Supporting Information

For

Rhodium(III)-catalyzed and MeOH-involved regioselective *mono*-alkenylation of *N*-arylureas with acrylates

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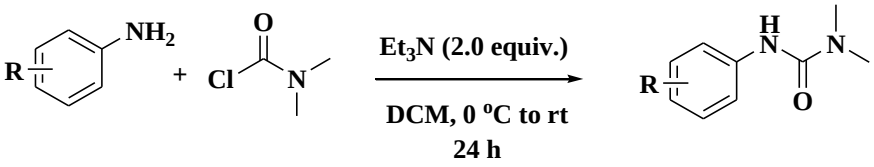
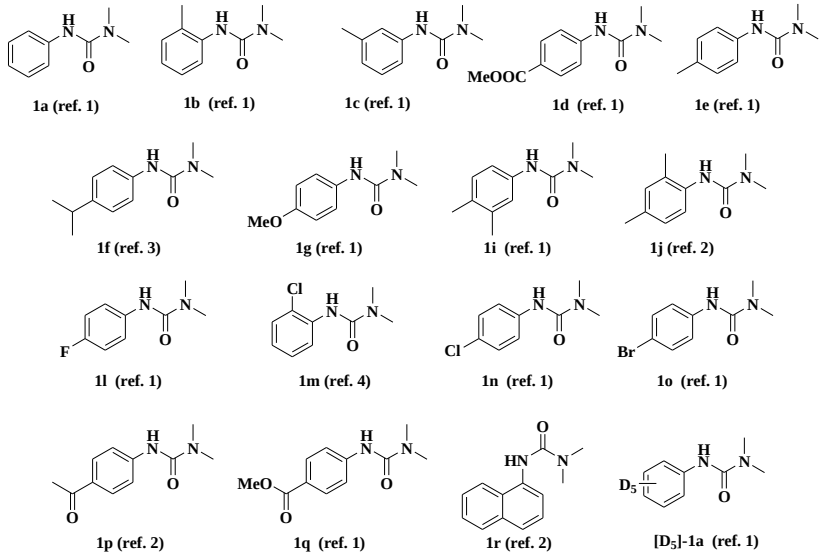
General information:

All commercial materials were used as received unless otherwise noted. ^{1}H and ^{13}C NMR spectra were recorded with Varian Mercury-Plus 400 NMR and Varian Mercury- Plus 500 NMR spectrometer as solutions (^{1}H 400 or 500 MHz; ^{13}C 100 or 125MHz) in $CDCl_3$ or CD_3OD or DMSO-d_6. Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to $CHCl_3$ (δ = 7.26 ppm; δ = 77.16 ppm) or CD_3OD (δ = 3.31 ppm; δ = 49.0 ppm) or DMSO-d_6 (δ = 5.50 ppm; δ = 39.52 ppm)as an internal standard. All coupling constants are absolute values and are expressed in Hz. The description of the signals include: s = singlet, d = doublet, t = triplet, m = multiplet and dd = doublet of doublets, at = apparent triplet, br = broad. High-resolution mass spectra were measured on an agilent TOF-G6230B mass spectrometer. Thin-layer chromatographies were done on pre-coated silica gel 60 F254 plates (Merck). Silica gel 60H (200-300 mesh) manufactured by Qingdao Haiyang Chemical Group Co. (China) was used for general chromatography.

General Experimental Procedure for the Synthesis of *N*-aryl urea:[1-4]



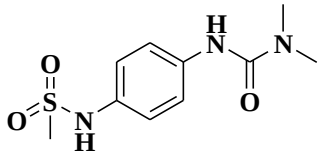
Aniline derivatives (1.00g, 10 mmol) and triethylamine (2.9 mL, 20 mmol) were dissolved in anhydrous CH_2Cl_2 (10 mL) in a 50 mL three neck round bottom flask followed by drop wise addition of chloroformic acid dimethyl amide (1.8 mL, 20 mmol) using a syringe. The reaction mixture was stirred overnight. After completion, the reaction was diluted with CH_2Cl_2 (30 mL), washed by sat. $NaHCO_3$ (30 mL), 2N HCl (30 mL), brine (20 mL) and dried over $MgSO_4$. The organic solvent was removed by evaporation. Purification by recrystallization in diethylehter afforded the corresponding *N*-arylurea as an off-white solid. The spectroscopic values are identical that of with literature.[1-4]



List of known *N*-aryl urea substrates

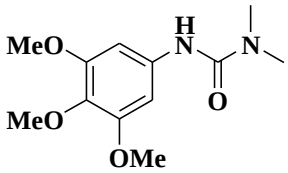
SPECTRAL DATA:

N-(4-(3,3-dimethylureido)phenyl)methanesulfonamide (1h)



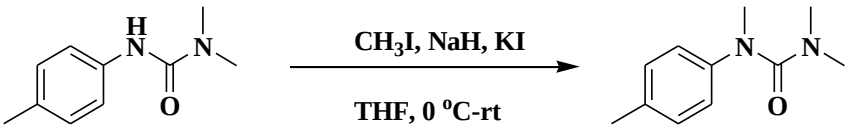
This compound was obtained as a white solid in 68% yield. **mp** : 208-209 ^{o}C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.39 (s, 1H), 8.27 (s, 1H), 7.41 (d, J = 8.8 Hz, 2H), 7.08 (d, J = 8.8 Hz, 2H), 2.91 (s, 6H), 2.90 (s, 3H); **^{13}C NMR** (100 MHz, $^{d6-}$DMSO) δ 155.8, 137.6, 131.9, 121.6, 120.6, 38.8, 36.2.; **HRMS** (ESI) calcd for 258.0907 ([M+H]$^{+}$), **found** 258.0899 ([M+H]$^{+}$).

1,1-dimethyl-3-(3,4,5-trimethoxyphenyl)urea (1k)



This compound was obtained as a white solid in 75% yield. **mp** : 141-142 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.69 (s,2H), 6.29 (s, 1H), 3.83 (s, 6H), 3.79 (s, 3H), 3.03(s, 6H); **^{13}C NMR** (100 MHz,$CDCl_3$) δ 155.9, 153.3, 135.5, 133.8, 97.6, 61.1, 56.2, 36.6; **HRMS** (ESI) calcd for 255.1339 ([M+H]$^{+}$), **found** 255.1339 ([M+H]$^{+}$).

Synthesis of 1,1,3-trimethyl-3-phenylurea

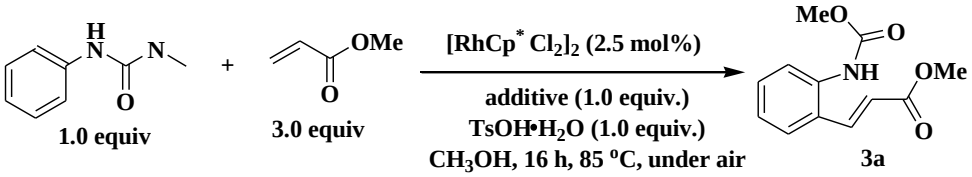


1e **1s**

To a solution of 1,1-dimethyl-3-*p*-tolylurea (0.5g, 2.81 mmol) in dry THF (30 mL) was added NaH (60 % in mineral oil, 0.11g, 4.22 mmol) in several portions, and then iodomethane (0.35 mL, 5.62 mmol) was added at 0 ℃. The reaction mixture was warmed to room temperature and stirred for further 5 hours. After complete consumption of the starting material monitored by TLC, water was added to the reaction mixture. The mixture was extracted with diethyl ether (3 x 40 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. Solvent was then removed under reduced pressure and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate = 4/1) to afford 1,1,3-trimethyl-3-*p*-tolylurea **1s** (oil, quantitatively). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.10 (d, J = 8.5 Hz, 2H), 6.93 (d, J = 8.4 Hz, 2H), 3.16 (s, 3H), 2.66 (s, 6H), 2.30 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.2, 144.6, 134.0, 130.1, 123.9, 39.9, 38.1, 20.9.; **HRMS** (ESI) calcd for 179.1184 ([M+H]$^{+}$), **found** 179.1180 ([M+H]$^{+}$).

Optimization of reaction conditions:

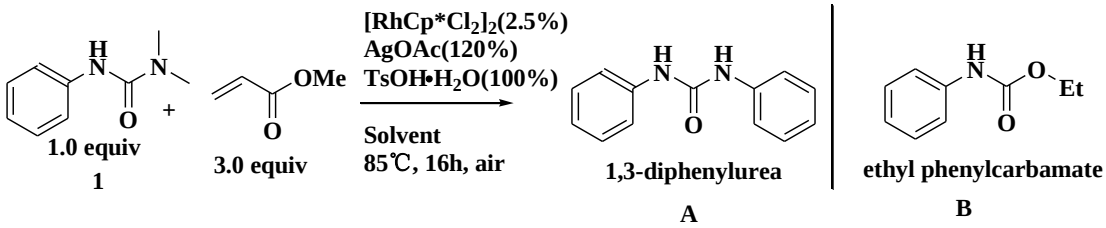
Table S1. Screening of additives



entry	additive	Yield (%)[a,b]
1	$Cu(OAc)_2$	N.R.
2	$AgSbF_6$	45
3	Ag_2CO_3	N.R.
4	AgOTf	56
5	$AgBF_4$	N.R.

[a] 0.3 M. [b] isolated yield.

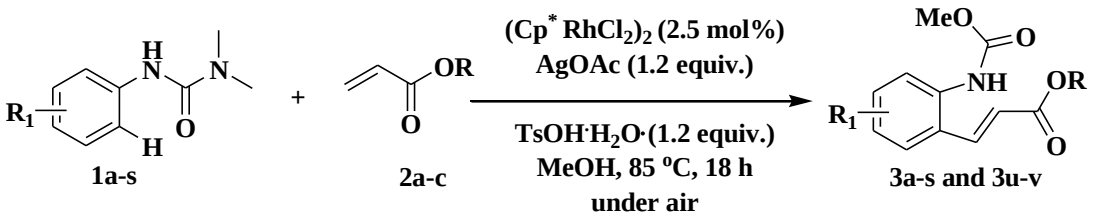
Table S2. Screening of solvents



entry	Solvent	Yield%[a,b]
1	DCE	(A) 90%
2	MeCN	(A) 55%
3	THF	(A) 86%
4	EtOH	(B) 92%

[a] 0.3 M. [b] isolated yield.

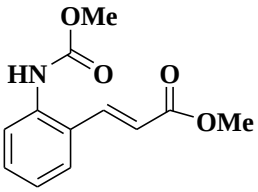
General procedure for the Rh(III)-catalyzed alkenylation reaction:



The mixture of $[Cp^*RhCl_2]_2$ (2.4 mg, 0.00375mmol, 0.025 equiv), substrate **1a-q** (0.15 mmol, 1.0 equiv), **2a-c** (0.45 mmol, 3.0 equiv), AgOAc (0.030g, 0.18mmol, 1.2equiv), $TsOH{\cdot}H_2O$ (0.029g, 0.15mmol) and MeOH (0.5 mL) were stirred at 85 ℃ for 18 h under air. The resulting mixture was cooled to room temperature, silica gel column directly to give the corresponding desired products **3a-q** and **3t-u**.

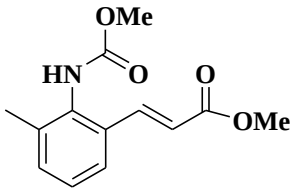
Characterizations of products:

(*E*)-methyl 3-(2-(methoxycarbonylamino)phenyl)acrylate (3a)



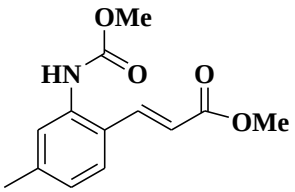
R_f = 0.6, 30% EtOAc in Hex; Compound **3a** was obtained as a white solid in 95% yield. **mp** : 122.5-123.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, J = 15.8 Hz, 1H), 7.74 (br, 1H), 7.51 (d, J = 7.4 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H), 6.78 (br, 1H), 6.38 (d, J = 15.8 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 154.6, 139.5, 136.2, 131.0, 127.3, 126.8, 125.1, 123.6, 120.4, 52.7, 52.0; **HRMS** (ESI) calcd for 236.0923 ($[M+H]^+$), **found** 236.0925 ($[M+H]^+$).

(*E*)-methyl 3-(2-(methoxycarbonylamino)-3-methylphenyl)acrylate (3b)



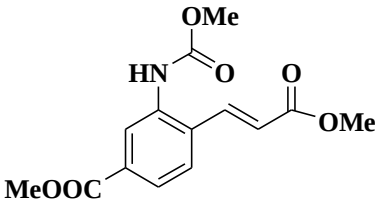
R_f = 0.6, 30% EtOAc in Hex; Compound **3b** was obtained as a white solid in 83% yield. **mp** : 133-134 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (d, J = 16.0 Hz, 1H), 7.82 (d, J = 7.7 Hz, 1H), 7.65 – 7.52 (m, 2H), 6.74 (d, J = 16.0 Hz, 1H), 6.59 (br, 1H), 4.13 (s, 6H), 2.62 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.4, 140.8, 136.8, 134.2, 132.7, 127.7, 127.0, 124.9, 119.8, 53.0, 51.9, 18.4; **HRMS** (ESI) calcd for 250.1079 ($[M+H]^+$), **found** 250.1073 ($[M+H]^+$).

(*E*)-methyl 3-(2-(methoxycarbonylamino)-4-methylphenyl)acrylate (3c)



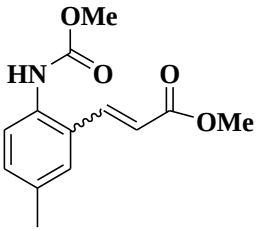
R_f = 0.6, 30% EtOAc in Hex; Compound **3c** was obtained as a white solid in 96% yield. **mp** : 149-150 ^{o}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, J = 15.8 Hz, 1H), 7.58 (br, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.00 (d, J = 8.0 Hz, 1H), 6.62 (s, 1H), 6.36 (d, J = 15.8 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 2.36 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.4, 154.6, 141.8, 139.3, 136.0, 127.3, 126.2, 123.9, 119.4, 52.8, 51.9, 21.7; **HRMS** (ESI) calcd for 250.1079 ($[M+H]^+$), **found** 250.1075 ($[M+H]^+$).

(E)-methyl 4-(3-methoxy-3-oxoprop-1-enyl)-3-(methoxycarbonyl)benzoate (**3d**)



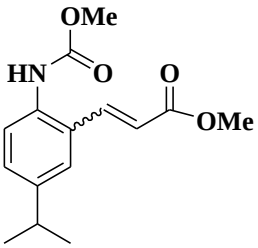
R_f = 0.5, 50% EtOAc in Hex; Compound **3d** was obtained as a white solid in 83% yield. **mp** : 168-169 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.86 - 7.79 (m, 2H), 7.56 (d, J = 8.2 Hz, 1H), 7.04 -7.02 (m, 1H), 6.45 (d, J = 15.9 Hz, 1H), 3.91 (s, 3H), 3.81 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 166.1, 154.5, 138.5, 136.2, 132.1, 131.0, 127.2, 125.9, 124.8, 122.2, 52.8, 52.4, 52.0; **HRMS** (ESI) calcd for 294.0978 ($[M+H]^+$), **found** 294.0972 ($[M+H]^+$).

(*E*)-methyl 3-(2-(methoxycarbonylamino)-5-methylphenyl)acrylate (3e)



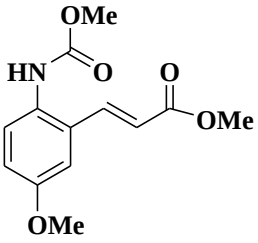
R_f = 0.6, 30% EtOAc in Hex; *E*:*Z*=96:4; Compound **3e** was obtained as a white solid in 94% yield. **mp** : 122-123 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, J = 15.9 Hz, 1H), 7.58 (br, 1H), 7.35 (s, 1H), 7.21 (d, J = 8.3 Hz, 1H), 6.67 (s, 1H), 6.40 (d, J = 15.9 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 2.33 (d, J = 12.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 154.8, 139.7, 135.1, 133.7, 131.9, 127.6, 124.1, 120.1, 52.7, 51.9, 21.0; **HRMS** (ESI) calcd for 250.1079 ($[M+H]^+$), **found** 250.1080 ($[M+H]^+$).

(*E*)-methyl 3-(4-isopropyl-2-(methoxycarbonylamino)phenyl)acrylate (3f)



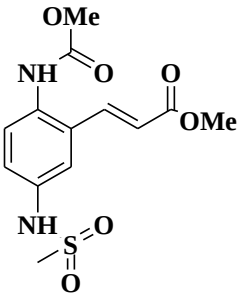
R_f = 0.6, 30% EtOAc in Hex; *E*:*Z*=97:3; Compound **3f** was obtained as a white solid in 93% yield. **mp** : 116-117 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 15.9 Hz, 1H), 7.59 (br, 1H), 7.36 (d, *J* = 1.8 Hz, 1H), 7.31-7.19 (m, 1H), 6.70 (br, 1H), 6.40 (d, *J* = 15.9 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 2.94-2.84(m, 1H), 1.24 (s, 3H), 1.23 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 154.9, 146.0, 139.9, 134.0, 129.3, 127.2, 125.1, 124.1, 112.0, 52.7, 51.9, 33.8, 24.0; **HRMS** (ESI) calcd for 278.1392 ($[M+H]^+$), **found** 278.1397 ($[M+H]^+$).

