Electronic Supplementary Information (ESI)

N,N'-Dioxide/ nickel(II)-catalyzed asymmetric Diels–Alder reaction of cyclopentadiene with 2,3-dioxopyrrolidines and 2-alkenoyl pyridines

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Contents

1. General method

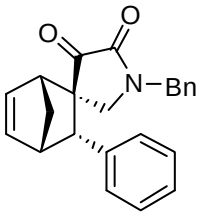
^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl3, δ = 7.26). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment. ^{13}C NMR spectra were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard (CDCl3, δ = 77.0). HRMS was recorded on a commercial apparatus (ESI Source). Enantiomeric excesses (ee) were determined by HPLC analysis using the corresponding commercial chiralpak column as stated in the experimental procedures at 25 °C. Optical rotations were reported as follows: $[a]^{T}_{D}$ (c g/100 mL, in solvent). Reactions were carried out with commercial available reagent in over dried apparatus. All the solvents were purified by usual methods before use. Chiral *N*,*N*′-dioxide ligands[1], 2,3-dioxopyrrolidines[2] and 2-alkenoyl pyridines[3] were prepared using literature method.

2. General procedure of the catalytic reactions

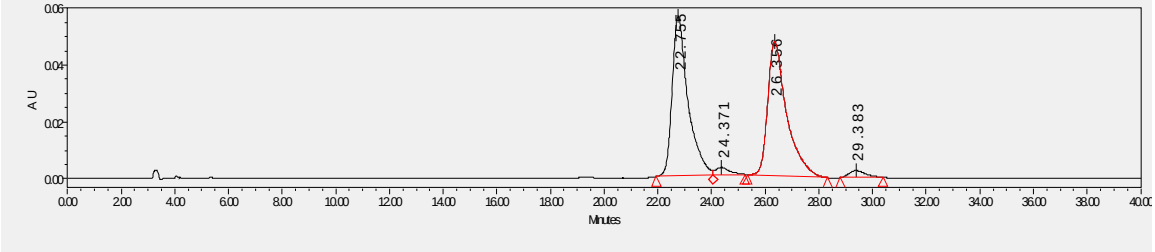
L-RaPr$_2$ (7.0 mg, 0.01 mmol), **1** or **4** (0.10 mmol) and Ni(OTf)$_2$ (3.6 mg, 0.01 mmol) were added to an over-dried reaction tube under nitrogen atmosphere. Then 1.0 mL anhydrous Cl_2CHCH_2Cl was added and the solution was stirred at 30 °C for 40 min. Subsequently, cyclopentadiene **2** (100μL) was added under 30 °C, and the reaction mixture continued stirring for 0.5-24 h. Need to be clearly explained, the diastereomer of the product was same point on TLC plate, but suffer somewhat separation after the chromatography on silica gel. For example, the dr value of **3a** varied from 93:7 to 97:3. To avoid the variation, all dr values were determined using the flash filtration as the isolated procedure. To get the exact yield, the product was further purified by a flash chromatography on silica gel (petroleum ether/ethyl acetate = 3:1-10:1). The enantiomeric excesses (ee) was determined by high-performance liquid chromatography (HPLC). Optical rotations, copies of CD spectra and copies of ^{1}H NMR and ^{13}C NMR spectra of products were determined using the flash chromatography on silica gel as the isolated procedure.

3. Product characterization data

(1R,2R,3S,4S)-1'-benzyl-3-phenylspiro[bicyclo[2.2.1]heptane-2,3'-pyrrolidin]-5-ene-4',5'-dione **3a**



Yield: 30.8 mg (90%), white amorphous solid, 93:7 dr, 97% ee; $[\alpha]^{17.3}_{D}$ = -84.8 (c = 0.59, CH_2Cl_2); HPLC (Daicel chiralcel ID, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 26.62 min, $t_{R(minor)}$ = 23.08 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 3H), 7.21 – 7.12 (m, 3H), 7.07 (dd, *J* = 6.0, 2.4 Hz, 1H), 6.89 (dd, *J* = 6.0, 2.4 Hz, 1H), 6.70 (dd, *J* = 5.6, 3.2 Hz, 1H), 6.17 (dd, *J* = 5.6, 3.2 Hz, 1H), 4.70 (d, *J* = 14.4 Hz, 1H), 4.15 (d, *J* = 14.4 Hz, 1H), 3.90 (d, *J* = 2.8 Hz, 1H), 3.27 (s, 1H), 3.01 (s, 1H), 2.97 (d, *J* = 11.2 Hz, 1H) 2.79 (d, *J* = 11.2 Hz, 1H), 2.31 (d, *J* = 9.2 Hz, 1H), 1.57 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.5, 159.8, 140.7, 138.8, 135.7, 134.4, 128.9, 128.5, 128.3, 128.1, 127.2, 58.8, 55.7, 51.9, 48.9, 48.4, 48.3, 47.8. ESI-HRMS calcd for [$C_{23}H_{21}NO_2$+ Na^+]: 366.1470, found 366.1470.



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3	26.356	2311304	47.98
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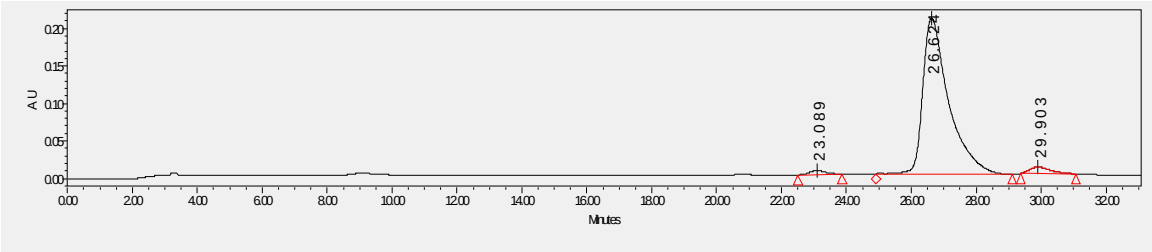

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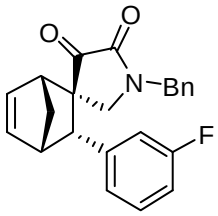
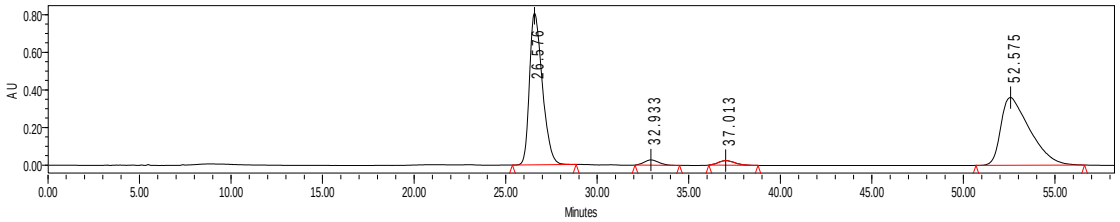
1	23.089	182165	1.49
2	26.624	11616673	95.30
3	29.903	391080	3.21

(1R,2R,3S,4S)-1'-benzyl-3-(3-fluorophenyl)spiro[bicyclo[2.2.1]heptane-2,3'-pyrrolidin]-5-ene-4',5'-dione **3b**



Yield: 32.9 mg (91%), white powder, 93:7 dr, 96% ee; $[\alpha]^{20.6}_{D}$ = -68.1 (c = 0.66, CH_2Cl_2); HPLC (Daicel chiralcel IC, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 54.68 min, $t_{R(minor)}$ = 27.48 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 3H), 7.15 – 7.06 (m, 3H), 6.88 – 6.81 (m, 1H), 6.67 (dd, *J* = 5.6, 3.2 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 2H), 6.21 (dd, *J* = 5.6, 3.2 Hz, 1H), 4.64 (d, *J* = 14.4 Hz, 1H), 4.30 (d, *J* = 14.4 Hz, 1H), 3.89 (d, *J* = 2.8 Hz, 1H), 3.25 (s, 1H), 3.08 – 2.94 (m, 2H), 2.78 (d, *J* = 11.6 Hz, 1H), 2.28 (d, *J* = 9.2 Hz, 1H), 1.57 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.0, 162.6 (d, *J* = 245 Hz), 159.5, 141.5 (d, *J* = 6.9 Hz), 140.5, 136.1, 134.3, 130.0 (d, *J* = 8.4 Hz), 128.9, 128.3, 128.2, 124.6 (d, *J* = 2.8 Hz), 115.1 (d, *J* = 21.6 Hz), 114.1 (d, *J* = 20.8 Hz), 58.1, 55.6, 52.1, 48.8, 48.4, 48.3, 47.8. ESI-HRMS calcd for [$C_{23}H_{20}FNO_2$+Na^+]: 384.1376, found 384,1371.



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1	26.576	39307903	48.07
2	32.933	1528148	1.87
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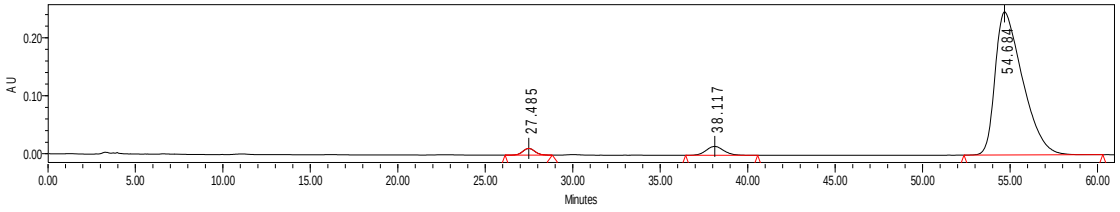

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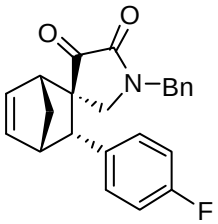
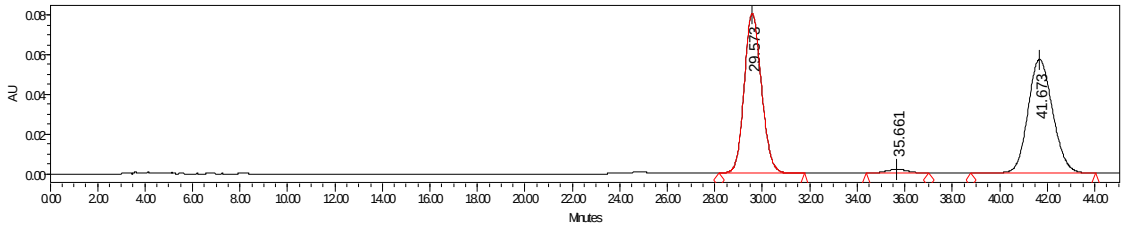
1	27.485	567283	1.99
2	38.117	1071392	3.76
3	54.684	26887686	94.26

(1R,2R,3S,4S)-1'-benzyl-3-(4-fluorophenyl)spiro[bicyclo[2.2.1]heptane-2,3'-pyrrolidin]-5-ene-4',5'-dione **3c**



Yield: 31.3 mg (87%), white powder, 92:8 dr, 95% ee; $[\alpha]^{25.0}_{D}$ = -67.6 (c = 0.63, CH_2Cl_2); HPLC (Daicel chiralcel IC, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 41.47 min, $t_{R(minor)}$ = 29.61 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 3H), 7.10 – 7.01 (m, 2H), 6.90 – 6.76 (m, 4H), 6.67 (dd, *J* = 5.6, 2.8 Hz, 1H), 6.22 (dd, *J* = 5.6, 3.2 Hz, 1H), 4.54 (d, *J* = 14.4 Hz, 1H), 4.35 (d, *J* = 14.4 Hz, 1H), 3.85 (d, *J* = 2.7 Hz, 1H), 3.23 (s, 1H), 3.08 – 2.94 (m, 2H), 2.76 (d, *J* = 11.6 Hz, 1H), 2.31 (d, *J* = 9.2 Hz, 1H), 1.57 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.5, 161.7 (d, *J* = 245 Hz), 159.6, 140.4, 136.1, 134.4 (d, *J* = 3.3 Hz),134.3, 130.0 (d, *J* = 7.8 Hz), 128.9, 128.4, 128.2, 115.3 (d, *J* = 21.1 Hz), 58.2, 55.4, 52.0, 48.7, 48.5, 48.3, 47.9. ESI-HRMS calcd for $[C_{23}H_{20}FNO_2+Na^+]$: 384.1376, found 384.1375.



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1	29.573	4115925	49.12
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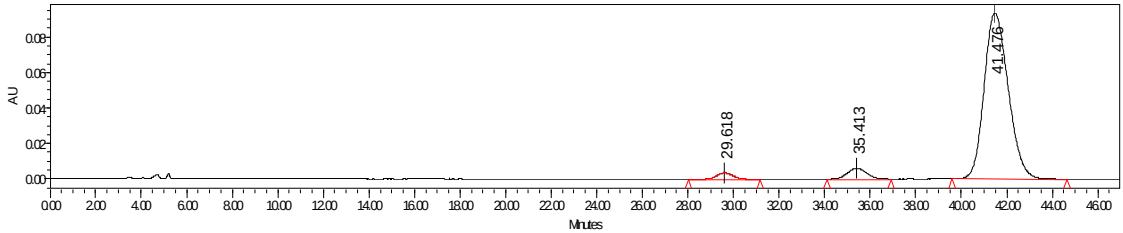

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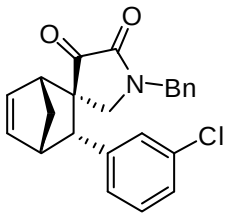
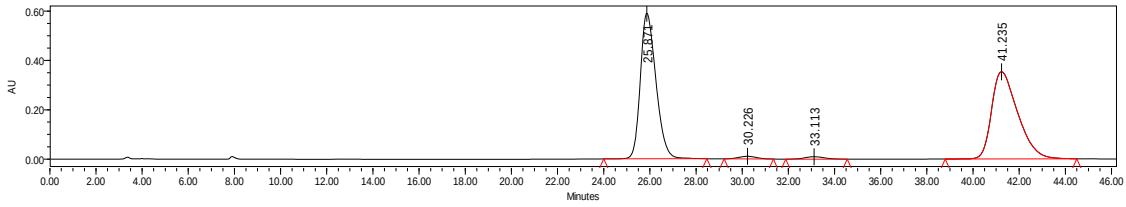
1	29.618	184680	2.48
2	35.413	367201	4.93
3	41.476	6890907	92.59

(1R,2R,3S,4S)-1'-benzyl-3-(3-chlorophenyl)spiro[bicyclo[2.2.1]heptane-2,3'-pyrrolidin]-5-ene-4',5'-dione **3d**



Yield: 34.3 mg (91%), white solid, 93:7 dr, 97% ee; $[\alpha]^{19.0}_{D}$ = -80.6 (c = 0.75, CH_2Cl_2); HPLC (Daicel chiralcel IC, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 40.37 min, $t_{R(minor)}$ = 25.67 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 3H), 7.14 – 7.02 (m, 4H), 6.91 (t, *J* = 1.6 Hz, 1H), 6.72 (d, *J* = 7.6 Hz, 1H), 6.68 (dd, *J* = 6.0, 3.2 Hz, 1H), 6.21 (dd, *J* = 6.0, 3.2 Hz, 1H), 4.63 (d, *J* = 14.4 Hz, 1H), 4.32 (d, *J* = 14.4 Hz, 1H), 3.86 (d, *J* = 2.8 Hz, 1H), 3.25 (s, 1H), 3.02 – 2.98 (m, 2H), 2.78 (d, *J* = 11.6 Hz, 1H), 2.28 (d, *J* = 8.8 Hz, 1H), 1.57 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.0, 159.5, 141.0, 140.4, 136.2, 134.4, 134.3, 129.8, 128.9, 128.4, 128.3, 128.2, 127.4, 126.9, 58.1, 55.6, 52.1, 48.8, 48.4, 48.3, 47.8. ESI-HRMS: calcd for $[C_{23}H_{20}{}^{34.9689}ClNO_2+Na^+]$ 400.1080, found 400.1079; ESI-HRMS: calcd for $[C_{23}H_{20}{}^{36.9659}ClNO_2+Na^+]$ 402.1051, found 402.1069.



	Retention Time	Area	% Area
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2	30.226	562901	0.99
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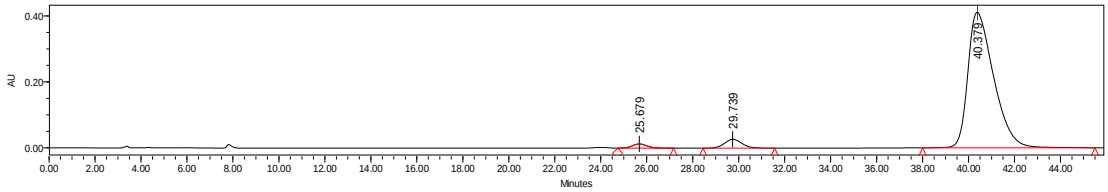
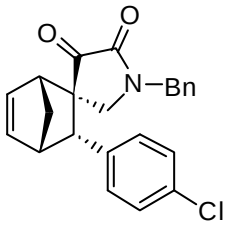
4	41.235	27720996	48.96

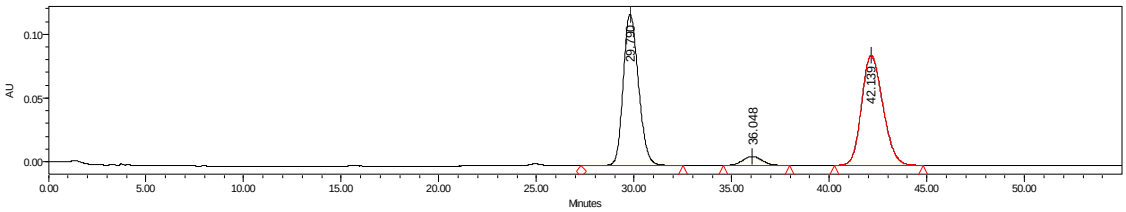


	Retention Time	Area	% Area
1	25.679	569298	1.68
2	29.739	1398259	4.13
3	40.379	31918263	94.19

(1R,2R,3S,4S)-1'-benzyl-3-(4-chlorophenyl)spiro[bicyclo[2.2.1]heptane-2,3'-pyrrolidin]-5-ene-4',5'-dione **3e**



Yield: 32.3 mg (86%), white powder, 93:7 dr, 95% ee; $[\alpha]^{23.0}_{D}$ = -76.0 (c = 0.65, CH_2Cl_2); HPLC (Daicel chiralcel IC, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 41.95 min, $t_{R(minor)}$ = 29.89 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 3H), 7.18 – 7.01 (m, 2H), 7.00 – 6.72 (m, 4H), 6.67 (dd, *J* = 5.6, 2.8 Hz, 1H), 6.22 (dd, *J* = 5.6, 2.8 Hz, 1H), 4.54 (d, *J* = 14.4 Hz, 1H), 4.35 (d, *J* = 14.4 Hz, 1H), 3.85 (d, *J* = 2.8 Hz, 1H), 3.24 (s, 1H), 3.11 – 2.94 (m, 2H), 2.76 (d, *J* = 11.6 Hz, 1H), 2.31 (d, *J* = 8.8 Hz, 1H), 1.57 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.5, 162.9, 160.5, 159.6, 140.4, 136.1, 134.5, 134.4, 134.3, 130.1, 129.9, 128.9, 128.4, 128.2, 115.5, 115.3, 58.2, 55.4, 52.0, 48.7, 48.5, 48.3, 47.9. ESI-HRMS: calcd for $[C_{23}H_{20}{}^{34.9689}ClNO_2+Na^+]$ 400.1080, found 400.1092; ESI-HRMS: calcd for $[C_{23}H_{20}{}^{36.9659}ClNO_2+Na^+]$ 402.1051, found 402.1088.



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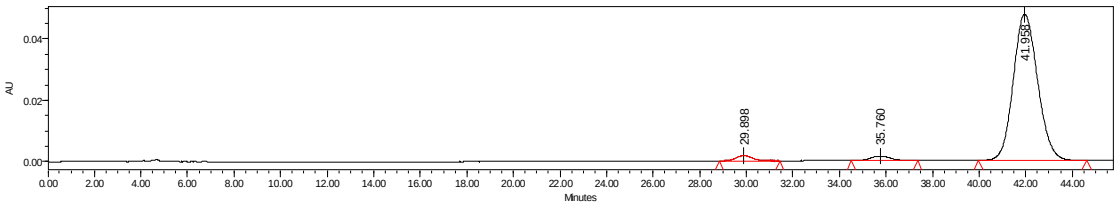
1	29.790	6446549	48.01
2	36.048	476441	3.55
3	42.139	6504205	48.44



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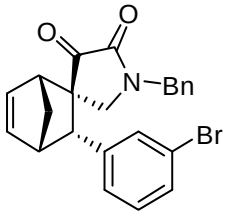
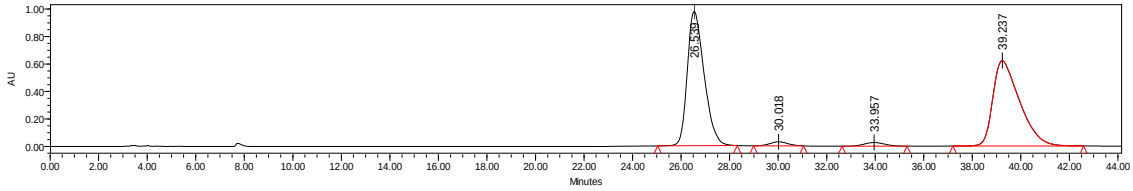
1	29.898	87517	2.42
2	35.760	85684	2.37
3	41.958	3441784	95.21

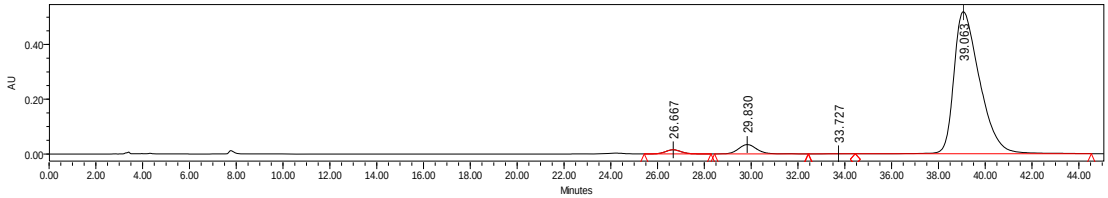
(1R,2R,3S,4S)-1'-benzyl-3-(3-bromophenyl)spiro[bicyclo[2.2.1]heptane-2,3'-pyrrolidin]-5-ene-4',5'-dione **3f**



Yield: 38.9 mg (92%), white amorphous solid, 94:6 dr, 97% ee; $[\alpha]^{18.1}_{D}$ = -87.5 (c = 0.81, CH_2Cl_2); HPLC (Daicel chiralcel IC, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 39.06 min, $t_{R(minor)}$ = 26.66 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 3H), 7.10 – 7.08 (m, 3H), 6.98 (t, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 6.67 (dd, *J* = 5.6, 2.8 Hz, 1H), 6.22 (dd, *J* = 5.6, 2.8 Hz, 1H), 4.64 (d, *J* = 14.4 Hz, 1H), 4.32 (d, *J* = 14.4 Hz, 1H), 3.85 (d, *J* = 2.8 Hz, 1H), 3.25 (s, 1H), 3.02 – 2.98 (m, 2H), 2.78 (d, *J* = 11.2 Hz, 1H), 2.28 (d, *J* = 8.8 Hz, 1H), 1.57 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.0, 159.5, 141.3, 140.3, 136.2, 134.3, 131.3, 130.3, 130.0, 128.9, 128.3, 128.2, 127.4, 122.7, 58.1, 55.6, 52.1, 48.8, 48.4, 48.3, 47.8. ESI-HRMS: calcd for $[C_{23}H_{20}{}^{78.9183}BrNO_2+Na^+]$ 444.0575, found 444.0573; ESI-HRMS: calcd for $[C_{23}H_{20}{}^{80.9163}BrNO_2+Na^+]$ 446.0555, found 446.0546.

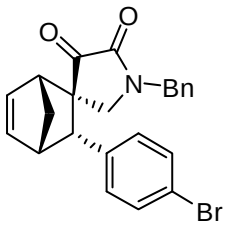


	Retention Time	Area	% Area
1	26.539	47122219	48.25
2	30.018	1521675	1.56
3	33.957	1585574	1.62
4	39.237	47436026	48.57

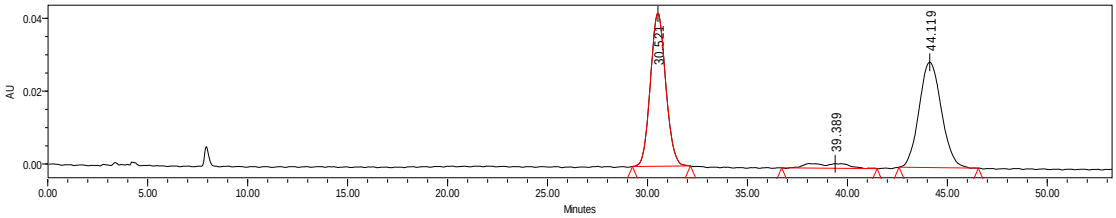


	Retention Time	Area	% Area
1	26.667	701020	1.66
2	29.830	1835033	4.36
3	33.727	19663	0.05
4	39.063	39548753	93.93

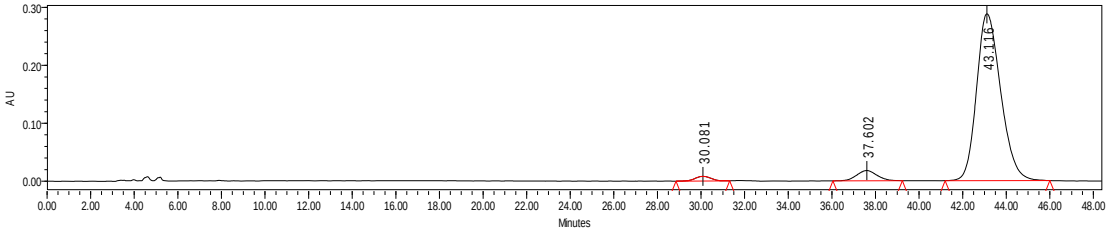
(1R,2R,3S,4S)-1'-benzyl-3-(4-bromophenyl)spiro[bicyclo[2.2.1]heptane-2,3'-pyrrolidin]-5-ene-4',5'-dione **3g**



Yield: 40.8 mg (97%), white amorphous solid, 93:7 dr, 96% ee; $[\alpha]^{22.8}_{D}$ = -80.5 (c = 0.82, CH_2Cl_2); HPLC (Daicel chiralcel IC, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 43.11 min, $t_{R(minor)}$ = 30.08 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 3H), 7.23 – 7.20 (m, 2H), 7.12 – 7.04 (m, 2H), 6.72 (d, *J* = 8.4 Hz, 2H), 6.65 (dd, *J* = 5.6, 2.8 Hz, 1H), 6.22 (dd, *J* = 5.6, 3.2 Hz, 1H), 4.46 (q, *J* = 14.4 Hz, 2H), 3.81 (d, *J* = 2.8 Hz, 1H), 3.23 (s, 1H), 3.06 – 2.95 (m, 2H), 2.76 (d, *J* = 11.2 Hz, 1H), 2.31 (d, *J* = 9.2 Hz, 1H), 1.57 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.3, 159.5, 140.4, 137.8, 136.2, 134.2, 131.6, 130.1, 128.9, 128.4, 128.3, 121.1, 58.4, 55.3, 52.1, 48.7, 48.3, 47.9. ESI-HRMS: calcd for $[C_{23}H_{20}{}^{78.9183}BrNO_2+Na^+]$ 444.0575, found 444.0580; ESI-HRMS: calcd for$[C_{23}H_{20}{}^{80.9163}BrNO_2+Na^+]$ 446.0555, found 446.0543.

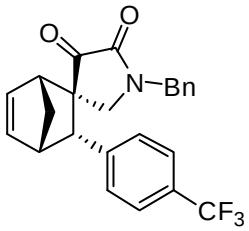


	Retention Time	Area	% Area
1	30.521	2236138	48.02
2	39.389	179965	3.86
3	44.119	2240571	48.12

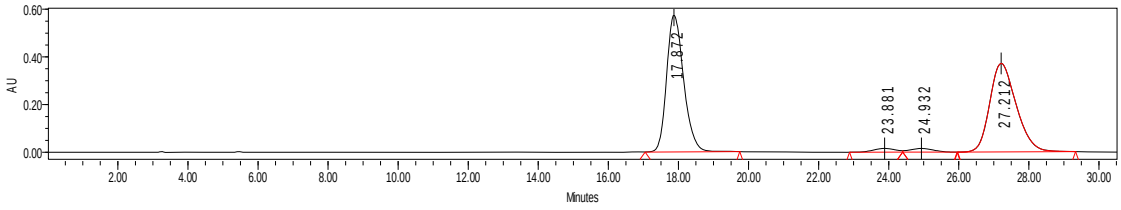


	Retention Time	Area	% Area
1	30.081	405185	1.71
2	37.602	1153697	4.88
3	43.116	22102811	93.41

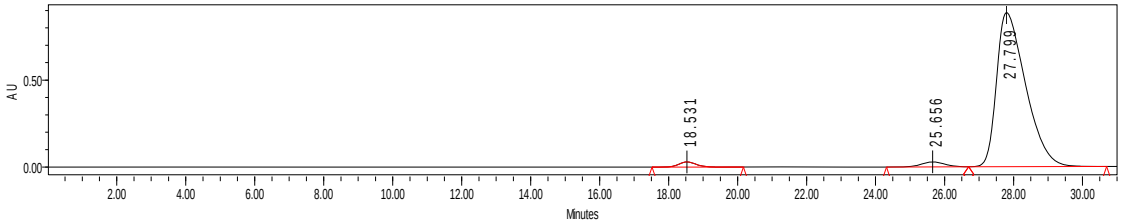
(1R,2R,3S,4S)-1'-benzyl-3-(4-(trifluoromethyl)phenyl)spiro[bicyclo[2.2.1]heptane-2,3'-pyrrolidin]-5-ene-4',5'-dione **3h**



Yield: 36.5 mg (89%), white amorphous solid, 94:6 dr, 96% ee; $[\alpha]^{18.6}_{D}$ = -60.8 (c = 0.73, CH_2Cl_2); HPLC (Daicel chiralcel IC, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 27.79 min, $t_{R(minor)}$ = 18.53 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.26 (m, 3H), 7.10 – 7.06 (m, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.68 (dd, *J* = 5.6, 2.8 Hz, 1H), 6.24 (dd, *J* = 5.6, 3.2 Hz, 1H), 4.48 (s, 2H), 3.94 (d, *J* = 2.4 Hz, 1H), 3.29 (s, 1H), 3.13 – 2.97 (m, 2H), 2.74 (d, *J* = 11.6 Hz, 1H), 2.33 (d, *J* = 8.8 Hz, 1H), 1.60 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 202.9, 159.4, 143.0, 140.4, 136.3, 134.3, 128.9, 128.8, 128.4, 128.4, 125.4 (q, 2C), 122.5, 58.3, 55.2, 52.3, 48.7, 48.4, 48.2, 47.7. ESI-HRMS calcd for $[C_{24}H_{20}F_3NO_2+Na^+]$: 434.1344, found 434.1343.

