Supplementary Information

Catalytic [2,3]-sigmatropic rearrangement of sulfonium ylides derived from azoalkenes: non-carbenoid Doyle−Kirmse reaction

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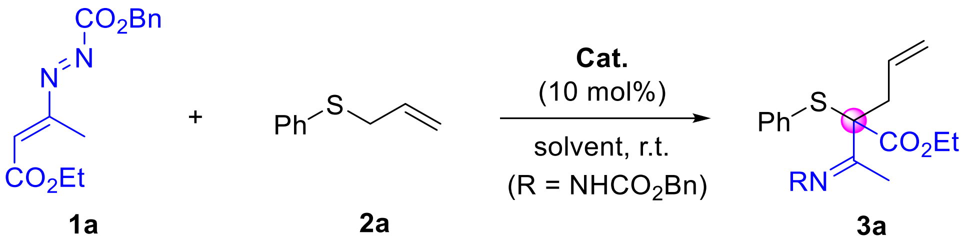
Contents

1. General Methods

Unless otherwise specified, all reactions were conducted under an inert atmosphere and anhydrous conditions. All the solvents were purified according to the standard procedures. All chemicals which are commercially available were employed without further purification. Thin - layer chromatography (TLC) was performed on silica gel plates (60F - 254) using UV - light (254 nm). Flash chromatography was conducted on silica gel (200–300 mesh). ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature in $CDCl_3$ on a 400 MHz NMR spectrometer. Chemical shifts were reported in parts per million (ppm). The data are reported as follows: for ^{1}H NMR, chemical shift in ppm from tetramethylsilane with the solvent as internal standard ($CDCl_3$ δ 7.26 ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or overlap of non-equivalent resonances), integration; for ^{13}C NMR, chemical shift in ppm from tetramethylsilane with the solvent as internal indicator ($CDCl_3$ δ 77.1 ppm), multiplicity with respect to protons. All high-resolution mass spectra were obtained on a Q-TOF Micro LC/MS System ESI spectrometer to be given in m/z. Azoalkenes **1** were either employed directly from commercial sources or prepared according to the literature[1]; thioethers **2** were synthesized according to modified literature-reported procedures[2-3].

2. Reaction optimization[a]

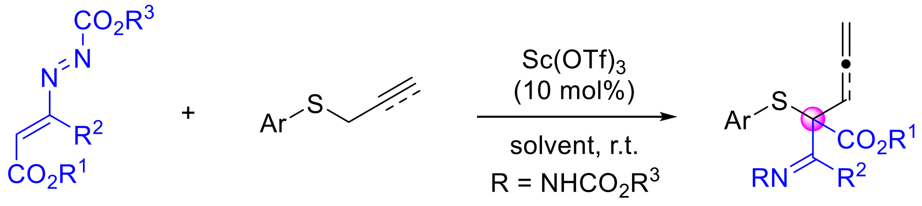


Entry	**Cat.**	Solvent	Additive	Yield (%)[b]
1	$Cu(OTf)_2$	CH_2Cl_2	-	64
2	$Ni(OTf)_2$	CH_2Cl_2	-	n.r.
3	$Fe(OTf)_3$	CH_2Cl_2	-	58
4	$In(OTf)_3$	CH_2Cl_2	-	34
5	$Sc(OTf)_3$	CH_2Cl_2	-	88
6	MsOH	CH_2Cl_2	-	41
7	$HNTf_2$	CH_2Cl_2	-	30
8	PA	CH_2Cl_2	-	Trace
9	$Sc(OTf)_3$	CH_3CN	-	87
10	$Sc(OTf)_3$	toluene	-	51
11	$Sc(OTf)_3$	THF	-	39
12	$Sc(OTf)_3$	CH_2Cl_2	3Å MS	44
13	$Sc(OTf)_3$	CH_2Cl_2	4Å MS	52
14	$Sc(OTf)_3$	CH_2Cl_2	5Å MS	70

[a]Reaction conditions: **1a** (0.12 mmol), **2a** (0.1 mmol), and **Cat.** (10 mol%) in the solvent specified (1 mL) at room temperature (r.t.) for 3d, n.r. = no reaction. [b]Isolated yields. PA = diphenyl phosphate.

3. Representative Procedures

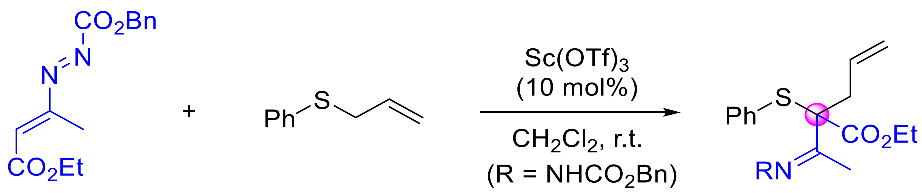
General Procedures for the synthesis of target products 3



1 2 3

Azoalkenes **1** (0.24 mmol) and thioethers **2** (0.2 mmol) (ratio of **1:2** = 1.2:1) were dissolved in CH_2Cl_2 (**3a-3y**) or CH_3CN (**3z-3c′**) and $Sc(OTf)_3$ (10 mol%) was added. The reaction mixture was stirred for 3 days at room temperature. After the completion of the reaction which was indicated by TLC, the solvents were removed in vacuo and the crude product was separated by flash column chromatography on silica gel (petroleum ether / ethyl acetate 8:1–4:1) to afford the target products **3**.

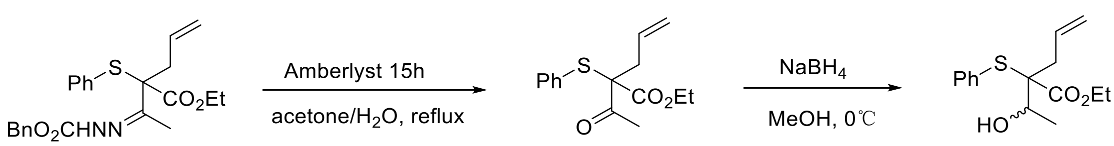
Procedure for the gram-scale reaction



1a 2a 3a

Azoalkene **1a** (1.04 g, 3.6 mmol), thioether **2a** (0.45 g, 3.0 mmol) were dissolved in CH_2Cl_2 and $Sc(OTf)_3$ (10 mol%) was added. The reaction mixture was stirred for 3 days at room temperature. After the completion of the reaction which was indicated by TLC, H_2O was added followed by extraction with CH_2Cl_2. The organic phase was dried on anhydrous sodium sulphate and evaporated under reduced pressure. The crude product was separated by flash column chromatography on silica gel (petroleum ether / ethyl acetate = 8:1 – 4:1) to afford the target products **3a** (1.12 g, 88% yield) as a white solid.

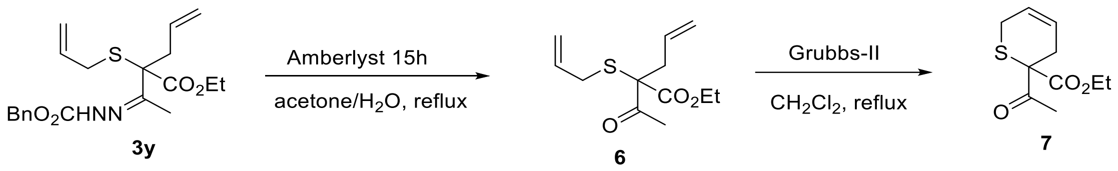
Derivatization of 3a and 3y into compounds 4-9



3a 4 5

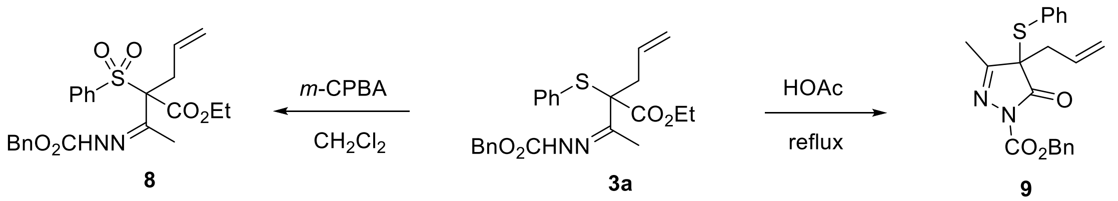
Compound **3a** (85.2 mg, 0.2 mmol) was refluxed in 10 mL of acetone/water (9:1 mixture) in the presence of Amberlyst-15h (100 mg) for 3 days (TLC check). The reaction mixture was filtered off and the solution was concentrated under reduced pressure and then extracted with ethyl acetate. The organic phase was dried on anhydrous sodium sulphate and evaporated under reduced pressure. The crude reaction mixture was purified by flash chromatography eluting with petroleum ether / ethyl acetate (10:1) mixtures to obtain ketone derivative **4** (37.8 mg, 68% yield) as a yellow oil.

To a stirred suspension of ketone derivative **4** (55.6 mg, 0.2 mmol, 1.0 equiv) in MeOH (5 mL) at 0 °C, $NaBH_4$ (11.4 mg, 0.3 mmol, 1.5 equiv) was slowly added. The resulting mixture was stirred at room temperature for 30 min. MeOH was removed under reduced pressure, and the residue was purified by flash chromatography (petroleum ether / ethyl acetate = 10:1) to afford alcohol **5** (54.3 mg, 97% yield, 4:1 dr) as a yellow oil.



Compound **3y** (78.0 mg, 0.2 mmol) was refluxed in 10 mL of acetone/water (9:1 mixture) in the presence of Amberlyst-15h (100 mg) for 7 days (TLC check). The reaction mixture was filtered off and the solution was concentrated under reduced pressure and then extracted with ethyl acetate. The organic phase was dried on anhydrous sodium sulphate and evaporated under reduced pressure. The crude reaction mixture was purified by flash chromatography eluting with petroleum ether / ethyl acetate (10:1) mixtures to obtain ketone derivative **6** (29.0 mg, 60% yield) as a yellow oil.

Ketone derivative **6** (48.4 mg, 0.2 mmol, 1.0 equiv), and Grubbs catalyst II (25.5 mg, 0.03 mmol, 15 mol%) were dissolved in CH_2Cl_2 (5 mL). The reaction mixture was stirred at 40 °C for 2 h, which was directly purified by flash column chromatography (petroleum ether / ethyl acetate = 10:1) to afford the title product **7** (39.4 mg, 92% yield) as a brown oil.

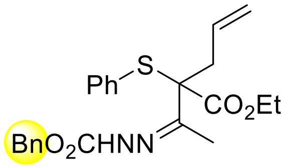


Compound **3a** (85.2 mg, 0.2 mmol) was dissolved in CH_2Cl_2 (5 mL), then *m*-CPBA (103.2 mg, 0.6 mmol, 3.0 equiv) was added. The reaction mixture was stirred at room temperature for 1h. After the completion of the reaction which was indicated by TLC, saturated $NaHCO_3$ aqueous solution was added followed by extraction with CH_2Cl_2. The organic phase was dried on anhydrous sodium sulphate and evaporated under reduced pressure. The crude product was separated by flash column chromatography on silica gel (petroleum ether / ethyl acetate = 2:1) to afford the sulfone derivative **8** (74.2 mg, 81% yield) as a yellow oil.

Compound **3a** (85.2 mg, 0.2 mmol) was dissolved in acetic acid (5 mL). The reaction mixture was refluxed at 130°C for 2h. After the completion of the reaction which was indicated by TLC, saturated $NaHCO_3$ aqueous solution was added followed by extraction with ethyl acetate. The organic phase was dried on anhydrous sodium sulphate and evaporated under reduced pressure. The crude product was separated by flash column chromatography on silica gel (petroleum ether / ethyl acetate = 2:1) to afford the title product **9** (49.4 mg, 65% yield) as a red oil.

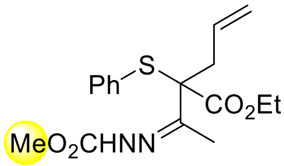
3. Characterization of Products

Benzyl-2-(3-(ethoxycarbonyl)-3-(phenylthio)hex-5-en-2-ylidene)hydrazine-1-carboxylate **3a:**



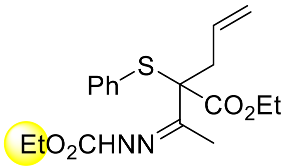
A white solid; 74.9 mg; isolated yield = 88%; m.p. 123.2-123.6°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.52 – 7.05 (m, 10H), 6.26 – 5.85 (m, 1H), 5.31 – 4.96 (m, 4H), 4.16 – 4.22(m, 2H), 3.04 – 2.52 (m, 2H), 1.90 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 153.4, 147.7, 136.8, 135.9, 133.4, 130.0, 129.5, 128.7, 128.6, 128.3, 118.5, 68.0, 67.3, 62.2, 38.4, 14.5, 14.2; HRMS (ESI) m/z calcd for $C_{23}H_{27}N_2O_4S^+$ $[M + H]^+$ = 427.1686, found = 427.1690.

Methyl-2-(3-(ethoxycarbonyl)-3-(phenylthio)hex-5-en-2-ylidene)hydrazine-1-carboxylate **3b:**



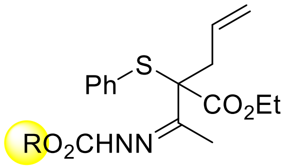
A white solid; 53.2 mg; isolated yield = 76%; m.p. 121.3-121.8°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.52 – 6.99 (m, 5H), 5.99 – 6.05 (m, 1H), 5.20 – 4.99 (m, 2H), 4.18 – 4.22 (m, 2H), 3.74 (s, 3H), 2.92 – 2.60 (m, 2H), 1.93 – 2.25 (m, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 154.5, 147.7, 136.9, 133.3, 130.0, 129.5, 128.7, 118.5, 67.8, 62.1, 52.9, 38.2, 14.5, 14.2; HRMS (ESI) m/z calcd for $C_{17}H_{23}N_2O_4S^+$ $[M + H]^+$ = 351.1373, found = 351.1369.

Ethyl-2-(3-(ethoxycarbonyl)-3-(phenylthio)hex-5-en-2-ylidene)hydrazine-1-carboxylate **3c:**



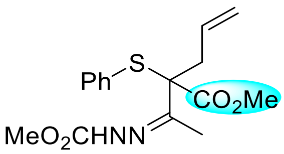
A yellow solid; 53.8 mg; isolated yield = 74%; m.p. 119.2-119.9°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.50 – 7.10 (m, 5H), 5.99 – 6.08 (m, 1H), 5.25 – 5.01 (m, 2H), 4.40 – 4.02 (m, 4H), 2.98 – 2.59 (m, 2H), 1.93 – 2.25 (m, 3H), 1.23 – 1.27 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 153.8, 147.3, 136.8, 133.4, 130.1, 129.5, 128.7, 118.5, 67.9, 62.1, 61.8, 38.3, 14.5, 14.4, 14.2; HRMS (ESI) m/z calcd for $C_{18}H_{25}N_2O_4S^+$ $[M + H]^+$ = 365.1530, found = 365.1529.

(9*H*-fluoren-9-yl)methyl-2-(3-(ethoxycarbonyl)-3-(phenylthio)hex-5-en-2-ylidene)hydrazine-1-carboxylate **3d,** R = fluorenylmethyl**:**



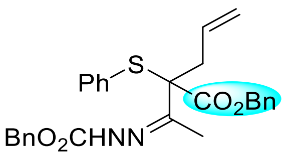
A white solid; 93.5 mg; isolated yield = 91%; m.p. 124.8-125.4℃; ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.74 – 7.76 (m, 2H), 7.68 – 7.54 (m, 2H), 7.36 – 7.41 (m, 4H), 7.34 – 7.22 (m, 5H), 6.29 – 5.94 (m, 1H), 5.15 (d, *J* = 12.3 Hz, 2H), 4.48 (m, 1H), 4.40 – 4.29 (s, 1H), 4.28 – 3.99 (m, 3H), 2.85 (m, 2H), 1.97 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 154.9, 147.9, 143.8, 143.5, 141.4, 141.3, 137.0, 133.5, 130.2, 129.5, 128.8, 127.8, 127.8, 127.1, 127.1, 125.4, 120.0, 120.0, 118.6, 68.0, 67.8, 62.2, 46.9, 38.5, 14.7, 14.3; HRMS (ESI) m/z calcd for $C_{30}H_{31}N_2O_4S^+$ $[M + H]^+$ = 515.1999, found = 515.2004.

Methyl-2-(3-(methoxycarbonyl)-3-(phenylthio)hex-5-en-2-ylidene)hydrazine-1-carboxylate **3e:**



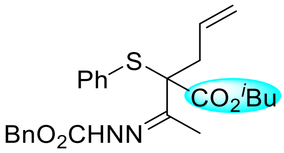
A white solid; 45.7 mg; isolated yield = 68%; m.p. 130.4-130.9℃; ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.51 – 7.08 (m, 5H), 6.21 – 5.85 (m, 1H), 5.27 – 4.82 (m, 2H), 3.98 – 3.49 (m, 6H), 2.63 – 2.82 (m, 2H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 154.7, 147.6, 136.9, 133.3, 130.0, 129.5, 128.7, 118.5, 67.9, 52.9, 52.8, 38.3, 14.6; HRMS (ESI) m/z calcd for $C_{16}H_{21}N_2O_4S^+$ $[M + H]^+$ = 337.1217, found = 337.1212.

Benzyl-2-(3-((benzyloxy)carbonyl)-3-(phenylthio)hex-5-en-2-ylidene)hydrazine-1-carboxylate **3f:**



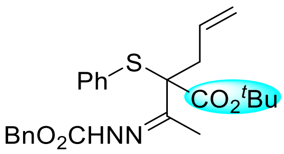
A yellow oil; 70.3 mg; isolated yield = 72%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.46 – 7.13 (m, 15H), 5.95– 6.05 (m, 1H), 5.34 – 4.77 (m, 6H), 2.66 – 2.89 (m, 2H), 1.80 – 2.23 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 153.6, 147.2, 136.9, 135.9, 135.0, 133.2, 129.9, 129.5, 128.8, 128.7, 128.6, 128.6, 128.5, 128.3, 118.6, 68.0, 67.8, 67.4, 38.4, 14.4; HRMS (ESI) m/z calcd for $C_{28}H_{29}N_2O_4S^+$ $[M + H]^+$ = 489.1843, found = 489.1846.

Benzyl-2-(3-(isobutoxycarbonyl)-3-(phenylthio)hex-5-en-2-ylidene)hydrazine-1-carboxylate **3g:**



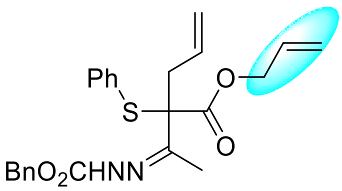
A yellow oil; 74.4 mg; isolated yield = 82%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.45 – 7.10 (m, 10H), 5.99 – 6.08 (m, 1H), 5.08 – 5.16 (m, 4H), 3.87 – 3.89 (m, 2H), 2.68 – 2.86 (m, 2H), 2.09 – 1.76 (m, 4H), 0.92 (d, J = 6.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 153.6, 147.9, 136.8, 135.9, 133.5, 130.0, 129.5, 128.7, 128.6, 128.3, 118.5, 72.5, 68.4, 67.4, 38.5, 27.6, 19.1, 14.6; HRMS (ESI) m/z calcd for $C_{25}H_{31}N_2O_4S^+$ $[M + H]^+$ = 455.1999, found = 455.2009.

Benzyl-2-(3-(*tert*-butoxycarbonyl)-3-(phenylthio)hex-5-en-2-ylidene)hydrazine-1-carboxylate **3h:**



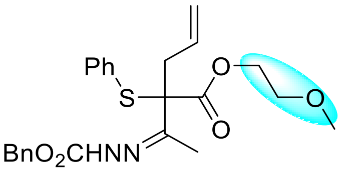
A yellow solid; 73.5 mg; isolated yield = 81%; m.p. 117.5-118.3°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.52 – 7.05 (m, 10H), 6.20 – 5.96 (m, 1H), 5.10 – 5.18 (m, 4H), 2.64 – 2.85 (m, 2H), 1.93 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 153.9, 148.2, 136.8, 136.0, 133.6, 132.2, 130.3, 129.3, 129.0, 128.9, 128.6, 128.5, 128.3, 127.8, 118.4, 83.3, 68.6, 67.1, 38.2, 27.9, 14.8; HRMS (ESI) m/z calcd for $C_{25}H_{30}N_2O_4SNa^+$ $[M + Na]^+$ = 477.1818, found = 477.1830.

Benzyl-2-(3-((allyloxy)carbonyl)-3-(phenylthio)hex-5-en-2-ylidene)hydrazine-1-carboxylate **3i:**



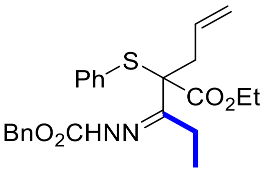
A yellow oil; 63.9 mg; isolated yield = 73%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.48 – 7.15 (m, 10H), 6.14 – 5.75 (m, 2H), 5.43 – 5.03 (m, 6H), 4.61 (d, J = 6.0 Hz, 2H), 2.79 (m, 2H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 153.3, 147.6, 136.8, 135.9, 133.3, 131.3, 129.9, 129.6, 128.7, 128.6, 128.5, 128.3, 119.6, 118.6, 68.0, 67.4, 66.7, 38.5, 14.5; HRMS (ESI) m/z calcd for $C_{24}H_{27}N_2O_4S^+$ $[M + H]^+$ = 439.1686, found = 439.1684.

Benzyl-2-(3-((2-methoxyethoxy)carbonyl)-3-(phenylthio)hex-5-en-2-ylidene)hydrazine-1-carboxylate **3j:**



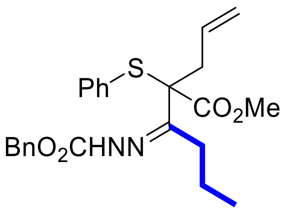
A yellow oil; 71.1 mg; isolated yield = 78%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.54 – 7.02 (m, 10H), 6.29 – 5.80 (m, 1H), 5.39 – 5.00 (m, 4H), 4.44 – 4.15 (m, 2H), 3.53 (t, *J* = 4.8 Hz, 2H), 3.32 (s, 3H), 2.67 – 2.90 (m, 2H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 153.5, 147.8, 136.9, 136.0, 133.4, 130.0, 129.5, 128.7, 128.5, 128.3, 128.1, 118.5, 70.0, 68.0, 67.3, 64.7, 58.8, 38.4, 14.4; HRMS (ESI) m/z calcd for $C_{24}H_{29}N_2O_5S^+$ $[M + H]^+$ = 457.1792, found = 457.1793.

Benzyl-2-(4-(ethoxycarbonyl)-4-(phenylthio)hept-6-en-3-ylidene)hydrazine-1-carboxylate **3k:**



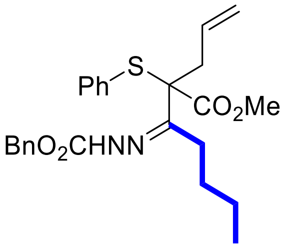
A yellow oil; 73.9 mg; isolated yield = 84%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.56 – 7.05 (m, 10H), 6.21 – 5.89 (m, 1H), 5.32 – 4.95 (m, 4H), 4.36 – 4.04 (m, 2H), 2.64 – 2.88 (m, 2H), 2.59 – 2.20 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 153.3, 151.6, 136.8, 135.9, 133.4, 130.2, 129.4, 128.6, 128.6, 128.3, 118.6, 68.3, 67.4, 62.1, 37.9, 21.8, 14.2, 9.9; HRMS (ESI) m/z calcd for $C_{24}H_{29}N_2O_4S^+$ $[M + H]^+$ = 441.1843, found = 441.1839.

Benzyl-2-(5-(methoxycarbonyl)-5-(phenylthio)oct-7-en-4-ylidene)hydrazine-1-carboxylate **3l:**



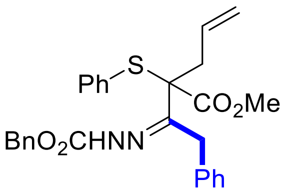
A yellow oil; 66.0 mg; isolated yield = 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.51 – 7.05 (m, 10H), 6.12 – 5.83 (m, 1H), 5.07 – 5.18 (m, 4H), 3.72 (s, 3H), 2.97 – 2.58 (m, 2H), 2.51 – 2.08 (m, 2H), 1.75 – 1.52 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 154.0, 150.7, 136.7, 135.9, 133.4, 130.1, 129.4, 128.7, 128.6, 128.3, 118.6, 68.3, 67.4, 52.7, 37.9, 30.9, 18.7, 14.8; HRMS (ESI) m/z calcd for $C_{24}H_{29}N_2O_4S^+$ $[M + H]^+$ = 441.1843, found = 441.1845.

Benzyl-2-(4-(methoxycarbonyl)-4-(phenylthio)non-1-en-5-ylidene)hydrazine-1-carboxylate **3m:**



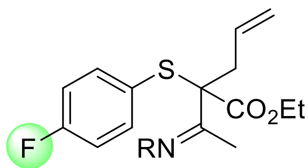
A yellow oil; 70.8 mg; isolated yield = 78%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.44 – 7.08 (m, 10H), 6.24 – 5.76 (m, 1H), 5.32 – 4.88 (m, 4H), 3.72 (s, 3H), 2.63 – 2.87 (m, 2H), 2.57 – 2.03 (m, 2H), 1.82 – 1.29 (m, 4H), 0.93 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 154.2, 150.7, 136.7, 135.9, 133.4, 130.1, 129.4, 128.7, 128.5, 128.3, 118.6, 68.3, 67.4, 52.6, 38.0, 28.6, 27.1, 23.4, 13.7; HRMS (ESI) m/z calcd for $C_{25}H_{31}N_2O_4S^+$ $[M + H]^+$ = 455.1999, found = 455.2000.

Benzyl-2-(3-(methoxycarbonyl)-1-phenyl-3-(phenylthio)hex-5-en-2-ylidene)hydrazine-1-carboxylate **3n:**



A red solid; 74.2 mg; isolated yield = 76%; m.p. 118.2-118.9℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.50 – 7.06 (m, 15H), 6.00 – 6.08 (m, 1H), 5.31 – 4.94 (m, 4H), 3.70 – 4.04 (m, 2H), 3.40 (s, 3H), 2.72 – 2.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 153.3, 147.9, 136.9, 135.9, 133.3, 133.0, 129.9, 129.6, 129.1, 128.8, 128.5, 128.2, 128.0, 127.3, 118.8, 68.7, 67.2, 52.4, 38.0, 34.7; HRMS (ESI) m/z calcd for $C_{28}H_{29}N_2O_4S^+$ $[M + H]^+$ = 489.1843, found = 489.1846.

Benzyl-2-(3-(ethoxycarbonyl)-3-((4-fluorophenyl)thio)hex-5-en-2-ylidene)hydrazine-1-carboxylate **3o:**

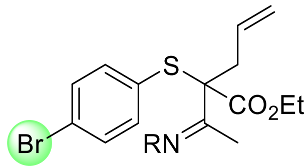


3o, R = $NHCO_2Bn$

A yellow solid; 63.9 mg; isolated yield = 72%; m.p. 112.9-113.7℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.30 – 7.37 (m, 7H), 6.91 – 6.95 (m, 2H), 6.29 – 5.83 (m, 1H), 5.31 – 4.93 (m, 4H), 4.16 – 4.22 (m, 2H), 2.62 – 2.85 (m, 2H), 1.90 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 163.8 (J = 250 Hz), 153.6, 147.5, 139.0 (J = 9 Hz), 135.9, 133.2, 128.6, 128.4, 125.4, 125.3, 118.7, 115.9 (J = 20

Hz), 68.0, 67.4, 62.2, 38.2, 14.4, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.33; HRMS (ESI) m/z calcd for $C_{23}H_{26}FN_2O_4S^+$ $[M + H]^+$ = 445.1592, found = 445.1591.

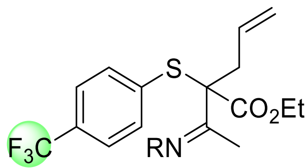
<u>Benzyl-2-(3-((4-bromophenyl)thio)-3-(ethoxycarbonyl)hex-5-en-2-ylidene)hydrazine-1-carboxylate **3p:**</u>



3p, R = $NHCO_2Bn$

A white solid; 88.7 mg; isolated yield = 88%; m.p. 102.6-103.1℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.41 – 7.30 (m, 7H), 7.24 – 7.16 (m, 2H), 5.93 – 5.99 (m, 1H), 5.30 – 4.99 (m, 4H), 4.15 – 4.19 (m, 2H), 2.63 – 2.87 (m, 2H), 1.89 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 153.6, 147.5, 138.2, 135.8, 133.0, 131.9, 129.3, 128.7, 128.6, 128.4, 128.4, 124.3, 118.8, 68.0, 67.5, 62.3, 38.3, 14.4, 14.2; HRMS (ESI) m/z calcd for $C_{23}H_{26}BrN_2O_4S^+$ $[M + H]^+$ = 505.0791, found = 505.0793.

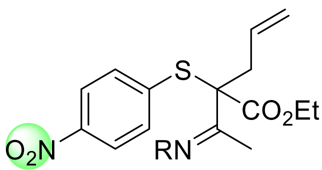
<u>Benzyl-2-(3-(ethoxycarbonyl)-3-((4-(trifluoromethyl)phenyl)thio)hex-5-en-2-ylidene) hydrazine-1-carboxylate **3q:**</u>



3q, R = $NHCO_2Bn$

A yellow solid; 75.1 mg; isolated yield = 76%; m.p. 96.4-96.8℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.48 (s, 4H), 7.35 (s, 5H), 5.94 – 6.01 (m, 1H), 5.43 – 4.93 (m, 4H), 4.17 – 4.23 (m, 2H), 2.68 – 2.93 (m, 2H), 1.89 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 153.3, 147.4, 136.3, 135.6 (*J* = 30 Hz), 132.8, 131.1 (*J* = 30 Hz), 128.7, 128.6, 128.4, 128.2, 127.9, 125.4, 125.4 (*J* = 3 Hz), 125.2, 123.9 (*J* = 271 Hz), 68.2, 67.5, 62.4, 38.4, 14.3, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.75; HRMS (ESI) m/z calcd for $C_{24}H_{26}F_3N_2O_4S^+$ $[M + H]^+$ = 495.1560, found = 495.1559.

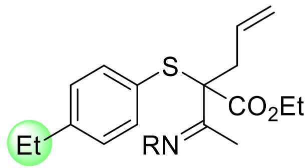
<u>Benzyl-2-(3-(ethoxycarbonyl)-3-((4-nitrophenyl)thio)hex-5-en-2-ylidene)hydrazine-1-carboxylate **3r:**</u>



3r, R = $NHCO_2Bn$

A yellow oil; 60.3 mg; isolated yield = 64%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.93 (s, 1H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.36 (s, 5H), 5.90 – 5.97 (m, 1H), 5.36 – 4.98 (m, 4H), 4.19 – 4.25 (m, 2H), 2.73 – 2.98 (m, 2H), 1.89 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 153.4, 147.8, 140.1, 135.6, 132.3, 128.6, 128.6, 128.3, 123.5, 119.3, 68.5, 67.7, 62.6, 38.5, 14.2, 14.1; HRMS (ESI) m/z calcd for $C_{23}H_{26}N_3O_6S^+$ $[M + H]^+$ = 472.1537, found = 472.1536.

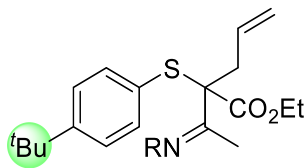
Benzyl-2-(3-(ethoxycarbonyl)-3-((4-ethylphenyl)thio)hex-5-en-2-ylidene)hydrazine-1-carboxylate **3s:**



3s, R = $NHCO_2Bn$

A yellow solid; 59.9 mg; isolated yield = 66%; m.p. 98.8-99.5℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.52 – 6.91 (m, 9H), 6.26 – 5.87 (m, 1H), 5.33 – 4.98 (m, 4H), 4.37 – 3.86 (m, 2H), 2.80 – 2.92 (m, 2H), 2.55 - 2.72 (m, 2H), 2.05 – 1.57 (m, 3H), 1.43 – 0.97 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 149.3, 146.0, 137.4, 136.9, 135.9, 133.7, 133.6, 129.5, 129.2, 129.0, 128.5, 128.3, 126.6, 125.9, 118.4, 67.9, 67.3, 62.1, 38.4, 28.6, 15.3, 14.5, 14.2; HRMS (ESI) m/z calcd for $C_{25}H_{31}N_2O_4S^+$ $[M + H]^+$ = 455.1999, found = 455.1999.

