

**Visible Light-Promoted Thiy Radical Generation from Sodium Sulfinates:
A Radical-Radical Coupling to Thioesters**

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General Methods:

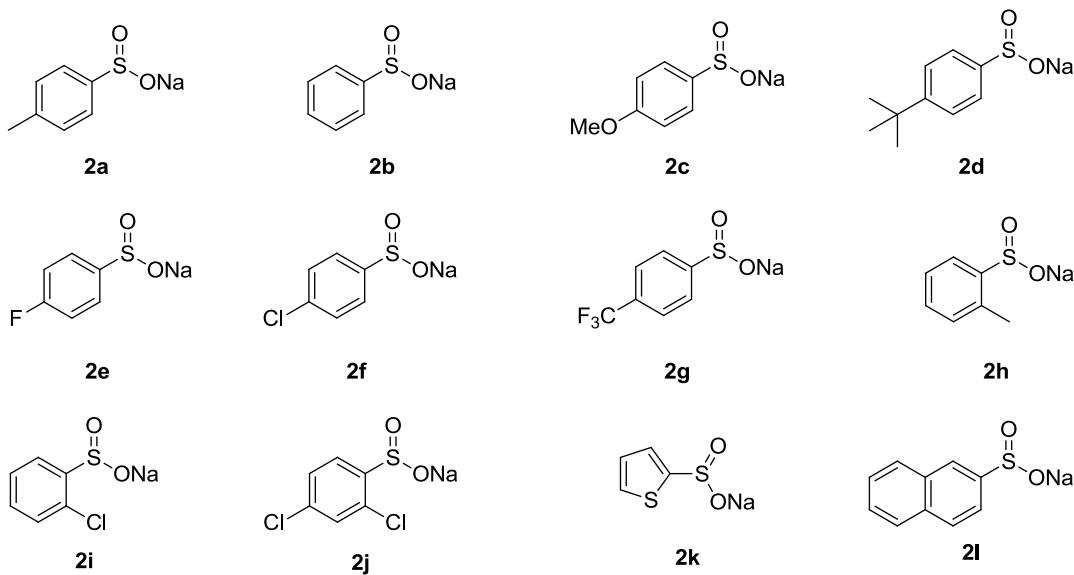
All reactions were carried out with oven-dried glassware. The progress of all reactions were monitored by TLC. HPLC grade solvents were used without further drying. Unless otherwise specified, all chemicals were purchased from Acros or Alfa Aesar and all solvents were purchased from Fischer Scientific. ¹H and ¹³C NMR spectra were recorded in CDCl₃, CD₃OD and D₂O as a solvent on JEOL 600 MHz Fourier transform spectrometers at ambient temperature. The coupling constant *J* is given in Hz. The chemical shifts are reported in ppm on a scale downfield from TMS as internal standard, and signal patterns are indicated as follows: s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, m = multiplet, br = broad. The infrared spectra were recorded on a Thermo Nicolet IR 300 Spectrometer. For high (HRMS) resolution, m/z ratios are reported as values in atomic mass units. Silica gel (32-64u, Dynamic Adsorbent, Inc.) was used for column chromatography. Melting points were recorded on a Buchi-B-450 melting point apparatus and the values were uncorrected.

General Procedure A for the Preparation of Sodium Aryl Sulfinates:

Sodium aryl sulfinates were prepared according to the literature procedure.¹

Sodium sulfite (20 mmol, 2 eq.), sodium bicarbonate (20 mmol, 2 eq.) and the corresponding aryl sulfonyl chloride (10 mmol, 1 eq.) were dissolved in distilled water (10 mL). The reaction mixture was stirred for 4 h at 80 °C. After cooling down to room temperature, water was removed *in vacuo*. 25 mL of ethanol was then added to this white residue and the resulting heterogeneous solution was filtered. The filtrate was concentrated under reduced pressure and the desired sodium aryl sulfinates were obtained as white crystalline powders in 82-96% yields.

Sodium aryl sulfinates **2a**, **2b** and **2f** are commercially available. ¹H and ¹³C NMR spectra of the known compounds **2c**, **2e** and **2l** are compared with literature values.¹⁻² Sodium aryl sulfinates **2d** and **2g-2k** are newly synthesized and characterized.

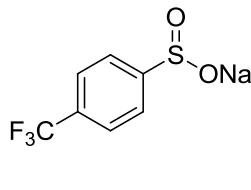


Characterization of Sodium Aryl Sulfinates:

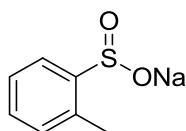
Sodium 4-methoxybenzenesulfinate (2c):¹ The product **2c** was prepared by the General Procedure A using 4-methoxybenzenesulfonyl chloride (2.07 g, 10.0 mmol). 1.78 g (92%); White solid; ¹H NMR (600 MHz, D₂O): δ 7.60-7.57 (m, 2H), 7.10-7.06 (m, 2H), 3.86 (s, 3H); ¹³C NMR (150 MHz, D₂O): δ 160.6, 146.0, 125.3, 114.4, 55.6.

Sodium 4-(*tert*-butyl)benzenesulfinate (2d): The product **2d** was prepared by the General Procedure A using 4-*tert*-butylbenzenesulfonyl chloride (2.3 g, 10.0 mmol). 2.09 g (96%); White solid; ¹H NMR (600 MHz, CD₃OD) δ 7.58 (d, *J* = 9.0 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 1.33 (s, 9H); ¹³C NMR (150 MHz, CD₃OD) δ 154.2, 153.8, 126.3, 125.0, 35.6, 31.7; IR(neat): 1079, 1044, 1035, 1022, 992, 975, 830, 745 cm⁻¹.

Sodium 4-fluorobenzenesulfinate (2e):¹ The product **2e** was prepared by the General Procedure A using 4-fluorobenzenesulfonyl chloride (1.95 g, 10.0 mmol). 1.68 g (92%); White solid; ¹H NMR (600 MHz, D₂O): δ 7.62-7.58 (m, 2H), 7.22-7.17 (m, 2H); ¹³C NMR (150 MHz, D₂O): δ 163.7 (d, *J* = 244.2 Hz), 149.5, 125.7 (d, *J* = 4.2 Hz), 115.8 (d, *J* = 21.6 Hz).



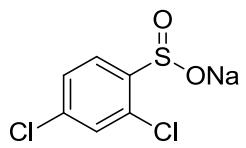
Sodium 4-(trifluoromethyl)benzenesulfinate (2g**):** The product **2g** was prepared by the General Procedure A using 4-(trifluoromethyl)benzenesulfonyl chloride (0.5 g, 2.04 mmol). 350.8 mg (74%); White solid; ¹H NMR (600 MHz, CD₃OD) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 7.8 Hz, 2H); ¹³C NMR (150 MHz, CD₃OD): δ 161.5, 132.3 (q, *J* = 31.5 Hz), 126.5 (q, *J* = 4.3 Hz), 126.2 (q, *J* = 270.0 Hz), 126.1; IR(neat): 1398, 1323, 1130, 1044, 974, 842, 694 cm⁻¹.



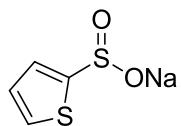
Sodium 2-methylbenzenesulfinate (2h**):** The product **2h** was prepared by the General Procedure A using *o*-toluenesulfonyl chloride (1.9 g, 10 mmol). 1.58 g (89%), (76% purity, contains corresponding sulfonate sodium salt impurity); White solid; ¹H NMR (600 MHz, CD₃OD) δ 7.80 (dd, *J* = 7.8, 2.4 Hz, 1H), 7.27-7.22 (m, 2H), 7.13 (d, *J* = 6.6 Hz, 1H), 2.56 (s, 3H); IR(neat): 1031, 967, 753, 717, 673 cm⁻¹.



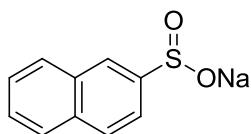
Sodium 2-chlorobenzenesulfinate (2i**):** The product **2i** was prepared by the General Procedure A using 2-chlorobenzenesulfonyl chloride (2.12 g, 10.0 mmol). 1.84 g (92%); White solid; ¹H NMR (600 MHz, D₂O) δ 7.70 (d, *J* = 7.2 Hz, 1H), 7.45-7.41 (m, 1H), 7.37 (d, *J* = 4.2 Hz, 2H); ¹³C NMR (150 MHz, D₂O): δ 149.6, 131.8, 131.6, 130.0, 127.9, 123.3; IR(neat): 1442, 1426, 1092, 1046, 1028, 974, 762, 753, 714, 653 cm⁻¹.



Sodium 2,4-dichlorobenzenesulfinate (2j**):** The product **2j** was prepared by the General Procedure A using 2,4-dichlorobenzenesulfonyl chloride (1.2 g, 5.0 mmol). 0.94 g (82%); White solid; ¹H NMR (600 MHz, D₂O): δ 7.62 (d, *J* = 8.4 Hz, 1H), 7.45-7.34 (m, 2H); ¹³C NMR (150 MHz, D₂O): δ 148.6, 136.1, 132.5, 129.5, 128.0, 124.7; IR(neat): 1570, 1443, 1366, 1105, 1031, 963, 867, 827, 802, 708 cm⁻¹.



Sodium thiophene-2-sulfinate (2k**):** The product **2k** was prepared by the General Procedure A using 2-thiophenesulfonyl chloride (1.82 g, 10.0 mmol). 1.57 g (93%); White solid; ¹H NMR (600 MHz, D₂O): δ 7.58 (d, *J* = 5.4 Hz, 1H), 7.33 (d, *J* = 3.6 Hz, 1H), 7.11 (dd, *J* = 4.2, 3.6 Hz, 1H); ¹³C NMR (150 MHz, D₂O): δ 158.3, 128.5, 127.7, 126.5; IR(neat): 1406, 1216, 1020, 971, 851, 716, 690 cm⁻¹.



Sodium naphthalene-2-sulfinate (2I): The product **2I** was prepared by the General Procedure A using 2-naphthalenesulfonyl chloride (2.3 g, 10.1 mmol). 1.98 g (91%), (85% purity, contains corresponding sodium sulfonate salt impurity); White solid; ^1H NMR spectrum for this compound are consistent with previously reported literature data.²² ^1H NMR (600 MHz, CD₃OD): δ 8.11 (s, 1H), 7.96-7.92 (m, 2H), 7.90-7.87 (m, 1H), 7.80 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.53-7.50 (m, 2H).

Experimental Setup for Light-Induced Reactions

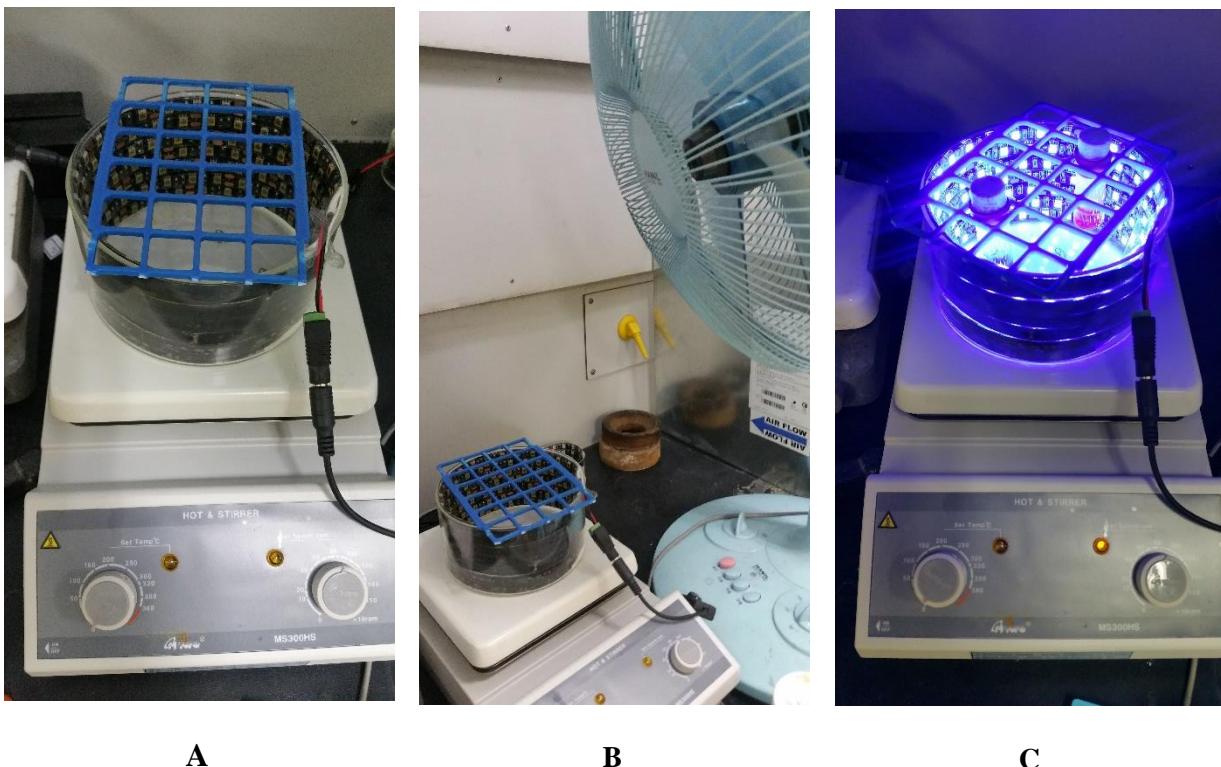


Figure S1. Pictures of a photochemistry reaction setup.

A—Homemade photoreactor, B – Cooling fan, C – Reaction setup

Features of LED tapes

Blue LED tape: 60 LED stripes (3 meter)

Blue light - $\lambda_{\text{max}} = 460 \text{ nm}$, 12-14W/meter

General Procedure B for the Synthesis of Thioesters:

To an oven-dried 10 mL vial equipped with a magnetic stir bar, sodium aryl sulfinate (0.2 mmol, 1.0 equiv.), HEH (0.4 mmol, 2.0 equiv.) and *fac*-Ir(ppy)₃ (0.003 mmol, 1.5 mol %) were added and the vial was sealed with a screw cap. The reaction vial was then purged with Ar. To this vial was added anhydrous dichloroethane (2.0 mL, 0.1 M) followed by aroyl chlorides (0.60 mmol, 3 equiv.) and DIPEA (0.60 mmol, 3.0 equiv.). The mixture was further purged with Ar for 5 mins and stirred with irradiation of blue LEDs (460 nm) for 6 h (distance app. 3 cm) at room temperature. After the reaction was complete by TLC, the solution was concentrated *in vacuo*, and the residue was purified by flash column chromatography (PE/DCM:2/1) to provide the desired product.

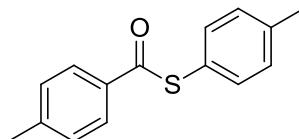
1 mmol scale reaction:

To an oven-dried 20 mL vial equipped with a magnetic stir bar, sodium aryl sulfinate **2a** (178.2 mg, 1 mmol), HEH (506.9 mg, 2 mmol) and *fac*-Ir(ppy)₃ (9.8 mg, 0.015 mmol, 1.5 mol %) were added and the vial was sealed with a screw cap. The reaction vial was then purged with Ar. To this vial was added anhydrous dichloroethane (10 mL, 0.1 M) followed by benzoyl chloride **1a** (0.35 mL, 3 mmol) and DIPEA (0.52 mL, 3 mmol). The mixture was further purged with Ar for 5 mins and stirred with irradiation of blue LEDs (460 nm) for 6 h (distance app. 3 cm) at room temperature. After the reaction was complete by TLC, the solution was concentrated *in vacuo*, and the residue was purified by flash column chromatography on silicagel (PE/DCM:2/1) to provide the desired thioester **3a** (208.8 mg, 91%) as a white solid.

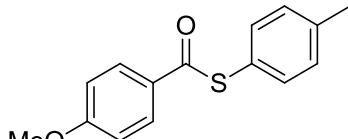
Characterization of Thioesters in Scheme 2 and 3:

S-p-Tolyl benzothioate (3a): The product **3a** was prepared by the General Procedure B using **2a** (36 mg, 0.2 mmol), 37.3 mg (81%); White solid; ¹H NMR and ¹³C NMR spectra for this compound are consistent with previously reported literature data.³ ¹H NMR (600 MHz, CDCl₃): δ 8.04 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.63-7.59 (m, 1H), 7.49 (*t*, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 2.41 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 190.7, 139.9, 136.8, 135.1, 133.7, 130.2, 128.8, 127.6, 123.9, 21.5.

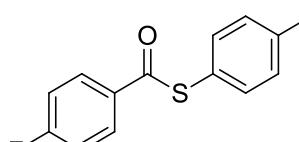




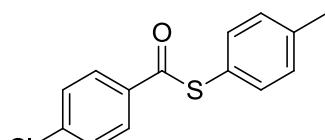
S-p-Tolyl 4-methylbenzothioate (3b): The product **3b** was prepared by the General Procedure B using **2a** (36 mg, 0.2 mmol). 31.0 mg (63%); White solid; ¹H NMR and ¹³C NMR spectra for this compound are consistent with previously reported literature data.⁴ ¹H NMR (600 MHz, CDCl₃): δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.27 (t, *J* = 7.8 Hz, 4H), 2.43 (s, 3H), 2.40 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 190.3, 144.6, 139.9, 135.2, 134.3, 130.2, 129.5, 127.7, 124.1, 21.9, 21.5.



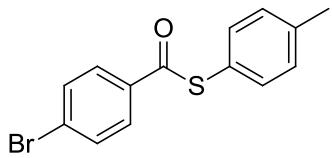
S-p-Tolyl 4-methoxybenzothioate (3c): The product **3c** was prepared by the General Procedure B using **2a** (36 mg, 0.2 mmol). 27.4 mg (53%); White solid; ¹H NMR and ¹³C NMR spectra for this compound are consistent with previously reported literature data.³ ¹H NMR (600 MHz, CDCl₃): δ 8.01 (d, *J* = 9.0 Hz, 2H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 9.0 Hz, 2H), 3.88 (s, 3H), 2.40 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 189.2, 164.0, 139.8, 135.3, 130.2, 129.8, 129.6, 124.1, 114.0, 55.7, 21.5.



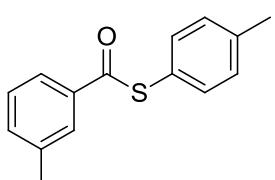
S-p-Tolyl 4-fluorobenzothioate (3d): The product **3d** was prepared by the General Procedure B using **2a** (36 mg, 0.2 mmol). 36.3 mg (73%); White solid, m.p. 71-73 °C; ¹H NMR (600 MHz, CDCl₃): δ 8.06 (dd, *J* = 8.4, 6.0 Hz, 2H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.16 (m, 2H), 2.41 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 189.3, 166.2 (d, *J* = 254.2 Hz), 140.1, 135.2, 133.2 (d, *J* = 2.8 Hz), 130.3, 130.2 (d, *J* = 10.5 Hz), 123.6, 116.0 (d, *J* = 21.6 Hz), 21.5; ¹⁹F NMR (564 MHz, CDCl₃): δ -104.3; IR(neat): 1676, 1597, 1504, 1234, 1199, 1155, 907, 843, 809, 635, 544, 480 cm⁻¹; HRMS (EI): m/z calcd for C₁₄H₁₁FOS [M]⁺ 246.0515 Found 246.0513.



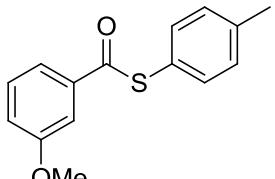
S-p-Tolyl 4-chlorobenzothioate (3e): The product **3e** was prepared by the General Procedure B using **2a** (36 mg, 0.2 mmol). 38.2 mg (72%); White solid; ¹H NMR and ¹³C NMR spectra for this compound are consistent with previously reported literature data.⁴ ¹H NMR (600 MHz, CDCl₃): δ 7.98-7.95 (m, 2H), 7.47-7.44 (m, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 2.41 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 189.6, 140.2, 140.1, 135.1, 130.3 (2C), 129.1, 128.9, 123.4, 21.5.



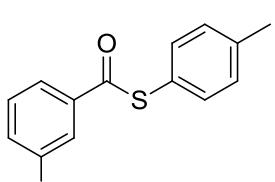
S-*p*-Tolyl 4-bromobenzothioate (3f): The product **3f** was prepared by the General Procedure B using **2a** (36 mg, 0.2 mmol). **3f:** 15.5 mg (25%) and **3a:** 14.3 mg (31%); White solid, m.p. 119-121 °C; ¹H NMR (600 MHz, CDCl₃): δ 7.90-7.77 (m, 2H), 7.64-7.61 (m, 2H), 7.39-7.36 (m, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 2.41 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 189.9, 140.2, 135.6, 135.1, 132.2, 130.3, 129.1, 128.8, 123.4, 21.6; IR(neat): 1678, 1203, 1174, 1069, 1001, 907, 835, 810, 772, 669, 634 cm⁻¹; HRMS (EI): m/z calcd for C₁₄H₁₁BrOS [M]⁺ 305.9714 Found 305.9711.



S-*p*-Tolyl 3-methylbenzothioate (3g): The product **3g** was prepared by the General Procedure B using **2a** (36 mg, 0.2 mmol). 42.3 mg (87%); White solid, m.p. 40-43 °C; ¹H NMR (600 MHz, CDCl₃): δ 7.83 (d, *J* = 7.2 Hz, 2H), 7.43-7.35 (m, 4H), 7.27 (d, *J* = 7.8 Hz, 2H), 2.43 (s, 3H), 2.41 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 190.8, 139.9, 138.7, 136.8, 135.1, 134.5, 130.2, 128.7, 128.0, 124.8, 124.0, 21.5, 21.4; IR(neat): 1678, 1492, 1245, 1160, 1149, 956, 939, 825, 806, 786, 696, 681, 673, 480 cm⁻¹; HRMS (EI): m/z calcd for C₁₅H₁₄OS [M]⁺ 242.0765 Found 242.0761.

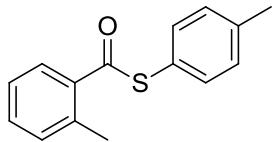


S-*p*-Tolyl 3-methoxybenzothioate (3h): The product **3h** was prepared by the General Procedure B using **2a** (36 mg, 0.2 mmol). 40.7 mg (78%); Gummy solid; ¹H NMR (600 MHz, CDCl₃): δ 7.65 (d, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 2.4 Hz, 1H), 7.41-7.37 (m, 3H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.15 (dd, *J* = 8.4, 3.0 Hz, 1H), 3.86 (s, 3H), 2.41 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 190.7, 159.9, 140.0, 138.1, 135.1, 130.2, 129.9, 123.9, 120.2, 120.1, 111.8, 55.6, 21.5; IR(neat): 1680, 1597, 1583, 1484, 1288, 1260, 1167, 1155, 1041, 959, 933, 808, 787, 694 cm⁻¹; HRMS (EI): m/z calcd for C₁₅H₁₄O₂S [M]⁺ 258.0715 Found 258.0720.

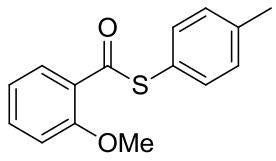


S-*p*-Tolyl 3-chlorobenzothioate (3i): The product **3i** was prepared by the General Procedure B using **2a** (36 mg, 0.2 mmol). 29.4 mg (56%); White solid, m.p. 62-64 °C; ¹H NMR (600 MHz, CDCl₃): δ 7.99 (t, *J* = 2.4 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.59-7.56 (m, 1H), 7.43 (t, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz,

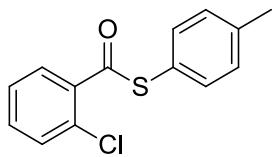
2H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 189.7, 140.3, 138.3, 135.1, 135.0, 133.6, 130.4, 130.2, 127.6, 125.7, 123.3, 21.5; IR(neat): 1694, 1669, 1195, 923, 806, 767, 731, 691, 669, 481 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{11}\text{ClOS} [\text{M}]^+$ 262.0219 Found 262.0216.



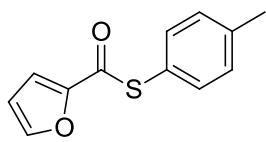
S-p-Tolyl 2-methylbenzothioate (3j): The product **3j** was prepared by the General Procedure B using **2a** (36 mg, 0.2 mmol). 40.5 mg (83%); White solid, m.p. 77-78 $^\circ\text{C}$; ^1H NMR (600 MHz, CDCl_3): δ 7.94 (d, $J = 7.2$ Hz, 1H), 7.45-7.38 (m, 3H), 7.32-7.27 (m, 4H), 2.49 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 192.8, 139.9, 137.5, 137.0, 135.0, 132.1, 131.9, 130.3, 128.8, 126.0, 124.8, 21.5, 20.9; IR(neat): 1689, 1670, 1455, 1193, 891, 810, 783, 762, 724, 681, 648 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{14}\text{OS} [\text{M}]^+$ 242.0765 Found 242.0765.



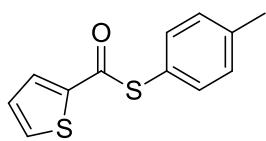
S-p-Tolyl 2-methoxybenzothioate (3k): The product **3k** was prepared by the General Procedure B using **2a** (36 mg, 0.2 mmol). 26.6 mg (51%); White solid, m.p. 58-59 $^\circ\text{C}$; ^1H NMR (600 MHz, CDCl_3): δ 7.86 (d, $J = 7.8$ Hz, 1H), 7.51 (t, $J = 7.8$ Hz, 1H), 7.41 (d, $J = 7.8$ Hz, 2H), 7.27 (d, $J = 6.6$ Hz, 2H), 7.03 (t, $J = 8.4$ Hz, 2H), 3.97 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 189.8, 158.3, 139.6, 135.0, 134.0, 130.1 (2C), 126.5, 125.3, 120.6, 112.2, 56.0, 21.5; IR(neat): 1696, 1650, 1595, 1485, 1463, 1435, 1250, 1190, 1162, 1089, 904, 891, 808, 758, 369 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{15}\text{H}_{14}\text{O}_2\text{S} [\text{M}]^+$ 258.0715 Found 258.0718.



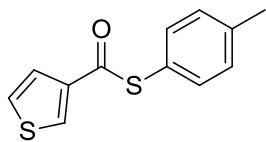
S-p-Tolyl 2-chlorobenzothioate (3l): The product **3l** was prepared by the General Procedure B using **2a** (36 mg, 0.2 mmol). 20.0 mg (38%); White solid, m.p. 91-92 $^\circ\text{C}$; ^1H NMR (600 MHz, CDCl_3): δ 7.76 (dd, $J = 8.4, 2.4$ Hz, 1H), 7.48-7.40 (m, 4H), 7.36 (td, $J = 7.2, 1.2$ Hz, 1H), 7.28 (d, $J = 7.2$ Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 190.8, 140.2, 137.3, 134.8, 132.5, 131.2, 131.0, 130.3, 129.3, 126.8, 124.0, 21.6; IR(neat): 1685, 1583, 1462, 1431, 1198, 900, 806, 764, 729, 716, 642, 480 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{11}\text{ClOS} [\text{M}]^+$ 262.0219 Found 262.0216.



S-p-Tolyl furan-2-carbothioate (3m): The product **3m** was prepared by the general procedure B using **2a** (36 mg, 0.2 mmol). 37.5 mg (85%); White solid; ¹H NMR and ¹³C NMR spectra for this compound are consistent with previously reported literature data.³ ¹H NMR (600 MHz, CDCl₃): δ 7.64-7.62 (m, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.29-7.25 (m, 3H), 6.59-6.57 (m, 1H), 2.41 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 179.3, 150.6, 146.5, 140.1, 135.2, 130.3, 122.7, 116.3, 112.5, 21.5.



S-p-Tolyl thiophene-2-carbothioate (3n): The product **3n** was prepared by the General Procedure B using **2a** (36 mg, 0.2 mmol). 37.3 mg (79%); White solid, m.p. 64-65 °C; ¹H NMR (600 MHz, CDCl₃): δ 7.92-7.90 (m, 1H), 7.66 (d, *J* = 4.8 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.16 (t, *J* = 4.2 Hz, 1H), 2.41 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 182.6, 141.6, 140.1, 135.1, 133.2, 131.6, 130.2, 128.1, 123.4, 21.5; IR(neat): 3101, 1659, 1596, 1511, 1407, 1233, 1203, 1179, 1084, 1052, 808, 741, 659, 484 cm⁻¹; HRMS (EI): m/z calcd for C₁₂H₁₀OS₂ [M]⁺ 234.0713 Found 234.0715.

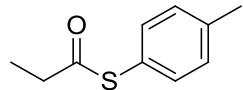


S-p-Tolyl thiophene-3-carbothioate (3o): The product **3o** was prepared by the General Procedure B using **2a** (36 mg, 0.2 mmol). 32.4 mg (68%); White solid, m.p. 72-74 °C; ¹H NMR (600 MHz, CDCl₃): δ 8.21-8.19 (m, 1H), 7.58 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.36 (dd, *J* = 4.8, 2.4 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 2.41 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 184.1, 140.5, 140.0, 135.0, 131.1, 130.2, 126.7, 126.3, 123.7, 21.5; IR(neat): 1661, 1229, 1158, 961, 843, 806, 793, 765, 684, 485 cm⁻¹; HRMS (EI): m/z calcd for C₁₂H₁₀OS₂ [M]⁺ 234.0713 Found 234.0715.

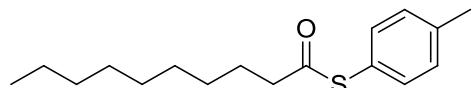


S-p-Tolyl naphthalene-1-carbothioate (3p): The product **3p** was prepared by the General Procedure B using **2a** (36 mg, 0.2 mmol). 43.8 mg (78%); White solid, m.p. 81-82 °C; ¹H NMR (600 MHz, CDCl₃): δ 8.54 (d, *J* = 9.0 Hz, 1H), 8.23-8.22 (m, 1H), 8.04 (d, *J* = 7.8 Hz, 1H), 7.90 (d, *J* = 7.2 Hz, 1H), 7.56-7.53 (m, 3H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 2.44 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 192.9, 140.0, 135.0, 134.9,

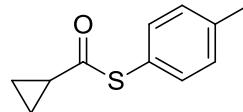
133.9, 133.3, 130.3, 129.5, 128.5, 128.2, 128.1, 126.8, 125.5, 124.9, 124.6, 21.6; IR(neat): 3048, 2920, 1683, 1657, 1507, 1493, 1224, 1171, 1055, 897, 805, 777, 763, 670, 480 cm⁻¹; HRMS (EI): m/z calcd for C₁₈H₁₄OS [M]⁺ 278.0765 Found 278.0764.



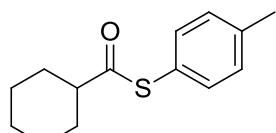
S-p-Tolyl propanethioate (3q): The product **3q** was prepared by the General Procedure B using **2a** (36 mg, 0.2 mmol). 16.7 mg (46%); Colorless liquid; ¹H NMR and ¹³C NMR spectra for this compound are consistent with previously reported literature data.³ ¹H NMR (600 MHz, CDCl₃): δ 7.30 (d, J = 7.8 Hz, 2H), 7.22 (d, J = 7.8 Hz, 2H), 2.67 (q, J = 7.2 Hz, 2H), 2.38 (s, 3H), 1.22 (t, J = 7.8 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 199.0, 139.7, 134.6, 130.1, 124.4, 37.1, 21.5, 9.8.



S-p-Tolyl decanethioate (3r): The product **3r** was prepared by the General Procedure B using **2a** (36 mg, 0.2 mmol). 33.1 mg (59%); Colorless liquid; ¹H NMR (600 MHz, CDCl₃): δ 7.29 (d, J = 7.8 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 2.64 (t, J = 7.2 Hz, 2H), 2.37 (s, 3H), 1.66-1.74 (m, 2H), 1.37-1.21 (m, 12H), 0.89 (t, J = 7.6 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 198.3, 139.7, 134.6, 130.1, 124.6, 43.8, 32.0, 29.5, 29.4 (2C), 29.1, 25.8, 22.8, 21.5, 14.3; IR(neat): 2925, 2855, 1709, 1494, 1465, 1018, 998, 958, 806 cm⁻¹; HRMS (EI): m/z calcd for C₁₇H₂₆OS [M]⁺ 278.1704 Found 278.1704.

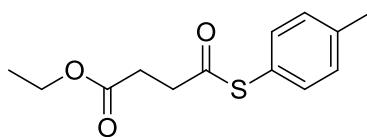


S-p-Tolyl cyclopropanecarbothioate (3s): The product **3s** was prepared by the General Procedure B using **2a** (36 mg, 0.2 mmol). 19.5 mg (50%); Colorless liquid; ¹H NMR (600 MHz, CDCl₃): δ 7.31 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 2.37 (s, 3H), 2.12-2.06 (m, 1H), 1.20 (dt, J = 8.5, 3.6 Hz, 2H), 0.99 (td, J = 7.8, 4.2 Hz, 2H); ¹³C NMR (150 MHz, CDCl₃): δ 198.2, 139.7, 134.7, 130.1, 124.4, 22.2, 21.5, 11.2; IR(neat): 2923, 2852, 1733, 1696, 1363, 1360, 1260, 1097, 1039, 979, 807, 773, 669 cm⁻¹; HRMS (EI): m/z calcd for C₁₁H₁₂OS [M]⁺ 192.0609 Found 192.0610.

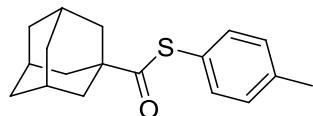


S-p-Tolyl cyclohexanecarbothioate (3t): The product **3t** was prepared by the General Procedure B using **2a** (36 mg, 0.2 mmol). 29.4 mg (62%); Gummy solid; ¹H NMR (600 MHz, CDCl₃): δ 7.28 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H),

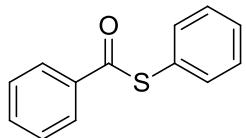
2.60 (tt, $J = 12.0, 3.6$ Hz, 1H), 2.37 (s, 3H), 1.99 (dd, $J = 13.8, 2.4$ Hz, 2H), 1.81 (dt, $J = 13.8, 3.6$ Hz, 2H), 1.71-1.64 (m, 1H), 1.57-1.47 (m, 2H), 1.36-1.21 (m, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 201.4, 139.5, 134.7, 130.1, 124.5, 52.6, 29.7, 25.7, 25.6, 21.5; IR(neat): 2931, 2855, 1704, 1494, 1449, 963, 806, 797, 767 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{18}\text{OS}$ [M] $^+$ 234.1078 Found 234.1081.



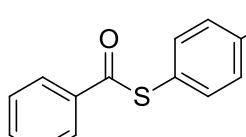
Ethyl 4-oxo-4-(*p*-tolylthio)butanoate (3u**):** The product **3u** was prepared by the General Procedure B using **2a** (36 mg, 0.2 mmol). 10.3 mg (20%); Colorless liquid; ^1H NMR (600 MHz, CDCl_3): δ 7.30 (d, $J = 8.4$ Hz, 2H), 7.21 (d, $J = 8.4$ Hz, 2H), 4.14 (q, $J = 7.2$ Hz, 2H), 2.98 (t, $J = 7.2$ Hz, 2H), 2.67 (t, $J = 7.2$ Hz, 2H), 2.37 (s, 3H), 1.26 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 196.9, 172.0, 139.9, 134.7, 130.2, 124.0, 61.0, 38.2, 29.4, 21.5, 14.3; IR(neat): 2981, 2925, 1732, 1705, 1494, 1375, 1204, 1067, 1019, 969, 809 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{13}\text{H}_{16}\text{O}_3\text{S}$ [M] $^+$ 252.0820 Found 252.0820.



S-*p*-Tolyl adamantane-1-carbothioate (3v**):** The product **3v** was prepared by the General Procedure B using **2a** (36 mg, 0.2 mmol). 23.5 mg (41%); White solid; ^1H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.⁵ ^1H NMR (600 MHz, CDCl_3): δ 7.26 (d, $J = 8.4$ Hz, 2H), 7.21 (d, $J = 7.8$ Hz, 2H), 2.37 (s, 3H), 2.09 (brs, 3H), 2.00 (brd, $J = 1.8$ Hz, 6H), 1.80-1.70 (m, 6H); ^{13}C NMR (150 MHz, CDCl_3): δ 204.8, 139.3, 135.1, 130.0, 124.5, 49.1, 39.4, 36.6, 28.4, 21.5.

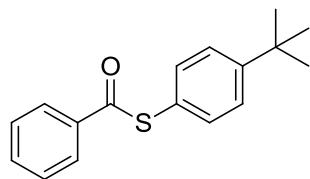


S-Phenyl benzothioate (3w**):** The product **3w** was prepared by the General Procedure B using **2b** (32.8 mg, 0.2 mmol). 36.4 mg (85%); White solid; ^1H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.³ ^1H NMR (600 MHz, CDCl_3): δ 8.04 (dd, $J = 8.4, 1.2$ Hz, 2H), 7.64-7.59 (m, 1H), 7.55-7.44 (m, 7H); ^{13}C NMR (150 MHz, CDCl_3): δ 190.3, 136.7, 135.2, 133.8, 129.7, 129.4, 128.9, 127.6, 127.5.

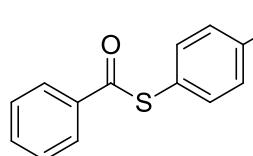


S-(4-Methoxyphenyl) benzothioate (3x**):** The product **3x** was prepared by the General Procedure B using **2c** (38.8 mg, 0.2 mmol). 41.4 mg (85%); White solid; ^1H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.^{2,6} ^1H NMR (600 MHz, CDCl_3): δ 8.05-8.01 (m, 2H), 7.62-7.58 (m, 1H),

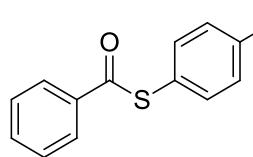
7.49 (t, $J = 7.8$ Hz, 2H), 7.44-7.40 (m, 2H), 7.01-6.98 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 191.2, 160.9, 136.8 (2C), 133.7, 128.9, 127.6, 118.0, 115.1, 55.5.



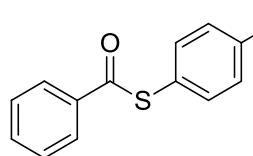
S-(4-(tert-Butyl)phenyl) benzothioate (3y): The product **3y** was prepared by the General Procedure B using **2d** (44.0 mg, 0.2 mmol). 38.8 mg (72%); White solid, m.p. 77-79 °C; ^1H NMR (600 MHz, CDCl_3): δ 8.06-8.02 (m, 2H), 7.63-7.59 (m, 1H), 7.52-7.47 (m, 4H), 7.47-7.43 (m, 2H), 1.36 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3): δ 190.8, 152.9, 136.8, 134.9, 133.7, 128.9, 127.6, 126.6, 123.9, 34.9, 31.4; IR(neat): 2963, 1680, 1448, 1204, 1176, 899, 827, 772, 686, 644 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{17}\text{H}_{18}\text{OS}$ [M] $^+$ 270.1078 Found 270.1076.



S-(4-Fluorophenyl) benzothioate (3z): The product **3z** was prepared by the General Procedure B using **2e** (36.4 mg, 0.2 mmol). 36.2 mg (78%); White solid; ^1H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.⁶ ^1H NMR (600 MHz, CDCl_3): δ 8.02 (d, $J = 7.8$ Hz, 2H), 7.62 (t, $J = 7.2$ Hz, 1H), 7.53-7.46 (m, 4H), 7.16 (t, $J = 7.8$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ 190.3, 163.8 (d, $J = 249.9$ Hz), 137.3 (d, $J = 8.7$ Hz), 136.5, 133.9, 128.9, 127.6, 122.7 (d, $J = 2.8$ Hz), 116.7 (d, $J = 21.4$ Hz); ^{19}F NMR (564 MHz, CDCl_3): δ -110.9.

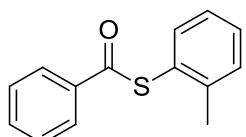


S-(4-Chlorophenyl) benzothioate (3aa): The product **3aa** was prepared by the General Procedure B using **2f** (40.0 mg, 0.2 mmol). 40.0 mg (80%); White solid; ^1H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.³ ^1H NMR (600 MHz, CDCl_3): δ 8.04-8.00 (m, 2H), 7.65-7.60 (m, 1H), 7.52-7.48 (m, 2H), 7.47-7.42 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3): δ 189.7, 136.4 (2C), 136.0, 134.0, 129.6, 128.9, 127.6, 125.9.

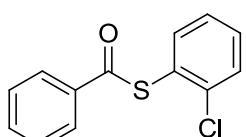


S-(4-(Trifluoromethyl)phenyl) benzothioate (3ab): The product **3ab** was prepared by the General Procedure B using **2g** (46.4 mg, 0.2 mmol). 41.9 mg (74%); White solid; ^1H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.⁶ ^1H NMR (600 MHz, CDCl_3): δ 8.05-8.01 (m, 2H), 7.71 (d, $J = 8.4$ Hz, 2H), 7.68-7.62 (m, 3H), 7.52 (t, $J = 7.8$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ 189.1,

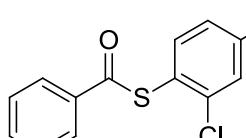
136.3, 135.4, 134.2, 132.3, 131.5 (q, $J = 33.0$ Hz), 129.0, 127.7, 126.1 (q, $J = 3.0$ Hz), 124.0 (q, $J = 270.0$ Hz); ^{19}F NMR (564 MHz, CDCl_3): δ -62.8.



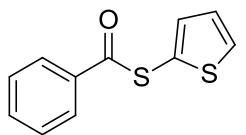
S-*o*-Tolyl benzothioate (3ac): The product **3ac** was prepared by the General Procedure B using **2h** (47.0 mg, 0.2 mmol, 76% purity). 35.4 mg (77%); White solid; ^1H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.⁶ ^1H NMR (600 MHz, CDCl_3): δ 8.11 (d, $J = 7.8$ Hz, 2H), 7.67 (t, $J = 7.8$ Hz, 1H), 7.58-7.51 (m, 3H), 7.44-7.41 (m, 2H), 7.34-7.29 (m, 1H), 2.46 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 189.8, 142.8, 136.9, 136.5, 133.7, 131.0, 130.4, 128.9, 127.7, 126.9, 126.8, 20.9.



S-(2-Chlorophenyl) benzothioate (3ad): The product **3ad** was prepared by the General Procedure B using **2i** (40.0 mg, 0.2 mmol). 26.5 mg (53%); White solid, m.p. 48-50 °C; ^1H NMR (600 MHz, CDCl_3): δ 8.06 (dd, $J = 8.4, 1.2$ Hz, 2H), 7.65-7.60 (m, 2H), 7.60-7.55 (m, 1H), 7.51 (t, $J = 7.8$ Hz, 2H), 7.42 (td, $J = 7.2, 1.8$ Hz, 1H), 7.35 (td, $J = 7.8, 1.8$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3): δ 188.4, 139.3, 137.8, 136.5, 134.0, 131.4, 130.5, 128.9, 127.8, 127.5, 127.1; IR(neat): 1682, 1580, 1452, 1433, 1206, 1177, 1037, 897, 771, 754, 684, 643 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{13}\text{H}_9\text{ClOS}$ [M]⁺ 248.0063 Found 248.0064.