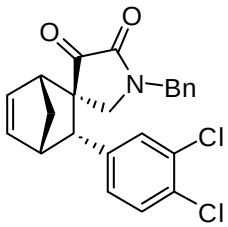


	Retention Time	Area	% Area
1	17.872	19392930	48.32
2	23.881	672190	1.67
3	24.932	698281	1.74
4	27.212	19368200	48.26

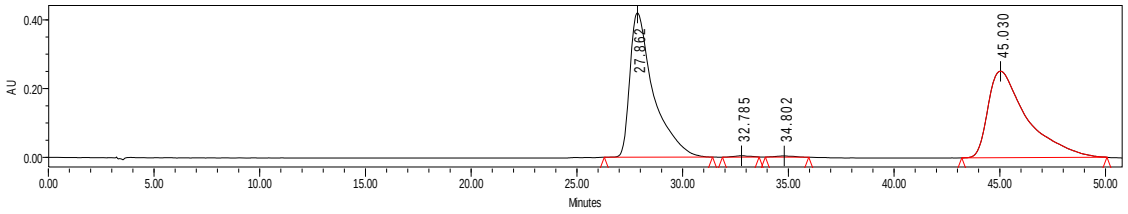


	Retention Time	Area	% Area
1	18.531	1053424	1.95
2	25.656	1358687	2.51
3	27.799	51740620	95.55

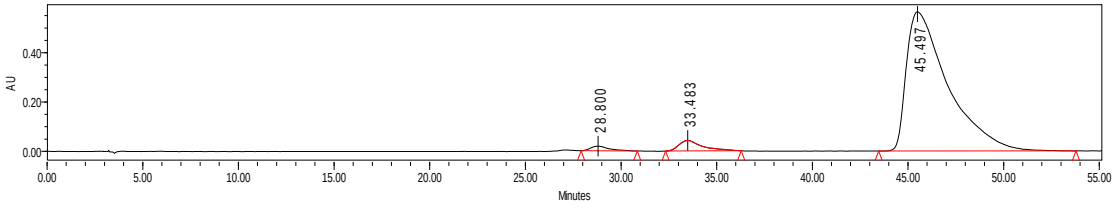
(1R,2R,3S,4S)-1'-benzyl-3-(3,4-dichlorophenyl)spiro[bicyclo[2.2.1]heptane-2,3'-pyrrolidin]-5-ene-4',5'-dione **3i**



Yield: 36.8 mg (90%), white amorphous solid, 93:7 dr, 97% ee; $[\alpha]^{18.4}_{D}$ = -92.5 (c = 0.74, CH_2Cl_2); HPLC (Daicel chiralcel IC, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 45.49 min, $t_{R(minor)}$ = 28.80 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 3H), 7.16 – 6.95 (m, 4H), 6.67 – 6.61 (m, 2H), 6.26 (dd, *J* = 5.6, 3.2 Hz, 1H), 4.49 (dd, *J* = 37.2, 14.4 Hz, 2H), 3.79 (d, *J* = 2.8 Hz, 1H), 3.22 (s, 1H), 3.11 – 2.98 (m, 2H), 2.76 (d, *J* = 11.6 Hz, 1H), 2.30 (d, *J* = 9.2 Hz, 1H), 1.58 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 202.9, 159.3, 140.1, 139.1, 136.6, 134.1, 132.6, 131.3, 130.4, 130.2, 128.9, 128.4, 128.3, 128.1, 57.8, 55.4, 52.2, 48.6, 48.5, 48.3, 47.9. ESI-HRMS: calcd for $[C_{23}H_{19}{}^{34.9689}Cl_2NO_2+Na^+]$ 434.0691, found 434.0690; ESI-HRMS: calcd for $[C_{23}H_{19}{}^{36.9659}Cl_2NO_2+Na^+]$ 436.0661, found 436.0666.



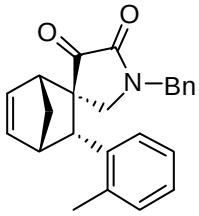
	Retention Time	Area	% Area
1	27.862	32423830	49.73
2	32.785	197461	0.30
3	34.802	197304	0.30
4	45.030	32376270	49.66



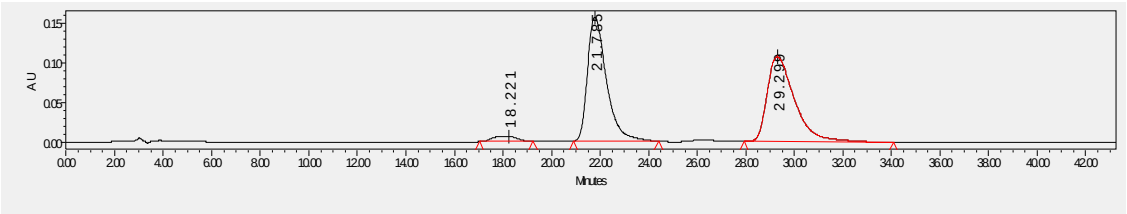
	Retention Time	Area	% Area
1	28.800	1252213	1.39
2	33.483	3612096	4.02
3	45.497	84928633	94.58

(1R,2R,3S,4S)-1'-benzyl-3-(o-tolyl)spiro[bicyclo[2.2.1]heptane-2,3'-pyrrolidin]-5-ene-4',5'-dione

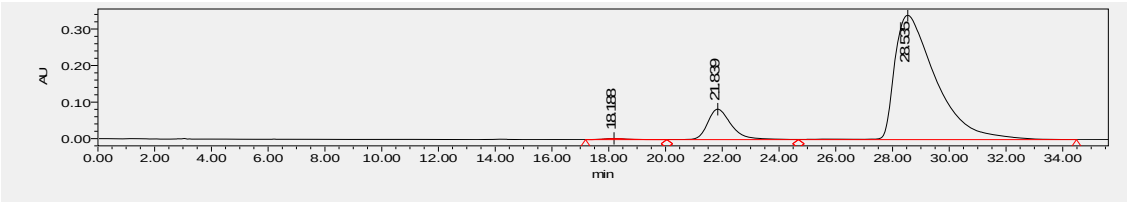
3j



Yield: 28.6 mg (80%), white amorphous solid, 90:10 dr, 75% ee; $[\alpha]^{20.1}_{D}$ = -58.6 (c = 0.57, CH_2Cl_2); HPLC (Chiralpak Lux 5u Cellulose-2, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 28.53 min, $t_{R(minor)}$ = 21.83 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.18 (m, 3H), 7.05 – 6.88 (m, 6H), 6.73 (dd, *J* = 5.6, 3.2 Hz, 1H), 6.06 (dd, *J* = 5.6, 3.2 Hz, 1H), 4.55 (d, *J* = 14.4 Hz, 1H), 4.27 (d, *J* = 14.4 Hz, 1H), 3.98 (d, *J* = 2.8 Hz, 1H), 3.18 (s, 1H), 2.93 (s, 1H), 2.85 (d, *J* = 11.6 Hz, 1H), 2.63 (d, *J* = 11.6 Hz, 1H), 2.23 (d, *J* = 9.2 Hz, 1H), 1.85 (s, 3H), 1.49 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 202.7, 159.5, 141.6, 137.8, 137.6, 135.2, 134.4, 130.8, 128.9, 128.2, 128.1, 127.4, 127.0, 125.9, 55.4, 53.9, 52.4, 48.7, 48.6, 48.2, 47.9, 21.0. ESI-HRMS calcd for [$C_{24}H_{23}NO_2$+Na^+]: 380.1626, found 380.1623.



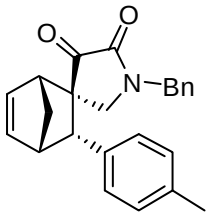
	Retention Time	Area	% Area
1	18.221	451977	2.59
2	21.785	8542732	48.96
3	29.299	8452552	48.45



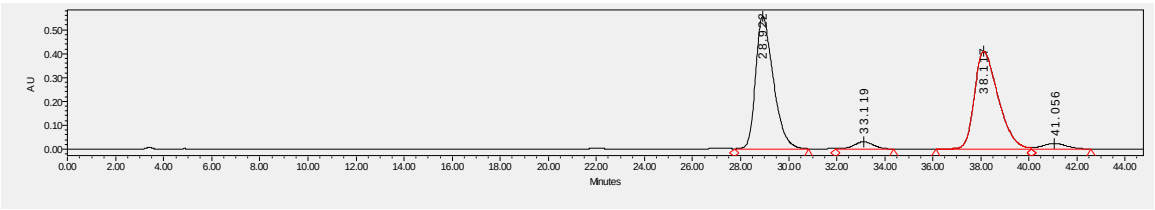
	Retention Time	Area	% Area
1	18.188	153528	0.39
2	21.839	4811609	12.28
3	28.535	34212948	87.33

(1R,2R,3S,4S)-1'-benzyl-3-(p-tolyl)spiro[bicyclo[2.2.1]heptane-2,3'-pyrrolidin]-5-ene-4',5'-dione

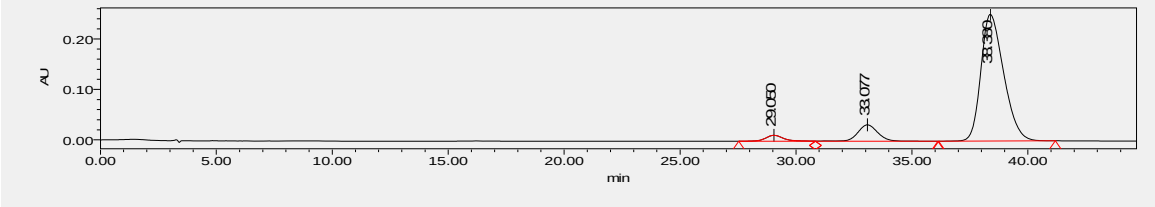
3k



Yield: 29.7 mg (83%), white amorphous solid, 92:8 dr, 93% ee; $[\alpha]^{18.8}_{D}$ = -101.7 (c = 0.59, CH_2Cl_2); HPLC (Daicel chiralcel IC, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 38.38 min, $t_{R(minor)}$ = 29.05 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.18 (m, 3H), 7.05 – 6.97 (m, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.69 (d, *J* = 8.0 Hz, 2H), 6.61 (dd, *J* = 5.6, 2.8 Hz, 1H), 6.10 (dd, *J* = 5.6, 3.2 Hz, 1H), 4.57 (d, *J* = 14.8 Hz, 1H), 4.16 (d, *J* = 14.4 Hz, 1H), 3.79 (d, *J* = 2.8 Hz, 1H), 3.17 (s, 1H), 2.98 – 2.86 (m, 2H), 2.73 (d, *J* = 11.6 Hz, 1H), 2.23 (d, *J* = 8.8 Hz, 1H), 2.20 (s, 3H), 1.48 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.7, 159.8, 140.8, 136.7, 135.7, 135.6, 134.4, 129.2, 128.8, 128.4, 128.4, 128.0, 58.7, 55.6, 51.9, 48.9, 48.4, 48.3, 47.9, 20.9. ESI-HRMS calcd for [$C_{24}H_{23}NO_2$+Na^+]: 380.1626, found 380.1623.

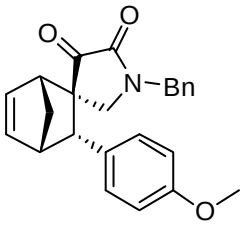


	Retention Time	Area	% Area
1	28.922	28386877	47.49
2	33.119	1694635	2.83
3	38.117	28039239	46.91
4	41.056	1654876	2.77

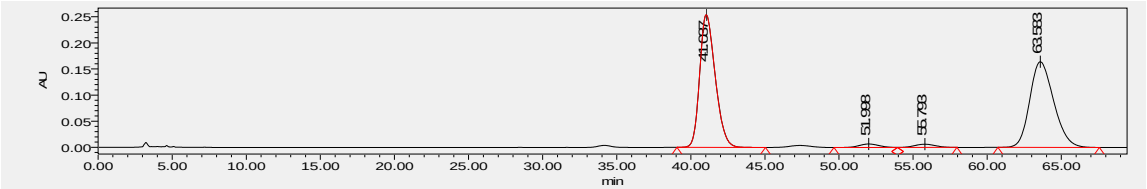


	Retention Time	Area	% Area
1	29.050	608575	3.10
2	33.077	1908644	9.71
3	38.380	17132471	87.19

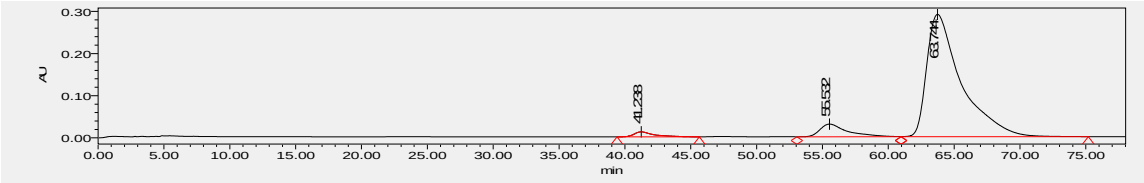
(1R,2R,3S,4S)-1'-benzyl-3-(4-methoxyphenyl)spiro[bicyclo[2.2.1]heptane-2,3'-pyrrolidin]-5-ene-4',5'-dione **3l**



Yield: 31.8 mg (85%), white power, 92:8 dr, 96% ee; $[\alpha]^{18.7}_{D}$ = -113.4 (c = 0.64, CH_2Cl_2); HPLC (Daicel chiralcel IC, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 63.74 min, $t_{R(minor)}$ = 41.23 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.26 (m, 3H), 7.07 – 7.04 (m, 2H), 6.83 – 6.77 (m, 2H), 6.71 – 6.65 (m, 3H), 6.18 (dd, *J* = 5.6, 2.8 Hz, 1H), 4.63 (d, *J* = 14.4 Hz, 1H), 4.23 (d, *J* = 14.4 Hz, 1H), 3.83 (d, *J* = 2.8 Hz, 1H), 3.76 (s, 3H), 3.22 (s, 1H), 3.03 – 2.94 (m, 2H), 2.82 (d, *J* = 11.6 Hz, 1H), 2.31 (d, *J* = 8.8 Hz, 1H), 1.55 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.8, 159.8, 158.5, 140.7, 135.7, 134.4, 130.7, 129.6, 128.8, 128.3, 128.1, 113.8, 58.4, 55.6, 55.2, 51.9, 48.8, 48.6, 48.3, 47.9. ESI-HRMS calcd for $[C_{24}H_{23}NO_3+Na^+]$: 396.1576, found 396.1572.

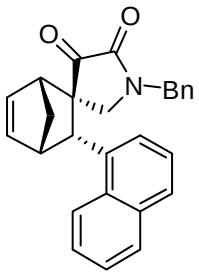


	Retention Time	Area	% Area
1	41.037	18501998	48.54
2	51.998	602585	1.58
3	55.793	584442	1.53
4	63.583	18425569	48.34

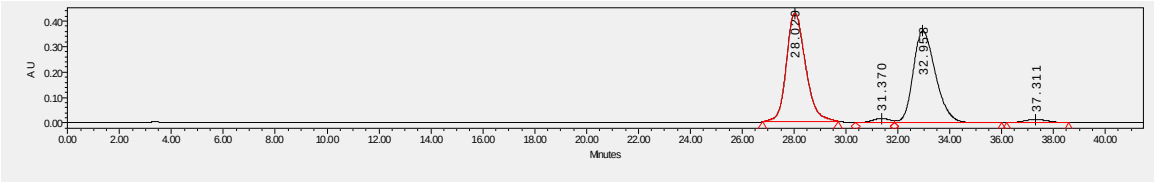


	Retention Time	Area	% Area
1	41.238	1215425	2.08
2	55.532	4364333	7.48
3	63.744	52753303	90.43

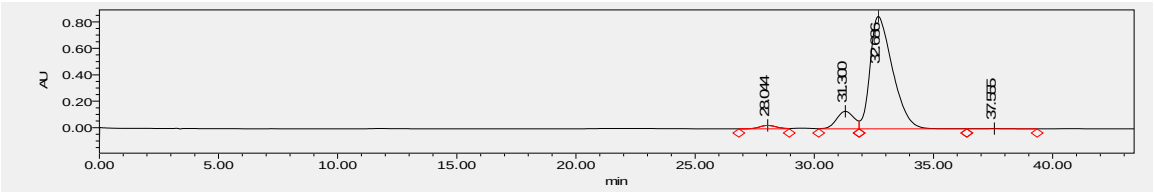
(1R,2R,3S,4S)-1'-benzyl-3-(naphthalen-1-yl)spiro[bicyclo[2.2.1]heptane-2,3'-pyrrolidin]-5-ene-4',5'-dione **3m**



Yield: 36.8 mg (94%), white power, 88:12 dr, 95% ee; $[\alpha]^{20.1}_{D}$ = 55.6 (c = 0.74, CH_2Cl_2); HPLC (Daicel chiralcel IC, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 32.68 min, $t_{R(minor)}$ = 28.04 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 -7.73(m, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.41-7.37 (m, 2H), 7.24-7.14 (m, 3H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.94 (m, 2H), 6.87 (dd, *J* = 5.6, 3.2 Hz, 1H), 6.49 (d, *J* = 7.2 Hz, 2H), 6.08 (dd, *J* = 5.6, 3.2 Hz, 1H), 4.51 (d, *J* = 2.4, 1H), 4.14 (s, 2H), 3.35 (s, 1H), 2.99 (s, 1H), 2.67 (d, *J* = 12.0 Hz, 1H), 2.43 (d, *J* = 9.2 Hz, 1H), 2.19 (d, *J* = 11.6 Hz,1H), 1.61 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 204.3, 159.5, 141.5, 135.5, 135.0, 133.9, 133.6, 132.5, 129.2, 128.6, 128.1, 127.7, 127.6, 126.9, 126.0, 124.9, 124.9, 122.9, 55.0, 54.8, 52.6, 48.5, 48.2, 47.9. ESI-HRMS calcd for [$C_{27}H_{23}NO_2$+Na^+]: 416.1626, found 416.1624.

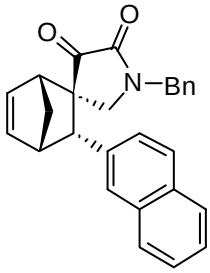


	Retention Time	Area	% Area
1	28.029	21703797	48.21
2	31.370	838350	1.86
3	32.958	21639571	48.07
4	37.311	838830	1.86

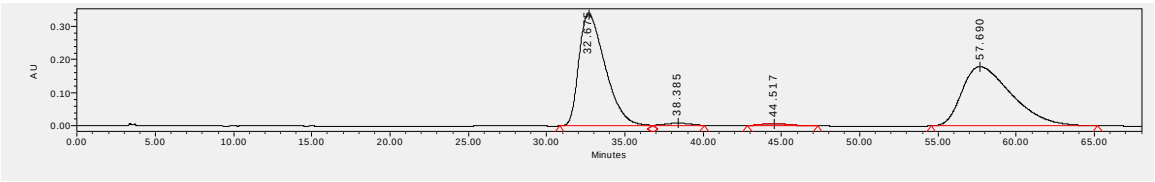


	Retention Time	Area	% Area
1	28.044	1343175	2.09
2	31.300	6786078	10.57
3	32.686	55800337	86.95
4	37.555	244147	0.38

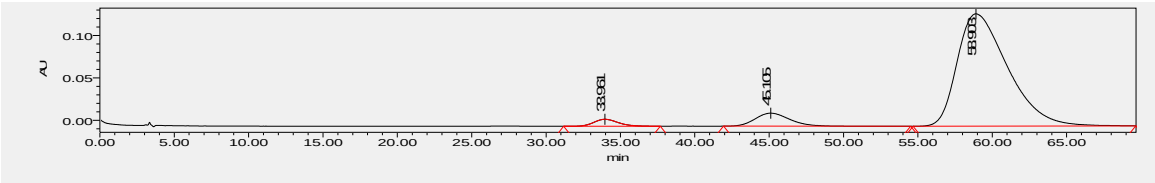
(1R,2R,3S,4S)-1'-benzyl-3-(naphthalen-2-yl)spiro[bicyclo[2.2.1]heptane-2,3'-pyrrolidin]-5-ene-4',5'-dione **3n**



Yield: 33.5 mg (85%), white power, 93:7 dr, 94% ee; $[\alpha]^{18.9}_{D}$ = -131.2 (c = 0.67, CH_2Cl_2); HPLC (Daicel chiralcel ASH, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 58.90 min, $t_{R(minor)}$ = 33.96 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.69 (m, 2H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.48 – 7.42 (m, 3H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.04 (t, *J* = 7.2 Hz, 2H), 6.94 – 6.86 (m, 3H), 6.82 (dd, *J* = 5.6, 3.2 Hz, 1H), 6.23 (dd, *J* = 5.6, 3.2 Hz, 1H), 4.57 (d, *J* = 14.4 Hz, 1H), 4.22 (d, *J* = 14.4 Hz, 1H), 4.07 (d, *J* = 2.8 Hz, 1H), 3.35 (s, 1H), 3.05 (s, 1H), 2.99 (d, *J* = 11.6 Hz, 1H), 2.81 (d, *J* = 11.6 Hz, 1H), 2.38 (d, *J* = 9.2 Hz, 1H), 1.62 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.7, 159.8, 140.8, 136.4, 135.8, 134.2, 133.2, 132.3, 128.7, 128.2, 127.9, 127.8, 127.6, 127.1, 126.6, 126.4, 126.1, 59.4, 55.5, 52.1, 48.9, 48.4, 48.3, 48.1. ESI-HRMS calcd for [$C_{27}H_{23}NO_2$+Na^+]: 416.1626, found 416.1629.

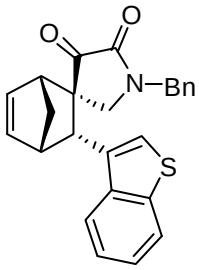


	Retention Time	Area	% Area
1	32.675	39330042	49.01
2	38.385	772908	0.96
3	44.517	767227	0.96
4	57.690	39377979	49.07

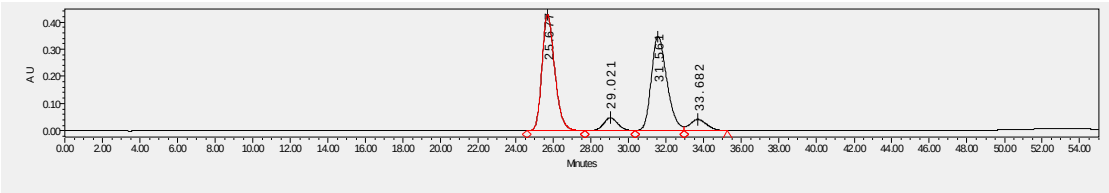


	Retention Time	Area	% Area
1	33.961	934769	2.70
2	45.105	2484534	7.18
3	58.903	31194493	90.12

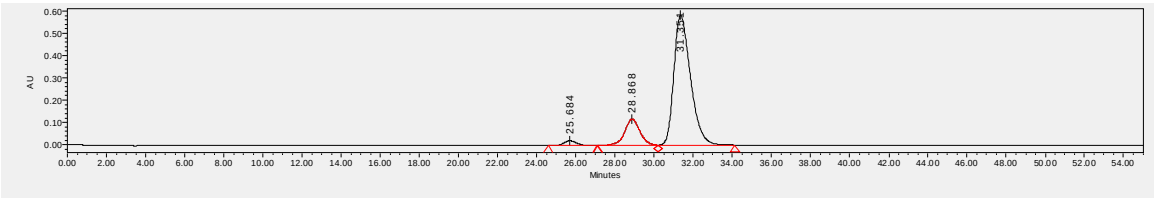
(1R,2R,3R,4S)-3-(benzo[b]thiophen-3-yl)-1'-benzylspiro[bicyclo[2.2.1]heptane-2,3'-pyrrolidin]-5-ene-4',5'-dione **3o**



Yield: 31.0 mg (78%), white power, 82:18 dr, 92% ee; $[\alpha]^{19.0}_{D}$ = 6.6 (c = 0.62, CH_2Cl_2); HPLC (Daicel chiralcel IC, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 31.35 min, $t_{R(minor)}$ = 25.68 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 1H), 7.32 – 7.22 (m, 2H), 7.17 – 7.05 (m, 2H), 7.06 – 6.85 (m, 3H), 6.75 (dd, *J* = 5.7, 2.8 Hz, 1H), 6.62 (d, *J* = 7.2 Hz, 1H), 6.13 (dd, *J* = 5.6, 3.2 Hz, 1H), 4.23 (q, *J* = 14.8 Hz, 2H), 4.10 (d, *J* = 2.8 Hz, 1H), 3.32 (s, 1H), 3.01 (s, 1H), 2.78 (d, *J* = 11.6 Hz, 1H), 2.43 (d, *J* = 11.6 Hz, 1H), 2.34 (d, *J* = 9.2 Hz, 1H), 1.57 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.9, 159.5, 140.8, 139.8, 138.9, 135.9, 134.7, 133.8, 128.7, 127.8, 127.8, 127.7, 124.9, 124.8, 122.9, 122.6, 121.3, 54.5, 52.4, 51.6, 48.7, 48.3, 48.1, 47.9. ESI-HRMS calcd for [$C_{25}H_{21}NO_2S$ +Na^+]: 422.1191, found 422.1194.

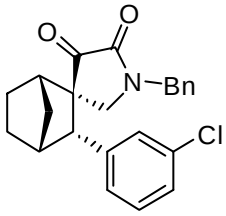


	Retention Time	Area	% Area
1	25.677	20051744	44.37
2	29.021	2528943	5.60
3	31.561	20032182	44.32
4	33.682	2583831	5.72

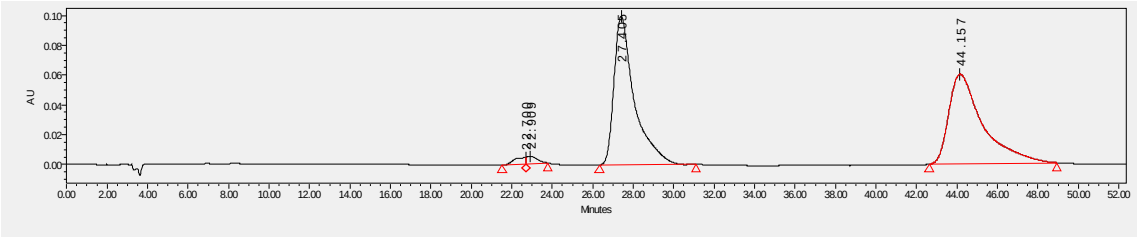


	Retention Time	Area	% Area
1	25.684	1018643	2.42
2	28.868	6513711	15.50
3	31.351	34481693	82.07

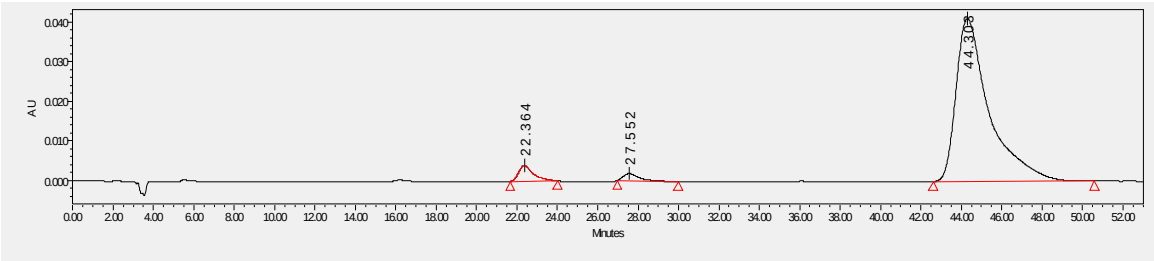
(1S,2R,3S,4R)-1'-benzyl-3-(3-chlorophenyl)spiro[bicyclo[2.2.1]heptane-2,3'-pyrrolidine]-4',5'-dione **6**



Yield: 25.8 mg (68%), white power, >95:5 dr, 96% ee; $[\alpha]^{15.7}_{D}$ = -49.8 (c = 0.52, CH_2Cl_2); HPLC (Daicel chiralcel IC, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 44.30 min, $t_{R(minor)}$ = 27.55 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 3H), 7.24 – 7.18 (m, 2H), 7.17 – 7.13 (m, 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 6.97 (s, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 4.73 (d, *J* = 14.4 Hz, 1H), 4.45 (d, *J* = 14.4 Hz, 1H), 3.53 (d, *J* = 2.8 Hz, 1H), 3.41 (d, *J* = 11.6 Hz, 1H), 3.18 (d, *J* = 11.6 Hz, 1H), 2.68 (s, 1H), 2.43 (s, 1H), 2.30 (d, *J* = 10.4 Hz, 1H), 1.73 – 1.66 (m, 1H), 1.61 – 1.49 (m, 1H), 1.48 – 1.39 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.3, 159.2, 139.9, 134.4, 134.3, 129.6, 129.0, 128.8, 128.5, 128.3, 127.1, 126.9, 53.3, 51.9, 48.6, 46.9, 46.4, 40.9, 37.1, 25.1, 21.8. ESI-HRMS calcd for [$C_{23}H_{22}ClNO_2$+Na^+]: 402.1237, found 402.1231.

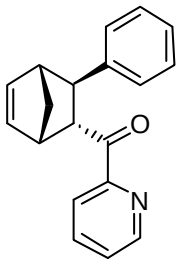


	Retention Time	Area	% Area
1	22.700	185798	1.30
2	22.909	188638	1.32
3	27.405	6947122	48.46
4	44.157	7014929	48.93

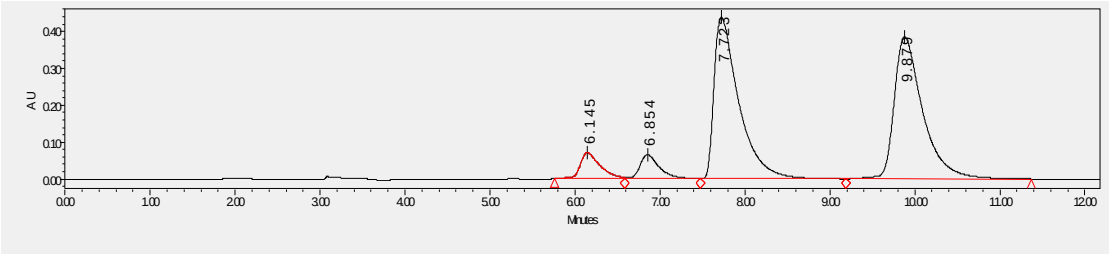


	Retention Time	Area	% Area
1	22.364	204620	4.10
2	27.552	100412	2.01
3	44.303	4685041	93.89

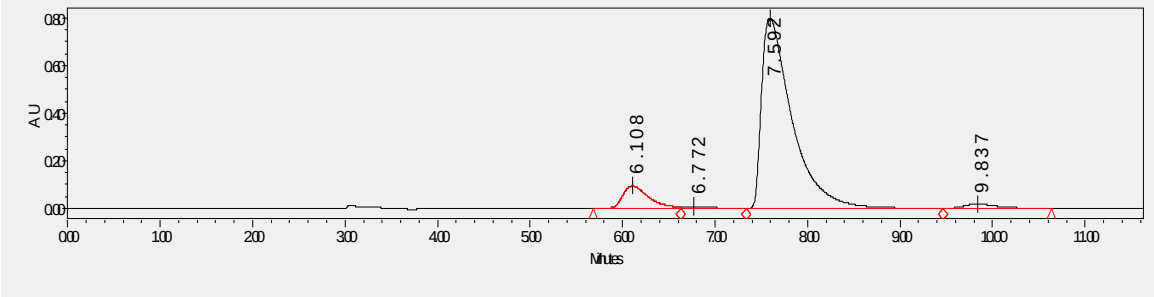
(1S,2R,3R,4R)-3-phenylbicyclo[2.2.1]hept-5-en-2-yl)(pyridin-2-yl)methanone **5a**



Yield: 24.5 mg (89%), colorless oil, 93:7 dr, 96% ee; $[\alpha]^{18.6}_{D}$ = -184.6 (c = 0.51, $CHCl_3$); HPLC (Daicel chiralcel ODH, *n*-hexane/*i*-PrOH 98/2, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 7.59 min, $t_{R(minor)}$ = 9.83 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.4 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.74 (td, *J* = 7.6, 1.6 Hz, 1H), 7.37 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 7.27 – 7.16 (m, 4H), 7.11 – 7.06 (m, 1H), 6.42 (dd, *J* = 5.6, 3.2 Hz, 1H), 5.75 (dd, *J* = 5.6, 2.8 Hz, 1H), 4.46 (dd, *J* = 5.2, 4.4 Hz, 1H), 3.47 (s, 1H), 3.38 (d, *J* = 4.4 Hz, 1H), 3.01 (s, 1H), 2.00 (d, *J* = 8.4 Hz, 1H), 1.54 (dd, *J* = 8.8, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 201.2, 153.6, 148.9, 144.6, 139.5, 136.9, 132.9, 128.4, 127.7, 126.9, 125.8, 122.2, 54.2, 49.4, 48.8, 48.2, 45.6. ESI-HRMS calcd for [$C_{19}H_{17}NO$ +Na^+]: 298.1208, found 298.1205.

