Supporting information

Iodine-mediated intramolecular electrophilic aromatic cyclization in allylamines: A general route to synthesis of quinolines, pyrazolo[4,3-*b*]pyridines and thieno[3,2-*b*]pyridines

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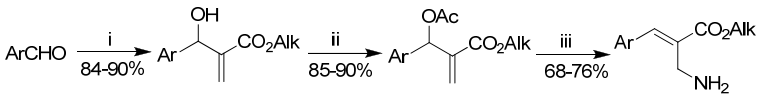
Contents

General

Melting points are uncorrected and were determined in capillary tubes on a Precision melting point apparatus containing silicon oil. IR spectra were recorded using a Perkin Elmer's RX I FTIR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded either on Bruker DPX-200 or Bruker Avance DRX-300 or Varian 600 MHz spectrometers, using TMS as an internal standard. The ESMS were recorded on Thermo Finnigan LCQ Advantage, Ion Trap Mass spectrometer. The HRMS spectra were recorded as EI-HRMS on Agilent 6520 Q-TOF, LC-MS/MS mass spectrometer.

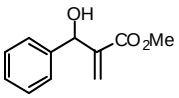
A general scheme that was followed for the preparation of allylamines is provided below. Only the spectroscopic details for the unreported Morita-Baylis-Hillman (MBH) adducts, corresponding acetates and allylamines are provided. For the reported compounds appropriate citations in which they appear are included.



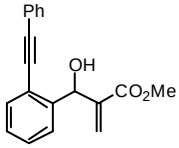
Scheme 1. *Reagents and conditions*: i) alkyl acrylate, DABCO, rt, 30 min to 3 d (for Ar = 4-OMe-C_6H_4 3 weeks); ii) AcCl, Pyridine, CH_2Cl_2, 0 ^{o}C to rt, 3 h; iii) MeOH-NH_3, rt, 1 h.

1. The MBH adducts were prepared according to the literature procedure.[1,2]

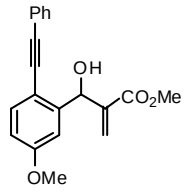
Methyl 2-(hydroxy(phenyl)methyl)acrylate.[1]



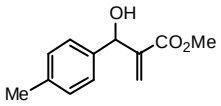
Methyl 2-(hydroxy(2-(phenylethynyl)phenyl)methyl)acrylate.[2] Yield: 89% (2.46 g from 2.0 g); yellow oil; R_f = 0.63 (hexanes: EtOAc, 3:2, v/v); IR (neat) ν: 1717 (CO_2Me), 3441 (OH) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.57-7.47 (m, 4H), 7.37-7.28 (m, 5H), 6.33 (s, 1H), 6.15 (s, 1H), 5.67 (s, 1H), 3.73 (s, 3H), 3.32 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 167.3, 142.8, 141.6, 132.3, 131.7, 128.8, 128.6, 128.1, 127.8, 126.9, 126.6, 123.2, 121.9, 94.8, 87.3, 70.92, 52.1. MS (ESI+): *m/z* = 293.1. ESI-HR-MS calculated for $C_{19}H_{16}O_3$ $[MH]^+$: 293.1178, found: 293.1182.



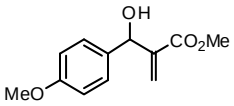
Methyl 2-(hydroxy(5-methoxy-2-(phenylethynyl)phenyl)methyl)acrylate. Yield: 88% (2.4 g from 2.0 g); yellow oil; R_f = 0.53 (hexanes: EtOAc, 3:2, v/v); IR (neat) ν: 1714 (CO_2Me), 3446 (OH) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.47-7.44 (m, 3H), 7.36-7.31 (m, 3H), 7.13 (d, J = 2.6 Hz, 1H), 6.84-6.80 (m, 1H), 6.32 (s, 1H), 6.12 (s, 1H), 5.66 (s, 1H), 3.83 (s, 3H), 3.75 (s, 3H), 3.36 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 167.3, 160.2, 144.7, 141.4, 133.8, 131.5, 128.5, 128.3, 127.1, 123.6, 114.0, 113.8, 112.1, 93.5, 87.3, 70.9, 55.6, 52.2. MS (ESI+): *m/z* = 323.2. ESI-HR-MS calculated for $C_{20}H_{18}O_4$ $[MH]^+$: 323.1283, found: 323.1285.



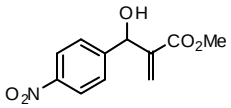
Methyl 2-(hydroxy(4-methylphenyl)methyl)acrylate.[3]



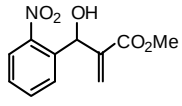
Methyl 2-(hydroxy(4-methoxyphenyl)methyl)acrylate.[4]



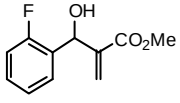
Methyl 2-(hydroxy(4-nitrophenyl)methyl)acrylate.[5]



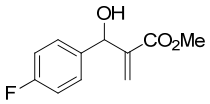
Methyl 2-(hydroxy(2-nitrophenyl)methyl)acrylate.[6]



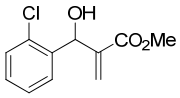
Methyl 2-((2-fluorophenyl)(hydroxy)methyl)acrylate.[1]



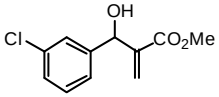
Methyl 2-((4-fluorophenyl)(hydroxy)methyl)acrylate.[1]



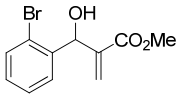
Methyl 2-((2-chlorophenyl)(hydroxy)methyl)acrylate.[1]



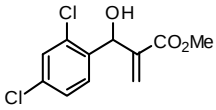
Methyl 2-((3-chlorophenyl)(hydroxy)methyl)acrylate.[7]



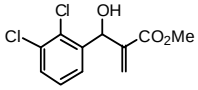
Methyl 2-((2-bromophenyl)(hydroxy)methyl)acrylate.[8]



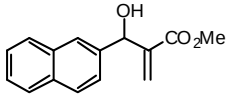
Methyl 2-((2,4-dichlorophenyl)(hydroxy)methyl)acrylate.[9]



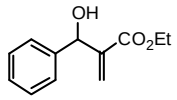
Methyl 2-((2,3-dichlorophenyl)(hydroxy)methyl)acrylate.[9]



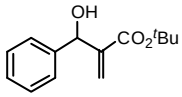
Methyl 2-(hydroxy(naphthalen-2-yl)methyl)acrylate.[7]



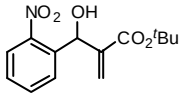
Ethyl 2-(hydroxy(phenyl)methyl)acrylate.[10]



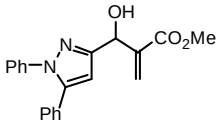
***tert*-Butyl 2-(hydroxy(phenyl)methyl)acrylate.**[11]



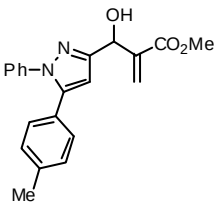
***tert*-Butyl 2-(hydroxy(2-nitrophenyl)methyl)acrylate.**[12]



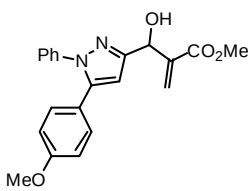
Methyl 2-((1,5-diphenyl-1*H*-pyrazol-3-yl)(hydroxy)methyl)acrylate.[13]



Methyl 2-(hydroxy(1-phenyl-5-(4-methylphenyl)-1*H*-pyrazol-3-yl)methyl)acrylate. Yield: 86% (2.28 g from 2.0 g); yellow oil; R_f = 0.29 (hexanes: EtOAc, 3:2, v/v); IR (neat) ν: 1714 (CO_2Me), 3446 (OH) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.31-7.26 (m, 5H), 7.08 (s, 4H), 6.44 (s, 1H), 6.39 (s, 1H), 6.05 (s, 1H), 5.73 (s, 1H), 3.79 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 167.1, 153.9, 144.3, 141.2, 140.2, 138.4, 129.3, 129.0, 128.8, 127.7, 127.6, 126.5, 125.5, 105.6, 68.7, 52.1, 21.4. MS (ESI+): *m/z* = 349.2. ESI-HR-MS calculated for $C_{21}H_{20}N_2O_3$ $[MH]^+$: 348.1474, found: 348.1479.



Methyl 2-(hydroxy(5-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-3-yl)methyl)acrylate. Yield: 87% (2.28 g from 2.0 g); yellow oil; R_f = 0.30 (hexanes: EtOAc, 3:2, v/v); IR (neat) *ν*: 1717 (CO_2Me), 3442 (OH) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.32-7.26 (m, 5H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 6.40 (d, *J* = 9.2



Hz, 2H), 6.05 (s, 1H), 5.73 (s, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.60 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 167.0, 159.8, 153.8, 144.0, 141.2, 140.2, 130.2, 129.0, 127.6, 126.5, 125.4, 123.0, 114.1, 105.4, 68.7, 55.4, 52.1. MS (ESI+): *m/z* = 365.2. ESI-HR-MS calculated for $C_{21}H_{20}N_2O_4$ $[MH]^+$: 365.1501, found: 365.1506.

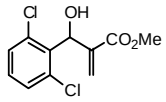
Methyl 2-(hydroxy(1-methyl-5-phenyl-1*H*-pyrazol-3-yl)methyl)acrylate Yield: 89% (2.6 g from 2.0 g); yellow oil; R_f = 0.13 (hexanes: EtOAc, 3:2, v/v); IR (neat) ν: 1731 (CO_2Me), 3444 (OH) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.48-7.43 (m, 5H), 6.42 (s, 1H), 6.31 (s, 1H), 6.09 (s, 1H), 5.71 (s, 1H), 3.89 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 167.0, 152.3, 144.8, 141.4, 130.7, 128.9, 128.8, 128.7, 126.1, 104.1, 68.5, 52.1, 37.6 ppm. MS (ESI+): *m/z* = 273.1. ESI-HR-MS calculated for $C_{15}H_{16}N_2O_3$ $[MH]^+$: 273.1239, found: 273.1236.

Methyl 2-(hydroxy(thiophen-2-yl)methyl)acrylate.[1]

Methyl 2-(hydroxy(5-methylthiophen-2-yl)methyl)acrylate. Yield: 84% (2.83 g from 2.0 g); yellow oil; R_f = 0.38 (hexanes: EtOAc, 3:2, v/v); IR (neat) ν: 1729 (CO_2Me), 3449 (OH) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.74 (d, *J* = 3.4 Hz, 1H), 6.59 (d, *J* = 3.2 Hz, 1H), 6.34 (s, 1H), 5.96 (s, 1H), 5.68 (d, *J* = 5.5 Hz, 1H), 3.76 (s, 3H), 3.16 (d, *J* = 6.3 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 166.6, 143.2, 141.5, 140.0, 125.9, 125.0, 124.9, 69.7, 52.1, 15.4. MS (ESI+): *m/z* = 195.0 [M-H_2O]. ESI-HR-MS calculated for $C_{10}H_{12}O_3S$ [M+Na]: 235.0405 found 235.0404.

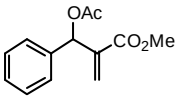
Methyl 2-((4-chloroquinolin-3-yl)(hydroxy)methyl)acrylate. Yield: 90% (2.6 g from 2.0 g); a white solid; mp: 142-143 ^{o}C; R_f = 0.30 (hexanes: EtOAc, 3:2, v/v); IR (KBr) ν: 1710 (CO_2Me), 3436 (OH) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.95 (s, 1H), 8.19 (d, *J* = 8.3 Hz, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 7.72 (t, *J* = 8.1 Hz, 1H), 7.63-7.58 (m, 1H), 6.42 (s, 1H), 6.23 (s, 1H), 5.83 (s, 1H), 4.49 (brs, 1H), 3.74 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 166.6, 149.9, 148.3, 141.0, 140.4, 131.2, 130.4, 129.6, 128.0, 127.3, 126.0, 124.5, 68.8, 52.3. MS (ESI+): *m/z* = 278.1. ESI-HR-MS calculated for $C_{14}H_{12}ClNO_3$ $[MH]^+$: 278.0584, found: 278.0589.

Methyl 2-((2,6-dichlorophenyl)(hydroxy)methyl)acrylate.[9]

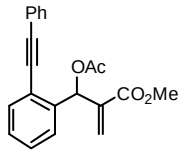


2. The MBH acetates were prepared from respective adducts according to the literature procedure.[1]

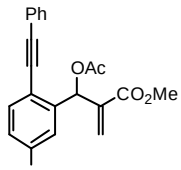
Methyl 2-(acetoxy(phenyl)methyl)acrylate.[1]



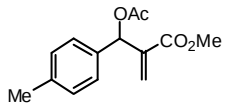
Methyl 2-(acetoxy(2-(phenylethynyl)phenyl)methyl)acrylate.[2] Yield: 90% (2.05 g from 2.0 g); yellow oil; R_f = 0.73 (hexanes: EtOAc, 3:2, v/v); IR (neat) ν: 1731 (CO_2Me and OCOMe) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.57-7.52 (m, 3H), 7.35-7.30 (m, 6H), 7.23 (s, 1H), 6.48 (s, 1H), 5.73 (s, 1 H), 3.69 (s, 3H), 2.11 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 169.5, 165.7, 139.4, 139.0, 132.6, 131.8, 128.6, 128.4, 127.5, 127.0, 123.2, 123.1, 95.0, 86.9, 71.6, 52.2, 21.1. MS (ESI+): *m/z* = 335.2. ESI-HR-MS calculated for $C_{21}H_{18}O_4$ $[MH]^+$: 335.1283 found 335.1288.



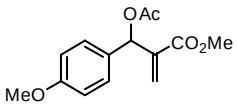
Methyl 2-(acetoxy(5-methoxy-2-(phenylethynyl)phenyl)methyl)acrylate. Yield: 88% (1.99 g from 2.0 g); an off white solid; mp: 123-124 ^oC; R_f = 0.67 (hexanes: EtOAc, 3:2, v/v); IR (neat) ν: 1724 (CO_2Me and OCOMe) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.51-7.48 (m, 3H), 7.33-7.29 (m, 3H), 7.18 (s, 1H), 6.90 (d, *J* = 2.5 Hz, 1H), 6.86-6.82 (m, 1H), 6.47 (s, 1H), 5.73 (s, 1H), 3.82 (s, 3H), 3.70 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 169.4, 165.7, 159.8, 141.2, 138.9, 134.0, 131.6, 128.5, 128.2, 127.8, 123.6, 115.3, 113.5, 113.4, 93.6, 86.9, 71.5, 55.5, 52.2, 21.1. MS (ESI+): *m/z* = 365.1. ESI-HR-MS calculated for $C_{22}H_{20}O_5$ $[MH]^+$: 365.1389, found: 365.1392.



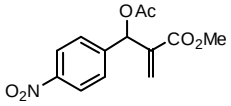
Methyl 2-(acetoxy(4-methylphenyl)methyl)acrylate.[3]



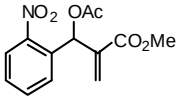
Methyl 2-(acetoxy(4-methoxyphenyl)methyl)acrylate.[14]



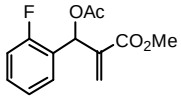
Methyl 2-(acetoxy(4-nitrophenyl)methyl)acrylate.[15]



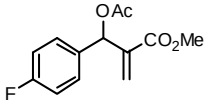
Methyl 2-(acetoxy(2-nitrophenyl)methyl)acrylate.[16]



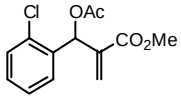
Methyl 2-(acetoxy(2-fluorophenyl)methyl)acrylate.[3]



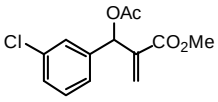
Methyl 2-(acetoxy(4-fluorophenyl)methyl)acrylate.[17]



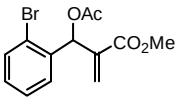
Methyl 2-(acetoxy(2-chlorophenyl)methyl)acrylate.[3]



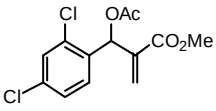
Methyl 2-(acetoxy(3-chlorophenyl)methyl)acrylate.[3]



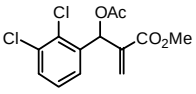
Methyl 2-(acetoxy(2-bromophenyl)methyl)acrylate.[18]



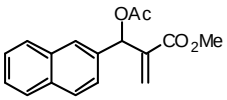
Methyl 2-(acetoxy(2,4-dichlorophenyl)methyl)acrylate.[17]



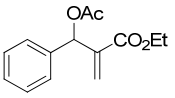
Methyl 2-(acetoxy(2,3-dichlorophenyl)methyl)acrylate.[9]

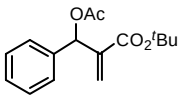


Methyl 2-(acetoxy(naphthalen-2-yl)methyl)acrylate.[7]



Ethyl 2-(acetoxy(phenyl)methyl)acrylate.[19]

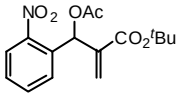


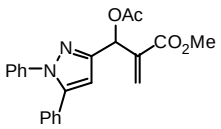


***tert*-Butyl 2-(acetoxy(phenyl)methyl)acrylate**.[14]

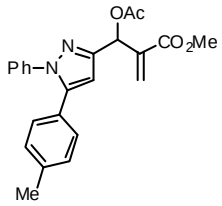
***tert*-Butyl 2-(acetoxy(2-nitrophenyl)methyl)acrylate**.[12]

Methyl 2-(acetoxy(1,5-diphenyl-1*H*-pyrazol-3-yl)methyl)acrylate.[13]

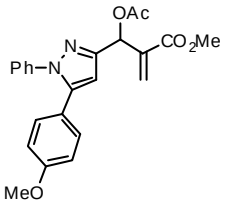




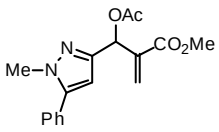
Methyl 2-(acetoxy(1-phenyl-5-(4-methylphenyl)-1*H*-pyrazol-3-yl)methyl)acrylate. Yield: 86% (1.92 g from 2.0 g); yellow oil; R_f = 0.6 (hexanes: EtOAc, 3:2, v/v); IR (neat) ν: 1729 (CO_2Me and OCOMe) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.31-7.26 (m, 5H), 7.08 (s, 4H), 6.87 (s, 1H), 6.48 (s, 1H), 6.46 (s, 1H), 6.03 (s, 1H), 3.77 (s, 3H), 2.32 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 169.9, 165.7, 150.5, 144.4, 140.3, 138.7, 129.3, 129.0, 128.8, 127.7, 127.5, 126.9, 125.5, 107.0, 68.3, 52.2, 21.4. MS (ESI+): *m/z* = 391.2. ESI-HR-MS calculated for $C_{23}H_{22}N_2O_4$ $[MH]^+$: 391.1658, found: 391.1662.



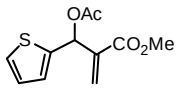
Methyl 2-(acetoxy(5-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-3-yl)methyl)acrylate. Yield: 87% (1.94 g from 2.0 g); yellow oil; R_f = 0.3 (hexanes: EtOAc, 3:2, v/v); IR (neat) ν: 1727. (CO_2Me and OCOMe) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.31-7.27 (m, 5H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.85 (s, 1H), 6.82 (s, 1H), 6.79 (s, 1H), 6.48 (s, 1H), 6.43 (s, 1H), 6.03 (s, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 169.6, 165.6, 159.7, 150.0, 143.8, 140.1, 138.6, 130.1, 128.9, 127.5, 126.7, 125.4, 122.7, 114.0, 106.6, 68.2, 55.3, 52.1, 21.2. MS (ESI+): *m/z* = 407.2. ESI-HR-MS calculated for $C_{23}H_{22}N_2O_5$ $[MH]^+$: 407.1607, found: 407.1612.



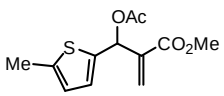
Methyl 2-(acetoxy(1-methyl-5-phenyl-1*H*-pyrazol-3-yl)methyl)acrylate. Yield: 89% (2.05 g from 2.0 g); yellow oil; R_f = 0.3 (hexanes: EtOAc, 3:2, v/v); IR (neat) ν: 1742. (CO_2Me and OCOMe) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.44-7.38 (m, 5H), 6.80 (s, 1H), 6.46 (s, 1H), 6.30 (s, 1H), 6.00 (s, 1H), 3.86 (s, 3H), 3.76 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 169.6, 165.6, 148.3, 144.5, 138.6, 130.4, 128.8, 128.7, 128.6, 126.2, 105.4, 68.1, 52.0, 37.7, 21.2. MS (ESI+): *m/z* = 315.1. ESI-HR-MS calculated for $C_{17}H_{18}N_2O_4$ $[MH]^+$: 315.1345, found: 315.1349.



Methyl 2-(acetoxy(thiophen-2-yl)methyl)acrylate.[1]

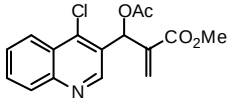


Methyl 2-(acetoxy(5-methylthiophen-2-yl)methyl)acrylate. Yield: 85% (2.04 g from 2.0 g); yellow oil; R_f = 0.54 (hexanes: EtOAc, 3:2, v/v); IR (neat) ν: 1745. (CO_2Me and OCOMe) cm^{-1}. ^1H NMR (300



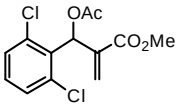
MHz, $CDCl_3$): δ (ppm) = 6.84 (t, J = 3.4 Hz, 2H), 6.60 (d, J = 2.6 Hz, 1H), 6.41 (s, 1H), 5.98 (s, 1H), 3.74 (s, 3H), 2.44 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 169.4, 165.3, 141.2, 139.5, 138.3, 127.4, 125.5, 125.1, 68.6, 52.2, 21.1, 15.4; mass (ES+): *m/z* = 255.1. ESI-HR-MS calculated for $C_{12}H_{14}O_4S$ $[MH]^+$: 255.0691, found: 255.0694.

Methyl 2-(acetoxy(4-chloroquinolin-3-yl)methyl)acrylate. Yield: 86% (1.98 g from 2.0 g); brown oil;



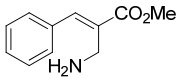
R_f = 0.67 (hexanes: EtOAc, 3:2, v/v); IR (neat): 1729 (CO_2Me and OCOMe) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.87 (s, 1H), 8.30 (d, J = 8.3 Hz, 1H), 8.12 (d, J = 8.3 Hz, 1H), 7.79 (s, 1H), 7.68 (d, J = 7.2 Hz, 1H), 6.56 (s, 1H), 5.90 (s, 1H), 5.29 (s, 1H), 3.74 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 169.4, 165.3, 149.7, 148.9, 142.3, 137.9, 130.9, 130.1, 128.5, 128.4, 126.4, 125.0, 70.3, 52.6, 21.3. MS (ESI+): *m/z* = 320.1. ESI-HR-MS calculated for $C_{16}H_{14}ClNO_4$ $[MH]^+$: 320.0690, found: 320.0695.

Methyl 2-(acetoxy(2,6-dichlorophenyl)methyl)acrylate.[9]

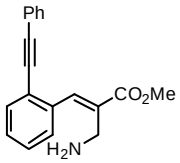


3: All primary allylamines from the MBH acetates were prepared according to the literature procedure.[9]

(*E*)-Methyl 2-(aminomethyl)-3-phenylacrylate (Table 2, entry 1, **1**).[8]

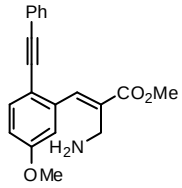


(*E*)-Methyl 2-(aminomethyl)-3-(2-(phenylethynyl)phenyl)acrylate (Table 2, entry 2, **1**)**.** Yield: 75%



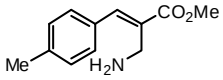
(1.31 g from 2.0 g); a brown solid; mp: 101-102 ^{o}C; R_f = 0.48 ($CHCl_3$: MeOH, 9:1, v/v); IR (KBr) ν: 1710 (CO_2Me), 3435 (NH_2) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.16 (s, 1H), 7.57 (d, J = 2.5 Hz, 1H), 7.52 (d, J = 3.4 Hz, 2H), 7.42 (s, 1H), 7.36-7.35 (m, 5H), 3.88 (s, 3H), 3.72 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 167.8, 142.0, 136.4, 132.4, 131.8, 130.1, 129.2, 128.9, 128.8 128.7, 128.6, 123.7, 123.0, 95.7, 87.4, 52.5, 38.0. MS (ESI+): *m/z* = 292.0. ESI-HR-MS calculated for $C_{19}H_{17}NO_2$ $[MH]^+$: 292.1338, found: 292.1342.

(*E*)-Methyl 2-(aminomethyl)-3-(5-methoxy-2-(phenylethynyl)phenyl)acrylate (Table 2, entry 3, **1**)**.**

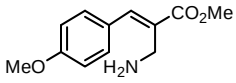


Yield: 74% (1.3 g from 2.0 g); a yellow solid; mp: 103-105 C; R_f = 0.48 ($CHCl_3$: MeOH, 9:1, v/v); IR (KBr) ν: 1705 (CO_2Me), 3432 (NH_2) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.10 (s, 1H), 7.52-7.47 (m, 3H), 7.33 (d, J = 3.7 Hz, 3H), 6.98 (s, 1H), 6.89 (d, J = 8.3 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 3.72 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 167.7, 159.7, 142.0, 137.9, 133.8, 131.5, 130.4, 128.6, 128.5, 123.3, 115.73, 115.1, 114.3, 94.1, 87.5, 55.7, 52.5, 38.1. MS (ESI+): *m/z* = 322.0. ESI-HR-MS calculated for $C_{20}H_{19}NO_3$ $[MH]^+$: 322.1443, found: 322.1448.

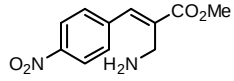
(*E*)-Methyl 2-(aminomethyl)-3-(4-methylphenyl)acrylate (Table 2, entry 4, **1**).[1]



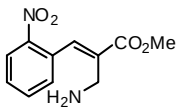
(*E*)-Methyl 2-(aminomethyl)-3-(4-methoxyphenyl)acrylate (Table 2, entry 5, **1**)**.**[20]



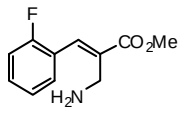
(*E*)-Methyl 2-(aminomethyl)-3-(4-nitrophenyl)acrylate (Table 2, entry 6, **1**)**.** Yield: 72 % (1.21 g from 2.0 g); a white solid; mp: 109-110 C; R_f = 0.51 ($CHCl_3$: MeOH, 9:1, v/v); IR (KBr) ν: 1708 (CO_2Me), 3435 (NH_2) cm^{-1}; H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ (ppm) = 8.28 (d, J = 8.4 Hz, 2H), 7.99 (s, 1H), 7.66 (d, J = 8.5 Hz, 2H), 3.90 (s, 3H), 3.85 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ (ppm) = 165.0, 146.8, 141.3, 139.1, 129.3, 128.5, 127.5, 122.8, 122.1, 51.6, 35.2. MS (ESI+): *m/z* = 237.0. ESI-HR-MS calculated for $C_{11}H_{12}N_2O_4$ $[MH]^+$: 237.0875, found: 237.0875.



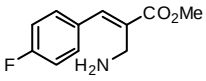
(*E*)-Methyl 2-(aminomethyl)-3-(2-nitrophenyl)acrylate (Table 2, entry 7, **1**)**.**[20]



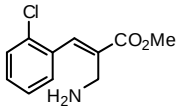
(*E*)-Methyl 2-(aminomethyl)-3-(2-fluorophenyl)acrylate (Table 2, entry 8, **1**)**.**[1]



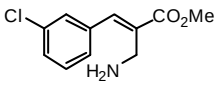
(*E*)-Methyl 2-(aminomethyl)-3-(4-fluorophenyl)acrylate (Table 2, entry 9, **1**).[1]



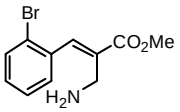
(*E*)-Methyl 2-(aminomethyl)-3-(2-chlorophenyl)acrylate (Table 2, entry 10, **1**).[1]



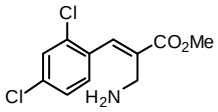
(*E*)-Methyl 2-(aminomethyl)-3-(3-chlorophenyl)acrylate (Table 2, entry 11, **1**). Yield: 70% (1.12 g from 2.0 g); colourless oil; R_f = 0.42 ($CHCl_3$: MeOH, 9:1, v/v); IR (KBr) ν: 1709 (CO_2Me), 3434 (NH_2) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.75 (s, 1H), 7.38 (s, 1H), 7.30-7.26 (m, 3H), 3.85 (s, 3H), 3.76 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 167.7, 141.0, 136.3, 134.8, 131.5, 130.2, 129.3, 127.4, 52.5, 37.9. MS (ESI+): *m/z* = 226.0. ESI-HR-MS calculated for $C_{11}H_{12}ClNO_2$ $[MH]^+$: 226.0635, found: 226.0639.



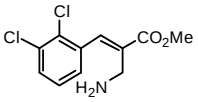
(*E*)-Methyl 2-(aminomethyl)-3-(2-bromophenyl)acrylate (Table 2, entry 12, **1**).[8]



(*E*)-Methyl 2-(aminomethyl)-3-(2,4-dichlorophenyl)acrylate (Table 2, entry 13, **1**).[1]

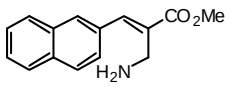


(*E*)-Methyl 2-(aminomethyl)-3-(2,3-dichlorophenyl)acrylate (Table 2, entry 14, **1**). Yield: 70% (1.2 g from 2.0 g); a white solid; mp:112-114 ^oC; R_f = 0.45 ($CHCl_3$: MeOH, 9:1, v/v); IR (KBr) ν: 1707 (CO_2Me), 3436 (NH_2) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.83

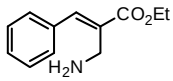


(s, 1H), 7.49 (d, J = 9.0 Hz, 1H), 7.40-7.36 (m, 1H), 7.30 (d, J = 7.7 Hz, 1H), 3.89 (s, 3H), 3.63 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ (ppm) = 166.2, 138.9, 134.6, 132.8, 131.3, 130.8, 130.3, 128.2, 127.2, 52.0, 37.0. MS (ESI+): m/z = 260.0. ESI-HR-MS calculated for $C_{11}H_{11}Cl_2NO_2$ $[MH]^+$: 260.0245 found: 260.0242.

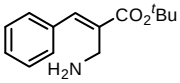
(*E*)-Methyl 2-(aminomethyl)-3-(naphthalen-2-yl)acrylate (Table 2, entry 15, **1**). Yield: 76% (1.29 g from 2.0 g); an off white solid; mp = 104-106 ^{o}C; R_f = 0.58 ($CHCl_3$: MeOH, 9:1, v/v); IR (KBr) ν: 1710 (CO_2Me), 3439 (NH_2) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.94 (s, 1H), 7.90-7.83 (m, 4H), 7.53-7.48 (m, 3H), 3.88 (s, 3H), 3.84 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 167.6, 140.4, 132.6, 131.7, 128.7, 127.9, 127.8, 127.1, 126.5, 126.1, 51.6, 37.8. MS (ESI+)*:* m/z = 242.1. ESI-HR-MS calculated for $C_{15}H_{15}NO_2$ $[MH]^+$: 242.1181, found: 242.1185.



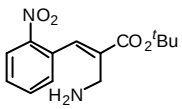
(*E*)-Ethyl 2-(aminomethyl)-3-phenylacrylate (Table 2, entry 16, **1**)**.**[21]



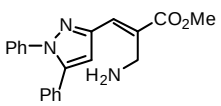
(*E*)-*tert*-Butyl 2-(aminomethyl)-3-phenylacrylate (Table 2, entry 17, **1**)**.**[22]



(*E*)-*tert*-Butyl 2-(aminomethyl)-3-(2-nitrophenyl)acrylate (Table 2, entry 18, **1**)**.** Yield: 74% (1.28 g from 2.0 g); a White solid; mp: 67-68 ^{o}C; R_f = 0.33 ($CHCl_3$: MeOH, 9:1, v/v); IR (KBr) ν: 1700 (CO_2Me), 3406 (NH_2) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.18 (dd, J_1 = 8.2 Hz, J_2 = 0.7 Hz, 1H), 7.94 (s, 1H), 7.71-7.67 (m, 1H), 7.54 (t, J = 7.5 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 3.50 (s, 2H), 1.57 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 166.1, 147.8, 139.5, 134.5, 131.7, 131.4, 130.8, 129.8, 125.2, 82.6, 38.0, 28.2. MS (ESI+): m/z = 278.9. ESI-HR-MS calculated for $C_{14}H_{18}N_2O_4$ $[MH]^+$: 279.1345; found: 279.1349

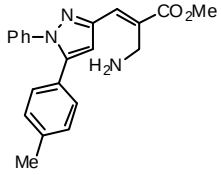


(*E*)-Methyl 2-(aminomethyl)-3-(1,5-diphenyl-1*H*-pyrazol-3-yl)acrylate (Table 2, entry 19, **1**). Yield: 71% (1.26 g from 2.0 g); a white solid; mp: 92-94 ^{o}C; R_f = 0.42 ($CHCl_3$: MeOH, 9:1, v/v); IR (KBr) ν:



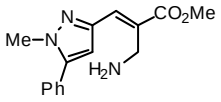
1708 (CO_2Me), 3435 (NH_2) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.71 (s, 1H), 7.33 (brs, 7H), 7.26-7.24 (m, 3H), 6.68 (s, 1H), 4.07 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 167.8, 147.2, 144.7, 139.5, 132.98, 129.7, 129.2, 128.9, 128.8, 128.2, 125.1, 111.1, 52.5, 37.6. MS (ESI+): *m/z* = 334.2. ESI-HR-MS calculated for $C_{20}H_{19}N_3O_2$ $[MH]^+$: 334.1556, found: 334.1561.

(*E*)-Methyl 2-(aminomethyl)-3-(1-phenyl-5-(4-methylphenyl)-1*H*-pyrazol-3-yl)acrylate (Table 2, entry 20, **1**). Yield: 71% (1.27 g from 2.0 g); a white solid; mp: 110-111 ^oC; R_f = 0.26 ($CHCl_3$: MeOH, 9:1, v/v); IR (KBr) ν: 1710 (CO_2Me), 3439 (NH_2) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.72 (s, 1H), 7.34 (s, 5H), 7.12 (s, 4H), 6.65 (s, 1H), 4.09 (s, 2H), 3.85 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 167.8, 147.1, 144.8, 139.6, 139.0, 133.16, 129.5, 129.2, 128.8, 128.2, 126.8, 125.2, 110.9, 52.5. MS (ESI+): *m/z* = 348.0. ESI-HR-MS calculated for $C_{21}H_{21}N_3O_2$ $[MH]^+$: 348.1712, found: 348.1704.

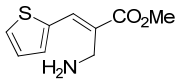


(*E*)-Methyl 2-(aminomethyl)-3-(5-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-3-yl)acrylate (Table 2, entry 21, **1**). Yield: 68% (1.21 g from 2.0 g); a pale yellow solid; mp: 104-105 ^oC; R_f = 0.26 ($CHCl_3$: MeOH, 9:1, v/v); IR (KBr) ν: 1708 (CO_2Me), 3437 (NH_2) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.75 (s, 1H), 7.34 (s, 5H), 7.14 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.63 (s, 1H), 4.14 (s, 2H), 3.83 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 167.6, 160.2, 147.0, 144.7, 139.6, 133.8, 130.3, 129.3, 128.2, 125.1, 121.9, 114.3, 110.7, 55.4, 52.6, 37.4. MS (ESI+): *m/z* = 364.2. ESI-HR-MS calculated for $C_{21}H_{21}N_3O_3$ $[MH]^+$: 364.1661, found: 364.1667.

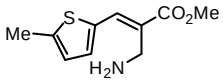
(*E*)-Methyl 2-(aminomethyl)-3-(1-methyl-5-phenyl-1*H*-pyrazol-3-yl)acrylate (Table 2, entry 22, **1**). Yield: 75% (1.29 g from 2.0 g); an off white solid; mp: 125-127 C; R_f = 0.23 ($CHCl_3$: MeOH, 9:1, v/v); IR (KBr) ν: 1710 (CO_2Me), 3436 (NH_2) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.66 (s, 1H), 7.47-7.46 (m, 3H), 7.43-7.42 (m, 2H), 6.50 (s, 1H), 4.06 (s, 2H), 3.94 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 168.0, 145.7, 145.4, 133.3, 129.9, 129.3, 129.1, 129.0, 128.7, 109.7, 52.5, 38.4, 37.5. MS (ESI+): *m/z* = 272.1. ESI-HR-MS calculated for $C_{15}H_{17}N_3O_2$ $[MH]^+$: 272.1399, found: 272.1404.



(E)-Methyl 2-(aminomethyl)-3-(thiophen-2-yl)acrylate (Table 2, entry 23, **1**).[1]

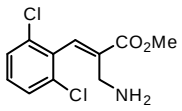


(*E*)-Methyl 2-(aminomethyl)-3-(5-methylthiophen-2-yl)acrylate (Table 2, entry 24, **1**). Yield: 75% (1.23 g from 2.0 g); a yellow solid; mp: 124-125 ^{o}C; R_f = 0.30 ($CHCl_3$: MeOH, 9:1, v/v); IR (KBr) ν: 1712 (CO_2Me), 3438 (NH_2) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.80 (s, 1H), 7.18 (d, J = 3.5 Hz, 1H), 6.82 (d, J = 3.4 Hz, 1H), 3.93 (s, 2H), 3.88 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 176.8, 168.3, 146.4, 135.0, 134.5, 126.4, 124.2, 52.4, 37.9, 15.8. MS (ESI+): *m/z* = 212.1. ESI-HR-MS calculated for $C_{10}H_{13}NO_2S$ $[MH]^+$: 212.0745, found: 212.0749.



(*E*)-Methyl 2-(aminomethyl)-3-(4-chloroquinolin-3-yl)acrylate (Table 2, entry 25, **1**). Yield: 76% (1.31 g from 2.0 g); a yellow solid; mp: 132-134 ^{o}C; R_f = 0.63 ($CHCl_3$: MeOH, 9:1, v/v); IR (KBr) ν: 1719 (CO_2Me), 3440 (NH_2) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ (ppm) = 8.28 (d, J = 8.3 Hz, 1H), 8.20 (s, 1H), 7.82 (d, J = 7.3 Hz, 1H), 7.70-7.65 (m, 1H), 7.48-7.43 (m, 2H), 4.69 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ (ppm) = 163.6, 151.0, 142.4, 141.9, 131.5, 130.7, 124.8, 122.7, 122.4, 118.3, 115.0, 106.2, 50.8, 42.0. MS (ESI+): *m/z* = 277.1. ESI-HR-MS calculated for $C_{10}H_{13}NO_2S$ $[MH]^+$: 277.0744, found: 277.0749.

(*E*)-Methyl 2-(aminomethyl)-3-(2,6-dichlorophenyl)acrylate (Table 2, entry 26, **1**).[9] Yield: 70% (1.20 g from 2.0 g); yellow solid; mp: 106-107 ^{o}C; R_f = 0.43 ($CHCl_3$: MeOH, 9:1, v/v); IR (KBr) ν: 1709 (CO_2Me), 3438 (NH_2) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.51 (s, 1 H), 7.42 (d, J = 7.9 Hz, 1H), 7.31 (d, J = 6.6 Hz, 2H), 3.95 (s, 3H), 3.40 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 166.8, 135.7, 135.4, 134.2, 132.8, 130.2, 128.3, 52.6, 39.2. MS (ESI+): *m/z* = 260.1. ESI-HR-MS calculated for $C_{11}H_{11}Cl_2NO_2$ $[MH]^+$: 260.0245, found: 260.0249.

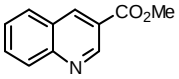


4. General procedure for the iodine-mediated reaction of allylamines as exemplified for the preparation of methyl quinoline-3-carboxylate (Table 2, entry 1, **2**) from (*E*)-methyl 2-(aminomethyl)-3-phenylacrylate (Table 2, entry 1, **1**).

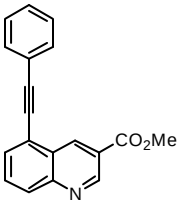
To a stirred solution of (*E*)-methyl 2-(aminomethyl)-3-phenylacrylate (0.29 g, 1.5 mmol) in $CHCl_3$ (15 mL) was added Iodine (1.14 g, 4.5 mmol). After 5 min K_2CO_3 (0.62 g, 4.5 mmol) was added and the

mixture was left for stirring at room temperature till completion of reaction (by TLC, 30 min). Thereafter the reaction was quenched by adding 10 mL of saturated solution of sodium thiosulphate. The mixture was partitioned in a separating funnel and the aqueous layer was further extracted with $CHCl_3$ (3 x 5 mL). The extracts were pooled, dried over anhyd. Na_2SO_4 and evaporated in vacuo to afford the crude product which was purified by column chromatography (silica gel, 20-40% EtOAc in hexanes) to get 0.24 g (84%) of the pure product **2** as a yellow solid**.**

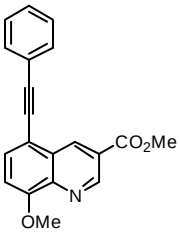
Methyl quinoline-3-carboxylate (Table 2, entry 1, **2**)**.**[23] Mp 70-72 ^oC; R_f = 0.58 (hexanes: EtOAc, 3:2, v/v); IR (KBr) ν: 1717 (CO_2Me) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.46 (d, J = 1.6 Hz, 1H), 8.86 (s, 1H), 8.17 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 7.8 Hz, 1H), 7.84 (t, J = 7.1 Hz, 1H), 7.63 (t, J = 7.2 Hz, 1H), 4.03 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 165.9, 150.1, 149.9, 138.9, 132.0, 129.6, 129.2, 127.6, 127.0, 123.1, 52.6. MS (ESI+): *m/z* = 188.0. ESI-HR-MS calculated for $C_{11}H_9NO_2$ $[MH]^+$: 188.0712, found: 188.0716.



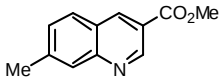
Methyl 5-(phenylethynyl)quinoline-3-carboxylate (Table 2, entry 2, **2**). Yield: 72% (0.31 g from 0.44 g); an off white solid; mp: 84-85 ^oC; R_f = 0.5 (hexanes: EtOAc, 3:2, v/v); IR (KBr) ν: 1723 (CO_2Me) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.47 (d, J = 1.5 Hz, 1H), 9.35 (d, J = 1.3 Hz, 1H), 8.14 (d, J = 6.2 Hz, 1H), 7.86-7.84 (m, 1H), 7.81-7.77 (m, 1H), 7.68-7.66 (m, 2H), 7.43-7.41 (m, 3H), 4.04 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 165.9, 150.6, 149.8, 137.2, 132.0, 131.5, 131.4, 130.5, 130.2, 129.1, 128.7, 127.4, 123.7, 123.0, 122.8, 96.2, 85.7, 52.8. MS (ESI+): *m/z* = 288.1. ESI-HR-MS calculated for $C_{19}H_{13}NO_2$ $[MH]^+$: 288.1025, found: 288.1029.



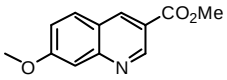
Methyl 8-methoxy-5-(phenylethynyl)quinoline-3-carboxylate (Table 2, entry 3, **2**). Yield: 73% (0.35 g from 0.48 g); an off white solid; mp: 85-86 ^oC; R_f = 0.32 (hexanes: EtOAc, 3:2, v/v); IR (KBr) ν: 1729 (CO_2Me) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.48 (d, J = 1.8 Hz, 1H), 9.34 (d, J = 1.7 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.65 (d, J = 4.5 Hz, 2H), 7.40 (d, J = 3.1 Hz, 3H), 7.16 (d, J = 8.1 Hz, 1H), 4.15 (s, 3H), 4.05 (s, 3H); ^{13} C NMR (75 MHz, $CDCl_3$): δ (ppm) = 166.0, 156.1, 149.4, 141.7, 137.7, 132.3, 131.9, 128.8, 128.7, 128.6, 124.3, 114.4, 109.8, 94.4, 86.2, 56.9, 53.0. MS (ESI+): *m/z* = 318.2. ESI-HR-MS calculated for $C_{20}H_{15}NO_3$ $[MH]^+$: 318.1130, found: 318.1134.



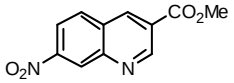
Methyl 7-methylquinoline-3-carboxylate (Table 2, entry 4, **2**)**.** Yield: 75% (0.23 g from 0.31 g); an off white solid; mp: 121-122 °C; R_f = 0.6 (hexanes: EtOAc, 3:2, v/v); IR (KBr) ν: 1719 (CO_2Me) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.41 (s, 1H), 8.79 (s, 1H), 7.94 (s, 1H), 7.82 (d, J = 8.3 Hz, 1H), 7.46 (d, J = 8.1 Hz, 1H), 4.01 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) = 166.1, 150.2, 142.9, 138.6, 129.9, 128.9, 128.6, 125.0, 122.3, 52.5, 22.3. MS (ESI+): *m/z* = 202.1. ESI-HR-MS calculated for $C_{12}H_{11}NO_2$ $[MH]^+$: 202.0868, found: 202.0872.



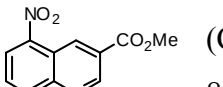
Methyl 7-methoxyquinoline-3-carboxylate (Table 2, entry 5, **2**). Yield: 84% (0.27 g from 0.33 g); a brown solid; mp: 110-112 °C; R_f = 0.46 (hexanes: EtOAc, 3:2, v/v); IR (KBr) ν: 1708 (CO_2Me) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.39 (s, 1H), 8.76 (s, 1H), 7.82 (d, J = 8.9 Hz, 1H), 7.49 (s, 1H), 7.28 (s, 1H), 4.02 (s, 3H), 4.00 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 166.2, 162.8, 152.1, 150.6, 138.3, 130.3, 122.2, 121.1, 120.9, 107.6, 55.8, 52.4. MS (ESI+): *m/z* = 218.1. ESI-HR-MS calculated for $C_{12}H_{11}NO_3$ $[MH]^+$: 218.0817, found: 218.0823.



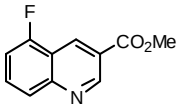
Methyl 7-nitroquinoline-3-carboxylate (Table 2, entry 6, **2**). Yield: 79% (0.28 g from 0.35 g); an off white solid; mp: 220-221 °C; R_f = 0.64 (hexanes: EtOAc, 3:2, v/v); IR (KBr) ν: 1708 (CO_2Me) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ (ppm) = 9.58 (s, 1H), 9.02 (s, 1H), 8.99 (s, 1H), 8.40 (d, J = 8.7 Hz, 1H), 8.20 (d, J = 8.5 Hz, 1H), 4.06 (s, 3H); ^{13} C NMR (150 MHz, $CDCl_3$ + DMSO-d_6): δ (ppm) = 164.5, 151.5, 138.5, 131.6, 130.0, 125.0, 124.4, 120.6, 111.7, 52.8. MS (ESI+): *m/z* = 233.1. ESI-HR-MS calculated for $C_{11}H_8N_2O_4$ $[MH]^+$: 233.0562, found: 233.0567.



Methyl 5-nitroquinoline-3-carboxylate (Table 2, entry 7, **2**).[24] Yield: 82% (0.29 g from 0.36 mg); a white solid; mp: 82-85 °C; R_f = 0.53 (hexanes: EtOAc, 3:2, v/v); IR (KBr) ν: 1707 (CO_2Me) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.63 (s, 1H), 9.57 (s, 1H), 8.50-8.44 (m, 2H), 7.93 (t, J = 7.9 Hz, 1H), 4.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 165.2, 151.5, 149.7, 146.3, 136.6, 134.6, 129.9, 125.7, 125.5, 120.2, 53.1. MS (ESI+): *m/z* = 233.1. ESI-HR-MS calculated for $C_{11}H_8N_2O_4$ $[MH]^+$: 233.0562, found: 233.0565.

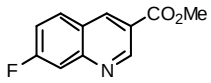


Methyl 5-fluoroquinoline-3-carboxylate (Table 2, entry 8, **2**). Yield: 81% (0.25 g from 0.31 g); a brown solid; mp: 135-136 °C; R_f = 0.73 (hexanes: EtOAc, 3:2, v/v); IR (KBr) ν: 1711

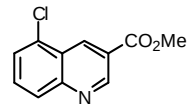


(CO_2Me) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.48 (d, J = 1.6 Hz, 1H), 9.12 (s, 1H), 7.98 (d, J = 8.6 Hz, 1 H), 7.81-7.77 (m, 1H), 7.32-7.29 (m, 1H), 4.04 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) = 165.6, 158.8 (d, J = 274.9 Hz), 151.3, 132.4 (d, J = 4.5 Hz), 131.8 (d, J = 9.0 Hz), 125.6 (d, J = 5.0 Hz), 123.4 (d, J = 2.7 Hz), 118.1 (d, J = 16.3 Hz), 111.30 (d, J = 19.9 Hz), 52.8. MS (ESI+): m/z = 206.0. ESI-HR-MS calculated for $C_{11}H_8FNO_2$ $[MH]^+$: 206.0617, found: 206.0622.

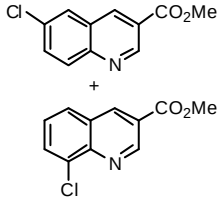
Methyl 7-fluoroquinoline-3-carboxylate (Table 2, entry 9, **2**). Yield: 80% (0.24 g from 0.31 g); a brown solid; mp = 134-135 ^oC; R_f = 0.53 (hexanes: EtOAc, 3:2, v/v); IR (KBr) ν: 1723 (CO_2Me) cm^{-1}.; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.45 (s, 1H), 8.84 (s, 1 H), 7.98-7.93 (m, 1H), 7.81-7.78 (m, 1H), 7.45-7.39 (m, 1H), 4.02 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) = 167.1, 164.6 (d, J = 252.5 Hz), 151.2, 138.7, 131.5 (d, J = 10.3 Hz), 124.0, 122.7, 118.3 (d, J = 10.3 Hz), 113.5 (d, J = 20.5 Hz), 52.7. MS (ESI+): m/z = 206.1. ESI-HR-MS calculated for $C_{11}H_8FNO_2$ $[MH]^+$: 206.0617, found: 206.0619.



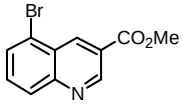
Methyl 5-chloroquinoline-3-carboxylate (Table 2, entry 10, **2**)**.** Yield: 83% (0.28 g from 0.34 g); an off white solid; mp: 80-82 ^oC; R_f = 0.51 (hexanes: EtOAc, 3:2, v/v); IR (KBr) ν: 1723 (CO_2Me) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.48 (d, J =1.6 Hz, 1H), 9.24 (s, 1H), 8.09 (d, J = 7.9 Hz, 1H), 7.75-7.71 (m, 2H), 4.05 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) = 165.6, 150.8, 150.6, 135.7, 132.8, 131.6, 128.7, 127.6, 125.4, 123.9, 52.8. MS (ESI+): m/z = 222.1. ESI-HR-MS calculated for $C_{11}H_8ClNO_2$ $[MH]^+$: 222.0322, found: 222.0325.



Methyl 6-chloroquinoline-3-carboxylate and methyl 8-chloroquinoline-3-carboxylate (Table 2, entry 11, **2**)**.** Yield: 77% (0.26 g from 0.34 g); a white solid; mp: 149-150 ^oC; R_f = 0.71 (hexanes: EtOAc, 3:2, v/v); IR (KBr) ν: 1725 (CO_2Me) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.56 (s, 1H), 9.44 (s, 1H), 8.88 (s, 1H), 8.77 (s, 1H), 8.11 (d, J = 8.7 Hz, 1H), 7.98-7.87 (m, 3H), 7.77 (d, J =8.8 Hz, 1H), 7.56-7.54 (m, 1H), 4.04 (s, 3H), 4.03 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) = 165.6, 150.7, 150.4, 139.4, 137.9, 133.5, 132.9, 132.1, 131.3, 128.4, 127.7, 127.6, 124.1, 124.0, 52.84, 52.80. MS (ESI+): m/z = 222.1. ESI-HR-MS calculated for $C_{11}H_8ClNO_2$ $[MH]^+$: 222.0322, found: not done.



Methyl 5-bromoquinoline-3-carboxylate (Table 2, entry 12, **2**)**.** Yield: 82% (0.32 g from 0.4 g); a white solid, mp = 107-109 ^oC; R_f = 0.51 (hexanes: EtOAc, 3:2, v/v); IR (KBr) ν: 1730.



(CO_2Me) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.46 (d, J = 1.7 Hz, 1H), 9.20 (s, 1H), 8.14 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 7.3 Hz, 1H), 7.71-7.66 (m, 1H), 4.05 (s, 3H); ^{13} C NMR (50 MHz, $CDCl_3$): δ (ppm) = 165.6, 150.8, 150.8, 138.3, 132.1, 131.4, 129.6, 126.7, 124.3, 123.4, 52.9. MS (ESI+): *m/z* = 266.1. ESI-HR-MS calculated for $C_{11}H_8BrNO_2$ $[MH]^+$: 265.9817, found: 265.9820.

