Supporting Information

Copper-Mediated Divergent Synthesis of Halogenated 1-Pyrrolines, 3-Azabicyclo[3.1.0]hex-2-enes and α, α-Dibromo imines from N-Allyl Enamine

Xiyan Duan, [a*] Junqi Wang, [a] Kun Liu, [a] Fengjiao Du, [a] Maolin He, [a] Wenxin Li, [a] Xinming Liu [a], Pu Liu [a*]

[a] *School of Chemistry & Chemical Engineering, Henan University of Science and Technology, Luoyang 471003, Henan, China;*

Fax: +86(379)64231914; +086-0379-64231914;

E-mail: duanxiyan@tju.edu.cn;

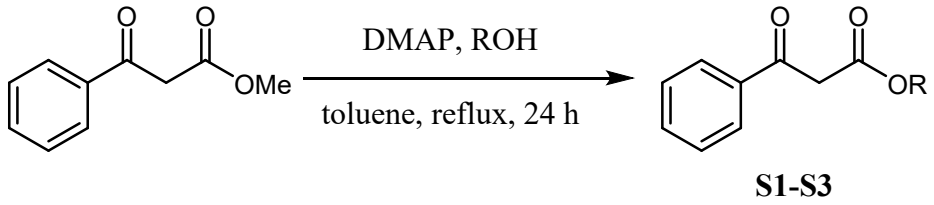
Contents

General Information

All reagents and solvent were commercial available with analytical grade and used as received. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. The used solvents were purified and dried according to common procedures. High-resolution mass spectra (HRMS) were obtained with a FTICR-MS (Ionspec 7.0T) spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 solution on a Bruker AV 400 MHz spectrometer. Chemical shifts are reported in parts per million (δ) relative to $CDCl_3$ (7.26 ppm) for ^{1}H NMR data and $CDCl_3$ (77.0 ppm) for ^{13}C NMR data or the peak of DMSO-d_6, defined at δ = 2.50 (^{1}H NMR) or δ = 39.5 (^{13}C NMR). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). Flash column chromatography was performed over silica gel 200−300 mesh, and the eluent was a mixture of ethyl acetate (EA) and petroleum ether (PE).

Experimental Procedure

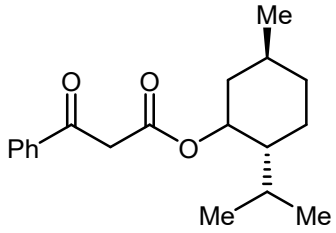
General Procedure A for the Synthesis of benzoylacetate **S1-S3**



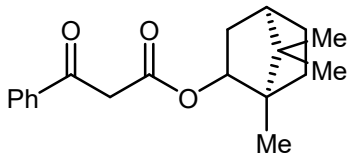
S1-S3

Scheme 1

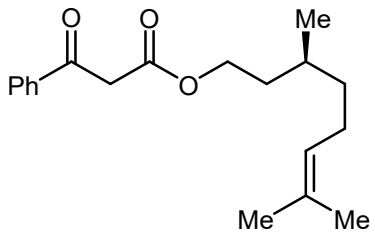
Methyl benzoylacetate (3.56 g, 20 mmol, 1.0 equiv) was dissolved in toluene (10 mL). DMAP (244 mg, 2 mmol, 0.1 equiv) and alcohol (30 mmol, 1.5 equiv) were then added to the solution. The reaction mixture was heated to reflux and stirred for 16 hours. After completion, the mixture was concentrated under reduced pressure and purified by flash chromatography (PE: EA = 100:1) on silica gel to afford products **S1**–**S3**.



(2R,5S)-2-isopropyl-5-methylcyclohexyl 3-oxo-3-phenylpropanoate (**S1**). The general procedure A was followed and purification by flash column chromatography afforded **S1** as a yellow oil (PE: EA = 100:1). Yield: 4.8 g, 79%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03–7.87 (m, 2H), 7.62–7.55 (m, 1H), 7.49–7.41 (m, 2H), 4.72 (td, J = 10.9, 4.4 Hz, 1H), 3.96 (q, J = 15.4 Hz, 2H), 2.05–1.97 (m, 1H), 1.77–1.59 (m, 4H), 1.54–1.38 (m, 2H), 1.36–1.23 (m, 2H), 0.88 (d, J = 6.5 Hz, 3H), 0.80 (d, J = 7.0 Hz, 3H), 0.68 (d, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.5, 167.1, 136.1, 133.6, 131.1, 128.7, 128.4, 126.0, 75.6, 46.8, 46.5, 40.5, 34.1, 31.3, 25.9, 23.1, 21.9, 20.7, 16.0. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{19}H_{26}NaO_3$: 325.1780; found: 325.1782.

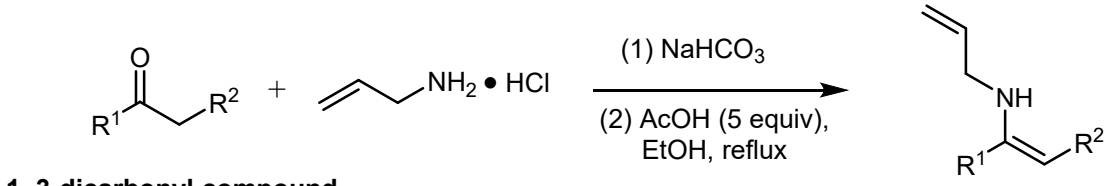


(1R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 3-oxo-3-phenylpropanoate (**S2**). The general procedure A was followed and purification by flash column chromatography afforded **S2** as a yellow oil (PE: EA = 100:1). Yield: 4.4 g, 74%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99–7.89 (m, 2H), 7.60–7.54 (m, 1H), 7.47–7.40 (m, 2H), 4.68 (dd, J = 7.7, 3.6 Hz, 1H), 3.94 (d, J = 3.2 Hz, 2H), 1.81–1.65 (m, 4H), 1.5–1.45 (m, 1H), 1.14–1.03 (m, 2H), 0.77 (s, 3H), 0.76 (s, 3H), 0.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.3, 166.9, 136.1, 133.6, 131.1, 128.7, 128.5, 125.9, 82.3, 48.6, 46.8, 46.1, 44.9, 38.5, 33.6, 26.9, 19.9, 19.5, 11.2. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{19}H_{24}NaO_3$: 323.1623; found: 323.1627.



(S)-3,7-dimethyloct-6-en-1-yl 3-oxo-3-phenylpropanoate (**S3**). The general procedure A was followed and purification by flash column chromatography afforded **S3** as a yellow oil (PE: EA = 100:1). Yield: 5.1 g, 85%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03–7.84 (m, 2H), 7.65–7.55 (m, 1H), 7.52–7.39 (m, 2H), 5.17–4.98 (m, 1H), 4.25–4.14 (m, 2H), 3.98 (s, 2H), 2.07–1.86 (m, 2H), 1.70–1.65 (m, 4H), 1.59 (s, 3H), 1.52–1.34 (m, 2H), 1.36–1.23 (m, 1H), 1.20–1.08 (m, 1H), 0.86 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.4, 167.5, 136.0, 133.7, 131.3, 128.7, 128.5, 126.0, 124.5, 87.4, 64.0, 46.0, 36.9, 35.2, 29.3, 25.7, 25.3, 19.2, 17.6. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{19}H_{26}NaO_3$: 325.1780; found: 325.1784.

General Procedure B for the Synthesis of N-allyl enamine **1a-1s**

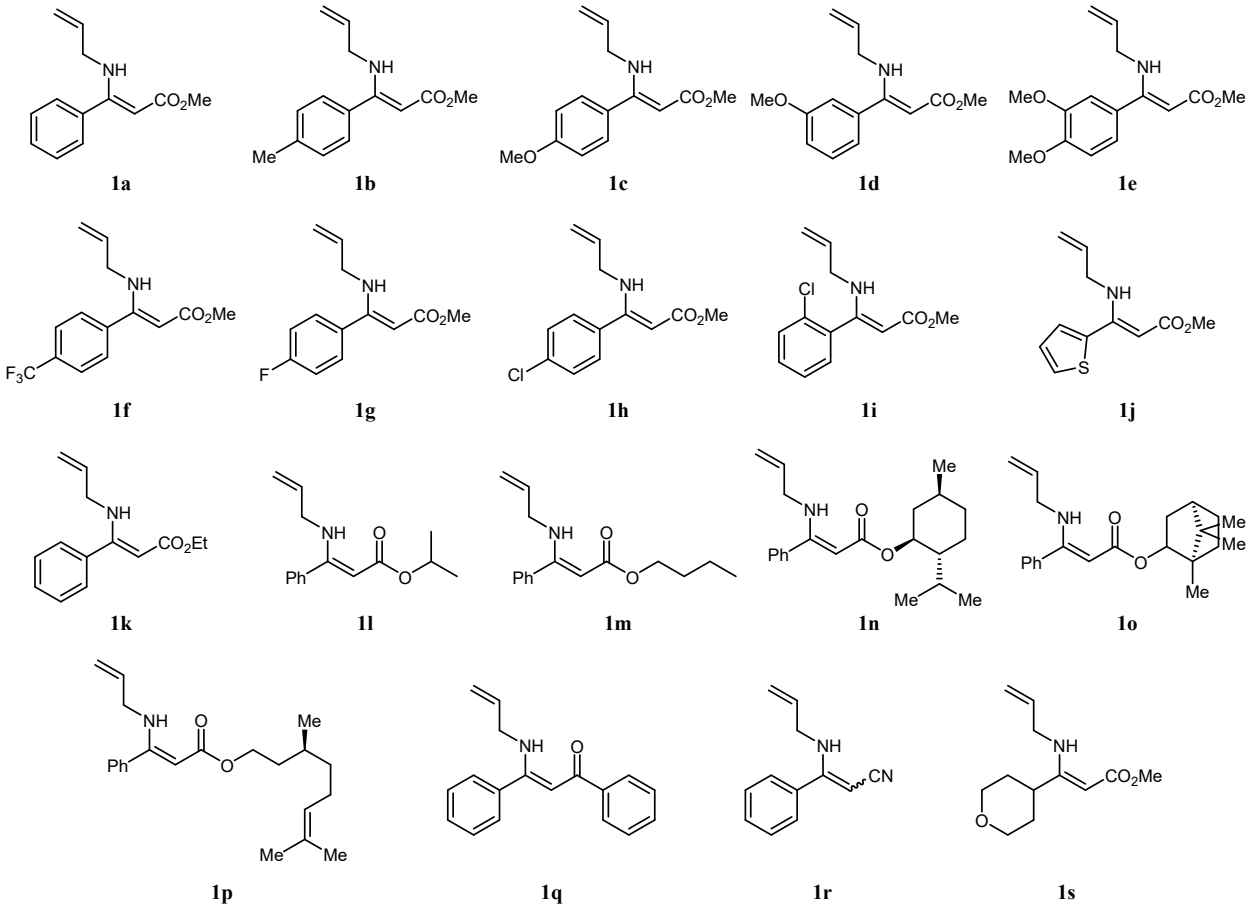


1, 3-dicarbonyl compound **1a-1s**

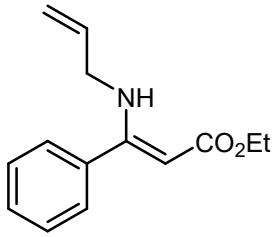
Scheme 2

Allylamine hydrochloride (50.0 mmol) and $NaHCO_3$ (50.0 mmol) were stirred at room temperature for 30 minutes. 1, 3-dicarbonyl compound (10.0 mmol), acetic acid (50.0 mmol), 4Å molecular sieves (1 g), and ethanol (20 mL) were then successively added. The reaction mixture was heated to reflux for 6 hours. After cooling, the mixture was filtered through a short pad of celite and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2, and the organic layer was washed with 1 M HCl solution and water, dried over Na_2SO_4, and concentrated. The crude product was purified by flash chromatography to afford N-allyl enamines **1a–1s**.

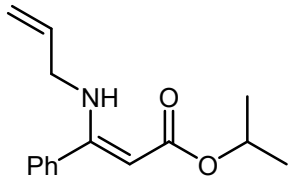
For the NMR data of compounds **1a**–**1j**, **1q**, and **1o**, please refer to our previous publication.[1]



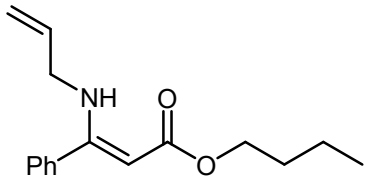
Scheme 3



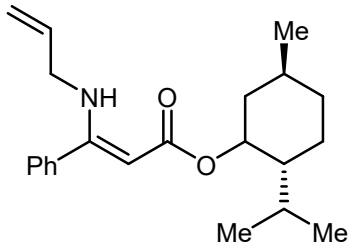
ethyl (Z)-3-(allylamino)-3-phenylacrylate (**1k**).[2] Ethyl 3-oxo-3-phenylpropanoate was used as a reaction substrate. The general procedure B was followed and purification by flash column chromatography afforded **1k** as a colorless oil (PE: EA = 100:1). Yield: 1.6 g, 70%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.61 (s, 1H), 7.44–7.29 (m, 5H), 5.88–5.66 (m, 1H), 5.27–5.03 (m, 2H), 4.63 (s, 1H), 4.15 (q, J = 7.1 Hz, 2H), 3.70–3.63 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 164.8, 135.9, 135.3, 129.2, 128.3, 127.7, 115.8, 85.9, 58.7, 46.8, 14.6.



isopropyl (Z)-3-(allylamino)-3-phenylacrylate (**1l**).[3] Isopropyl 3-oxo-3-phenylpropanoate was used as a reaction substrate. The general procedure B was followed and purification by flash column chromatography afforded **1l** as a colorless oil (PE: EA = 100:1). Yield: 1.8 g, 75%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.62 (s, 1H), 7.41–7.31 (m, 5H), 5.90–5.66 (m, 1H), 5.25–5.16 (m, 1H), 5.13–5.08 (m, 1H), 5.07–5.00 (m, 1H), 4.61 (s, 1H), 3.76–3.60 (m, 2H), 1.26 (d, J = 6.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.0, 164.6, 136.0, 135.4, 129.2, 128.3, 127.8, 115.8, 86.4, 65.6, 46.8, 22.2.

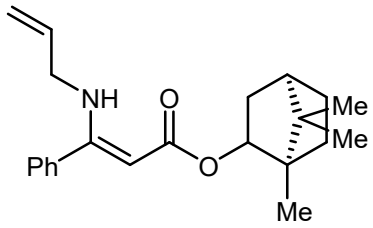


butyl (Z)-3-(allylamino)-3-phenylacrylate (**1m**). Butyl 3-oxo-3-phenylpropanoate was used as a reaction substrate. The general procedure B was followed and purification by flash column chromatography afforded **1m** as a colorless oil (PE: EA = 100:1). Yield: 1.7 g, 67%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.61 (s, 1H), 7.41–7.32 (m, 5H), 5.86–5.68 (m, 1H), 5.27–5.17 (m, 1H), 5.15–5.06 (m, 1H), 4.64 (s, 1H), 4.10 (t, J = 6.7 Hz, 2H), 3.71–3.63 (m, 2H), 1.66–1.61 (m, 2H), 1.47–1.36 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 164.7, 136.0, 135.4, 129.2, 128.3, 127.8, 115.8, 85.9, 62.7, 46.8, 31.1, 19.2, 13.8. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{16}H_{21}NNaO_2$: 282.1470; found: 282.1474.

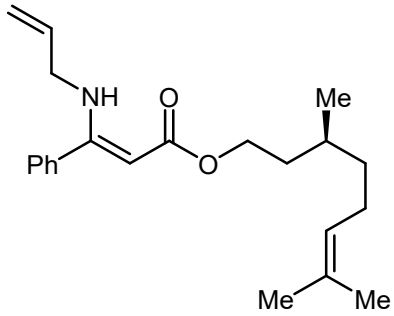


(2R,5S)-2-isopropyl-5-methylcyclohexyl (Z)-3-(allylamino)-3-phenylacrylate (**1n**). **S1** was used as a reaction substrate. The general procedure B was followed and purification by flash column

chromatography afforded **1n** as a colorless oil (PE:EA = 100:1). Yield: 2.3 g, 68%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.61 (s, 1H), 7.45–7.30 (m, 5H), 5.94–5.71 (m, 1H), 5.27–5.15 (m, 1H), 5.14–5.05 (m, 1H), 4.70 (td, J = 10.8, 4.3 Hz, 1H), 4.62 (s, 1H), 3.74–3.63 (m, 2H), 2.15–2.04 (m, 1H), 2.01–1.89 (m, 1H), 1.71–1.63 (m, 2H), 1.60–1.46 (m, 1H), 1.45–1.31 (m, 1H), 1.15–0.95 (m, 2H), 0.95–0.84 (m, 7H), 0.80 (d, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 164.5, 136.0, 135.4, 129.2, 128.2, 127.8, 115.8, 86.4, 72.2, 47.2, 46.9, 41.5, 34.4, 31.5, 26.2, 23.7, 22.1, 20.8, 16.6. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{22}H_{31}NNaO_2$: 364.2252; found: 364.2256.

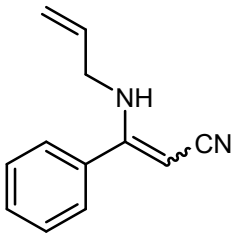


(1R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl (Z)-3-(allylamino)-3-phenylacrylate (**1o**). **S2** was used as a reaction substrate. The general procedure B was followed and purification by flash column chromatography afforded **1o** as a colorless solid (PE: EA = 100:1). Yield: 2.0 g, 59%; mp 49-50 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (s, 1H), 7.44–7.31 (m, 5H), 5.88–5.69 (m, 1H), 5.28–5.15 (m, 1H), 5.14–5.05 (m, 1H), 4.73–4.66 (m, 1H), 4.61 (s, 1H), 3.73–3.59 (m, 2H), 1.87 – 1.77 (m, 2H), 1.74–1.65 (m, 2H), 1.59–1.50 (m, 1H), 1.23–1.04 (m, 2H), 0.98 (s, 3H), 0.87 (s, 3H), 0.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 164.4, 136.0, 135.4, 129.1, 128.2, 127.8, 115.7, 86.5, 79.2, 48.6, 46.9, 46.8, 45.1, 39.1, 33.9, 27.1, 20.2, 19.9, 11.5. HRMS (ESI): m/z [M + Na] $^+$ calcd for $C_{22}H_{29}NNaO_2$: 362.2096; found: 362.2097.



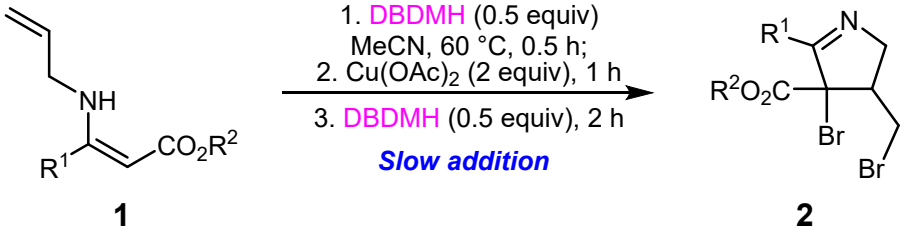
(S)-3,7-dimethyloct-6-en-1-yl (Z)-3-(allylamino)-3-phenylacrylate (**1p**). **S3** was used as a reaction substrate. The general procedure B was followed and purification by flash column chromatography afforded **1p** as a colorless oil (PE: EA = 100:1). Yield: 2.5 g, 72%; ^{1}H NMR (400 MHz, $CDCl_3$):

δ = 8.61 (s, 1H), 7.41–7.32 (m, 5H), 5.94–5.66 (m, 1H), 5.28–5.17 (m, 1H), 5.15–5.04 (m, 2H), 4.64 (s, 1H), 4.23–4.04 (m, 2H), 3.67 (tt, J = 6.6, 1.7 Hz, 2H), 2.08–1.92 (m, 2H), 1.73–1.66 (m, 4H), 1.62–1.54 (m, 4H), 1.52–1.43 (m, 1H), 1.41–1.32 (m, 1H), 1.24–1.13 (m, 1H), 0.93 (d, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 164.7, 135.9, 135.3, 131.1, 129.2, 128.3, 127.7, 124.7, 115.7, 85.9, 61.3, 46.8, 37.0, 35.8, 29.6, 25.7, 25.4, 19.4, 17.6. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{22}H_{31}NNaO_2$: 364.2252; found: 364.2256.



3-(allylamino)-3-phenylacrylonitrile (**1r**).[2] 3-oxo-3-phenylpropanenitrile was used as a reaction substrate. The general procedure B was followed and purification by flash column chromatography afforded **1r** as a red oil (PE: EA = 5:1). Yield: 1.5 g, 80%. Isolated as a *E*/*Z* mixture (*E*: *Z* = 0.23:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.52 (m, 2H), 7.46–7.38 (m, 3H), 5.96–5.76 (m, 1H), 5.34–5.24 (m, 2H), 4.56 (s, 1H), 4.06 (s, 1H), 3.80–3.66 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.0, 135.7, 132.1, 130.4, 128.8, 127.7, 121.4, 118.0, 62.1, 46.3.

General Procedure C for the synthesis of dibromo 1-pyrrolines **2a-2m**

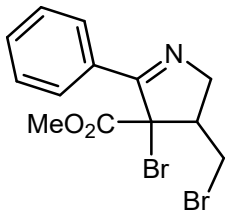


1 **2**

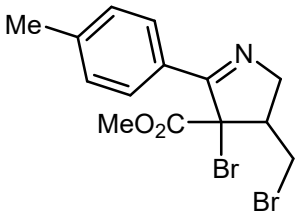
Scheme 4

To a solution of N-allyl enamine **1** (1 mmol) in MeCN (1.5 mL), DBDMH (0.5 mmol) was added. The mixture was stirred at 60 °C for 30 minutes, after which $Cu(OAc)_2$ (2 mmol) was added. After 1 hour, an additional portion of DBDMH (0.5 mmol) was added in 5 batches over 2 hours. Upon completion (monitored by TLC), the reaction mixture was cooled to room temperature, and CH_2Cl_2 (50 mL) was added. The organic layer was washed with brine (15 mL ×

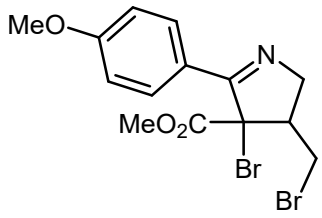
2), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a residue. The residue was purified by flash column chromatography to yield dibromo 1-pyrrolines **2**.



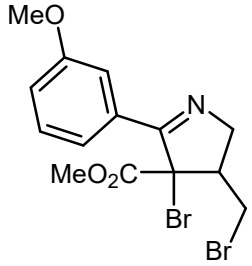
methyl 4-bromo-3-(bromomethyl)-5-phenyl-3,4-dihydro-2H-pyrrole-4-carboxylate (**2a**). The general procedure C was followed and purification by flash column chromatography afforded **2a** as a colorless oil (PE: EA = 10:1). Yield: 242 mg, 65%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88–7.85 (m, 1H), 7.48–7.36 (m, 4H), 4.33 (dd, J = 16.4, 6.7 Hz, 1H), 3.75 (s, 3H), 3.72–3.56 (m, 3H), 3.30–3.16 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.9, 168.5, 131.2, 131.1, 128.6, 127.8, 70.5, 62.9, 54.3, 53.8, 30.1. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{13}H_{14}Br_2NO_2$: 373.9391; found: 373.9394.



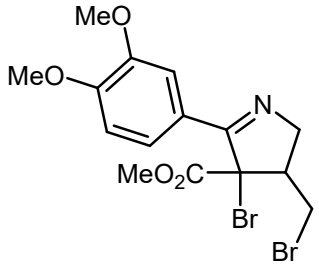
methyl 4-bromo-3-(bromomethyl)-5-(p-tolyl)-3,4-dihydro-2H-pyrrole-4-carboxylate (**2b**). The general procedure C was followed and purification by flash column chromatography afforded **2b** as a white solid (PE: EA = 10:1). Yield: 236 mg, 61%; mp: 106-107 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.69 (m, 2H), 7.22–7.14 (m, 2H), 4.40–4.23 (m, 1H), 3.76 (s, 3H), 3.73–3.54 (m, 3H), 3.29–3.17 (m, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.8, 168.6, 141.5, 129.3, 128.3, 127.7, 70.6, 62.8, 54.3, 53.8, 30.2, 21.4. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{16}Br_2NO_2$: 387.9548; found: 387.9548.



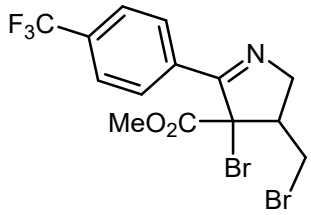
methyl 4-bromo-3-(bromomethyl)-5-(4-methoxyphenyl)-3,4-dihydro-2H-pyrrole-4-carboxylate (**2c**). The general procedure C was followed and purification by flash column chromatography afforded **2c** as a white solid (PE: EA = 8:1). Yield: 254 mg, 63%; mp 103-104 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.75 (m, 2H), 6.93–6.84 (m, 2H), 4.28 (dd, J = 16.3, 6.7 Hz, 1H), 3.82 (s, 3H), 3.75 (s, 3H), 3.72–3.51 (m, 3H), 3.28–3.16 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.2, 168.6, 161.8, 129.4, 123.6, 113.9, 70.6, 62.7, 55.3, 54.3, 53.8, 30.2. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{16}Br_2NO_3$: 403.9497; found: 403.9501.



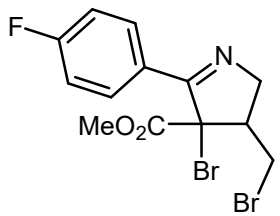
methyl 4-bromo-3-(bromomethyl)-5-(3-methoxyphenyl)-3,4-dihydro-2H-pyrrole-4-carboxylate (**2d**). The general procedure C was followed and purification by flash column chromatography afforded **2d** as a white solid (PE: EA = 10:1). Yield: 222 mg, 55%; mp 85-86 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.48 (m, 1H), 7.44–7.38 (m, 1H), 7.33–7.27 (m, 1H), 7.05–6.98 (m, 1H), 4.34 (dd, J = 16.4, 6.7 Hz, 1H), 3.83 (s, 3H), 3.77 (s, 3H), 3.70–3.57 (m, 3H), 3.32–3.19 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 168.2, 159.7, 131.7, 129.6, 120.4, 118.5, 112.5, 70.4, 62.2, 55.4, 54.4, 53.6, 29.8. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{16}Br_2NO_3$: 403.9497; found: 403.9494.



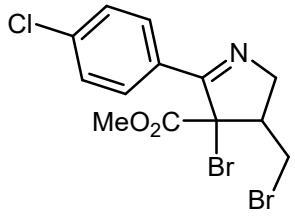
Methyl 4-bromo-3-(bromomethyl)-5-(3,4-dimethoxyphenyl)-3,4-dihydro-2H-pyrrole-4-carboxylate (**2e**). The general procedure C was followed and purification by flash column chromatography afforded **2e** as a colorless oil (PE: EA = 5:1). Yield: 165 mg, 38%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.48 (m, 1H), 7.40–7.32 (m, 1H), 6.85–6.80 (m, 1H), 4.28 (dd, J = 16.3, 6.7 Hz, 1H), 3.89 (s, 6H), 3.76 (s, 3H), 3.69–3.52 (m, 3H), 3.30–3.19 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.4, 168.7, 151.5, 149.0, 123.7, 121.0, 110.4, 110.3, 70.7, 62.6, 55.9, 55.8, 54.3, 53.9, 30.1. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{15}H_{18}Br_2NO_4$: 433.9603; found: 433.9604.



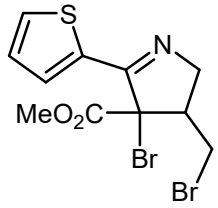
methyl 4-bromo-3-(bromomethyl)-5-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2H-pyrrole-4-carboxylate (**2f**). The general procedure C was followed and purification by flash column chromatography afforded **2f** as a white solid (PE: EA = 10:1). Yield: 300 mg, 68%; mp 109-110 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, J = 8.2 Hz, 2H), 7.66 (d, J = 8.3 Hz, 2H), 4.38 (dd, J = 16.7, 6.7 Hz, 1H), 3.77 (s, 3H), 3.73–3.59 (m, 3H), 3.30–3.19 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.9, 168.2, 134.5, 132.6 (q, J = 32 Hz), 128.2, 125.5 (q, J = 4 Hz), 123.7 (d, J = 271 Hz), 70.1, 63.1, 54.5, 53.8, 29.9. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{13}Br_2F_3NO_2$: 441.9265; found: 441.9269.



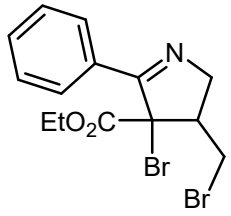
methyl 4-bromo-3-(bromomethyl)-5-(4-fluorophenyl)-3,4-dihydro-2H-pyrrole-4-carboxylate (**2g**). The general procedure C was followed and purification by flash column chromatography afforded **2g** as a colorless oil (PE: EA = 10:1). Yield: 260 mg, 67%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94–7.80 (m, 2H), 7.14–6.99 (m, 2H), 4.30 (dd, J = 16.4, 6.7 Hz, 1H), 3.75 (s, 3H), 3.70–3.51 (m, 3H), 3.28–3.17 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.7, 168.3, 165.6 (d, J = 250 Hz), 130.0 (d, J = 8 Hz), 127.4 (d, J = 4 Hz), 115.7 (d, J = 22 Hz), 70.4, 62.8, 54.4, 53.8, 30.0. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{13}H_{13}Br_2FNO_2$: 391.9297; found: 391.9301.



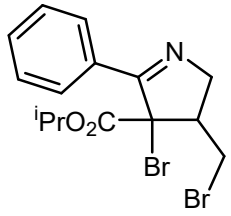
methyl 4-bromo-3-(bromomethyl)-5-(4-chlorophenyl)-3,4-dihydro-2H-pyrrole-4-carboxylate (**2h**). The general procedure C was followed and purification by flash column chromatography afforded **2h** as a white solid (PE: EA = 10:1). Yield: 210 mg, 52%; mp: 108-109 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.75 (m, 2H), 7.39–7.33 (m, 2H), 4.32 (dd, J = 16.6, 6.7 Hz, 1H), 3.76 (s, 3H), 3.72–3.54 (m, 3H), 3.27–3.17 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.9, 168.3, 137.3, 129.6, 129.1, 128.8, 70.2, 62.9, 54.4, 53.8, 30.0. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{13}H_{13}Br_2ClNO_2$: 407.9002; found: 407.8999.



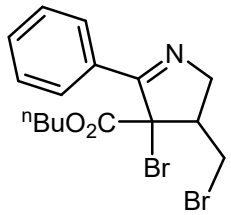
methyl 4-bromo-3-(bromomethyl)-5-(thiophen-2-yl)-3,4-dihydro-2H-pyrrole-4-carboxylate (**2j**). The general procedure C was followed and purification by flash column chromatography afforded **2j** as a colorless oil (PE: EA = 10:1). Yield: 121 mg, 32%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.36 (m, 2H), 7.08–7.02 (m, 1H), 4.29 (dd, J = 16.4, 6.8 Hz, 1H), 3.82 (s, 3H), 3.71–3.50 (m, 3H), 3.38–3.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.1, 164.7, 135.2, 130.2, 129.1, 127.8, 70.5, 62.8, 54.5, 53.7, 30.1. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{11}H_{12}Br_2NO_2S$: 379.8956; found: 379.8958.



ethyl 4-bromo-3-(bromomethyl)-5-phenyl-3,4-dihydro-2H-pyrrole-4-carboxylate (**2k**). The general procedure C was followed and purification by flash column chromatography afforded **2k** as a white solid (PE: EA = 10:1). Yield: 252 mg, 65%; mp: 65-66 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93–7.83 (m, 2H), 7.47–7.34 (m, 3H), 4.33 (dd, J = 16.4, 6.7 Hz, 1H), 4.21 (q, J = 7.2 Hz, 2H), 3.77–3.55 (m, 3H), 3.30–3.15 (m, 1H), 1.11 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 167.7, 131.3, 131.0, 128.4, 127.8, 70.9, 63.7, 62.9, 53.7, 30.2, 13.7. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{16}Br_2NO_2$: 387.9548; found: 387.9549.

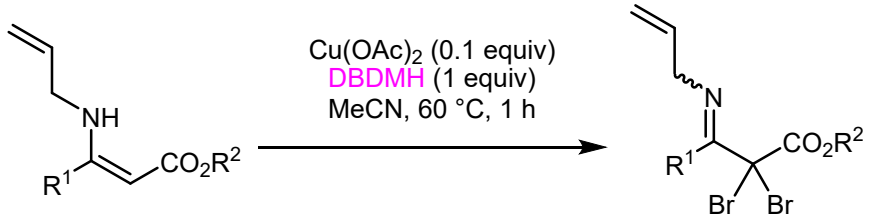


isopropyl 4-bromo-3-(bromomethyl)-5-phenyl-3,4-dihydro-2H-pyrrole-4-carboxylate (**2l**). The general procedure C was followed and purification by flash column chromatography afforded **2l** as a colorless oil (PE: EA = 10:1). Yield: 261 mg, 65%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93–7.81 (m, 2H), 7.49–7.34 (m, 3H), 5.18–4.85 (m, 1H), 4.30 (dd, J = 16.3, 6.7 Hz, 1H), 3.75–3.51 (m, 3H), 3.38–3.11 (m, 1H), 1.22 (d, J = 6.3 Hz, 3H), 0.95 (d, J = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 167.0, 131.4, 131.0, 128.4, 127.9, 71.7, 71.3, 62.9, 53.7, 30.1, 21.4, 20.9. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{15}H_{18}Br_2NO_2$: 401.9704; found: 401.9707.



butyl 4-bromo-3-(bromomethyl)-5-phenyl-3,4-dihydro-2H-pyrrole-4-carboxylate (**2m**). The general procedure C was followed and purification by flash column chromatography afforded **2m** as a colorless oil (PE: EA = 10:1). Yield: 203 mg, 49%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97–7.79 (m, 2H), 7.46–7.34 (m, 3H), 4.33 (dd, J = 16.4, 6.7 Hz, 1H), 4.22–4.07 (m, 2H), 3.75–3.56 (m, 3H), 3.28–3.14 (m, 1H), 1.55–1.39 (m, 2H), 1.21–1.06 (m, 2H), 0.78 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 167.8, 131.3, 131.0, 128.5, 127.8, 70.9, 67.5, 62.9, 53.7, 30.1, 30.1, 18.8, 13.4. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{16}H_{20}Br_2NO_2$: 415.9861; found: 415.9864.

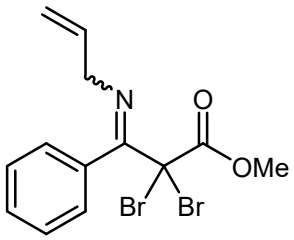
General Procedure D for the Synthesis of dibromo imines **3a-3h**



1 **3**

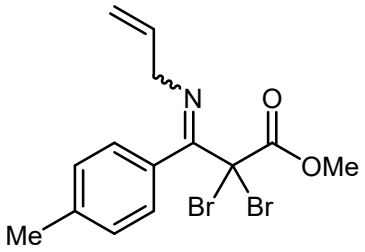
Scheme 5

To a solution of N-allyl enamine **1** (1 mmol) in MeCN (1.5 mL) was added DBDMH (1 mmol) and $Cu(OAc)_2$ (0.1 mmol). The reaction mixture was heated to 60 °C and stirred for 1 h. After TLC confirmed reaction completion, the mixture was cooled to room temperature, and CH_2Cl_2 (50 mL) was added. The reaction mixture was washed with brine (15 mL×2). The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford a residue. This residue was purified via flash column chromatography to yield dibromo imines **3**.

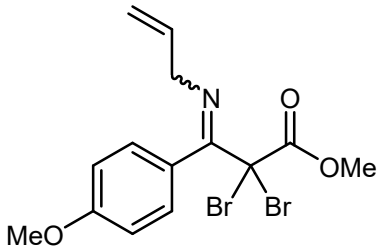


methyl 3-(allylimino)-2,2-dibromo-3-phenylpropanoate (**3a**). The general procedure D was followed and purification by flash column chromatography afforded **3a** as a yellow oil (PE: EA = 70:1). Yield: 354 mg, 95%. Isolated as a *E*/*Z* mixture (*E*: *Z* = 1:8); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.44 (m, 3H), 7.42–7.37 (m, 2H), 5.99–5.81 (m, 1H), 5.15–5.06 (m, 2H), 3.92 (s, 3H),

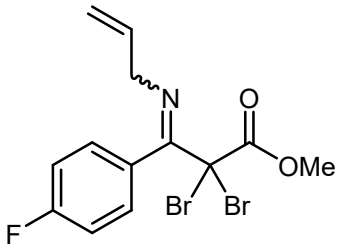
3.87–3.83 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 165.4, 134.5, 131.8, 129.5, 129.0, 128.1, 115.6, 61.4, 55.8, 54.7. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{13}H_{13}Br_2NO_2Na$: 395.9211; found: 395.9206.



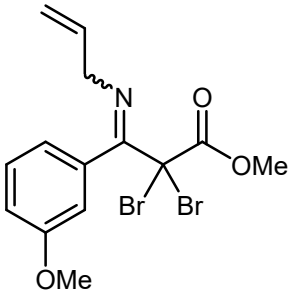
methyl 3-(allylimino)-2,2-dibromo-3-(p-tolyl)propanoate (**3b**). The general procedure D was followed and purification by flash column chromatography afforded **3b** as a yellow oil (PE: EA = 80:1). Yield: 329 mg, 85%. Isolated as a *E*/*Z* mixture (*E*: *Z* = 1:13); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.24 (m, 4H), 6.02–5.76 (m, 1H), 5.19–5.04 (m, 2H), 3.91 (s, 3H), 3.88–3.83 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.7, 165.5, 139.5, 134.6, 128.9, 128.8, 128.8, 115.5, 61.7, 55.8, 54.6, 21.3. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{16}Br_2NO_2$: 387.9548; found: 387.9550.



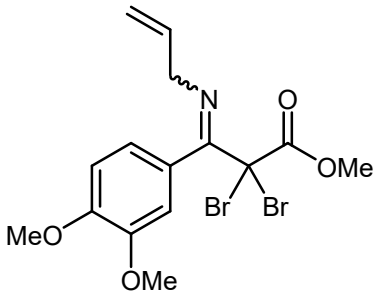
methyl 3-(allylimino)-2,2-dibromo-3-(4-methoxyphenyl)propanoate (**3c**). The general procedure D was followed and purification by flash column chromatography afforded **3c** as a yellow oil (PE: EA = 80:1). Yield: 318 mg, 79%. Isolated as a *E*/*Z* mixture (*E*: *Z* = 1:17); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.28 (m, 2H), 6.97–6.92 (m, 2H), 5.97–5.77 (m, 1H), 5.14–5.02 (m, 2H), 3.88 (s, 3H), 3.86–3.83 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 165.5, 160.3, 134.6, 130.5, 123.9, 115.5, 113.5, 62.1, 55.9, 55.2, 54.6. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{16}Br_2NO_3$: 403.9497; found: 403.9502.



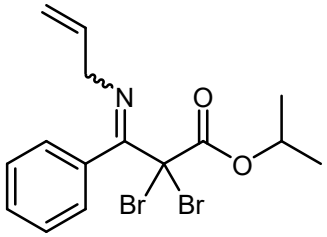
methyl 3-(allylimino)-2,2-dibromo-3-(4-fluorophenyl)propanoate (**3d**). The general procedure D was followed and purification by flash column chromatography afforded **3d** as a yellow oil (PE:EA = 80:1). Yield: 348 mg, 89%. Isolated as a *E*/*Z* mixture (*E*: *Z* = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.34 (m, 2H), 7.18–7.10 (m, 2H), 5.98–5.55 (m, 1H), 5.18–5.02 (m, 2H), 3.96–3.87 (m, 3H), 3.84–3.77 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7, 165.3, 163.2 (d, *J* = 249 Hz), 134.3, 131.1(d, *J* = 8 Hz), 127.7(d, *J* = 4 Hz), 115.7, 115.4 (d, *J* = 21 Hz), 61.4, 55.9, 54.7. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{13}H_{13}Br_2FNO_2$: 391.9297; found: 391.9300.



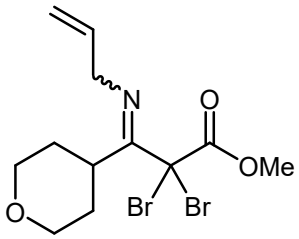
methyl 3-(allylimino)-2,2-dibromo-3-(3-methoxyphenyl)propanoate (**3e**). The general procedure D was followed and purification by flash column chromatography afforded **3e** as a yellow oil (PE: EA = 80:1). Yield: 367 mg, 91%. Isolated as a *E*/*Z* mixture (*E*: *Z* = 1:13); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.32 (m, 1H), 7.00–6.89 (m, 3H), 5.97–5.80 (m, 1H), 5.15–5.03 (m, 2H), 3.90 (s, 3H), 3.86–3.83 (m, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.2, 165.4, 159.1, 134.6, 133.0, 129.2, 121.3, 115.5, 114.9, 114.8, 61.2, 55.9, 55.3, 54.7. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{16}Br_2NO_3$: 403.9497; found: 403.9497.



methyl 3-(allylimino)-2,2-dibromo-3-(3,4-dimethoxyphenyl)propanoate (**3f**). The general procedure D was followed and purification by flash column chromatography afforded **3f** as a yellow oil (PE: EA = 80:1). Yield: 372 mg, 86%. Isolated as a *E*/*Z* mixture (*E*: *Z* = 1:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.95–6.86 (m, 3H), 6.03–5.77 (m, 1H), 5.18–4.92 (m, 2H), 3.91 (s, 3H), 3.89 (s, 3H), 3.88–3.85 (m, 4H), 3.80–3.72 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3, 165.5, 149.8, 148.4, 134.7, 124.0, 121.8, 115.4, 112.3, 110.5, 61.9, 56.0, 56.0, 55.8, 54.6. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{15}H_{18}Br_2NO_4$: 433.9603; found: 433.9607.



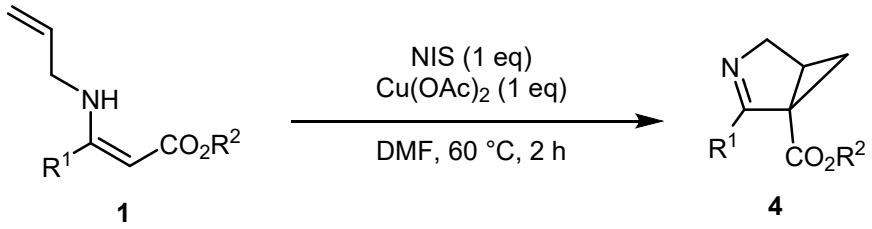
isopropyl 3-(allylimino)-2,2-dibromo-3-phenylpropanoate (**3g**). The general procedure D was followed and purification by flash column chromatography afforded **3g** as a yellow oil (PE: EA = 80:1). Yield: 361 mg, 90%. Isolated as a *E*/*Z* mixture (*E*: *Z* = 1:6); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.41 (m, 3H), 7.41–7.33 (m, 2H), 5.99–5.79 (m, 1H), 5.19–5.01 (m, 3H), 3.91–3.77 (m, 2H), 1.31 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.4, 164.2, 134.5, 132.1, 129.4, 129.0, 128.0, 115.8, 72.6, 62.4, 56.1, 21.3. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{15}H_{18}Br_2NO_2$: 401.9704; found: 401.9708.



methyl 3-(allylimino)-2,2-dibromo-3-(tetrahydro-2H-pyran-4-yl)propanoate (**3h**). The general procedure D was followed and purification by flash column chromatography afforded **3h** as a white solid (PE: EA = 10:1). Yield: 286 mg, 75%. Isolated as a *E*/*Z* mixture (*E*: *Z* = 1:5); mp: 62-63 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.05–5.79 (m, 1H), 5.17–4.96 (m, 2H), 4.42–4.35 (m, 2H), 4.06–4.01 (m, 2H), 3.83 (s, 3H), 3.51–3.43 (m, 2H), 3.40–3.31 (m, 1H), 2.28–2.13 (m, 2H),

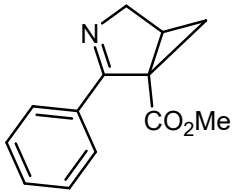
1.89–1.83 (m, 2H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8, 165.2, 134.5, 115.4, 68.0, 65.0, 54.5, 53.0, 39.7, 30.1. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{12}H_{18}Br_2NO_3$: 381.9653; found: 381.9656.

General Procedure E for the Synthesis of 3-azabicyclo[3.1.0]hex-2-enes **4a-4r**

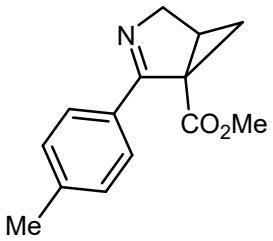


Scheme 6

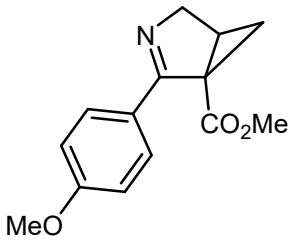
To a solution of N-allyl enamine **1** (1 mmol) in DMF (1.5 mL) was added NIS (1 mmol) and $Cu(OAc)_2$ (1 mmol). The reaction mixture was stirred at 60 °C for 2 h. After TLC confirmed reaction completion, the reaction mixture was cooled to room temperature, and EtOAc (50 mL) was introduced. The reaction mixture was washed with brine (15 mL×2). The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford a residue. This residue was purified via flash column chromatography to yield 3-azabicyclo[3.1.0]hex-2-enes **4**.



