

A Convenient Allenoate-Based Synthesis of 2-Quinolin-2-yl Malonates and β -Ketoesters

Philipp Selig^{a*} and William Raven^b

^aInstitute of Organic Chemistry, RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany

*Phone: +49 241 809 4697, Fax: +49 241 809 2127, E-mail: Philipp.Selig@rwth-aachen.de

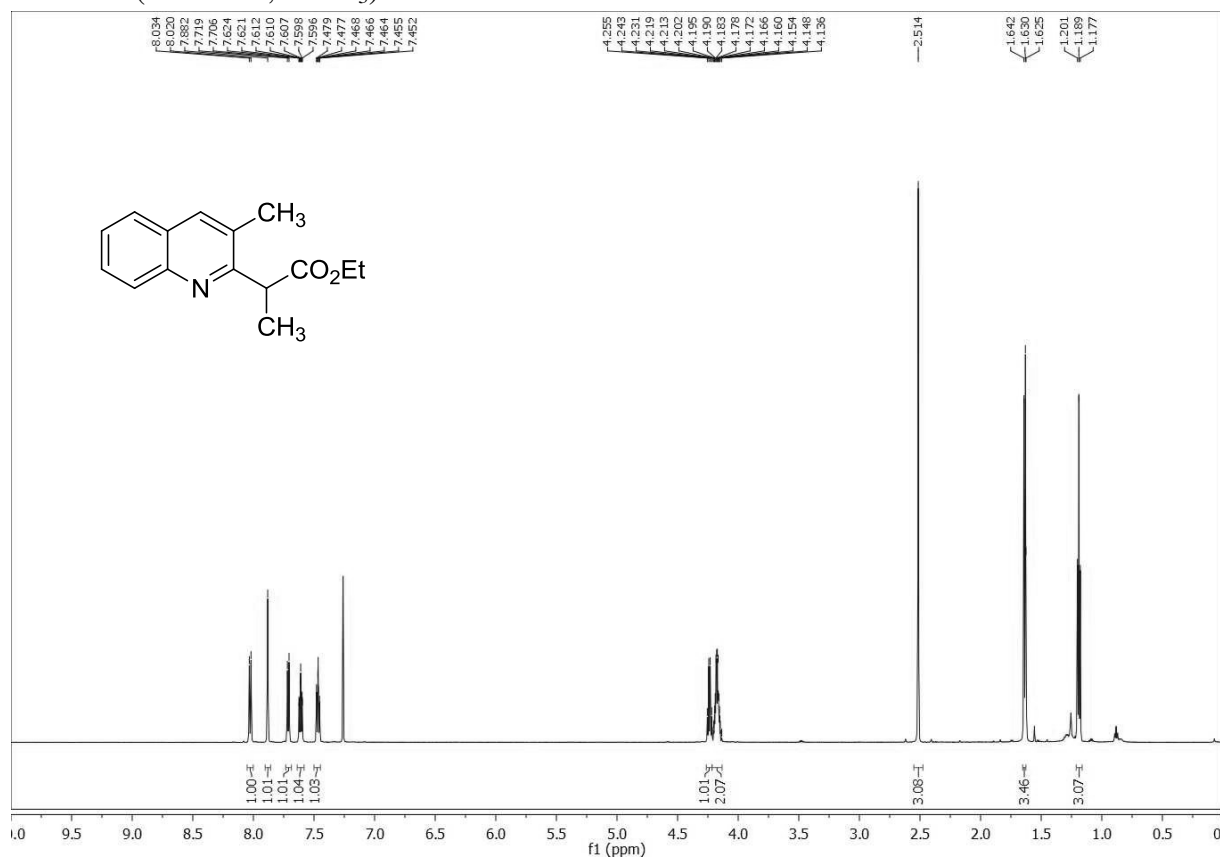
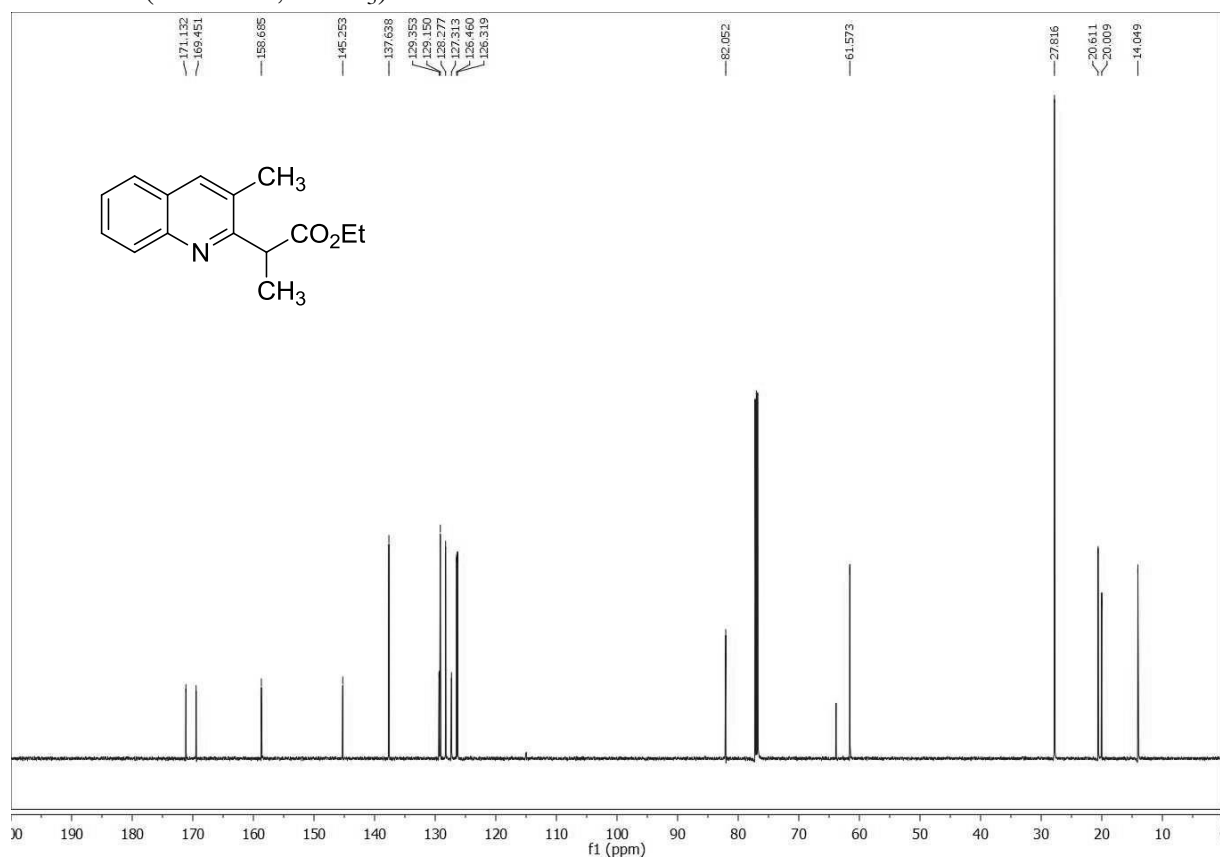
^bInstitute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany

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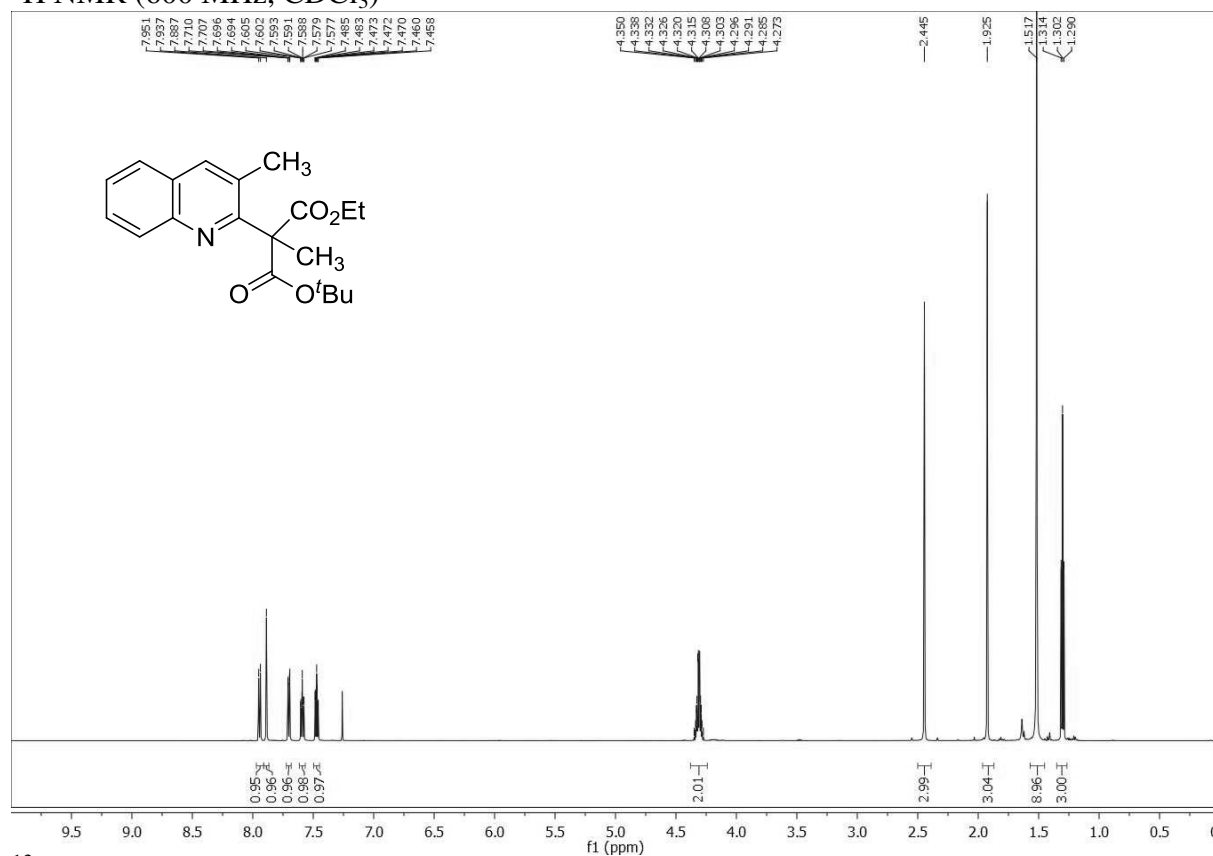
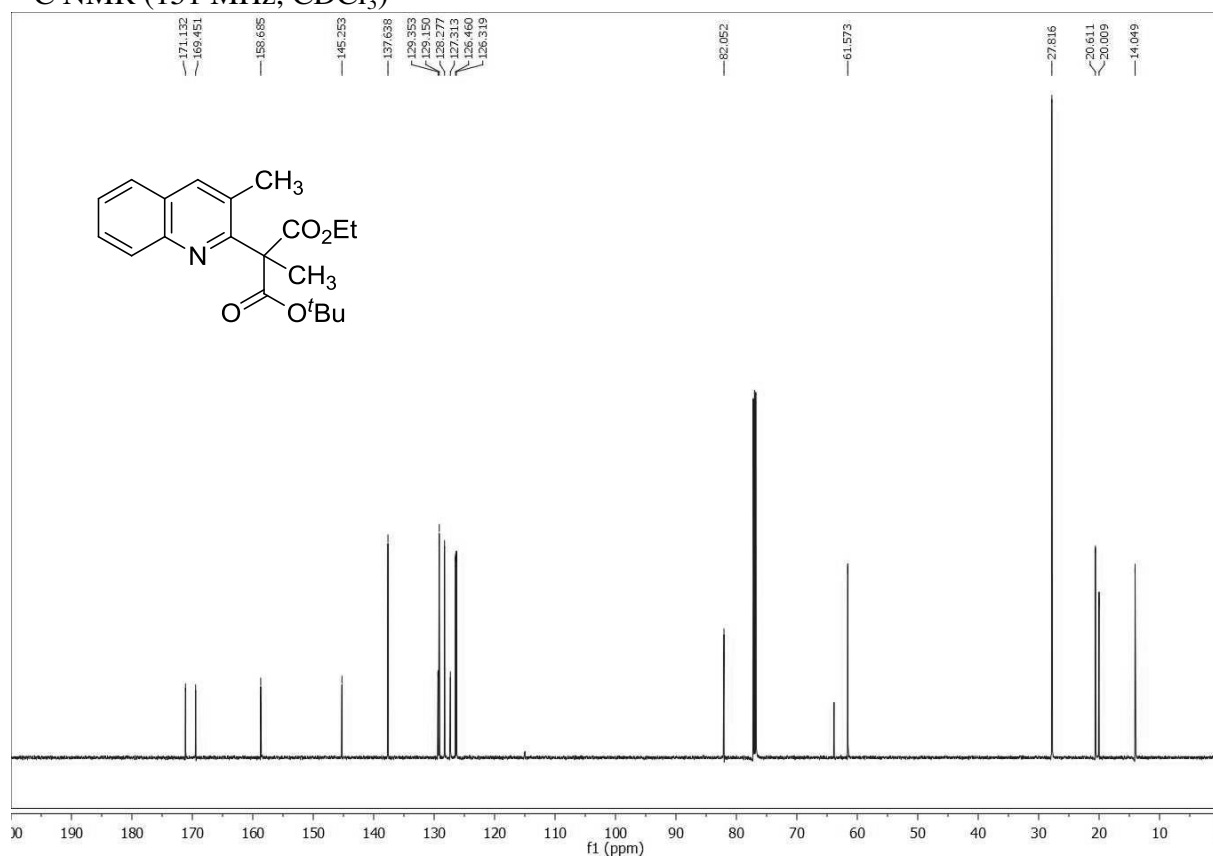
ethyl 2-(3-methylquinolin-2-yl)propanoate

3

 ^1H NMR (600 MHz, CDCl_3) ^{13}C NMR (151 MHz, CDCl_3)

1-tert-butyl 3-ethyl 2-methyl-2-(3-methylquinolin-2-yl)malonate

4a

 ^1H NMR (600 MHz, CDCl_3) ^{13}C NMR (151 MHz, CDCl_3)

11a

Chemical structure: CC1=CC=C2C(=C1)N(C2)C(C(=O)OCC)C(=O)OC(C)(C)C

¹H NMR spectrum (CDCl₃) showing peaks from 0.9 to 7.9 ppm. Integration values are provided below the peaks.

Chemical Shift (ppm)	Integration
7.867, 7.853, 7.850, 7.849, 7.713, 7.711, 7.700, 7.697, 7.603, 7.601, 7.592, 7.589, 7.587, 7.578, 7.575, 7.484, 7.482, 7.473, 7.471, 7.469, 7.459, 7.457	1.00, 1.04, 1.04, 1.06, 1.05
4.334, 4.332, 4.330, 4.316, 4.310, 4.304, 4.298, 4.292, 4.285, 4.280, 4.274, 4.268, 4.262, 4.255, 4.244	2.07
2.435, 2.433, 2.416, 2.411, 2.409, 2.404, 2.402, 2.396	5.06
1.501, 1.499, 1.276, 1.274, 1.264, 1.261, 1.257, 1.252, 1.149, 1.137, 1.135, 1.125, 1.111, 1.100, 0.939, 0.927	9.14, 5.84, 3.20

