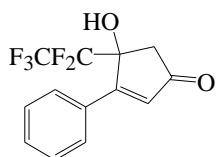
22% total isolated yield (107 mg), yellow solid. Melting point: 67.4-71.0 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 2.86 (d, $J=18.5$ Hz, 1H), 3.08 (d, $J=18.5$ Hz, 1H), 6.68 (s, 1H), 7.44 (dd, $J=7.8$ Hz, $J=4.9$ Hz, 1H), 7.71 (d, $J=7.8$ Hz, 1H), 7.88 (t, $J=7.8$ Hz), 8.16 (broad s, 1H), 8.64 (d, $J=4.9$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 46.46, 81.51 (q, $^2J_{\text{CF}}=30.9$ Hz), 123.32, 125.22, 128.15 (q, $^1J_{\text{CF}}=287.2$ Hz), 134.53, 137.91, 148.26, 152.83, 162.36, 201.11 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -78.76 ppm; IR (KBr): 3407, 3128, 3070, 2989, 2937, 1735, 1611 cm^{-1} ; MS (EI) m/z : 243 [M^+]; HRMS (EI) calcd for $\text{C}_{11}\text{H}_8\text{NO}_2\text{F}_3$: 243.0507, found 243.0464.

4-Hydroxy-3-(2-thienyl)-4-trifluoromethylcyclopent-2-en-1-one (6l)



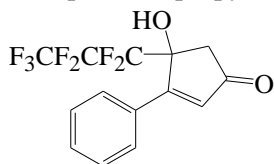
34% total isolated yield (168 mg), brown solid. Melting point: 104.7-105.9 °C; ^1H NMR (400 MHz, CDCl_3): δ 2.74 (d, $J=18.0$ Hz, 1H), 3.10 (d, $J=18.0$ Hz, 1H), 4.03 (s, 1H), 6.49 (s, 1H), 7.15 (dd, $J=5.1$ Hz, $J=3.9$ Hz, 1H), 7.59 (d, $J=5.1$ Hz, 1H), 7.82 (d, $J=3.9$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 47.15, 80.86 (q, $^2J_{\text{CF}}=31.5$ Hz), 124.62 (q, $^1J_{\text{CF}}=285.5$ Hz), 128.73, 129.95, 131.62, 133.09, 133.91, 161.19, 200.24 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -78.38 ppm; IR (KBr): 3259, 3121, 2988, 2935, 1699, 1585 cm^{-1} ; MS (EI) m/z : 248 [M^+]; HRMS (EI) calcd for $\text{C}_{10}\text{H}_7\text{O}_2\text{F}_3\text{S}$: 248.0119, found 248.0084.

4-Hydroxy-4-pentafluoroethyl-3-phenylcyclopent-2-en-1-one (6o)



41% total isolated yield (241 mg), yellow solid. Melting point: 99.7-101.5 °C; ^1H NMR (400 MHz, CDCl_3): δ 2.77 (d, $J=18.5$ Hz, 1H), 3.23 (d, $J=18.5$ Hz, 1H), 4.22 (s, 1H), 6.49 (s, 1H), 7.40-7.46 (m, 3H), 7.77 (d, $J=7.3$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 47.40 (dd, $^3J_{\text{CF}}=5.0$ Hz, $^3J_{\text{CF}}=2.5$ Hz), 81.75 (t, $^2J_{\text{CF}}=24.4$ Hz), 114.19 (tq, $^1J_{\text{CF}}=261.5$ Hz, $^2J_{\text{CF}}=35.6$ Hz), 118.84 (qt, $^1J_{\text{CF}}=288.0$ Hz, $^2J_{\text{CF}}=35.6$ Hz), 128.46, 128.55, 130.88, 132.98, 134.07, 169.64, 201.60 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -78.95, -119.91 (d, $^2J_{\text{FF}}=275.8$ Hz), -120.80 (d, $^2J_{\text{FF}}=275.8$ Hz) ppm; IR (KBr): 3361, 3061, 3020, 2937, 1701, 1596 cm^{-1} ; MS (EI) m/z : 292 [M^+]; HRMS (EI) calcd for $\text{C}_{13}\text{H}_9\text{O}_2\text{F}_5$: 292.0523, found 292.0514.

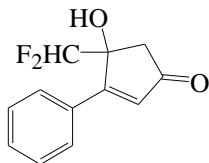
4-Heptafluoropropyl-4-hydroxy-3-phenylcyclopent-2-en-1-one (6p)



25% total isolated yield (169 mg), yellow solid. Melting point: 122.5-123.3 °C; ^1H NMR (400 MHz, CDCl_3): δ 2.78 (d, $J=18.5$ Hz, 1H), 3.25 (d, $J=18.5$ Hz, 1H), 3.75 (s, 1H), 6.50 (s, 1H), 7.40-7.47 (m, 3H), 7.74 (d, $J=7.3$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 47.28 (dd, $^3J_{\text{CF}}=5.8$ Hz, $^3J_{\text{CF}}=3.3$ Hz), 82.54 (t, $^2J_{\text{CF}}=24.8$ Hz), 109.87 (t.sext, $^1J_{\text{CF}}=269.0$ Hz, $^2J_{\text{CF}}=37.1$ Hz), 115.80 (tt, $^1J_{\text{CF}}=260.7$ Hz, $^2J_{\text{CF}}=29.4$ Hz), 117.53 (tq, $^1J_{\text{CF}}=285.5$ Hz, $^2J_{\text{CF}}=34.8$ Hz), 128.43, 128.55, 130.83, 133.13, 134.17, 169.96, 201.80 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -81.07, -116.10 (d, $^2J_{\text{FF}}=282.3$ Hz), -117.49 (d, $^2J_{\text{FF}}=282.3$ Hz), -122.66 (d,

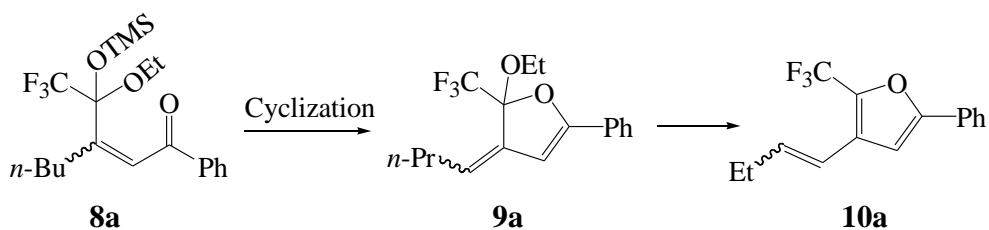
$^2J_{\text{FF}}=290.3$ Hz), -123.51 (d, $^2J_{\text{FF}}=290.3$ Hz) ppm; IR (KBr): 3209, 3089, 3019, 2947, 1684, 1606 cm^{-1} ; MS (EI) m/z: 342 [M^+]; HRMS (EI) calcd for $\text{C}_{14}\text{H}_9\text{O}_2\text{F}_7$: 342.0491, found 342.0489.

4-Difluoromethyl-4-hydroxy-3-phenylcyclopent-2-en-1-one (6g)



27% total isolated yield (120 mg), yellow solid. Melting point: 50.1-53.0 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 2.57 (d, $J=18.5$ Hz, 1H), 3.13 (d, $J=18.5$ Hz, 1H), 4.06 (broad s, 1H), 6.03 (dd, $^2J_{\text{HF}}=56.8$ Hz, $^2J_{\text{HF}}=54.9$ Hz, 1H), 6.49 (s, 1H), 7.41-7.49 (m, 3H), 7.81-7.84 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 44.59, 81.01 (t, $^2J_{\text{CF}}=24.8$ Hz), 107.89, 114.37 (t, $^1J_{\text{CF}}=247.9$ Hz), 128.44, 129.02, 131.20, 131.96, 169.46, 203.56 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -127.11 (dd, $^2J_{\text{FF}}=289.0$ Hz, $^2J_{\text{HF}}=54.9$ Hz, 1F), -132.92 (dd, $^2J_{\text{FF}}=289.0$ Hz, $^2J_{\text{HF}}=56.8$ Hz, 1F) ppm; IR (KBr): 3354, 3078, 3026, 2979, 2935, 1683, 1597 cm^{-1} ; MS (EI) m/z: 224 [M^+]; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{10}\text{O}_2\text{F}_2$: 224.0649, found 224.0620.

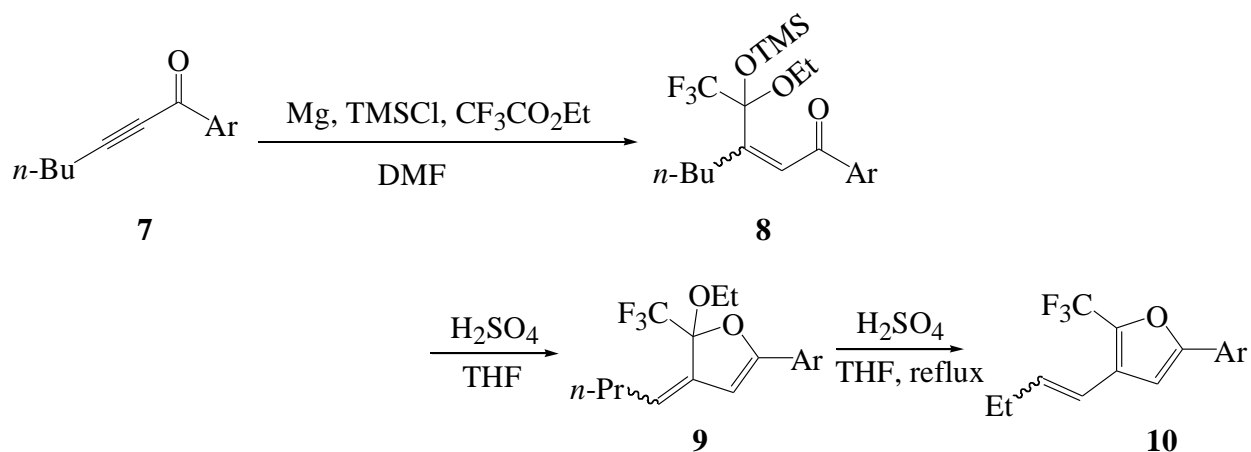
Table S2. Investigation on cyclization reaction conditions of 8



entry	reagent	solvent ^a	temp (°C)	time	isolated yield (%)	
					9a	10a
1 ^b	1.1 equiv <i>n</i> -Bu ₄ NF	THF (7.5)	-15	2 h	0	0
2 ^c	1.1 equiv <i>n</i> -Bu ₄ NF	THF (7.5)	-15 to rt	24 h	34	0
3	CF ₃ COOH	CF ₃ COOH (10)	rt	15 h	complex	
4	10 equiv H ₂ SO ₄	THF (2.5)	rt	3 h	91 ^d	0
5	10 equiv TsOH·H ₂ O	THF (20)	6	6 h	0	0
6	10 equiv H ₂ SO ₄	THF (5)	70	16 h	^e	trace
7	10 equiv H ₂ SO ₄	THF (3)	70	8 h	trace	62
8	10 equiv H ₂ SO ₄	THF (2)	70	3 h	trace	74
9	10 equiv H ₂ SO ₄	THF (1.5)	70	40 min	0	75 ^f
10	10 equiv H ₂ SO ₄	THF (1)	70	10 min	0	75 ^f
11	10 equiv H ₂ SO ₄	no solvent	70	-	complex	
12	10 equiv H ₂ SO ₄	THF (1.5)	50	8 h	trace	66
13	5 equiv H ₂ SO ₄	THF (1.5)	70	10 h	trace	40

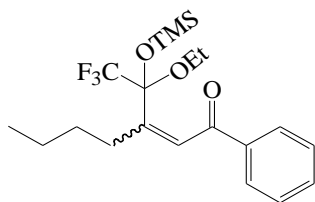
Reaction Conditions: **8a** (0.5 mmol), N₂ atmosphere. ^a Concentration in parentheses (mmol/mL). ^b 2.0 mmol of **8a**. ^c 1.2 mmol of **8a**. ^d Isomers ratio was determined by gas chromatography, 14:1. Total yield of **9a** from **7a** is 78%. ^e Main product was **9a**. ^f Isomers ratio was determined by gas chromatography, *E/Z* = 14:1.

General procedure for trifluoroacetylation of alkynyl ketones **7**



Under the nitrogen atmosphere, to a 100 mL four-necked flask, Mg turnings (3 equiv), DMF (5 mL), chlorotrimethylsilane (4 equiv) and ethyl trifluoroacetate (11 equiv) were added in order, and then the mixture was stirred for 30 min at 25 °C. To this mixture, alkynyl ketone **1** (2 mmol) in DMF (15 mL) was added dropwise within 30 min at 0 °C. After the addition, the reaction mixture was cooled to -10 °C and stirred for additional 2 hours. Then, 1M sulfuric acid (50 mL) was added carefully, and this mixture was stirred for 30 minutes. The products were extracted with diethyl ether, and combined organic layers were washed by saturated sodium bicarbonate solution and brine in sequence and dried over anhydrous sodium sulfate. At this step, intermediate **8** could be isolated by flash column chromatography (hexane/ethyl acetate = 10:1). For the second step, under the nitrogen atmosphere, to the crude products in THF (1.5 M), conc. sulfuric acid (10 equiv) was added carefully. Trifluoroacetylated diene **9** could be isolated by flash chromatography (hexane/acetone = 100:1) after 14 hours stirring, subsequent addition of saturated aqueous sodium bicarbonate, extraction with diethyl ether 3 times, washing with brine and dryness over anhydrous sodium sulfate. For synthesis of furan **10**, the reaction mixture of **8** shown above was stirred at 70 °C for 0.5 - 3 hours. After the reaction, saturated aqueous sodium bicarbonate was added, and the product was extracted with diethyl ether 3 times, and combined organic layers were washed with brine and dried over anhydrous sodium sulfate. The product furan **10** was purified by column chromatography on neutral silica gel (hexane/acetone = 100:1).

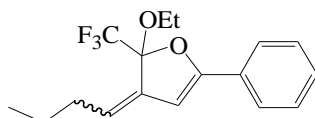
3-(1-Ethoxy-2,2,2-trifluoro-1-trimethylsiloxyethyl)-1-phenylhept-2-en-1-one (8a, Z/E = 18:1)



90% isolated yield (720 mg), pale yellow oil.

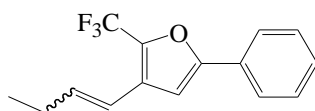
Z-isomer. ^1H NMR (400 MHz, CDCl_3): δ -0.17 (s, 9H), 0.97 (t, $J=7.3$ Hz, 3H), 1.20 (t, $J=7.3$ Hz, 3H), 1.39-1.69 (m, 4H), 2.10-2.29 (m, 2H), 3.39-3.54 (m, 2H), 6.25 (s, 1H), 7.44 (t, $J=7.3$ Hz, 2H), 7.53 (t, $J=7.3$ Hz, 1H), 7.94 (d, $J=7.3$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 0.33, 13.96, 14.50, 22.68, 29.59, 30.89, 58.48, 99.06 (q, $^2J_{\text{CF}}=32.0$ Hz), 122.49 (q, $^1J_{\text{CF}}=290.2$ Hz), 128.17, 129.44, 131.79, 132.90, 136.44, 140.64, 195.45 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -77.47 ppm; IR (neat): 3061, 2960, 2934, 2874, 1676, 1583 cm^{-1} ; MS (EI) m/z : 402 [M^+]; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{29}\text{O}_3\text{F}_3\text{Si}$: 402.1838, found 402.1854.

3-Butylidene-2-ethoxy-5-phenyl-2-trifluoromethyl-2,3-dihydrofuran (9a, isomers ratio = 14:1)



78% total isolated yield (487 mg), colorless oil. Major isomer. ^1H NMR (400 MHz, CDCl_3): δ 0.96 (t, $J=7.4$ Hz, 3H), 1.25 (t, $J=7.4$ Hz, 3H), 1.52 (sext, $J=7.4$ Hz, 2H), 2.26 (q, $J=7.4$ Hz, 2H), 3.51-3.63 (m, 2H), 5.61 (t, $J=7.4$ Hz, 1H), 6.23 (s, 1H), 7.36-7.42 (m, 3H), 7.68 (d, $J=7.4$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 13.66, 15.10, 22.60, 31.80, 59.13, 99.00, 105.86 (q, $^2J_{\text{CF}}=32.8$ Hz), 121.52 (q, $^1J_{\text{CF}}=284.4$ Hz), 124.92, 125.27, 128.54, 129.17, 129.56, 134.40, 159.17 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -85.17 ppm; IR (neat): 3059, 2962, 2933, 2873, 1659 cm^{-1} ; MS (EI) m/z : 312 [M^+]; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{19}\text{O}_2\text{F}_3$: 312.1337, found 312.1306.

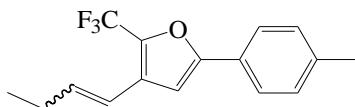
3-(1-Butenyl)-5-phenyl-2-trifluoromethylfuran (10a, E/Z = 14:1)



64% total isolated yield (338 mg), colorless oil. E-isomer. ^1H NMR (400 MHz, CDCl_3): δ 1.12 (t, $J=7.3$ Hz, 3H), 2.27 (quint, $J=7.3$ Hz, 2H), 6.25 (td, $J=7.3$ Hz, $J=15.8$ Hz, 1H), 6.45 (d, $J=15.8$ Hz, 1H), 6.82 (s, 1H), 7.35 (t, $J=7.3$ Hz, 1H), 7.43 (t, $J=7.3$ Hz, 2H), 7.72 (d, $J=7.3$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 13.26, 26.07, 103.51, 116.44, 120.27 (q, $^1J_{\text{CF}}=267.3$ Hz), 124.47, 127.43 (q, $^3J_{\text{CF}}=2.5$ Hz), 128.76, 128.77,

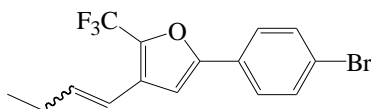
129.23, 134.86 (q, $^2J_{CF}=40.8$ Hz), 137.35, 155.13 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -61.10 ppm; IR (neat): 3055, 2967, 2936, 2876, 1664 cm^{-1} ; MS (EI) m/z : 266 [M^+]; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{13}\text{OF}_3$: 266.0919, found 266.0944.

3-(1-Butenyl)- 5-*p*-tolyl-2-trifluoromethylfuran (**10b**, *E/Z* = 13:1)



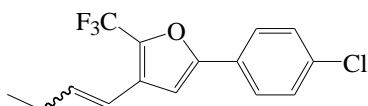
60% total isolated yield (337 mg), colorless oil. *E*-isomer. ^1H NMR (400 MHz, CDCl_3): δ 1.11 (t, $J=7.5$ Hz, 3H), 2.26 (quint, $J=7.5$ Hz, 2H), 2.39 (s, 3H), 6.23 (dt, $J=17.3$ Hz, $J=7.5$ Hz, 1H), 6.44 (d, $J=17.3$ Hz, 1H), 6.76 (s, 1H), 7.22 (d, $J=7.5$ Hz, 2H), 7.60 (d, $J=7.5$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 13.29, 21.32, 26.07, 102.82, 116.53, 120.31 (q, $^1J_{CF}=267.3$ Hz), 124.44, 126.56, 127.37 (q, $^3J_{CF}=2.5$ Hz), 129.46, 134.53 (q, $^2J_{CF}=40.3$ Hz), 137.18, 138.83, 155.38 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -61.04 ppm; IR (neat): 3029, 2967, 2935, 2876, 1664 cm^{-1} ; MS (EI) m/z : 280 [M^+]; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{15}\text{OF}_3$: 280.1075, found 280.1049.

5-(4-Bromophenyl)- 3-(1-Butenyl)-2-trifluoromethylfuran (**10c**, *E/Z* = 13:1)



59% total isolated yield (405 mg), colorless oil. *E*-isomer. ^1H NMR (400 MHz, CDCl_3): δ 1.10 (t, $J=7.4$ Hz, 3H), 2.26 (quint, $J=7.4$ Hz, 2H), 6.23 (dt, $J=15.8$ Hz, $J=7.4$ Hz, 1H), 6.42 (d, $J=15.8$ Hz, 1H), 6.81 (s, 1H), 7.53-7.57 (m, 4H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 13.24, 26.06, 104.05, 116.24, 120.13 (q, $^1J_{CF}=268.1$ Hz), 122.82, 125.92, 127.51 (q, $^3J_{CF}=2.5$ Hz), 128.11, 131.99, 135.11 (q, $^2J_{CF}=40.8$ Hz), 137.63, 154.01 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -61.18 ppm; IR (neat): 3055, 2967, 2935, 2876, 1664 cm^{-1} ; MS (EI) m/z : 344 [M^+]; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{12}\text{OF}_3\text{Br}$: 344.0024, found 344.0024.

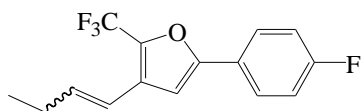
3-(1-Butenyl)-5-(4-chlorophenyl)-2-trifluoromethylfuran (**10d**, *E/Z* = 13:1)



59% total isolated yield (354 mg), colorless oil. *E*-isomer. ^1H NMR (400 MHz, CDCl_3): δ 1.11 (t, $J=7.5$ Hz, 3H), 2.26 (quint, $J=7.5$ Hz, 2H), 6.23 (dt, $J=15.8$ Hz, $J=7.5$ Hz, 1H), 6.42 (d, $J=15.8$ Hz, 1H), 6.80 (s, 1H), 7.39 (d, $J=7.5$ Hz, 2H), 7.62 (d, $J=7.5$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 13.25, 26.07, 104.00,

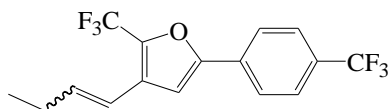
116.29, 120.16 (q, $^1J_{\text{CF}}=267.9$ Hz), 125.72, 127.51 (q, $^3J_{\text{CF}}=2.5$ Hz), 127.74, 129.07, 134.67, 135.13 (q, $^2J_{\text{CF}}=40.6$ Hz), 137.60, 154.03 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -61.19 ppm; IR (neat): 3054, 2968, 2936, 2877, 1663 cm^{-1} ; MS (EI) m/z : 300 [M^+]; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{12}\text{OF}_3\text{Cl}$: 300.0529, found 300.0558.

3-(1-Butenyl)-5-(4-fluorophenyl)-2-trifluoromethylfuran (**10e**, $E/Z > 25:1$)



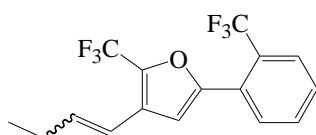
61% total isolated yield (348 mg), colorless oil. *E*-isomer. ^1H NMR (400 MHz, CDCl_3): δ 1.10 (t, $J=7.4$ Hz, 3H), 2.26 (quint, $J=7.4$ Hz, 2H), 6.22 (dt, $J=15.6$ Hz, $J=7.4$ Hz, 1H), 6.43 (d, $J=15.6$ Hz, 1H), 6.75 (s, 1H), 7.11 (t, $J=8.7$ Hz, 2H), 7.67 (dd, $J=8.7$ Hz, $J=5.4$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 13.26, 26.07, 103.25, 115.92 (d, $^2J_{\text{CF}}=22.3$ Hz), 116.34, 120.19 (q, $^1J_{\text{CF}}=267.3$ Hz), 125.56, 126.40 (d, $^3J_{\text{CF}}=7.4$ Hz), 127.45, 134.85 (q, $^2J_{\text{CF}}=40.6$ Hz), 137.47, 154.22, 162.94 (d, $^1J_{\text{CF}}=249.1$ Hz) ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -61.16, -112.03 (m) ppm; IR (neat): 3053, 2967, 2934, 2877, 1664 cm^{-1} ; MS (EI) m/z : 284 [M^+]; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{12}\text{OF}_4$: 284.0824, found 284.0819.

3-(1-Butenyl)-2-trifluoromethyl-5-(4-trifluoromethylphenyl)furan (**10f**, $E/Z = 15:1$)



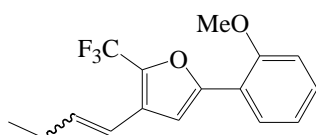
55% total isolated yield (367 mg), colorless oil. *E*-isomer. ^1H NMR (400 MHz, CDCl_3): δ 1.12 (t, $J=7.3$ Hz, 3H), 2.27 (quint, $J=7.3$ Hz, 2H), 6.26 (dt, $J=15.8$ Hz, $J=7.3$ Hz, 1H), 6.43 (d, $J=15.8$ Hz, 1H), 6.92 (s, 1H), 7.66 (d, $J=8.6$ Hz, 2H), 7.78 (d, $J=8.6$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 13.19, 26.08, 105.37, 116.10, 120.07 (q, $^1J_{\text{CF}}=268.2$ Hz), 123.94 (q, $^1J_{\text{CF}}=272.3$ Hz), 124.57, 125.83 (q, $^3J_{\text{CF}}=3.9$ Hz), 127.59 (q, $^3J_{\text{CF}}=2.5$ Hz), 130.47 (q, $^2J_{\text{CF}}=32.6$ Hz), 132.35, 135.74 (q, $^2J_{\text{CF}}=40.8$ Hz), 137.91, 153.48 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -61.33, -62.95 ppm; IR (neat): 3056, 2969, 2938, 2879, 1664 cm^{-1} ; MS (EI) m/z : 334 [M^+]; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{12}\text{OF}_6$: 334.0792, found 334.0754.

3-(1-Butenyl)-2-trifluoromethyl-5-(2-trifluoromethylphenyl)furan (**10g**, $E/Z = 20:1$)



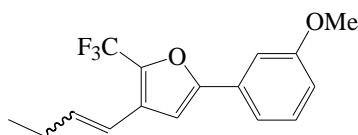
41% total isolated yield (276 mg), colorless oil. *E*-isomer. ^1H NMR (400 MHz, CDCl_3): δ 1.11 (t, $J=7.6$ Hz, 3H), 2.26 (quint, $J=7.6$ Hz, 2H), 6.24 (dt, $J=15.8$ Hz, $J=7.6$ Hz, 1H), 6.44 (d, $J=15.8$ Hz, 1H), 6.84 (s, 1H), 7.51 (t, $J=7.6$ Hz, 1H), 7.62 (t, $J=7.6$ Hz, 1H), 7.75 (d, $J=7.6$ Hz, 1H), 7.79 (d, $J=7.6$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 13.20, 26.08, 108.71, 116.20, 120.10 (q, $^1J_{\text{CF}}=268.1$ Hz), 123.72 (q, $^1J_{\text{CF}}=273.9$ Hz), 126.73 (q, $^3J_{\text{CF}}=5.5$ Hz), 127.13 (m), 127.46 (q, $^2J_{\text{CF}}=31.4$ Hz), 128.07, 129.06, 130.42, 131.85, 135.80 (q, $^2J_{\text{CF}}=40.8$ Hz), 137.66, 151.76 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -59.74, -61.42 ppm; IR (neat): 3056, 2968, 2936, 2877, 1664 cm^{-1} ; MS (EI) m/z : 334 [M^+]; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{12}\text{OF}_6$: 334.0792, found 334.0759.

3-(1-Butenyl)-5-(2-methoxyphenyl)-2-trifluoromethylfuran (**10h**, *E/Z* = 9:1)



54 % total isolated yield (319 mg), pale yellow solid. *E*-isomer. Melting point: 30.2-31.8 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 1.12 (t, $J=7.3$ Hz, 3H), 2.26 (quint, $J=7.3$ Hz, 2H), 3.98 (s, 3H), 6.27 (dt, $J=15.6$ Hz, $J=7.3$ Hz, 1H), 6.45 (d, $J=15.6$ Hz, 1H), 6.99 (d, $J=7.3$ Hz, 1H), 7.04 (t, $J=7.3$ Hz, 1H), 7.09 (s, 1H), 7.32 (t, $J=7.3$ Hz, 1H), 7.86 (d, $J=7.3$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 13.33, 26.09, 55.46, 108.31, 111.05, 116.75, 118.26, 120.49 (q, $^1J_{\text{CF}}=267.3$ Hz), 120.80, 126.66, 127.31 (q, $^3J_{\text{CF}}=2.5$ Hz), 129.54, 133.90 (q, $^2J_{\text{CF}}=40.4$ Hz), 136.96, 151.49, 156.04 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -60.99 ppm; IR (neat): 3054, 2966, 2936, 2841, 1664 cm^{-1} ; MS (EI) m/z : 296 [M^+]; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{15}\text{O}_2\text{F}_3$: 296.1024, found 296.1049.

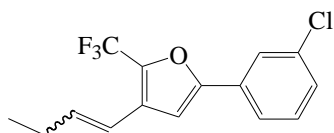
3-(1-Butenyl)-5-(3-methoxyphenyl)-2-trifluoromethylfuran (**10i**, *E/Z* = 13:1)



45% total isolated yield (266 mg), colorless oil. *E*-isomer. ^1H NMR (400 MHz, CDCl_3): δ 1.11 (t, $J=7.4$ Hz, 3H), 2.26 (quint, $J=7.4$ Hz, 2H), 3.87 (s, 3H), 6.24 (dt, $J=16.1$ Hz, $J=7.4$ Hz, 1H), 6.44 (d, $J=16.1$ Hz, 1H), 6.81 (s, 1H), 6.90 (ddd, $J=7.8$ Hz, $J=2.3$ Hz, $J=1.5$ Hz, 1H), 7.23 (dd, $J=2.3$ Hz, $J=1.5$ Hz, 1H), 7.29 (dt, $J=7.8$ Hz, $J=1.5$ Hz, 1H), 7.32 (t, $J=7.8$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 13.27, 26.07, 55.34, 103.85, 109.81, 114.62, 116.43, 117.05, 120.25 (q, $^1J_{\text{CF}}=266.6$ Hz), 127.41 (q, $^3J_{\text{CF}}=2.5$ Hz), 129.90, 130.50,

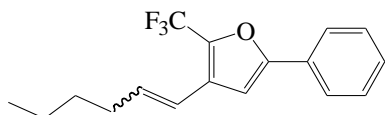
134.89 (q, $^2J_{\text{CF}}=40.8$ Hz), 137.38, 154.96 (q, $^4J_{\text{CF}}=1.7$ Hz), 159.95 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -61.12 ppm; IR (neat): 3119, 3056, 3005, 2966, 2838, 1663 cm^{-1} ; MS (EI) m/z : 296 [M^+]; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{15}\text{O}_2\text{F}_3$: 296.1024, found 296.1049.

3-(1-Butenyl)-5-(3-chlorophenyl)-2-trifluoromethylfuran (**10j**, $E/Z = 13:1$)



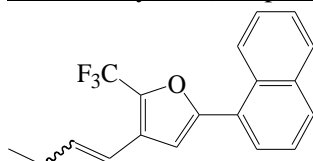
63% total isolated yield (376 mg), colorless oil. *E*-isomer. ^1H NMR (400 MHz, CDCl_3): δ 1.11 (t, $J=7.4$ Hz, 3H), 2.26 (quint, $J=7.4$ Hz, 2H), 6.24 (dt, $J=15.6$ Hz, $J=7.4$ Hz, 1H), 6.42 (d, $J=15.6$ Hz, 1H), 6.83 (s, 1H), 7.31 (dt, $J=7.8$ Hz, $J=1.6$ Hz, 1H), 7.34 (t, $J=7.8$ Hz, 1H), 7.57 (dt, $J=7.8$ Hz, $J=1.6$ Hz, 1H), 7.68 (t, $J=1.6$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 13.21, 26.07, 104.52, 116.18, 120.09 (q, $^1J_{\text{CF}}=268.1$ Hz), 122.49, 124.46, 127.47, 128.69, 130.08, 130.82, 134.88, 135.26 (q, $^2J_{\text{CF}}=40.6$ Hz), 137.70, 153.55 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -61.23 ppm; IR (neat): 3067, 3011, 2967, 2935, 2876, 1664 cm^{-1} ; MS (EI) m/z : 300 [M^+]; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{12}\text{OF}_3\text{Cl}$: 300.0529, found 300.0535.

3-(1-Hexenyl)-5-phenyl-2-trifluoromethylfuran (**10k**, $E/Z = 15:1$)



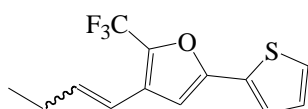
68% total isolated yield (399 mg), colorless oil. *E*-isomer. ^1H NMR (400 MHz, CDCl_3): δ 0.95 (t, $J=7.3$ Hz, 3H), 1.36-1.51 (m, 4H), 2.24 (q, $J=7.3$ Hz, 2H), 6.20 (dt, $J=14.1$ Hz, $J=7.3$ Hz, 1H), 6.44 (d, $J=14.1$ Hz, 1H), 6.82 (s, 1H), 7.35 (t, $J=7.6$ Hz, 1H), 7.42 (t, $J=7.6$ Hz, 2H), 7.71 (d, $J=7.6$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 13.88, 22.25, 31.20, 32.72, 103.58, 117.31, 120.27 (q, $^1J_{\text{CF}}=267.6$ Hz), 124.51, 127.43 (q, $^3J_{\text{CF}}=2.5$ Hz), 128.77, 128.79, 129.28, 134.89 (q, $^2J_{\text{CF}}=40.6$ Hz), 135.99, 155.14 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -61.12 ppm; IR (neat): 3085, 3055, 2959, 2929, 2859, 1664 cm^{-1} ; MS (EI) m/z : 294 [M^+]; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{17}\text{OF}_3$: 294.1231, found 294.1256.

3-(1-Butenyl)-5-(1-naphthalenyl)-2-trifluoromethylfuran (**10l**, $E/Z = 14:1$)



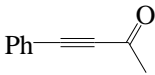
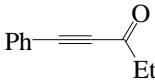
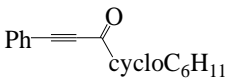
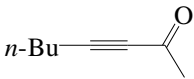
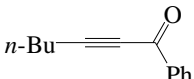
47% total isolated yield (297 mg), colorless oil. *E*-isomer. ^1H NMR (400 MHz, CDCl_3): δ 1.15 (t, $J=7.3$ Hz, 3H), 2.30 (quint, $J=7.3$ Hz, 2H), 6.31 (dt, $J=15.8$ Hz, $J=7.3$ Hz, 1H), 6.54 (d, $J=15.8$ Hz, 1H), 6.90 (s, 1H), 7.51-7.62 (m, 3H), 7.77 (d, $J=7.3$ Hz, 1H), 7.91-7.93 (m, 2H), 8.34 (d, $J=7.3$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 13.31, 26.12, 107.96, 116.53, 120.37 (q, $^1J_{\text{CF}}=267.6$ Hz), 125.02, 125.16, 126.19, 126.91, 127.01, 127.08, 127.12 (q, $^3J_{\text{CF}}=2.5$ Hz), 128.65, 129.83, 130.37, 133.88, 135.35 (q, $^2J_{\text{CF}}=40.6$ Hz), 137.47, 154.85 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -61.01 ppm; IR (neat): 3054, 3011, 2967, 2935, 2876, 2852, 1664 cm^{-1} ; MS (EI) m/z : 316 [M^+]; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{15}\text{OF}_3$: 316.1075, found 316.1080.

3-(1-Butenyl)-5-thienyl-2-trifluoromethylfuran (**10m**, *E/Z* = 11:1)

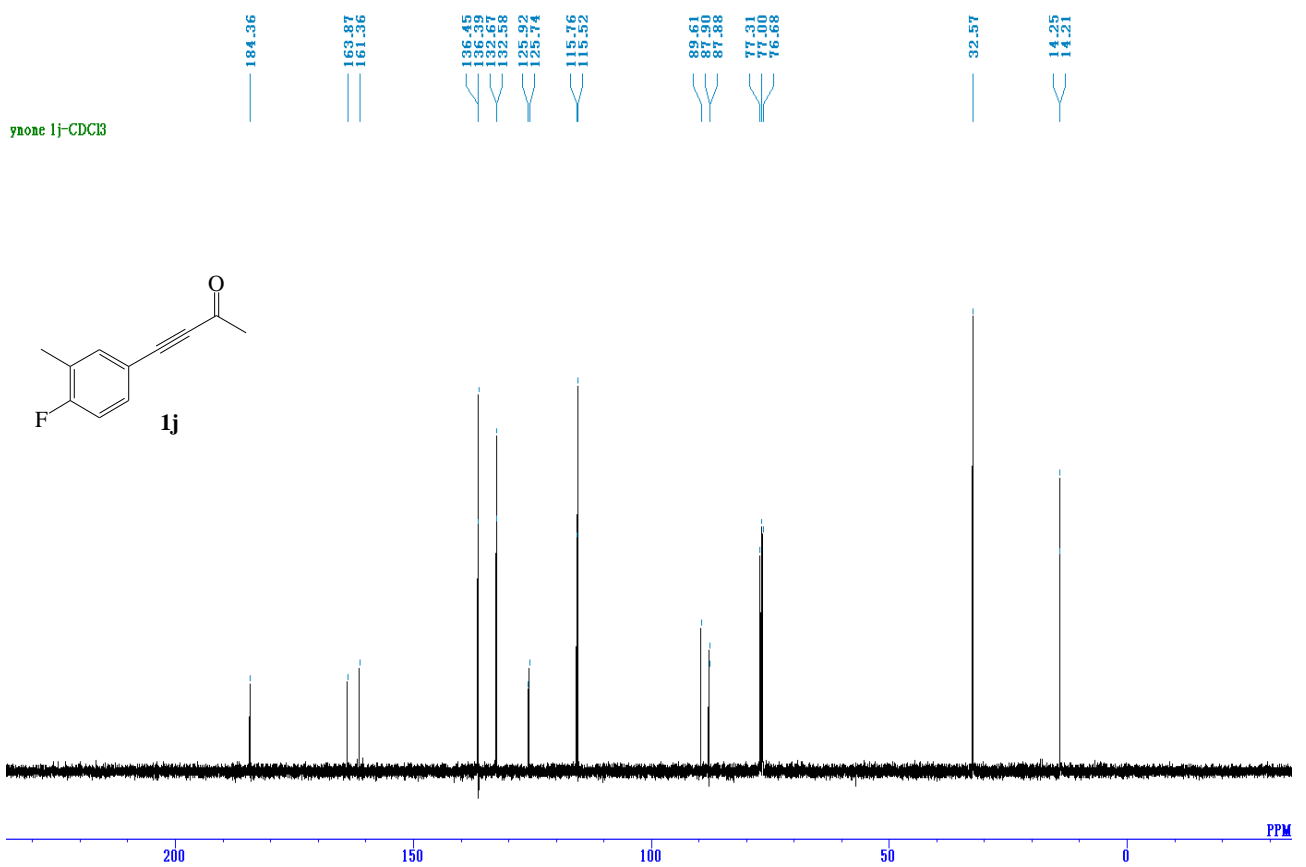
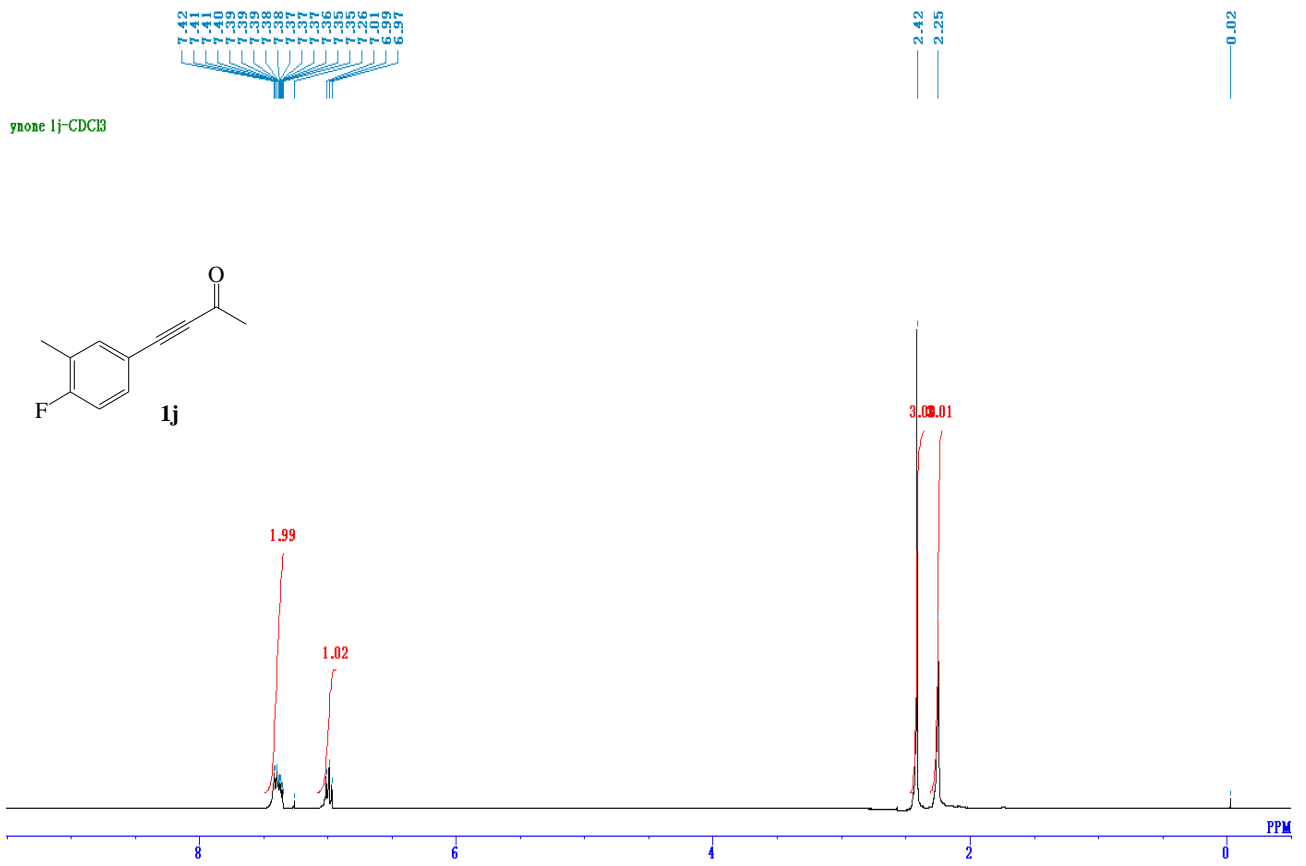


28% total isolated yield (151 mg), colorless oil, *E*-isomer. ^1H NMR (400 MHz, CDCl_3): δ 1.10 (t, $J=7.4$ Hz, 3H), 2.25 (quint, $J=7.4$ Hz, 2H), 6.21 (dt, $J=15.6$ Hz, $J=7.4$ Hz, 1H), 6.41 (d, $J=15.6$ Hz, 1H), 6.65 (s, 1H), 7.07 (dd, $J=5.1$ Hz, $J=3.7$ Hz, 1H), 7.31 (dd, $J=5.1$ Hz, $J=1.0$ Hz, 1H), 7.37 (dd, $J=3.7$ Hz, $J=1.0$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 13.26, 26.07, 103.49, 116.24, 120.12 (q, $^1J_{\text{CF}}=267.6$ Hz), 124.72, 125.95, 127.48 (q, $^3J_{\text{CF}}=2.5$ Hz), 127.82, 131.79, 134.34 (q, $^2J_{\text{CF}}=40.6$ Hz), 137.63, 150.63 ppm; ^{19}F NMR (376 MHz, CDCl_3): δ -61.23 ppm; IR (neat): 3120, 3078, 3054, 2967, 2934, 2876, 1663 cm^{-1} ; MS (EI) m/z : 272 [M^+]; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{11}\text{OF}_3\text{S}$: 272.0483, found 272.0501.

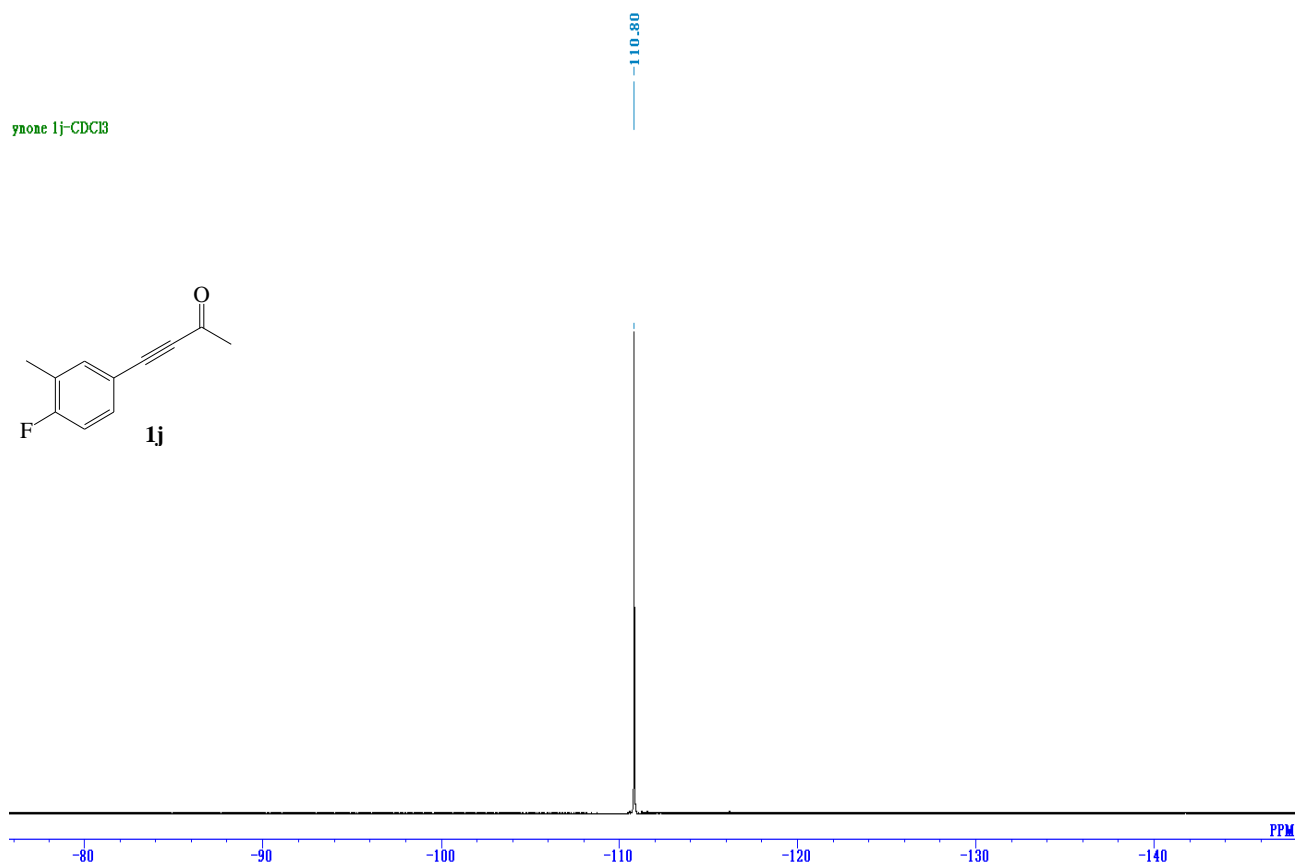
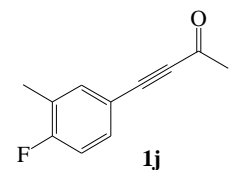
Table S3. Reduction potential of substrates

substrate		reduction potential (V vs. Ag/AgCl)
	1a	-1.70
	1b	-1.83
	1n	-1.75
	1m	-2.23
	7a	-1.63
TMSCl		No Wave (0 to -3.00 V)
CF ₃ COOEt	2a	No Wave (0 to -3.00 V)

Working electrode: Pt, Counter electrode: Pt, Reference electrode: Ag/AgCl, Solvent: DMF, Supporting electrolyte: 1% *n*-Bu₄NClO₄, Scan rate: 200 mVs⁻¹.