Methyl 5,7-dichloroquinoline-3-carboxylate (Table 2, entry 13, **2**)**.** Yield: 73% (0.28 g from 0.39 g); a white solid; mp: 149-151 ^oC; R_f = 0.79 (hexanes: EtOAc, 3:2, v/v); IR (KBr) ν: 1731 (CO_2Me) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.48 (s, 1H), 9.18 (s, 1H), 8.09 (s, 1H), 7.70 (s, 1H), 4.04 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) = 165.3, 151.9, 137.4, 135.6, 133.7, 128.5, 128.0, 124.0, 52.9. MS (ESI+): *m/z* = 256.2. ESI-HR-MS calculated for $C_{11}H_7Cl_2NO_2$ $[MH]^+$: 255.9932, found: 255.9937.

Methyl 5,6-dichloroquinoline-3-carboxylate (Table 2, entry 14, **2**)**.** Yield: 77% (0.29 g from 0.39 g); a yellow solid; mp: 121-122 ^oC; R_f = 0.67 (hexanes: EtOAc, 3:2, v/v); IR (KBr) ν: 1727 (CO_2Me) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.46 (d, J = 1.5 Hz, 1H), 9.23 (s, 1H), 8.04 (d, J = 9.0 Hz, 1H), 7.85 (d, J = 9.0 Hz, 1H), 4.05 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) = 165.3, 150.7, 148.9, 135.6, 133.0, 132.2, 130.4, 129.5, 126.3, 124.6, 52.9. MS (ESI+): *m/z* = 256.2. ESI-HR-MS calculated for $C_{11}H_7Cl_2NO_2$ $[MH]^+$: 255.9932, found: 255.9935

Methyl benzo[*h*]quinoline-3-carboxylate (Table 2, entry 15, **2**).[25] Yield: 28% (0.1 g from 0.36 g); an off white solid; mp: 124-125 ^oC; R_f = 0.89 (hexanes: EtOAc, 3:2, v/v); IR (KBr) ν: 1717. (CO_2Me) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.54 (d, J =1.6 Hz, 1 H), 9.34-9.32 (m, 1H), 8.83 (s, 1H), 7.95-7.86 (m, 2H), 7.76 (d, J = 5.8 Hz, 3H), 4.04 (s, 3H); ^{13}C NMR (75 MHz, Acetone-d_6): δ (ppm) = 166.3, 149.5, 138.4, 135.6, 131.8, 130.2, 129.5, 128.9, 128.2, 126.7, 126.2, 125.7, 124.7, 52.7. MS (ESI+): *m/z* = 238.1. ESI-HR-MS calculated for $C_{15}H_{11}NO_2$ $[MH]^+$: 238.0868, found: 238.0871.

Ethyl quinoline-3-carboxylate (Table 2, entry 16, **2**)**.** Yield: 82% (0.25 g from 0.31 g); an orange solid; mp: 68-69 ^oC; R_f = 0.76 (hexanes: EtOAc, 3:2, v/v); IR (KBr) ν: 1720 (CO_2Me) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.46 (s, 1H), 8.85 (s, 1H), 8.17 (d, J = 8.5 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.86-7.81 (m, 1H), 7.62 (t, J = 7.3 Hz, 1H), 4.49 (q, J = 7.0 Hz, 2H), 1.47 (t,

J = 7.0 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) = 165.5, 150.1, 149.9, 138.8, 131.9, 129.5, 129.2, 127.5, 126.9, 123.4, 61.6, 14.5. MS (ESI+): *m/z* = 202.1. ESI-HR-MS calculated for $C_{12}H_{11}NO_2$ $[MH]^+$: 202.0868; found: 202.0872.

***tert*-Butyl quinoline-3-carboxylate** (Table 2, entry 17, **2**). Yield: 80% (0.27 g from 0.35 g); an off white solid; mp: 57-58 ^{o}C; R_f = 0.76 (hexanes: EtOAc, 3:2, v/v); IR (KBr) ν: 1716 (CO_2Me) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.41 (d, *J* = 1.9 Hz, 1H), 8.77 (d, *J* = 1.5 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.84-7.79 (m, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 1.66 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 164.6, 150.4, 149.8, 138.5, 131.7, 129.6, 129.2, 127.4, 127.0, 124.9, 82.3, 28.4. MS (ESI+): *m/z* = 229.9. ESI-HR-MS calculated for $C_{14}H_{15}NO_2$ $[MH]^+$: 230.1181; found: 230.1185.

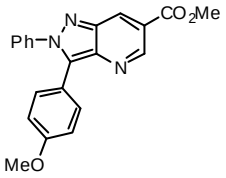
***tert*-Butyl 5-nitroquinoline-3-carboxylate:** (Table 2, entry 18, **2**) Yield: 76% (0.31 g from 0.42 g); a yellow solid; m p: 98-100 ^{o}C; R_f = 0.60 (hexanes: EtOAc, 3:2, v/v); IR (KBr) ν: 1717 (CO_2Me) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.54 (s, 1H), 9.51 (d, *J* = 1.8 Hz, 1H), 8.48-8.46 (m, 1H), 8.44-8.41 (m, 1H), 7.90 (t, *J* = 7.9 Hz, 1H), 1.67 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 163.7, 151.7, 149.5, 146.4, 136.5, 134.2, 129.5, 127.4, 125.3, 120.2, 83.2, 28.3. MS (ESI+): *m/z* = 275.0. ESI-HR-MS calculated for $C_{14}H_{14}N_2O_4$ $[MH]^+$: 275.1032; found: 275.1035.

Methyl 2,3-diphenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (Table 2, entry 19, **2**).[26] Yield: 69% (0.34 g from 0.52 g); a white solid; mp: 109-110 ^{o}C; R_f = 0.68 (hexanes: EtOAc, 3:2, v/v); IR (KBr): 1714 (CO_2Me) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.23 (s, 1H), 8.84 (s, 1H), 7.55-7.53 (m, 2H), 7.46-7.42 (m, 5H), 7.40 (s, 3H), 4.02 (s, 3H). MS (ESI+): *m/z* = 330.3. ESI-HR-MS calculated for $C_{20}H_{15}N_3O_2$ $[MH]^+$: 330.1243, found: 330.1247.

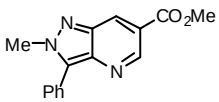
Methyl 2-phenyl-3-(4-methylphenyl)-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (Table 2, entry 20, **2**).[26] Yield: 72% (0.37 g from 0.52 g); an off white solid; mp: 112-113 ^{o}C; R_f = 0.72 (hexanes: EtOAc, 3:2, v/v); IR (KBr) ν: 1716 (CO_2Me) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.21 (d, *J* = 1.2 Hz, 1H), 8.82 (s, 1H), 7.49-7.47 (m, 6H), 7.44-7.41 (m, 1H), 7.22 (d, *J* = 7.8 Hz, 2H), 4.001 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) = 166.3, 148.6, 141.0, 140.4, 139.2, 136.7, 130.0, 129.7,

129.4, 129.3, 126.1, 125.2, 124.4, 52.6, 21.5. MS (ESI+): *m/z* = 344.3. ESI-HR-MS calculated for $C_{21}H_{17}N_3O_2$ $[MH]^+$: 344.1399, found: 344.1403.

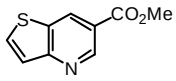
Methyl 3-(4-methoxyphenyl)-2-phenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (Table 2, entry 21, **2**).[26] Yield: 71% (0.38 g from 0.54 g); a yellow solid; mp: 164-165 ^oC; R_f = 0.6 (hexanes: EtOAc, 3:2, v/v); IR (KBr) ν: 1721 (CO_2Me) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.21 (d, *J* = 1.5 Hz, 1H), 8.81 (d, *J* = 1.6 Hz, 1H), 7.49-7.46 (m, 7H), 6.94 (d, *J* = 8.6 Hz, 2H), 4.02 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) = 166.3, 160.2, 148.4, 140.9, 140.4, 139.0, 136.5, 131.4, 129.4, 129.2, 126.1, 124.3, 120.4, 114.5, 55.5, 52.6. MS (ESI+): *m/z* = 360.3. ESI-HR-MS calculated for $C_{21}H_{17}N_3O_3$ $[MH]^+$: 360.1348, found: 360.1343.



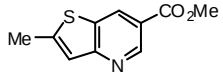
Methyl 2-methyl-3-phenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (Table 2, entry 22, **2**).[26] Yield: 73% (0.29 g from 0.41 g); a yellow solid; mp: 128-129 ^oC; R_f = 0.42 (hexanes: EtOAc, 3:2, v/v); IR (KBr) ν: 1716 (CO_2Me) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.16 (d, *J* = 1.7 Hz, 1H), 8.75 (d, *J* = 1.8 Hz, 1H), 7.72-7.69 (m, 2H), 7.60 (t, *J* = 7.0 Hz, 2H), 7.54-7.46 (m, 1H), 4.31 (s, 3H), 4.00 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 166.2, 148.2, 139.9, 139.2, 137.1, 130.1, 129.5, 129.3, 128.6, 128.0, 123.8, 52.6, 40.1. MS (ESI+): *m/z* = 268.2. ESI-HR-MS calculated for $C_{15}H_{13}N_3O_2$: 268.1086, found: 268.1090.



Methyl thieno[3,2-*b*]pyridine-6-carboxylate (Table 2, entry 23, **2**).[27] Yield: 75% (0.28 g from 0.3 g); a light brown solid; mp: 101-102 ^oC; R_f = 0.61 (hexanes: EtOAc, 3:2, v/v); IR (KBr) ν: 1706.67 (CO_2Me) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.29 (s, 1 H), 8.85 (s, 1H), 7.96 (d, *J* = 5.6 Hz, 1H), 7.63 (d, *J* = 5.1 Hz, 1H), 4.00 (s, 3H). MS (ESI+): *m/z* = 194.1. ESI-HR-MS calculated for $C_9H_7NO_2S$ $[MH]^+$: 194.0276 found: 194.0279.



Methyl 2-methylthieno[3,2-*b*]pyridine-6-carboxylate (Table 2, entry 24, **2**)**.** Yield: 71% (0.22 g from 0.32 g); a yellow solid; mp: 103-104 ^oC; R_f = 0.50 (hexanes: EtOAc, 3:2, v/v); IR (KBr) ν: 1703 (CO_2Me) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.22 (s, 1H), 8.70 (s, 1H), 7.30 (s, 1H), 3.99 (s, 3 H), 2.71 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 166.3, 159.7, 150.8, 148.3, 132.9, 131.5, 123.2, 120.4, 52.5, 17.3. MS (ESI+): *m/z* = 208.2. ESI-HR-MS calculated for $C_{10}H_9NO_2S$ $[MH]^+$: 208.0432, found: 208.0428.



Methyl benzo[*h*][1,6]naphthyridine-3-carboxylate (Table 2, entry 25, **2**)**.** Yield: 87% (0.27 g from 0.36 g); a pale yellow solid; mp: 115-117 ^{o}C; R_f = 0.41 (hexanes: EtOAc, 3:2, v/v); IR (KBr) ν: 1719 (CO_2Me) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.71 (s, 1H), 9.38 (s, 1H), 9.19 (d, J = 8.1 Hz, 1H), 8.99 (s, 1H), 8.24 (d, J = 8.1 Hz, 1H), 7.92 (t, J = 7.2 Hz, 1H), 7.81 (t, J = 7.3 Hz, 1H), 4.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 165.3, 153.5, 152.9, 151.0, 147.6, 138.2, 131.7, 129.7, 128.2, 124.9, 124.8, 124.6, 119.8, 52.9. MS (ESI+): *m/z* = 239.2. ESI-HR-MS calculated for $C_{14}H_{10}N_2O_2$ [MH]+: 239.0821 found: 239.0826.

References:

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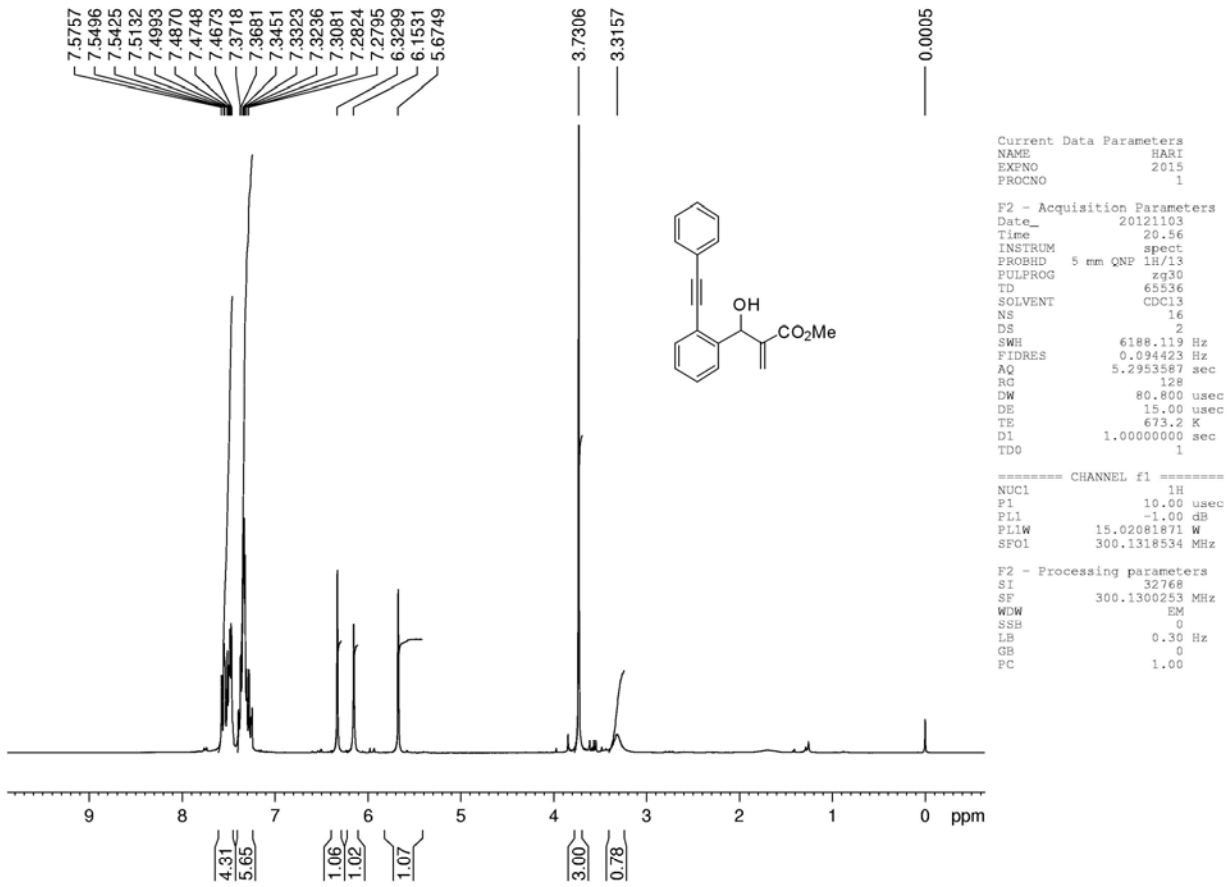


Fig. S-1: ^{1}H spectrum of methyl 2-(hydroxy(2-(phenylethynyl)phenyl)methyl)acrylate.

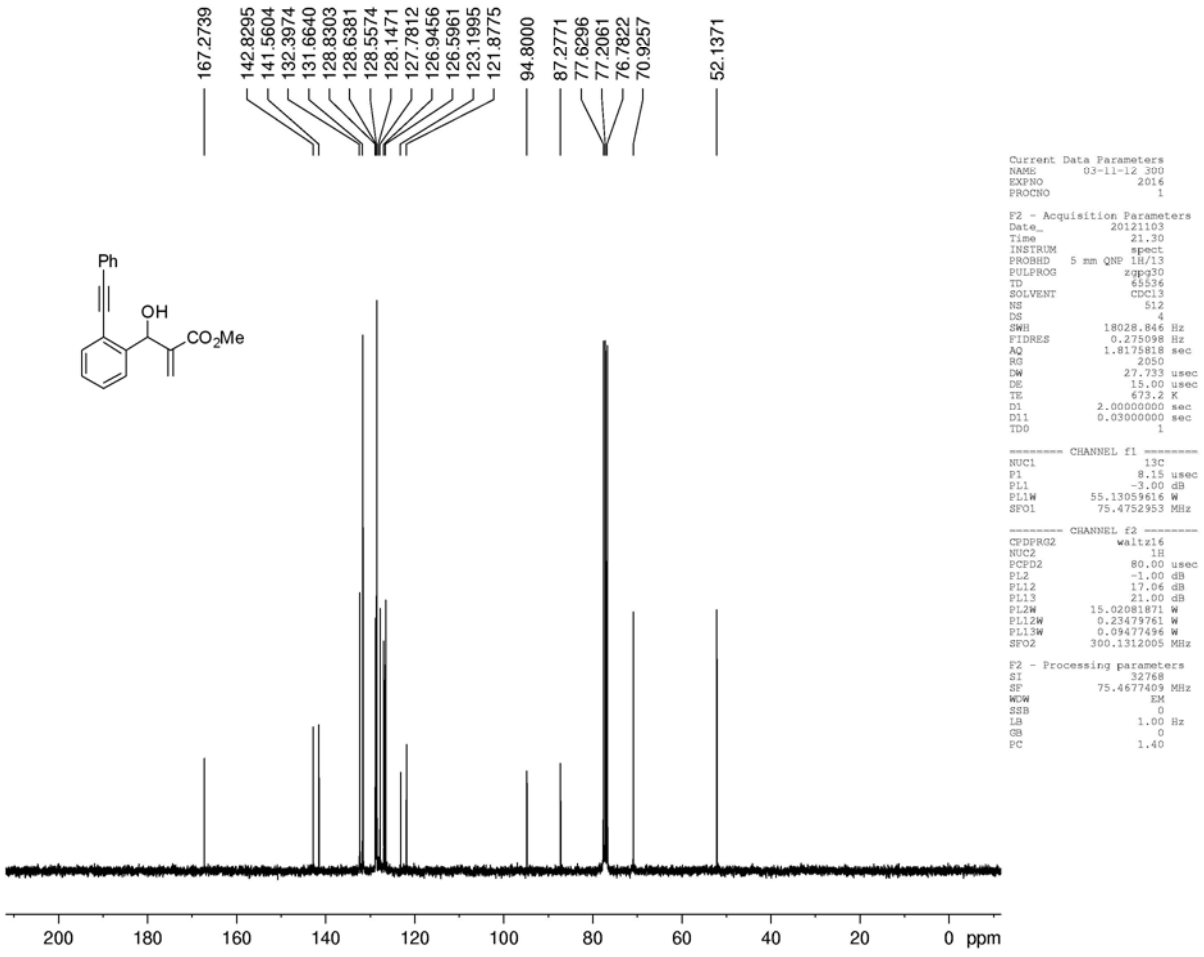


Fig. S-2: ^{13}C spectrum of methyl 2-(hydroxy(2-(phenylethynyl)phenyl)methyl)acrylate.

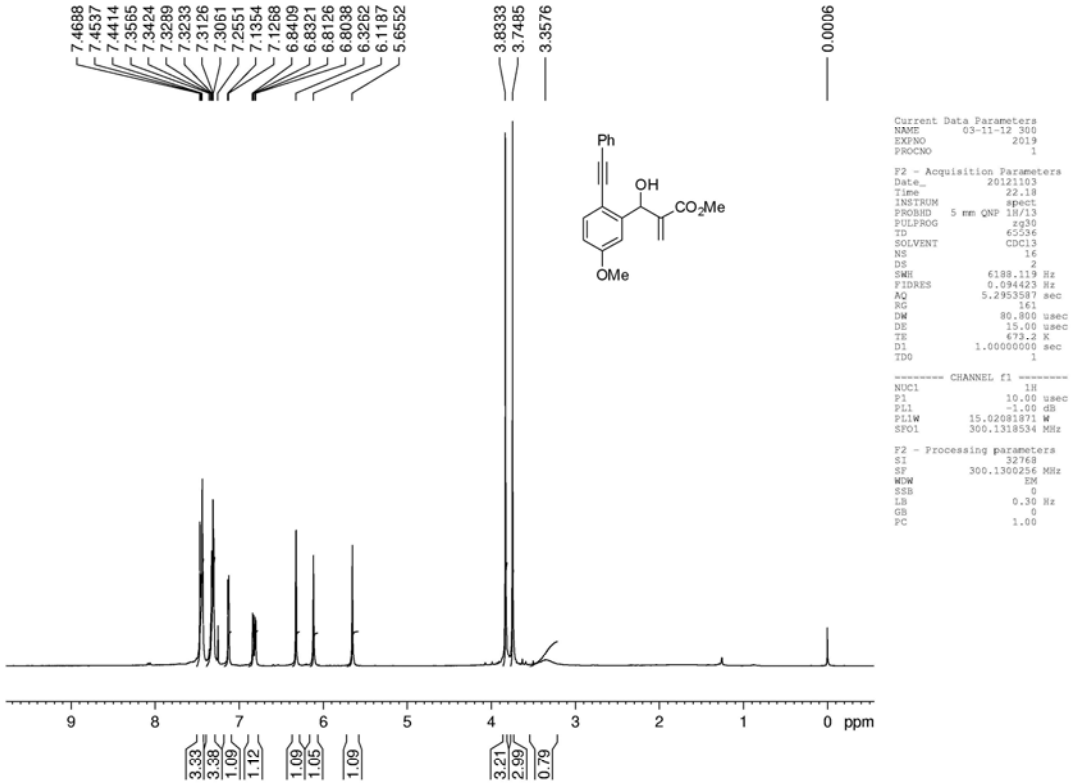
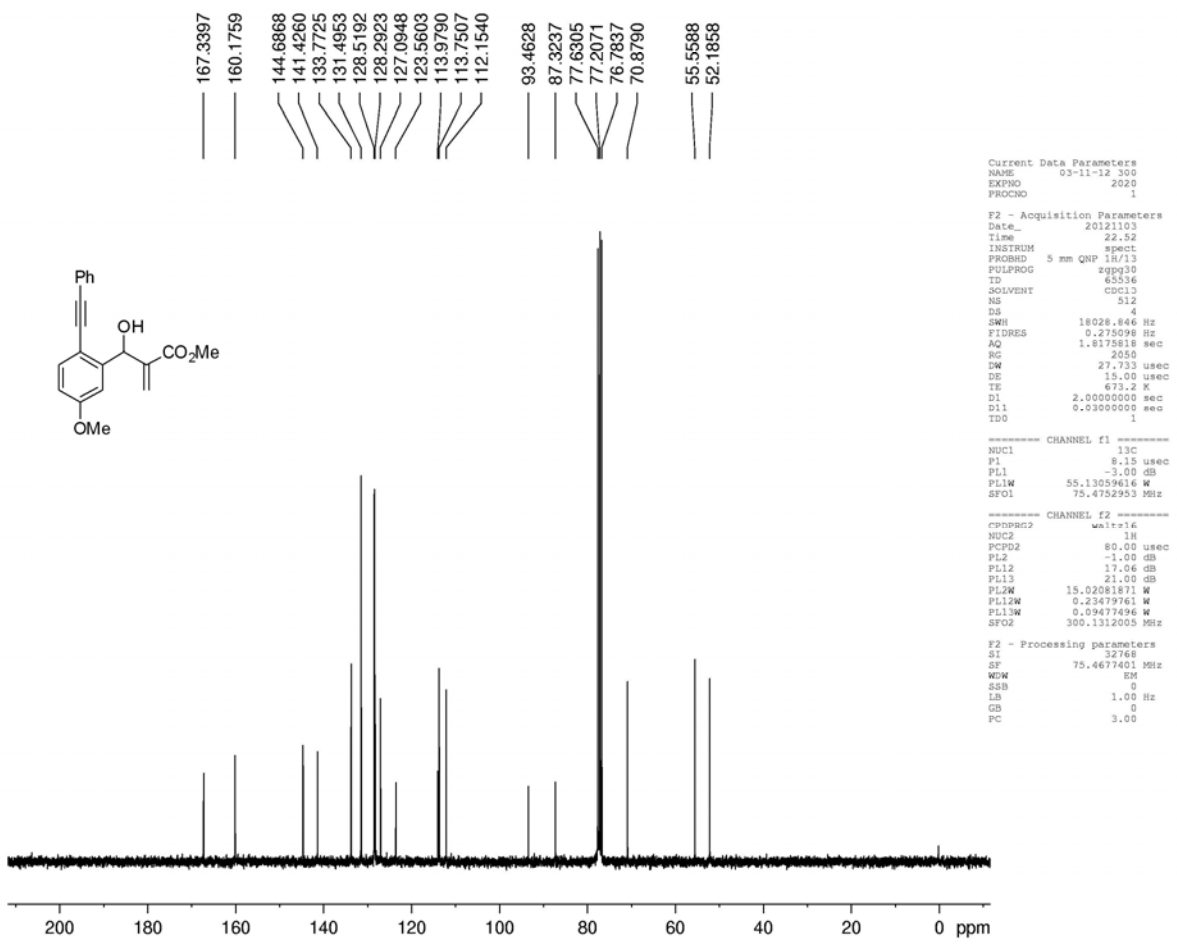


Fig. S-3: ^{1}H spectrum of methyl 2-(hydroxy(5-methoxy-2-(phenylethynyl)phenyl)methyl)acrylate.



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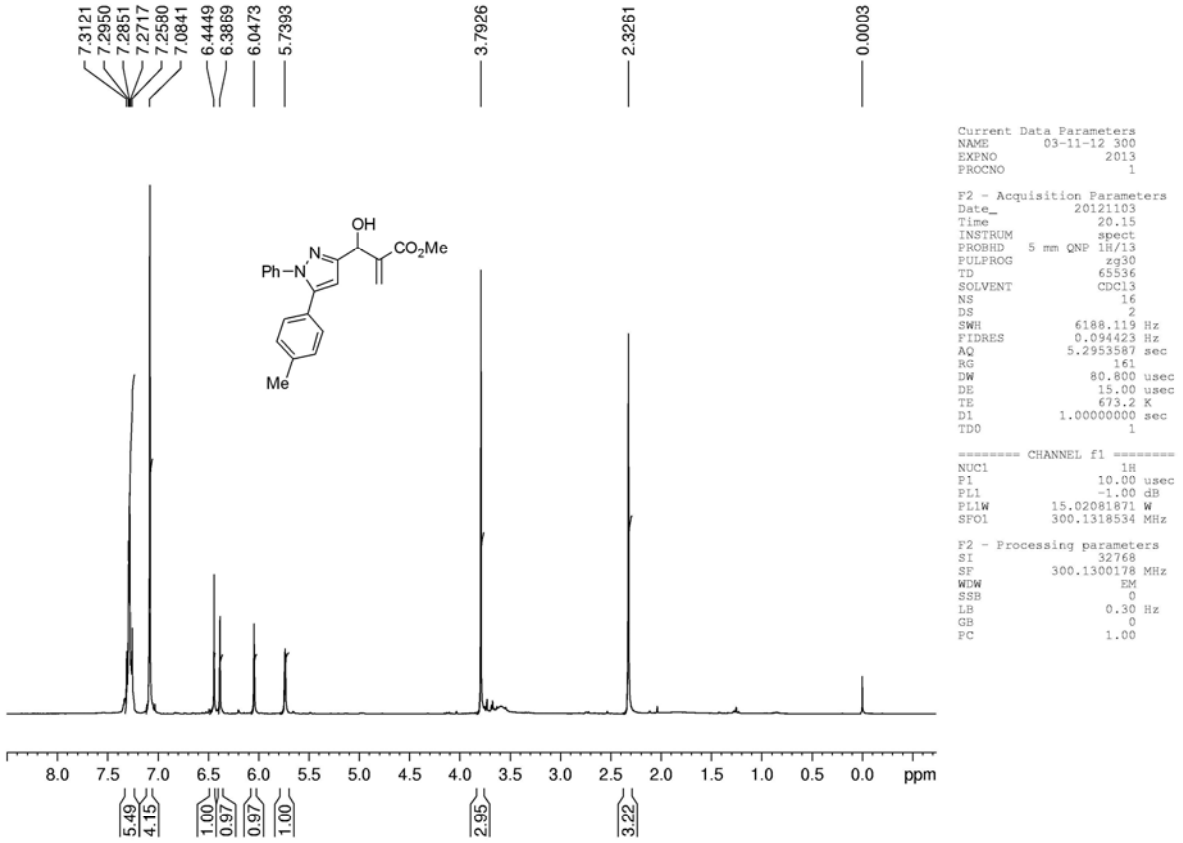


Fig. S-5: ^{1}H spectrum of methyl 2-(hydroxy(1-phenyl-5-(4-methylphenyl)-1*H*-pyrazol-3-yl)methyl)acrylate.

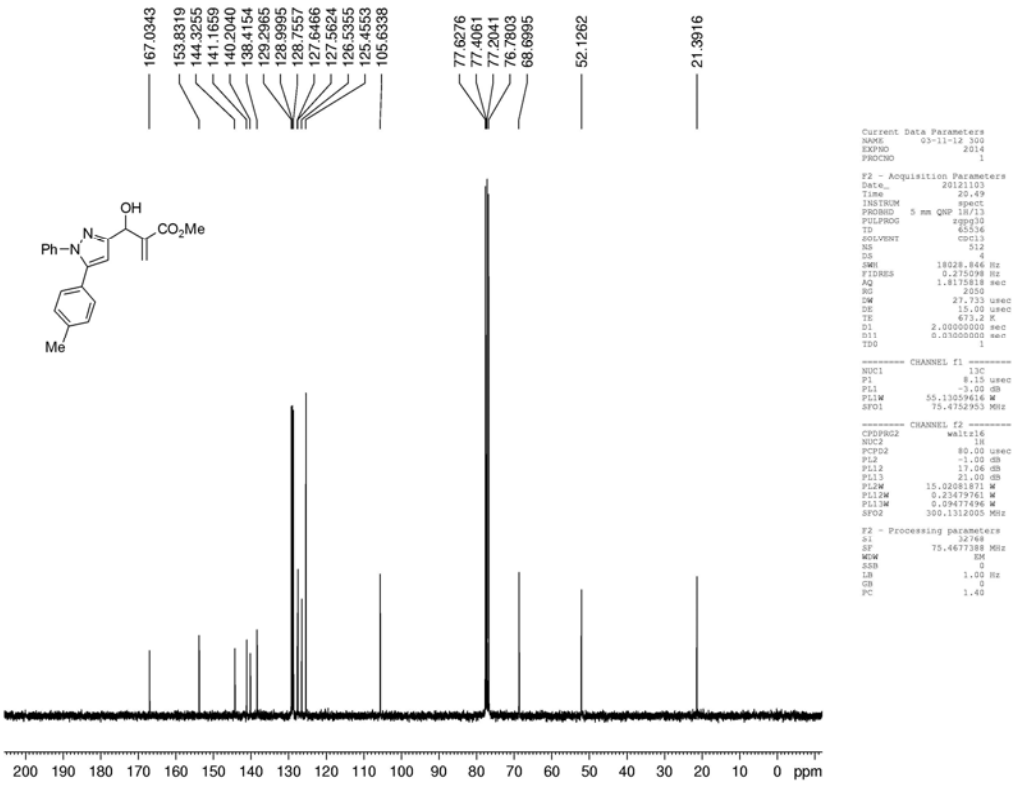


Fig. S-6: ^{13}C spectrum of methyl 2-(hydroxy(1-phenyl-5-(4-methylphenyl)-1*H*-pyrazol-3-yl)methyl)acrylate.

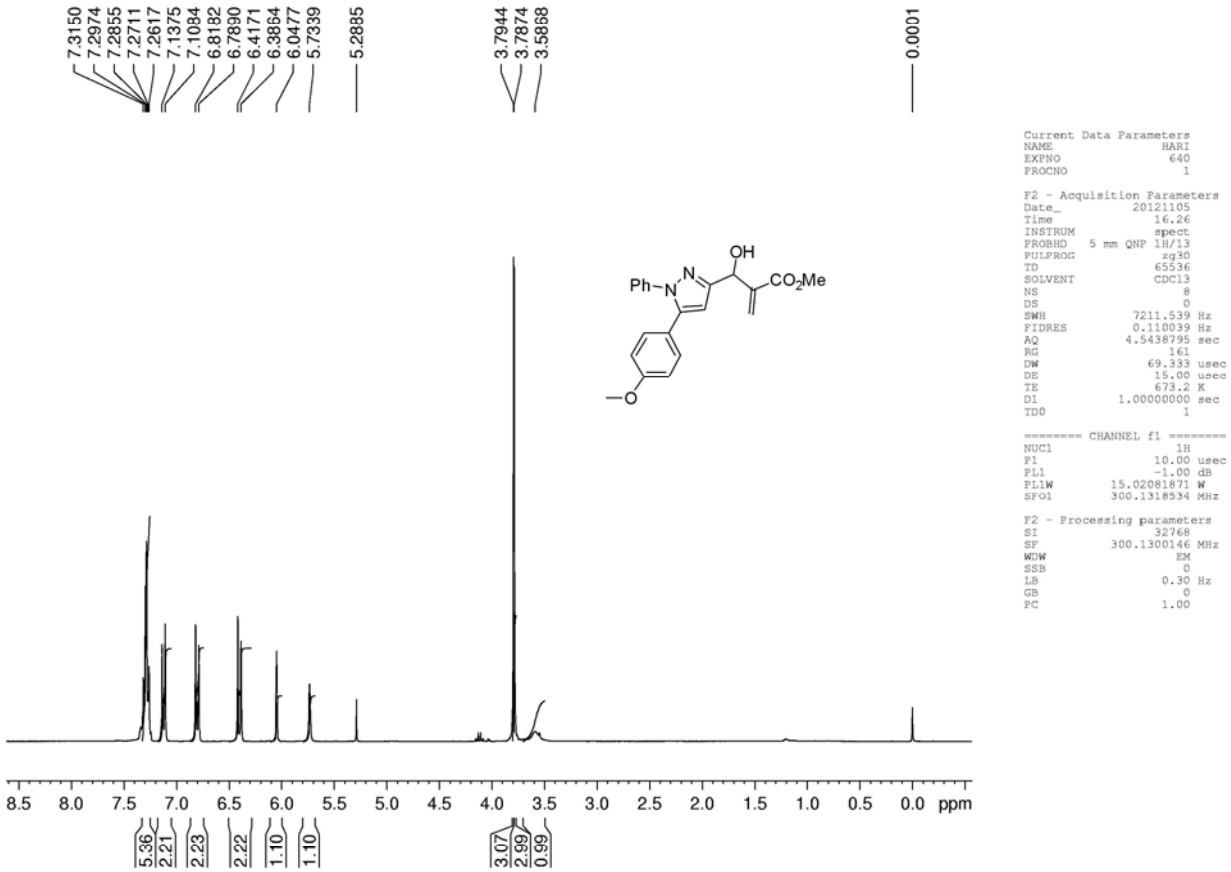
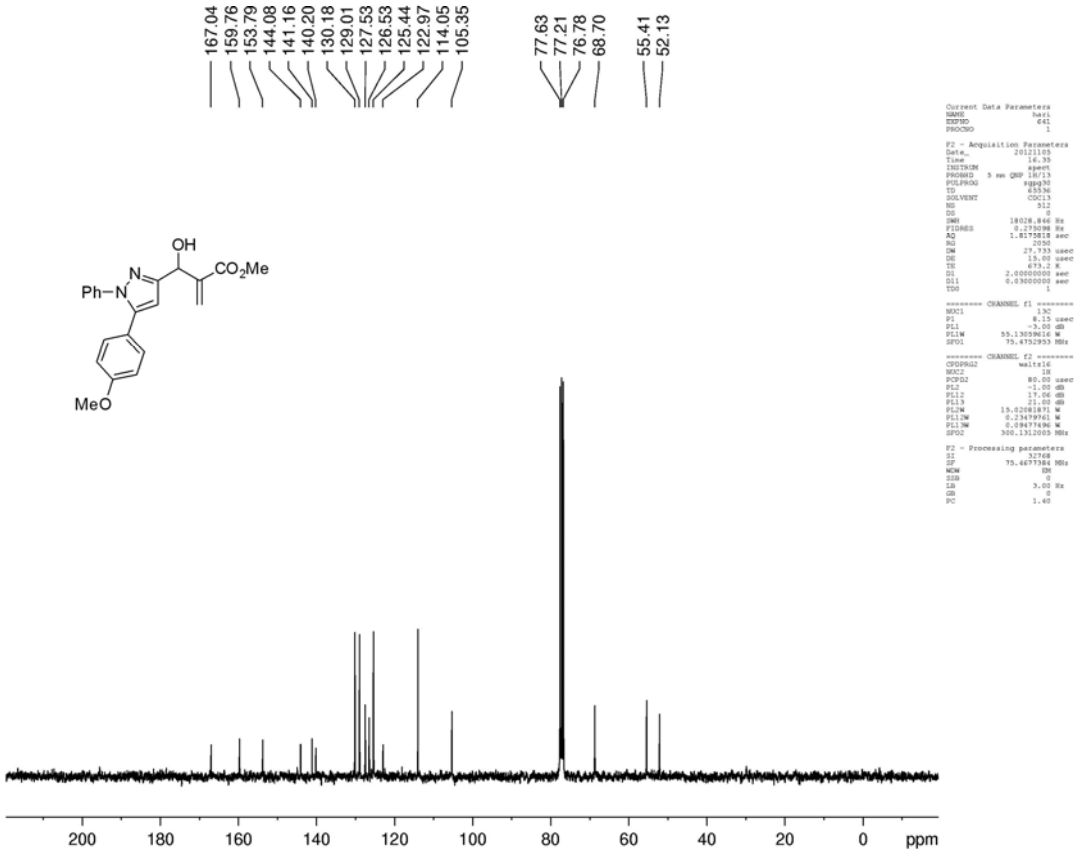


Fig. S-7: ^{1}H spectrum of methyl 2-(hydroxy(5-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-3-yl)methyl)acrylate.



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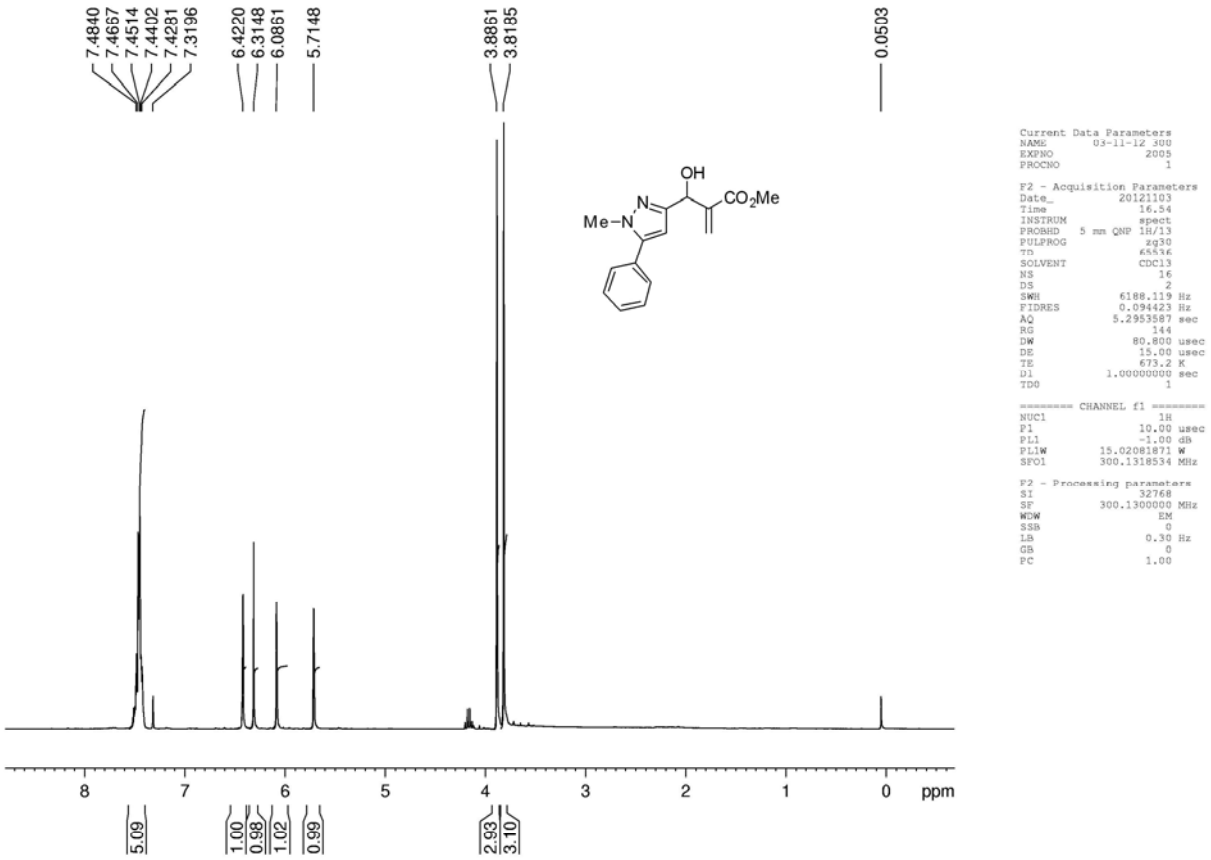
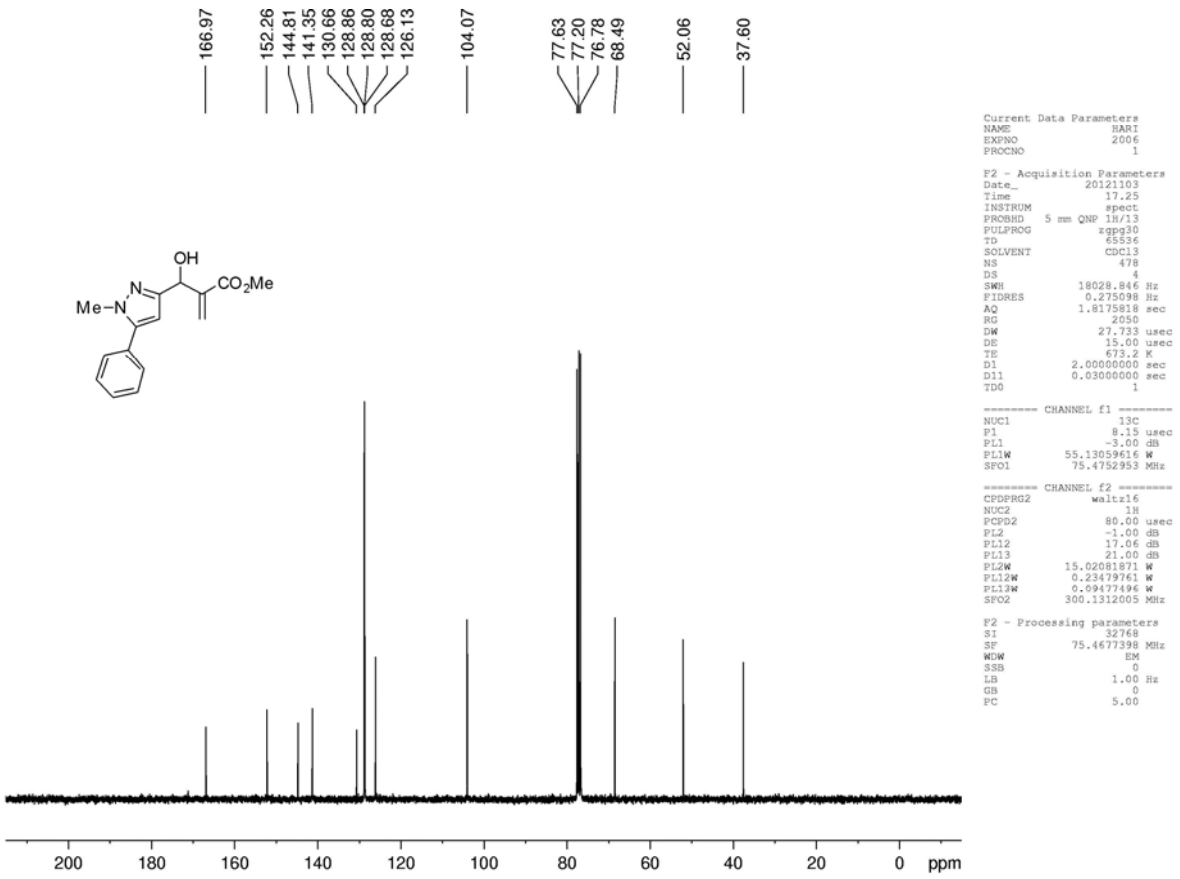


Fig. S-9: ^{1}H spectrum of methyl 2-(hydroxy(1-methyl-5-phenyl-1*H*-pyrazol-3-yl)methyl)acrylate.



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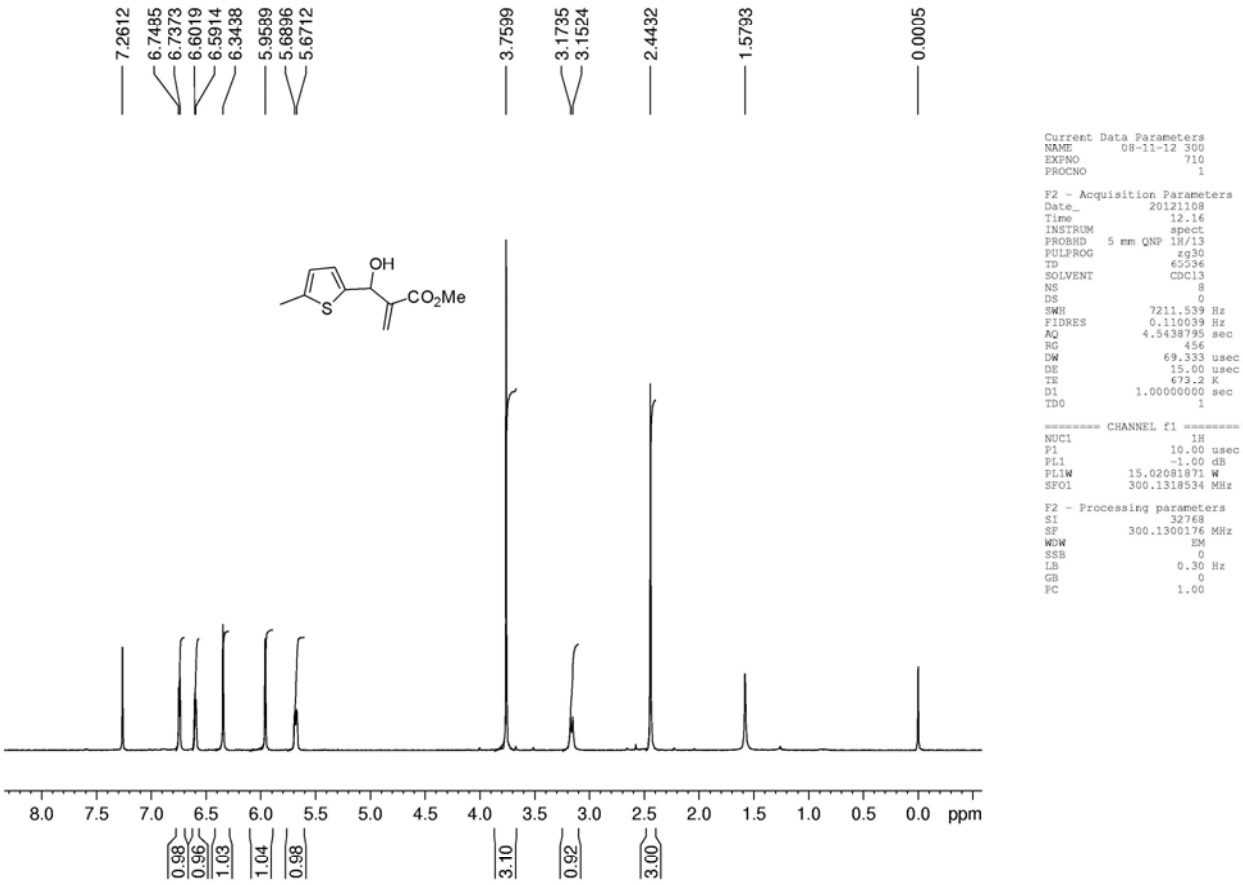


Fig. S-11: ^{1}H spectrum of methyl 2-(hydroxy(5-methylthiophen-2-yl)methyl)acrylate.

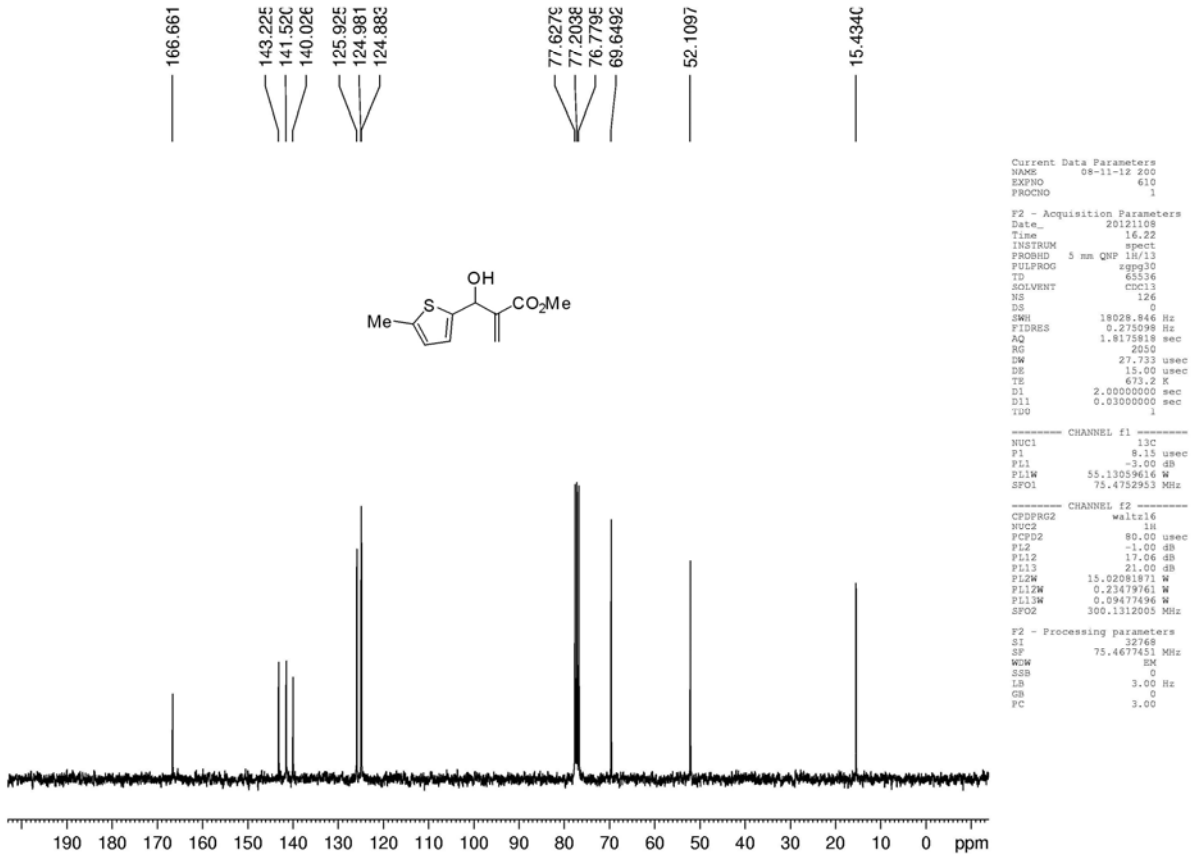


Fig. S-12: ^{13}C spectrum of methyl 2-(hydroxy(5-methylthiophen-2-yl)methyl)acrylate.

