Supporting Information

for

Asymmetric approach to bicyclo[2.2.1]heptane-1-carboxylates via a formal [4+2] cycloaddition reaction enabled by organocatalysis

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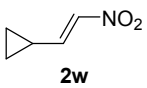
General Information

All non-aqueous reactions were run under a positive pressure of nitrogen. Anhydrous solvents were obtained using standard drying techniques. Commercial grade reagents were used without further purification unless stated otherwise. Flash chromatography was performed on 300-400 mesh silica gel with the indicated solvent systems. ^{1}H NMR were recorded on a Bruker 400 (400 MHz) spectrometer and chemical shifts are reported in ppm down field from TMS, using TMS (0.00 ppm) or residual chloroform (7.26 ppm) as an internal standard. Data are reported as: (s = singlet, br = broad, d = doublet, t = triplet, q = quartet, quint = quintuplet, hept = heptalet, m = multiplet; *J* = coupling constant in Hz, integration.). ^{13}C NMR spectra were recorded on a Bruker 400 (100 MHz) spectrometer, using proton decoupling unless otherwise noted. Chemical shifts are reported in ppm down field from TMS, using the central resonance of $CDCl_3$ (77.00 ppm) as the internal standard. $[\alpha]^D$ values were given in 10^{-1} deg cm^2 g^{-1}. HRMS were recorded by using either FTMS-7 or IonSpec 4.7 spectrometers.

General Procedure for the Perparation of Nitroolefin

All nitroolefins were prepared according to the literature procedures[1].

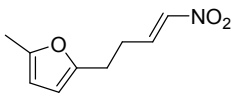
(E)-(2-nitrovinyl)cyclopropane



2w

68% yield as whiteless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.14 (d, *J* = 13.3 Hz, 1H), 6.78 (dd, J_1 = 13.0 Hz, J_2 = 11.0 Hz, 1H), 1.65-1.60 (m, 1H), 1.17-1.12 (m, 2H), 0.82-0.78 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.8, 137.3, 11.5, 9.7; **IR** (thin film): 3108, 3013, 1640, 1514, 1374, 1347, 1195, 1060, 939, 865 cm^{-1}; **LRMS** (ESI): 136 $(M+Na)^+$; **HRMS** (MALDI): calcd for $C_5H_7N_1O_2Na$ $(M+Na)^+$: 136.0369, found: 136.0370.

(E)-2-methyl-5-(4-nitrobut-3-en-1-yl)furan



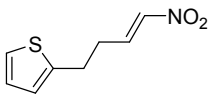
2q

30% yield as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.31-7.24 (m, 1H), 6.99 (br d, *J* = 13.3 Hz, 1H), 5.91-5.90 (m, 1H), 5.86-5.85 (m, 1H), 2.82-2.79 (m, 2H), 2.63-2.57 (m, 2H), 2.25 (s,

[1] J. C Anderson, A. J.Blake, M. Mills and P. D. Ratcliffe, *Org. Lett.* 2008, **10**, 4141 - 4143.

3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.2, 151.2, 106.7, 106.1, 27.2, 26.4, 13.5; **IR** (thin film): 3447, 3105, 2924, 1684, 1650, 1611, 1554, 1523, 1352, 1023, 960, 789 cm^{-1}; **LRMS** (EI): 181 $(M)^+$; **HRMS** (EI): calcd for $C_9H_{11}N_1O_3$ $(M)^+$: 181.0739, found: 181.0735.

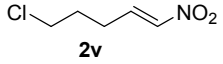
(E)-2-(4-nitrobut-3-en-1-yl)thiophene



2r

32% yield as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.31-7.24 (m, 1H), 7.16 (dd, J_1 = 5.0 Hz, J_2 = 1.0 Hz, 1H), 6.98 (br dt, J_1 = 13.3 Hz, J_2 = 1.3 Hz, 1H), 6.94 (dd, J_1 = 5.0 Hz, J_2 = 3.5 Hz, 1H), 6.82 (dd, J_1 = 3.6 Hz, J_2 = 1.0 Hz, 1H), 3.07 (t, J = 7.3 Hz, 2H), 2.65 (qd, J_1 = 7.4 Hz, J_2 = 1.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 142.0, 140.6, 140.4, 127.1, 125.1, 124.0, 30.4, 28.1; **IR** (thin film): 3106, 2922, 2854, 1648, 1523, 1440, 1351, 952, 849, 702 cm^{-1}; **LRMS** (ESI): 206 $(M+Na)^+$; **HRMS** (ESI): calcd for $C_8H_9N_1O_2S_1Na$ $(M+Na)^+$: 206.0246, found: 206.0247.

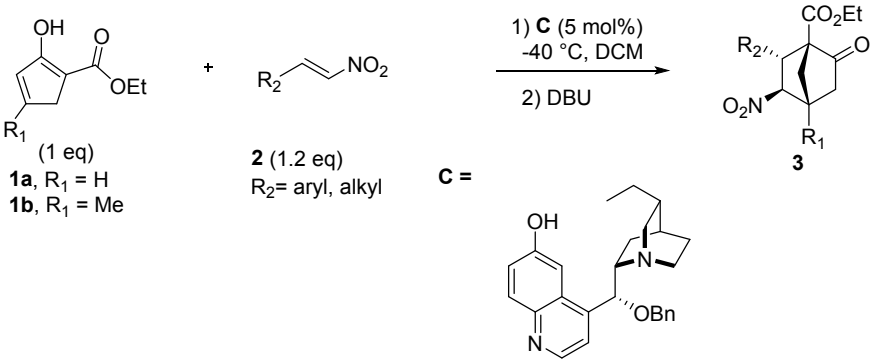
(E)-5-chloro-1-nitropent-1-ene



2v

20% yield as yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.29-7.22 (m, 1H), 7.03 (d, J = 13.6 Hz, 1H), 3.59 (t, J = 6.3 Hz, 2H), 2.48 (q, J = 7.3 Hz, 2H), 2.04-1.99 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 140.6, 140.4, 43.6, 30.3, 25.6; **IR** (thin film): 3106, 2961, 2870, 1651, 1526, 1445, 1356, 959, 731 cm^{-1}; **LRMS** (EI): 114 $(M-Cl)^+$; **HRMS** (EI): calcd for $C_5H_8N_1O_2$ $(M-Cl)^+$: 114.0555, found: 114.0553.

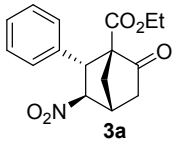
General Procedure for Tandem Michael Addition



To a solution of enone **1** (0.20 mmol, 1.0 equiv) and the nitroolefin **2** (0.24 mmol, 1.2 equiv) in CH_2Cl_2 (1.0 mL) at -40°C was added **C** (4.0 mg, 0.01 mmol). The resulting mixture was stirred at that temperature until enone **1** is consumed as indicated by TLC. Then, DBU (15 μL, 0.5 equiv) was added and the mixture was allowed to stir at that temperature until completion as indicated by TLC. The reaction mixture was loaded

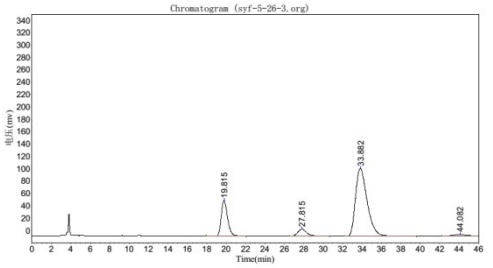
onto a plug of silica gel and eluted with ethyl acetate to remove the catalyst. The eluent was concentrated in *vacuo* to give the crude mixture, which was used for the crude ^{1}H NMR to determine the diastereoselectivity before purified by flash chromatography on silica gel to give **3**.

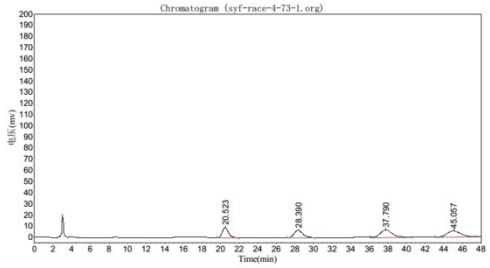
ethyl (1S,2R,3S,4S)-3-nitro-6-oxo-2-phenylbicyclo[2.2.1]heptane-1-carboxylate



3a
mixture

51.0 mg, 84% yield as whiteless oily mixture; *dr* = 3.2/1; (major) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.33-7.28 (m, 3H), 7.16 (d, *J* = 7.2 Hz, 2H), 4.85 (br d, *J* = 4.5 Hz, 1H), 4.49 (br d, *J* = 4.5 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.35 (br d, *J* = 4.3 Hz, 1H), 2.70 (m, 1H), 2.62 (dd, J_1 = 18.4 Hz, J_2 = 5.0 Hz, 1H), 2.39-2.33 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 3H); **LRMS** (ESI): 326 (M+Na) $^+$; **HRMS** (DART): calcd for $C_{16}H_{18}N_1O_5$ (M+H) $^+$: 304.1179, found: 304.1180; (major) 94% ee, (minor) 57% ee; enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-propanol = 90/10, 1.0 mL/min, 214 nm, 25 °C).





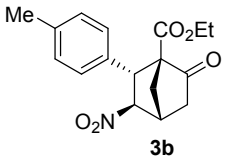
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.815	57919.898	2581302.750	20.4843
2		27.815	11012.028	702427.750	5.5742
3		33.882	109594.898	9055622.000	71.8620
4		44.082	2523.111	262049.203	2.0795
Total			181049.936	12601401.703	100.0000

Results

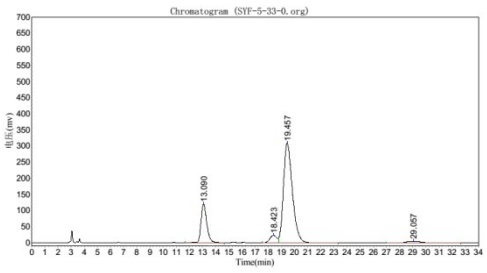
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.523	9155.654	419583.250	20.8387
2		28.390	6568.818	428562.594	21.2847
3		37.790	6596.396	583642.688	28.9868
4		45.057	5496.483	581689.188	28.8898
Total			27817.352	2013477.719	100.0000

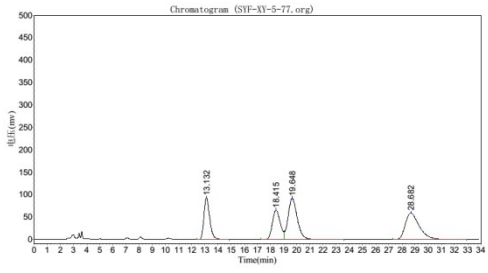
ethyl (1S,2R,3S,4S)-3-nitro-6-oxo-2-(p-tolyl)bicyclo[2.2.1]heptane-1-carboxylate



3b
mixture

50.0 mg, 78% yield as whiteless oily mixture; *dr* = 3.1/1; (major) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.11 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 8.1 Hz, 2H), 4.83 (br d, *J* = 4.5 Hz, 1H), 4.44 (br d, *J* = 4.5 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.33 (br d, *J* = 4.5 Hz, 1H), 2.69 (m, 1H), 2.61 (dd, J_1 = 18.3 Hz, J_2 = 5.0 Hz, 1H), 2.38-2.32 (m, 2H), 2.31 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); **LRMS** (ESI): 340 (M+Na) $^+$; **HRMS** (DART): calcd for $C_{17}H_{20}N_1O_5$ (M+H) $^+$: 318.1336, found: 318.1336; (major) 95% ee, (minor) 66% ee; enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-propanol = 90/10, 1.0 mL/min, 214 nm, 25 °C).





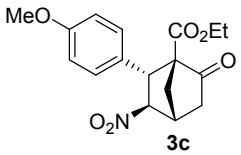
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.090	120152.805	3716240.750	18.9635
2		18.423	22794.195	847130.625	4.3228
3		19.457	308267.188	14670578.000	74.8621
4		29.057	4826.687	362850.000	1.8516
Total			456040.874	19596799.375	100.0000

Results

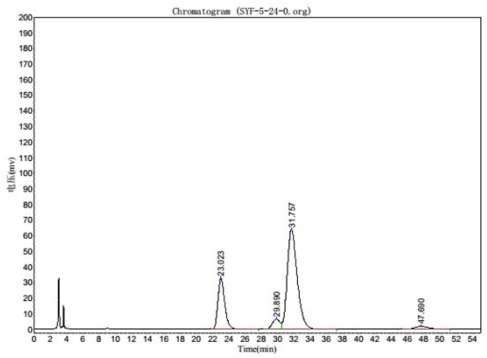
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.132	92674.977	2803947.500	19.7060
2		18.415	64781.398	2704305.250	19.0057
3		19.648	91339.641	4414443.500	31.0244
4		28.682	58829.367	4306231.000	30.2639
Total			307625.383	14228927.250	100.0000

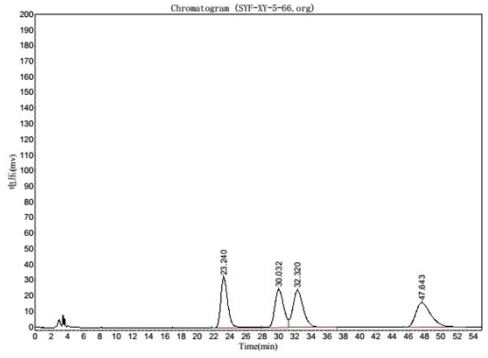
ethyl (1S,2R,3S,4S)-2-(4-methoxyphenyl)-3-nitro-6-oxobicyclo[2.2.1]heptane-1-carboxylate



3c
mixture

49.0 mg, 74% yield as whiteless oily mixture; *dr* = 2.0/1; (major) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.07 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 4.81 (br d, *J* = 4.5 Hz, 1H), 4.43 (br d, *J* = 4.7 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 3H), 3.33 (br d, *J* = 4.3 Hz, 1H), 2.69 (m, 1H), 2.61 (dd, J_1 = 18.6 Hz, J_2 = 5.0 Hz, 1H), 2.36-2.31 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H); **LRMS** (ESI): 356 $(M+Na)^+$; **HRMS** (DART): calcd for $C_{17}H_{20}N_1O_6$ $(M+H)^+$: 334.1285, found: 334.1285; (major) 92% ee, (minor) 66% ee; enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-propanol = 90/10, 1.0 mL/min, 214 nm, 25 °C).





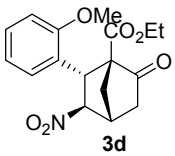
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.023	32489.758	1914059.625	23.6886
2		29.890	6535.704	432118.875	5.3479
3		31.757	63940.281	5501289.500	68.0844
4		47.690	1757.785	232633.016	2.8791
Total			104723.528	8080101.016	100.0000

Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.240	32118.309	1929084.125	24.4544
2		30.032	24247.342	1836604.875	23.2821
3		32.320	23630.512	2108448.750	26.7281
4		47.643	15545.538	2014362.375	25.5354
Total			95541.700	7888500.125	100.0000

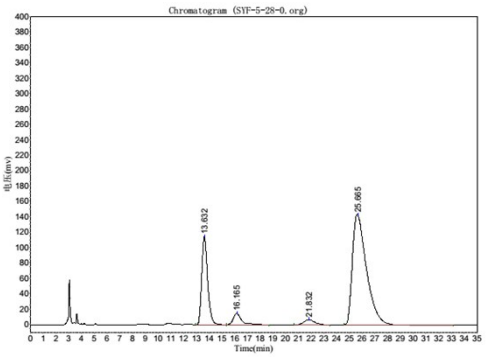
ethyl (1S,2R,3S,4S)-2-(2-methoxyphenyl)-3-nitro-6-oxobicyclo[2.2.1]heptane-1-carboxylate

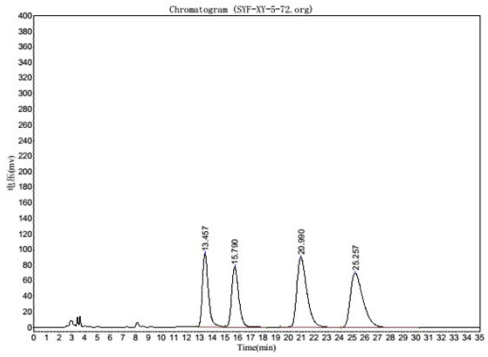


3d
mixture

50.0 mg, 75% yield as whiteless oily mixture; *dr* = 2.6/1; (major) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.22 (d, *J* = 8.5 Hz, 1H), 6.88 (t, *J* = 7.0

Hz, 2H), 6.83 (d, J = 8.3 Hz, 1H), 4.95 (br d, J = 5.0 Hz, 1H), 4.59 (br d, J = 5.0 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.70 (s, 3H), 3.18 (br d, J = 4.8 Hz, 1H), 2.77 (m, 1H), 2.48 (dd, J_1 = 18.3 Hz, J_2 = 5.2 Hz, 1H), 2.28-2.22 (m, 2H), 1.21 (t, J = 7.1 Hz, 3H); **LRMS** (ESI): 316 $(M+Na)^+$; **HRMS** (DART): calcd for $C_{14}H_{16}N_1O_6$ $(M+H)^+$: 294.0972, found: 294.0973; (major) 94% ee, (minor) 73% ee; enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-propanol = 90/10, 1.0 mL/min, 214 nm, 25 °C).





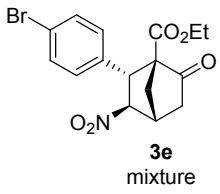
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.632	114680.188	3715609.250	23.6393
2		16.165	14546.220	647852.188	4.1217
3		21.832	6672.500	380041.906	2.4179
4		25.665	143410.000	10974416.000	69.8210
Total			279308.907	15717919.344	100.0000

Results

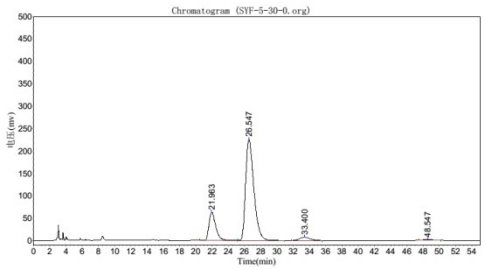
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.457	94470.453	3101393.000	19.4554
2		15.790	77485.828	3038431.500	19.0604
3		20.990	90089.805	4972928.500	31.1957
4		25.257	70083.641	4828319.500	30.2885
Total			332129.727	15941072.500	100.0000

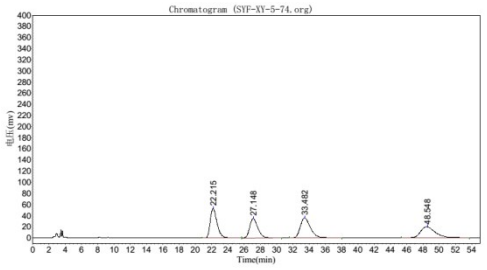
ethyl (1S,2R,3S,4S)-2-(4-bromophenyl)-3-nitro-6-oxobicyclo[2.2.1]heptane-1-carboxylate



3e
mixture

64.0 mg, 84% yield as whiteless oily mixture; *dr* = 3.5/1; (major) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44 (d, J = 8.5 Hz, 2H), 7.04 (d, J = 8.5 Hz, 2H), 4.77 (br d, J = 4.5 Hz, 1H), 4.43 (br d, J = 4.8 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.36 (br d, J = 4.3 Hz, 1H), 2.67 (m, 1H), 2.62 (dd, J_1 = 18.6 Hz, J_2 = 5.0 Hz, 1H), 2.37 (d, J = 11.5 Hz, 1H), 2.32 (dd, J_1 = 18.6 Hz, J_2 = 4.5 Hz, 1H), 1.23 (t, J = 7.1 Hz, 3H); **LRMS** (ESI): 404 $(M+Na)^+$; **HRMS** (DART): calcd for $C_{16}H_{17}N_1O_5Br_1$ $(M+H)^+$: 382.0285, found: 382.0283; (major) 97% ee, (minor) 71% ee; enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-propanol = 90/10, 1.0 mL/min, 214 nm, 25 °C).





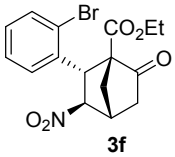
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.963	62834.762	3594762.750	17.9429
2		26.547	225186.625	15710889.000	78.4195
3		33.400	7217.997	603569.438	3.0127
4		48.547	1406.706	125189.102	0.6249
Total			296646.089	20034410.289	100.0000

Results

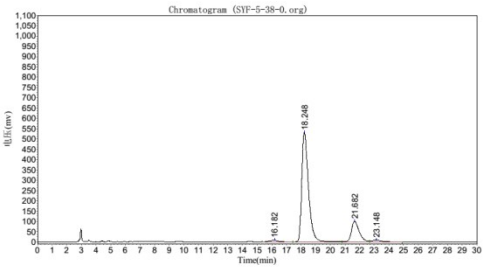
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.215	53406.258	3105871.250	27.9966
2		27.148	34828.930	2422488.250	21.8365
3		33.482	35976.910	3126883.500	28.1860
4		48.548	19472.805	2438503.750	21.9809
Total			143684.902	11093746.750	100.0000

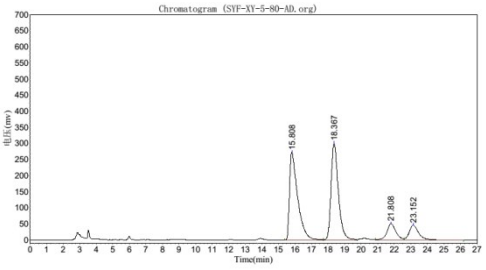
ethyl (1S,2S,3S,4S)-2-(2-bromophenyl)-3-nitro-6-oxobicyclo[2.2.1]heptane-1-carboxylate



3f
mixture

61.0 mg, 80% yield as whiteless oily mixture; *dr* = 4.0/1; (major) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.29-7.25 (m, 1H), 7.15 (t, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 5.09 (br d, *J* = 5.0 Hz, 1H), 4.71 (br d, *J* = 5.3 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.30 (br d, *J* = 4.5 Hz, 1H), 2.80 (m, 1H), 2.66 (dd, J_1 = 18.5 Hz, J_2 = 5.0 Hz, 1H), 2.44-2.34 (m, 2H), 1.14 (t, *J* = 7.1 Hz, 3H); **LRMS** (ESI): 404 $(M+Na)^+$; **HRMS** (DART): calcd for $C_{16}H_{17}N_1O_5Br_1$ $(M+H)^+$: 382.0285, found: 382.0286; (major) 98% ee, (minor) 95% ee; enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-propanol = 90/10, 1.0 mL/min, 214 nm, 25 °C).





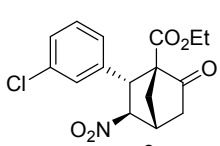
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.182	9121.641	345931.156	1.6208
2		18.248	533764.063	16879820.000	79.0881
3		21.682	100039.828	3707230.750	17.3697
4		23.148	9495.144	410067.969	1.9213
Total			652420.675	21343049.875	100.0000

Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.808	272406.813	9320372.000	41.9474
2		18.367	300121.344	9185688.000	41.3413
3		21.808	50513.379	1900389.375	8.5529
4		23.152	45587.648	1812727.125	8.1584
Total			668629.184	22219176.500	100.0000

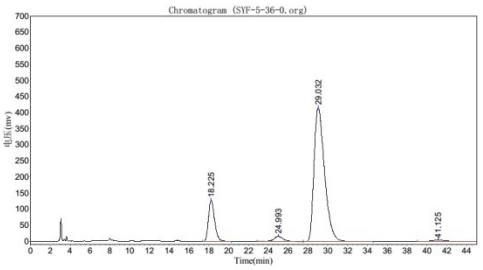
ethyl (1S,2R,3S,4S)-2-(3-chlorophenyl)-3-nitro-6-oxobicyclo[2.2.1]heptane-1-carboxylate

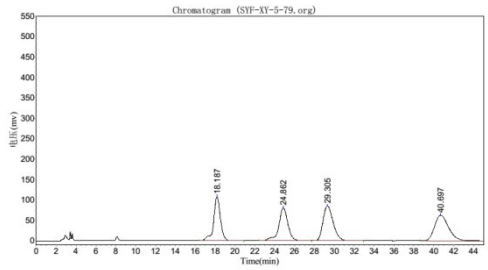


3g
mixture

57.0 mg, 84% yield as whiteless oily mixture; *dr* = 4.7/1; (major) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.29-7.24 (m, 2H), 7.19 (s, 1H),

7.02 (d, J = 7.3 Hz, 1H), 4.80 (br d, J = 4.8 Hz, 1H), 4.45 (br d, J = 4.5 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.37 (br d, J = 4.5 Hz, 1H), 2.67 (m, 1H), 2.63 (dd, J_1 = 18.4 Hz, J_2 = 5.1 Hz, 1H), 2.38-2.32 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H); **LRMS** (ESI): 360 $(M+Na)^+$; **HRMS** (DART): calcd for $C_{16}H_{17}N_1O_5Cl_1$ $(M+H)^+$: 338.0790, found: 338.0790; (major) 98% ee, (minor) 72% ee; enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-propanol = 90/10, 1.0 mL/min, 214 nm, 25 °C).