уложне 1j-CDCl3

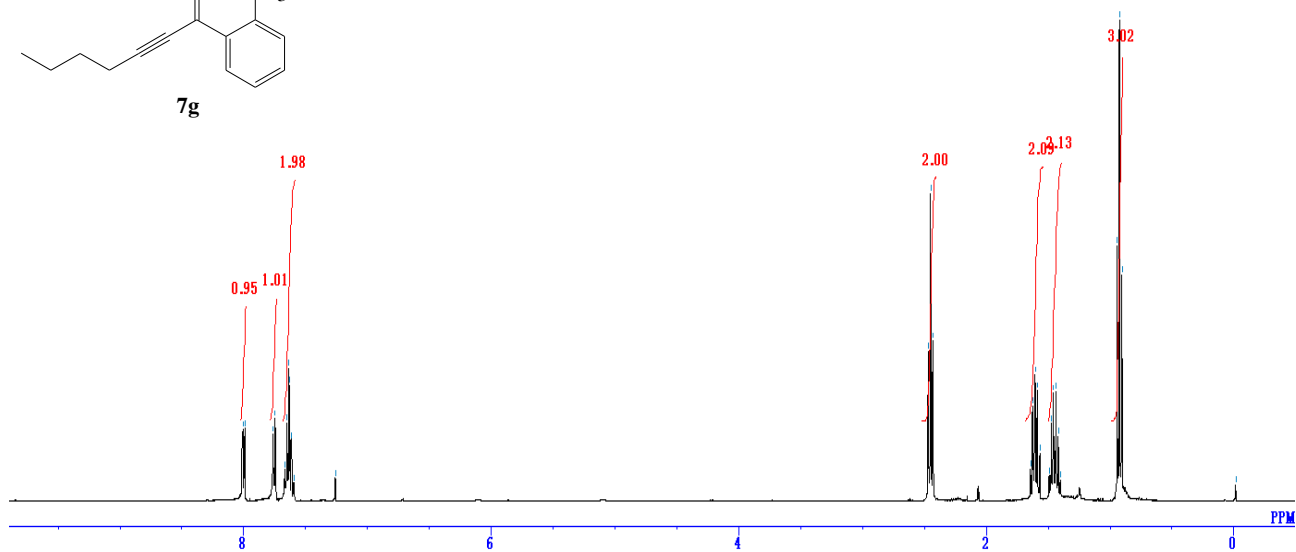
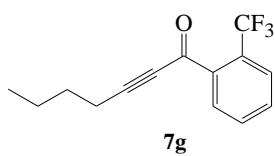


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7.99
7.76
7.75
7.67
7.65
7.63
7.62
7.58

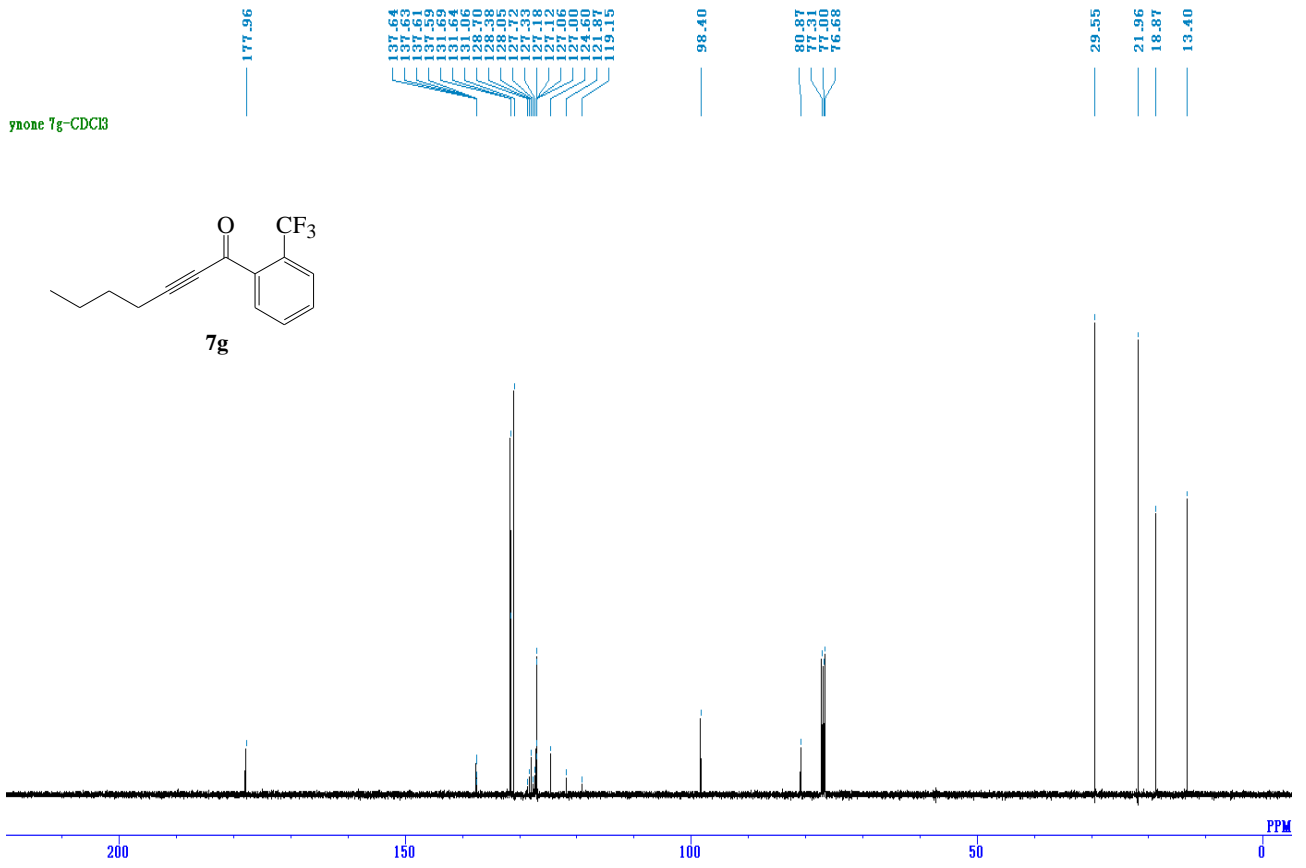
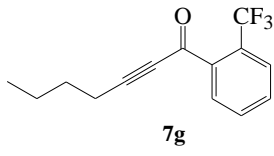
2.47
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1.63
1.59
1.57
1.50
1.46
1.44
1.42
0.95
0.91

0.01

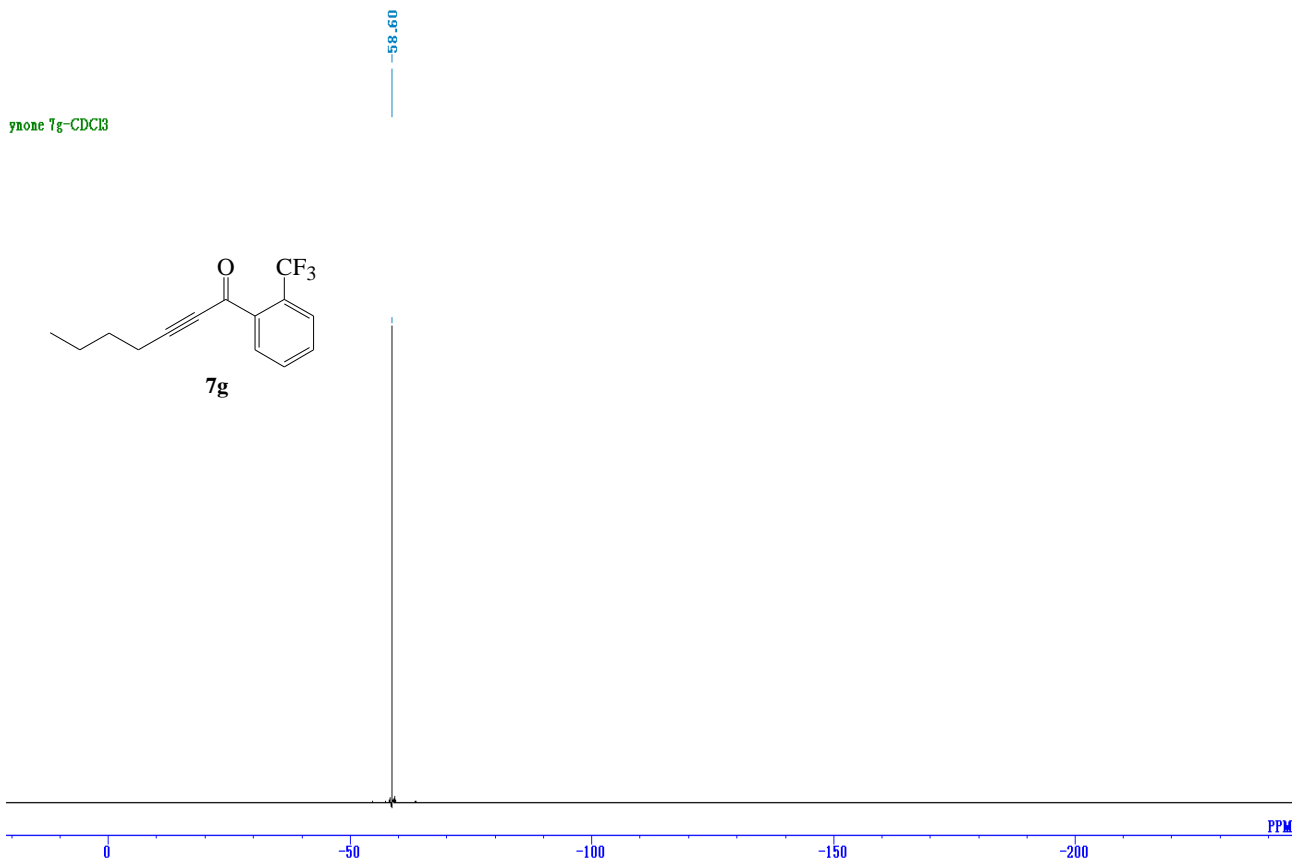
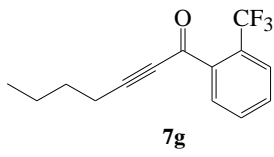
уложне 7g-CDCl3



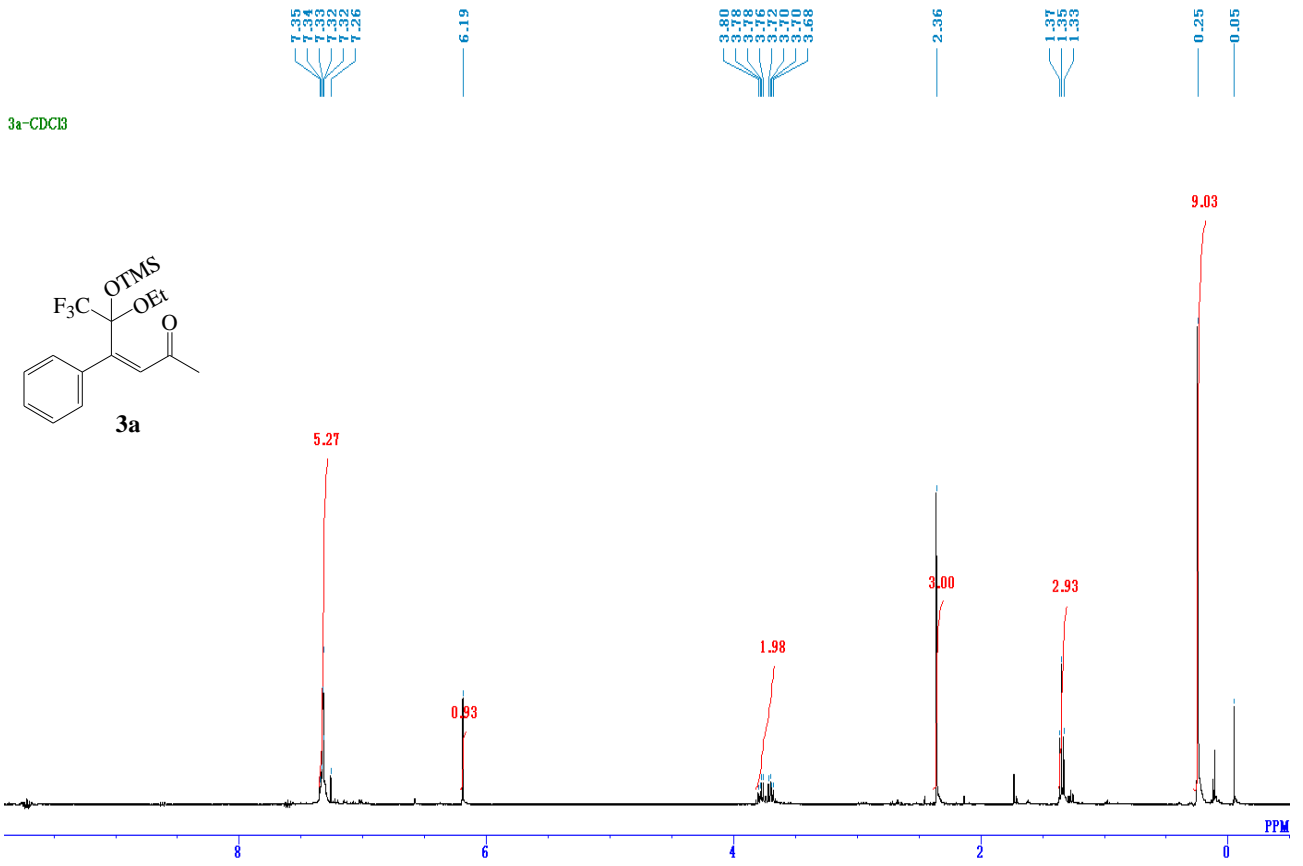
ynone 7g-CDCl₃



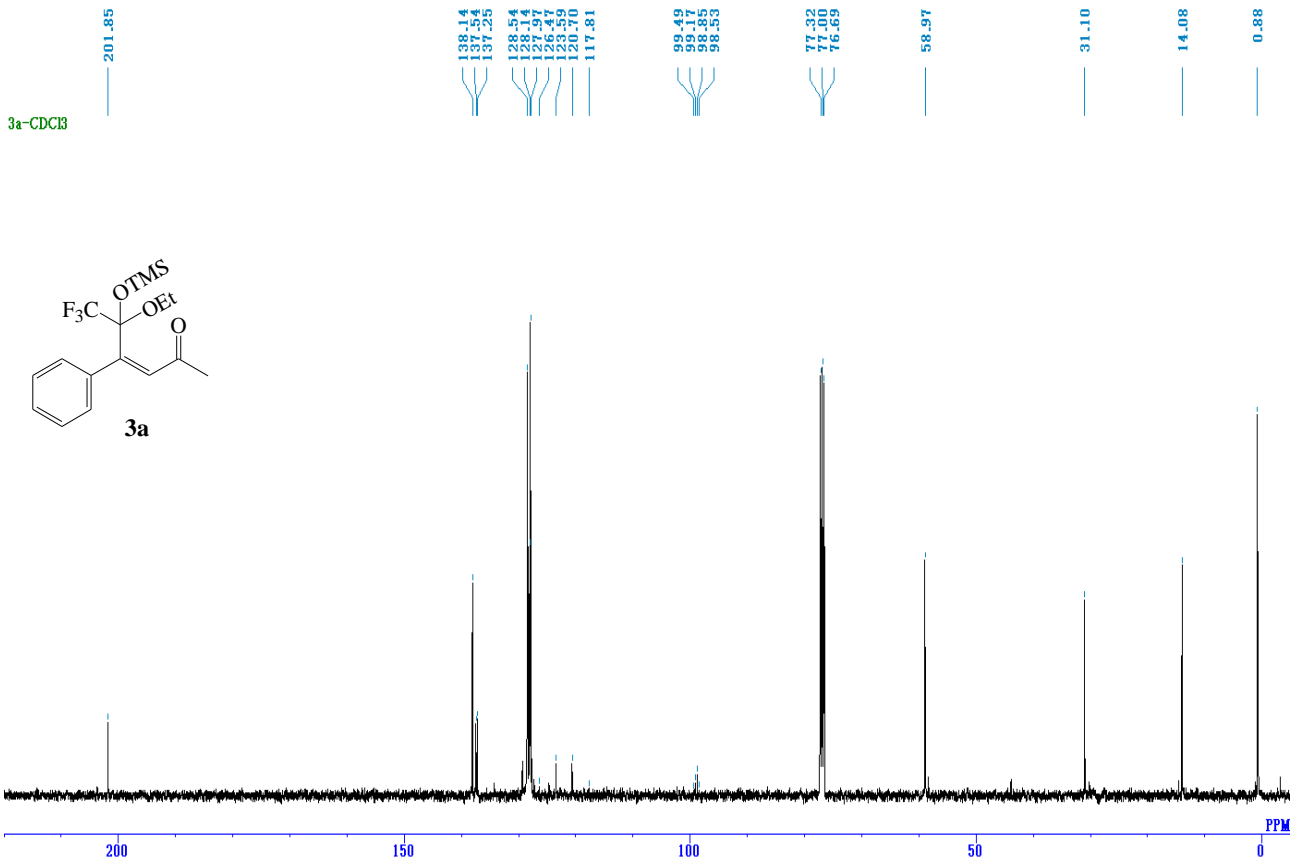
ynone 7g-CDCl₃



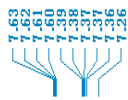
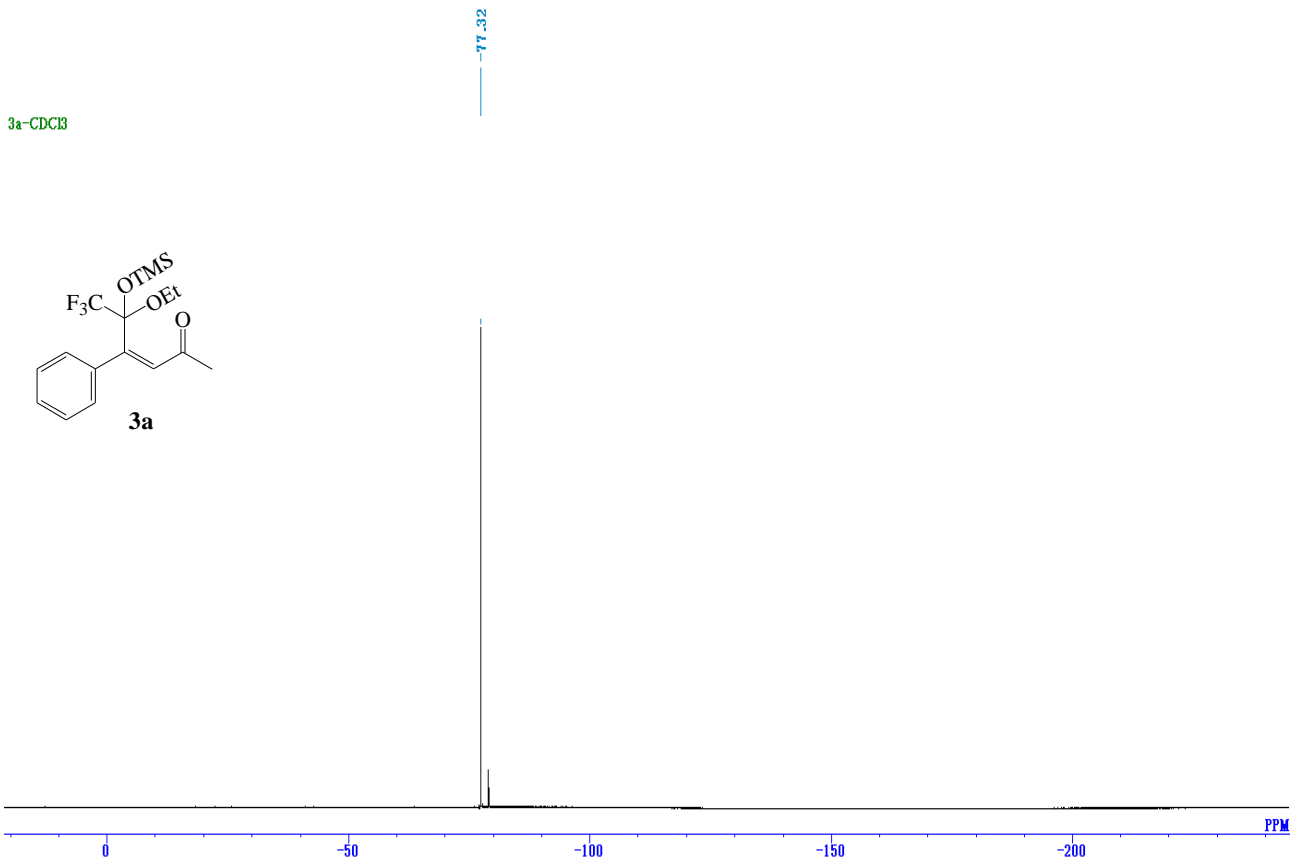
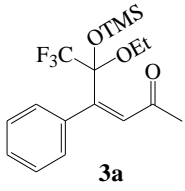
3a-CDCl3



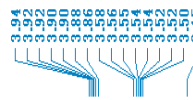
3a-CDCl3



3a-CDCl3



6.48



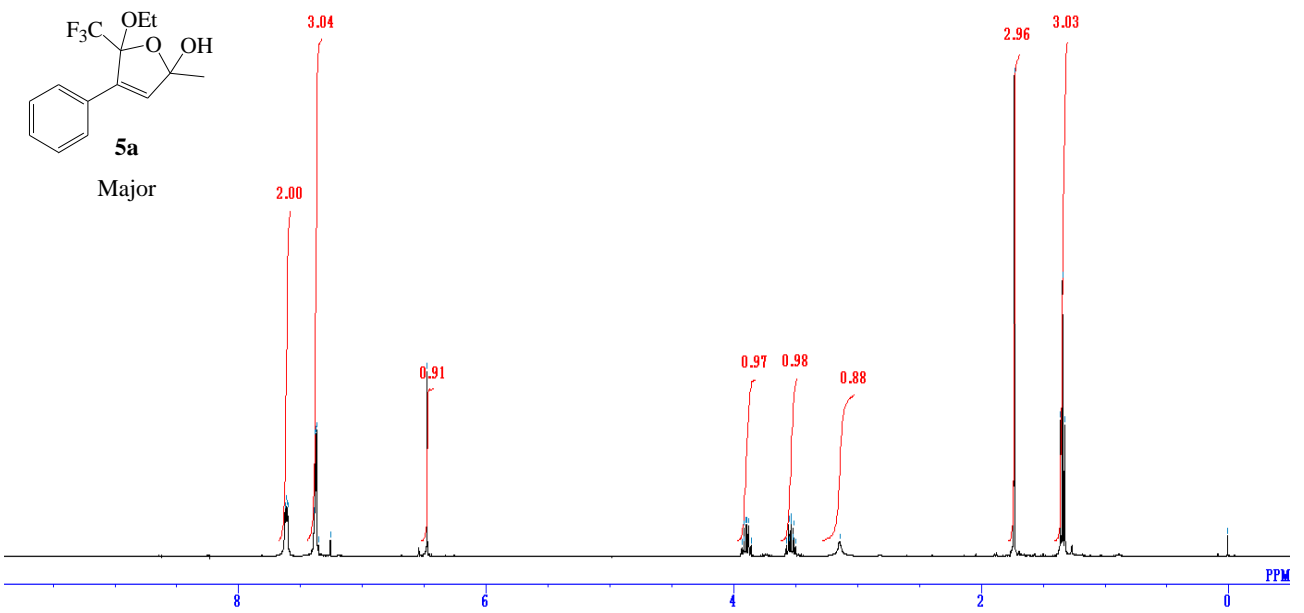
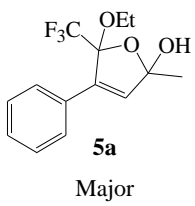
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1.36

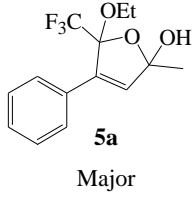
1.33

0.01

5a major-CDCl3



5a major-CDCl3



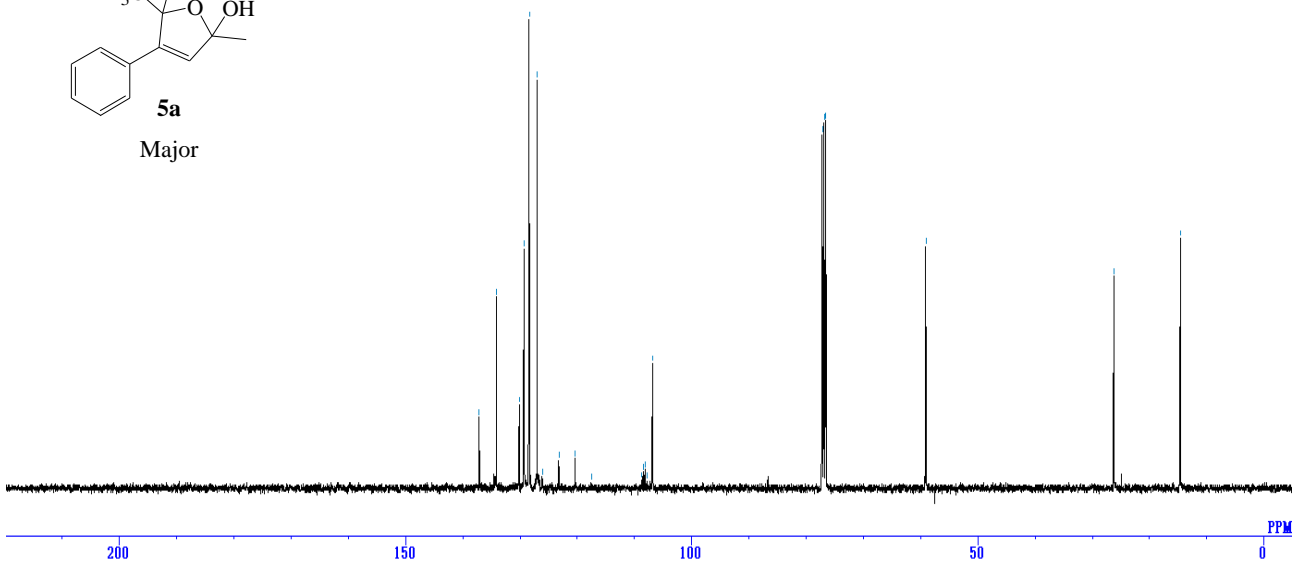
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107.90
106.91

77.31
77.00
76.68

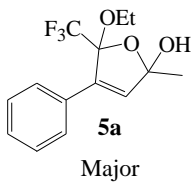
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26.38

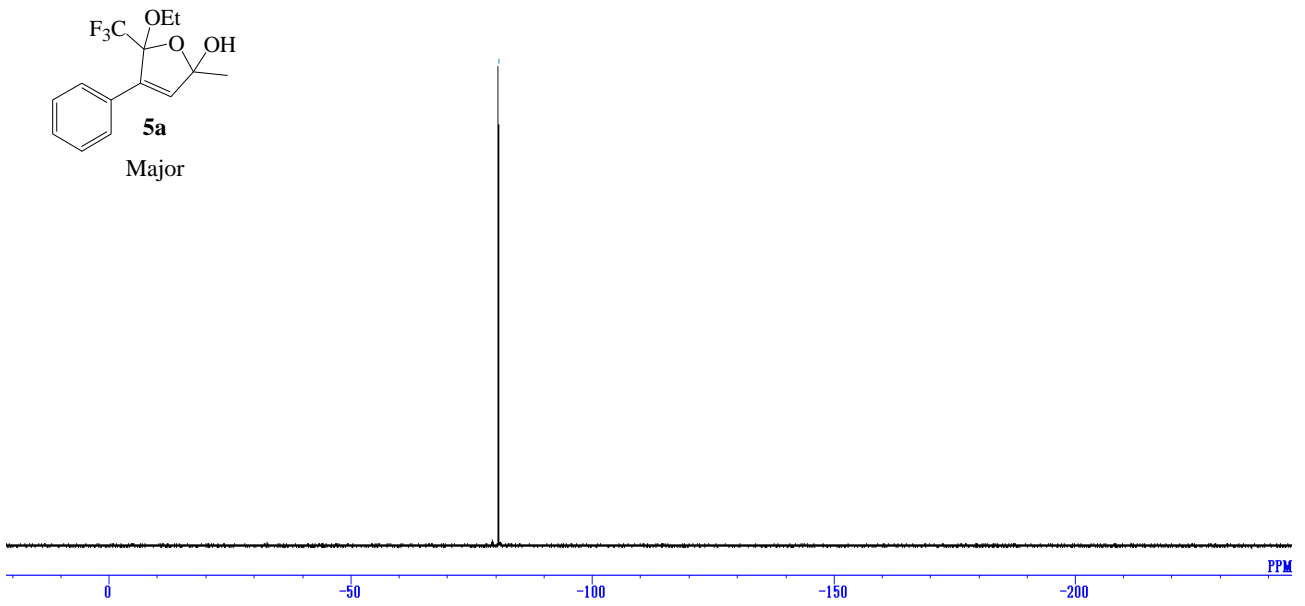
14.75



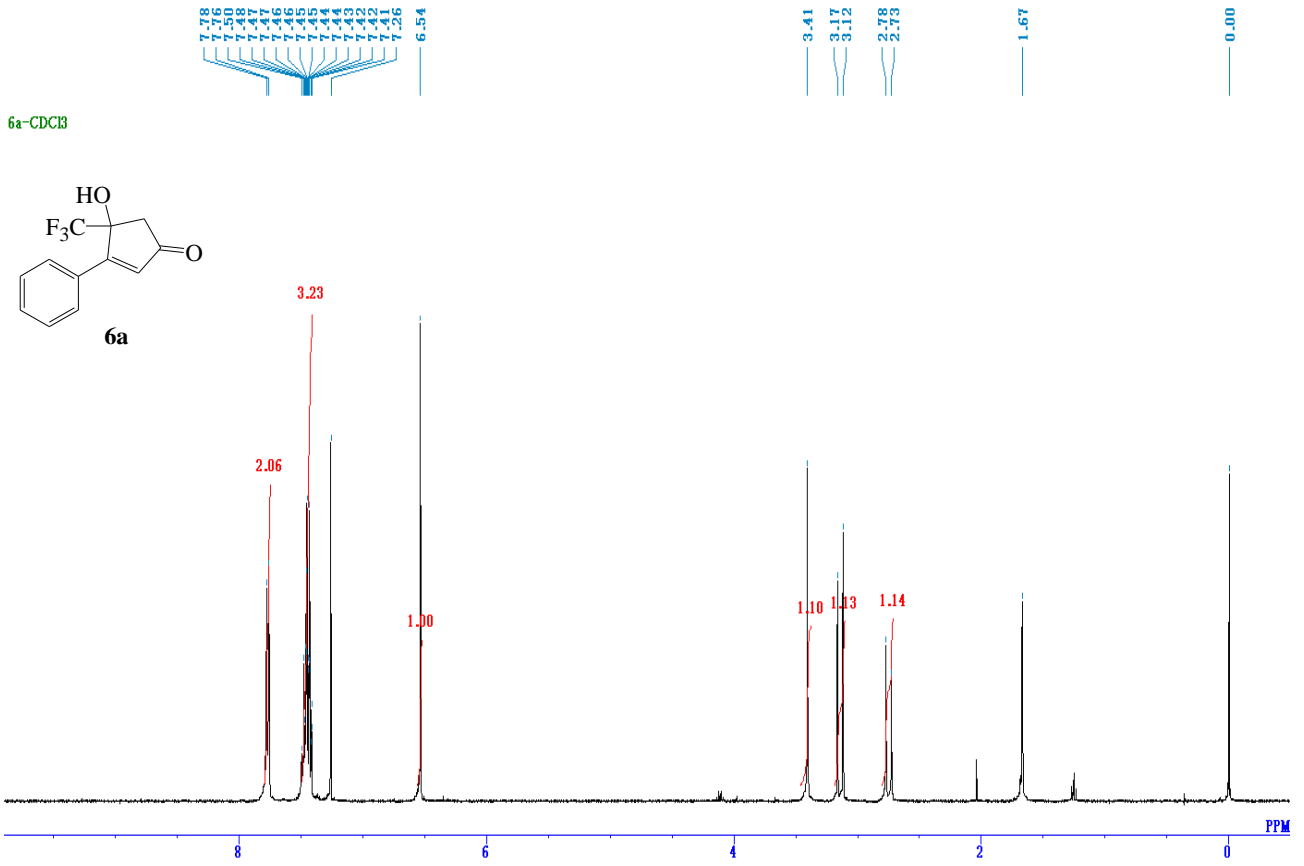
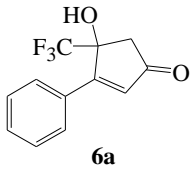
5a major-CDCl3



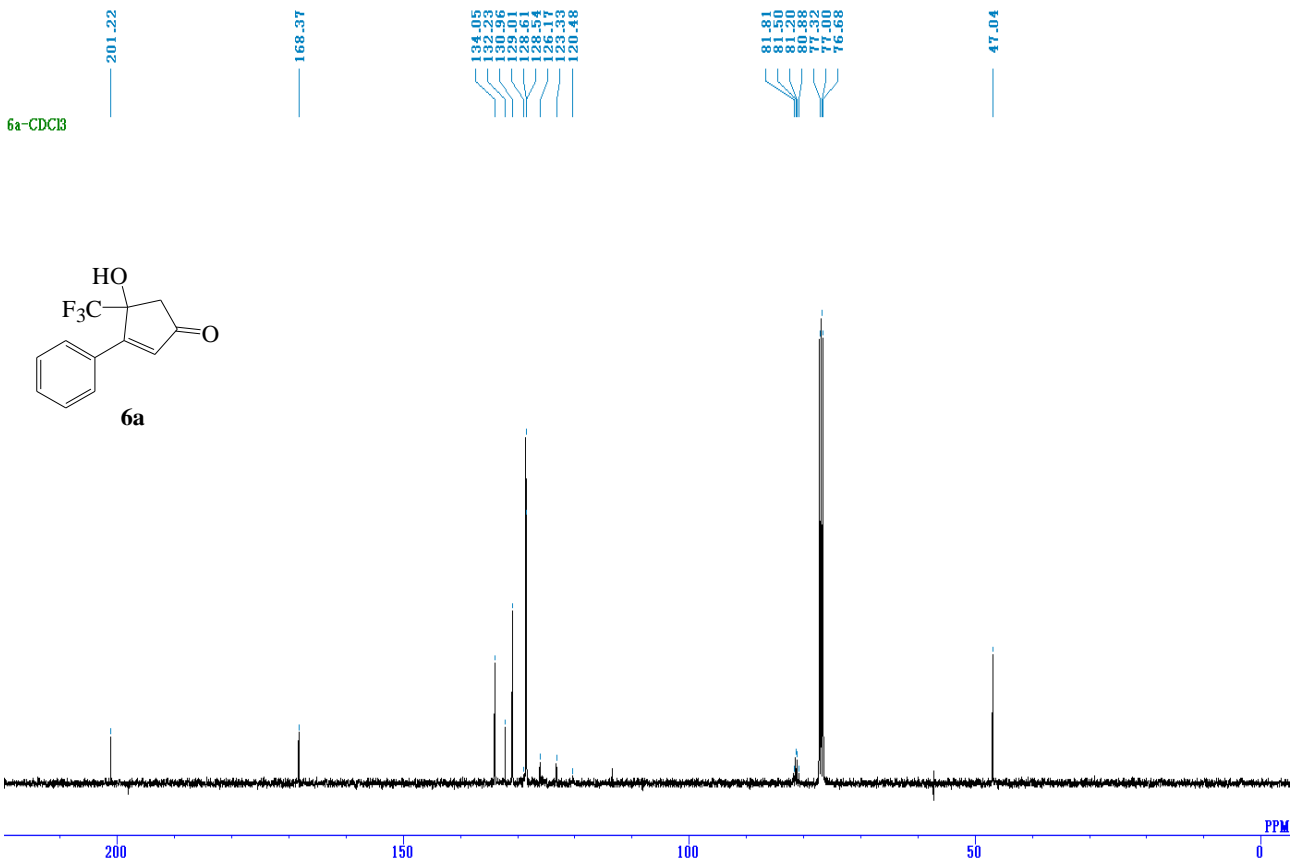
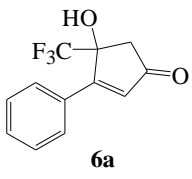
-80.47



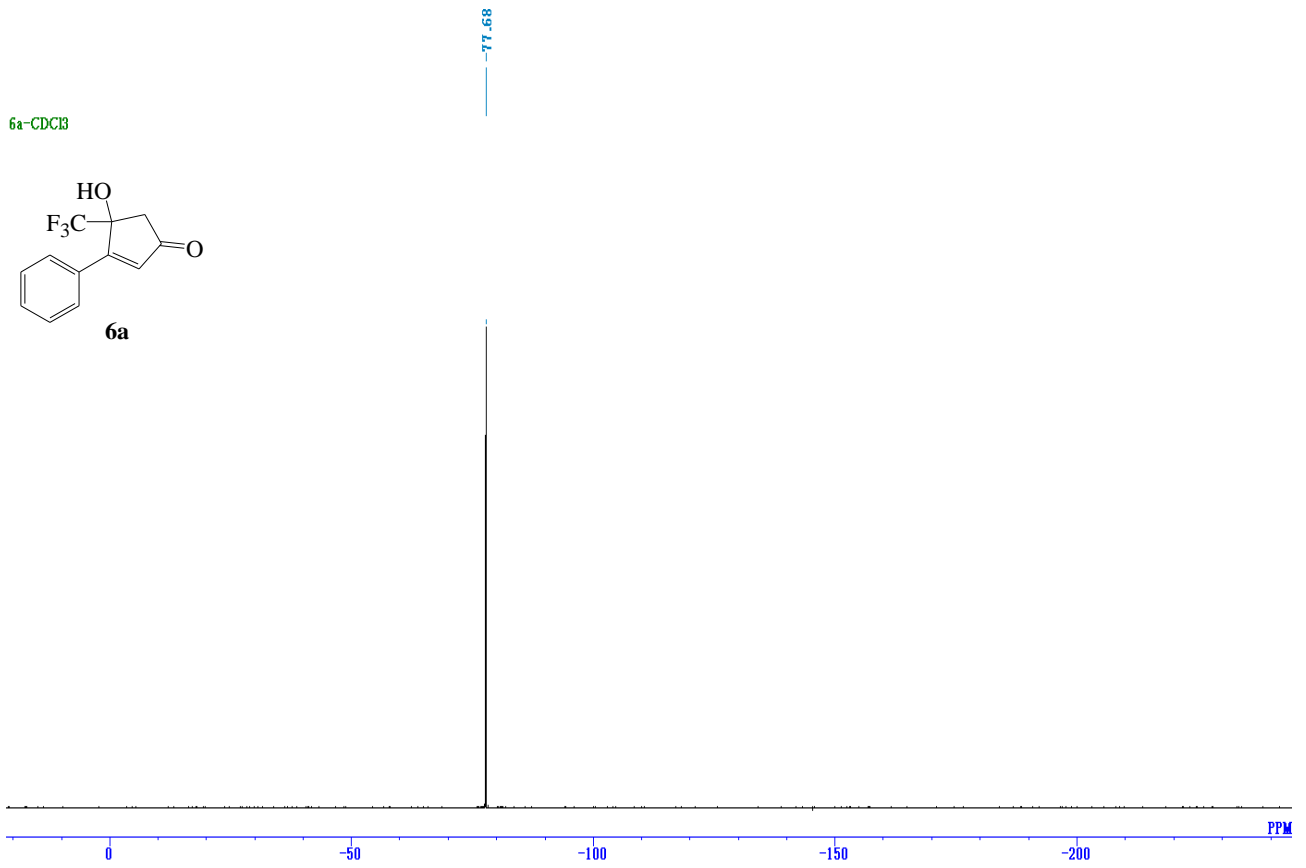
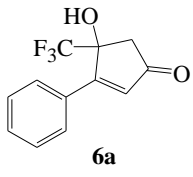
6a-CDCl₃



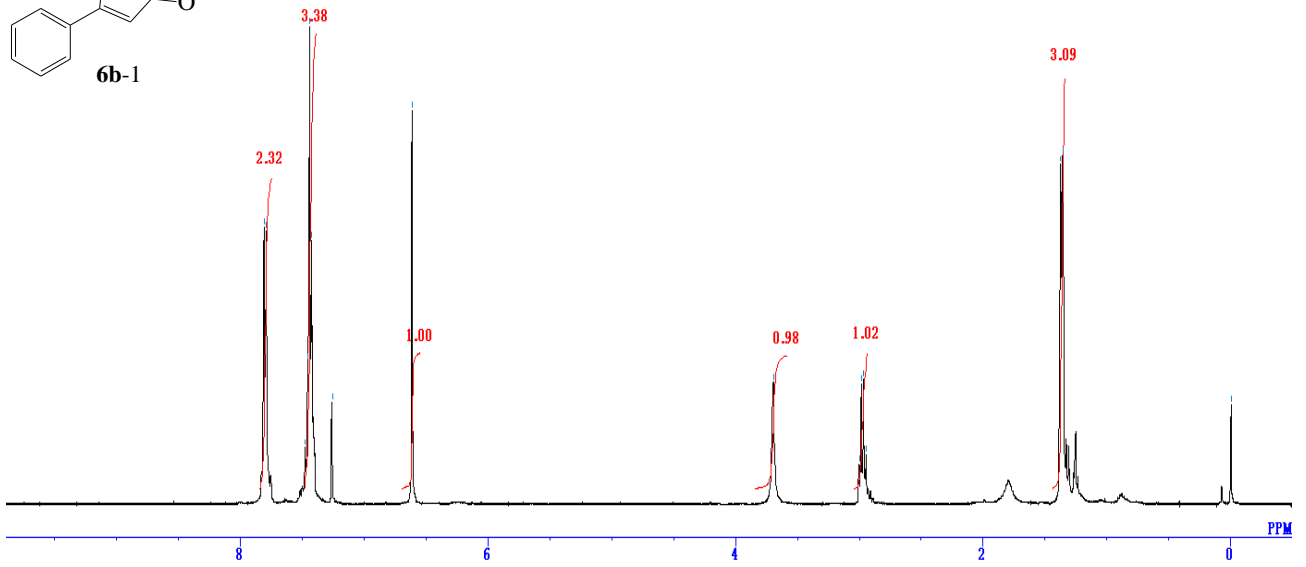
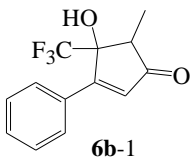
6a-CDCl₃

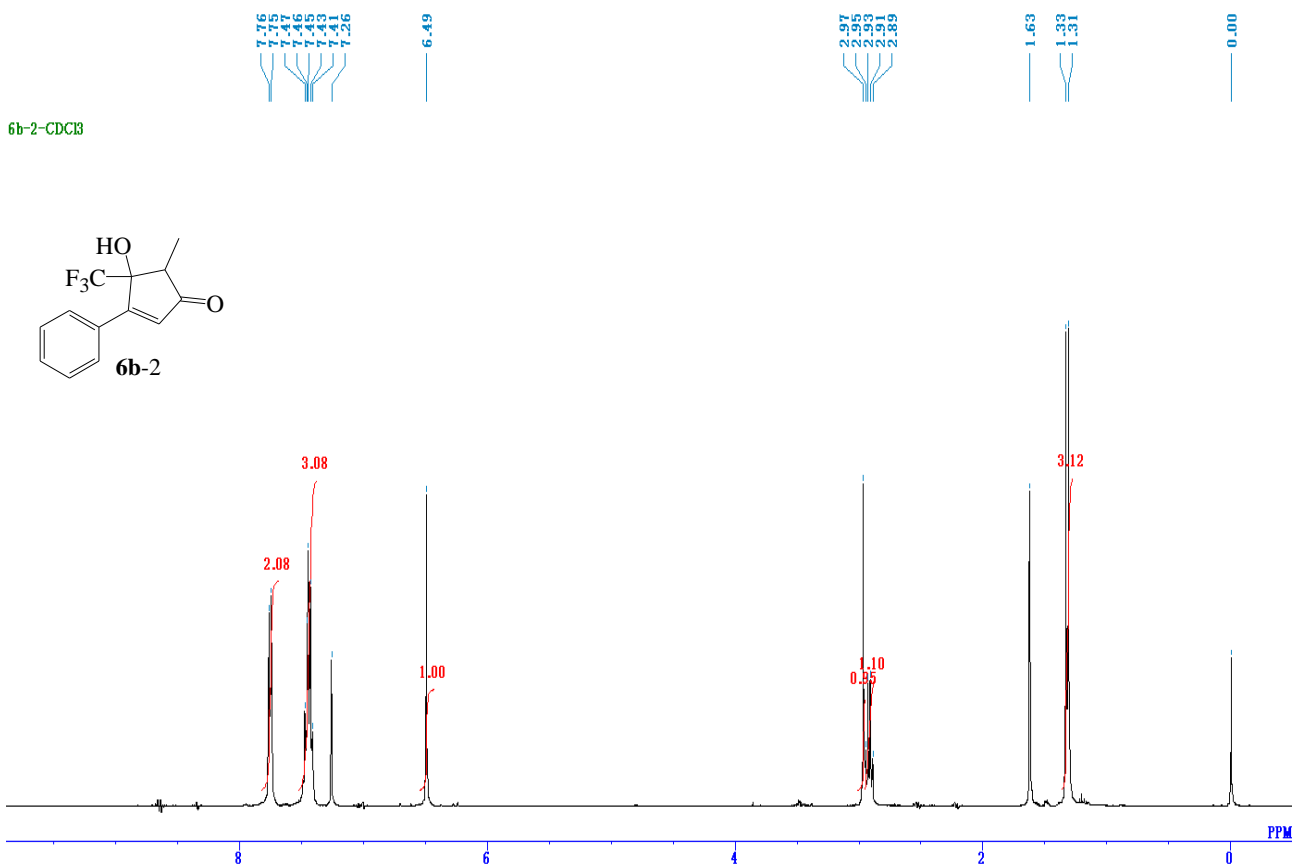
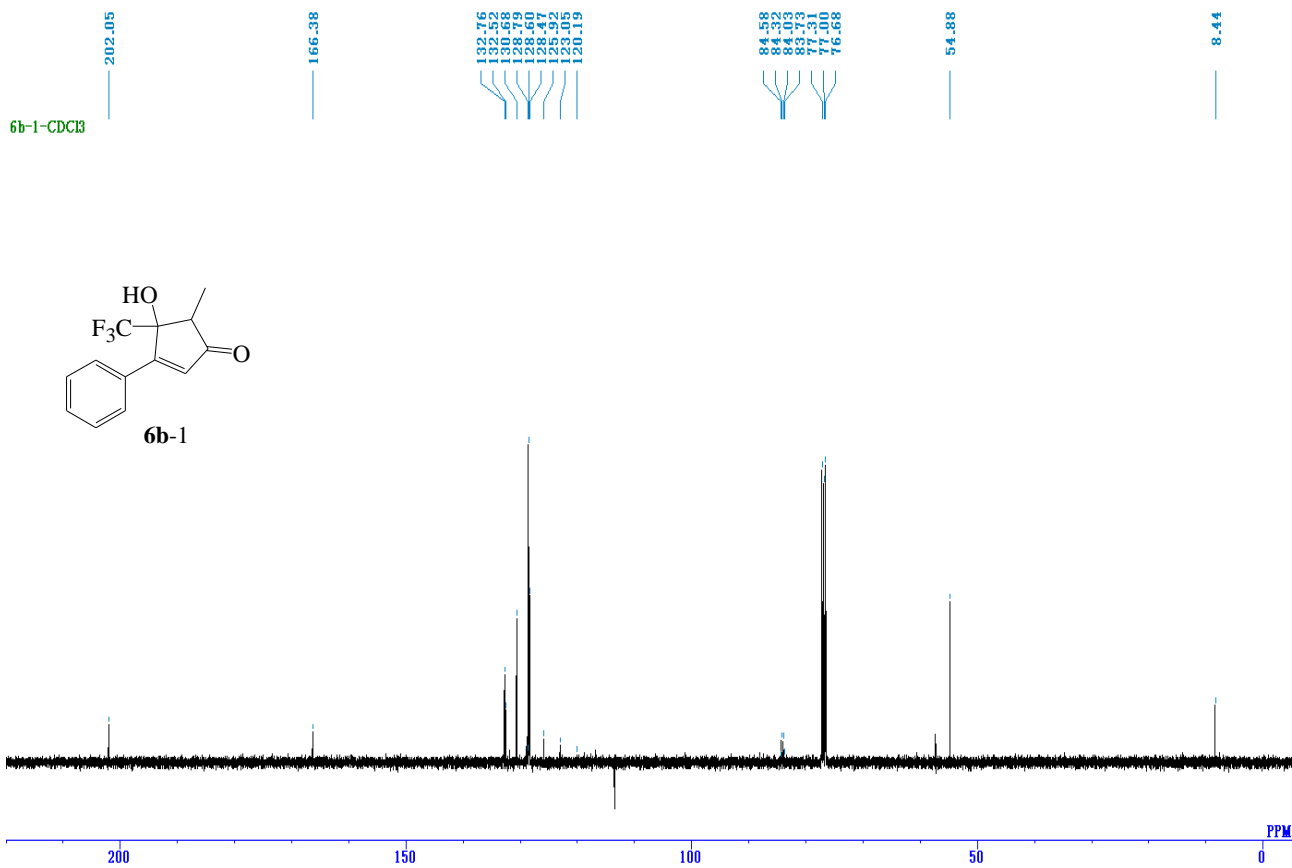