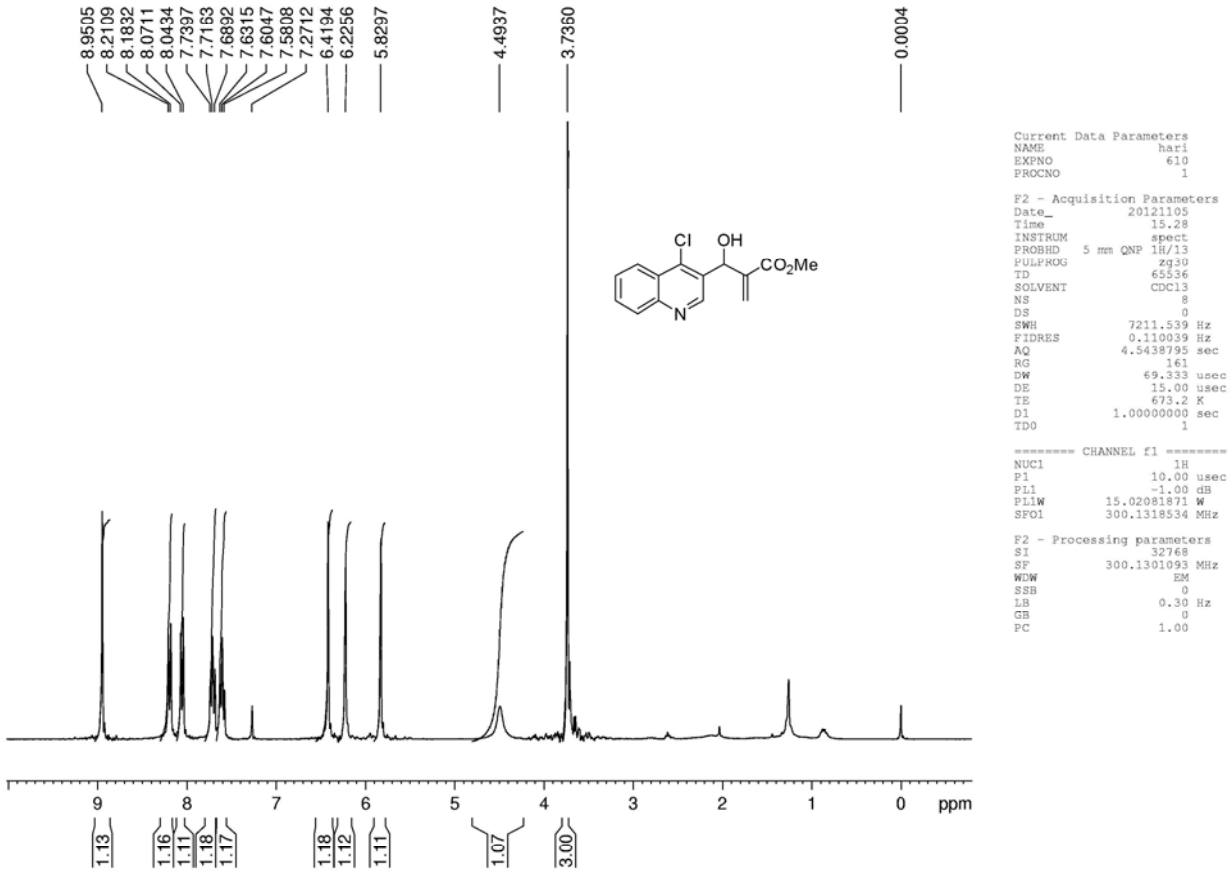


Fig. S-13: ^{1}H spectrum of methyl 2-((4-chloroquinolin-3-yl)(hydroxy)methyl)acrylate.

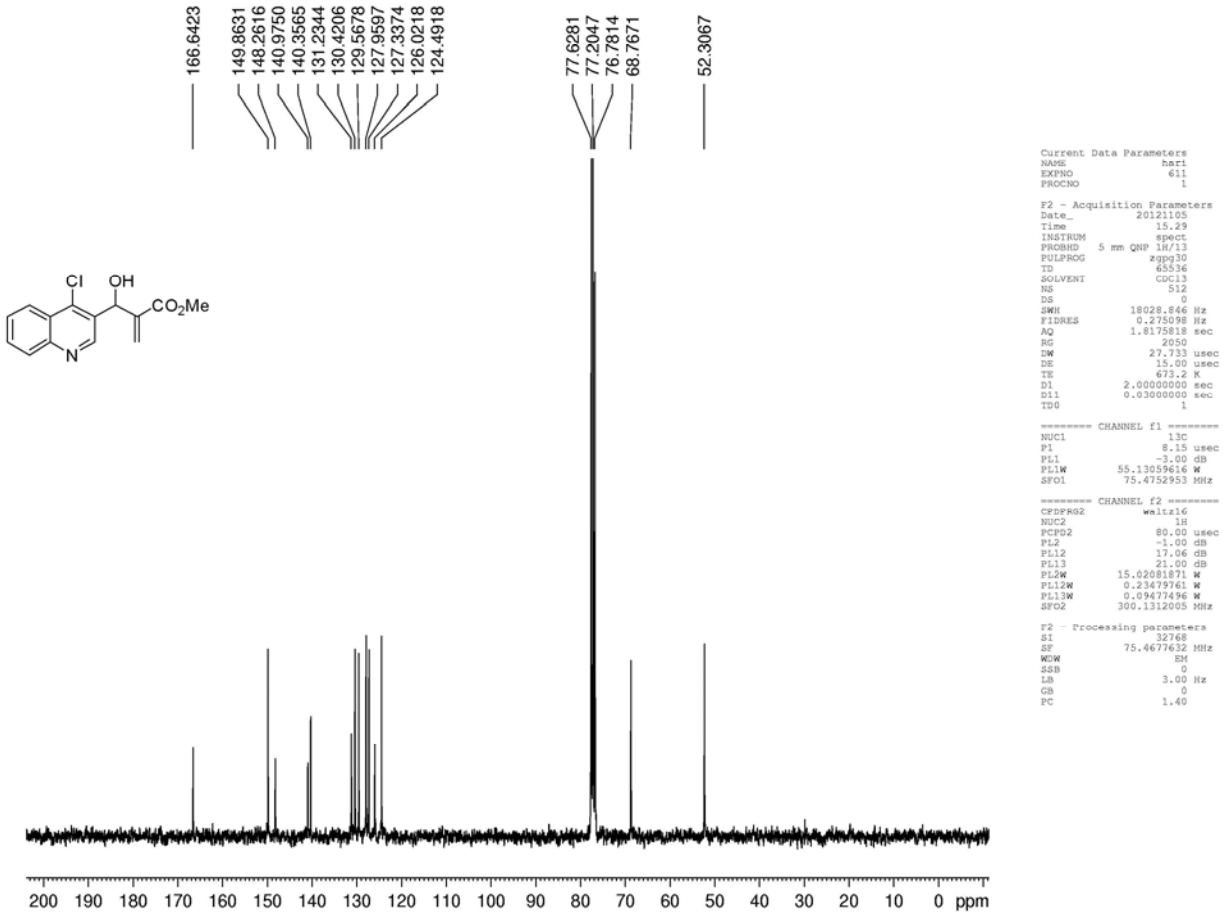


Fig. S-14: ^{13}C spectrum of methyl 2-((4-chloroquinolin-3-yl)(hydroxy)methyl)acrylate.

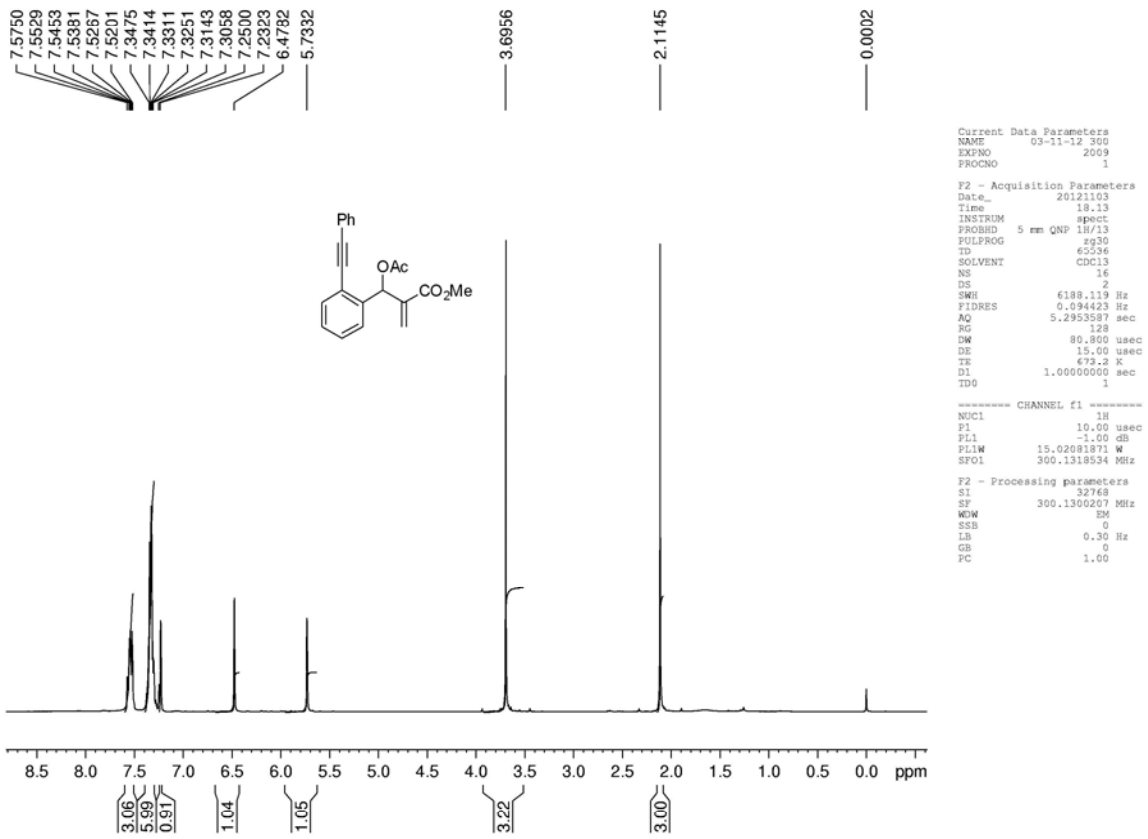
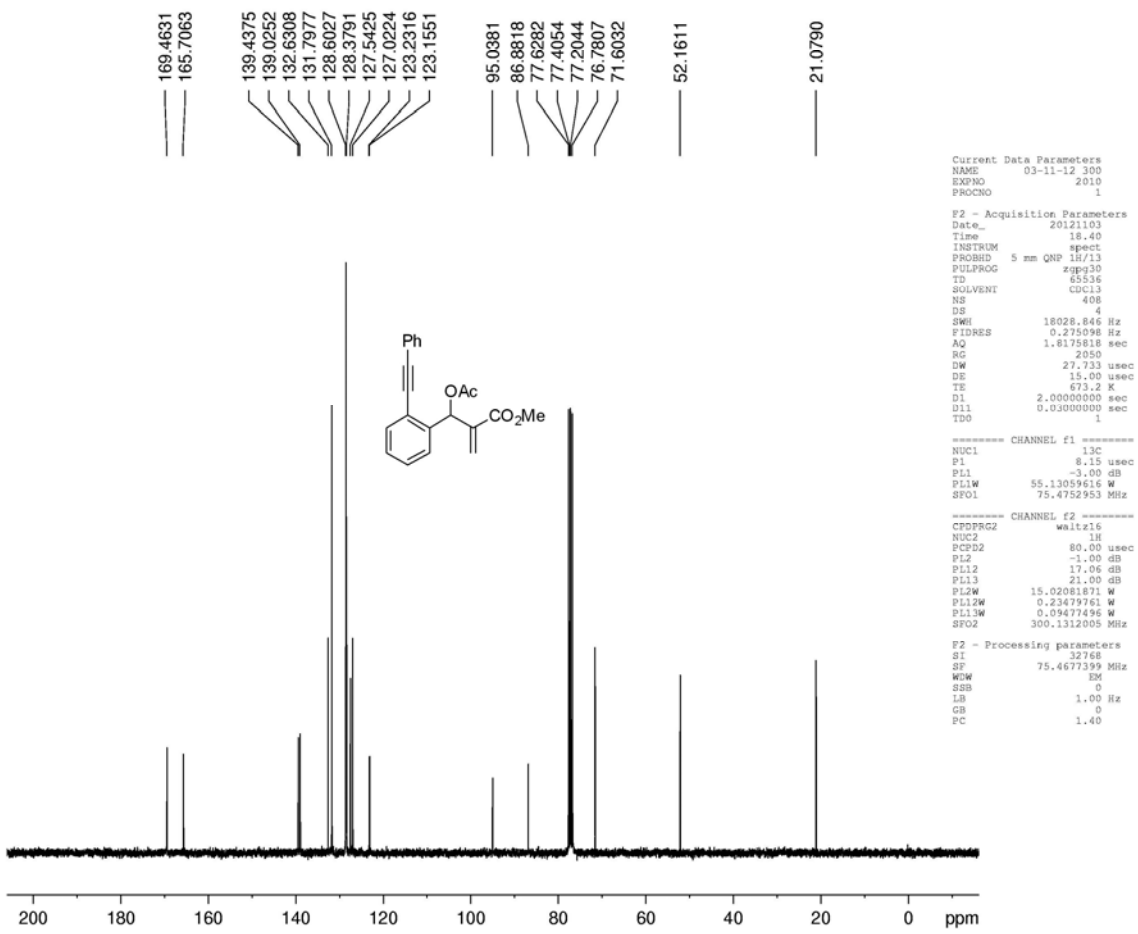


Fig. S-15: ^{1}H spectrum of methyl 2-(acetoxy(2-(phenylethynyl)phenyl)methyl)acrylate.



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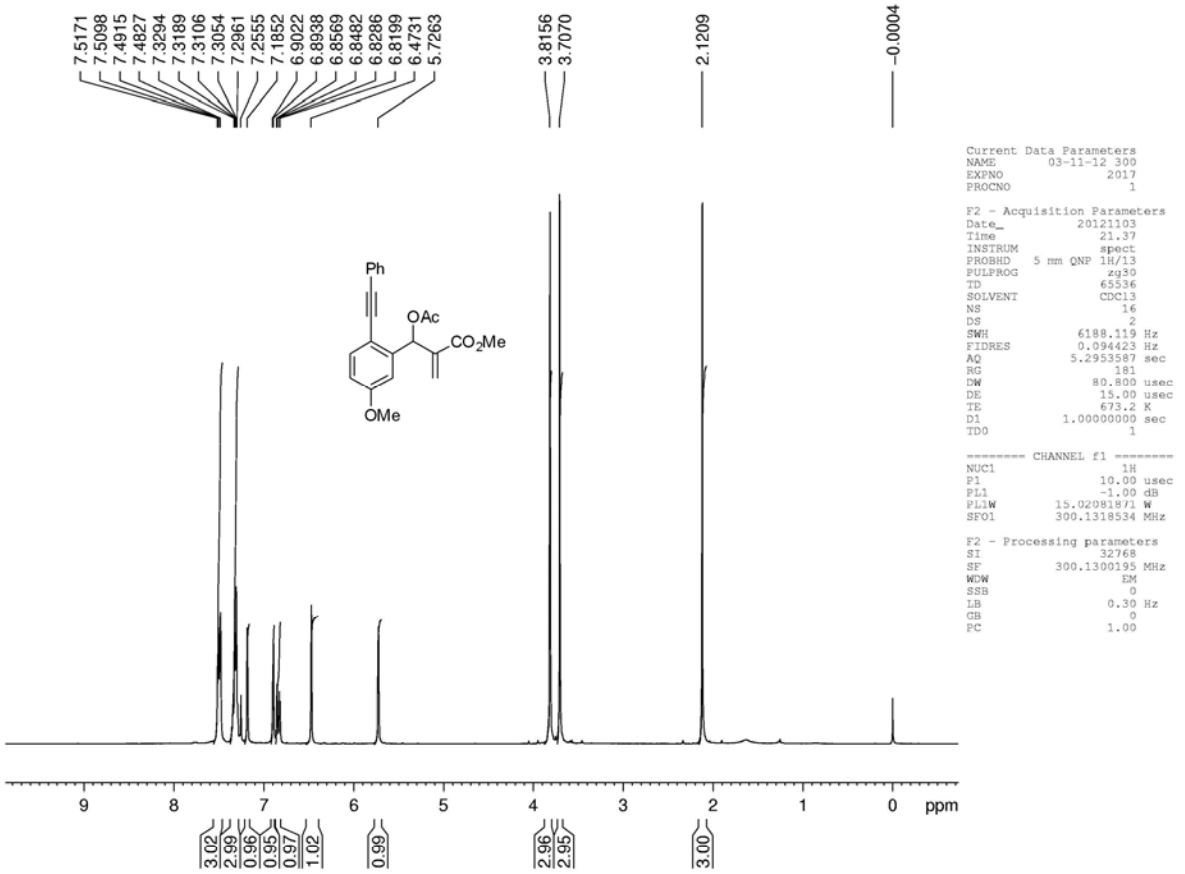


Fig. S-17: ^{1}H spectrum of methyl 2-(acetoxy(5-methoxy-2-(phenylethynyl)phenyl)methyl)acrylate.

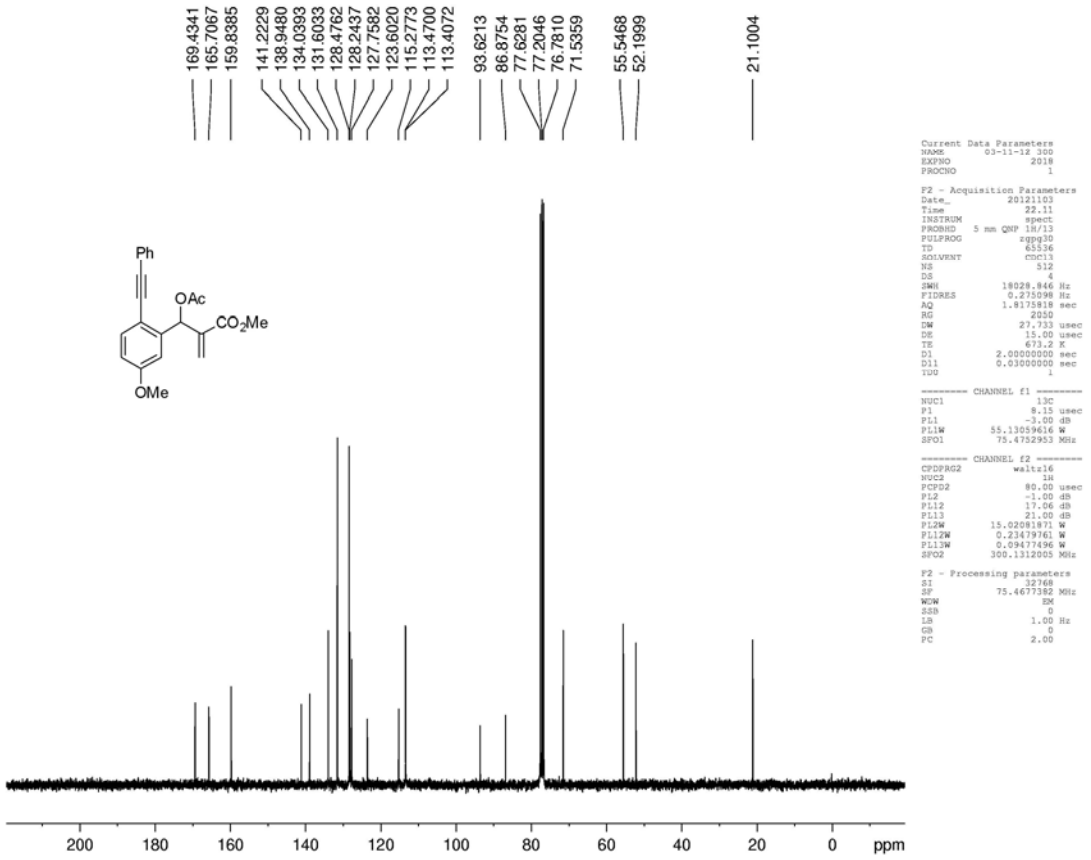


Fig. S-18: ^{13}C spectrum of methyl 2-(acetoxy(5-methoxy-2-(phenylethynyl)phenyl)methyl)acrylate.

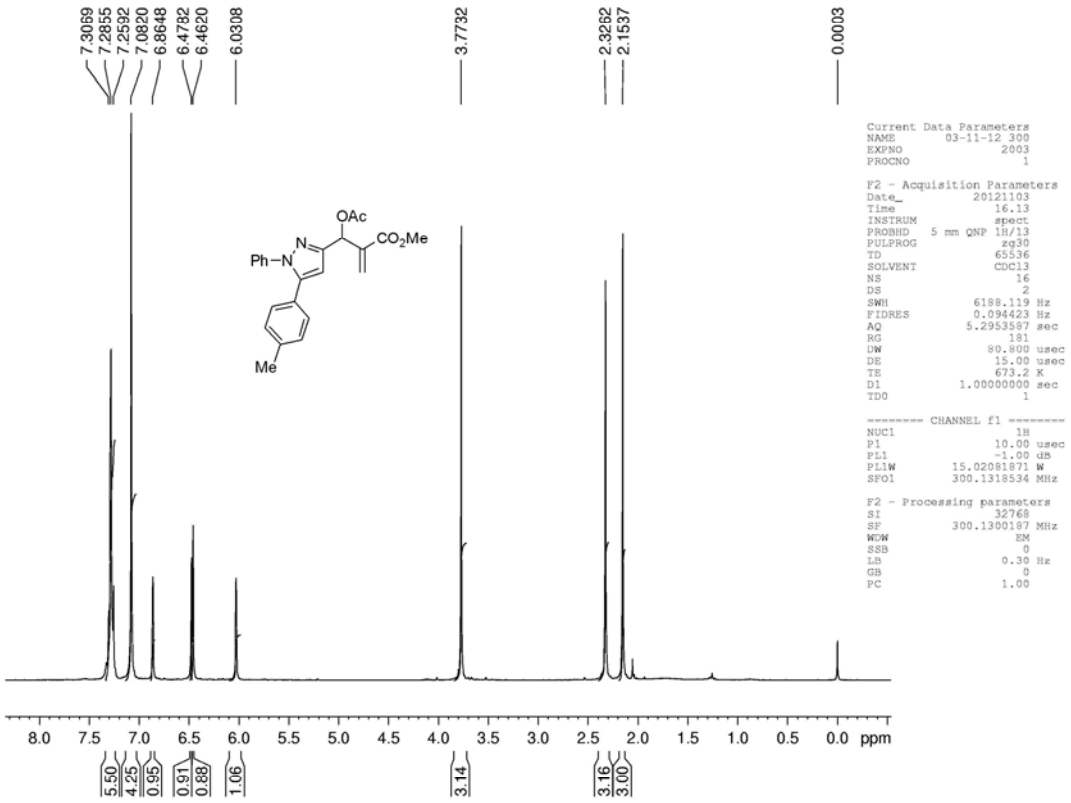


Fig. S-19: ^{1}H spectrum of methyl 2-(acetoxy(1-phenyl-5-(4-methylphenyl)-1*H*-pyrazol-3-yl)methyl)acrylate.

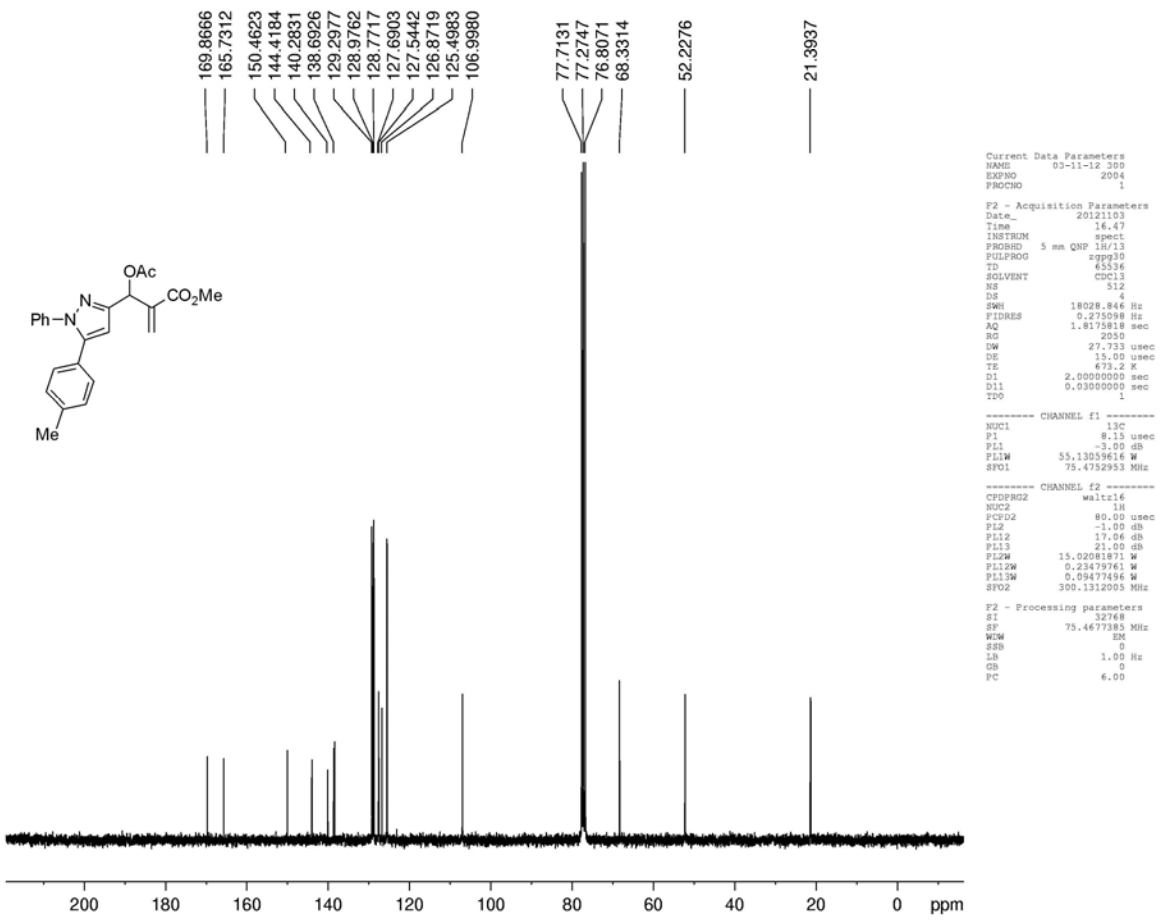


Fig. S-20: ^{13}C spectrum of methyl 2-(acetoxy(1-phenyl-5-(4-methylphenyl)-1*H*-pyrazol-3-yl)methyl)acrylate.

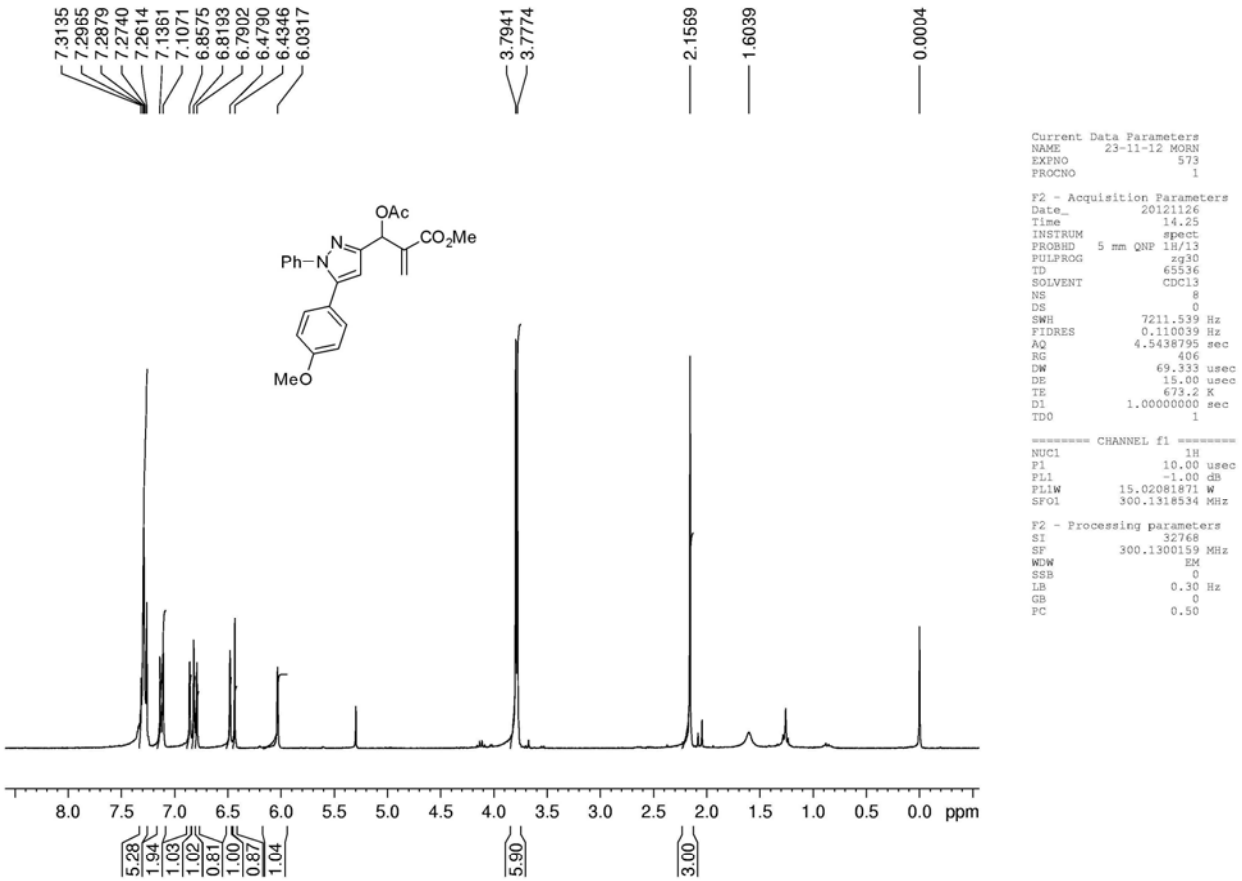


Fig. S-21: ^{1}H spectrum of methyl 2-(acetoxy(5-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-3-yl)methyl)acrylate.

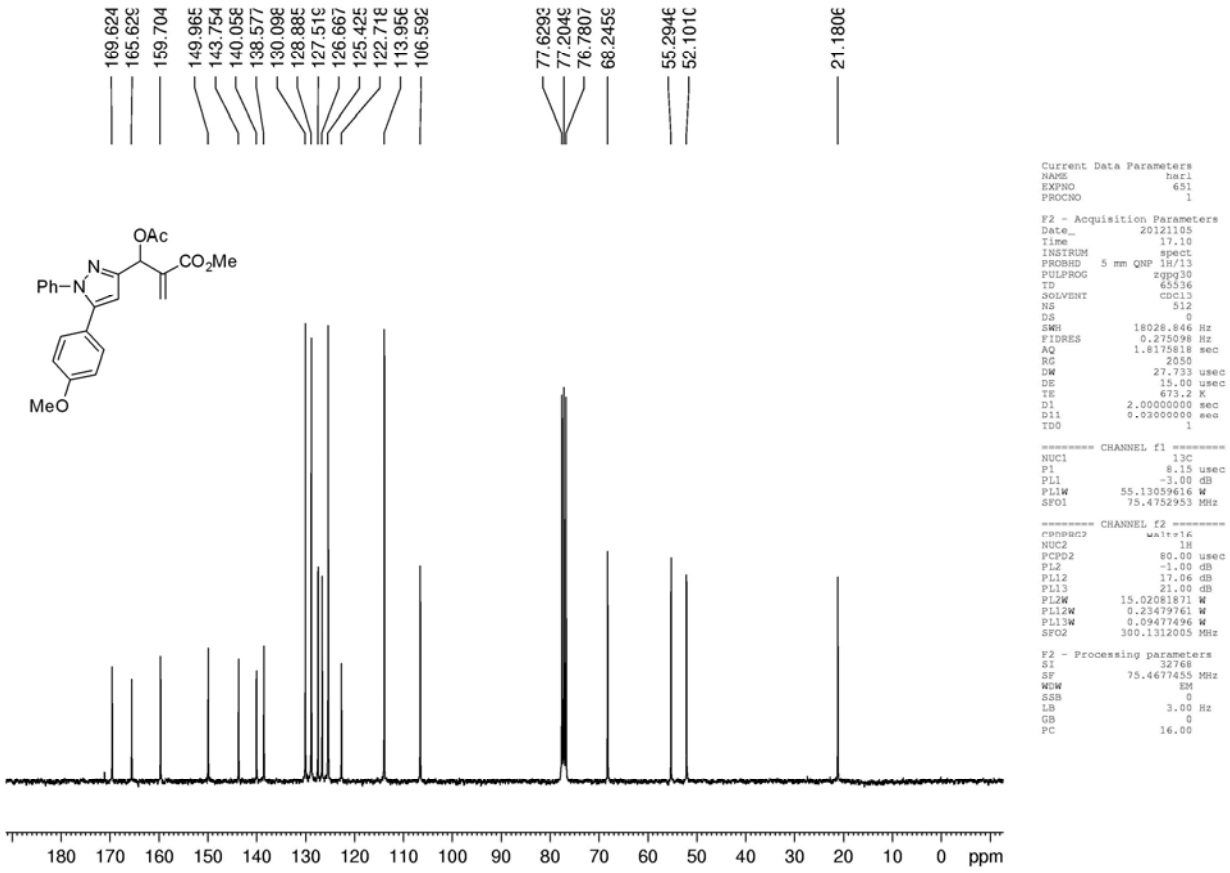


Fig. S-22: ^{13}C spectrum of methyl 2-(acetoxy(5-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-3-yl)methyl)acrylate.

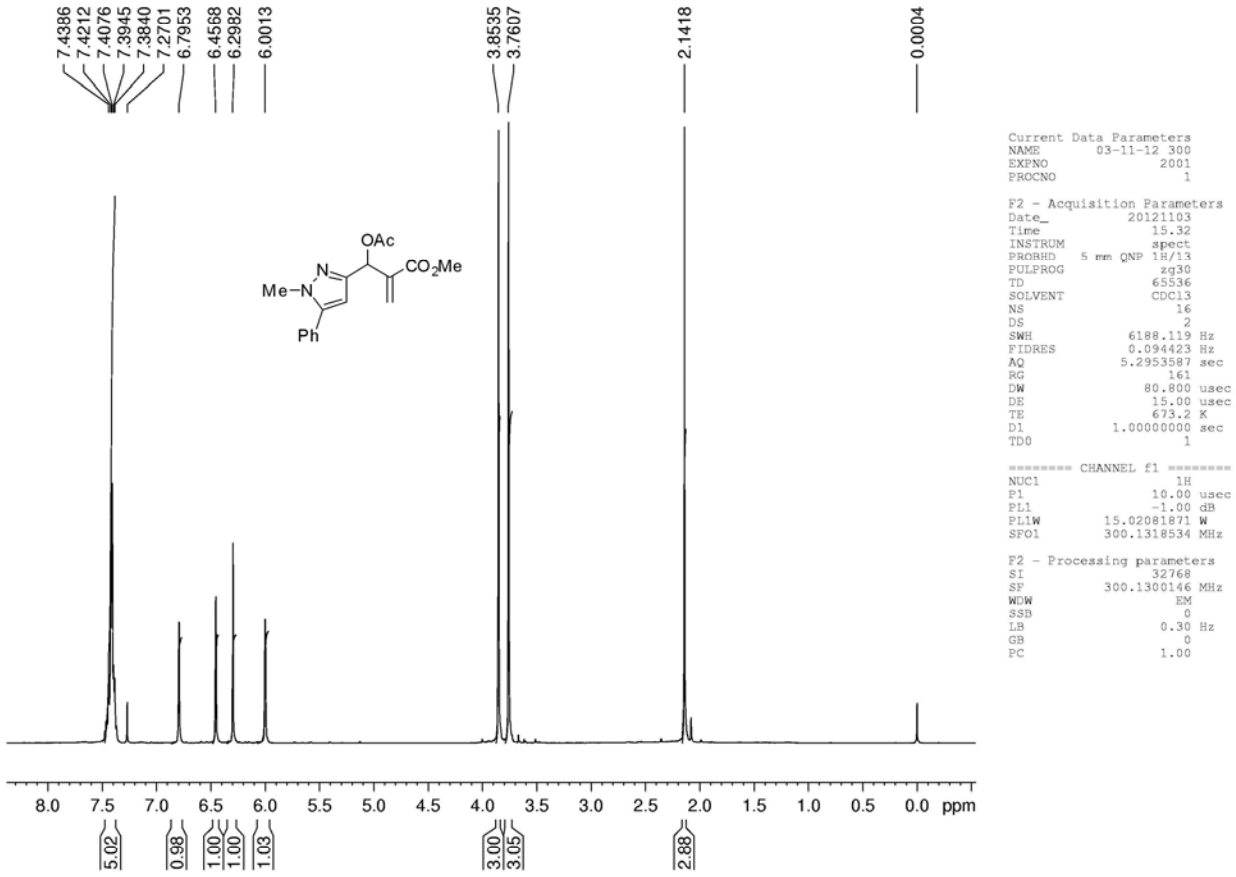


Fig. S-23: ^{1}H spectrum of methyl 2-(acetoxy(1-methyl-5-phenyl-1*H*-pyrazol-3-yl)methyl)acrylate.

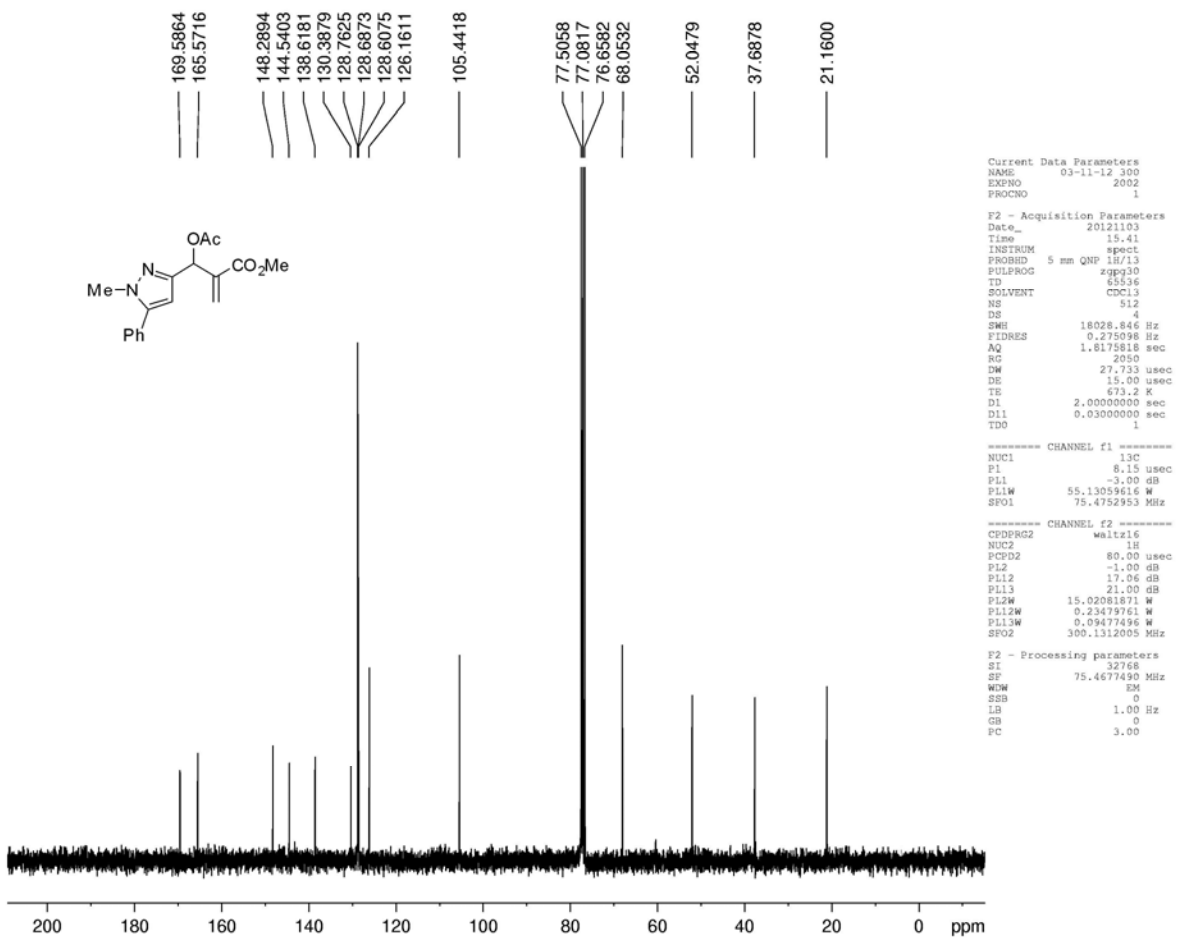


Fig. S-24: ^{13}C spectrum of methyl 2-(acetoxy(5-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-3-yl)methyl)acrylate.

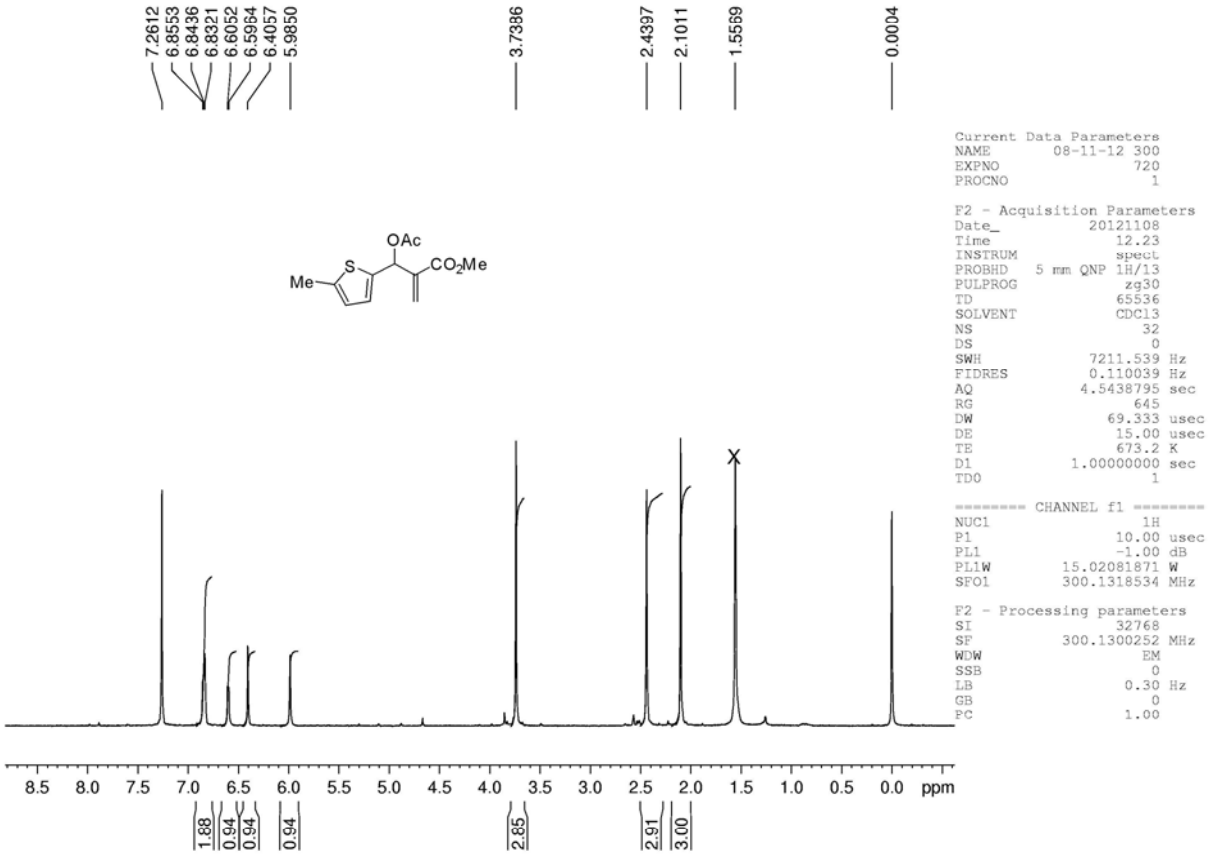


Fig. S-25: ^{1}H spectrum of methyl 2-(acetoxy(5-methylthiophen-2-yl)methyl)acrylate.

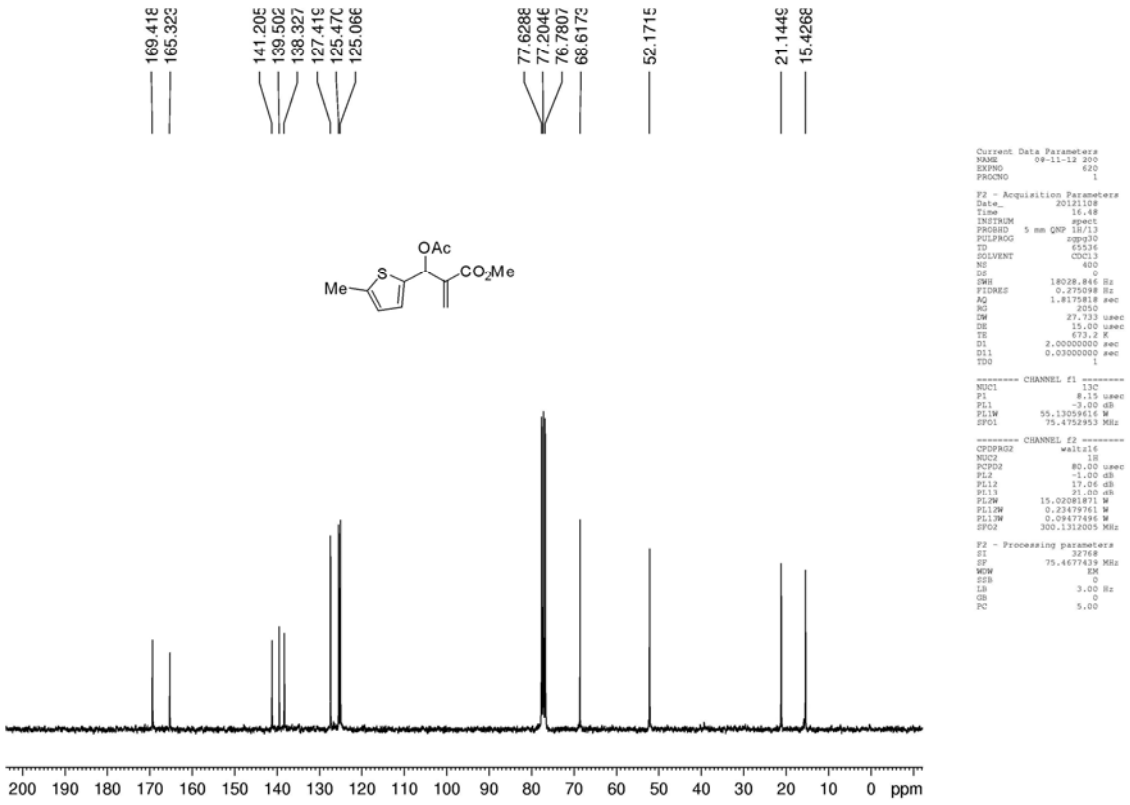


Fig. S-26: ^{13}C spectrum of methyl 2-(acetoxy(5-methylthiophen-2-yl)methyl)acrylate.

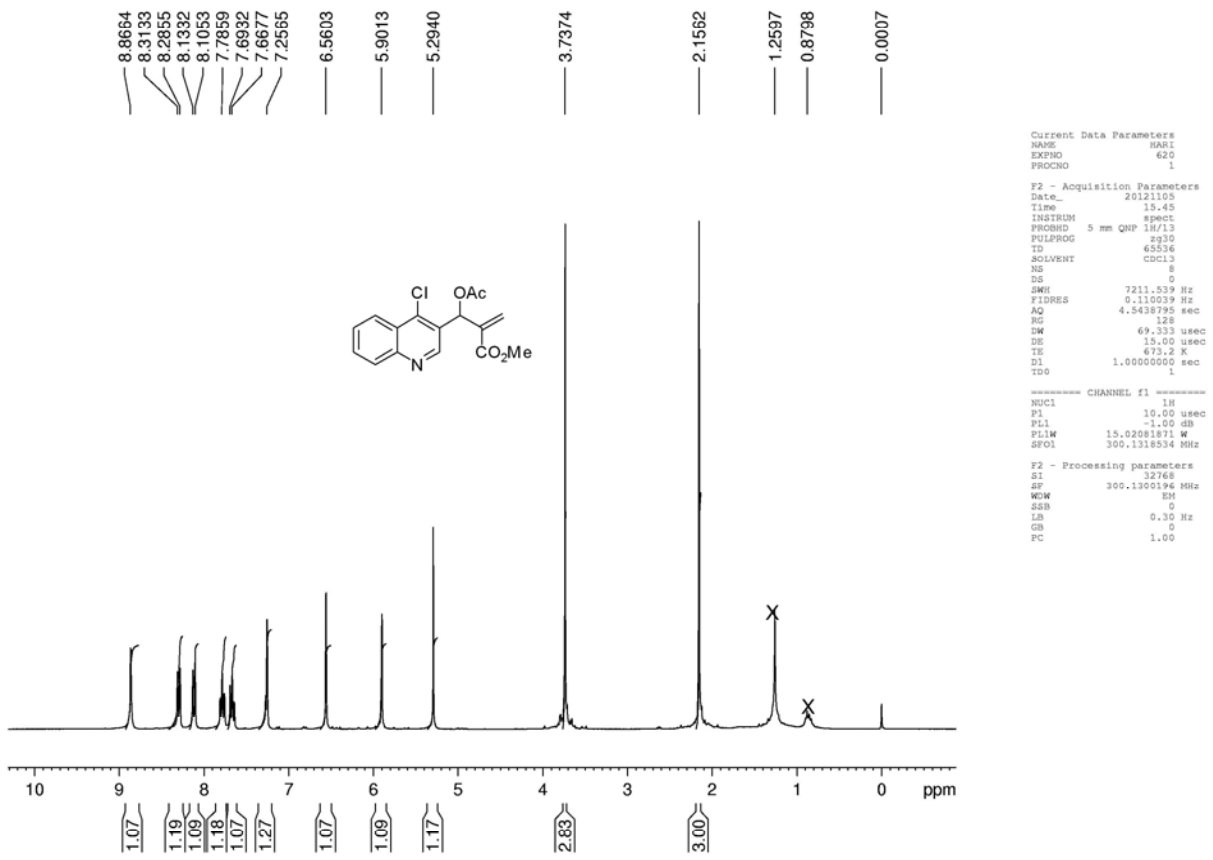


Fig. S-27: ^{1}H spectrum of methyl 2-(acetoxy(4-chloroquinolin-3-yl)methyl)acrylate.

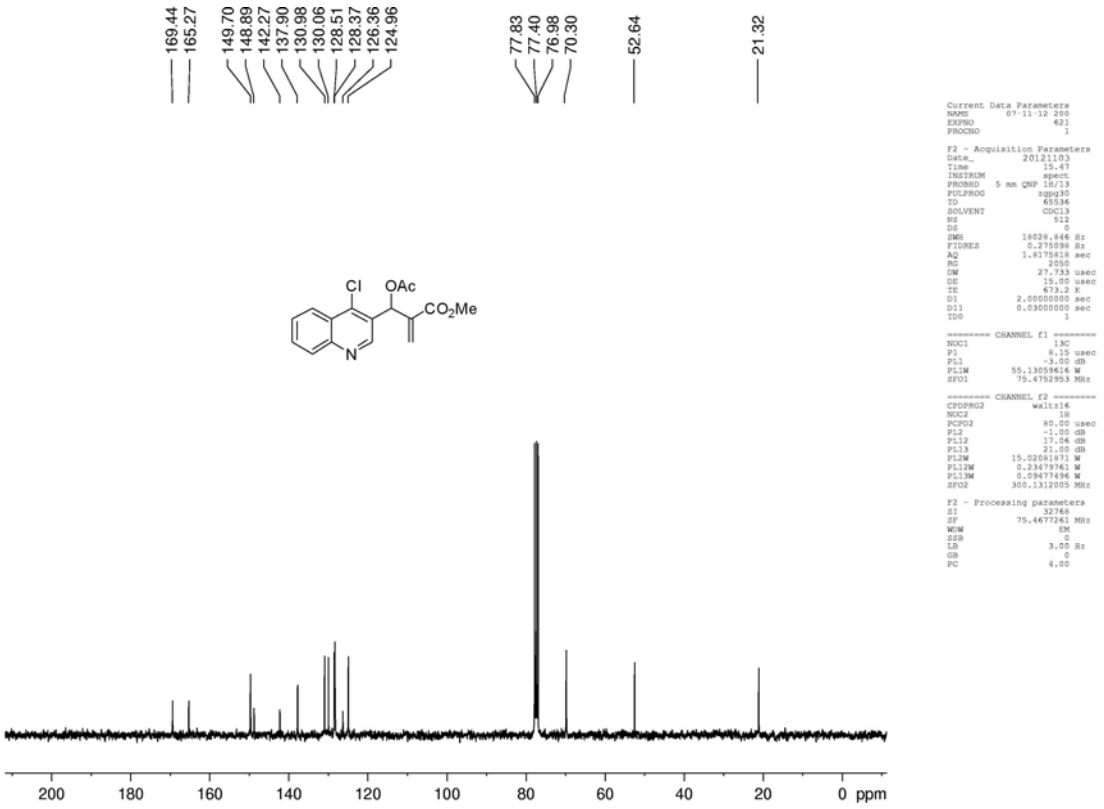


Fig. S-28: ^{13}C spectrum of methyl 2-(acetoxy(4-chloroquinolin-3-yl)methyl)acrylate.