(*E*)-methyl 3-(5-methoxy-2-(methoxycarbonylamino)phenyl)acrylate (3g)



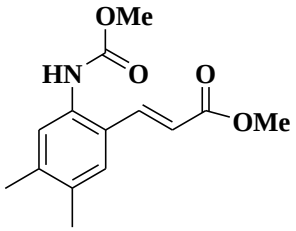
R_f = 0.4, 30% EtOAc in Hex; Compound **3g** was obtained as a white solid in 98% yield. **mp** : 137-138 ^{o}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 15.8 Hz, 1H), 7.50 (br, 1H), 7.04 (s, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.45 (br, 1H), 6.38 (d, *J* = 15.9 Hz, 1H), 4.06 - 3.45 (m, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.2, 157.3, 155.2, 139.6, 129.3, 126.5, 120.5, 117.1, 111.5, 55.7, 52.8, 52.0; **HRMS** (ESI) calcd for 266.1028 ($[M+H]^+$), **found** 266.1026 ($[M+H]^+$).

(*E*)-methyl 3-(2-(methoxycarbonylamino)-5-(methylsulfonamido)phenyl)acrylate (3h)



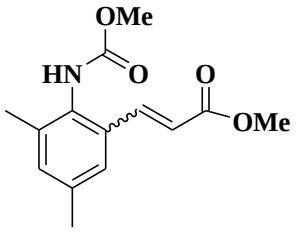
R_f = 0.3, 50% EtOAc in Hex; Compound **3h** was obtained as a white solid in 86% yield. **mp** : 159-160 ^{o}C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.34 (s, 1H), 7.77 (d, *J* = 16.0 Hz, 1H), 7.48 (s, 1H), 7.34 (d, *J* = 8.8 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 1H), 6.39 (d, *J* = 16.0 Hz, 1H), 3.74 (s, 3H), 3.64 (s, 3H), 3.00 (s, 3H).**^{13}C NMR** (100 MHz, DMSO-d_6) δ 166.4, 155.1, 140.1, 136.4, 132.8, 129.5, 127.6, 122.9, 118.8, 117.7, 51.9, 51.6; **HRMS** (ESI) calcd for 329.0807 ($[M+H]^+$), **found** 329.0802 ($[M+H]^+$).

(*E*)-methyl 3-(2-(methoxycarbonylamino)-4,5-dimethylphenyl)acrylate (3i)



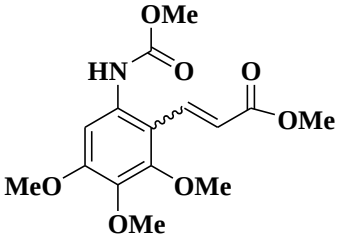
R_f = 0.6, 30% EtOAc in Hex; Compound **3i** was obtained as a white solid in 92% yield. **mp** : 131-132 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, J = 16.0 Hz, 1H), 7.28 (s, 1H), 7.10 (s, 1H), 6.38 (d, J = 16.0 Hz, 1H), 6.19 (br, 1H), 3.79 (s, 6H), 2.32 (s, 3H), 2.24 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 140.9, 137.5, 136.7, 133.6, 132.4, 131.7, 125.3, 119.5, 52.9, 51.8, 21.1, 18.2; **HRMS** (ESI) calcd for 264.1236 ($[M+H]^+$), **found** 264.1237 ($[M+H]^+$).

(*E*)-methyl 3-(2-(methoxycarbonylamino)-3,5-dimethylphenyl)acrylate (3j)



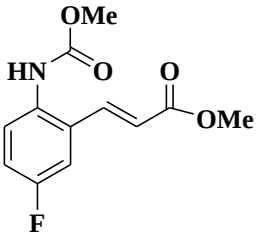
R_f = 0.6, 30% EtOAc in Hex; *E*:*Z*=96:4; Compound **3j** was obtained as a white solid in 86% yield. **mp** : 118.5-119.5 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, J = 15.8 Hz, 1H), 7.44 (s, 1H), 7.29 (s, 1H), 6.65 (br, 1H), 6.34 (d, J = 15.8 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 2.25 (s, 3H), 2.22 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 154.9, 140.5, 139.5, 133.9, 128.0, 118.8, 52.7, 51.8, 20.0, 19.4; **HRMS** (ESI) calcd for 264.1236 ($[M+H]^+$), **found** 264.1240 ($[M+H]^+$).

(*E*)-methyl 3-(2,3,4-trimethoxy-6-(methoxycarbonylamino)phenyl)acrylate (3k)



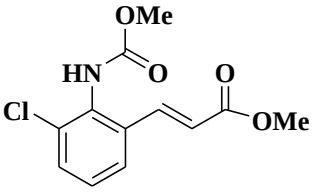
R_f = 0.4, 50% EtOAc in Hex; *E*/*Z*= 89:11; Compound **3k** was obtained as a white solid in 85% yield. **mp** : 141-142 ^{o}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69 (d, J = 16.3 Hz, 1H), 7.30 (br, 1H), 6.68 (br, 1H), 6.53 (d, J = 16.3 Hz, 1H), 3.95-3.62 (m, 15H). **^{13}C NMR** (125MHz, $CDCl_3$) δ 168.0, 155.0, 154.5, 153.6, 153.2, 136.5, 132.8, 121.3, 61.1, 61.0, 56.1, 52.7, 51.9; **HRMS** (ESI) calcd for 326.1240 ($[M+H]^+$), **found** 326.1237 ($[M+H]^+$).

(*E*)-methyl 3-(5-fluoro-2-(methoxycarbonylamino)phenyl)acrylate (3l)



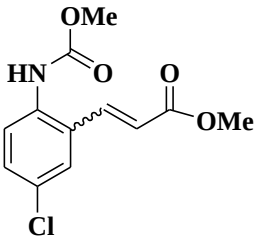
R_f = 0.5, 30% EtOAc in Hex; Compound **3l** was obtained as a white solid in 89% yield. **mp** : 157-158 ^oC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 (d, J = 15.8 Hz, 1H), 7.66 (br, 1H), 7.22 (dd, J = 9.1, 2.9 Hz, 1H), 7.14-7.04 (m, 1H), 6.54 (br, 1H), 6.38 (d, J = 15.8 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.7, 159.9 (d, J = 243.7 Hz), 154.6, 138.2, 132.0 (d, J = 1.9 Hz), 126.0, 121.5, 117.8 (d, J = 22.7 Hz), 113.3 (d, J = 23.4 Hz), 52.7, 52.0; **HRMS** (ESI) calcd for 254.0829 ($[M+H]^+$), **found** 254.0821 ($[M+H]^+$).

(*E*)-methyl 3-(3-chloro-2-(methoxycarbonylamino)phenyl)acrylate (3m)



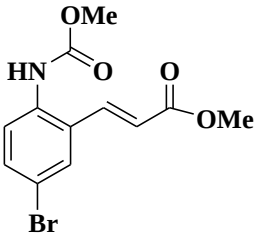
R_f = 0.4, 30% EtOAc in Hex; Compound **3m** was obtained as a white solid in 80% yield. **mp** : 163-164 ^oC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (d, J = 16.0 Hz, 1H), 7.55 (d, J = 7.8 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.29-7.16 (m, 1H), 6.53-6.30 (d, J = 16.0 Hz, 1H; br, 1H), 3.80 (s, 3H), 3.78 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.1, 155.1, 140.3, 134.2, 133.2, 131.0, 128.0, 125.8, 120.4, 53.3, 52.0; **HRMS** (ESI) calcd for 270.0533, 272.0504 ($[M+H]^+$), **found** 270.0535, 272.0514 ($[M+H]^+$).

(*E*)-methyl 3-(5-chloro-2-(methoxycarbonylamino)phenyl)acrylate (3n)



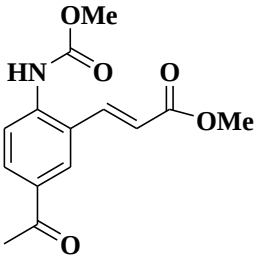
R_f = 0.5, 30% EtOAc in Hex; *E*/*Z*= 93:7; Compound **3n** was obtained as a white solid in 92% yield. **mp** : 147-148 ^oC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81-7.66 (m, 2H), 7.47 (d, J = 2.4 Hz, 1H), 7.34 (dd, J = 8.8, 2.4 Hz, 1H), 6.68 (br, 1H), 6.39 (d, J = 15.8 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H). **^{13}C NMR** (100MHz, $CDCl_3$) δ 166.9, 154.4, 138.1, 134.7, 130.9, 130.4, 127.1, 121.9, 52.9, 52.2; **HRMS** (ESI) calcd for 270.0533, 272.0504 ($[M+H]^+$), **found** 270.0552, 272.0525 ($[M+H]^+$).

(*E*)-methyl 3-(5-bromo-2-(methoxycarbonylamino)phenyl)acrylate (3o)



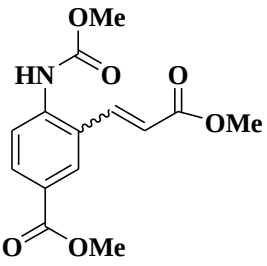
R_f = 0.3, 30% EtOAc in Hex; Compound **3o** was obtained as a white solid in 90% yield. **mp** : 166-167^{o}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73 (d, J = 15.8 Hz, 1H), 7.68 (br, 1H), 7.61 (d, J = 2.1 Hz, 1H), 7.47 (dd, J = 8.7, 2.1 Hz, 1H), 6.71 (br, 1H), 6.38 (d, J = 15.8 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.8, 154.3, 138.0, 135.2, 133.7, 130.0, 128.1, 124.7, 121.9, 118.0, 52.9, 52.1; **HRMS** (ESI) calcd for 314.0028, 316.0007([M+H]$^+$), **found** 314.0050, 316.0029 ([M+H]$^+$).

(*E*)-methyl 3-(5-acetyl-2-(methoxycarbonylamino)phenyl)acrylate (3p)



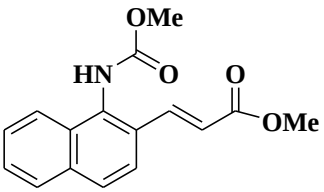
R_f = 0.3, 40% EtOAc in Hex; Compound **3p** was obtained as a white solid in 72% yield. **mp** : 150-151 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11-8.09 (m, 2H), 7.96 (d, J = 8.6 Hz, 1H), 7.79 (d, J = 15.7 Hz, 1H), 6.91 (br, 1H), 6.48 (d, J = 15.7 Hz, 1H), 3.83 (s, 3H), 3.83 (s, 3H), 2.59 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.6, 166.8, 153.7, 140.3, 138.3, 132.9, 131.2, 128.0, 124.8, 122.6, 120.9, 53.0, 52.2, 26.6; **HRMS** (ESI) calcd for 278.1028 ([M+H]$^+$), **found** 278.1026 ([M+H]$^+$).

(*E*)-methyl 3-(3-methoxy-3-oxoprop-1-enyl)-4-(methoxycarbonylamino)benzoate (3q)



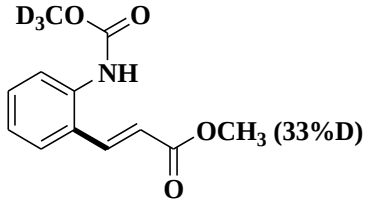
R_f = 0.5, 50% EtOAc in Hex; *E*/*Z*= 89:11; Compound **3q** was obtained as a white solid in 68% yield. **mp** : 171-172 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 8.11-7.98 (m, 2H), 7.79 (d, J = 15.7 Hz, 1H), 6.89 (br, 1H), 6.48 (d, J = 15.7 Hz, 1H), 3.92 (s, 3H), 3.83 (s, 3H), 3.82 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 166.3, 153.8, 140.2, 138.2, 132.2, 129.3, 125.9, 124.8, 122.4,121.0, 53.0, 52.4, 52.2; **HRMS** (ESI) calcd for 294.0978 ([M+H]$^+$), **found** 294.0980 ([M+H]$^+$).

(*E*)-methyl 3-(1-(methoxycarbonylamino)naphthalen-2-yl)acrylate (3r)



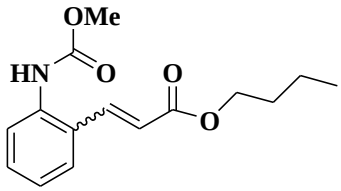
R_f = 0.6, 30% EtOAc in Hex; Compound **3r** was obtained as a white solid in 90% yield. **mp** :183-184 ^oC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09 (d, J = 16.0 Hz, 1H), 7.99 (d, J = 7.0 Hz, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.80 (d, J = 8.7 Hz, 1H), 7.70 (d, J = 8.7 Hz, 1H), 7.61- 7.46 (m, 2H), 6.66 (br, 1H), 6.53 (d, J = 16.0 Hz, 1H), 3.82 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.4, 155.8 140.3, 135.0, 132.1, 131.1, 129.7, 128.4, 127.6, 123.4, 123.1, 120.1, 53.2, 52.0; **HRMS** (ESI) calcd for 286.1079 ($[M+H]^+$), **found** 286.1068 ($[M+H]^+$).

(*E*)-methyl 3-(2-(d_3-methoxycarbonylamino)phenyl)acrylate (3t)



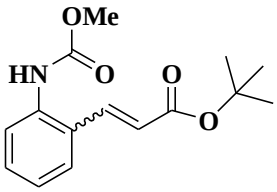
R_f = 0.6, 30% EtOAc in Hex; Compound **3t** was obtained as a white solid in 85% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, J = 15.8 Hz, 1H), 7.74 (br, 1H), 7.52-7.50 (m, 1H), 7.40-7.36 (m, 1H), 7.15 (t, J = 7.8 Hz, 1H), 6.74 (br, 1H), 6.39 (d, J = 15.8 Hz, 1H), 3.80 (s, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.2, 154.6, 139.5, 136.2, 131.1, 127.4, 126.7, 125.1, 123.6, 120.6, 52.0 .

(*E*)-butyl 3-(2-(methoxycarbonylamino)phenyl)acrylate (3u)



R_f = 0.6, 30% EtOAc in Hex; *E*/*Z*= 97:3; Compound **3u** was obtained as a white solid in 91% yield. **mp** : 84-85 ^oC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, J = 15.8 Hz, 1H), 7.76 (br, 1H), 7.52 (d, J = 7.8 Hz, 1H), 7.38 (t, J = 7.8 Hz, 1H), 7.15 (t, J = 7.8 Hz, 1H), 6.72 (br, 1H), 6.39 (d, J = 15.8 Hz, 1H), 4.21 (t, J = 6.7 Hz, 2H), 3.79 (s, 3H), 1.72 – 1.65 (m, 2H), 1.48-1.38 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 154.6, 139.2, 136.2, 131.0, 129.2, 127.4, 125.1, 123.4, 121.1, 64.8, 52.8, 30.9, 19.3, 13.8; **HRMS** (ESI) calcd for 278.1392 ($[M+H]^+$), **found** 278.1388 ($[M+H]^+$).

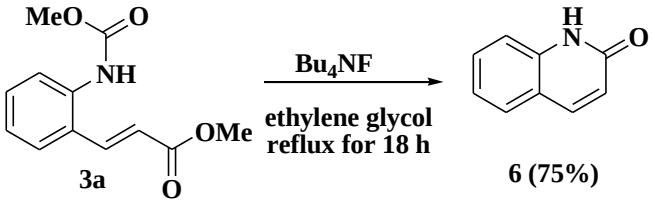
(*E*)-tert-butyl 3-(2-(methoxycarbonylamino)phenyl)acrylate (3v)



R_f = 0.6, 30% EtOAc in Hex; *E*/*Z*= 97:3; Compound **3v** was obtained as an oily liquid in 88%

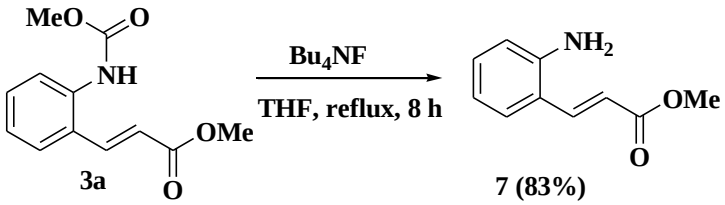
yield.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (br, 1H), 7.73 (d, J = 15.8 Hz, 1H), 7.50 (d, J = 7.8 Hz, 1H), 7.36 (t, J = 7.8 Hz, 1H), 7.13 (t, J = 7.8 Hz, 1H), 6.70 (br, 1H), 6.32 (d, J = 15.8 Hz, 1H), 3.78 (s,3H), 1.53 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.1, 154.5, 138.1, 136.1, 130.7, 129.1, 128.9, 127. 4, 125.0, 123.1, 81.0, 52.7, 28.3; **HRMS** (ESI) calcd for 278.1392 ($[M+H]^+$), **found** 278.1395 ($[M+H]^+$).

Synthesis of quinolin-2(1*H*)-one (6)



A mixture of compound 3a (0.047g, 0.2 mmol), TBAF (0.26g, 1mmol) and ethylene glycol (0.5 ml) ware added into a 5 mL flask, The resulting mixture was refluxed for 15 h. After cooling, the mixture was poured into H_2O (10 mL) and the solid was filtered and washed with Et_2O and CH_2Cl_2 to give **6** (0.022g, 75%) as a brown solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.71 (br, 1H), 7.82 (d, J = 9.5 Hz, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.50-7.54 (m, 1H), 7.39 (d, J = 8.2 Hz, 1H), 7.21-7.24 (m, 1H), 6.71 (d, J = 9.5 Hz, 1H).

Synthesis of (*E*)-methyl 3-(2-aminophenyl)acrylate (7)



A solution of **3a** (0.047g, 0.2 mmol) and TBAF (1mL, 1 M in THF, 1mmol) in dry THF (1 mL) was stirred under argon . The reaction mixture was refluxed for 8 h. After cooling, a solution of NH_4Cl satd. (5 mL) was added and the aqueous phase was extracted with EtOAc (3 x10 mL). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate = 3/1) to afford Compound **7** as a brown solid (0.029g, 83%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, J = 15.8 Hz, 1H), 7.38 (dd, J = 7.8, 1.2 Hz, 1H), 7.22 – 7.10 (m, 1H), 6.77 (t, J = 7.5 Hz, 1H), 6.70 (d, J = 8.1 Hz, 1H), 6.36 (d, J = 15.8 Hz, 1H), 3.98 (s, 2H), 3.80 (s, 3H).