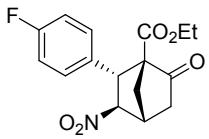
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.225	127588.258	5400825.500	14.4985
2		24.993	15392.483	942582.688	2.5304
3		29.032	416262.063	30579294.000	82.0902
4		41.125	3446.720	328159.688	0.8809
Total			562689.523	37250861.875	100.0000

Results

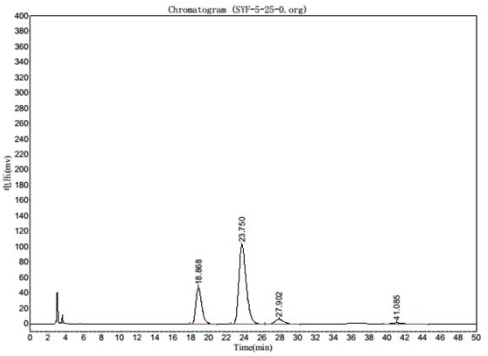
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.187	108147.930	5140532.500	22.8189
2		24.862	80567.656	5178572.000	22.9878
3		29.305	85789.383	6089493.000	27.0314
4		40.697	62853.141	6118876.500	27.1618
Total			337358.109	22527474.000	100.0000

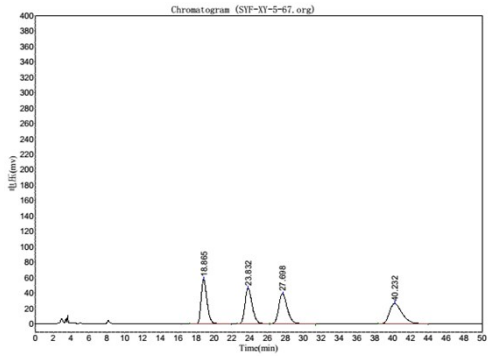
ethyl (1S,2R,3S,4S)-2-(4-fluorophenyl)-3-nitro-6-oxobicyclo[2.2.1]heptane-1-carboxylate



3h
mixture

55.0 mg, 86% yield as whiteless oily mixture; *dr* = 2.8/1; (major) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.14 (dd, J_1 = 8.5 Hz, J_2 = 5.2 Hz, 2H), 7.00 (t, J = 8.5 Hz, 2H), 4.78 (br d, J = 4.5 Hz, 1H), 4.46 (br d, J = 4.5 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.36 (br d, J = 4.2 Hz, 1H), 2.68 (m, 1H), 2.63 (dd, J_1 = 18.9 Hz, J_2 = 5.3 Hz, 1H), 2.40-2.30 (m, 2H), 1.22 (t, J = 7.1 Hz, 3H); **LRMS** (ESI): 344 $(M+Na)^+$; **HRMS** (DART): calcd for $C_{16}H_{17}N_1O_5F_1$ $(M+H)^+$: 322.1085, found: 322.1086; (major) 96% ee, (minor) 69% ee; enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-propanol = 90/10, 1.0 mL/min, 214 nm, 25 °C).





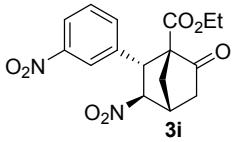
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.868	47563.359	2119458.500	24.8766
2		23.750	102525.063	5873936.500	68.9437
3		27.902	5779.370	391254.125	4.5922
4		41.085	1268.843	135251.688	1.5875
Total			157136.635	8519900.813	100.0000

Results

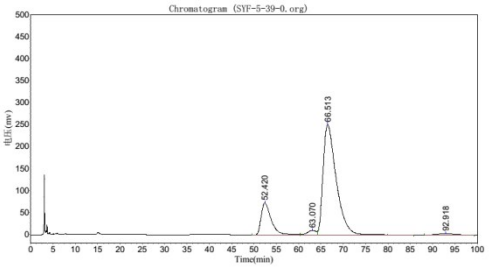
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.865	58380.719	2614985.000	24.8398
2		23.832	46349.578	2613761.500	24.8281
3		27.698	39132.691	2630770.000	24.9897
4		40.232	26567.328	2667903.500	25.3424
Total			170430.316	10527420.000	100.0000

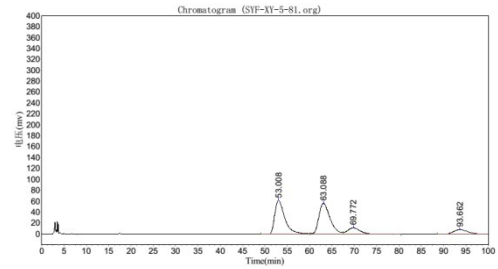
ethyl (1S,2R,3S,4S)-3-nitro-2-(3-nitrophenyl)-6-oxobicyclo[2.2.1]heptane-1-carboxylate



3i
mixture

57.0 mg, 82% yield as whiteless oily mixture; *dr* = 4.2/1; (major) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.17-8.15 (m, 1H), 8.08 (s, 1H), 7.53-7.52 (m, 2H), 4.84 (br d, *J* = 4.8 Hz, 1H), 4.57 (br d, *J* = 4.8 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.45 (br d, *J* = 4.1 Hz, 1H), 2.72-2.67 (m, 2H), 2.44 (m, 1H), 2.62 (dd, J_1 = 14.5 Hz, J_2 = 4.2 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H); **LRMS** (ESI): 371 (M+Na) $^+$; **HRMS** (DART): calcd for $C_{16}H_{17}N_2O_7$ (M+H) $^+$: 349.1030, found: 349.1031; (major) 99% ee, (minor) 87% ee; enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-propanol = 90/10, 1.0 mL/min, 214 nm, 25 °C).





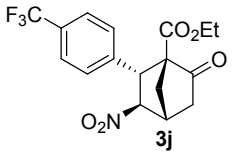
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		52.420	72417.703	11193890.000	17.4453
2		63.070	10200.488	1331449.750	2.0750
3		66.513	250516.828	51042492.000	79.5479
4		92.918	2468.140	597899.438	0.9318
Total			335603.159	64165731.188	100.0000

Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		53.008	62499.746	10051435.000	40.6558
2		63.088	57144.371	10042653.000	40.6202
3		69.772	11957.935	2574926.750	10.4150
4		93.662	8535.871	2054255.625	8.3090
Total			140137.923	24723270.375	100.0000

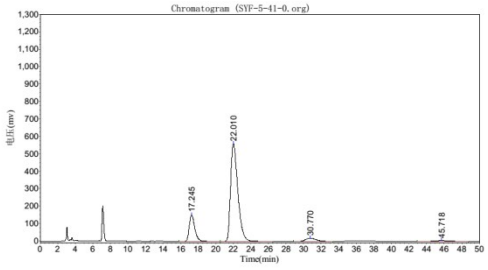
ethyl (1S,2R,3S,4S)-3-nitro-6-oxo-2-(4-(trifluoromethyl)phenyl)bicyclo[2.2.1]heptane-1-carboxylate

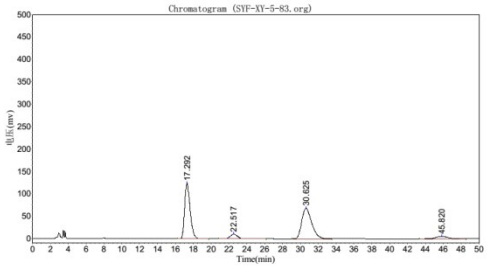


3j
mixture

59.0 mg, 80% yield as whiteless oily mixture; *dr* = 4.2/1; (major) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.30 (d,

J = 8.0 Hz, 2H), 4.81 (br d, *J* = 4.5 Hz, 1H), 4.53 (br d, *J* = 4.6 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.40 (br d, *J* = 4.5 Hz, 1H), 2.69 (m, 1H), 2.66 (dd, J_1 = 18.9 Hz, J_2 = 5.1 Hz, 1H), 2.41-2.32 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H); **LRMS** (ESI): 394 $(M+Na)^+$; **HRMS** (DART): calcd for $C_{17}H_{17}N_1O_5F_3$ $(M+H)^+$: 372.1053, found: 372.1054; (major) 97% ee, (minor) 65% ee; enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-propanol = 90/10, 1.0 mL/min, 214 nm, 25 °C).





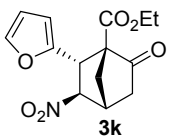
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.245	151322.203	6530857.000	16.1932
2		22.010	559936.813	31980200.000	79.2944
3		30.770	17624.750	1375681.500	3.4110
4		45.718	4064.427	444218.000	1.1014
Total			732948.193	40330956.500	100.0000

Results

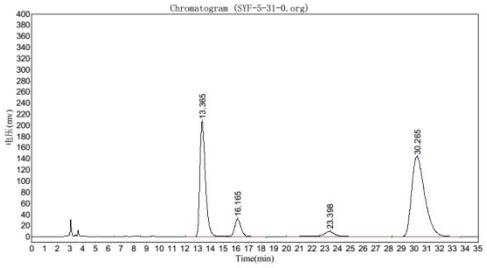
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.292	123946.844	5358558.500	45.0376
2		22.517	10373.171	670557.688	5.6359
3		30.625	68140.789	5351810.000	44.9809
4		45.820	4914.000	517030.969	4.3455
Total			207374.803	11897957.156	100.0000

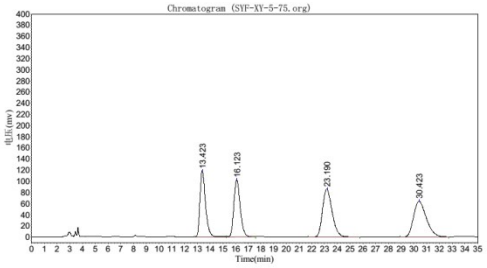
ethyl (1S,2R,3S,4S)-2-(furan-2-yl)-3-nitro-6-oxobicyclo[2.2.1]heptane-1-carboxylate



3k
mixture

43.0 mg, 73% yield as whiteless oily mixture; *dr* = 1.3/1; (major) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30 (br s, 1H), 6.34-6.26 (m, 2H), 5.02 (br d, *J* = 3.8 Hz, 1H), 4.57 (br d, *J* = 4.1 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.37 (br d, *J* = 4.5 Hz, 1H), 2.57-2.52 (m, 1H), 2.55 (dd, J_1 = 18.3 Hz, J_2 = 5.5 Hz, 1H), 2.45-2.25 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); **LRMS** (ESI): 404 $(M+Na)^+$; **HRMS** (DART): calcd for $C_{16}H_{17}N_1O_5Br_1$ $(M+H)^+$: 382.0285, found: 382.0283; (major) 92% ee, (minor) 70% ee; enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-propanol = 90/10, 1.0 mL/min, 214 nm, 25 °C).





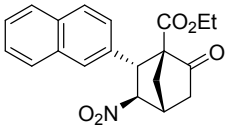
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.365	205997.219	6261158.000	34.2137
2		16.165	31256.191	1109459.125	6.0626
3		23.398	9050.028	652472.500	3.5654
4		30.265	143409.328	10277074.000	56.1584
Total			389712.767	18300163.625	100.0000

Results

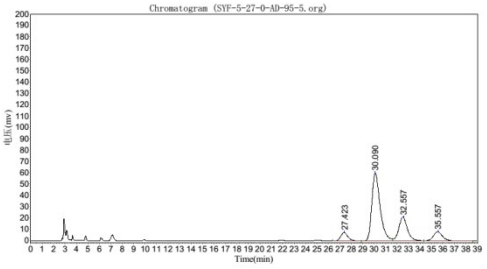
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.423	118645.781	3607238.000	22.3091
2		16.123	102768.578	3565635.750	22.0518
3		23.190	85876.875	4505474.500	27.8643
4		30.423	64100.289	4491009.000	27.7748
Total			371391.523	16169357.250	100.0000

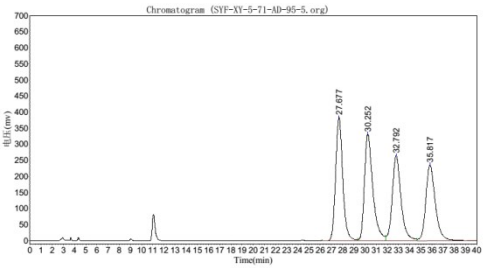
ethyl (1S,2R,3S,4S)-2-(naphthalen-2-yl)-3-nitro-6-oxobicyclo[2.2.1]heptane-1-carboxylate



3l
mixture

65.0 mg, 77% yield as whiteless oily mixture; *dr* = 1.9/1; (major) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.83-7.78 (m, 3H), 7.64 (s, 1H), 7.51-7.46 (m, 2H), 7.25 (d, *J* = 8.2 Hz, 1H), 4.97 (br d, *J* = 4.5 Hz, 1H), 4.66 (br d, *J* = 4.5 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.40 (br d, *J* = 3.8 Hz, 1H), 2.76 (m, 1H), 2.66 (dd, J_1 = 18.5 Hz, J_2 = 5.2 Hz, 1H), 2.50-2.38 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H); **LRMS** (ESI): 376 $(M+Na)^+$; **HRMS** (DART): calcd for $C_{20}H_{20}N_1O_5$ $(M+H)^+$: 354.1336, found: 354.1336; (major) 81% ee, (minor) 35% ee; enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-propanol = 95/5, 1.0 mL/min, 214 nm, 25 °C).





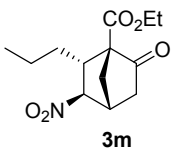
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		27.423	7512.302	342529.969	6.8672
2		30.090	59513.793	3042959.000	61.0067
3		32.557	21025.396	1122709.500	22.5086
4		35.557	8219.698	479709.250	9.6174
Total			96271.189	4987907.719	100.0000

Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		27.677	383787.844	17081098.000	27.1708
2		30.252	331356.313	17360102.000	27.6146
3		32.792	264579.813	14439829.000	22.9693
4		35.817	235687.875	13984634.000	22.2453
Total			1215411.844	62865663.000	100.0000

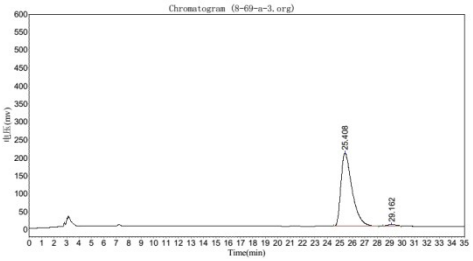
ethyl (1S,2R,3S,4S)-3-nitro-6-oxo-2-propylbicyclo[2.2.1]heptane-1-carboxylate



3m

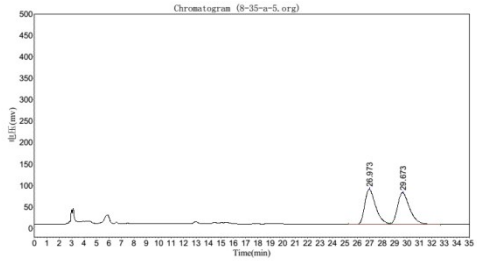
45.3 mg, 83% yield as whiteless oil; *dr* = 18/1; $[\alpha]_D^{27}$ 38.6 (*c* = 2.10, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.31 (br d, *J* = 2.8 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.21 (br d, *J* = 4.8 Hz, 1H), 3.13 (br dt, J_1 = 11.8 Hz, J_2 = 3.0 Hz, 1H), 2.53 (ddd, J_1 = 11.3 Hz, J_2 = 4.2 Hz, J_3 =

2.0 Hz, 1H), 2.46 (dd, J_1 = 18.3 Hz, J_2 = 5.0 Hz, 1H), 2.24 (d, J = 11.3 Hz, 1H), 2.06 (dd, J_1 = 18.3 Hz, J_2 = 4.5 Hz, 1H), 1.94-1.85 (m, 1H), 1.54-1.36 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H), 1.08-0.98 (m, 1H), 0.93 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.6, 168.3, 92.0, 66.1, 61.5, 45.8, 41.7, 40.3, 40.0, 33.5, 21.1, 14.1, 13.6; **IR** (thin film): 2962, 2932, 2874, 1764, 1729, 1549, 1466, 1370, 1272, 1228, 1186, 1070, 1016, 979, 768 cm^{-1}; **LRMS** (ESI): 292 (M+Na)$^+$; **HRMS** (MALDI): calcd for $C_{13}H_{19}N_1O_5Na$ (M+Na)$^+$: 292.1155, found: 292.1160; 98% ee; enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-propanol = 98/2, 1.0 mL/min, 214 nm, 25 °C).



Results

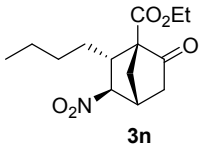
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		25.408	203582.984	12618090.000	98.8650
2		29.162	2978.825	144861.016	1.1350
Total			206561.809	12762951.016	100.0000



Results

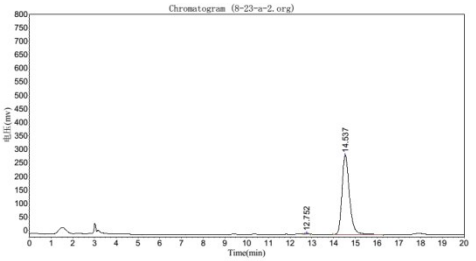
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		26.973	82035.008	5042539.500	50.1091
2		29.673	74115.250	5020581.500	49.8909
Total			156150.258	10063121.000	100.0000

ethyl (1S,2S,3R,4R)-2-butyl-3-nitro-6-oxobicyclo[2.2.1]heptane-1-carboxylate



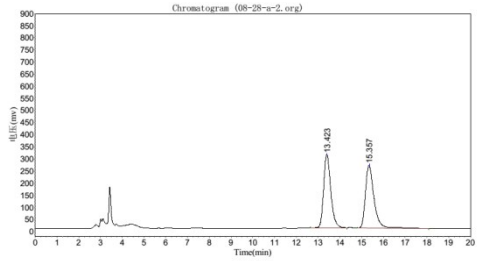
3n

50.7 mg, 90% yield as whiteless oil; *dr* = 17/1; **[α]**$_D^{26}$ 36.3 (*c* = 2.235, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.30 (br d, J = 3.0 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.20 (br d, J = 4.8 Hz, 1H), 3.12 (br dt, J_1 = 9.0 Hz, J_2 = 3.0 Hz, 1H), 2.54 (ddd, J_1 = 11.3 Hz, J_2 = 4.3 Hz, J_3 = 2.0 Hz, 1H), 3.12 (dd, J_1 = 18.3 Hz, J_2 = 5.3 Hz, 1H), 2.24 (d, J = 11.3 Hz, 1H), 2.05 (dd, J_1 = 18.3 Hz, J_2 = 4.5 Hz, 1H), 1.99-1.90 (m, 1H), 1.42-1.26 (m, 4H), 1.28 (t, J = 7.1 Hz, 3H), 1.06-0.96 (m, 1H), 0.89 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.6, 168.3, 92.0, 66.2, 61.5, 46.0, 41.8, 40.3, 40.0, 31.1, 29.9, 22.2, 14.1, 13.8; **IR** (thin film): 2960, 2872, 1762, 1728, 1550, 1468, 1370, 1273, 1227, 1186, 1070, 768 cm^{-1}; **LRMS** (ESI): 306 (M+Na)$^+$; **HRMS** (MALDI): calcd for $C_{14}H_{21}N_1O_5Na$ (M+Na)$^+$: 306.1312, found: 306.1316; 99% ee; enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-propanol = 98/2, 1.0 mL/min, 214 nm, 25 °C).



Results

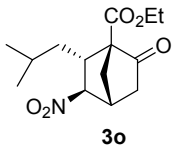
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.752	3581.539	46991.191	0.6662
2		14.537	294796.844	7006686.500	99.3338
Total			298378.383	7053677.691	100.0000



Results

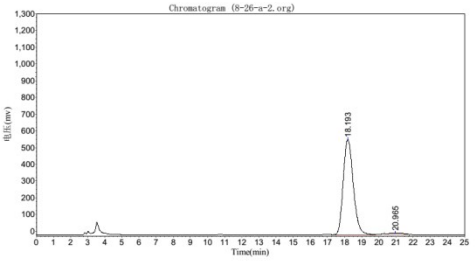
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.423	304989.031	7104016.500	49.8059
2		15.357	260061.094	7159381.000	50.1941
Total			565050.125	14263397.500	100.0000

ethyl (1S,2R,3S,4S)-2-isobutyl-3-nitro-6-oxobicyclo[2.2.1]heptane-1-carboxylate



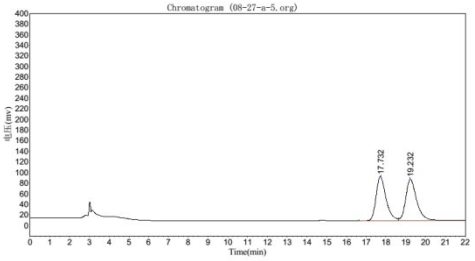
3o

48.7 mg, 86% yield as whiteless oil; *dr* > 20/1; $[\alpha]_D^{26}$ 35.1 (*c* = 2.385, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.31 (br d, *J* = 2.5 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.26 (br d, *J* = 12.1 Hz, 1H), 3.20 (br d, *J* = 4.5 Hz, 1H), 2.54 (ddd, J_1 = 11.3 Hz, J_2 = 4.1 Hz, J_3 = 2.0 Hz, 1H), 3.12 (dd, J_1 = 18.3 Hz, J_2 = 5.3 Hz, 1H), 2.46 (dd, J_1 = 18.3 Hz, J_2 = 5.0 Hz, 1H), 2.24 (d, *J* = 11.3 Hz, 1H), 2.07 (dd, J_1 = 18.3 Hz, J_2 = 4.5 Hz, 1H), 1.73-1.64 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 10.5 Hz, 1H), 0.92 (d, *J* = 5.3 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.7, 168.3, 92.4, 66.2, 43.8, 41.7, 40.6, 40.6, 39.8, 26.4, 23.7, 20.9, 14.1; **IR** (thin film): 2960, 2931, 2872, 1763, 1729, 1551, 1467, 1370, 1325, 1270, 1325, 1270, 1185, 1072, 1015, 768 cm^{-1}; **LRMS** (ESI): 306 $(M+Na)^+$; **HRMS** (MALDI): calcd for $C_{14}H_{21}N_1O_5Na$ $(M+Na)^+$: 306.1312, found: 306.1318; 98% ee; enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-propanol = 99/1, 1.0 mL/min, 214 nm, 25 °C).