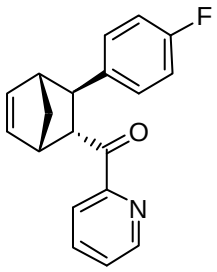


	Retention Time	Area	% Area
1	6.145	1168584	5.81
2	6.854	1057562	5.26
3	7.723	8892787	44.22
4	9.879	8993362	44.72

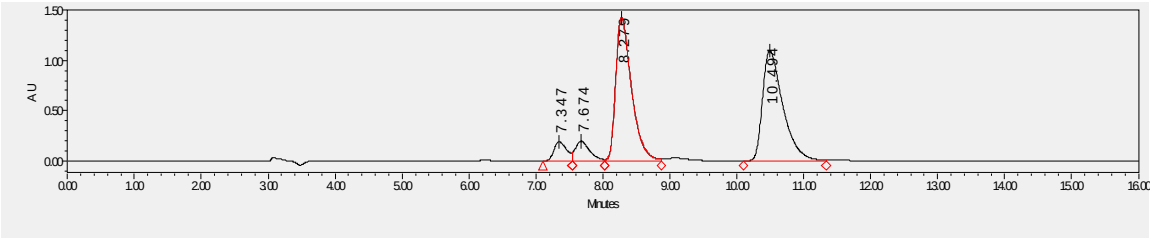


	Retention Time	Area	% Area
1	6.108	1828121	8.85
2	6.772	161746	0.78
3	7.592	18245128	88.37
4	9.837	411754	1.99

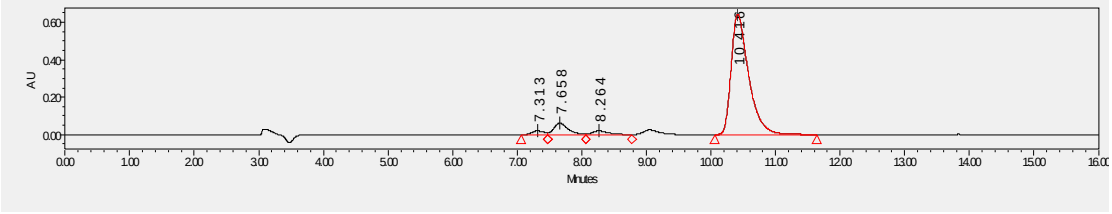
(1S,2R,3R,4R)-3-(4-fluorophenyl)bicyclo[2.2.1]hept-5-en-2-yl)(pyridin-2-yl)methanone **5b**



Yield: 25.2 mg (86%), colorless oil, 93:7 dr, 95% ee; $[\alpha]^{12.7}_{D}$ = -132.6 (c = 0.47, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 10.41 min, $t_{R(minor)}$ = 8.26 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (ddd, *J* = 4.4, 1.6, 0.8 Hz, 1H), 7.96 – 7.90 (m, 1H), 7.75 (td, *J* = 7.6, 1.6 Hz, 1H), 7.39 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 7.20 – 7.17 (m, 2H), 6.91 – 6.85 (m, 2H), 6.41 (dd, *J* = 5.6, 3.2 Hz, 1H), 5.75 (dd, *J* = 5.6, 2.8 Hz, 1H), 4.39 (dd, *J* = 5.2, 3.6 Hz, 1H), 3.47 (s, 1H), 3.34 (d, *J* = 4.8 Hz, 1H), 2.97 (d, *J* = 1.2 Hz, 1H), 1.96 (d, *J* = 8.4 Hz, 1H), 1.54 (dd, *J* = 8.8, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 201.0, 161.6 (d, *J* = 242 Hz), 153.5, 148.9, 140.3, 139.4, 136.9, 132.9, 128.9 (d, *J* = 0.8 Hz), 127.0, 122.3, 115.2 (d, *J* = 21.0 Hz), 54.5, 49.4, 48.7, 48.2, 44.9. ESI-HRMS calcd for [$C_{19}H_{16}FNO$ +H^+]: 294.1294, found 294.1292.

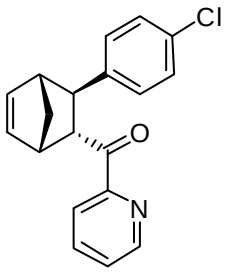


	Retention Time	Area	% Area
1	7.347	2510371	4.83
2	7.674	2913663	5.61
3	8.279	23414745	45.06
4	10.494	23126754	44.50

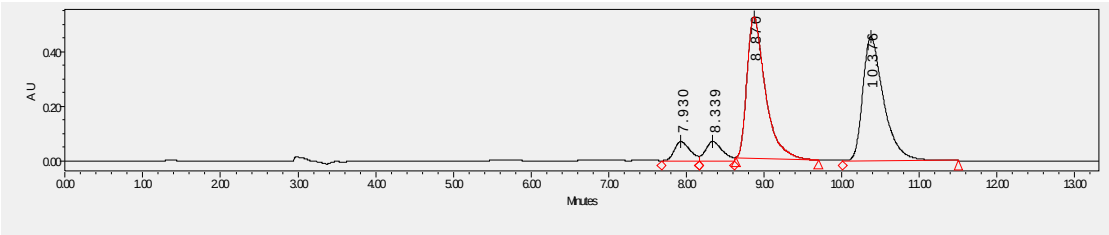


	Retention Time	Area	% Area
1	7.313	253709	1.87
2	7.658	932058	6.87
3	8.264	328303	2.42
4	10.416	12050878	88.84

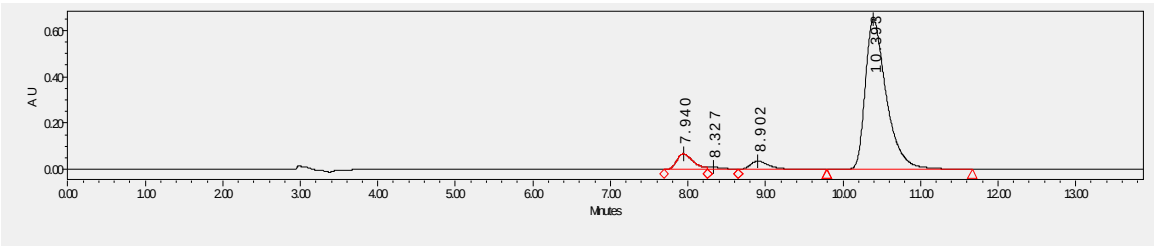
(1S,2R,3R,4R)-3-(4-chlorophenyl)bicyclo[2.2.1]hept-5-en-2-yl)(pyridin-2-yl)methanone **5c**



Yield: 27.8 mg (90%), colorless oil, 92:8 dr, 88% ee; $[\alpha]^{10.6}_{D}$ = -132.4 (c = 0.48, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 10.39 min, $t_{R(minor)}$ = 8.90 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 4.4 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.76 (td, *J* = 7.6, 1.6 Hz, 1H), 7.39 (ddd, *J* = 7.2, 4.8, 0.8 Hz, 1H), 7.20 – 7.15 (m, 4H), 6.41 (dd, *J* = 5.2, 3.2 Hz, 1H), 5.76 (dd, *J* = 5.2, 2.4 Hz, 1H), 4.38 (dd, *J* = 4.8, 3.2 Hz, 1H), 3.47 (s, 1H), 3.34 (dd, *J* = 4.8, 1.2 Hz, 1H), 2.98 (s, 1H), 1.94 (d, *J* = 8.4 Hz, 1H), 1.56 (d, *J* = 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.9, 153.4, 148.9, 143.2, 139.3, 136.9, 133.0, 131.5, 128.9, 128.4, 127.0, 122.3, 54.4, 49.3, 48.7, 48.2, 45.0. ESI-HRMS: calcd for $[C_{19}H_{16}{}^{34.9689}ClNO+Na^+]$ 332.0818, found 400.0811; ESI-HRMS: calcd for $[C_{19}H_{16}{}^{36.9659}ClNO+Na^+]$ 334.0789, found 402.0786.

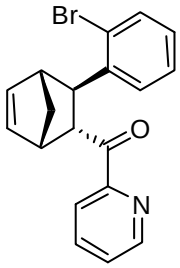


	Retention Time	Area	% Area
1	7.930	966341	5.10
2	8.339	1056042	5.57
3	8.870	8489093	44.80
4	10.376	8435721	44.52

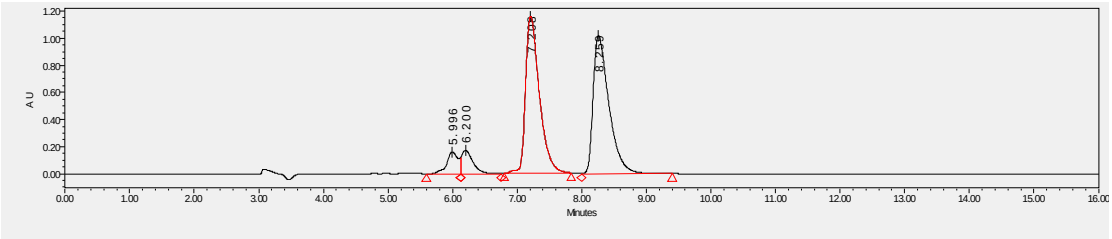


	Retention Time	Area	% Area
1	7.940	983477	7.06
2	8.327	128991	0.93
3	8.902	604612	4.34
4	10.393	12221224	87.68

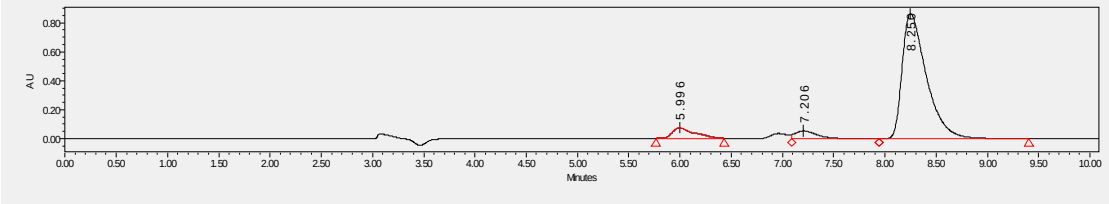
(1S,2R,3R,4R)-3-(2-bromophenyl)bicyclo[2.2.1]hept-5-en-2-yl)(pyridin-2-yl)methanone **5d**



Yield: 28.9 mg (82%), colorless oil, 92:8 dr, 90% ee; $[\alpha]^{9.8}_{D}$ = -91.5 (c = 0.58, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 8.25 min, $t_{R(minor)}$ = 7.20 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 4.4 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.75 (td, *J* = 7.6, 1.6 Hz, 1H), 7.46 (ddd, *J* = 10.8, 7.6, 1.2 Hz, 2H), 7.38 (ddd, *J* = 7.6, 4.0, 0.8 Hz, 1H), 7.25 – 7.20 (m, 1H), 6.98 (td, *J* = 8.0, 1.6 Hz, 1H), 6.46 (dd, *J* = 5.6, 3.2 Hz, 1H), 5.83 (dd, *J* = 5.6, 2.8 Hz, 1H), 4.61 (dd, *J* = 4.8, 3.6 Hz, 1H), 3.53 (d, *J* = 4.0 Hz, 1H), 3.41 (s, 1H), 2.99 (d, *J* = 1.2 Hz, 1H), 1.92 (d, *J* = 8.4 Hz, 1H), 1.52 (dd, *J* = 8.9, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.4, 153.6, 148.8, 143.4, 138.5, 136.9, 133.7, 133.2, 127.9, 127.4, 127.2, 126.9, 126.4, 122.3, 51.2, 49.9, 48.5, 47.5, 46.3. ESI-HRMS: calcd for $[C_{19}H_{16}{}^{78.9183}BrNO + Na^+]$ 376.0313, found 376.0315; ESI-HRMS: calcd for $[C_{19}H_{16}{}^{80.9163}BrNO + Na^+]$ 378.0292, found 378.0287.

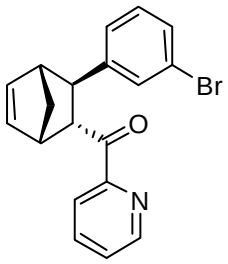


	Retention Time	Area	% Area
1	5.996	1983504	5.15
2	6.200	2054120	5.34
3	7.208	17258436	44.83
4	8.259	17203587	44.69

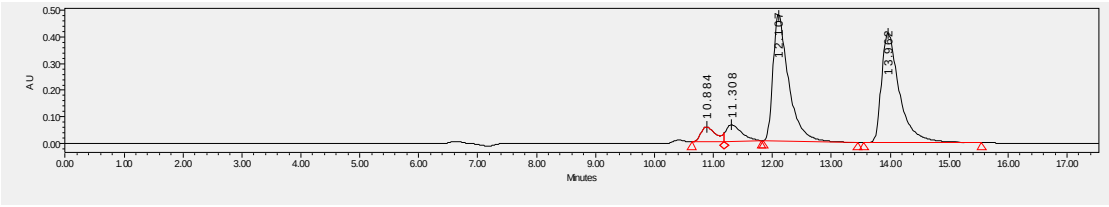


	Retention Time	Area	% Area
1	5.996	1067570	6.68
2	7.206	789406	4.94
3	8.250	14113809	88.37

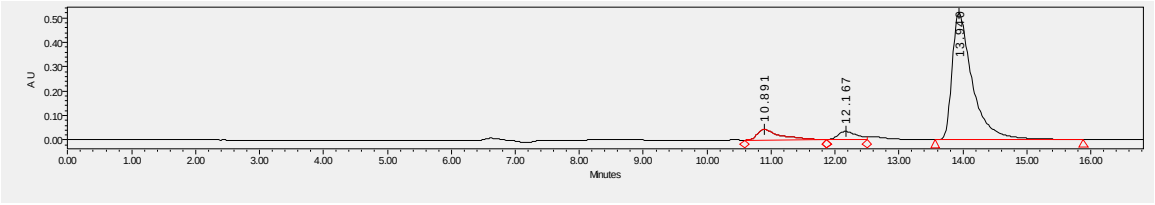
(1S,2R,3R,4R)-3-(3-bromophenyl)bicyclo[2.2.1]hept-5-en-2-yl)(pyridin-2-yl)methanone **5e**



Yield: 26.2 mg (74%), colorless oil, 90:10 dr, 88% ee; $[\alpha]^{8.8}_{D}$ = -133.9 (c = 0.52, CH_2Cl_2); HPLC (Daicel chiralcel ID-Chiralpak Lux 5u Cellulose-2, *n*-hexane/*i*-PrOH 90/10, 0.9 mL/min, 254 nm) $t_{R(major)}$ = 13.94 min, $t_{R(minor)}$ = 12.16 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 – 8.59 (m, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.76 (td, *J* = 7.6, 1.6 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.21 – 7.13 (m, 2H), 7.06 (t, *J* = 8.0 Hz, 1H), 6.40 (dd, *J* = 5.6, 3.2 Hz, 0H), 5.75 (dd, *J* = 5.6, 2.4 Hz, 1H), 4.38 (dd, *J* = 5.2, 3.2 Hz, 1H), 3.49 (s, 0H), 3.34 (d, *J* = 4.4 Hz, 1H), 2.99 (d, *J* = 1.2 Hz, 1H), 1.96 (d, *J* = 8.4 Hz, 1H), 1.56 (dd, *J* = 8.4, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 199.7, 152.3, 147.9, 146.1, 138.2, 135.9, 132.0, 129.5, 128.9, 127.9, 126.0, 125.4, 121.5, 121.2, 53.4, 48.1, 47.7, 47.2, 44.2. ESI-HRMS: calcd for $[C_{19}H_{16}{}^{78.9183}BrNO + Na^+]$ 376.0313, found 376.0309; ESI-HRMS: calcd for $[C_{19}H_{16}{}^{80.9163}BrNO + Na^+]$ 378.0292, found 378.0285.

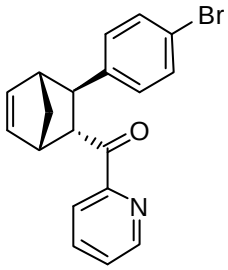


	Retention Time	Area	% Area
1	10.884	995501	5.06
2	11.308	1119589	5.69
3	12.107	8753920	44.50
4	13.962	8804460	44.75

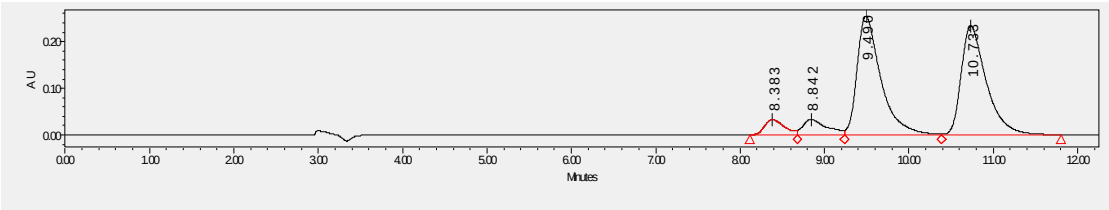


	Retention Time	Area	% Area
1	10.891	1143982	8.52
2	12.167	742971	5.53
3	13.940	11542197	85.95

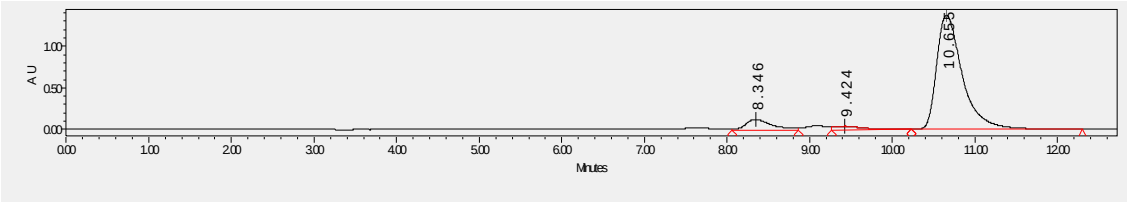
(1S,2R,3R,4R)-3-(4-bromophenyl)bicyclo[2.2.1]hept-5-en-2-yl)(pyridin-2-yl)methanone **5f**



Yield: 29.1 mg (82%), colorless oil, 91:9 dr, 93% ee; $[\alpha]^{9.5}_{D}$ = -117.5 (c = 0.58, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 10.65 min, $t_{R(minor)}$ = 9.42 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.4 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.81 (td, *J* = 8.0, 1.6 Hz, 1H), 7.47 – 7.44 (m, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.47 (dd, *J* = 5.2, 3.2 Hz, 1H), 5.82 (dd, *J* = 4.8, 2.8 Hz, 1H), 4.45 (dd, *J* = 5.2, 3.6 Hz, 1H), 3.54 (s, 1H), 3.38 (d, *J* = 4.4 Hz, 1H), 3.04 (s, 1H), 2.00 (d, *J* = 8.4 Hz, 1H), 1.61 (dd, *J* = 8.8, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.9, 153.4, 148.9, 143.7, 139.3, 136.9, 133.0, 131.4, 129.4, 127.0, 122.3, 119.6, 54.4, 49.2, 48.7, 48.2, 45.1. ESI-HRMS: calcd for $[C_{19}H_{16}{}^{78.9183}BrNO + Na^+]$ 376.0313, found 376.0307; ESI-HRMS: calcd for $[C_{19}H_{16}{}^{80.9163}BrNO + Na^+]$ 378.0292, found 378.0287.

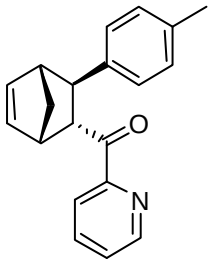


	Retention Time	Area	% Area
1	8.383	524459	4.80
2	8.842	640541	5.86
3	9.490	4955975	45.37
4	10.733	4801411	43.96

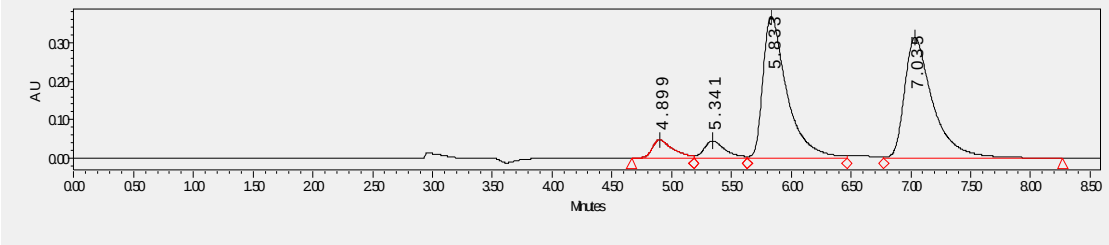


	Retention Time	Area	% Area
1	8.346	2724355	8.08
2	9.424	1044746	3.10
3	10.655	29966718	88.83

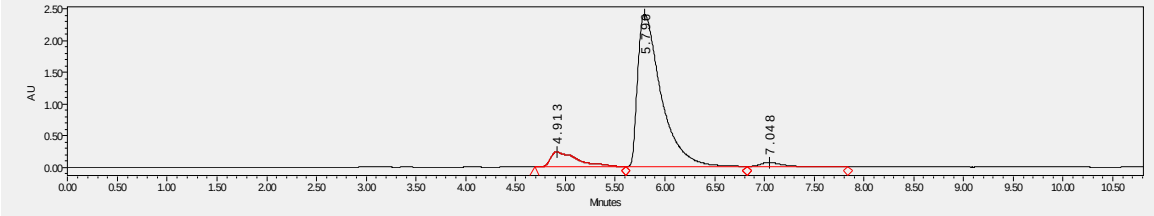
Pyridin-2-yl((1S,2R,3R,4R)-3-(p-tolyl)bicyclo[2.2.1]hept-5-en-2-yl)methanone **5g**



Yield: 24.2 mg (84%), colorless oil, 94:6 dr, 94% ee; $[\alpha]^{9.2}_{D}$ = -165.9 (c = 0.48, CH_2Cl_2); HPLC (Daicel chiralcel ODH, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 5.79 min, $t_{R(minor)}$ = 7.04 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (ddd, *J* = 4.8, 1.6, 0.8 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.74 (td, *J* = 7.6, 1.6 Hz, 1H), 7.37 (ddd, *J* = 7.2, 4.8, 1.2 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.42 (dd, *J* = 5.6, 3.2 Hz, 1H), 5.74 (dd, *J* = 5.6, 2.8 Hz, 1H), 4.45 (dd, *J* = 5.2, 3.6 Hz, 1H), 3.46 (s, 1H), 3.33 (d, *J* = 4.8 Hz, 1H), 2.97 (d, *J* = 1.6 Hz, 1H), 2.23 (s, 1H), 1.99 (d, *J* = 8.4 Hz, 1H), 1.52 (dd, *J* = 8.4, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 201.2, 153.6, 148.9, 141.6, 139.5, 136.8, 135.3, 132.8, 129.1, 127.6, 126.9, 122.2, 54.2, 49.6, 48.7, 48.2, 45.3, 20.9. ESI-HRMS calcd for [$C_{20}H_{19}NO$ +H^+]: 290.1545 found 290.1545.

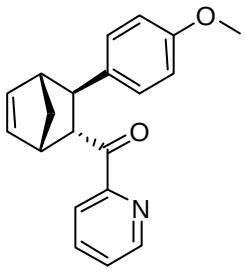


	Retention Time	Area	% Area
1	4.899	573869	5.03
2	5.341	552634	4.84
3	5.833	5141228	45.07
4	7.035	5139210	45.05

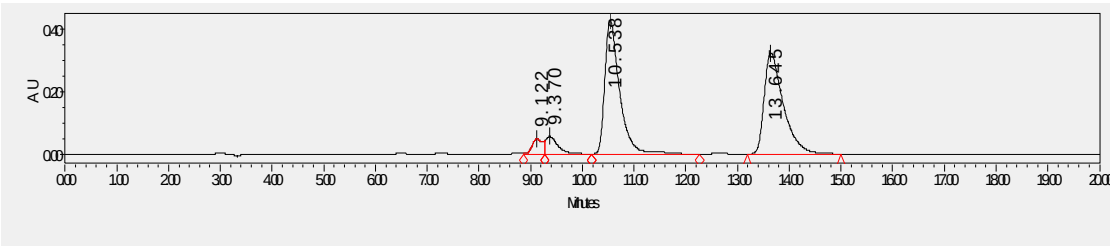


	Retention Time	Area	% Area
1	4.913	4702711	10.26
2	5.796	39820456	86.85
3	7.048	1323996	2.89

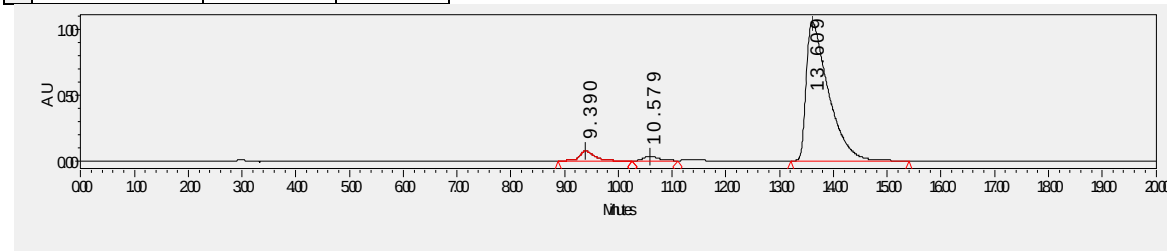
(1S,2R,3R,4R)-3-(4-methoxyphenyl)bicyclo[2.2.1]hept-5-en-2-yl)(pyridin-2-yl)methanone **5h**



Yield: 20.2 mg (77%), colorless oil, 95:5 dr, 96% ee; $[\alpha]^{8.6}_{D}$ = -159.6 (c = 0.40, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 13.60 min, $t_{R(minor)}$ = 10.57 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (ddd, *J* = 4.8, 1.6, 0.8 Hz, 1H), 7.93 (dd, *J* = 6.8, 0.8 Hz, 1H), 7.75 (td, *J* = 7.6, 2.0 Hz, 1H), 7.38 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 7.19 – 7.14 (m, 2H),, 6.79 – 6.69 (m, 2H), 6.41 (dd, *J* = 5.6, 3.2 Hz, 1H), 5.74 (dd, *J* = 5.6, 2.8 Hz, 1H), 4.42 (dd, *J* = 5.2, 3.6 Hz, 1H), 3.70 (s, 3H), 3.45 (s, 1H), 3.31 (d, *J* = 4.0 Hz, 1H), 2.95 (d, *J* = 1.2 Hz, 1H), 1.99 (d, *J* = 8.4 Hz, 1H), 1.53 (dd, *J* = 8.4, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 201.2, 157.7, 153.6, 148.9, 139.5, 136.9, 136.7, 132.7, 128.6, 126.9, 122.2, 113.8, 55.3, 54.3, 49.7, 48.7, 48.2, 44.9. ESI-HRMS calcd for [$C_{20}H_{19}NO_2$ +Na^+]: 328.1313 found 328.1304.

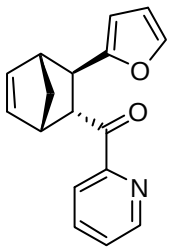


	Retention Time	Area	% Area
1	9.122	678662	3.70
2	9.370	910517	4.96
3	10.538	8496215	46.29
4	13.645	8269338	45.05

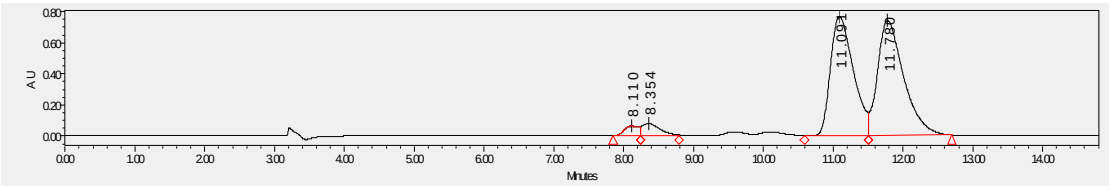


	Retention Time	Area	% Area
1	9.390	1415444	4.38
2	10.579	681190	2.11
3	13.609	30231216	93.51

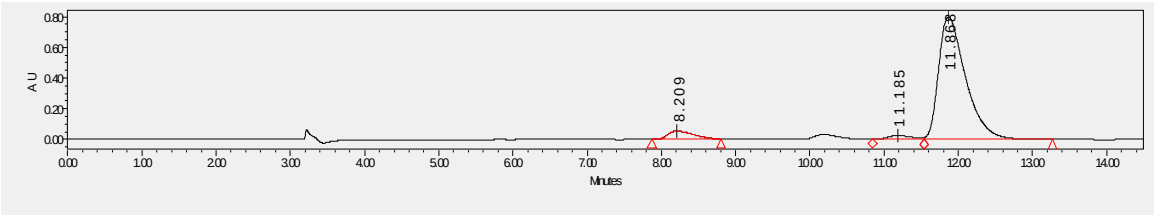
(1S,2R,3R,4R)-3-(furan-2-yl)bicyclo[2.2.1]hept-5-en-2-yl)(pyridin-2-yl)methanone **5i**



Yield: 20.5 mg (77%), colorless oil, 94:6 dr, 94% ee; $[\alpha]^{14.2}_{D}$ = -120.9 (c = 0.41, CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 98/2, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 11.86 min, $t_{R(minor)}$ = 11.18 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.75 (td, *J* = 7.6, 1.6 Hz, 1H), 7.40 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 7.24 (d, *J* = 0.8 Hz, 1H), 6.34 (dd, *J* = 5.6, 3.2 Hz, 1H), 6.20 (dd, *J* = 3.2, 2.0 Hz, 1H), 6.03 (d, *J* = 3.2 Hz, 1H), 5.72 (dd, *J* = 5.6, 2.8 Hz, 1H), 4.52 (dd, *J* = 4.8, 3.6 Hz, 1H), 3.46 (s, 1H), 3.32 (d, *J* = 4.0 Hz, 1H), 3.00 (d, *J* = 1.6 Hz, 1H), 1.97 (d, *J* = 8.4 Hz, 1H), 1.49 (dd, *J* = 8.4, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.4, 158.1, 153.4, 148.9, 141.1, 138.4, 136.9, 132.8, 126.9, 122.3, 110.1, 104.8, 52.2, 49.2, 48.6, 48.2, 39.7. ESI-HRMS calcd for [$C_{17}H_{15}NO_2$+Na^+]: 288.1000, found 288.0996.

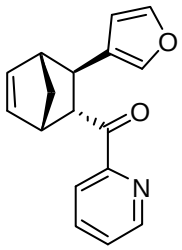


	Retention Time	Area	% Area
1	8.110	873514	2.26
2	8.354	1361632	3.52
3	11.091	17309949	44.77
4	11.780	19120757	49.45

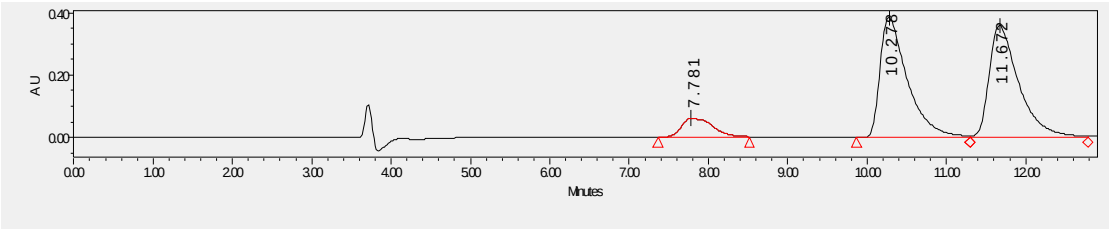


	Retention Time	Area	% Area
1	8.209	1256417	5.71
2	11.185	578678	2.63
3	11.868	20157900	91.66

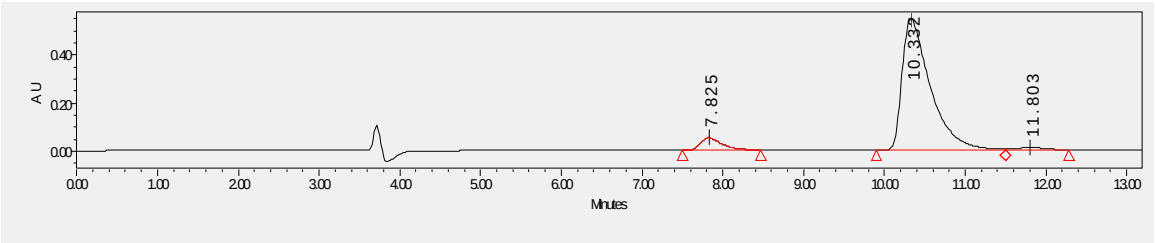
(1S,2R,3R,4R)-3-(furan-3-yl)bicyclo[2.2.1]hept-5-en-2-yl)(pyridin-2-yl)methanone **5j**



Yield: 17.4 mg (66%), colorless oil, 94:6 dr, 96% ee; $[\alpha]^{12.3}_{D}$ = -136.5 (c = 0.35, CH_2Cl_2); HPLC (Daicel chiralcel ODH, *n*-hexane/*i*-PrOH 99/1, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 10.33 min, $t_{R(minor)}$ = 11.80 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.4 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.76 (td, *J* = 7.6, 1.6 Hz, 1H), 7.40 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 7.29 – 7.24 (m, 2H), 6.36 (dd, *J* = 5.6, 3.2 Hz, 1H), 6.27 (d, *J* = 0.8 Hz, 1H), 5.71 (dd, *J* = 5.6, 2.8 Hz, 1H), 4.34 (dd, *J* = 4.8, 3.2 Hz, 1H), 3.43 (s, 1H), 3.14 (d, *J* = 4.8 Hz, 1H), 2.87 (d, *J* = 1.6 Hz, 1H), 1.86 (d, *J* = 8.4 Hz, 1H), 1.50 (dd, *J* = 8.4, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.9, 153.5, 148.9, 142.8, 138.7, 138.6, 136.9, 132.4, 128.7, 126.9, 122.2, 110.8, 53.6, 49.8, 48.5, 48.4, 37.1. ESI-HRMS calcd for $[C_{17}H_{15}NO_2+Na^+]$: 288.1000, found 288.1002.