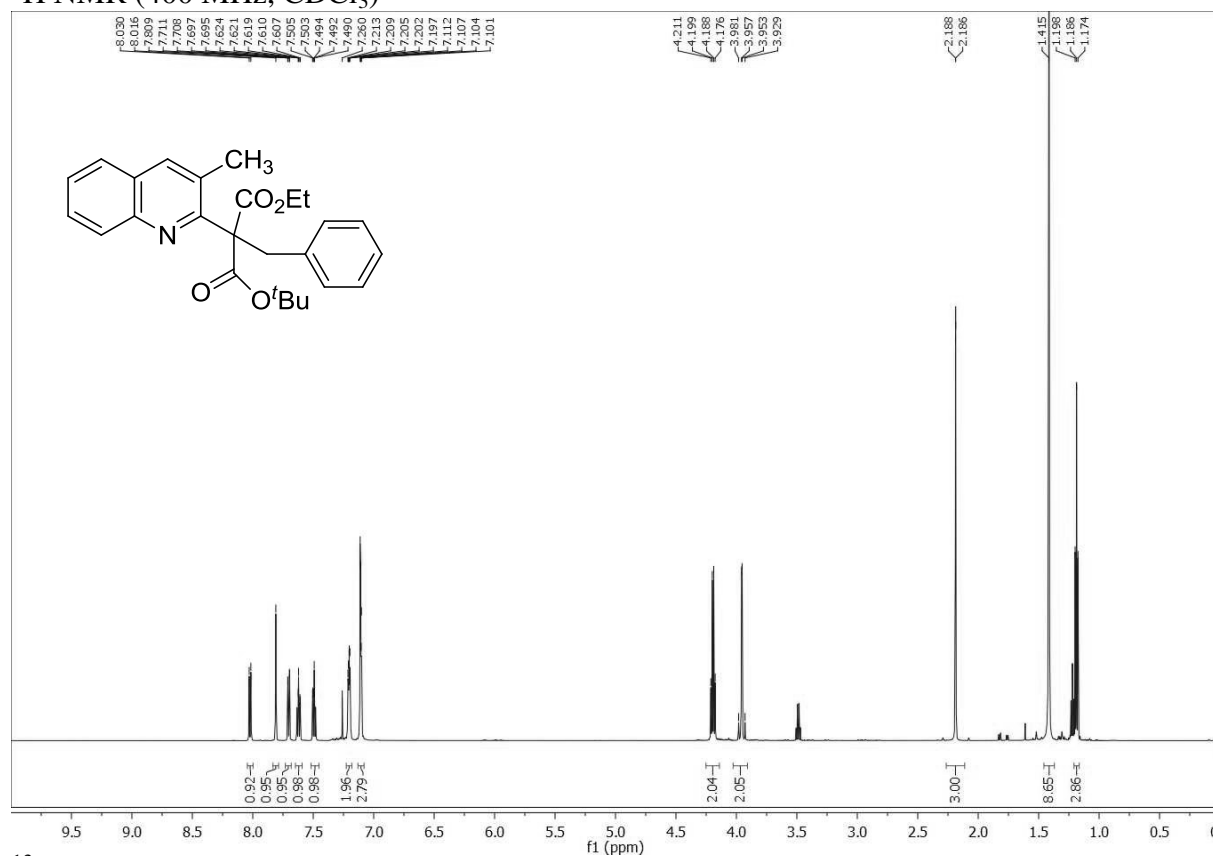
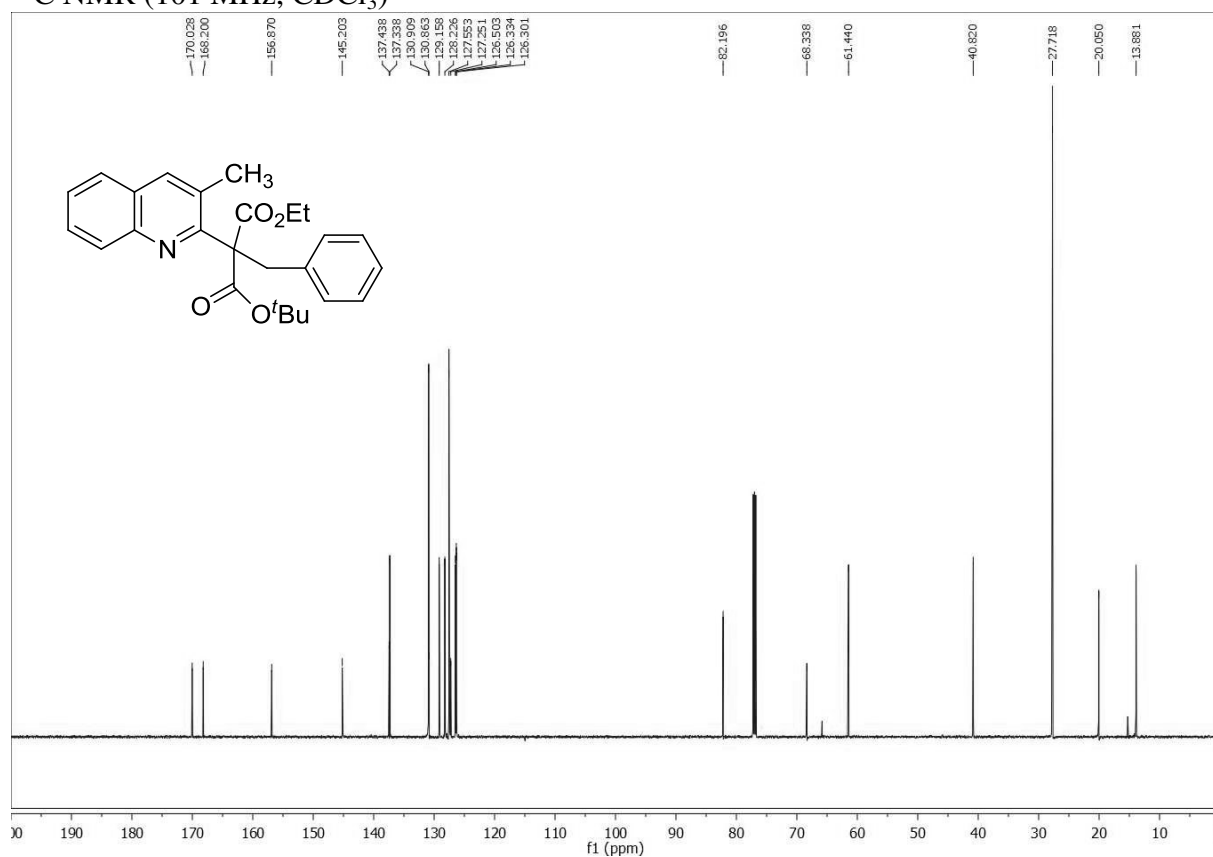
Chemical structure of **1-methyl-2-(1-ethoxy-1-propyl)-3-(tert-butoxy)pyridine** is shown above the ¹³C NMR spectrum. The spectrum displays peaks corresponding to the structure, with the following chemical shifts (ppm) labeled above the peaks:

- 170.913, 169.277
- 157.417
- 145.208
- 136.989
- 130.223, 129.211, 128.145, 127.202
- 126.400, 126.316
- 81.822
- 67.161
- 61.283
- 36.118
- 27.639
- 19.950, 18.885, 14.668, 14.053

The x-axis is labeled f1 (ppm) and ranges from 0 to 200.

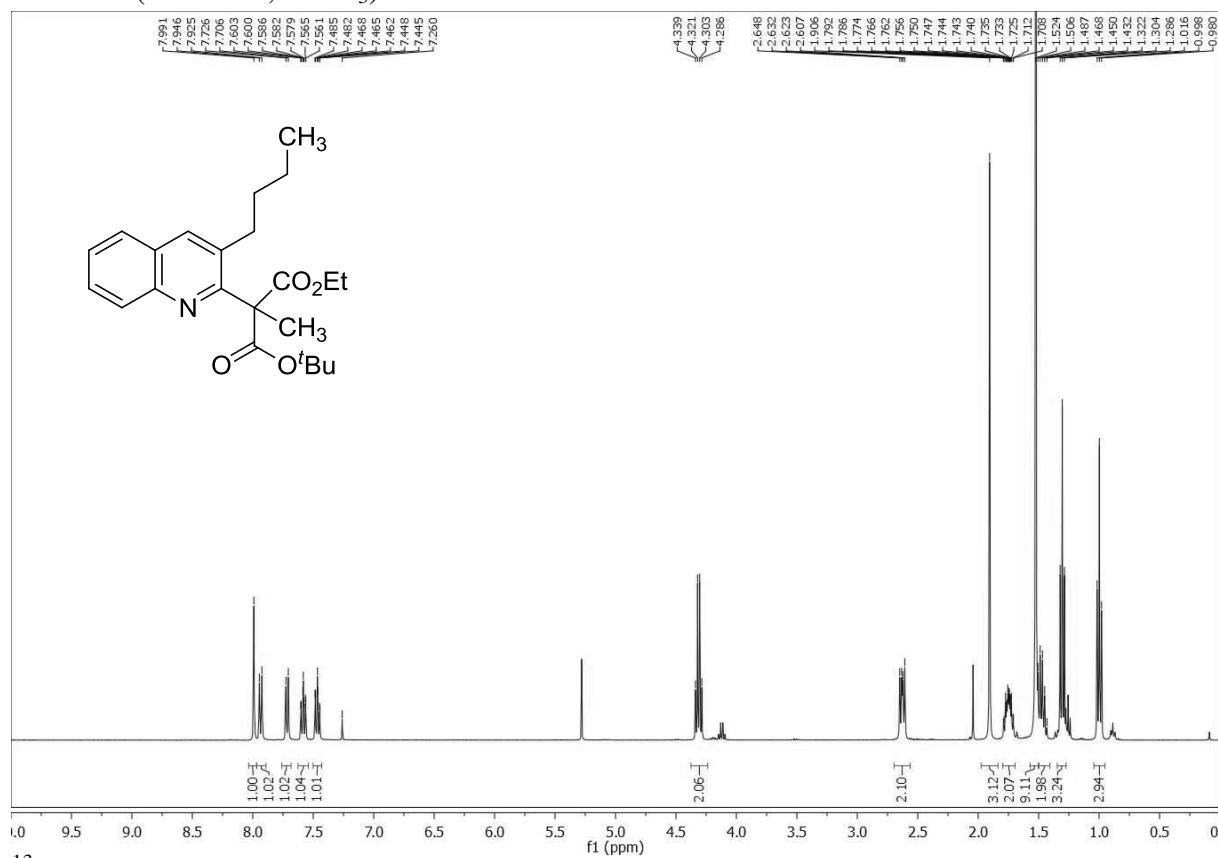
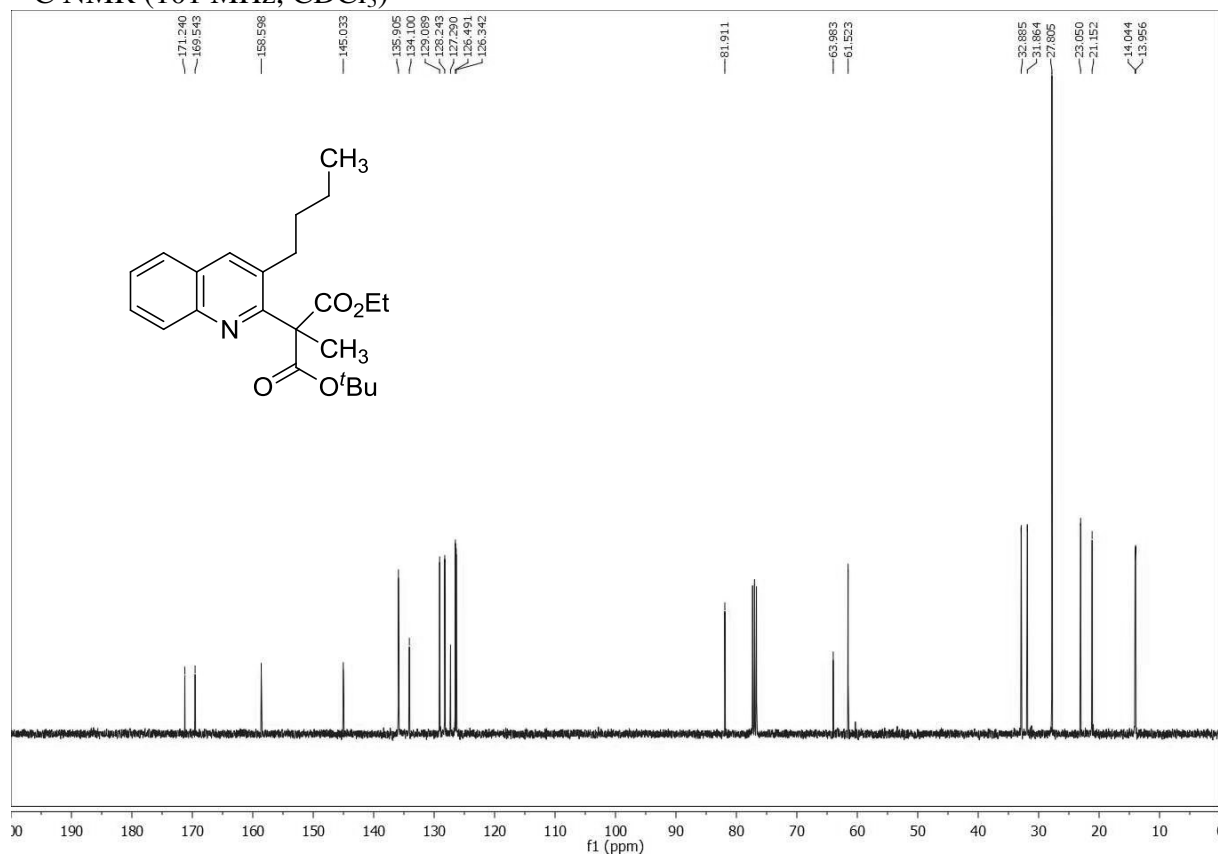
1-tert-butyl 3-ethyl 2-benzyl-2-(3-methylquinolin-2-yl) malonate

12a

 ^1H NMR (400 MHz, CDCl_3) ^{13}C NMR (101 MHz, CDCl_3)

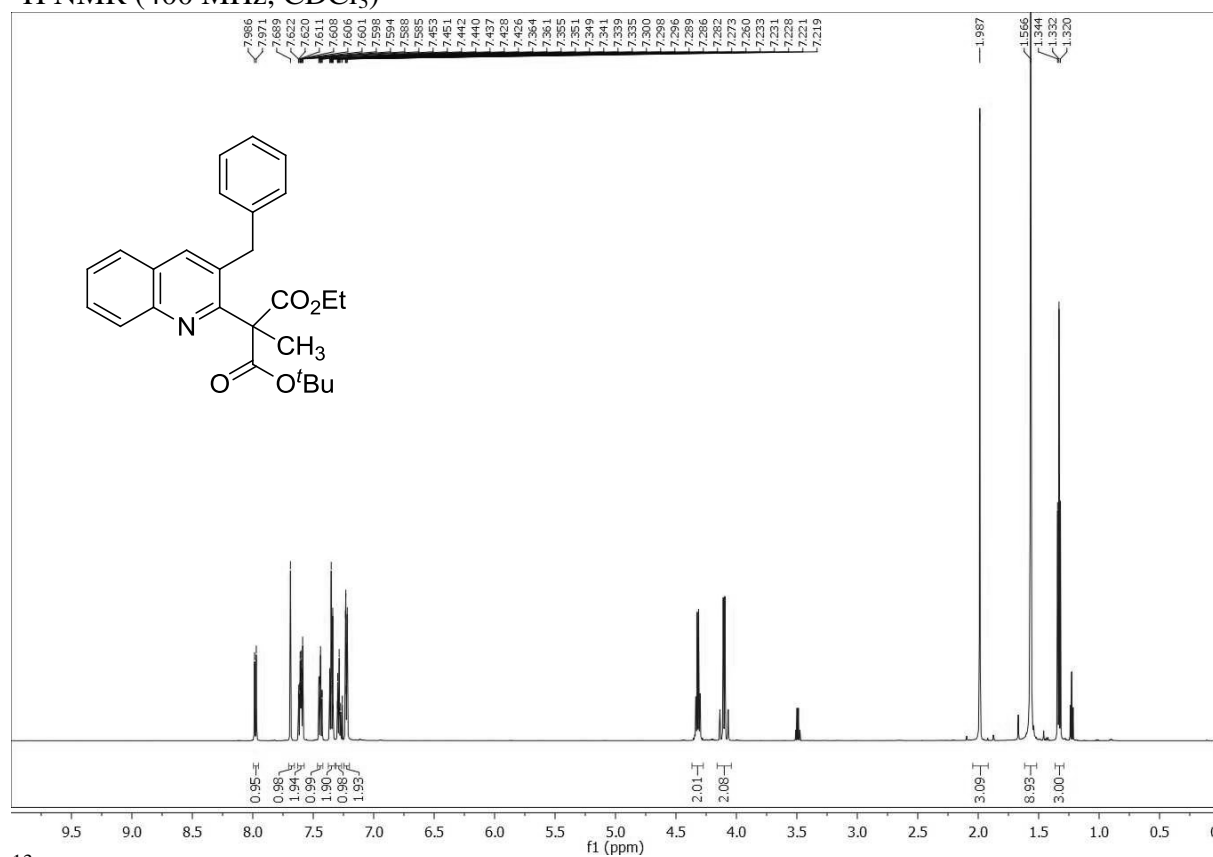
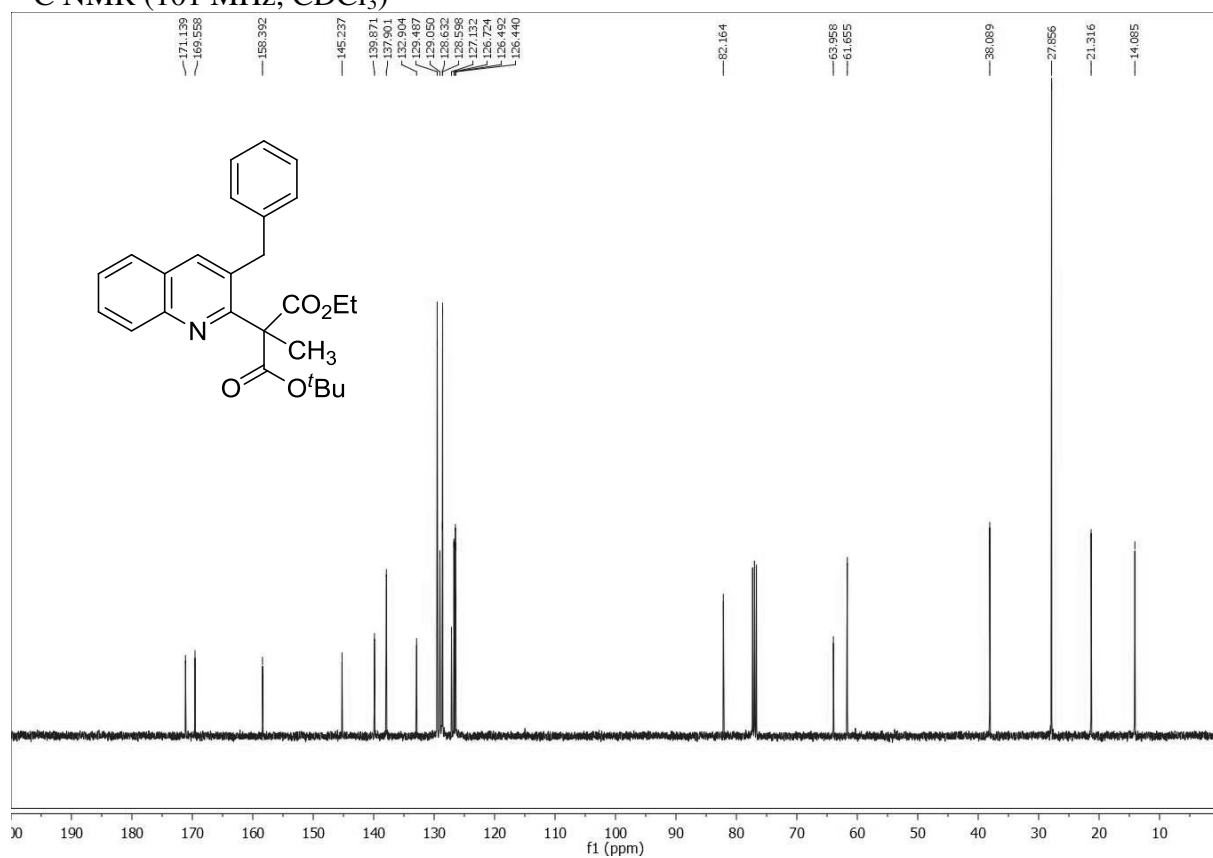
1-tert-butyl 3-ethyl 2-(3-butylquinolin-2-yl)-2-methylmalonate