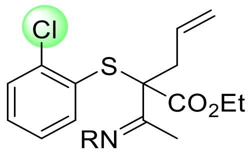
Benzyl-2-(3-((4-(tert-butyl)phenyl)thio)-3-(ethoxycarbonyl)hex-5-en-2-ylidene)hydrazine-1-carboxylate **3t:**



3t, R = $NHCO_2Bn$

A yellow oil; 72.3 mg; isolated yield = 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.44 – 7.12 (m, 9H), 6.00 – 6.06(m, 1H), 5.36 – 4.89 (m, 4H), 4.16 – 4.21 (m, 2H), 2.98 – 2.59 (m, 2H), 1.90 (s, 3H), 1.44 – 1.04 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 152.8, 147.8, 136.5, 135.9, 133.6, 128.6, 128.3, 126.5, 125.8, 118.4, 67.9, 67.3, 62.1, 38.5, 34.7, 31.2, 14.5, 14.2; HRMS (ESI) m/z calcd for $C_{27}H_{35}N_2O_4S^+$ $[M + H]^+$ = 483.2312, found = 483.2316.

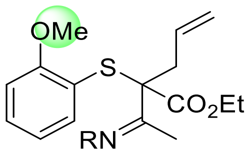
Benzyl-2-(3-((2-chlorophenyl)thio)-3-(ethoxycarbonyl)hex-5-en-2-ylidene)hydrazine-1-carboxylate **3u:**



3u, R = $NHCO_2Bn$

A yellow oil; 74.5 mg; isolated yield = 81%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.34 – 7.48 (m, 7H), 7.10 – 7.22 (m, 2H), 6.29 – 5.96 (m, 1H), 5.09 – 5.22 (m, 4H), 4.17 – 4.23 (m, 2H), 2.73 – 2.91 (m, 2H), 1.91 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 149.2, 143.0, 135.9, 134.4, 131.2, 128.7, 126.0, 125.4, 124.8, 123.8, 123.6, 122.0, 113.8, 63.6, 62.6, 57.5, 33.8, 9.7, 9.4; HRMS (ESI) m/z calcd for $C_{23}H_{26}ClN_2O_4S^+$ $[M + H]^+$ = 461.1296, found = 461.1303.

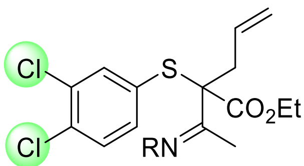
<u>Benzyl-2-(3-(ethoxycarbonyl)-3-((2-methoxyphenyl)thio)hex-5-en-2-ylidene)hydrazine-1-carboxylate **3v:**</u>



3v, R = $NHCO_2Bn$

A yellow solid; 77.5 mg; isolated yield = 85%; m.p. 103.7-104.2℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.54 – 7.23 (m, 7H), 6.74 – 6.85 (m, 2H), 6.35 – 5.92 (m, 1H), 5.35 – 4.98 (m, 4H), 4.14 – 4.20 (m, 2H), 3.71 (s, 3H), 2.66 – 2.83 (m, 2H), 1.92 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 156.8, 149.4, 143.9, 135.2, 131.3, 129.4, 127.0, 123.8, 123.5, 115.8, 113.2, 112.9, 106.4, 63.3, 62.4, 57.3, 50.8, 33.5, 9.6, 9.4; HRMS (ESI) m/z calcd for $C_{24}H_{29}N_2O_5S^+$ $[M + H]^+$ = 457.1792, found = 457.1799.

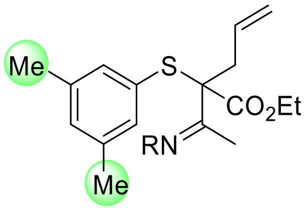
<u>Benzyl-2-(3-((3,4-dichlorophenyl)thio)-3-(ethoxycarbonyl)hex-5-en-2-ylidene)hydrazine-1-carboxylate **3w:**</u>



3w, R = $NHCO_2Bn$

A white solid; 72.1 mg; isolated yield = 73%; m.p. 93.1-93.9℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 6.85 (m, 9H), 5.91 – 5.97 (m, 1H), 5.34 – 4.99 (m, 4H), 4.16 – 4.21 (m, 2H), 2.61 – 2.85 (m, 2H), 1.90 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 153.9, 147.3, 138.1, 135.9, 135.8, 134.1, 132.8, 132.4, 130.5, 130.4, 128.6, 128.3, 119.0, 68.3, 67.5, 62.4, 38.2, 14.5, 14.2; HRMS (ESI) m/z calcd for $C_{23}H_{25}Cl_2N_2O_4S^+$ $[M + H]^+$ = 495.0907, found = 495.0911.

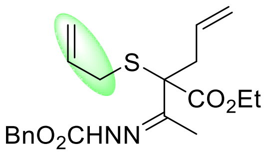
<u>Benzyl-2-(3-((3,5-dimethylphenyl)thio)-3-(ethoxycarbonyl)hex-5-en-2-ylidene)hydrazine-1-carboxylate **3x:**</u>



3x, R = $NHCO_2Bn$

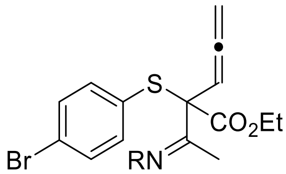
A yellow solid; 73.5 mg; isolated yield = 81%; m.p. 97.5-98.1℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 6H), 6.90 – 6.93 (m, 3H), 6.29 – 5.82 (m, 1H), 5.06 – 5.17 (m, 4H), 4.15 – 4.21 (m, 2H), 2.63 – 2.83 (m, 2H), 2.19 (s, 6H), 1.91 (s, 3H), 1.23 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 153.7, 148.0, 138.1, 136.0, 134.4, 133.7, 131.2, 129.3, 128.6, 128.6, 128.5, 128.4, 128.3, 118.3, 67.9, 67.3, 62.1, 38.4, 21.0, 14.6, 14.2; HRMS (ESI) m/z calcd for $C_{25}H_{31}N_2O_4S^+$ $[M + H]^+$ = 455.1999, found = 455.1999.

Benzyl-2-(3-(allylthio)-3-(ethoxycarbonyl)hex-5-en-2-ylidene)hydrazine-1-carboxylate **3y:**



A yellow oil; 66.3 mg; isolated yield = 85%; ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.34 – 7.40 (m, 5H), 6.01 – 5.63 (m, 2H), 5.44 – 5.09 (m, 6H), 4.18 (q, J = 7.1 Hz, 2H), 3.32 – 2.77 (m, 4H), 1.87 (s, 3H), 1.23 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 153.8, 148.7, 135.9, 133.7, 133.2, 128.6, 128.4, 118.5, 117.8, 67.5, 65.1, 62.0, 38.4, 31.9, 14.2, 13.8; HRMS (ESI) m/z calcd for $C_{20}H_{27}N_2O_4S^+$ $[M + H]^+$ = 391.1686, found = 391.1682.

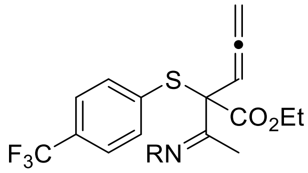
Benzyl-2-(3-((4-bromophenyl)thio)-3-(ethoxycarbonyl)hexa-4,5-dien-2-ylidene)hydrazine-1-carboxylate **3z:**



3z, R = $NHCO_2Bn$

A red oil; 68.3 mg; isolated yield = 68%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.34 – 7.41 (m, 9H), 5.78 (t, J = 6.7 Hz, 1H), 5.19 – 5.25 (m, 2H), 4.87 (d, J = 6.7 Hz, 2H), 4.13 – 4.18 (m, 2H), 1.84 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9, 168.6, 153.9, 148.8, 138.3, 135.8, 131.7, 130.1, 128.6, 128.5, 124.1, 90.8, 79.0, 67.7, 66.6, 62.4, 14.6, 14.0; HRMS (ESI) m/z calcd for $C_{23}H_{24}BrN_2O_4S^+$ $[M + H]^+$ = 503.0635, found = 503.0631.

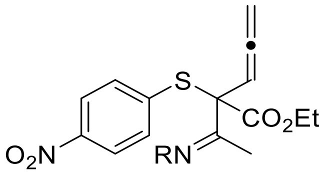
Benzyl-2-(3-(ethoxycarbonyl)-3-((4-(trifluoromethyl)phenyl)thio)hexa-4,5-dien-2-ylidene)hydrazine-1-carboxylate **3a′:**



3a′, R = $NHCO_2Bn$

A red solid; 73.8 mg; isolated yield = 75%; m.p. 95.1-95.6°C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.34 – 7.67 (m, 9H), 5.83 (t, *J* = 6.6 Hz, 1H), 5.20 – 5.29 (m, 2H), 4.88 (d, *J* = 6.7 Hz, 2H), 4.37 – 4.06 (m, 2H), 1.84 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.1, 168.5, 153.6, 146.9, 136.2, 135.7, 130.8 (*J* = 32 Hz), 129.0, 128.7, 128.6, 128.5, 125.3, 123.9 (*J* = 271 Hz), 122.6, 90.8, 79.2, 67.7, 66.7, 62.6, 14.5, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.74; HRMS (ESI) m/z calcd for $C_{24}H_{24}F_3N_2O_4S^+$ $[M + H]^+$ = 493.1403, found = 493.1406.

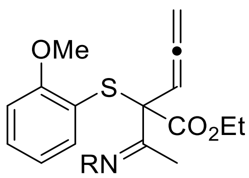
Benzyl-2-(3-(ethoxycarbonyl)-3-((4-nitrophenyl)thio)hexa-4,5-dien-2-ylidene)hydrazine-1-carboxylate **3b′:**



3b′, R = $NHCO_2Bn$

A yellow oil; 62.8 mg; isolated yield = 67%; ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 – 8.04 (m, 2H), 7.79 (s, 1H), 7.63 – 7.70 (m, 2H), 7.36 – 7.39 (m, 5H), 5.88 – 5.91 (t, *J* = 6.5 Hz, 1H), 5.20 – 5.29 (m, 2H), 4.91 (d, *J* = 6.7 Hz, 2H), 4.45 – 3.89 (m, 2H), 1.84 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 168.3, 153.9, 148.8, 147.5, 141.0, 135.6, 134.9, 128.7, 128.6, 128.5, 123.3, 90.6, 79.6, 67.8, 66.9, 62.8, 14.3, 14.1; HRMS (ESI) m/z calcd for $C_{23}H_{24}N_3O_6S^+$ $[M + H]^+$ = 470.1380, found = 470.1377.

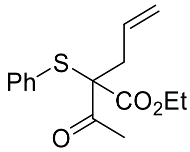
Benzyl-2-(3-(ethoxycarbonyl)-3-((2-methoxyphenyl)thio)hexa-4,5-dien-2-ylidene)hydrazine-1-carboxylate **3c′:**



3c′, R = $NHCO_2Bn$

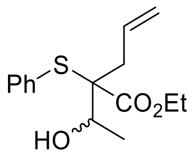
A yellow oil; 58.1 mg; isolated yield = 64%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.65 – 7.27 (m, 7H), 6.77 – 6.87 (m, 2H), 5.82 (t, *J* = 6.6 Hz, 1H), 5.18 (t, *J* = 17.1 Hz, 2H), 4.82 – 4.84 (m, 2H), 4.17 – 4.22 (m, 2H), 3.75 (s, 3H), 1.89 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.0, 168.9, 161.1, 154.9, 147.2, 139.8, 135.9, 131.5, 128.7, 128.7, 128.5, 128.3, 120.6, 118.3, 110.9, 91.0, 78.5, 67.4, 66.3, 62.2, 55.7, 14.5, 14.1; HRMS (ESI) m/z calcd for $C_{24}H_{27}N_2O_5S^+$ [M + H]$^+$ = 455.1635, found = 455.1632.

Ethyl 2-acetyl-2-(phenylthio)pent-4-enoate **4:**



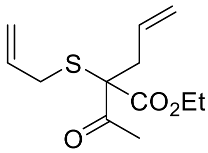
A yellow oil; 37.8 mg; isolated yield = 68%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.42 (m, 5H), 6.13 – 5.78 (m, 1H), 5.26 – 4.96 (m, 2H), 4.22 – 4.27 (m, 2H), 2.48 – 2.68 (m, 2H), 2.36 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 168.6, 136.8, 132.2, 123.0, 129.1, 129.0, 119.1, 70.3, 62.4, 36.6, 26.4, 14.1; HRMS (ESI) m/z calcd for $C_{15}H_{18}O_3SNa^+$ [M + Na]$^+$ = 301.0869, found = 301.0864.

Ethyl 2-(1-hydroxyethyl)-2-(phenylthio)pent-4-enoate **5:**



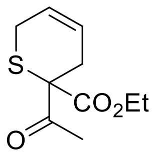
A yellow oil; 54.3 mg; dr = 4:1; isolated yield = 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.14 (m, 5H), 6.21 – 5.55 (m, 1H), 5.09 – 5.13 (m, 2H), 4.29 – 3.87 (m, 3H), 3.13 – 3.15 (m, 1H), 2.80 – 2.33 (m, 2H), 1.33 – 1.39 (m, 3H), 1.30 – 1.02 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 137.0, 133.7, 130.1, 129.6, 128.8, 118.0, 70.1, 62.9, 61.5, 36.6, 17.7, 14.0; HRMS (ESI) m/z calcd for $C_{15}H_{20}O_3SNa^+$ [M + Na]$^+$ = 303.1025, found = 303.1030.

Ethyl 2-acetyl-2-(allylthio)pent-4-enoate **6:**



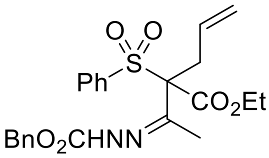
A yellow oil; 29.0 mg; isolated yield = 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95 – 5.65 (m, 2H), 5.09 – 5.22 (m, 4H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.76 – 3.07 (m, 4H), 2.30 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 168.8, 132.5, 131.9, 119.1, 118.6, 67.2, 62.3, 36.6, 32.1, 25.8, 14.0; HRMS (ESI) m/z calcd for $C_{12}H_{18}O_3SNa^+$ [M + Na]$^+$ = 265.0869, found = 265.0863.

Ethyl 2-acetyl-3,6-dihydro-2*H*-thiopyran-2-carboxylate **7:**



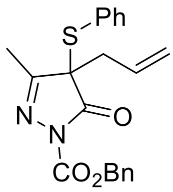
A brown oil; 39.4 mg; isolated yield = 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.16 – 5.58 (m, 2H), 4.24 – 4.30 (m, 2H), 2.51 – 3.07 (m, 4H), 2.34 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 169.3, 126.4, 121.9, 62.6, 61.2, 29.8, 24.9, 24.8, 14.0; HRMS (ESI) m/z calcd for $C_{10}H_{14}O_3SNa^+$ $[M + Na]^+$ = 237.0556, found = 237.0556.

<u>Benzyl 2-(3-(ethoxycarbonyl)-3-(phenylsulfonyl)hex-5-en-2-ylidene)hydrazine-1-carboxylate **8:**</u>



A yellow oil; 74.2 mg; isolated yield = 81%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.95 – 7.15 (m, 10H), 5.78 – 5.86 (m, 1H), 5.31 – 4.87 (m, 4H), 4.10 – 4.27 (m, 2H), 3.78 – 2.31 (m, 2H), 2.25 – 1.70 (m, 3H), 1.40 – 1.06 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 152.9, 136.8, 134.7, 131.9, 130.5, 128.6, 128.6, 128.5, 119.6, 83.4, 67.6, 62.5, 36.8, 15.9, 14.0; HRMS (ESI) m/z calcd for $C_{23}H_{26}N_2O_6SNa^+$ [M + Na]$^+$ = 481.1404, found = 481.1414.

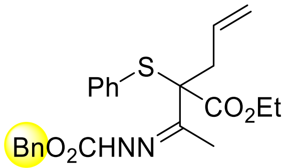
<u>Benzyl 4-allyl-3-methyl-5-oxo-4-(phenylthio)-4,5-dihydro-1*H*-pyrazole-1-carboxylate **9:**</u>



A red oil; 49.4 mg; isolated yield = 65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 6.95 (m, 10H), 5.58 – 5.40 (m, 1H), 5.30 – 4.94 (m, 4H), 2.52 – 2.87 (m, 2H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 160.3, 148.3, 136.0, 134.9, 130.7, 129.4, 129.3, 128.5, 128.5, 128.5, 127.0, 121.2, 68.5, 62.2, 36.2, 14.0; HRMS (ESI) m/z calcd for $C_{21}H_{20}N_2O_3SNa^+$ [M + Na]$^+$ = 403.1087, found = 403.1088.

4. X-ray single crystal data for compound 3a

Compound 3a:



CCDC:2234932

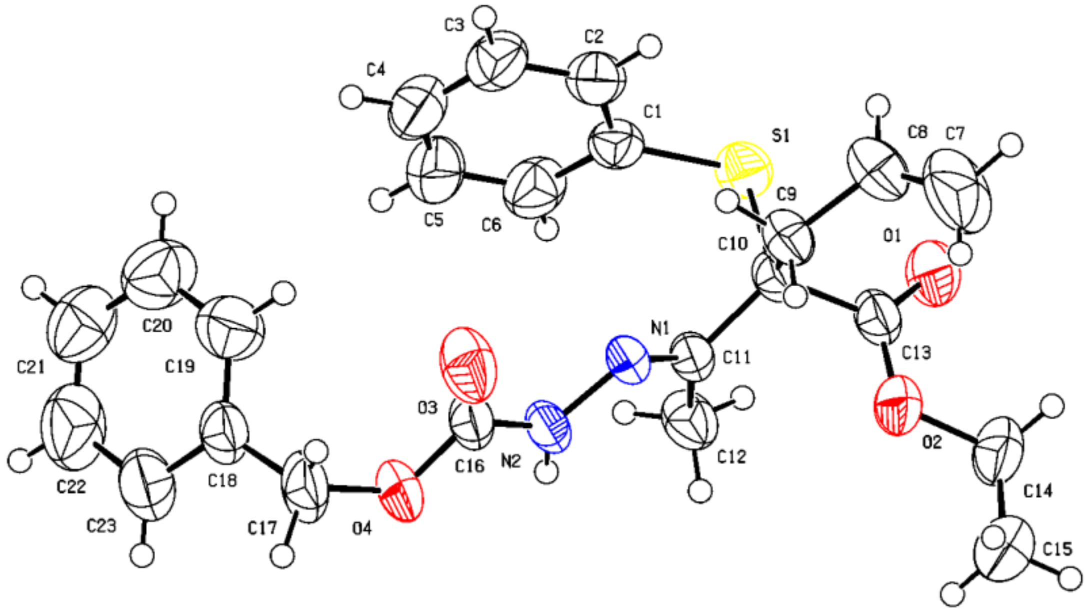
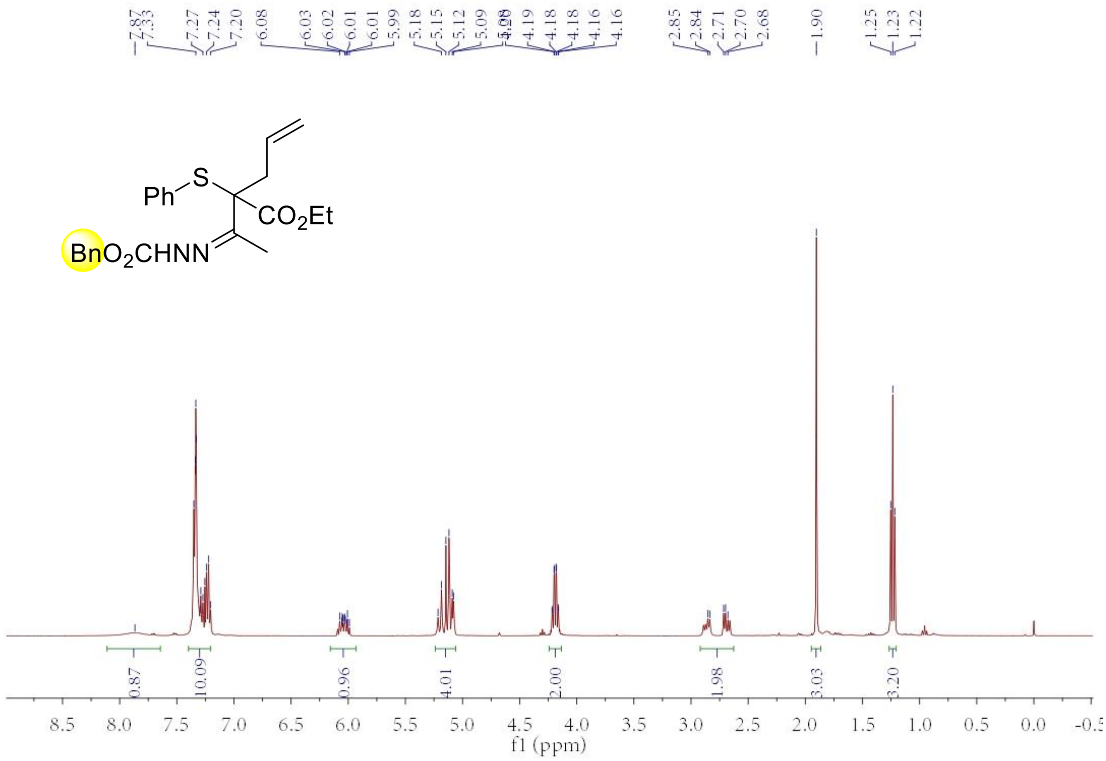


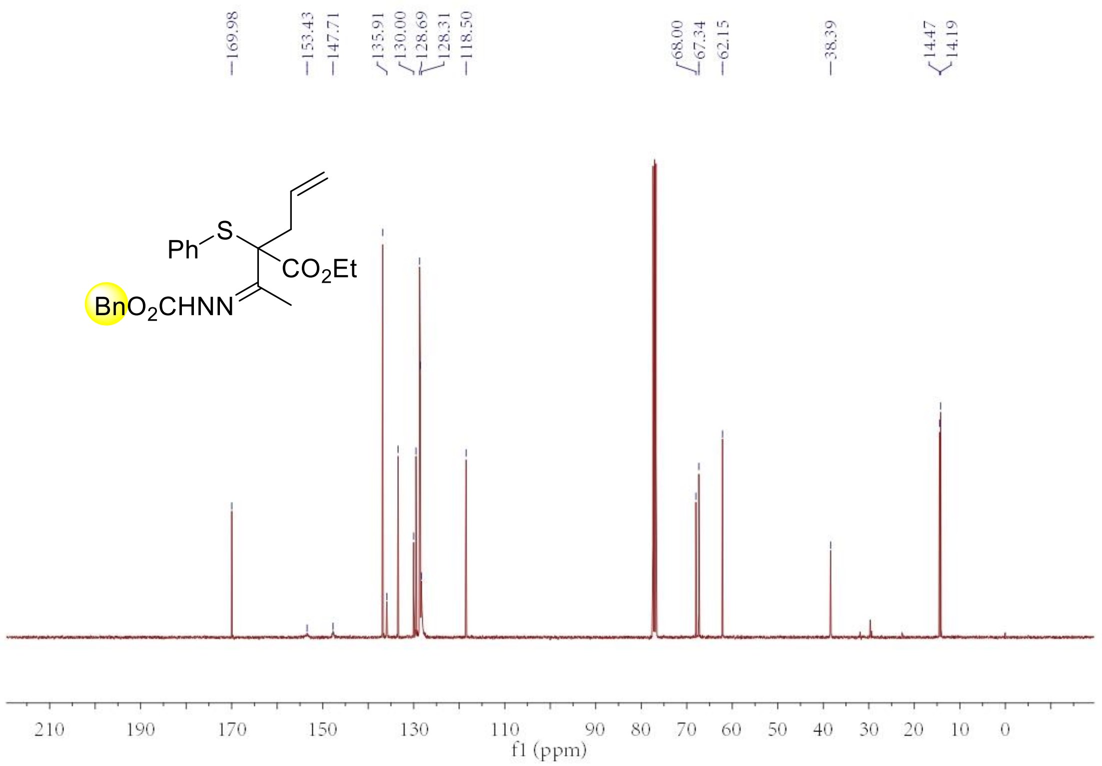
Table 1 Crystal data and structure refinement for 202209176.

Identification code	202209176
Empirical formula	$C_{23}H_{26}N_2O_4S$
Formula weight	426.52
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.8940(8)
b/Å	13.8863(6)
c/Å	14.5801(9)
α/°	90
β/°	108.178(7)
γ/°	90
Volume/Å^3	2287.9(2)
Z	4
ρ_{calc}g/cm^3	1.238
μ/mm^{-1}	1.506
F(000)	904.0
Crystal size/mm^3	0.17 × 0.13 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.824 to 134.158
Index ranges	-14 ≤ h ≤ 10, -10 ≤ k ≤ 16, -17 ≤ l ≤ 17
Reflections collected	8969
Independent reflections	4075 [R_{int} = 0.0276, R_{sigma} = 0.0357]
Data/restraints/parameters	4075/0/273
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0504, wR_2 = 0.1357
Final R indexes [all data]	R_1 = 0.0627, wR_2 = 0.1500
Largest diff. peak/hole / e Å^{-3}	0.42/-0.24

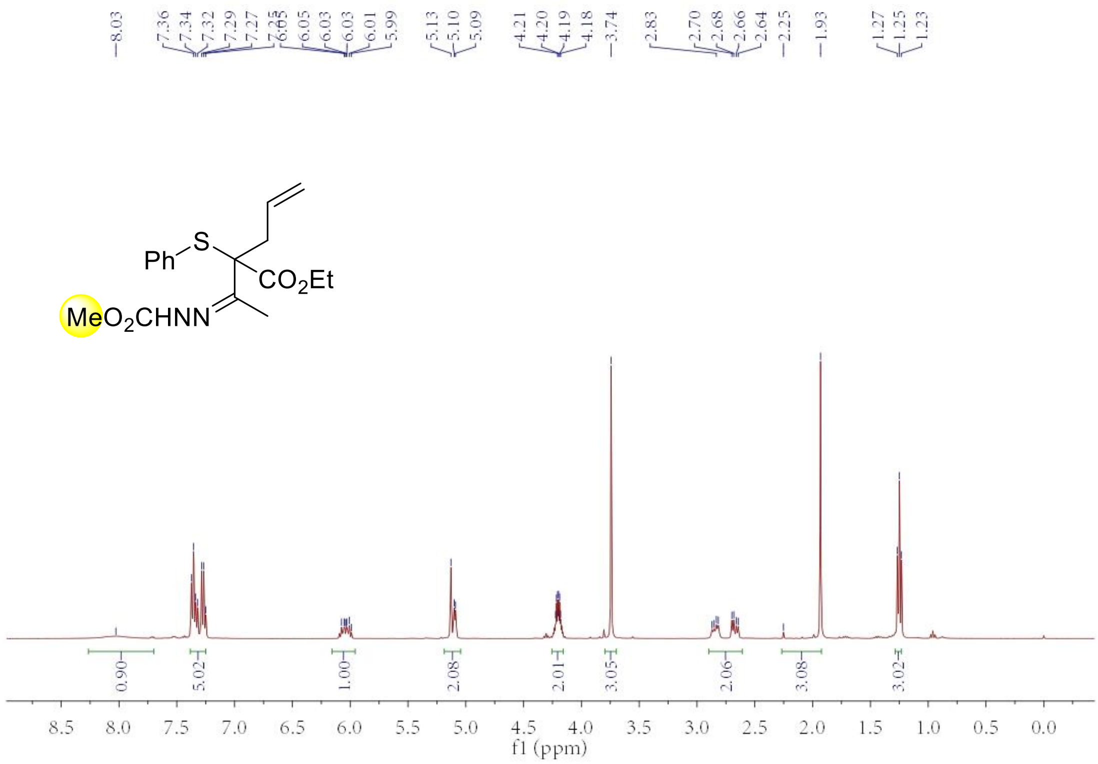
5. NMR Spectra

3a





3b



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6.03
6.03
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5.13
5.10
5.09
4.21
4.20
4.19
4.18
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2.66
2.64
2.25
1.93
1.27
1.25
1.23
Ph
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1.00
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2.01
3.05
2.06
3.08
3.02
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7.5
7.0
6.5
6.0
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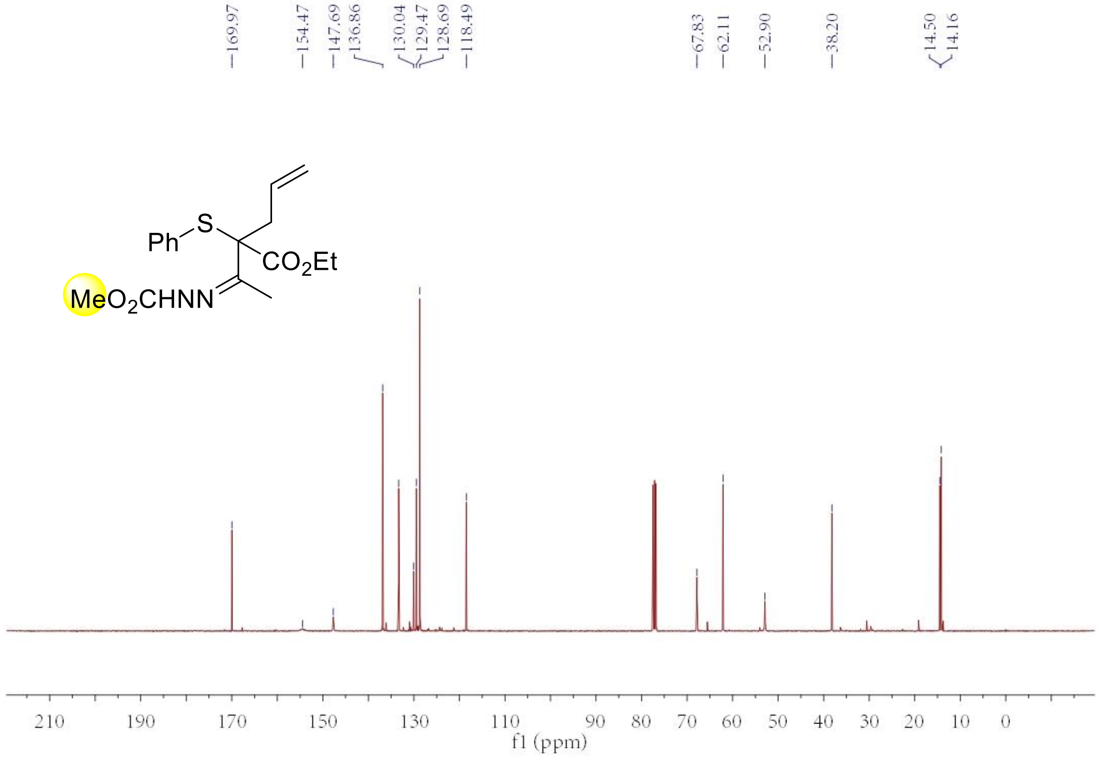
f1 (ppm)