Crystallographic data:

X-ray structural analysis was performed on a Bruker SMART CCD diffractometer at 296 K. Single crystal of **3a** was obtained by recrystallization in ethyl acetate and petroleum (1 : 3) at room temperature.

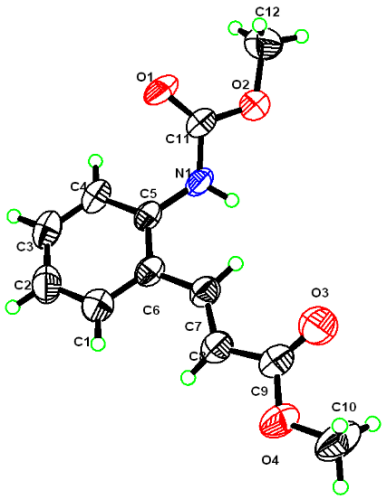


Figure 1. ORTEP plot of compound **3a**. All H atoms have been omitted for clarity.

Table 1. Crystal data

$C_{12}H_{13}NO_4$	Z = 2
M_r = 235.23	F(000) = 248
Triclinic, $P\bar{1}$	D_x = 1.301 Mg m^{-3}
a = 4.9045 (4) Å	Mo $K\alpha$ radiation, λ = 0.71073 Å
b = 10.4027 (10) Å	Cell parameters from 3298 reflections
c = 12.0076 (10) Å	θ = 2.5–26.2 °
α = 83.328 (4) °	μ = 0.10 mm^{-1}
β = 80.762 (6) °	T = 296 K
γ = 89.239 (6) °	Block, colourless
V = 600.58 (9) Å^3	0.3 × 0.15 × 0.12 mm

Table 2. Data collection

Bruker APEX-II CCD diffractometer	1846 reflections with $I > 2\sigma(I)$
graphite	R_{int} = 0.030
ϕ and ω scans	θ_{max} = 27.6 °, θ_{min} = 1.7 °
Absorption correction: multi-scan	h = -6→6

SADABS2008/1 (Bruker,2008) was used for absorption correction. wR2(int) was 0.0746 before and 0.0511 after correction. The Ratio of minimum to maximum transmission is 0.8920. The λ/2 correction factor is 0.0015.	
T_{min} = 0.665, T_{max} = 0.746	k = -12→13
9835 measured reflections	l = -15→15
2736 independent reflections	

Table 3. Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.081	H-atom parameters constrained
$wR(F^2)$ = 0.277	$w = 1/[\sigma^2(F_o^2) + (0.1194P)^2 + 0.6842P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.07	$(\Delta/\sigma)_{max} < 0.001$
2736 reflections	$\Delta\rangle_{max}$ = 0.32 e Å^{-3}
156 parameters	$\Delta\rangle_{min}$ = -0.27 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table4. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
O1	-0.3954 (5)	0.7593 (3)	0.0093 (3)	0.0729 (9)

O2	-0.0091 (5)	0.8689 (3)	-0.0691 (2)	0.0596 (7)
O3	0.5430 (8)	0.8853 (3)	0.3312 (3)	0.0954 (12)
O4	0.6530 (6)	0.7522 (3)	0.4748 (2)	0.0703 (8)
N1	0.0174 (5)	0.7134 (3)	0.0687 (2)	0.0465 (7)
H1	0.1831	0.7424	0.0627	0.056*
C1	-0.0118 (8)	0.4657 (4)	0.3178 (4)	0.0595 (9)
H1A	0.0648	0.4492	0.3840	0.071*
C2	-0.1890 (9)	0.3753 (4)	0.2915 (4)	0.0678 (11)
H2	-0.2327	0.2995	0.3401	0.081*
C3	-0.3008 (8)	0.3988 (4)	0.1920 (4)	0.0616 (10)
H3	-0.4213	0.3387	0.1744	0.074*
C4	-0.2359 (7)	0.5090 (4)	0.1197 (3)	0.0514 (9)
H4	-0.3101	0.5231	0.0528	0.062*
C5	-0.0572 (6)	0.6015 (3)	0.1460 (3)	0.0424 (7)
C6	0.0545 (6)	0.5810 (3)	0.2471 (3)	0.0451 (8)
C7	0.2291 (7)	0.6797 (3)	0.2771 (3)	0.0495 (8)
H7	0.2391	0.7589	0.2319	0.059*
C8	0.3759 (7)	0.6694 (4)	0.3618 (3)	0.0521 (8)
H8	0.3811	0.5909	0.4072	0.062*
C9	0.5286 (7)	0.7807 (4)	0.3836 (3)	0.0537 (9)
C10	0.8014 (11)	0.8568 (5)	0.5077 (5)	0.0877 (16)
H10A	0.8886	0.9096	0.4409	0.132*
H10B	0.9394	0.8220	0.5509	0.132*
H10C	0.6748	0.9085	0.5531	0.132*
C11	-0.1516 (6)	0.7781 (3)	0.0036 (3)	0.0469 (8)
C12	-0.1616 (11)	0.9469 (5)	-0.1443 (4)	0.0795 (13)
H12A	-0.0372	1.0046	-0.1963	0.119*
H12B	-0.2971	0.9964	-0.1008	0.119*
H12C	-0.2523	0.8920	-0.1861	0.119*

Table 5. Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}

O1	0.0308 (12)	0.098 (2)	0.089 (2)	-0.0045 (12)	-0.0211 (12)	0.0087 (17)
O2	0.0509 (14)	0.0609 (16)	0.0666 (16)	-0.0059 (11)	-0.0161 (12)	0.0043 (12)
O3	0.125 (3)	0.072 (2)	0.103 (3)	-0.026 (2)	-0.065 (2)	0.0022 (19)
O4	0.0698 (18)	0.084 (2)	0.0659 (17)	-0.0090 (15)	-0.0325 (14)	-0.0148 (15)
N1	0.0292 (12)	0.0595 (17)	0.0523 (16)	-0.0063 (11)	-0.0107 (11)	-0.0058 (13)
C1	0.054 (2)	0.062 (2)	0.062 (2)	-0.0057 (17)	-0.0117 (17)	-0.0035 (18)
C2	0.063 (2)	0.059 (2)	0.079 (3)	-0.0148 (18)	-0.005 (2)	-0.001 (2)
C3	0.0483 (19)	0.060 (2)	0.078 (3)	-0.0130 (16)	-0.0053 (18)	-0.0215 (19)
C4	0.0375 (16)	0.063 (2)	0.056 (2)	-0.0072 (14)	-0.0052 (14)	-0.0195 (17)
C5	0.0274 (13)	0.0506 (18)	0.0490 (17)	0.0005 (12)	-0.0013 (12)	-0.0111 (14)
C6	0.0346 (14)	0.0510 (18)	0.0506 (18)	0.0009 (13)	-0.0056 (13)	-0.0121 (14)
C7	0.0473 (17)	0.054 (2)	0.0492 (18)	-0.0054 (14)	-0.0122 (14)	-0.0092 (15)
C8	0.0455 (17)	0.059 (2)	0.054 (2)	-0.0022 (15)	-0.0109 (15)	-0.0090 (16)
C9	0.0447 (17)	0.066 (2)	0.054 (2)	0.0001 (16)	-0.0119 (15)	-0.0144 (17)
C10	0.082 (3)	0.093 (3)	0.106 (4)	0.000 (3)	-0.051 (3)	-0.039 (3)
C11	0.0365 (15)	0.057 (2)	0.0498 (18)	-0.0013 (13)	-0.0111 (13)	-0.0120 (15)
C12	0.085 (3)	0.074 (3)	0.084 (3)	-0.001 (2)	-0.036 (3)	0.006 (2)

Table 6. Geometric parameters (Å, º)

O1—C11	1.204 (4)	C3—C4	1.364 (6)
O2—C11	1.331 (4)	C4—H4	0.9300
O2—C12	1.437 (5)	C4—C5	1.405 (4)
O3—C9	1.189 (5)	C5—C6	1.404 (5)
O4—C9	1.340 (5)	C6—C7	1.458 (4)
O4—C10	1.443 (5)	C7—H7	0.9300
N1—H1	0.8600	C7—C8	1.331 (5)
N1—C5	1.415 (4)	C8—H8	0.9300
N1—C11	1.350 (4)	C8—C9	1.459 (5)
C1—H1A	0.9300	C10—H10A	0.9600
C1—C2	1.385 (6)	C10—H10B	0.9600
C1—C6	1.397 (5)	C10—H10C	0.9600
C2—H2	0.9300	C12—H12A	0.9600

C2—C3	1.389 (6)	C12—H12B	0.9600
C3—H3	0.9300	C12—H12C	0.9600
C11—O2—C12	116.5 (3)	C8—C7—C6	127.4 (4)
C9—O4—C10	116.1 (4)	C8—C7—H7	116.3
C5—N1—H1	117.5	C7—C8—H8	119.9
C11—N1—H1	117.5	C7—C8—C9	120.2 (4)
C11—N1—C5	125.0 (3)	C9—C8—H8	119.9
C2—C1—H1A	119.3	O3—C9—O4	122.2 (4)
C2—C1—C6	121.5 (4)	O3—C9—C8	126.7 (4)
C6—C1—H1A	119.3	O4—C9—C8	111.1 (3)
C1—C2—H2	120.3	O4—C10—H10A	109.5
C1—C2—C3	119.4 (4)	O4—C10—H10B	109.5
C3—C2—H2	120.3	O4—C10—H10C	109.5
C2—C3—H3	119.6	H10A—C10—H10B	109.5
C4—C3—C2	120.7 (3)	H10A—C10—H10C	109.5
C4—C3—H3	119.6	H10B—C10—H10C	109.5
C3—C4—H4	119.9	O1—C11—O2	123.9 (3)
C3—C4—C5	120.2 (3)	O1—C11—N1	126.3 (3)
C5—C4—H4	119.9	O2—C11—N1	109.8 (3)
C4—C5—N1	119.9 (3)	O2—C12—H12A	109.5
C6—C5—N1	119.9 (3)	O2—C12—H12B	109.5
C6—C5—C4	120.1 (3)	O2—C12—H12C	109.5
C1—C6—C5	118.0 (3)	H12A—C12—H12B	109.5
C1—C6—C7	121.8 (3)	H12A—C12—H12C	109.5
C5—C6—C7	120.2 (3)	H12B—C12—H12C	109.5
C6—C7—H7	116.3		
N1—C5—C6—C1	-176.3 (3)	C5—N1—C11—O2	-172.5 (3)
N1—C5—C6—C7	5.0 (4)	C5—C6—C7—C8	-171.4 (3)
C1—C2—C3—C4	0.6 (6)	C6—C1—C2—C3	0.8 (6)
C1—C6—C7—C8	10.0 (6)	C6—C7—C8—C9	-176.7 (3)

C2—C1—C6—C5	-2.0 (5)	C7—C8—C9—O3	-1.3 (6)
C2—C1—C6—C7	176.7 (4)	C7—C8—C9—O4	177.4 (3)
C2—C3—C4—C5	-0.9 (6)	C10—O4—C9—O3	1.3 (6)
C3—C4—C5—N1	177.7 (3)	C10—O4—C9—C8	-177.5 (4)
C3—C4—C5—C6	-0.3 (5)	C11—N1—C5—C4	36.2 (5)
C4—C5—C6—C1	1.7 (5)	C11—N1—C5—C6	-145.8 (3)
C4—C5—C6—C7	-177.0 (3)	C12—O2—C11—O1	-0.3 (6)
C5—N1—C11—O1	8.0 (6)	C12—O2—C11—N1	-179.7 (3)

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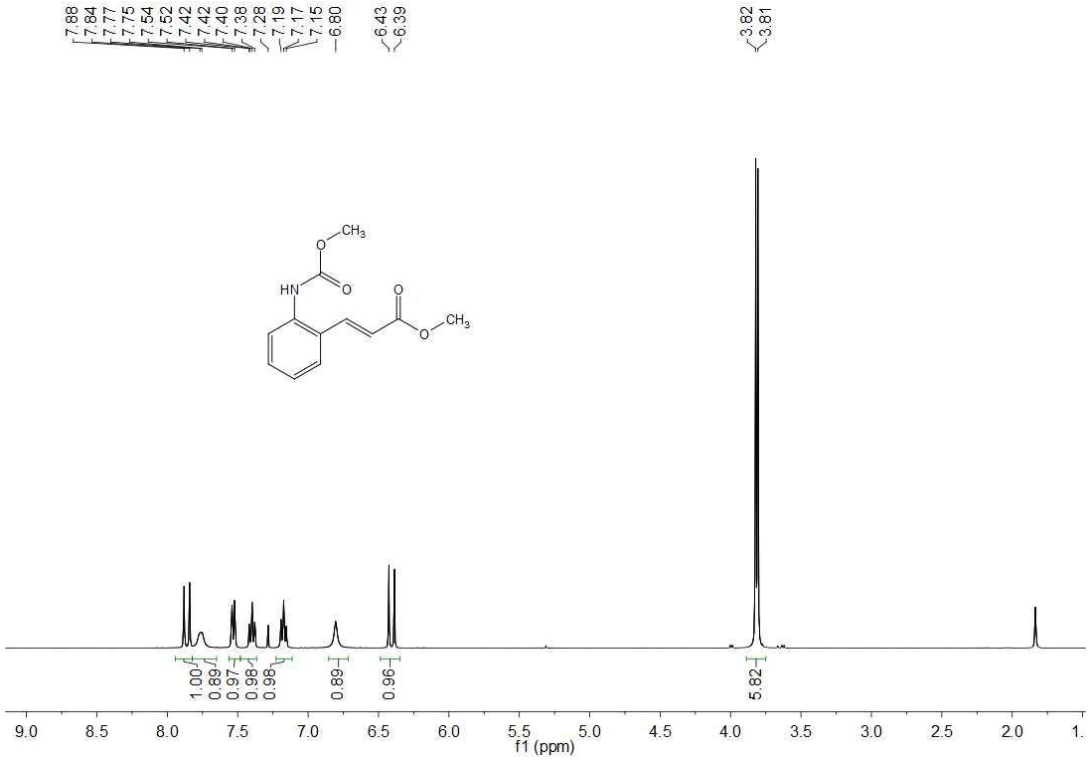
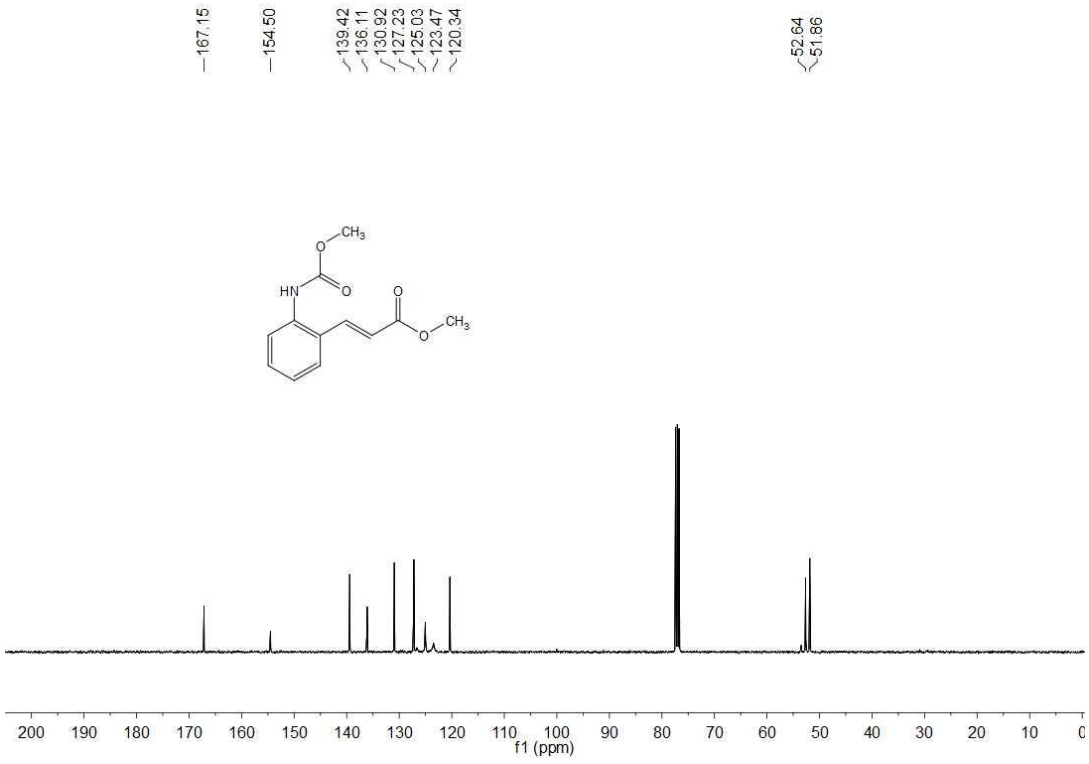
^{1}H and ^{13}C NMR spectra of products

