Supplementary Information

1,2-Acyl migration with α-imino rhodium carbenoids leading to substituted 1-naphthols

Tomoya Miura,[‡,]* Shunsuke Moritani, Yota Shiratori and Masahiro Murakami*

Department of Synthetic Chemistry and Biological Chemistry, Kyoto University
Katsura, Kyoto 615-8510, Japan

[‡] Current Address: Division of Applied Chemistry, Okayama University
Tsushimanaka, Okayama 700-8530, Japan.

E-mail: tmiura@okayama-u.ac.jp; murakami@sbchem.kyoto-u.ac.jp

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1. General Methods:

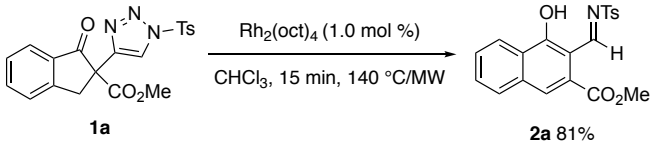
All reactions were carried out under a nitrogen atmosphere unless otherwise noted. For microwave syntheses, Initiator+ (Biotage) was used. IR measurements were performed on an Affinity-1S spectrometer fitted with a Pike Technologies MIRacle Single Reflection ATR adapter. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECZ400S/L1 (^{1}H at 400.44 MHz and ^{13}C at 100.69 MHz) and a JEOL JNM-ECZ500R (^{1}H at 500.16 MHz and ^{13}C at 125.77 MHz) spectrometer. NMR data were obtained in $CDCl_3$ unless otherwise noted. Proton chemical shifts were referenced to the residual proton signal of the solvent at 7.26 ppm ($CHCl_3$). Carbon chemical shifts were referenced to the carbon signal of the solvent at 77.0 ppm ($CDCl_3$). High-resolution mass spectra were recorded on JEOL JMS-SX102A (EI) and Thermo Fisher Scientific EXACTIVE Plus (ESI, APCI, DART) spectrometer. Preparative thin-layer chromatography (PTLC) was performed on silica gel plates with PF254 indicator (Merck). Flash column chromatography was performed with silica gel 60N (Kanto).

2. Materials:

All chemicals and anhydrous solvents were obtained from commercial suppliers and used without further purification unless otherwise noted. Chloroform, amylene added (FUJIFILM Wako) was distilled from P_2O_5. $Rh_2(oct)_4$ (TCI), $Rh_2(piv)_4$ (Aldrich) and $Rh_2(esp)_2$ (Aldrich) were obtained from commercial suppliers. Molecular sieves 4 Å (Nacalai) was obtained from commercial suppliers and dried under vacuum at 250 °C for 12 h before use. 6w% Distilled water was added into aluminium oxide 90 active base (basic Al_2O_3) (Merck) before use.

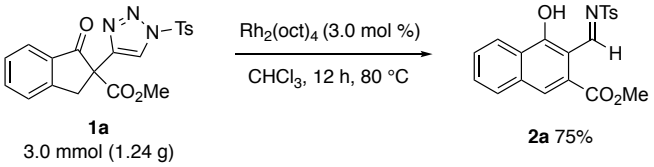
1-Indanones **s1, s3, s5, s8, s11, s14, s17, s21, s24** [1-indanone (TCI), 2-methyl-1-indanone (Aldrich), 3-phenyl-1-indanone (Aldrich), 5-fluoro-1-indanone (TCI), 5-chloro-1-indanone (TCI), 5-bromo-1-indanone (TCI), 5-hydroxy-1-indanone (Aldrich), 6-methyl-1-indanone (Aldrich), 6-hydroxy-1-indanone (TCI)], cyclic ketone **s28** [2-oxocyclopentanecarboxylate (TCI)] and diketones **s30, s32** [2-phenyl-1,3-indandione (Aldrich), 1,2-cyclohexanedione (TCI)] and were used.

3. Typical procedure for the Rh-catalysed 1,2-acyl migration (Scheme 2):



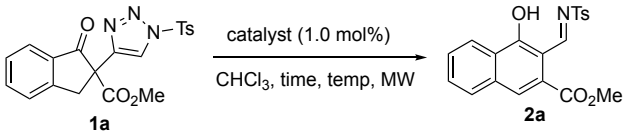
A 2-5 mL Biotage® microwave vial was charged with $Rh_2(oct)_4$ (0.90 mg, 1.0 μmol, 1.0 mol %), freshly prepared triazole **1a** (41 mg, 0.10 mmol) and $CHCl_3$ (2.0 mL). The vial was capped with a Teflon pressure cap. The reaction mixture was heated at 140 °C under microwave irradiation. After 15 minutes, the reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 4:1 to 2:1) to give the corresponding 2-imino-1-naphthol **2a** (31 mg, 0.082 mmol, 81%) as a light-yellow solid.

Without microwave conditions:



Triazole **1a** (1.2 g, 3.0 mmol), $Rh_2(oct)_4$ (72 mg, 0.092 mmol, 3 mol %) and chloroform (60 mL) were added to an oven-dried 100 mL two-necks flask equipped with a stirrer bar. The reaction mixture was stirred for 12 hours at 80 °C. The reaction mixture was cooled to room temperature, and concentrated under reduced pressure. The light-green powder was purified by reprecipitation (DCM/hexane = 1:10) and washed with hexane (15 mL x 3) to give **2a** (0.87 g, 2.3 mmol, 75%).

4. Optimization of reaction conditions.

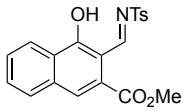


Entry	Rh catalyst	time (min)	temp (°C)	Yield **2a**	(recov. **1a**)
1	$Rh_2(oct)_4$	15	140	81%[a]	(0%)
2	not add	15	140	>1%[b]	(100%)
3	$Rh_2(oct)_4$	15	100	53%[a]	(7%)
4	$Rh_2(oct)_4$	15	80	3%[b]	(84%)
5	$Rh_2(oct)_4$	60	100	65%[a]	(0%)
6	$Rh_2(opiv)_4$	15	140	52%[a]	(0%)
7	$Rh_2(esp)_2$	15	140	47%[a]	(0%)
8	CuTC[c]	15	140	>1%[b]	(100%)

[a]Isolated yields. [b]Yields were determined by ^1H NMR using CH_2Br_2 as the internal standard. [c]10 mol %.

5. Characterizations of products (2a-2j, 8, 10 and 12)

3-Methoxycarbonyl-2-(*N*-tosyl-iminomethyl)-1-naphthol (2a) (Scheme 2)

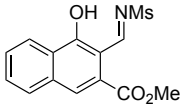


The reaction was carried out on 0.10 mmol (41 mg) scale. The crude mixture was purified by flash silica gel column chromatography (hexane/ethyl acetate = 4:1) to give **2a** in 81% yield (31 mg, 0.081 mmol).

When the reaction was carried out on 1.0 mmol (0.41 g) scale, the reaction temperature was at 120 ℃. The crude mixture was purified by flash silica gel column chromatography (hexane/ethyl acetate = 4:1) to give **2a** in 89% yield (0.34 g, 0.89 mmol).

IR (ATR): 2951, 1705, 1549, 1329, 1152 cm^{-1}; ^1H NMR: δ = 2.44 (s, 3H), 4.00 (s, 3H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.65 (td, *J* = 8.0, 1.2 Hz, 1H), 7.71 (td, *J* = 8.0, 1.2 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 8.04 (s, 1H), 8.41 (d, *J* = 8.4 Hz, 1H), 10.17 (s, 1H); ^{13}C NMR: δ = 21.7, 52.8, 107.8, 124.86, 124.91, 126.4, 127.3, 127.9, 128.7, 128.9, 130.0, 131.5, 135.4, 135.5, 144.8, 164.3, 166.6, 171.2; HRMS (APCI$^+$): Calcd for $C_{20}H_{18}O_5NS^+$, $[M+H]^+$ 384.0906. Found *m/z* 384.0900.

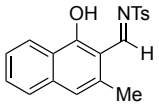
2-(*N*-Mesyl-iminomethyl)-3-methoxycarbonyl-1-naphthol (2b) (Scheme 2)



This reaction was carried out on 0.20 mmol (67 mg) scale. The crude mixture was purified by recrystallization (DCM/hexane = 1:20) to give **2b** in 86% yield (53 mg, 0.17 mmol).

IR (ATR): 2953, 1707, 1587, 1312, 1140, 1036 cm^{-1}; ^1H NMR: δ = 3.22 (s, 3H), 4.00 (s, 3H), 7.70 (td, *J* = 8.4, 1.6 Hz, 1H), 7.76 (td, *J* = 8.0, 1.6 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 8.09 (s, 1H), 8.49 (d, *J* = 8.0 Hz, 1H), 10.19 (s, 1H); ^{13}C NMR: δ = 41.1, 52.9, 107.6, 125.0, 125.1, 126.4, 127.4, 128.8, 129.0, 131.7, 135.6, 164.4, 166.6, 172.7. HRMS (ESI$^+$): Calcd for $C_{14}H_{13}NO_5SNa^+$, $[M+Na]^+$ 330.0407. Found *m/z* 330.0413.

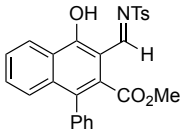
3-Methyl-2-(*N*-tosyl-iminomethyl)-1-naphthol (2c) (Table 1, entry 1)



This reaction was carried out on 0.10 mmol (37 mg) scale. The crude mixture was purified by flash silica gel column chromatography (hexane/ethyl acetate = 1:1) to give **2c** in 76% yield (26 mg, 0.076 mmol).

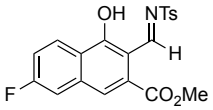
IR (ATR): 2924, 1715, 1638, 1578, 1489, 1319, 1152 cm^{-1}; ^1H NMR: δ = 2.44 (s, 3H), 2.62 (s, 3H), 7.09 (s, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.41-7.47 (m, 1H), 7.57-7.65 (m, 2H), 7.90 (d, *J* = 8.4 Hz, 2H), 8.31 (d, *J* = 8.4 Hz, 1H), 9.47 (s, 1H) ; ^{13}C NMR: δ = 19.7, 21.7, 110.0, 120.3, 123.9, 124.7, 125.6, 126.9, 127.7, 130.0, 131.3, 135.0, 135.7, 138.0, 144.7, 164.5, 168.3 ; HRMS (ESI$^+$): Calcd for $C_{19}H_{17}NO_3SNa^+$, $[M+Na]^+$ 362.0821. Found *m/z* 362.0826.

3-Methyl-4-phenyl-2-(*N*-tosyl-iminomethyl)-1-naphthol (2d) (Table 1, entry 2)



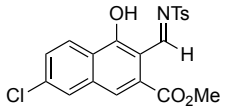
This reaction was carried out on 0.10 mmol (49 mg) scale. The crude mixture was purified by flash silica gel column chromatography (hexane/ethyl acetate = 2:1) to give **2d** in 87% yield (38 mg, 0.082 mmol).
IR (ATR): 2924, 1717, 1587, 1558, 1258, 1155, 1084 cm^{-1}; ^{1}H NMR: δ = 2.45 (s, 3H), 3.55 (s, 3H), 7.28-7.63 (m, 10H), 7.89 (d, *J* = 8.0 Hz, 2H), 8.45-8.51 (m, 1H), 9.20 (s, 1H); ^{13}C NMR: δ = 21.7, 52.5, 106.4, 124.8, 125.0, 127.2, 127.4, 127.9, 128.0, 128.3, 130.0, 130.1, 130.9, 131.2, 131.5, 135.2, 136.0, 136.8, 145.0, 163.0, 168.0, 169.2; HRMS (ESI^+): Calcd for $C_{26}H_{21}NO_5SNa^+$, $[M+Na]^+$ 482.1033. Found *m/z* 482.1031.

6-Fluoro-3-methoxycarbonyl-2-(*N*-tosyl-iminomethyl)-1-naphthol (2e) (Table 1, entry 3)



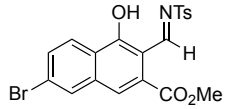
This reaction was carried out on 0.10 mmol (42 mg) scale. The crude mixture was purified by flash silica gel column chromatography (hexane/ethyl acetate = 2:1) to give **2e** in 77% yield (30.8 mg, 0.077 mmol).
IR (ATR): 2953, 1748, 1713, 1593, 1196, 1173 cm^{-1}; ^{1}H NMR: δ = 2.17 (s, 1H), 2.44 (s, 3H), 4.01 (s, 3H), 7.34-7.41 (m, 3H), 7.45 (dd, *J* = 5.2, 2.4 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 2H) 7.95 (s, 1H), 8.43 (dd, *J* = 6.0, 5.2 Hz, 1H), 10.13 (s, 1H); ^{13}C NMR: δ = 21.7, 52.9, 107.5, 112.8 (d, *J* = 21.1 Hz), 118.4 (d, *J* = 23.9 Hz), 123.2, 123.8 (d, *J* = 4.7 Hz), 127.9, 128.1 (d, *J* = 10.5 Hz), 128.9, 130.0, 135.4, 137.2 (d, *J* = 10.5 Hz), 144.9, 164.1, 164.2(d, J = 253.9 Hz), 166.3, 170.9; HRMS (ESI^+): Calcd for $C_{20}H_{16}FNO_5SNa^+$, $[M+Na]^+$ 424.0625. Found *m/z* 424.0632.

6-Chloro-3-methoxycarbonyl-2-(*N*-tosyl-iminomethyl)-1-naphthol (2f) (Table 1, entry 4)



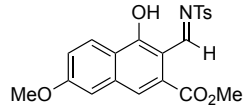
This reaction was carried out on 0.10 mmol (45 mg) scale. The crude mixture was purified by flash silica gel column chromatography (hexane/ethyl acetate = 2:1) to give **2f** in 91% yield (38 mg, 0.091 mmol).
IR (ATR): 2949, 1719, 1707, 1582, 1321, 1248, 1157, 1086 cm^{-1}; ^{1}H NMR: δ = 2.44 (s, 3H), 4.01 (s, 3H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.57 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.81 (d, *J* = 2.0 Hz, 1H), 7.89-7.94 (m, 3H), 8.35 (d, *J* = 8.4 Hz, 1H)10.14 (s, 1H); ^{13}C NMR: δ =21.7, 53.0, 108.0, 123.6, 124.6, 126.6, 127.7, 128.0, 128.9, 129.4, 130.0, 135.3, 136.2, 137.9, 145.0, 164.0, 166.3, 170.9; HRMS (ESI^+): Calcd for $C_{20}H_{16}ClNO_5SNa^+$, $[M+H]^+$ 440.0330. Found *m/z* 440.0336.

6-Bromo-3-methoxycarbonyl-2-(*N*-tosyl-iminomethyl)-1-naphthol (2g) (Table 1, entry 5)



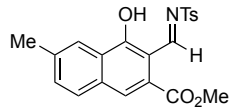
This reaction was carried out on 0.10 mmol (49 mg) scale. The crude mixture was purified by flash silica gel column chromatography (hexane/ethyl acetate = 2:1) to give **2g** in 82% yield (38 mg, 0.082 mmol).
IR (ATR): 2957, 1748, 1717, 1593, 1395, 1194, 1173 cm^{-1}; ^1H NMR: δ = 2.44 (s, 3H), 4.01 (s, 3H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.72 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.92(d, *J* = 8.4 Hz, 2H), 7.93 (s, 1H), 8.00 (s, 1H), 8.27 (d, *J* = 8.8 Hz, 1H), 10.14 (s, 1H); ^{13}C NMR: δ = 21.7, 53.0, 108.1, 123.5, 124.9, 126.47, 126.50, 128.0, 128.8, 130.0, 131.0, 132.0, 135.3, 136.4, 145.0, 164.1, 166.2, 170.9; HRMS (ESI^+): Calcd for $C_{20}H_{16}BrNO_5SNa^+$, $[M+Na]^+$ 483.9825. Found *m/z* 483.9825.

6-Methoxy-3-methoxycarbonyl-2-(*N*-tosyl-iminomethyl)-1-naphthol (2h) (Table 1, entry 6)



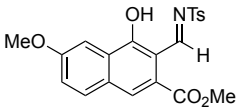
This reaction was carried out on 0.10 mmol (45 mg) scale. The crude mixture was purified by flash silica gel column chromatography (hexane/ethyl acetate = 2:1) to give **2h** in 78% yield (32 mg, 0.078 mmol).
IR (ATR): 2970, 1717, 1489, 1321, 1161, 1026 cm^{-1}; ^1H NMR: δ = 2.43 (s, 3H), 3.95 (s, 3H), 3.99 (s, 3H), 7.12 (d, *J* = 2.4 Hz, 1H), 7.22 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.906 (d, *J* = 8.4 Hz, 2H), 7.907 (s, 1H), 8.30 (d, *J* = 9.2 Hz, 1H), 10.10 (s, 1H); ^{13}C NMR: δ = 21.6, 52.8, 55.6, 106.7, 107.9, 120.2, 120.9, 124.0, 126.8, 127.8, 128.3, 129.9, 135.8, 137.8, 144.6, 162.2, 164.4, 166.6, 170.8; HRMS (ESI^+): Calcd for $C_{21}H_{19}NO_6SNa^+$, $[M+Na]^+$436.0825. Found *m/z* 436.0822.

7-Methyl-3-methoxycarbonyl-2-(*N*-tosyl-iminomethyl)-1-naphthol (2i) (Table 1, entry 7)



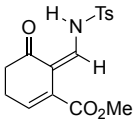
This reaction was carried out on 0.10 mmol (44 mg) scale. The crude mixture was purified by flash silica gel column chromatography (hexane/ethyl acetate = 2:1) to give **2i** in 86% yield (35 mg, 0.086 mmol).
IR (ATR): 2922, 1719, 1585, 1323, 1155, 1086 cm^{-1}; ^1H NMR: δ = 2.45 (s, 3H), 4.00 (s, 3H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.89-7.94 (m, 3H), 7.99 (s, 1H), 8.27 (d, *J* = 9.6 Hz, 1H), 10.14 (s, 1H); ^{13}C NMR: δ = 21.7, 53.0, 108.1, 123.5, 124.9, 126.47, 126.50, 128.0, 128.8, 130.0, 131.0, 132.0, 135.3, 136.4, 145.0, 164.1, 166.2, 170.9; HRMS (ESI^+): Calcd for $C_{21}H_{20}NO_5S^+$, $[M+H]^+$ 420.0876. Found *m/z* 420.0874.

7-Methoxy-3-methoxycarbonyl-2-(*N*-tosyl-iminomethyl)-1-naphthol (2j) (Table 1, entry 8)



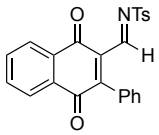
This reaction was carried out on 0.10 mmol (45 mg) scale. The crude mixture was purified by flash silica gel column chromatography (hexane/ethyl acetate = 1:1) to give **2j** in 99% yield (34 mg, 0.099 mmol).
IR (ATR): 2959, 1703, 1585, 1292, 1215, 1153 cm^{-1}; ^{1}H NMR: δ = 2.41 (s, 3H), 3.69 (s, 3H), 3.80 (s, 3H), 3.91 (d, *J* = 17.2 Hz, 1H), 4.10 (d, *J* = 17.2 Hz, 1H), 7.16 (d, *J* = 2.4 Hz, 1H), 7.24 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 8.54 (s, 1H); ^{13}C NMR: δ = 21.7, 36.7, 53.4, 55.6, 60.1, 106.1, 123.5, 125.6, 127.1, 128.7, 130.3, 132.8, 134.6, 143.7, 146.6, 147.3, 159.8, 169.1, 198.5; HRMS (ESI^+): Calcd for $C_{21}H_{19}NO_6SNa^+$, $[M+Na]^+$ 436.0825. Found *m/z* 436.0832.

3-Methoxylcarbonyl-2-(*N*-tosylaminomethylene)-3-cyclohexen-1-one (8) (Scheme 6)



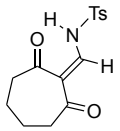
A 2-5 mL Biotage® microwave vial was charged with $Rh_2(oct)_4$ (1.8 mg, 2.0 μmol, 1.0 mol %), freshly prepared triazole **6** (78.3 mg, 0.22 mmol) and $CHCl_3$ (4.0 mL). The vial was capped with a Teflon pressure cap. The reaction mixture was heated at 140 °C under microwave irradiation. After 15 minutes, 1 M HCl (diethyl ether solution, 20 μL, 10 mol %) was directly added to the reaction mixture. It was further stirred at 30 min. Then, it was concentrated under reduced pressure. The residue was purified by recrystallization (DCM/hexane = 1:20) to give **8** (48.1 mg, 0.14 mmol, 67%) as a white solid.
IR (ATR): 3098, 2953, 1703, 1645, 1558, 1248, 1157, 1086 cm^{-1}; ^{1}H NMR: δ =2.41 (s, 3H), 2.42-2.52 (m, 4H), 3.80 (s, 3H), 6.94 (t, *J* = 4.8 Hz, 1H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 8.04 (d, *J* = 11.2 Hz, 1H), 11.90 (d, *J* = 11.2 Hz, 1H); ^{13}C NMR: δ = 21.6, 22.5, 36.5, 52.1, 108.0, 126.8, 128.3, 130.0, 135.0, 136.9, 138.9, 144.5, 165.8, 201.9; HRMS (ESI^+): Calcd for $C_{16}H_{17}NO_5SNa^+$, $[M+Na]^+$ 358.0720. Found *m/z* 358.0726.

3-Phenyl-2-(*N*-tosyl-iminomethyl)-1,4-naphthalenedione (10) (Scheme 7)



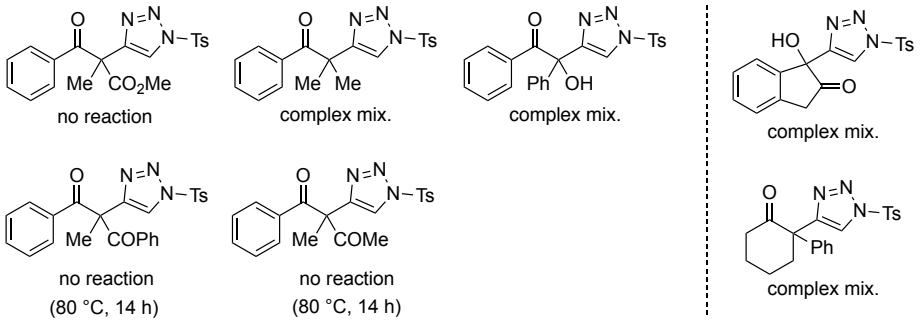
This reaction was carried out on 0.10 mmol (45 mg) scale. The crude mixture was purified by recrystallization (DCM/hexane = 1:20) to give **10** in 87 % yield (36 mg, 0.087 mmol).
IR (ATR): 3063, 1665, 1593, 1323, 1287, 1155, 1088 cm^{-1}; ^{1}H NMR: δ = 2.46 (s, 3H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 7.6Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.80-7.84 (m,2H), 8.13-8.20 (m, 2H), 8.90 (s, 1H); ^{13}C NMR(500 MHz): δ = 21.7, 126.7, 127.0, 128.1, 128.3, 129.8, 130.2, 130.35, 130.36, 131.65, 131.67, 133.6, 134.4, 134.6, 135.5, 145.0, 150.2, 166.3, 181.9, 183.6; HRMS ($APCI^+$): Calcd for $C_{24}H_{18}NO_4S^+$, $[M+H]^+$ 416.0951. Found *m/z* 416.0953.

2-(*N*-Tosylaminomethylene)-1,3-cycloheptadione (12) (Scheme 8)



This reaction was carried out on 0.20 mmol (67 mg) scale. The crude mixture was purified by recrystallization (diethyl ether/hexane = 1:20) to give **12** in 89 % yield (55 mg, 0.18 mmol).
IR (ATR): 3138, 2945, 1680, 1612, 1533, 1360, 1265, 1163, 1084 cm^{-1}; ^{1}H NMR: δ = 1.80-1.92 (m, 4H), 2.43 (s, 3H), 2.62-2.72 (m, 4H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 8.07 (d, *J* = 11.2 Hz, 1H), 12.26 (d, *J* = 11.2 Hz, 1H); ^{13}C NMR: δ = 21.3, 21.5, 21.6, 40.2, 40.6, 117.0, 127.2, 130.2, 135.6, 145.4, 149.7, 199.6, 202.8; HRMS (ESI^{+}): Calcd for $C_{15}H_{17}NO_4SNa^{+}$, $[M+Na]^{+}$330.0770. Found *m/z* 330.0777.

6. Limitations



7. X-ray Crystallography of 2c (CCDC# 2110557)

For **2c**, X-ray diffraction measurements were performed with a Rigaku AFC10 diffractometer with Rigaku Saturn Kappa CCD system equipped with a MicroMax-007 HF/VariMax rotating-anode X-ray generator with confocal monochromated Mo Kα radiation.

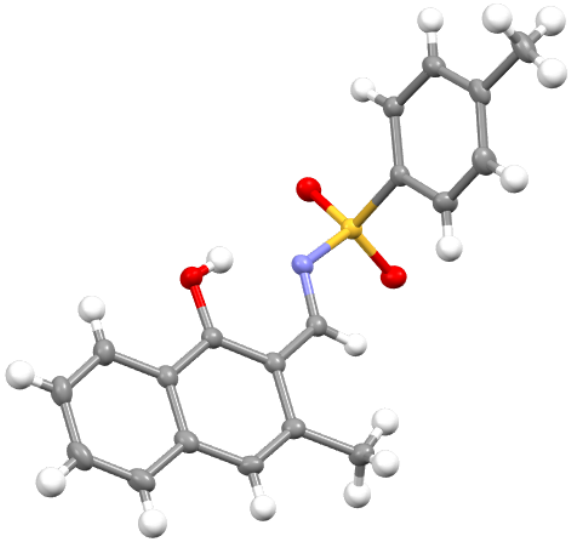


Fig *S1* Molecular structure of **2c** with thermal ellipsoids at 50% probability level.

Table *S1* Crystal data and structure refinement of **2c**

Empirical formula	$C_{19}H_{17}NO_3S$
Formula weight	339.41
Temperature	293 K
Wavelength	0.71075 Å
Crystal system	*Triclinic*
Space group	*P-1* (No. 2)
Cell constants:	
a	6.478(2) Å
b	8.078(3) Å
c	15.574(5) Å
α	81.981(8) °
β	89.271(9) °
γ	88.832(8) °
Volume	806.8(5) $Å^3$
Z	2
Density (calculated)	1.397 Mg/m^3
Absorption coefficient	0.218 mm^{-1}
F(000)	356
Crystal size	0.20 x 0.20 x 0.20 mm^3
Theta range for data collection	3.028 to 27.480 °

Index ranges	$-8 \leq h \leq 7, -10 \leq k \leq 10, -20 \leq l \leq 15$
Reflections collected	6488
Independent reflected	3545 [*R*(int)= 0.020]
Completeness to theta = 27.5 °	95.5%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Max. and min. transmission	0.957 and 0.815
Data/ restraints/ parameters	3545/ 0/ 217
Goodness-of-fit on F^2	1.089
Final R indices [I>2sigma(I)]	R = 0.0526, wR = 0.1554
R indices (all data)	R = 0.0468, wR = 0.1506
Largest diff. peak and hole	0.67 and -0.72 e·Å^{-3}

Table *S2* Atomic coordinates and equivalent isotropic displacement parameters for **2c**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U (eq)
S1	0.22744(7)	0.26011(6)	0.16909(3)	0.01888(17)
O1	0.1549(2)	0.15088(19)	0.43405(9)	0.0262(3)
O2	0.1065(2)	0.11781(17)	0.15886(9)	0.0255(3)
O3	0.4256(2)	0.27811(19)	0.12670(9)	0.0253(3)
N1	0.2536(3)	0.2563(2)	0.27554(10)	0.0203(4)
C1	0.4286(3)	0.3029(2)	0.30351(12)	0.0194(4)
C2	0.4725(3)	0.2913(2)	0.39436(12)	0.0197(4)
C3	0.3341(3)	0.2100(2)	0.45574(12)	0.0204(4)
C4	0.3835(3)	0.1847(2)	0.54586(12)	0.0213(4)
C5	0.2457(4)	0.1027(3)	0.60853(13)	0.0266(5)
C6	0.2987(4)	0.0766(3)	0.69436(14)	0.0303(5)
C7	0.4901(4)	0.1317(3)	0.72028(14)	0.0323(5)
C8	0.6247(4)	0.2120(3)	0.66079(14)	0.0304(5)
C9	0.5746(3)	0.2419(3)	0.57148(12)	0.0236(4)
C10	0.7112(3)	0.3261(3)	0.50820(13)	0.0243(4)
C11	0.6641(3)	0.3517(2)	0.42226(12)	0.0214(4)
C12	0.8088(3)	0.4449(3)	0.35687(13)	0.0266(5)
C13	0.0771(3)	0.4419(2)	0.13891(11)	0.0186(4)
C14	-0.1210(3)	0.4295(2)	0.10893(12)	0.0215(4)
C15	-0.2348(3)	0.5757(3)	0.08294(13)	0.0245(4)
C16	-0.1530(3)	0.7318(3)	0.08741(12)	0.0239(4)
C17	0.0470(4)	0.7399(3)	0.11904(14)	0.0286(5)
C18	0.1631(3)	0.5967(3)	0.14423(14)	0.0251(4)

C19	-0.2761(4)	0.8891(3)	0.05786(14)	0.0329(5)

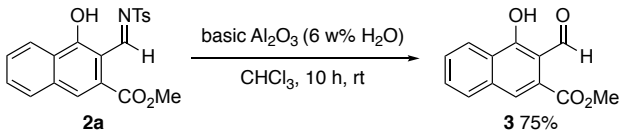
Table *S3* Bond lengths [Å] and angles [°] for **2c**.

S1	-	O2		1.4324(15)
S1	-	O3		1.4369(16)
S1	-	N1		1.6646(17)
S1	-	C13		1.757(2)
O1	-	C3		1.330(3)
N1	-	C1		1.301(3)
C1	-	C2		1.437(3)
C2	-	C3		1.406(3)
C2	-	C11		1.437(3)
C3	-	C4		1.429(3)
C4	-	C9		1.411(3)
C4	-	C5		1.418(3)
C5	-	C6		1.371(3)
C6	-	C7		1.409(3)
C7	-	C8		1.369(3)
C8	-	C9		1.419(3)
C9	-	C10		1.426(3)
C10	-	C1		1 1.363(3)
C11	-	C1		2 1.508(3)
C13	-	C1		4 1.381(3)
C13	-	C1		8 1.393(3)
C14	-	C1		5 1.393(3)
C15	-	C1		6 1.389(3)
C16	-	C1		7 1.398(3)
C16	-	C1		9 1.506(3)
C17	-	C1		8 1.380(3)

O2	-	S1	-	O3	118.87(9)
O2	-	S1	-	N1	105.74(9)
O3	-	S1	-	N1	110.04(9)
O2	-	S1	-	C13	108.56(9)
O3	-	S1	-	C13	109.33(9)
N1	-	S1	-	C13	103.13(8)
C1	-	N1	-	S1	117.90(14)
N1	-	C1	-	C2	122.14(18)
C3	-	C2	-	C1	119.75(18)
C3	-	C2	-	C11	119.94(17)

C1	-	C2	-	C11	120.16(18)
O1	-	C3	-	C2	122.82(18)
O1	-	C3	-	C4	116.65(18)
C2	-	C3	-	C4	120.52(18)
C9	-	C4	-	C5	120.31(18)
C9	-	C4	-	C3	118.50(18)
C5	-	C4	-	C3	121.19(19)
C6	-	C5	-	C4	120.1(2)
C5	-	C6	-	C7	119.9(2)
C8	-	C7	-	C6	120.9(2)
C7	-	C8	-	C9	120.8(2)
C4	-	C9	-	C8	118.07(19)
C4	-	C9	-	C10	119.97(18)
C8	-	C9	-	C10	122.0(2)
C11	-	C10	-	C9	121.76(19)
C10	-	C11	-	C2	119.29(18)
C10	-	C11	-	C12	120.73(19)
C2	-	C11	-	C12	119.98(17)
C14	-	C13	-	C18	121.30(18)
C14	-	C13	-	S1	119.93(15)
C18	-	C13	-	S1	118.76(15)
C13	-	C14	-	C15	118.81(19)
C16	-	C15	-	C14	121.2(2)
C15	-	C16	-	C17	118.60(18)
C15	-	C16	-	C19	120.7(2)
C17	-	C16	-	C19	120.7(2)
C18	-	C17	-	C16	121.14(19)
C17	-	C18	-	C13	118.97(19)

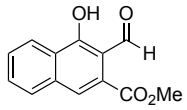
8. Procedure for hydrolysis of 2a (Scheme 4)



2a **3** 75%

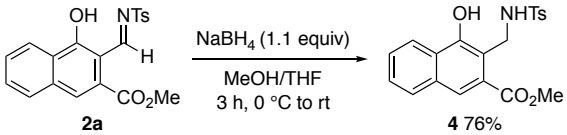
The 1-naphthol **2a** (83 mg, 0.22 mmol), basic Al_2O_3 (6% w/w water, 0.56 g) and $CHCl_3$ (4.0 mL) were added to a 10 mL Schlenk flask equipped with a stirrer bar. After 10 hours, the reaction mixture was filtered and under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 2:1) to give **3** (37 mg, 0.16 mmol, 75%) as a light-yellow solid.

2-Formyl-3-methoxycarbonyl-1-naphthol (3)



IR (ATR) 2963, 2926, 1701, 1618, 1460, 1306, 1030 cm^{-1}; ^1H NMR: δ = 4.00 (s, 3H), 7.66 (td, *J* = 7.2, 1.2 Hz, 1H), 7.72 (td, *J* = 7.2, 1.2 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.99 (s, 1H), 8.47 (d, *J* = 8.0 Hz, 1H), 10.72 (s, 1H); ^{13}C NMR: δ = 52.7, 111.6, 124.0, 124.6, 126.6, 127.1, 128.5, 128.8, 131.2, 135.4, 164.0, 166.6, 197.4 ; HRMS (APCI$^+$): Calcd for $C_{13}H_{11}O_4^+$, $[M+H]^+$ 231.0652. Found *m/z* 231.0657.

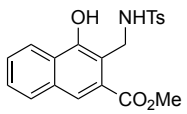
9. Procedure for reduction of 2a (Scheme 4)



2a **4** 76%

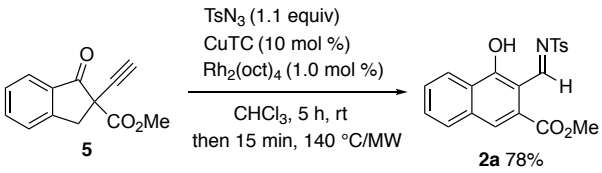
The 1-naphthol **2a** (83 mg, 0.22 mmol) and THF (3.0 mL) were added to a 10 mL Schlenk flask equipped with a stirrer bar. $NaBH_4$ (9.3 mg, 0.24 mmol, 1.1 equiv) and MeOH (2.0 mL) was added to the reaction mixture at 0 °C. Then, the ice bath was removed. The reaction mixture was stirred at room temperature. After 3 hours, the reaction mixture was diluted with water (5.0 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic phase was washed with brine (30 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by reprecipitation (diethyl ether/hexane = 1:10) to give **4** (64 mg, 0.17 mmol, 76%) as a white solid.

3-Methoxycarbonyl-2-(*N*-tosylaminomethyl)-1-naphthol (4)



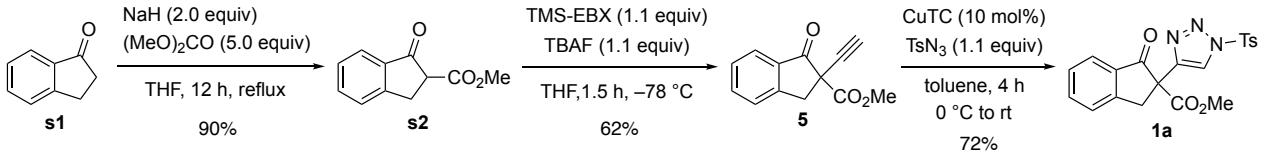
IR (ATR) 3399, 3285, 1701, 1595, 1508, 1406, 1304, 1248, 1134, 1043cm^{-1}; ^1H NMR: δ =2.40 (s, 3H), 3.93 (s, 3H), 4.45 (d, *J* = 7.2 Hz, 2H), 5.98 (t, *J* = 6.8 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.56 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.62 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.80 (d, *J* =8.4 Hz, 2H), 7.83 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.98 (s, 1H), 8.09 (s, 1H), 8.39 (dd, *J* = 8.4 Hz, 1H); ^{13}C NMR: δ = 21.5, 40.0, 52.4, 116.4, 123.2, 124.8, 126.6, 127.5, 128.1, 128.5, 129.7, 132.8, 137.5, 143.5, 152.0, 168.4 ; HRMS (ESI$^+$): Calcd for $C_{20}H_{19}NO_5SNa^+$, $[M+Na]^+$ 408.0876. Found *m/z* 408.0885.

10. All-in one-pot reaction (Scheme 5)



A 2-5 mL Biotage® microwave vial was charged with 2-ethynyl-2-methoxycarbonyl-1-indanone **5** (44 mg, 0.20 mmol), CuTC (4.0 mg, 0.020 mmol, 10 mol %), $Rh_2(oct)_4$ (1.6 mg, 2.0 μmol, 1.0 mol %) and $CHCl_3$ (4.0 mL). Tosyl azide (42 mg, 0.22 mmol, 1.1 equiv) was added dropwise. The vial was capped with a Teflon pressure cap. The resulting mixture was stirred at room temperature. After 5 hours, the reaction mixture was heated at 140 °C under microwave irradiation. After 15 minutes, the reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 2:1) to give the corresponding 2-imino-1-naphthol **2a** (61.7 mg, 0.16 mmol, 78%).

11. Synthetic procedure for triazole substrates (1a-1j, 5, 6, 9 and 11)



Scheme *S1* Synthesis of Triazole **1a**.

2-Methoxycarbonyl-1-indanone (s2)

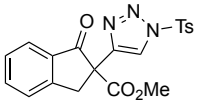
1-Indanone (**s1**, 0.66 g, 5.0 mmol), 60 w% sodium hydride (0.43 g, 11 mmol, 2.1 equiv), dimethoxy carbonate (2.1 mL, 25 mmol, 5 equiv) and THF (30 mL) were added to an oven-dried 100 mL two-necks flask equipped with a stirrer bar. The reaction mixture was refluxed at 70 °C. After 12 hours, the reaction mixture was cooled to room temperature, and acidified with 1 M HCl aq. The resulting mixture was extracted with diethyl ether (3 x 30 mL). The combined organic phase was washed with brine (30 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 4:1) to give 2-metoxycarbonyl-1-indanone (**s2**, 0.86 g, 4.5 mmol, 90%) as a light-yellow solid. The analytical data of **s2** was matched well with already reported one.[1]

2-Ethynyl-2-methoxycarbonyl-1-indanone (5)

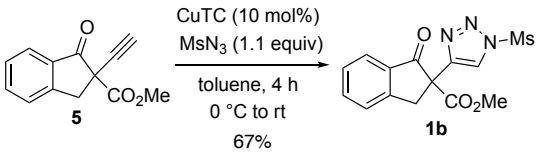
2-Methoxycarbonyl-1-indanone (**s2**, 0.57 g, 3.0 mmol), TMS-EBX (1.1 g, 3.3 mmol, 1.1 equiv) and THF (45 mL) were added to an oven-dried 50 mL two-necks flask equipped with a stirrer bar. Then, the reaction mixture was cooled to –78 °C. TBAF (1 M in THF, 3.3 mL, 1.1 equiv) was added via syringe. After 1.5 hours, it was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 4:1) to give 2-ethynyl-2-methoxycarbonyl-1-indanone (**5**, 0.40 g, 1.9 mmol, 62%) as a light-yellow solid. The analytical data of **5** was matched well with already reported one.[1]

2-Methoxycarbonyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1-indanone (1a)

2-Ethynyl-2-metoxycarbonyl-1-indanone (**5**, 1.9 g, 8.7 mmol), CuTC (0.17 g, 0.87 mmol, 10 mol %) and toluene (44 mL) was added to an oven-dried 100 mL two-necks flask equipped with a stirrer bar. Then, the reaction mixture was cooled to 0 °C. Tosyl azide (1.3 mL, 8.7 mmol, 1.0 equiv) was added dropwise. The resulting mixture was stirred at room temperature. After 4 hours, the reaction mixture was diluted with saturated NH_4Cl aq. (10 mL) and extracted with ethyl acetate (3 x 30 mL). The combined organic phase was washed with brine (30 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 2:1) to give 2-Methoxycarbonyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1-indanone (**1a**, 2.6 g, 6.3 mmol, 72%) as a white solid.