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MeO2CHNN
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110
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30
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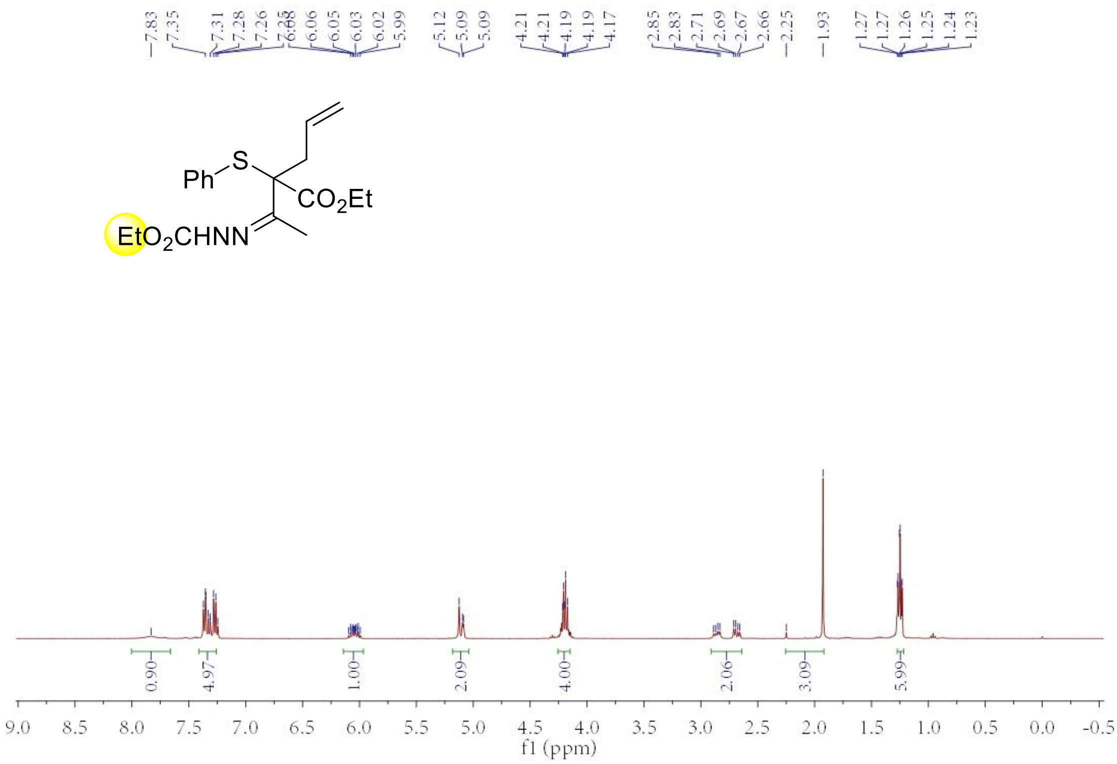
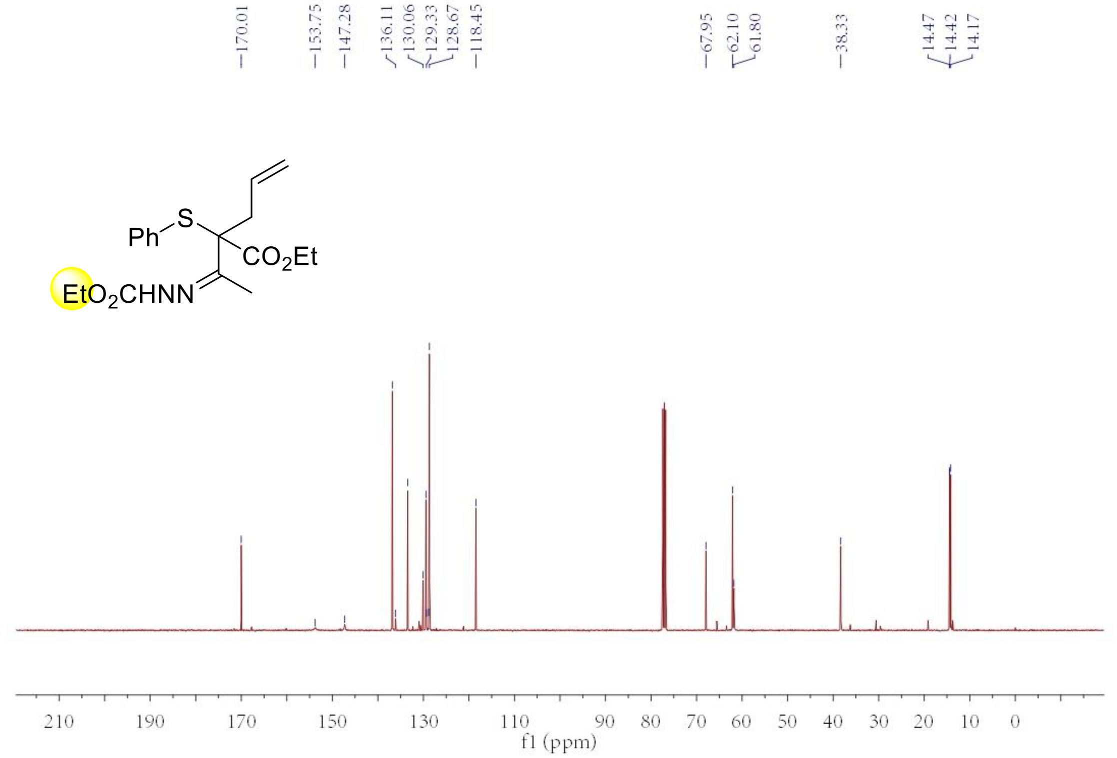
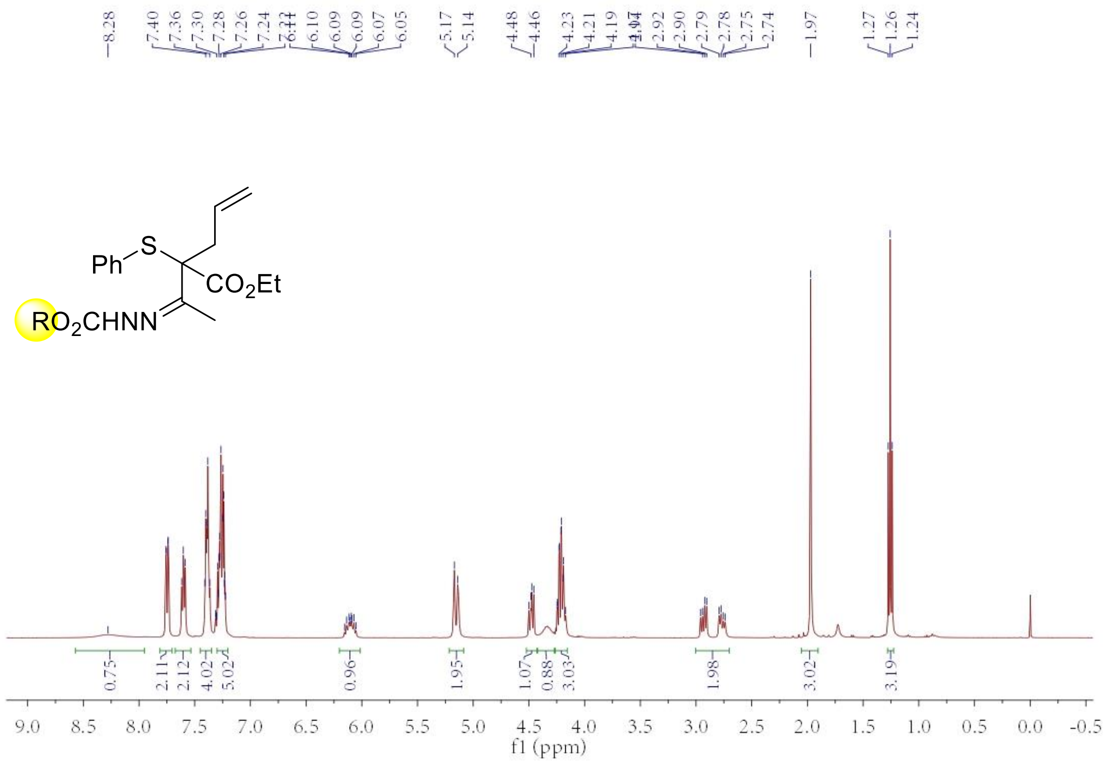
f1 (ppm)

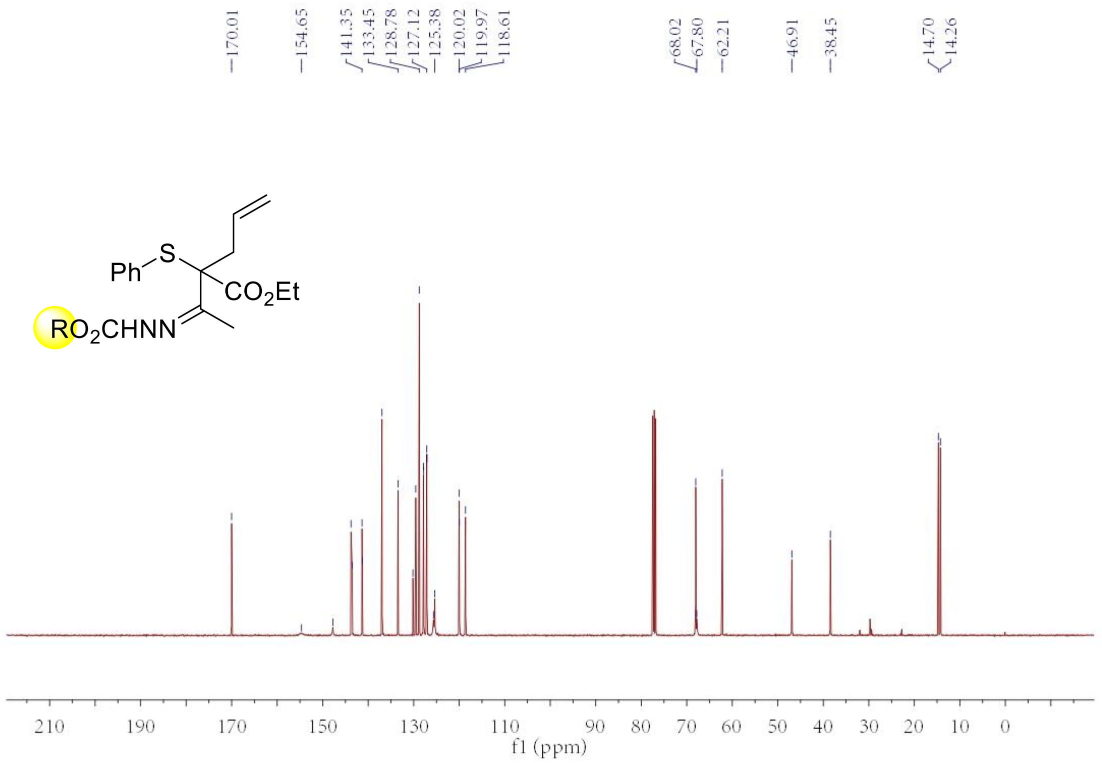
3c





3d, R = fluorenylmethyl





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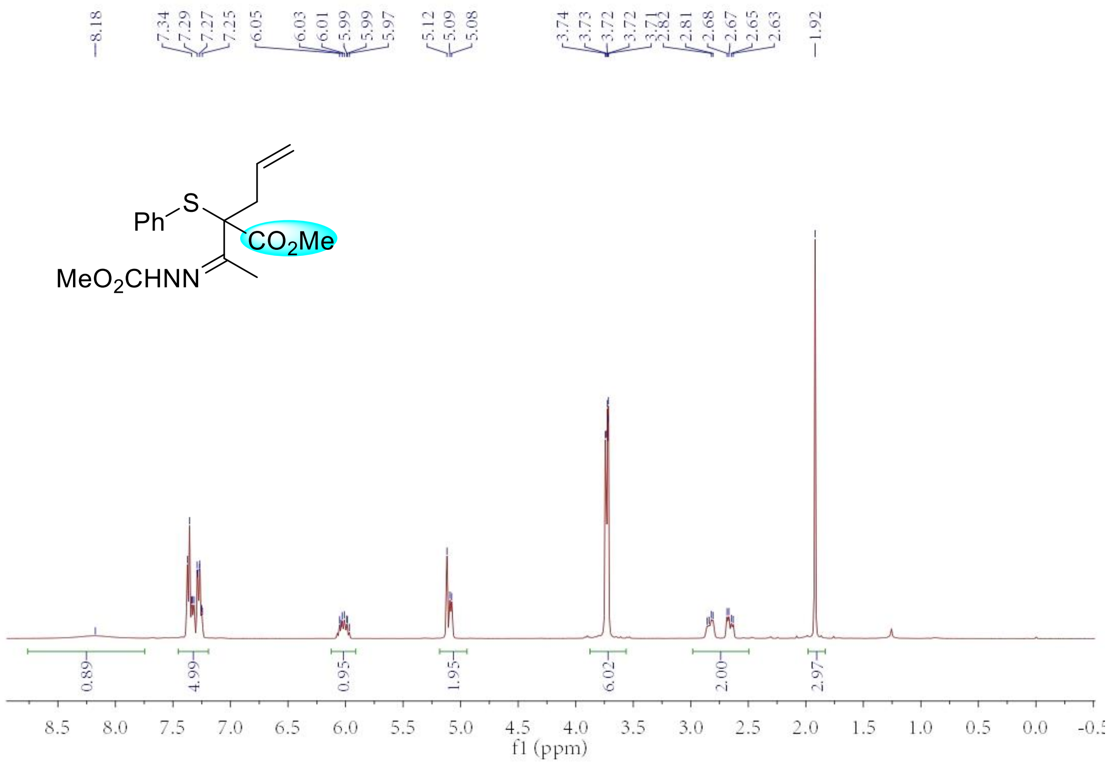

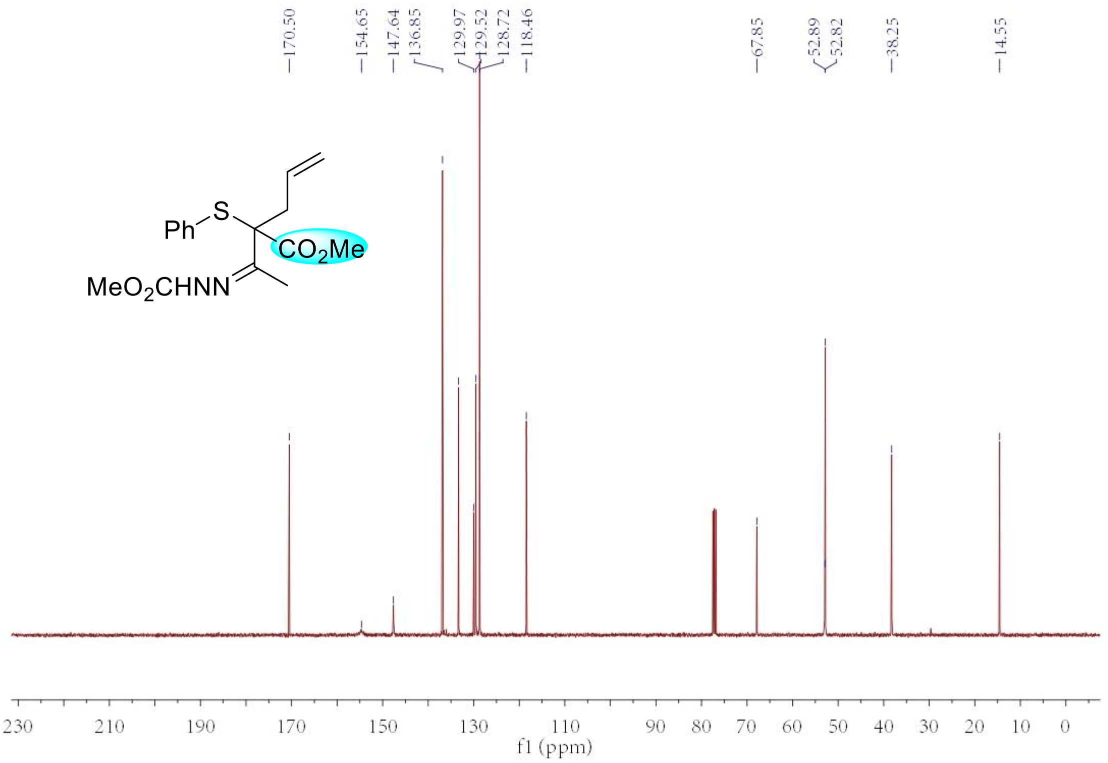

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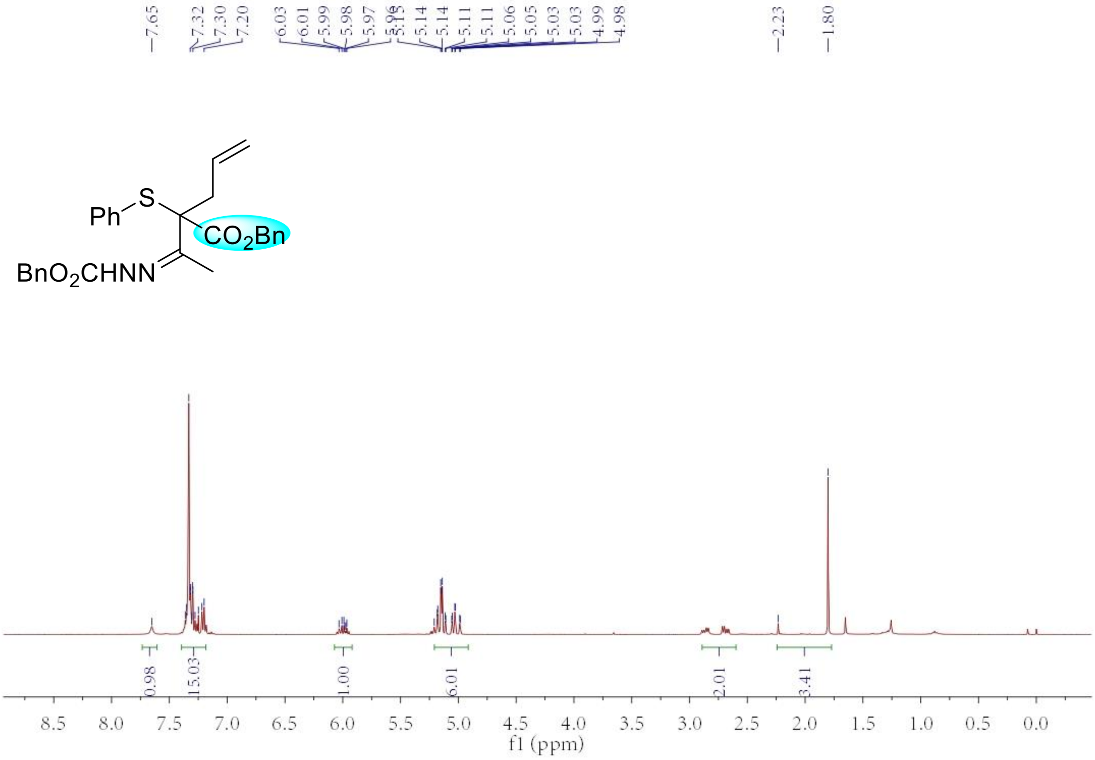
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5.11
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5.03
5.03
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Ph
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BnO2CHNN
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1.00
6.01
2.01
3.41
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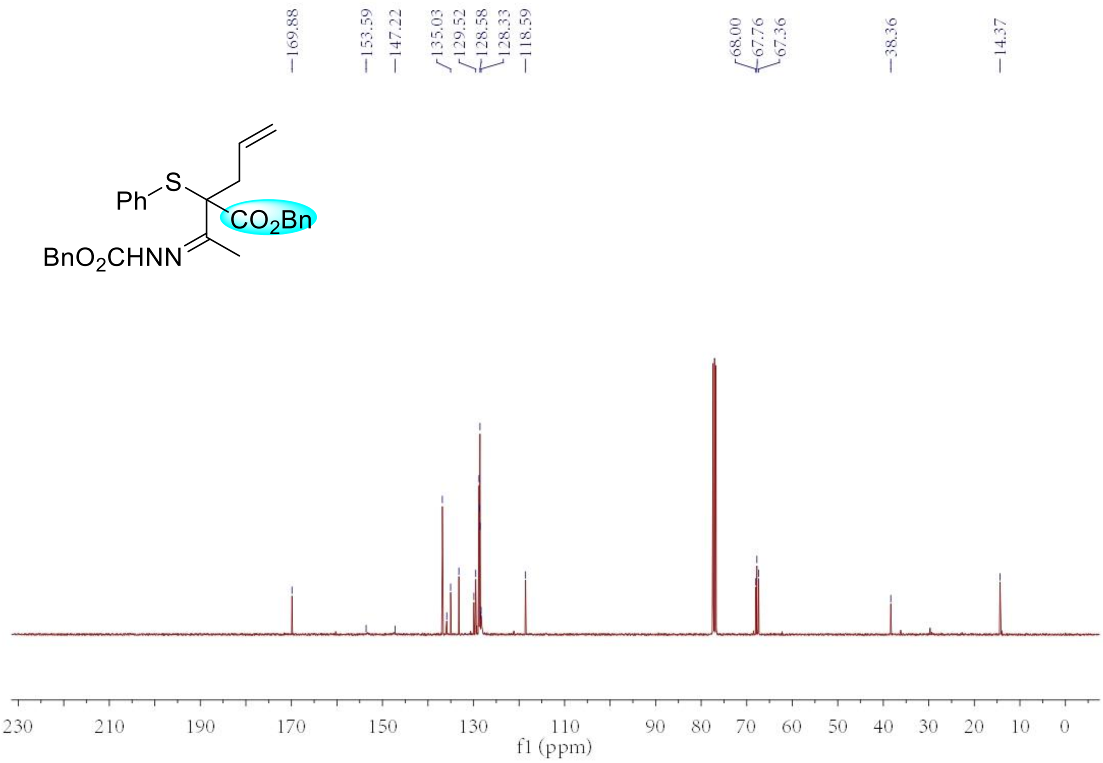
f1 (ppm)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BnO2CHNN
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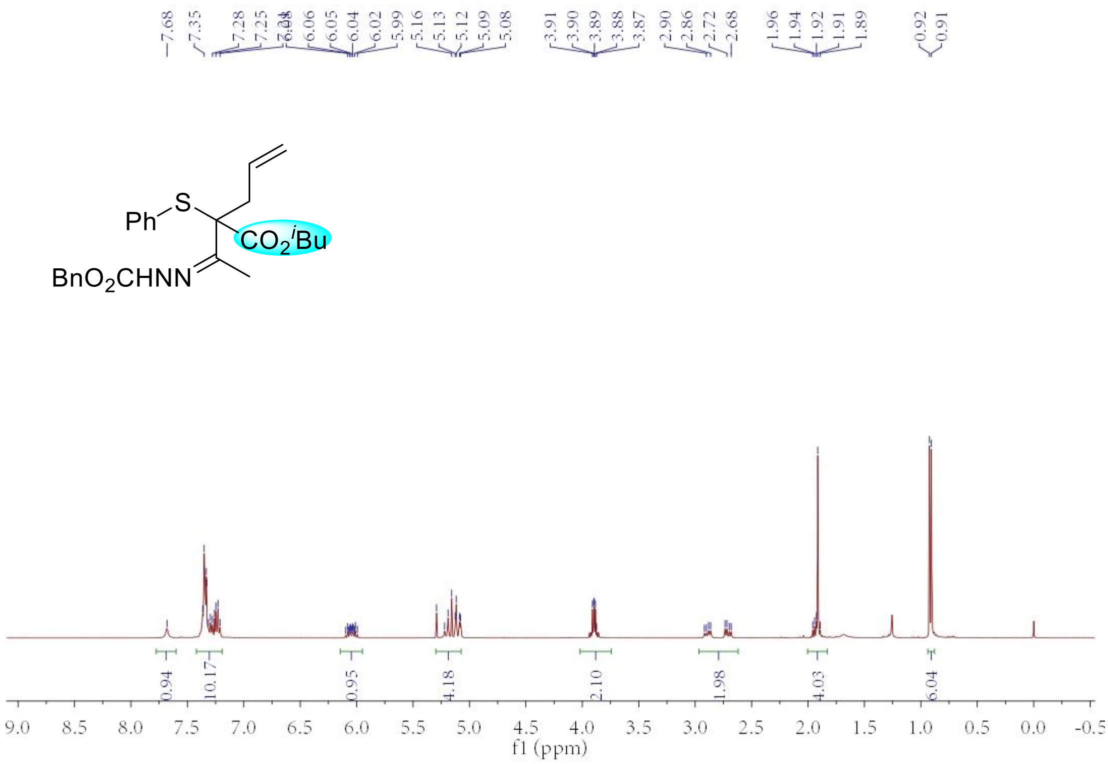
f1 (ppm)

3g



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5.09
5.08
3.91
3.90
3.89
3.88
3.87
2.90
2.86
2.72
2.68
1.96
1.94
1.92
1.91
1.89
0.92
0.91
Ph
S
$CO_2{}^iBu$
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10.17
0.95
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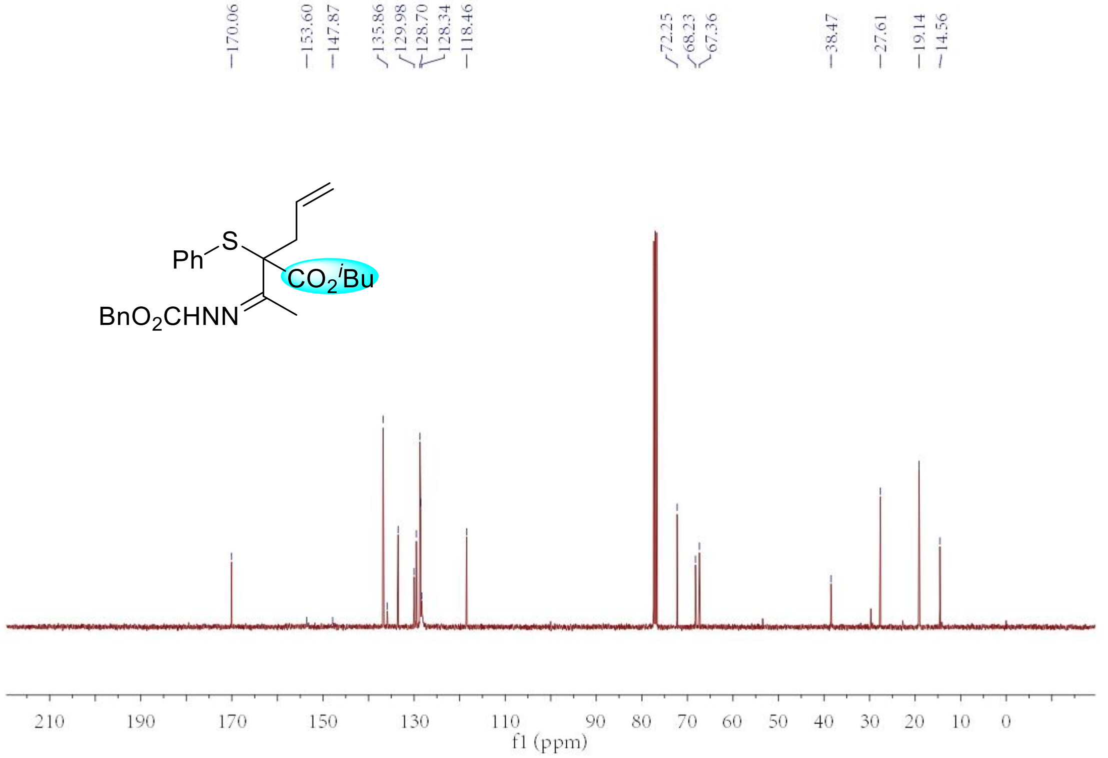
6.04
f1 (ppm)



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Ph
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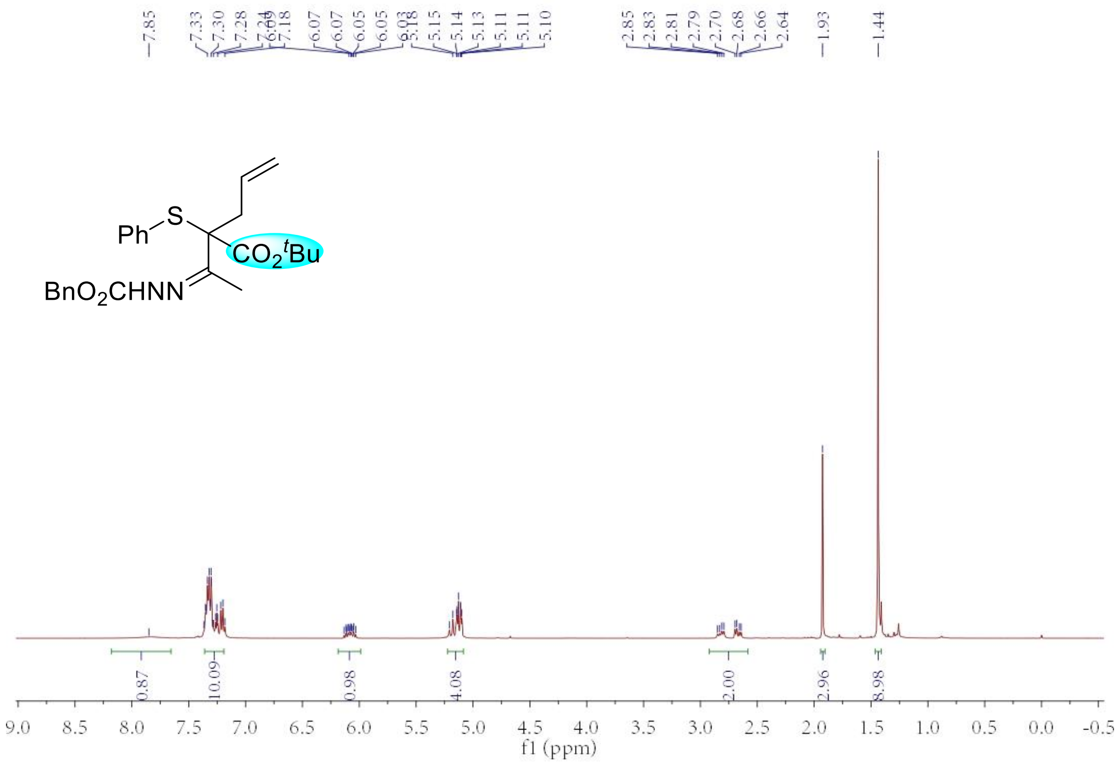
BnO_2CHNN
f1 (ppm)

3h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5.11
5.10
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2.79
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2.68
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1.44
Ph
S
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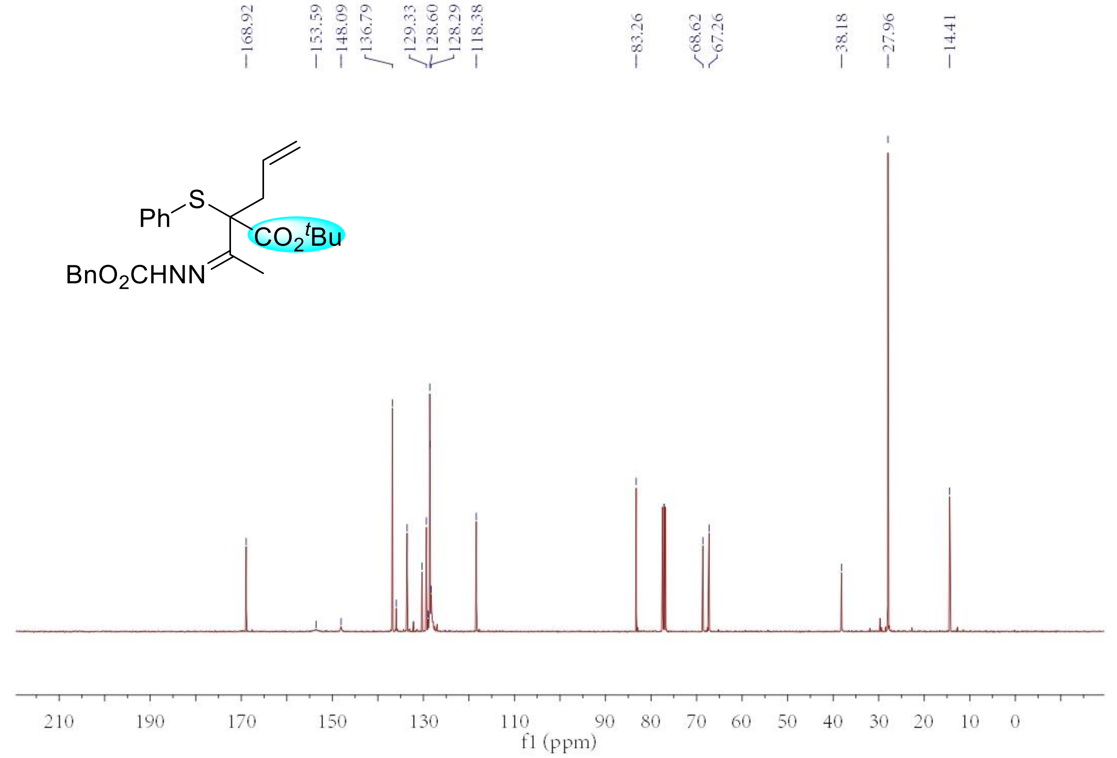
f1 (ppm)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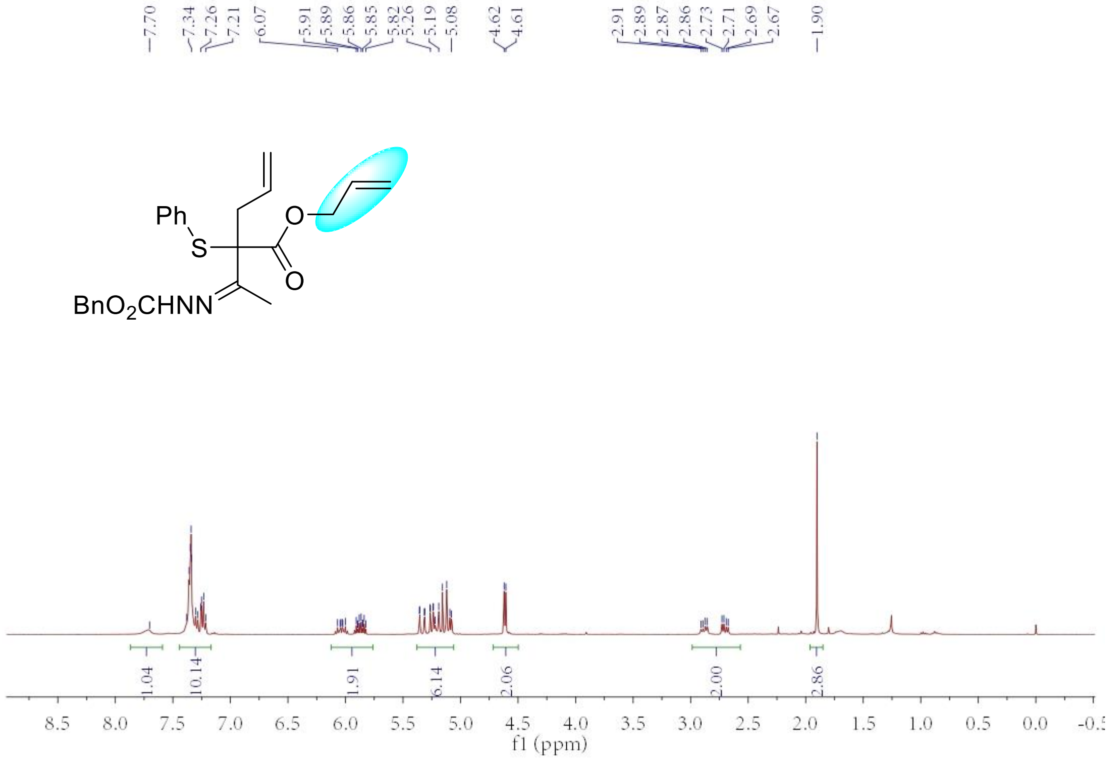
f1 (ppm)

