

Supporting Information

Catalytic asymmetric synthesis of 1,3-enyne scaffolds: design and synthesis of conjugated nitro dienynes as novel Michael acceptors and development of new synthetic methodology

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1. General Information

¹H-NMR and ¹³C-NMR spectra were recorded at 300 MHz and 400 MHz spectrophotometer. Chemical shifts (δ) are expressed in ppm, and *J* values are given in Hz. The enantiomeric excess was determined by chiral HPLC with *n*-hexane and *i*-propanol as eluents. High resolution mass spectrometry (HRMS) was recorded on a VG Auto Spec-3000 spectrometer. Optical rotations were measured on a JASCO DIP-370 polarimeter. All chemicals and solvents were used as received without further purification unless otherwise stated. Flash column chromatography was performed on silica gel (230–400 mesh).

2. Representative Procedure for the Synthesis of Alcohols 3

To a solution of (*E*)-(2-bromovinyl)benzene **2a** (1.82 g, 10 mmol) in dry diethylamine (25 mL) was added Pd(PPh₃)₄ (46 mg, 0.04 mmol, 0.004 eq), CuI (25 mg, 0.13 mmol, 0.013 eq) and propargylic alcohol (560 mg, 10 mmol) and the resulting mixture was stirred for 36 h at room temperature. The solvent was removed under reduced pressure, and the crude was purified by flash silica gel chromatography to give the desired alcohol **3a** (1.34 g, 85%). ¹H NMR (300 MHz, CDCl₃): δ = 7.24 (m, 5H), 6.92 (d, *J* = 16.2 Hz, 1H), 6.13 (m, 1H), 4.44 (s, 2H), 2.44 (brs, 1H); ¹³C NMR (75 MHz, CDCl₃), δ = 141.9, 136.0, 128.8, 126.3, 107.5, 89.5, 84.9, 51.6. HRMS: calcd for C₁₁H₁₀O [M]⁺ 158.0732, found 158.0735.

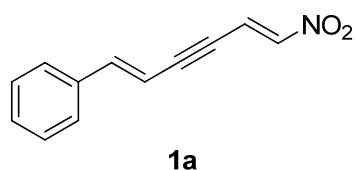
3. Representative Procedure for the Synthesis of Aldehydes 4

To a solution of **3a** (790 mg, 5 mmol) in THF/DMSO (14 mL, V_{THF}/V_{DMSO} = 6/1) was added IBX (1.68 g, 6 mmol, 1.2 eq) and the resulting mixture was stirred for 8 h at room temperature. The organic layer was

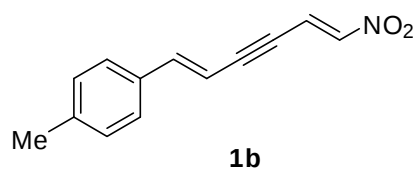
washed with saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution and brine. The organic phase was dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure, and the crude was purified by flash silica gel chromatography to give the desired aldehyde **4a** (640 mg, 82%). ^1H NMR (400 MHz, CDCl_3): δ = 9.35 (s, 1H), 7.45 (m, 2H), 7.38 (m, 3H), 7.29 (m, 1H), 6.27 (d, J = 16.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ = 176.5, 149.0, 134.9, 130.4, 129.0, 127.2, 104.7, 95.0, 90.4. HRMS: calcd for $\text{C}_{11}\text{H}_8\text{O}$ $[\text{M}]^+$ 156.0568, found 156.0575.

4. Representative Procedure for the Synthesis of Conjugated Nitro Dienynes 1

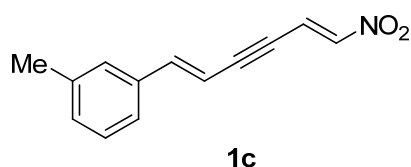
A slurry of LiAlH_4 (3.8 mg, 0.1 mmol, 0.1 eq) in dry THF (4 mL) was stirred for 30 min at 0°C , and then nitromethane (305 mg, 5 mmol, 5eq) was added. After 30 min, **4** (1 mmol) was added in one portion. The mixture was stirred until the reaction was complete (monitored by TLC). Then 1N HCl was added and the reaction mixture was extracted with dichloromethane. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to give the nitro alcohol product which was used without purification for the next step. To a solution of the nitro alcohol (0.9 mmol, 1eq) in dry dichloromethane (3 mL) was added trifluoroacetic anhydride (198 mg, 0.945 mmol, 1.05 eq) and triethylamine (190 mg, 1.89 mmol, 2.1 eq) at 0°C . The reaction mixture was stirred at 0°C until the reaction was complete (monitored by TLC). Then the organic layer was washed with saturated aqueous NH_4Cl solution and brine. The organic layer was dried over Na_2SO_4 , filtered and concentrated under reduced pressure, and the crude was purified by flash silica gel chromatography to give **1**.



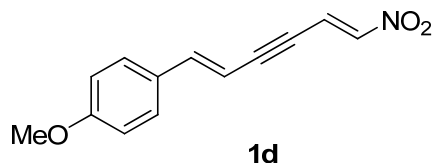
((1E,5E)-6-Nitrohexa-1,5-dien-3-ynyl)benzene (1a): ^1H NMR (300 MHz, CDCl_3): δ = 7.41 (m, 2H), 7.38 (m, 3H), 7.35 (m, 2H), 7.13 (d, J = 16.2 Hz, 1H), 6.31 (dd, J = 16.2 Hz, J = 1.5 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ = 146.2, 145.2, 135.3, 130.0, 129.0, 127.0, 121.2, 106.4, 105.2, 84.3. HRMS: calcd for $\text{C}_{12}\text{H}_9\text{NO}_2$ $[\text{M}]^+$ 199.0633, found 199.0637.



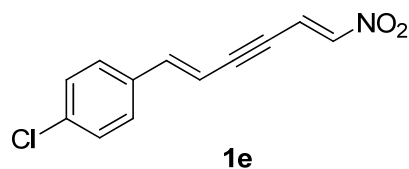
1-Methyl-4-((1E,5E)-6-nitrohexa-1,5-dien-3-ynyl)benzene (1b): ^1H NMR (300 MHz, CDCl_3): δ = 7.33 (m, 4H), 7.19 (m, 3H), 6.26 (dd, J = 16.2 Hz, J = 1.8 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ = 146.3, 144.9, 140.4, 132.6, 129.7, 126.9, 121.3, 105.7, 105.2, 84.1, 21.4. HRMS: calcd for $\text{C}_{13}\text{H}_{11}\text{NO}_2$ $[\text{M}]^+$ 213.0790, found 213.0792.



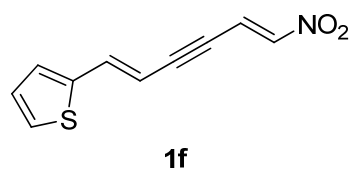
1-Methyl-3-((1E,5E)-6-nitrohexa-1,5-dien-3-ynyl)benzene (1c): ^1H NMR (300 MHz, CDCl_3): δ = 7.20 (m, 2H), 7.16 (m, 3H), 7.09 (m, 1H), 7.00 (d, J = 16.5 Hz, 1H), 6.21 (dd, J = 16.2 Hz, J = 2.1 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ = 146.4, 145.1, 138.7, 135.2, 130.9, 128.9, 127.6, 124.2, 121.2, 105.1, 105.4, 84.2, 21.4. HRMS: calcd for $\text{C}_{13}\text{H}_{11}\text{NO}_2$ $[\text{M}]^+$ 213.0790, found 213.0792.



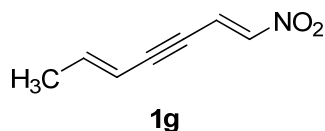
1-Methoxy-4-((1E,5E)-6-nitrohexa-1,5-dien-3-ynyl)benzene (1d): ^1H NMR (400 MHz, CDCl_3): δ = 7.31 (d, J = 8.7 Hz, 2H), 7.23 (d, J = 9.0 Hz, 2H), 7.02 (d, J = 16.2 Hz, 1H), 6.81 (d, J = 8.8 Hz, 2H), 6.11 (dd, J = 16.2 Hz, J = 2.4 Hz, 1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ = 161.2, 146.0, 144.7, 128.6, 128.1, 121.5, 114.4, 106.3, 103.8, 84.1, 55.4. HRMS: calcd for $\text{C}_{13}\text{H}_{11}\text{NO}_3$ $[\text{M}]^+$ 229.0739, found 229.0739.



1-Chloro-4-((1E,5E)-6-nitrohexa-1,5-dien-3-ynyl)benzene (1e): ^1H NMR (300 MHz, CDCl_3): δ = 7.35 (m, 4H), 7.29 (m, 2H), 7.06 (d, J = 16.2 Hz, 1H), 6.28 (d, J = 15.9 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ = 145.2, 145.7, 135.7, 133.7, 129.1, 128.0, 120.8, 106.9, 104.4, 84.5. HRMS: calcd for $\text{C}_{12}\text{H}_8\text{ClNO}_2$ $[\text{M}]^+$ 233.0244, found 233.0238.



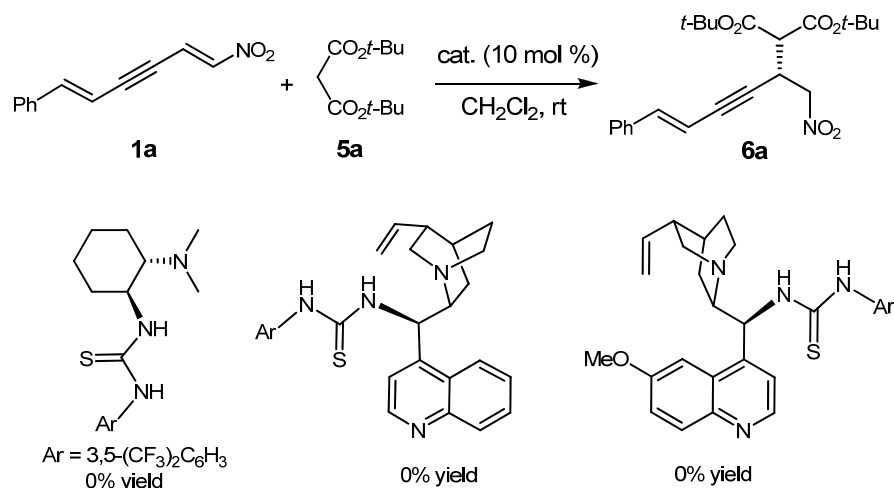
2-((1E,5E)-6-Nitrohexa-1,5-dien-3-ynyl)thiophene (1f): ^1H NMR (300 MHz, CDCl_3): δ = 7.34 (m, 1H), 7.30 (m, 3H), 7.17 (d, J = 3.6 Hz, 1H), 7.05 (m, 1H), 6.13 (dd, J = 15.9 Hz, J = 2.1 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ = 145.1, 140.6, 138.8, 129.4, 128.3, 127.8, 121.2, 105.4, 84.9. HRMS: calcd for $\text{C}_{10}\text{H}_7\text{NO}_2\text{S}$ $[\text{M}]^+$ 205.0198, found 205.0203.



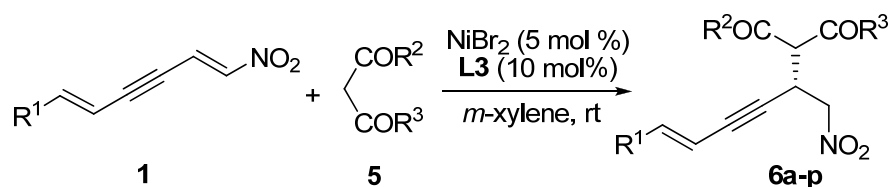
((1E,5E)-1-Nitrohepta-1,5-dien-3-yne (1g): ^1H NMR (300 MHz, CDCl_3): δ = 7.21 (m, 2H), 6.18 (m, 1H), 5.61 (m, 1H), 1.85 (dd, J = 6.9 Hz, J = 1.5 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ = 145.0, 144.3, 121.2, 109.1, 102.2, 86.3, 16.6. HRMS: calcd for $\text{C}_7\text{H}_7\text{NO}_2$ $[\text{M}]^+$ 137.0477, found 137.0475.

5. Catalytic Enantioselective Conjugate Addition of 1,3-Dicarbonyl Compounds to Nitro Dienynes

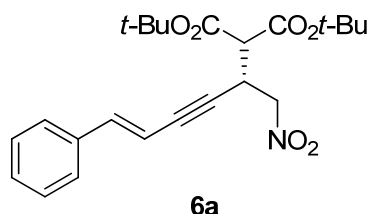
(A) Attempts with Bifunctional Tertiary Amine-Thiourea Catalysts



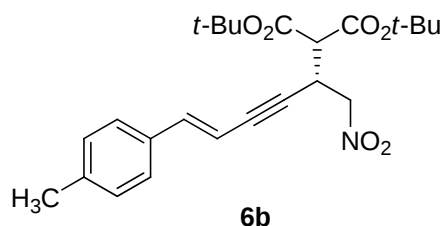
(B) Representative Procedure for Ni(II)-Catalyzed Enantioselective Conjugate Addition of 1,3-Dicarbonyl Compounds to Nitro Dienynes



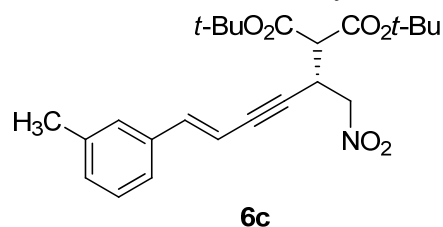
To a solution of catalyst $\text{NiBr}_2/2\text{L3}$ (5 mol %) in *m*-xylene (0.5 mL) was added 1,3-dicarbonyl compounds **5** (0.3 mmol, 1.5 eq) and nitro dienynes **1** (0.2 mmol). The reaction mixture was stirred at room temperature until the reaction was complete (monitored by TLC). The solvent was removed under reduced pressure and the crude was purified by flash silica gel chromatography to give **6**.



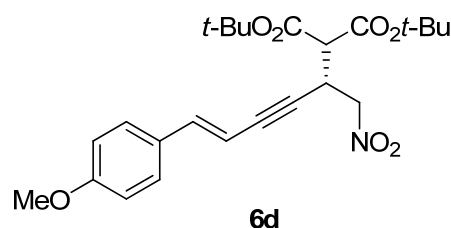
(S,E)-Di-tert-butyl 2-(1-nitro-6-phenylhex-5-en-3-yn-2-yl)malonate (6a): $[\alpha]_{\text{D}}^{20} = +14.1$ (*c* 1.0 CHCl_3). ^1H NMR (300 MHz, CDCl_3): δ = 7.29 (m, 5H), 6.87 (d, J = 16.2 Hz, 1H), 6.04 (dd, J = 16.2 Hz, J = 1.8 Hz, 1H), 4.77-4.71 (m, 2H), 4.04-4.00 (m, 1H), 3.54 (d, J = 7.8 Hz, 1H), 1.46 (s, 18H); ^{13}C NMR (75 MHz, CDCl_3): δ = 166.1, 165.8, 142.4, 135.9, 128.8, 128.7, 128.3, 126.3, 107.1, 85.8, 84.5, 83.1, 82.9, 76.4, 55.0, 30.9, 27.9, 27.9. HRMS: calcd for $\text{C}_{23}\text{H}_{29}\text{NO}_6$ $[\text{M}]^+$ 415.1995, found 415.1985. HPLC (Chiralcel OJ-H, *i*-propanol/*n*-hexane = 10/90, flow rate 0.8 mL/min, λ = 254 nm): t_{major} = 14.489 min, t_{minor} = 26.307 min.



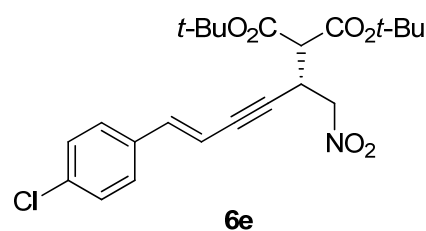
(*S,E*)-Di-*tert*-butyl 2-(1-nitro-6-*p*-tolylhex-5-en-3-yn-2-yl)malonate (6b): $[\alpha]_D^{20} = + 2.1$ (*c* 1.0 CHCl₃). ¹H NMR (300 MHz, CDCl₃): δ = 7.23 (m, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.84 (d, *J* = 16.5 Hz, 1H), 5.98 (dd, *J* = 16.2 Hz, *J* = 2.1 Hz, 1H), 4.80-4.65 (m, 2H), 4.04-3.97 (m, 1H), 3.53 (d, *J* = 8.1 Hz, 1H), 2.33 (s, 3H), 1.49 (s, 18H); ¹³C NMR (75 MHz, CDCl₃): δ = 166.1, 165.8, 142.3, 138.9, 133.2, 129.4, 129.0, 128.6, 126.2, 106.0, 85.4, 84.7, 83.0, 82.9, 76.5, 55.0, 31.0, 27.9, 27.8, 21.3. HRMS: calcd for C₂₄H₃₁NO₆ [M]⁺ 429.2151, found 429.2141. HPLC (Chiralpak AD-H, *i*-propanol/*n*-hexane = 15/85, flow rate 0.8 mL/min, λ = 254 nm): *t*_{major} = 12.377 min, *t*_{minor} = 17.939 min.



(*S,E*)-Di-*tert*-butyl 2-(1-nitro-6-*m*-tolylhex-5-en-3-yn-2-yl)malonate (6c): $[\alpha]_D^{20} = + 53.9$ (*c* 1.0 CHCl₃). ¹H NMR (300 MHz, CDCl₃): δ = 7.00 (m, 4H), 6.75 (d, *J* = 16.2 Hz, 1H), 5.94 (dd, *J* = 16.5 Hz, *J* = 1.8 Hz, 1H), 4.73-4.58 (m, 2H), 3.97-3.92 (m, 1H), 3.45 (d, *J* = 7.8 Hz, 1H), 2.25 (s, 3H), 1.41 (s, 18H); ¹³C NMR (75 MHz, CDCl₃): δ = 166.1, 165.8, 142.5, 138.3, 135.9, 129.7, 128.6, 127.0, 123.5, 106.8, 85.7, 84.5, 83.0, 82.9, 76.5, 54.9, 30.9, 27.9, 27.8, 21.3. HRMS: calcd for C₂₄H₃₁NO₆ [M]⁺ 429.2151, found 429.2141. HPLC (Chiralpak AD-H, *i*-propanol/*n*-hexane = 10/90, flow rate 0.8 mL/min, λ = 254 nm): *t*_{major} = 11.085 min, *t*_{minor} = 14.531 min.

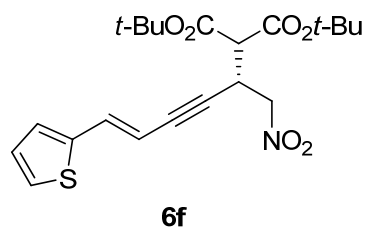


(*S,E*)-Di-*tert*-butyl 2-(6-(4-methoxyphenyl)-1-nitrohex-5-en-3-yn-2-yl)malonate (6d): $[\alpha]_D^{20} = + 21.5$ (*c* 1.0 CHCl₃). ¹H NMR (300 MHz, CDCl₃): δ = 7.30 (m, 2H), 6.81 (m, 3H), 5.89 (dd, *J* = 16.2 Hz, *J* = 1.8 Hz, 1H), 4.76-4.70 (m, 2H), 4.01-3.99 (m, 1H), 3.80 (s, 3H), 3.53 (d, *J* = 8.1 Hz, 1H), 1.47 (s, 18H); ¹³C NMR (75 MHz, CDCl₃): δ = 166.2, 165.8, 160.2, 141.9, 128.8, 127.6, 114.2, 104.6, 85.0, 84.8, 83.0, 82.9, 76.5, 55.3, 55.0, 31.1, 27.9, 27.8. HRMS: calcd for C₂₄H₃₁NO₇ [M]⁺ 445.2101, found 445.2111. HPLC (Chiralpak AD-H, *i*-propanol/*n*-hexane = 15/85, flow rate 0.8 mL/min, λ = 254 nm): *t*_{major} = 19.327 min, *t*_{minor} = 29.451 min.

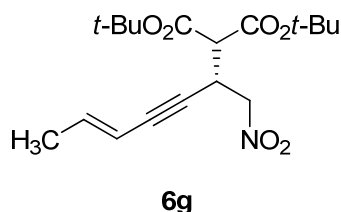


(*S,E*)-Di-*tert*-butyl 2-(6-(4-chlorophenyl)-1-nitrohex-5-en-3-yn-2-yl)malonate (6e): $[\alpha]_D^{20} = + 18.5$ (*c* 1.0 CHCl₃). ¹H NMR (300 MHz, CDCl₃): δ = 7.28 (m, 4H), 6.82 (dd, *J* = 16.2 Hz, *J* = 1.2 Hz, 1H), 6.02 (dd, *J* = 16.2 Hz, *J* = 1.2 Hz, 1H), 4.82-4.71 (m, 2H), 4.05-3.99 (m, 1H), 3.60 (d, *J* = 8.1 Hz, 1H), 1.46 (s, 18H); ¹³C NMR (75 MHz, CDCl₃): δ = 166.1, 165.7, 141.0, 134.5, 134.4, 128.9, 127.5, 107.7, 86.5, 84.1,

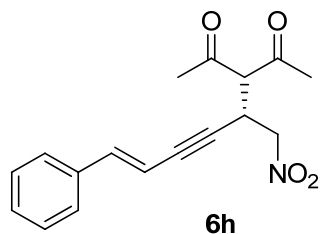
83.1, 82.9, 76.4, 54.9, 30.9, 27.8. HRMS: calcd for $C_{23}H_{28}ClNO_6 [M]^+$ 449.1605, found 449.1607. HPLC (Chiralpak AD-H, *i*-propanol/*n*-hexane = 15/85, flow rate 0.8 mL/min, λ = 254 nm): t_{major} = 16.253 min, t_{minor} = 21.103 min.



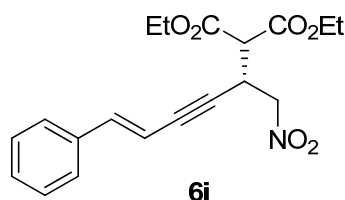
(S,E)-Di-tert-butyl 2-(1-nitro-6-(thiophen-2-yl)hex-5-en-3-yn-2-yl)malonate (6f): $[\alpha]_D^{20} = + 14.8$ (*c* 1.0 $CHCl_3$). 1H NMR (300 MHz, $CDCl_3$): δ = 7.18 (d, J = 4.8 Hz, 1H), 6.95 (m, 3H), 5.84 (dd, J = 15.9 Hz, J = 2.1 Hz, 1H), 4.80-4.64 (m, 2H), 4.05-3.97 (m, 1H), 3.52 (d, J = 7.8 Hz, 1H), 1.49 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.1, 165.7, 140.9, 135.2, 127.7, 127.3, 125.7, 106.1, 86.2, 84.2, 83.0, 82.9, 76.4, 54.9, 30.9, 27.9, 27.8. HRMS: calcd for $C_{21}H_{27}NO_6S [M]^+$ 421.1559, found 421.1551. HPLC (Chiralpak AD-H, *i*-propanol/*n*-hexane = 8/92, flow rate 0.8 mL/min, λ = 254 nm): t_{major} = 16.895 min, t_{minor} = 28.858 min.



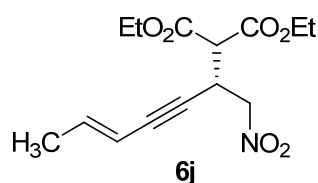
(S,E)-Di-tert-butyl 2-(1-nitrohept-5-en-3-yn-2-yl)malonate (6g): $[\alpha]_D^{20} = + 12.0$ (*c* 1.0 $CHCl_3$). 1H NMR (300 MHz, $CDCl_3$): δ = 5.86 (m, 1H), 5.31 (m, 1H), 4.72-4.58 (m, 2H), 3.96-3.89 (m, 1H), 3.46 (d, J = 7.8 Hz, 1H), 1.73 (dd, J = 6.9 Hz, J = 1.5 Hz, 3H), 1.41 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.1, 165.8, 139.8, 109.0, 88.1, 83.0, 82.8, 82.0, 76.6, 55.1, 30.9, 27.8, 27.8, 15.9. HRMS: calcd for $C_{18}H_{27}NO_6 [M]^+$: 354.1917, found 354.1924. HPLC (Chiralpak AD-H, *i*-propanol/*n*-hexane = 5/95, flow rate 0.8 mL/min, λ = 220 nm): t_{major} = 10.784 min, t_{minor} = 12.733 min.



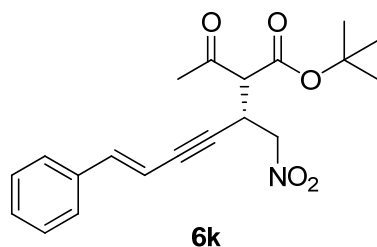
(S,E)-3-(1-Nitro-6-phenylhex-5-en-3-yn-2-yl)pentane-2,4-dione (6h): $[\alpha]_D^{20} = + 107.4$ (*c* 1.0 $CHCl_3$). 1H NMR (300 MHz, $CDCl_3$): δ = 7.19 (m, 5H), 6.79 (d, J = 16.2 Hz, 1H), 5.94 (dd, J = 16.2 Hz, J = 1.8 Hz, 1H), 4.55-4.37 (m, 1H), 4.37 (m, 1H), 4.09 (d, J = 9.6 Hz, 1H), 4.03-3.98 (m, 1H), 2.27 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.9, 200.5, 142.9, 135.7, 129.0, 128.8, 106.5, 85.5, 85.2, 76.2, 68.3, 30.7, 30.2, 29.9. HRMS: calcd for $C_{17}H_{17}NO_4 [M]^+$ 299.1158, found 299.1154. HPLC (Chiralcel OD-H, *i*-propanol/*n*-hexane = 20/80, flow rate 0.8 mL/min, λ = 254 nm): t_{minor} = 30.673 min, t_{major} = 43.743 min.



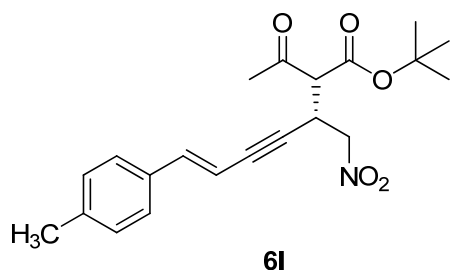
(*S,E*)-Diethyl 2-(1-nitro-6-phenylhex-5-en-3-yn-2-yl)malonate (6i): $[\alpha]_{\text{D}}^{20} = +10.9$ (*c* 1.0 CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ = 7.18 (m, 5H), 6.79 (d, *J* = 16.2 Hz, 1H), 5.96 (dd, *J* = 16.4 Hz, *J* = 2.0 Hz, 1H), 4.74-4.62 (m, 2H), 4.21-4.03 (m, 4H), 4.00 (m, 1H), 3.69 (d, *J* = 7.6 Hz, 1H), 1.20 (t, *J* = 7.2 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): δ = 166.8, 166.5, 142.7, 135.8, 128.9, 128.7, 128.3, 126.3, 106.9, 85.2, 84.7, 76.2, 62.3, 53.2, 30.9, 14.0. HRMS: calcd for C₁₉H₂₁NO₆ [M]⁺ 359.1369, found 359.1367. HPLC (Chiralpak AD-H, *i*-propanol/*n*-hexane = 10/90, flow rate 0.8 mL/min, λ = 254 nm): *t*_{major} = 23.013 min, *t*_{minor} = 24.885 min.



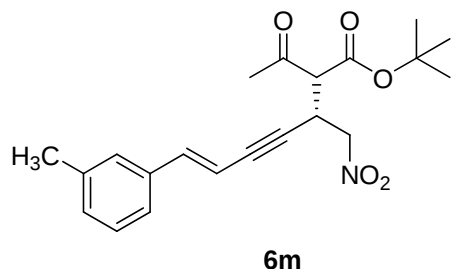
(*S,E*)-diethyl 2-(1-nitrohept-5-en-3-yn-2-yl)malonate (6j): $[\alpha]_{\text{D}}^{20} = +11.2$ (*c* 1.0 CHCl₃). ¹H NMR (300 MHz, CDCl₃): δ = 5.95 (m, 1H), 5.37 (d, *J* = 10.8 Hz, 1H), 4.78-4.67 (m, 2H), 4.20 (q, *J* = 6.9 Hz, 4H), 4.10-4.04 (m, 1H), 3.74 (d, *J* = 7.6 Hz, 1H), 1.78 (d, *J* = 7.6 Hz, 3H), 1.25 (t, *J* = 7.2 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃): δ = 166.8, 166.5, 140.1, 108.9, 87.5, 82.3, 76.3, 62.2, 53.3, 30.9, 15.8, 14.0. HPLC (Chiralpak AD-H, *i*-propanol/*n*-hexane = 10/90, flow rate 0.8 mL/min, λ = 220 nm): *t*_{major} = 11.133 min, *t*_{minor} = 13.044 min.



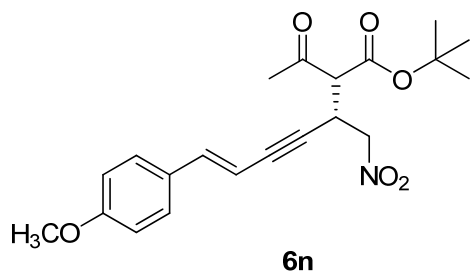
(*2S,3S,E*)-tert-Butyl 2-acetyl-3-(nitromethyl)-7-phenylhept-6-en-4-ynoate (6k): $[\alpha]_{\text{D}}^{20} = +193.4$ (*c* 1.0 CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ = 7.28 (m, 5H), 6.87 (dd, *J* = 16.4 Hz, *J* = 2.4 Hz, 1H), 6.10-6.04 (m, 1H), 4.76-4.59 (m, 2H), 4.02 (m, 1H), 3.84 (m, 1H), 2.35 (s, 3H), 1.51 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ = 200.6, 200.4, 166.0, 165.7, 142.6, 142.5, 135.9, 135.8, 128.9, 128.7, 126.3, 107.0, 106.8, 85.9, 85.8, 84.6, 84.5, 83.7, 83.5, 76.4, 76.3, 61.3, 60.7, 30.3, 30.2, 29.9, 27.8, 27.8. HRMS: calcd for C₂₀H₂₃NO₅ [M]⁺ 357.1576, found 357.1587. HPLC (Chiralpak AD-H, *i*-propanol/*n*-hexane = 10/90, flow rate 0.8 mL/min, λ = 254 nm): *t*_{major} = 18.698 min, *t*_{major} = 20.253 min, *t*_{minor} = 23.325 min, *t*_{minor} = 32.434 min.



(2S,3S,E)-tert-Butyl 2-acetyl-3-(nitromethyl)-7-p-tolylhept-6-en-4-ynoate (6l): $[\alpha]_D^{20} = + 49.1$ (*c* 1.0 CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ = 7.15 (m, 2H), 7.03 (d, *J* = 7.6 Hz, 2H), 6.76 (dd, *J* = 16.0 Hz, *J* = 2.8 Hz, 1H), 5.95-5.90 (m, 1H), 4.65-4.50 (m, 2H), 3.91 (m, 1H), 3.74 (m, 1H), 2.36 (m, 6H), 1.42 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ = 200.7, 200.4, 166.0, 165.7, 142.6, 142.5, 139.0, 133.2, 129.4, 126.2, 105.8, 105.7, 85.4, 85.3, 84.9, 84.8, 83.7, 83.5, 76.4, 76.3, 61.4, 60.7, 30.3, 30.2, 29.9, 27.9, 27.8, 21.3. HRMS: calcd for C₂₁H₂₅NO₅ [M]⁺ 371.1733, found 371.1714. HPLC (Chiralpak AD-H, *i*-propanol/*n*-hexane = 15/85, flow rate 0.8 mL/min, λ = 254 nm): *t*_{major} = 13.796 min, *t*_{minor} = 18.950 min, *t*_{major} = 22.171 min, *t*_{minor} = 30.138 min.

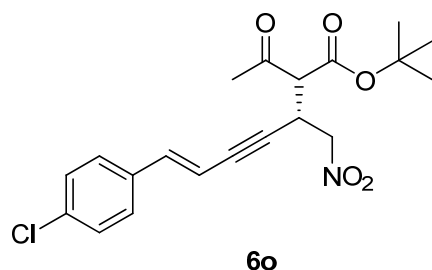


(2S,3S,E)-tert-Butyl 2-acetyl-3-(nitromethyl)-7-m-tolylhept-6-en-4-ynoate (6m): $[\alpha]_D^{20} = + 15.8$ (*c* 1.0 CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ = 7.01 (m, 4H), 6.76 (dd, *J* = 16.4 Hz, *J* = 2.4 Hz, 1H), 5.99-5.94 (m, 1H), 4.65-4.50 (m, 2H), 3.91 (m, 1H), 3.75 (m, 1H), 2.26 (m, 6H), 1.42 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ = 200.6, 200.4, 166.0, 165.7, 142.7, 142.6, 138.3, 135.8, 129.7, 128.6, 127.0, 123.5, 106.7, 106.6, 85.6, 85.5, 84.8, 84.7, 83.7, 83.5, 76.3, 76.3, 61.4, 60.7, 30.3, 30.2, 29.9, 27.9, 27.8, 21.3. HRMS: calcd for C₂₁H₂₅NO₅ [M]⁺ 371.1733, found 371.1714. HPLC (Chiralpak AD-H, *i*-propanol/*n*-hexane = 8/92, flow rate 0.8 mL/min, λ = 254 nm): *t*_{major} = 15.251 min, *t*_{major} = 16.988 min, *t*_{minor} = 20.623 min, *t*_{minor} = 25.614 min.

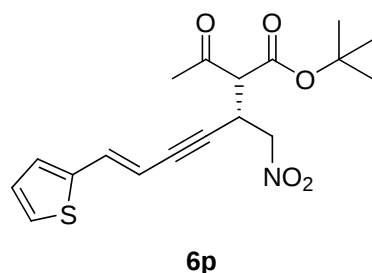


(2S,3S,E)-tert-Butyl 2-acetyl-7-(4-methoxyphenyl)-3-(nitromethyl)hept-6-en-4-ynoate (6n): $[\alpha]_D^{20} = + 30.9$ (*c* 1.0 CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ = 7.19 (m, 2H), 6.75 (m, 3H), 5.86-5.80 (m, 1H), 4.65-4.49 (m, 2H), 3.93 (m, 1H), 3.73 (m, 1H), 3.72 (s, 3H), 2.26 (s, 3H), 1.41 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ = 200.7, 200.4, 166.0, 165.7, 160.3, 142.1, 142.0, 128.7, 127.7, 114.2, 104.5, 104.3, 85.0, 84.94, 84.9, 83.7, 83.5, 76.4, 76.3, 61.4, 60.7, 55.3, 30.3, 30.2, 29.9, 27.8. HRMS: calcd for C₂₁H₂₅NO₆

$[M]^+$ 387.1682, found 387.1685. HPLC (Chiralpak AD-H, *i*-propanol/*n*-hexane = 15/85, flow rate 0.8 mL/min, λ = 254 nm): t_{major} = 22.033 min, t_{minor} = 29.813 min, t_{major} = 35.636 min, t_{minor} = 53.109 min.



(2S,3S,E)-tert-Butyl 2-acetyl-7-(4-chlorophenyl)-3-(nitromethyl)hept-6-en-4-ynoate (6o): $[\alpha]_D^{20}$ = +25.5 (*c* 1.0 CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ = 7.16 (m, 4H), 6.72 (dd, *J* = 16.0 Hz, *J* = 2.8 Hz, 1H), 5.92 (m, 1H), 4.64-4.50 (m, 2H), 3.93 (m, 1H), 3.75 (m, 1H), 2.26 (s, 3H), 1.41 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ = 200.5, 200.3, 165.9, 165.6, 141.2, 141.1, 134.5, 134.4, 134.3, 128.9, 127.5, 107.6, 107.5, 86.5, 86.4, 84.3, 84.2, 83.7, 83.5, 76.3, 76.2, 61.3, 60.6, 30.3, 30.2, 29.9, 27.8, 27.8. HRMS: calcd for C₂₀H₂₂ClNO₅ $[M]^+$ 391.1187, found 391.1185. HPLC (Chiralpak AD-H, *i*-propanol/*n*-hexane = 15/85, flow rate 0.8 mL/min, λ = 254 nm): t_{major} = 19.636 min, t_{minor} = 23.127 min, t_{major} = 24.854 min, t_{minor} = 33.263 min.



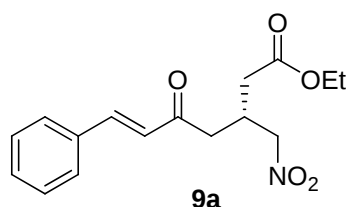
(2S,3S,E)-tert-Butyl 2-acetyl-3-(nitromethyl)-7-(thiophen-2-yl)hept-6-en-4-ynoate (6p): $[\alpha]_D^{20}$ = +33.7 (*c* 1.0 CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ = 7.12 (d, *J* = 4.8 Hz, 1H), 6.89 (m, 3H), 5.82-5.76 (m, 1H), 4.65-4.50 (m, 2H), 3.92 (m, 1H), 3.74 (m, 1H), 2.26 (s, 3H), 1.42 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ = 200.6, 200.3, 166.0, 165.6, 140.9, 135.4, 135.3, 127.7, 127.4, 125.8, 125.7, 106.0, 105.9, 86.1, 86.0, 84.4, 84.3, 83.7, 83.6, 76.3, 76.2, 61.3, 60.6, 30.3, 30.2, 30.0, 27.9, 27.8. HRMS: calcd for C₁₈H₂₁NO₅S $[M]^+$ 363.1140, found 363.1133. HPLC (Chiralpak AD-H, *i*-propanol/*n*-hexane = 8/92, flow rate 0.8 mL/min, λ = 254 nm): t_{major} = 19.870 min, t_{major} = 21.575 min, t_{minor} = 28.670 min, t_{minor} = 34.248 min.

7. Representative Procedure for the Synthesis of Acyclic α,β -Enone Acids 8

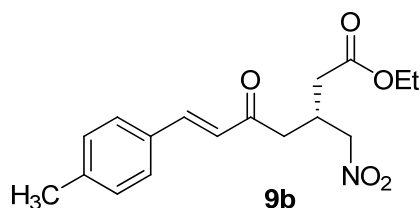
To a solution of **6a** (415 mg, 1 mmol) in toluene (20 mL) was added TsOH (38 mg, 0.2 eq). The reaction mixture was stirred for 6 h under reflux. After removal of solvent, the crude product was purified through column chromatography on silica gel to afford the compound **8a** (233 mg, 84%). $[\alpha]_D^{20}$ = +6.7 (*c* 1.0 CHCl₃). ¹H NMR (300 MHz, CDCl₃): δ = 7.54 (m, 3H), 7.40 (m, 3H), 6.70 (d, *J* = 16.2 Hz, 1H), 4.64 (d, *J* = 5.7 Hz, 2H), 3.19 (m, 1H), 2.92 (m, 2H), 2.65 (d, *J* = 6.3 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ = 197.1, 176.5, 143.9, 134.0, 131.0, 129.1, 128.5, 125.5, 77.5, 41.1, 35.0, 29.6. HRMS: calcd for C₁₄H₁₅NO₅ $[M]^+$ 277.0950, found 277.0955.

8 Representative Procedure for the Synthesis of Acyclic α,β -Enone Esters 9

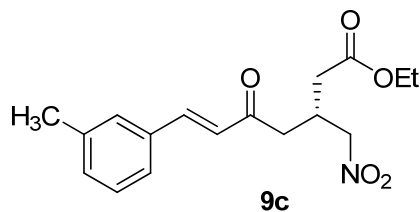
To a solution of compound **8** (0.8 mmol) in absolute ethanol (10 mL) was added thionylchloride (95 mg, 0.8 mmol). The reaction mixture was stirred for 3 h under reflux. The solvent was removed under reduced pressure, and the mixture was diluted with AcOEt. The organic layer was washed with saturated aqueous NaHCO₃ solution and brine. The organic layer was dried over Na₂SO₄, filtered and concentrated under reduced pressure, and the crude product was purified through column chromatography on silica gel to afford compounds **9a-f**.



