

Supporting Information

Stereospecific assembly of tetrahydroquinolines via tandem ring-opening/oxidative cyclization of donor-acceptor cyclopropanes with *N*-alkyl anilines

Bijay Ketan Das, Sourav Pradhan and Tharmalingam Punniyamurthy*

Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781039, India

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General Information. Cu(OTf)₂ (98%), Cu(OAc)₂ (98%), CuCl₂ (97%) and CuBr₂ (99.9%) were purchased from Aldrich and used as received. Cyclopropanes^{1,2} and *N*-alkyl anilines³ were prepared according to the reported procedure. Column chromatography was performed with Rankem silica gel (60-120 mesh). Bruker Avance III 400 and Bruker Avance III 600 spectrometers were used for recording NMR spectra using CDCl₃ as a solvent and Me₄Si as an internal standard. Chemical shifts (δ) and spin-spin coupling constants (J) are reported in ppm and Hz, respectively, and other data are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, dd = doublet of doublet and br s = broad singlet. Melting points were determined with a Büchi B-540 apparatus and are uncorrected. Optical rotation was determined using Perkin Elmer-343 Polarimeter. HPLC analysis was carried out with Waters-2489 instrument using Daicel Chiralcel AD-H column using *iso*-propanol and hexane as eluent. FT-IR spectra were collected on Thermo Fisher Scientific IR spectrometer. Q-ToF ESI-MS instrument (model HAB 273) was used for recording mass spectra. Single crystal X-ray data were collected using Bruker SMART APEX-II CCD diffractometer, which is equipped with 1.75 kW sealed-tube Mo-K α irradiation ($\lambda = 0.71073$ Å) at 298(2) K. The crystal structure was solved by direct method using SHELXL-97 (Göttingen, Germany) and refined with full-matrix least squares on F² using SHELXL-97.

General Procedure for the Synthesis of Tetrahydroquinolines

N-Alkyl aniline **1** (0.2 mmol), cyclopropane **2** (0.24 mmol) and Cu(OTf)₂ (0.02 mmol, 7.2 mg) were stirred at room temperature for 6 h. Then, K₂CO₃ (0.2 mmol, 22 mg) and DMF (2 mL) were added and the resulting mixture was stirred at 100 °C for 12 h under air. The progress of the reaction was monitored using TLC with ethyl acetate and hexane as an eluent. After completion, the reaction mixture was cooled to room temperature and diluted with ethyl acetate (10 mL). The resultant mixture was washed with ice cold brine (5 mL) and cold water (5 mL). The aqueous solution was extracted with ethyl acetate (2 x 5 mL). Drying (Na₂SO₄) and evaporation of the solvent gave a residue that was purified on a silica gel column chromatography using hexane and ethyl acetate as an eluent to give analytically pure tetrahydroquinoline scaffolds.

Procedure for the Enantiospecific Synthesis of Tetrahydroquinolines

N-Alkyl aniline **1** (0.2 mmol), chiral cyclopropane (*R*)-**2a'** (0.24 mmol) and Cu(OTf)₂ (0.02 mmol, 7.2 mg) were subjected to the above described general procedure for the tetrahydroquinoline synthesis. The enantiomeric excess was determined using chiral HPLC.

Crystal Data and Structure Refinement

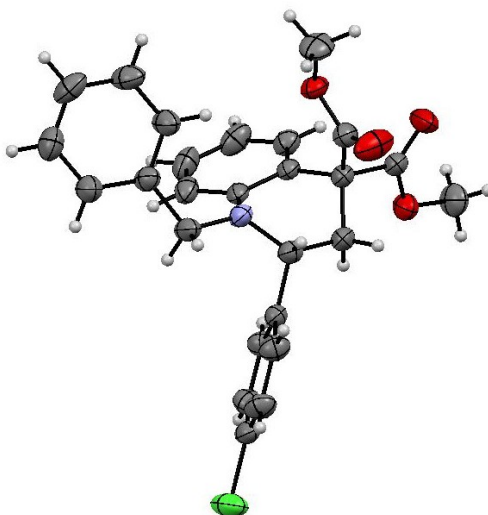


Figure S1. ORTEP diagram of dimethyl 1-benzyl-2-(4-chlorophenyl)-2,3-dihydroquinoline-4,4(1*H*)-dicarboxylate **4d** with 50% ellipsoid (CCDC 1902908).

Identification code	4d
Empirical formula	C ₂₆ H ₂₄ ClNO ₄
Formula weight	449.91
Crystal habit, colour	block /Colorless
Crystal size, mm ³	0.4 x 0.3 x 0.2
Temperature, <i>T</i> /K	296 K
Wavelength, λ/Å	0.71073
Crystal system	'Triclinic'
Space group	'P -1'
Unit cell dimensions	a = 9.8937(9)Å b = 11.1906(10)Å c = 11.7431(8)Å α = 68.403(7) β = 71.507(7) γ = 82.528(7)
Volume, V/Å ³	1146.32(18)

Z	2
Calculated density, Mg·m ⁻³	1.303
Absorption coefficient, μ/mm^{-1}	0.199
<i>F</i> (000)	472
θ range for data collection	2.23 to 25°
Limiting indices	-11 ≤ <i>h</i> ≤ 11, -13 ≤ <i>k</i> ≤ 13, -13 ≤ <i>l</i> ≤ 13
Reflection collected / unique	4056/2736
Completeness to θ	99.90% ($\theta = 25^\circ$)
Absorption correction	Multi-scan
Max. and min. transmission	1.000 and 0.867
Refinement method	'SHELXL-2014/7 (Sheldrick, 2014)'
Data / restraints / parameters	4056/0/ 291
Goodness-of-fit on <i>F</i> ²	1.070
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0521, <i>wR</i> 2 = 0.1084
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0833, <i>wR</i> 2 = 0.1386

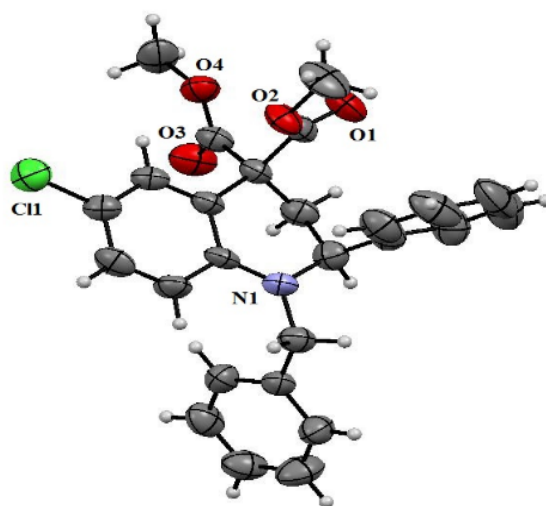
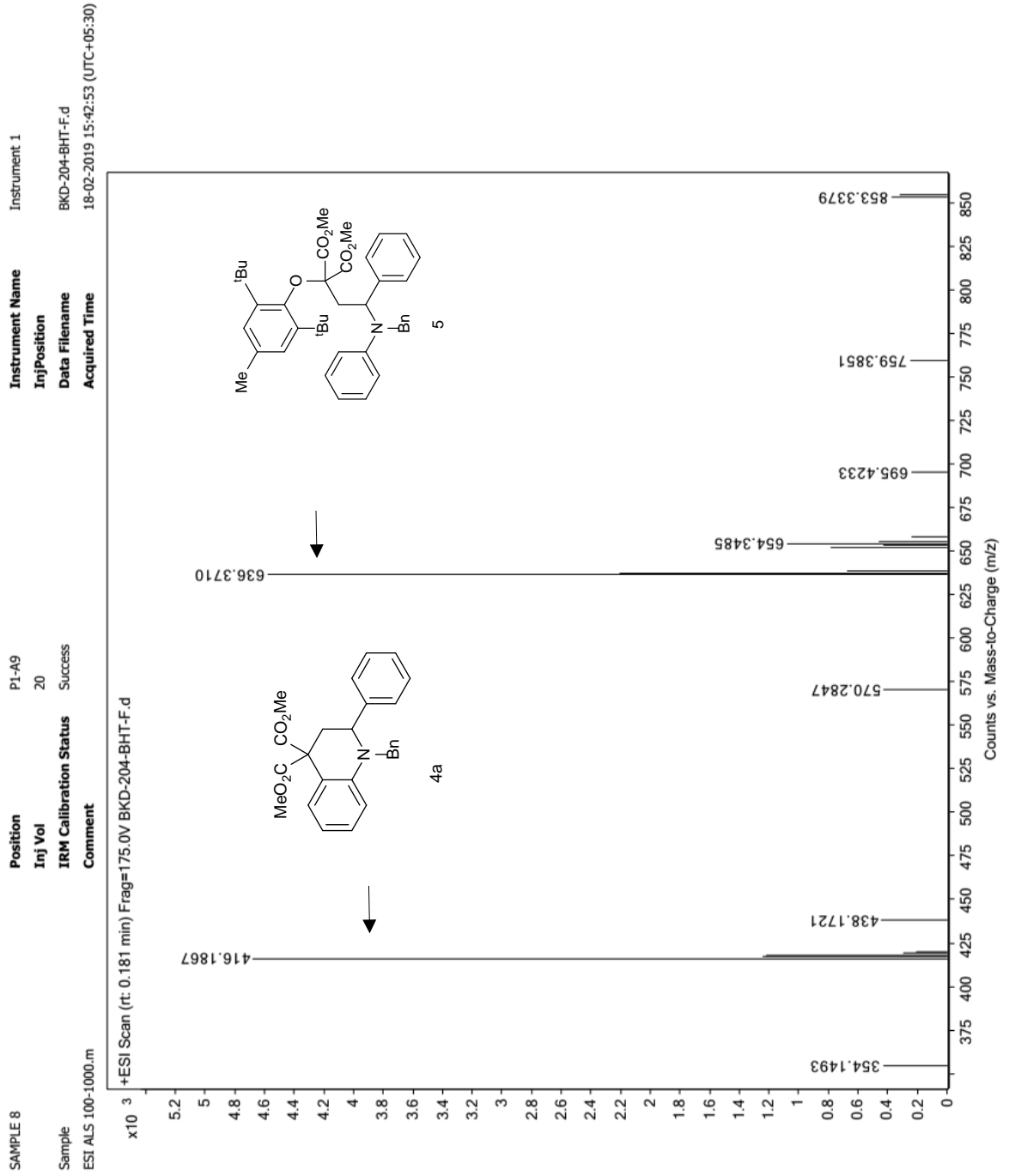


Figure S2. ORTEP diagram of dimethyl (*S*)-1-benzyl-6-chloro-2-phenyl-2,3-dihydroquinoline-4,4(*1H*)-dicarboxylate **4p'** with 50% ellipsoid (CCDC 1902927).

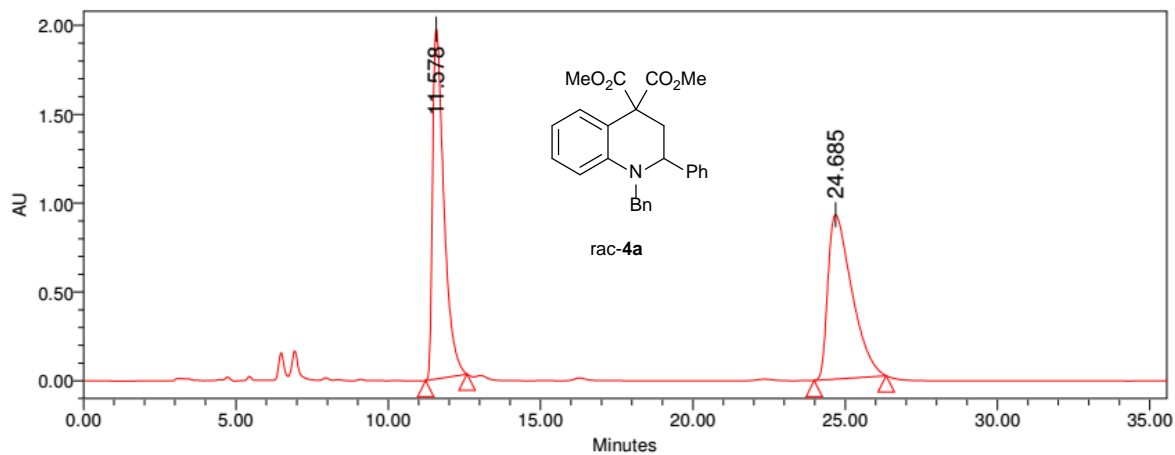
Identification code	4p'
Empirical formula	C ₂₆ H ₂₄ ClNO ₄
Formula weight	449.91
Crystal habit, colour	block /colorless
Crystal size, mm ³	0.4 x 0.3 x 0.2
Temperature, <i>T</i> /K	296 K
Wavelength, $\lambda/\text{\AA}$	0.71073

Crystal system	'monoclinic'
Space group	'P 21'
Unit cell dimensions	a = 10.5583(10)Å b = 9.7573(7)Å c = 11.7032(11)Å α = 90 β = 106.984(11) γ = 90
Volume, V/Å ³	1153.09(19)
Z	2
Calculated density, Mg·m ⁻³	1.296
Absorption coefficient, μ/mm ⁻¹	0.198
F(000)	472
θ range for data collection	2.28 to 28°
Limiting indices	-14 ≤ h ≤ 10, -12 ≤ k ≤ 7, -8 ≤ l ≤ 15
Reflection collected / unique	3728/2194
Completeness to θ	99.90% (θ = 28°)
Absorption correction	Multi-scan
Max. and min. transmission	1.000 and 0.768
Refinement method	'SHELXT 2018/2 (Sheldrick, 2018)'
Data / restraints / parameters	3728/1/ 291
Goodness-of-fit on F ²	1.031
Final R indices [I > 2σ(I)]	R1 = 0.0713, wR2 = 0.1584
R indices (all data)	R1 = 0.1065, wR2 = 0.1989

ESI-MS of the reaction of mixture of 1a and 2a in the presence of BHT after 4 h

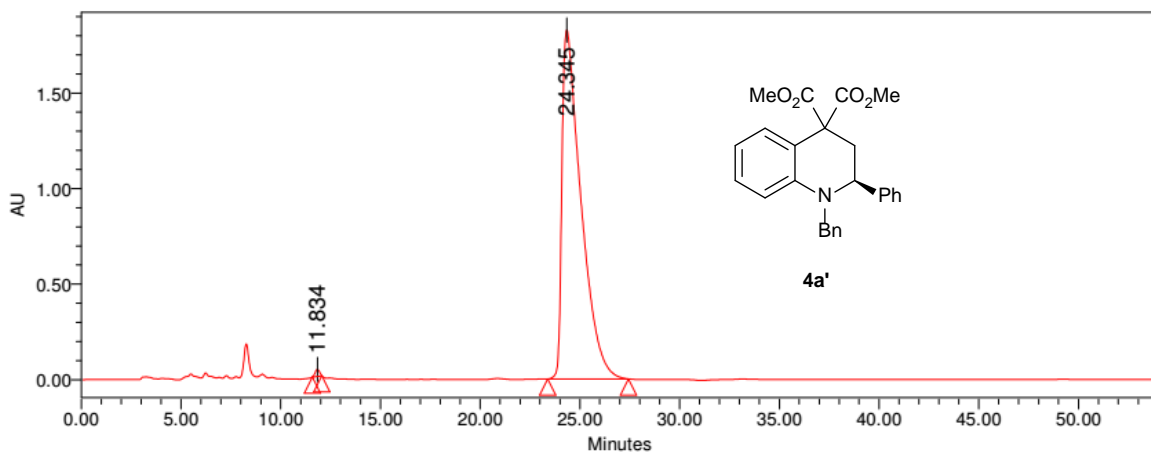


HPLC chromatograms



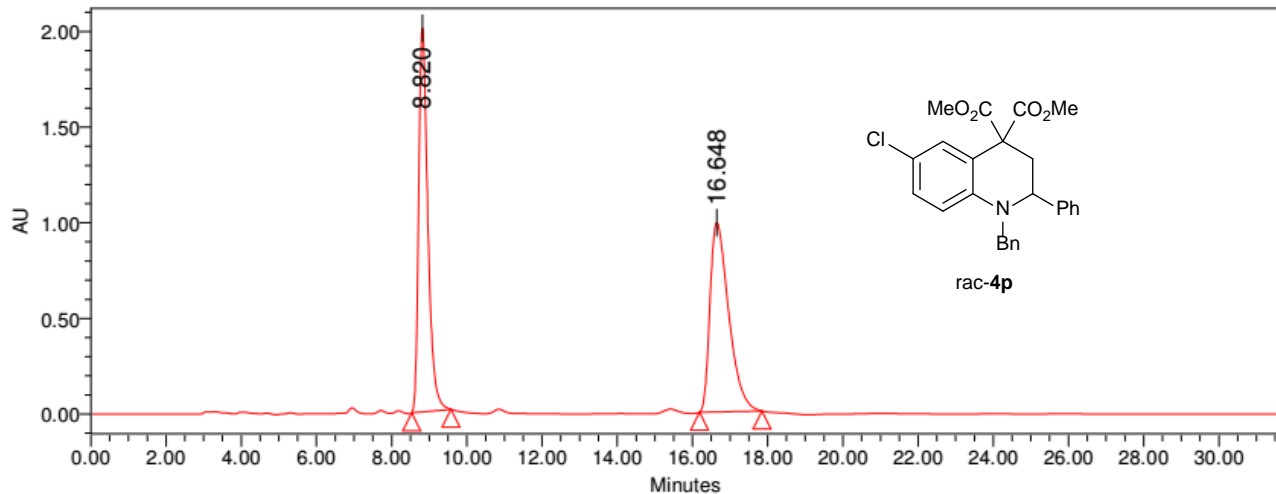
Peak Results

	RT	Height (μV)	% Area
1	11.578	1970222	49.96
2	24.685	924902	50.04



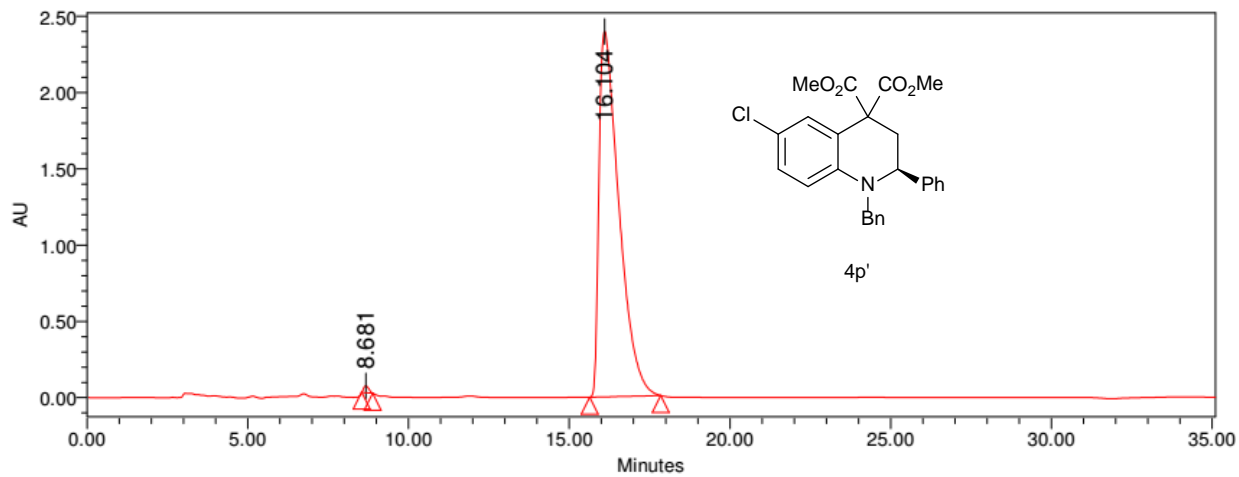
Peak Results

	RT	Height (μV)	% Area
1	11.834	36313	0.46
2	24.345	1827164	99.54



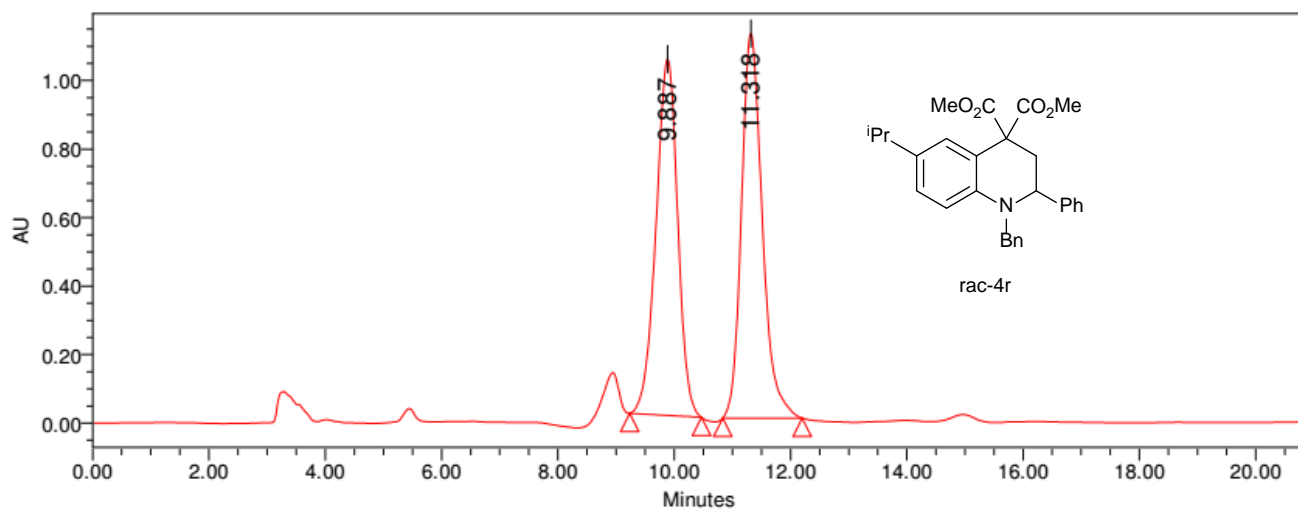
Peak Results

	RT	Height (μV)	% Area
1	8.820	2008296	49.82
2	16.648	989772	50.18



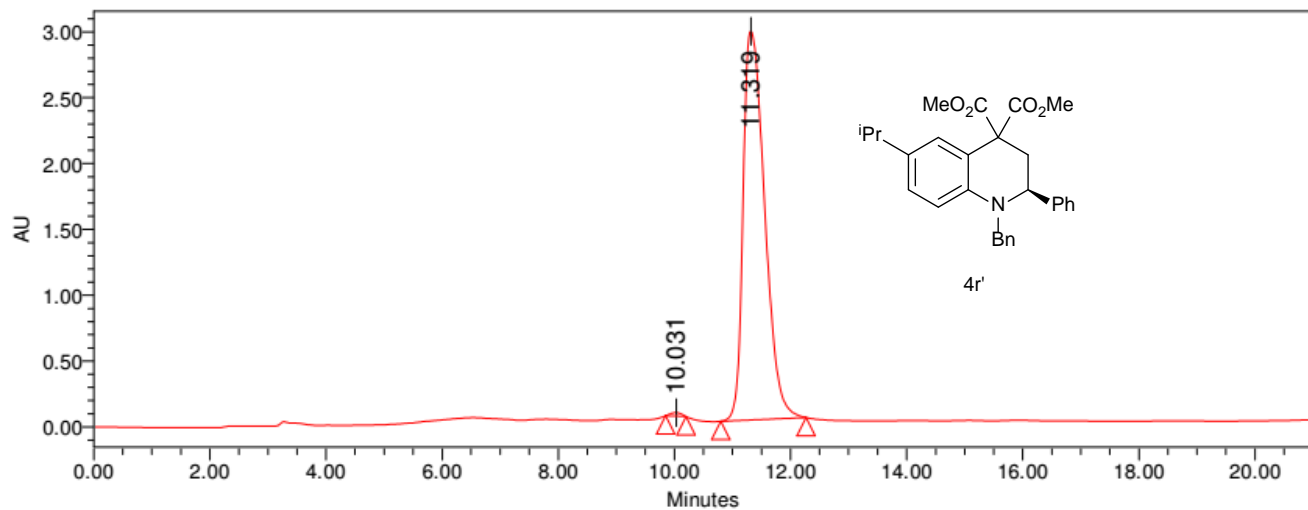
Peak Results

	RT	Height (μV)	% Area
1	8.681	44552	0.47
2	16.104	2396437	99.53



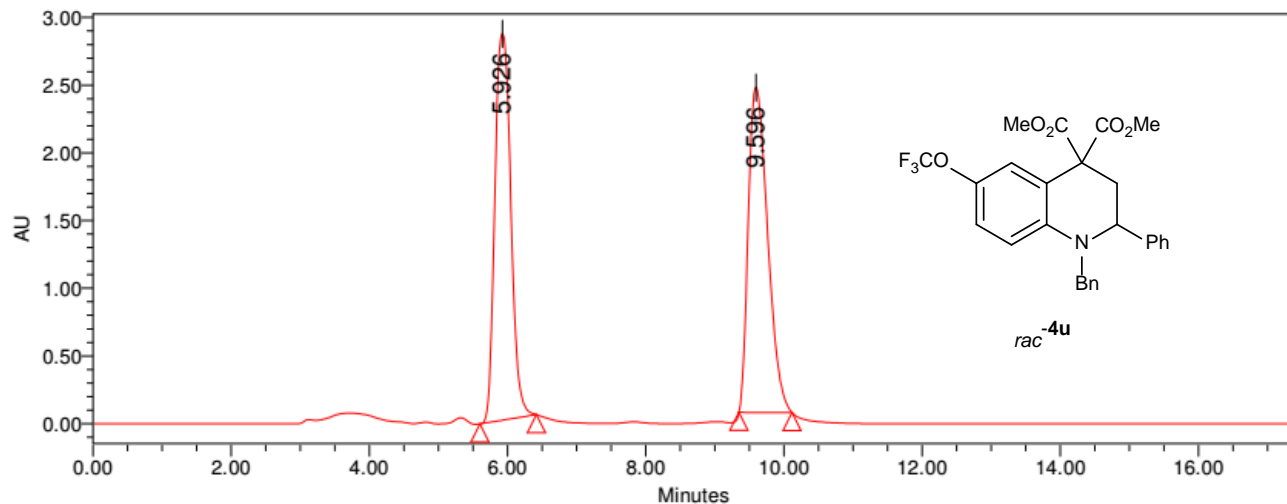
Peak Results

	RT	Height (μV)	% Area
1	9.887	1040759	49.11
2	11.318	1123176	50.89



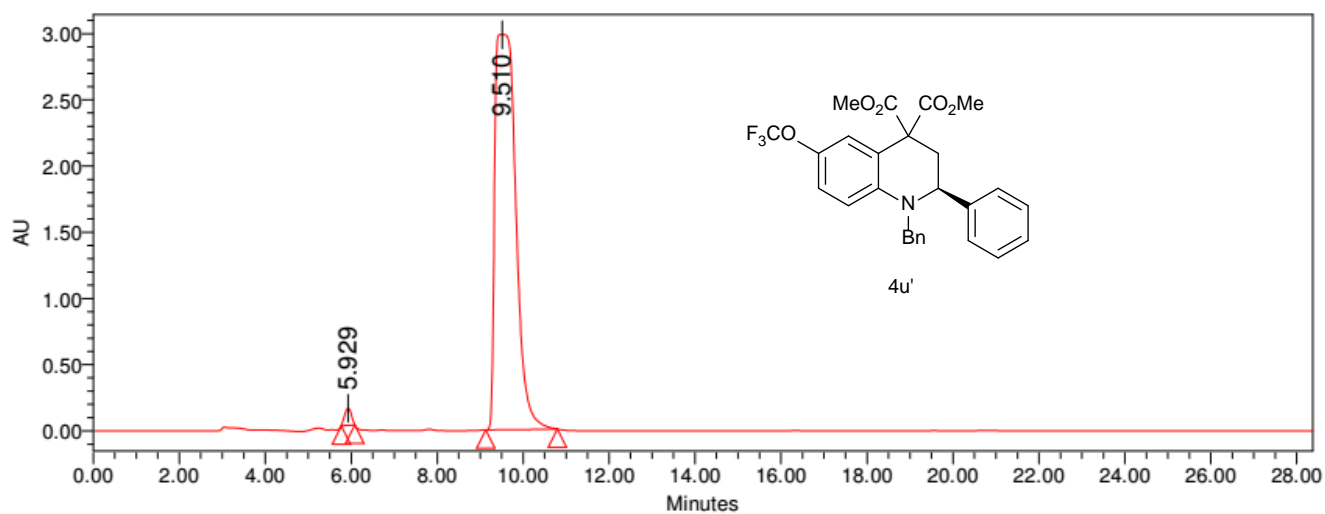
Peak Results

	RT	Height (μV)	% Area
1	10.031	26543	0.45
2	11.319	2952909	99.55



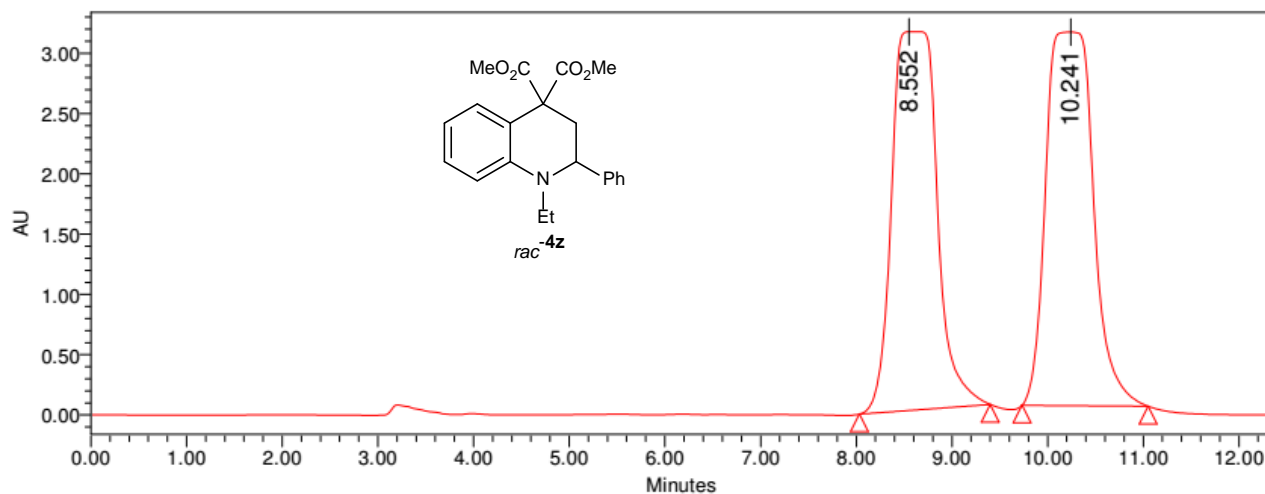
Peak Results

	RT	Height (μV)	% Area
1	5.926	2860023	49.53
2	9.596	2400387	50.47



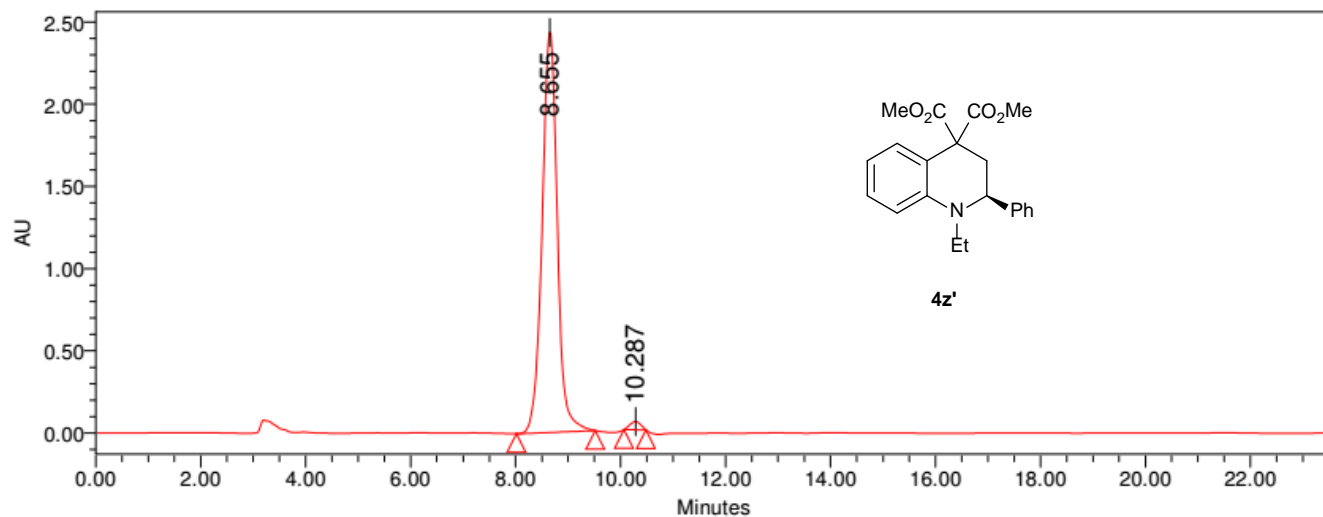
Peak Results

	RT	Height (μV)	% Area
1	5.929	129262	1.36
2	9.510	2984269	98.64



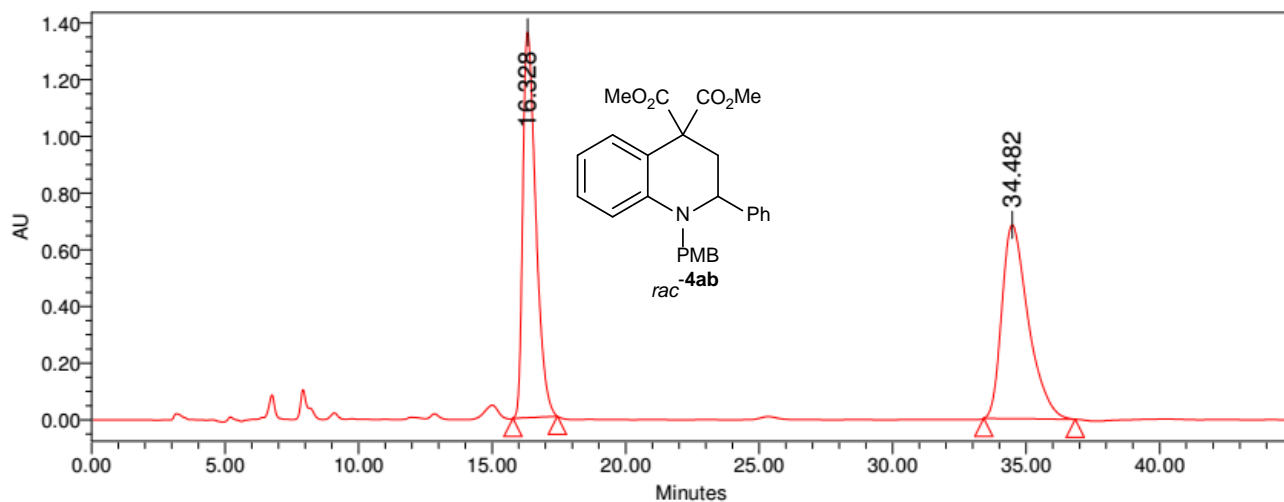
Peak Results

	RT	Height (μV)	% Area
1	8.552	3141971	49.13
2	10.241	3098548	50.87



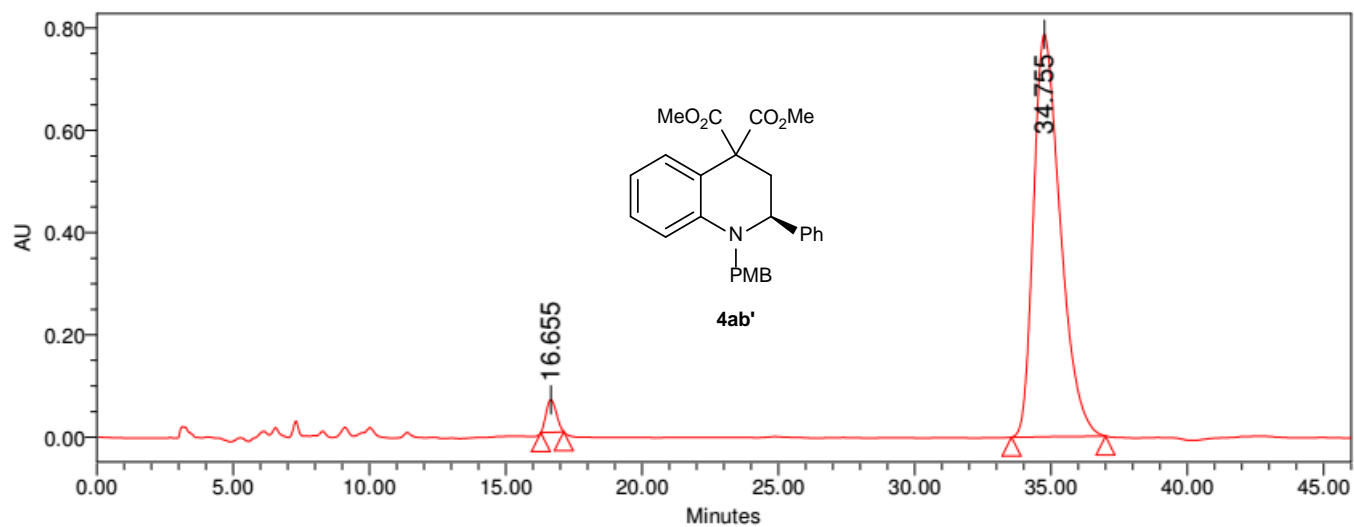
Peak Results

	RT	Height (μV)	% Area
1	8.655	2436560	98.54
2	10.287	50203	1.46



Peak Results

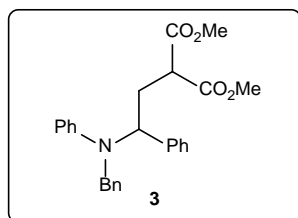
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1	16.328	1360558	49.21
2	34.482	683393	50.79



Peak Results

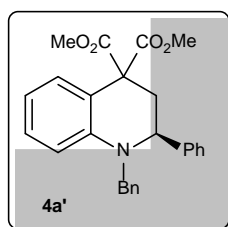
	RT	Height (μV)	% Area
1	16.655	63704	2.98
2	34.755	787287	97.02

Characterization Data



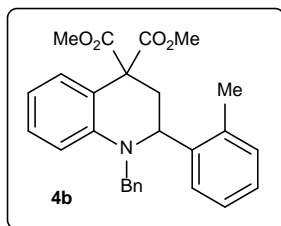
Dimethyl 2-(2-(benzyl(phenyl)amino)-2-phenylethyl) malonate **3**.

Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.42$; thick liquid; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.42-7.34 (m, 5H), 7.32-7.23 (m, 7H), 6.95 (d, $J = 8.4$ Hz, 2H), 6.86 (t, $J = 7.2$ Hz, 1H), 5.26 (t, $J = 7.8$, 1H), 4.43 (d, $J = 16.8$ Hz, 1H), 4.35 (d, $J = 16.8$ Hz, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 3.76-3.74 (m, 1H), 2.77-2.69 (m, 2H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 169.9, 169.8, 149.4, 139.5, 139.2, 129.2, 128.7, 128.5, 127.9, 127.7, 127.0, 126.6, 118.7, 116.2, 52.8, 52.8, 50.0, 49.1, 31.1; FT-IR (neat) 3061, 3029, 2953, 2847, 1731, 1628, 1598, 1501, 1452, 1436, 1265, 1223, 1155, 1064, 751, 697 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{28}\text{NO}_4$: 418.2013 found: 418.2011.



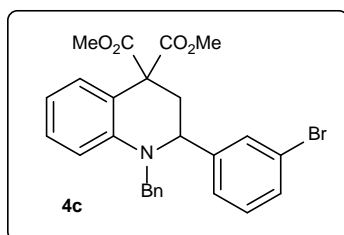
(S)-Dimethyl 1-benzyl-2-phenyl-2,3-dihydroquinoline-4,4(1H)-dicarboxylate **4a'**.

Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.43$; sticky liquid; yield 81% (67 mg); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.22-7.03 (m, 10H), 7.01 (d, $J = 7.8$ Hz, 2H), 6.66-6.64 (m, 2H), 4.58 (d, $J = 16.8$ Hz, 1H), 4.47-4.45 (m, 1H), 3.98 (d, $J = 16.8$ Hz, 1H), 3.68 (s, 3H), 3.45 (s, 3H), 2.90-2.87 (m, 1H), 2.64-2.60 (m, 1H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 171.7, 171.3, 145.0, 141.9, 138.1, 129.5, 129.0, 128.7, 128.5, 127.6, 127.4, 127.09, 127.01, 119.8, 117.0, 113.5, 59.1, 57.1, 53.2, 52.8, 52.7, 38.3; FT-IR (neat) 3062, 3028, 2952, 1733, 1602, 1495, 1451, 1240, 1099 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{26}\text{NO}_4$: 416.1856, found: 416.1860; $[\alpha]_{\text{D}}^{25} = +42.00$ ($c = 0.1$, CHCl_3); HPLC: >99% ee [CHIRALCEL AD-H, hexane/ i PrOH = 90:10, flow rate: 1 mL /min, $\lambda = 254$ nm, $t_{\text{R}} = 24.34$ min (major), 11.83 min (minor)].



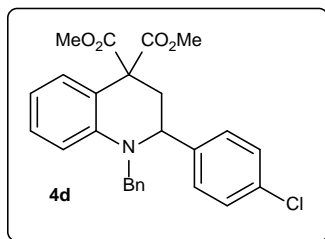
Dimethyl 1-benzyl-2-(*o*-tolyl)-2,3-dihydroquinoline-4,4(1*H*)-dicarb-

oxylate 4b. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.42$; sticky liquid; yield 67% (56 mg); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.17-7.09 (m, 5H), 7.07-7.02 (m, 4H), 6.96 (d, $J = 7.8$ Hz, 2H), 6.73 (d, $J = 8.4$ Hz, 1H), 6.66 (t, $J = 7.8$, 1H), 4.62-4.58 (m, 2H), 3.92 (d, $J = 16.2$ Hz, 1H), 3.67 (s, 3H), 3.47 (s, 3H), 2.80 (dd, $J = 13.8, 4.8$ Hz, 1H), 2.51 (dd, $J = 13.8, 9.0$ Hz, 1H), 2.07 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 171.7, 171.4, 145.6, 139.7, 137.9, 135.9, 130.83, 130.81, 129.5, 129.1, 128.6, 127.4, 127.3, 127.1, 126.4, 119.8, 116.9, 113.6, 57.2, 53.2, 52.9, 52.8, 36.5, 18.8; FT-IR (neat) 3027, 2951, 1734, 1602, 1495, 1453, 1240, 1135, 1101, 1025, 748, 699 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{28}\text{NO}_4$: 430.2013, found: 430.2014.



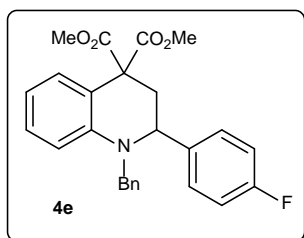
Dimethyl 1-benzyl-2-(3-bromophenyl)-2,3-dihydroquinoline-

4,4(1*H*)-dicarboxylate 4c. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.43$; sticky liquid; yield 76% (75 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.31-7.27 (m, 2H), 7.19-7.02 (m, 7H), 7.00-6.97 (m, 2H), 6.72-6.65 (m, 2H), 4.61 (d, $J = 16.4$ Hz, 1H), 4.42-4.38 (m, 1H), 3.96 (d, $J = 16.4$ Hz, 1H), 3.67 (s, 3H), 3.53 (s, 3H), 2.85 (dd, $J = 13.6, 5.2$ Hz, 1H), 2.55 (dd, $J = 13.6, 9.2$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.5, 171.2, 144.9, 144.7, 137.8, 130.9, 130.5, 130.3, 129.6, 129.1, 128.6, 127.25, 127.22, 126.1, 122.8, 120.0, 117.5, 113.8, 58.7, 57.1, 53.2, 52.9, 38.3; FT-IR (neat) 3028, 2951, 2924, 2853, 1733, 1601, 1572, 1496, 1450, 1434, 1342, 1240, 1067, 1026, 749, 697 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{25}\text{BrNO}_4$: 494.0961, found: 494.0962.



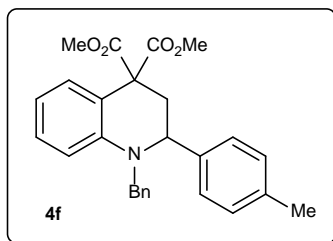
Dimethyl 1-benzyl-2-(4-chlorophenyl)-2,3-dihydroquinoline-

4,4(1H)-dicarboxylate 4d. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.46$; colorless crystal; mp 122-123 °C; yield 75% (67 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.27-7.05 (m, 11H), 6.76-6.73 (m, 2H), 4.65 (d, $J = 16.4$ Hz, 1H), 4.50-4.47(m, 1H), 4.01 (d, $J = 16.4$ Hz, 1H), 3.75 (s, 3H), 3.57 (s, 3H), 2.93 (dd, $J = 13.6, 5.2$ Hz, 1H), 2.62 (dd, $J = 13.6, 8.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.5, 171.3, 145.0, 140.6, 137.8, 133.4, 129.6, 129.1, 128.93, 128.91, 128.6, 127.23, 127.20, 120.0, 117.4, 113.7, 58.5, 57.1, 53.2, 52.95, 52.90, 38.4; FT-IR (KBr) 3028, 2951, 1733, 1601, 1575, 1495, 1493, 1450, 1343, 1240, 1089, 1014, 937, 835, 751, 699 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{25}\text{ClNO}_4$: 450.1467, found: 450.1468.



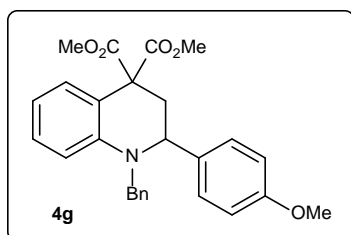
Dimethyl 1-benzyl-2-(4-fluorophenyl)-2,3-dihydroquinoline-4,4(1H)-

dicarboxylate 4e. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.36$; sticky liquid; yield 74% (64 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.18-7.04 (m, 7H), 7.00-6.97 (m, 2H), 6.90-6.86 (m, 2H), 6.68-6.64 (m, 2H), 4.57 (d, $J = 16.8$ Hz, 1H), 4.44-4.40 (m, 1H), 3.95 (d, $J = 16.8$ Hz, 1H), 3.67 (s, 3H), 3.51 (s, 3H), 2.86 (dd, $J = 13.6, 5.2$ Hz, 1H), 2.56 (dd, $J = 13.6, 9.2$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 171.6, 171.3, 163.1 ($J_{\text{C-F}} = 244.2$ Hz), 145.0, 138.0, 137.7 ($J_{\text{C-F}} = 3.1$ Hz), 129.6, 129.15, 129.13 ($J_{\text{C-F}} = 7.8$ Hz), 128.6, 127.18, 127.14, 119.9, 117.3, 115.6 ($J_{\text{C-F}} = 21.3$ Hz), 113.7, 58.5, 57.2, 53.2, 52.9, 52.8, 38.5; ^{19}F NMR (377 MHz, CDCl_3) δ -114.91; FT-IR (neat) 3030, 2952, 2922, 2852, 1733, 1644, 1602, 1502, 1451, 1345, 1235, 1161, 1100, 1059, 841, 749, 699 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{25}\text{FNO}_4$: 434.1762, found: 434.1763.



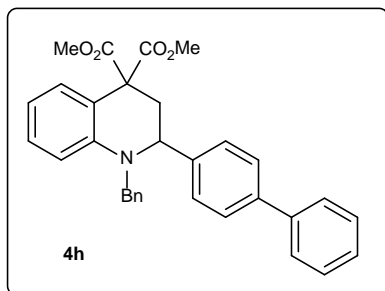
Dimethyl 1-benzyl-2-(*p*-tolyl)-2,3-dihydroquinoline-4,4(1*H*)-

dicarboxylate 4f. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.47$; sticky liquid; yield 68% (58 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.18-6.98 (m, 11H), 6.66-6.62 (m, 2H), 4.57 (d, $J = 16.8$ Hz, 1H), 4.43-4.39 (m, 1H), 3.98 (d, $J = 16.8$ Hz, 1H), 3.67 (s, 3H), 3.49 (s, 3H), 2.87-2.83 (m, 1H), 2.61-2.55 (m, 1H), 2.24 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.7, 171.4, 145.2, 139.0, 138.2, 137.3, 129.49, 129.42, 129.0, 128.5, 127.4, 127.1, 126.9, 120.0, 117.0, 113.6, 59.0, 57.3, 53.1, 52.8, 52.6, 38.6, 21.2; FT-IR (neat) 3025, 2952, 2923, 2853, 1733, 1602, 1496, 1451, 1346, 1240, 1126, 1103, 1026, 824, 753, 699, 667 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{28}\text{NO}_4$: 430.2013, found: 430.2014.

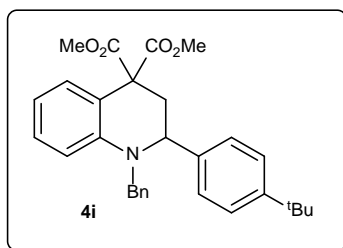


Dimethyl 1-benzyl-2-(4-methoxyphenyl)-2,3-dihydroquinoline-

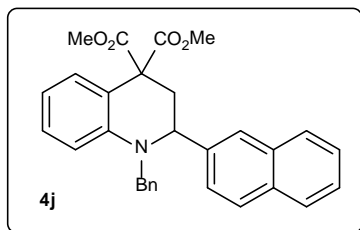
4,4(1*H*)-dicarboxylate 4g. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.50$; brown sticky liquid; yield 62% (60 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.18-6.99 (m, 9H), 6.75-6.73 (m, 2H), 6.67-6.63 (m, 2H), 4.56 (d, $J = 16.8$ Hz, 1H), 4.41-4.37 (m, 1H), 3.98 (d, $J = 16.8$ Hz, 1H), 3.70 (s, 3H), 3.68 (s, 3H), 3.52 (s, 3H), 2.85 (dd, $J = 13.6, 4.8$ Hz, 1H), 2.58 (dd, $J = 13.6, 9.2$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.7, 171.5, 159.1, 145.3, 138.3, 133.9, 129.5, 129.1, 128.6, 128.5, 127.1, 126.9, 119.9, 117.0, 114.1, 113.6, 58.6, 57.3, 55.5, 53.2, 52.9, 52.6, 38.6; FT-IR (neat) 3027, 2952, 2849, 1733, 1603, 1509, 1451, 1302, 1245, 1173, 1030, 836, 751, 699 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{28}\text{NO}_5$: 446.1962, found: 481. 446.1985.



Dimethyl 2-([1,1'-biphenyl]-4-yl)-1-benzyl-2,3-dihydroquinoline-4,4(1H)-dicarboxylate 3h. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.41$; sticky liquid; yield 73% (71 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.58-7.51 (m, 4H), 7.45-7.41 (m, 2H), 7.36-7.32 (m, 1H), 7.28-7.10 (m, 9H), 6.78-6.72 (m, 2H), 4.71 (d, $J = 16.8$ Hz, 1H), 4.61-4.57 (m, 1H), 4.13 (d, $J = 16.8$ Hz, 1H), 3.77 (s, 3H), 3.54 (s, 3H), 3.01 (dd, $J = 13.6, 5.2$ Hz, 1H), 2.74 (dd, $J = 13.6, 8.8$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.7, 171.4, 145.1, 141.1, 140.9, 140.6, 138.1, 129.5, 129.1, 129.0, 128.6, 127.9, 127.5, 127.4, 127.2, 127.2, 127.0, 119.9, 117.1, 113.6, 59.0, 57.2, 53.2, 52.8, 38.4; FT-IR (neat) 3027, 2951, 2852, 1733, 1601, 1495, 1450, 1347, 1103, 1026, 843, 698, 667 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{32}\text{H}_{30}\text{NO}_4$: 492.2169, found: 492.2170.

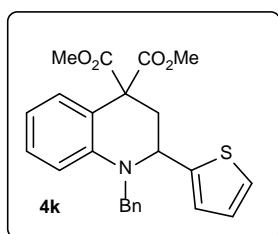


Dimethyl 1-benzyl-2-(4-(tert-butyl)phenyl)-2,3-dihydroquinoline-4,4(1H)-dicarboxylate 3i. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.56$; sticky liquid; yield 67% (63 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.22-7.01 (m, 11H), 6.65-6.62 (m, 2H), 4.57 (d, $J = 16.8$ Hz, 1H), 4.48-4.44 (m, 1H), 4.02 (d, $J = 16.8$ Hz, 1H), 3.67 (s, 3H), 3.40 (s, 3H), 2.89 (dd, $J = 13.6, 5.2$ Hz, 1H), 2.64 (dd, $J = 13.6, 8.4$ Hz, 1H), 1.21 (s, 9H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.7, 171.3, 150.4, 145.0, 138.7, 138.3, 129.4, 129.1, 128.5, 127.1, 127.0, 126.9, 125.5, 119.5, 116.9, 113.3, 58.9, 57.1, 53.1, 52.7, 38.1, 34.6, 31.5; FT-IR (neat) 3028, 2954, 2868, 1733, 1602, 1496, 1451, 1435, 1345, 1240, 1026, 839, 750, 697 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{30}\text{H}_{34}\text{NO}_4$: 472.2482, found: 472.2491.



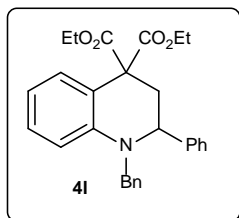
Dimethyl 1-benzyl-2-(naphthalen-2-yl)-2,3-dihydroquinoline-

4,4(1H)-dicarboxylate 4j. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.37$; semi solid; yield 71% (66 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.74-7.66 (m, 3H), 7.54 (s, 1H), 7.40-7.37 (m, 2H), 7.28-7.26 (m, 1H), 7.18-7.05 (m, 5H), 7.01-6.98 (m, 2H), 6.73-6.66 (m, 2H), 4.65-4.59 (m, 2H), 4.03 (d, $J = 16.8$ Hz, 1H), 3.70 (s, 3H), 3.38 (s, 3H), 2.93 (dd, $J = 13.6, 5.2$ Hz, 1H), 2.70 (dd, $J = 13.6, 9.2$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.7, 171.4, 145.2, 139.5, 138.1, 133.4, 133.1, 129.6, 129.0, 128.7, 128.6, 128.0, 127.8, 127.2, 127.0, 126.6, 126.4, 126.1, 125.1, 120.1, 117.2, 113.7, 59.3, 57.4, 53.2, 52.8, 52.7, 38.4; FT-IR (neat) 3026, 2951, 2923, 2852, 1733, 1601, 1496, 1450, 1436, 1351, 1239, 1129, 1100, 1058, 1026, 751, 698 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{30}\text{H}_{28}\text{NO}_4$: 466.2013, found: 466.2015.



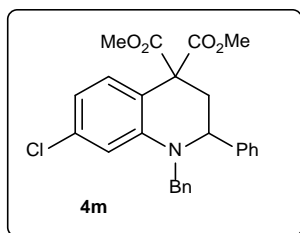
Dimethyl 1-benzyl-2-(thiophen-2-yl)-2,3-dihydroquinoline-4,4(1H)-

dicarboxylate 4k. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.36$; brown sticky liquid; yield 61% (51 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.20-7.03 (m, 8H), 6.82-6.80 (m, 1H), 6.77-6.76 (m, 1H), 6.70-6.64 (m, 2H), 4.73 (dd, $J = 8.8, 4.8$ Hz, 1H), 4.60 (d, $J = 16.4$ Hz, 1H), 4.08 (d, $J = 16.8$ Hz, 1H), 3.67 (s, 3H), 3.59 (s, 3H), 2.97 (dd, $J = 13.6, 4.8$ Hz, 1H), 2.69 (dd, $J = 13.6, 9.2$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.5, 171.4, 146.1, 144.7, 138.2, 129.5, 129.1, 128.6, 127.2, 127.1, 126.5, 126.0, 125.1, 120.3, 117.7, 114.4, 57.3, 55.0, 53.2, 53.0, 52.9, 39.4; FT-IR (neat) 3028, 2952, 2922, 2851, 1733, 1602, 1494, 1435, 1355, 1242, 1199, 1023, 851, 750, 700 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{24}\text{NO}_4\text{S}$: 422.1421, found: 422.1423.



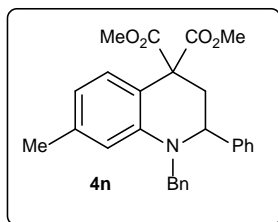
Diethyl 1-benzyl-2-phenyl-2,3-dihydroquinoline-4,4(1H)-dicarboxylate

4l. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.41$; sticky liquid; yield 81% (71 mg); ^1H NMR (600 MHz, CDCl_3) δ 7.22-7.10 (m, 9H), 7.07-7.04 (m, 1H), 7.02-7.00 (m, 2H), 6.67-6.64 (m, 2H), 4.57 (d, $J = 16.8$ Hz, 1H), 4.49-4.46 (m, 1H), 4.25-4.20 (m, 1H), 4.13-4.07 (m, 1H), 4.02-3.96 (m, 2H), 3.88-3.82 (m, 1H), 2.87-2.84 (m, 1H), 2.61-2.56 (m, 1H), 1.19-1.17 (m, 3H), 1.12-1.09 (m, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 171.1, 171.0, 145.2, 142.2, 138.2, 129.3, 129.2, 128.7, 128.5, 127.7, 127.5, 127.1, 126.9, 119.9, 117.0, 113.5, 62.0, 61.9, 59.4, 57.1, 52.8, 38.3, 14.2, 14.1; FT-IR (neat) 3029, 2981, 1730, 1602, 1495, 1451, 1299, 1237, 1094, 1059, 1029, 862, 747, 701 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{30}\text{NO}_4$: 444.2169, found: 444.2177.

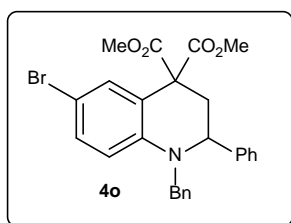


Dimethyl 1-benzyl-7-chloro-2-phenyl-2,3-dihydroquinoline-4,4(1H)-dicarboxylate. 4m

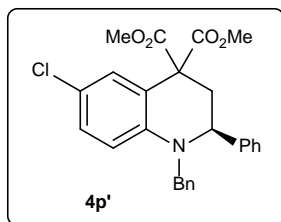
4m Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.47$; sticky liquid; yield 64% (57 mg); ^1H NMR (600 MHz, CDCl_3) δ 7.23-7.13 (m, 6H), 7.07 (d, $J = 7.8$ Hz, 2H), 7.00-6.95 (m, 3H), 6.65-6.60 (m, 2H), 4.55 (d, $J = 16.8$ Hz, 1H), 4.48-4.45 (m, 1H), 3.98 (d, $J = 16.8$ Hz, 1H), 3.67 (s, 3H), 3.40 (s, 3H), 2.88-2.85 (m, 1H), 2.63-2.59 (m, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 171.3, 170.9, 146.1, 141.2, 137.2, 135.3, 130.2, 128.8, 128.7, 127.8, 127.38, 127.32, 127.0, 118.0, 116.9, 113.0, 58.9, 56.5, 53.3, 52.9, 52.6, 37.7; FT-IR (neat) 3028, 2951, 1734, 1597, 1562, 1494, 1451, 1432, 1357, 1240, 1105, 1055, 1027, 849, 754, 700 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{25}\text{ClNO}_4$: 450.1467, found: 450.1469.



Dimethyl 1-benzyl-7-methyl-2-phenyl-2,3-dihydroquinoline-4,4(1H)-dicarboxylate 4n. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.51$; sticky liquid; yield 62% (53 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.22-7.08 (m, 8H), 7.02-6.99 (m, 2H), 6.95 (d, $J = 8.0$ Hz, 1H), 6.52-6.47 (m, 2H), 4.62 (d, $J = 16.4$ Hz, 1H), 4.42 (dd, $J = 8.4, 4.8$ Hz, 1H), 3.97 (d, $J = 16.8$ Hz, 1H), 3.67 (s, 3H), 3.43 (s, 3H), 2.86 (dd, $J = 13.6, 5.2$ Hz, 1H), 2.61 (dd, $J = 13.6, 8.4$ Hz, 1H), 2.16 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.8, 171.5, 145.1, 142.0, 139.4, 138.3, 129.0, 128.69, 128.60, 127.6, 127.5, 127.2, 127.0, 118.1, 116.9, 114.0, 59.0, 56.9, 53.2, 52.8, 52.7, 38.3, 21.9; FT-IR (neat) 3026, 2949, 2924, 2852, 1734, 1609, 1505, 1449, 1238, 1135, 1026, 940, 754, 700 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{28}\text{NO}_4$: 430.2013, found: 430.2014.



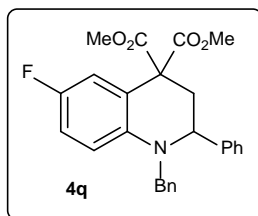
Dimethyl 1-benzyl-6-bromo-2-phenyl-2,3-dihydroquinoline-4,4(1H)-dicarboxylate 4o. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.47$; semi solid; yield 71% (70 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.24-7.07 (m, 10H), 7.99-6.97 (m, 2H), 6.53-6.50 (m, 1H), 4.52-4.45 (m, 2H), 3.99 (d, $J = 16.8$ Hz, 1H), 3.70 (s, 3H), 3.47 (s, 3H), 2.90-2.85 (m, 1H), 2.62-2.56 (m, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.1, 170.8, 144.1, 141.5, 137.5, 132.2, 131.7, 128.8, 128.7, 127.8, 127.4, 127.2, 127.0, 121.6, 115.1, 108.9, 59.3, 56.9, 53.4, 53.1, 52.8, 38.1; FT-IR (neat) 3029, 2952, 2922, 2852, 1734, 1594, 1493, 1452, 1347, 1239, 1132, 1025, 802, 754, 700 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{25}\text{BrNO}_4$: 494.0961, found: 494.0962.



(S)-Dimethyl 1-benzyl-6-chloro-2-phenyl-2,3-dihydroquinoline-

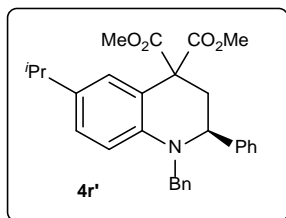
4,4(1H)-dicarboxylate 4p'. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.44$; crystalline solid; mp 165-166 °C; yield 72% (65 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.23-7.07 (m, 8H), 7.03-6.97 (m, 4H), 6.57 (d, $J = 8.8$ Hz, 1H), 4.52-4.45 (m, 2H), 3.99 (d, $J = 16.8$ Hz, 1H), 3.69 (s, 3H), 3.46 (s, 3H), 2.88 (dd, $J = 13.6, 5.2$ Hz, 1H), 2.60 (dd, $J = 13.6, 8.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.1, 170.8, 143.7, 141.5, 137.6, 129.4, 128.9, 128.8, 128.7, 127.8, 127.4, 127.2, 127.0, 121.8, 121.2, 114.6, 59.2, 56.9, 53.3, 53.0, 52.9, 38.2; FT-IR (KBr) 3028, 2951, 1734, 1599, 1494, 1452, 1346, 1239, 1134, 1061, 1025, 803, 753, 700 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{25}\text{ClNO}_4$: 450.1467, found: 450.1465; $[\alpha]_{\text{D}}^{25} = +32.00$ ($c = 0.1$, CHCl_3); HPLC: >99% *ee* [CHIRALCEL AD-H, hexane/*i*PrOH = 90:10, flow rate: 1 mL /min, $\lambda = 254$ nm, $t_{\text{R}} = 16.10$ min (major), 8.68 min (minor)].

BB



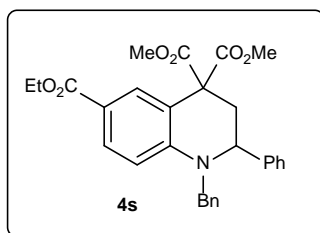
Dimethyl 1-benzyl-6-fluoro-2-phenyl-2,3-dihydroquinoline-4,4(1H)-

dicarboxylate 4q. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.40$; sticky liquid; yield 68% (58 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.23-7.07 (m, 8H), 7.00-6.98 (m, 2H), 6.84-6.76 (m, 2H), 6.56 (dd, $J = 9.2, 4.8$ Hz, 1H), 4.49-4.41 (m, 2H), 3.97 (d, $J = 16.8$ Hz, 1H), 3.69 (s, 3H), 3.49 (s, 3H), 2.89 (dd, $J = 13.6, 5.2$ Hz, 1H), 2.58 (dd, $J = 13.6, 9.2$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 171.1, 170.8, 155.8 ($J_{\text{C-F}} = 234.3$ Hz), 141.8, 141.6, 137.9, 128.7, 128.6, 127.7, 127.4, 127.1, 121.0 ($J_{\text{C-F}} = 7.2$ Hz), 116.2, 116.0, 115.8 ($J_{\text{C-F}} = 23.55$ Hz), 114.4 ($J_{\text{C-F}} = 7.9$ Hz), 59.3, 57.1, 53.3, 53.2, 53.0, 38.5; ^{19}F NMR (377 MHz, CDCl_3) δ -127.87; FT-IR (neat) 3028, 2953, 1733, 1602, 1499, 1453, 1434, 1243, 1166, 1024, 803, 755, 701 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{25}\text{FNO}_4$: 434.1762, found: 434.1764.



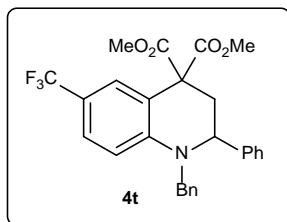
(S)-Dimethyl 1-benzyl-6-isopropyl-2-phenyl-2,3-dihydroquino-line-

4,4(1H)-dicarboxylate 4r'. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.58$; brown oil; yield 66% (60 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.20-7.09 (m, 8H), 7.02-7.00 (m, 2H), 6.95-6.92 (m, 1H), 6.90-6.89 (m, 1H), 6.60 (d, $J = 8.4$ Hz, 1H), 4.54 (d, $J = 16.4$ Hz, 1H), 4.41 (dd, $J = 9.2, 4.8$ Hz, 1H), 3.96 (d, $J = 16.4$ Hz, 1H), 3.68 (s, 3H), 3.46 (s, 3H), 2.86 (dd, $J = 13.6, 5.2$ Hz, 1H), 2.78-2.68 (m, 1H), 2.60 (dd, $J = 13.6, 8.8$ Hz, 1H), 1.14 (d, $J = 7.6$ Hz, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.7, 171.5, 143.3, 142.2, 138.5, 137.2, 128.6, 128.5, 127.6, 127.5, 127.35, 127.30, 127.1, 126.9, 119.4, 113.4, 59.2, 57.3, 53.1, 53.0, 52.7, 38.5, 33.1, 24.2; FT-IR (neat) 3028, 2958, 2871, 1733, 1615, 1505, 1452, 1351, 1239, 1089, 1061, 1026, 949, 814, 752, 700 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{29}\text{H}_{32}\text{NO}_4$: 458.2326, found: 458.2331; $[\alpha]_D^{25} = +32.00$ ($c = 0.1$, CHCl_3); HPLC: >99% *ee* [CHIRALCEL AD-H, hexane/*i*PrOH = 97:03, flow rate: 1 mL/min, $\lambda = 254$ nm, $t_R = 11.31$ min (major), 10.03 min (minor)].



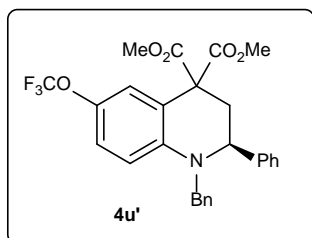
6-Ethyl 4,4-dimethyl 1-benzyl-2-phenyl-2,3-dihydroquino-line-

4,4,6(1H)-tricarboxylate 4s. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.35$; sticky liquid; yield 62% (58 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.76-7.74 (m, 2H), 7.25-7.14 (m, 6H), 7.10-7.07 (m, 2H), 7.00-6.97 (m, 2H), 6.66 (d, $J = 8.8$ Hz, 1H), 4.67 (d, $J = 16.8$ Hz, 1H), 4.56 (dd, $J = 8.0, 5.2$ Hz, 1H), 4.23 (q, $J = 7.2$ Hz, 2H), 4.07 (d, $J = 17.2$ Hz, 1H), 3.70 (s, 3H), 3.43 (s, 3H), 2.92-2.88 (m, 1H), 2.67 (dd, $J = 13.6, 8.8$ Hz, 1H), 1.26 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.3, 170.8, 166.7, 148.5, 141.0, 137.1, 131.3, 131.2, 128.9, 128.8, 127.9, 127.39, 127.37, 126.9, 118.8, 118.7, 112.4, 60.4, 59.4, 56.7, 53.3, 53.0, 52.6, 37.6, 14.6; FT-IR (neat) 3027, 2981, 2953, 2852, 1734, 1705, 1608, 1512, 1451, 1308, 1241, 1171, 1061, 1026, 929, 756, 700 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{29}\text{H}_{30}\text{NO}_6$: 488.2068, found: 488.2069.



Dimethyl 1-benzyl-2-phenyl-6-(trifluoromethyl)-2,3-dihydroqui-

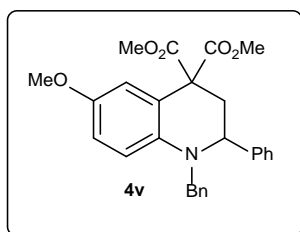
noline-4,4(*1H*)-dicarboxylate 4t. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.37$; colorless solid; mp 116-117 °C; yield 77% (74 mg); ^1H NMR (600 MHz, CDCl_3) δ 7.30-7.27 (m, 2H), 7.24-7.14 (m, 6H), 7.08 (d, $J = 7.2$ Hz, 2H), 7.01 (d, $J = 7.2$ Hz, 2H), 6.67 (d, $J = 9.0$ Hz, 1H), 4.62-4.56 (m, 2H), 4.07 (d, $J = 16.8$ Hz, 1H), 3.70 (s, 3H), 3.40 (s, 3H), 2.92 (dd, $J = 13.8, 5.4$ Hz, 1H), 2.68 (dd, $J = 13.8, 9.0$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 171.0, 170.6, 147.4, 140.9, 137.1, 128.89, 128.87, 128.0, 127.4, 127.3, 126.8, 126.7 (q, $J = 3.5$ Hz), 126.6 (q, $J = 3.8$ Hz), 125.8 (q, $J = 268.9$ Hz), 118.8, 118.6 (q, $J = 32.2$ Hz), 112.7, 59.3, 56.5, 53.4, 53.0, 52.8, 37.4; ^{19}F NMR (377 MHz, CDCl_3) δ -61.02; FT-IR (KBr) 3030, 2953, 1735, 1619, 1519, 1494, 1453, 1435, 1334, 1273, 1156, 1123 1087, 754, 700 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{25}\text{F}_3\text{NO}_4$: 484.1730, found: 484.1734.



(*S*)-Dimethyl 1-benzyl-2-phenyl-6-(trifluoromethoxy)-2,3-dihydro-

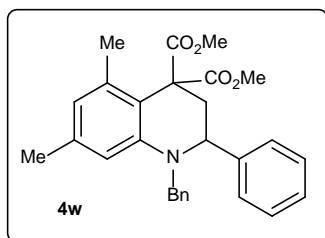
droquinoline-4,4(*1H*)-dicarboxylate 4u'. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.36$; semi solid; yield 69% (68 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.24-7.08 (m, 8H), 7.02-6.97 (m, 3H), 6.94-6.90 (m, 1H), 6.59 (d, $J = 9.2$ Hz, 1H), 4.54-4.48 (m, 2H), 4.03 (d, $J = 16.8$ Hz, 1H), 3.69 (s, 3H), 3.44 (s, 3H), 2.89 (dd, $J = 13.6, 4.8$ Hz, 1H), 2.63 (dd, $J = 13.6, 8.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.0, 170.7, 144.0, 141.4, 139.9, 137.6, 128.8, 128.7, 127.9, 127.4, 127.2, 126.9, 122.7, 122.4, 122.1 (q, $J = 254.1$ Hz), 120.1, 113.8, 59.4, 56.9, 53.3, 53.1, 53.0, 37.9; ^{19}F NMR (377 MHz, CDCl_3) δ -58.38; FT-IR (neat) 3029, 2956, 2924, 2853, 1737, 1604, 1502, 1454, 1435, 1377, 1261, 1162, 1025, 804, 762, 700 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{25}\text{F}_3\text{NO}_5$: 500.1679, found: 500.1680; $[\alpha]_D^{25} = +46.00$ ($c = 0.1$, CHCl_3); HPLC:

>97% *ee* [CHIRALCEL AD-H, hexane/*i*PrOH = 90:10, flow rate: 1 mL /min, λ = 254 nm, t_R = 9.51 min (major), 5.92 min (minor)].