3i



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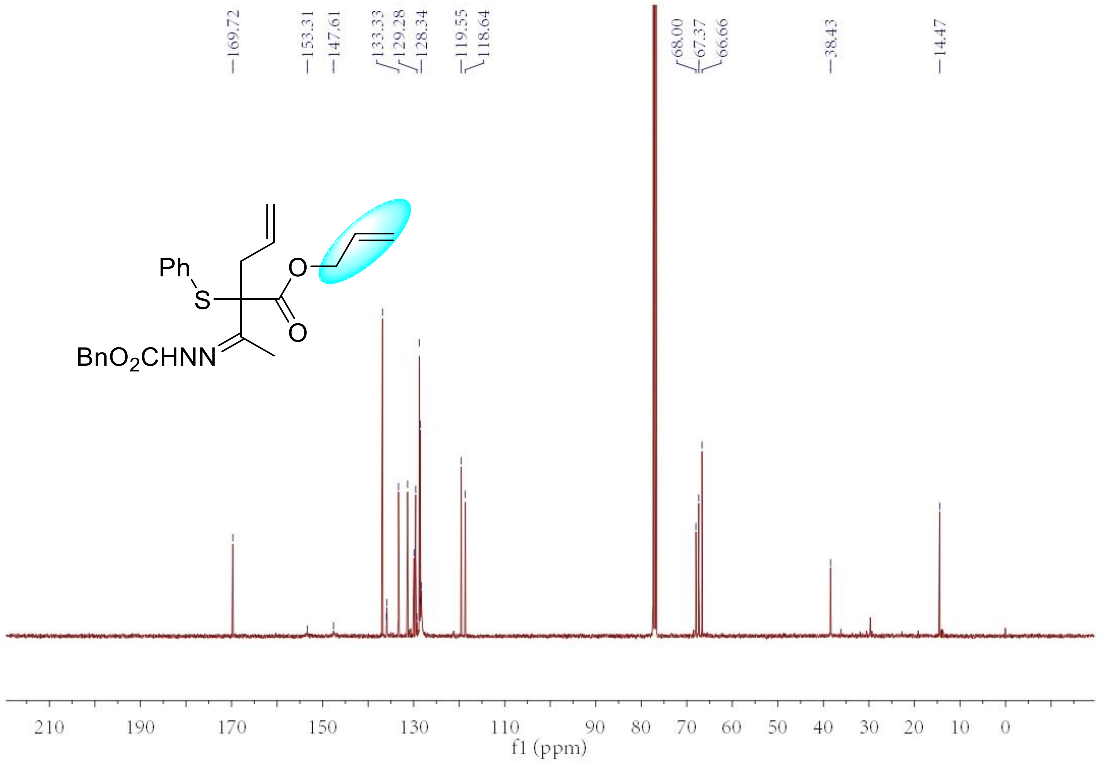

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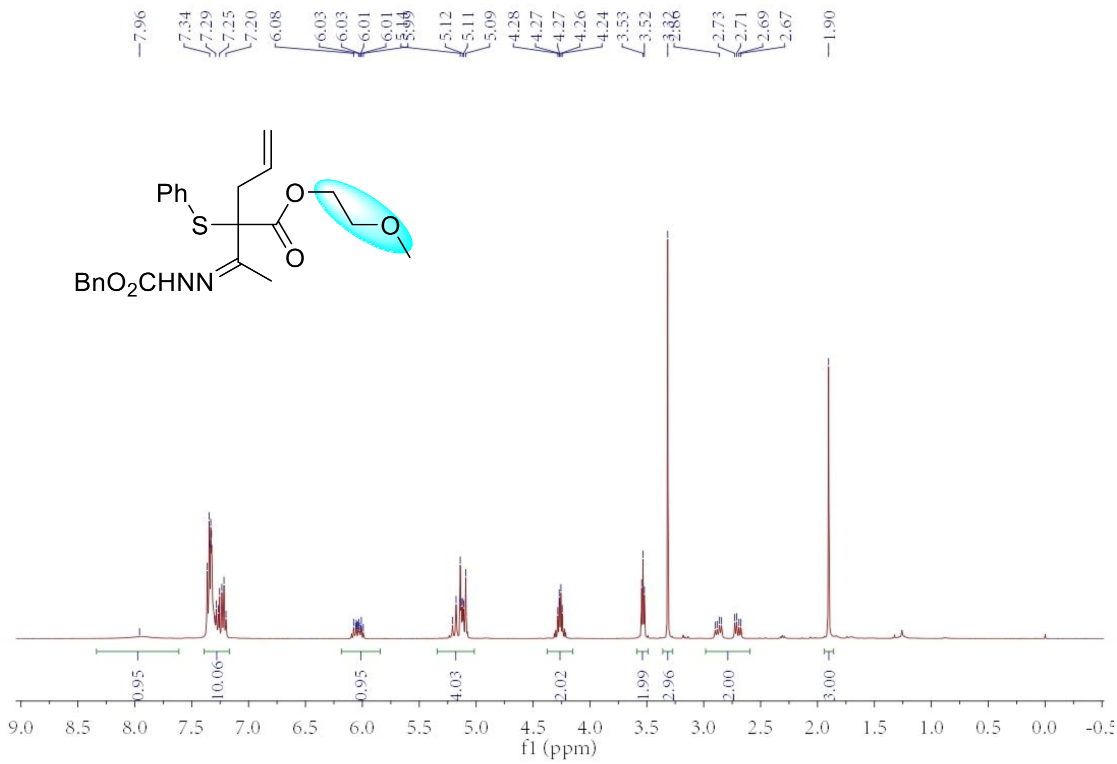
3j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4.27
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3.52
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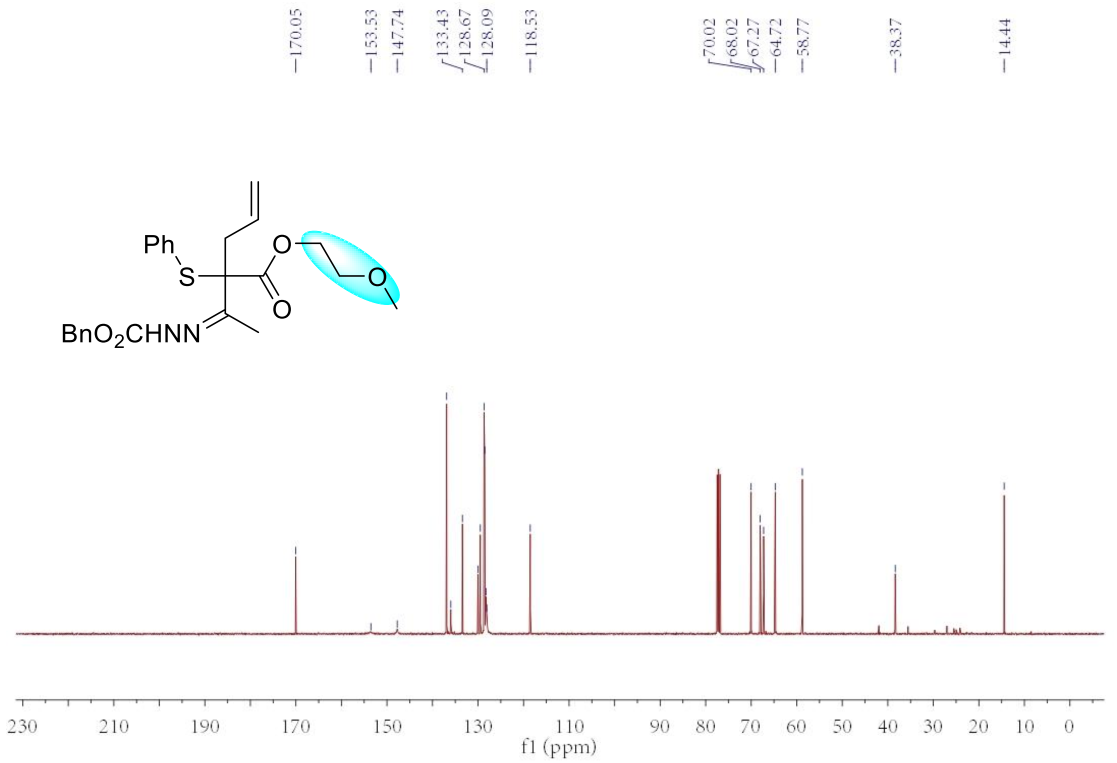
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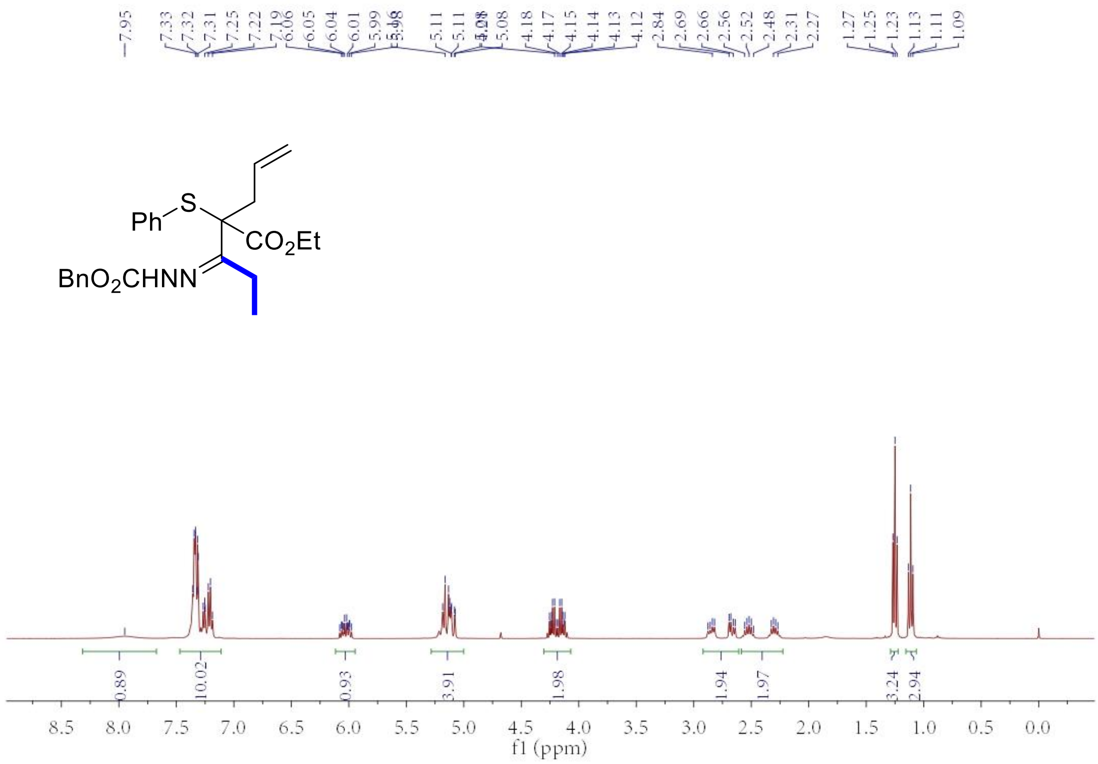
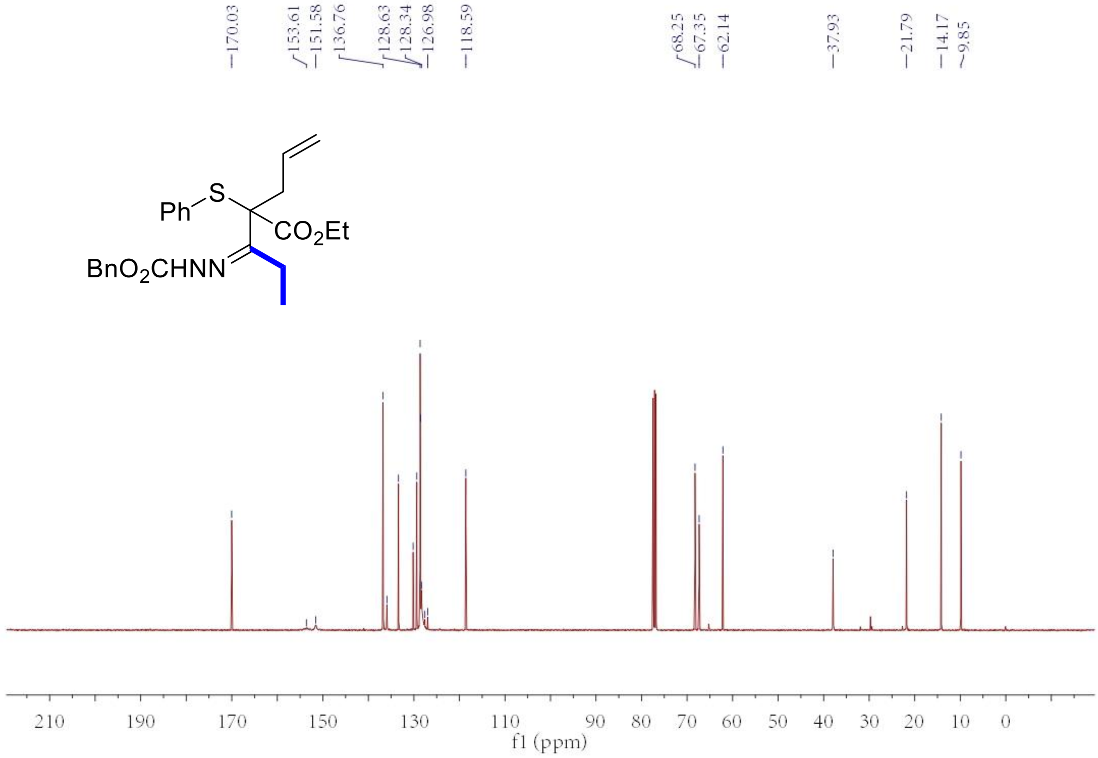
f1 (ppm)

3k





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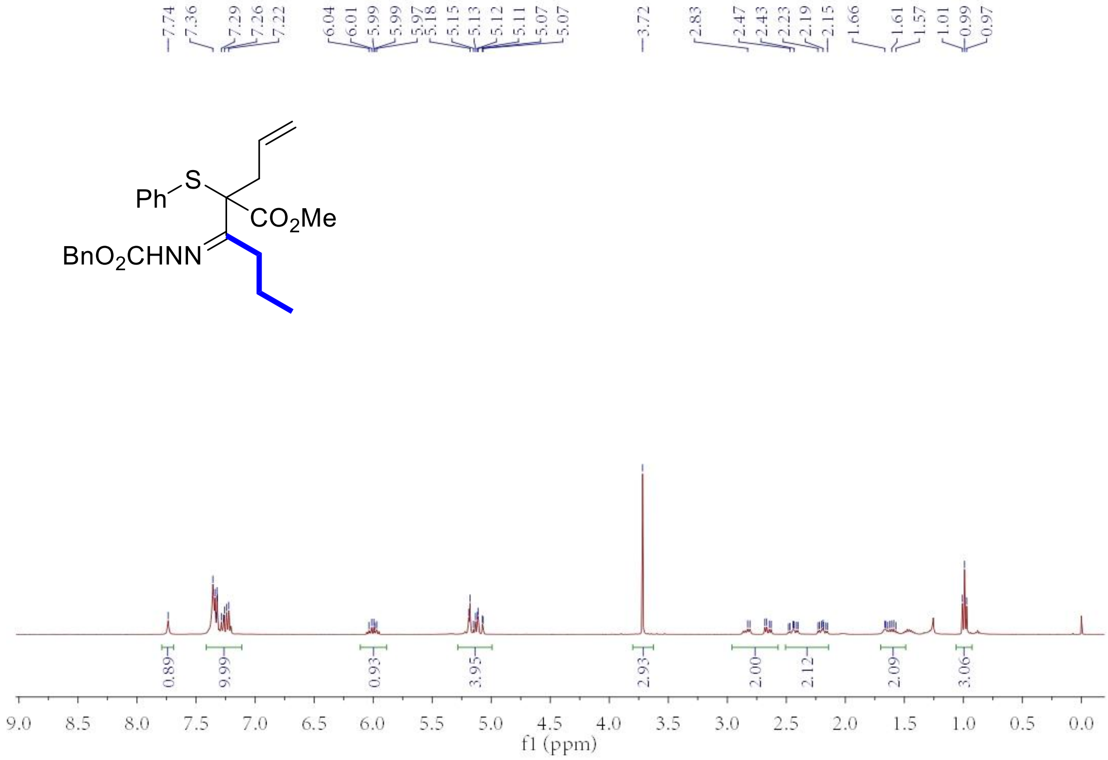
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0.97
Ph
S
CO2Me
BnO2CHNN
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2.00
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2.09
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8.0
7.5
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6.0
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1.0
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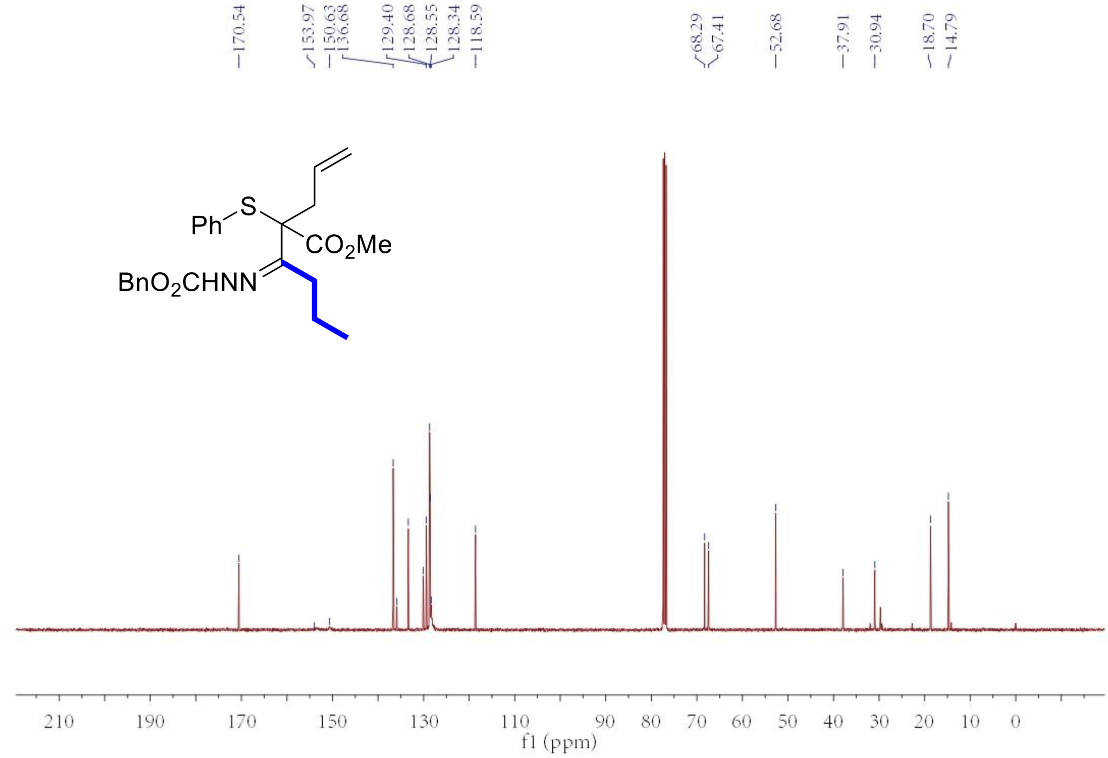
0.0
f1 (ppm)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30.94
18.70
14.79
Ph
S
CO2Me
BnO2CHNN
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170
150
130
110
90
80
70
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50
40
30
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10
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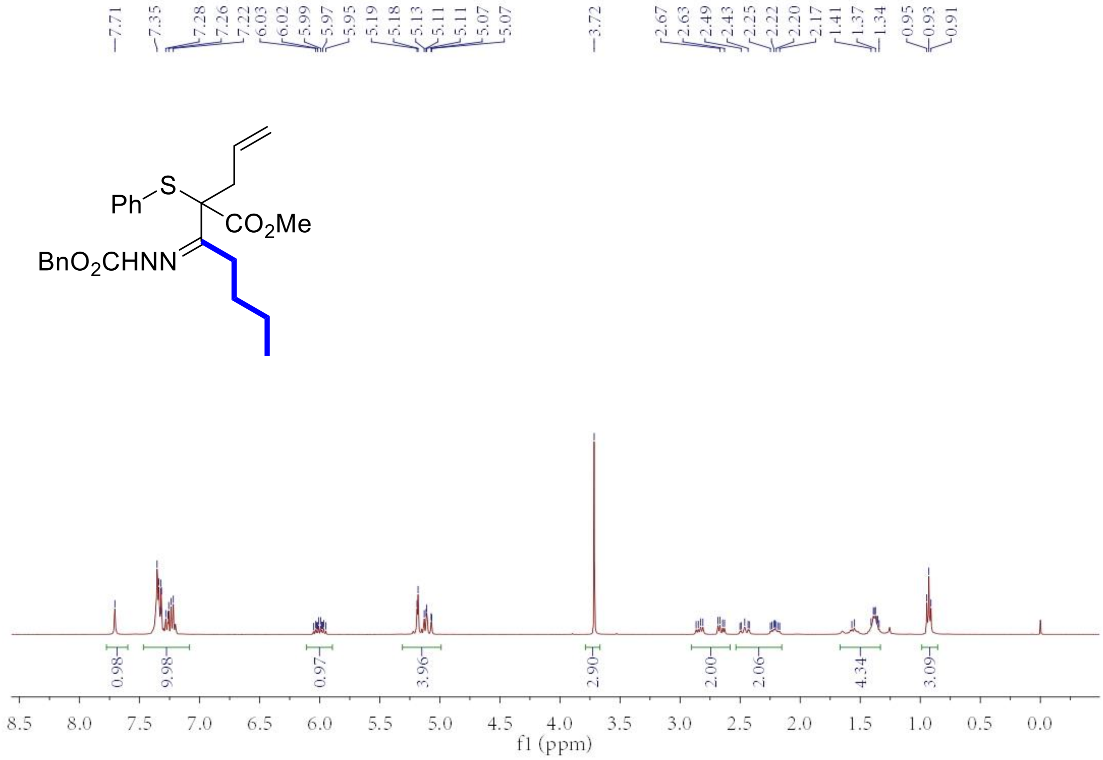
f1 (ppm)

3m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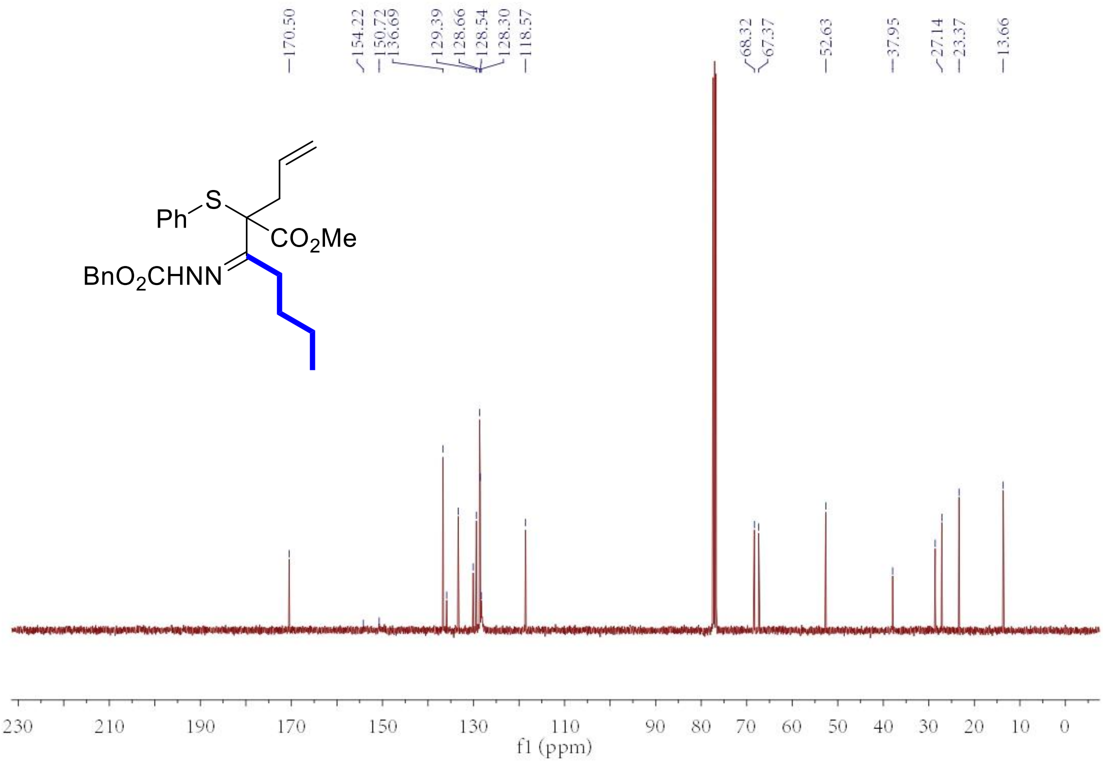
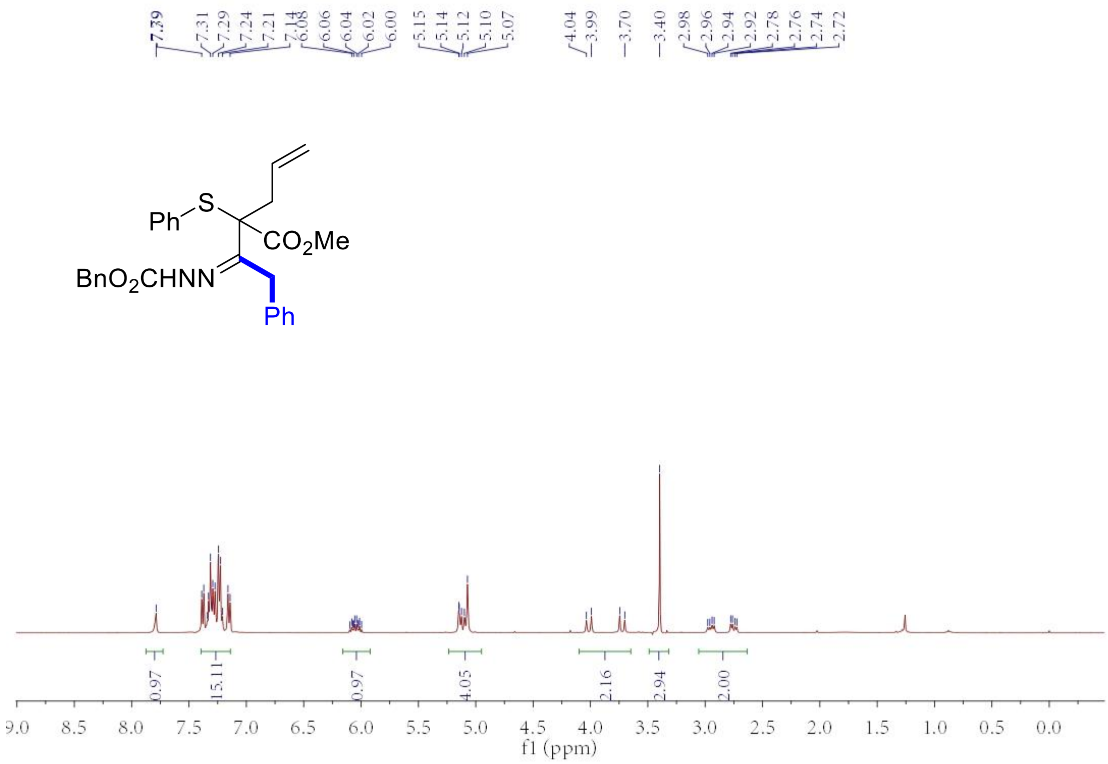
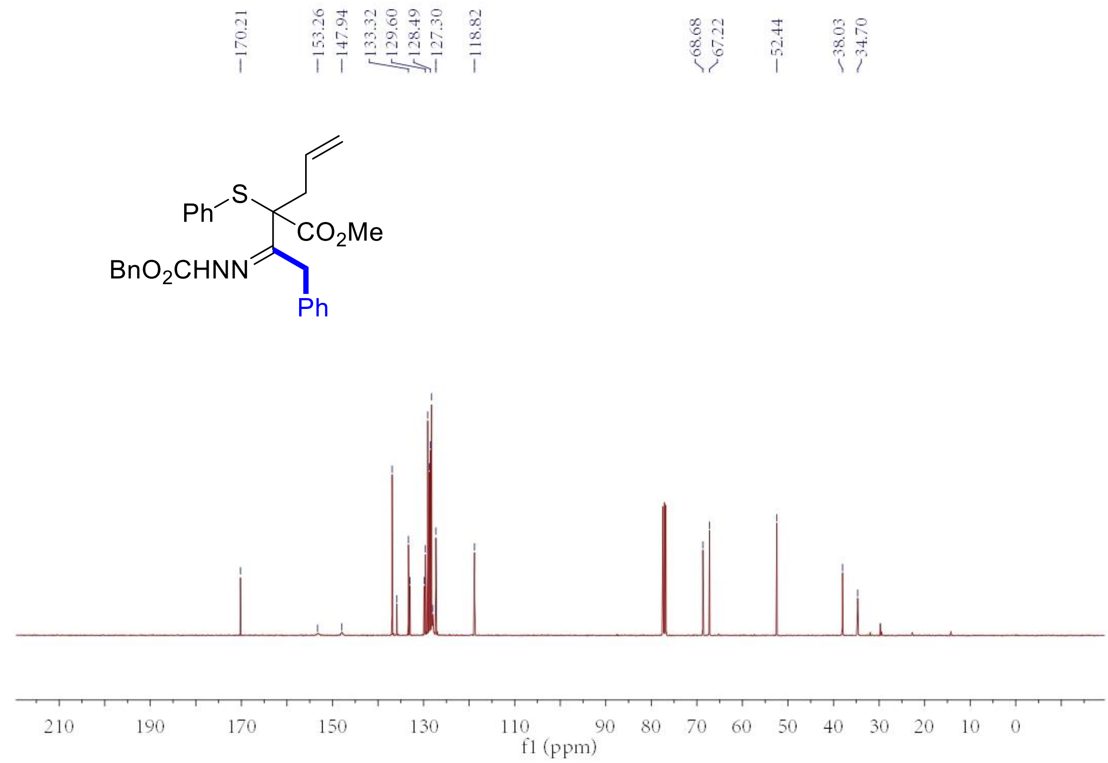
2.67
2.63
2.49
2.43
2.25
2.22
2.20
2.17
1.41
1.37
1.34
0.95
0.93
0.91
Ph
S
CO2Me
BnO2CHNN
0.98
9.98
0.97
3.96
2.90
2.00
2.06
4.34
3.09
f1 (ppm)