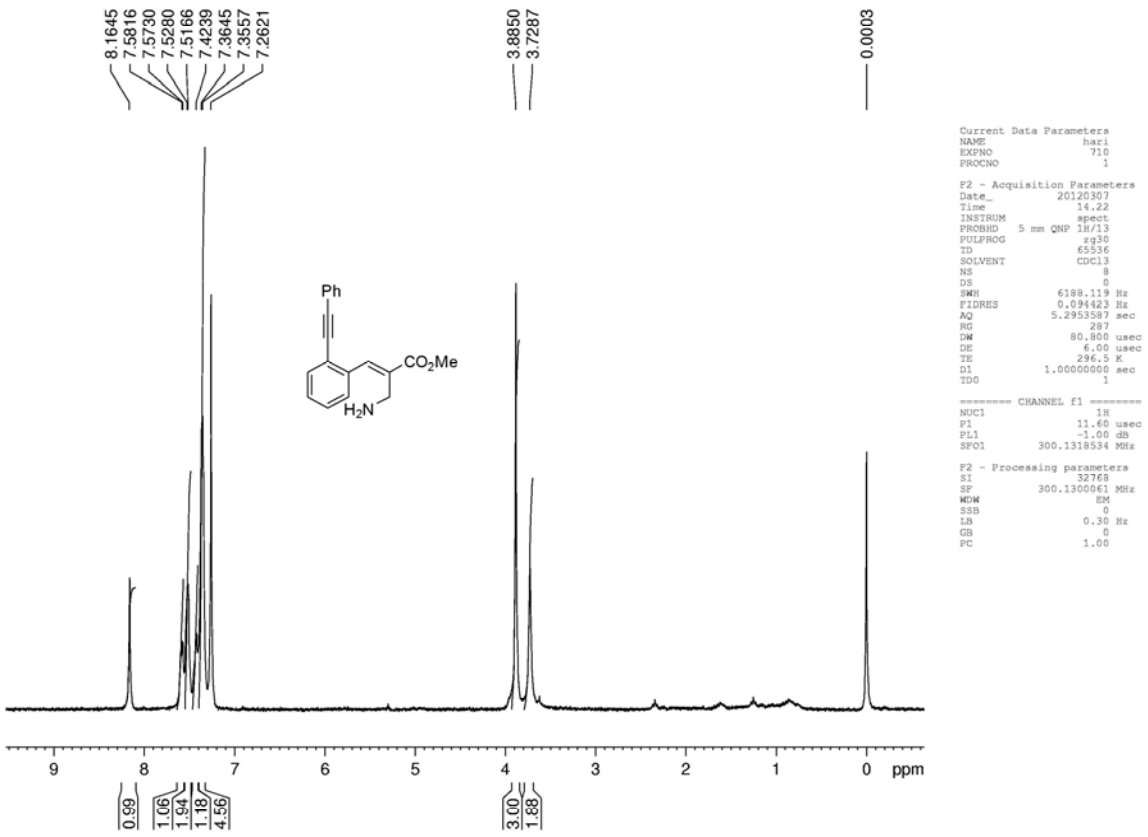


Fig. S-29: ^{1}H spectrum of (*E*)-methyl 2-(aminomethyl)-3-(2-(phenylethynyl)phenyl)acrylate (Table 2, entry 2, **1**).

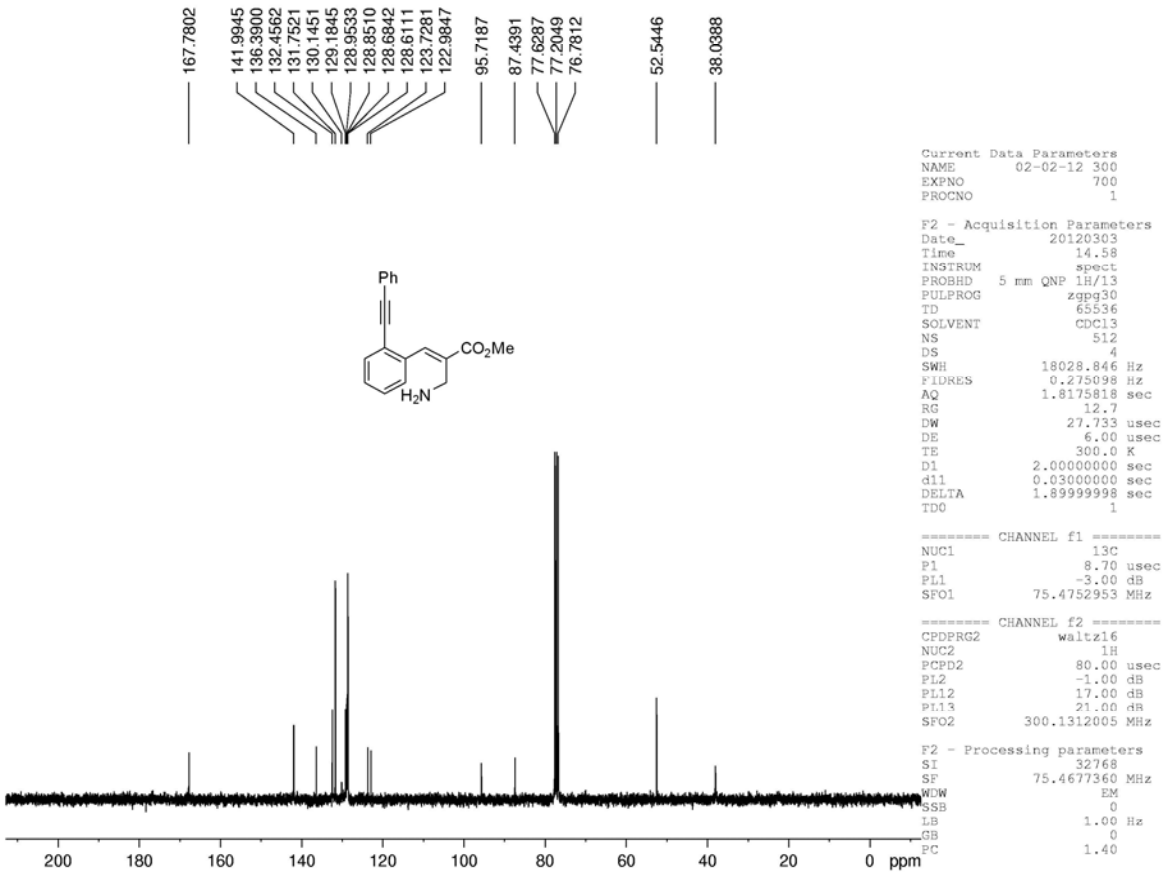


Fig. S-30: ^{13}C spectrum of (*E*)-methyl 2-(aminomethyl)-3-(2-(phenylethynyl)phenyl)acrylate (Table 2, entry 2, **1**).

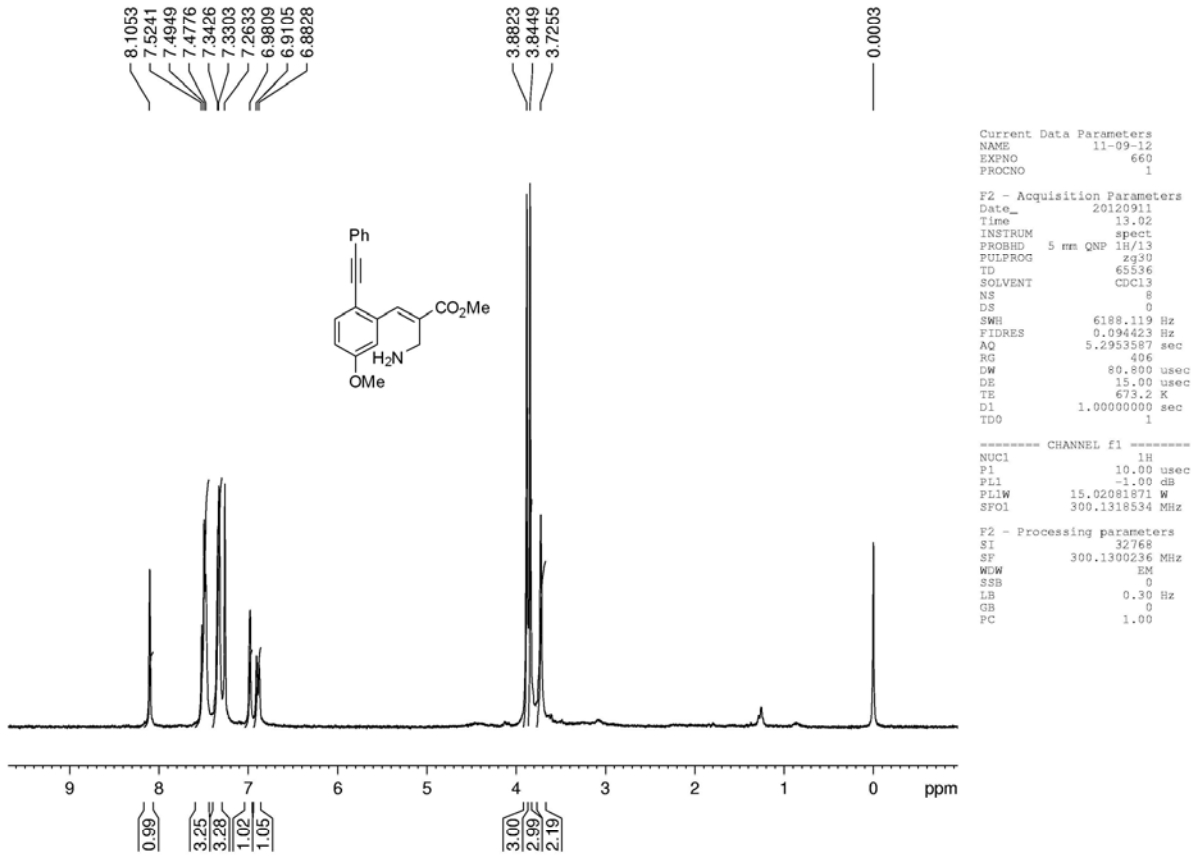
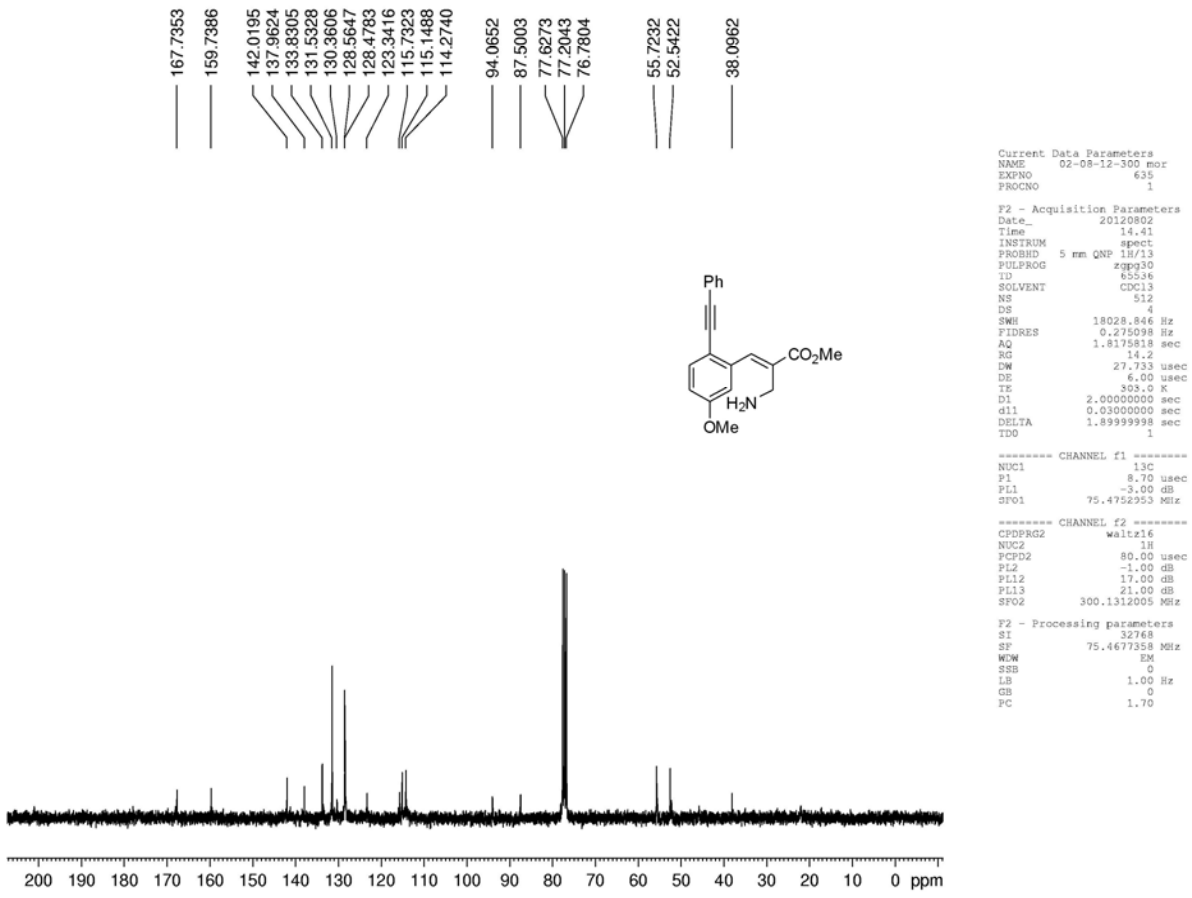


Fig. S-31: ^{1}H spectrum of (*E*)-methyl 2-(aminomethyl)-3-(5-methoxy-2-(phenylethynyl)phenyl)acrylate (Table 2, entry 3, **1**).

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DE                6.00 usec
TE                303.0 K
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PL1               -3.00 dB
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PL13              21.00 dB
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Fig. S-32: ^{13}C spectrum of (*E*)-methyl 2-(aminomethyl)-3-(5-methoxy-2-(phenylethynyl)phenyl)acrylate (Table 2, entry 3, **1**).

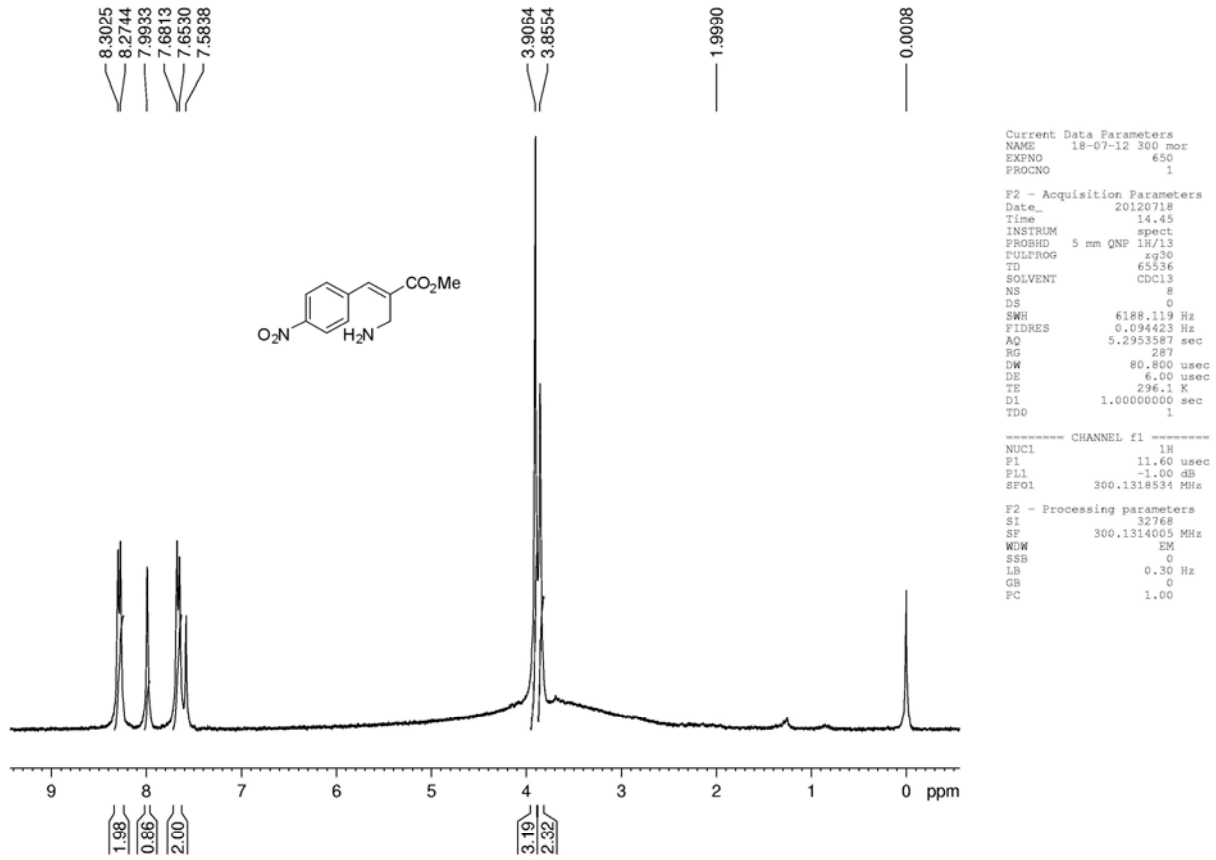
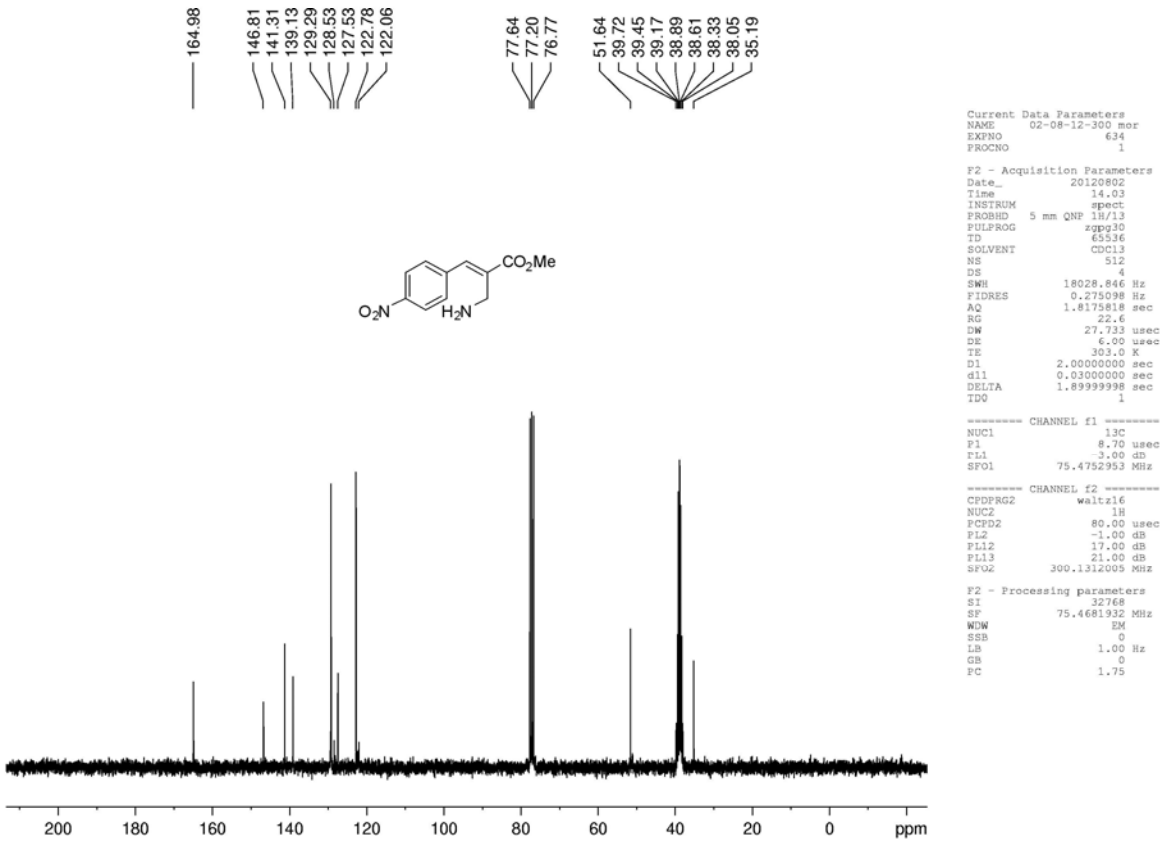


Fig. S-33: ^{1}H spectrum of (*E*)-methyl 2-(aminomethyl)-3-(4-nitrophenyl)acrylate (Table 2, entry 6, **1**).

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PL12              17.00 dB
PL13              21.00 dB
SFO2        300.1312005 MHz

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Fig. S-34: ^{13}C spectrum of (*E*)-methyl 2-(aminomethyl)-3-(4-nitrophenyl)acrylate (Table 2, entry 6, **1**).

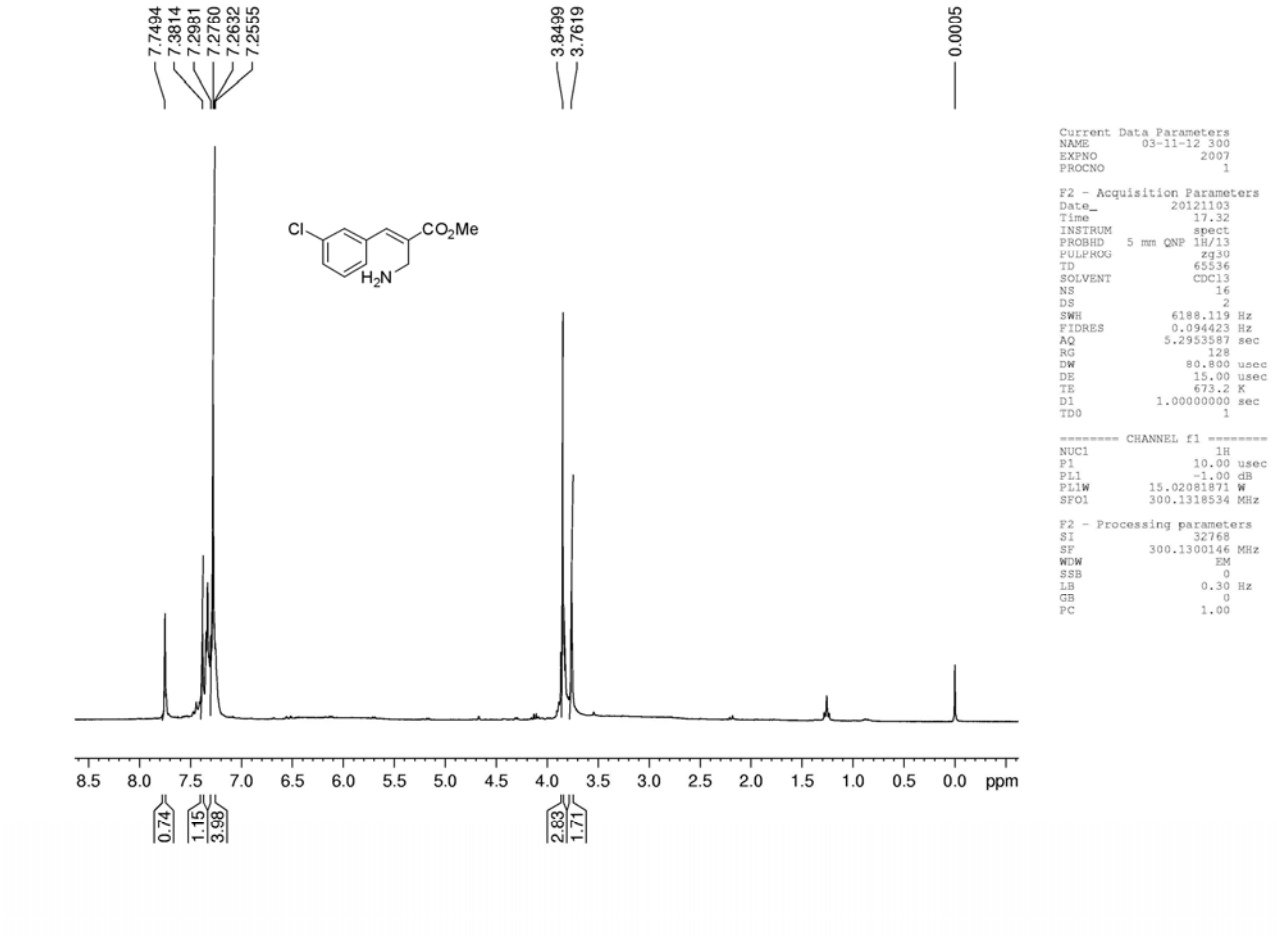


Fig. S-35: ^{1}H spectrum of (*E*)-methyl 2-(aminomethyl)-3-(3-chlorophenyl)acrylate (Table 2, entry 11, **1**).

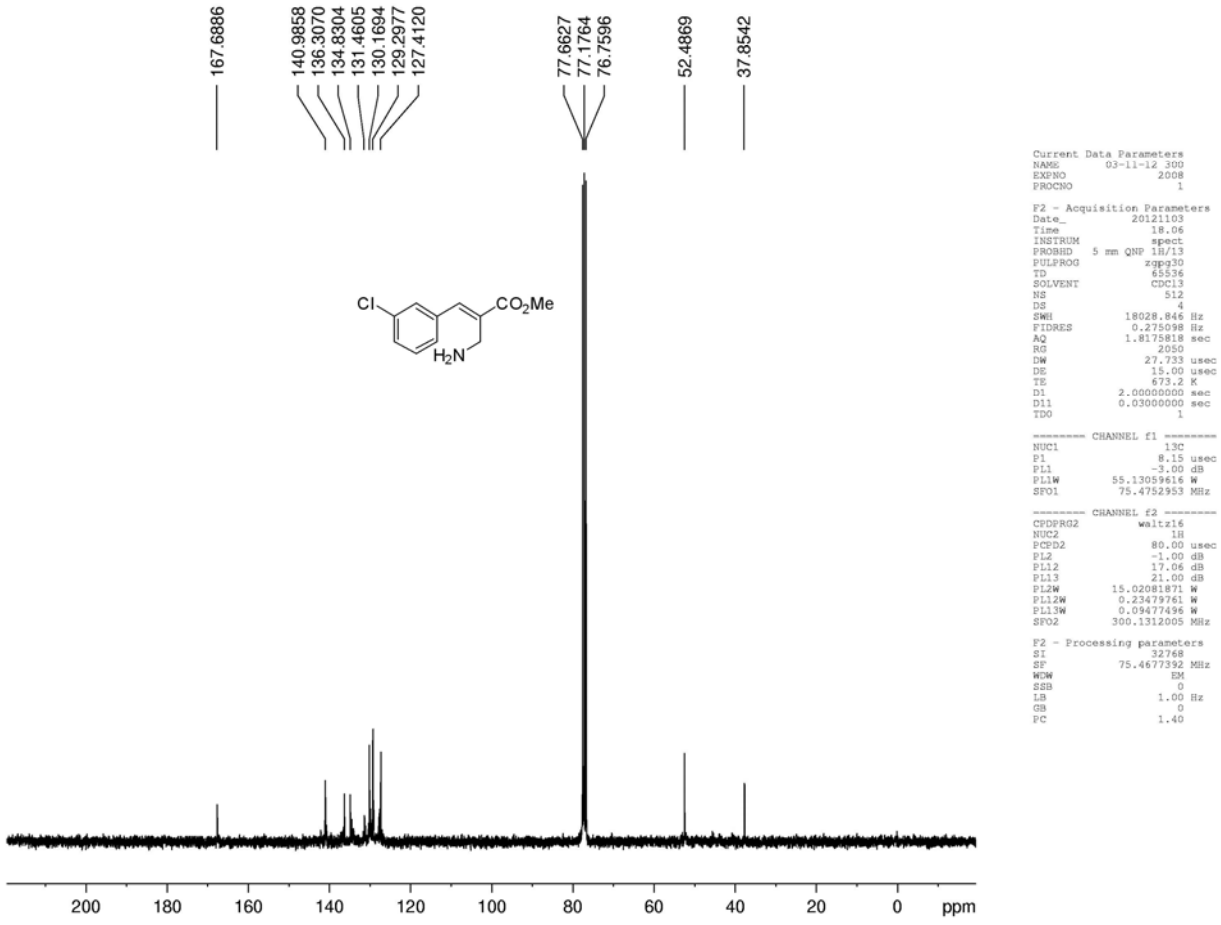


Fig. S-36: ^{13}C spectrum of (*E*)-methyl 2-(aminomethyl)-3-(3-chlorophenyl)acrylate (Table 2, entry 11, **1**).

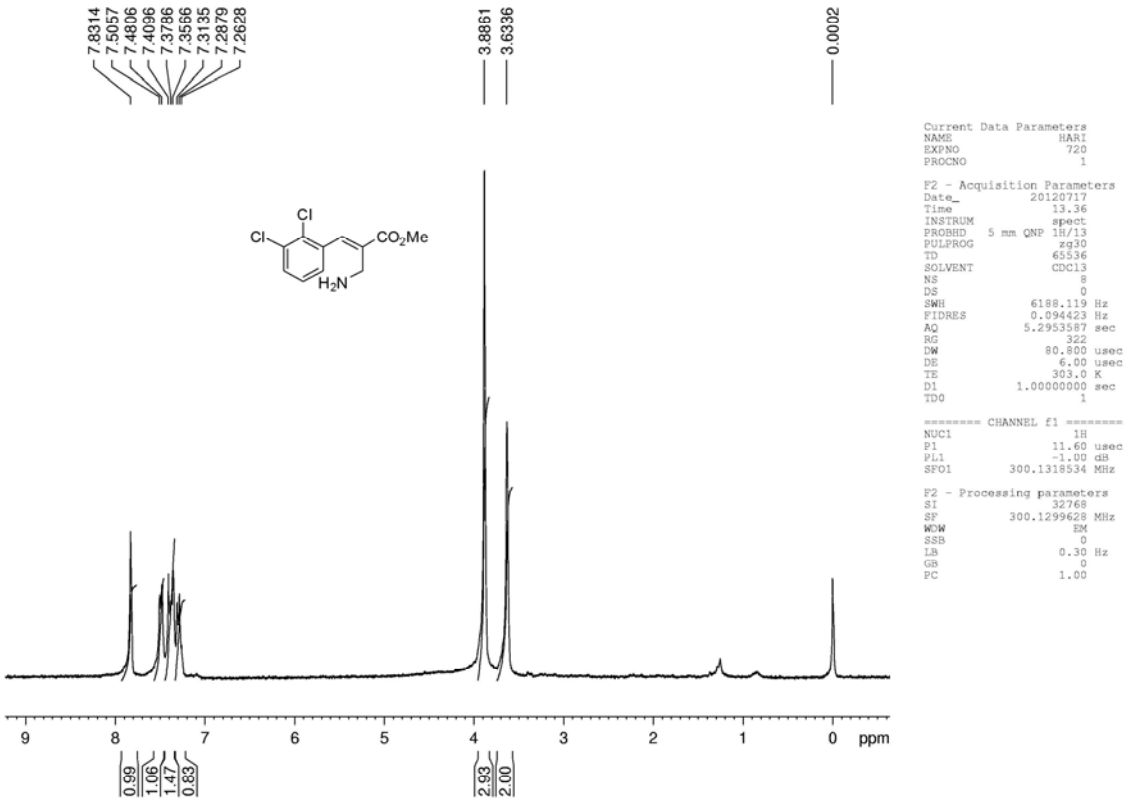


Fig. S-37: ^{1}H spectrum of (*E*)-methyl 2-(aminomethyl)-3-(2,3-dichlorophenyl)acrylate (Table 2, entry 14, **1**).

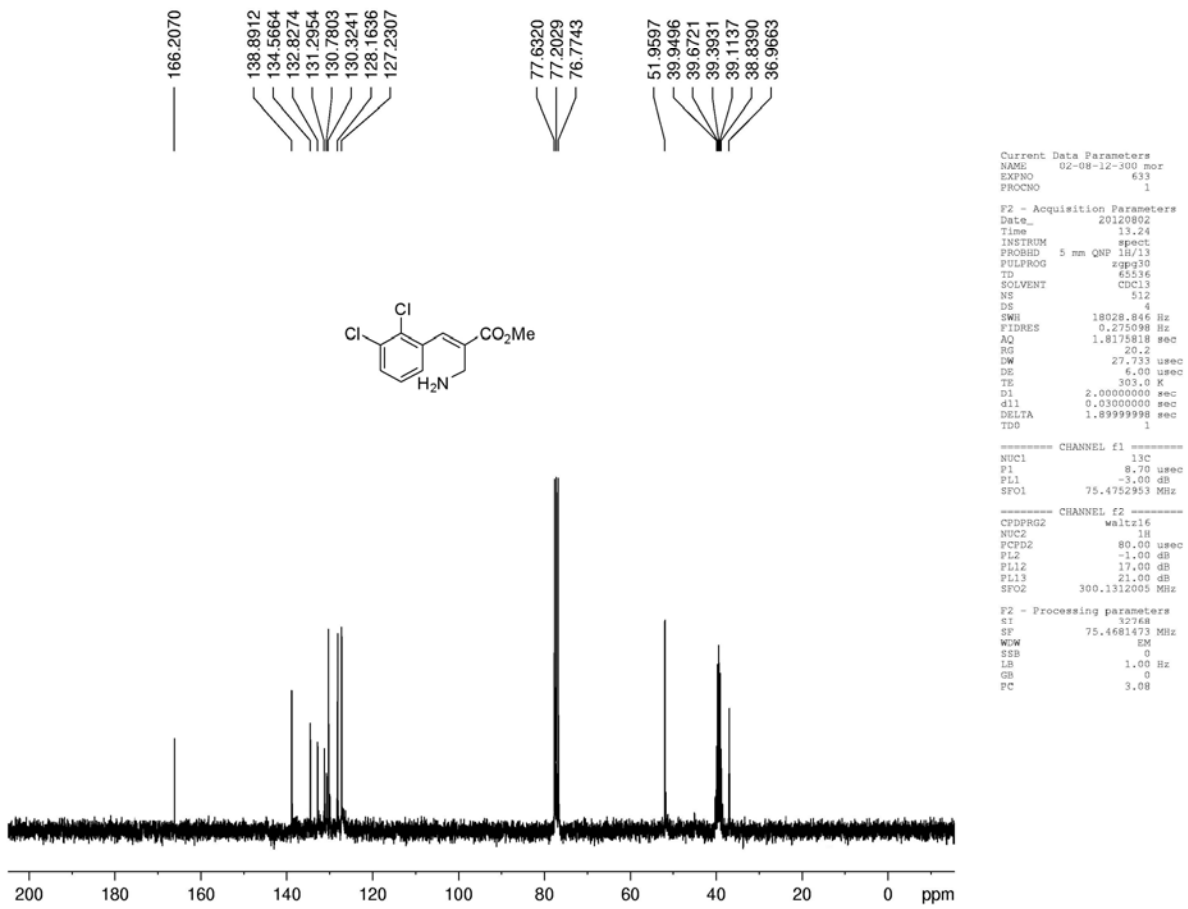


Fig. S-38: ^{13}C spectrum of (*E*)-methyl 2-(aminomethyl)-3-(2,3-dichlorophenyl)acrylate (Table 2, entry 14, **1**).

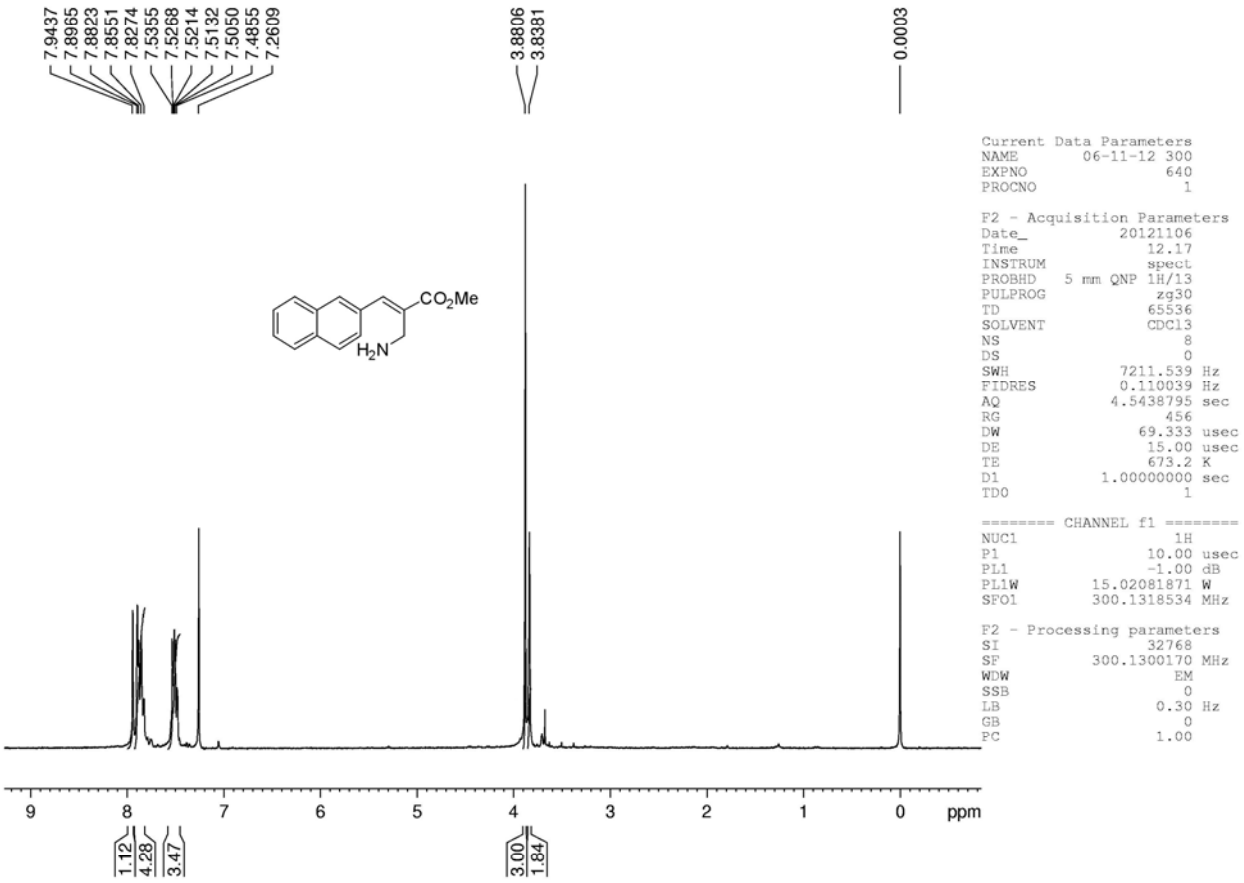


Fig. S-39: ^{1}H spectrum of (*E*)-methyl 2-(aminomethyl)-3-(naphthalen-2-yl)acrylate (Table 2, entry 15, **1**).

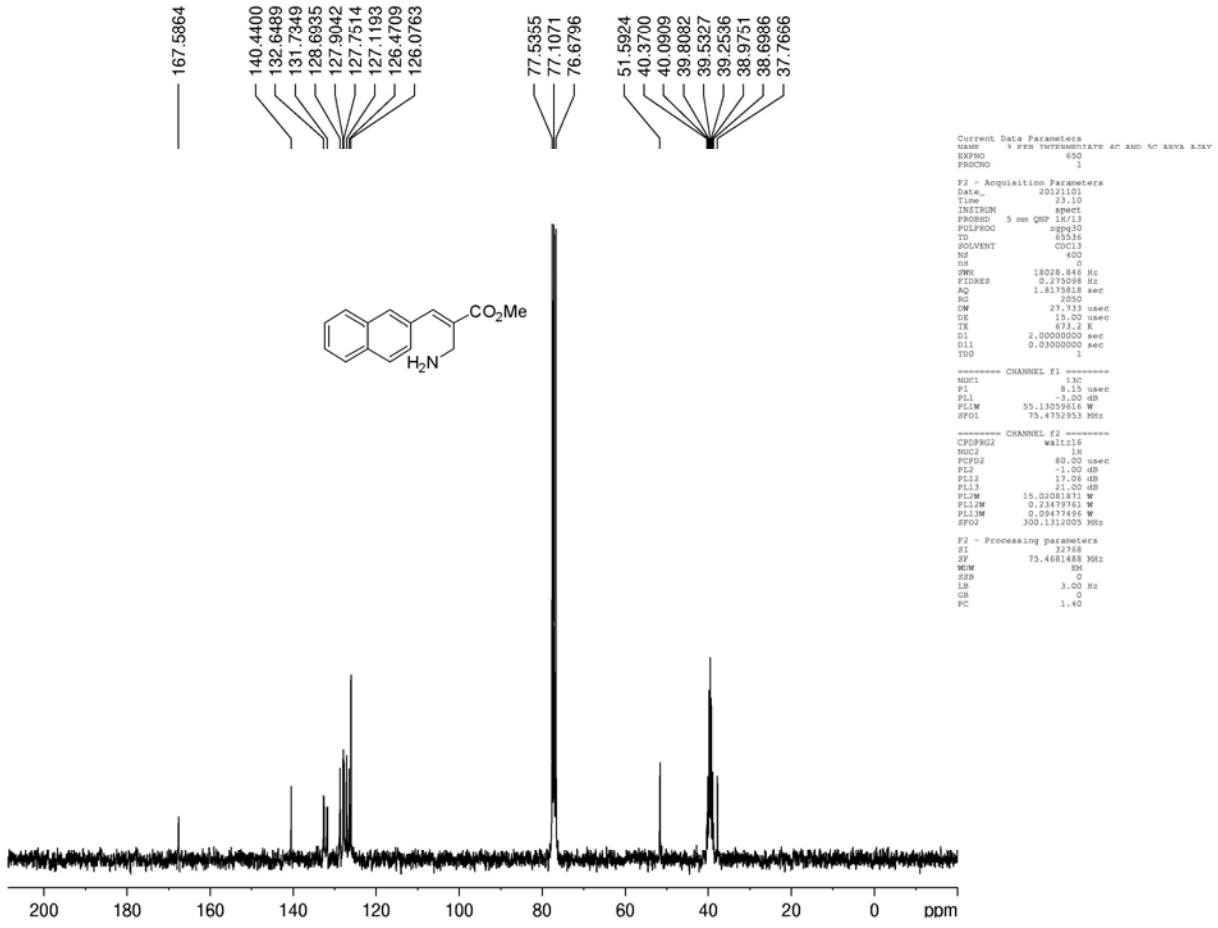


Fig. S-40: ^{13}C spectrum of (*E*)-methyl 2-(aminomethyl)-3-(naphthalen-2-yl)acrylate (Table 2, entry 15, **1**).

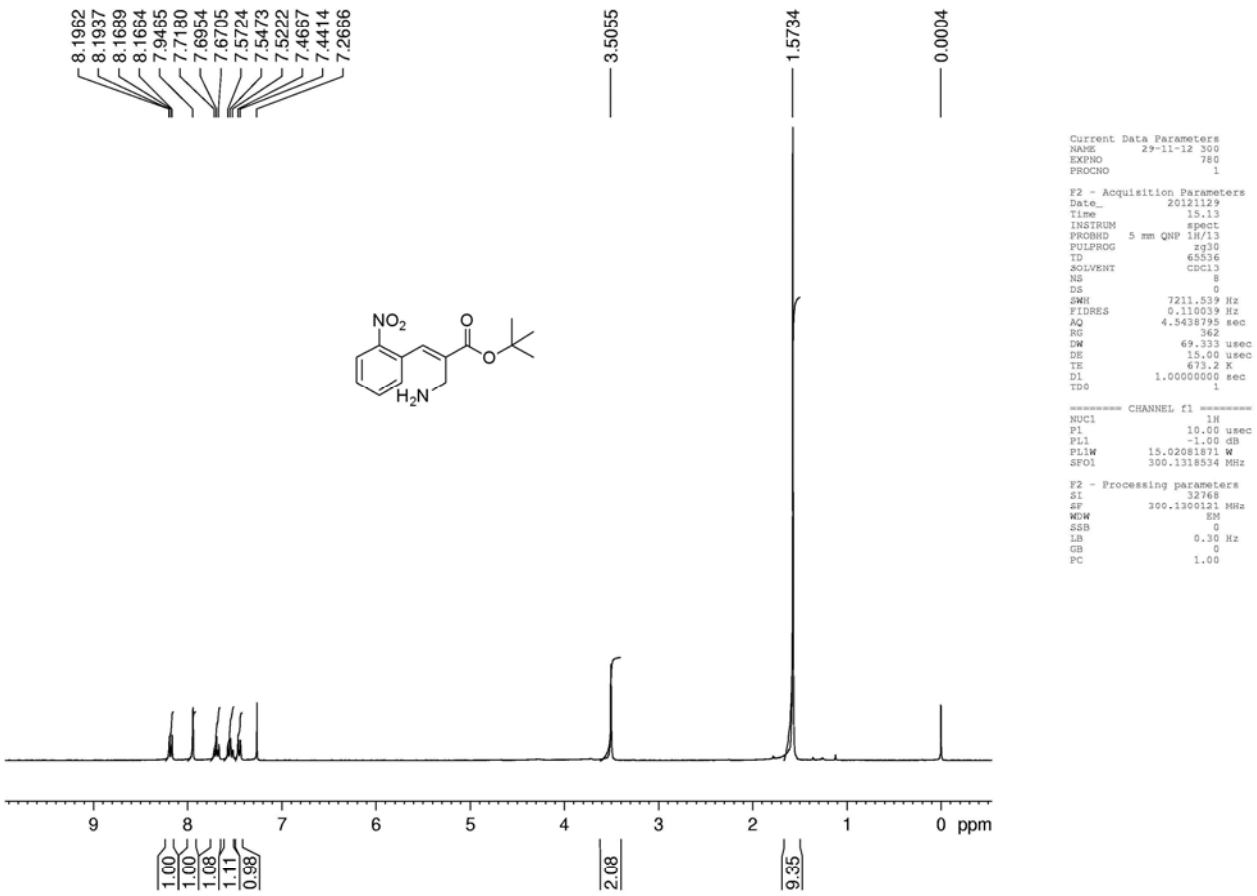


Fig. S-41: ^{1}H spectrum of (*E*)-*tert*-butyl 2-(aminomethyl)-3-(2-nitrophenyl)acrylate (Table 2, entry 18, **1**).

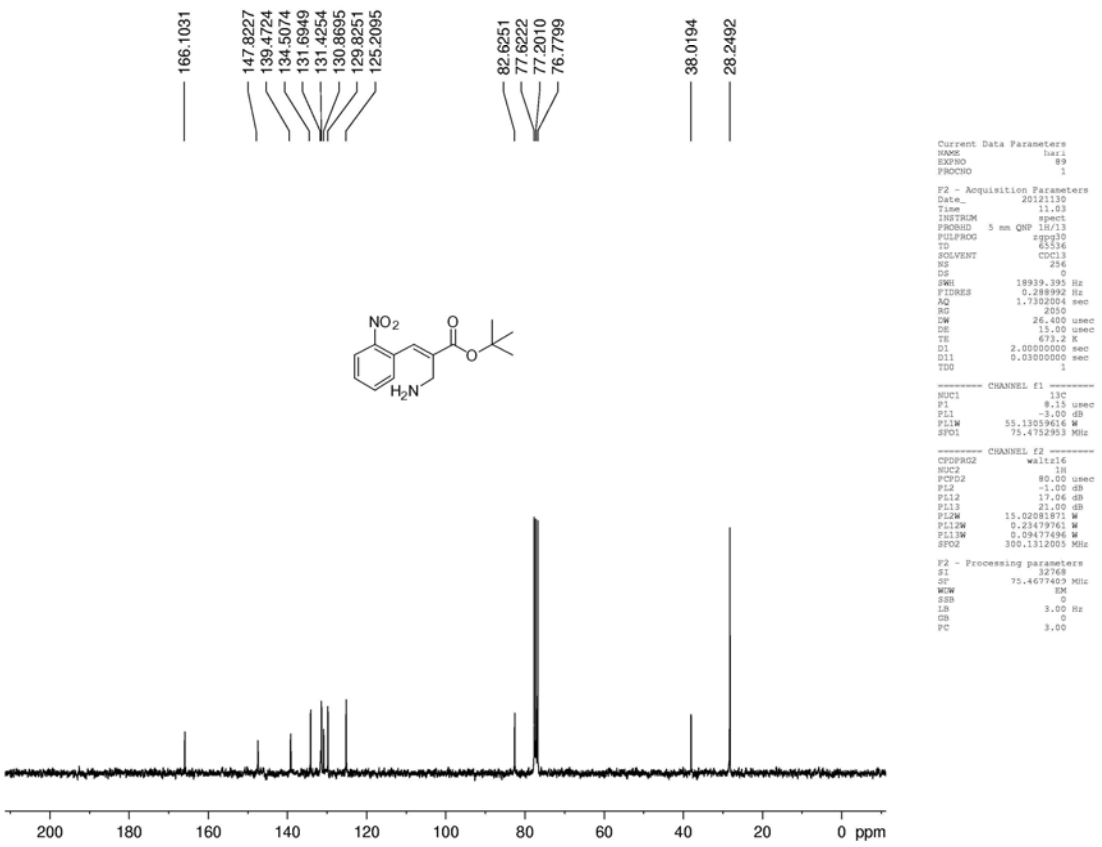


Fig. S-42: ^{13}C spectrum of (*E*)-*tert*-butyl 2-(aminomethyl)-3-(2-nitrophenyl)acrylate (Table 2, entry 18, **1**).

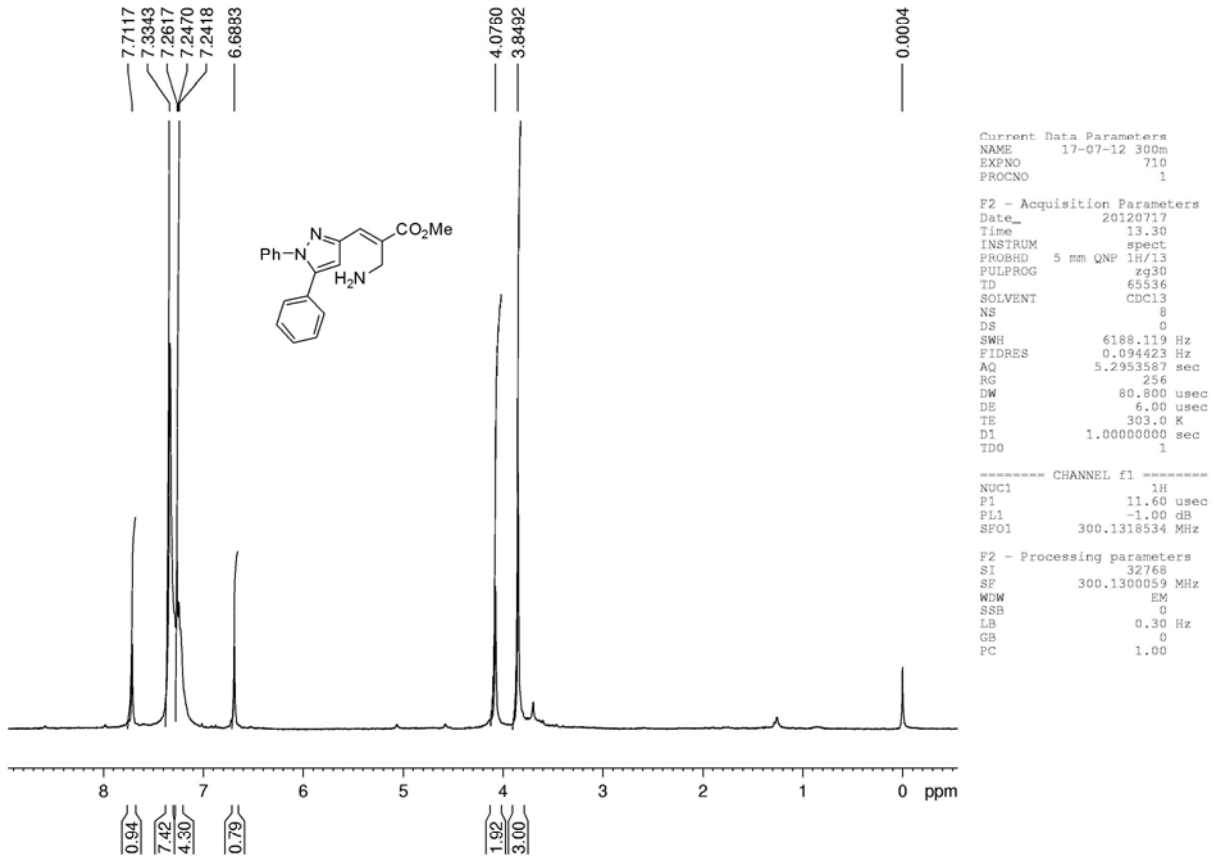


Fig. S-43: ^{1}H spectrum of (*E*)-methyl 2-(aminomethyl)-3-(1,5-diphenyl-1*H*-pyrazol-3-yl)acrylate (Table 2, entry 19, **1**).