Results

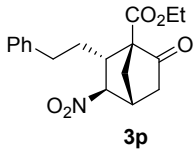
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.193	567990.250	23184314.000	98.8330
2		20.965	4558.042	273749.719	1.1670
Total			572548.292	23458063.719	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.732	83029.461	2898681.000	49.2447
2		19.232	77557.086	2987595.750	50.7553
Total			160586.547	5886276.750	100.0000

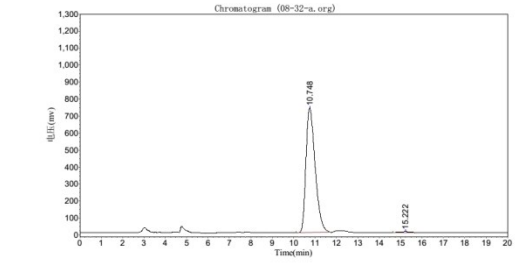
ethyl(1S,2R,3S,4S)-3-nitro-6-oxo-2-phenethylbicyclo[2.2.1]heptane-1-carboxylate



3p

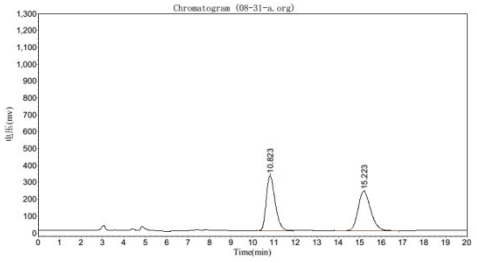
58.0 mg, 88% yield as whiteless oil; *dr* > 20/1; $[\alpha]_D^{27}$ 14.8 (*c* = 2.92, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.28-7.25 (m, 2H), 7.20-7.18 (m, 1H), 7.17-7.13 (m, 2H), 4.33 (br d, *J* = 2.5 Hz, 1H), 4.21 (q,

J = 7.1 Hz, 2H), 3.18 (br d, J = 4.8 Hz, 1H), 3.13 (br dt, J_1 = 11.8 Hz, J_2 = 3.0 Hz, 1H), 2.84-2.77 (m, 1H), 2.74-2.67 (m, 1H), 2.50 (ddd, J_1 = 11.3 Hz, J_2 = 4.3 Hz, J_3 = 2.0 Hz, 1H), 2.44 (dd, J_1 = 18.3 Hz, J_2 = 5.2 Hz, 1H), 2.36-2.27 (m, 1H), 2.22 (d, J = 11.3 Hz, 1H), 2.05 (dd, J_1 = 18.3 Hz, J_2 = 4.3 Hz, 1H), 1.41-1.31 (m, 1H), 1.26 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.6, 168.2, 140.2, 128.6, 128.3, 126.3, 92.0, 66.2, 51.6, 45.5, 41.7, 40.4, 39.9, 33.9, 33.0, 14.1; **IR** (thin film): 3027, 2983, 2926, 1763, 1728, 1549, 1496, 1455, 1370, 1325, 1271, 1187, 1143, 1072, 751, 702 cm^{-1}; **LRMS** (ESI): 354 (M+Na) $^+$; **HRMS** (MALDI): calcd for $C_{18}H_{21}N_1O_5Na$ (M+Na) $^+$: 354.1312, found: 354.1316; 99% ee; enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-propanol = 7/3, 1.0 mL/min, 214 nm, 25 °C).



Results

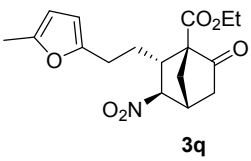
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.748	730533.250	21792006.000	99.4081
2		15.222	3759.440	129762.273	0.5919
Total			734292.690	21921768.273	100.0000



Results

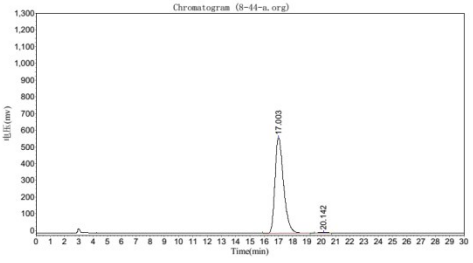
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.823	324912.438	9442068.000	49.6984
2		15.223	233158.469	9556678.000	50.3016
Total			558070.906	18998746.000	100.0000

ethyl (1S,2R,3S,4S)-2-(2-(5-methylfuran-2-yl)ethyl)-3-nitro-6-oxobicyclo [2.2.1] heptane-1-carboxylate



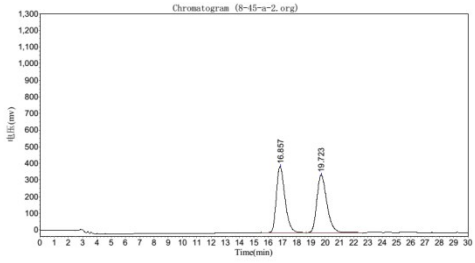
3q

56.0 mg, 84% yield as yellow oil; *dr* > 20/1; **[α]**$_D^{27}$ 24.3 (*c* = 2.74, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.86 (d, J = 2.5 Hz, 1H), 5.82 (d, J = 2.5 Hz, 1H), 4.28 (br d, J = 2.5 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 3.19-3.17 (m, 2H), 2.80-2.67 (m, 2H), 2.50 (ddd, J_1 = 11.6 Hz, J_2 = 4.3 Hz, J_3 = 1.8 Hz, 1H), 2.46 (dd, J_1 = 18.6 Hz, J_2 = 5.3 Hz, 1H), 2.35-2.27 (m, 1H), 2.23 (d, J = 11.6 Hz, 1H), 2.23 (s, 3H), 2.07 (dd, J_1 = 18.3 Hz, J_2 = 4.3 Hz, 1H), 1.40-1.32 (m, 1H), 1.28 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.5, 168.2, 151.8, 150.8, 106.5, 106.0, 91.8, 66.3, 61.6, 45.3, 41.7, 40.3, 39.7, 30.0, 26.4, 14.1, 13.4; **IR** (thin film): 2982, 2924, 1764, 1727, 1551, 1451, 1371, 1324, 1272, 1228, 1186, 1079, 1021, 787 cm^{-1}; **LRMS** (ESI): 358 (M+Na) $^+$; **HRMS** (MALDI): calcd for $C_{17}H_{21}N_1O_6Na$ (M+Na) $^+$: 358.1261, found: 358.1267; 99% ee; enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-propanol = 9/1, 1.0 mL/min, 214 nm, 25 °C).



Results

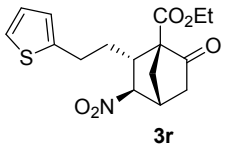
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.003	573002.875	23787278.000	99.5788
2		20.142	2581.329	100619.438	0.4212
Total			575584.204	23887897.438	100.0000



Results

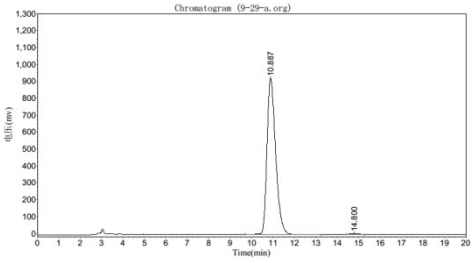
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.857	403145.969	17480550.000	49.8881
2		19.723	350258.156	17558978.000	50.1119
Total			753404.125	35039528.000	100.0000

ethyl (1S,2R,3S,4S)-3-nitro-6-oxo-2-(2-(thiophen-2-yl)ethyl)bicyclo[2.2.1]heptane -1-carboxylate



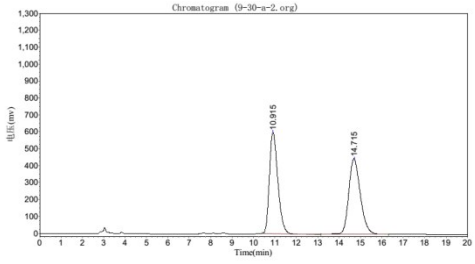
3r

60.4 mg, 90% yield as whiteless oil; *dr* = 20/1; $[\alpha]_D^{24}$ 22.4 (*c* = 2.99, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.13 (dd, J_1 = 5.0 Hz, J_2 = 0.8 Hz, 1H), 6.89 (dd, J_1 = 5.0 Hz, J_2 = 3.5 Hz, 1H), 6.77 (br d, *J* = 2.7 Hz, 1H), 4.33 (br d, *J* = 2.7 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.20 (br d, *J* = 4.5 Hz, 1H), 3.16 (br dt, J_1 = 12.1 Hz, J_2 = 3.0 Hz, 1H), 3.04-2.95 (m, 2H), 2.51 (ddd, J_1 = 11.3 Hz, J_2 = 4.2 Hz, J_3 = 2.0 Hz, 1H), 2.46 (dd, J_1 = 18.3 Hz, J_2 = 5.1 Hz, 1H), 2.42-2.36 (m, 1H), 2.24 (d, *J* = 11.3 Hz, 1H), 2.07 (dd, J_1 = 18.3 Hz, J_2 = 4.3 Hz, 1H), 1.46-1.40 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.5, 168.1, 142.8, 126.9, 125.0, 123.7, 91.7, 66.2, 61.6, 45.3, 41.7, 40.2, 39.9, 33.4, 28.1, 14.1; **IR** (thin film): 2982, 2924, 2855, 1763, 1727, 1549, 1370, 1272, 1187, 1143, 1076, 1034, 850, 702 cm^{-1}; **LRMS** (ESI): 360 $(M+Na)^+$; **HRMS** (MALDI): calcd for $C_{16}H_{19}N_1O_5SNa$ $(M+Na)^+$: 360.0876, found: 360.0872; 99% ee; enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-propanol = 7/3, 1.0 mL/min, 214 nm, 25 °C).



Results

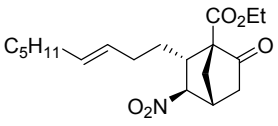
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.887	922891.500	25931952.000	99.5710
2		14.800	4036.170	111723.016	0.4290
Total			926927.670	26043675.016	100.0000



Results

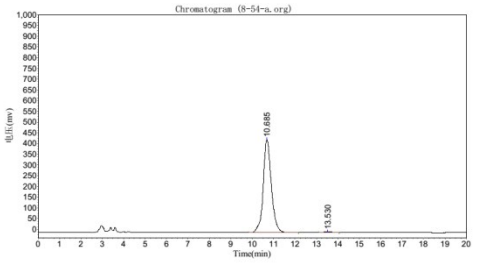
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.915	601636.625	16738582.000	49.7666
2		14.715	446936.688	16895586.000	50.2334
Total			1048573.313	33634168.000	100.0000

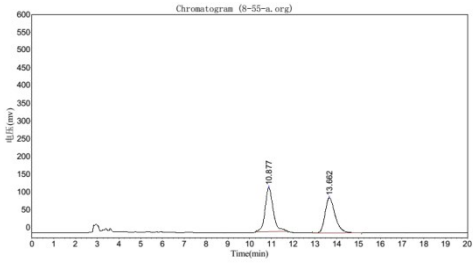
ethyl (1S,2R,3S,4S)-3-nitro-2-((E)-non-3-en-1-yl)-6-oxobicyclo[2.2.1]heptane-1-carboxylate



3s

63.3 mg, 90% yield as whiteless oil; *dr* > 20/1; $[\alpha]_D^{27}$ 21.4 (*c* = 2.945, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.42-5.37 (m, 1H), 5.33-5.28 (m, 1H), 4.33 (br d, *J* = 3.1 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.18-3.14 (m, 2H), 2.50 (ddd, J_1 = 11.3 Hz, J_2 = 4.3 Hz, J_3 = 2.0 Hz, 1H), 2.45 (dd, J_1 = 18.3 Hz, J_2 = 5.2 Hz, 1H), 2.23 (d, *J* = 11.3 Hz, 1H), 2.18-2.12 (m, 1H), 2.10-2.00 (m, 3H), 1.98-1.91 (m, 2H), 1.35-1.21 (m, 6H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.12-1.07 (m, 1H), 0.88 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.6, 168.3, 132.6, 127.6, 92.0, 66.2, 61.5, 45.2, 41.8, 40.5, 39.8, 32.5, 31.4, 31.2, 30.7, 29.0, 22.5, 14.1, 14.0; **IR** (thin film): 2926, 2856, 1728, 1550, 1466, 1370, 1325, 1270, 1185, 973, 767, 736 cm^{-1}; **LRMS** (ESI): 374 $(M+Na)^+$; **HRMS** (MALDI): calcd for $C_{19}H_{29}N_1O_5Na$ $(M+Na)^+$: 374.1938, found: 374.1942; 99% ee; enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-propanol = 9/1, 1.0 mL/min, 214 nm, 25 °C).





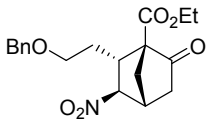
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.685	434213.094	11475779.000	99.2906
2		13.530	2997.040	81988.672	0.7094
Total			437210.134	11557767.672	100.0000

Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.877	123544.461	3152401.000	50.0663
2		13.662	98660.594	3144050.250	49.9337
Total			222205.055	6296451.250	100.0000

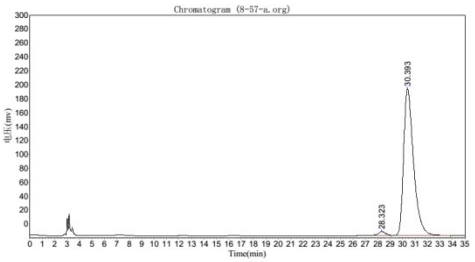
ethyl (1S,2R,3S,4S)-2-(2-(benzyloxy)ethyl)-3-nitro-6-oxobicyclo[2.2.1]heptane-1-carboxylate

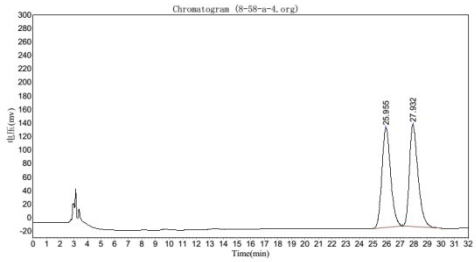


3t

59.8 mg, 83% yield as whiteless oil; *dr* > 20/1; $[\alpha]_D^{27}$ 37.4 (*c* = 2.99, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.35-7.23 (m, 5H), 4.62 (br d, *J* = 2.7 Hz, 1H), 4.42 (d, *J* = 11.8 Hz, 1H), 4.37 (d, *J* = 11.8 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.65-3.60 (m, 1H), 3.54 (td, J_1 = 9.0 Hz, J_2 = 4.0 Hz, 1H), 3.36 (br d, *J* = 11.8 Hz, 1H), 3.14 (br d, *J* = 4.5 Hz, 1H), 2.43 (ddd, J_1 = 11.3 Hz, J_2 = 4.3 Hz, J_3 = 2.0 Hz, 1H), 2.42 (dd, J_1 = 18.3 Hz, J_2 = 5.3 Hz, 1H), 2.27-2.20 (m, 1H), 2.19 (d, *J* = 11.3 Hz, 1H), 2.07 (dd, J_1 = 18.3 Hz, J_2 = 4.5 Hz, 1H), 1.40-1.32 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.9, 168.4, 137.8, 128.4, 128.0, 127.8, 92.2, 73.4, 69.1, 66.3, 61.5, 44.2, 41.9, 40.8, 39.2, 30.7, 14.1; **IR** (thin film): 3031, 2982, 2922, 2864, 2800, 1763, 1728, 1552, 1455, 1371, 1325, 1274, 1184, 1100, 1070, 1016, 737, 700 cm^{-1}; **LRMS** (ESI): 384

(M+Na) $^{+}$; **HRMS** (MALDI): calcd for $C_{19}H_{23}N_1O_6Na$ (M+Na) $^{+}$: 344.1418, found: 384.1421; 98% ee; enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-propanol = 98/2, 1.0 mL/min, 214 nm, 25 °C).





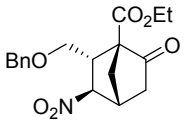
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		28.323	5051.045	198745.484	1.6691
2		30.393	210946.109	11708573.000	98.3309
Total			215997.154	11907318.484	100.0000

Results

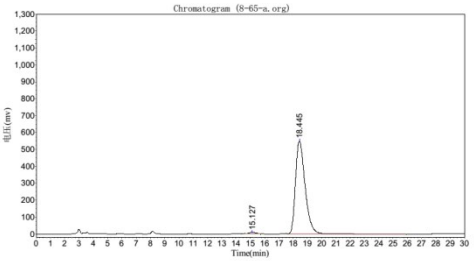
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		25.955	147155.469	6578937.000	49.8888
2		27.932	150674.516	6608256.500	50.1112
Total			297829.984	13187193.500	100.0000

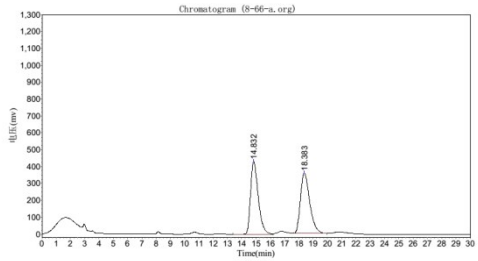
ethyl (1S,2R,3S,4S)-2-((benzyloxy)methyl)-3-nitro-6-oxobicyclo[2.2.1]heptane-1-carboxylate



3u

61.2 mg, 88% yield as whiteless oil; *dr* = 20/1; $[\alpha]_D^{27}$ -0.86 (*c* = 2.65, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.35-7.25 (m, 5H), 4.83 (br d, *J* = 2.7 Hz, 1H), 4.45 (d, *J* = 11.3 Hz, 1H), 4.35 (d, *J* = 11.3 Hz, 1H), 4.25 (m, 2H), 3.90 (dd, J_1 = 10.3 Hz, J_2 = 3.7 Hz, 1H), 3.83 (dd, J_1 = 10.3 Hz, J_2 = 3.0 Hz, 1H), 3.30 (br d, *J* = 3.5 Hz, 1H), 3.21 (br d, *J* = 4.8 Hz, 1H), 2.38 (ddd, J_1 = 11.3 Hz, J_2 = 4.2 Hz, J_3 = 2.0 Hz, 1H), 2.33 (dd, J_1 = 18.1 Hz, J_2 = 5.2 Hz, 1H), 2.20-2.15 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.1, 168.7, 137.4, 128.5, 127.9, 127.9, 87.6, 73.5, 66.7, 64.6, 61.5, 47.5, 40.8, 40.2, 39.1, 14.1; **IR** (thin film): 3031, 2982, 2929, 2870, 1763, 1732, 1549, 1497, 1455, 1370, 1316, 1276, 1186, 1118, 1073, 1035, 740, 700 cm^{-1}; **LRMS** (ESI): 370 (M+Na) $^{+}$; **HRMS** (MALDI): calcd for $C_{18}H_{21}N_1O_6Na$ (M+Na) $^{+}$: 370.1261, found: 370.1267; 98% ee; enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-propanol = 9/1, 1.0 mL/min, 214 nm, 25 °C).





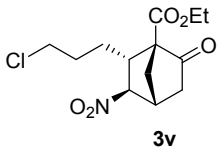
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.127	9128.390	301519.156	1.1652
2		18.445	549607.938	25574566.000	98.8348
Total			558736.327	25876085.156	100.0000

Results

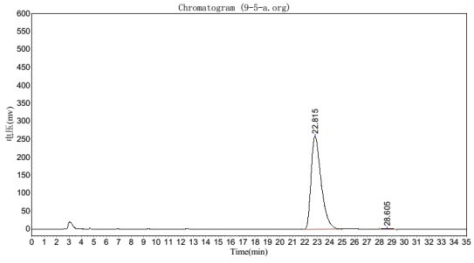
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.832	430005.563	16088310.000	49.7041
2		18.383	358914.250	16279896.000	50.2959
Total			788919.813	32368206.000	100.0000

ethyl (1S,2R,3S,4S)-2-(3-chloropropyl)-3-nitro-6-oxobicyclo[2.2.1]heptane-1-carboxylate



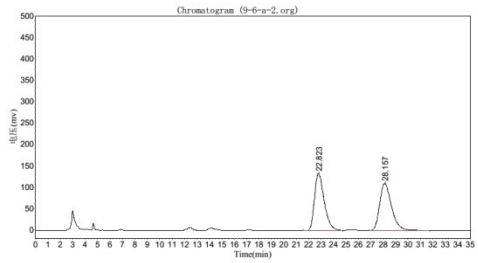
3v

53.7 mg, 89% yield as whiteless oil; *dr* > 20/1; $[\alpha]_D^{27}$ 37.3 (*c* = 2.685, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.31 (br d, *J* = 2.7 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.61-3.56 (m, 1H), 3.53-3.47 (m, 1H), 3.27 (br d, *J* = 4.7 Hz, 1H), 3.09 (br dt, J_1 = 11.6 Hz, J_2 = 3.0 Hz, 1H), 2.49 (dd, J_1 = 18.3 Hz, J_2 = 5.2 Hz, 1H), 2.49 (ddd, J_1 = 11.6 Hz, J_2 = 4.2 Hz, J_3 = 2.0 Hz, 1H), 2.27 (d, *J* = 11.6 Hz, 1H), 2.11-2.05 (m, 2H), 1.96-1.89 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.32-1.24 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.4, 168.2, 91.7, 66.2, 61.7, 45.6, 44.1, 41.6, 40.1, 40.0, 30.8, 28.9, 14.1; **IR** (thin film): 2983, 2934, 2872, 1763, 1728, 1549, 1371, 1318, 1276, 1188, 1142, 1066, 1016, 769 cm^{-1}; **LRMS** (ESI): 326 $(M+Na)^+$; **HRMS** (MALDI): calcd for $C_{13}H_{18}N_1O_5ClNa$ $(M+Na)^+$: 326.0766, found: 326.0774; 99% ee; enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-propanol = 9/1, 1.0 mL/min, 214 nm, 25 °C).



Results

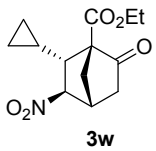
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.815	258892.578	14482225.000	99.5234
2		28.605	1449.546	69352.797	0.4766
Total			260342.124	14551577.797	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.823	132947.969	7288267.000	49.6379
2		28.157	109895.703	7394591.000	50.3621
Total			242843.672	14682858.000	100.0000

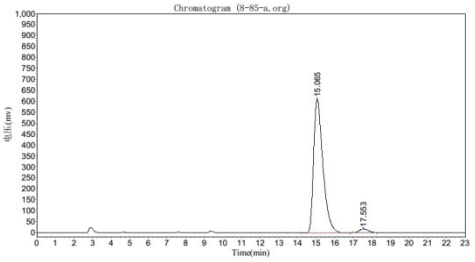
ethyl (1S,2R,3S,4S)-2-cyclopropyl-3-nitro-6-oxobicyclo[2.2.1]heptane-1-carboxylate



3w

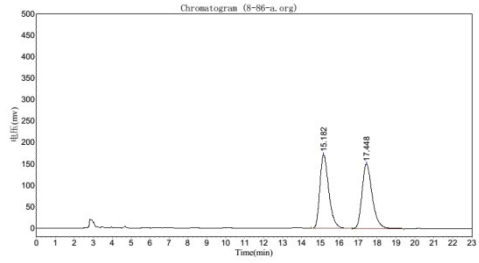
38.5 mg, 73% yield as whiteless oil; *dr* = 10/1; $[\alpha]_D^{27}$ 4.15 (*c* = 1.925, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.40 (br d, *J* = 2.3 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.22 (br d, *J* = 4.5 Hz, 1H), 2.70 (br dd, J_1 = 8.3 Hz, J_2 = 3.8 Hz, 1H), 2.49 (dd, J_1 = 18.3 Hz, J_2 = 5.2 Hz, 1H), 2.52-2.46 (m, 1H), 2.25 (d, *J* = 12.3 Hz, 1H), 2.13 (dd, J_1 = 18.3 Hz, J_2 = 4.2 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.68-0.62 (m, 2H), 0.60-0.52 (m, 2H), 0.37-0.34 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.5, 168.2, 91.4, 66.3, 61.5, 50.5, 41.9, 41.0, 39.7, 14.1, 11.8, 5.8, 2.8 ; **IR** (thin film): 3086, 2984, 2937, 1732, 1549, 1467, 1371, 1325, 1277, 1234, 1192, 976, 763 cm^{-1}; **LRMS** (ESI): 290 $(M+Na)^+$; **HRMS** (MALDI): calcd for

$C_{13}H_{17}N_1O_5Na$ $(M+Na)^+$: 290.0999, found: 290.1001; 95% ee; enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-propanol = 9/1, 1.0 mL/min, 214 nm, 25 °C).