13a

 ^1H NMR (400 MHz, CDCl_3) ^{13}C NMR (101 MHz, CDCl_3)

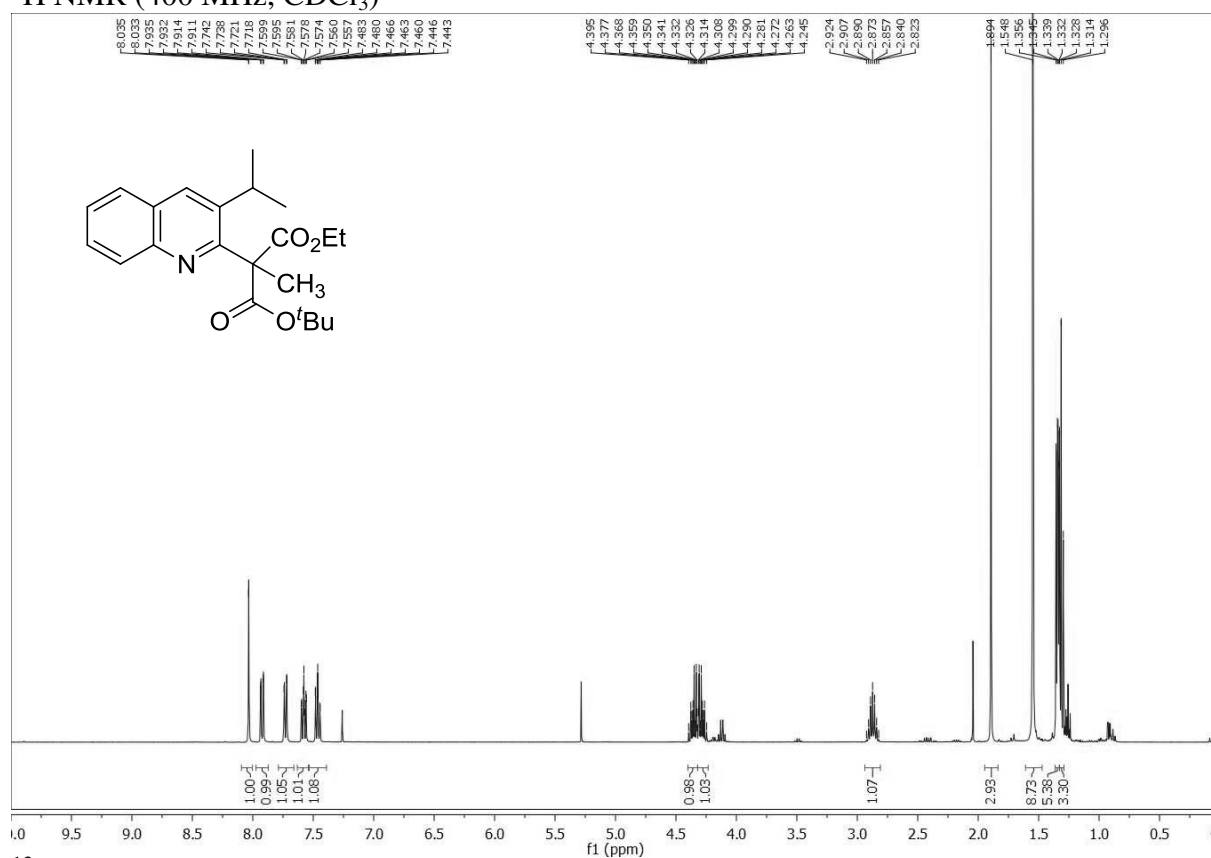
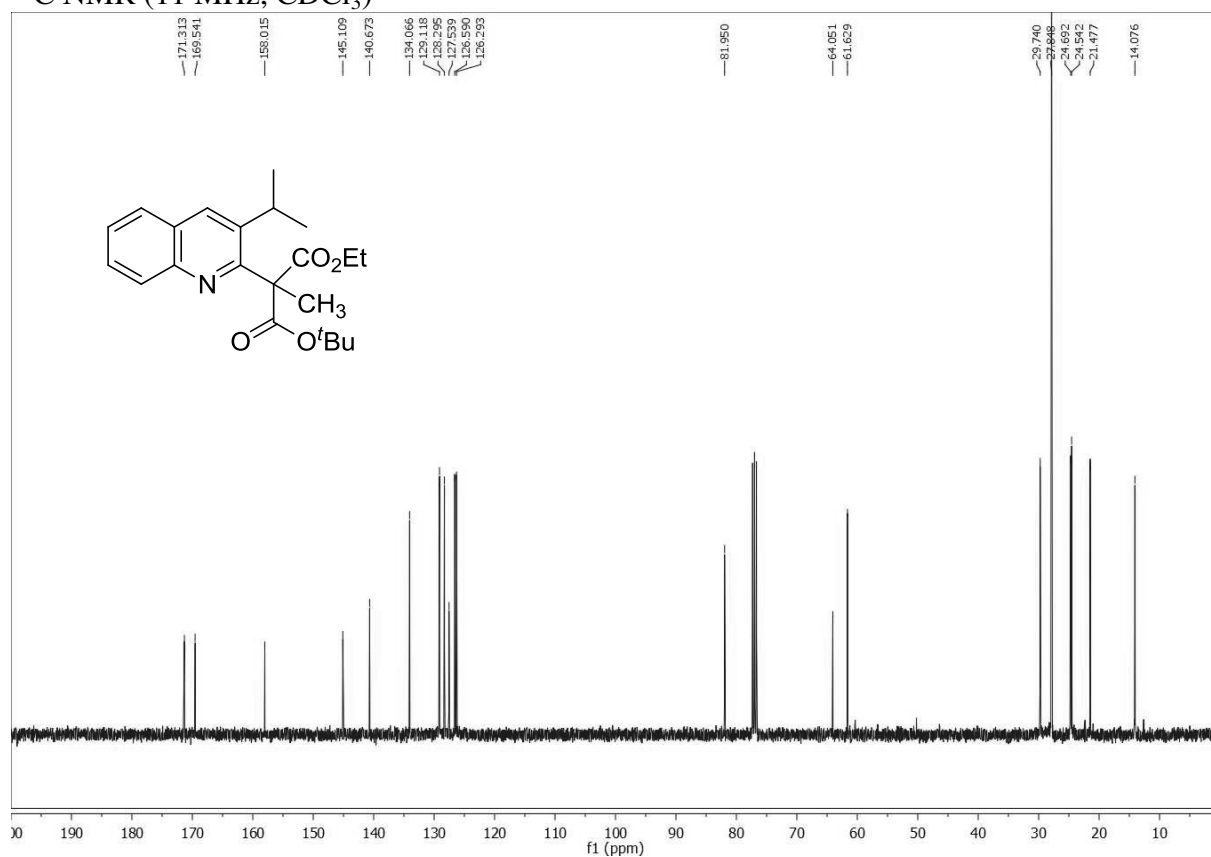
1-tert-butyl 3-ethyl 2-(3-benzylquinolin-2-yl)-2-methylmalonate

14a

 ^1H NMR (400 MHz, CDCl_3) ^{13}C NMR (101 MHz, CDCl_3)

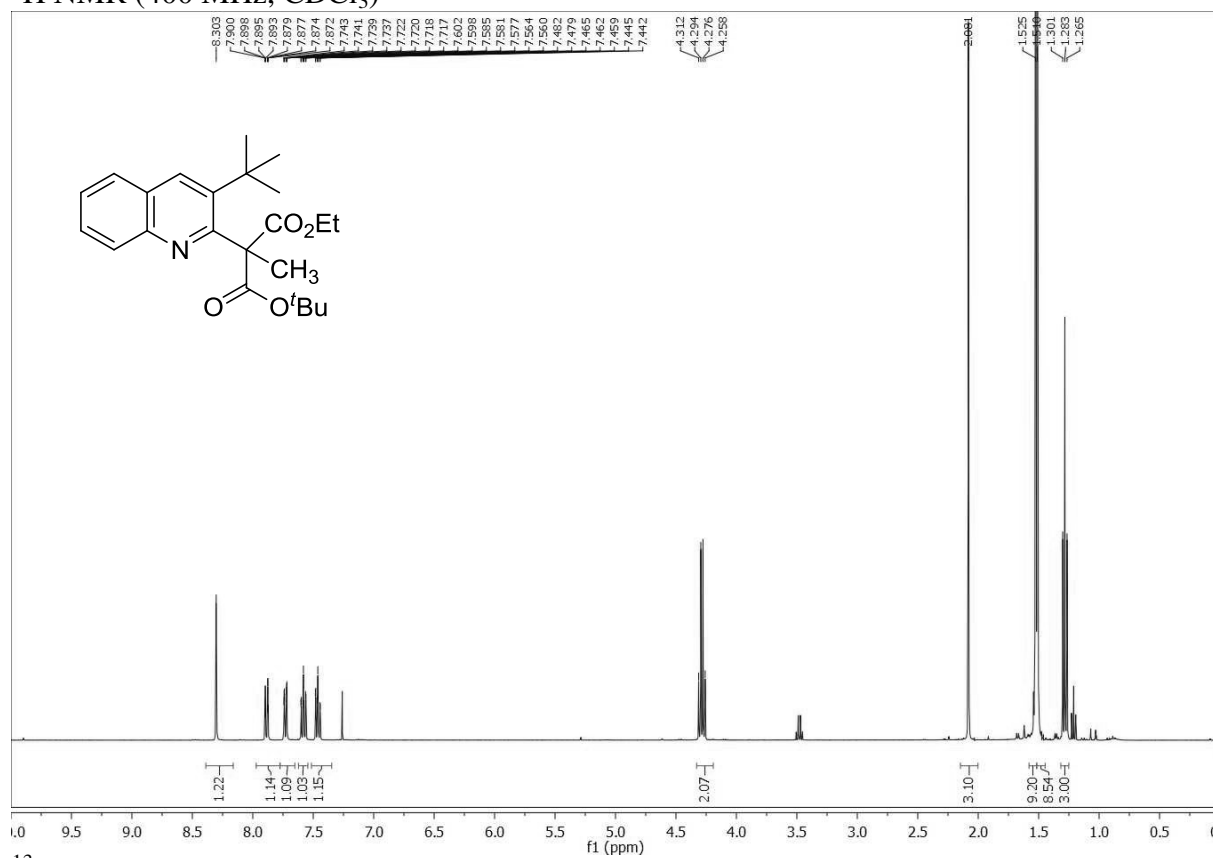
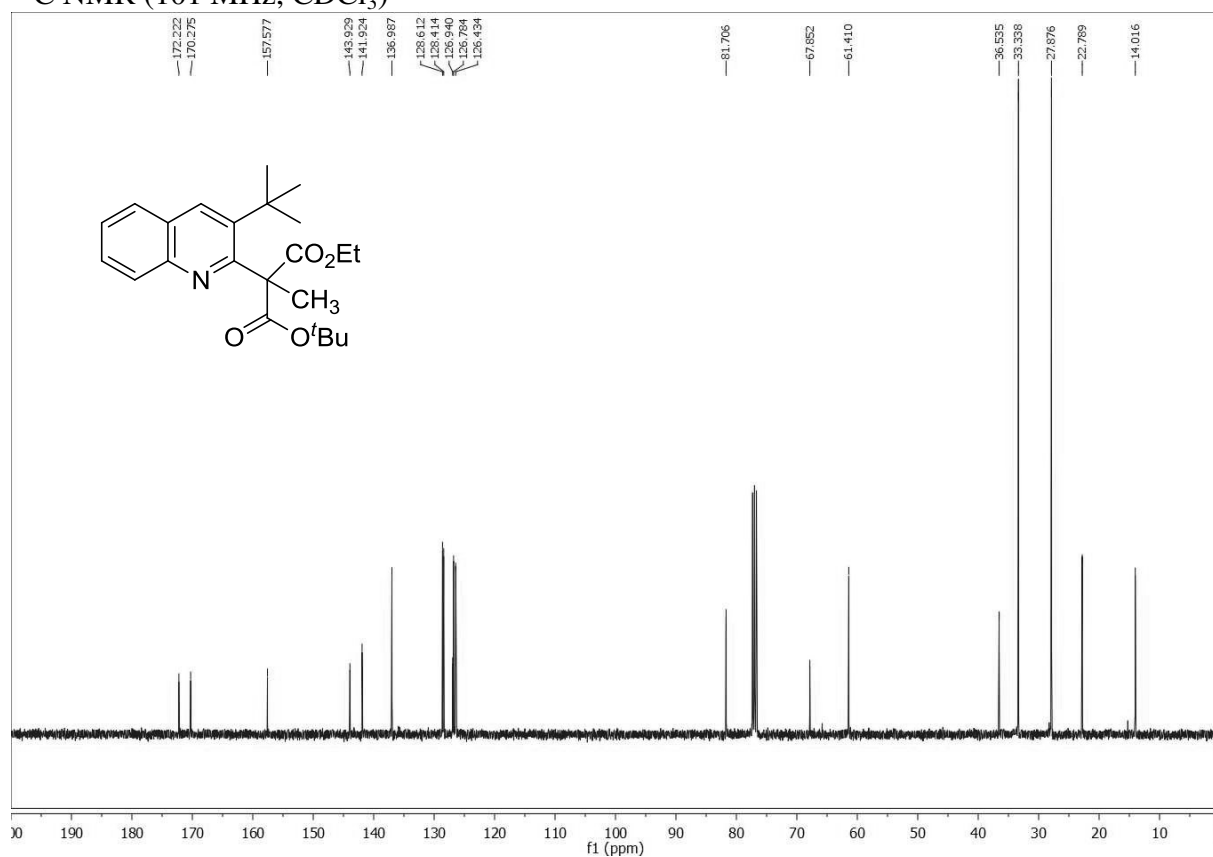
1-tert-butyl 3-ethyl 2-(3-isopropylquinolin-2-yl)-2-methylmalonate