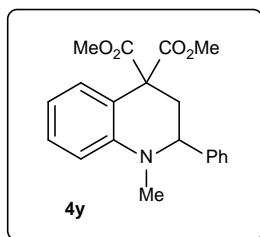
Dimethyl 1-benzyl-6-methoxy-2-phenyl-2,3-dihydroquinoline-

4,4(1H)-dicarboxylate 4v. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.47; sticky liquid; yield 56% (50 mg); ^1H NMR (600 MHz, CDCl_3) δ 7.22-7.10 (m, 8H), 7.01 (d, J = 7.2 Hz, 2H), 6.69-6.66 (m, 2H), 6.60 (d, J = 9.0 Hz, 1H), 4.48 (d, J = 16.2 Hz, 1H), 4.39-4.37 (m, 1H), 3.92 (d, J = 16.2 Hz, 1H), 3.68 (s, 3H), 3.67 (s, 3H), 3.52 (s, 3H), 2.89-2.86 (m, 1H), 2.57-2.53 (m, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 171.5, 171.3, 151.3, 142.3, 139.5, 138.4, 128.7, 128.5, 127.6, 127.5, 127.2, 126.9, 121.5, 115.0, 114.8, 114.7, 59.2, 57.5, 55.8, 53.26, 53.24, 53.0, 39.0; FT-IR (neat) 2953, 2924, 2852, 1734, 1501, 1453, 1242, 1053, 803, 755, 701 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{28}\text{NO}_5$: 446.1962, found: 446.1972.



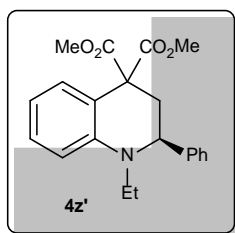
Dimethyl 1-benzyl-5,7-dimethyl-2-phenyl-2,3-dihydroquinoline-

4,4(1H)-dicarboxylate 4w. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.57; sticky liquid; yield 51% (45 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.23-7.10 (m, 9H), 6.95-6.92 (m, 2H), 6.46 (s, 1H), 6.37 (s, 1H), 4.61 (d, J = 16.4 Hz, 1H), 4.37 (dd, J = 9.2, 5.2 Hz, 1H), 3.92 (d, J = 16.4 Hz, 1H), 3.67 (s, 3H), 3.43 (s, 3H), 2.78 (dd, J = 13.2, 5.2 Hz, 1H), 2.56 (dd, J = 13.2, 9.2 Hz, 1H), 2.12 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 172.2, 172.0, 145.8, 142.4, 138.5, 138.3, 138.1, 128.7, 128.5, 127.6, 127.4, 127.3, 126.9, 122.1, 117.5, 112.9, 56.4, 53.4, 53.1, 52.8, 40.6, 21.7, 20.8; FT-IR (neat) 3027, 2950, 2924, 2856, 1732, 1605, 1572, 1451, 1343, 1234, 1073, 1028, 823, 751, 700 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{30}\text{NO}_4$: 444.2169, found: 444.2179.



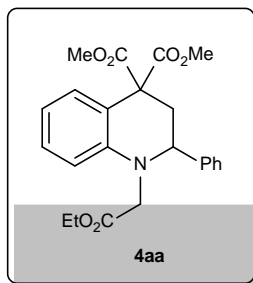
Dimethyl 1-methyl-2-phenyl-2,3-dihydroquinoline-4,4(1H)-dicar-

boxylate 4y. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.60$; sticky liquid; yield 75% (51 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.27-7.24 (m, 2H), 7.20-7.17 (m, 4H), 7.07-7.05 (m, 1H), 6.70-6.65 (m, 2H), 4.29-4.27 (m, 1H), 3.71 (s, 3H), 3.53 (s, 3H), 2.78 (dd, $J = 13.8, 4.2$ Hz, 1H), 2.65 (s, 3H), 2.45-2.41(m, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.74, 171.72, 146.4, 142.6, 129.6, 129.4, 128.8, 127.6, 127.2, 118.9, 116.7, 112.9, 60.8, 57.2, 53.3, 52.9, 38.9, 37.9; FT-IR (neat) 3026, 2953, 2921, 2852, 1735, 1690, 1604, 1495, 1450, 1351, 1239, 1100, 1061, 751, 701 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{22}\text{NO}_4$: 340.1543, found: 340.1544.



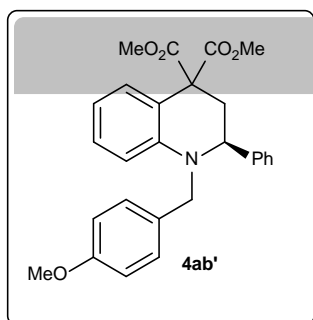
(S)-Dimethyl 1-ethyl-2-phenyl-2,3-dihydroquinoline-4,4(1H)-dicar-

boxylate 4z'. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.61$; semi solid; yield 72% (51 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.25-7.12 (m, 6H), 7.04-7.02 (m, 1H), 6.76 (d, $J = 8.8$ Hz, 1H), 6.65-6.61 (m, 1H), 4.35(dd, $J = 9.6, 4.4$ Hz, 1H), 3.68 (s, 3H), 3.50 (s, 3H), 3.43-3.34 (m, 1H), 2.89-2.80 (m, 1H), 2.76-2.71 (m, 1H), 2.50-2.43 (m, 1H), 0.88 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.8, 171.6, 145.0, 142.8, 129.47, 129.43, 128.7, 127.6, 127.4, 119.8, 116.6, 113.5, 58.3, 57.3, 53.1, 52.8, 43.2, 38.7, 11.2; FT-IR (neat) 3029, 2952, 1733, 1602, 1573, 1495, 1452, 1344, 1255, 1203, 1096, 1058, 1023 749, 703 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{24}\text{NO}_4$: 354.1700, found: 354.1706; $[\alpha]_{\text{D}}^{25} = +12.00$ ($c = 0.1$, CHCl_3); HPLC: >97% *ee* [CHIRALCEL AD-H, hexane/*i*PrOH = 97:03, flow rate: 1 mL /min, $\lambda = 254$ nm, $t_R = 10.28$ min (major), 8.65 min (minor)].



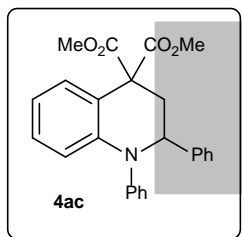
Dimethyl 1-(2-ethoxy-2-oxoethyl)-2-phenyl-2,3-dihydroquinoline-

4,4(1H)-dicarboxylate 4aa. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.47$; sticky liquid; yield 62% (51 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.34-7.25 (m, 5H), 7.21-7.17 (m, 2H), 6.79-6.75 (m, 1H), 6.68-6.65 (m, 1H), 4.60 (dd, $J = 10.8, 3.6$ Hz, 1H), 4.09-4.01 (m, 2H), 3.80 (s, 3H), 3.65 (s, 3H), 2.84 (dd, $J = 13.6, 4.0$ Hz, 1H), 2.55 (dd, $J = 13.6, 10.8$ Hz, 1H), 1.11 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.9, 171.4, 170.7, 145.3, 142.0, 130.3, 129.5, 129.0, 128.1, 127.6, 119.2, 117.8, 112.9, 60.9, 60.0, 57.4, 53.2, 53.0, 51.0, 38.5, 14.2; FT-IR (neat) 2953, 1733, 1603, 1495, 1454, 1435, 1334, 1236, 1193, 1126, 1093, 1026, 749, 703 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{26}\text{NO}_6$: 412.1755, found: 412.1756.



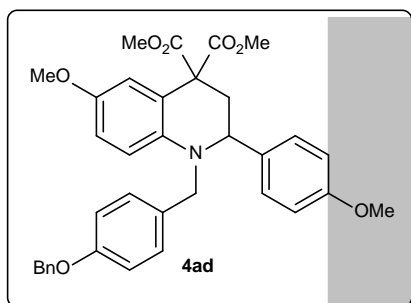
(S)-Dimethyl 1-(4-methoxybenzyl)-2-phenyl-2,3-dihydroquinoline-

4,4(1H)-dicarboxylate 4ab'. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.63$; sticky liquid; yield 71% (63 mg); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.22-7.01 (m, 7H), 6.91 (d, $J = 8.8$ Hz, 1H), 6.70-6.62 (m, 4H), 4.53 (d, $J = 16.4$ Hz, 1H), 4.42-4.39 (m, 1H), 3.89 (d, $J = 16.4$ Hz, 1H), 3.67 (s, 3H), 3.66 (s, 3H), 3.46 (s, 3H), 2.88-2.83 (m, 1H), 2.60-2.54 (m, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.7, 171.3, 158.7, 145.2, 142.1, 129.9, 129.5, 128.9, 128.7, 128.4, 127.6, 127.4, 120.1, 117.0, 113.9, 113.6, 58.8, 57.2, 55.4, 53.1, 52.8, 52.0, 38.5; FT-IR (neat) 3028, 2951, 2838, 1733, 1603, 1509, 1453, 1245, 1175, 1102, 1060, 815, 751, 702 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{28}\text{NO}_5$: 446.1962 found: 446.1969; $[\alpha]_{\text{D}}^{25} = -42.00$ ($c = 0.1$, CHCl_3); HPLC: >94% *ee* [CHIRALCEL AD-H, hexane/*i*PrOH = 90:10, flow rate: 1 mL/min, $\lambda = 254$ nm, $t_{\text{R}} = 34.75$ min (major), 16.65 min (minor)].



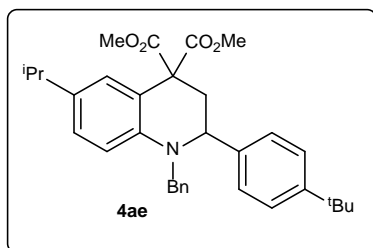
Dimethyl 1,2-diphenyl-2,3-dihydroquinoline-4,4(1H)-dicarboxylate 4ac.

Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.47$; semi solid; yield 68% (54 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.21-7.05 (m, 9H), 6.90-6.78 (m, 5H), 4.72-4.68 (dd, $J = 9.2, 6.0$ Hz, 1H), 3.62 (s, 3H), 3.58 (s, 3H), 3.09 (dd, $J = 13.6, 5.6$ Hz, 1H), 2.61 (dd, $J = 13.6, 9.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.5, 171.0, 147.6, 144.2, 143.1, 129.2, 129.0, 128.7, 128.4, 127.3, 127.0, 124.5, 123.6, 123.5, 120.13, 120.11, 60.5, 57.4, 53.3, 53.0, 40.6; FT-IR (neat) 3029, 2952, 1733, 1594, 1492, 1449, 1383, 1314, 1249, 1129, 1095, 1056, 1026, 751, 699 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{24}\text{NO}_4$: 402.1700, found: 402.1703.

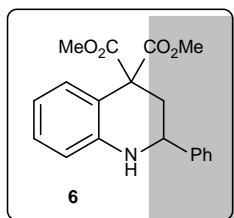


Dimethyl 1-(4-(benzyloxy)benzyl)-6-methoxy-2-(4-

methoxyphenyl)-2,3-dihydroquinoline-4,4(1H)-dicarboxylate 4ad. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.47$; thick liquid; yield 75% (87 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.43-7.30 (m, 5H), 7.10 (d, $J = 8.8$ Hz, 2H), 6.99 (d, $J = 8.8$ Hz, 2H), 6.86-6.68 (m, 7H), 5.02 (s, 2H), 4.49 (d, $J = 16.0$ Hz, 1H), 4.36-4.33 (m, 1H), 3.90 (d, $J = 16.0$ Hz, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.72 (s, 3H), 3.64 (s, 3H), 2.90 (dd, $J = 13.6, 5.2$ Hz, 1H), 2.57 (dd, $J = 13.6, 9.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.5, 171.4, 159.0, 157.8, 151.3, 139.8, 137.2, 134.4, 130.7, 128.7, 128.6, 128.5, 128.1, 127.6, 121.8, 115.0, 114.9, 114.84, 114.80, 114.0, 70.1, 58.3, 57.7, 55.8, 55.4, 53.1, 53.0, 52.3, 39.3; FT-IR (neat) 2951, 2836, 1733, 1610, 1584, 1509, 1454, 1245, 1172, 1032, 832, 744, 698 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{35}\text{H}_{36}\text{NO}_7$: 582.2486, found: 582.2485.

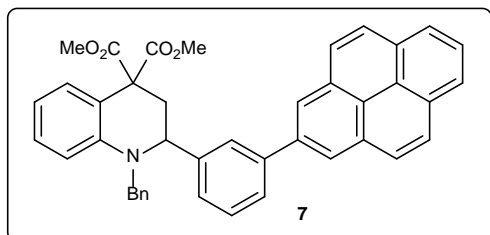


Dimethyl 1-benzyl-2-(4-(tert-butyl)phenyl)-6-isopropyl-2,3-dihydroquinoline-4,4(1H)-dicarboxylate 4ae. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.68$; sticky liquid; yield 78% (80 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.21-7.08 (m, 5H), 7.05-7.01 (m, 4H), 6.94-6.88 (m, 2H), 6.59 (d, $J = 8.4$ Hz, 1H), 4.54 (d, $J = 16.8$ Hz, 1H), 4.43-4.40 (m, 1H), 4.01 (d, $J = 16.8$ Hz, 1H), 3.68 (s, 3H), 3.42 (s, 3H), 2.86 (dd, $J = 13.6, 4.8$ Hz, 1H), 2.76-2.69 (m, 1H), 2.62 (dd, $J = 13.6, 8.8$ Hz, 1H), 1.21 (s, 9H), 1.14 (d, $J = 6.8$, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.9, 171.6, 150.4, 143.3, 138.9, 138.7, 137.0, 128.5, 127.4, 127.28, 127.23, 127.1, 126.8, 125.5, 119.1, 113.3, 59.0, 57.3, 53.1, 53.0, 52.7, 38.3, 34.6, 33.1, 31.5, 24.3, 24.2; FT-IR (neat) 3026, 2958, 2869, 1735, 1615, 1508, 1453, 1434, 1360, 1239, 1142, 1081, 1025, 810, 756, 699 cm^{-1} ; HRMS (ESI) m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{33}\text{H}_{40}\text{NO}_4$: 514.2952, found: 514.2961.

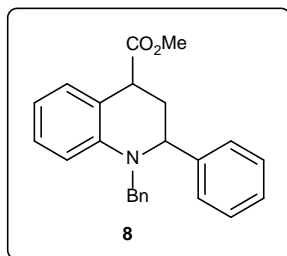


Dimethyl 2-phenyl-2,3-dihydroquinoline-4,4(1H)-dicarboxylate 6.⁴ Anisole (2 mL) was added to a stirring solution of **4ab** (0.1 mmol, 50 mg) in TFA (1.5 mL, 1 mmol) and the resultant mixture was heated to reflux for 4 h. The reaction was quenched by addition of sat. aq. NaHCO_3 (5 mL) and extracted with CH_2Cl_2 (10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography to give **6**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.37$; yellow solid; mp 124-125 $^\circ\text{C}$; yield 89% (29 mg); ^1H NMR (400 MHz, CDCl_3) δ 7.47-7.44 (m, 2H), 7.40-7.29 (m, 4H), 7.15-7.10 (m, 1H), 6.76-6.72 (m, 1H), 6.60-6.58 (m, 1H), 4.47-4.43 (m, 1H), 4.17 (brs, 1H), 3.80 (s, 3H), 3.74 (s, 3H), 2.81 (dd, $J = 13.2, 2.8$ Hz, 1H), 2.32 (dd, $J = 13.2, 11.6$ Hz, 1H); ^{13}C NMR (100

MHz, CDCl₃) δ 172.2, 171.7, 144.8, 142.9, 131.1, 129.3, 128.9, 128.2, 126.9, 117.7, 115.7, 115.3, 57.5, 53.7, 53.3, 53.1, 38.6; FT-IR (neat) 3028, 2952, 2848, 1731, 1607, 1490, 1434, 1321, 1253, 1126, 1059, 751, 701 cm⁻¹; HRMS (ESI) m/z [M+H]⁺ calcd for C₁₉H₂₀NO₄: 326.1387, found: 326.1397.



Dimethyl 1-benzyl-2-(3-(pyren-2-yl)phenyl)-2,3-dihydroquinoline-4,4(1H)-dicarboxylate 7. Tetrahydroquinoline **4c** (0.1 mmol, 50 mg), Pd(PPh₃)₄ (2 mol %, 2.3 mg), pyrene-1-boronic acid (0.2 mmol, 50 mg), Na₂CO₃ (0.2 mmol, 22 mg) and H₂O (50 μ L) were refluxed in toluene:EtOH (1:1, 2 mL) for 4 h under N₂ atmosphere. After completion, the reaction mixture was cooled to room temperature and passed through a short pad of celite using CH₂Cl₂ (10 mL). Evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and ethyl acetate as an eluent to give **7**. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.32; semi solid; yield 91% (56 mg); ¹H NMR (600 MHz, CDCl₃) δ 8.13-8.09 (m, 3H), 8.07 (d, J = 9.0 Hz, 1H), 8.02 (s, 2H), 7.96-7.93 (m, 2H), 7.76 (s, 1H), 7.45-7.39 (m, 3H), 7.25-7.23 (m, 1H), 7.21-7.18 (m, 2H), 7.16-7.13 (m, 1H), 7.11-7.05 (m, 4H), 6.69-6.65 (m, 2H), 4.70 (d, J = 16.8 Hz, 1H), 4.61-4.58 (m, 1H), 4.18 (d, J = 16.8 Hz, 1H), 3.70 (s, 3H), 3.52 (s, 3H), 3.01 (dd, J = 13.8, 4.8 Hz, 1H), 2.76 (dd, J = 13.2, 8.4 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 171.7, 171.5, 145.2, 142.2, 141.6, 138.2, 137.4, 131.6, 131.1, 130.8, 130.0, 129.7, 129.6, 129.2, 128.7, 128.5, 127.8, 127.7, 127.66, 127.61, 127.19, 127.11, 126.4, 126.2, 125.3, 125.2, 125.1, 125.07, 125.04, 124.8, 119.6, 117.2, 113.6, 59.4, 57.2, 53.3, 53.2, 53.0, 38.4; FT-IR (neat) 2924, 2853, 1732, 1602, 1456, 1451, 1239, 1083, 1029, 848, 750 cm⁻¹; HRMS (ESI) m/z [M+H]⁺ calcd for C₄₂H₃₄NO₄: 616.2482, found: 616.2489.



Methyl 1-benzyl-2-phenyl-1,2,3,4-tetrahydroquinoline-4-carboxylate

8.⁵ Tetrahydroquinoline **4a** (41.6 mg, 0.1 mmol), LiCl (12.7 mg, 0.3 mmol) and H₂O (1 drop) were stirred in DMSO (2 mL) at 130 °C for 12 h. The mixture was cooled to room temperature, washed with brine (5 mL) and extracted with ethyl acetate (10 mL). Evaporation of the solvent gave a residue that was purified by silica gel column chromatography using hexane and ethyl acetate as an eluent to furnish **8** in 77% yield as a 6:5 mixture of diastereomers.

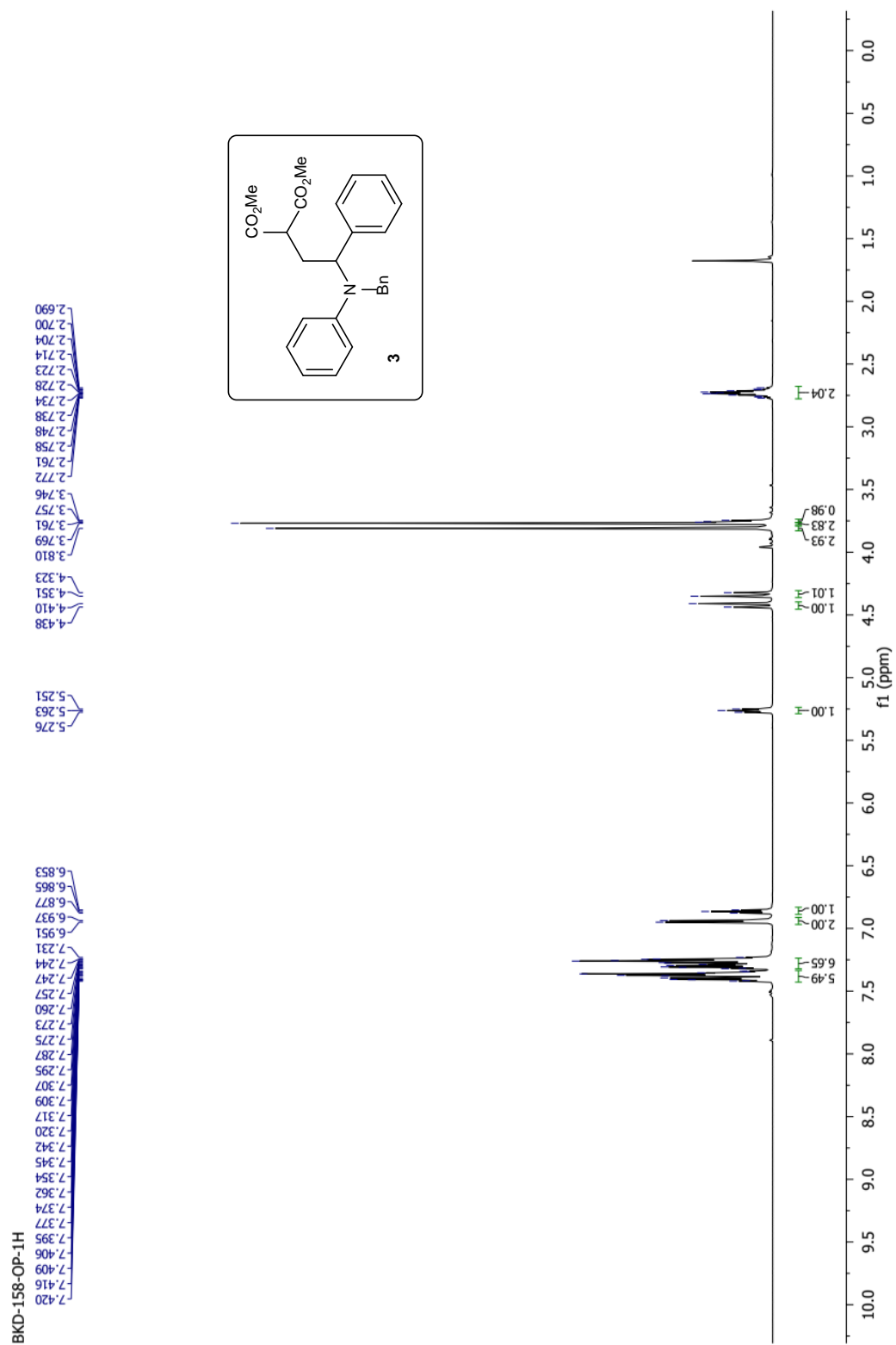
Data for major diastereomer. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.60$; liquid; yield 42% (15 mg); ¹H NMR (400 MHz, CDCl₃) δ 7.23-7.09 (m, 10H), 7.06-7.01 (m, 1H), 6.96-6.94 (m, 1H), 6.64-6.59 (m, 2H), 4.69 (d, $J = 17.2$ Hz, 1H), 4.58 (t, $J = 5.2$ Hz, 1H), 4.093 (d, $J = 17.6$ Hz, 1H), 3.75 (t, $J = 5.6$ Hz, 1H), 3.20 (s, 3H), 2.73-2.68 (m, 1H), 2.47-2.41 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 173.7, 145.1, 141.8, 138.5, 130.4, 128.7, 128.5, 127.4, 127.0, 126.6, 118.9, 116.4, 112.0, 60.6, 53.0, 51.9, 42.0 32.9; FT-IR (neat) 3028, 2952, 1734, 1602, 1494, 1400, 1451, 1196, 1162, 1124, 1014 cm⁻¹; HRMS (ESI) m/z [M+H]⁺ calcd for C₂₄H₂₄NO₂: 358.1802, found: 358.1803.

Data for minor diastereomer. Analytical TLC on silica gel, 1:9 ethyl acetate/hexane $R_f = 0.63$; sticky liquid; yield 35% (12 mg); ¹H NMR (600 MHz, CDCl₃) δ 7.25-7.10 (m, 10H), 7.03-7.00 (m, 1H), 6.95 (d, $J = 7.8$ Hz, 1H), 6.60-6.54 (m, 2H), 4.66 (t, $J = 5.4$ Hz, 1H), 4.63 (d, $J = 17.4$ Hz, 1H), 4.14 (d, $J = 17.4$ Hz, 1H), 3.67 (s, 3H), 3.62-3.59 (m, 1H), 2.57-2.52 (m, 1H), 2.19-2.16 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 174.7, 144.9, 143.2, 138.3, 128.9, 128.8, 128.7, 128.1, 127.6, 127.0, 126.9, 126.6, 119.2, 116.4, 111.7, 59.8, 52.9, 52.2, 40.6, 33.4; FT-IR (neat) 3018, 2952, 1733, 1601, 1400, 1451, 1250, 1162, 1123, 1013 cm⁻¹; HRMS (ESI) m/z [M+H]⁺ calcd for C₂₄H₂₄NO₂: 358.1802, found: 358.1804.

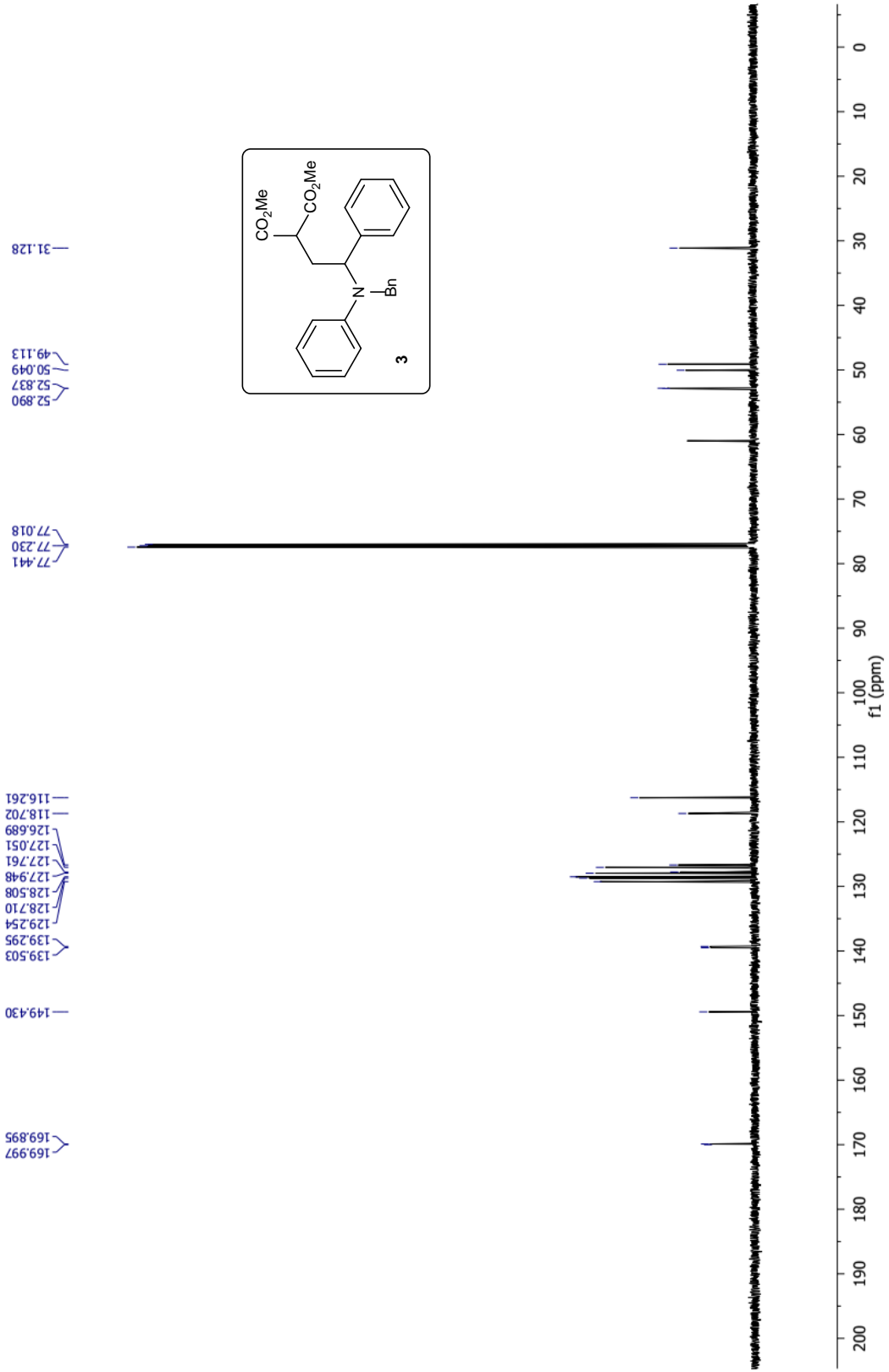
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2. For preparation of chiral cyclopropane, see: K. Sapeta and M. A. Kerr, *J. Org. Chem.*, 2007, **72**, 8597.
3. Preparation of *N*-alkylanilines, see: X. Ling, Y. Xiong, R. Huang, X. Zhang, S. Zhang and C. Chen, *J. Org. Chem.* 2013, **78**, 5218.
4. F. Burg, M. Gicquel, S. Breitenlechner, A. Pothig and T. Bach, *Angew. Chem., Int. Ed.*, 2018, **57**, 2953.
5. S. Das, S. Chakrabarty, C. G. Daniliuc and A. Studer, *Org. Lett.* 2016, **18**, 2784.

NMR spectra



BKD-158-OP-13C



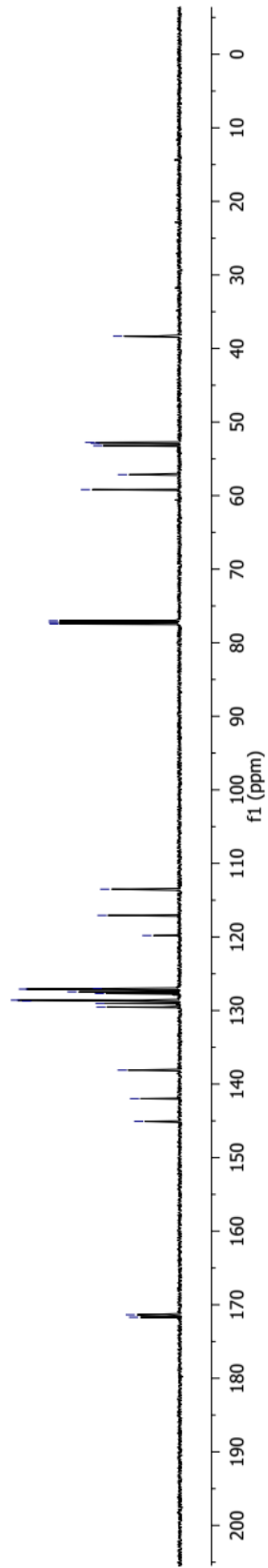
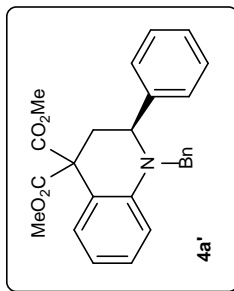
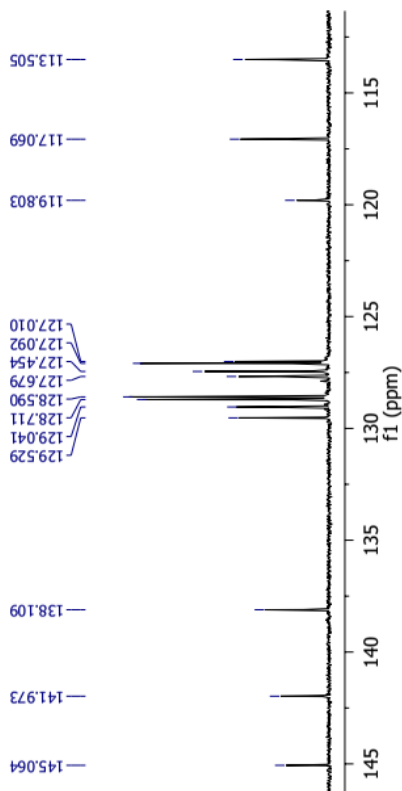
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57.151
53.217
52.875
52.755
38.321

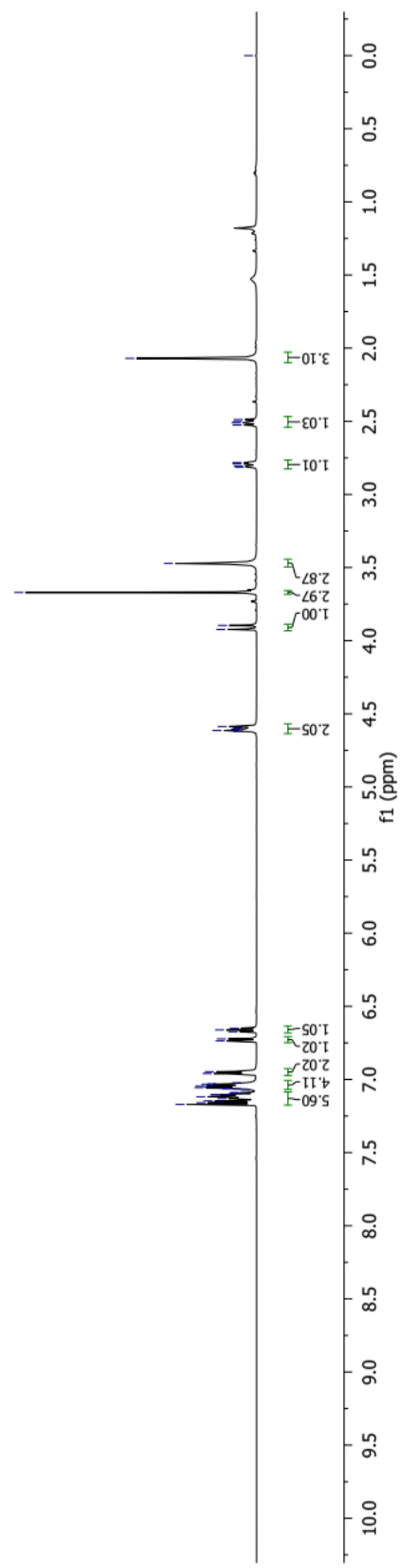
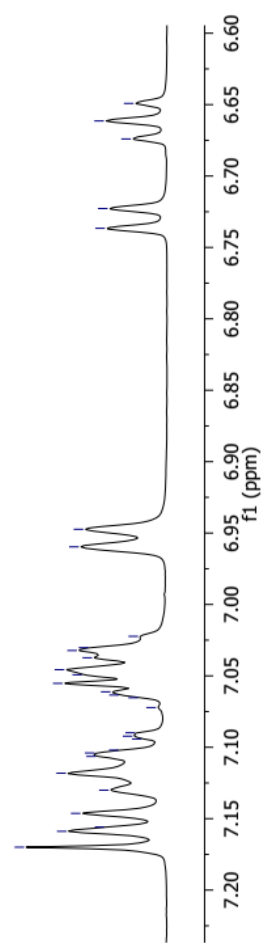
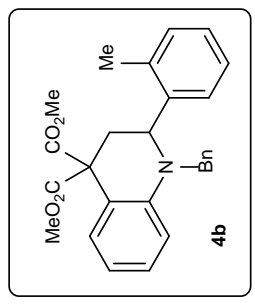
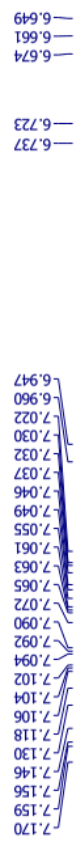
77.441
77.230
77.018

145.064
141.973
138.109
129.064
129.529
129.041
128.711
128.590
127.679
127.454
127.092
127.010
119.803
117.069
113.505