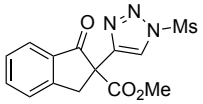
IR (ATR): 3184, 1744, 1721, 1589, 1387, 1175 cm^{-1}; ^1H NMR: δ = 2.42 (s, 3H), 3.70 (s, 3H), 4.02 (d, *J* = 17.6 Hz, 1H), 4.22 (d, *J* = 17.6 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 8.57 (s, 1H); ^{13}C NMR: δ = 21.8, 37.2, 53.5, 59.4, 123.7, 125.4, 126.5, 128.0, 128.7, 130.4, 132.8, 133.4, 136.1, 143.6, 147.3, 153.6, 169.0, 198.6; HRMS (ESI^+): Calcd for $C_{20}H_{17}N_3O_5SNa^+$, $[M+Na]^+$ 434.0781. Found *m/z* 434.0777.



Scheme *S2* Synthesis of Triazole **1b**

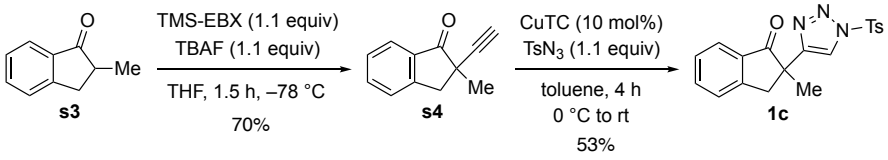
2-Methoxycarbonyl-2-(1-mesyl-1,2,3-triazol-4-yl)-1-indanone (1b)

2-Ethynyl-2-metoxycarbonyl-1-indanone (**5**, 0.40 g, 1.9 mmol), CuTC (37 mg, 0.20 mmol, 10 mol %) and toluene (10 mL) was added to an oven-dried 50 mL two-necks flask equipped with a stirrer bar. Then, the reaction mixture was cooled to 0 °C. Mesyl azide (0.25 g, 2.0 mmol, 1.1 equiv) was added dropwise. The resulting mixture was stirred at room temperature. After 4 hours, the reaction mixture was diluted with saturated NH_4Cl aq. (10 mL) and extracted with ethyl acetate (3 x 15 mL). The combined organic phase was washed with brine (30 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 2:1) and recrystallization (DCM / hexane = 1:1) to give 2-methoxycarbonyl-2-(1-mesyl-1,2,3-triazol-4-yl)-1-indanone (**1b**, 0.42 g, 1.2 mmol, 67%) as a white solid.



IR (ATR): 3159, 2924, 1742, 1713, 1369, 1194, 1169 cm^{-1}; ^1H NMR: δ = 3.51 (s, 3H), 3.74 (s, 3H), 4.07 (d, *J* = 17.6 Hz, 1H), 4.27 (d, *J* = 17.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 8.55 (s, 1H); ^{13}C NMR: δ = 37.3, 42.7, 53.6, 59.5, 123.8, 125.5, 126.5,

128.2, 133.4, 136.2, 143.9, 153.6, 169.0, 198.5. HRMS (ESI$^+$): Calcd for $C_{14}H_{13}N_3O_5SNa^+$, $[M+Na]^+$ 358.0468. Found *m/z* 358.0470.



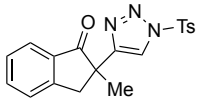
Scheme *S3* Synthesis of Triazole **1c**

2-Ethynyl-2-methyl-1-indanone (s4)

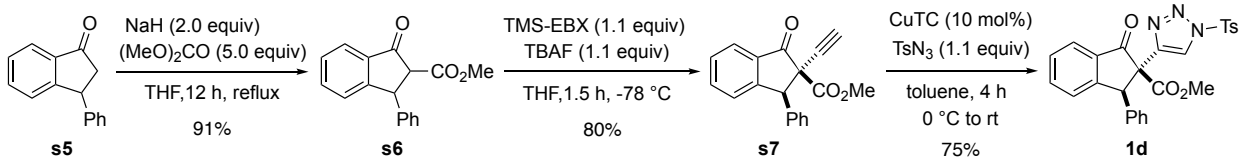
2-Methyl-1-indanone (**s3**, 0.17 g, 1.1 mmol), TMS-EBX (0.38 g, 1.2 mmol, 1.1 equiv) and THF (20 mL) were added to an oven-dried 50 mL two-necks flask equipped with a stirrer bar. Then, the reaction mixture was cooled to –78 ℃. TBAF (1 M in THF, 1.2 mL, 1.1 equiv) was added via syringe. After 1.5 hours, it was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 4:1) to give 2-ethynyl-2-methyl-1-indanone (**s4**, 0.14 g, 0.81 mmol, 70%) as a yellow oil.

2-Methyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1-indanone (1c)

2-Ethynyl-2-methyl-1-indanone (**s4**, 58 mg, 0.34 mmol), CuTC (8.5 mg, 0.040 mmol, 10 mol %) and toluene (2.0 mL) was added to an oven-dried 50 mL two-necks flask equipped with a stirrer bar. Then, the reaction mixture was cooled to 0 ℃. Tosyl azide (93 mg, 0.47 mmol, 1.1 equiv) was added dropwise. The resulting mixture was stirred at room temperature. After 4 hours, the reaction mixture was diluted with saturated NH_4Cl aq. (5.0 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic phase was washed with brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by recrystallization (diethyl ether / hexane = 1:1) to give 2-methyl -2-(1-tosyl-1,2,3-triazol-4-yl)-1-indanone (**1c**, 0.66 g, 0.18 mmol, 53%) as a white solid.



IR (ATR): 3148, 1703, 1179, 1003 cm^{-1}; ^{1}H NMR: δ = 1.59 (s, 3H), 2.42 (s, 3H), 3.29 (d, *J* = 17.6 Hz, 1H), 3.98 (d, *J* = 17.6 Hz, 1H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 8.18 (s, 1H); ^{13}C NMR: δ = 21.8, 25.8, 41.0, 48.0, 120.8, 124.8, 126.7, 127.8, 128.7, 130.4, 132.9, 134.1, 135.6, 147.2, 149.8, 152.5, 206.4; HRMS (ESI$^+$): Calcd for $C_{19}H_{17}N_3O_3SNa^+$, $[M+Na]^+$ 390.0883. Found *m/z* 390.0879.



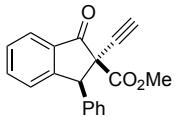
Scheme *S4* Synthesis of Triazole **1d.**

2-Methoxycarbonyl-3-phenyl-1-indanone (s6)

3-Phenyl-1-indanone (**s5**, 0.83 g, 4.0 mmol), 60 w% sodium hydride (0.32 g, 8.0 mmol, 2.0 equiv), dimethoxy carbonate (1.7 mL, 20 mmol, 5.0 equiv) and THF (24 mL) were added to an oven-dried 50 mL two-necks flask equipped with a stirrer bar. The reaction mixture was refluxed at 70 ℃. After 12 hours, the reaction mixture was cooled to room temperature, and acidified with 1 M HCl aq. The resulting mixture was extracted with diethyl ether (3 x 30 mL). The combined organic phase was washed with brine (30 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 4:1) to give 2-methoxycarbonyl-3-phenyl-1-indanone (**s6**, 0.97 g, 3.6 mmol, 91%) as a light-yellow solid. The analytical data of **s6** was matched well with already reported one.[2]

2-Ethynyl-2-methoxycarbonyl-3-phenyl-1-indanone (s7)

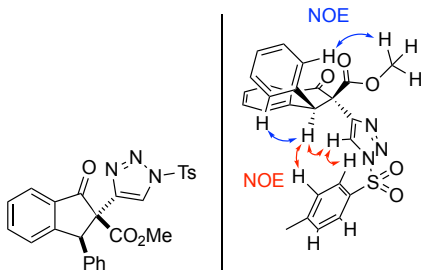
2-Methoxycarbonyl-3-phenyl-1-indanone (**s6**, 0.40 g, 1.5 mmol), TMS-EBX (0.69 g, 2.0 mmol, 1.1 equiv) and THF (20 mL) were added to an oven-dried 50 mL two-necks flask equipped with a stirrer bar. Then, the reaction mixture was cooled to –78 ℃. TBAF (1 M in THF, 2.0 mL, 1.1 equiv) was added via syringe. After 1.5 hours, it was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 2:1) and recrystallization (DCM/hexane = 1:10) to give 2-ethynyl-2-methoxycarbonyl-1-indanone (**s7**, 0.35 g, 1.2 mmol, 80%) as a light-red solid.



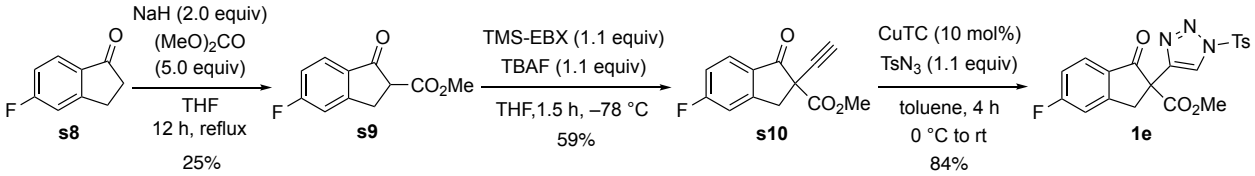
IR (ATR): 3275, 2947, 1746, 1715, 1601, 1288, 1202, 1179, 1130; ^{1}H NMR: δ = 2.60 (s, 1H), 3.15 (s, 3H), 5.12 (s, 1H), 7.19-7.24 (m, 2H), 7.29-7.36 (m, 3H), 7.40 (d, *J* = 6.8 Hz, 1H), 7.53 (t, *J* = 6.8 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.93 (d, *J* = 7.6 HZ, 1H); ^{13}C NMR: δ = 52.5, 58.5, 62.1, 73.9, 79.8, 125.2, 126.7, 128.2, 128.4, 128.8, 129.2, 135.3, 135.8, 136.5, 152.8, 166.8, 196.2; HRMS (APCI$^+$): Calcd for $C_{19}H_{15}O_3^+$, $[M+H]^+$ 291.1016. Found *m/z* 291.1016.

2-Methoxycarbonyl-3-phenyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1-indanone (1d)

2-Ethynyl-2-methoxycarbonyl-3-phenyl-1-indanone (**s7**, 0.35 g, 1.2 mmol), CuTC (25 mg, 0.13 mmol, 10 mol %) and toluene (6.0 mL) was added to an oven-dried Schlenk tube equipped with a stirrer bar. Then, the reaction mixture was cooled to 0 ℃. Tosyl azide (0.22 g, 1.2 mmol, 1.1 equiv) was added dropwise. The resulting mixture was stirred at room temperature. After 4 hours, the reaction mixture was diluted with saturated NH_4Cl aq. (5.0 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic phase was washed with brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was again washed with a small amount of DCM to give 2-methoxycarbonyl-3-phenyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1-indanone (**1d**, 0.44 g, 0.89 mmol, 75%) as a white solid. Relative configuration was determined by NOE spectra.



IR (ATR): 3146, 1749, 1719, 1395, 1194, 1179 cm^{-1};^{1}H NMR: δ = 2.45 (s, 3H), 3.15 (s, 3H), 5.94 (s, 1H), 7.22-7.31 (m, 5H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 8.53 (s, 1H); ^{13}C NMR: δ = 21.8, 52.2, 54.4, 65.8, 123.9, 124.9, 127.0, 127.9, 128.2, 128.6, 128.8, 129.6, 130.4, 132.8, 135.4, 135.9, 137.3, 143.9, 147.3, 154.5, 168.5, 199.0; HRMS (ESI$^+$): Calcd for $C_{26}H_{21}N_3O_5SNa^+$, $[M+Na]^+$ 510.1094. Found *m/z* 510.1095.



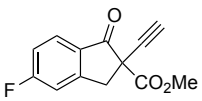
Scheme *S5* Synthesis of Triazole **1e**

5-Fluoro-2-methoxycarbonyl-1-indanone (s9)

5-Fluoro-1-indanone (**s8**, 0.46 g, 3.1 mmol), 60 w% sodium hydride (0.25 g, 6.3 mmol, 2.0 equiv), dimethoxy carbonate (1.3 mL, 14 mmol, 5 equiv) and THF (8.0 mL) were added to an oven-dried 50 mL two-necks flask equipped with a stirrer bar. The reaction mixture was refluxed at 70 °C. After 12 hours, the reaction mixture was cooled to room temperature, and acidified with 1 M HCl aq. The resulting mixture was extracted with ethyl acetate (3 x 10 mL). The combined organic phase was washed with brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was washed with DCM and reprecipitation (diethyl ether/hexane =1/1) to give 5-fluoro-2-methoxycarbonyl-1-indanone (**s9**, 0.16 g, 0.79 mmol, 25%) as a light-yellow solid. The analytical data of **s9** was matched well with already reported one.[3]

2-Ethynyl-5-fluoro-2-methoxycarbonyl-1-indanone (s10)

5-Fluoro-2-methoxycarbonyl-1-indanone (**s9**, 0.16 g, 0.77 mmol), TMS-EBX (0.29 g, 0.84 mmol, 1.1 equiv) and THF (13 mL) were added to an oven-dried 50 mL two-necks flask equipped with a stirrer bar. Then, the reaction mixture was cooled to –78 °C. TBAF (1 M in THF, 0.85 mL, 1.1 equiv) was added via syringe. After 1.5 hours, it was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 2:1) to give 2-ethynyl-5-fluoro-2-methoxycarbonyl-1-indanone (**s10**, 0.11 g, 0.45 mmol, 59%) as a red solid.

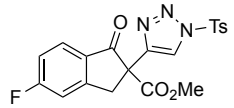


IR (ATR): 3736, 3267, 3742, 1721, 1425, 1248, 1186 cm^{-1}; ^{1}H NMR: δ = 2.44 (s, 1H), 3.49 (d, *J* = 17.6 Hz, 1H), 3.80 (s, 3H), 3.92 (d, *J* = 17.2 Hz, 1H), 7.06-7.19 (m, 2H), 7.76-7.86 (m, 1H); ^{13}C NMR: δ = 40.2, 53.9,

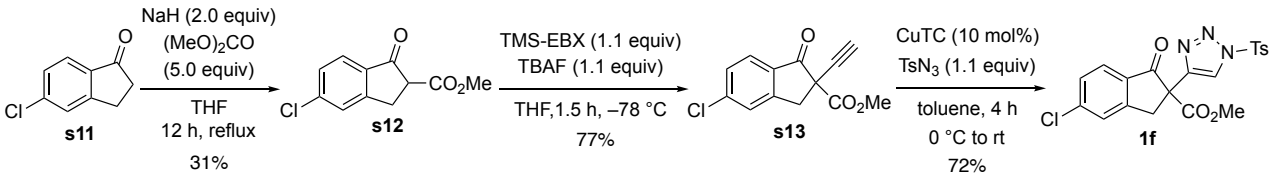
55.5, 72.6, 79.5, 113.2 (d, J = 22.0 Hz), 116.8 (d, *J* = 24.0 Hz), 128.2 (d, *J* = 11.5Hz), 129.4, 155.1(d, *J* = 10.5 Hz), 167.8, 167.9 (d, *J* = 258.8Hz), 193.9; HRMS (ESI$^+$): Calcd for $C_{13}H_9FO_3Na^+$, $[M+Na]^+$ 255.0428. Found *m/z* 255.0426.

2-Methoxycarbonyl-5-fluoro-2-(1-tosyl-1,2,3-triazol-4-yl)-1-indanone (1e)

2-Ethynyl-5-fluoro-2-methoxycarbonyl-1-indanone (**s10**, 84 mg, 0.36 mmol), CuTC (7.5 mg, 0.039 mmol, 10 mol %) and toluene (2.0 mL) were added to an oven-dried Schlenk tube equipped with a stirrer bar. Then, the reaction mixture was cooled to 0 °C. Tosyl azide (89 mg, 0.45 mmol, 1.1 equiv) was added dropwise. The resulting mixture was stirred at room temperature. After 4 hours, the reaction mixture was diluted with saturated NH_4Cl aq. (3.0 mL) and extracted with ethyl acetate (3 x 5.0 mL). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 2/1) and reprecipitation (diethyl ether/hexane = 1/1) to give 2-methoxycarbonyl-5-fluoro-2-(1-tosyl-1,2,3-triazol-4-yl)-1-indanone (**1e**, 0.13 g, 0.30 mmol, 84%) as a white solid.



IR (ATR): 3152, 2955, 1748, 1717, 1593, 1395, 1172 cm^{-1}; ^{1}H NMR: δ = 2.44 (s, 3H), 3.72 (s, 3H), 4.00 (d, *J* = 18.0 Hz, 1H), 4.22 (d, *J* = 17.4 Hz, 1H), 7.12 (t, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.78 (dd, *J* = 8.4, 5.2 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 2H), 8.57 (s, 1H); ^{13}C NMR: δ = 21.8, 36.9, 53.6, 59.8, 113.3 (d, *J* = 24.0 Hz), 116.6 (d, *J* = 24.0 Hz), 123.7, 127.8 (d, *J* = 10.5 Hz), 128.8, 129.7, 130.4, 132.7, 143.3, 147.4, 156.7 (d, *J* = 10.5 Hz), 167.9 (d, *J* = 257.8 Hz), 168.7, 196.6; HRMS (ESI$^+$): Calcd for $C_{20}H_{16}FN_3O_5SNa^+$, $[M+Na]^+$ 452.0687. Found *m/z* 452.0686.



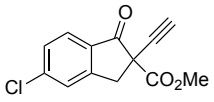
Scheme *S6* Synthesis of Triazole **1f.**

5-Chloro-2-methoxycarbonyl-1-indanone (s12)

5-Chloro-1-indanone (**s11**, 0.50 g, 3.0 mmol), 60 w% sodium hydride (0.24 g, 6.1 mmol, 2.0 equiv), dimethoxy carbonate (1.3 mL, 14 mmol, 5.0 equiv) and THF (6.0 mL) were added to an oven-dried 50 mL two-necks flask equipped with a stirrer bar. The reaction mixture was refluxed at 70 °C. After 12 hours, the reaction mixture was cooled to room temperature, and acidified with 1 M HCl aq. The resulting mixture was extracted with ethyl acetate (3 x 10 mL). The combined organic phase was washed with brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was again washed with a small amount of DCM and reprecipitation (DCM/hexane =1/20) to give 5-chloro-2-metoxycarbonyl-1-indanone (**s12**, 0.23 g, 0.93 mmol, 31%) as a light-yellow solid. The analytical data of **s12** was matched well with already reported one.[3]

5-Chloro-2-ethynyl-2-methoxycarbonyl-1-indanone (s13)

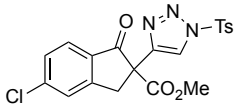
5-Chloro-2-methoxycarbonyl-1-indanone (**s12**, 0.13 g, 0.56 mmol), TMS-EBX (0.21 g, 0.62 mmol, 1.1 equiv) and THF (10 mL) were added to an oven-dried Schlenk tube equipped with a stirrer bar. Then, the reaction mixture was cooled to –78 °C. TBAF (1 M in THF, 0.70 mL, 1.1 equiv) was added via syringe. After 1.5 hours, it was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 2:1) to give 5-chloro-2-ethynyl-2-methoxycarbonyl-1-indanone (**s13**, 0.11 g, 0.43 mmol, 77%) as a red solid.



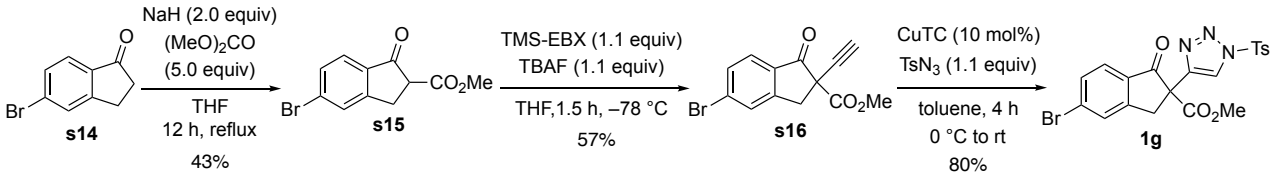
IR (ATR): 3264, 2955, 1744, 1719, 1599, 1263, 1190 cm^{-1}; ^1H NMR: δ = 2.45 (s, 1H), 3.49 (d, *J* = 17.6 Hz, 1H), 3.81 (s, 3H), 3.92 (d, *J* = 17.2 Hz, 1H), 7.40-7.44 (m, 1H), 7.49-7.52 (m, 1H), 7.76 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR: δ =40.1, 54.0, 55.4, 72.7, 79.4, 126.6, 126.9, 129.2, 131.5, 142.9, 153.5, 167.8, 194.4; HRMS (ESI^+): Calcd for $C_{13}H_9ClO_3Na^+$, $[M+Na]^+$ 271.0132. Found *m/z* 271.0130.

5-Chloro-2-methoxycarbonyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1-indanone (1f)

5-Chloro-2-ethynyl-2-methoxycarbonyl-1-indanone (**s13**, 91 mg, 0.36 mmol), CuTC (7.1 mg, 0.037 mmol, 10 mol %) and toluene (2.0 mL) were added to an oven-dried Schlenk tube equipped with a stirrer bar. Then, the reaction mixture was cooled to 0 °C. Tosyl azide (90 mg, 0.45 mmol, 1.1 equiv) was added dropwise. The resulting mixture was stirred at room temperature. After 4 hours, the reaction mixture was diluted with saturated NH_4Cl aq. (3.0 mL) and extracted with ethyl acetate (3 x 5.0 mL). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 2/1) to give 5-chloro-2-methoxycarbonyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1-indanone (**1f**, 0.12 g, 0.26 mmol, 72%) as a white solid.



IR (ATR): 3154, 2957, 1748, 1717, 1593, 1395, 1194, 1175 cm^{-1}; ^1H NMR: δ = 2.42 (s, 3H), 3.71 (s, 3H), 3.98 (d, *J* = 17.6 Hz, 1H), 4.20 (d, *J* = 18.0 Hz, 1H), 7.31-7.42 (m, 3H), 7.54 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 2H), 8.56 (s, 1H); ^{13}C NMR: δ = 21.8, 36.8, 53.6, 59.6, 123.7, 126.4, 126.7, 128.8, 128.9, 130.4, 131.8, 132.8, 142.8, 143.3, 147.4, 155.0, 168.6, 197.1; HRMS (ESI^+): Calcd for $C_{20}H_{16}ClN_3O_5SNa^+$, $[M+Na]^+$ 468.0391. Found *m/z* 468.0391.



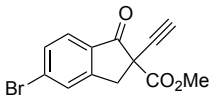
Scheme *S7* Synthesis of Triazole **1g.**

5-Bromo-2-methoxycarbonyl-1-indanone (s15)

5-Bromo-1-indanone (**s14**, 0.63 g, 3.0 mmol), 60 w% sodium hydride (0.24 g, 6.1 mmol, 2.0 equiv), dimethoxy carbonate (1.3 mL, 14 mmol, 5.0 equiv) and THF (6.0 mL) were added to an oven-dried 50 mL two-necks flask equipped with a stirrer bar. The reaction mixture was refluxed at 70 ℃. After 12 hours, the reaction mixture was cooled to room temperature, and acidified with 1 M HCl aq. The resulting mixture was extracted with ethyl acetate (3 x 10 mL). The combined organic phase was washed with brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was washed with DCM to give 5-bromo-2-metoxycarbonyl-1-indanone (**s15**, 0.35 g, 1.3 mmol, 43%) as a light-purple solid. The analytical data of **s15** was matched well with already reported one.[3]

5-Bromo-2-ethynyl-2-methoxycarbonyl-1-indanone (s16)

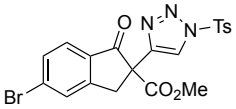
5-Bromo-2-methoxycarbonyl-1-indanone (**s15**, 0.27 g, 1.0 mmol), TMS-EBX (0.38 g, 1.1 mmol, 1.1 equiv) and THF (17 mL) were added to an oven-dried Schlenk tube equipped with a stirrer bar. Then, the reaction mixture was cooled to –78 ℃. TBAF (1 M in THF, 1.1 mL, 1.1 equiv) was added via syringe. After 1.5 hours, it was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 2:1) and recrystallization (DCM/hexane = 1/10) to give 5-bromo-2-ethynyl-2-methoxycarbonyl-1-indanone (**s16**, 0.17 g, 0.57 mmol, 57%) as a red solid.



IR (ATR): 3260, 2955, 1742, 1722, 1595, 1261, 1057 cm^{-1}; ^1H NMR: δ = 2.44 (s, 1H), 3.49 (d, *J* = 17.2 Hz, 1H), 3.80 (s, 3H), 3.92 (d, *J* = 17.2 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.65-7.72 (m, 2H); ^{13}C NMR: δ = 40.0, 54.0, 55.3, 72.7, 79.3, 126.9, 129.7, 131.7, 131.9, 132.0, 153.6, 167.7, 194.6; HRMS (ESI^+): Calcd for $C_{13}H_9BrO_3Na^+$, $[M+Na]^+$ 314.9627. Found *m/z* 314.9626.

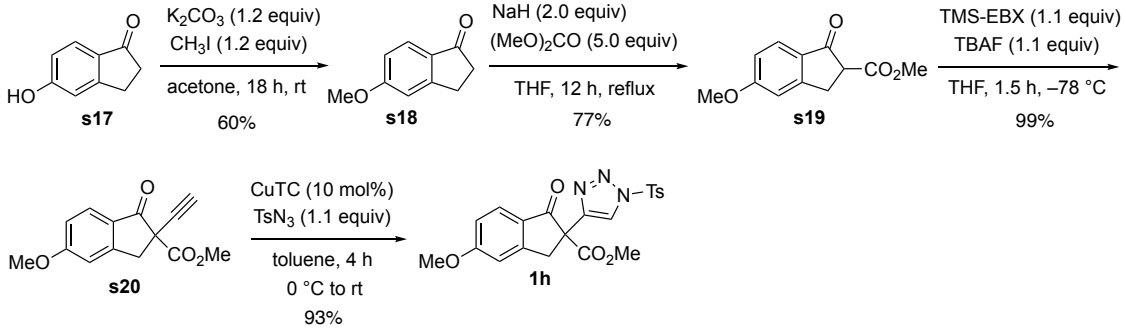
5-Bromo-2-methoxycarbonyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1-indanone (1g)

5-Bromo-2-ethynyl-2-methoxycarbonyl-1-indanone (**s16**, 0.16 g, 0.53 mmol), CuTC (11.2 mg, 0.059 mmol, 10 mol %) and toluene (3.0 mL) were added to an oven-dried Schlenk tube equipped with a stirrer bar. Then, the reaction mixture was cooled to 0 ℃. Tosyl azide (0.11 g, 0.56 mmol, 1.1 equiv) was added dropwise. The resulting mixture was stirred at room temperature. After 4 hours, the reaction mixture was diluted with saturated NH_4Cl aq. (3.0 mL) and extracted with ethyl acetate (3 x 5.0 mL). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 2/1) to give 5-bromo-2-methoxycarbonyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1-indanone (**1g**, 0.21 g, 0.43 mmol, 80%) as a white solid.



IR (ATR): 2955, 1749, 1717, 1593, 1395, 1194, 1175 cm^{-1}; ^1H NMR: δ = 2.44 (s, 3H), 3.72 (s, 3H), 3.87 (d, *J* = 17.6 Hz, 1H), 4.21 (d, *J* = 18.0 Hz, 1H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.74 (s, 1H), 8.00 (d, *J* = 8.4 Hz, 2H), 8.56 (s, 1H); ^{13}C NMR: δ = 21.7, 36.8, 53.6, 59.5, 123.7, 126.4,

128.7, 129.8, 130.4, 131.7, 132.2, 132.7, 143.2, 147.3, 155.0, 168.5, 197.3; HRMS (ESI^+): Calcd for $C_{20}H_{16}BrN_3O_5SNa^+$, $[M+Na]^+$ 511.9886. Found *m/z* 511.9887.



Scheme *S8* Synthesis of Triazole **1h.**

5-Methoxy-1-indanone (s18)

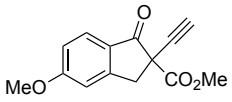
5-Hydroxy-1-indanone (**s17**, 0.74 g, 5.0 mmol), potassium carbonate (0.83 g, 6.0 mmol, 1.2 equiv), iodomethane (0.40 mL, 6.0 mmol, 1.2 equiv) and acetone (10 mL) were added to an oven-dried 50 mL two-necks flask equipped with a stirrer bar. The reaction mixture was stirred at room temperature. After 18 hours, it was concentrated under reduced pressure. The residue was diluted with water (10 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic phase was washed with brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 2:1) to give 5-methoxy-1-indanone (**s18**, 0.49 g, 3.0 mmol, 60%) as a yellow solid. The analytical data of **s18** was matched well with already reported one.[4]

5-Methoxy-2-methoxycarbonyl-1-indanone (s19)

5-Methoxy-1-indanone (**s19**, 0.48 g, 3.0 mmol), 60 w% sodium hydride (0.26 g, 6.0 mmol, 2.0 equiv), dimethoxy carbonate (1.3 mL, 14 mmol, 5.0 equiv) and THF (8.0 mL) were added to an oven-dried 50 mL two-necks flask equipped with a stirrer bar. The reaction mixture was refluxed at 70 ℃. After 12 hours, the reaction mixture was cooled to room temperature, and acidified with 1 M HCl aq. The resulting mixture was extracted with ethyl acetate (3 x 10 mL). The combined organic phase was washed with brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (hexane/ethyl acetate = 2:1) to give 5-methoxy-2-methoxycarbonyl-1-indanone (**s19**, 0.56 g, 2.3 mmol, 77%) as a light-orange solid. The analytical data of **s19** was matched well with already reported one.[3]

2-Ethynyl-5-methoxy-2-methoxycarbonyl-1-indanone (s20)

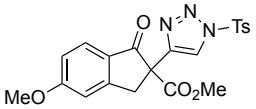
5-Methoxy-2-methoxycarbonyl-1-indanone (**s19**, 0.49 g, 2.2 mmol), TMS-EBX (0.87 g, 2.5 mmol, 1.1 equiv) and THF (40 mL) were added to an oven-dried 50 mL two-necks flask equipped with a stirrer bar. Then, the reaction mixture was cooled to –78 ℃. TBAF (1 M in THF, 2.5 mL, 1.1 equiv) was added via syringe. After 1.5 hours, it was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 2:1) to give 2-ethynyl-5-methoxy-2-methoxycarbonyl-1-indanone (**s20**, 0.57 g, 2.3 mmol, 99%) as a red solid.



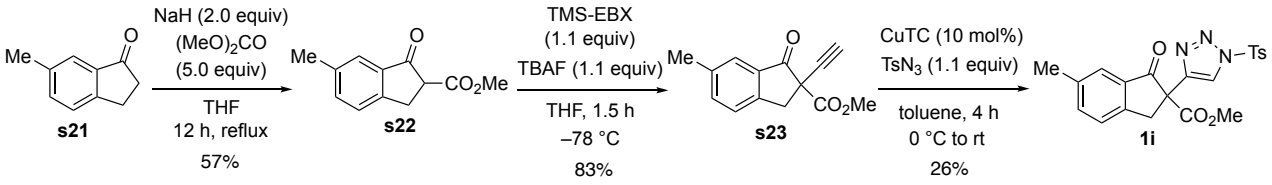
IR (ATR): 3258, 2953, 1724, 1701, 1591, 1433, 1254, 1092 cm^{-1}; ^1H NMR: δ = 2.43 (s, 1H), 3.46 (d, *J* = 17.2 Hz, 1H), 3.81 (s, 3H), 3.90 (d, *J* = 17.2 Hz, 1H), 3.91 (s, 3H), 6.91 (d, *J* = 2.0 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR: δ = 40.4, 53.8, 55.5, 55.8, 72.2, 80.2, 109.4, 116.5, 126.0, 127.6, 155.4, 166.4, 168.4, 193.8; HRMS (ESI^+): Calcd for $C_{14}H_{12}O_4Na^+$, $[M+Na]^+$ 267.0628. Found *m/z* 267.0624.

5-Methoxy-2-methoxycarbonyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1-indanone (1h)

2-Ethynyl-5-methoxy-2-methoxycarbonyl-1-indanone (**s20**, 0.40 g, 1.6 mmol), CuTC (31.5 mg, 0.16 mmol, 10 mol %) and toluene (8.0 mL) were added to an oven-dried 50 mL two-necks flask equipped with a stirrer bar. Then, the reaction mixture was cooled to 0 °C. Tosyl azide (0.38 g, 1.9 mmol, 1.1 equiv) was added dropwise. The resulting mixture was stirred at room temperature. After 4 hours, the reaction mixture was diluted with saturated NH_4Cl aq. (20 mL) and extracted with ethyl acetate (3 x 20 mL). The combined organic phase was washed with brine (30 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography (hexane/ethyl acetate = 2/1) and recrystallization (DCM/hexane = 1/10) to give 5-methoxy-2-methoxycarbonyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1-indanone (**1h**, 0.66 g, 1.5 mmol, 93%) as a white solid.



IR (ATR): 3144, 2972, 1730, 1705, 1601, 1406, 1260, 1196, 1088 cm^{-1}; ^1H NMR: δ = 2.39 (s, 3H), 3.68 (s, 3H), 3.86 (s, 3H), 3.95 (d, *J* = 17.2 Hz, 1H), 4.13 (d, *J* = 17.6 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 1H), 6.94 (s, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 2H), 8.56 (s, 1H); ^{13}C NMR: δ = 21.6, 37.0, 53.3, 55.7, 59.6, 109.2, 116.4, 123.6, 126.2, 127.0, 128.6, 130.3, 132.7, 143.9, 147.2, 156.8, 166.4, 169.1, 196.3; HRMS (ESI^+): Calcd for $C_{21}H_{19}N_3O_6SNa^+$, $[M+Na]^+$ 464.0887. Found *m/z* 464.0881.



Scheme *S9* Synthesis of Triazole **1i.**

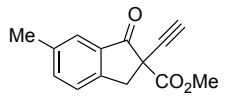
6-Methyl-2-methoxycarbonyl-1-indanone (s22)

6-Methyl-1-indanone (**s21**, 0.73 g, 5.0 mmol), 60 w% sodium hydride (0.41 g, 10 mmol, 2.0 equiv), dimethoxy carbonate (2.2 mL, 10 mmol, 5.0 equiv) and THF (13 mL) were added to an oven-dried 50 mL two-necks flask equipped with a stirrer bar. The reaction mixture was refluxed at 70 °C. After 12 hours, the reaction mixture was cooled to room temperature, and acidified with 1 M HCl aq. The resulting mixture was extracted with ethyl acetate (3 x 10 mL). The combined organic phase was washed with brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography

(hexane/ethyl acetate = 2:1) and recrystallization (DCM/hexane = 1/10) to give 6-methyl-2-methoxycarbonyl-1-indanone (**s22**, 0.58 g, 2.9 mmol, 57%) as a light-orange solid. The analytical data of **s22** was matched well with already reported one.[3]

2-Ethynyl-6-methyl-2-methoxycarbonyl-1-indanone (s23)

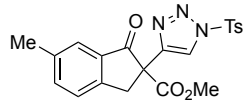
6-Methyl-2-methoxycarbonyl-1-indanone (**s22**, 0.58 g, 2.9 mmol), TMS-EBX (1.1 g, 3.2 mmol, 1.1 equiv) and THF (40 mL) were added to an oven-dried 50 mL two-necks flask equipped with a stirrer bar. Then, the reaction mixture was cooled to –78 ℃. TBAF (1 M in THF, 3.2 mL, 1.1 equiv) was added via syringe. After 1.5 hours, it was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 2:1) and recrystallization (DCM/hexane = 1/10) to give 2-ethynyl-6-methyl-2-methoxycarbonyl-1-indanone (**s23**, 0.54 g, 2.4 mmol, 83%) as a light-orange solid.



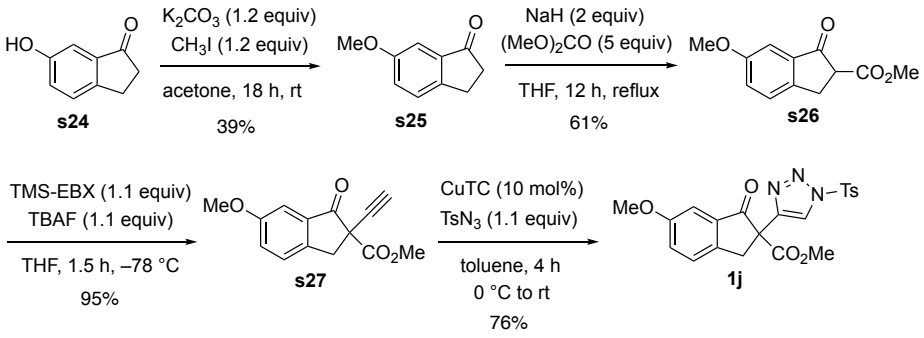
IR (ATR): 3264, 2959, 1740, 1719, 1431, 1263, 1204, 1180 cm^{-1}; ^1H NMR: δ = 2.40-2.43 (m, 4H), 3.47 (d, *J* = 16.8 Hz, 1H), 3.78 (s, 3H), 3.89 (d, *J* = 16.8 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.63 (s, 1H); ^{13}C NMR: δ = 21.0, 40.2, 53.8, 55,6, 72.2, 80.0, 125.7, 126.0, 133.2, 137.4, 138.4, 149.6, 168.3, 195.9; HRMS (ESI^+): Calcd for $C_{14}H_{12}O_3Na^+$, $[M+Na]^+$ 251.0679. Found *m/z* 251.0675.

6-Methyl-2-methoxycarbonyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1-indanone (1i)

2-Ethynyl-6-methyl-2-methoxycarbonyl-1-indanone (**s23**, 0.48 g, 2.1 mmol), CuTC (40 mg, 0.21 mmol, 10 mol %) and toluene (11 mL) were added to an oven-dried 50 mL two-necks flask equipped with a stirrer bar. Then, the reaction mixture was cooled to 0 ℃. Tosyl azide (0.44 g, 2.2 mmol, 1.1 equiv) was added dropwise. The resulting mixture was stirred at room temperature. After 4 hours, the reaction mixture was diluted with saturated NH_4Cl aq. (20 mL) and extracted with ethyl acetate (3 x 20 mL). The combined organic phase was washed with brine (30 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was again washed with a small amount of DCM to give 6-methyl-2-methoxycarbonyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1-indanone (**1i**, 0.23 g, 0.54 mmol, 26%) as a white solid.



IR (ATR): 3167, 1734, 1713, 1395, 1229, 1198, 1175 cm^{-1}; ^1H NMR: δ = 2.40 (s, 3H), 2.43 (s, 3H), 3.70 (s, 3H), 3.96 (d, *J* = 17.6 Hz, 1H), 4.16 (d, *J* = 17.6 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.56 (s, 1H), 8.00 (d, *J* = 8.4 Hz, 2H), 8.55 (s, 1H); ^{13}C NMR: δ = 21.0, 21.7, 36.9, 53.4, 59.7, 123.6, 125.2, 126.1, 128.7, 130.4, 132.8, 133.5, 137.4, 138.1, 143.8, 147.3, 151.1, 169.1, 198.6; HRMS (ESI^+): Calcd for $C_{21}H_{19}N_3O_5SNa^+$, $[M+Na]^+$ 448.0938. Found *m/z* 448.0933.