Results

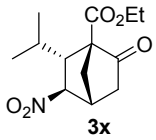
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.065	610267.563	21133782.000	97.4396
2		17.553	16244.895	555322.625	2.5604
Total			626512.457	21689104.625	100.0000



Results

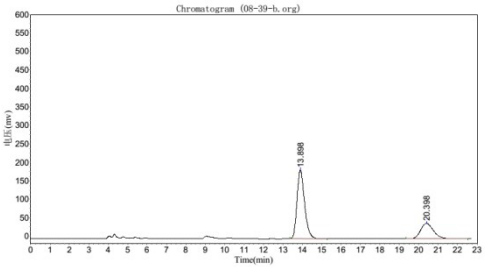
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.182	171919.625	5629288.500	50.0628
2		17.448	150674.484	5615170.000	49.9372
Total			322594.109	11244458.500	100.0000

ethyl (1S,2R,3S,4S)-2-isopropyl-3-nitro-6-oxobicyclo[2.2.1]heptane-1-carboxylate



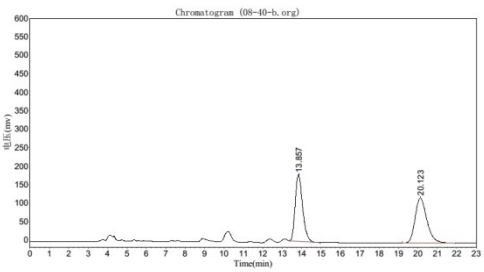
3x

27.5 mg, 69% yield as whiteless oil; *dr* = 10/1; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.39 (br d, J = 2.5 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.19 (br d, J = 4.6 Hz, 1H), 3.16 (dd, J_1 = 11.1 Hz, J_2 = 3.8 Hz, 1H), 2.60 (ddd, J_1 = 11.3 Hz, J_2 = 4.3 Hz, J_3 = 2.0 Hz, 1H), 2.47 (dd, J_1 = 18.5 Hz, J_2 = 5.2 Hz, 1H), 2.17 (d, J = 11.1 Hz, 1H), 2.09 (dd, J_1 = 18.5 Hz, J_2 = 4.5 Hz, 1H), 1.46-1.44 (m, 1H), 1.31 (t, J = 7.1 Hz, 3H), 1.03 (d, J = 6.5 Hz, 3H), 0.93 (d, J = 5.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 204.7, 168.8, 91.7, 64.4, 61.4, 52.7, 42.5, 42.2, 40.5, 31.8, 21.1, 20.8, 14.1; **IR** (thin film): 2967, 2878, 1768, 1728, 1550, 1466, 1372, 1333, 1273, 1192, 1069, 1019, 761 cm^{-1}; **LRMS** (ESI): 292 $(M+Na)^+$; **HRMS** (ESI): calcd for $C_{13}H_{19}N_1O_5Na$ $(M+Na)^+$: 292.1155, found: 292.1154; 46% ee; enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-propanol = 8/2, 0.7 mL/min, 214 nm, 25 °C).



Results

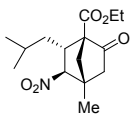
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.898	185199.797	5100325.500	72.7715
2		20.398	41361.875	1908360.500	27.2285
Total			226561.672	7008686.000	100.0000



Results

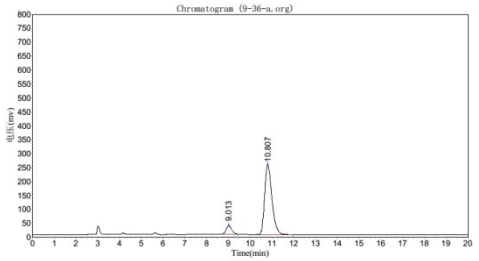
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.857	183910.781	5034179.500	50.0686
2		20.123	120084.516	5020380.500	49.9314
Total			303995.297	10054560.000	100.0000

ethyl (1S,2R,3R,4S)-2-isobutyl-4-methyl-3-nitro-6-oxobicyclo[2.2.1]heptane-1-carboxylate



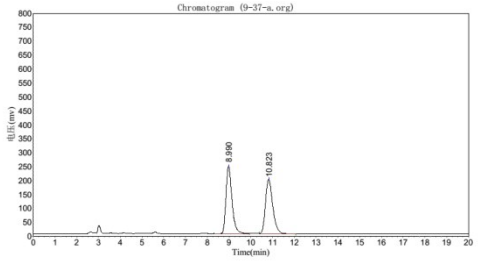
3ob

46.0 mg, 78% yield as whiteless oil; *dr* = 6/1; **[α]**$_D^{24}$ 33.2 (*c* = 2.245, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.28 (br d, *J* = 4.5 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.30 (br dt, J_1 = 12.6 Hz, J_2 = 3.3 Hz, 1H), 2.72 (dd, J_1 = 11.3 Hz, J_2 = 4.5 Hz, 1H), 2.30 (d, *J* = 18.4 Hz, 1H), 2.12-2.04 (m, 2H), 1.68 (ddd, J_1 = 13.3 Hz, J_2 = 10.3 Hz, J_3 = 3.0 Hz, 1H), 1.56-1.51 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.23 (s, 3H), 1.00 (td, J_1 = 13.3 Hz, J_2 = 3.7 Hz, 1H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.7, 168.1, 97.2, 66.6, 61.4, 49.2, 47.0, 45.1, 44.1, 40.0, 26.6, 23.6, 20.9, 16.8, 14.1; **IR** (thin film): 2961, 2936, 2874, 1765, 1730, 1552, 1466, 1369, 1271, 1220, 1181, 1066, 1019, 771 cm^{-1}; **LRMS** (ESI): 320 (M+Na) $^+$; **HRMS** (MALDI): calcd for $C_{15}H_{23}N_1O_5Na$ (M+Na) $^+$: 320.1468, found: 320.1468; 84% ee; enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-propanol = 95/5, 1.0 mL/min, 214 nm, 25 °C).



Results

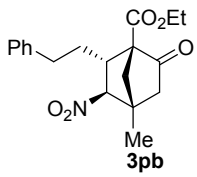
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.013	29863.732	528298.438	8.2814
2		10.807	251952.516	5851060.000	91.7186
Total			281816.248	6379358.438	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.990	241249.000	4696420.500	50.7901
2		10.823	195693.000	4550303.000	49.2099
Total			436942.000	9246723.500	100.0000

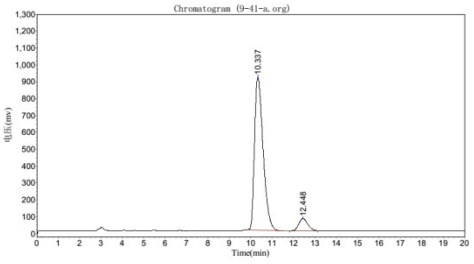
ethyl (1S,2R,3R,4S)-4-methyl-3-nitro-6-oxo-2-phenethylbicyclo[2.2.1]heptane-1-carboxylate



3pb

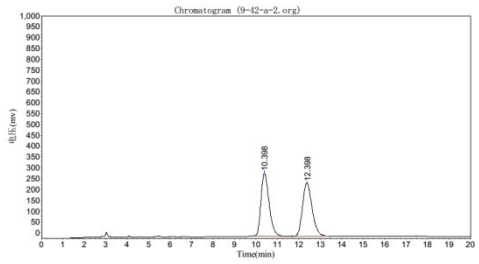
50.0 mg, 73% yield as a white solid; *dr* = 6.5/1; **[α]**$_D^{24}$ 20.7 (*c* = 2.435, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.28-7.24 (m, 2H), 7.20-7.17 (m, 1H), 7.10-7.08 (m, 2H), 4.34 (br d, *J* = 3.3 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.17 (br dt, J_1 = 12.3 Hz, J_2 = 3.5 Hz, 1H), 2.75-2.71 (m, 1H), 2.70 (dd, J_1 = 11.3 Hz, J_2 = 4.5 Hz, 1H), 2.62-2.54 (m, 1H), 2.35-2.29 (m, 1H), 2.30 (d, *J* = 18.3 Hz, 1H), 2.10 (dd, J_1 = 18.3 Hz, J_2 = 4.5 Hz, 1H), 2.04 (dd, J_1 = 11.0 Hz, J_2 = 1.0 Hz, 1H), 1.39-1.31 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.22 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.5, 168.0, 139.8, 128.6, 128.3, 126.4, 96.8, 66.6, 61.5, 49.1, 47.0, 46.4, 44.0, 33.8, 32.4, 16.8, 14.1; **IR** (thin film): 2960, 2928, 1760, 1716, 1551, 1457, 1369, 1313, 1180, 1079, 763 cm^{-1}; **LRMS** (ESI): 368 (M+Na) $^+$; **HRMS** (MALDI): calcd for $C_{19}H_{23}N_1O_5Na$ (M+Na) $^+$: 368.1468, found:

368.1466; 84% ee; enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-propanol = 8/2, 1.0 mL/min, 214 nm, 25 °C).



Results

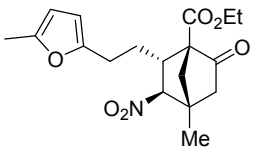
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.337	906921.000	25236970.000	92.2554
2		12.448	71625.695	2118587.750	7.7446
Total			978546.695	27355557.750	100.0000



Results

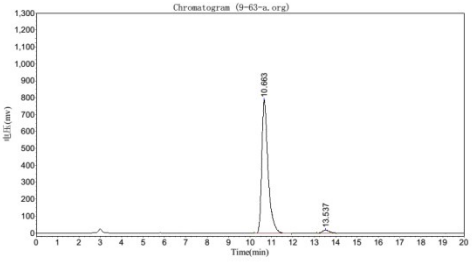
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.398	291728.219	7845304.000	50.1453
2		12.398	246655.281	7799825.500	49.8547
Total			538383.500	15645129.500	100.0000

ethyl (1S,2R,3R,4S)-4-methyl-2-(2-(5-methylfuran-2-yl)ethyl)-3-nitro-6-oxobicyclo [2.2.1] heptane-1-carboxylate



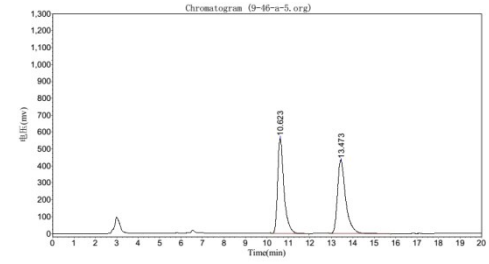
3qb

55.6 mg, 80% yield as whiteless oil; *dr* = 13/1; $[\alpha]_D^{25}$ 34.5 (*c* = 2.615, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.83-5.81 (m, 2H), 4.30 (br d, *J* = 3.5 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.21 (br dt, J_1 = 12.3 Hz, J_2 = 3.5 Hz, 1H), 2.71 (dd, J_1 = 11.0 Hz, J_2 = 4.5 Hz, 1H), 2.67-2.59 (m, 2H), 2.30 (d, *J* = 18.3 Hz, 1H), 2.32-2.26 (m, 1H), 2.22 (s, 3H), 2.10 (dd, J_1 = 18.3 Hz, J_2 = 4.5 Hz, 1H), 2.04 (d, *J* = 11.3 Hz, 1H), 1.35-1.26 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.22 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.6, 168.0, 151.4, 151.0, 106.6, 106.0, 96.6, 66.6, 61.5, 49.1, 46.9, 46.3, 43.9, 29.7, 26.3, 16.8, 14.1, 13.4; **IR** (thin film): 2965, 2924, 1763, 1728, 1553, 1463, 1369, 1320, 1270, 1220, 1181, 1075, 1021, 785 cm^{-1}; **LRMS** (ESI): 372 $(M+Na)^+$; **HRMS** (MALDI): calcd for $C_{18}H_{23}N_1O_6Na$ $(M+Na)^+$: 372.1418, found: 372.1423; 95% ee; enantiomeric excess was determined by HPLC with a Chiralcel PC-2 column (*n*-hexane/*i*-propanol = 9/1, 1.0 mL/min, 214 nm, 25 °C).



Results

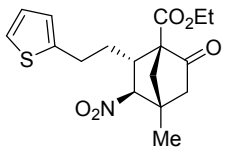
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.663	788303.063	16169880.000	97.6327
2		13.537	17315.244	392072.063	2.3673
Total			805618.307	16561952.063	100.0000



Results

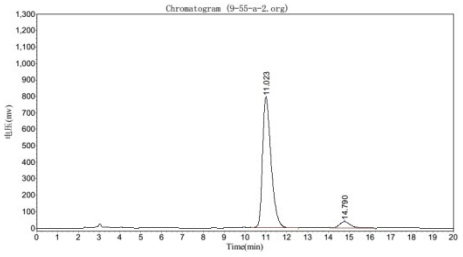
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.623	564303.750	11511607.000	50.0513
2		13.473	433839.750	11488002.000	49.9487
Total			998143.500	22999609.000	100.0000

ethyl (1S,2R,3R,4S)-4-methyl-3-nitro-6-oxo-2-(2-(thiophen-2-yl)ethyl)bicyclo [2.2.1]heptane-1-carboxylate



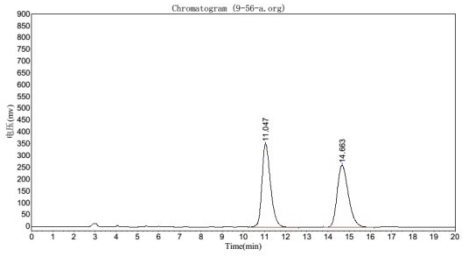
3rb

51.8 mg, 74% yield as a white solid; *dr* = 8/1; $[\alpha]_D^{25}$ 29.0 (*c* = 2.515, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.13 (dd, J_1 = 5.0 Hz, J_2 = 0.8 Hz, 1H), 6.88 (dd, J_1 = 5.0 Hz, J_2 = 3.5 Hz, 1H), 6.72 (br d, *J* = 3.1 Hz, 1H), 4.33 (br d, *J* = 3.2 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.22 (br dt, J_1 = 12.0 Hz, J_2 = 3.5 Hz, 1H), 2.97-2.91 (m, 1H), 2.88-2.82 (m, 1H), 2.71 (dd, J_1 = 11.3 Hz, J_2 = 4.6 Hz, 1H), 2.38-2.33 (m, 1H), 2.32 (d, *J* = 18.3 Hz, 1H), 2.11 (dd, J_1 = 18.3 Hz, J_2 = 4.5 Hz, 1H), 2.05 (dd, J_1 = 11.1 Hz, J_2 = 0.7 Hz, 1H), 1.46-1.39 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.23 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.5, 168.0, 142.3, 126.9, 125.1, 123.8, 96.6, 66.6, 61.6, 49.1, 47.0, 46.2, 44.0, 32.9, 28.1, 16.8, 14.1; **IR** (thin film): 2967, 2932, 1763, 1728, 1552, 1463, 1368, 1320, 1269, 1221, 1180, 1072, 735, 702 cm^{-1}; **LRMS** (ESI): 374 $(M+Na)^+$; **HRMS** (MALDI): calcd for $C_{17}H_{21}N_1O_5SNa$ $(M+Na)^+$: 374.1033, found: 374.1035; 88% ee; enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-propanol = 8/2, 1.0 mL/min, 214 nm, 25 °C).



Results

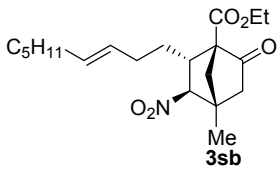
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.023	792471.438	22698942.000	94.1588
2		14.790	37898.398	1408155.500	5.8412
Total			830369.836	24107097.500	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.047	352975.781	9924279.000	50.5828
2		14.663	262936.969	9695593.000	49.4172
Total			615912.750	19619872.000	100.0000

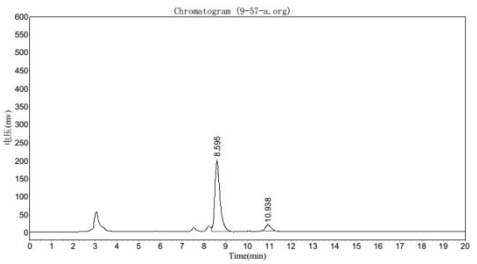
ethyl (1S,2R,3R,4S)-4-methyl-3-nitro-2-((E)-non-3-en-1-yl)-6-oxobicyclo[2.2.1] heptane-1-carboxylate



3sb

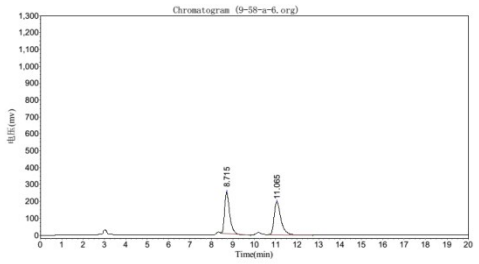
54.3 mg, 74% yield as whiteless oil; *dr* = 6.3/1; $[\alpha]_D^{25}$ 19.5 (*c* = 2.425, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.39-5.34 (m, 1H), 5.27-5.22 (m, 1H), 4.30 (br d, *J* = 3.5 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.21 (br dt, J_1 = 9.3 Hz, J_2 = 3.2 Hz, 1H), 2.73 (dd, J_1 = 11.1 Hz, J_2 = 4.3 Hz, 1H), 2.30 (d, *J* = 18.3 Hz, 1H), 2.12-1.90 (m, 7H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.35-1.23 (m, 6H), 1.23 (s, 3H), 1.12-1.04 (m, 1H), 0.88 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.7, 168.1, 132.8, 127.3, 96.7, 66.5, 61.4, 49.1, 46.9, 46.3, 44.0, 32.5, 31.4, 30.7, 30.7, 29.0, 22.5, 16.8, 14.1, 14.0; **IR** (thin

film): 2926, 2856, 1763, 1733, 1553, 1464, 1369, 1313, 1271, 1071, 972, 740 cm^{-1}; **LRMS** (ESI): 388 $(M+Na)^+$; **HRMS** (MALDI): calcd for $C_{20}H_{31}N_1O_5Na$ $(M+Na)^+$: 388.2094, found: 388.2095; 83% ee; enantiomeric excess was determined by HPLC with a Chiralcel PC-2 column (*n*-hexane/*i*-propanol = 95/5, 1.0 mL/min, 214 nm, 25 °C).



Results

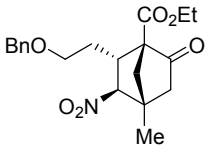
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.595	194510.719	3230816.000	91.3819
2		10.938	16652.969	304692.375	8.6181
Total			211163.688	3535508.375	100.0000



Results

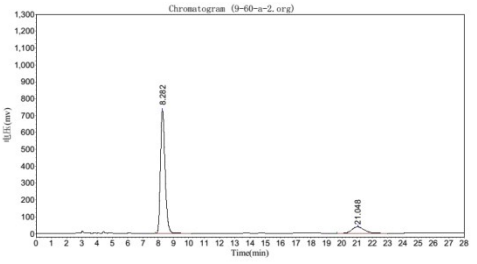
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.715	254643.469	4368531.000	50.1196
2		11.065	197016.859	4347677.000	49.8804
Total			451660.328	8716208.000	100.0000

ethyl (1S,2R,3R,4S)-2-(2-(benzyloxy)ethyl)-4-methyl-3-nitro-6-oxobicyclo [2.2.1] heptane-1-carboxylate



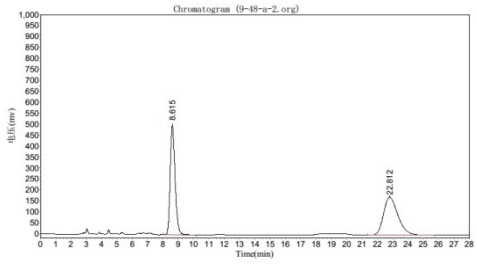
3tb

57.3 mg, 76% yield as whiteless oil; *dr* = 8/1; $[\alpha]_D^{25}$ 30.1 (*c* = 2.865, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36-7.24 (m, 5H), 4.51 (br d, *J* = 3.3 Hz, 1H), 4.41 (d, *J* = 11.8 Hz, 1H), 4.35 (d, *J* = 11.8 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.57-3.52 (m, 1H), 3.43 (td, J_1 = 8.1 Hz, J_2 = 4.0 Hz, 1H), 3.37 (ddd, J_1 = 11.8 Hz, J_2 = 3.5 Hz, J_3 = 2.8 Hz, 1H), 2.62 (dd, J_1 = 11.0 Hz, J_2 = 4.5 Hz, 1H), 2.27 (d, *J* = 18.3 Hz, 1H), 2.19 (m, 1H), 2.08 (dd, J_1 = 18.3 Hz, J_2 = 4.5 Hz, 1H), 2.02 (br d, *J* = 11.0 Hz, 1H), 1.40-1.31 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.21 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 206.0, 168.2, 137.7, 128.4, 128.1, 127.8, 96.9, 73.4, 68.9, 66.6, 61.5, 49.2, 46.8, 45.7, 43.6, 30.6, 17.0, 14.1; **IR** (thin film): 2964, 2918, 2860, 1761, 1728, 1552, 1456, 1369, 1323, 1266, 1180, 1096, 1070, 742 cm^{-1}; **LRMS** (ESI): 398 $(M+Na)^+$; **HRMS** (MALDI): calcd for $C_{20}H_{25}N_1O_6Na$ $(M+Na)^+$: 398.1574, found: 398.1578; 75% ee; enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (*n*-hexane/*i*-propanol = 7/3, 1.0 mL/min, 214 nm, 25 °C).



Results

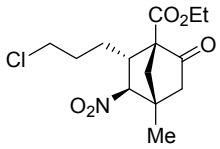
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.282	732653.500	15381043.000	87.6531
2		21.048	38010.223	2166596.500	12.3469
Total			770663.723	17547639.500	100.0000



Results

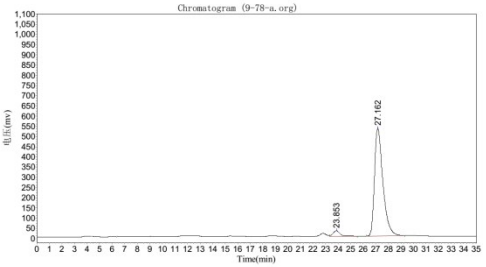
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.615	498831.750	11093012.000	49.6696
2		22.812	172650.828	11240610.000	50.3304
Total			671482.578	22333622.000	100.0000

ethyl (1S,2R,3R,4S)-2-(3-chloropropyl)-4-methyl-3-nitro-6-oxobicyclo[2.2.1] heptane-1-carboxylate



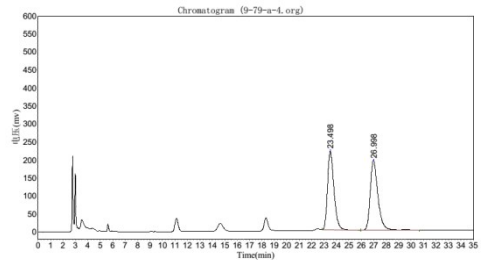
3vb

50.3 mg, 79% yield as whiteless oil; *dr* > 20/1; $[\alpha]_D^{21}$ 254.1 (*c* = 2.515, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.31 (br d, *J* = 3.6 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.54-3.50 (m, 1H), 3.48-3.44 (m, 1H), 3.18 (br dt, J_1 = 12.1 Hz, J_2 = 3.8 Hz, 1H), 2.74 (dd, J_1 = 11.0 Hz, J_2 = 4.5 Hz, 1H), 2.33 (d, *J* = 18.3 Hz, 1H), 2.12 (dd, J_1 = 18.3 Hz, J_2 = 4.5 Hz, 1H), 2.08 (br d, *J* = 11.0 Hz, 1H), 2.08-2.03 (m, 1H), 1.83-1.75 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.25 (s, 3H), 1.25-1.19 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 205.3, 168.0, 96.7, 66.5, 61.6, 49.2, 47.0, 46.7, 44.2, 43.9, 30.8, 28.4, 16.7, 14.1; **IR** (thin film): 2965, 2935, 1762, 1728, 1552, 1463, 1369, 1315, 1272, 1222, 1182, 769 cm^{-1}; **LRMS** (ESI): 340 $(M+Na)^+$; **HRMS** (MALDI): calcd for $C_{14}H_{20}N_1O_5ClNa$ $(M+Na)^+$: 340.0922, found: 340.0921; 92% ee; enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (*n*-hexane/*i*-propanol = 98/2, 1.0 mL/min, 214 nm, 25 °C).