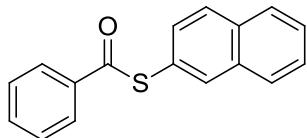


S-(2,4-Dichlorophenyl) benzothioate (3ae): The product **3ae** was prepared by the General Procedure B using **2j** (46.6 mg, 0.2 mmol). 28.2 mg (50%); White solid, m.p. 96-98 °C; ^1H NMR (600 MHz, CDCl_3): δ 8.05-8.02 (m, 2H), 7.64 (t, $J = 7.2$ Hz, 1H), 7.58 (d, $J = 1.8$ Hz, 1H), 7.54 (d, $J = 7.8$ Hz, 1H), 7.51 (t, $J = 7.8$ Hz, 2H), 7.34 (dd, $J = 8.4, 1.8$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3): δ 188.0, 140.1, 138.4, 137.0, 136.2, 134.2, 130.4, 129.0, 127.9, 127.8, 125.8; IR(neat): 1685, 1458, 1458, 1450, 1209, 1178, 1097, 901, 862, 827, 766, 679, 637 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{13}\text{H}_8\text{Cl}_2\text{OS}$ [M]⁺ 281.9673 Found 281.9678.

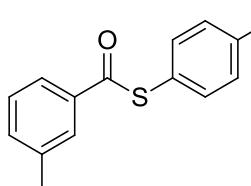


S-Thiophen-2-yl benzothioate (3af): The product **3af** was prepared by the General Procedure B using **2k** (34.0 mg, 0.2 mmol). 26.0 mg (59%); White solid, m.p. 58-60 °C; ^1H NMR (600 MHz, CDCl_3): δ 8.02 (d, $J = 7.8$ Hz, 2H), 7.65-7.60 (m, 2H), 7.50

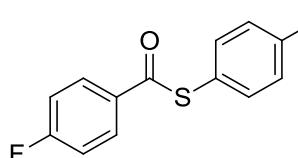
(t, $J = 7.2$ Hz, 2H), 7.27-7.25 (m, 1H), 7.17 (t, $J = 4.6$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3): δ 190.0, 136.5, 136.1, 134.1, 132.3, 129.0, 128.1, 127.7, 124.3; IR(neat): 3092, 1671, 1445, 1402, 1203, 1177, 893, 848, 771, 726, 684, 669, 643 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{11}\text{H}_8\text{OS}_2$ [M] $^+$ 220.0017 Found 220.0020.



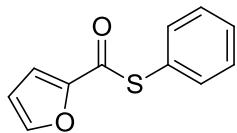
S-Naphthalen-2-yl benzothioate (3ag): The product **3ag** was prepared by the General Procedure B using **2l** (51.0 mg, 0.2 mmol, 85% purity). 36.0 mg (68%); White solid; ^1H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.⁷ ^1H NMR (600 MHz, CDCl_3): δ 8.09-8.05 (m, 3H), 7.93 (d, $J = 8.4$ Hz, 1H), 7.88 (dd, $J = 7.2, 16.2$ Hz, 2H), 7.63 (t, $J = 7.2$ Hz, 1H), 7.59-7.47 (m, 5H); ^{13}C NMR (150 MHz, CDCl_3): δ 190.5, 136.8, 135.1, 133.9, 133.8, 133.6, 131.5, 129.0, 128.9, 128.1, 127.9, 127.7, 127.3, 126.7, 124.8.



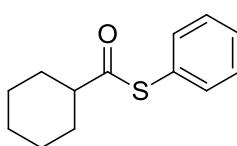
S-(4-Chlorophenyl) 3-methylbenzothioate (3ah): The product **3ah** was prepared by the General Procedure B using **2f** (40.0 mg, 0.2 mmol). 36.3 mg (69%); White solid, m.p. 66-68 °C; ^1H NMR (600 MHz, CDCl_3): δ 7.83-7.81 (m, 2H), 7.45-7.41 (m, 5H), 7.38 (t, $J = 8.4$ Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 189.9, 138.9, 136.5, 136.4, 136.0, 134.8, 129.6, 128.8, 128.1, 126.1, 124.9, 21.5; IR(neat): 1667, 1601, 1387, 1245, 1150, 816, 792, 784, 694, 486 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{11}\text{ClOS}$ [M] $^+$ 262.0219 Found 262.0216.



S-(4-Methoxyphenyl) 4-fluorobenzothioate (3ai): The product **3ai** was prepared by the General Procedure B using **2c** (38.8 mg, 0.2 mmol). 38.8 mg (74%); White solid, m.p. 66-68 °C; ^1H NMR (600 MHz, CDCl_3): δ 8.07-8.03 (m, 2H), 7.41 (d, $J = 9.0$ Hz, 2H), 7.19-7.12 (m, 2H), 6.99 (d, $J = 7.8$ Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 189.8, 166.2 (d, $J = 254.2$ Hz), 161.0, 136.8, 133.1, 130.1 (d, $J = 10.0$ Hz), 117.7, 116.0 (d, $J = 23.1$ Hz), 115.1, 55.5; ^{19}F NMR (564 MHz, CDCl_3): δ -104.2; IR(neat): 1670, 1593, 1505, 1495, 1250, 1201, 1155, 1028, 905, 825, 669, 636, 618 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{14}\text{H}_{11}\text{FO}_2\text{S}$ [M] $^+$ 262.0464 Found 262.0460.



S-Phenyl furan-2-carbothioate (3aj): The product **3aj** was prepared by the General Procedure B using **2b** (32.8 mg, 0.2 mmol). 28.7 mg (70%); White solid; ^1H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.³ ^1H NMR (600 MHz, CDCl_3): δ 7.63 (d, $J = 2.4$ Hz, 1H), 7.54-7.49 (m, 2H), 7.47-7.44 (m, 3H), 7.27 (d, $J = 3.6$ Hz, 1H), 6.58 (dd, $J = 3.6, 2.4$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3): δ 178.8, 150.5, 146.6, 135.3, 129.8, 129.4, 126.3, 116.4, 112.6.



S-Phenyl cyclohexanecarbothioate (3ak): The product **3ak** was prepared by the General Procedure B using **2b** (32.8 mg, 0.2 mmol). 28.5 mg (65%); White solid; ^1H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.⁸ ^1H NMR (600 MHz, CDCl_3): δ 7.40 (s, 5H), 2.61 (tt, $J = 11.4, 3.6$ Hz, 1H), 2.01 (brd, $J = 11.4$ Hz, 2H), 1.82 (dt, $J = 13.2, 7.2$ Hz, 2H), 1.70-1.65 (m, 1H), 1.58-1.48 (m, 2H), 1.36-1.20 (m, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 200.9, 134.7, 129.3, 129.2, 128.1, 52.7, 29.7, 25.7, 25.6.



S-(4-Fluorophenyl) cyclohexanecarbothioate (3al): The product **3al** was prepared by the General Procedure B using **2e** (36.4 mg, 0.2 mmol). 29.1 mg (61%); White solid, m.p. 35-37 °C; ^1H NMR (600 MHz, CDCl_3): δ 7.38-7.34 (m, 2H), 7.12-7.07 (m, 2H), 2.60 (tt, $J = 12.0, 3.6$ Hz, 1H), 2.02-1.95 (m, 2H), 1.82 (dt, $J = 13.8, 3.6$ Hz, 2H), 1.70-1.65 (m, 1H), 1.56-1.45 (m, 2H), 1.36-1.18 (m, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 200.9, 163.5 (d, $J = 248.4$ Hz), 136.8 (d, $J = 8.5$ Hz), 123.4 (d, $J = 2.8$ Hz), 116.5 (d, $J = 21.6$ Hz), 52.6, 29.6, 25.7, 25.6; ^{19}F NMR (564 MHz, CDCl_3): δ -111.6; IR(neat): 2933, 2856, 1705, 1591, 1450, 1231, 1157, 963, 829, 796, 767 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{13}\text{H}_{15}\text{FOS}$ [M]⁺ 238.0828 Found 238.0825.

p-Tolyl disulfide (4a): ^1H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.⁹ ^1H NMR (600 MHz, CDCl_3): δ 7.39 (d, $J = 7.8$ Hz, 4H); 7.11 (d, $J = 7.2$ Hz, 4H), 2.32 (s, 6H); ^{13}C NMR (150 MHz, CDCl_3) δ 137.6, 134.0, 129.9, 128.7, 21.2.

Time- Resolved Fluorescence Lifetime Measurements:

Time-resolved fluorescence study was carried out using a confocal microscope (MicroTime-200, Picoquant, Germany). A single-mode pulsed diode laser (375 nm with 30 ps pulse width and < 1 μ W power) was used as an excitation source. A dichroic mirror (Z375RDC, AHF), a long pass filter (HQ405lp, AHF), a bandpass filter (500-550 nm, Thorlabs) and an avalanche photodiode detector (PDM series, MPD) were used to collect emission photons from the samples. Exponential fitting for the obtained fluorescence decays was accomplished using the Symphotime-64 software (Ver. 2.2).

The fluorescence lifetime of *fac*-Ir(ppy)₃ (0.05 mM) was measured in the presence of quenchers such as 10 mM of benzoyl chloride **1a**, sodium aryl sulfinate **2a**, Hantzsch ester (HEH), or DIPEA in Ar-saturated DCE (similar molar ratio of catalyst and quencher with the optimized reaction condition). The chart in Figure S2 displays lifetime changes of *fac*-Ir(ppy)₃ depending on the kinds of quencher, where τ and τ_0 correspond to the observed fluorescence lifetimes in the presence and absence of quenchers respectively. As described in Figure S2, lifetime decrease of photocatalyst *fac*-Ir(ppy)₃ was observed in the presence of DIPEA, Sulfinate, and HEH ($\tau_0 > \tau$). It should be noticed that the fluorescence lifetime was the most significantly decreased upon the addition of HEH quencher. In contrast, when solution of benzoyl chloride **1a** was employed, lifetime remained unchanged ($\tau_0/\tau \sim 1$). Based on these results DIPEA, Sulfinate, and HEH are reductive quenchers in the excited state of *fac*-Ir(ppy)₃, where HEH is the most effective one. This finding strongly supports our mechanistic proposal in Scheme 5 of the manuscript that excited Ir(III)* catalyst is reduced to Ir(II) by HEH, DIPEA and sulfinate, not oxidized to Ir(IV) by benzoyl chloride.

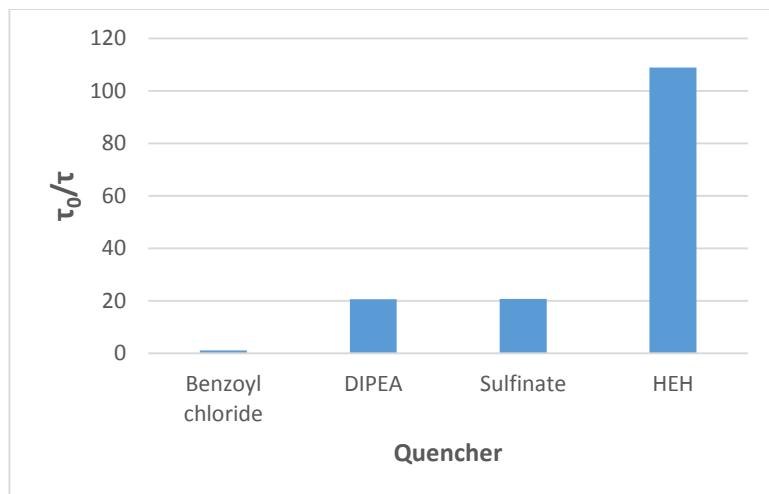
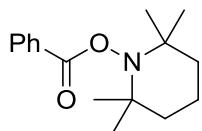
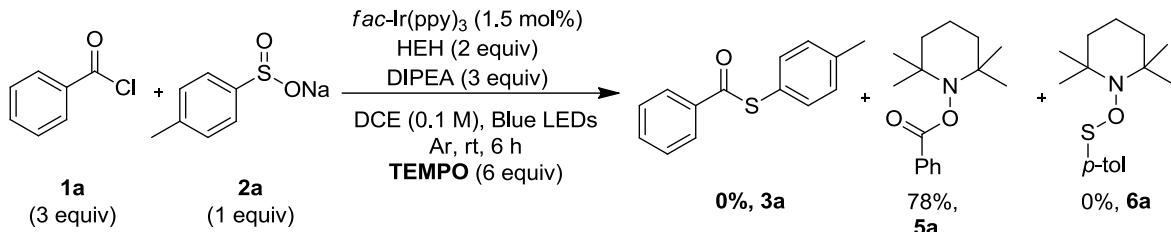


Figure S2: lifetime changes of *fac*-Ir(ppy)₃ in the presence of quencher (benzoyl chloride **1a**, DIPEA, sodium arylsulfinate **2a** and HEH)

Control Experiments A: Radical trapping experiment

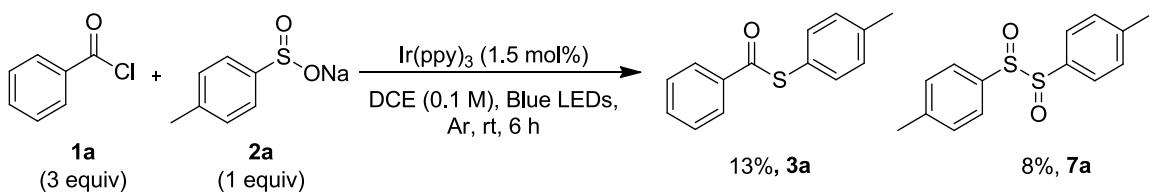
An oven-dried 10 mL vial charged with sodium aryl sulfinate **2a** (36 mg, 0.2 mmol), HEH (102 mg, 0.4 mmol), *fac*-Ir(ppy)₃ (1.96 mg, 1.5 mol %) and TEMPO (189.4 mg, 1.21 mmol) was screw capped and purged with Ar (evacuated and backfilled with Ar). After the addition of anhydrous dichloroethane (2.0 mL, 0.1 M), benzoyl chloride **1a** (70.4 μ L, 0.60 mmol) and DIPEA (0.11 mL, 0.60 mmol) were added to this vial. The mixture was further purged with Ar for 5 mins and then irradiated by blue LEDs (460 nm) with stirring for 6 h (distance app. 3 cm) at room temperature. After the reaction was complete by TLC (no starting materials were left, but the desired thioester product (**3a**) was not detected by TLC), the solvent was removed under reduced pressure. The reaction product (TEMPO-acyl adduct, 2,2,6,6-tetramethylpiperidin-1-yl benzoate (**5a**)) was isolated by flash column chromatography on silica gel (Hexanes/DCM (2/1)) in 78% yield (123.20 mg, yield is based on amount of benzoyl chloride used) as a white solid. The control experiment A suggested that our reaction proceeds *via* radical pathway and the acyl radical intermediate can be generated from the corresponding aryloyl chlorides. Sulfide radical trapped TEMPO adduct (**6a**) was not detected by either TLC or Mass.

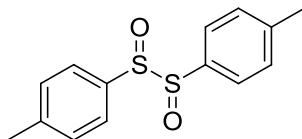


2,2,6,6-Tetramethylpiperidin-1-yl benzoate (5a): ¹H NMR and ¹³C NMR spectra for this compound are consistent with previously reported literature data.¹⁰ ¹H NMR (CDCl₃, 600 MHz): δ 8.12 (d, *J* = 7.8 Hz, 2H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 1.87-1.69 (m, 3H), 1.68-1.47 (m, 3H), 1.32 (s, 6H), 1.17 (s, 6H); ¹³C NMR (CDCl₃, 150 MHz): δ 165.7, 132.2, 129.1, 128.9, 127.8, 59.8, 38.4, 31.3, 20.2, 16.4.

Control Experiments B:

Sodium aryl sulfinate **2a** (36 mg, 0.2 mmol) and *fac*-Ir(ppy)₃ (1.96 mg, 1.5 mol %) were added to an oven-dried 10 mL vial equipped with a magnetic stir bar. The vial was screw capped and purged with Ar (evacuated and backfilled with Ar). Anhydrous dichloroethane (2.0 mL, 0.1 M) was added followed by addition of benzoyl chloride **1a** (70.4 μl, 0.60 mmol). The mixture was further purged with argon for 5 mins and stirred at room temperature under irradiation of blue LEDs (460 nm) for 6 h (distance app. 3 cm). The solution was then concentrated in *vacuo*. The crude reaction mixture was purified by flash column chromatography on silica gel using Hexanes/DCM (2/1) as eluent to provide thioester (**3a**, 5.8 mg) and 4-methyl-phenyl-disulfoxide (**7a**, 2.3 mg) in 13 and 8% yield respectively. This control experiment B suggested that the radical reaction pathway could not proceed efficiently without HEH and DIPEA reductants.

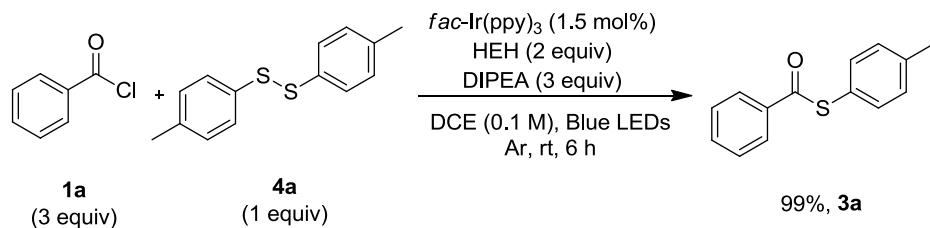




4-Methyl-phenyl-disulfoxide (7a): ^1H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.¹¹ ^1H NMR (CDCl_3 , 600 MHz): δ 7.46 (d, $J = 7.8$ Hz, 2H), 7.25-7.19 (m, 4H), 7.14 (d, $J = 8.4$ Hz, 2H), 2.42 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 144.7, 142.2, 140.6, 136.6, 130.3, 129.5, 127.7, 124.7, 21.8, 21.6.

Control Experiments C:

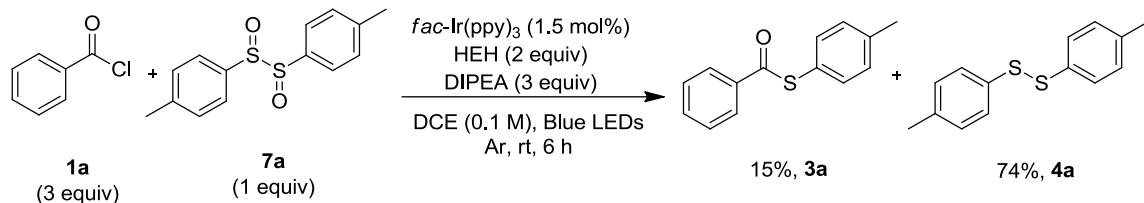
To an Ar purged 10 mL vial charged with *p*-tolyl disulfide **4a** (49.3 mg, 0.2 mmol), HEH (102 mg, 0.4 mmol) and *fac*-Ir(ppy)₃ (1.96 mg, 1.5 mol %) was added anhydrous dichloroethane (2.0 mL, 0.1 M) followed by addition of benzoyl chloride **1a** (70.4 μl , 0.60 mmol) and DIPEA (0.11 mL, 0.60 mmol). The mixture was then further purged with Ar for 5 mins and stirred under irradiation of blue LEDs (460 nm) for 6 h (distance app. 3 cm) at room temperature. After the reaction was complete by TLC, the solvent was removed under reduced pressure. The crude reaction mixture was purified by flash column chromatography on silica gel using Hexanes/DCM (2/1) as an eluent to afford thioester (**3a**, 91.1 mg) in 99% yield as a white solid. This control experiment C suggested that the disulfide could be a source of thio radical in our reaction.



Control Experiments D:

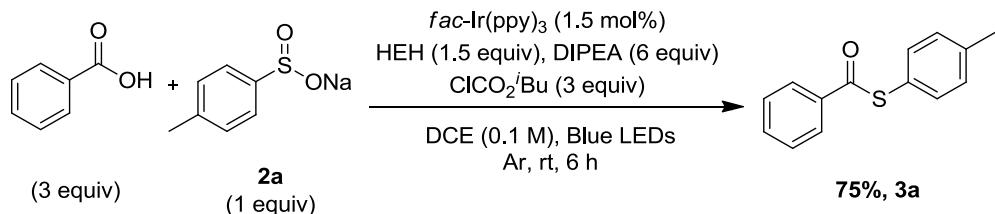
To an Ar purged 10 mL vial charged with *p*-tolyl disulfoxide **7a** (55.8 mg, 0.2 mmol), HEH (102 mg, 0.4 mmol) and *fac*-Ir(ppy)₃ (1.96 mg, 1.5 mol %) was added anhydrous dichloroethane (2.0 mL, 0.1 M) followed by the addition of benzoyl chloride **1a** (70.4 μl , 0.60 mmol) and DIPEA (0.11 mL, 0.60 mmol). The mixture was then further purged with Ar for 5 mins and stirred under irradiation of blue LEDs (460 nm) for 6 h (distance app. 3 cm) at room temperature. After the reaction was complete by TLC, the solvent

was removed under reduced pressure. The crude reaction mixture was purified by flash column chromatography on silica gel using Hexanes/DCM (2/1) as an eluent to afford thioester **3a** and *p*-tolyl disulfide **4a** in 15% (13.8 mg) and 74% (36.8 mg) yield, respectively.



Control Experiments E: Mixed Anhydride

To an oven-dried 10 mL vial charged with benzoic acid (75.3 mg, 0.6 mmol), sodium aryl sulfinate **2a** (36 mg, 0.2 mmol), HEH (102 mg, 0.4 mmol) and *fac*-Ir(ppy)₃ (1.96 mg, 1.5 mol %) under Ar, was added anhydrous dichloroethane (2.0 mL, 0.1 M) followed by addition of isobutyl chloroformate (78 μ L, 0.6 mmol) and DIPEA (0.21 mL, 1.2 mmol). The mixture was then further purged with Ar for 5 mins and stirred under irradiation of blue LEDs (460 nm) for 6 h (distance app. 3 cm) at room temperature. After the reaction was complete by TLC, the solvent was removed in *vacuo*. The crude reaction mixture was purified by flash column chromatography on silica gel using Hexanes/DCM (2/1) as an eluent to afford thioester (**3a**, 34.6 mg) in 75% yield as a white solid.

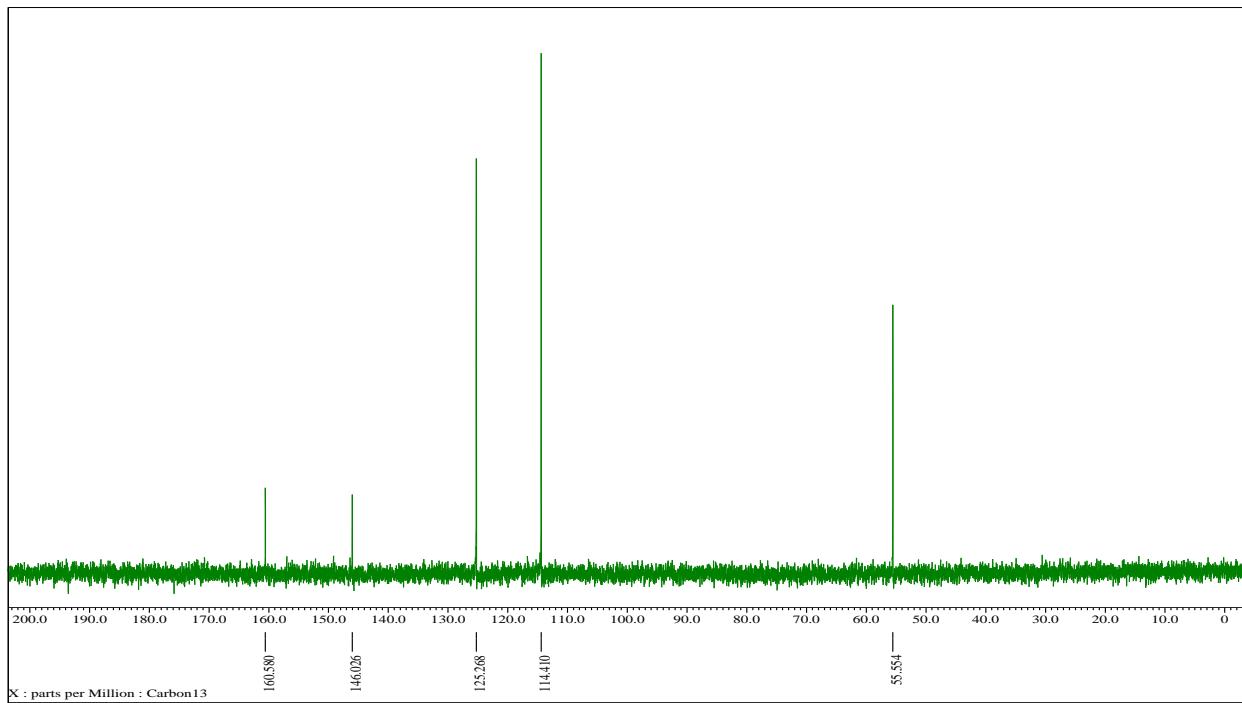
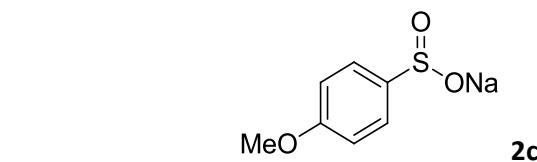
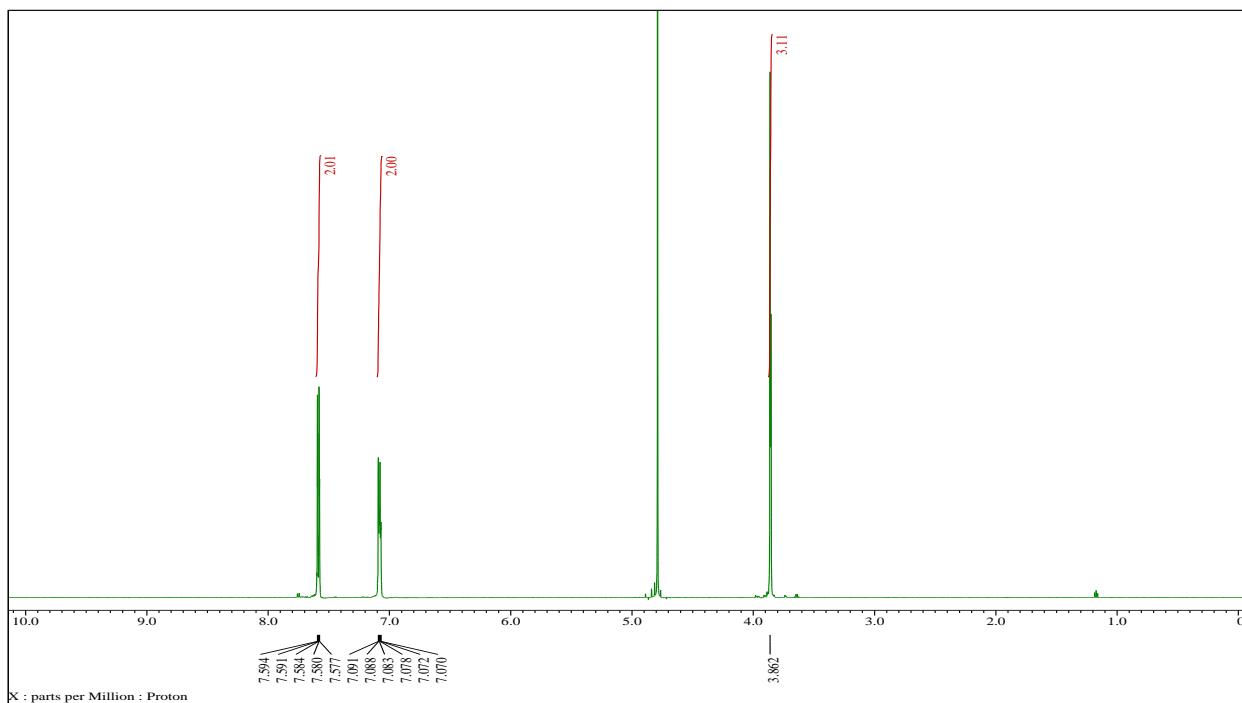


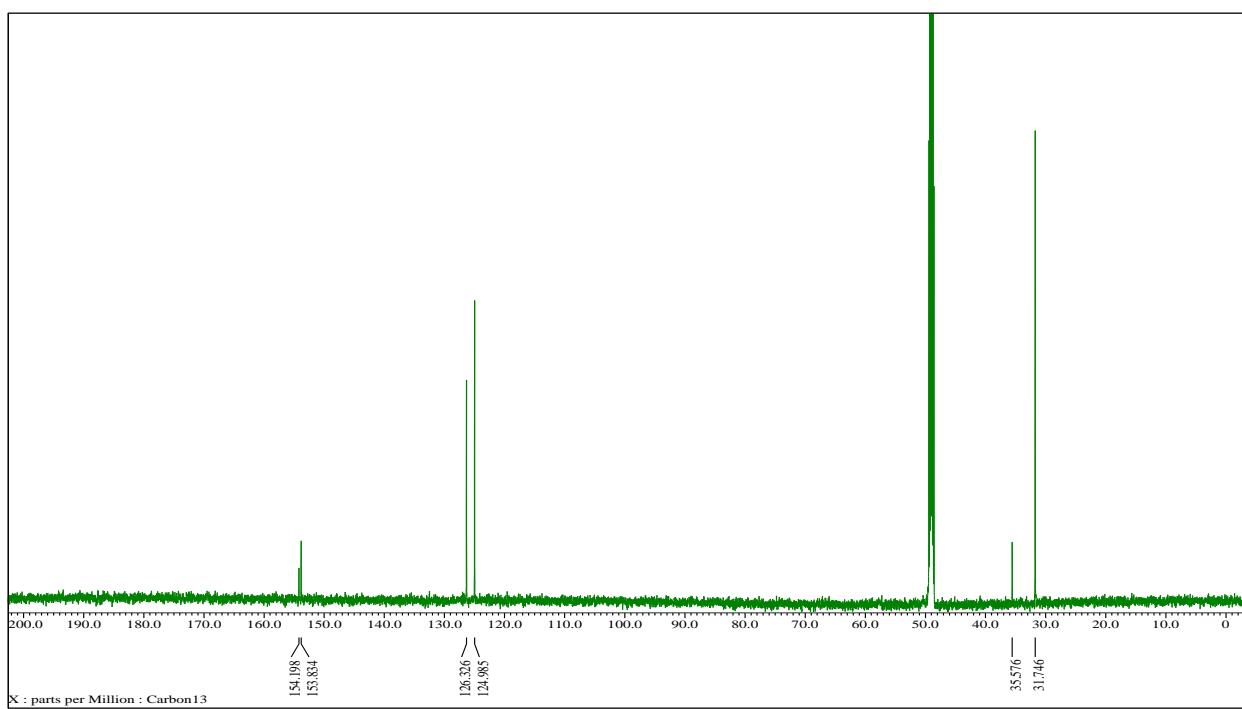
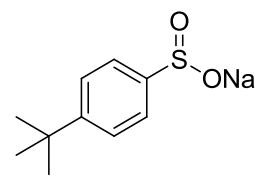
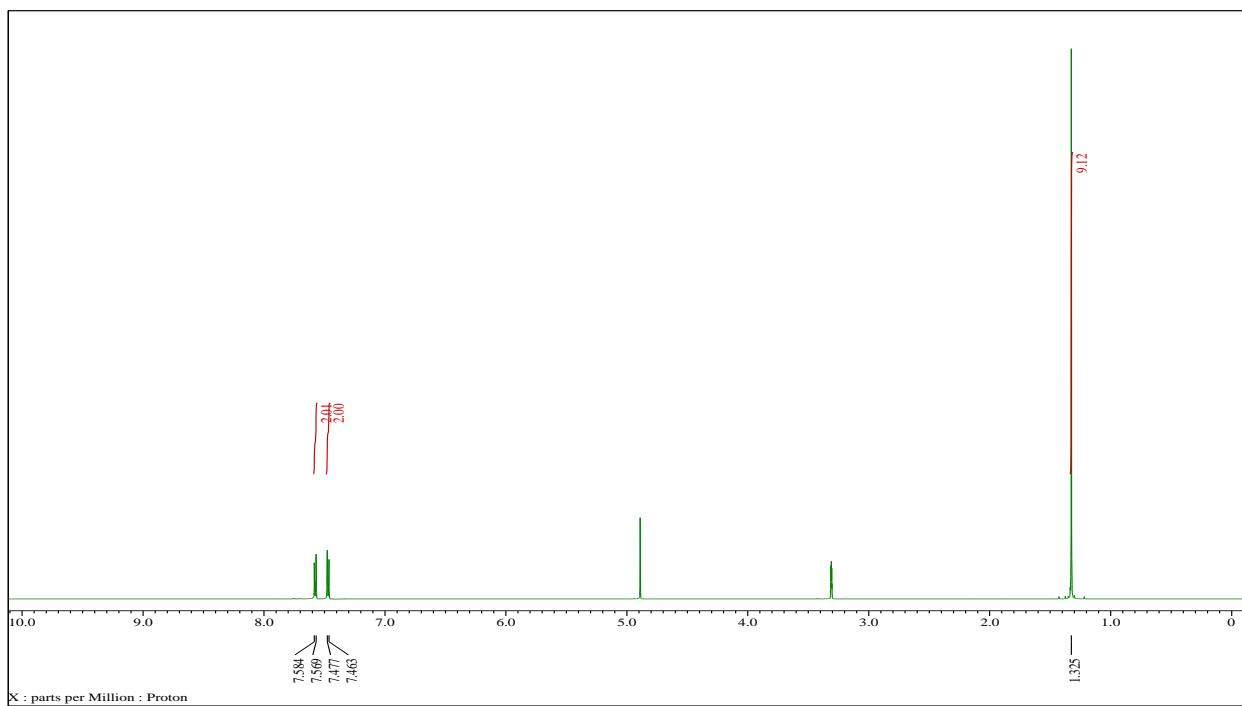
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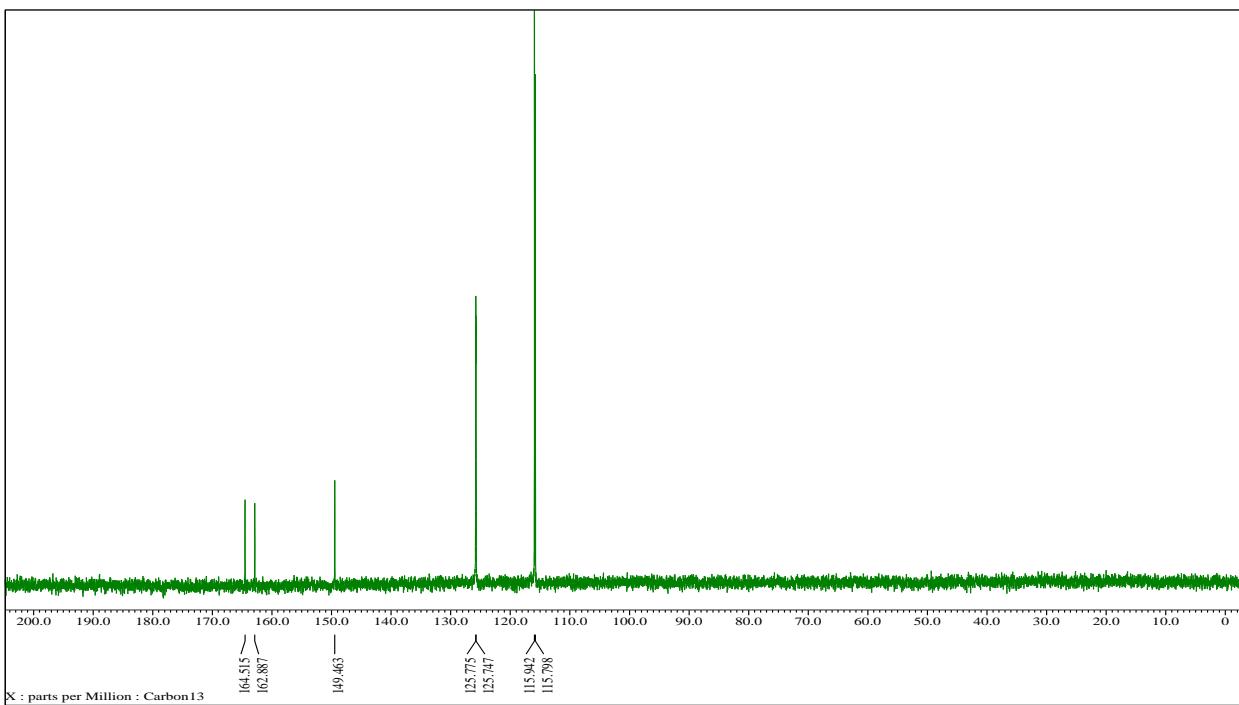
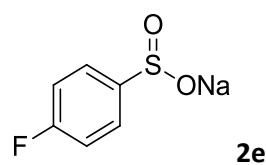
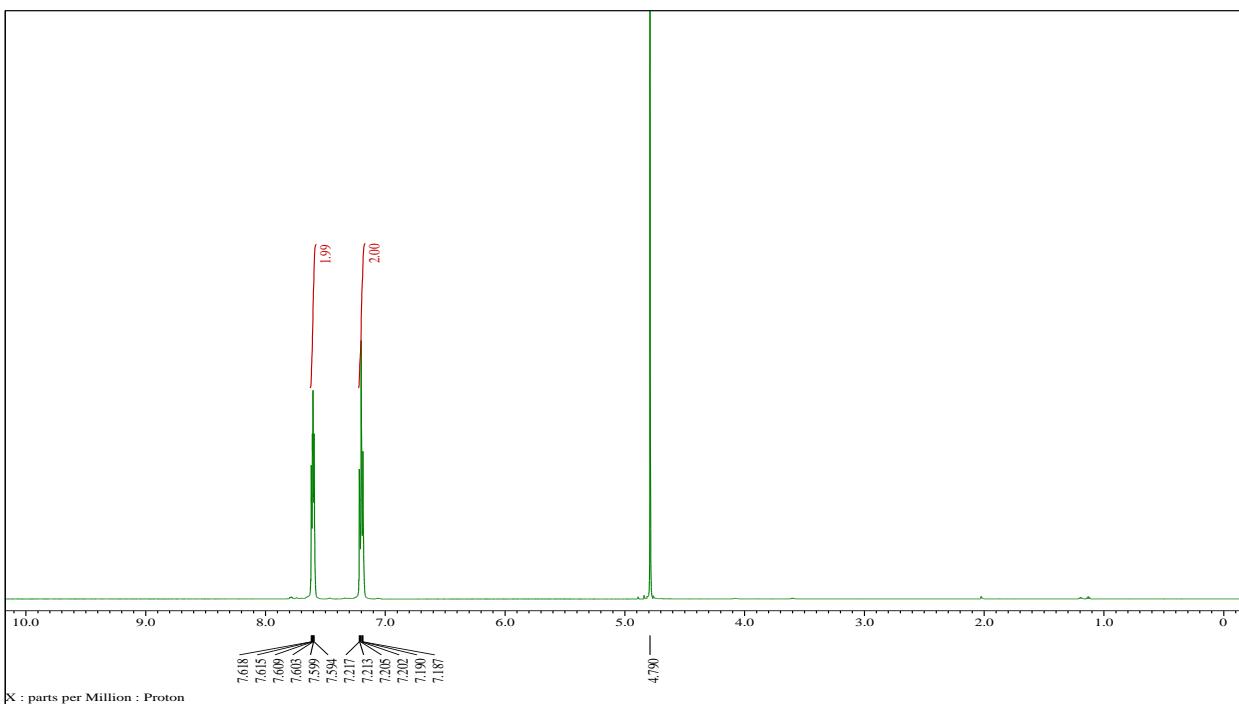
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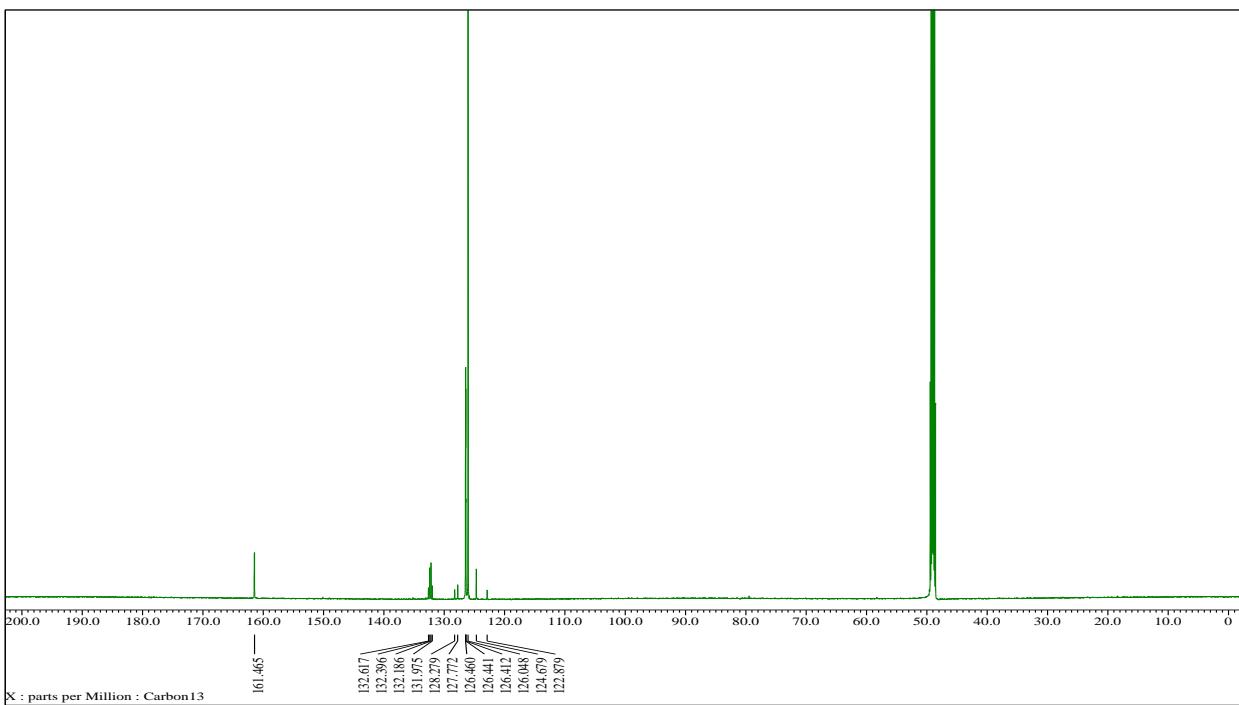
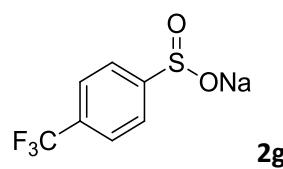
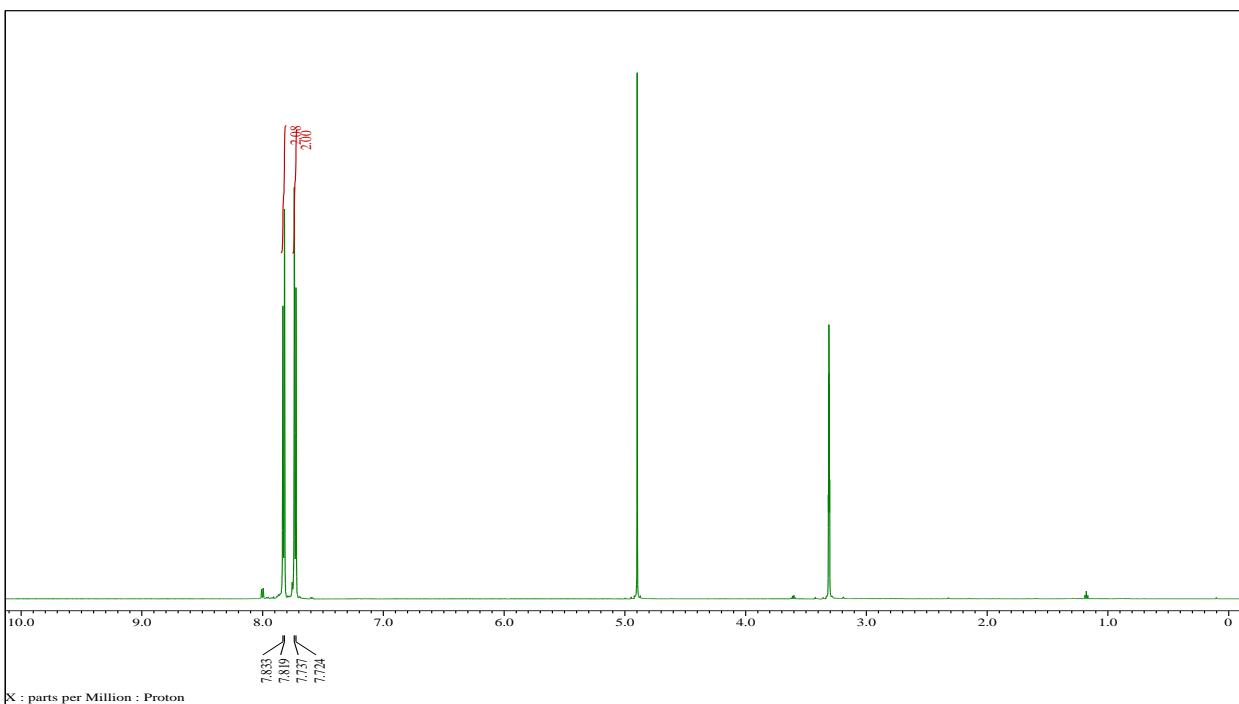
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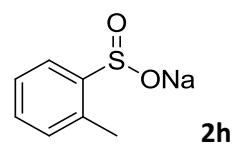
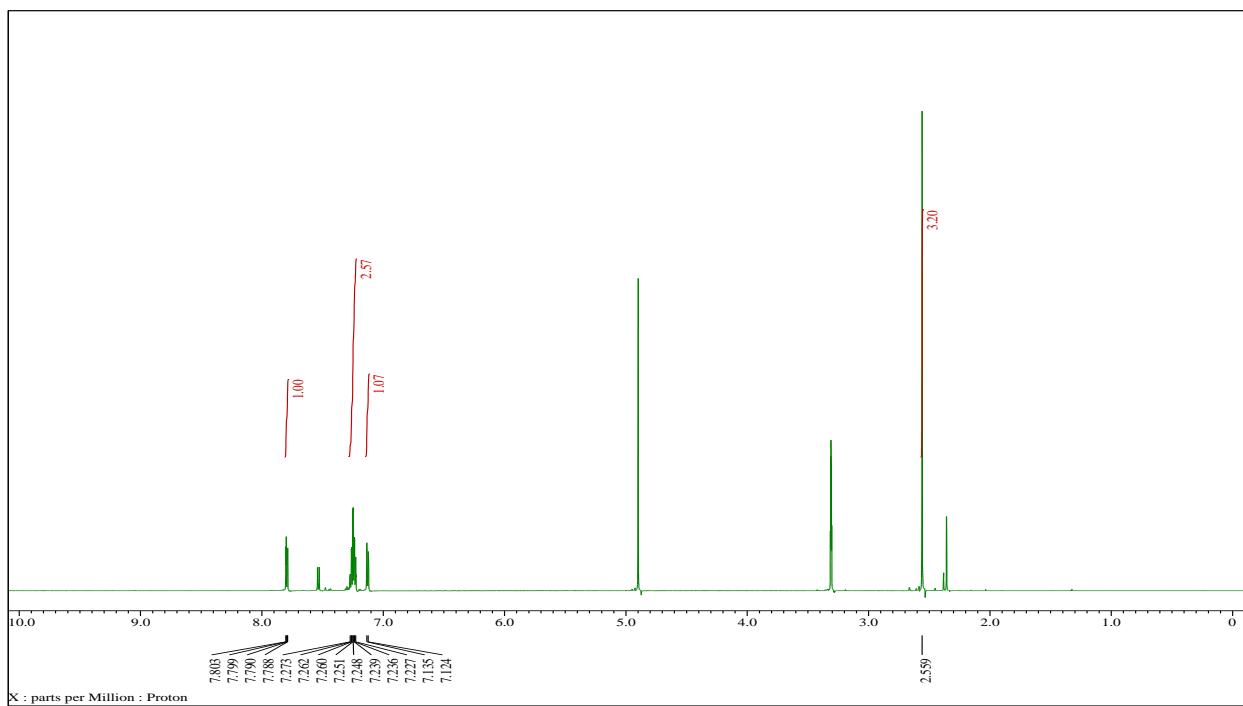
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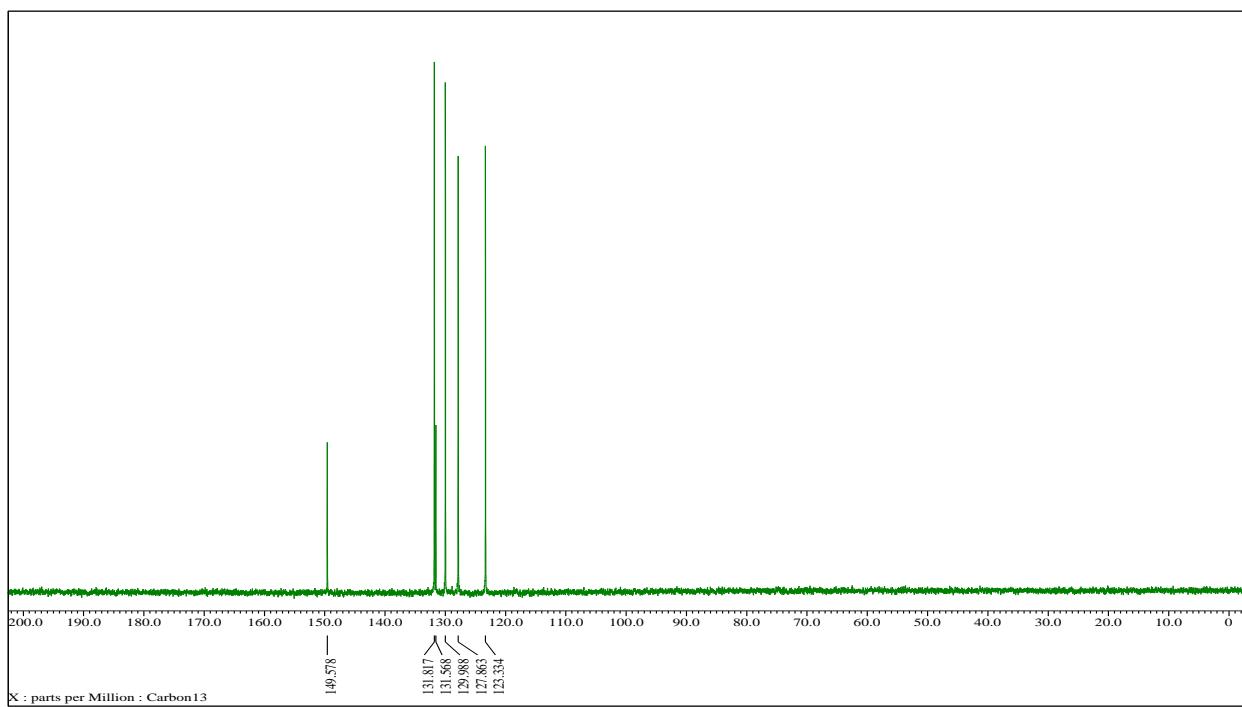
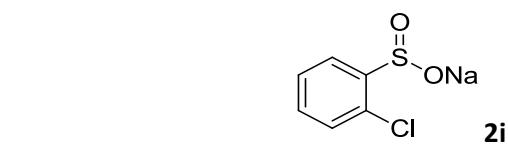
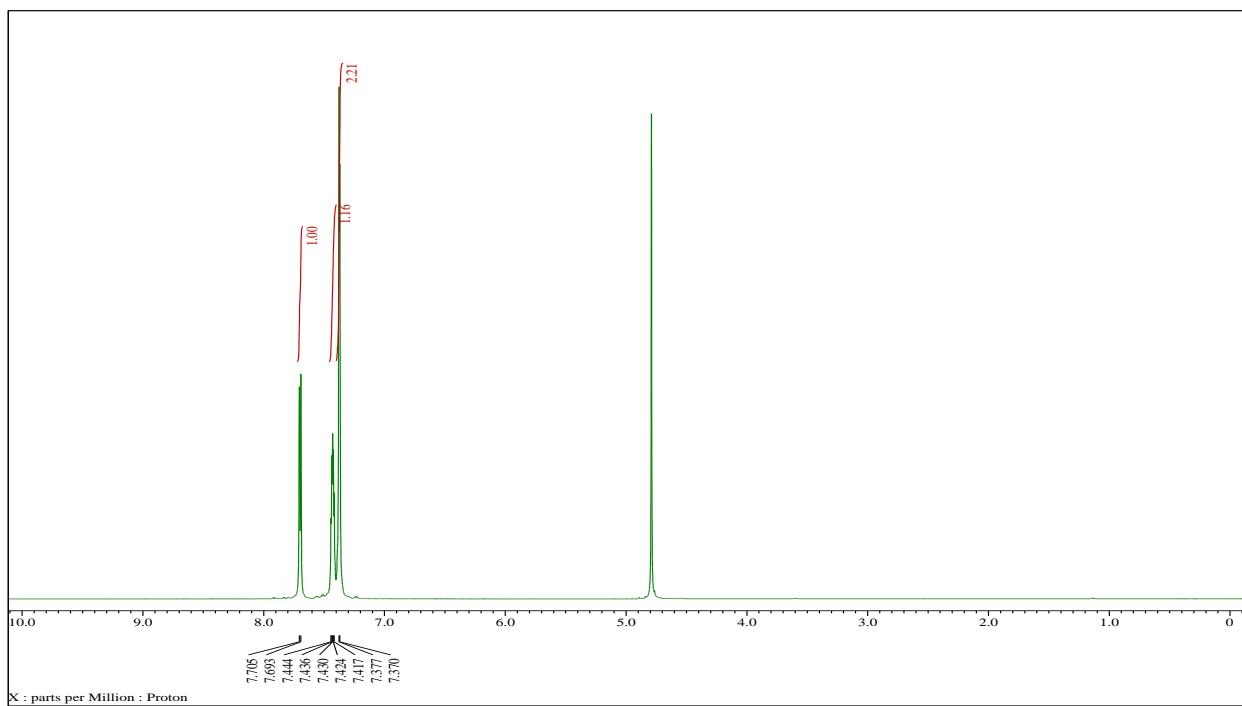