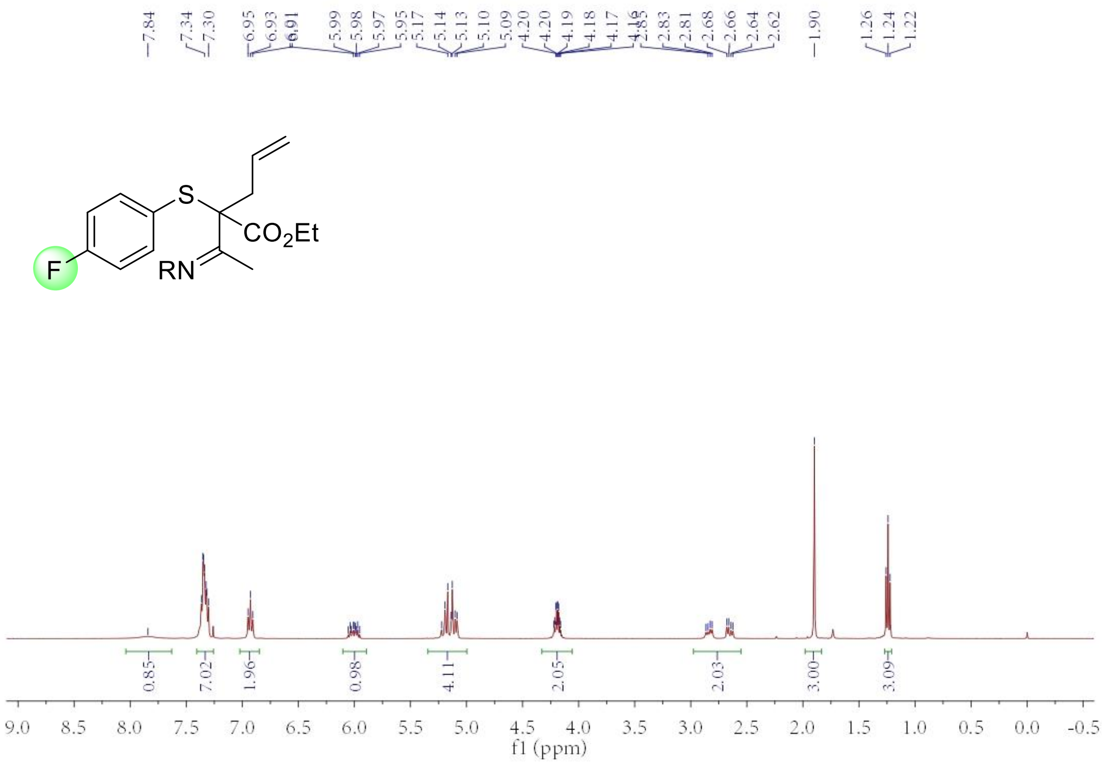

170.50
154.22
150.72
136.69
129.39
128.66
128.54
128.30
118.57
68.32
67.37
52.63
37.95
27.14
23.37
13.66
Ph
S
CO2Me
BnO2CHNN
f1 (ppm)

3n

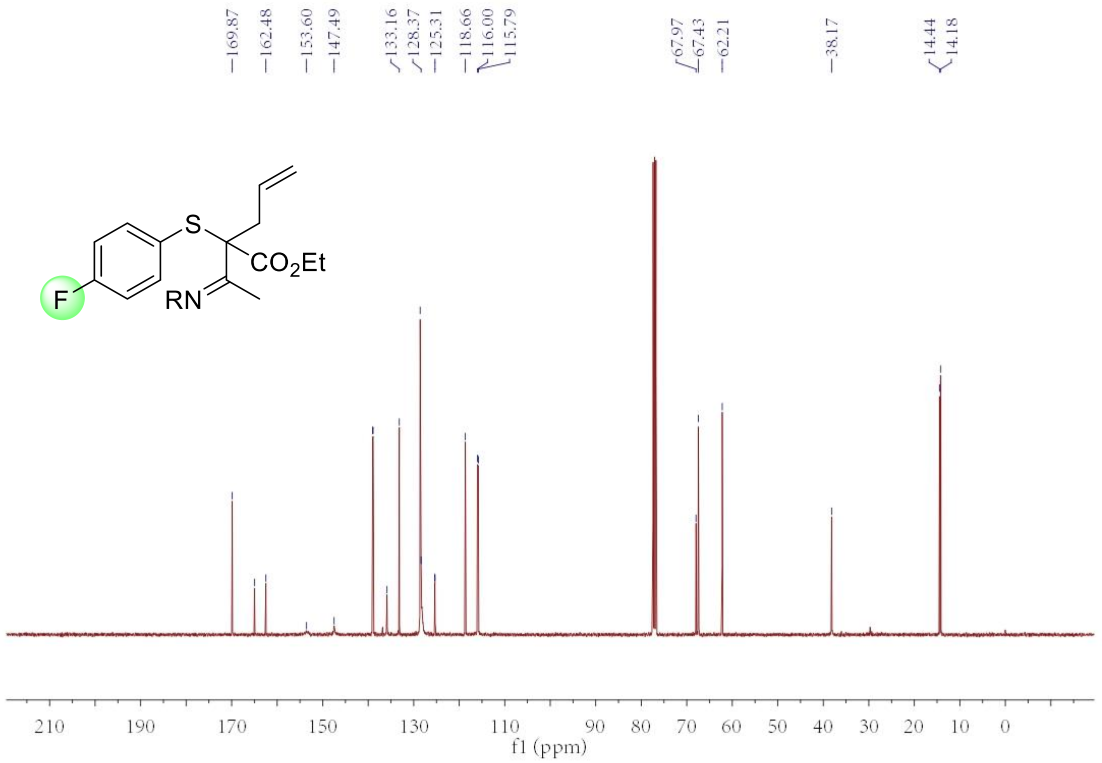




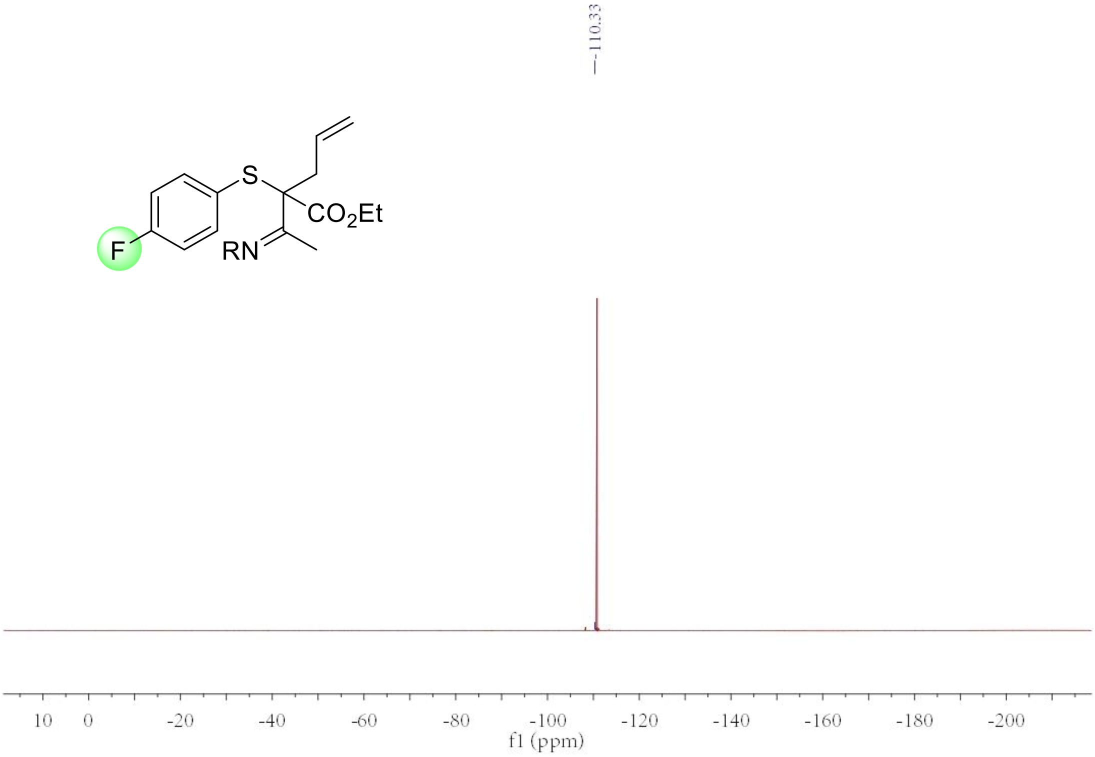
3o, R = $NHCO_2Bn$



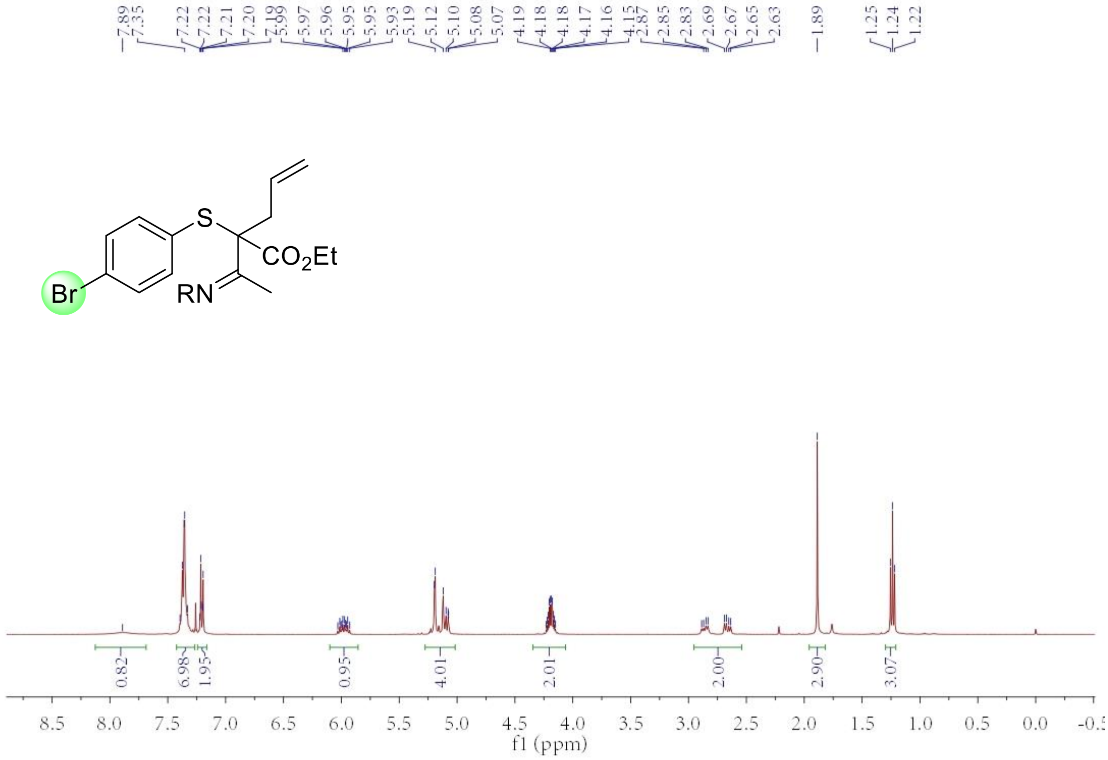
7.84
7.34
7.30
6.95
6.93
6.91
5.99
5.98
5.97
5.95
5.17
5.14
5.13
5.10
5.09
4.20
4.19
4.18
4.17
4.16
2.85
2.83
2.81
2.68
2.66
2.64
2.62
1.90
1.26
1.24
1.22
S
CO2Et
F
RN
0.85
7.02
1.96
0.98
4.11
2.05
2.03
3.00
3.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



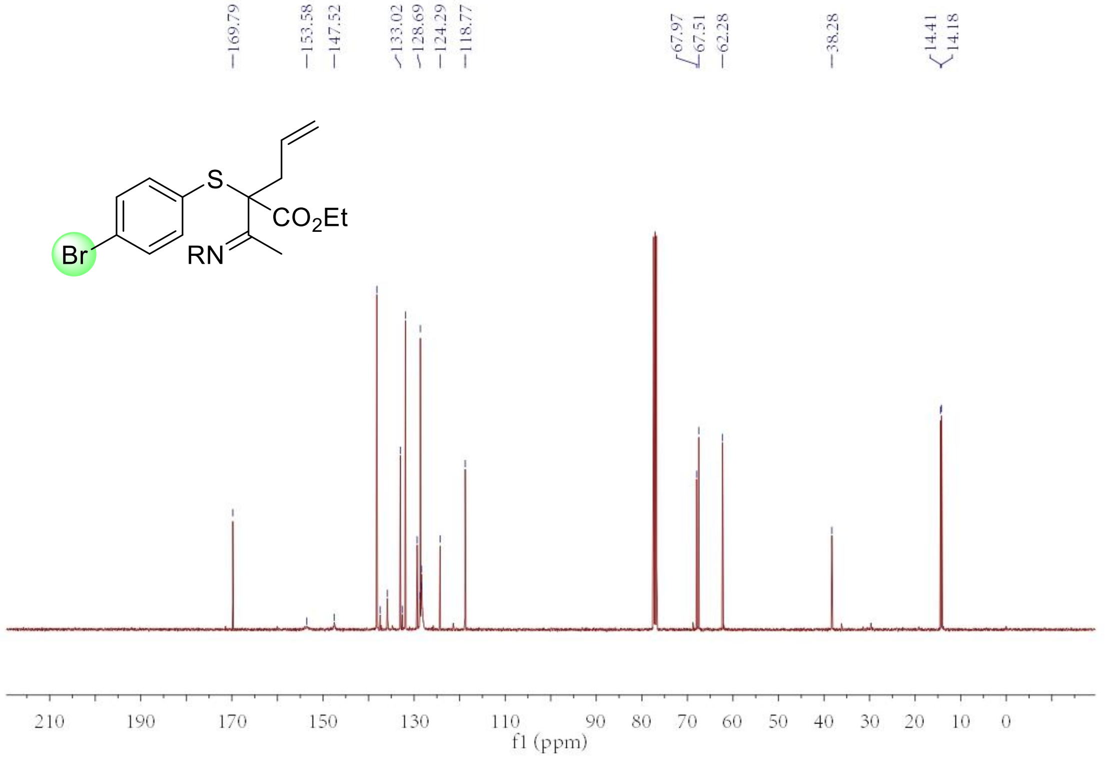
169.87
162.48
153.60
147.49
133.16
128.37
125.31
118.66
116.00
115.79
67.97
67.43
62.21
38.17
14.44
14.18
S
CO2Et
F
RN
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-110.33
S
CO2Et
F
RN
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

3p, R = $NHCO_2Bn$

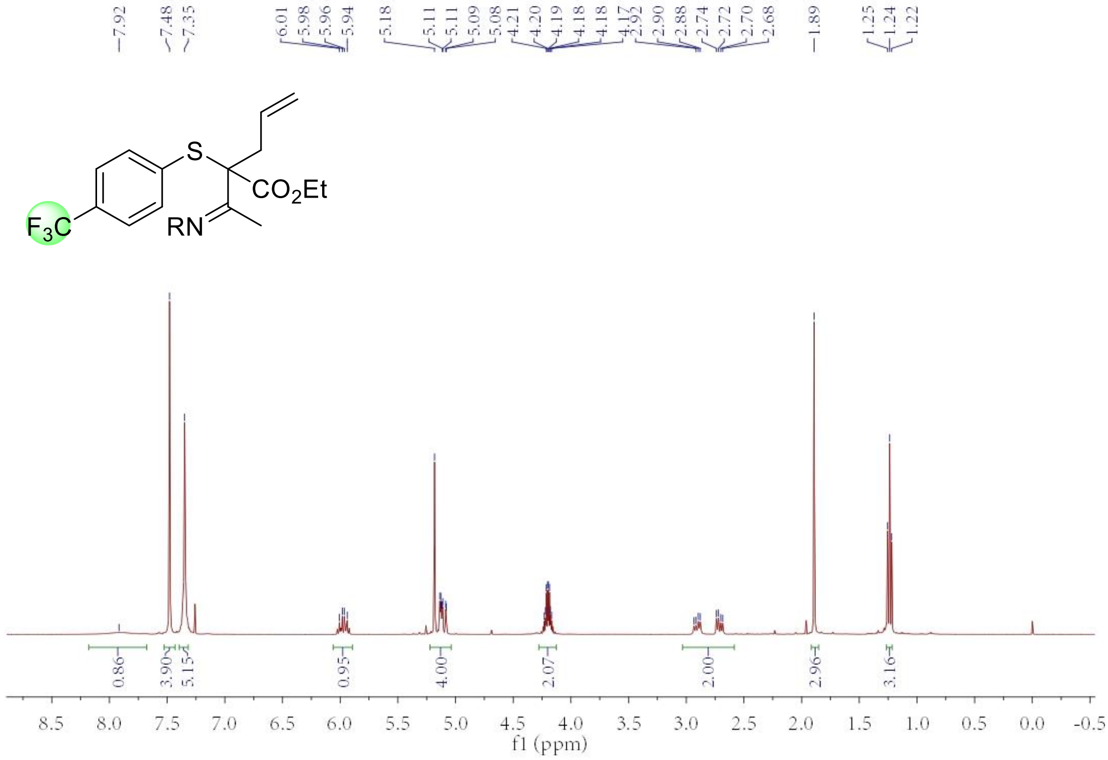


7.89
7.35
7.22
7.22
7.21
7.20
7.19
5.99
5.97
5.96
5.95
5.95
5.93
5.19
5.12
5.10
5.08
5.07
4.19
4.18
4.18
4.17
4.16
4.15
2.87
2.85
2.83
2.69
2.67
2.65
2.63
1.89
1.25
1.24
1.22
S
CO_2Et
Br
RN
0.82
6.98
1.95
0.95
4.01
2.01
2.00
2.90
3.07
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

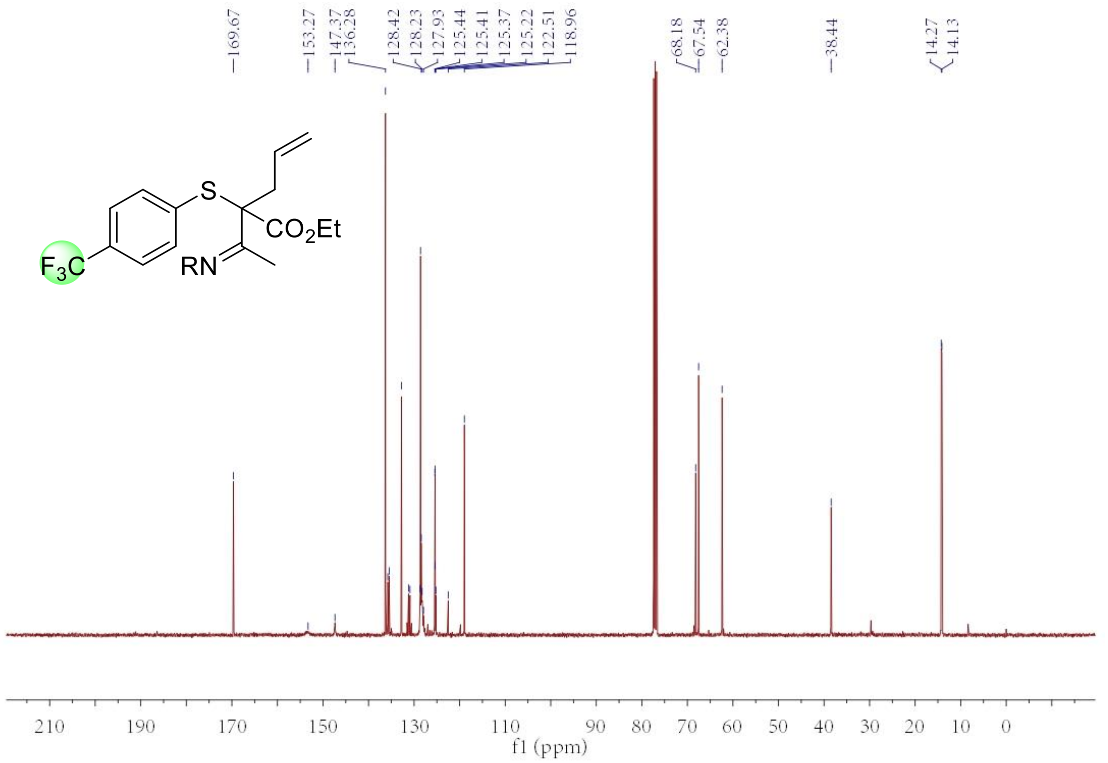


169.79
153.58
147.52
133.02
128.69
124.29
118.77
67.97
67.51
62.28
38.28
14.41
14.18
S
CO_2Et
Br
RN
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

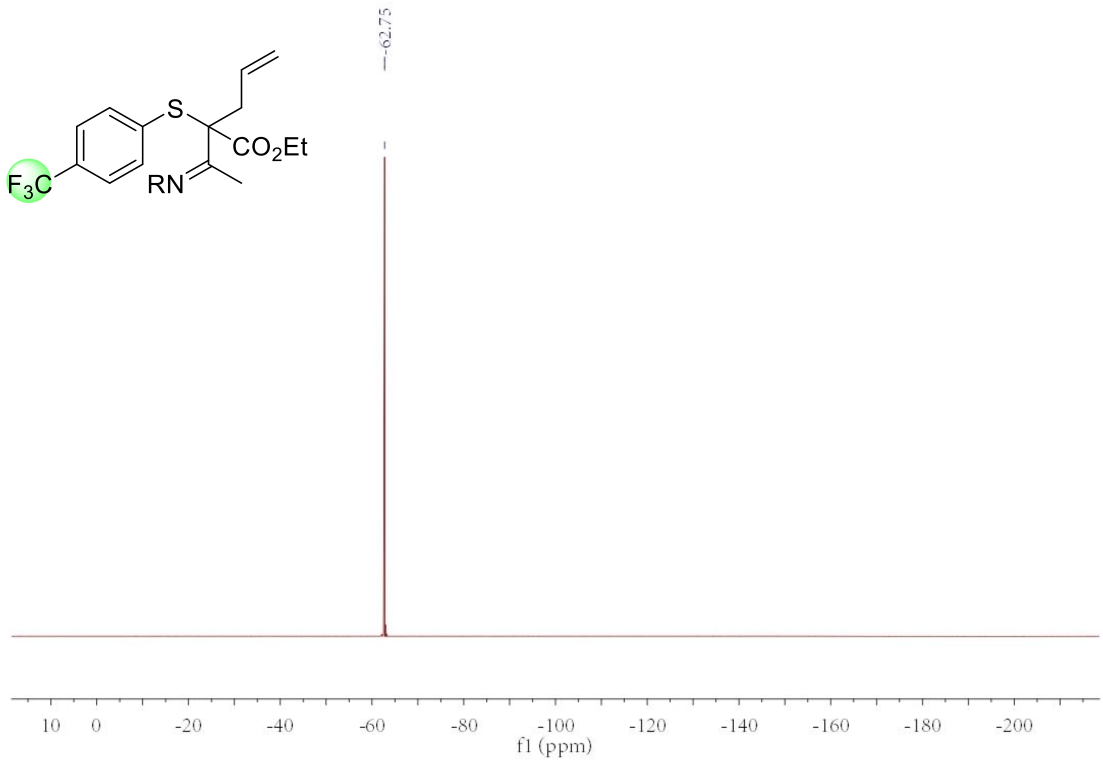
3q, R = $NHCO_2Bn$



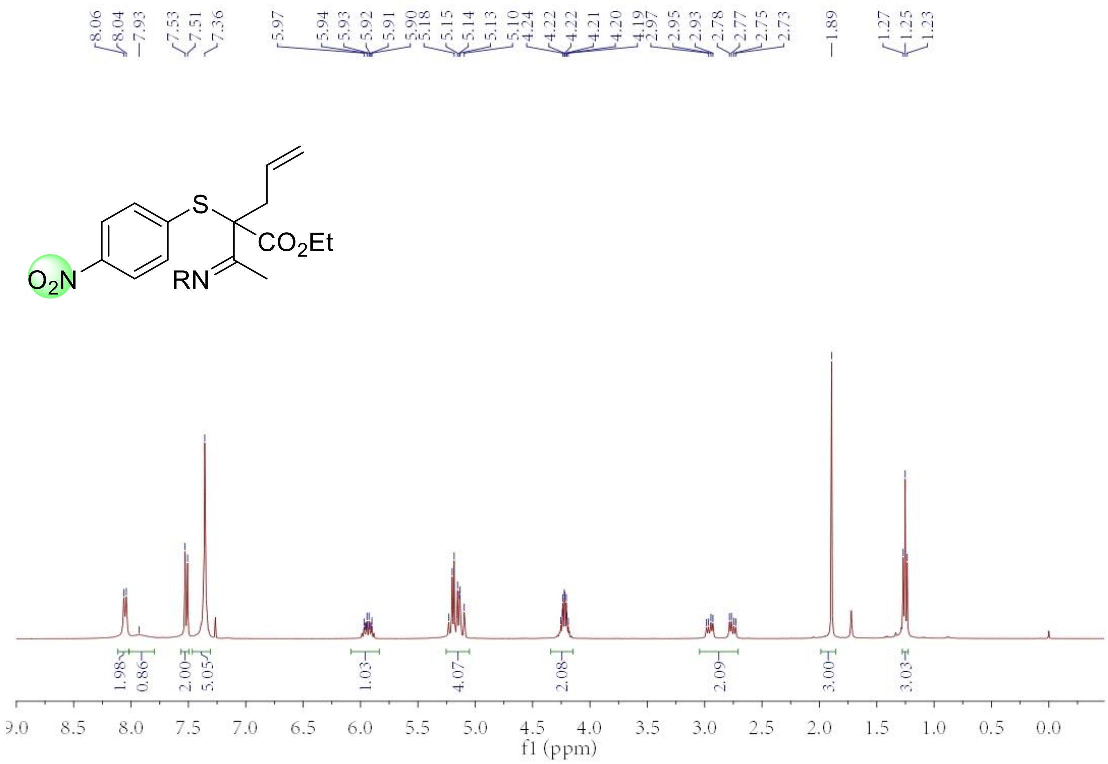
7.92
7.48
7.35
6.01
5.98
5.96
5.94
5.18
5.11
5.11
5.09
5.08
4.21
4.20
4.19
4.18
4.18
4.17
2.92
2.90
2.88
2.74
2.72
2.70
2.68
1.89
1.25
1.24
1.22
S
CO2Et
F3C
RN
0.86
3.90
5.15
0.95
4.00
2.07
2.00
2.96
3.16
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

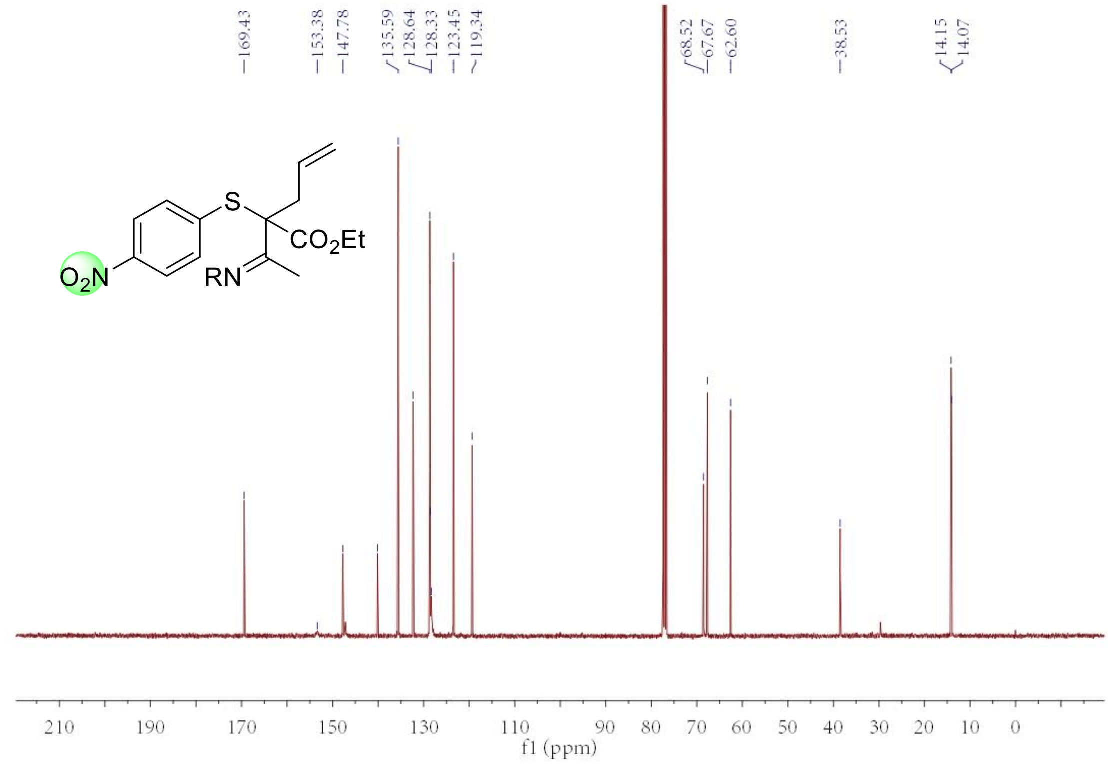


169.67
153.27
147.37
136.28
128.42
128.23
127.93
125.44
125.41
125.37
125.22
122.51
118.96
68.18
67.54
62.38
38.44
14.27
14.13
S
CO2Et
F3C
RN
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