Results

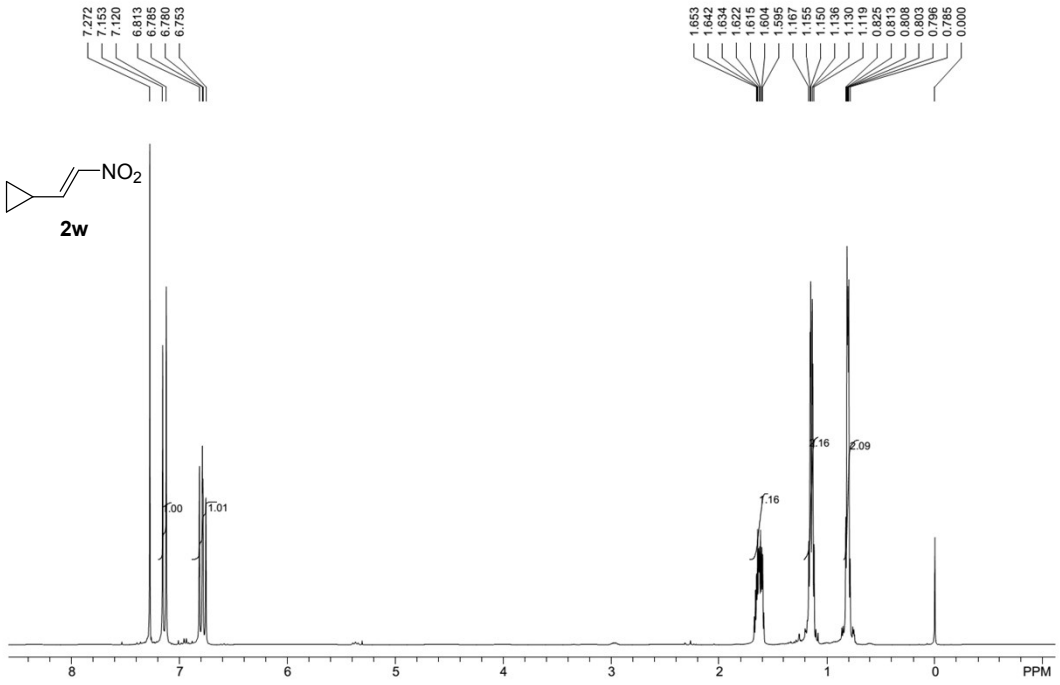
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.853	27242.900	1074370.625	4.2108
2		27.162	527020.750	24440236.000	95.7892
Total			554263.650	25514606.625	100.0000

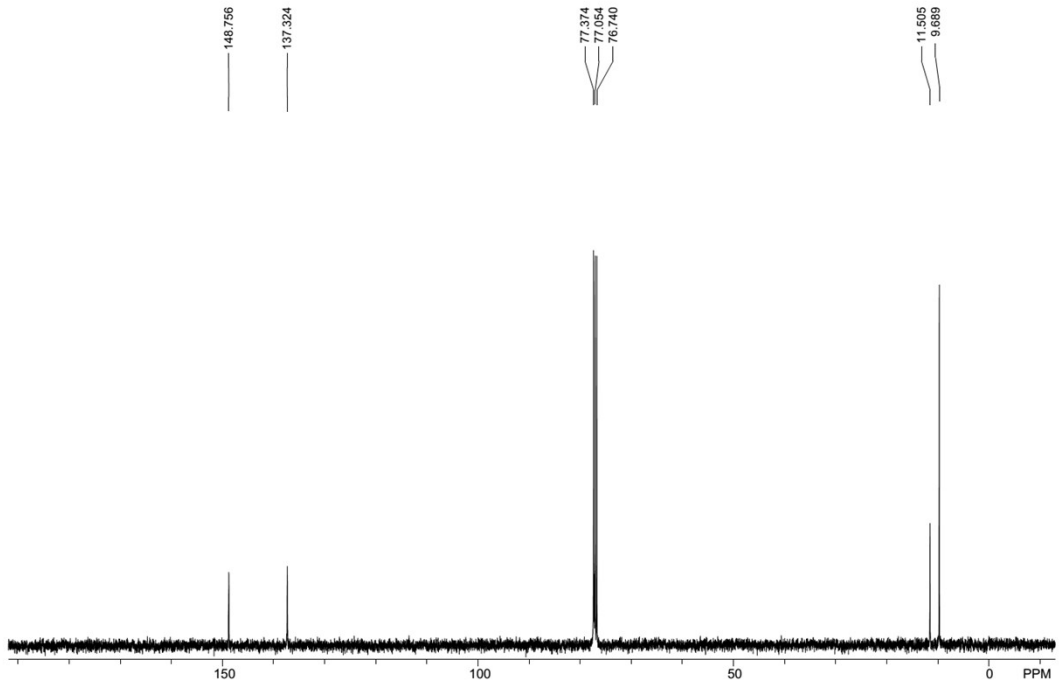


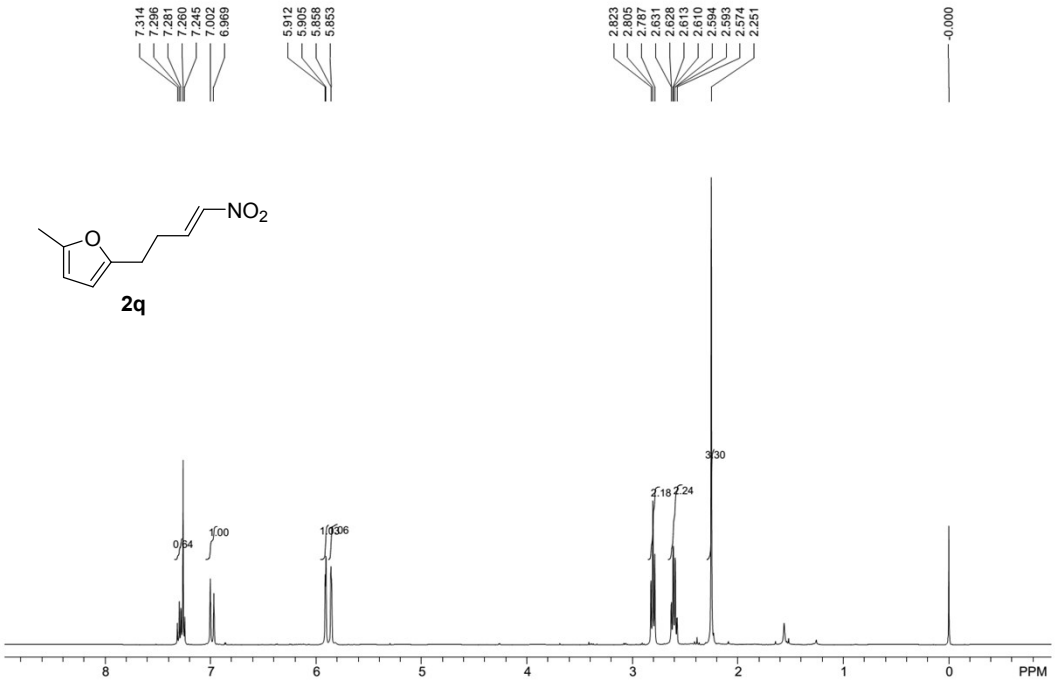
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.498	220209.344	8176009.000	50.7946
2		26.998	193779.297	7920215.500	49.2054
Total			413988.641	16096224.500	100.0000