(R,E)-Ethyl 3-(nitromethyl)-5-oxo-7-phenylhept-6-enoate (9a): $[\alpha]_D^{20} = +34.6$ (*c* 1.0 CHCl₃). ¹H NMR (300 MHz, CDCl₃): δ = 7.54 (m, 3H), 7.40 (m, 3H), 6.70 (d, *J* = 16.2 Hz, 1H), 4.64 (d, *J* = 6.0 Hz, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.16 (m, 1H), 2.92 (d, *J* = 6.0 Hz, 2H), 2.56 (dd, *J* = 6.6 Hz, *J* = 1.2 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ = 197.1, 171.2, 143.6, 134.1, 130.9, 129.0, 128.4, 125.7, 77.8, 60.9, 41.2, 35.4, 29.9, 14.2. HRMS: calcd for C₁₆H₁₉NO₅ [M]⁺ 305.1263, found 305.1263. HPLC (Chiralcel OD-H, *i*-propanol/*n*-hexane = 25/75, flow rate 1.0 mL/min, λ = 254 nm): *t*_{major} = 22.688 min. *t*_{minor} = 25.380 min.

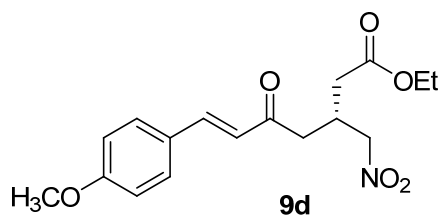


(R,E)-Ethyl 3-(nitromethyl)-5-oxo-7-p-tolylhept-6-enoate (9b): $[\alpha]_D^{20} = +16.8$ (*c* 1.0 CHCl₃). ¹H NMR (300 MHz, CDCl₃): δ = 7.54 (d, *J* = 16.2 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 6.66 (d, *J* = 16.2 Hz, 1H), 4.64 (d, *J* = 6.0 Hz, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.19 (m, 1H), 2.91 (d, *J* = 6.3 Hz, 2H), 2.56 (d, *J* = 6.6 Hz, 2H), 2.39 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ = 197.2, 171.2, 143.7, 141.4, 131.4, 129.8, 128.4, 124.8, 77.8, 60.8, 41.1, 35.4, 30.0, 21.5, 14.1. HRMS: calcd for C₁₇H₂₁NO₅ [M]⁺ 319.1420, found 319.1422. HPLC (Chiralpak AD-H, *i*-propanol/*n*-hexane = 25/75, flow rate 1.0 mL/min, λ = 254 nm): *t*_{minor} = 15.534 min. *t*_{major} = 17.527 min.

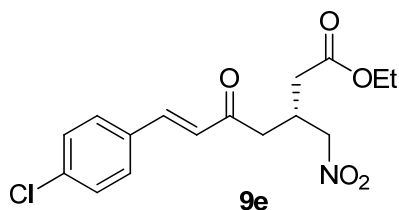


(R,E)-Ethyl 3-(nitromethyl)-5-oxo-7-m-tolylhept-6-enoate (9c): $[\alpha]_D^{20} = +15.7$ (*c* 1.0 CHCl₃). ¹H NMR (300 MHz, CDCl₃): δ = 7.46 (d, *J* = 16.2 Hz, 1H), 7.29-7.16 (m, 4H), 6.61 (d, *J* = 16.2 Hz, 1H), 4.56 (d, *J* = 6.0 Hz, 2H), 4.05 (q, *J* = 7.2 Hz, 2H), 3.08 (m, 1H), 2.83 (d, *J* = 5.4 Hz, 2H), 2.48 (d, *J* = 6.6

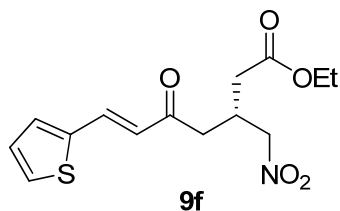
Hz, 2H), 2.30 (s, 3H), 1.17 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): $\delta = 197.2, 171.2, 143.8, 138.7, 134.1, 131.7, 129.1, 128.9, 125.7, 125.5, 77.8, 60.9, 41.2, 35.4, 30.0, 21.3, 14.2$. HRMS: calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_5$ $[\text{M}]^+$ 319.1420, found 319.1422. HPLC (Chiralcel OD-H, *i*-propanol/*n*-hexane = 25/75, flow rate 1.0 mL/min, $\lambda = 254$ nm): $t_{\text{major}} = 20.877$ min, $t_{\text{minor}} = 22.677$ min.



(*R,E*)-Ethyl 7-(4-methoxyphenyl)-3-(nitromethyl)-5-oxohept-6-enoate (9d): $[\alpha]_{\text{D}}^{20} = + 47.4$ (c 1.0 CHCl_3). ^1H NMR (300 MHz, CDCl_3): $\delta = 7.41$ (m, 3H), 6.83 (d, $J = 8.7$ Hz, 2H), 6.50 (d, $J = 16.2$ Hz, 1H), 4.56 (d, $J = 8.7$ Hz, 2H), 4.05 (q, $J = 7.2$ Hz, 2H), 3.77 (s, 3H), 3.10 (m, 1H), 2.81 (d, $J = 6.6$ Hz, 2H), 2.48 (d, $J = 6.6$ Hz, 2H), 1.16 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): $\delta = 197.0, 171.3, 161.9, 143.4, 130.2, 126.8, 123.5, 114.5, 77.8, 60.8, 55.4, 41.1, 35.4, 30.1, 14.1$. HRMS calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_6$ $[\text{M}]^+$ 335.1369, found 335.1373. HPLC (Chiralpak AD-H, *i*-propanol/*n*-hexane = 25/75, flow rate 1.0 mL/min, $\lambda = 254$ nm): $t_{\text{minor}} = 22.324$ min, $t_{\text{major}} = 24.617$ min.



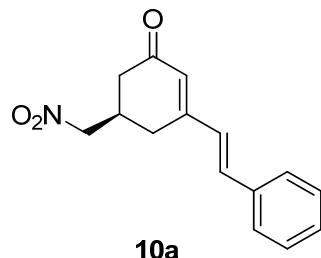
(*R,E*)-Ethyl 7-(4-chlorophenyl)-3-(nitromethyl)-5-oxohept-6-enoate (9e): $[\alpha]_{\text{D}}^{20} = + 5.0$ (c 1.0 CHCl_3). ^1H NMR (300 MHz, CDCl_3): $\delta = 7.39$ (m, 3H), 7.29 (d, $J = 8.4$ Hz, 2H), 6.59 (d, $J = 16.2$ Hz, 1H), 4.56 (d, $J = 6.0$ Hz, 2H), 4.05 (q, $J = 7.2$ Hz, 2H), 3.10 (m, 1H), 2.83 (d, $J = 6.3$ Hz, 2H), 2.48 (dd, $J = 6.6$ Hz, $J = 1.8$ Hz, 2H), 1.17 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): $\delta = 196.9, 171.2, 142.1, 136.8, 132.6, 129.5, 129.3, 126.0, 77.7, 60.9, 41.4, 35.4, 29.9, 14.1$. HRMS: calcd for $\text{C}_{16}\text{H}_{18}\text{ClNO}_5$ $[\text{M}]^+$ 339.0874, found 339.0863. HPLC (Chiralpak AD-H, *i*-propanol/*n*-hexane = 25/75, flow rate 1.0 mL/min, $\lambda = 254$ nm): $t_{\text{minor}} = 17.749$ min, $t_{\text{major}} = 18.749$ min.



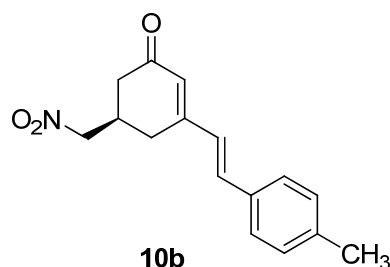
(*R,E*)-Ethyl 3-(nitromethyl)-5-oxo-7-(thiophen-2-yl)hept-6-enoate (9f): $[\alpha]_{\text{D}}^{20} = + 15.4$ (c 1.0 CHCl_3). ^1H NMR (300 MHz, CDCl_3): $\delta = 7.61$ (d, $J = 15.6$ Hz, 1H), 7.35 (d, $J = 4.8$ Hz, 1H), 7.24 (d, $J = 3.6$ Hz, 1H), 6.99 (m, 1H), 6.42 (d, $J = 15.9$ Hz, 1H), 4.56 (d, $J = 6.0$ Hz, 2H), 4.05 (q, $J = 7.2$ Hz, 2H), 3.09 (m, 1H), 2.79 (d, $J = 6.9$ Hz, 2H), 2.47 (dd, $J = 6.6$ Hz, $J = 1.2$ Hz, 2H), 1.17 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): $\delta = 196.6, 171.2, 139.5, 135.9, 132.2, 129.4, 128.4, 124.3, 77.7, 60.9, 41.3, 35.3, 30.0, 14.2$. HRMS: calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_5\text{S}$ $[\text{M}]^+$ 311.0827, found 311.0831. HPLC (Chiralpak AD-H, *i*-propanol/*n*-hexane = 25/75, flow rate 1.0 mL/min, $\lambda = 254$ nm): $t_{\text{minor}} = 14.387$ min, $t_{\text{major}} = 15.332$ min.

9 Representative Procedure for the Synthesis of Cyclic Dienones 10

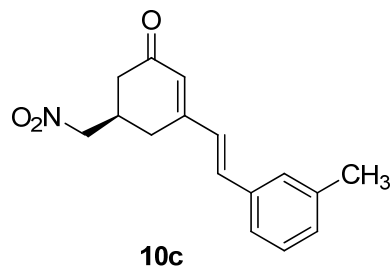
To a solution of compound **6** (0.5 mmol) in toluene (10 mL) was added TsOH (19 mg, 0.2 eq). The reaction mixture was stirred for 6-8 h under reflux. After removal of solvent, the crude product was purified through column chromatography on silica gel to afford the compounds **10a-f**.



(R,E)-5-(Nitromethyl)-3-styrylcyclohex-2-enone (10a): $[\alpha]_D^{20} = -35.1$ (*c* 1.0 CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ = 7.41 (d, *J* = 7.2 Hz, 2H), 7.28 (m, 3H), 6.91 (d, *J* = 16.4 Hz, 1H), 6.80 (d, *J* = 16.0 Hz, 1H), 6.06 (s, 1H), 4.41 (d, *J* = 6.8 Hz, 2H), 2.98-2.93 (m, 1H), 2.80 (dd, *J* = 17.2 Hz, *J* = 4.4 Hz, 1H), 2.53 (dd, *J* = 16.4 Hz, *J* = 4.0 Hz, 1H), 2.33 (m, 1H), 2.20 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 196.4, 154.3, 136.2, 135.6, 129.5, 129.0, 128.3, 127.7, 127.4, 79.3, 40.5, 33.4, 28.4. HRMS: calcd for C₁₅H₁₅NO₃ [M]⁺ 257.1052, found 257.1049. HPLC (Chiralpak AD-H, *i*-propanol/*n*-hexane = 15/85, flow rate 0.9 mL/min, λ = 254 nm): *t*_{major} = 26.038 min, *t*_{minor} = 27.549 min.

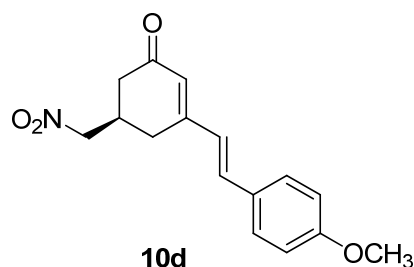


(R,E)-3-(4-Methylstyryl)-5-(nitromethyl)cyclohex-2-enone (10b): $[\alpha]_D^{20} = -49.5$ (*c* 1.0 CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ = 7.32 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 16.4 Hz, 1H), 6.76 (d, *J* = 16.4 Hz, 1H), 6.05 (s, 1H), 4.41 (d, *J* = 6.8 Hz, 2H), 2.98-2.93 (m, 1H), 2.80 (dd, *J* = 17.2 Hz, *J* = 4.4 Hz, 1H), 2.53 (dd, *J* = 16.4 Hz, *J* = 4.0 Hz, 1H), 2.32 (m, 1H), 2.30 (s, 3H), 2.20 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 196.4, 154.6, 138.9, 136.3, 132.8, 129.7, 127.4, 127.3, 79.4, 40.5, 33.4, 28.4, 21.4. HRMS: calcd for C₁₆H₁₇NO₃ [M]⁺ 271.1208, found 271.1201. HPLC (Chiralpak AD-H, *i*-propanol/*n*-hexane = 20/80, flow rate 0.8 mL/min, λ = 254 nm): *t*_{major} = 19.799 min, *t*_{minor} = 21.017 min.

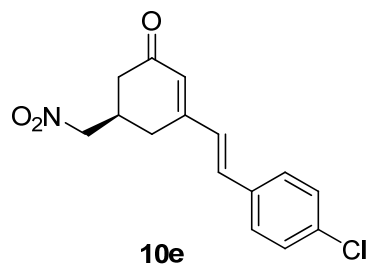


(R,E)-3-(3-Methylstyryl)-5-(nitromethyl)cyclohex-2-enone (10c): $[\alpha]_D^{20} = -67.5$ (*c* 1.0 CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ = 7.17 (m, 3H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.89 (d, *J* = 16.4 Hz, 1H), 6.79 (d, *J* = 16.0 Hz, 1H), 6.05 (s, 1H), 4.40 (d, *J* = 6.8 Hz, 2H), 2.97-2.92 (m, 1H), 2.79 (dd, *J* = 17.2 Hz, *J* = 4.4

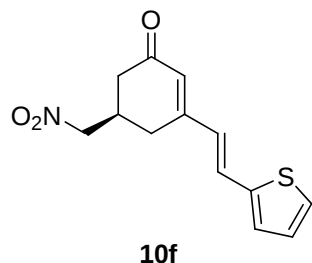
Hz, 1H), 2.52 (dd, $J = 16.4$ Hz, $J = 4.0$ Hz, 1H), 2.34 (m, 1H), 2.29 (s, 3H), 2.19 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 196.5, 154.5, 138.6, 136.4, 135.5, 130.4, 128.9, 128.1, 127.5, 124.7, 79.3, 40.5, 33.4, 28.4, 21.4$. HRMS: calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_3$ $[\text{M}]^+$ 271.1208, found 271.1201. HPLC (Chiralpak AD-H, *i*-propanol/*n*-hexane = 20/80, flow rate 0.8 mL/min, $\lambda = 254$ nm): $t_{\text{major}} = 41.541$ min, $t_{\text{minor}} = 48.319$ min.



(*R,E*)-3-(4-methoxystyryl)-5-(nitromethyl)cyclohex-2-enone (10d): $[\alpha]_{\text{D}}^{20} = -25.7$ (*c* 1.0 CHCl_3). ^1H NMR (400 MHz, CDCl_3): $\delta = 7.36$ (d, $J = 8.8$ Hz, 2H), 6.82 (m, 3H), 6.68 (d, $J = 16.0$ Hz, 1H), 6.02 (s, 1H), 4.40 (d, $J = 6.8$ Hz, 2H), 3.76 (s, 3H), 2.97-2.91 (m, 1H), 2.78 (dd, $J = 16.8$ Hz, $J = 4.4$ Hz, 1H), 2.51 (dd, $J = 16.4$ Hz, $J = 4.0$ Hz, 1H), 2.30 (m, 1H), 2.19 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 196.4, 160.8, 154.8, 135.9, 129.0, 128.6, 128.3, 126.8, 126.0, 114.5, 79.4, 55.4, 40.4, 33.4, 28.4$. HRMS: calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_4$ $[\text{M}]^+$ 287.1158, found 287.1162. HPLC (Chiralpak AD-H, *i*-propanol/*n*-hexane = 20/80, flow rate 0.8 mL/min, $\lambda = 254$ nm): $t_{\text{major}} = 36.051$ min, $t_{\text{minor}} = 39.681$ min.

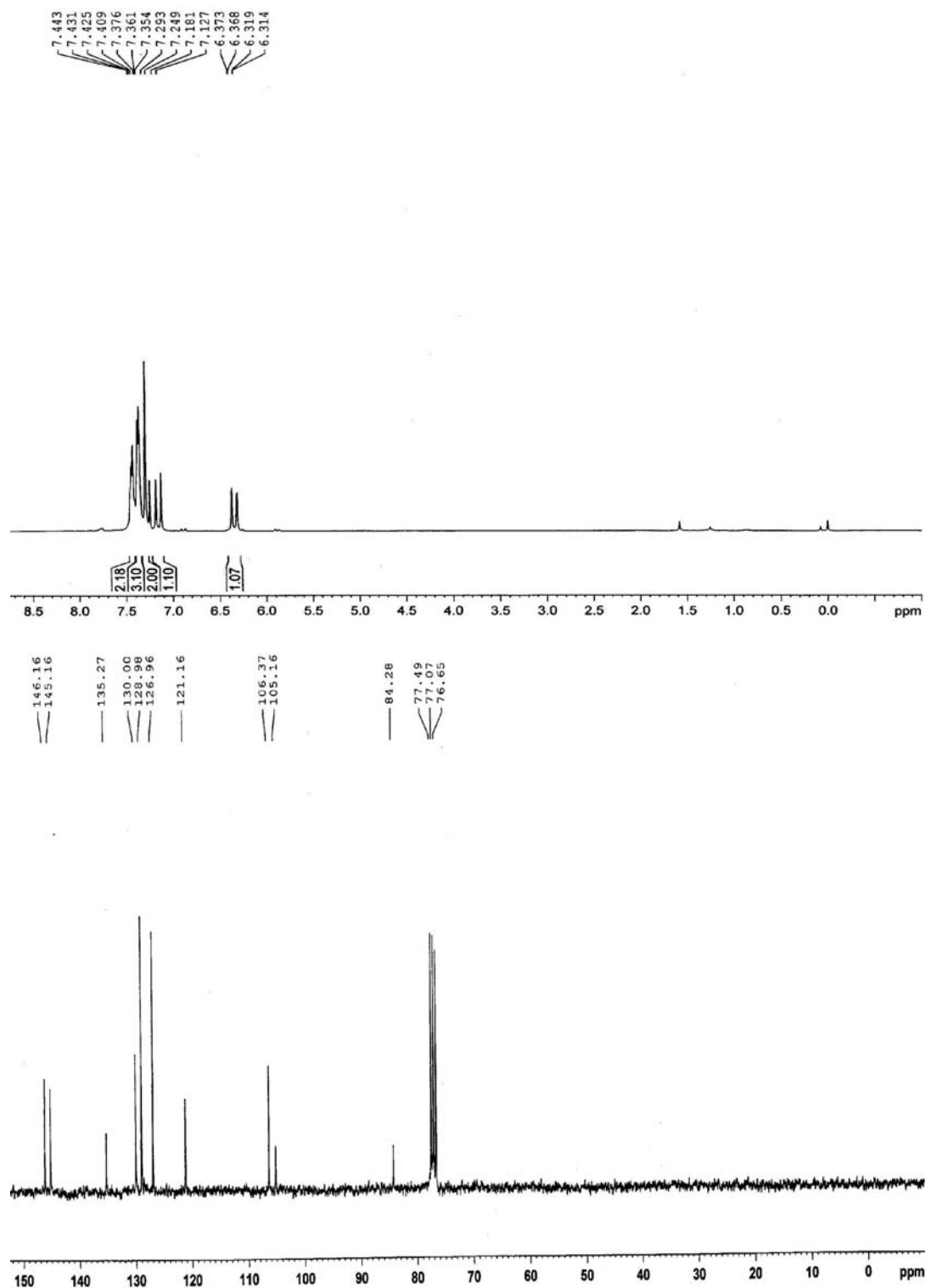
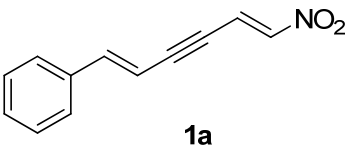


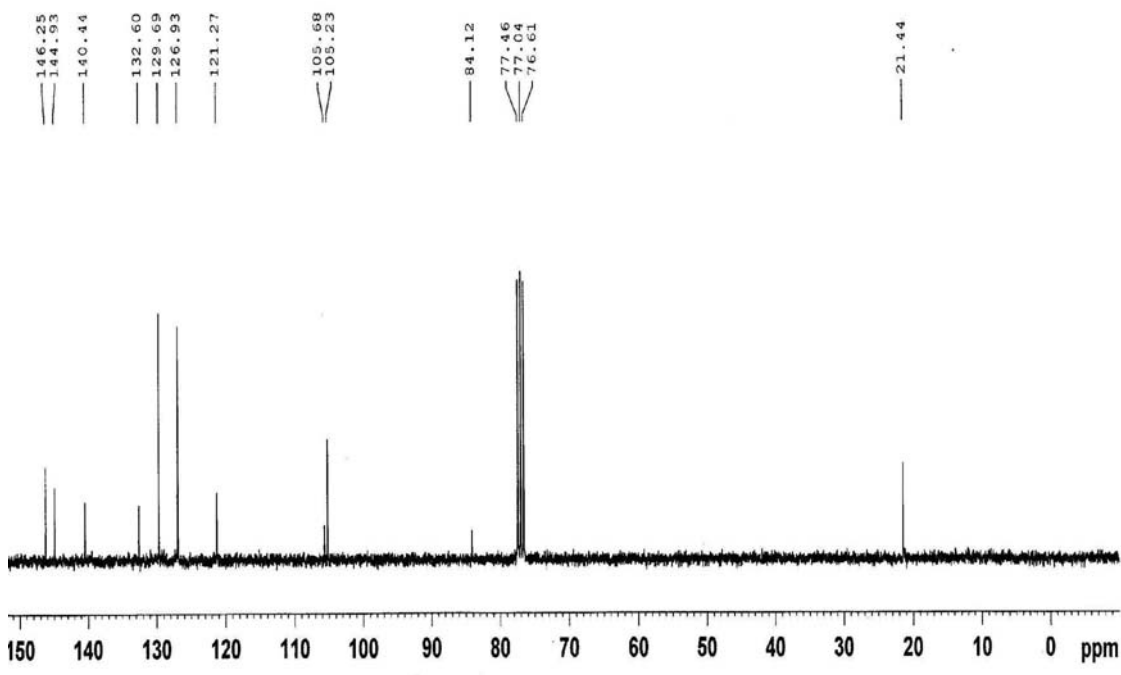
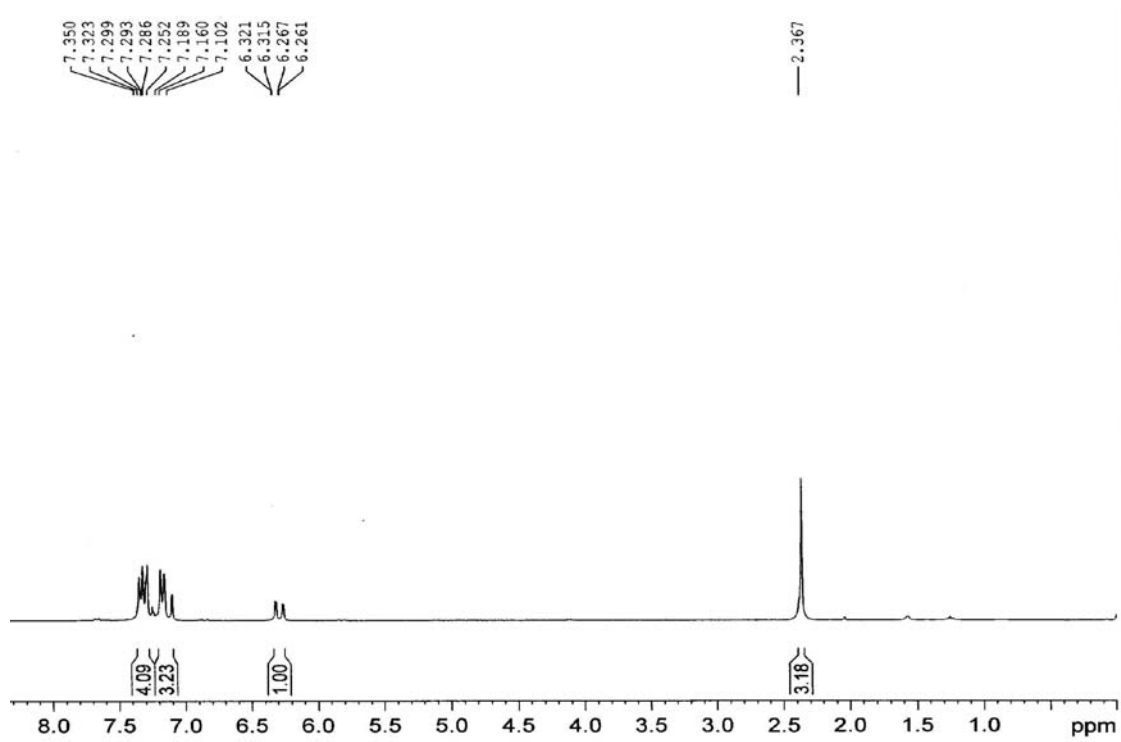
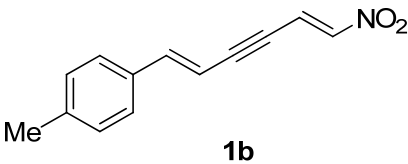
(*R,E*)-3-(4-Chlorostyryl)-5-(nitromethyl)cyclohex-2-enone (10e): $[\alpha]_{\text{D}}^{20} = -97.2$ (*c* 1.0 CHCl_3). ^1H NMR (400 MHz, CDCl_3): $\delta = 7.34$ (d, $J = 8.8$ Hz, 2H), 7.28 (m, 2H), 6.86 (d, $J = 16.0$ Hz, 1H), 6.77 (d, $J = 16.4$ Hz, 1H), 6.06 (s, 1H), 4.41 (m, 2H), 2.98-2.93 (m, 1H), 2.78 (dd, $J = 17.2$ Hz, $J = 4.4$ Hz, 1H), 2.53 (dd, $J = 16.4$ Hz, $J = 4.0$ Hz, 1H), 2.32 (m, 1H), 2.20 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 196.3, 153.9, 135.3, 134.7, 134.1, 129.2, 128.8, 128.6, 128.0, 79.3, 40.5, 33.4, 28.4$. HRMS: calcd for $\text{C}_{15}\text{H}_{14}\text{ClNO}_3$ $[\text{M}]^+$ 291.0622, found 291.0658. HPLC (Chiralpak AD-H, *i*-propanol/*n*-hexane = 20/80, flow rate 0.8 mL/min, $\lambda = 254$ nm): $t_{\text{major}} = 28.544$ min, $t_{\text{minor}} = 30.154$ min.

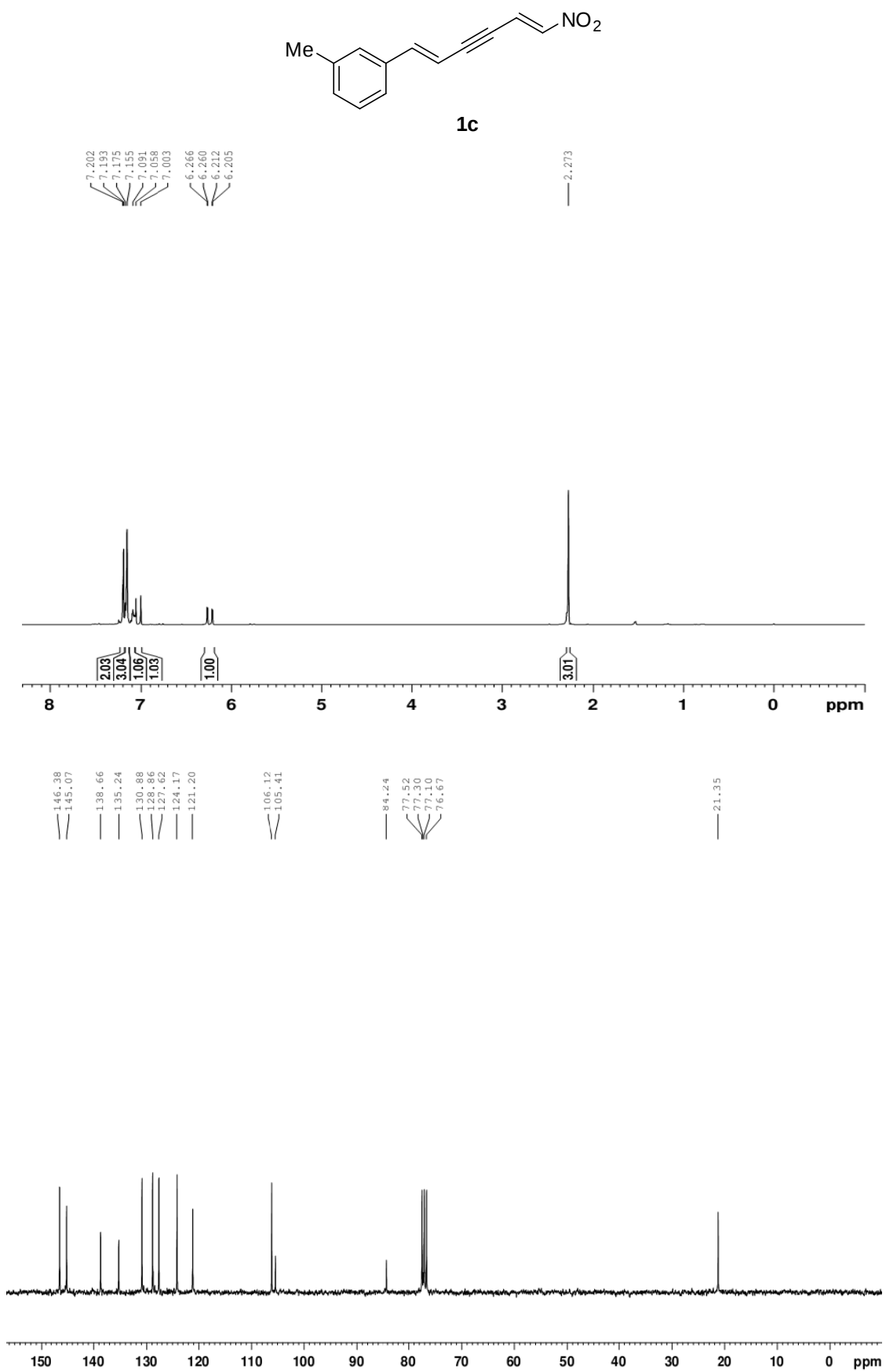


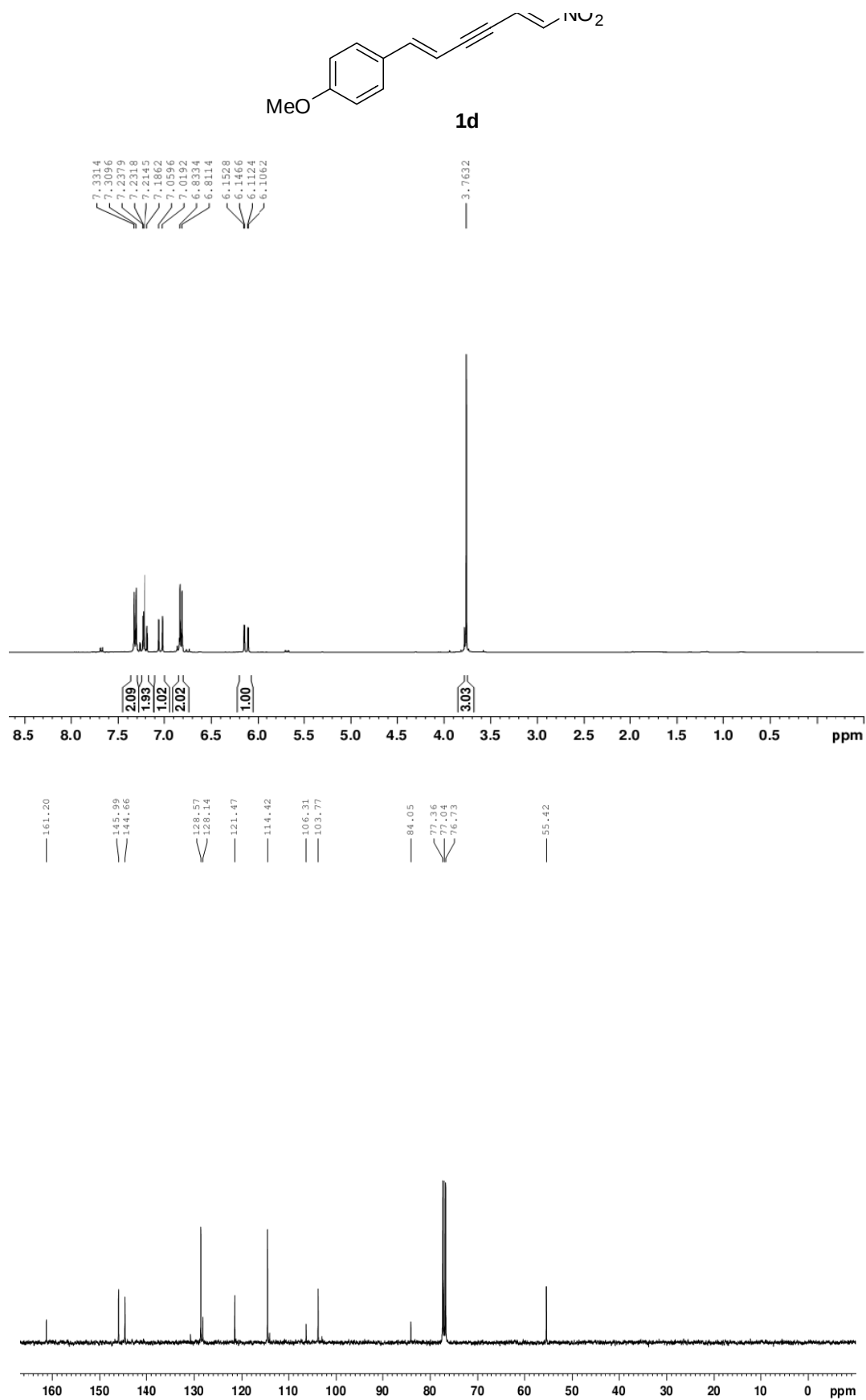
(*R,E*)-5-(Nitromethyl)-3-(2-(thiophen-2-yl)vinyl)cyclohex-2-enone (10f): $[\alpha]_{\text{D}}^{20} = 40.0$ (*c* 1.0 CHCl_3). ^1H NMR (400 MHz, CDCl_3): $\delta = 7.27$ (m, 1H), 7.10 (m, 2H), 6.96 (m, 1H), 6.60 (d, $J = 16.0$ Hz, 1H), 6.02 (s, 1H), 4.40 (m, 2H), 2.99-2.90 (m, 1H), 2.74 (dd, $J = 16.4$ Hz, $J = 4.0$ Hz, 1H), 2.52 (dd, $J = 16.4$ Hz, $J = 4.0$ Hz, 1H), 2.26 (m, 1H), 2.19 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 196.2, 154.0, 141.2,$

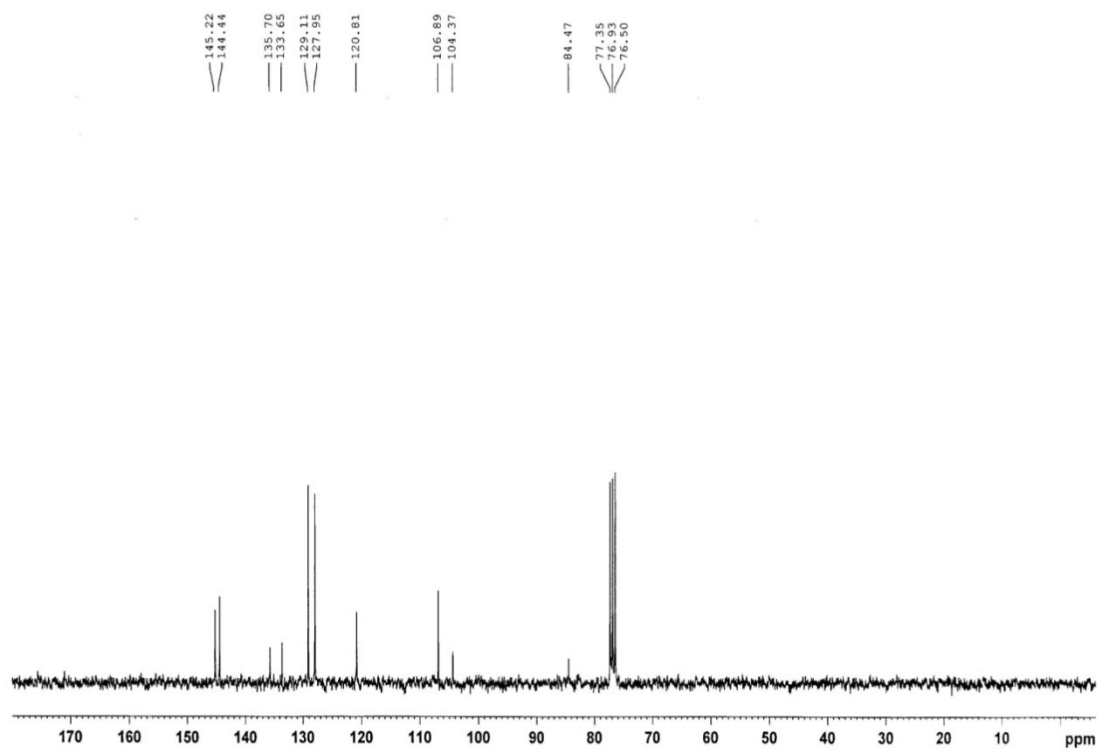
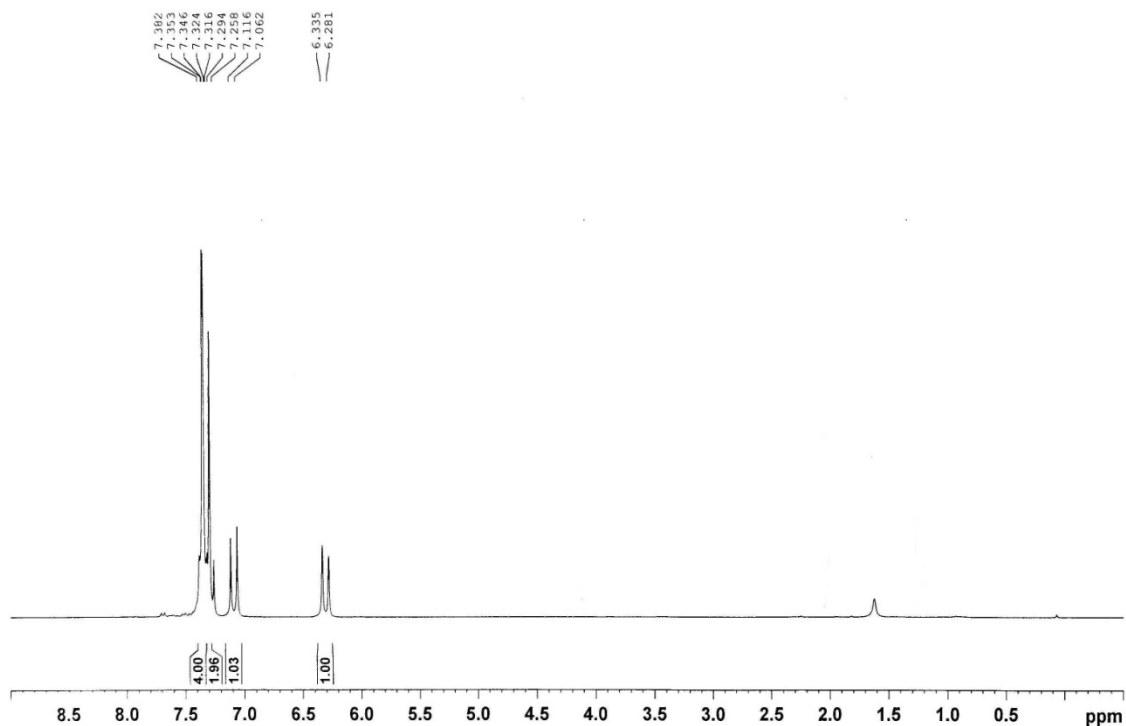
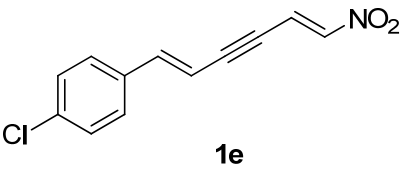
129.3, 129.0, 128.2, 127.5, 127.5, 127.2, 79.3, 40.4, 33.4, 28.3. HRMS: calcd for $C_{13}H_{13}NO_3S [M]^+$ 263.0616, found 263.0624. HPLC (Chiralpak AD-H, *i*-propanol/*n*-hexane = 15/85, flow rate 0.9 mL/min, $\lambda = 254$ nm): $t_{\text{major}} = 26.262$ min, $t_{\text{minor}} = 28.679$ min.