^{1}H and ^{13}C NMR spectra of 3a





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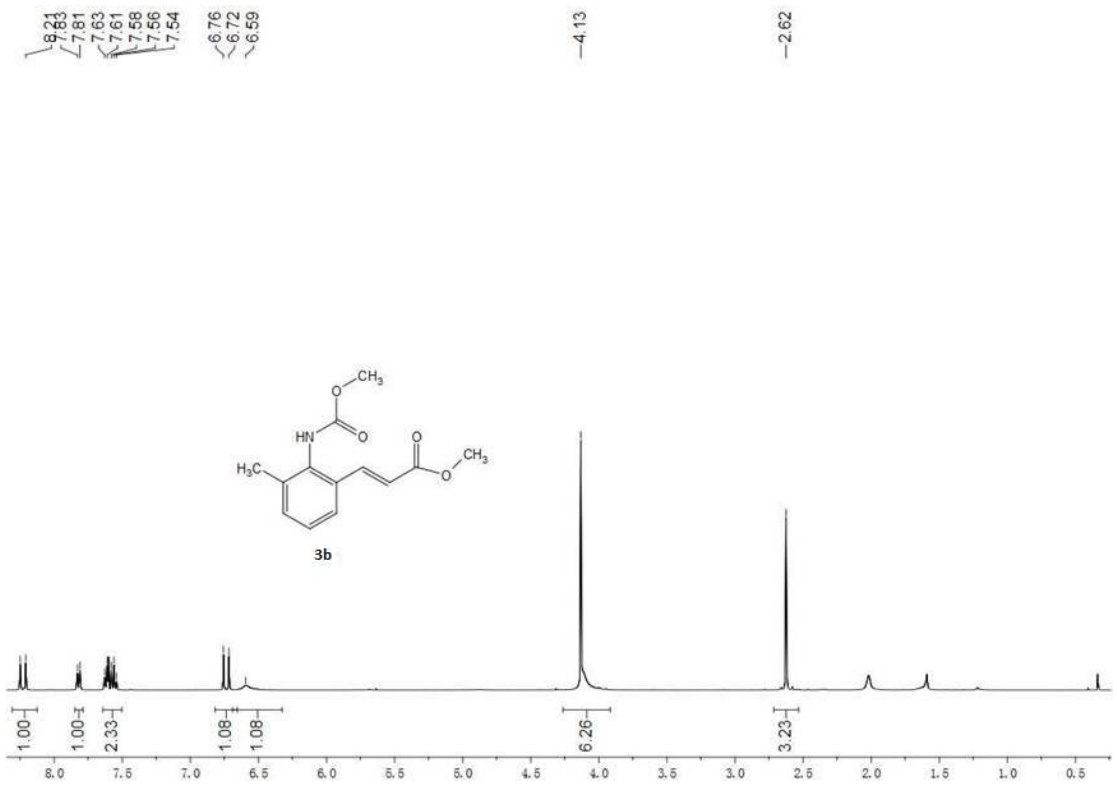

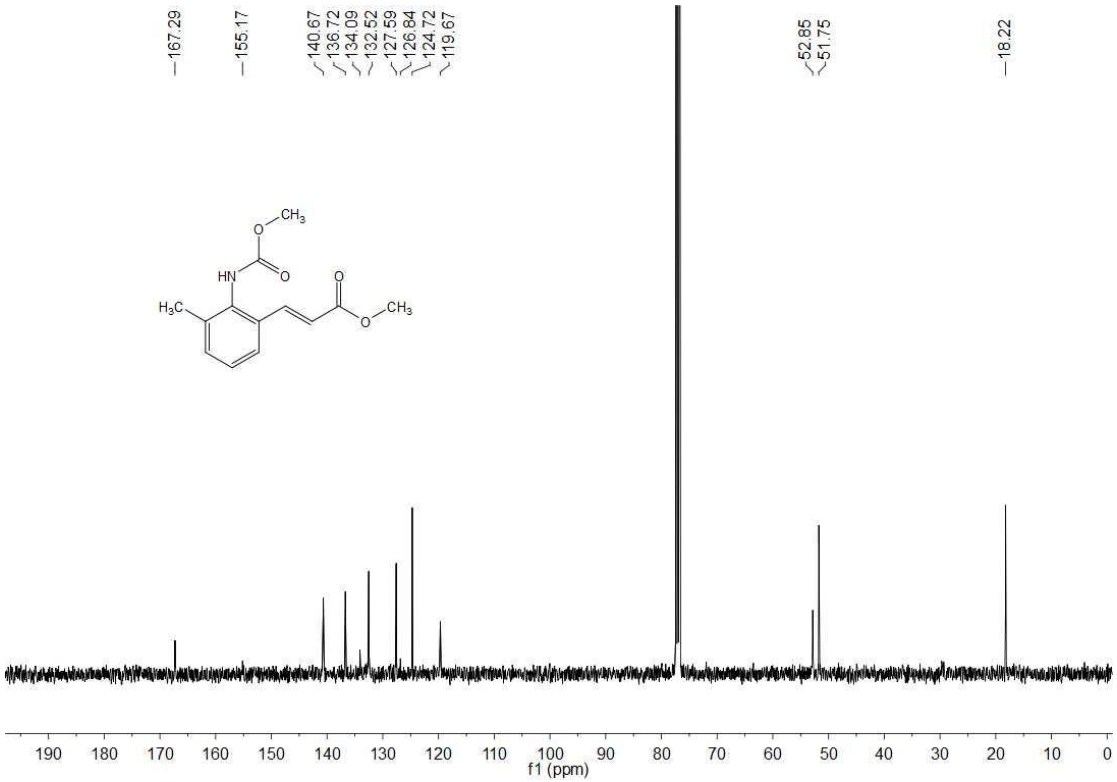

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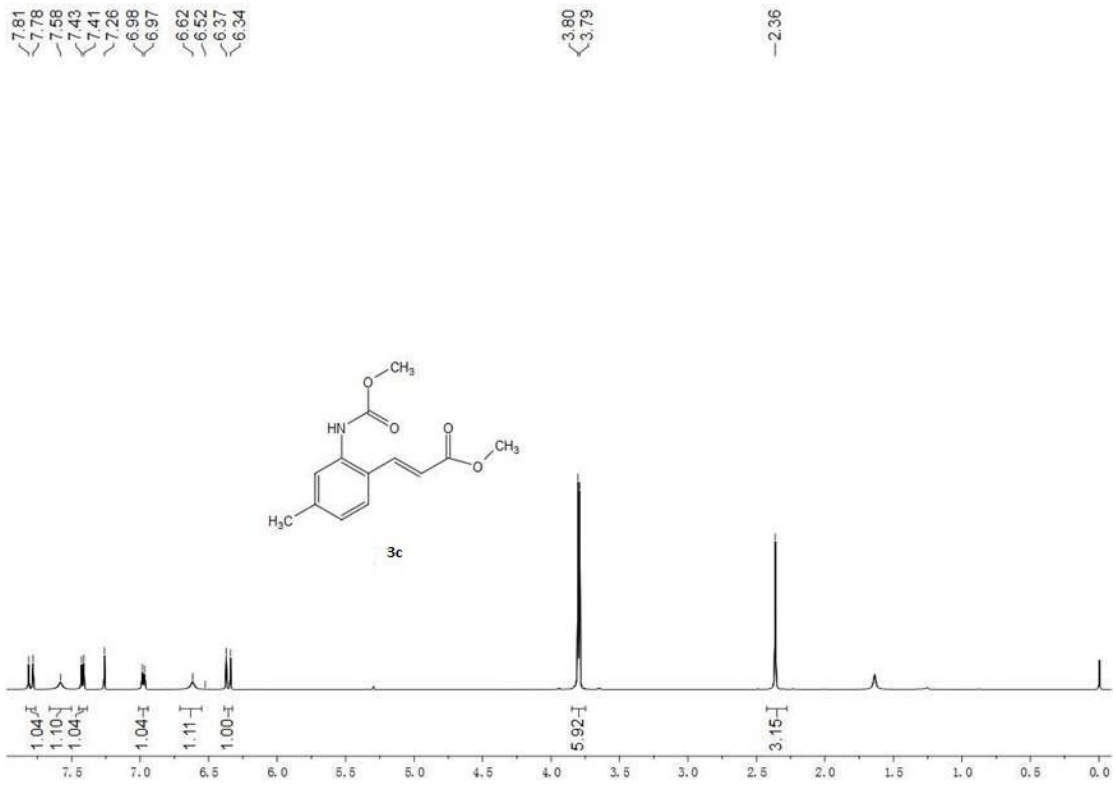

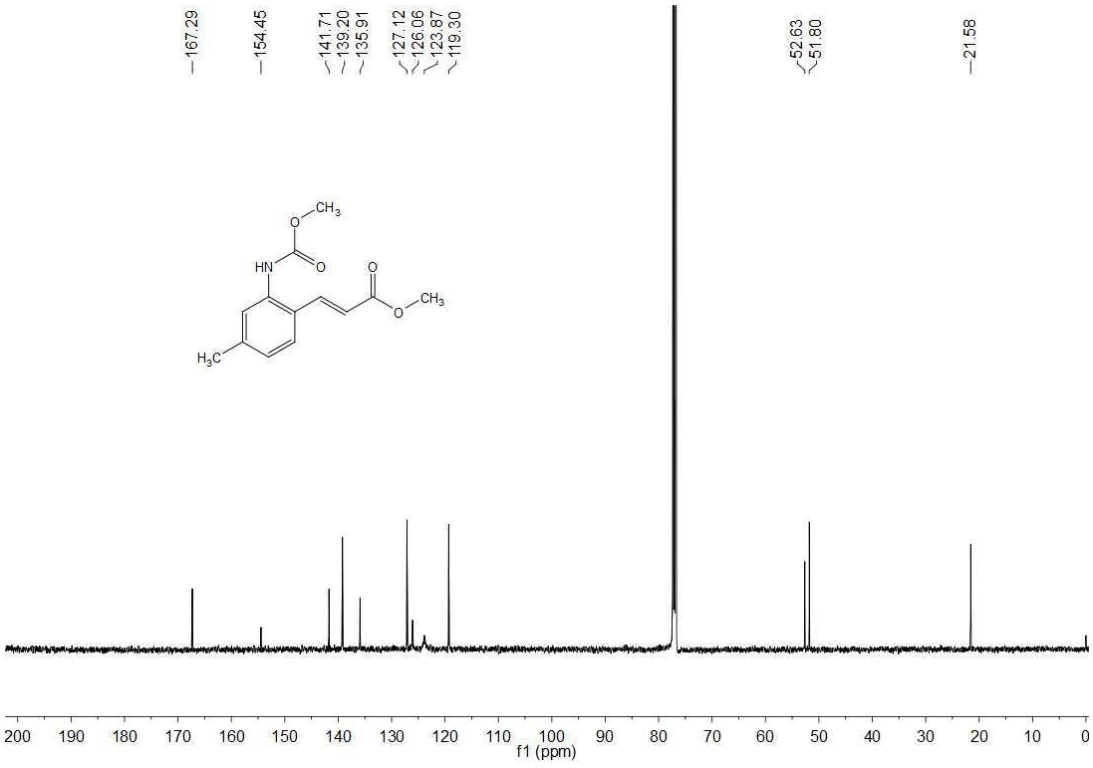

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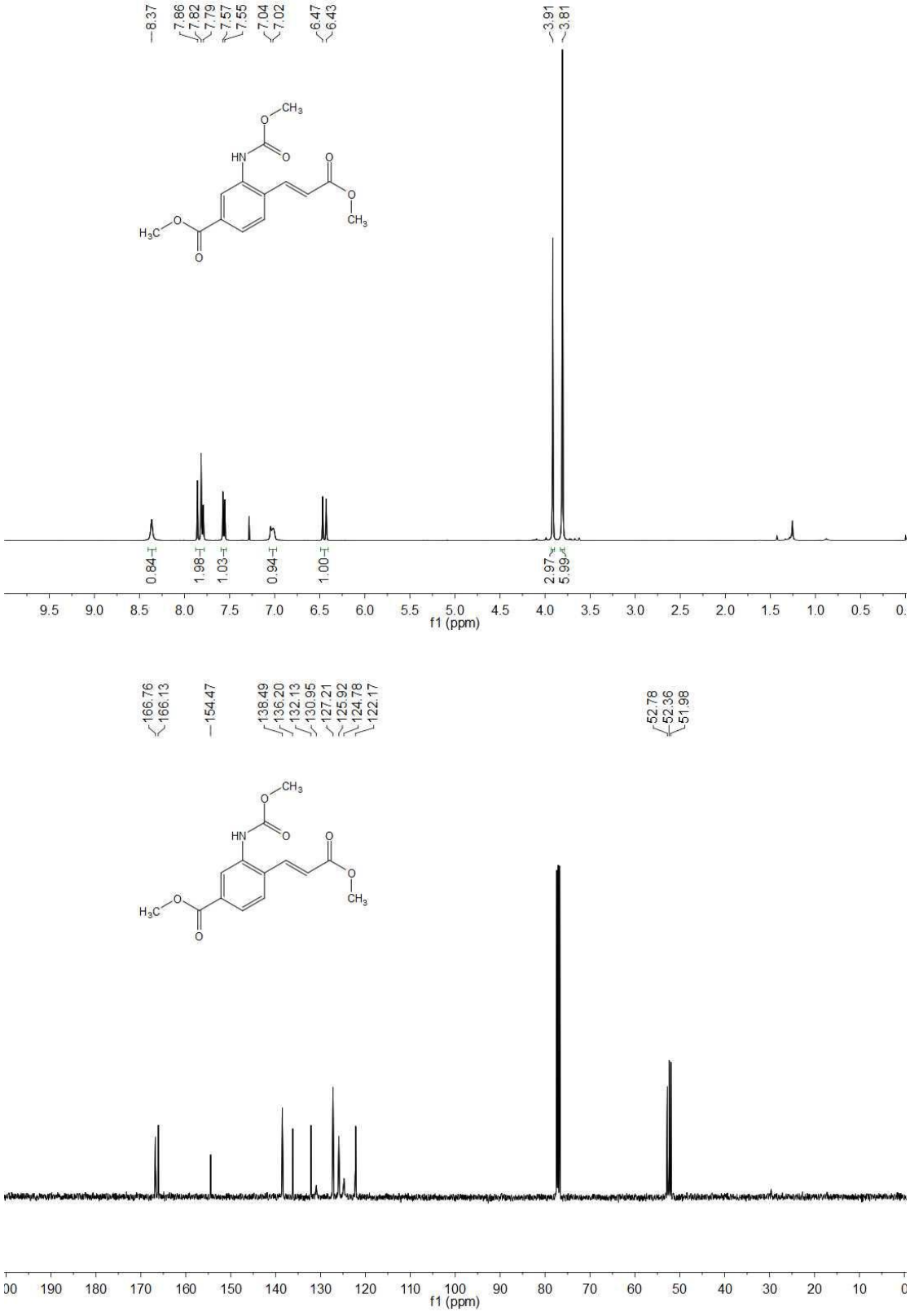