Spectral Data



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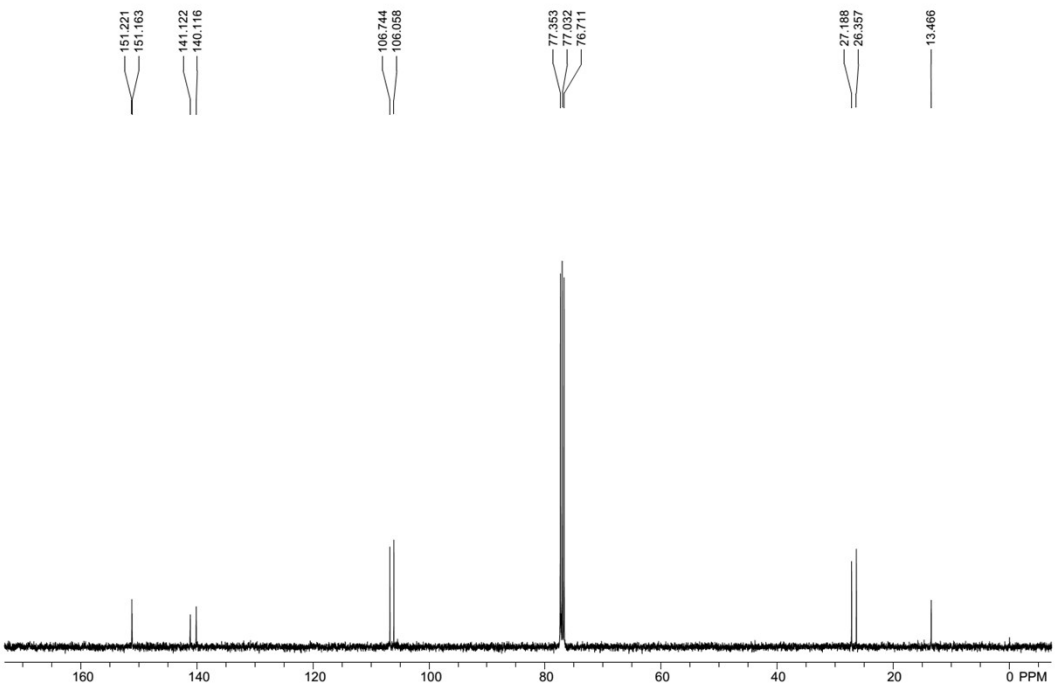
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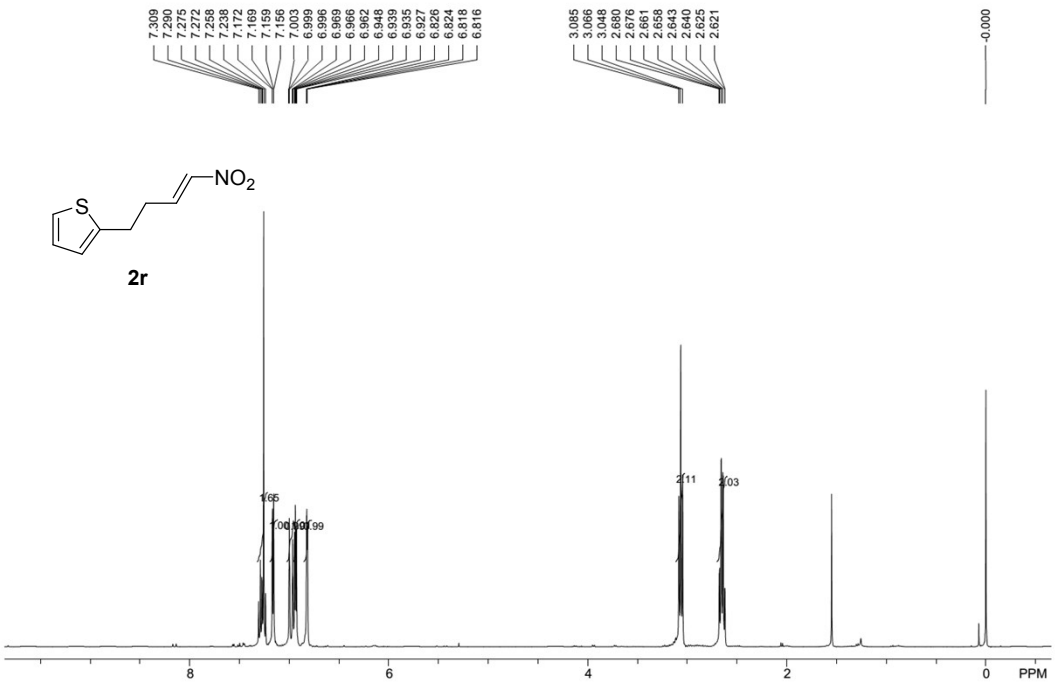
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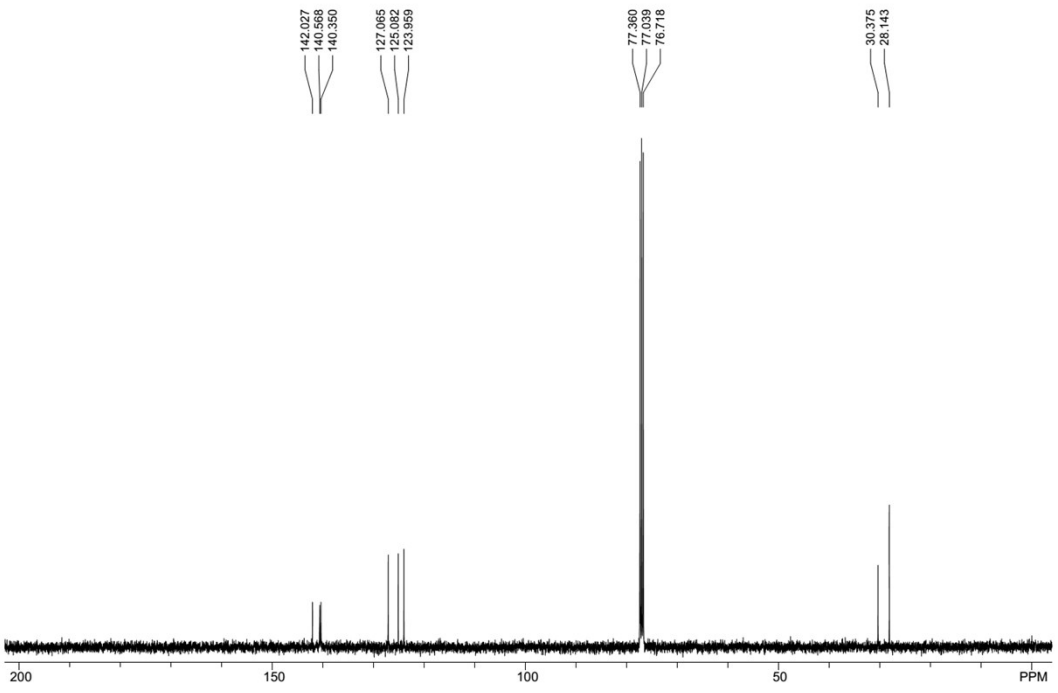
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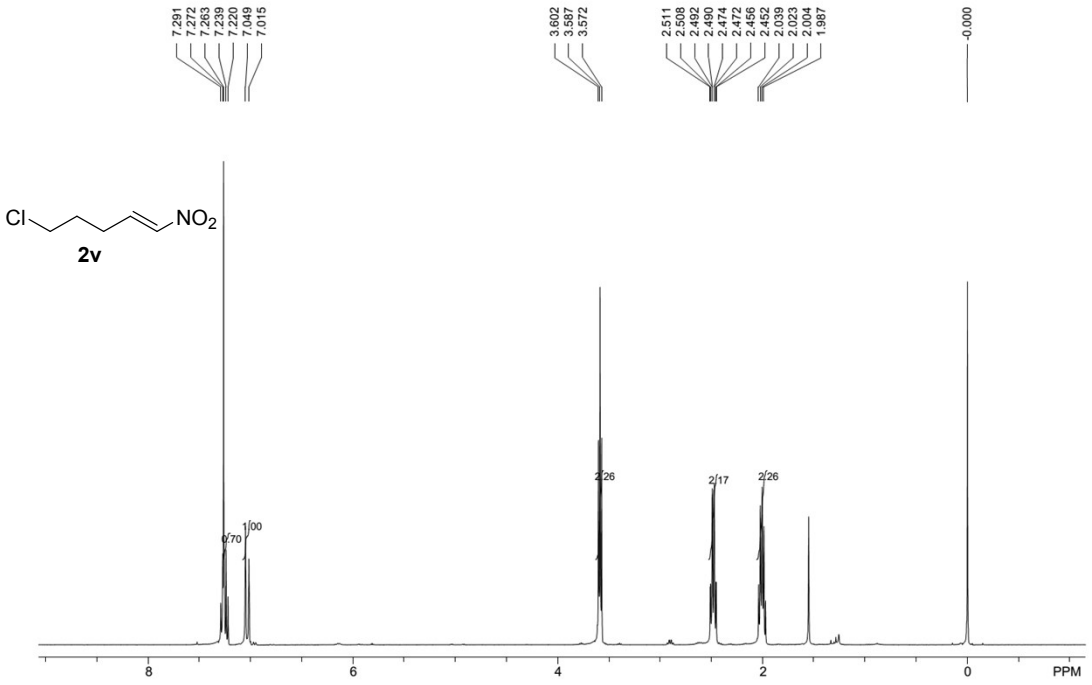
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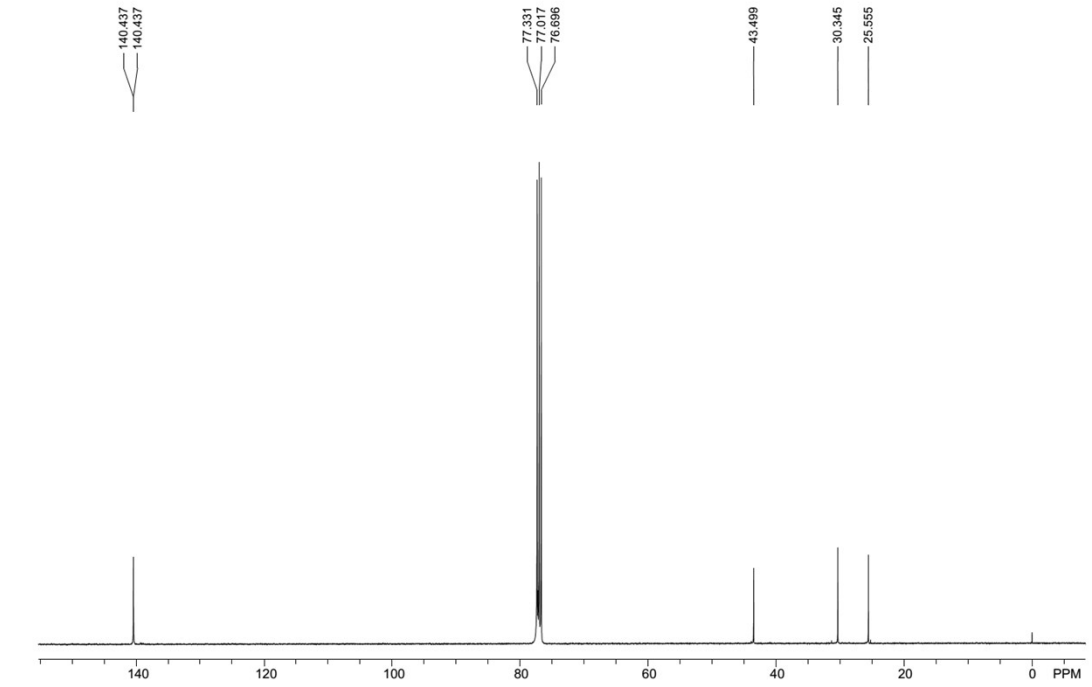
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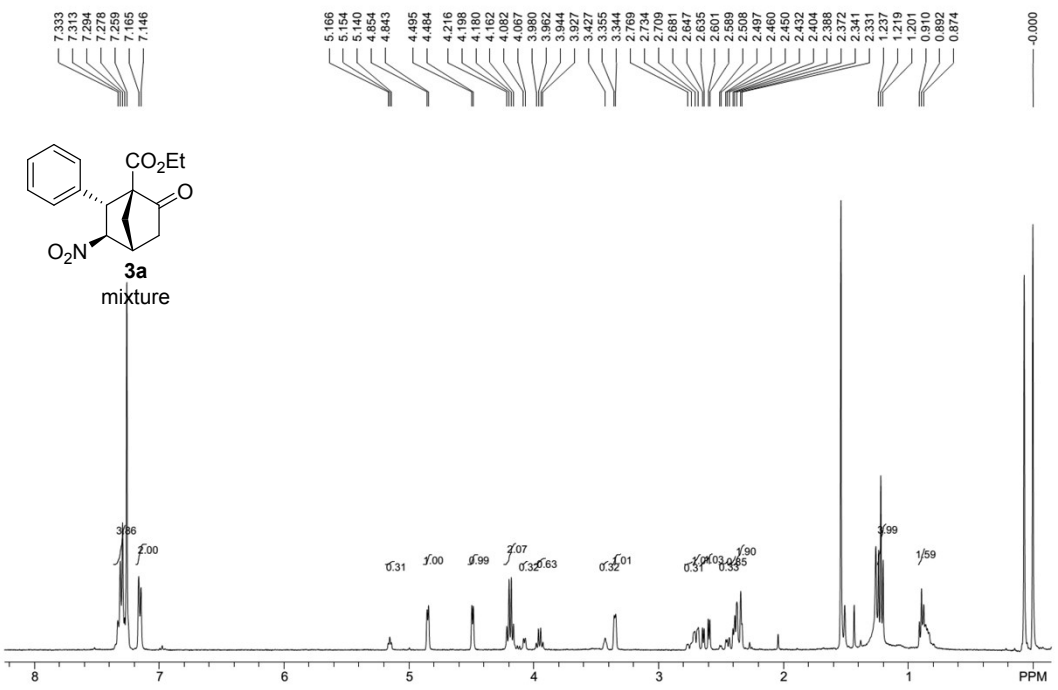
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O2N
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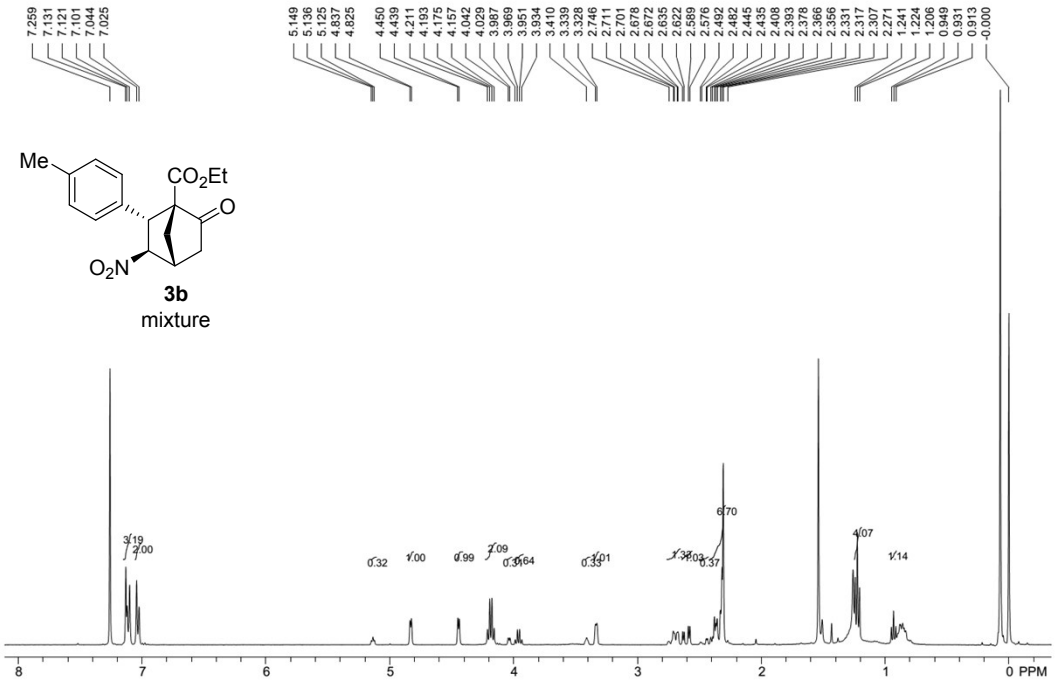
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CO2Et
O
O2N
3b
mixture
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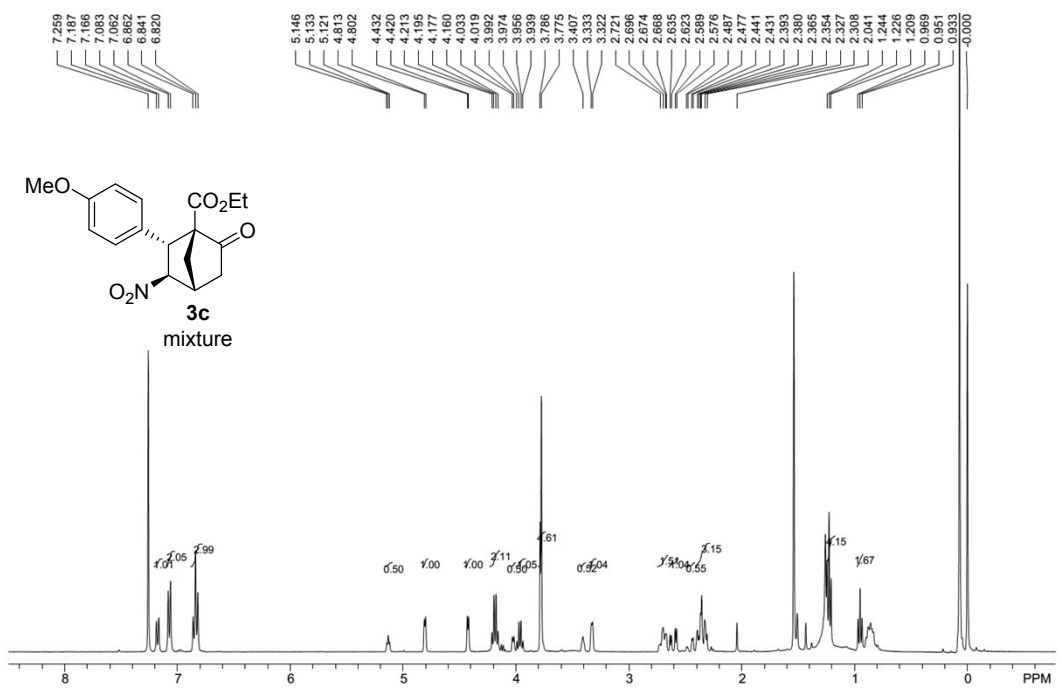
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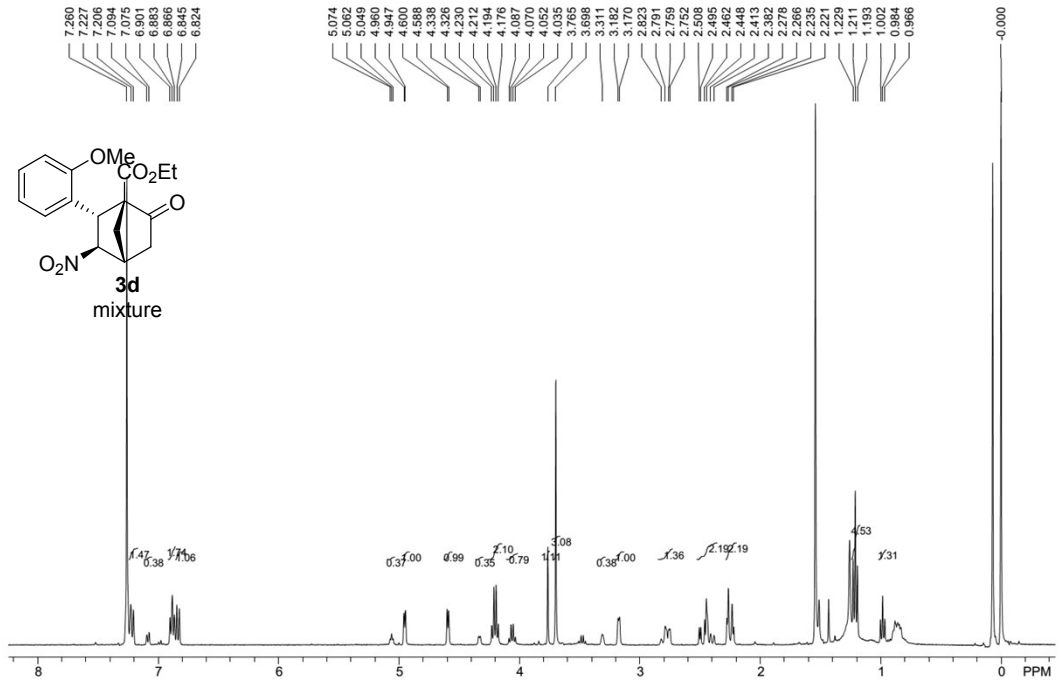
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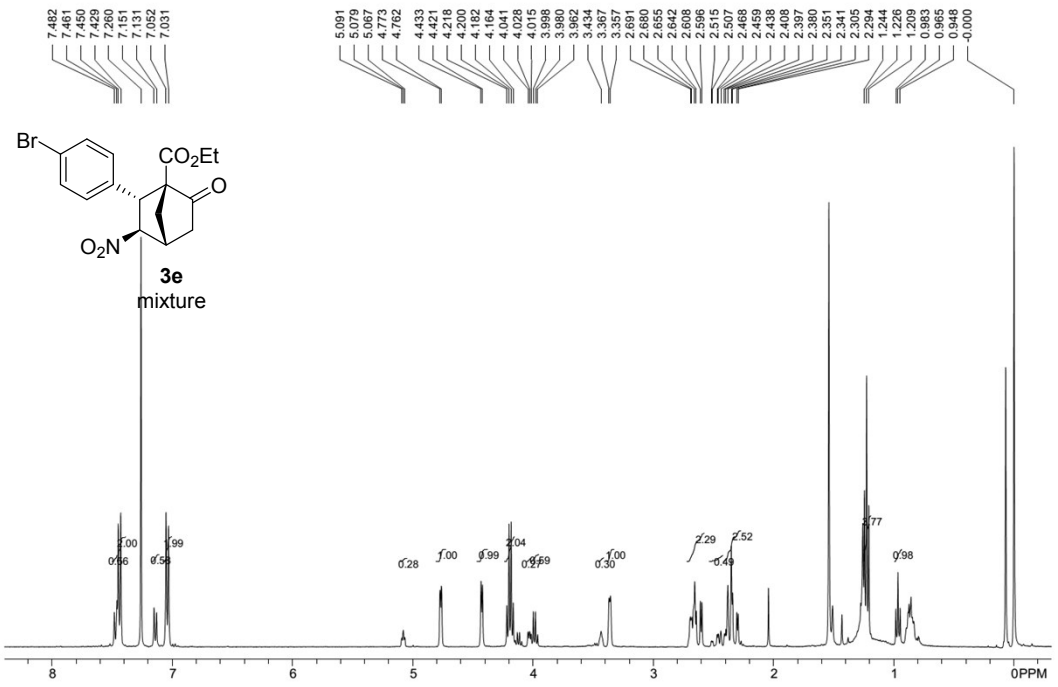
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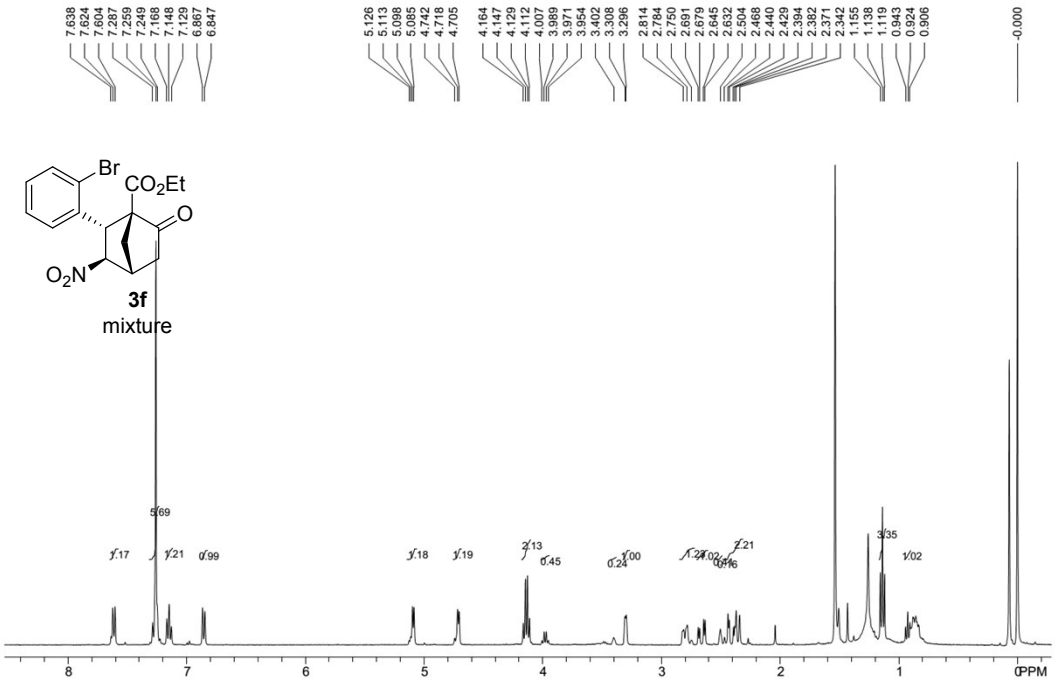
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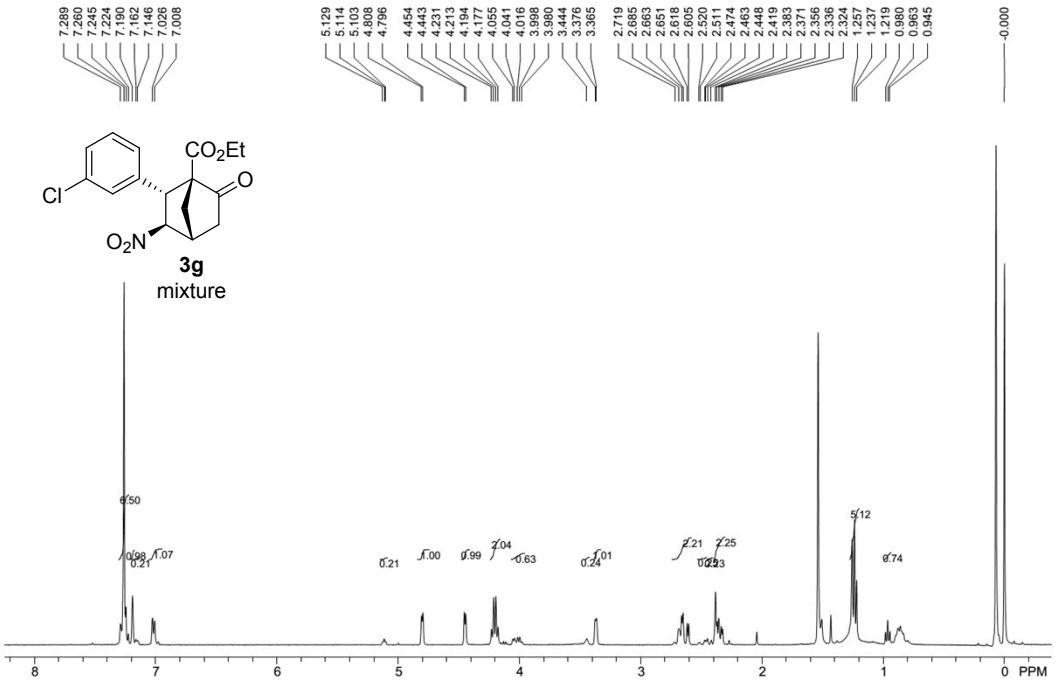
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O
Cl
O2N
3g
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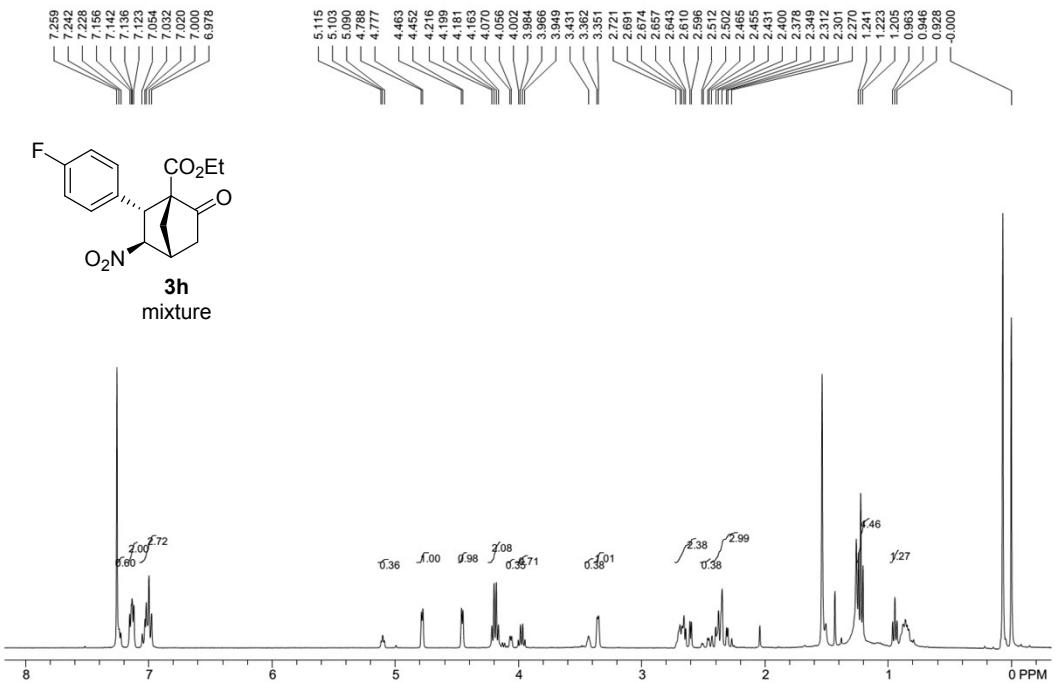