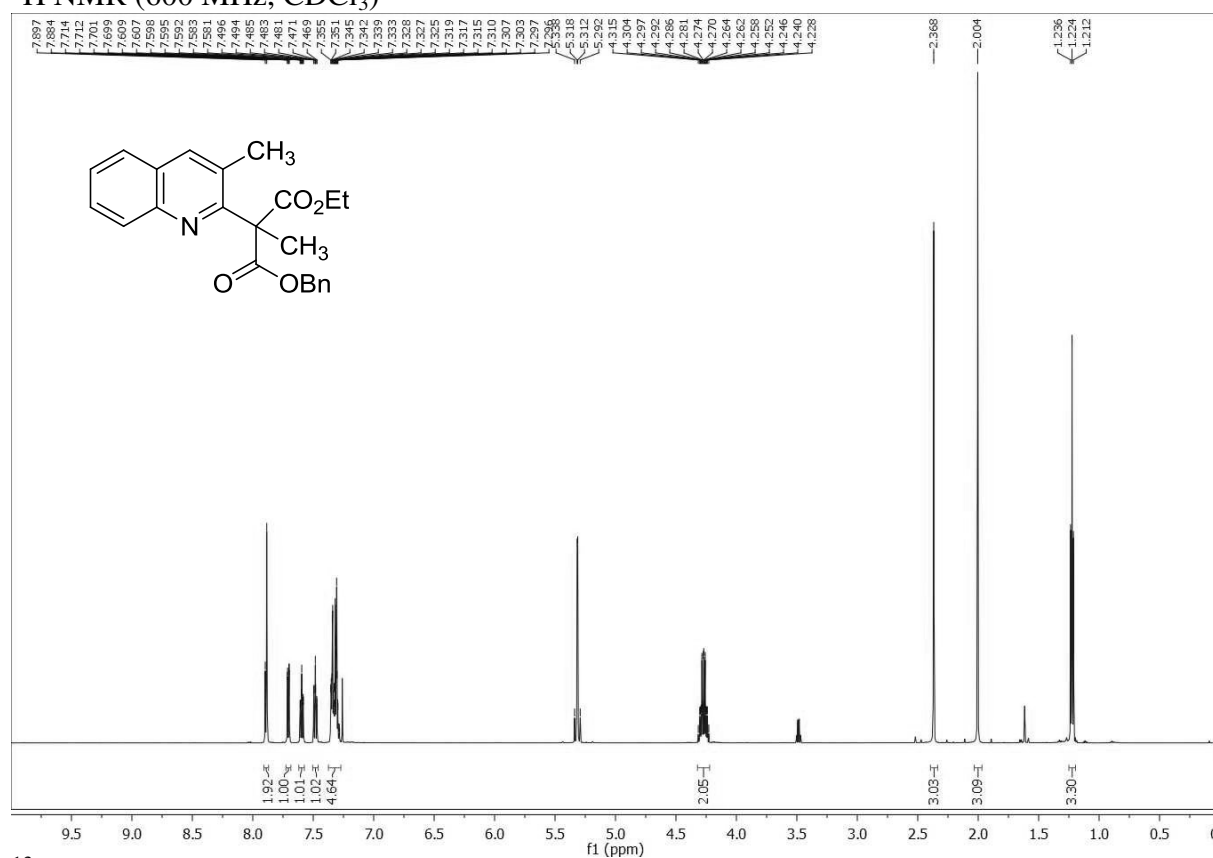
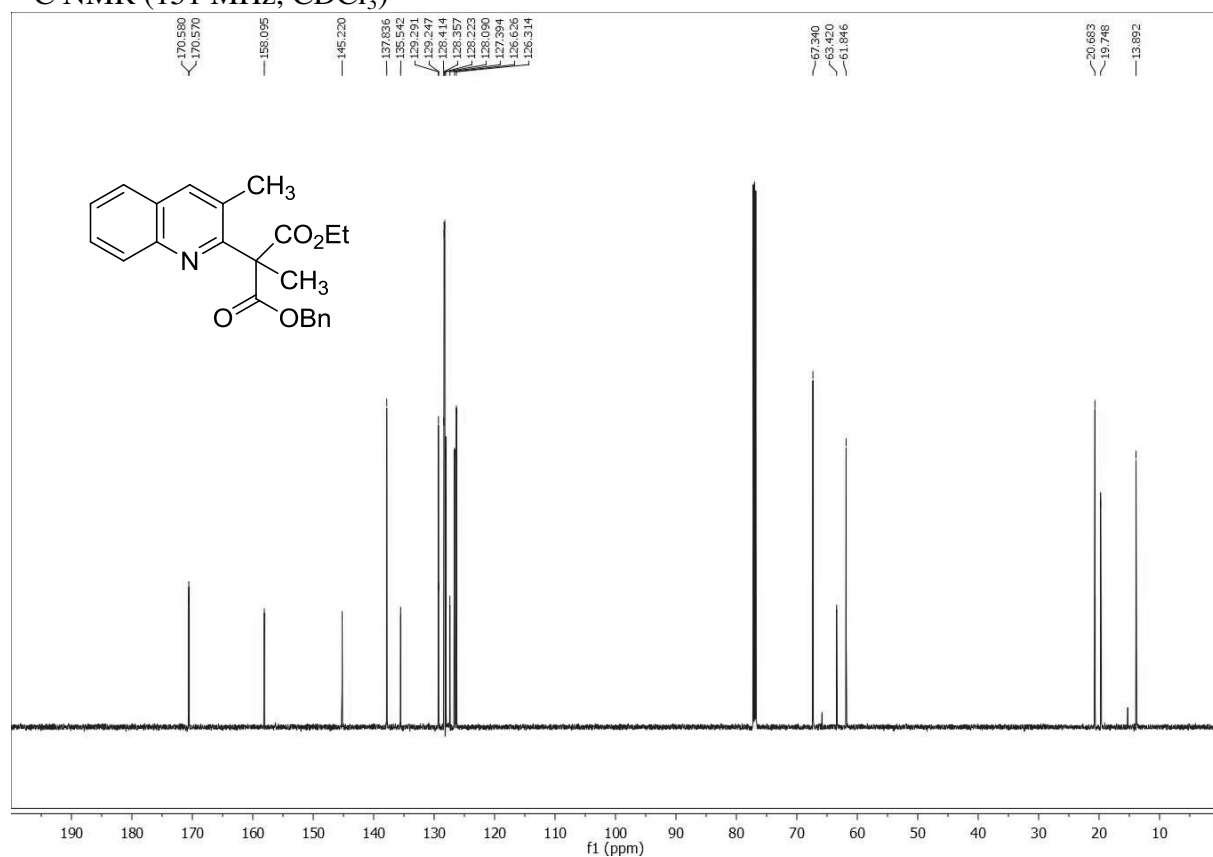
15a

 ^1H NMR (400 MHz, CDCl_3) ^{13}C NMR (11 MHz, CDCl_3)

1-tert-butyl 3-ethyl 2-(3-(tert-butyl)quinolin-2-yl)-2-methylmalonate

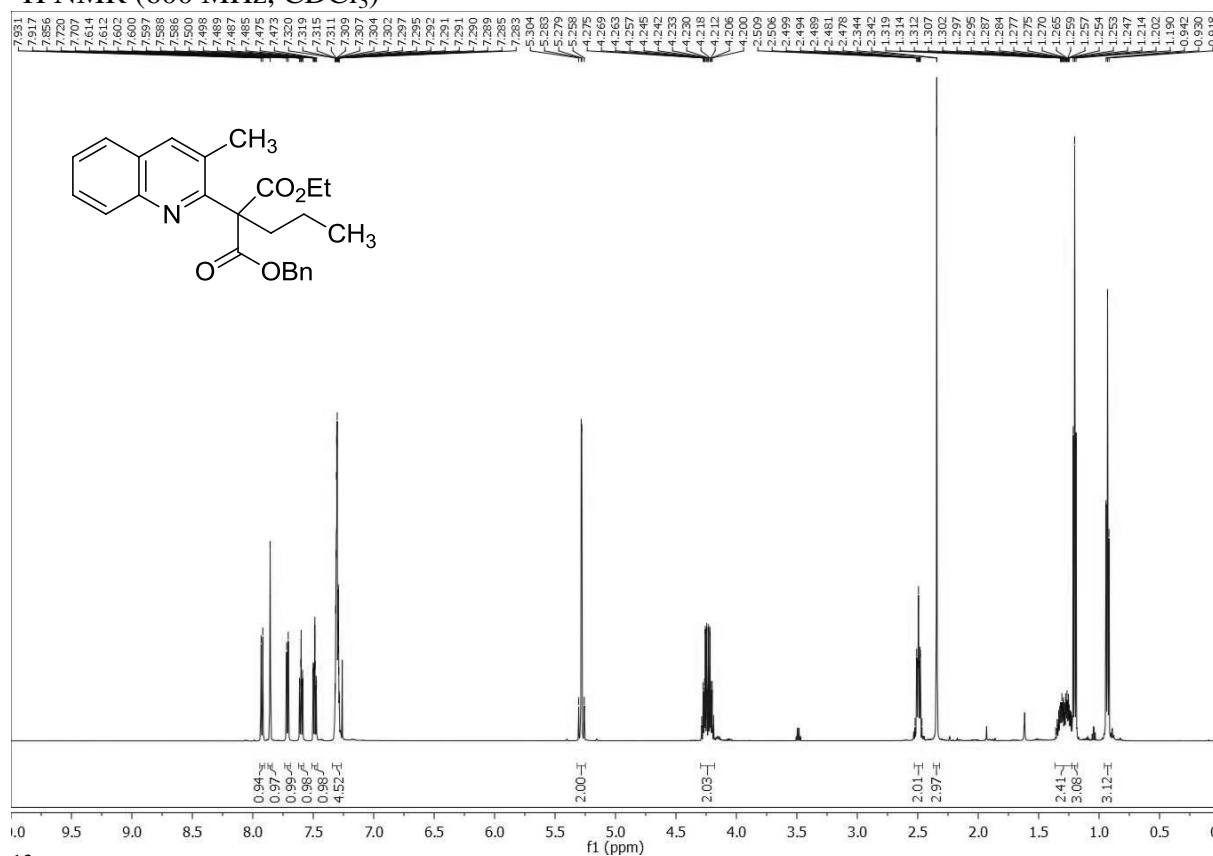
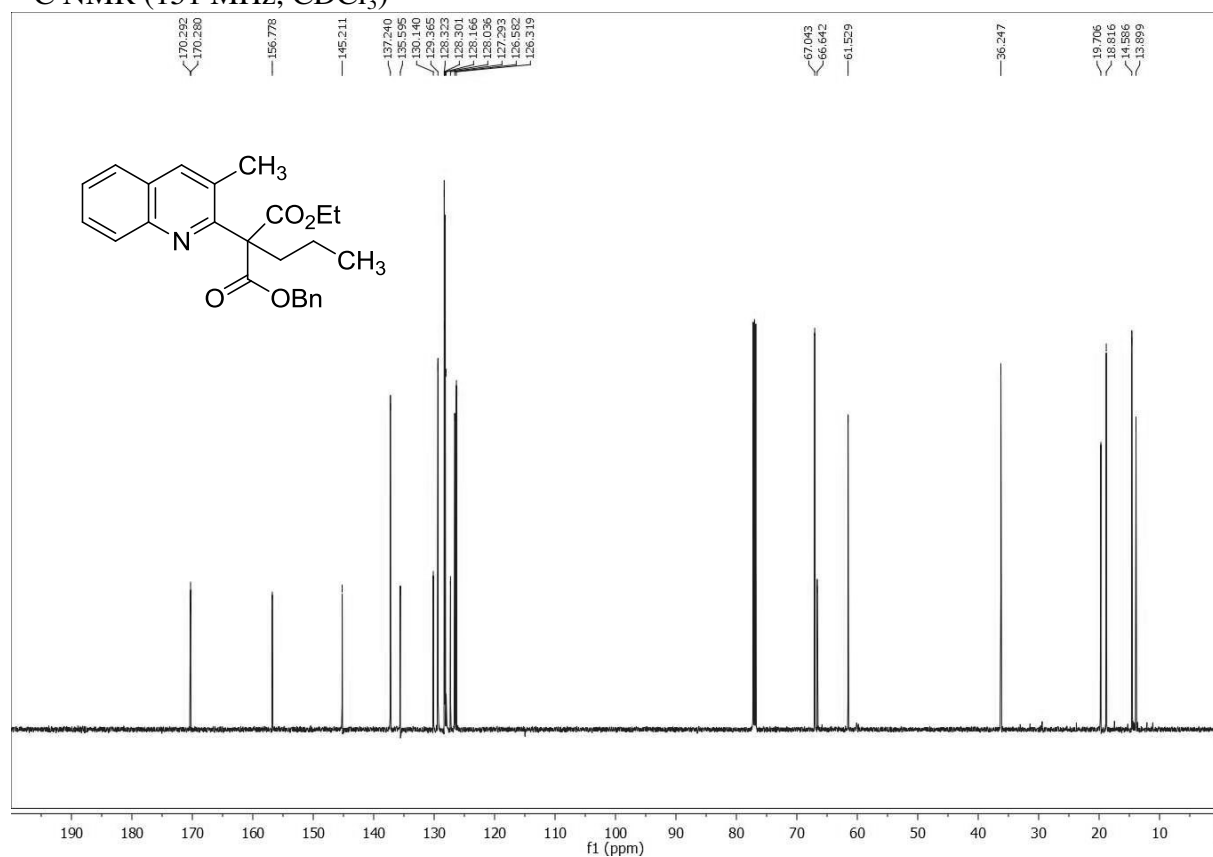
16a

 ^1H NMR (400 MHz, CDCl_3) ^{13}C NMR (101 MHz, CDCl_3)

1-benzyl 3-ethyl 2-methyl-2-(3-methylquinolin-2-yl)malonate**4b** ^1H NMR (600 MHz, CDCl_3) ^{13}C NMR (151 MHz, CDCl_3)

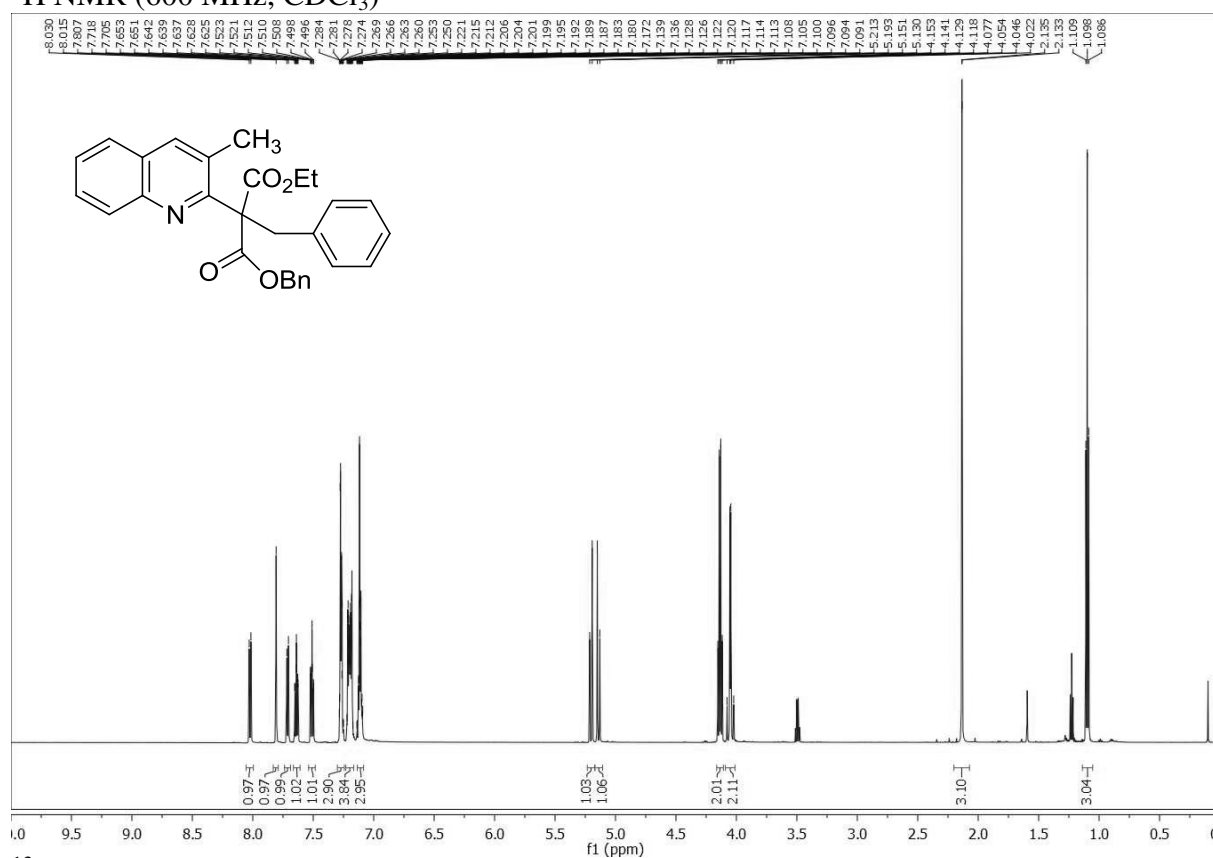
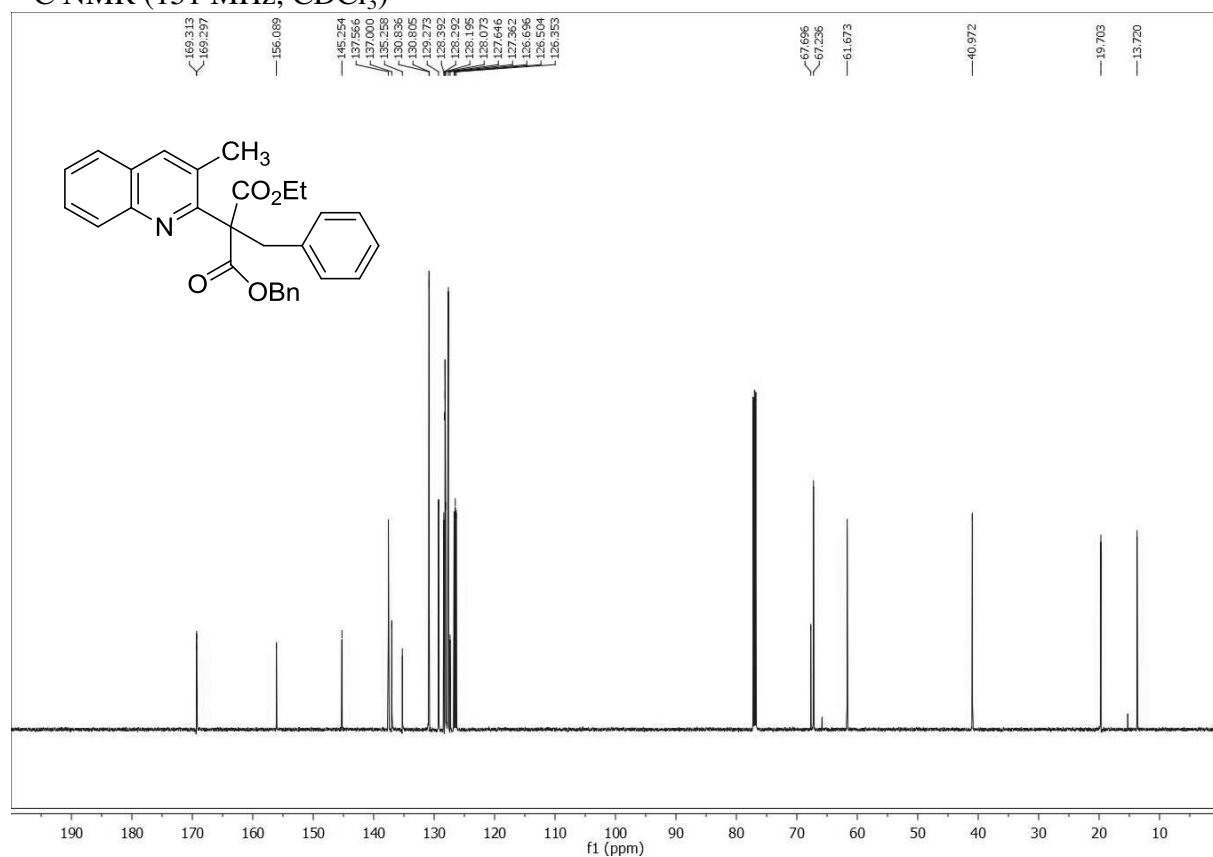
1-benzyl 3-ethyl 2-(3-methylquinolin-2-yl)-2-propylmalonate