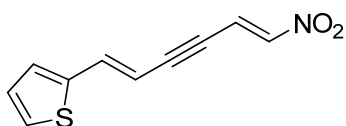




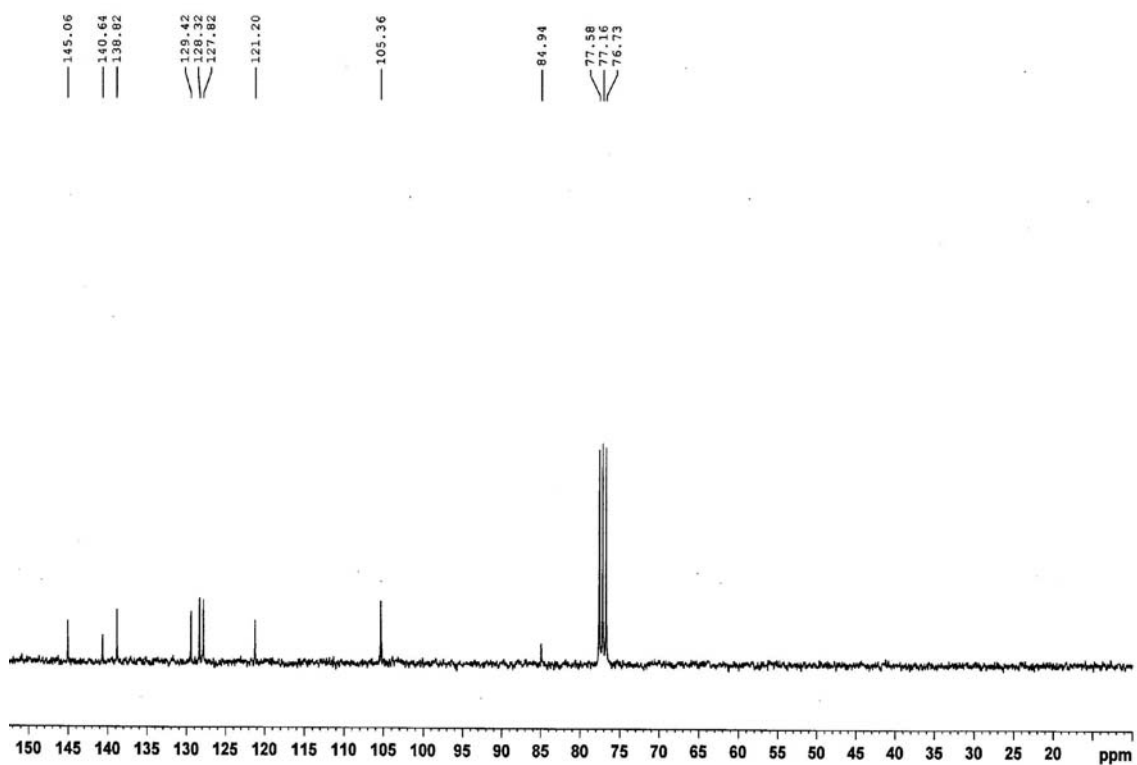
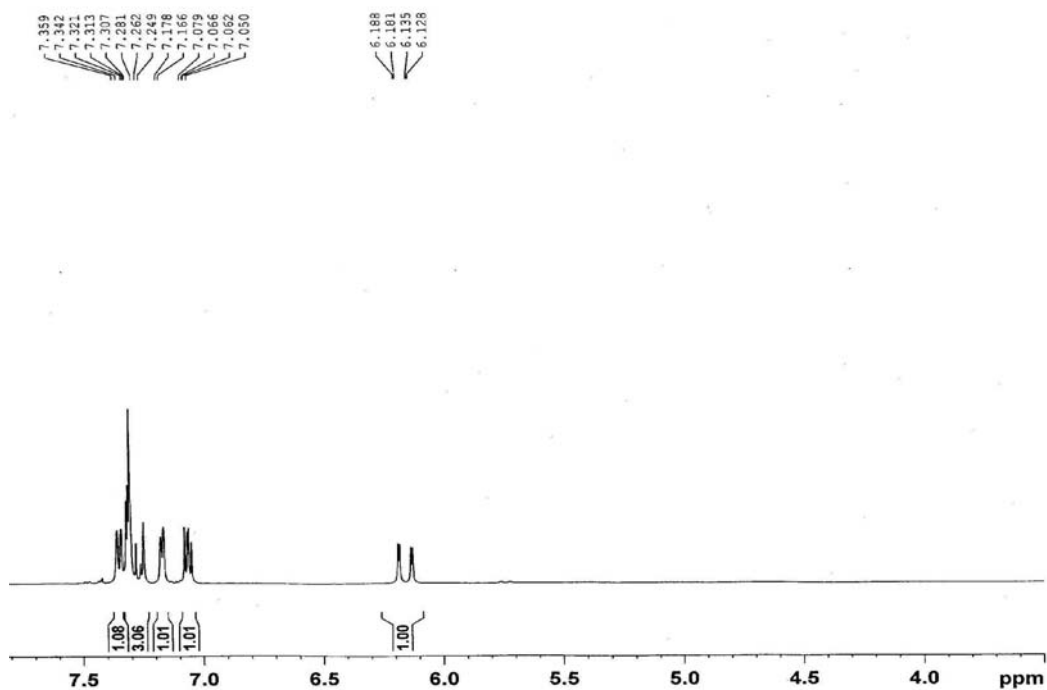






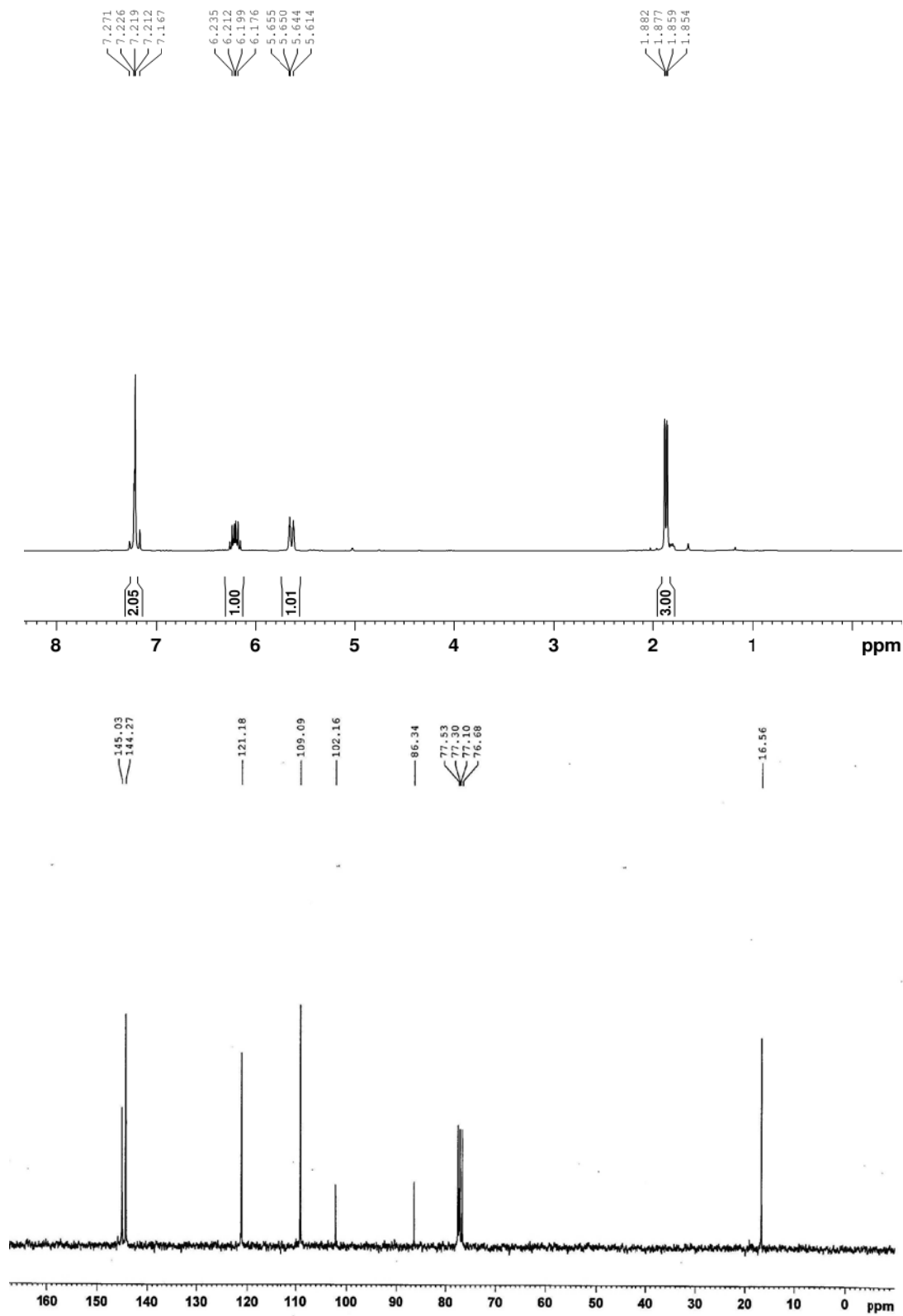


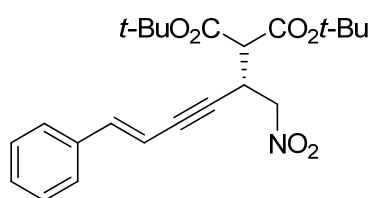
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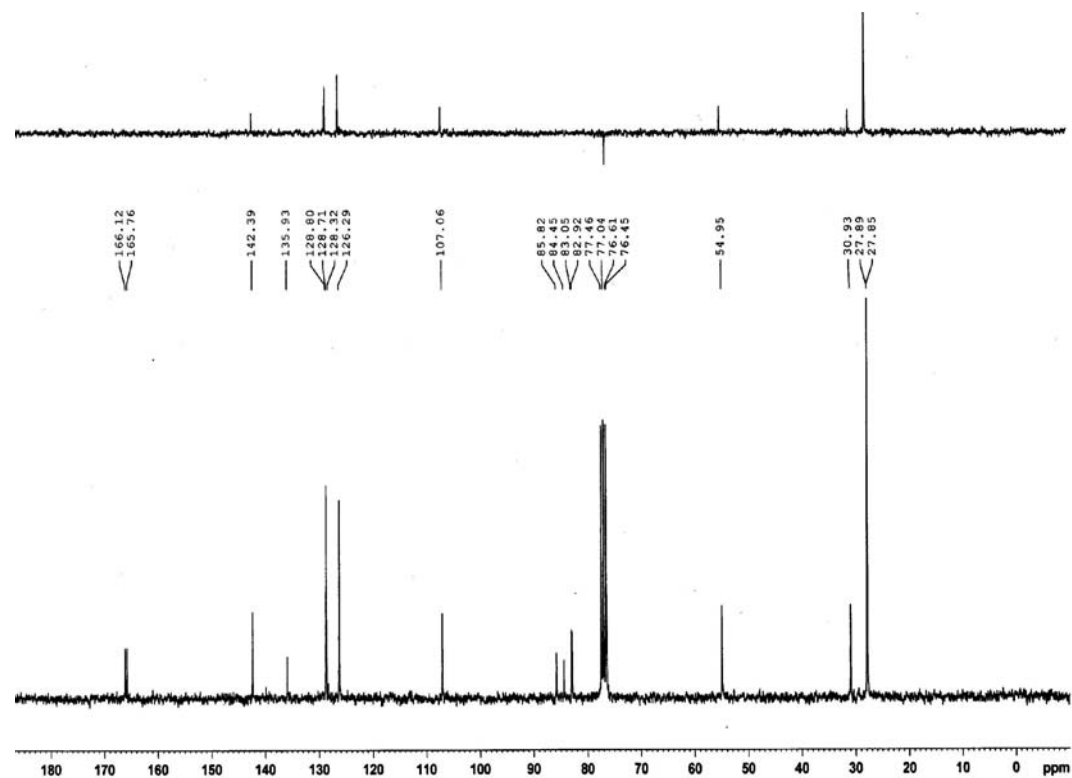
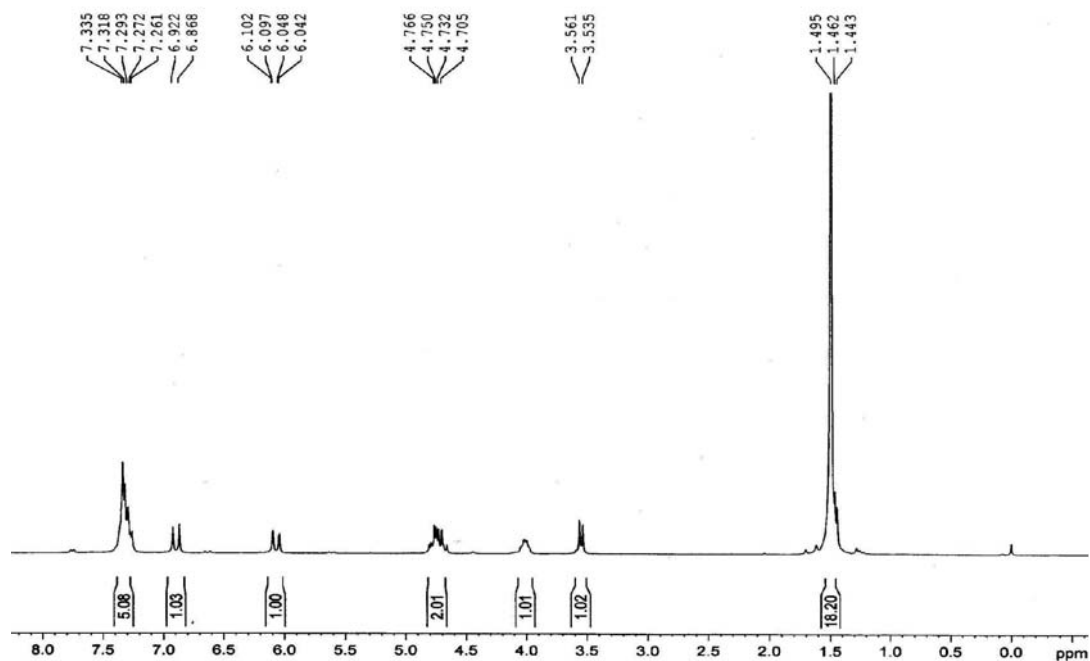


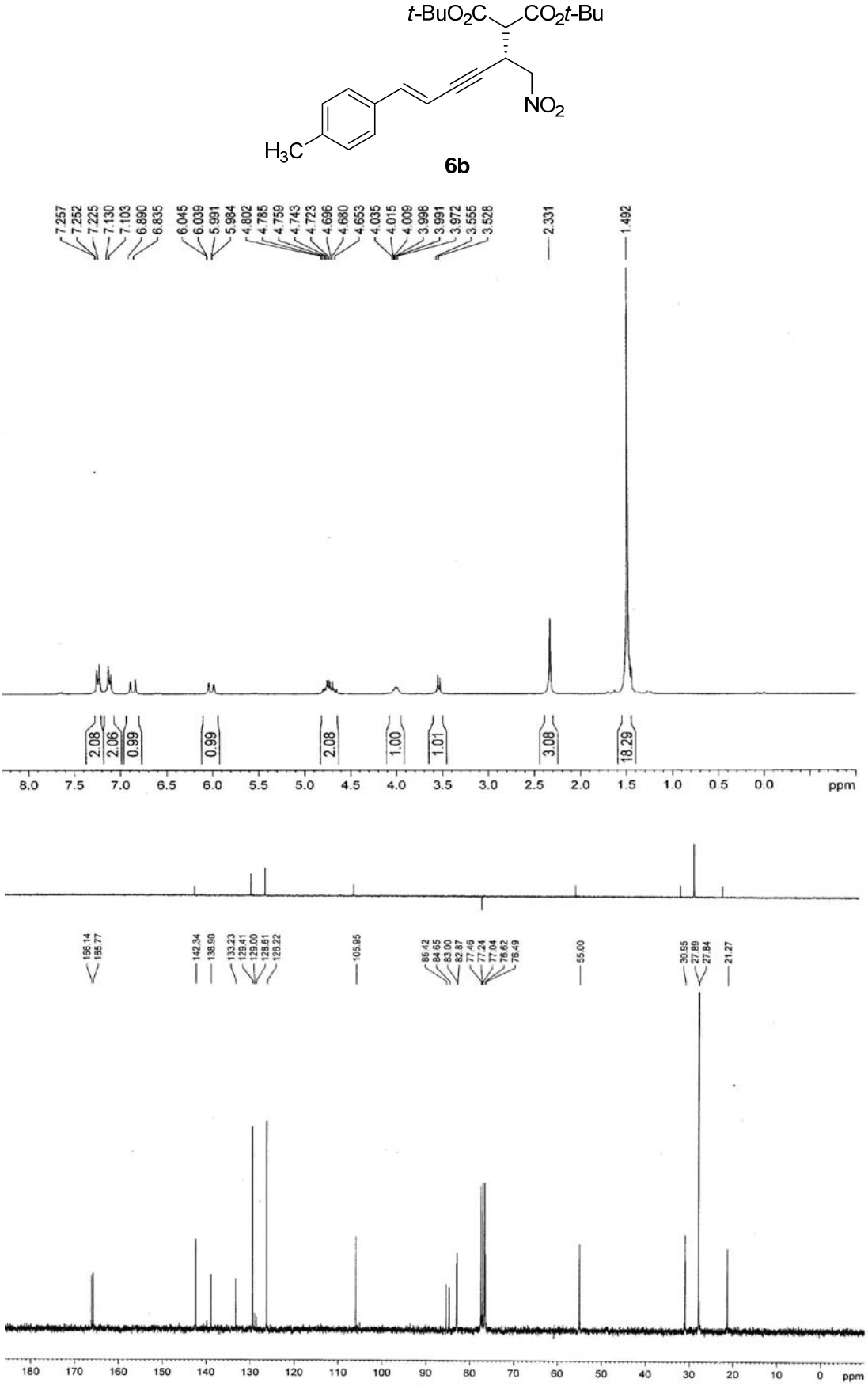
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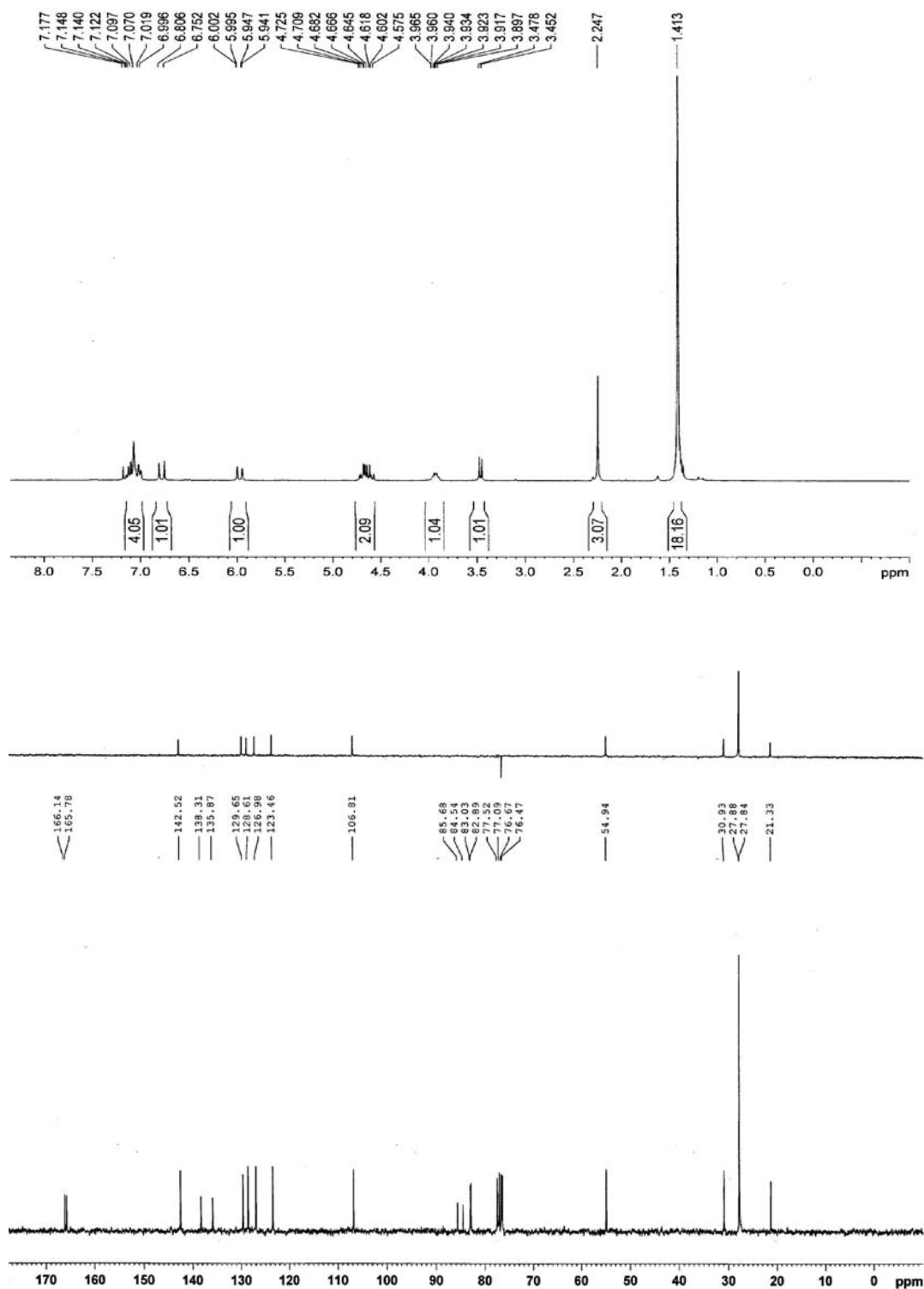
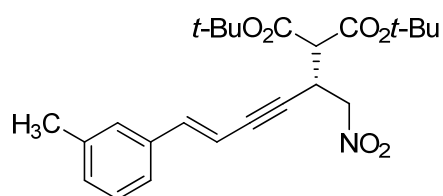


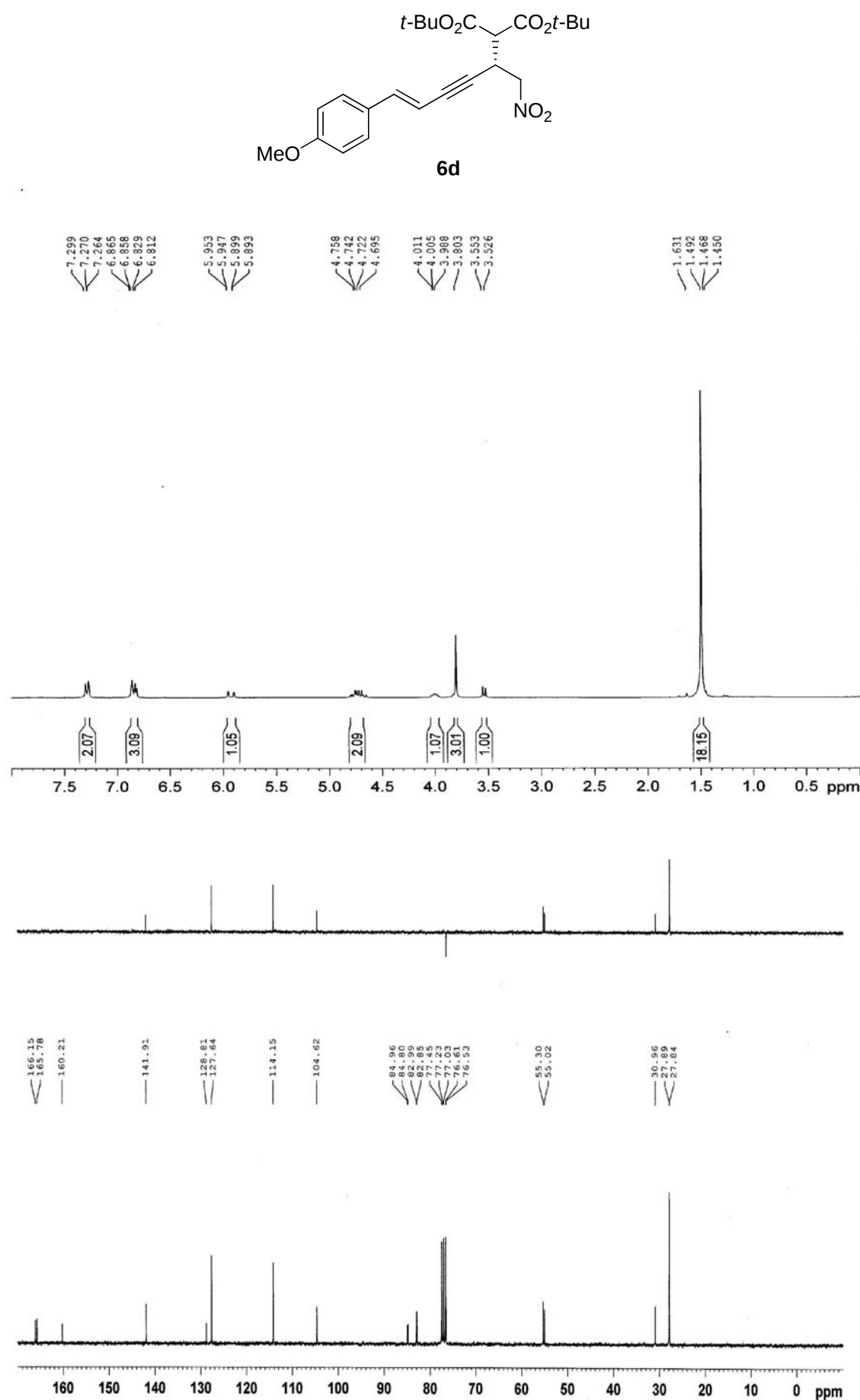


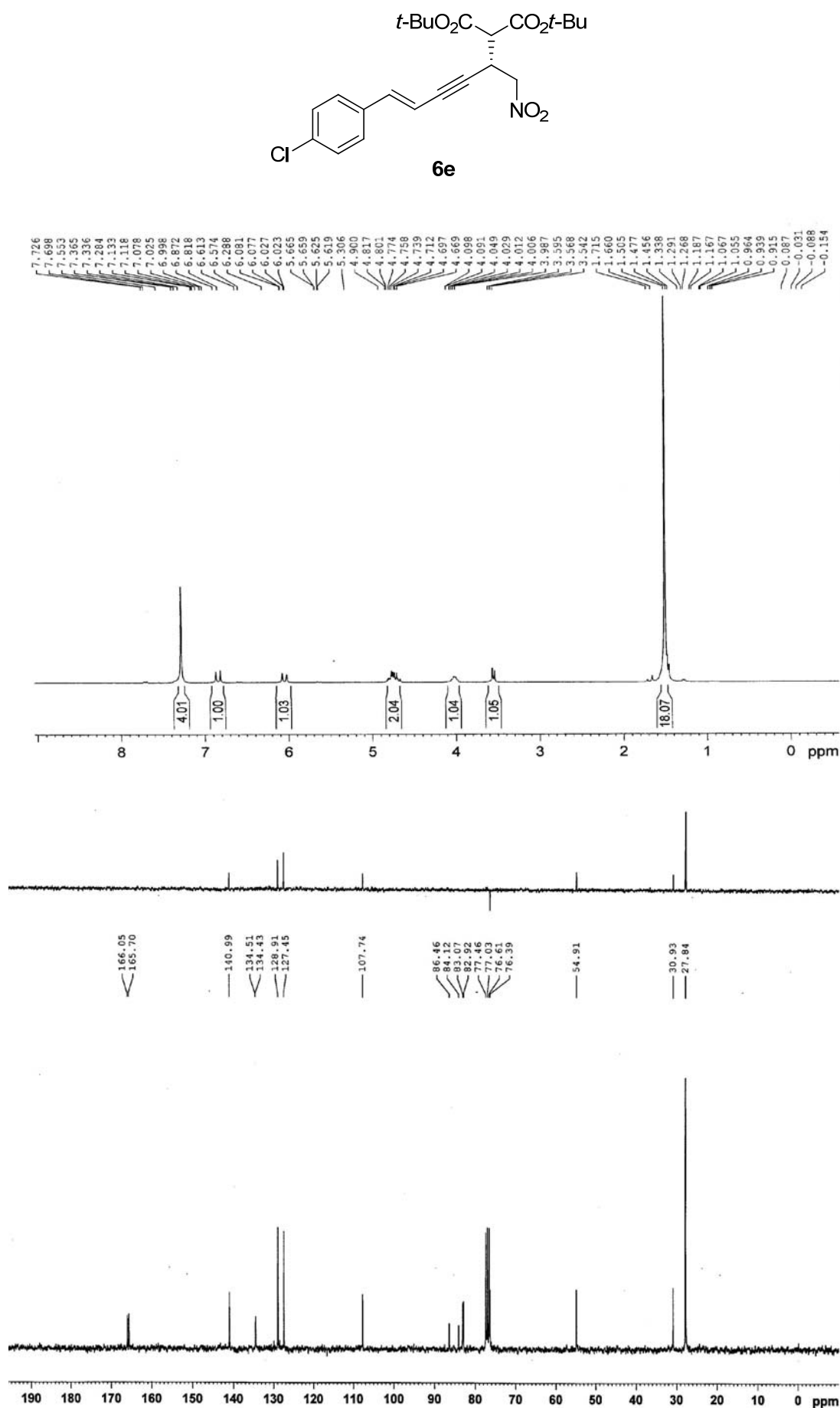
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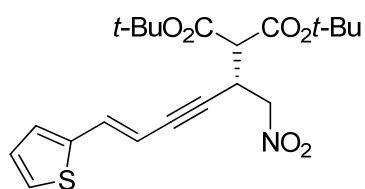