Scheme *S10* Synthesis of Triazole **1j.**

6-Methoxy-1-indanone (s25)

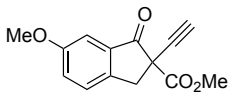
6-Hydroxy-1-indanone (**s24**, 0.86 g, 4.8 mmol), potassium carbonate (0.83 g, 6.0 mmol, 1.2 equiv), iodomethane (0.40 mL, 6.0 mmol, 1.2 equiv) and acetone (10 mL) were added to an oven-dried 50 mL two-necks flask equipped with a stirrer bar. The reaction mixture was stirred at room temperature. After 18 hours, it was concentrated under reduced pressure. The residue was added water (10 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic phase was washed with brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 2:1) to give 6-methoxy-1-indanone (**s25**, 0.30 g, 1.7 mmol, 39%) as a yellow solid. The analytical data of **s25** was matched well with already reported one.[4,5]

6-Methoxy-2-methoxycarbonyl-1-indanone (s26)

6-Methoxy-1-indanone (**s25**, 0.30 g, 1.7 mmol), 60 w% sodium hydride (0.15 g, 0.37 mmol, 2.0 equiv), dimethoxy carbonate (1.0 mL, 11 mmol, 5 equiv) and THF (6.0 mL) were added to an oven-dried 50 mL two-necks flask equipped with a stirrer bar. The reaction mixture was refluxed at 70 °C. After 12 hours, the reaction mixture was cooled to room temperature, and acidified with 1 M HCl aq. The resulting mixture was extracted with ethyl acetate (3 x 10 mL). The combined organic phase was washed with brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (hexane/ethyl acetate = 2:1) to give 6-methoxy-2-methoxycarbonyl-1-indanone (**s26**, 0.25 g, 1.1 mmol, 61%) as a yellow oil. The analytical data of **s26** was matched well with already reported one.[3]

2-Ethynyl-6-methoxy-2-methoxycarbonyl-1-indanone (s27)

6-Methoxy-2-methoxycarbonyl-1-indanone (**s26**, 0.24 g, 1.1 mmol), TMS-EBX (0.42 g, 1.2 mmol, 1.1 equiv) and THF (18 mL) were added to an oven-dried 50 mL two-necks flask equipped with a stirrer bar. Then, the reaction mixture was cooled to –78 °C. TBAF (1 M in THF, 1.2 mL, 1.1 equiv) was added via syringe. After 1.5 hours, it was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 2:1) and recrystallization (DCM/hexane = 1/10) to give 2-ethynyl-6-methoxy-2-methoxycarbonyl-1-indanone (**s27**, 0.25 g, 1.0 mmol, 95%) as a white solid.

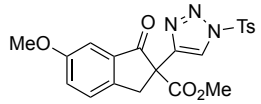


IR (ATR): 3275, 2968, 1748, 1717, 1491, 1306, 1267, 1020 cm^{-1}; ^1H NMR: δ = 2.44 (s, 1H), 3.45 (d, *J* = 16.8 Hz, 1H), 3.80 (s, 3H), 3.84 (s, 3H), 3.84 (d, *J* = 16.4 Hz, 1H), 7.20-7.29 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 1H); ^{13}C

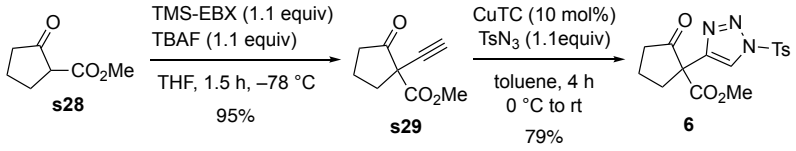
NMR: δ = 39.8, 53.8, 55.6, 55.9, 72.3, 79.9, 106.5, 125.7, 127.0, 134.2, 145.1, 159.9, 168.2, 195.8; HRMS (ESI^+): Calcd for $C_{14}H_{12}O_4Na^+$, $[M+Na]^+$ 267.0628. Found *m/z* 267.0625.

6-Methoxy-2-methoxycarbonyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1-indanone (1j)

2-Ethynyl-6-methoxy-2-methoxycarbonyl-1-indanone (**s27**, 0.22 g, 0.9 mmol), CuTC (19 mg, 0.10 mmol, 10 mol %) and toluene (5.0 mL) were added to an oven-dried 50 mL two-necks flask equipped with a stirrer bar. Then, the reaction mixture was cooled to 0 ℃. Tosyl azide (0.22 g, 1.1 mmol, 1.1 equiv) was added dropwise. The resulting mixture was stirred at room temperature. After 4 hours, the reaction mixture was diluted with saturated NH_4Cl aq. (20 mL) and extracted with ethyl acetate (3 x 20 mL). The combined organic phase was washed with brine (30 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was washed with a small amount of DCM to give 6-methoxy-2-methoxycarbonyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1-indanone (**1j**, 0.30 g, 0.69 mmol, 76%) as a white solid.



IR (ATR): 3192, 2955, 1748, 1715, 1491, 1398, 1221, 1194, 1173 cm^{-1}; ^1H NMR: δ = 2.41 (s,3H), 3.69 (s, 3H), 3.80 (s, 3H), 3.91 (d, *J* = 17.2 Hz, 1H), 4.10 (d, *J* = 17.2 Hz, 1H), 7.16 (d, *J* = 2.4 Hz, 1H), 7.24 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 8.54 (s, 1H); ^{13}C NMR: δ = 21.7, 36.7, 53.4, 55.6, 60.1, 106.1, 123.5, 125.6, 127.1, 128.7, 130.3, 132.8, 134.6, 143.7, 146.6, 147.3, 159.8, 169.1, 198.5; HRMS (ESI^+): Calcd for $C_{21}H_{19}N_3O_6SNa^+$, $[M+Na]^+$ 464.0887. Found *m/z* 464.0886.



Scheme *S11* Synthesis of Triazole **6**

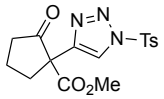
2-Ethynyl-2-methoxycarbonyl-1-cyclopentanone (s29)

2-Methoxycarbonyl-1-cyclopentanone (**s28**, 0.72 g, 5.0 mmol), TMS-EBX (1.9 g, 5.5 mmol, 1.1 equiv) and THF (80 mL) were added to an oven-dried 100 mL two-necks flask equipped with a stirrer bar. Then, the reaction mixture was cooled to –78 ℃. TBAF (1 M in THF, 5.5 mL, 1.1 equiv) was added via syringe. After 1.5 hours, it was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 2:1) to give 2-ethynyl-2-methoxycarbonyl-1-cyclopentanone (**s29**, 0.79 g, 4.8 mmol, 95%) as a white solid.

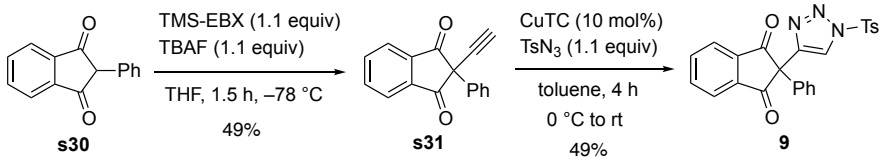
2-Methoxycarbonyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1-cyclopentanone (6)

2-Ethynyl-2-methoxycarbonyl-1-cyclopentanone (**s29**, 0.79 g, 4.8 mmol), CuTC (0.10 g, 0.50 mmol, 10 mol %) and toluene (24 mL) were added to an oven-dried 50 mL two-necks flask equipped with a stirrer bar. Then, the reaction mixture was cooled to 0 ℃. Tosyl azide (1.1 g, 5.5 mmol, 1.1 equiv) was added dropwise.

The resulting mixture was stirred at room temperature. After 4 hours, the reaction mixture was diluted with saturated NH_4Cl aq. (20 mL) and extracted with ethyl acetate (3 x 20 mL). The combined organic phase was washed with brine (30 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 2:1) to give 2-methoxycarbonyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1-cyclopentanone (**6**, 1.4 g, 3.8 mmol, 79%) as a white solid.



IR (ATR): 3165, 2957, 1763, 1724, 1391, 1192, 1167 cm^{-1}; ^1H NMR: δ = 2.02-2.22 (m, 2H), 2.33-2.46 (m, 4H), 2.47-2.59 (m, 1H), 2.77-2.95 (m, 2H), 3.73 (s, 3H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 2H), 8.36 (s, 1H); ^{13}C NMR: δ = 20.0, 21.8, 34.0, 37.6, 53.2, 59.3, 123.2, 128.7, 130.4, 132.7, 143.4, 147.3, 169.3, 210.9 ; HRMS (ESI^+): Calcd for $C_{16}H_{17}N_3O_5SNa^+$, $[M+Na]^+$ 386.0781. Found *m/z* 386.0781.



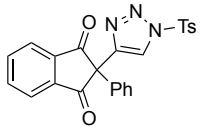
Scheme *S12* Synthesis of Triazole **9**

2-Ethynyl-2-phenyl-1,3-indandione (s31)

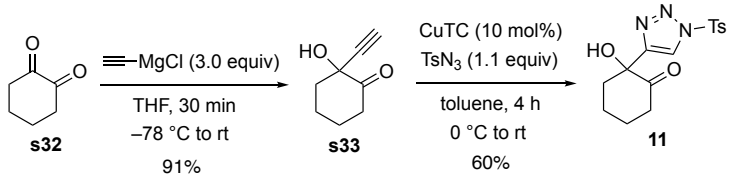
2-Phenyl-1,3-indandione (**s30**, 1.1 g, 5.0 mmol), TMS-EBX (1.9 g, 5.5 mmol, 1.1 equiv) and THF (80 mL) were added to an oven-dried 200 mL two-necks flask equipped with a stirrer bar. Then, the reaction mixture was cooled to –78 °C. TBAF (1 M in THF, 5.5 mL, 1.1 equiv) was added via syringe. After 1.5 hours, it was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 4:1) to give 2-ethynyl-2-phenyl-1,3-indandione (**s31**, 0.61 g, 2.5 mmol, 49%) as an orange solid. The analytical data of **s31** was matched well with already reported one.[7]

2-Phenyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1,3-indandione (9)

2-Ethynyl-2-phenyl-1,3-indandione (**s31**, 0.47 g, 1.9 mmol), CuTC (39 mg, 0.20 mmol, 10 mol %) and toluene (20 mL) were added to an oven-dried 50 mL two-necks flask equipped with a stirrer bar. Then, the reaction mixture was cooled to 0 °C. Tosyl azide (0.58 g, 2.1 mmol, 1.1 equiv) was added dropwise. The resulting mixture was stirred at room temperature. After 4 hours, the reaction mixture was diluted with saturated NH_4Cl aq. (20 mL) and extracted with ethyl acetate (3 x 20 mL). The combined organic phase was washed with brine (30 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was washed by DCM/hexane = 1/1 to give 2-phenyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1,3-indandione (**9**, 0.41 g, 0.93 mmol, 49%) as a white solid.



IR (ATR): 3161, 1748, 1701, 1395, 1196, 1182 cm^{-1}; ^1H NMR: δ = 2.44 (s, 3H), 7.29-7.41 (m, 5H), 7.43-7.49 (m, 2H), 7.89 (dd, *J* = 7.6, 3.2 Hz, 2H), 7.91 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 2H), 8.07 (dd, *J* = 5.6, 3.2 Hz, 2H); ^{13}C NMR: δ = 21.8, 60.9, 124.2, 124.4, 127.7, 128.7, 128.9, 129.2, 130.5, 132.6, 134.3, 136.5, 141.4, 146.1, 147.5, 196.7 ; HRMS (APCI$^+$): Calcd for $C_{24}H_{18}N_3O_4S^+$, $[M+H]^+$ 444.1013. Found *m/z* 444.1016.



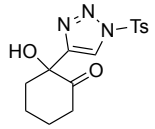
Scheme *S13* Synthesis of Triazole **11**

2-Ethynyl-2-hydroxy-1-cyclohexanone (s33)

1,2-Cyclohexadione (**s32**, 0.34 g, 3.0 mmol) and THF (8.0 mL) were added to an oven-dried 50 mL two-necks flask equipped with a stirrer bar. Then, the reaction mixture was cooled to –78 ℃. Ethynyl magnesium chloride (0.5 M in THF, 18 mL, 3 equiv) was added via syringe. The resulting mixture stirred at room temperature. After 30 minutes, it was diluted with iced water (10 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic phase was washed with brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 2:1) to give 2-ethynyl-2-hydroxy-1-cyclohexanone (**s33**, 0.38 g, 2.7 mmol, 91%) as an orange oil. The analytical data of **s33** was matched well with already reported one.[8]

2-Hydroxy-2-(1-tosyl-1,2,3-triazol-4-yl)-1-cyclohexanone (11)

2-Ethynyl-2-hydroxy-1-cyclohexanone (**s33**, 0.38 g, 2.7 mmol), CuTC (52 mg, 0.27 mmol, 10 mol %) and toluene (15 mL) was added to an oven-dried 50 mL two-necks flask equipped with a stirrer bar. Then, the reaction mixture was cooled to 0 ℃. Tosyl azide (0.57 g, 2.9 mmol, 1.1 equiv) was added dropwise. The resulting mixture was stirred at room temperature. After 4 hours, the reaction mixture was diluted with saturated NH_4Cl aq. (20 mL) and extracted with ethyl acetate (3 x 20 mL). The combined organic phase was washed with brine (30 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 2:1) to give 2-hydroxy-2-(1-tosyl-1,2,3-triazol-4-yl)-1-cyclohexanone (**11**, 0.54 g, 1.6 mmol, 60%) as a white solid.



IR (ATR): 3493, 3129, 2955, 1713, 1393, 1192, 1175, 1011 cm^{-1}; ^1H NMR: δ = 1.67-1.84 (m, 2H), 1.90 (dt, *J* = 13.6, 4.0 Hz, 1H), 2.13-2.25 (m, 2H), 2.46 (s, 3H), 2.51-2.64 (m, 2H), 3.04 (dt, *J* =14.0, 5.6 Hz, 1H), 7.39 (d, *J* =8.4 Hz, 2H), 8.00 (d, *J* = 8.4 HZ, 2H), 8.15 (s, 1H); ^{13}C NMR: δ = 21.7, 21.9, 28.0, 38.3, 42.0, 76.1, 121.9, 128.9, 130.5, 132.7, 147.6, 149.8, 209.6; HRMS (ESI$^+$): Calcd for $C_{15}H_{17}N_3O_4SNa^+$, $[M+Na]^+$358.0832. Found *m/z* 358.0836.

12. Reference

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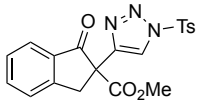
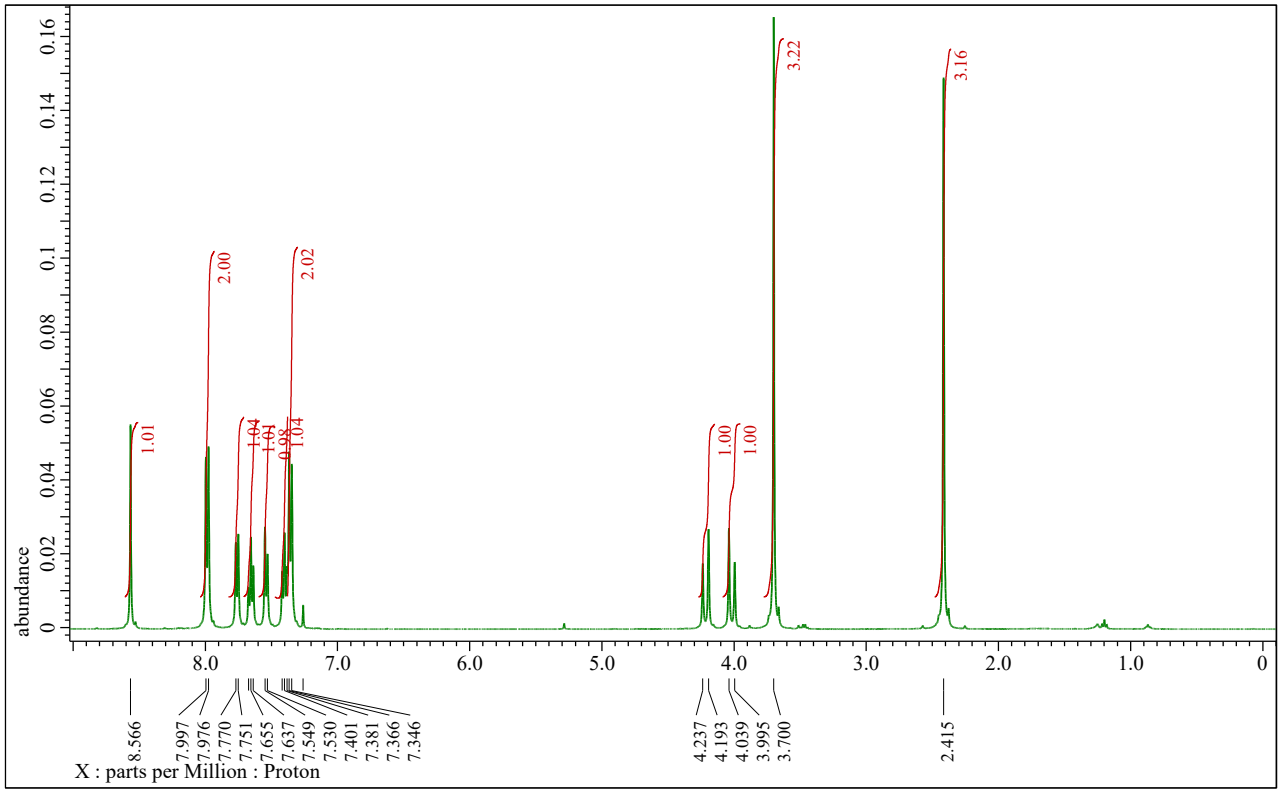
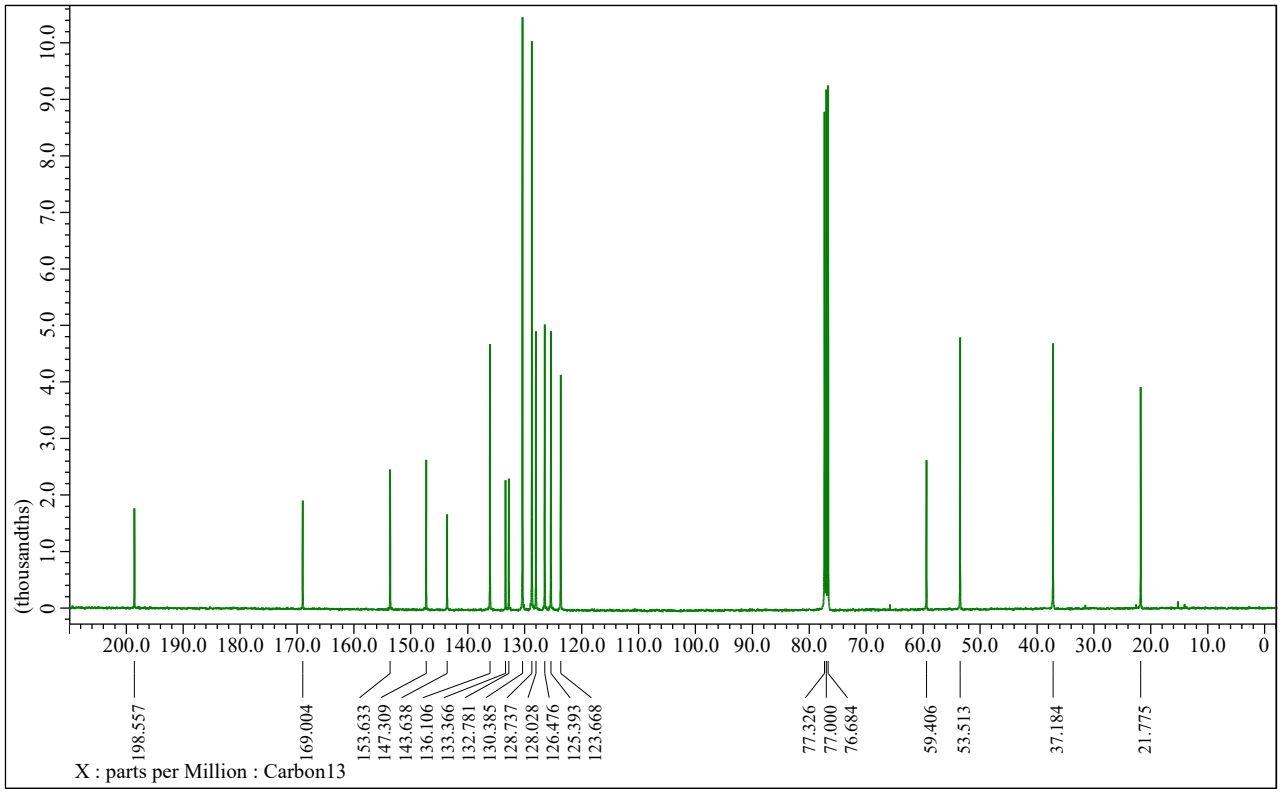
13. ^{1}H and ^{13}C NMR charts

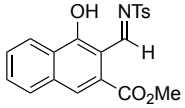
2-Methoxycarbonyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1-indanone (1a)

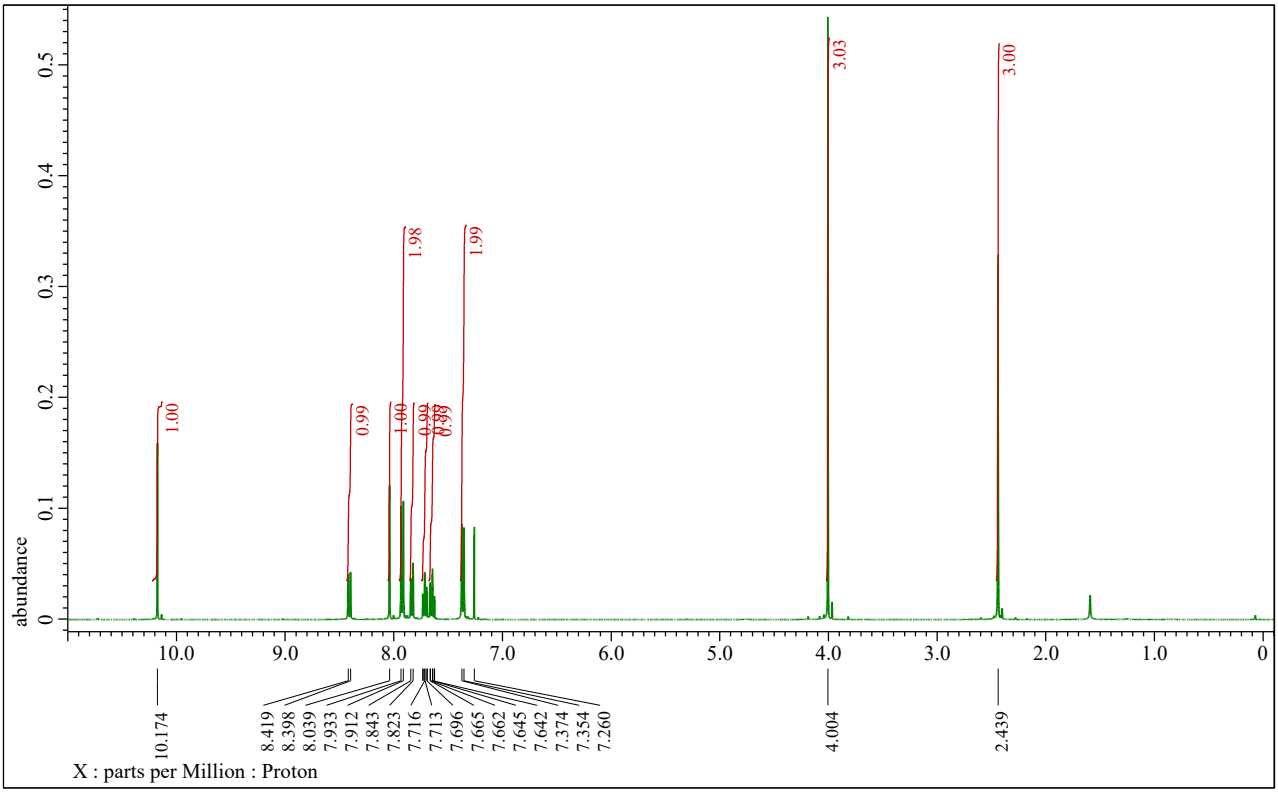


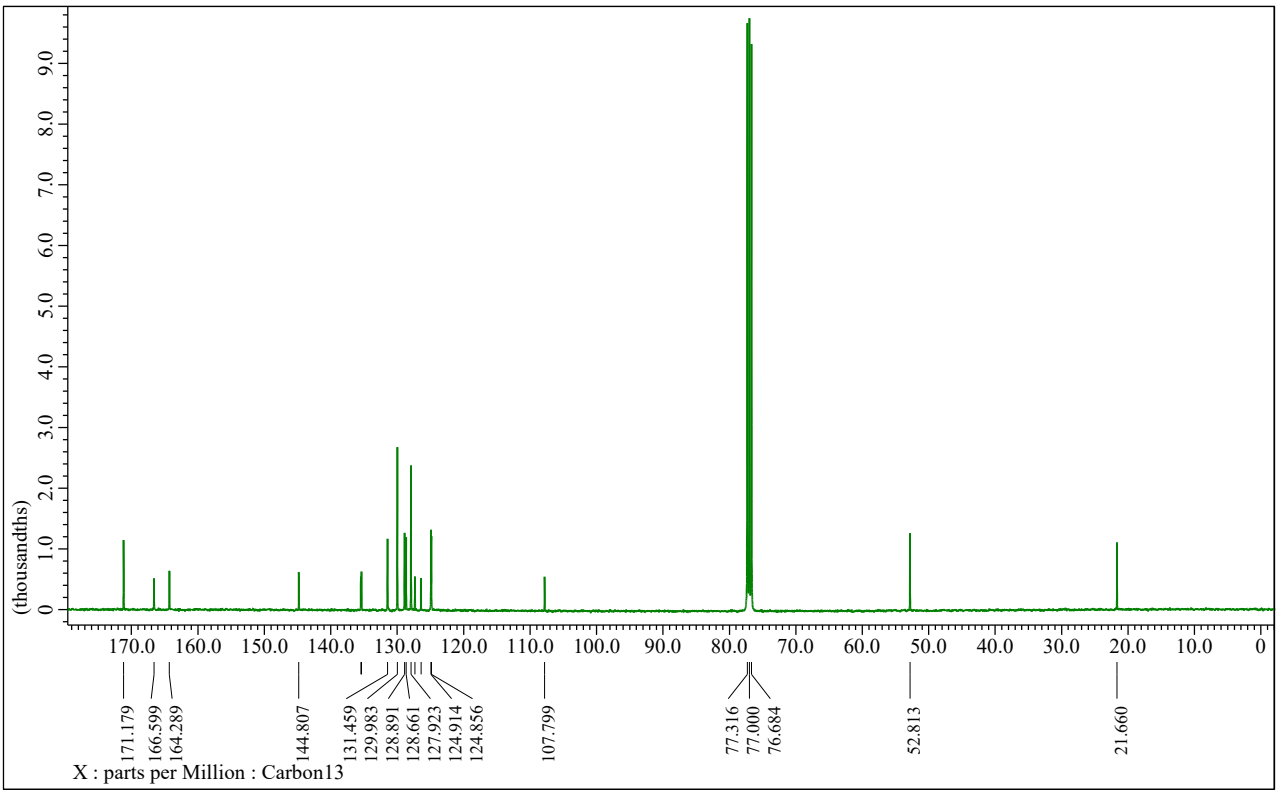




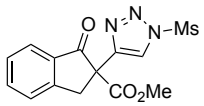
3-Methoxycarbonyl-2-(*N*-tosyl-iminomethyl)-1-naphthol (2a)

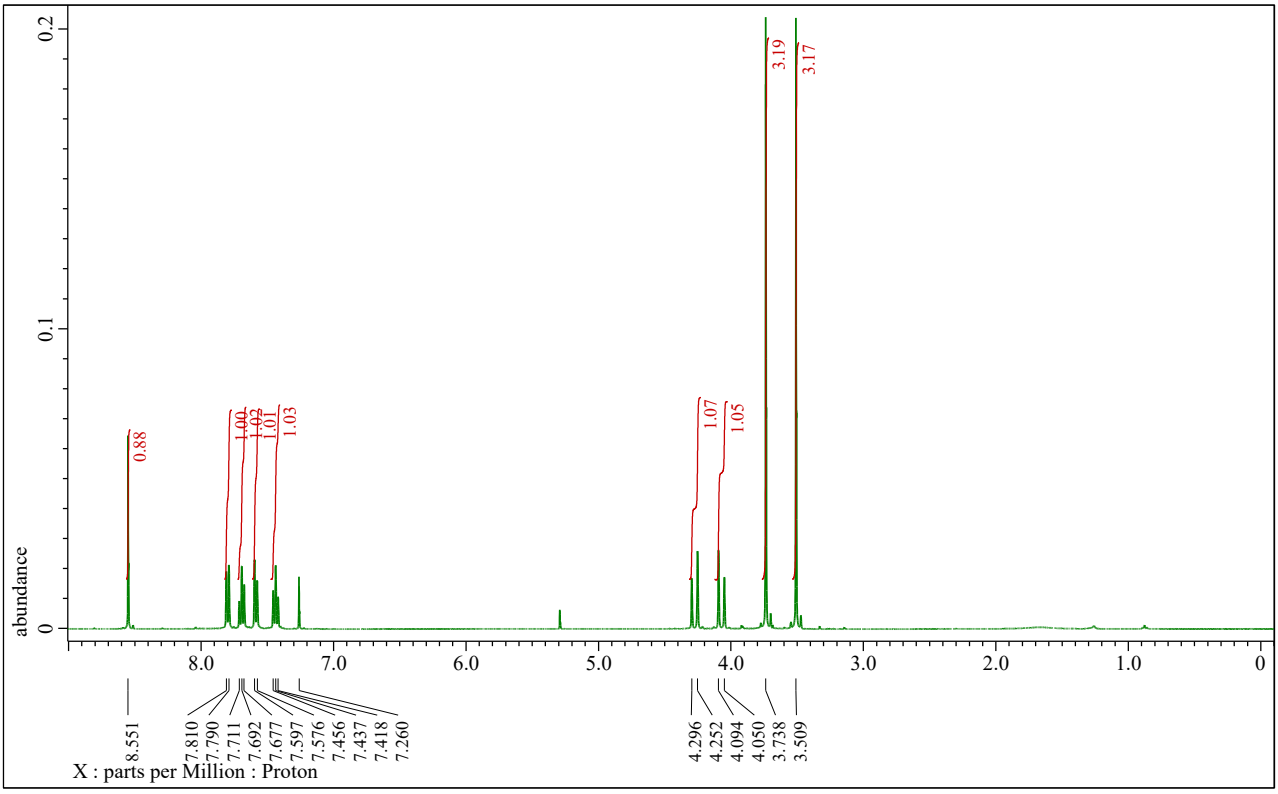


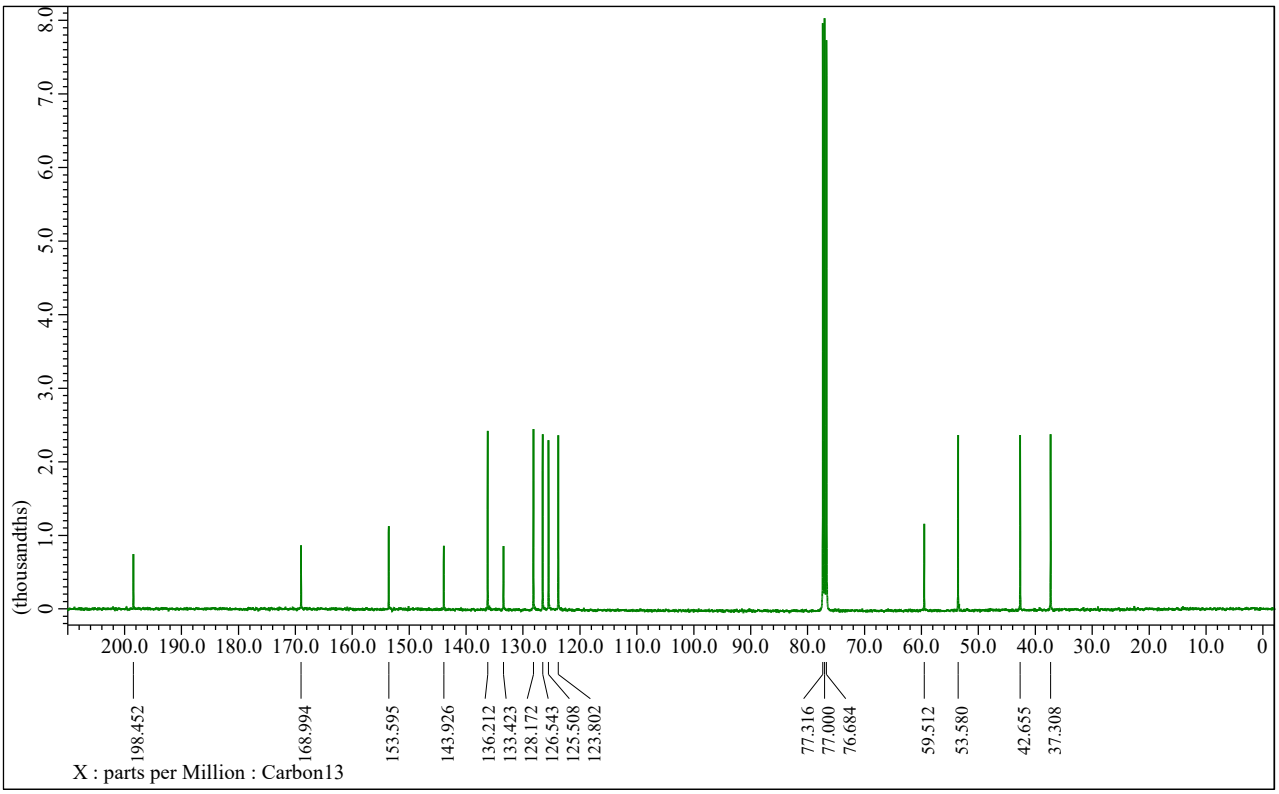




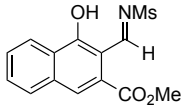
2-Methoxycarbonyl-2-(1-mesyl-1,2,3-triazol-4-yl)-1-indanone (1b)

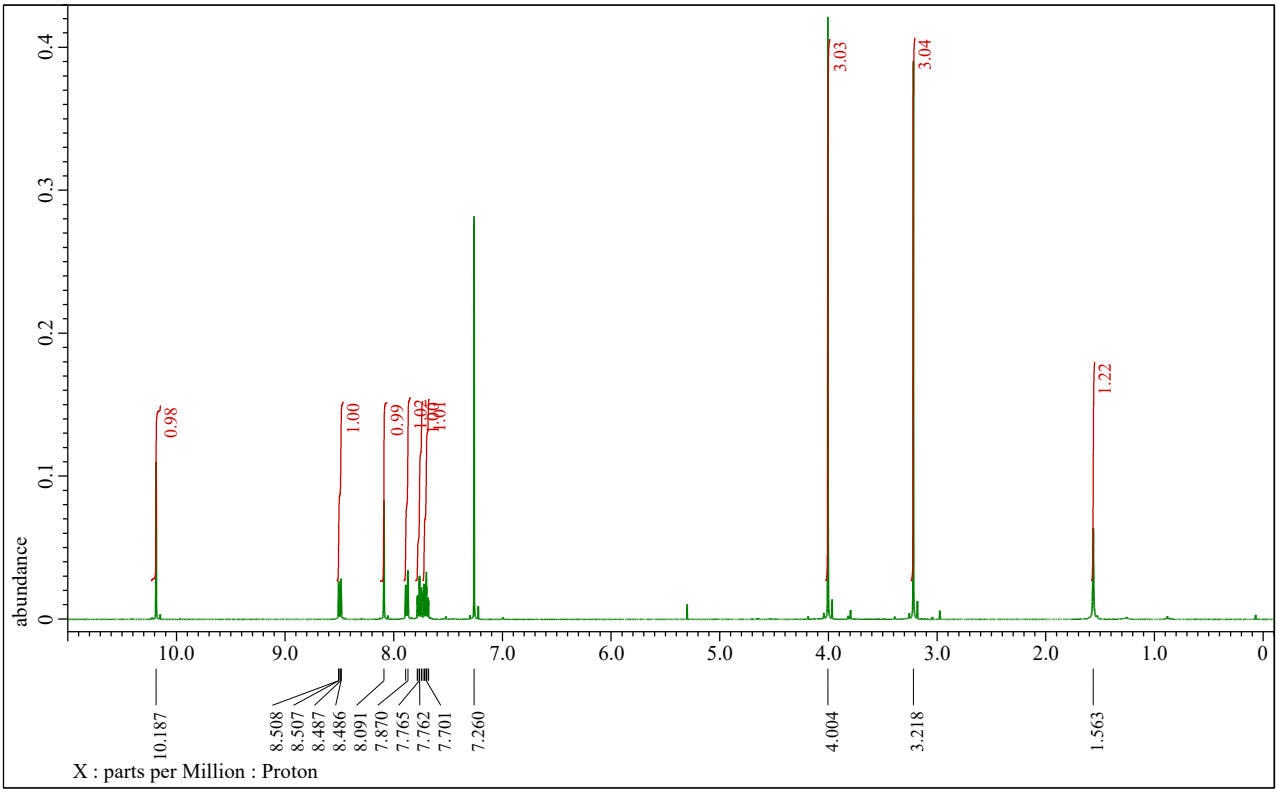


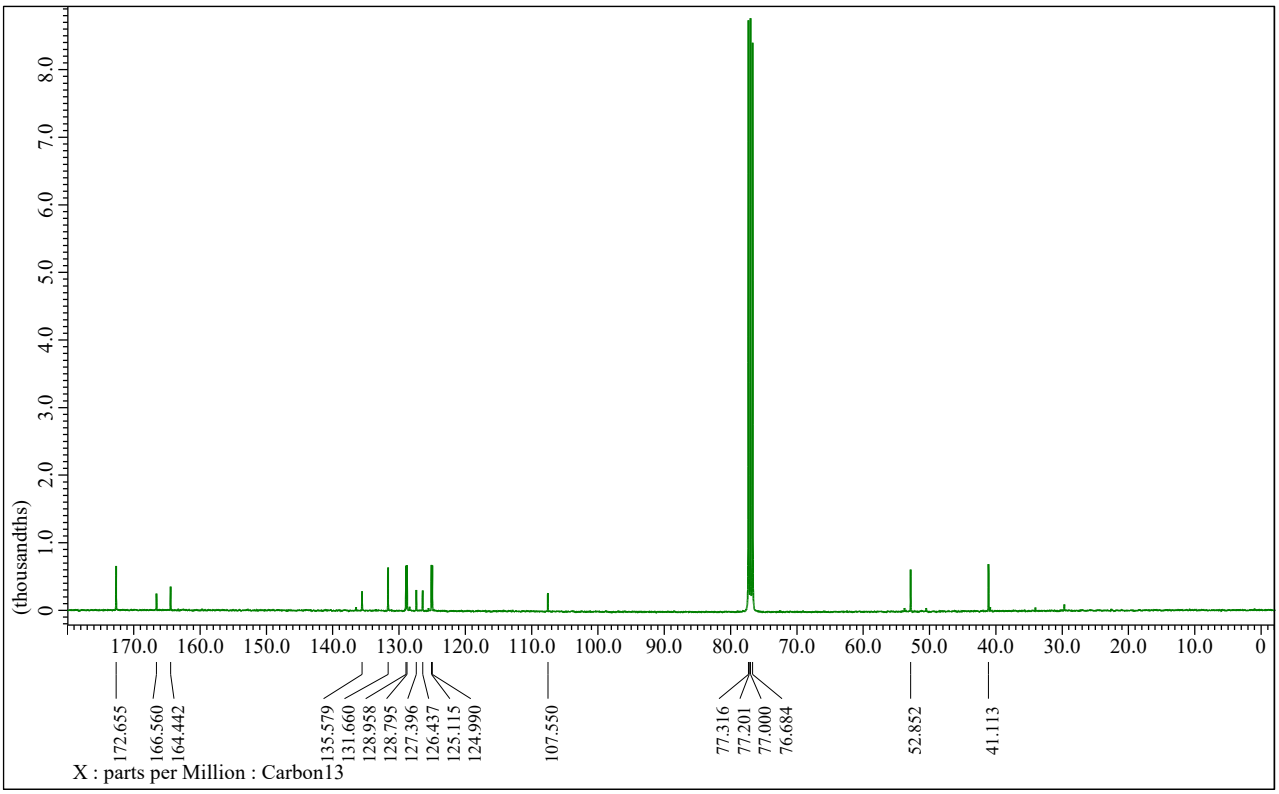




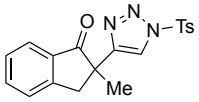
2-(*N*-Mesyl-iminomethyl)-3-methoxycarbonyl-1-naphthol (2b)