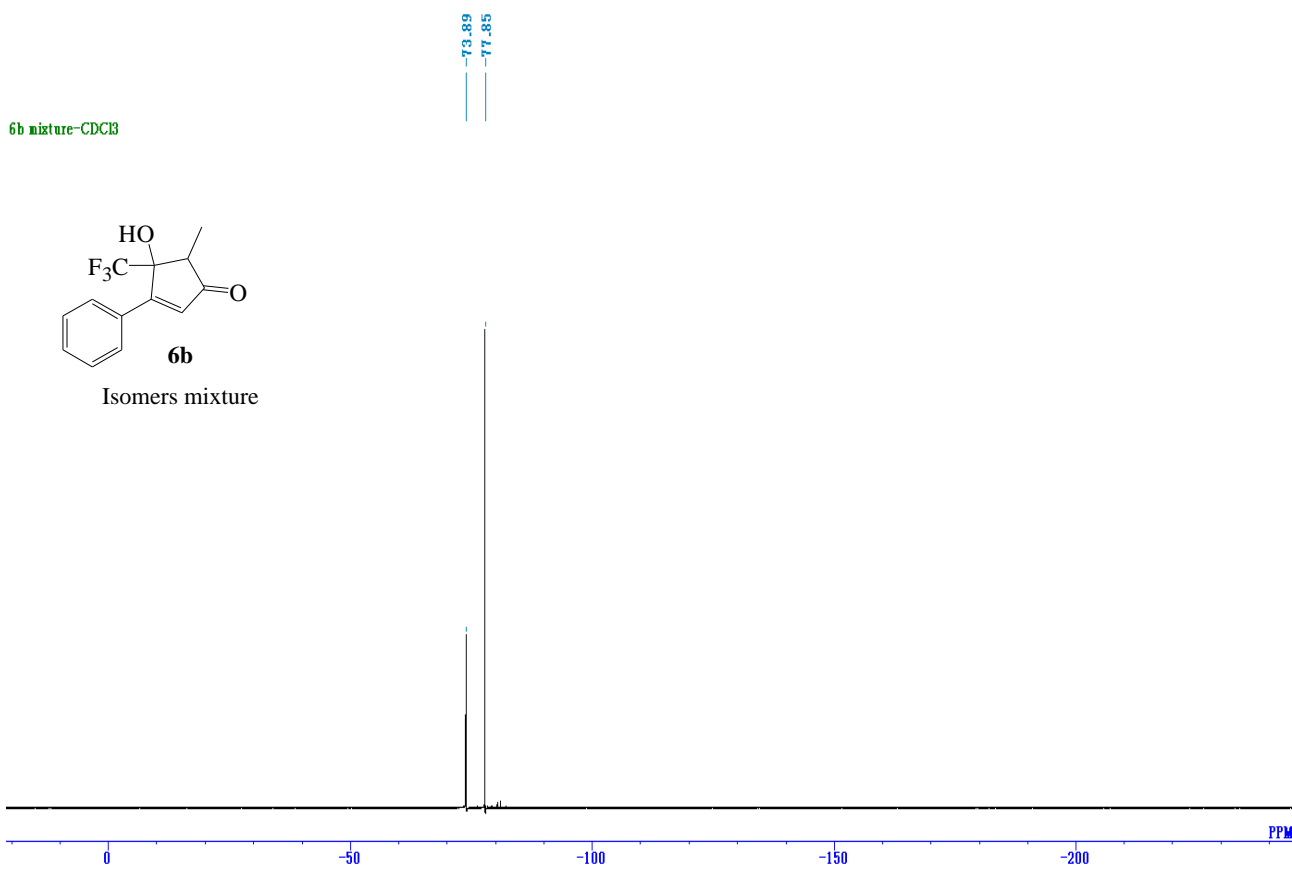
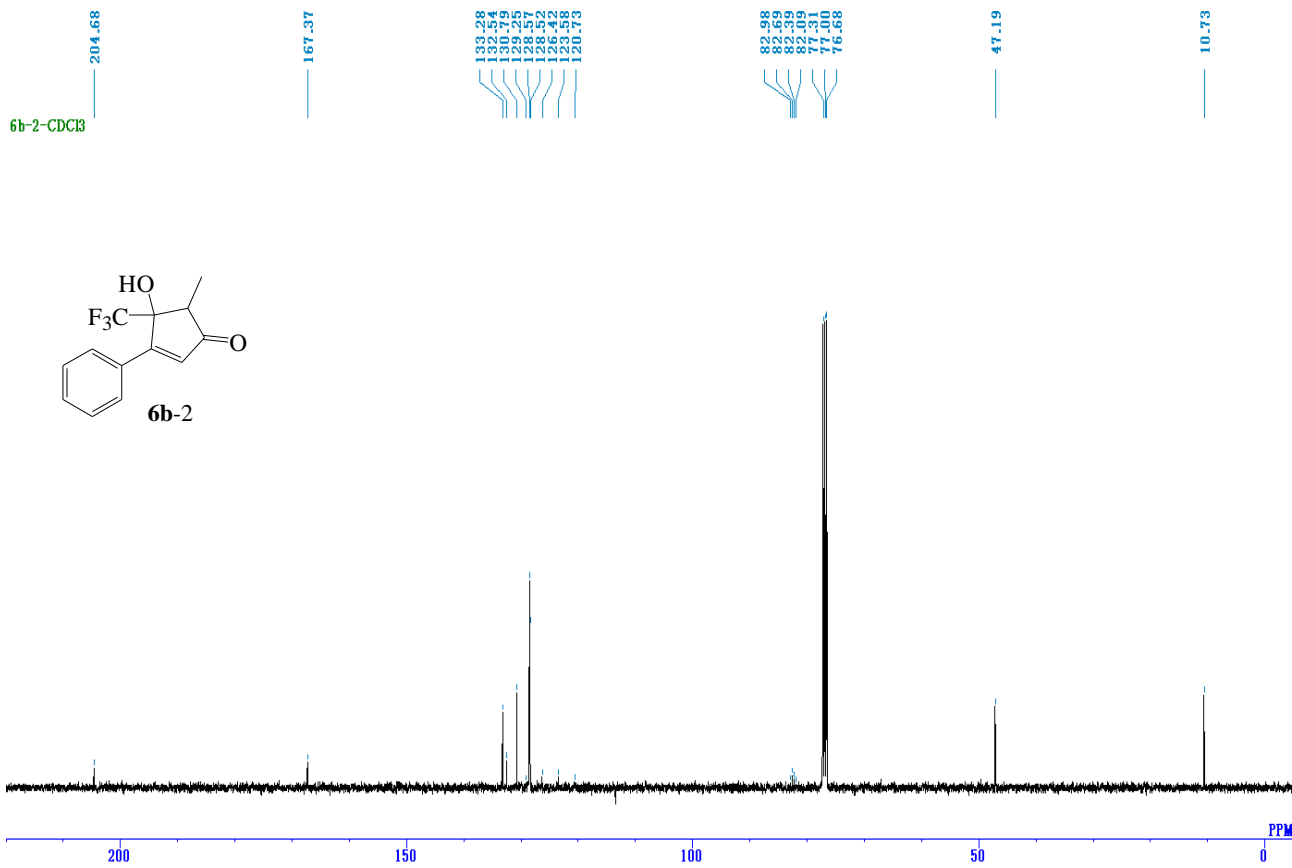
6a-CDCl₃



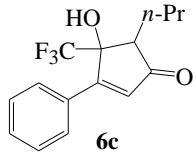
6b-1-CDCl₃



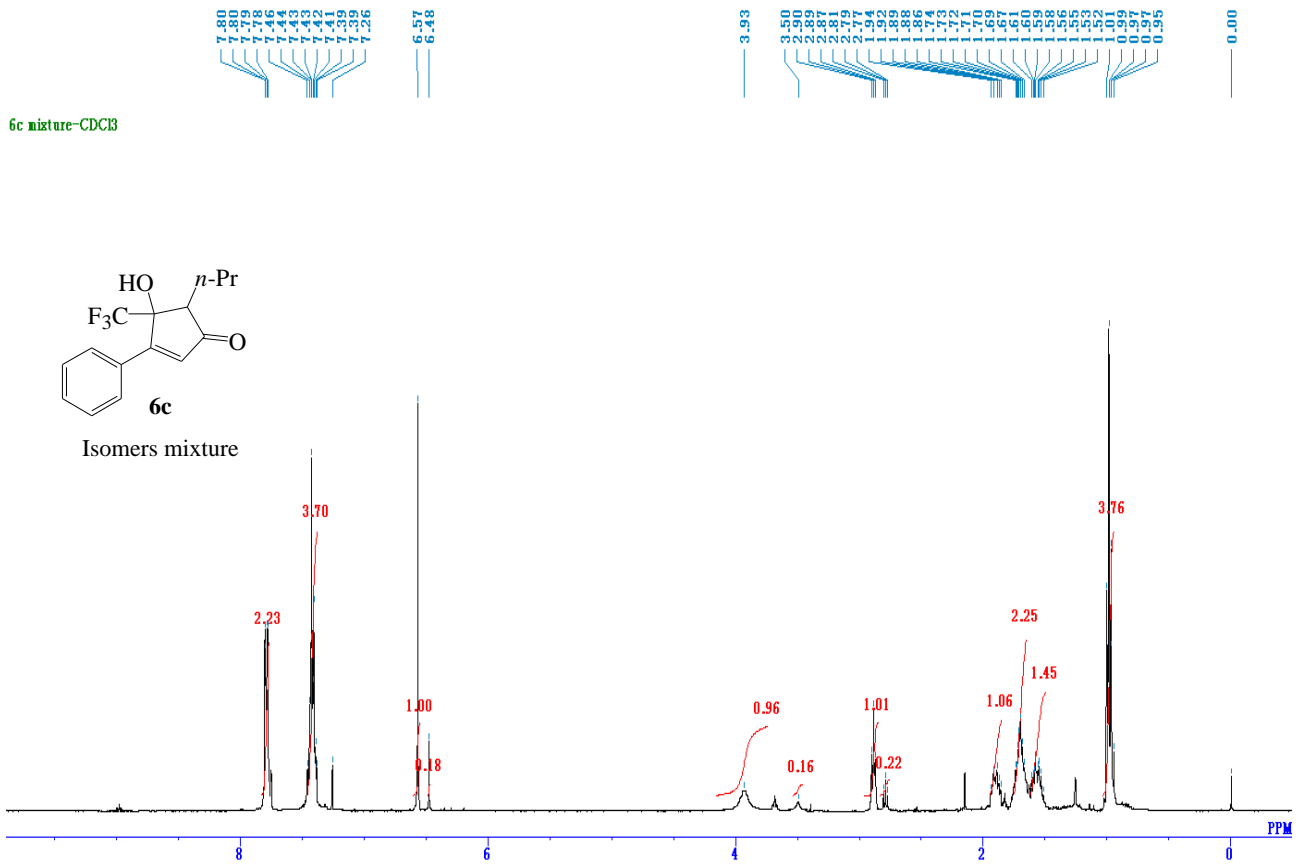




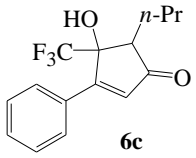
6c mixture-CDCl3



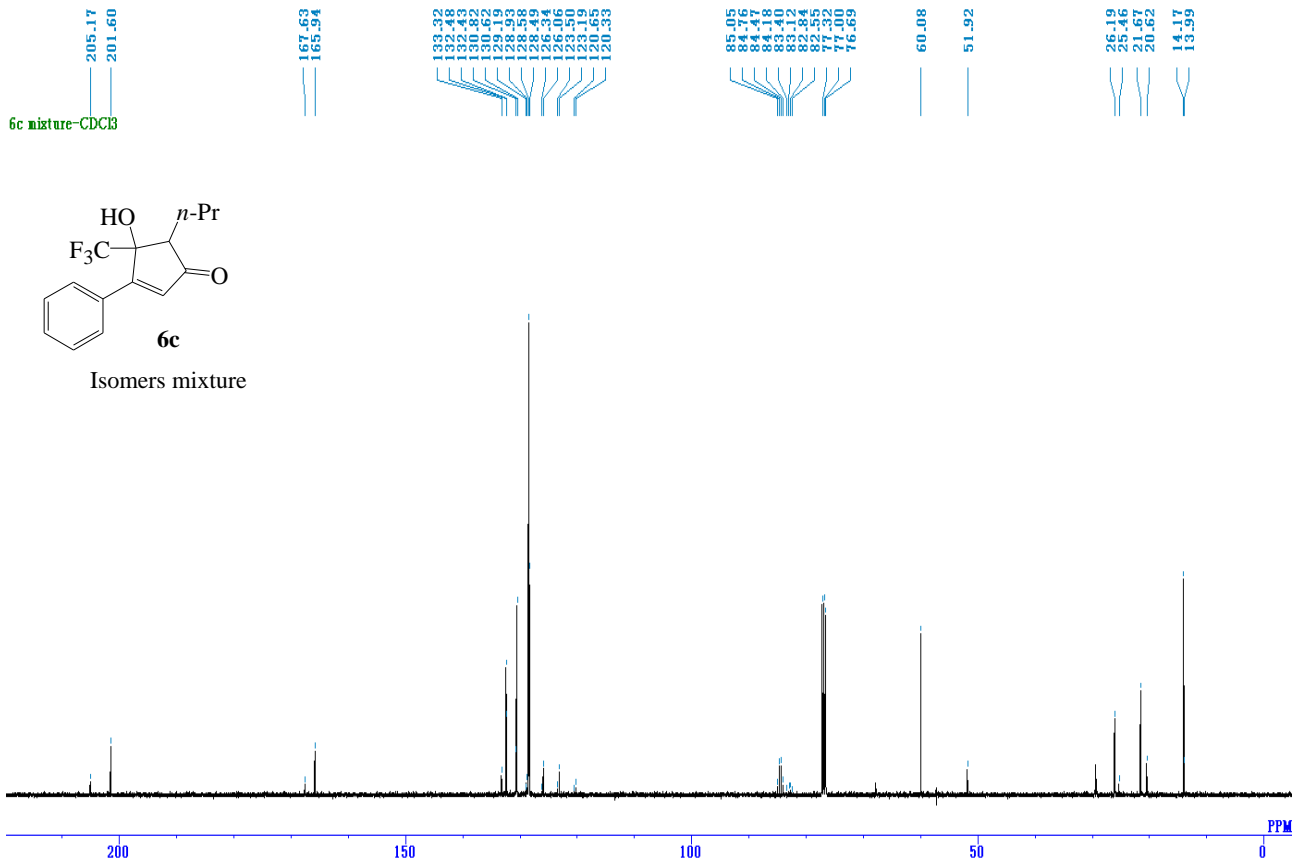
Isomers mixture



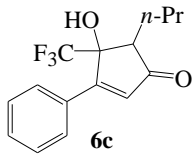
6c mixture-CDCl3



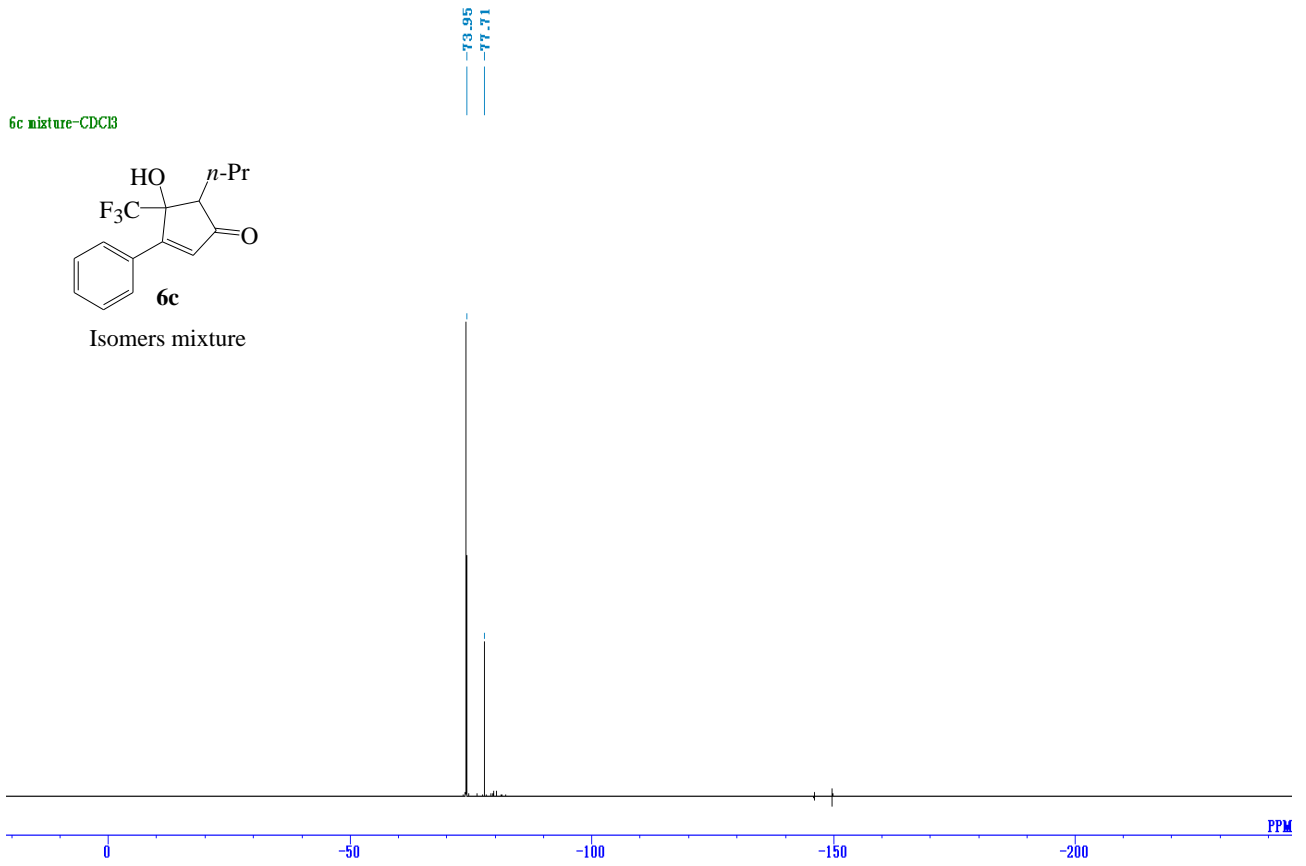
Isomers mixture



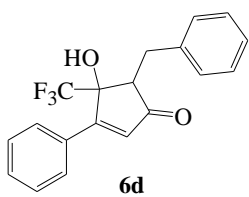
6c mixture-CDCl₃



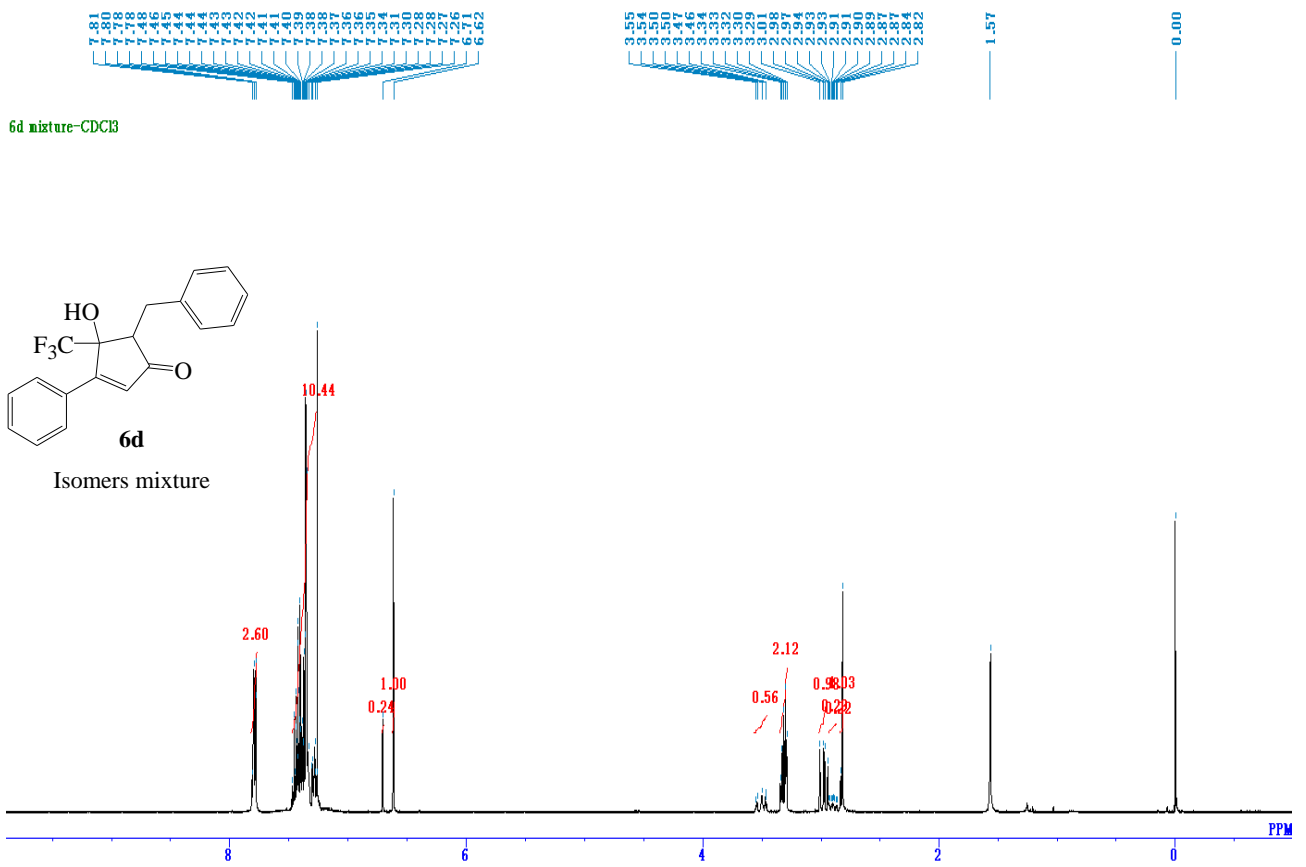
Isomers mixture

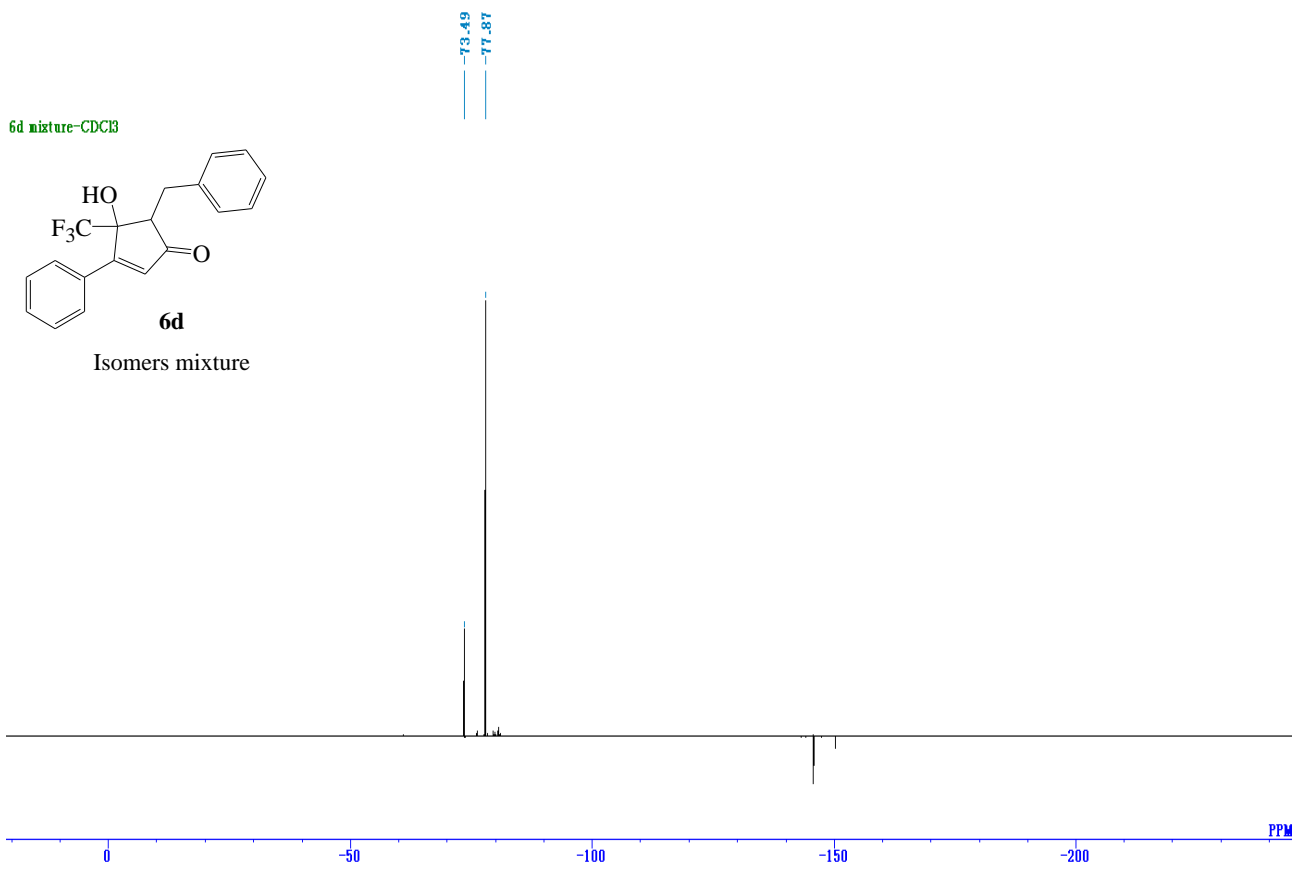
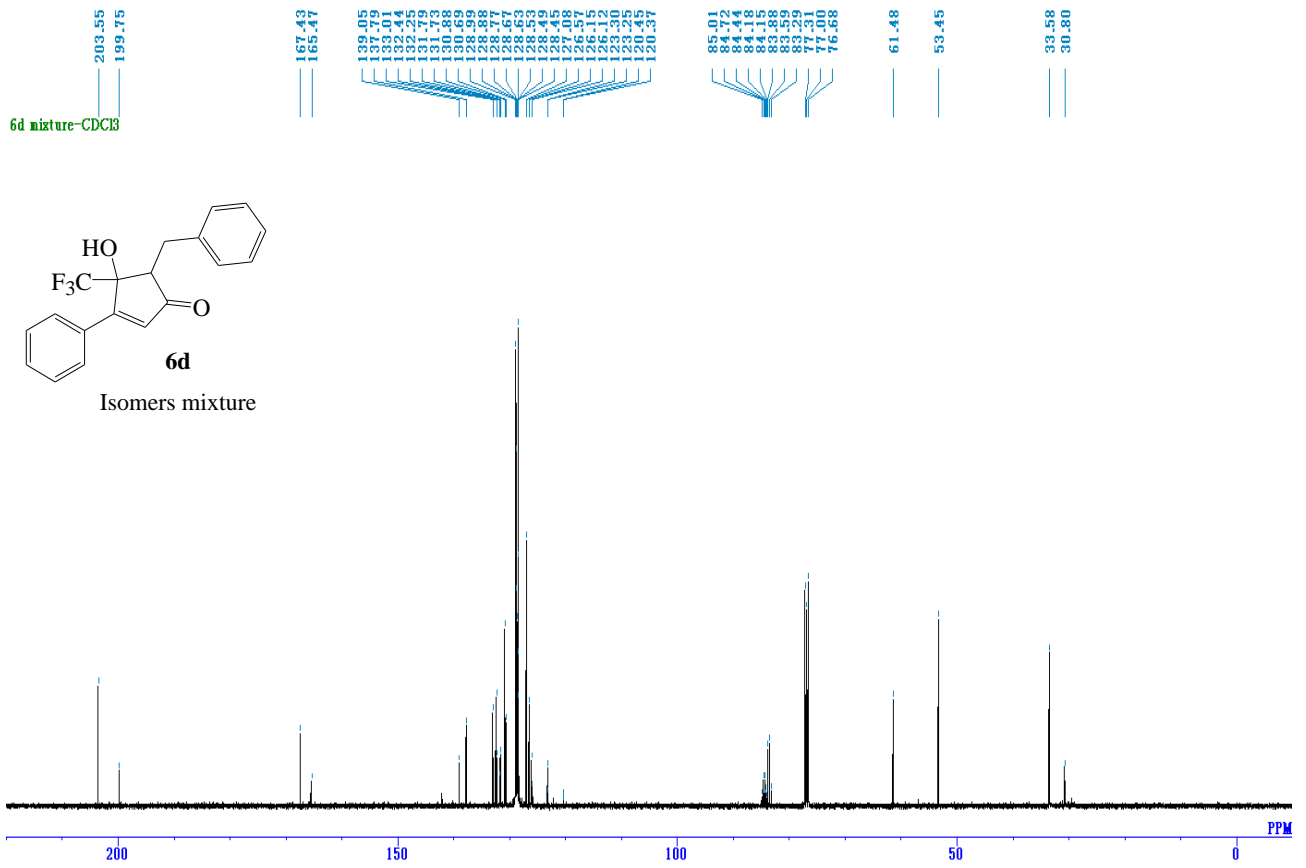


6d mixture-CDCl₃

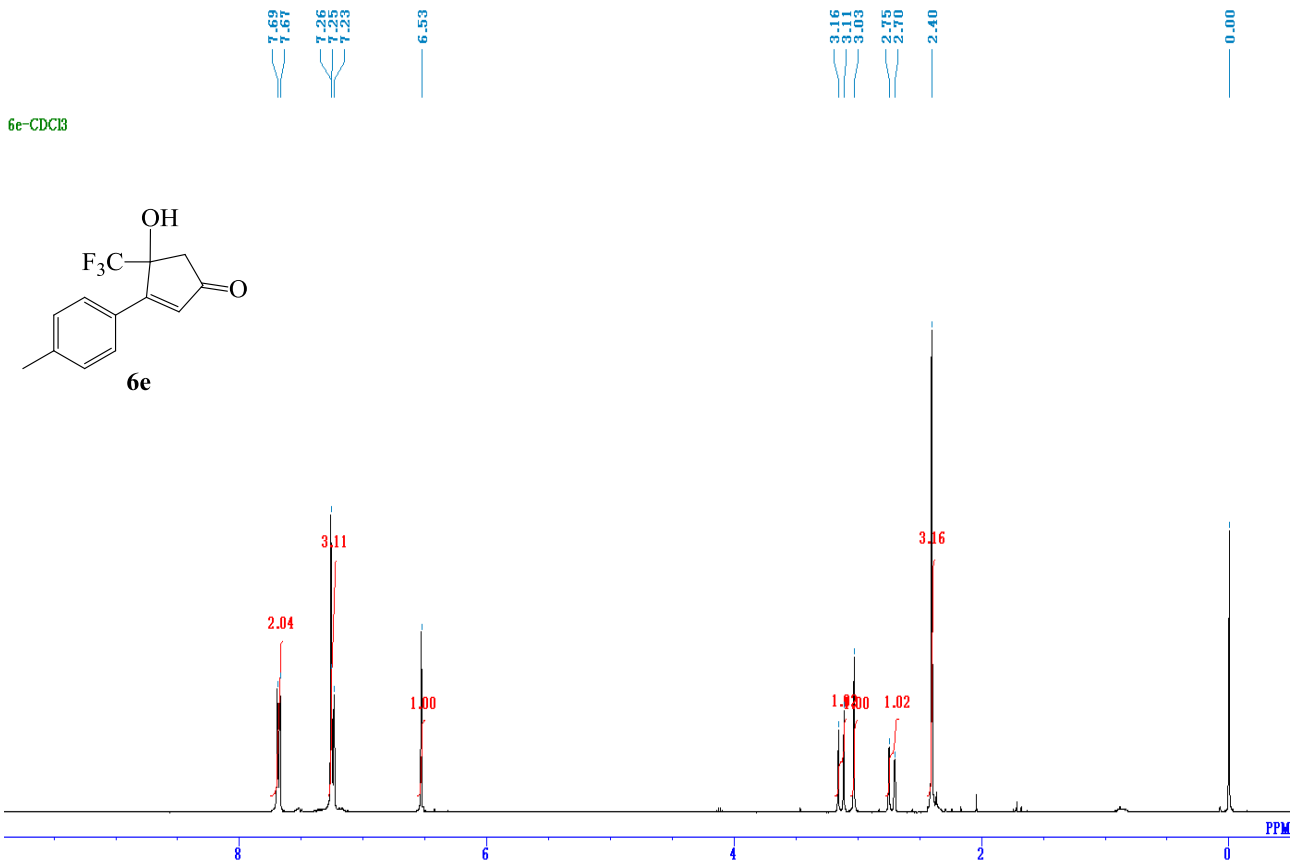
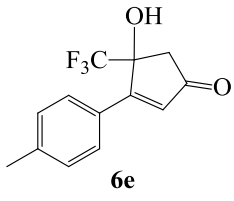


Isomers mixture

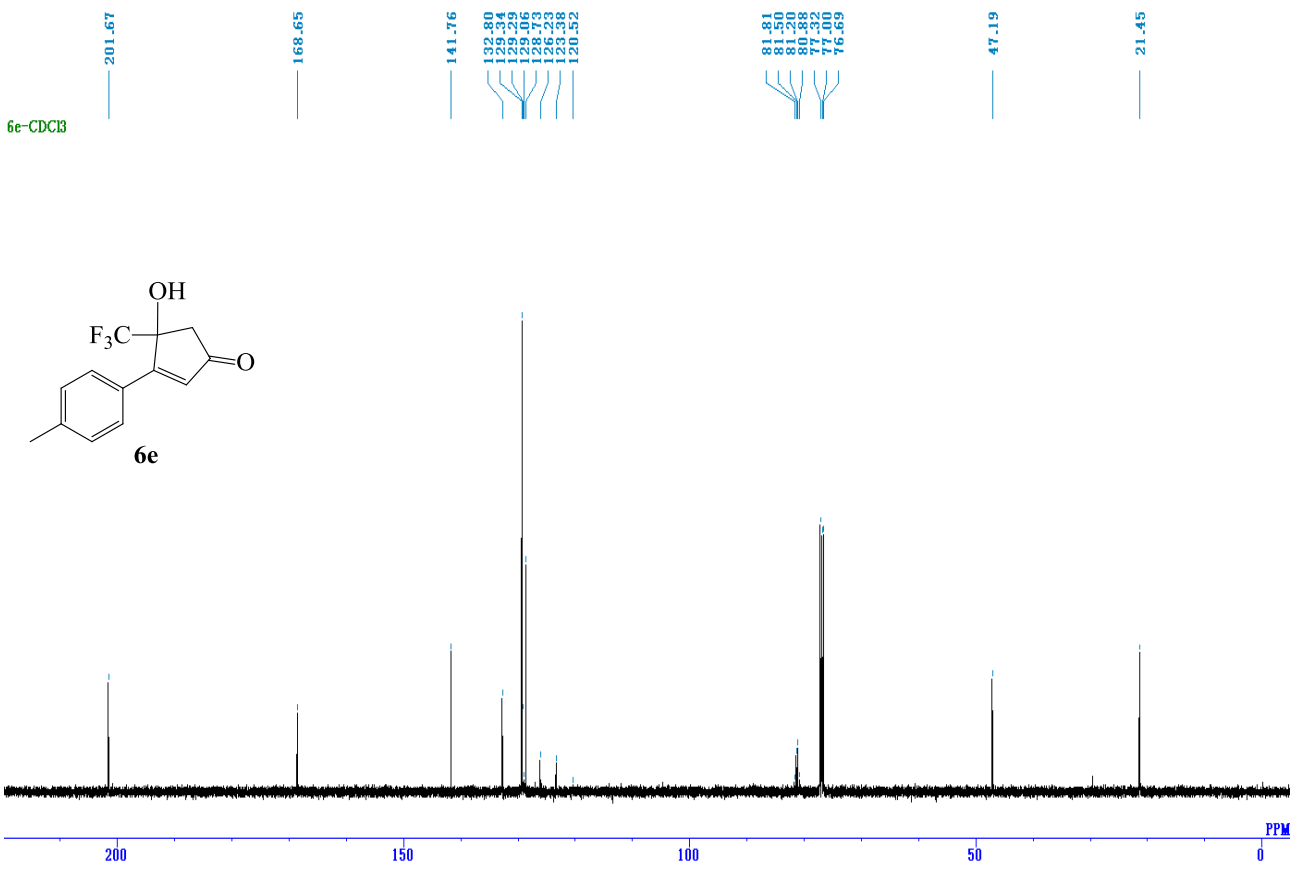
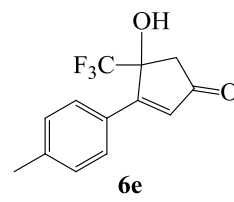




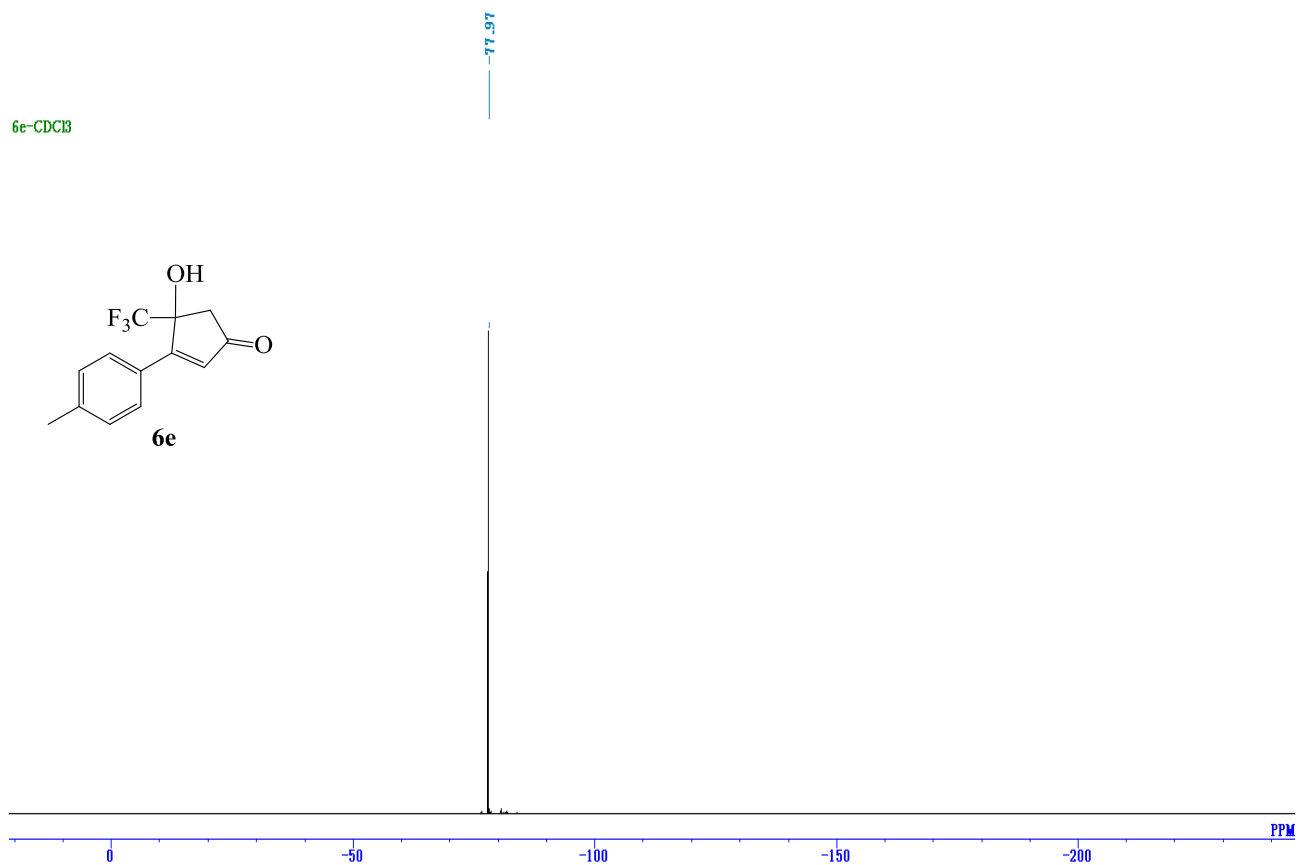
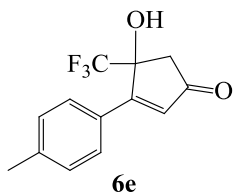
6e-CDCl3



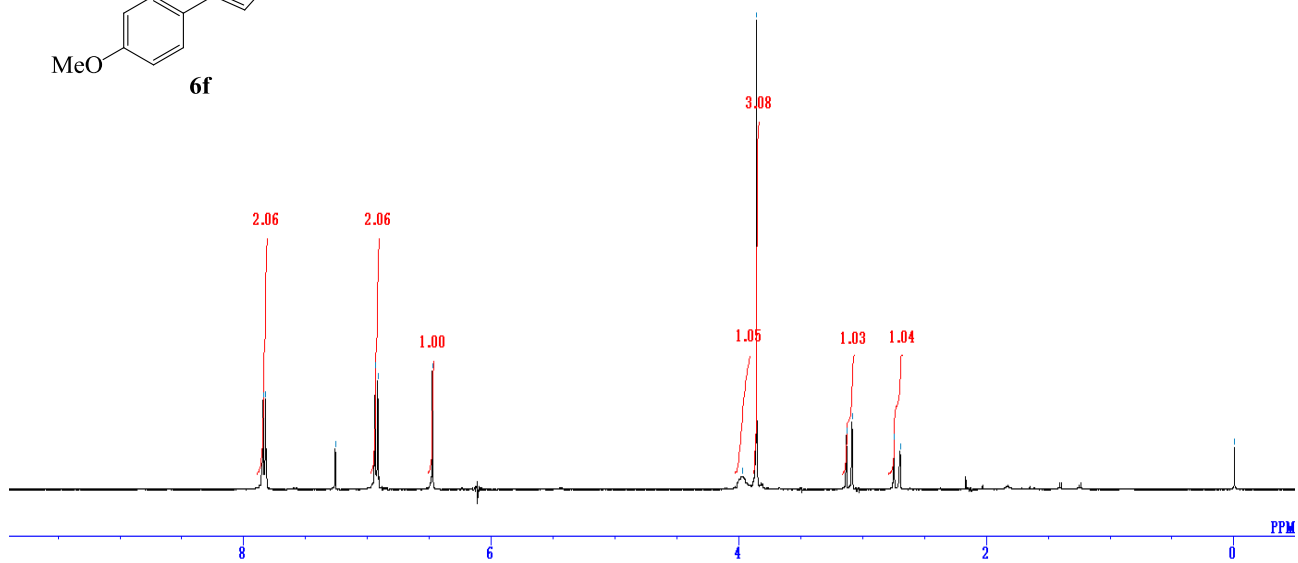
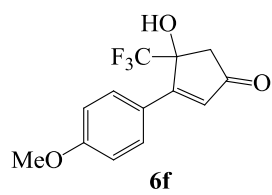
6e-CDCl3