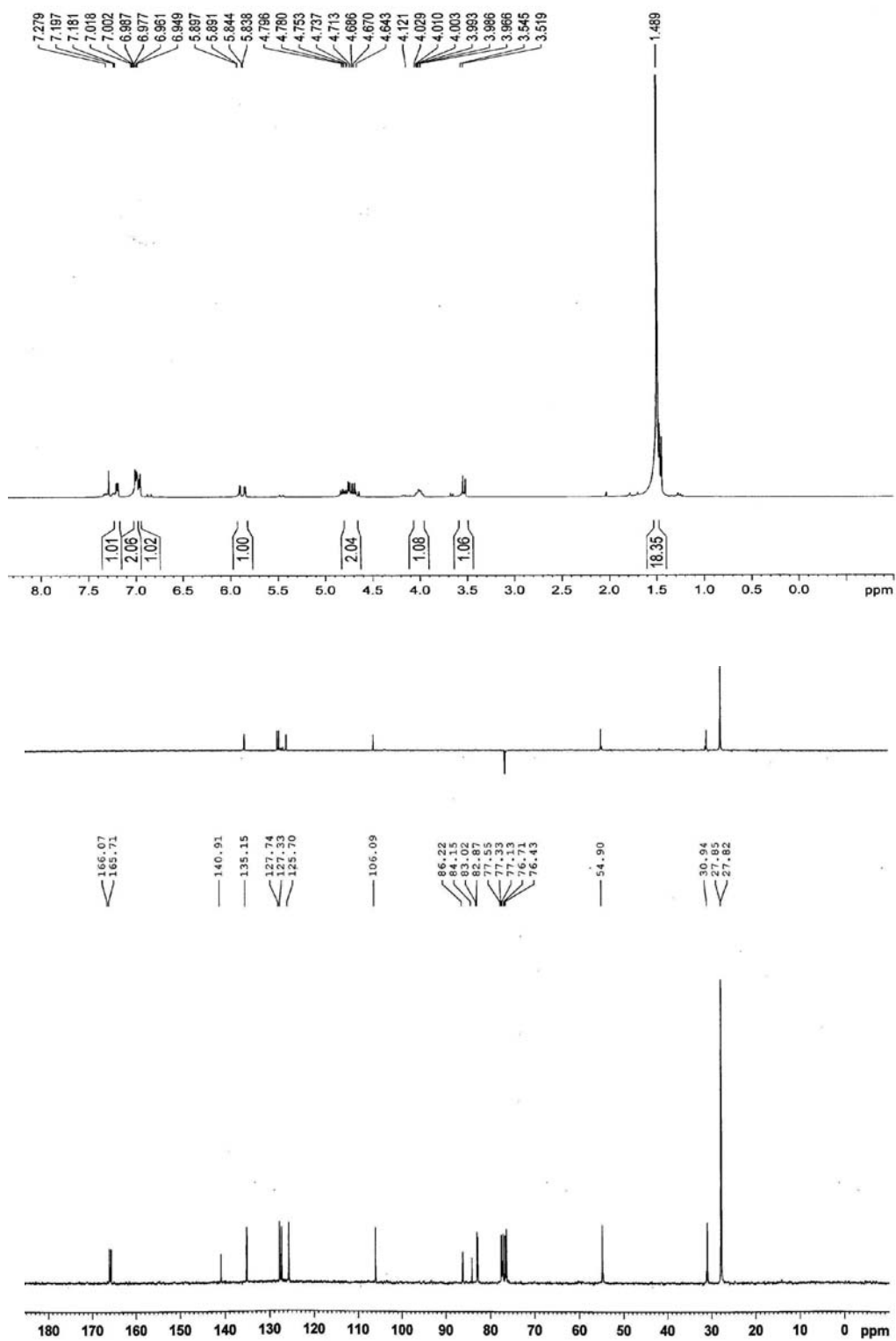


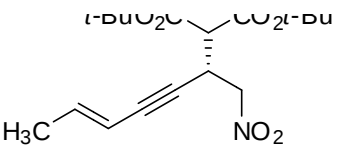




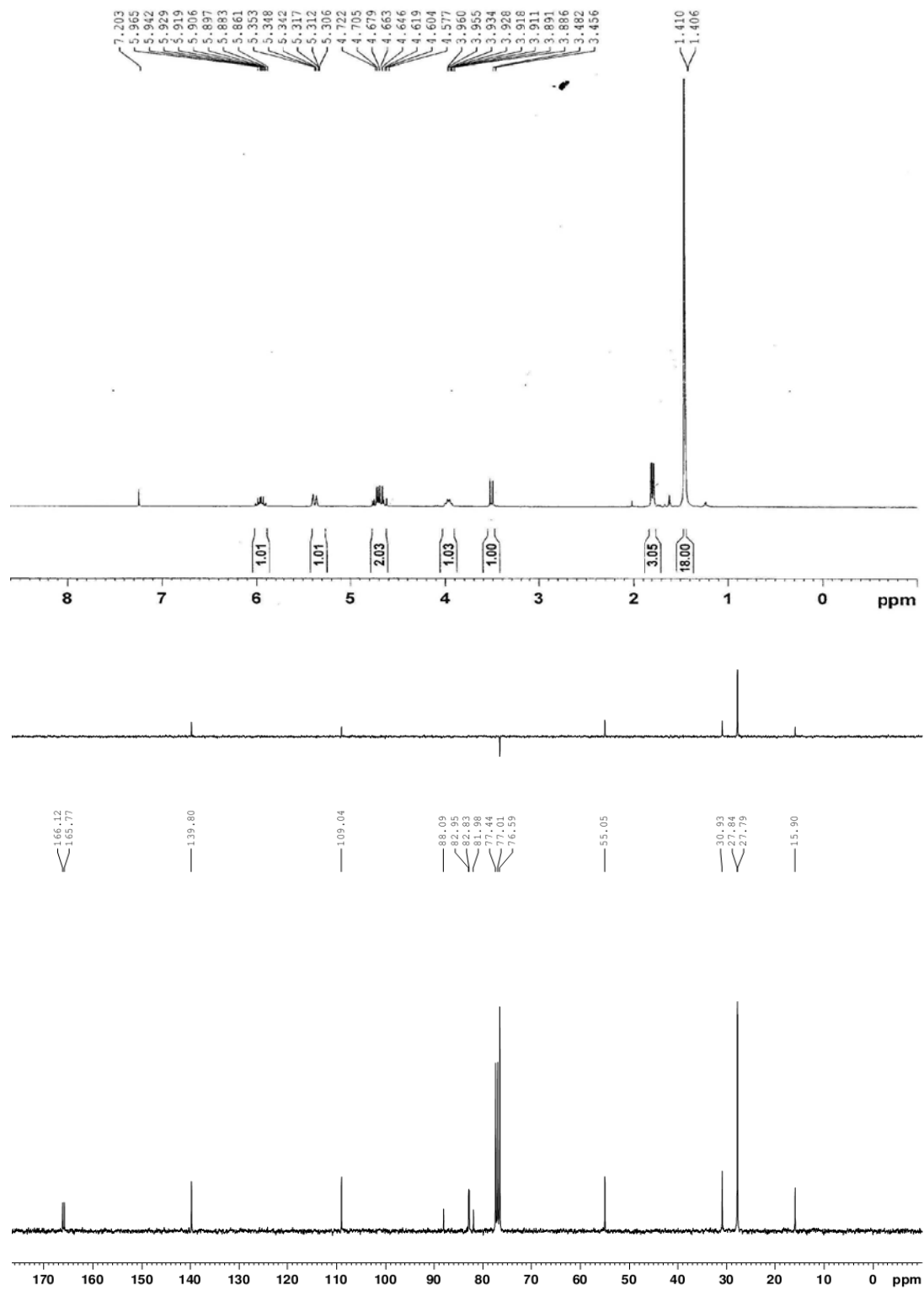


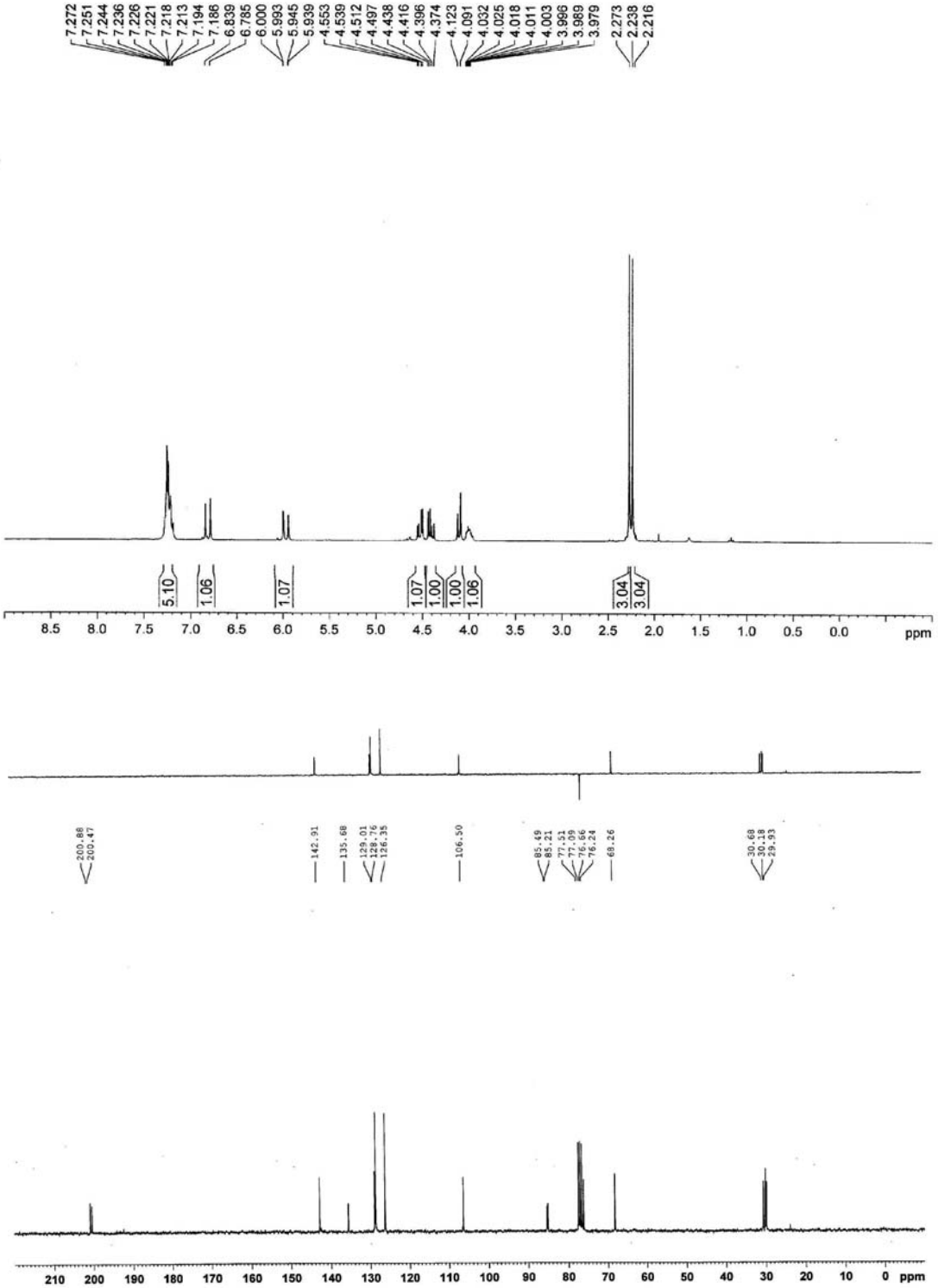
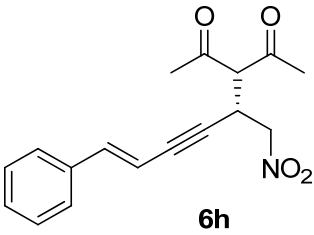
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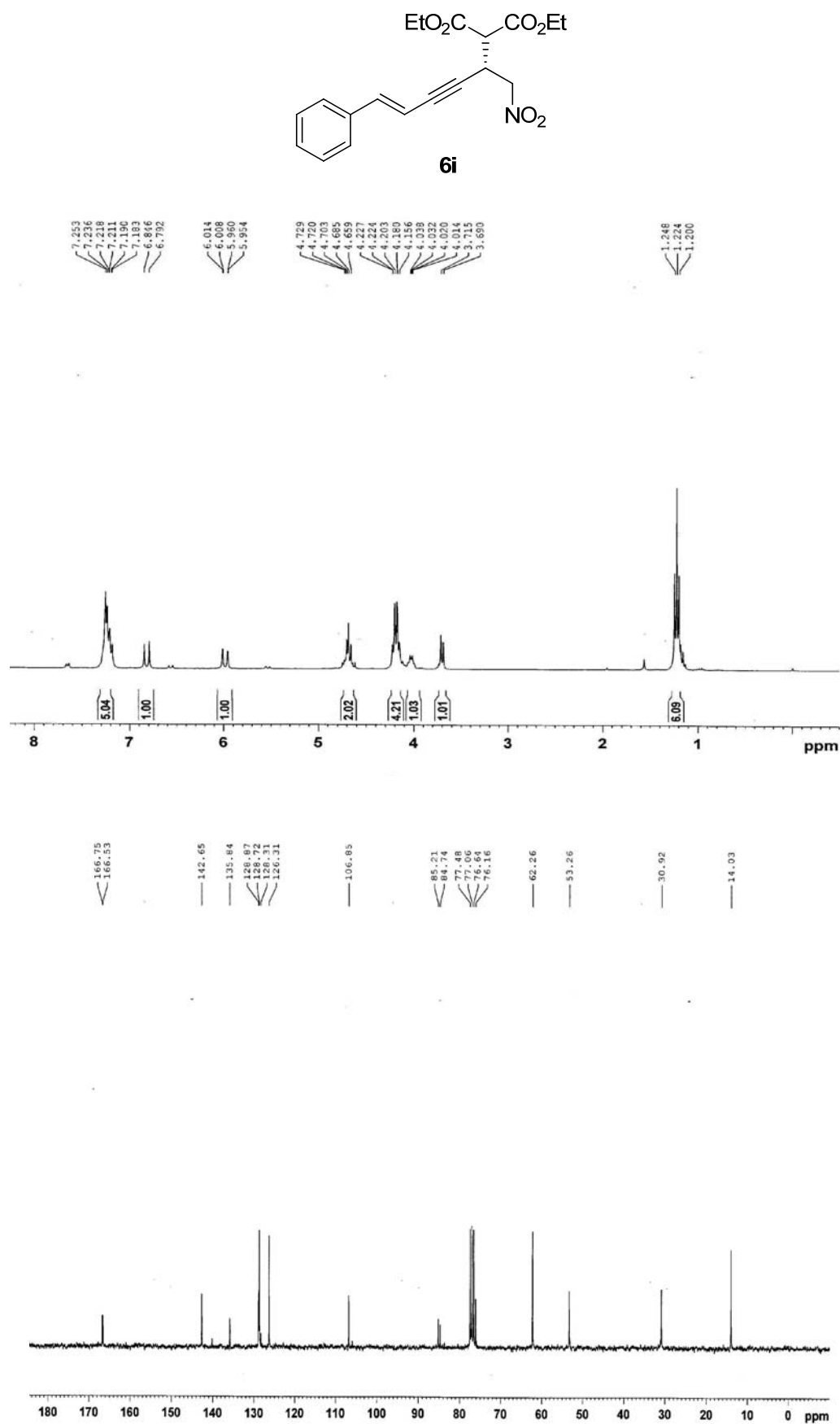


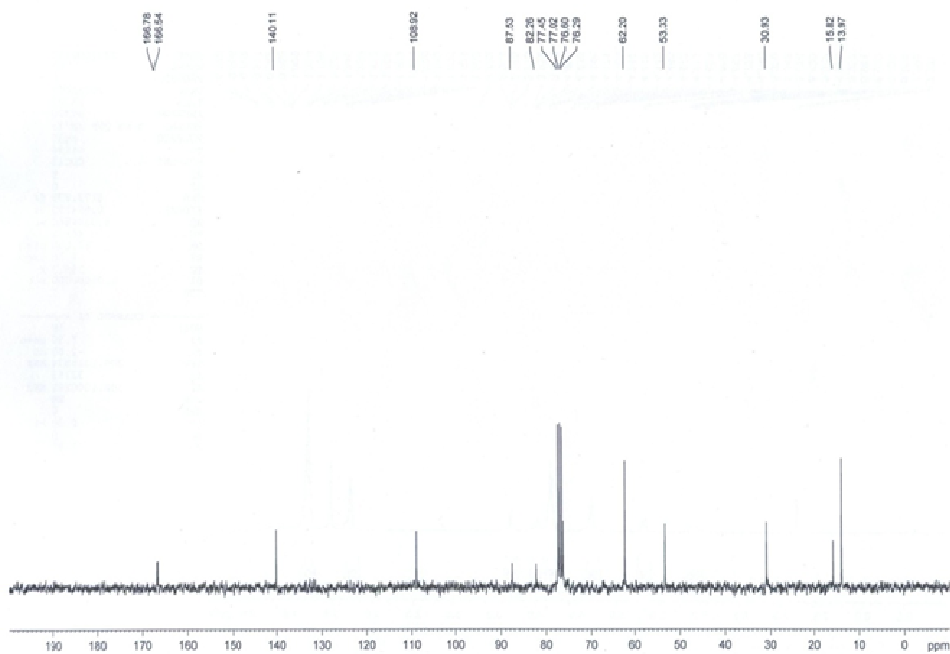
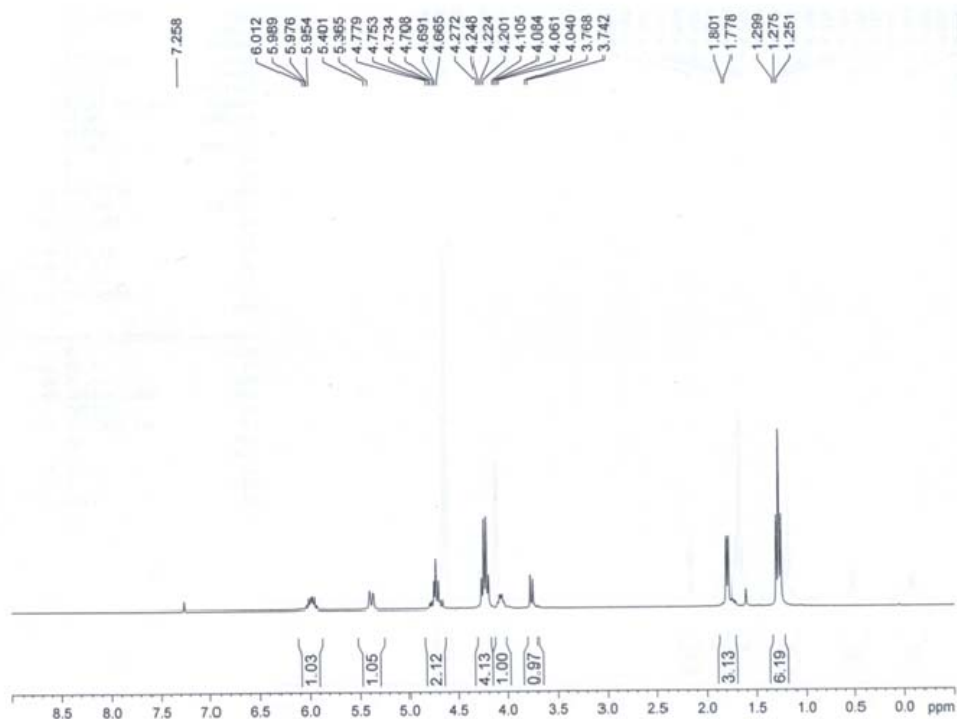
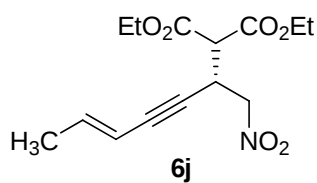


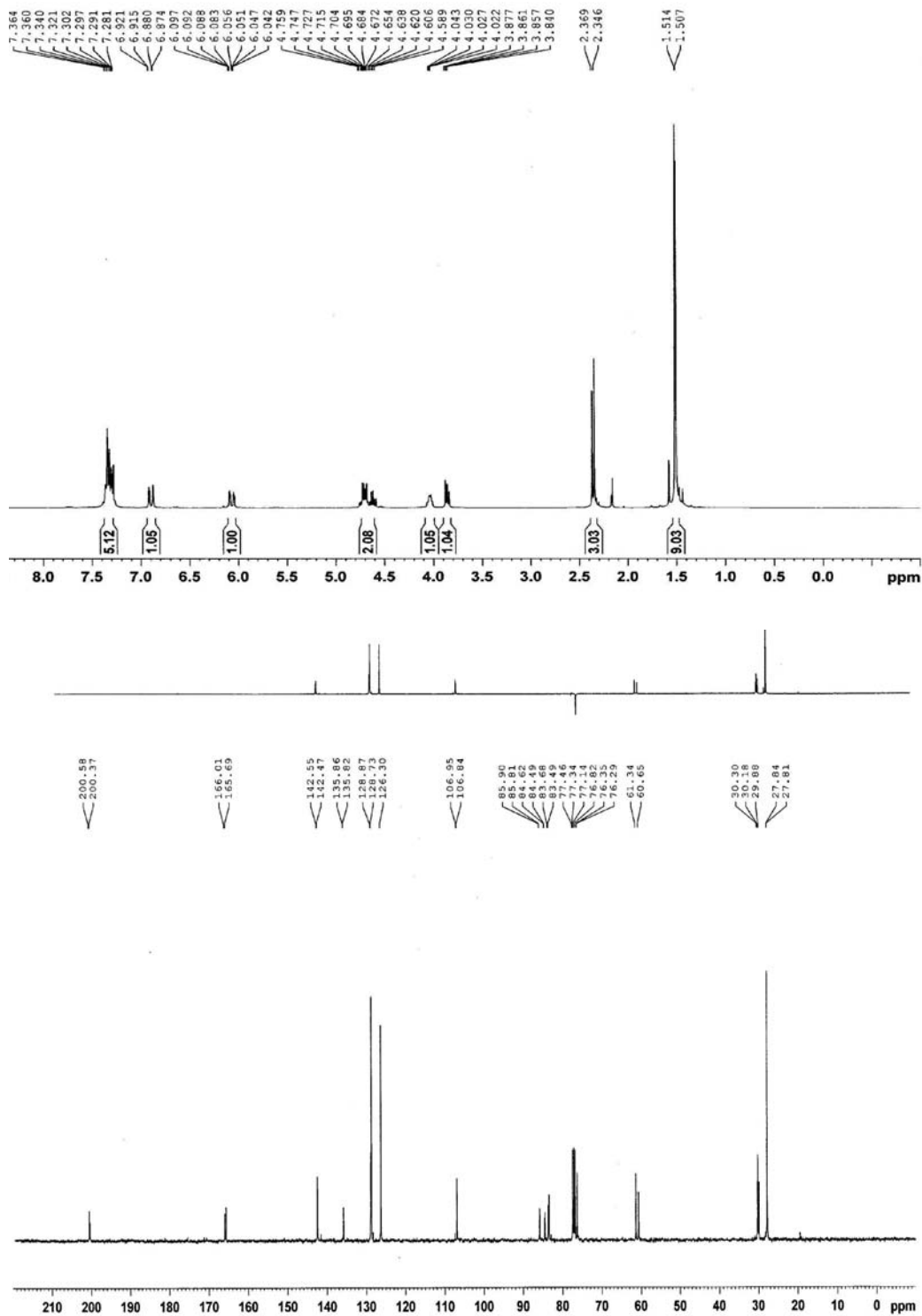
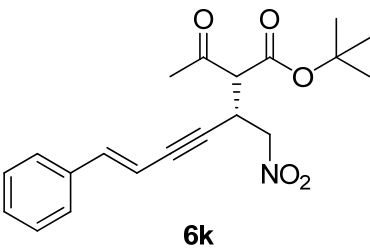
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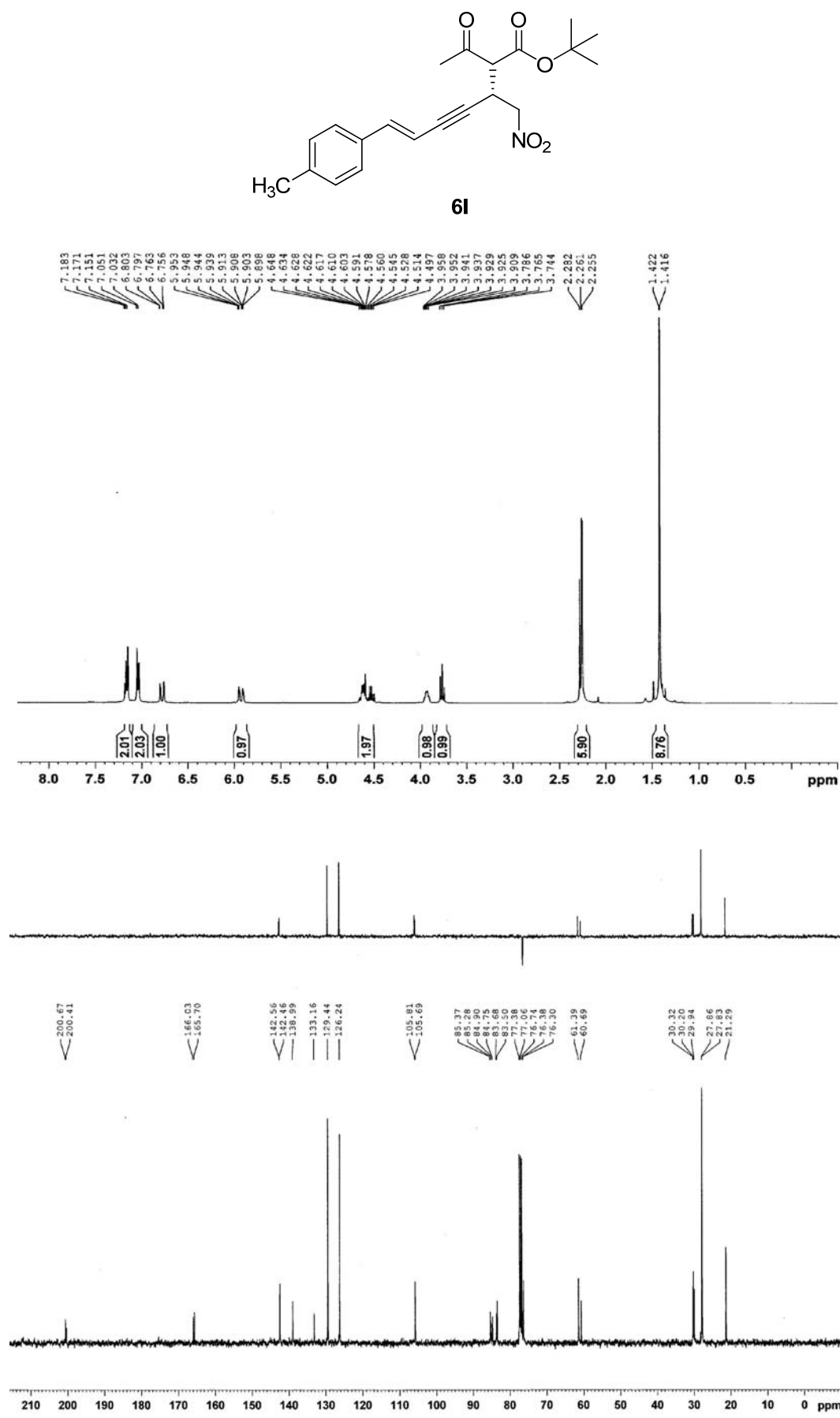


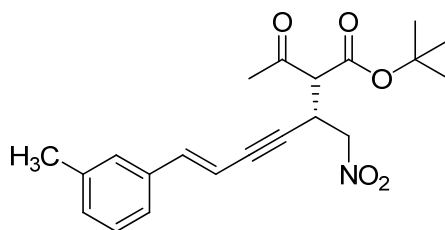




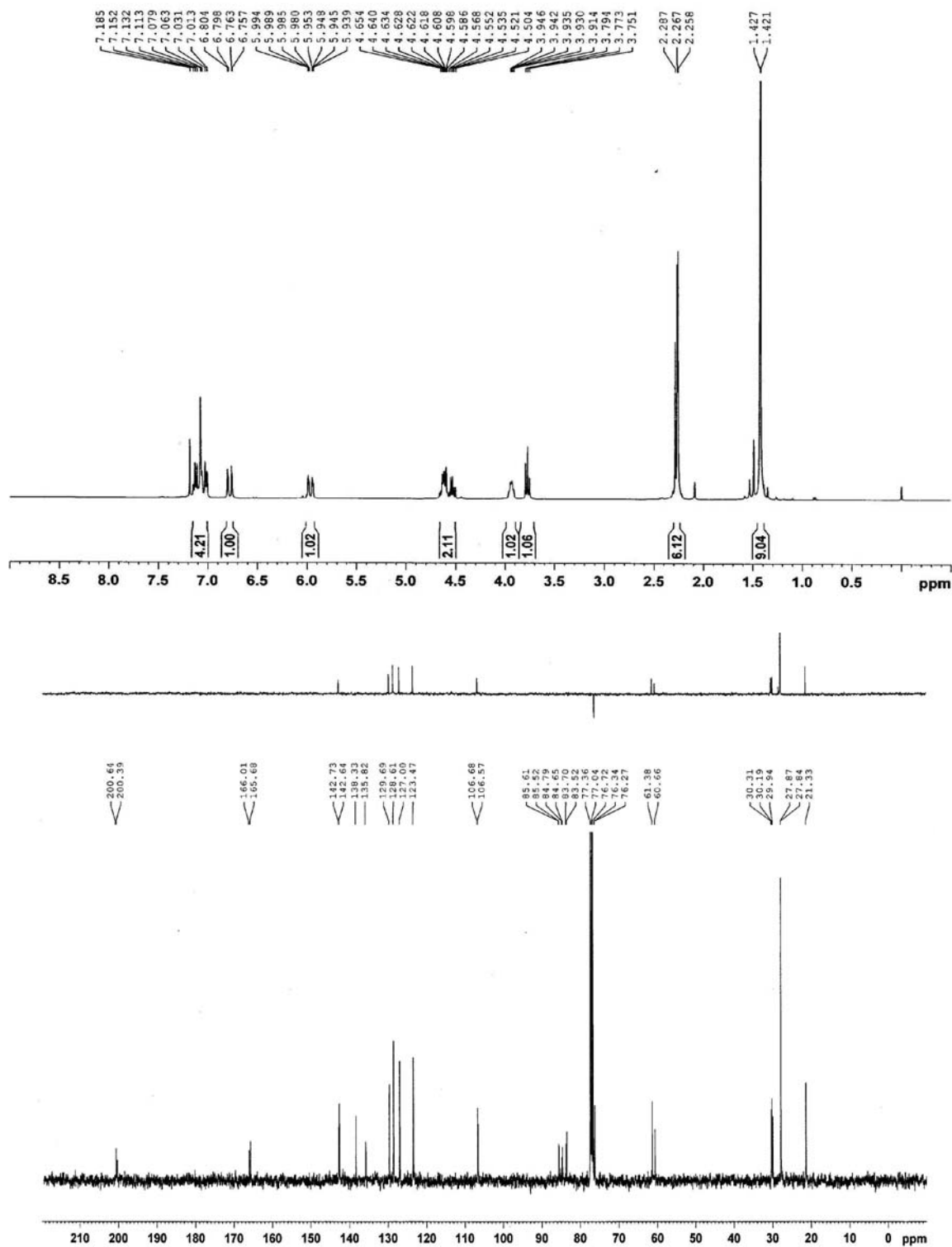


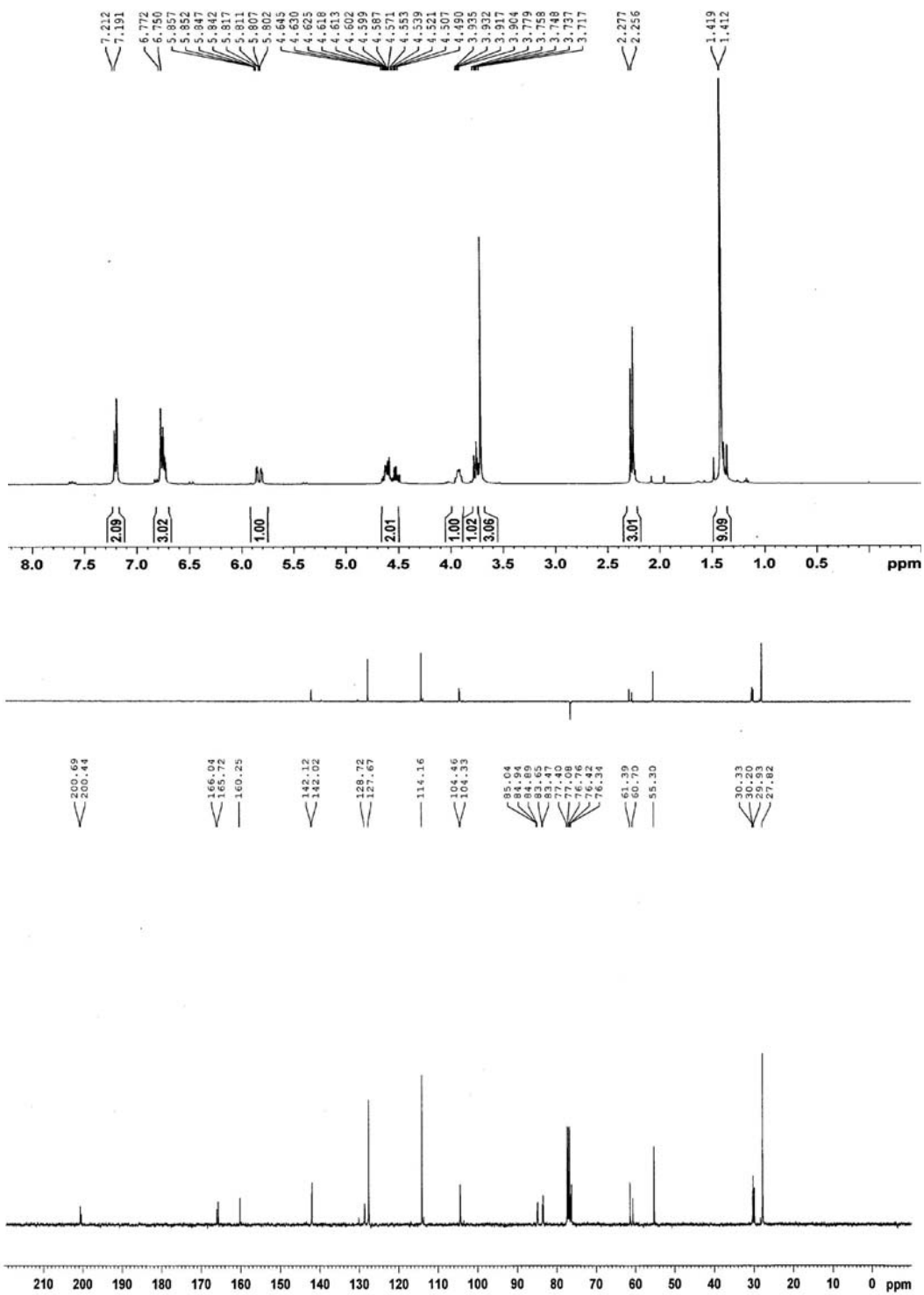
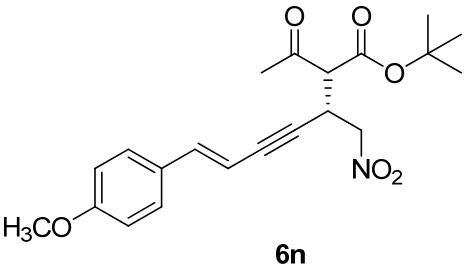


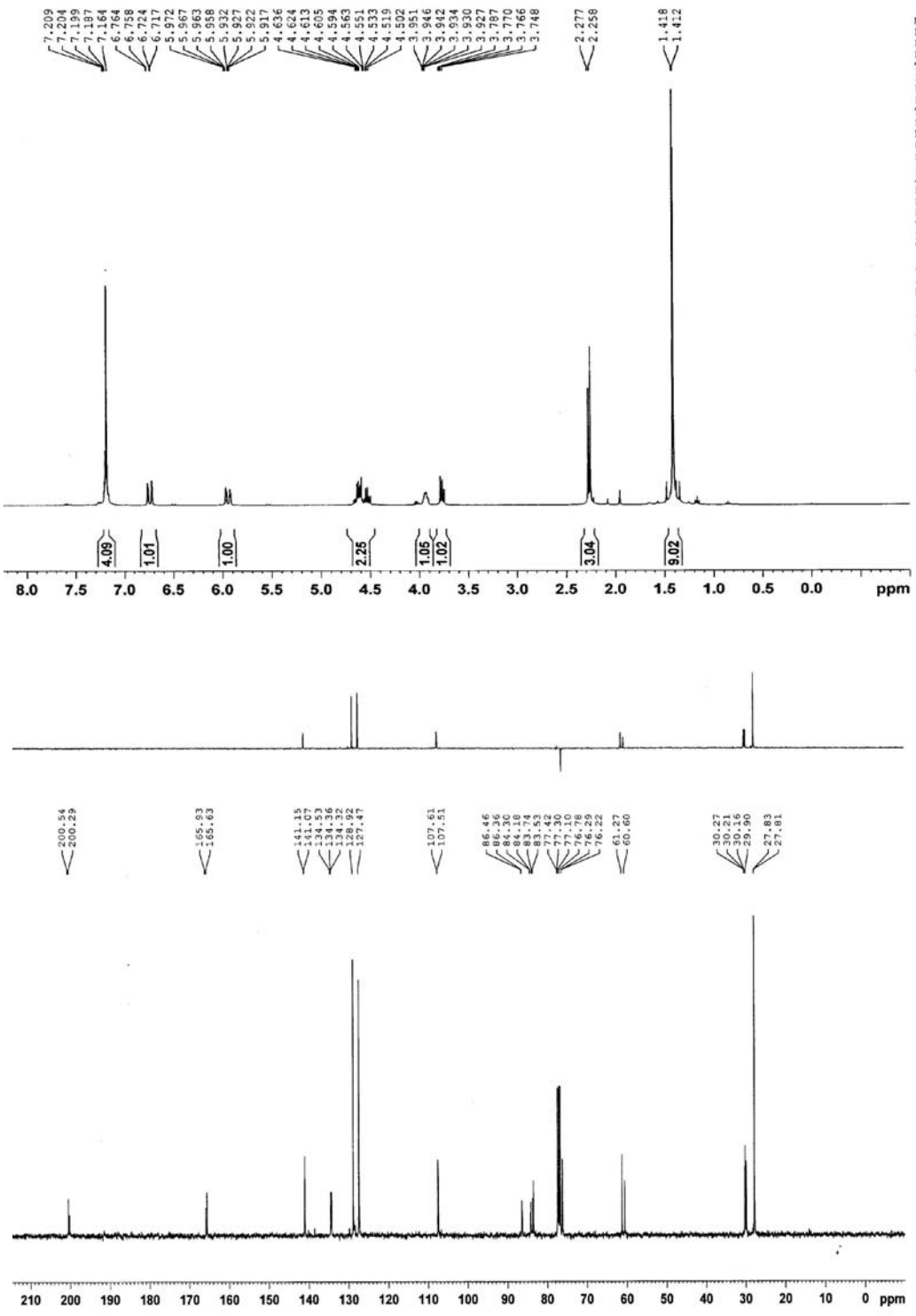
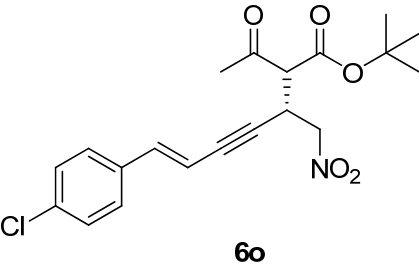


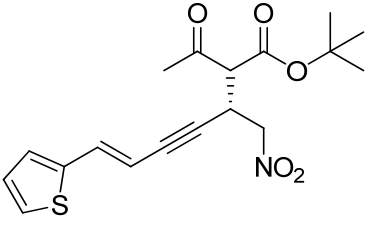


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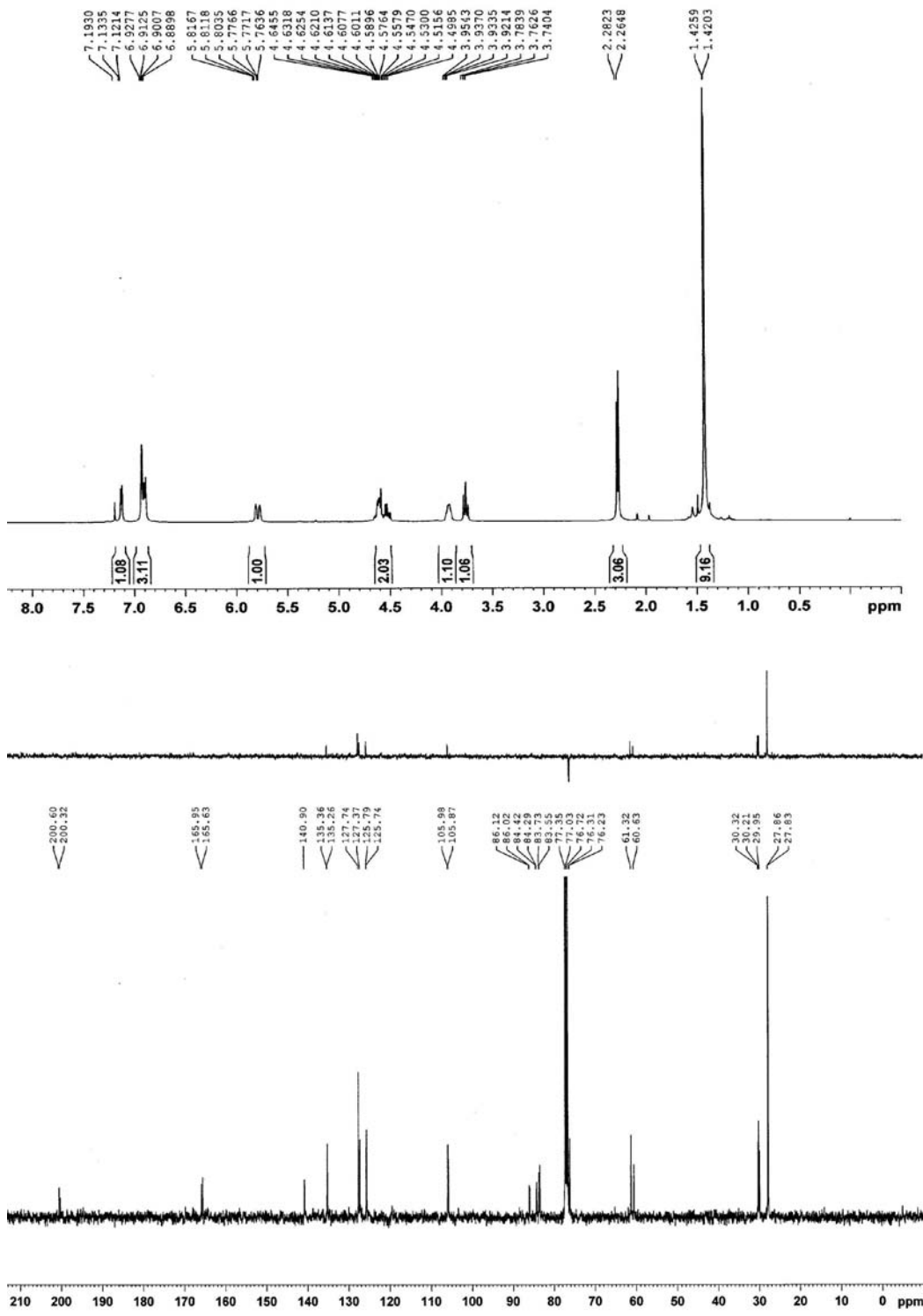


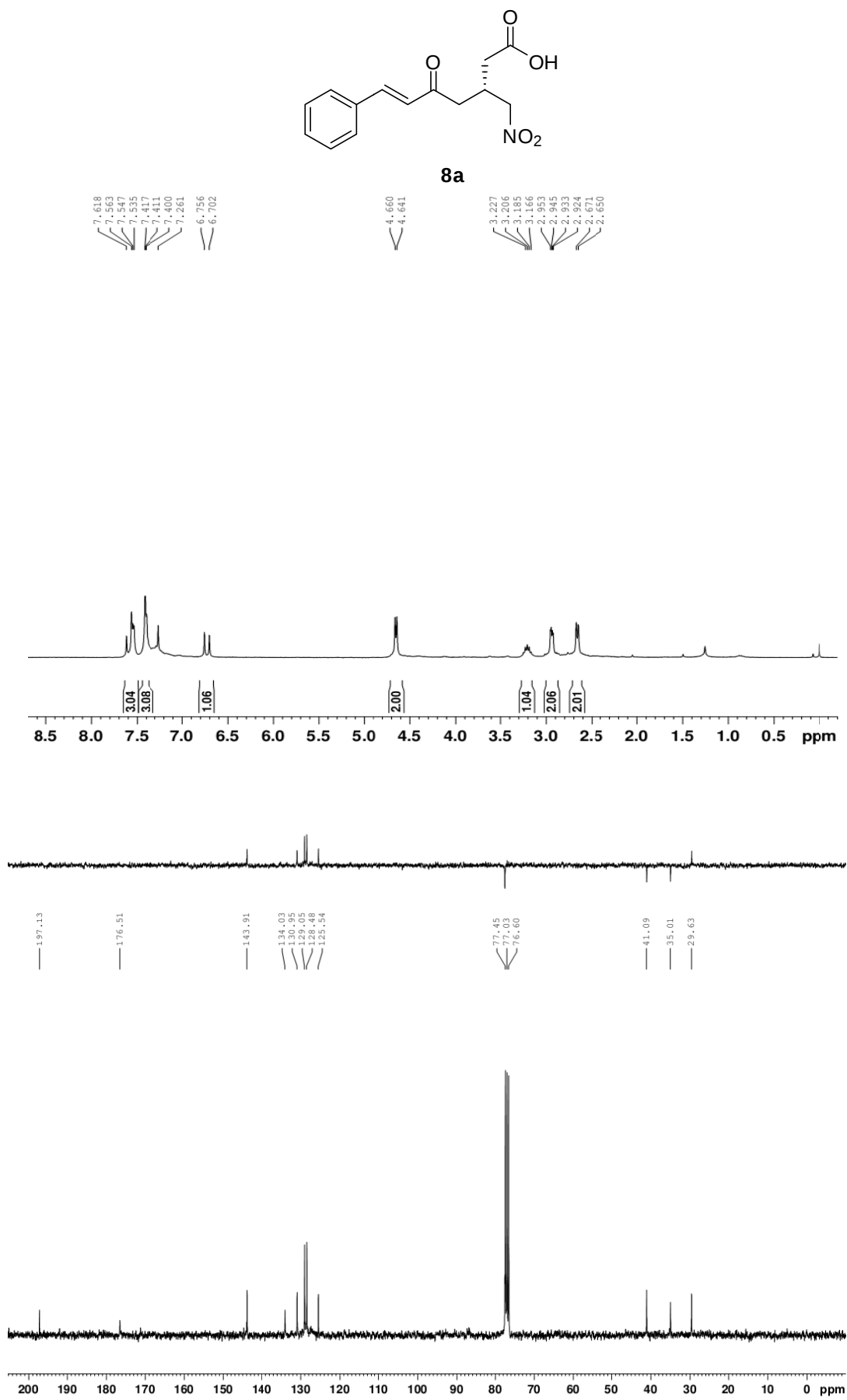


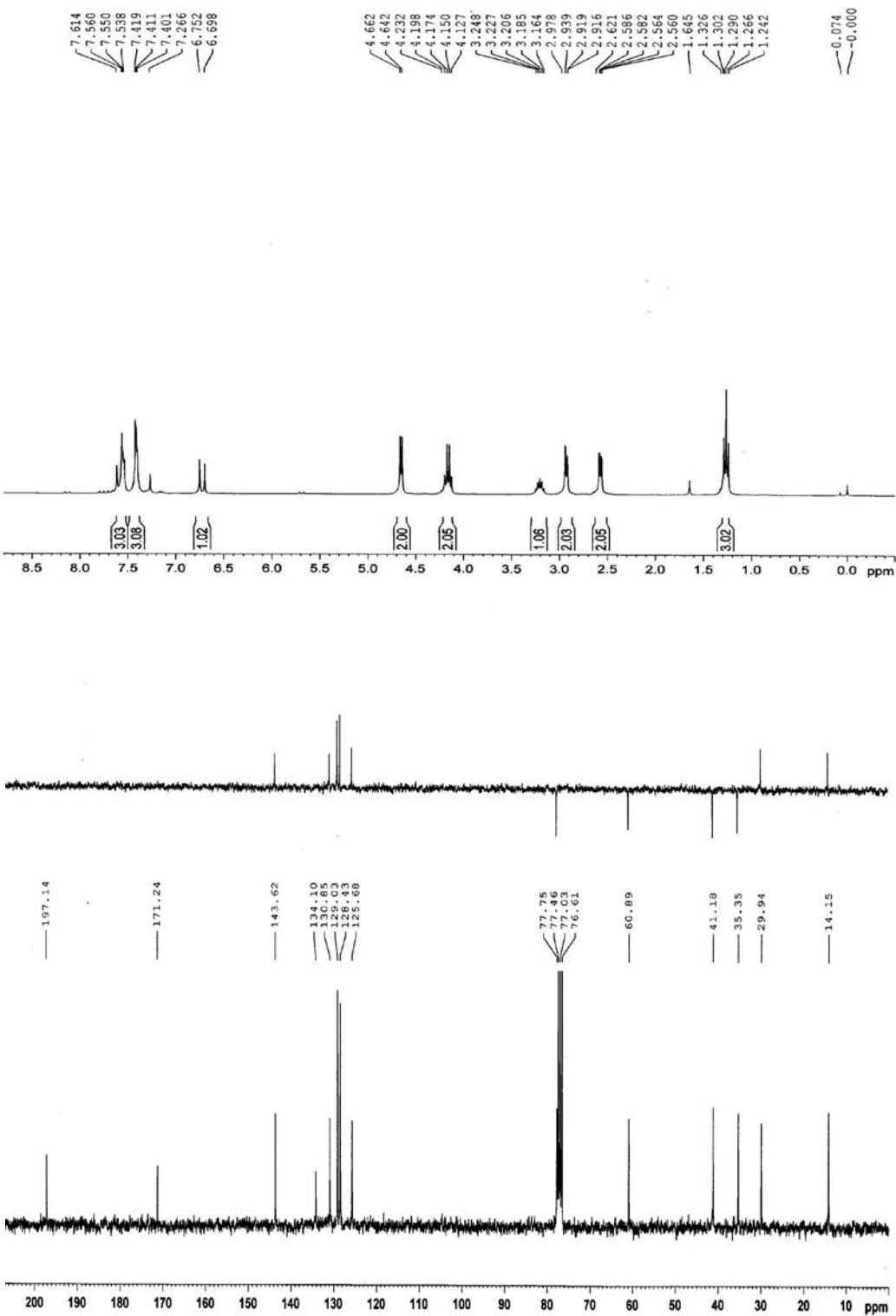
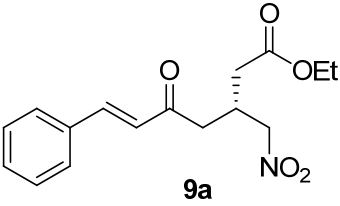