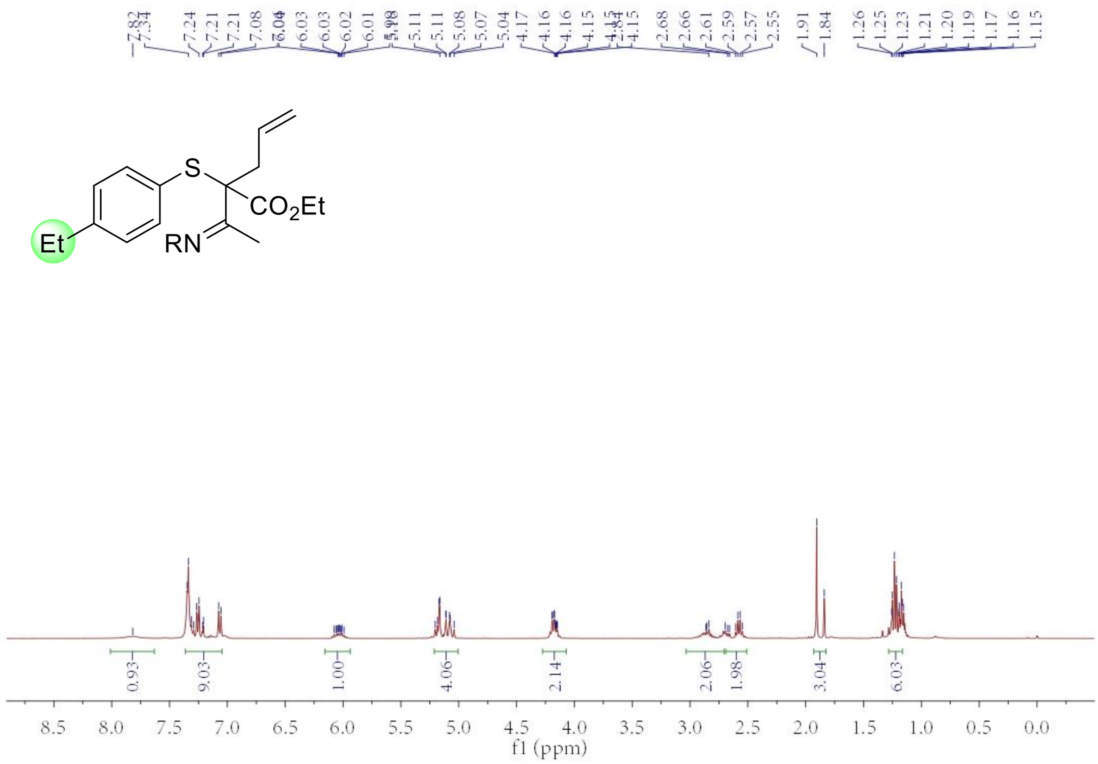

S
CO2Et
RN
F3C
-62.75
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

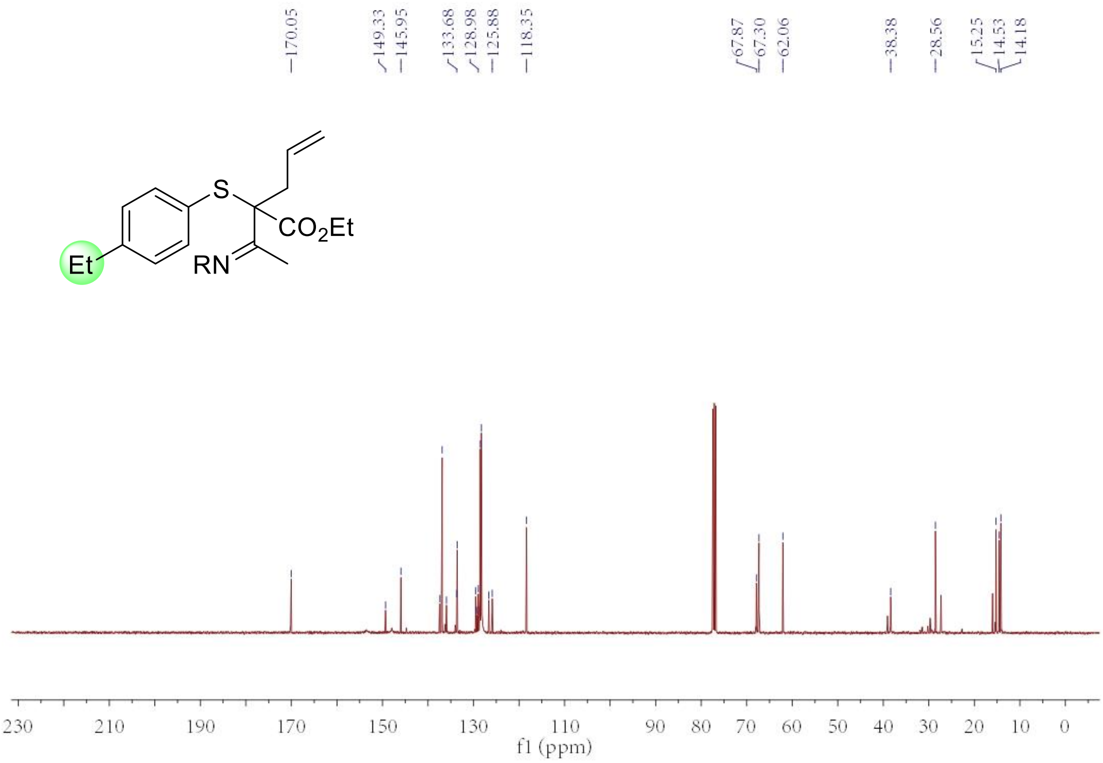
3r, R = $NHCO_2Bn$



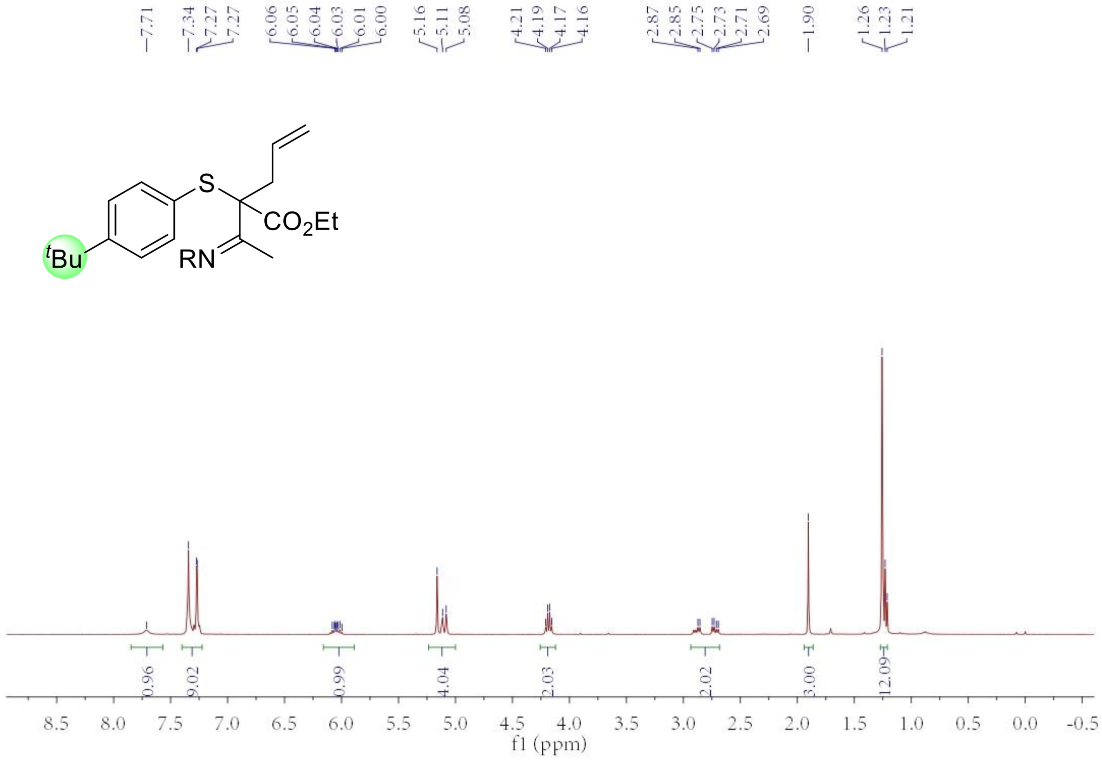


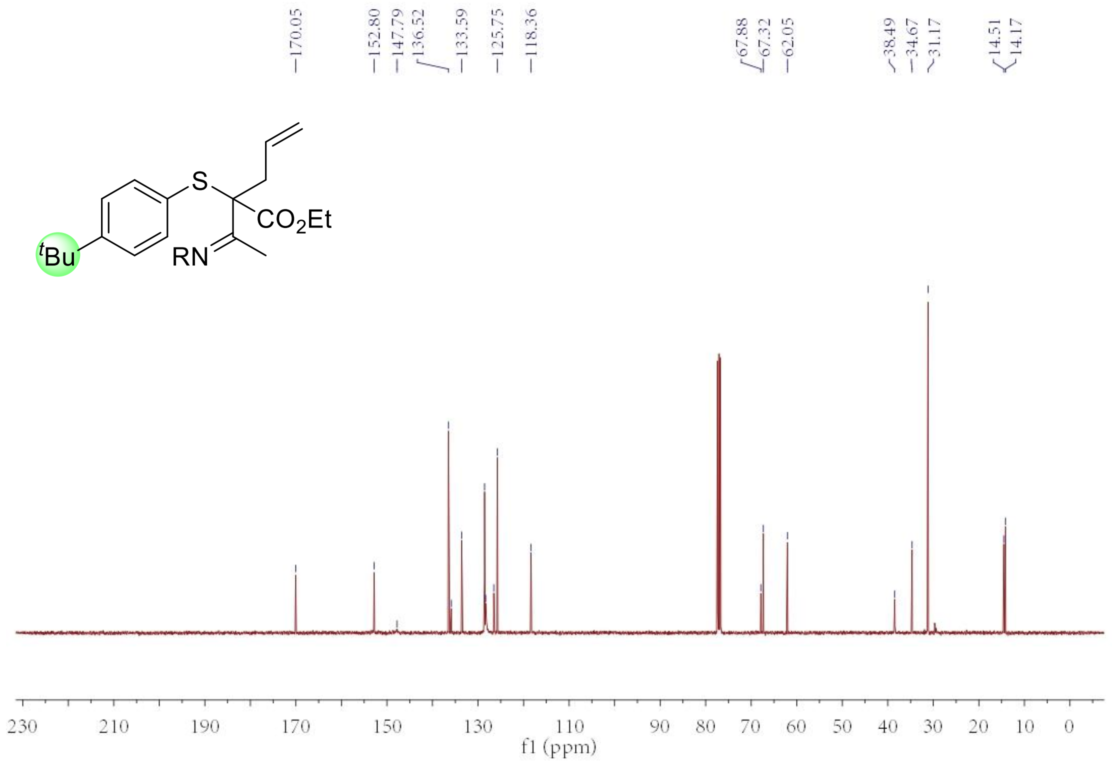
3s, R = $NHCO_2Bn$



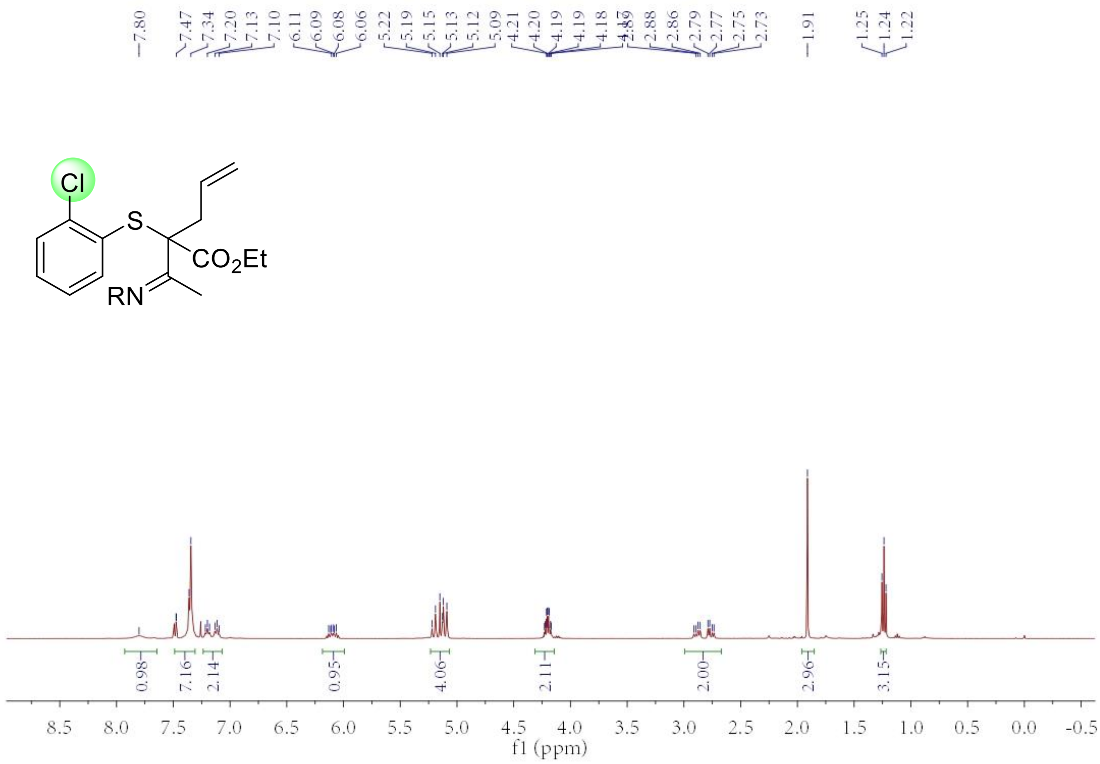


3t, R = $NHCO_2Bn$

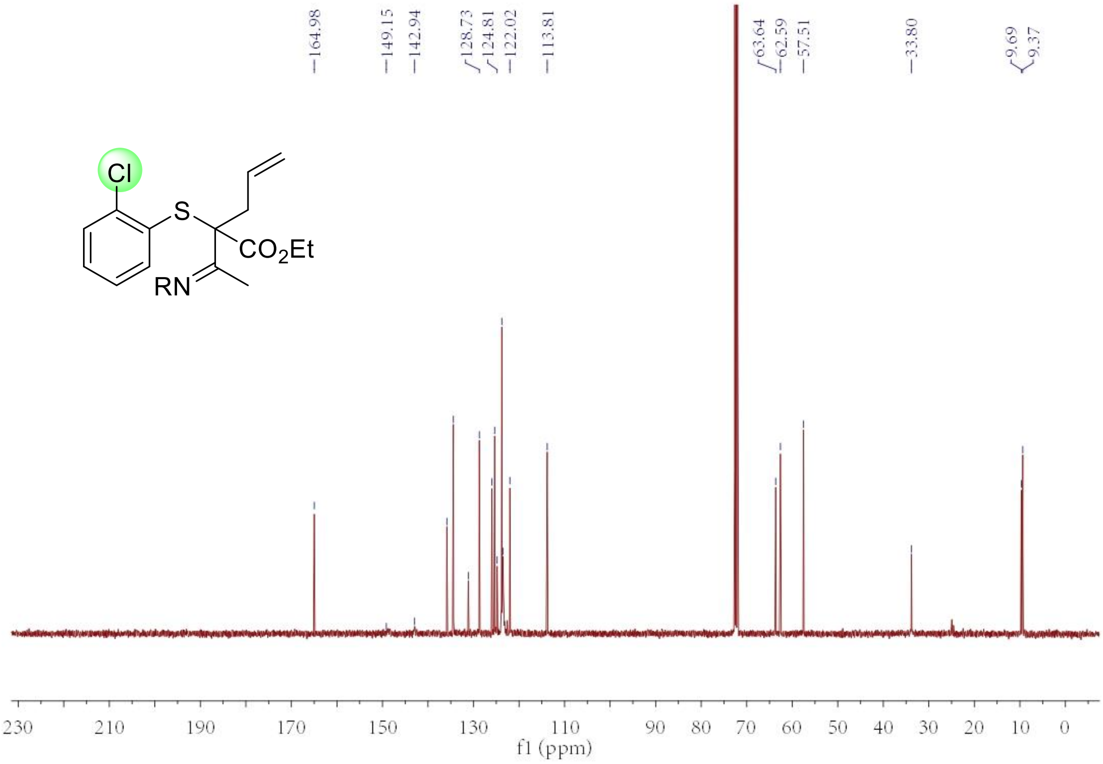

7.71
7.34
7.27
7.27
6.06
6.05
6.04
6.03
6.01
6.00
5.16
5.11
5.08
4.21
4.19
4.17
4.16
2.87
2.85
2.75
2.73
2.71
2.69
1.90
1.26
1.23
1.21
S
CO2Et
tBu
RN
0.96
9.02
0.99
4.04
2.03
2.02
3.00
12.09
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


170.05
152.80
147.79
136.52
133.59
125.75
118.36
67.88
67.32
62.05
38.49
34.67
31.17
14.51
14.17
S
CO2Et
tBu
RN
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3u, R = $NHCO_2Bn$

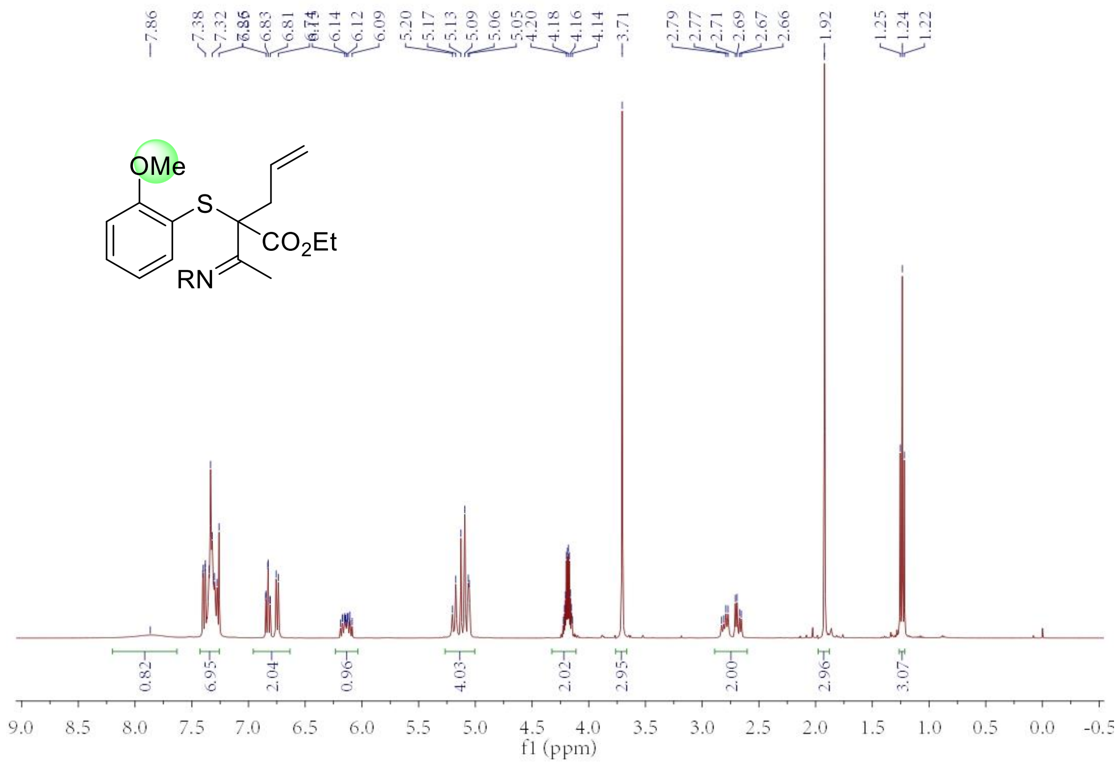


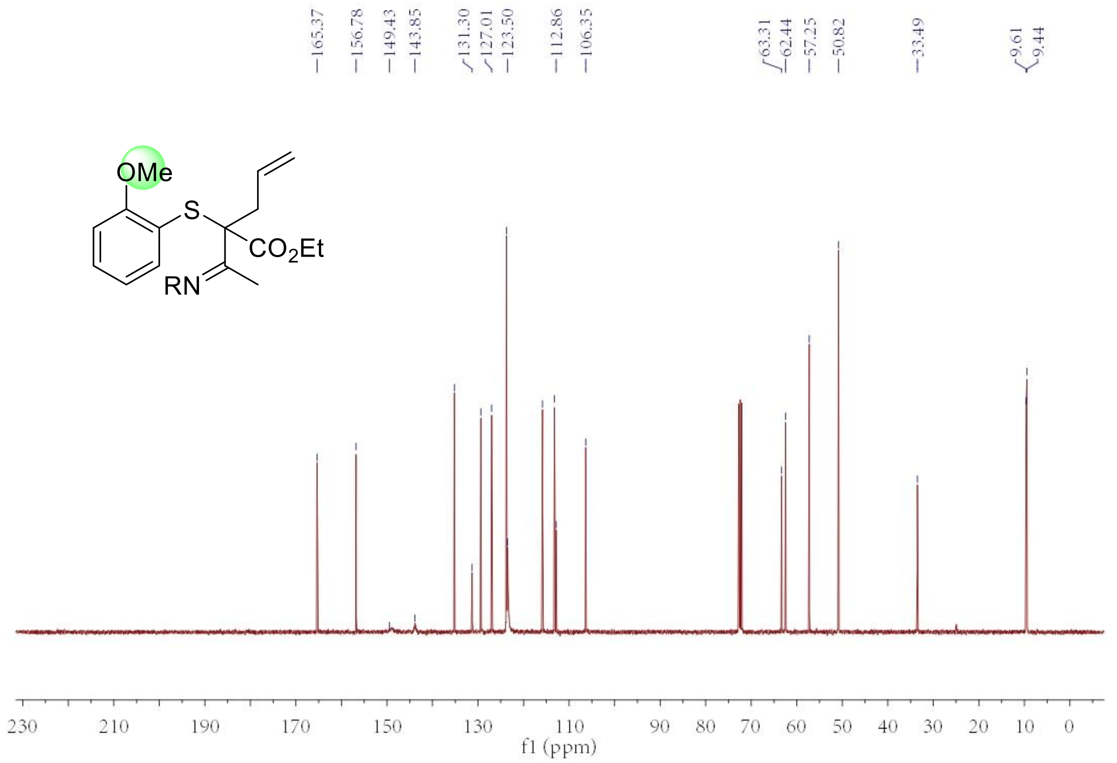
7.80
7.47
7.34
7.20
7.13
7.10
6.11
6.09
6.08
6.06
5.22
5.19
5.15
5.13
5.12
5.09
4.21
4.20
4.19
4.19
4.18
2.88
2.86
2.79
2.77
2.75
2.73
1.91
1.25
1.24
1.22
Cl
S
CO2Et
RN
0.98
7.16
2.14
0.95
4.06
2.11
2.00
2.96
3.15
f1 (ppm)



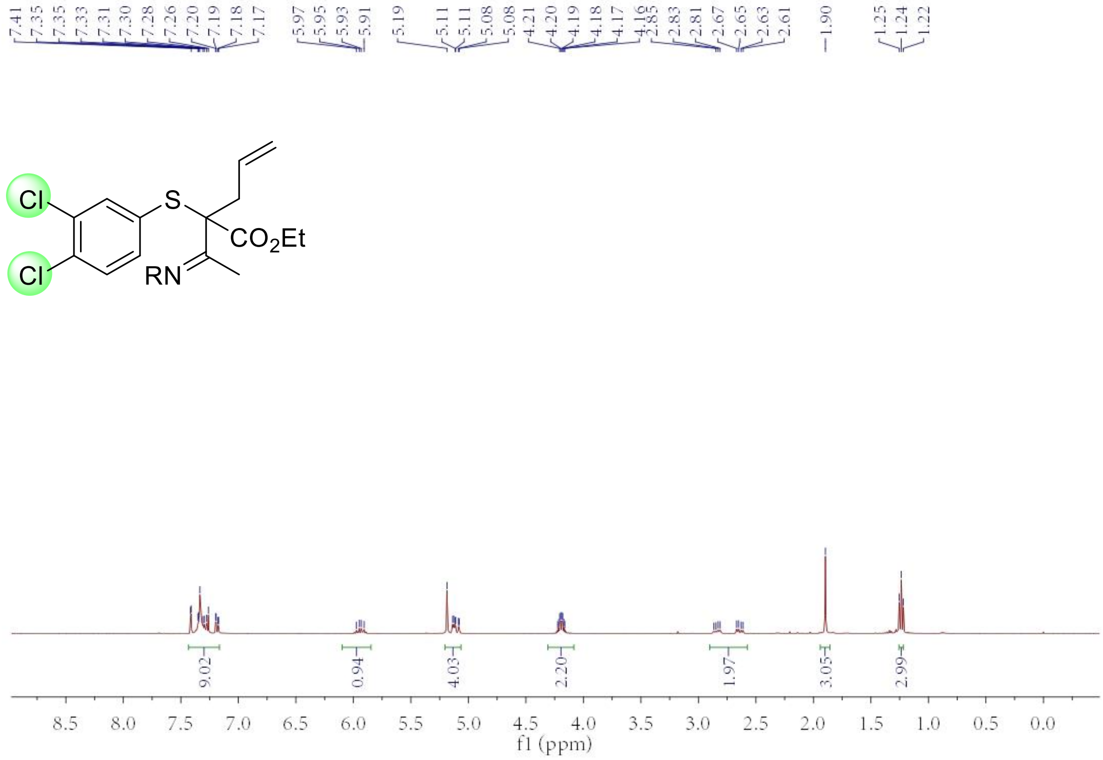
164.98
149.15
142.94
128.73
124.81
122.02
113.81
63.64
62.59
57.51
33.80
9.69
9.37
Cl
S
CO2Et
RN
f1 (ppm)

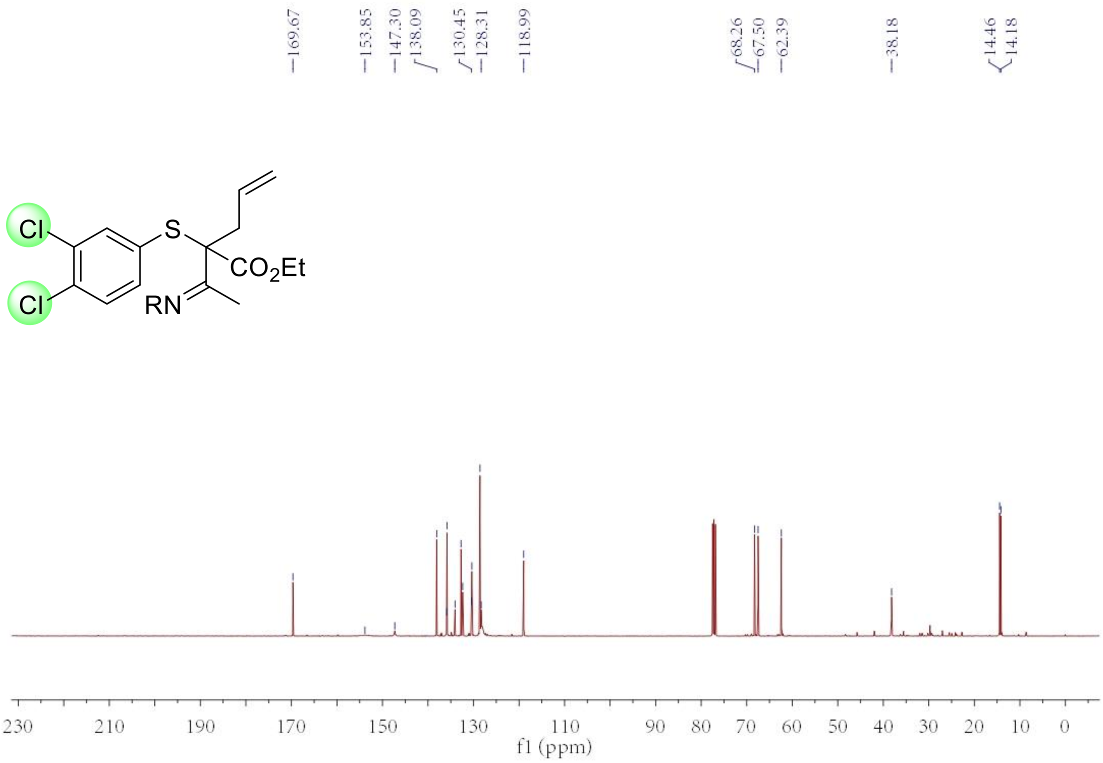
3v, R = $NHCO_2Bn$


OMe
S
CO2Et
RN
0.82
6.95
2.04
0.96
4.03
2.02
2.95
2.00
2.96
3.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

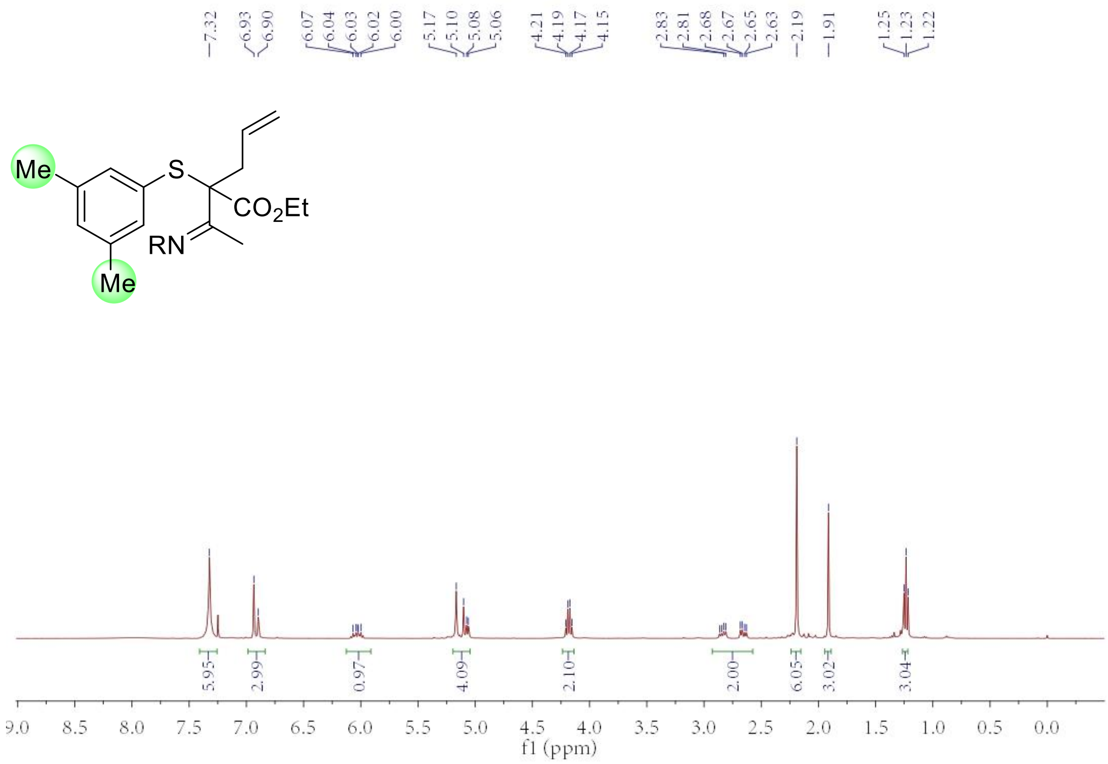

165.37
156.78
149.43
143.85
131.30
127.01
123.50
112.86
106.35
63.31
62.44
57.25
50.82
33.49
9.61
9.44
OMe
S
CO2Et
RN
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

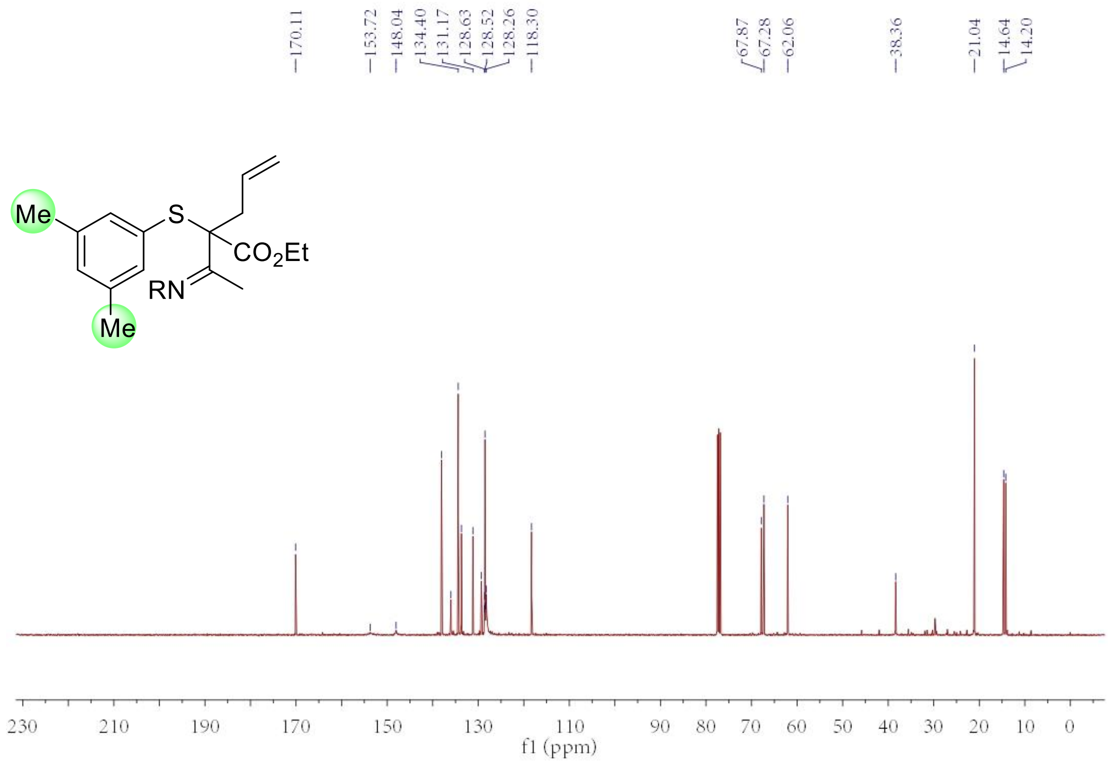
3w, R = $NHCO_2Bn$



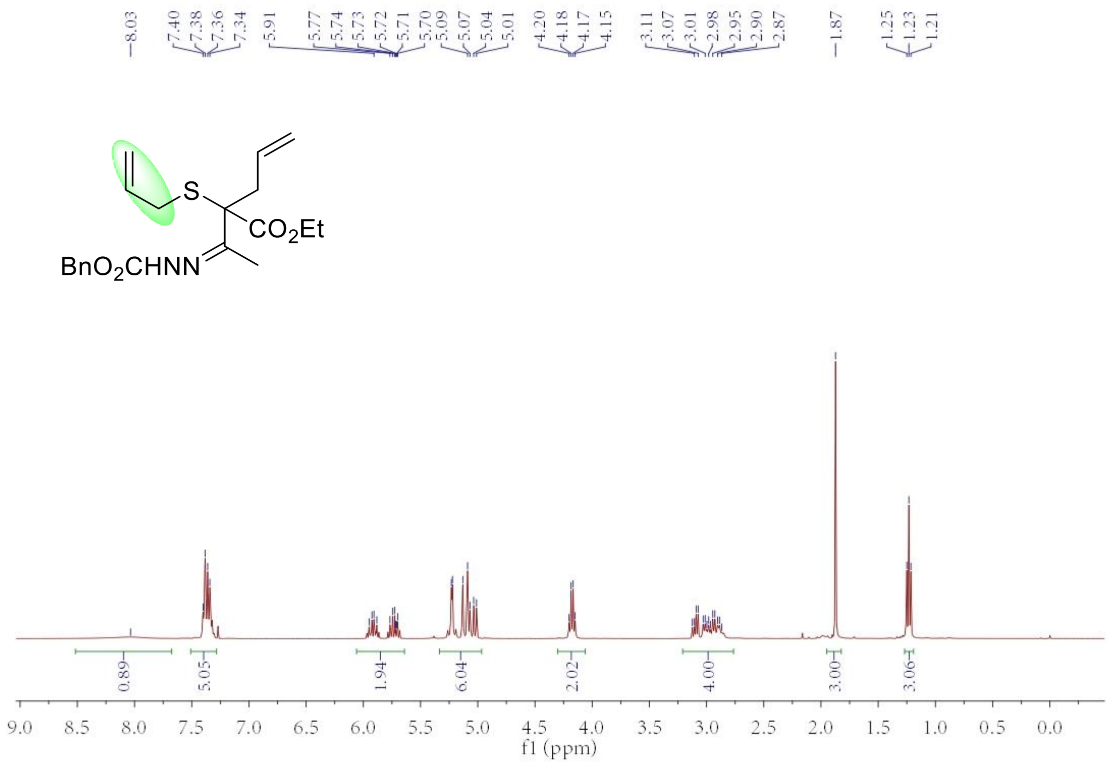


3x, R = $NHCO_2Bn$

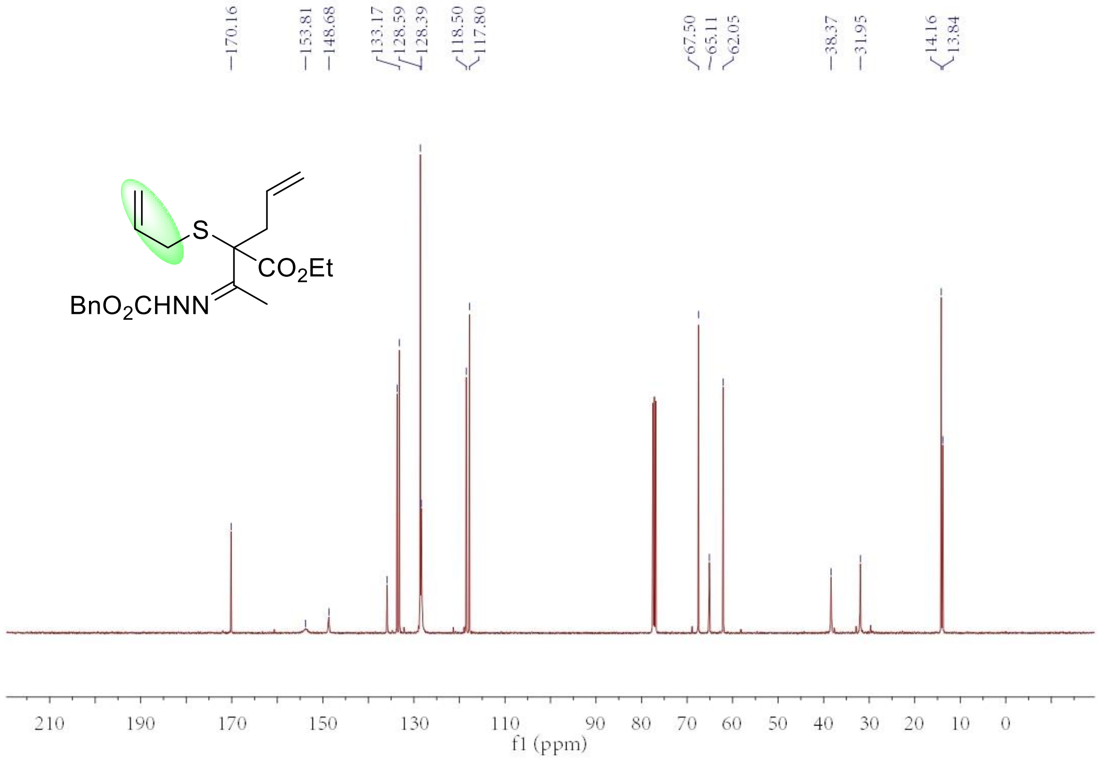

7.32
6.93
6.90
6.07
6.04
6.03
6.02
6.00
5.17
5.10
5.08
5.06
4.21
4.19
4.17
4.15
2.83
2.81
2.68
2.67
2.65
2.63
2.19
1.91
1.25
1.23
1.22
Me
S
CO2Et
RN
Me
5.95
2.99
0.97
4.09
2.10
2.00
6.05
3.02
3.04
f1 (ppm)