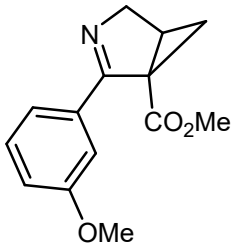
methyl 2-phenyl-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4a**). The general procedure E was followed and purification by flash column chromatography afforded **4a** as a yellow oil (PE: EA = 5:1). Yield: 194 mg, 90%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82–7.64 (m, 2H), 7.46–7.37 (m, 3H), 4.24–3.98 (m, 2H), 3.60 (s, 3H), 2.62–2.50 (m, 1H), 2.13 (dd, J = 8.5, 4.2 Hz, 1H), 0.95–0.85 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.6, 170.3, 133.6, 130.4, 128.2, 128.0, 61.7, 52.0, 40.7, 31.8, 21.5. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{13}H_{14}NO_2$: 216.1025; found: 216.1027.



methyl 2-(p-tolyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4b**). The general procedure E was followed and purification by flash column chromatography afforded **4b** as a yellow oil (PE: EA = 5:1). Yield: 188 mg, 82%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75–7.51 (m, 2H), 7.24–7.16 (m, 2H), 4.26–3.95 (m, 2H), 3.61 (s, 3H), 2.58–2.50 (m, 1H), 2.39 (s, 3H), 2.17–2.07 (m, 1H), 0.95–0.73 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.5, 170.4, 140.7, 130.8, 129.0, 128.1, 61.6, 52.1, 40.7, 31.8, 21.5, 21.4. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{16}NO_2$: 230.1181; found: 230.1186.

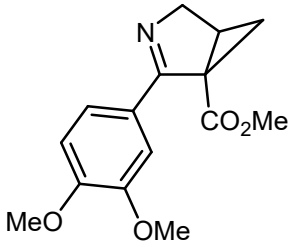


methyl 2-(4-methoxyphenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4c**).[4] The general procedure E was followed and purification by flash column chromatography afforded **4c** as a yellow oil (PE: EA = 5:1). Yield: 196 mg, 80%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.58 (m, 2H), 6.95–6.85 (m, 2H), 4.21–3.96 (m, 2H), 3.83 (s, 3H), 3.61 (s, 3H), 2.57–2.47 (m, 1H), 2.10 (dd, J = 8.5, 4.2 Hz, 1H), 0.88–0.82 (m, 1H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.8, 170.4, 161.4, 129.8, 126.3, 113.6, 61.4, 55.3, 52.1, 40.5, 31.9, 21.5.

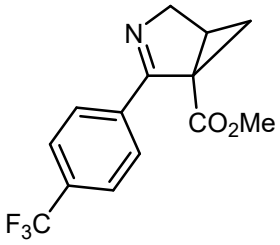


methyl 2-(3-methoxyphenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4d**). The general procedure E was followed and purification by flash column chromatography afforded **4d** as a

yellow oil (PE: EA = 5:1). Yield: 206 mg, 84%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.31 (m, 1H), 7.31–7.26 (m, 2H), 7.03–6.92 (m, 1H), 4.27–3.95(m, 2H), 3.83 (s, 3H), 3.61 (s, 3H), 2.64–2.43 (m, 1H), 2.11 (dd, J = 8.5, 4.2 Hz, 1H), 0.91–0.83 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.5, 170.3, 159.5, 135.0, 129.2, 120.9, 116.9, 112.3, 61.8, 55.3, 52.1, 40.8, 31.9, 21.4. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{16}NO_3$: 246.1130; found: 246.1134.

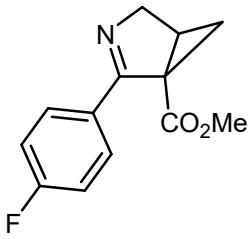


methyl 2-(3,4-dimethoxyphenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4e**). The general procedure E was followed and purification by flash column chromatography afforded **4e** as a yellow oil (PE: EA = 3:1). Yield: 187 mg, 68%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, J = 1.9 Hz, 1H), 7.20 (dd, J = 8.3, 1.9 Hz, 1H), 6.84 (d, J = 8.3 Hz, 1H), 4.17–3.96 (m, 2H), 3.90 (s, 6H), 3.61 (s, 3H), 2.61–2.40 (m, 1H), 2.09 (dd, J = 8.5, 4.2 Hz, 1H), 0.89–0.77 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.8, 170.5, 151.0, 148.8, 126.5, 122.0, 110.1, 110.0, 61.5, 55.8, 55.8, 52.1, 40.5, 32.0, 21.3. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{15}H_{18}NO_4$: 276.1236; found: 276.1241.

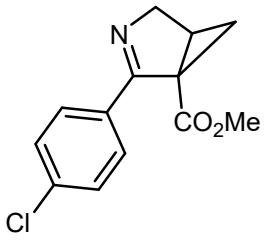


methyl 2-(4-(trifluoromethyl)phenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4f**). The general procedure E was followed and purification by flash column chromatography afforded **4f** as a yellow solid (PE: EA = 5:1). Yield: 156 mg, 55%; mp: 57-58 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, J = 8.1 Hz, 2H), 7.66 (d, J = 8.2 Hz, 2H), 4.25–4.02 (m, 2H), 3.61 (s, 3H), 2.66–2.55 (m, 1H), 2.15 (dd, J = 8.6, 4.2 Hz, 1H), 0.95–0.85 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.5, 170.0, 137.1, 131.9 (q, J = 32 Hz), 128.4, 125.2 (q, J = 4 Hz), 123.9 (d, J = 270 Hz), 62.0,

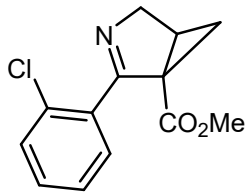
52.1, 40.7, 32.1, 21.9. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{14}H_{13}F_3NO_2$: 284.0898; found: 284.0902.



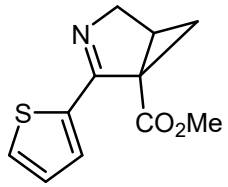
methyl 2-(4-fluorophenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4g**).[3] The general procedure E was followed and purification by flash column chromatography afforded **4g** as a yellow solid (PE: EA = 5:1). Yield: 214 mg, 92%; mp: 65-66 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.66 (m, 2H), 7.12–7.03 (m, 2H), 4.20–3.95 (m, 2H), 3.61 (s, 3H), 2.64–2.50 (m, 1H), 2.12 (dd, J = 8.5, 4.1 Hz, 1H), 0.91–0.81 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.3, 170.2, 164.0 (d, J = 248 Hz), 130.1 (d, J = 9 Hz),130.0 (d, J = 4 Hz) 115.3 (d, J = 22 Hz), 61.6, 52.1, 40.6, 32.1, 21.7.



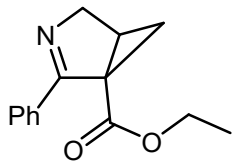
methyl 2-(4-chlorophenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4h**). The general procedure E was followed and purification by flash column chromatography afforded **4h** as a yellow oil (PE: EA = 5:1). Yield: 149 mg, 60%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 8.5 Hz, 2H), 4.23–4.01 (m, 2H), 3.63 (s, 3H), 2.65–2.54 (m, 1H), 2.15 (dd, J = 8.5, 4.2 Hz, 1H), 0.95–0.85 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.5, 170.1, 136.4, 132.2, 129.4, 128.5, 61.7, 52.1, 40.6, 32.1, 21.7. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{13}H_{13}ClNO_2$: 250.0635; found: 250.0639.



methyl 2-(2-chlorophenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4i**). The general procedure E was followed and purification by flash column chromatography afforded **4i** as a yellow oil (PE: EA = 5:1). Yield: 137 mg, 55%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71–7.63 (m, 1H), 7.42–7.27 (m, 3H), 4.16–3.97 (m, 2H), 3.54 (s, 3H), 2.78–2.66 (m, 1H), 2.18 (dd, J = 8.5, 4.2 Hz, 1H), 1.11–1.02 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.9, 170.2, 134.5, 132.9, 131.0, 130.7, 129.7, 126.7, 61.4, 51.9, 43.2, 34.2, 24.2. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{13}H_{13}ClNO_2$: 250.0635; found: 250.0639.

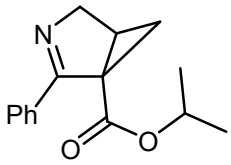


methyl 2-(thiophen-2-yl)-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4j**). The general procedure E was followed and purification by flash column chromatography afforded **4j** as a yellow solid (PE: EA = 5:1). Yield: 111 mg, 50%; mp: 115-116 ºC ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (dd, J = 13.1, 4.3 Hz, 2H), 7.10–6.99 (dd, J = 5.0, 3.8 Hz, 1H), 4.21–3.90 (m, 2H), 3.69 (s, 3H), 2.63–2.42 (m, 1H), 2.06 (dd, J = 8.6, 4.3 Hz, 1H), 0.89–0.76 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.9, 166.1, 137.8, 130.2, 129.0, 127.3, 61.2, 52.1, 40.9, 32.6, 21.4. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{11}H_{12}NO_2S$: 222.0589; found: 222.0593.

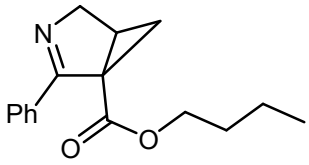


ethyl 2-phenyl-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4k**).[3] The general procedure E was followed and purification by flash column chromatography afforded **4k** as a yellow oil (PE: EA = 5:1). Yield: 195 mg, 85%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (dd, J = 7.9, 1.6 Hz, 2H), 7.47–7.33 (m, 3H), 4.27–3.91 (m, 4H), 2.63–2.46 (m, 1H), 2.11 (dd, J = 8.5, 4.1 Hz, 1H), 1.03 (t, J =

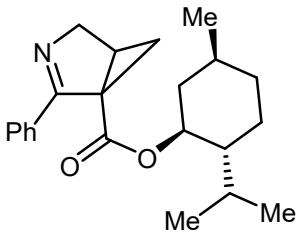
7.1 Hz, 3H), 0.92–0.82 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.7, 169.9, 133.9, 130.2, 128.1, 128.1, 61.9, 60.9, 40.9, 31.8, 21.4, 13.8.



isopropyl 2-phenyl-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4l**).[3] The general procedure E was followed and purification by flash column chromatography afforded **4l** as a yellow oil (PE: EA = 5:1). Yield: 241 mg, 99%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.63 (m, 2H), 7.43–7.36 (m, 3H), 5.04–4.87 (m, 1H), 4.23–3.95 (m, 2H), 2.62–2.38 (m, 1H), 2.10 (dd, J = 8.5, 4.1 Hz, 1H), 1.09 (d, J = 6.3 Hz, 3H), 0.94 (d, J = 6.2 Hz, 3H), 0.88–0.85 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.1, 169.3, 133.9, 130.2, 128.1, 128.0, 68.6, 61.8, 41.2, 31.6, 21.6, 21.3, 21.2.

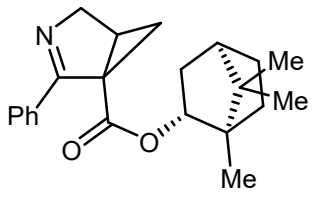


butyl 2-phenyl-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4m**). The general procedure E was followed and purification by flash column chromatography afforded **4m** as a yellow oil (PE: EA = 5:1). Yield: 149 mg, 58%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.65 (m, 2H), 7.45–7.35 (m, 3H), 4.22–3.99 (m, 3H), 3.95–3.87 (m, 1H), 2.59–2.47 (m, 1H), 2.11 (dd, J = 8.5, 4.1 Hz, 1H), 1.44–1.27 (m, 2H), 1.09–0.95 (m, 2H), 0.90–0.85 (m, 1H), 0.74 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.8, 170.0, 134.0, 130.2, 128.1, 128.0, 64.8, 41.0, 31.9, 30.3, 21.5, 18.7, 13.5. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{16}H_{20}NO_2$: 258.1494; found: 258.1493.

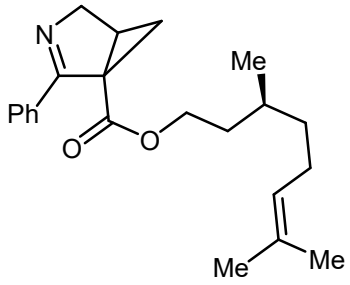


(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 2-phenyl-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4n**).[3] The general procedure E was followed and purification by flash column

chromatography afforded **4n** (dr = 1:4, determined by ^{1}H NMR) as a yellow oil (PE: EA = 5:1). Yield: 275 mg, 81%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77–7.62 (m, 2H), 7.46–7.32 (m, 3H), 4.68–4.43 (m, 1H), 4.24–4.08 (m, 1H), 4.07–3.92 (m, 1H), 2.56–2.35 (m, 1H), 2.15–2.02 (m, 1H), 2.01–1.89 (m, 1H), 1.87–1.64 (m, 1H), 1.63–1.48 (m, 2H), 1.45–1.32 (m, 1H), 1.08–0.90 (m, 2H), 0.89–0.78 (m, 5H), 0.77–0.70 (m, 2H), 0.58–0.47 (dd, J = 20.1, 6.9 Hz, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.2, 169.2, 134.2, 130.2, 128.2, 127.8, 75.4, 75.1, 62.2, 46.7, 46.4, 40.4, 40.3, 34.0, 31.3, 31.2, 26.6, 24.8, 23.7, 22.6, 21.9, 21.8, 21.1, 20.8, 20.4, 16.7, 15.5. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{22}H_{30}NO_2$: 340.2277; found: 340.2281.

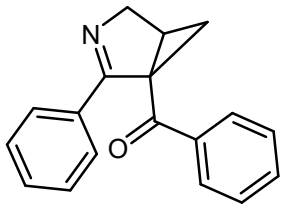


(1R,2R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2-phenyl-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4o**). The general procedure E was followed and purification by flash column chromatography afforded **4o** (dr = 1:2.75, determined by ^{1}H NMR) as a yellow oil (PE: EA = 10:1). Yield: 250 mg, 74%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.67 (m, 2H), 7.47–7.32 (m, 3H), 4.76–4.52 (m, 1H), 4.23–3.96 (m, 2H), 2.56–2.42 (m, 1H), 2.19–2.03 (m, 1H), 1.66–1.54 (m, 3H), 1.53–1.28 (m, 2H), 1.11–0.95 (m, 2H), 0.91–0.84 (m, 1H), 0.76–0.69 (m, 5H), 0.62 (s, 1H), 0.49–0.35 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.9, 169.5, 134.0, 130.3, 128.3, 128.2, 128.1, 128.1, 82.2, 81.5, 61.8, 48.7, 48.5, 46.8, 46.6, 44.8, 41.4, 41.0, 39.0, 37.9, 33.7, 33.6, 31.8, 26.9, 21.3, 21.2, 19.9, 19.4, 19.0, 11.1, 10.9. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{22}H_{28}NO_2$: 338.2120; found: 338.2122.

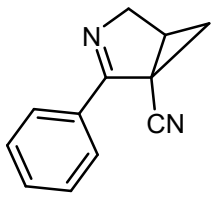


(S)-3,7-dimethyloct-6-en-1-yl 2-phenyl-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4p**). The general procedure E was followed and purification by flash column chromatography afforded **4p**

(dr = 1:1, determined by ^{1}H NMR) as a yellow oil (PE: EA = 10:1). Yield: 302 mg, 89%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82–7.66 (m, 2H), 7.45–7.35 (m, 3H), 5.11–4.92 (m, 1H), 4.20–4.07 (m, 2H), 4.06–3.91 (m, 2H), 2.58–2.46 (m, 1H), 2.17–2.07 (m, 1H), 1.91–1.77 (m, 2H), 1.67 (s, 3H), 1.58 (s, 3H), 1.50–1.33 (m, 1H), 1.26–0.95 (m, 4H), 0.91–0.84 (m, 1H), 0.78–0.65 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.7, 170.0, 170.0, 134.0, 134.0, 131.2, 131.2, 130.2, 130.2, 128.2, 128.1, 128.0, 128.0, 124.5, 63.4, 63.4, 61.9, 61.8, 41.0, 36.9, 36.7, 35.2, 35.0, 31.9, 31.9, 29.1, 28.9, 25.7, 25.3, 25.2, 21.5, 21.4, 19.1, 19.0, 17.6, 17.6. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{22}H_{30}NO_2$: 340.2277; found: 340.2281.

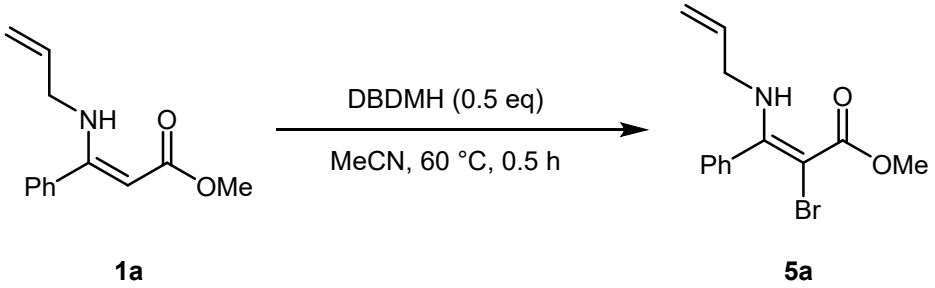


phenyl(2-phenyl-3-azabicyclo[3.1.0]hex-2-en-1-yl)methanone (**4q**).[2] The general procedure E was followed and purification by flash column chromatography afforded **4q** as a yellow solid (PE: EA = 5:1). Yield: 240 mg, 92%; mp: 115-116 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76–7.60 (m, 4H), 7.41–7.34 (m, 1H), 7.31–7.13 (m, 5H), 4.53–4.26 (m, 2H), 2.69–2.54 (m, 1H), 2.37 (dd, J = 8.3, 4.2 Hz, 1H), 0.82 (t, J = 4.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.1, 175.2, 137.2, 133.1, 132.8, 130.6, 128.4, 128.4, 128.2, 128.1, 62.5, 47.7, 32.9, 18.6.



2-phenyl-3-azabicyclo[3.1.0]hex-2-ene-1-carbonitrile (**4r**).[2] The general procedure E was followed and purification by flash column chromatography afforded **4r** as a yellow solid (PE: EA = 5:1). Yield: 58 mg, 32%; mp: 47-48 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10–7.88 (m, 2H), 7.58–7.40 (m, 3H), 4.34–4.04 (m, 2H), 2.90–2.73 (m, 1H), 1.89 (dd, J = 8.7, 4.6 Hz, 1H), 1.00 (dd, J = 5.5, 5.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.5, 131.5, 131.4, 128.7, 128.2, 118.7, 62.0, 29.8, 24.7, 22.9.

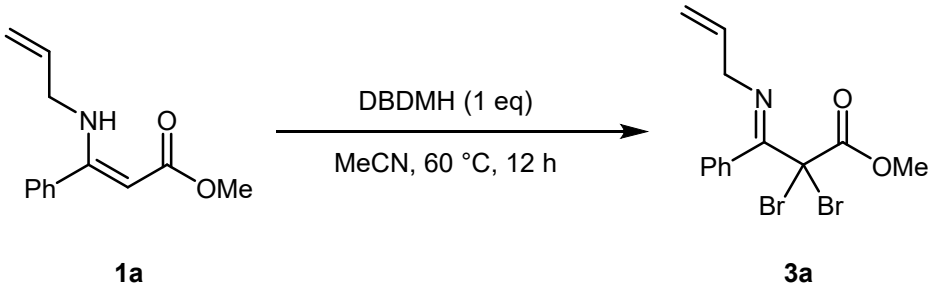
Control experiment



1a **5a**

Scheme 7

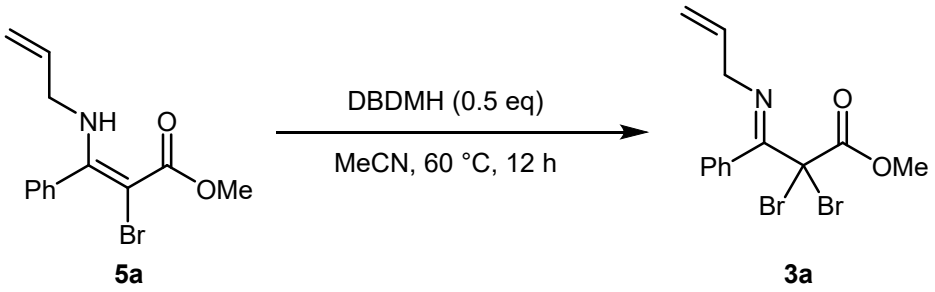
To a solution of N-allyl enamine **1** (1 mmol) in MeCN (1.5 mL) was added DBDMH (0.5 mmol). The reaction mixture was stirred at 60 °C for 0.5 h, then cooled to room temperature. DCM (50 mL) was added, and the mixture was washed with brine (15 mL × 2). The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure to obtain a residue. This residue was purified by flash column chromatography to yield **5a** as a colorless oil (PE: EA = 100:1).[1] Yield: 274 mg, 93%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.32 (s, 1H), 7.45–7.41 (m, 3H), 7.23–7.19 (m, 2H), 5.76–5.66 (m, 1H), 5.18–5.07 (m, 2H), 3.80 (s, 3H), 3.54–3.48 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.1, 163.7, 135.6, 134.7, 129.1, 128.5, 128.3, 127.7, 116.1, 51.9, 47.8.



1a **3a**

Scheme 8

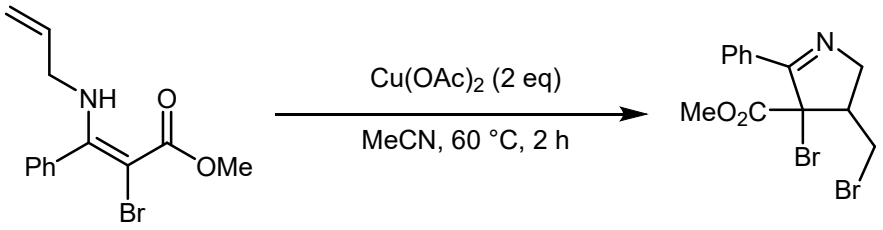
To a solution of N-allyl enamine **1** (1 mmol) in MeCN (1.5 mL), DBDMH (1 mmol) was added. The reaction mixture was stirred at 60 °C for 12 h, then cooled to room temperature. DCM (50 mL) was added, and the mixture was washed with brine (15 mL × 2). The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure to obtain a residue. This residue was purified by flash column chromatography to yield **3a** as a colorless oil (PE: EA = 100:1). Yield: 291 mg, 78%.



5a **3a**

Scheme 9

To a solution of **5a** (1 mmol) in MeCN (1.5 mL), , DBDMH (0.5 mmol) was added. The reaction mixture was stirred at 60 °C for 12 h, then cooled to room temperature. DCM (50 mL) was added, and the reaction mixture was washed with brine (15 mL×2). The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure to obtain a residue. This residue was purified by flash column chromatography to yield **3a** as a colorless oil (PE: EA = 100:1). Yield: 283 mg, 76%.



5a **2a**

Scheme 10

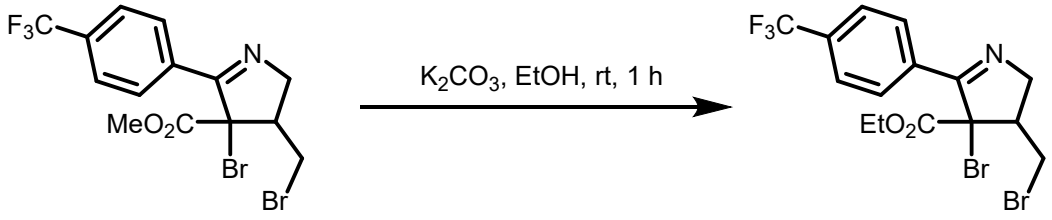
To a solution of **5a** (1 mmol) in MeCN (1.5 mL), $Cu(OAc)_2$ (2 mmol) was added. The reaction mixture was stirred at 60 °C for 2 h, then cooled to room temperature. DCM (50 mL) was added, and the mixture was washed with brine (15 mL × 2). The organic layer was dried over with Na_2SO_4, filtered and concentrated under reduced pressure to obtain a residue. This residue was purified by flash column chromatography to yield **2a** as a colorless oil (PE: EA = 10:1). Yield: 149 mg, 40%.

1a **4a**

Scheme 11

To a solution of N-allyl enamine **1a** (1 mmol) in DMF (1.5 mL), NIS (1 mmol) was added. The reaction mixture was stirred at room temperature for 4 h. After monitoring the reaction to completion by TLC, the reaction mixture was cooled to room temperature, and EtOAc (50 mL) was added. The reaction mixture was washed with brine (15 mL×2), and the organic layer was dried over with Na_2SO_4, filtered and concentrated under reduced pressure to obtain a residue. This residue was purified by flash column chromatography to yield 3-azabicyclo[3.1.0]hex-2-enes **4a** as a yellow oil (PE:EA = 5:1). Yield: 49 mg, 23%.

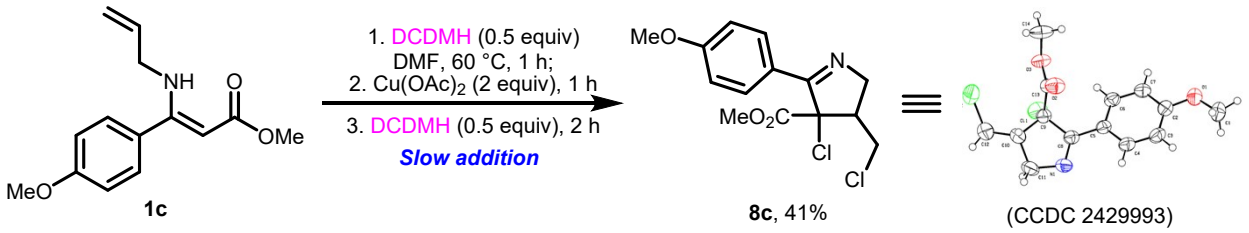
Application



2f **7f**, 96%

Scheme 12

To a solution of dibromo 1-pyrrolines **2f** (1 mmol) in EtOH (1.5 mL), K_2CO_3 (1.5 mmol) was added. The mixture was stirred at room temperature for 1 h. Upon completion (monitored by TLC), the reaction mixture was cooled to room temperature, and EtOAc (50 mL) was added. The organic layer was washed with brine (15 mL × 2), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a residue. The residue was purified by flash column chromatography to yield **7f** as a yellow oil (PE:EA = 10:1). Yield: 437 mg, 96%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, J = 8.3 Hz, 2H), 7.66 (d, J = 8.3 Hz, 2H), 4.39 (dd, J = 16.7, 6.7 Hz, 1H), 4.23 (qd, J = 7.1, 0.7 Hz, 2H), 3.73–3.61 (m, 3H), 3.32–3.19 (m, 1H), 1.15 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.6, 167.2, 134.0, 133.0 (q, J = 32 Hz), 128.5, 125.5 (q, J = 3 Hz), 123.6 (d, J = 271 Hz), 70.2, 64.0, 62.6, 53.3, 29.7, 13.7. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{15}H_{15}Br_2F_3NO_2$: 455.9422; found: 455.9420.



Scheme 13

To a solution of N-allyl enamine **1c** (1 mmol) in DMF (1.5 mL), DCDMH (0.5 mmol) was added. The mixture was stirred at 60 °C for 1 h, after which $Cu(OAc)_2$ (2 mmol) was added. After 1 hour, an additional portion of DCDMH (0.5 mmol) was added in 5 batches over 2 hours. Upon completion (monitored by TLC), the reaction mixture was cooled to room temperature, and EtOAc (50 mL) was added. The organic layer was washed with brine (15 mL × 2), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a residue. The residue was purified by flash column chromatography to yield **8c** as a yellow solid (PE:EA = 10:1). Yield: 129 mg, 41%; mp 88-89 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.72 (m, 2H), 6.92–6.86 (m, 2H), 4.37–4.30 (m, 1H), 3.94–3.85 (m, 2H), 3.83 (s, 3H), 3.76 (s, 3H), 3.74–3.69 (m, 1H), 3.52–3.36 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.3, 168.7, 161.8, 131.0, 129.3, 123.5, 114.0, 61.9, 55.3, 54.1, 53.6, 41.3, 25.8. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{16}Cl_2NO_3$: 316.0507; found: 316.0508.

X-Ray crystallographic studies

Method of crystallization: A solution of **2f**, **4j** and **8c** in CH_2Cl_2 was left in the hood, and the solvent was allowed to evaporate slowly. The crystal structures have been deposited at the Cambridge Crystallographic Data Centre. CCDC 2402930 (**2f**), CCDC 2429981 (**4j**) and 2429993 (**8c**) which contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via the internet at https://www.ccdc.cam.ac.uk/structures/

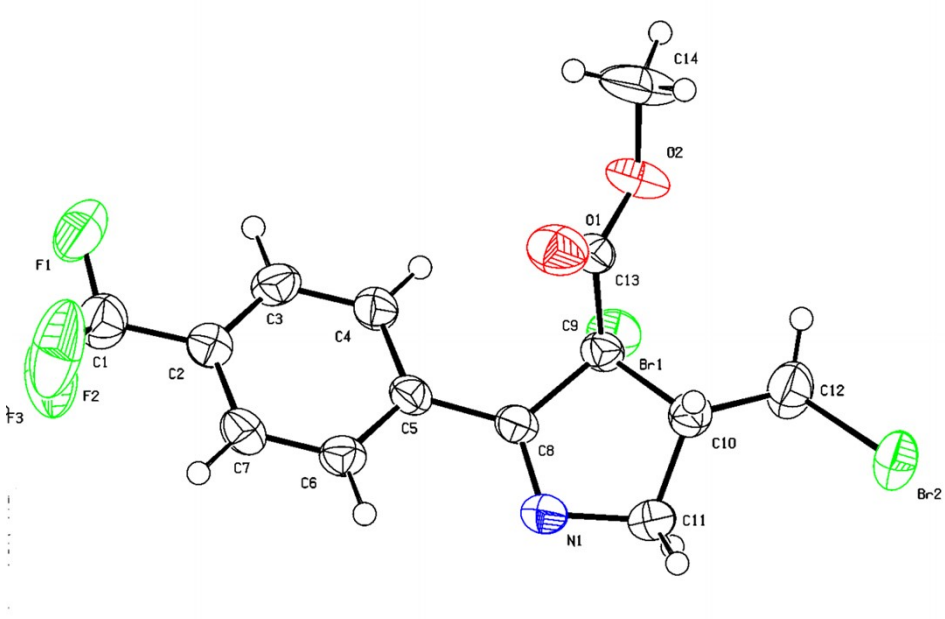


Figure S1. ORTEP X-ray structure of **2f**

Table S1. Crystal data and structure refinement for **2f**

Empirical formula	$C_{14}H_{12}Br_2F_3NO_2$
Formula weight	443.07
Temperature	296.15 K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, P-1
Unit cell dimensions	a= 7.8205(4) Å alpha = 69.3080(10)° b= 9.2042(4) Å beta = 77.6970(10)° c= 11.7867(5) Å gamma = 86.335(2)°
Volume	775.41(6) $Å^3$
Z, Calculated density	2, 1.898 g/cm^3
Absorption coefficient	5.264 mm^{-1}
F(000)	432.0
Crystal size	0.22×0.2×0.18 mm^3
Theta range for data collection	5.332 to 56.658°
Index ranges	-10<=h<=10, -11<=k<=12, -15<=l<=15
Reflections collected	14548
Independent reflections	3807 [R(int) = 0.0408, R(sigma) = 0.0527]
Completeness to theta = 28.329°	98.2 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3807 / 0 / 200
Goodness-of-fit on F^2	1.017
Final R indices [I>2sigma(I)]	R1 = 0.0438, wR2 = 0.0924
R indices (all data)	R1 = 0.0867, wR2 = 0.1080

Extinction coefficient	n/a
Largest diff. peak and hole	0.93 and -0.52 e. Å $^{-3}$

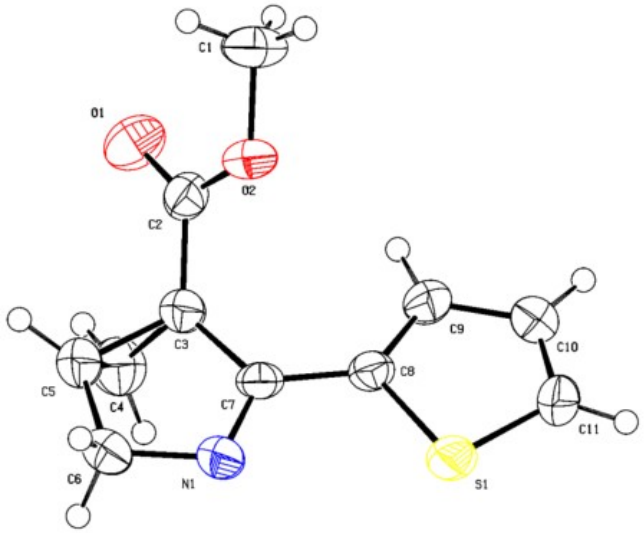


Figure S2. ORTEP X-ray structure of **4j**

Table S2. Crystal data and structure refinement for **4j**

Empirical formula	$C_{11}H_{11}NO_2S$
Formula weight	221.27
Temperature	296.15 K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/n$
Unit cell dimensions	a= 6.601(3) Å alpha = 90° b= 6.611(3) Å beta = 97.223(14)° c= 24.701(9) Å gamma = 90°
Volume	1069.4(8) Å^3
Z, Calculated density	4, 1.374 g/cm^3
Absorption coefficient	0.281 mm^{-1}
F(000)	464.0
Crystal size	0.22×0.2×0.18 mm^3
Theta range for data collection	6.234 to 50.06°
Index ranges	-7<=h<=7, -6<=k<=7, -29<=l<=29
Reflections collected	11335
Independent reflections	1858 [R(int) = 0.0518, R(sigma) = 0.0407]
Completeness to theta = 25.030°	98.5 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1858 / 0 / 137
Goodness-of-fit on F^2	1.064

Final R indices [I>2sigma(I)]	R1 = 0.0536, wR2 = 0.1166
R indices (all data)	R1 = 0.0818, wR2 = 0.1306
Extinction coefficient	n/a
Largest diff. peak and hole	0.19 and -0.26 e. Å $^{-3}$

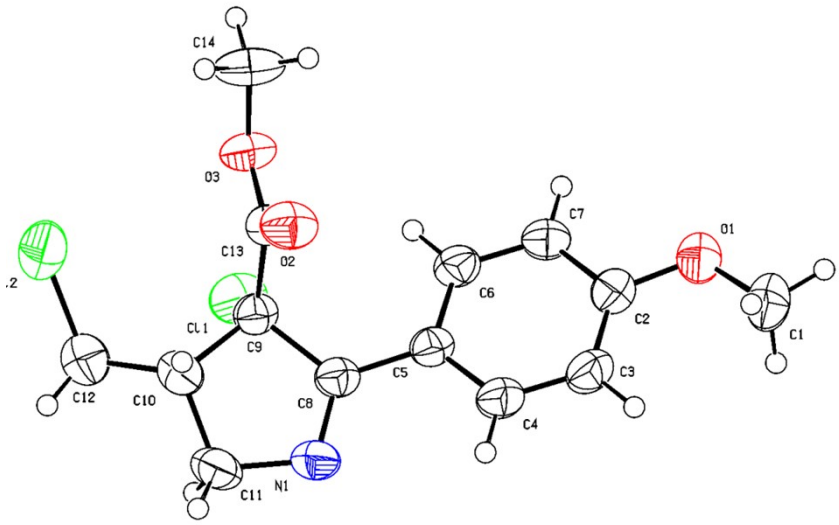


Figure S3. ORTEP X-ray structure of **8c**

Table S3. Crystal data and structure refinement for **8c**

Empirical formula	$C_{14}H_{15}Cl_2NO_3$
Formula weight	316.17
Temperature	296.15 K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, P-1
Unit cell dimensions	a= 7.1404(6) Å alpha = 102.274(3)° b= 9.9152(10) Å beta = 95.146(2)° c= 11.5518(10) Å gamma =111.046(2)°
Volume	733.38(12) Å^3
Z, Calculated density	2, 1.432 g/cm^3
Absorption coefficient	0.448 mm^{-1}
F(000)	328.0
Crystal size	0.22×0.2×0.18 mm^3
Theta range for data collection	5.046 to 50.096°
Index ranges	-8<=h<=7, -11<=k<=11, -13<=l<=13
Reflections collected	9849
Independent reflections	2563 [R(int) = 0.0510, R(sigma) = 0.0613]
Completeness to theta = 25.048°	98.8 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2563 / 0 / 183

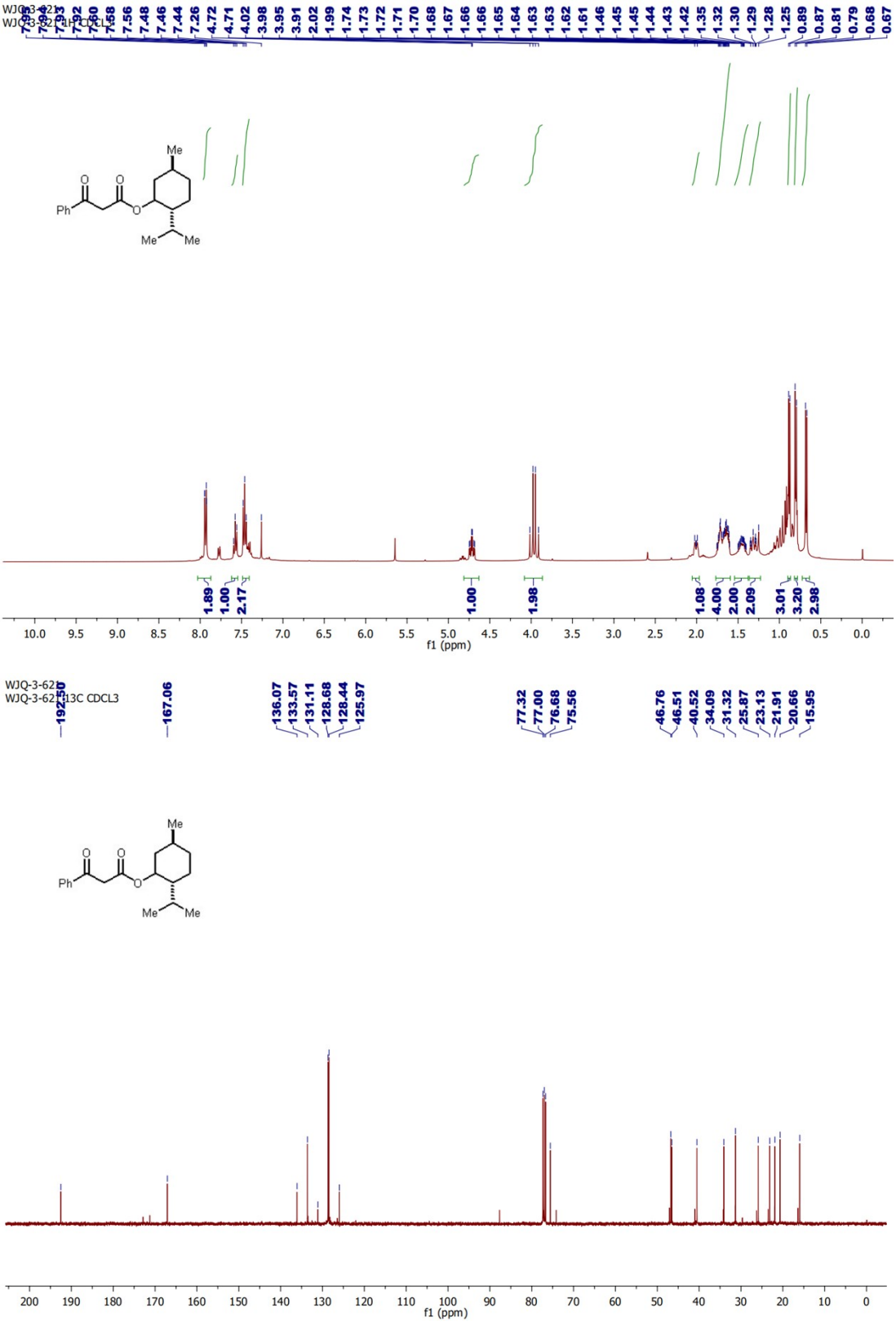
Goodness-of-fit on F^2	1.013
Final R indices [I>2sigma(I)]	R1 = 0.0516, wR2 = 0.0847
R indices (all data)	R1 = 0.1116, wR2 = 0.1063
Extinction coefficient	n/a
Largest diff. peak and hole	0.25 and -0.29 e. Å $^{-3}$

References

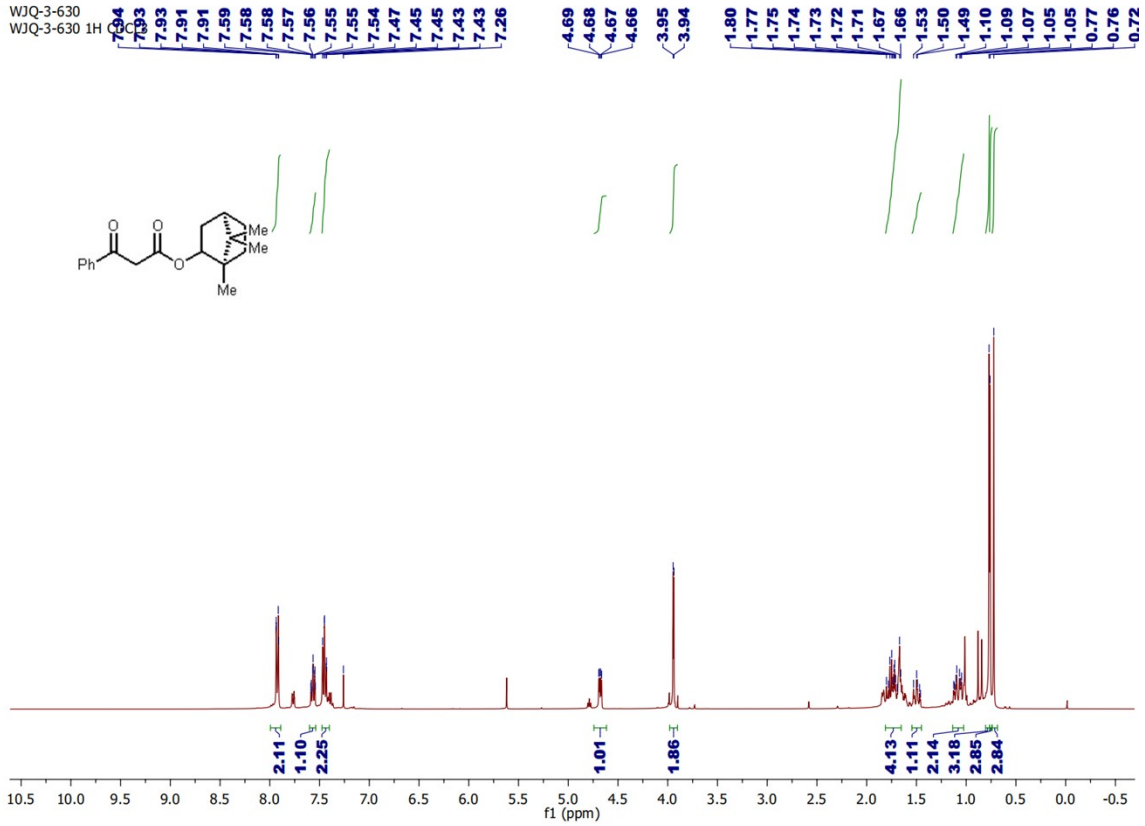
1. Duan, X.-Y.; Wang, J.-Q.; Li, H.; Du, F.-J.; Chen, R.; Lian, W.-D.; Shi, M.-X., Tandem site-selective bromination and highly regioselective Heck reaction of N-allyl enaminones: chemodivergent synthesis of polysubstituted pyrroles and pyridines. Organic Chemistry Frontiers **2024**, 11(19), 5532-5537.
2. Toh, K. K.; Biswas, A.; Wang, Y.-F.; Tan, Y. Y.; Chiba, S., Copper-Mediated Oxidative Transformation of N-Allyl Enamine Carboxylates toward Synthesis of Azaheterocycles. *Journal of the American Chemical Society* **2014**, *136* (16), 6011-6020.
3. Baidya, M.; Kumbhakar, P.; De Sarkar, S., Metal-Free Electrocatalytic Synthesis of Fused Azabicycles from N-Allyl Enamine Carboxylates. Organic Letters **2024**, 26(13), 2651-2655.
4. Zhai, S.-X.; Dong, H.-R.; Chen, Z.-B.; Hu, Y.-M.; Dong, H.-S., Cascade synthesis of 3-aza-bicyclo[3.1.0]hex-2-ene derivatives from N-allyl enamines. *Tetrahedron* **2014**, *70* (44), 8405-8412.