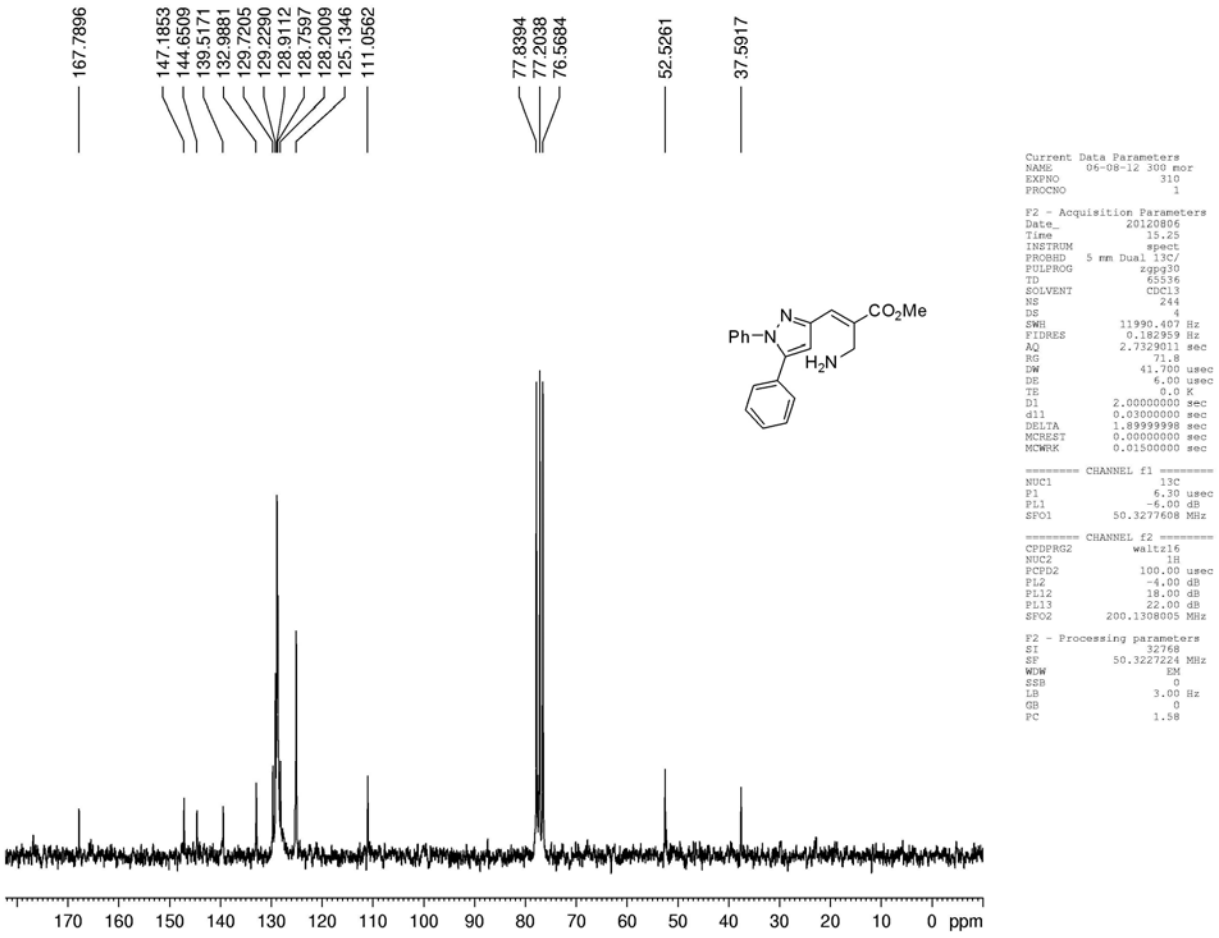


Fig. S-44: ^{13}C spectrum of (*E*)-methyl 2-(aminomethyl)-3-(1,5-diphenyl-1*H*-pyrazol-3-yl)acrylate (Table 2, entry 19, **1**).

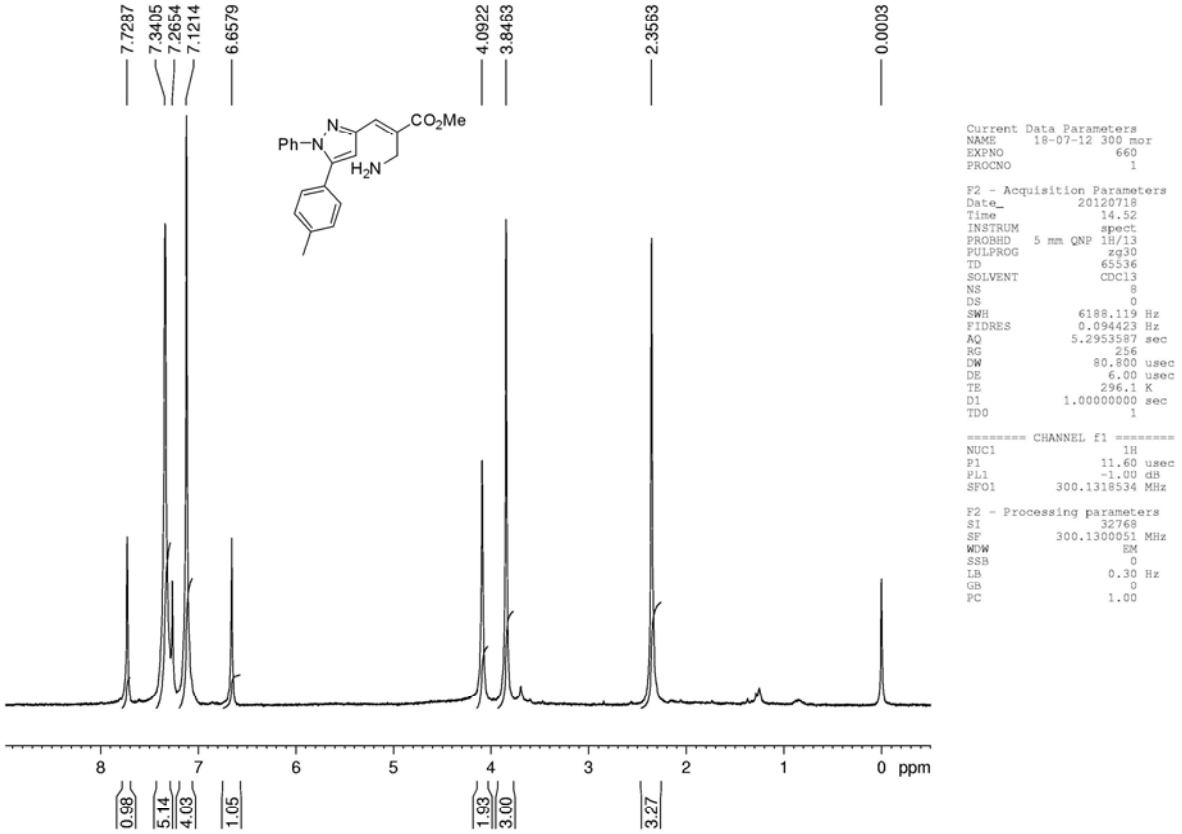


Fig:S-45 ^{1}H spectrum of (*E*)-methyl 2-(aminomethyl)-3-(1-phenyl-5-(4-methylphenyl)-1*H*-pyrazol-3-yl)acrylate (Table 2, entry 20, **1**).

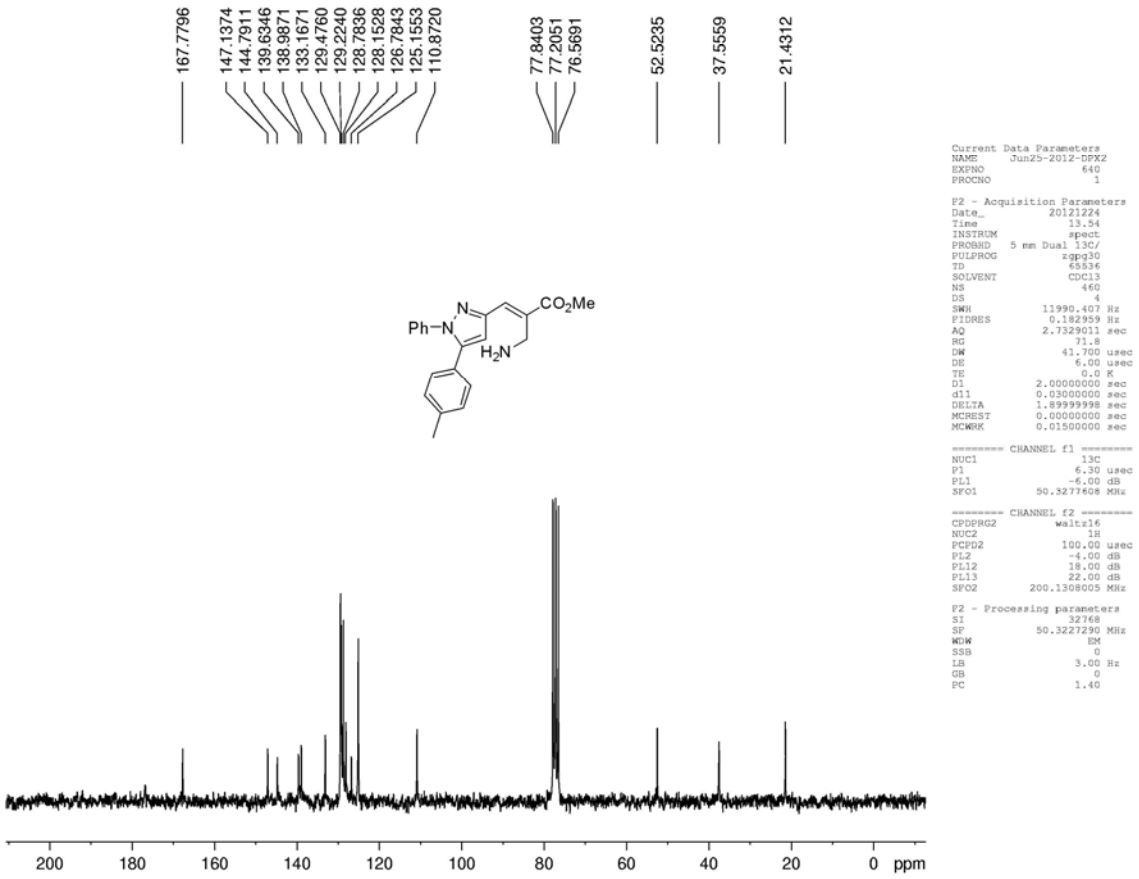


Fig. S-46: ^{13}C spectrum of (*E*)-methyl 2-(aminomethyl)-3-(1,5-diphenyl-1*H*-pyrazol-3-yl)acrylate (Table 2, entry 20, **1**).

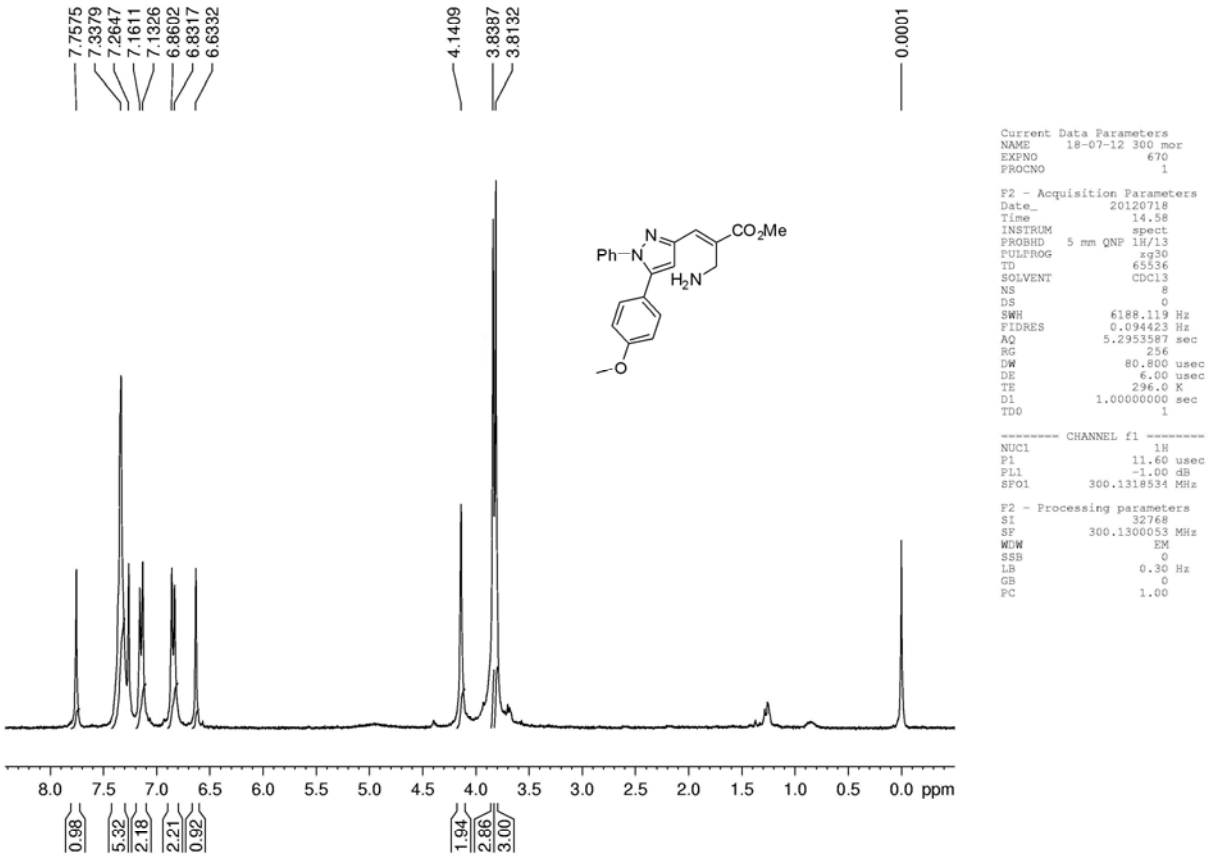


Fig. S-47: ^{1}H spectrum of (*E*)-methyl 2-(aminomethyl)-3-(5-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-3-yl)acrylate (Table 2, entry 21, **1**).

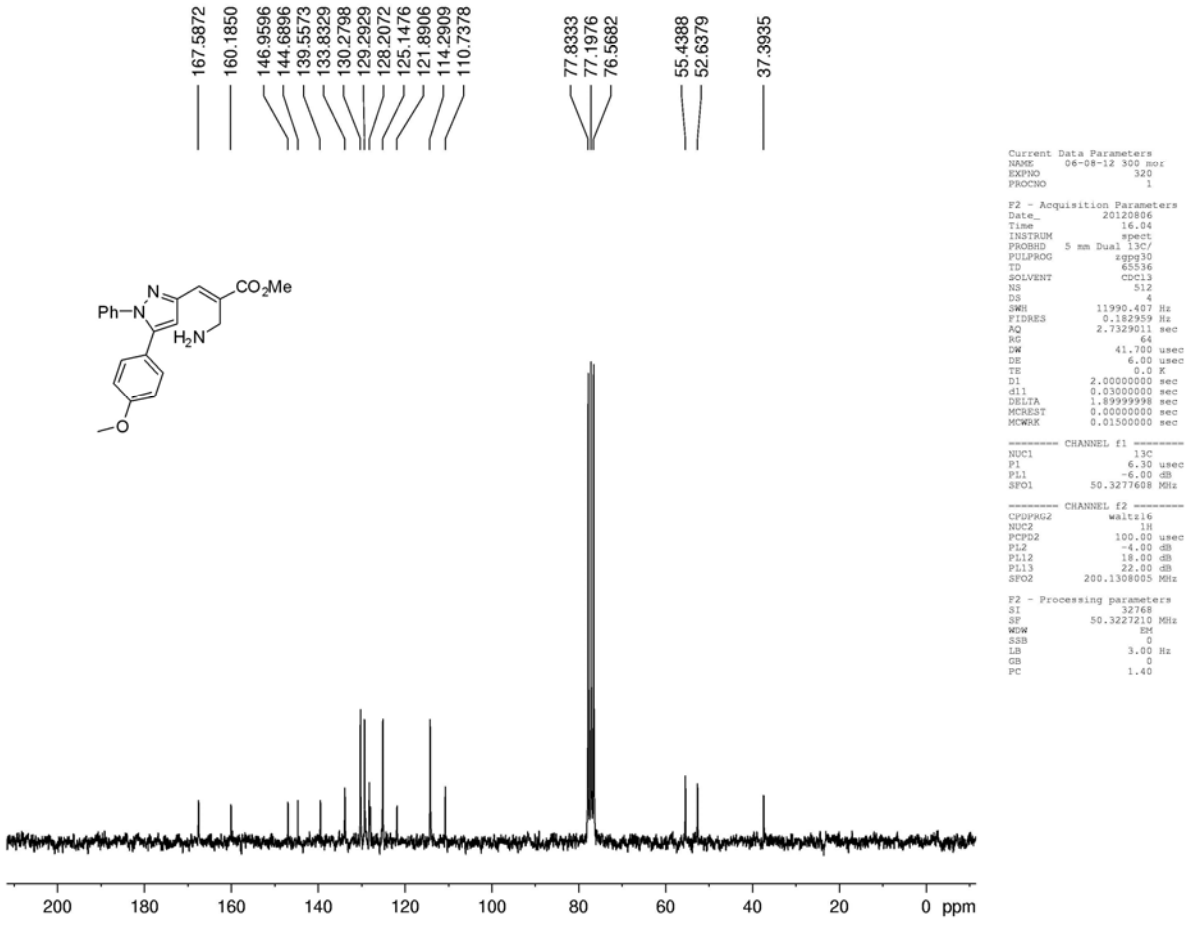


Fig. S-48: ^{13}C spectrum of (*E*)-methyl 2-(aminomethyl)-3-(5-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-3-yl)acrylate (Table 2, entry 21, **1**).

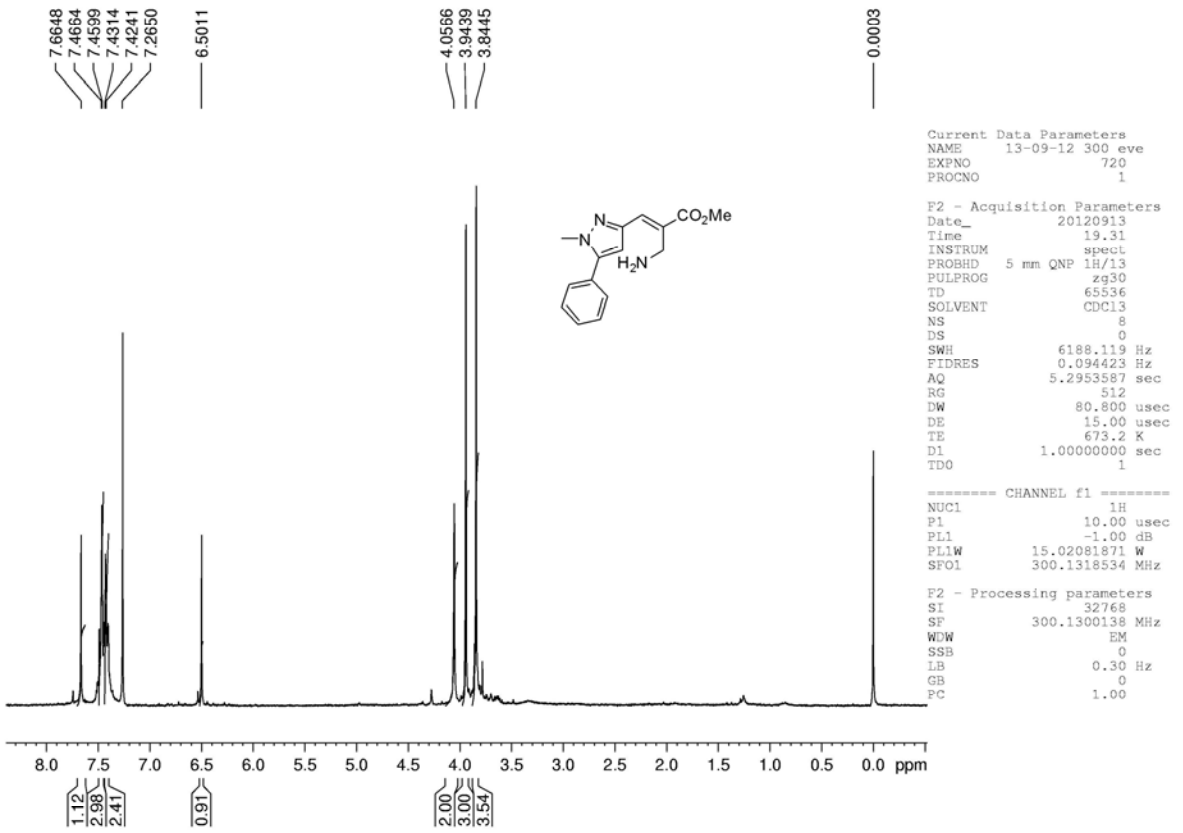


Fig. S-49: ^{1}H spectrum of (*E*)-methyl 2-(aminomethyl)-3-(1-methyl-5-phenyl-1*H*-pyrazol-3-yl)acrylate (Table 2, entry 22, **1**).

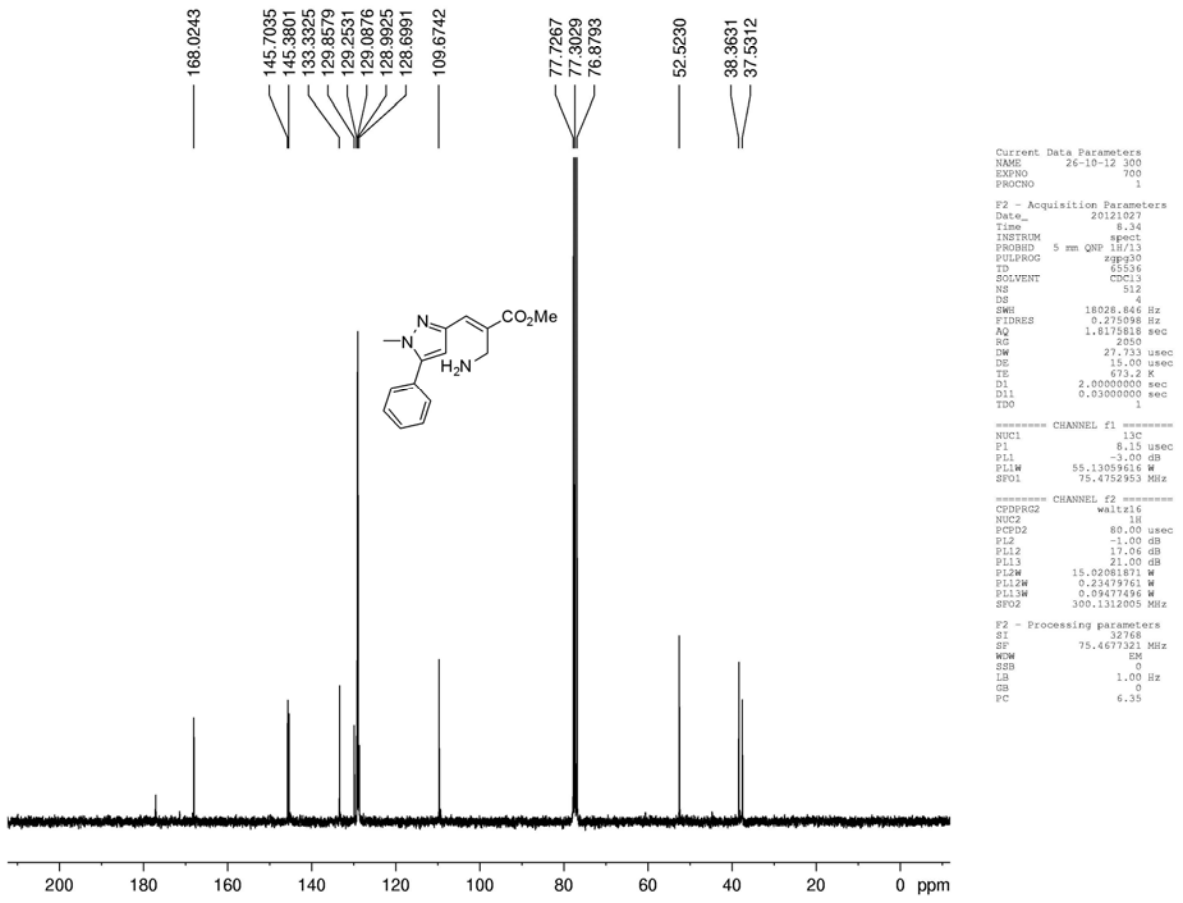


Fig. S-50: ^{13}C spectrum of (*E*)-methyl 2-(aminomethyl)-3-(5-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-3-yl)acrylate (Table 2, entry 22, **1**).

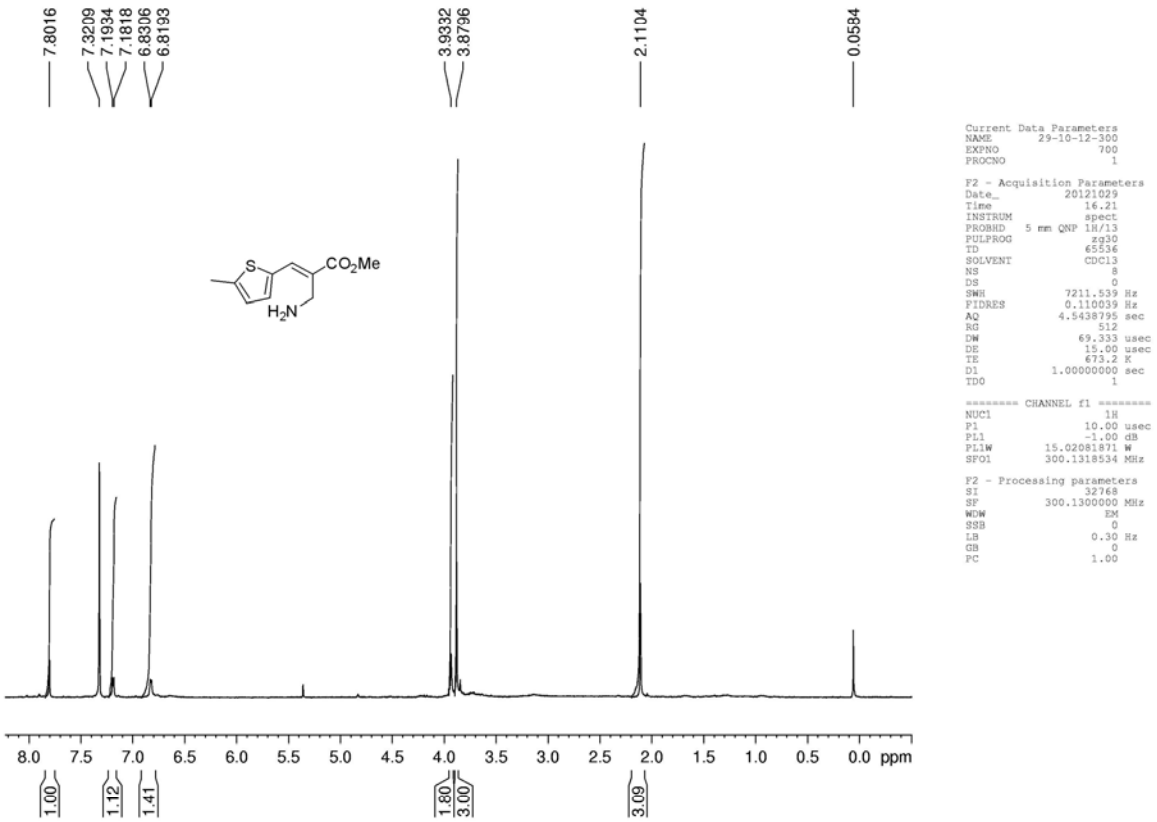


Fig. S-51: ^{1}H spectrum of (*E*)-methyl 2-(aminomethyl)-3-(5-methylthiophen-2-yl)acrylate (Table 2, entry 24, **1**).

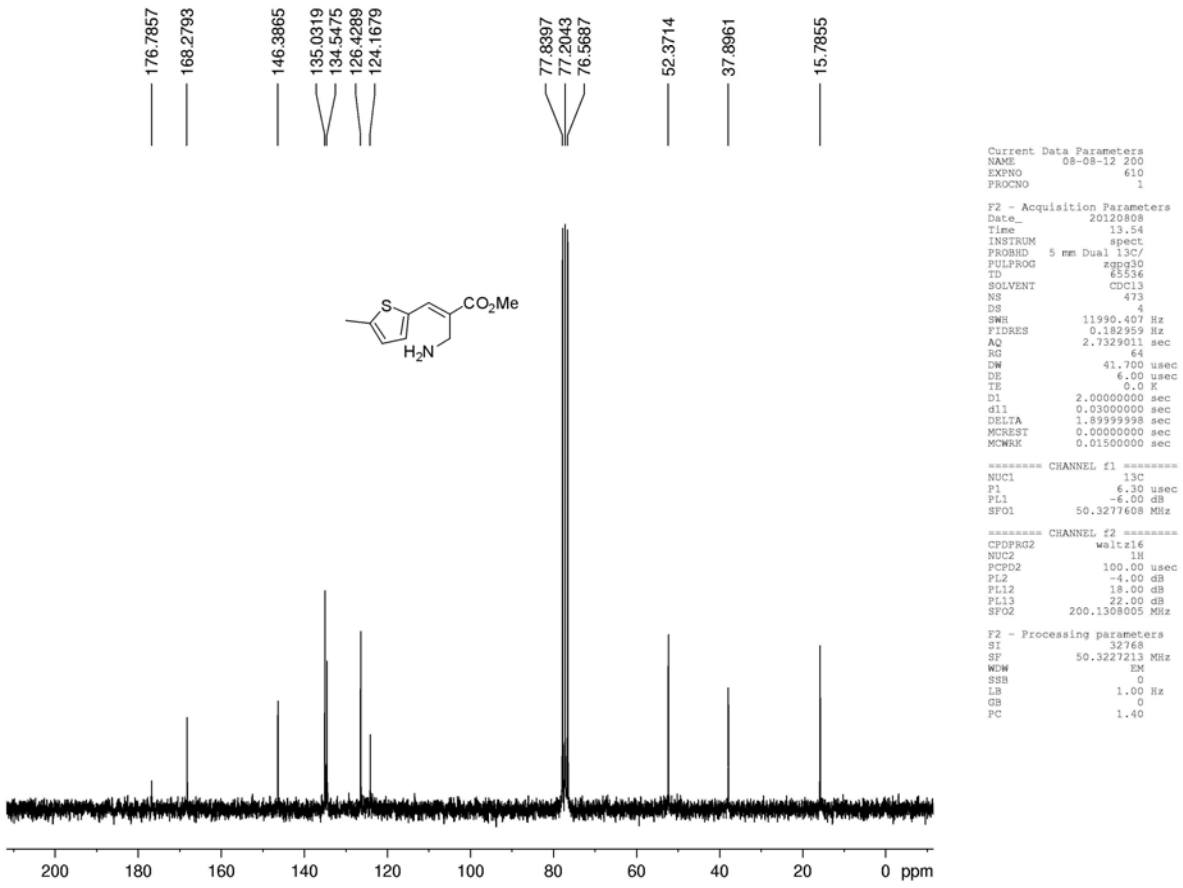


Fig. S-52: ^{13}C spectrum of (*E*)-methyl 2-(aminomethyl)-3-(5-methylthiophen-2-yl)acrylate (Table 2, entry 24, **1**).

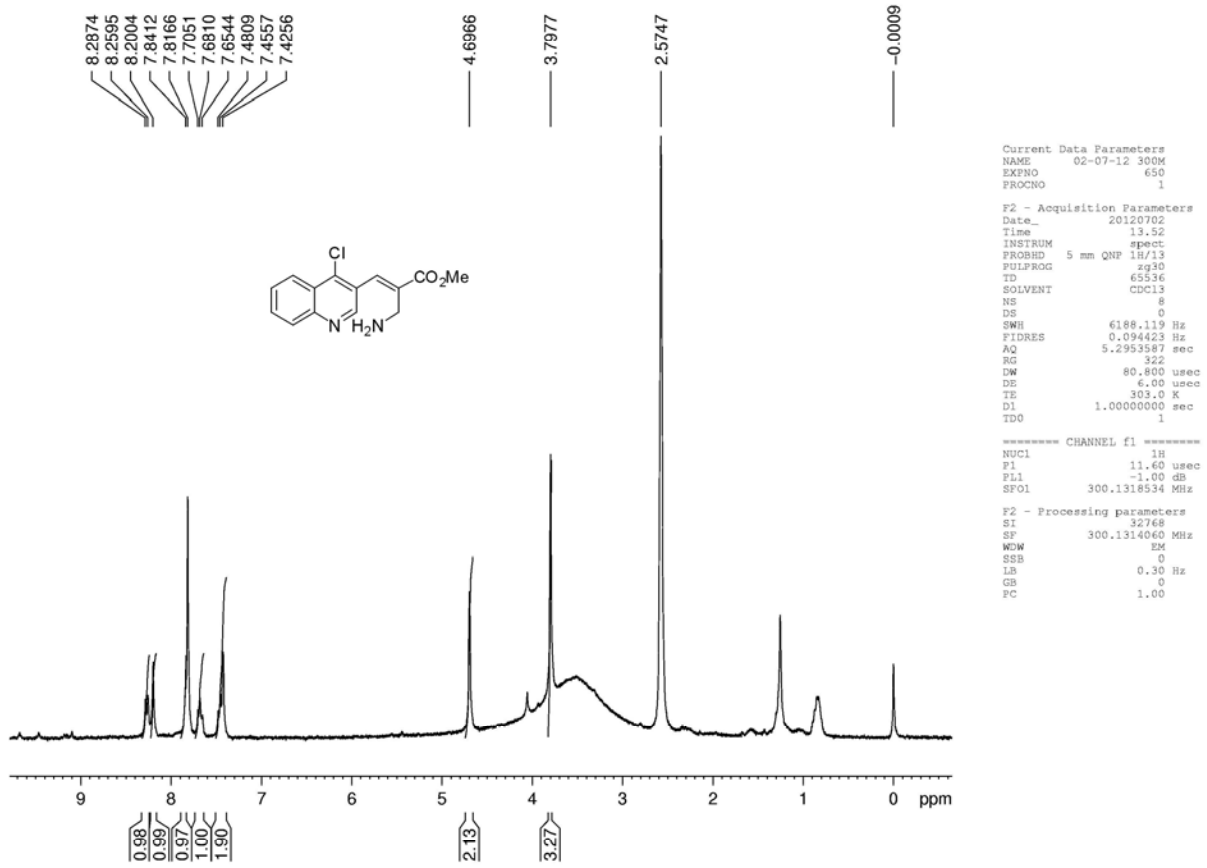


Fig. S-53: ^{1}H spectrum of (*E*)-methyl 2-(aminomethyl)-3-(4-chloroquinolin-3-yl)acrylate (Table 2, entry 25, **1**).

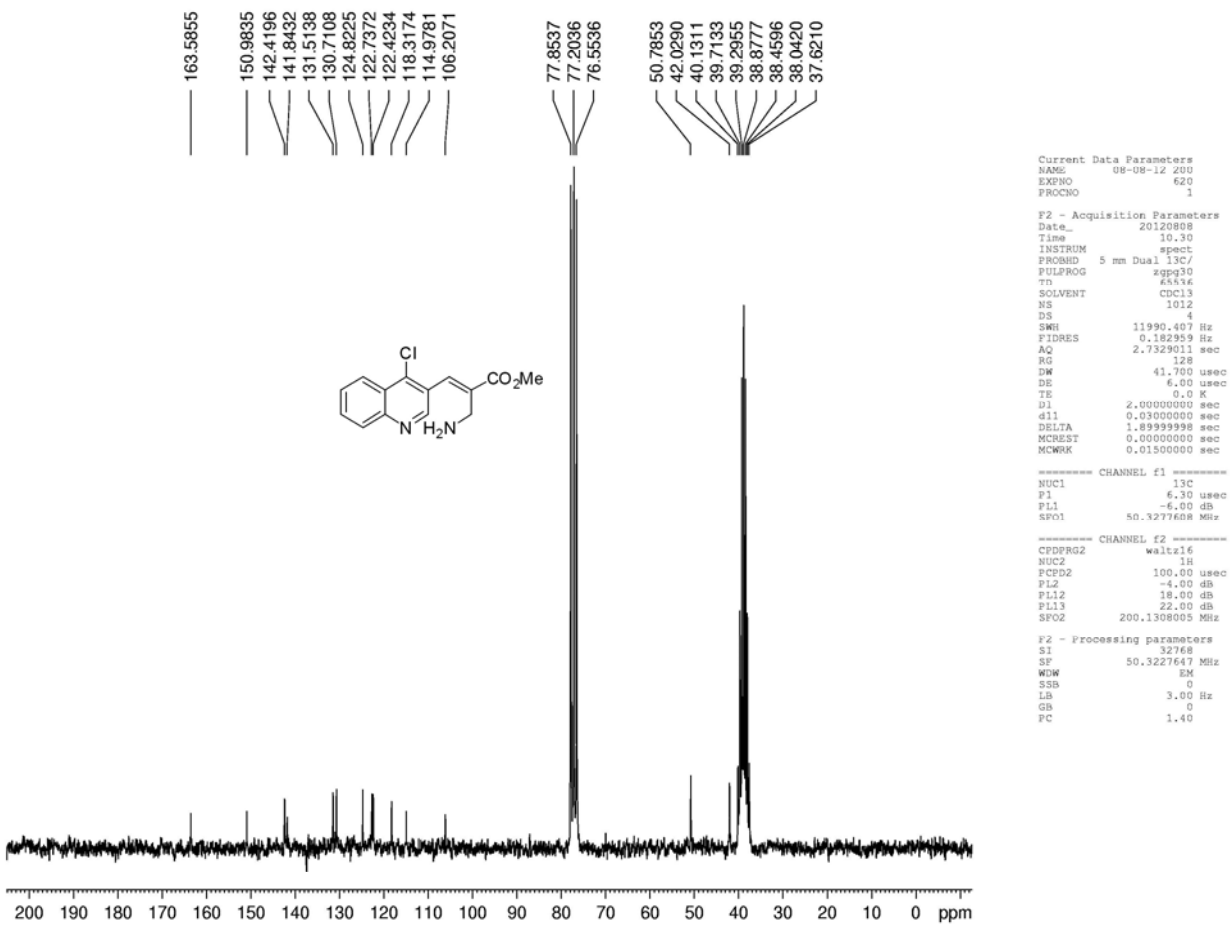


Fig. S-54: ^{13}C spectrum of (*E*)-methyl 2-(aminomethyl)-3-(4-chloroquinolin-3-yl)acrylate (Table 2, entry 25, **1**).

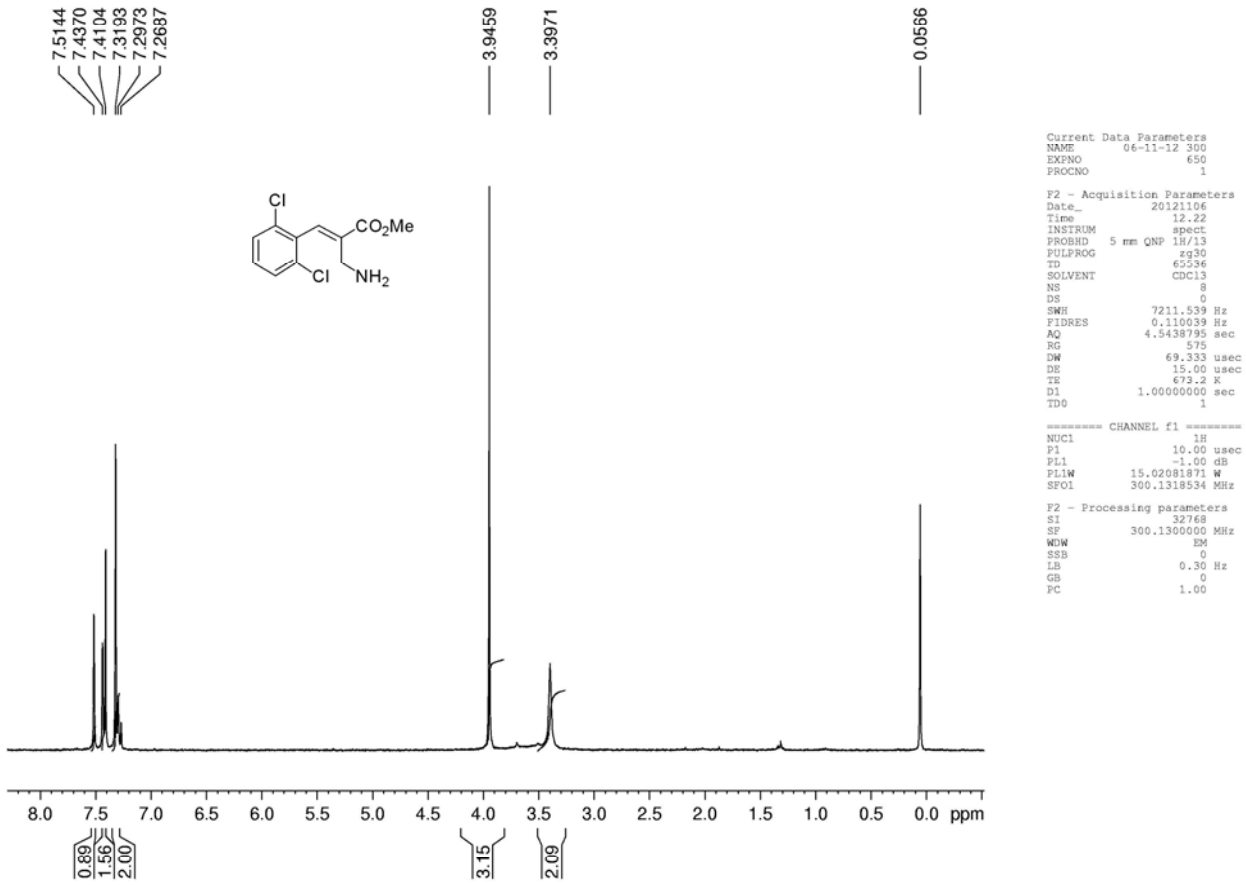


Fig. S-55: ^{1}H spectrum of (*E*)-methyl 2-(aminomethyl)-3-(2,6-dichlorophenyl)acrylate (Table 2, entry 26, **1**).

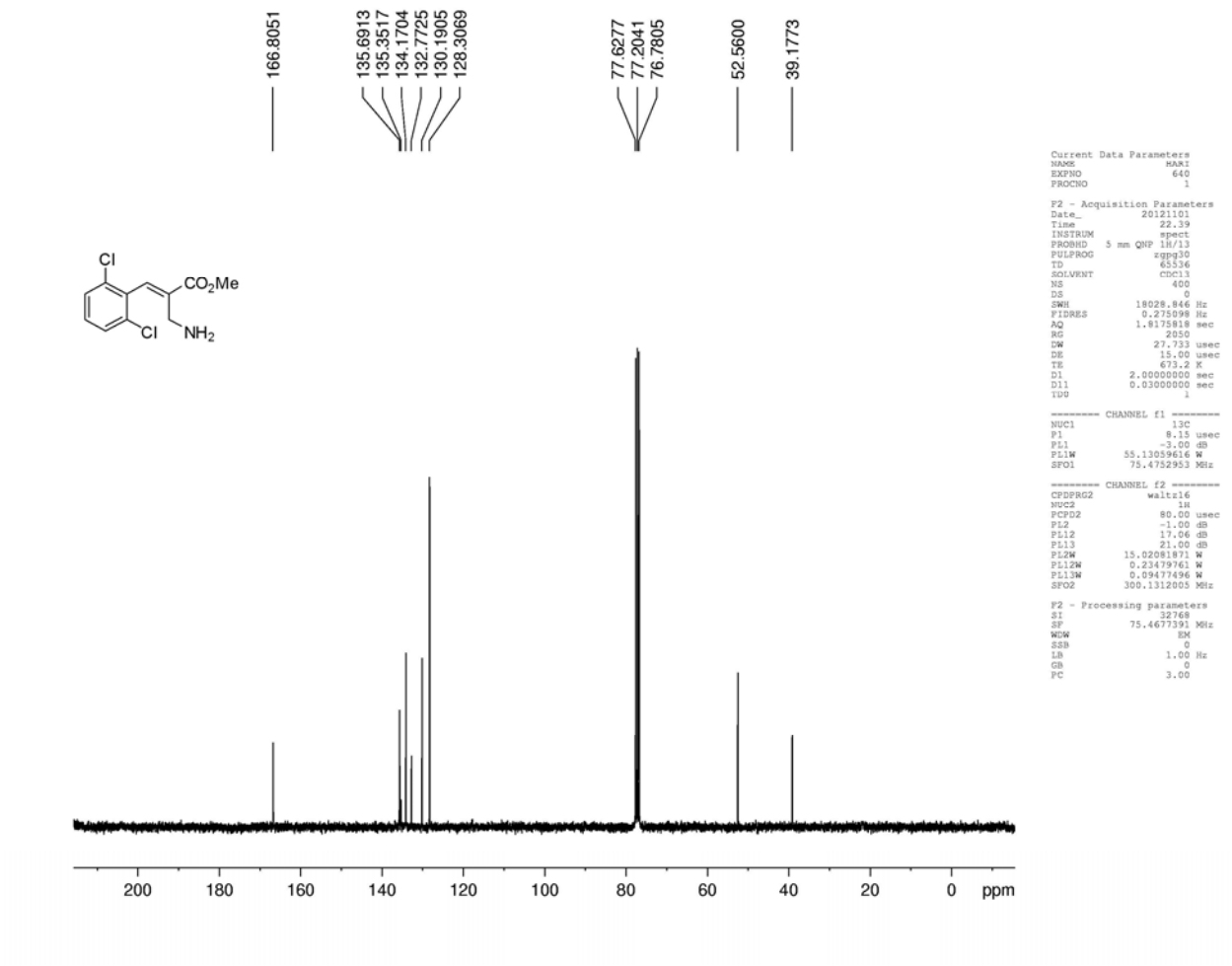


Fig. S-56: ^{13}C spectrum of (*E*)-methyl 2-(aminomethyl)-3-(2,6-dichlorophenyl)acrylate (Table 2, entry 26, **1**).

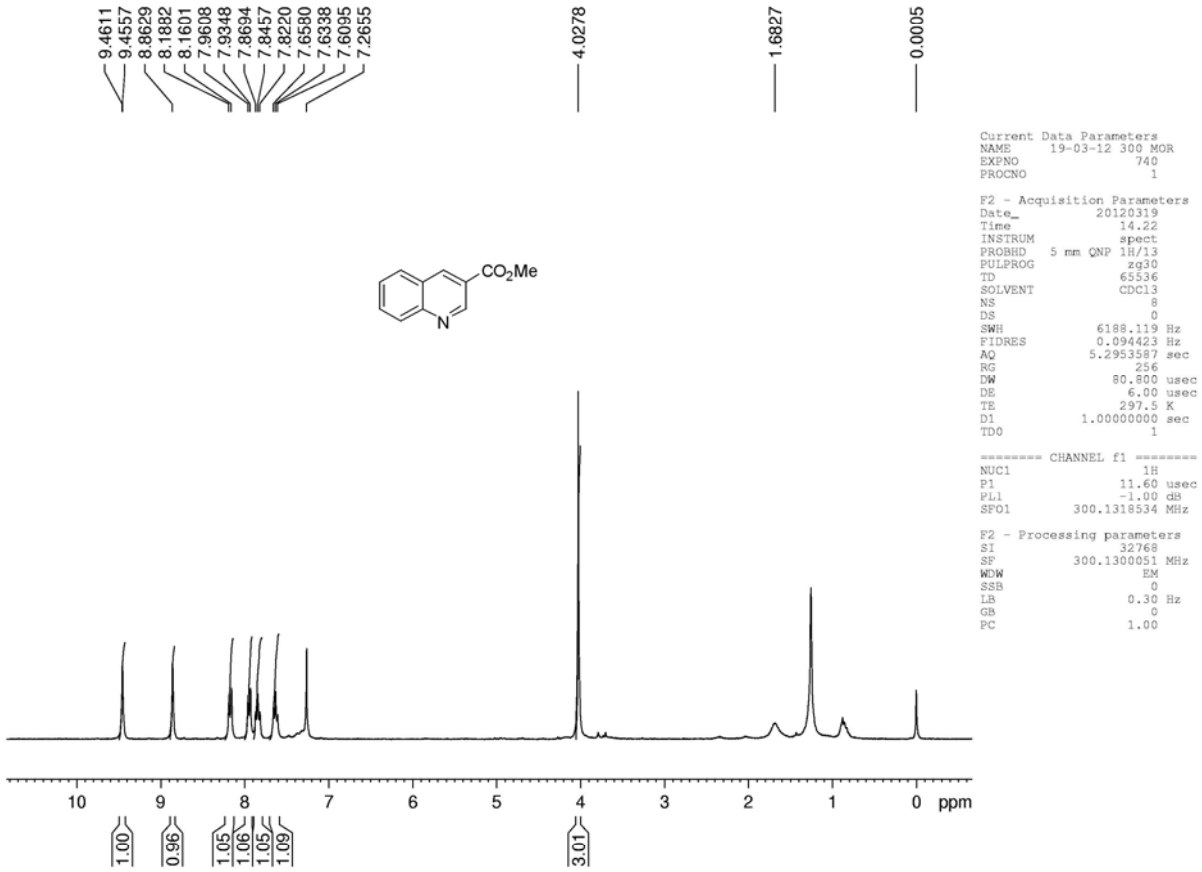


Fig. S-57: ^{1}H spectrum of methyl quinoline-3-carboxylate (Table 2, entry 1, **2**).

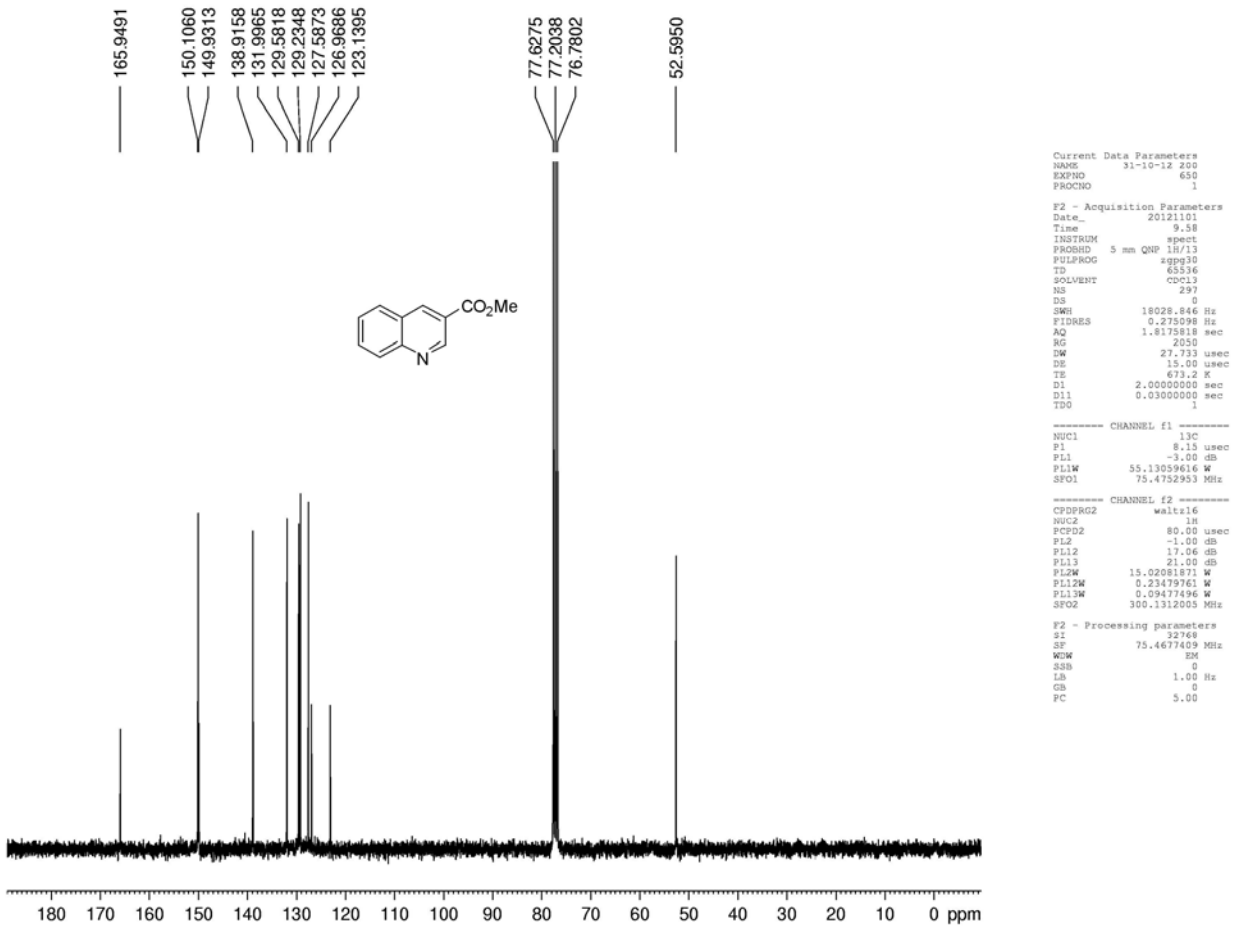


Fig. S-58: ^{13}C spectrum of methyl quinoline-3-carboxylate (Table 2, entry 1, **2**).