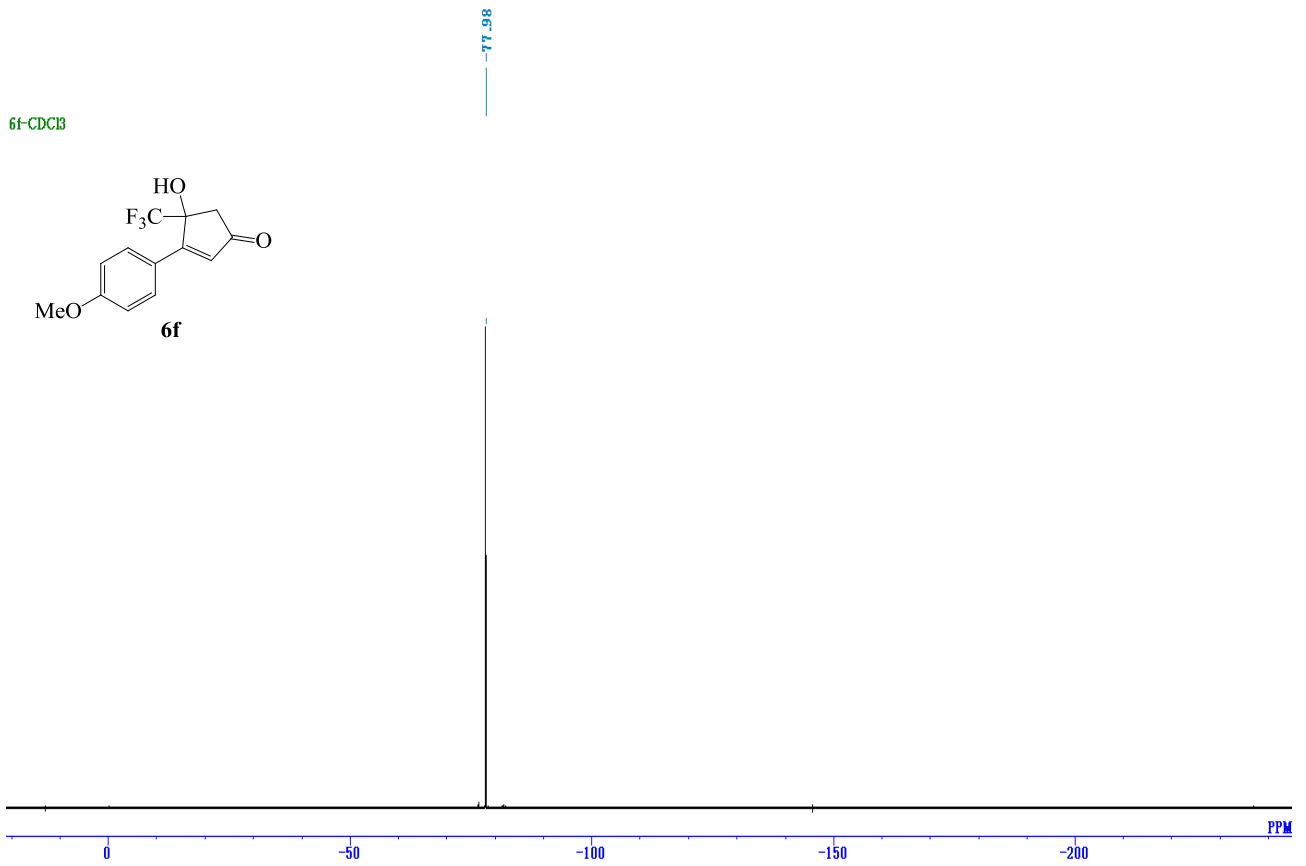
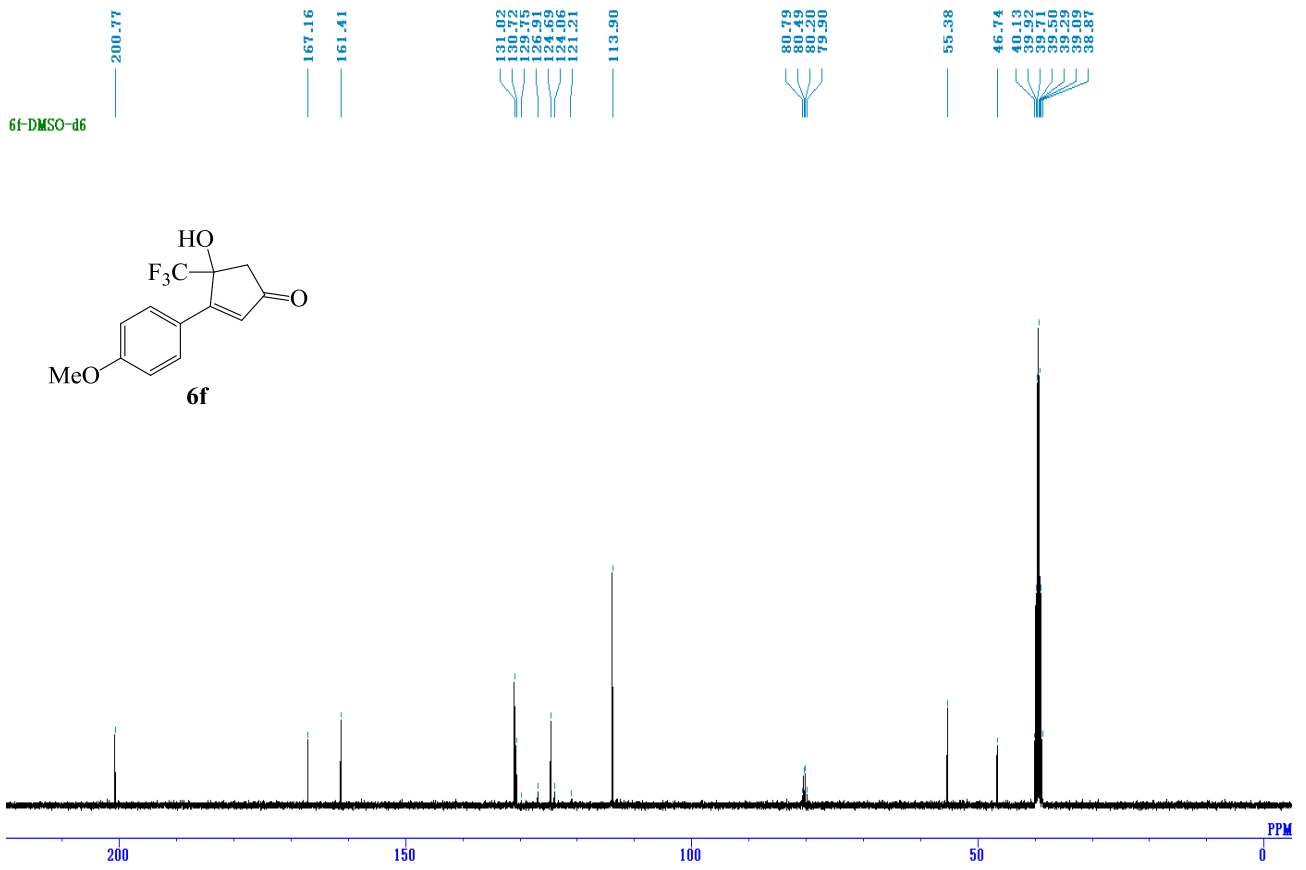


6e-CDCl₃

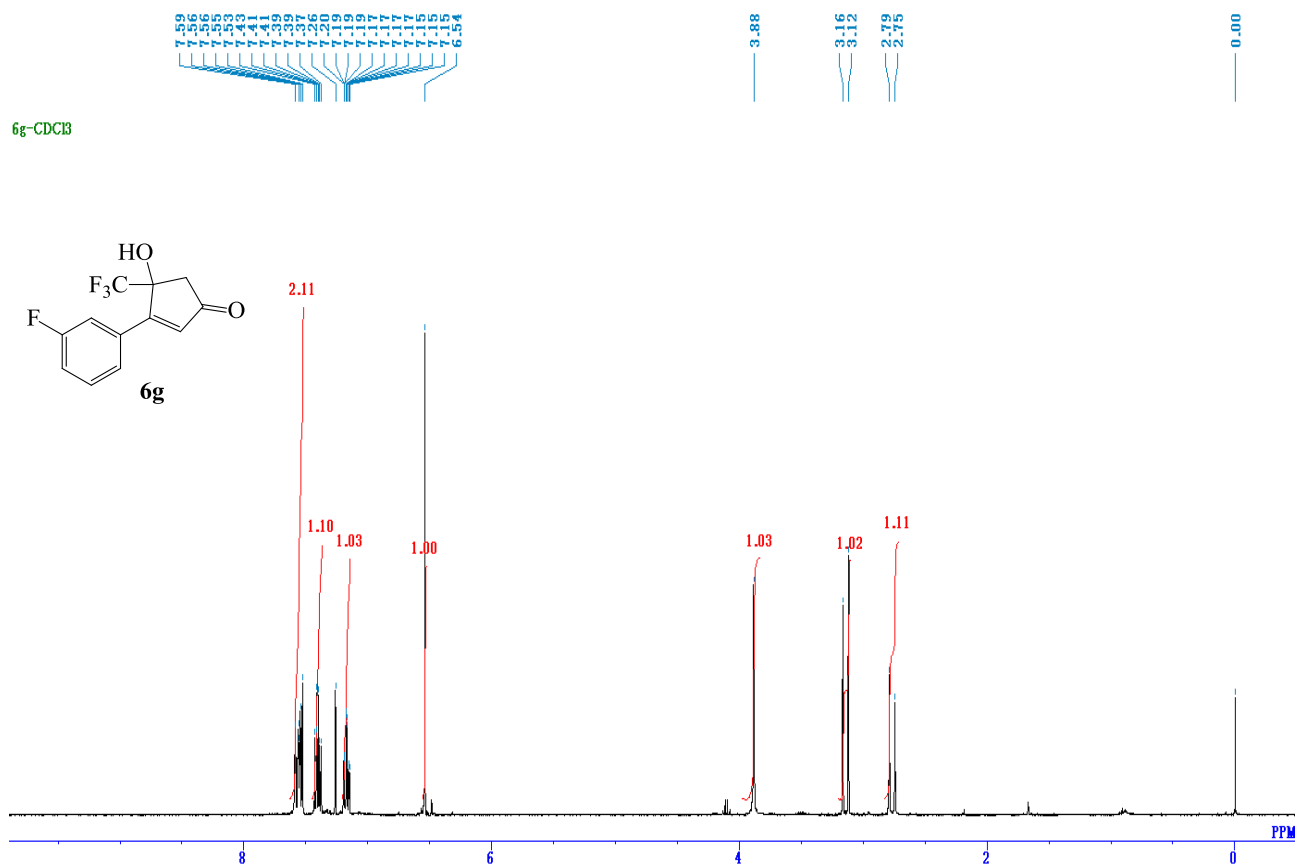
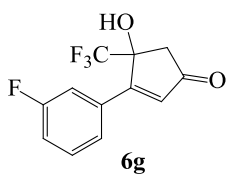


6f-CDCl₃

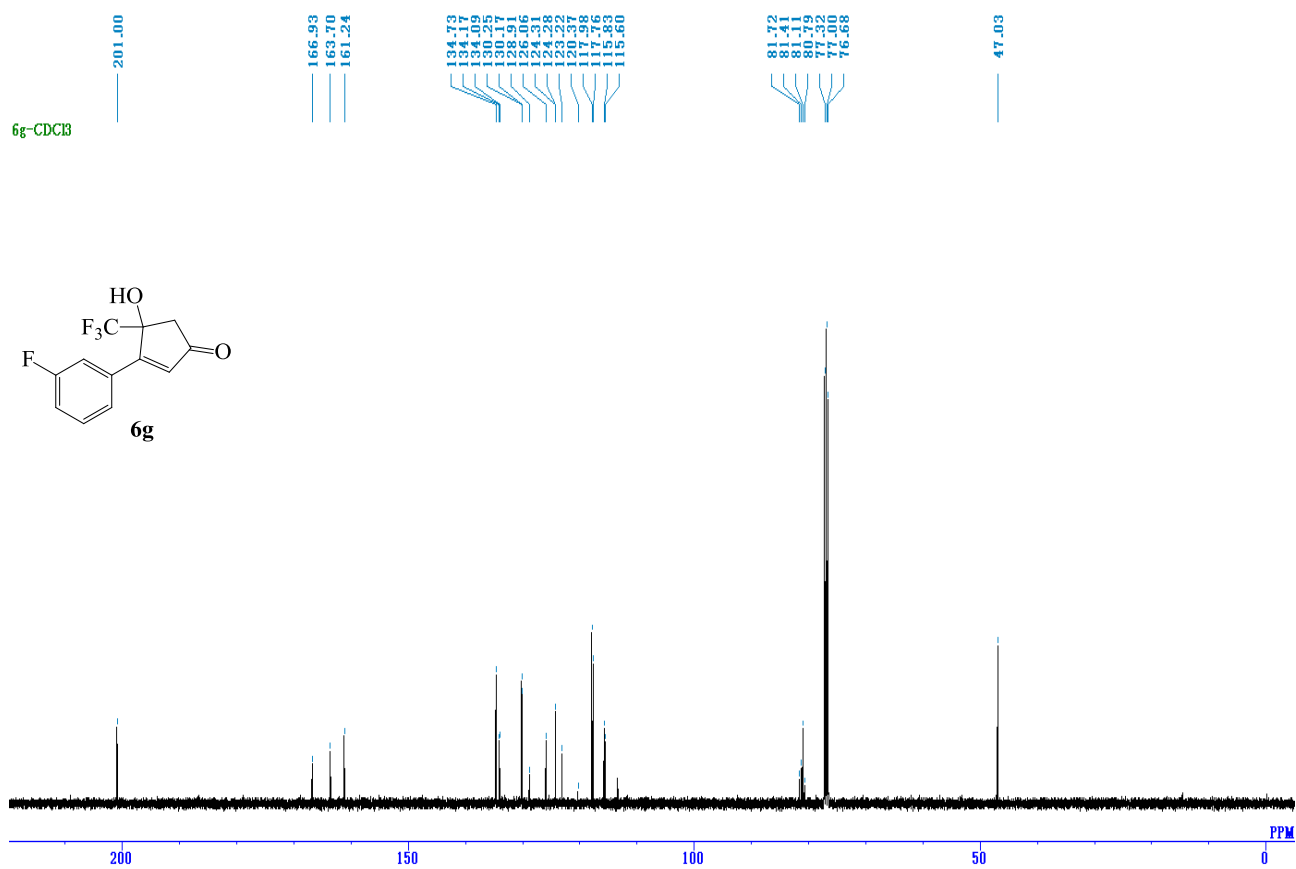
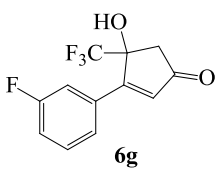




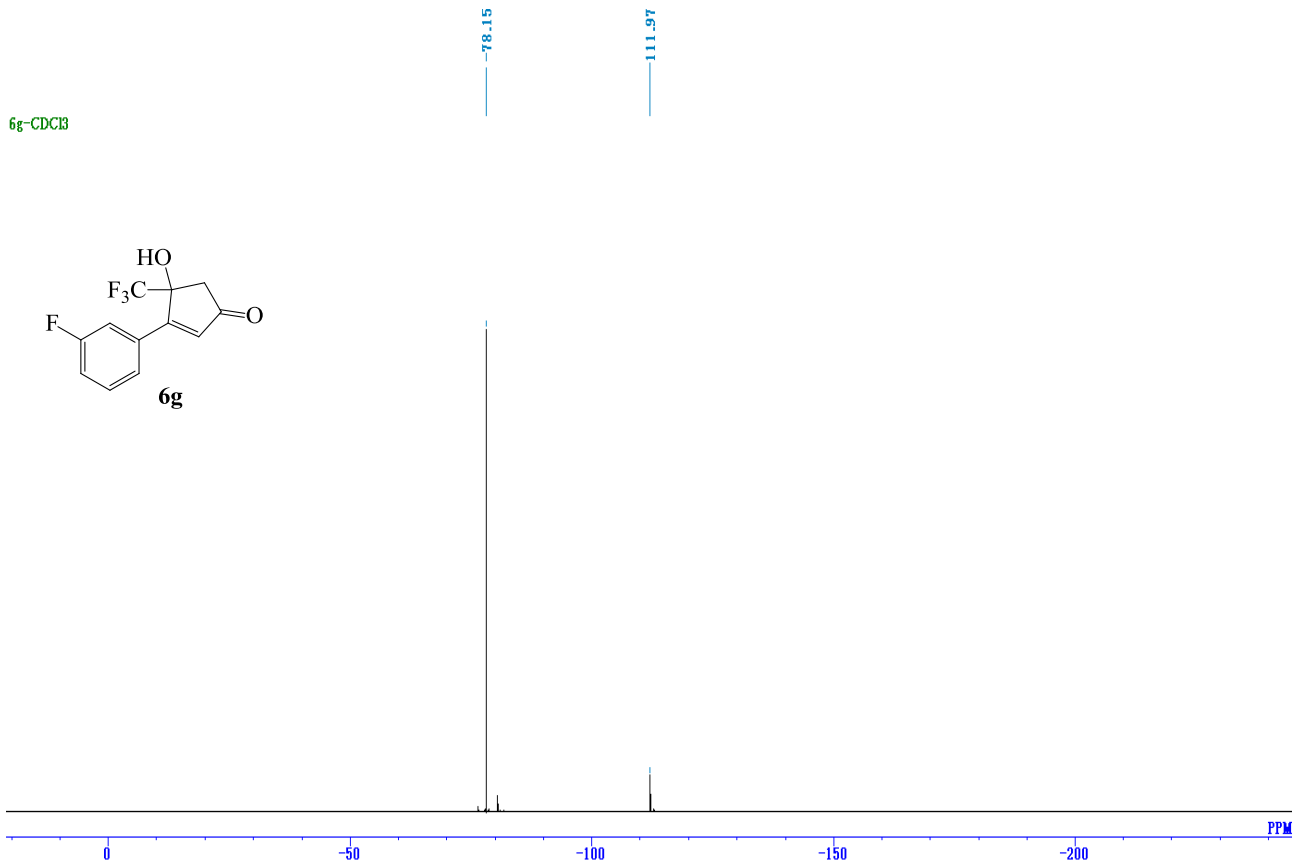
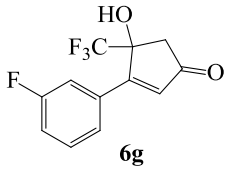
6g-CDCl₃



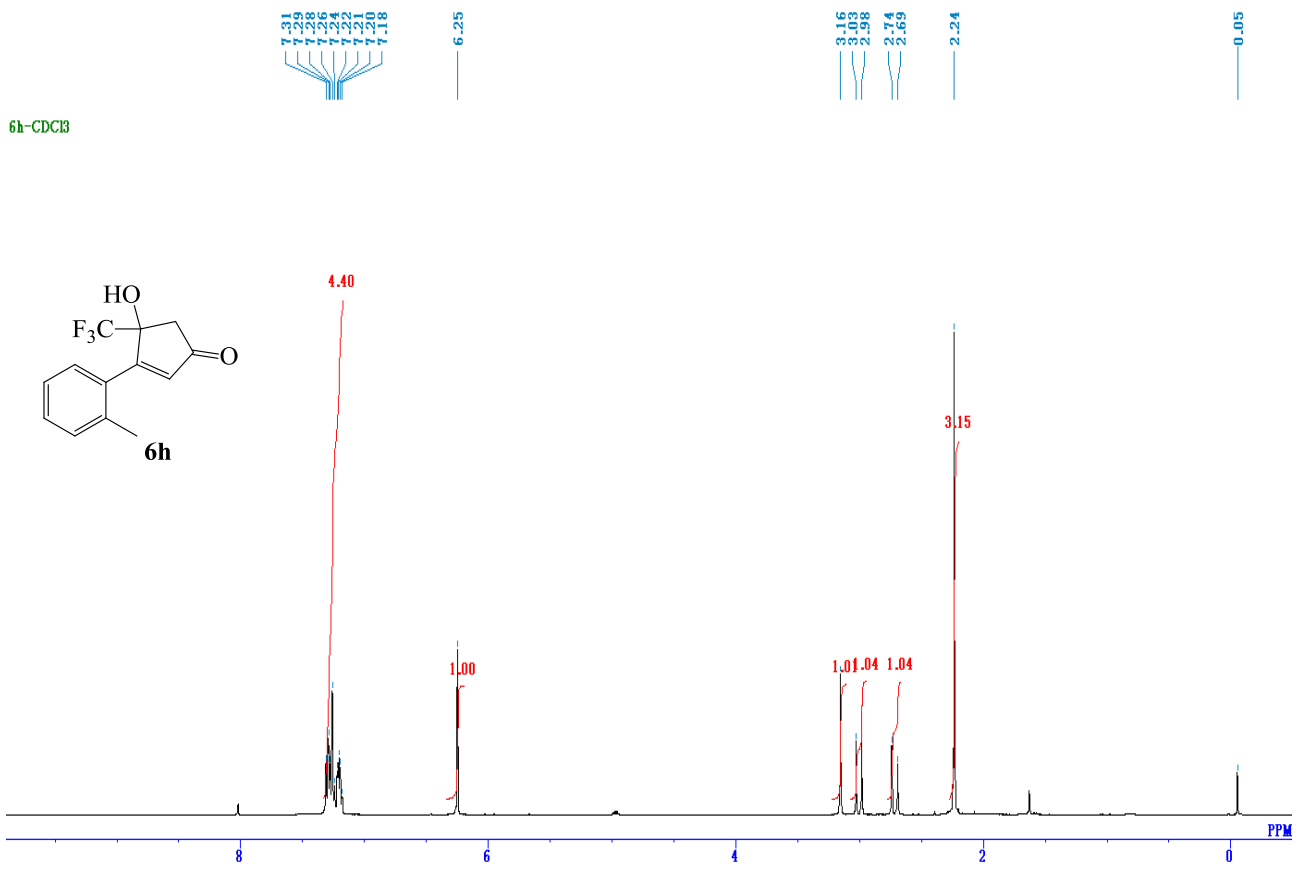
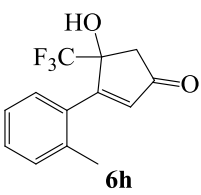
6g-CDCl₃

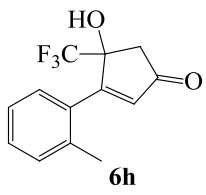
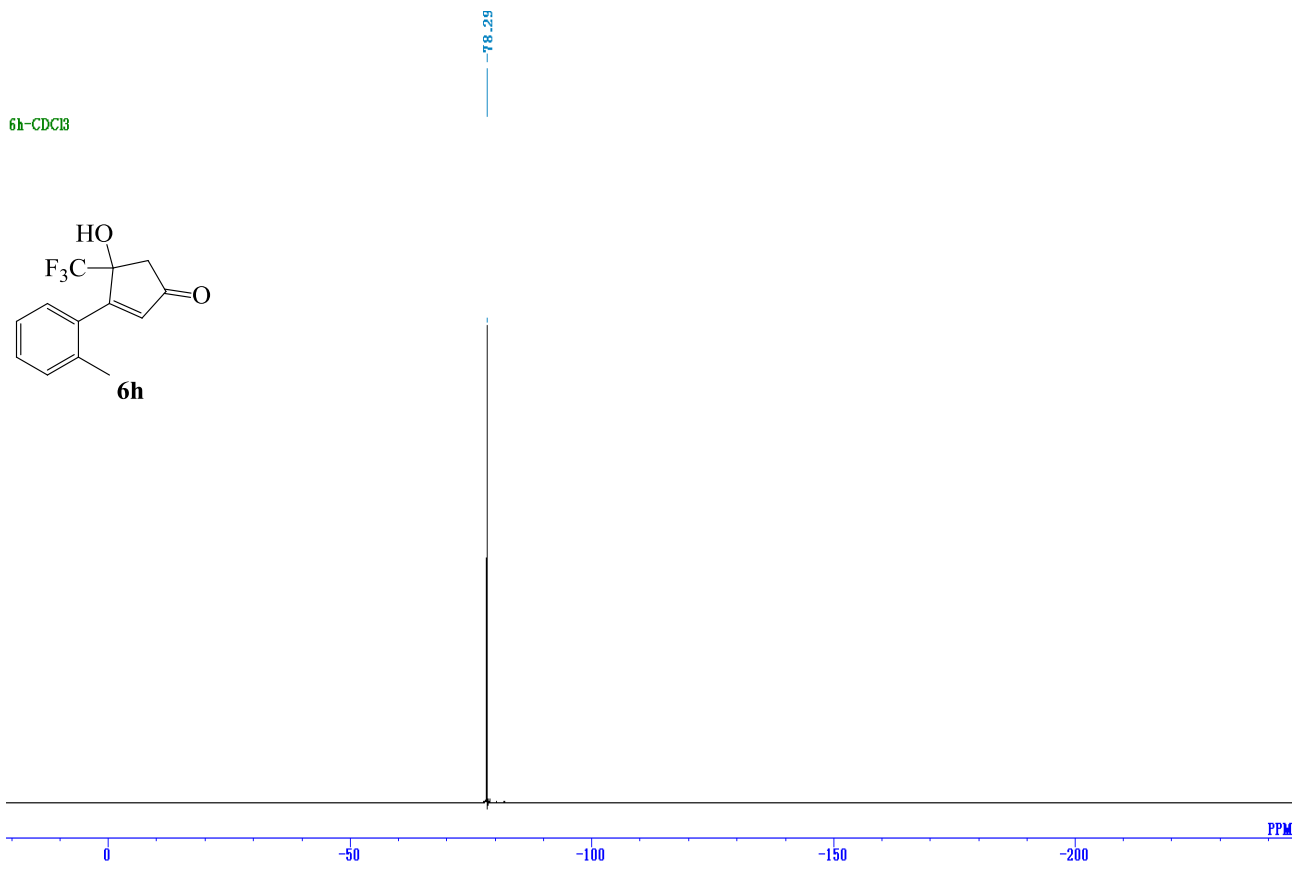
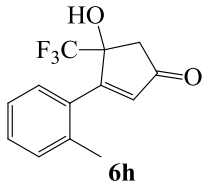
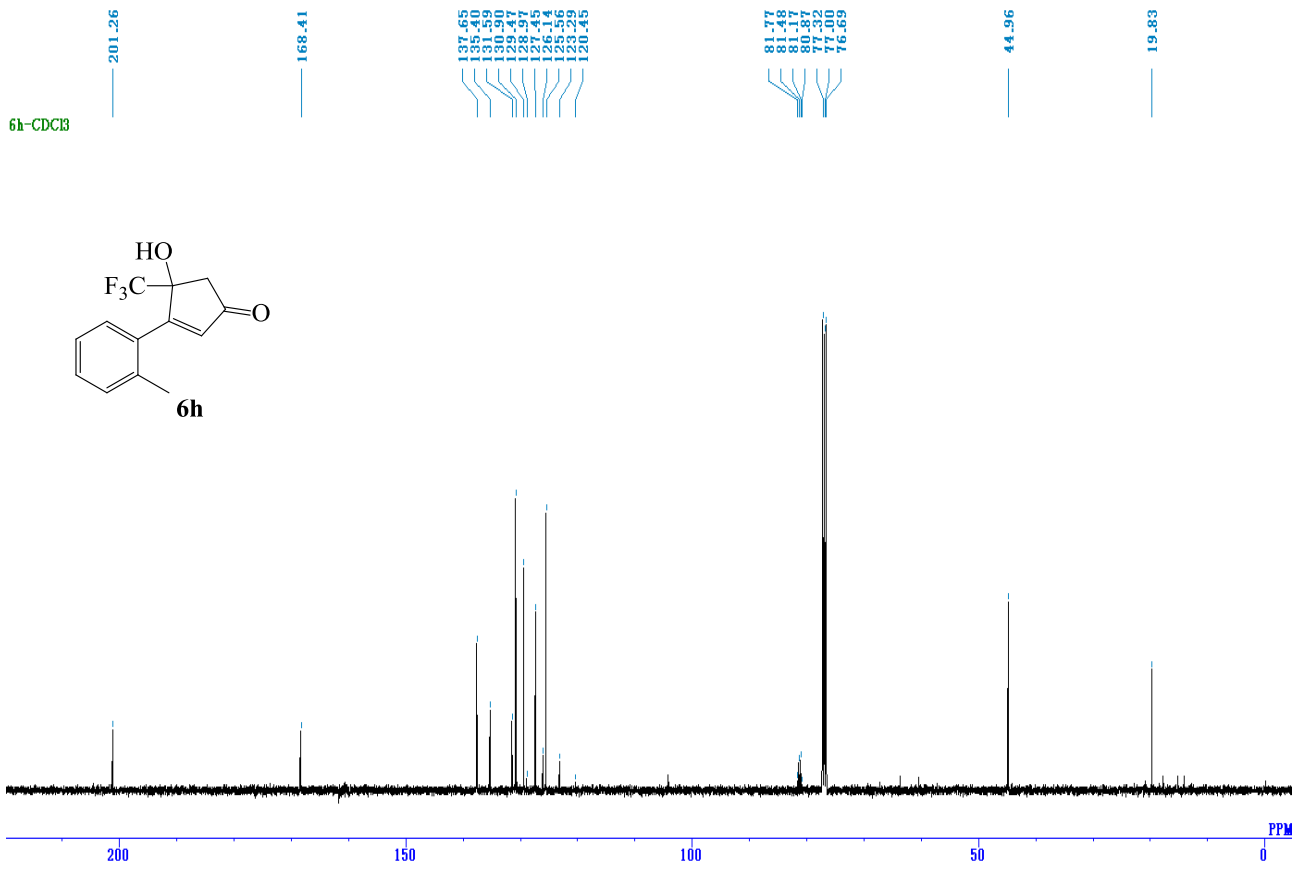


6g-CDCl₃



6h-CDCl₃





6i-CDCB

7.79
7.77
7.71
7.62
7.60
7.57
7.55
7.26

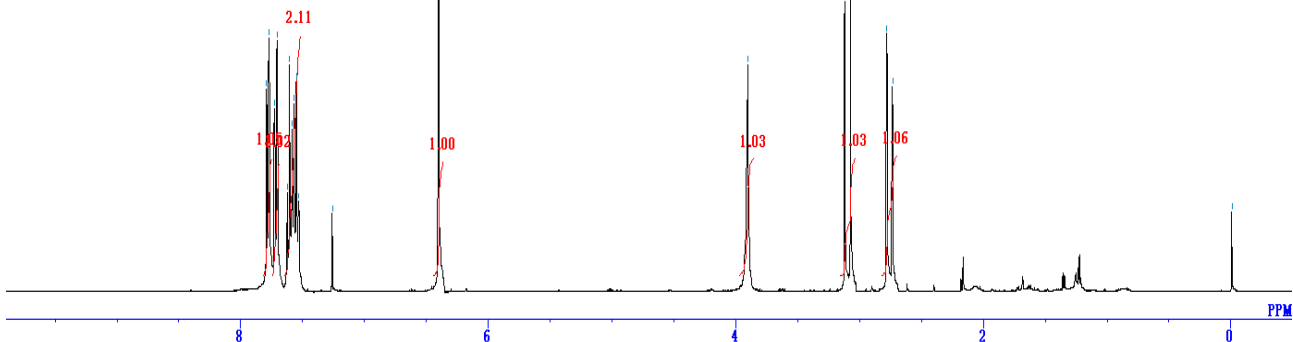
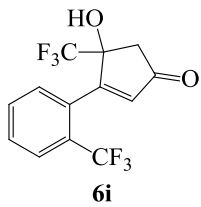
6.40

3.90

3.12
3.07

2.78
2.74

0.01



6i-CDCB

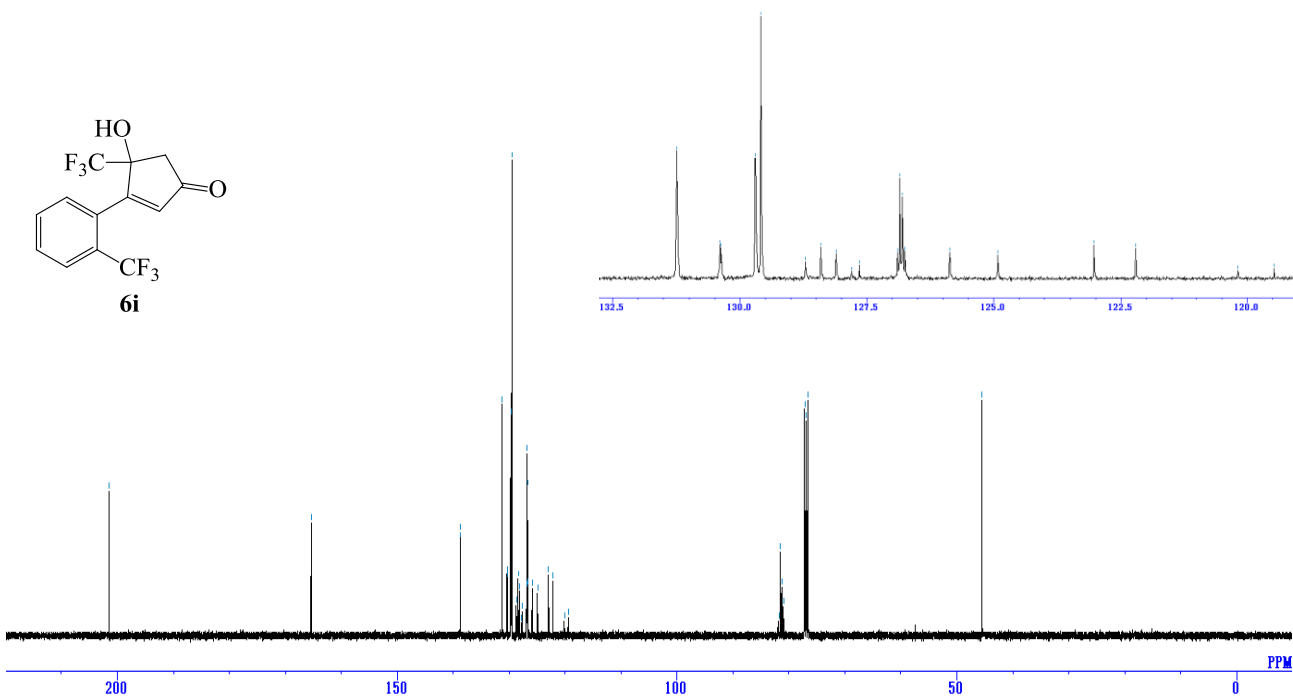
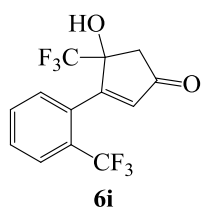
201.46

165.39

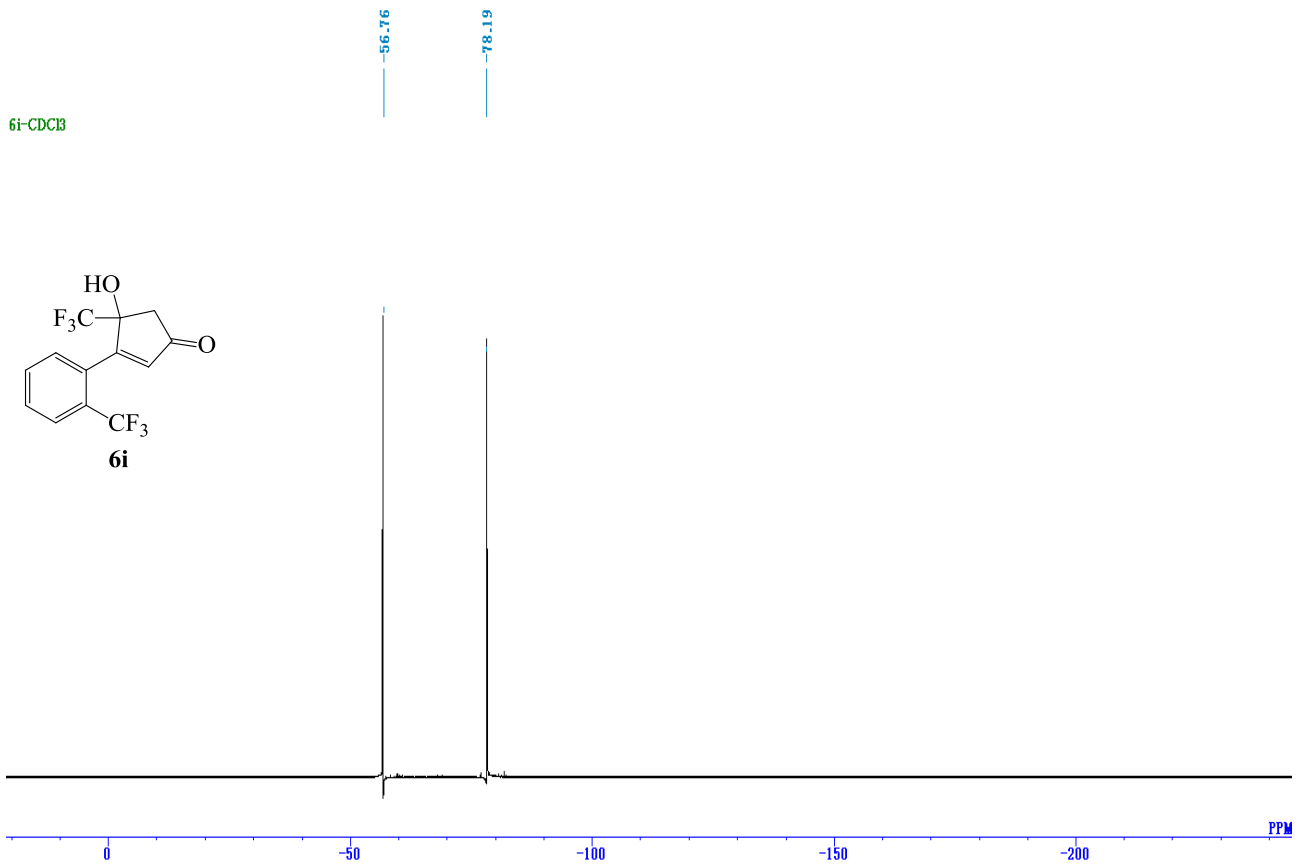
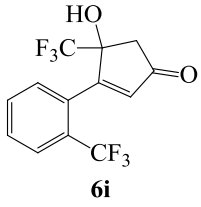
138.71
138.69
131.26
130.48
129.70
129.59
128.71
128.11
127.81
127.65
126.85
126.80
126.75
124.92
123.03
122.20
121.43
119.48

81.92
81.59
80.59
77.31
77.00
76.68

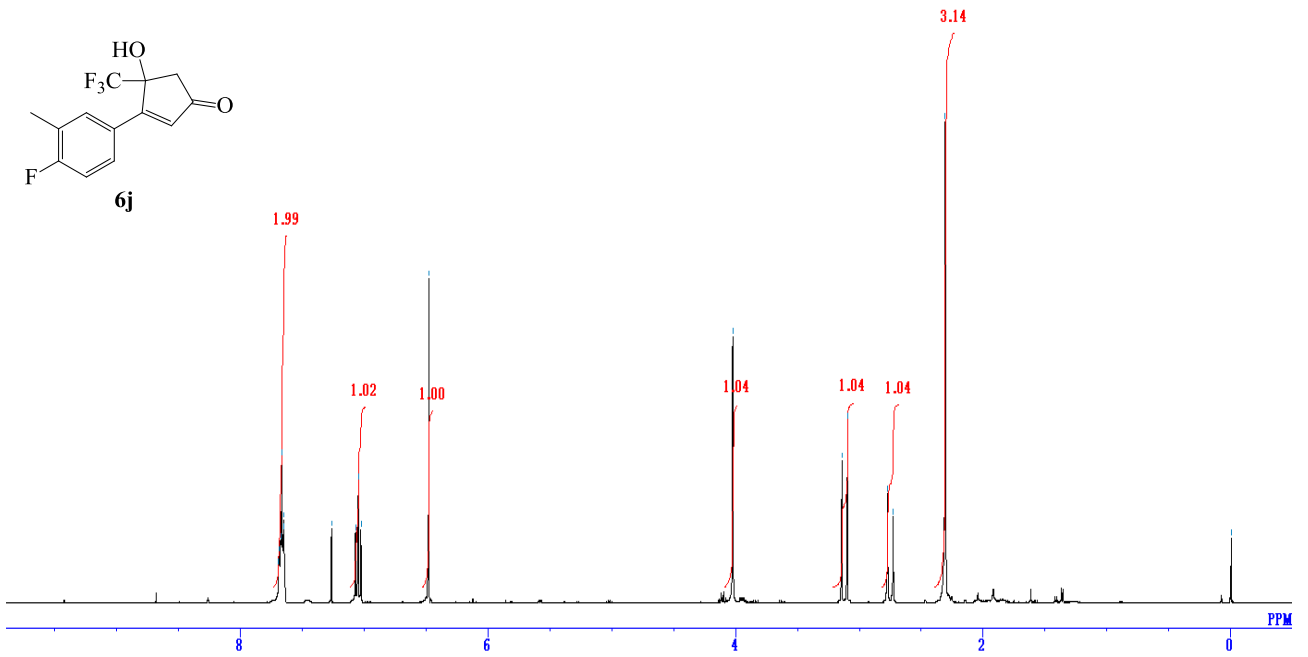
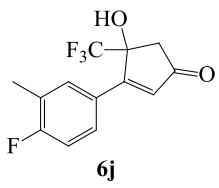
45.67

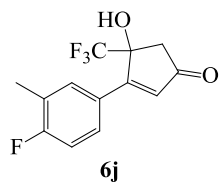
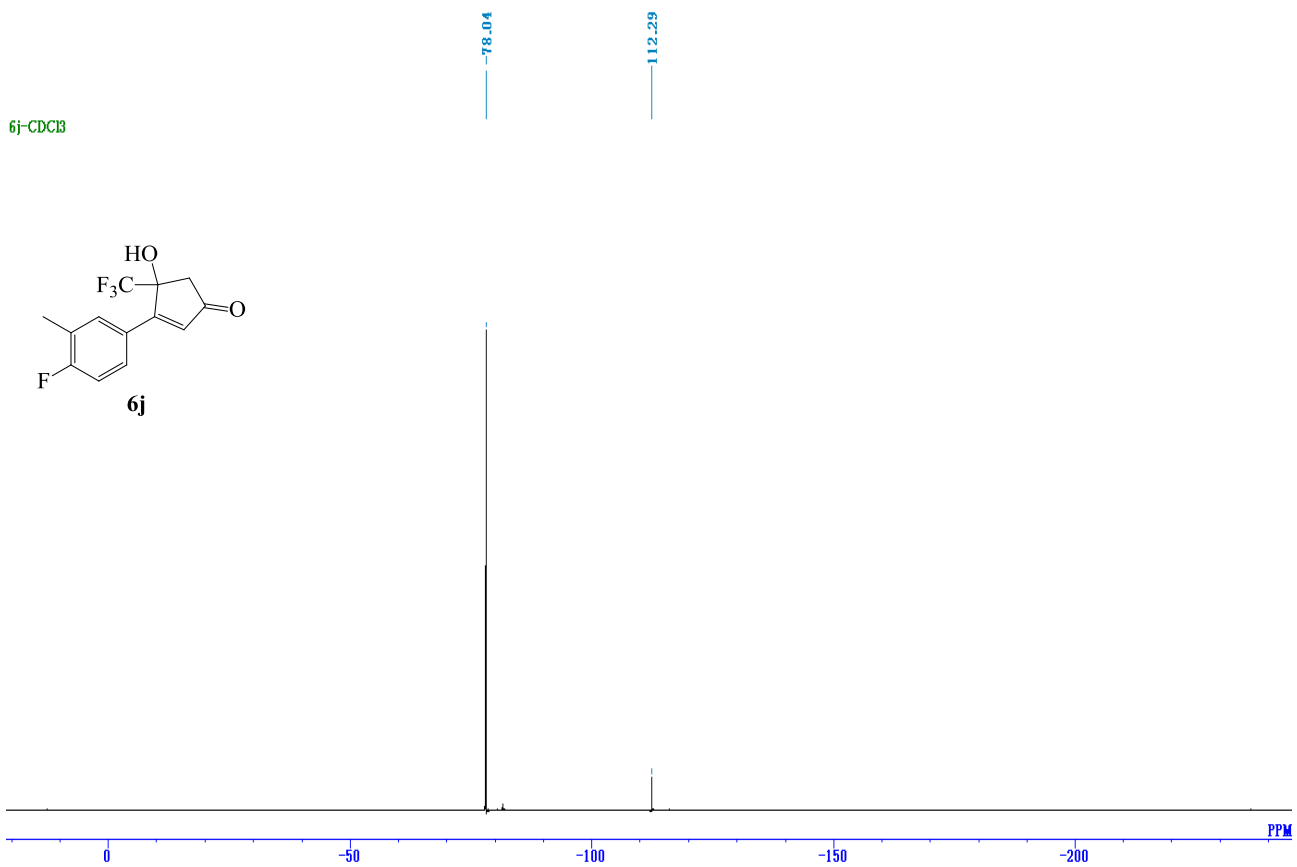
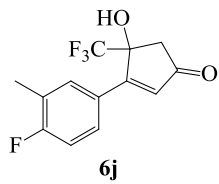
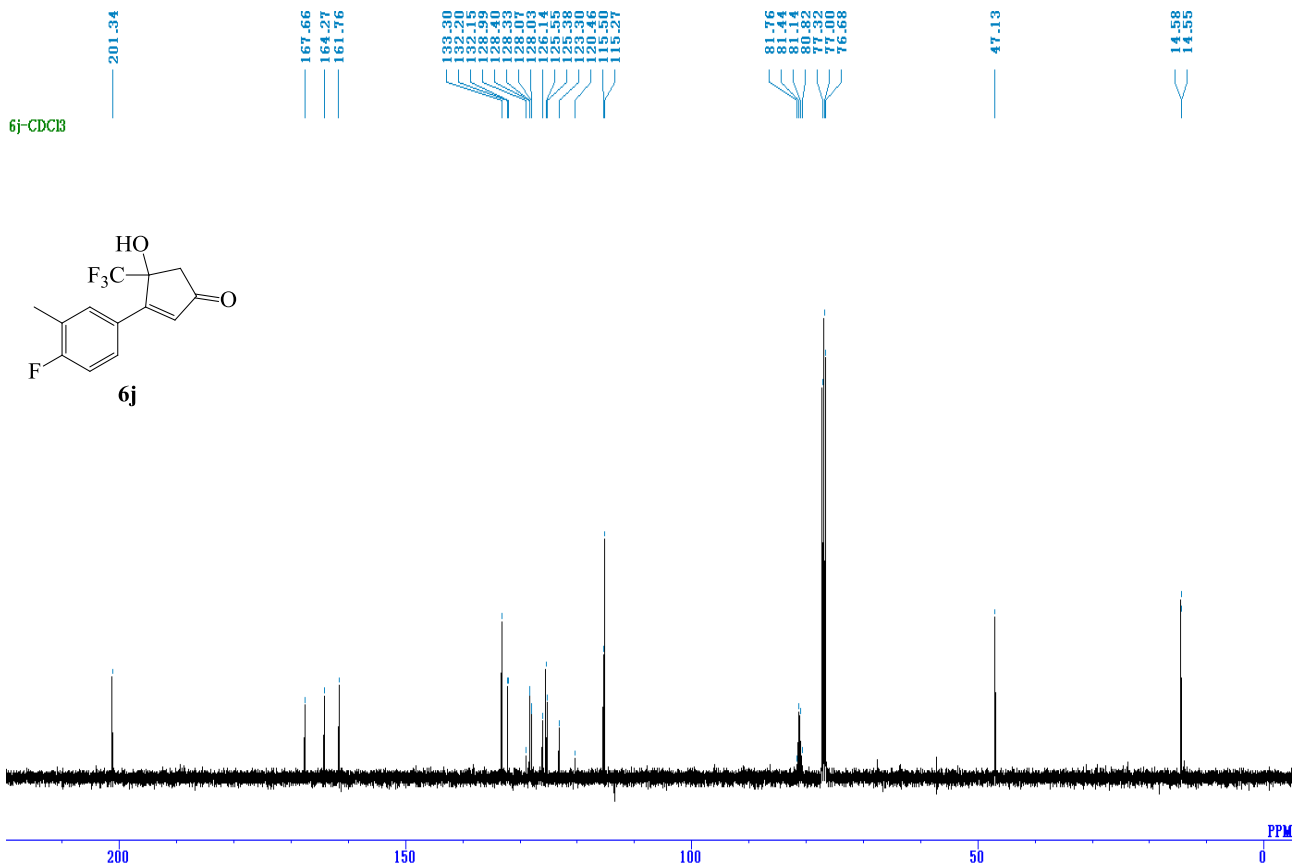