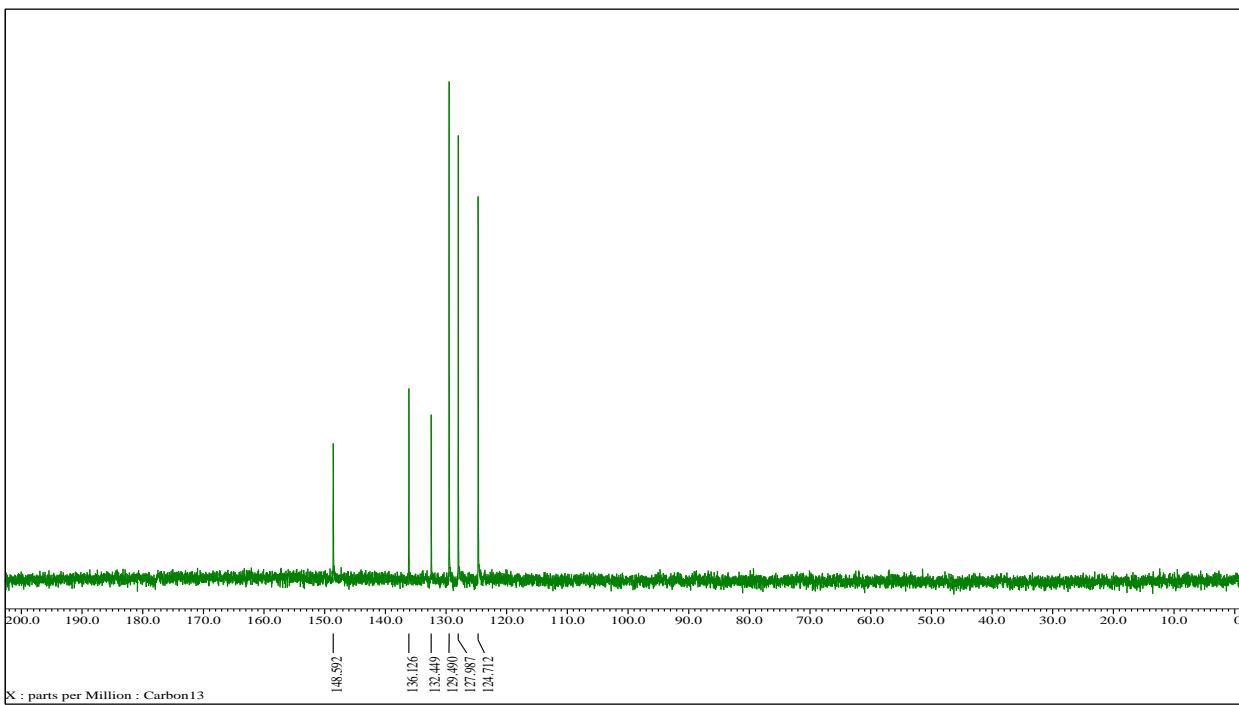
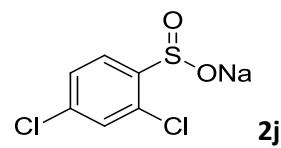
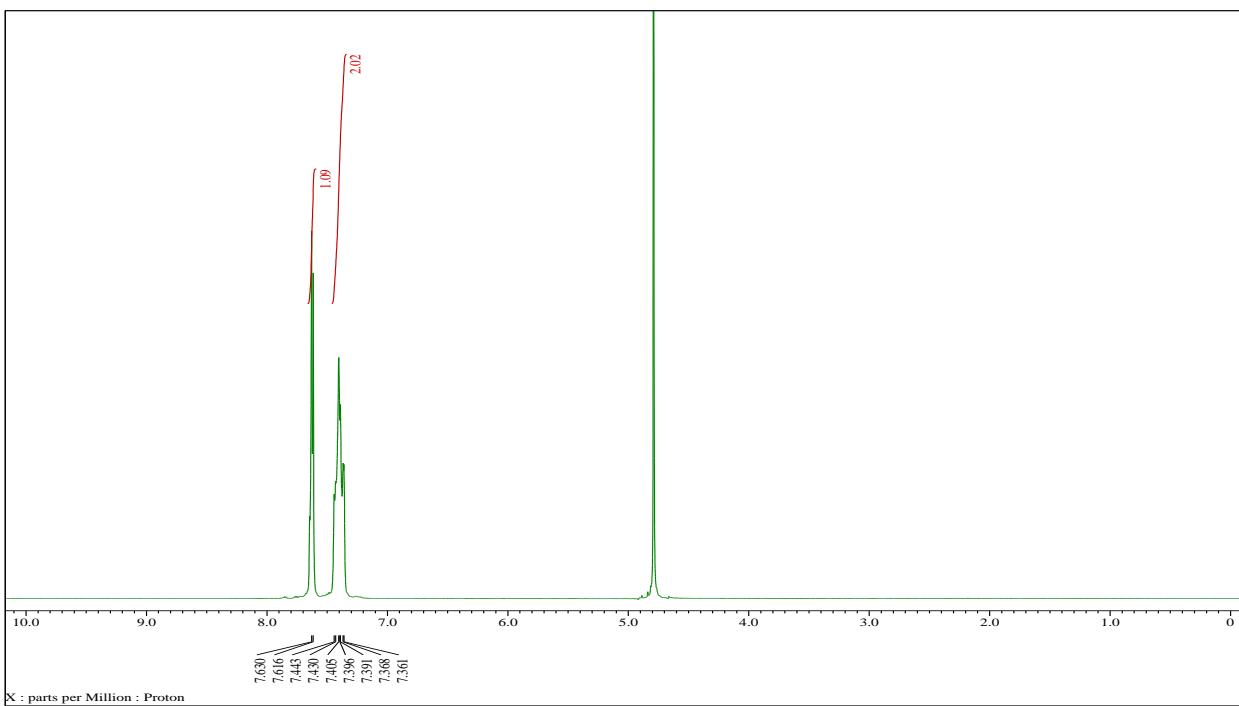


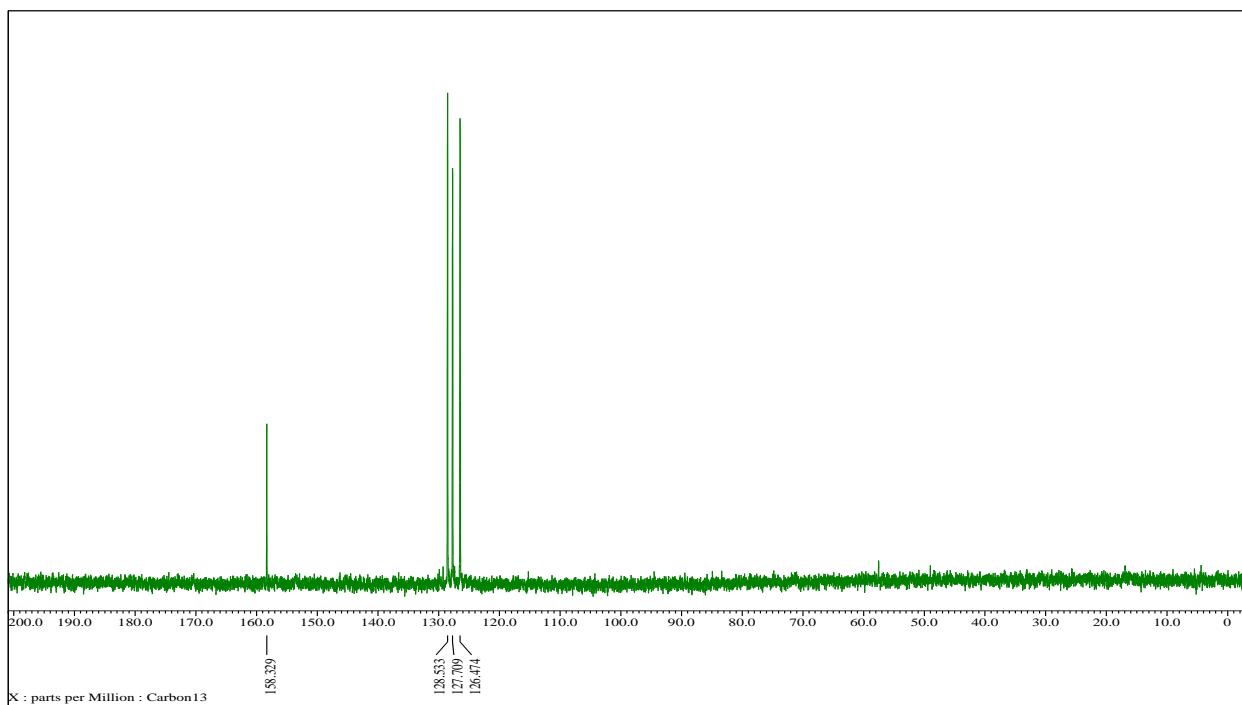
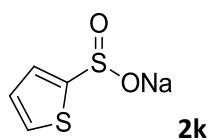
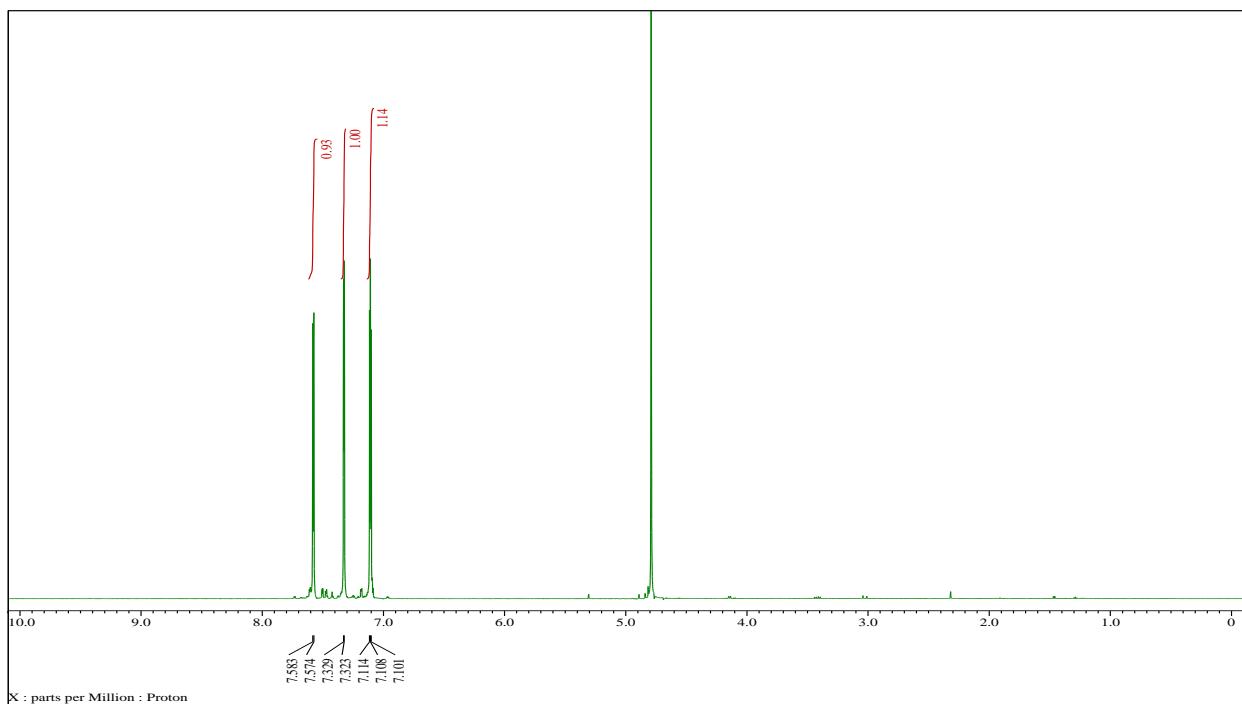


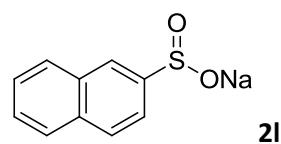
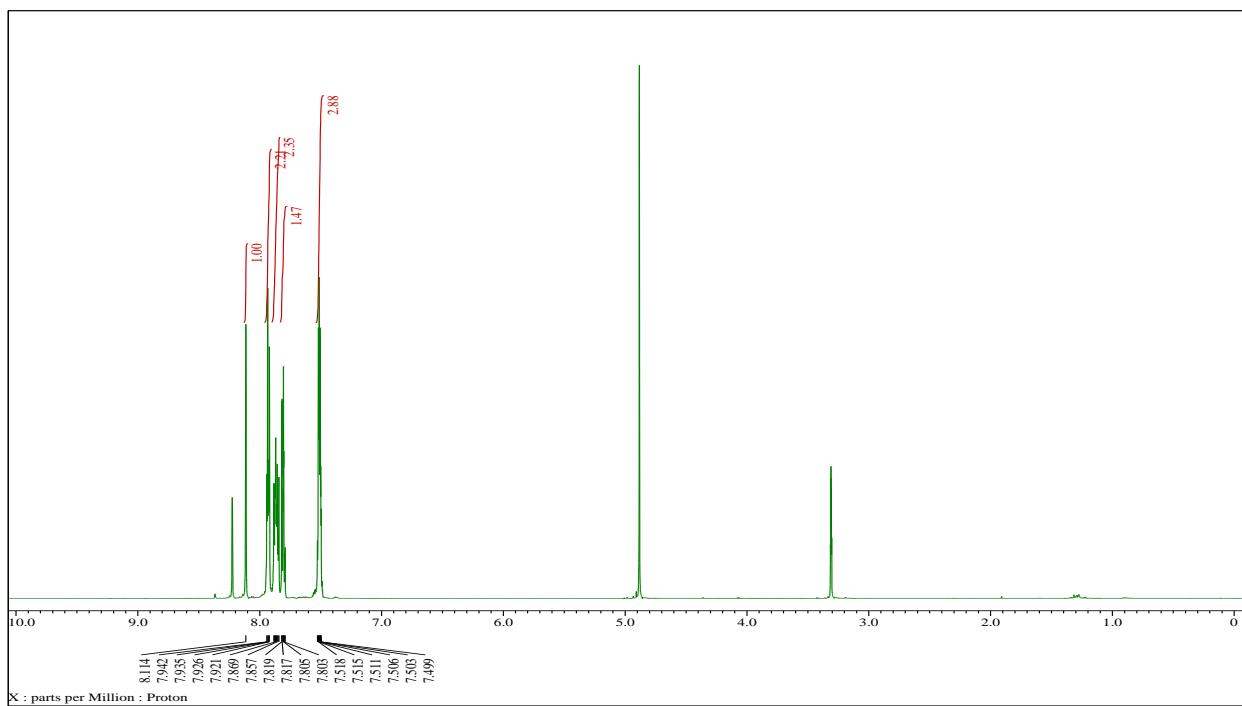


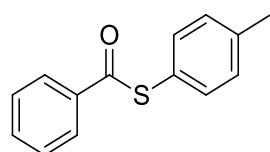
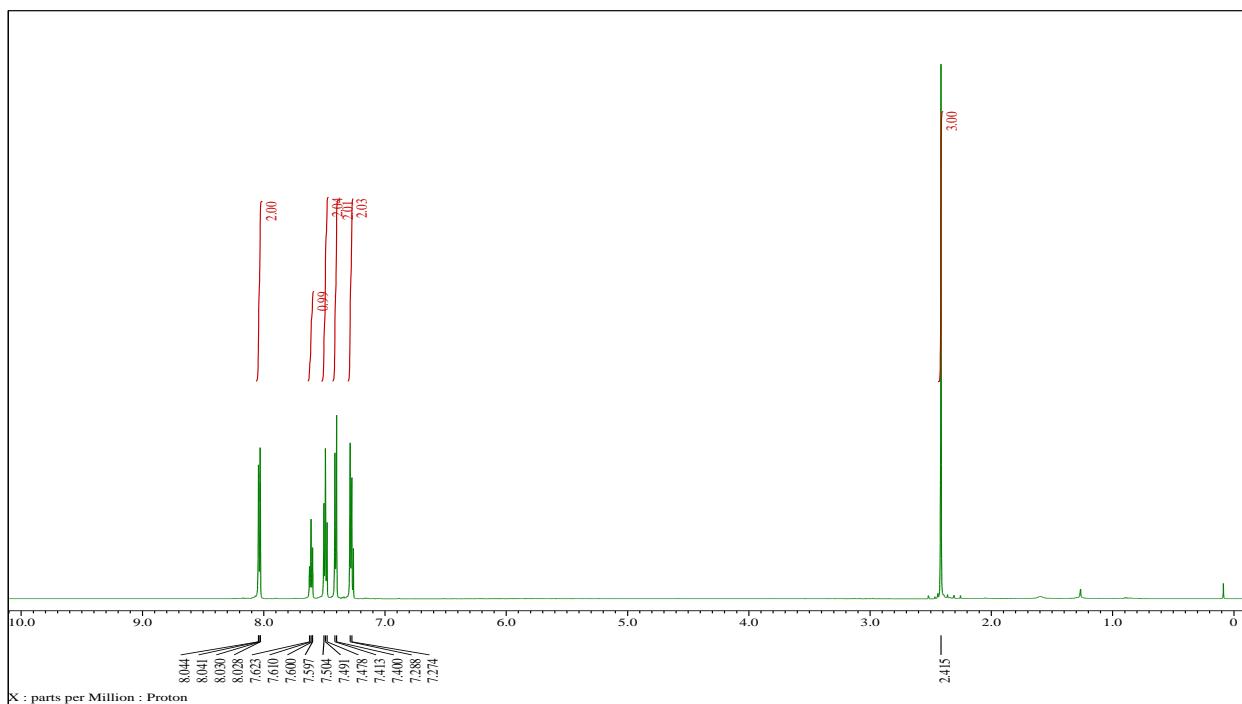




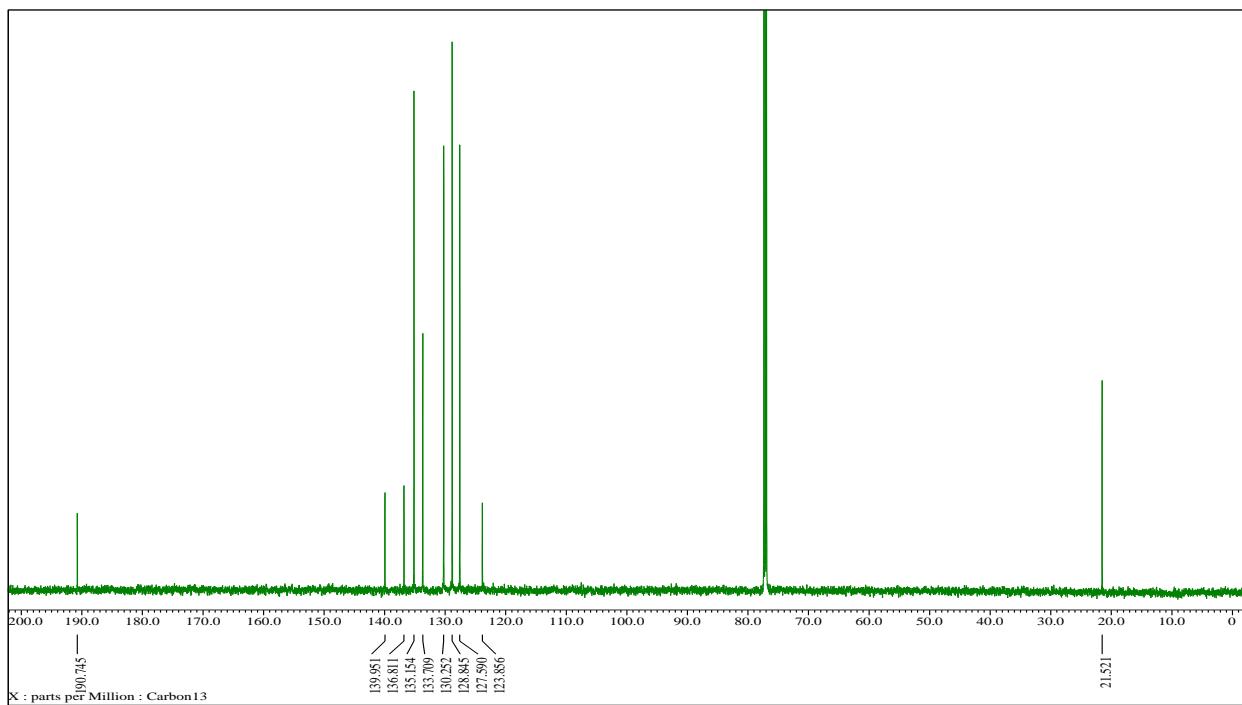


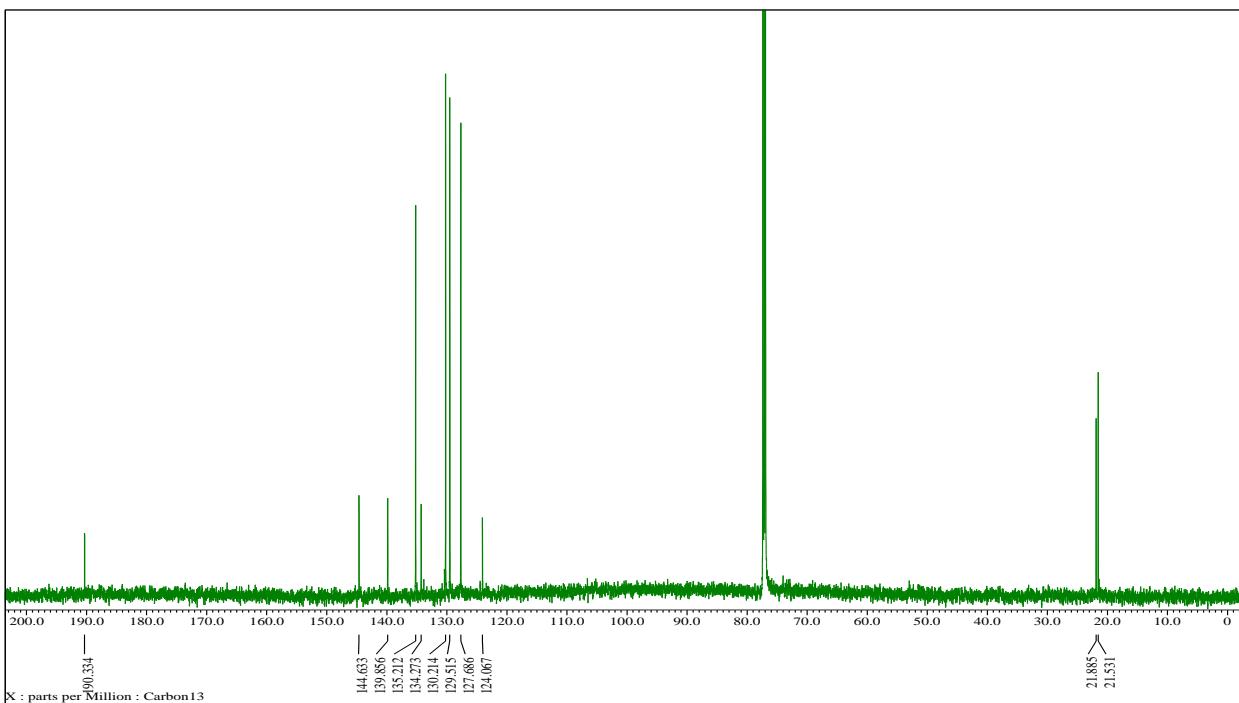
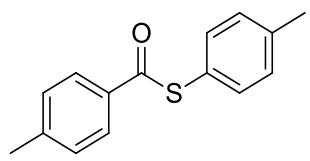
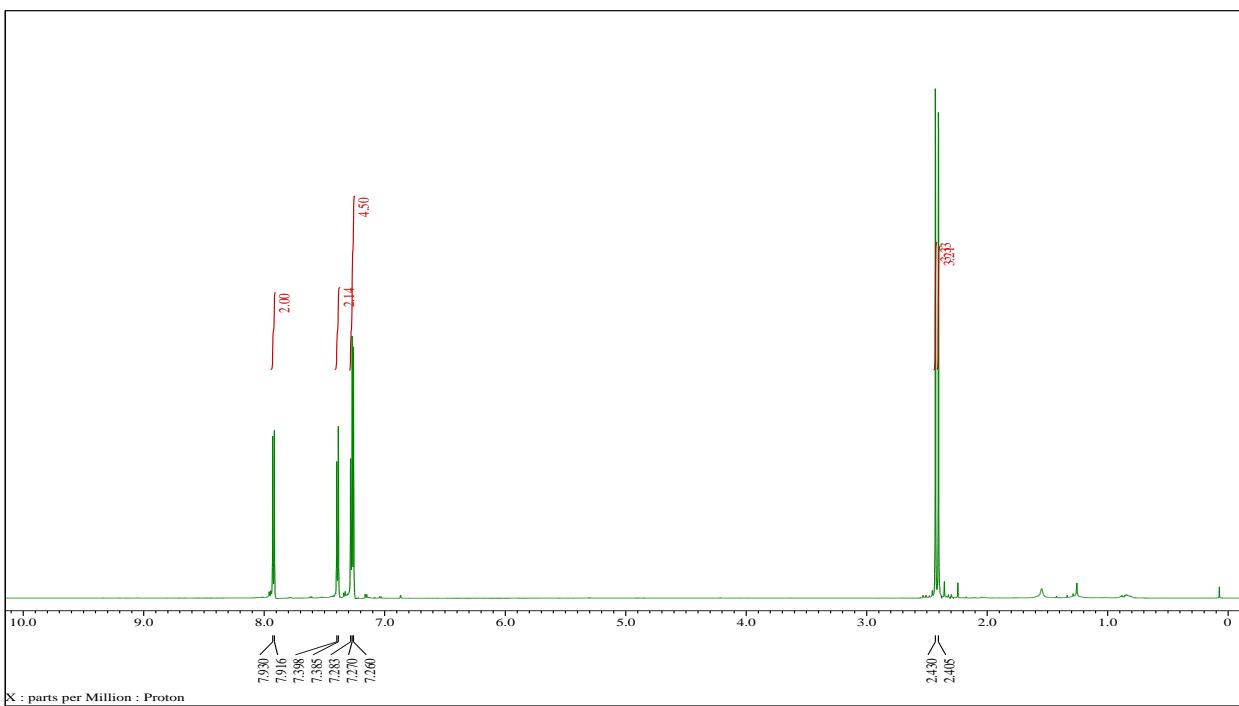


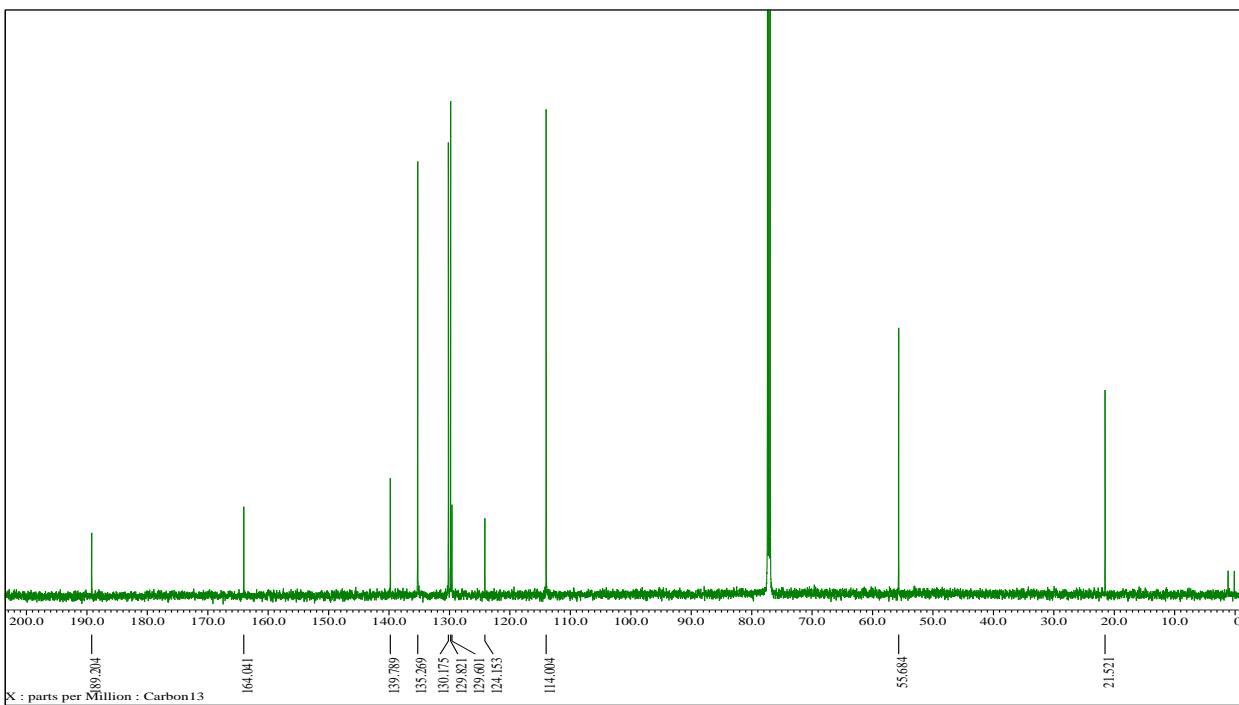
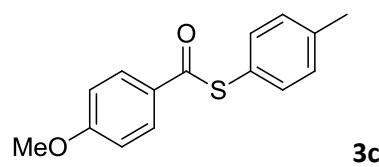
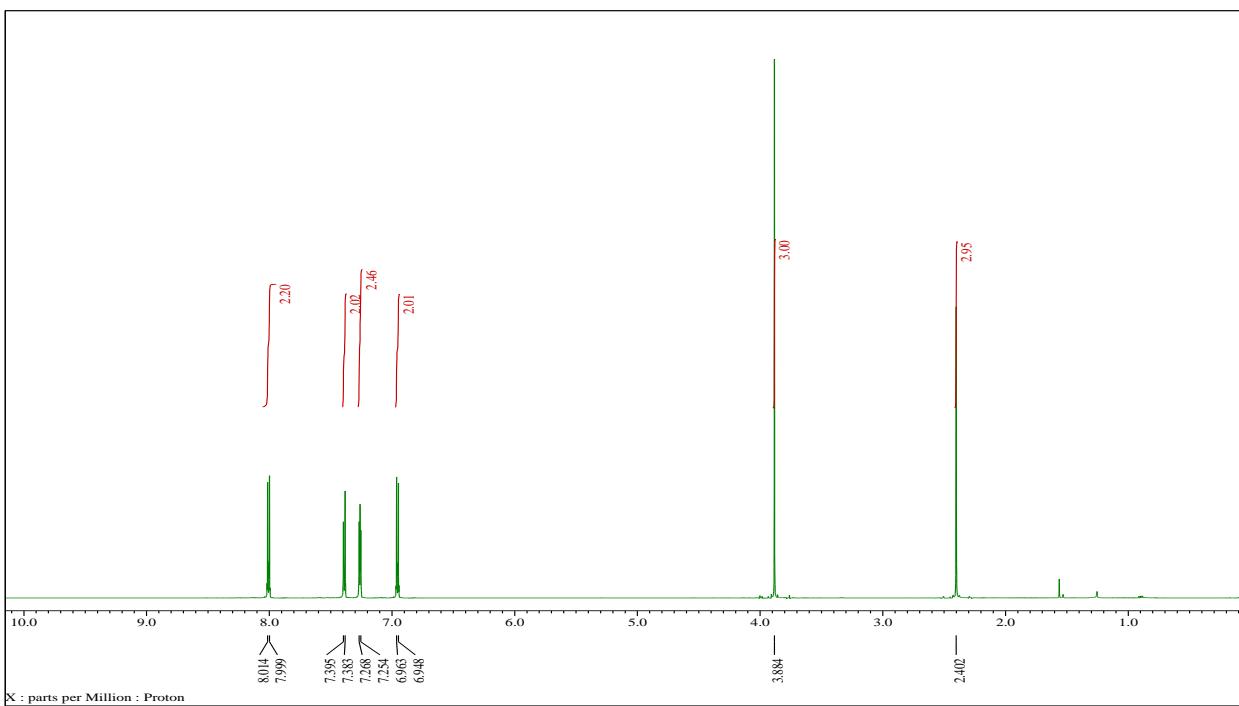