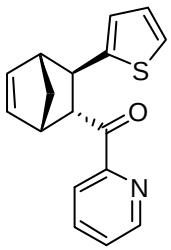


	Retention Time	Area	% Area
1	7.781	1616374	8.02
2	10.278	9233618	45.84
3	11.672	9293263	46.14

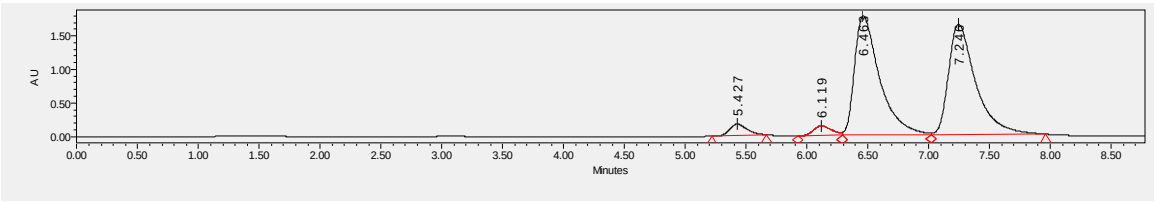


	Retention Time	Area	% Area
1	7.825	979526	6.72
2	10.332	13325998	91.45
3	11.803	266252	1.83

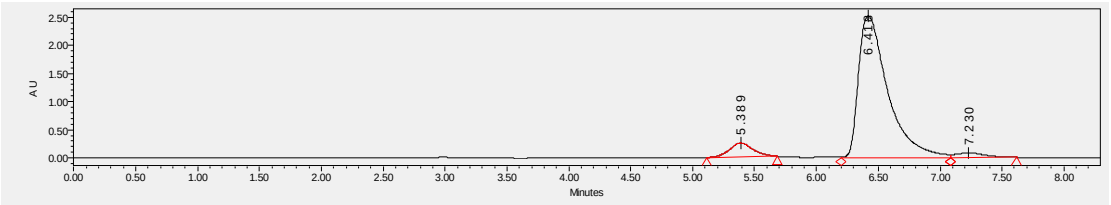
Pyridin-2-yl((1S,2R,3R,4R)-3-(thiophen-2-yl)bicyclo[2.2.1]hept-5-en-2-yl)methanone **5k**



Yield: 23.3 mg (83%), white solid, 94:6 dr, 94% ee; $[\alpha]^{17.5}_{D}$ = -104.9 (c = 0.47, CH_2Cl_2); HPLC (Daicel chiralcel ODH, *n*-hexane/*i*-PrOH 98/2, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 6.41 min, $t_{R(minor)}$ = 7.23 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (ddd, *J* = 4.8, 2.0, 1.2 Hz, 1H), 7.96 – 7.89 (m, 1H), 7.75 (td, *J* = 7.6, 1.6 Hz, 1H), 7.39 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 7.09 – 7.01 (m, 1H), 6.88 – 6.79 (m, 2H), 6.38 (dd, *J* = 5.6, 3.2 Hz, 1H), 5.73 (dd, *J* = 5.6, 2.8 Hz, 1H), 4.50 (dd, *J* = 4.8, 3.6 Hz, 1H), 3.56 (dd, *J* = 4.8, 1.6 Hz, 1H), 3.48 (s, 1H), 2.98 (s, 1H), 2.04 (d, *J* = 8.4 Hz, 1H), 1.57 (dd, *J* = 8.4, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.4, 153.4, 149.0, 148.9, 138.7, 136.9, 132.7, 127.0, 126.7, 123.7, 123.0, 122.3, 55.7, 51.5, 48.6, 48.6, 41.6. ESI-HRMS calcd for [$C_{17}H_{15}NOS$+Na^+]: 304.0772, found 304.0763.

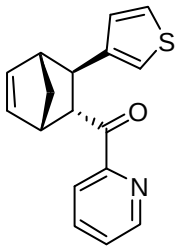


	Retention Time	Area	% Area
1	5.427	1714771	3.15
2	6.119	1512808	2.78
3	6.463	25599509	46.98
4	7.246	25663800	47.10

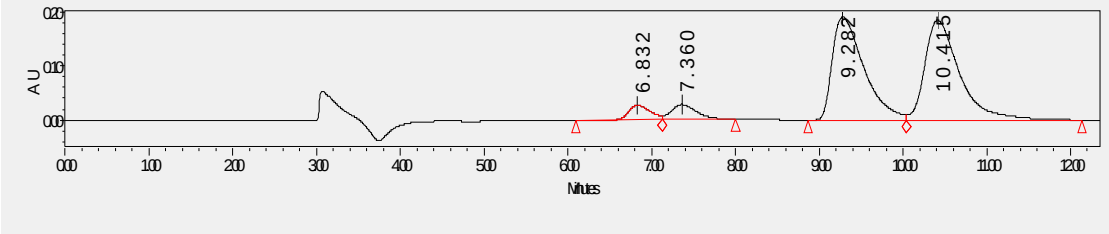


	Retention Time	Area	% Area
1	5.389	3314705	7.21
2	6.418	41354150	89.92
3	7.230	1320626	2.87

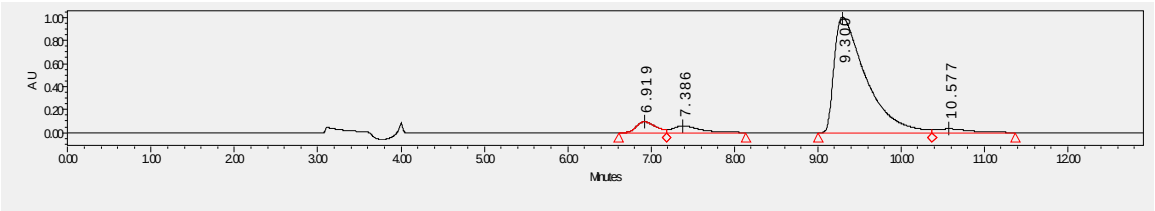
Pyridin-2-yl((1S,2R,3R,4R)-3-(thiophen-3-yl)bicyclo[2.2.1]hept-5-en-2-yl)methanone **5l**



Yield: 21.1 mg (75%), white solid, 95:5 dr, 94% ee; $[\alpha]^{14.9}_{D}$ = -109.1 (c = 0.42, CH_2Cl_2); HPLC (Daicel chiralcel ODH, *n*-hexane/*i*-PrOH 98/2, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 9.30 min, $t_{R(minor)}$ = 10.57 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.4 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.75 (td, *J* = 7.6, 1.6 Hz, 1H), 7.39 (dd, *J* = 6.4, 4.8 Hz, 1H), 7.17 (dd, *J* = 4.8, 2.8 Hz, 1H), 7.02 – 6.88 (m, 2H), 6.38 (dd, *J* = 5.6, 3.2 Hz, 1H), 5.73 (dd, *J* = 5.6, 2.8 Hz, 1H), 4.45 (dd, *J* = 4.8, 3.6 Hz, 1H), 3.45 (s, 1H), 3.36 (d, *J* = 4.8 Hz, 1H), 2.98 (d, *J* = 1.2 Hz, 1H), 1.94 (d, *J* = 8.4 Hz, 1H), 1.53 (dd, *J* = 8.4, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.9, 153.5, 148.9, 145.8, 138.9, 136.9, 132.6, 128.2, 126.9, 125.3, 122.2, 119.4, 54.0, 49.9, 48.6, 48.4, 41.6. ESI-HRMS calcd for [$C_{17}H_{15}NOS$+Na^+]: 304.0772, found 304.0773.

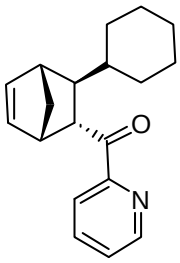


	Retention Time	Area	% Area
1	6.832	475446	4.20
2	7.360	564852	4.99
3	9.282	4988934	44.04
4	10.415	5298160	46.77

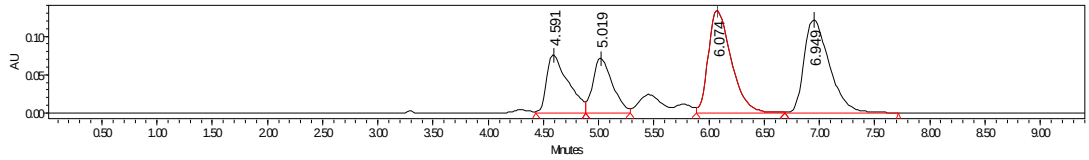


	Retention Time	Area	% Area
1	6.919	1489575	4.99
2	7.386	1236658	4.14
3	9.300	26323483	88.16
4	10.577	810476	2.71

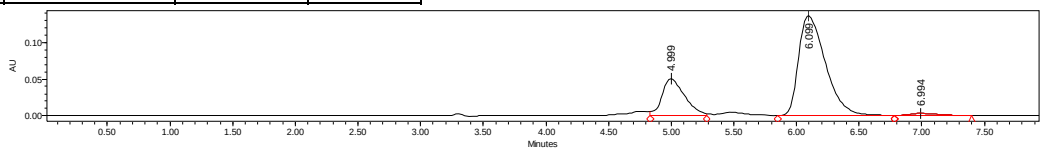
(1S,2R,3R,4R)-3-cyclohexylbicyclo[2.2.1]hept-5-en-2-yl)(pyridin-2-yl)methanone **5m**



Yield: 22.1 mg (79%), colorless oil, 77:23 dr, 96% ee; HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH 98/2, 1.0 mL/min, 254 nm) $t_{R(major)}$ = 6.09 min, $t_{R(minor)}$ = 6.99 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.4 Hz, 1H), 8.06 (d, *J* = 7.6 Hz, 0.23H), 7.98 (d, *J* = 8.0 Hz, 0.77H), 7.82 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 5.6 Hz, 1H), 6.33 (s, 1H), 6.19 (s, 0.23H), 5.69 (t, *J* = 2.4 Hz, 0.77H), 4.12 (s, 0.78H), 3.51 (d, *J* = 4.4 Hz, 0.22H), 3.30 (s, 0.75H), 3.00 (s, 0.25H), 2.89 (d, *J* = 16.8 Hz, 1H), 1.99 – 1.56 (m, 7H), 1.29 – 0.85 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.9, 153.7, 148.8, 139.4, 136.9, 131.7, 126.8, 122.2, 51.4, 48.5, 48.1, 47.8, 44.7, 42.3, 32.9, 32.5, 26.6, 26.5, 26.3. ESI-HRMS calcd for [$C_{19}H_{23}NO+H^+$]: 282.1852, found 282.1864.



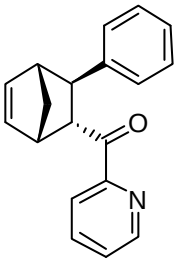
	Retention Time	Area	% Area
1	4.591	1032015	17.92
2	5.019	880697	15.29
3	6.074	1923229	33.39
4	6.949	1923134	33.39



	Retention Time	Area	% Area
1	4.999	622921	23.18
2	6.099	2020720	75.20
3	6.994	43526	1.62

4. Determination methods of relative and absolute configurations of products 5

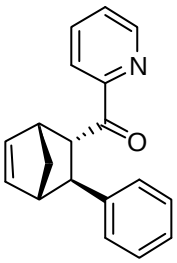
The relative and absolute configurations of products **5** were determined by optical rotations and spectral data. The configuration of **5a** was the opposite enantiomer of the product reported in the literature.[3]



DA product *endo*-**5a** (93:7 dr and 96% ee) we obtained: $[\alpha]^{18.6}_{D}$ = -184.6 (c = 0.51, $CHCl_3$).

HPLC (Daicel chiralcel ODH, *n*-hexane/*i*-PrOH 98/2, 1.0 mL/min, 254 nm) Major *exo* t_R = 6.108 min, minor *exo* t_R = 6.772 min, major *endo* (−) t_R = 7.592 min, minor *endo* (+) t_R = 9.837 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.4 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.74 (td, *J* = 7.6, 1.6 Hz, 1H), 7.37 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 7.27 – 7.16 (m, 4H), 7.11 – 7.06 (m, 1H), 6.42 (dd, *J* = 5.6, 3.2 Hz, 1H), 5.75 (dd, *J* = 5.6, 2.8 Hz, 1H), 4.46 (dd, *J* = 5.2, 4.4 Hz, 1H), 3.47 (s, 1H), 3.38 (d, *J* = 4.4 Hz, 1H), 3.01 (s, 1H), 2.00 (d, *J* = 8.4 Hz, 1H), 1.54 (dd, *J* = 8.8, 2.0 Hz, 1H).

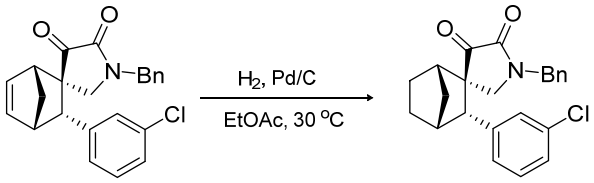


DA product *endo*-**5a** (>98% de and 90% ee) reported in literature: $[\alpha]^{25}_{D}$ = +176.6 (c = 0.81, $CHCl_3$).

HPLC (Daicel chiralcel ODH, *n*-hexane/*i*-PrOH 98/2, 1.0 mL/min, 254 nm) Major *exo* t_R = 6.5 min, minor *exo* t_R = 7.2 min, minor *endo* (−) t_R = 7.9 min, major *endo* (+) t_R = 9.5 min.

1H NMR (300 MHz, $CDCl_3$,) δ 8.67 (1H, d, *J* = 4.8 Hz), 8.00 (1H, d, *J* = 7.8 Hz), 7.81 (1H, dt, *J* = 1.7, 7.7 Hz), 7.44 (1H, ddd, *J* = 1.2, 4.8, 7.5 Hz), 7.37-7.22 (m, 4H), 7.15 (tt, *J* = 1.7, 6.9Hz), 6.49 (1H, dd, *J* = 3.2, 5.6 Hz), 5.82 (1H, dd, *J* = 2.8, 5.6 Hz), 4.53 (1H, dd, *J* = 3.4, 5.2 Hz), 3.54 (1H, s), 3.45 (1H, dd, *J* = 1.3, 5.0 Hz), 3.08 (1H, s), 2.06 (1H, d, *J* = 8.4 Hz), 1.61 (1H, dd, *J* = 1.7, 8.5 Hz).

5. Experimental procedure for the reduction of 3d



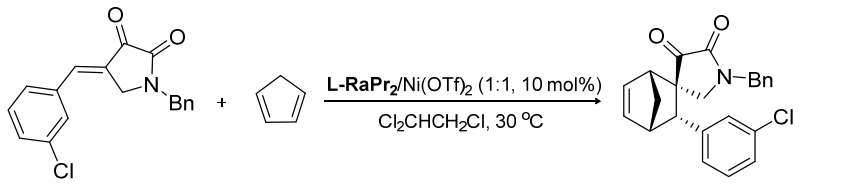
3d >95:5 d.r., 97% ee

6 68% yield, >95:5 d.r., 96% ee

To a solution of **3d** (37.7 mg, 0.1 mmol) in EtOAc (1.0 mL) at 30 °C, under magnetic stirring

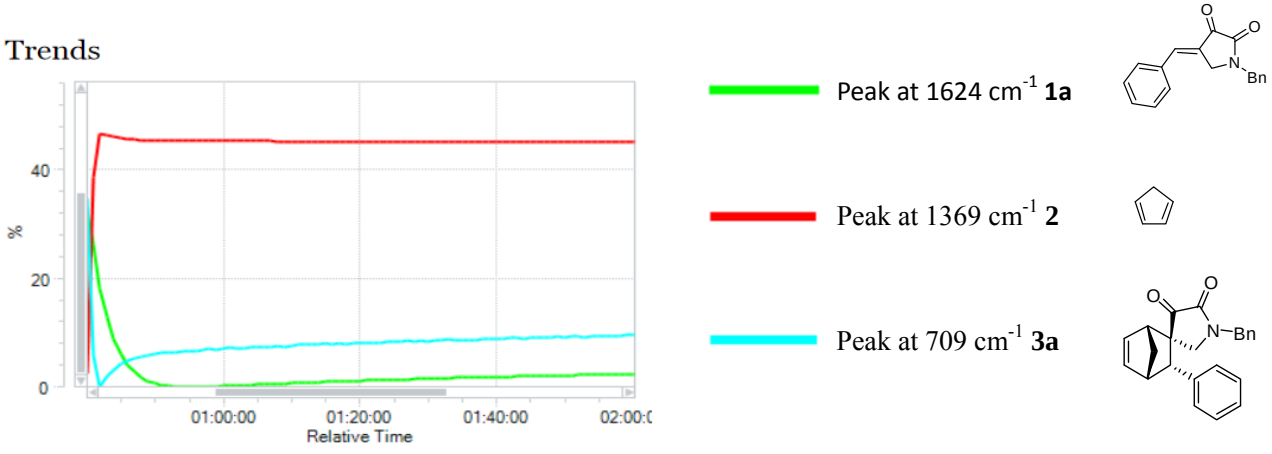
and hydrogen atmosphere, was added Pd/C (1.8 mg). The mixture was allowed to stir for 3 h. After complete consumption of starting material, the product **6** was purified on silica gel chromatography (EtOAc: Pet = 1: 3). The results were 68% yield, > 95:5 d.r. and 96% ee.

6. Gram scale experiment

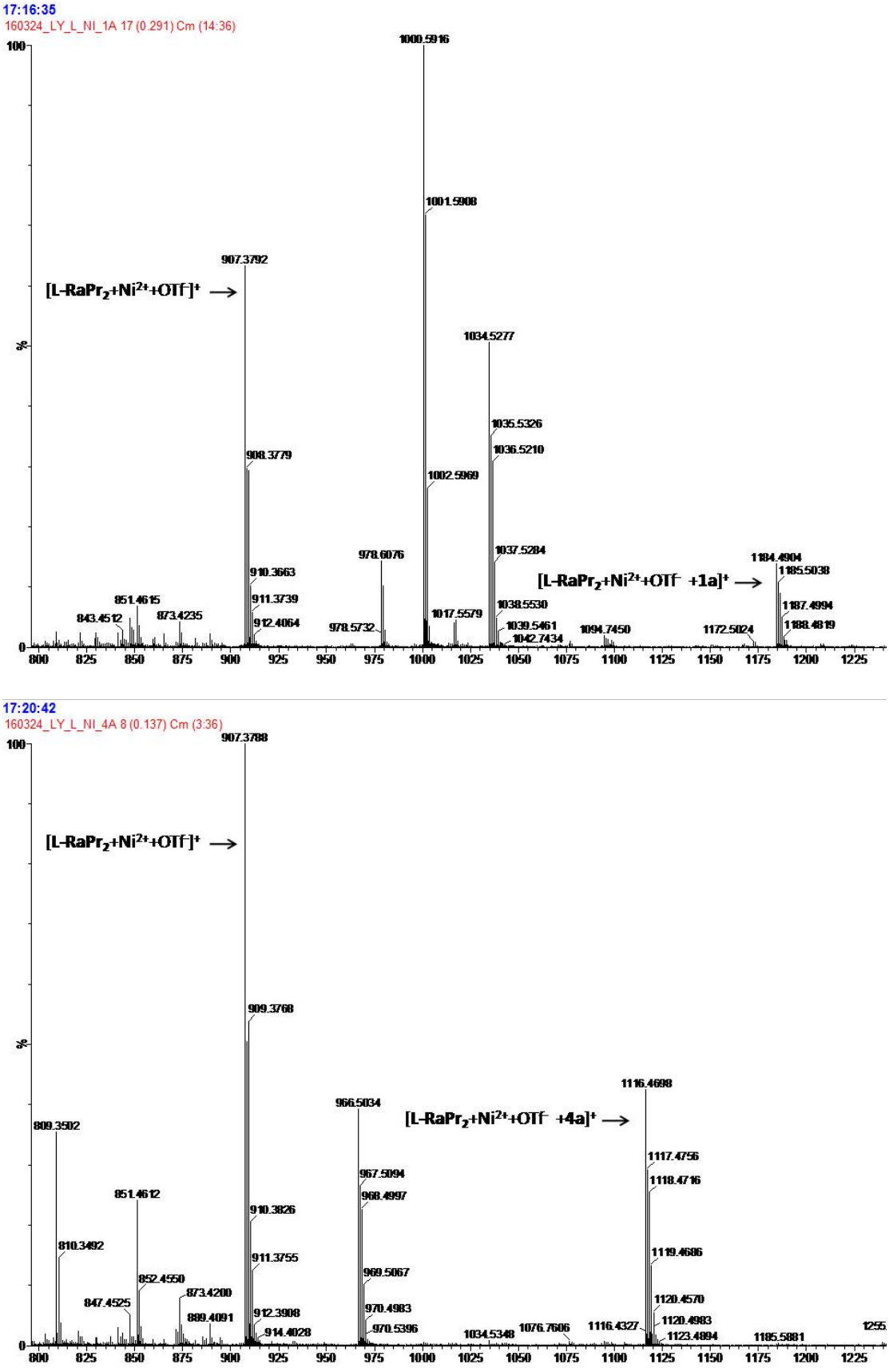


L-RaPr$_2$ (245 mg, 0.35 mmol), Ni(OTf)$_2$ (126 mg, 0.35 mmol), and **1d** (1.09 g, 3.5 mmol) in Cl_2CHCH_2Cl (3.5 mL) were added to an over-dried reaction tube under nitrogen atmosphere and then stirred at 30 °C for 1 h. Subsequently, cyclopentadiene **2** (3.5 mL) was added under 30 °C, the reaction mixture continued stirring for 1 h. After completion, the residue was purified by flash chromatography on silica gel to afford the desired product **3d** (1.313 g, 99% yield) as a white solid. The product was determined by HPLC and NMR analysis.

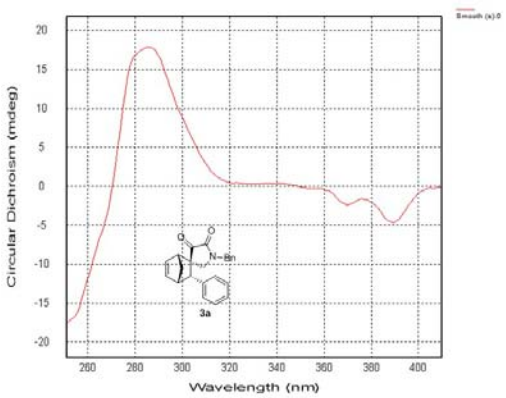
7. Operando IR experiments

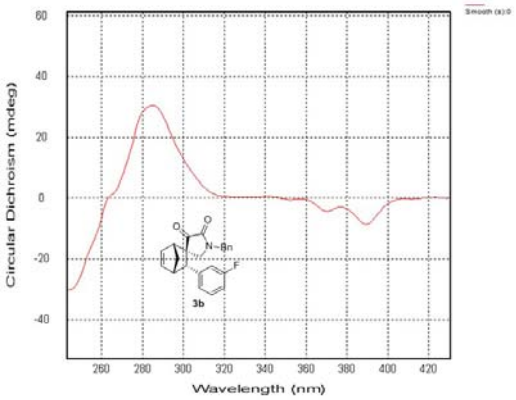


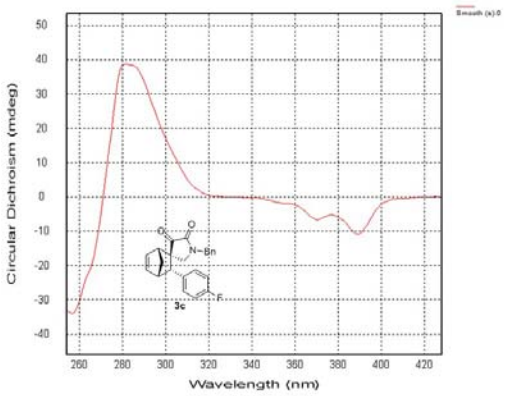
8. ESI-MS analysis of the solution of catalyst/substrate

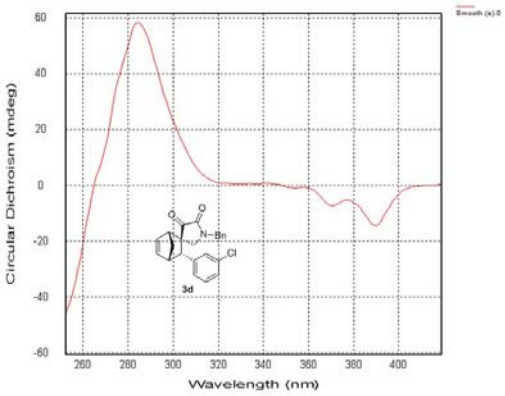


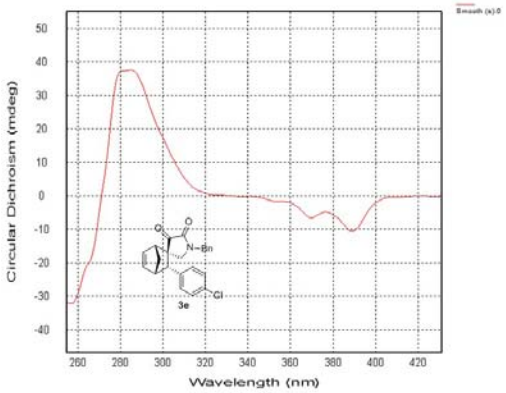
9. Copies of CD Spectra and their Absolute Configurations