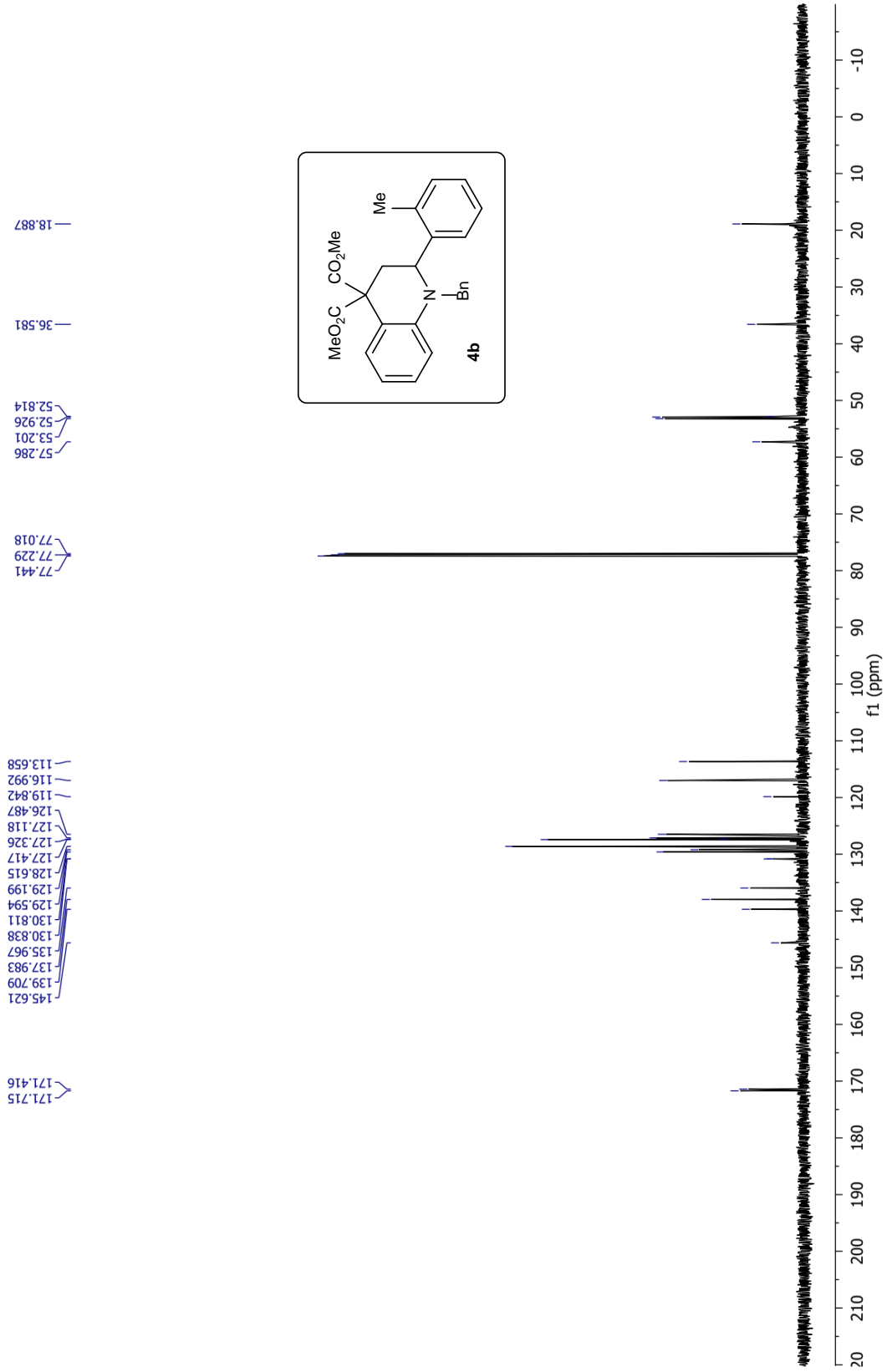
171.706
171.365



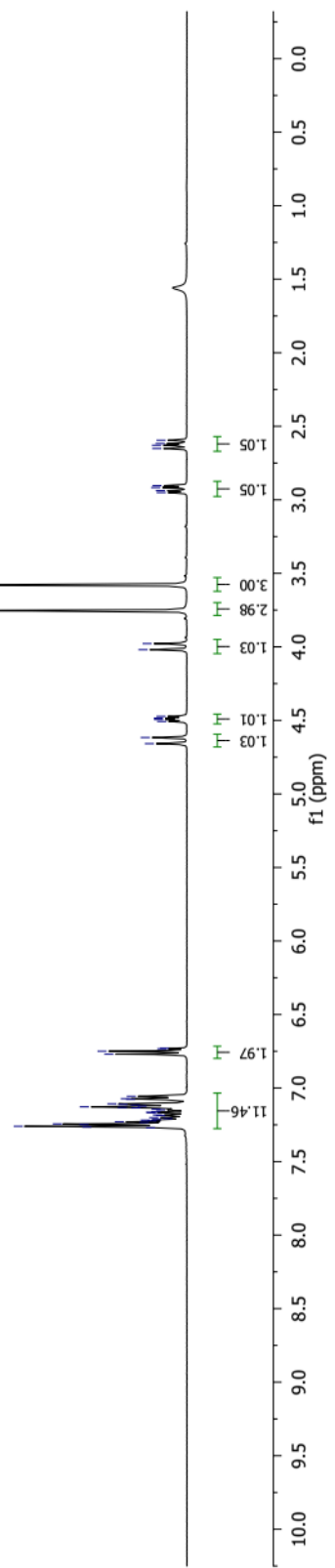
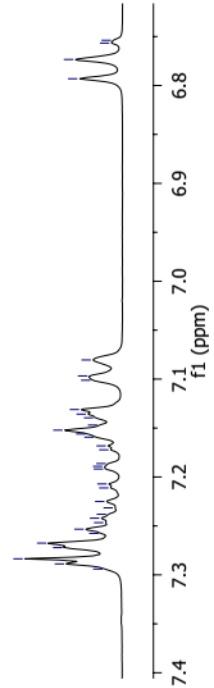
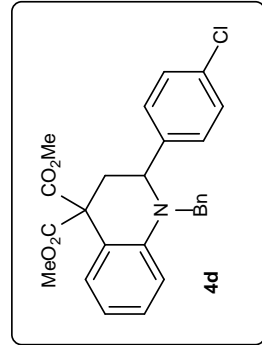
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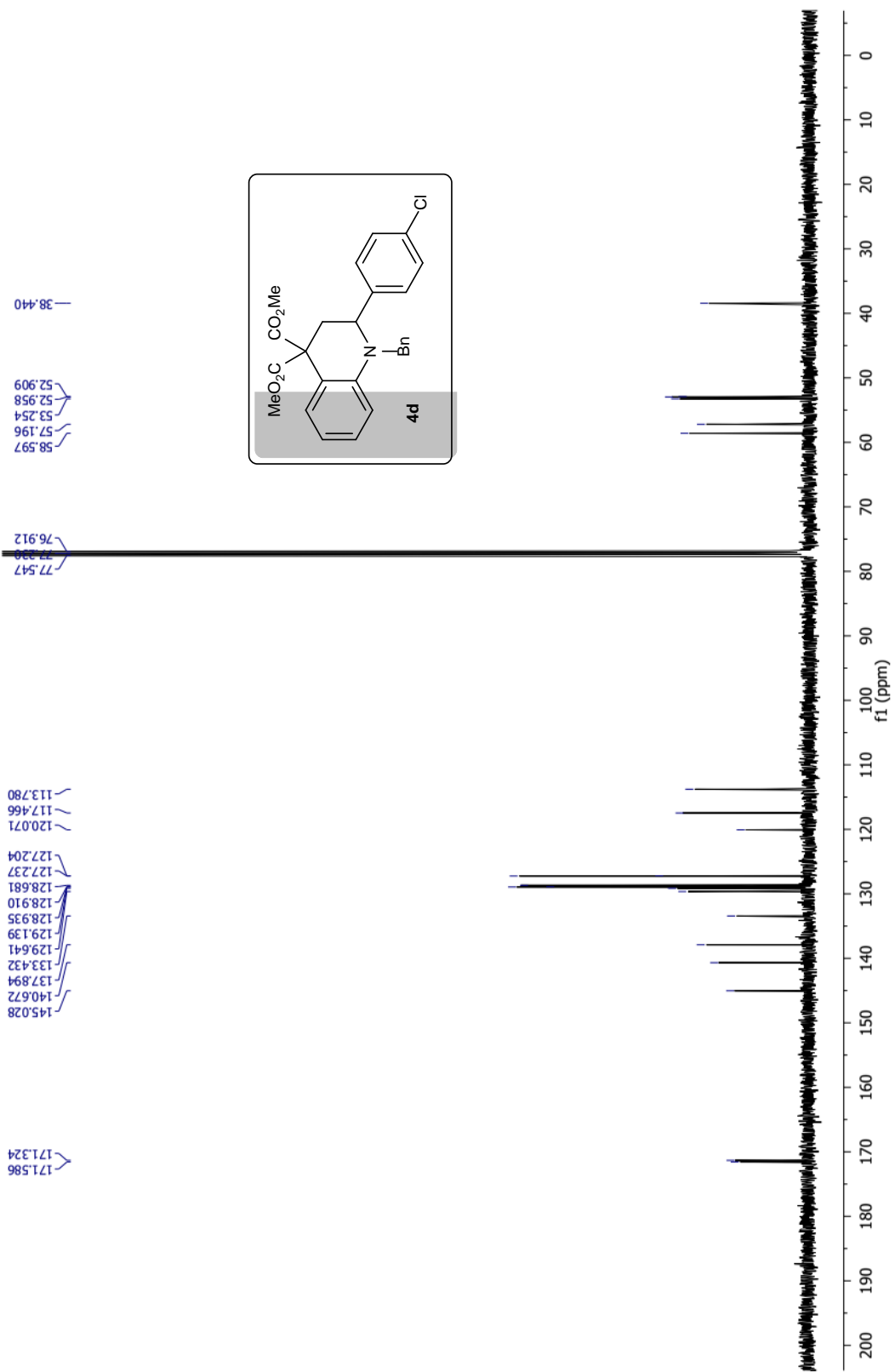
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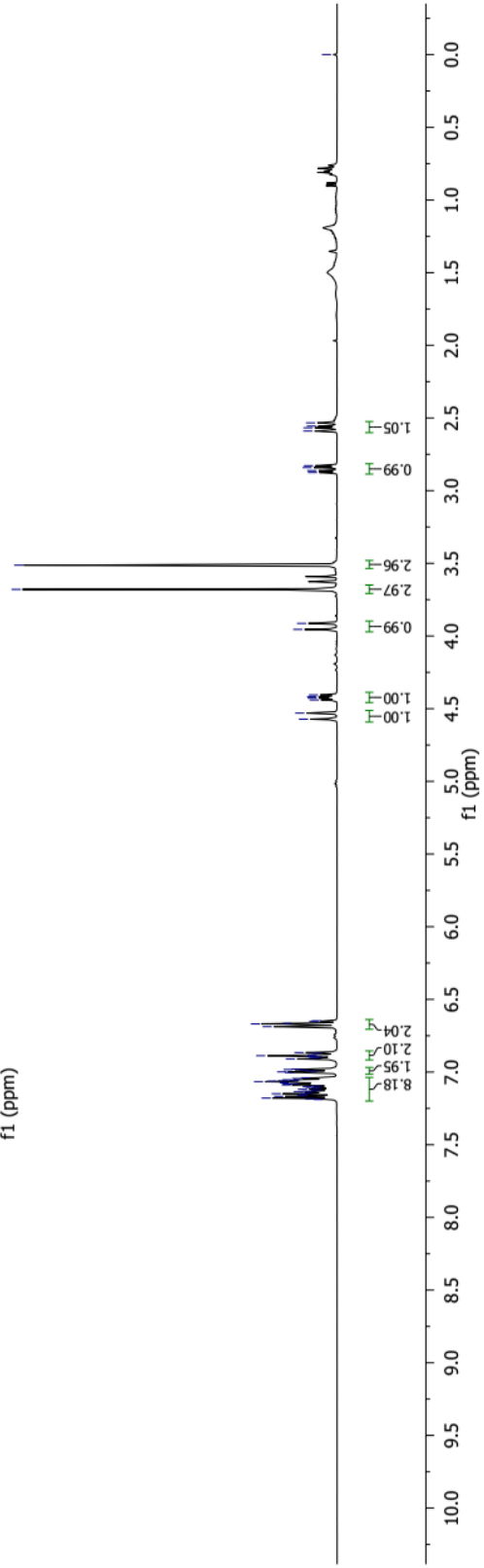
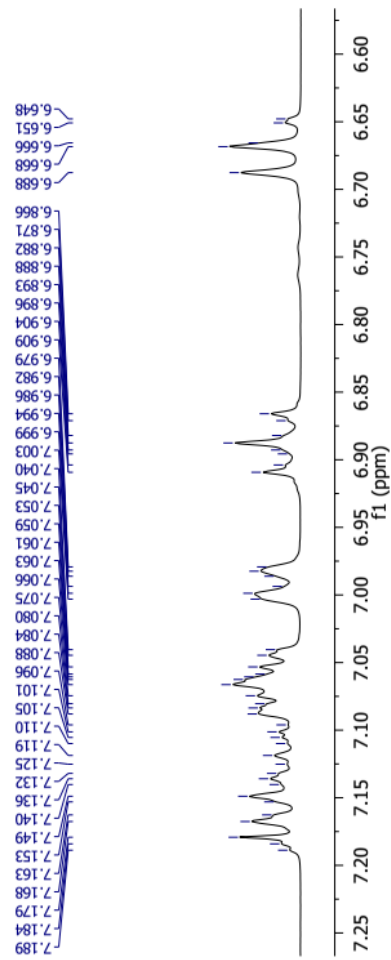
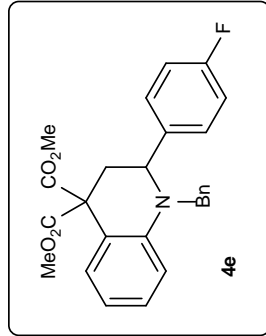
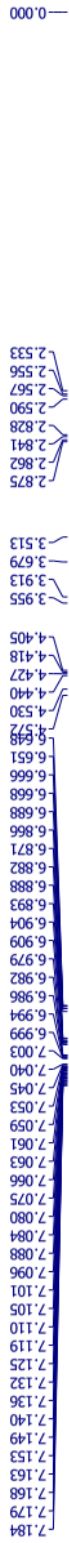
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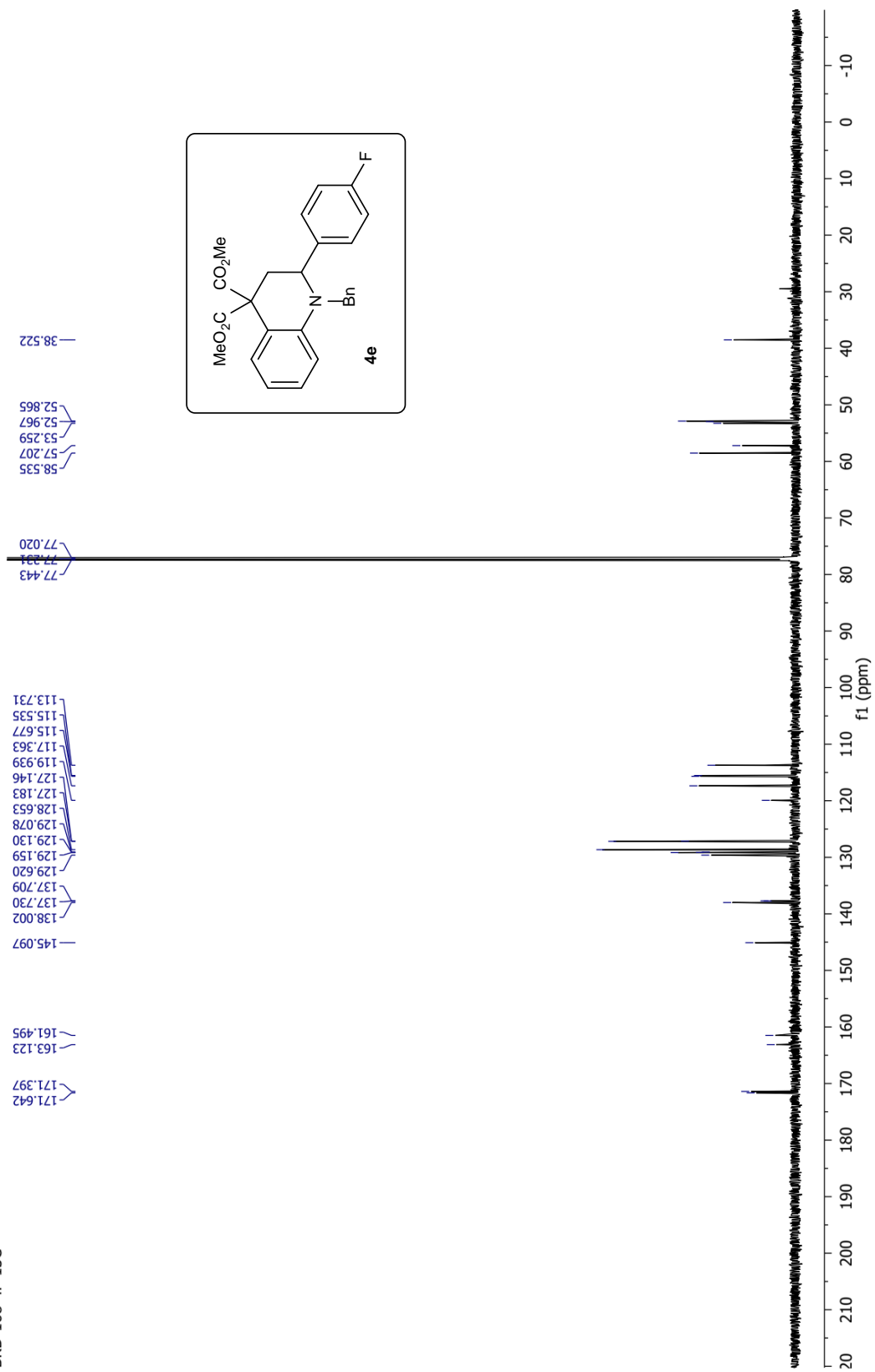
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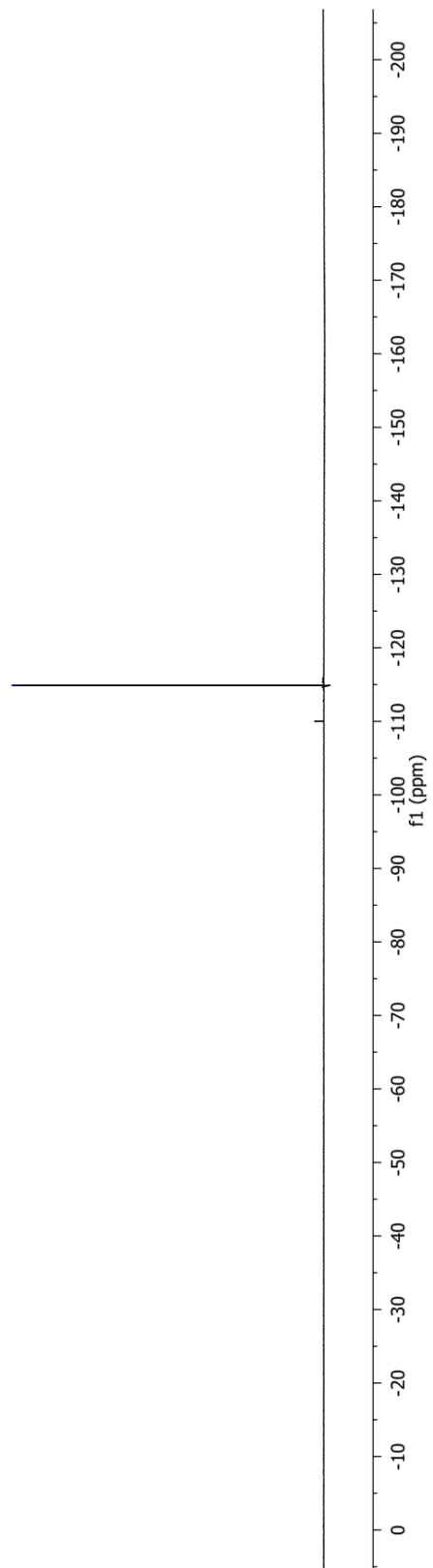
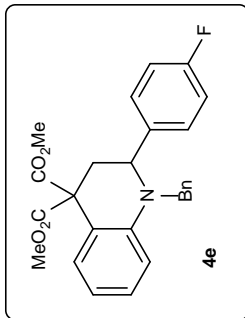


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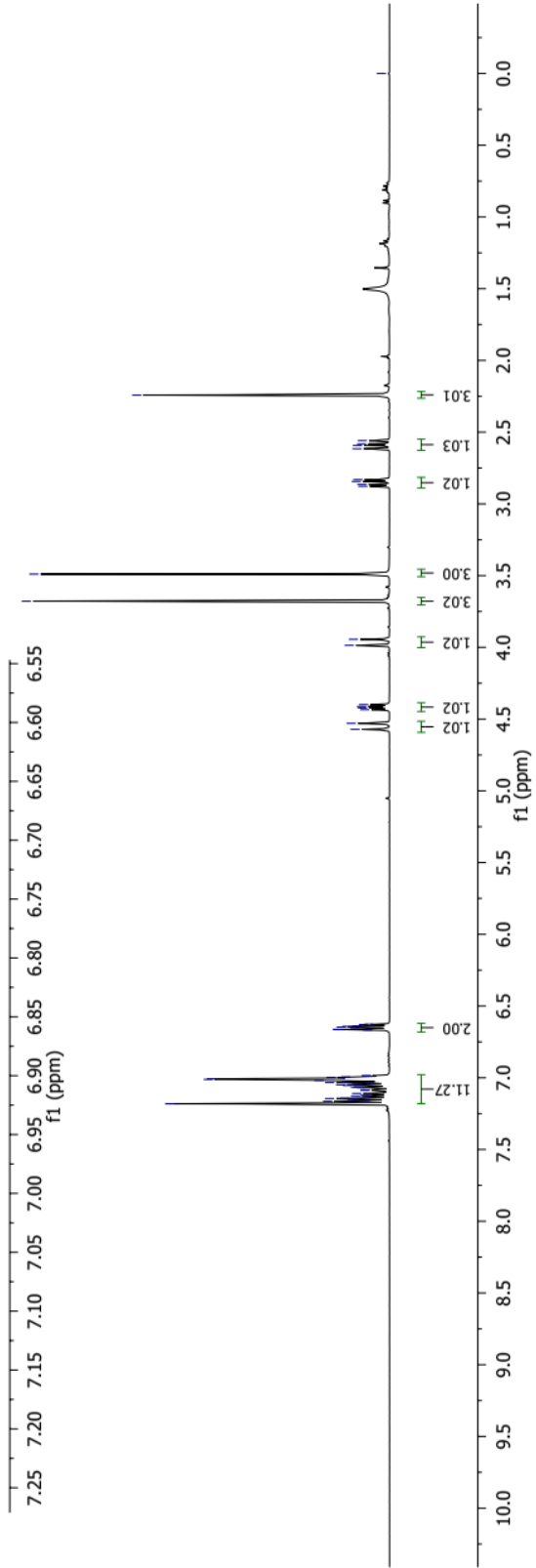
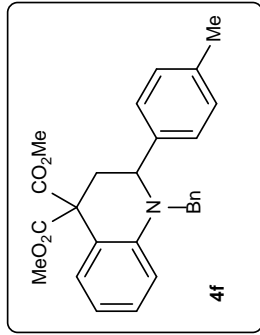