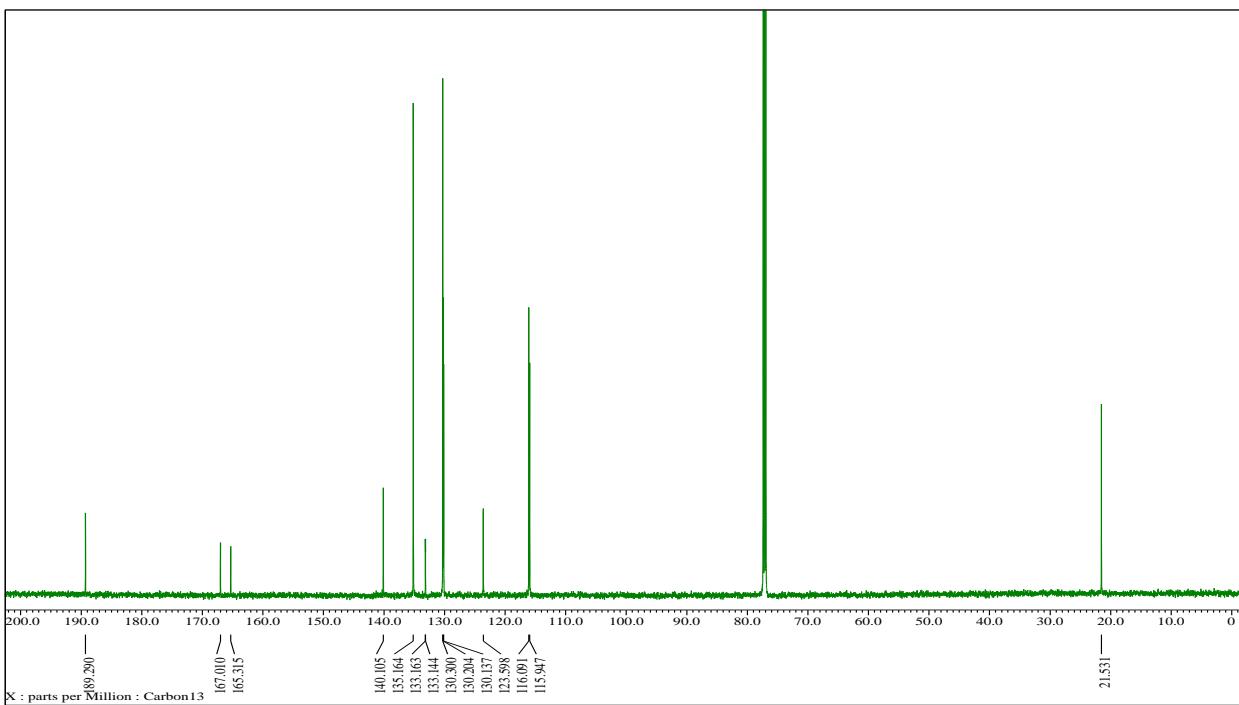
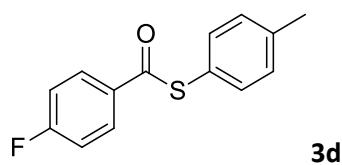
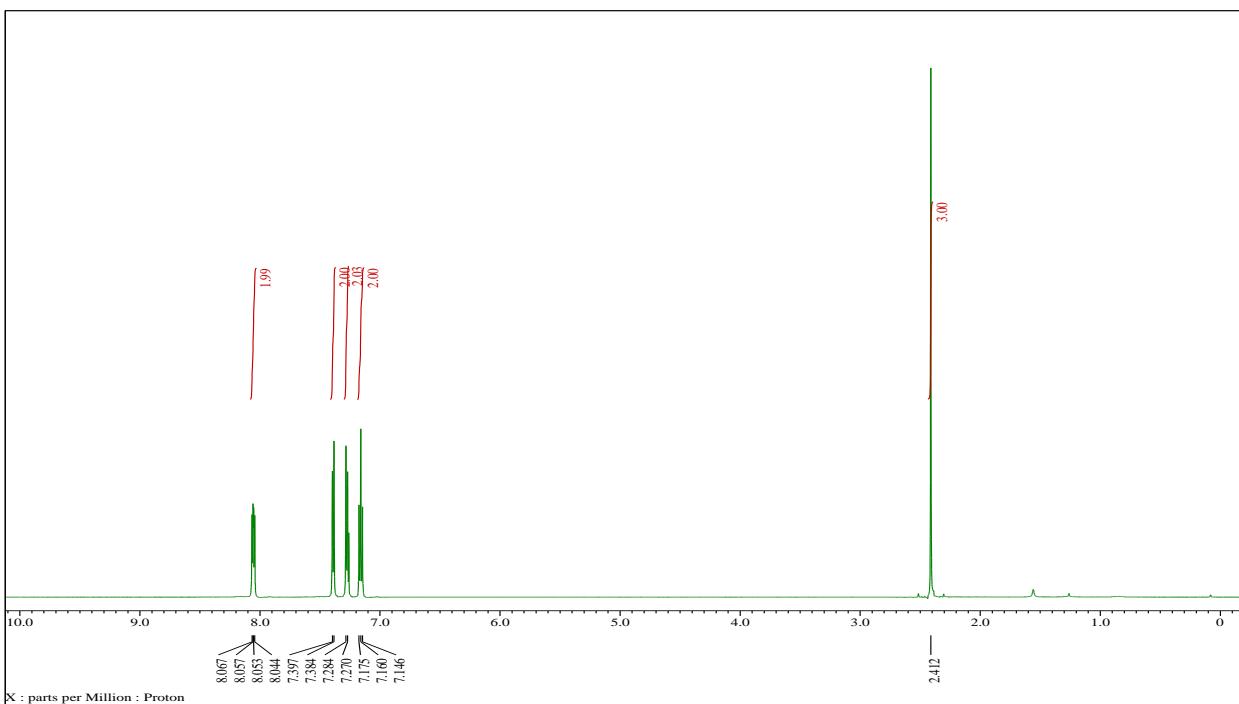


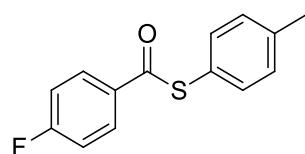
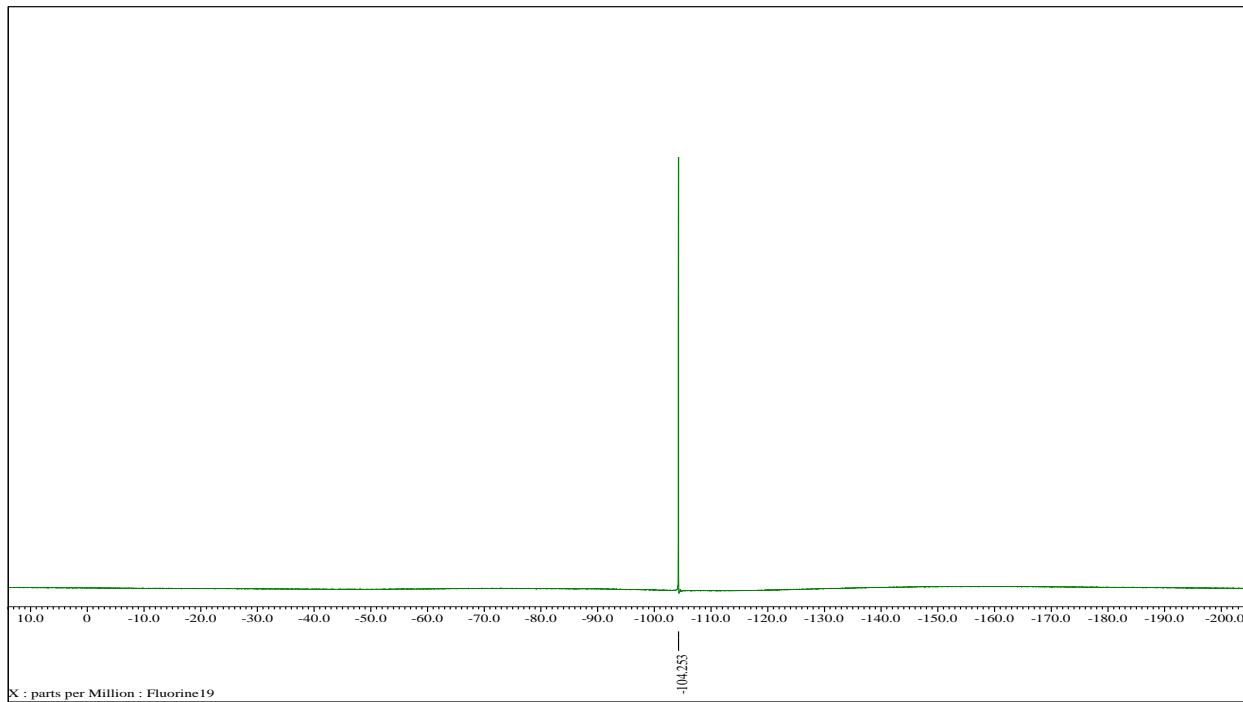
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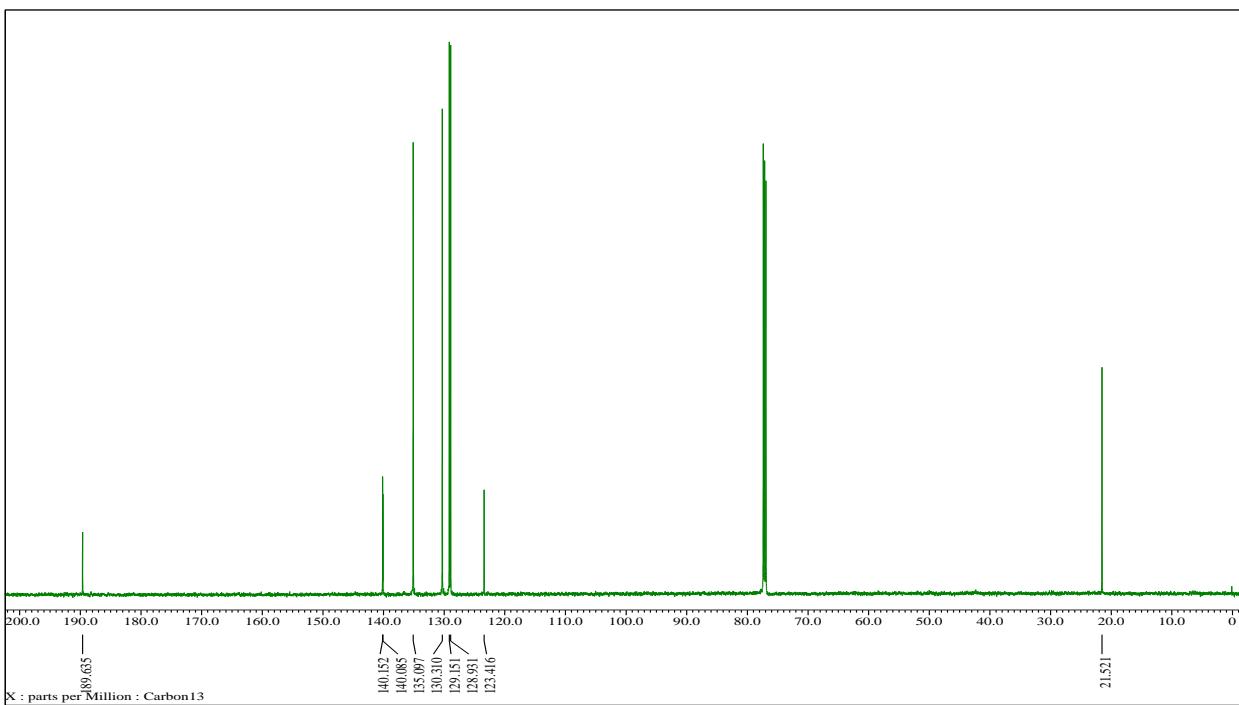
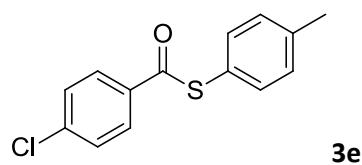
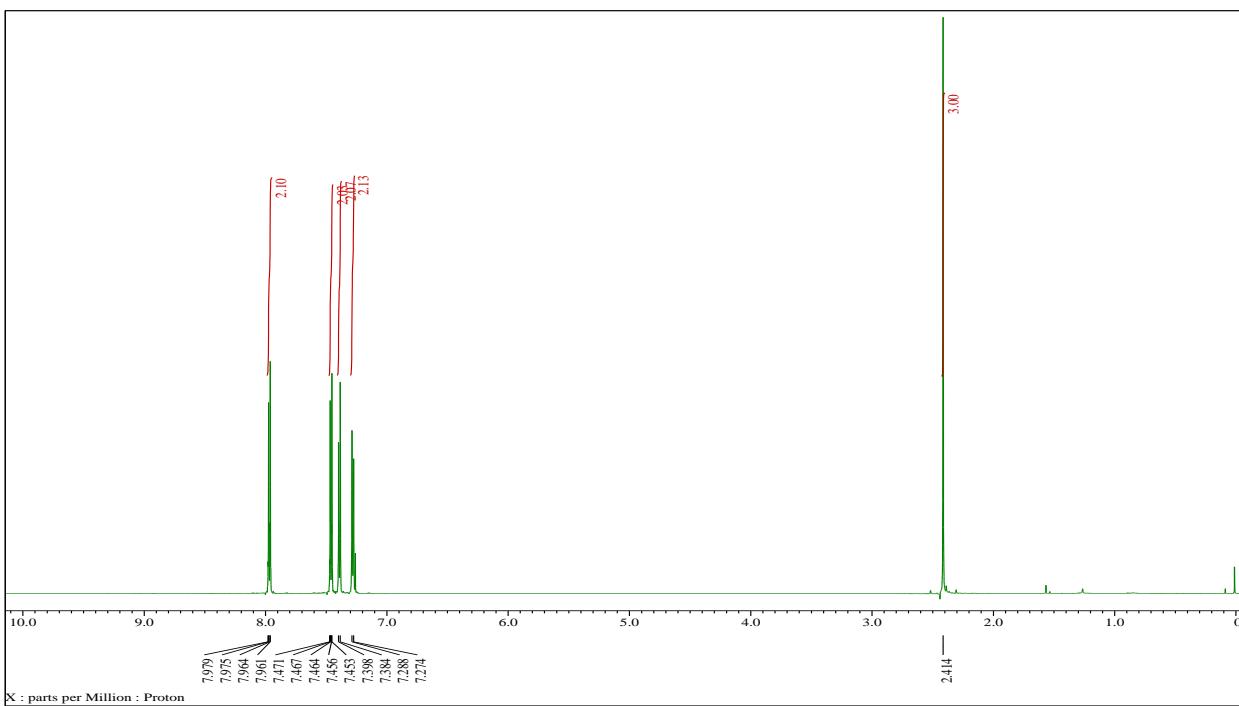


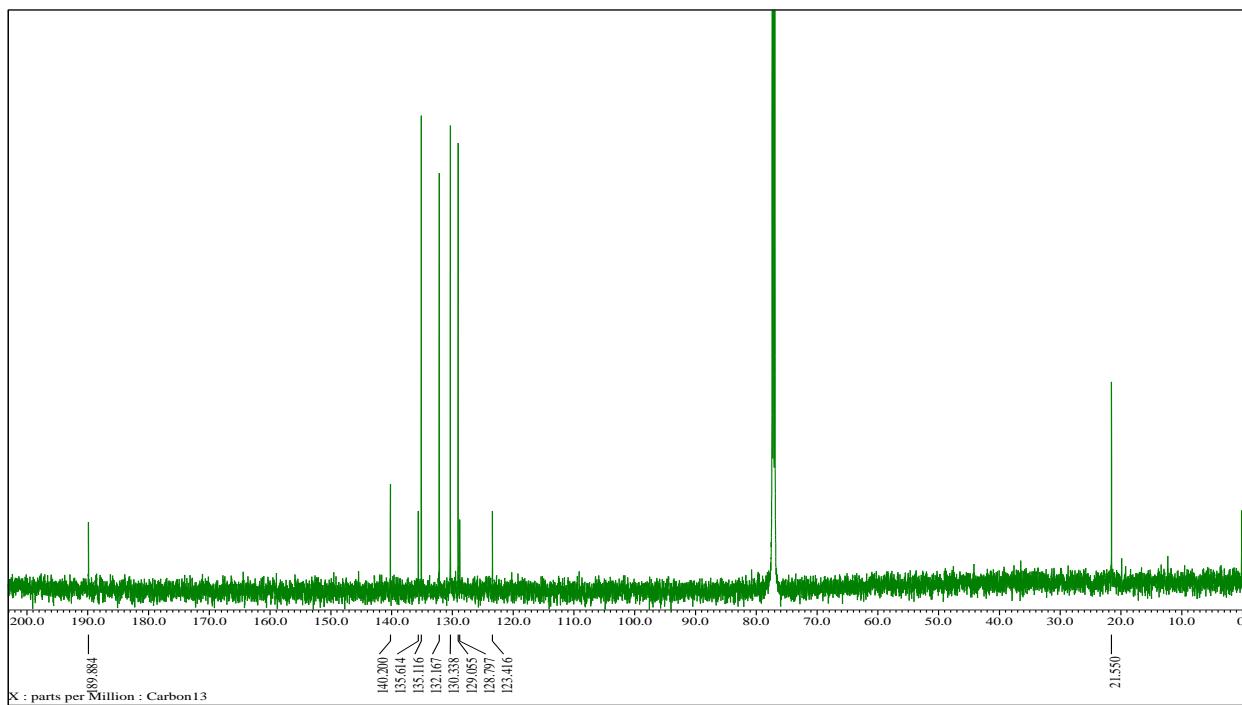
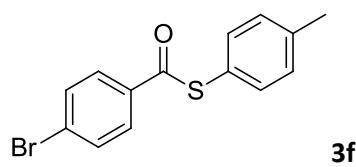
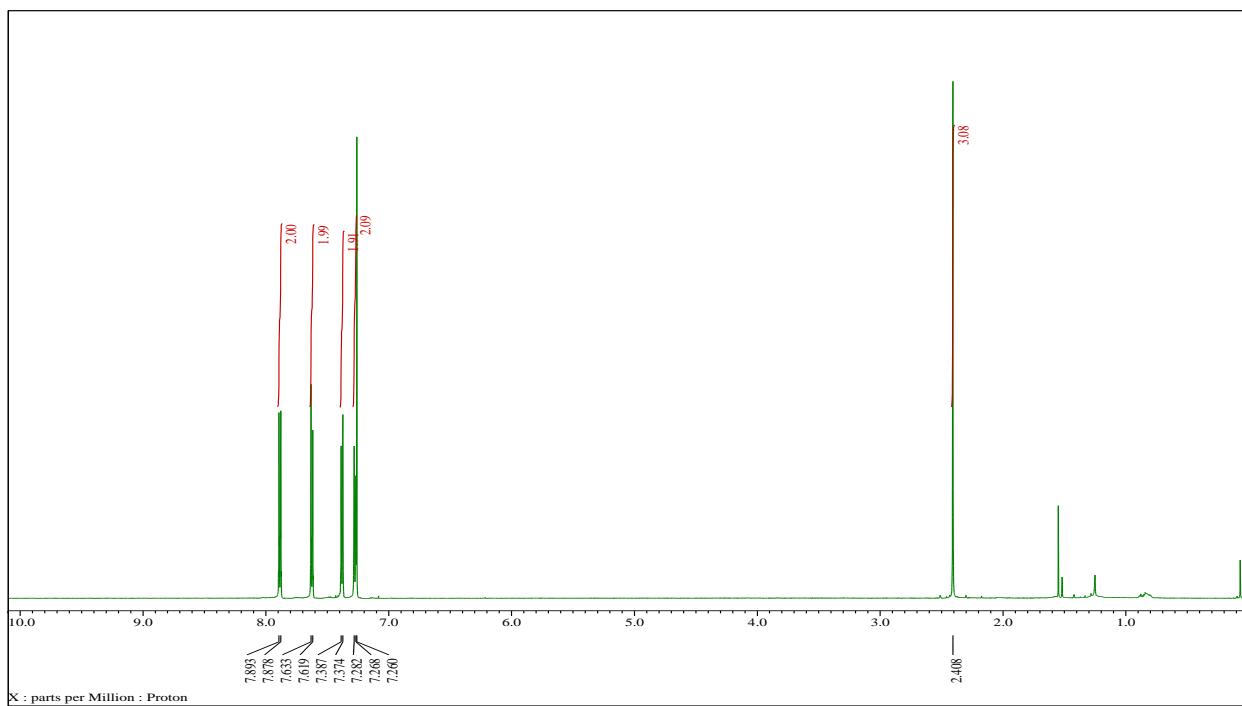


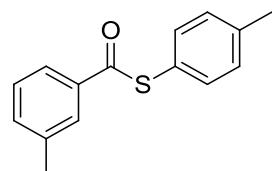
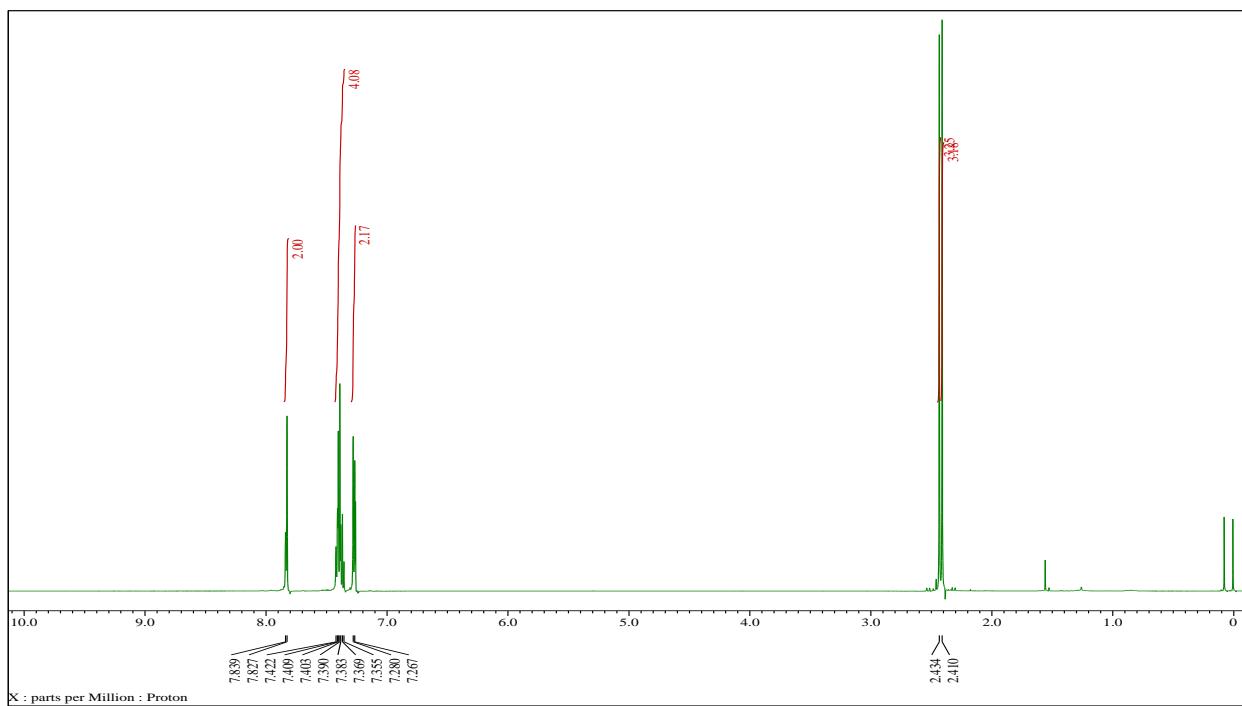




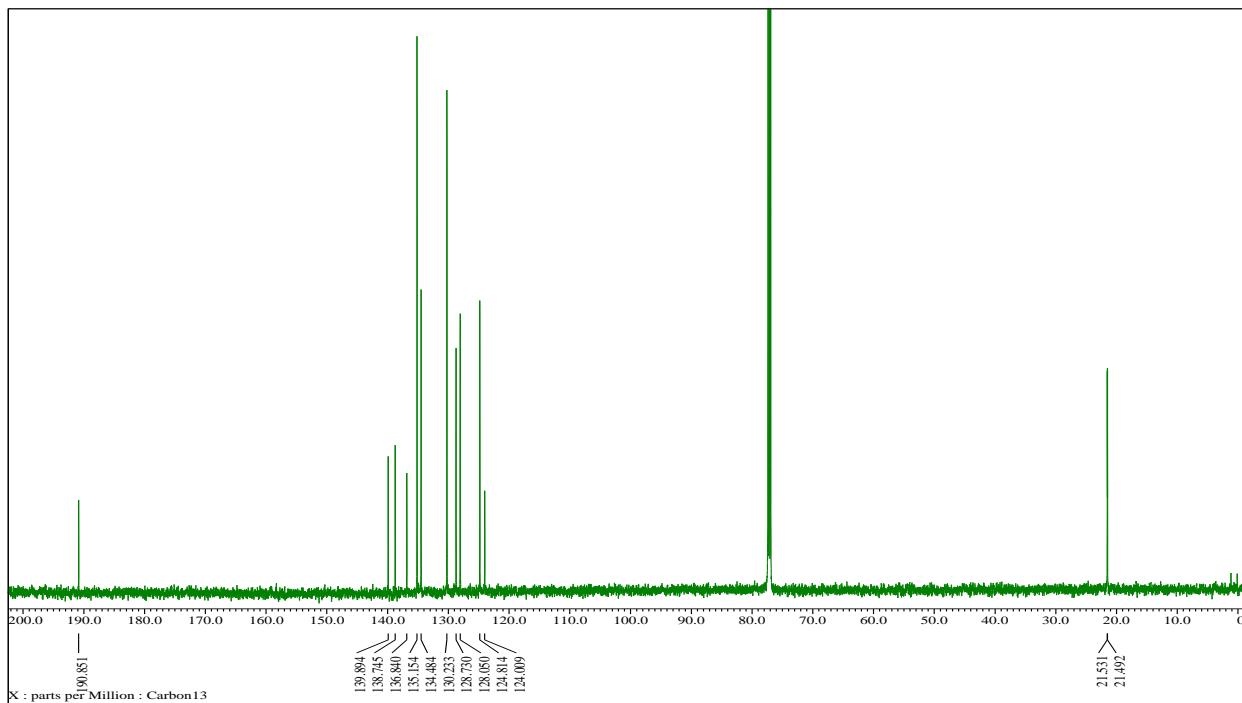
¹⁹F NMR of 3d

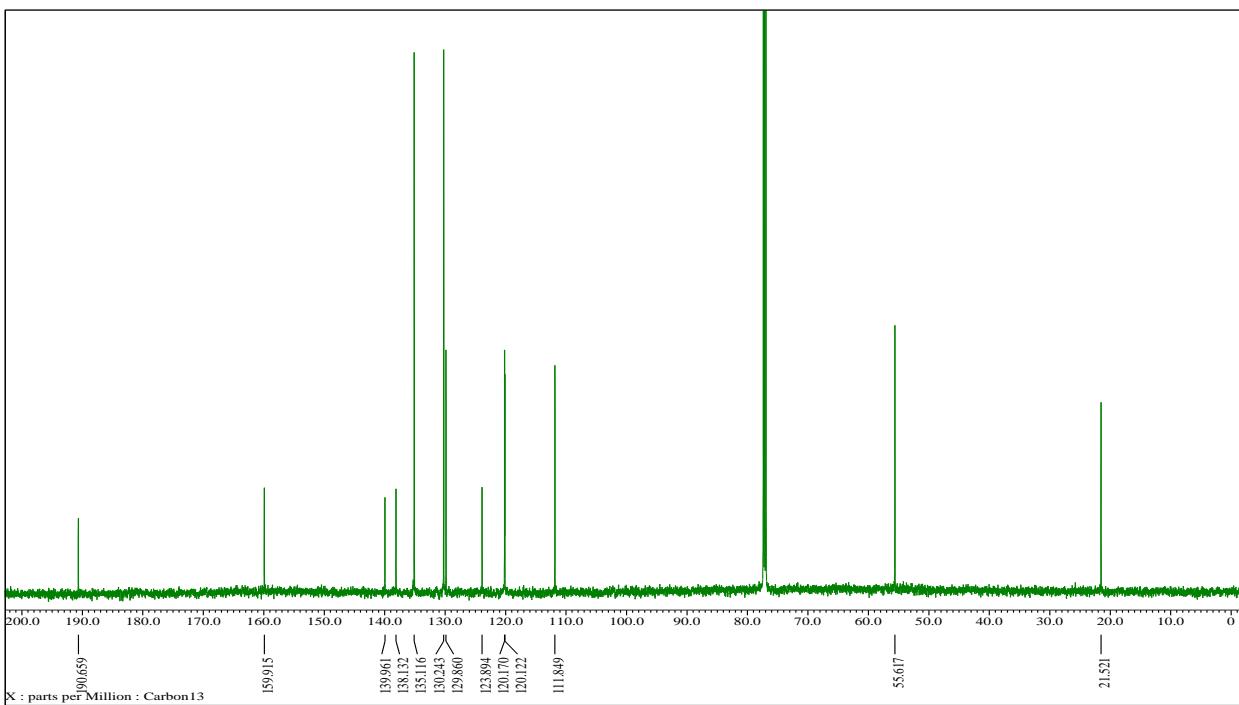
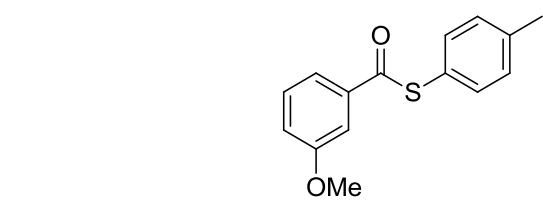
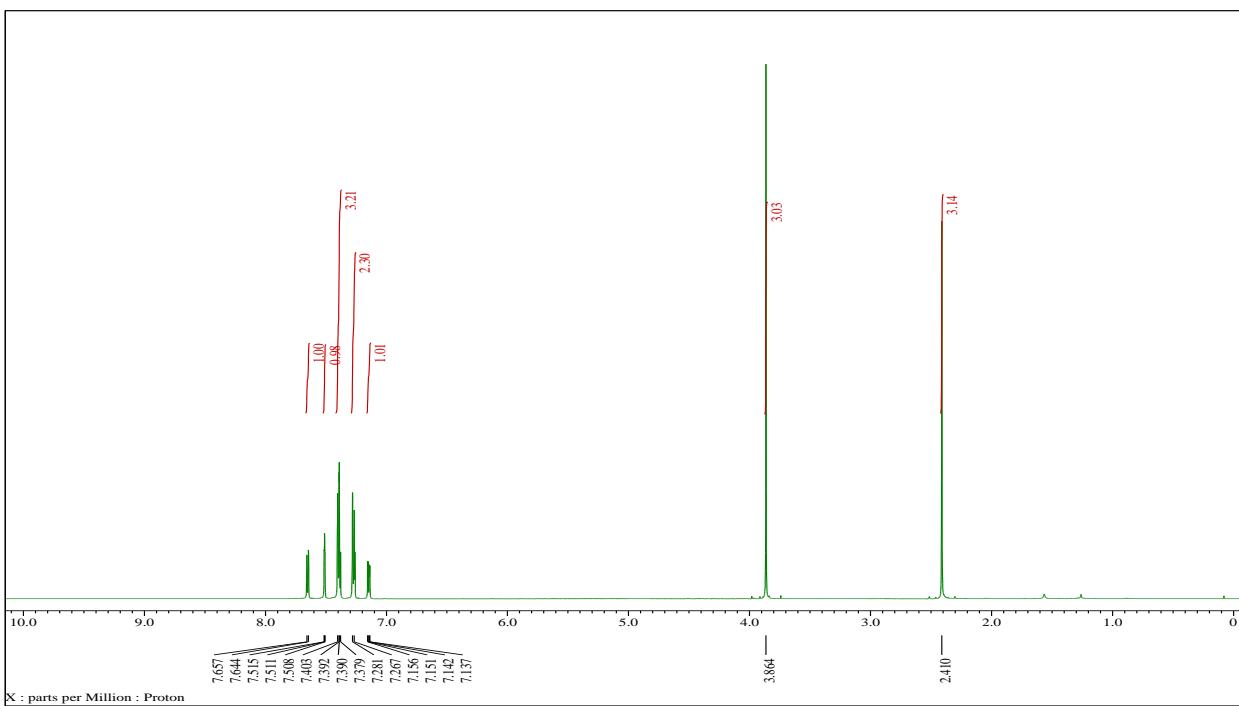


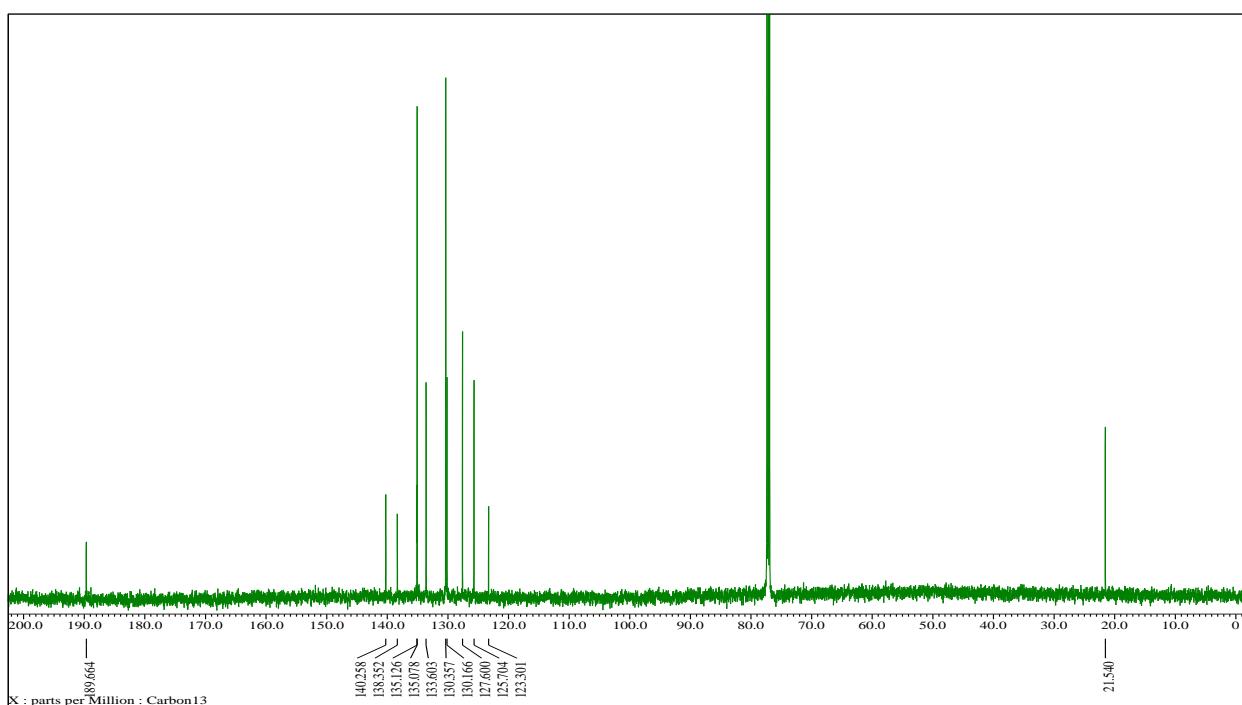
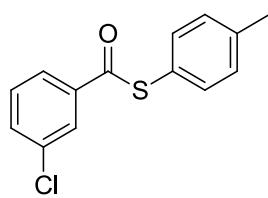
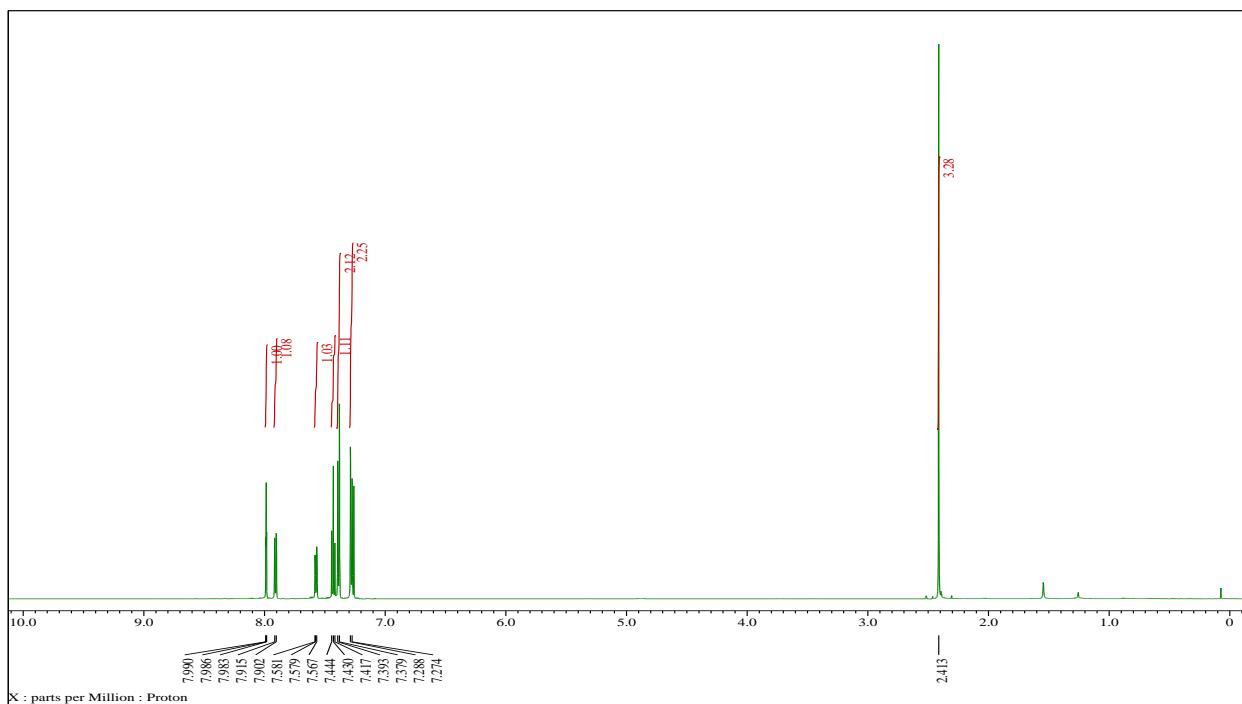


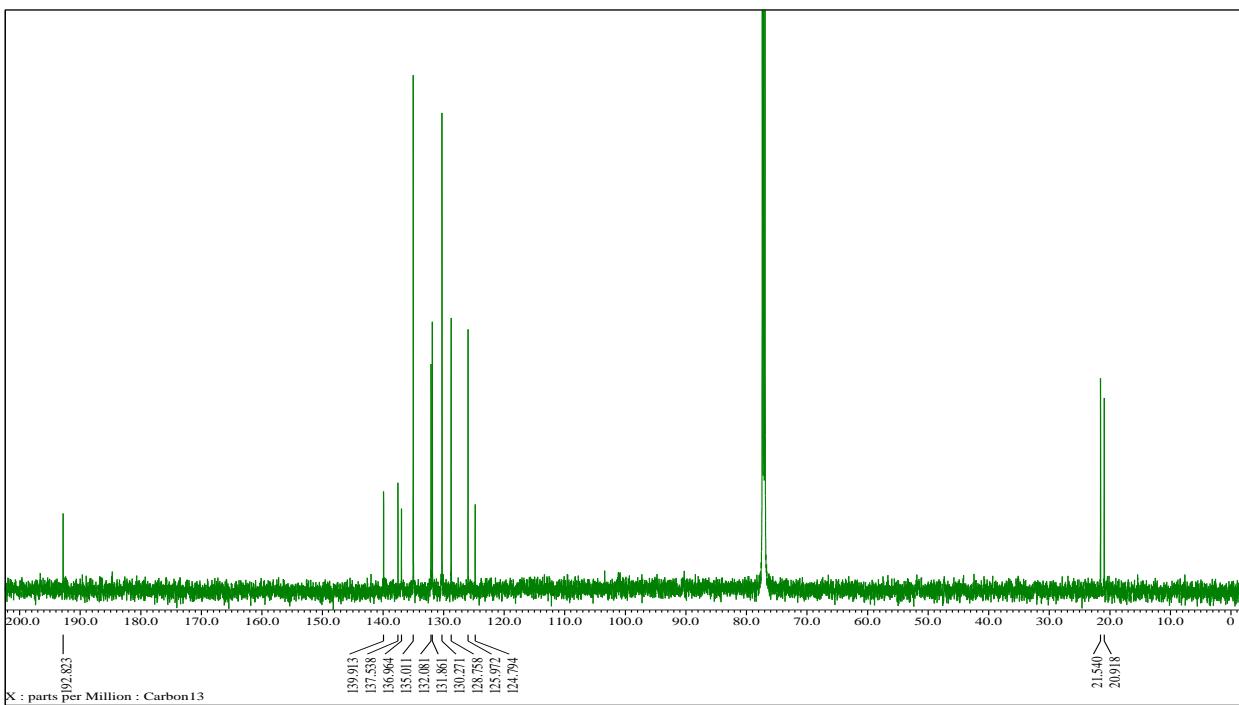
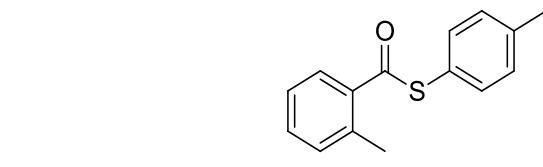
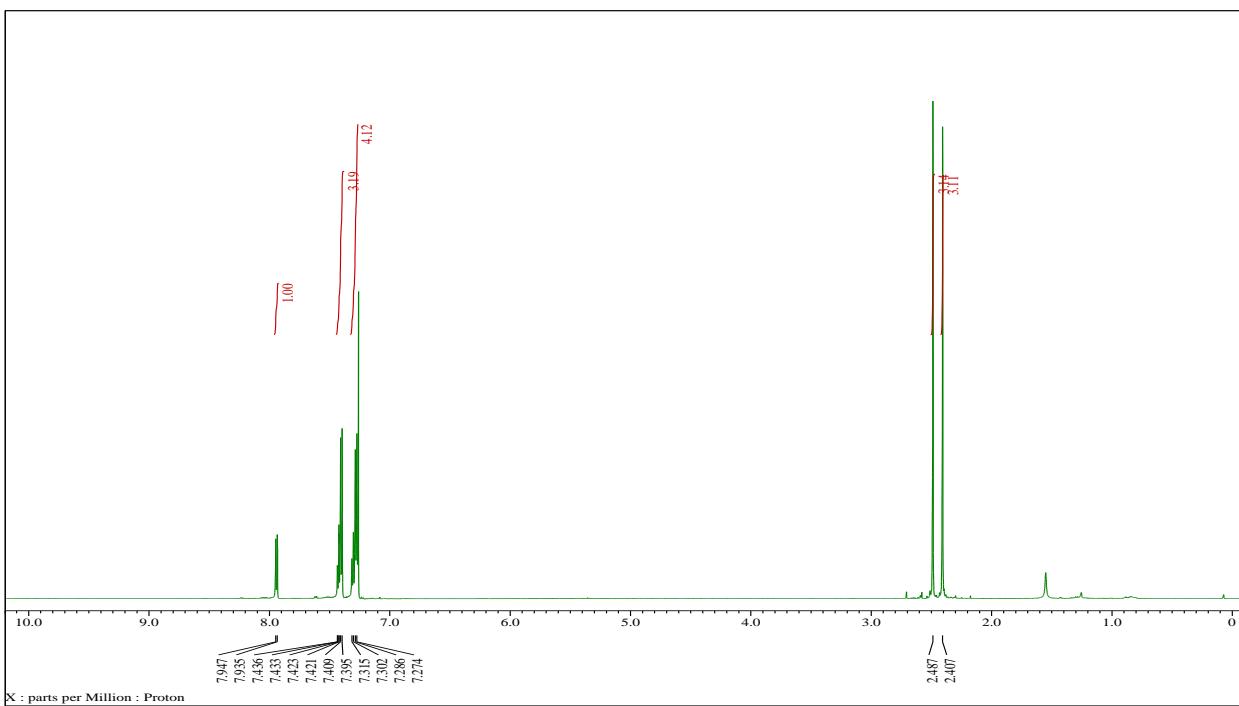