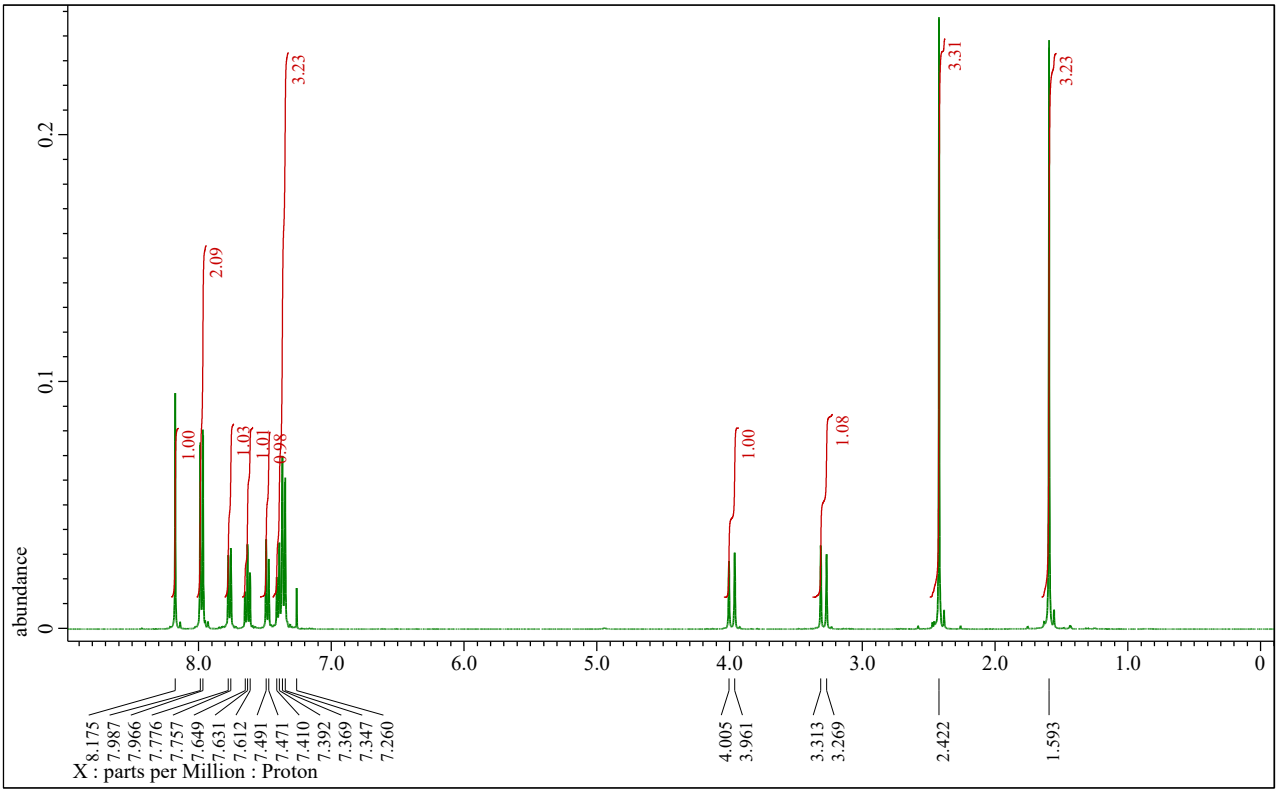


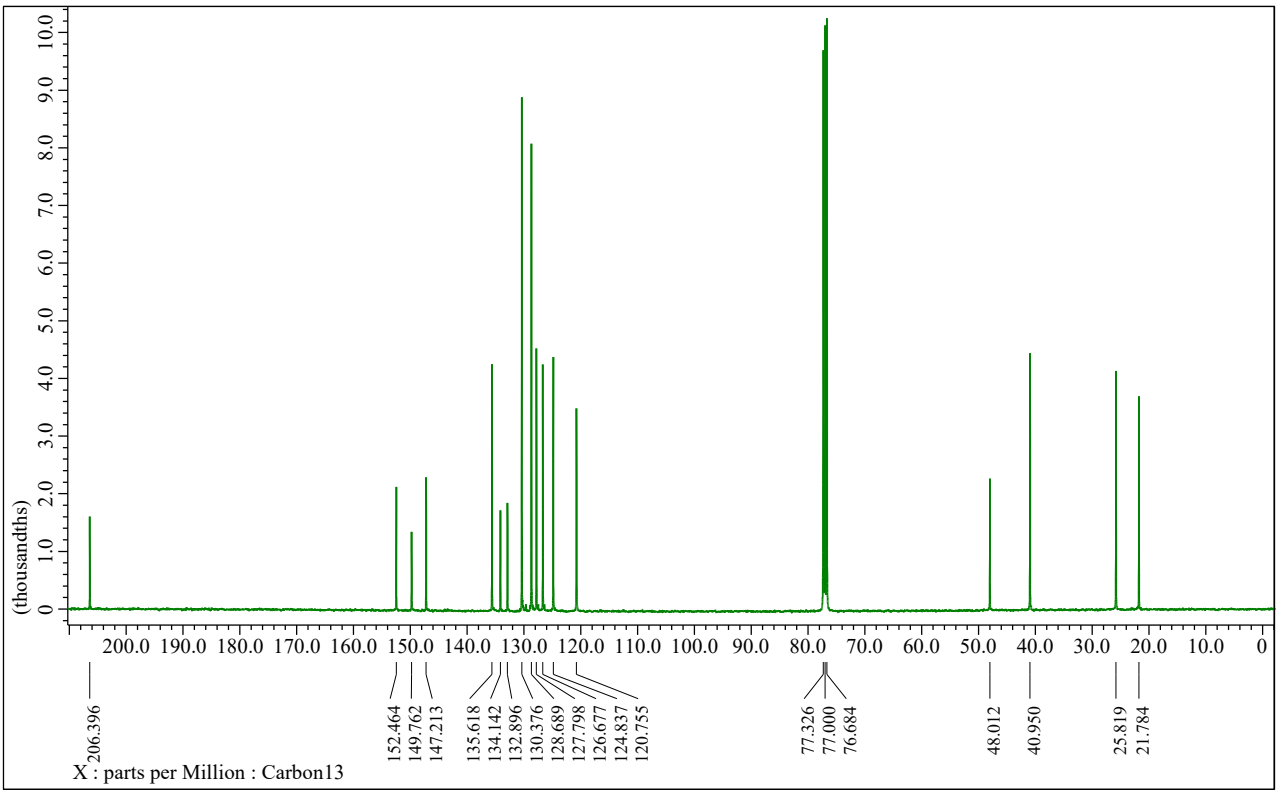




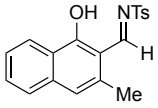
2-Methyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1-indanone (1c)

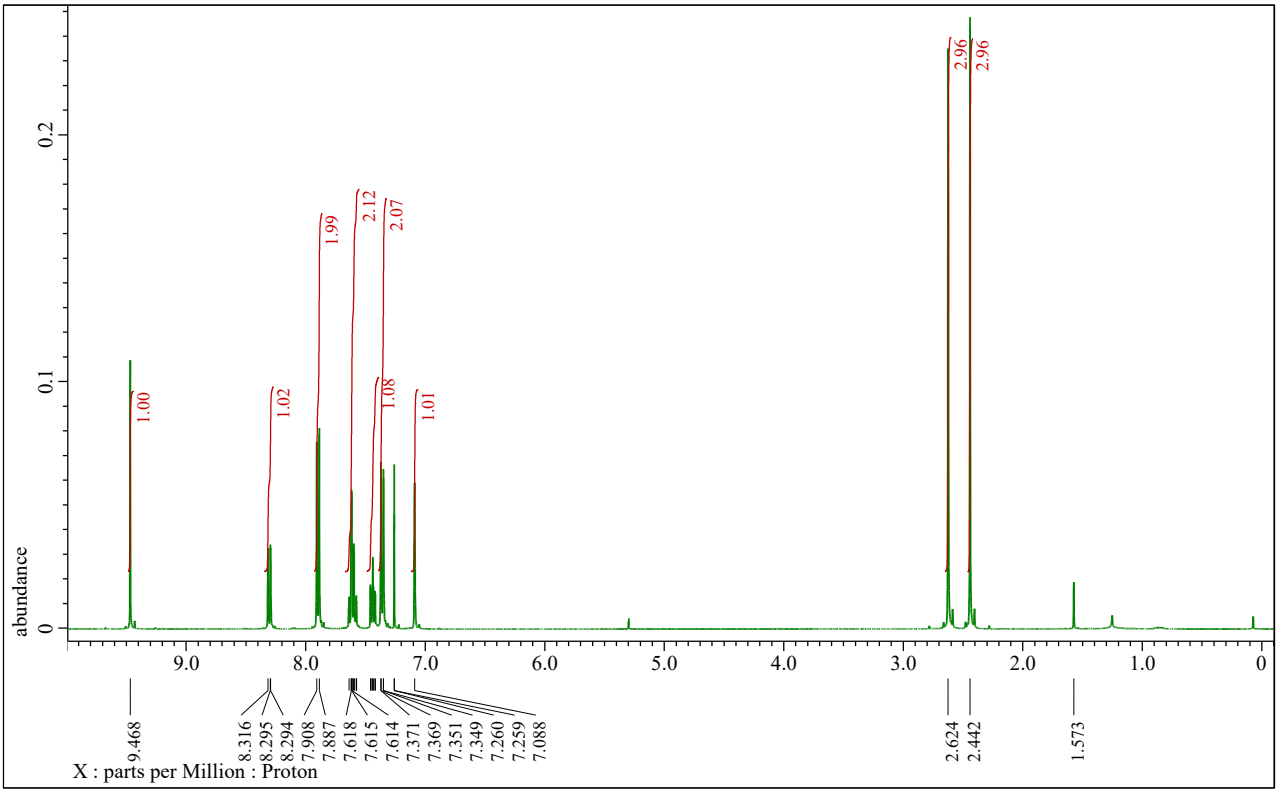


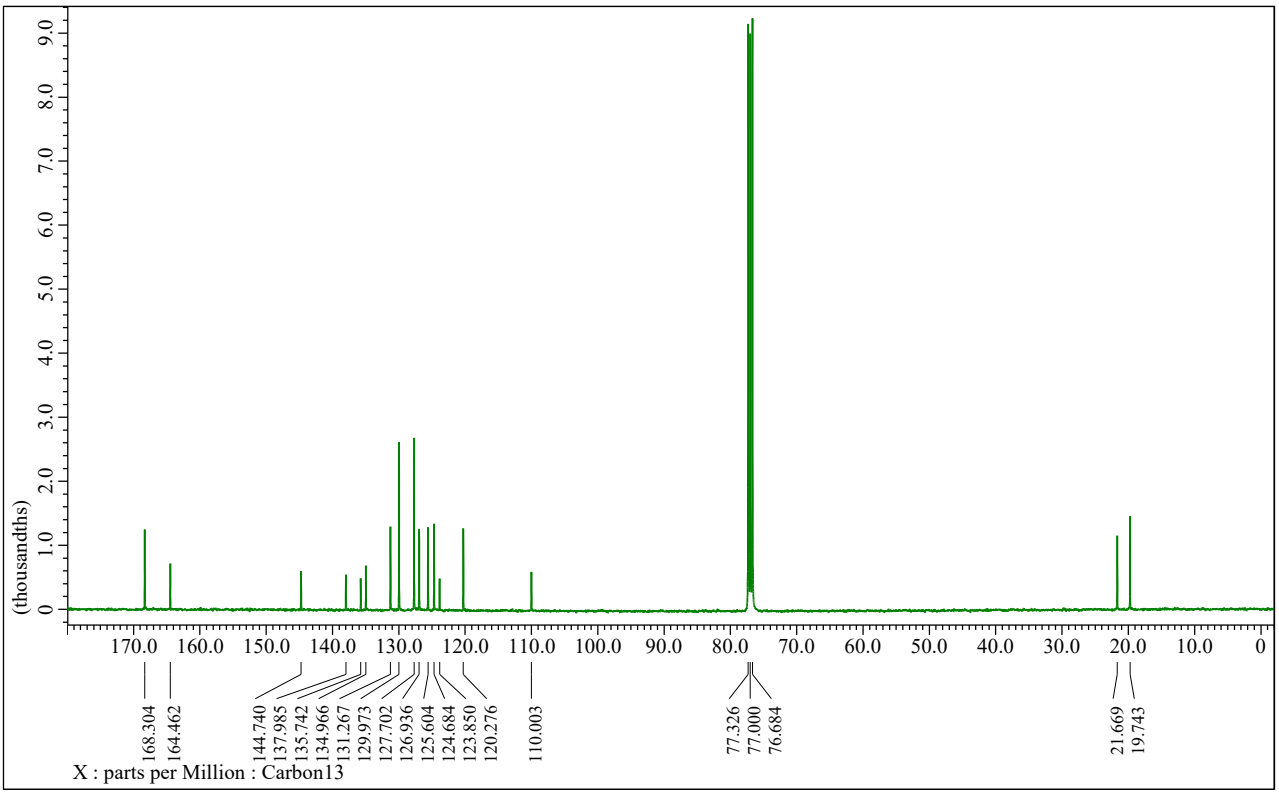




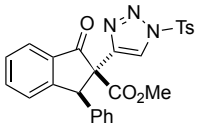
3-Methyl-2-(*N*-tosyl-iminomethyl)-1-naphthol (2c)

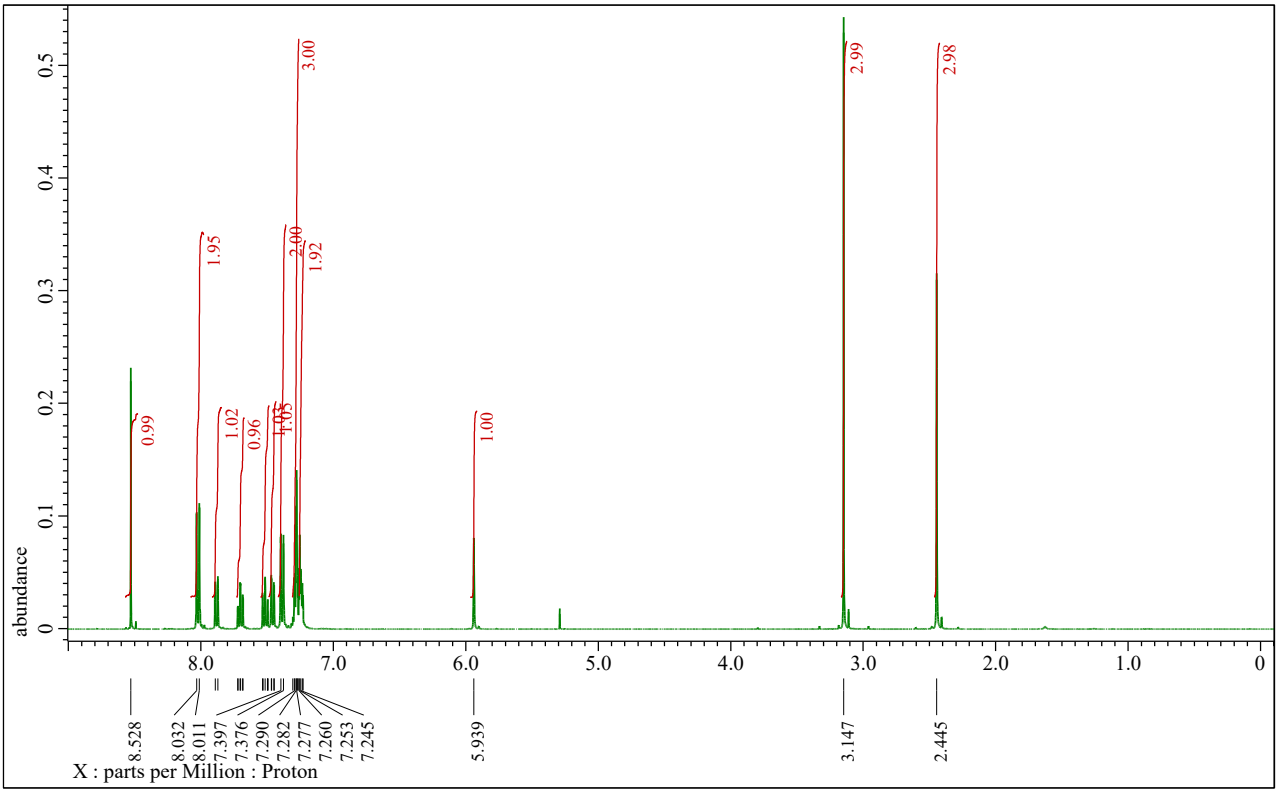


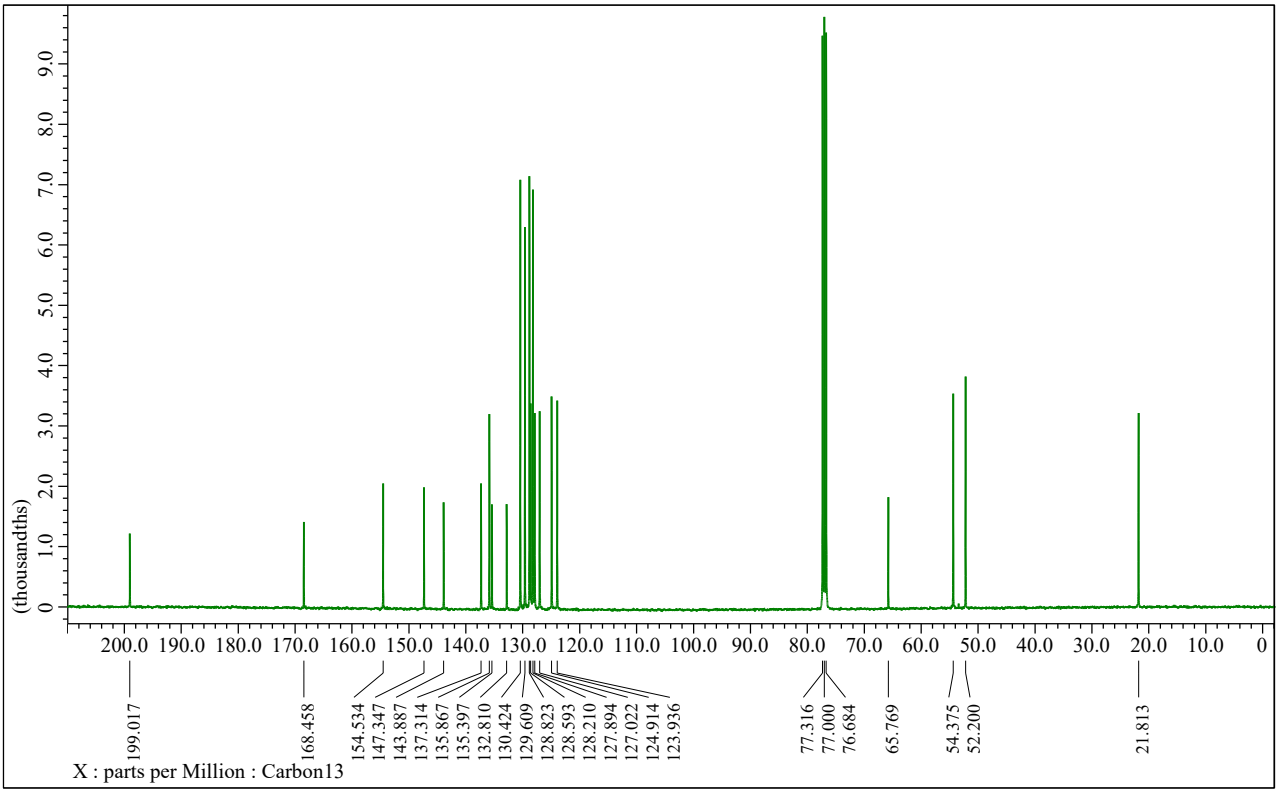




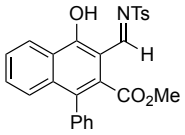
2-Methoxycarbonyl-3-phenyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1-indanone (1d)

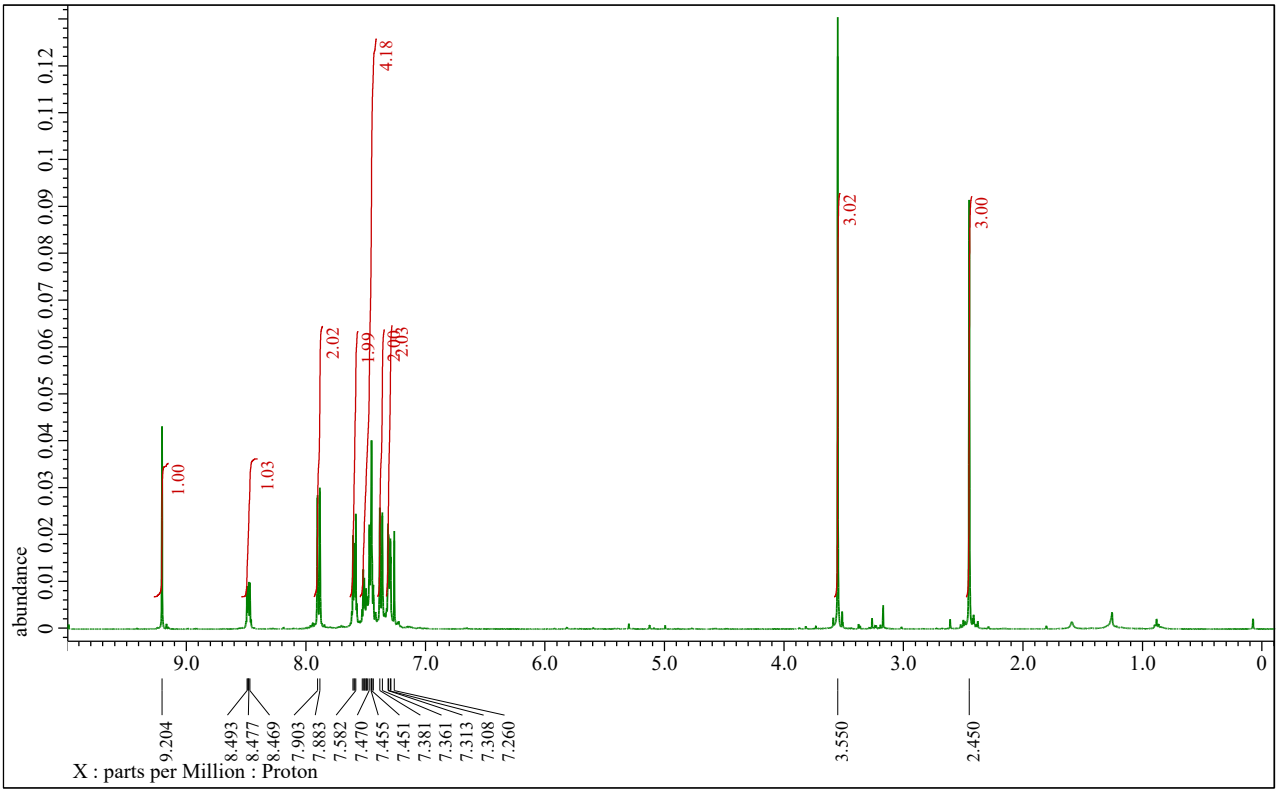


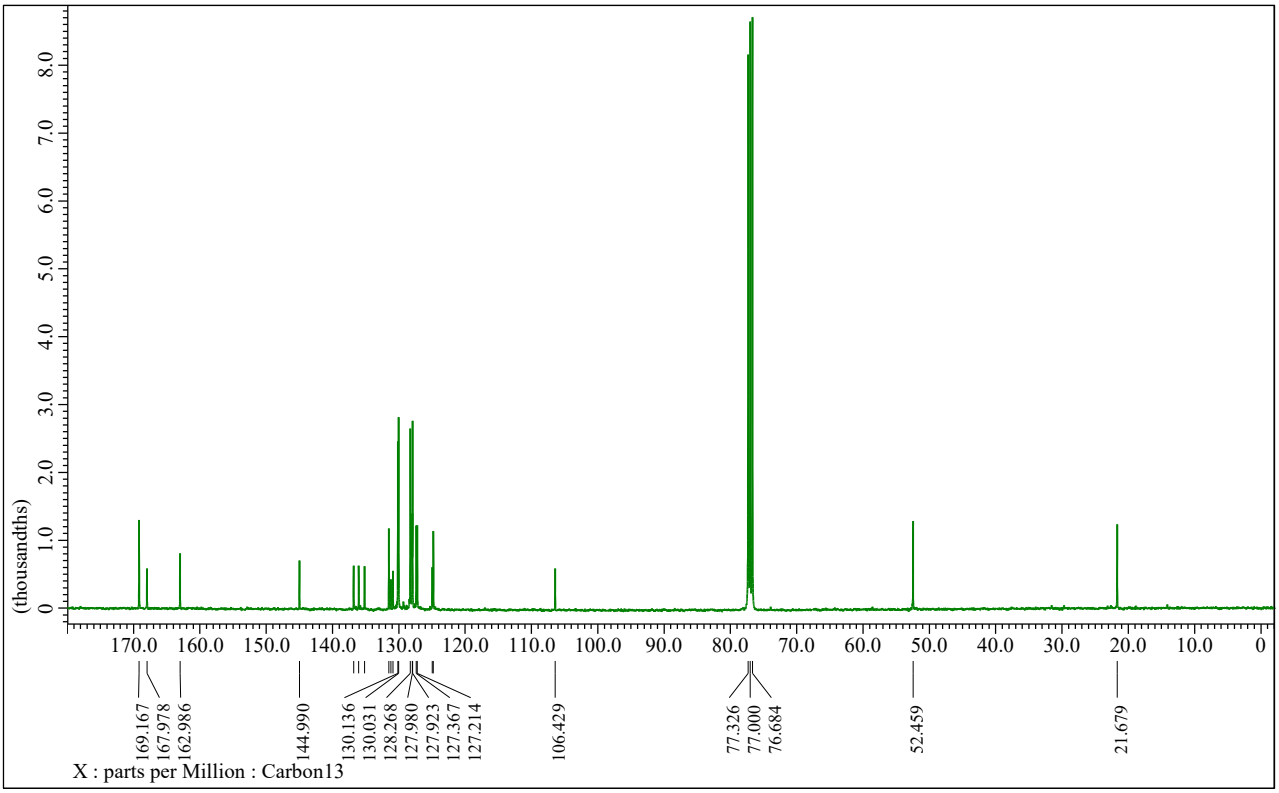




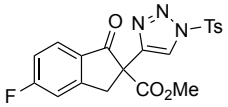
3-Methyl-4-phenyl-2-(*N*-tosyl-iminomethyl)-1-naphthol (2d)

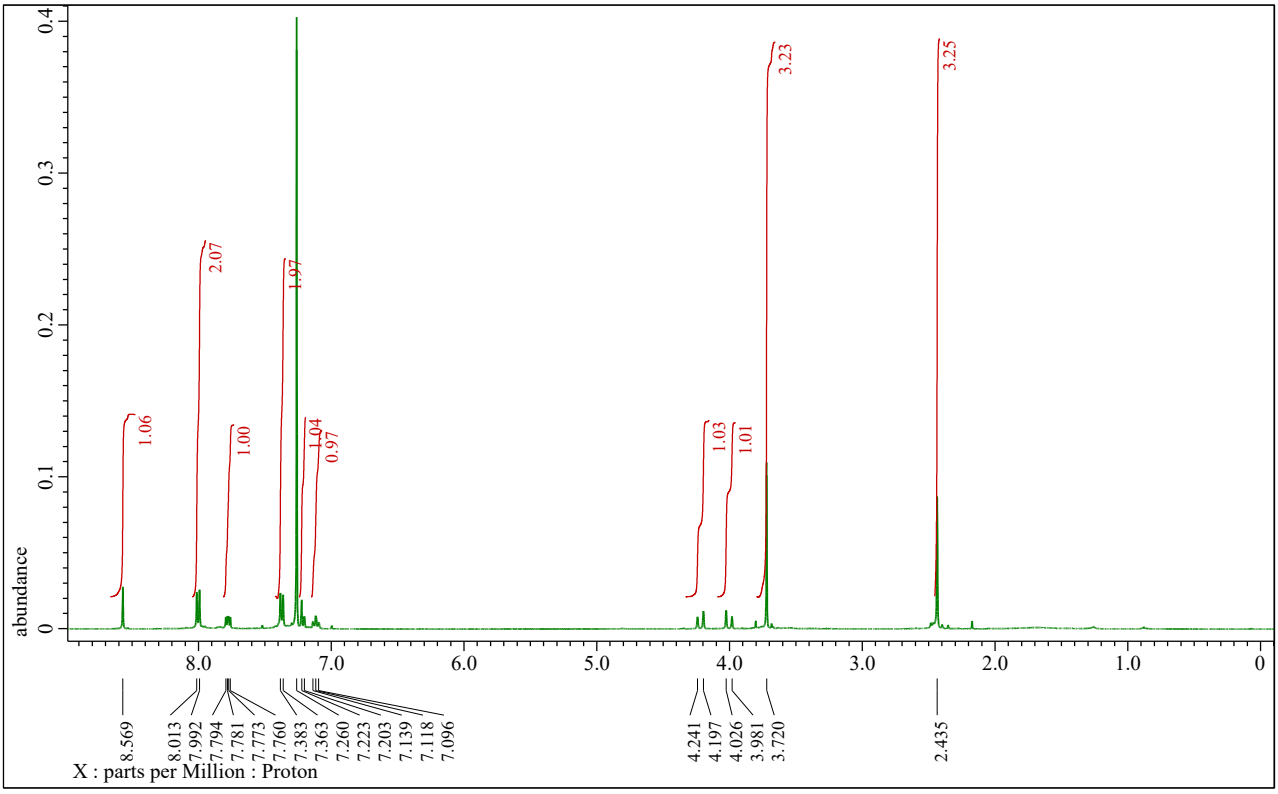


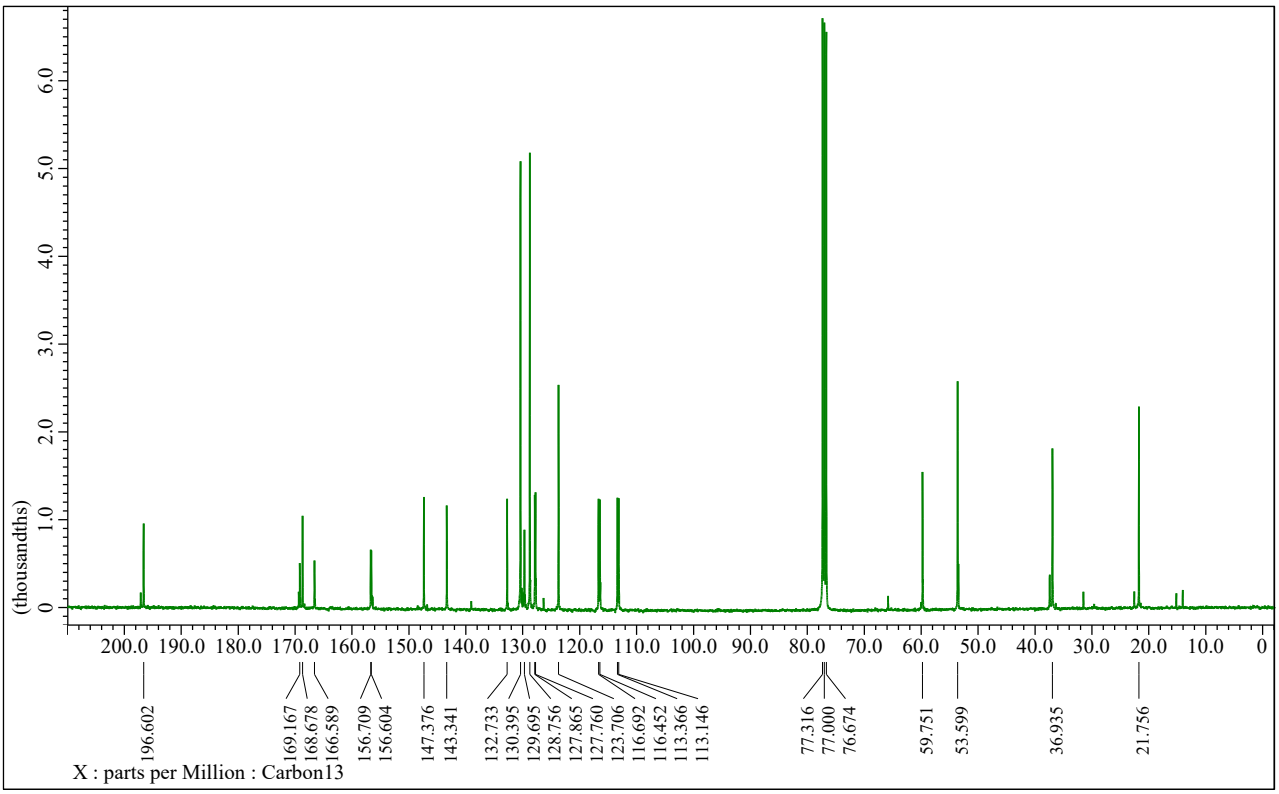




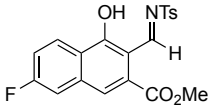
2-Methoxycarbonyl-5-fluoro-2-(1-tosyl-1,2,3-triazol-4-yl)-1-indanone (1e)

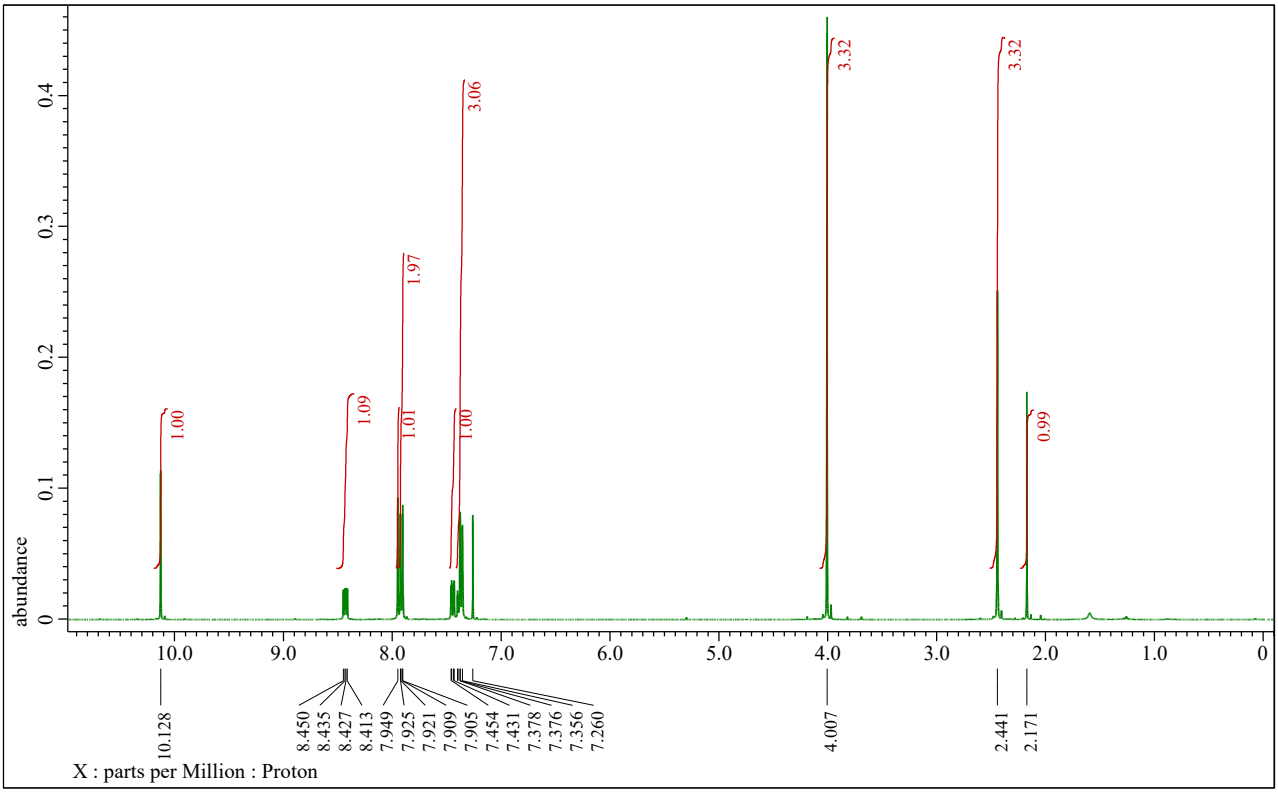


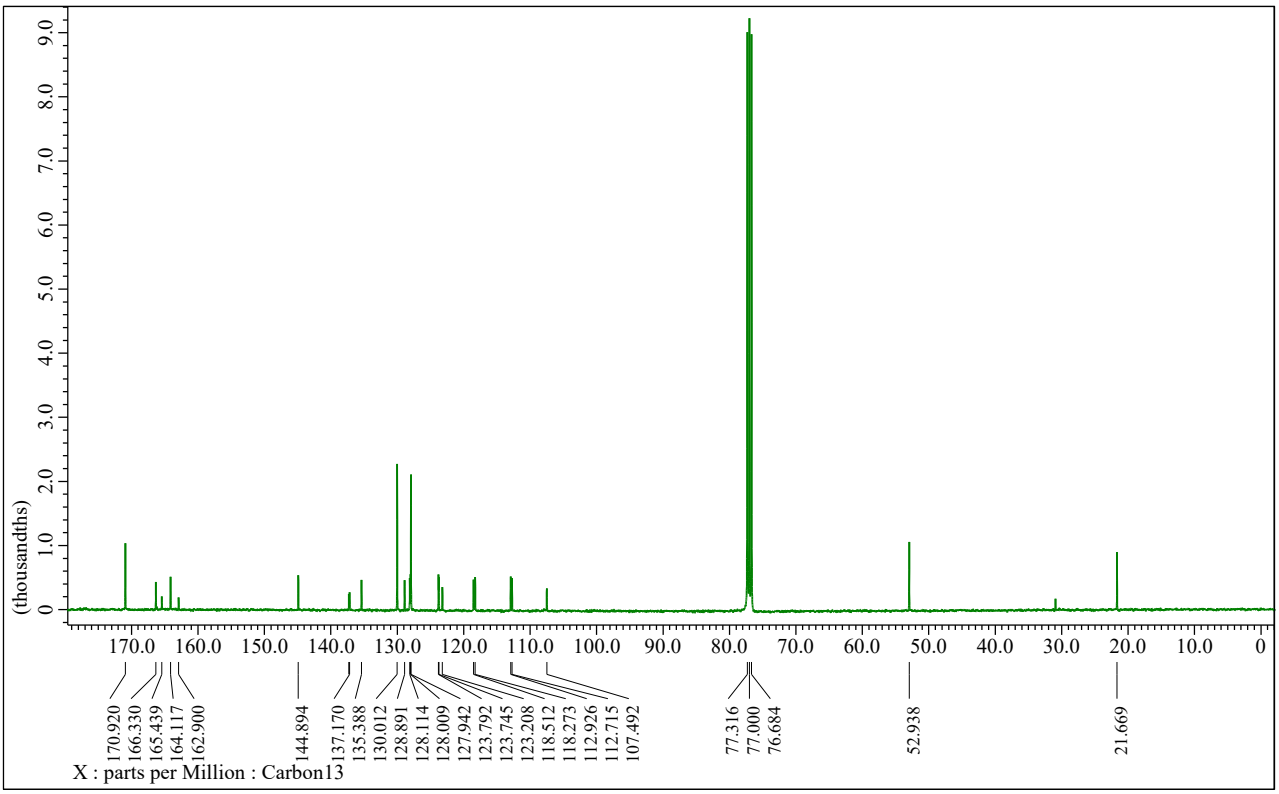




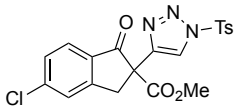
6-Fluoro-3-methoxycarbonyl-2-(*N*-tosyl-iminomethyl)-1-naphthol (2e)