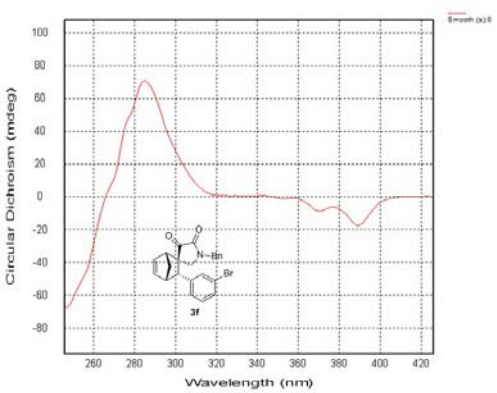


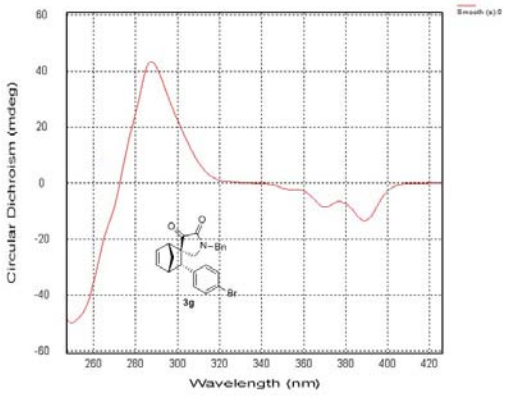


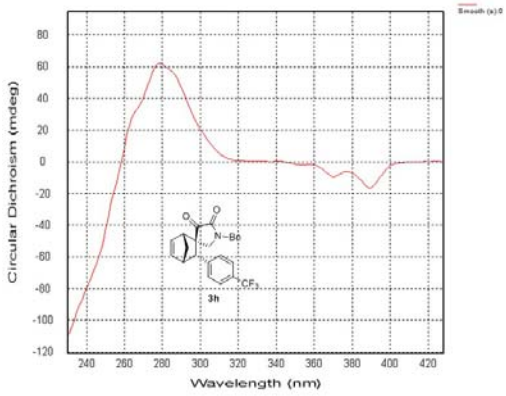


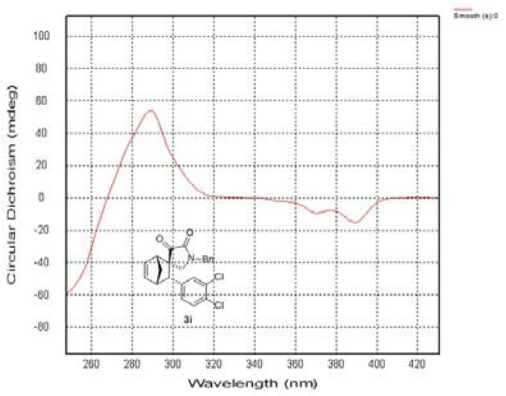


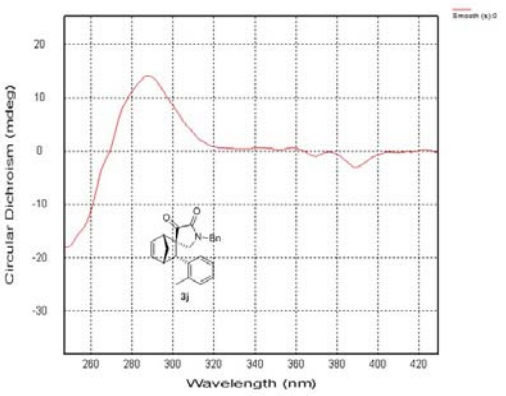


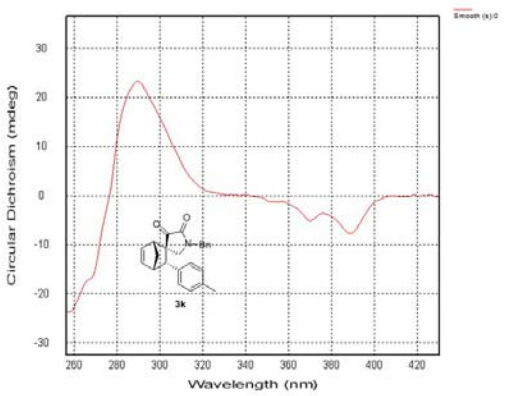


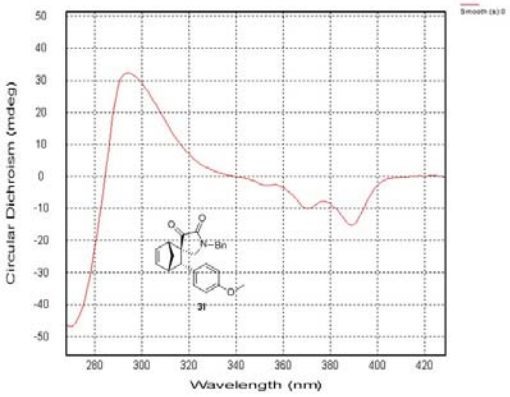


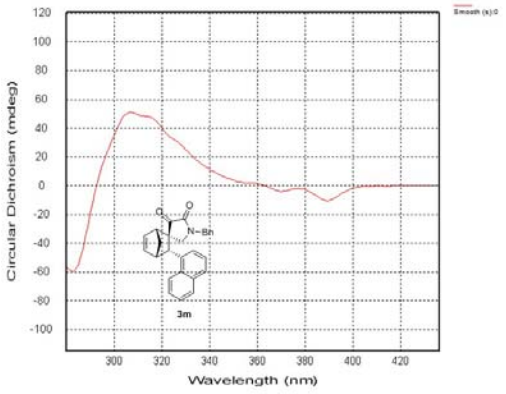


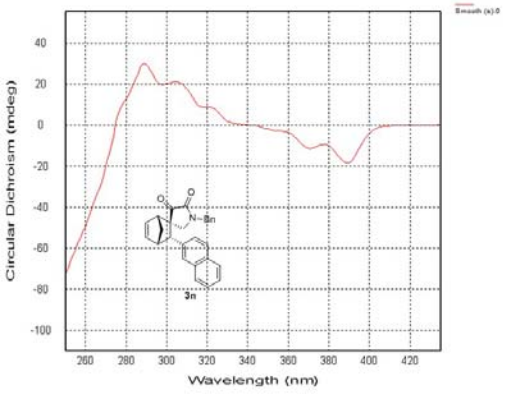

Circular Dichroism (mdeg)
Wavelength (nm)
3i

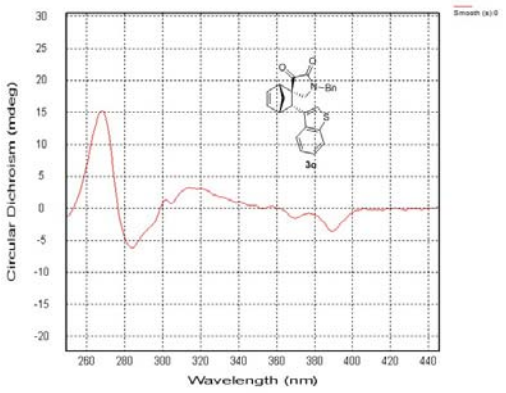

Circular Dichroism (mdeg)
Wavelength (nm)
3j

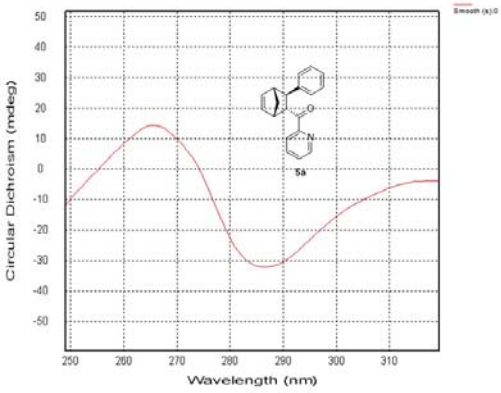

Circular Dichroism (mdeg)
Wavelength (nm)
3k

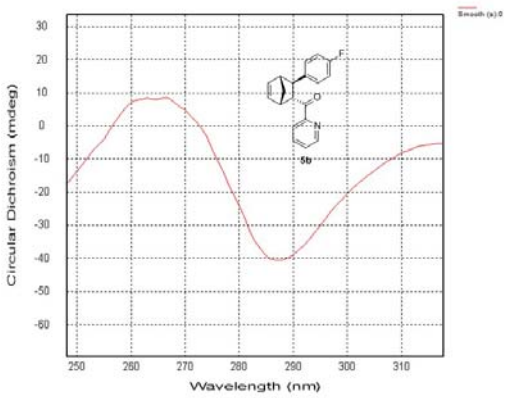

Circular Dichroism (mdeg)
Wavelength (nm)
3l

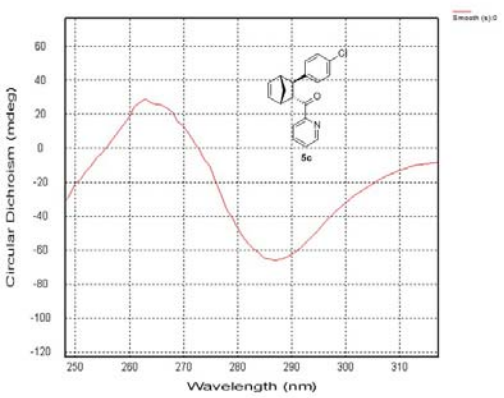

Circular Dichroism (mdeg)
Wavelength (nm)
3m

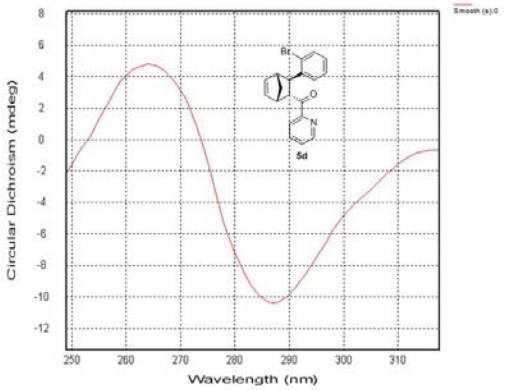

Circular Dichroism (mdeg)
Wavelength (nm)
3n

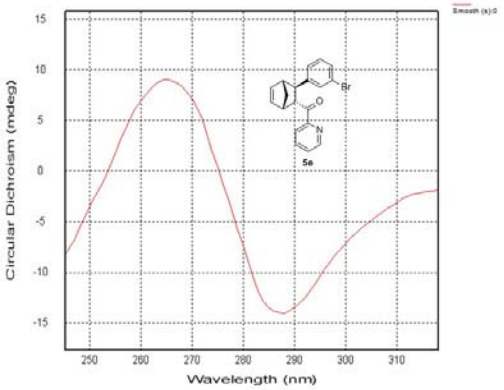

Circular Dichroism (mdeg)
Wavelength (nm)
3q

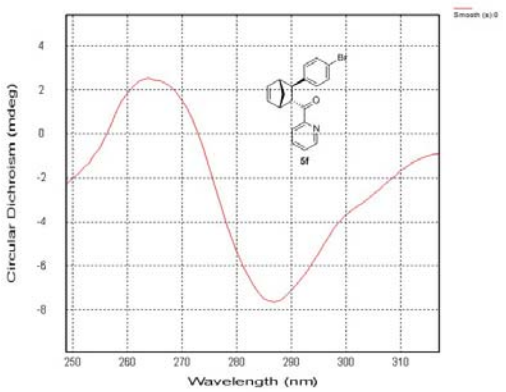

Circular Dichroism (mdeg)
Wavelength (nm)
5a

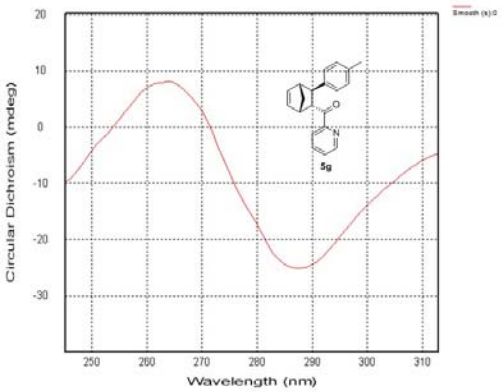

Circular Dichroism (mdeg)
Wavelength (nm)
5b

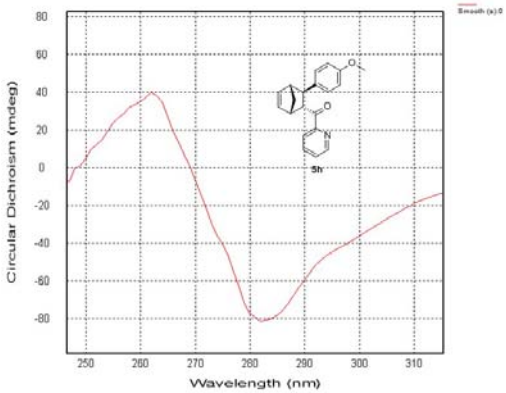

Circular Dichroism (mdeg)
Wavelength (nm)
5c

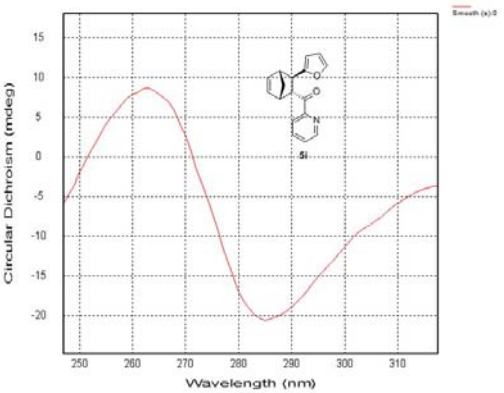

Circular Dichroism (mdeg)
Wavelength (nm)
5d

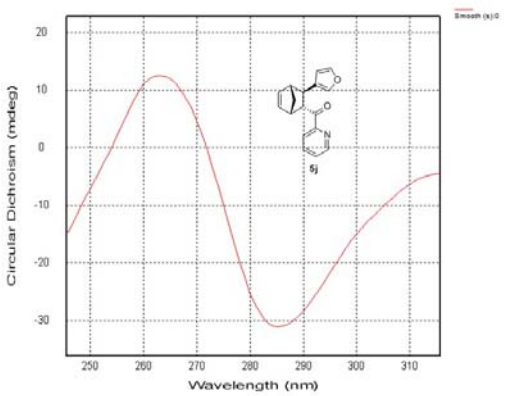

Circular Dichroism (mdeg)
Wavelength (nm)
5e

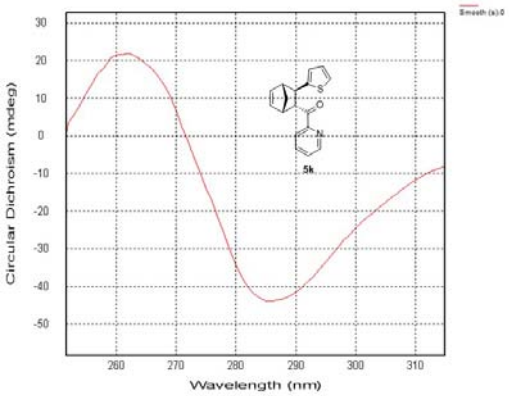

Circular Dichroism (mdeg)
Wavelength (nm)
5f

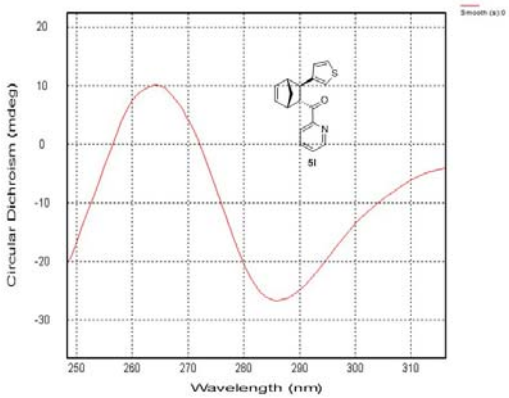

Circular Dichroism (mdeg)
Wavelength (nm)
5g


Circular Dichroism (mdeg)
Wavelength (nm)
5h


Circular Dichroism (mdeg)
Wavelength (nm)
5i

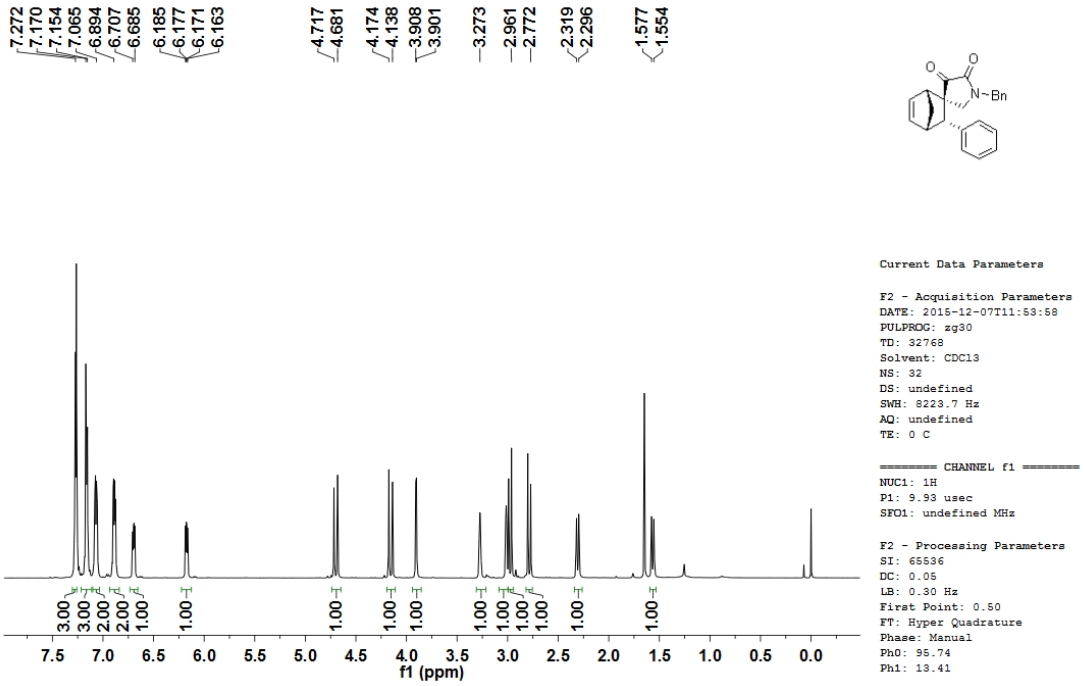

Circular Dichroism (mdeg)
Wavelength (nm)
5j

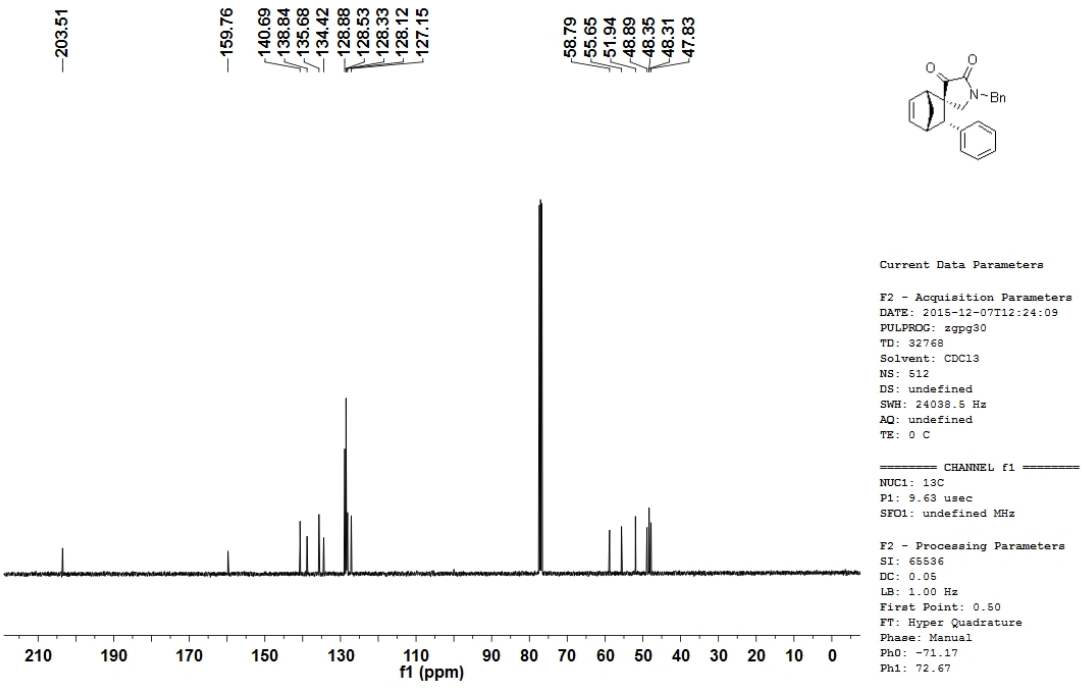

Circular Dichroism (mdeg)
Wavelength (nm)
5k


Circular Dichroism (mdeg)
Wavelength (nm)
5l

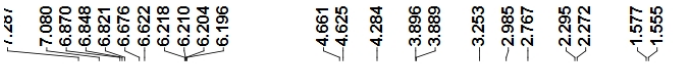
10. Copies of ^{1}H NMR and ^{13}C NMR Spectra for Products

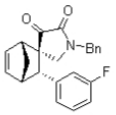
3a

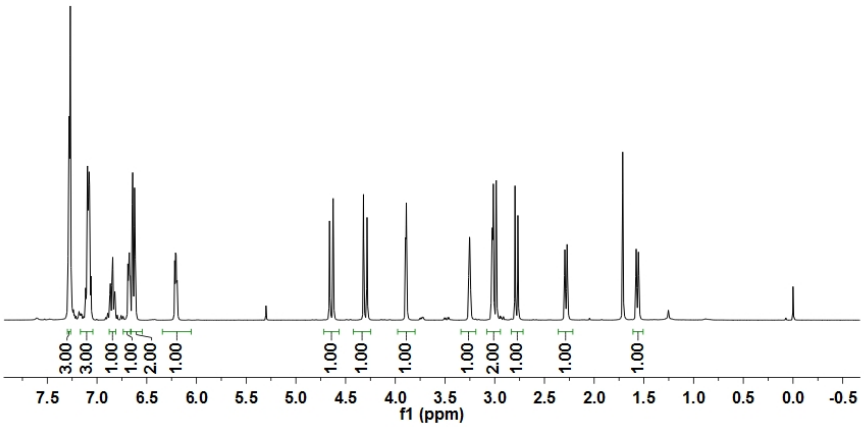




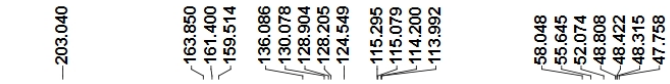
3b

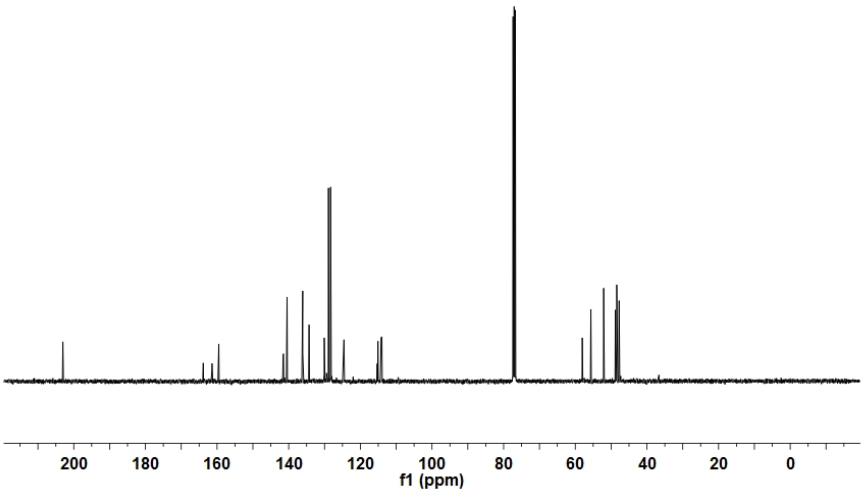






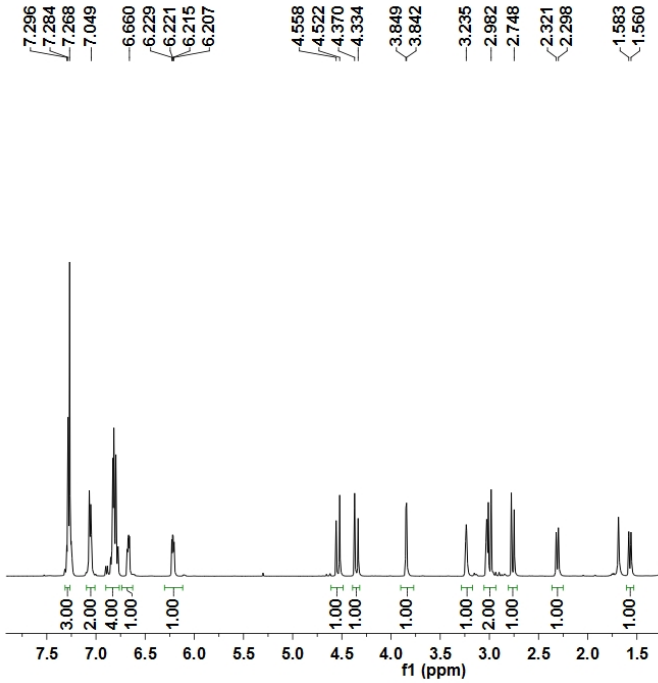

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-11-18T18:02:23
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 32
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 95.65
Ph1: 16.11
```

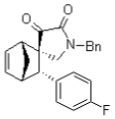




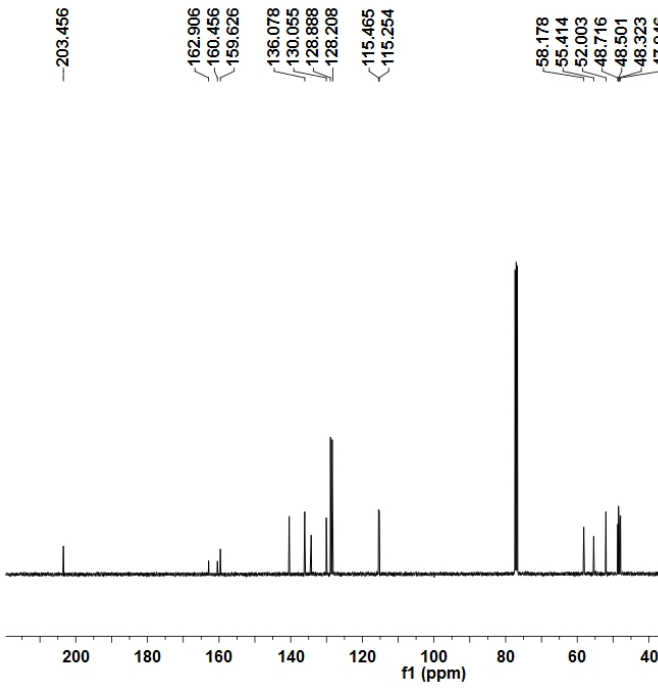

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-11-18T18:32:37
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -52.96
Ph1: 52.30
```

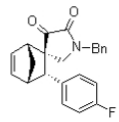
3c





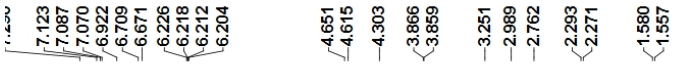

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-11-18T20:24:26
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 32
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -263.23
Ph1: 14.47
```

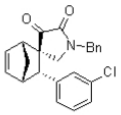


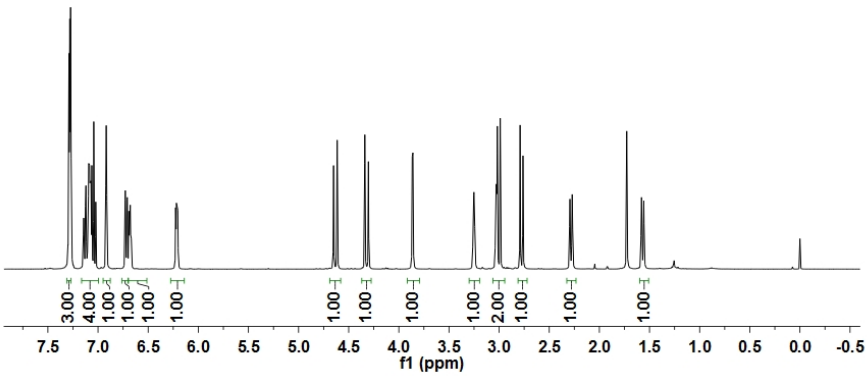



```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-11-18T20:54:38
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -63.48
Ph1: 64.77
```

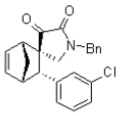
3d

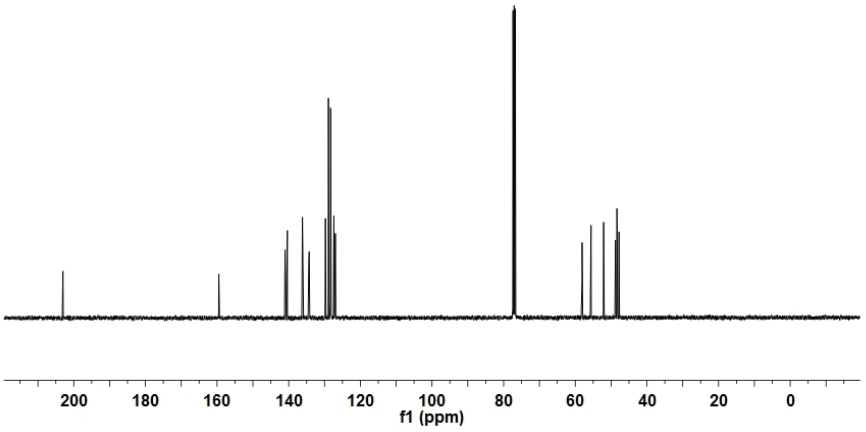






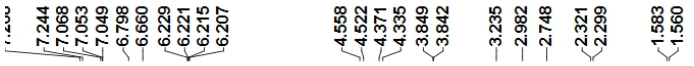

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-11-18T18:38:14
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 32
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 95.86
Ph1: 16.83
```

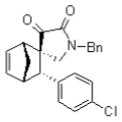


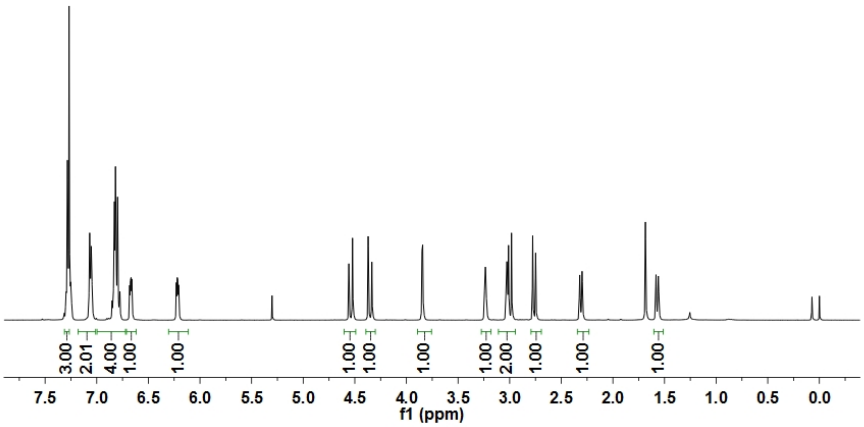



```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-11-18T19:08:25
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -61.97
Ph1: 70.58
```

3e





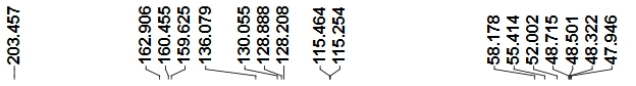


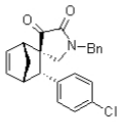
Current Data Parameters

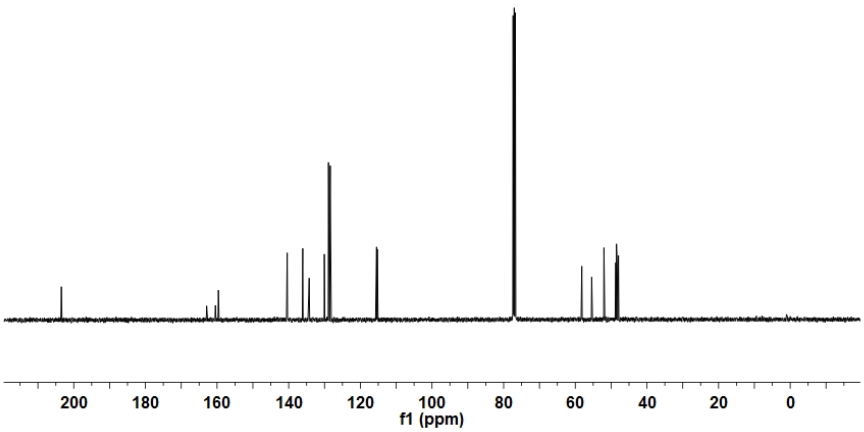
F2 - Acquisition Parameters
DATE: 2015-11-18T21:00:15
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 32
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 95.81
Ph1: 17.41







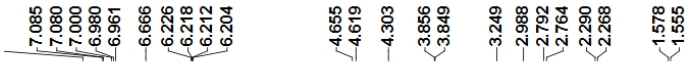
Current Data Parameters

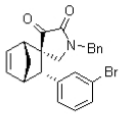
F2 - Acquisition Parameters
DATE: 2015-11-18T21:30:27
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C

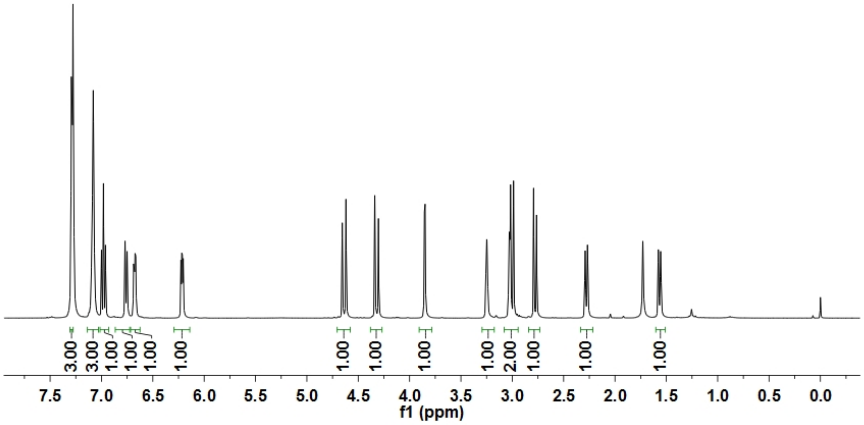
======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -57.03
Ph1: 52.29

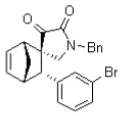
3f

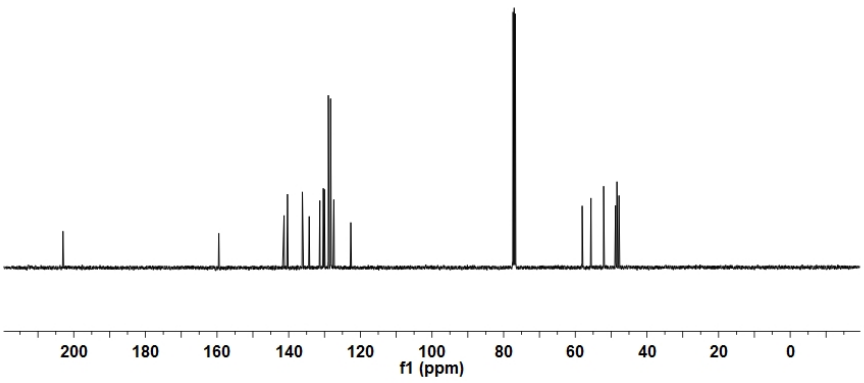






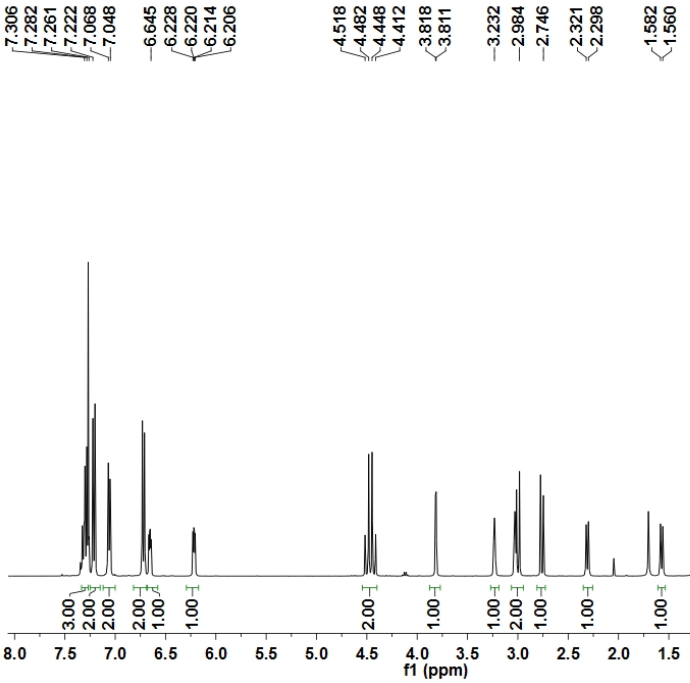

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-11-18T19:14:04
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 32
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -263.96
Ph1: 16.43
```

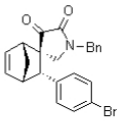




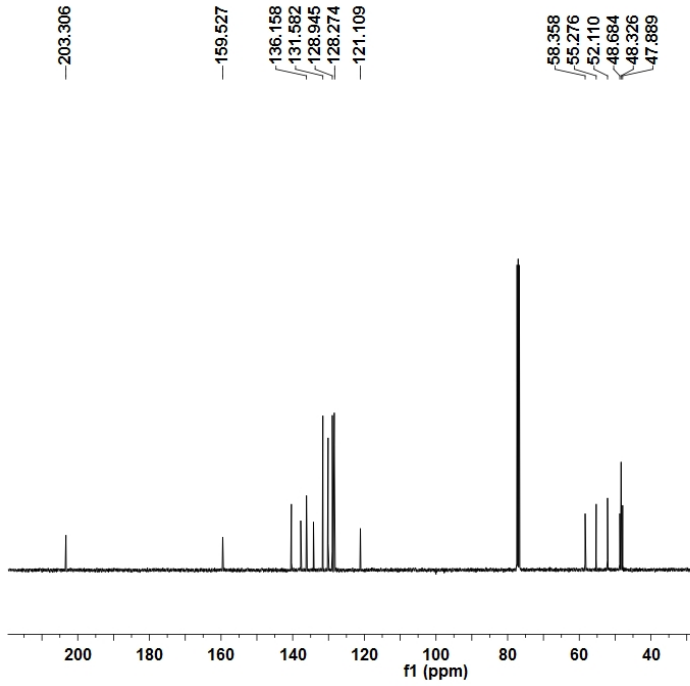

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-11-18T19:44:16
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -60.93
Ph1: 67.62
```