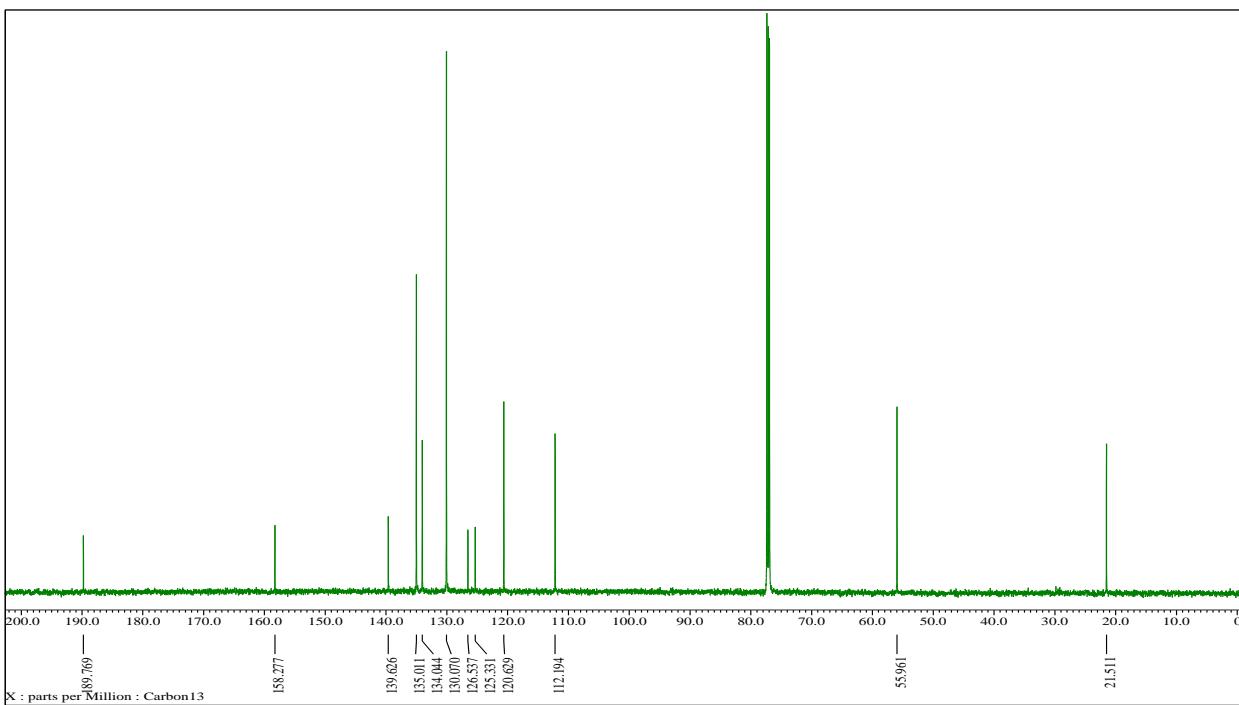
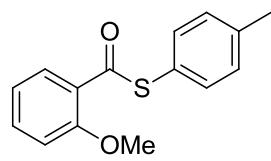
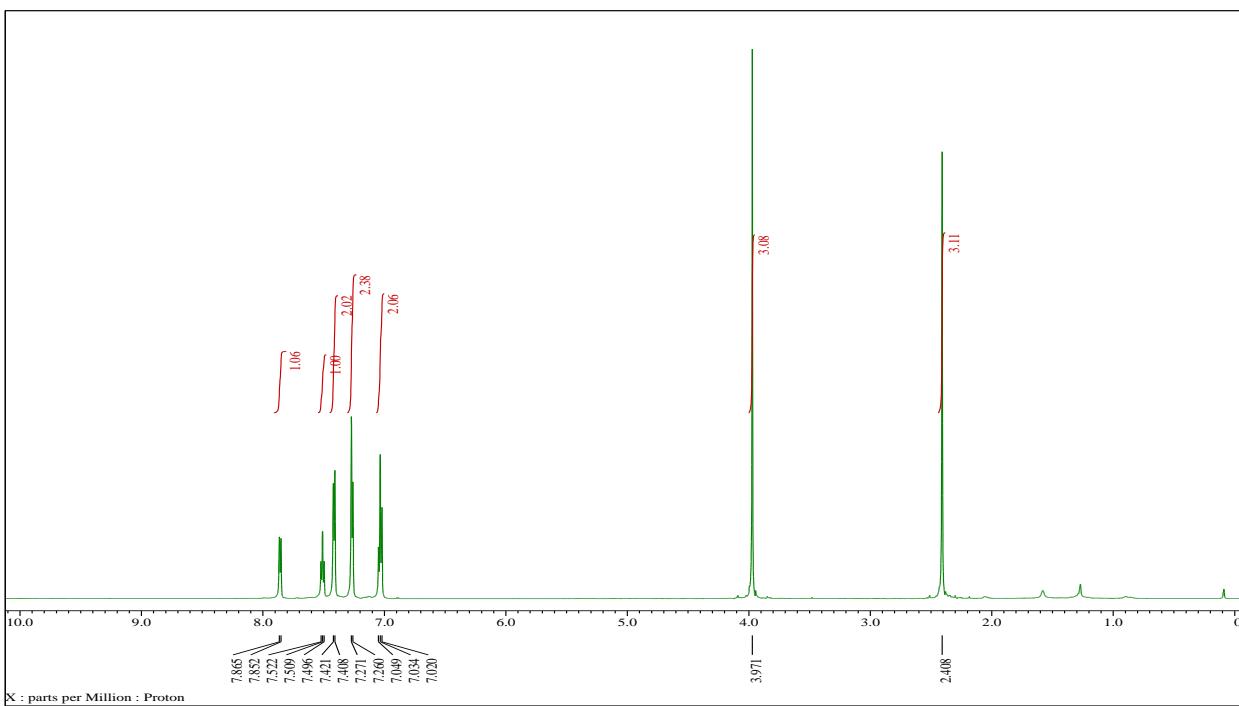
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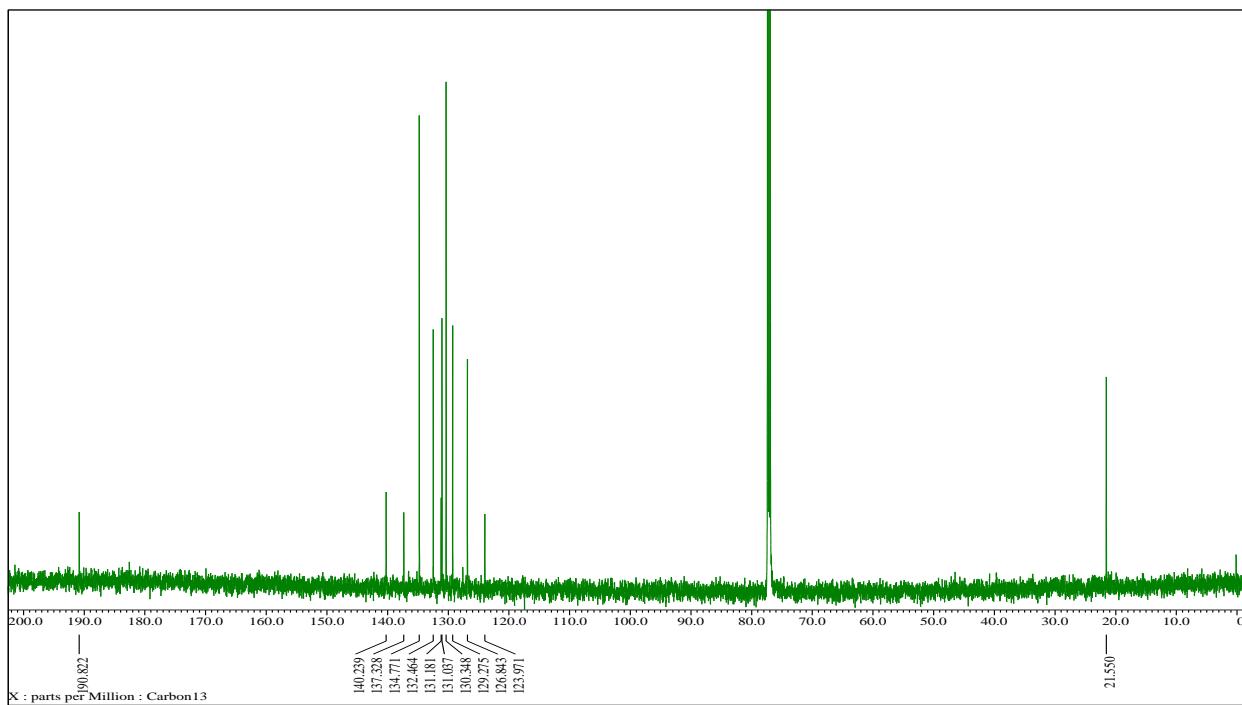
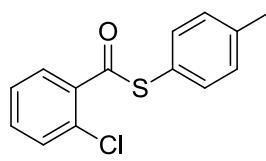
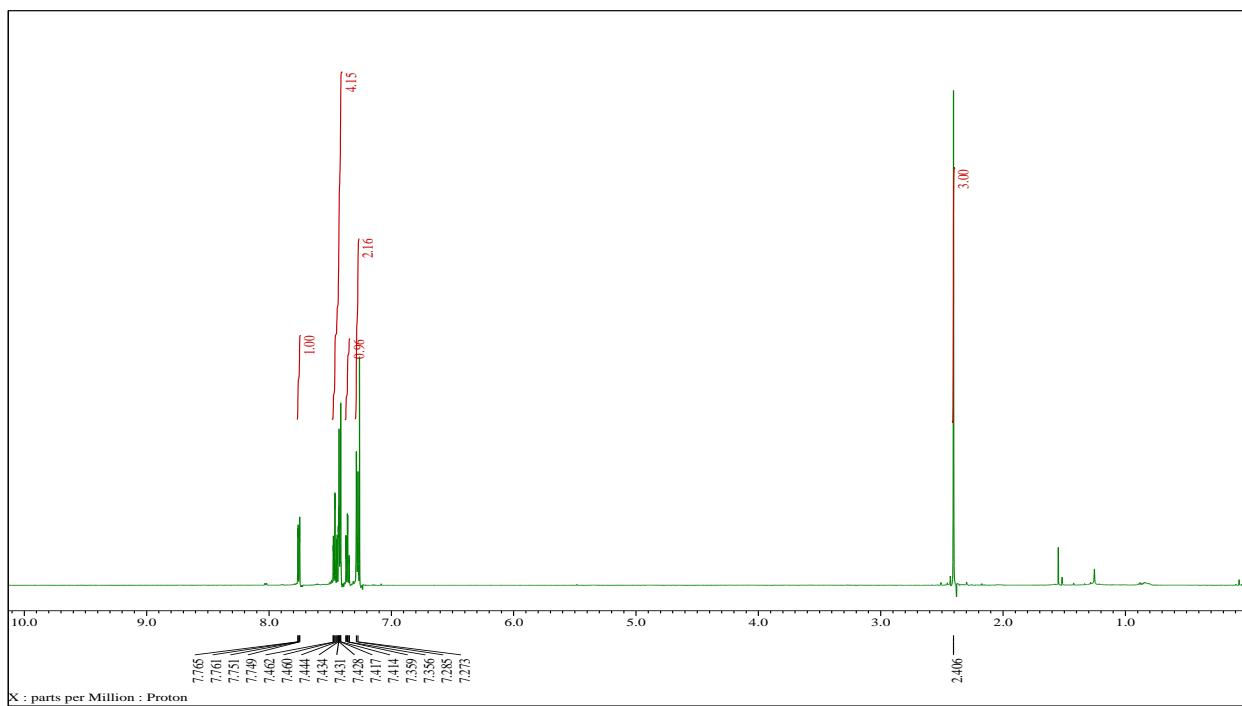


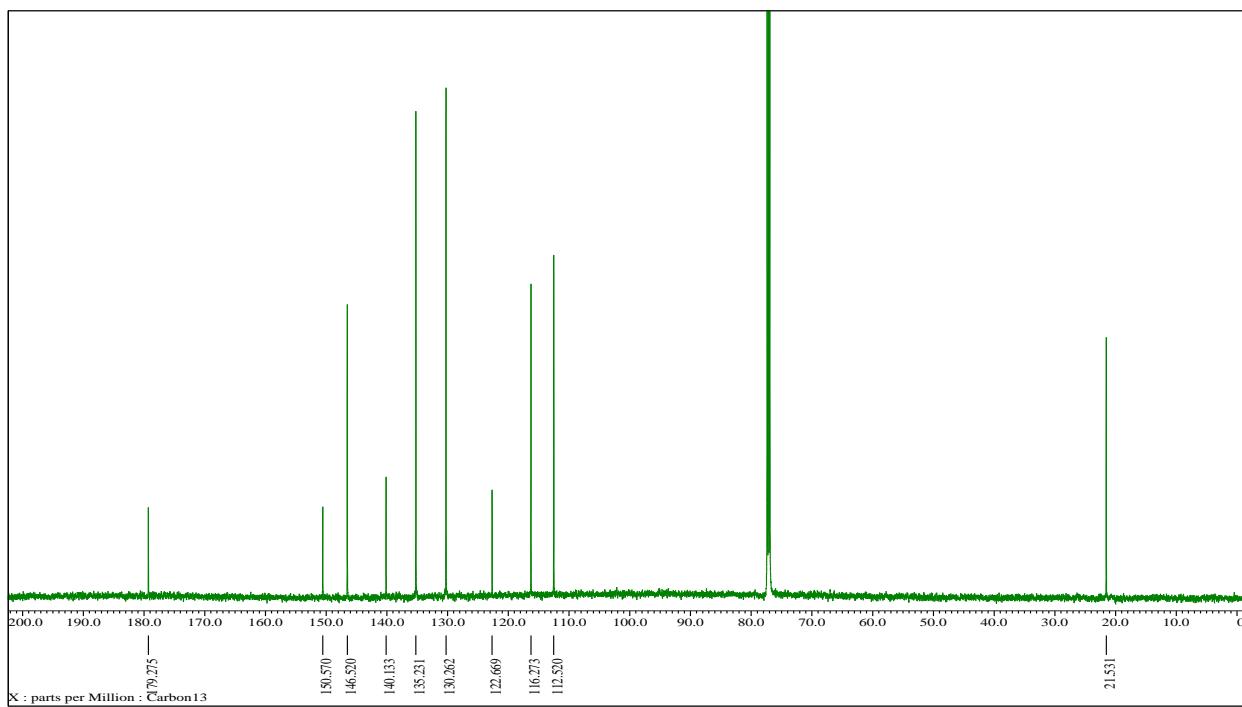
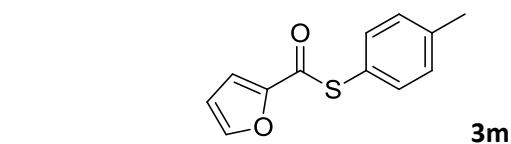
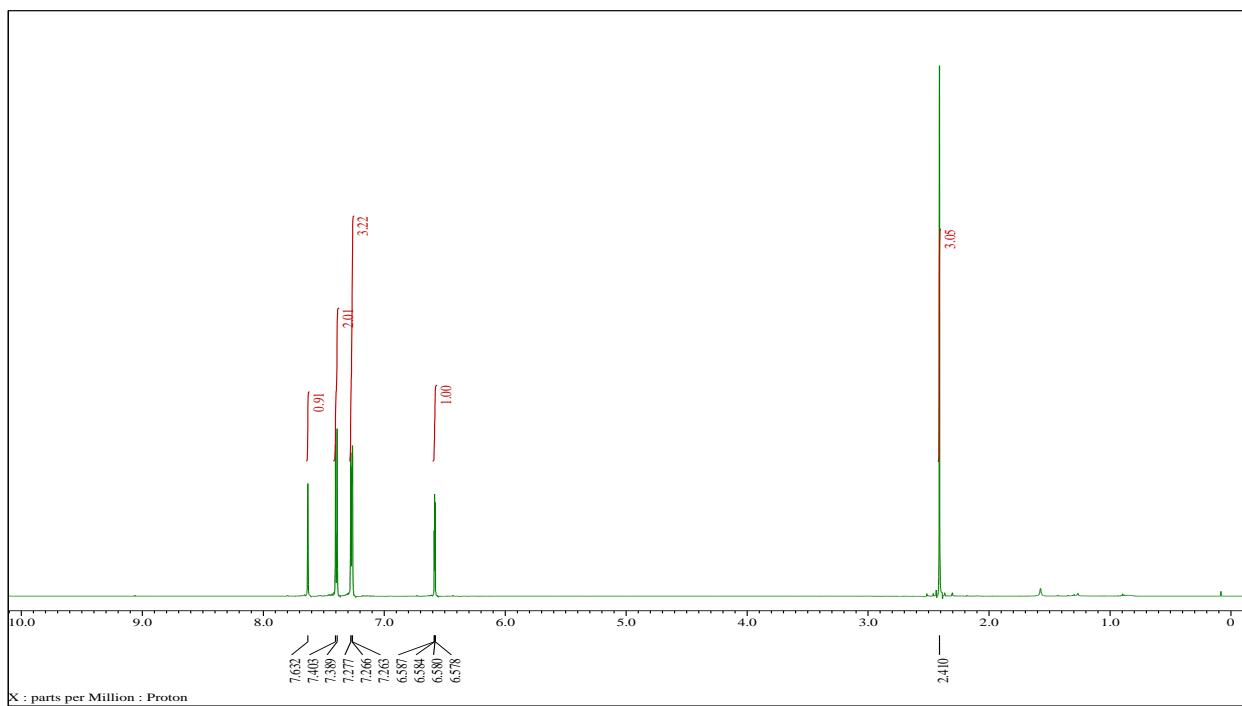


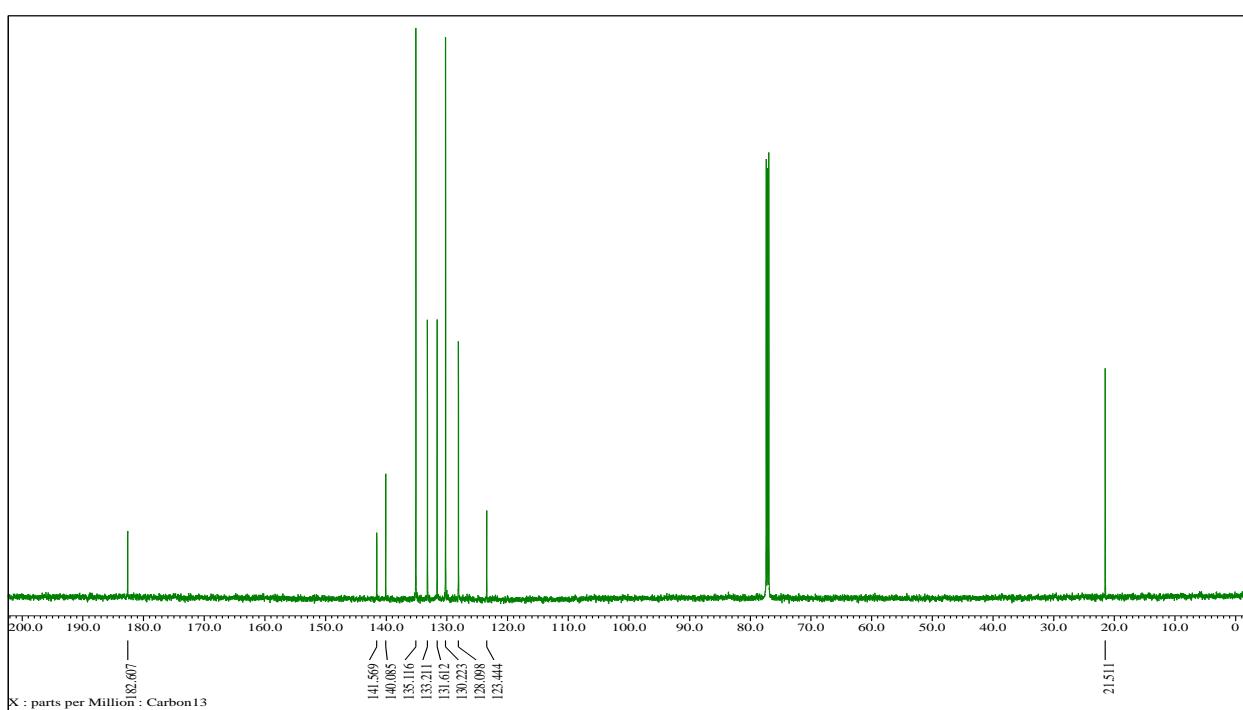
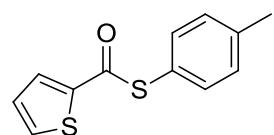
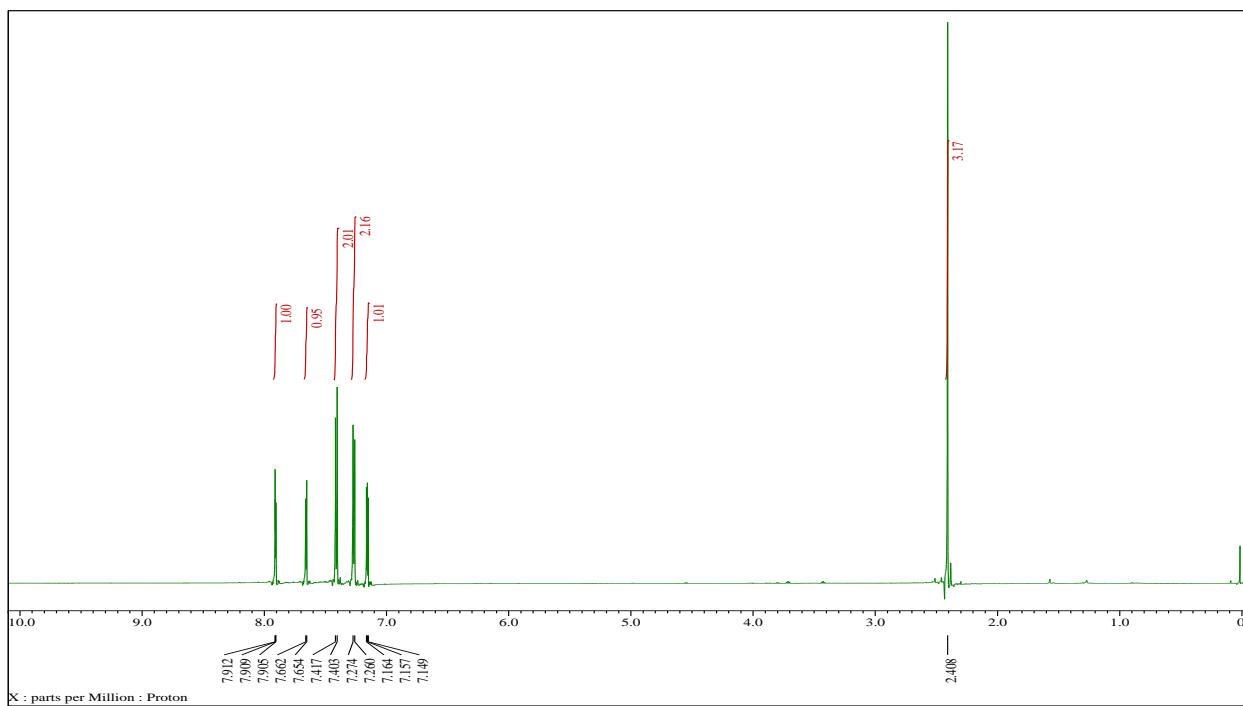


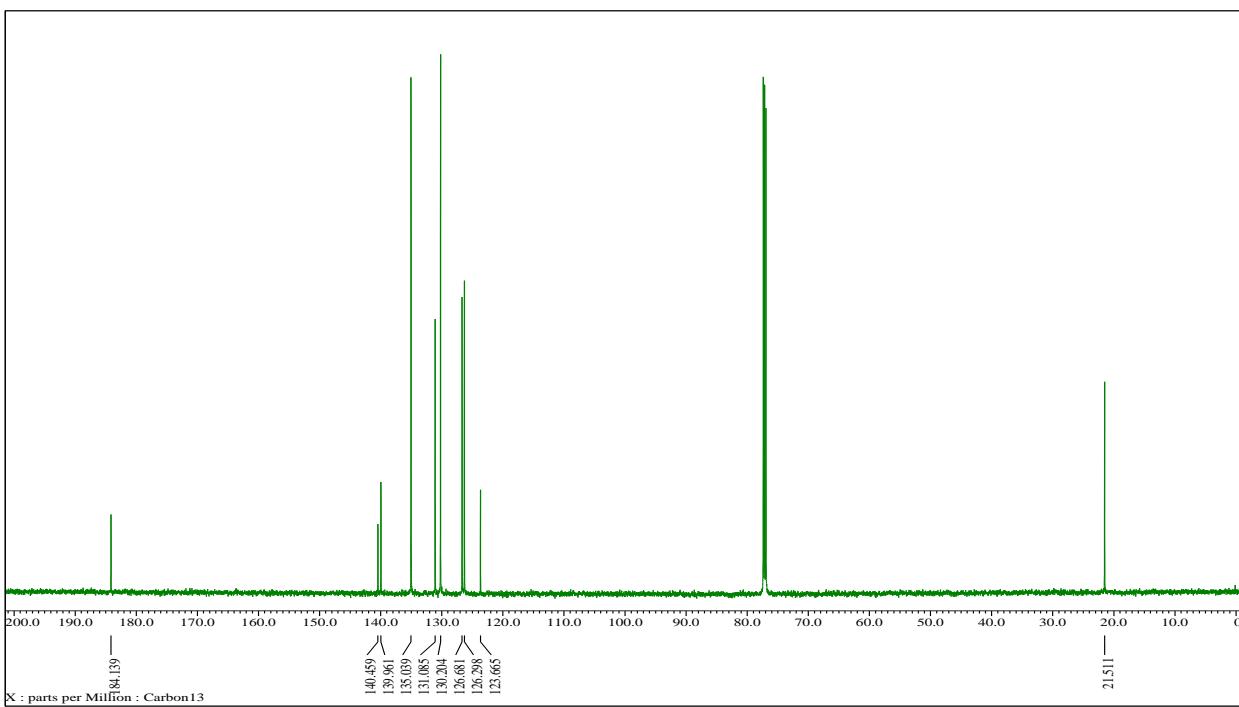
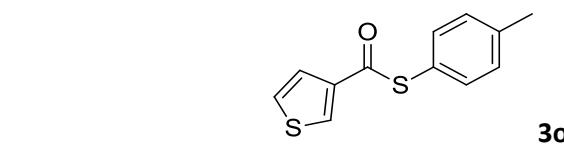
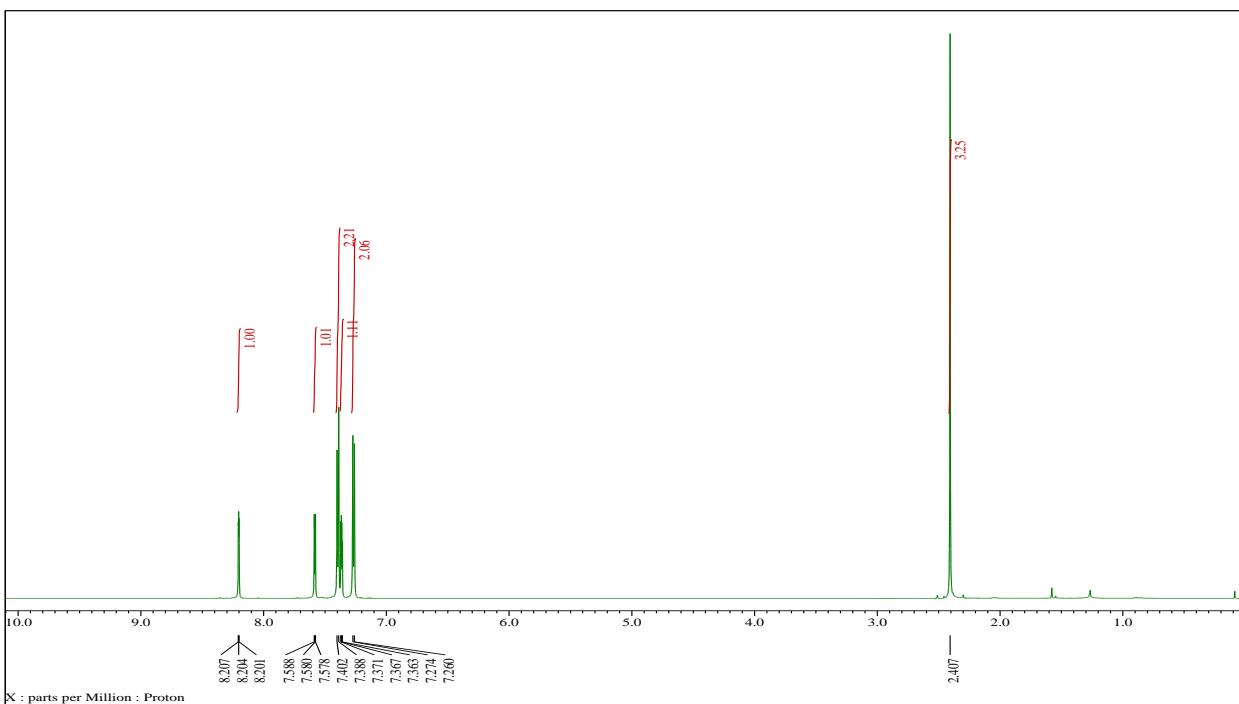


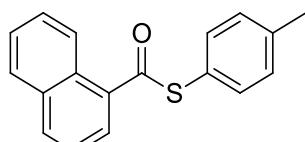
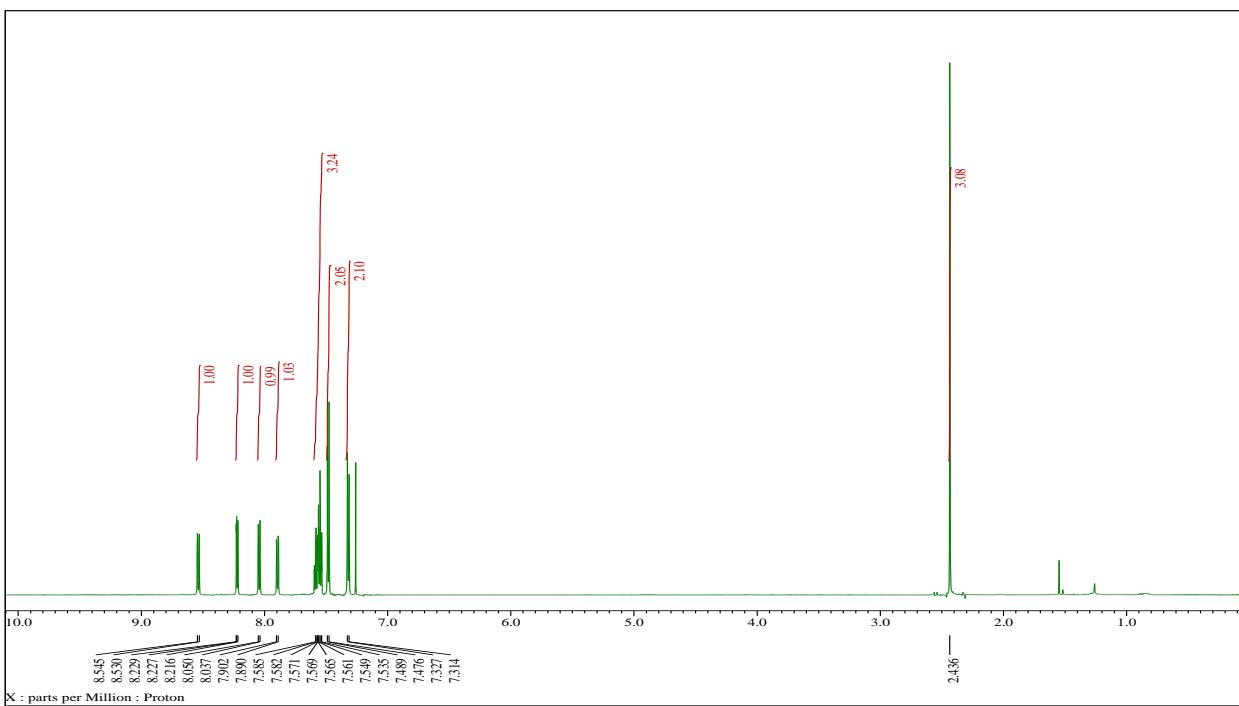




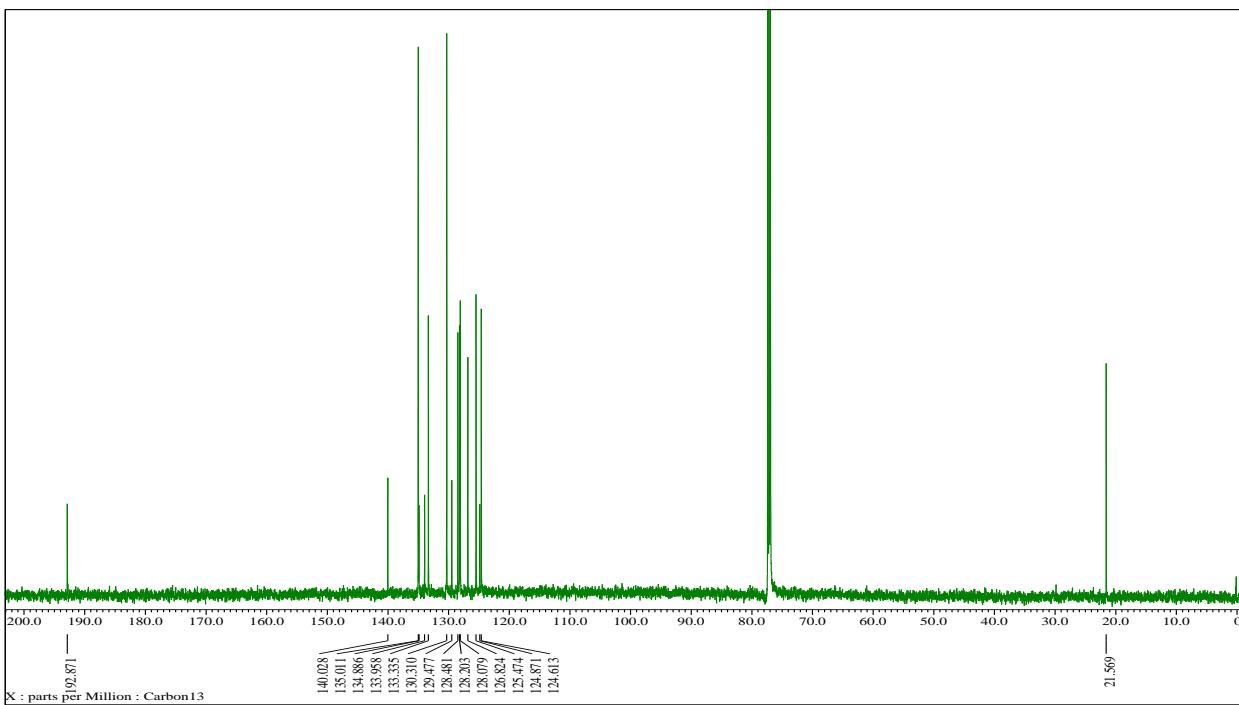


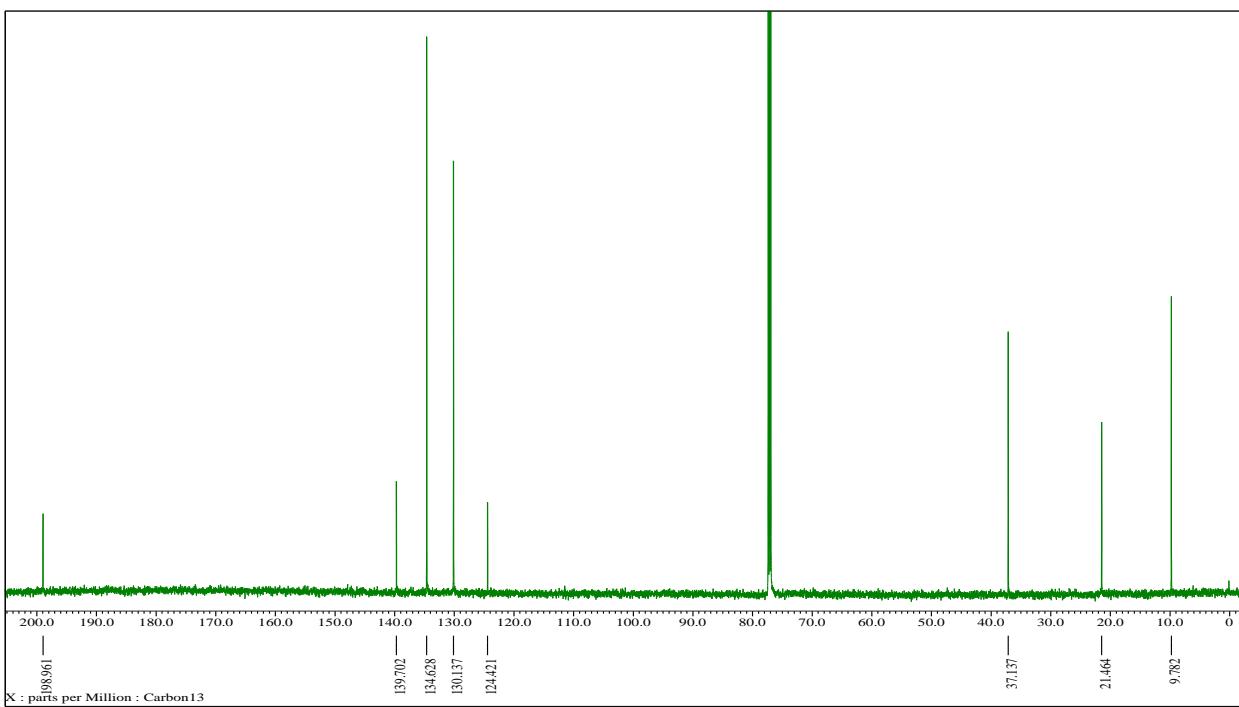
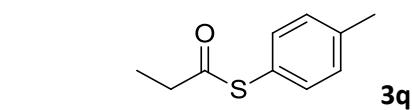
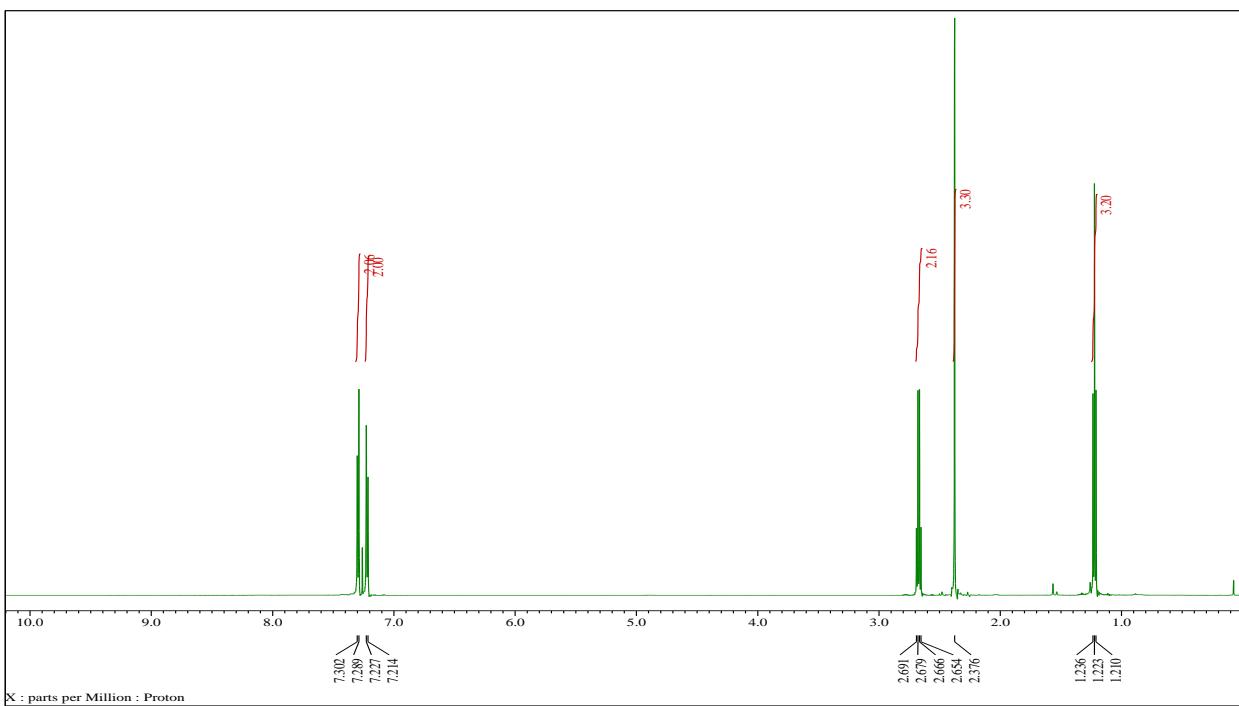


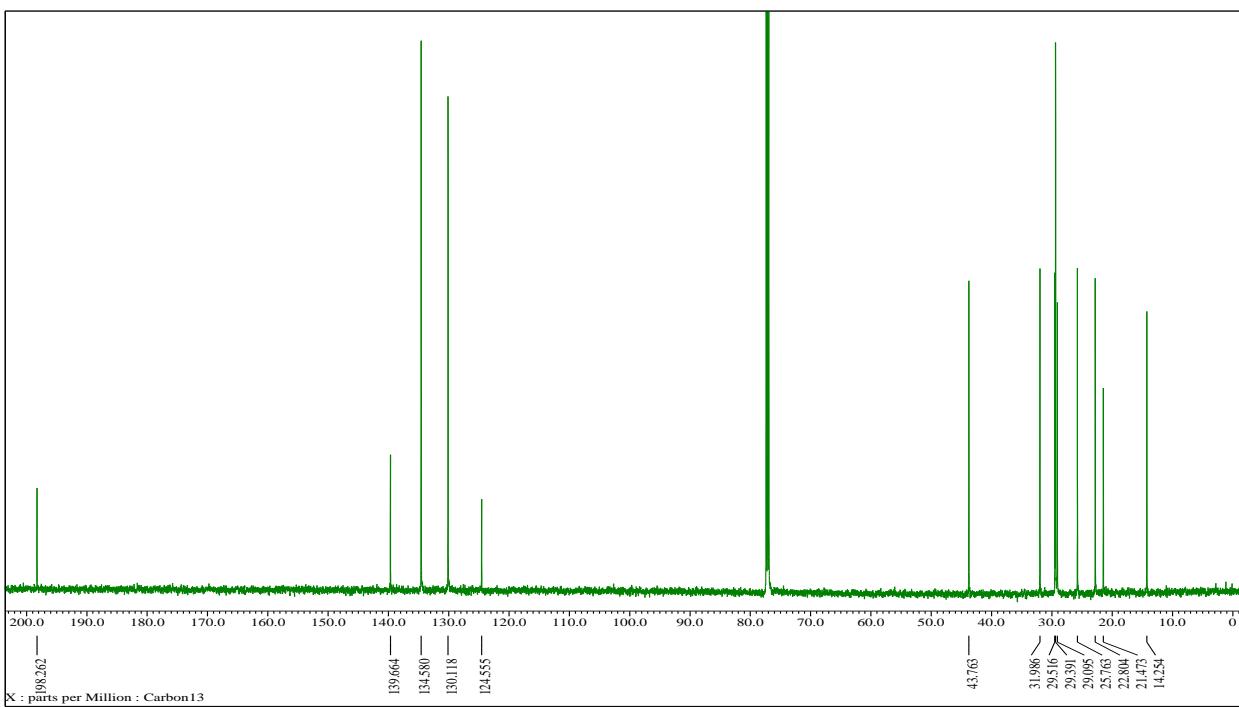
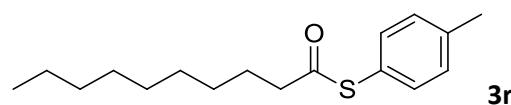
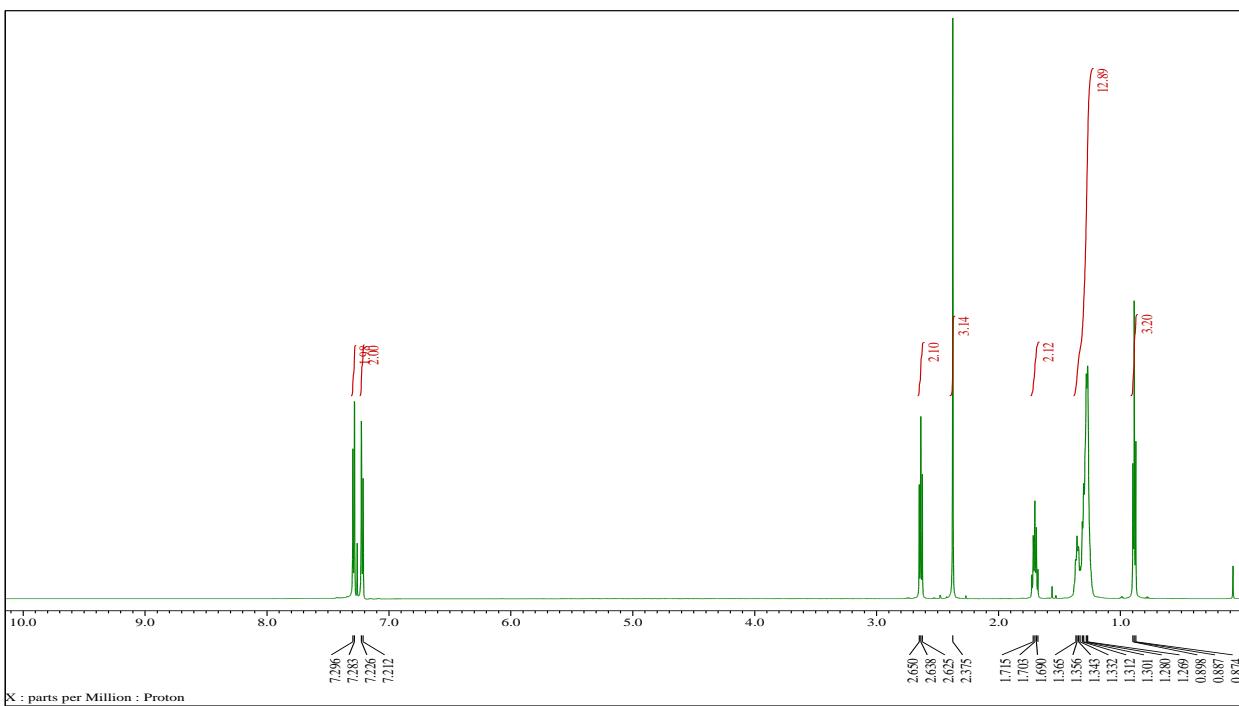