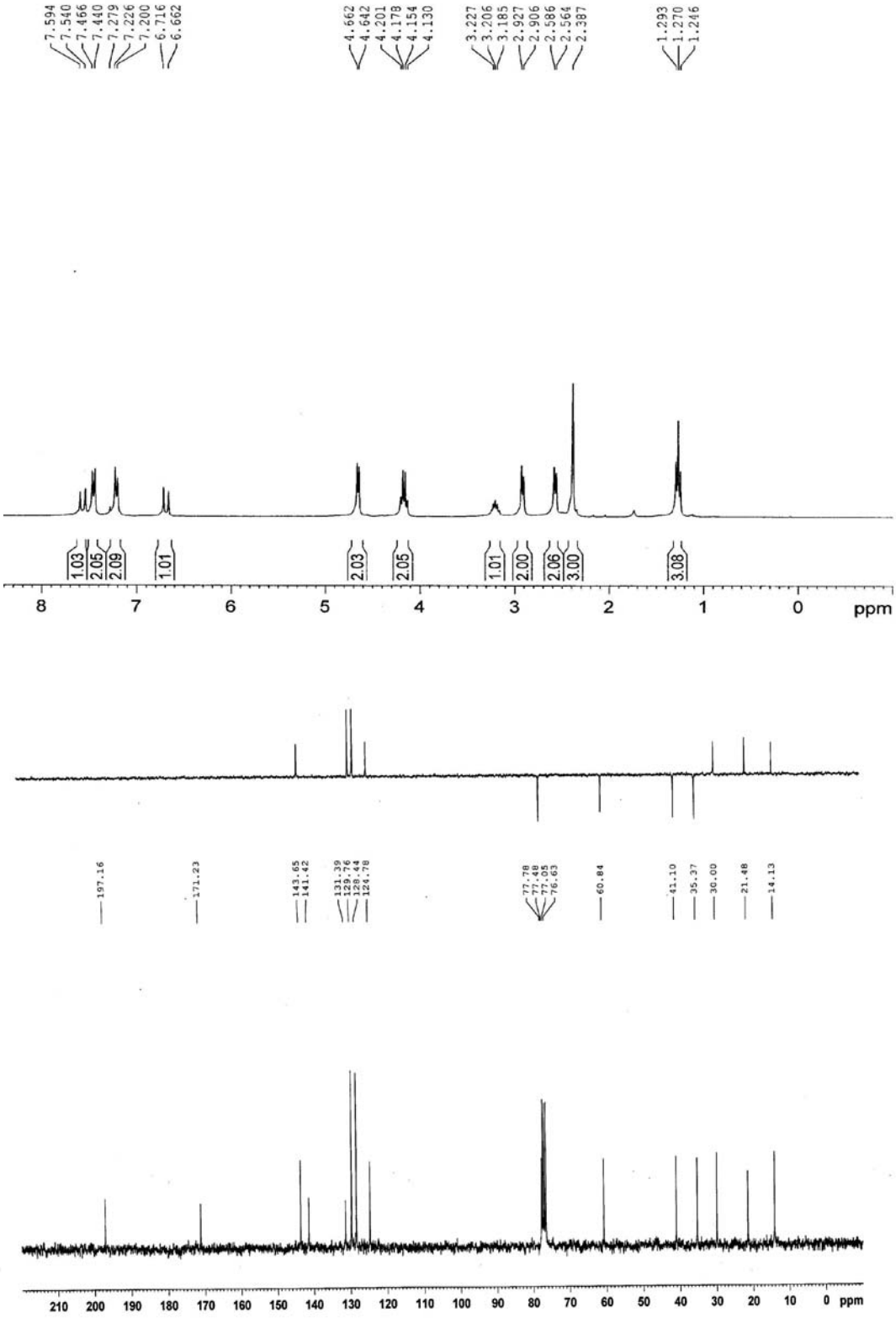
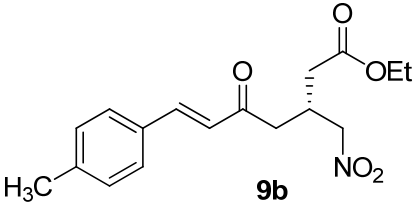


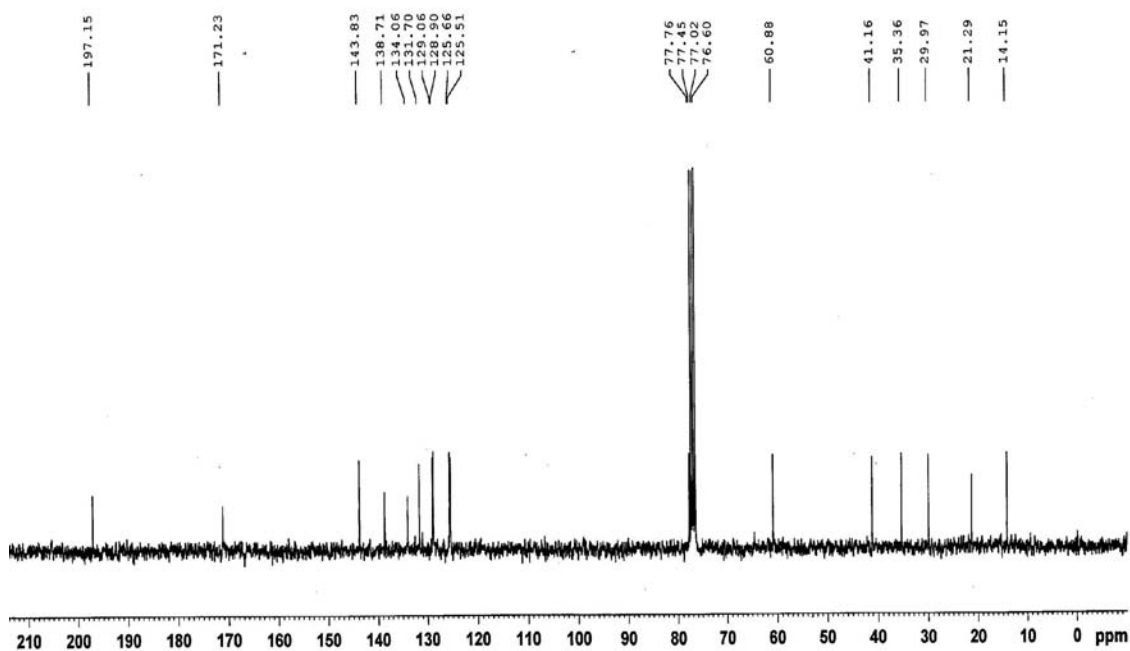
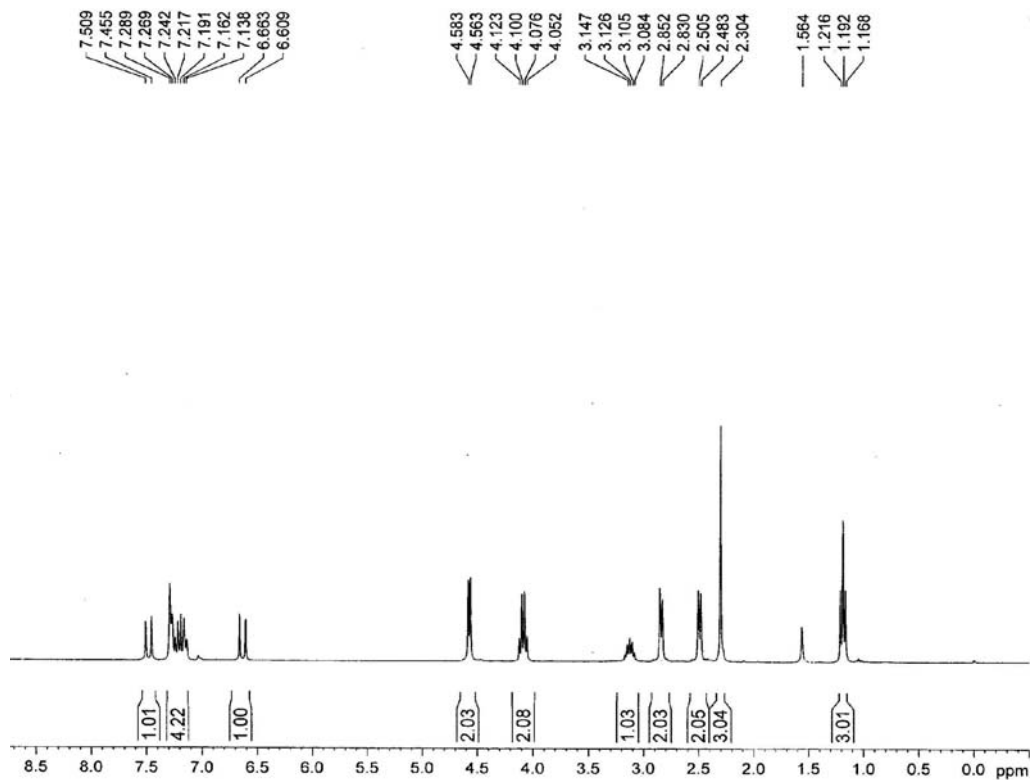
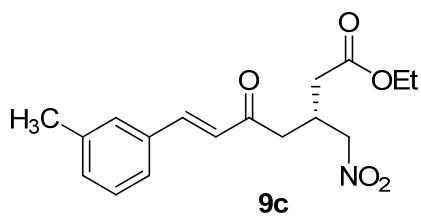
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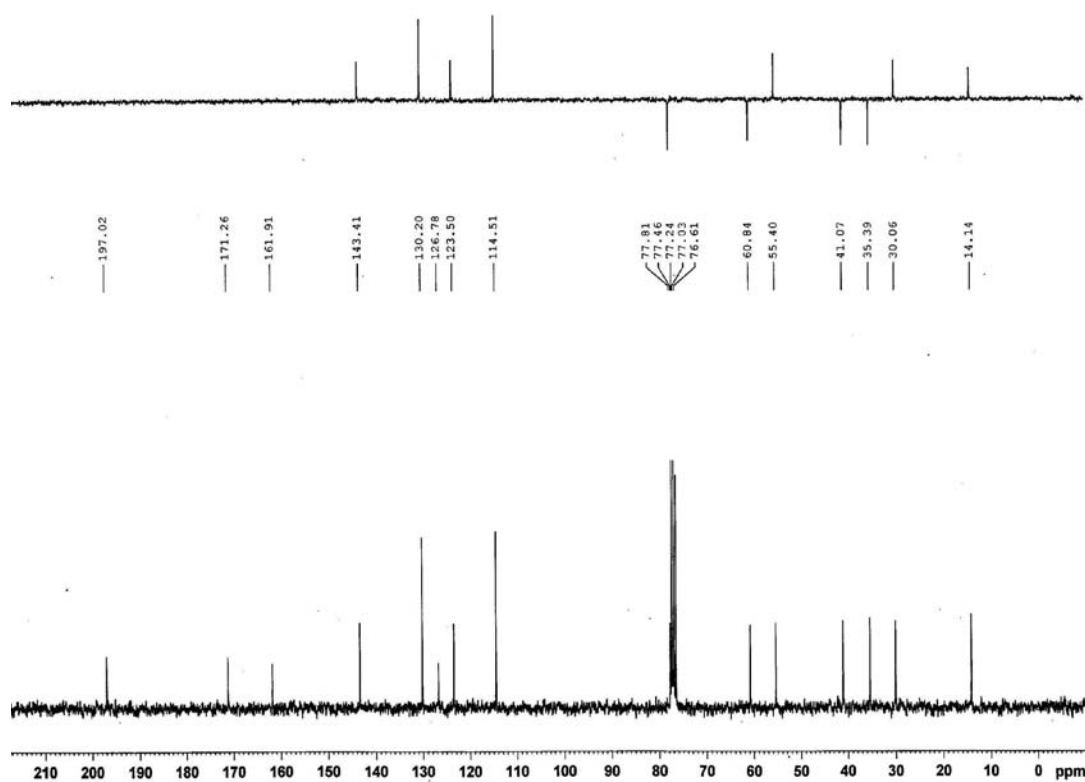
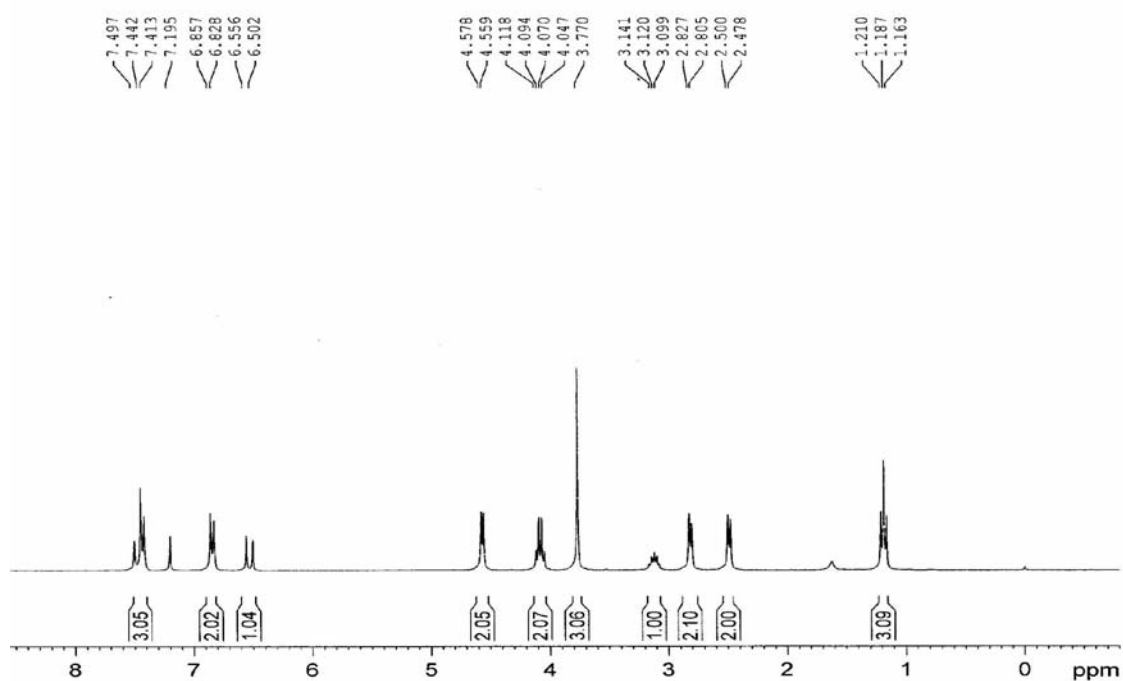
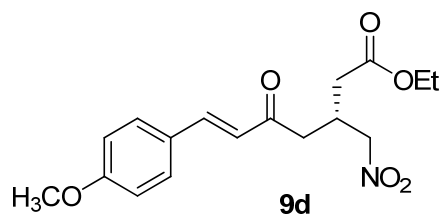


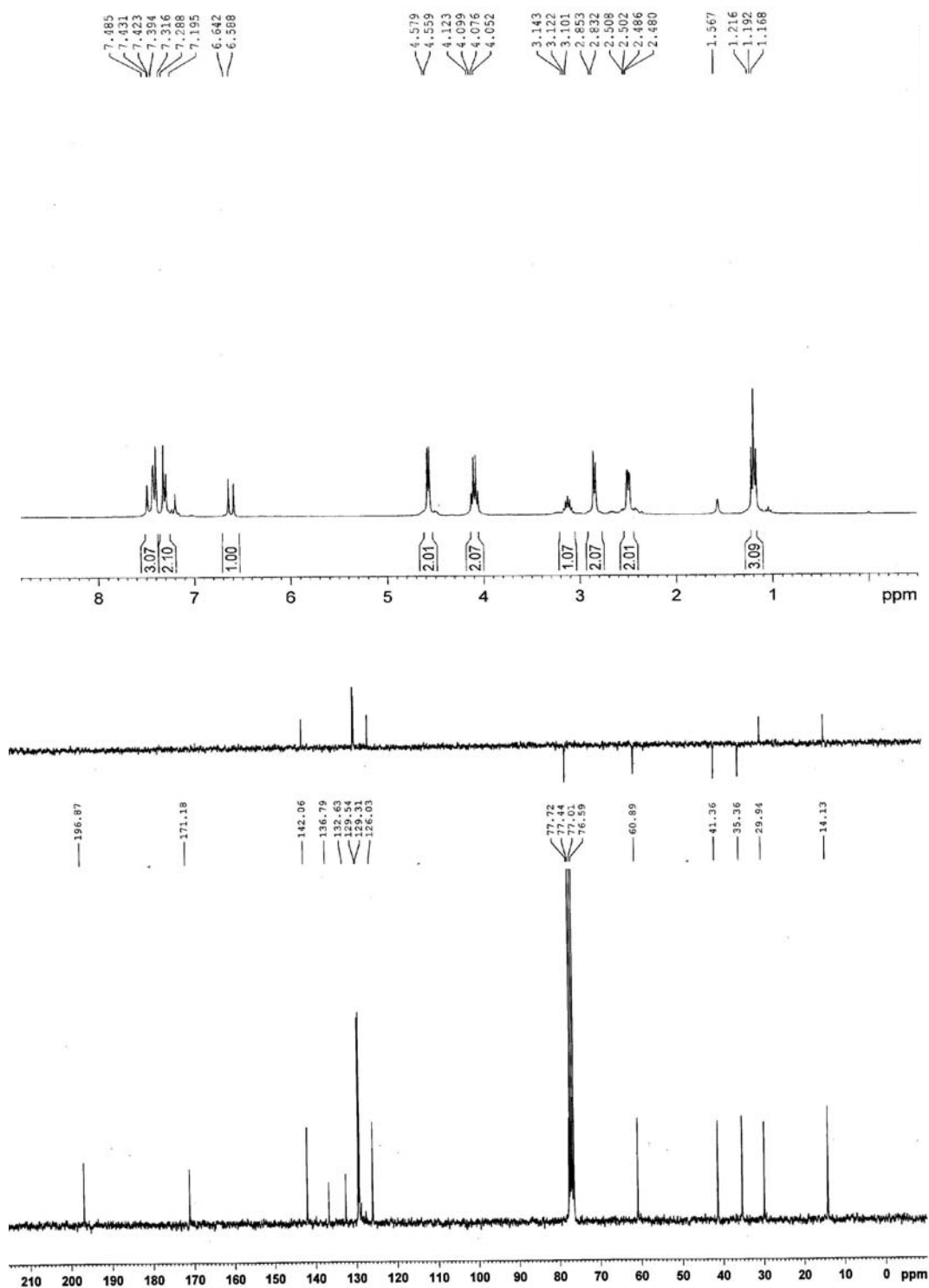
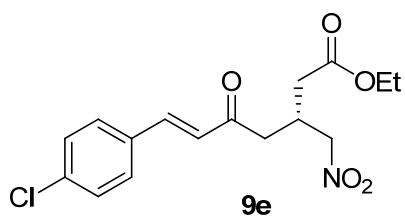


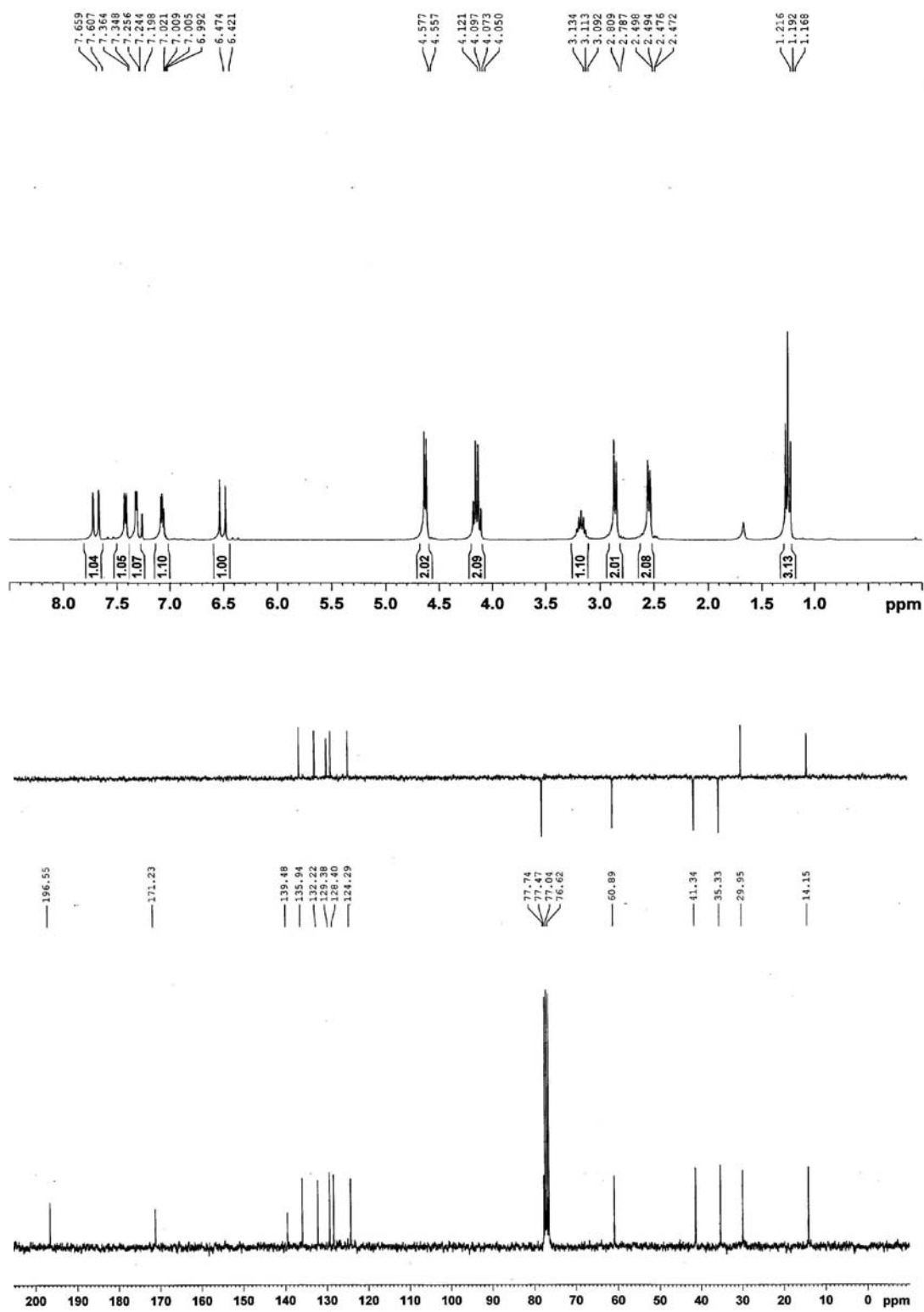
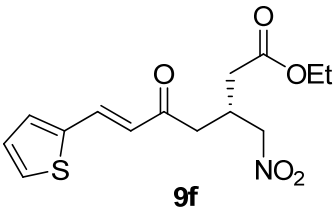


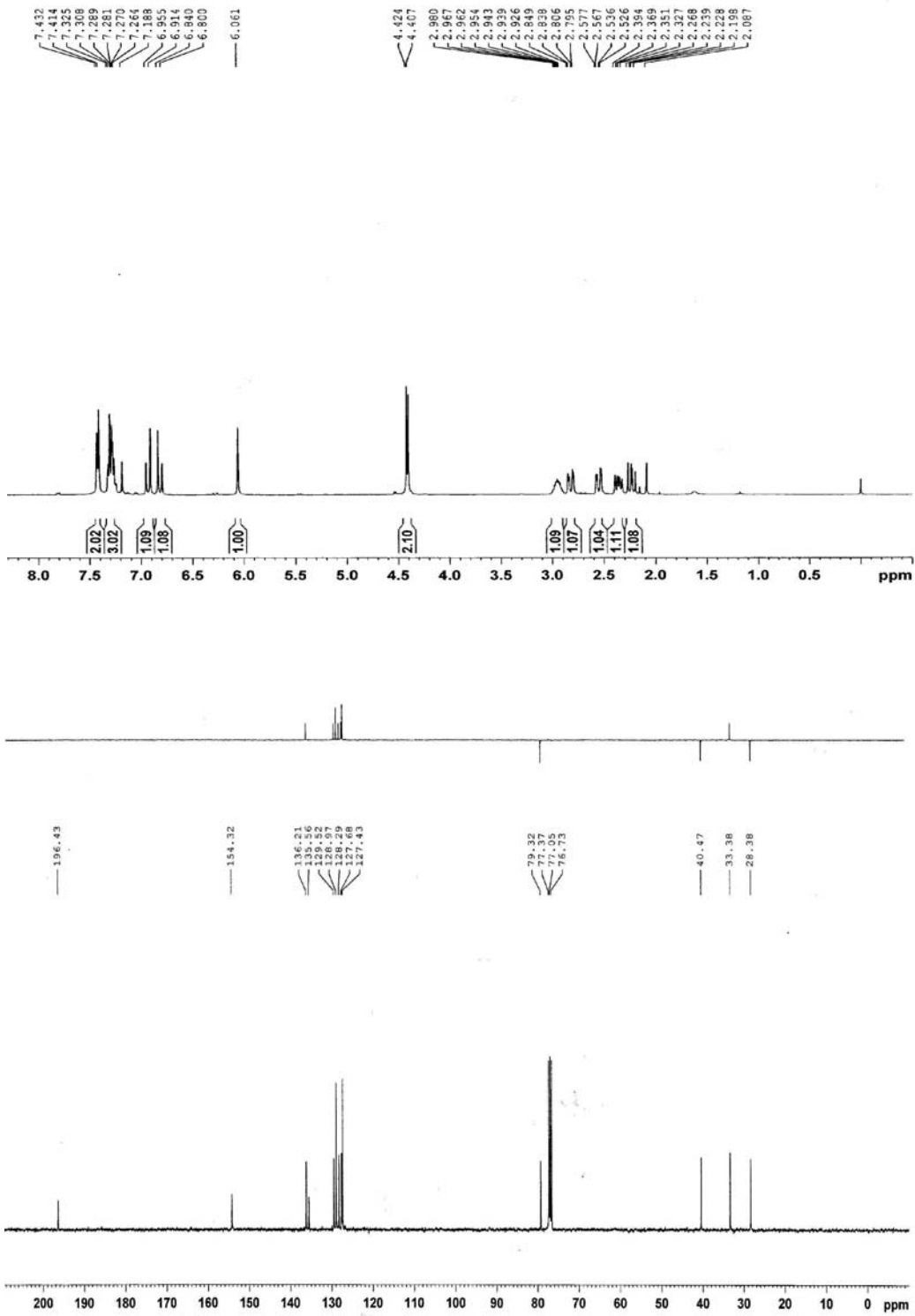
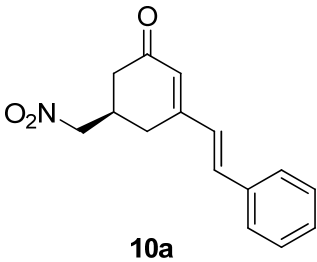


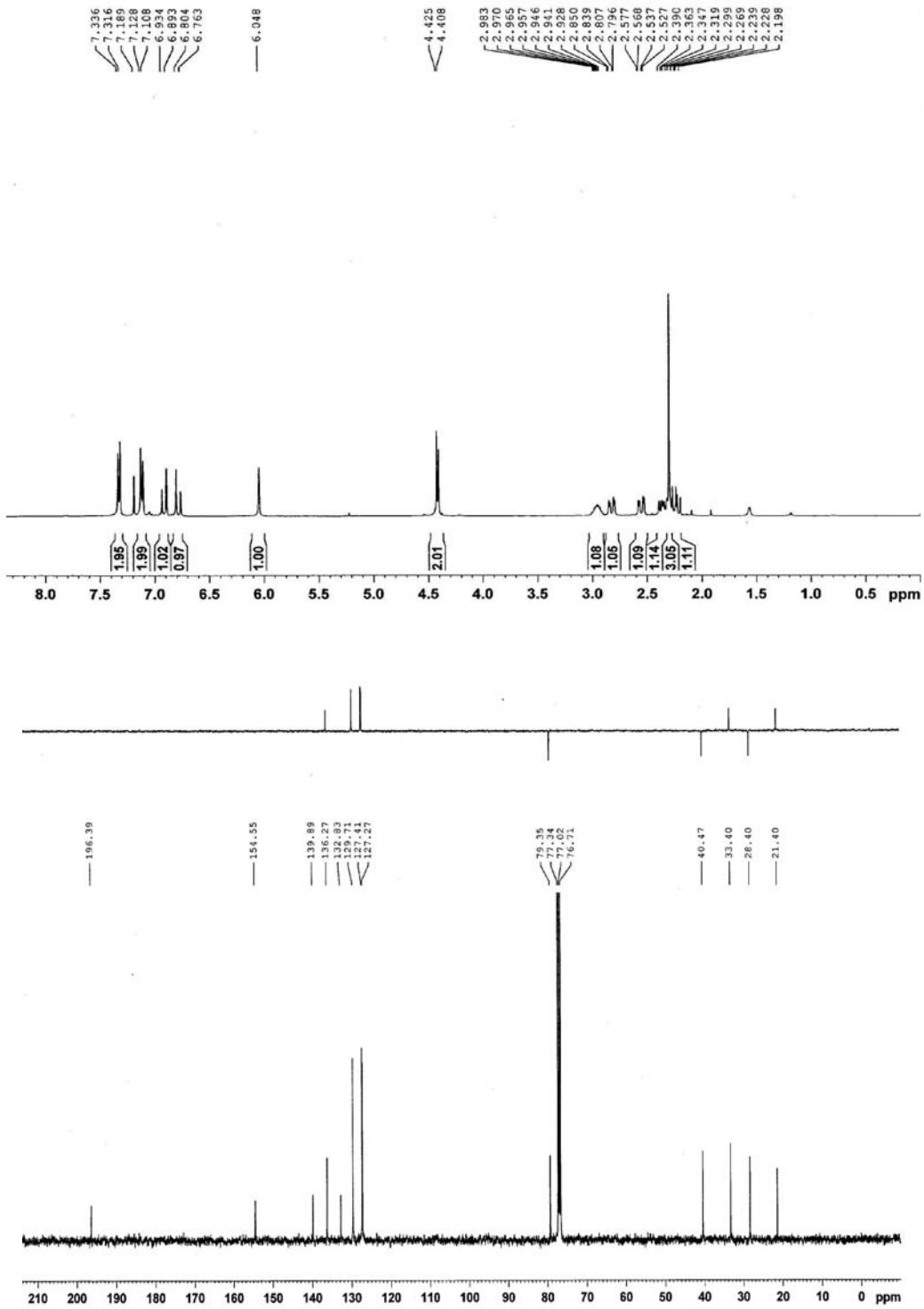
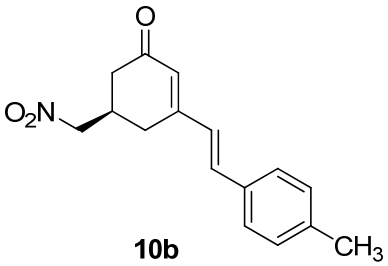


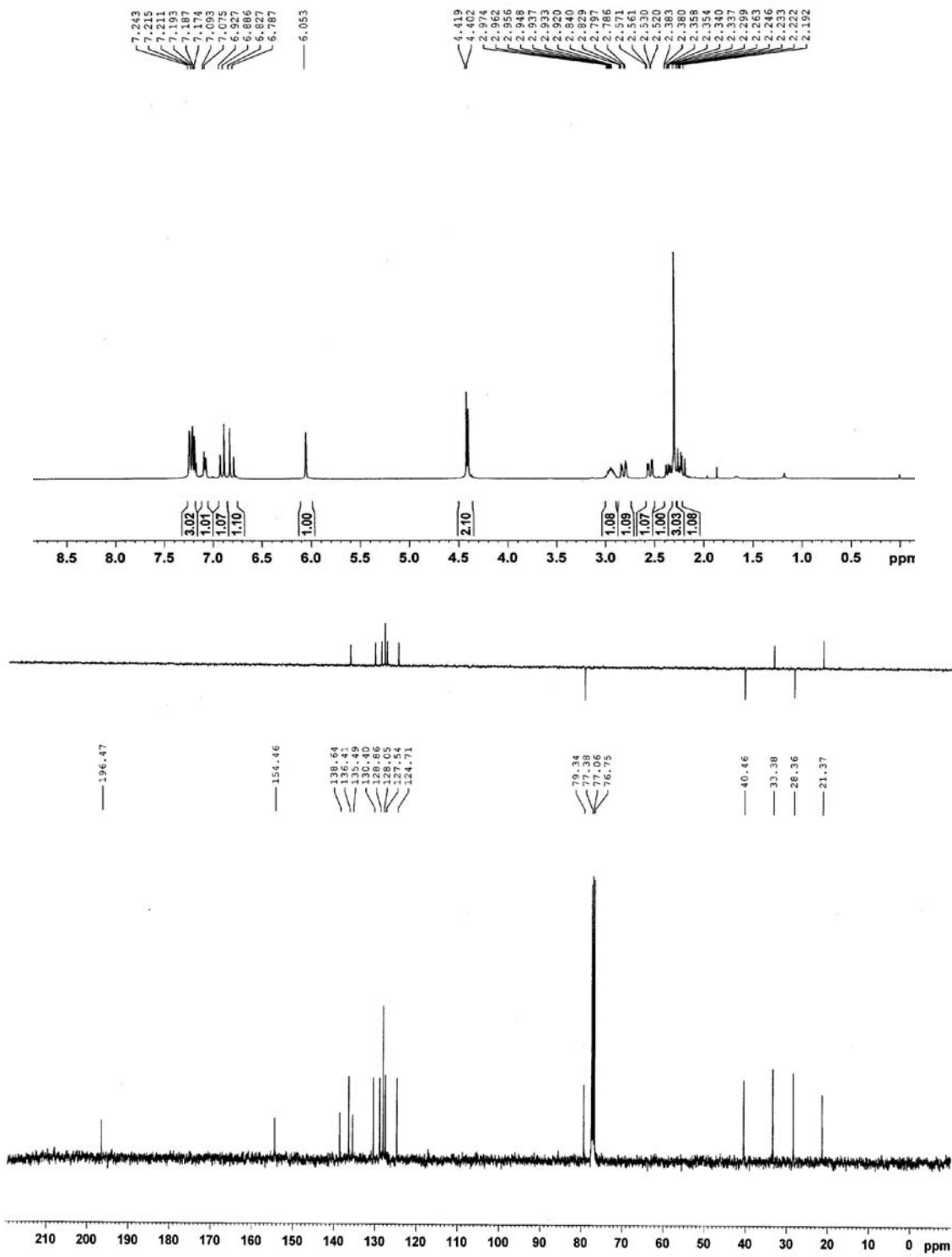
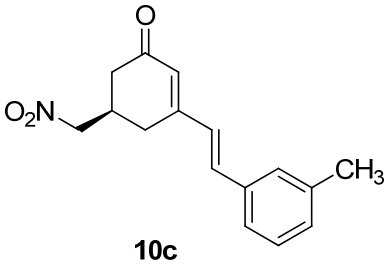


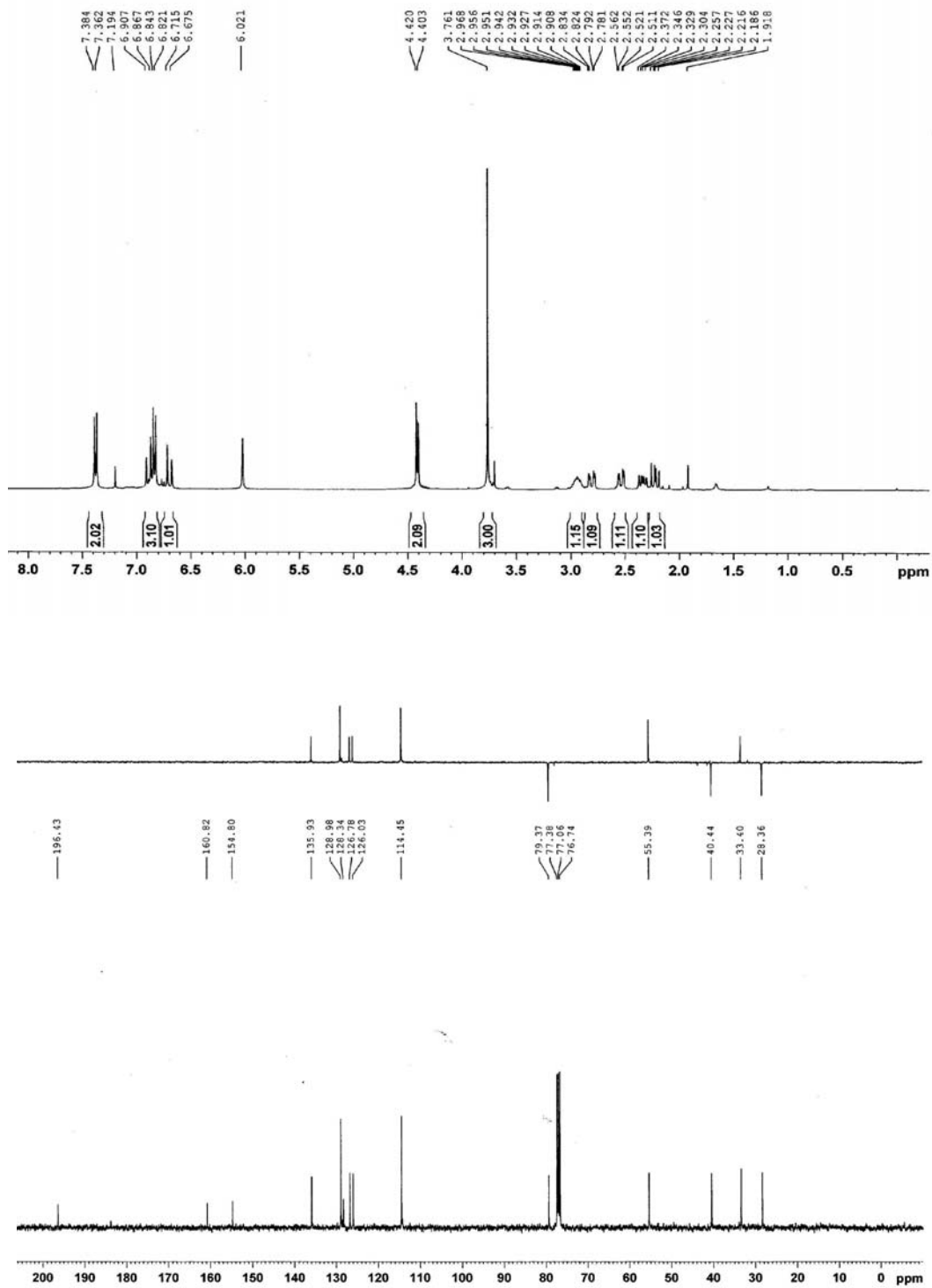
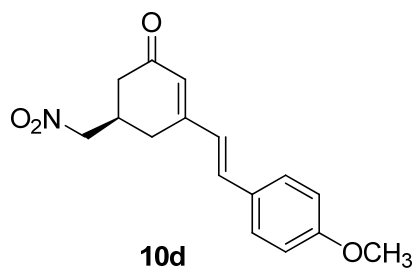