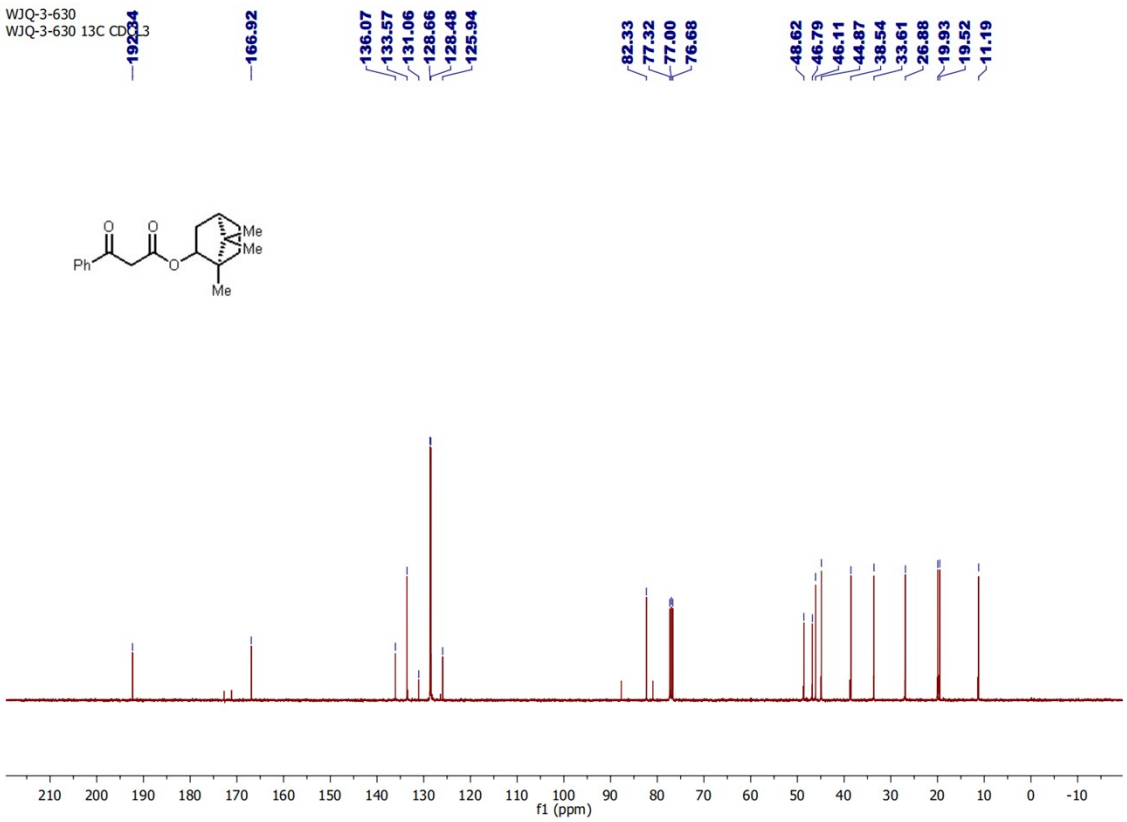
NMR Spectra

(2R,5S)-2-isopropyl-5-methylcyclohexyl 3-oxo-3-phenylpropanoate (**S1**)

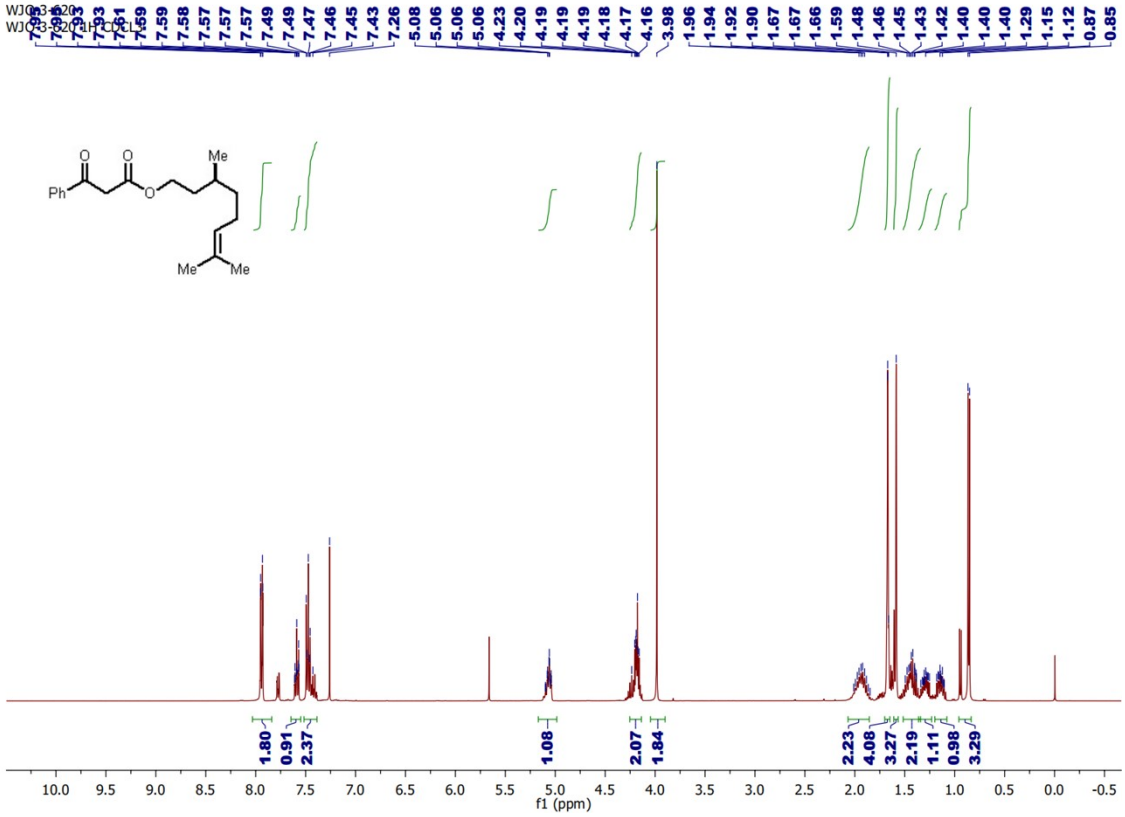


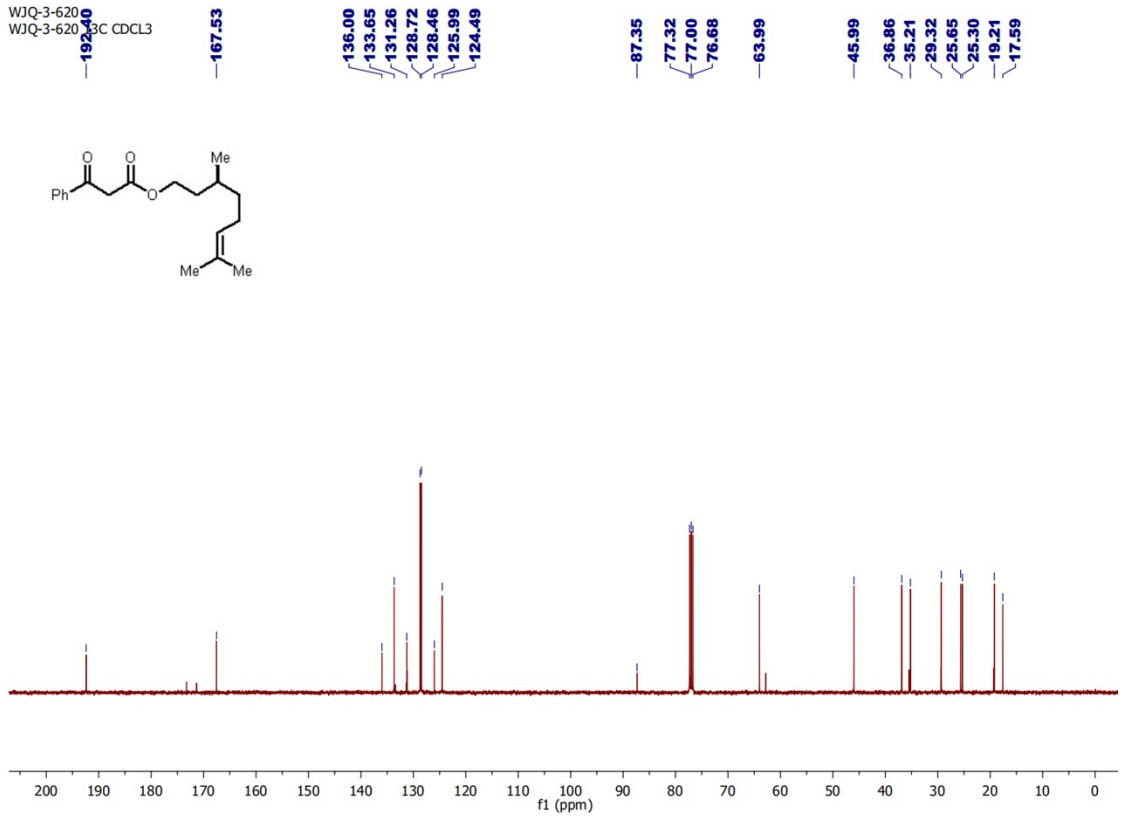
(1R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 3-oxo-3-phenylpropanoate (**S2**)



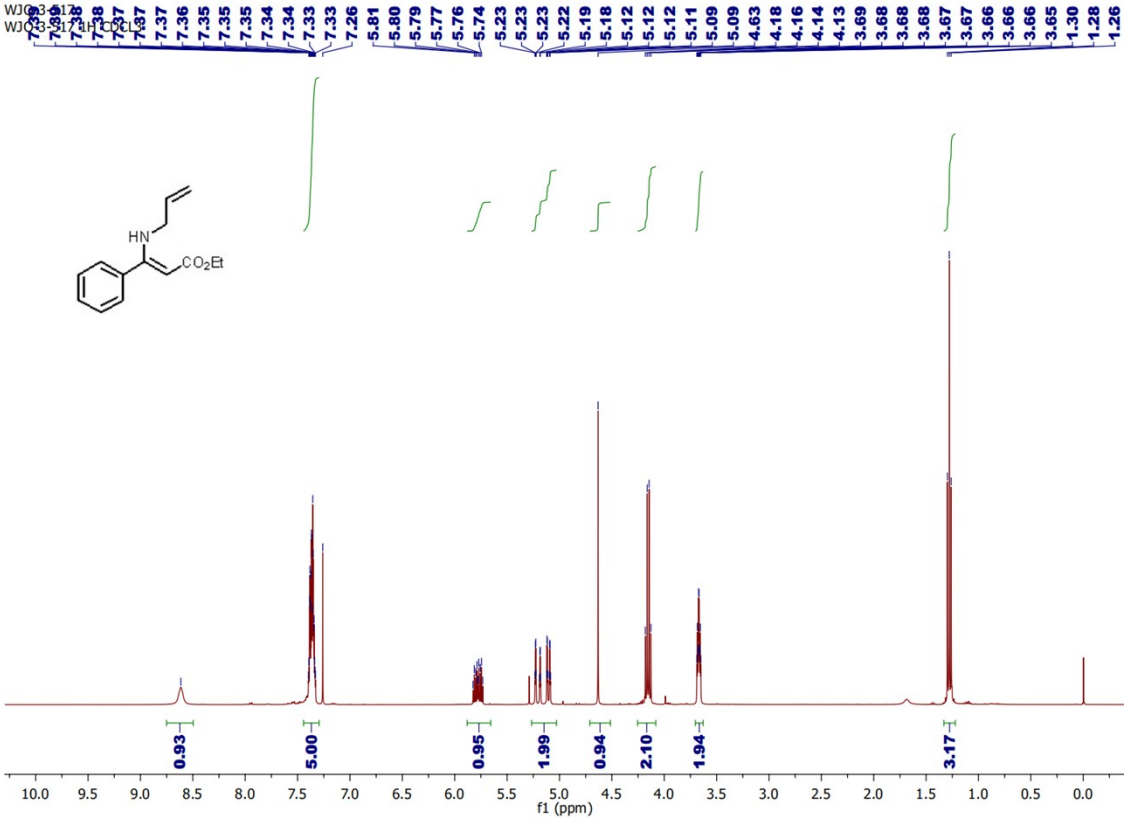


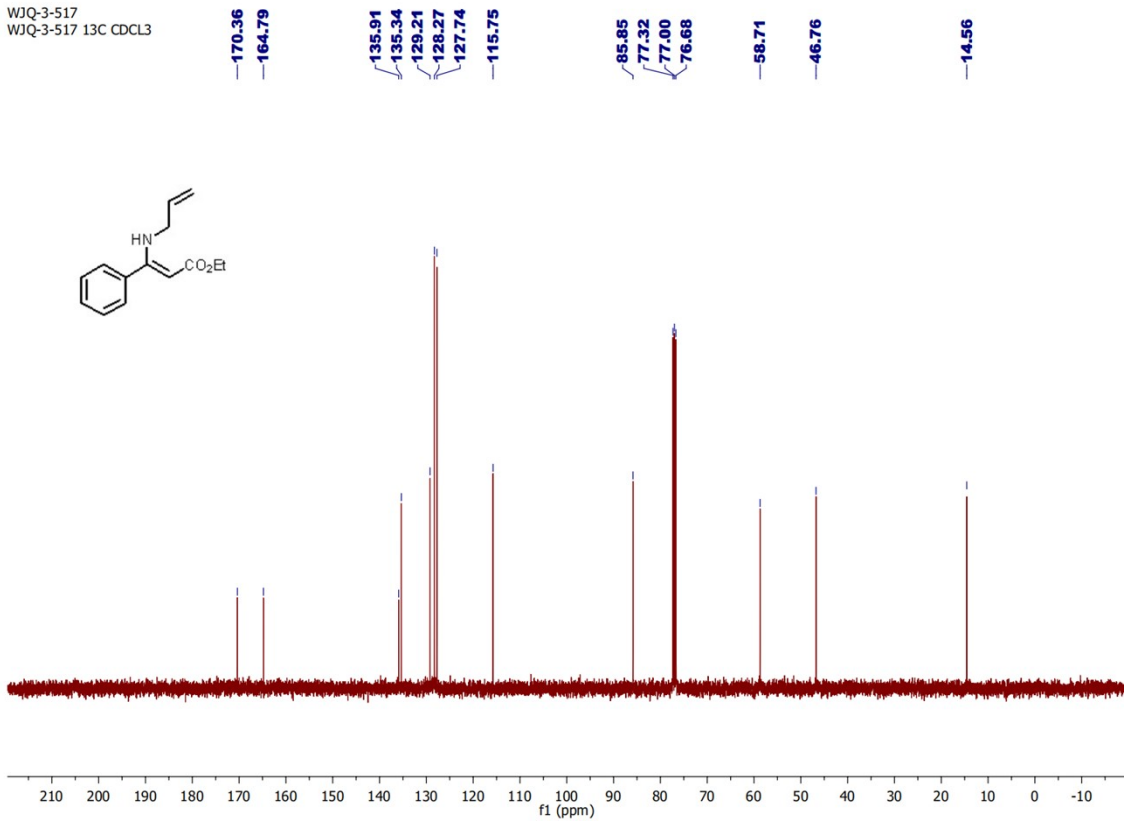
(S)-3,7-dimethyloct-6-en-1-yl 3-oxo-3-phenylpropanoate (**S3**)



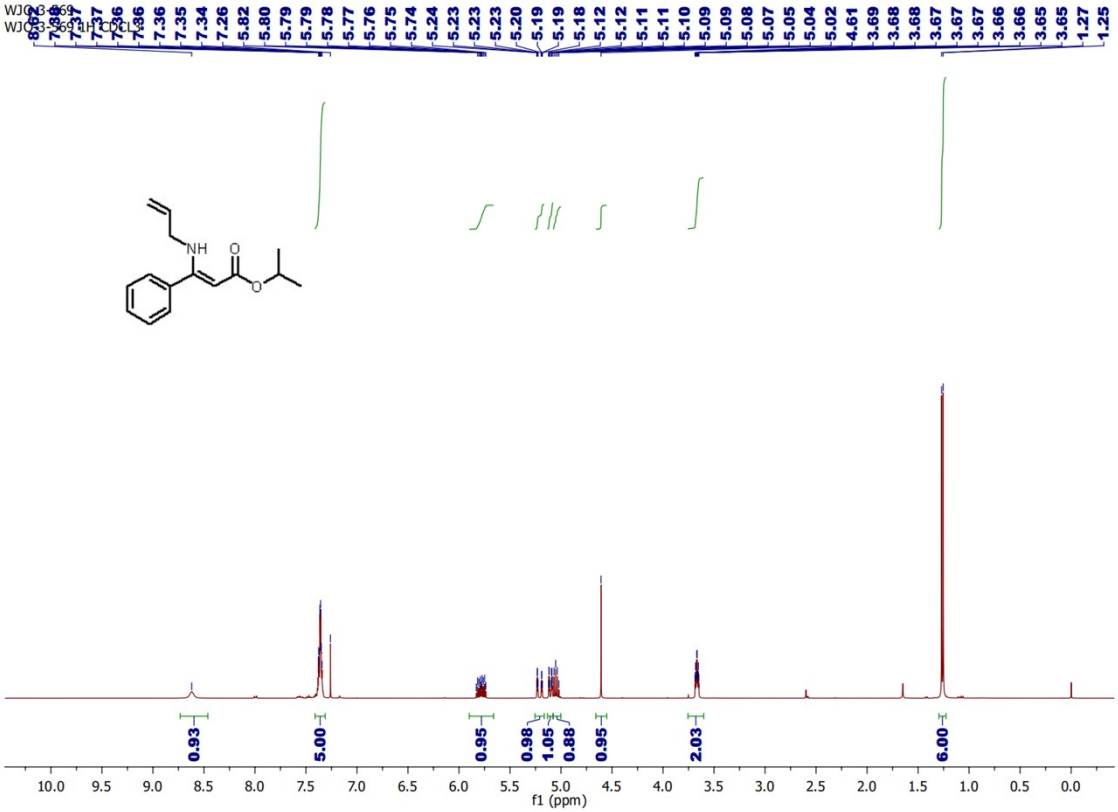


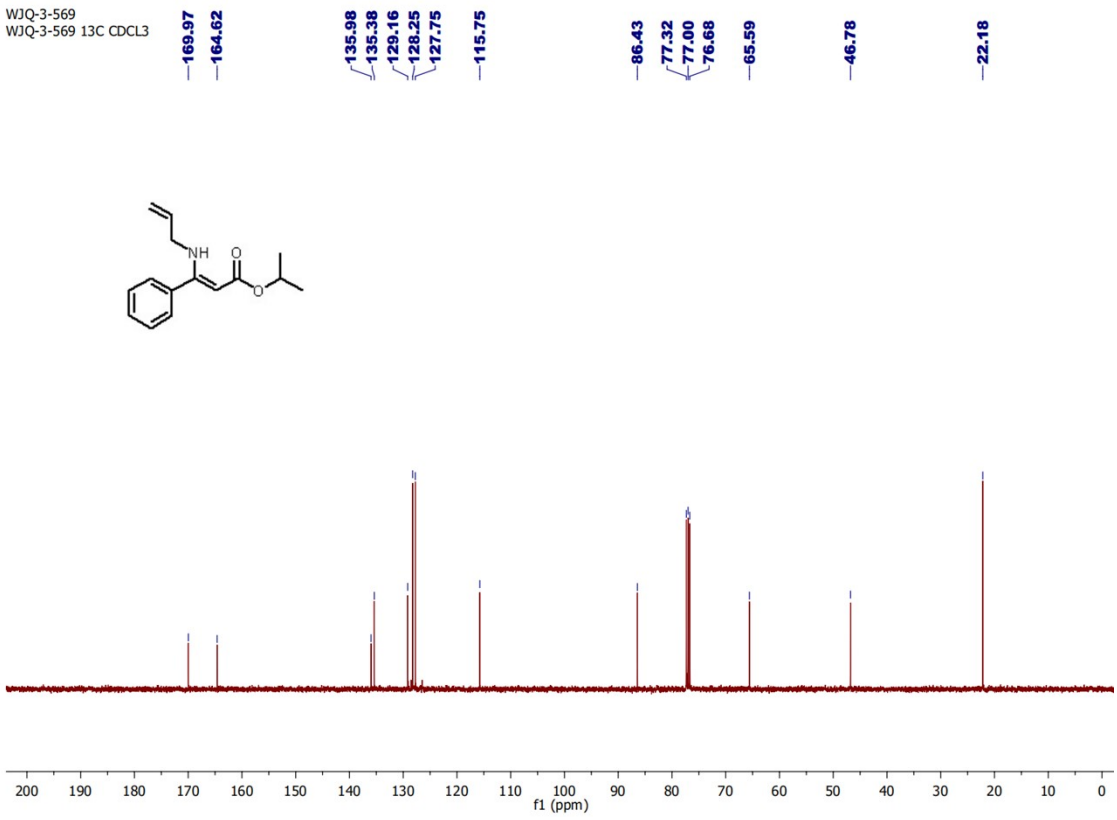
ethyl (Z)-3-(allylamino)-3-phenylacrylate (**1k**)



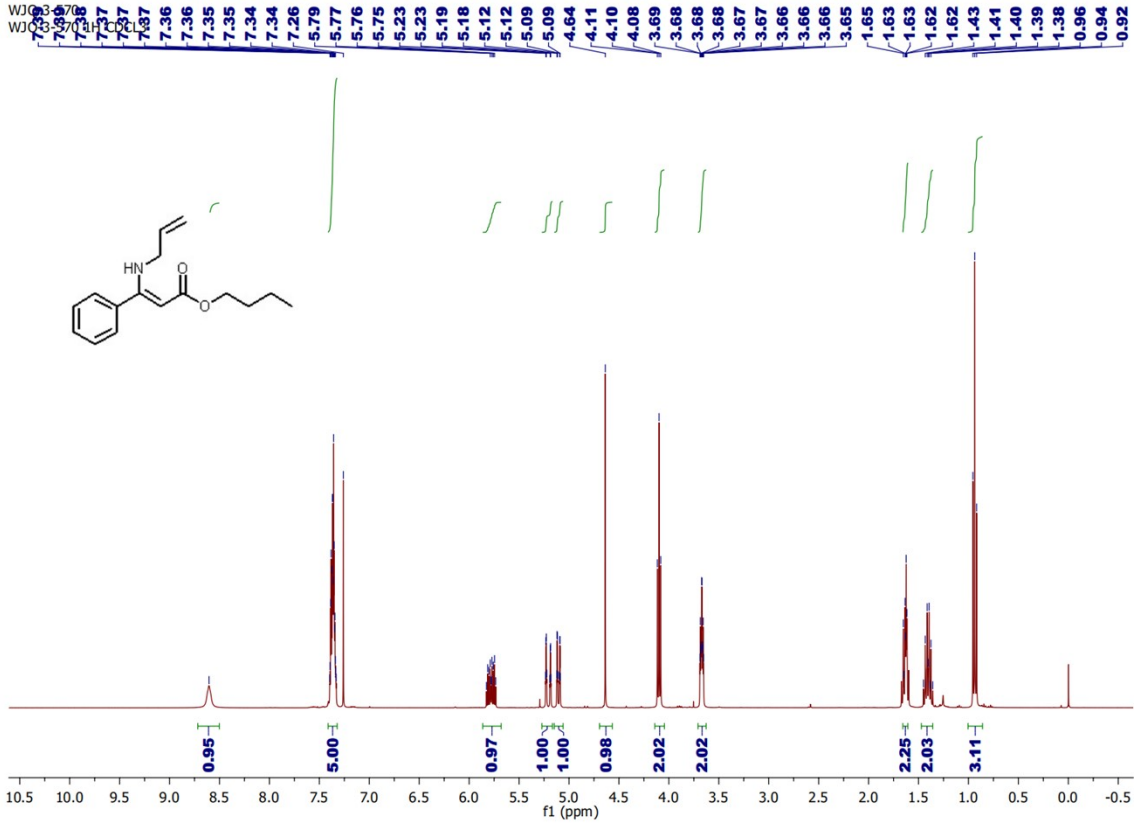


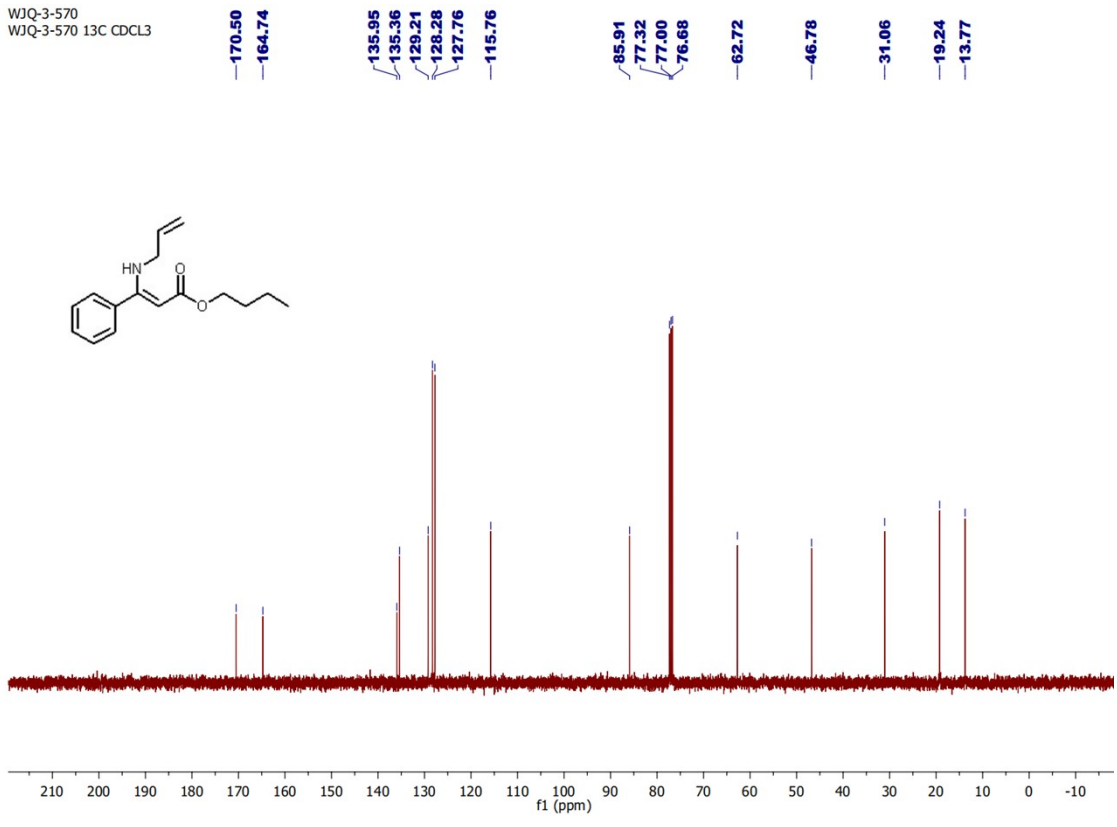
isopropyl (Z)-3-(allylamino)-3-phenylacrylate (**1l**)



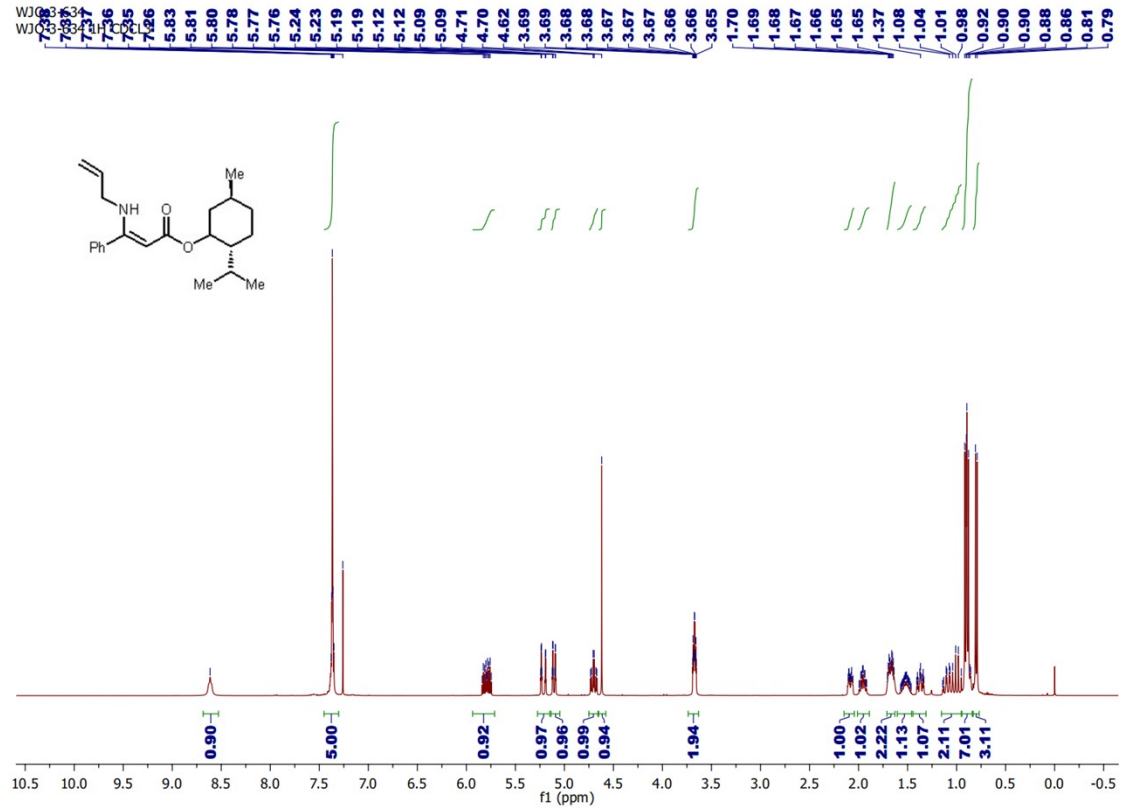


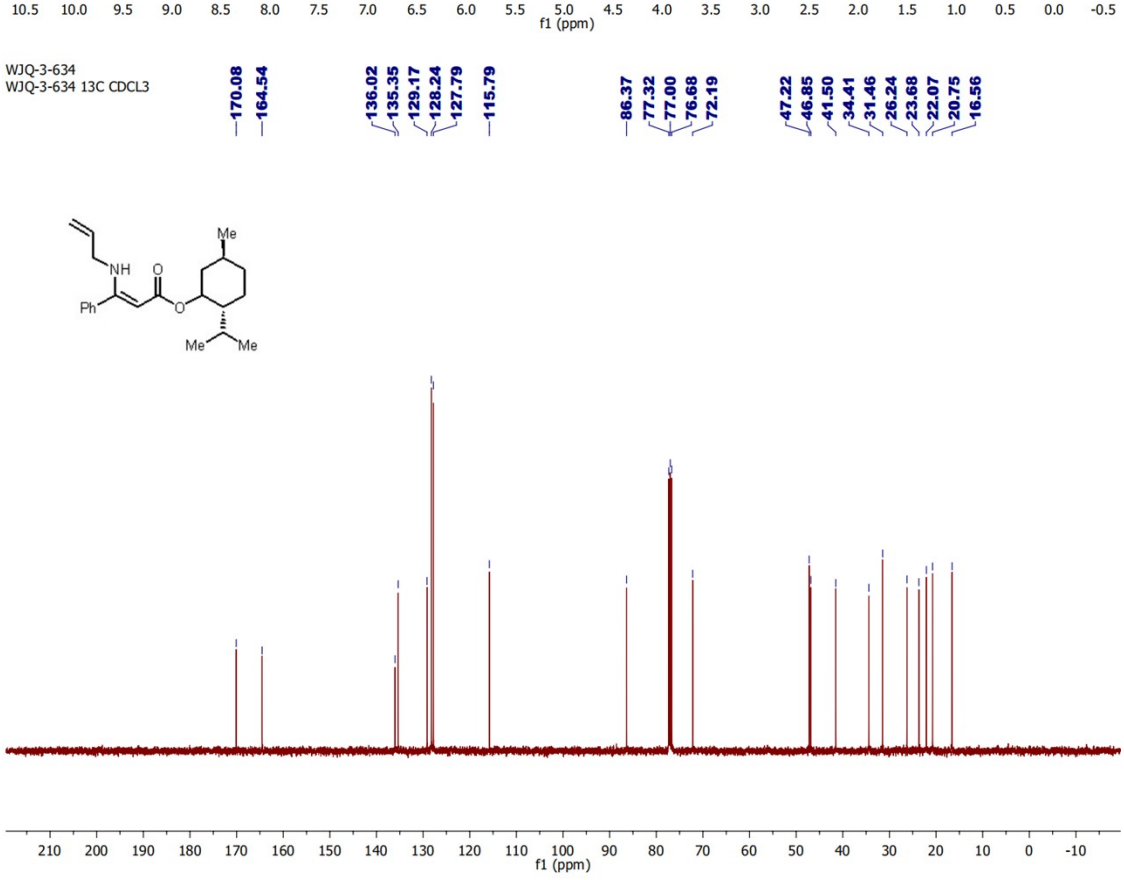
butyl (Z)-3-(allylamino)-3-phenylacrylate (**1m**)



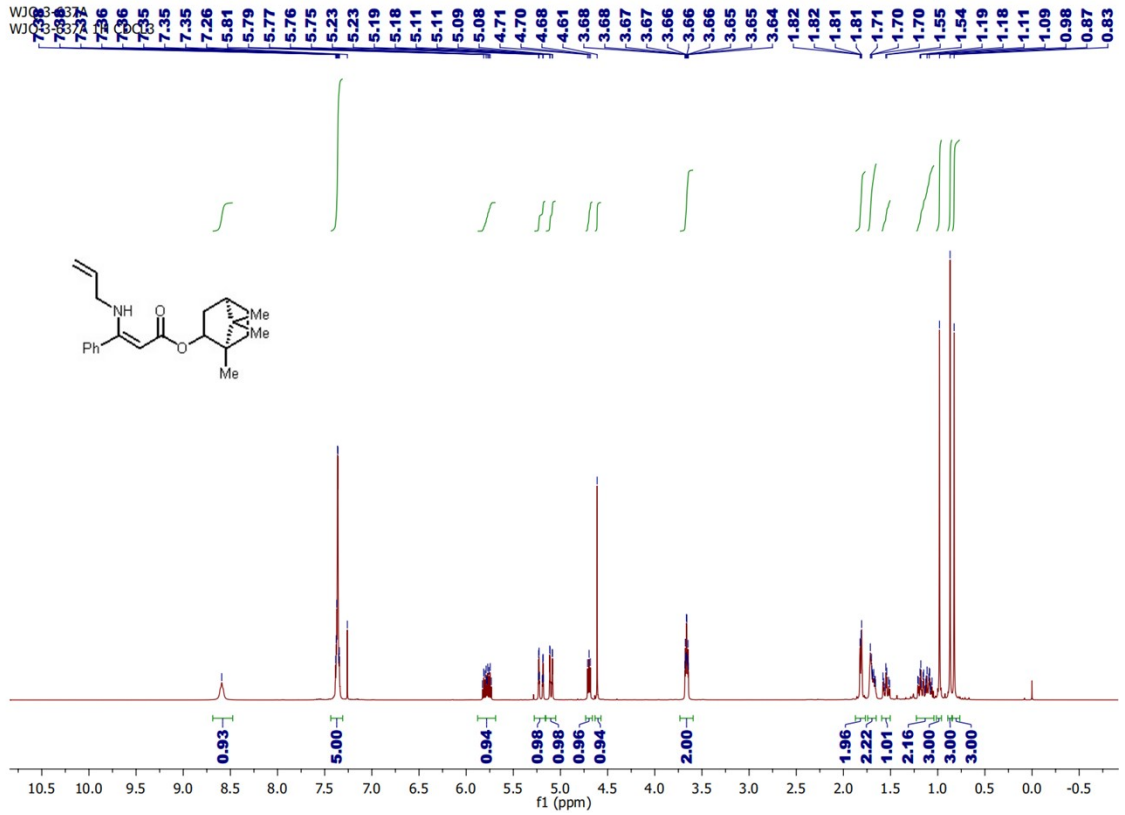


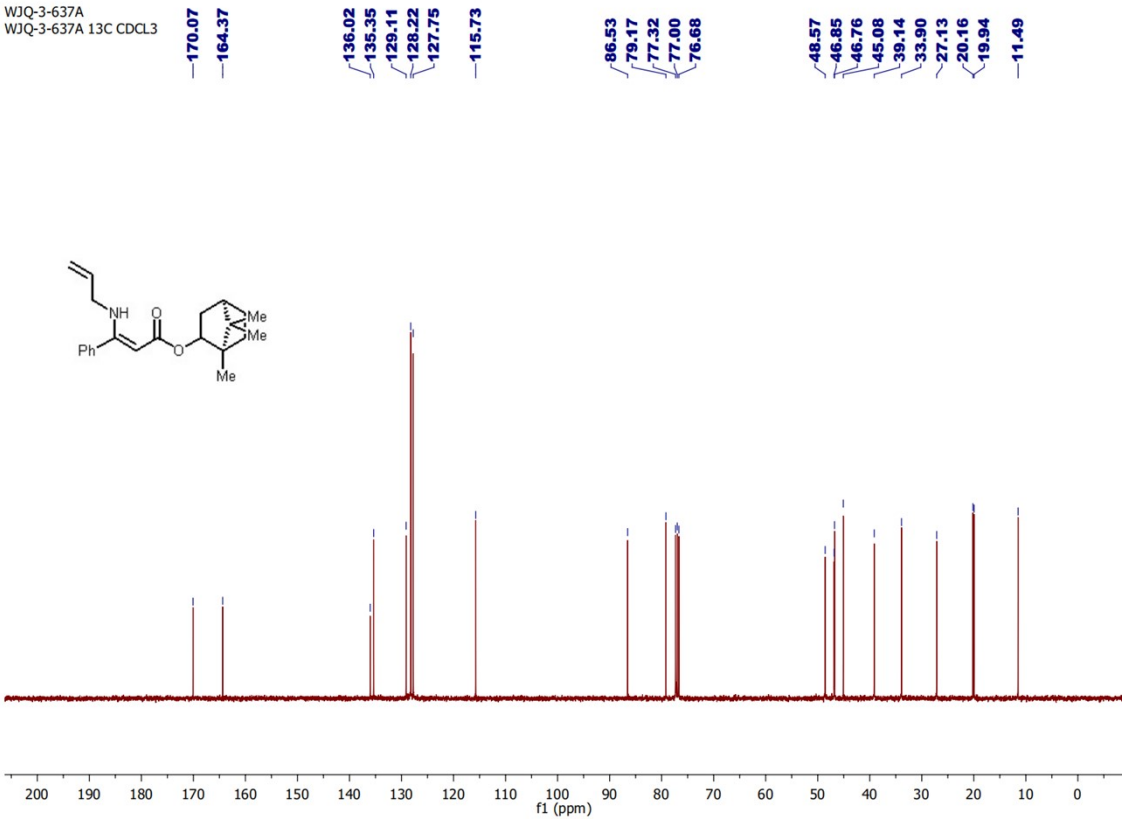
(2R,5S)-2-isopropyl-5-methylcyclohexyl (Z)-3-(allylamino)-3-phenylacrylate (**1n**)



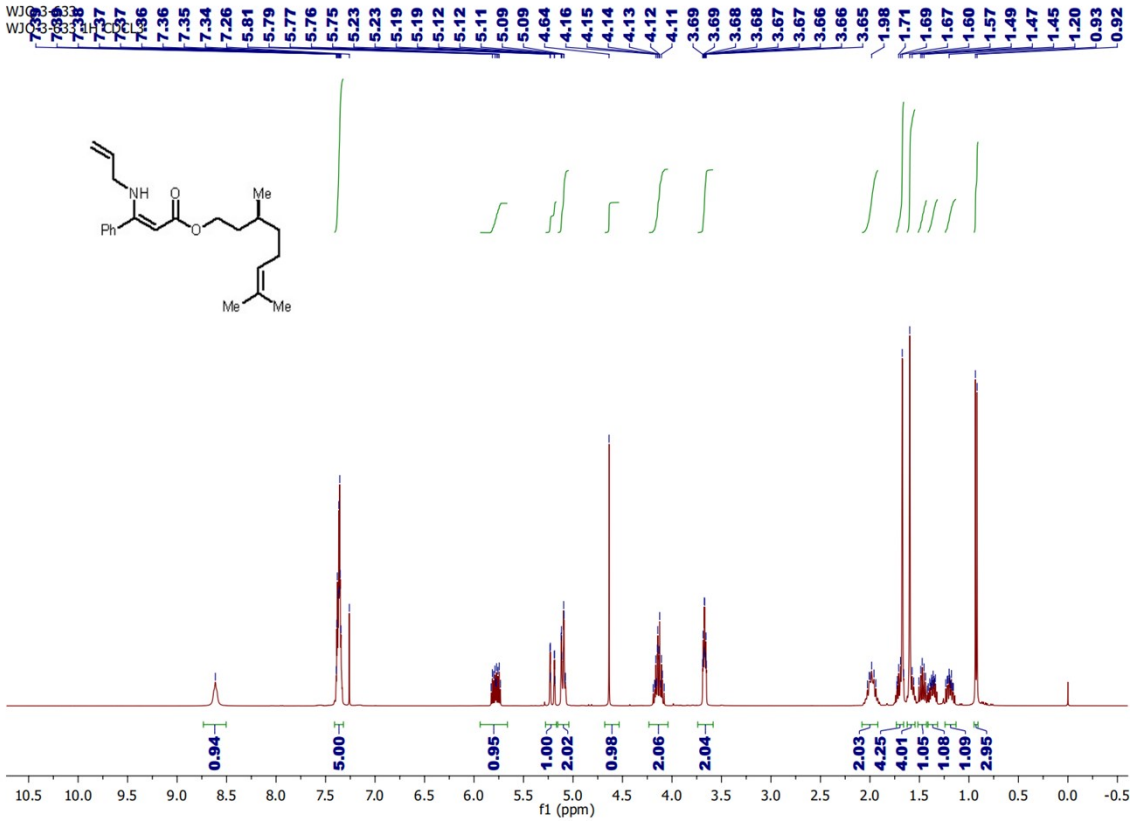


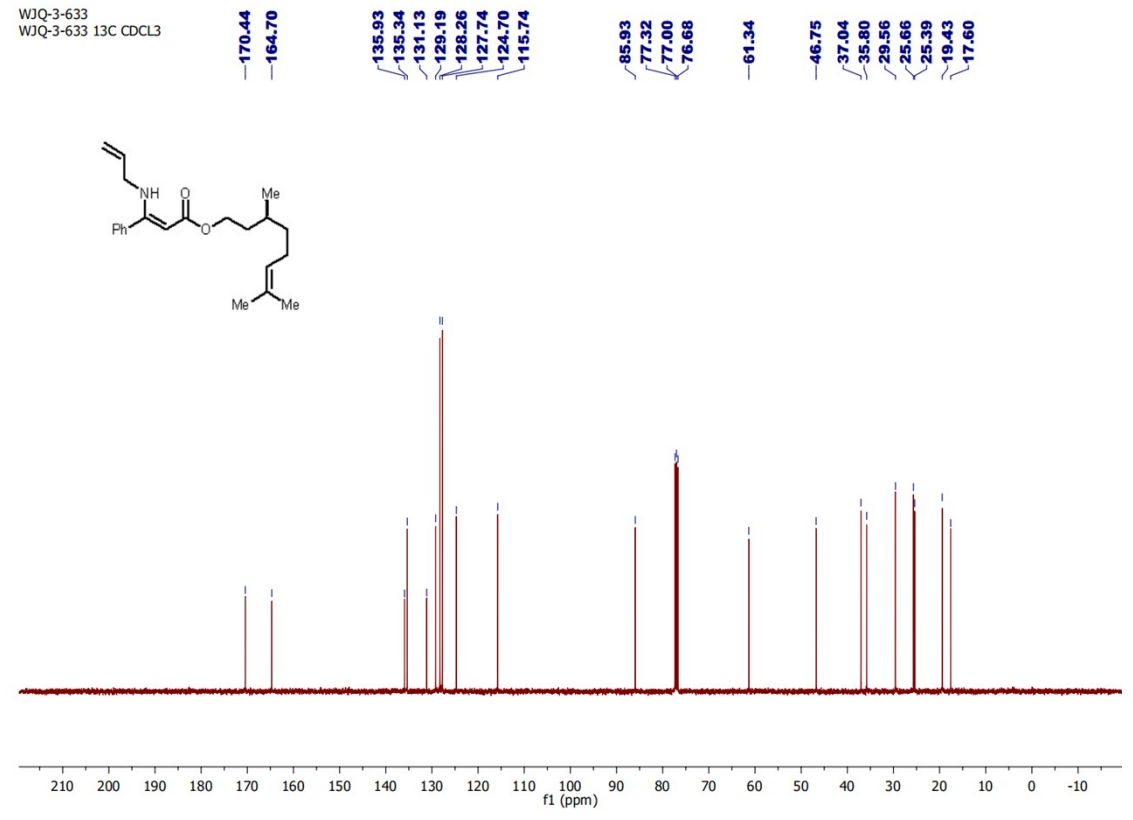
(1R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl (Z)-3-(allylamino)-3-phenylacrylate (**1o**)



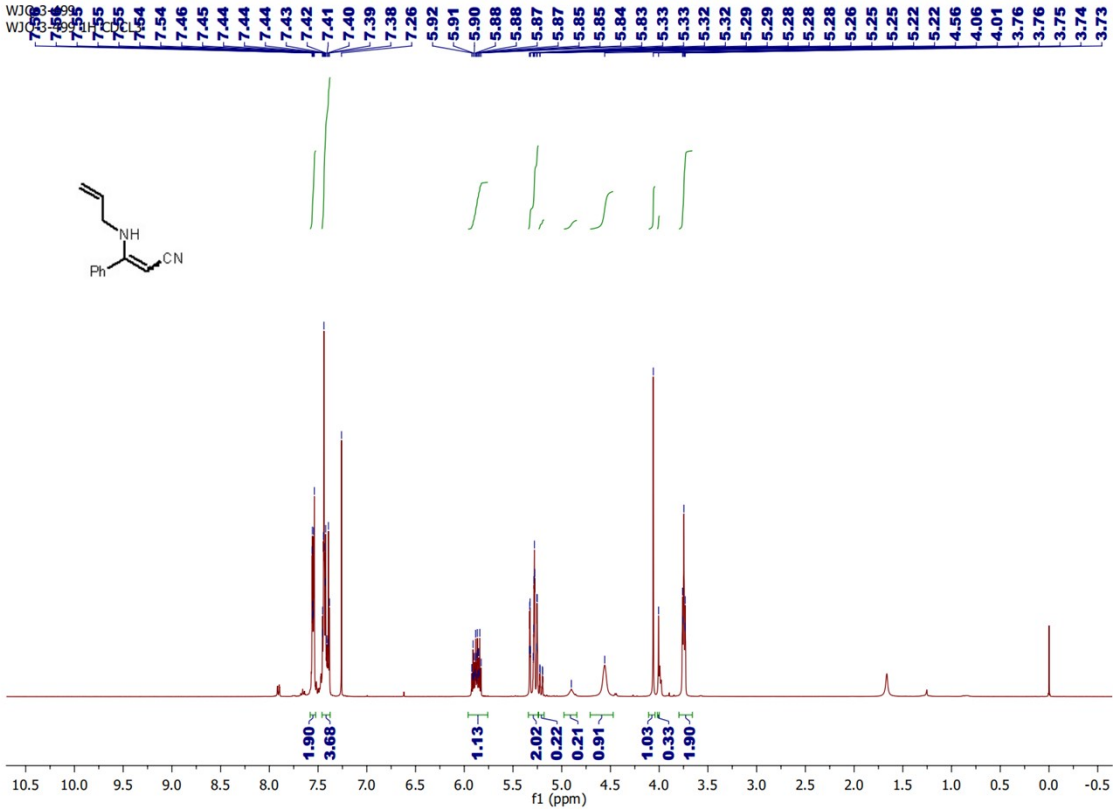


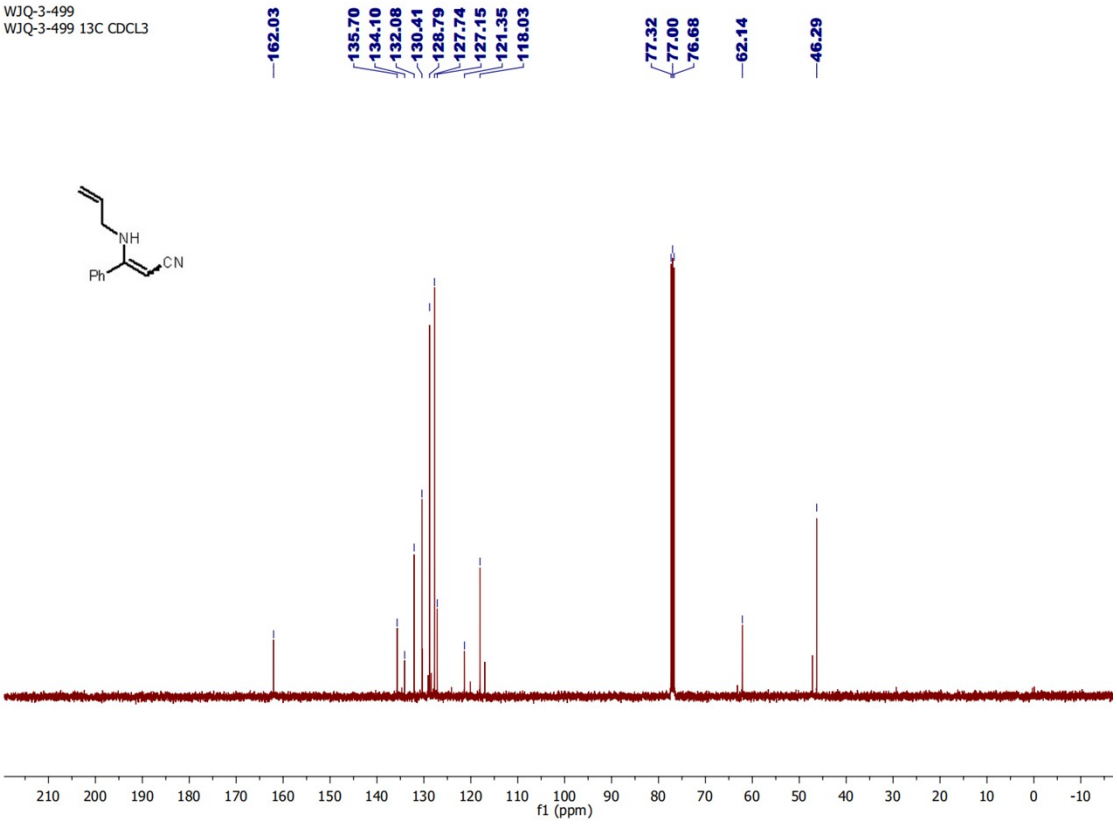
(S)-3,7-dimethyloct-6-en-1-yl (Z)-3-(allylamino)-3-phenylacrylate (**1p**)