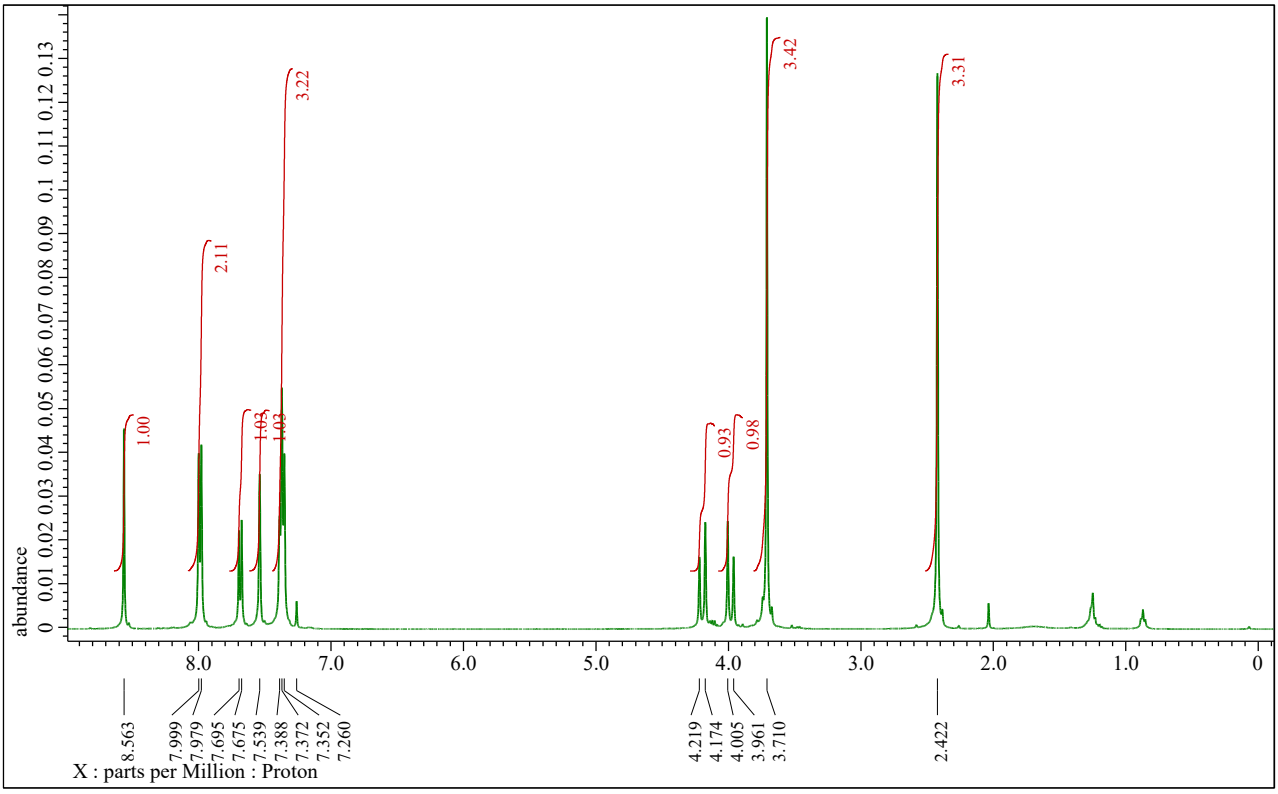


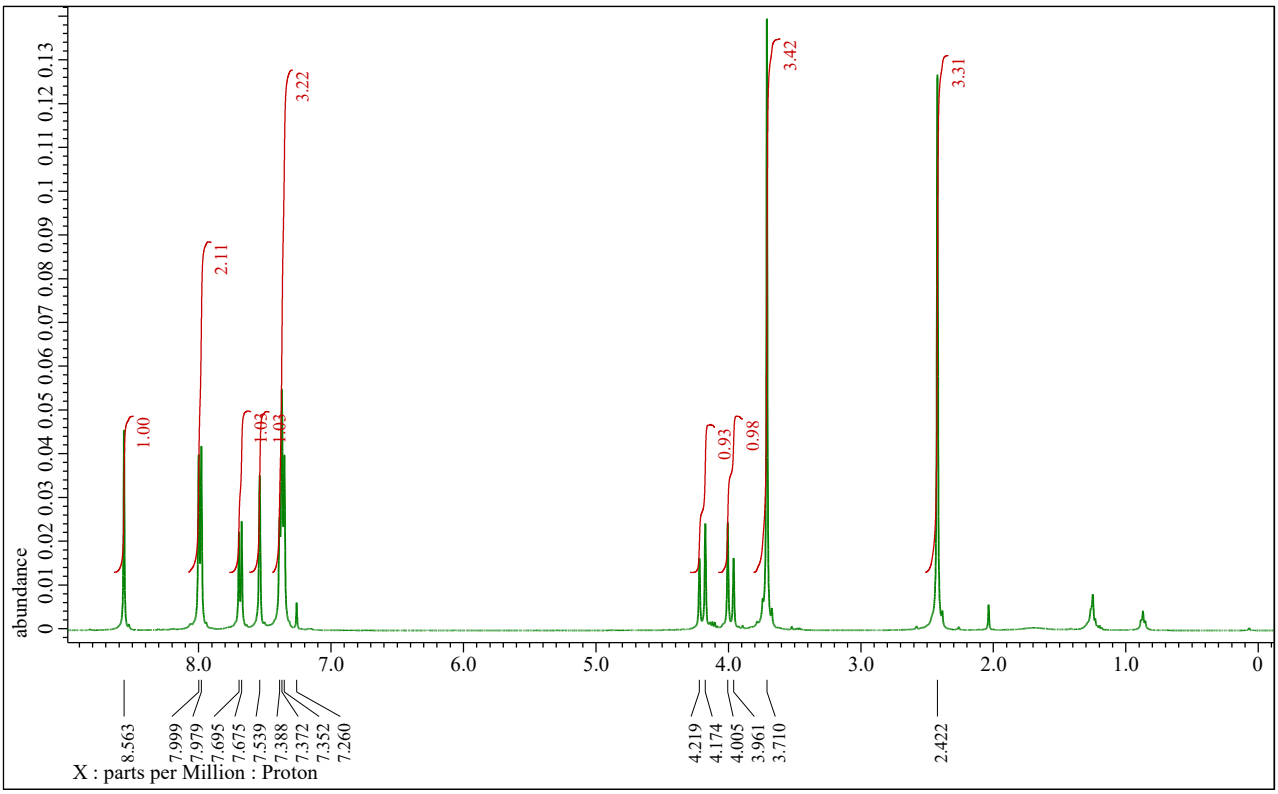




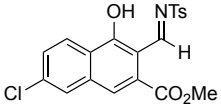
5-Chloro-2-methoxycarbonyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1-indanone (1f)

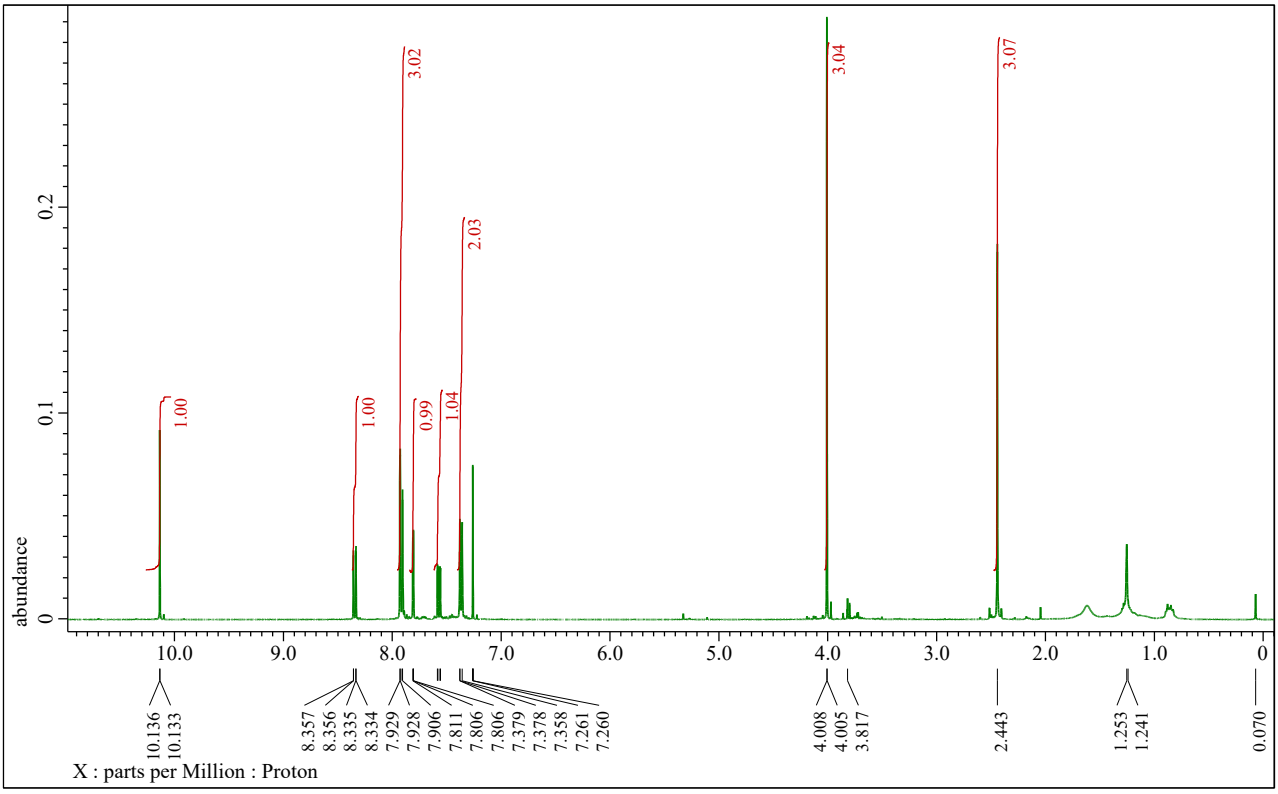


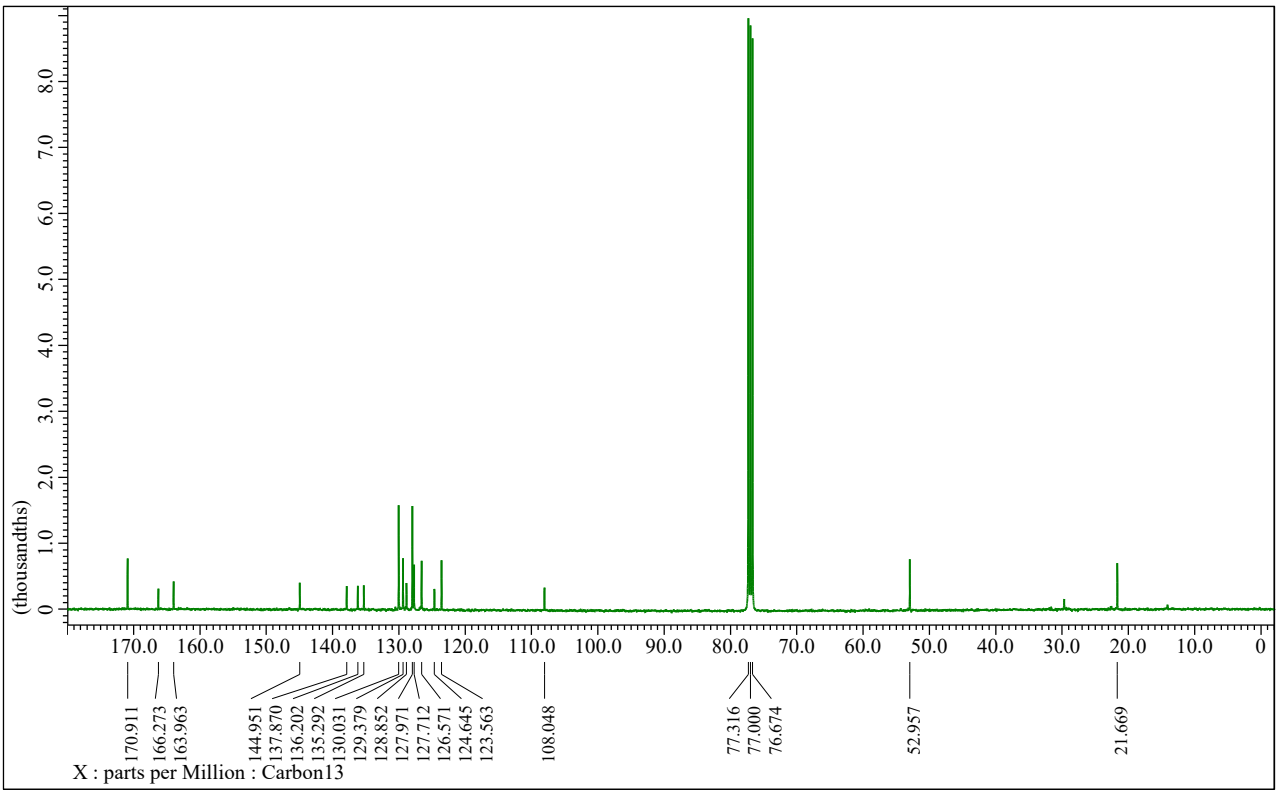




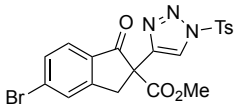
6-Chloro-3-methoxycarbonyl-2-(*N*-tosyl-iminomethyl)-1-naphthol (2f)

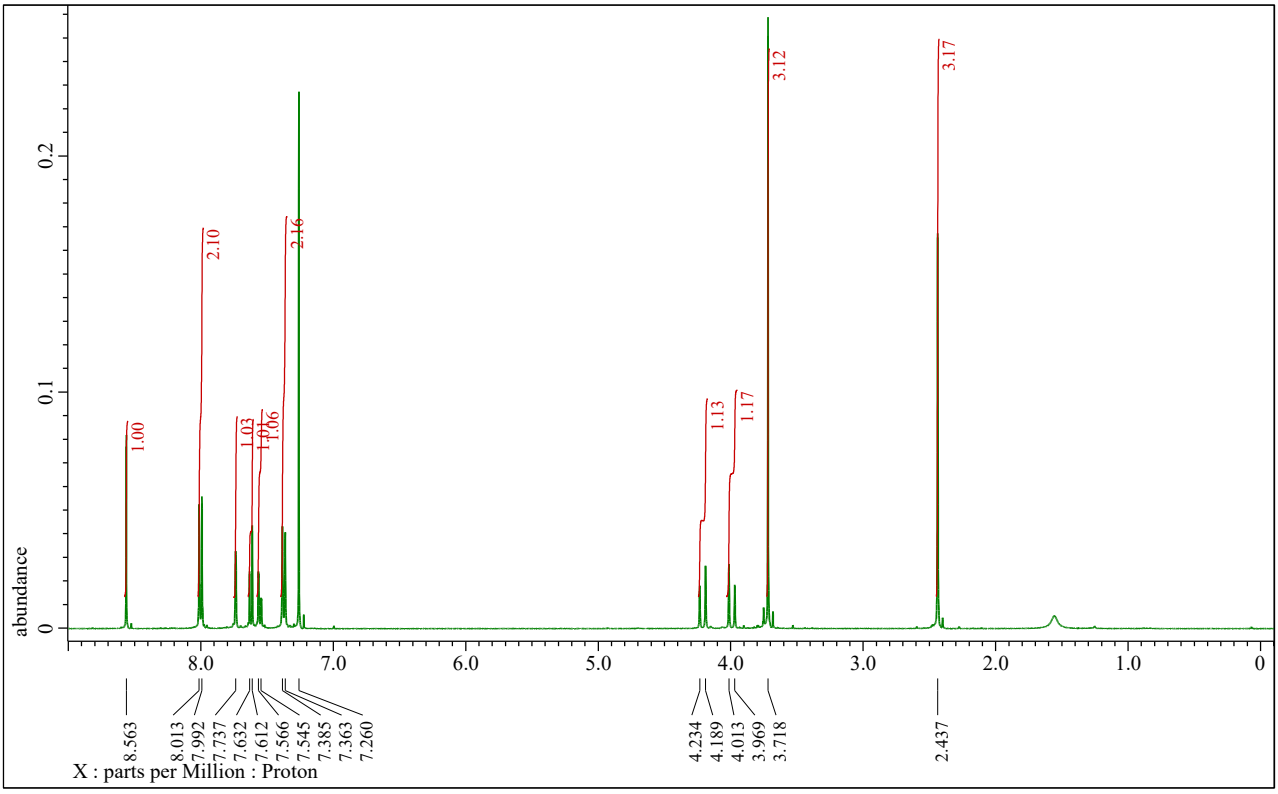


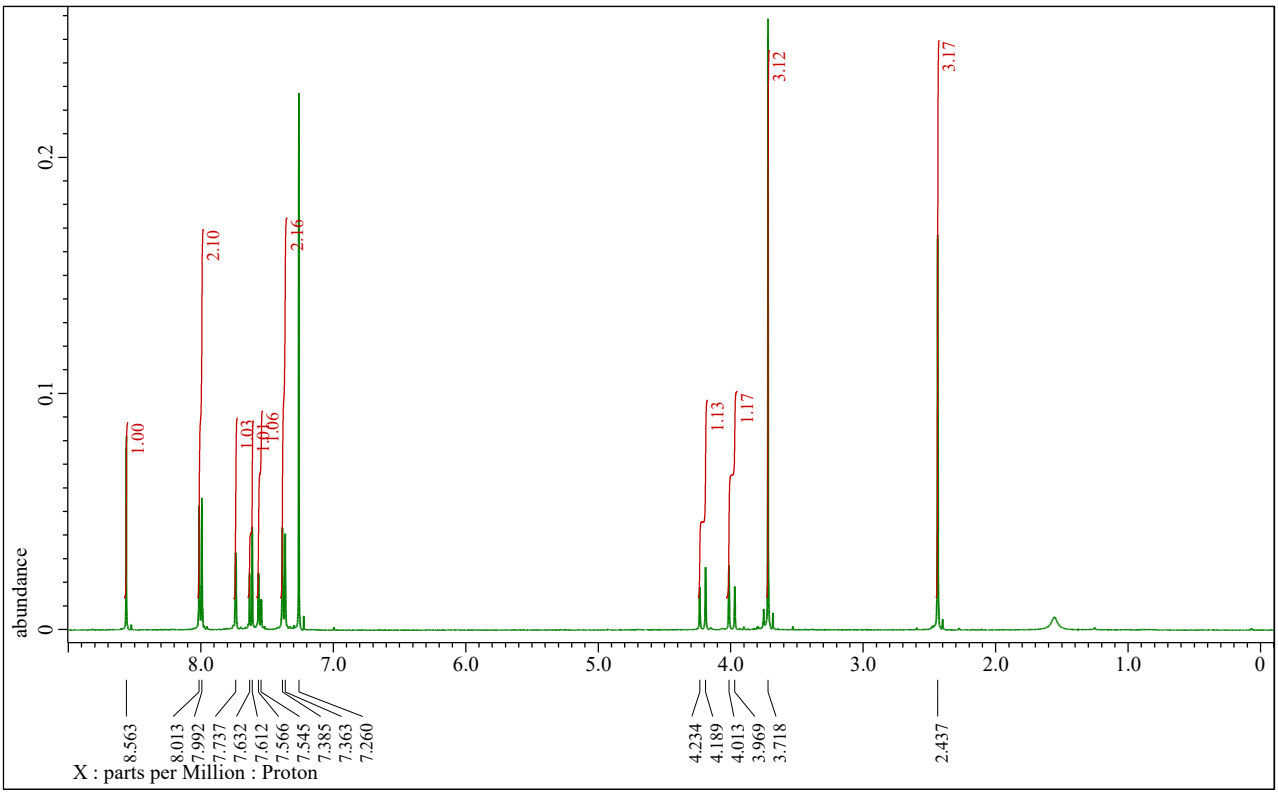




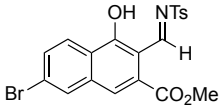
5-Bromo-2-methoxycarbonyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1-indanone (1g)

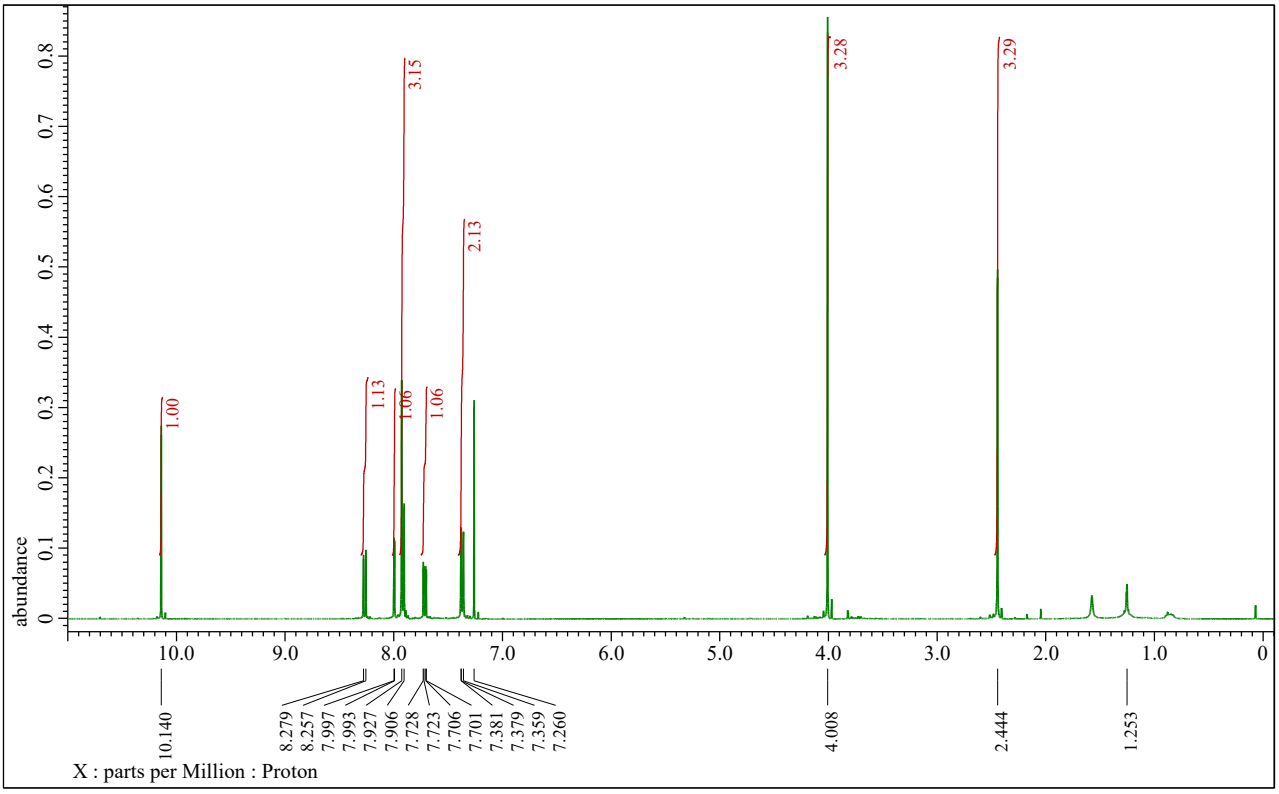


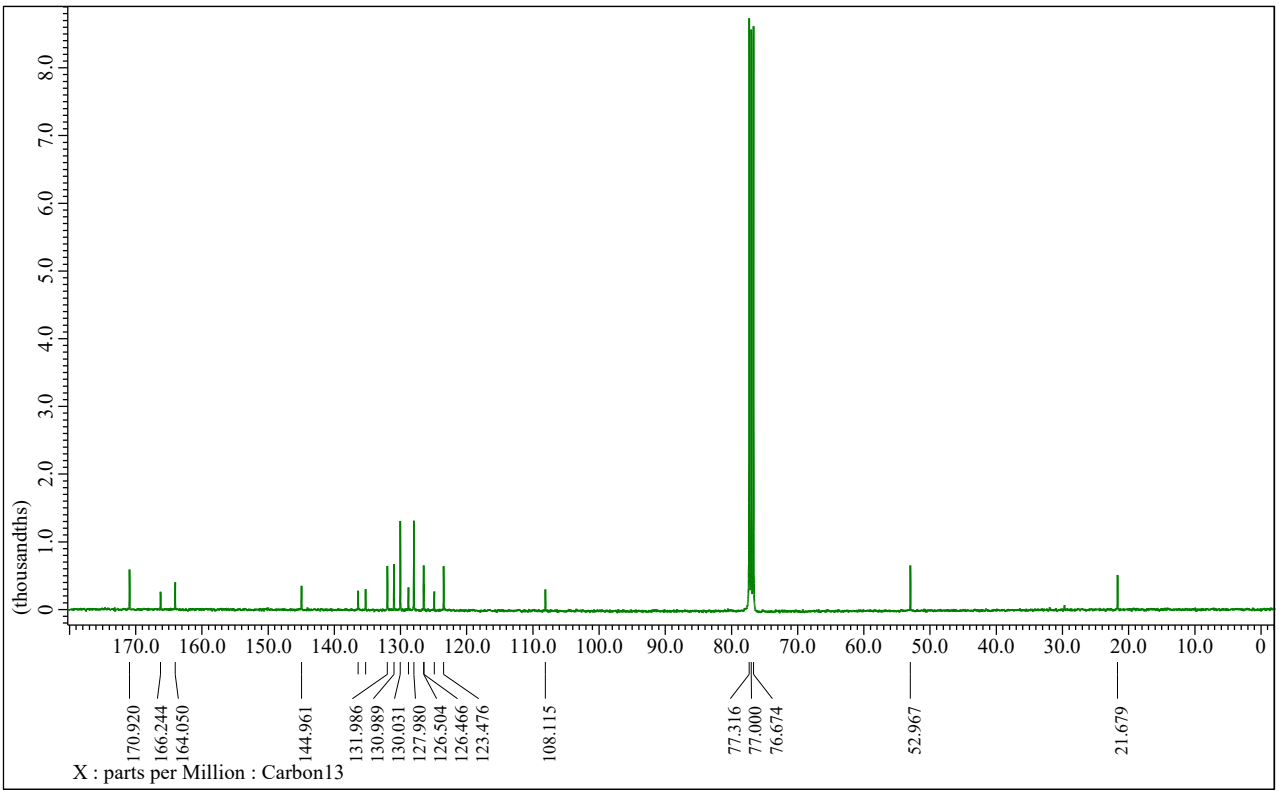




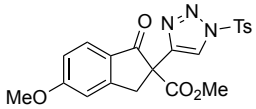
6-Bromo-3-methoxycarbonyl-2-(*N*-tosyl-iminomethyl)-1-naphthol (2g)

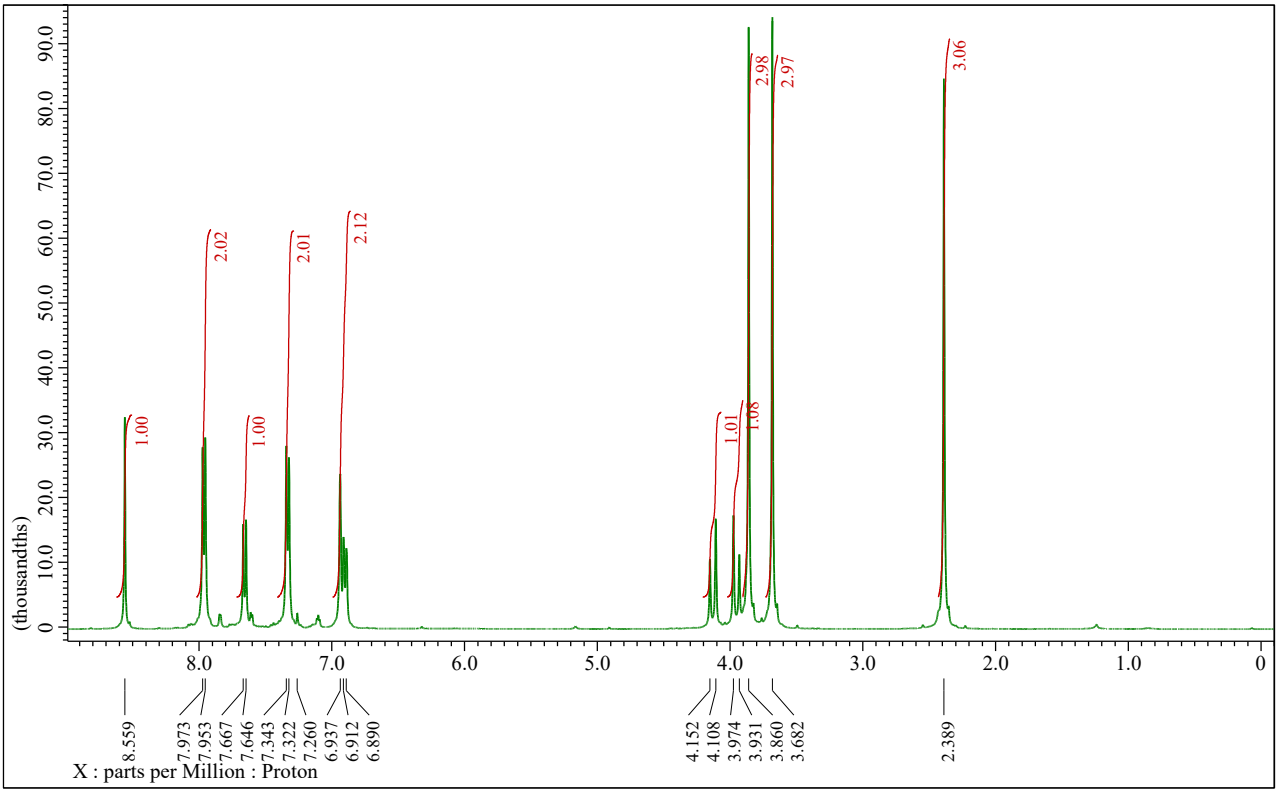


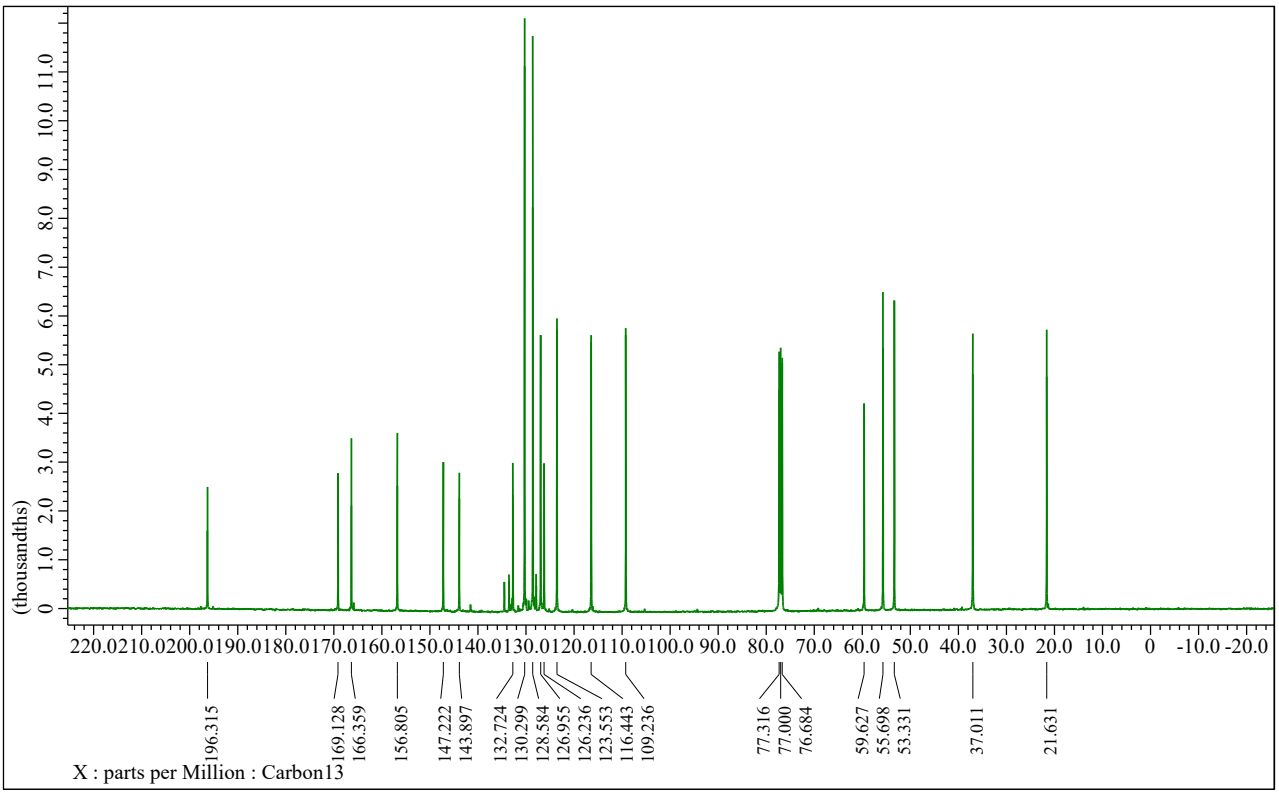




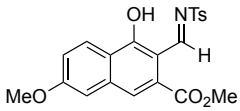
1h: 5-methoxy-2-methoxycarbonyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1-indanone

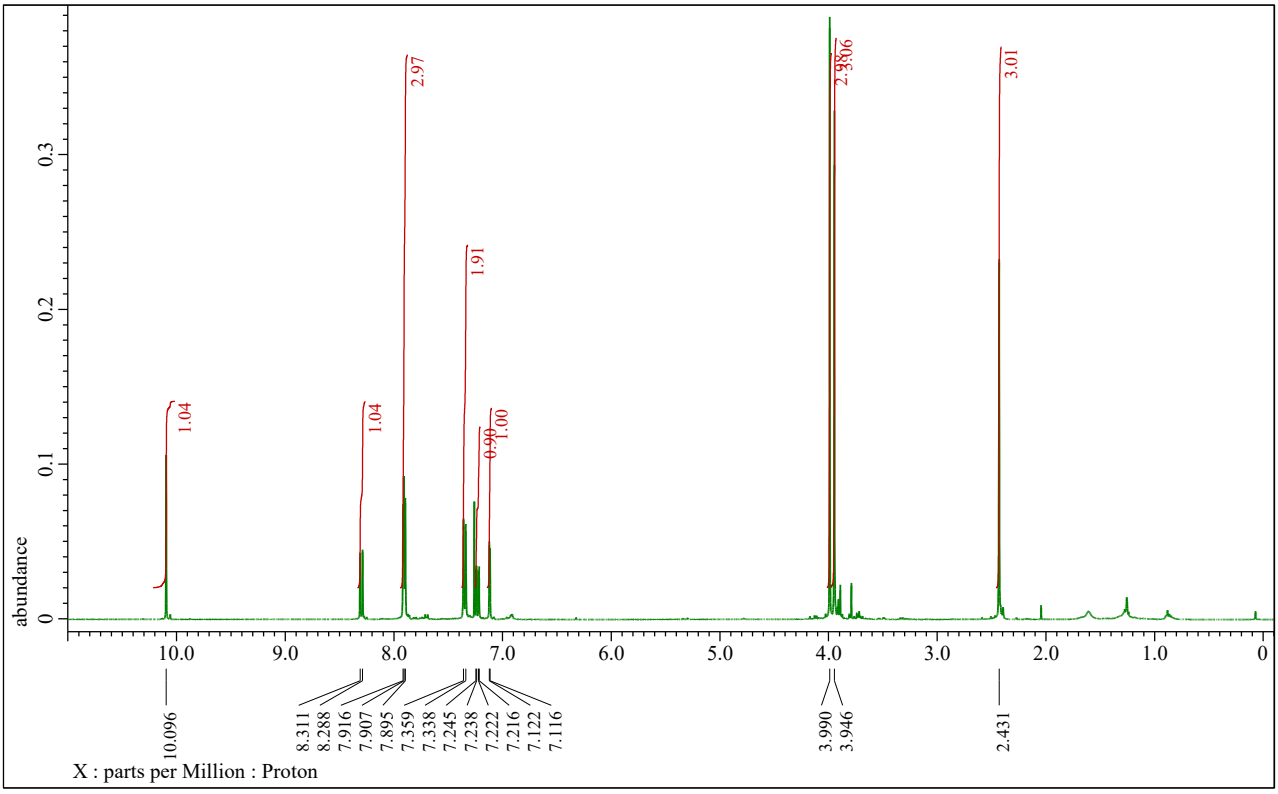


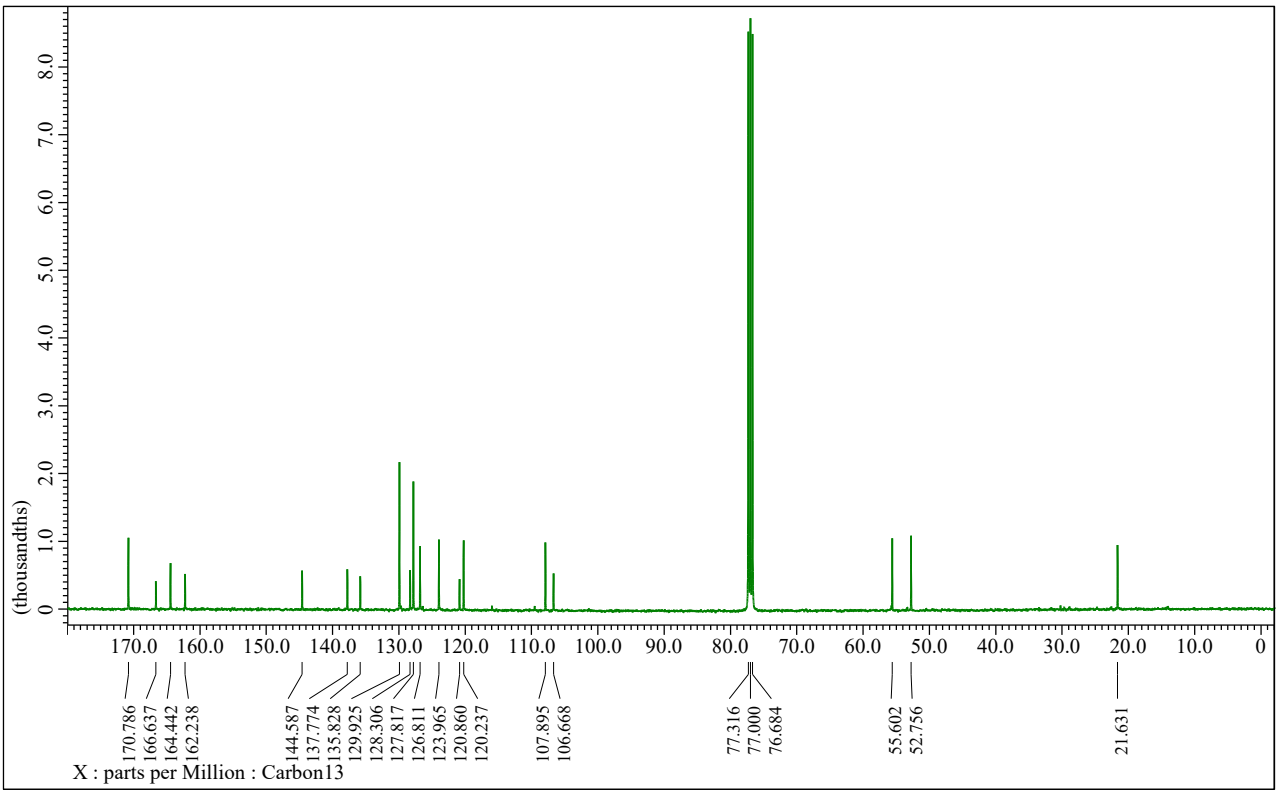




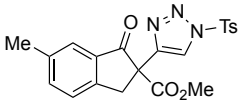
6-Methoxy-3-methoxycarbonyl-2-(*N*-tosyl-iminomethyl)-1-naphthol (2h)