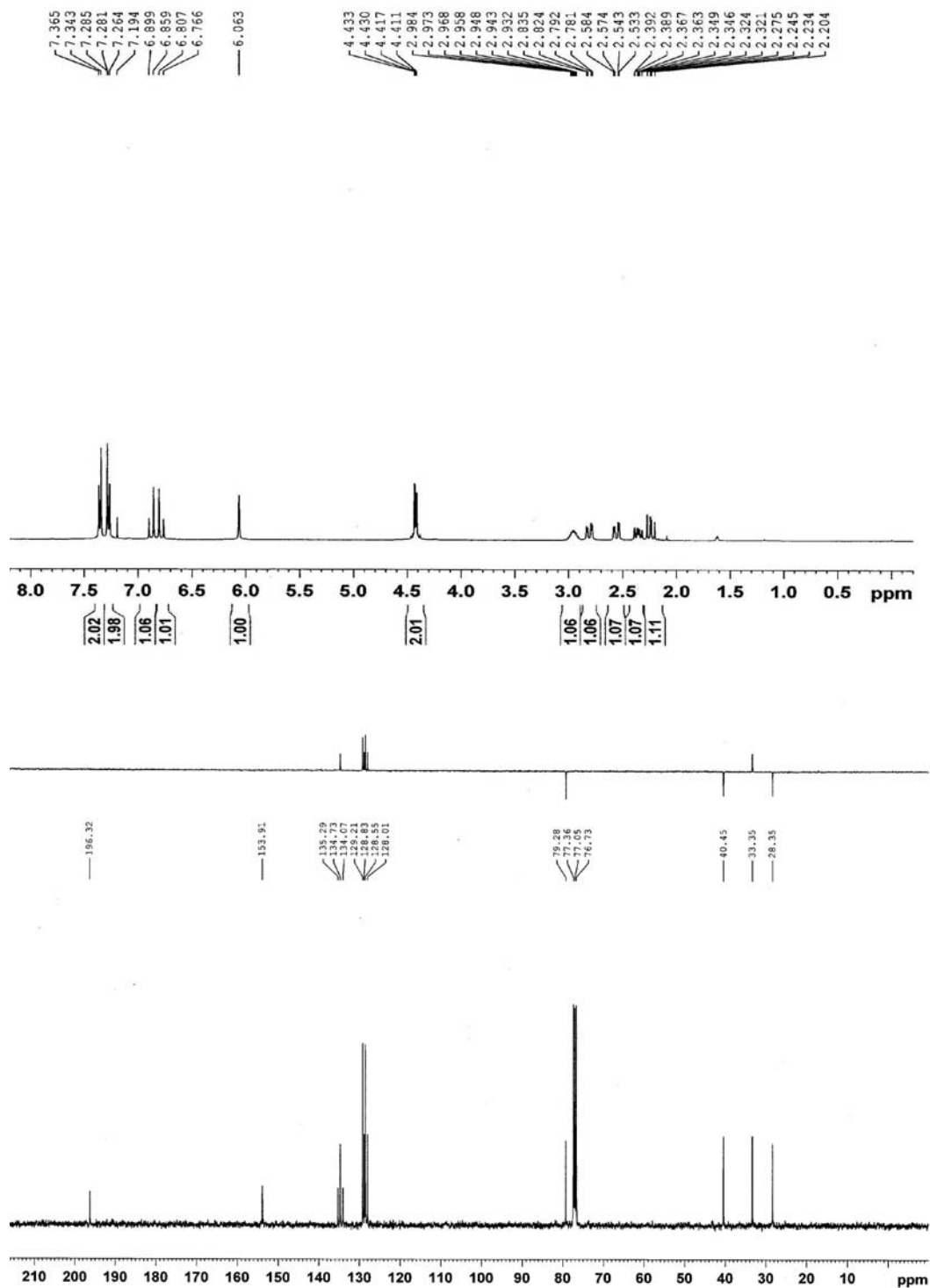
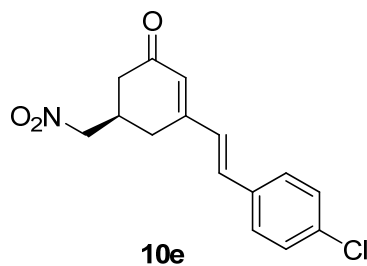


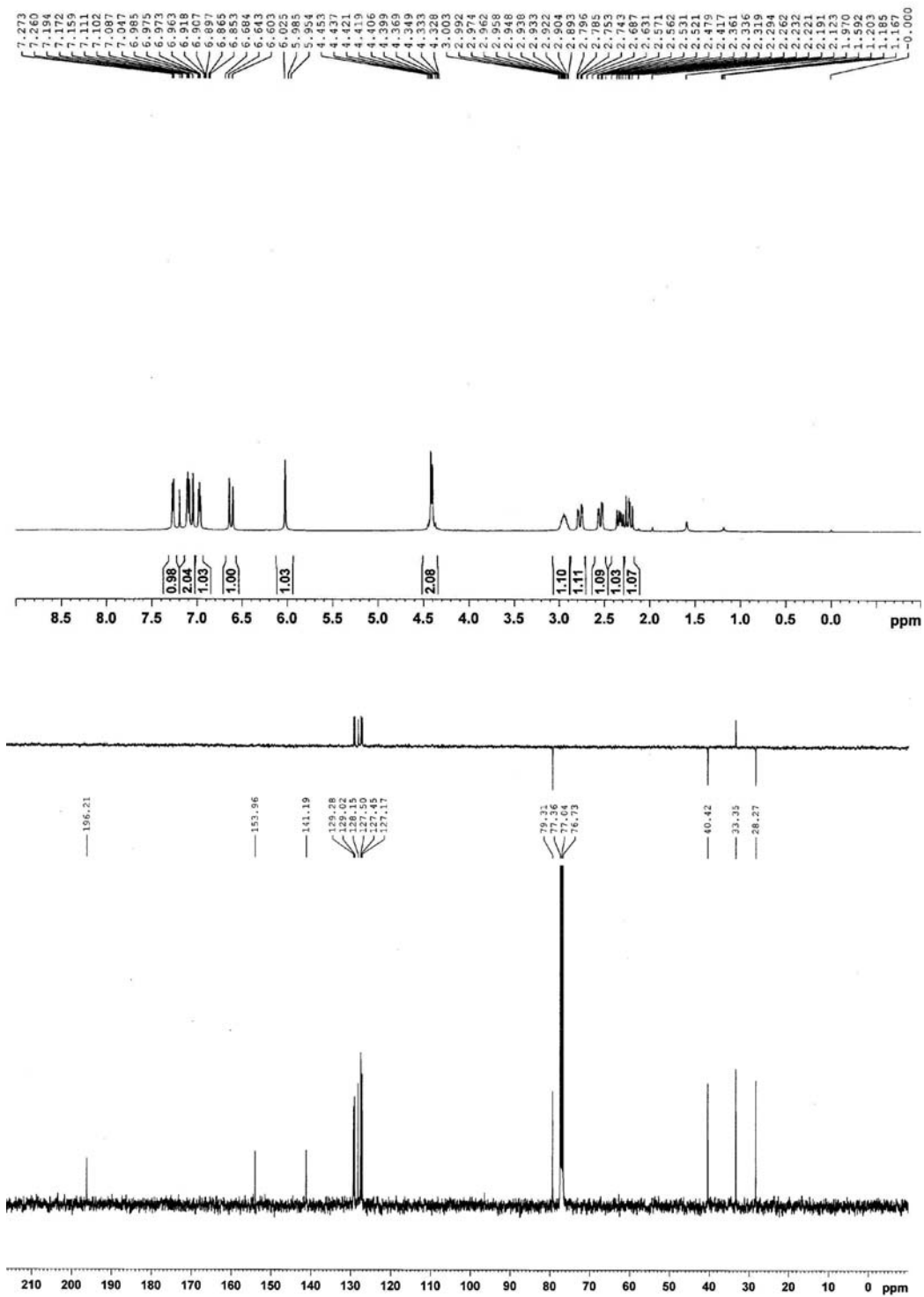


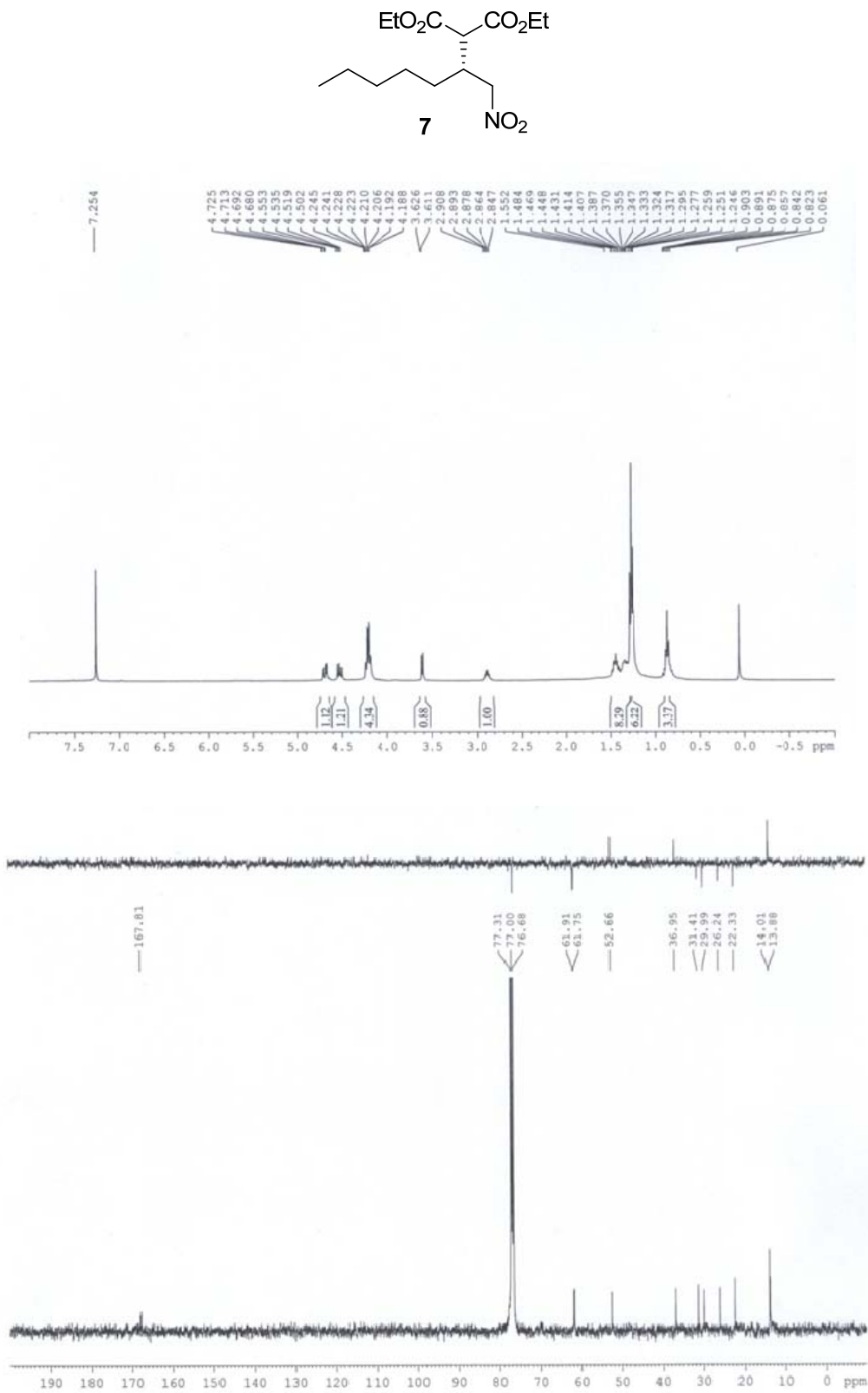


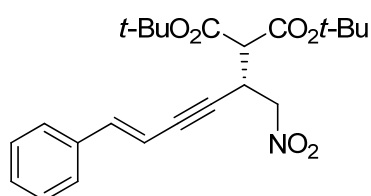




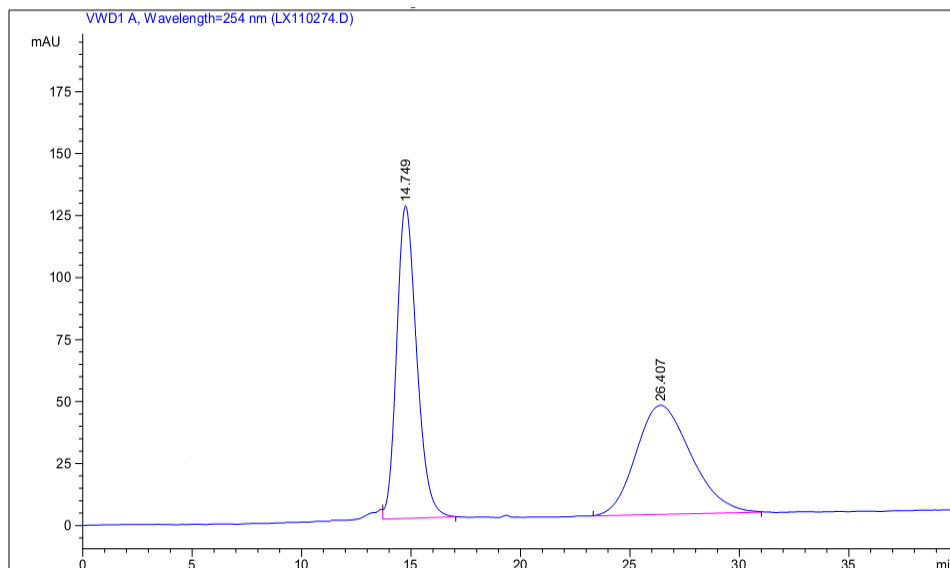




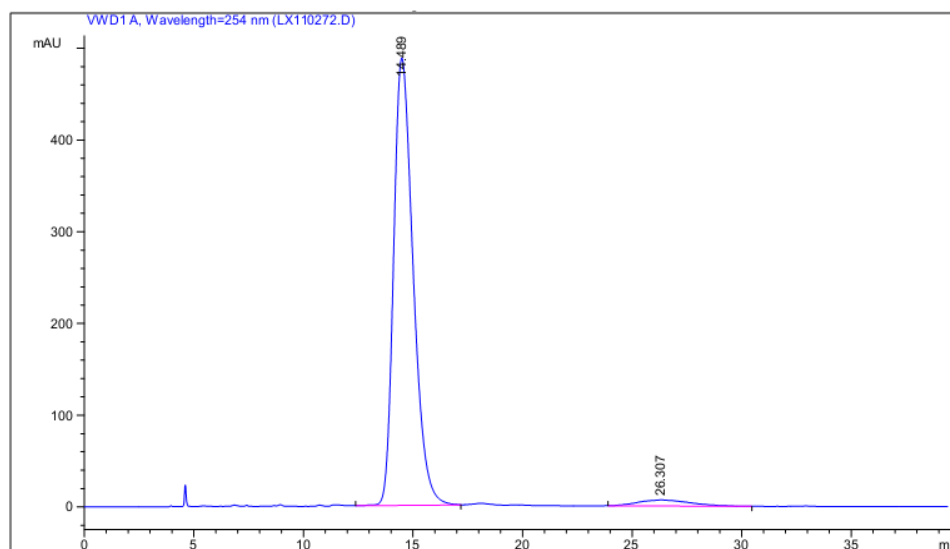




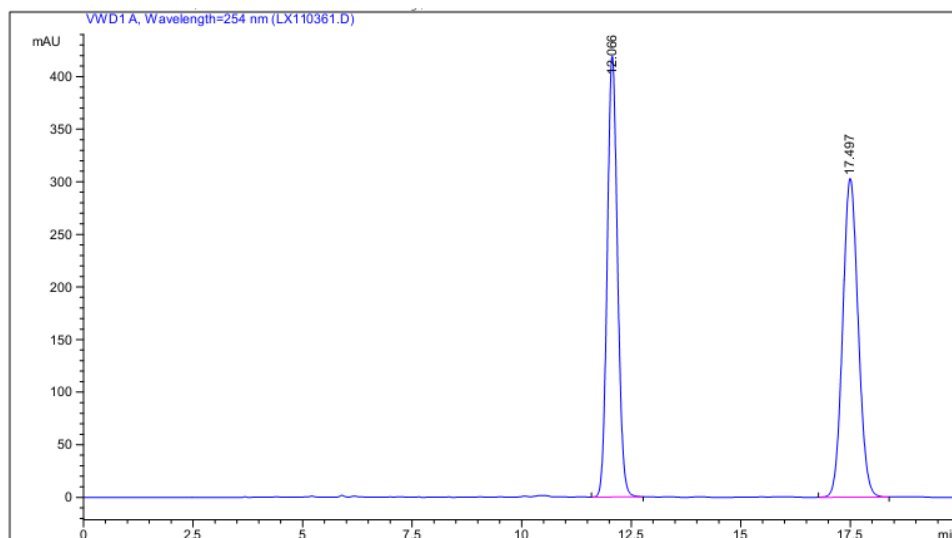
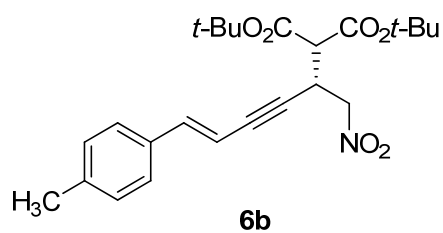
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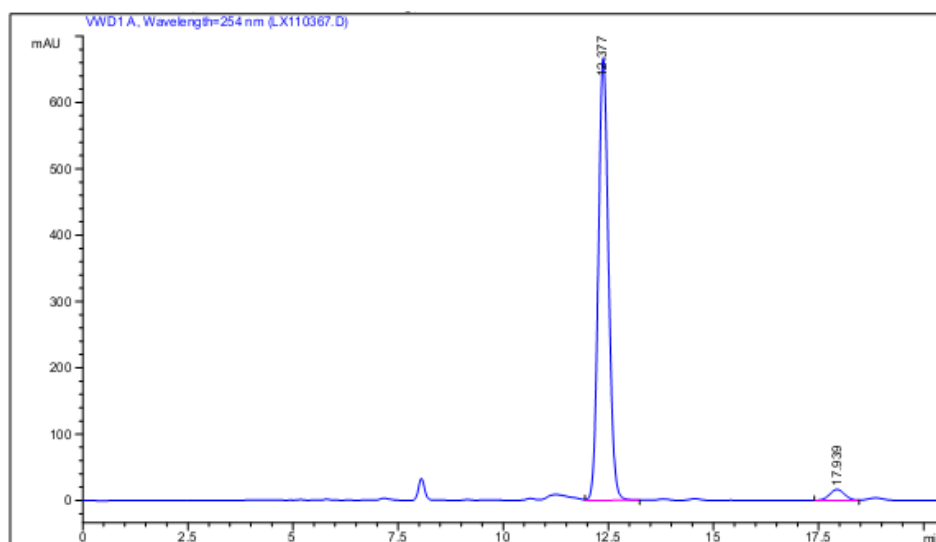
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	14.749	VB	0.9788	8025.40137	126.02297	51.0291
2	26.407	BB	2.4781	7701.71582	43.98695	48.9709



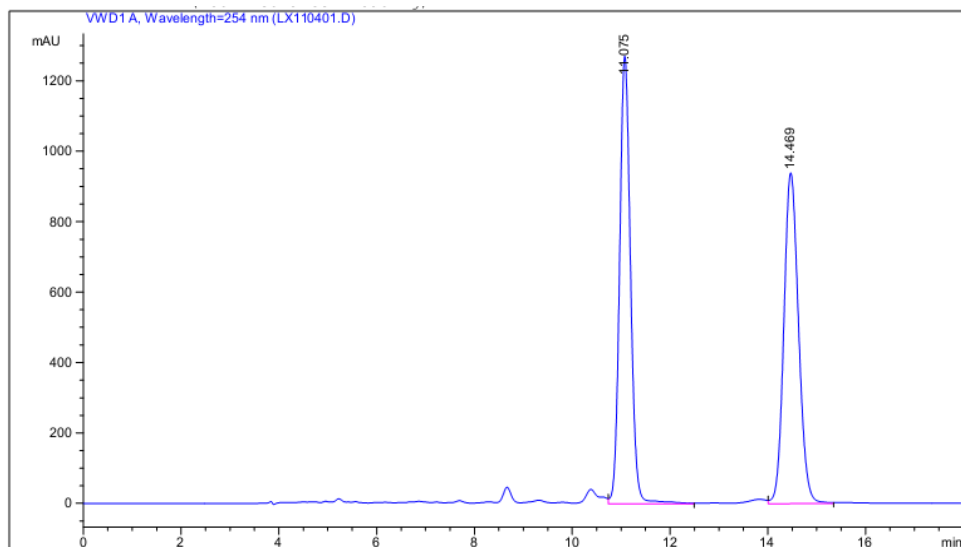
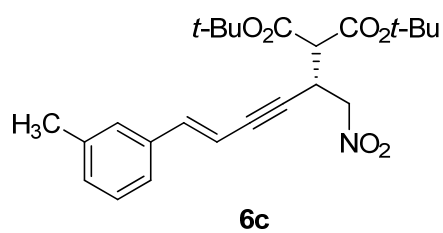
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	14.489	VB	0.9544	3.01449e4	487.51428	96.5154
2	26.307	BB	1.9783	1088.34949	6.46104	3.4846



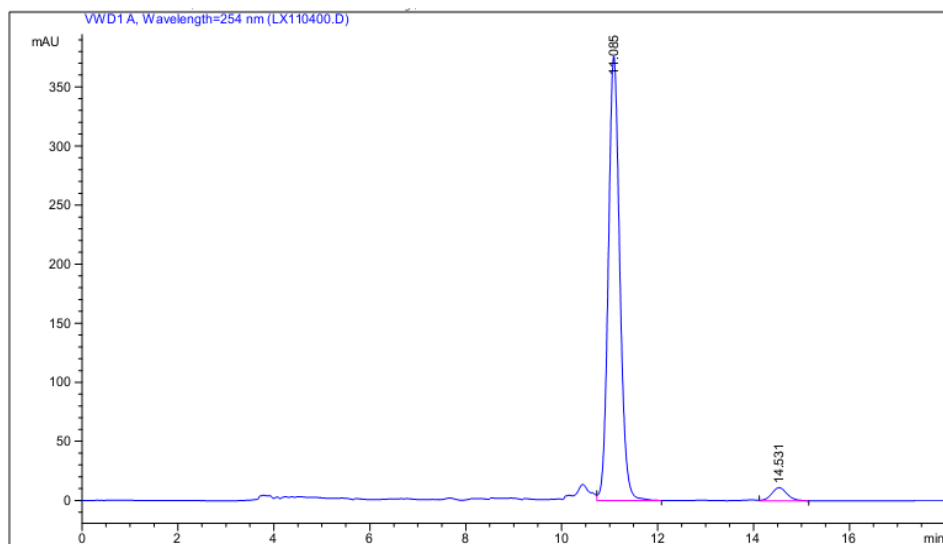
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	12.066	VB	0.2527	6827.85352	418.97421	47.8924
2	17.497	BP	0.3821	7428.78613	303.01572	52.1076



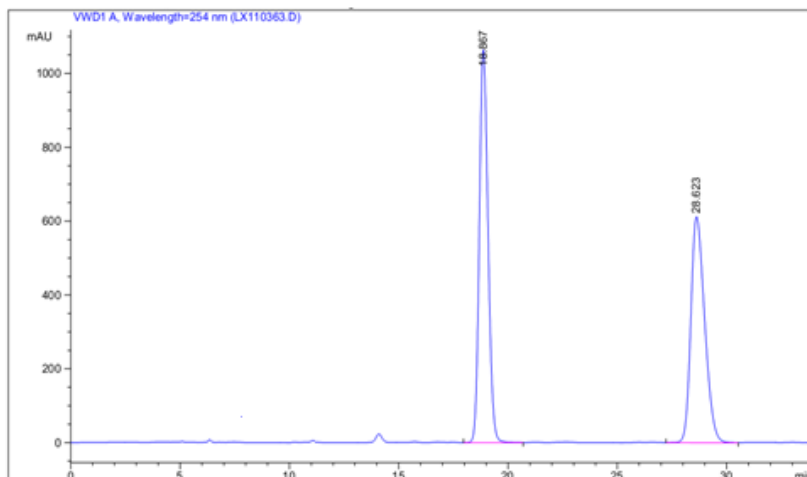
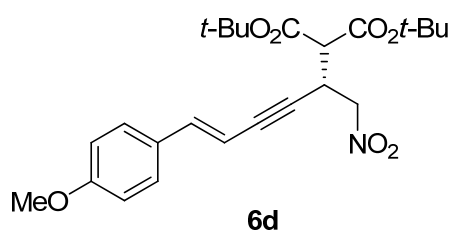
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	12.377	VB	0.2626	1.12520e4	666.25238	96.4097
2	17.939	VV	0.3892	419.02063	16.68033	3.5903



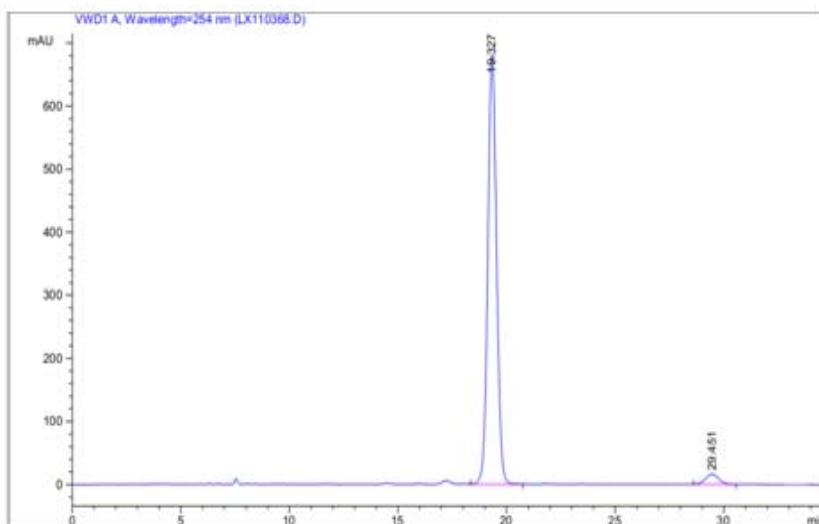
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	11.075	VB	0.2392	1.97148e4	1271.20801	50.1489
2	14.469	VV	0.3249	1.95977e4	939.33478	49.8511



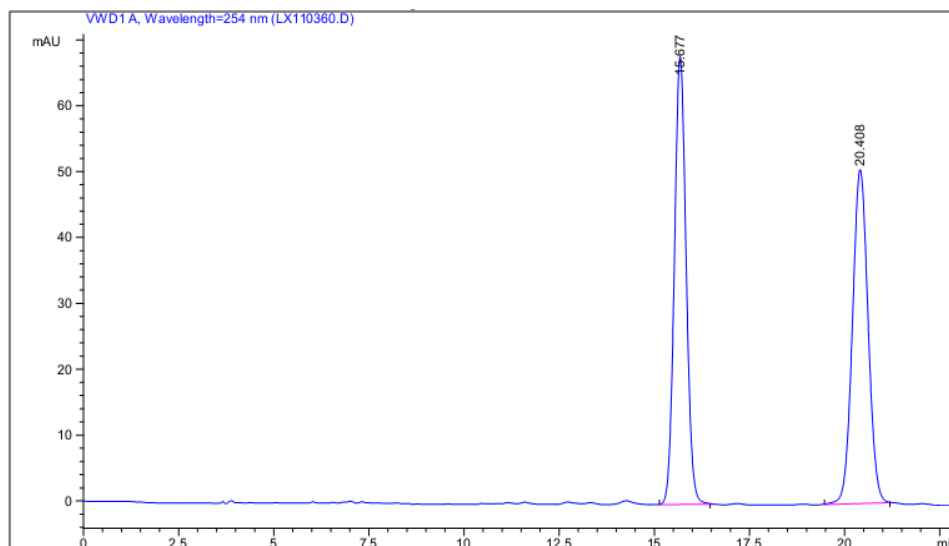
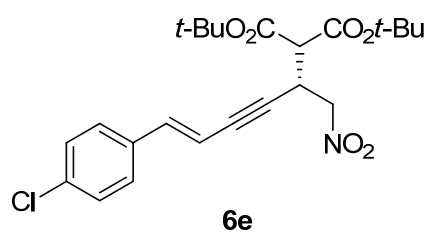
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	11.085	VB	0.2557	6217.59717	375.74512	96.2535
2	14.531	VB	0.3378	242.00644	11.01695	3.7465



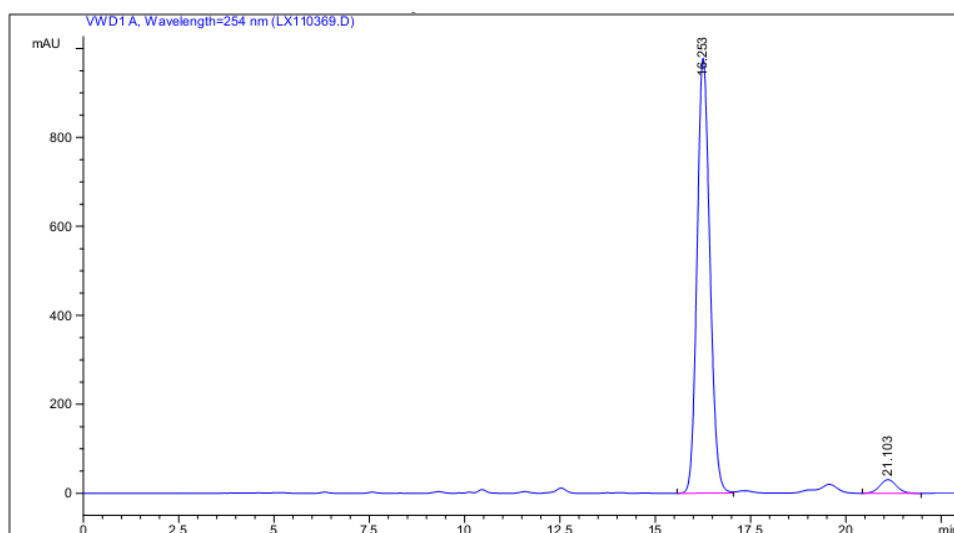
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.867	VB	0.4307	2.94668e4	1064.40369	52.2726
2	28.623	VB	0.6818	2.69047e4	611.94617	47.7274



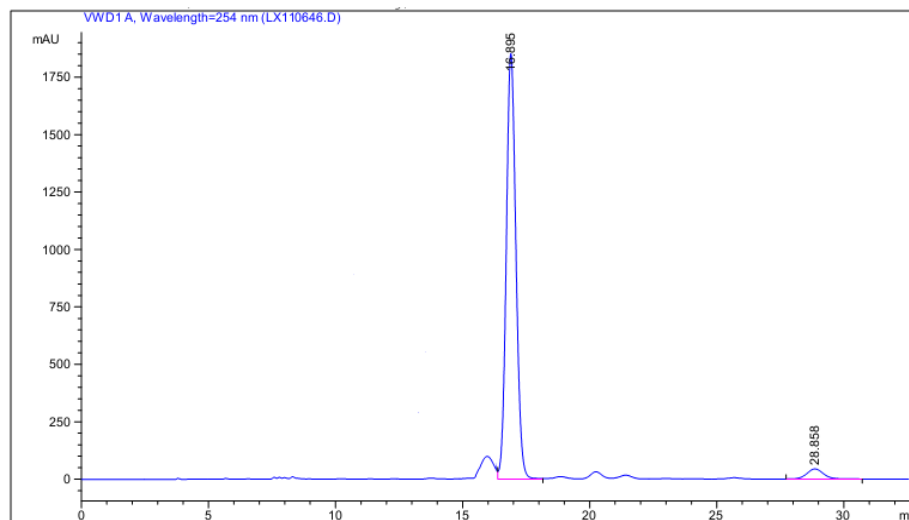
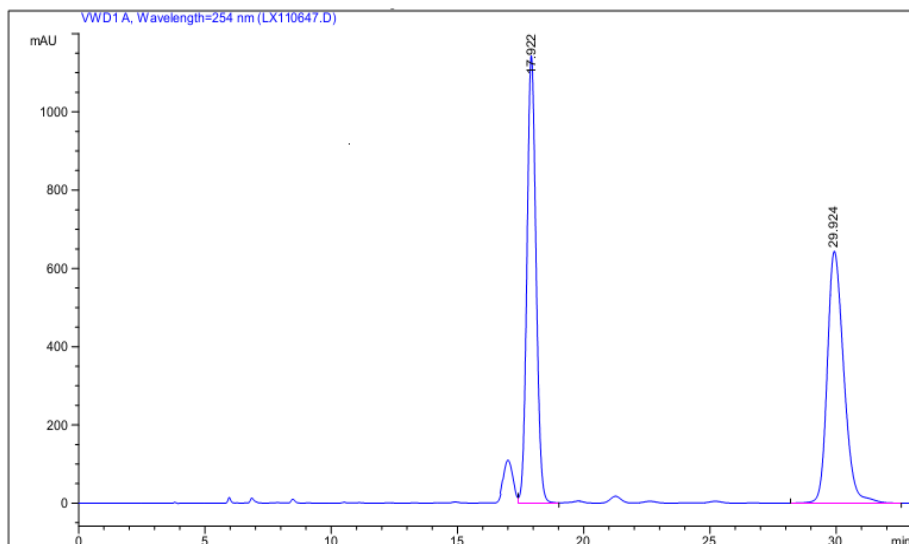
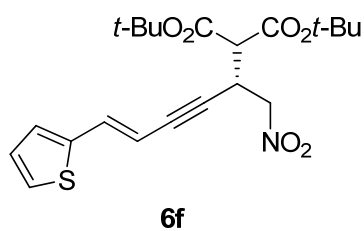
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.327	VB	0.4332	1.89839e4	680.57690	96.5092
2	29.451	BB	0.6590	686.66217	16.24774	3.4908

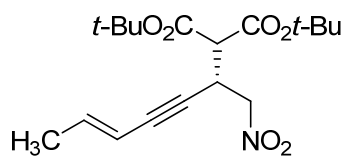


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.677	BB	0.3330	1457.16614	68.00014	50.1893
2	20.408	BB	0.4421	1446.17517	50.68524	49.8107

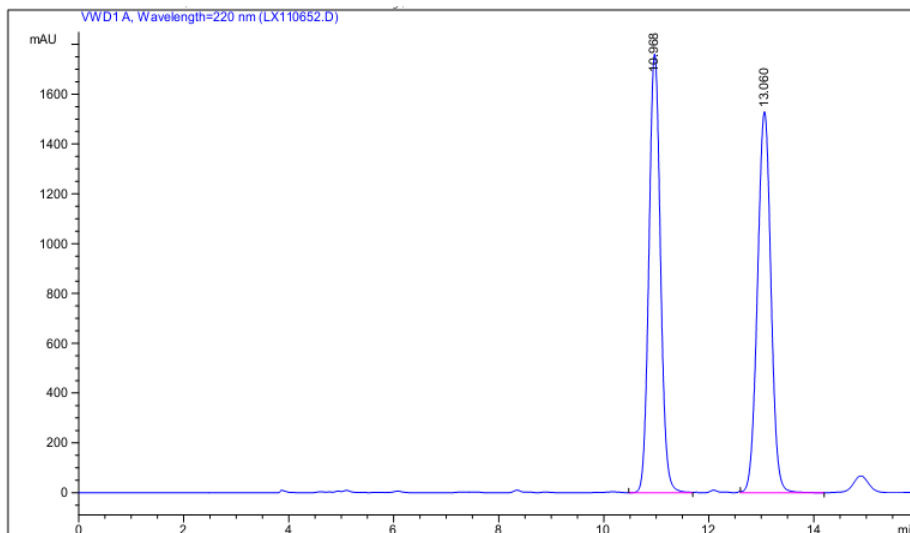


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.253	BV	0.3632	2.28744e4	977.85846	96.1126
2	21.103	BB	0.4705	925.17468	30.49139	3.8874

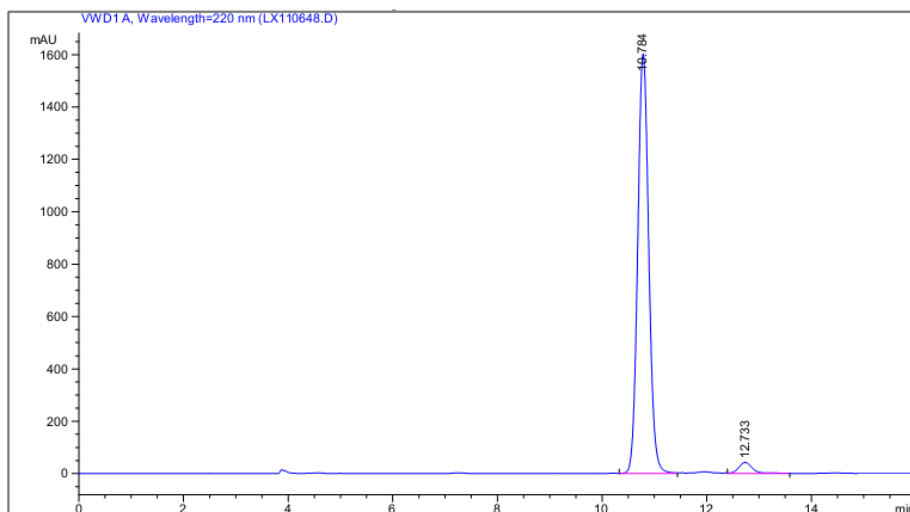




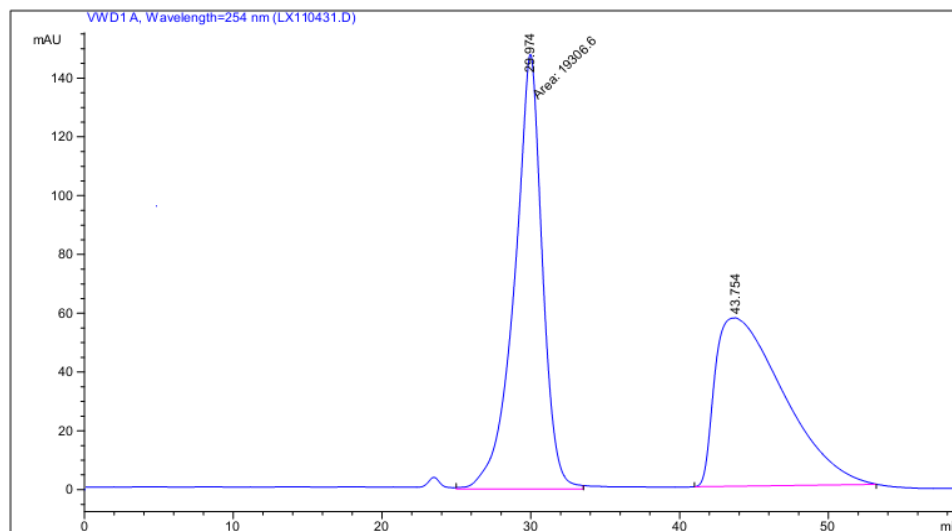
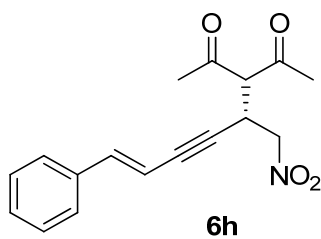
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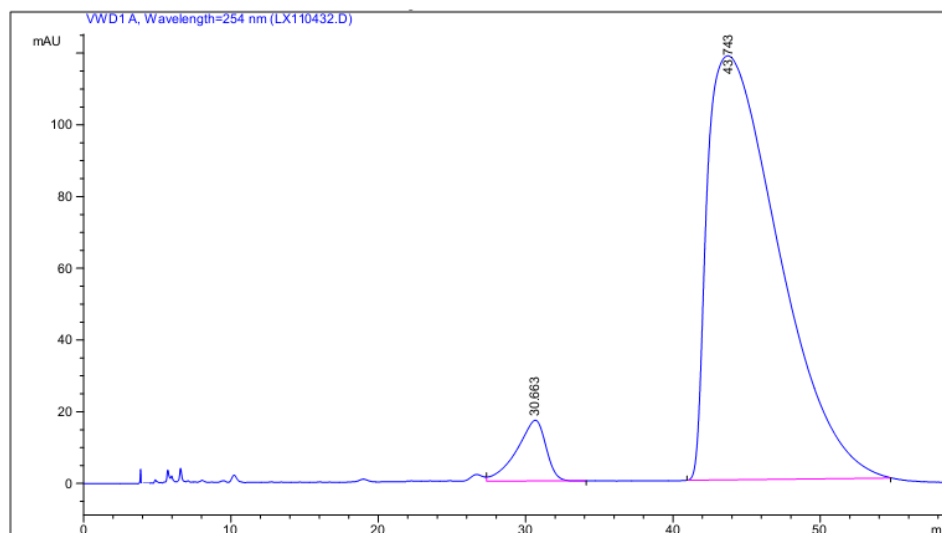
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.968	VV	0.2390	2.68565e4	1761.30798	49.6630
2	13.060	VB	0.2789	2.72210e4	1529.95825	50.3370