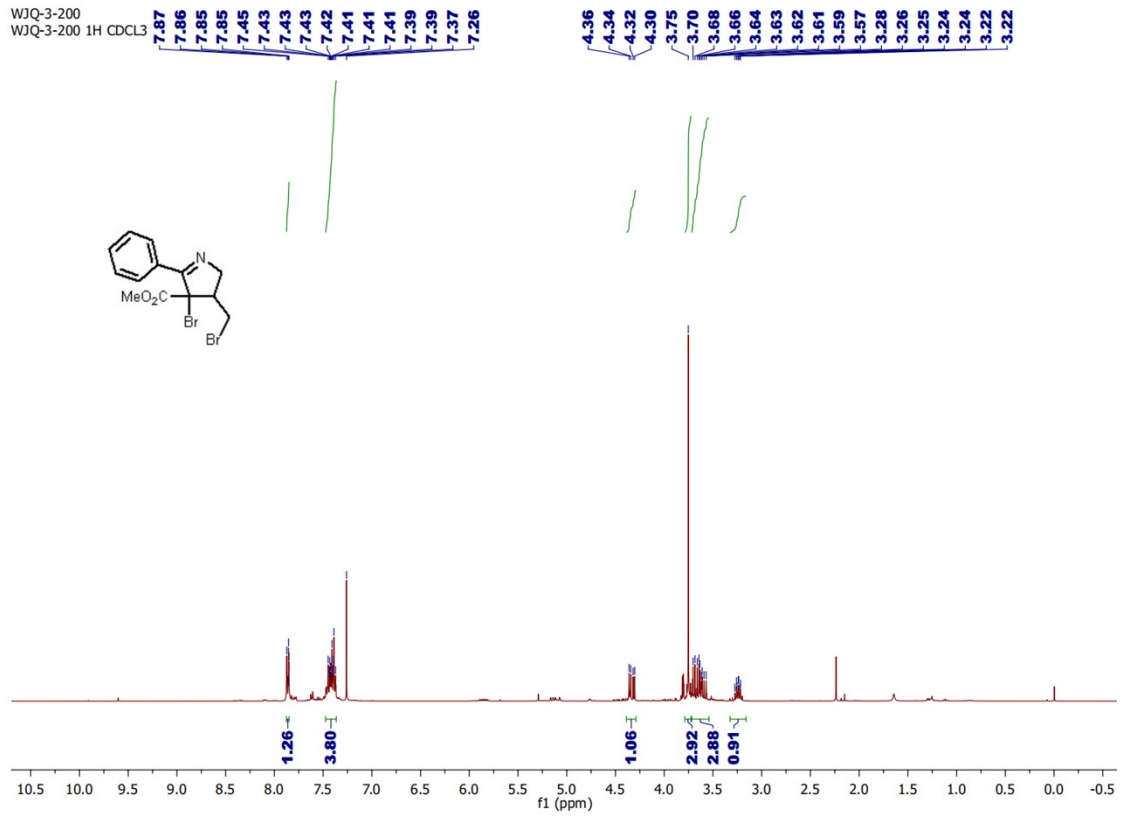


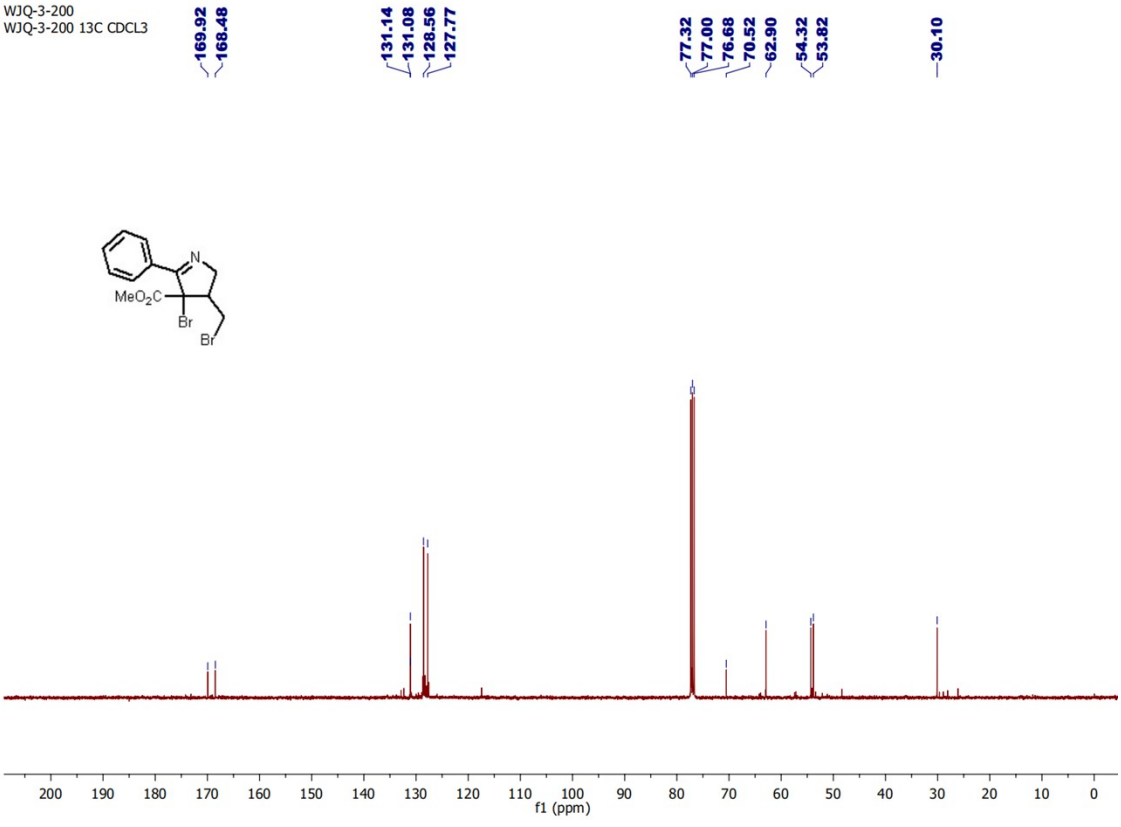
3-(allylamino)-3-phenylacrylonitrile (**1r**)



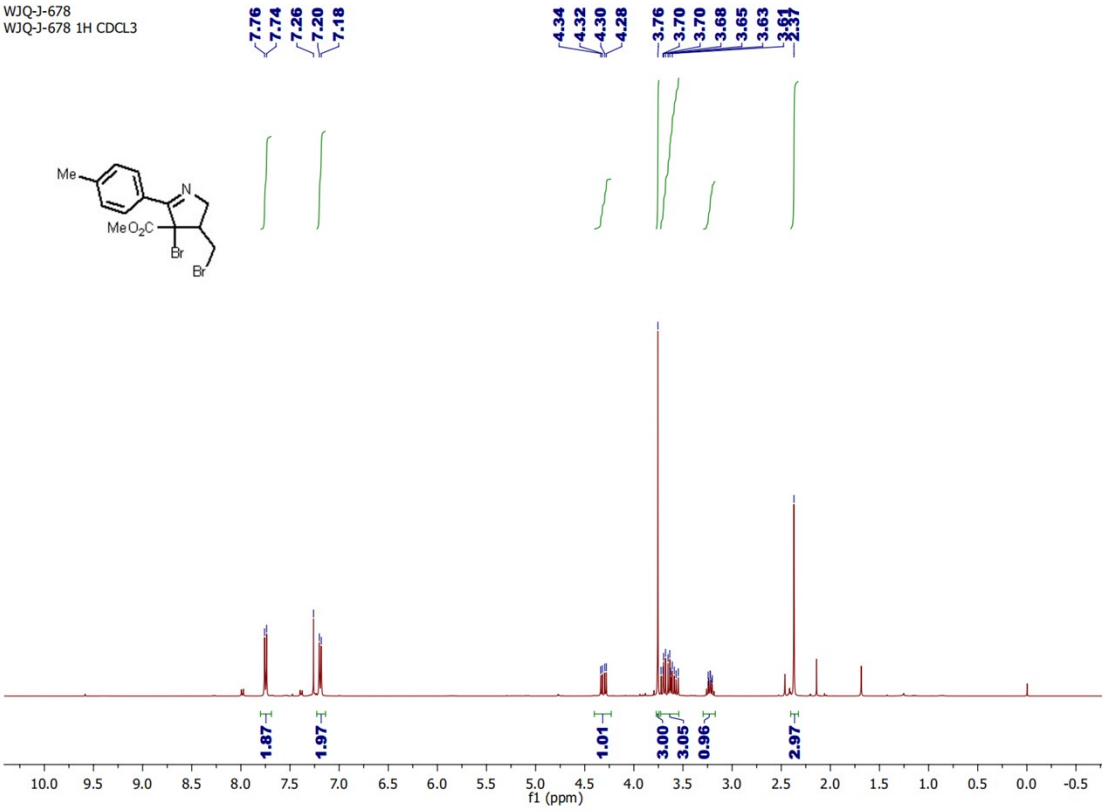


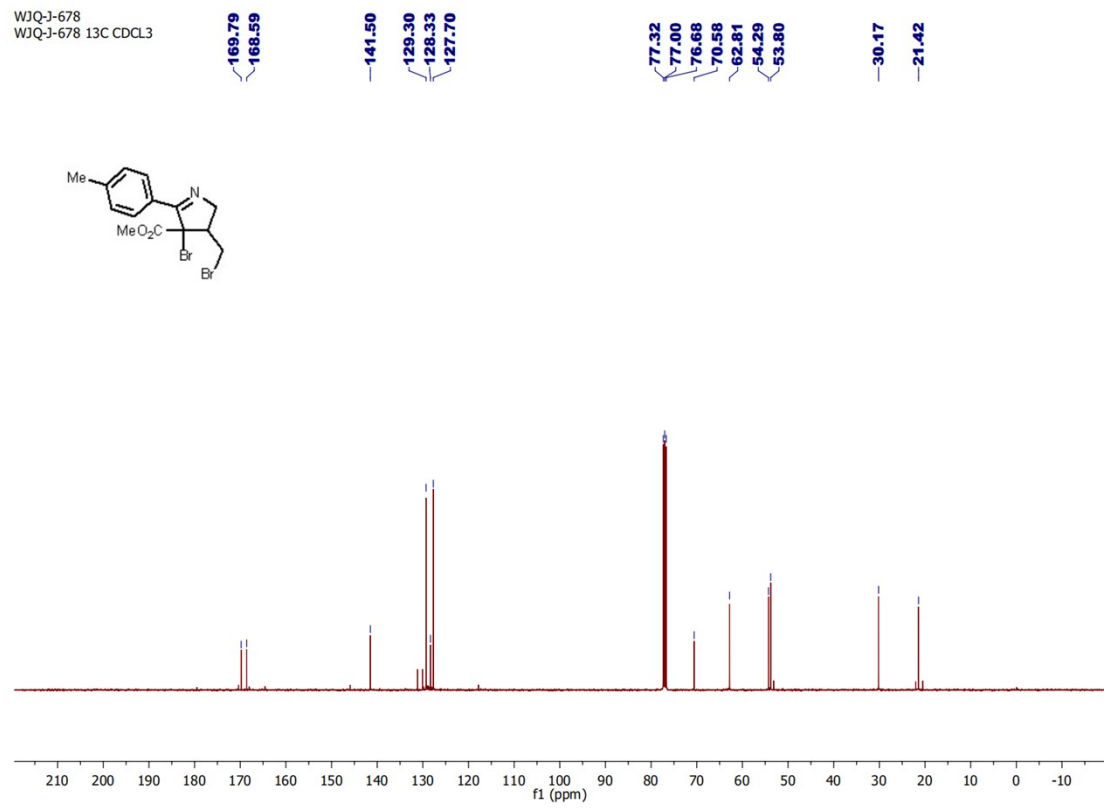
methyl 4-bromo-3-(bromomethyl)-5-phenyl-3,4-dihydro-2H-pyrrole-4-carboxylate (**2a**)



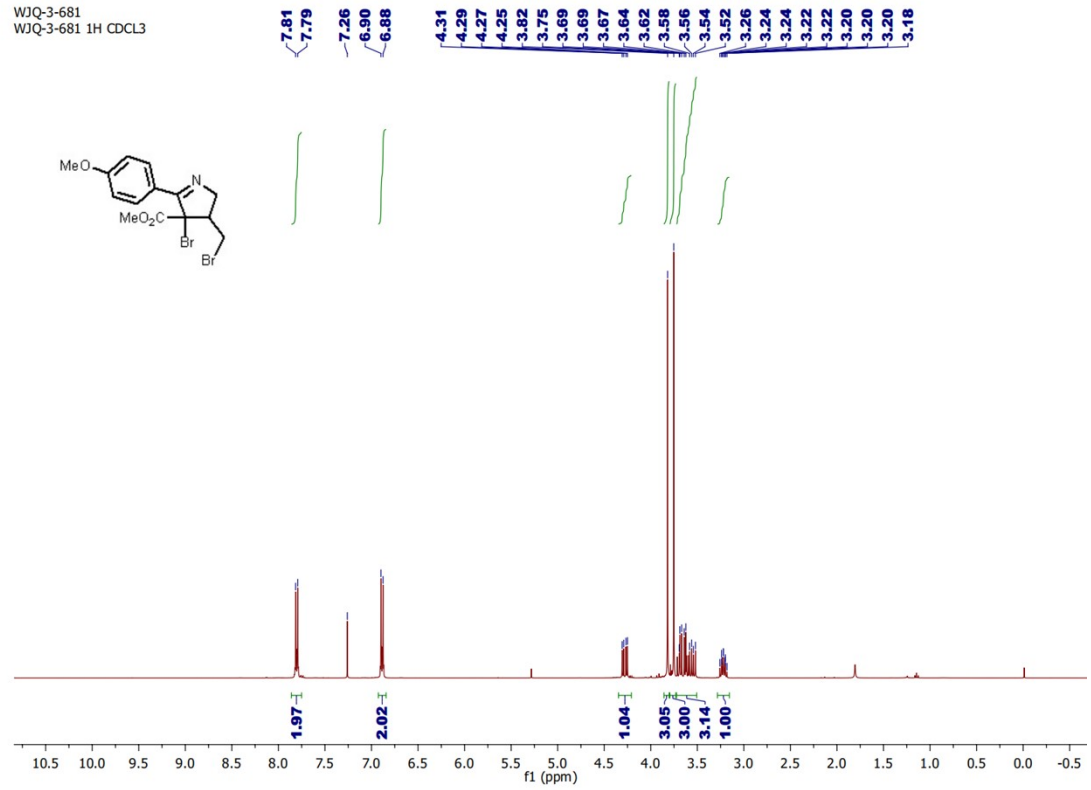


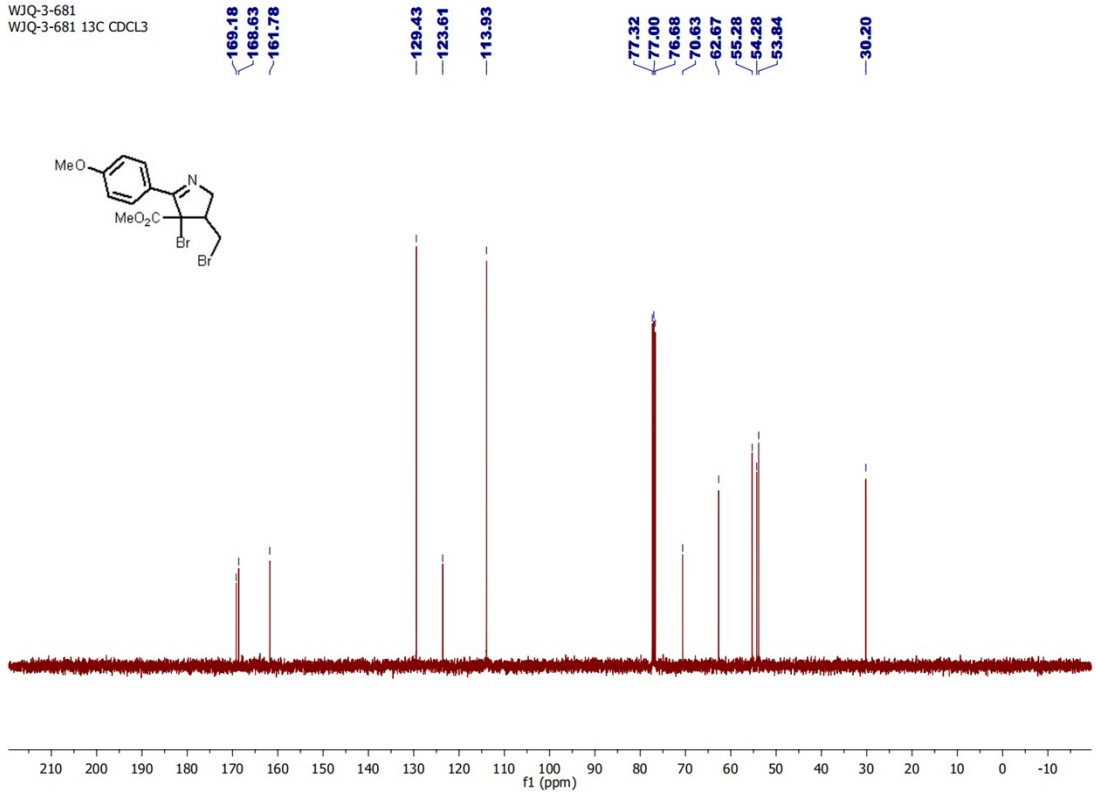
methyl 4-bromo-3-(bromomethyl)-5-(p-tolyl)-3,4-dihydro-2H-pyrrole-4-carboxylate (**2b**)



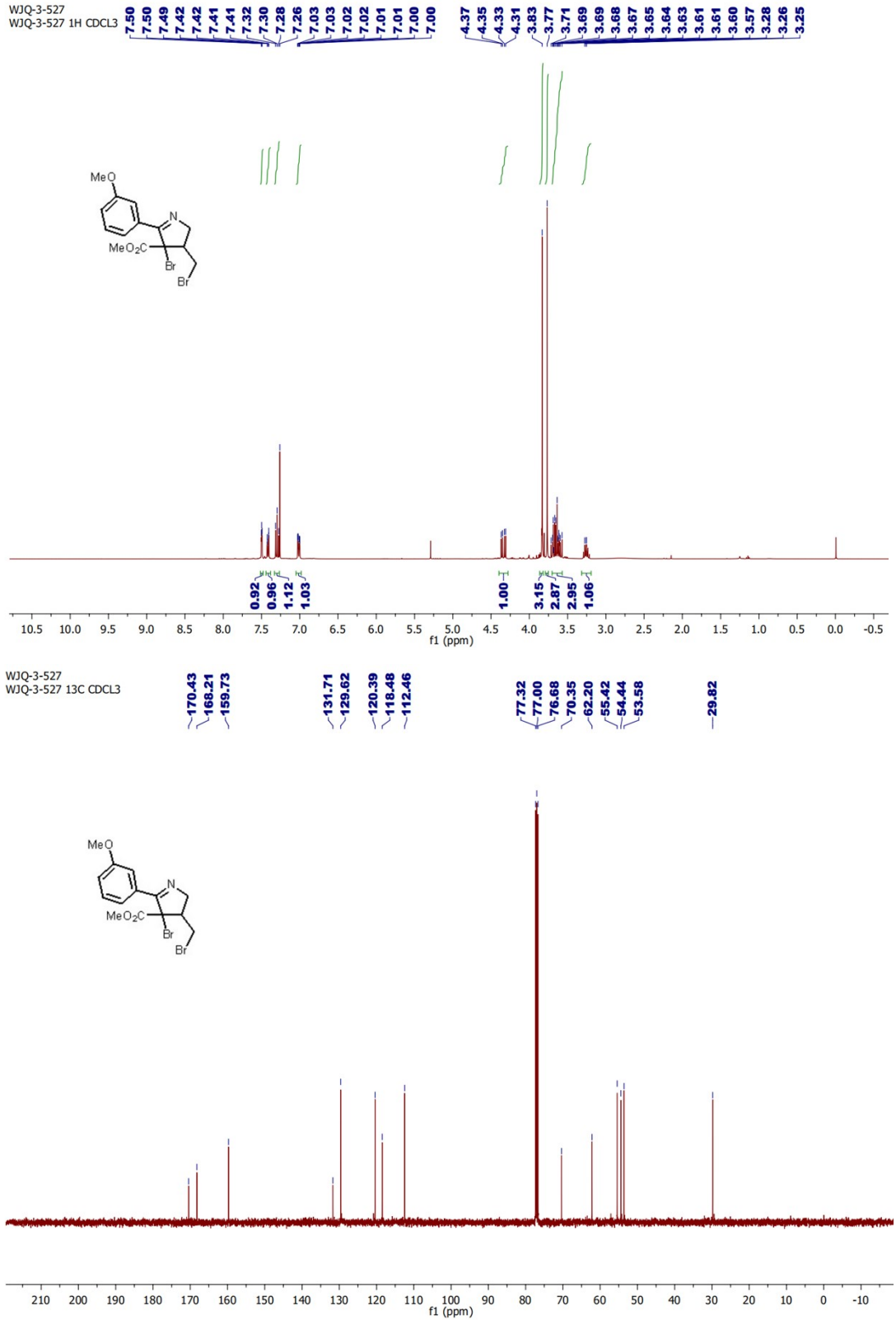


methyl 4-bromo-3-(bromomethyl)-5-(4-methoxyphenyl)-3,4-dihydro-2H-pyrrole-4-carboxylate (**2c**)

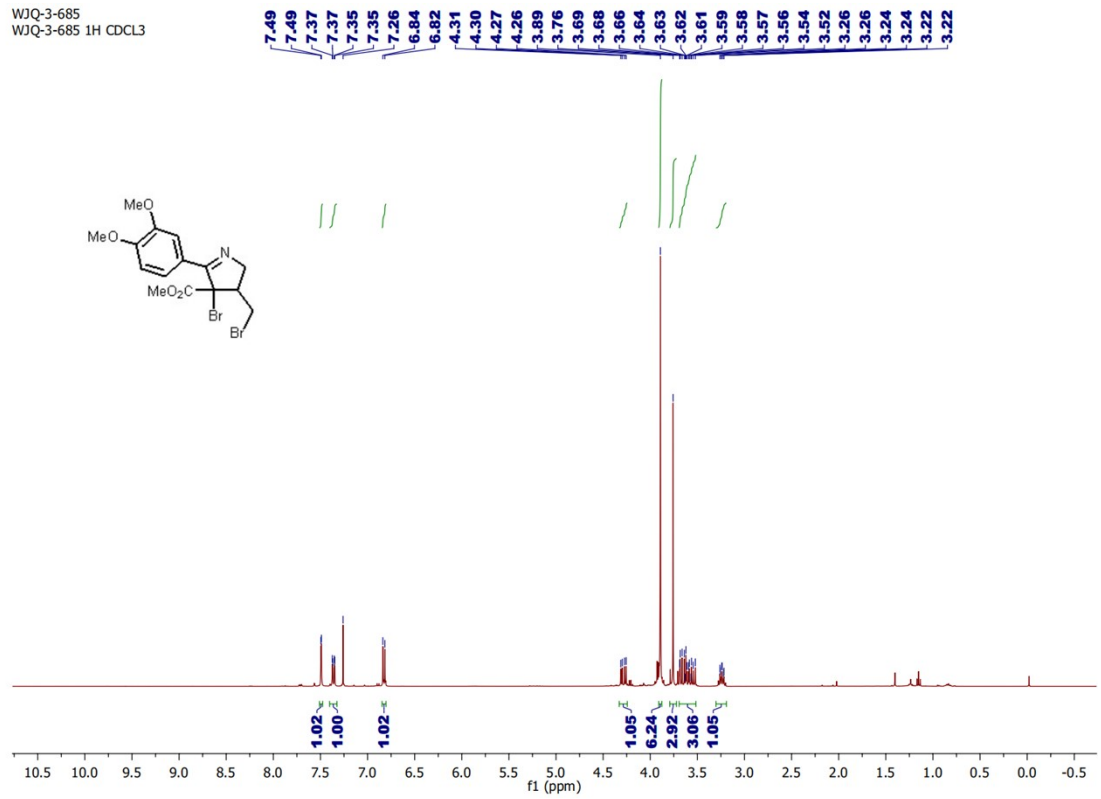


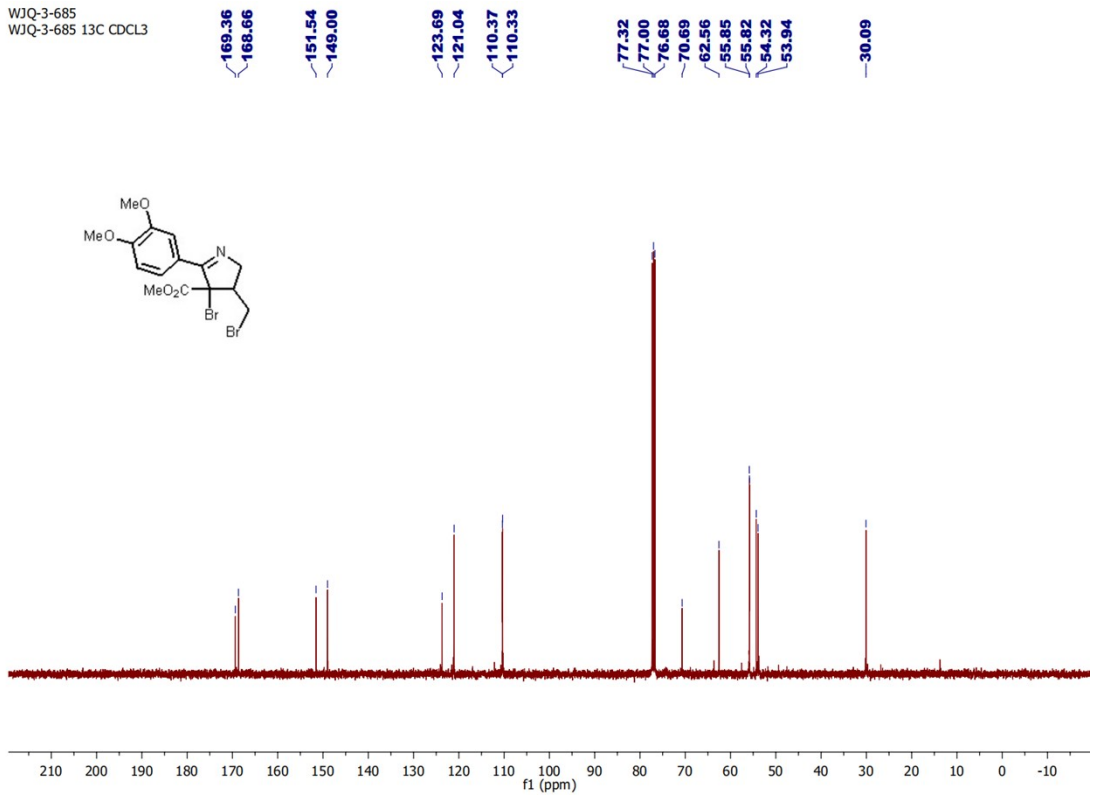


methyl 4-bromo-3-(bromomethyl)-5-(3-methoxyphenyl)-3,4-dihydro-2H-pyrrole-4-carboxylate (**2d**)

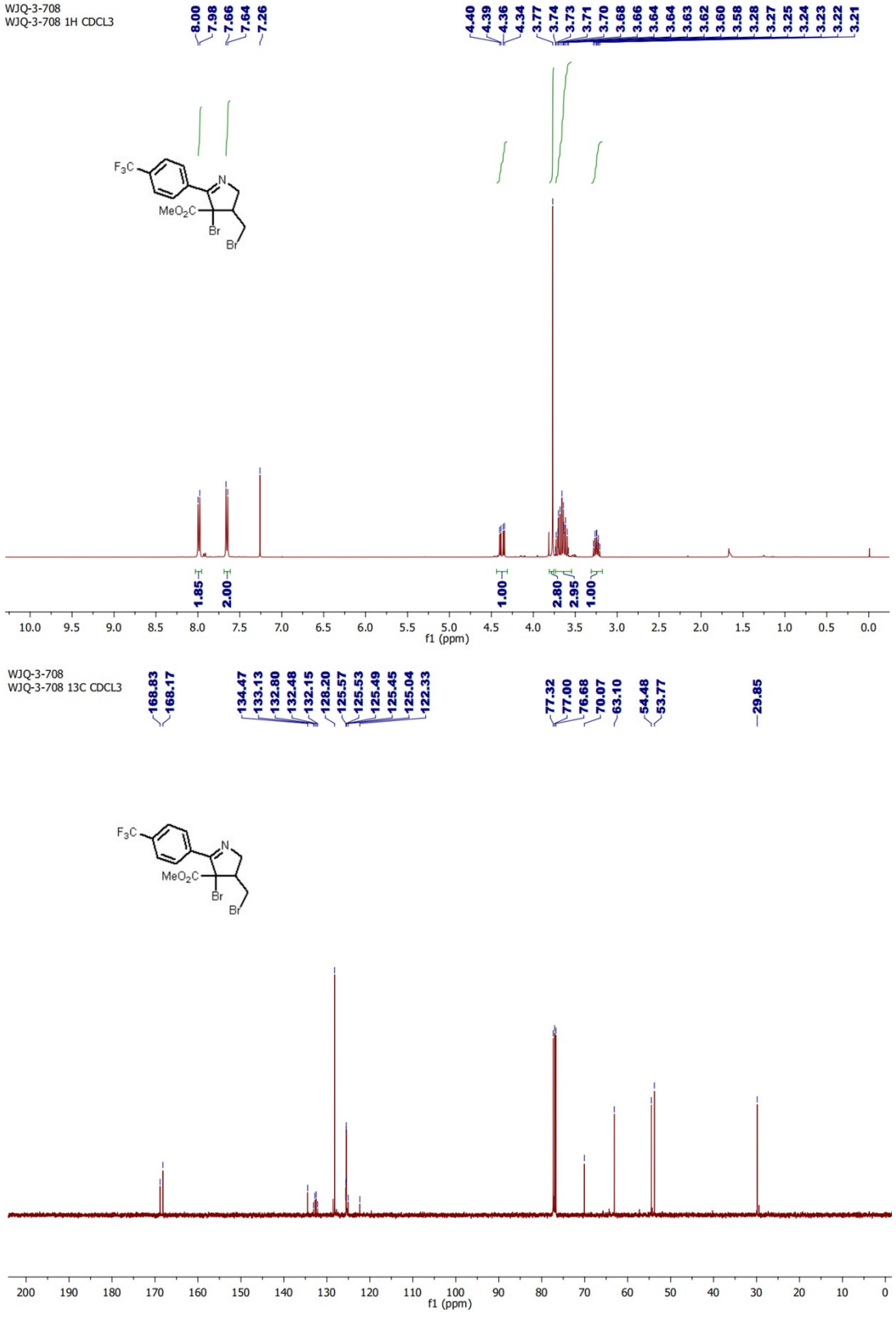


Methyl 4-bromo-3-(bromomethyl)-5-(3,4-dimethoxyphenyl)-3,4-dihydro-2H-pyrrole-4-carboxylate (**2e**)

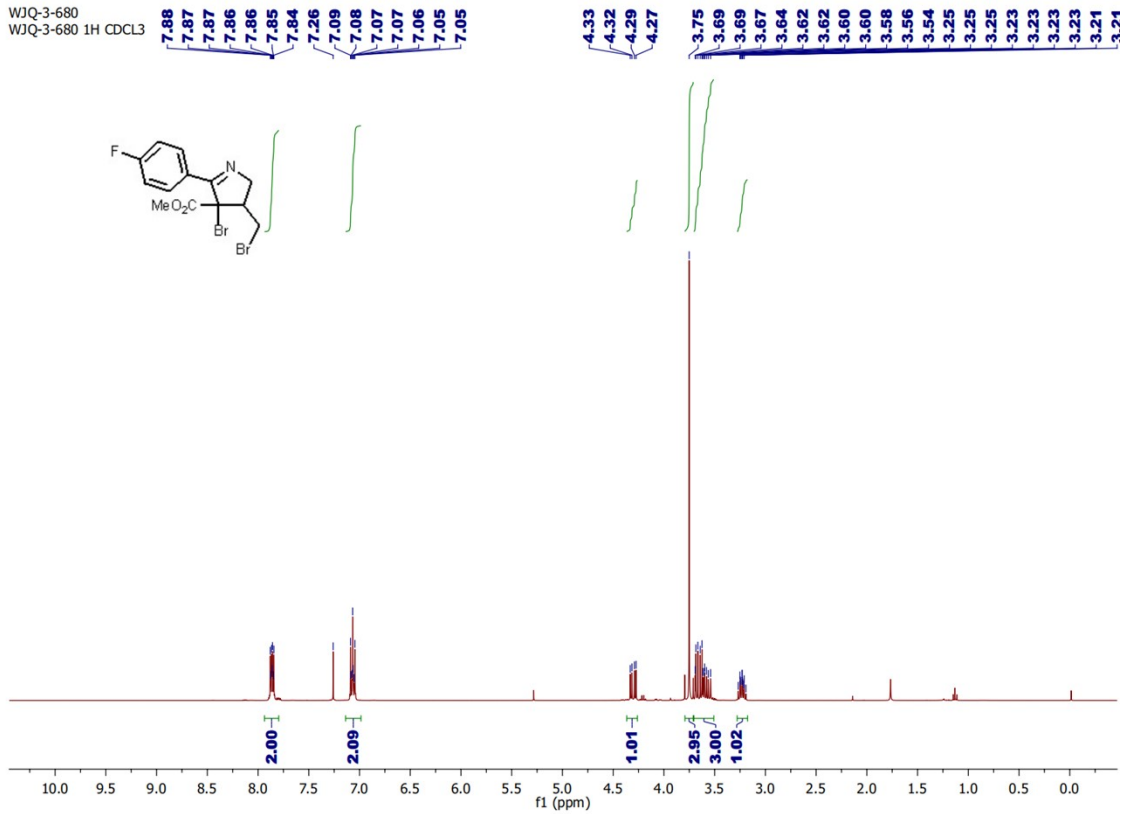


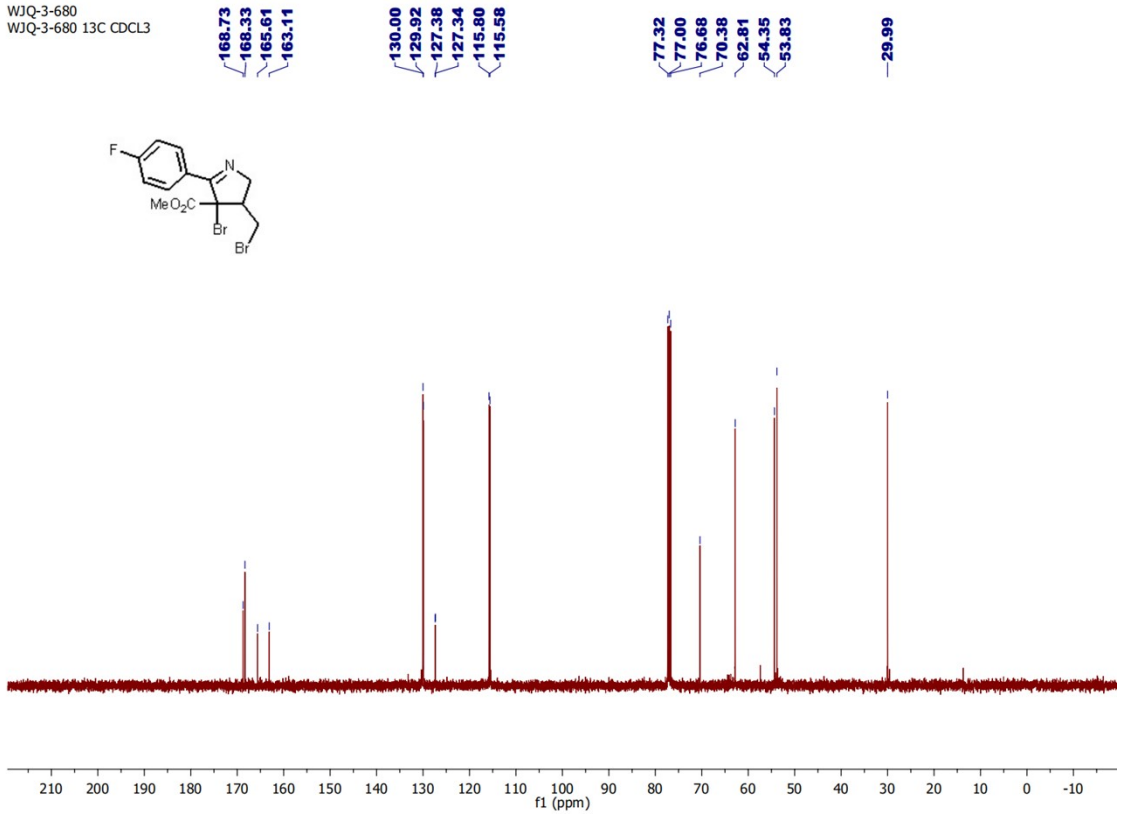


methyl 4-bromo-3-(bromomethyl)-5-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2H-pyrrole-4-carboxylate (**2f**)

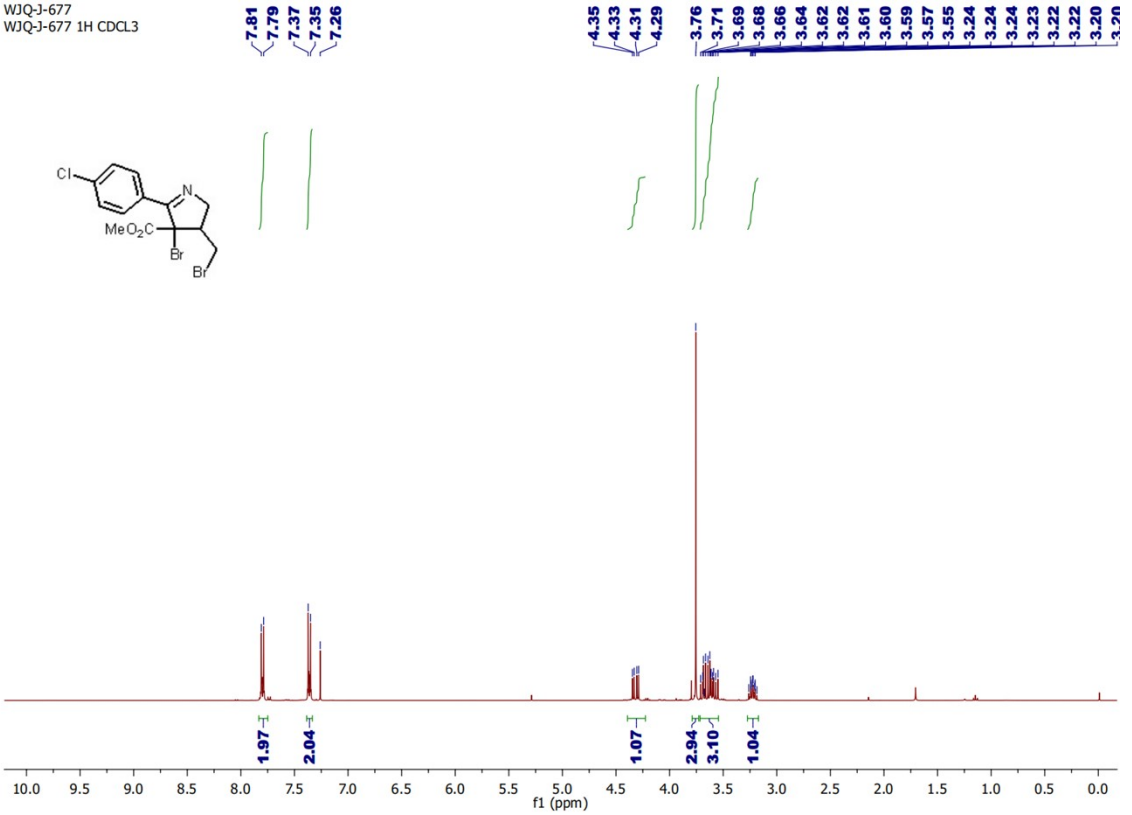


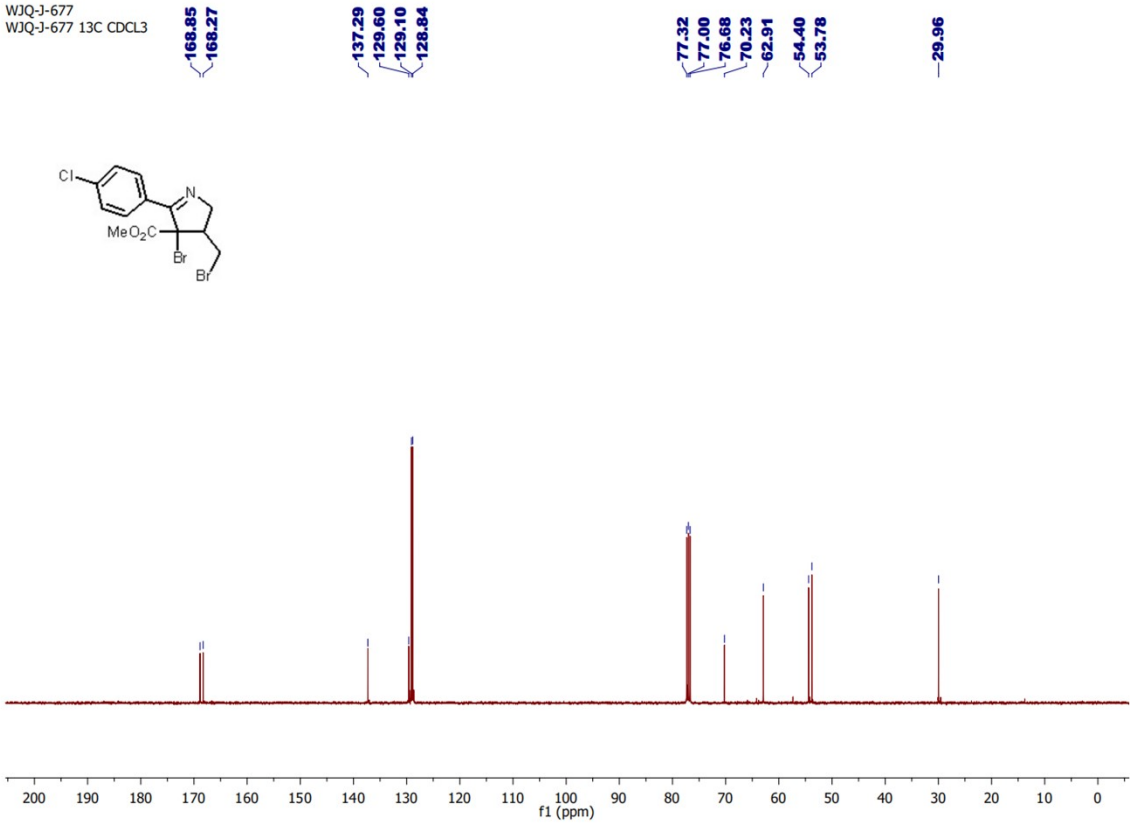
methyl 4-bromo-3-(bromomethyl)-5-(4-fluorophenyl)-3,4-dihydro-2H-pyrrole-4-carboxylate (**2g**)