11b

¹H NMR (600 MHz, CDCl₃) ^{13}C NMR (151 MHz, CDCl_3)

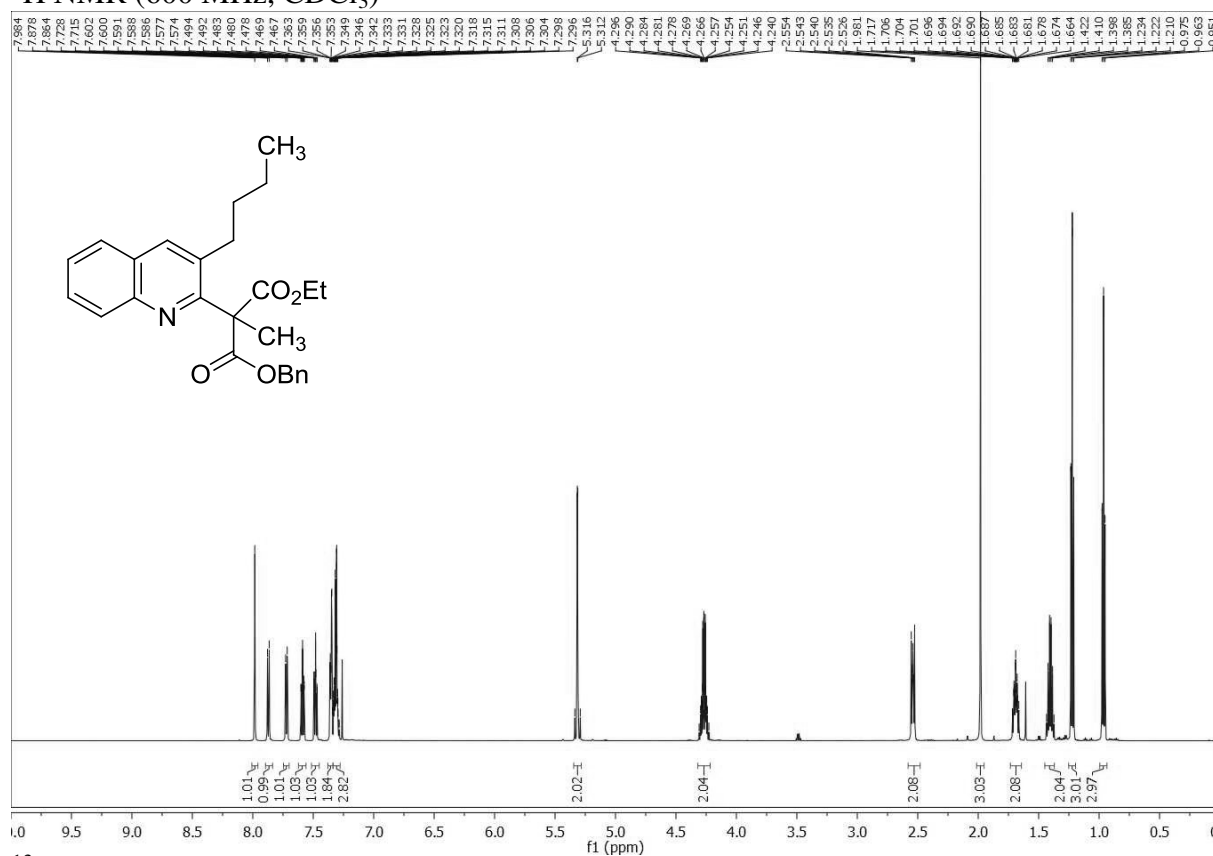
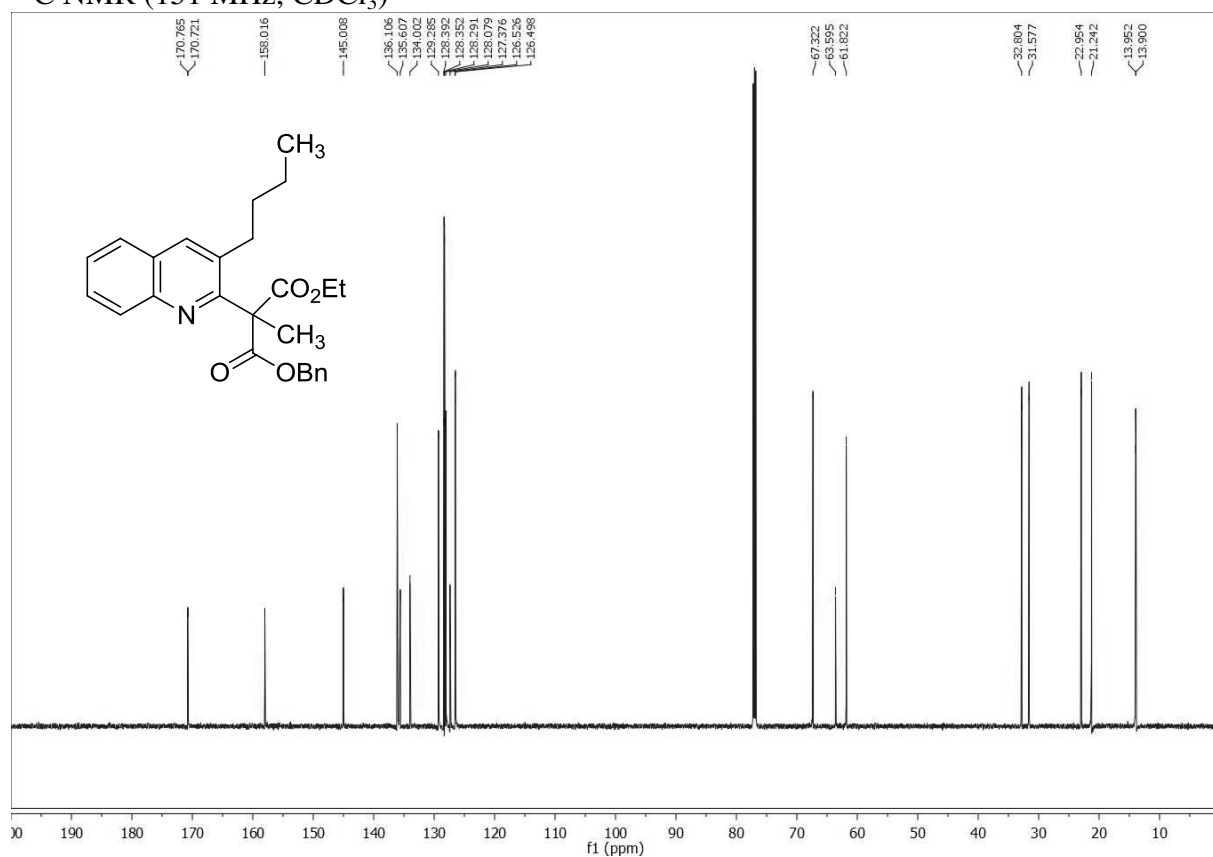
1-benzyl 3-ethyl 2-benzyl-2-(3-methylquinolin-2-yl)malonate

12b

 ^1H NMR (600 MHz, CDCl_3) ^{13}C NMR (151 MHz, CDCl_3)

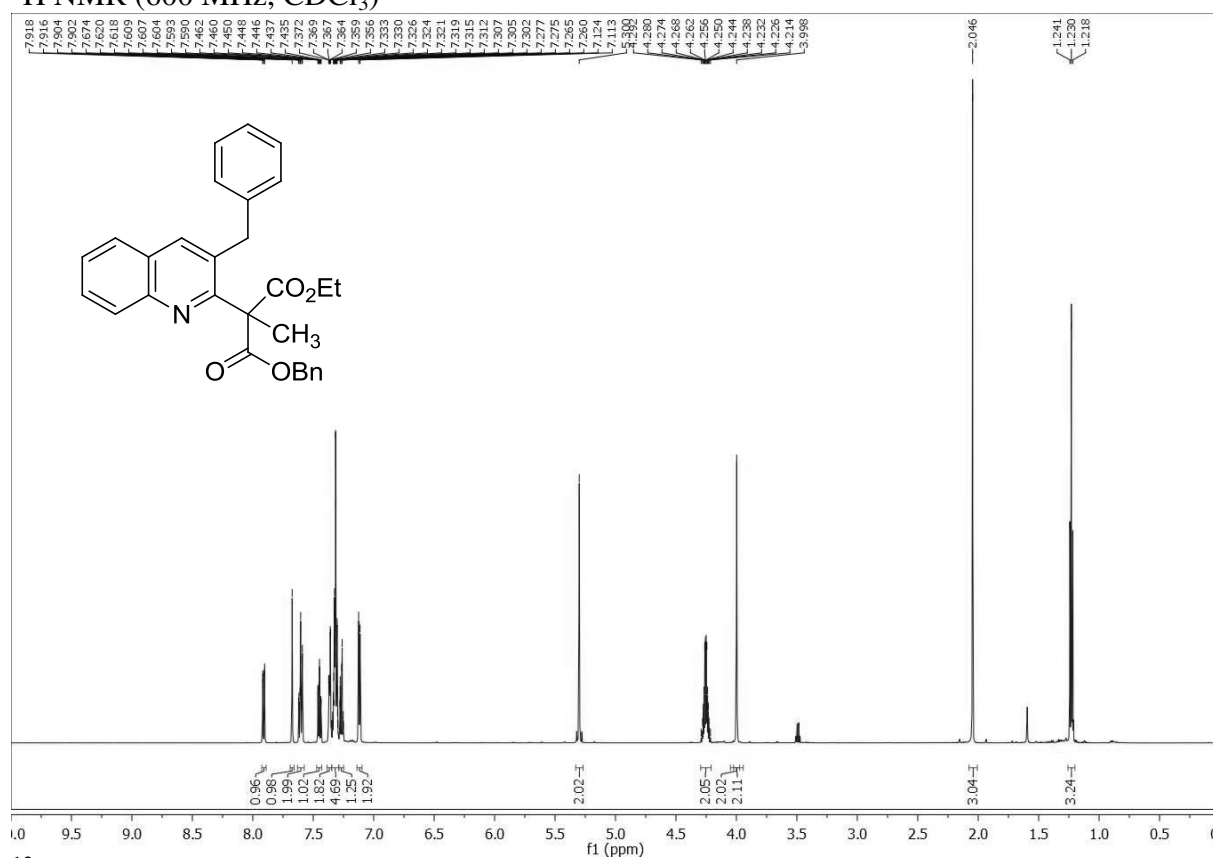
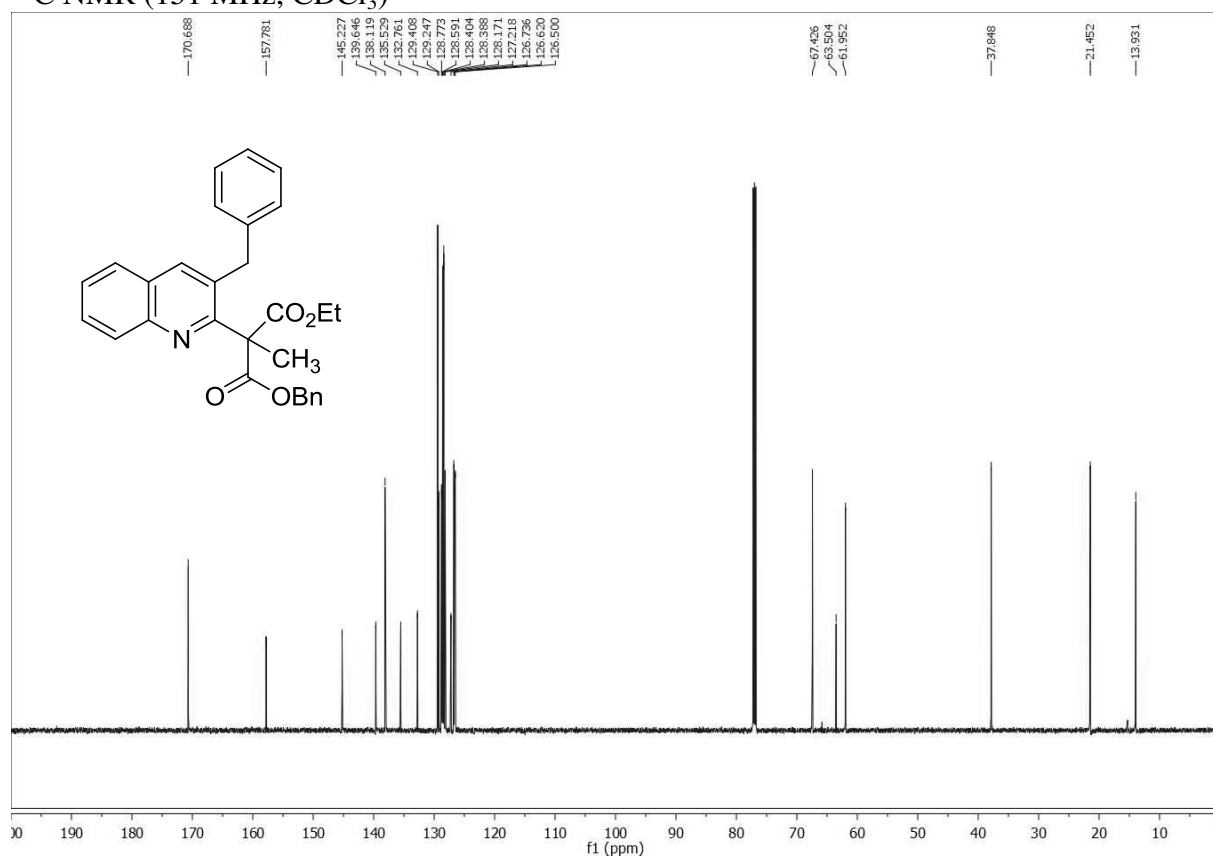
1-benzyl 3-ethyl 2-(3-butylquinolin-2-yl)-2-methylmalonate

13b

¹H NMR (600 MHz, CDCl₃) ^{13}C NMR (151 MHz, CDCl_3)

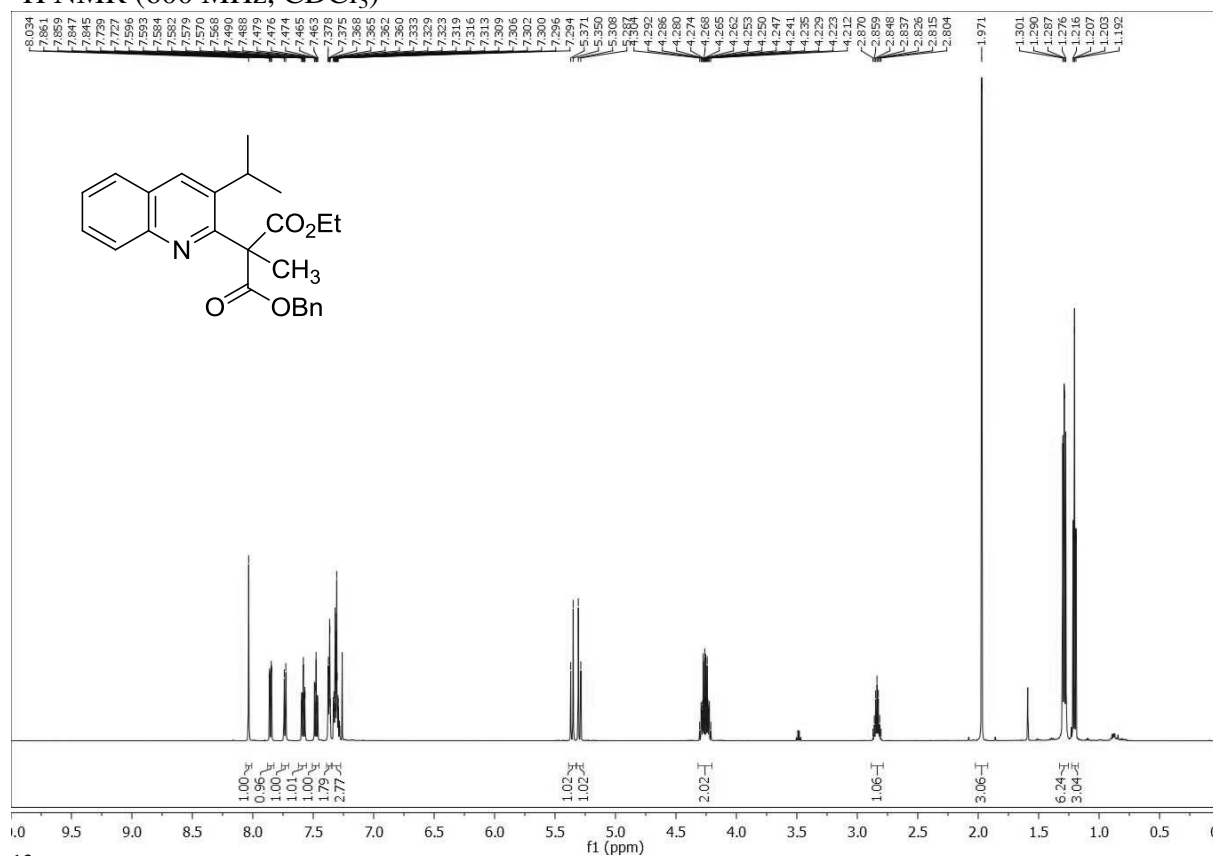
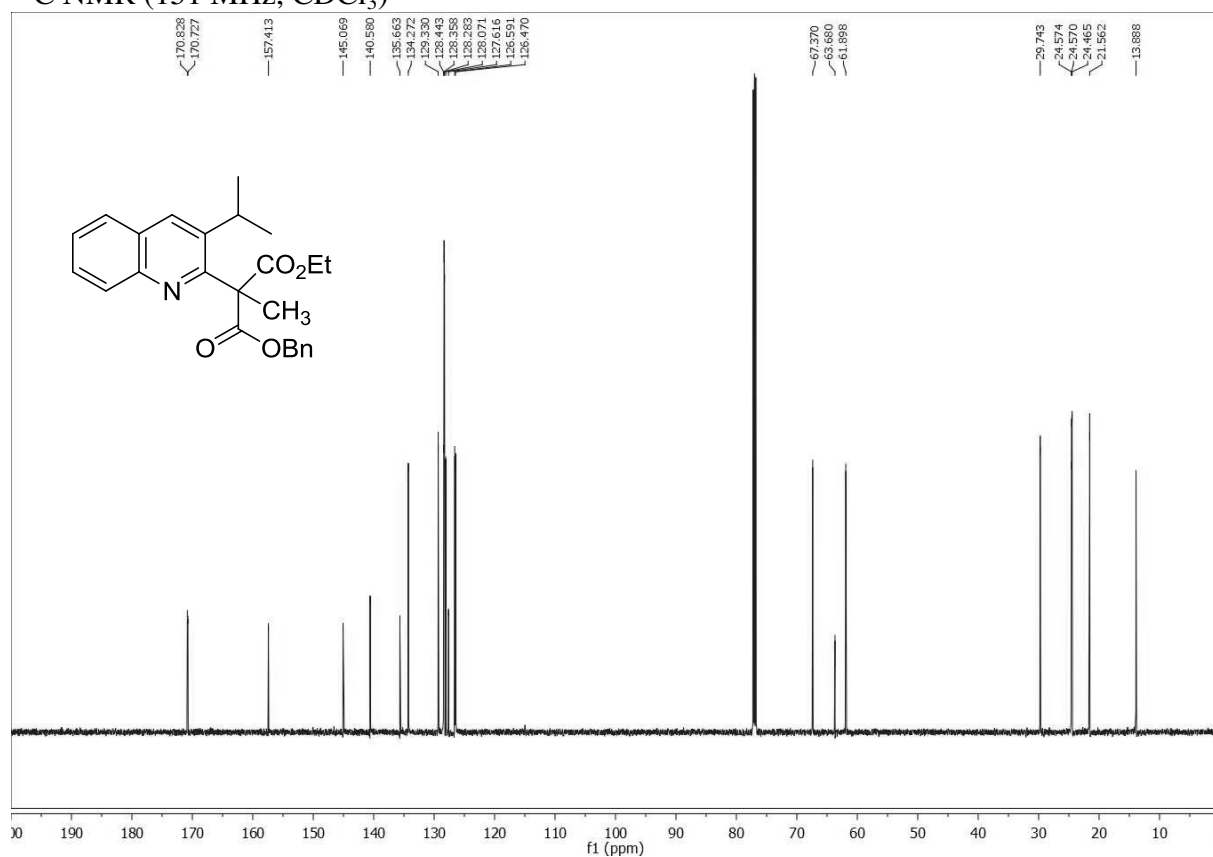
1-benzyl 3-ethyl 2-(3-benzylquinolin-2-yl)-2-methylmalonate