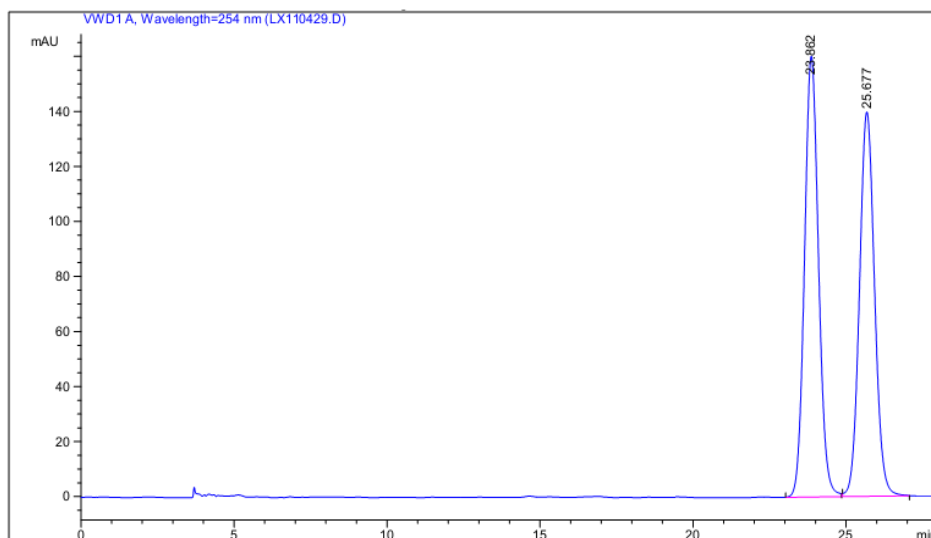
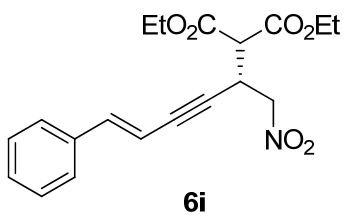
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.784	VV	0.2274	2.34358e4	1602.06628	96.9207
2	12.733	VB	0.2722	744.58997	41.72990	3.0793



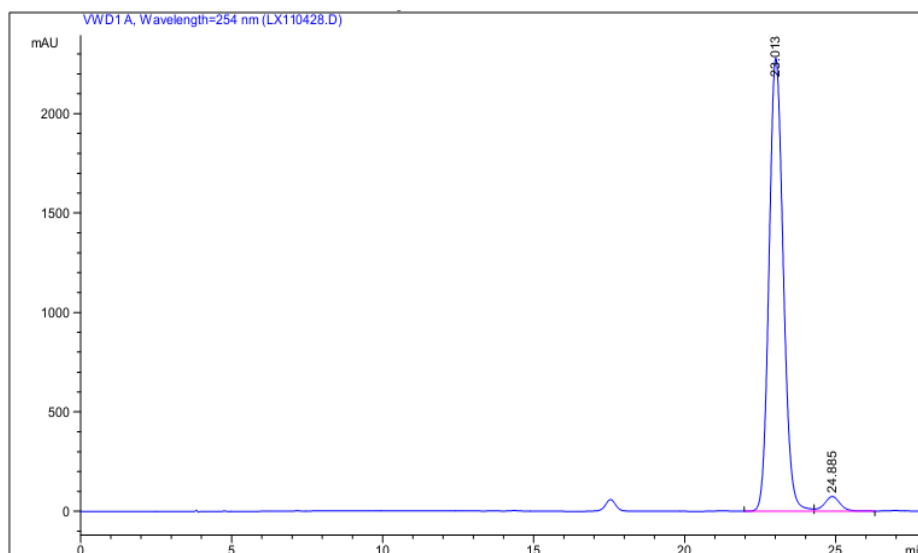
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	29.974	MM	2.1543	1.90436e4	147.33232	49.6981
2	43.758	MM	5.5771	1.92749e4	57.60180	50.3019



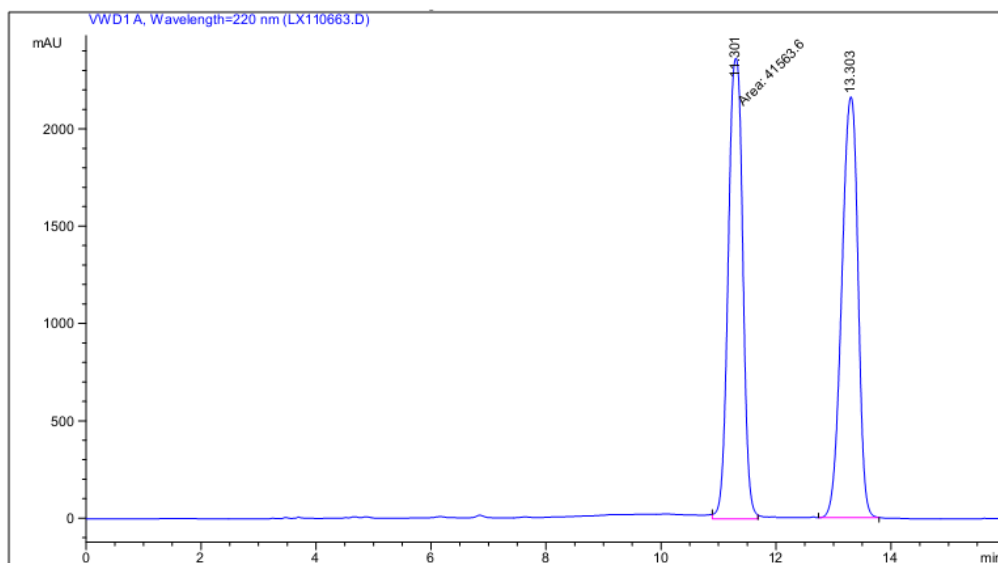
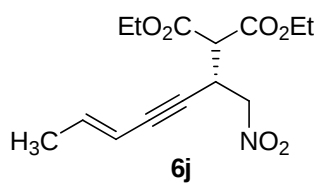
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	30.673	MM	2.2088	2205.99731	16.64542	5.1794
2	43.743	MM	5.6754	4.03859e4	118.59822	94.8206



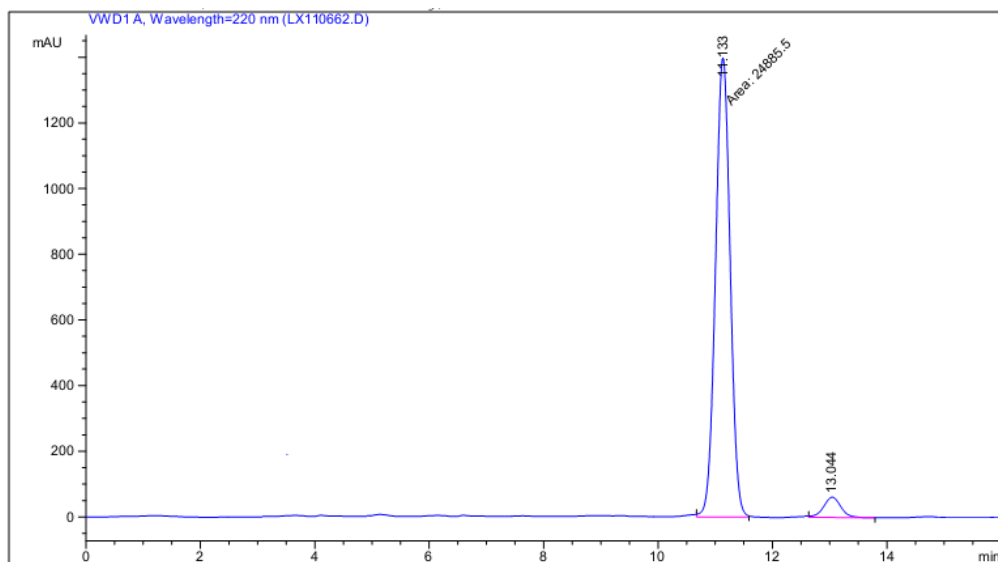
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	23.862	BB	0.4932	5091.74121	160.14915	51.5087
2	25.677	BB	0.5314	4793.46533	139.68375	48.4913



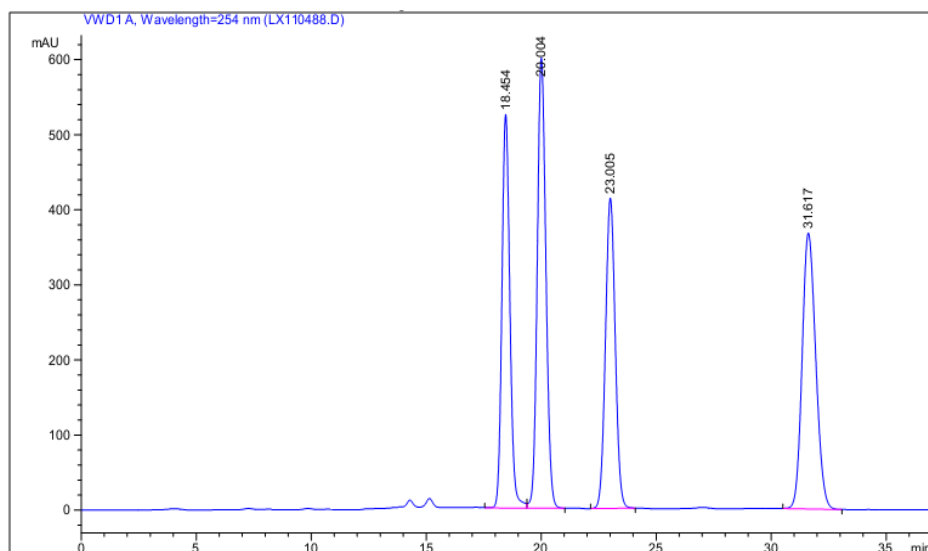
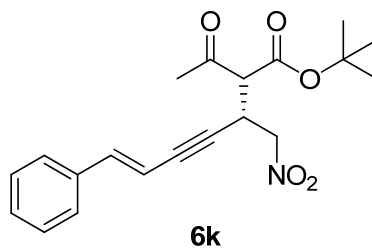
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	23.013	VV	0.5101	7.46082e4	2278.93555	96.4653
2	24.885	VB	0.5575	2733.77930	74.27536	3.5347



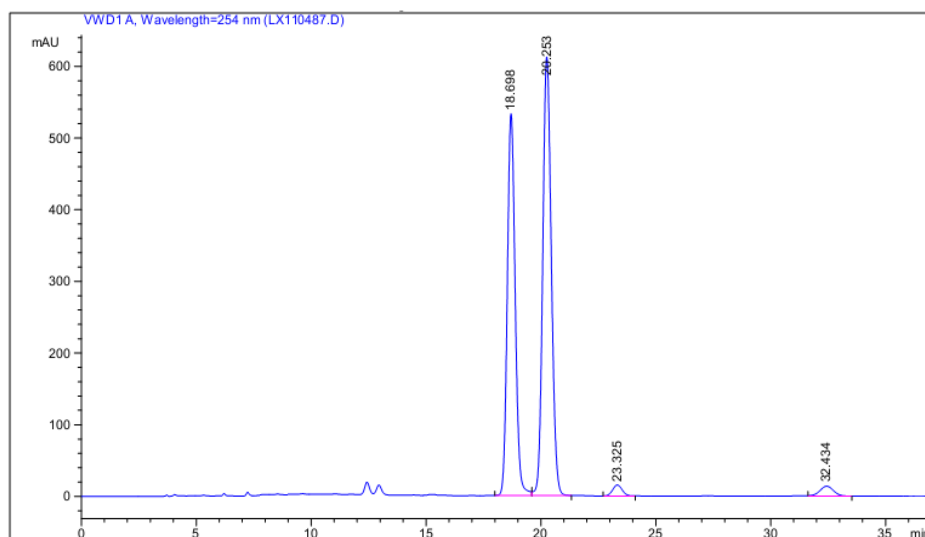
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	11.301	MM	0.2927	4.15636e4	2366.92920	49.5053
2	13.303	VBA	0.3103	4.23942e4	2161.93604	50.4947



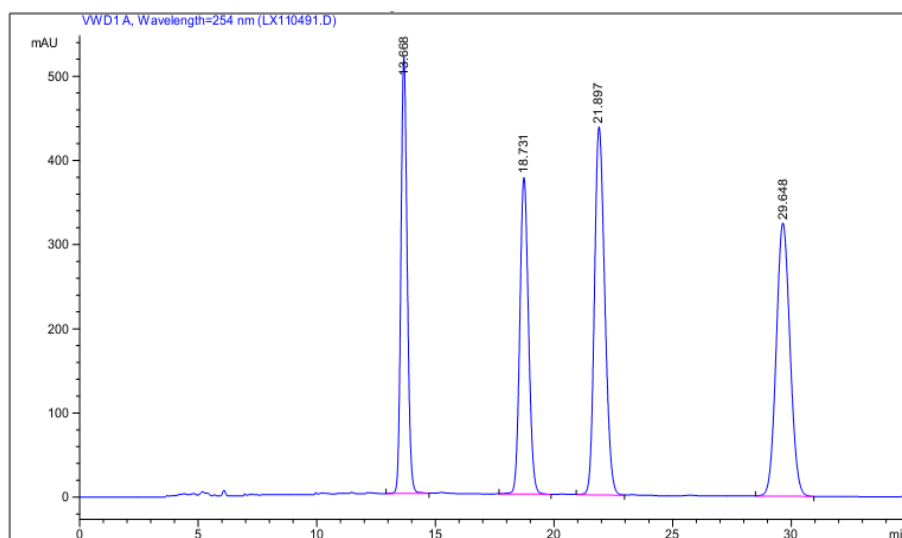
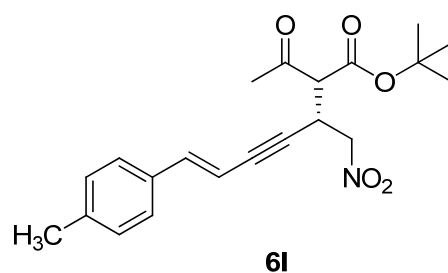
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	11.133	MM	0.2967	2.48855e4	1398.05542	95.1109
2	13.044	VBA	0.3217	1279.23132	61.41025	4.8891



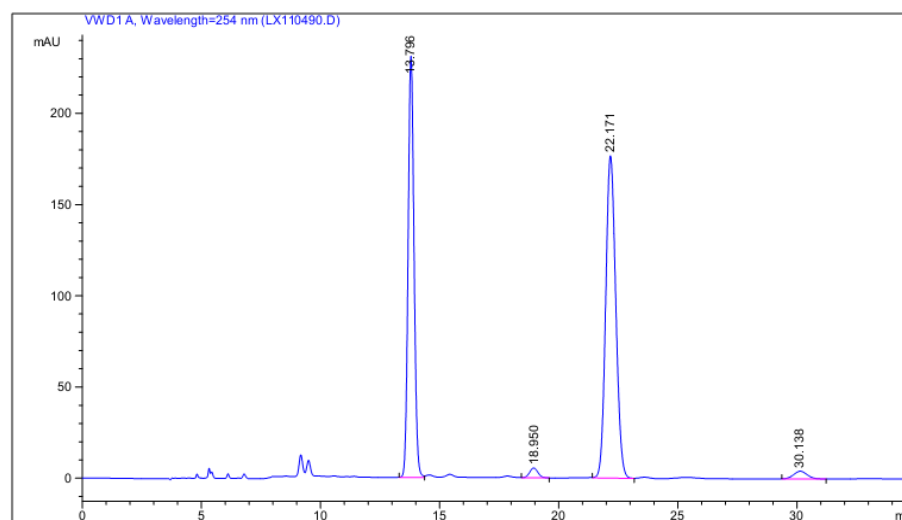
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	18.454	VV	0.3706	1.25973e4	524.28192	22.7019
2	20.004	VB	0.4054	1.56061e4	599.86371	28.1240
3	23.005	PB	0.4606	1.21915e4	413.30658	21.9706
4	31.617	BB	0.6392	1.50953e4	367.63858	27.2035



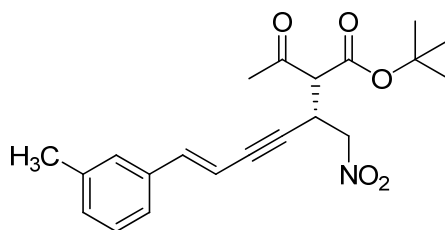
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	18.698	BV	0.3696	1.26882e4	532.74786	42.9150
2	20.253	VB	0.4027	1.58523e4	611.83472	53.6167
3	23.325	BB	0.4564	450.75418	15.40602	1.5246
4	32.434	BB	0.6482	574.69714	13.86342	1.9438



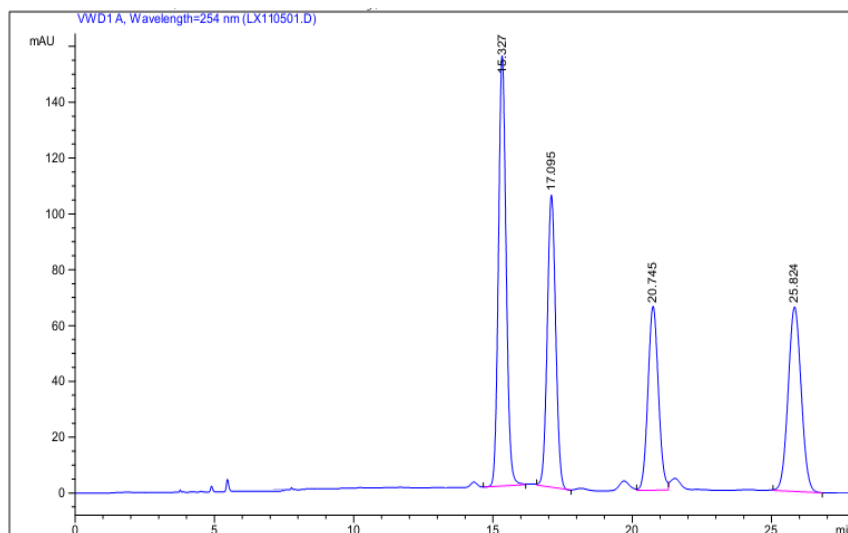
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.668	BB	0.2839	9498.48242	517.74823	20.9598
2	18.731	BB	0.3948	9536.74121	376.10510	21.0443
3	21.897	BB	0.4688	1.32062e4	437.25113	29.1416
4	29.648	BB	0.6288	1.30761e4	324.54590	28.8543



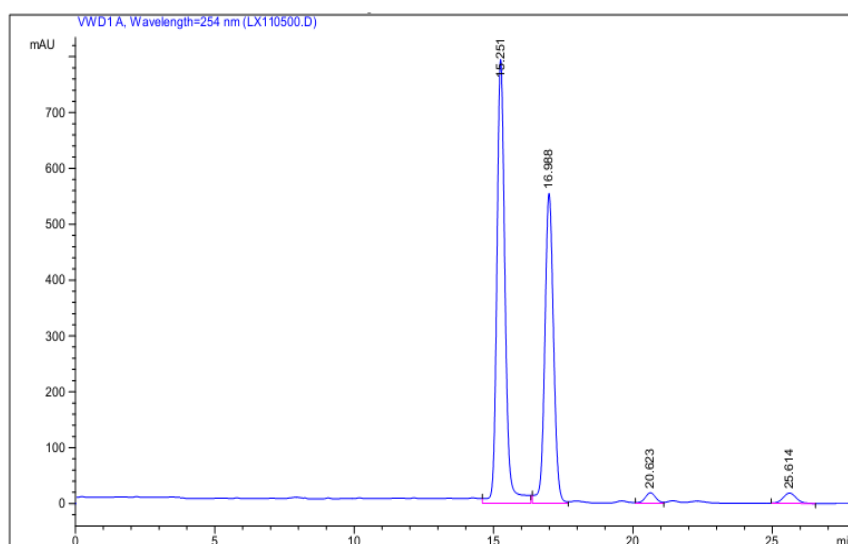
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.796	BV	0.2686	3991.90234	230.99382	42.1611
2	18.950	VP	0.3763	131.07944	5.40212	1.3844
3	22.171	BB	0.4585	5178.53271	176.66638	54.6939
4	30.138	BB	0.6258	166.69319	4.20256	1.7606



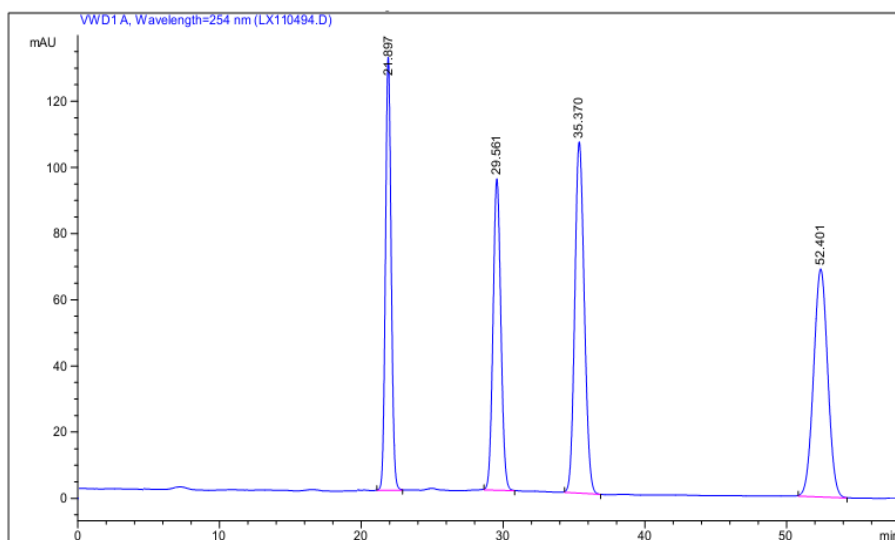
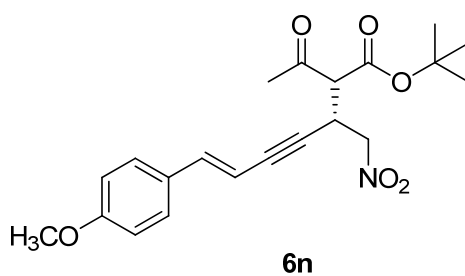
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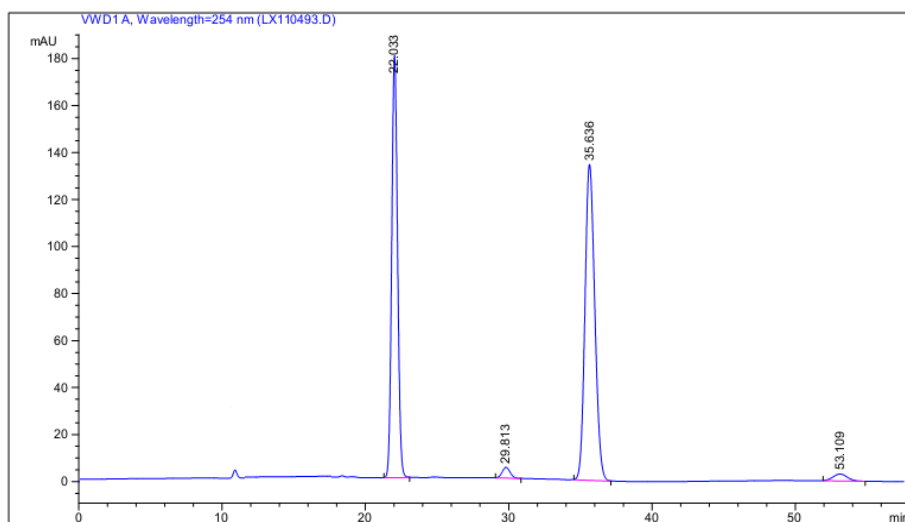
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.327	VB	0.2978	2954.43701	154.16777	32.7694
2	17.095	BP	0.3257	2190.50879	104.64998	24.2962
3	20.745	VV	0.4066	1719.77490	65.86095	19.0750
4	25.824	BP	0.5064	2151.12671	66.09227	23.8594



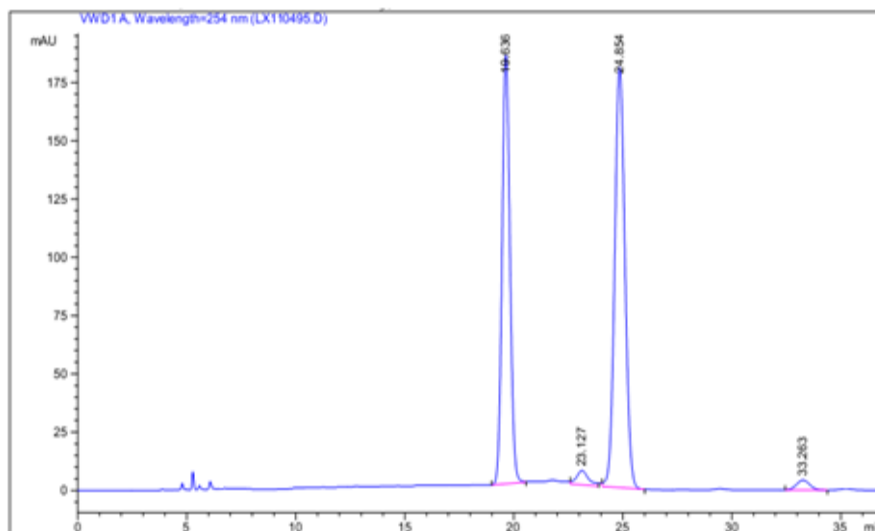
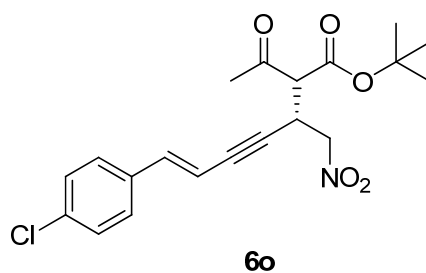
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.251	MM	0.3206	1.51020e4	785.11163	54.3510
2	16.988	MM	0.3522	1.15931e4	548.63275	41.7229
3	20.623	VV	0.4115	500.56805	18.68864	1.8015
4	25.614	BP	0.4988	590.31915	18.29192	2.1245



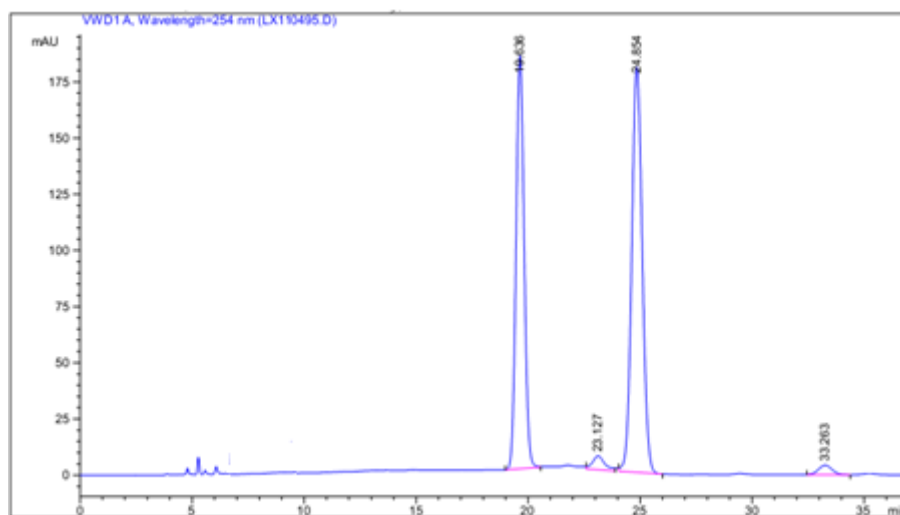
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	21.897	BB	0.4353	3674.01978	130.84093	21.6030
2	29.561	BB	0.5996	3615.94702	94.12921	21.2615
3	35.370	BP	0.7308	4954.11572	106.17180	29.1299
4	52.401	BB	1.0804	4762.91797	68.88592	28.0056



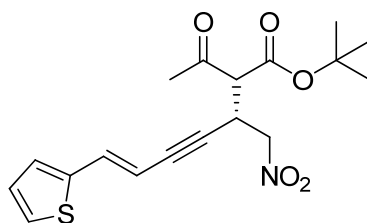
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	22.033	BB	0.4407	5080.89258	179.62541	42.8926
2	29.813	BB	0.6074	177.24985	4.56479	1.4963
3	35.636	BB	0.7402	6382.84912	134.46750	53.8836
4	53.109	BP	1.0044	204.63301	2.94989	1.7275



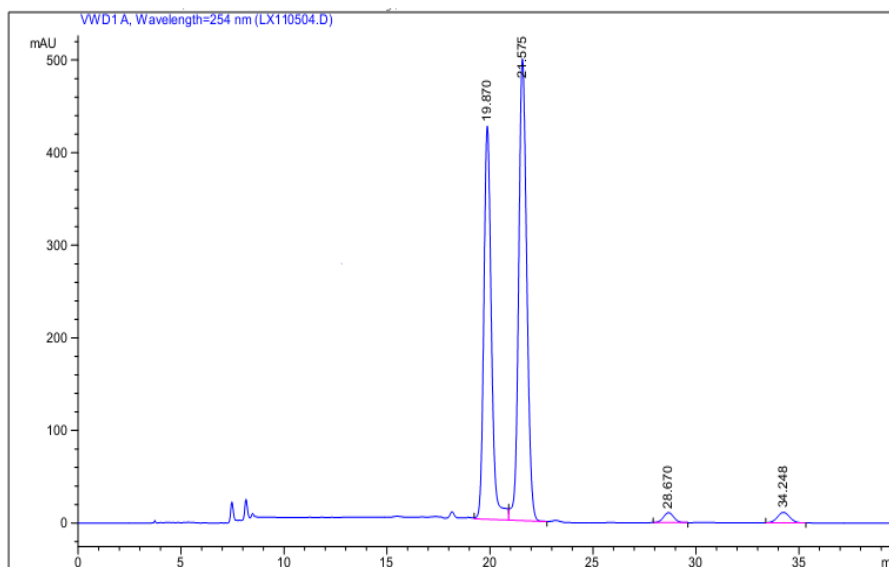
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	19.233	VB	0.3815	7234.70898		295.74445	22.7031
2	22.627	BV	0.4653	7474.11719		249.97382	23.4544
3	24.346	VP	0.5008	8825.29102		274.13116	27.6945
4	32.286	BP	0.6684	8332.51660		194.62424	26.1481



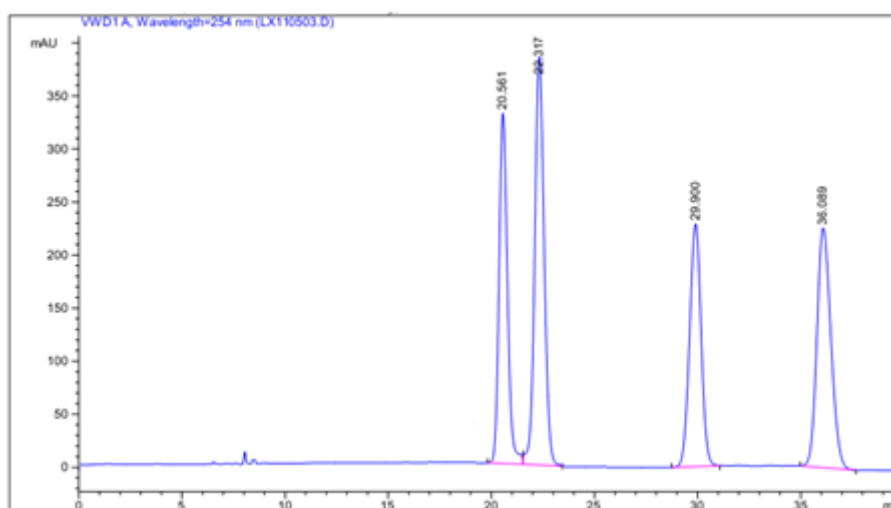
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	19.636	PB	0.3919	4614.14355		183.81404	42.3057
2	23.127	BB	0.5603	235.12903		6.14028	2.1558
3	24.854	BP	0.5083	5876.15186		180.33162	53.8767
4	33.263	BP	0.6376	181.24321		4.27284	1.6618



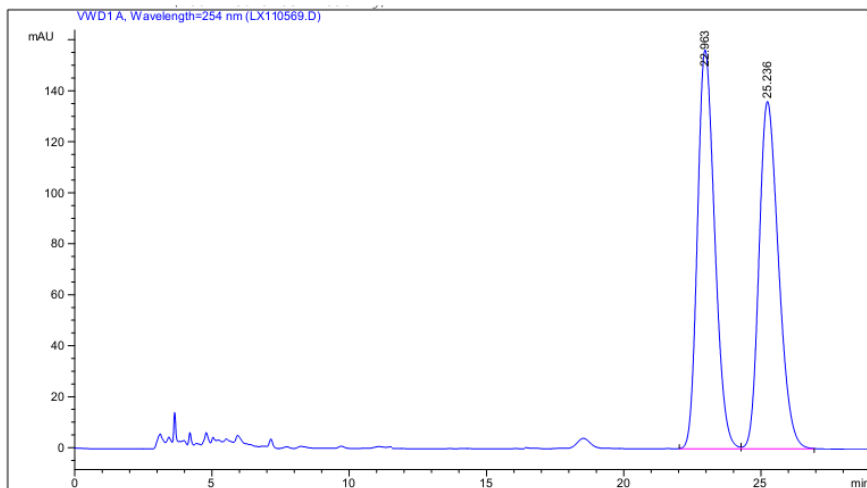
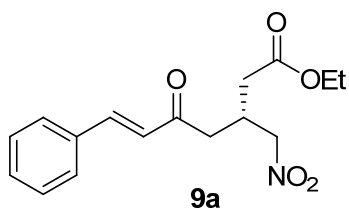
6p



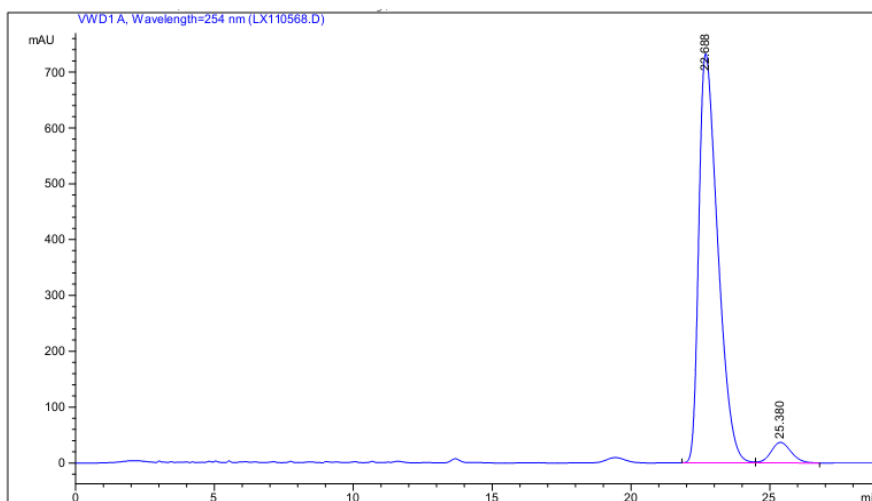
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.561	BB	0.4342	9319.78613	330.10413	22.7478
2	22.317	BB	0.4857	1.21638e4	384.36755	29.6895
3	29.900	BB	0.6042	8872.78711	228.62059	21.6568
4	36.089	BP	0.7320	1.06136e4	225.71568	25.9059



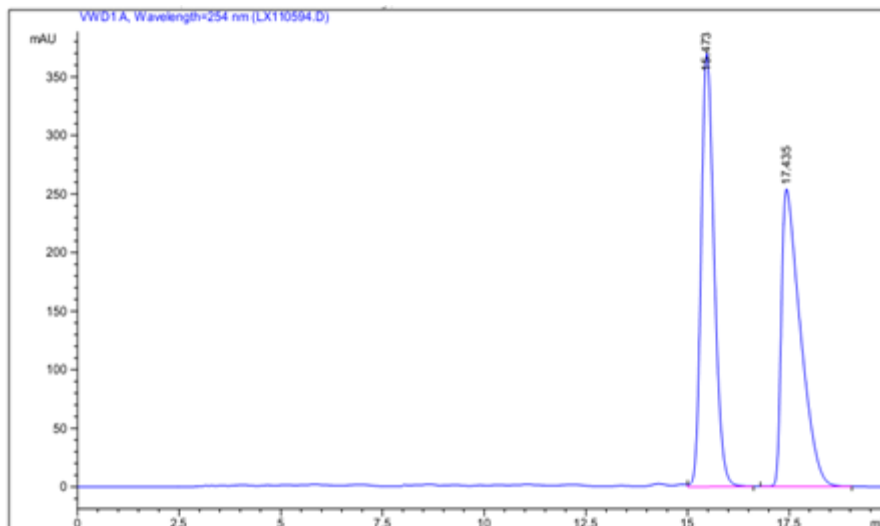
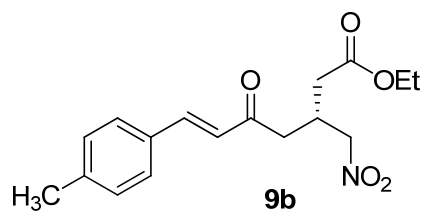
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.870	MM	0.4063	1.02697e4	421.27780	42.0676
2	21.575	MM	0.4480	1.32932e4	494.54681	54.4527
3	28.670	BB	0.5500	379.63522	10.79679	1.5551
4	34.248	BP	0.6386	469.84955	11.35348	1.9246