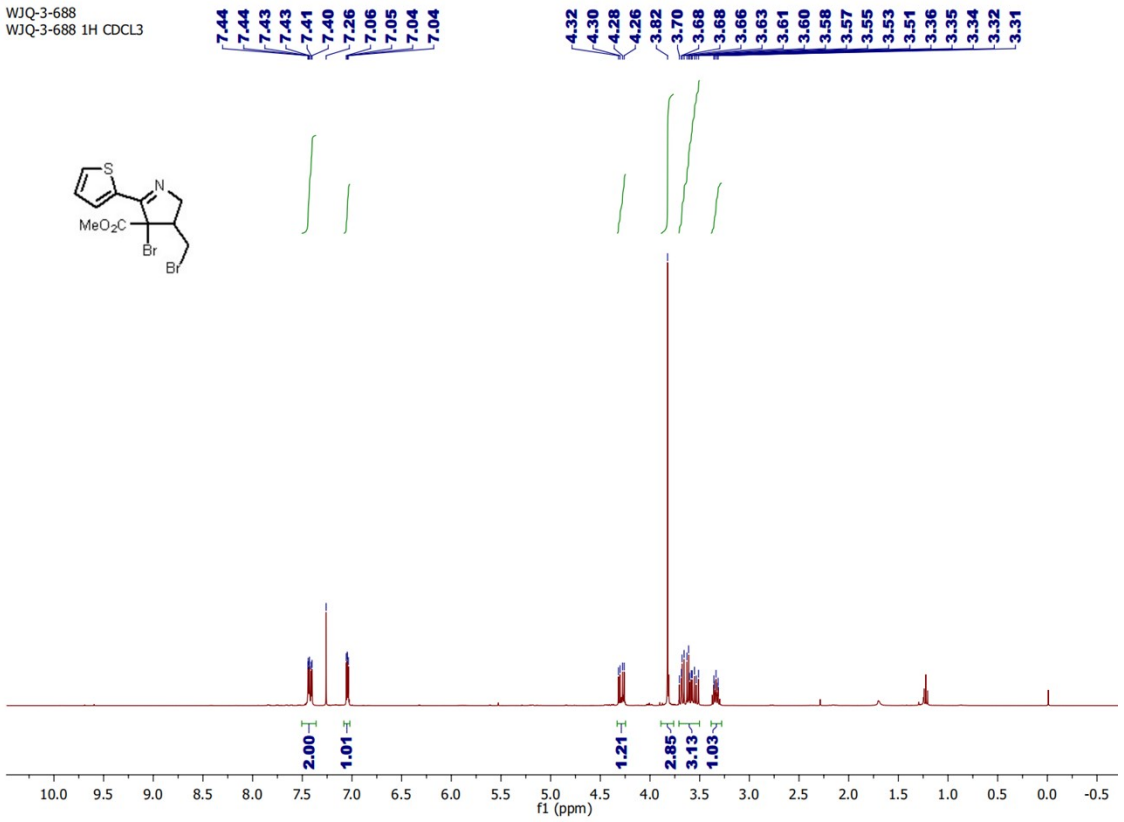


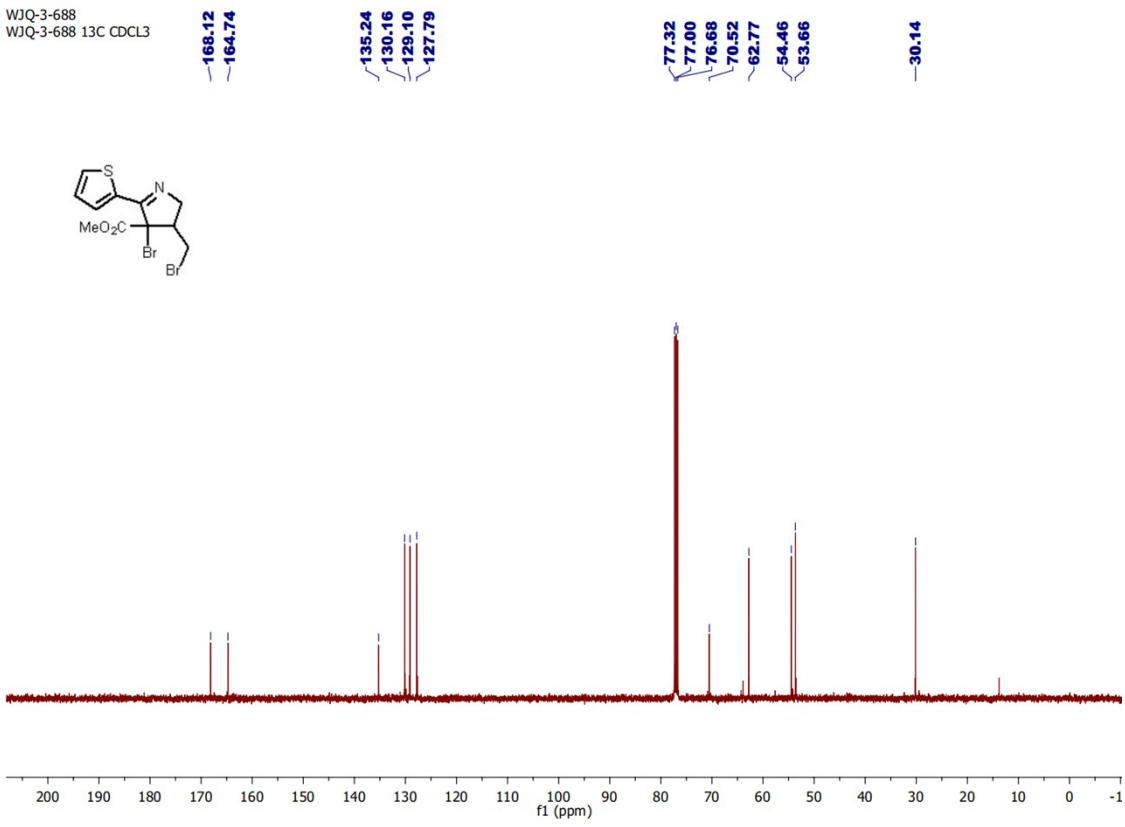
methyl 4-bromo-3-(bromomethyl)-5-(4-chlorophenyl)-3,4-dihydro-2H-pyrrole-4-carboxylate (**2h**)



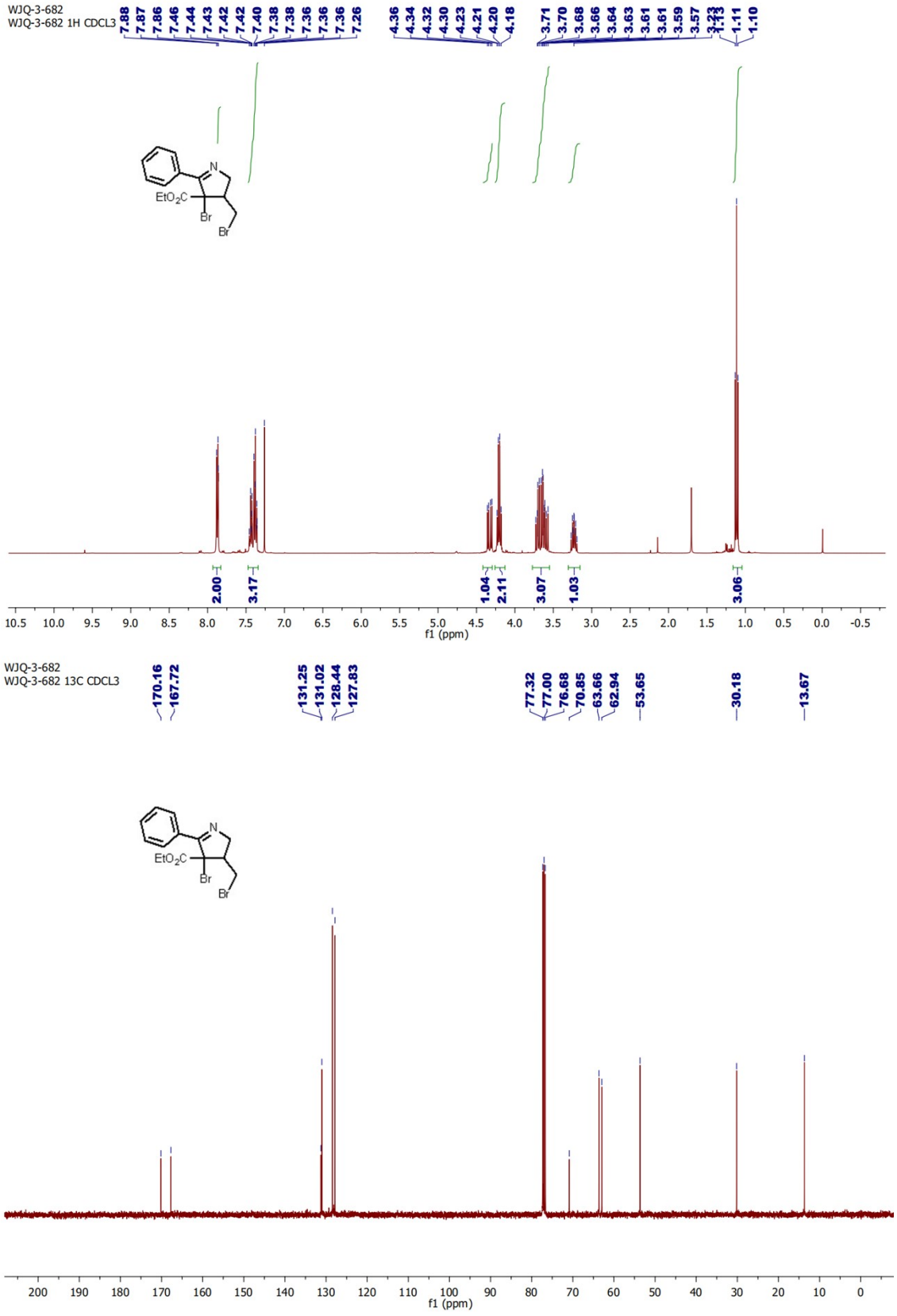


methyl 4-bromo-3-(bromomethyl)-5-(thiophen-2-yl)-3,4-dihydro-2H-pyrrole-4-carboxylate (**2j**)

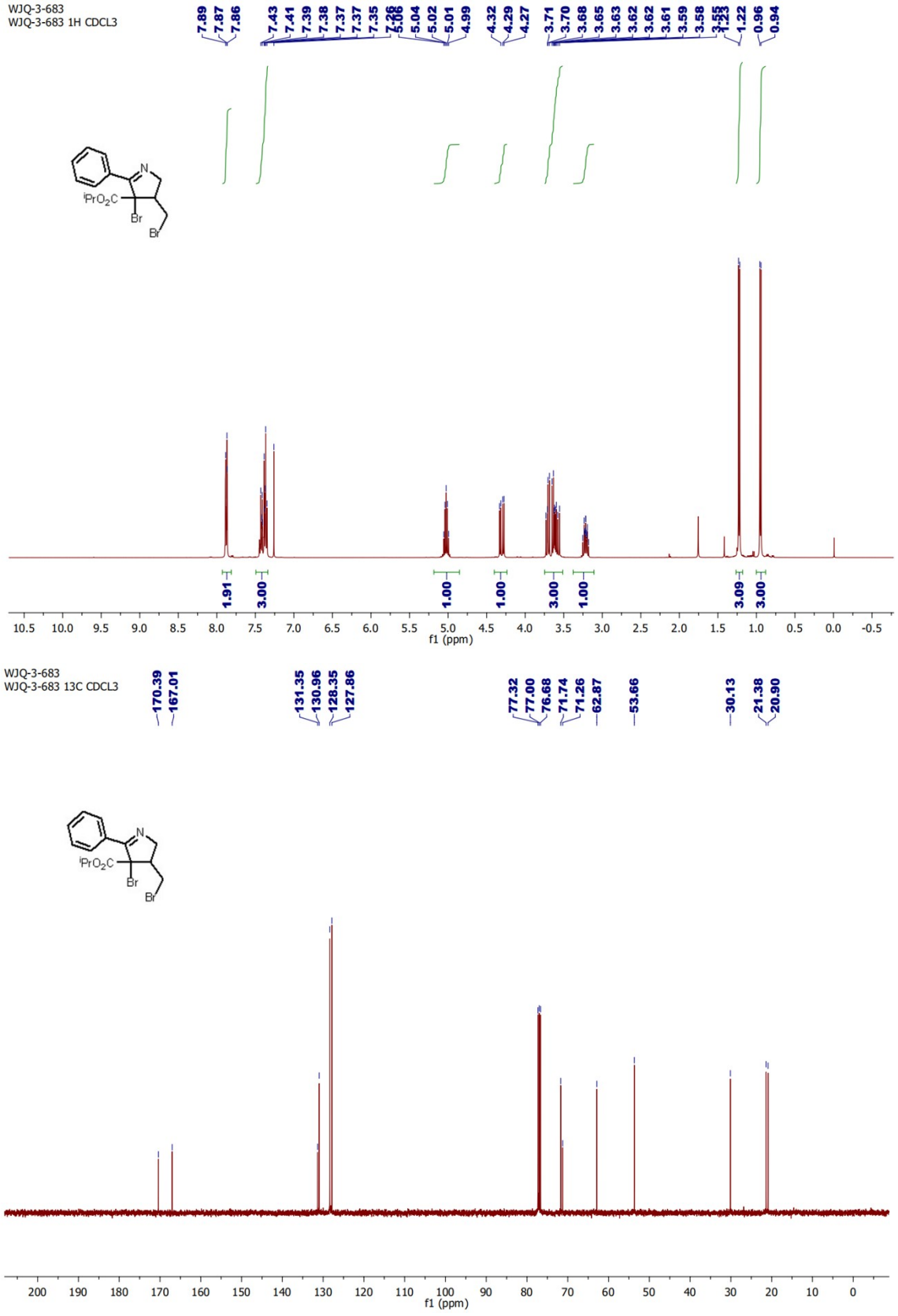




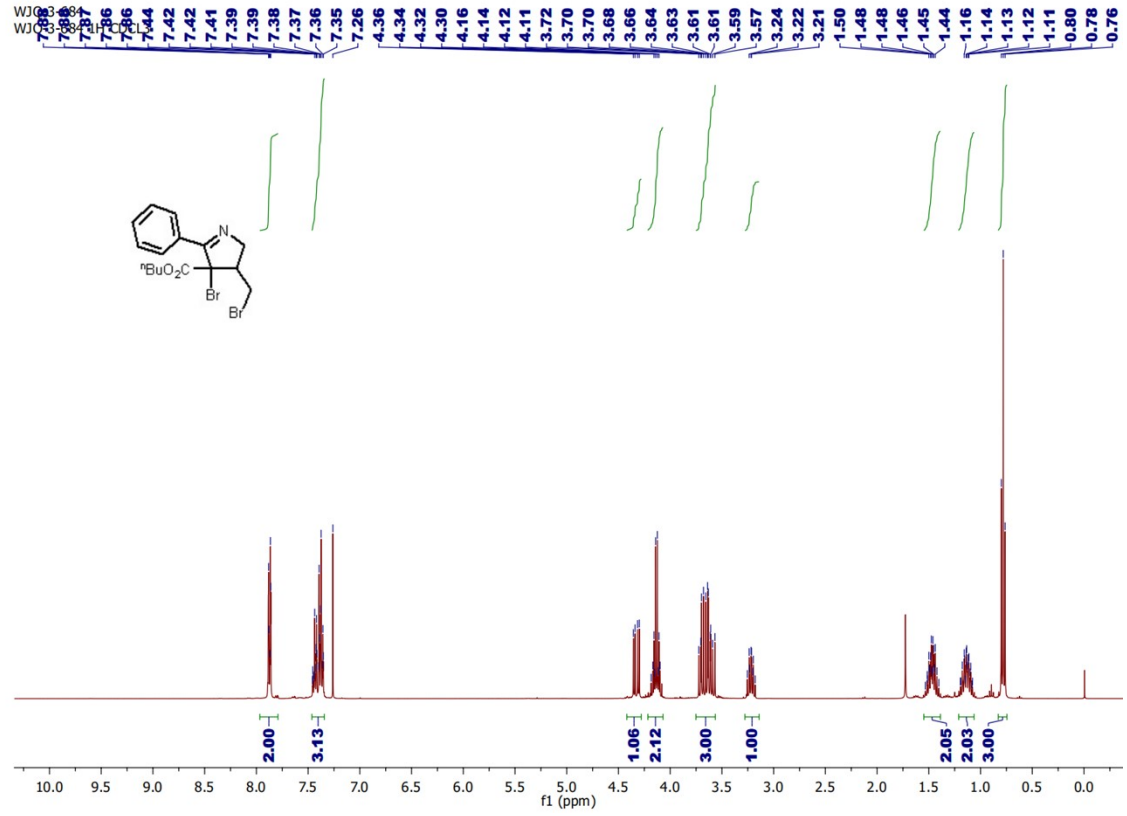
ethyl 4-bromo-3-(bromomethyl)-5-phenyl-3,4-dihydro-2H-pyrrole-4-carboxylate (**2k**)

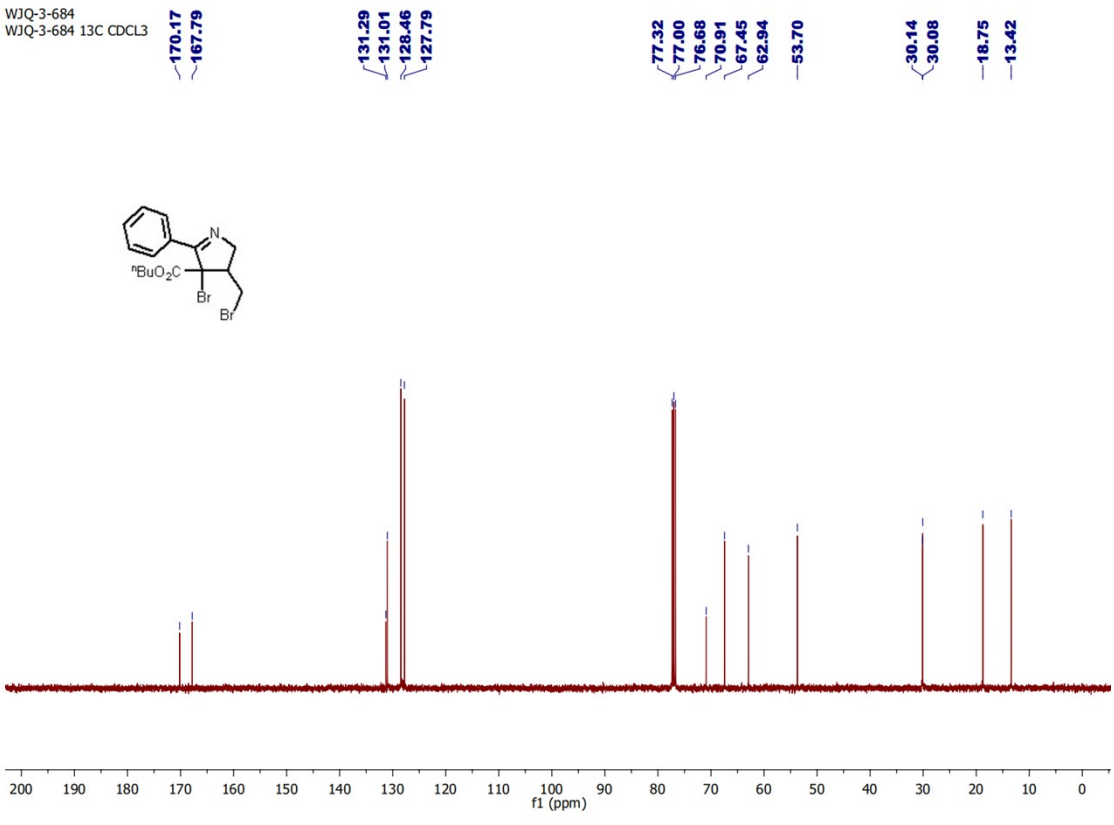


isopropyl 4-bromo-3-(bromomethyl)-5-phenyl-3,4-dihydro-2H-pyrrole-4-carboxylate (**2l**)

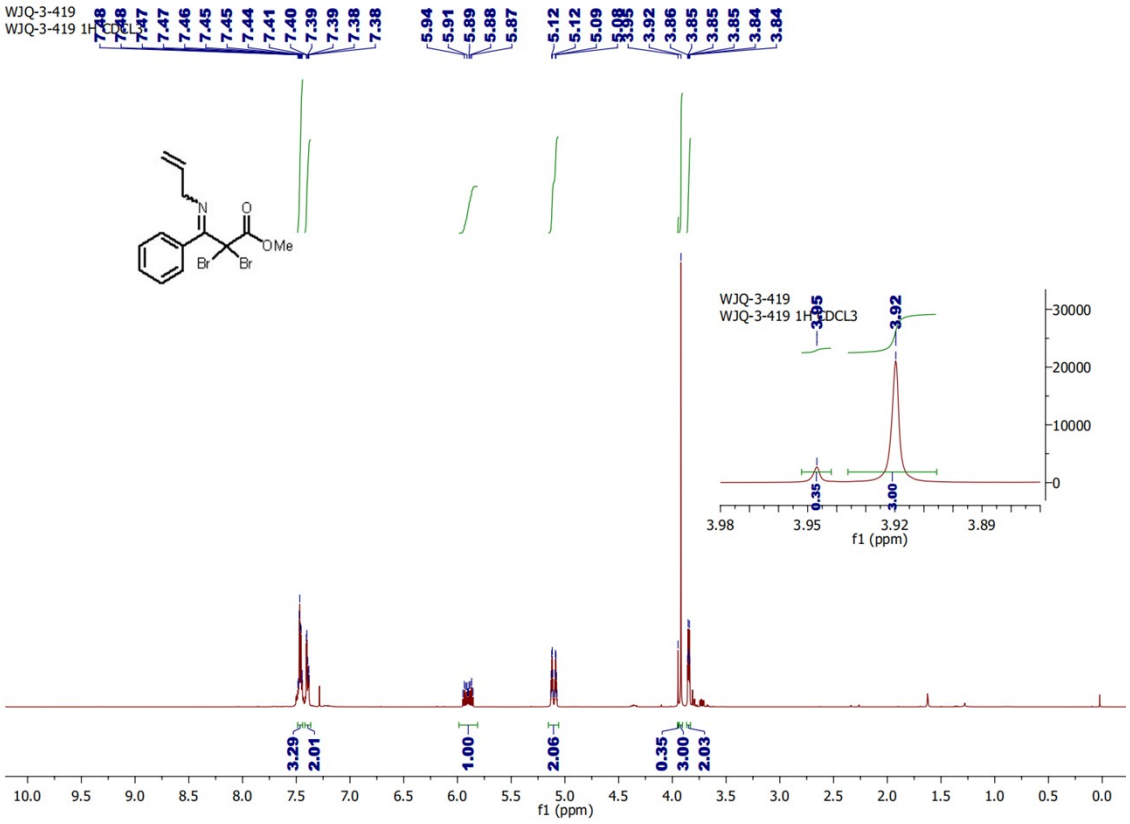


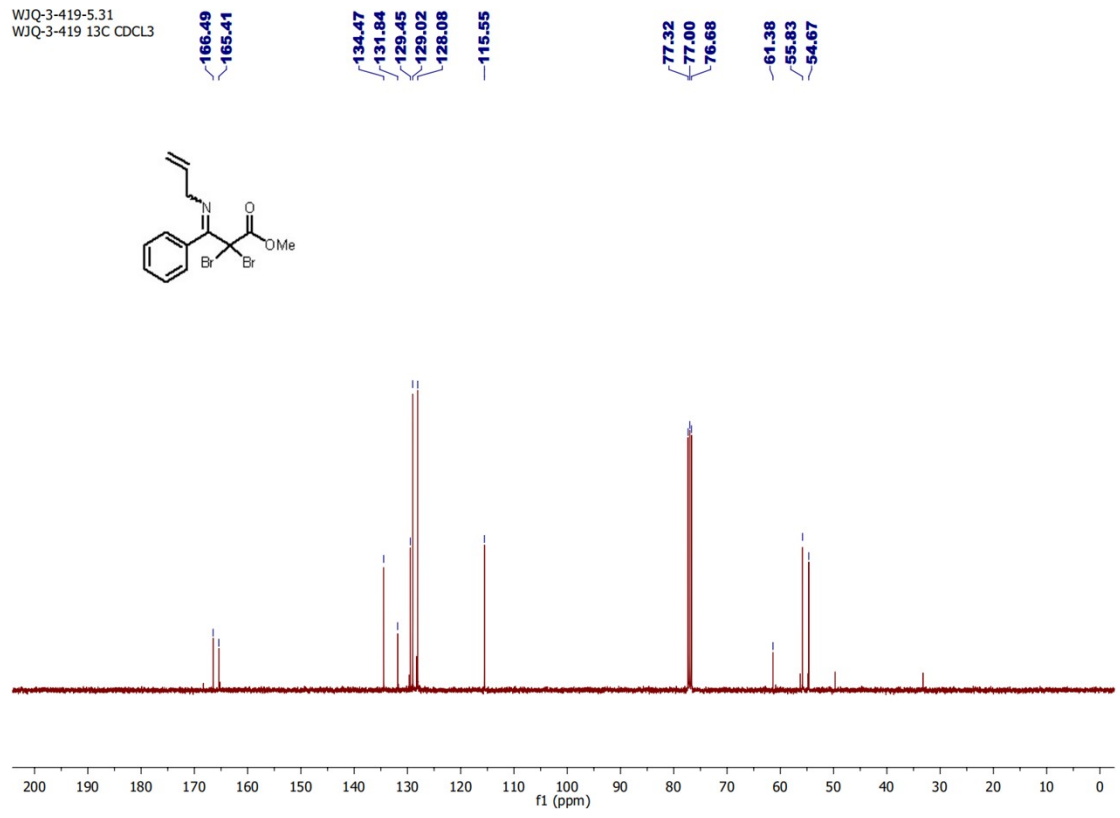
butyl 4-bromo-3-(bromomethyl)-5-phenyl-3,4-dihydro-2H-pyrrole-4-carboxylate (**2m**)



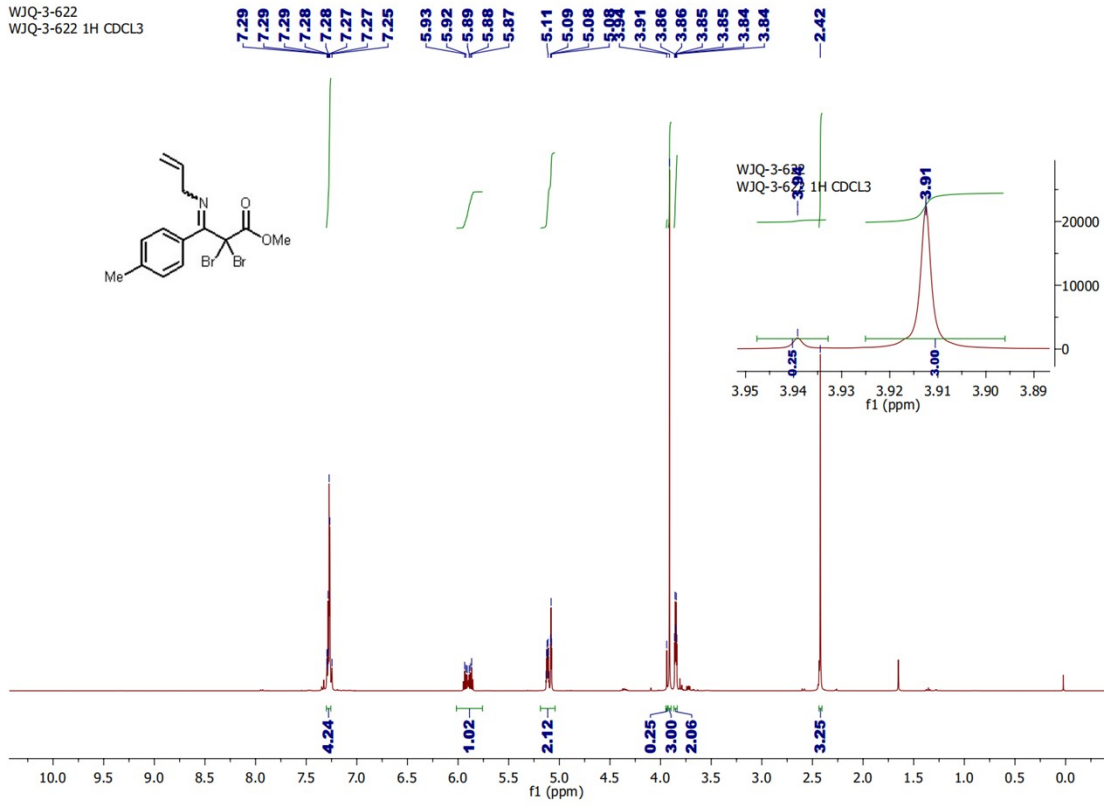


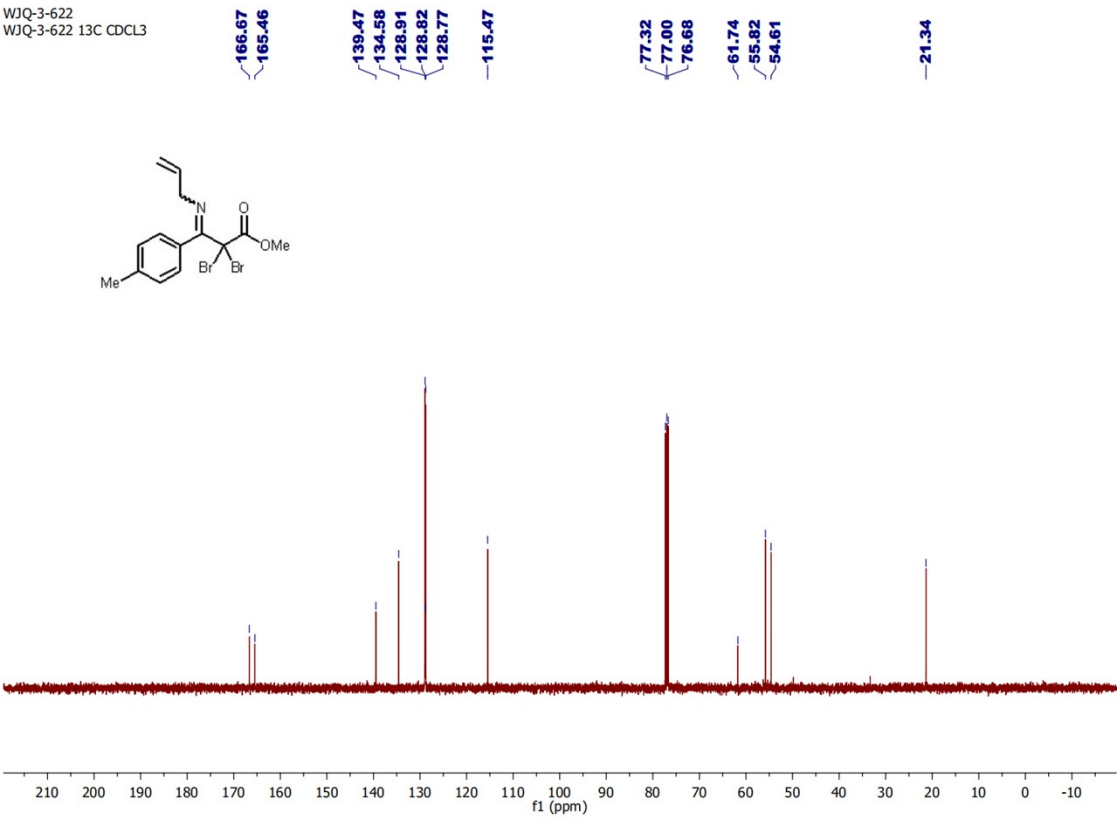
methyl 3-(allylimino)-2,2-dibromo-3-phenylpropanoate (**3a**)



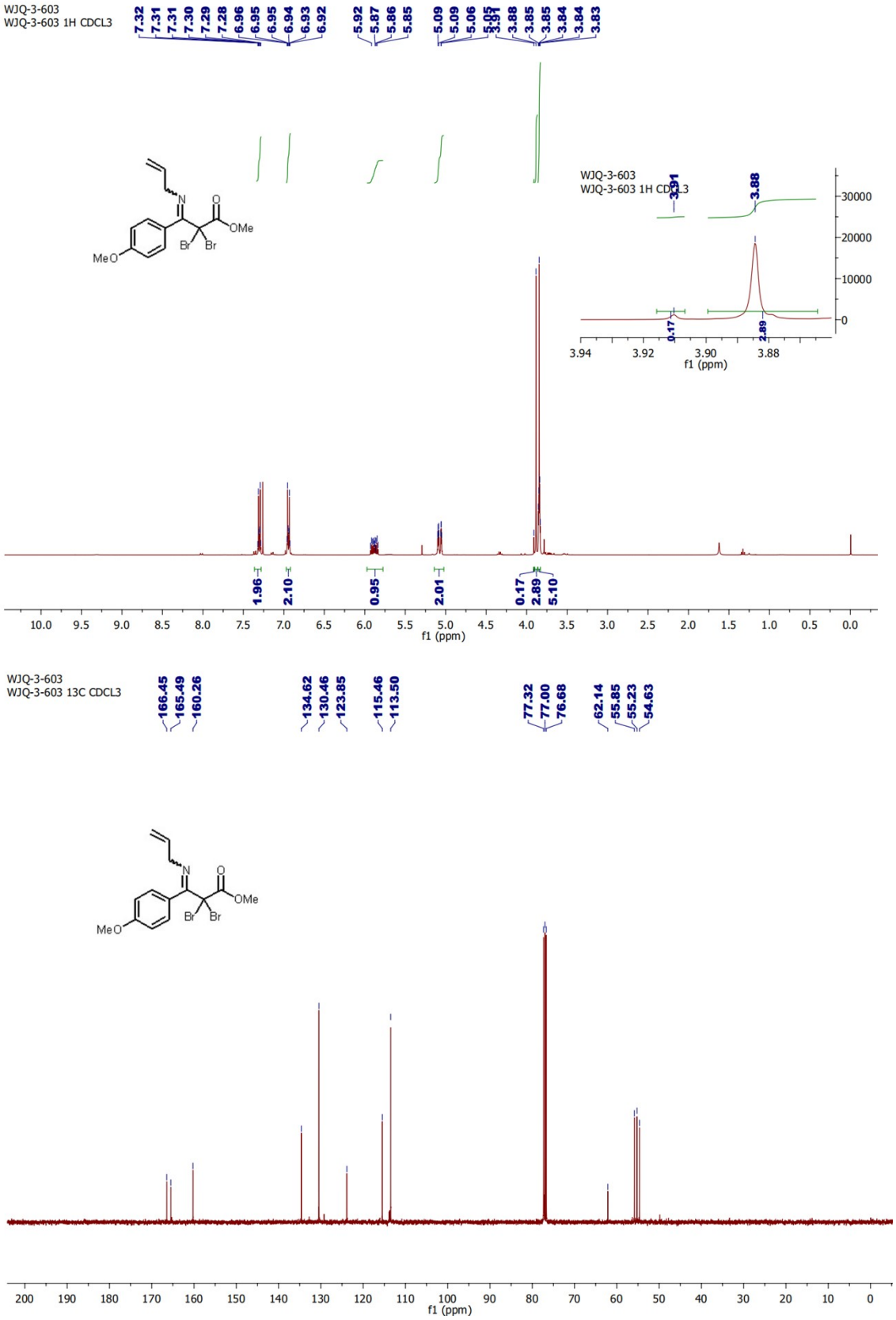


methyl 3-(allylimino)-2,2-dibromo-3-(p-tolyl)propanoate (**3b**)

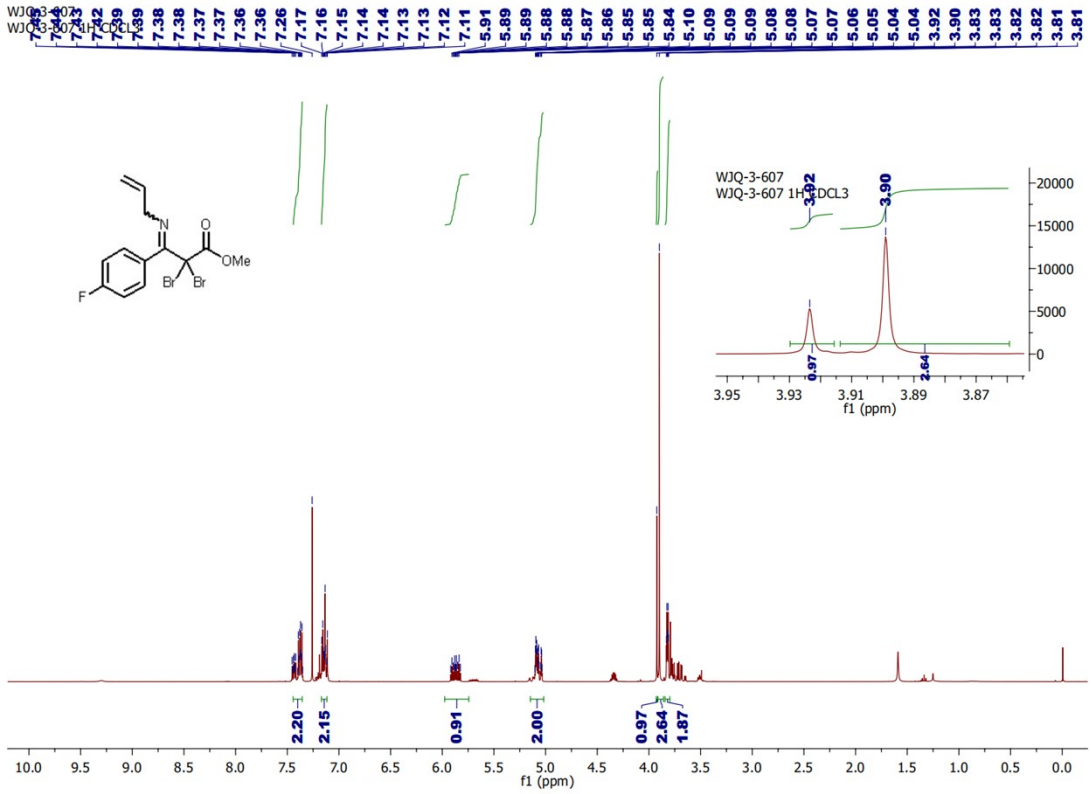


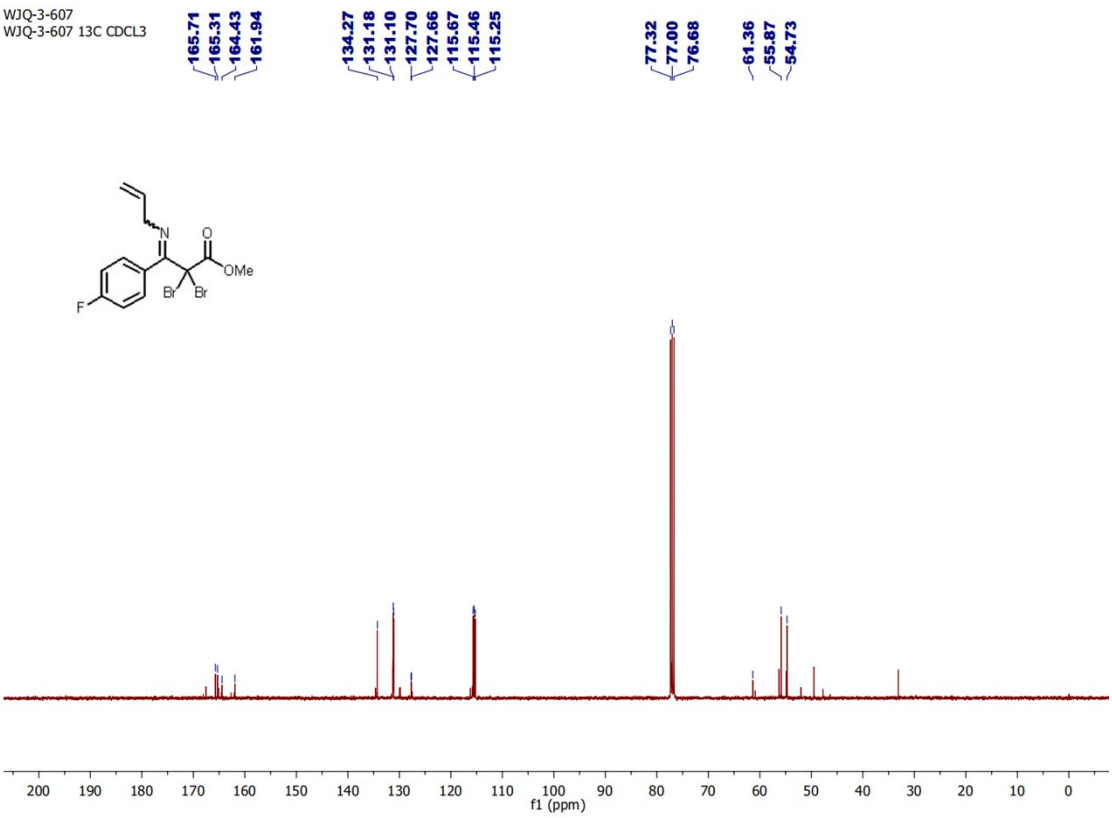


methyl 3-(allylimino)-2,2-dibromo-3-(4-methoxyphenyl)propanoate (**3c**)

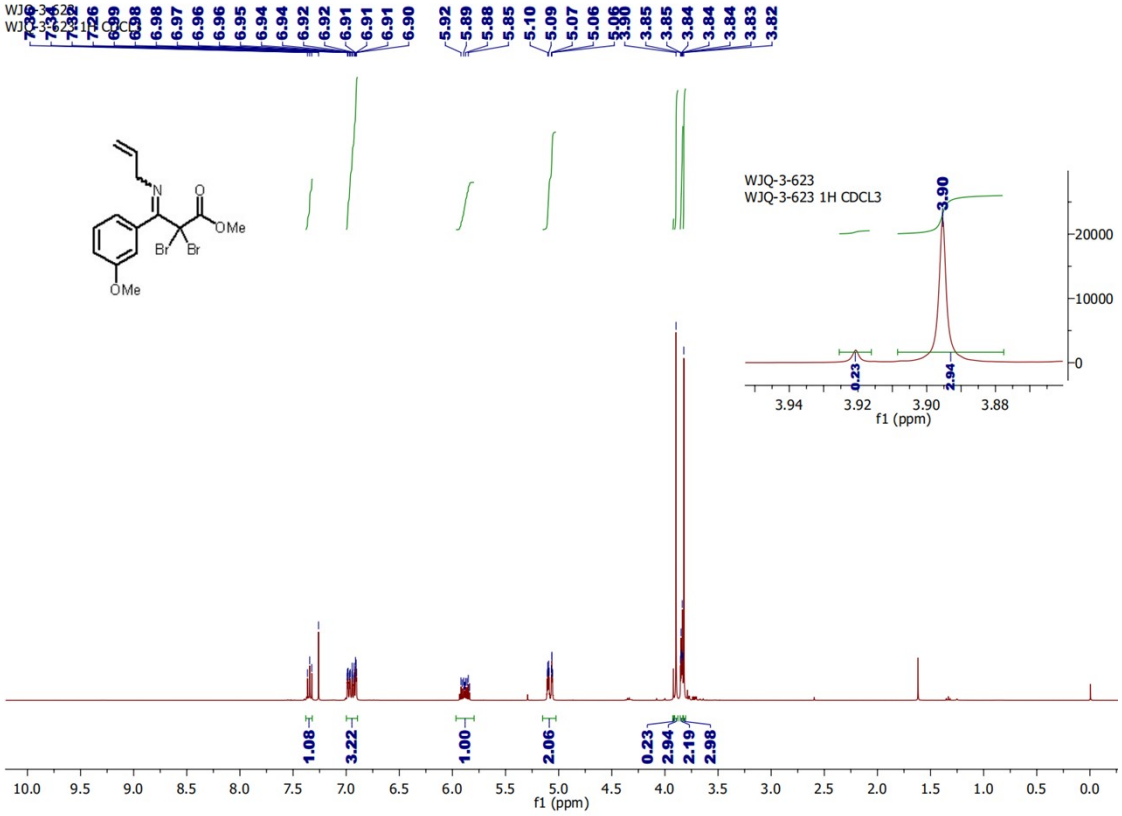


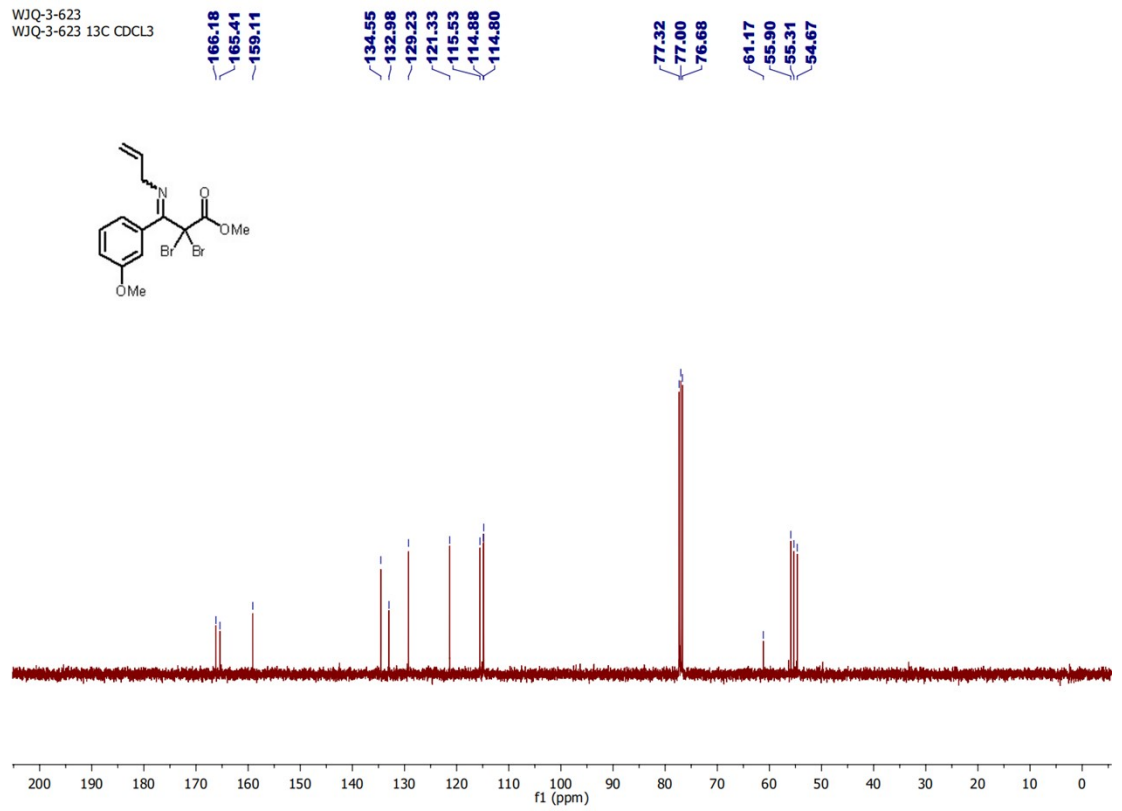
methyl 3-(allylimino)-2,2-dibromo-3-(4-fluorophenyl)propanoate (**3d**)