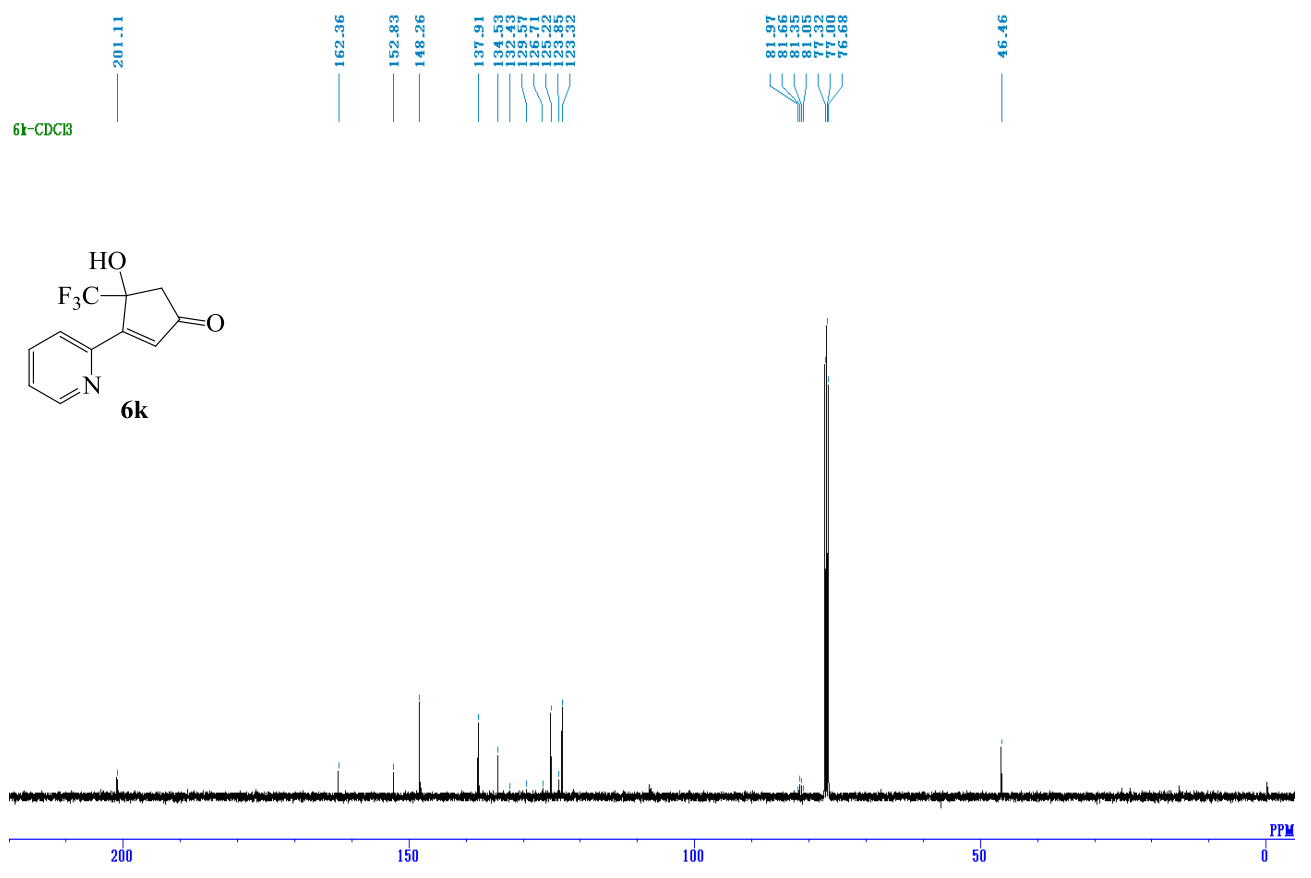
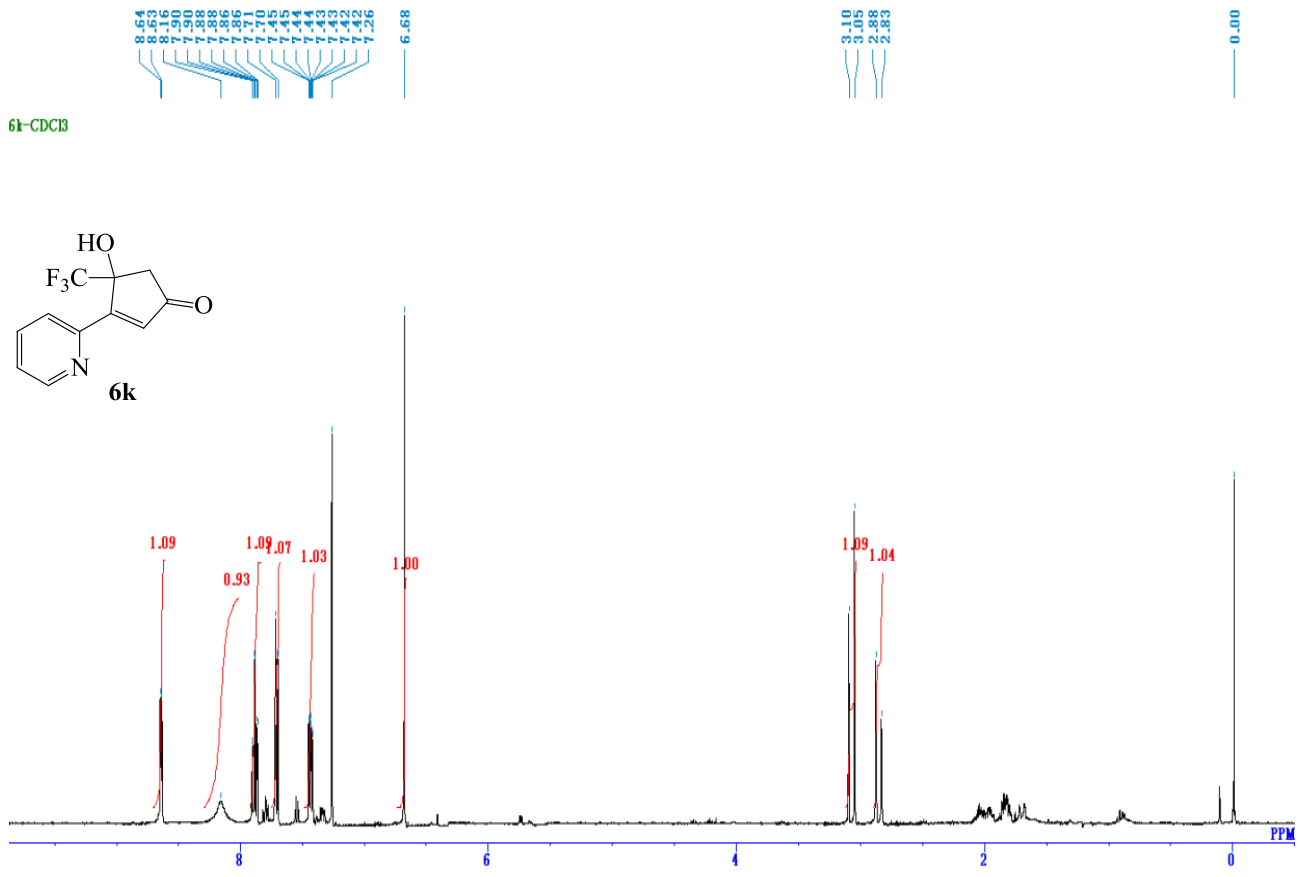
6i-CDCl₃



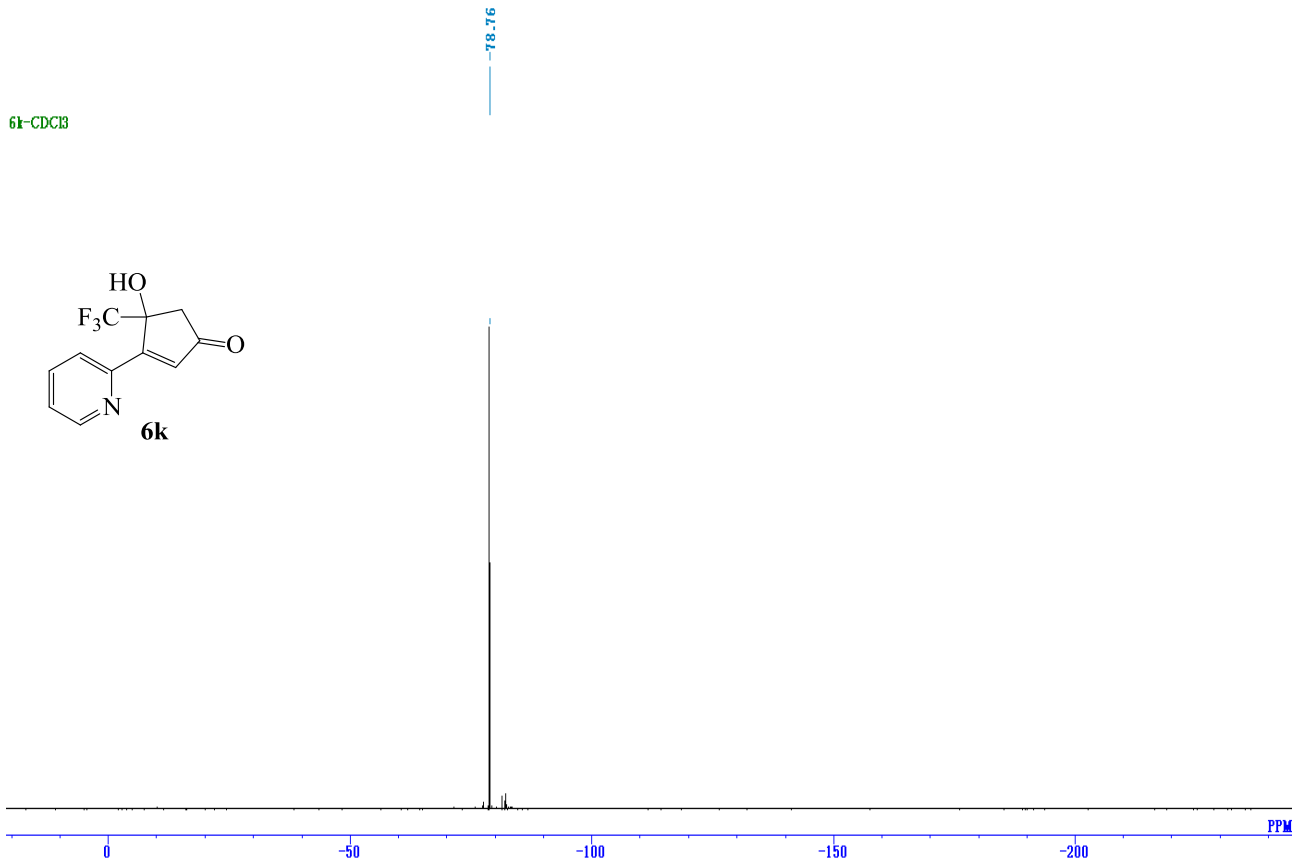
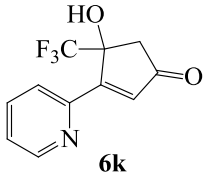
6j-CDCl₃







6k-CDCl₃



7.82
7.81
7.58
7.58
7.26
7.16
7.15
7.14

6.49

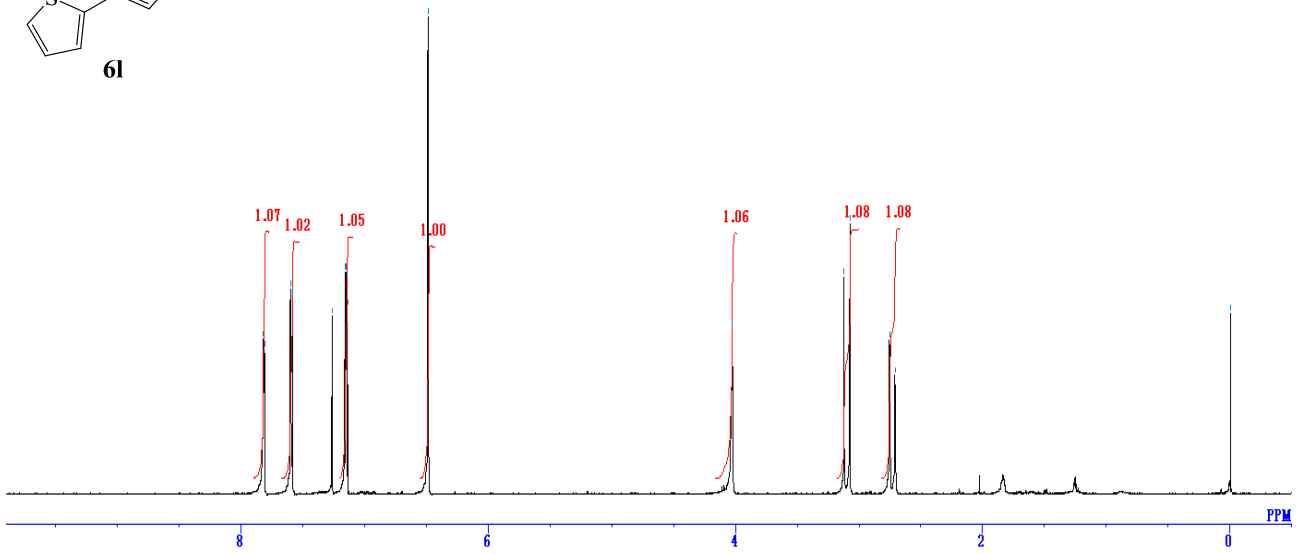
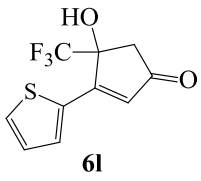
4.03

3.12
3.08

2.76
2.71

0.00

6l-CDCl₃



1.07

1.02

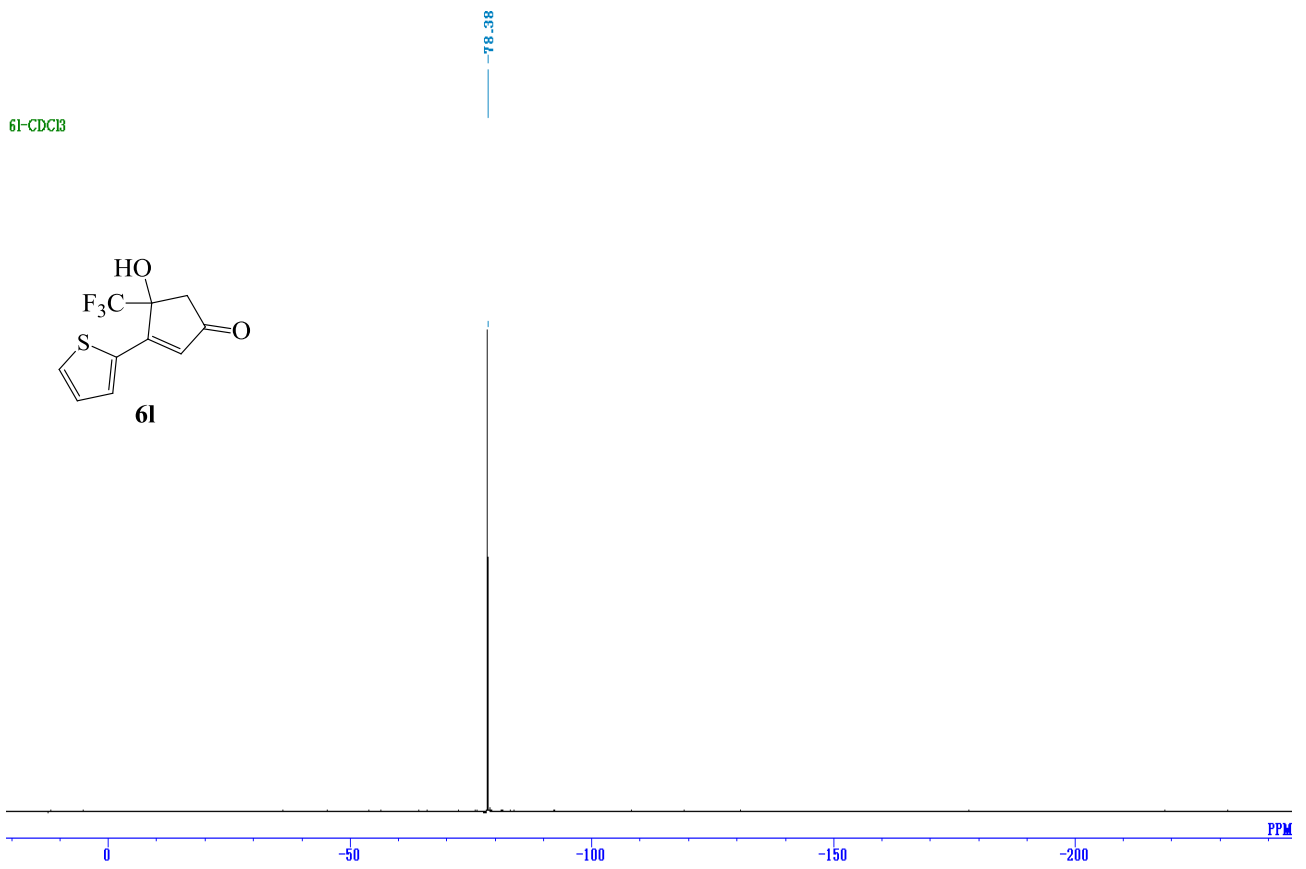
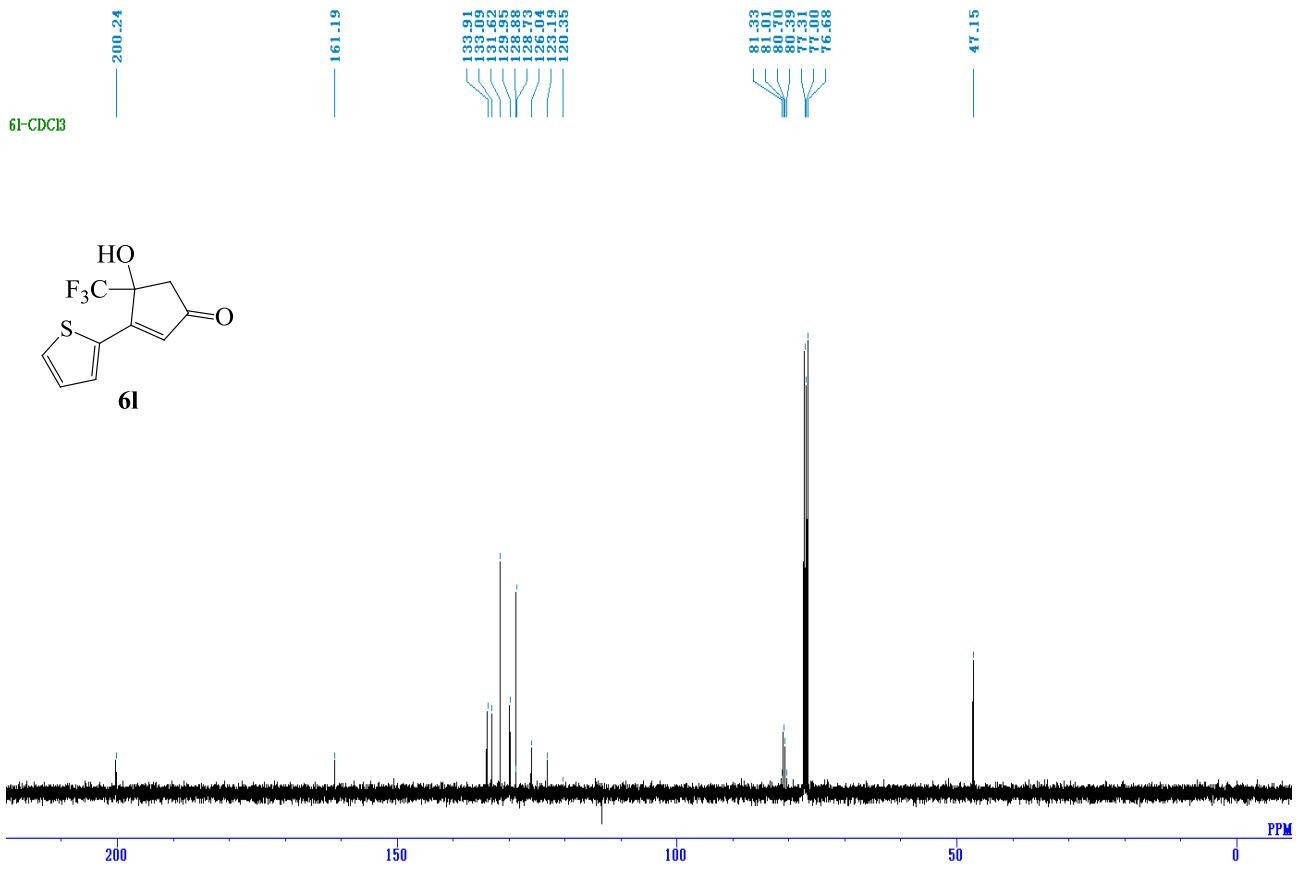
1.05

1.00

1.06

1.08

1.08



60-CDCl₃

7.78
7.76
7.48
7.46
7.46
7.43
7.42
7.41
7.39
7.26

6.49

4.22

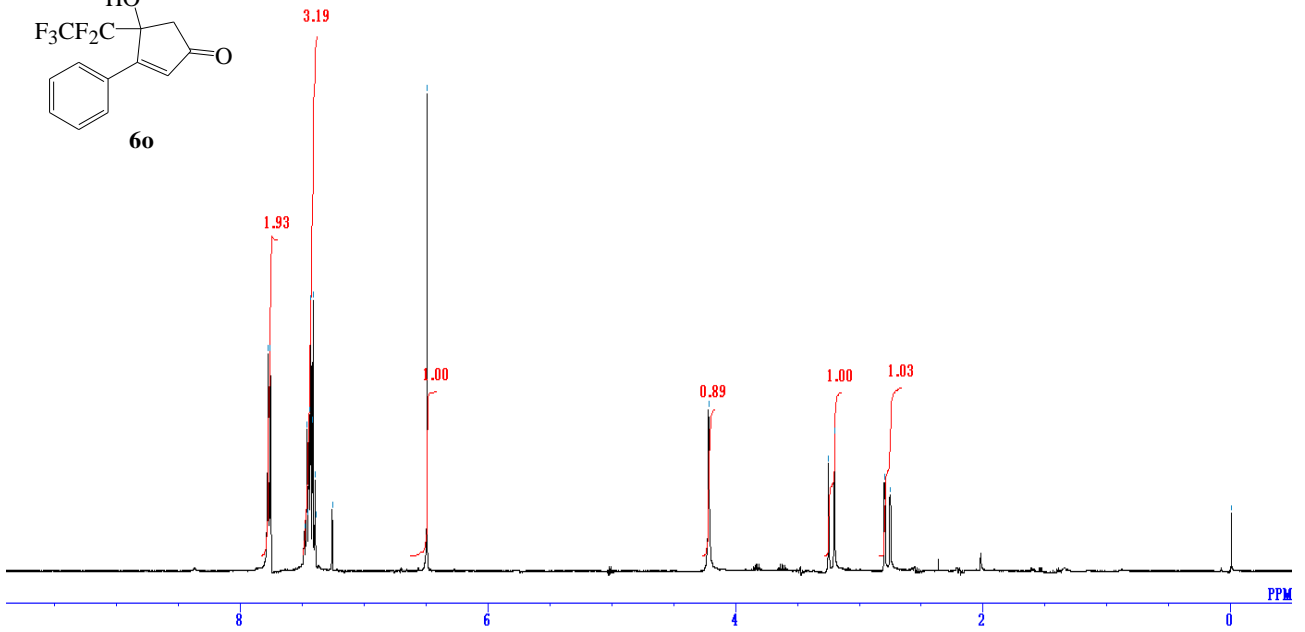
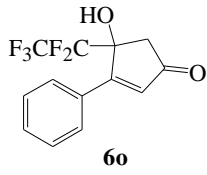
3.25

3.20

2.80

2.75

0.00



60-CDCl₃

201.60

169.64

134.07
132.98
130.88
128.32
128.32
123.49
123.14
122.78
122.68
120.27
119.91
117.75
117.36
117.04
117.00
116.29
116.29
114.90
114.72
114.37
114.37
114.18
114.01
113.82
113.76
111.41
111.05

81.98

81.49

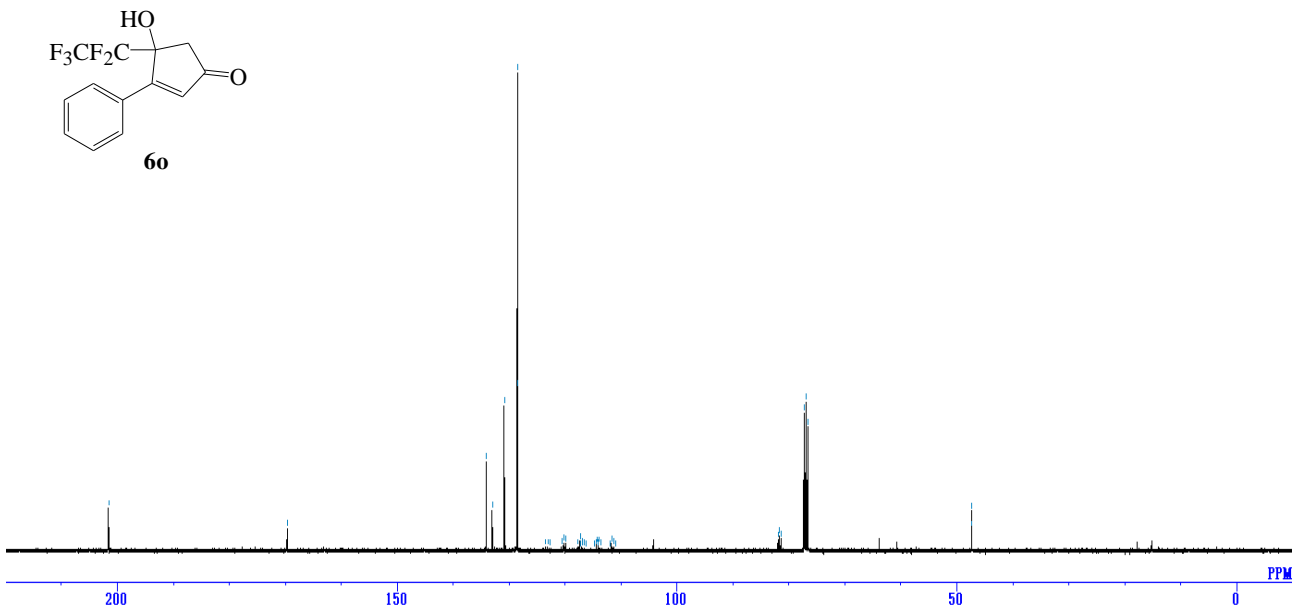
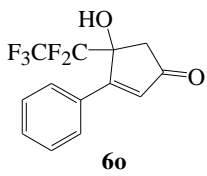
77.02

76.68

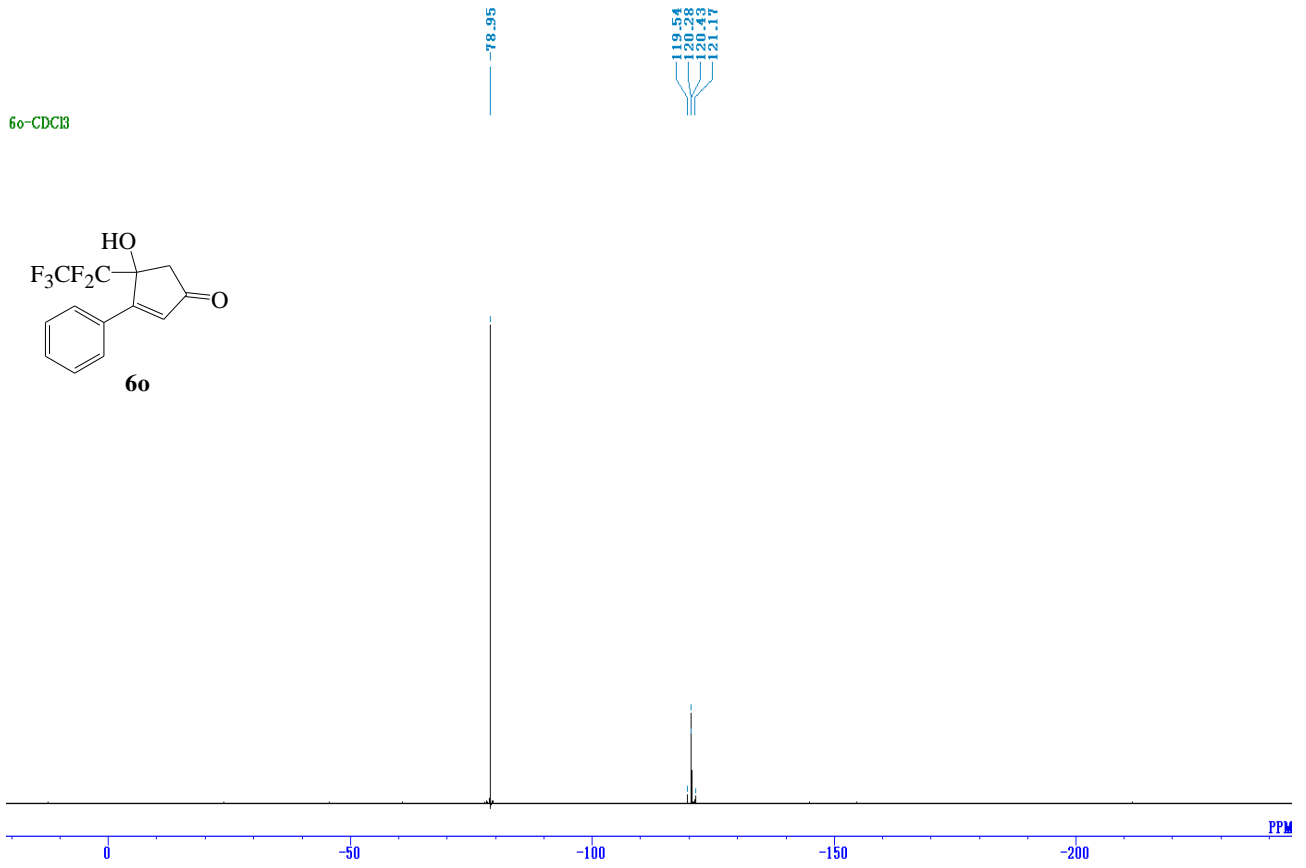
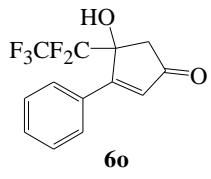
47.44

47.42

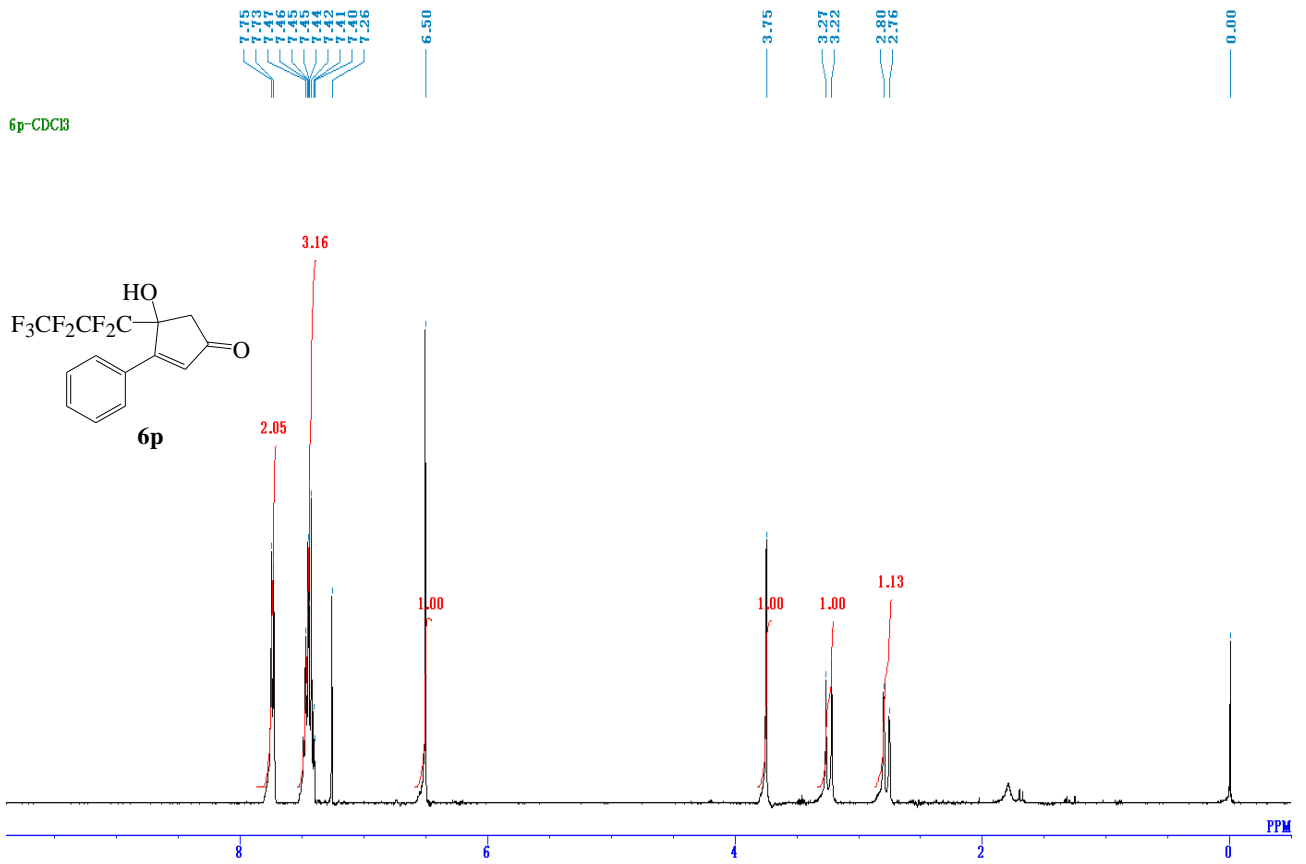
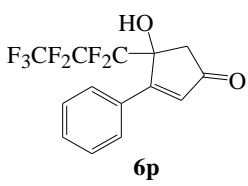
47.37

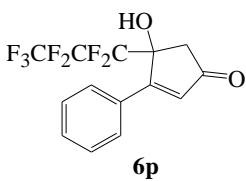
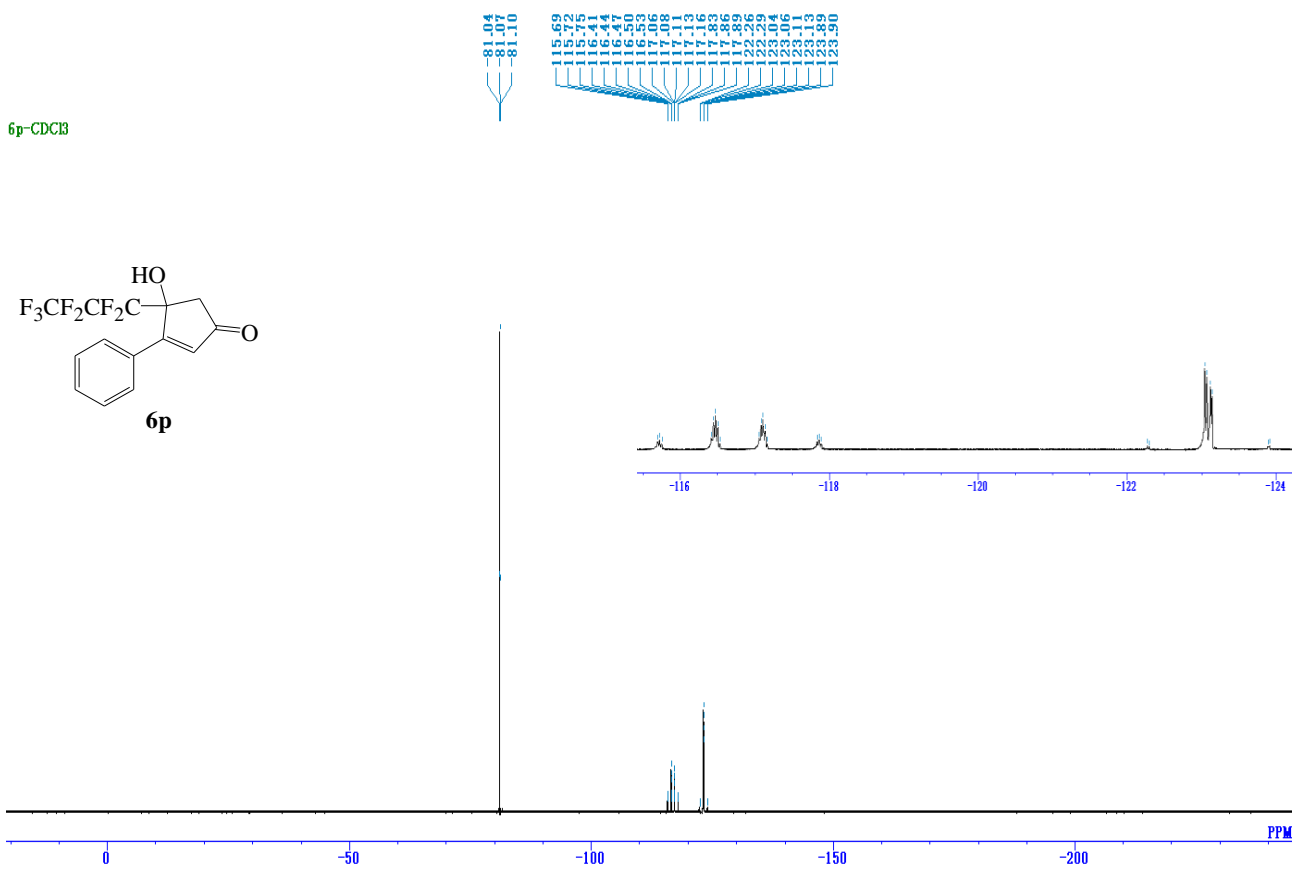
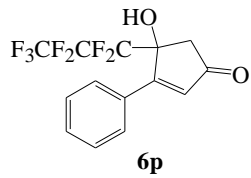
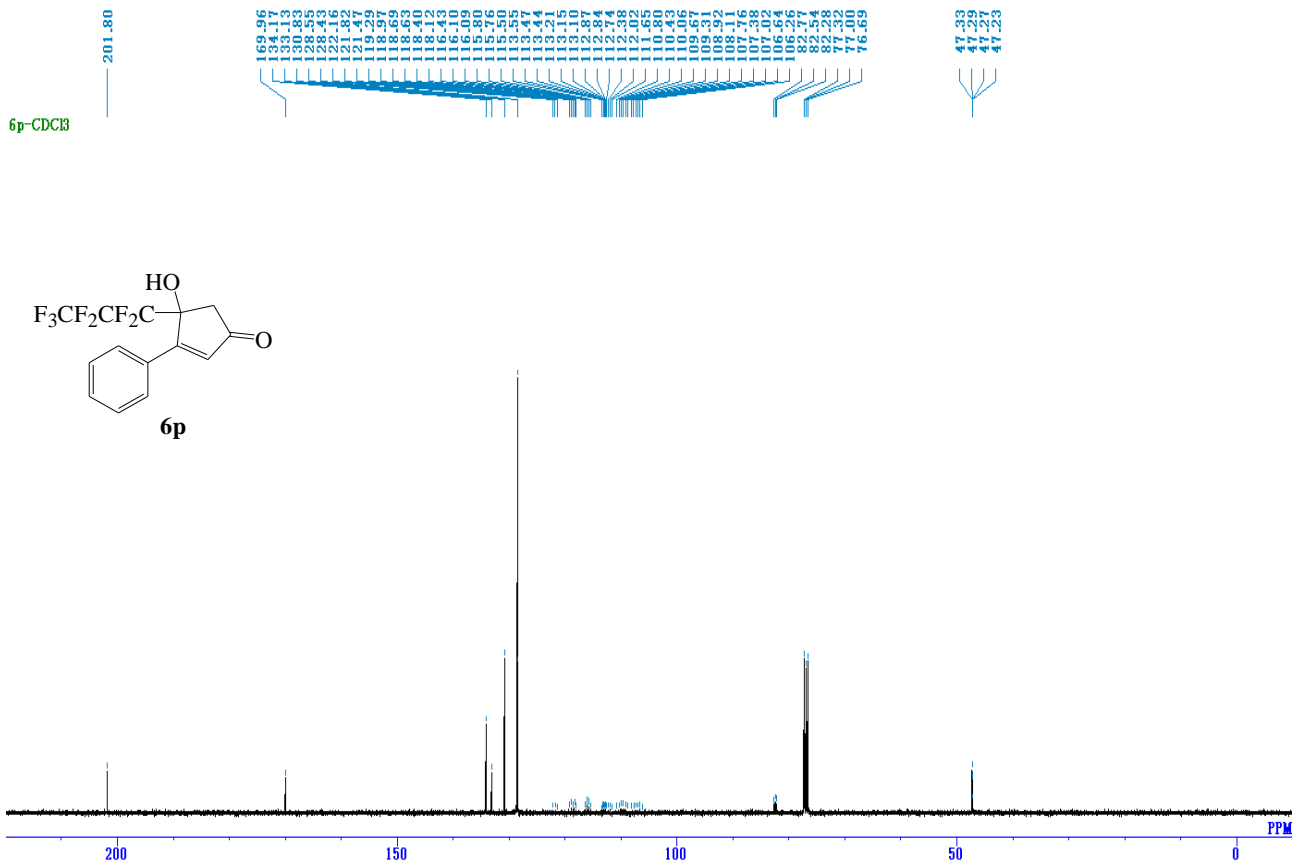


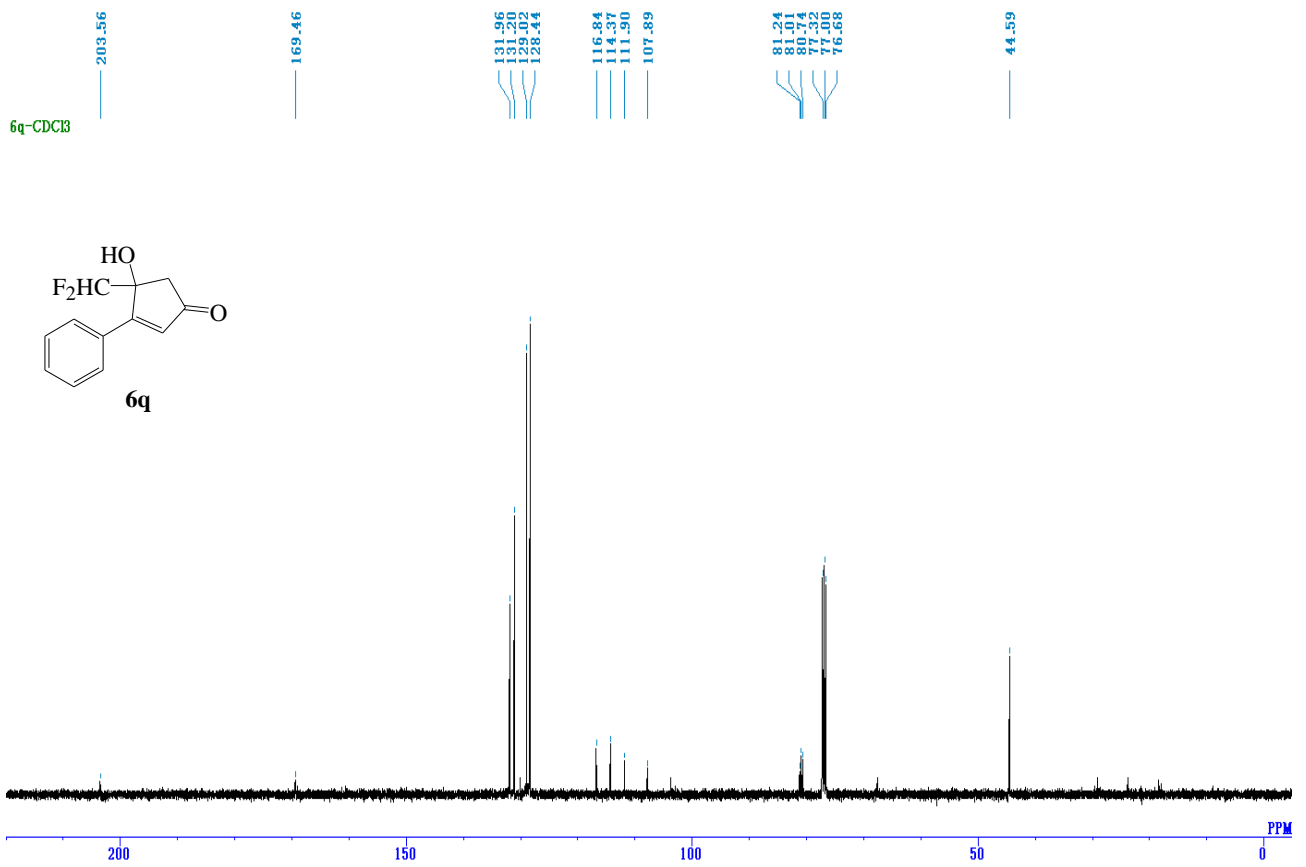
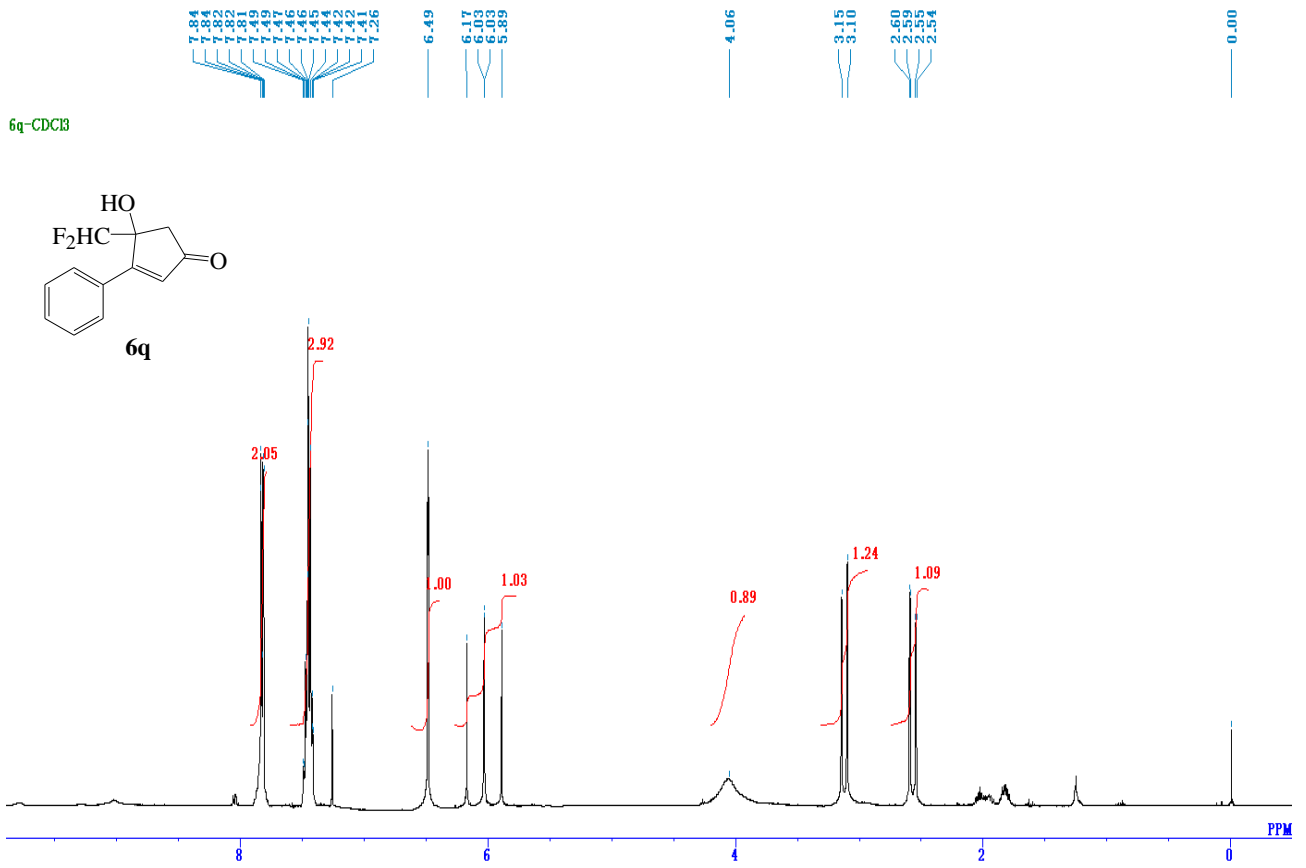
6o-CDCB3