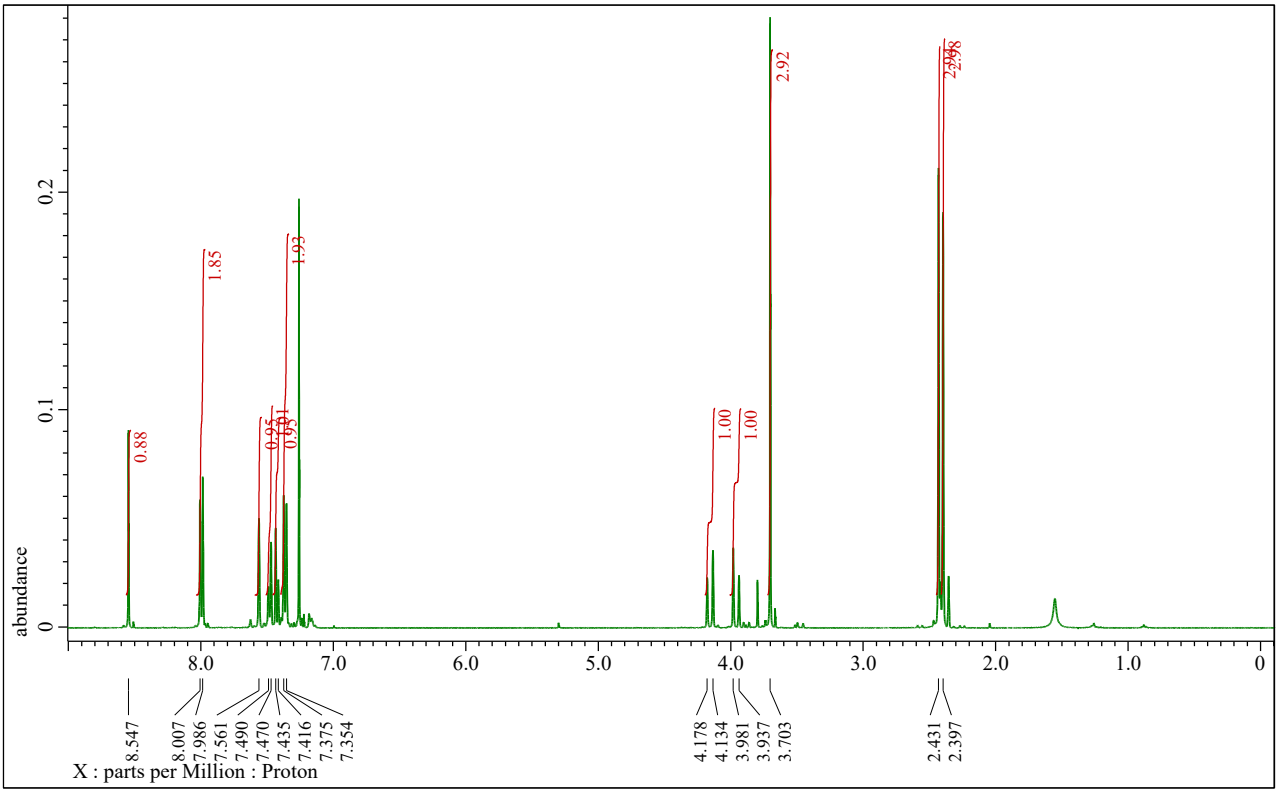


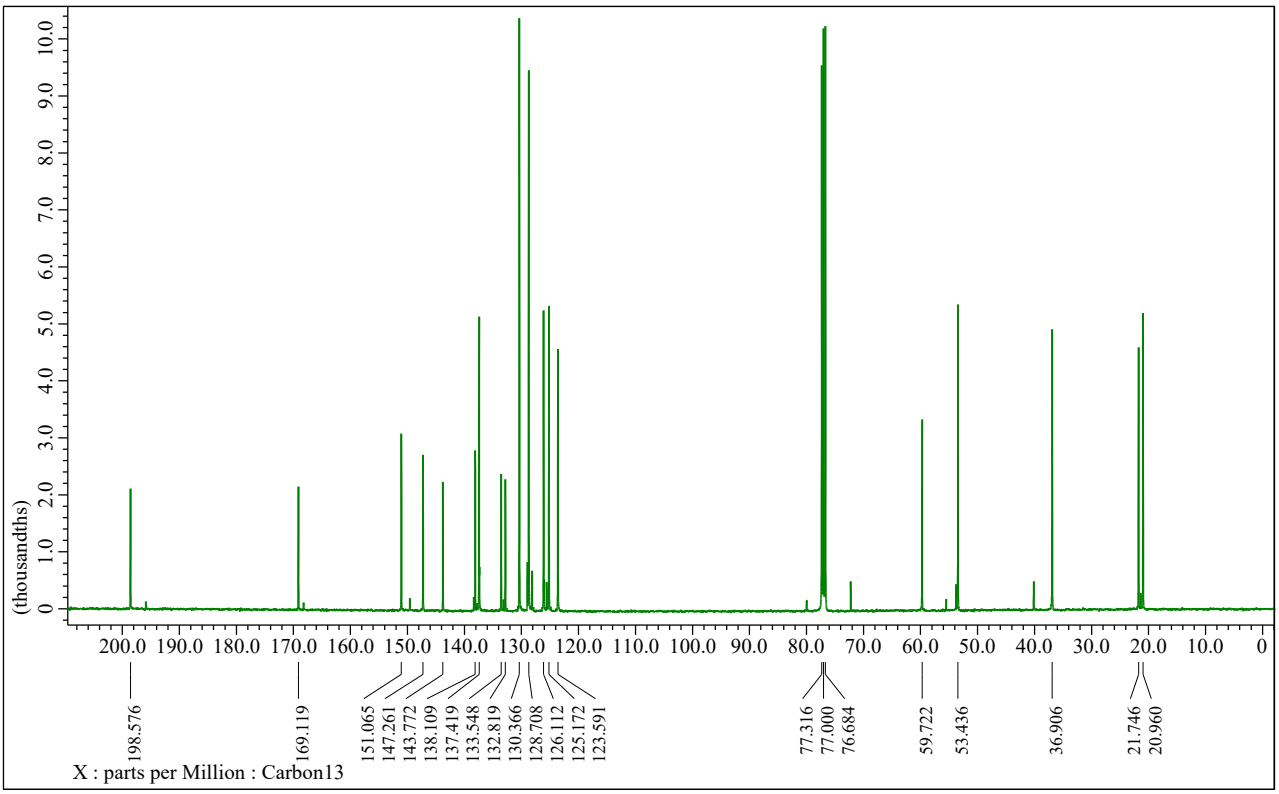




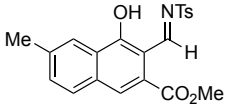
6-Methyl-2-methoxycarbonyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1-indanone (1i)

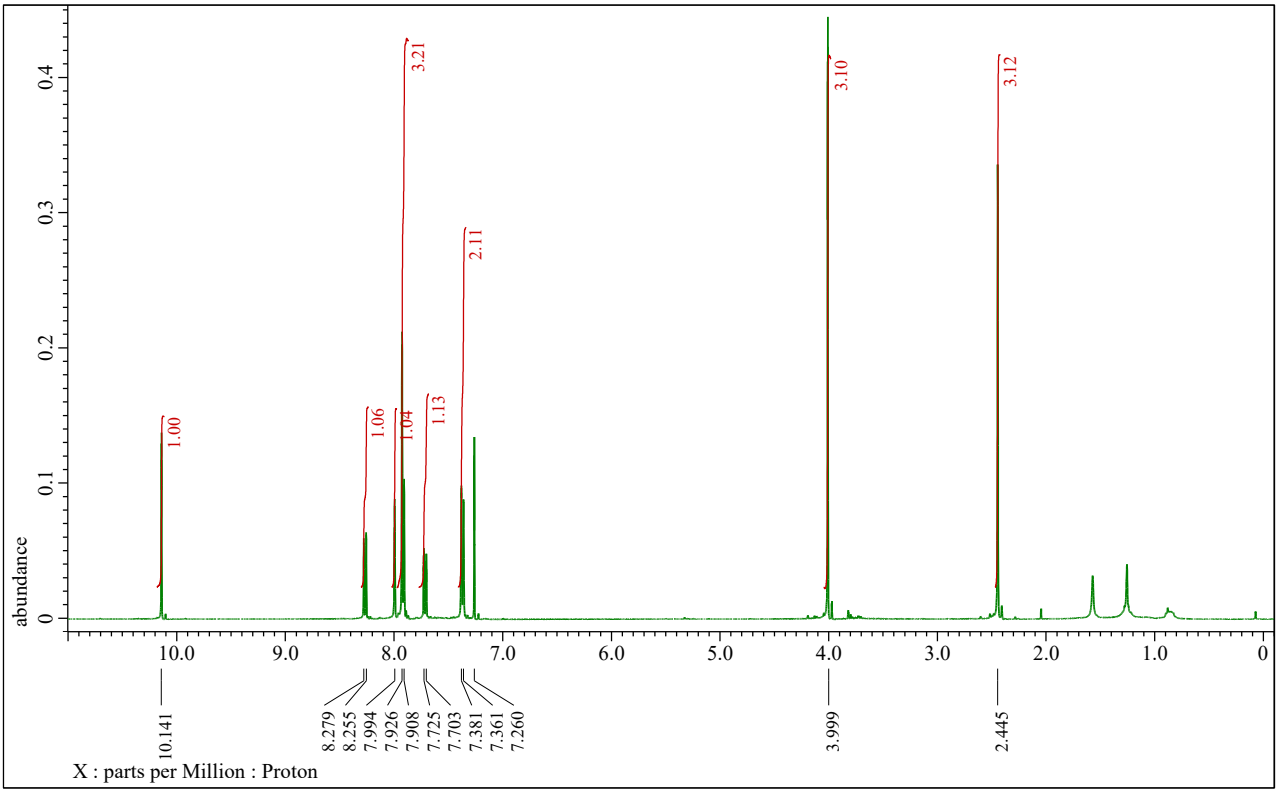


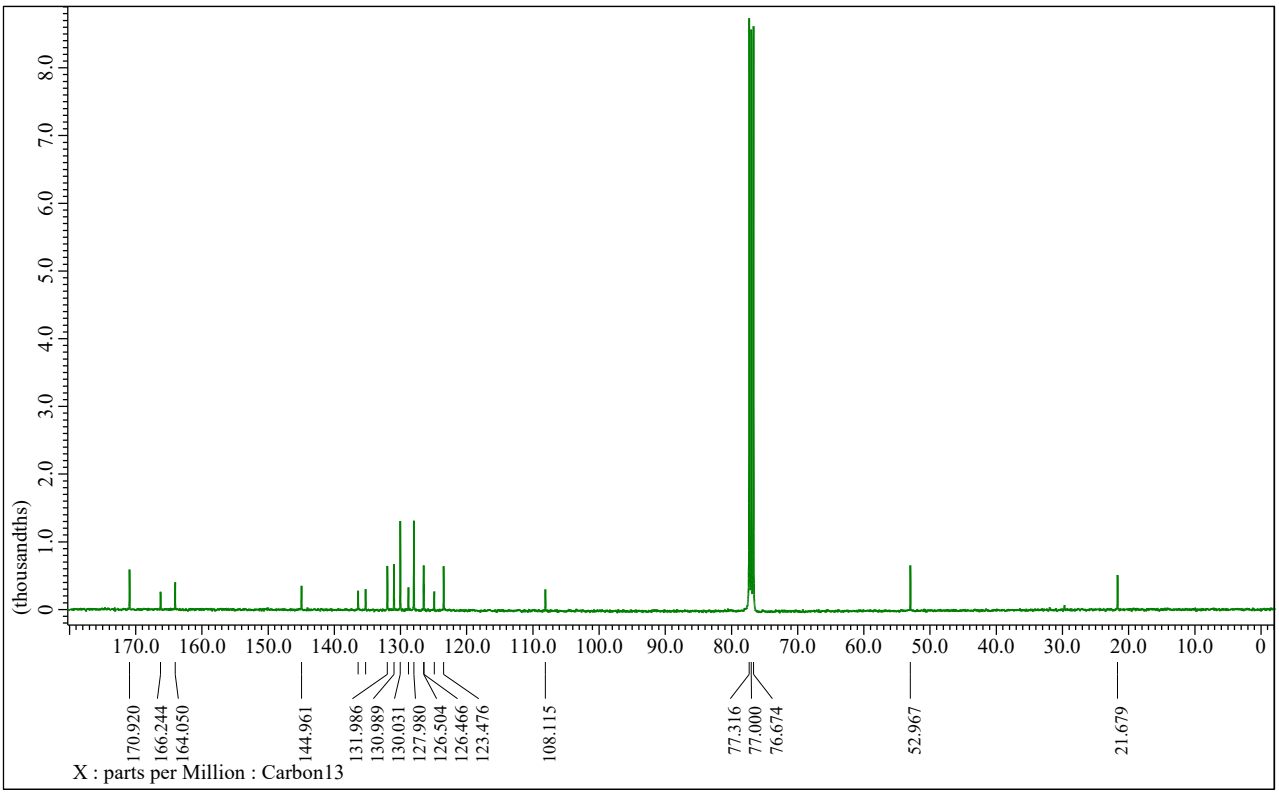




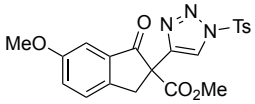
7-Methyl-3-methoxycarbonyl-2-(*N*-tosyl-iminomethyl)-1-naphthol (2i)

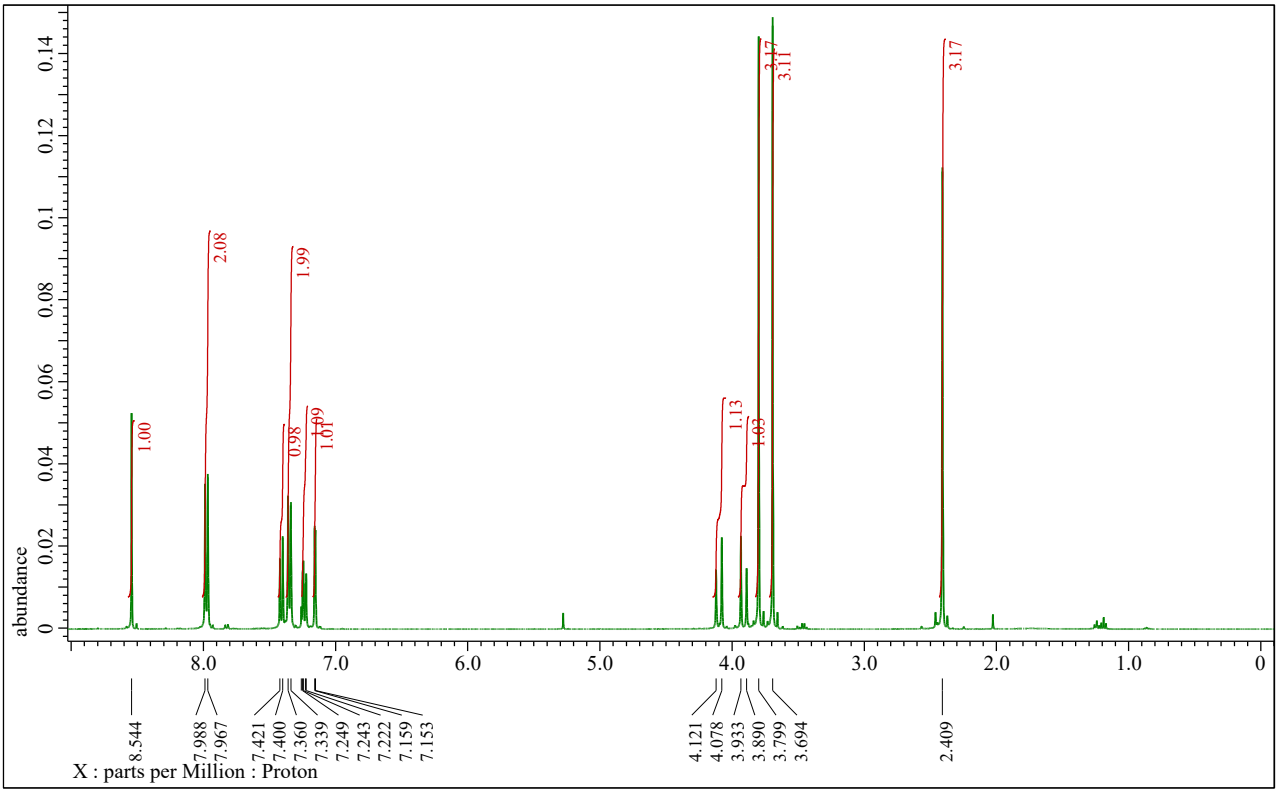


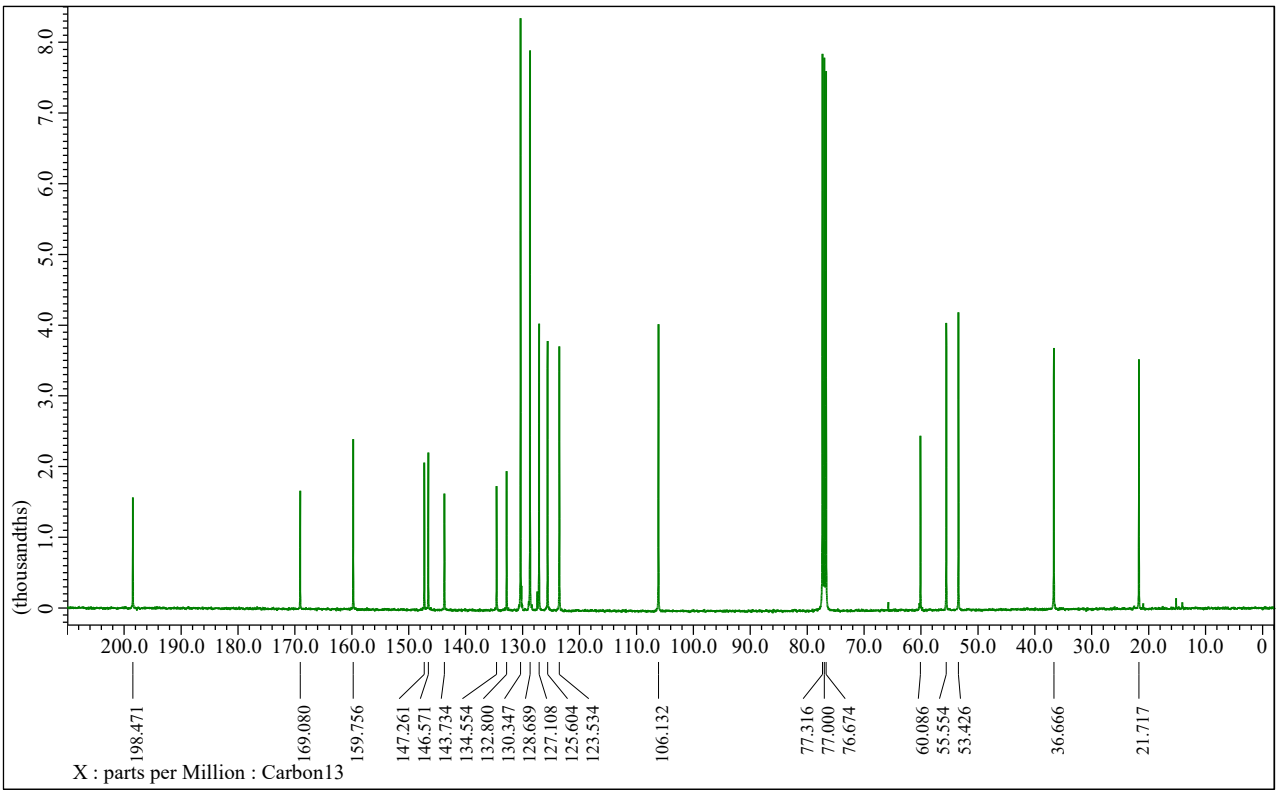




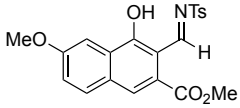
6-Methoxy-2-methoxycarbonyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1-indanone (1j)

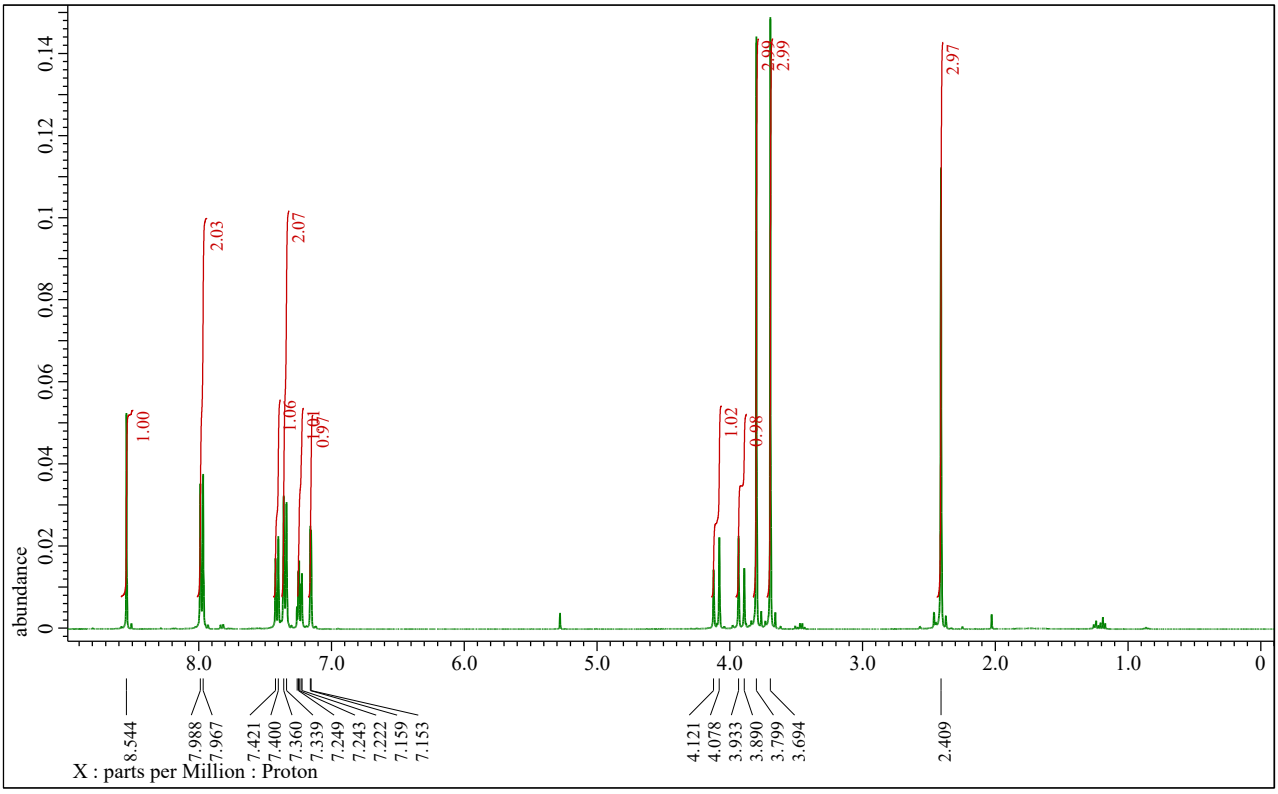


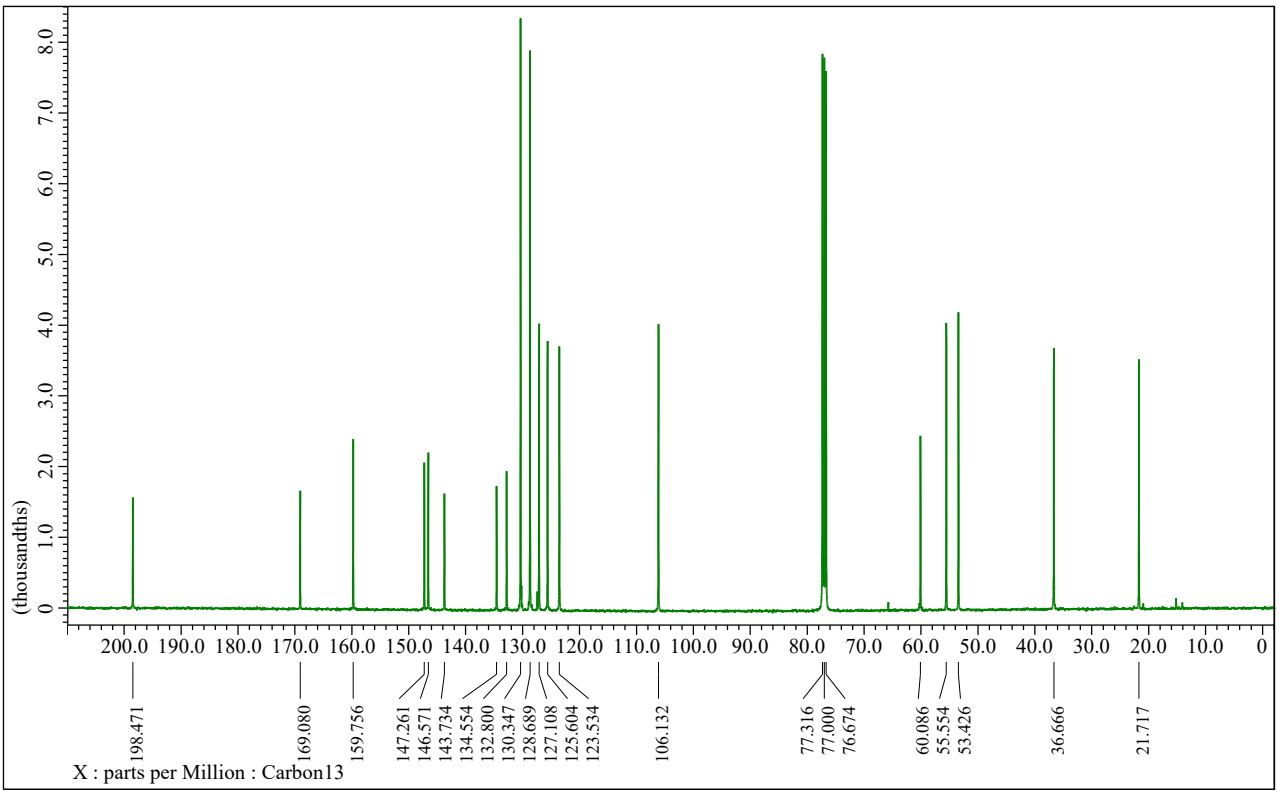




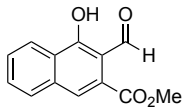
7-Methoxy-3-methoxycarbonyl-2-(*N*-tosyl-iminomethyl)-1-naphthol (2j)

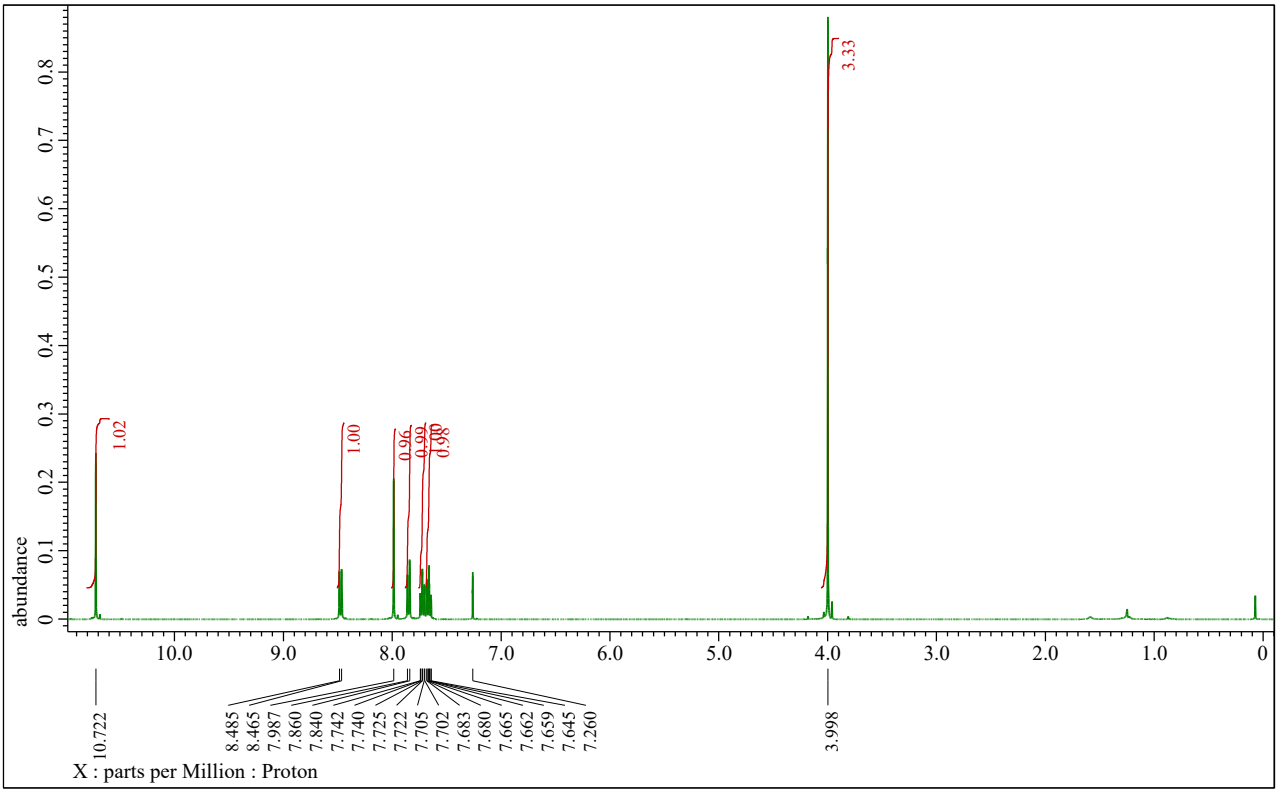


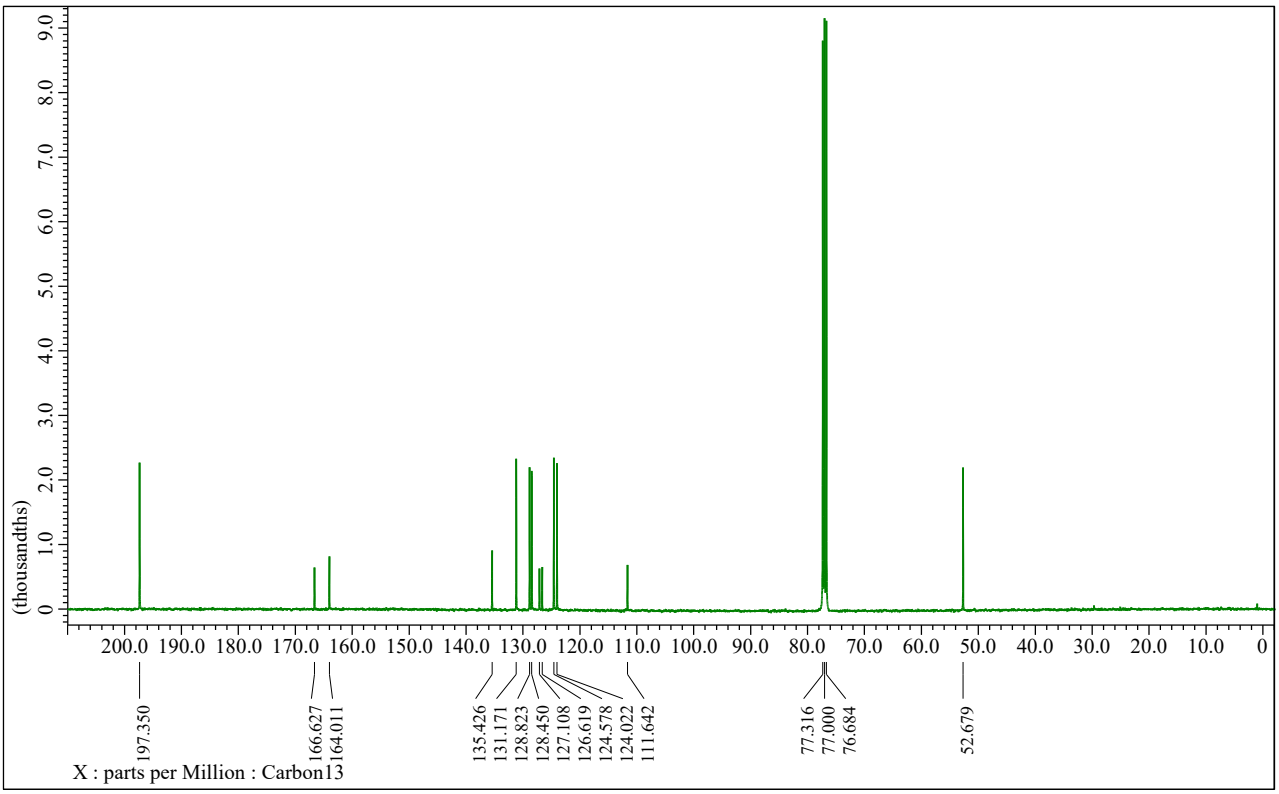




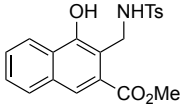
2-Formyl-3-methoxycarbonyl-1-naphthol (3)

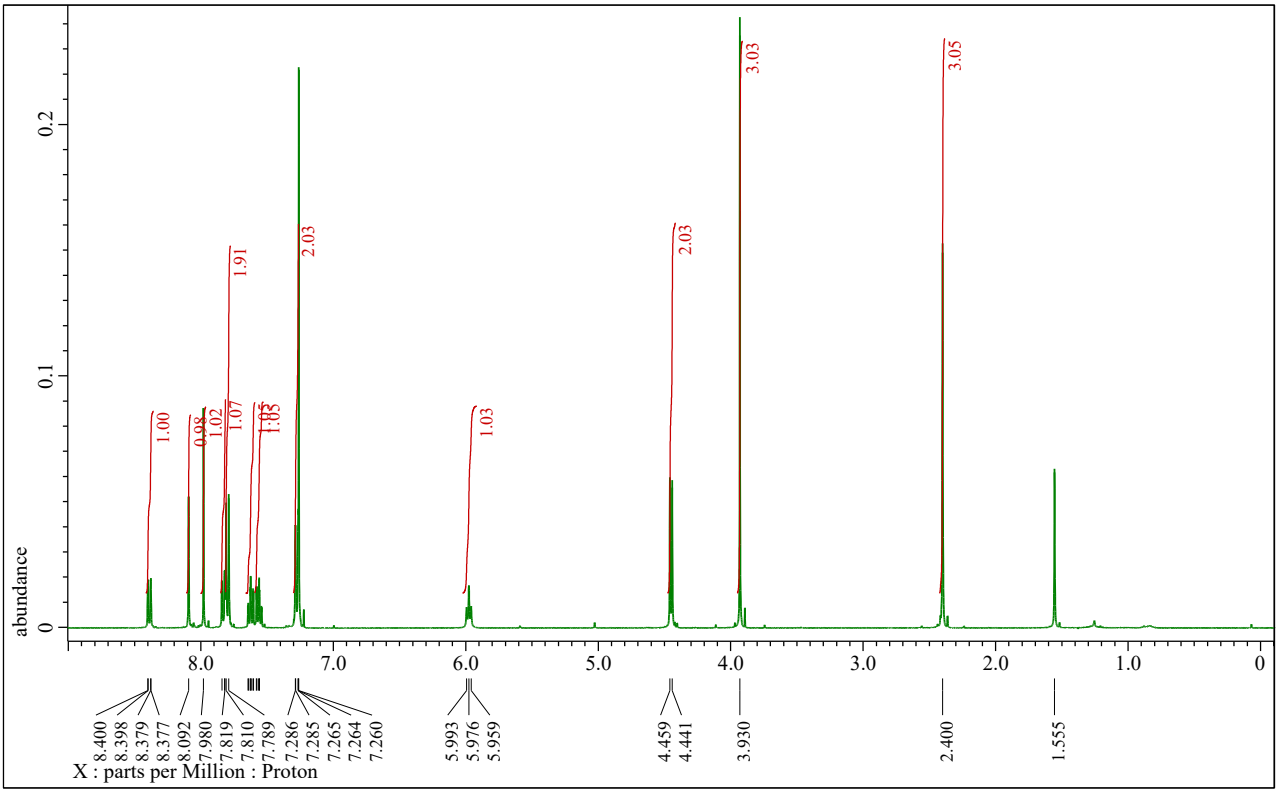


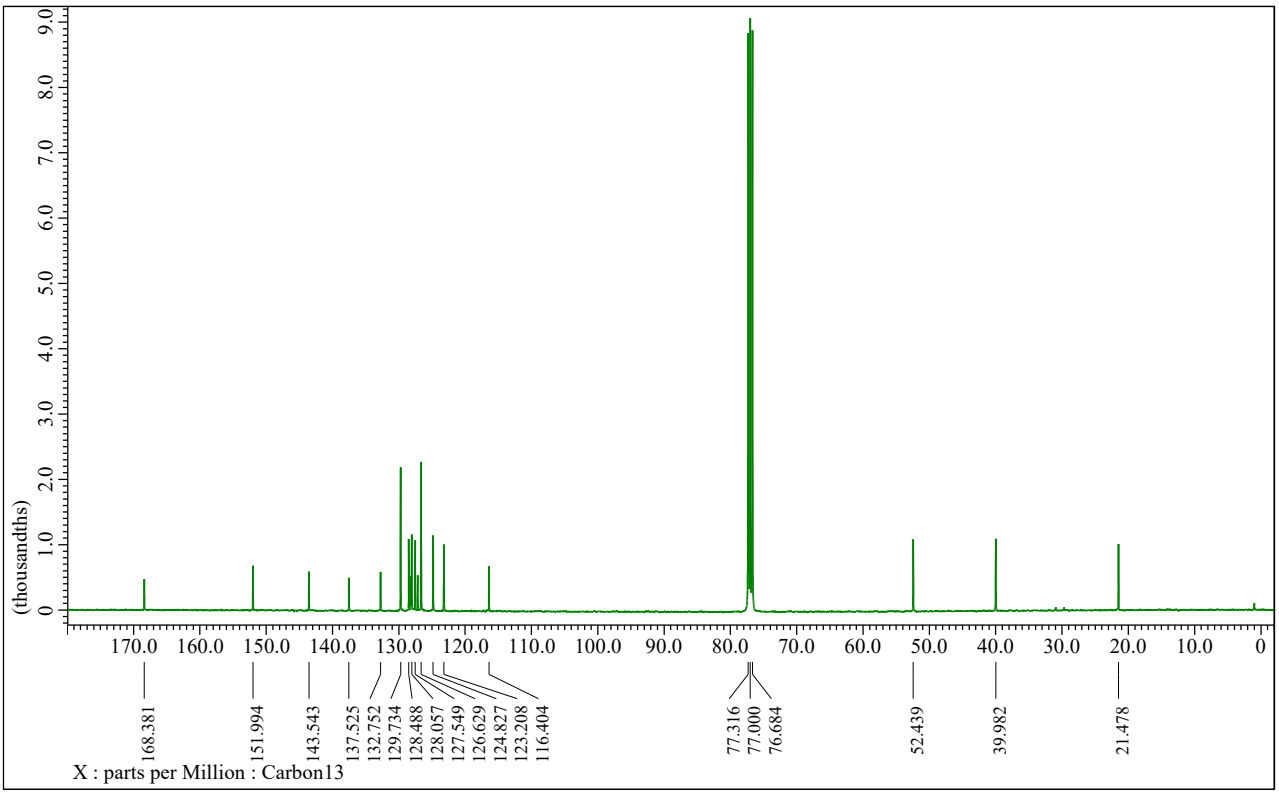




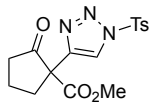
3-Methoxycarbonyl-2-(*N*-tosylaminomethyl)-1-naphthol (4)