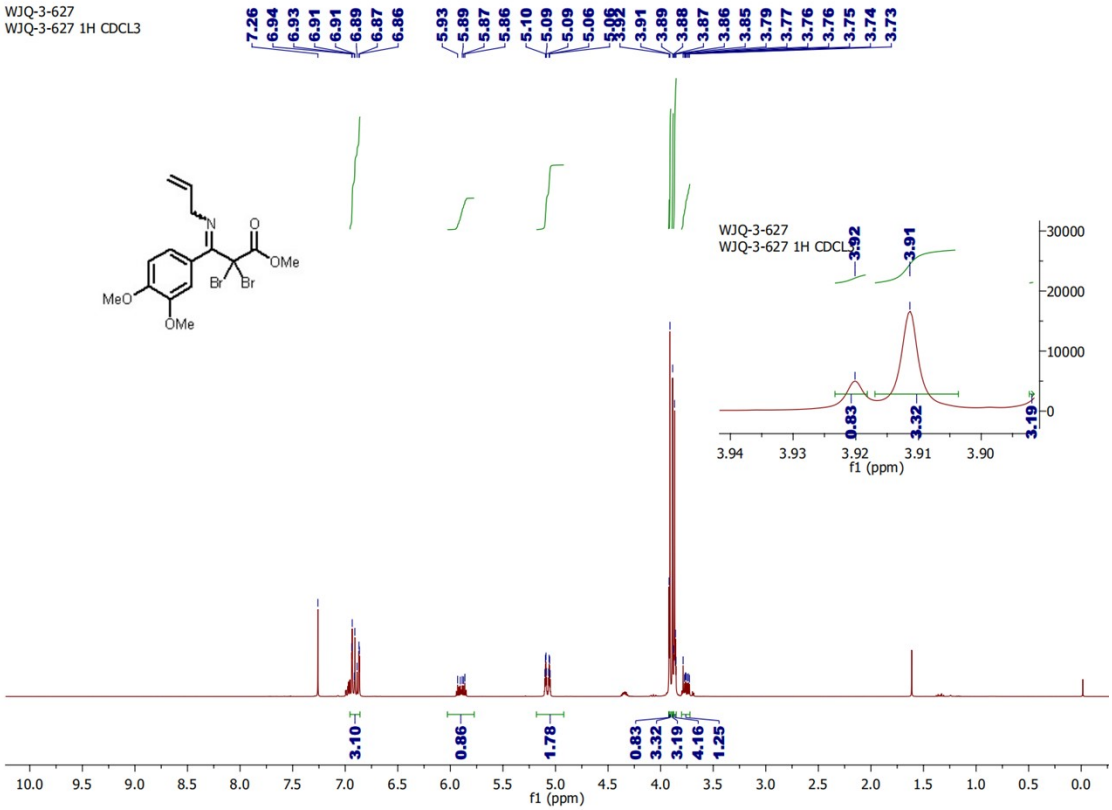


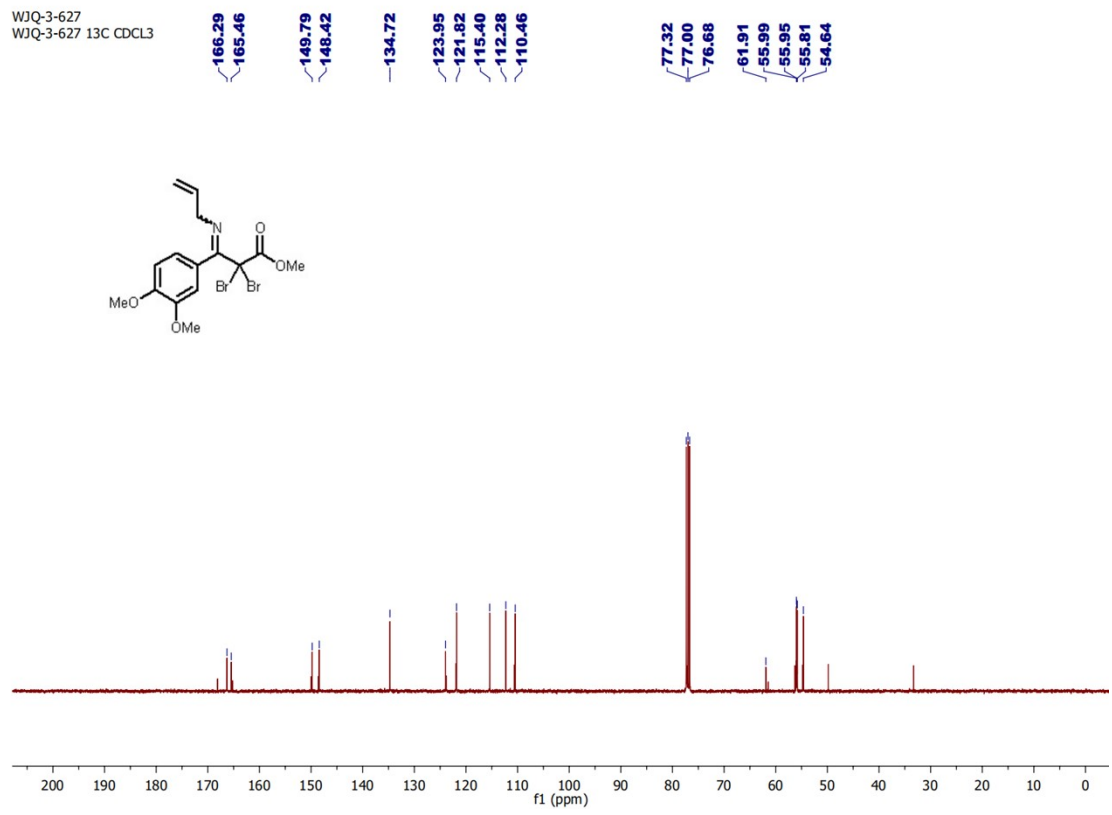
methyl 3-(allylimino)-2,2-dibromo-3-(3-methoxyphenyl)propanoate (**3e**)



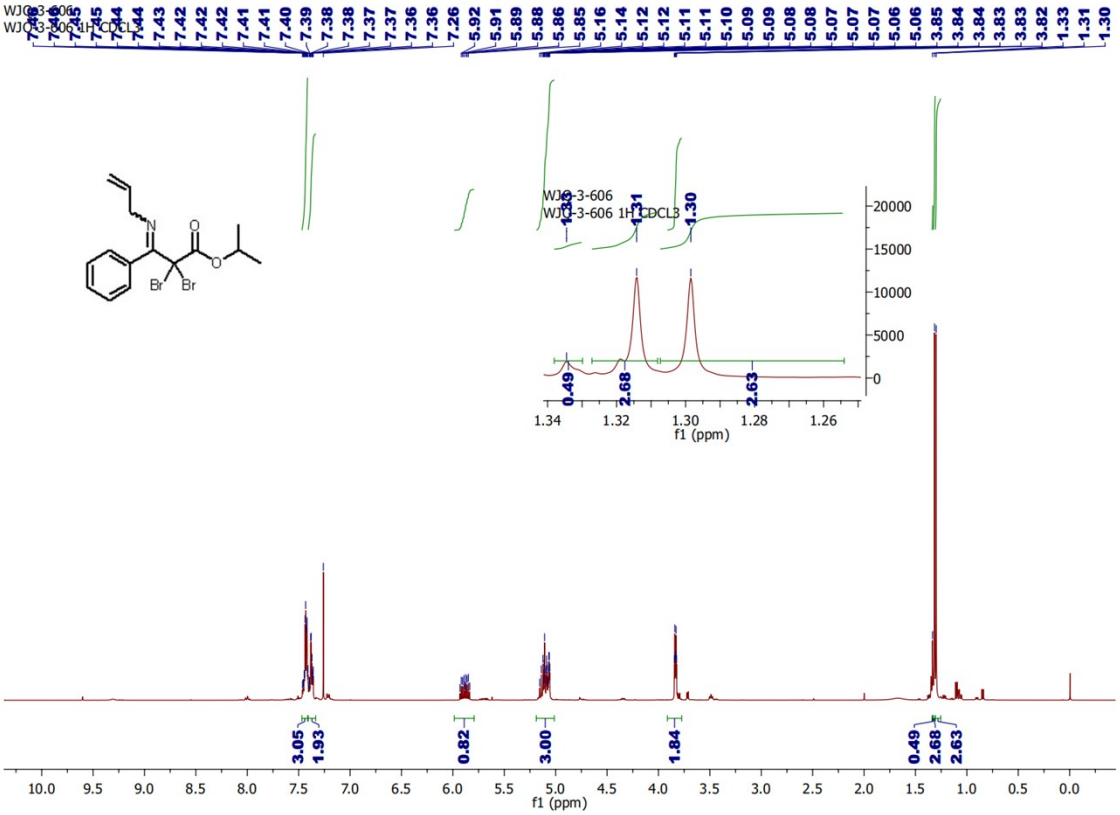


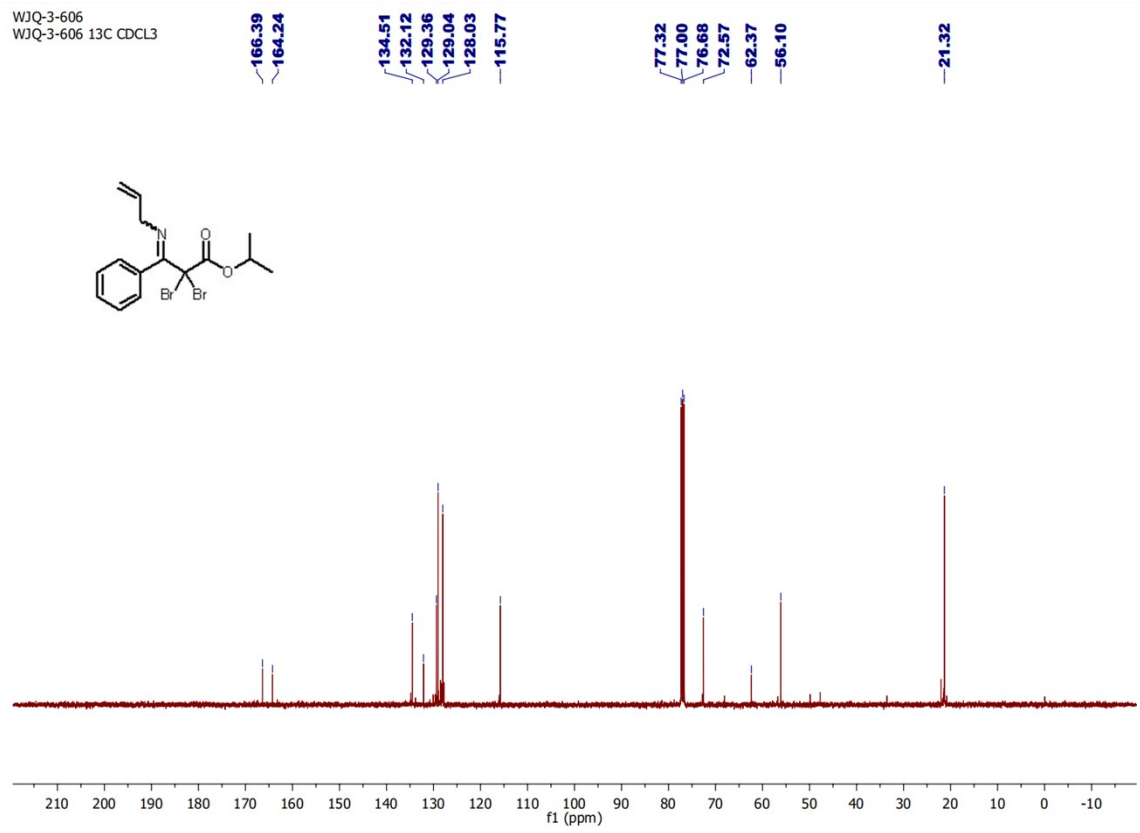
methyl 3-(allylimino)-2,2-dibromo-3-(3,4-dimethoxyphenyl)propanoate (**3f**)



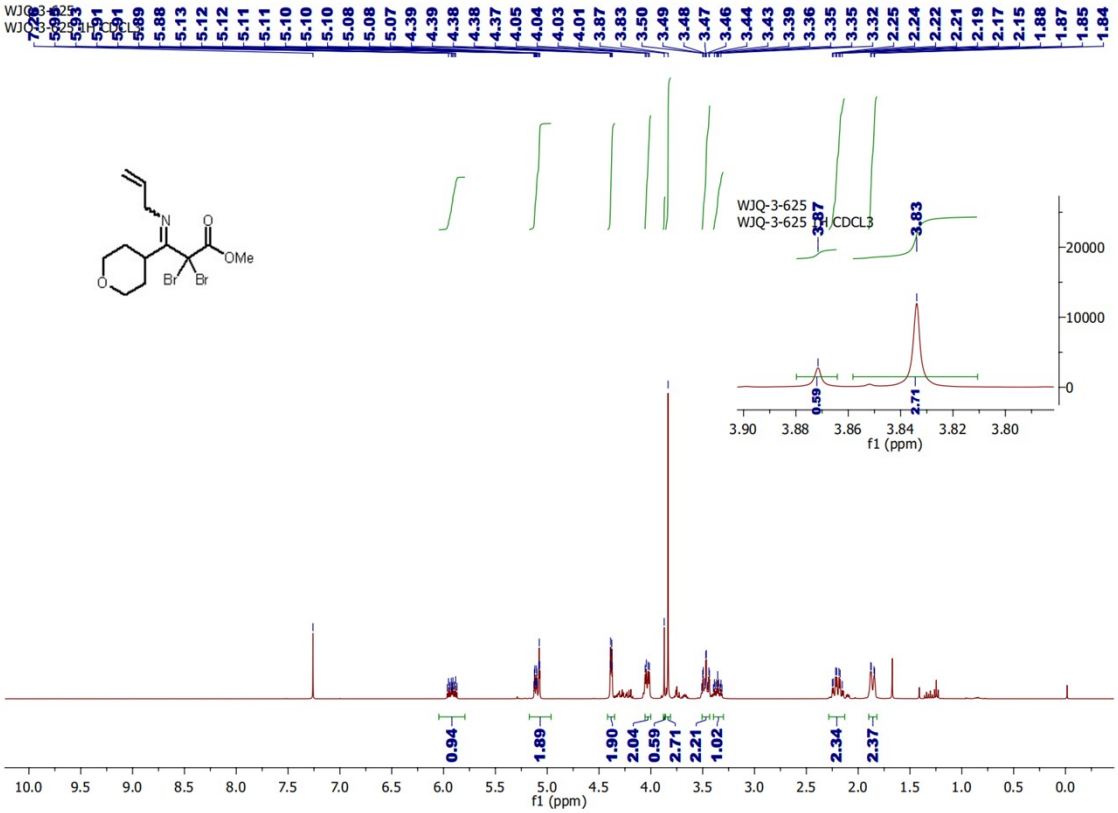


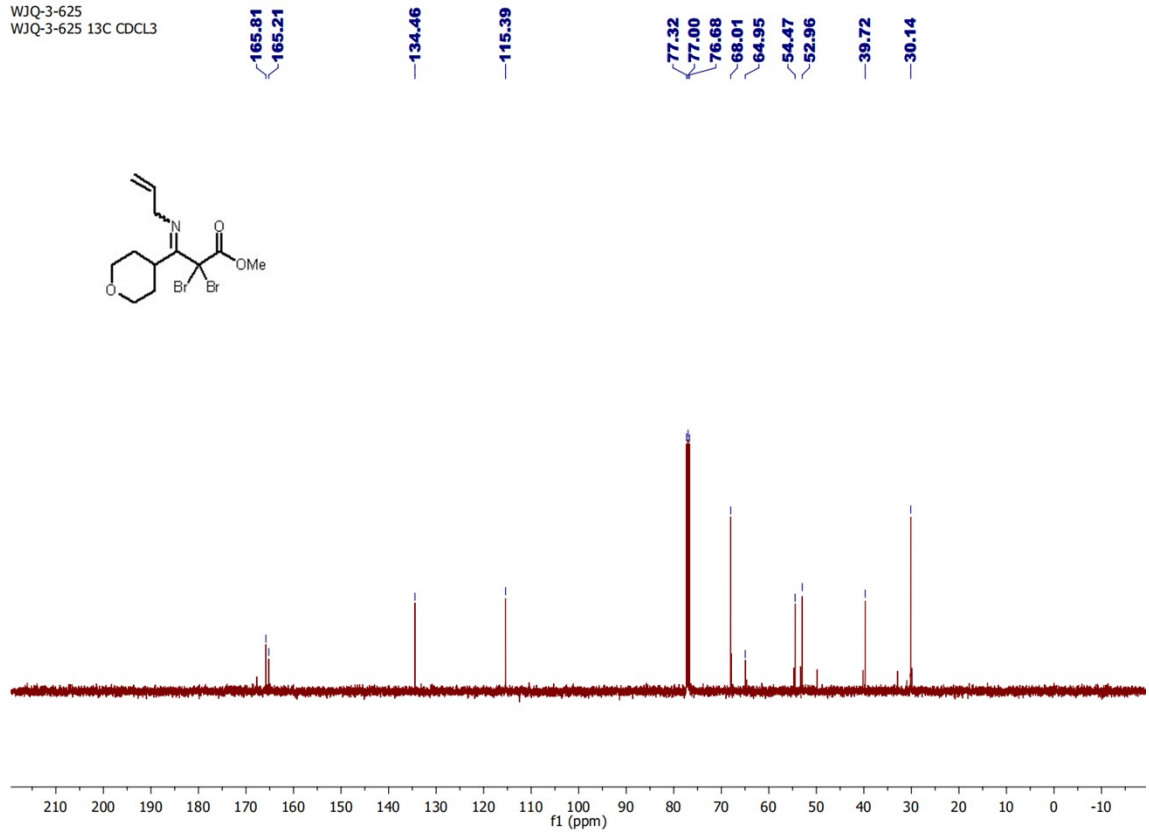
isopropyl 3-(allylimino)-2,2-dibromo-3-phenylpropanoate (**3g**)



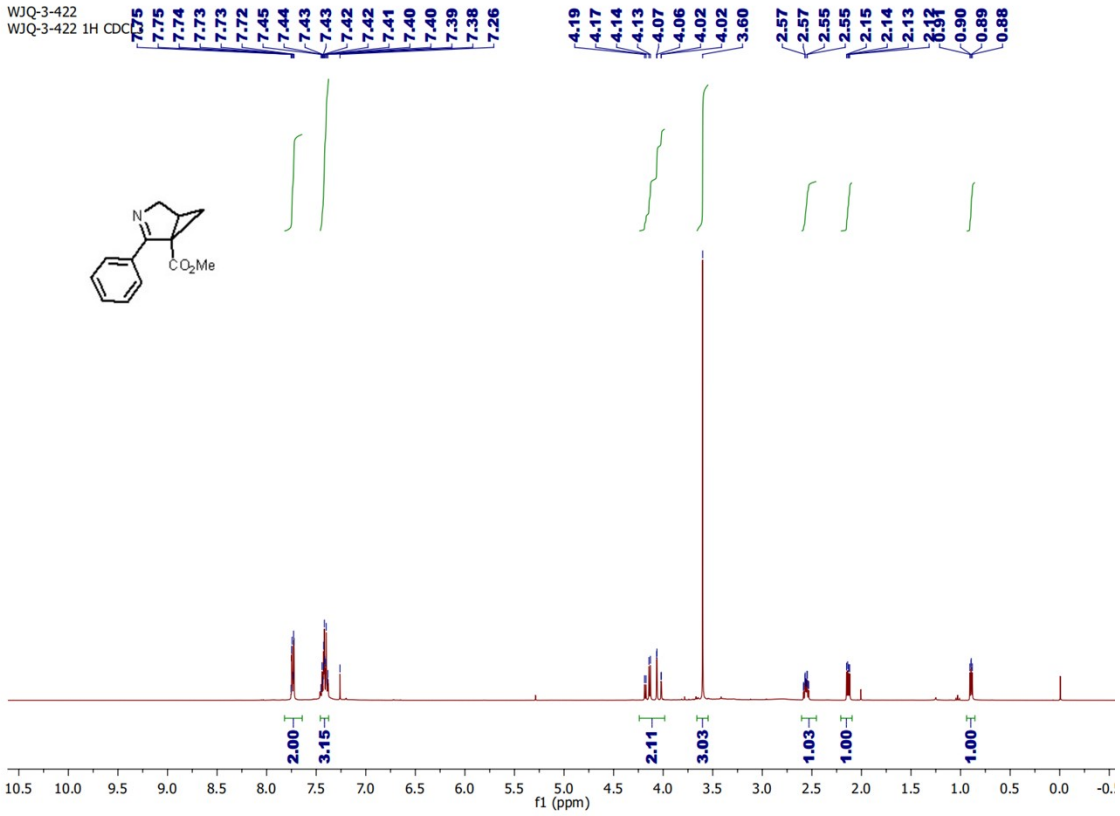


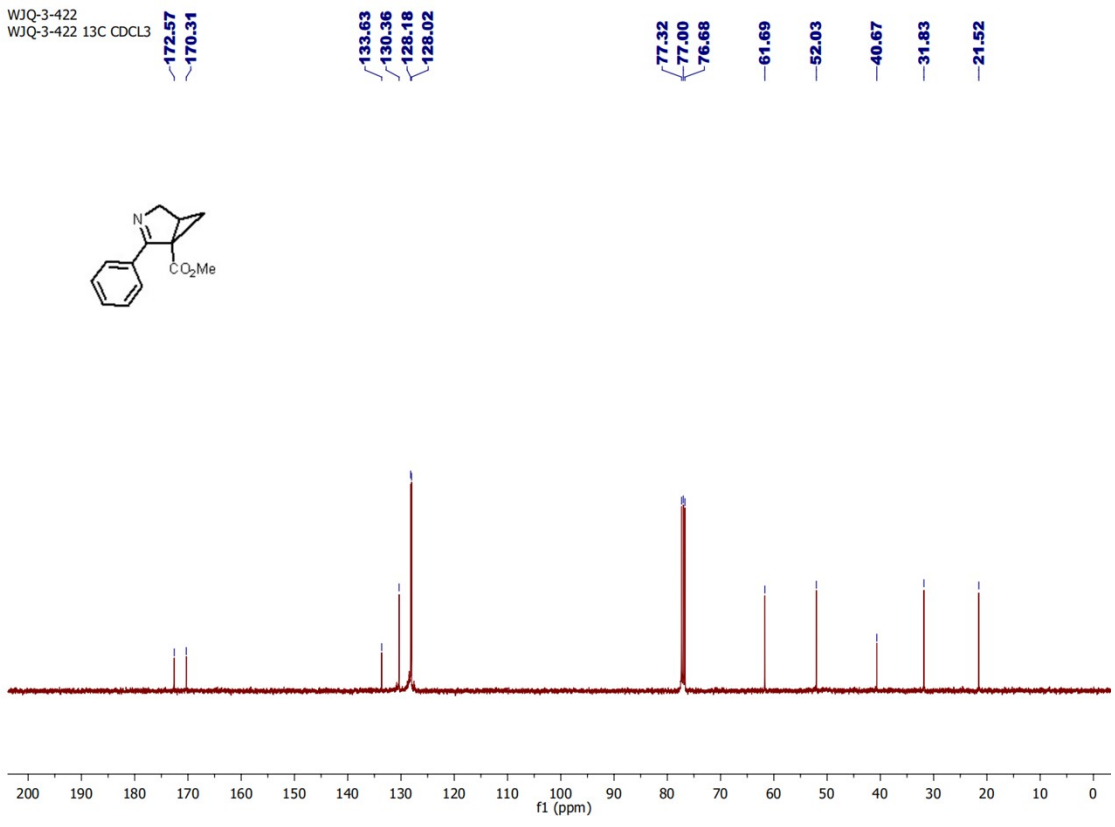
methyl 3-(allylimino)-2,2-dibromo-3-(tetrahydro-2H-pyran-4-yl)propanoate (**3h**)



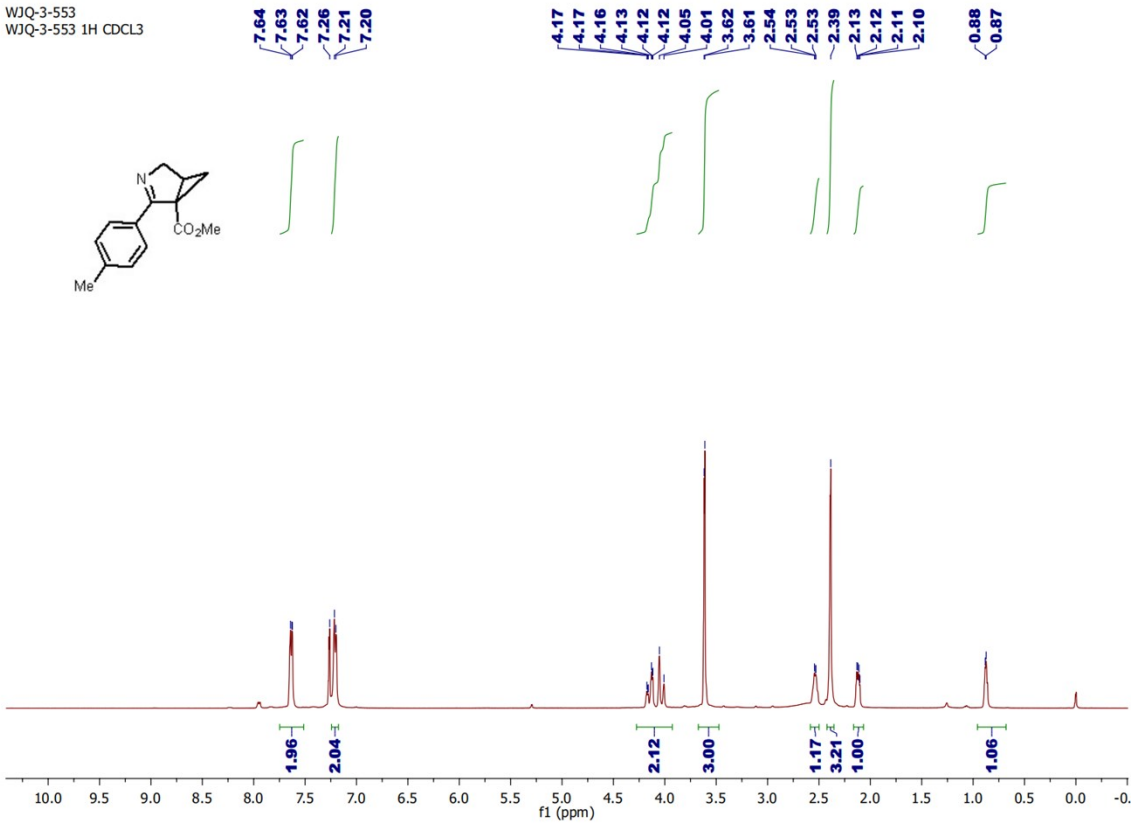


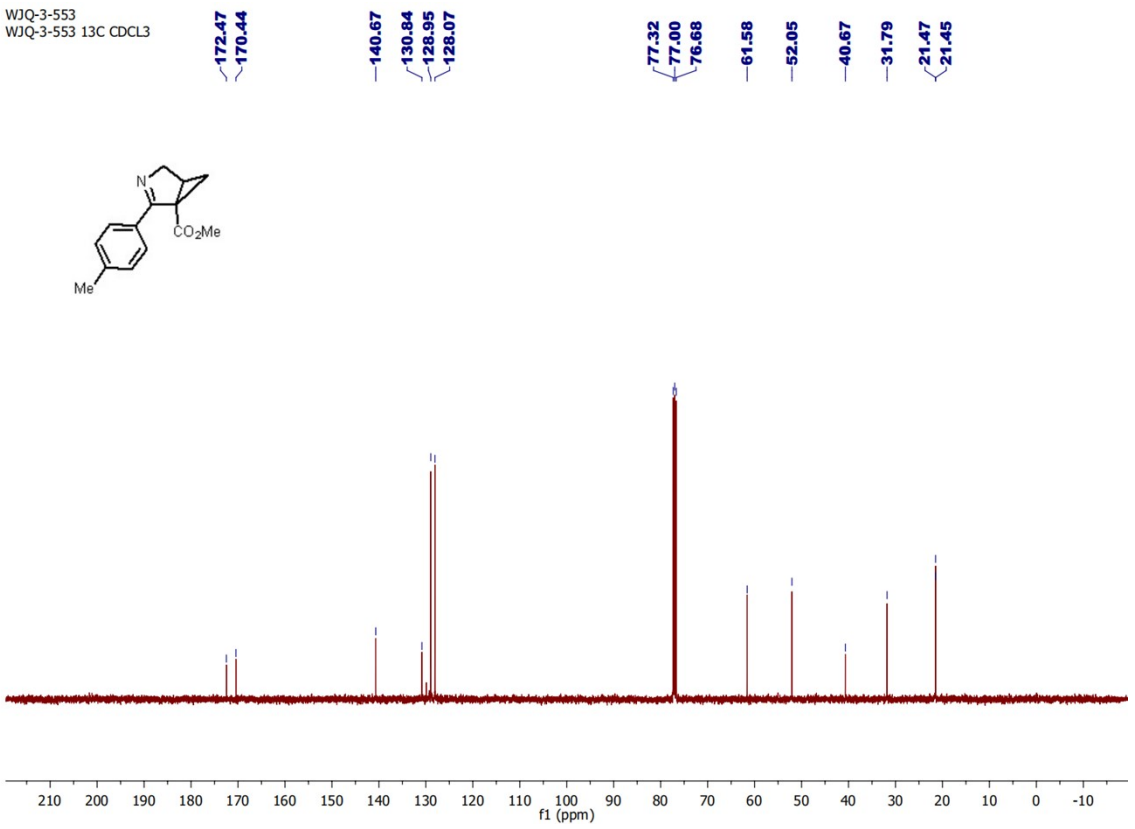
methyl 2-phenyl-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4a**)



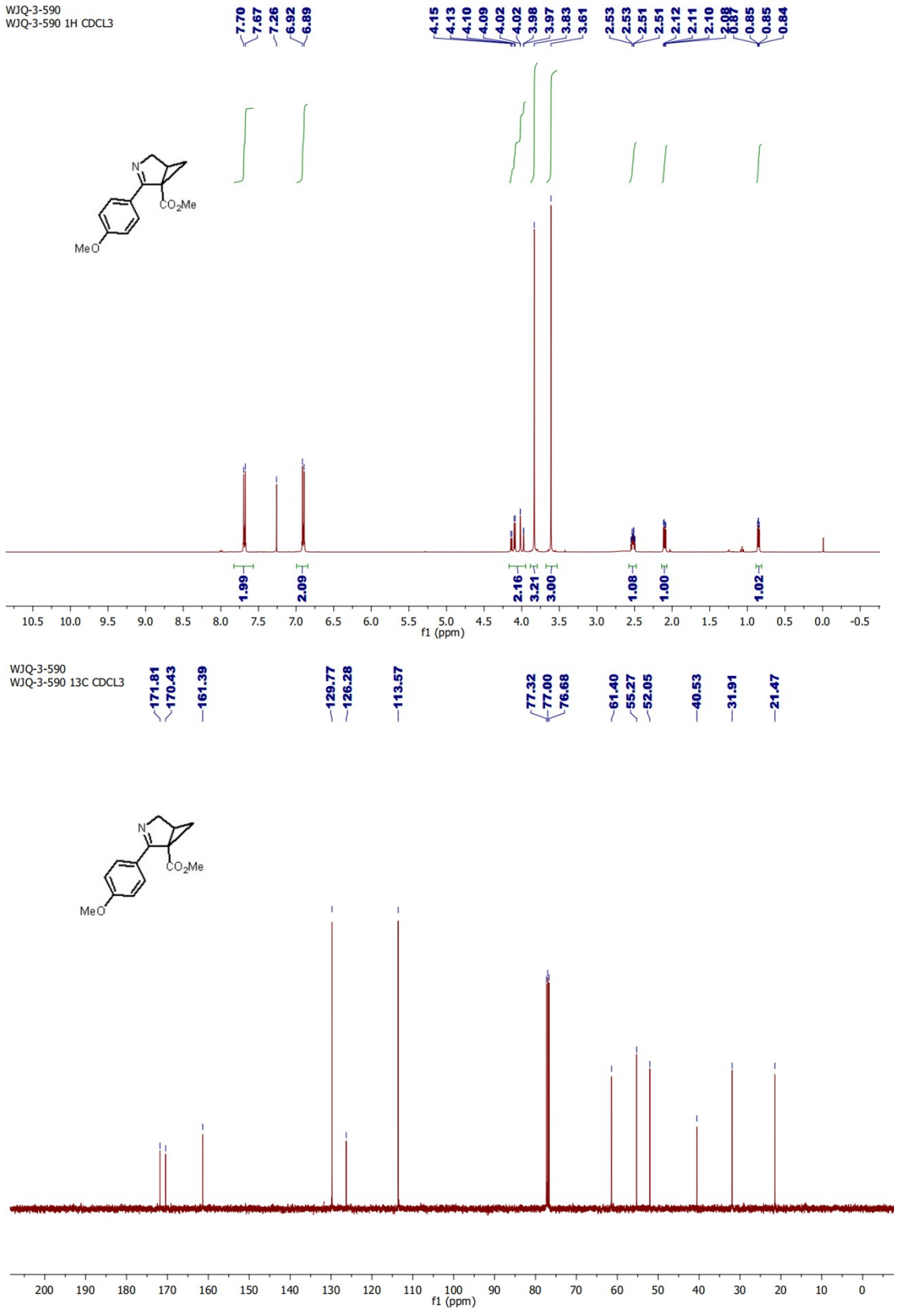


methyl 2-(p-tolyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4b**)

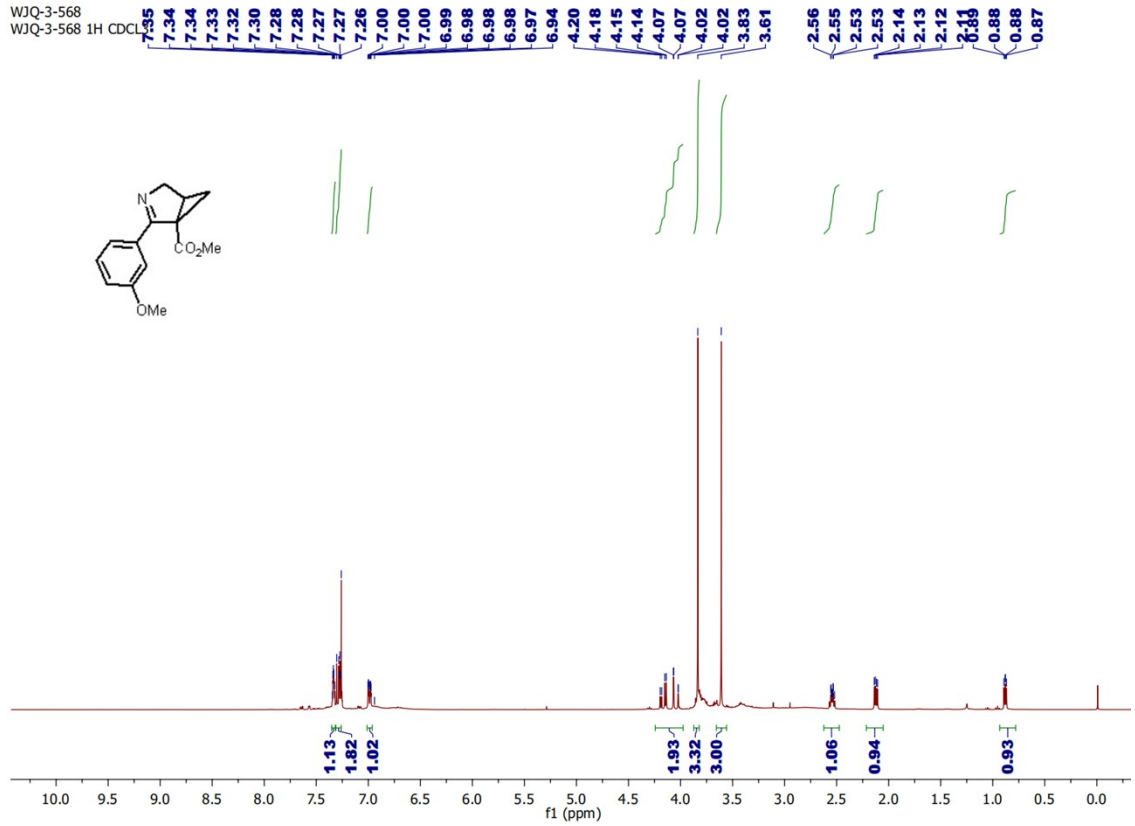


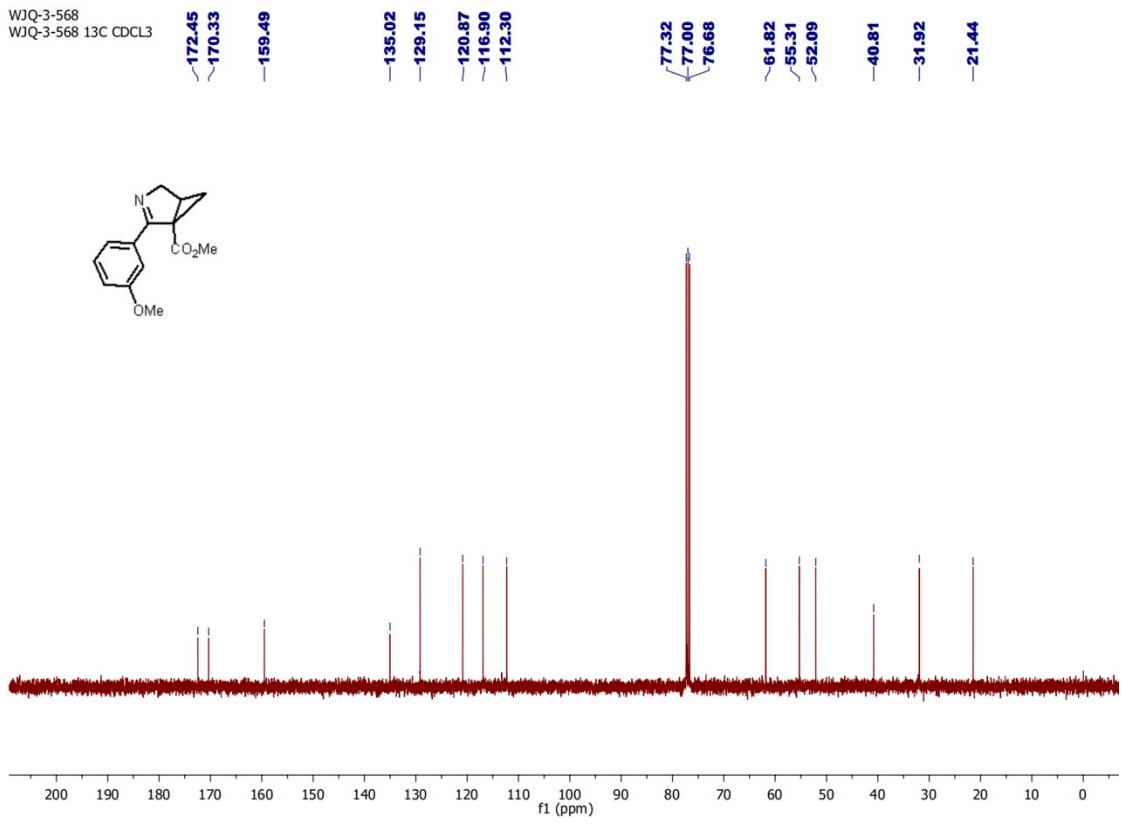


methyl 2-(4-methoxyphenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4c**)

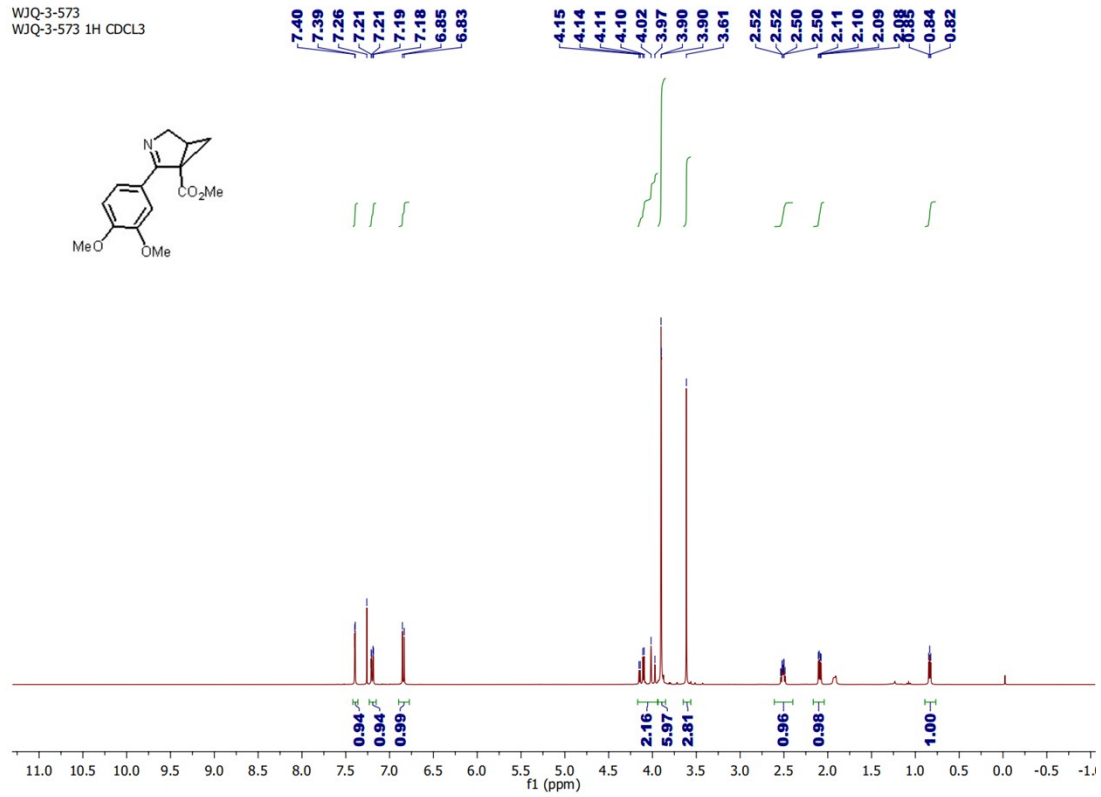


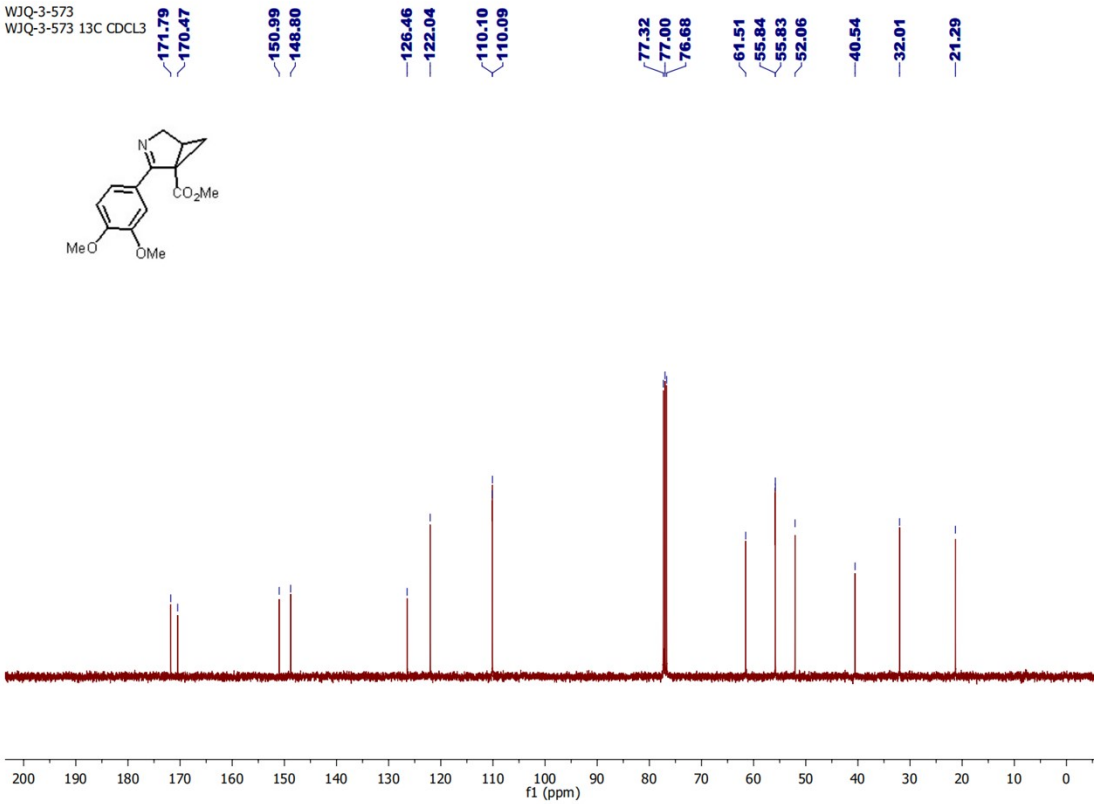
methyl 2-(3-methoxyphenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4d**)