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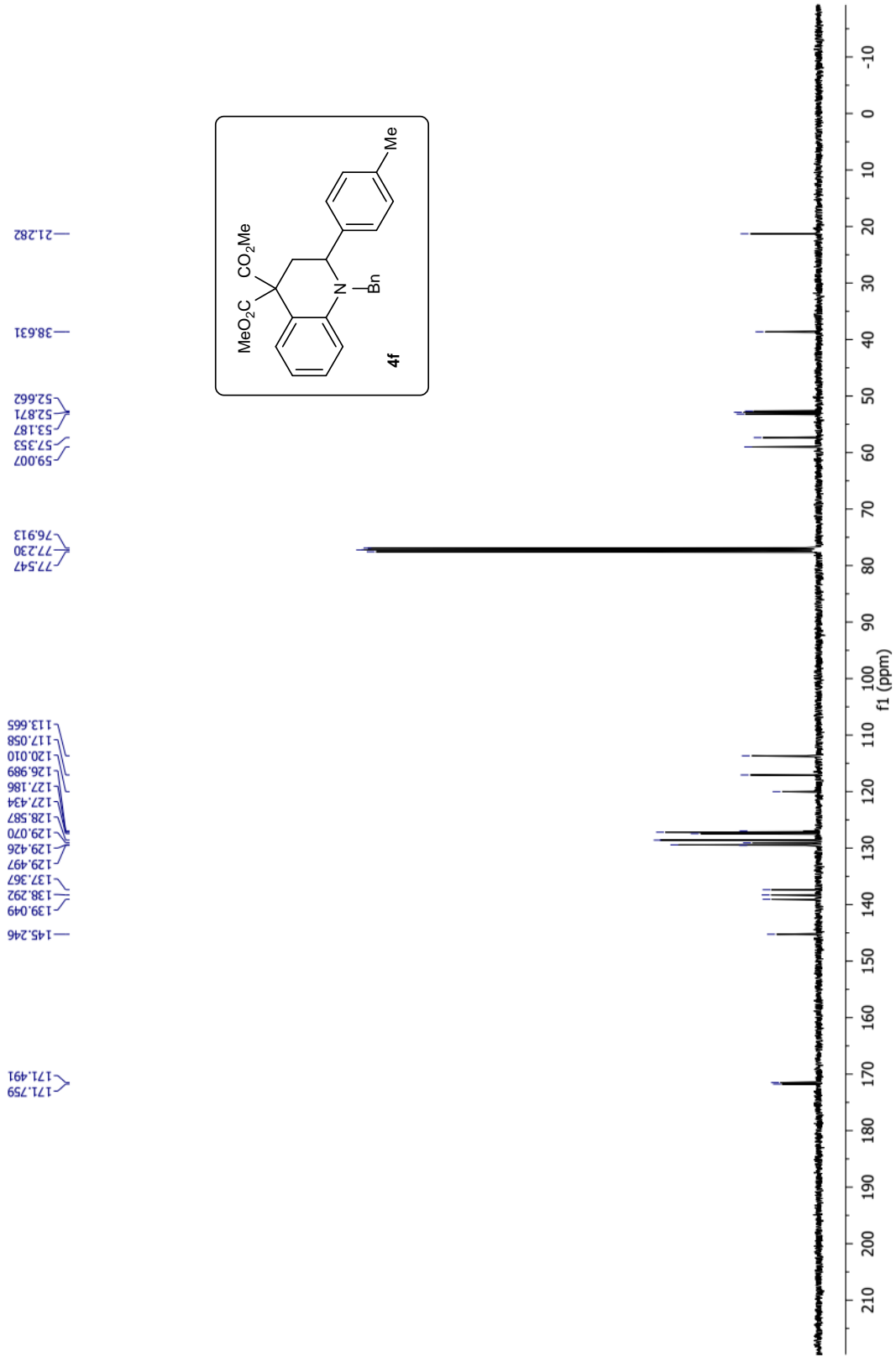
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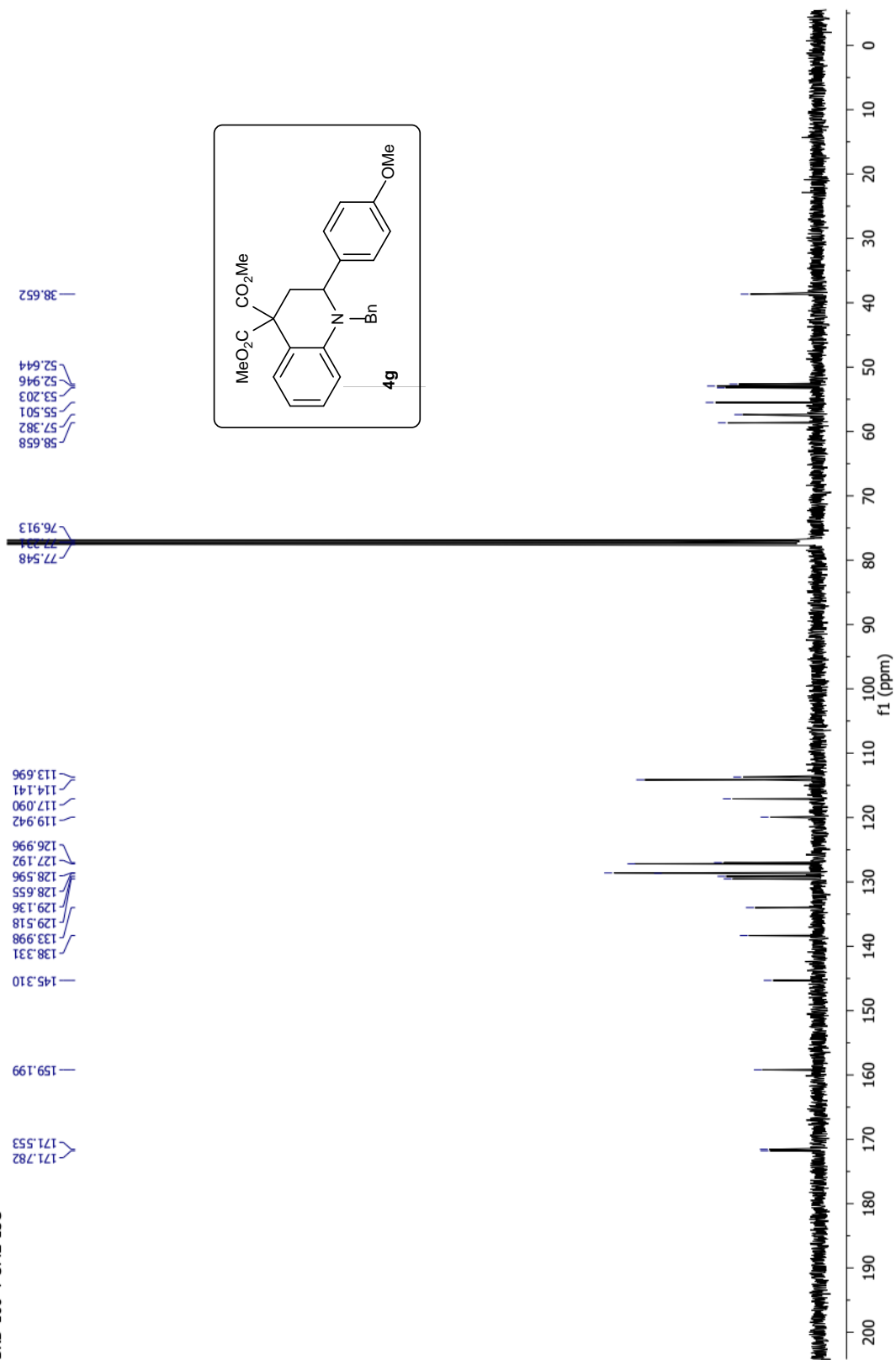
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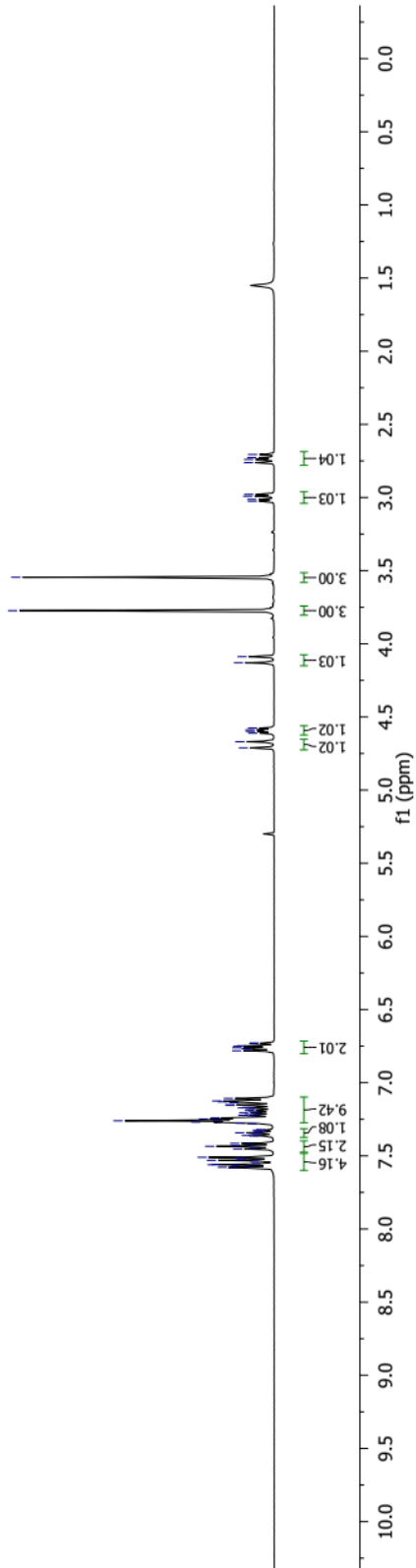
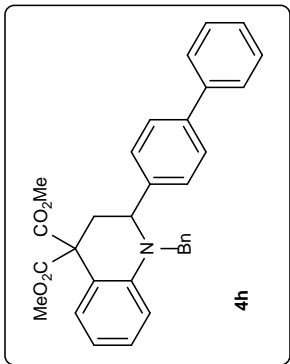
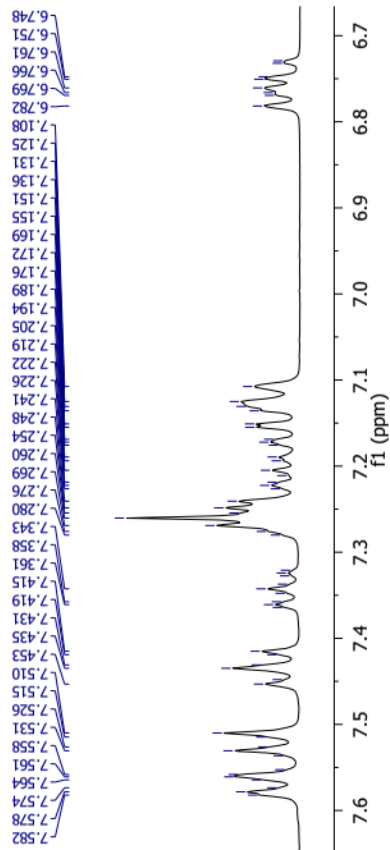
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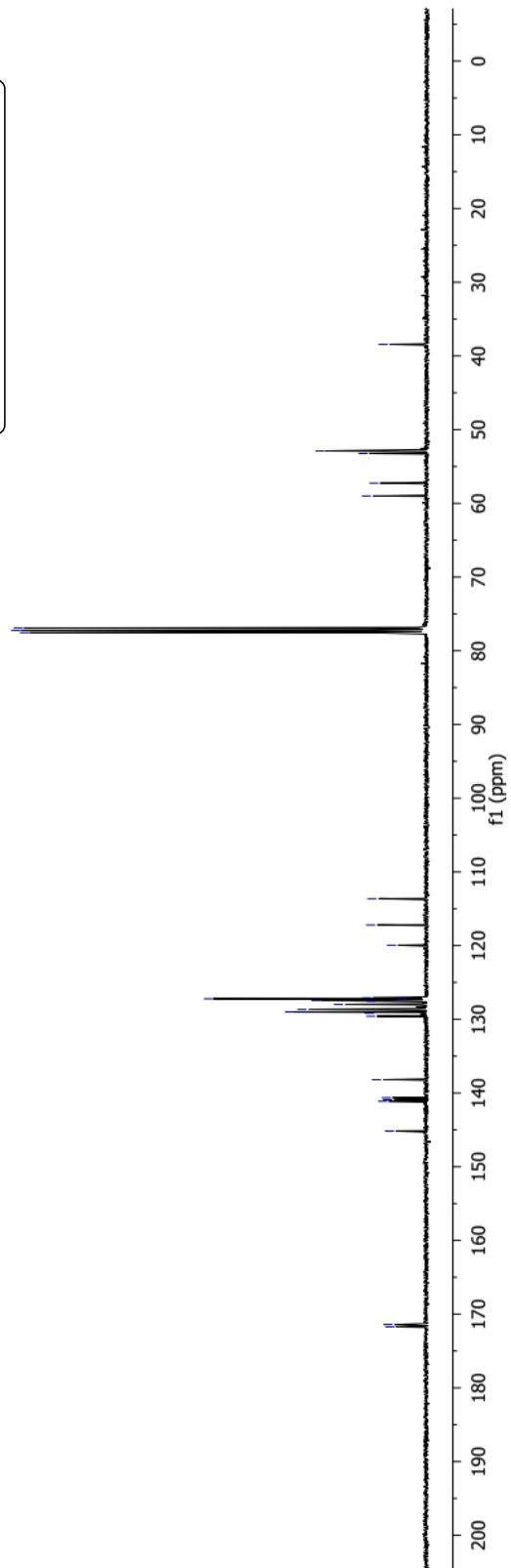
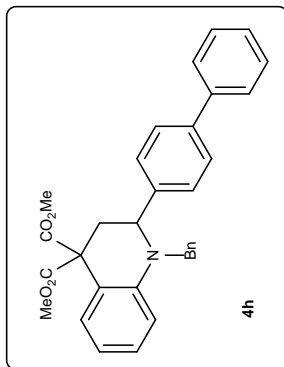
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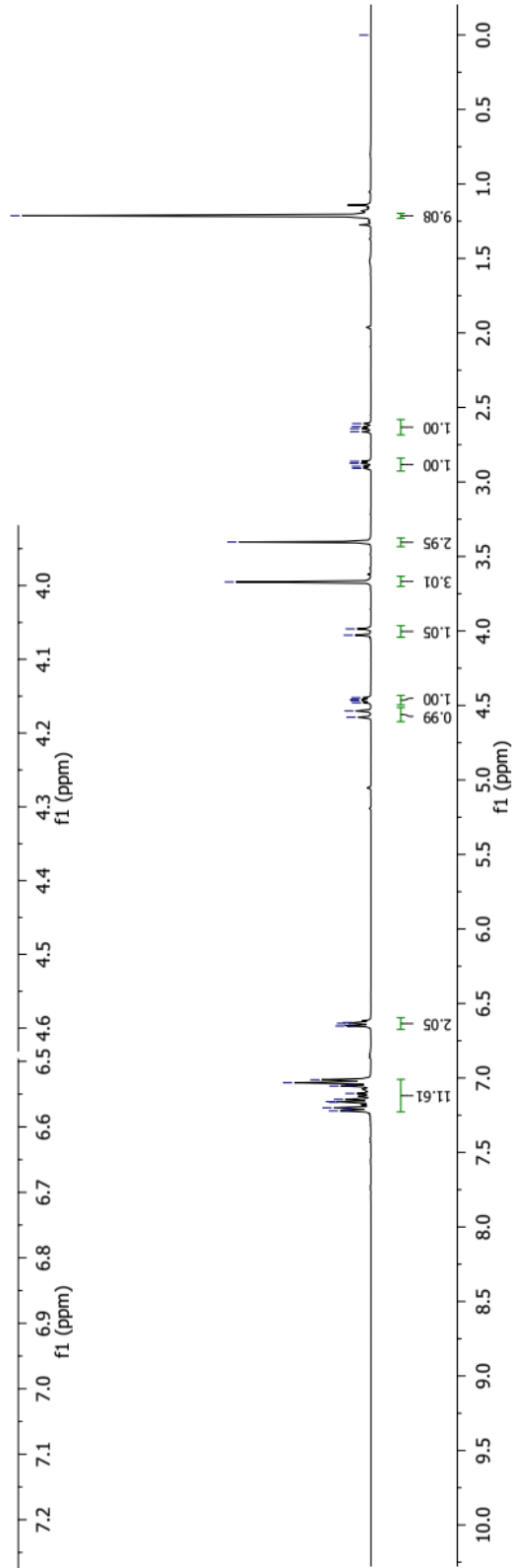
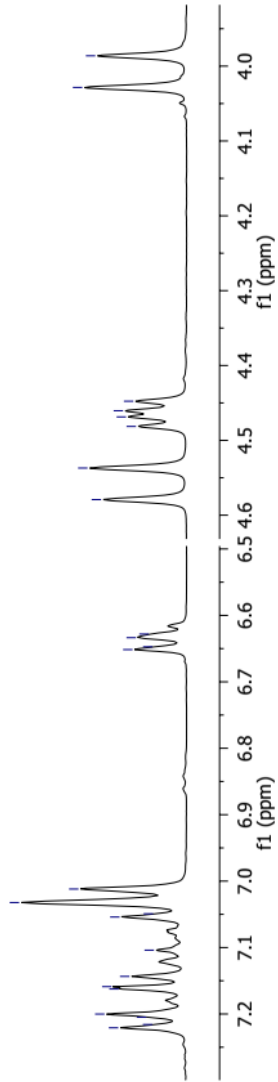
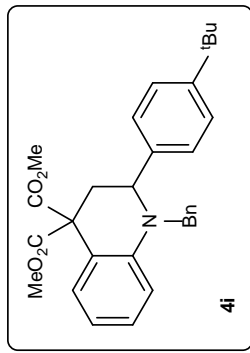
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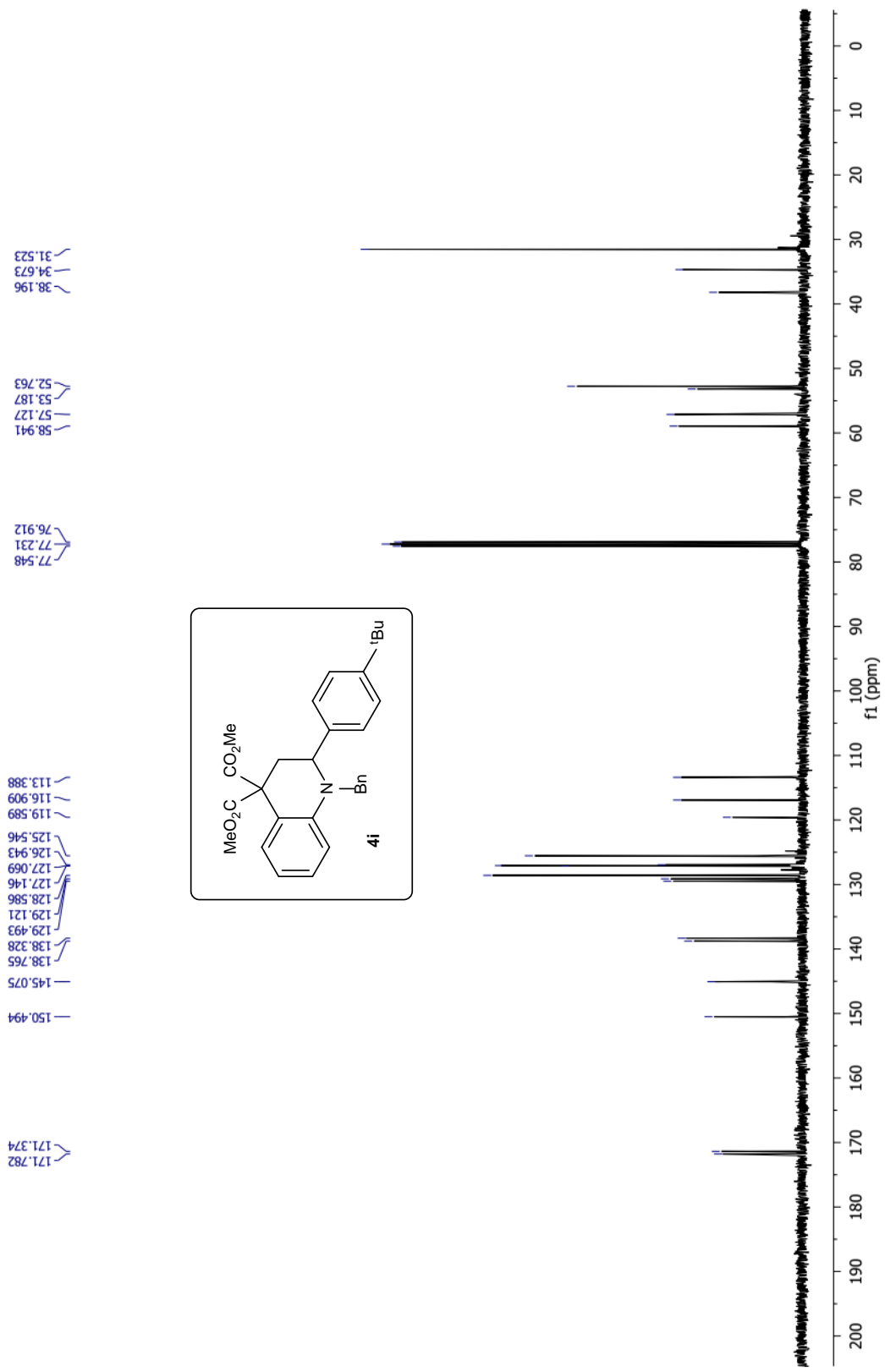
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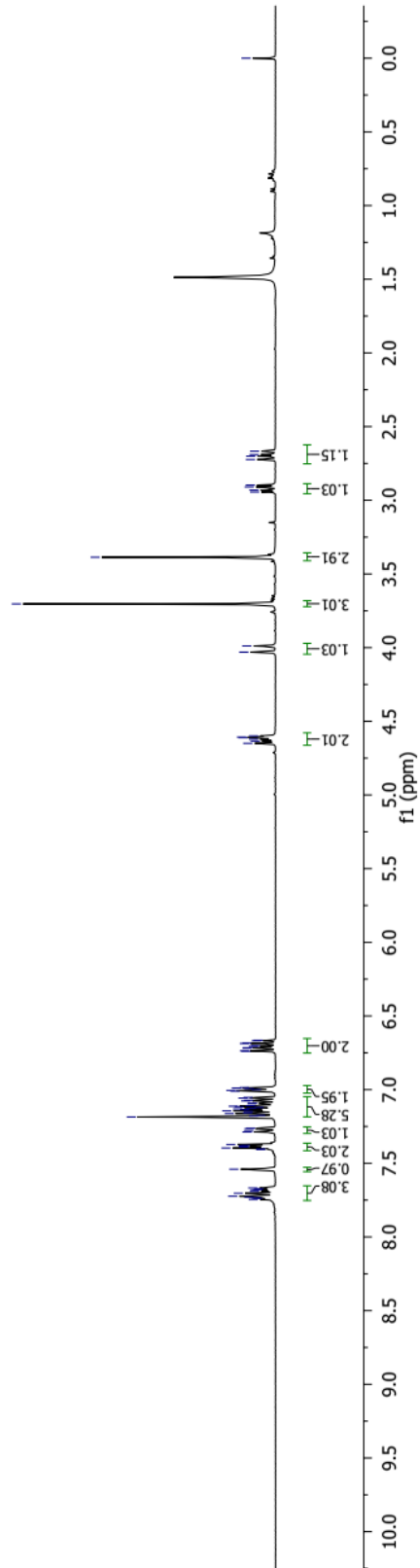
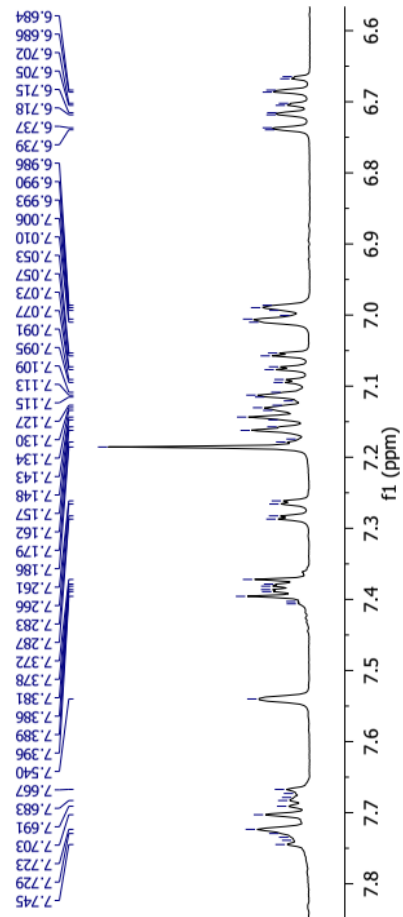
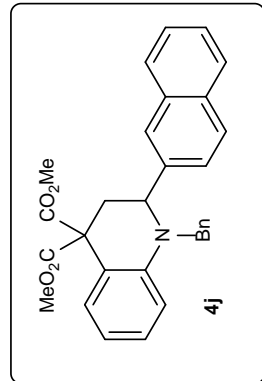
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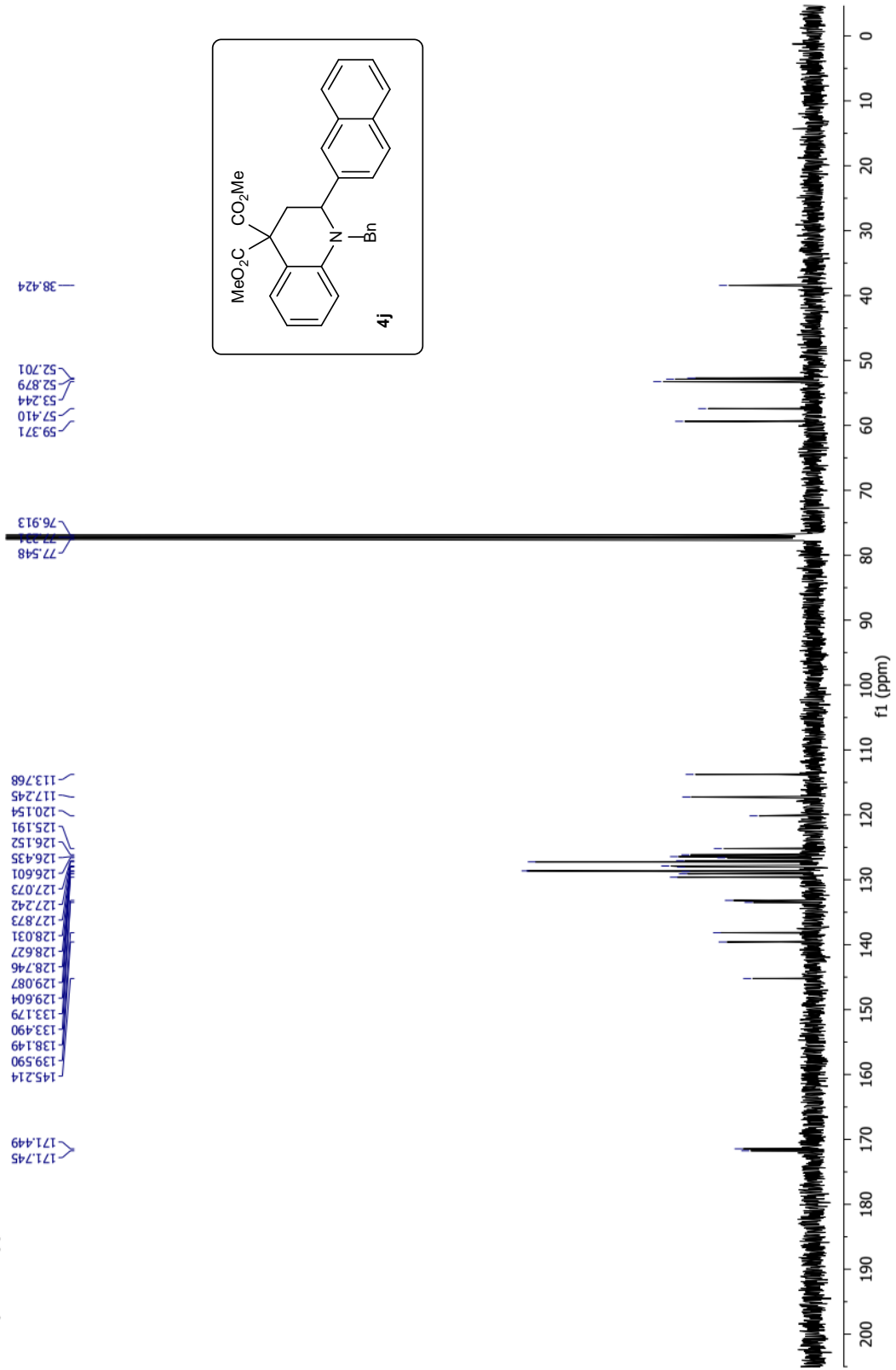
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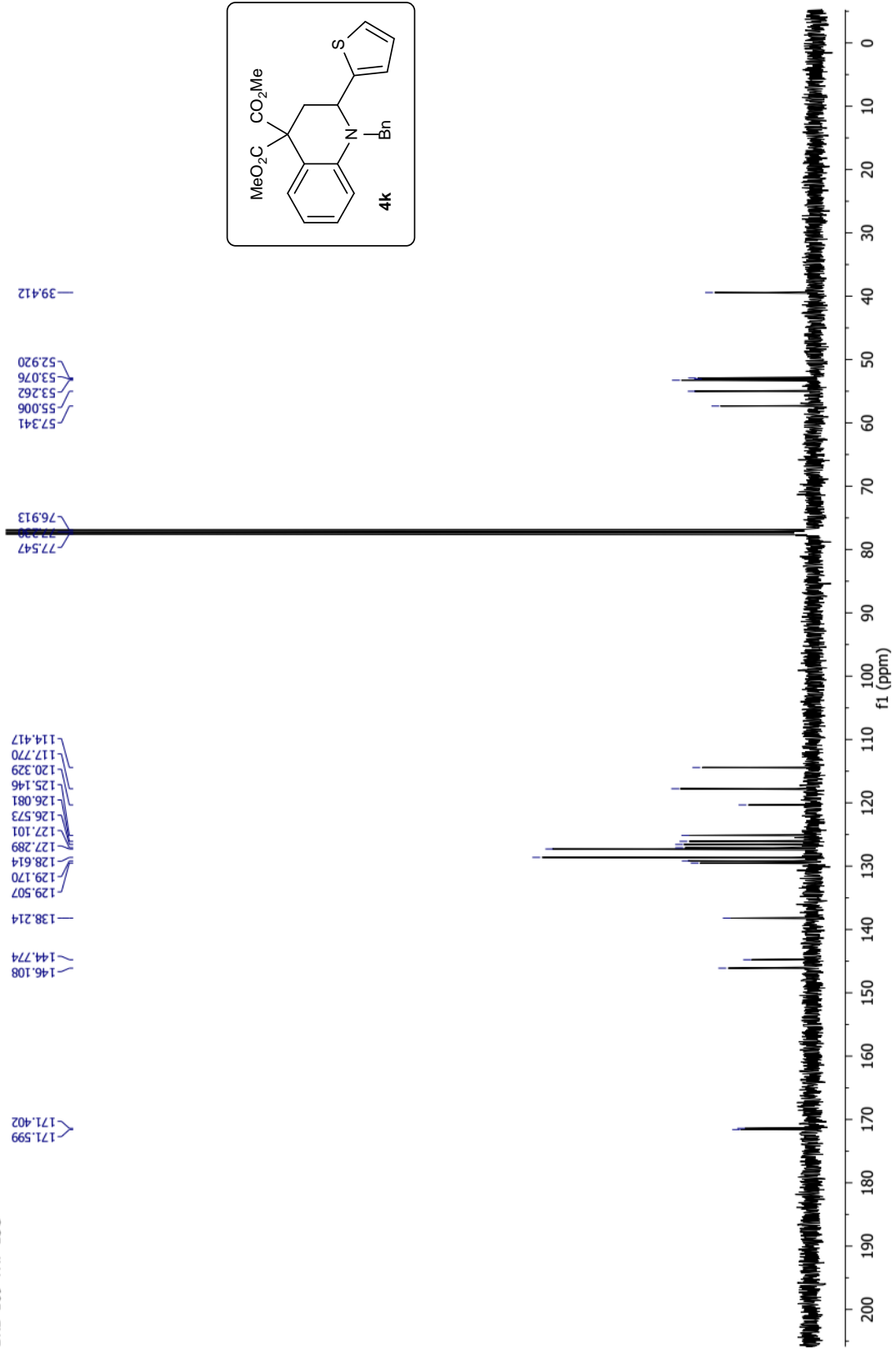
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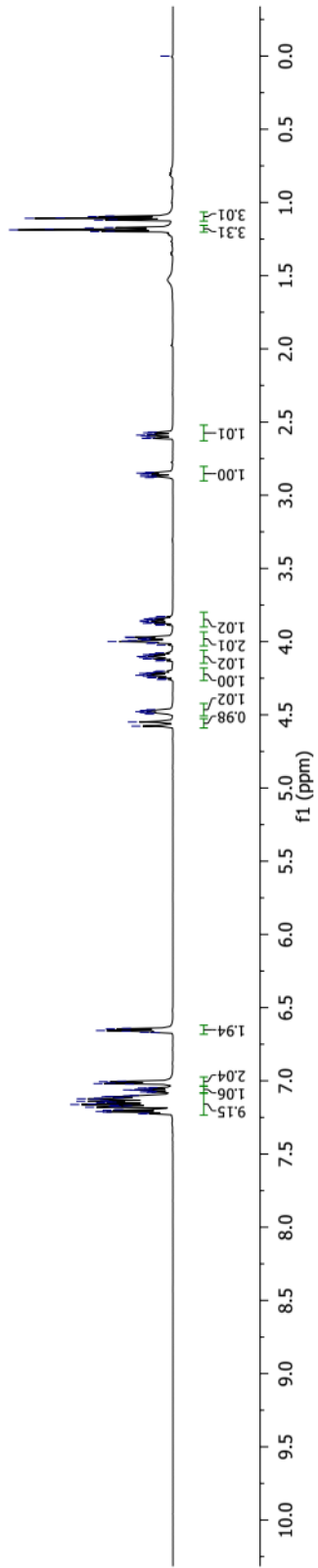
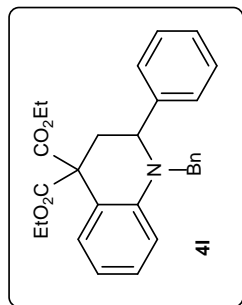
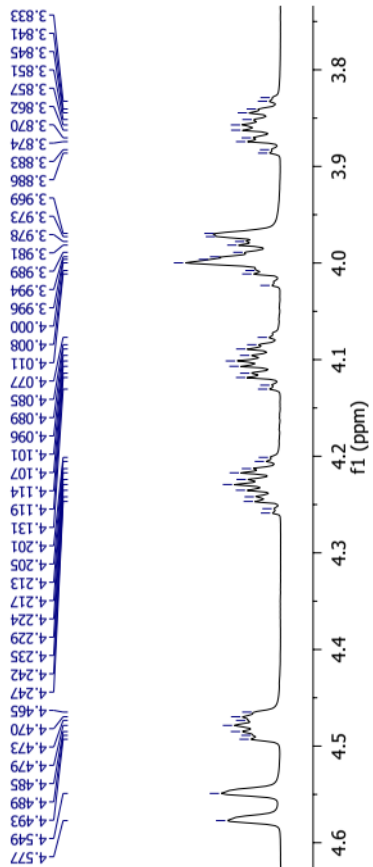
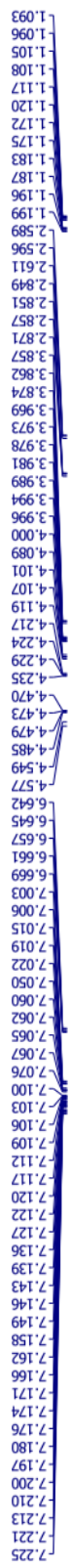
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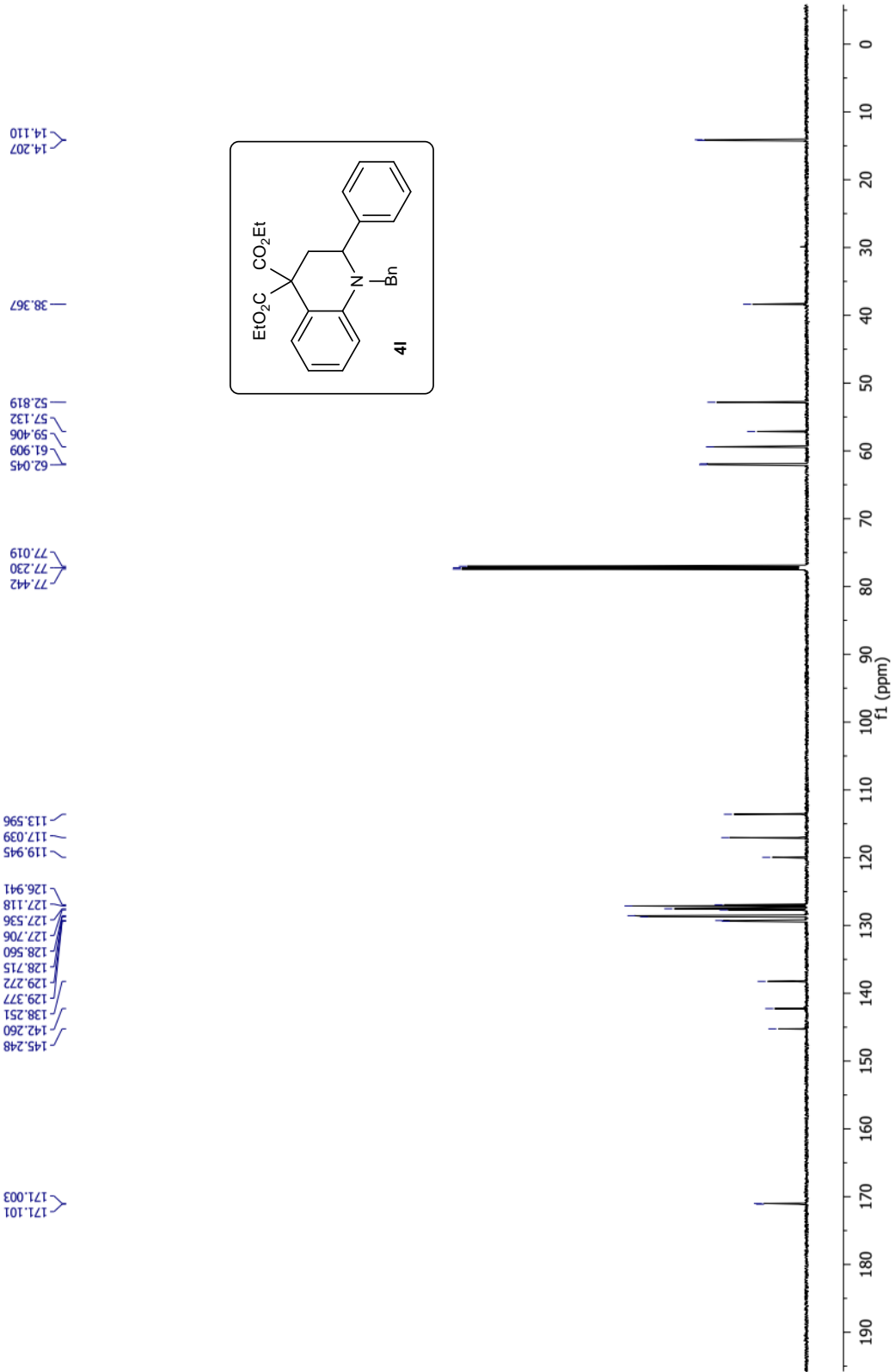
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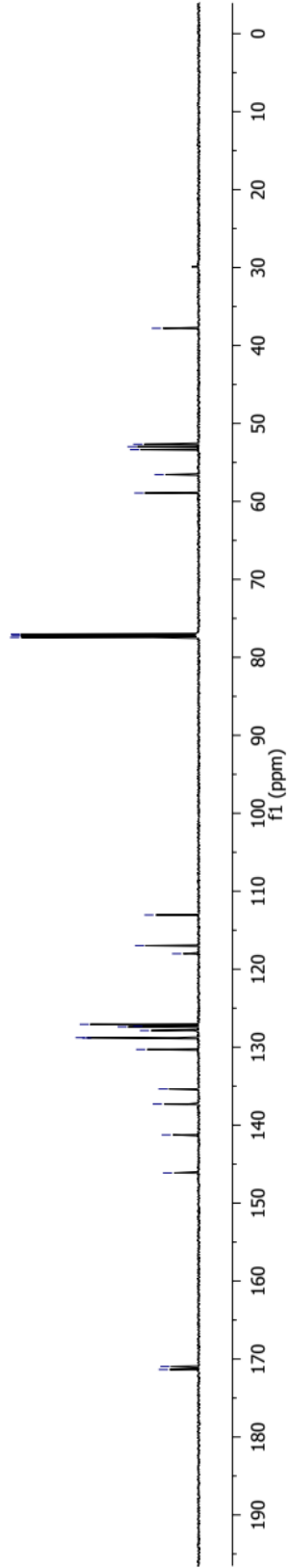
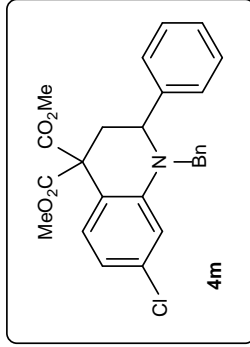
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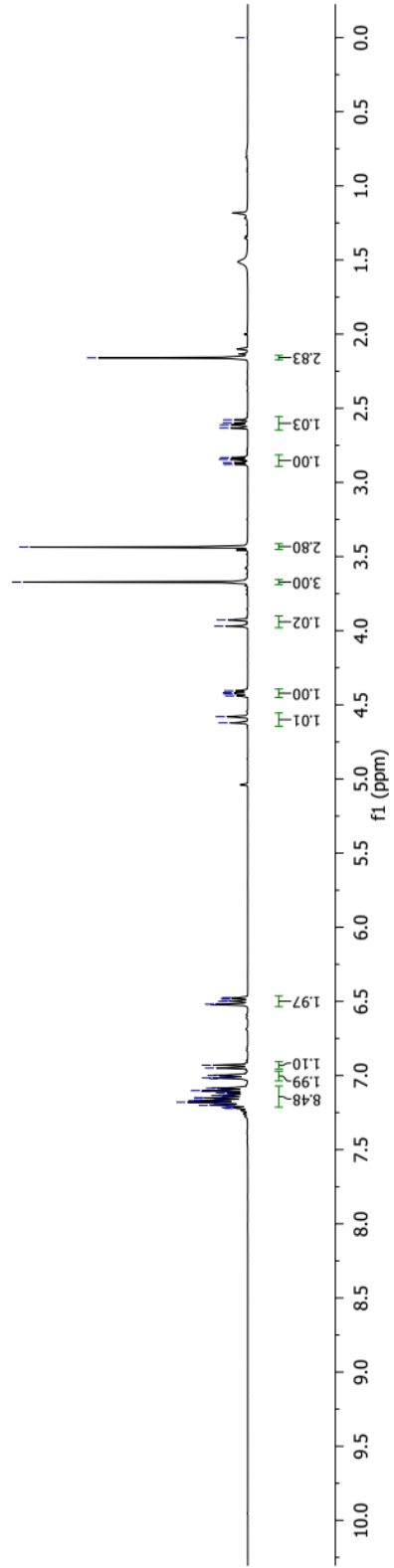
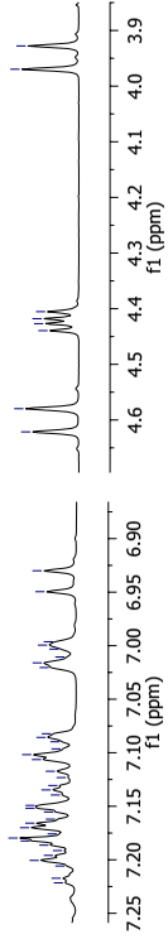
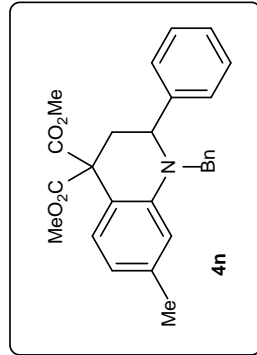
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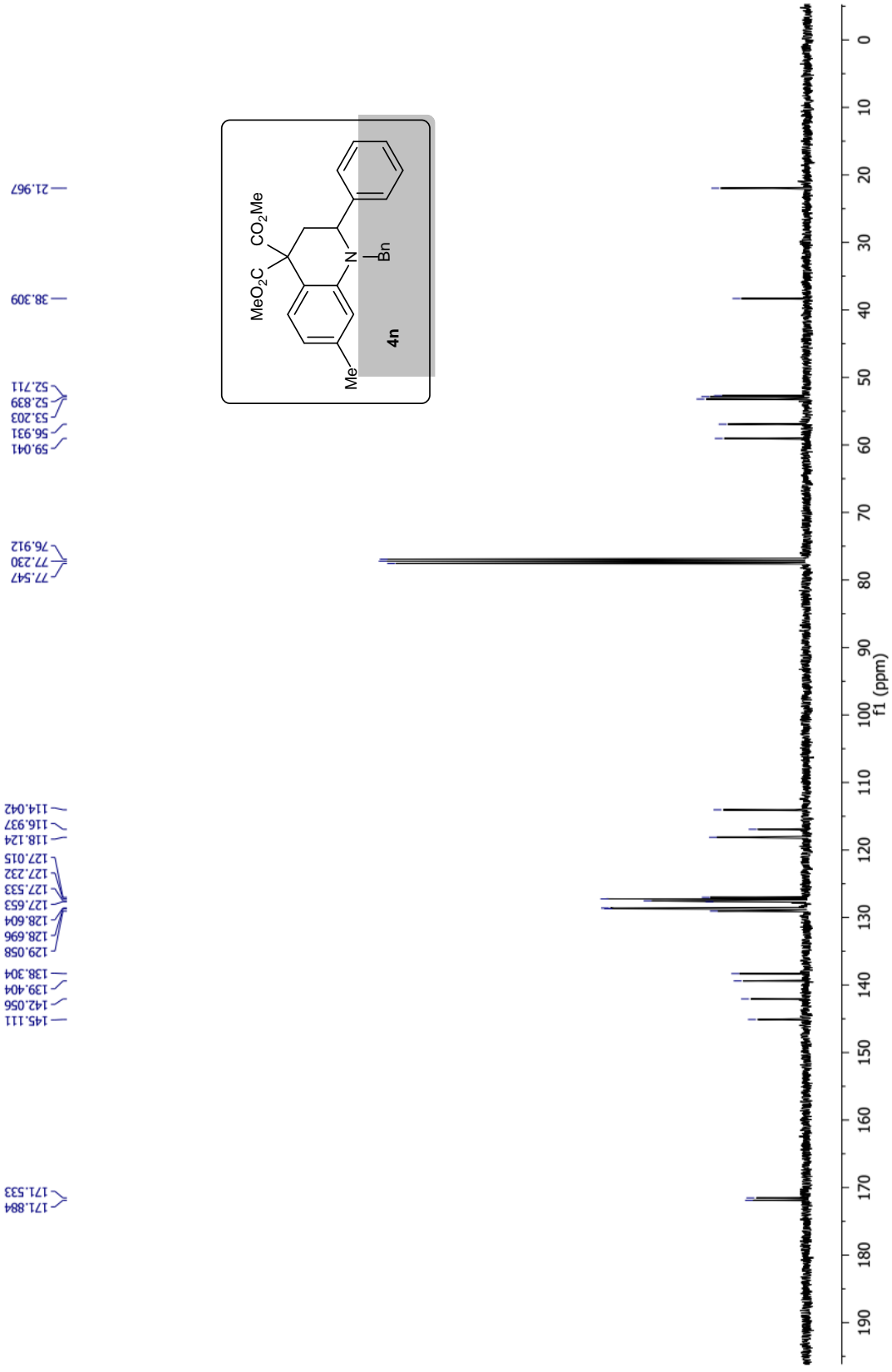
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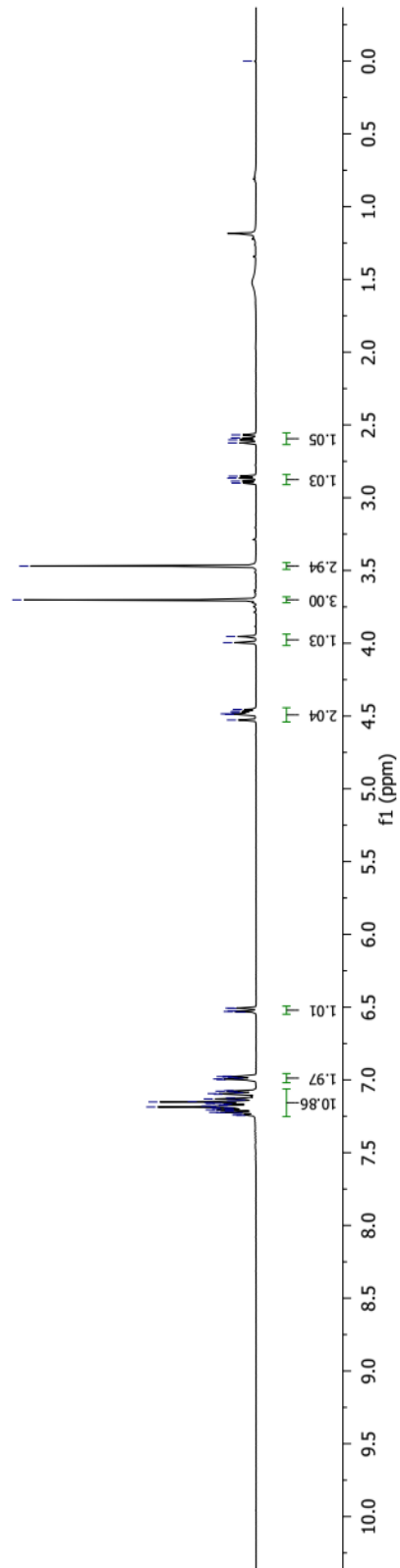
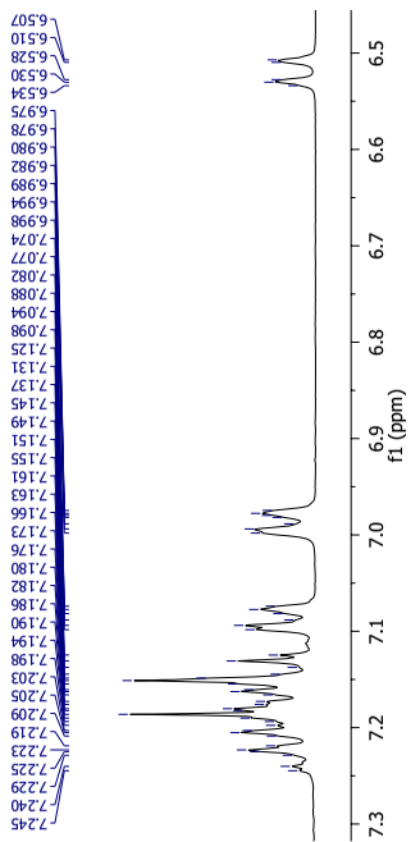
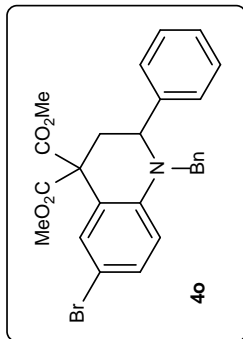
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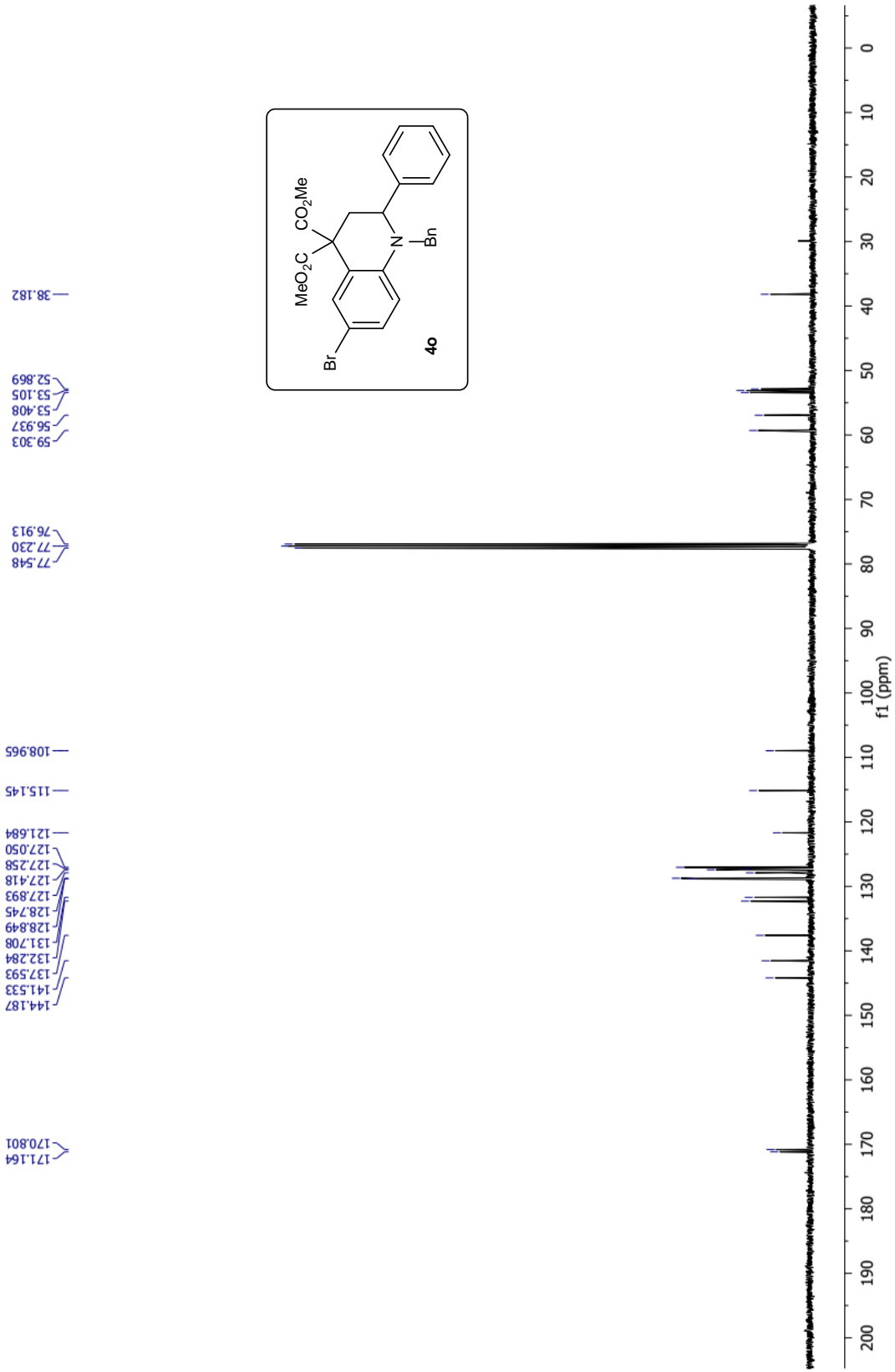
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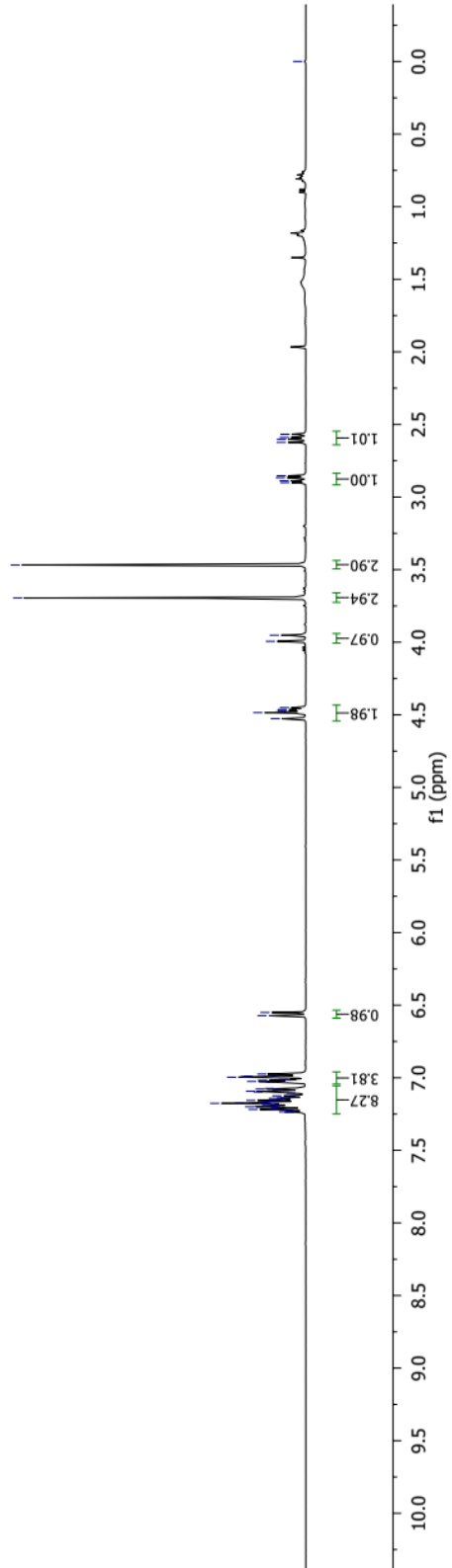
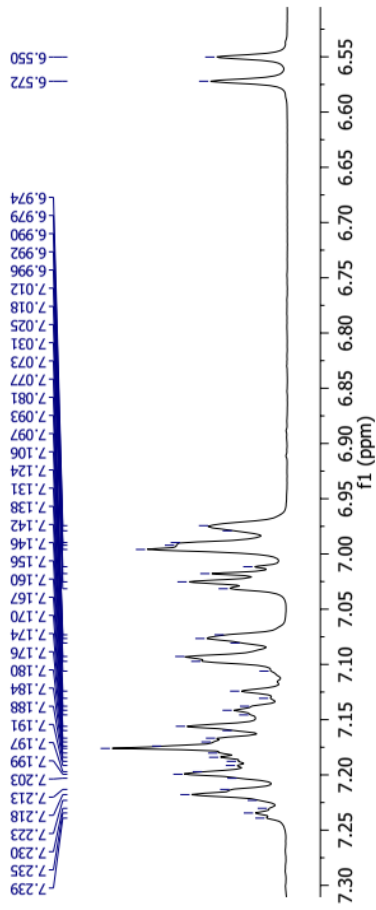
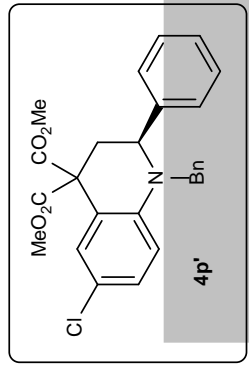
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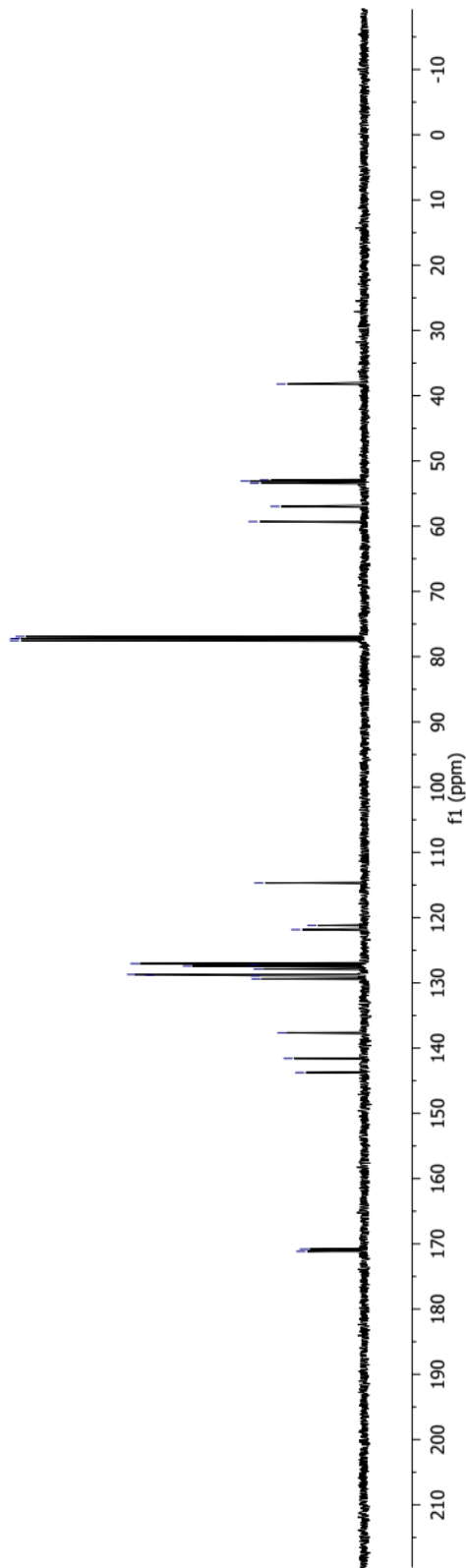
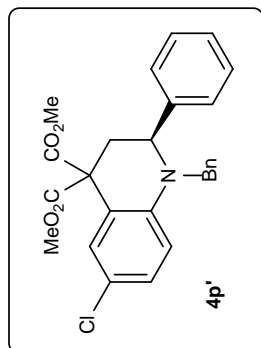
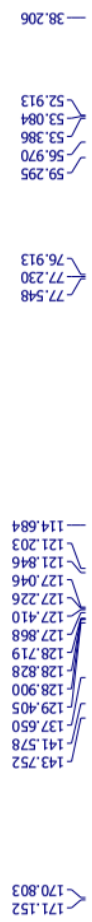
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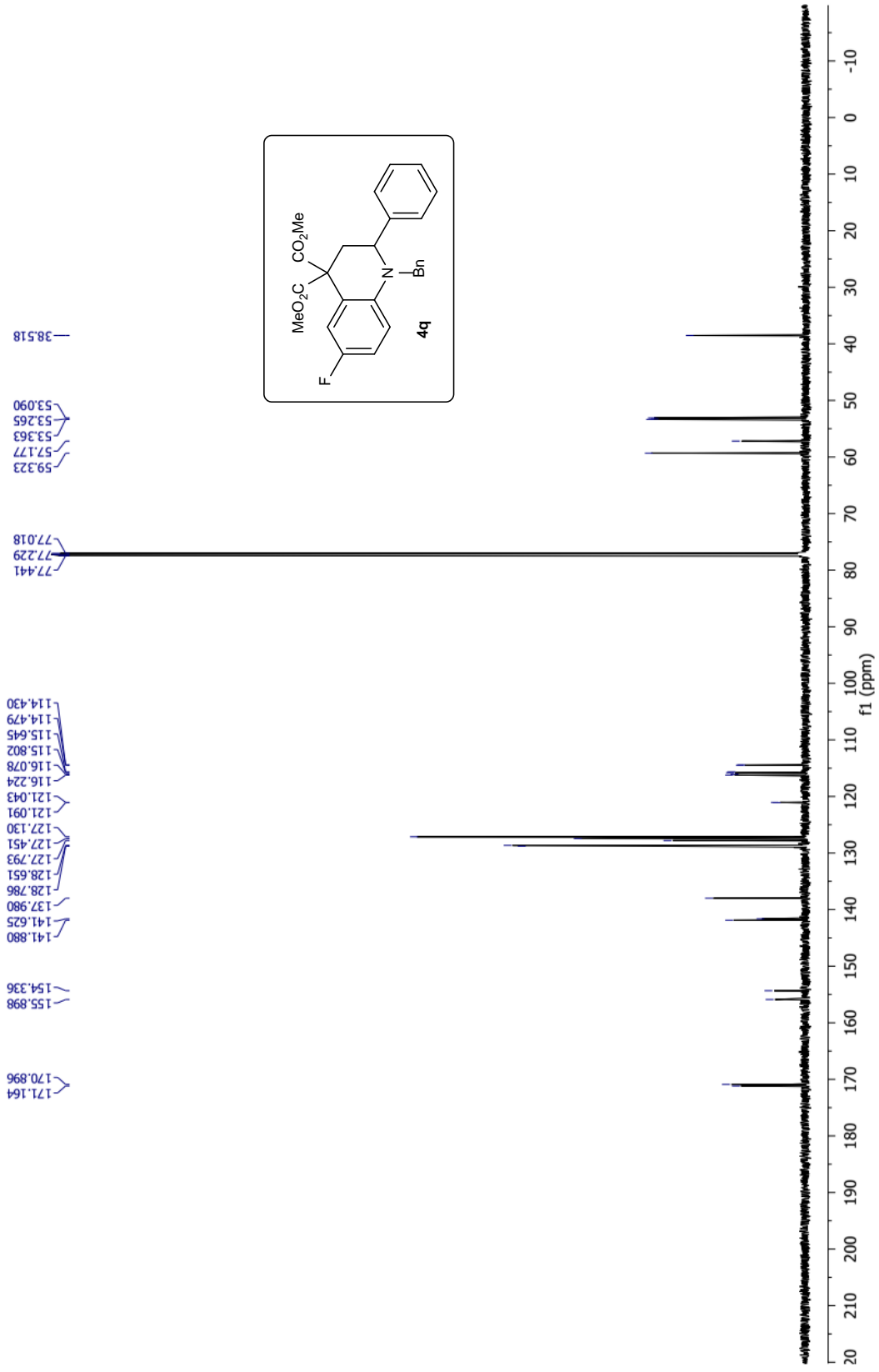
BKD-176-4CL-AM-1H