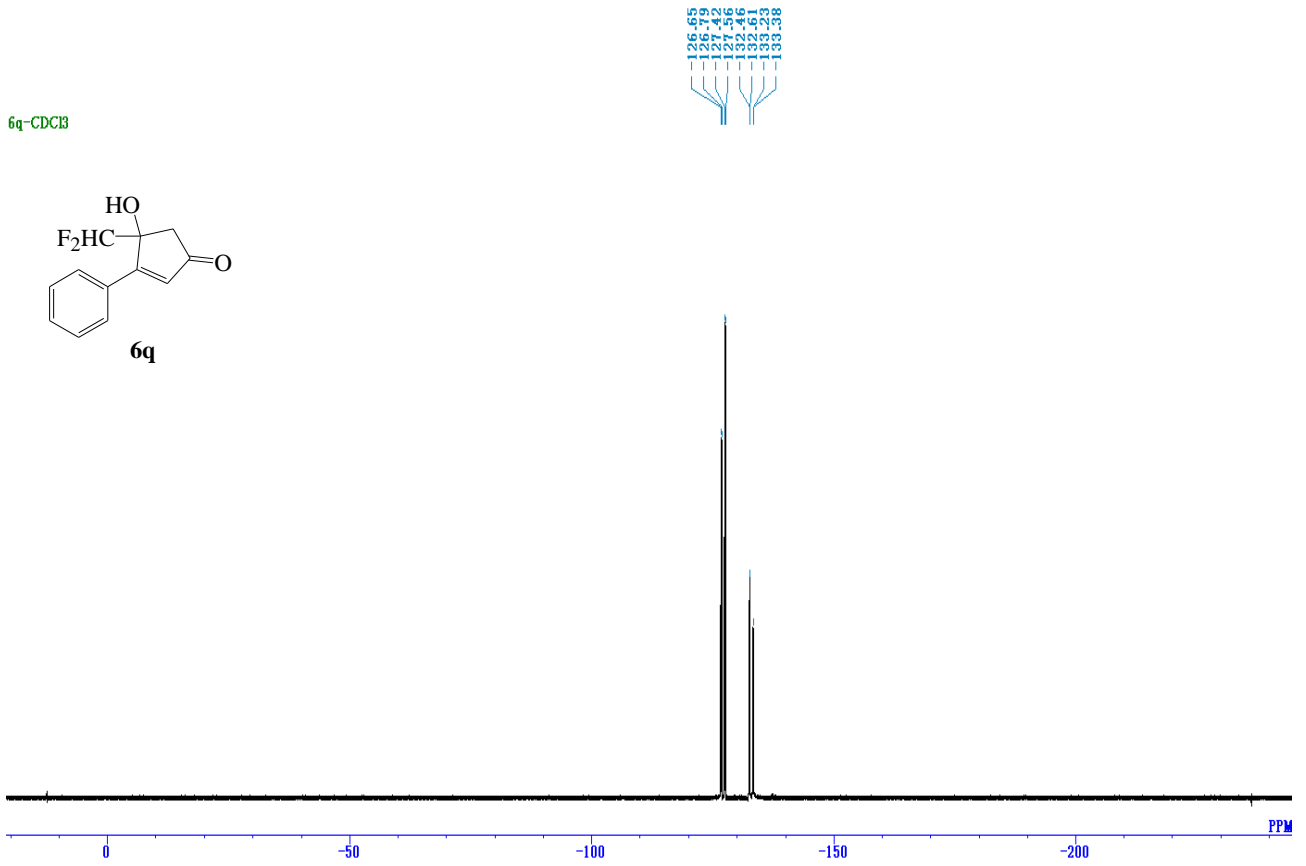
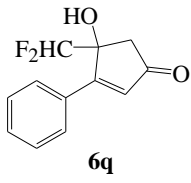
6p-CDCB3



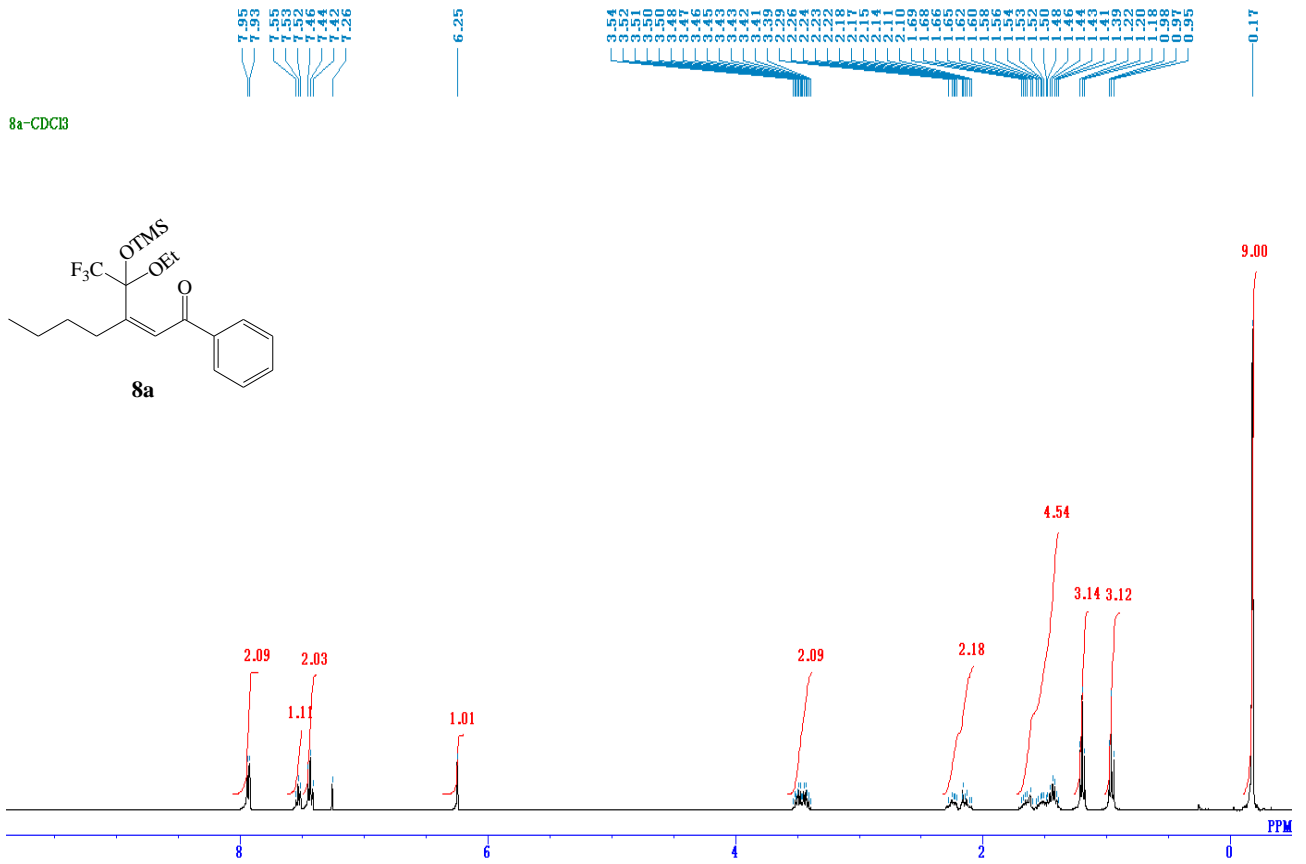
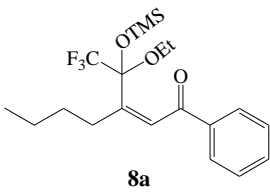


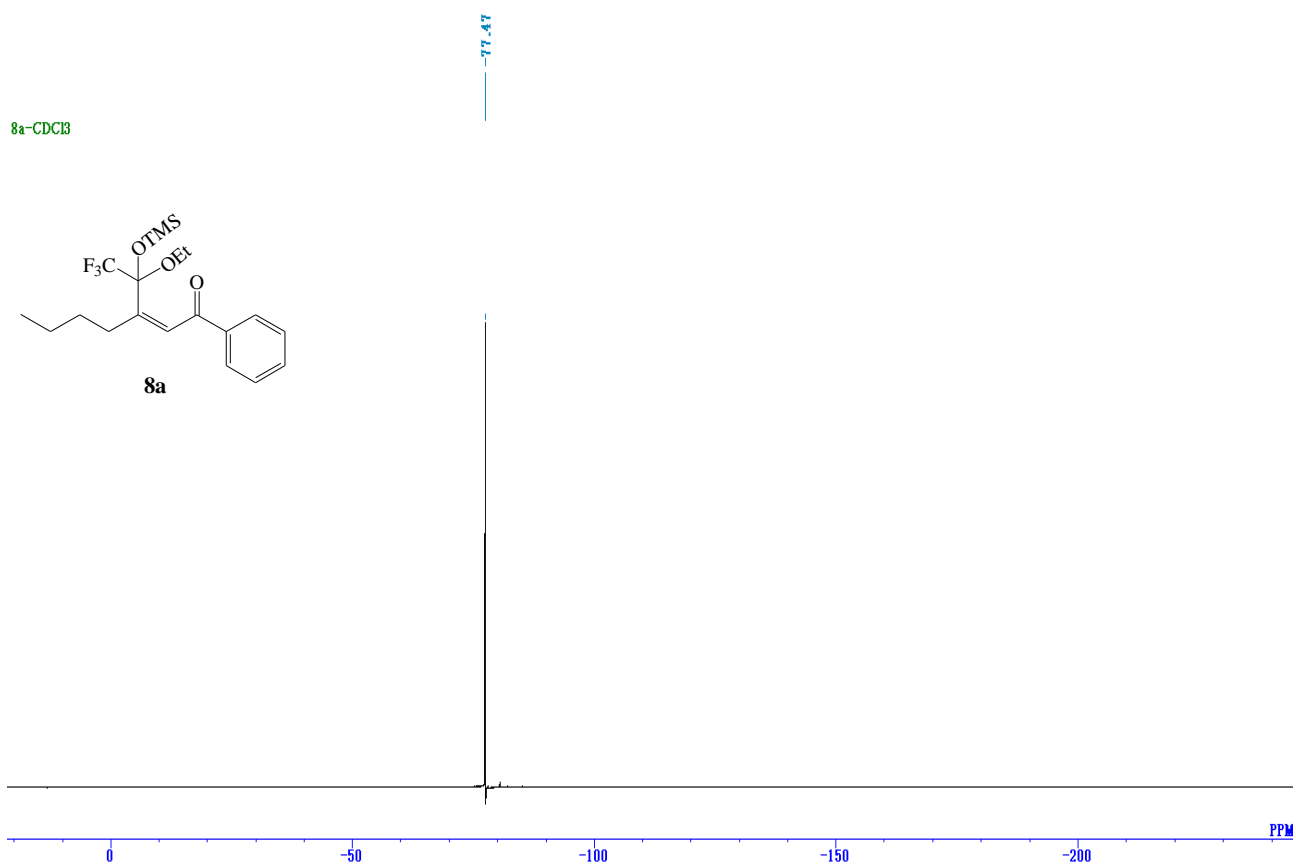
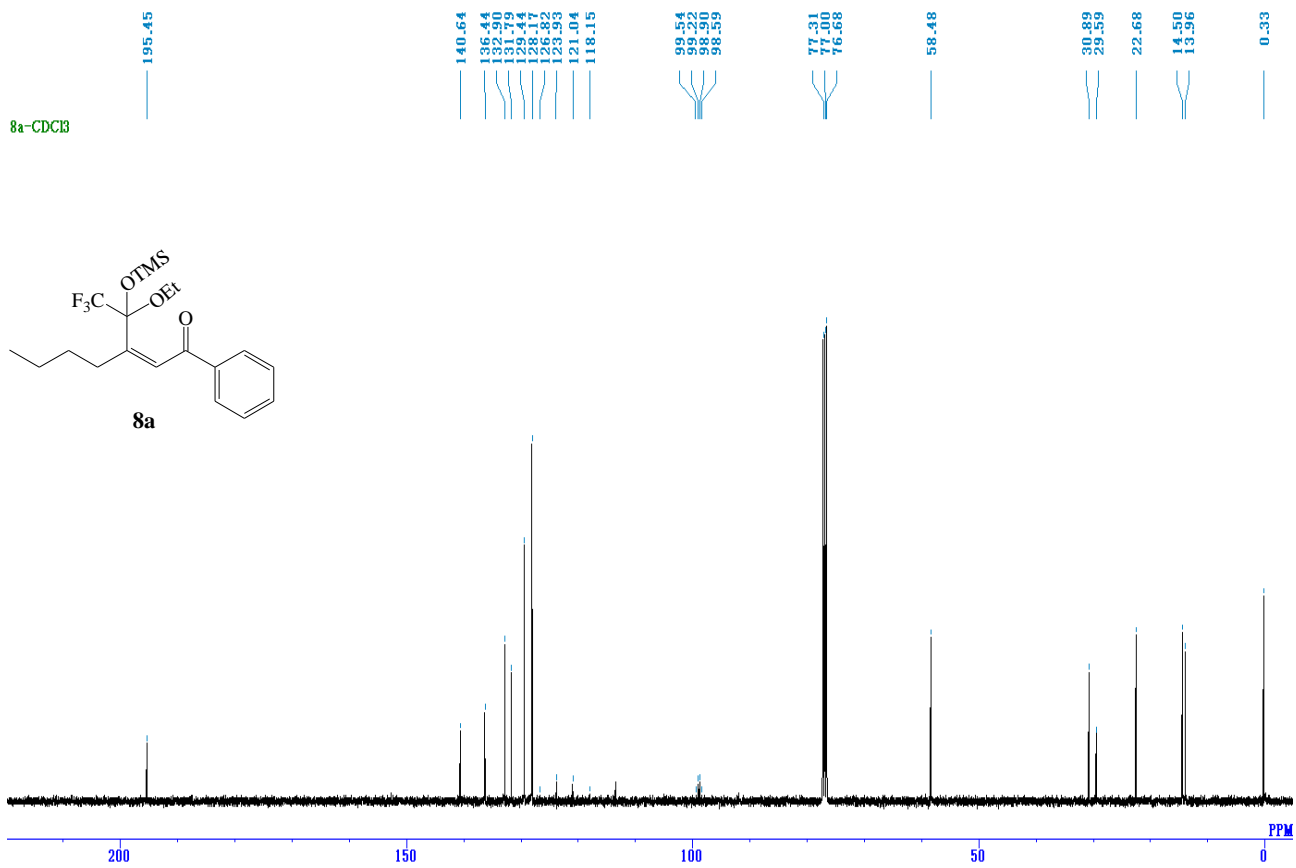


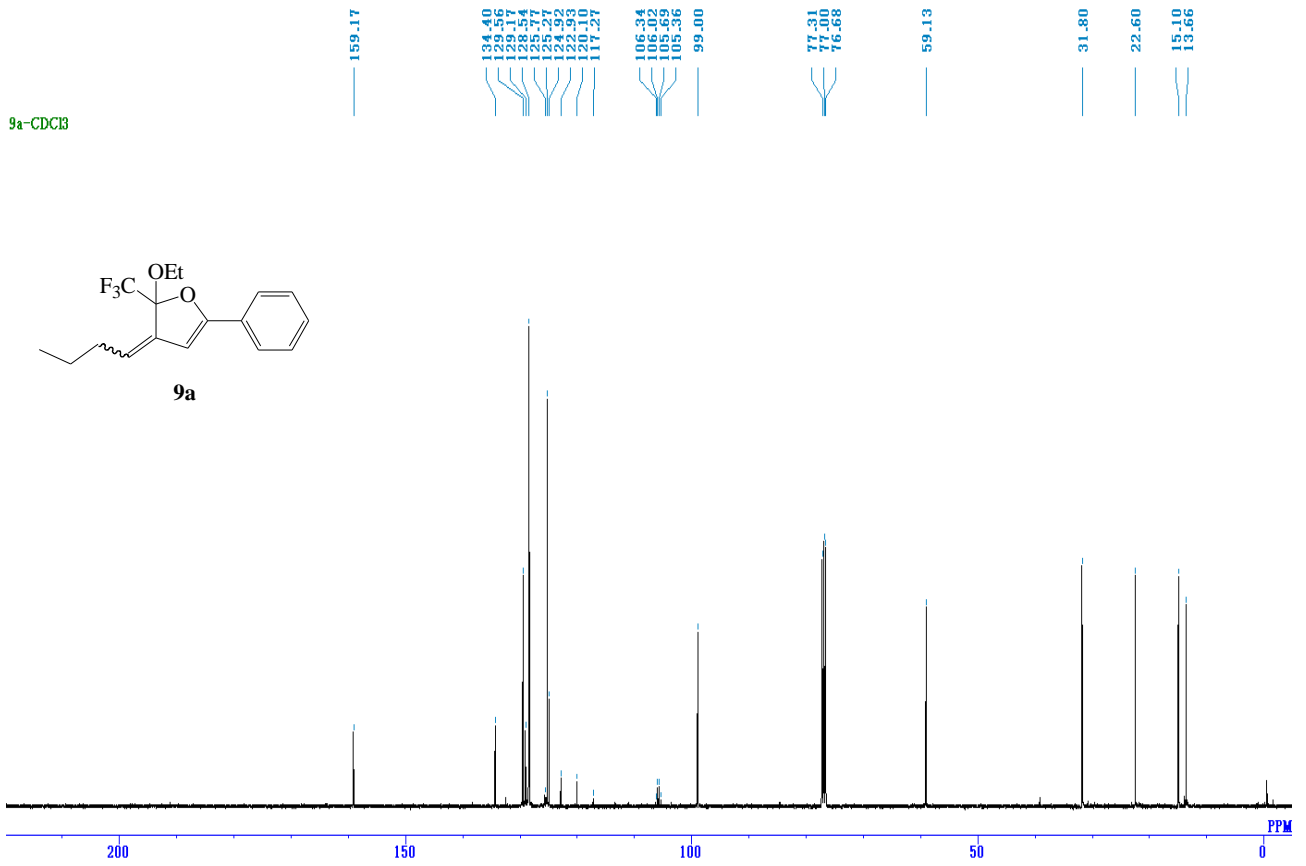
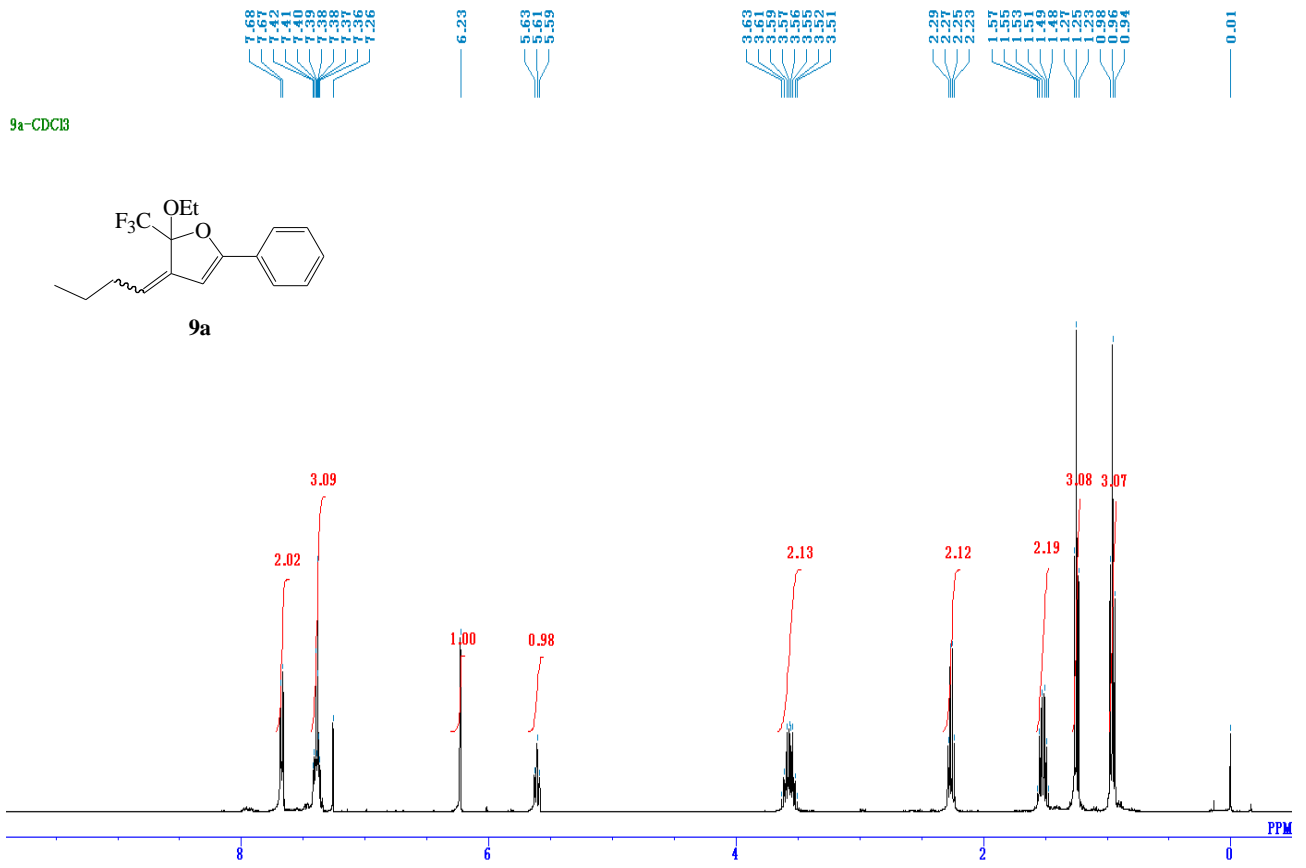
6q-CDCl₃



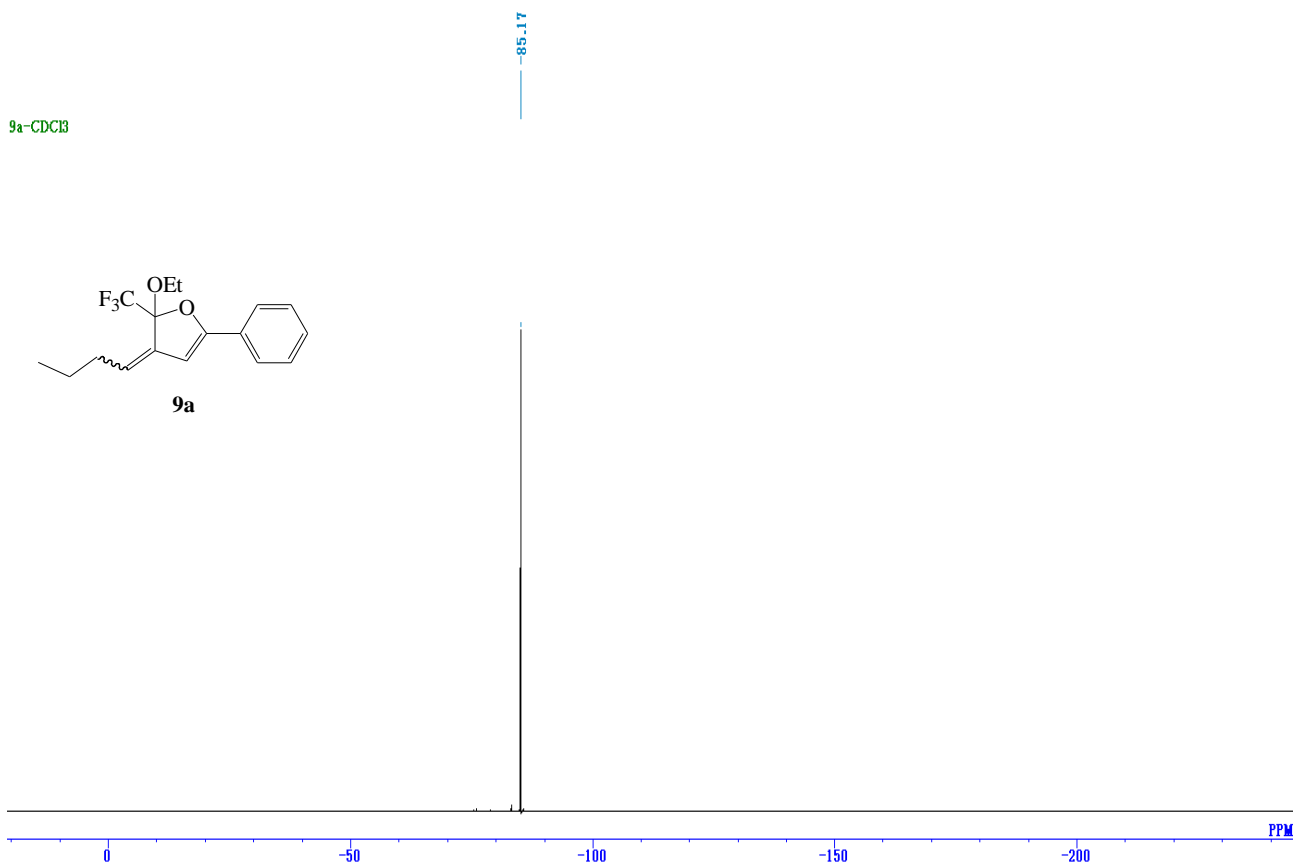
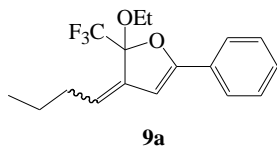
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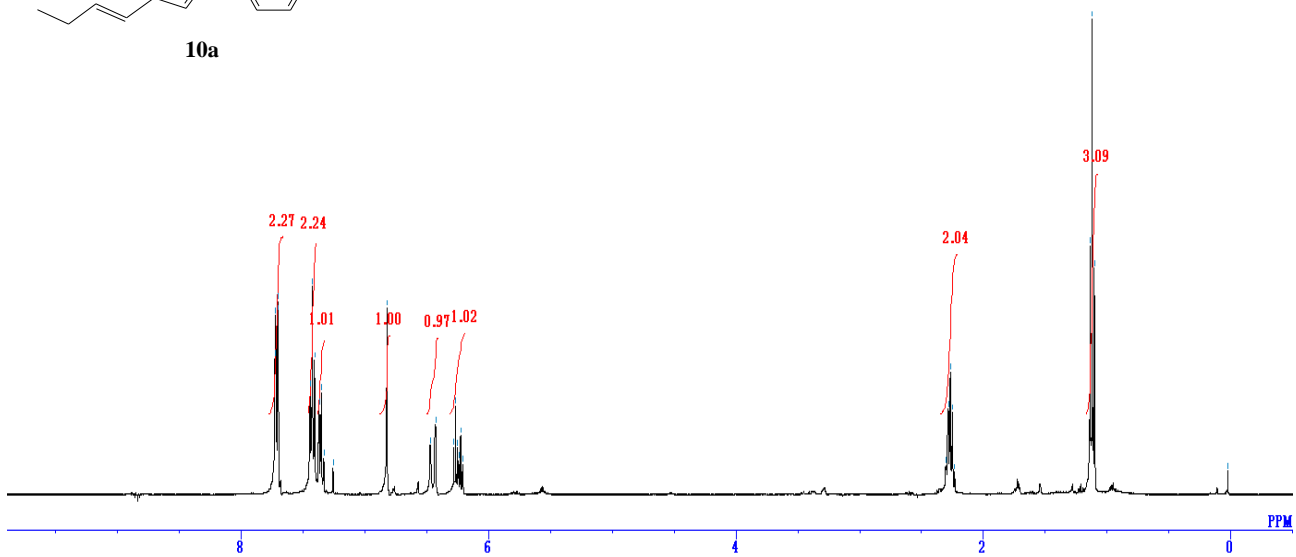
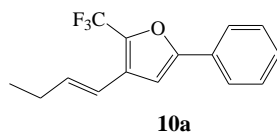




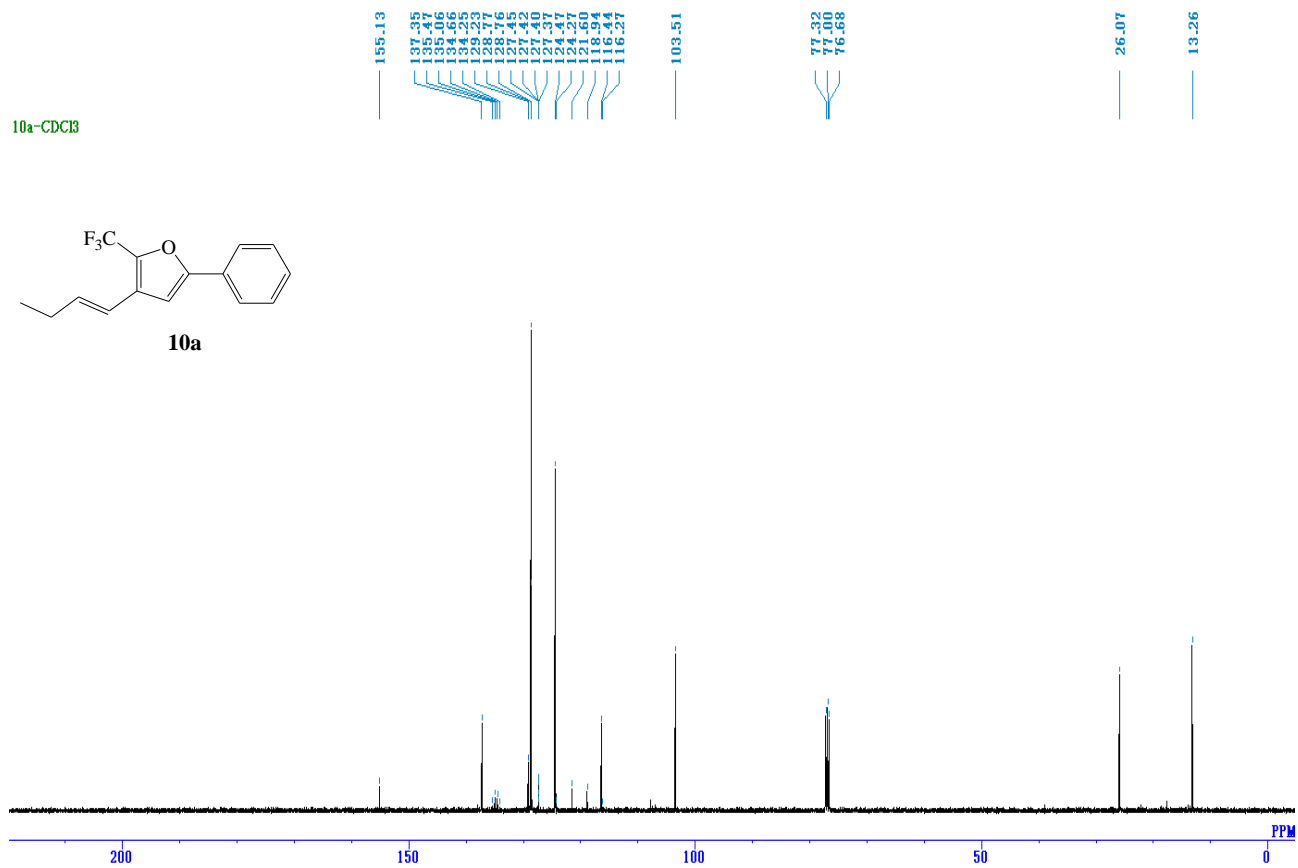
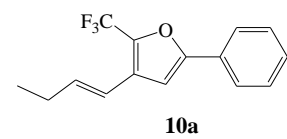
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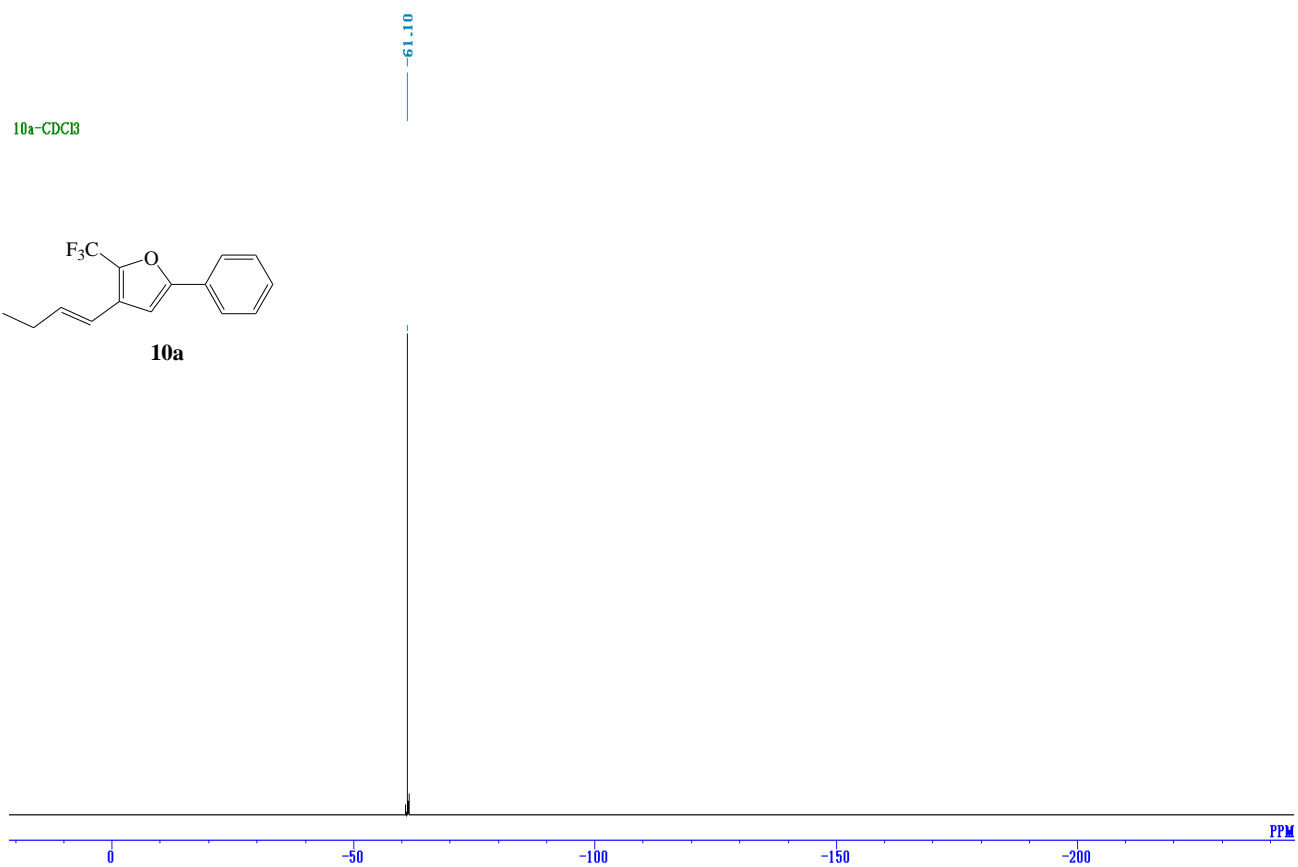
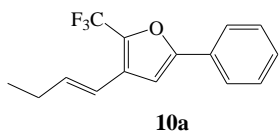
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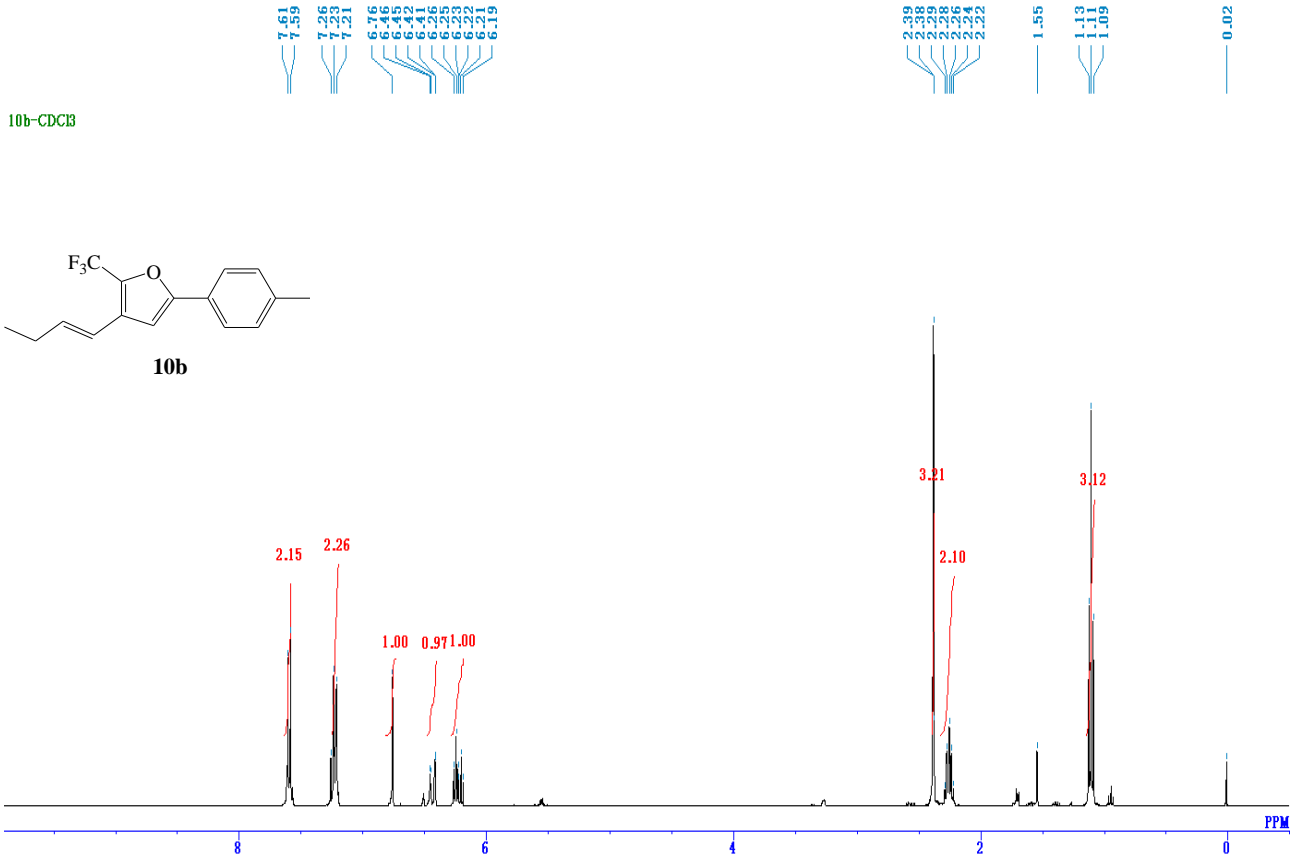
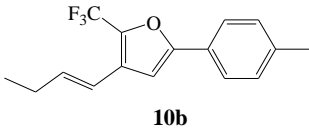
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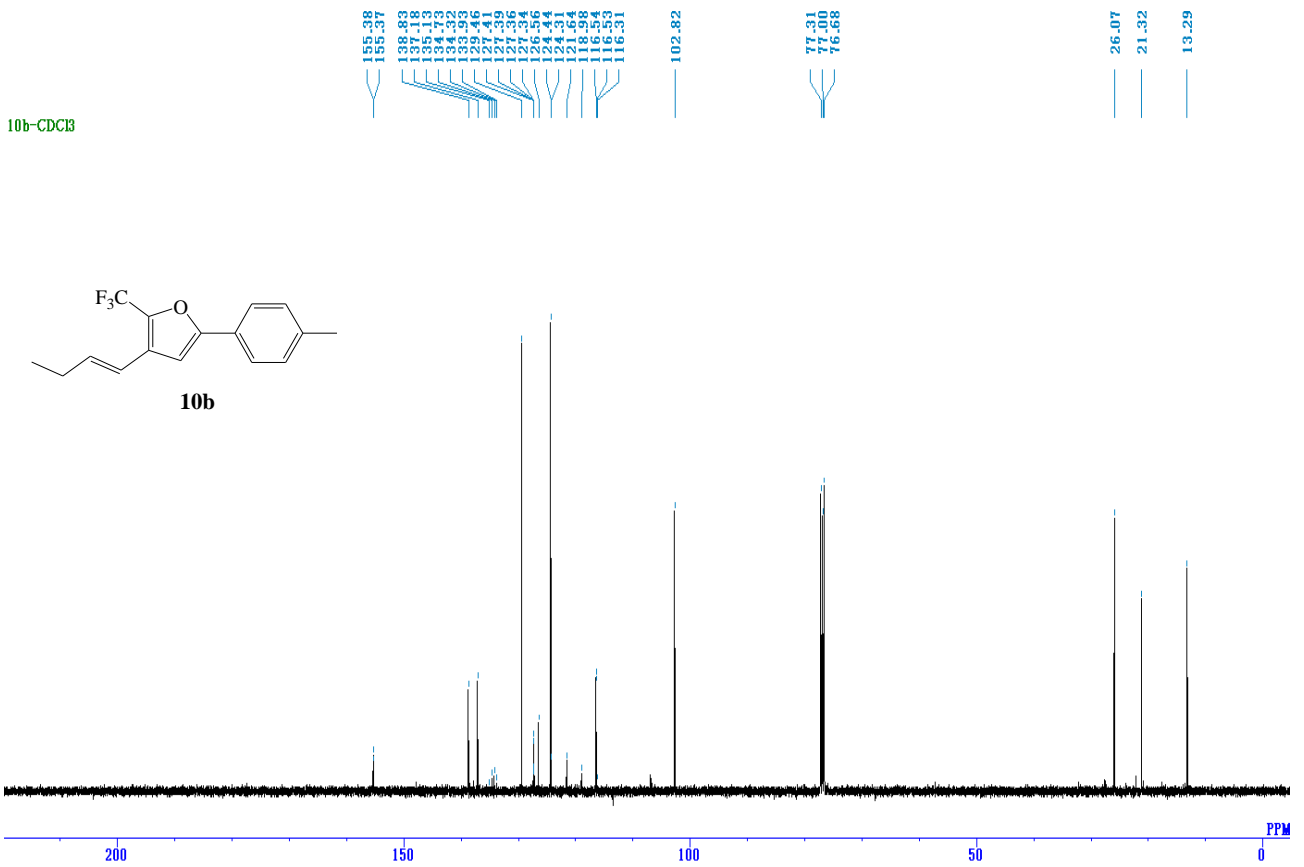
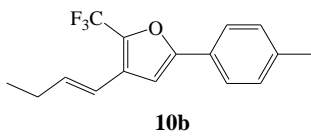
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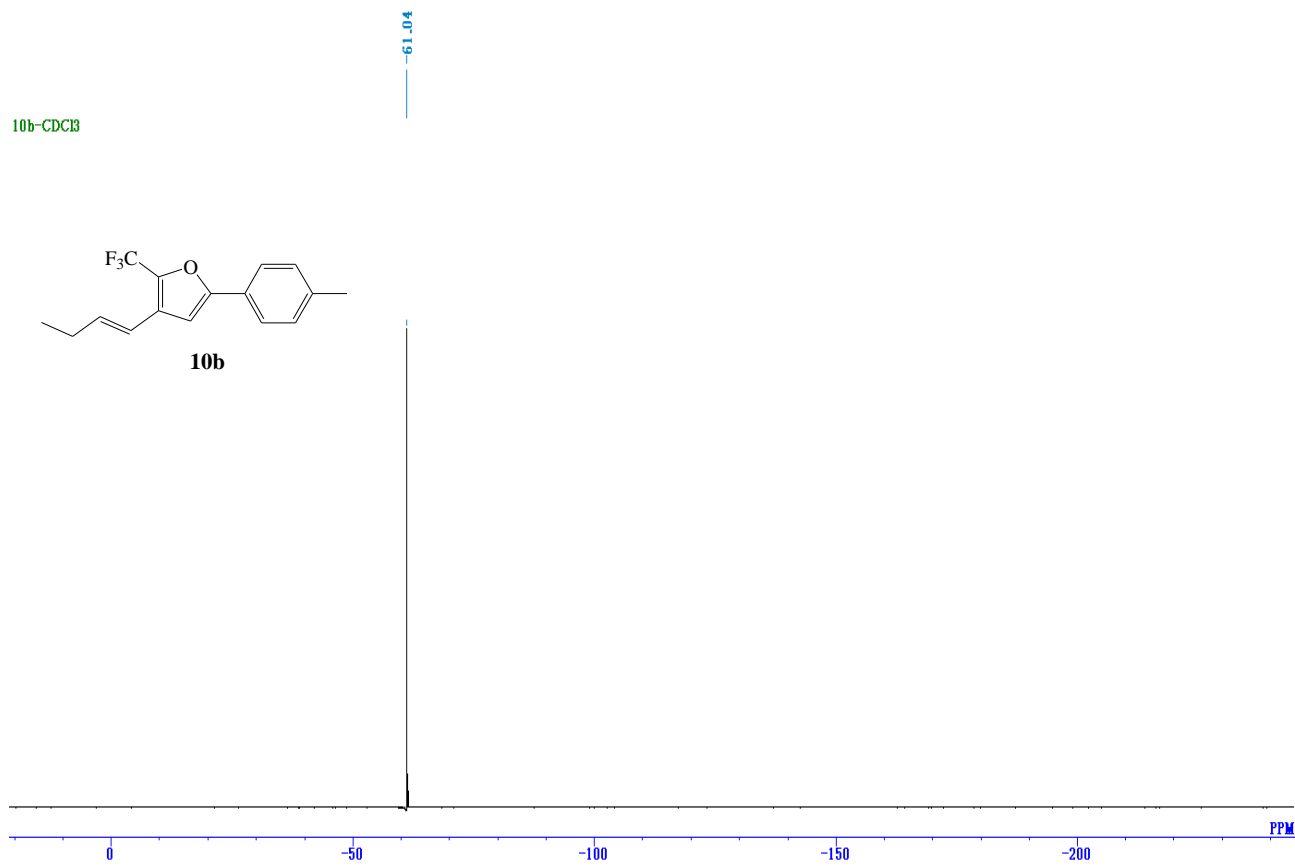
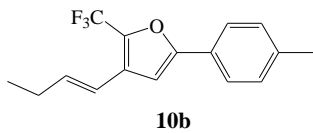
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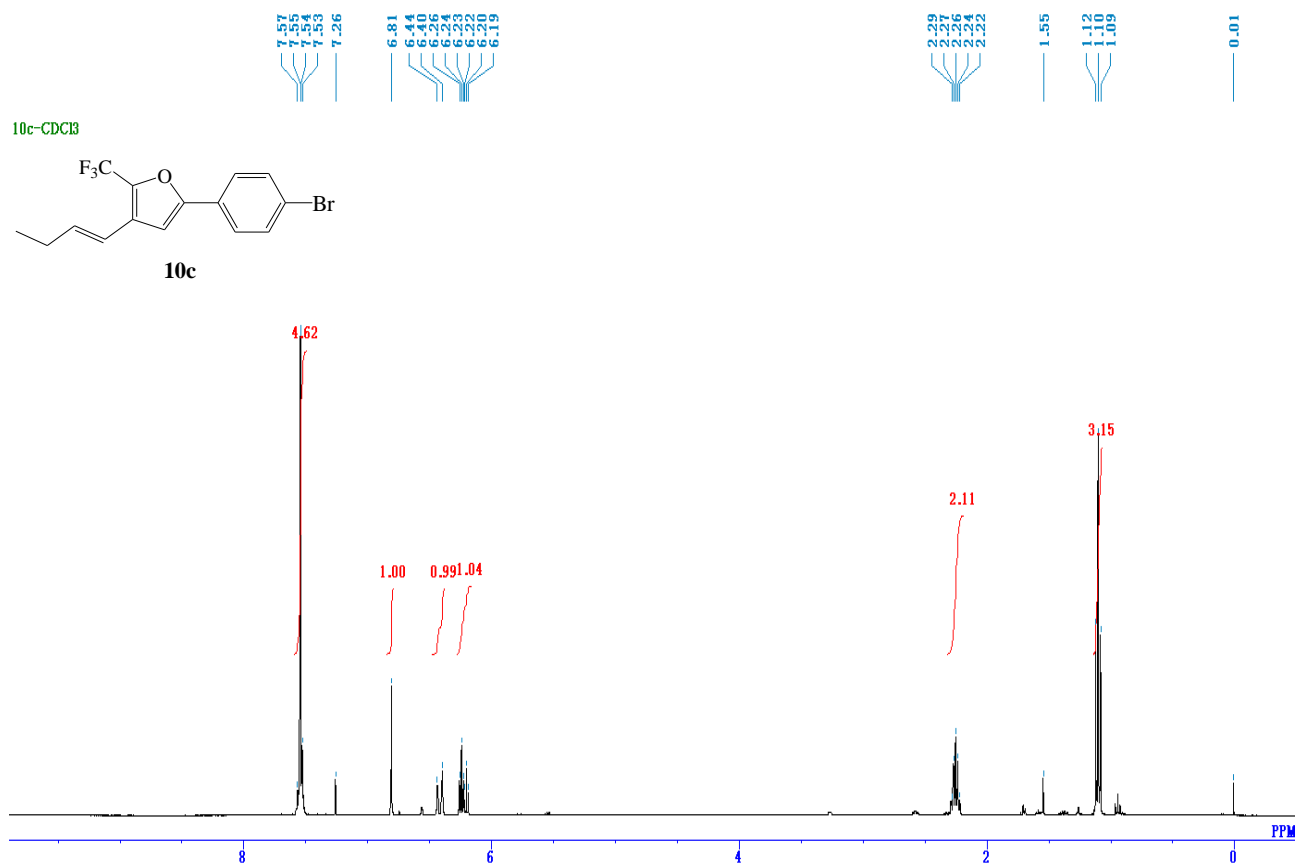
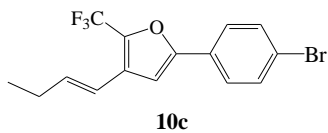
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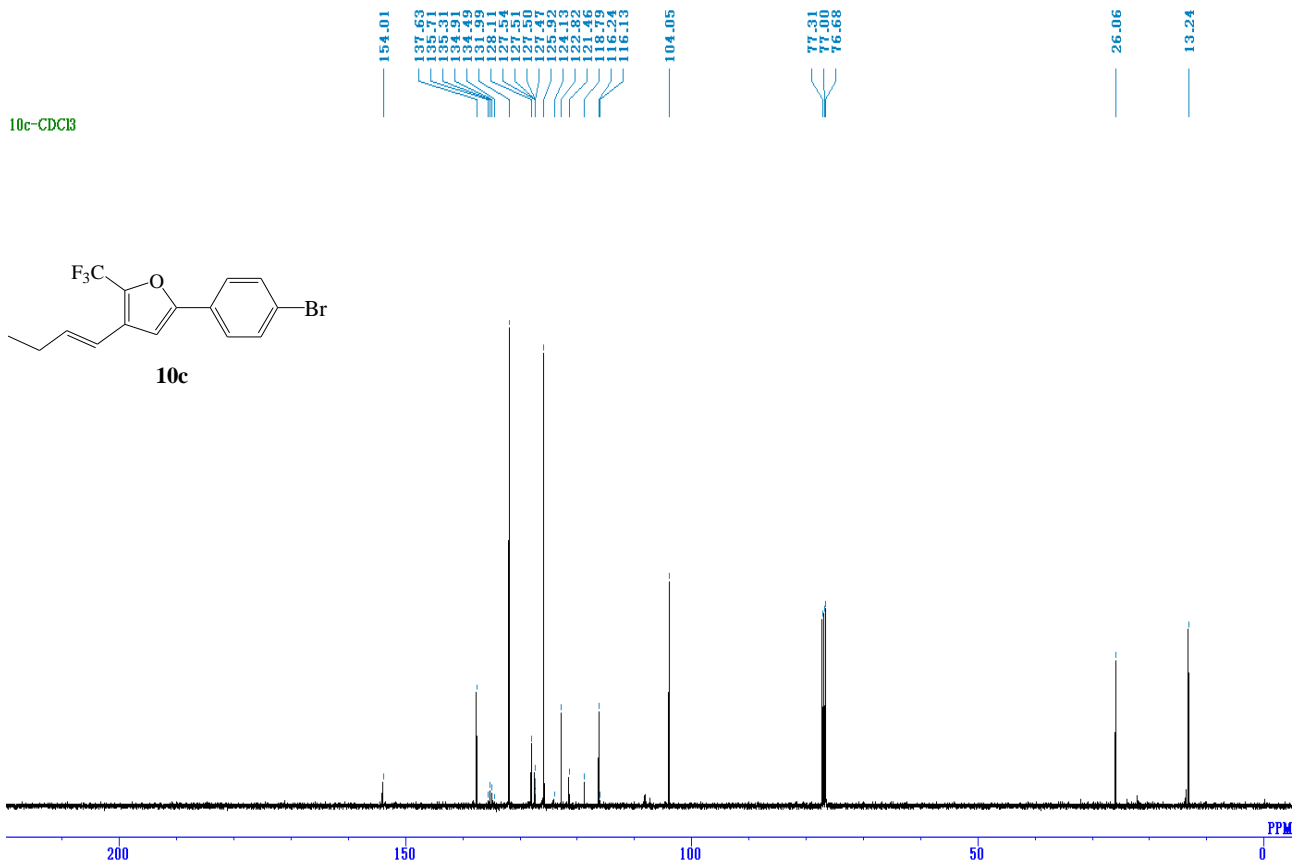
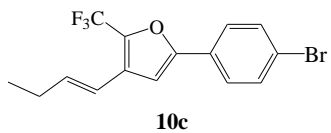
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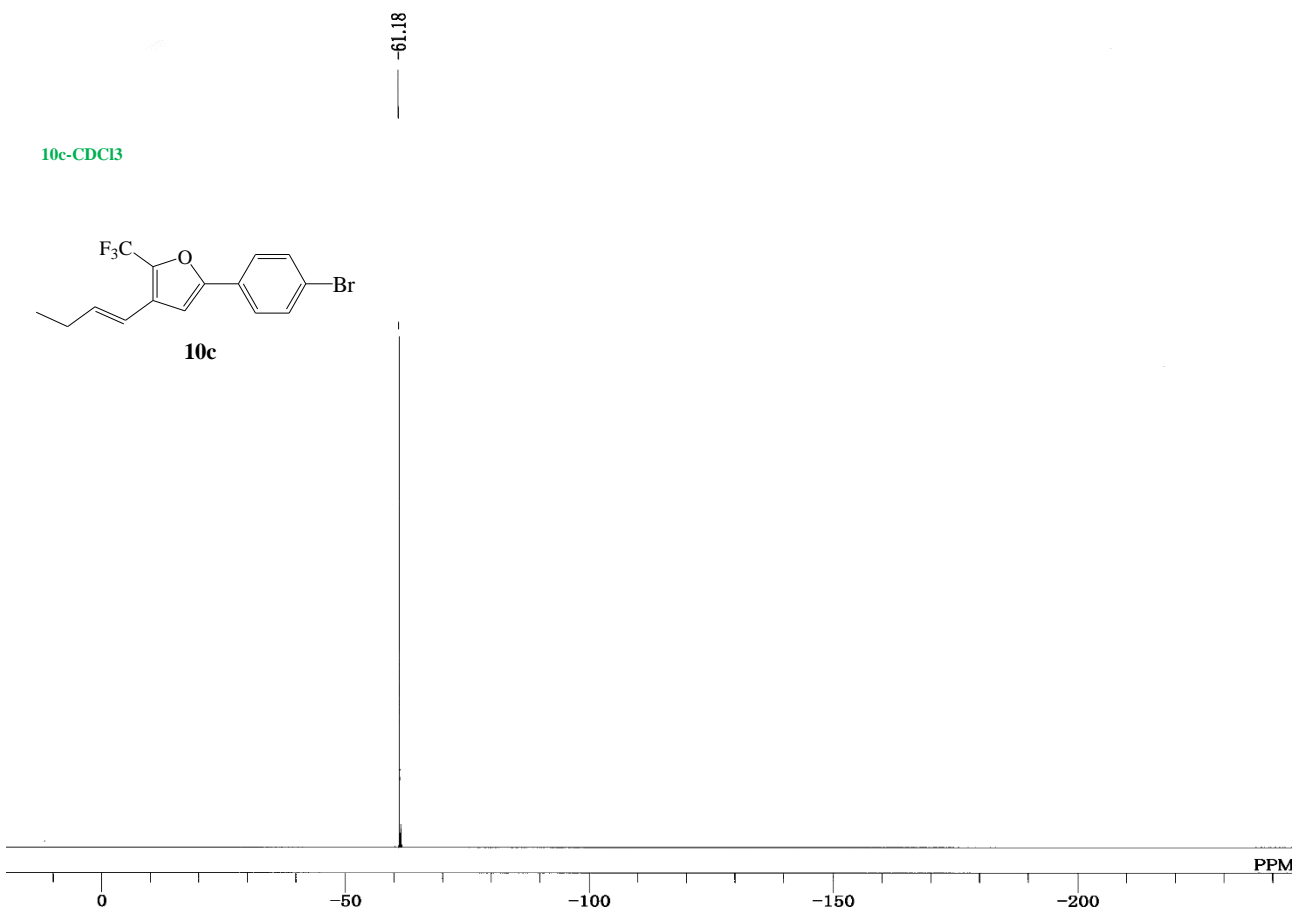
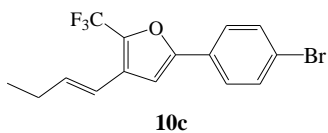
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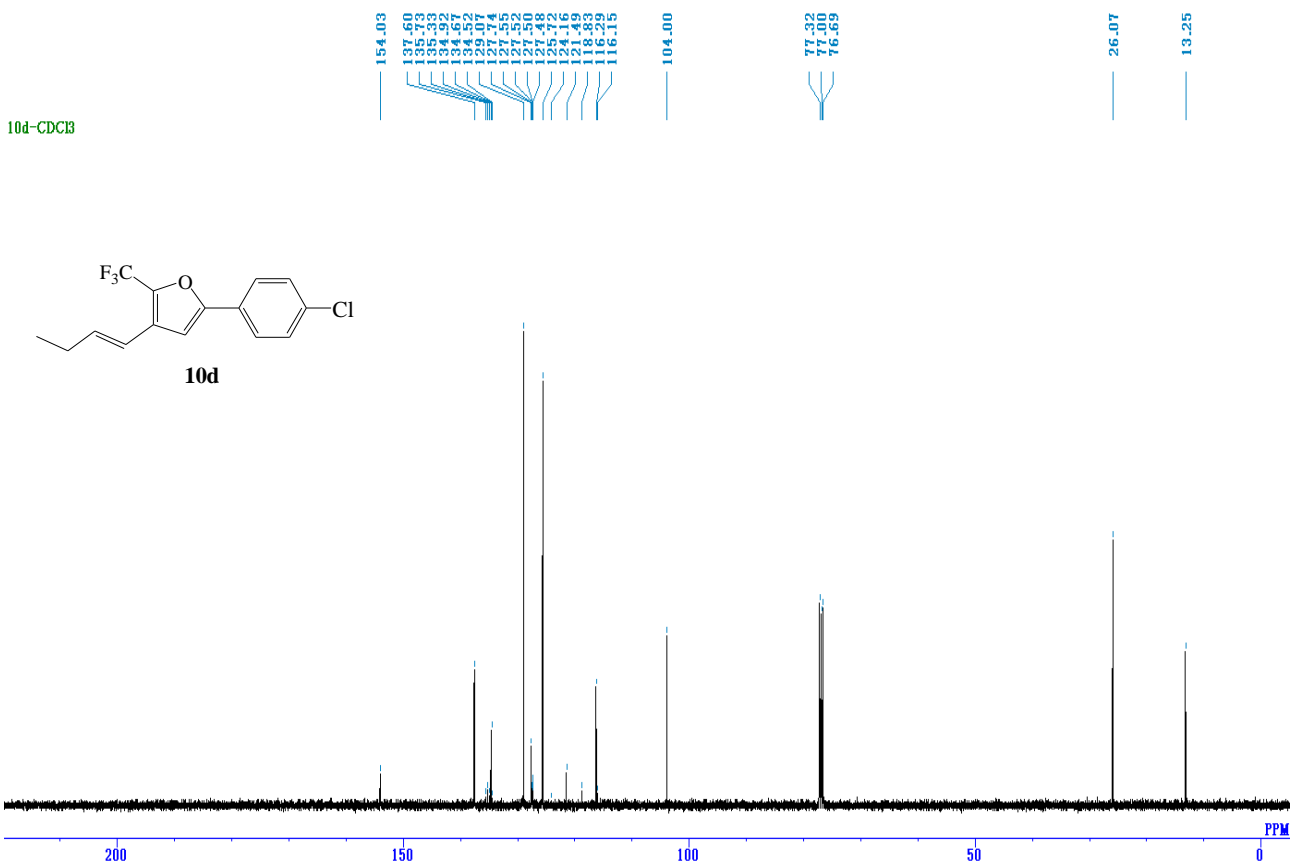
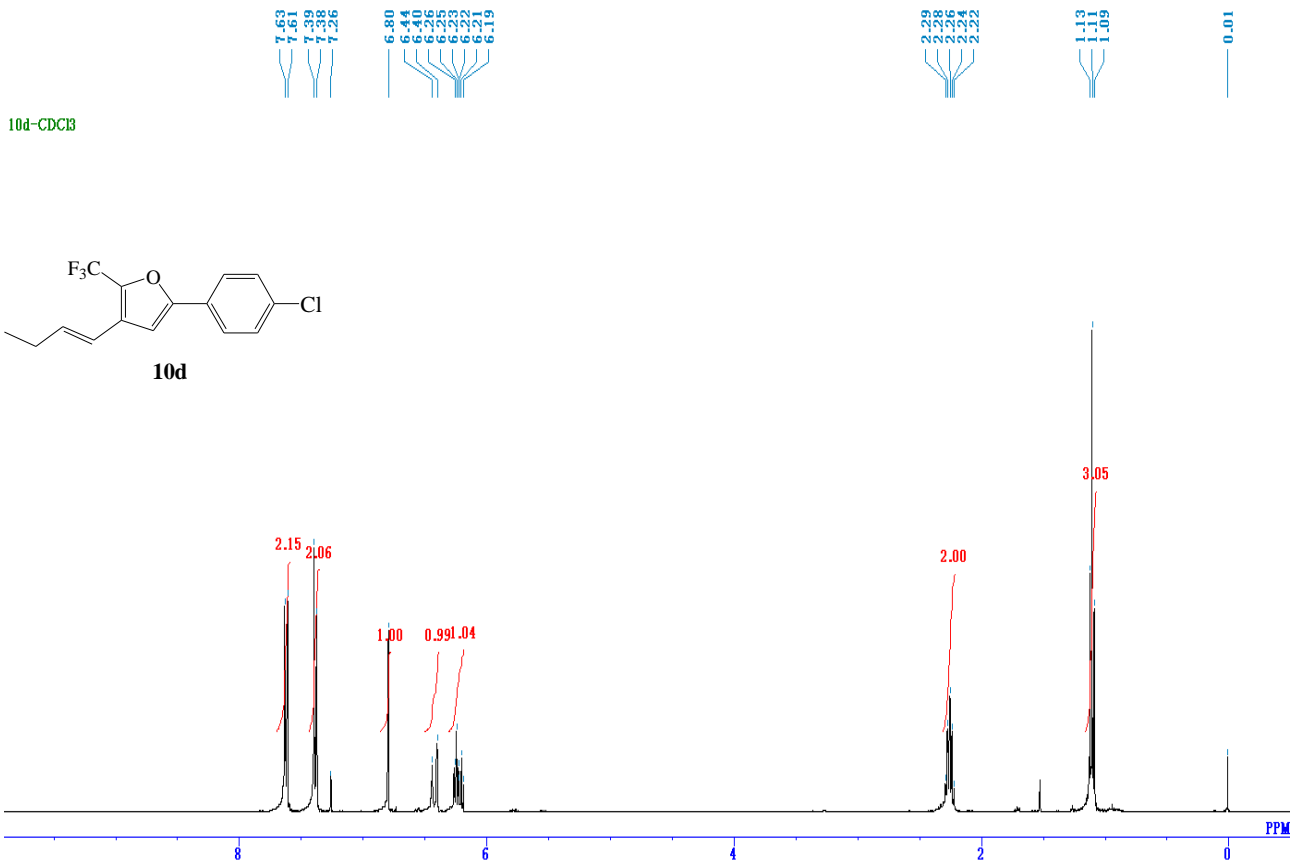