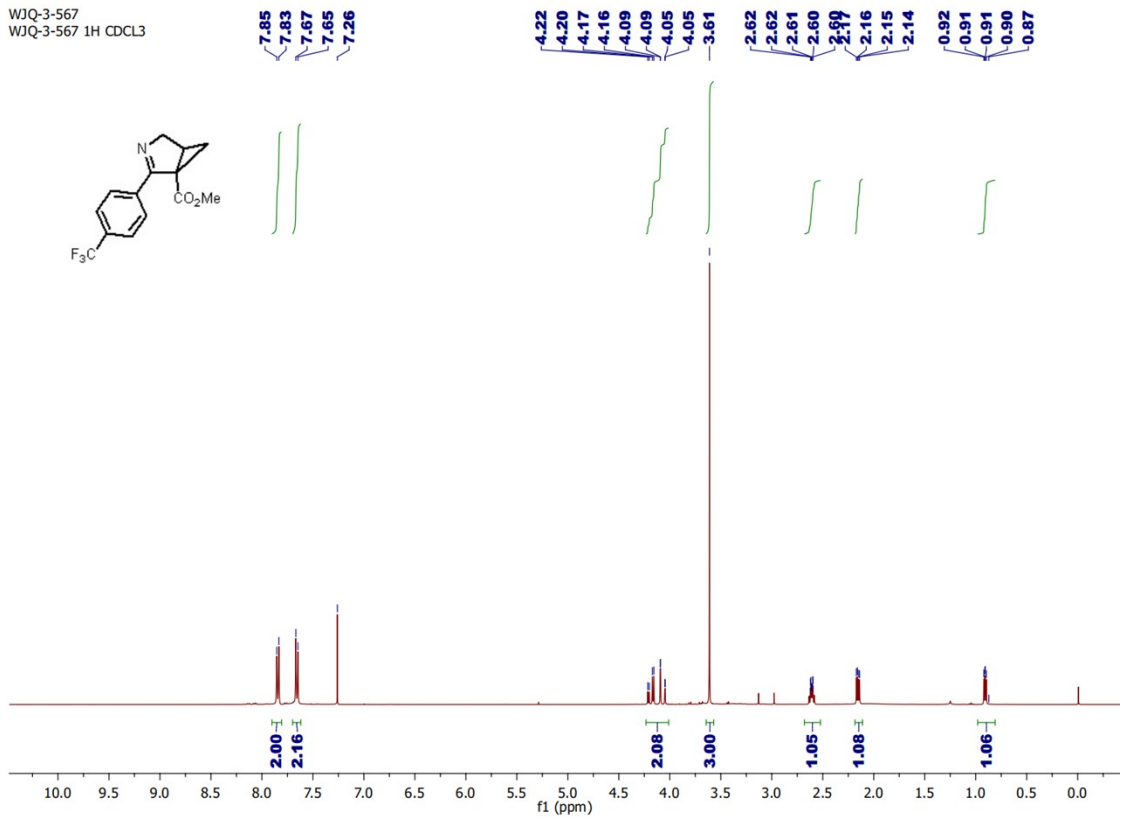


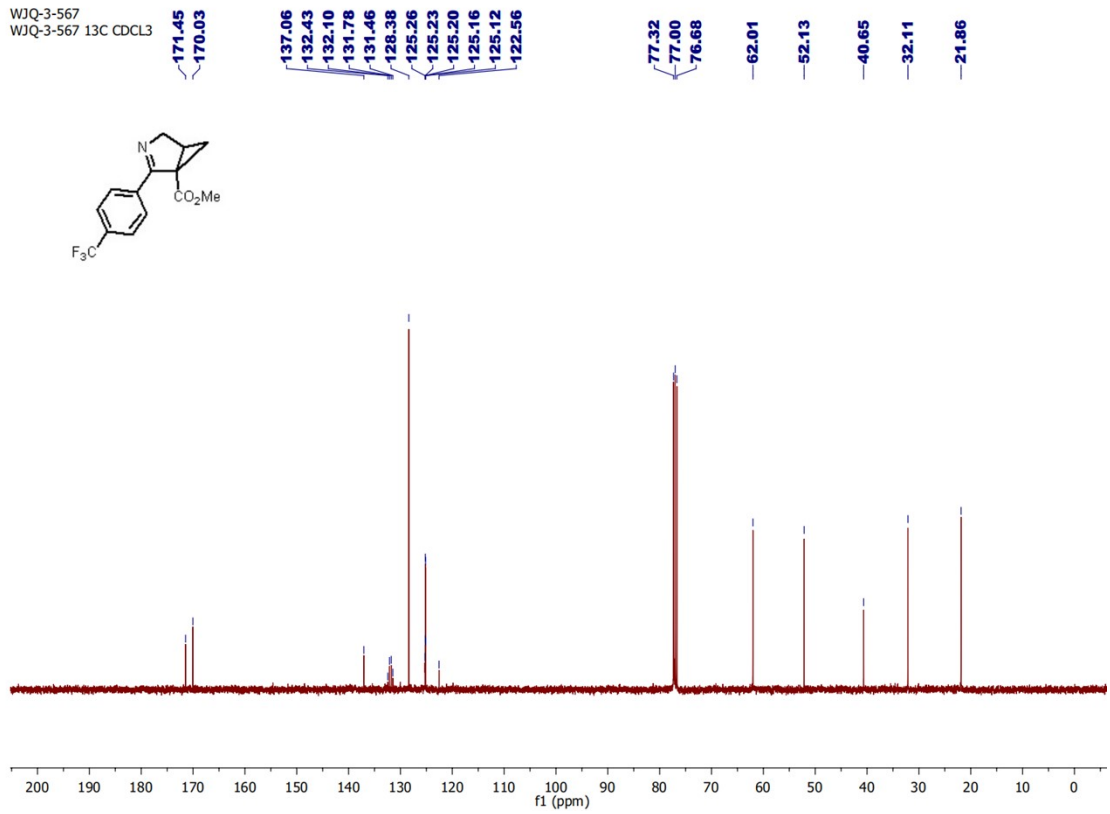
methyl 2-(3,4-dimethoxyphenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4e**)



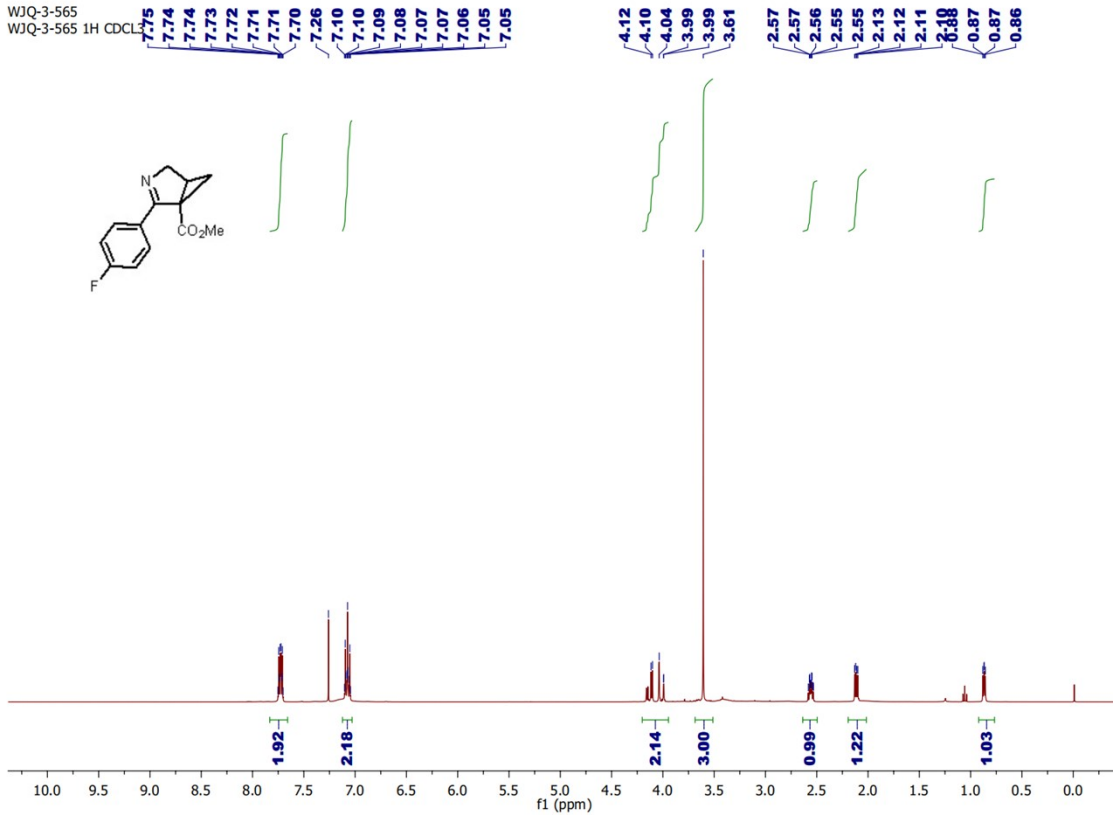


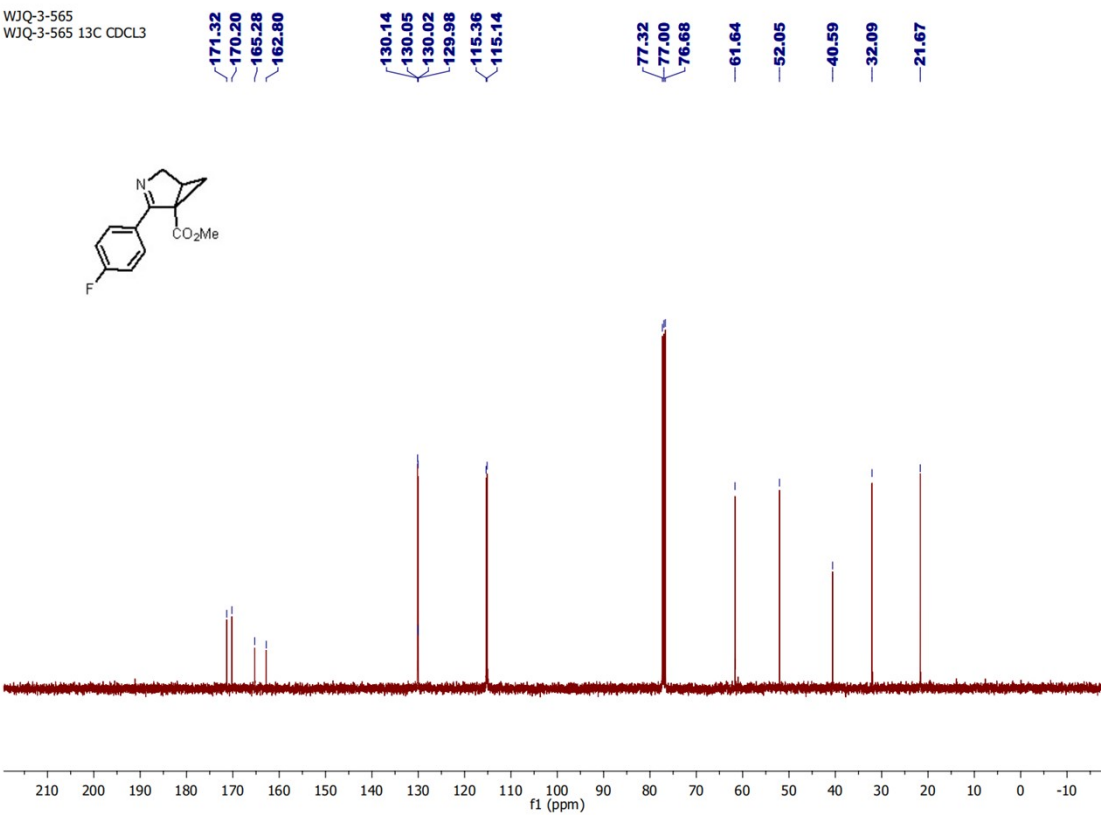
methyl 2-(4-(trifluoromethyl)phenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4f**)



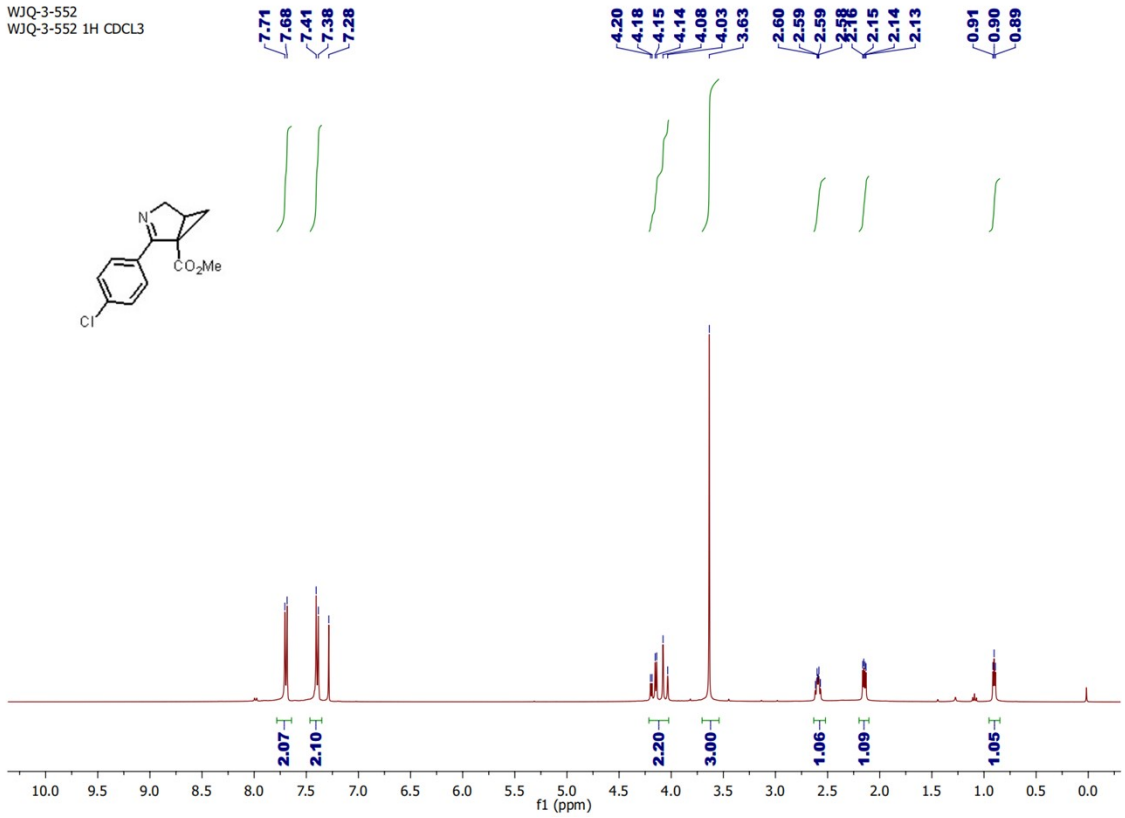


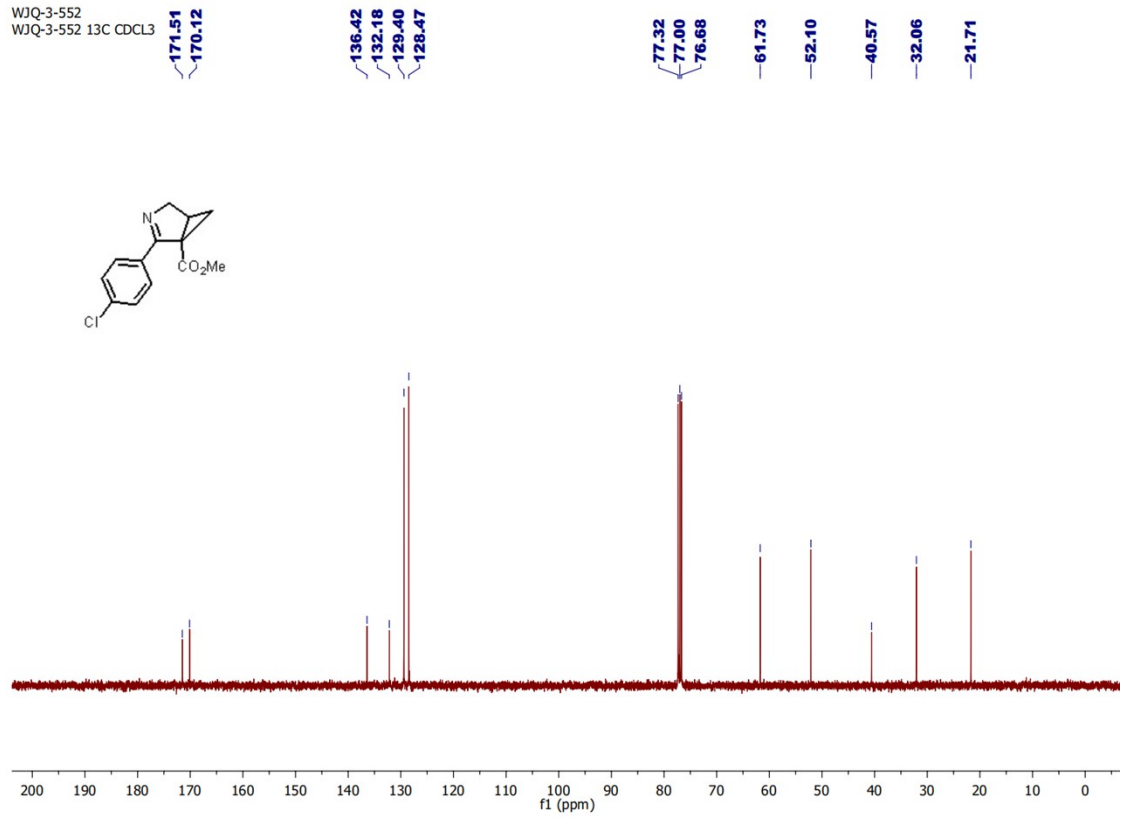
methyl 2-(4-fluorophenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4g**)



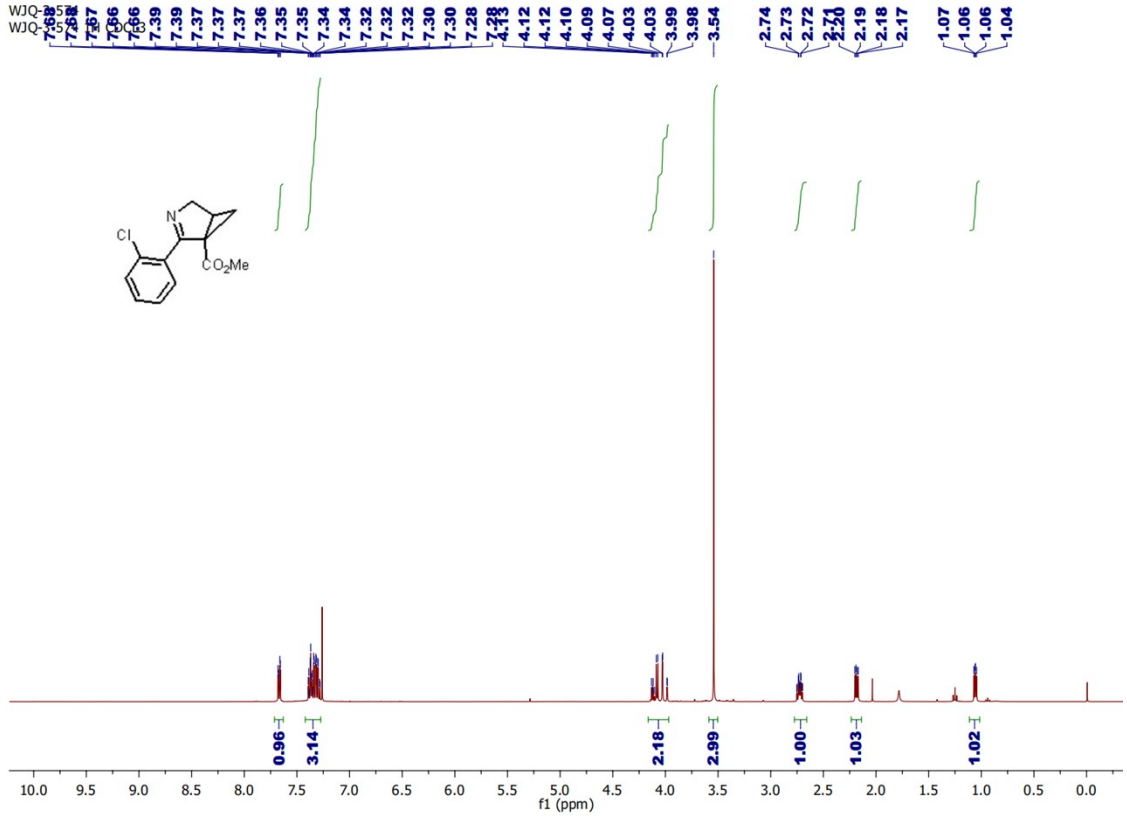


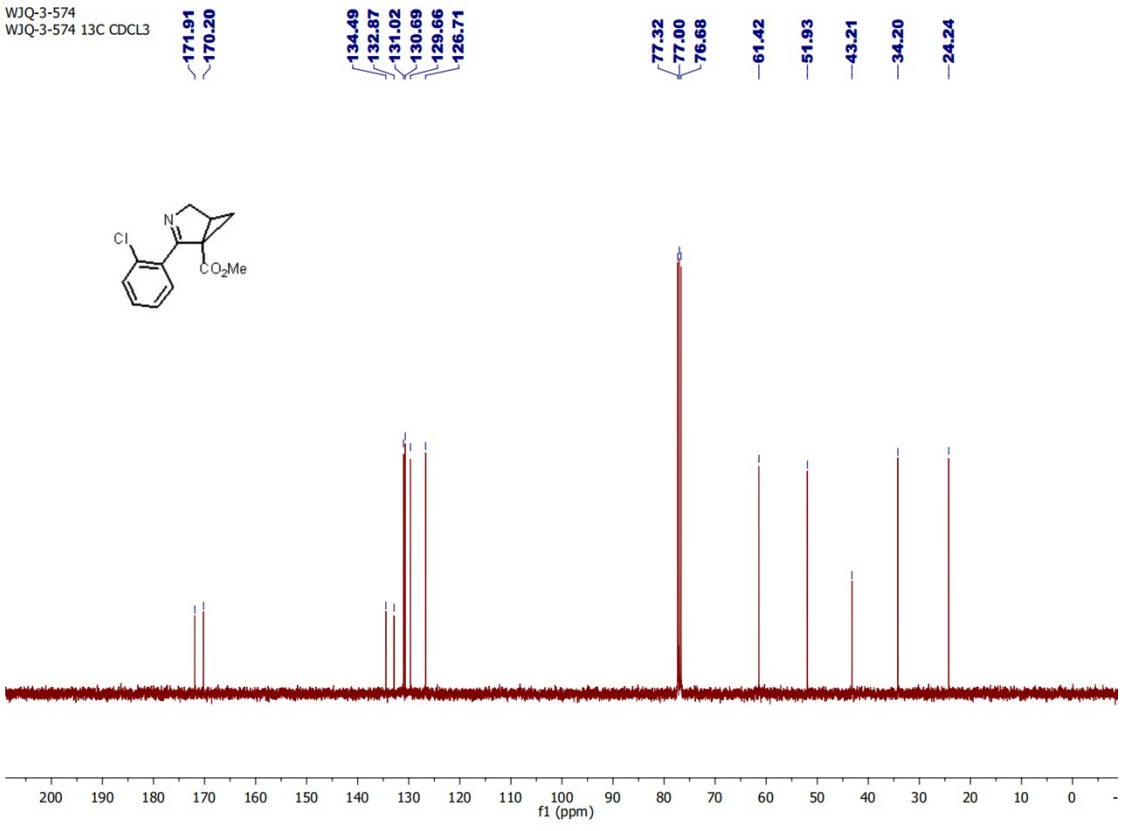
methyl 2-(4-chlorophenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4h**)



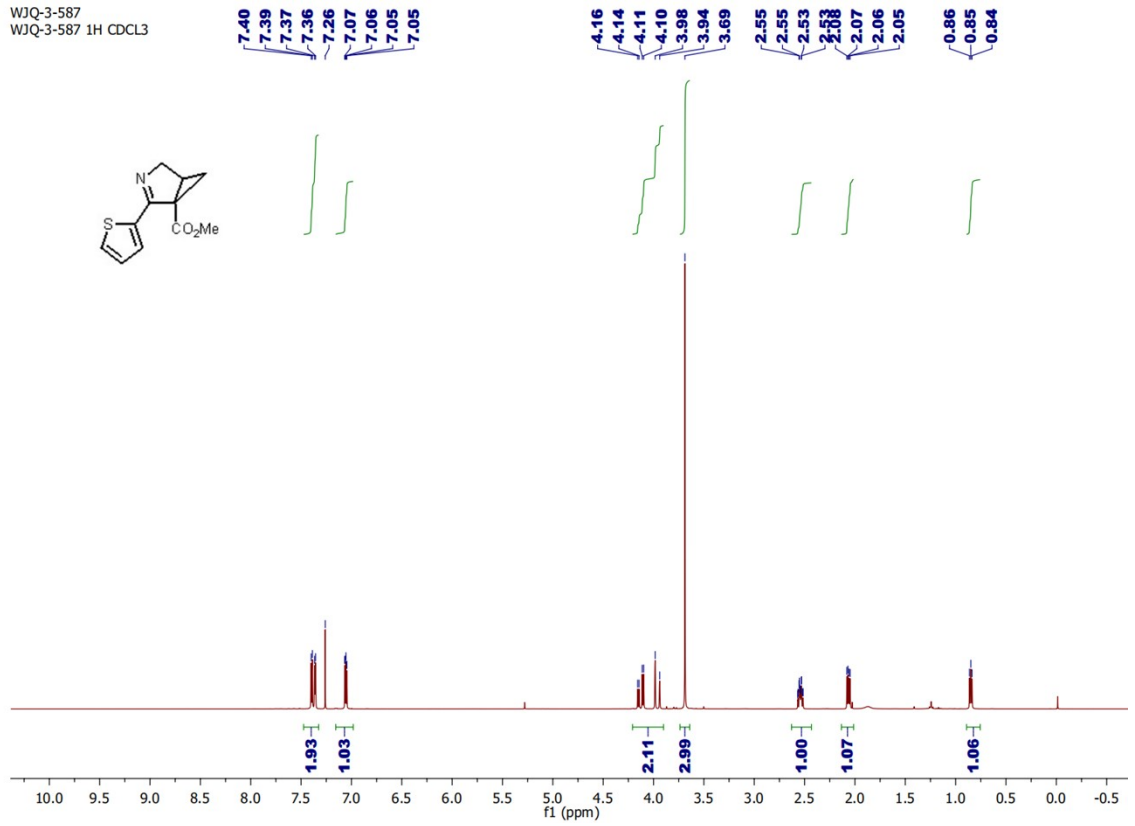


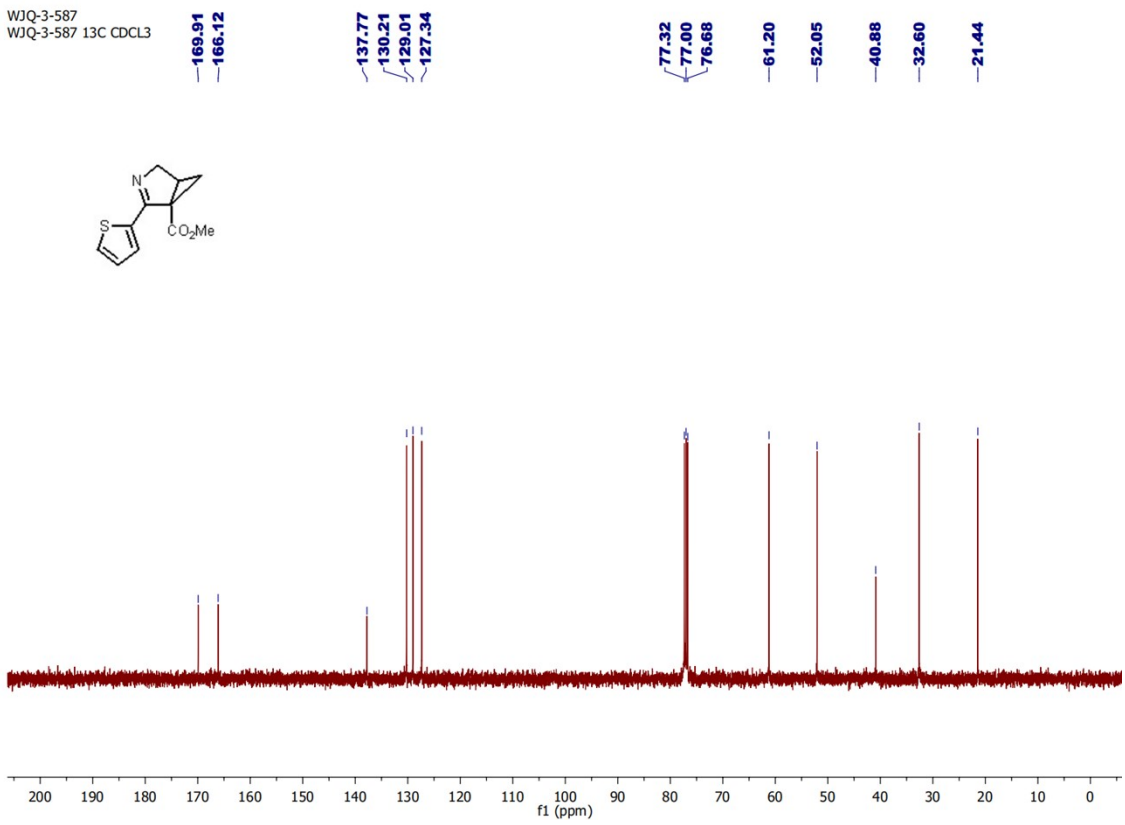
methyl 2-(2-chlorophenyl)-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4i**)



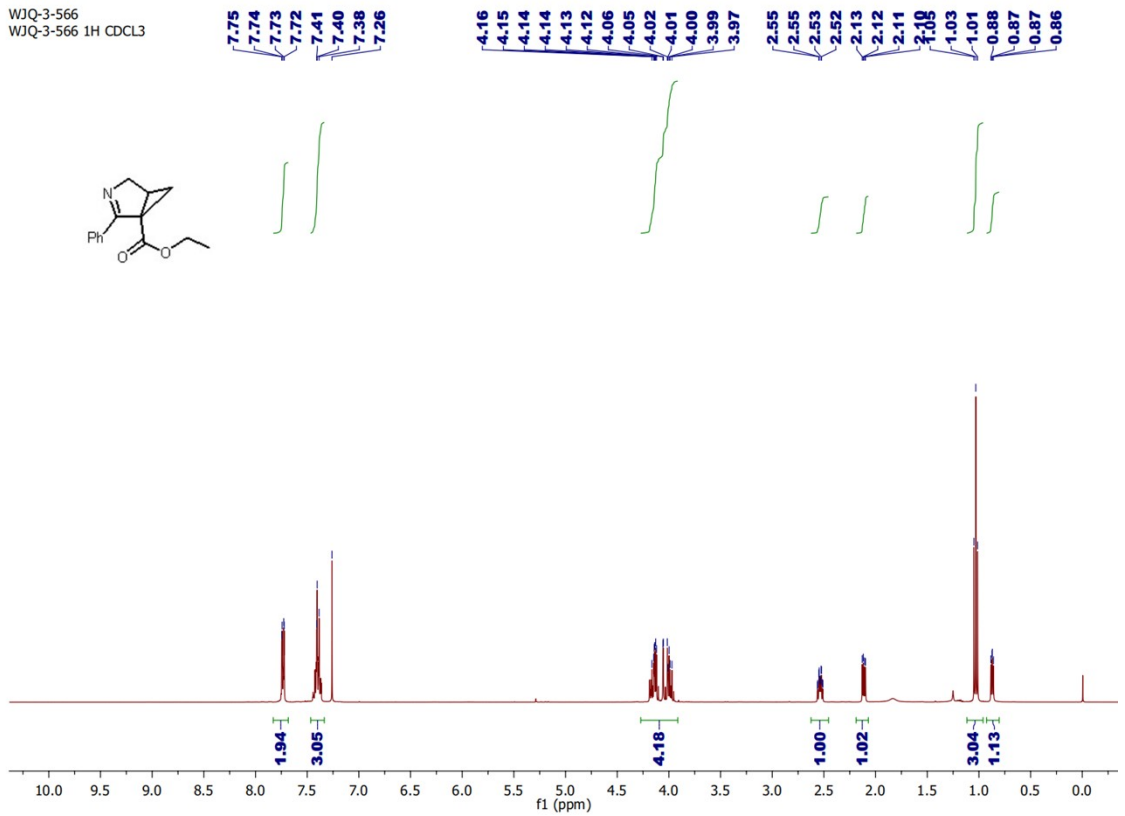


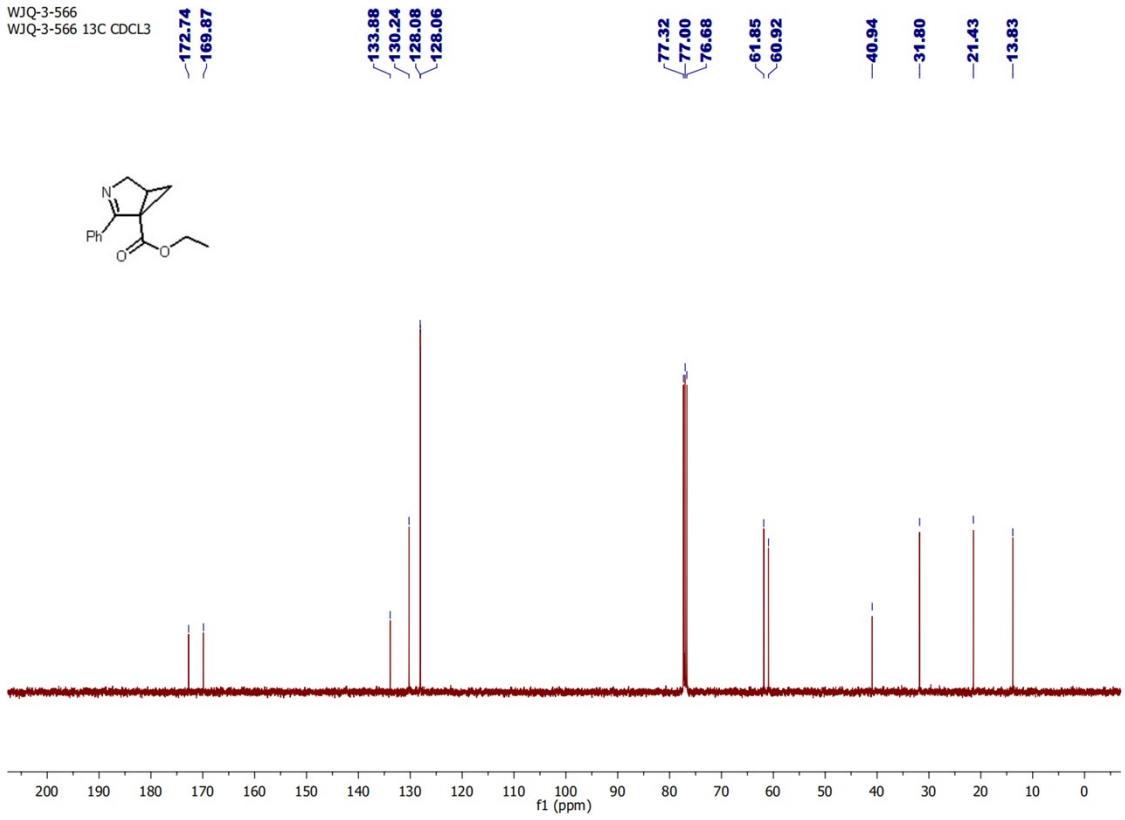
methyl 2-(thiophen-2-yl)-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4j**)



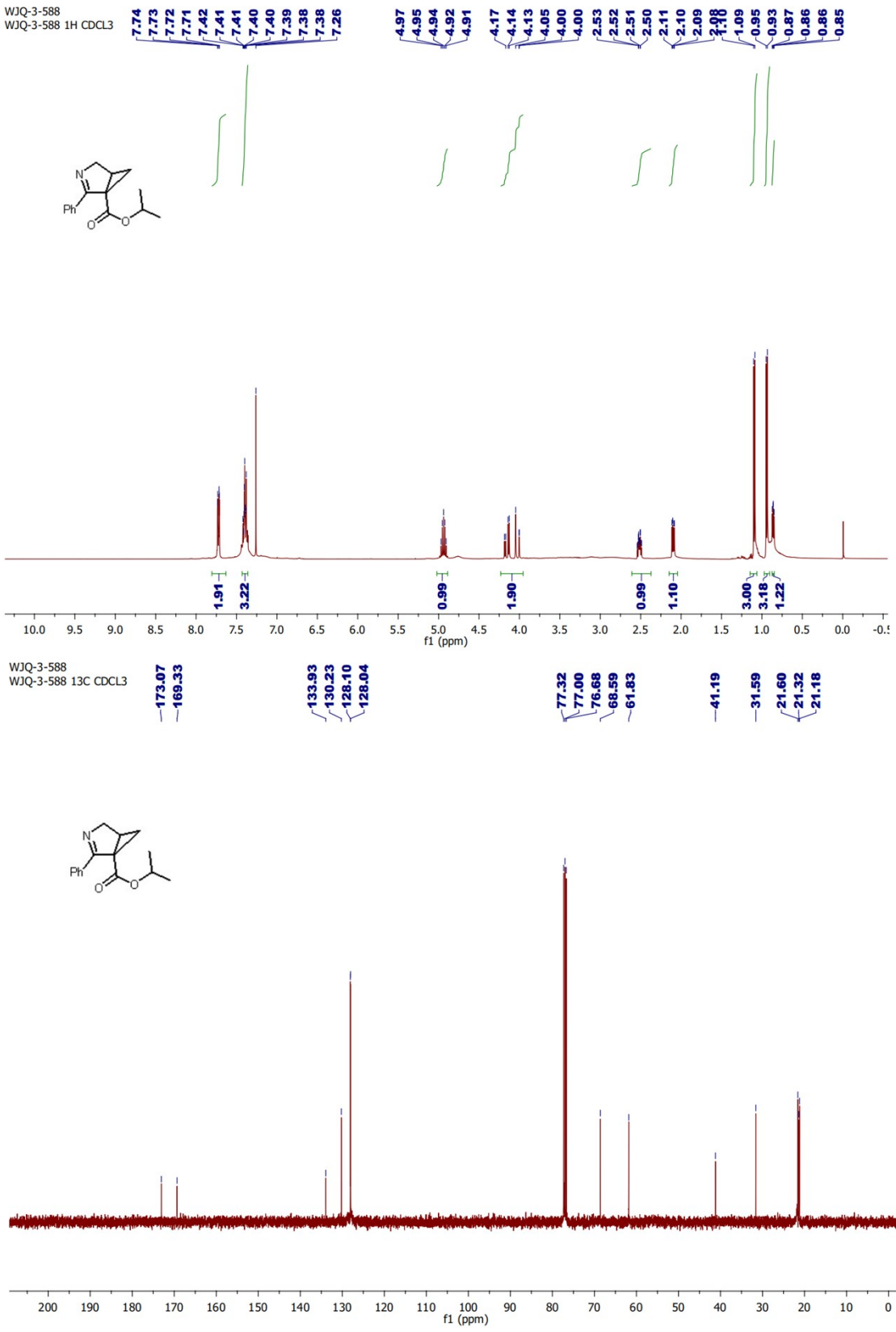


ethyl 2-phenyl-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4k**)

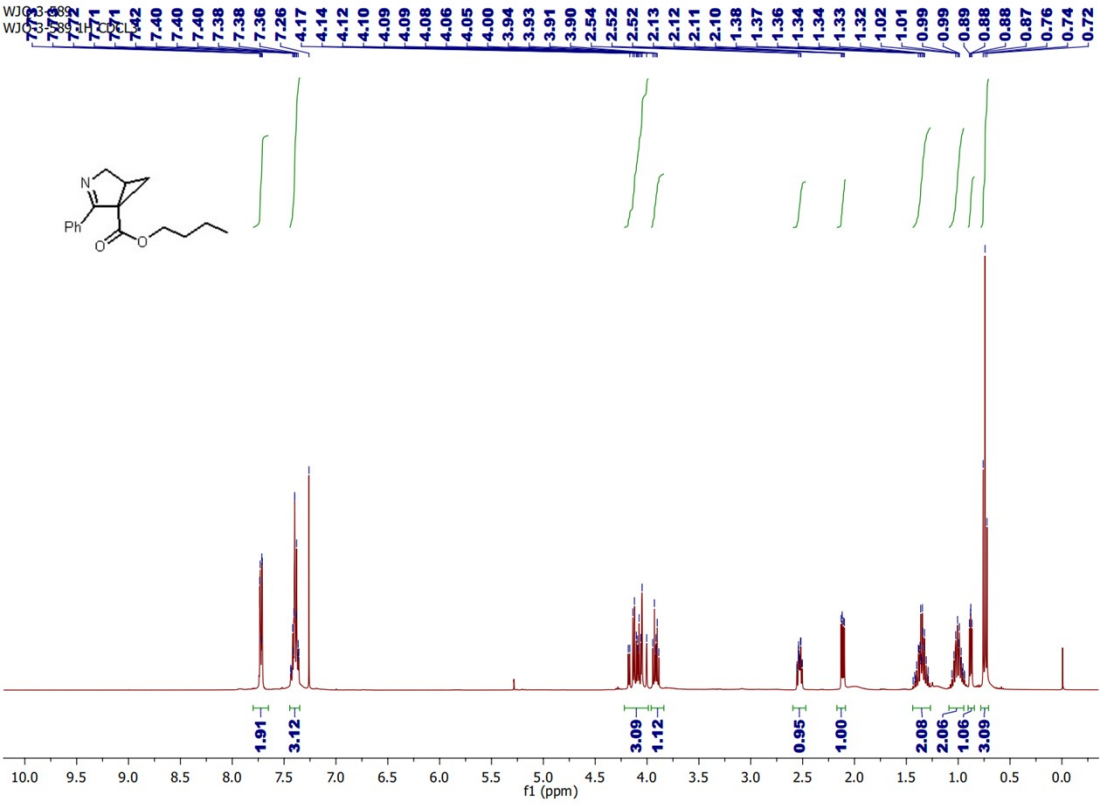


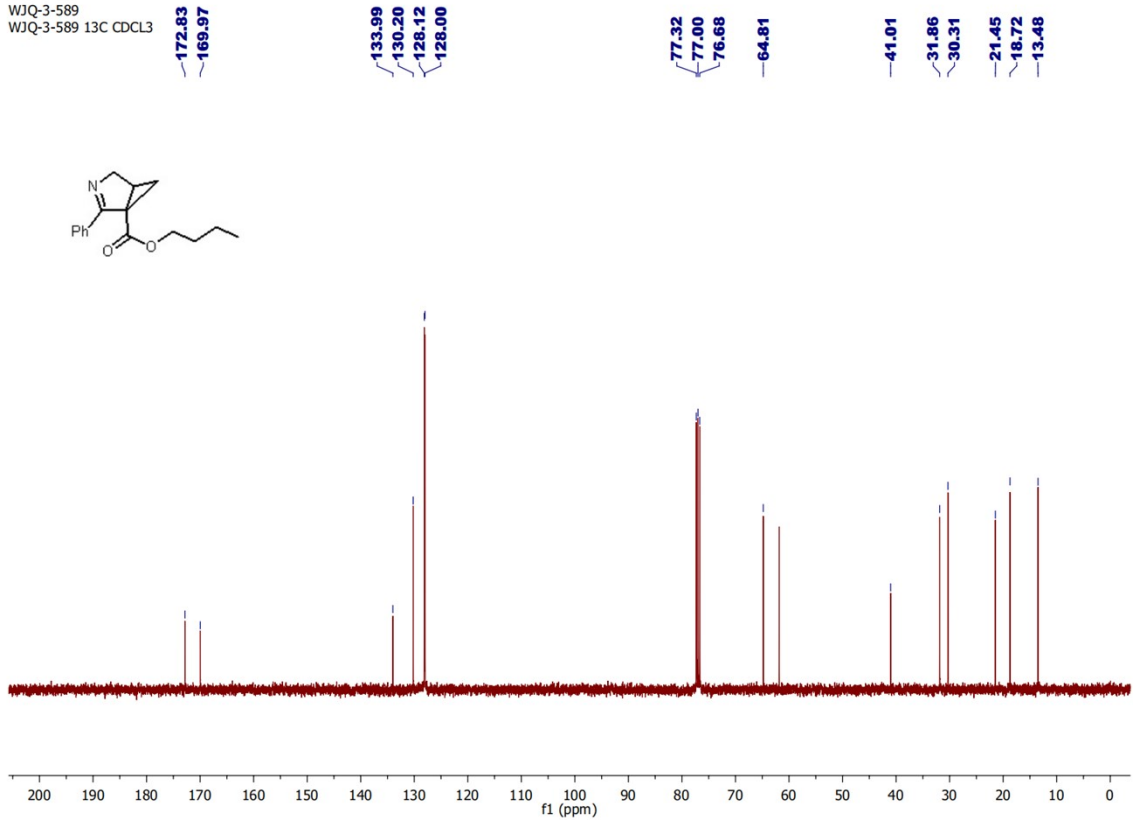


isopropyl 2-phenyl-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4l**)