14b

 ^1H NMR (600 MHz, CDCl_3) ^{13}C NMR (151 MHz, CDCl_3)

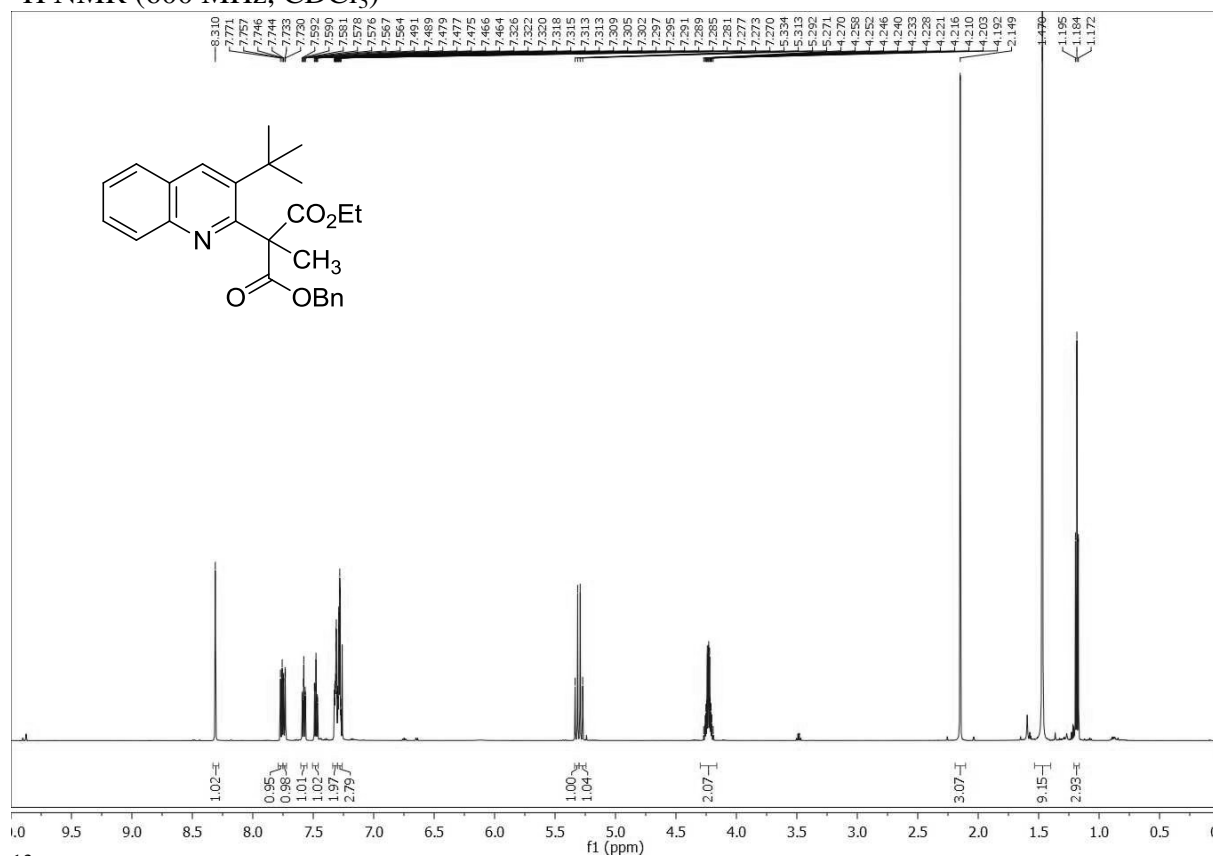
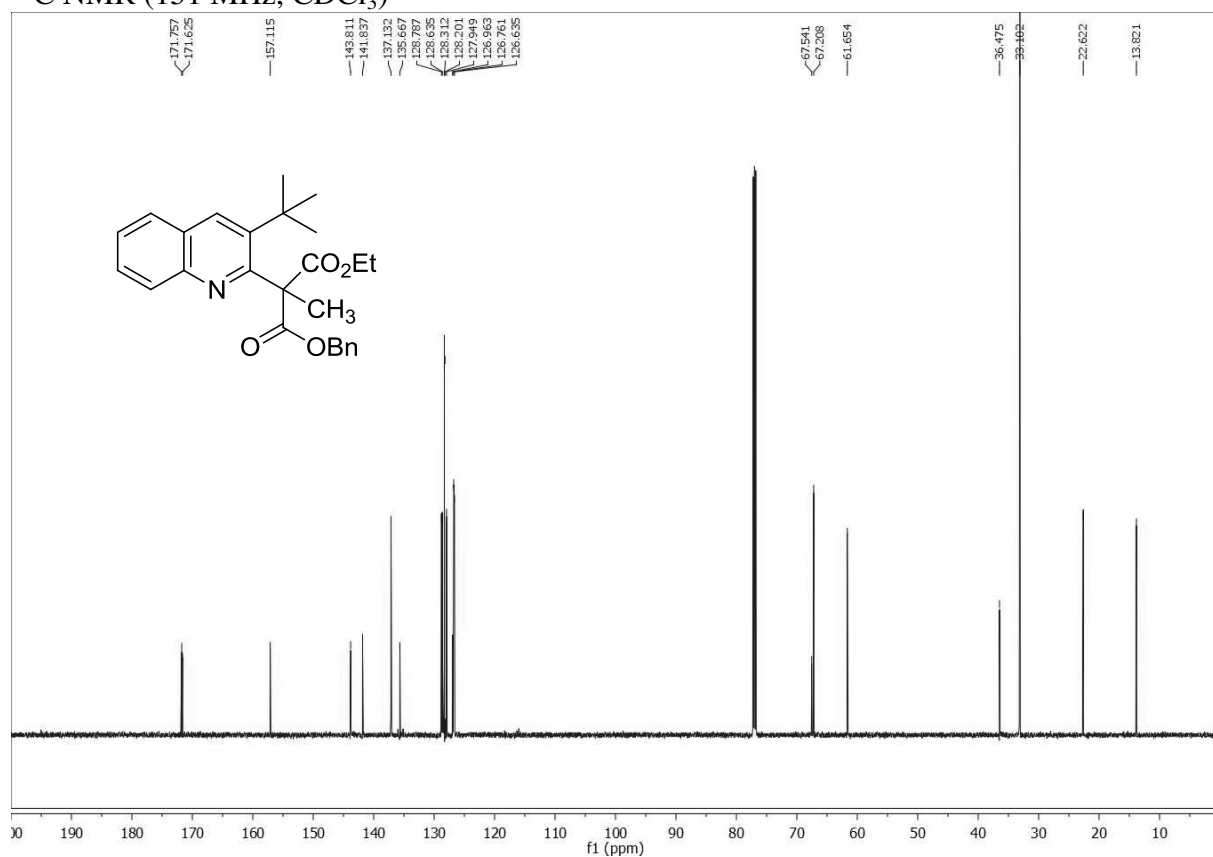
1-benzyl 3-ethyl 2-(3-isopropylquinolin-2-yl)-2-methylmalonate

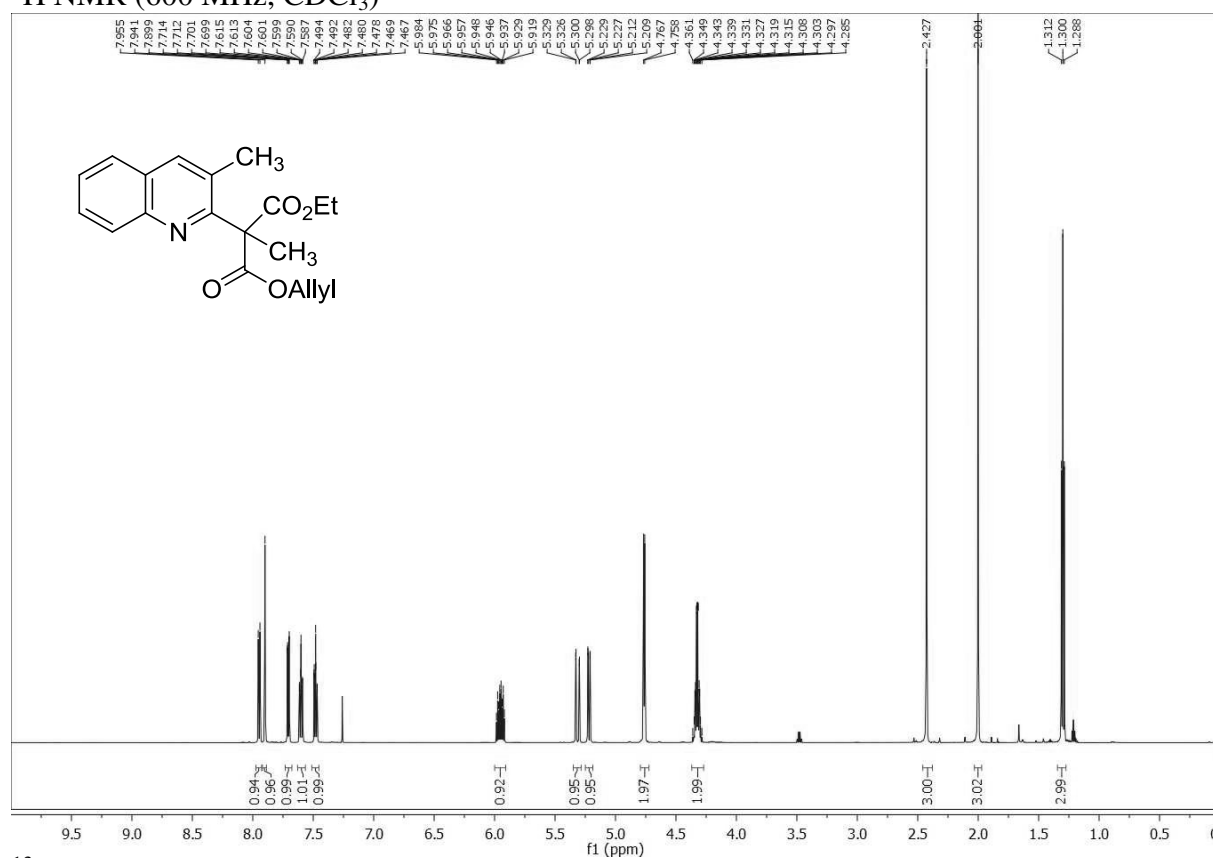
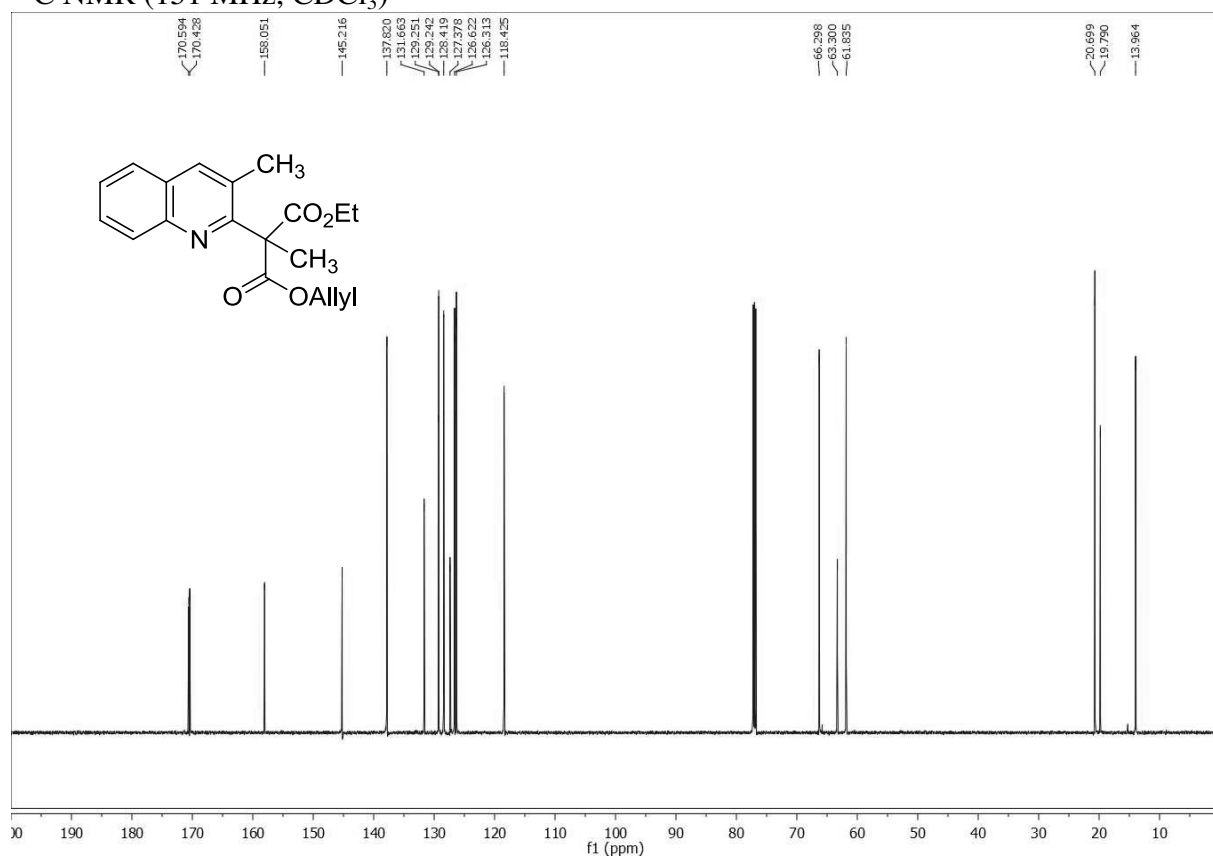
15b

 ^1H NMR (600 MHz, CDCl_3) ^{13}C NMR (151 MHz, CDCl_3)