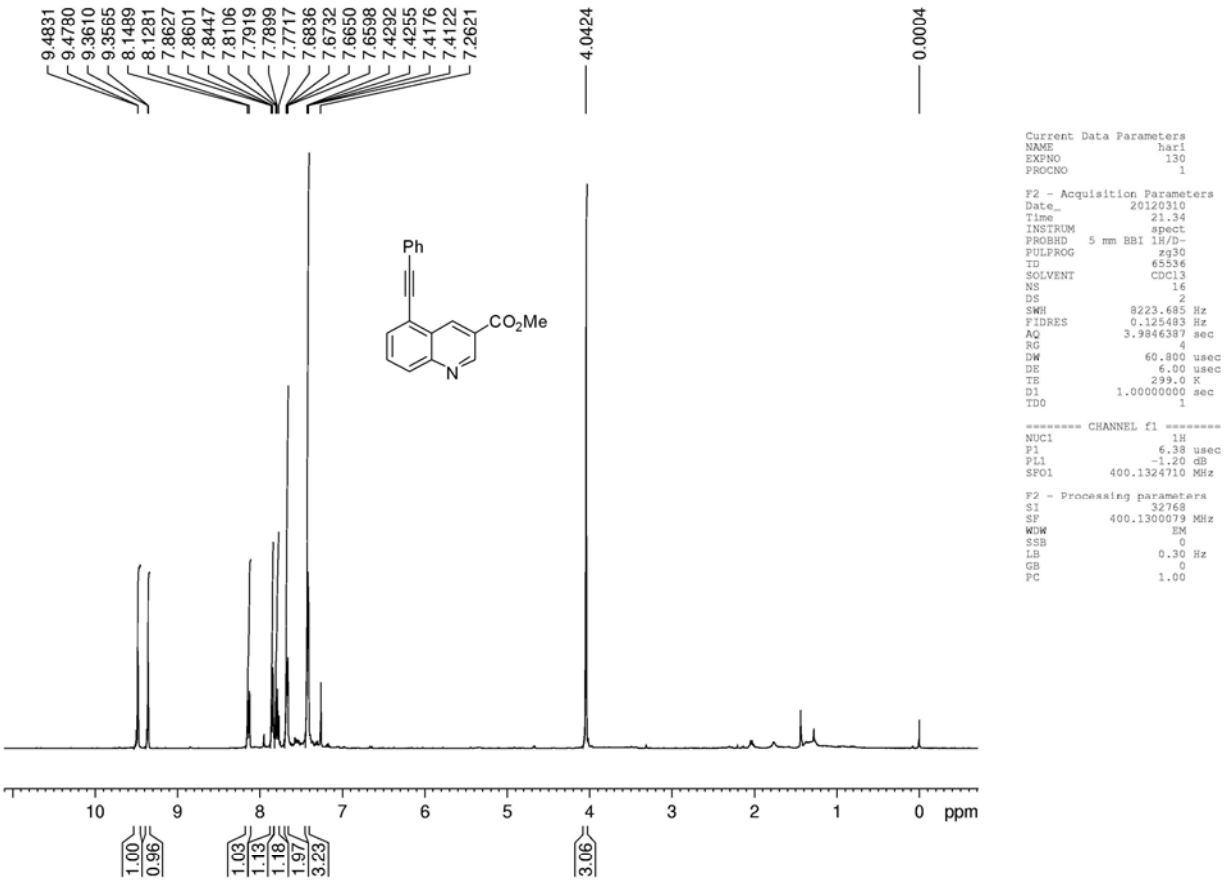


Fig. S-59: ^{1}H spectrum of methyl 5-(phenylethynyl)quinoline-3-carboxylate (Table 2, entry 2, **2**).

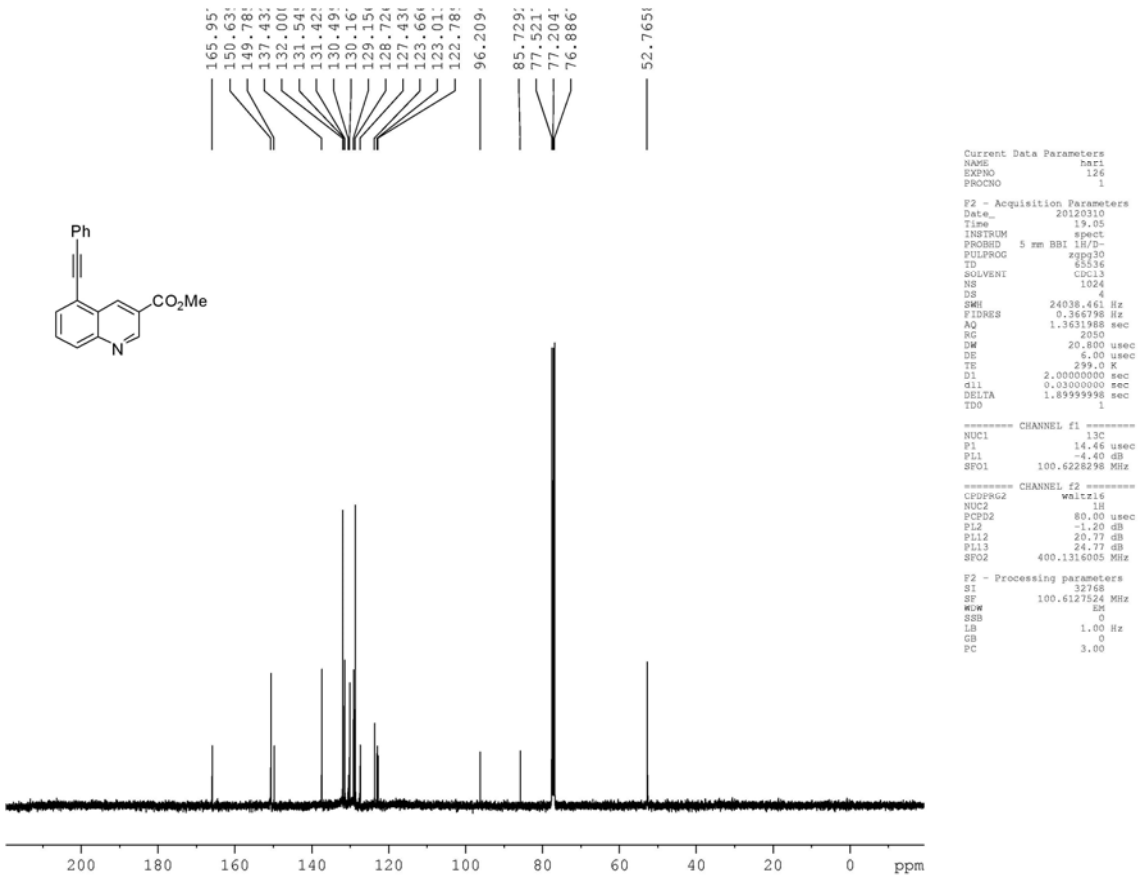


Fig. S-60: ^{13}C spectrum of methyl 5-(phenylethynyl)quinoline-3-carboxylate (Table 2, entry 2, **2**).

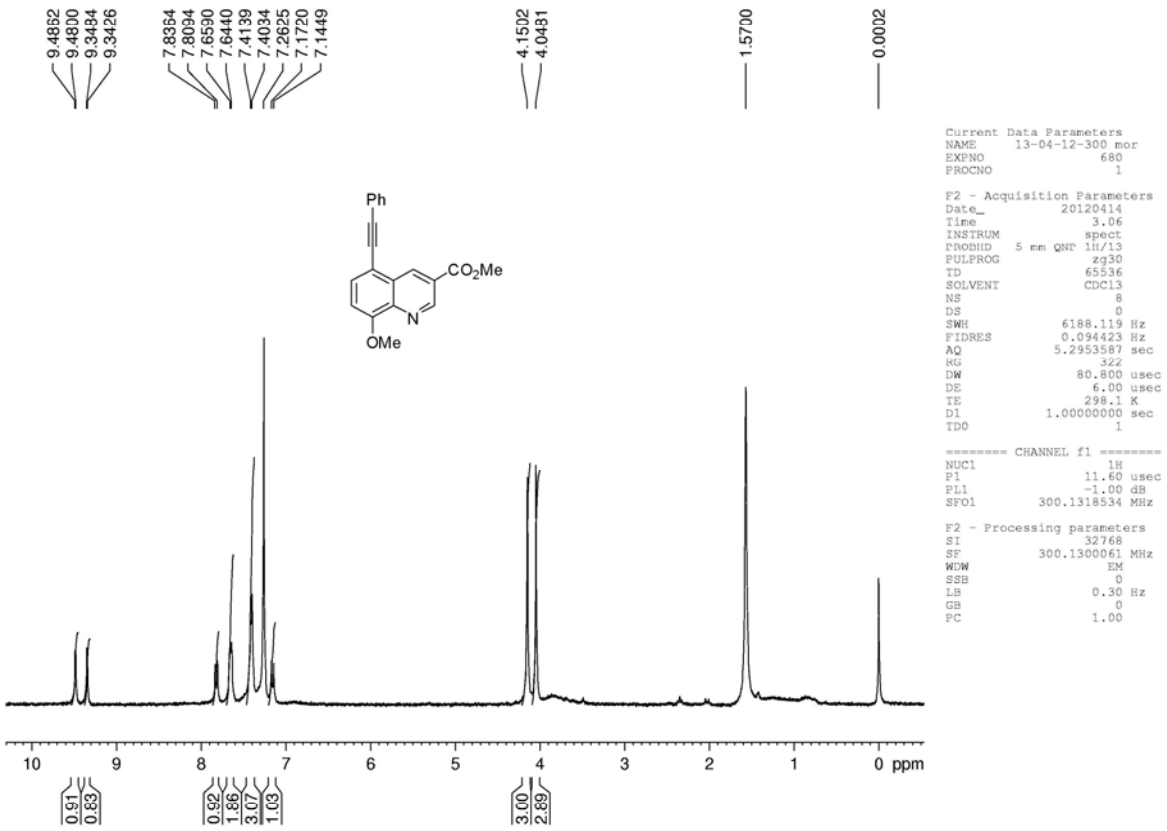


Fig. S-61: ^{1}H spectrum of methyl 8-methoxy-5-(phenylethynyl)quinoline-3-carboxylate (Table 2, entry 3, **2**).

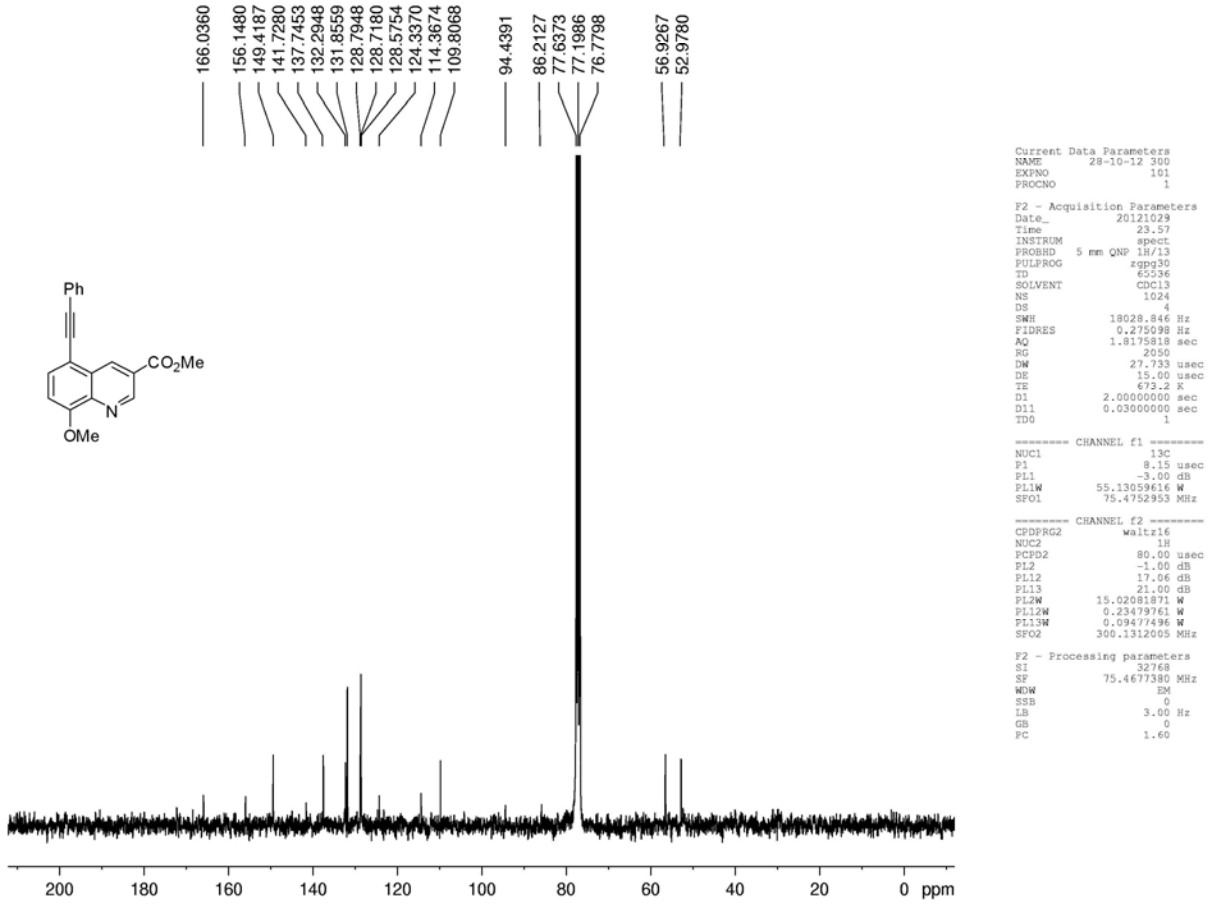


Fig. S-62: ^{13}C spectrum of methyl 8-methoxy-5-(phenylethynyl)quinoline-3-carboxylate (Table 2, entry 3, **2**).

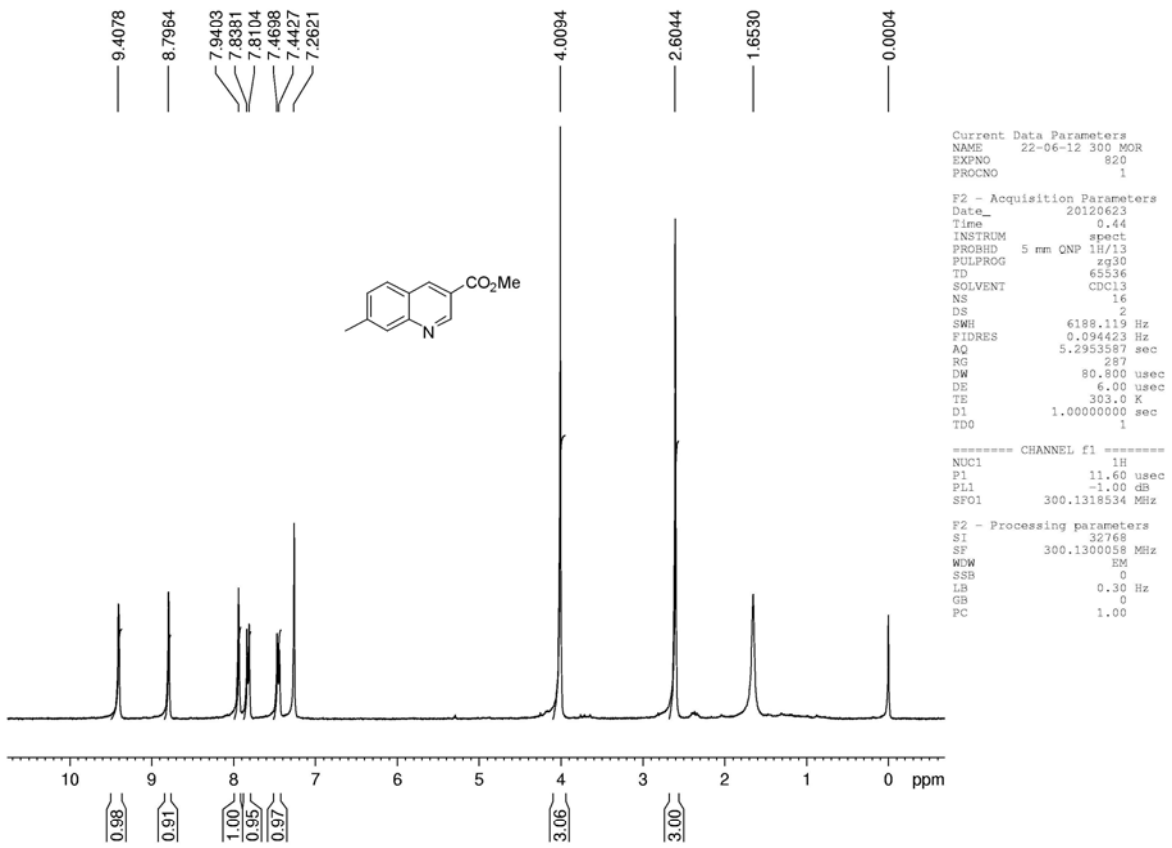


Fig. S-63: ^{1}H spectrum of methyl 7-methylquinoline-3-carboxylate (Table 2, entry 4, **2**).

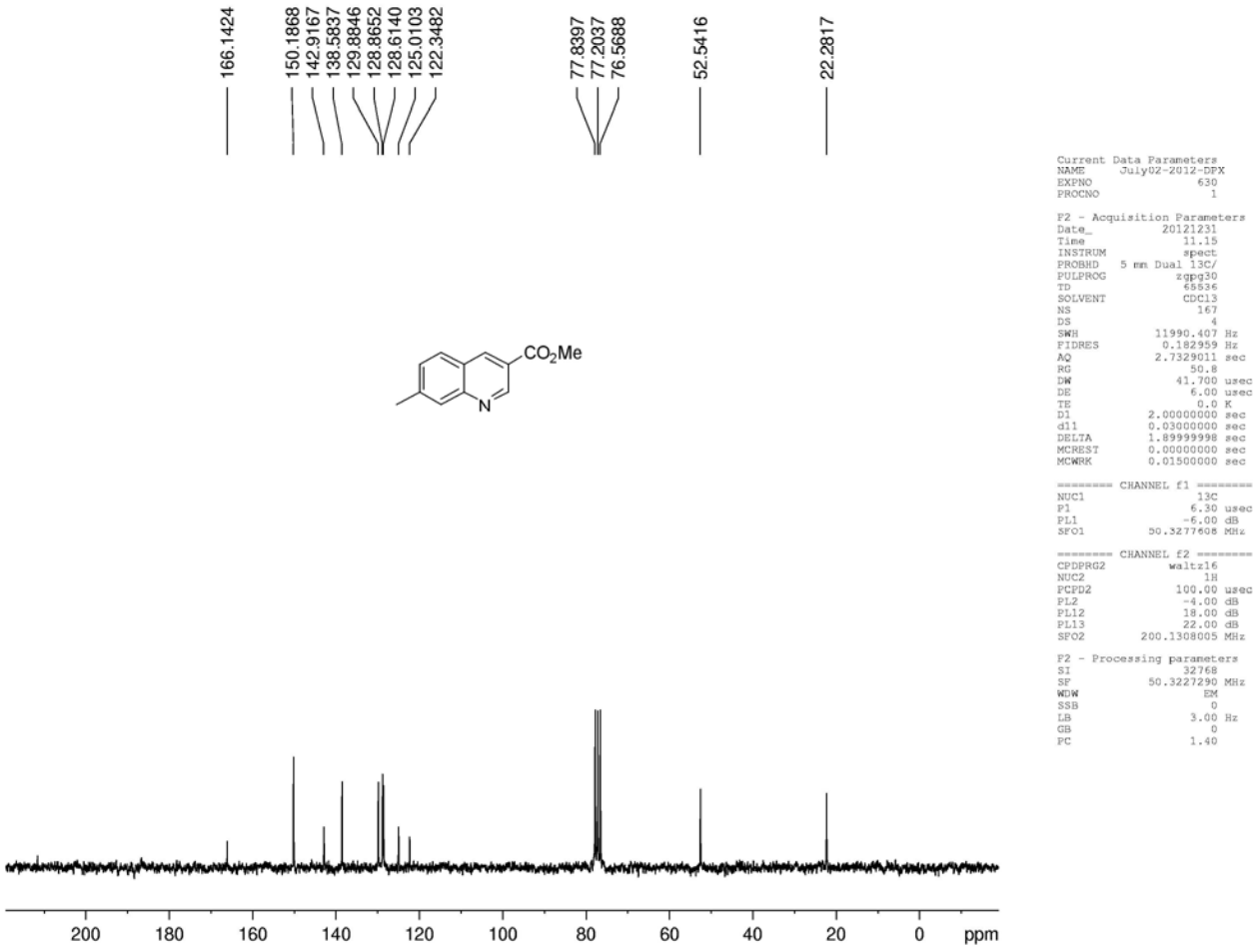


Fig. S-64: ^{13}C spectrum of methyl 7-methylquinoline-3-carboxylate (Table 2, entry 4, **2**).

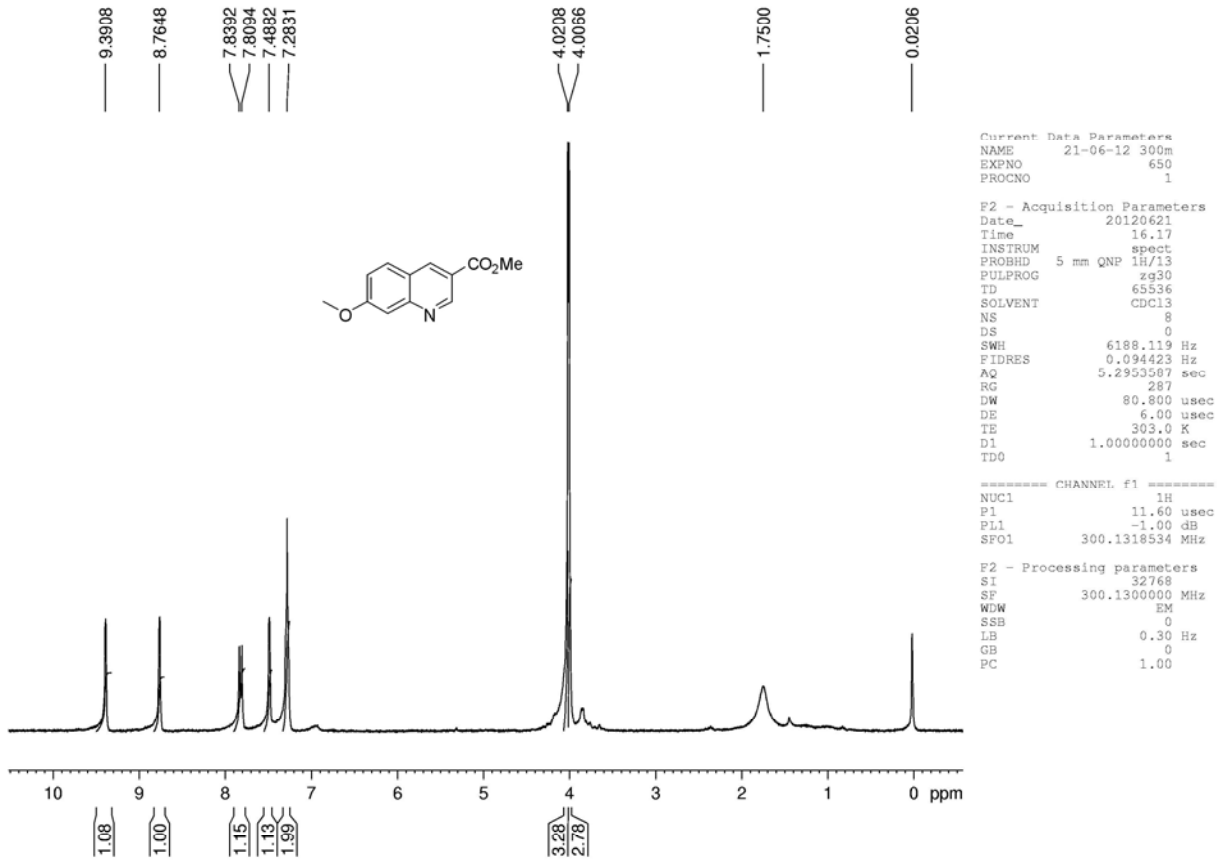


Fig. S-65: ^{1}H spectrum of methyl 7-methoxyquinoline-3-carboxylate (Table 2, entry 5, **2**).

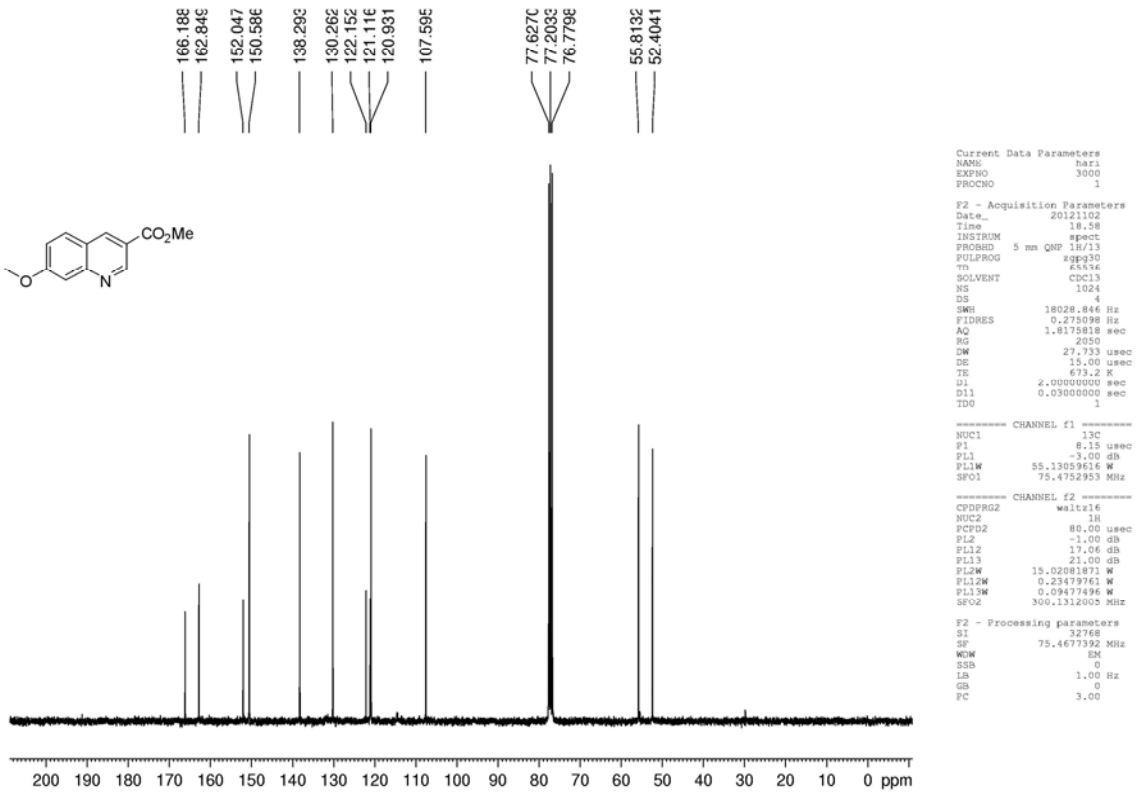


Fig. S-66: ^{13}C spectrum of methyl 7-methoxyquinoline-3-carboxylate (Table 2, entry 5, **2**).

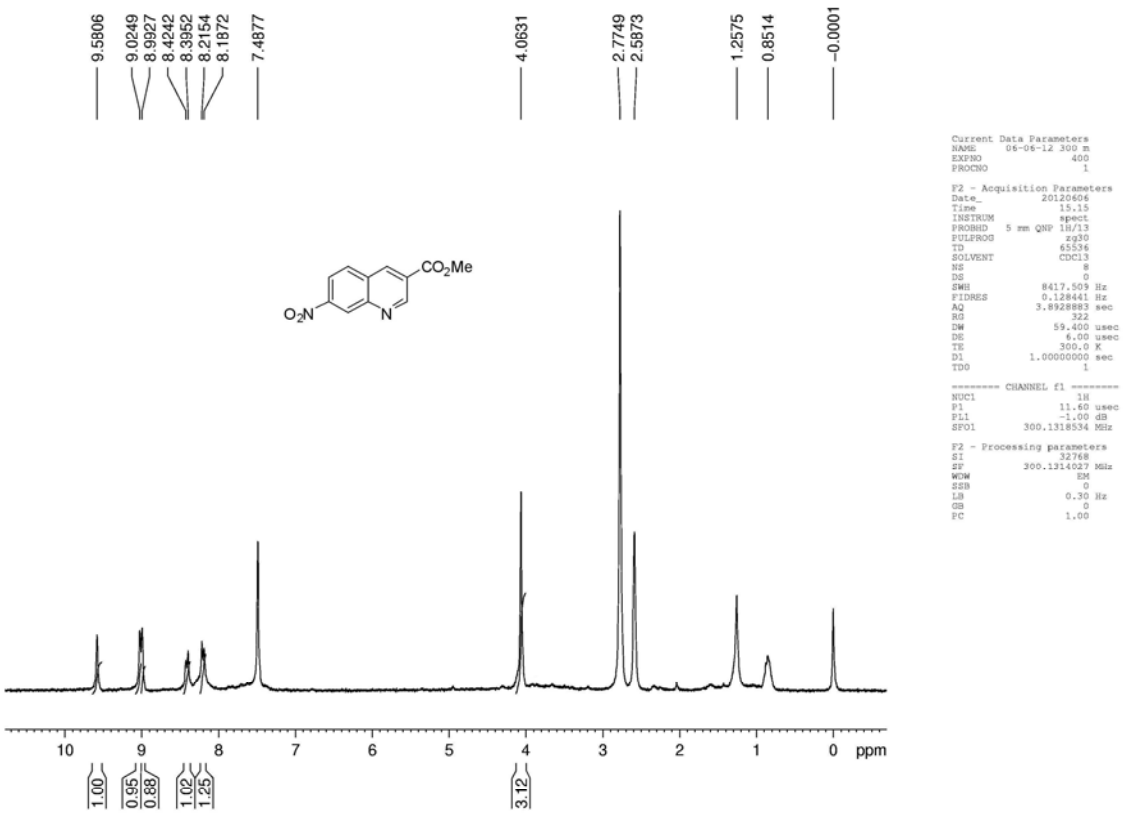


Fig. S-67: ^{1}H spectrum of methyl 7-nitroquinoline-3-carboxylate (Table 2, entry 6, **2**).

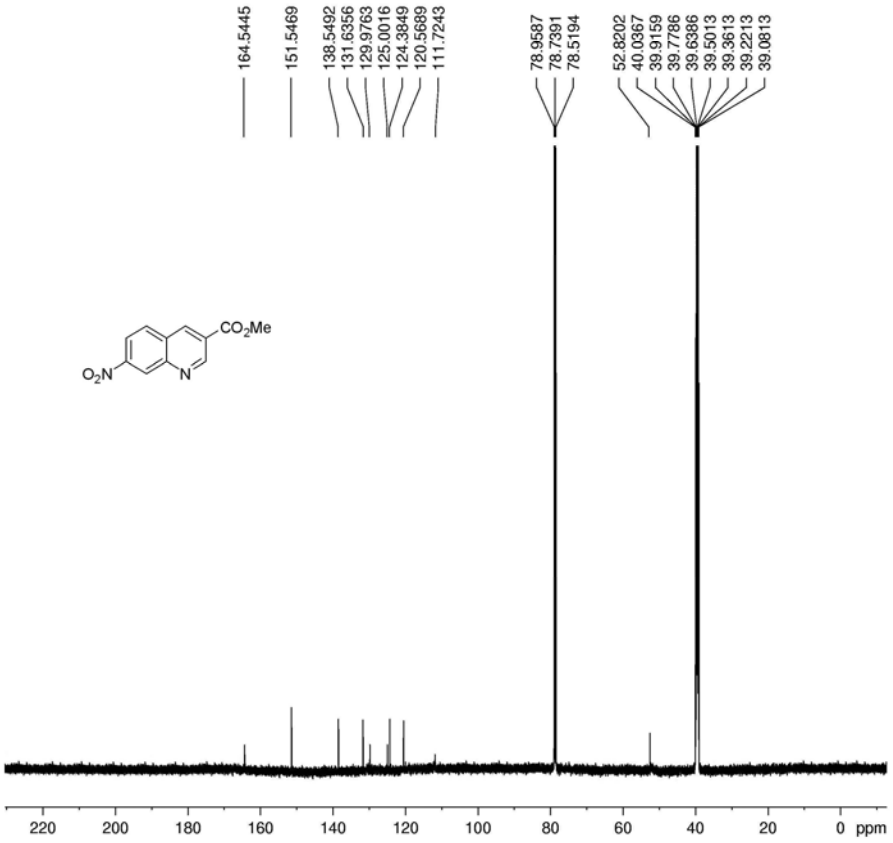


Fig. S-68: ^{13}C spectrum of methyl 7-nitroquinoline-3-carboxylate (Table 2, entry 6, **2**).

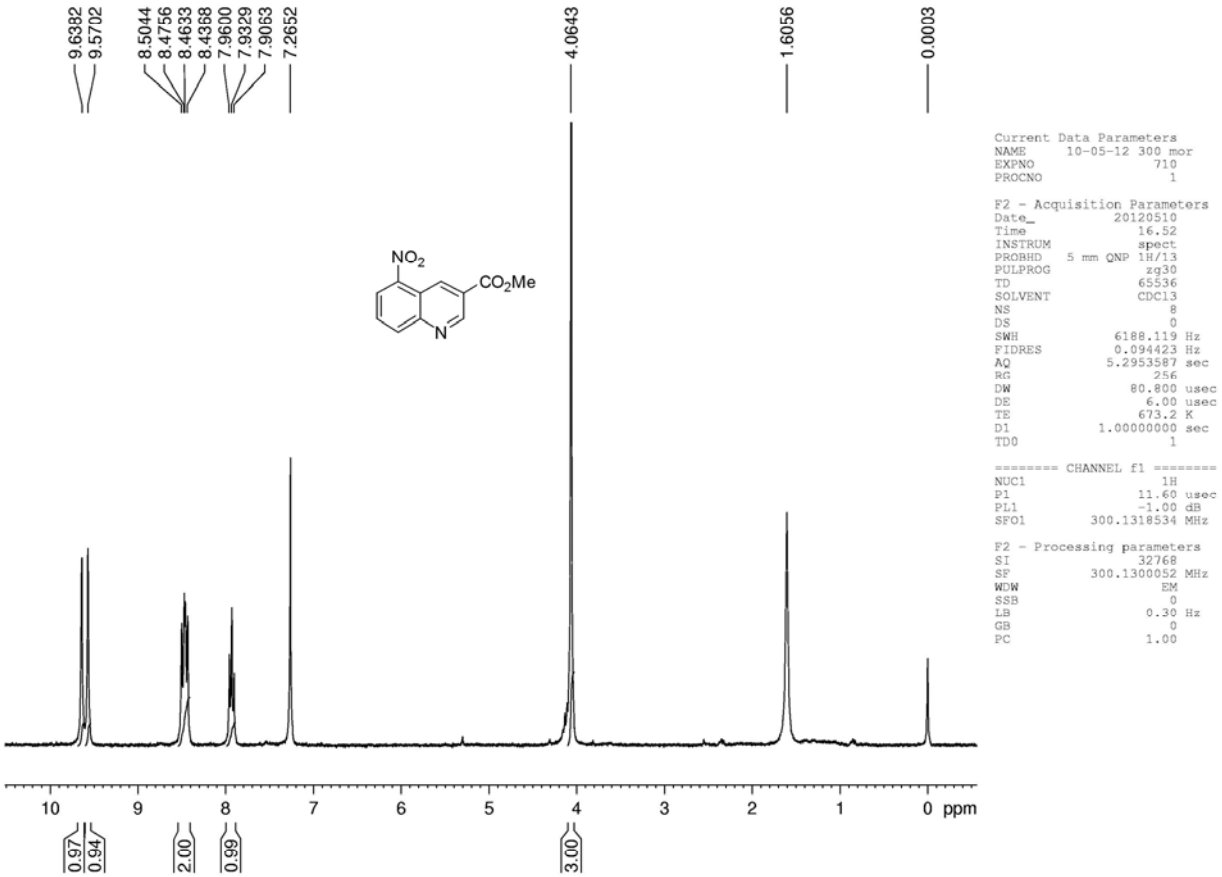


Fig. S-69: ^{1}H spectrum of methyl 5-nitroquinoline-3-carboxylate (Table 2, entry 7, **2**).

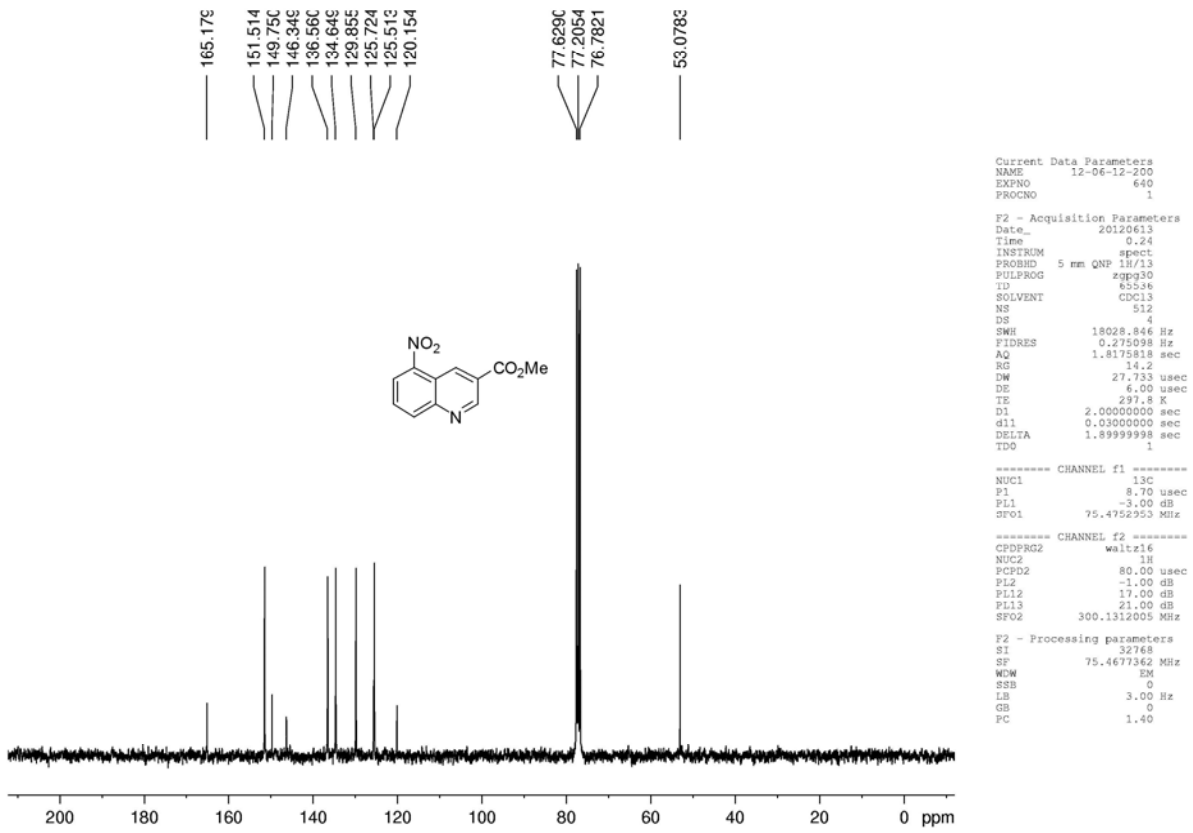


Fig. S-70: ^{13}C spectrum of methyl 5-nitroquinoline-3-carboxylate (Table 2, entry 7, **2**).

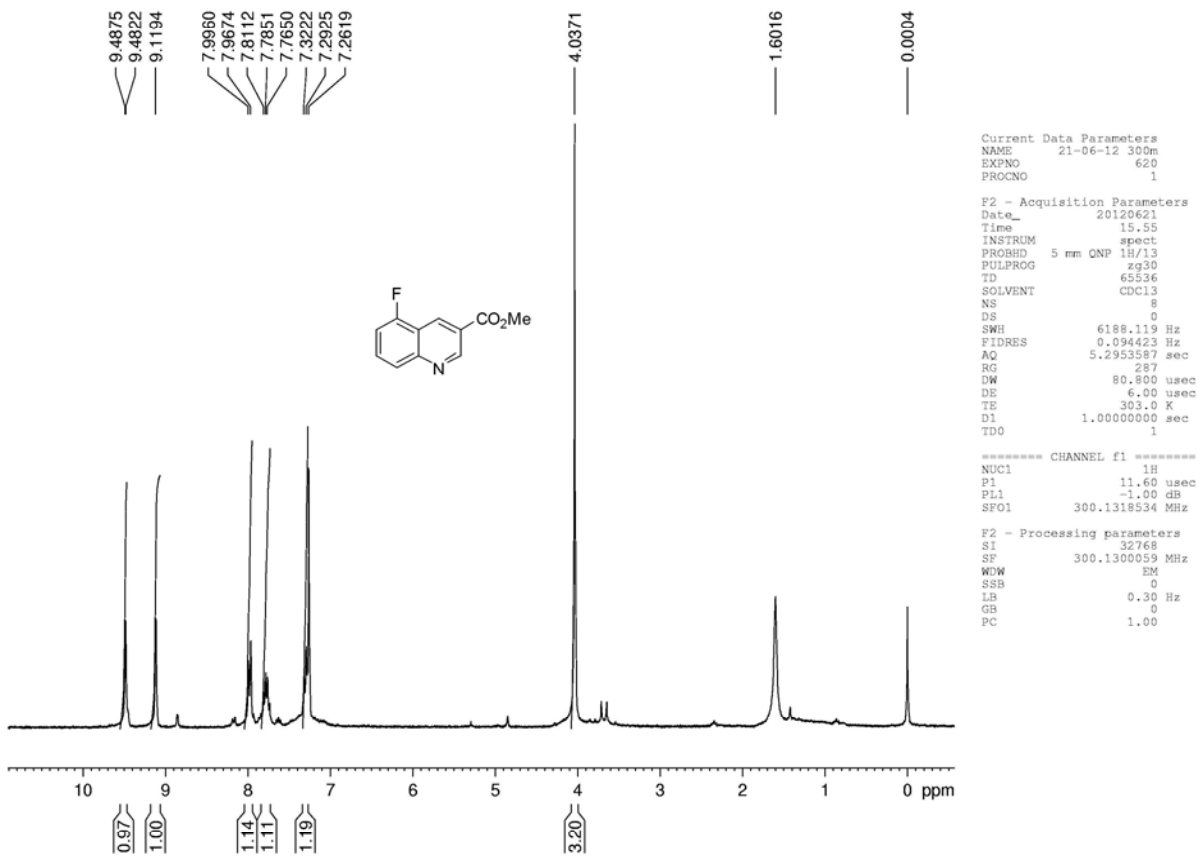


Fig. S-71: ^{1}H spectrum of methyl 5-fluoroquinoline-3-carboxylate (Table 2, entry 8, **2**).

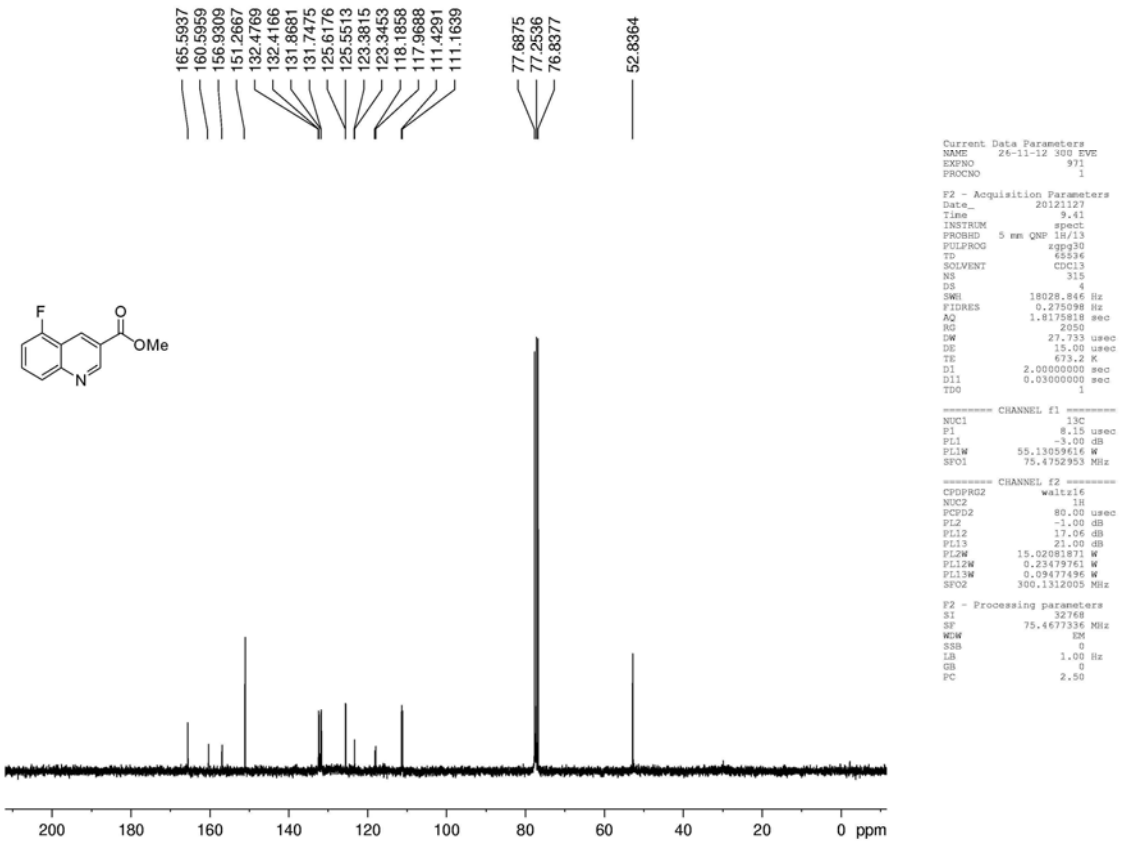


Fig. S-72: ^{13}C spectrum of methyl 5-fluoroquinoline-3-carboxylate (Table 2, entry 8, **2**).

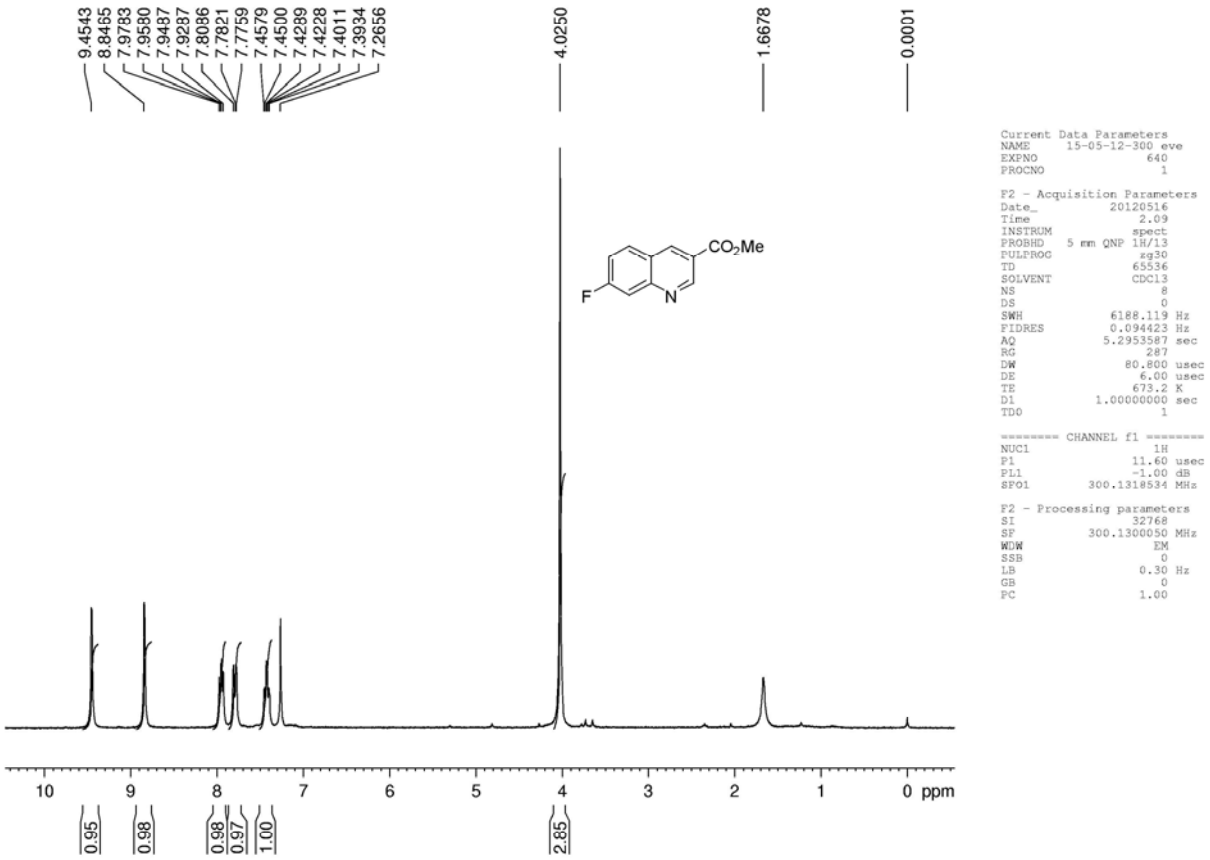


Fig. S-73: ^{1}H spectrum of methyl 7-fluoroquinoline-3-carboxylate (Table 2, entry 9, **2**).

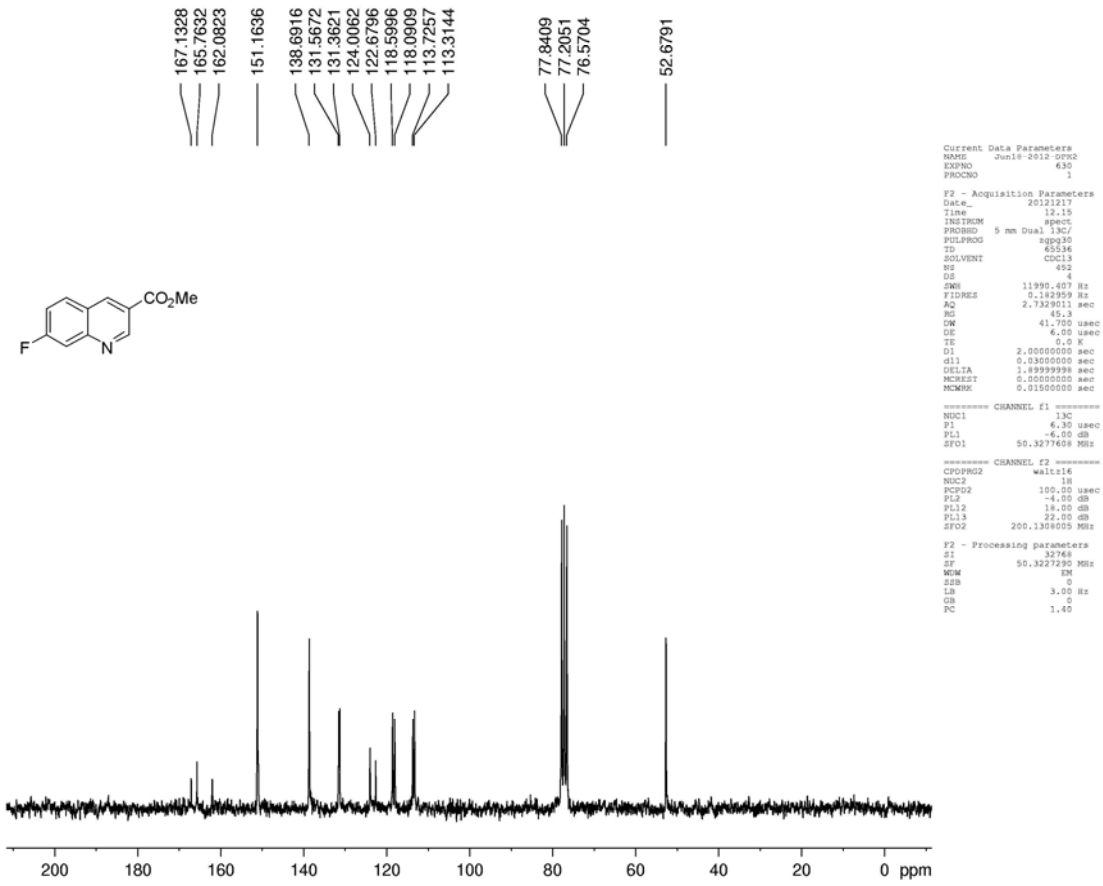


Fig. S-74: ^{13}C spectrum of methyl 7-fluoroquinoline-3-carboxylate (Table 2, entry 9, **2**).