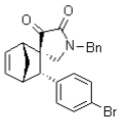
3g





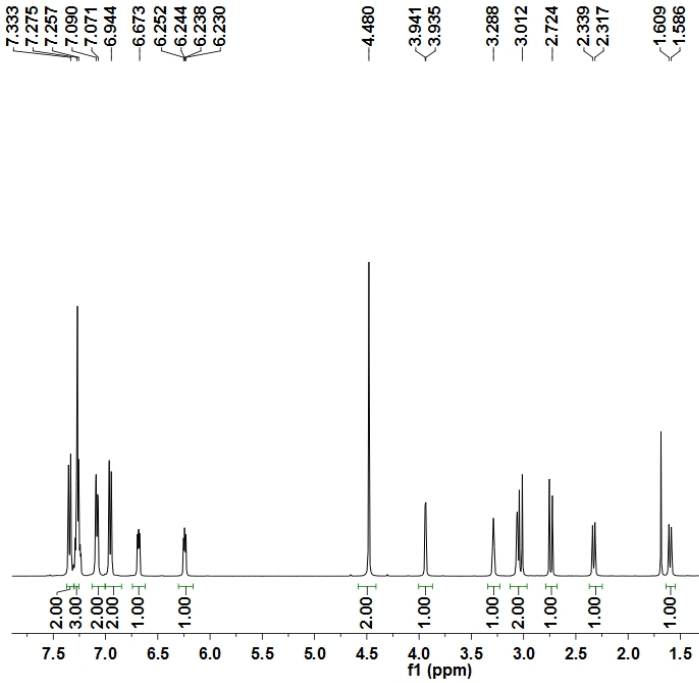

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-11-18T21:36:03
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 32
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 93.93
Ph1: 19.54
```

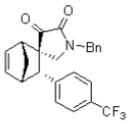




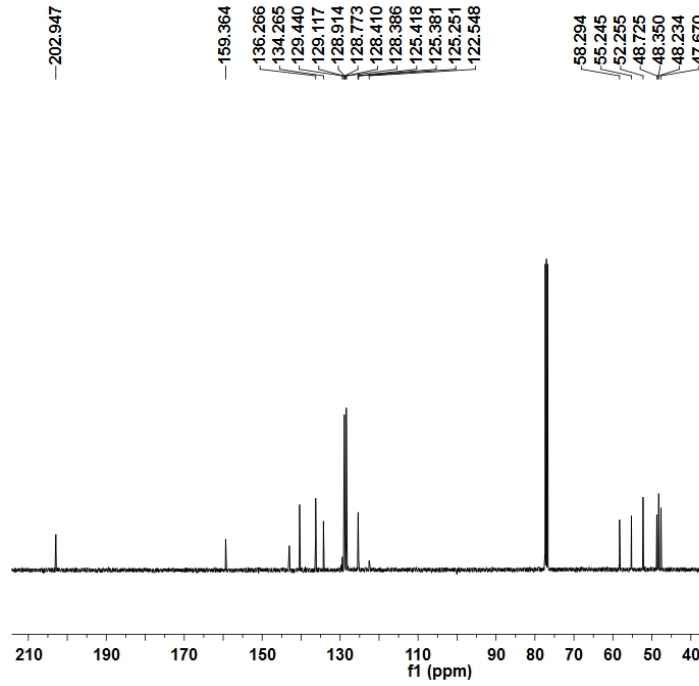

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-11-18T22:06:15
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -58.55
Ph1: 61.33
```

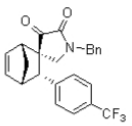
3i





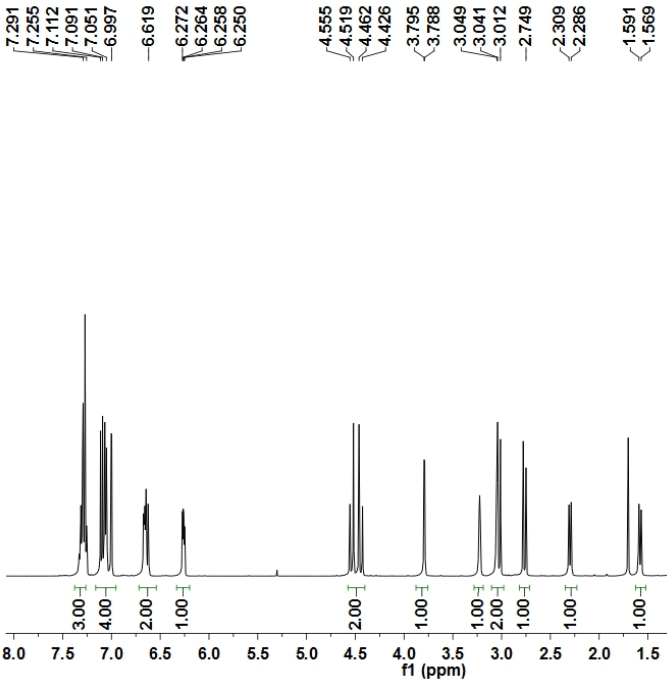

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-11-19T18:33:15
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 32
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 96.35
Ph1: 16.12
```

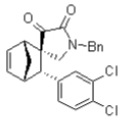





```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-11-19T19:03:27
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -65.75
Ph1: 69.77
```

3i



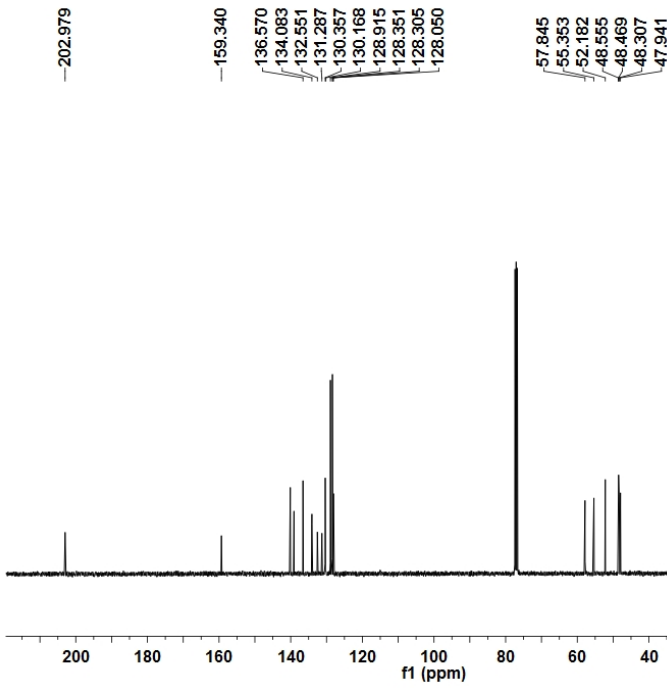


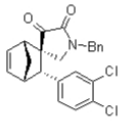
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-11-20T00:31:18
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 32
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 96.15
Ph1: 16.16





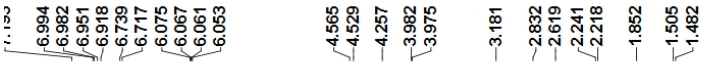
Current Data Parameters

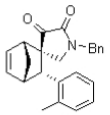
F2 - Acquisition Parameters
DATE: 2015-11-20T01:01:30
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C

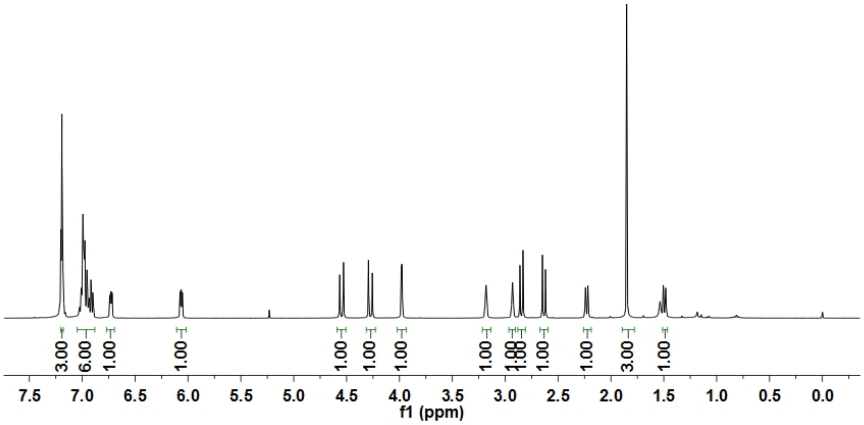
======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -51.10
Ph1: 39.03

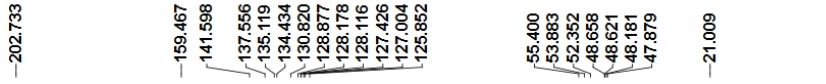
3j

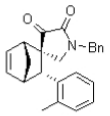


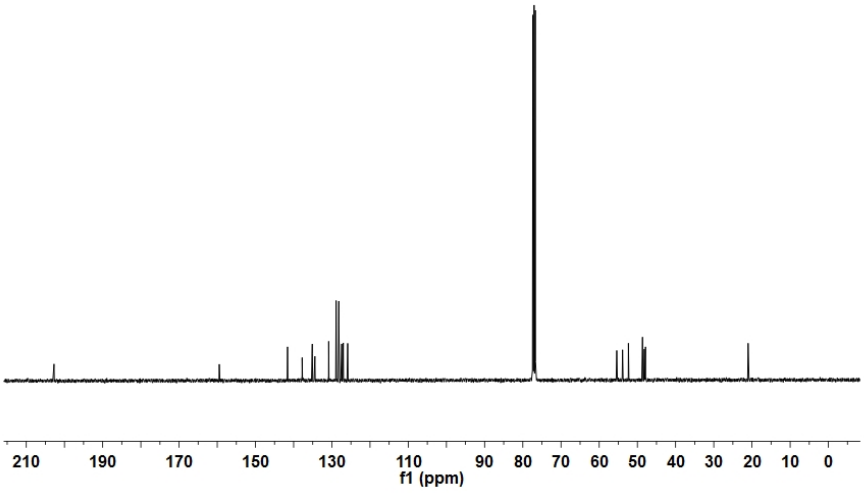





```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-01-23T01:51:27
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 64
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 97.73
Ph1: 11.56
```

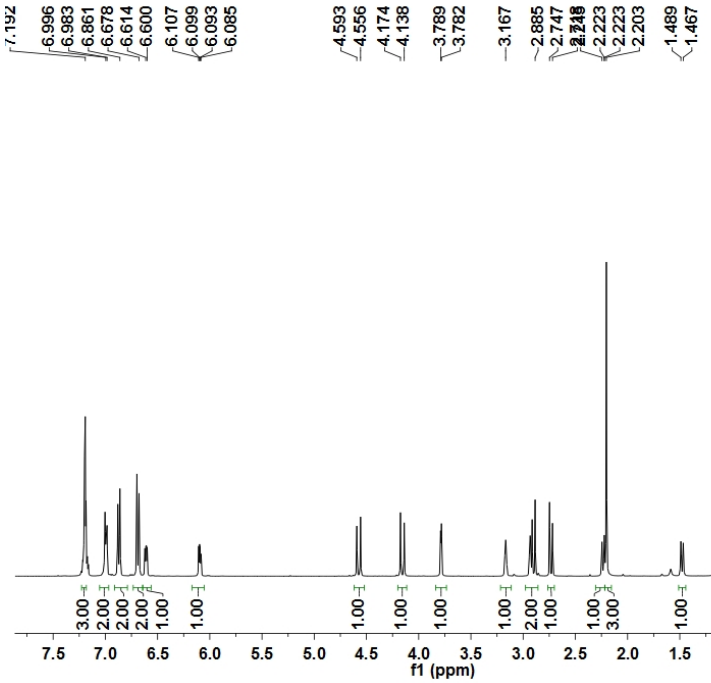




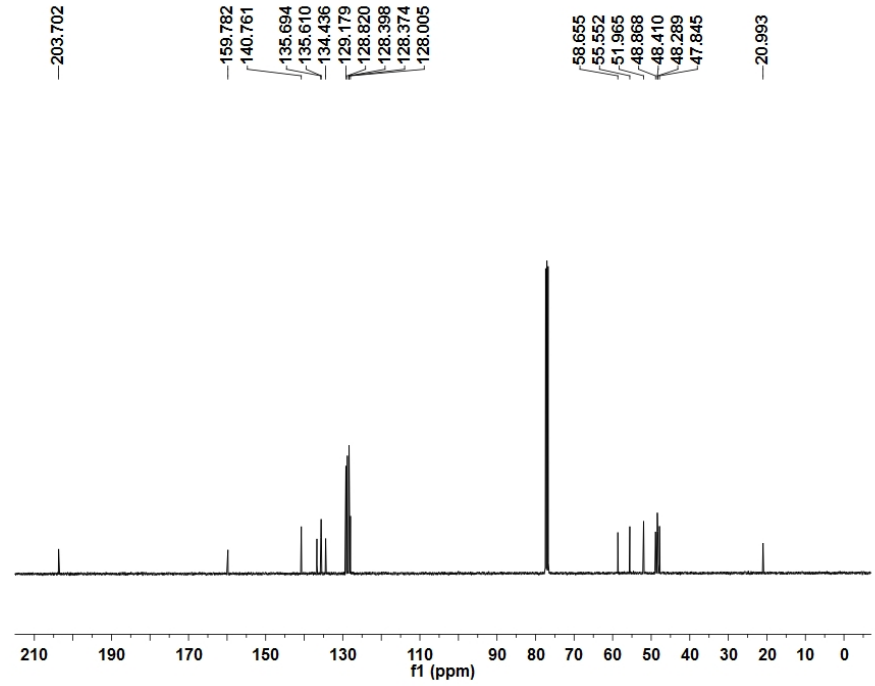



```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-01-23T02:50:53
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 1024
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -60.74
Ph1: 53.53
```

3k

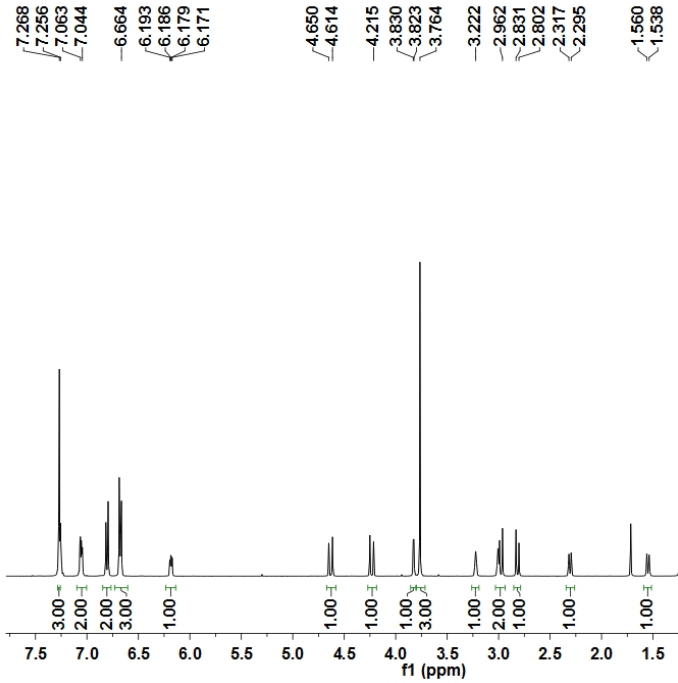


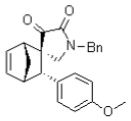

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-01-23T20:15:15
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 64
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 98.23
Ph1: 14.49
```



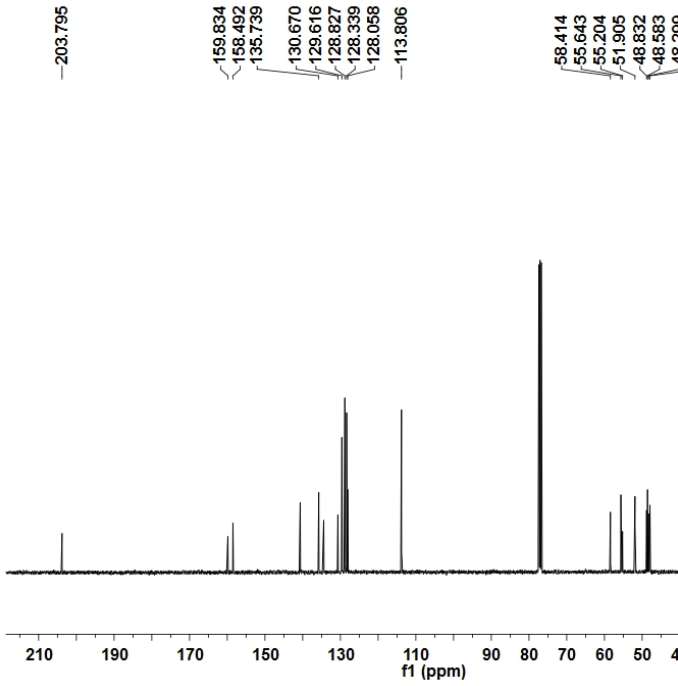

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-01-23T21:14:41
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 1024
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -72.07
Ph1: 75.38
```

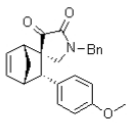
3l





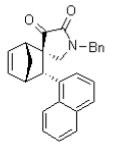

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-11-19T17:57:26
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 94.69
Ph1: 17.79
```

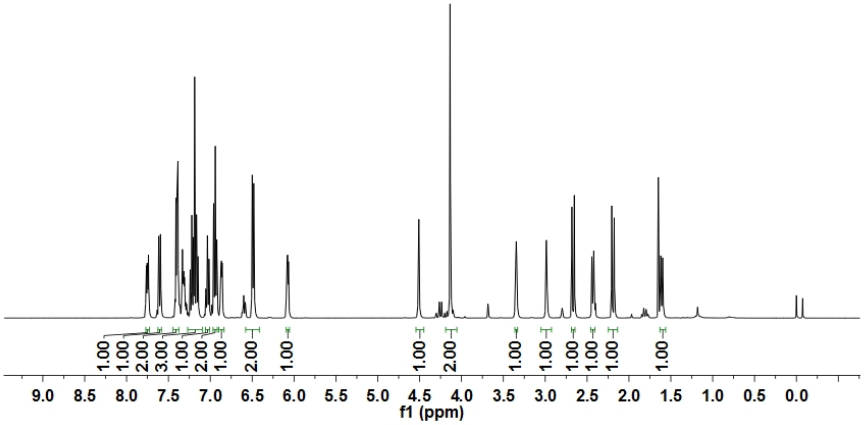




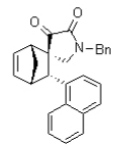

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-11-19T18:27:38
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -68.92
Ph1: 71.95
```

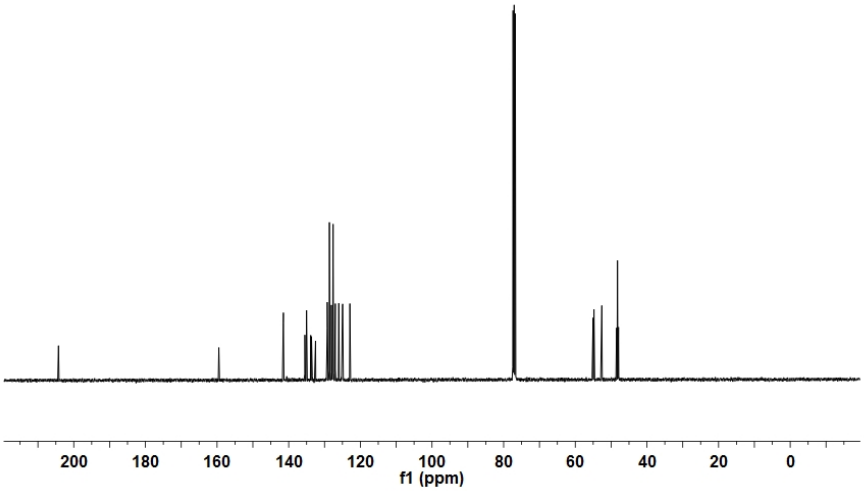
3m





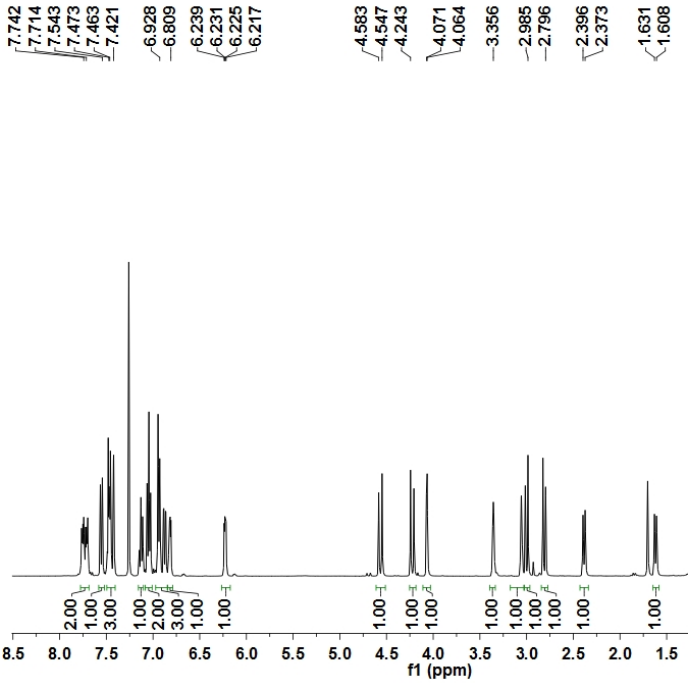

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-11-17T12:55:09
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 32
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 93.31
Ph1: 21.31
```

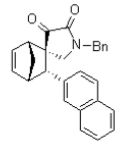




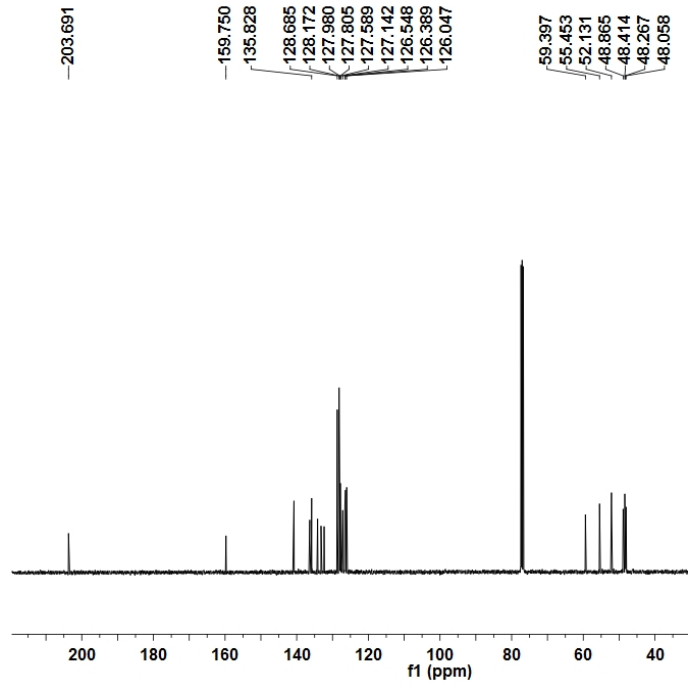

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-01-23T00:14:09
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 1024
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -64.14
Ph1: 58.05
```

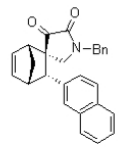
3n





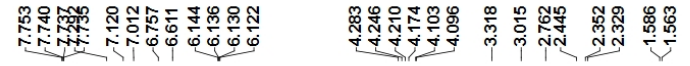

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-11-17T13:31:04
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 32
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 96.52
Ph1: 13.35
```

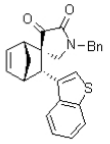


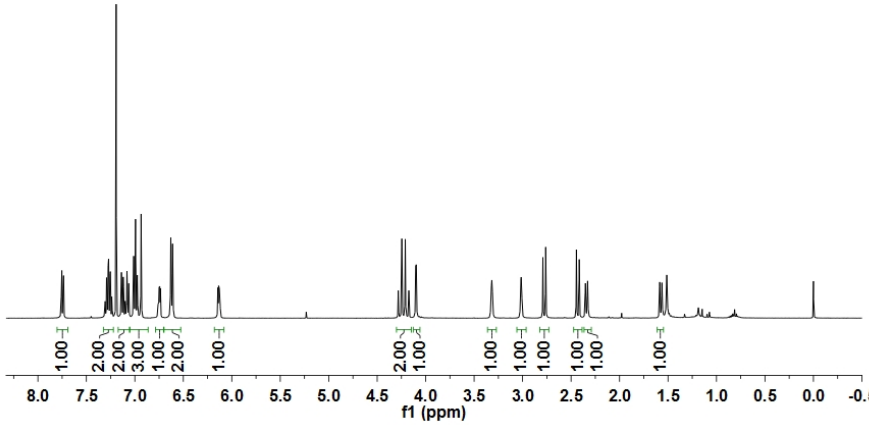



```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-11-17T14:01:15
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -66.70
Ph1: 64.81
```

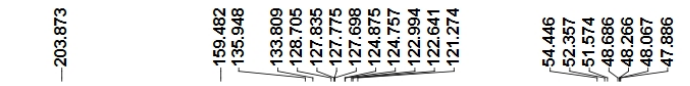
3o

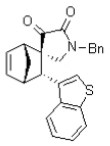


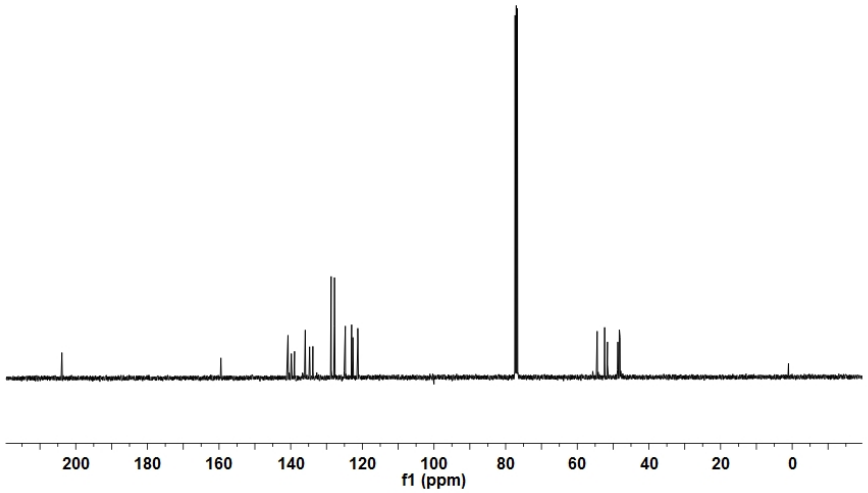





```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-01-23T19:07:13
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 64
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 100.77
Ph1: 4.98
```

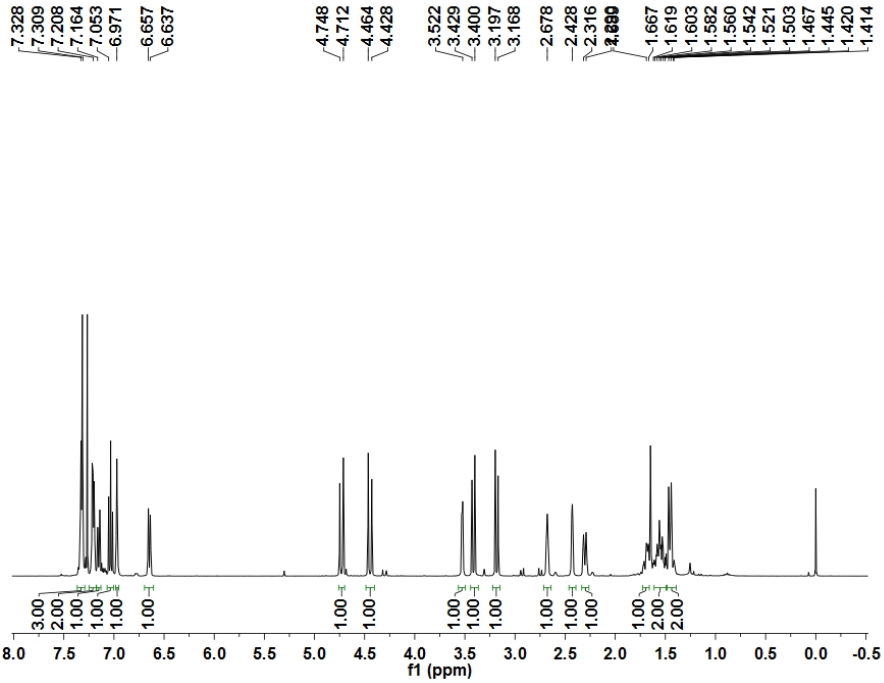




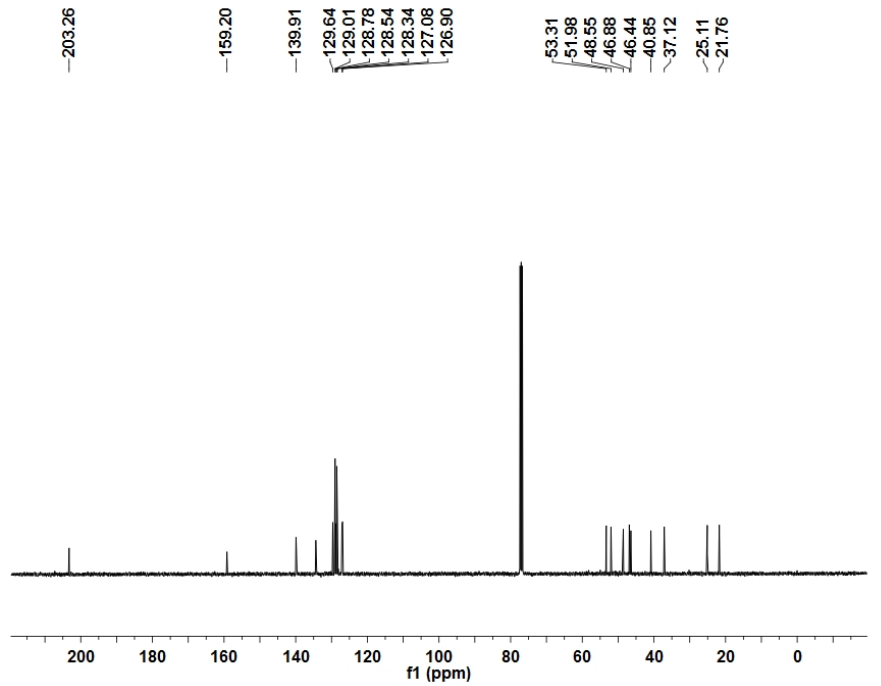



```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-11-20T00:25:34
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -76.10
Ph1: 79.02
```