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O
F
O2N
3h
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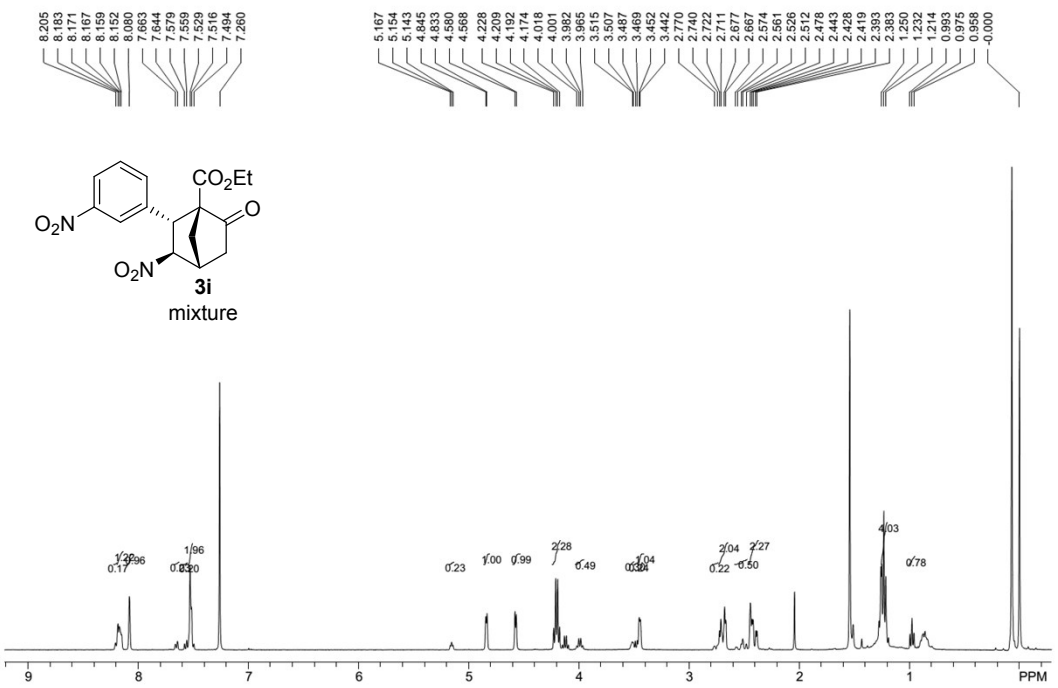
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O
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O2N
3i
mixture
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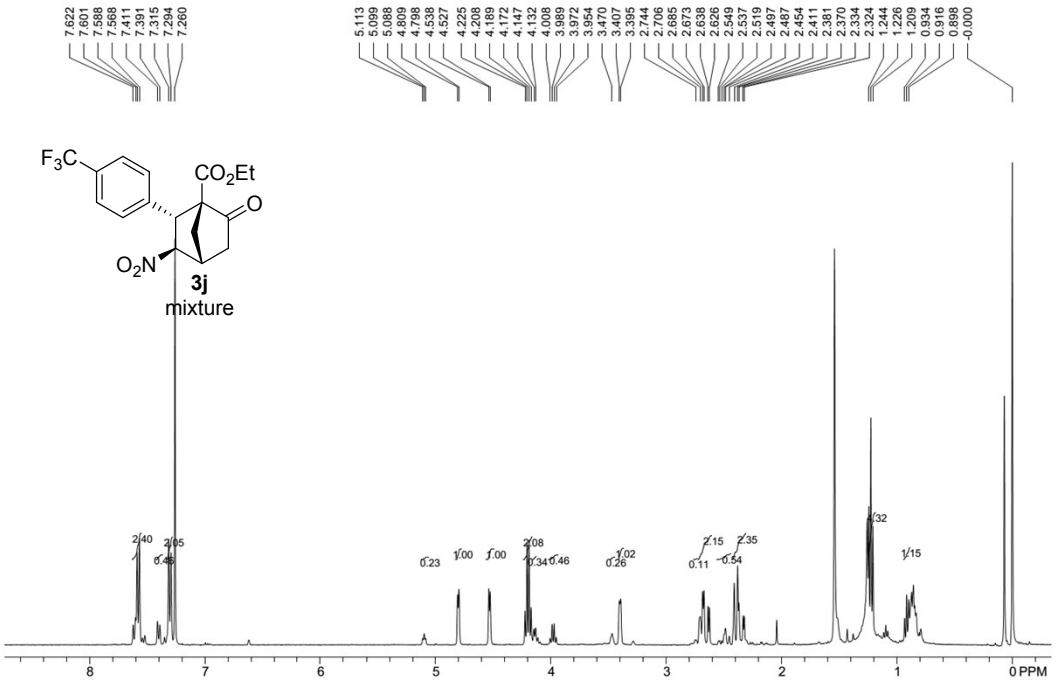
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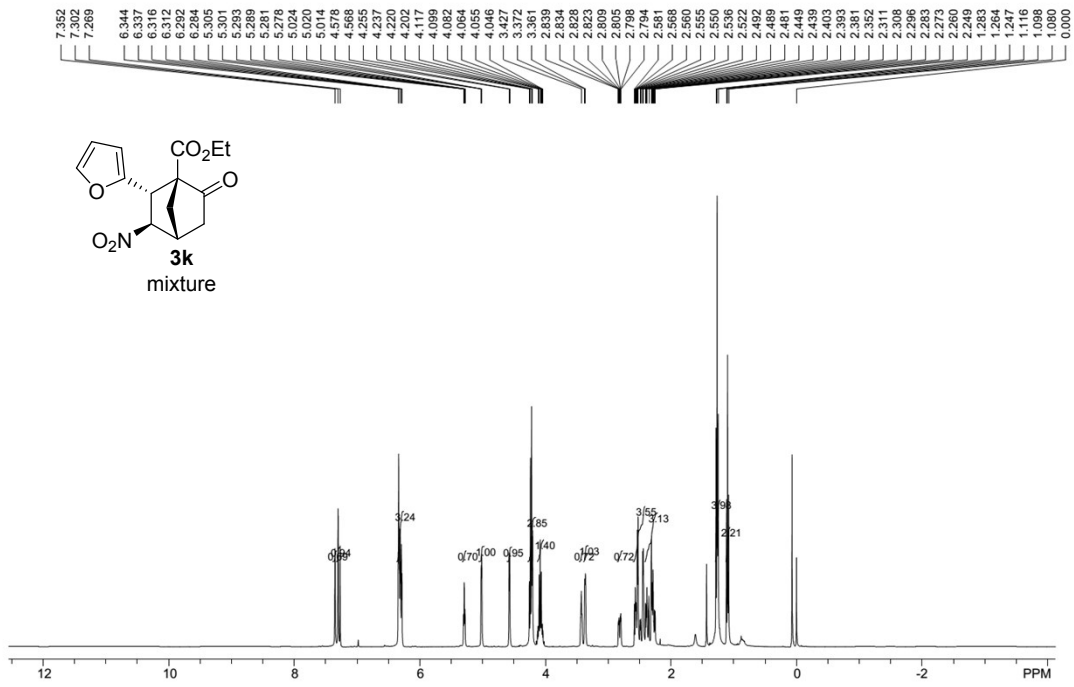
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O
O2N
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mixture
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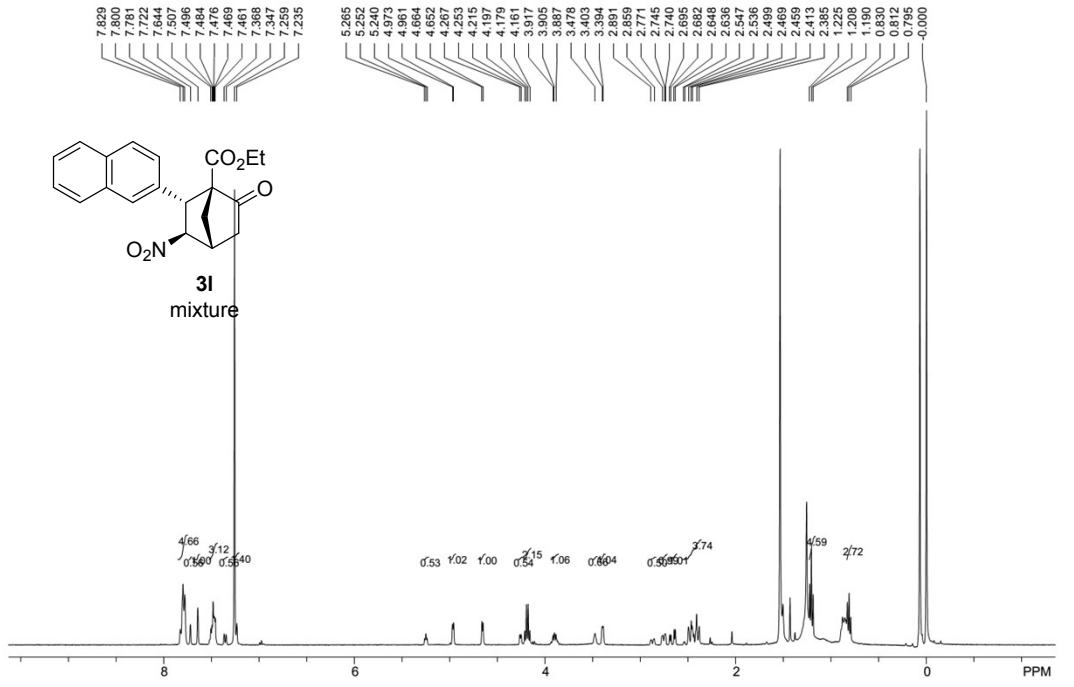
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O2N
3l
mixture
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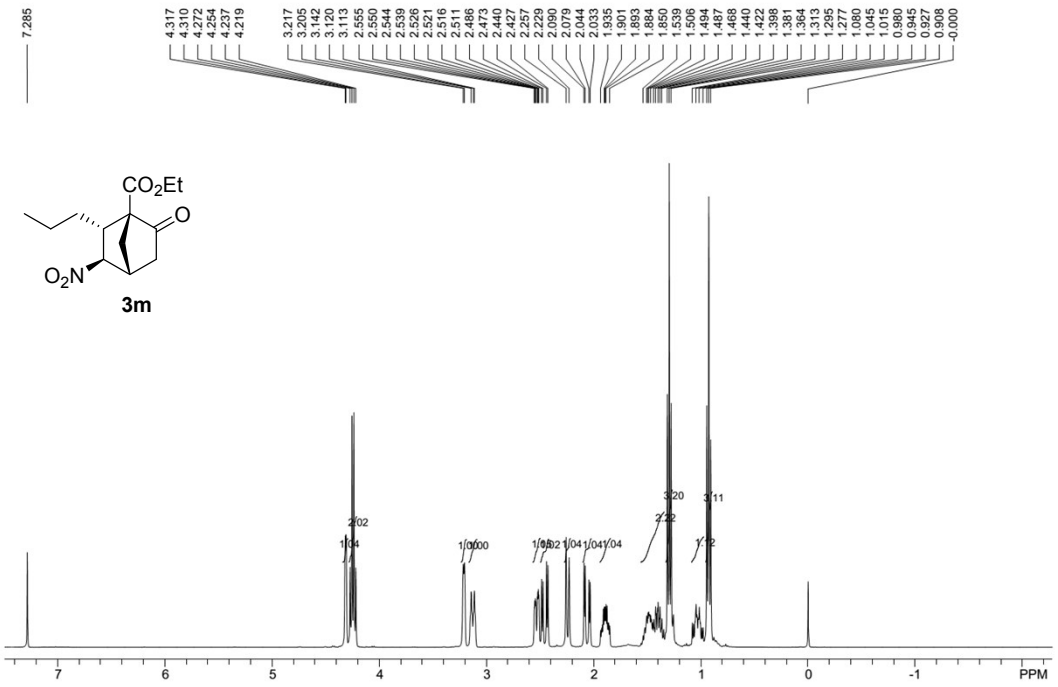
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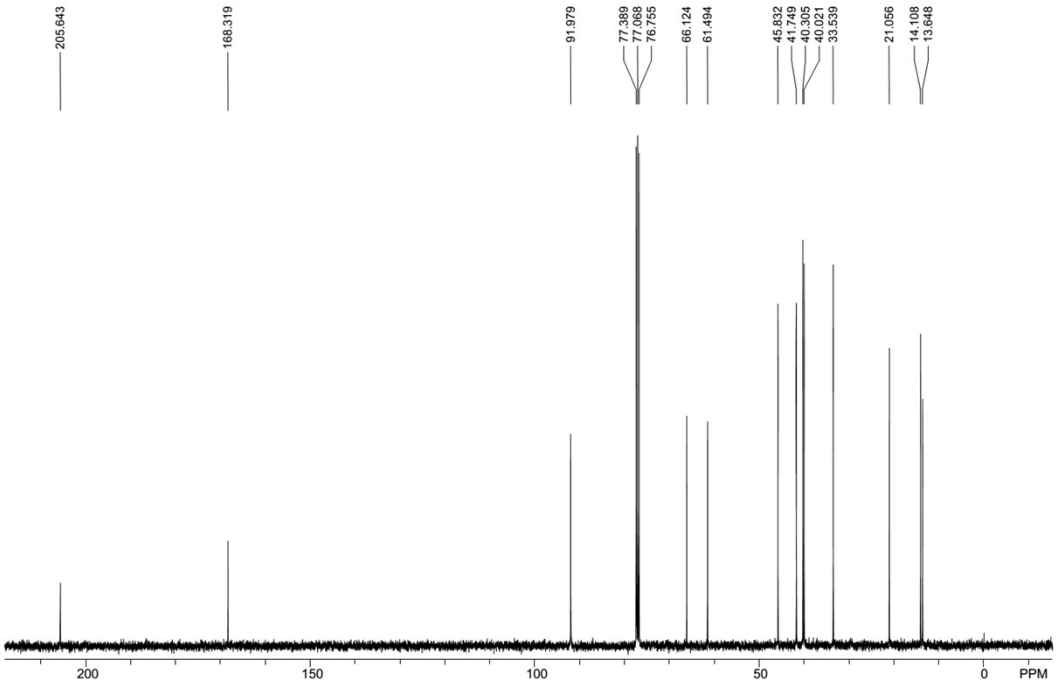
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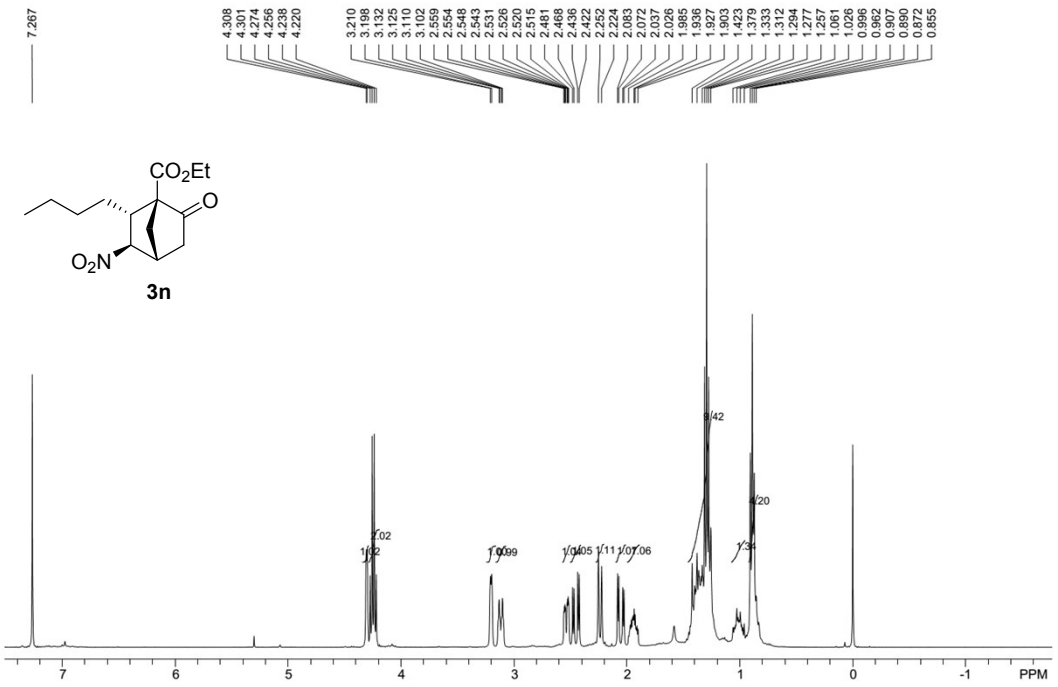
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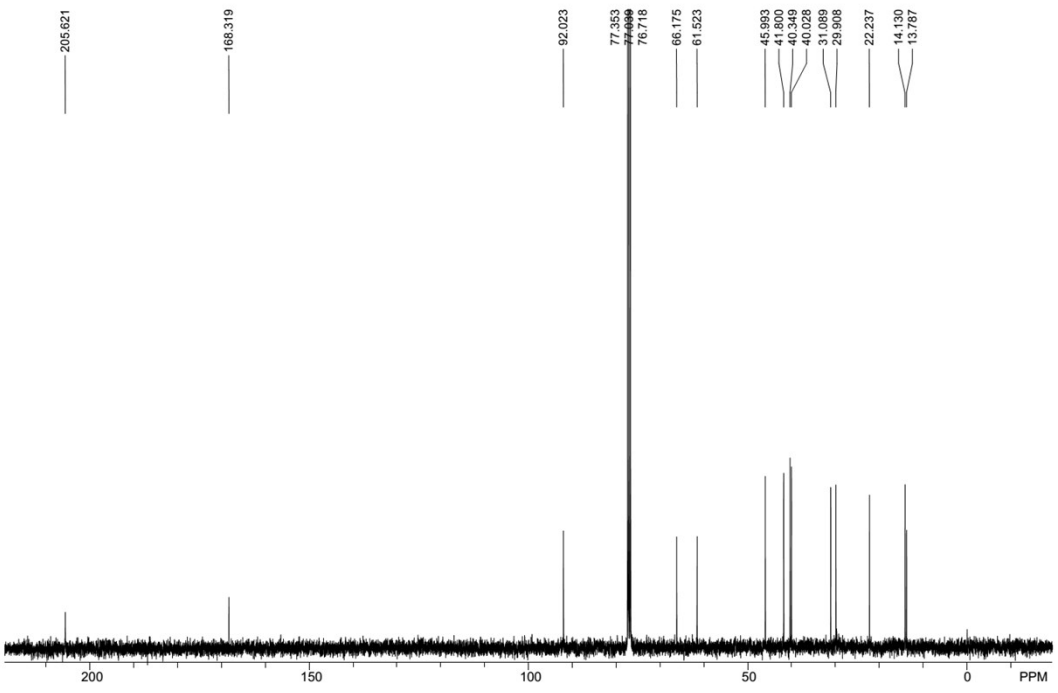
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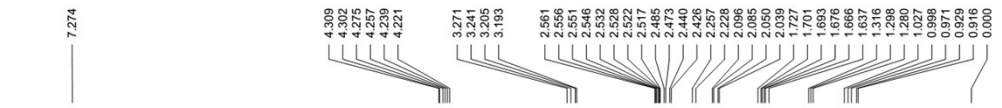
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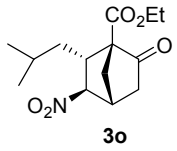
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O2N