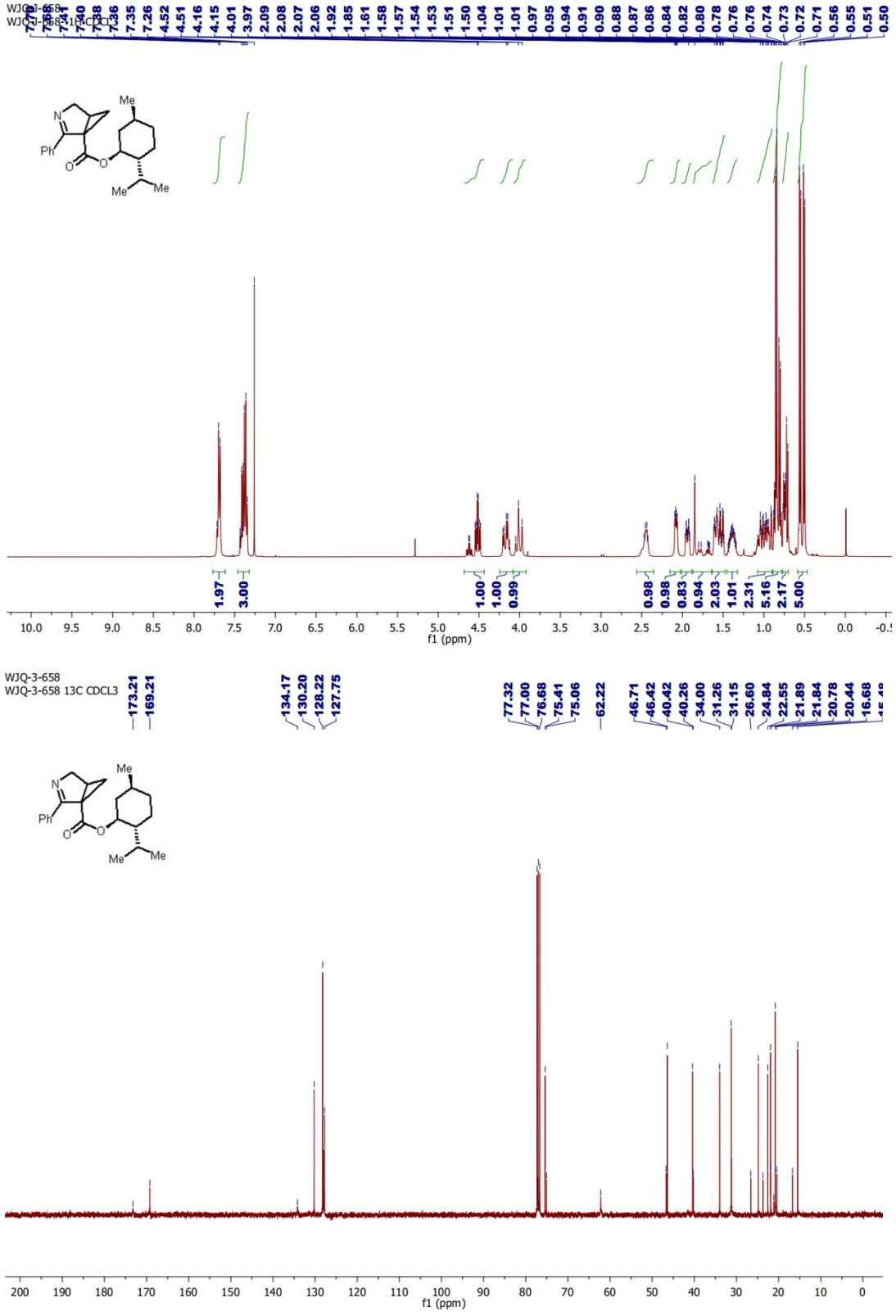


butyl 2-phenyl-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4m**)

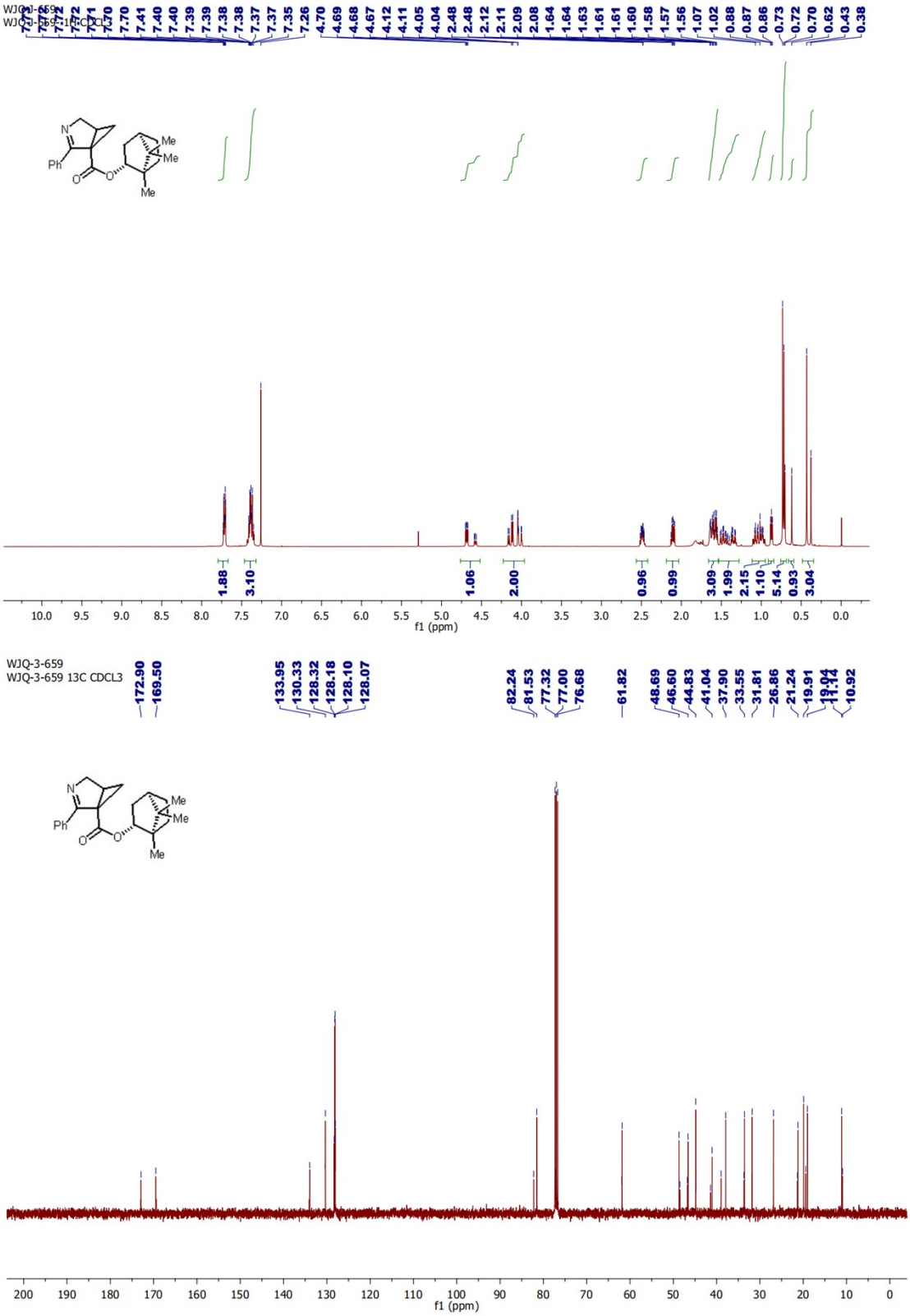




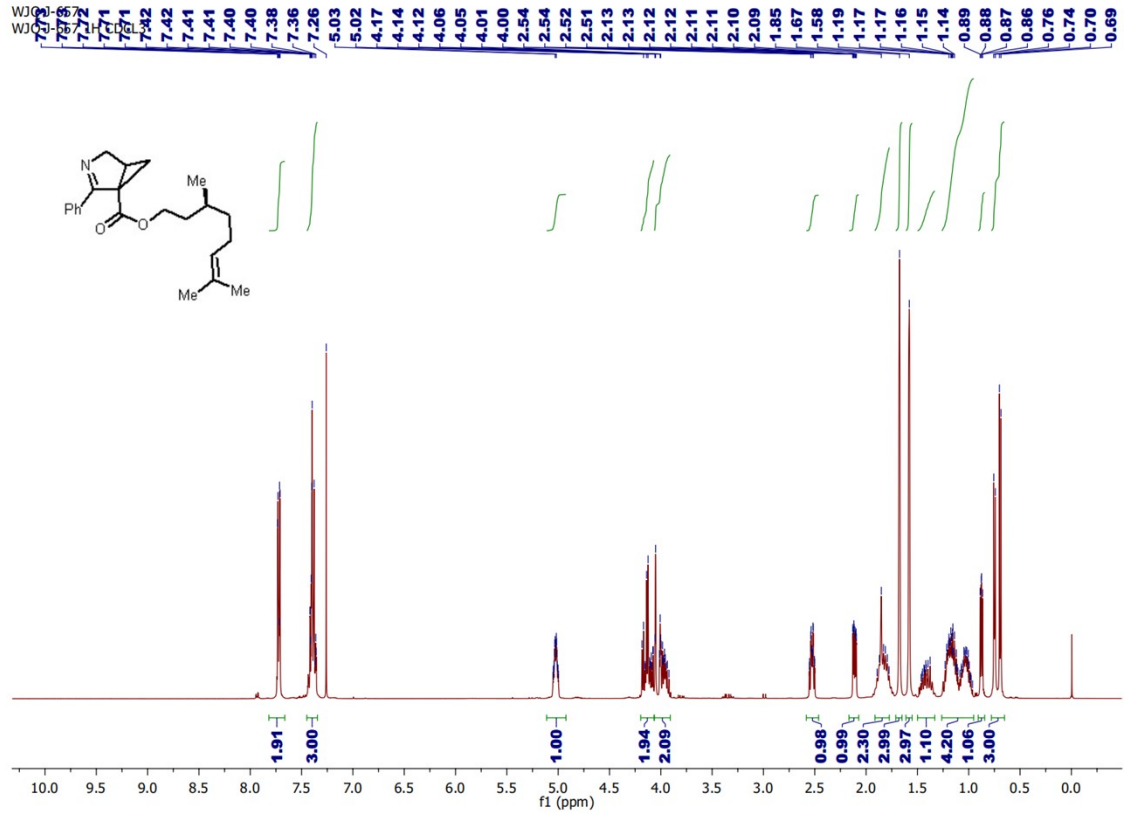
(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 2-phenyl-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4n**)

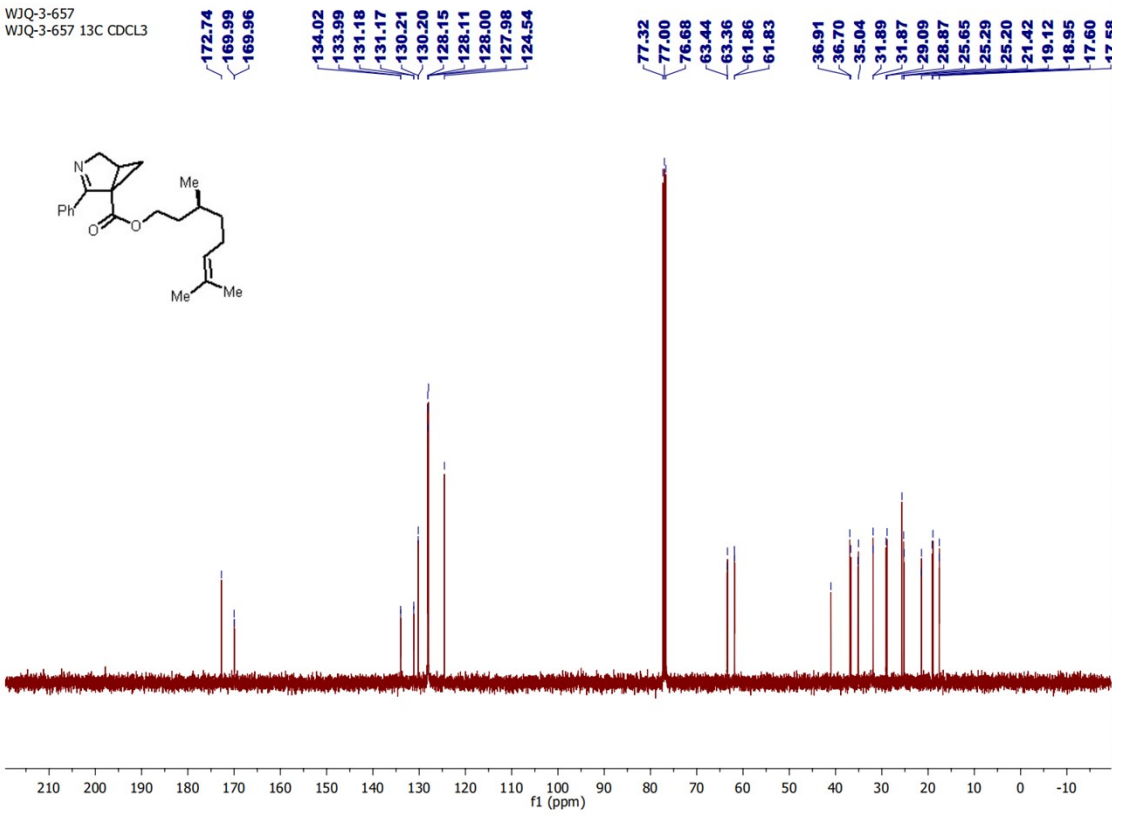


(1R,2R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2-phenyl-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4o**)

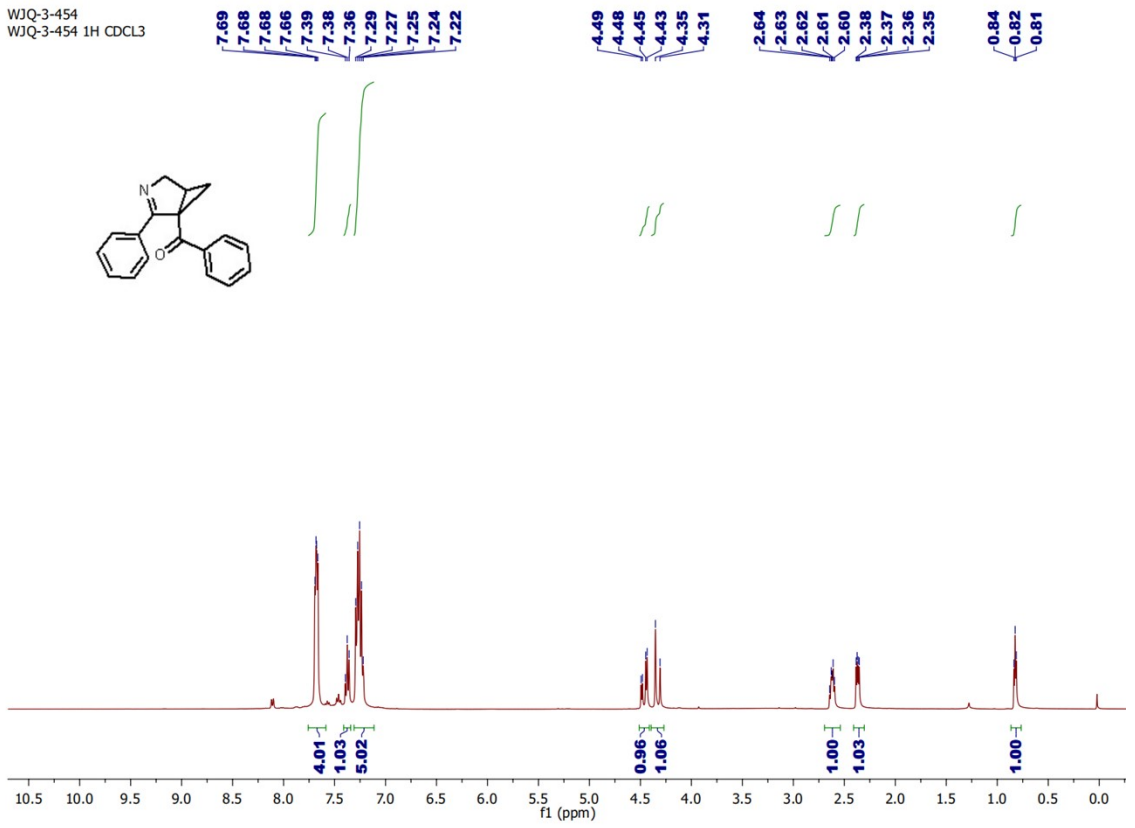


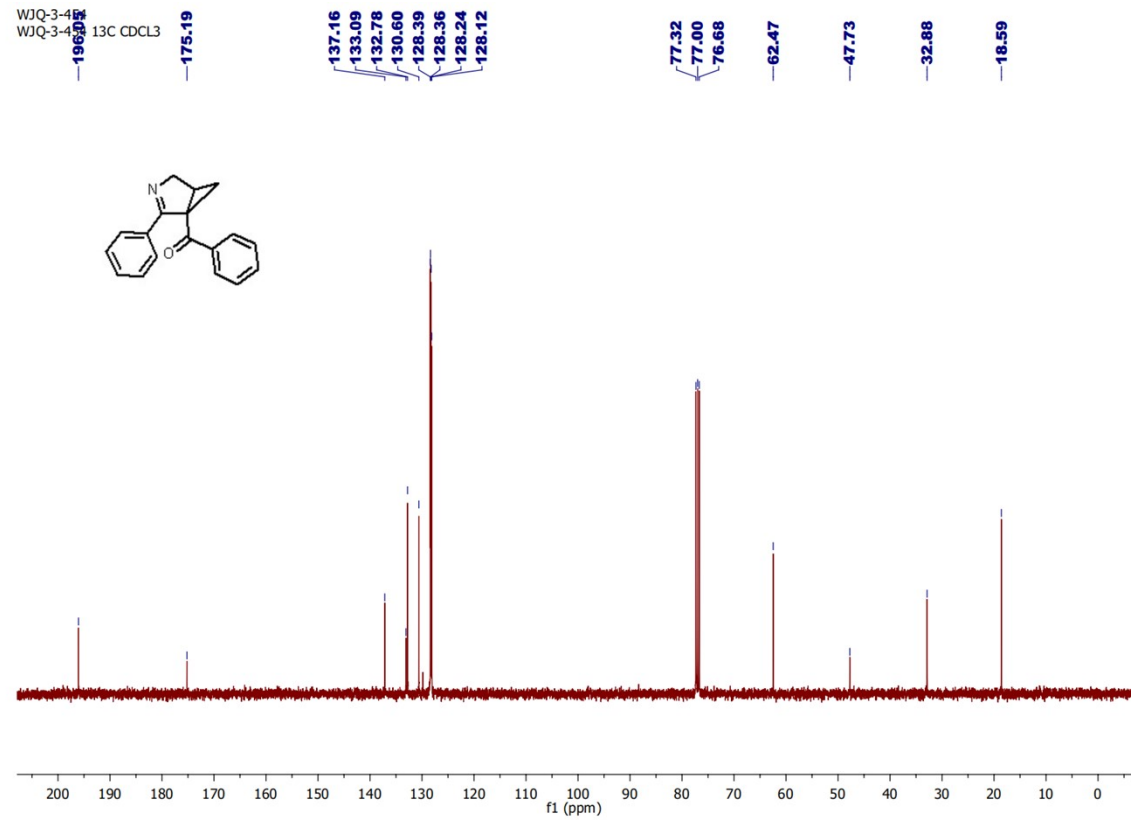
(S)-3,7-dimethyloct-6-en-1-yl 2-phenyl-3-azabicyclo[3.1.0]hex-2-ene-1-carboxylate (**4p**)



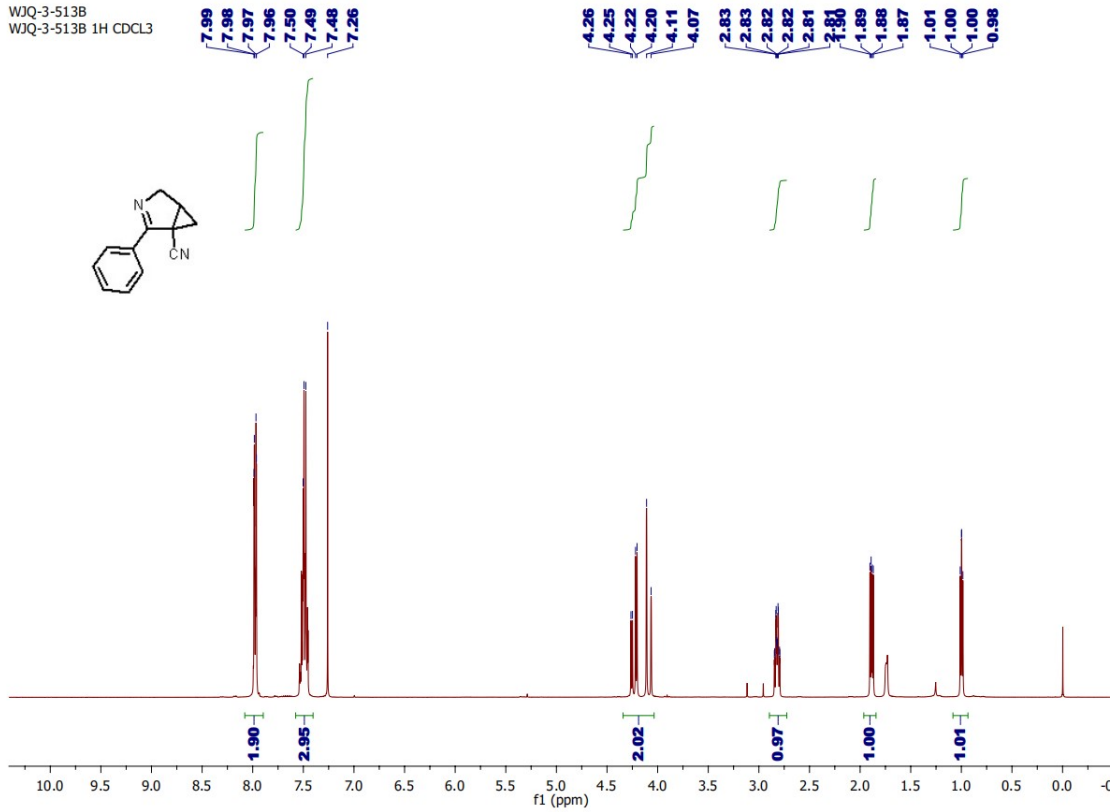


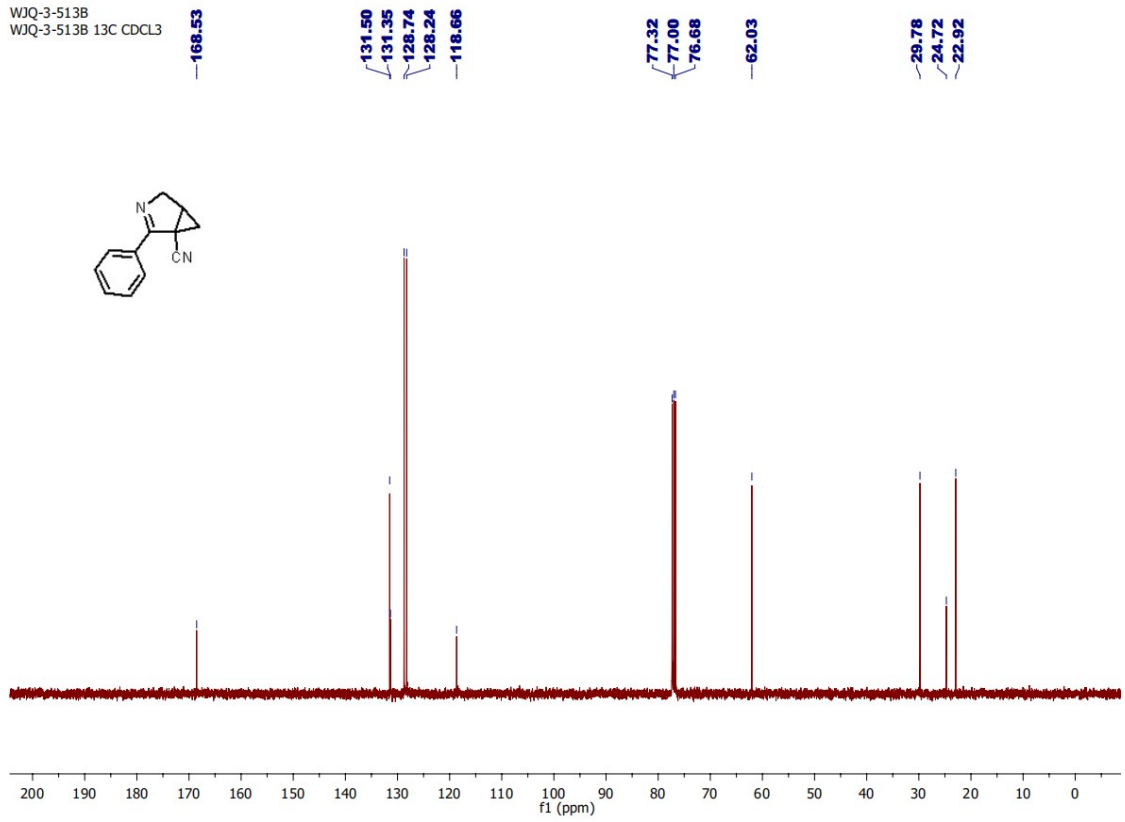
phenyl(2-phenyl-3-azabicyclo[3.1.0]hex-2-en-1-yl)methanone (**4q**)



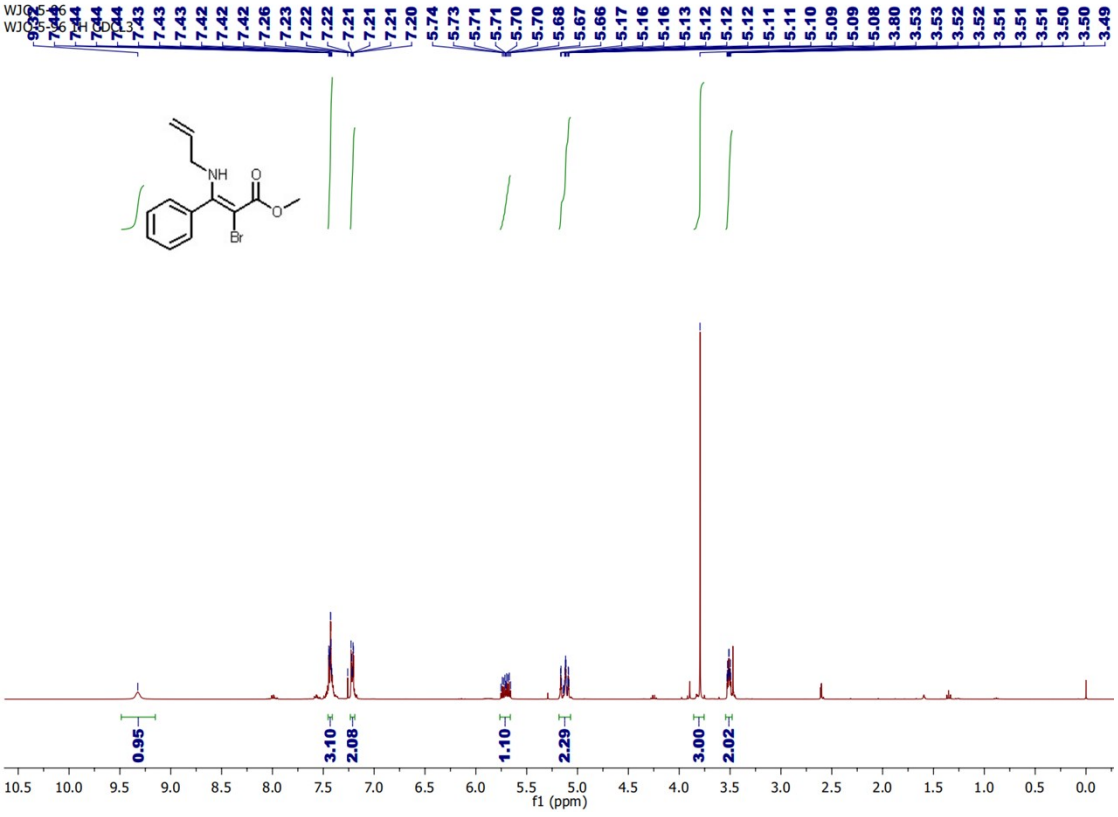


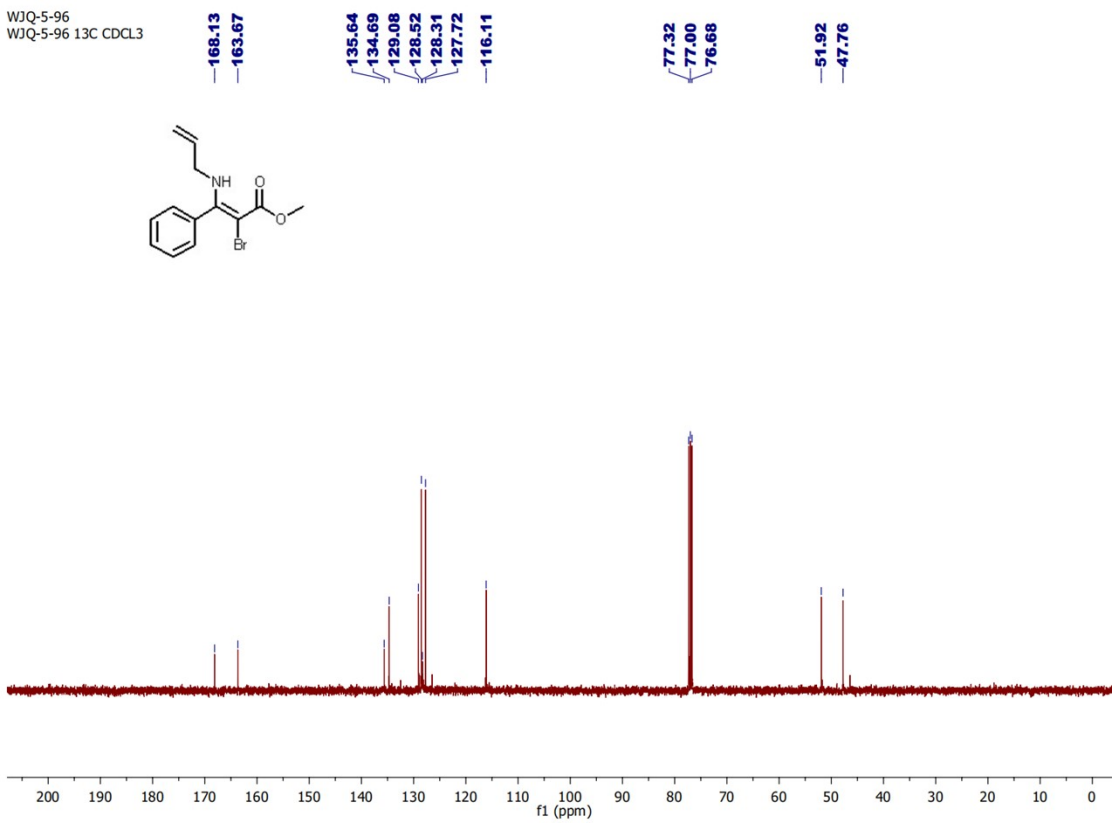
2-phenyl-3-azabicyclo[3.1.0]hex-2-ene-1-carbonitrile (**4r**)



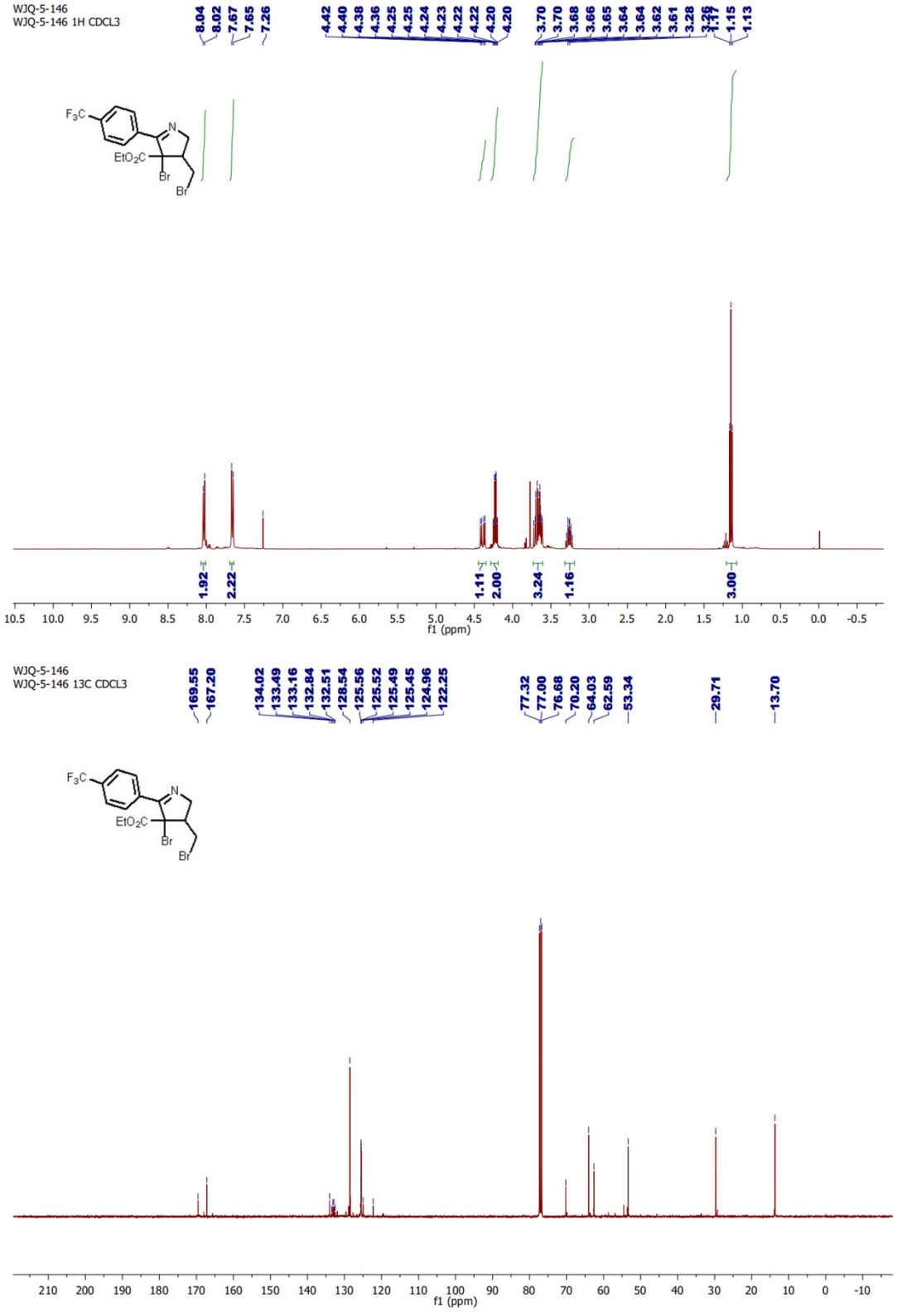


methyl (E)-3-(allylamino)-2-bromo-3-phenylacrylate (**5a**)



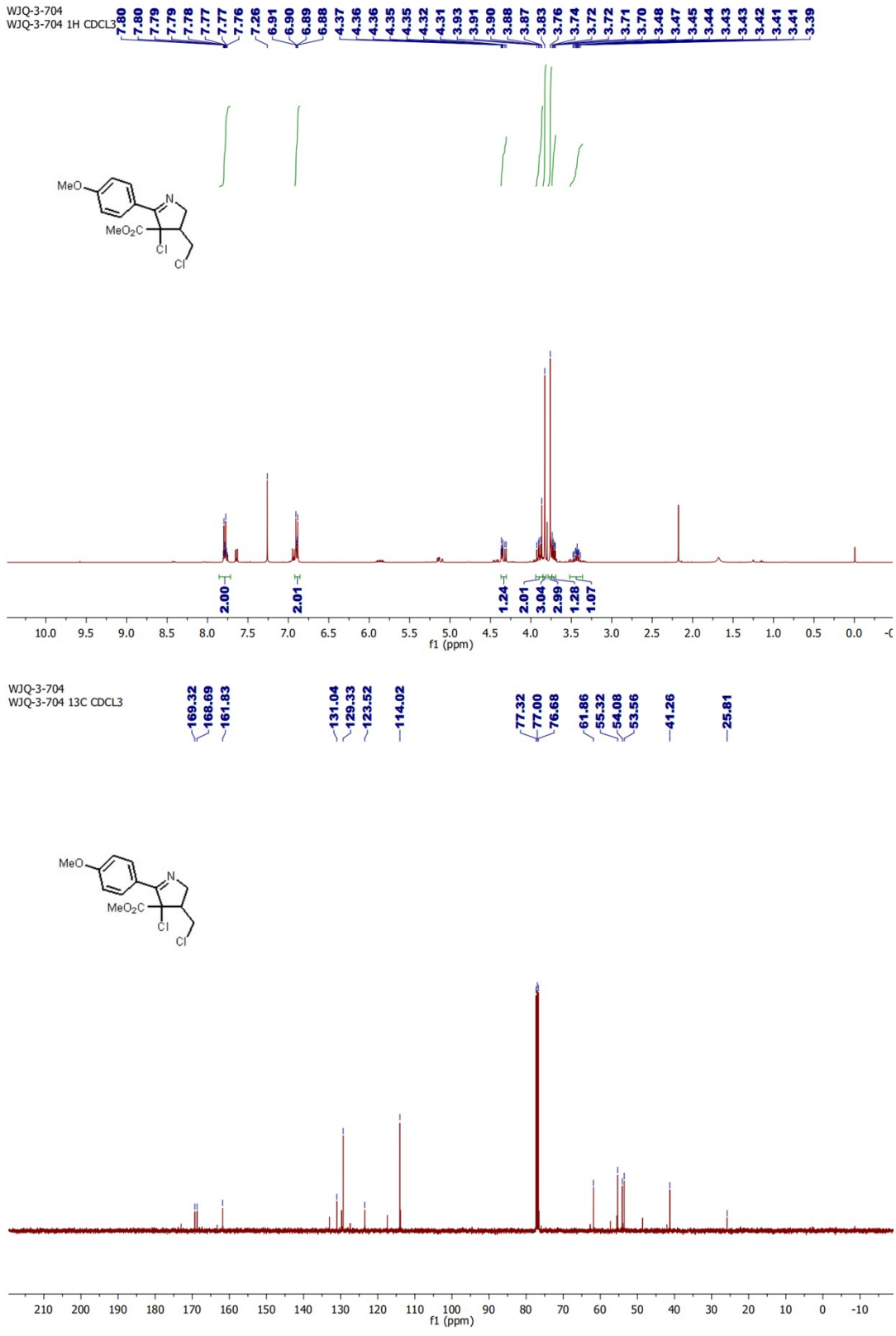


ethyl 4-bromo-3-(bromomethyl)-5-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2H-pyrrole-4-carboxylate **(7f)**



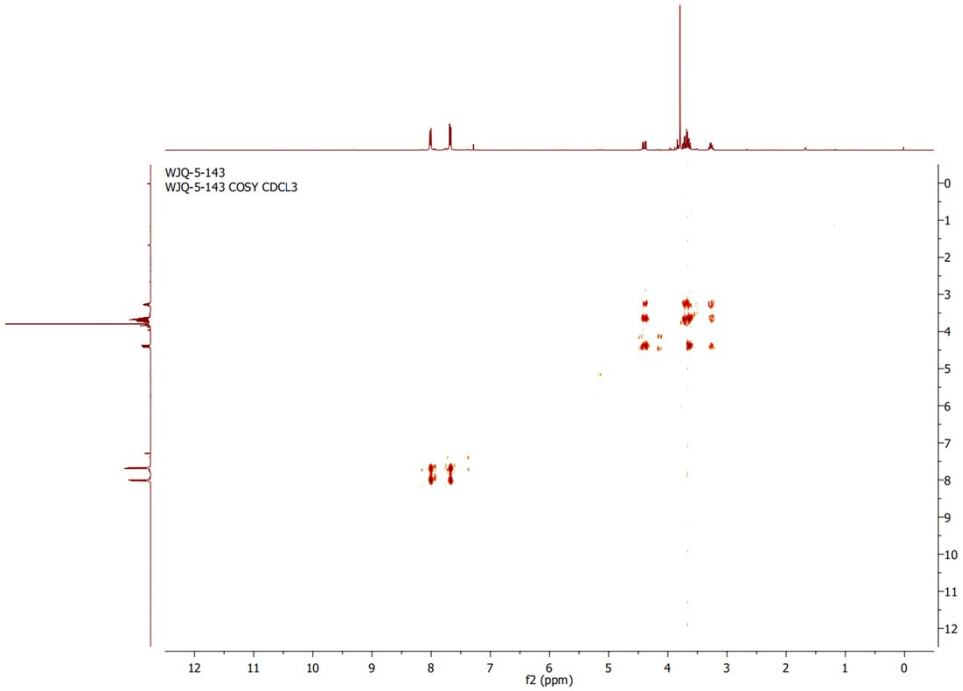
methyl 4-chloro-3-(chloromethyl)-5-(4-methoxyphenyl)-3,4-dihydro-2H-pyrrole-4-carboxylate

(8c)

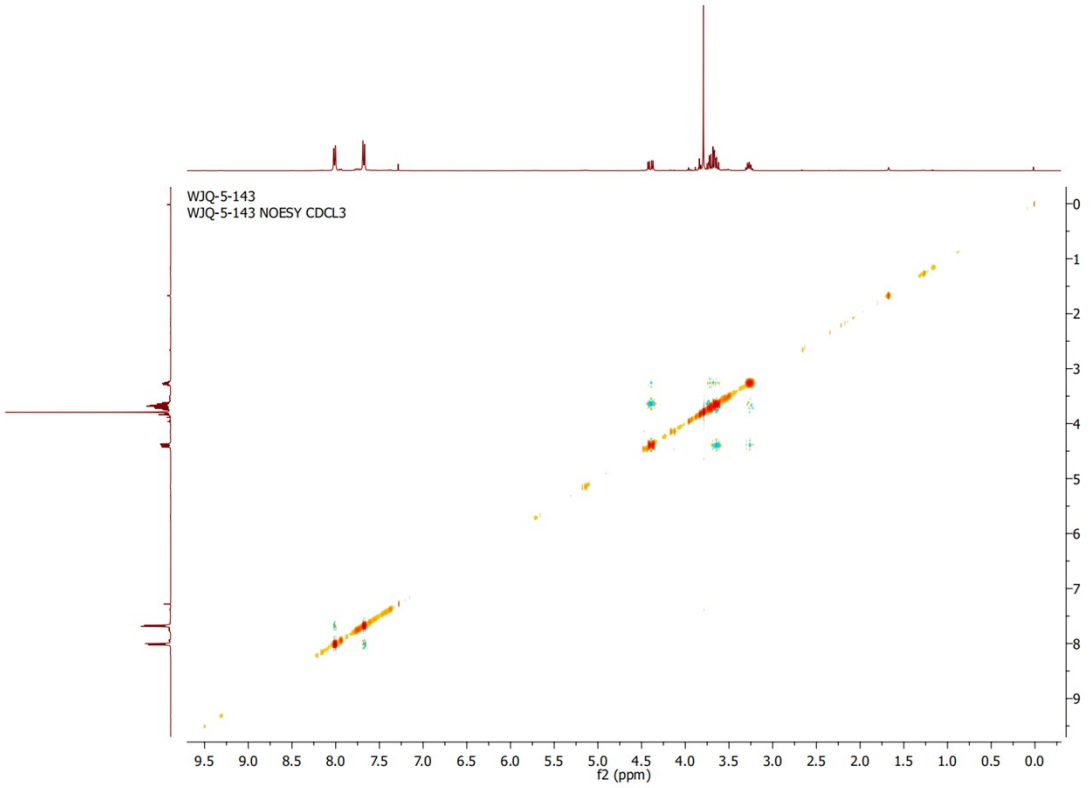


2D NMR spectra

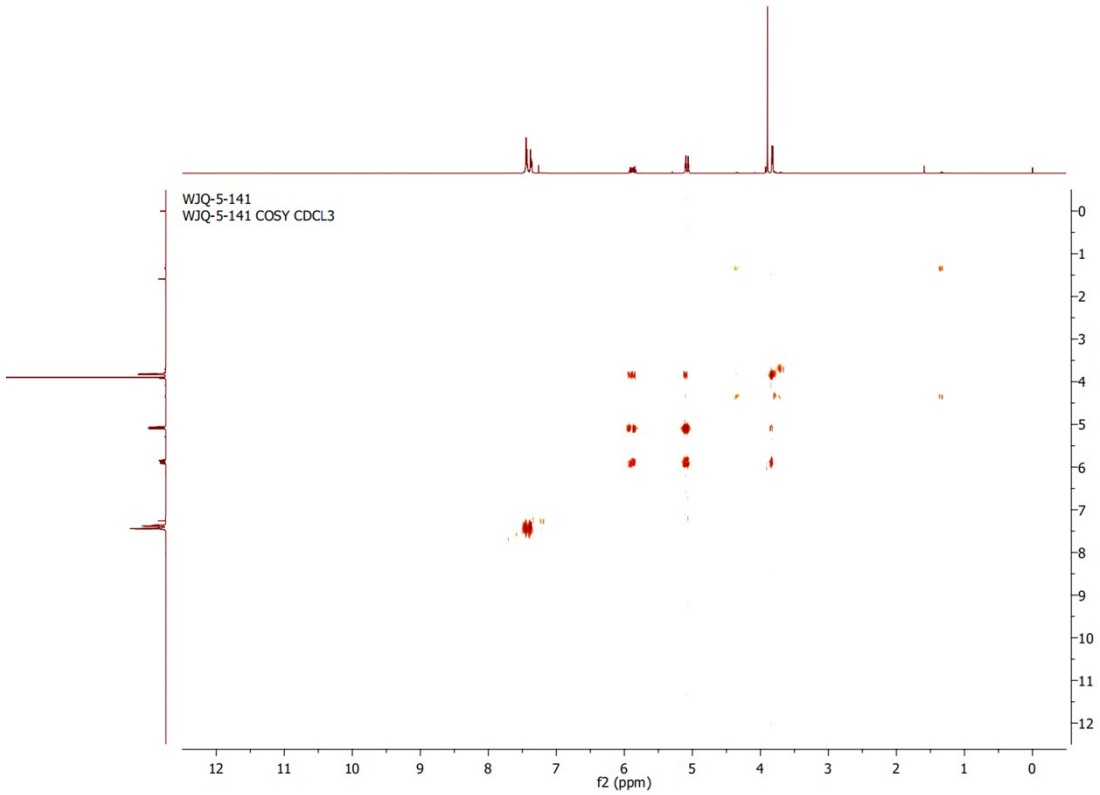
COSY spectra of compound **2f** (400 MHz, $CDCl_3$)



NOESY spectra of compound **2f** (400 MHz, $CDCl_3$)



COSY spectra of compound **3a** (400 MHz, $CDCl_3$)



NOESY spectra of compound **3a** (400 MHz, $CDCl_3$)