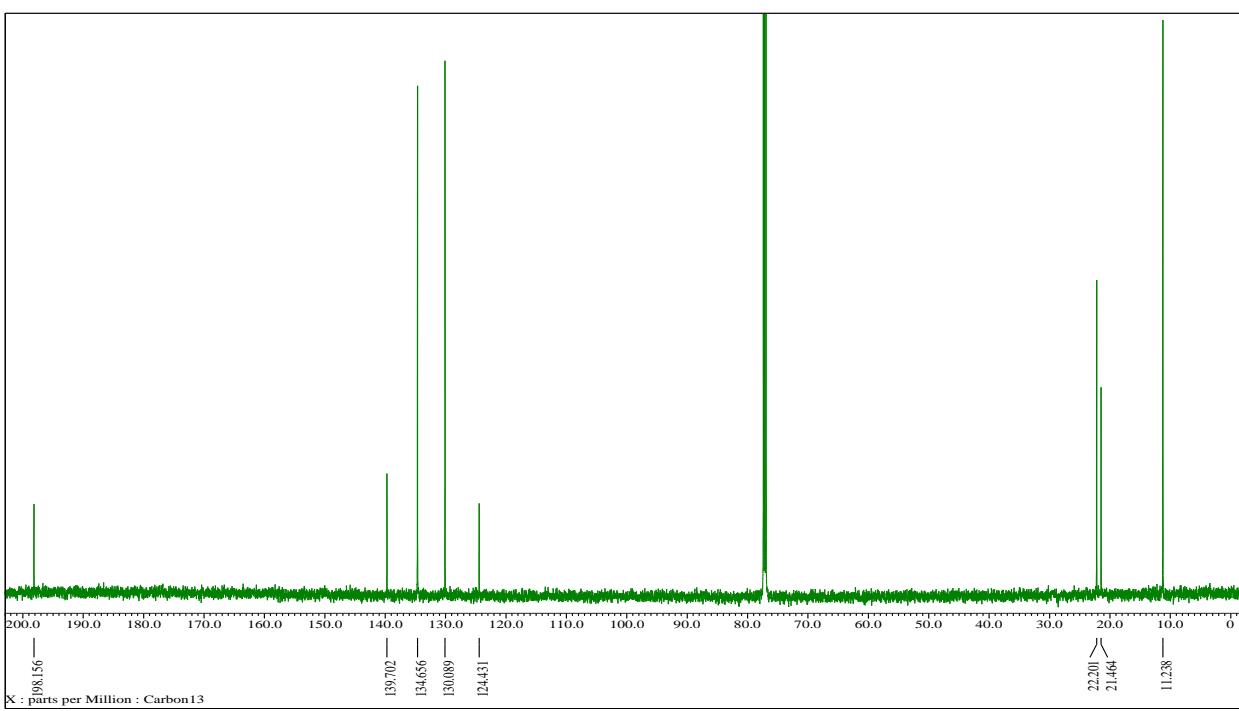
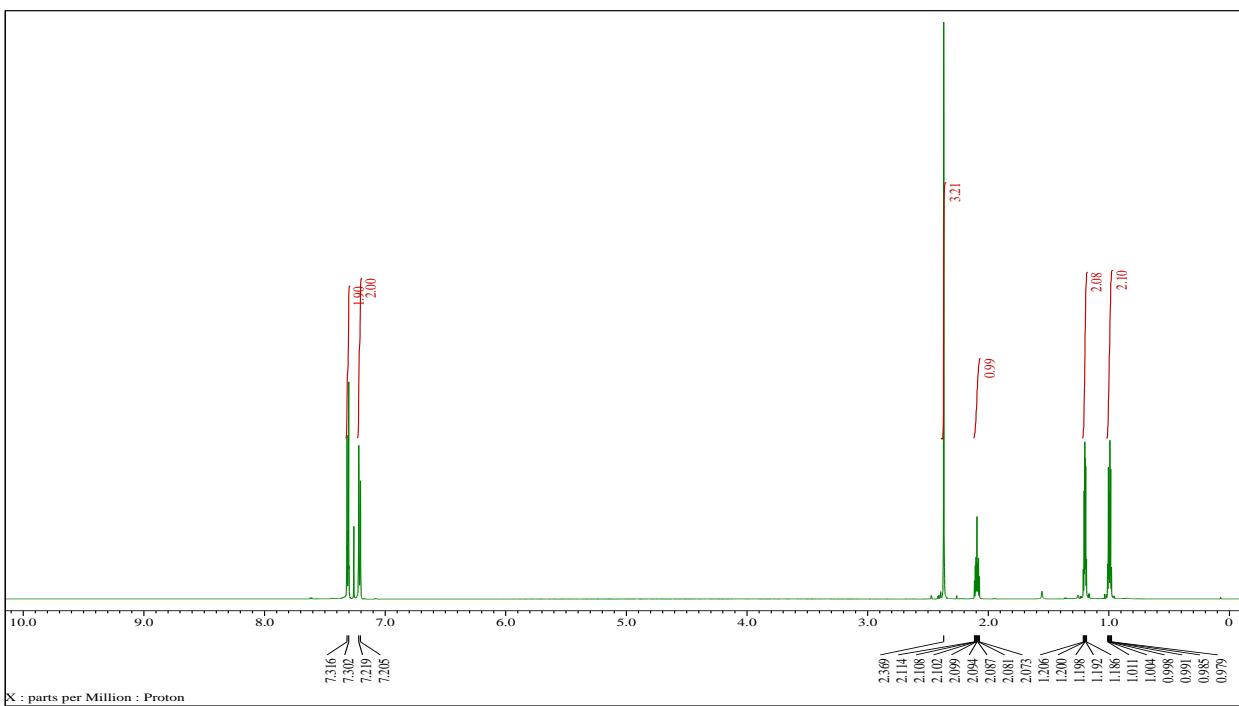


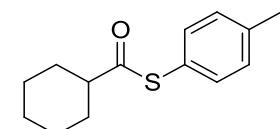
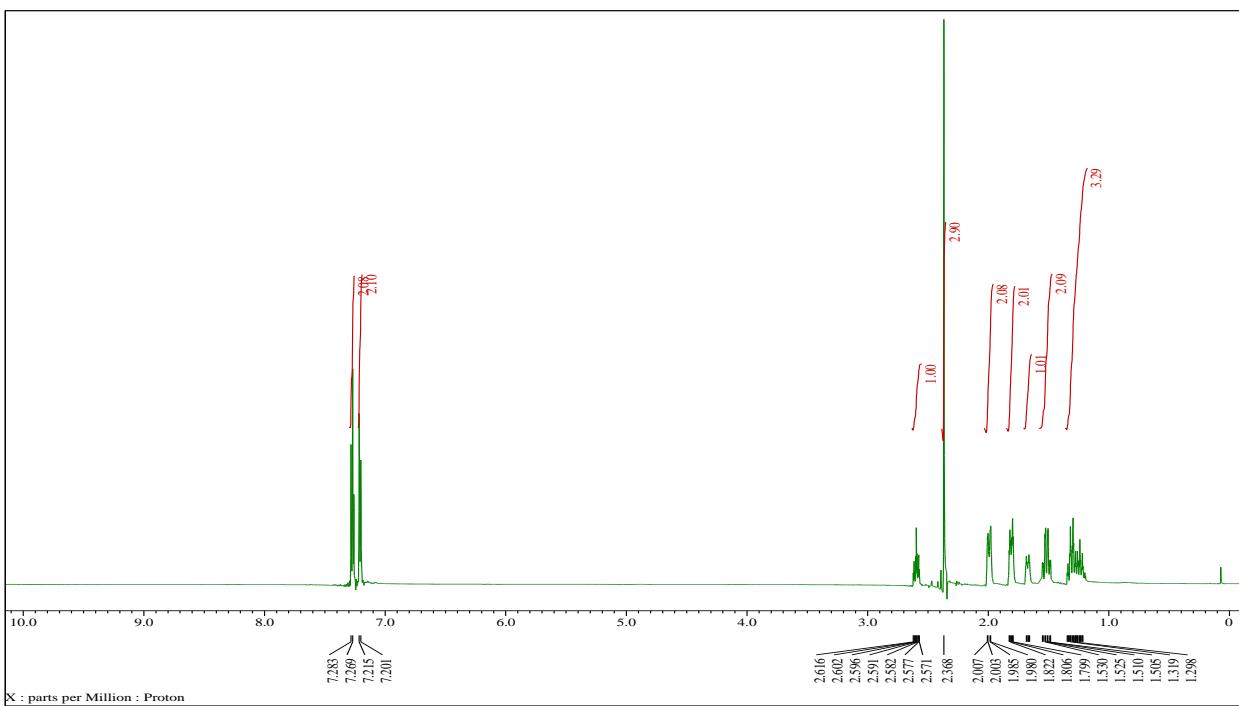
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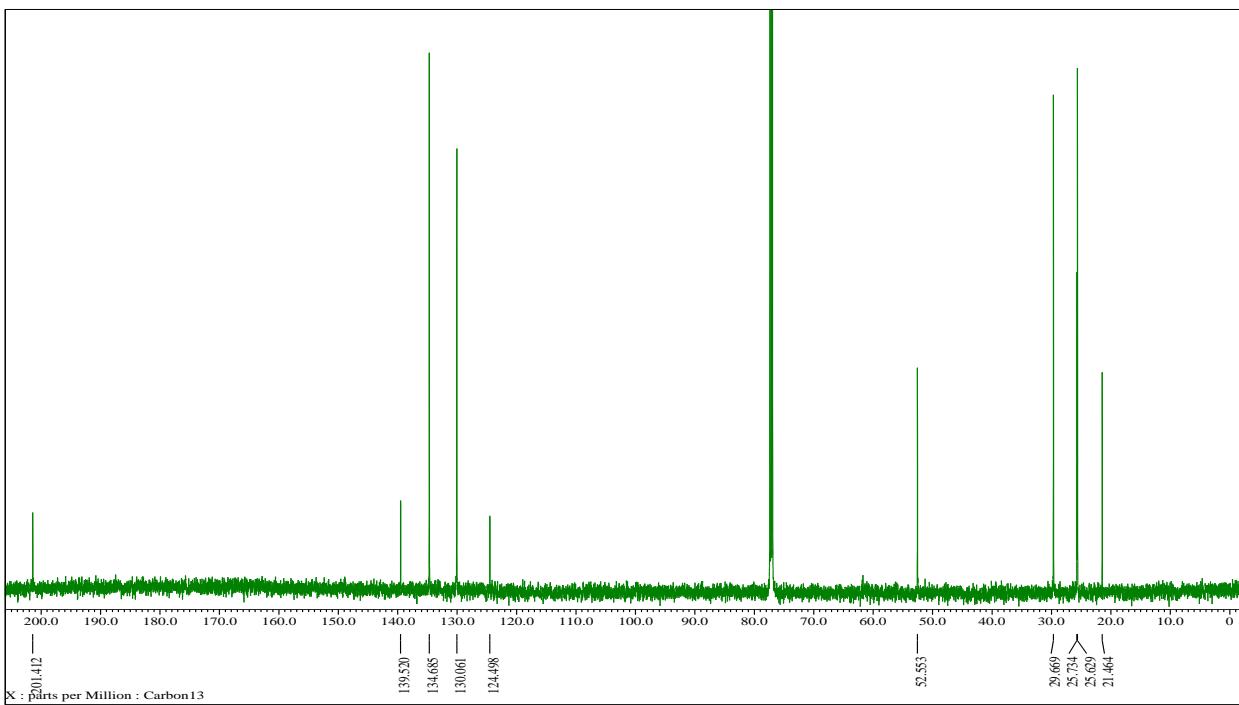


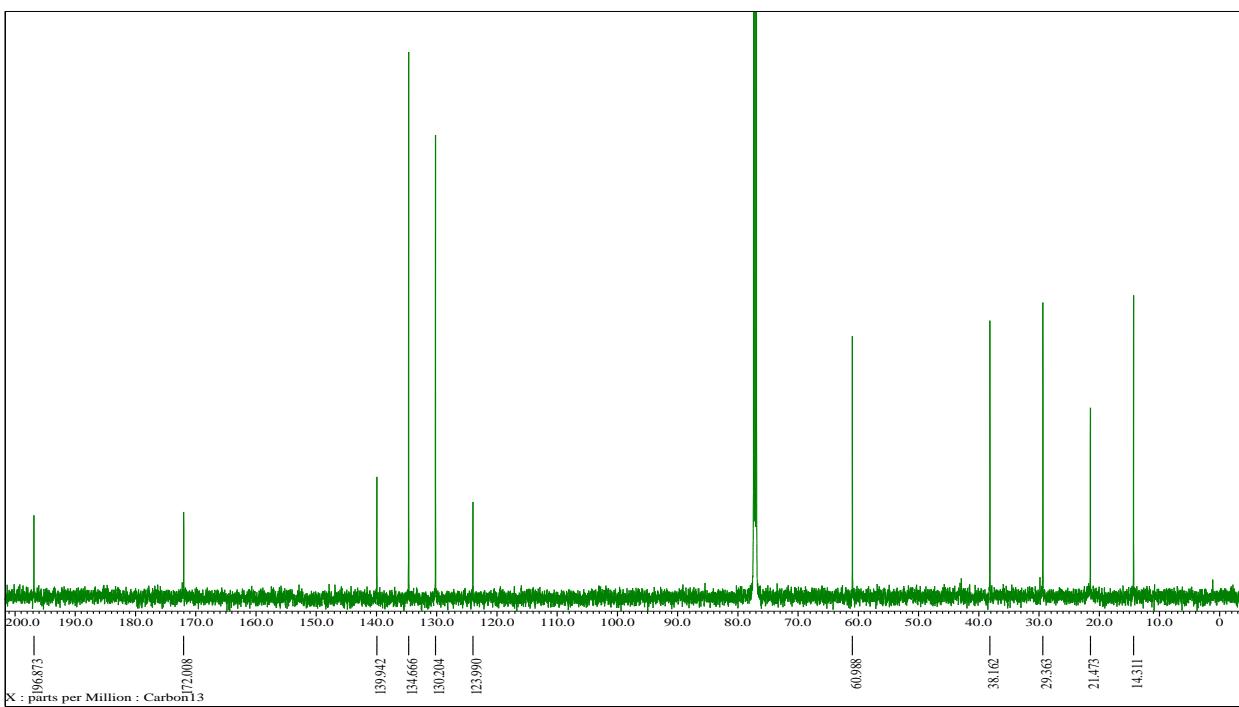
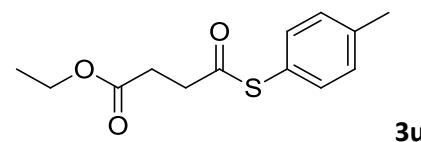
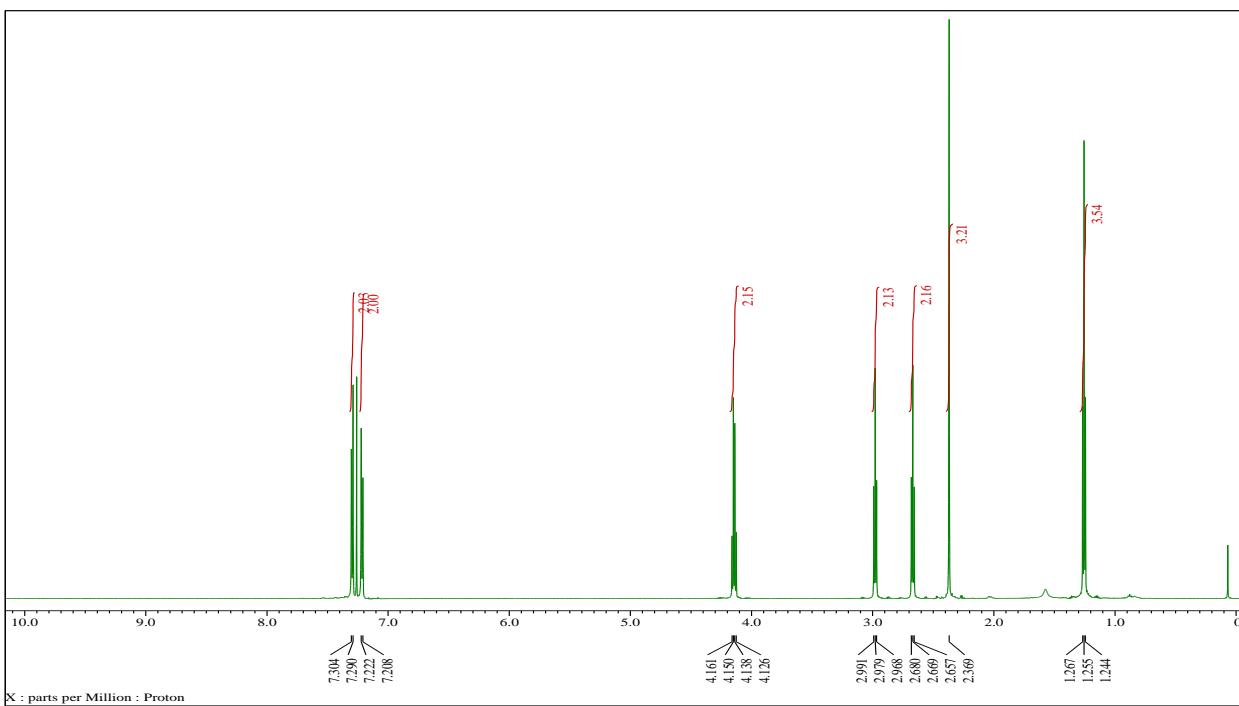


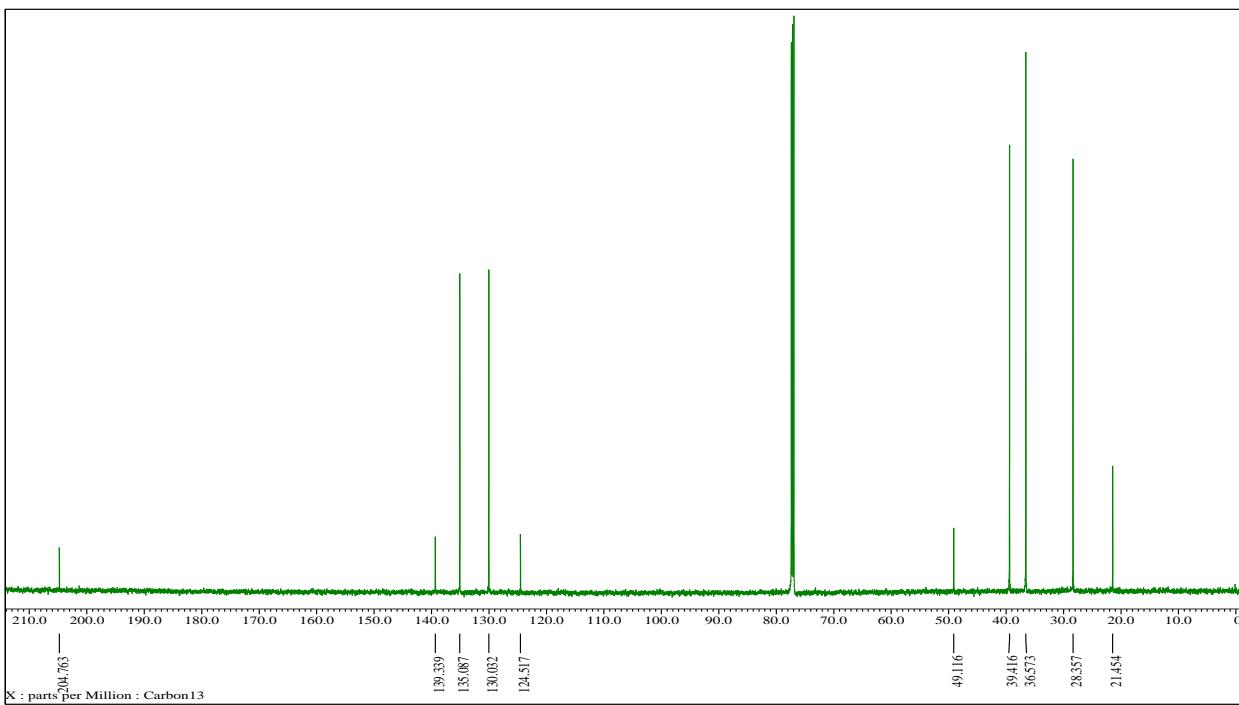
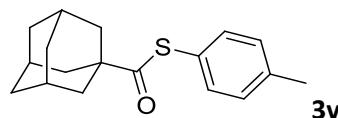
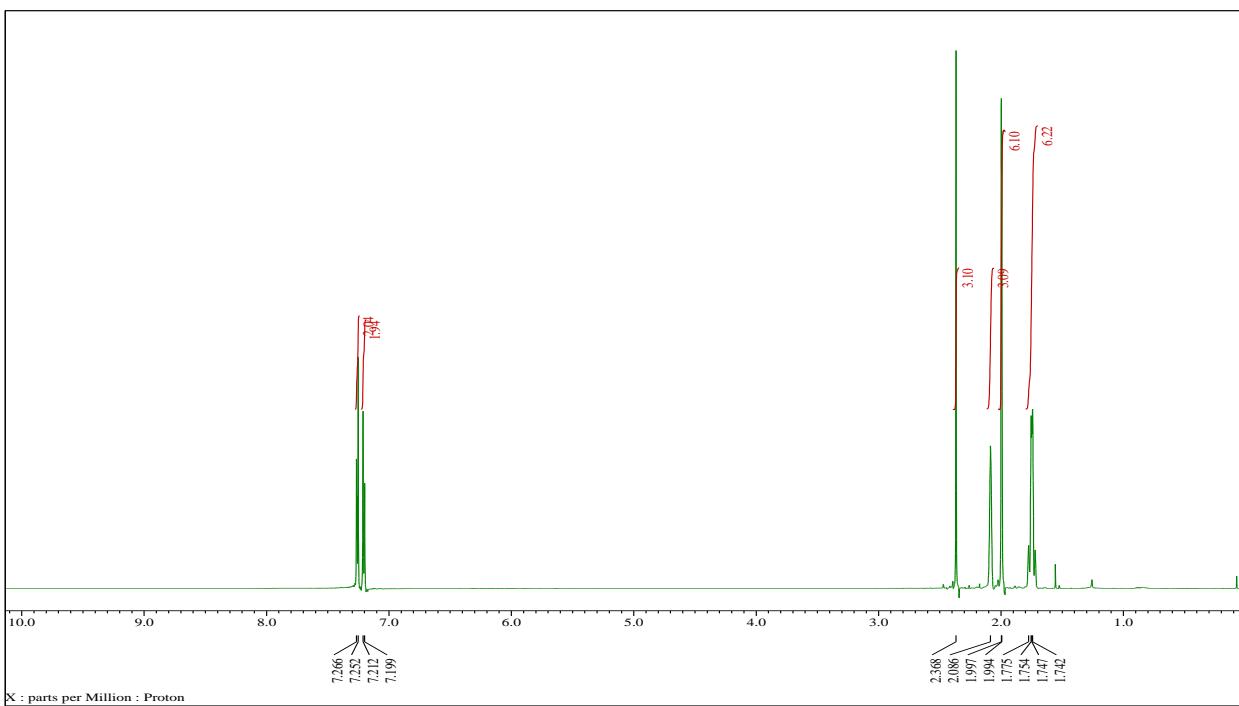


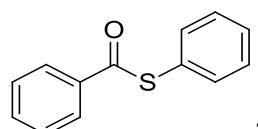
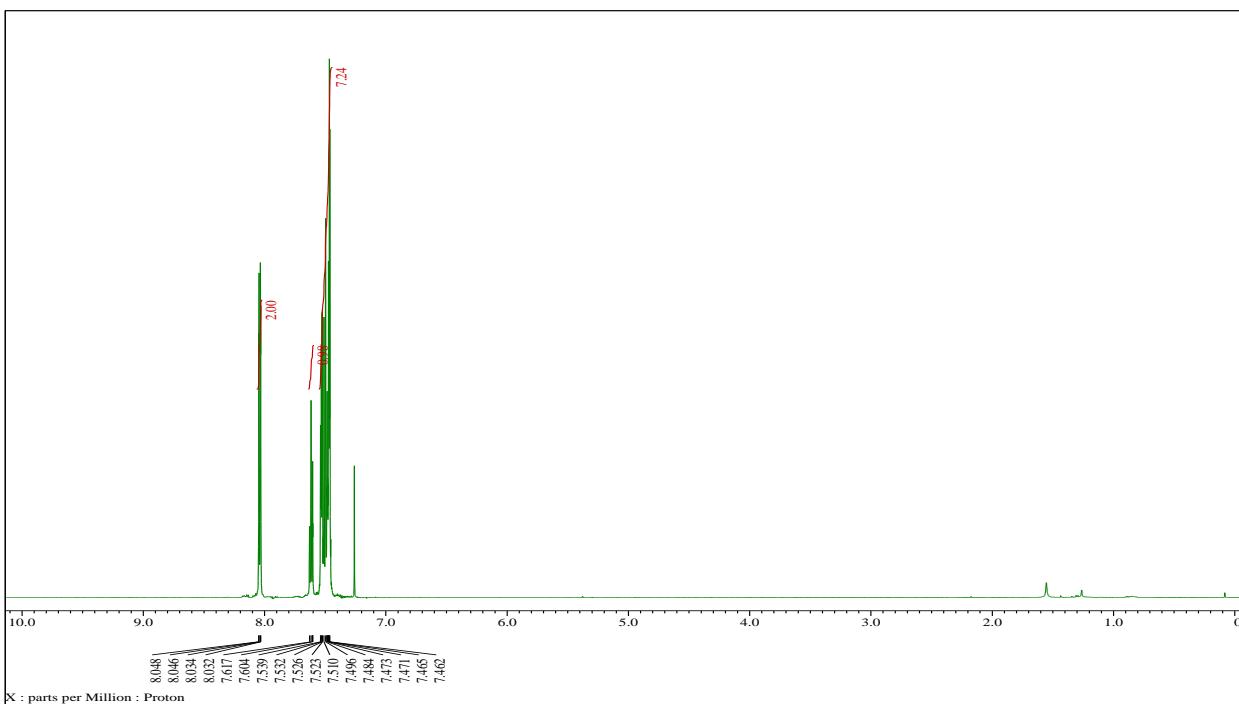


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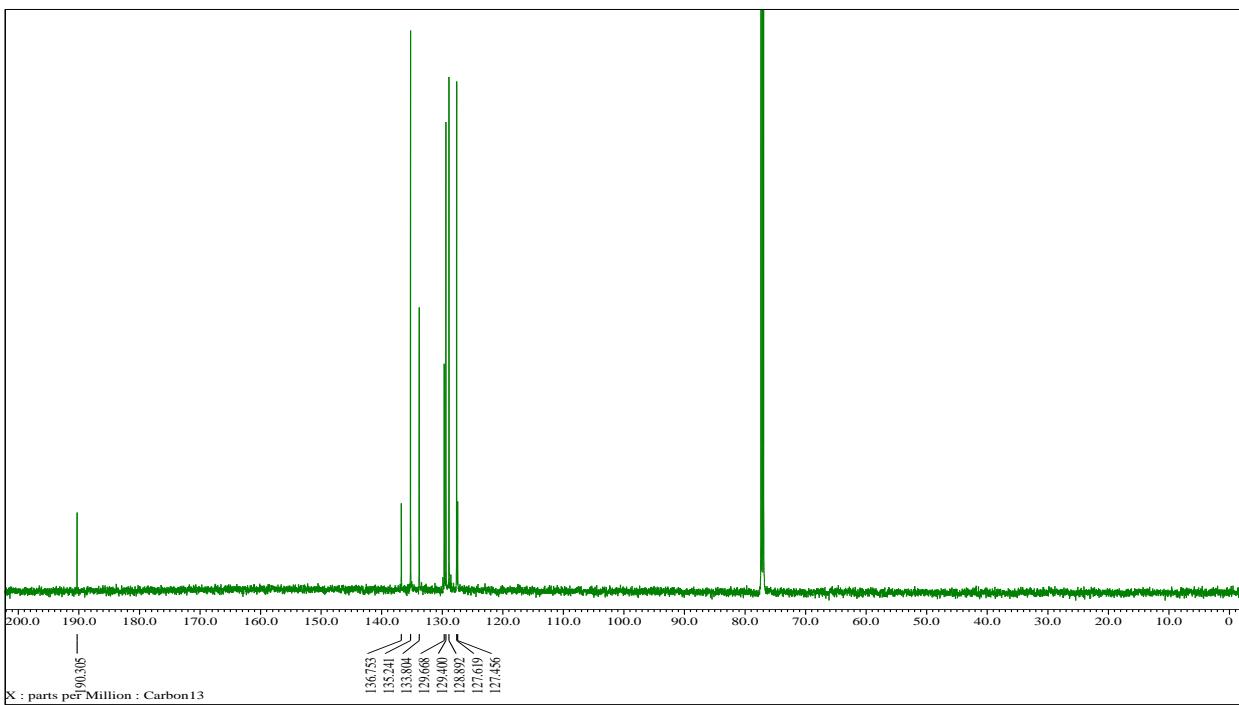


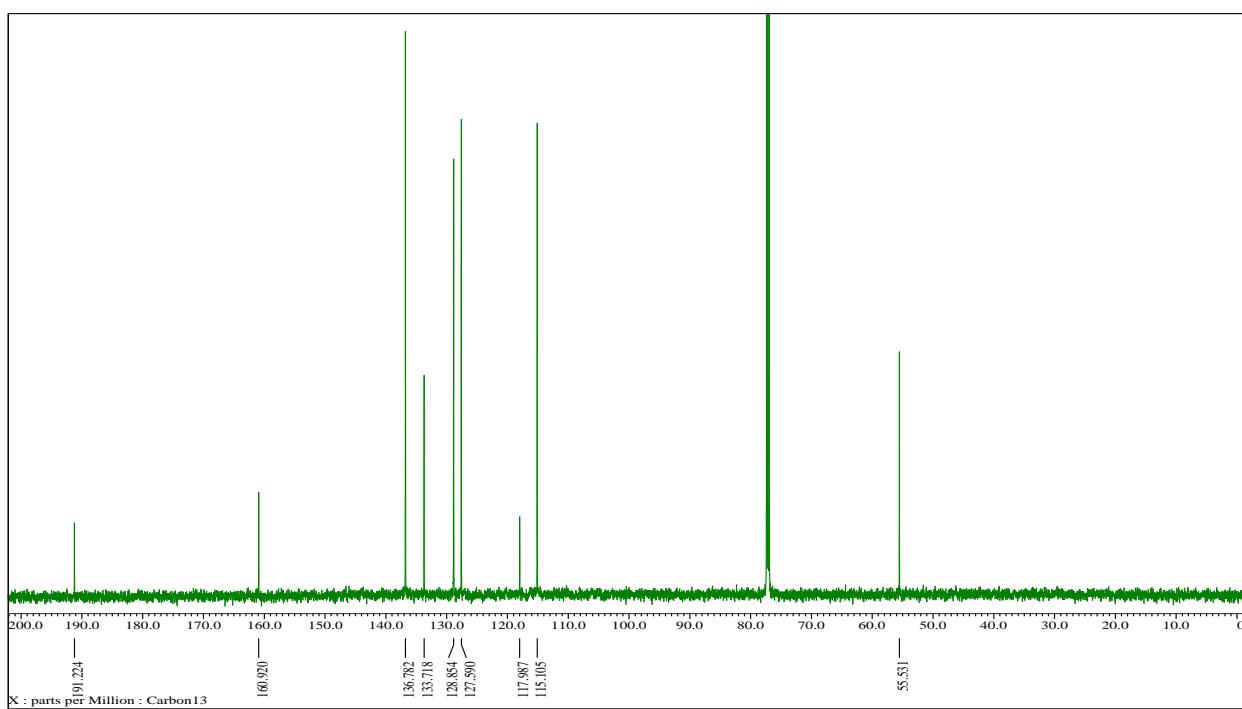
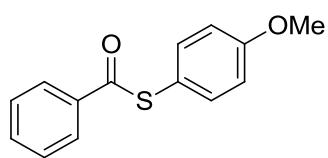
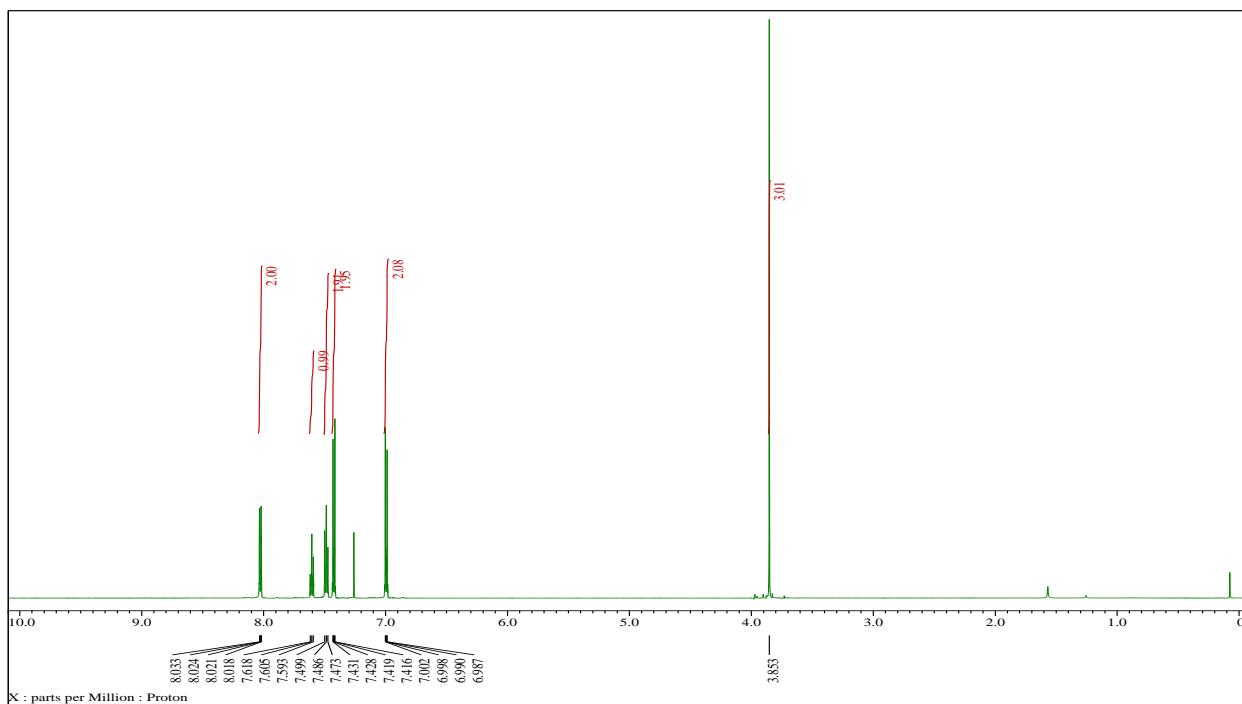


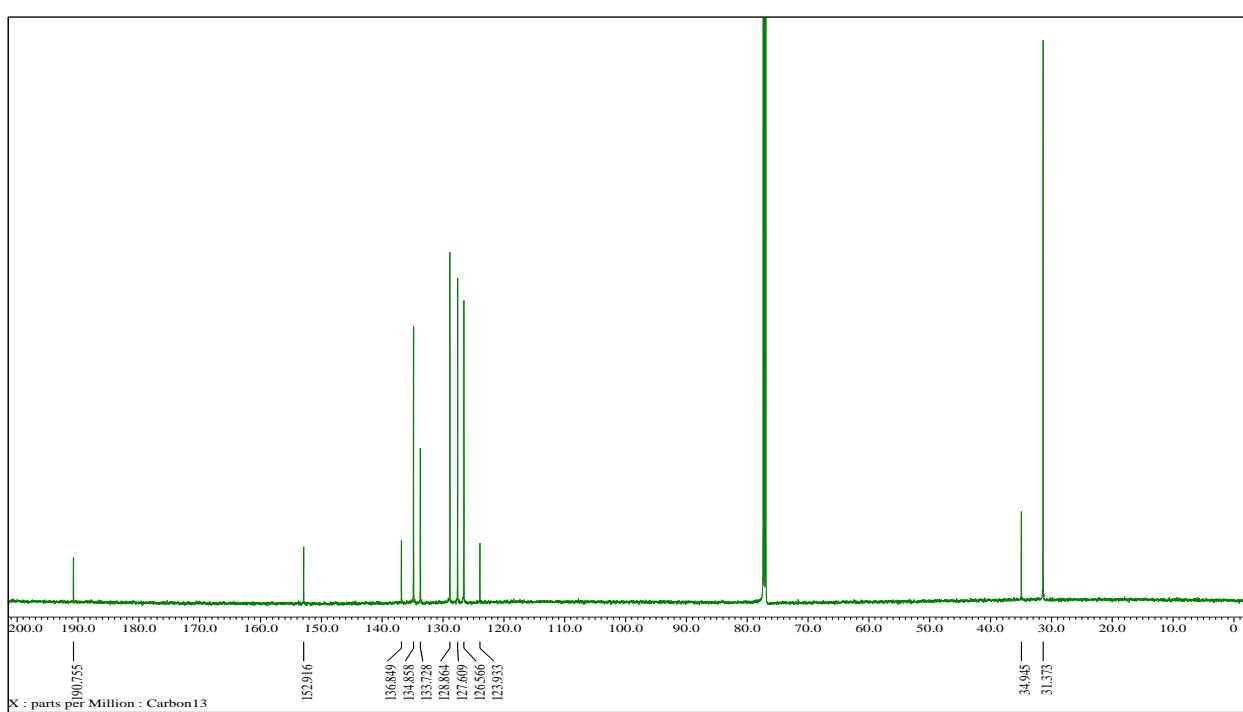
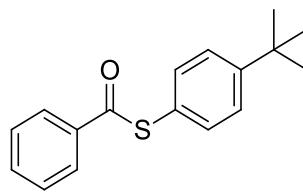
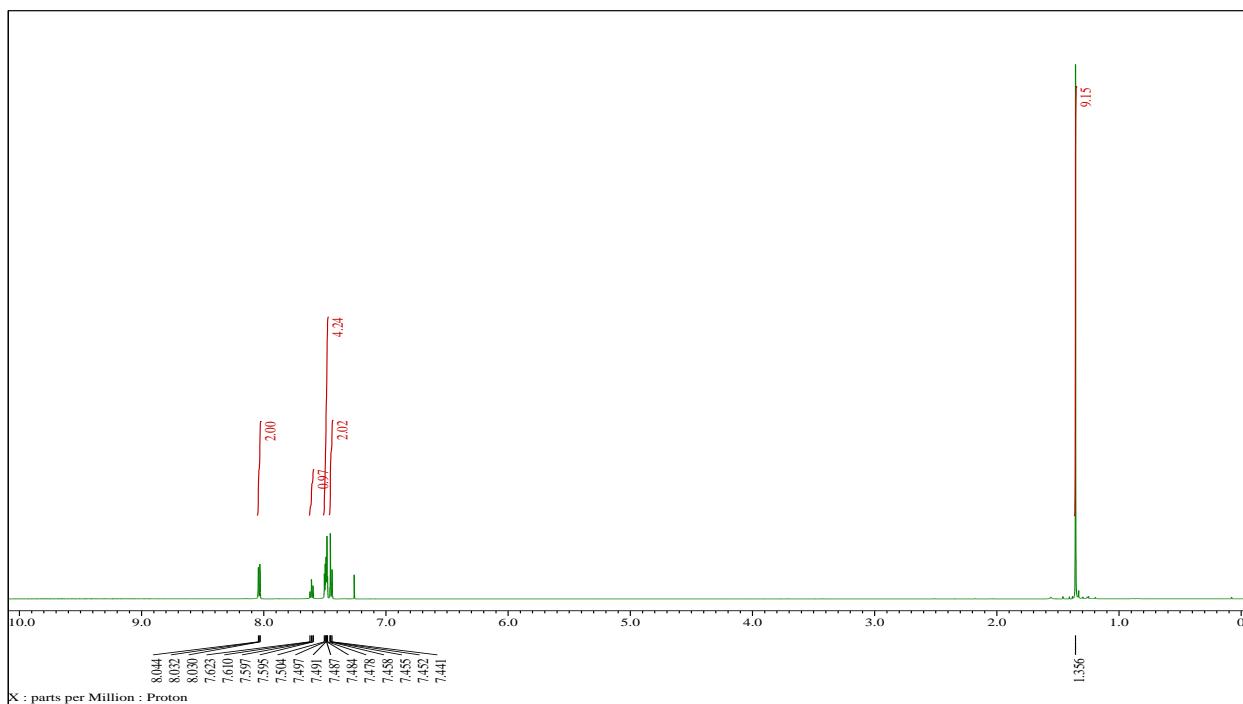