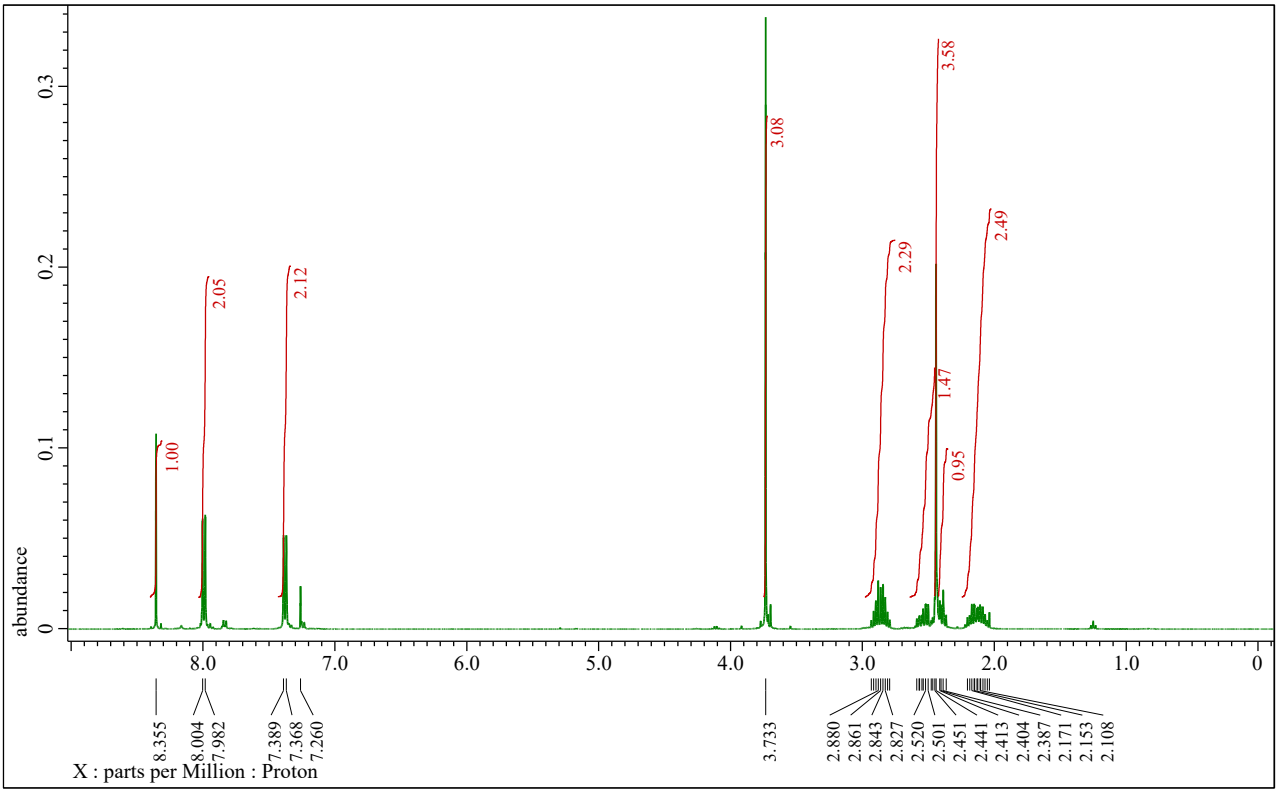


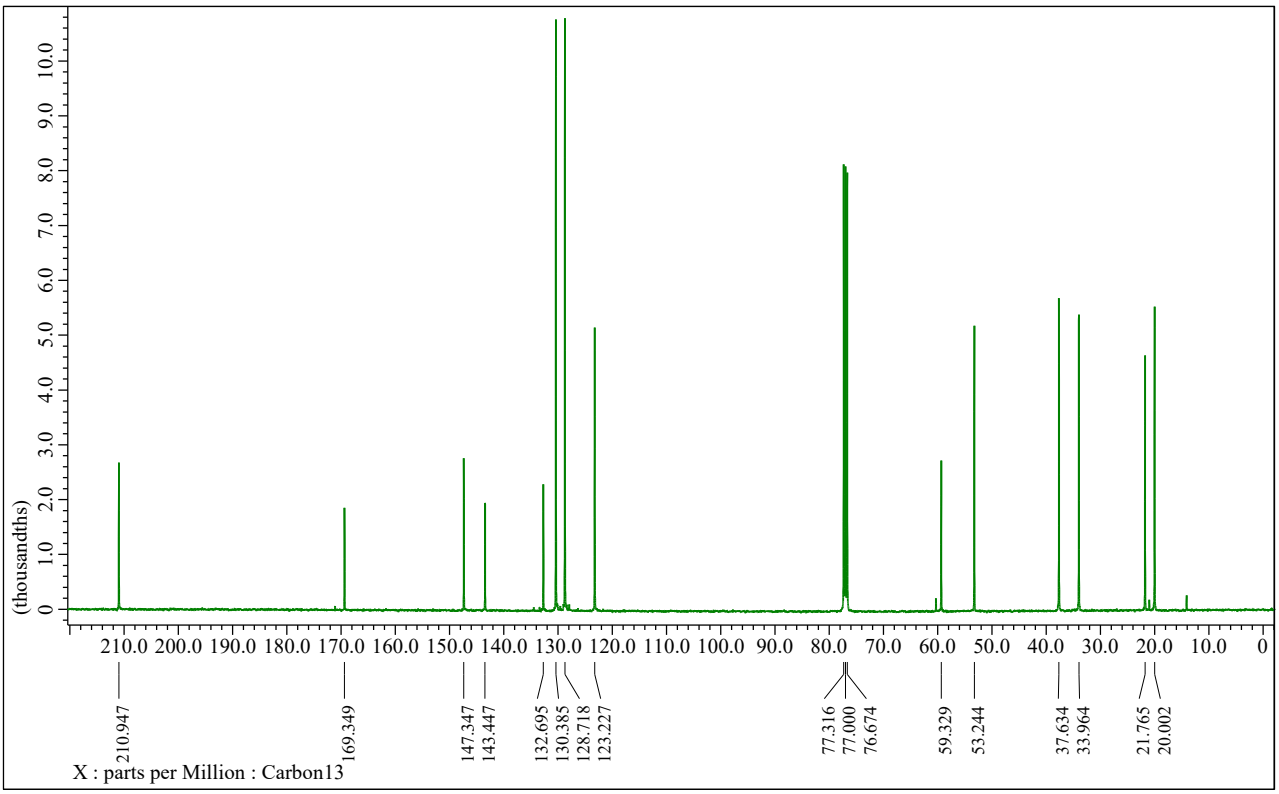




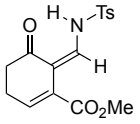
2-Methoxycarbonyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1-cyclopentanone (6)

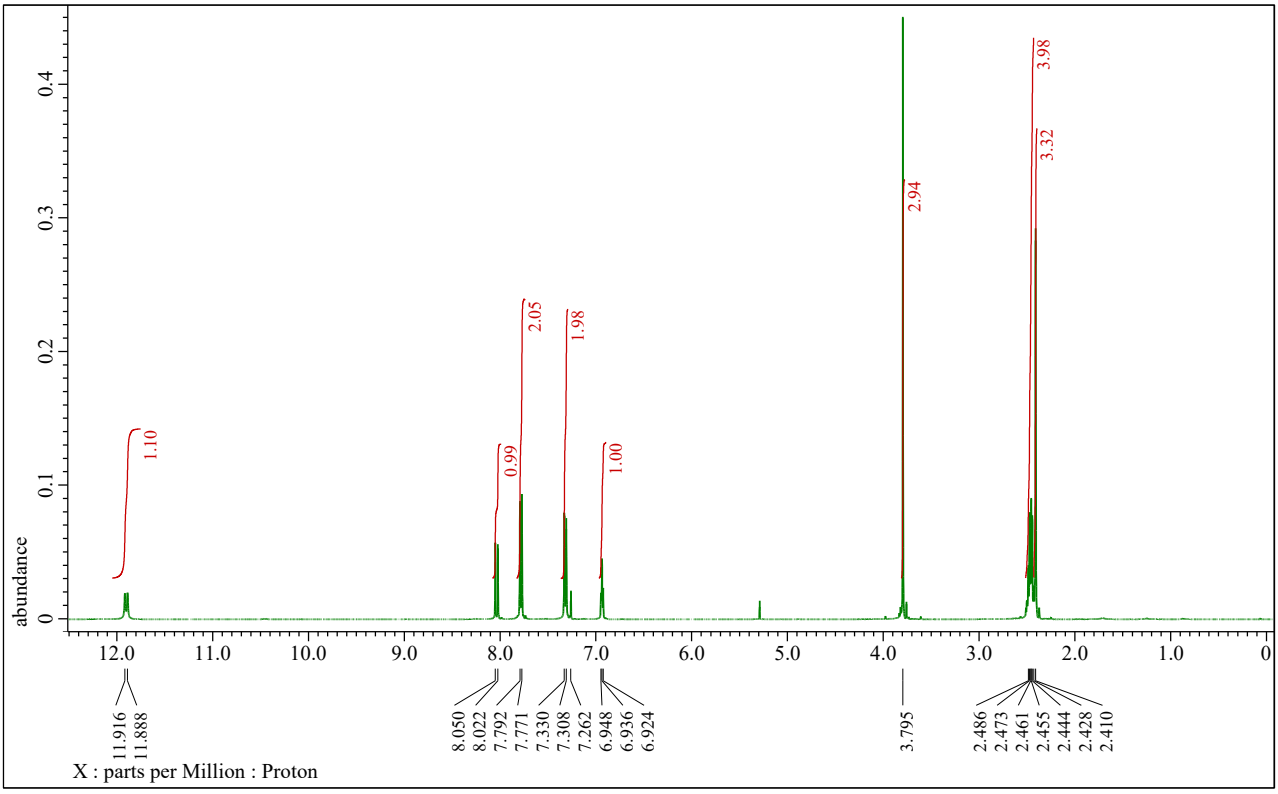


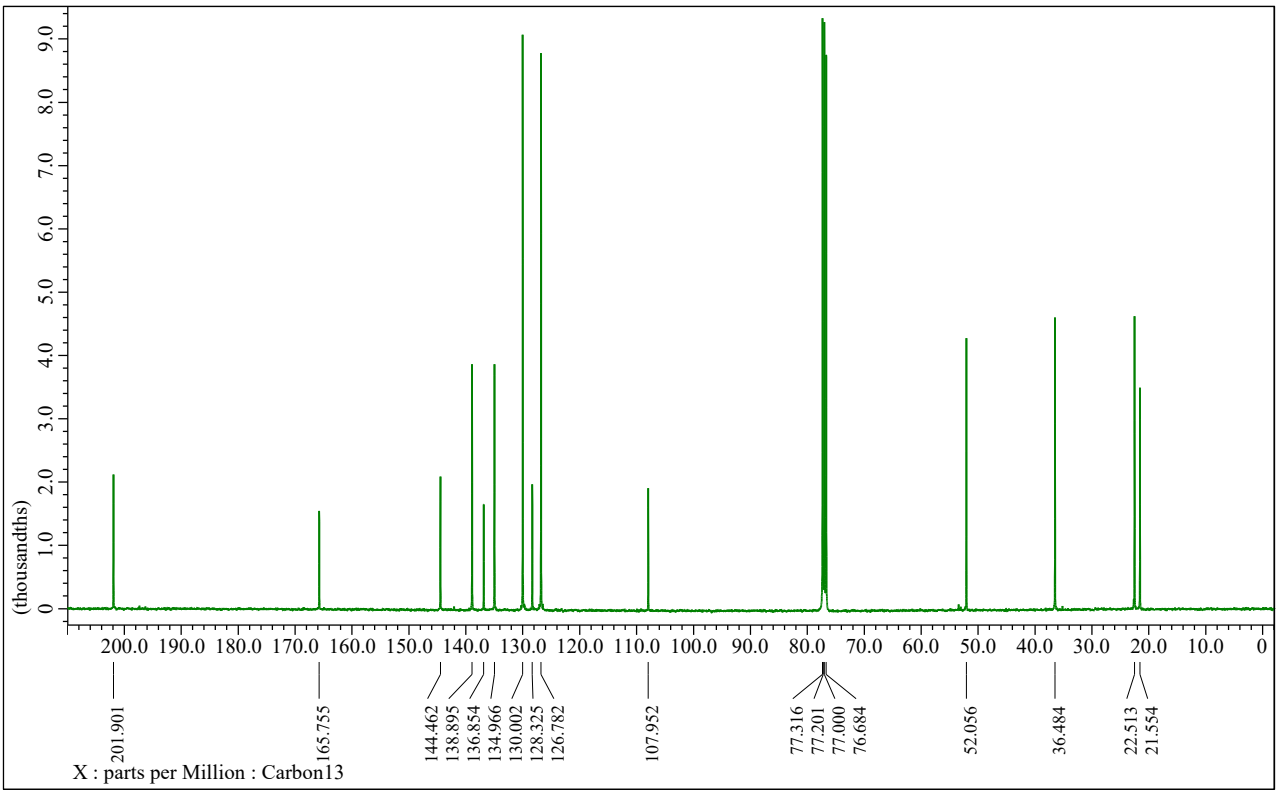




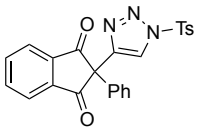
3-Methoxylcarbonyl-2-(*N*-tosylaminomethylene)-3-cyclohexen-1-one (8)

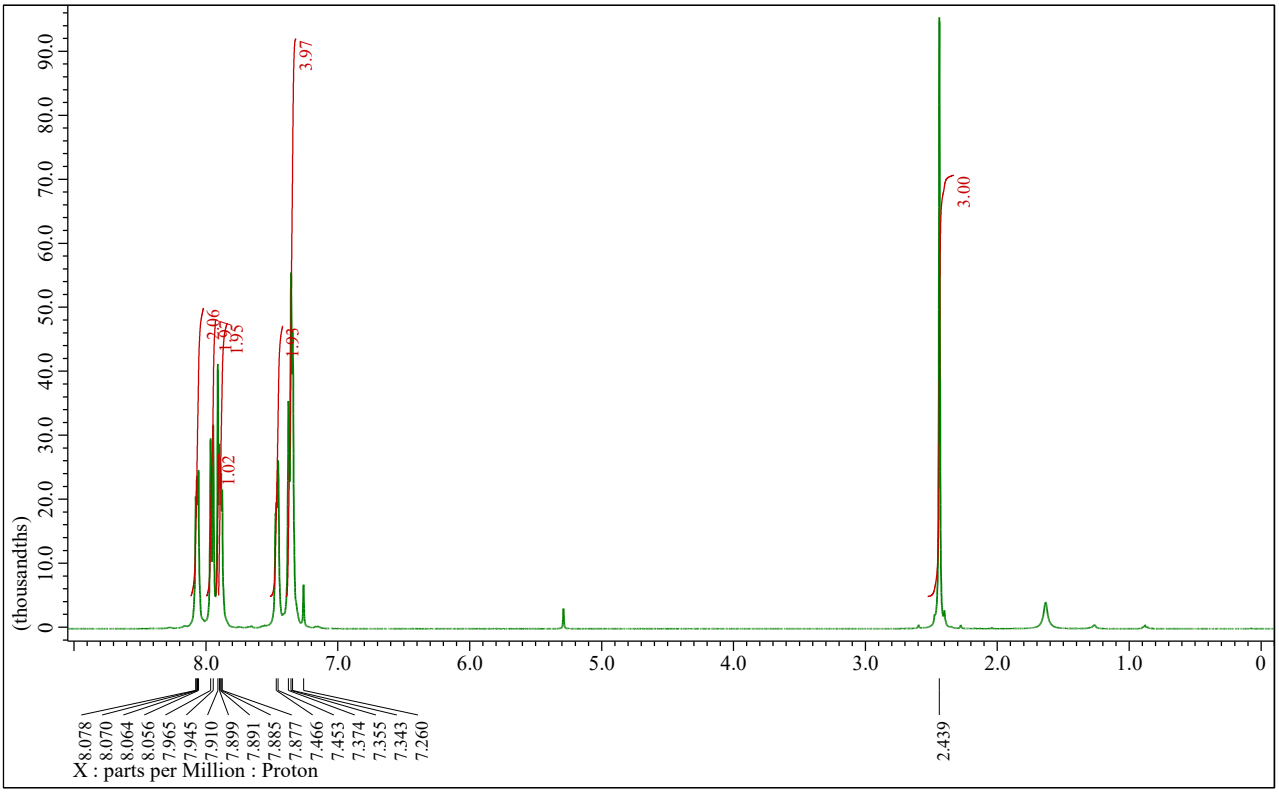


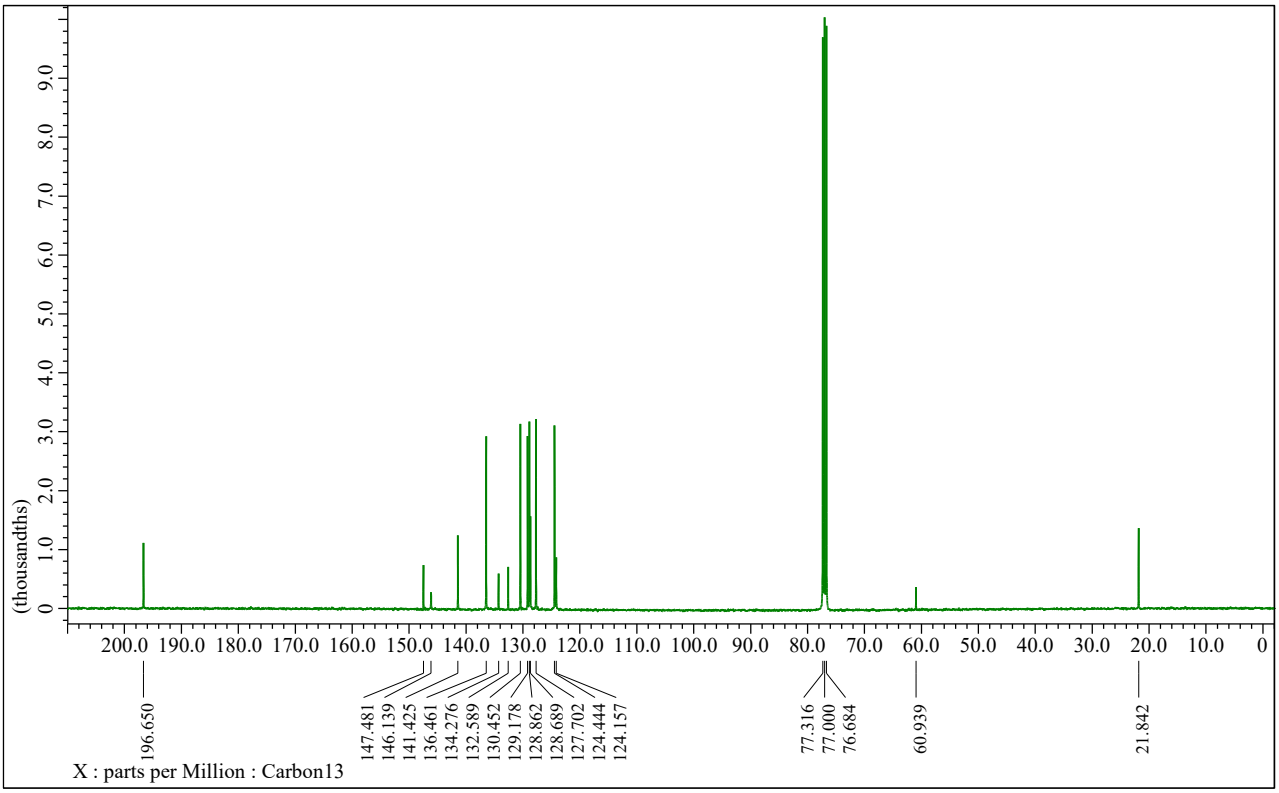




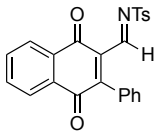
2-Phenyl-2-(1-tosyl-1,2,3-triazol-4-yl)-1,3-indandione (9)

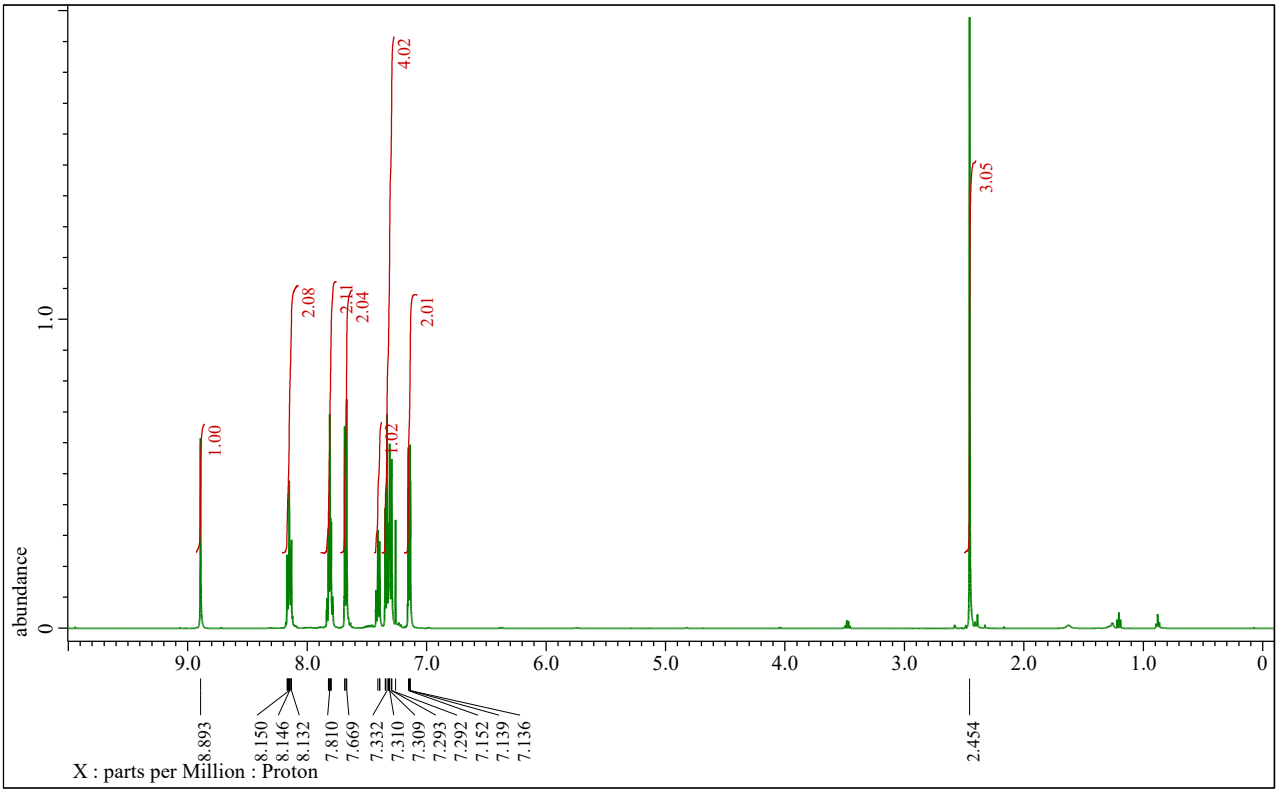


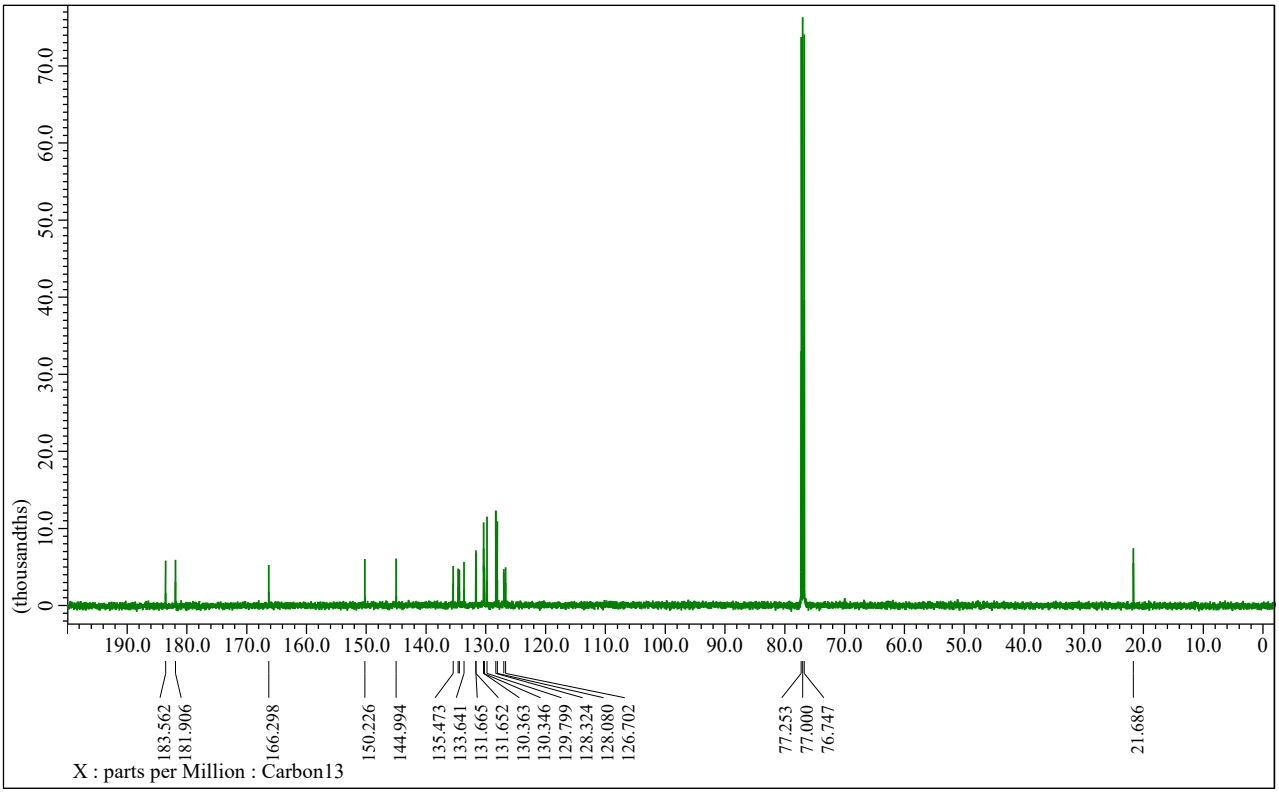




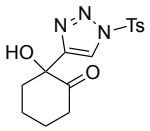
3-Phenyl-2-(*N*-tosyl-iminomethyl)-1,4-naphthalenedione (10)

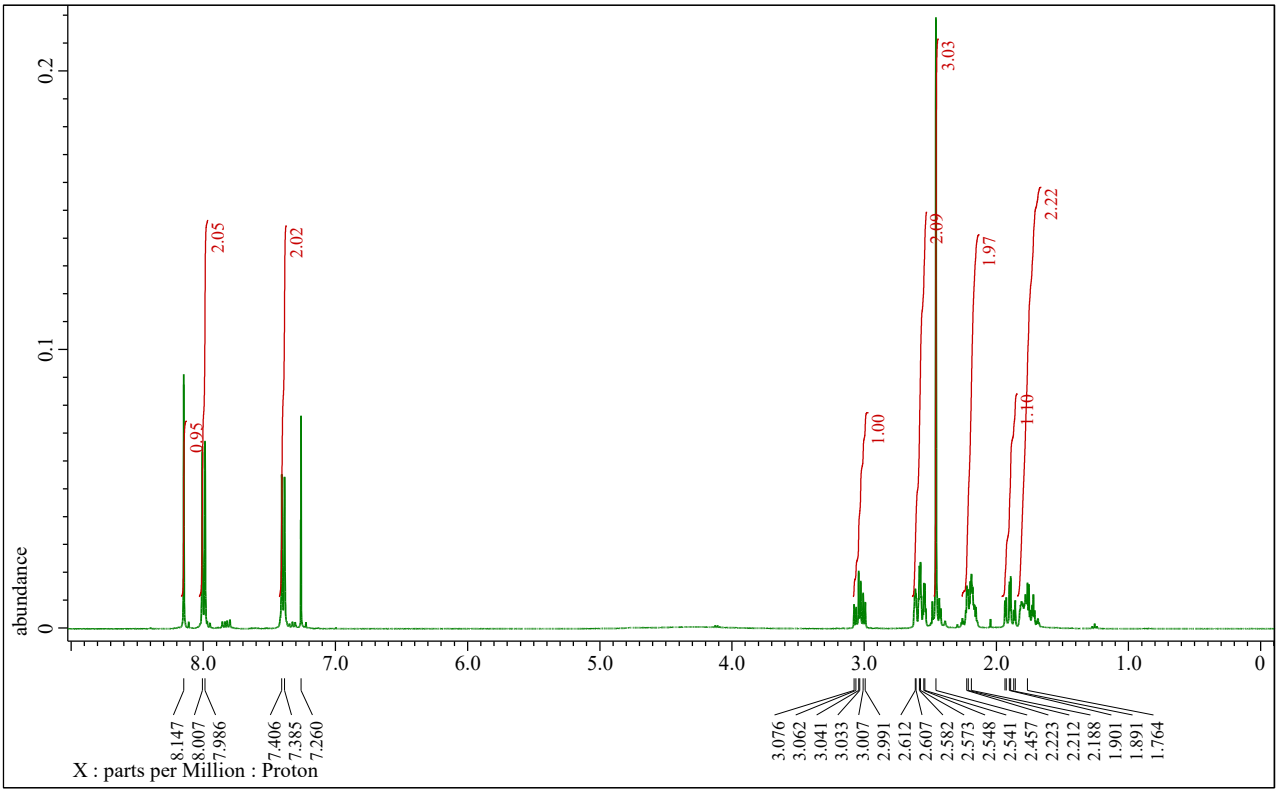


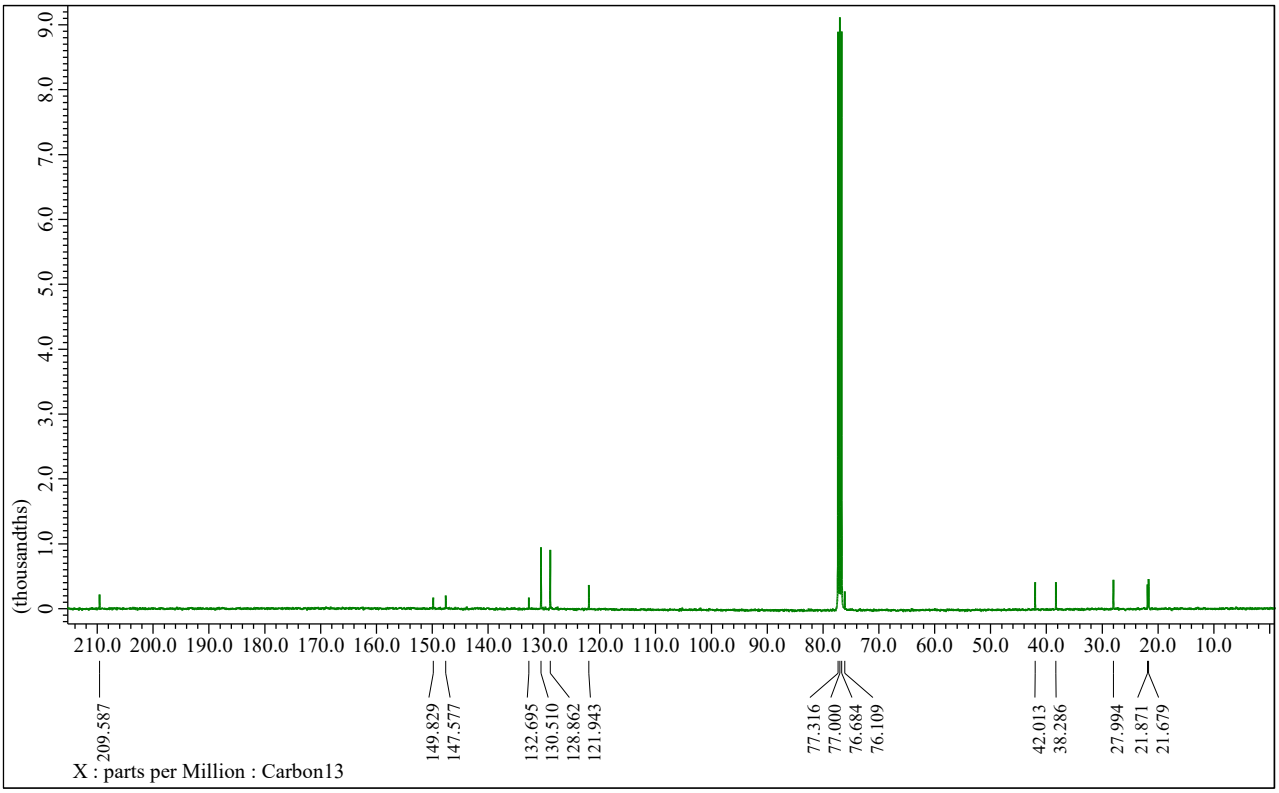




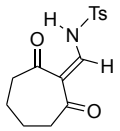
2-Hydroxy-2-(1-tosyl-1,2,3-triazol-4-yl)-1-cyclohexanone (11)

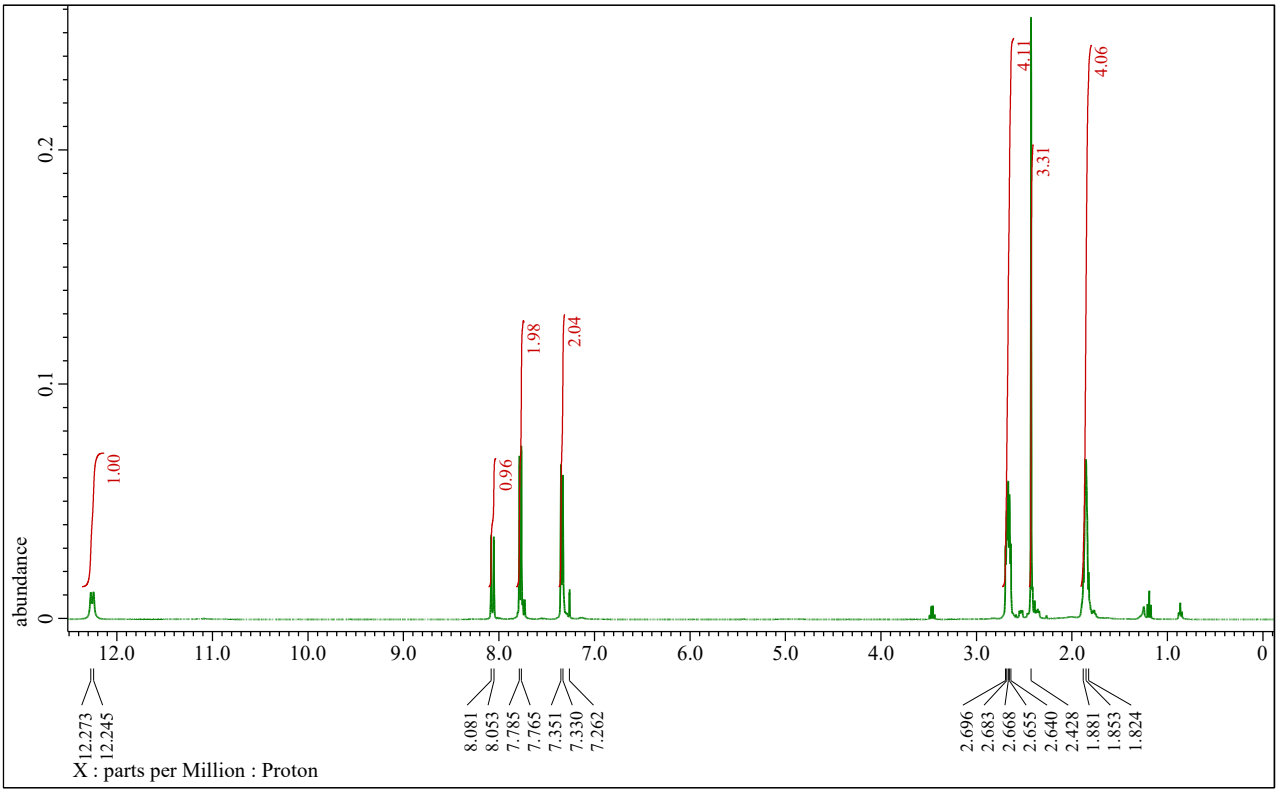


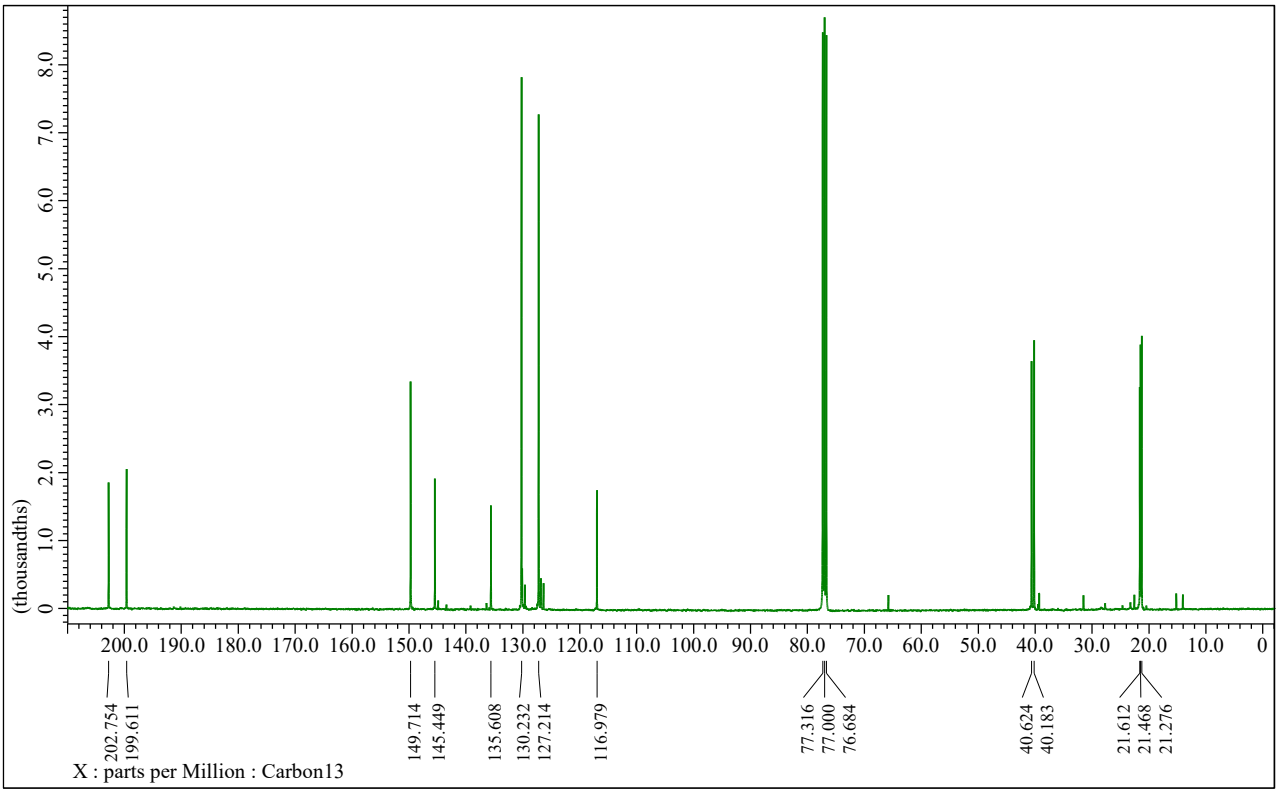




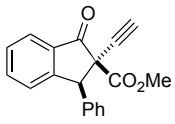
2-(*N*-Tosylaminomethylene)-1,3-cycloheptadione (12)