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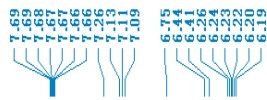
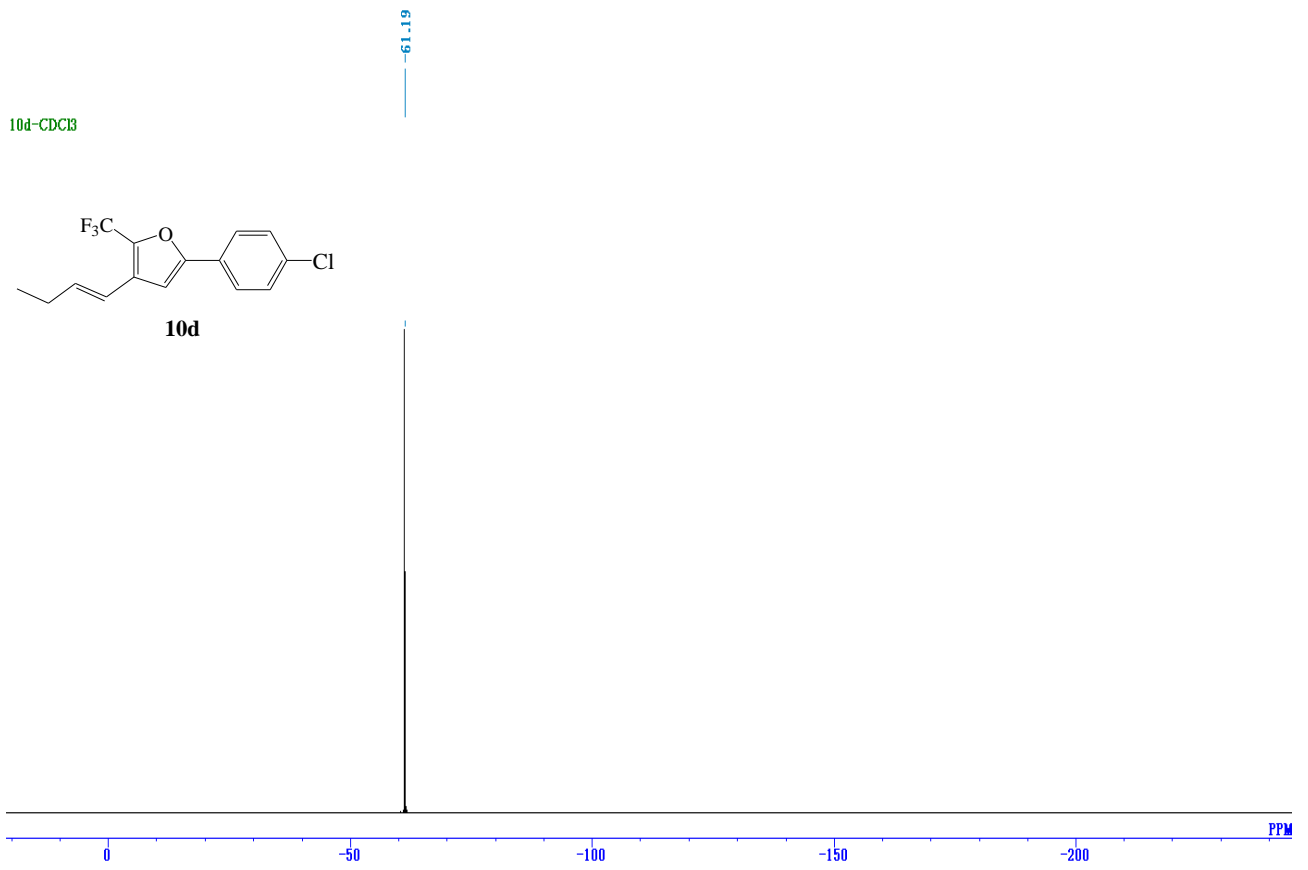
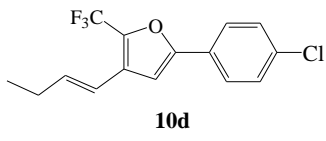


10c-CDCl3

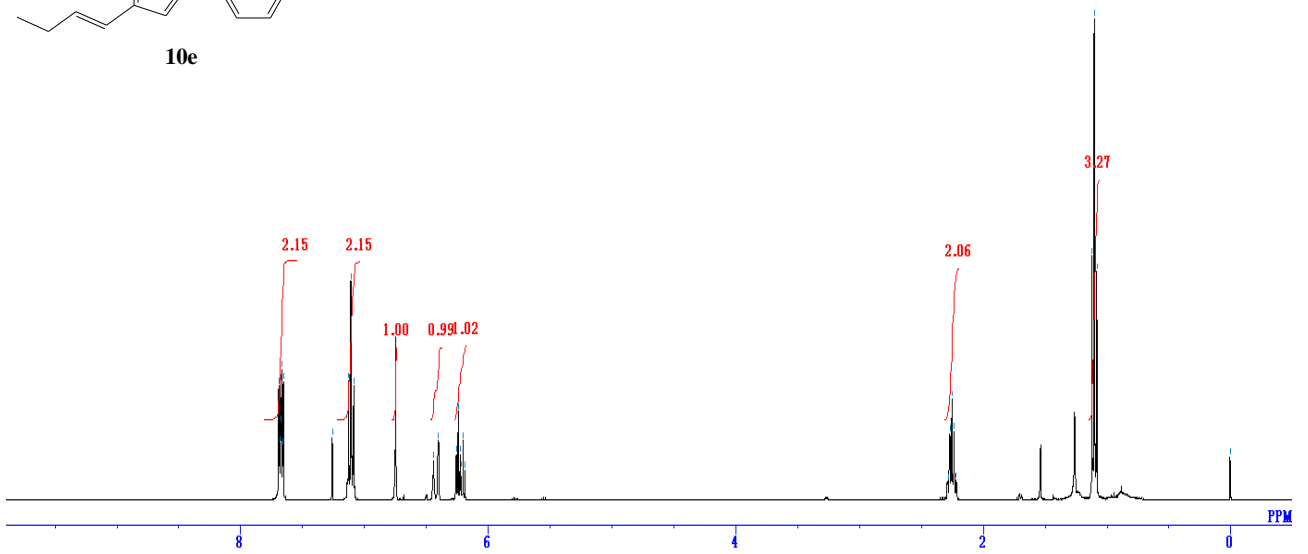
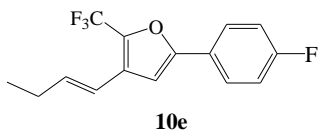




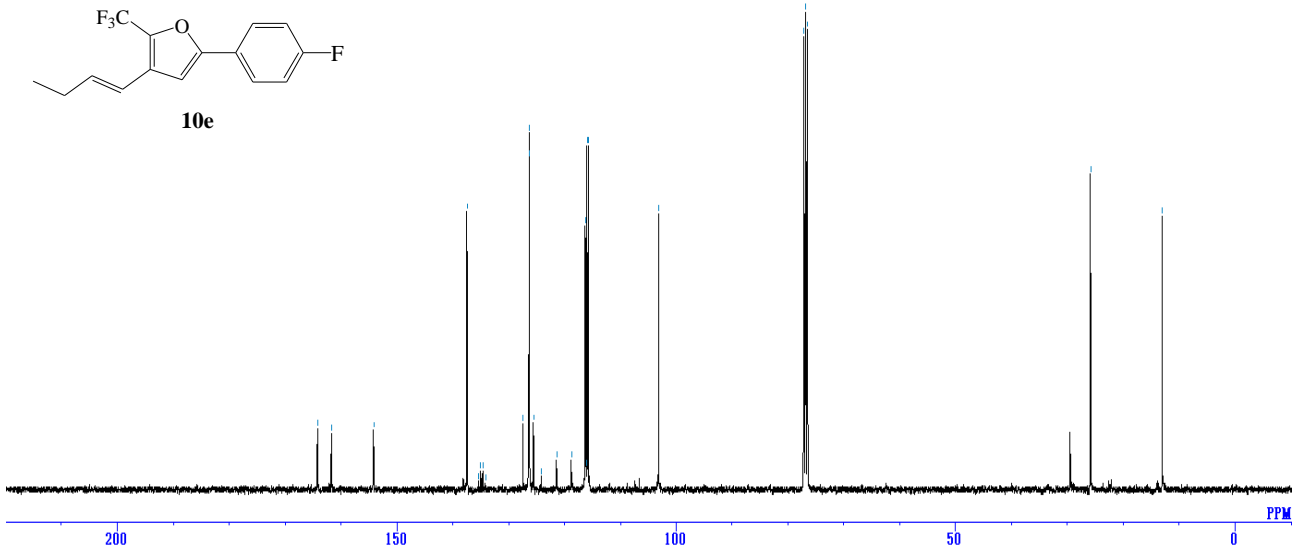
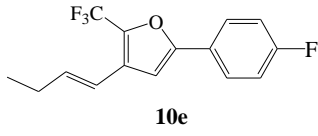
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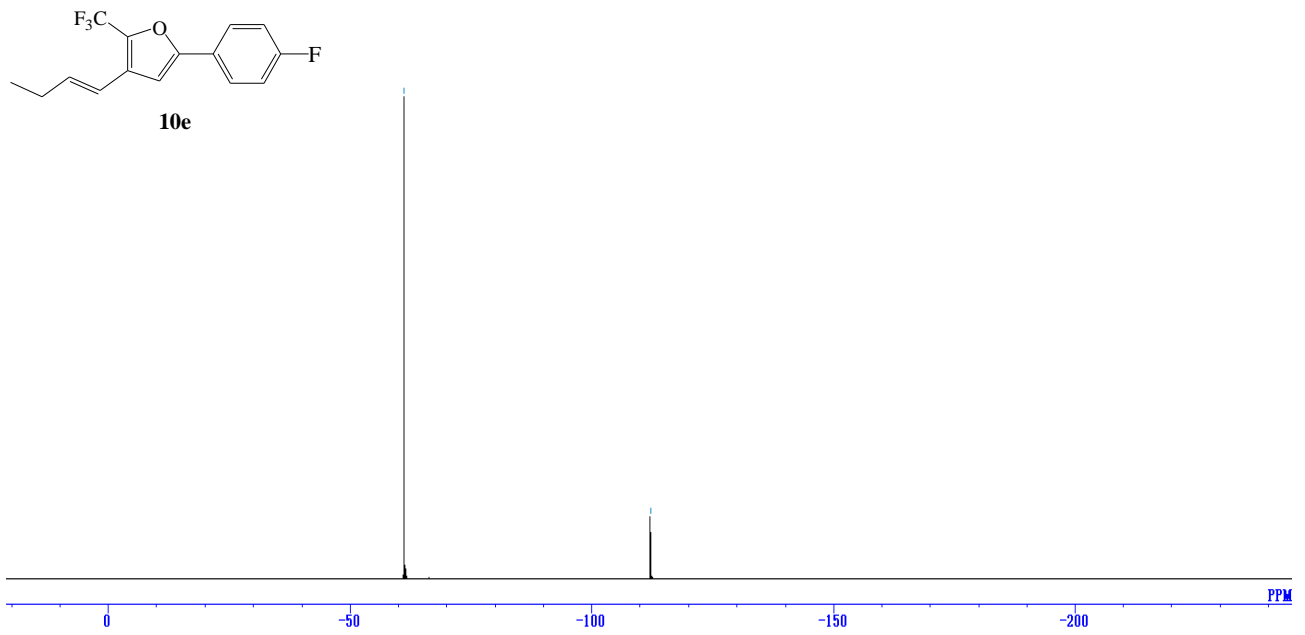
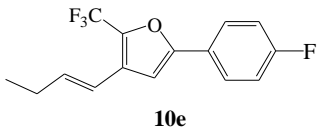
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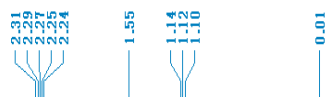
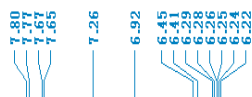


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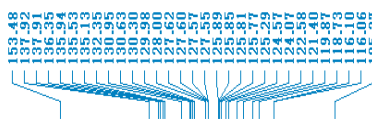
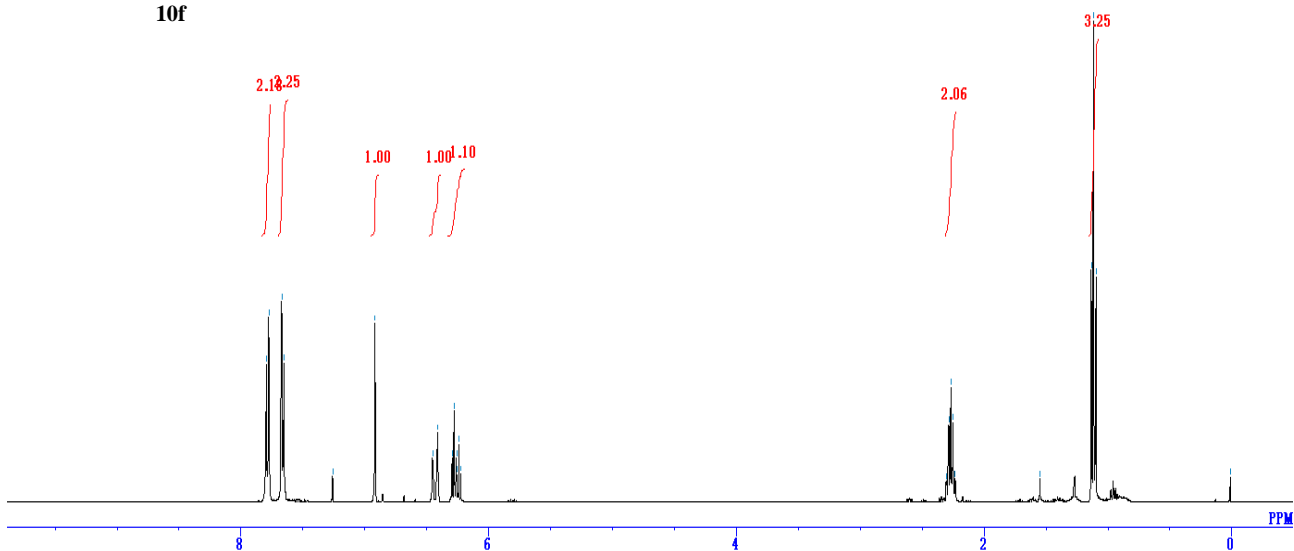
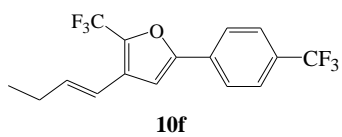


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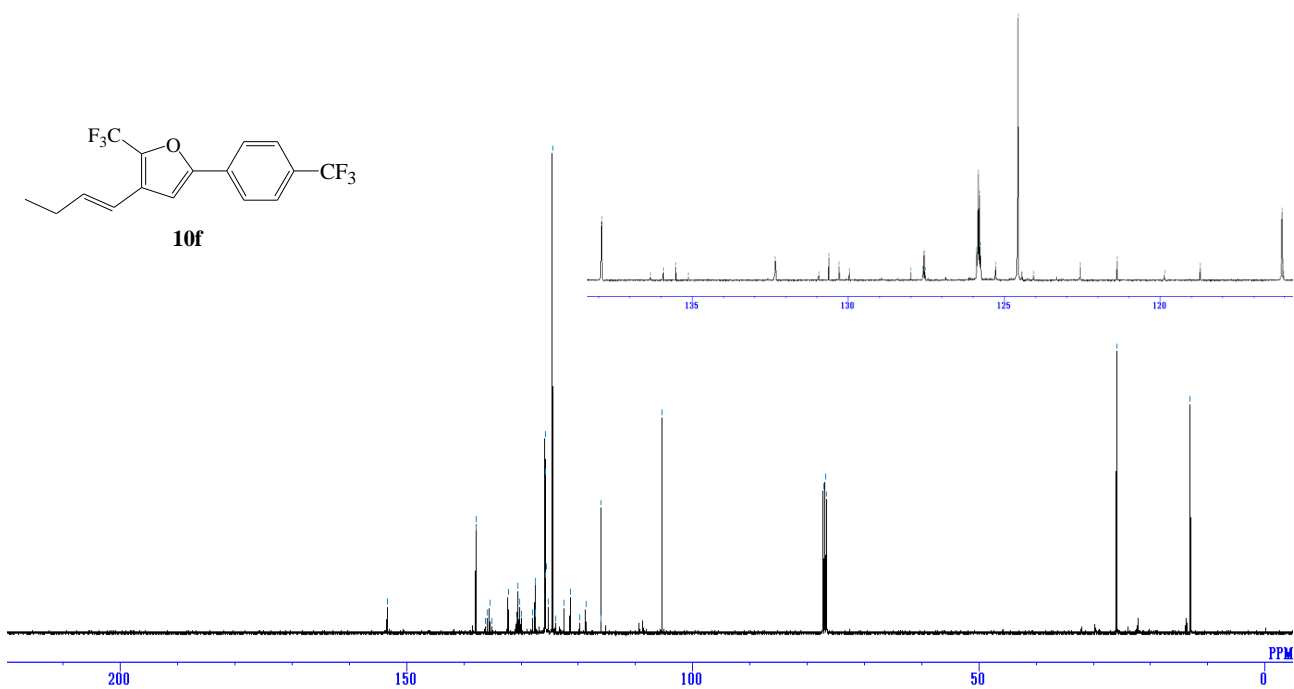
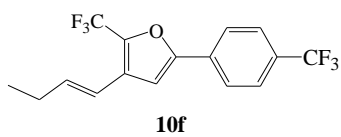




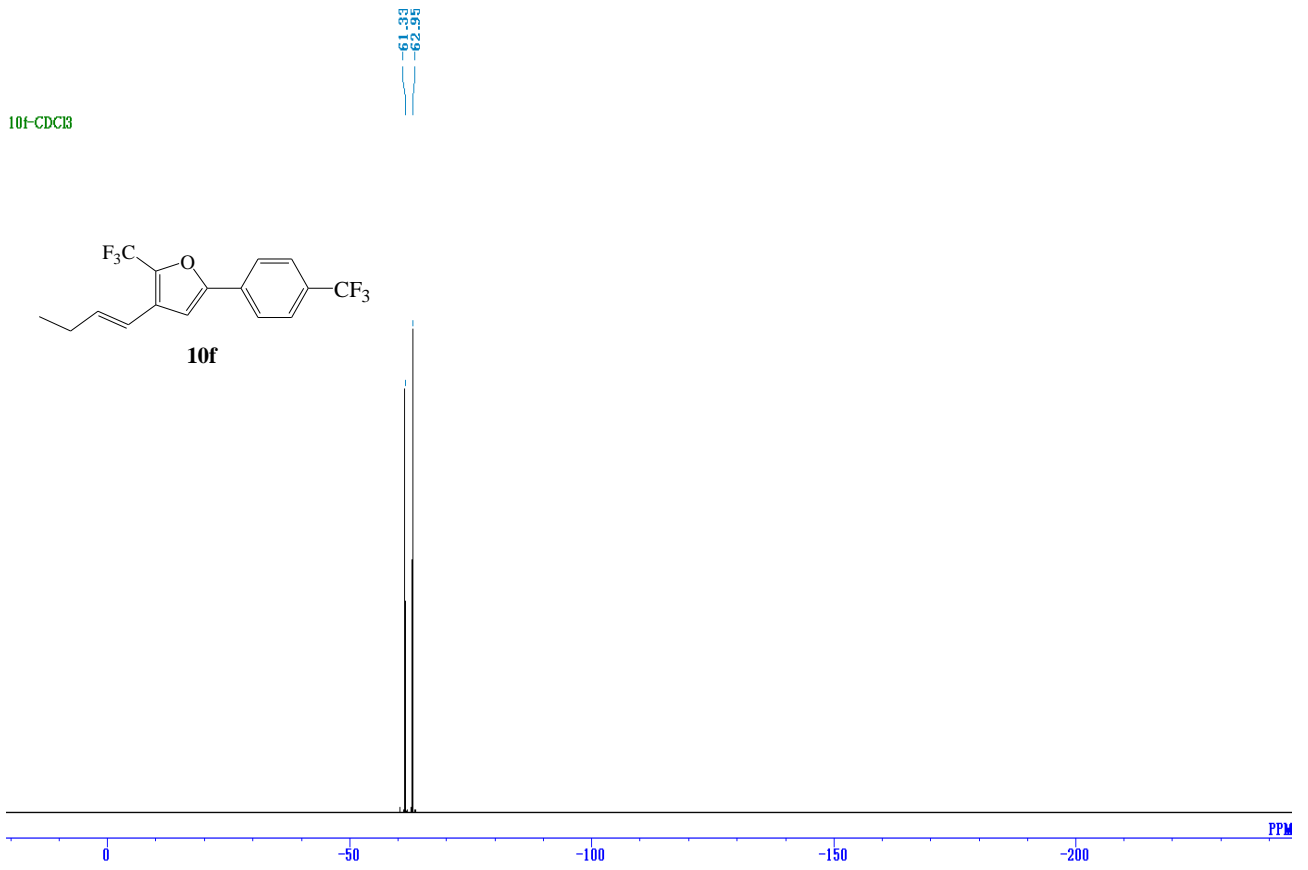
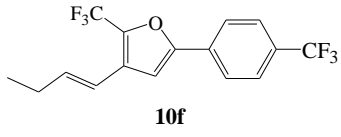
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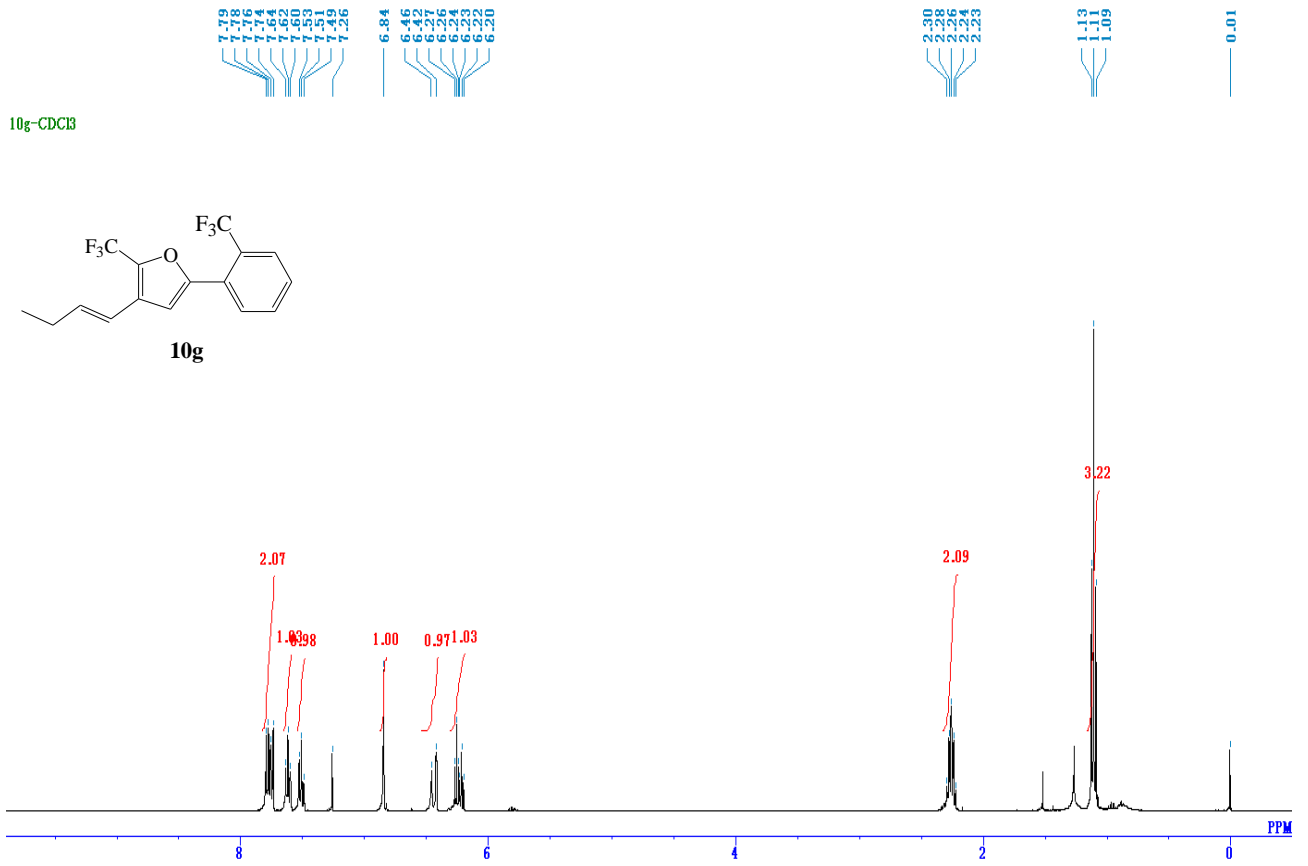
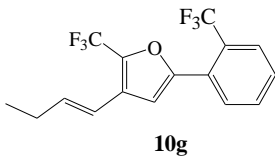
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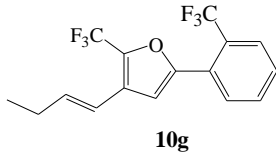
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10g-CDCl3



10g-CDCl₃

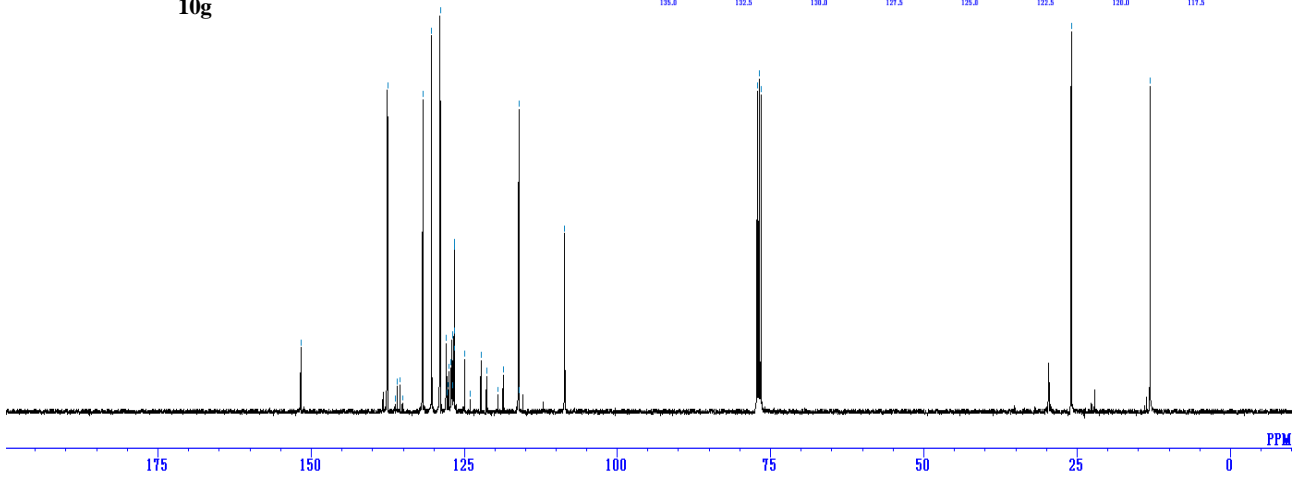
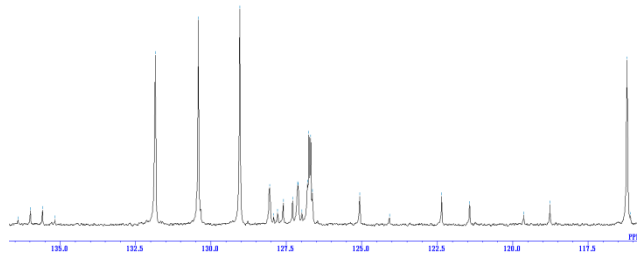


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137.66
136.41
135.59
135.19
131.85
129.06
128.07
127.93
127.60
127.30
127.14
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126.60
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125.08
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116.20
108.71

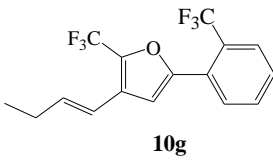
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26.08