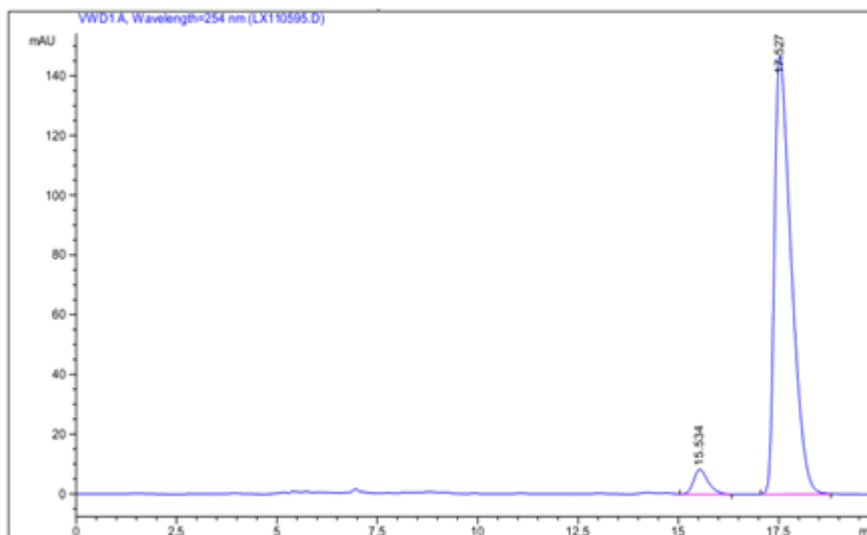
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	22.963	BV	0.6770	6812.94971	156.44388	50.3669
2	25.236	VB	0.7672	6713.70020	136.20755	49.6331



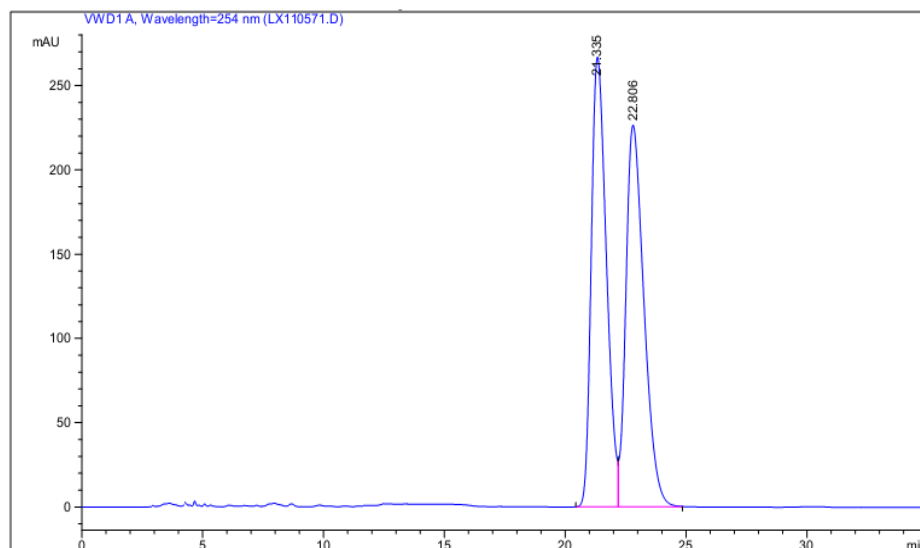
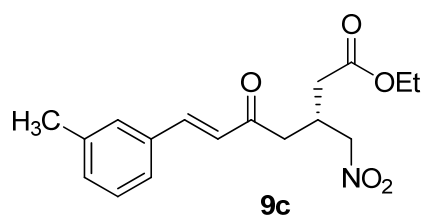
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	22.688	BV	0.7304	3.47123e4	732.65015	94.9450
2	25.380	VB	0.7795	1848.13745	36.80548	5.0550



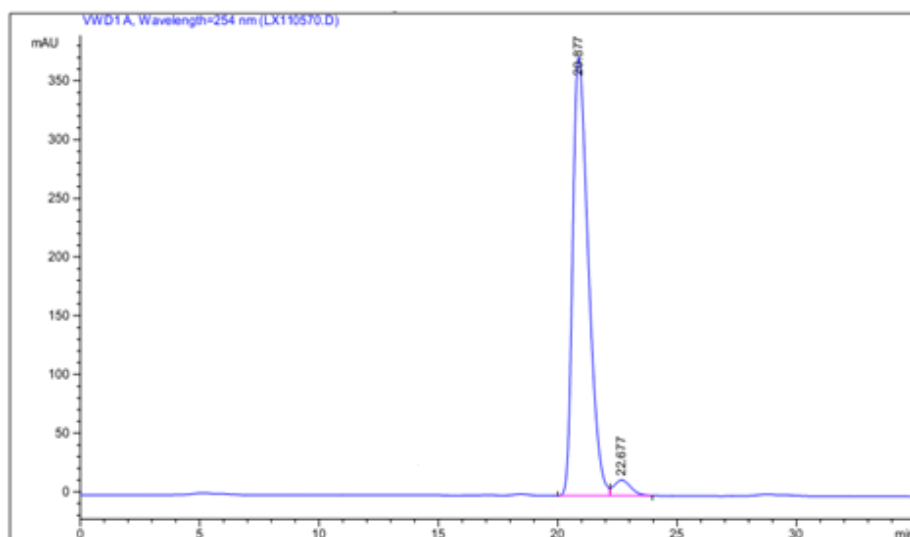
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.473	VB	0.3433	8205.07715	369.78949	49.8454
2	17.435	BB	0.4783	8255.97852	253.91743	50.1546



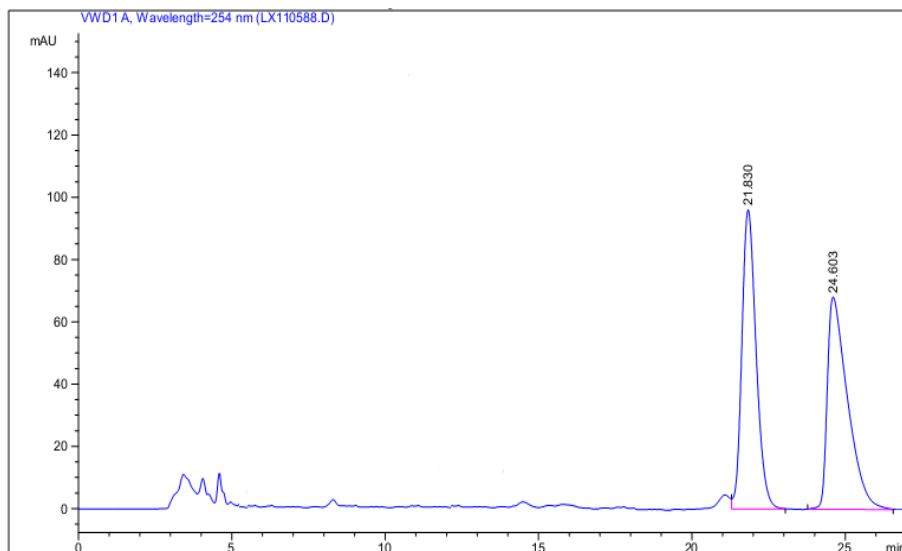
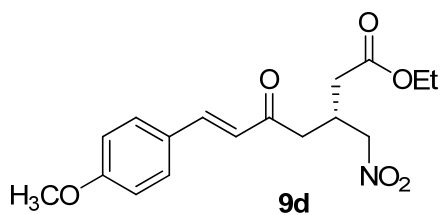
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.534	VB	0.3820	212.22447	8.36133	4.7285
2	17.527	BB	0.4400	4275.93018	146.93484	95.2715



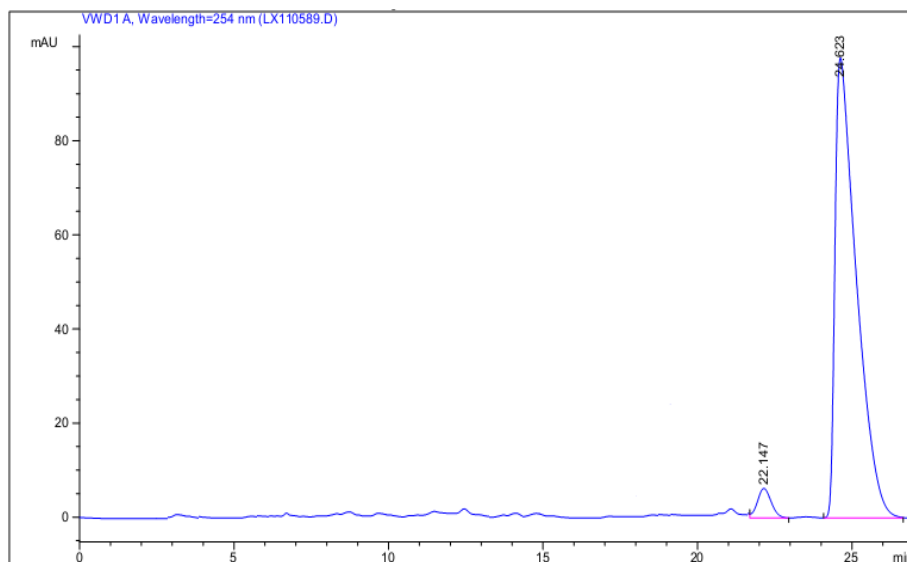
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	21.335	BV	0.6757	1.15932e4	266.87305	49.5918
2	22.806	VB	0.7980	1.17841e4	226.40678	50.4082



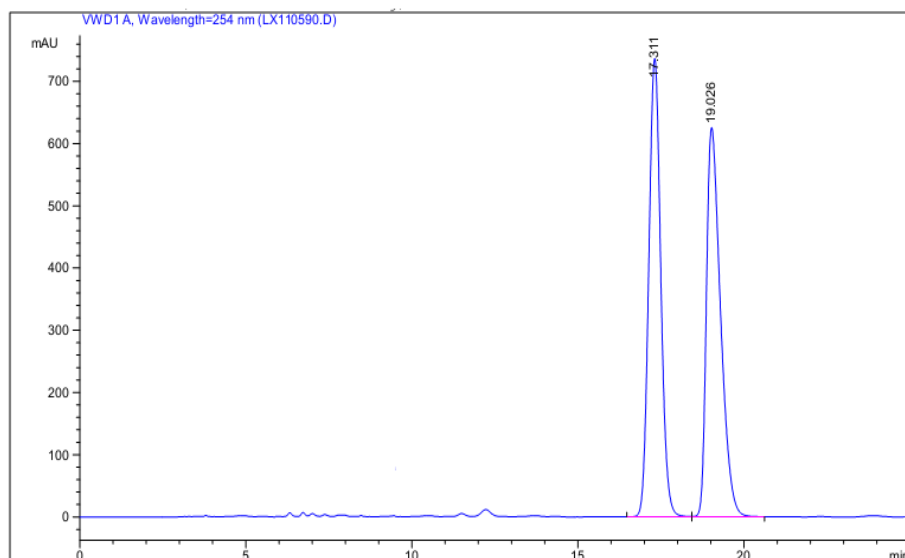
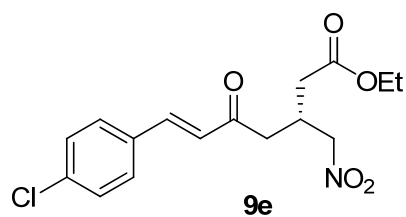
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	20.877	BV	0.7028	1.70300e4	373.14520	96.2609
2	22.677	VB	0.7489	661.50134	13.30664	3.7391



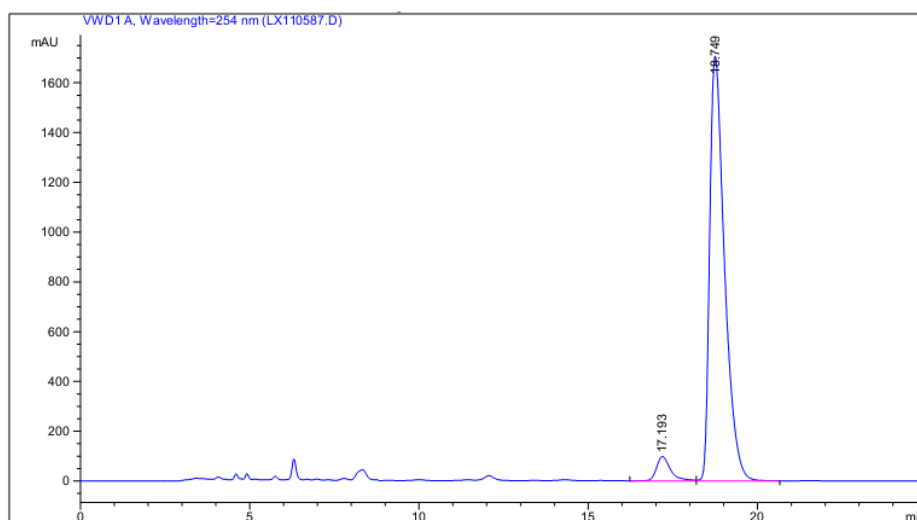
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]
1	21.830	VB	0.4974	3102.83276	49.7642	96.13017
2	24.603	BB	0.6786	3132.23193	50.2358	68.19067



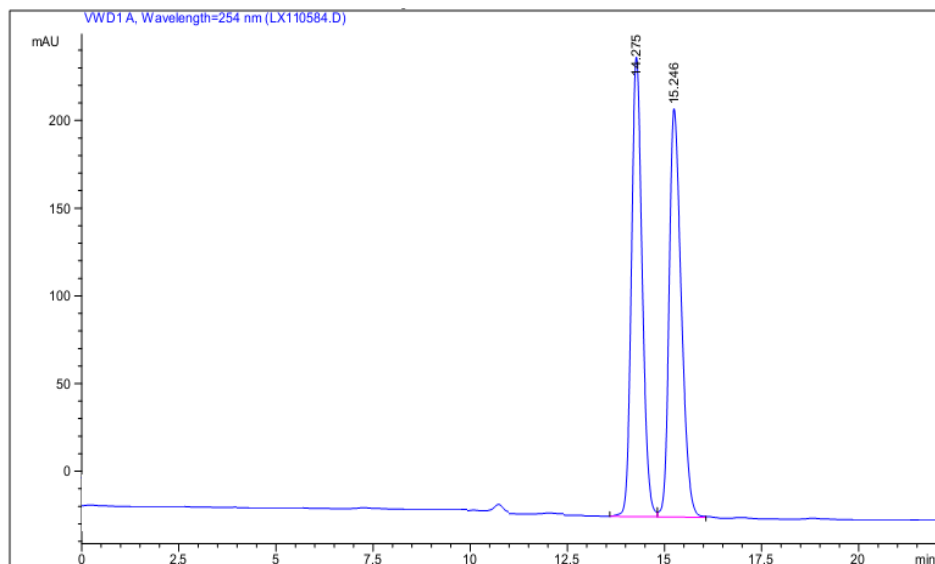
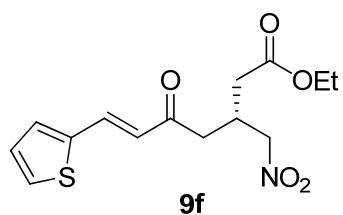
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]
1	22.324	VB	0.4949	310.35349	3.6478	9.79309
2	24.617	BB	0.7496	8197.54102	96.3522	155.34393



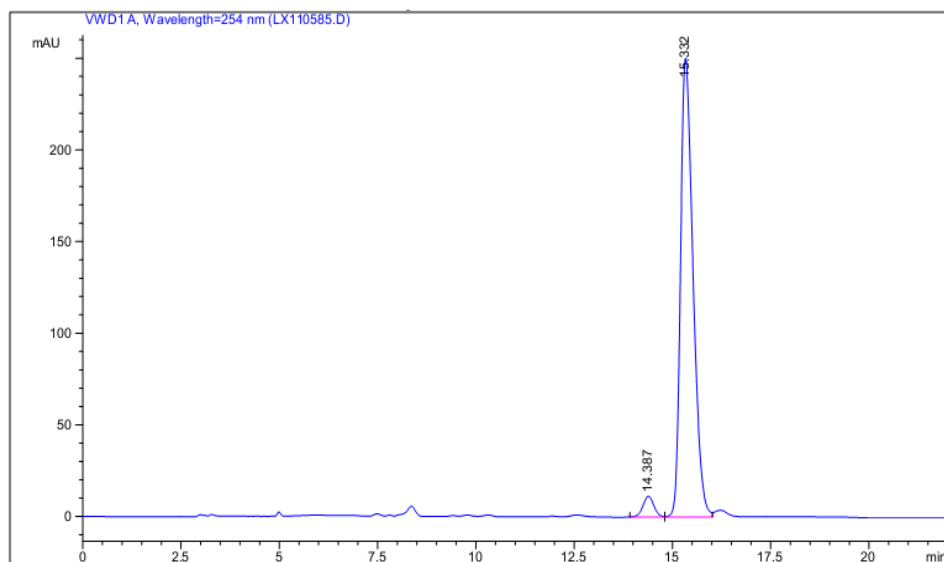
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]
1	17.311	VV	0.3907	1.84153e4	49.9736	736.51123
2	19.026	VB	0.4516	1.84347e4	50.0264	625.48175



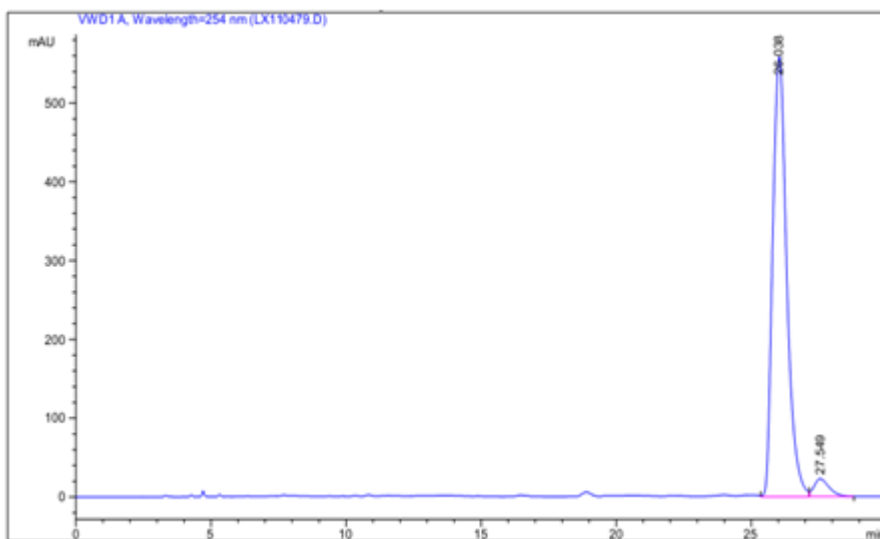
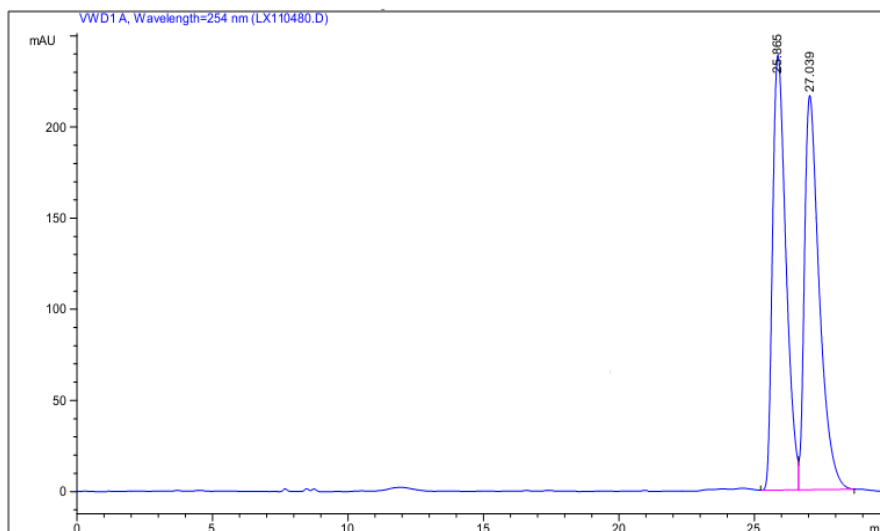
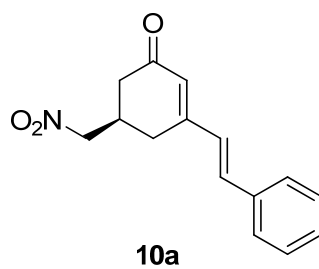
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]
1	17.193	VV	0.4294	2785.83862	5.0906	97.51108
2	18.749	VB	0.4630	5.19389e4	94.9094	1705.52844

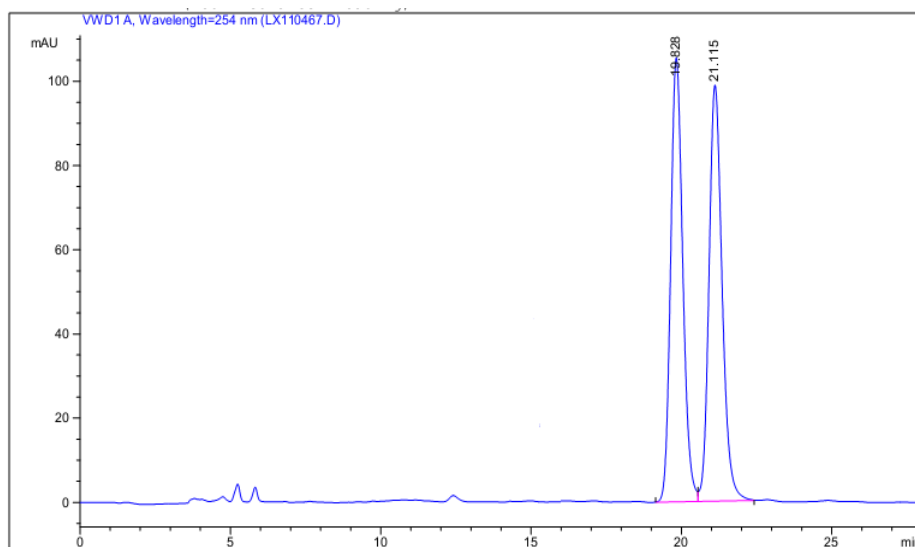
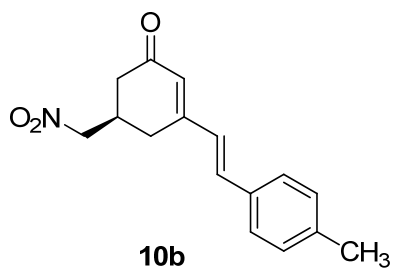


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.275	BV	0.2971	5037.64746	262.03149	49.9316
2	15.246	VB	0.3348	5051.44580	232.71236	50.0684

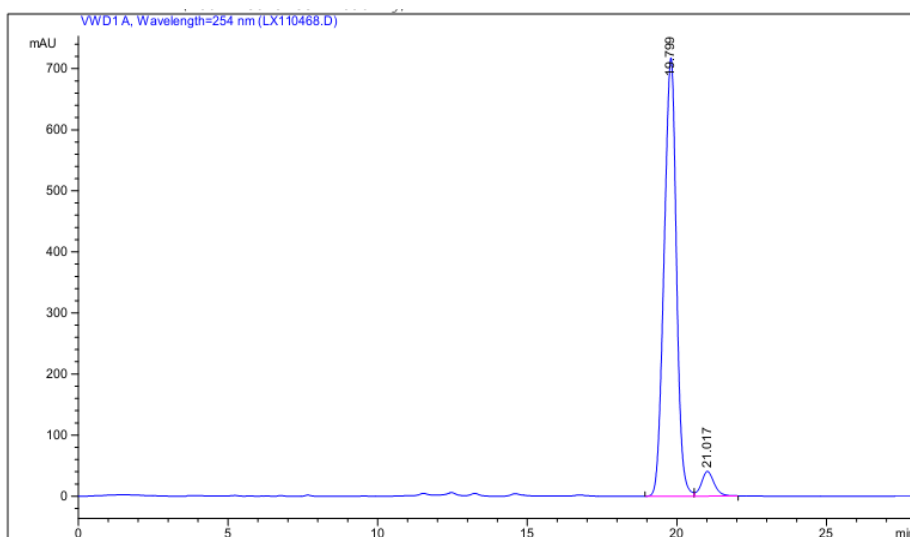


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.387	BV	0.3032	222.18466	11.39554	3.8650
2	15.332	VV	0.3393	5526.49609	250.17061	96.1350

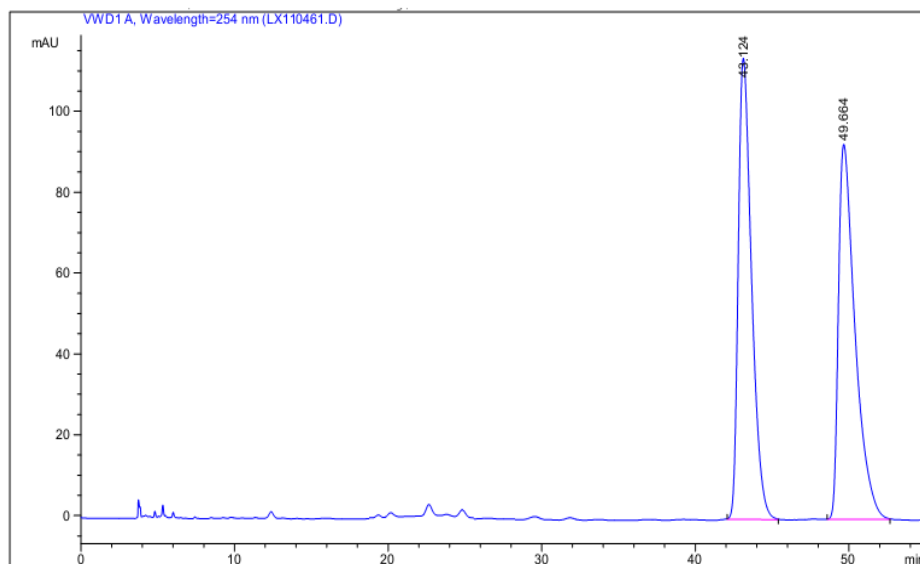
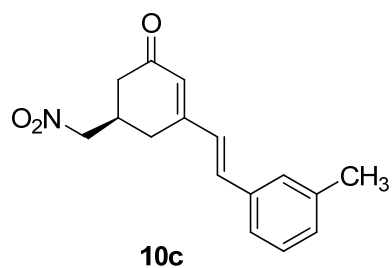




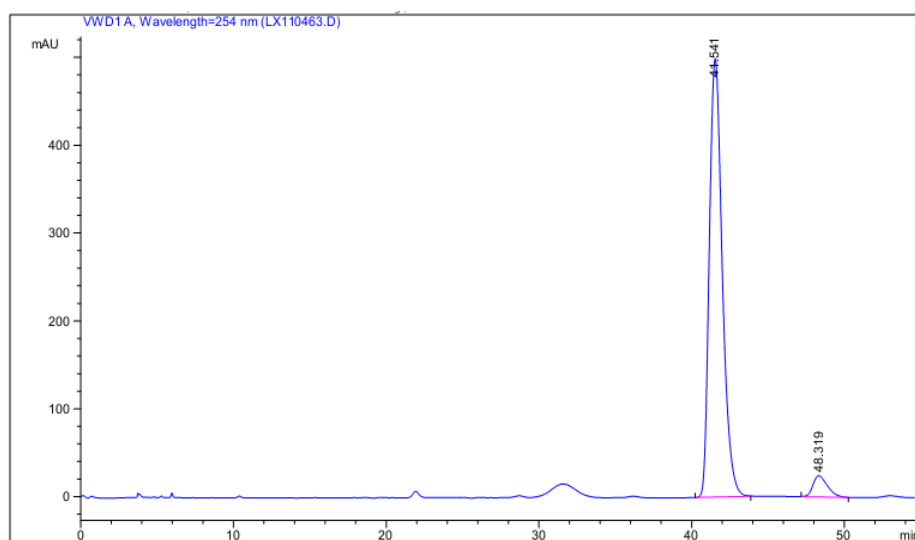
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	19.828	BV	0.4317	2954.92383	105.46574	49.6892
2	21.115	VB	0.4639	2991.88647	98.81908	50.3108



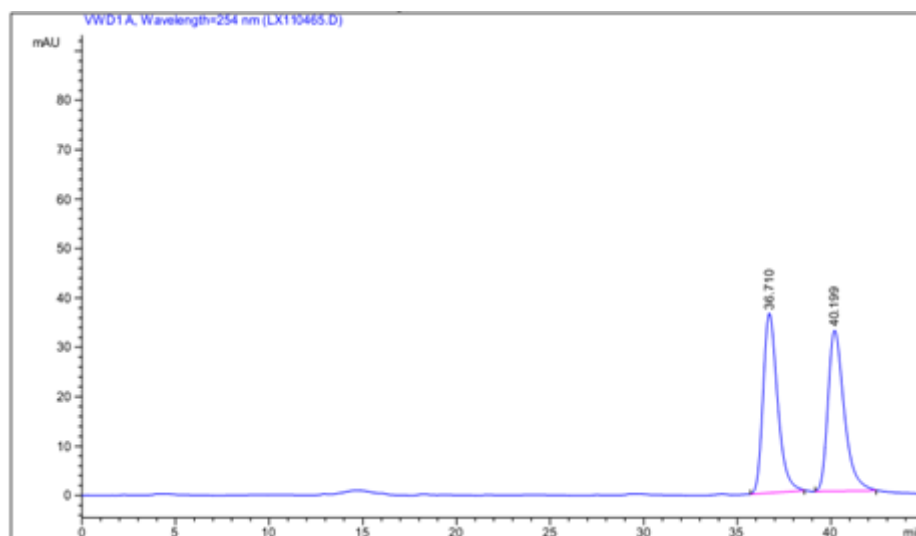
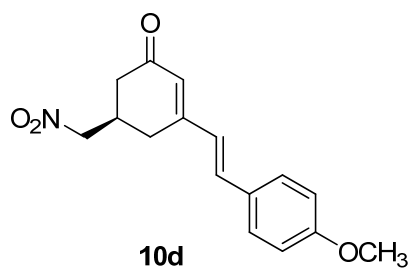
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	19.799	BV	0.4472	2.05222e4	717.66412	94.5120
2	21.017	VB	0.4515	1191.65369	40.27441	5.4880



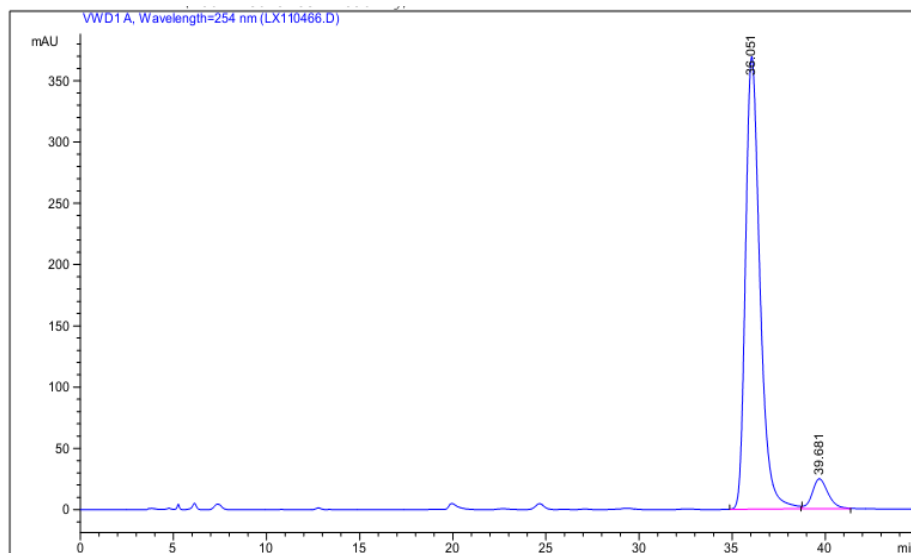
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	43.124	BB	0.9189	6862.68213	114.06327	49.6070
2	49.664	BB	1.1172	6971.40576	92.73961	50.3930



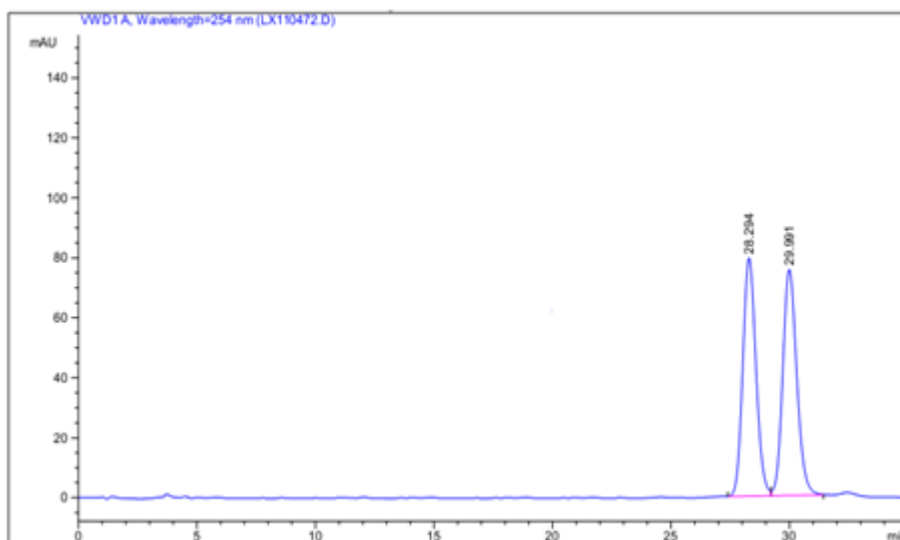
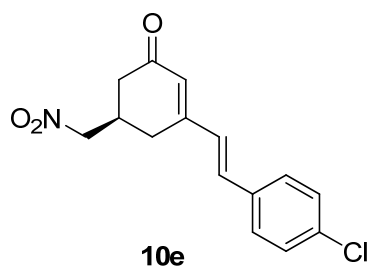
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	41.541	BB	0.9187	2.93198e4	498.85928	94.8920
2	48.319	BB	0.9817	1578.28040	24.12177	5.1080



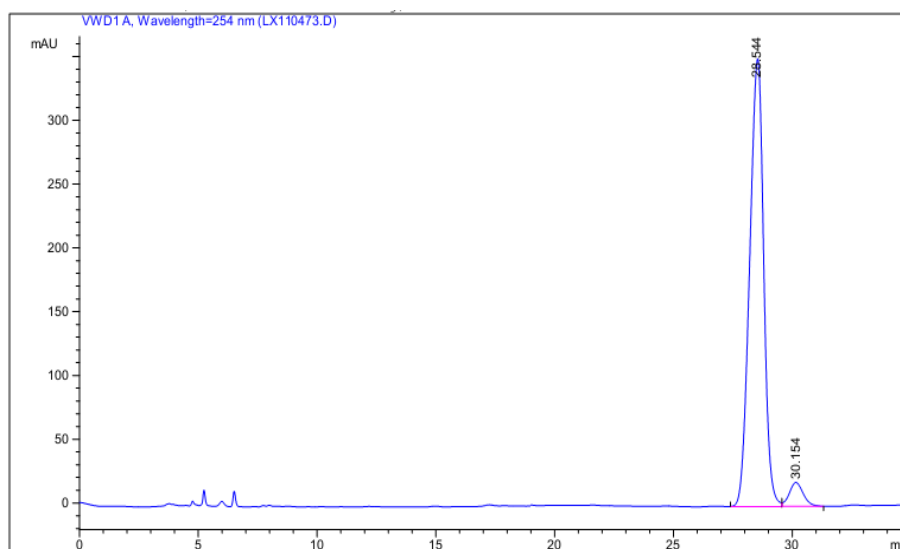
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	36.710	BB	0.8198	1966.99304	36.39786	50.0320
2	40.199	BB	0.9126	1964.47876	32.53901	49.9680



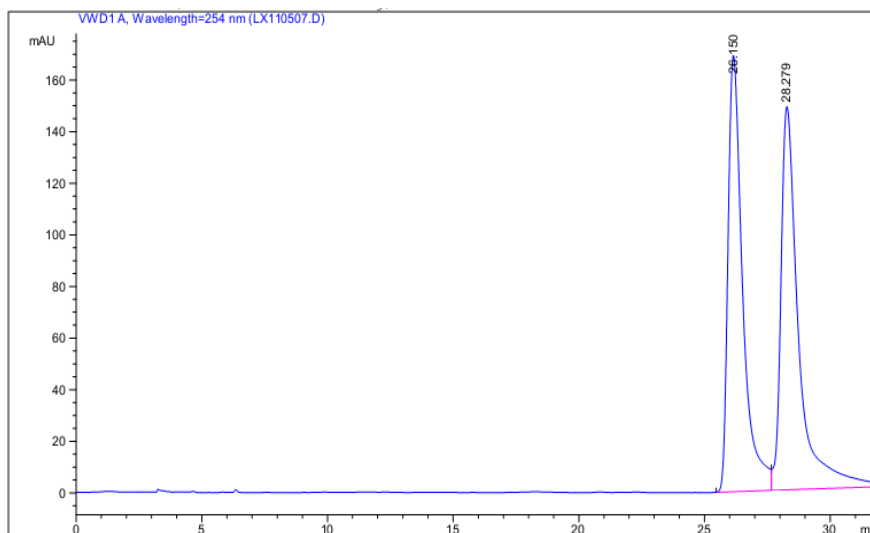
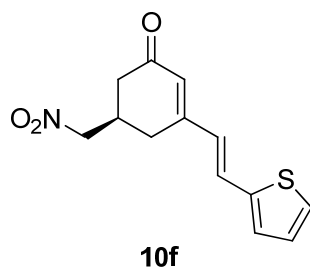
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	36.051	MM	0.8972	1.98680e4	369.06573	93.4676
2	39.681	MM	0.9469	1388.57190	24.44158	6.5324



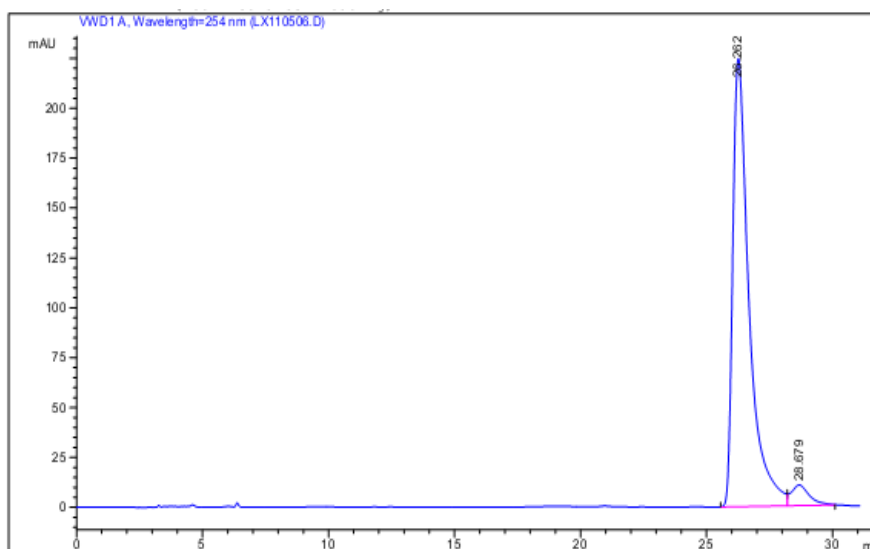
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.294	BV	0.6009	3069.03223	79.39937	49.7415
2	29.991	VB	0.6359	3100.92847	75.34604	50.2585



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.544	BV	0.6423	1.43742e4	350.98071	94.9070
2	30.154	VB	0.6309	771.35779	18.71167	5.0930



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.150	BV	0.6078	6844.27979	169.03355	48.3901
2	28.279	VB	0.7189	7299.69385	148.53635	51.6099



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.262	BV	0.6683	1.00877e4	224.53786	95.1135
2	28.679	VB	0.7226	518.26581	10.29704	4.8865