6

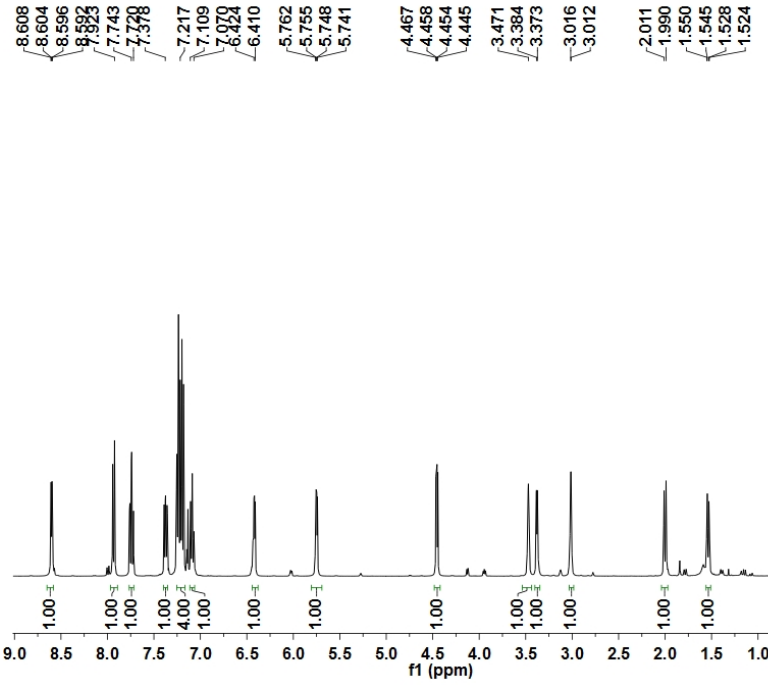


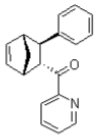

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-07T12:29:28
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 32
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 94.38
Ph1: 17.71
```



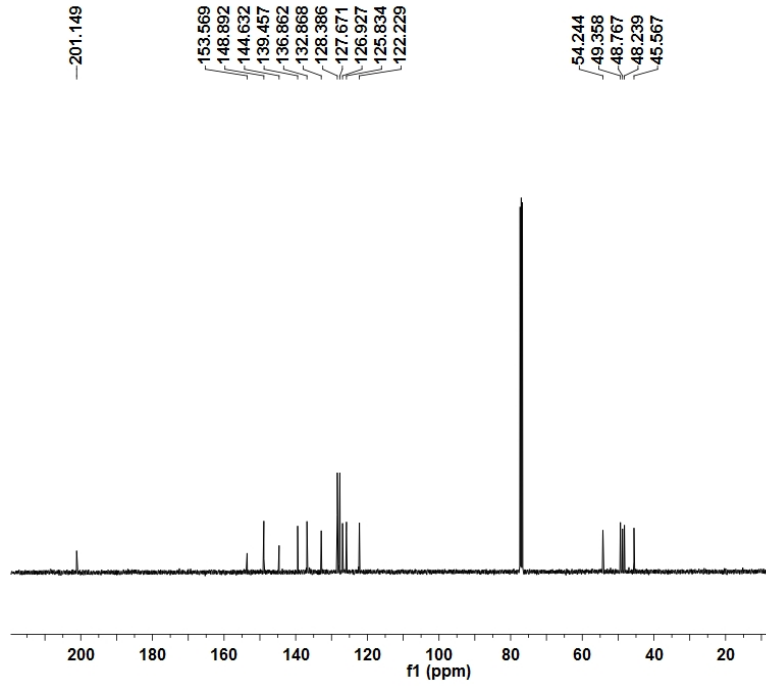

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-07T12:59:40
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -64.75
Ph1: 61.55
```

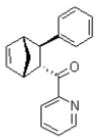
5a





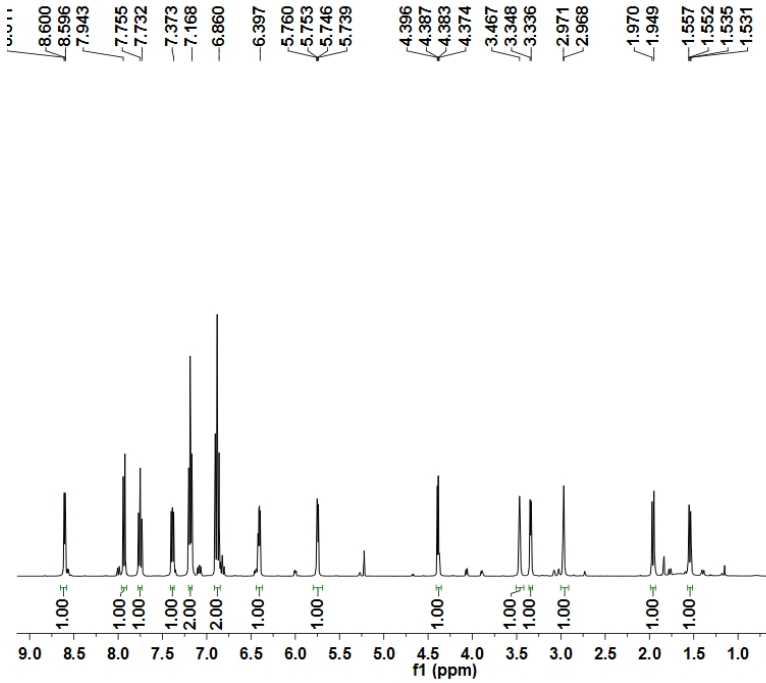

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-02-19T12:09:55
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 64
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 293.7 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -263.60
Ph1: 15.88
```

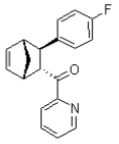




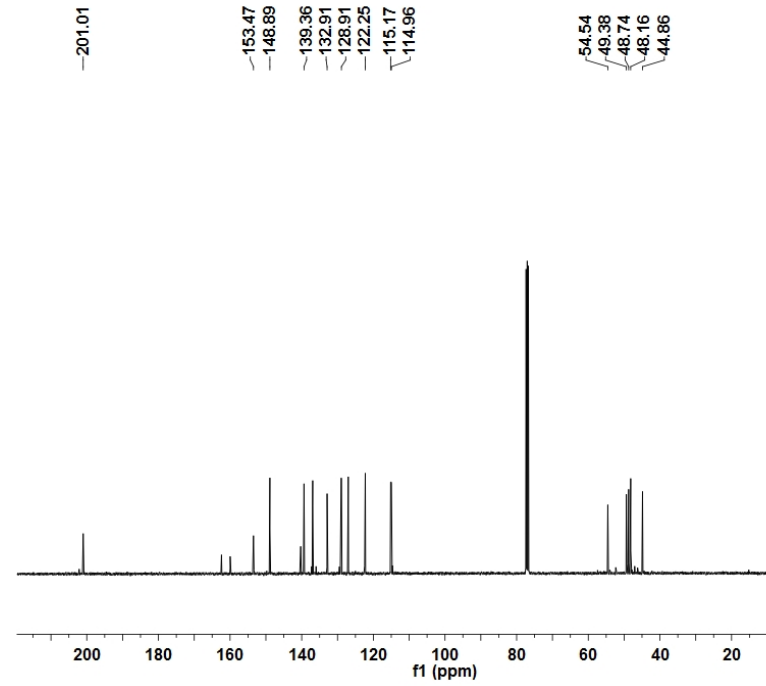

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-01-14T12:16:43
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -72.44
Ph1: 71.79
```

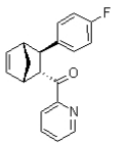
5b





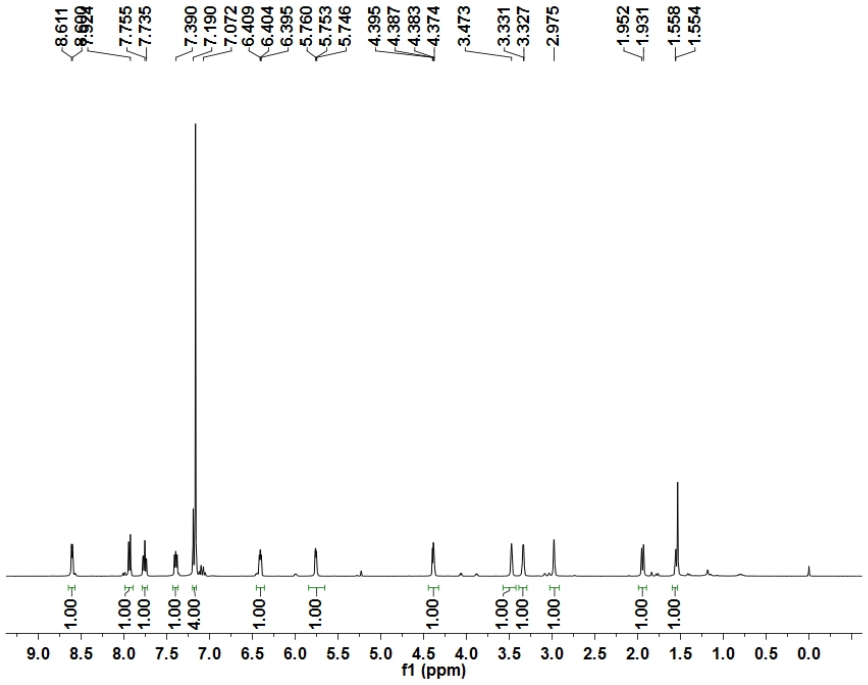

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-02-19T13:17:21
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 64
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 293.8 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 95.14
Ph1: 16.13
```

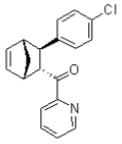




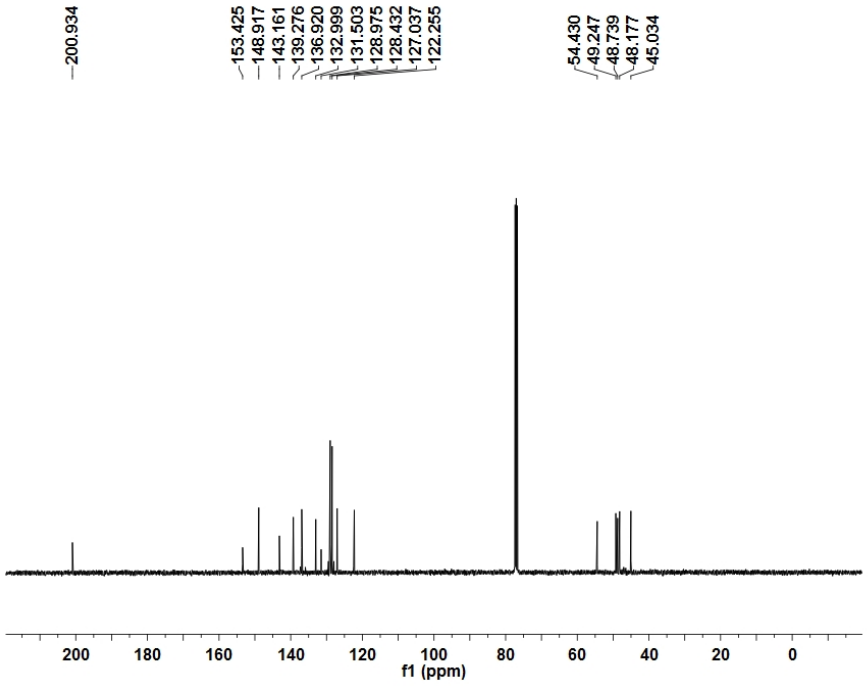

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-02-19T14:16:48
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 1024
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 294.1 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -65.65
Ph1: 56.77
```

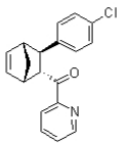
5c





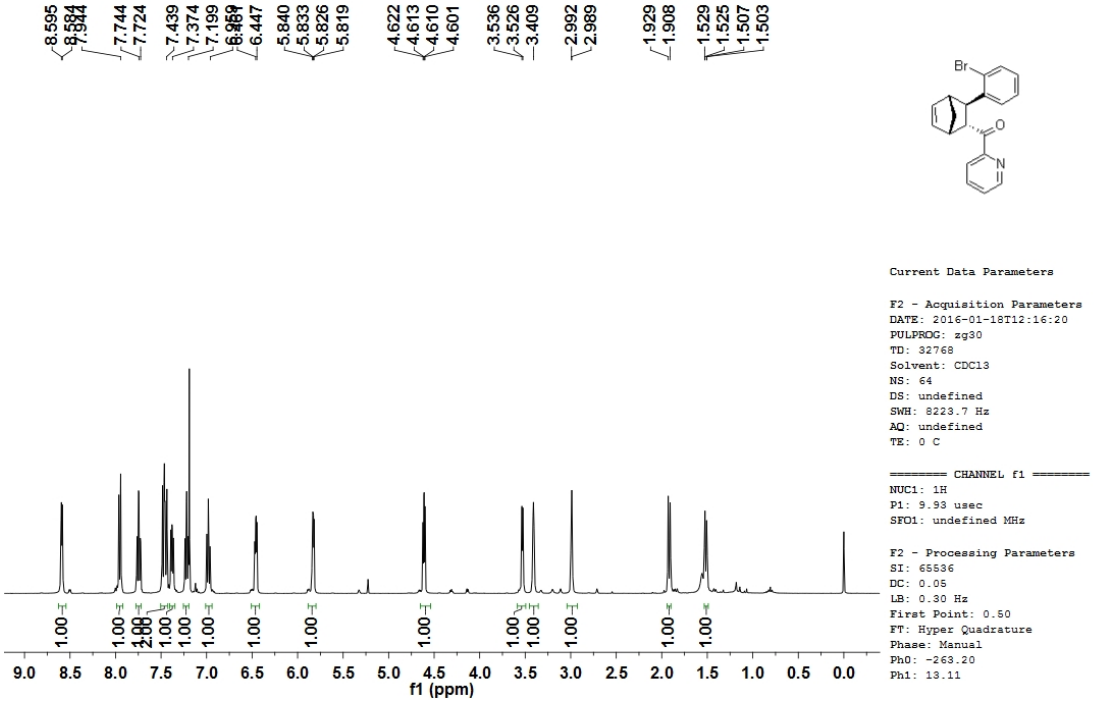

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-01-14T13:02:59
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 64
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 99.19
Ph1: 11.43
```

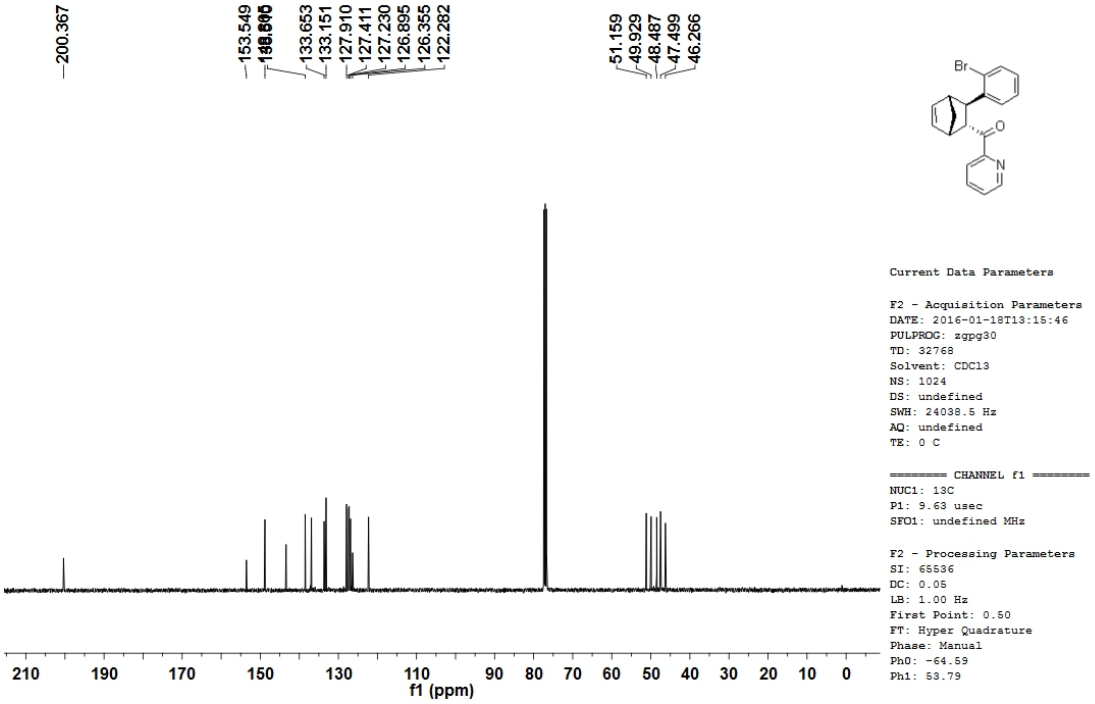




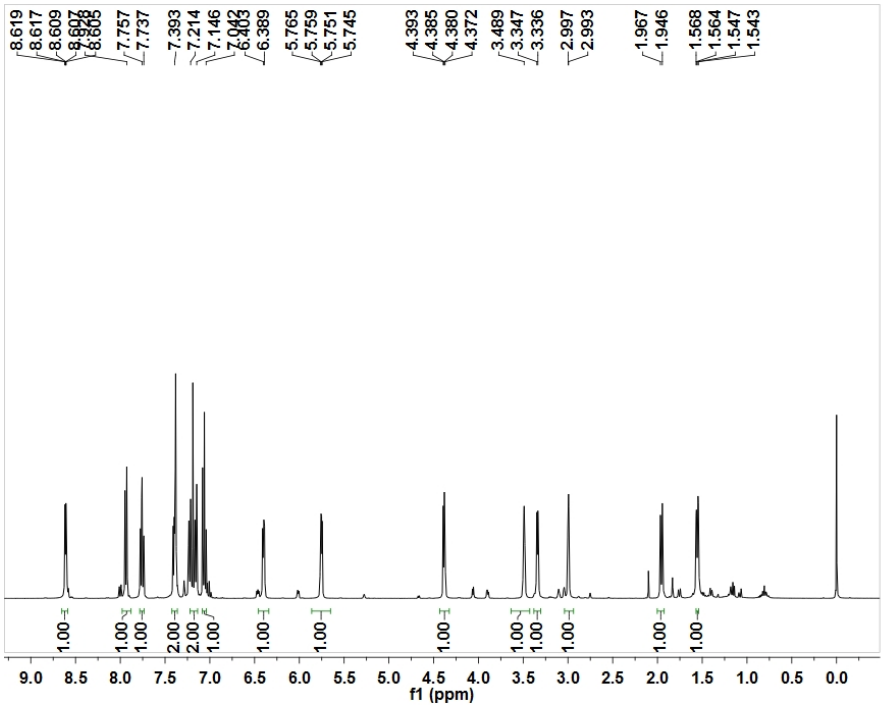

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-01-14T13:33:11
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -70.99
Ph1: 63.55
```

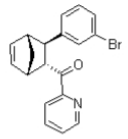
5d


8.595
8.584
7.744
7.724
7.439
7.374
7.199
6.447
5.840
5.833
5.826
5.819
4.622
4.613
4.610
4.601
3.536
3.526
3.409
2.992
2.989
1.929
1.908
1.529
1.525
1.507
1.503
Br
O
N
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2016-01-18T12:16:20
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 64
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 C
======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -263.20
Ph1: 13.11
f1 (ppm)

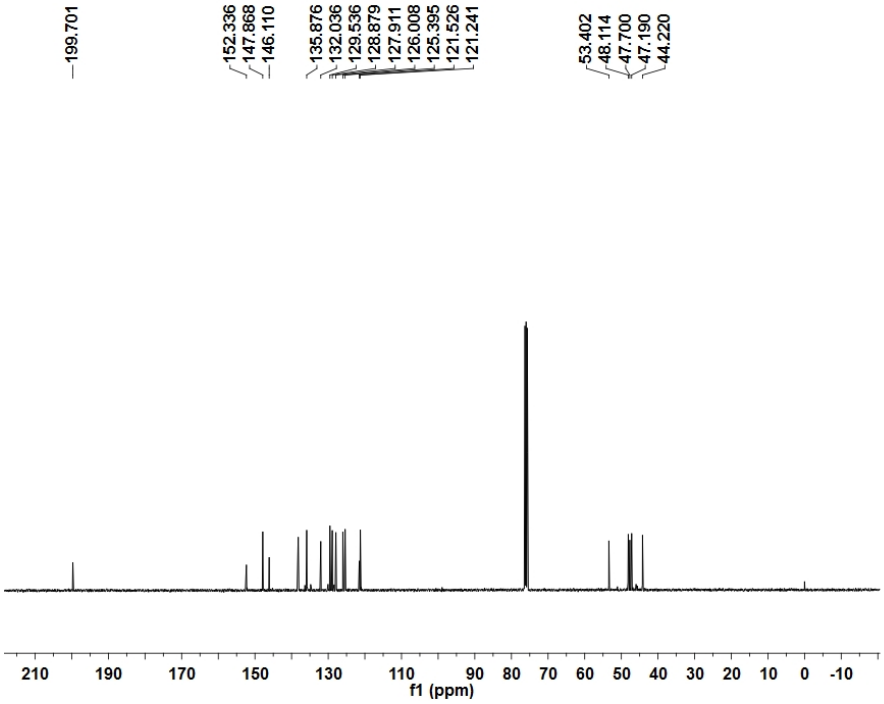

200.367
153.549
133.653
133.151
127.910
127.411
127.230
126.895
126.355
122.282
51.159
49.929
48.487
47.499
46.266
Br
O
N
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2016-01-18T13:15:46
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 1024
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C
======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -64.59
Ph1: 53.79
f1 (ppm)

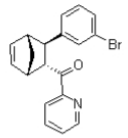
5e





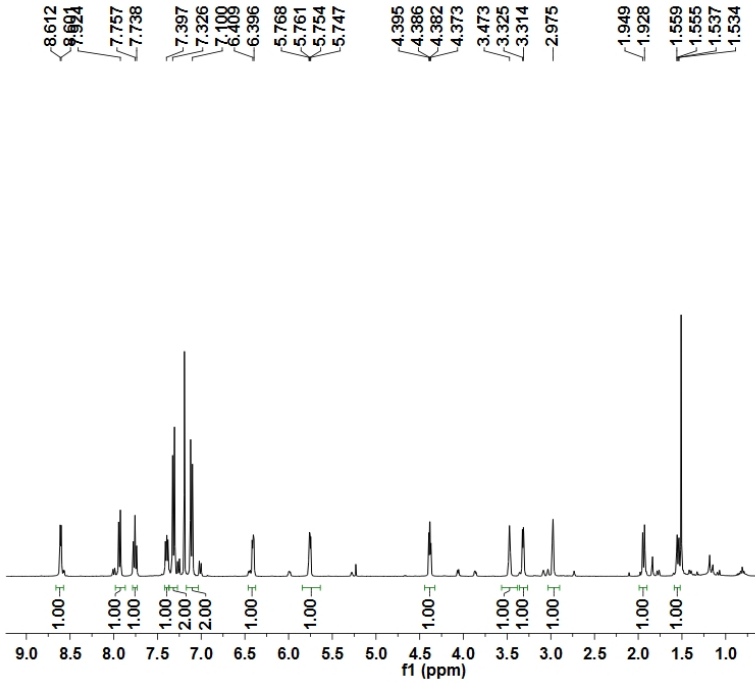

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-01-18T13:23:49
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 64
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 96.05
Ph1: 12.09
```

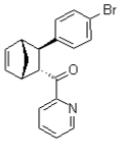




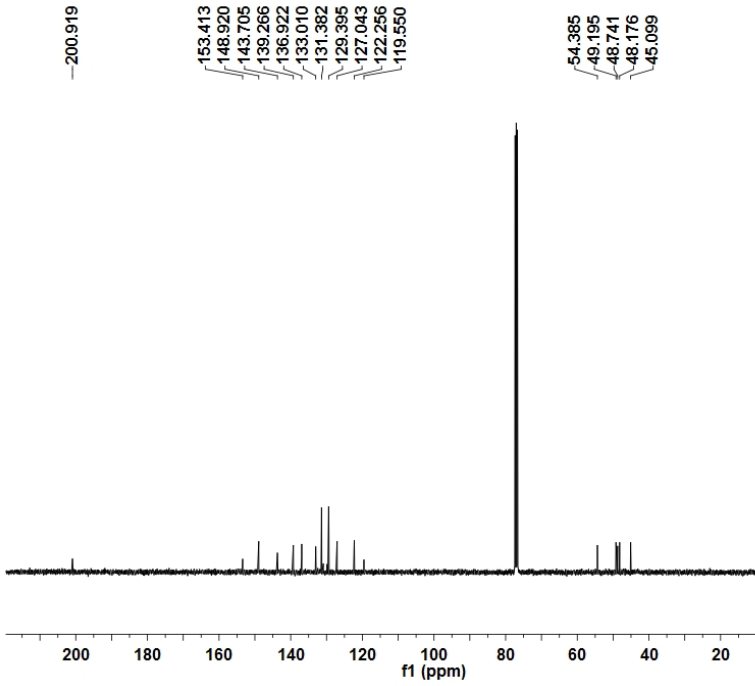

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-01-18T14:23:15
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 1024
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -74.51
Ph1: 75.40
```

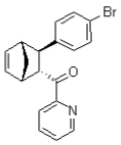
5f





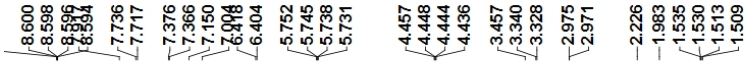

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-01-14T13:41:08
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 64
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 101.01
Ph1: 8.18
```

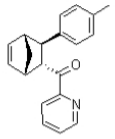


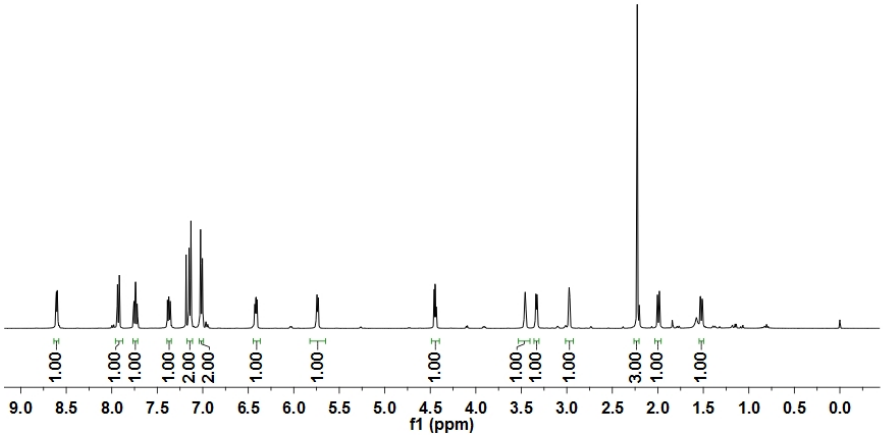



```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-01-14T14:11:19
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -15.18
Ph1: -14.30
```

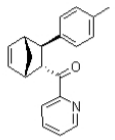
5g

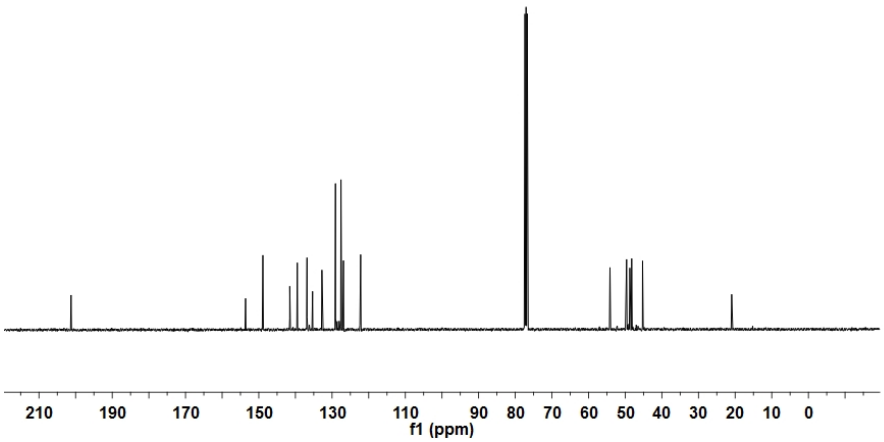






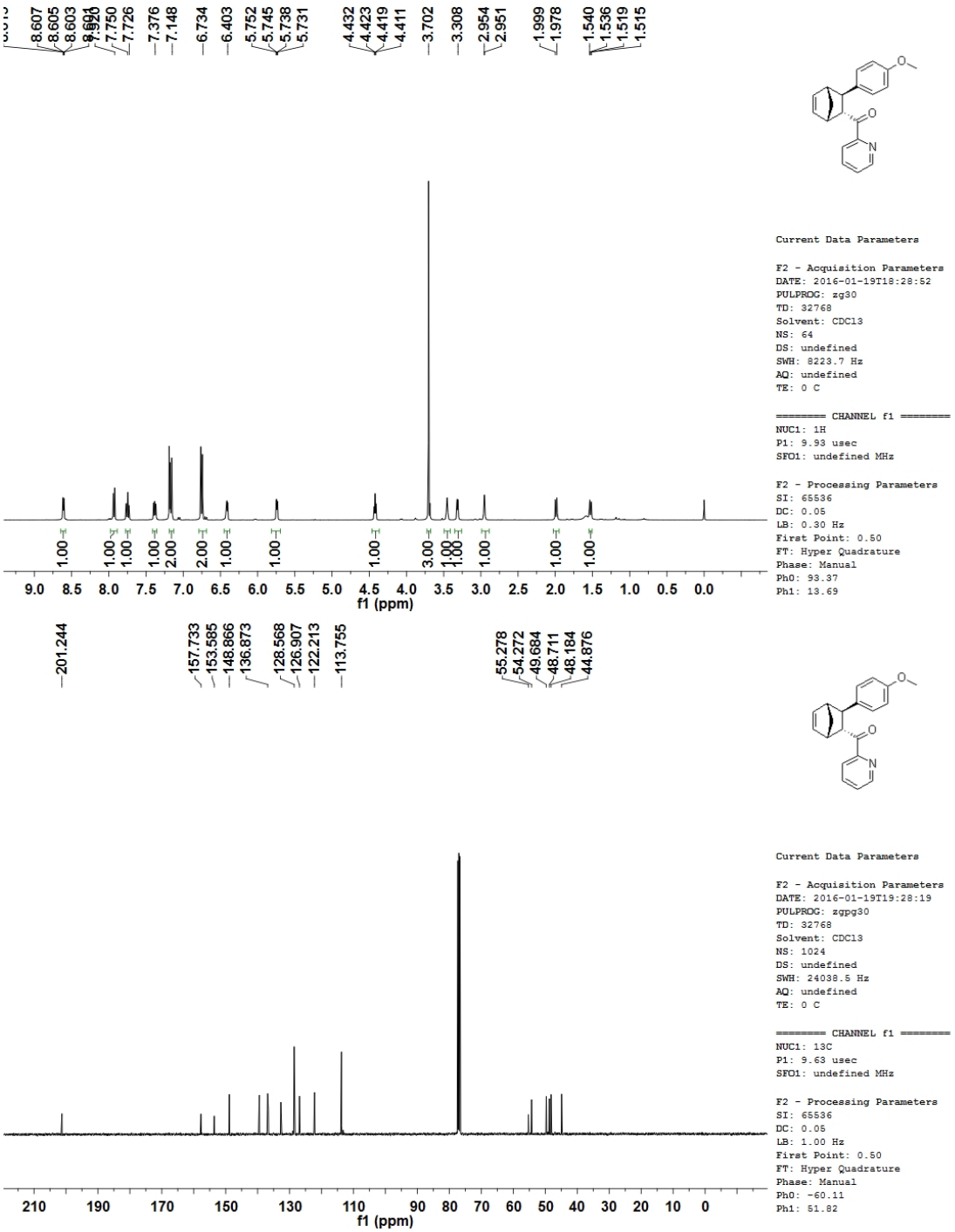

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-01-19T17:21:17
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 64
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 93.59
Ph1: 14.65
```