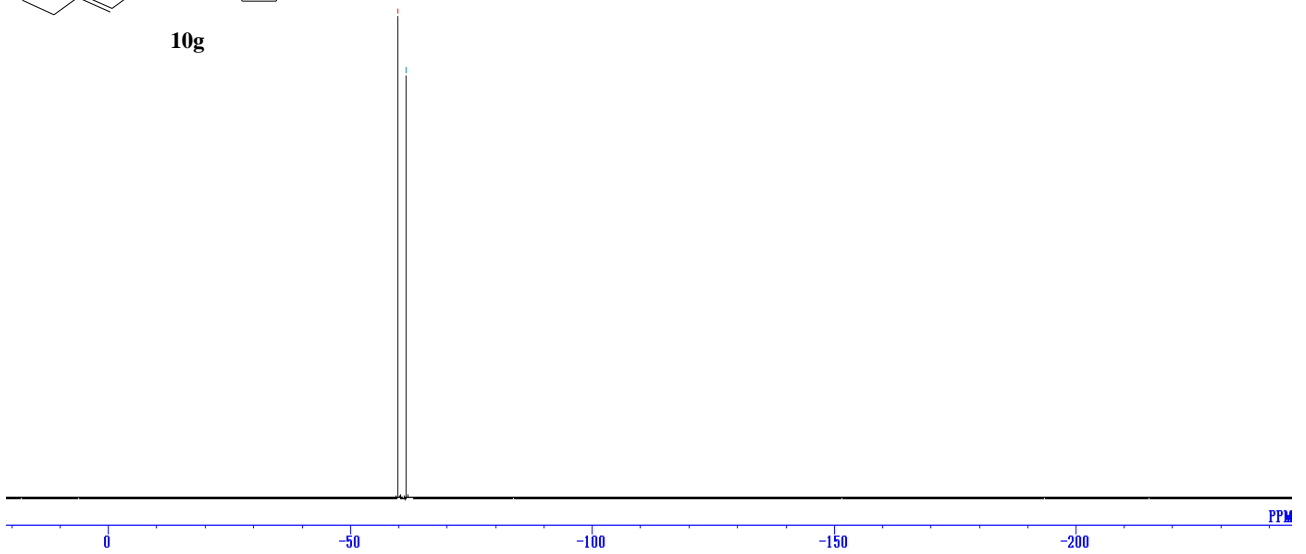
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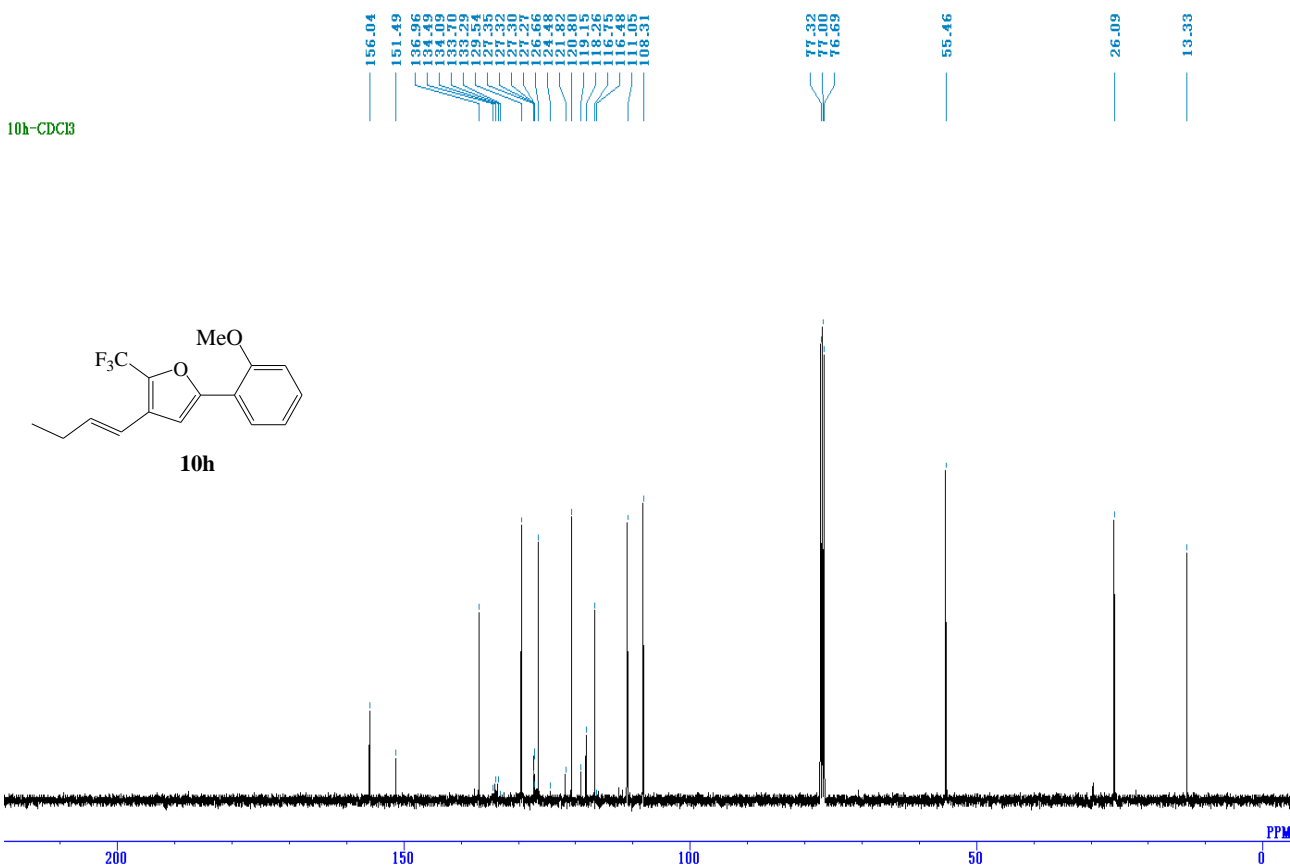
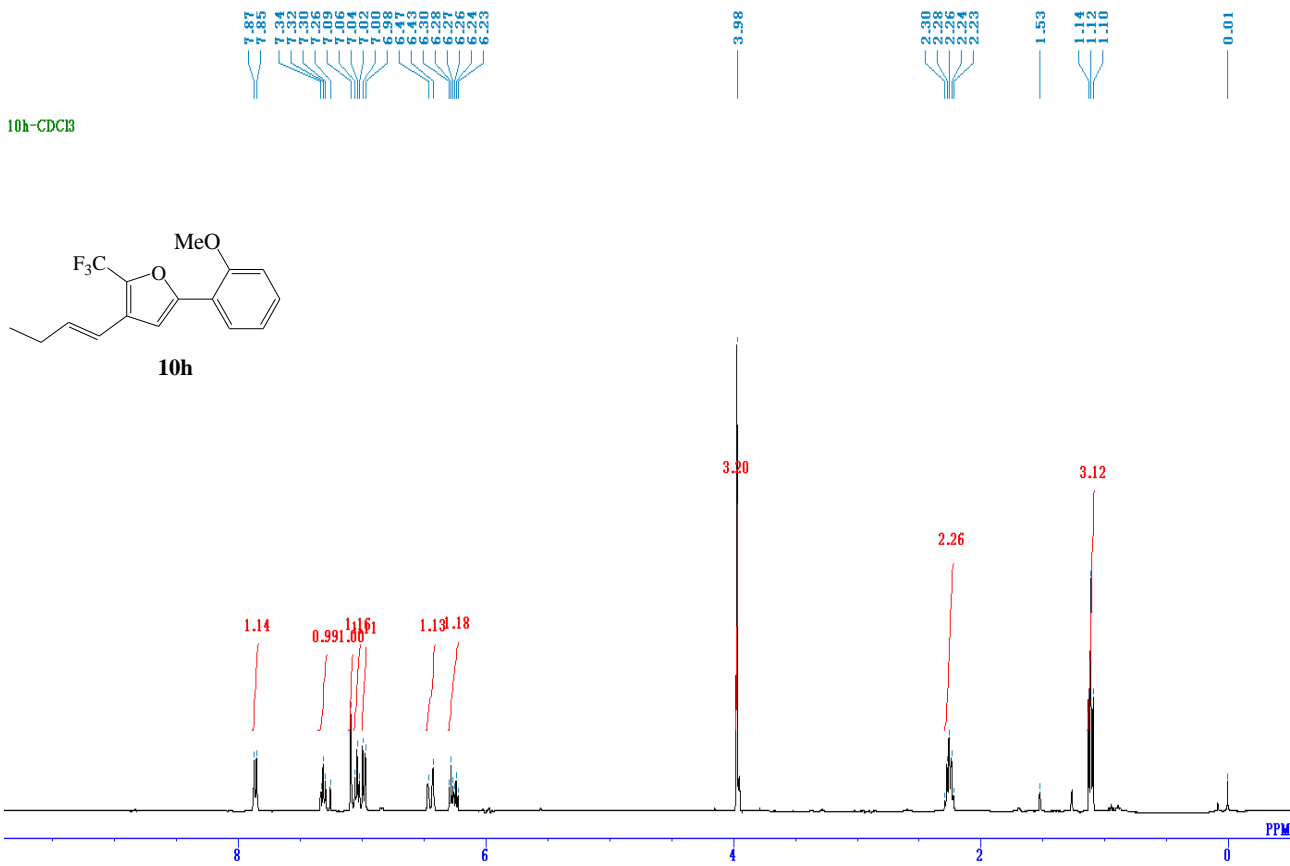


10g-CDCl₃

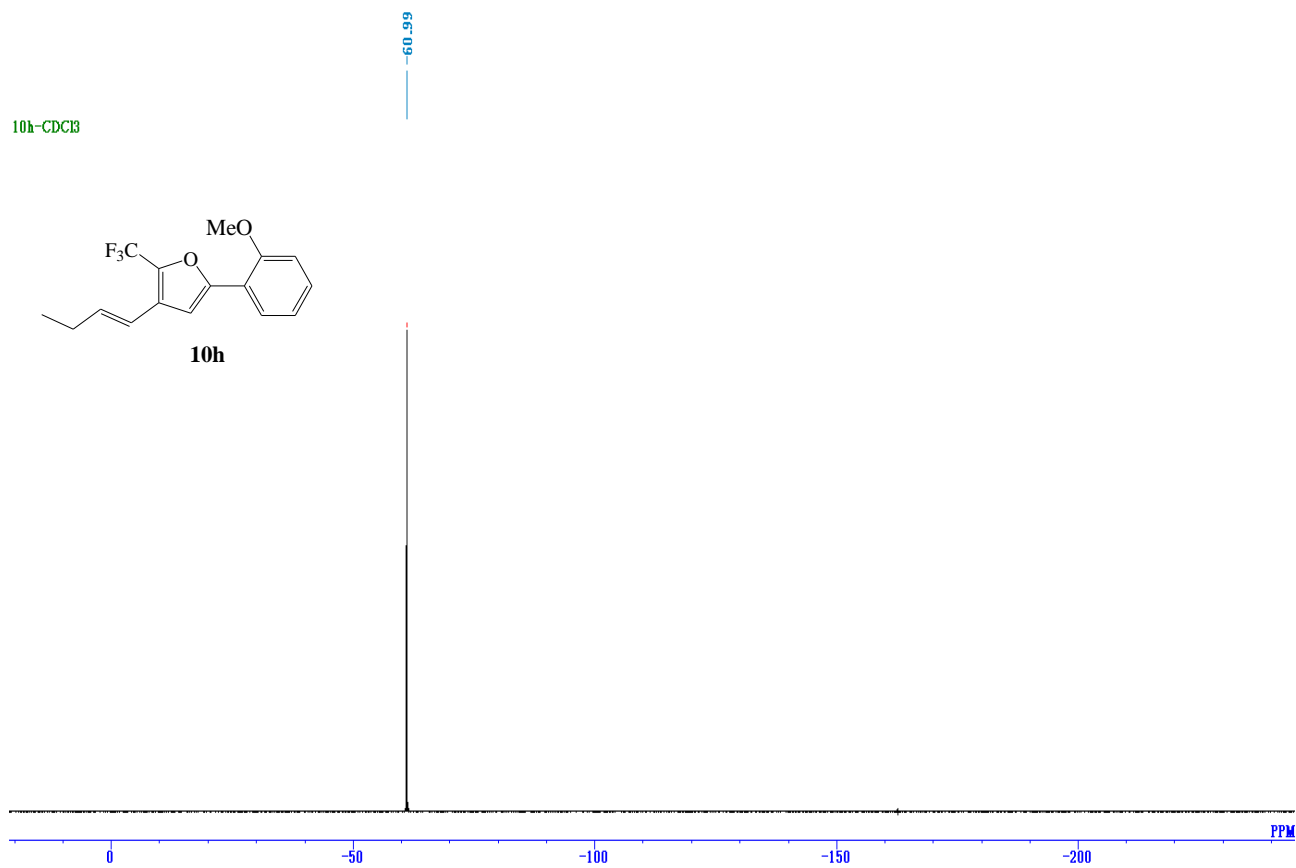
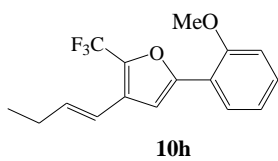


-69.74
-69.42

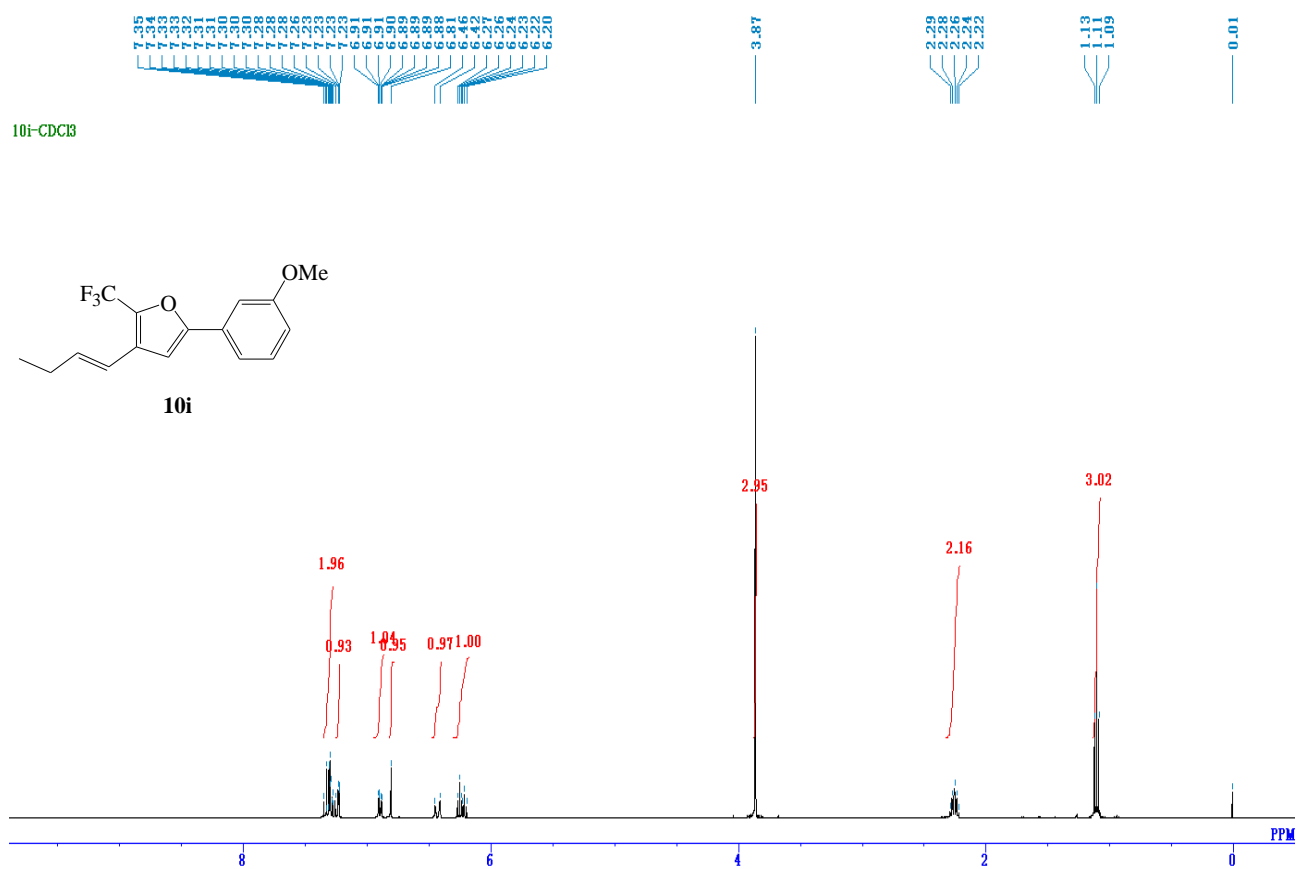
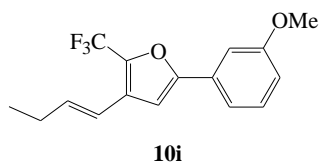




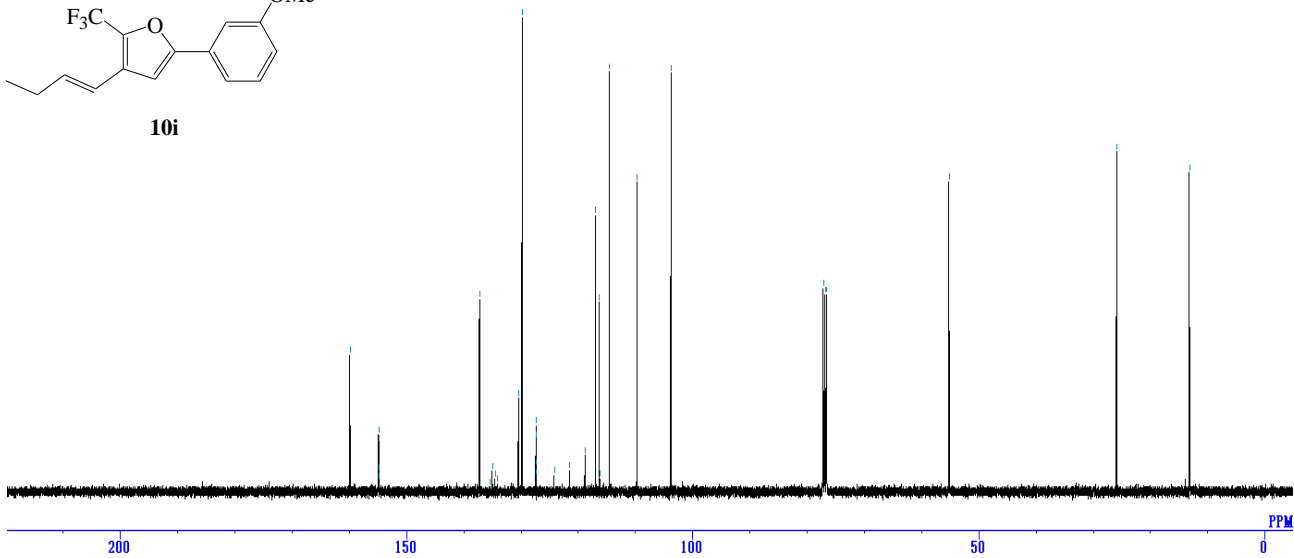
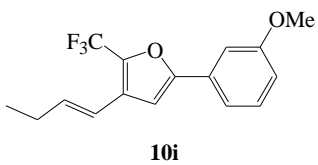
10h-CDCl3



10i-CDCl3

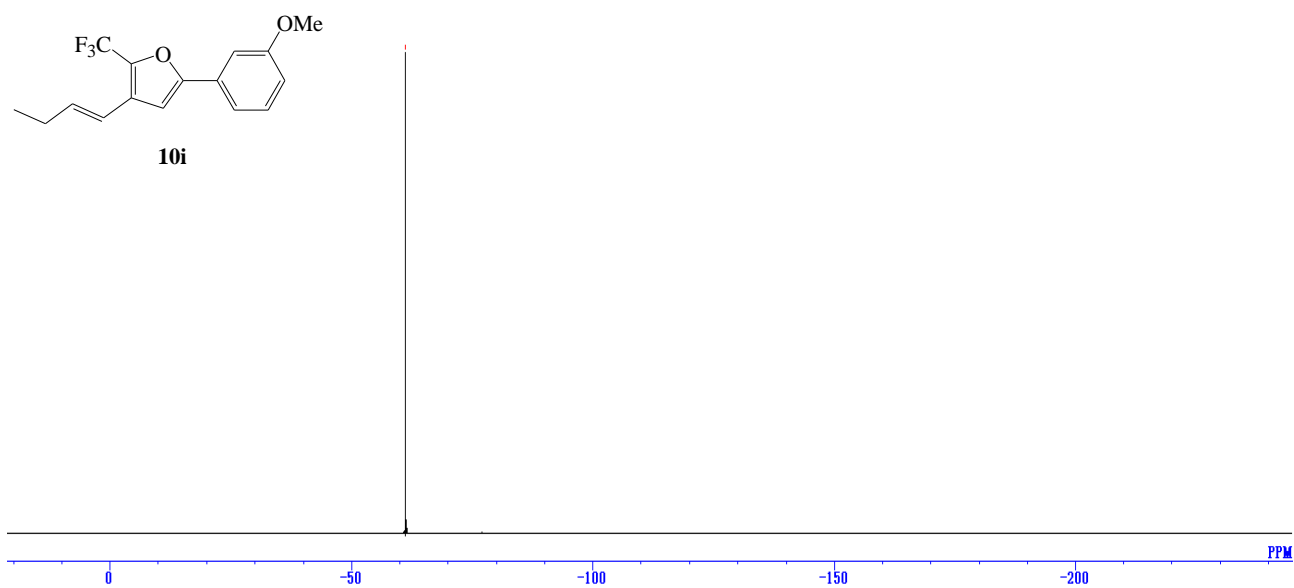
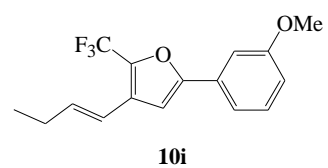


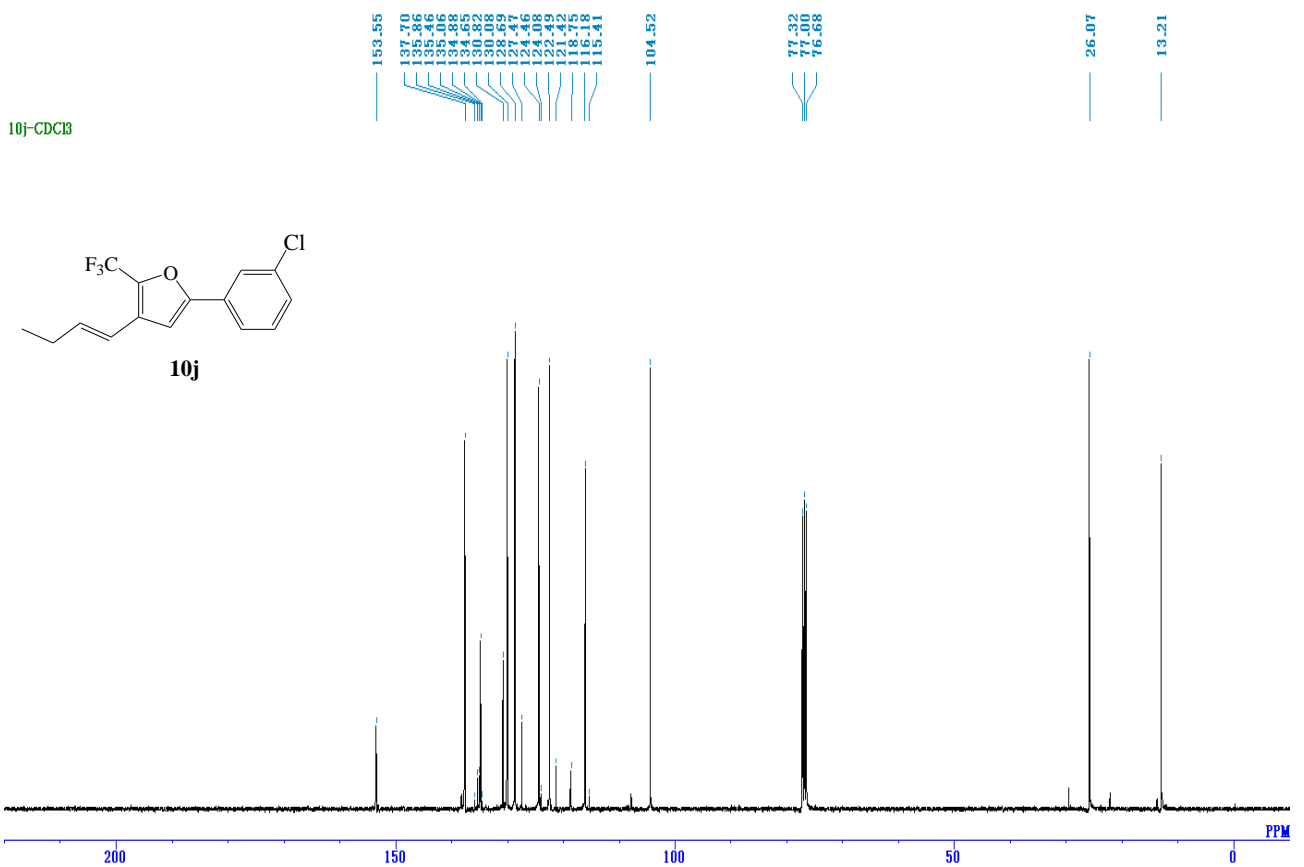
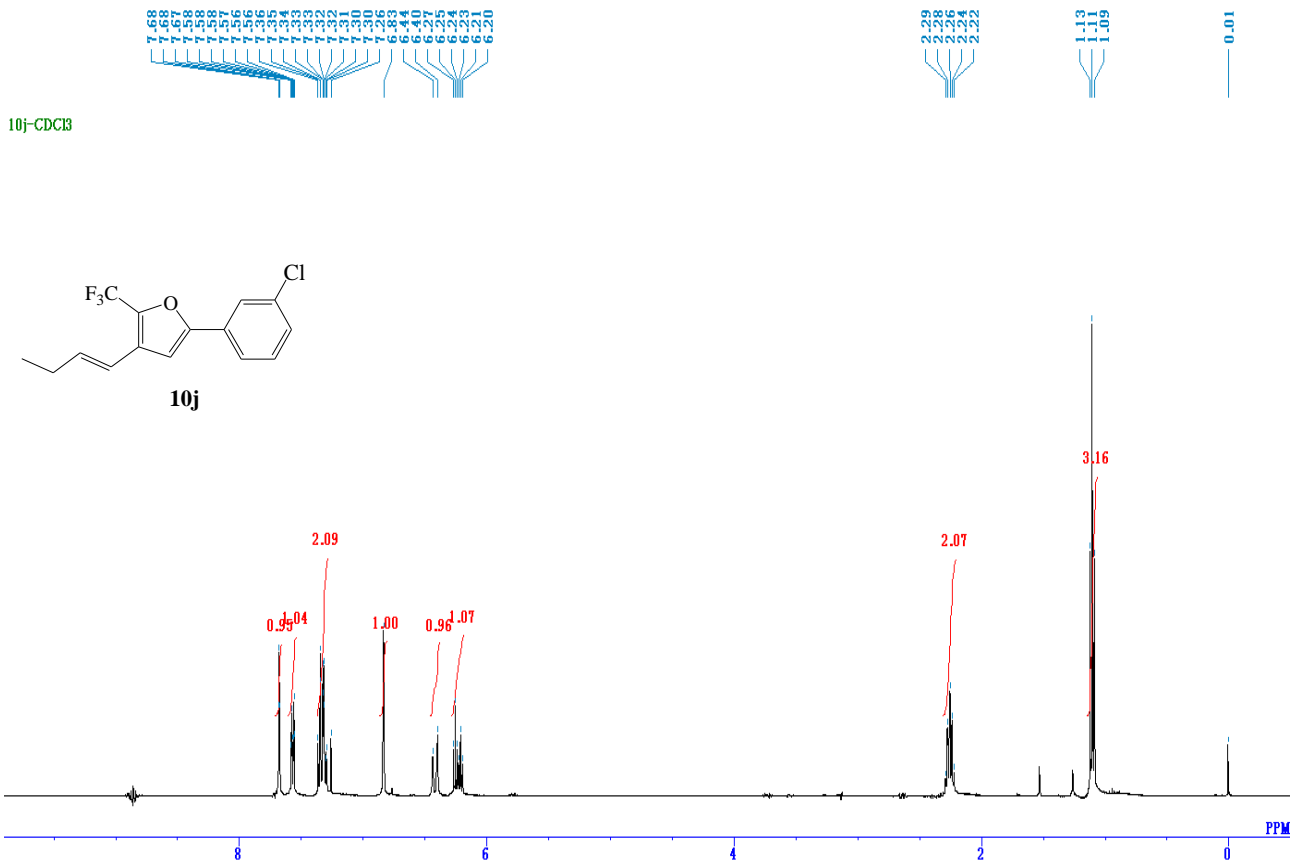
10i -CDCl₃



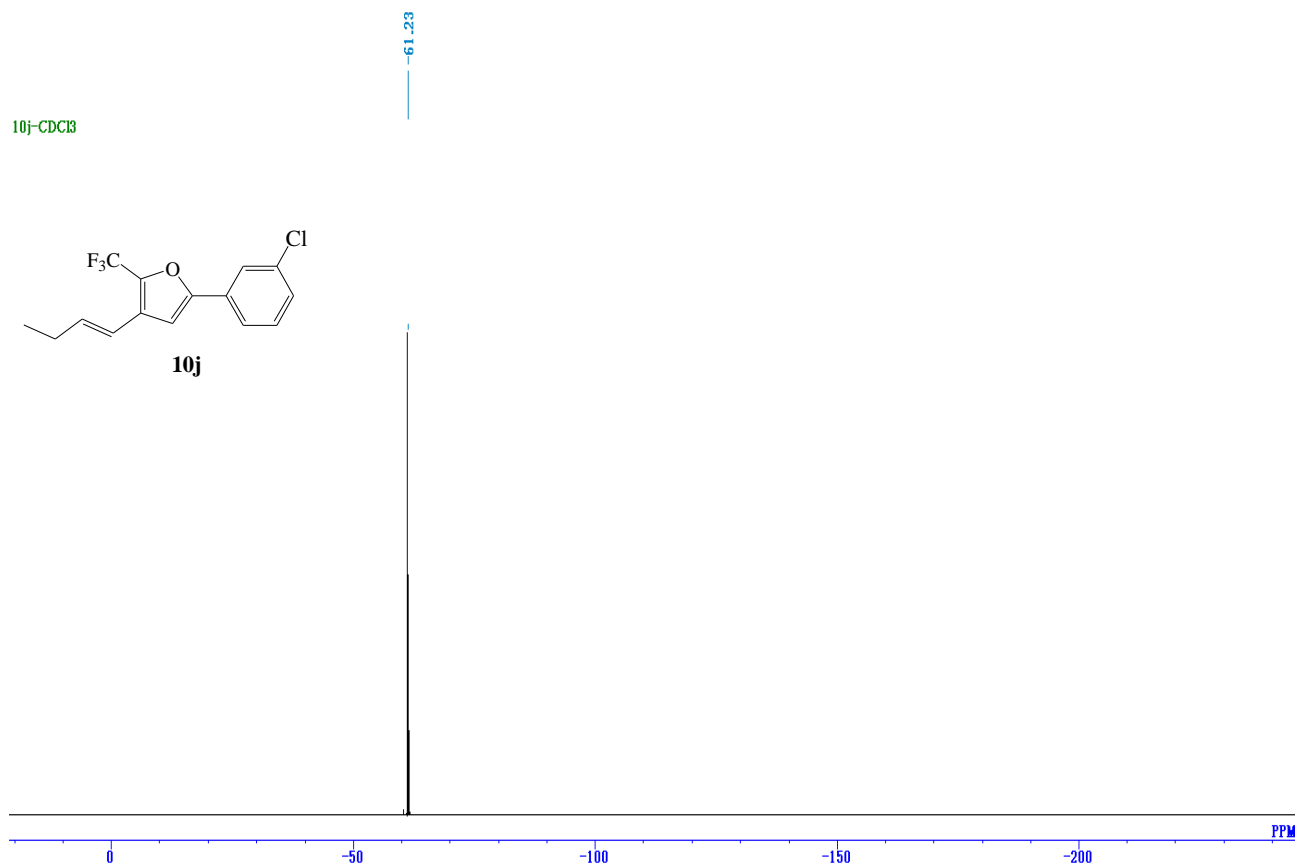
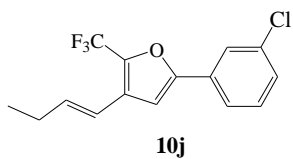
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-61.12





10j-CDCl3

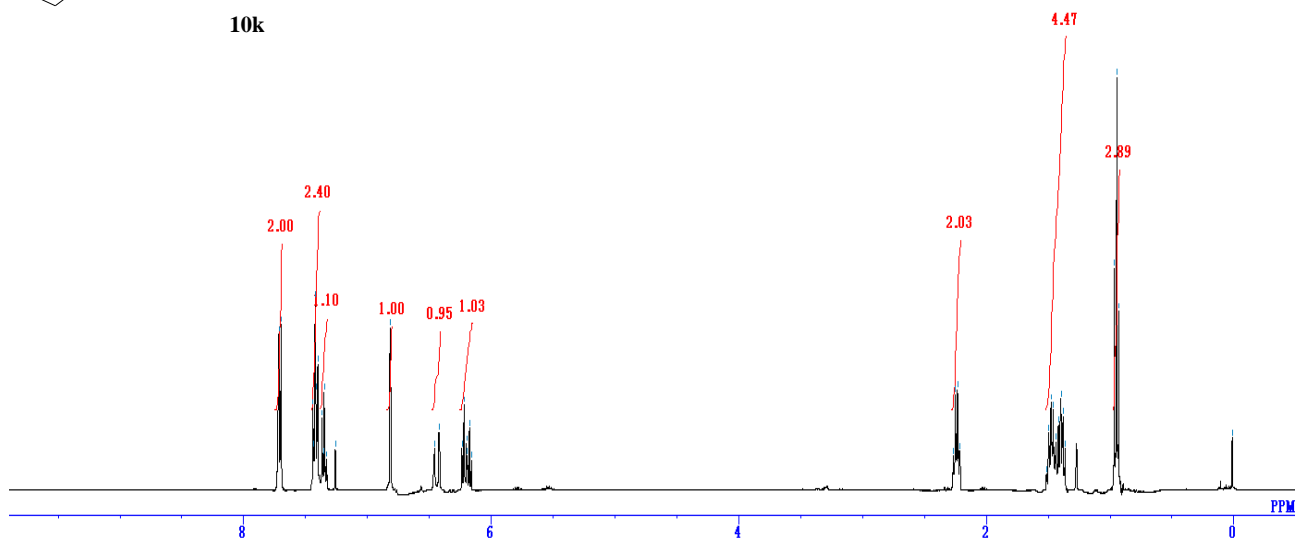
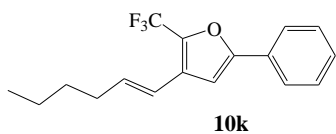


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7.70
7.44
7.42
7.42
7.37
7.35
7.35
7.26
6.82
6.45
6.23
6.22
6.20
6.18

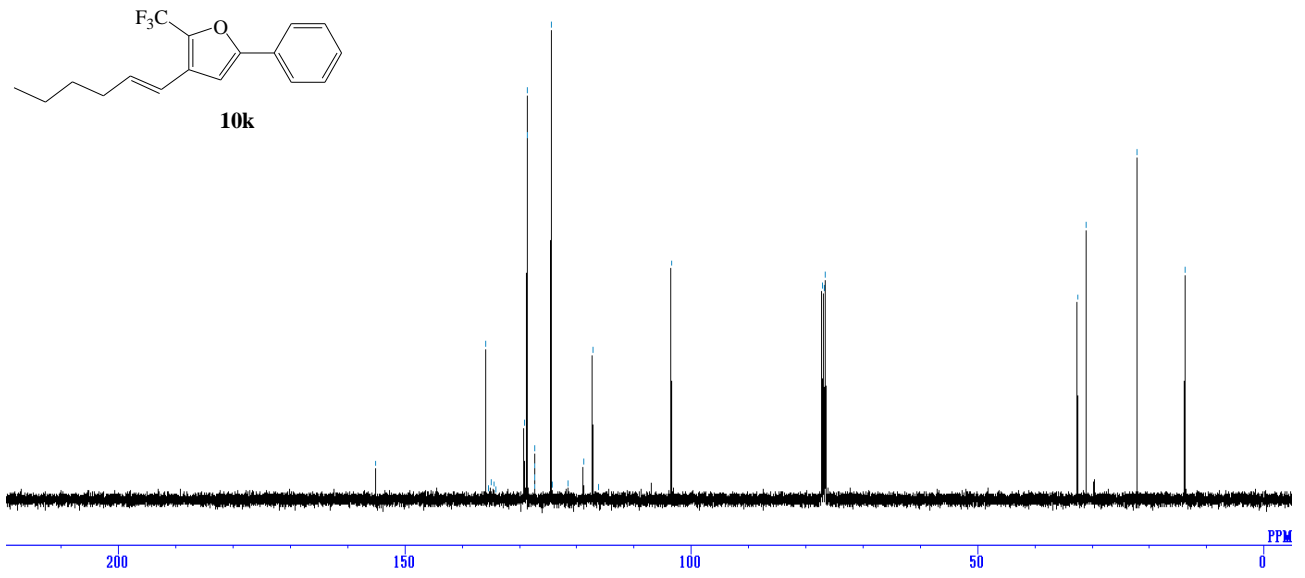
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1.44
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1.40
1.36
0.97
0.95

0.02

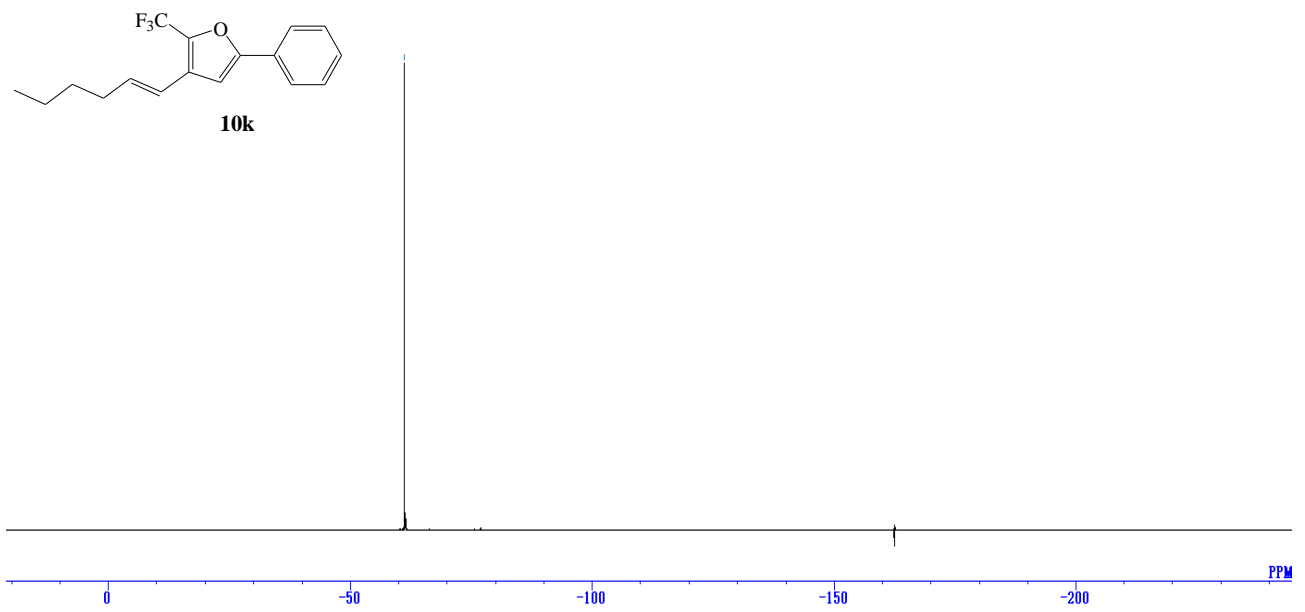
10k-CDCl3



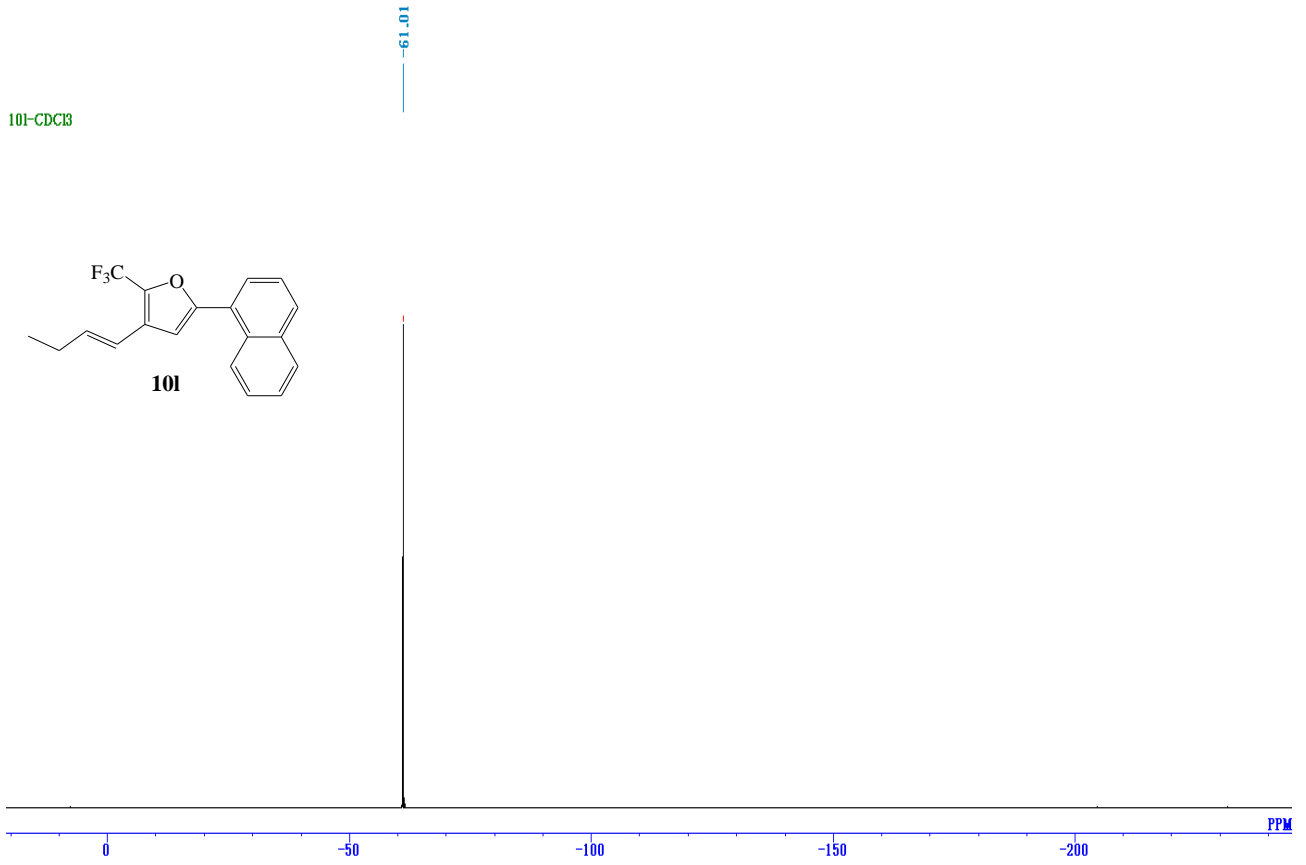
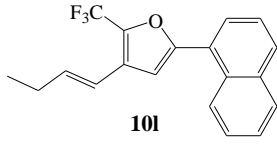
101-CDCl3



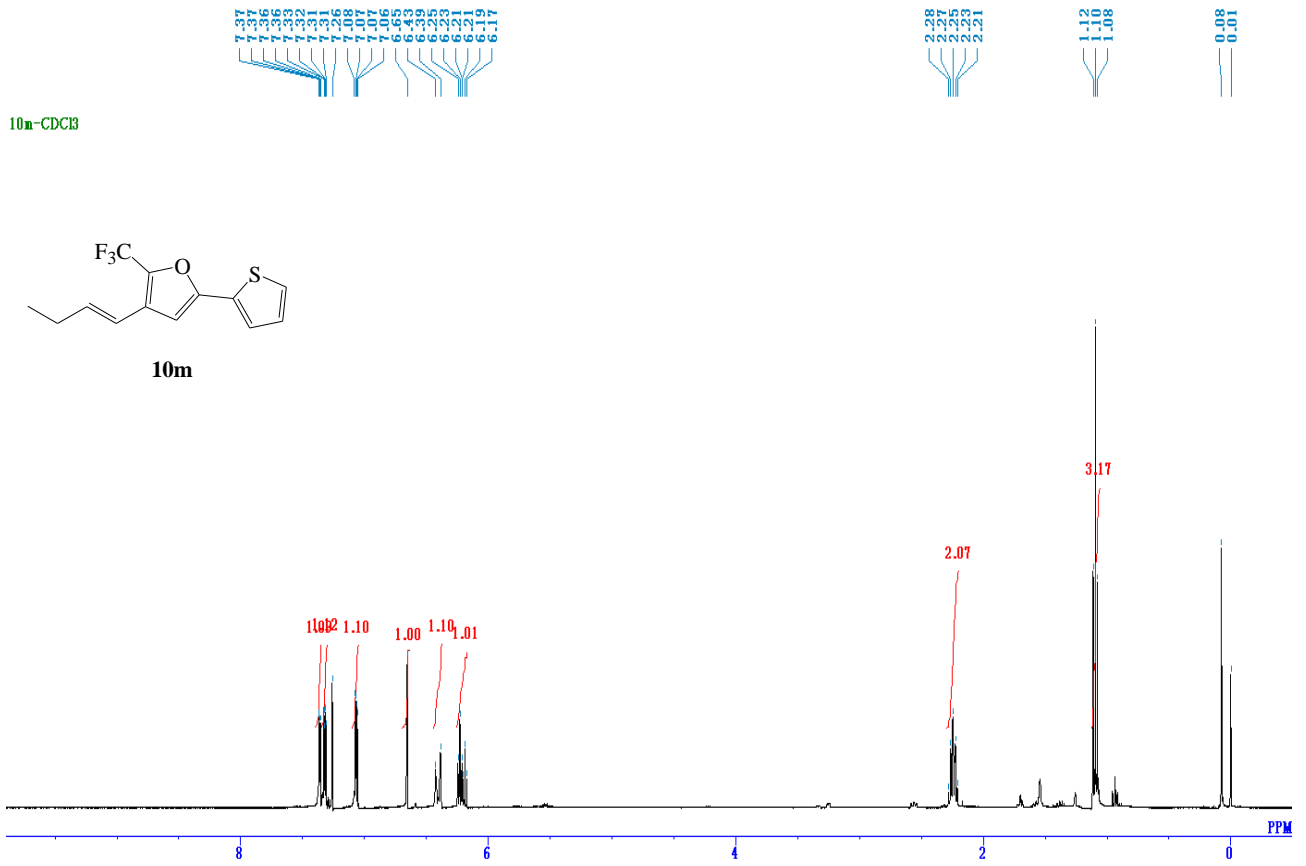
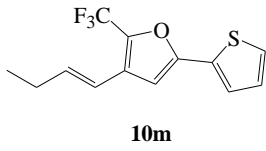
101-CDCl3



10l-CDCl3



10m-CDCl3



10m-CDCl3

150.63
134.92
134.54
134.14
133.79
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127.50
127.49
127.44
125.95
124.12
121.45
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116.24
116.12

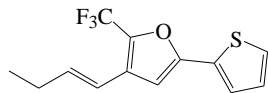
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77.32
77.00
76.69

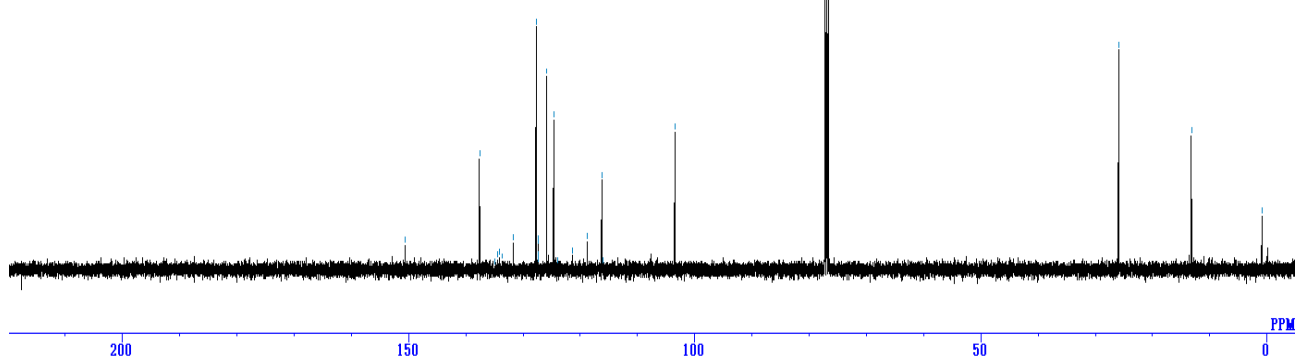
26.07

13.26

1.01

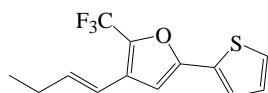


10m



10m-CDCl3

61.23



10m