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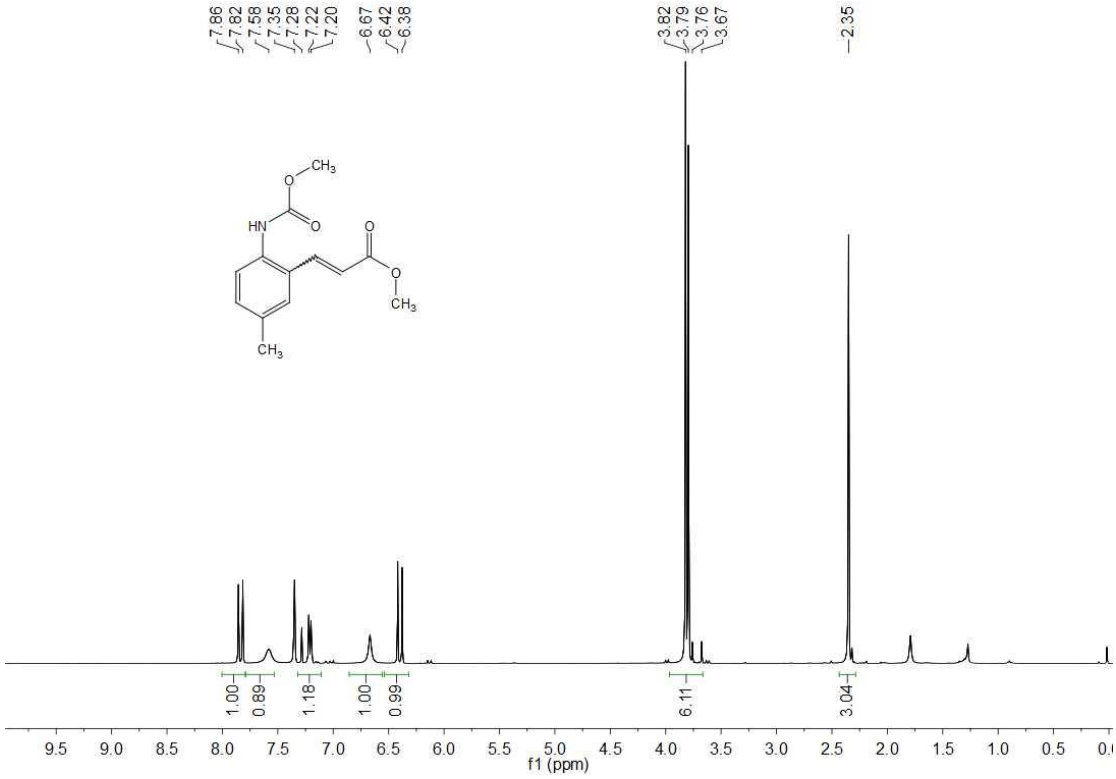
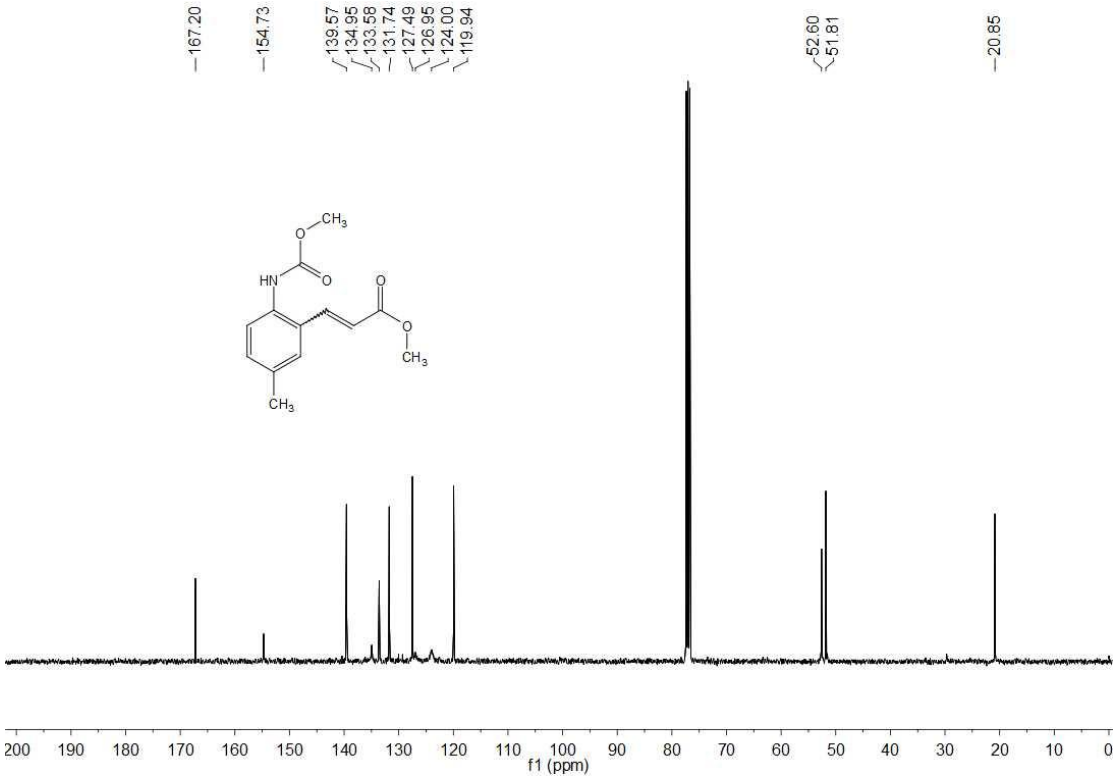
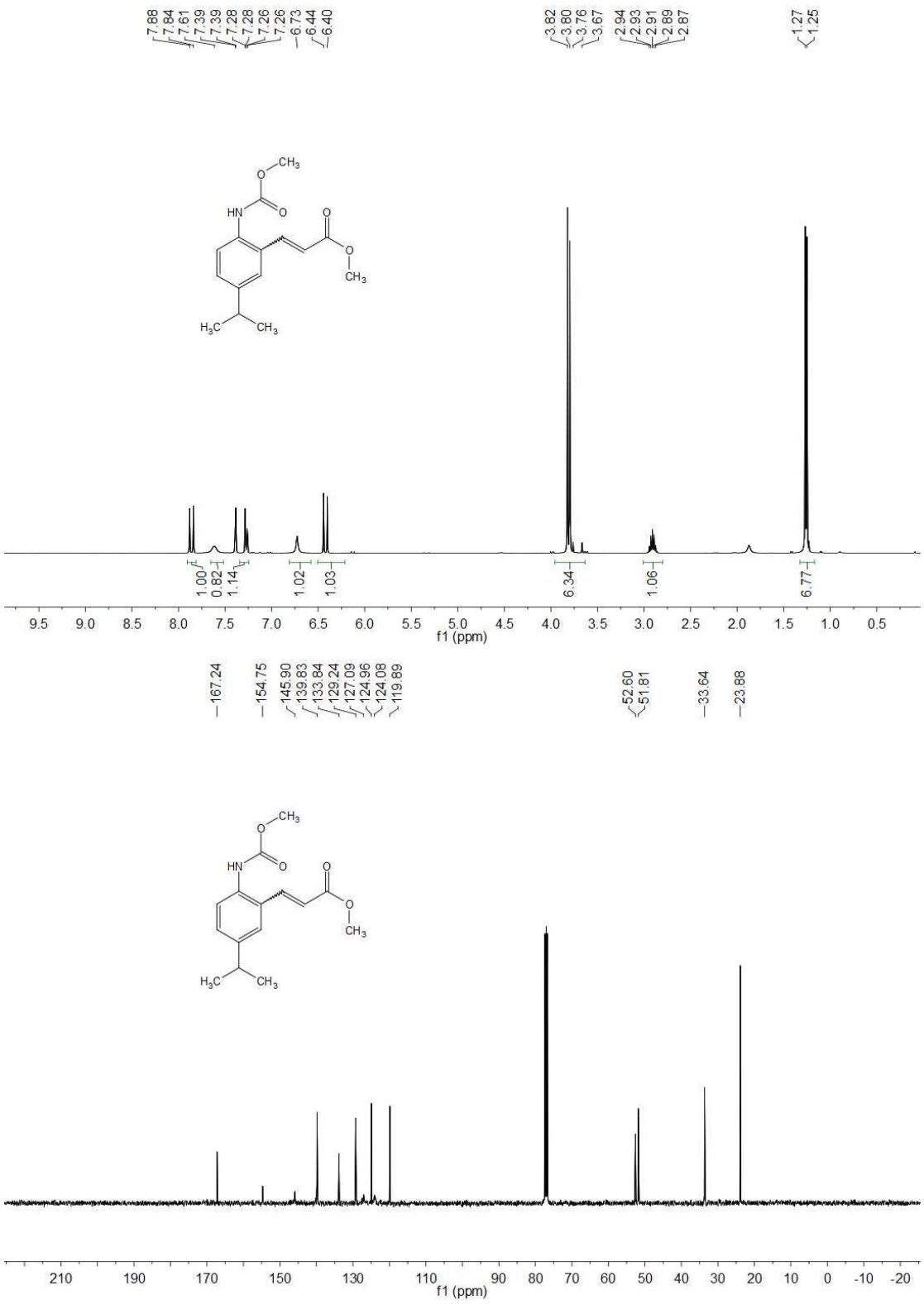
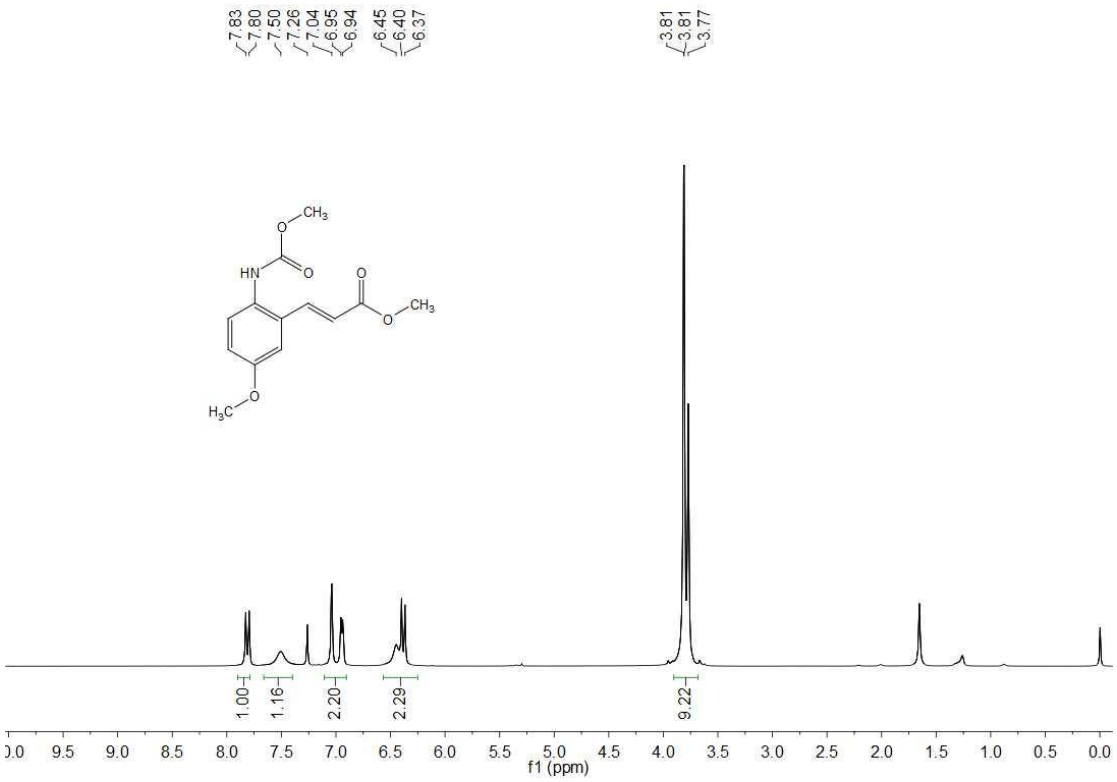


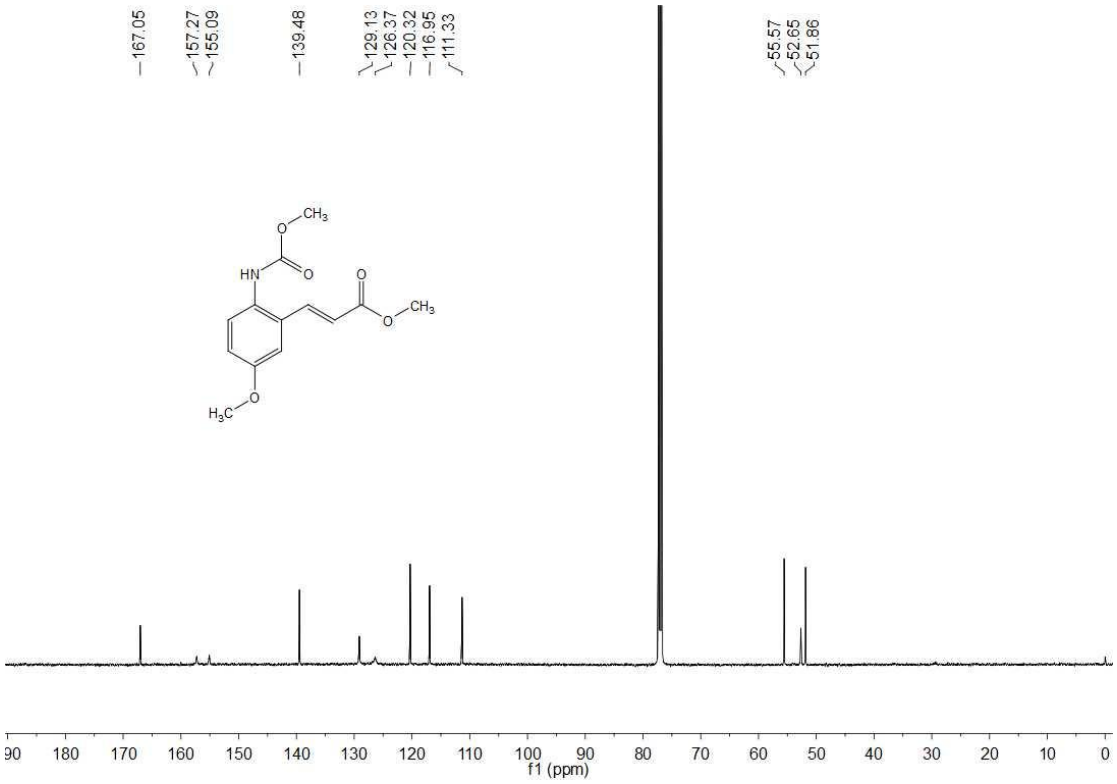