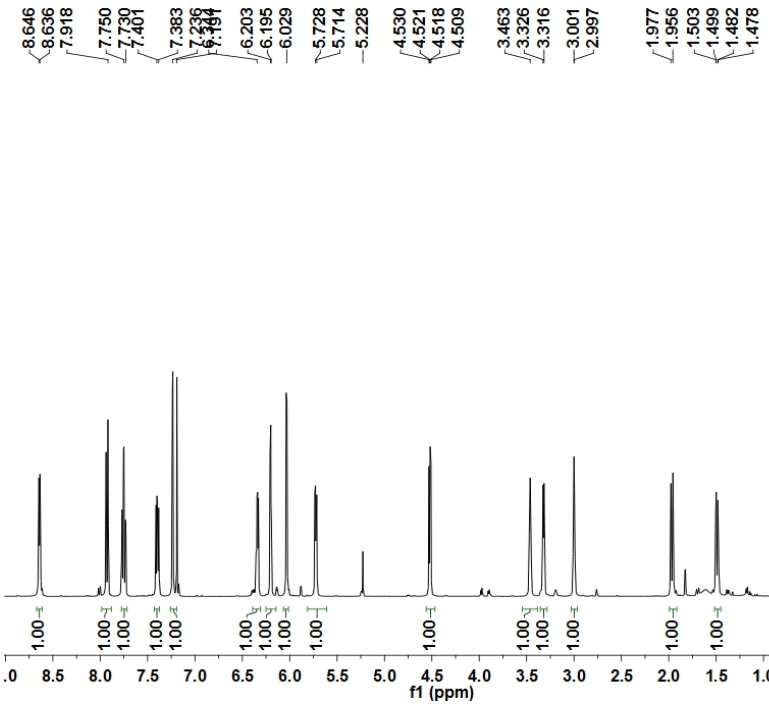


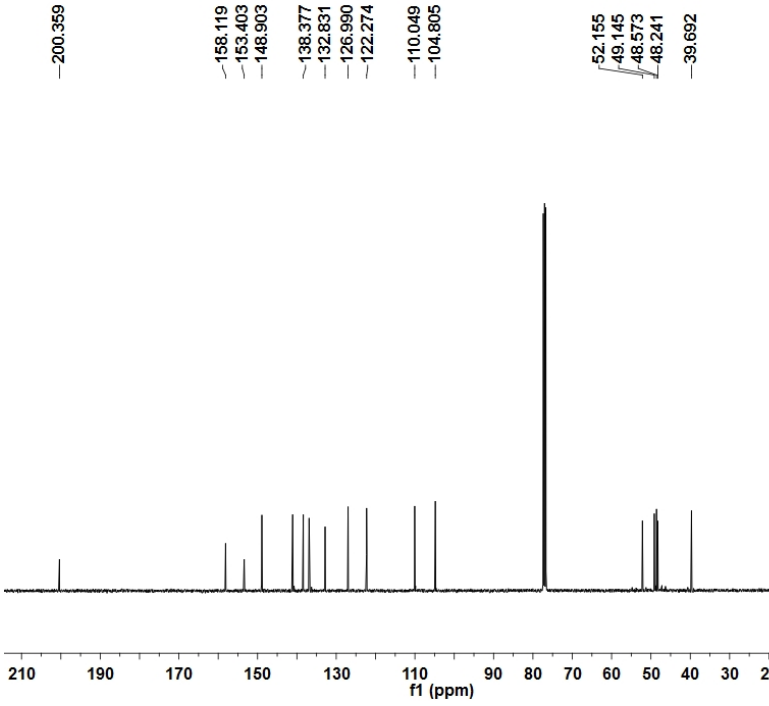

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-01-19T18:20:52
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 1024
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -62.41
Ph1: 56.28
```

5h

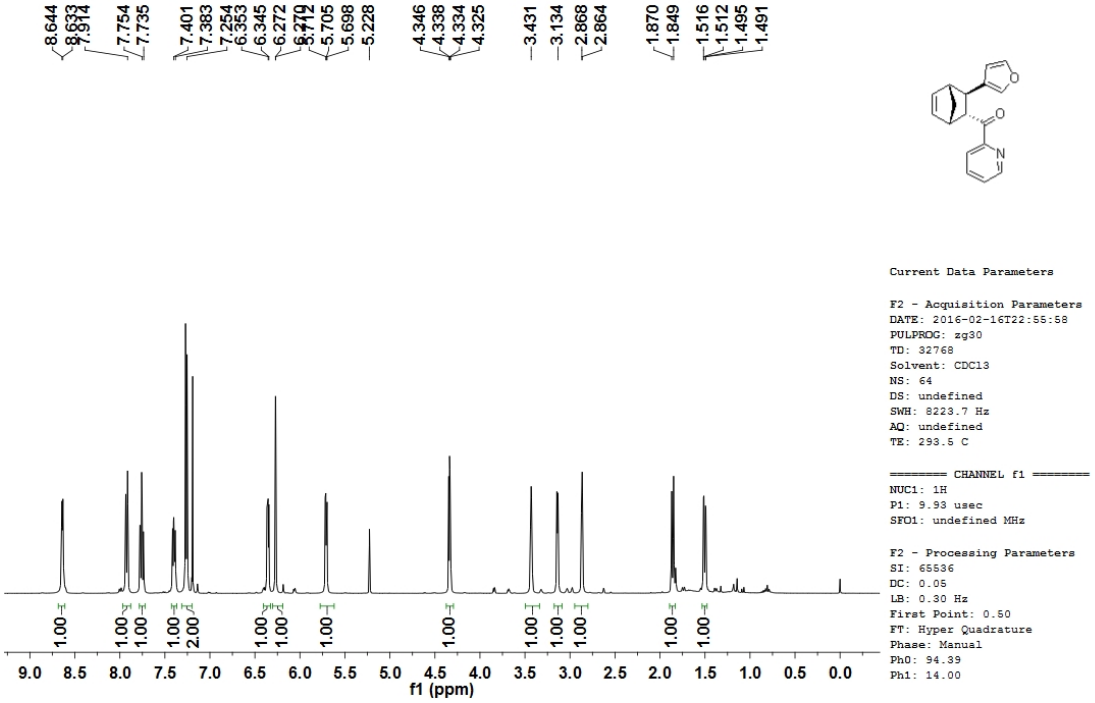

8.607
8.605
8.603
7.750
7.726
7.376
7.148
6.734
6.403
5.752
5.745
5.738
5.731
4.432
4.423
4.419
4.411
3.702
3.308
2.954
2.951
1.999
1.978
1.540
1.536
1.519
1.515
O
N
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2016-01-19T18:28:52
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 64
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 C
======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 93.37
Ph1: 13.69
1.00
1.00
1.00
2.00
2.00
1.00
1.00
1.00
3.00
1.00
1.00
1.00
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
201.244
157.733
153.585
148.866
136.873
128.568
126.907
122.213
113.755
55.278
54.272
49.684
48.711
48.184
44.876
O
N
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2016-01-19T19:28:19
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 1024
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C
======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -60.11
Ph1: 51.82
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

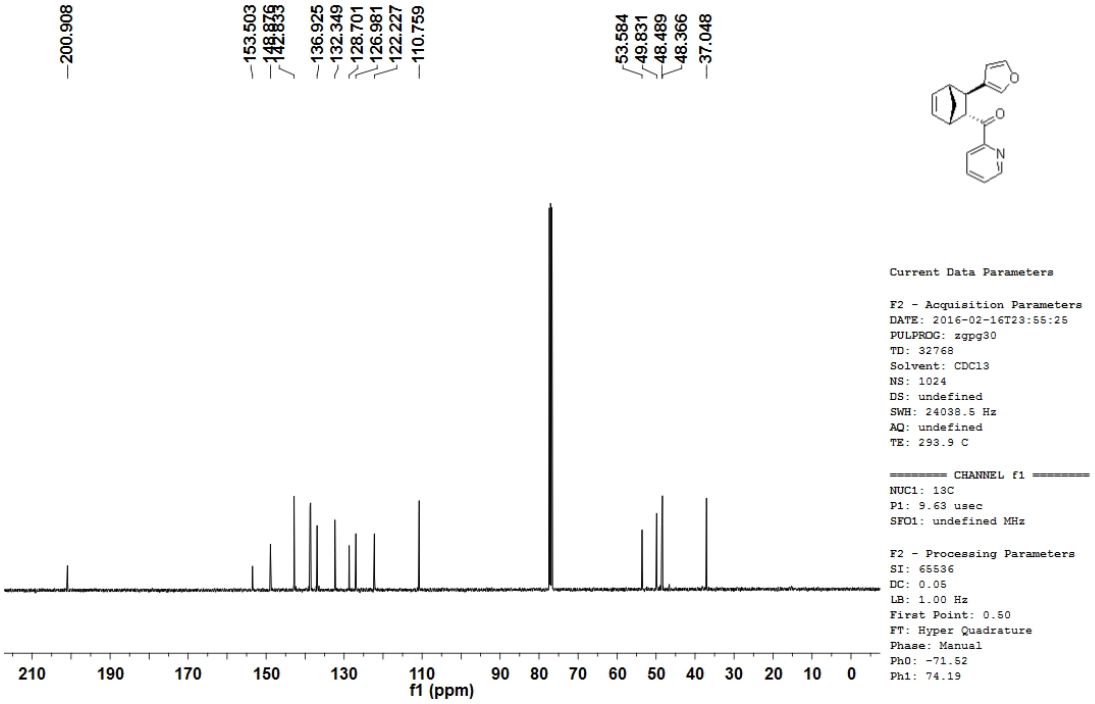
5i


8.646
8.636
7.918
7.750
7.730
7.401
7.383
7.236
6.203
6.195
6.029
5.728
5.714
5.228
4.530
4.521
4.518
4.509
3.463
3.326
3.316
3.001
2.997
1.977
1.956
1.503
1.499
1.482
1.478
O
O
N
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2016-02-16T21:48:32
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 64
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 293.5 C
======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 95.05
Ph1: 14.98
1.00
f1 (ppm)

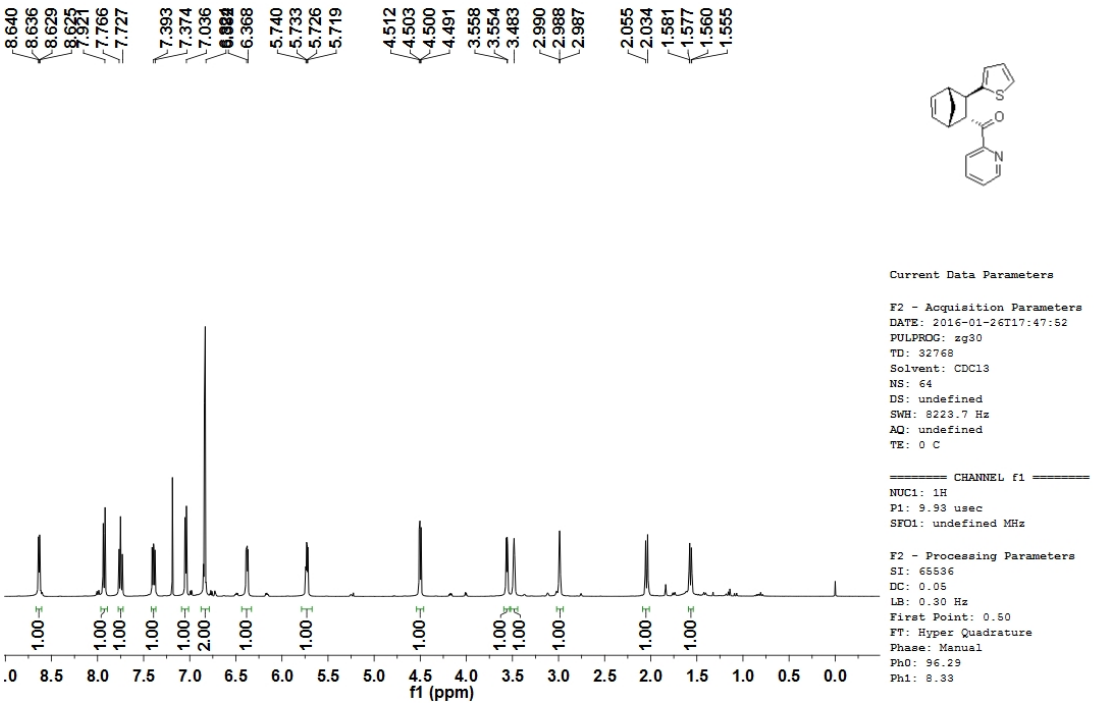

200.359
158.119
153.403
148.903
138.377
132.831
126.990
122.274
110.049
104.805
52.155
49.145
48.573
48.241
39.692
O
O
N
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2016-02-16T22:47:58
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 1024
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 293.9 C
======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -51.61
Ph1: 49.54
f1 (ppm)

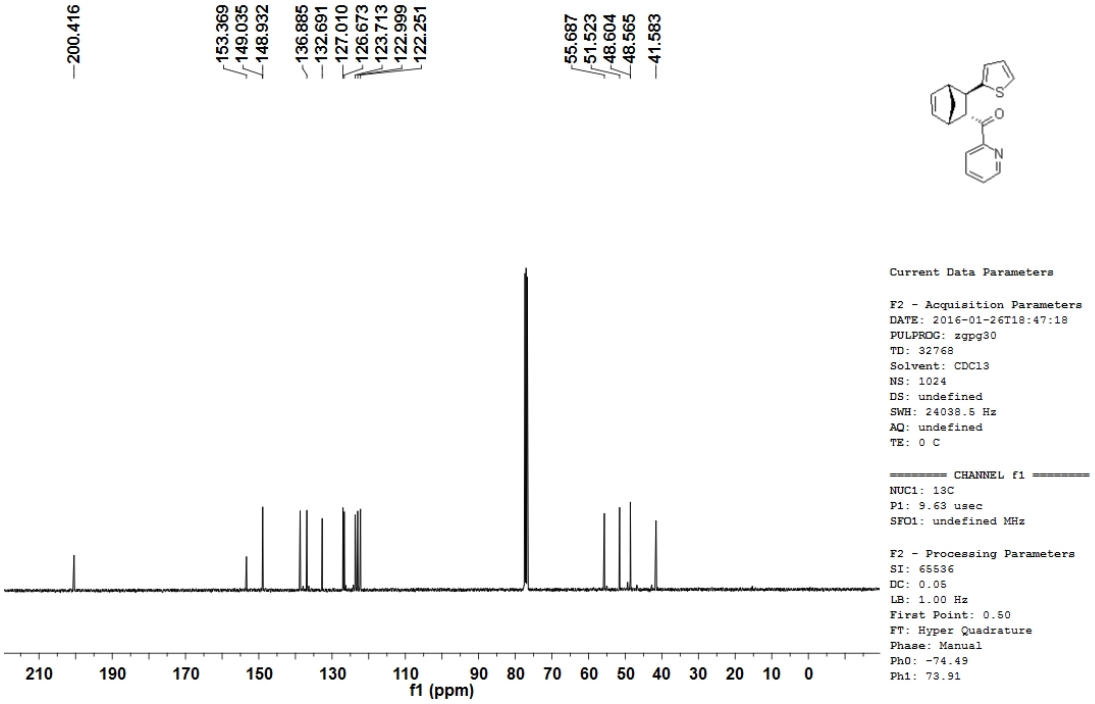
5j


8.644
8.633
8.614
7.754
7.735
7.401
7.383
7.254
6.353
6.345
6.272
5.705
5.698
5.228
4.346
4.338
4.334
4.325
3.431
3.134
2.868
2.864
1.870
1.849
1.516
1.512
1.495
1.491
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2016-02-16T22:55:58
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 64
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 293.5 C
======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 94.39
Ph1: 14.00
f1 (ppm)

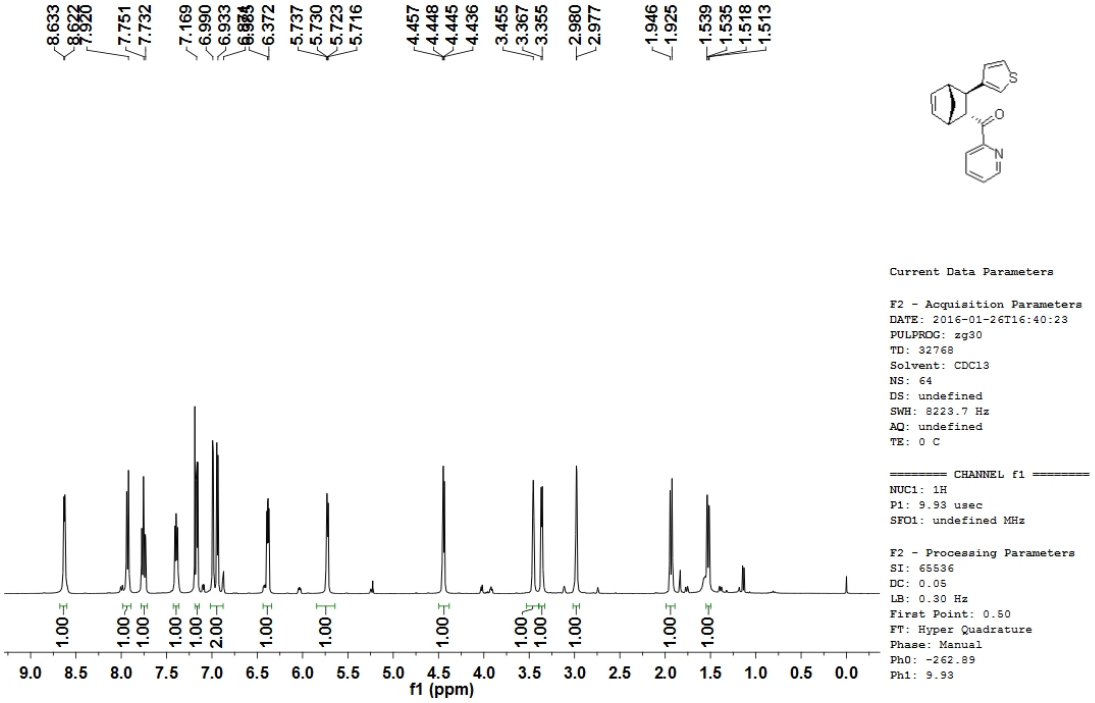

200.908
153.503
136.925
132.349
128.701
126.981
122.227
110.759
53.584
49.831
48.489
48.366
37.048
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2016-02-16T23:55:25
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 1024
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 293.9 C
======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -71.52
Ph1: 74.19
f1 (ppm)

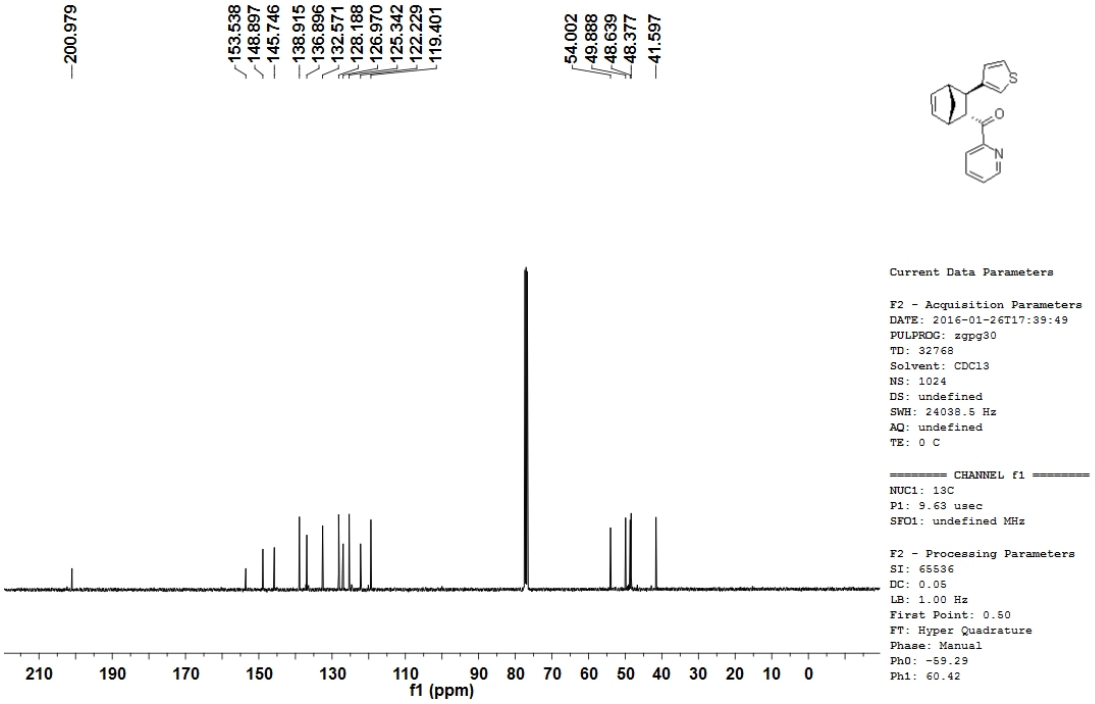
5k


8.640
8.636
8.629
8.625
7.766
7.727
7.393
7.374
7.036
6.368
5.740
5.733
5.726
5.719
4.512
4.503
4.500
4.491
3.558
3.554
3.483
2.990
2.988
2.987
2.055
2.034
1.581
1.577
1.560
1.555
1.00
2.00
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2016-01-26T17:47:52
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 64
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 C
CHANNEL f1
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 96.29
Ph1: 8.33

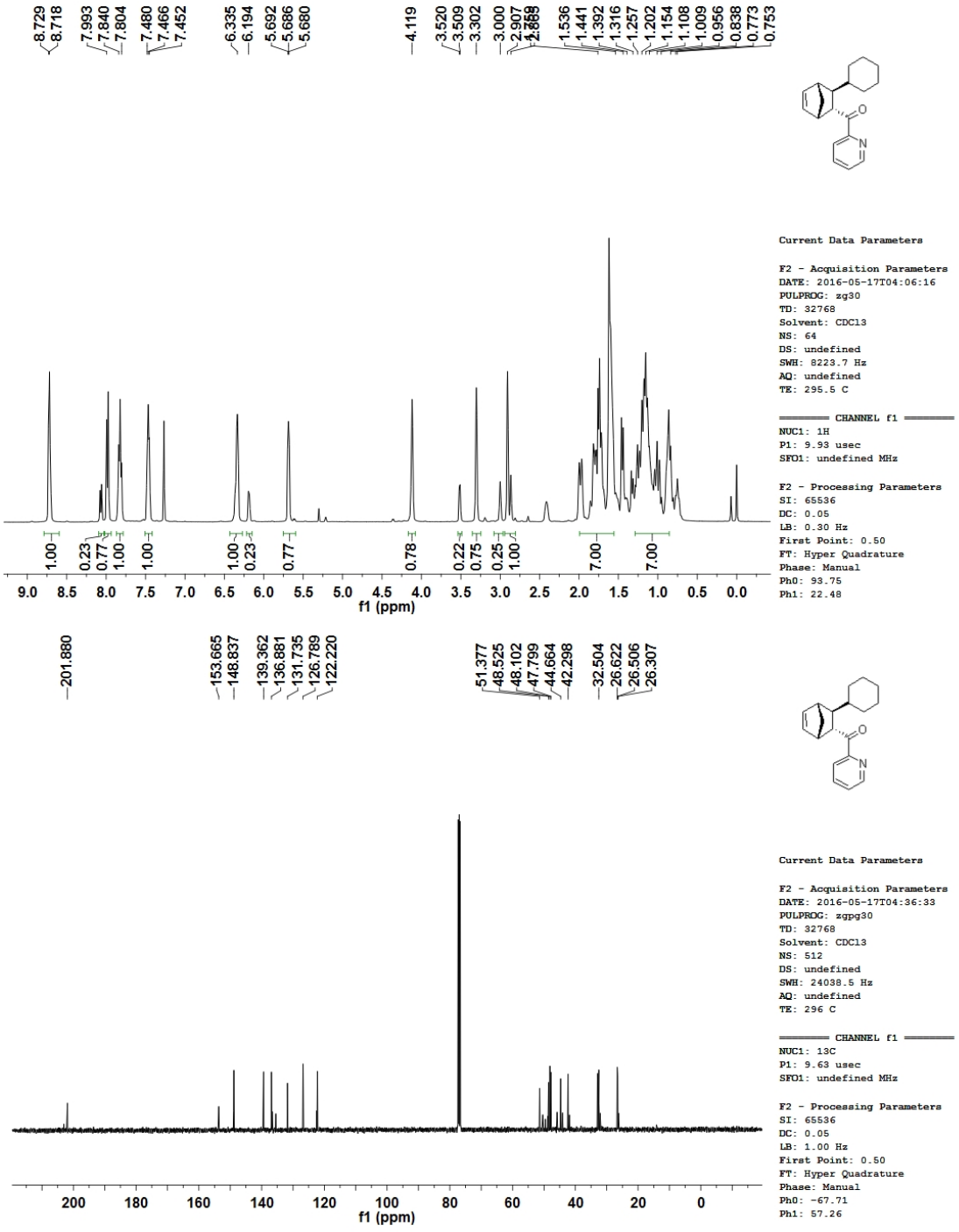

200.416
153.369
149.035
148.932
136.885
132.691
127.010
126.673
123.713
122.999
122.251
55.687
51.523
48.604
48.565
41.583
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2016-01-26T18:47:18
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 1024
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C
CHANNEL f1
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -74.49
Ph1: 73.91

5l

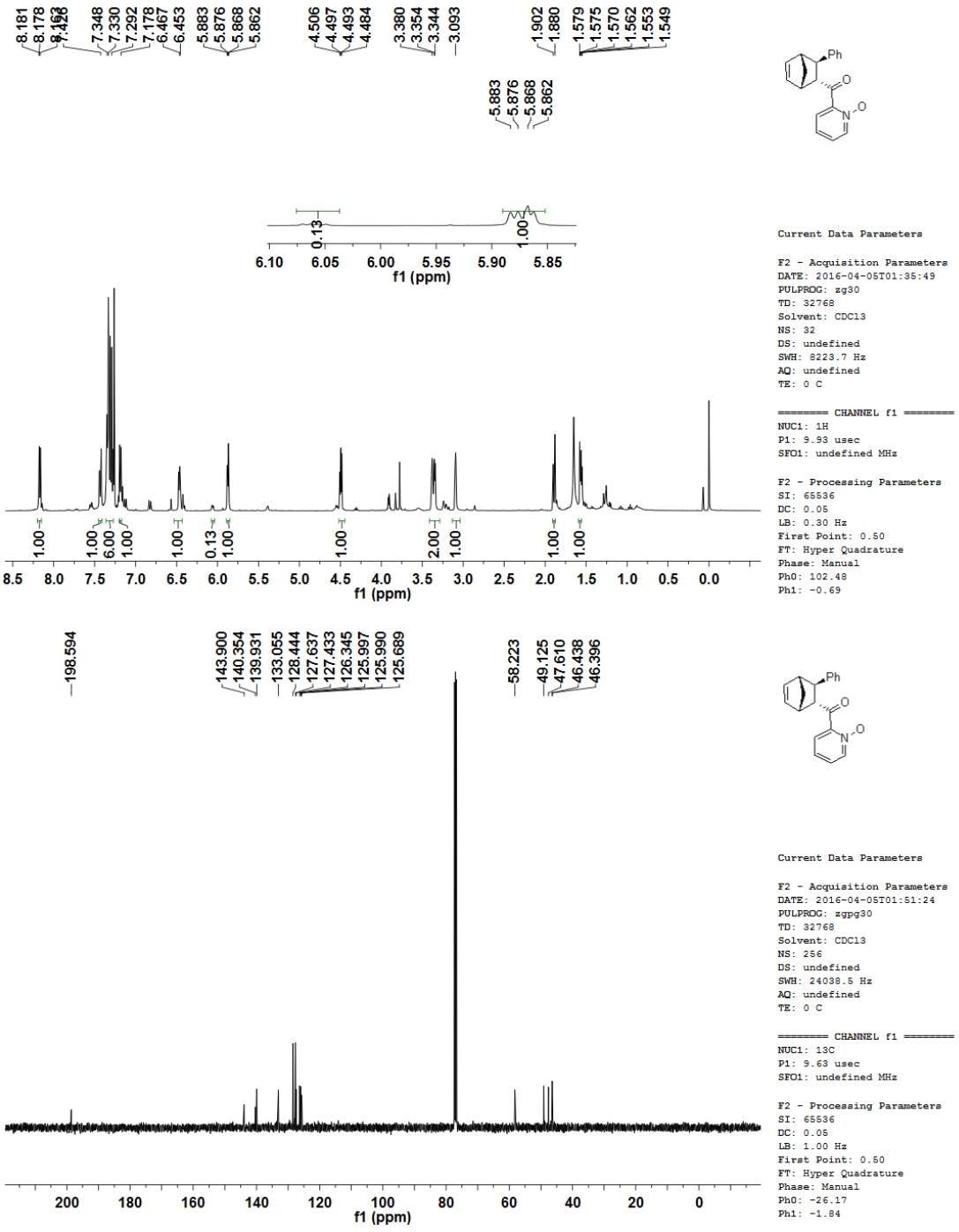

8.633
8.622
7.920
7.751
7.732
7.169
6.990
6.933
6.372
5.737
5.730
5.723
5.716
4.457
4.448
4.445
4.436
3.455
3.367
3.355
2.980
2.977
1.946
1.925
1.539
1.535
1.518
1.513
S
O
N
1.00
1.00
1.00
1.00
2.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2016-01-26T16:40:23
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 64
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 C
======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -262.89
Ph1: 9.93


200.979
153.538
148.897
145.746
138.915
136.896
132.571
128.188
126.970
125.342
122.229
119.401
54.002
49.888
48.639
48.377
41.597
S
O
N
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2016-01-26T17:39:49
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 1024
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C
======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -59.29
Ph1: 60.42

5m


8.729
8.718
7.993
7.840
7.804
7.480
7.466
7.452
6.335
6.194
5.692
5.686
5.680
4.119
3.520
3.509
3.302
3.000
2.907
1.536
1.441
1.392
1.316
1.257
1.202
1.154
1.108
1.009
0.956
0.838
0.773
0.753
1.00
0.23
0.77
1.00
1.00
1.00
0.23
0.77
0.78
0.22
0.75
0.25
1.00
7.00
7.00
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2016-05-17T04:06:16
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 64
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 295.5 C
CHANNEL f1
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 93.75
Ph1: 22.48
201.880
153.665
148.837
139.362
136.881
131.735
126.789
122.220
51.377
48.525
48.102
47.799
44.664
42.298
32.504
26.622
26.506
26.307
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2016-05-17T04:36:33
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 296 C
CHANNEL f1
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -67.71
Ph1: 57.26

5p


8.181
8.178
7.348
7.330
7.292
7.178
6.467
6.453
5.883
5.876
5.868
5.862
4.506
4.497
4.493
4.484
3.380
3.354
3.344
3.093
1.902
1.880
1.579
1.575
1.570
1.562
1.553
1.549
Ph
O
N
O
0.13
1.00
6.10 6.05 6.00 5.95 5.90 5.85
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2016-04-05T01:35:49
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 32
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 C
======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 102.48
Ph1: -0.69
1.00 1.00 6.00 1.00 1.00 0.13 1.00 1.00 2.00 1.00 1.00 1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
198.594
143.900
140.354
139.931
133.055
128.444
127.637
127.433
126.345
125.997
125.990
125.689
58.223
49.125
47.610
46.438
46.396
Ph
O
N
O
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2016-04-05T01:51:24
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C
======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -26.17
Ph1: -1.84
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

11. References

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2. (a) X. Chen, L. Zhu, L. Fang, S. Yan and J. Lin, *RSC Adv*., 2014, **4**, 9926; (b) S. Zhang, Y.-C. Luo, X.-Q. Hu, Z.-Y. Wang, Y.-M. Liang and P.-F. Xu, *J. Org. Chem*. 2015, **80**, 7288.
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