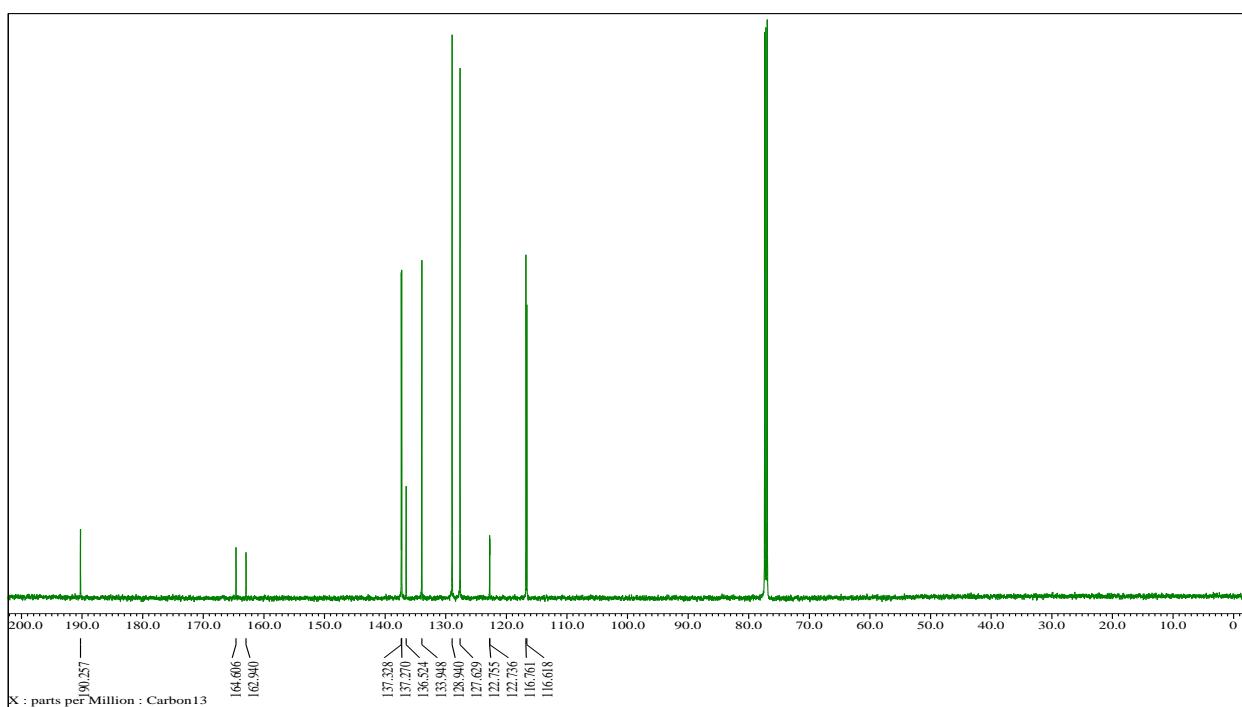
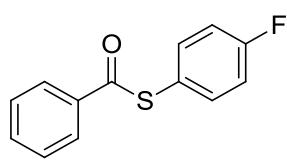
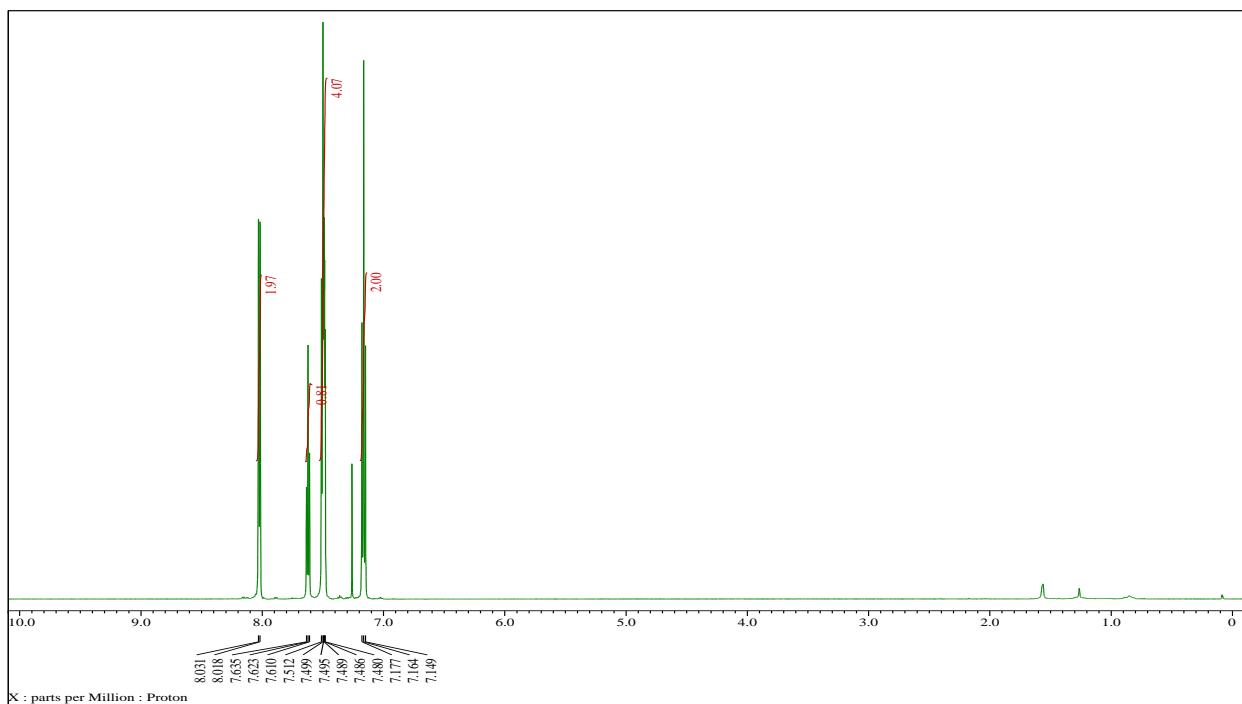


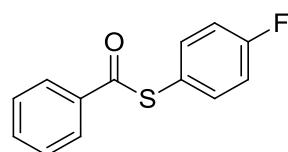
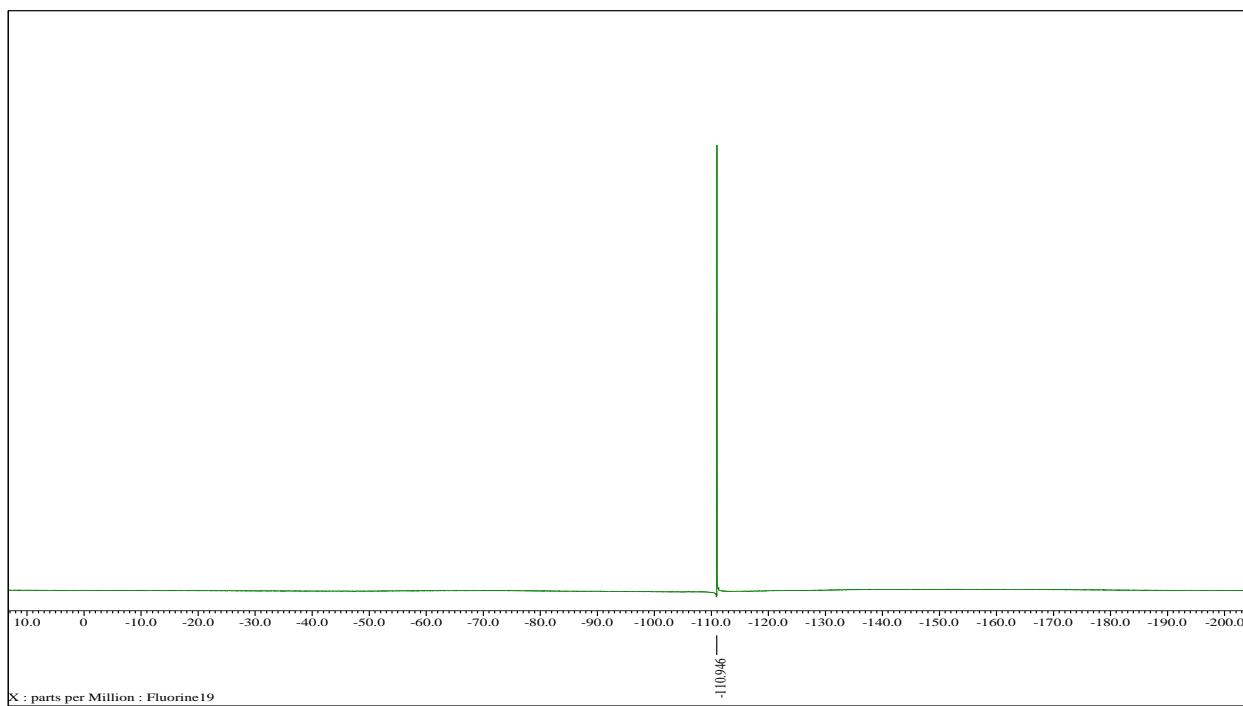
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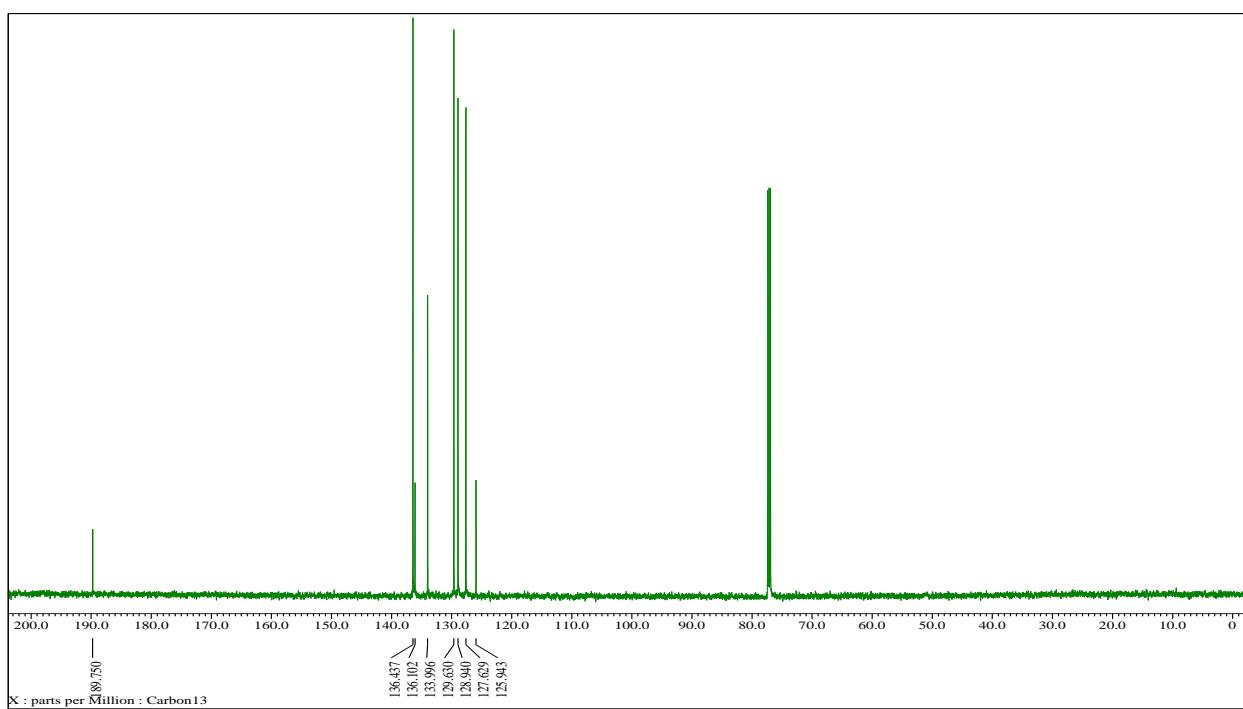
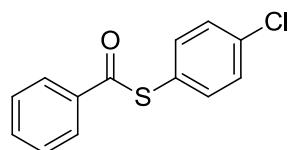
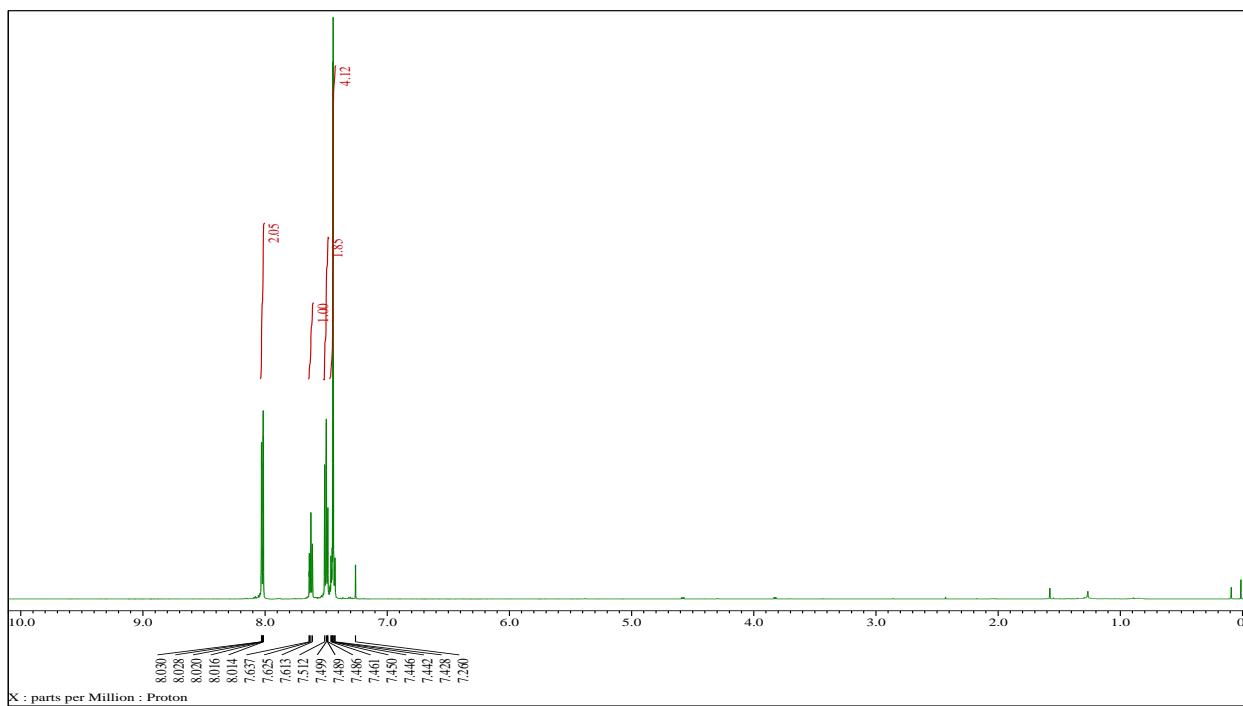


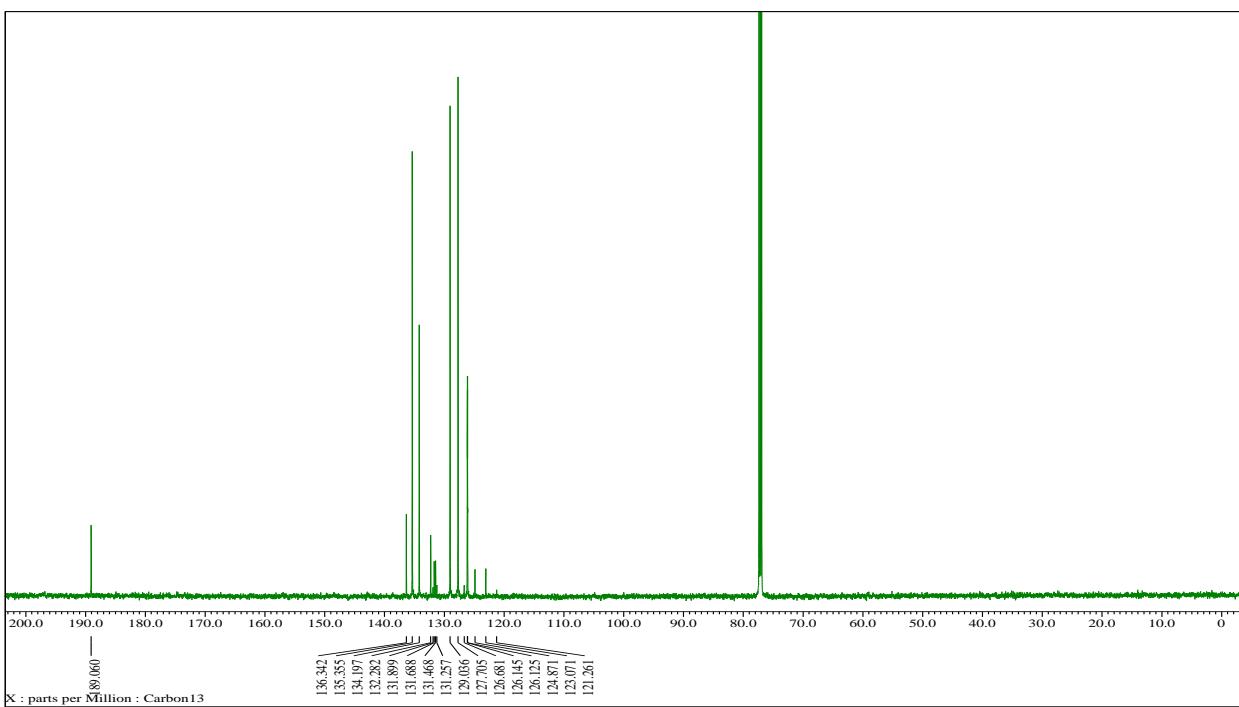
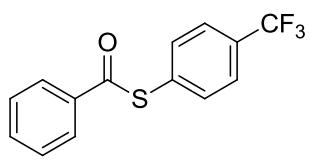
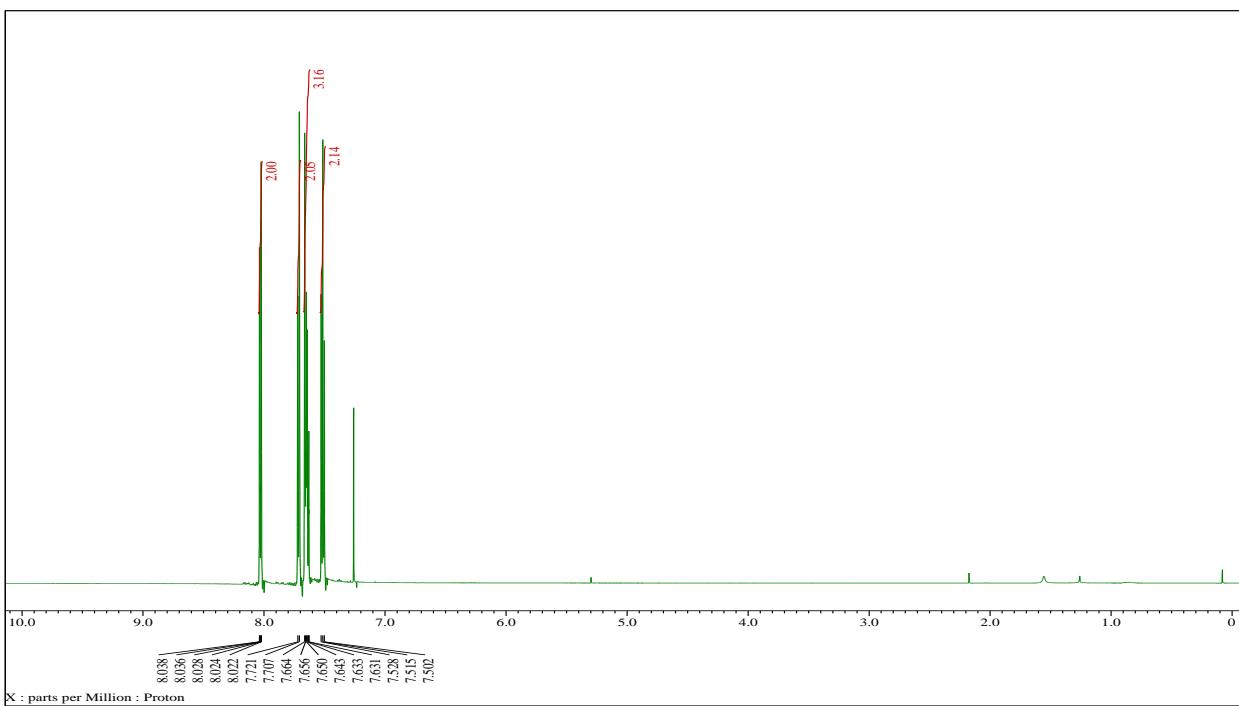


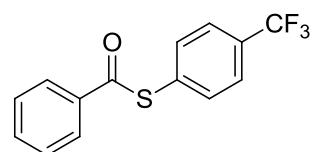
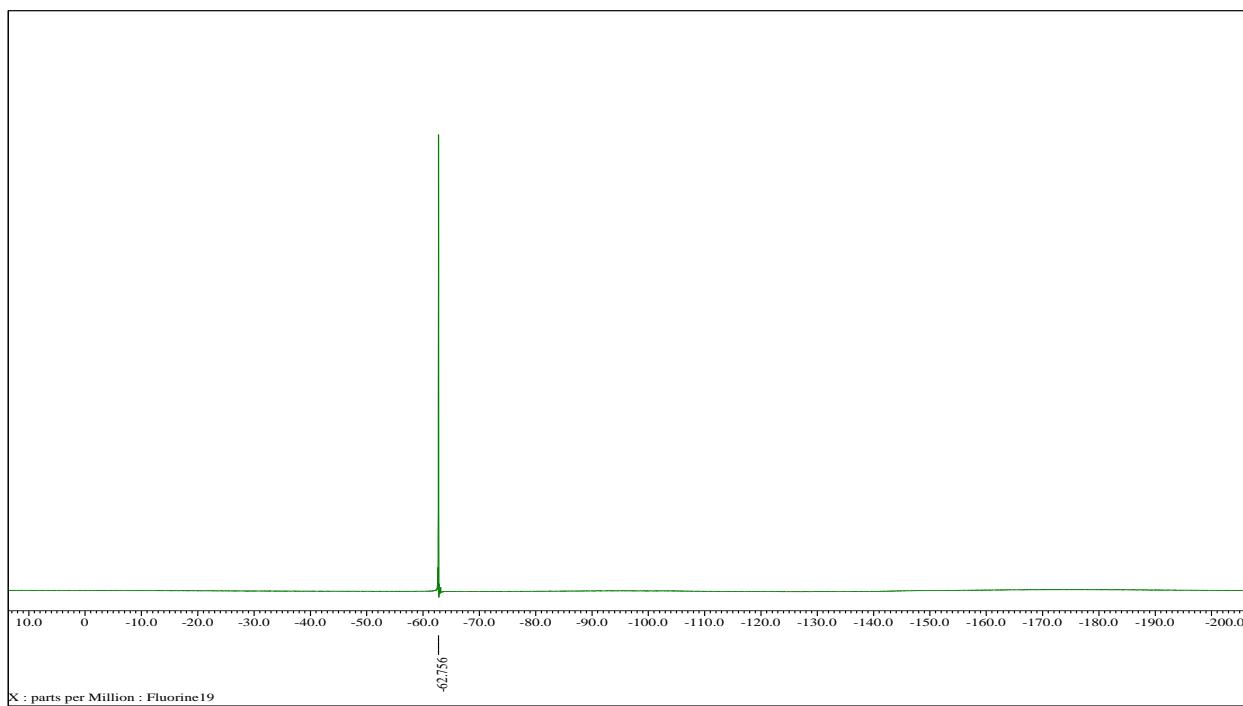




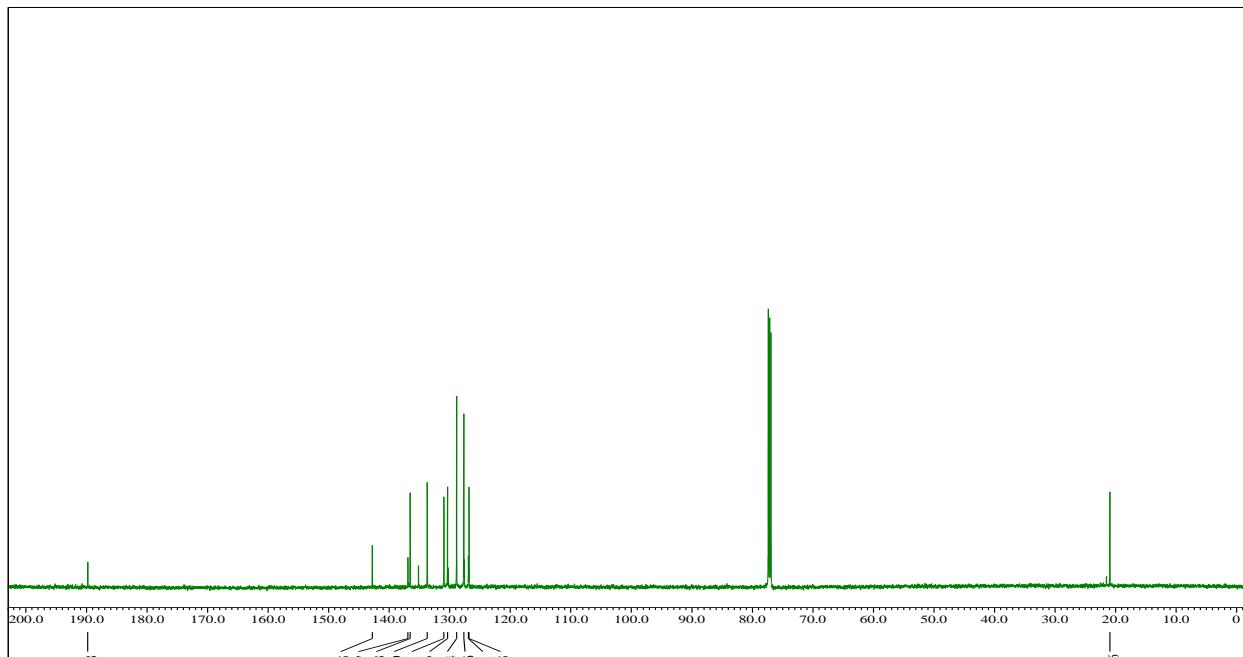
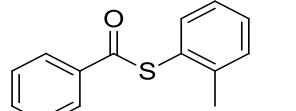
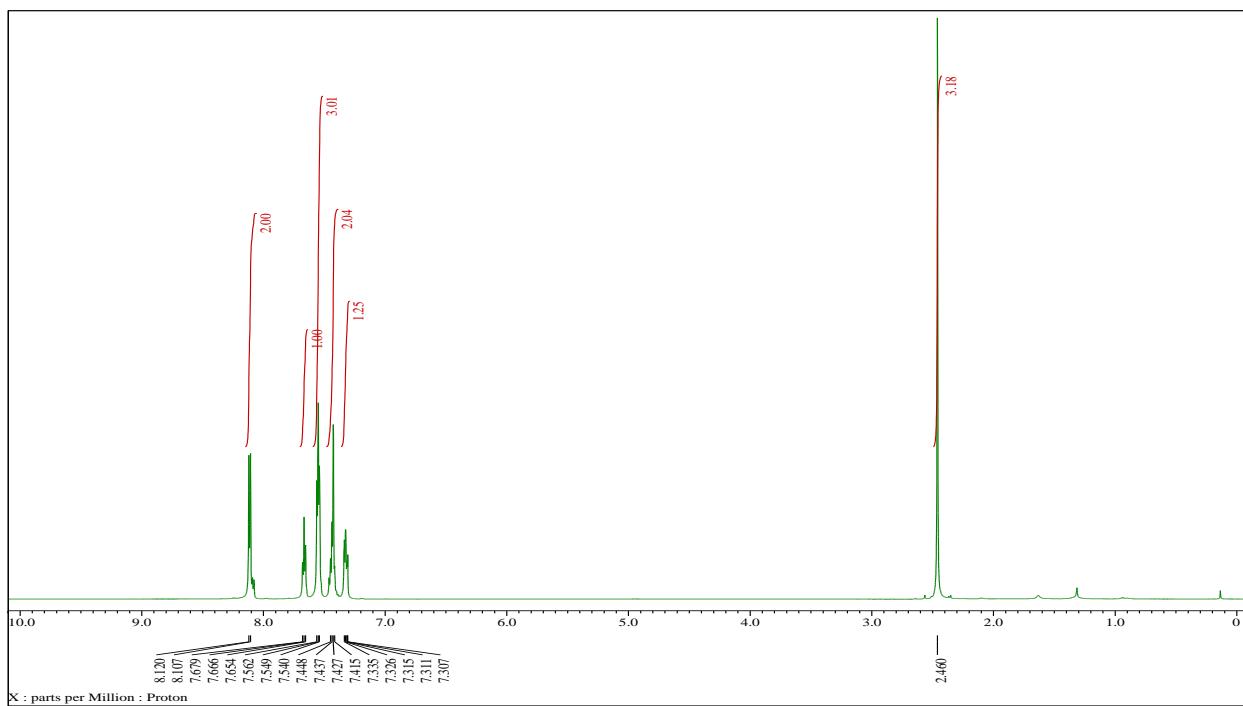
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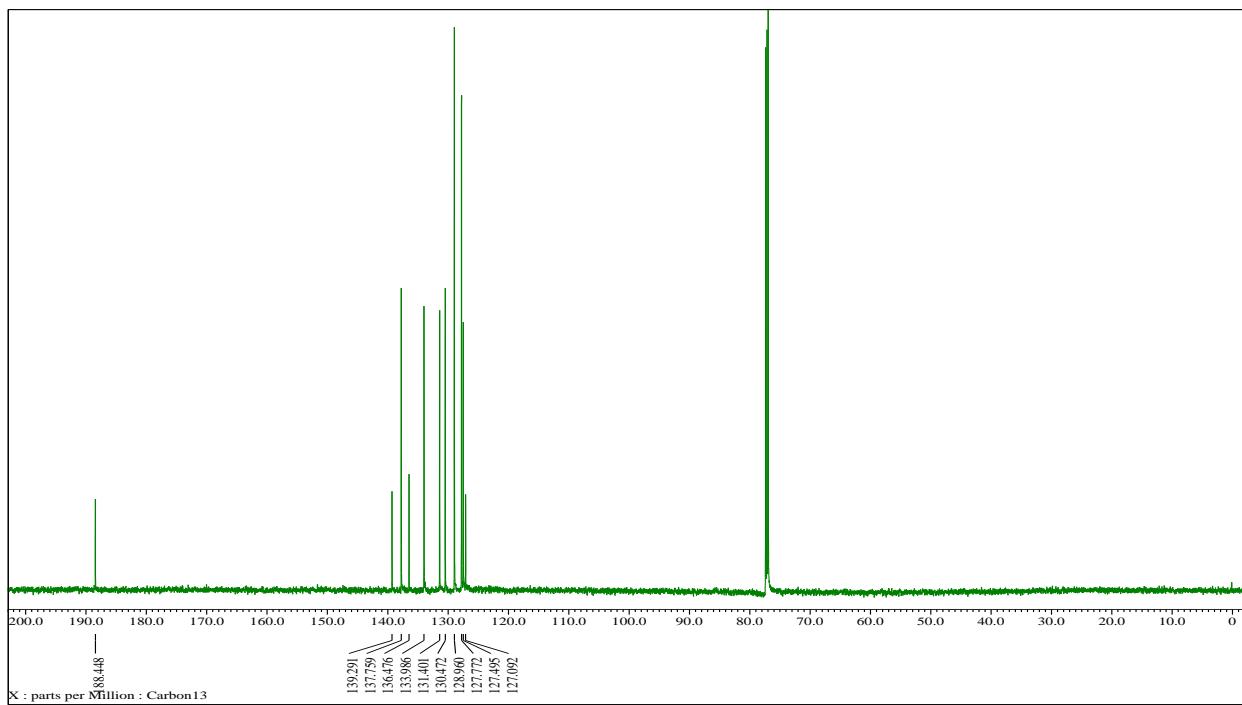
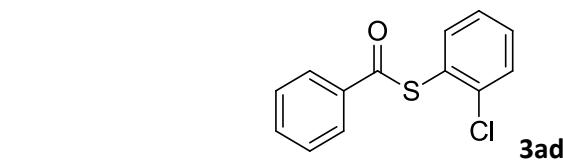
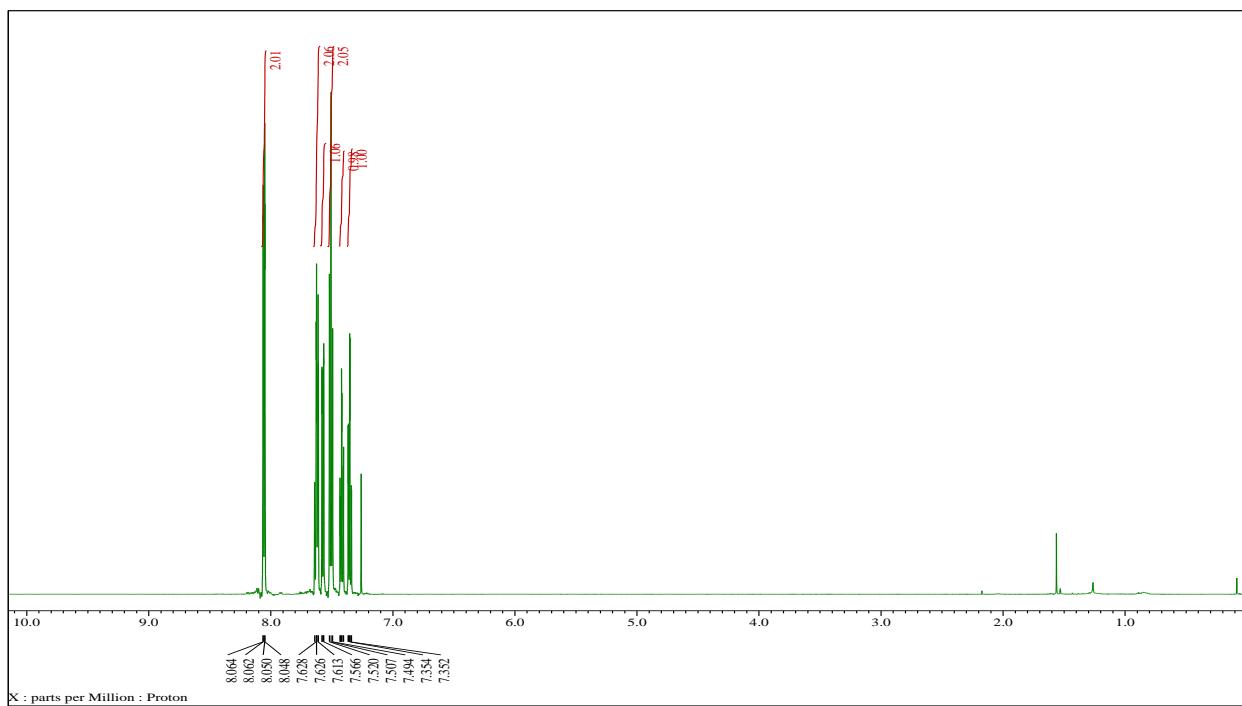


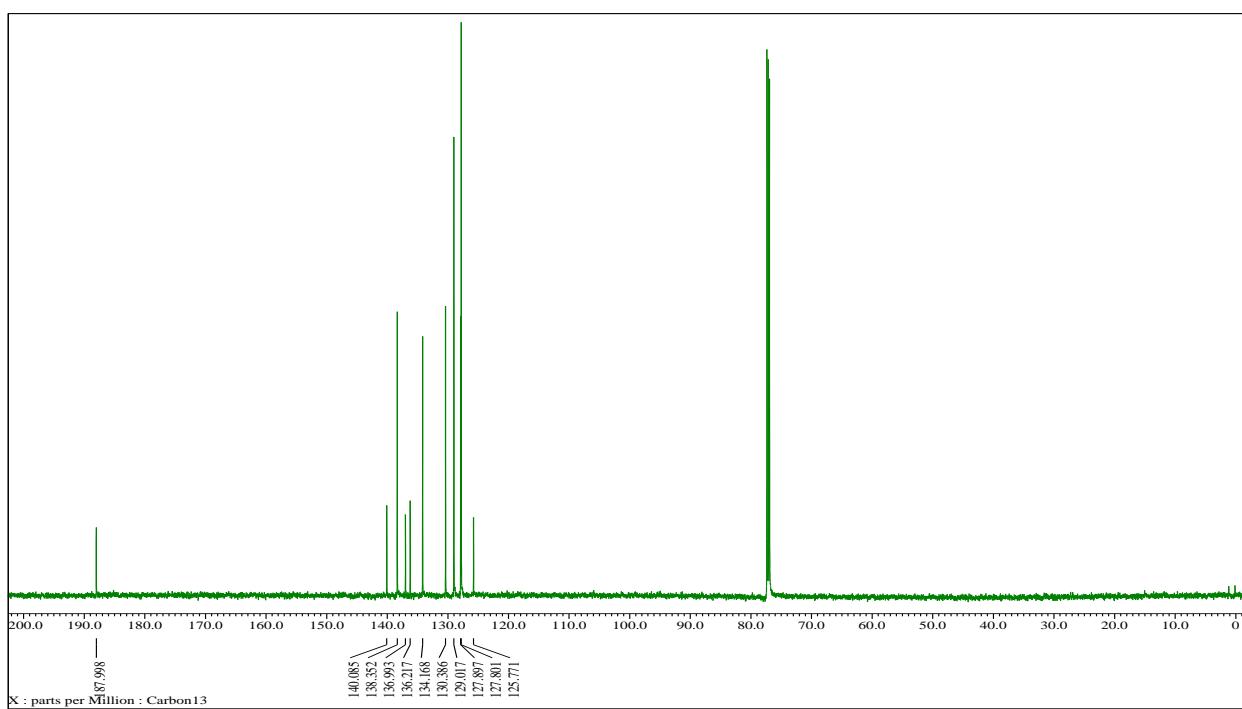
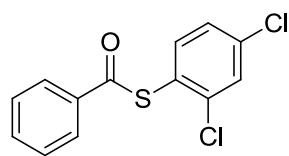
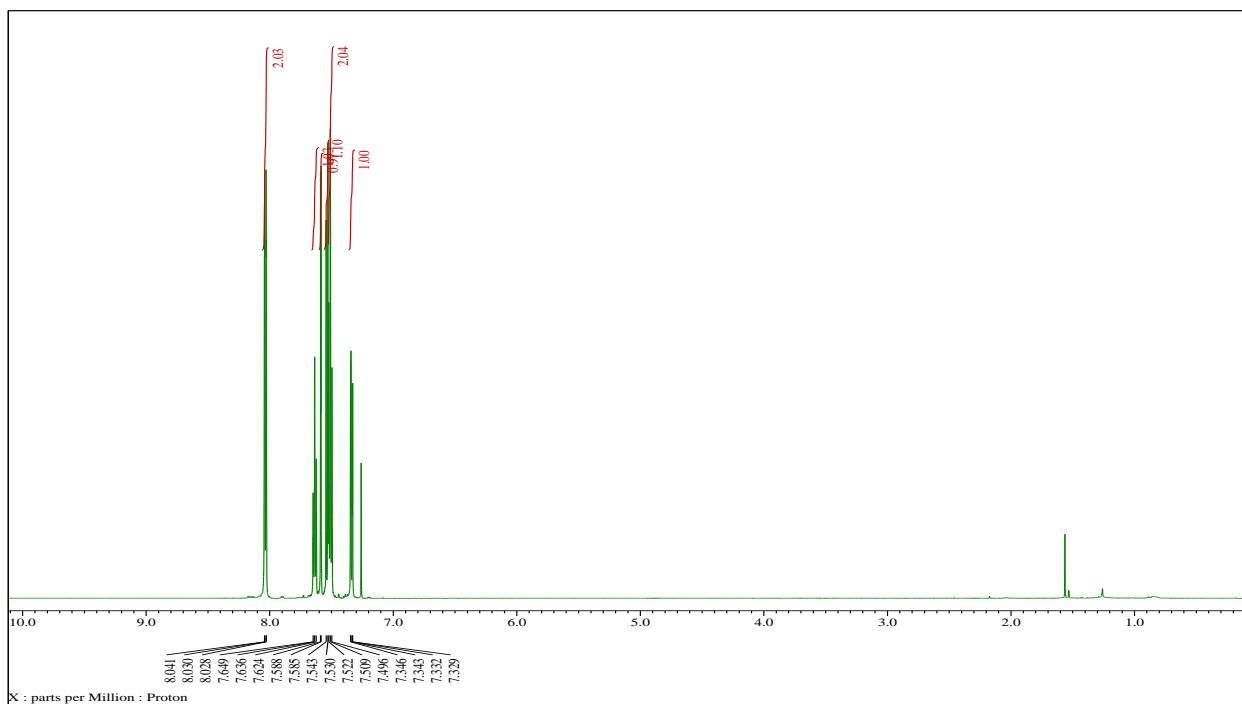


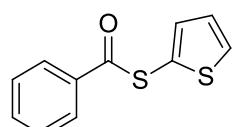
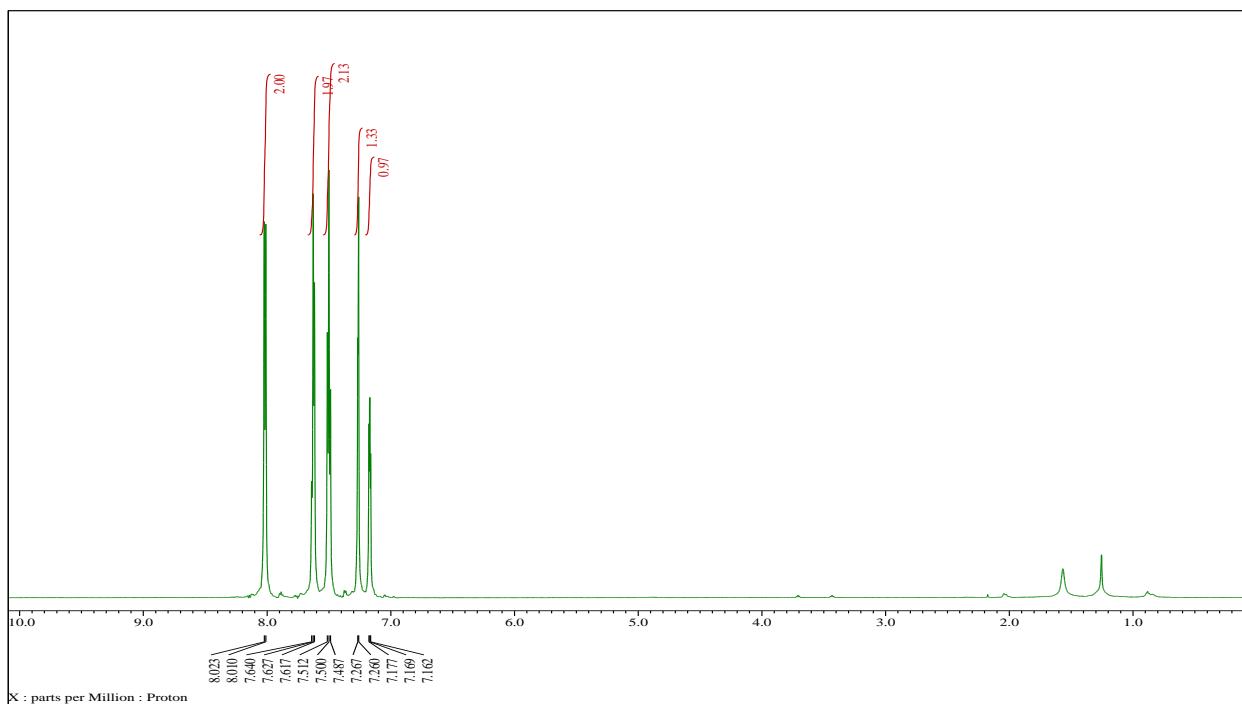