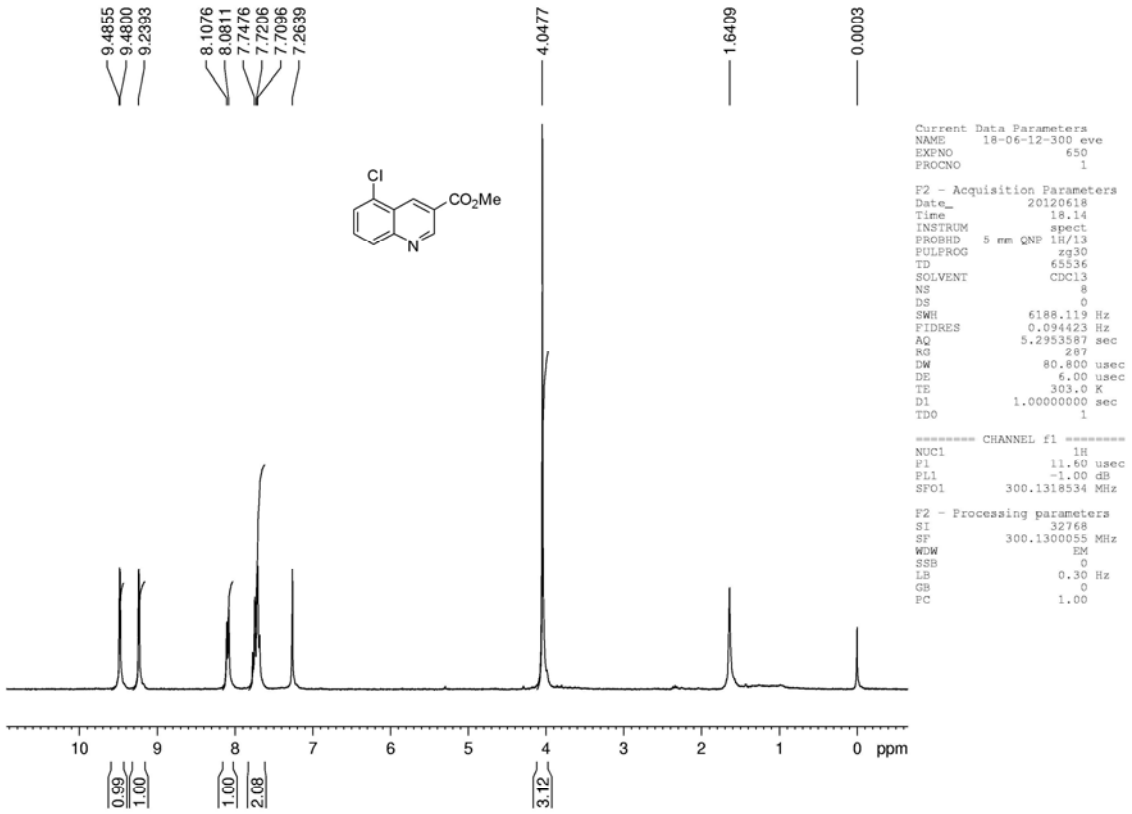


Fig.S-75: ^{1}H spectrum of methyl 5-chloroquinoline-3-carboxylate (Table 2, entry 10, **2**).

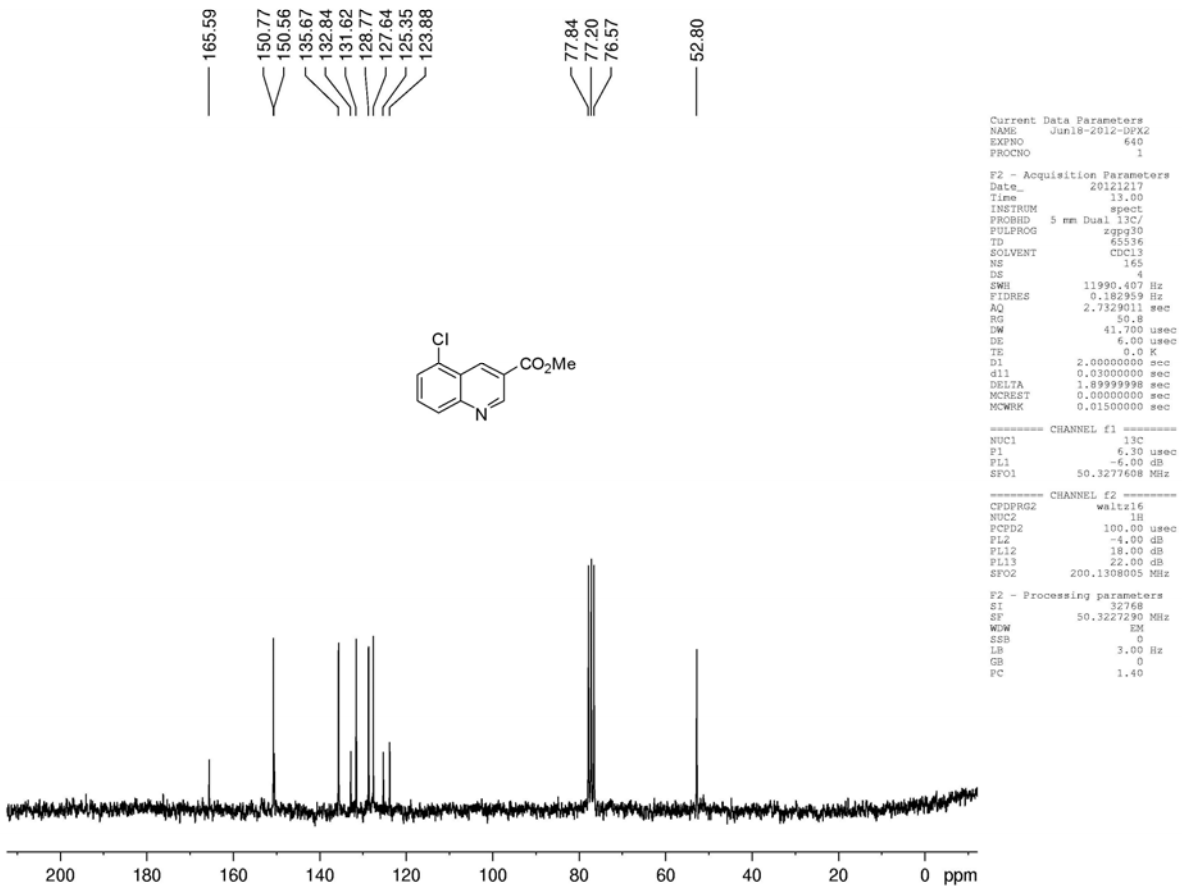


Fig. S-76: ^{13}C spectrum of methyl 5-chloroquinoline-3-carboxylate (Table 2, entry 10, **2**).

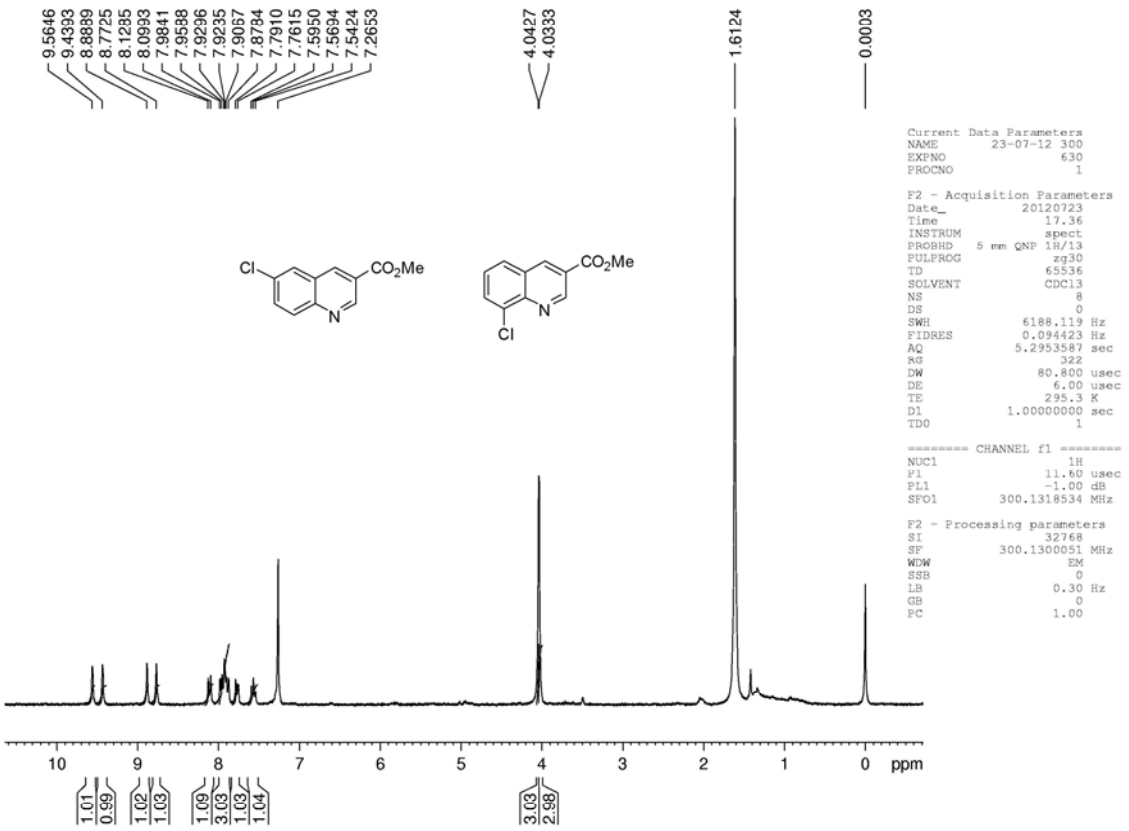


Fig. S-77: ^{1}H spectrum of methyl 6-chloroquinoline-3-carboxylate and methyl 8-chloroquinoline-3-carboxylate (Table 2, entry 11, **2**).

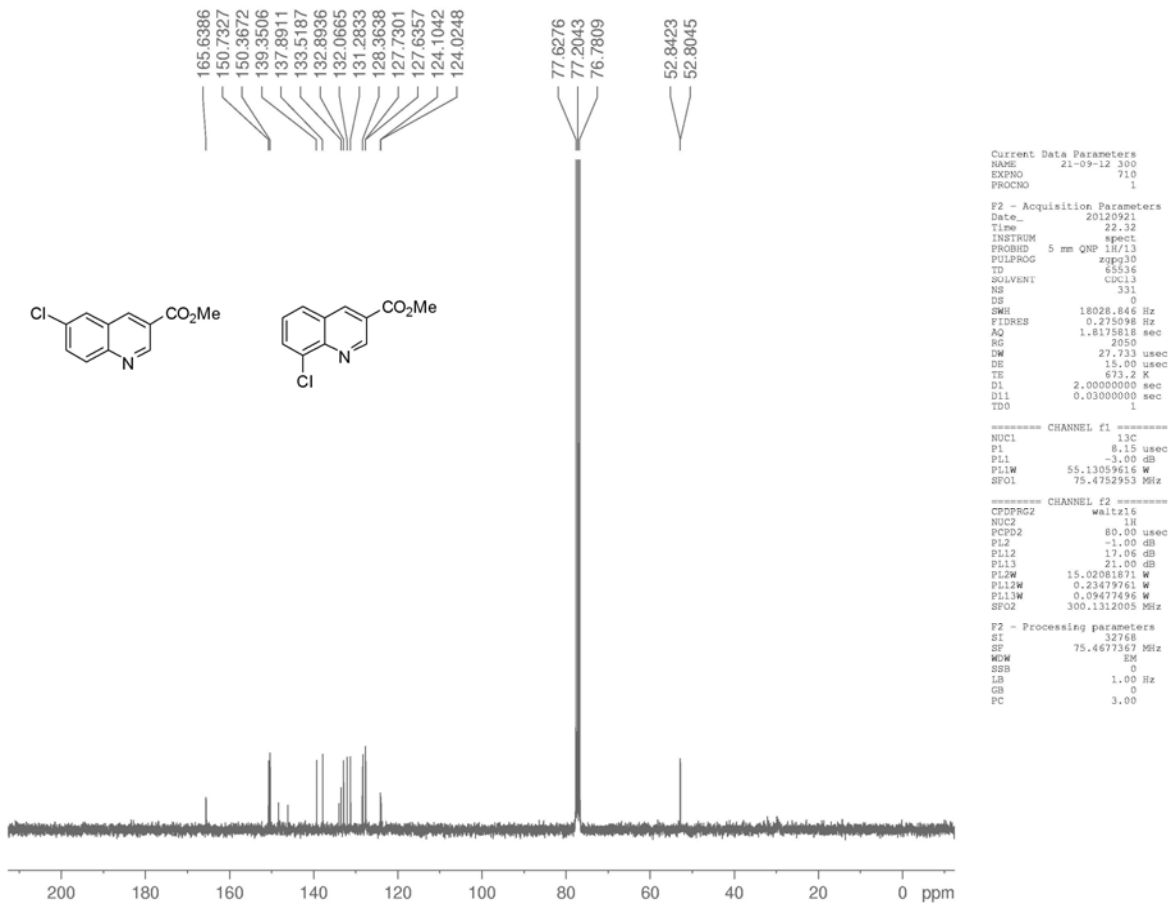


Fig. S-78: ^{13}C spectrum of methyl 6-chloroquinoline-3-carboxylate and methyl 8-chloroquinoline-3-carboxylate (Table 2, entry 11, **2**).

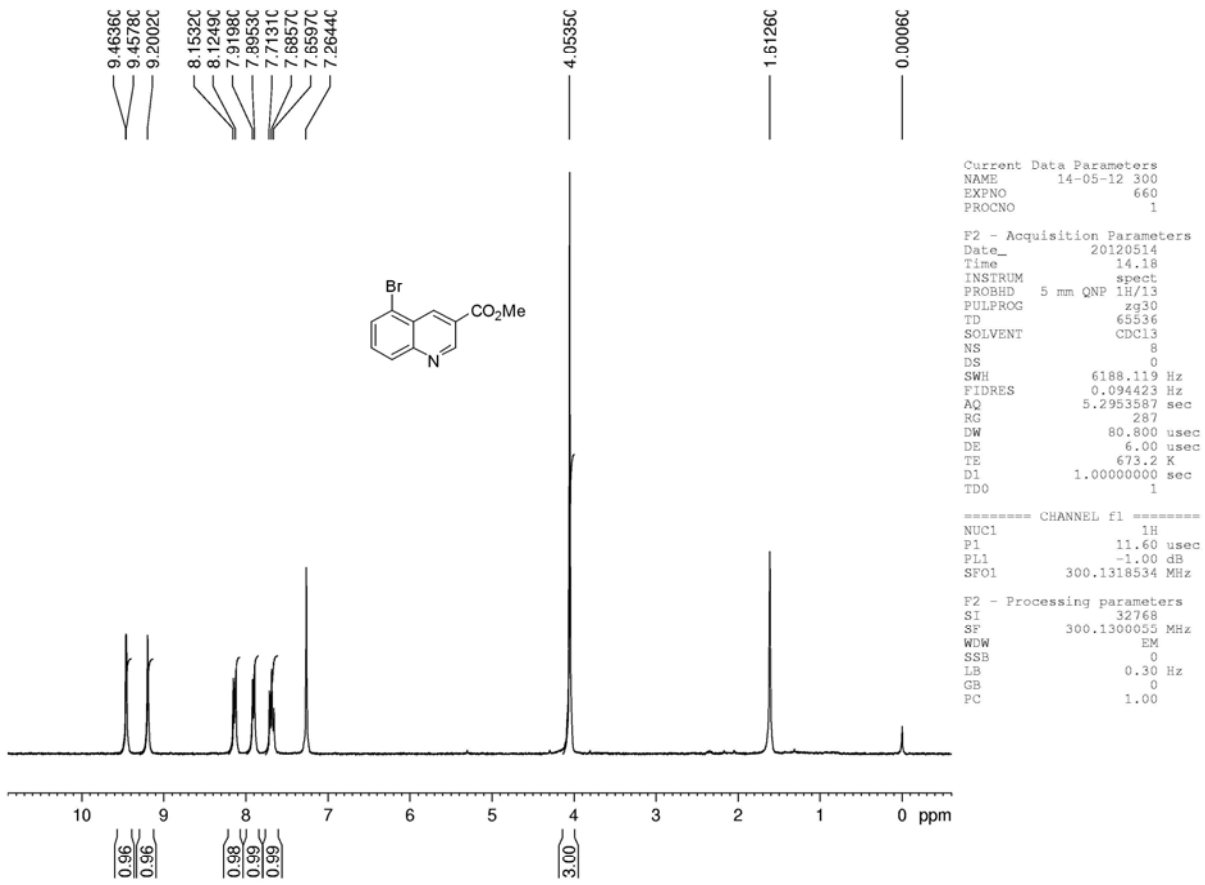


Fig. S-79: ^{1}H spectrum of methyl 5-bromoquinoline-3-carboxylate (Table 2, entry 12, **2**).

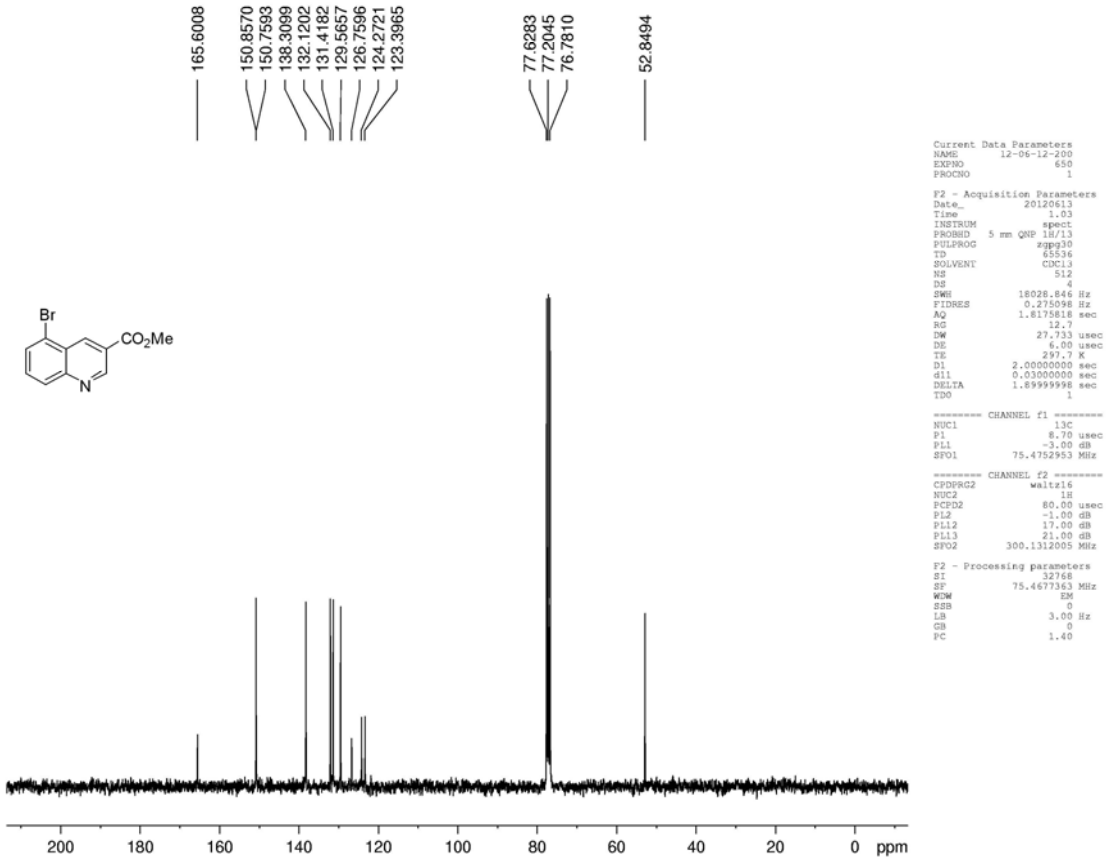


Fig. S-80: ^{13}C spectrum of methyl 5-bromoquinoline-3-carboxylate (Table 2, entry 12, **2**).

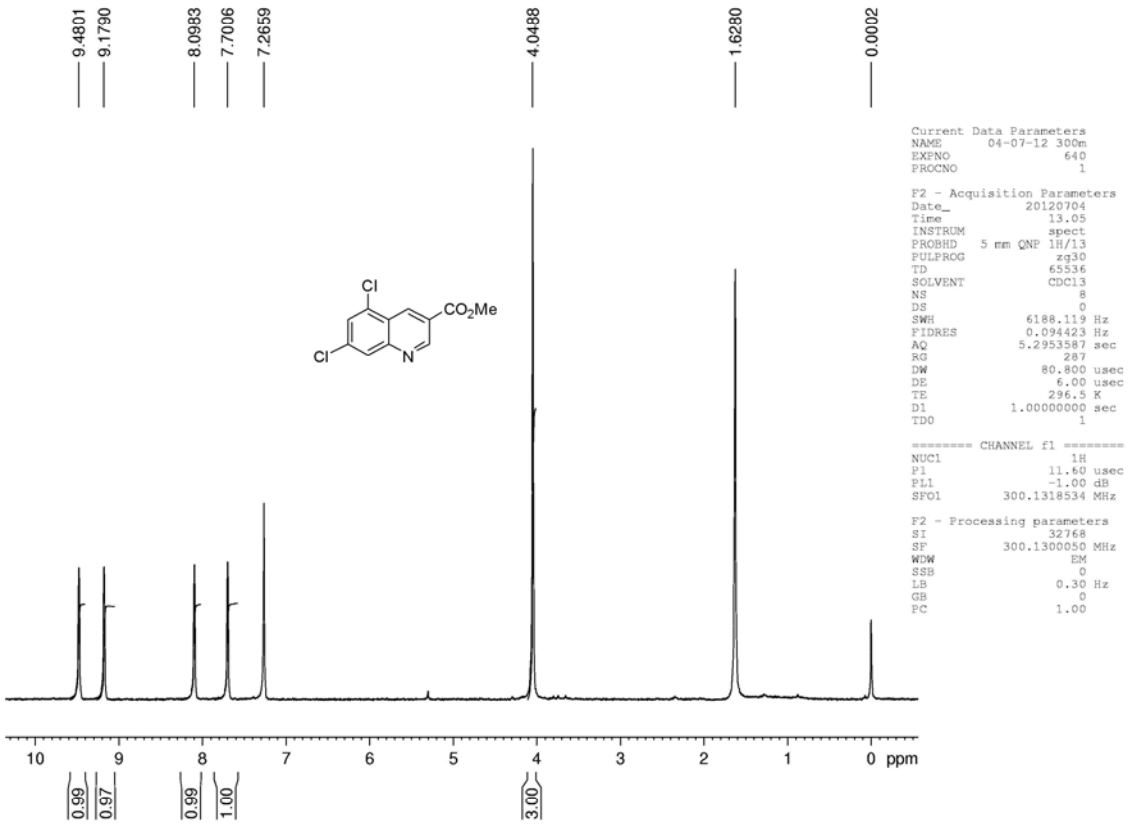


Fig. S-81: ^{1}H spectrum of methyl 5,7-dichloroquinoline-3-carboxylate (Table 2, entry 13, **2**).

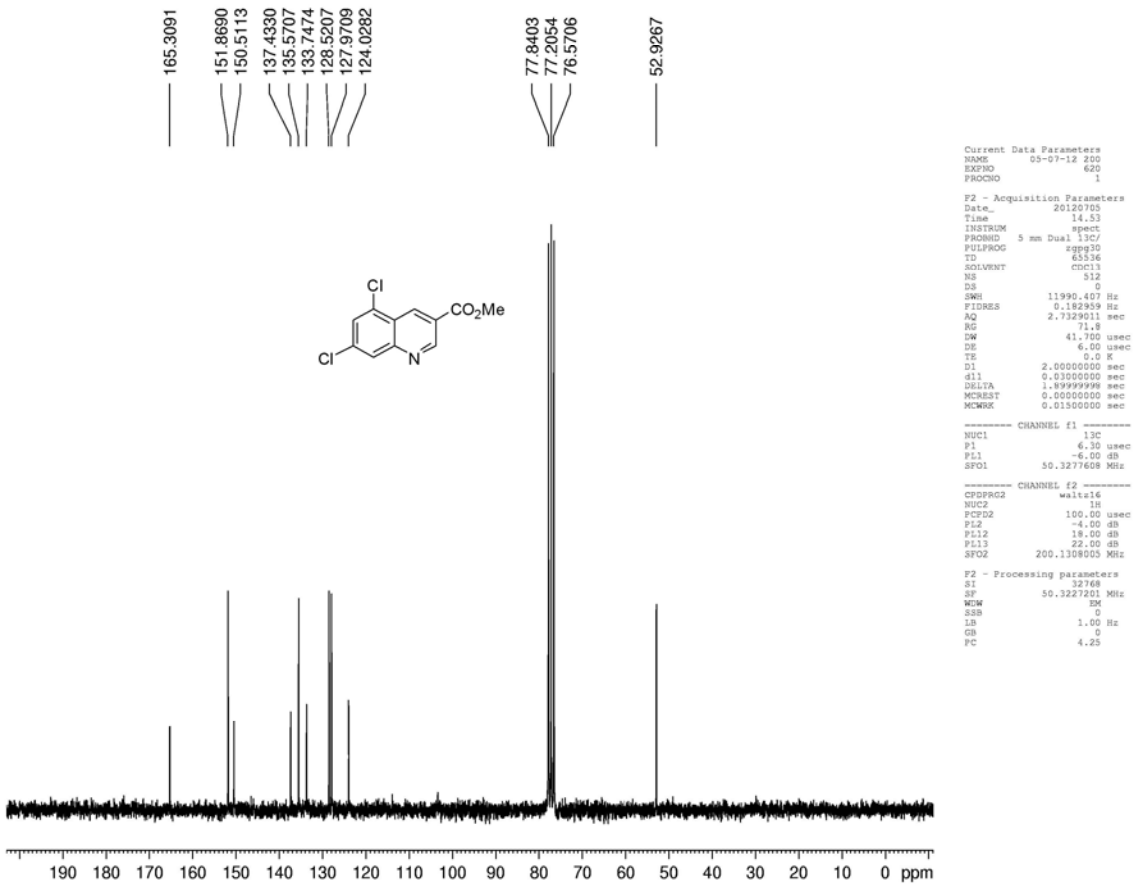


Fig: S-82. ^{13}C spectrum of methyl 5,7-dichloroquinoline-3-carboxylate (Table 2, entry 13, **2**).

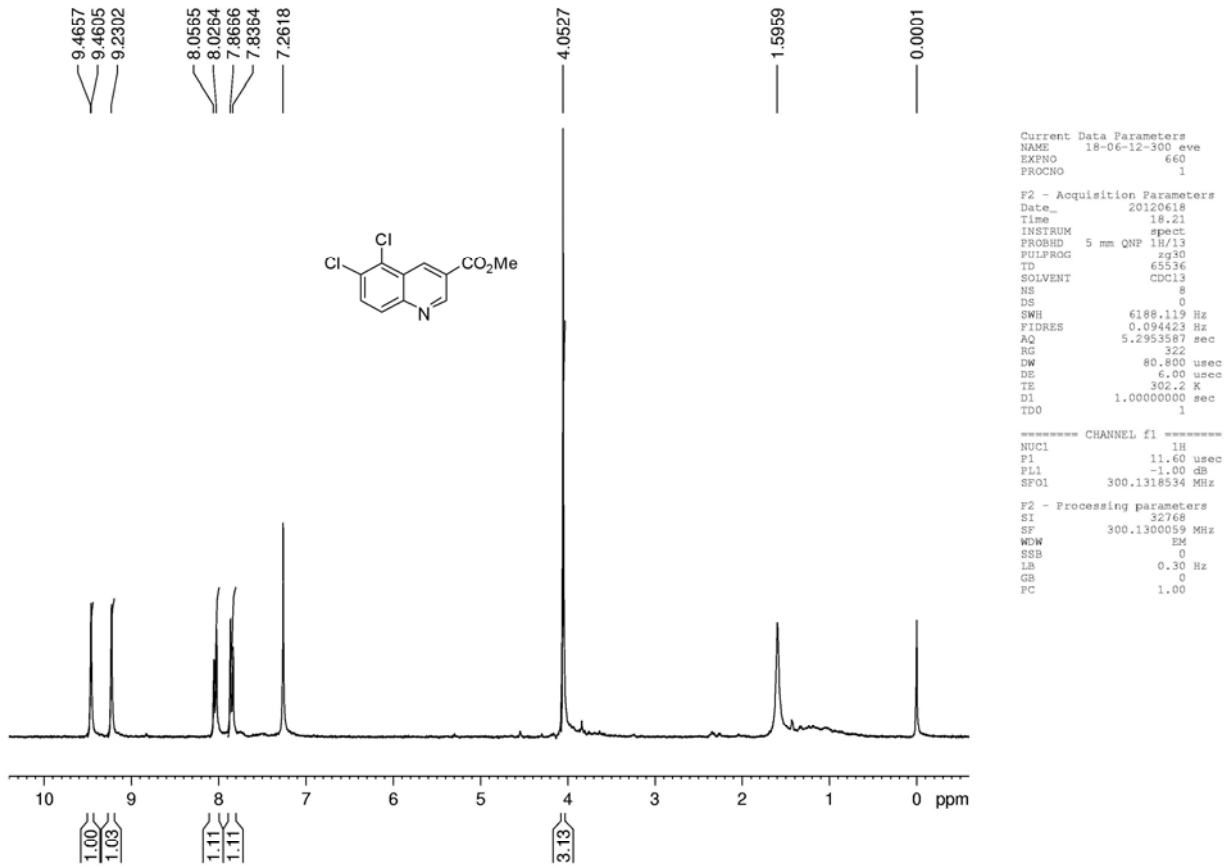


Fig. S-83: ^{1}H spectrum of methyl 5,6-dichloroquinoline-3-carboxylate (Table 2, entry 14, **2**).

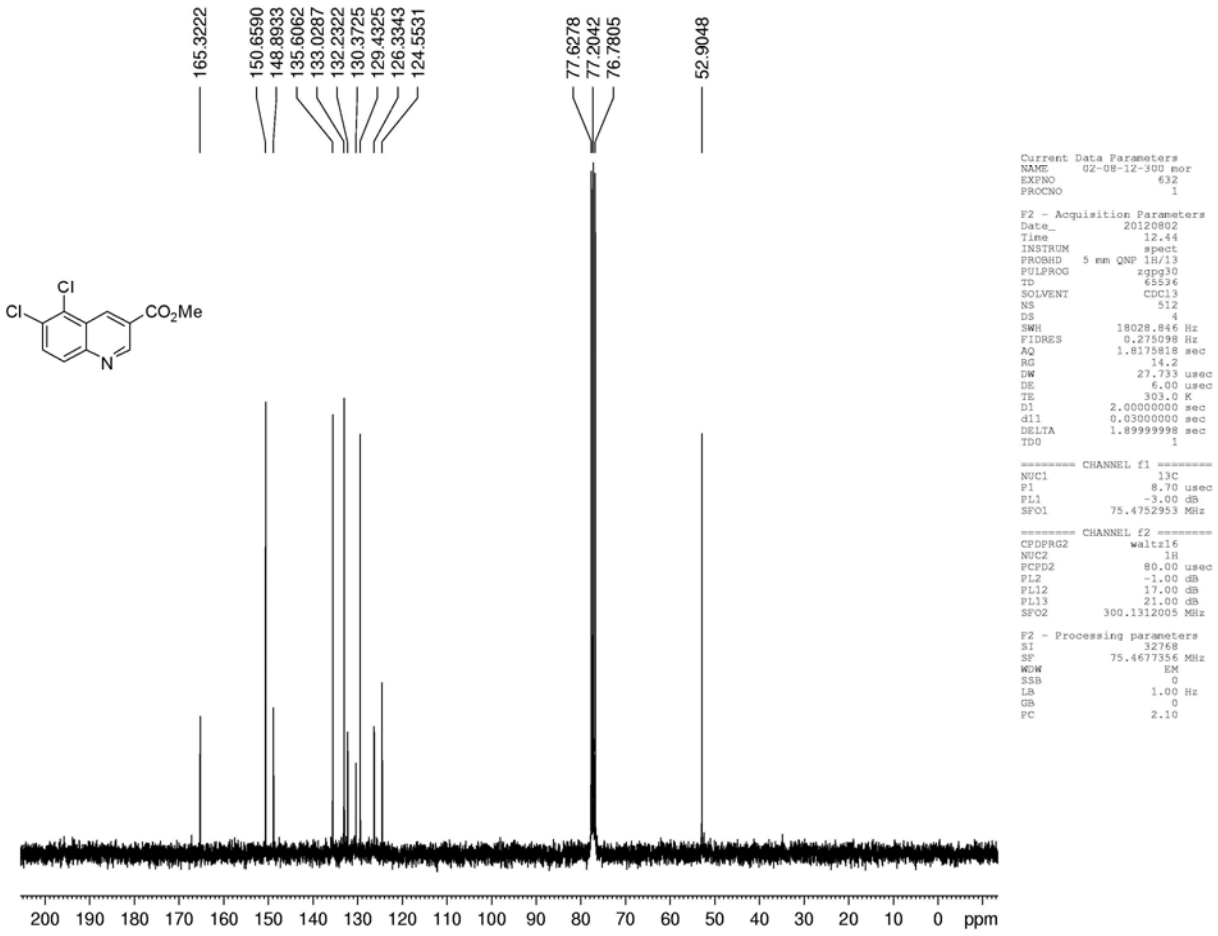


Fig. S-84: ^{13}C spectrum of methyl 5,6-dichloroquinoline-3-carboxylate(Table 2, entry 14, **2**).

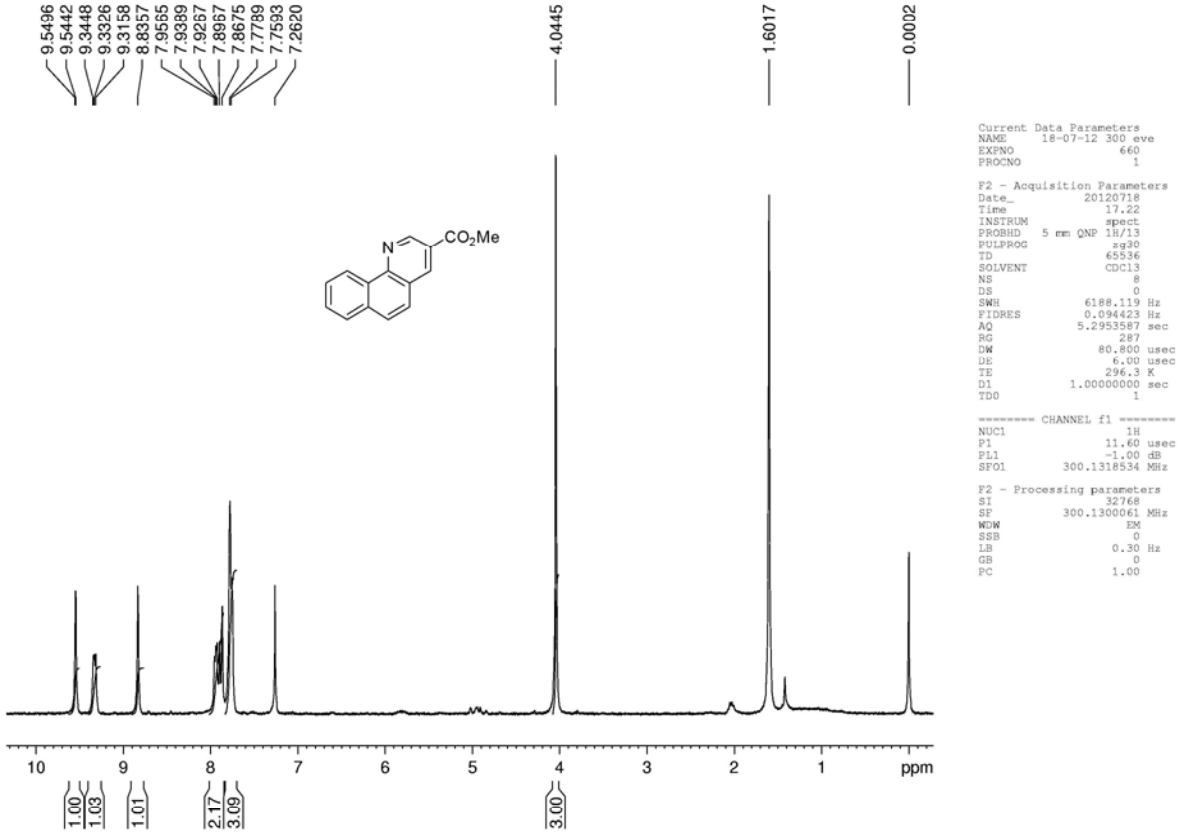


Fig. S-85: ^{1}H spectrum of methyl benzo[*h*]quinoline-3-carboxylate (Table 2, entry 15, **2**).

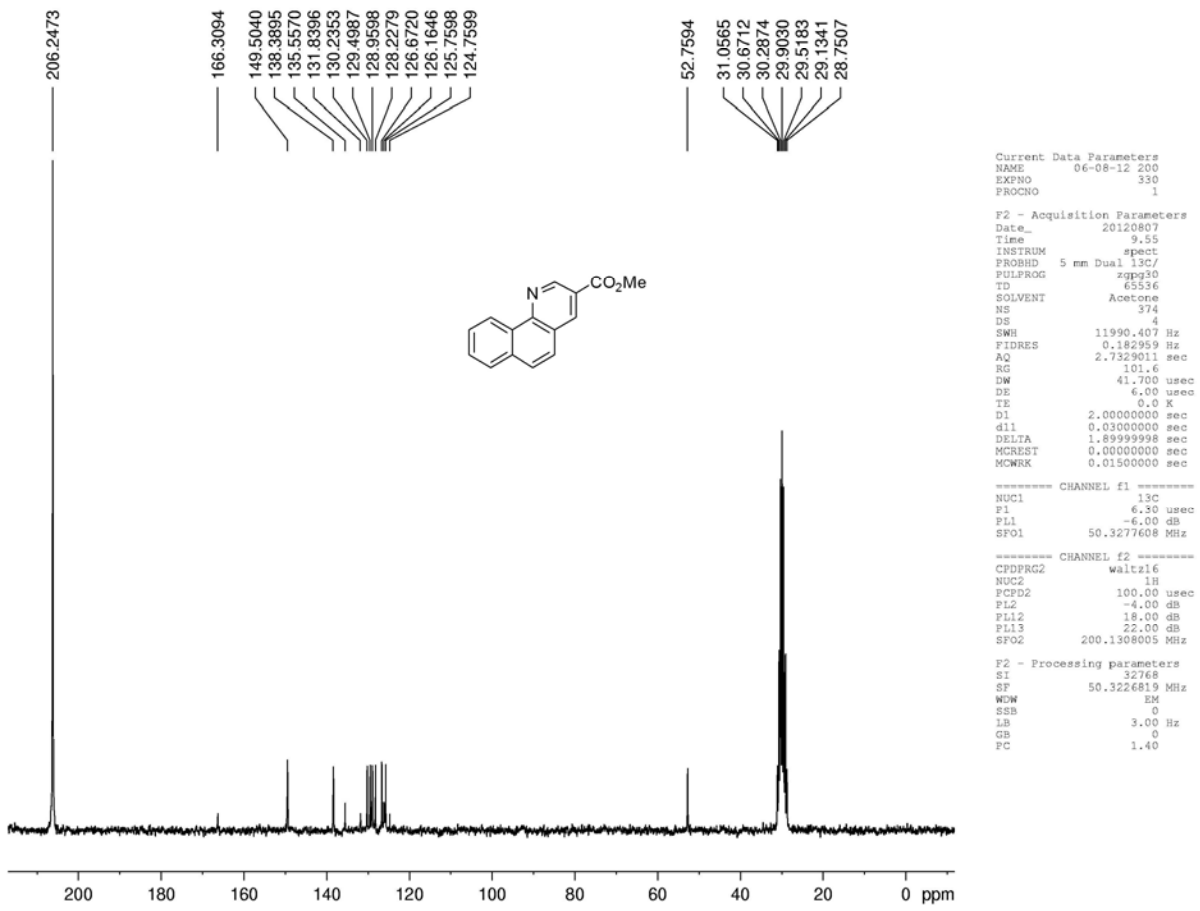


Fig. S-86: ^{13}C spectrum of methyl benzo[*h*]quinoline-3-carboxylate (Table 2, entry 15, **2**).

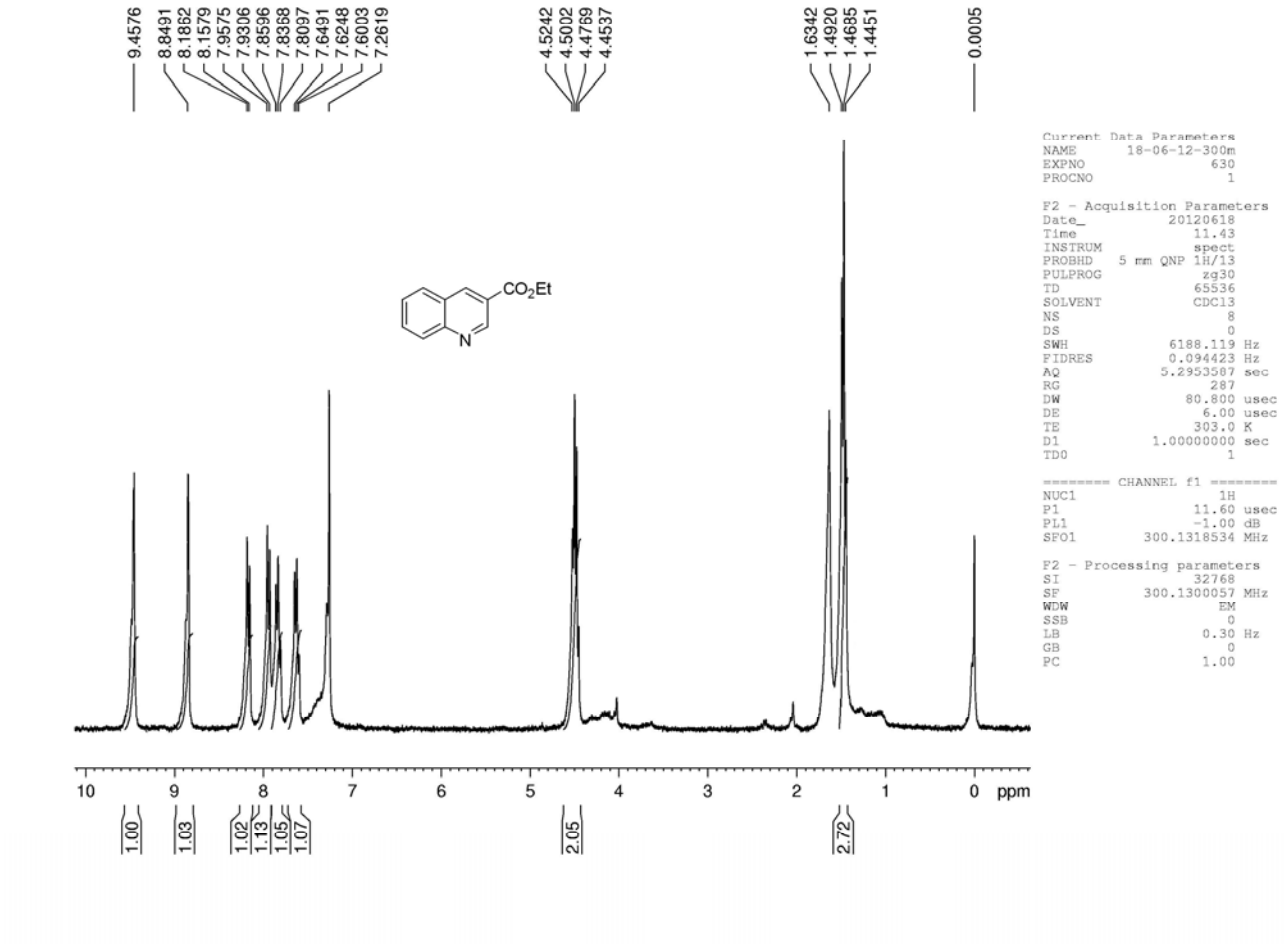


Fig. S-87: ^{1}H spectrum of ethyl quinoline-3-carboxylate (Table 2, entry 16, **2**).

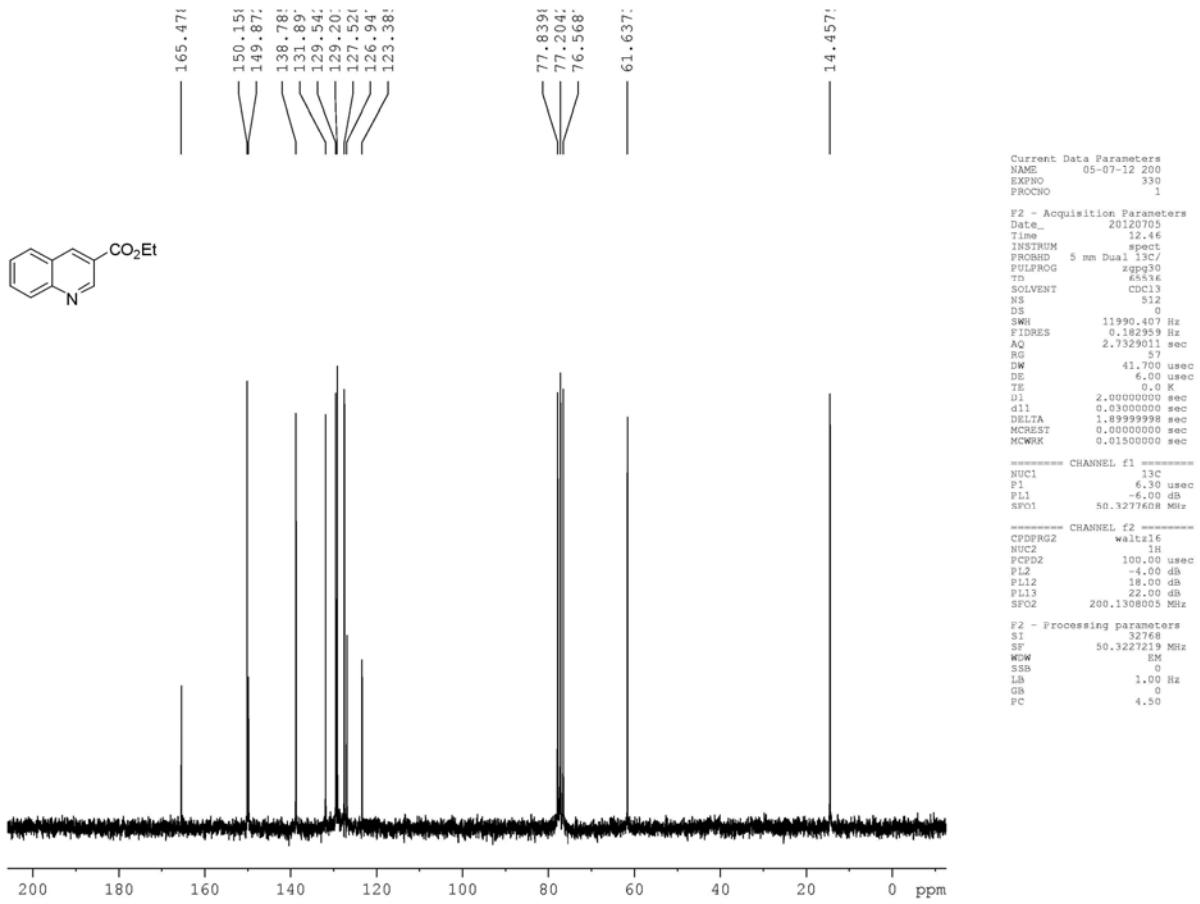


Fig. S-88: ^{13}C spectrum of ethyl quinoline-3-carboxylate (Table 2, entry 16, **2**).

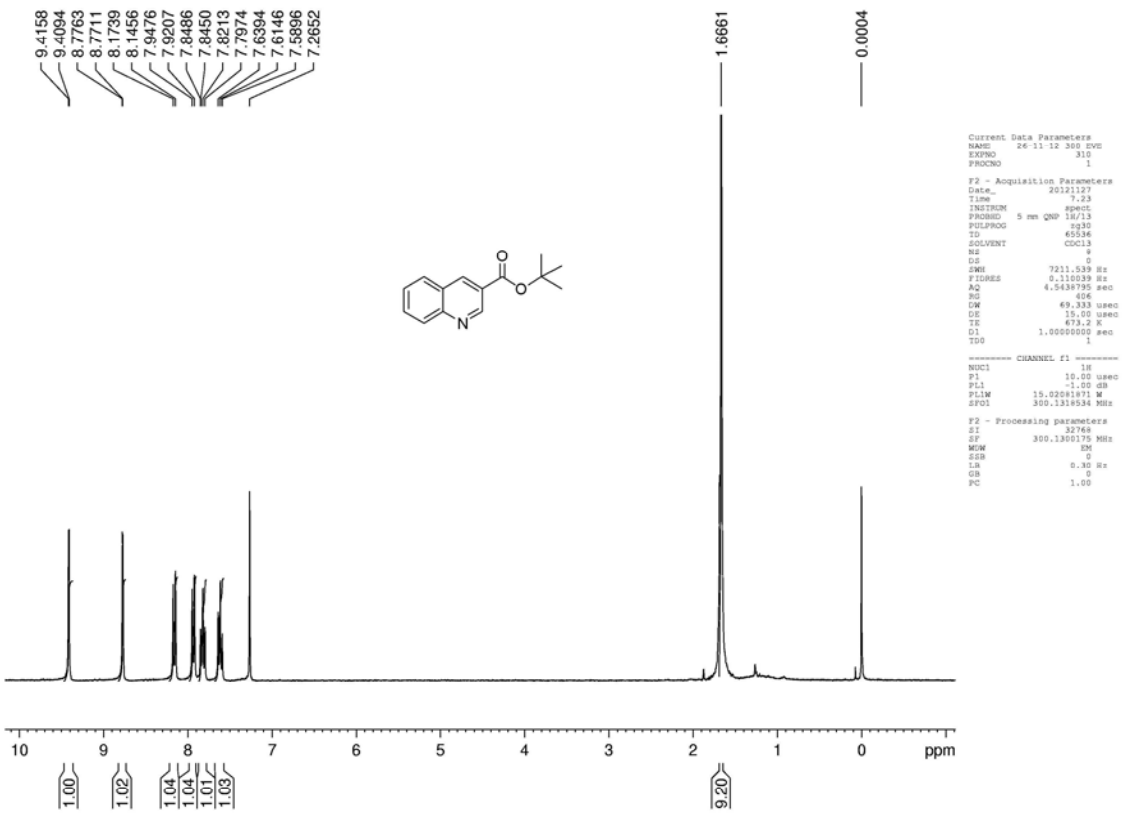


Fig. S-89: ^{1}H spectrum of *tert*-butyl quinoline-3-carboxylate (Table 2, entry 17, **2**).