BKD-176-4CL-AM-13C

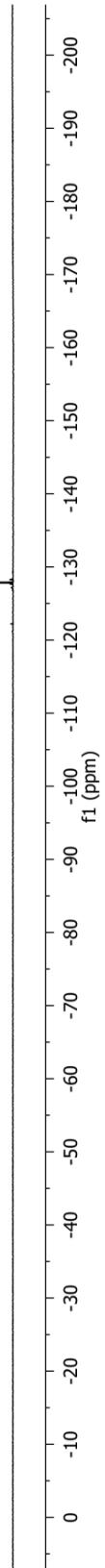
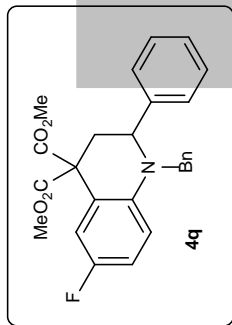


BKD-179-4-F-13C

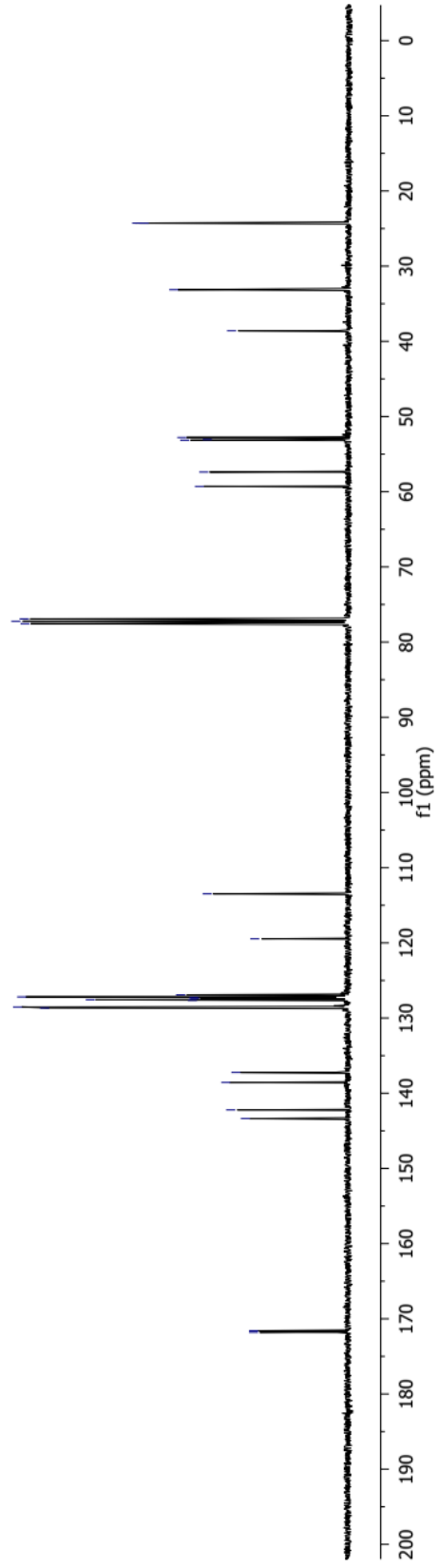
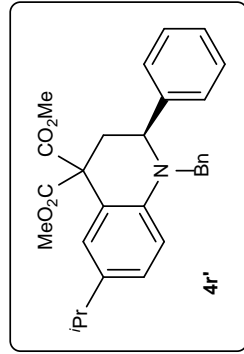


BKD-179-4F-19F

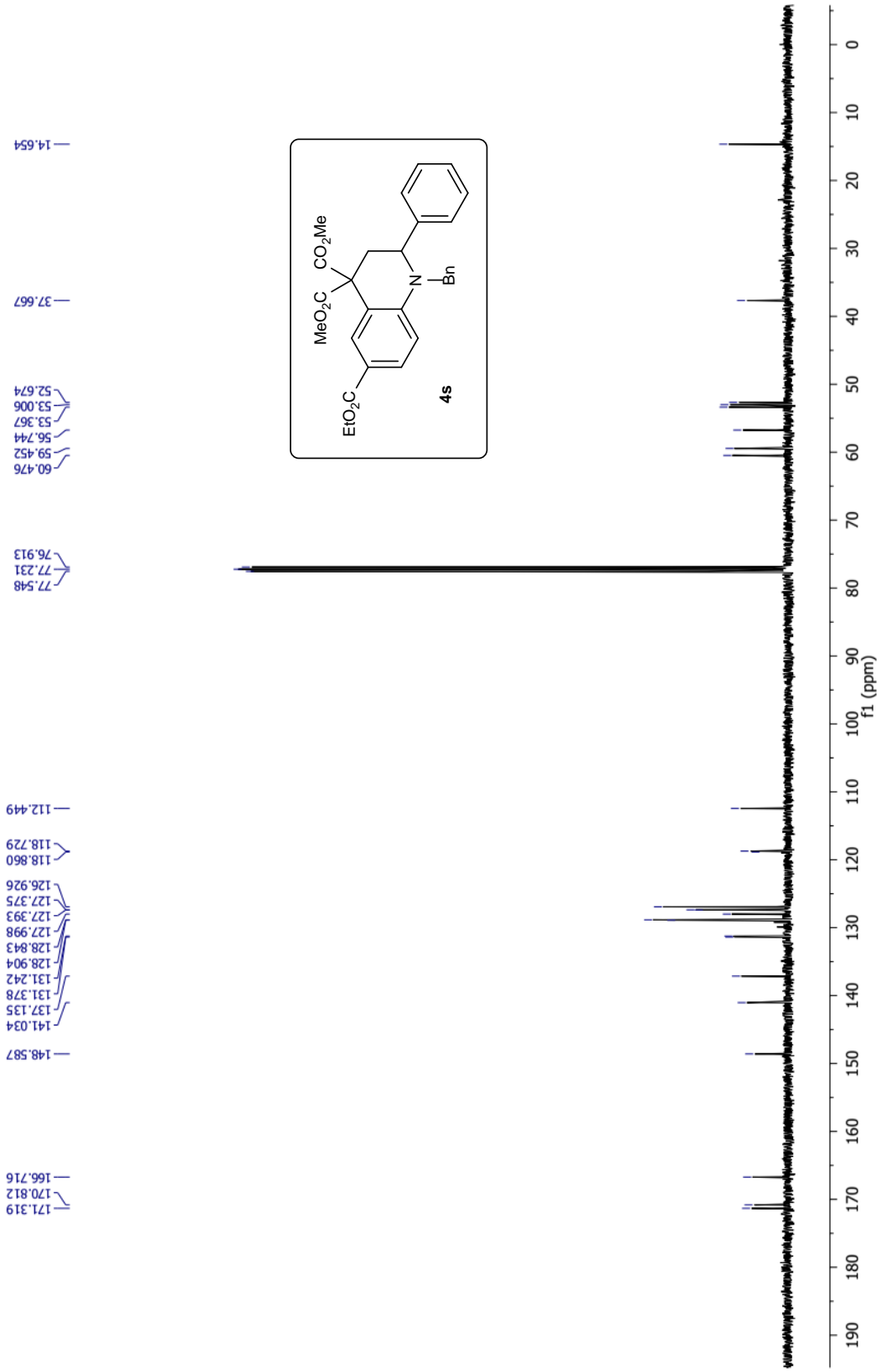
— -127.871



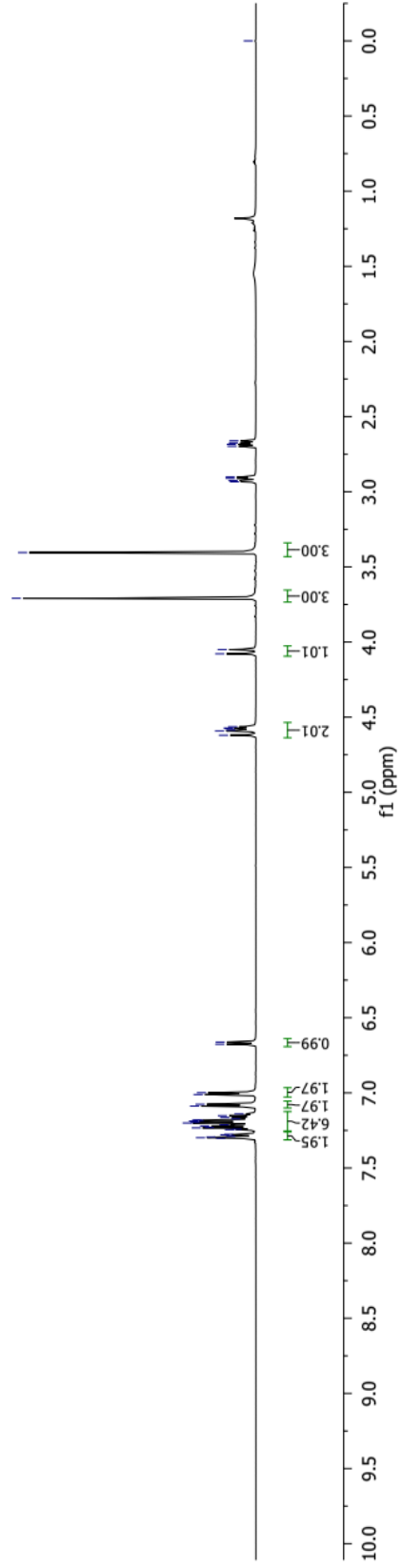
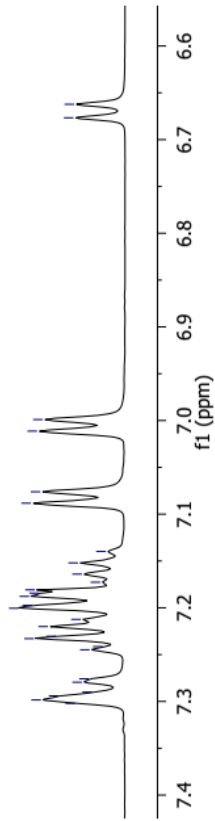
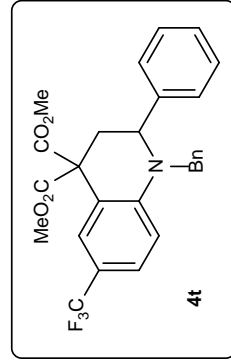
BKD-189-ISP-13C



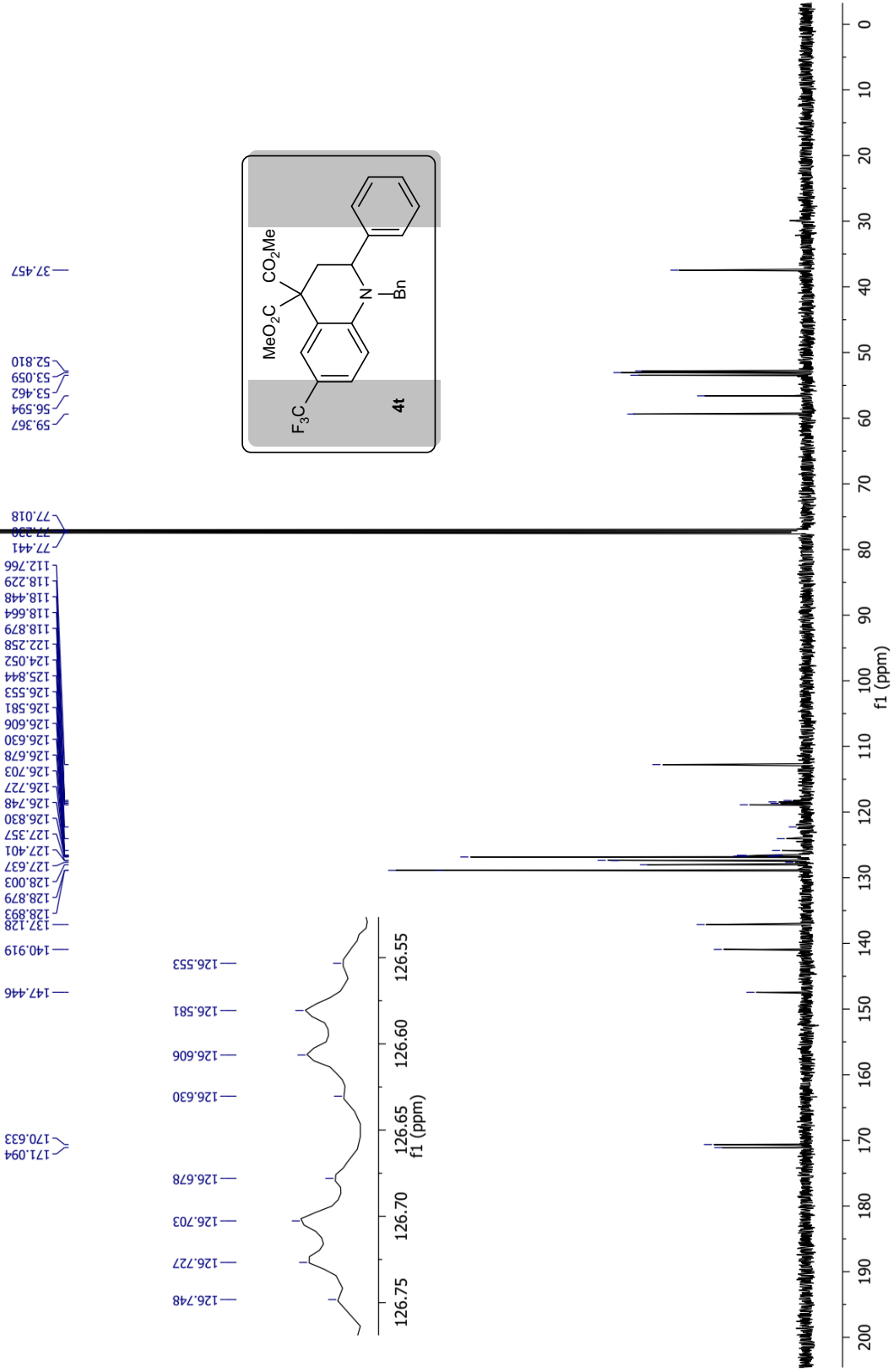
BKD-182-CO2ET-13C



BKD-181-CF3-1H

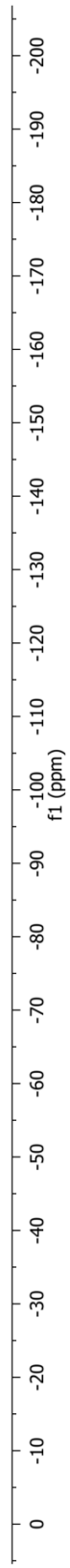
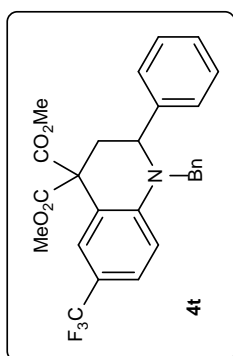


BKD-181-CF3-13C

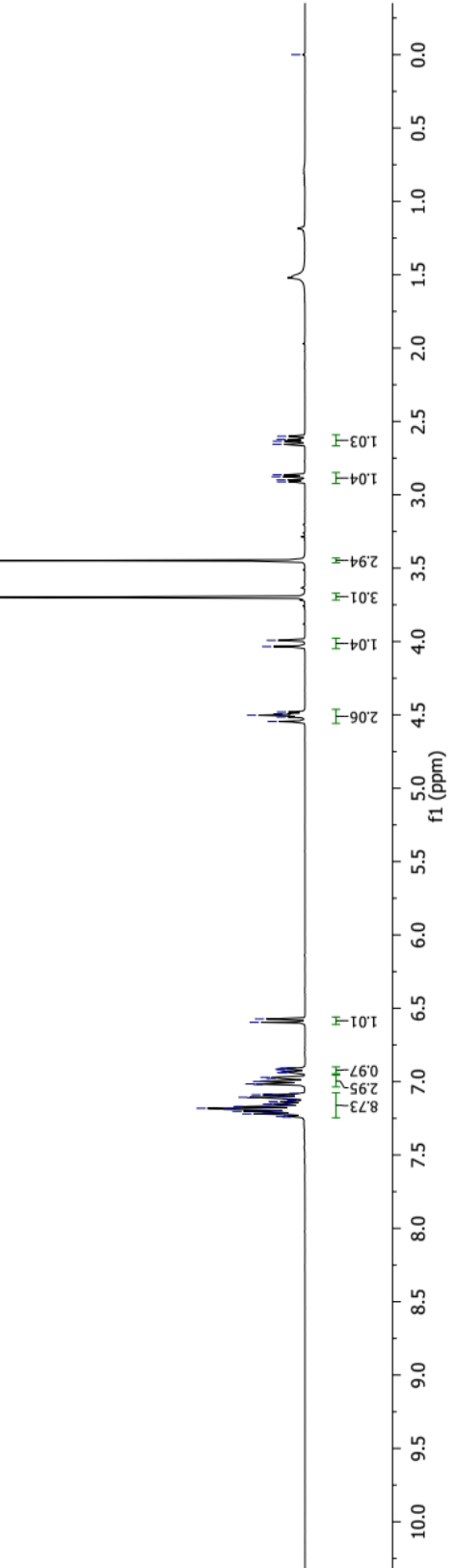
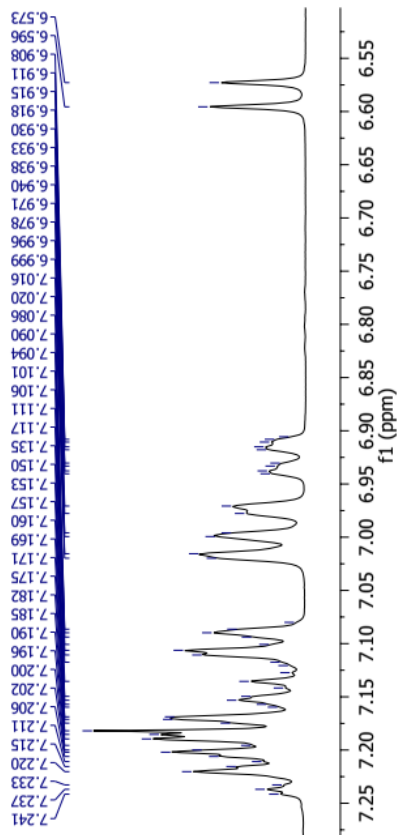
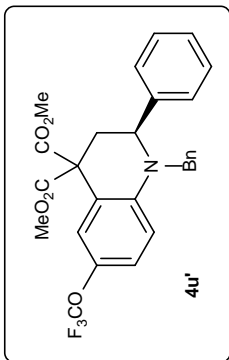