^{1}H and ^{13}C NMR spectra of 3f



^{1}H and ^{13}C NMR spectra of 3g





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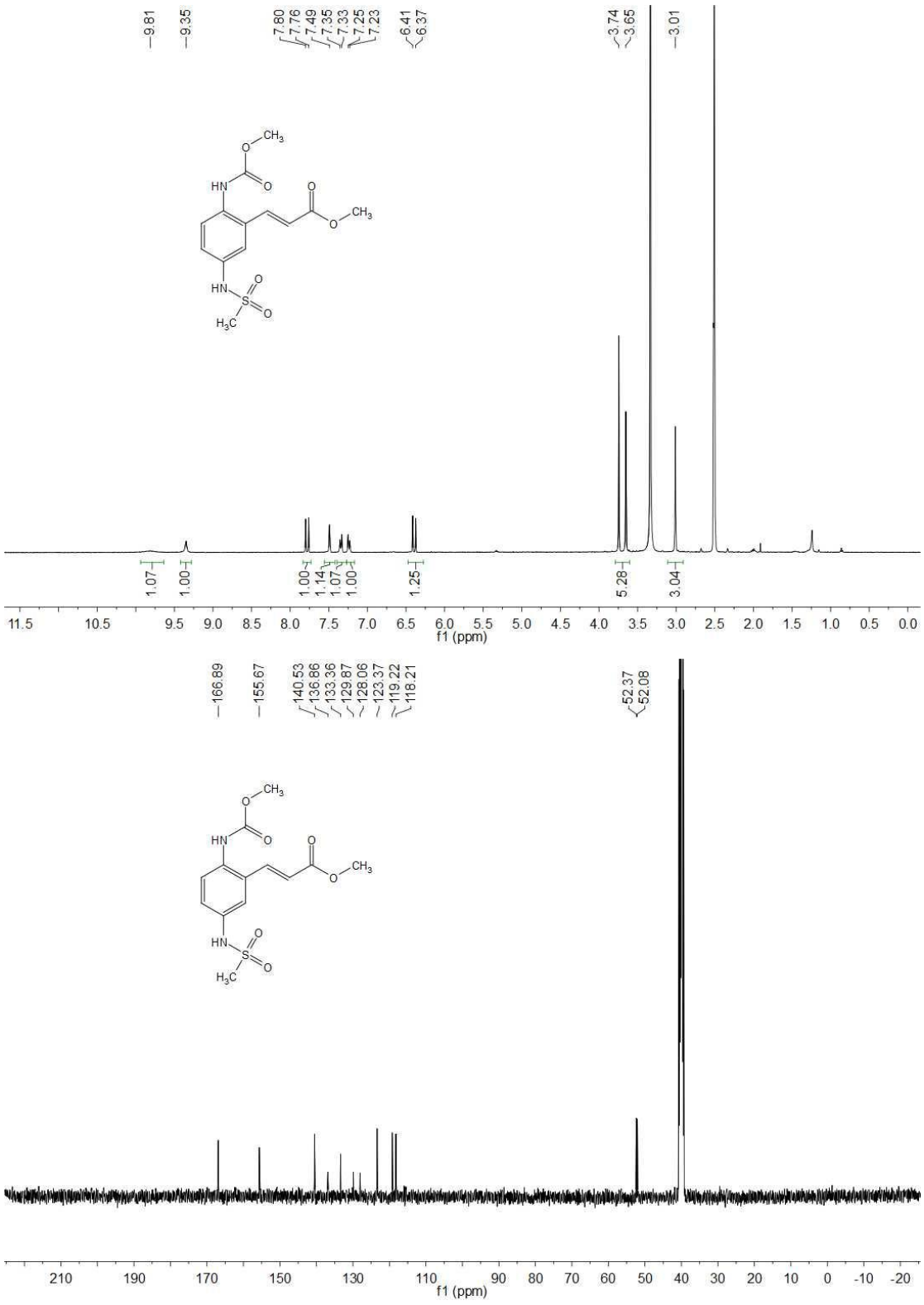
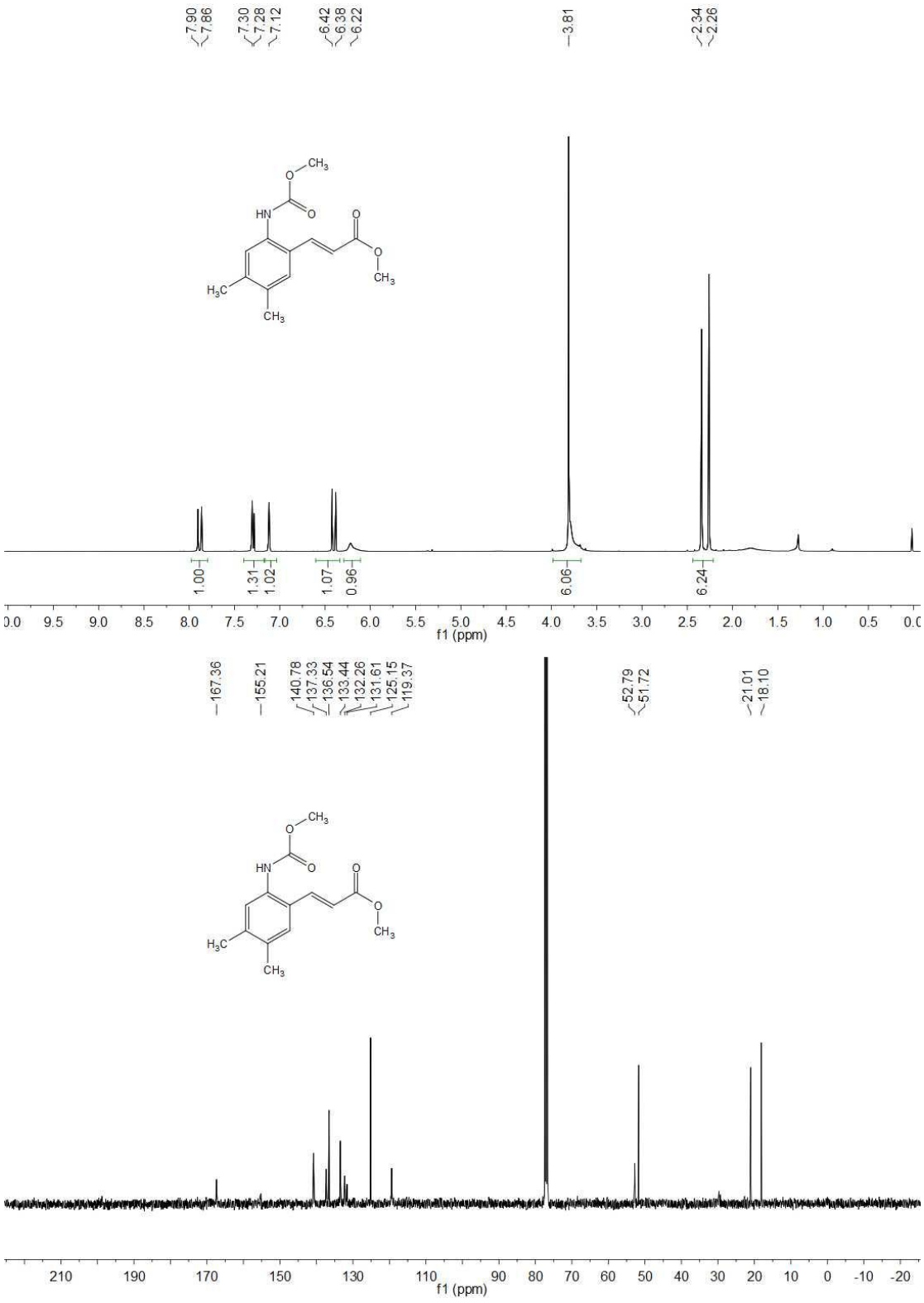
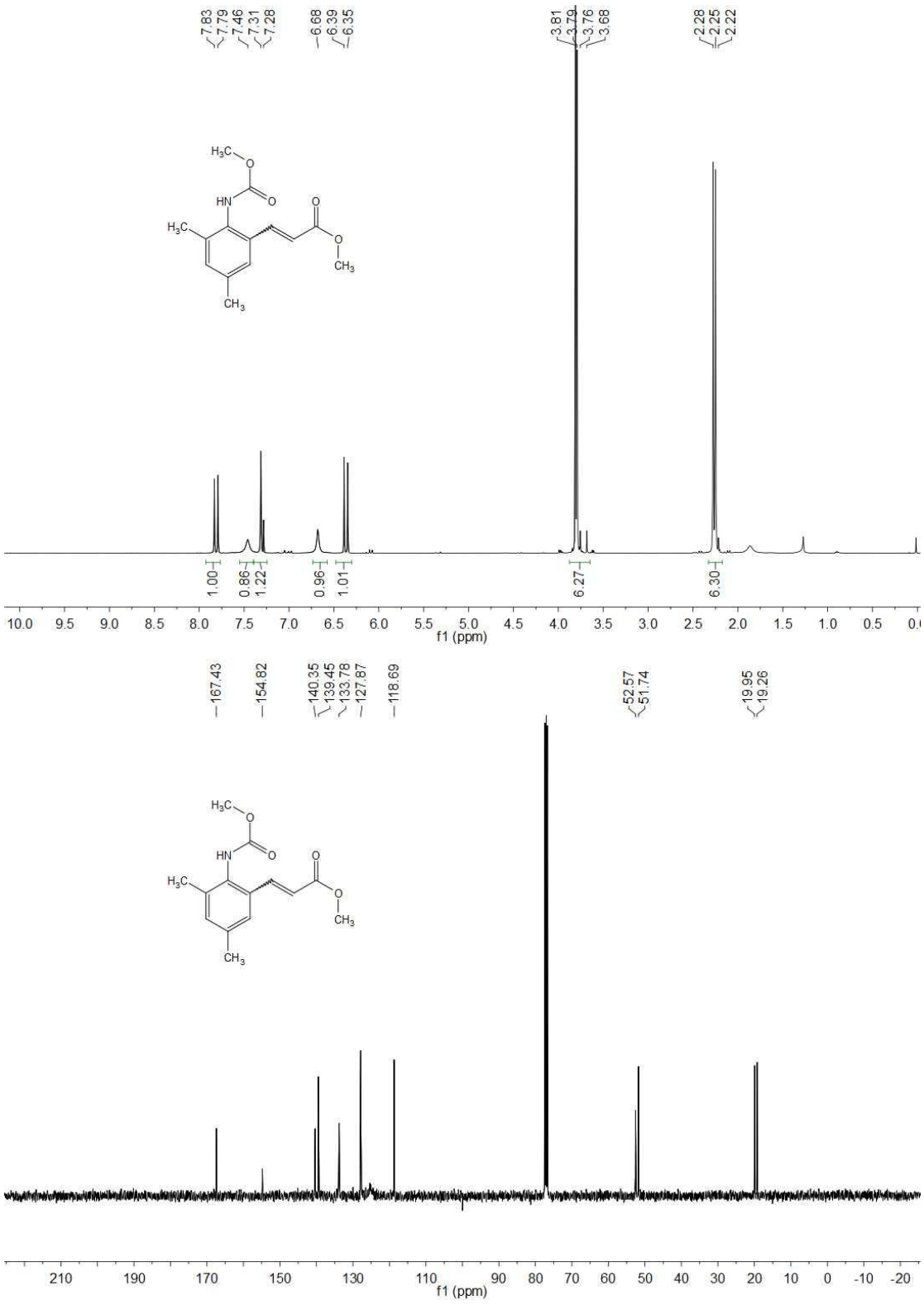