1-benzyl 3-ethyl 2-(3-(tert-butyl)quinolin-2-yl)-2-methylmalonate

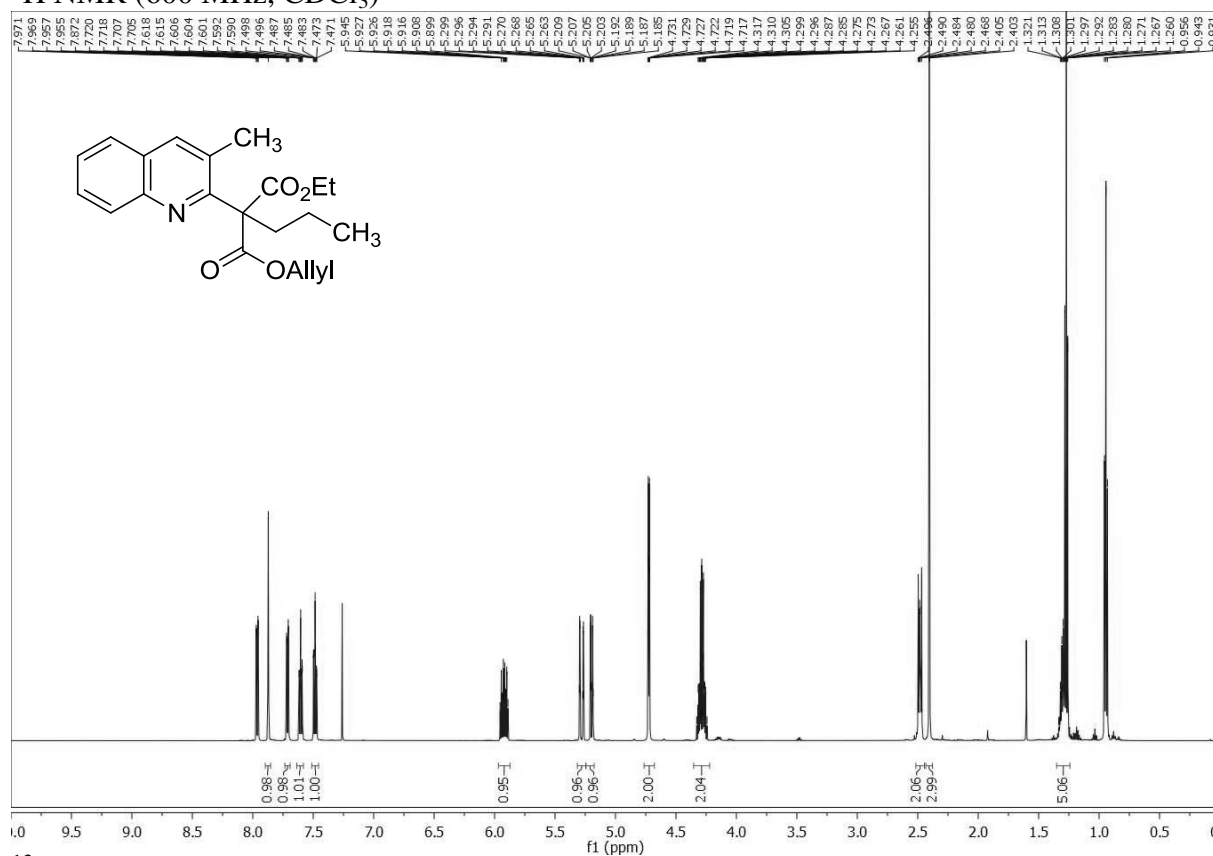
16b

 ^1H NMR (600 MHz, CDCl_3) ^{13}C NMR (151 MHz, CDCl_3)

1-allyl 3-ethyl 2-methyl-2-(3-methylquinolin-2-yl)malonate**4c** ^1H NMR (600 MHz, CDCl_3) ^{13}C NMR (151 MHz, CDCl_3)

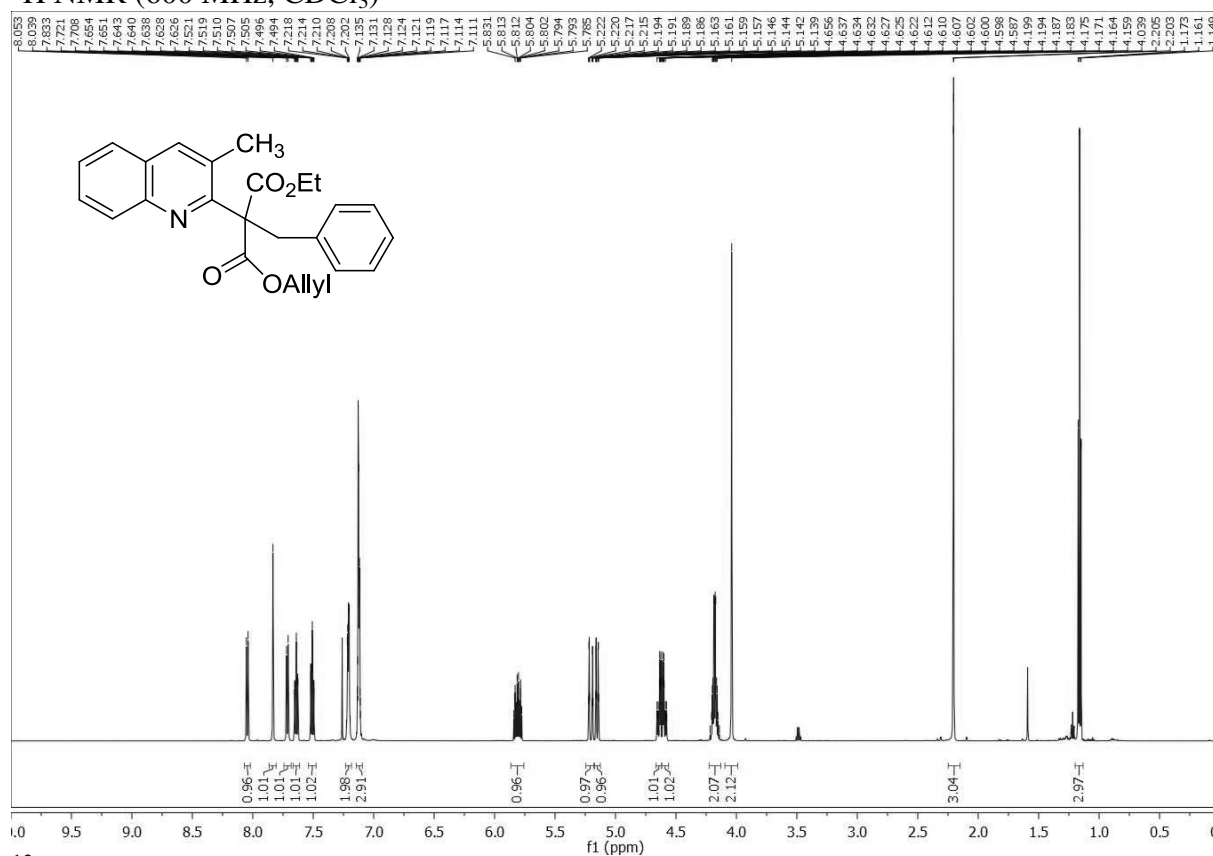
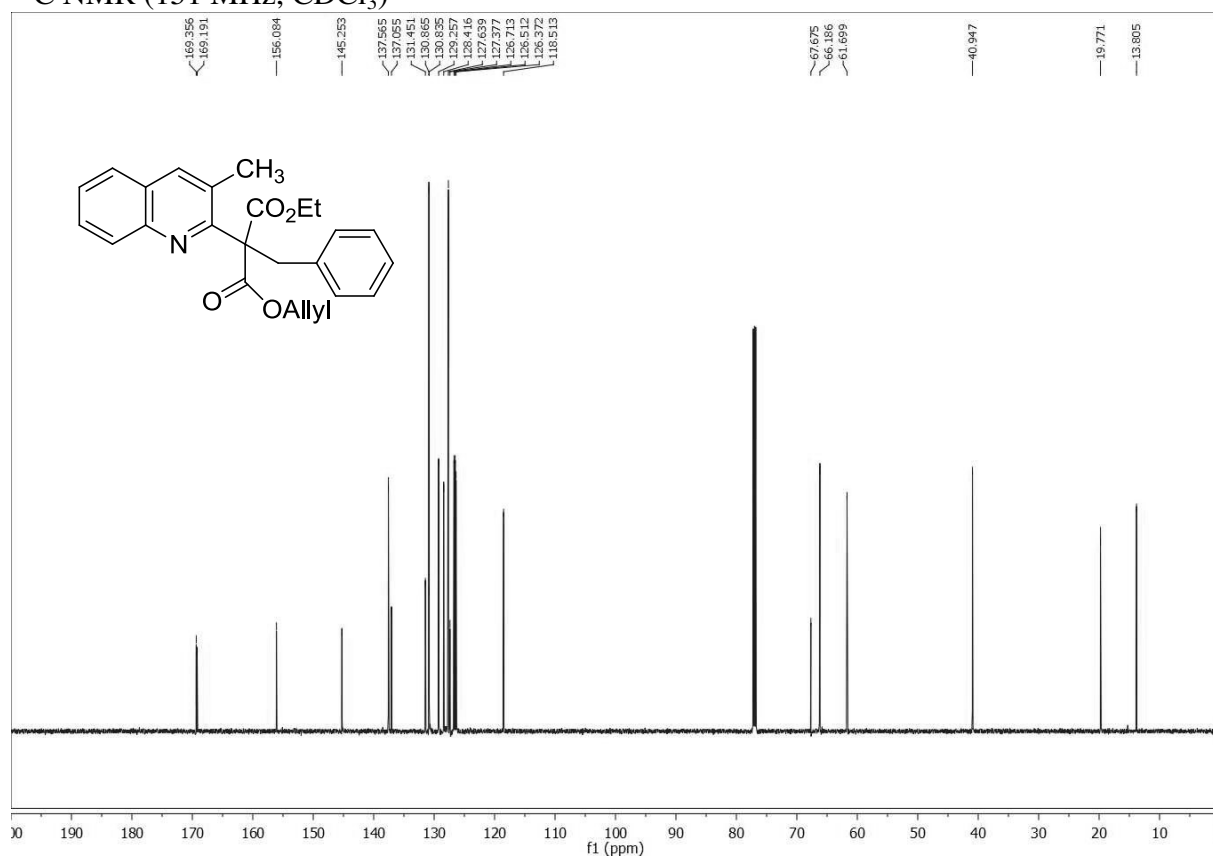
1-allyl 3-ethyl 2-(3-methylquinolin-2-yl)-2-propylmalonate

11c

 ^1H NMR (600 MHz, CDCl_3)

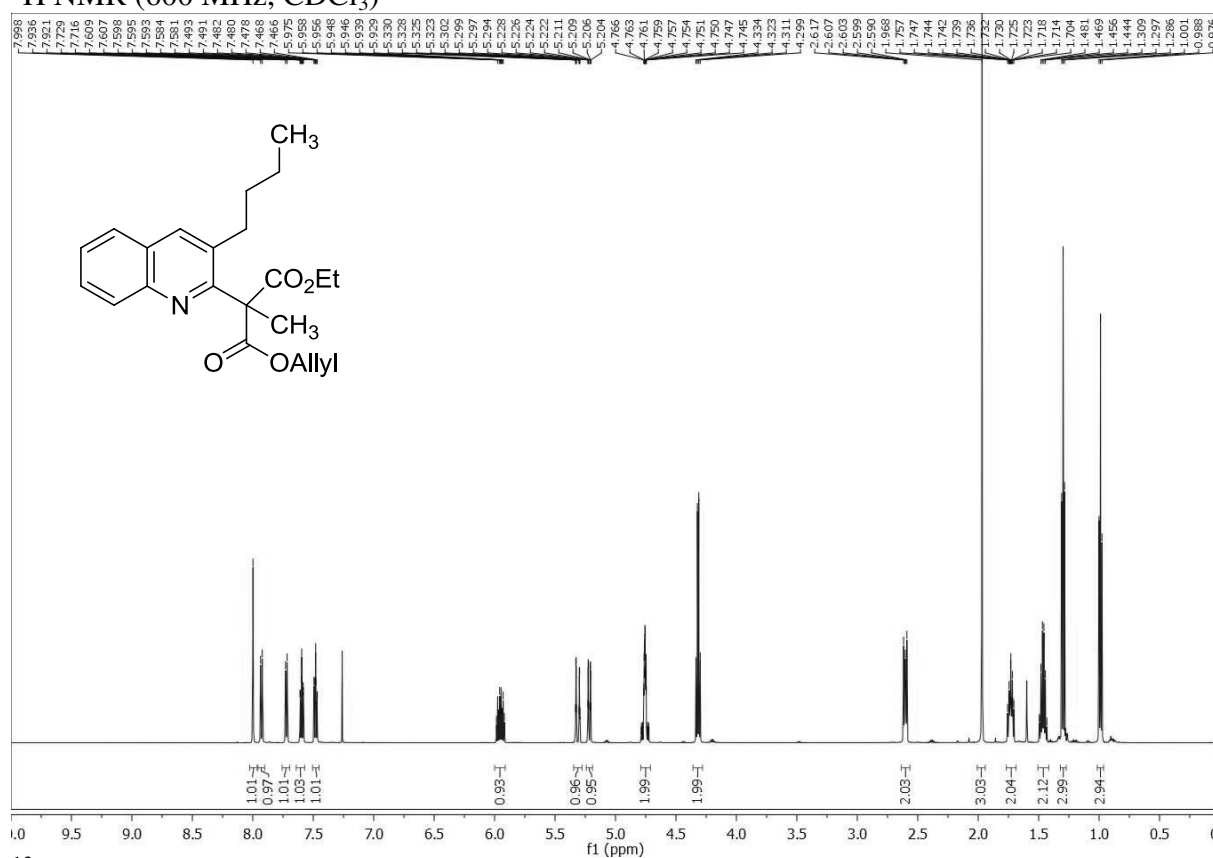
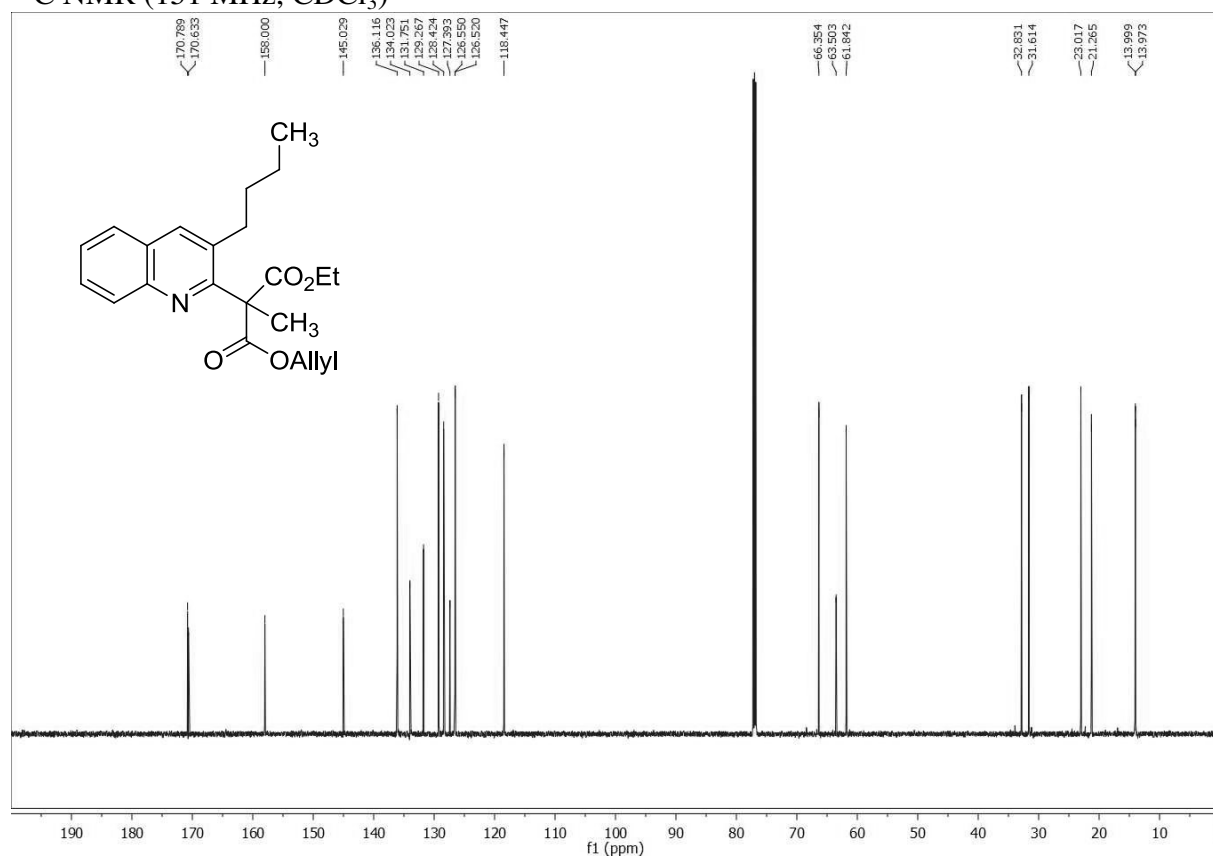
1-allyl 3-ethyl 2-benzyl-2-(3-methylquinolin-2-yl)malonate

12c

¹H NMR (600 MHz, CDCl₃) ^{13}C NMR (151 MHz, CDCl_3)

1-allyl 3-ethyl 2-(3-butylquinolin-2-yl)-2-methylmalonate

13c

 ^1H NMR (600 MHz, CDCl_3) ^{13}C NMR (151 MHz, CDCl_3)

14c

Chemical structure: CCOC(=O)C(C)(C(=O)OCC)c1cc(Cc2ccccc2)c3ccccc13

¹H NMR spectrum (CDCl₃) showing peaks from 1.0 to 7.8 ppm. The x-axis is labeled 'f1 (ppm)'.