BKD-181-CF3-19F

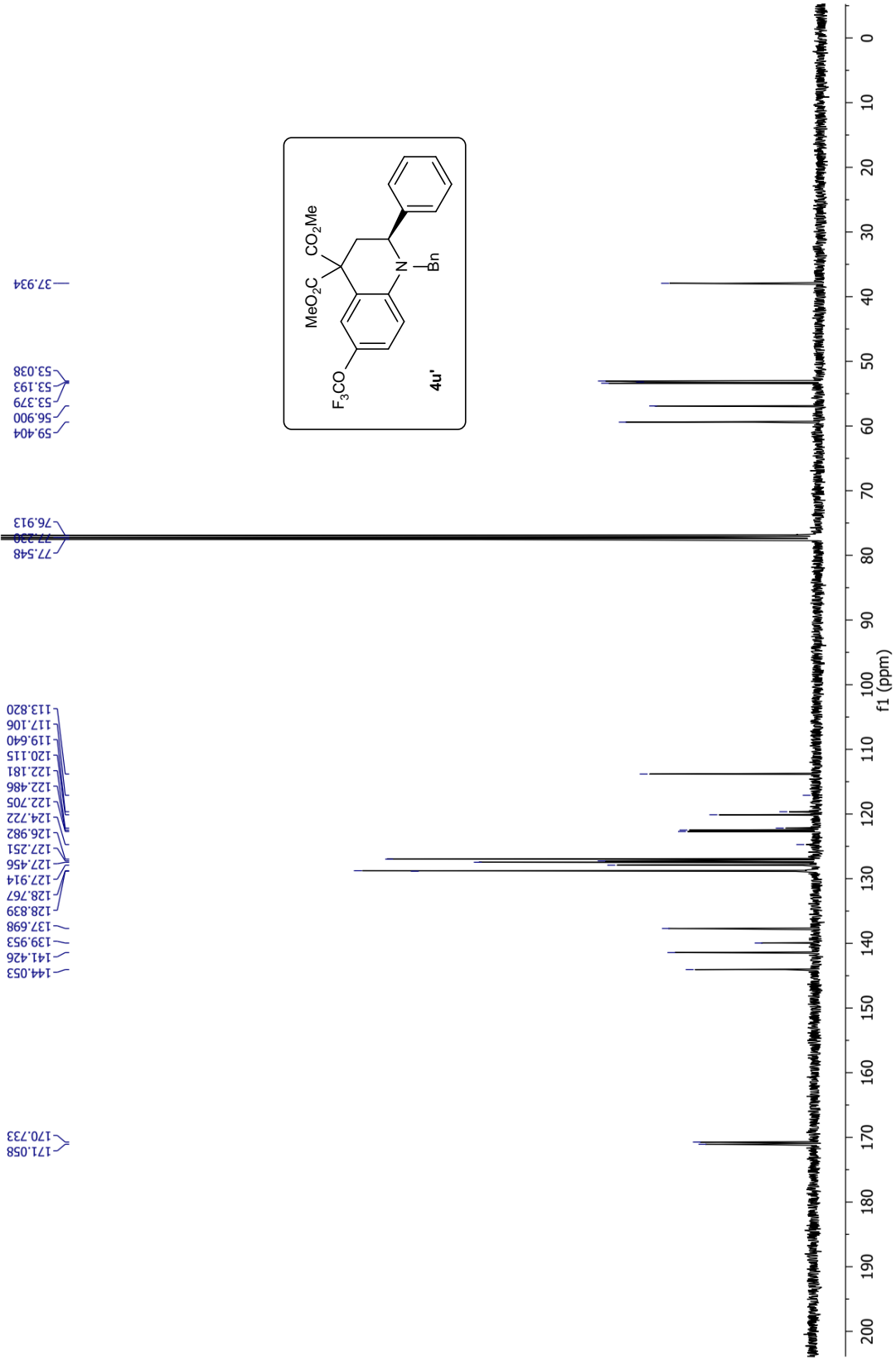
— -61.022



BKD-177-OCF3-1H

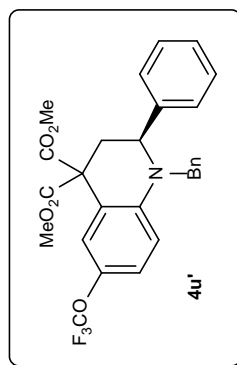


BKD-177-OCF3-13C

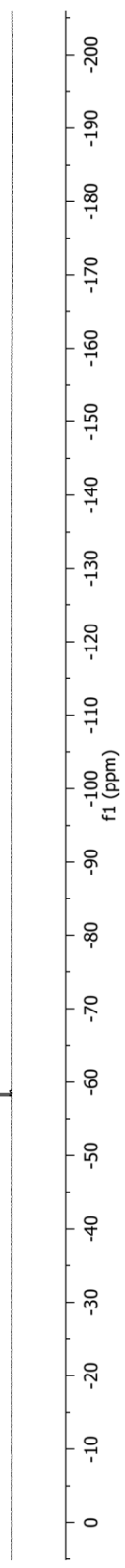


BKD-177-OCF3-19F

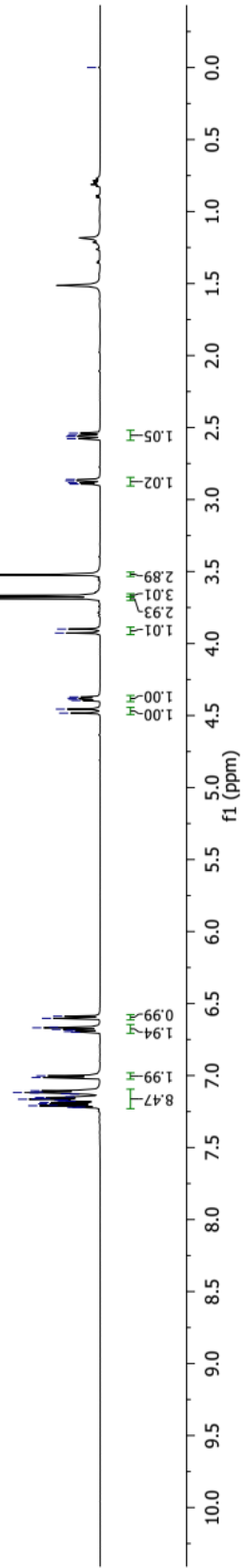
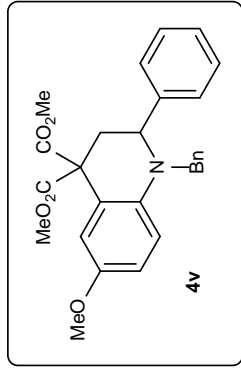
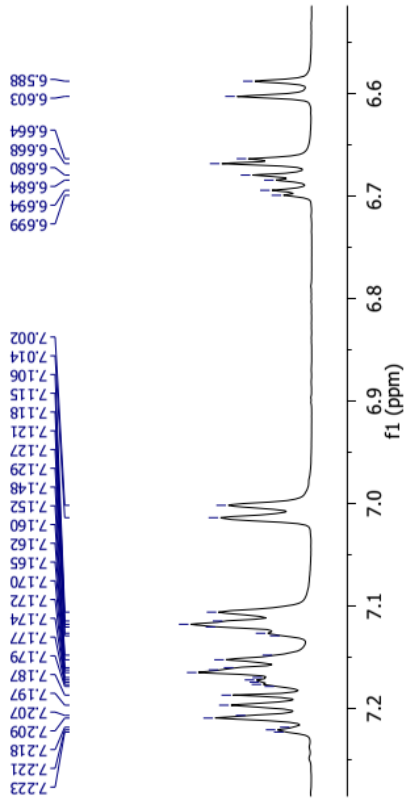
— 58.388



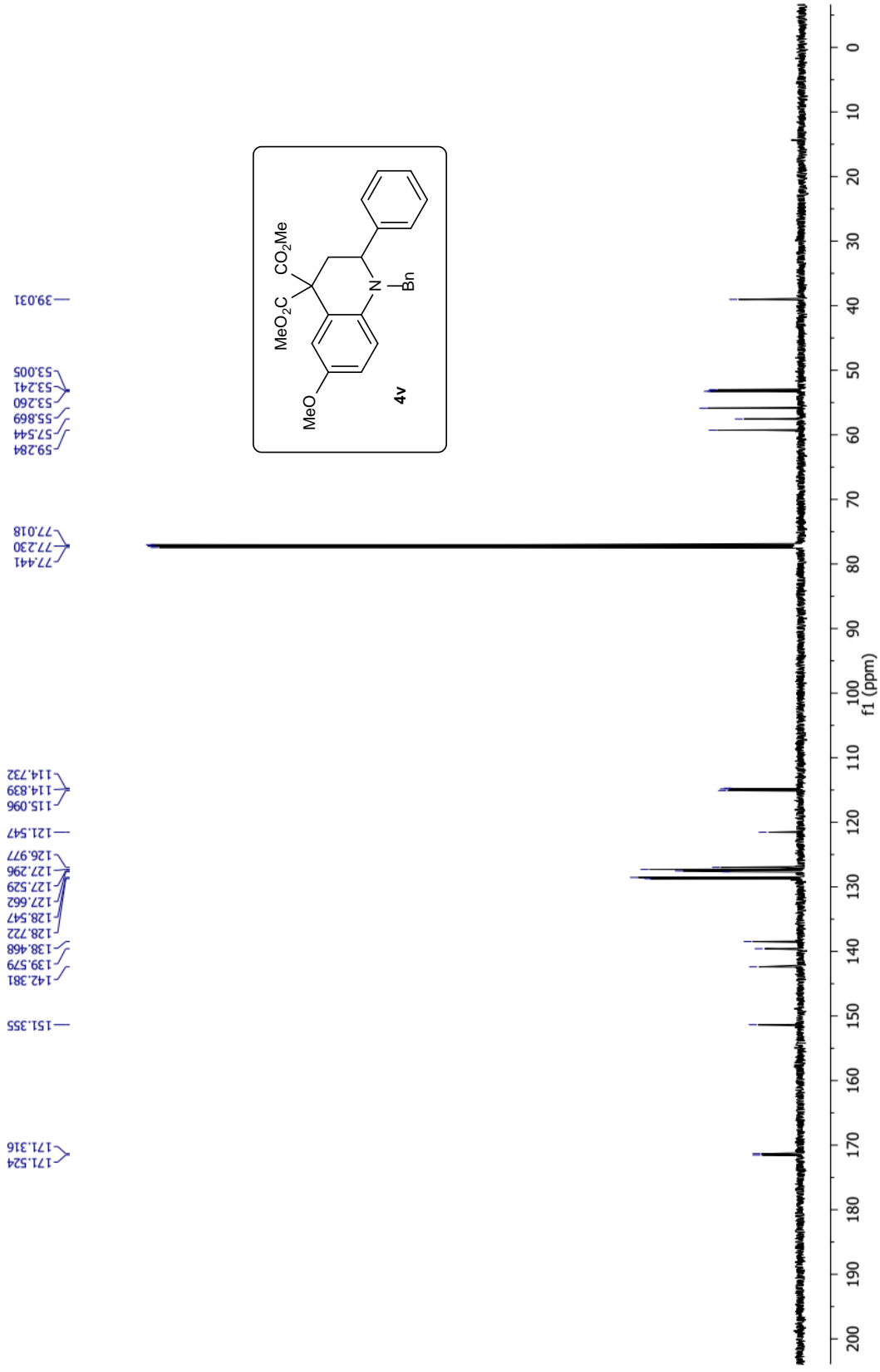
S79



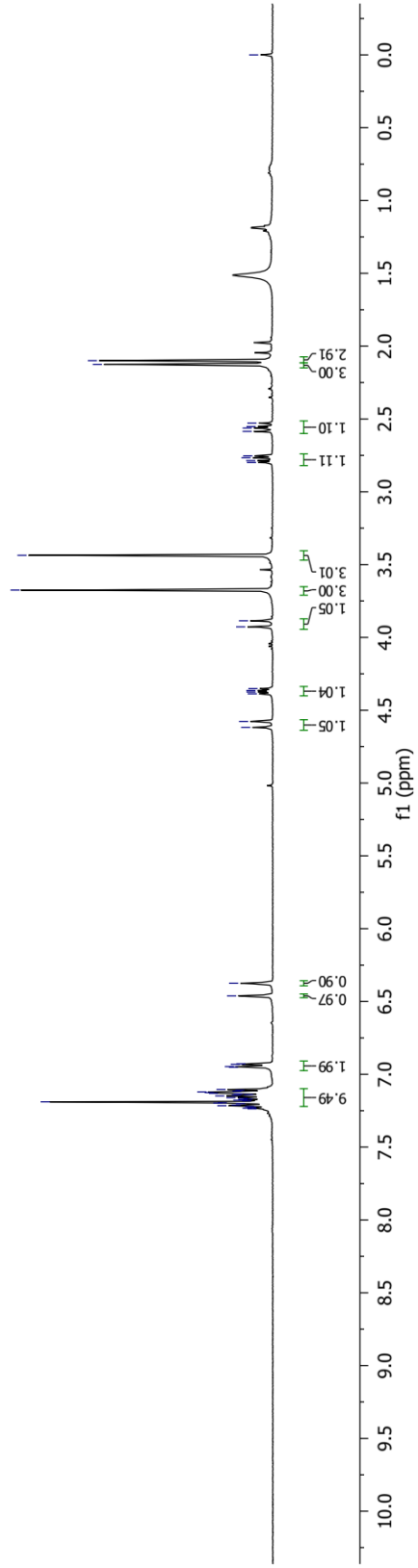
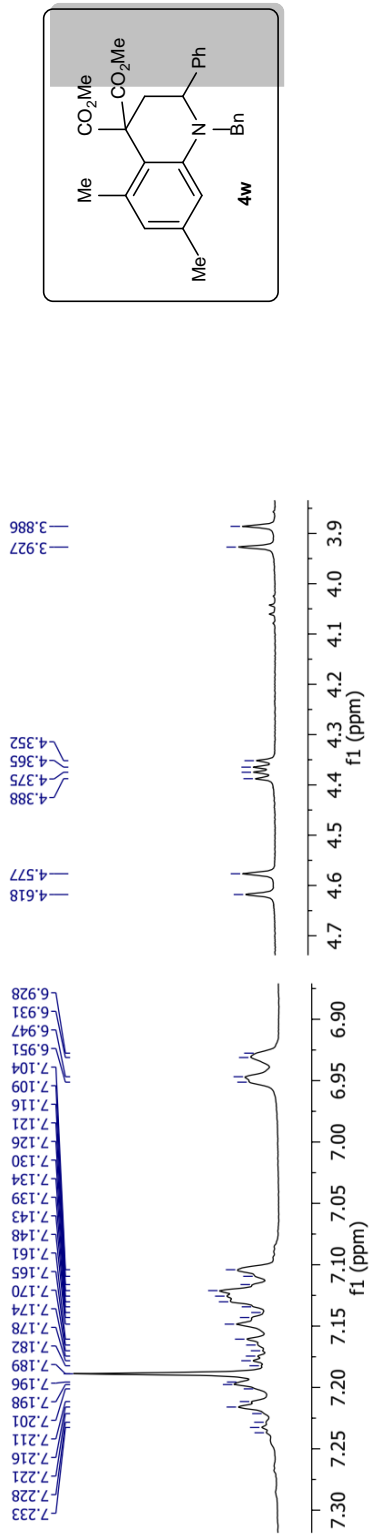
BKD-173-40ME-1H



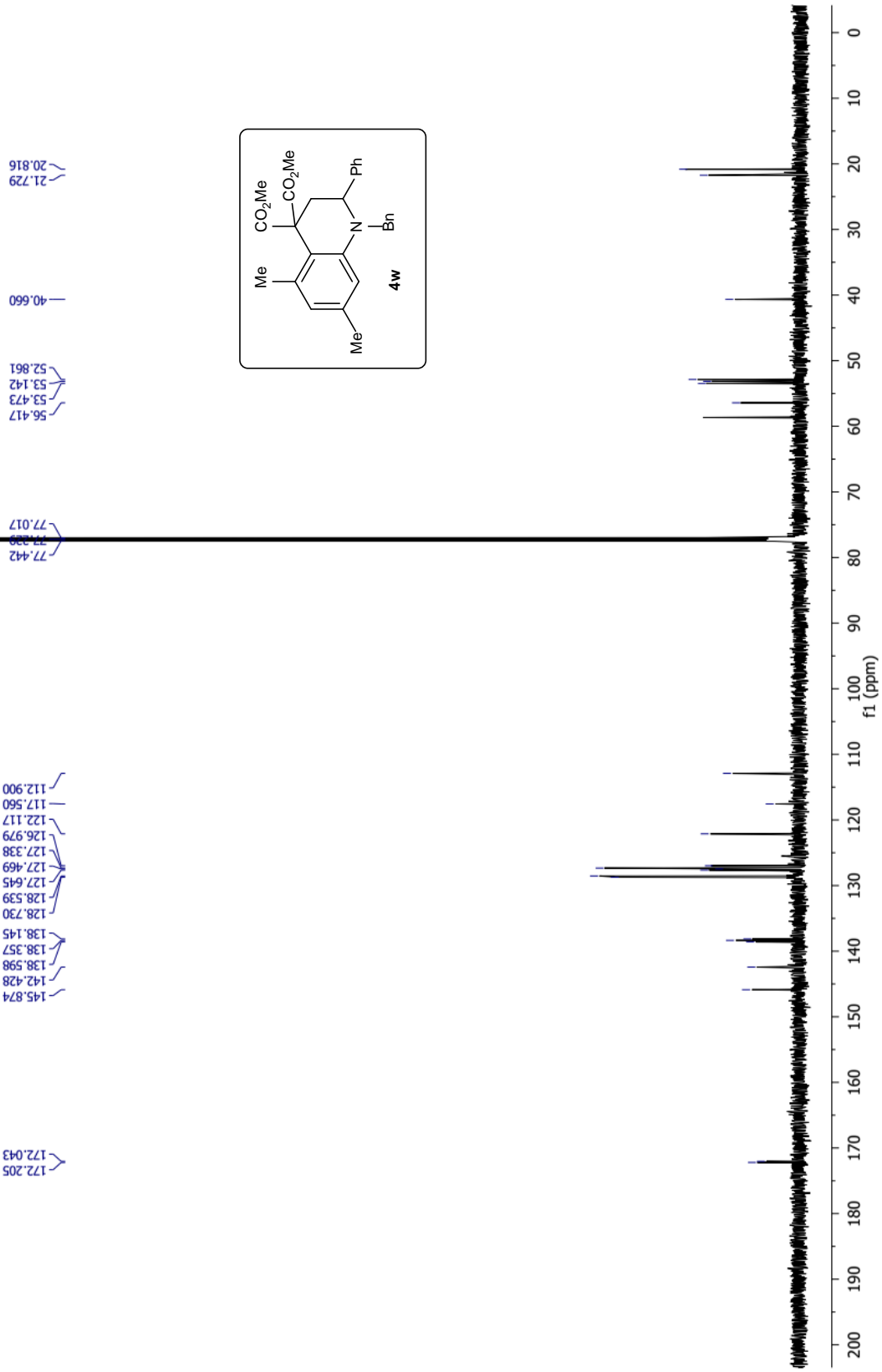
BKD-173-4OME-13C



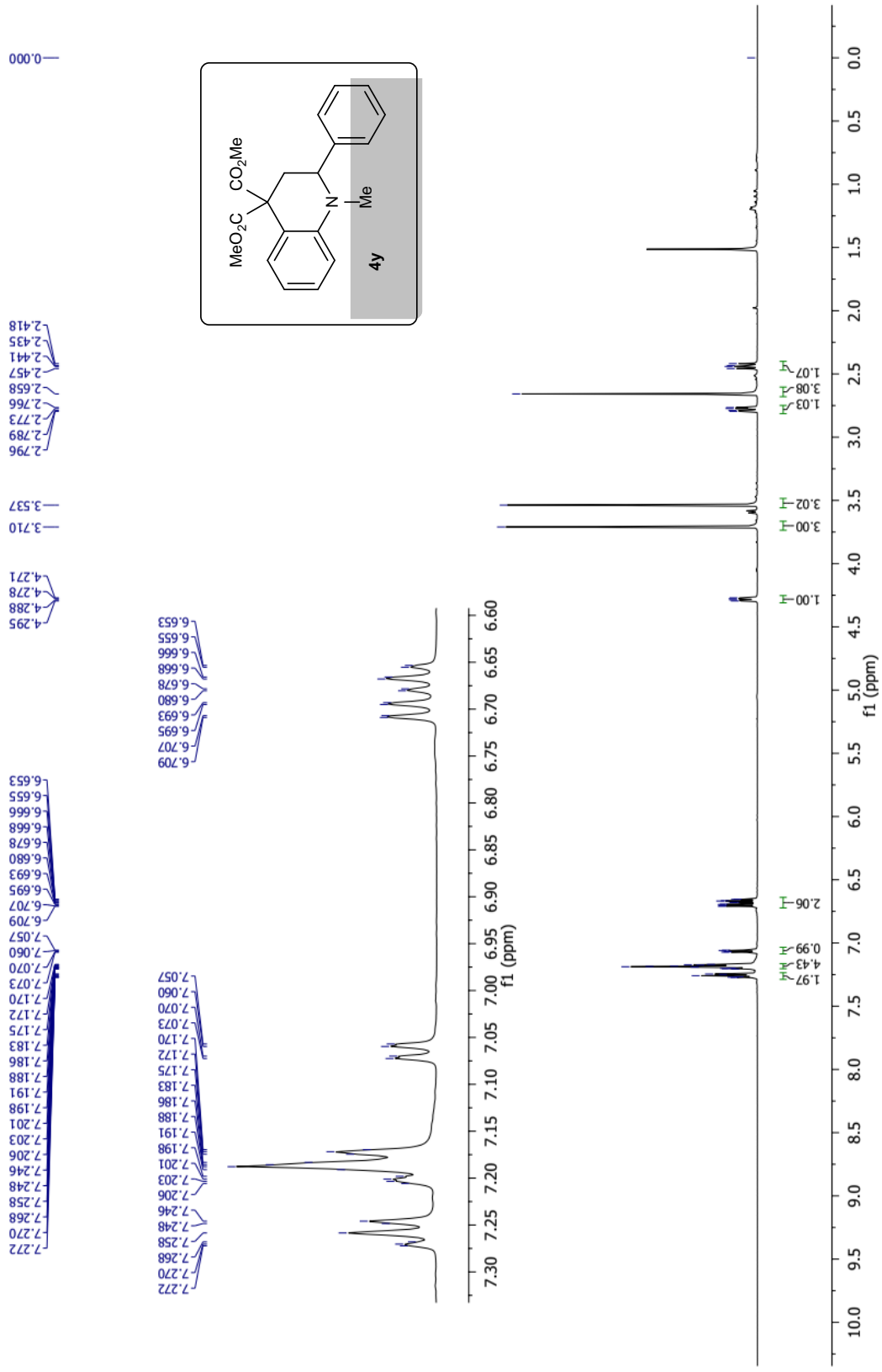
BKD-188-35-ME-1H



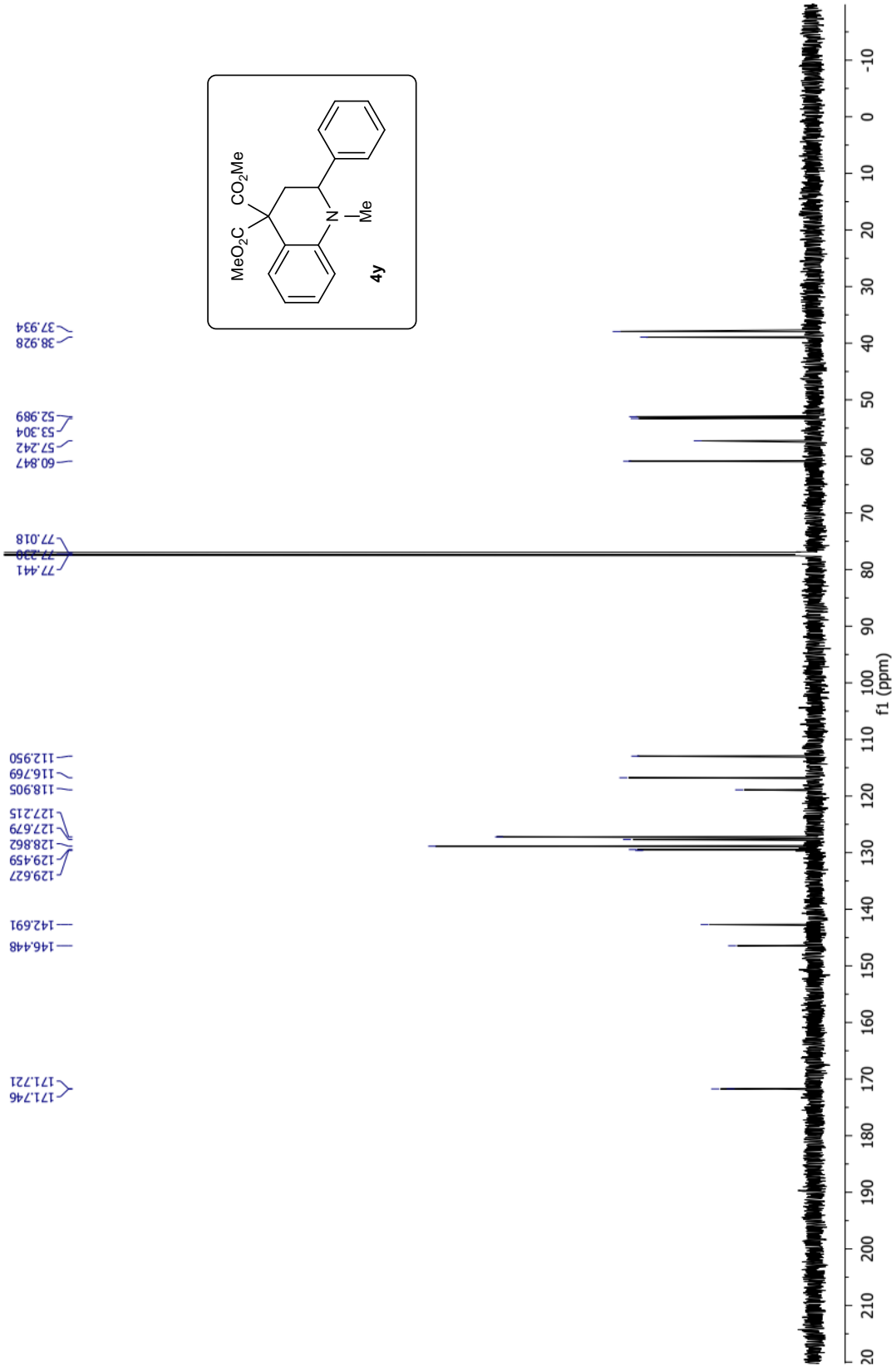
BKD-188-35-ME-13C



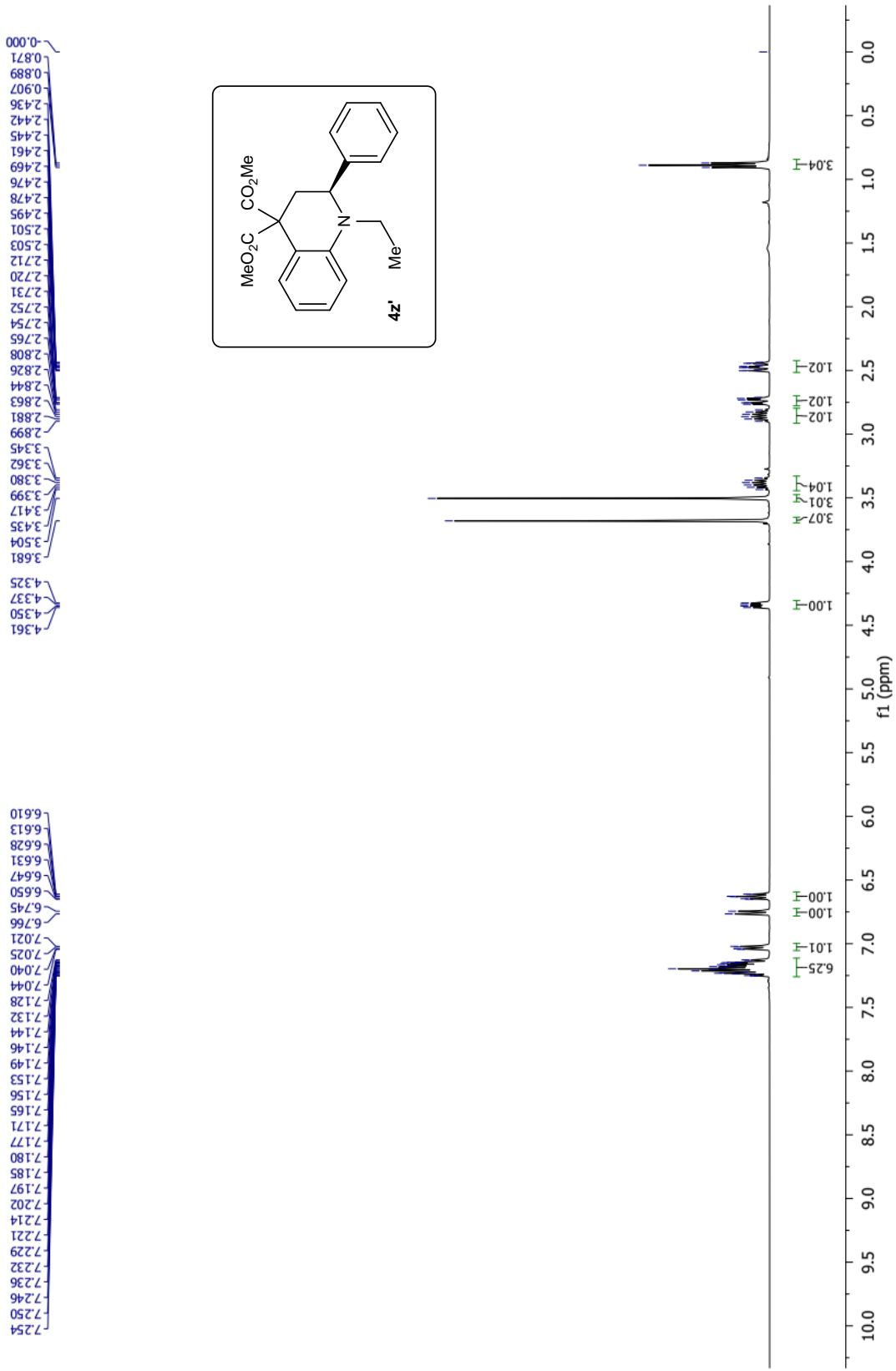
BKD-152-NME-1H



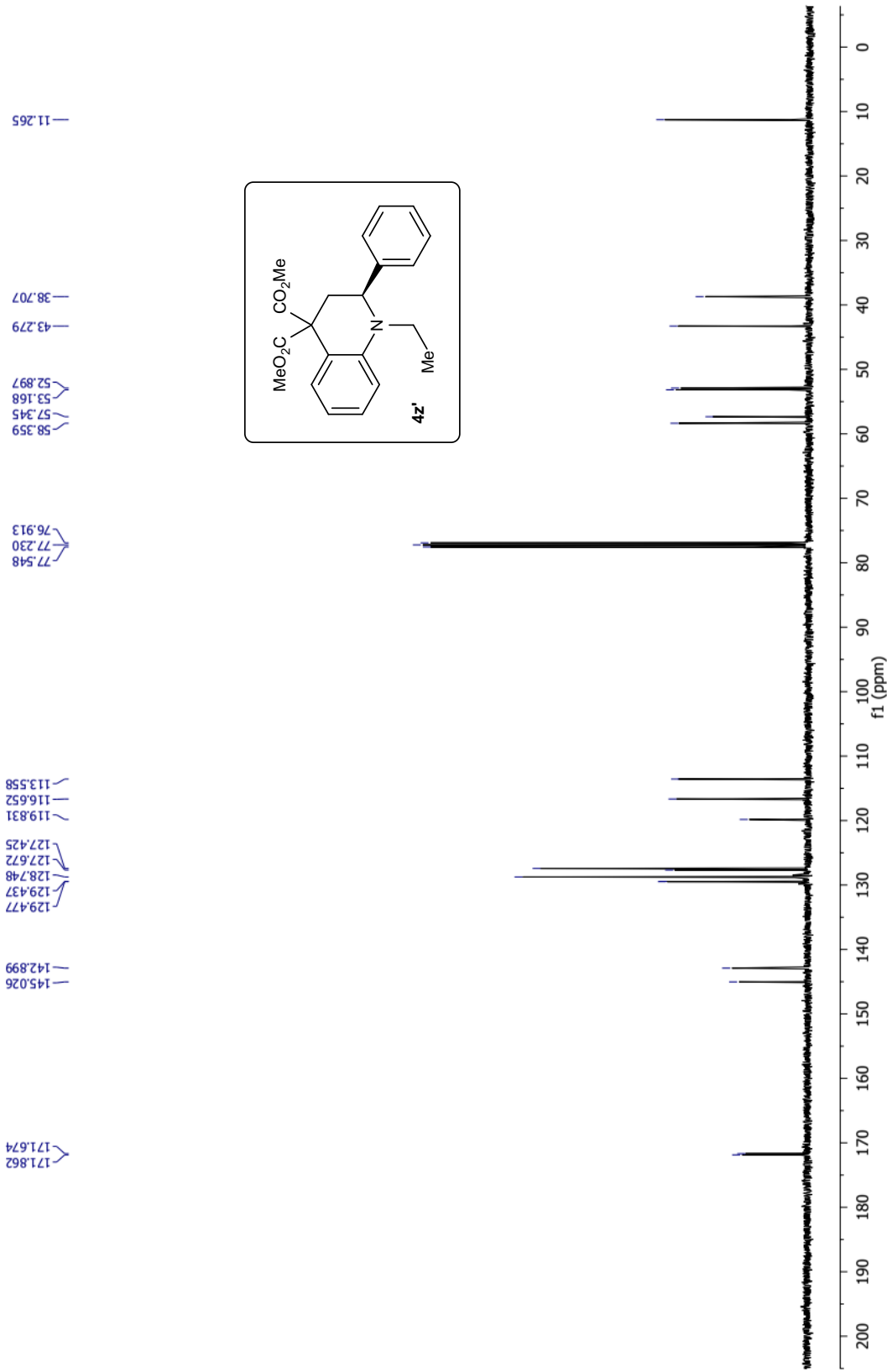
BKD-152-NME-13C



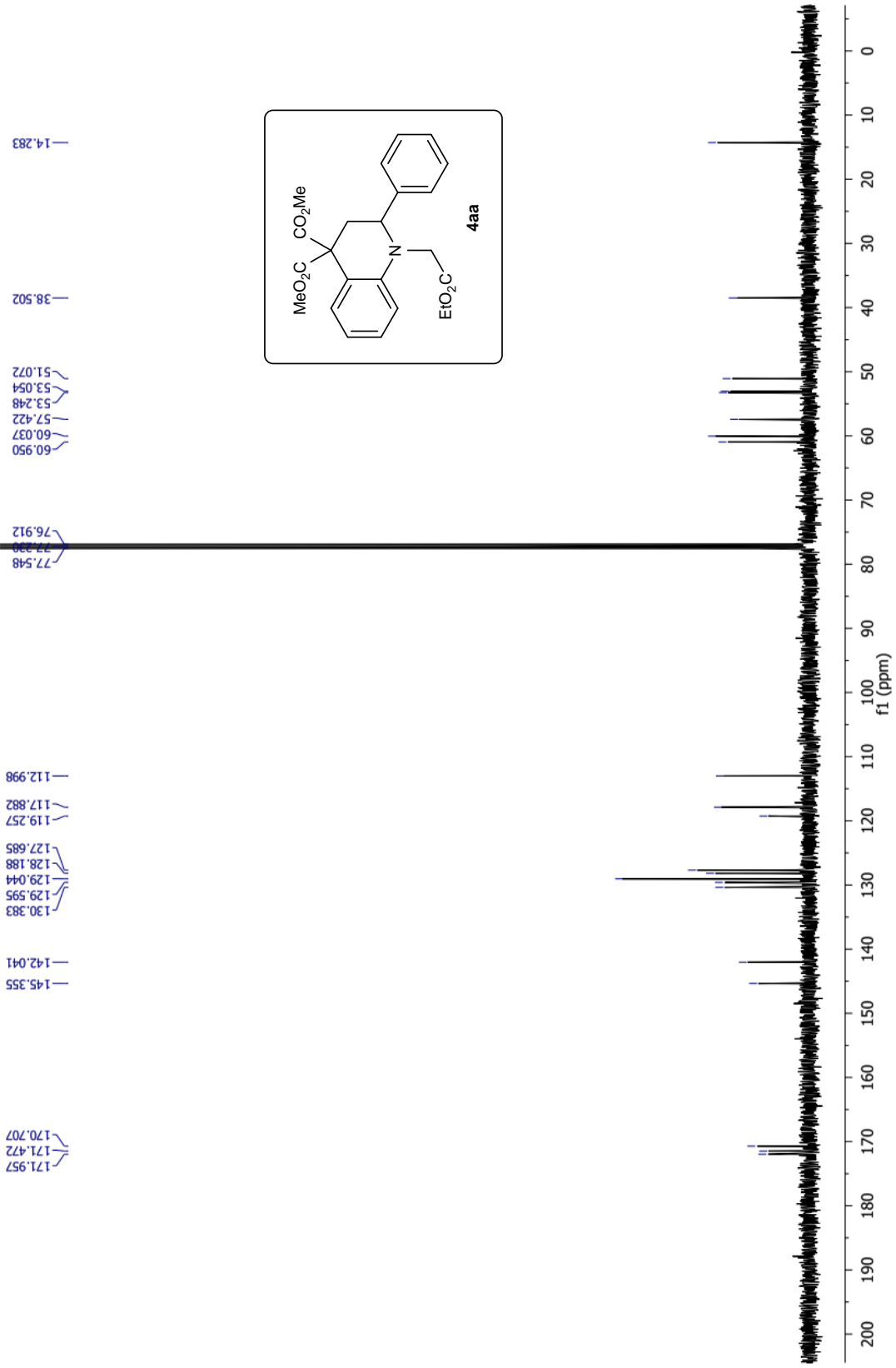
BKD-184-NET-1H



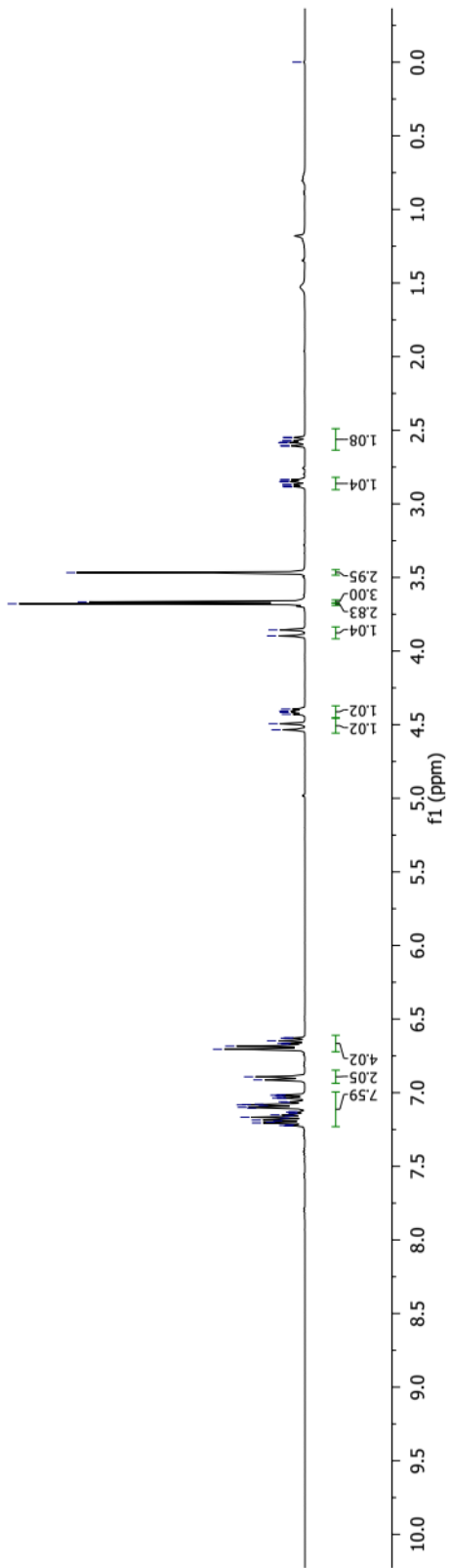
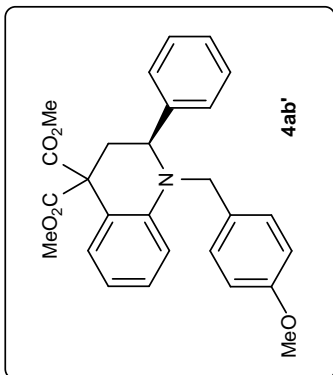
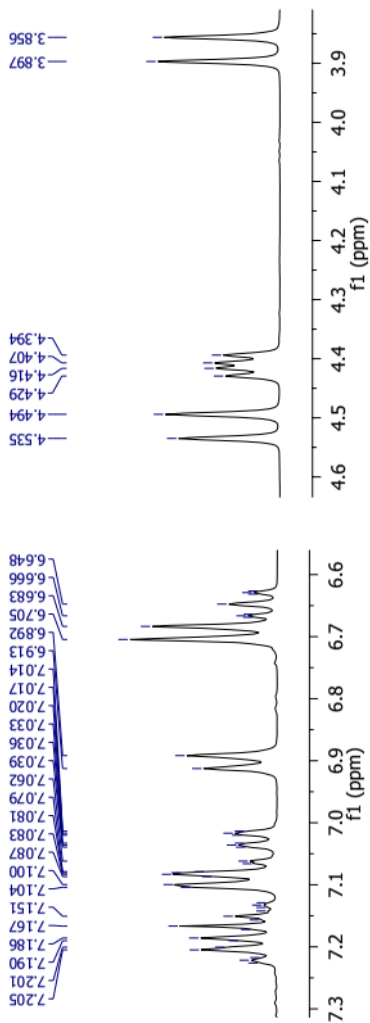
BKD-184-NET-13C