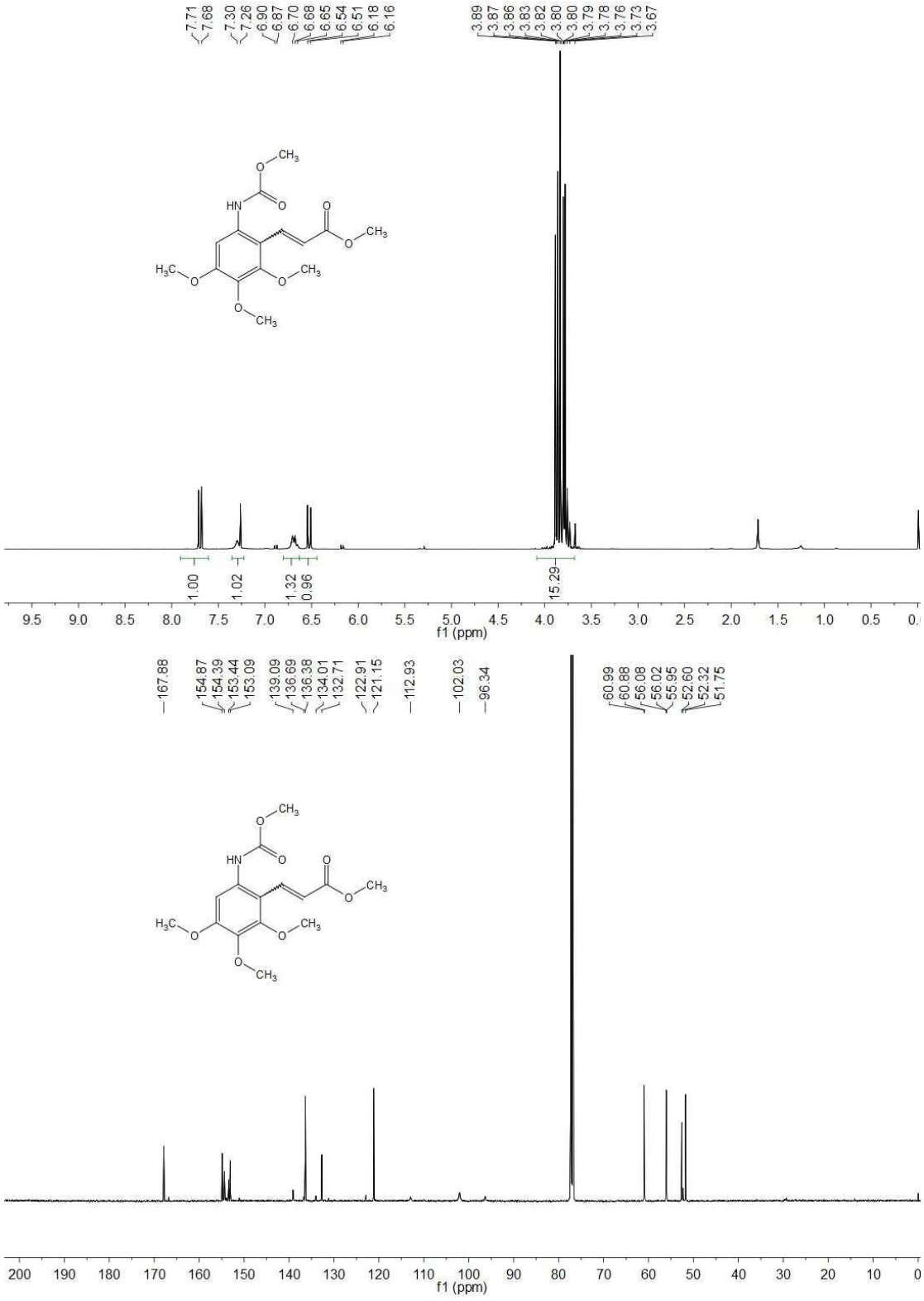
^{1}H and ^{13}C NMR spectra of 3i



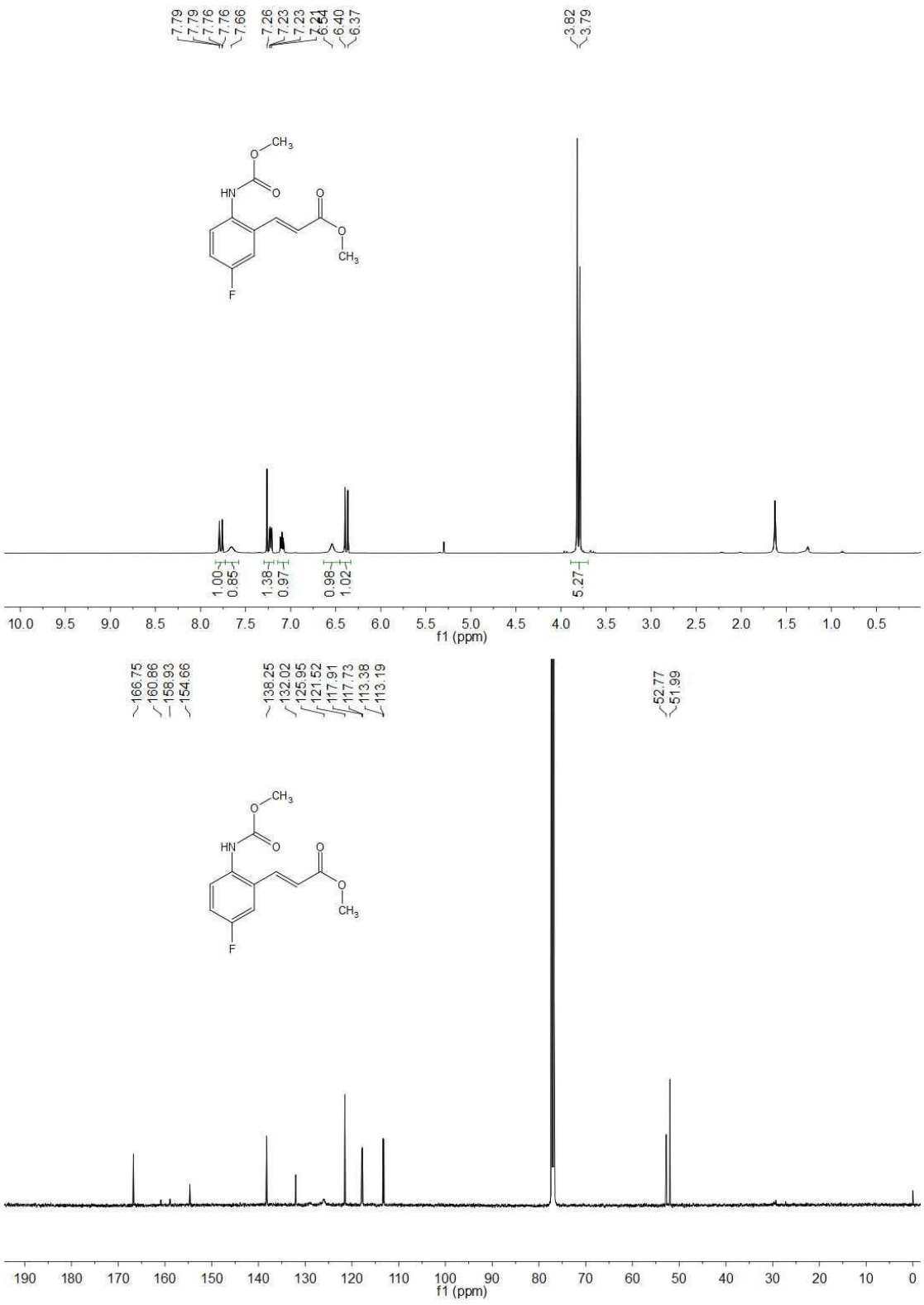
^{1}H and ^{13}C NMR spectra of 3j



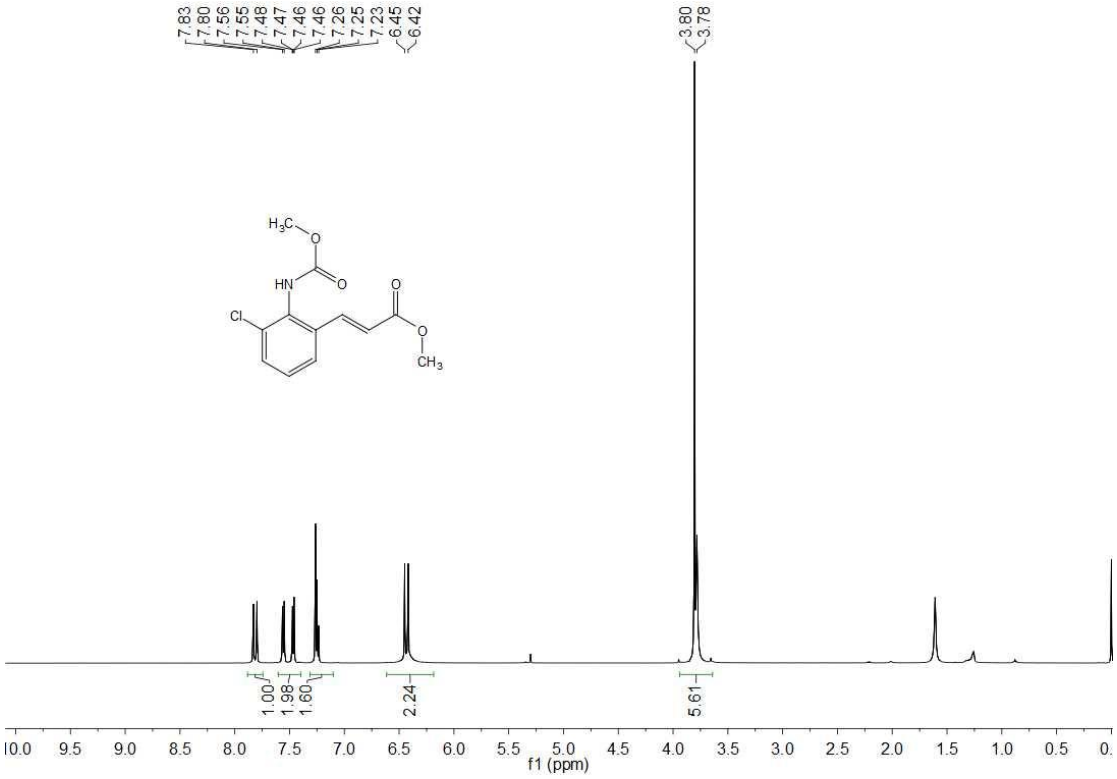
^{1}H and ^{13}C NMR spectra of 3k

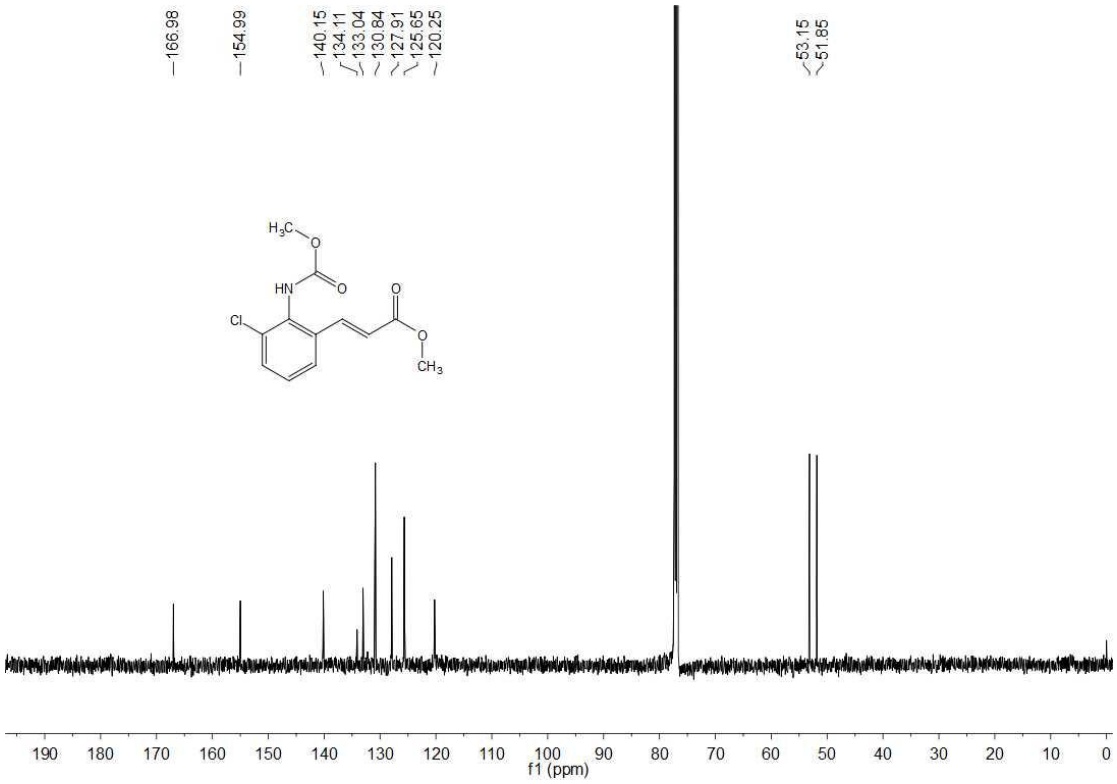


^{1}H and ^{13}C NMR spectra of 3l



^{1}H and ^{13}C NMR spectra of 3m





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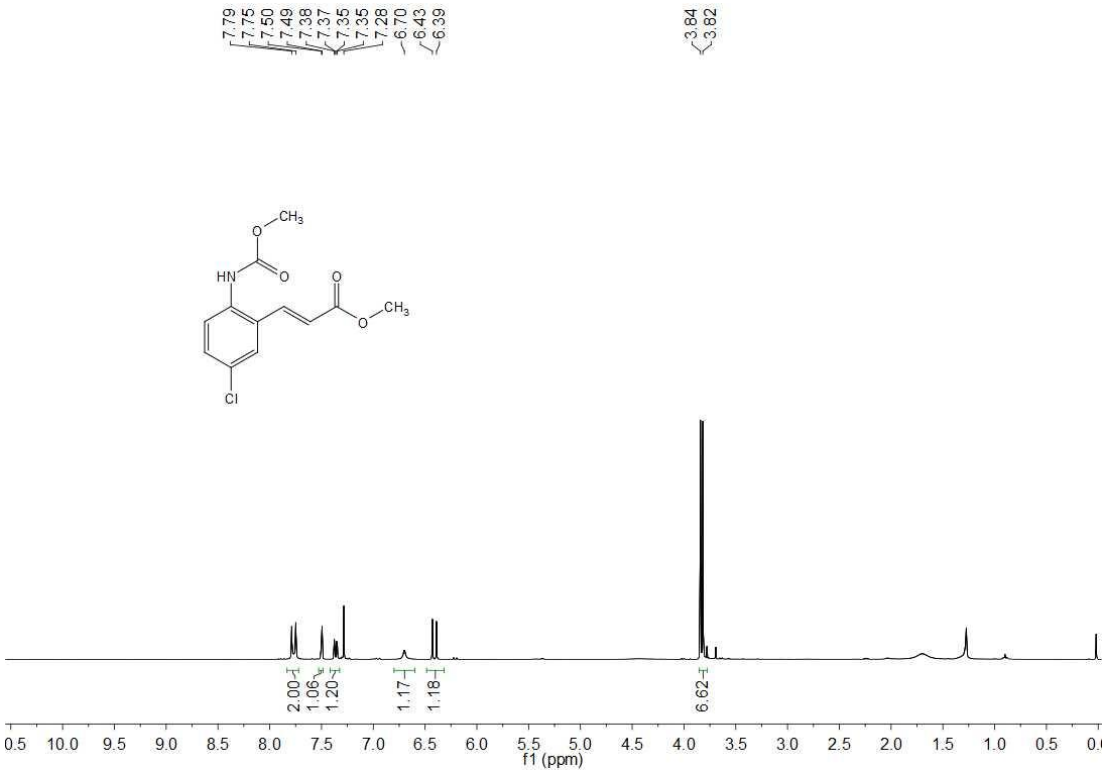
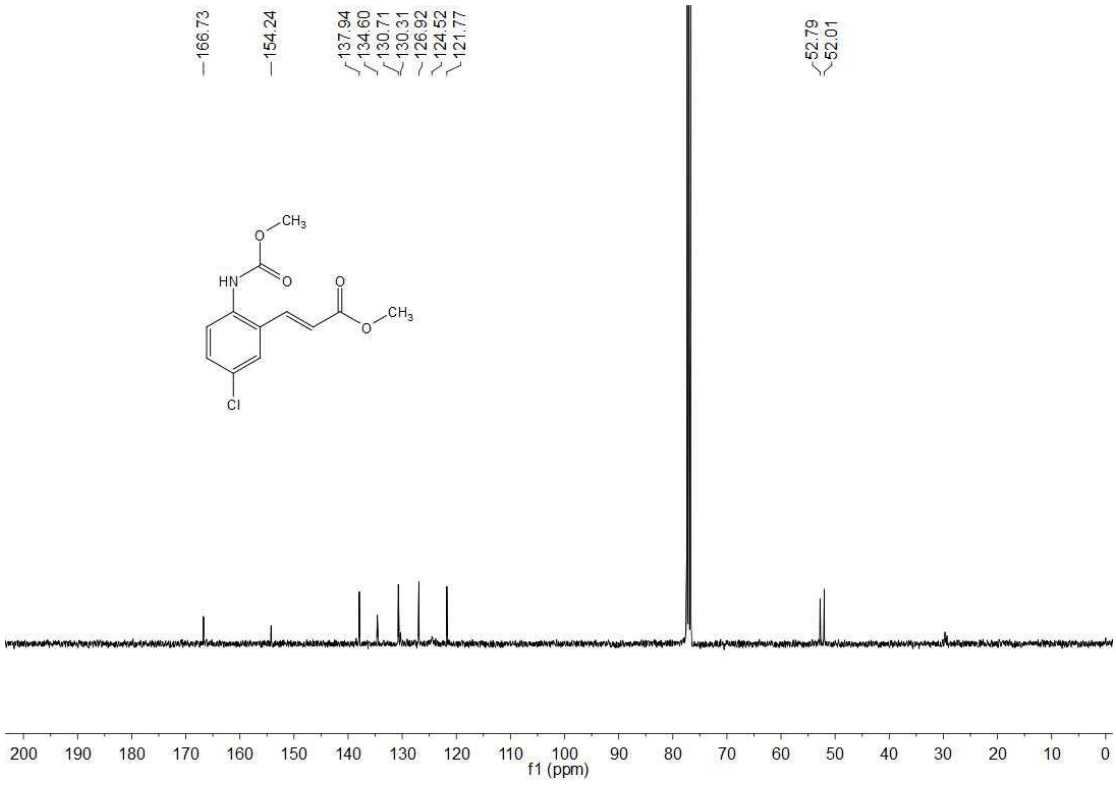
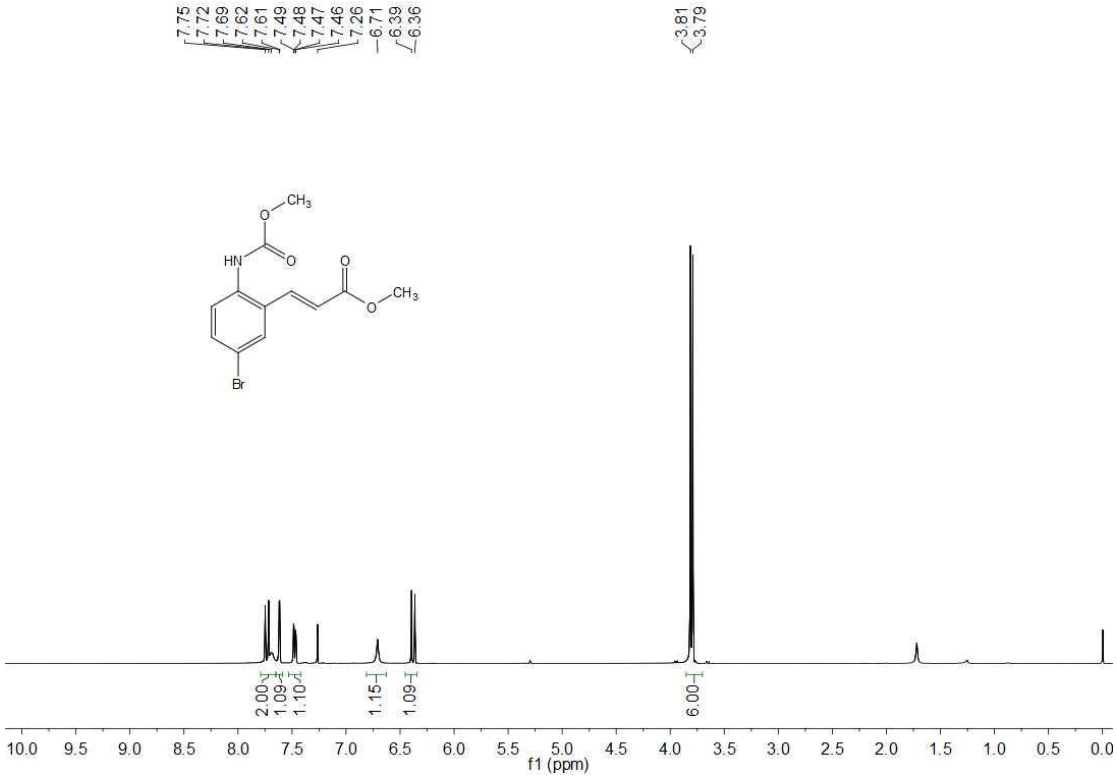
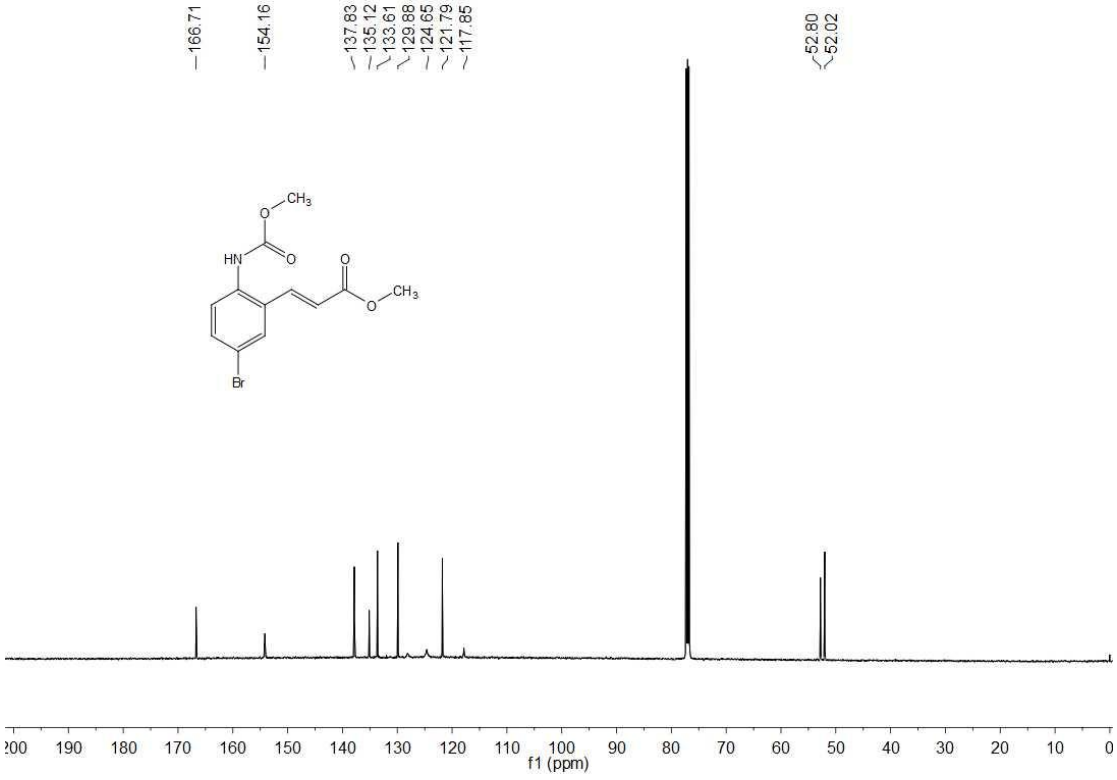