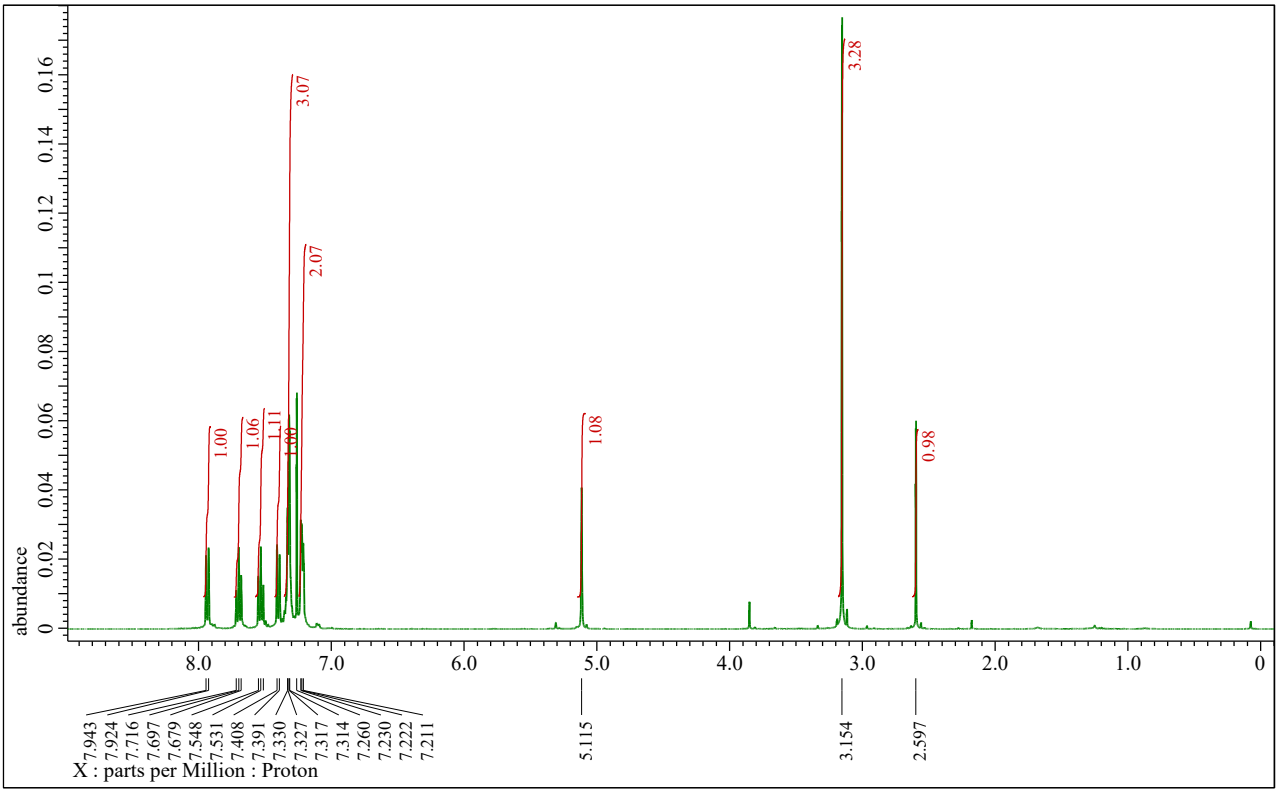


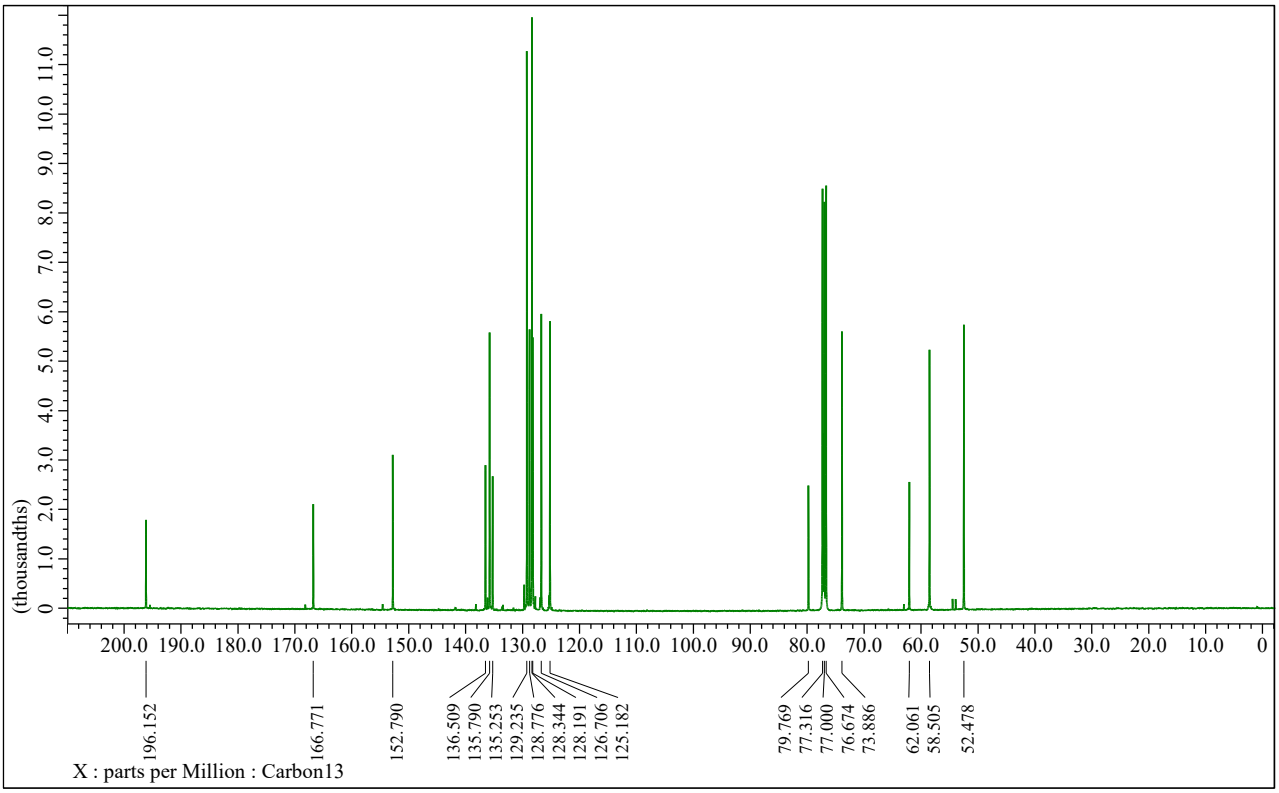




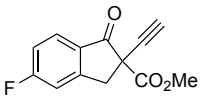
2-Ethynyl-2-methoxycarbonyl-3-phenyl-1-indanone (s7)

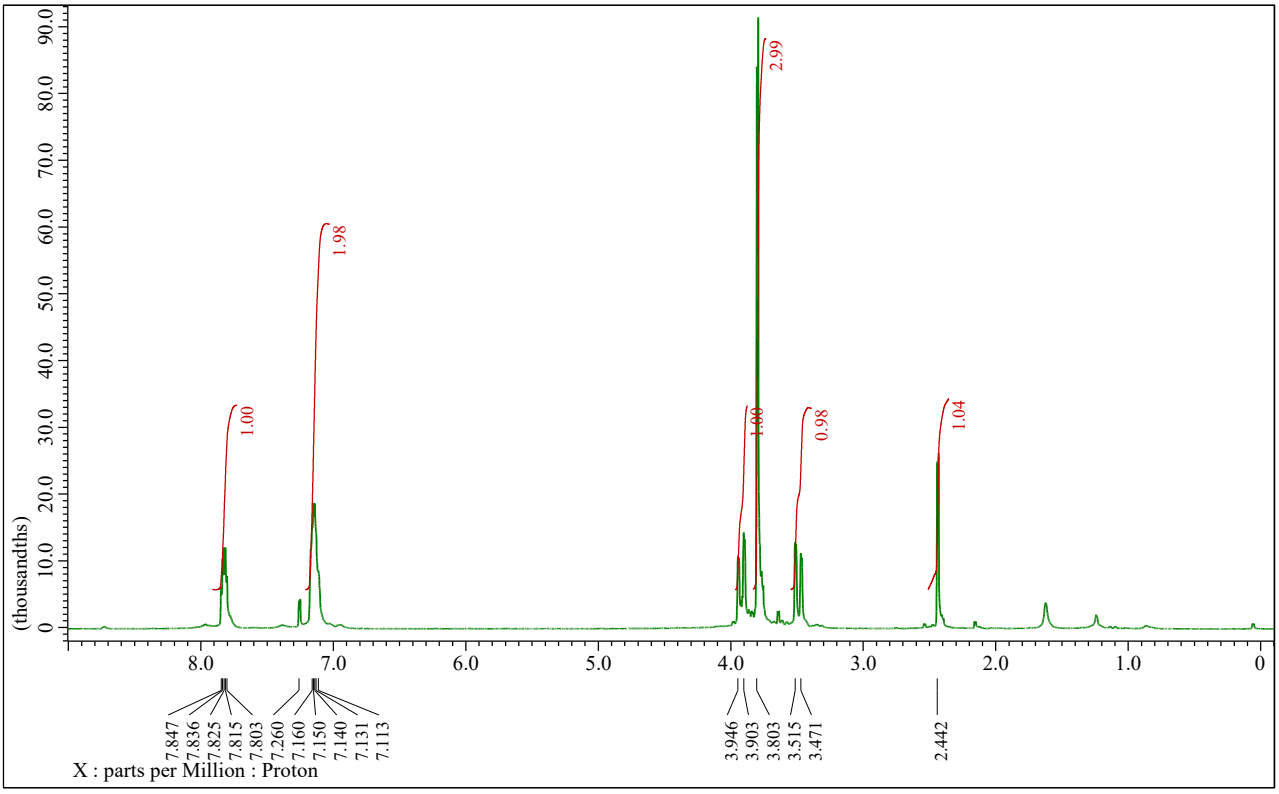


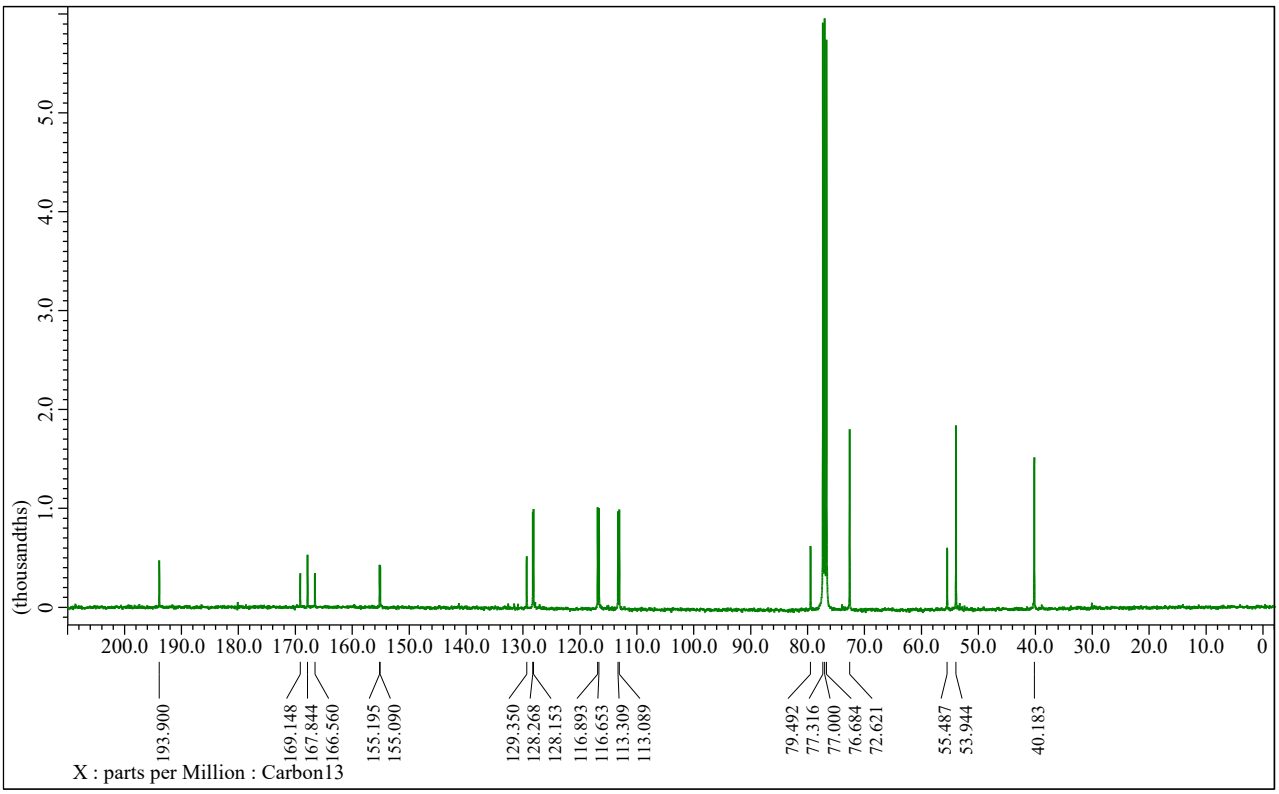




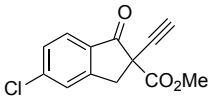
2-Ethynyl-5-fluoro-2-methoxycarbonyl-1-indanone (s10)

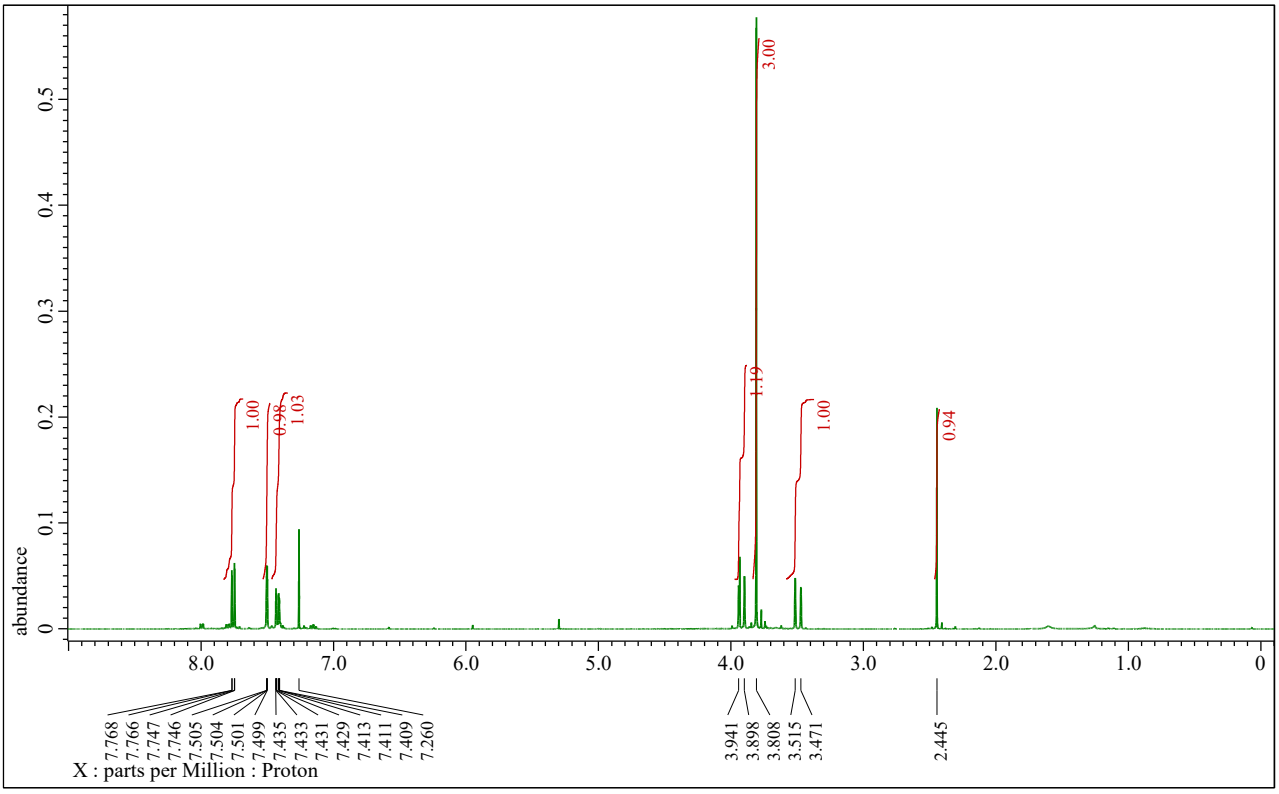


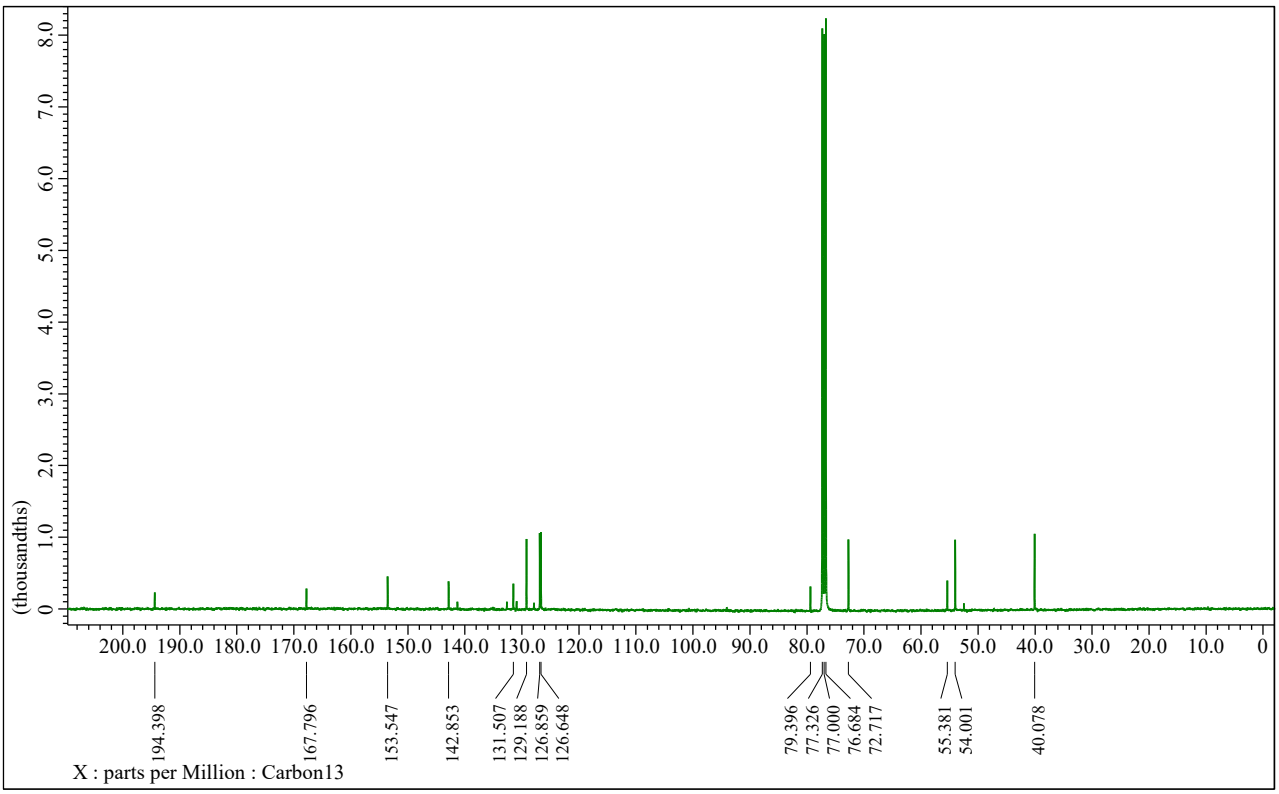




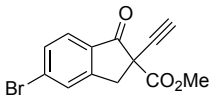
5-Chloro-2-ethynyl-2-methoxycarbonyl-1-indanone (s13)

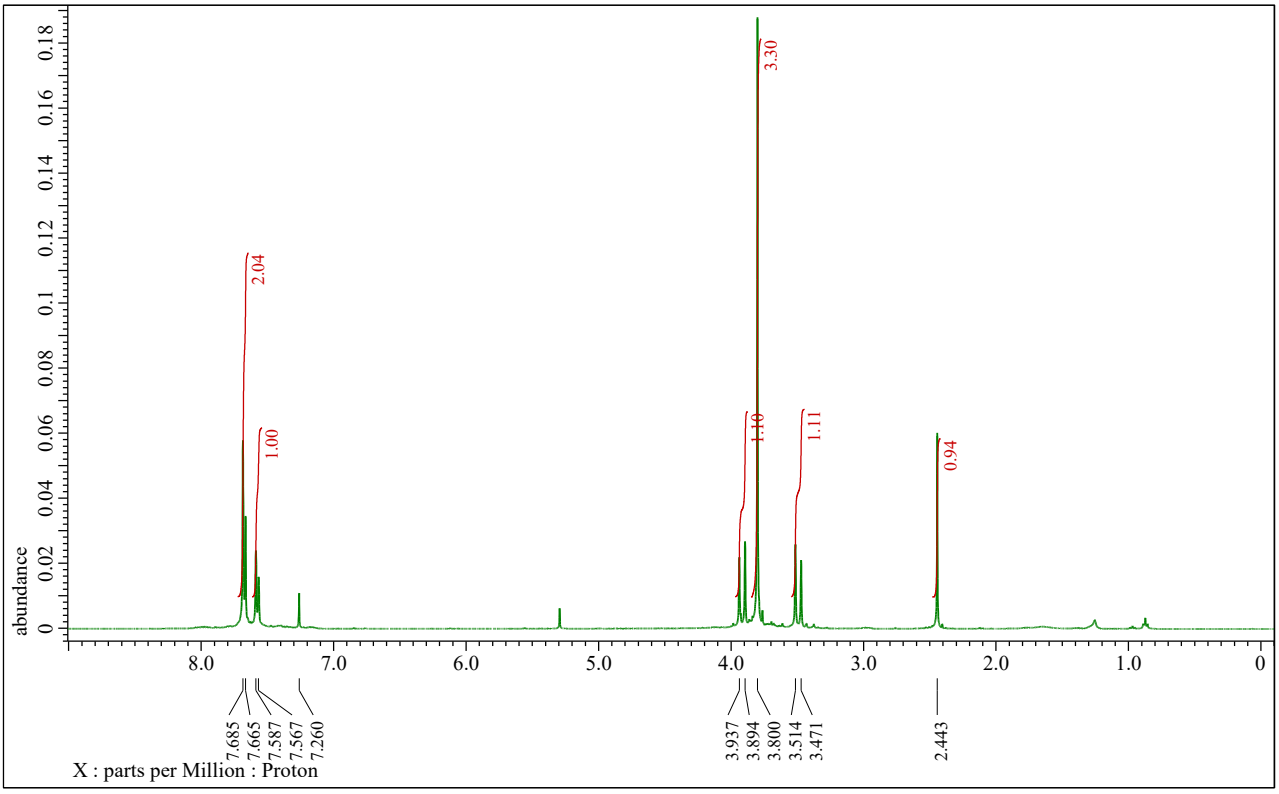


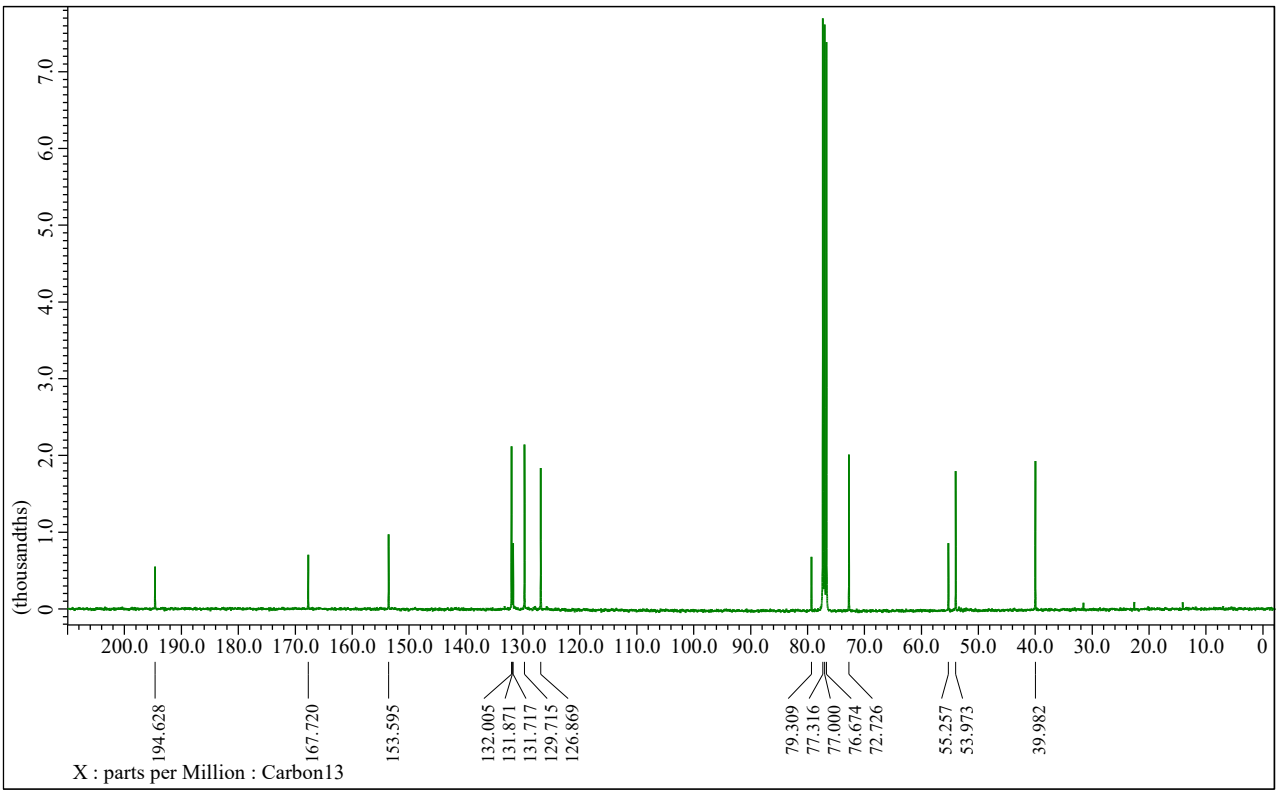




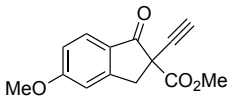
5-Bromo-2-ethynyl-2-methoxycarbonyl-1-indanone (s16)

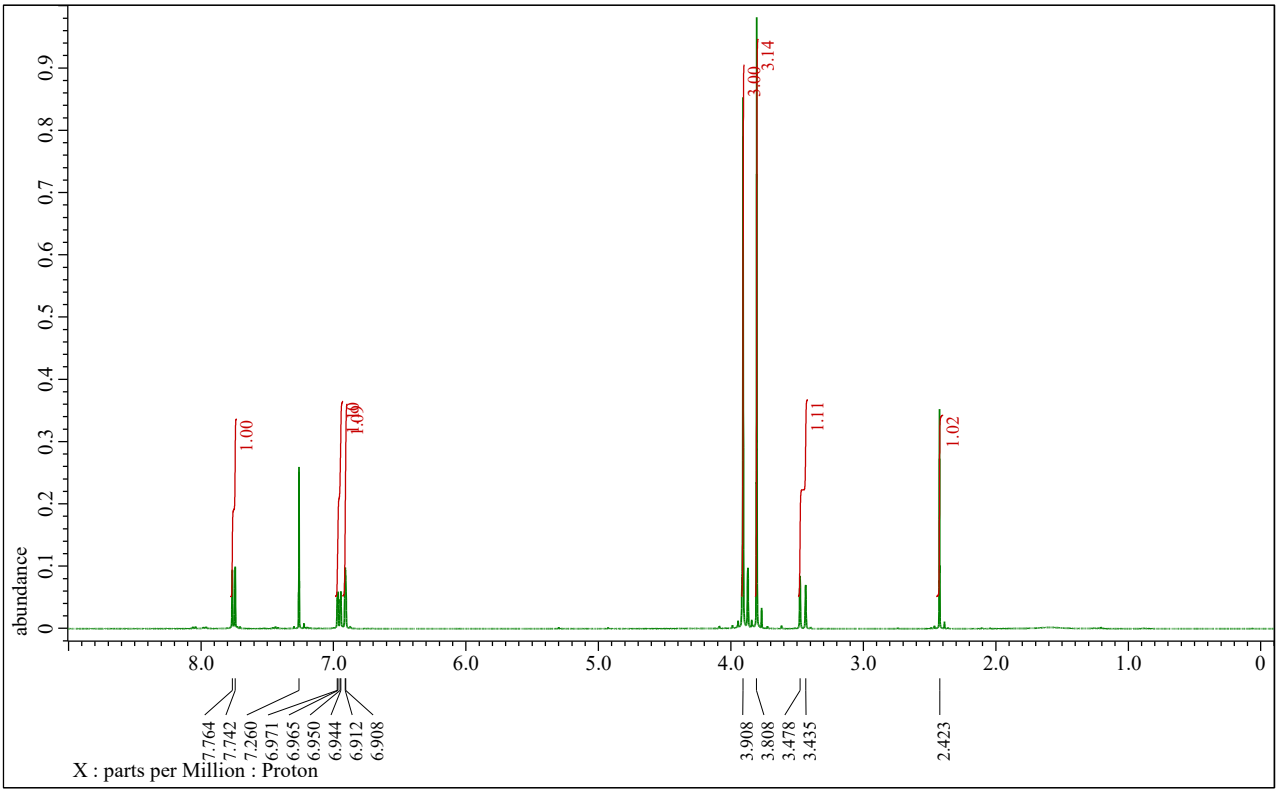


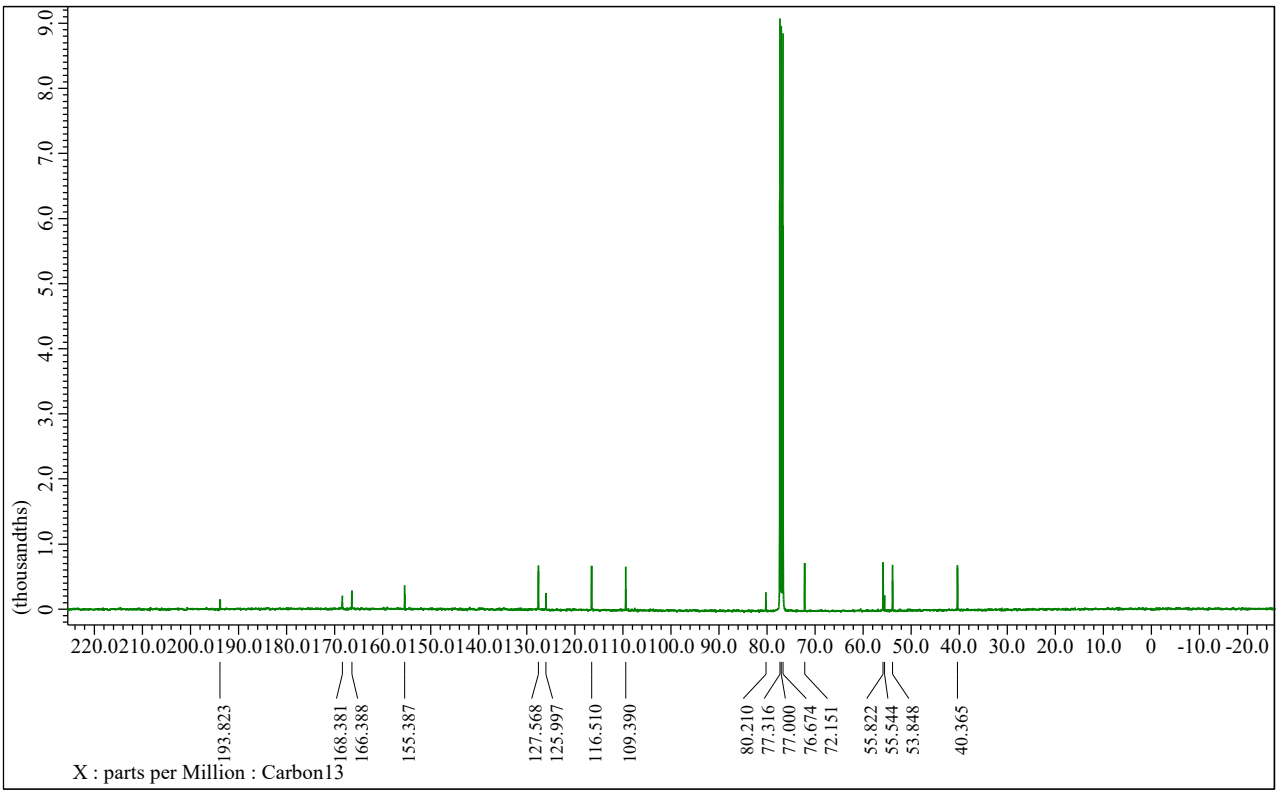




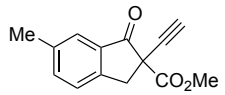
2-Ethynyl-5-methoxy-2-methoxycarbonyl-1-indanone (s20)

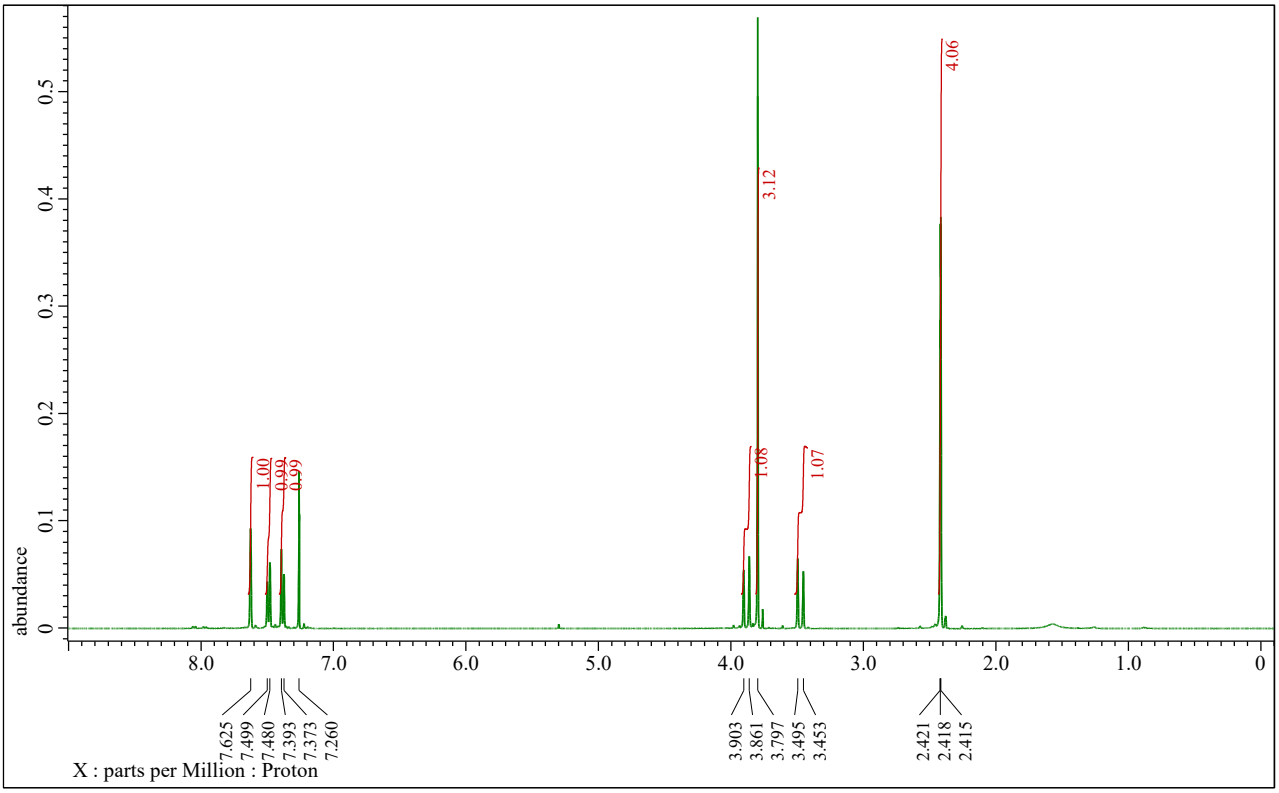


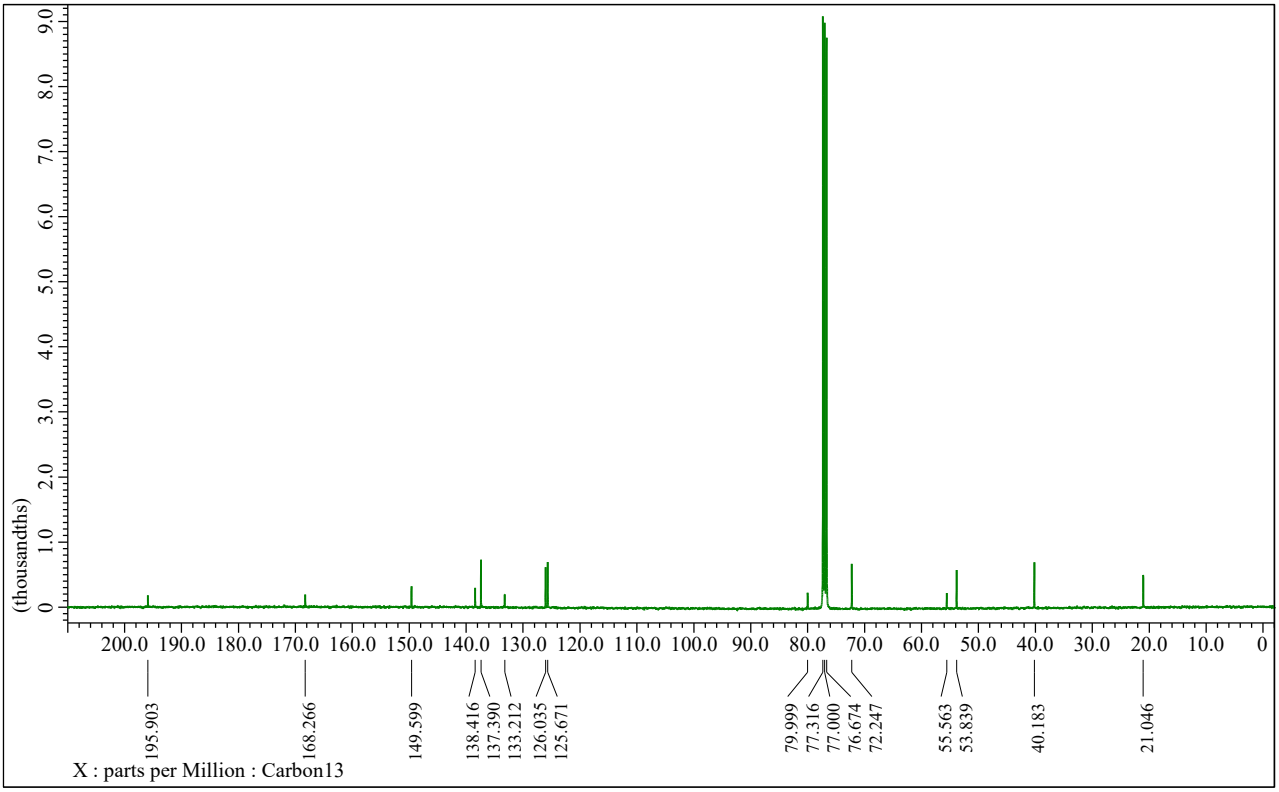




6-Methyl-2-methoxycarbonyl-1-indanone (s22)







2-Ethynyl-6-methoxy-2-methoxycarbonyl-1-indanone (s27)