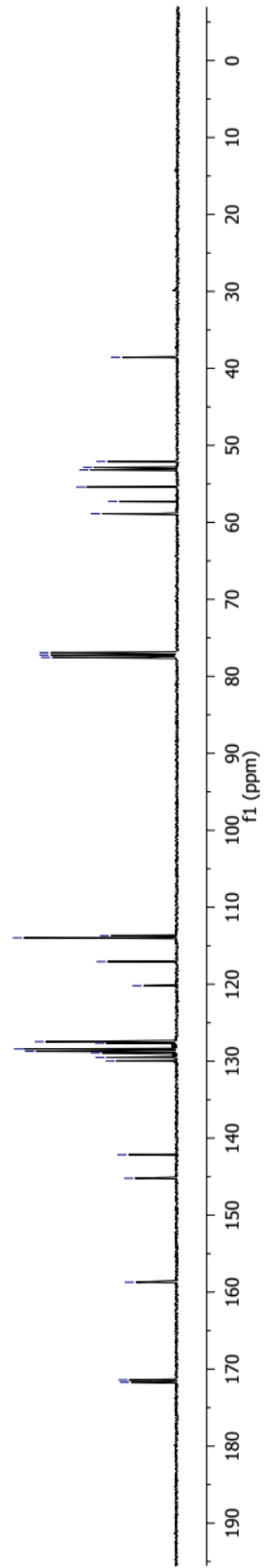
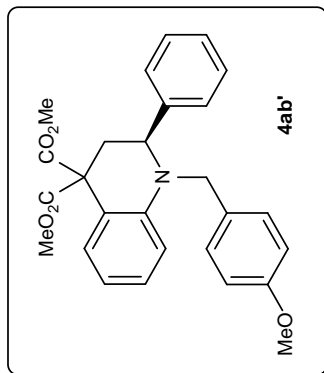
BKD-134-N-CO2ET-13C



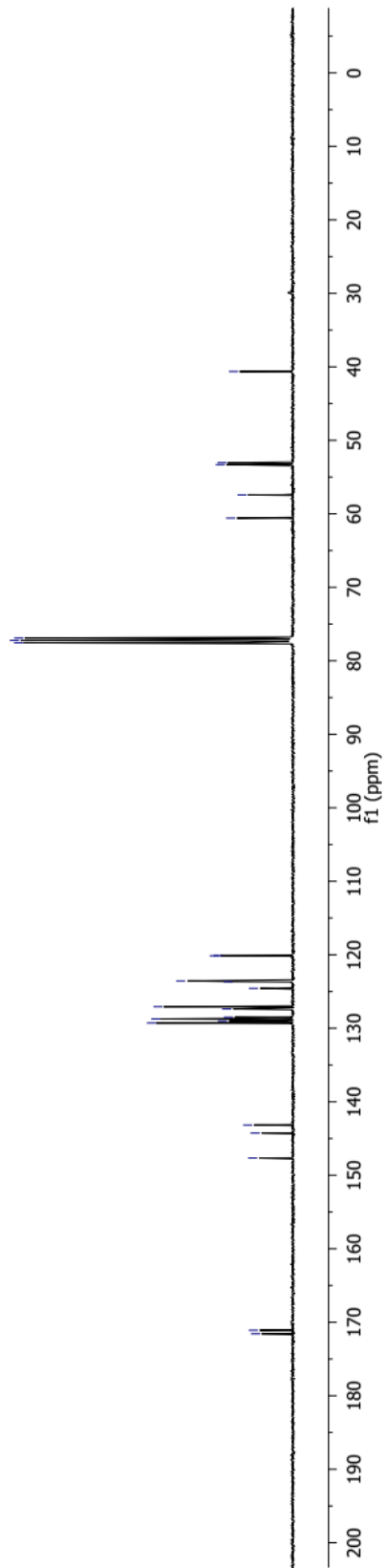
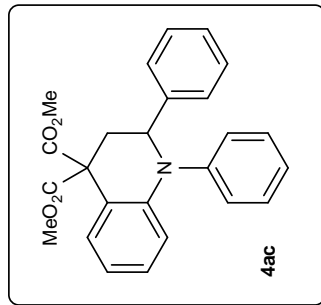
BKD-191-POME-1H



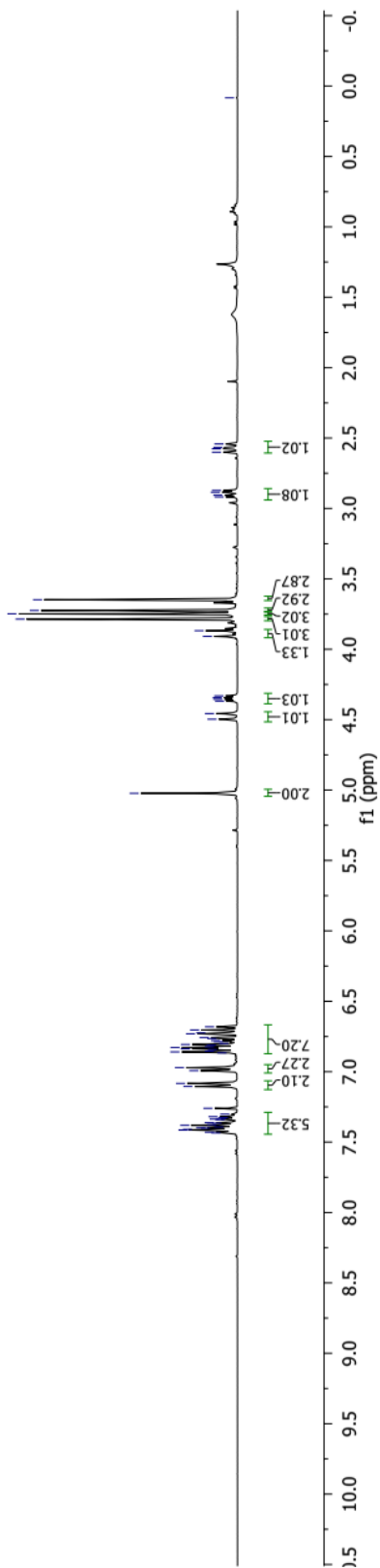
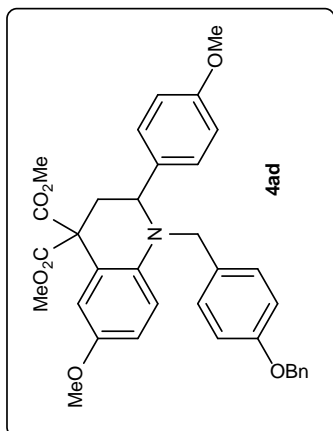
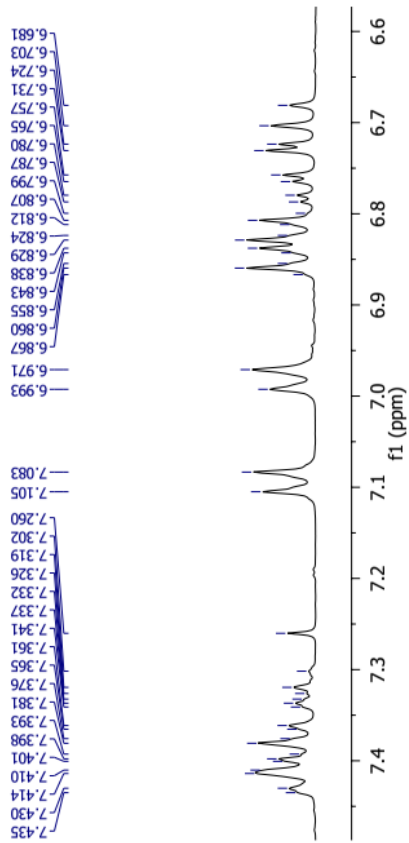
BKD-191-POME-13C



BKD-183-NPH-13C

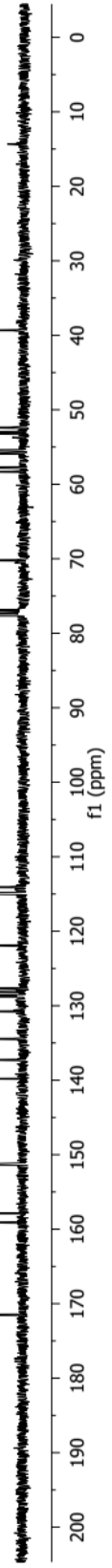
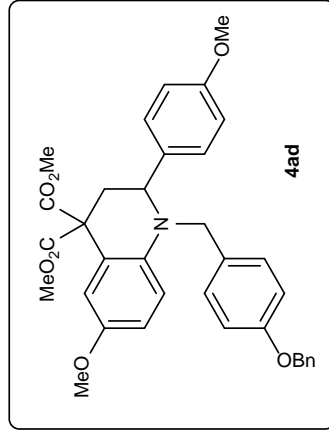


BKD-202-ERM-1H

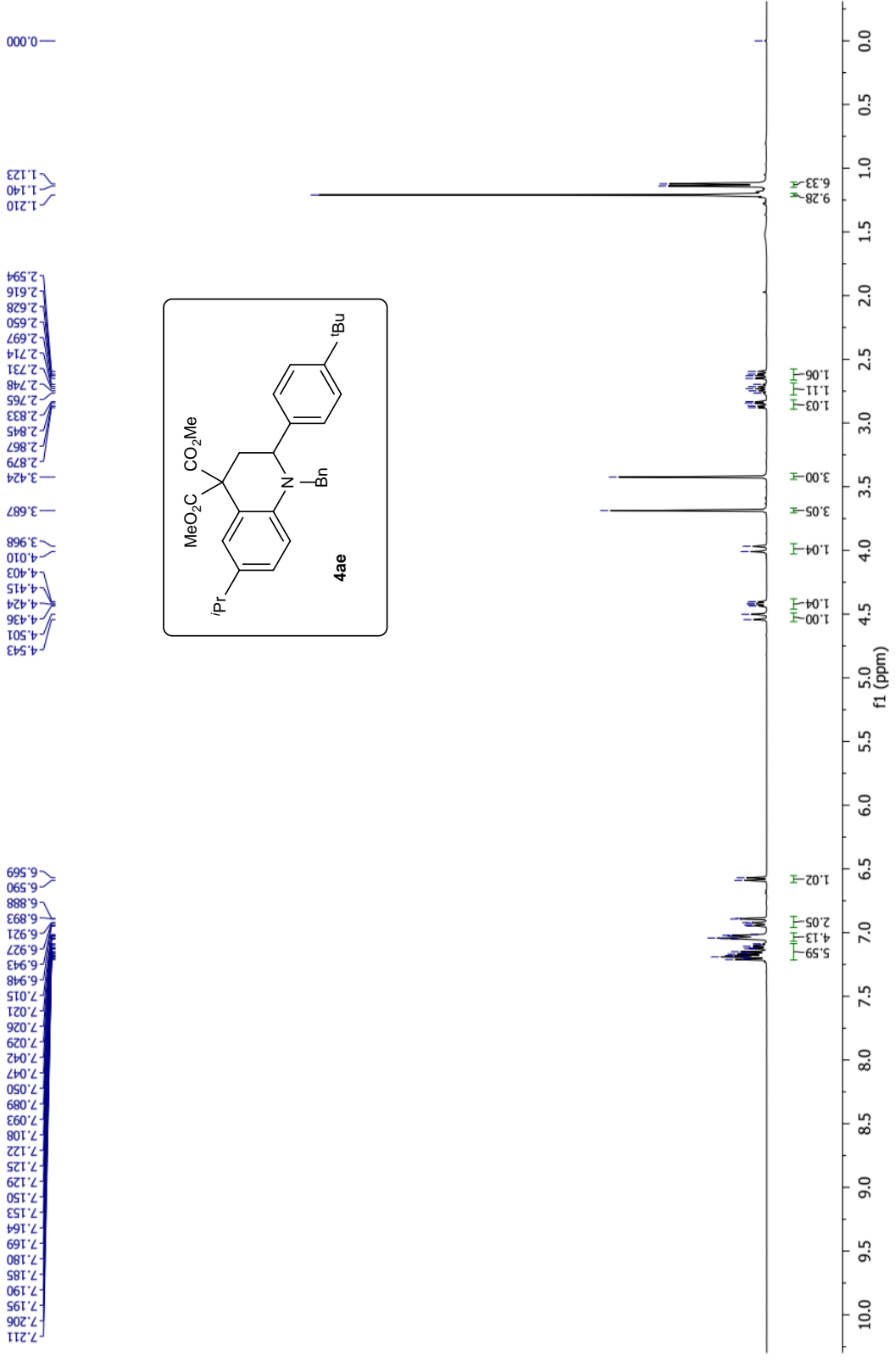


BKD-202-ERM-13C

171.531
171.418
159.076
157.872
151.340
139.800
137.267
134.412
130.739
128.764
128.632
128.578
128.132
127.674
121.877
115.001
114.954
114.844
114.807
114.053
77.548
77.230
76.913
70.195
58.300
57.717
55.869
55.459
53.180
53.004
52.369
39.351



BKD-199-TBU-ISP-1H



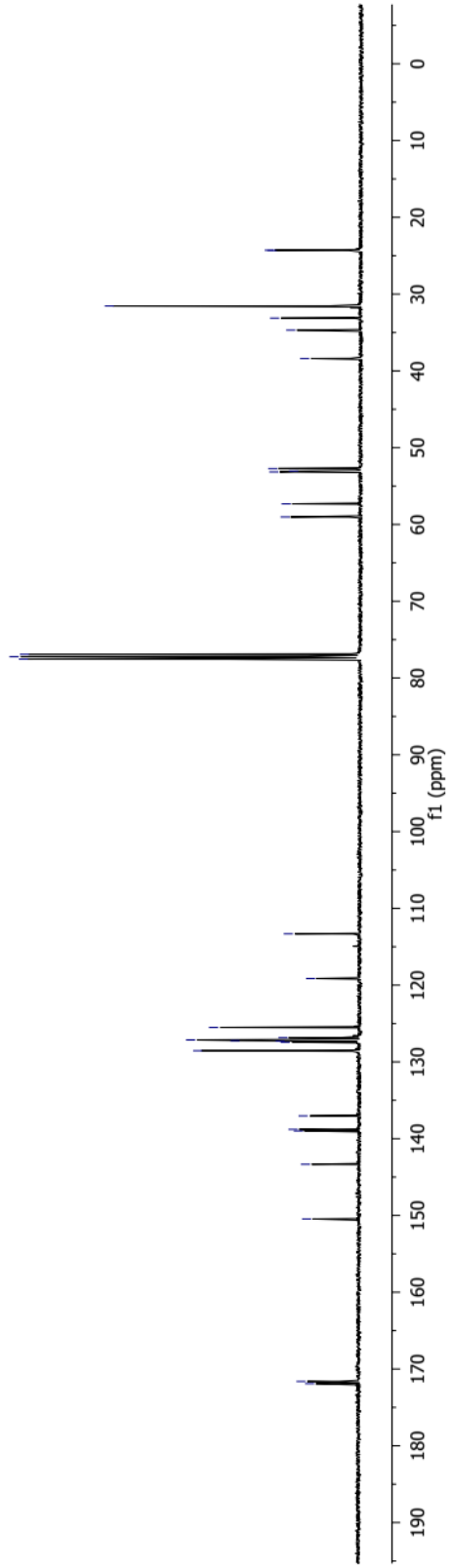
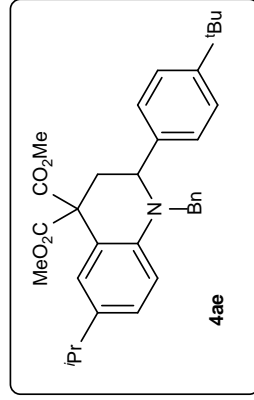
BKD-199-TBU-ISP-13C

171.908
171.611

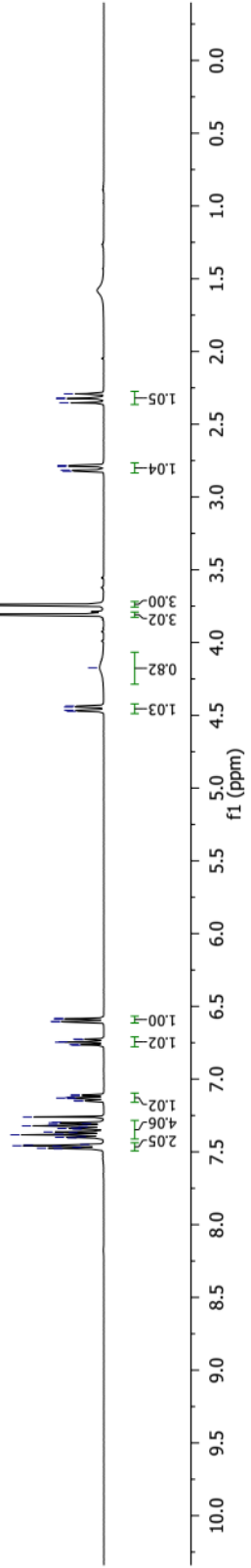
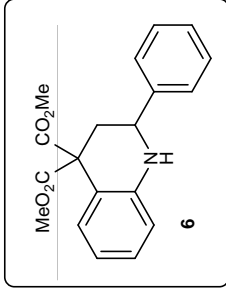
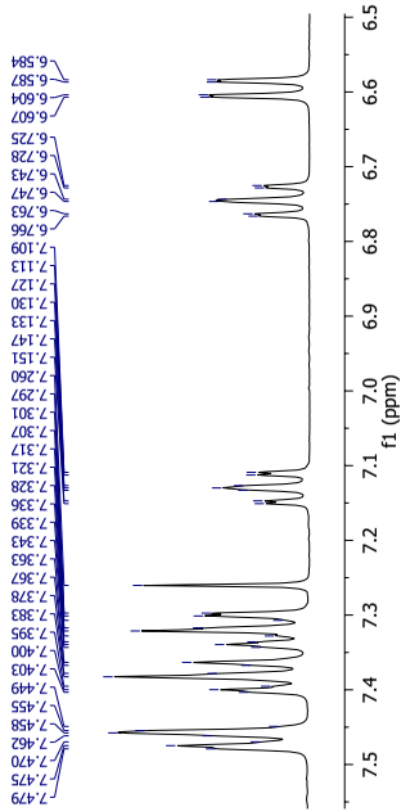
150.453
143.339
138.990
138.794
137.030
128.546
127.441
127.285
127.236
127.138
126.842
125.509
119.141
113.321

77.547
77.231
76.913

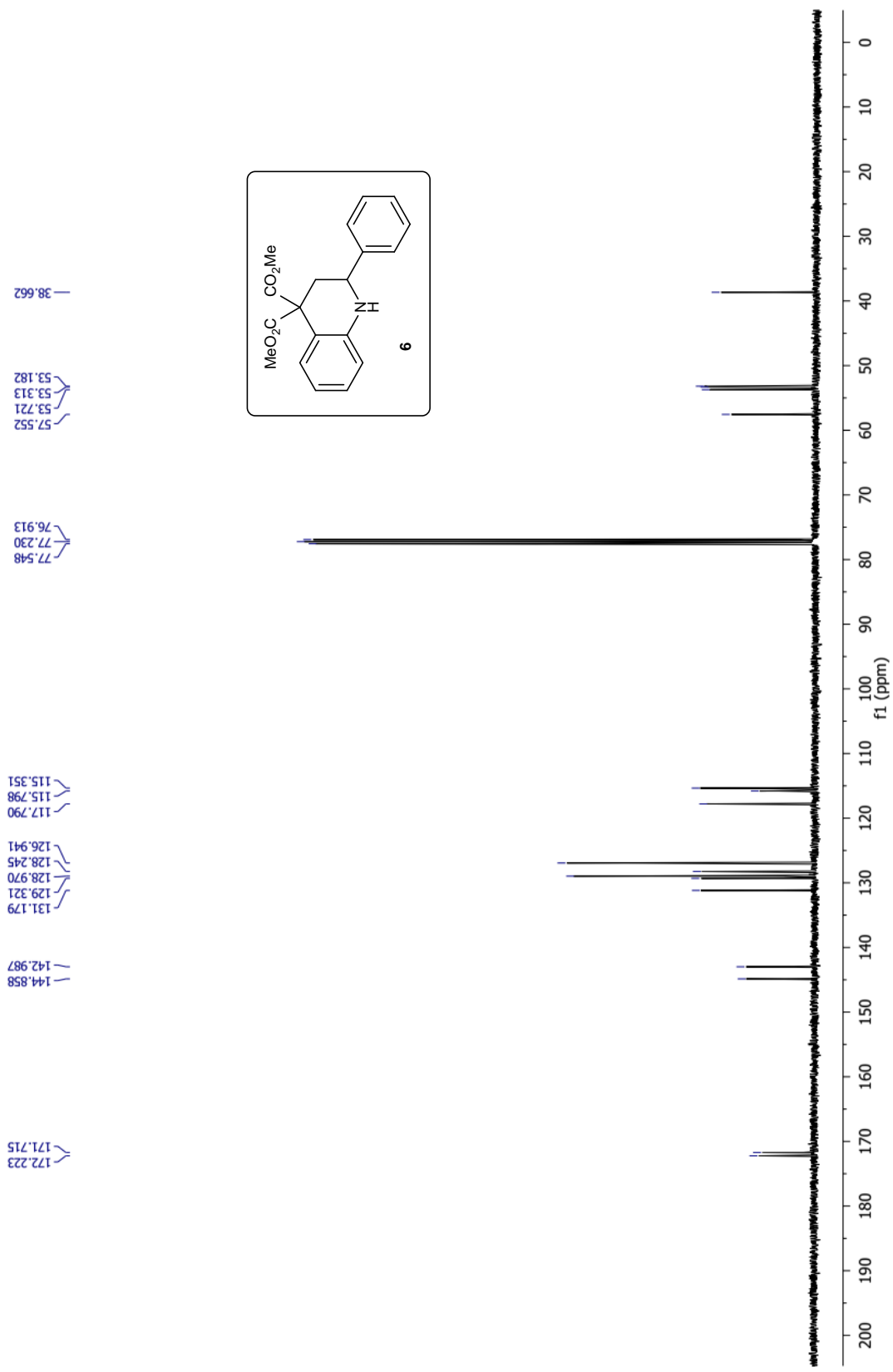
59.024
57.320
53.154
53.045
52.720
38.384
34.692
33.125
31.547
24.318
24.280



BKD-194-TFA-1H



BKD-194-TFA-13C



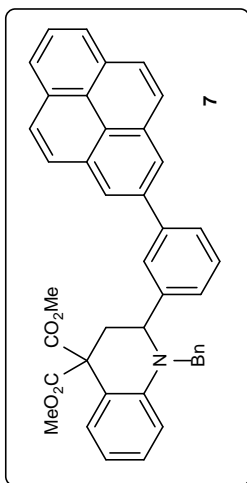
BKD-206-PYR

59.436
57.266
53.307
53.263
53.038
38.445

145.232
142.236
141.676
138.232
137.481
131.661
131.125
130.813
130.078
129.711
129.626
129.202
128.705
128.562
127.800
127.768
127.666
127.611
127.198
127.117
126.412
126.223
125.347
125.280
125.115
125.076
125.047
124.852
119.684
117.234
113.693
77.441
77.229
77.017

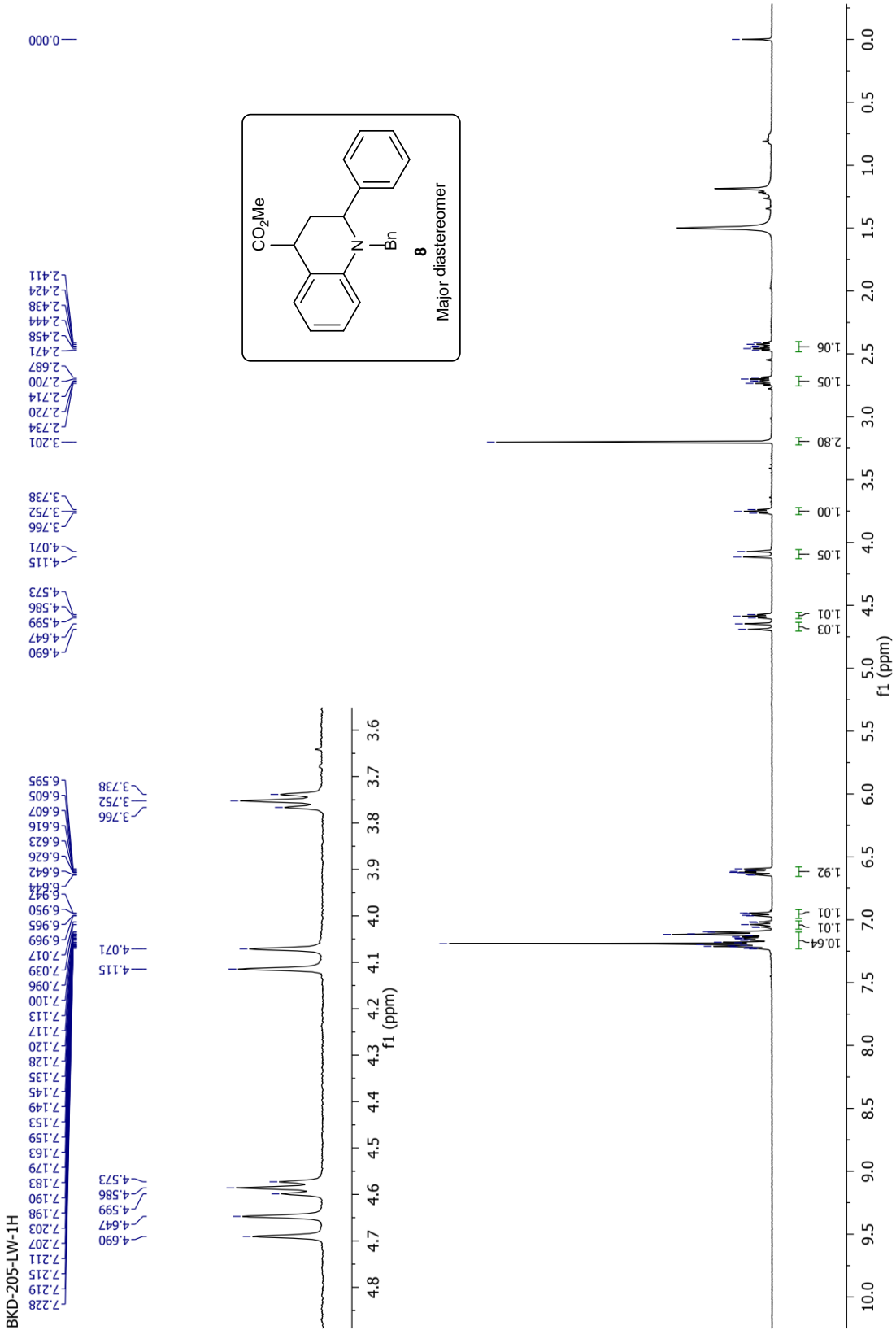
171.532
171.745

145.232
142.236
141.676
138.232
137.481
131.661
131.125
130.813
130.078
129.711
129.626
129.202
128.705
128.562
127.800
127.768
127.666
127.611
127.198
127.117
126.412
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125.347
125.280
125.115
125.076
125.047
124.852
119.684
117.234
113.693

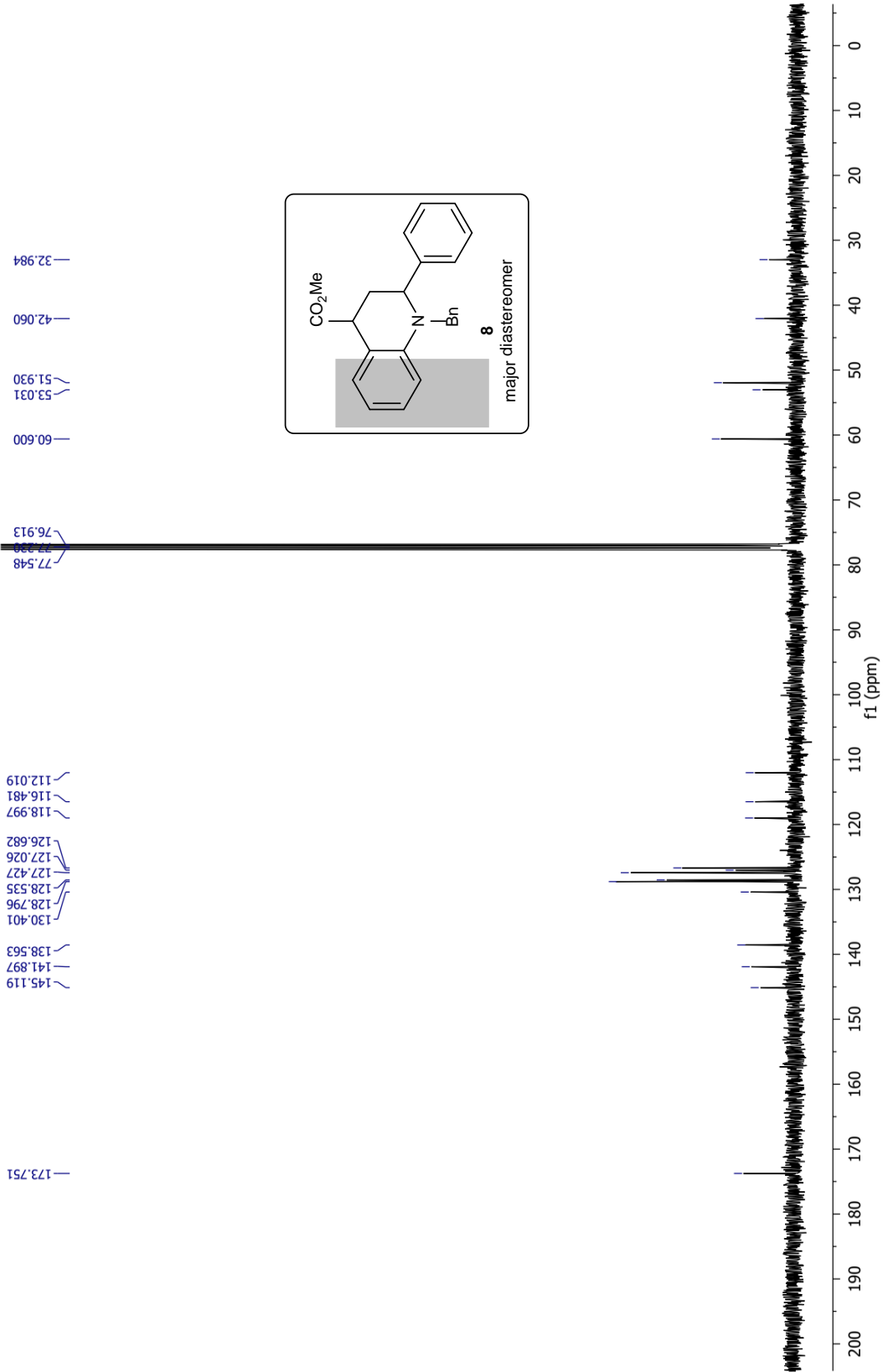


48 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112
f1 (ppm)

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

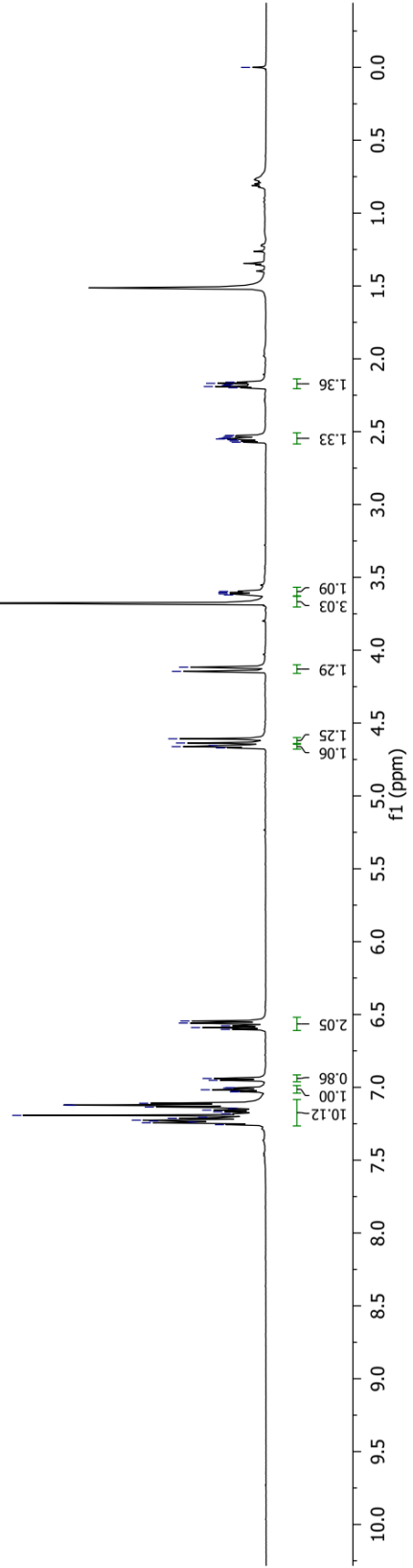
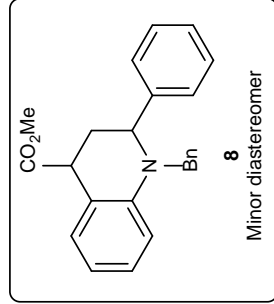


BKD-205-LW-13C



BKD-205-LCL-UP-1H

7.256
7.244
7.238
7.231
7.226
7.213
7.206
7.193
7.182
7.168
7.156
7.145
7.135
7.123
7.121
7.109
7.101
7.028
7.017
7.005
7.002
6.992
6.939
6.603
6.590
6.578
6.559
6.545



BKD-205-LCL-13C