170.11
153.72
148.04
134.40
131.17
128.63
128.52
128.26
118.30
67.87
67.28
62.06
38.36
21.04
14.64
14.20
Me
S
CO2Et
RN
Me
f1 (ppm)

3y

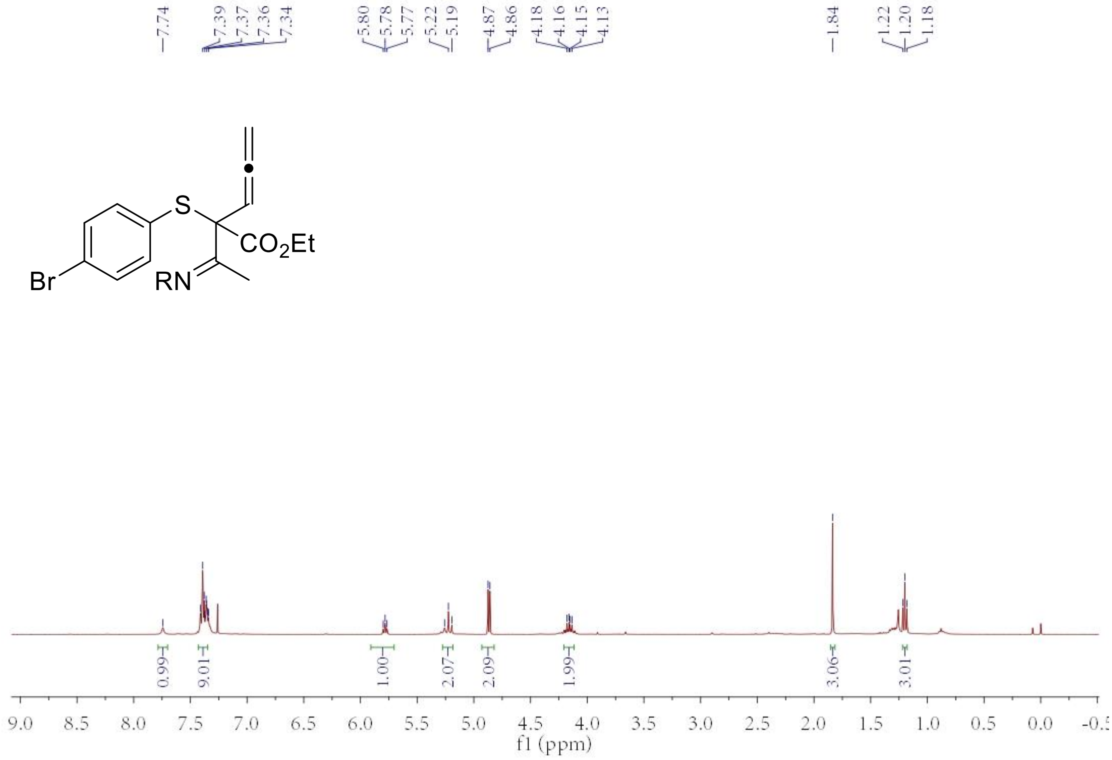


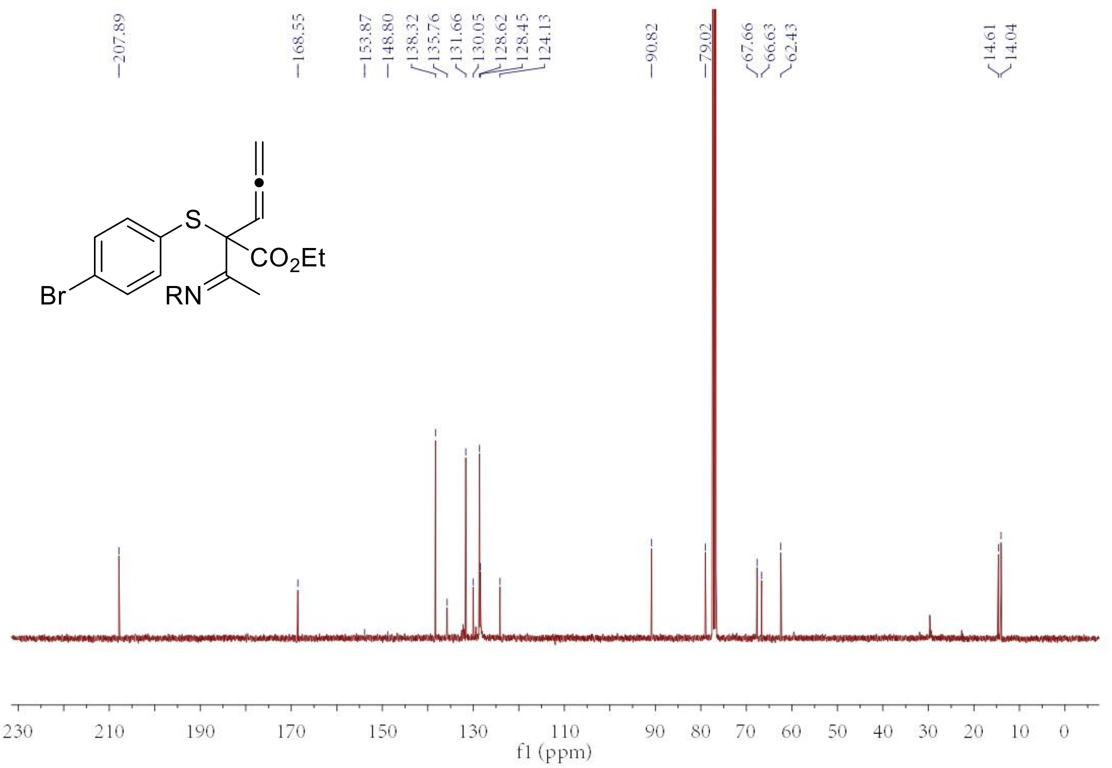
8.03
7.40
7.38
7.36
7.34
5.91
5.77
5.74
5.73
5.72
5.71
5.70
5.09
5.07
5.04
5.01
4.20
4.18
4.17
4.15
3.11
3.07
3.01
2.98
2.95
2.90
2.87
1.87
1.25
1.23
1.21
S
CO2Et
BnO2CHNN
0.89
5.05
1.94
6.04
2.02
4.00
3.00
3.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



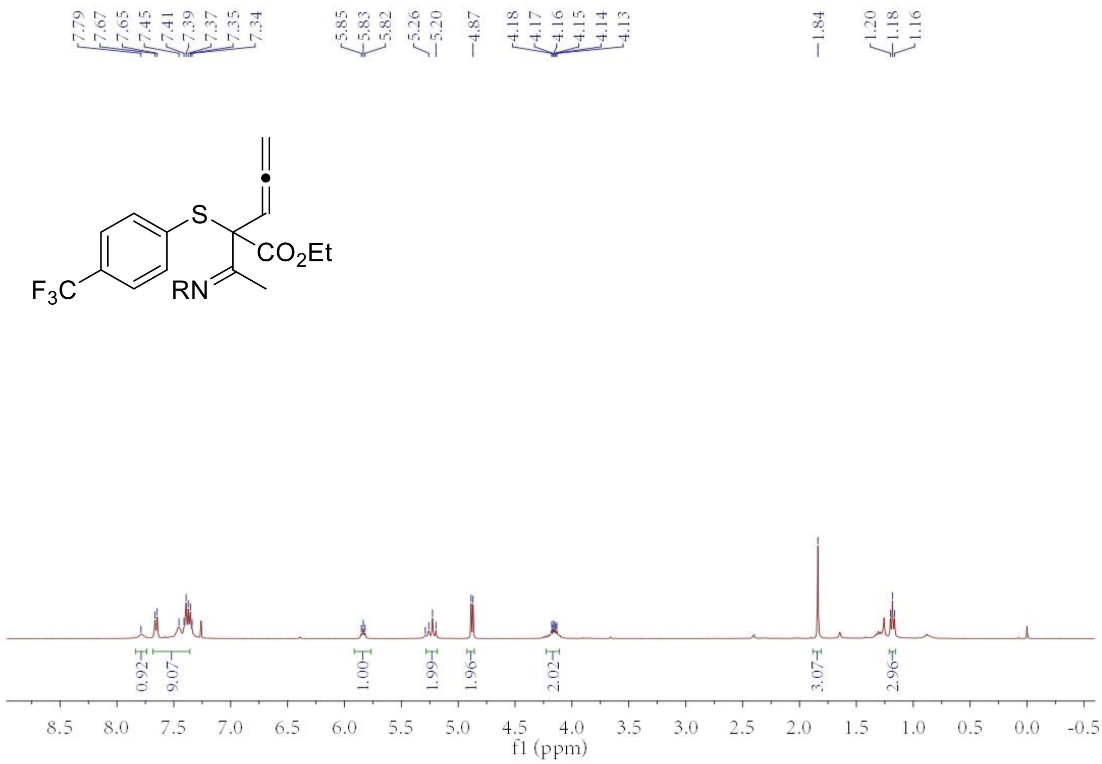
170.16
153.81
148.68
133.17
128.59
128.39
118.50
117.80
67.50
65.11
62.05
38.37
31.95
14.16
13.84
S
CO2Et
BnO2CHNN
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

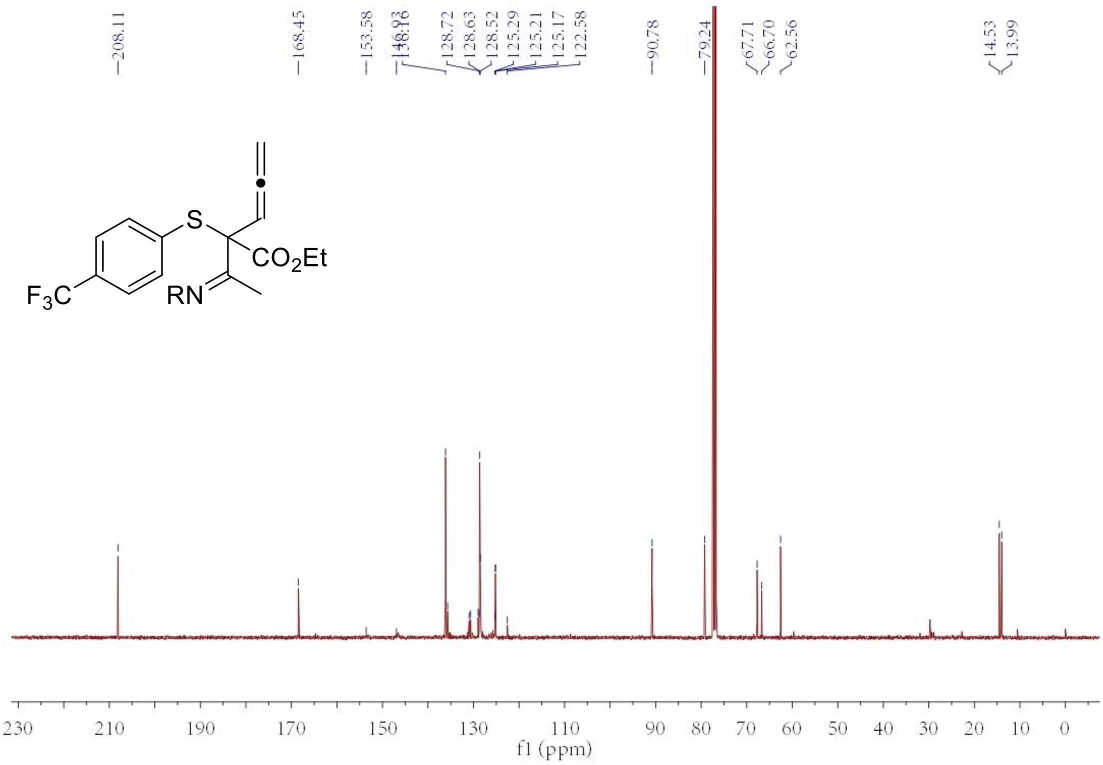
3z，R=NHCO$_2$Bn

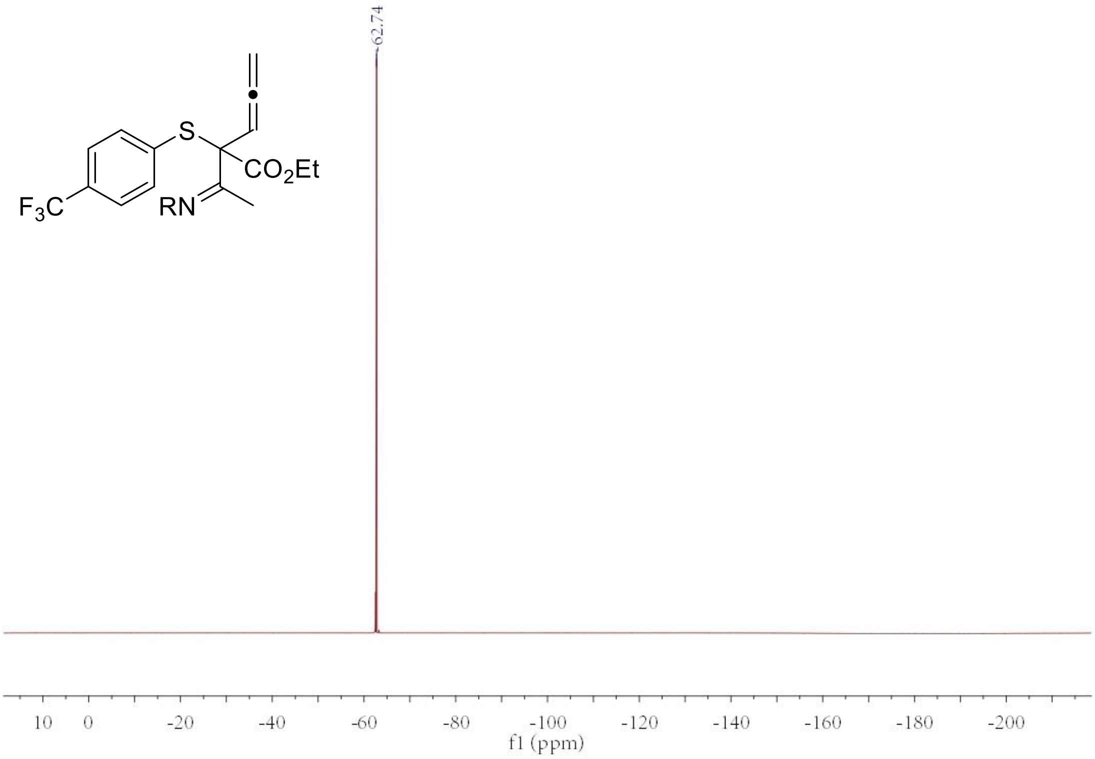




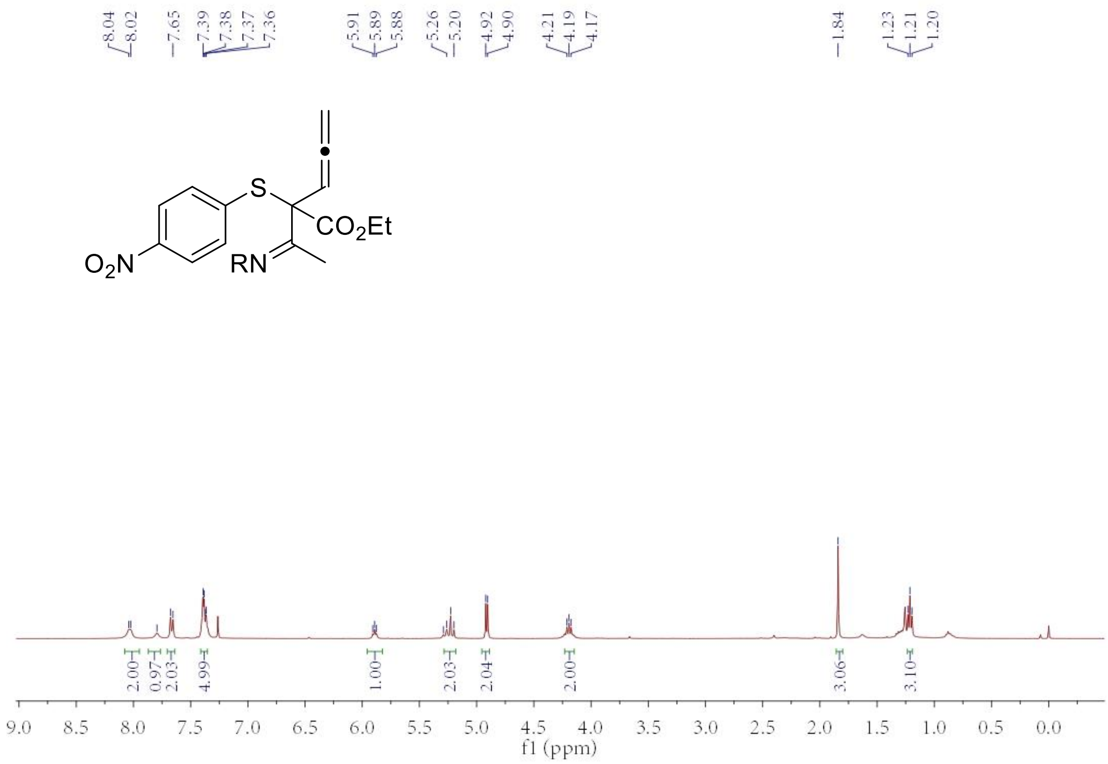
3a′，R=NHCO₂Bn



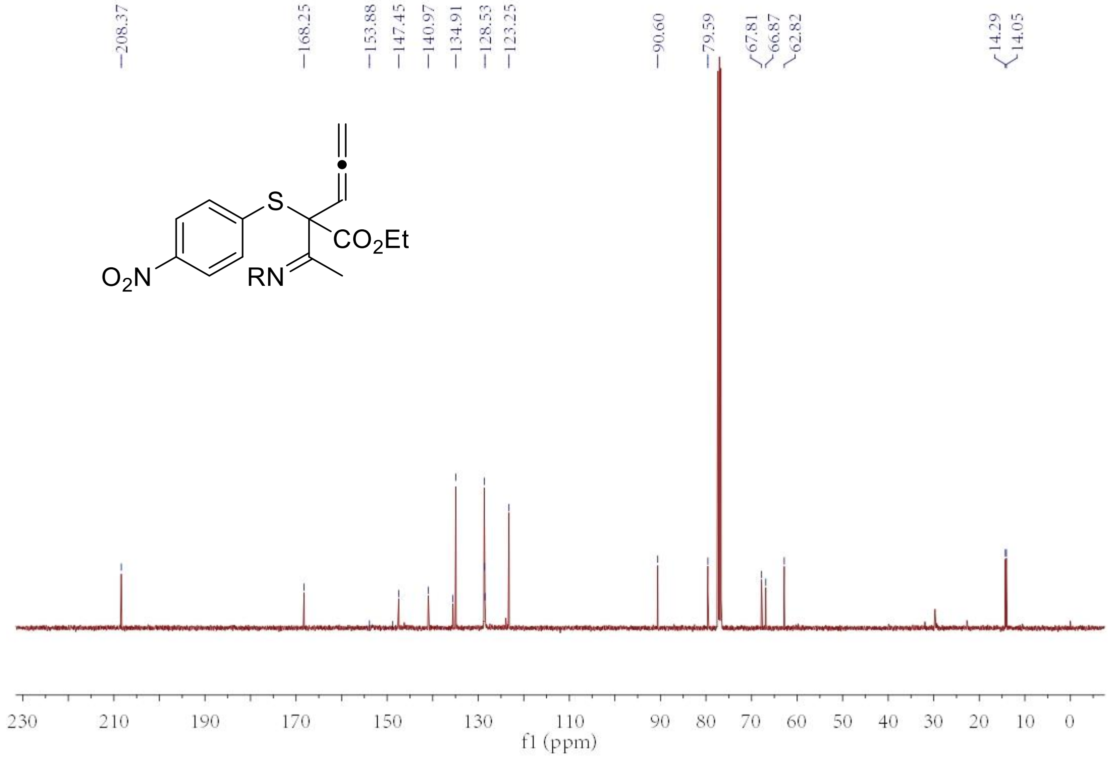



-62.74
S
CO2Et
F3C
RN
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

3b′，R=NHCO₂Bn

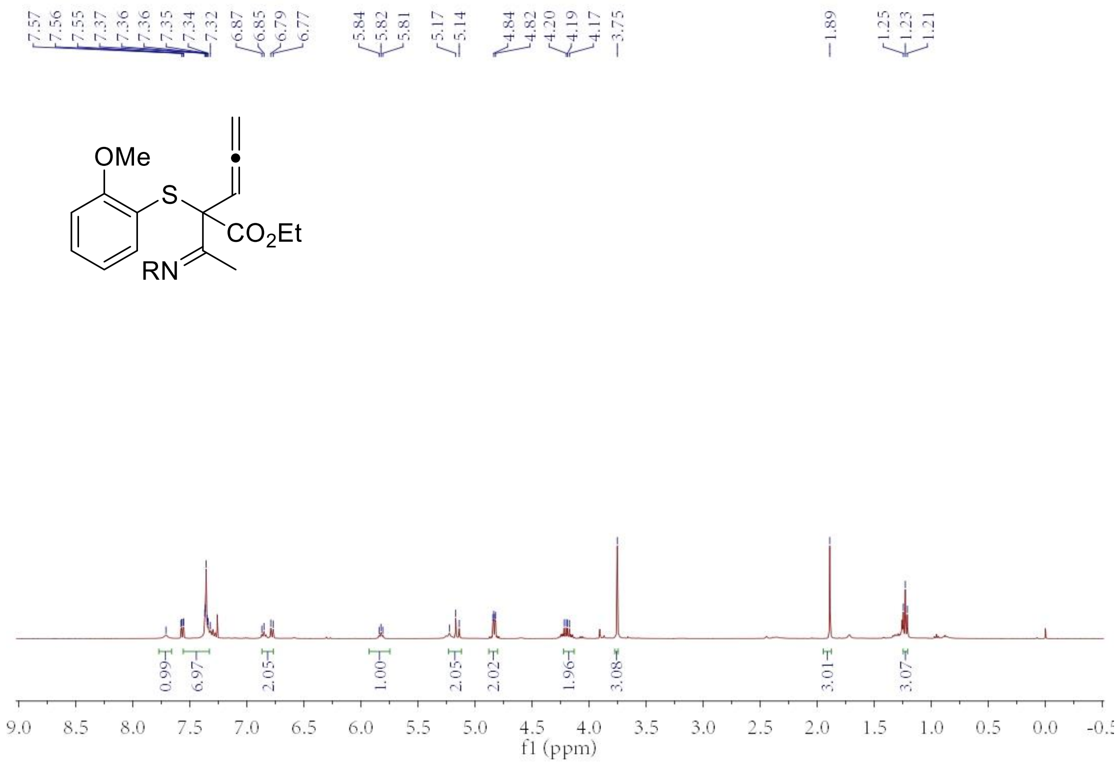


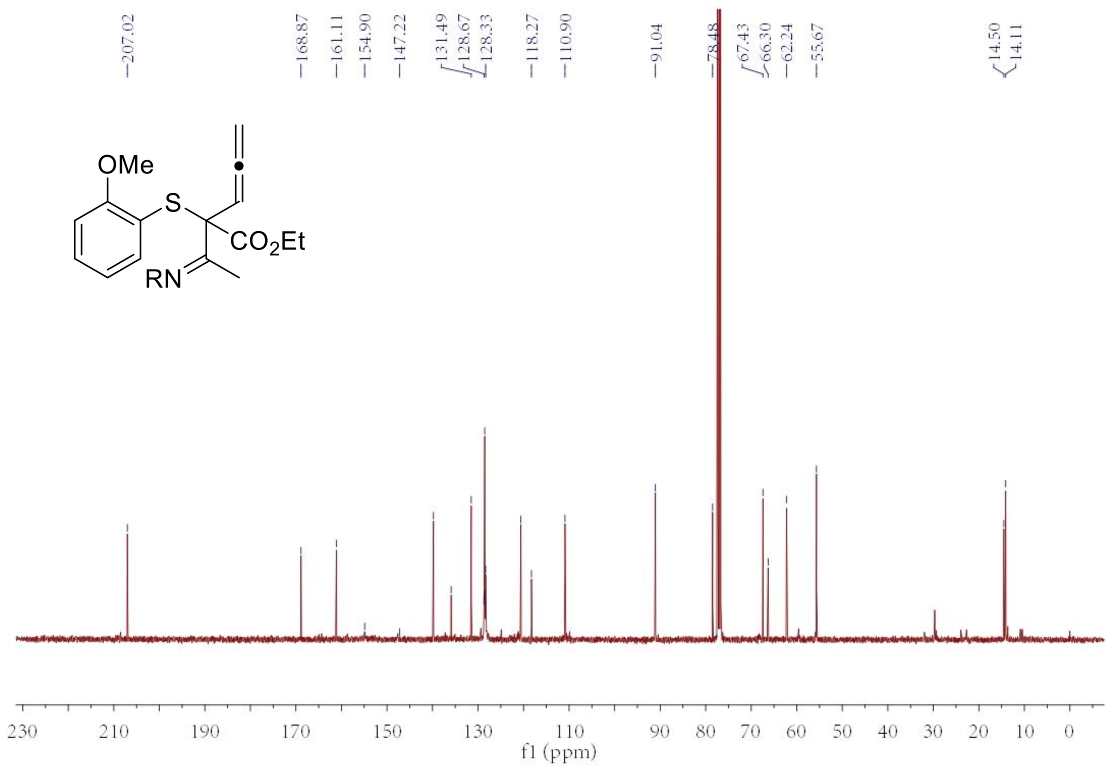
8.04
8.02
7.65
7.39
7.38
7.37
7.36
5.91
5.89
5.88
5.26
5.20
4.92
4.90
4.21
4.19
4.17
1.84
1.23
1.21
1.20
S
CO2Et
O2N
RN
2.00
0.97
2.03
4.99
1.00
2.03
2.04
2.00
3.06
3.10
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



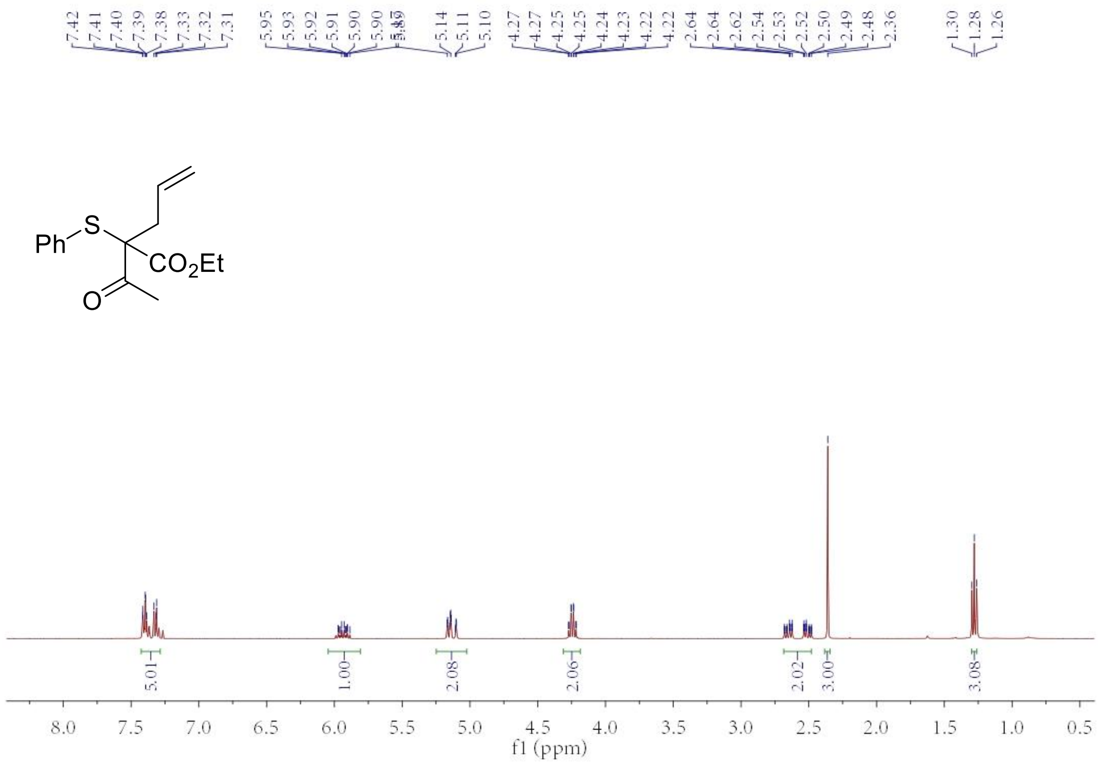
208.37
168.25
153.88
147.45
140.97
134.91
128.53
123.25
90.60
79.59
67.81
66.87
62.82
14.29
14.05
S
CO2Et
O2N
RN
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