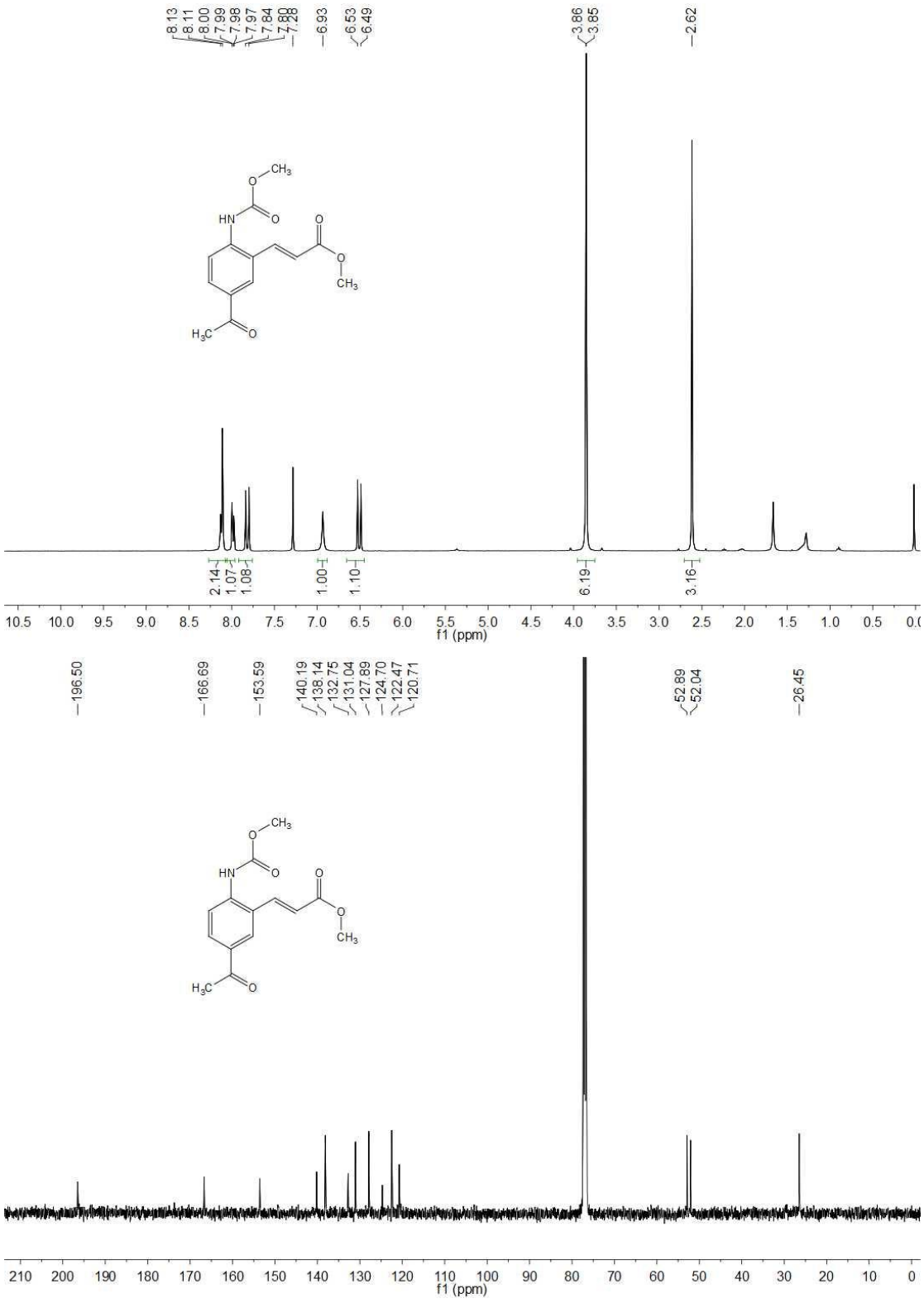


^{1}H and ^{13}C NMR spectra of 3o

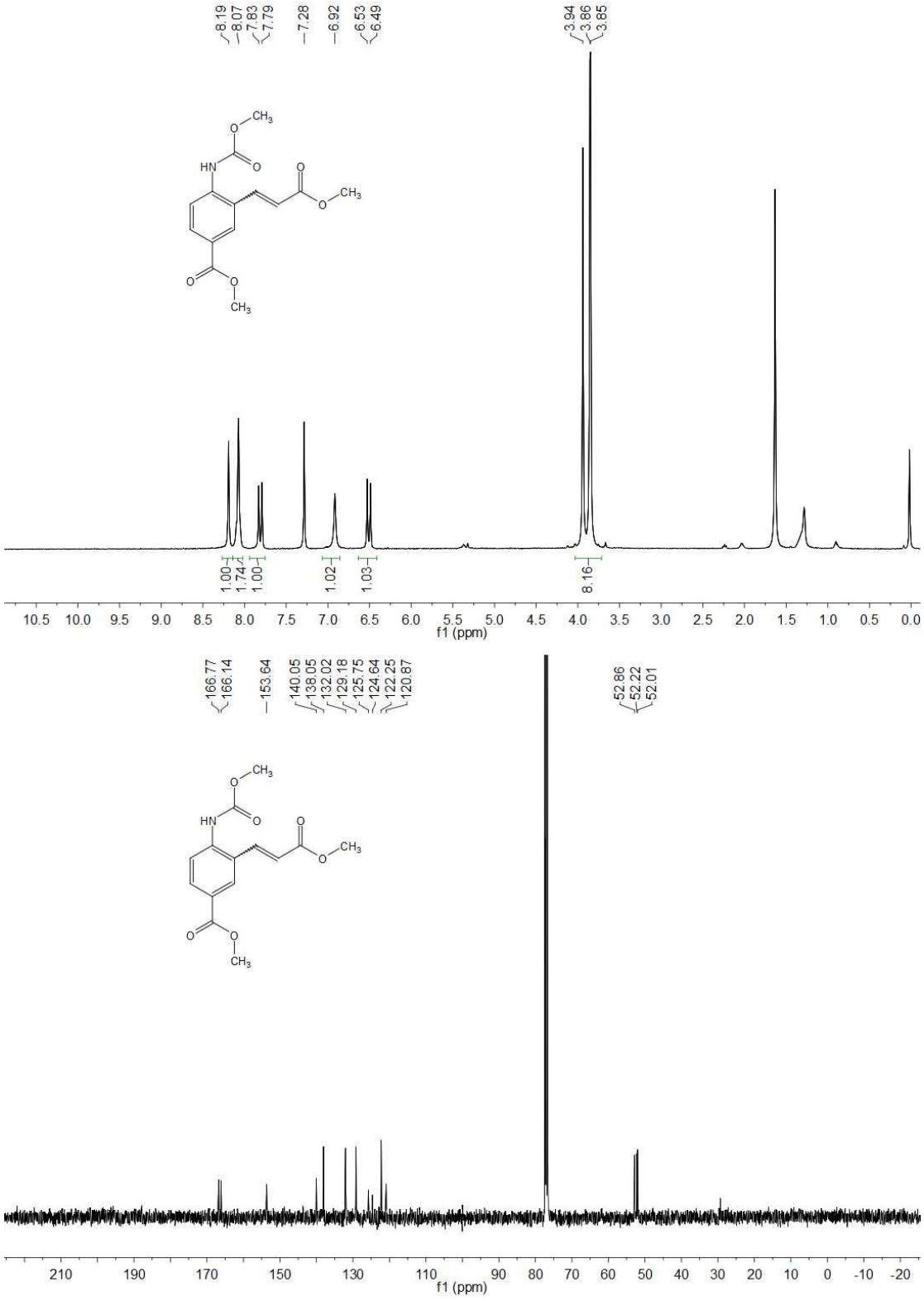




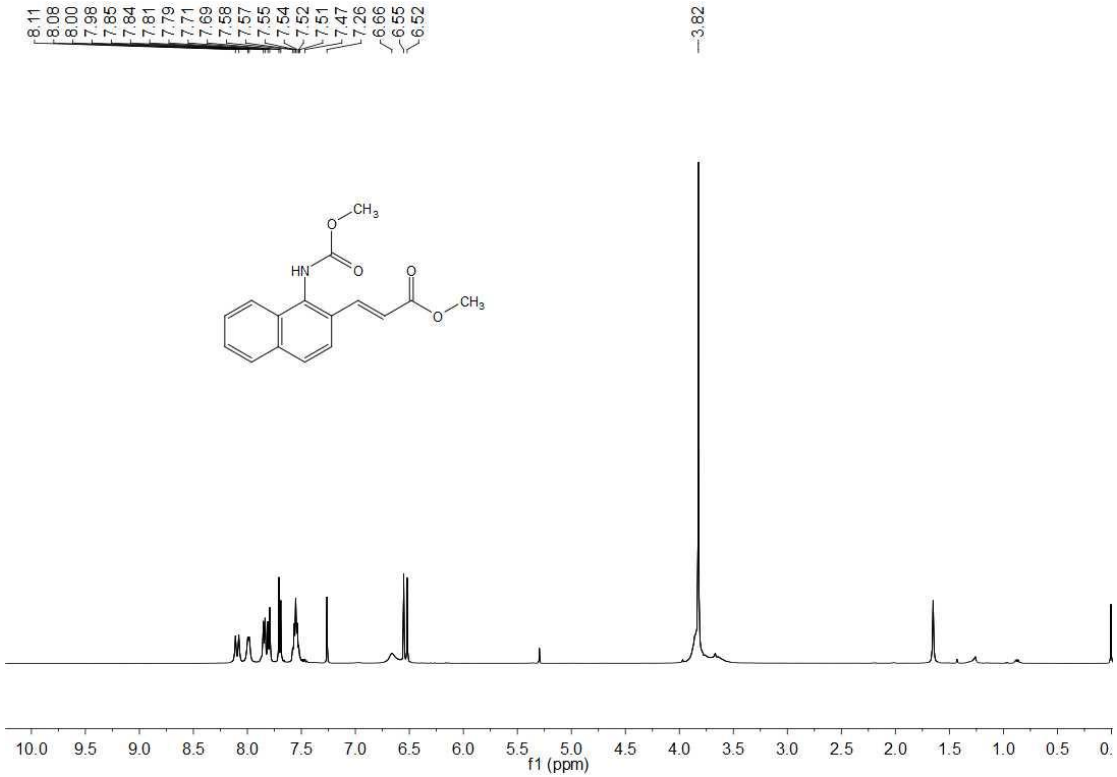
^{1}H and ^{13}C NMR spectra of 3p

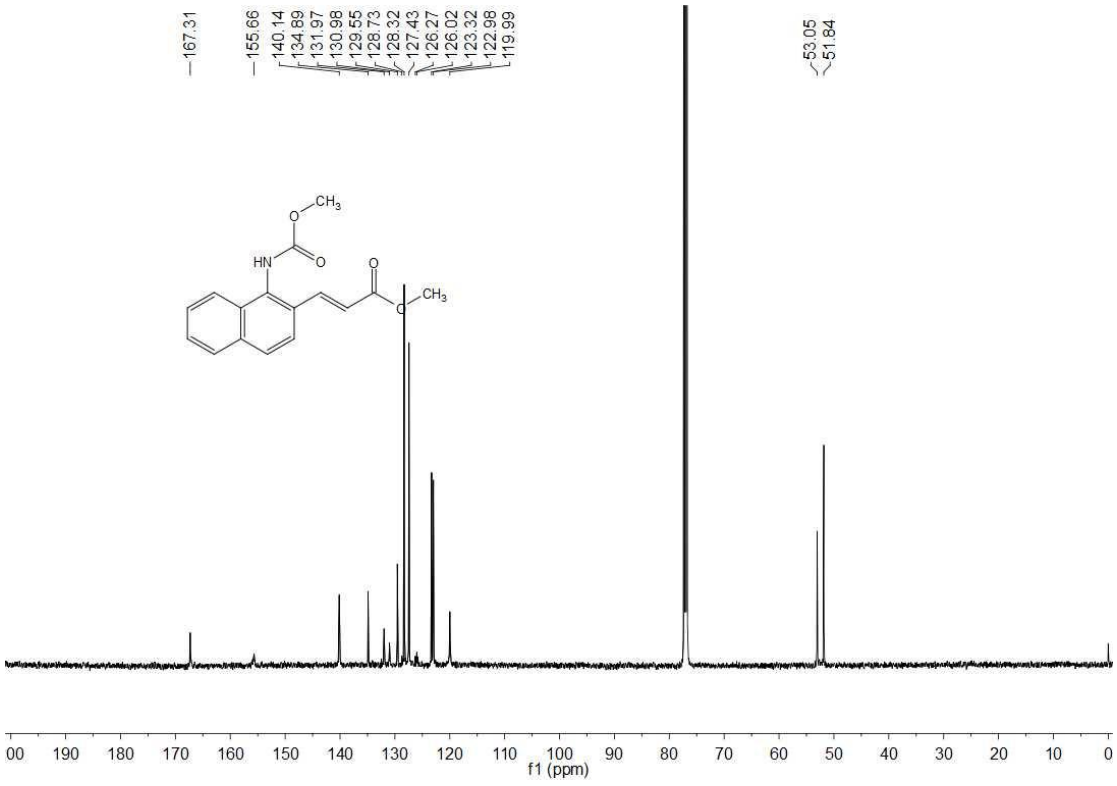


^{1}H and ^{13}C NMR spectra of 3q

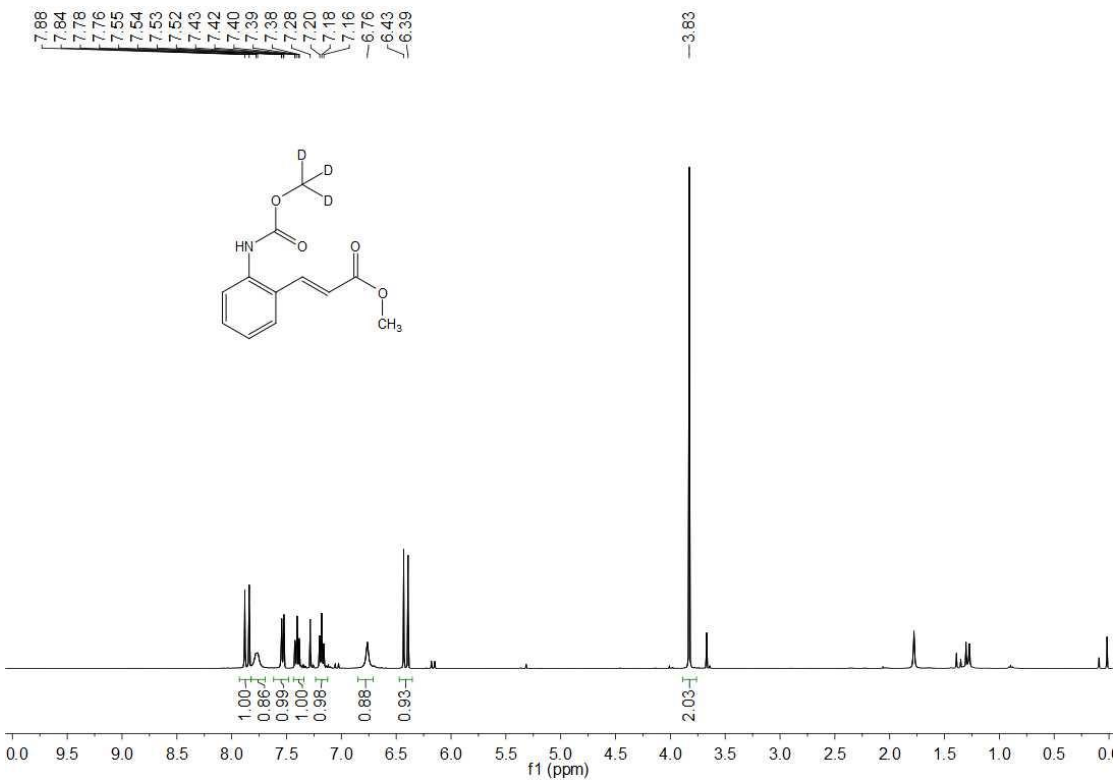


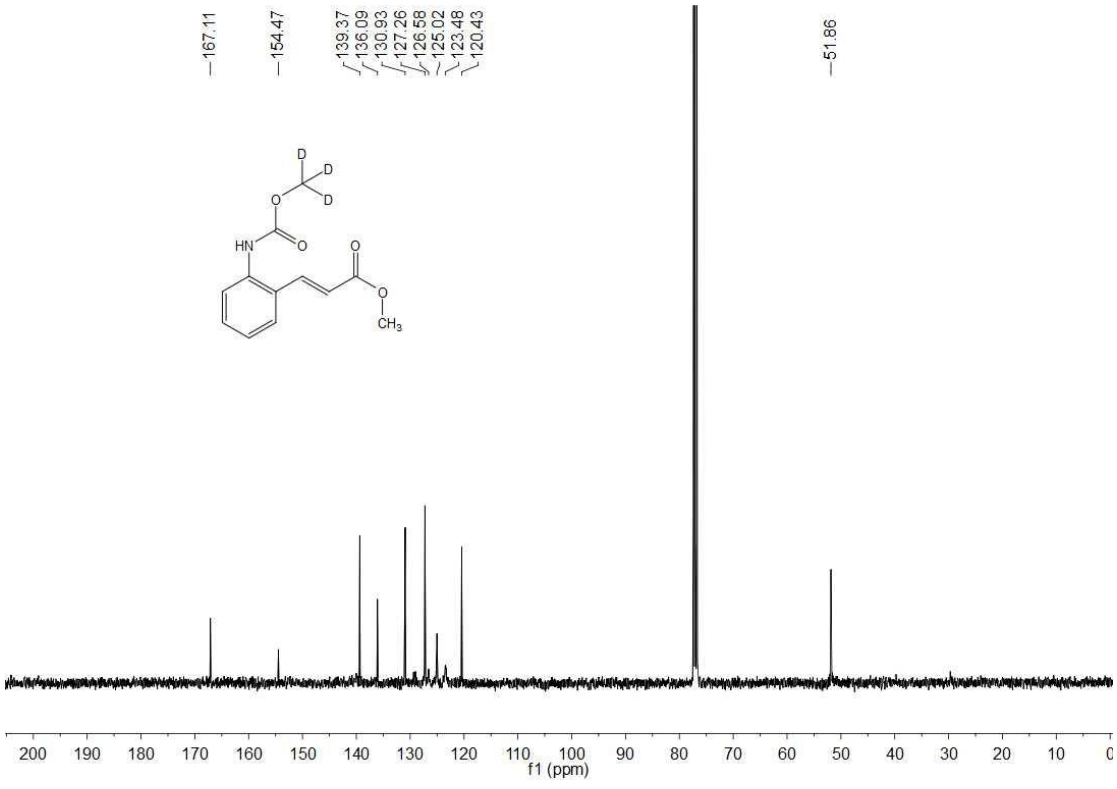
^{1}H and ^{13}C NMR spectra of 3r



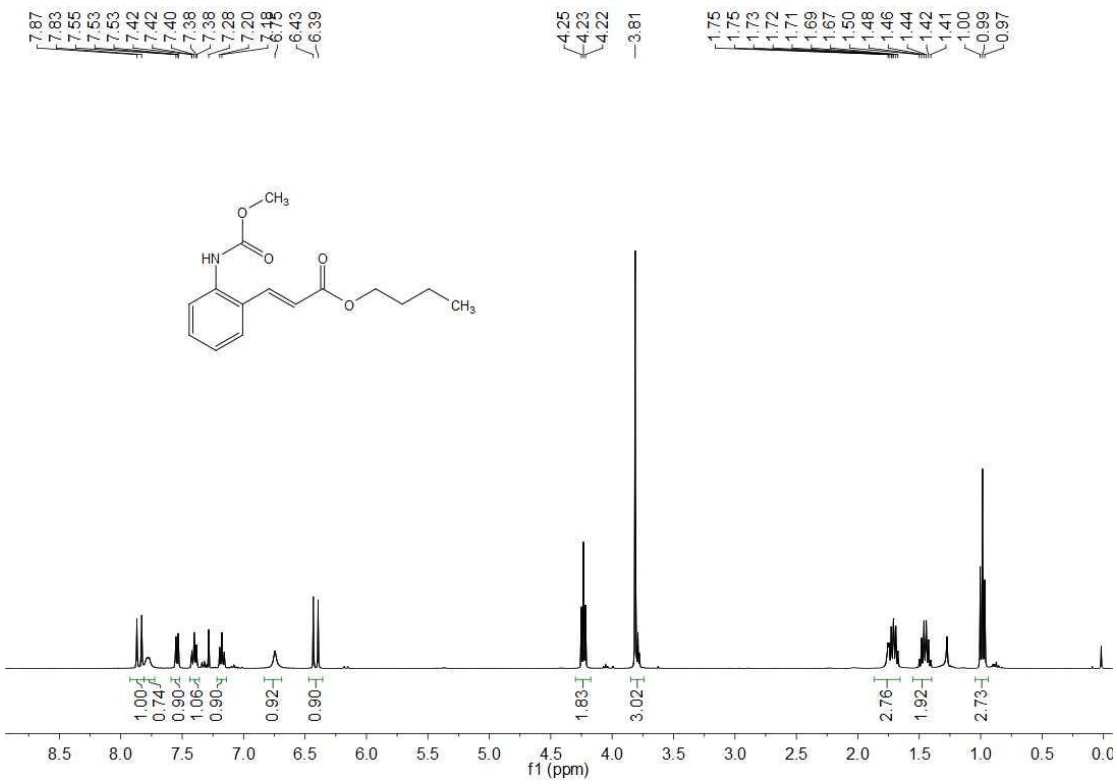


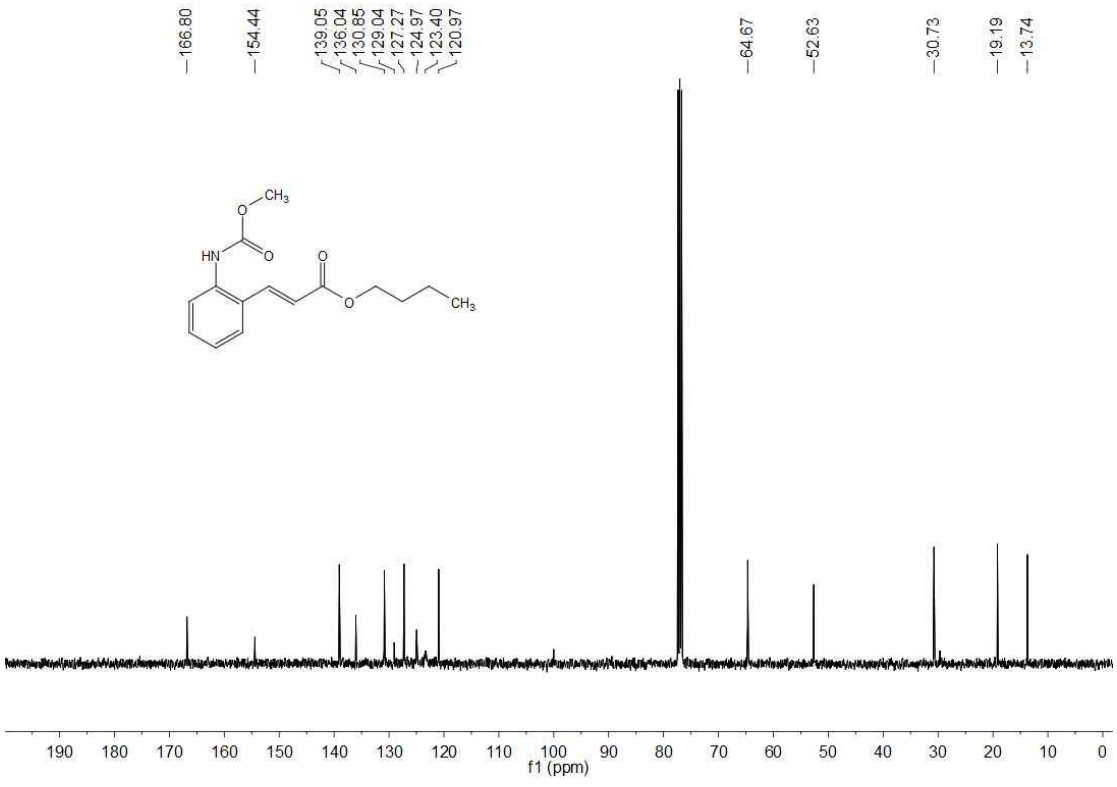
^{1}H and ^{13}C NMR spectra of 3t





^{1}H and ^{13}C NMR spectra of 3u





^{1}H and ^{13}C NMR spectra of 3v