Peak list (ppm): 7.899, 7.897, 7.895, 7.893, 7.698, 7.631, 7.628, 7.619, 7.617, 7.614, 7.611, 7.609, 7.605, 7.603, 7.598, 7.596, 7.594, 7.592, 7.590, 7.588, 7.586, 7.584, 7.582, 7.580, 7.578, 7.576, 7.574, 7.572, 7.570, 7.568, 7.566, 7.564, 7.562, 7.560, 7.558, 7.556, 7.554, 7.552, 7.550, 7.548, 7.546, 7.544, 7.542, 7.540, 7.538, 7.536, 7.534, 7.532, 7.530, 7.528, 7.526, 7.524, 7.522, 7.520, 7.518, 7.516, 7.514, 7.512, 7.510, 7.508, 7.506, 7.504, 7.502, 7.500, 7.498, 7.496, 7.494, 7.492, 7.490, 7.488, 7.486, 7.484, 7.482, 7.480, 7.478, 7.476, 7.474, 7.472, 7.470, 7.468, 7.466, 7.464, 7.462, 7.460, 7.458, 7.456, 7.454, 7.452, 7.450, 7.448, 7.446, 7.444, 7.442, 7.440, 7.438, 7.436, 7.434, 7.432, 7.430, 7.428, 7.426, 7.424, 7.422, 7.420, 7.418, 7.416, 7.414, 7.412, 7.410, 7.408, 7.406, 7.404, 7.402, 7.400, 7.398, 7.396, 7.394, 7.392, 7.390, 7.388, 7.386, 7.384, 7.382, 7.380, 7.378, 7.376, 7.374, 7.372, 7.370, 7.368, 7.366, 7.364, 7.362, 7.360, 7.358, 7.356, 7.354, 7.352, 7.350, 7.348, 7.346, 7.344, 7.342, 7.340, 7.338, 7.336, 7.334, 7.332, 7.330, 7.328, 7.326, 7.324, 7.322, 7.320, 7.318, 7.316, 7.314, 7.312, 7.310, 7.308, 7.306, 7.304, 7.302, 7.300, 7.298, 7.296, 7.294, 7.292, 7.290, 7.288, 7.286, 7.284, 7.282, 7.280, 7.278, 7.276, 7.274, 7.272, 7.270, 7.268, 7.266, 7.264, 7.262, 7.260, 7.258, 7.256, 7.254, 7.252, 7.250, 7.248, 7.246, 7.244, 7.242, 7.240, 7.238, 7.236, 7.234, 7.232, 7.230, 7.228, 7.226, 7.224, 7.222, 7.220, 7.218, 7.216, 7.214, 7.212, 7.210, 7.208, 7.206, 7.204, 7.202, 7.200, 7.198, 7.196, 7.194, 7.192, 7.190, 7.188, 7.186, 7.184, 7.182, 7.180, 7.178, 7.176, 7.174, 7.172, 7.170, 7.168, 7.166, 7.164, 7.162, 7.160, 7.158, 7.156, 7.154, 7.152, 7.150, 7.148, 7.146, 7.144, 7.142, 7.140, 7.138, 7.136, 7.134, 7.132, 7.130, 7.128, 7.126, 7.124, 7.122, 7.120, 7.118, 7.116, 7.114, 7.112, 7.110, 7.108, 7.106, 7.104, 7.102, 7.100, 7.098, 7.096, 7.094, 7.092, 7.090, 7.088, 7.086, 7.084, 7.082, 7.080, 7.078, 7.076, 7.074, 7.072, 7.070, 7.068, 7.066, 7.064, 7.062, 7.060, 7.058, 7.056, 7.054, 7.052, 7.050, 7.048, 7.046, 7.044, 7.042, 7.040, 7.038, 7.036, 7.034, 7.032, 7.030, 7.028, 7.026, 7.024, 7.022, 7.020, 7.018, 7.016, 7.014, 7.012, 7.010, 7.008, 7.006, 7.004, 7.002, 7.000, 6.998, 6.996, 6.994, 6.992, 6.990, 6.988, 6.986, 6.984, 6.982, 6.980, 6.978, 6.976, 6.974, 6.972, 6.970, 6.968, 6.966, 6.964, 6.962, 6.960, 6.958, 6.956, 6.954, 6.952, 6.950, 6.948, 6.946, 6.944, 6.942, 6.940, 6.938, 6.936, 6.934, 6.932, 6.930, 6.928, 6.926, 6.924, 6.922, 6.920, 6.918, 6.916, 6.914, 6.912, 6.910, 6.908, 6.906, 6.904, 6.902, 6.900, 6.898, 6.896, 6.894, 6.892, 6.890, 6.888, 6.886, 6.884, 6.882, 6.880, 6.878, 6.876, 6.874, 6.872, 6.870, 6.868, 6.866, 6.864, 6.862, 6.860, 6.858, 6.856, 6.854, 6.852, 6.850, 6.848, 6.846, 6.844, 6.842, 6.840, 6.838, 6.836, 6.834, 6.832, 6.830, 6.828, 6.826, 6.824, 6.822, 6.820, 6.818, 6.816, 6.814, 6.812, 6.810, 6.808, 6.806, 6.804, 6.802, 6.800, 6.798, 6.796, 6.794, 6.792, 6.790, 6.788, 6.786, 6.784, 6.782, 6.780, 6.778, 6.776, 6.774, 6.772, 6.770, 6.768, 6.766, 6.764, 6.762, 6.760, 6.758, 6.756, 6.754, 6.752, 6.750, 6.748, 6.746, 6.744, 6.742, 6.740, 6.738, 6.736, 6.734, 6.732, 6.730, 6.728, 6.726, 6.724, 6.722, 6.720, 6.718, 6.716, 6.714, 6.712, 6.710, 6.708, 6.706, 6.704, 6.702, 6.700, 6.698, 6.696, 6.694, 6.692, 6.690, 6.688, 6.686, 6.684, 6.682, 6.680, 6.678, 6.676, 6.674, 6.672, 6.670, 6.668, 6.666, 6.664, 6.662, 6.660, 6.658, 6.656, 6.654, 6.652, 6.650, 6.648, 6.646, 6.644, 6.642, 6.640, 6.638, 6.636, 6.634, 6.632, 6.630, 6.628, 6.626, 6.624, 6.622, 6.620, 6.618, 6.616, 6.614, 6.612, 6.610, 6.608, 6.606, 6.604, 6.602, 6.600, 6.598, 6.596, 6.594, 6.592, 6.590, 6.588, 6.586, 6.584, 6.582, 6.580, 6.578, 6.576, 6.574, 6.572, 6.570, 6.568, 6.566, 6.564, 6.562, 6.560, 6.558, 6.556, 6.554, 6.552, 6.550, 6.548, 6.546, 6.544, 6.542, 6.540, 6.538, 6.536, 6.534, 6.532, 6.530, 6.528, 6.526, 6.524, 6.522, 6.520, 6.518, 6.516, 6.514, 6.512,

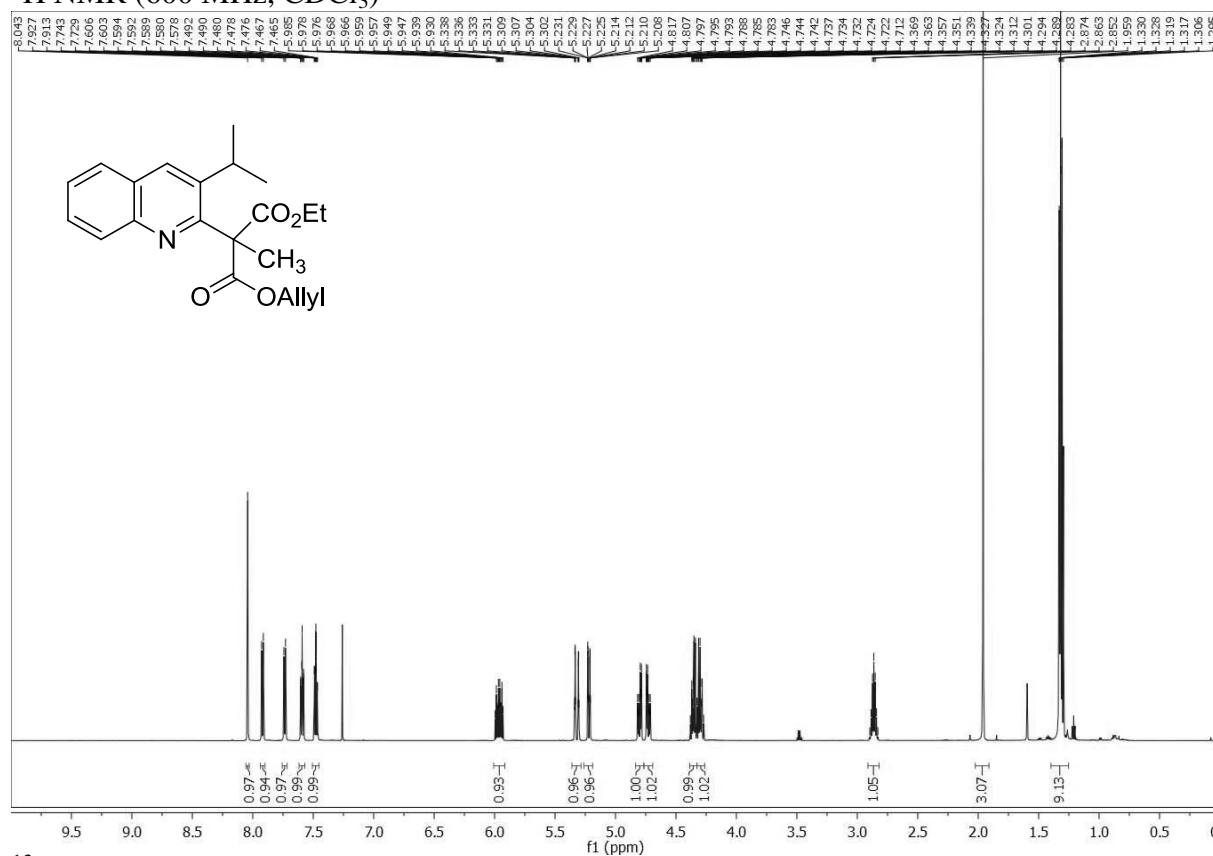
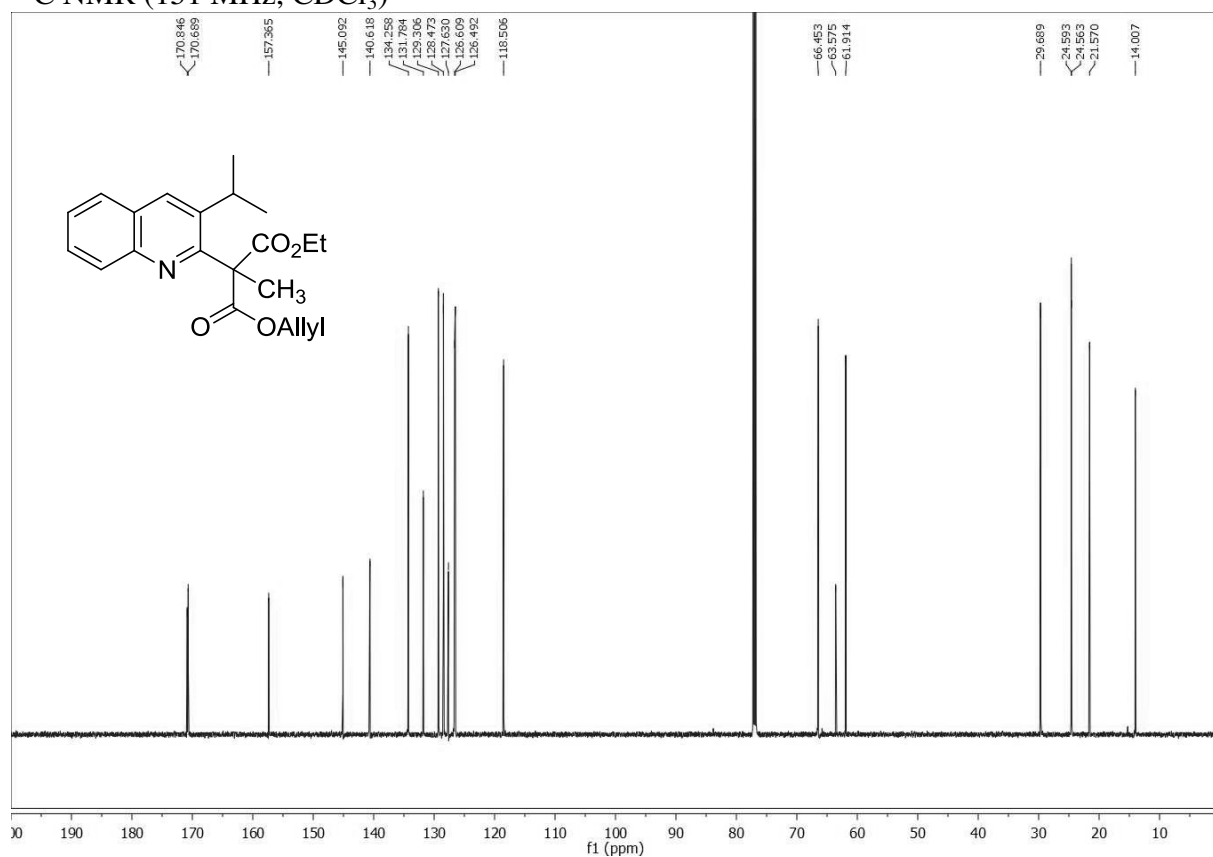
¹³C NMR (101 MHz, CDCl₃)

Chemical structure of compound 10: CCOC(=O)C1=C(C(=O)OCC)C2=CC=CC=C2N=C1Cc3ccccc3

Peak list (ppm): 170.715, 170.569, 157.750, 145.240, 139.672, 138.121, 132.784, 132.783, 132.438, 129.219, 128.797, 128.623, 127.219, 126.749, 126.633, 126.544, 118.552, 66.429, 63.410, 61.956, 37.893, 21.441, 14.022.

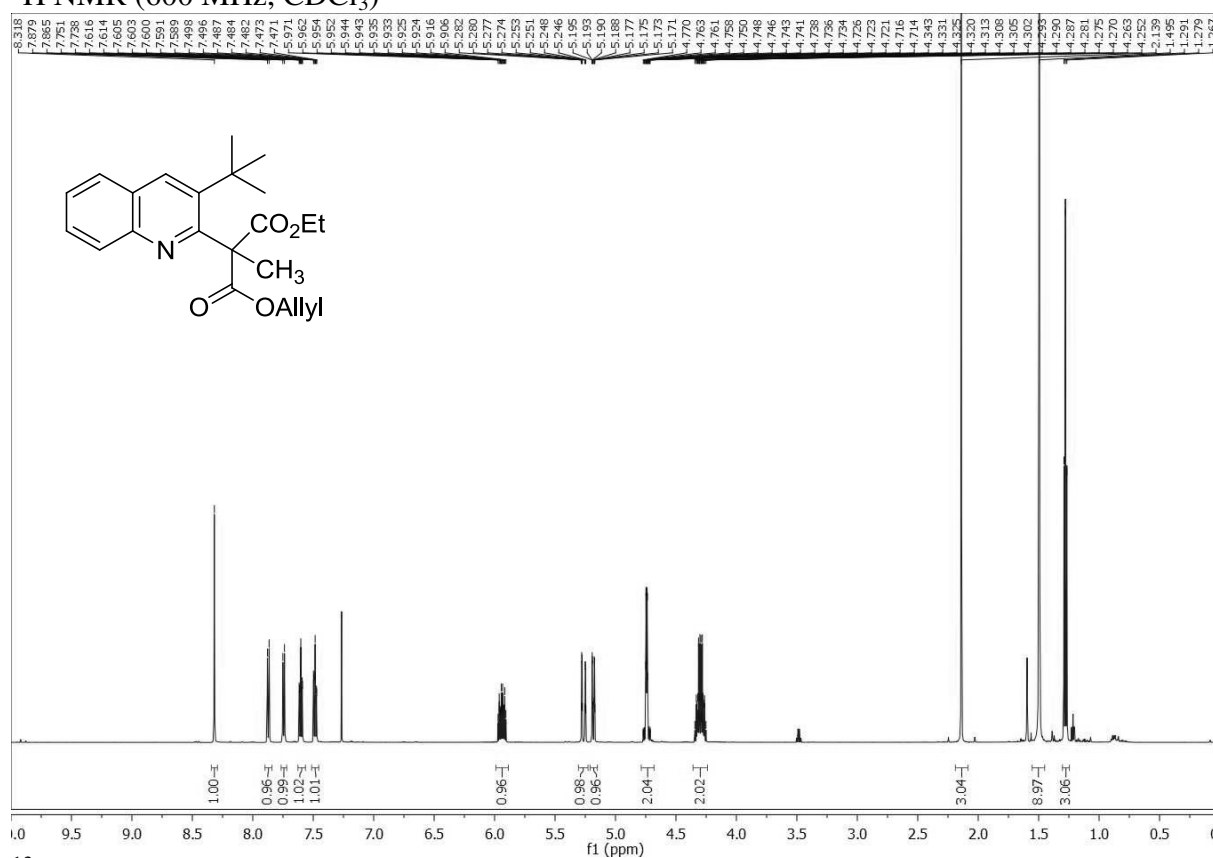
1-allyl 3-ethyl 2-(3-isopropylquinolin-2-yl)-2-methylmalonate

15c

 ^1H NMR (600 MHz, CDCl_3) ^{13}C NMR (151 MHz, CDCl_3)

1-allyl 3-ethyl 2-(3-(tert-butyl)quinolin-2-yl)-2-methylmalonate

16c

 ^1H NMR (600 MHz, CDCl_3) ^{13}C NMR (151 MHz, CDCl_3)