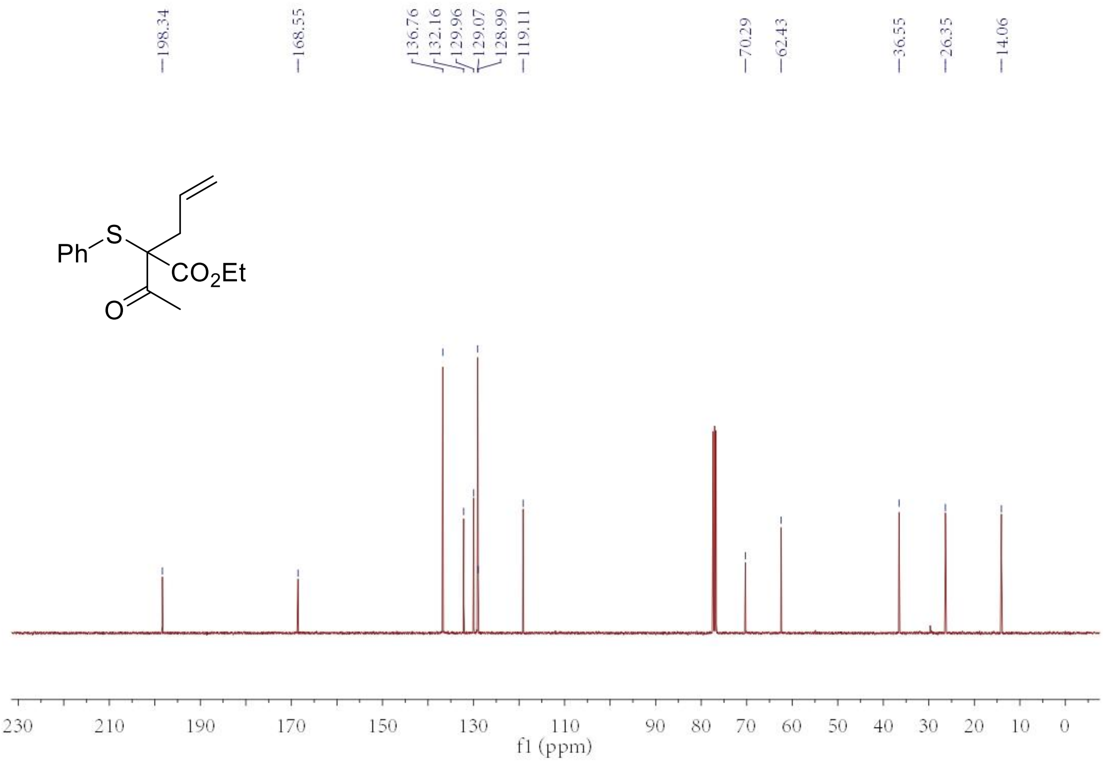
3c′，R=NHCO$_2$Bn


7.57 7.56 7.55 7.37 7.36 7.36 7.35 7.34 7.32 6.87 6.85 6.79 6.77 5.84 5.82 5.81 5.17 5.14 4.84 4.82 4.20 4.19 4.17 3.75 1.89 1.25 1.23 1.21
OMe
S
CO2Et
RN
0.99 6.97 2.05 1.00 2.05 2.02 1.96 3.08 3.01 3.07
f1 (ppm)

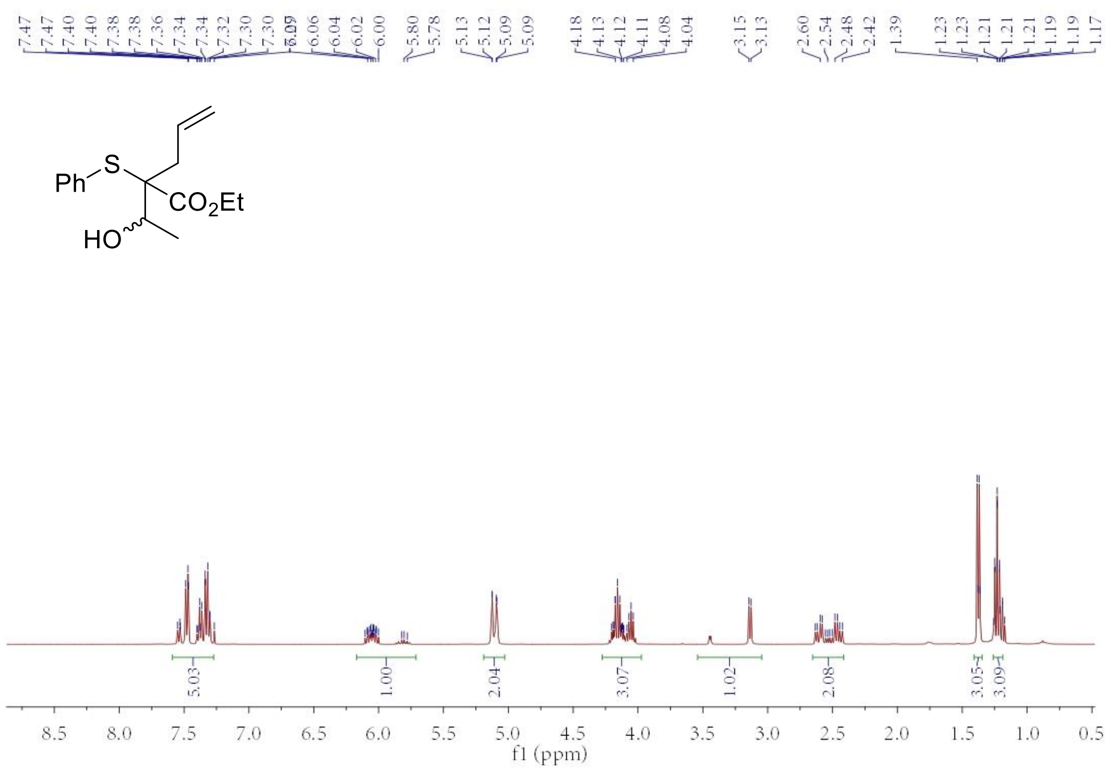

207.02 168.87 161.11 154.90 147.22 131.49 128.67 128.33 118.27 110.90 91.04 78.48 67.43 66.30 62.24 55.67 14.50 14.11
OMe
S
CO2Et
RN
f1 (ppm)

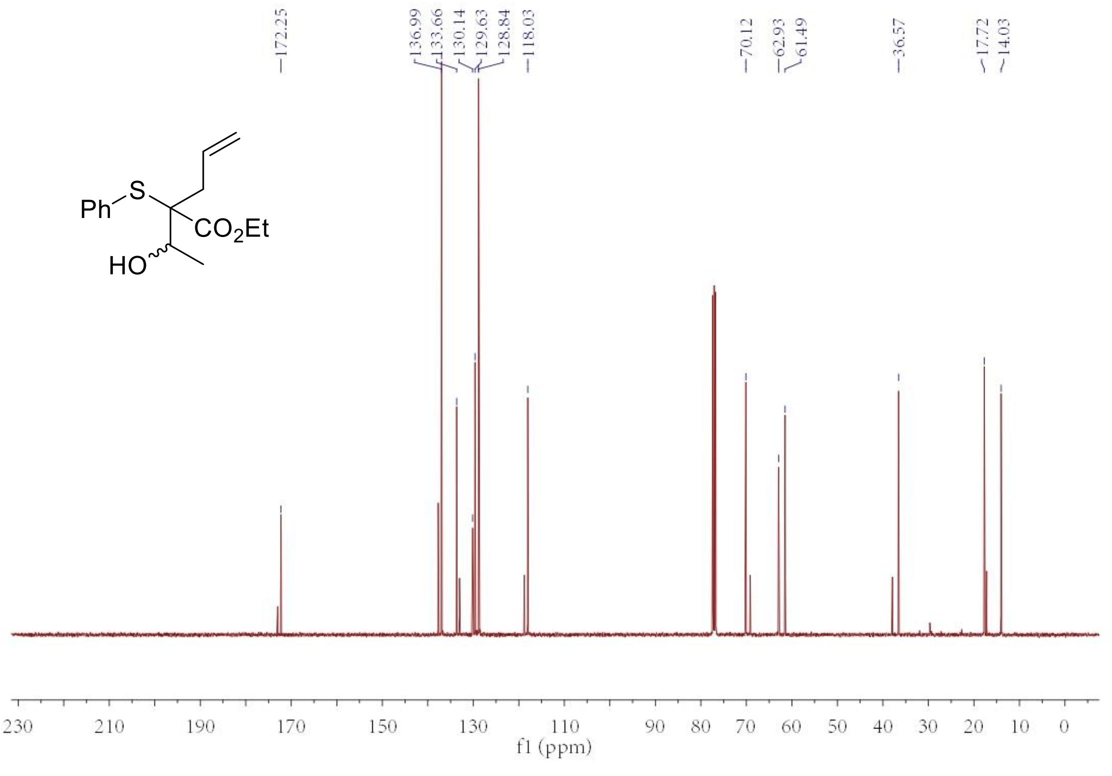
4





5





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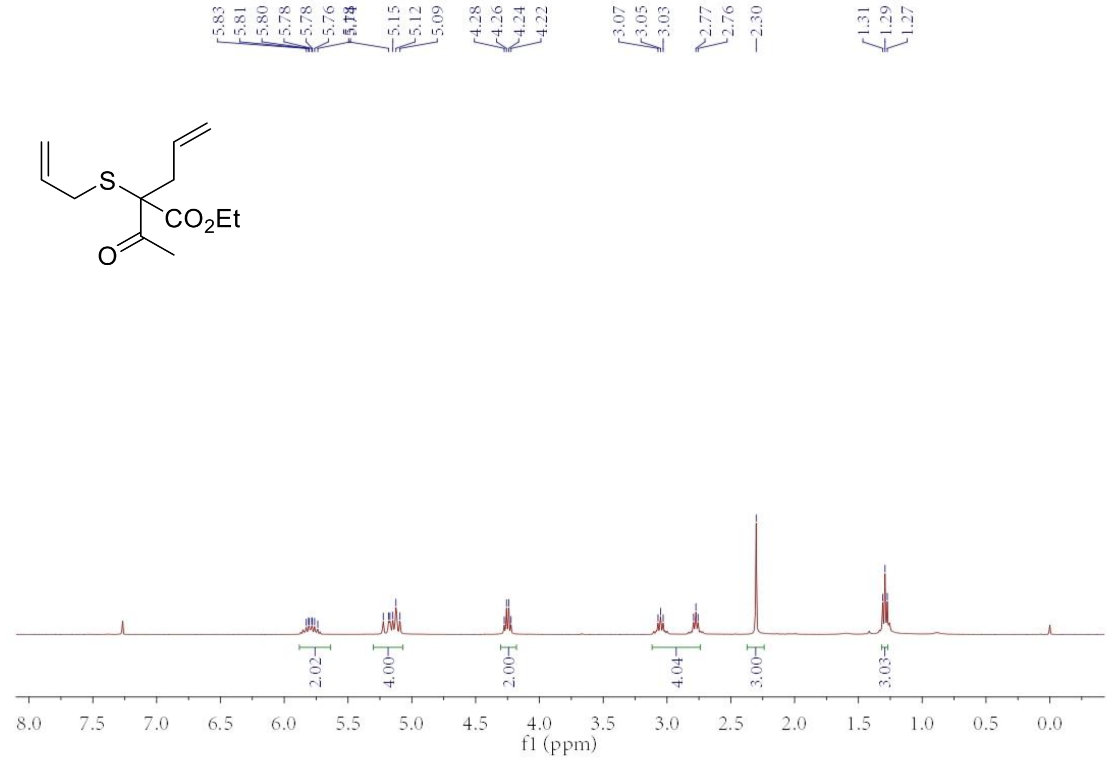
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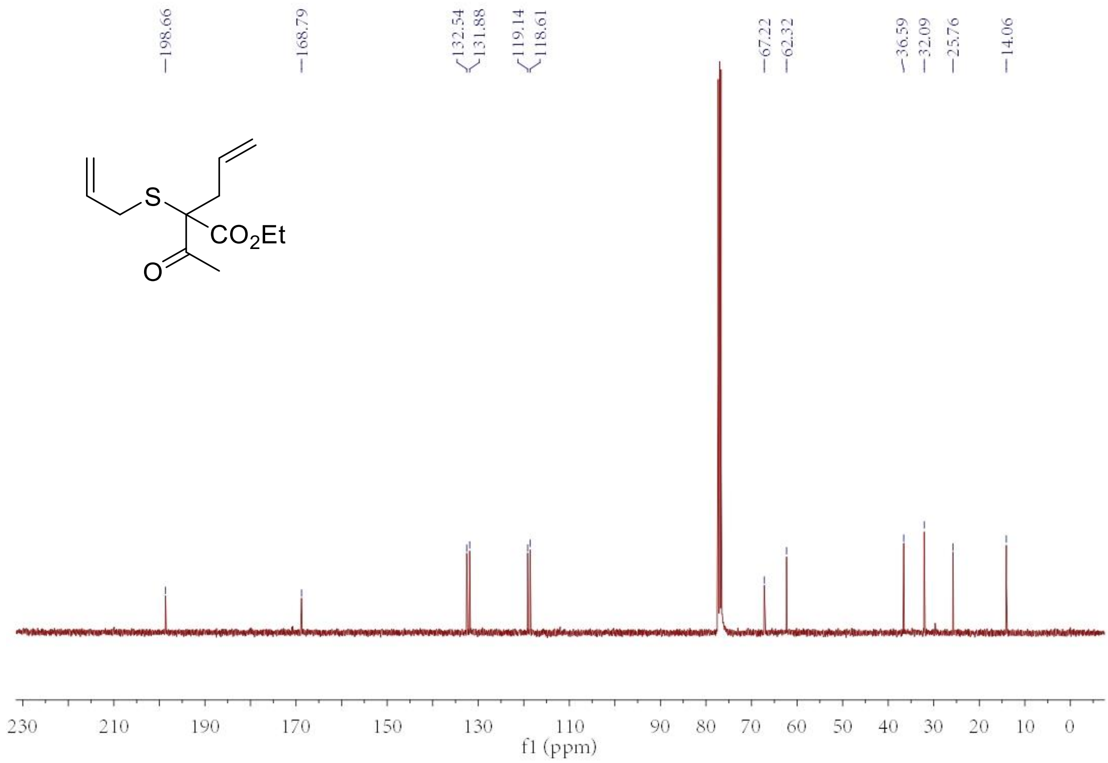
5.81
5.80
5.78
5.78
5.76
5.15
5.12
5.09
4.28
4.26
4.24
4.22
3.07
3.05
3.03
2.77
2.76
2.30
1.31
1.29
1.27
S
CO_2Et
O
2.02
4.00
2.00
4.04
3.00
3.03
f1 (ppm)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168.79
132.54
131.88
119.14
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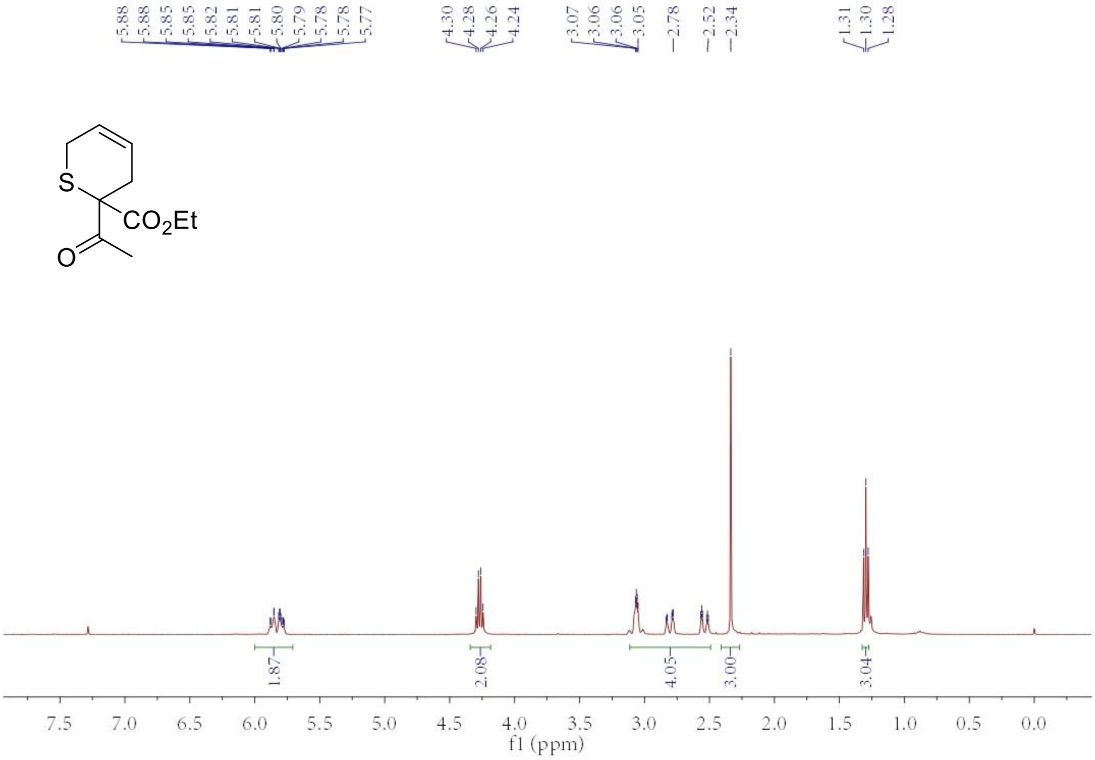
67.22
62.32
36.59
32.09
25.76
14.06
S
CO_2Et
O
f1 (ppm)

7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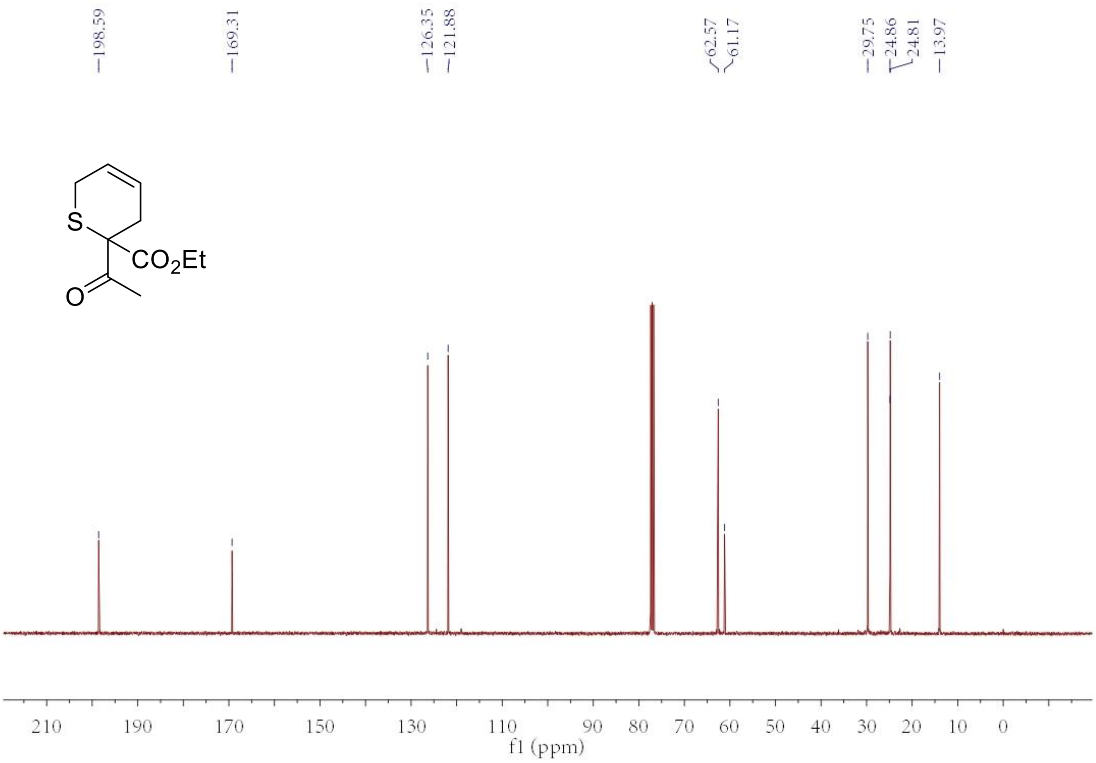
5.88
5.85
5.85
5.82
5.81
5.81
5.80
5.79
5.78
5.78
5.77
4.30
4.28
4.26
4.24
3.07
3.06
3.06
3.05
2.78
2.52
2.34
1.31
1.30
1.28
S
CO2Et
O
1.87
2.08
4.05
3.00
3.04
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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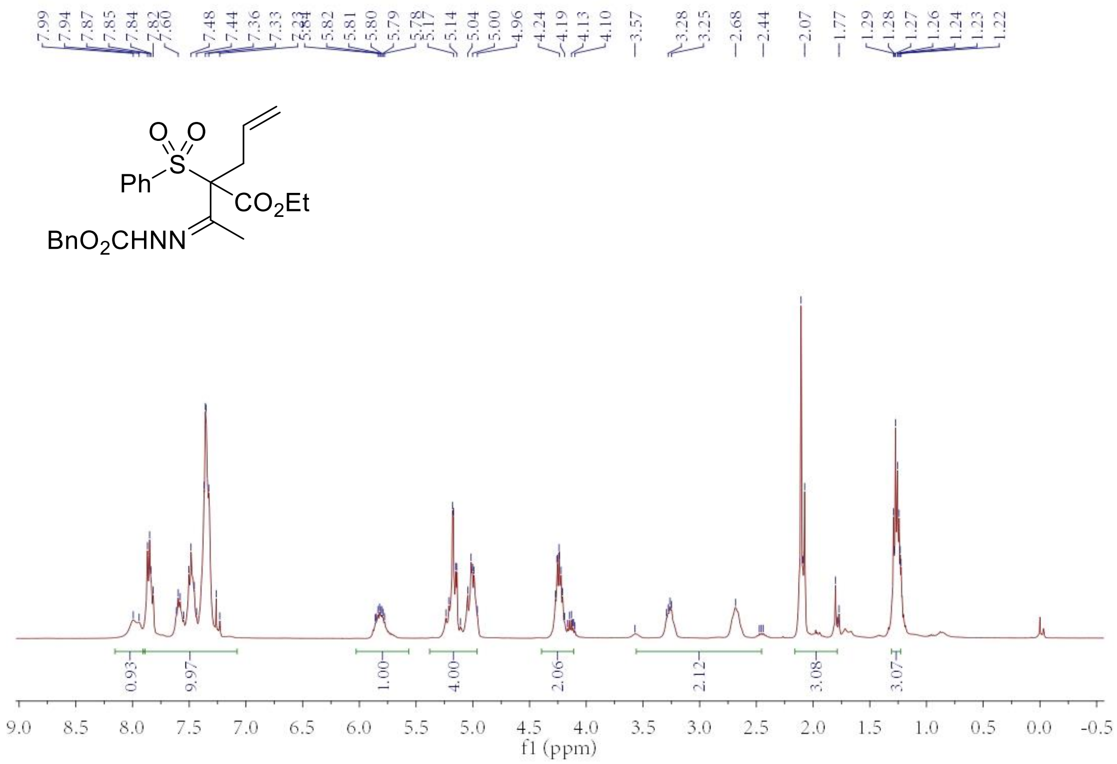
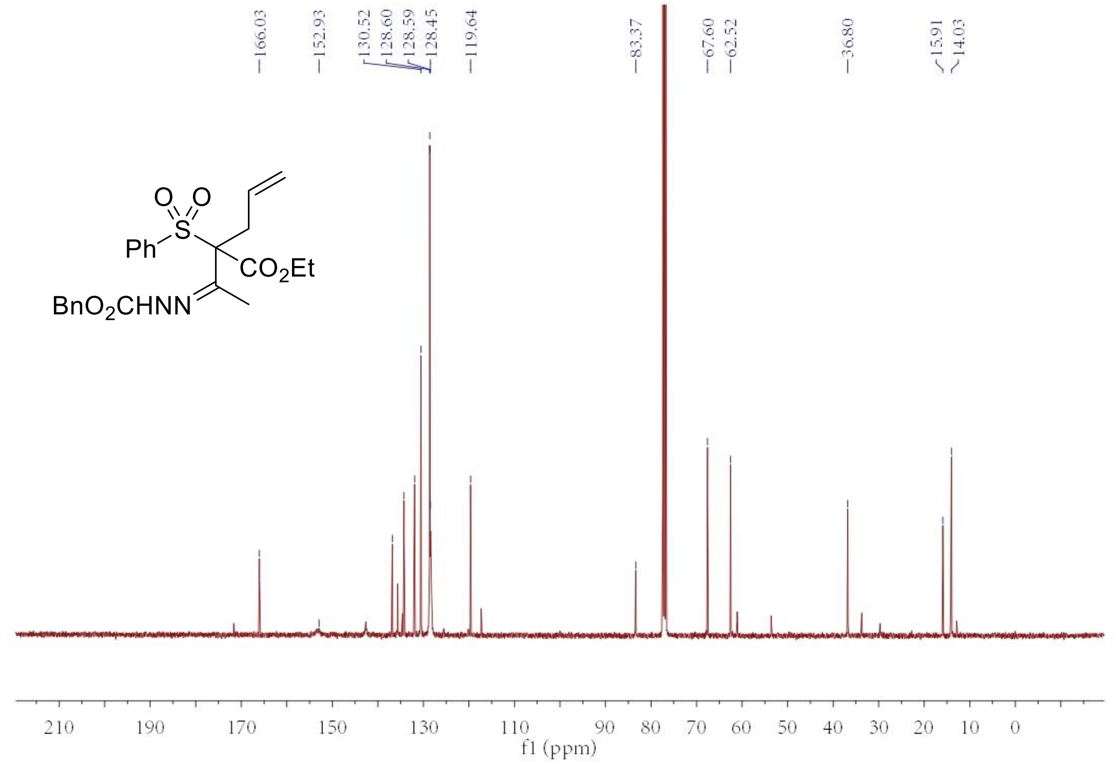
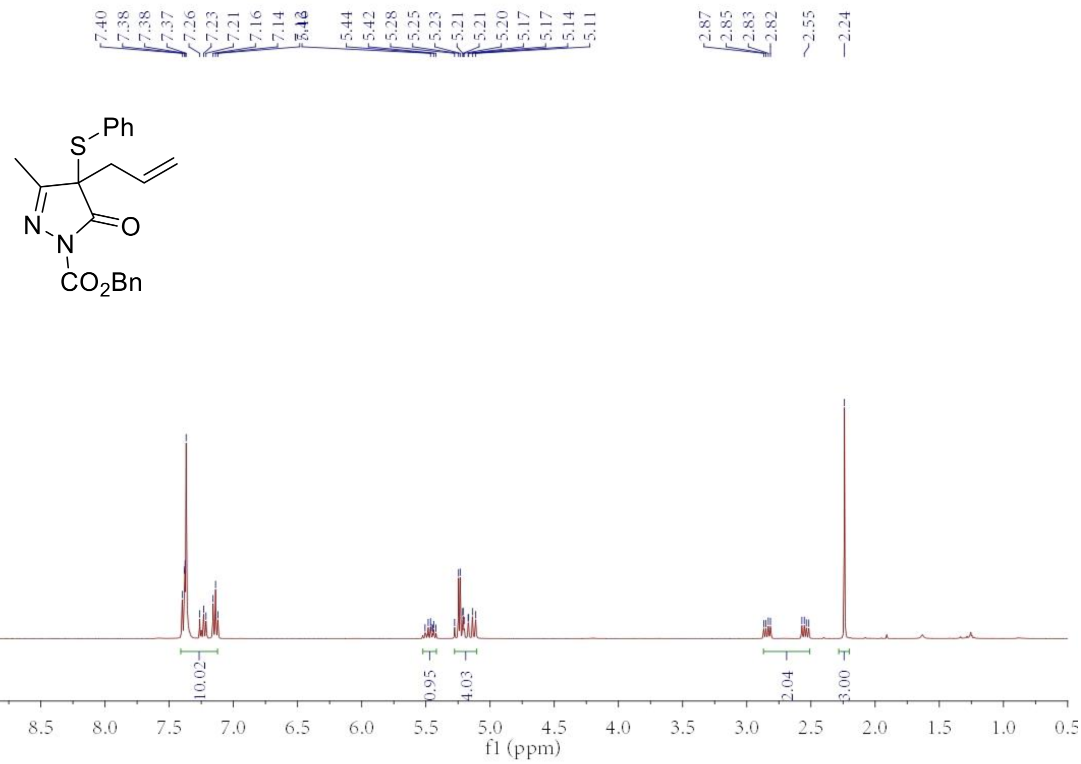
169.31
126.35
121.88
62.57
61.17
29.75
24.86
24.81
13.97
S
CO2Et
O
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

8

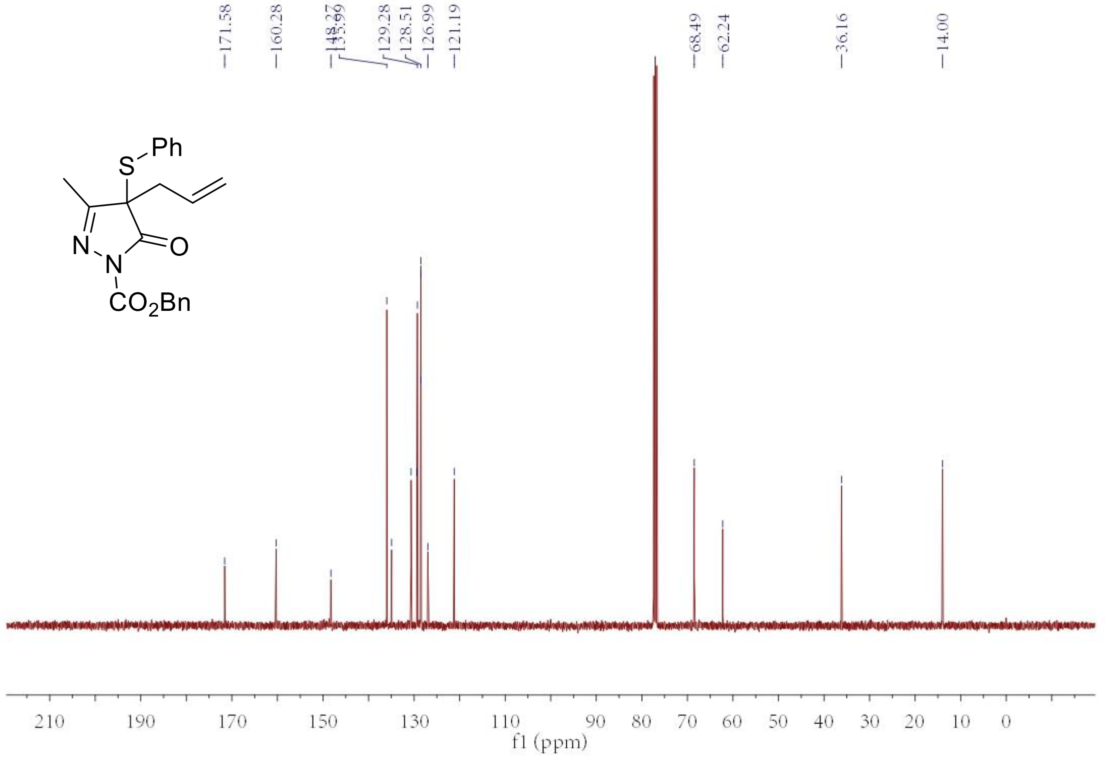




9



7.40
7.38
7.38
7.37
7.26
7.23
7.21
7.16
7.14
5.44
5.42
5.28
5.25
5.23
5.21
5.21
5.20
5.17
5.14
5.11
2.87
2.85
2.83
2.82
2.55
2.24
S
Ph
N
N
O
CO2Bn
10.02
0.95
4.03
2.04
3.00
f1 (ppm)



171.58
160.28
129.28
128.51
126.99
121.19
68.49
62.24
36.16
14.00
S
Ph
N
N
O
CO2Bn
f1 (ppm)

6. References

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[3] Wagh, Sachin Bhausaheb; Singh, Rahulkumar Rajmani; Sahani, Rajkumar Lalji; Liu, R.-S. *Org. Lett.* **2019**, *21*, 8, 2755–2758.