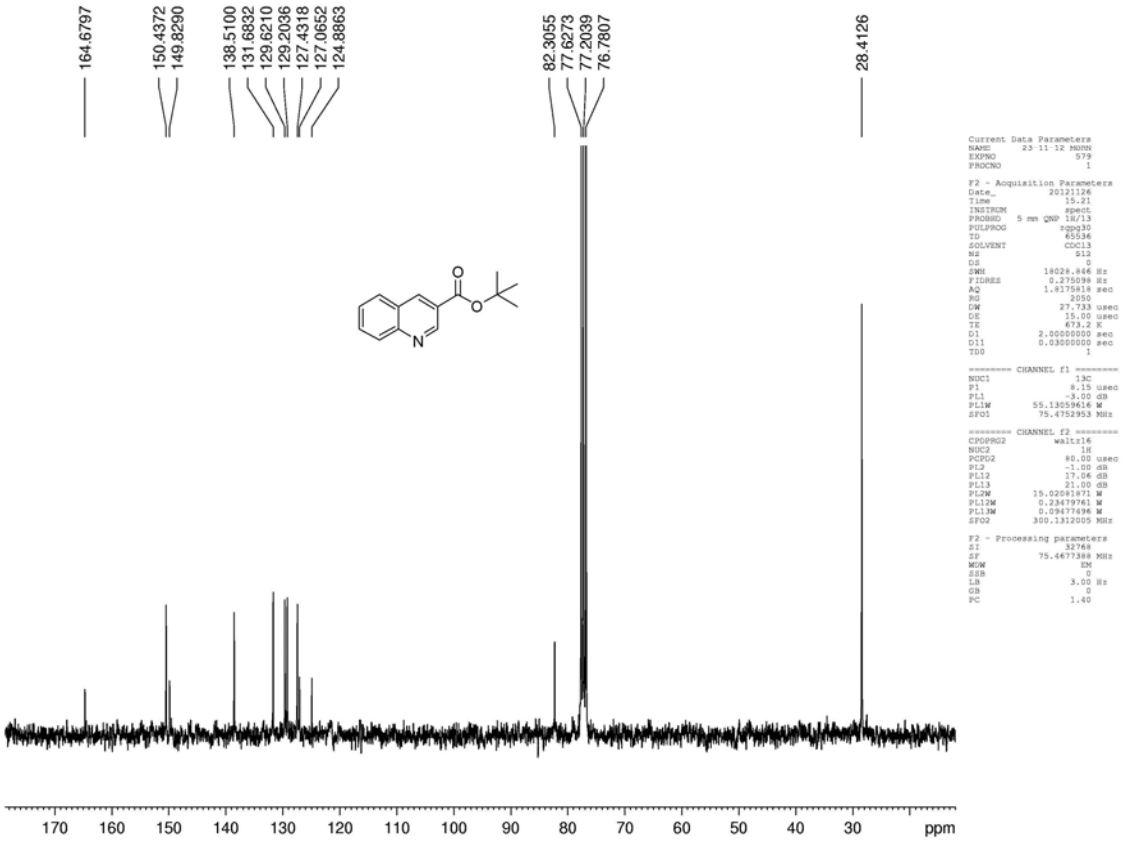


Fig. S-90: ^{13}C spectrum of *tert*-butyl quinoline-3-carboxylate (Table 2, entry 17, **2**).

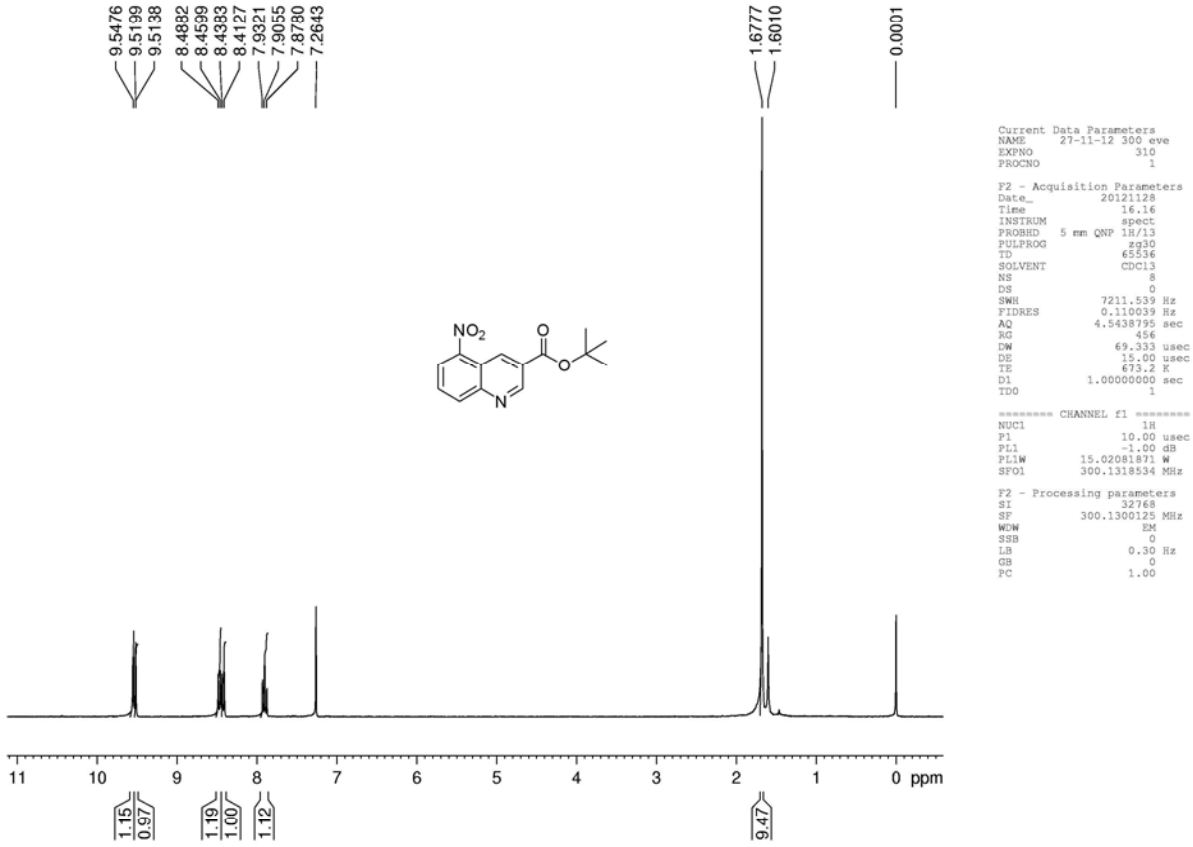


Fig. S-91: ^{1}H spectrum of *tert*-butyl 5-nitroquinoline-3-carboxylate (Table 2, entry 18, **2**).

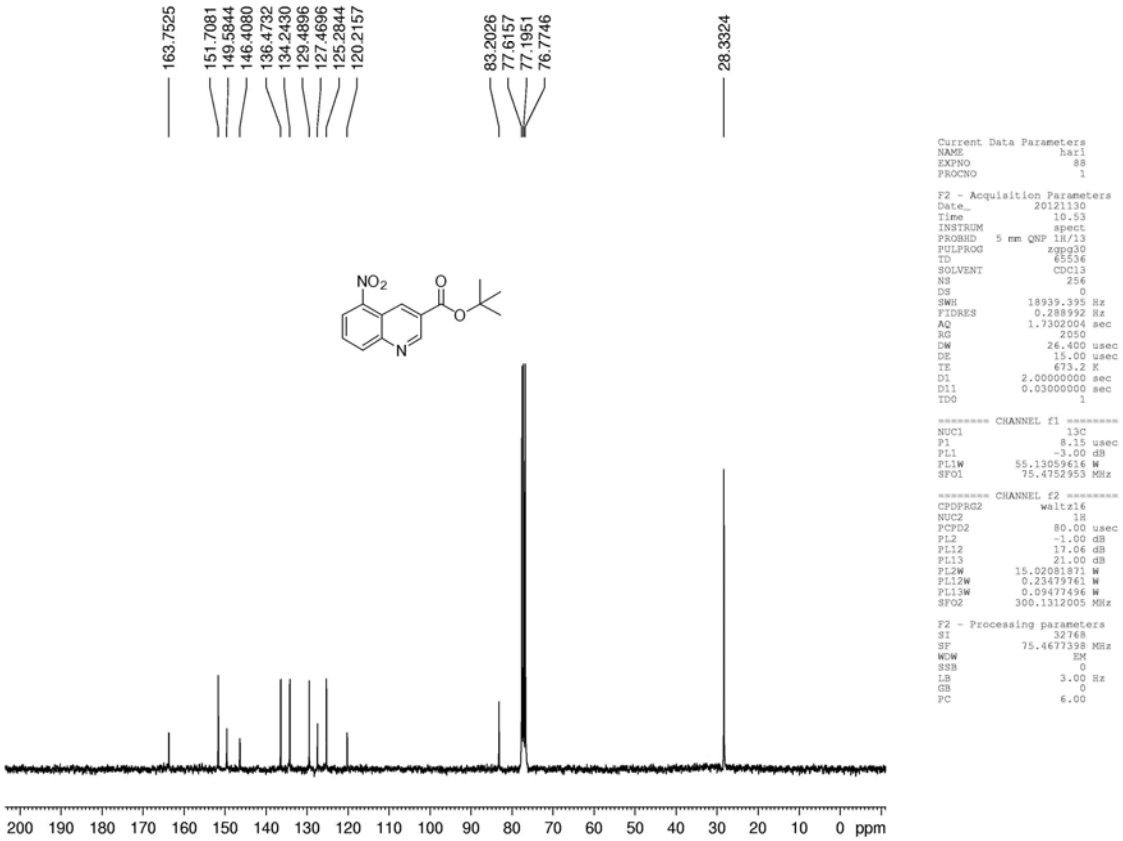


Fig. S-92: ^{13}C spectrum of *tert*-butyl 5-nitroquinoline-3-carboxylate (Table 2, entry 18, **2**).

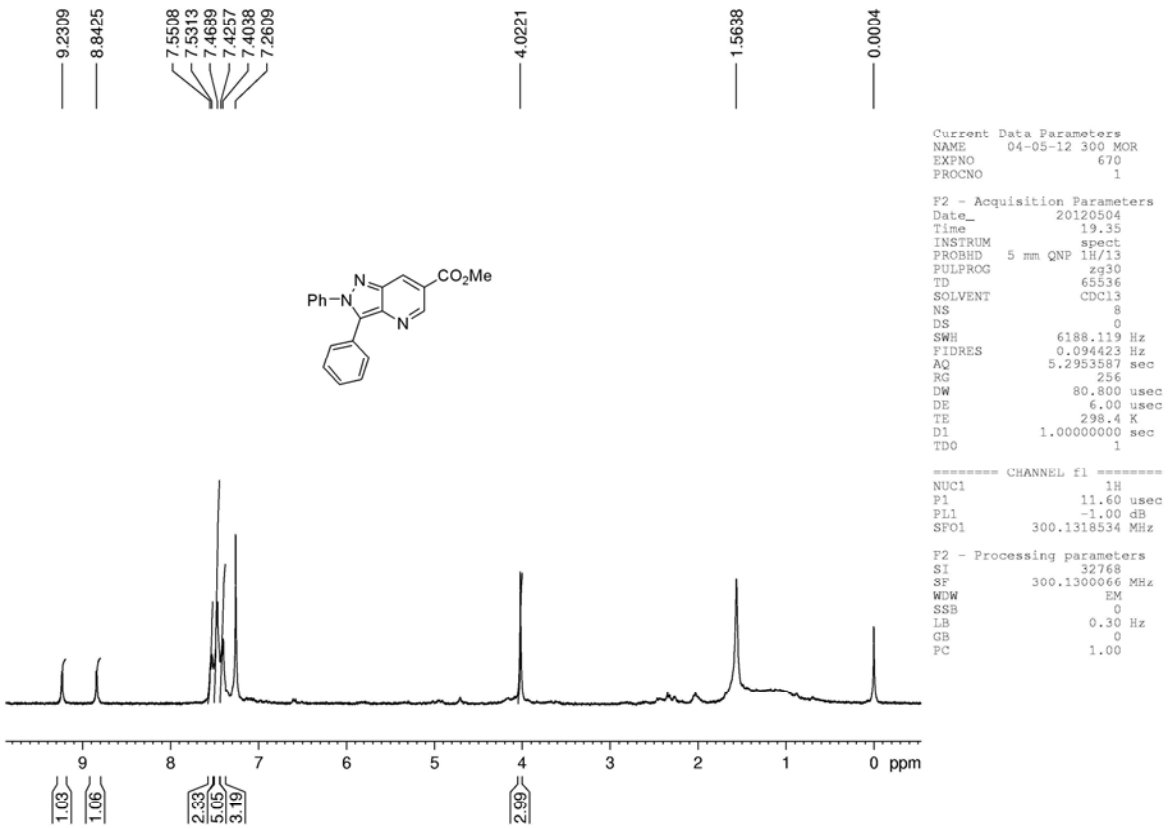


Fig. S-93: ^{1}H spectrum of methyl 2,3-diphenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (Table 2, entry 19, **2**).

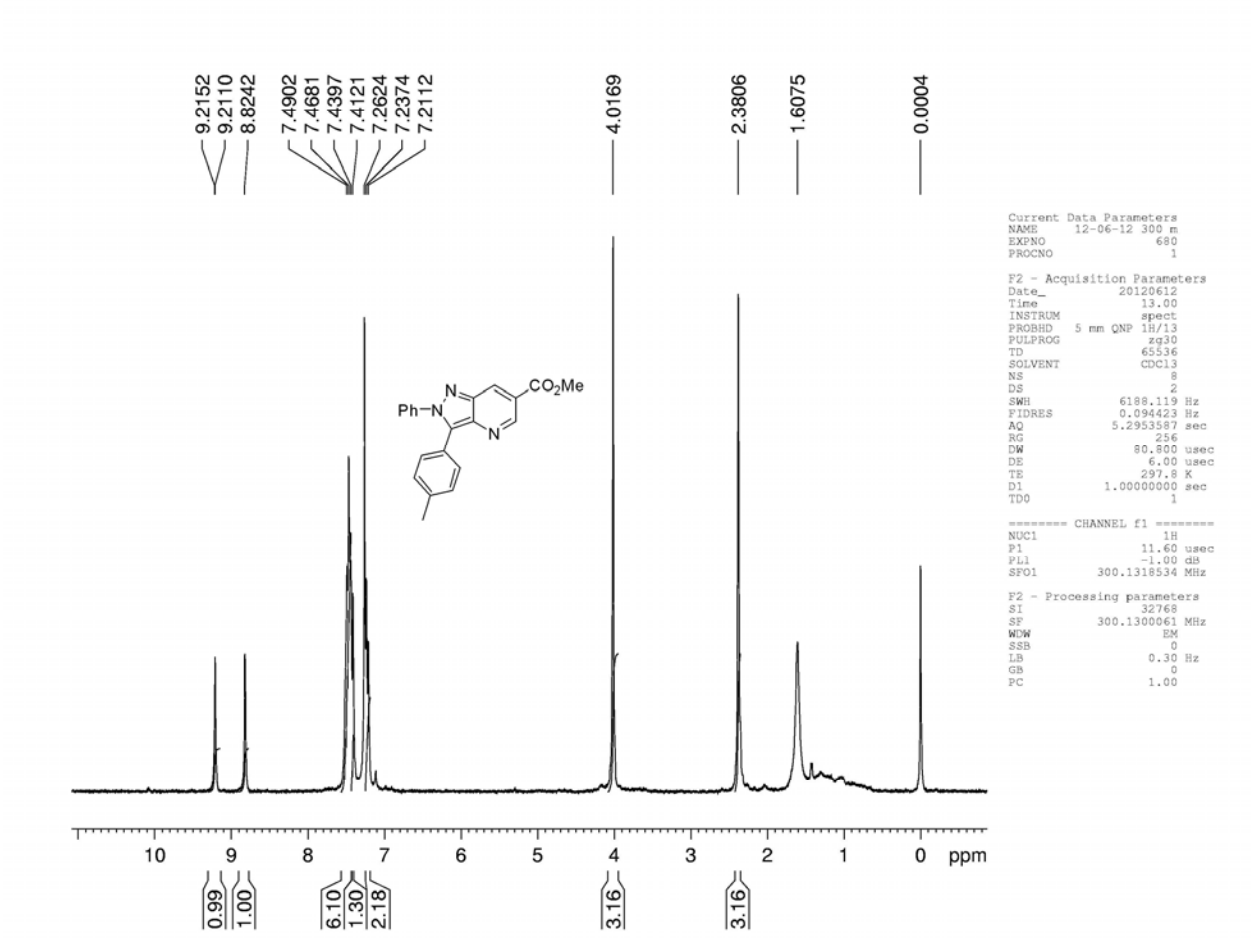


Fig. S-94: ^{1}H spectrum of methyl 2-phenyl-3-(4-methylphenyl)-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (Table 2, entry 20, **2**).

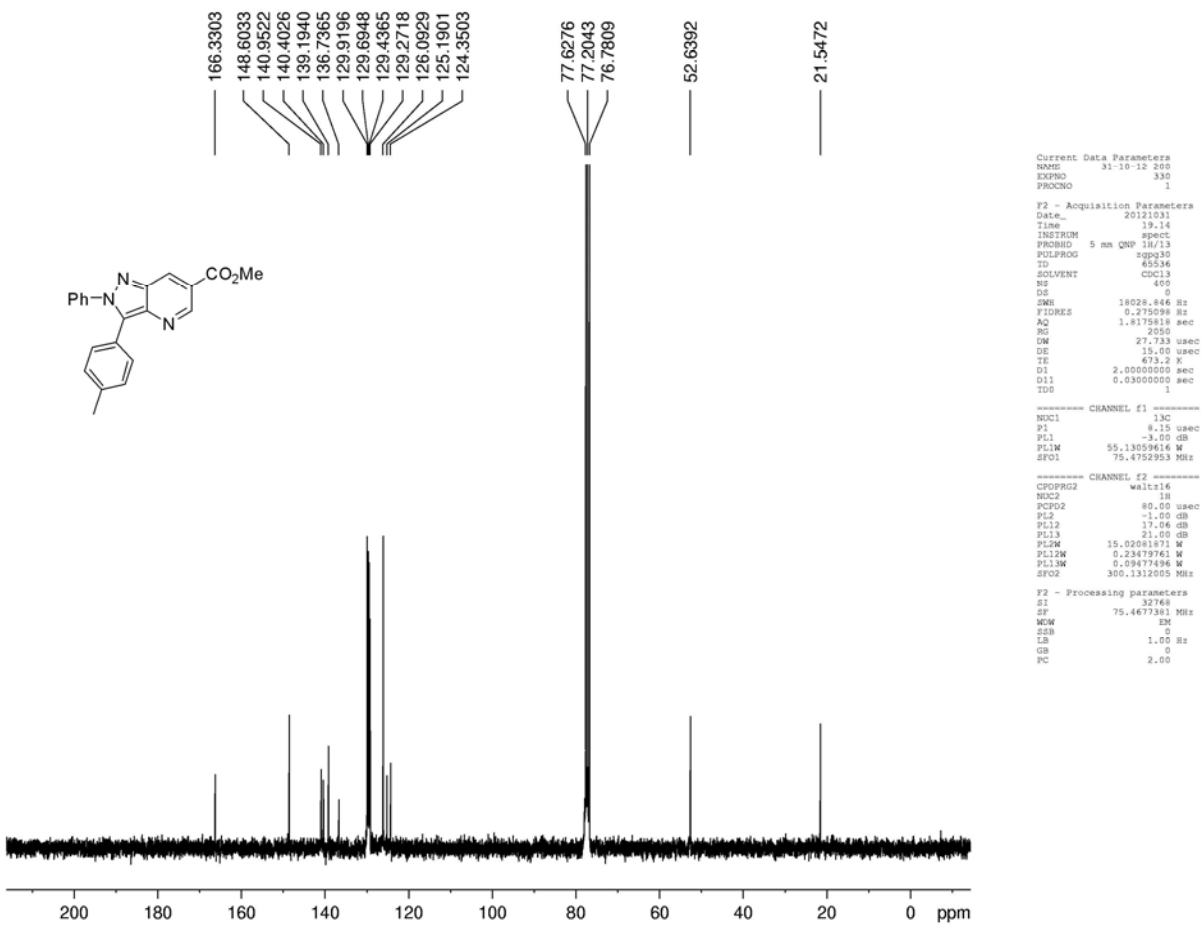


Fig. S-95: ^{13}C spectrum of methyl 2-phenyl-3-(4-methylphenyl)-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (Table 2, entry 20, **2**).

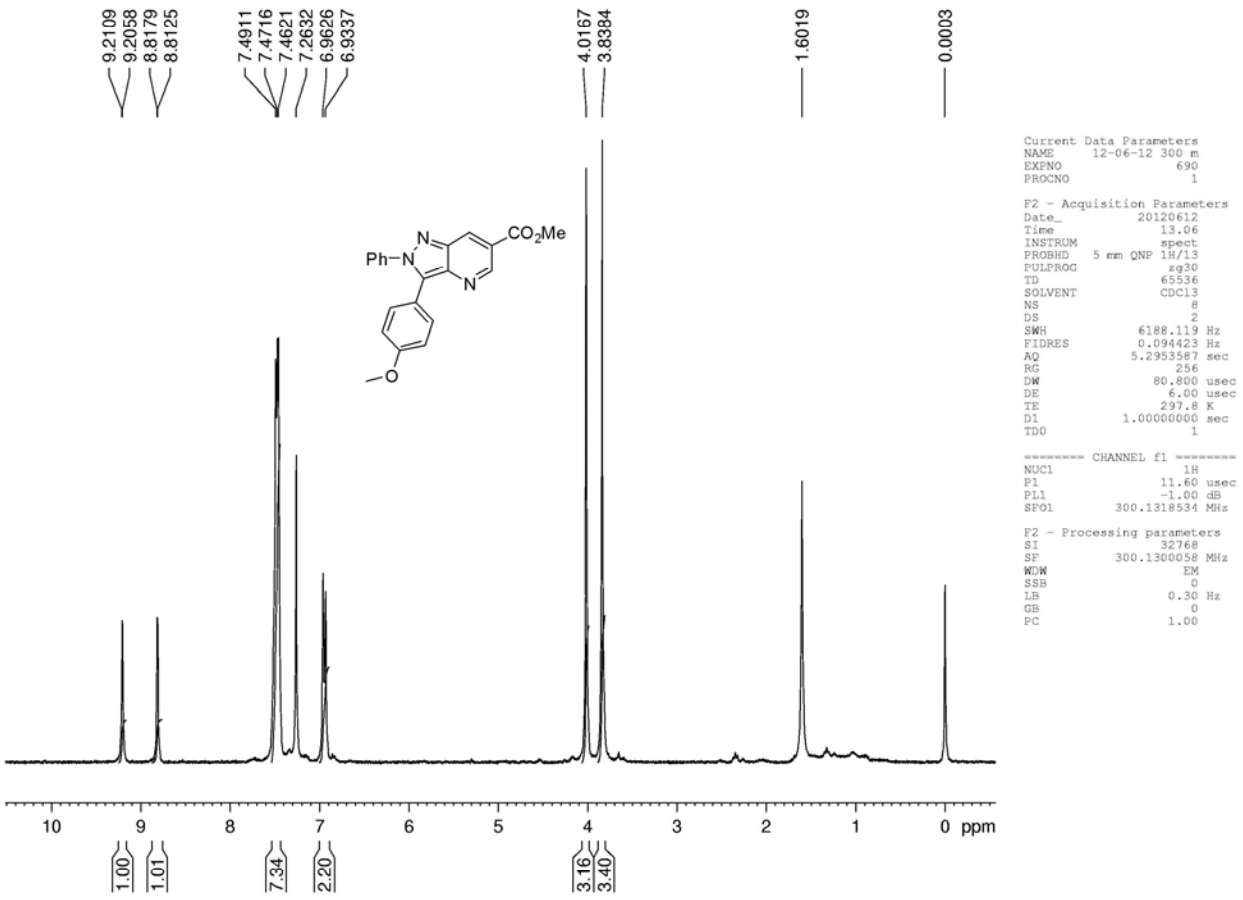
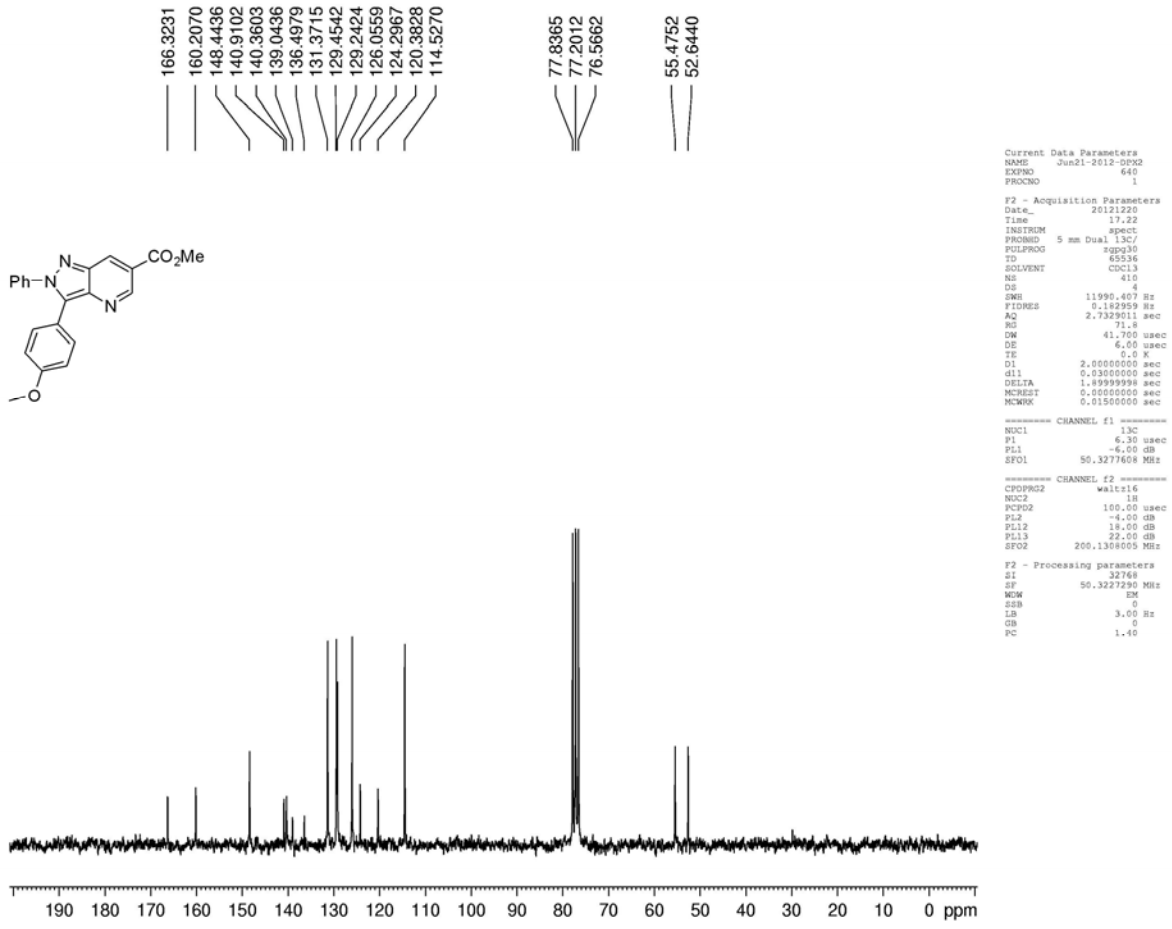


Fig. S-96: ^{1}H spectrum of methyl 3-(4-methoxyphenyl)-2-phenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (Table 2, entry 21, **2**).



Current Data Parameters
NAME Jun21-2012-DPX2
EXPNO 640
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121220
Time 17.22
INSTRUM spect
PROBHD 5 mm Dual 13C/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 410
DS 4
SWH 11990.407 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 71.8
DW 41.700 usec
DE 6.00 usec
TE 0.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 6.30 usec
PL1 -6.00 dB
SFO1 50.3277608 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -4.00 dB
PL12 18.00 dB
PL13 22.00 dB
SFO2 200.1308005 MHz

F2 - Processing parameters
SI 32768
SF 50.3227290 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

Fig. S-97: ^{13}C spectrum of methyl 2-phenyl-3-(4-methylphenyl)-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (Table 2, entry 21, **2**).

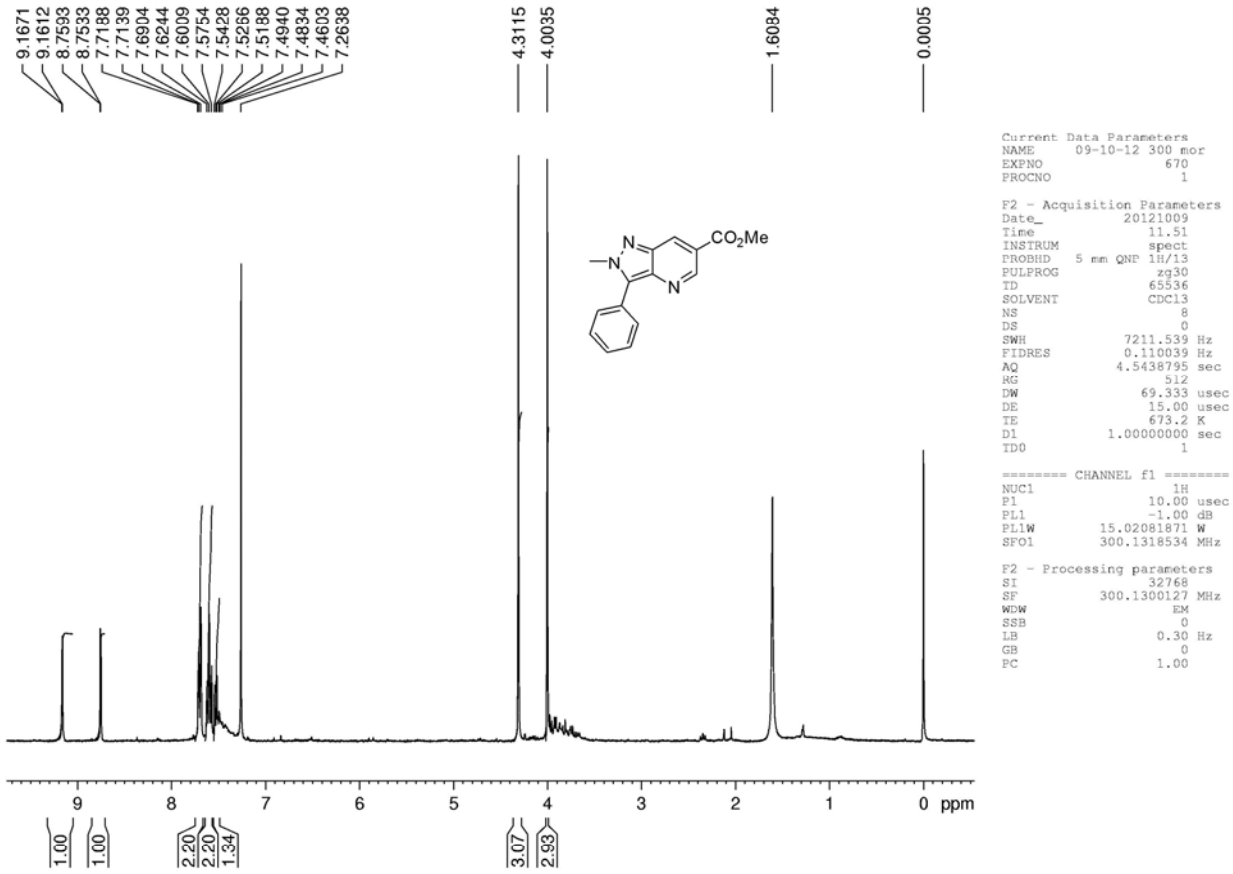


Fig. S-98: ^{1}H spectrum of methyl 2-methyl-3-phenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (Table 2, entry 22, **2**).

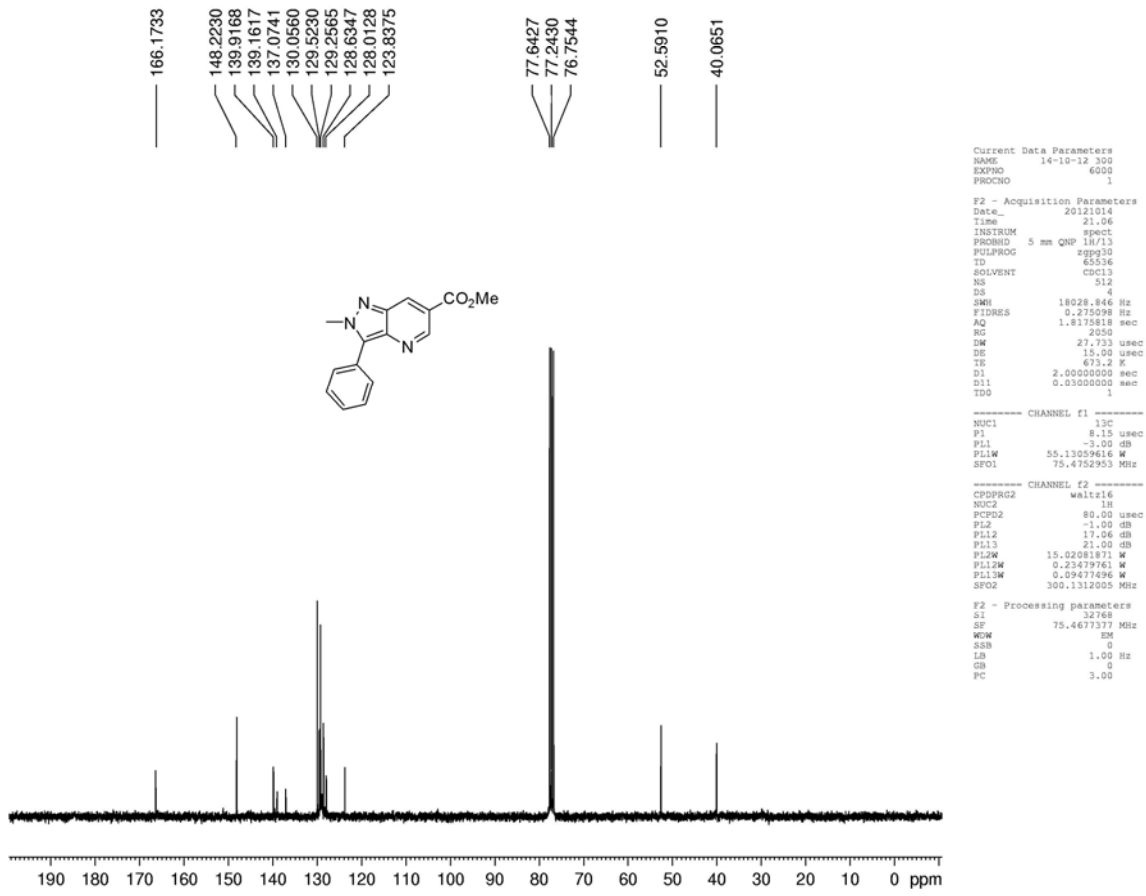


Fig. S-99: ^{13}C spectrum of methyl 2-methyl-3-phenyl-2*H*-pyrazolo[4,3-*b*]pyridine-6-carboxylate (Table 2, entry 22, **2**).

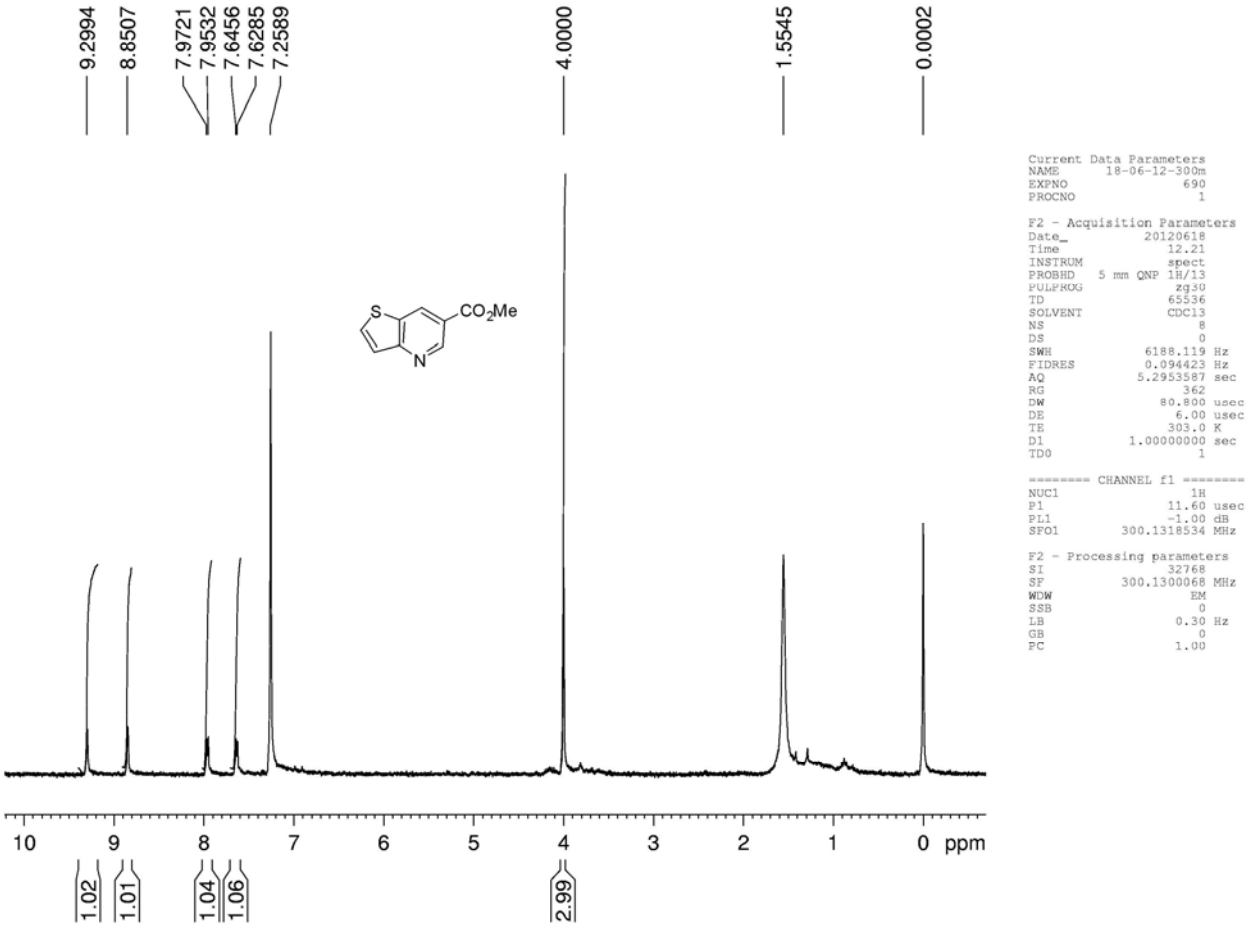


Fig. S-100: ^{1}H spectrum of methyl thieno[3,2-*b*]pyridine-6-carboxylate (Table 2, entry 23, **2**).

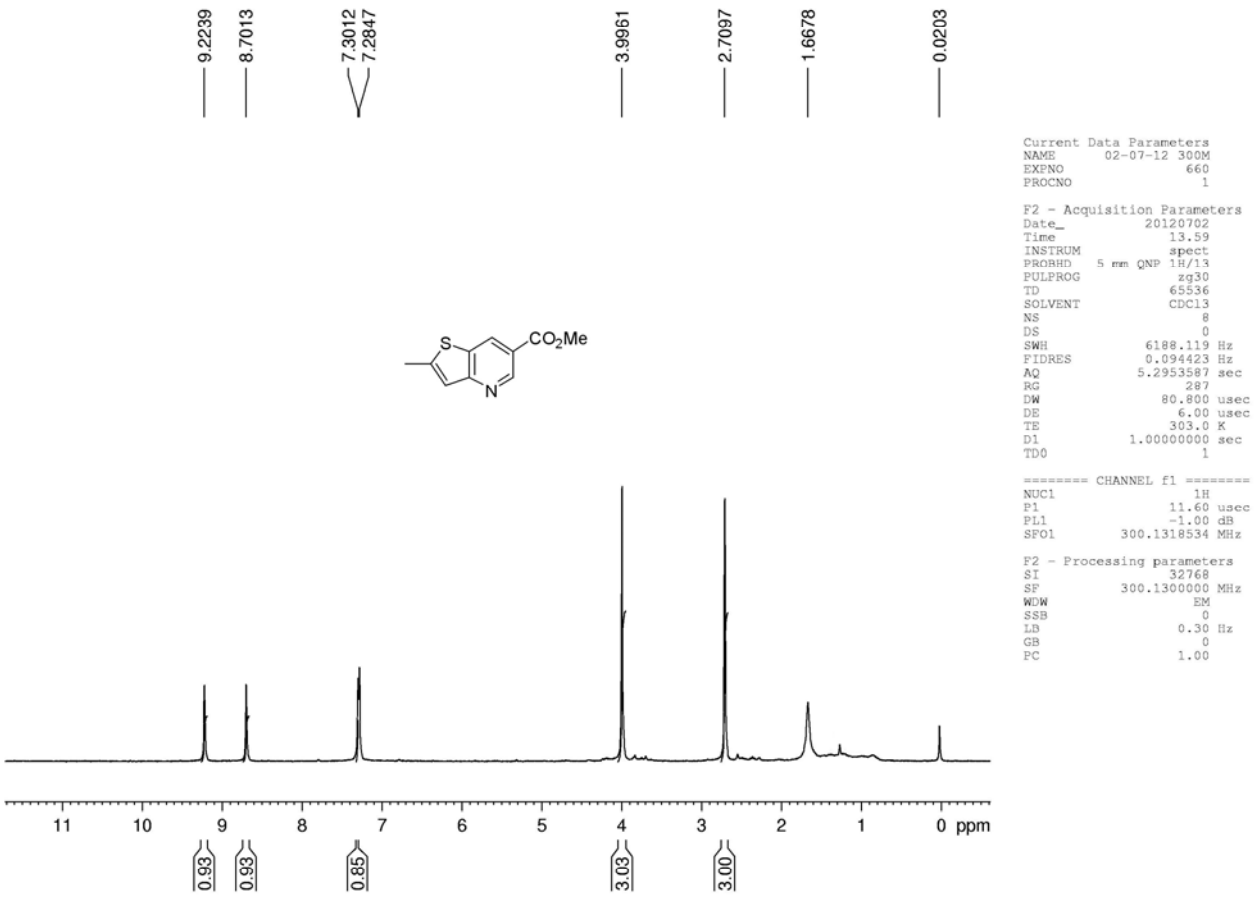


Fig. S-101: ^{1}H spectrum of methyl 2-methylthieno[3,2-*b*]pyridine-6-carboxylate (Table 2, entry 24, **2**).

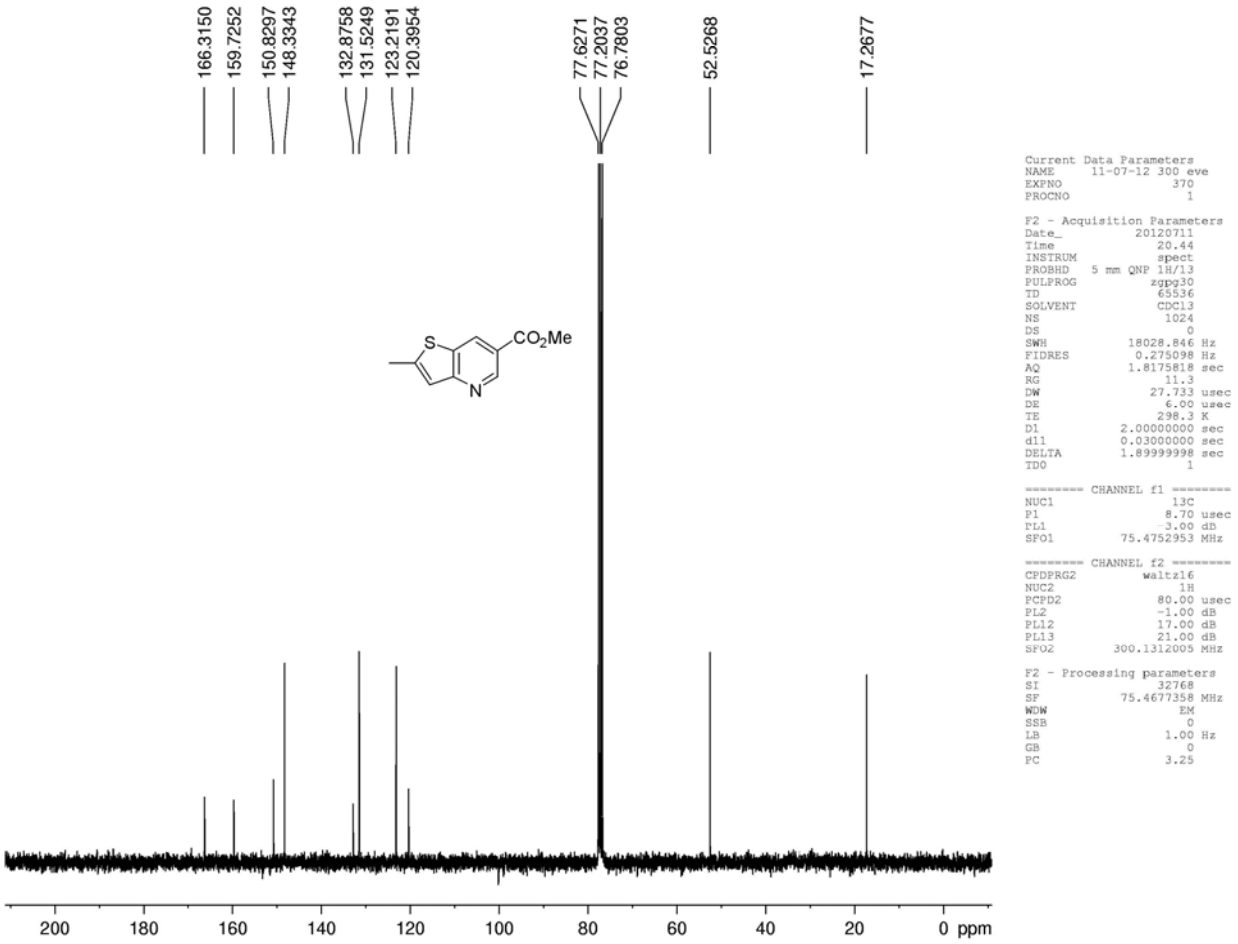


Fig. S-102: ^{13}C spectrum of methyl 2-methylthieno[3,2-*b*]pyridine-6-carboxylate (Table 2, entry 24, **2**).

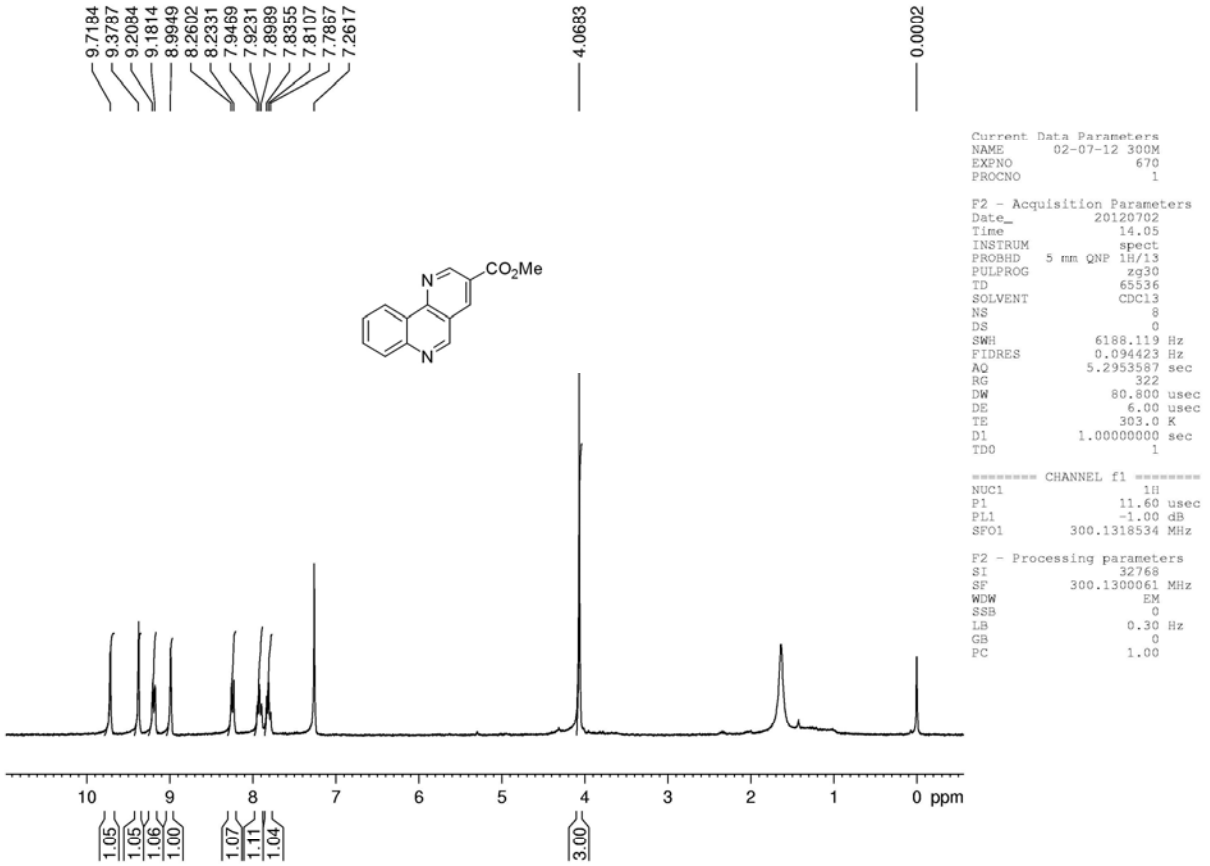


Fig. S-103: ^{1}H spectrum of methyl benzo[*h*][1,6]naphthyridine-3-carboxylate (Table 2, entry 25, **2**).

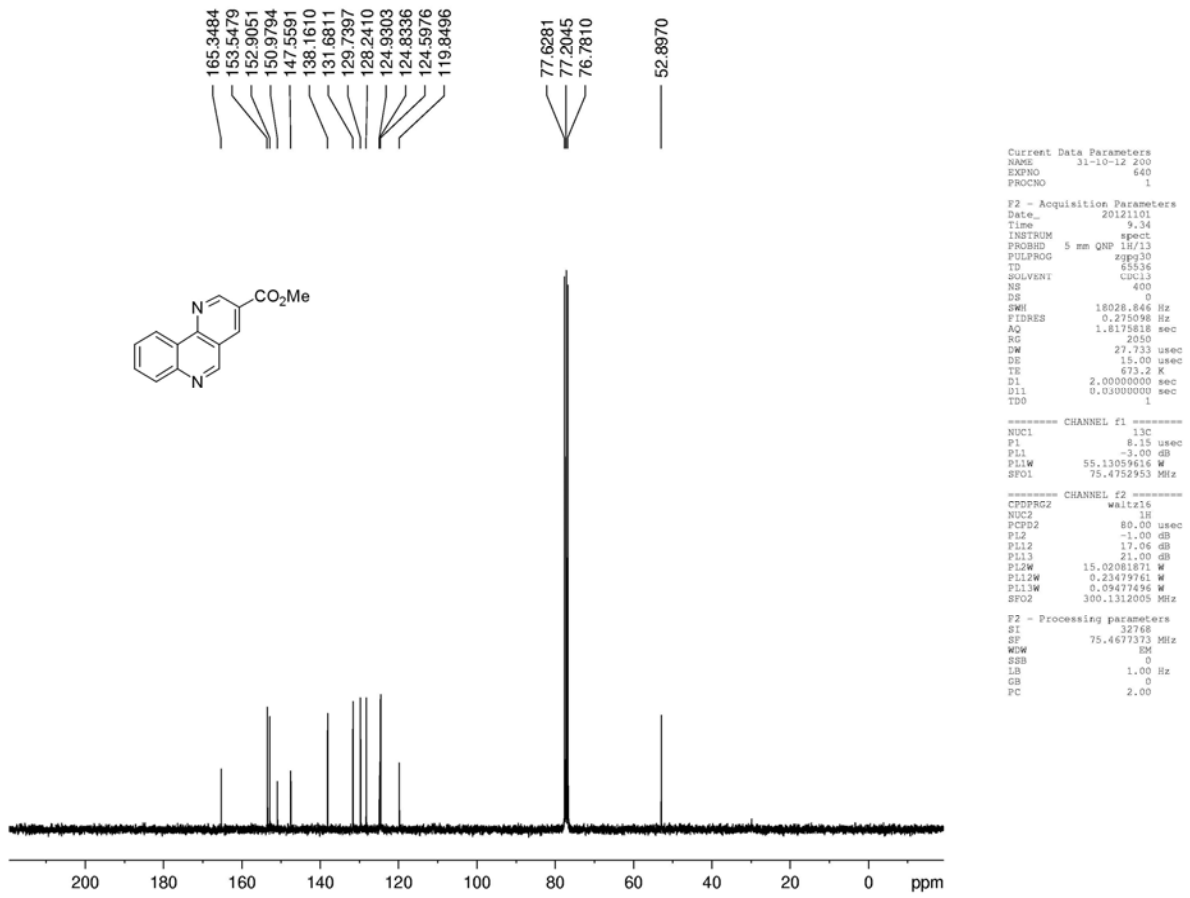


Fig. S-104: ^{13}C spectrum of methyl benzo[*h*][1,6]naphthyridine-3-carboxylate (Table 2, entry 25, **2**).