¹⁹F NMR of 3ab

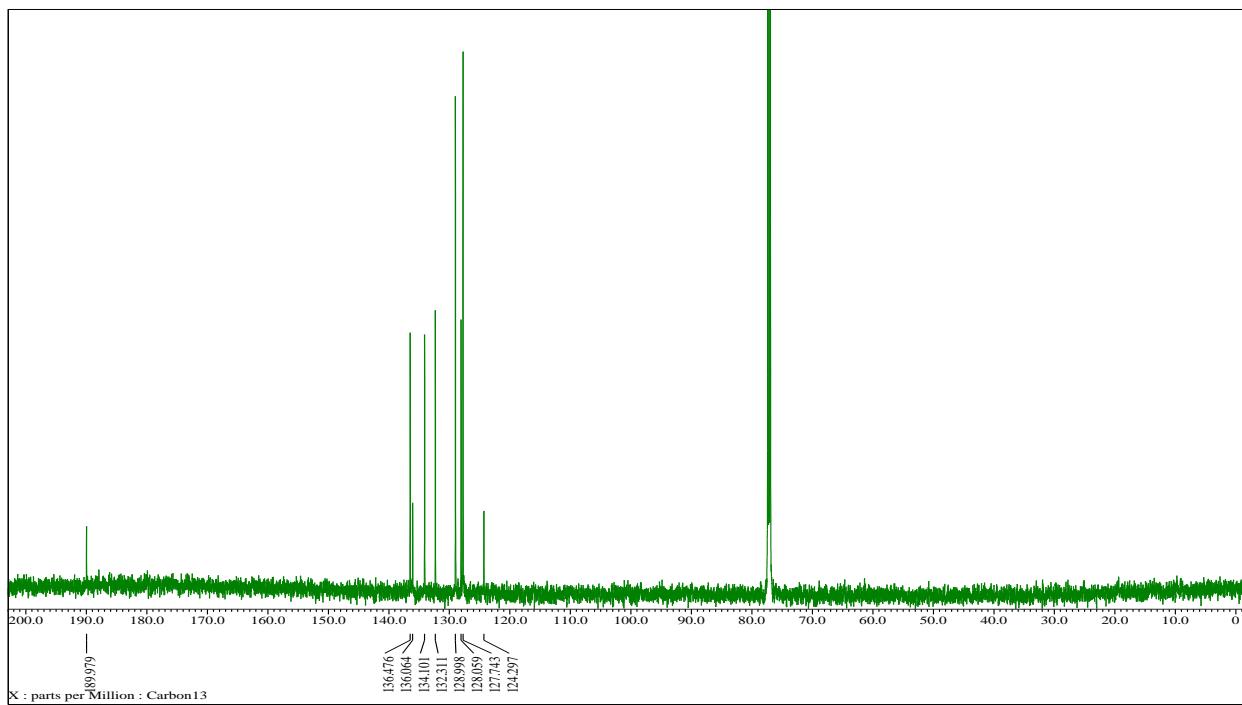


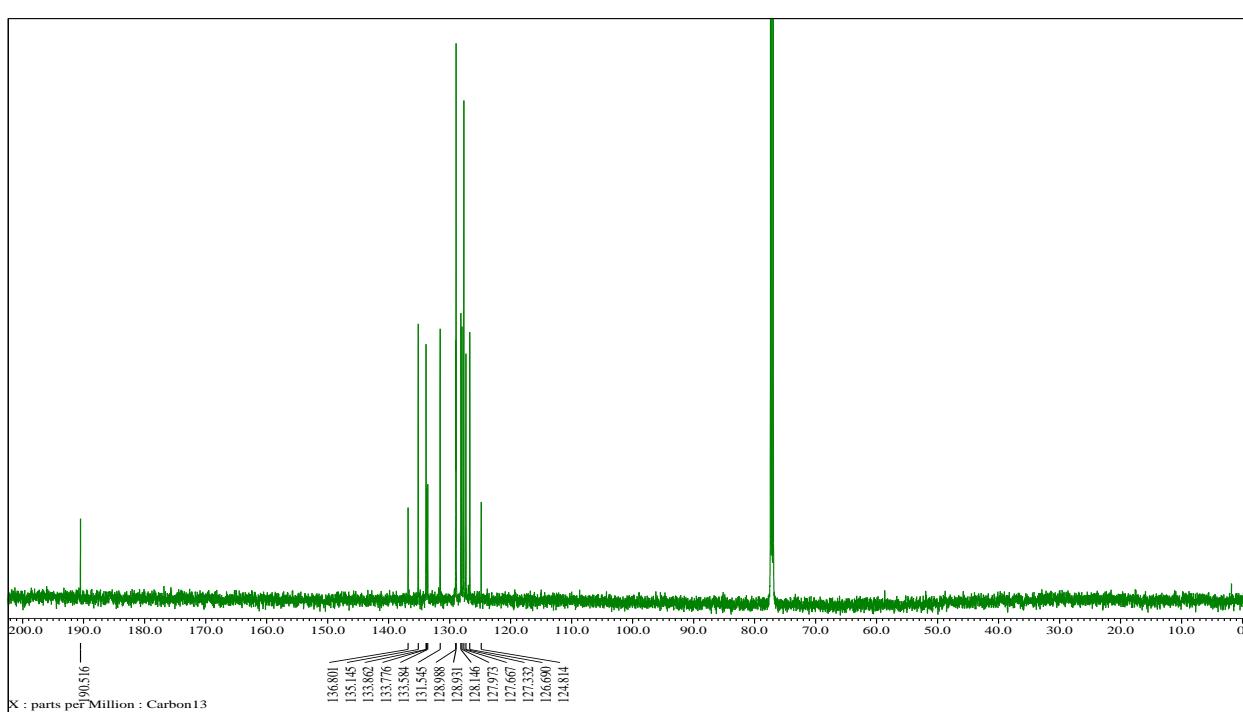
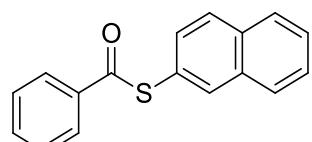
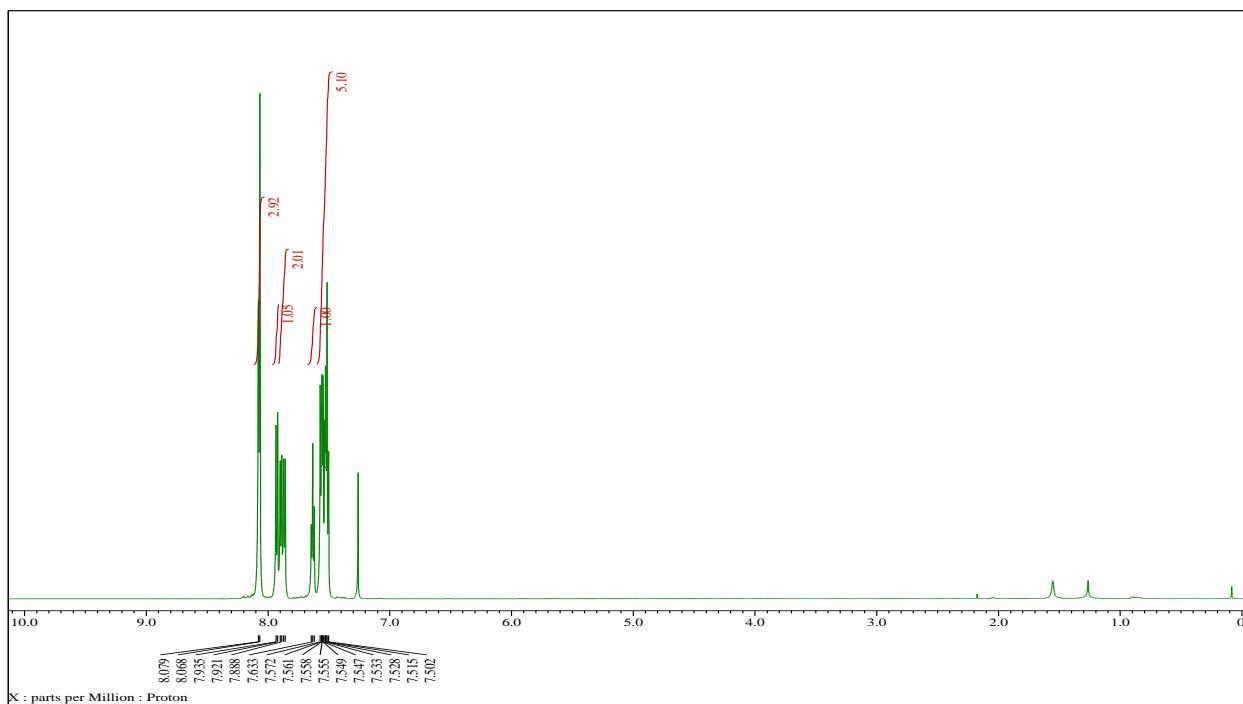


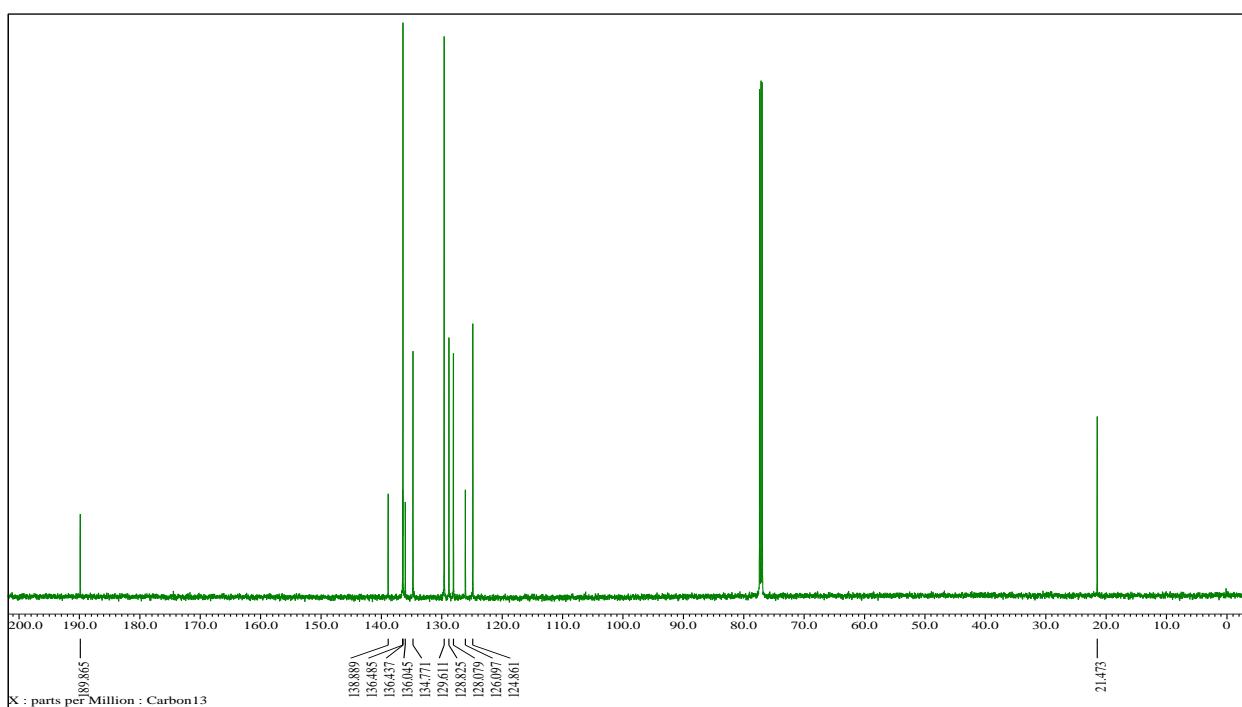
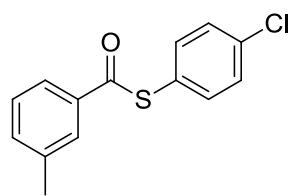
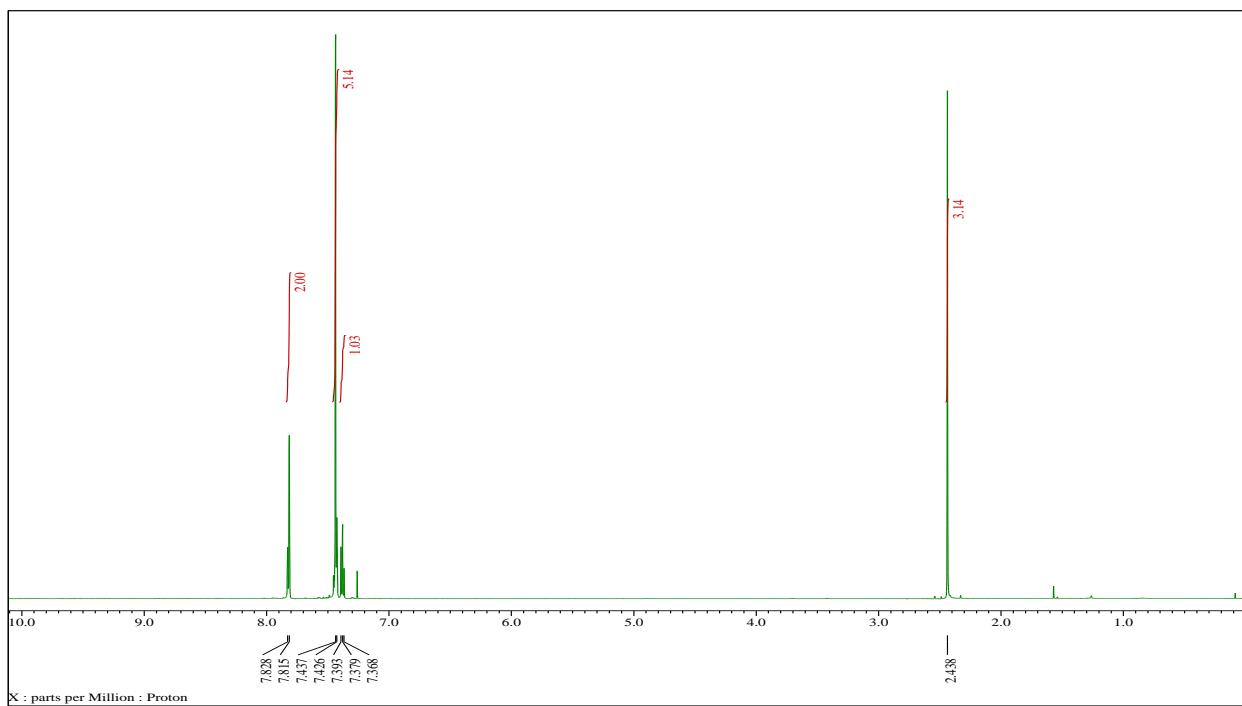


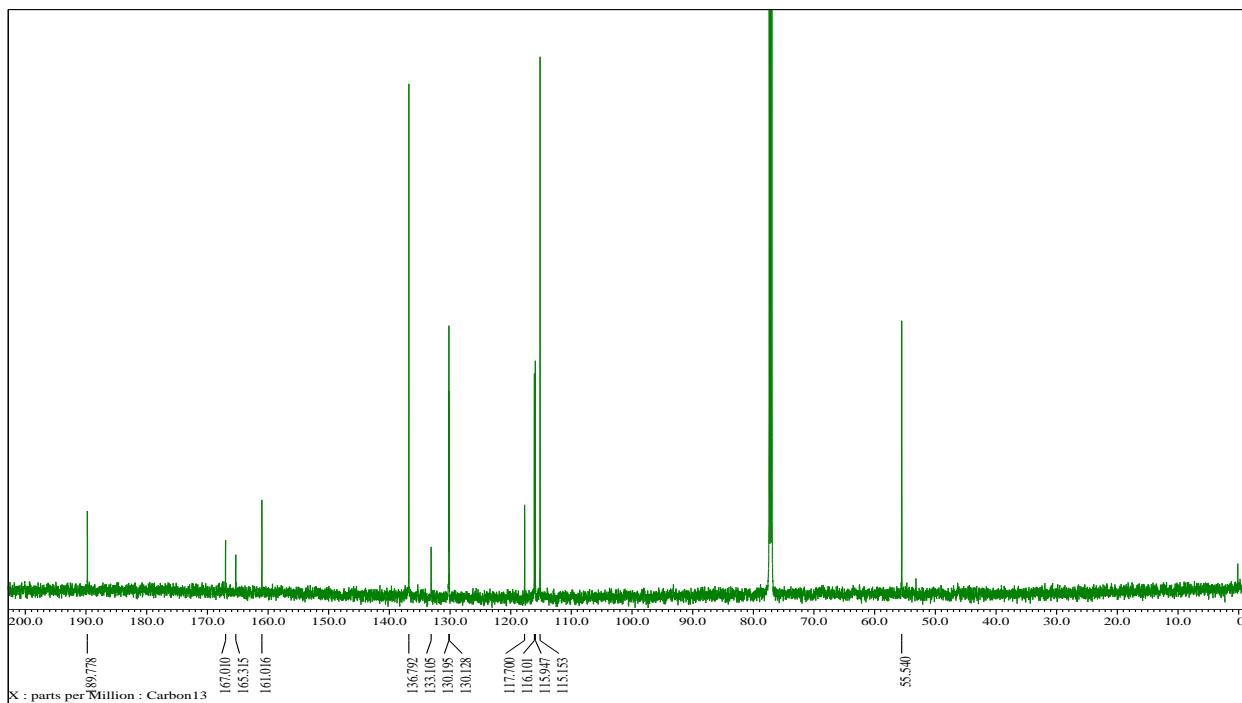
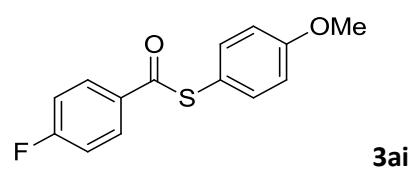
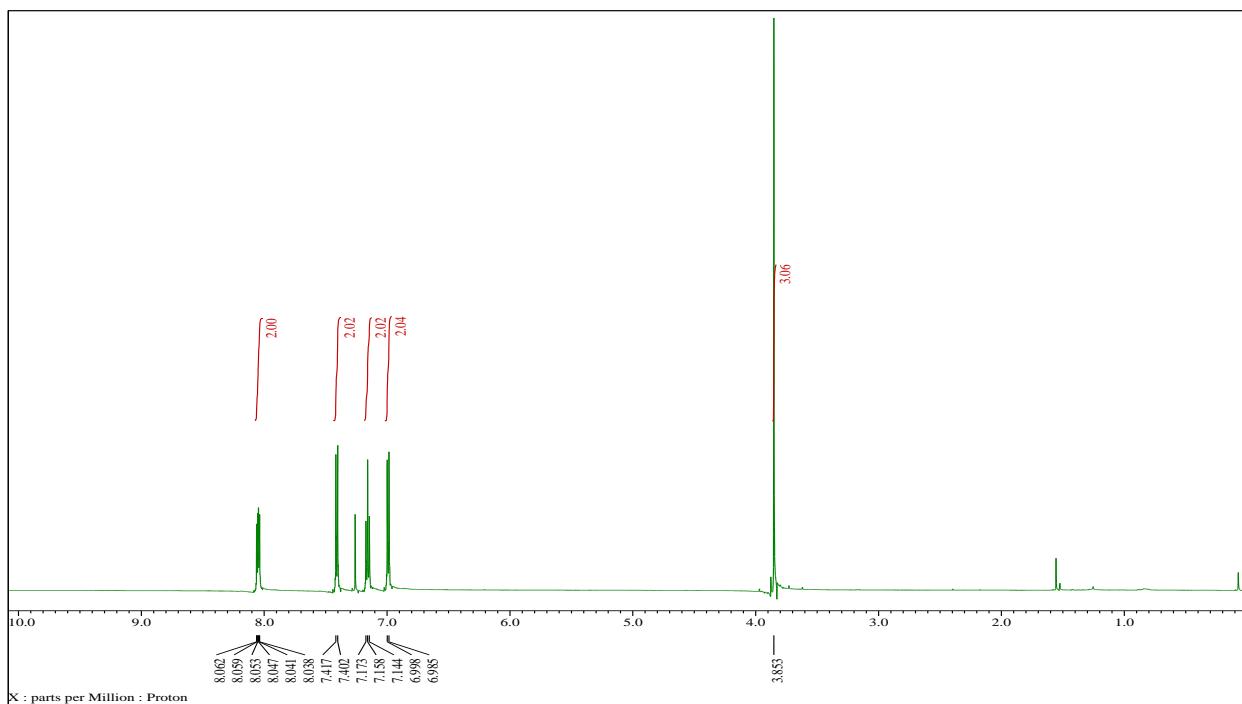


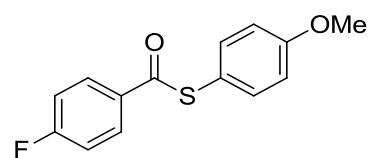
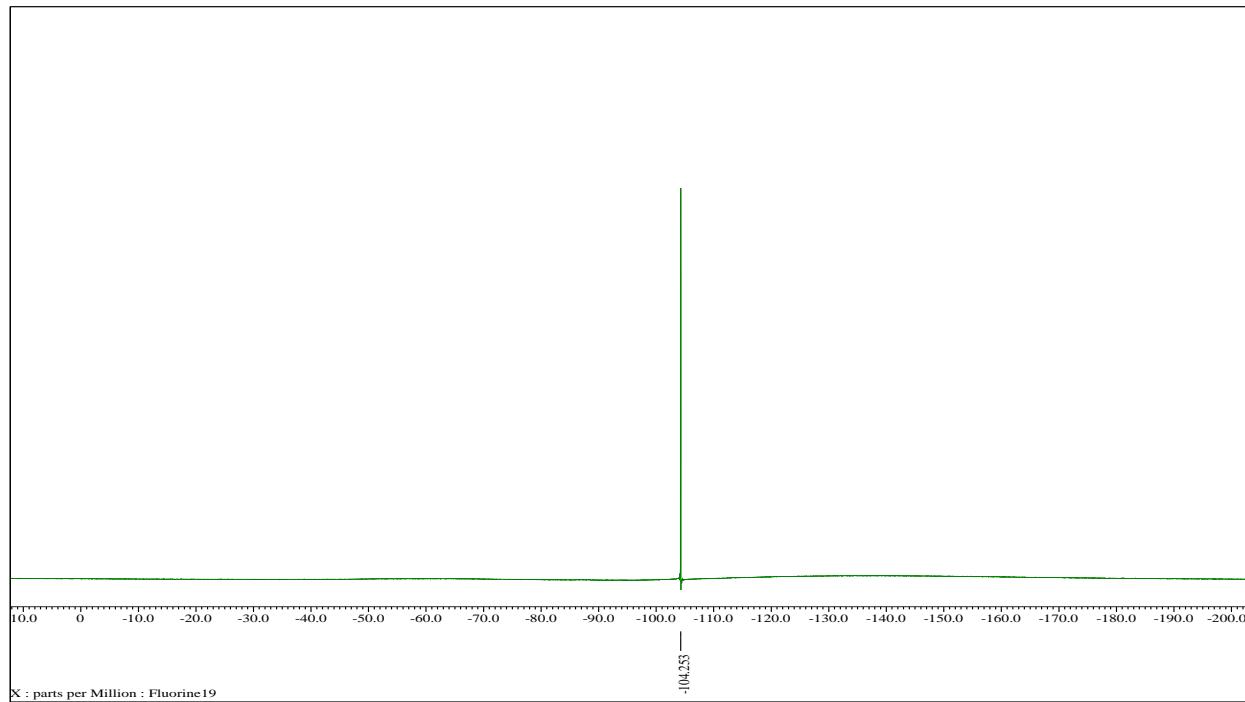
3af



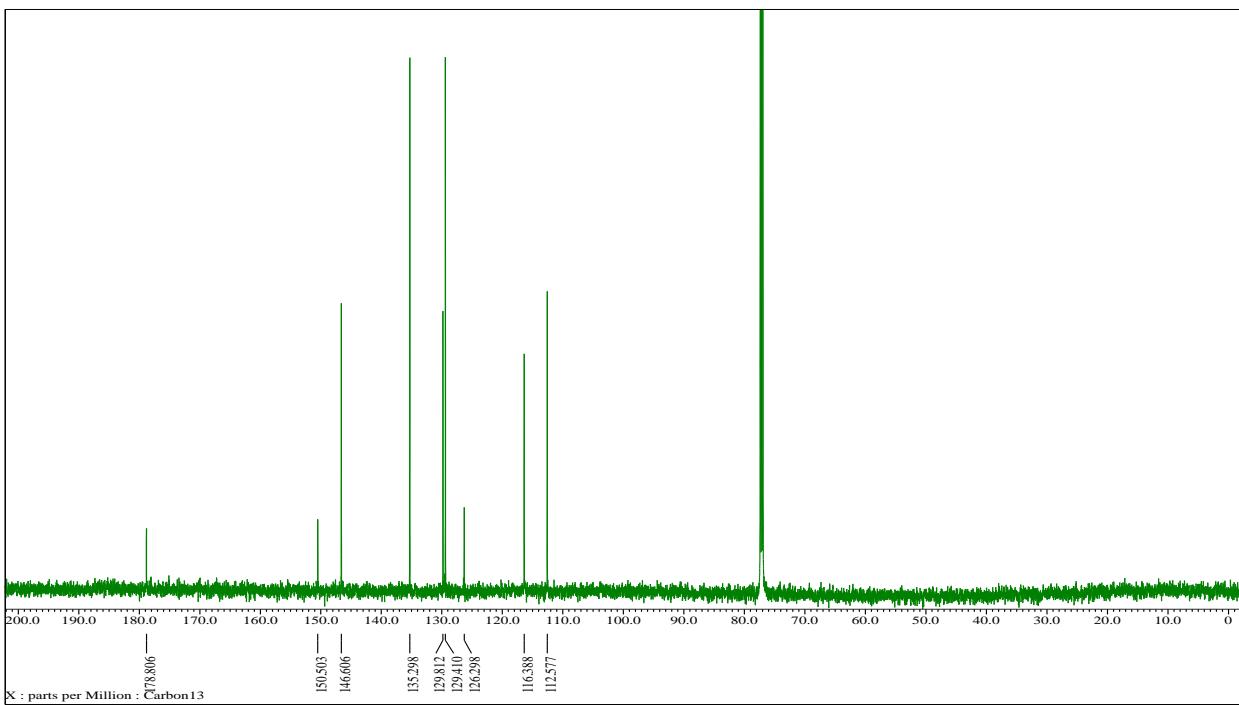
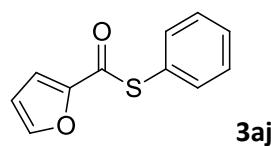
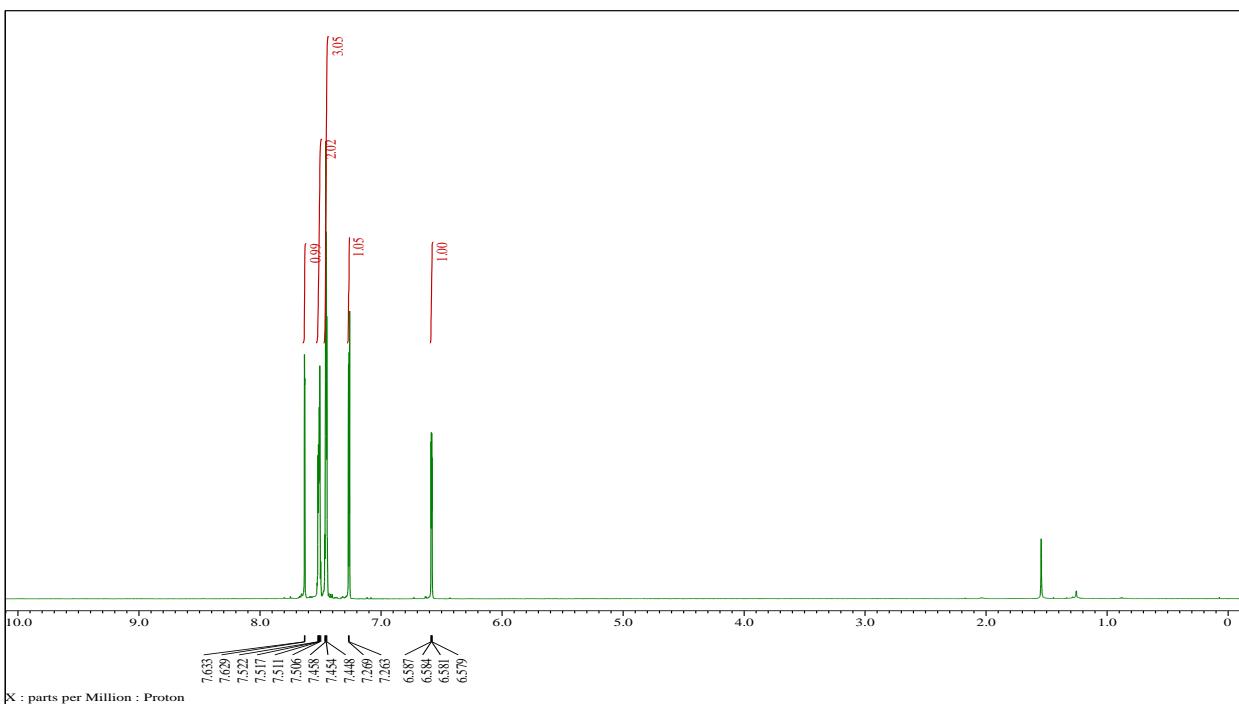


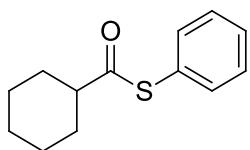
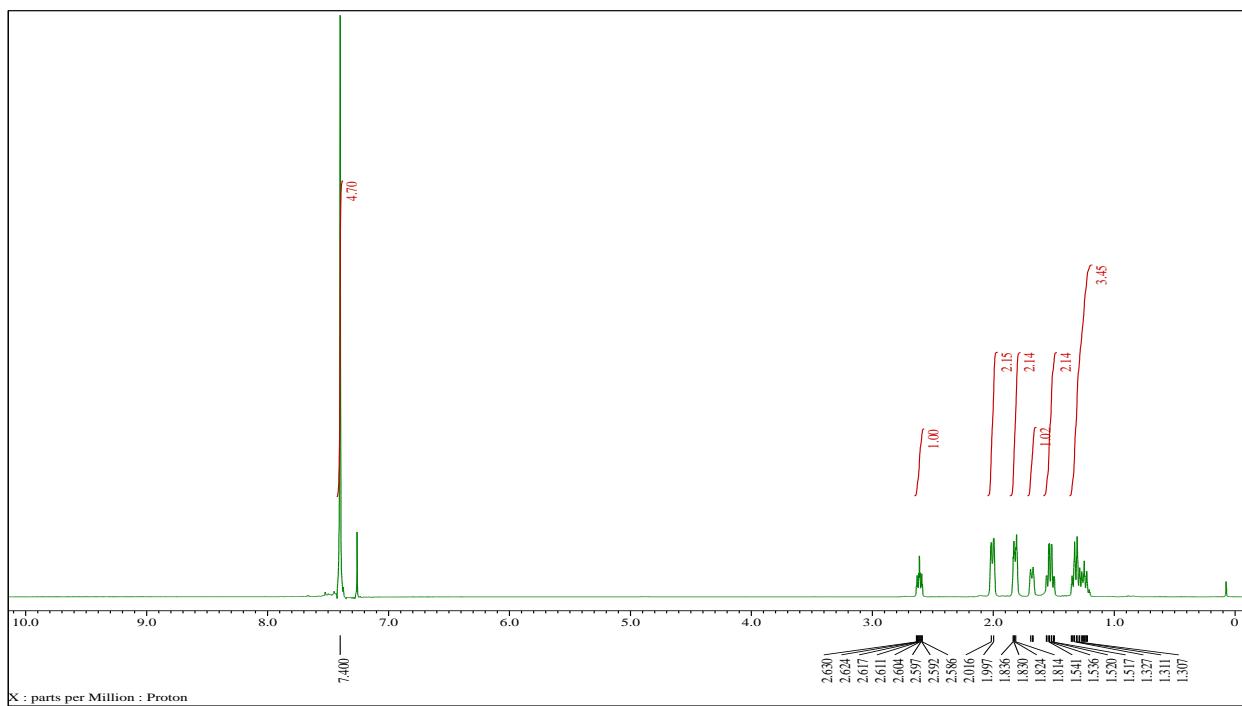




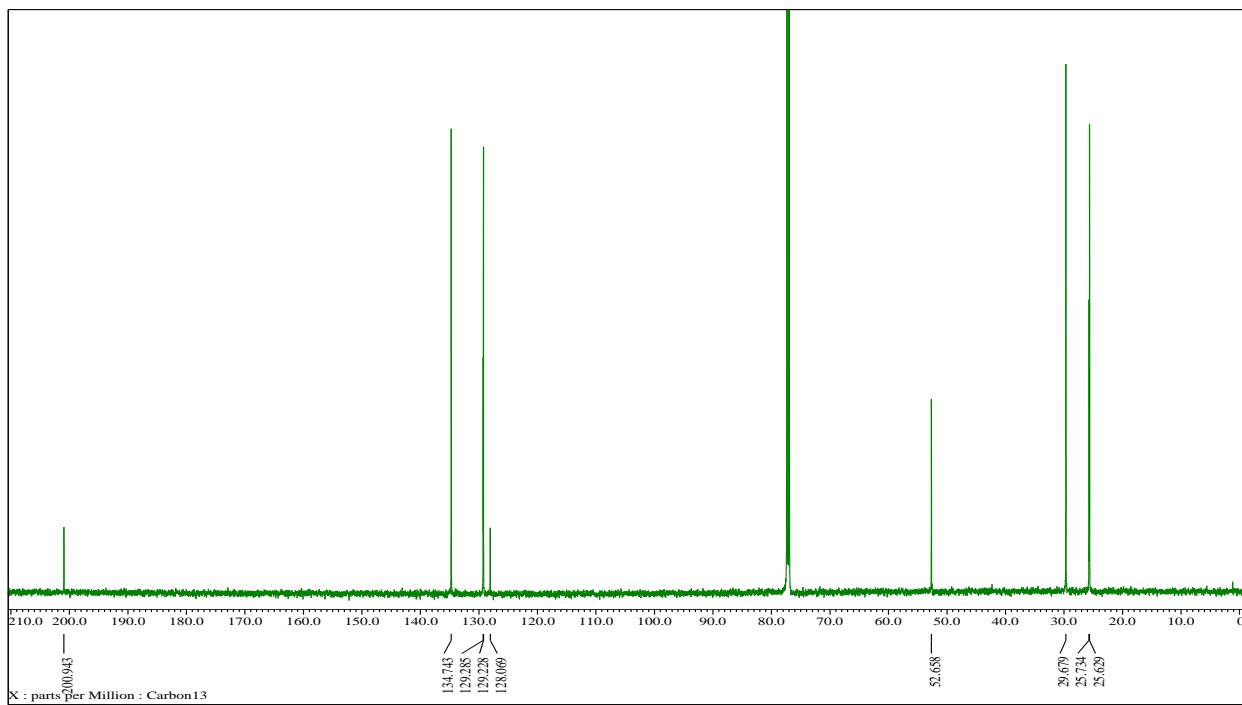


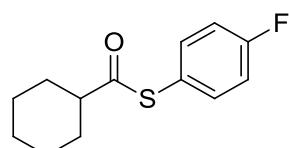
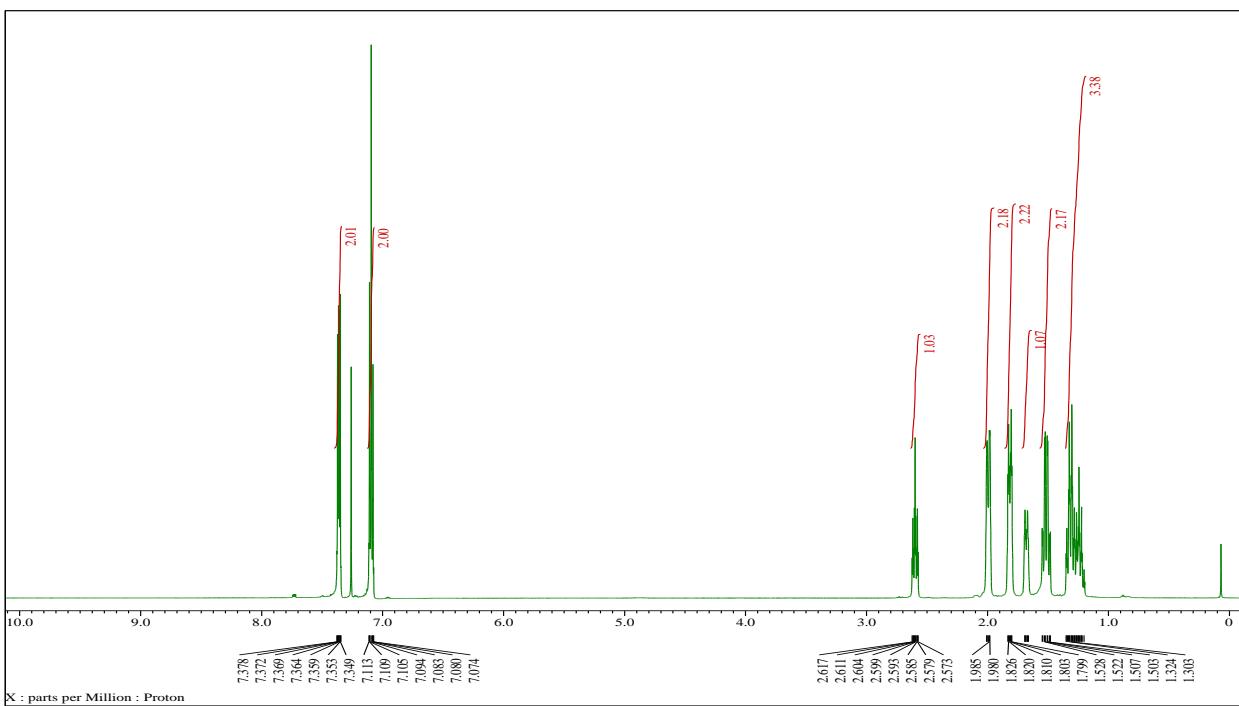
¹⁹F NMR of 3ai



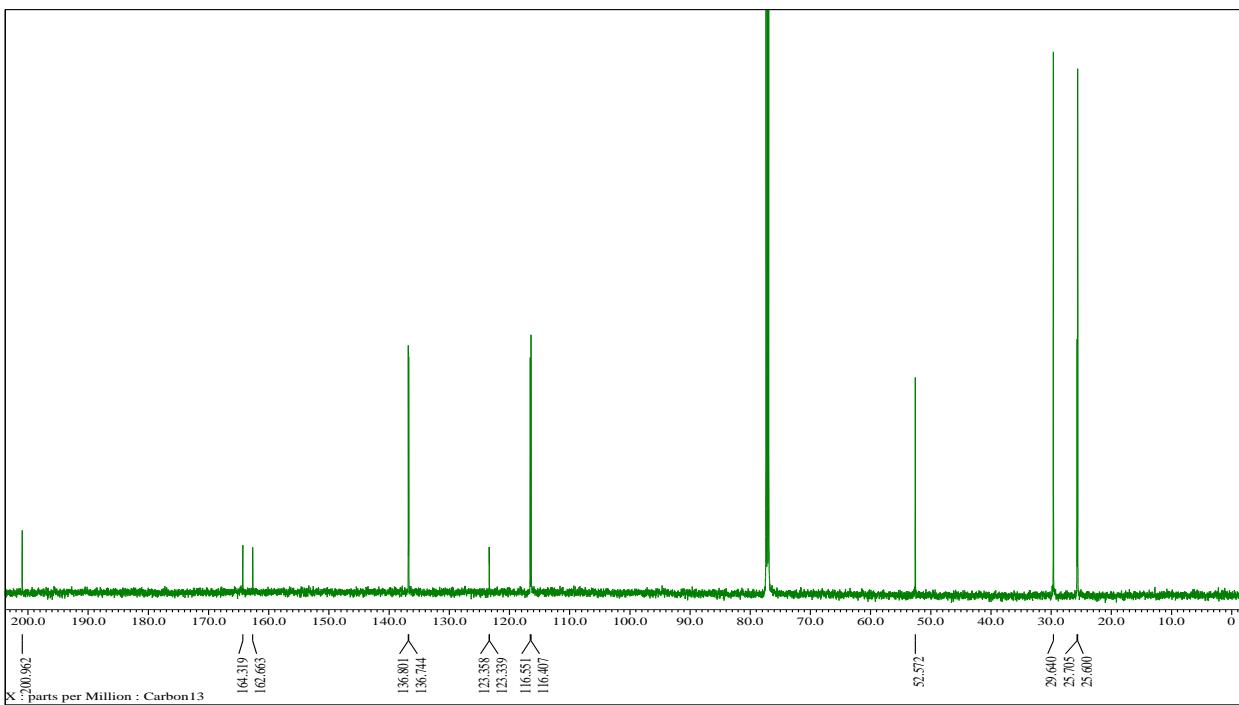


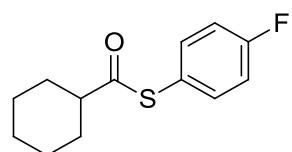
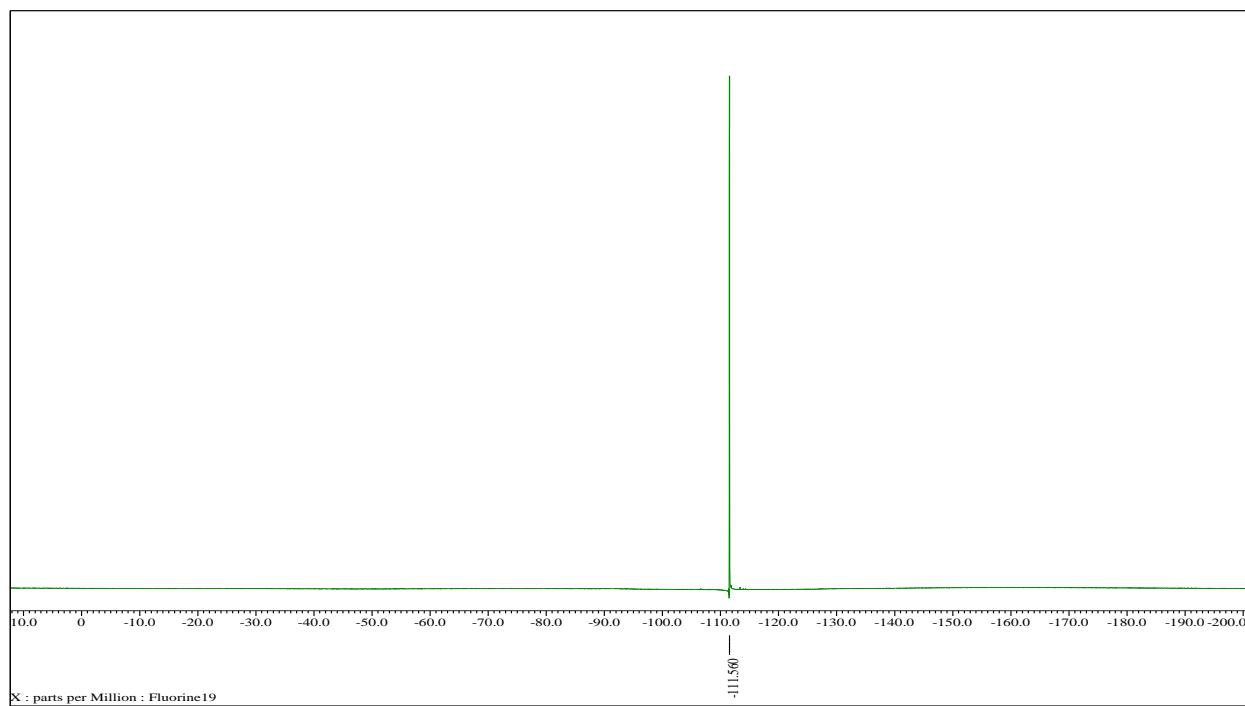
3ak





3al





¹⁹F NMR of 3al