3o

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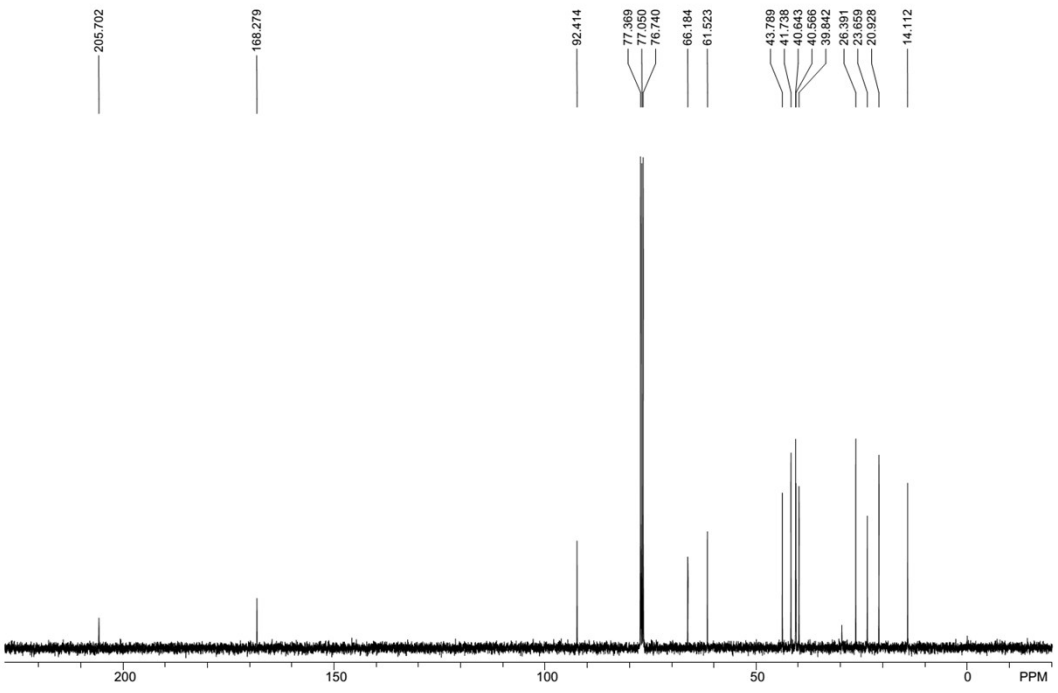
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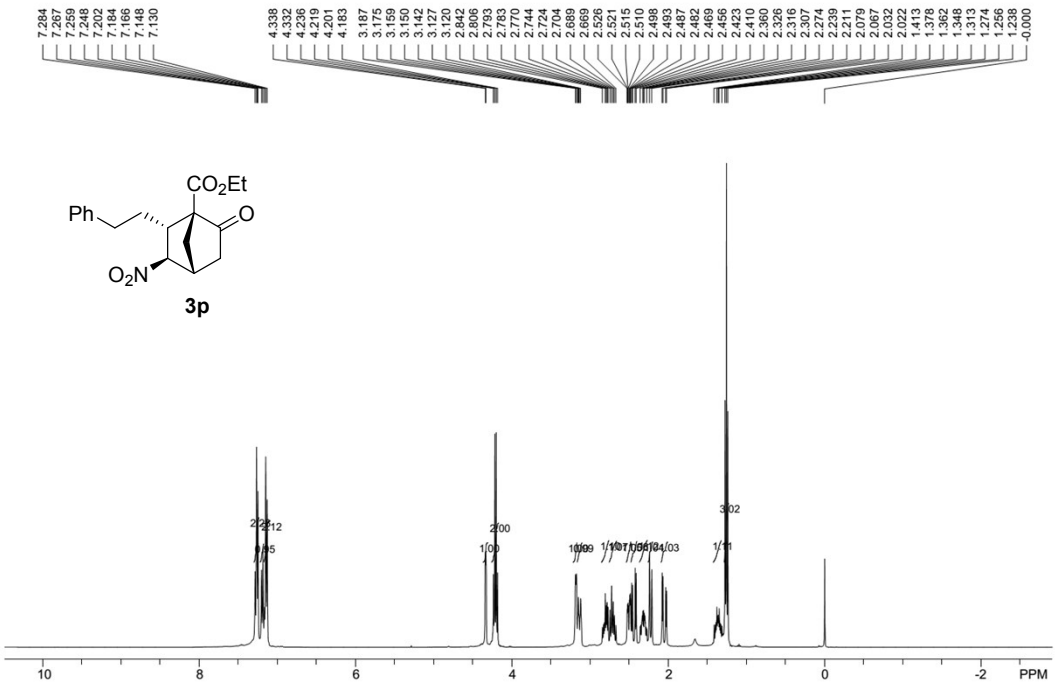
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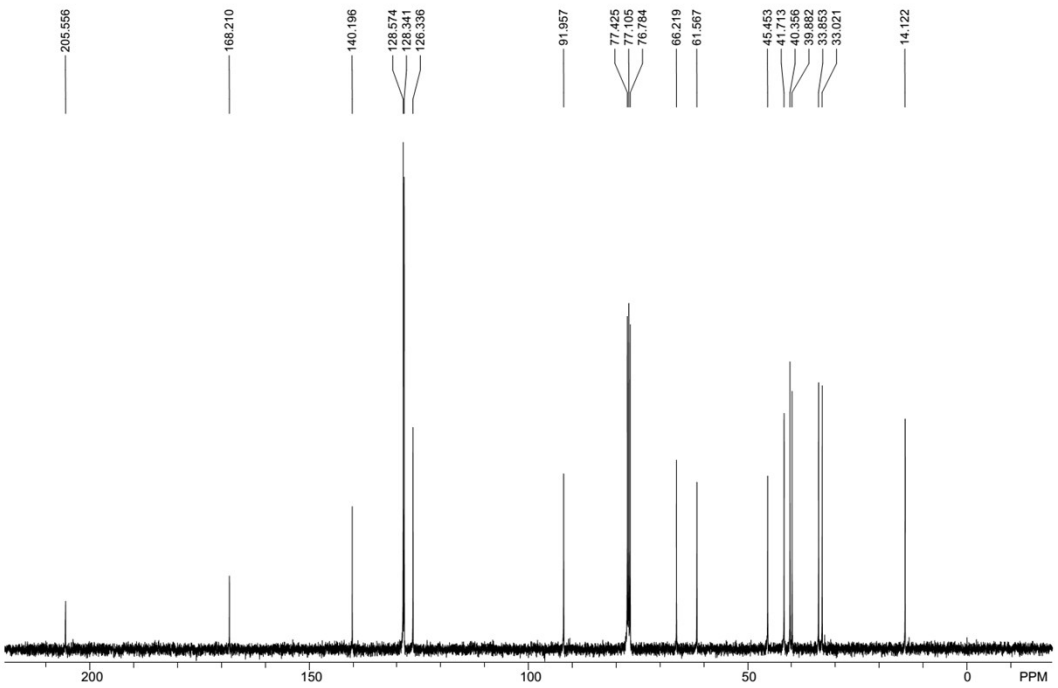
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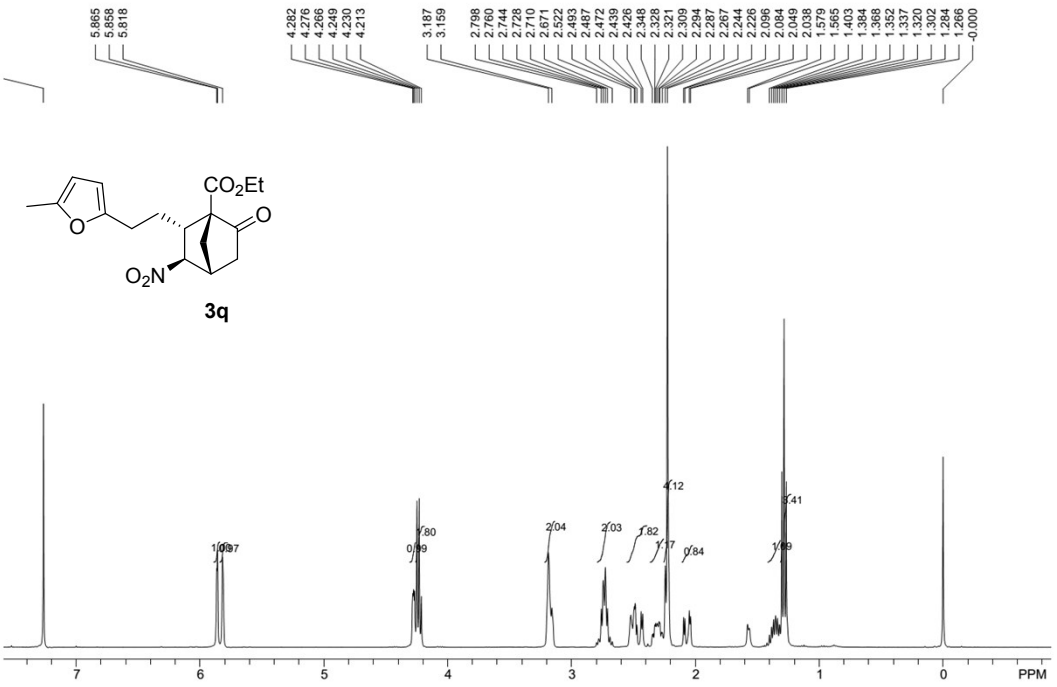
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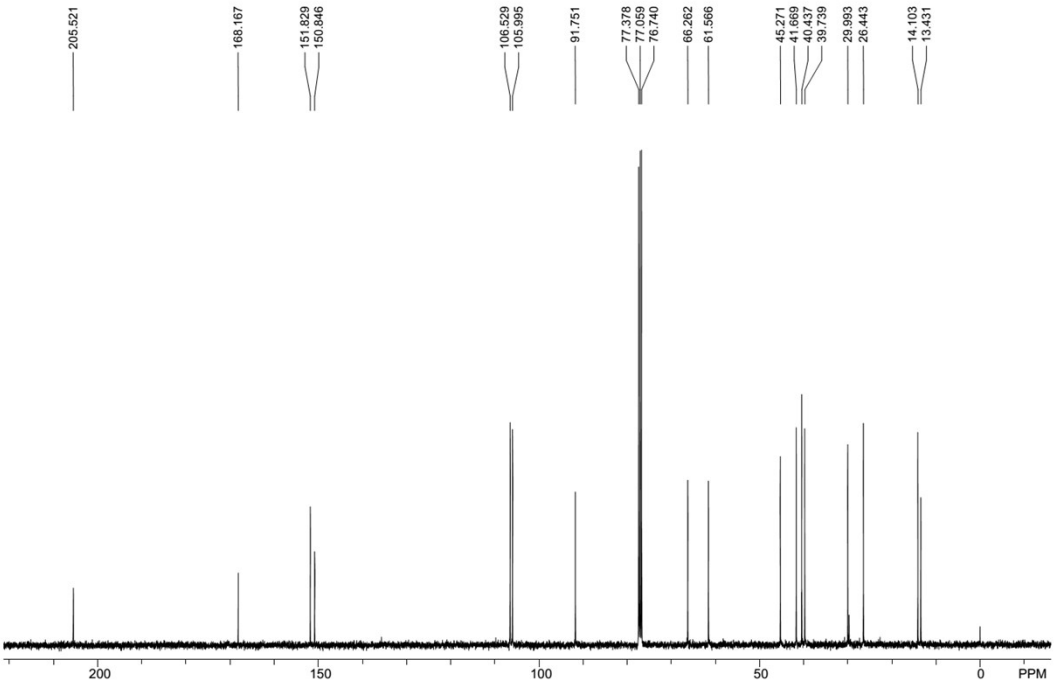
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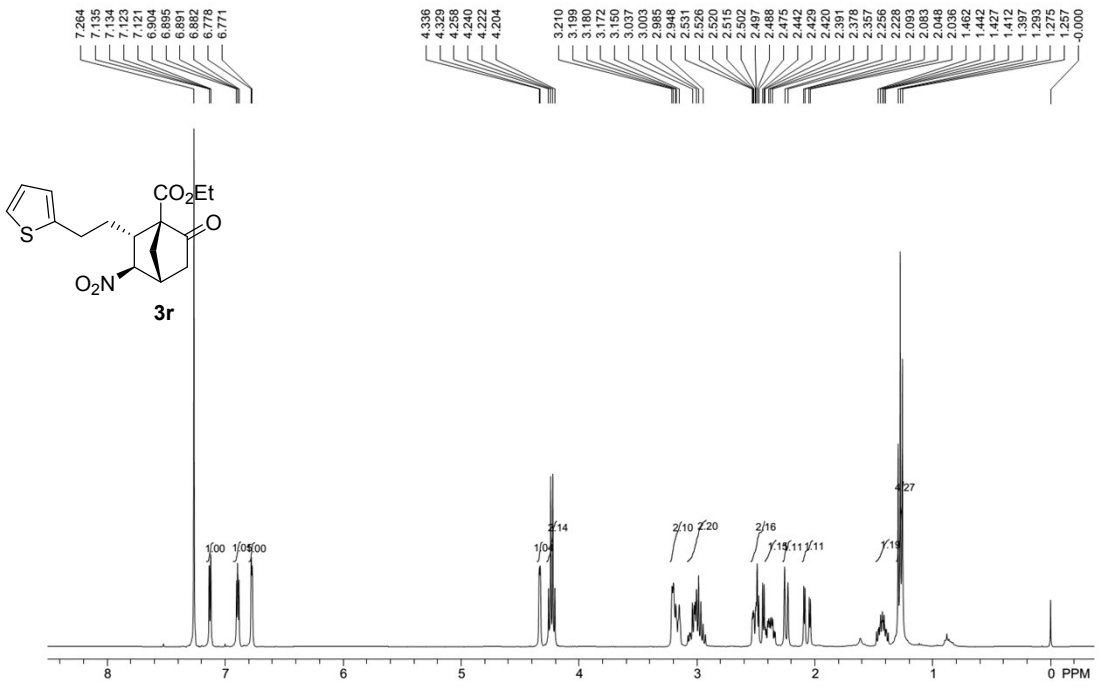
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S
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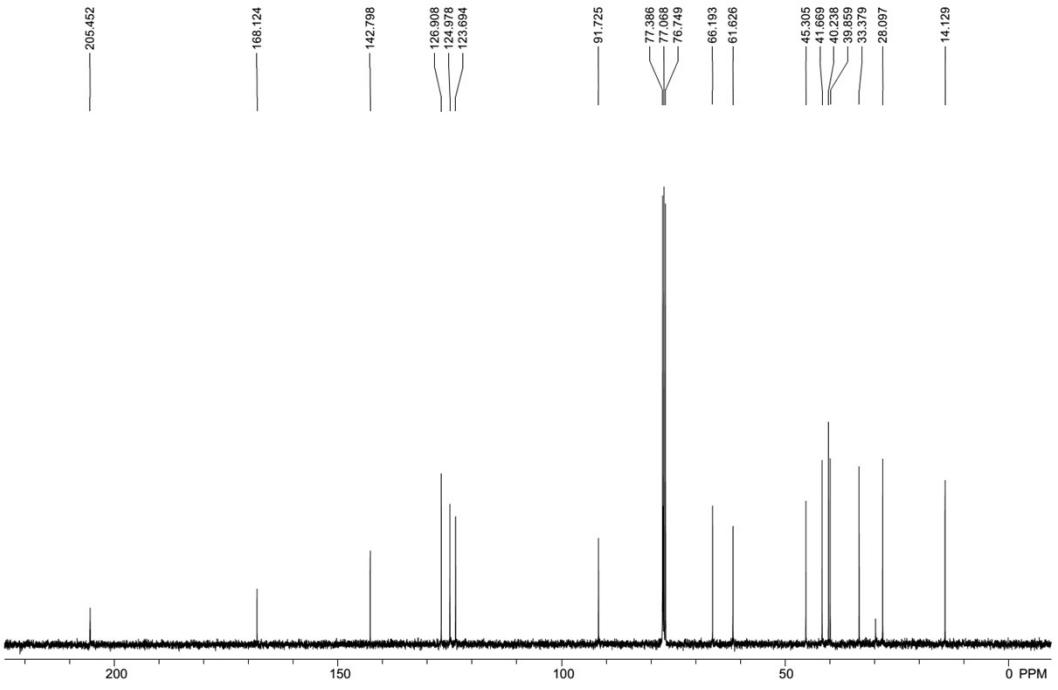
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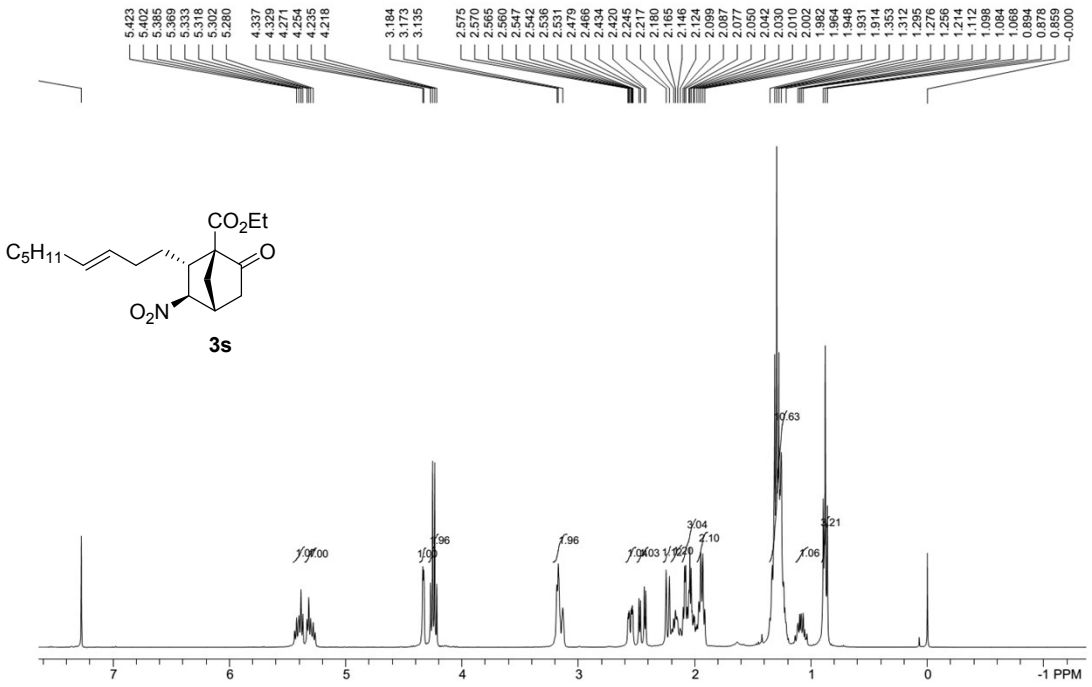
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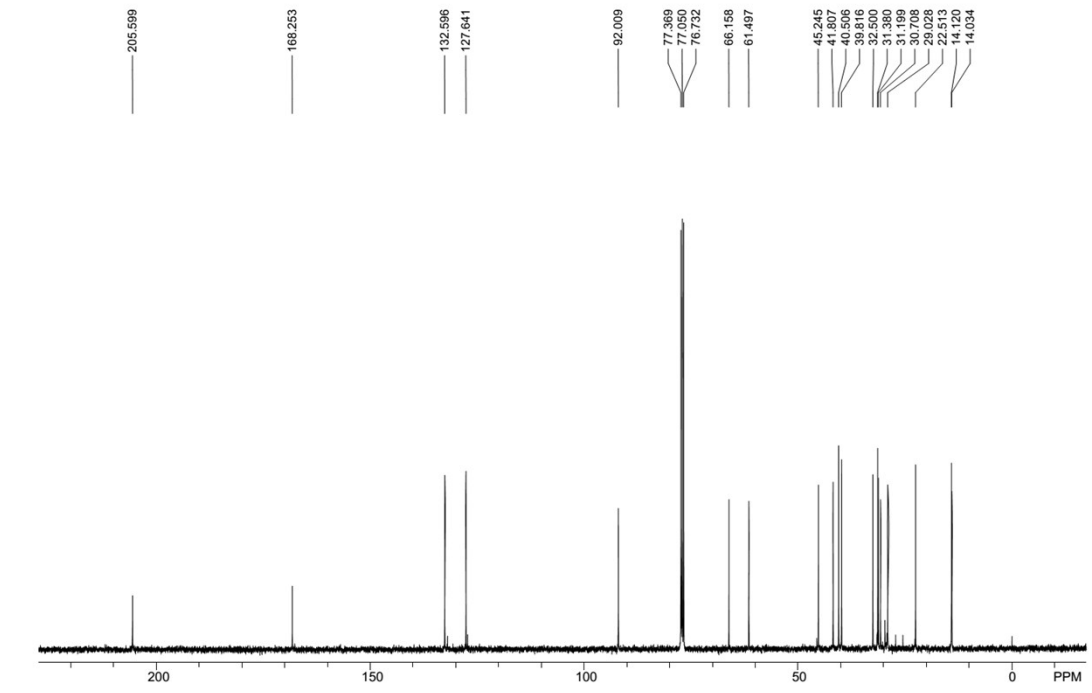
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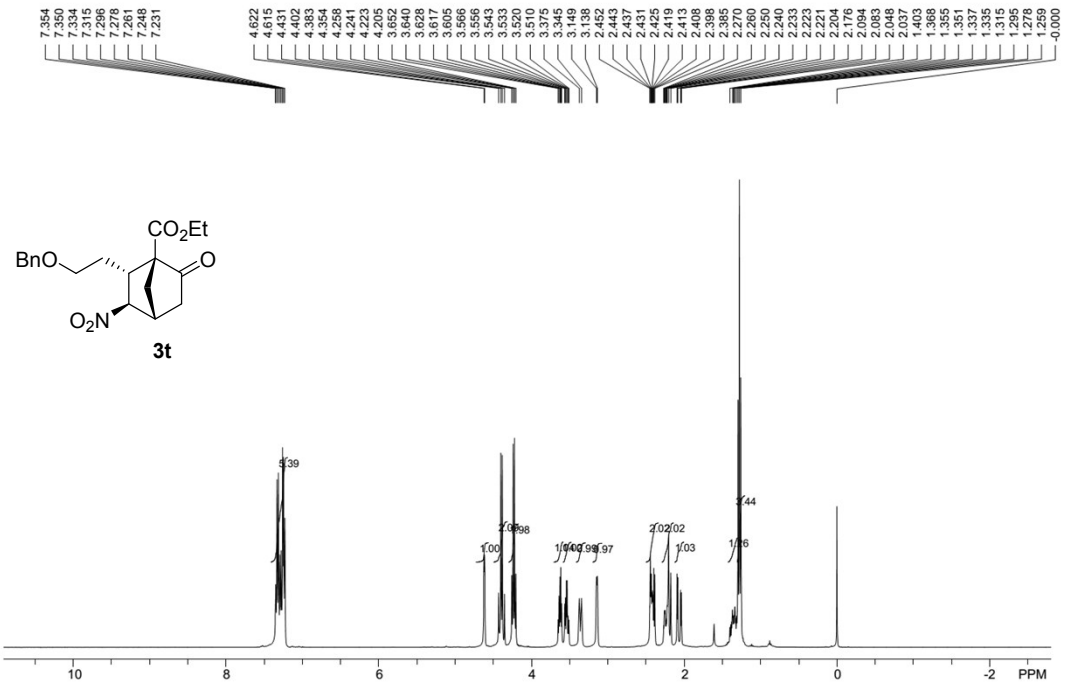
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BnO
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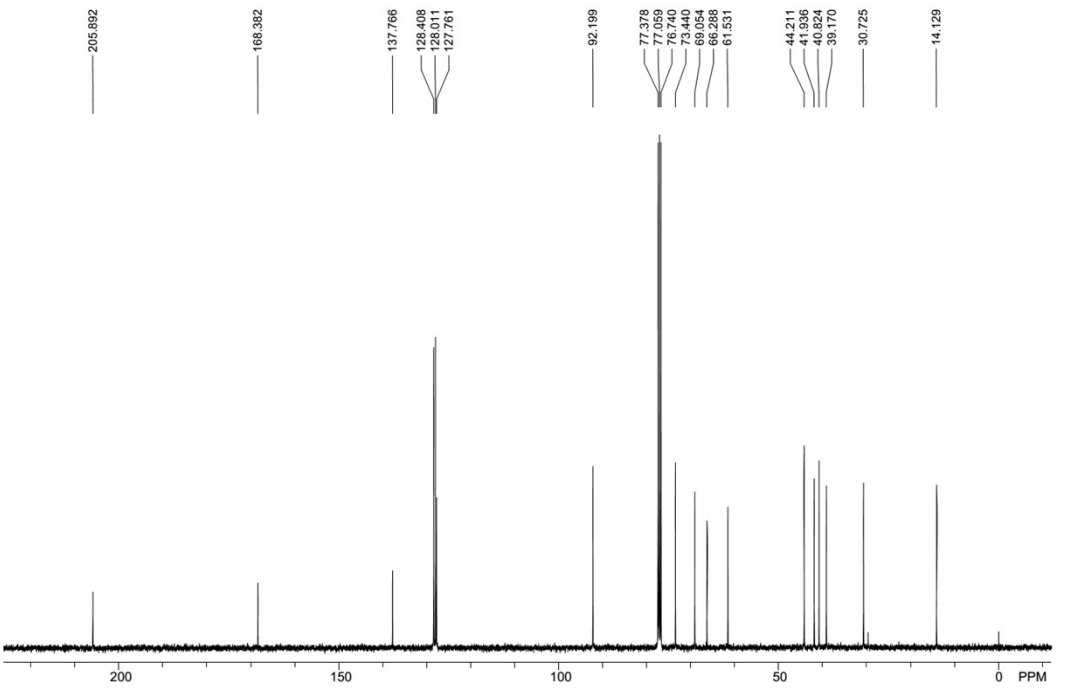
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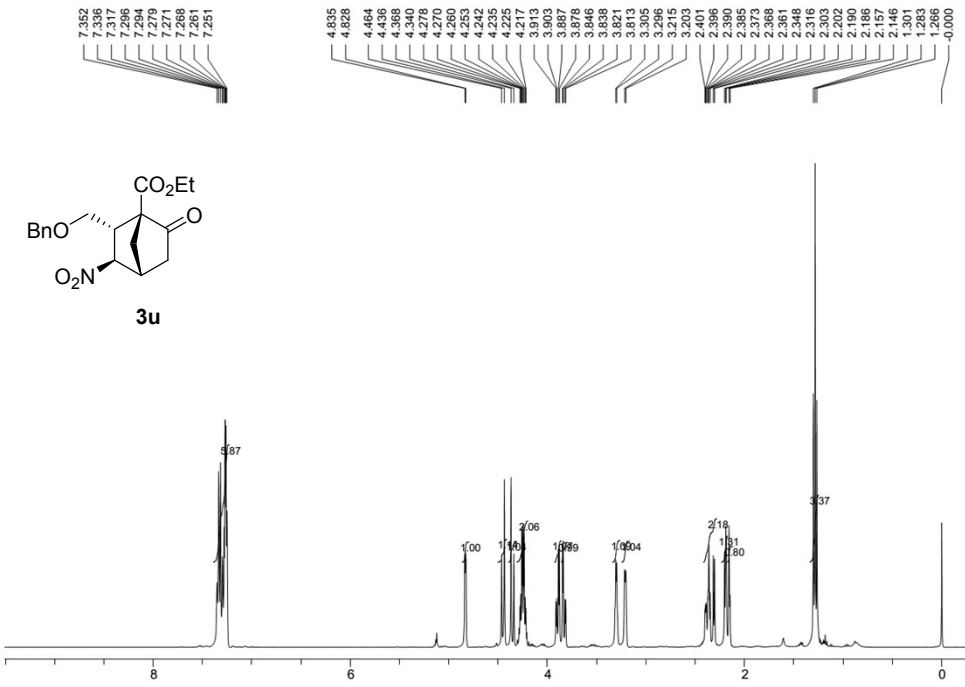
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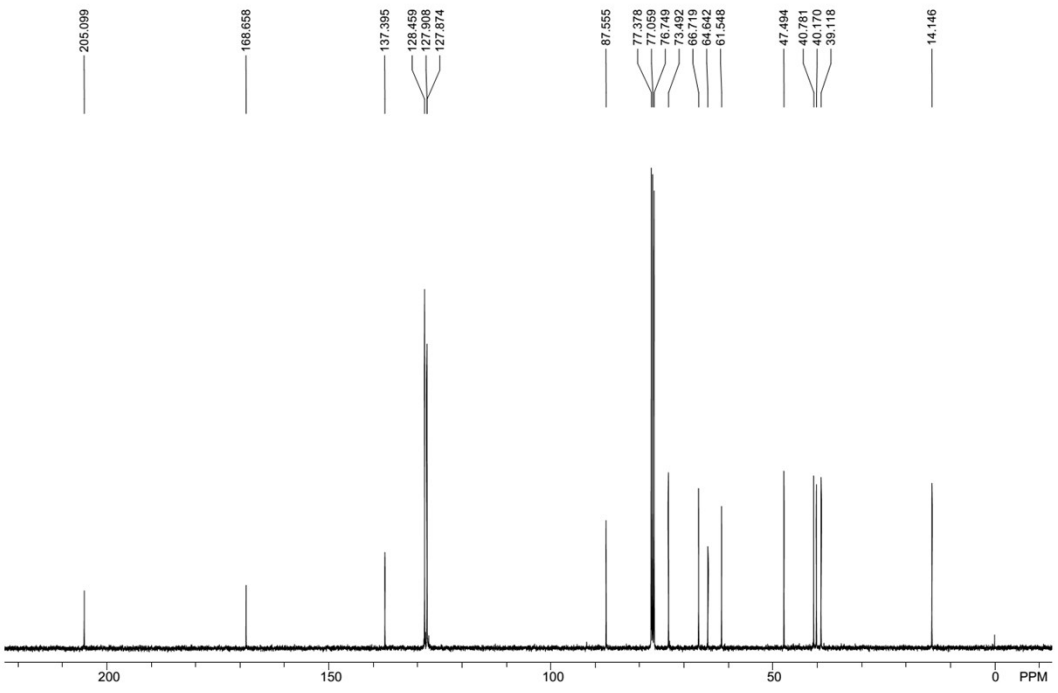
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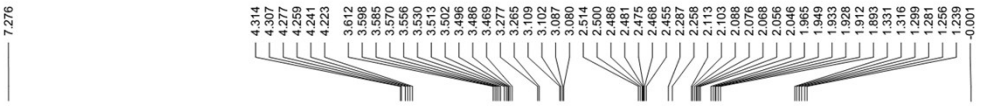
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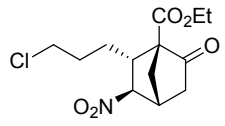
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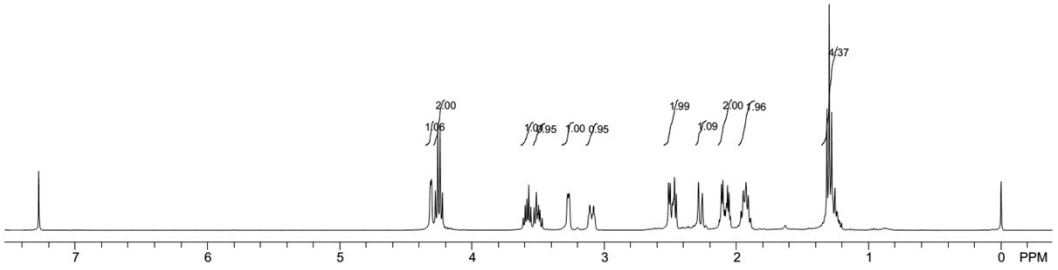
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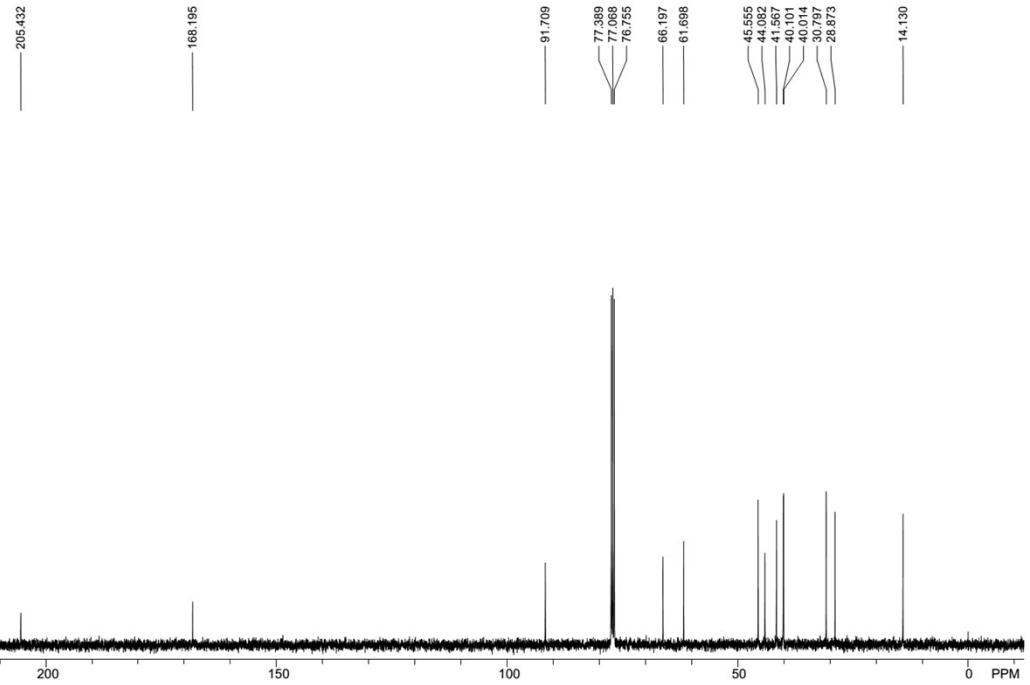
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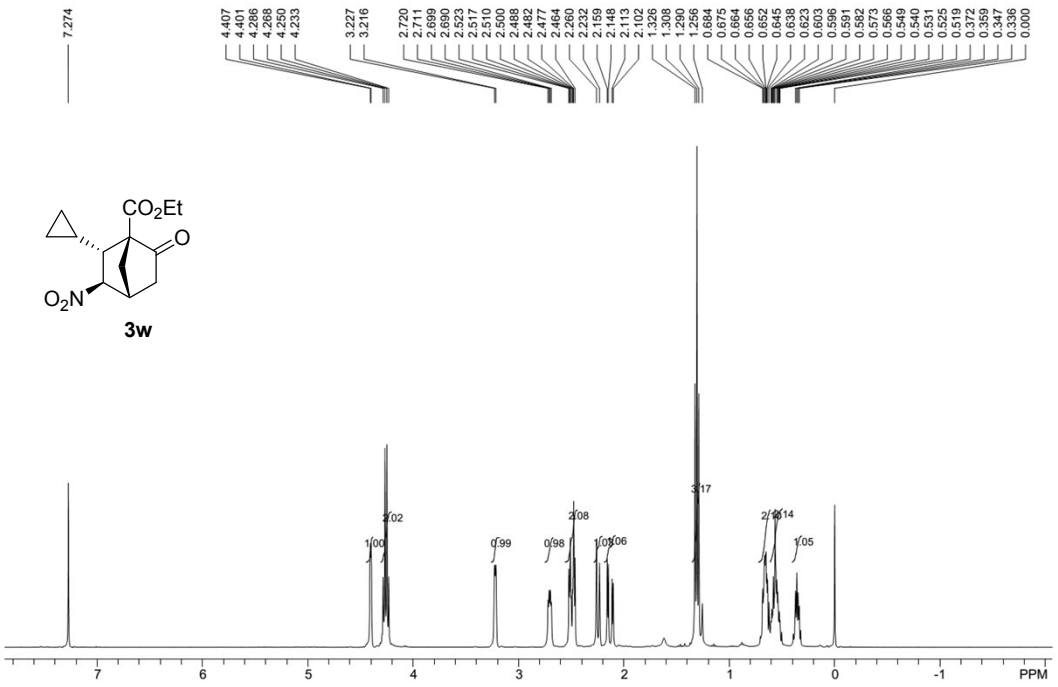
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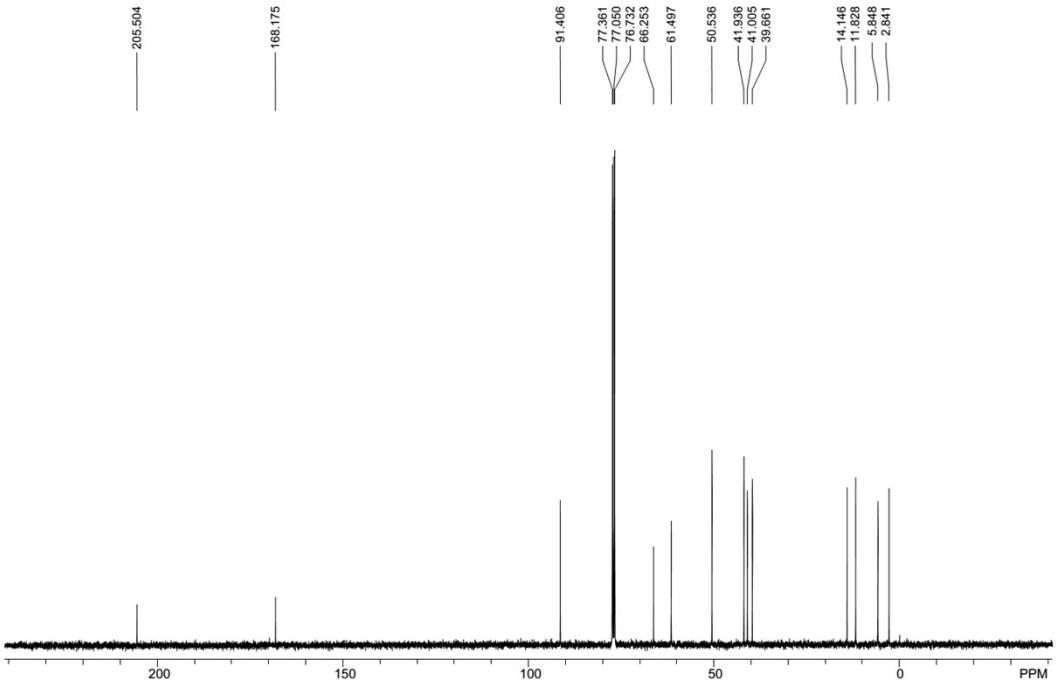
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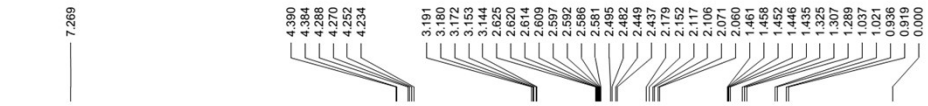
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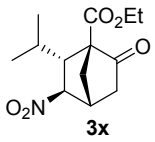
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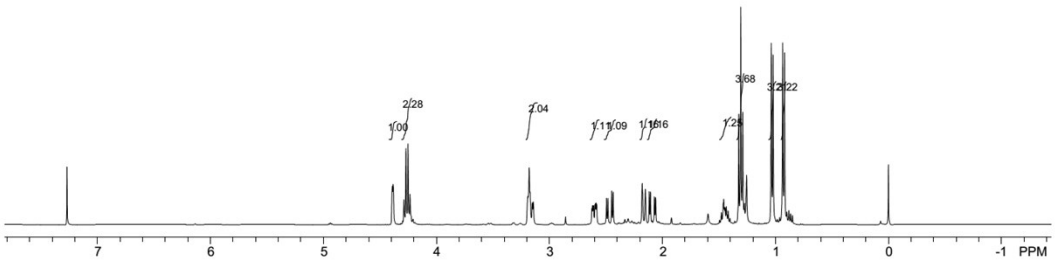
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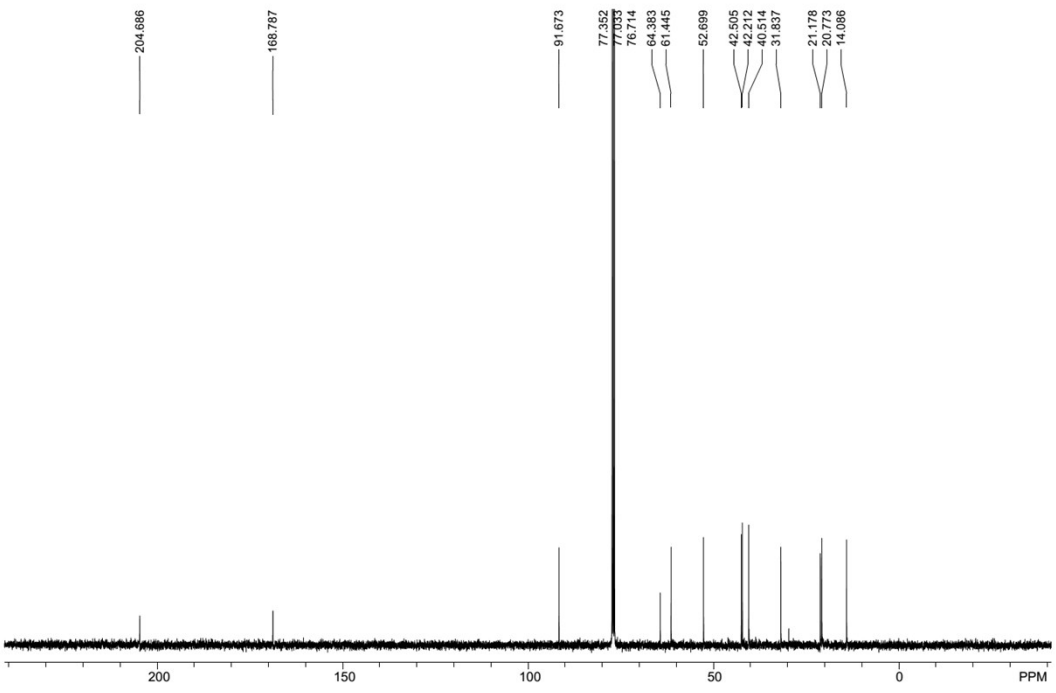
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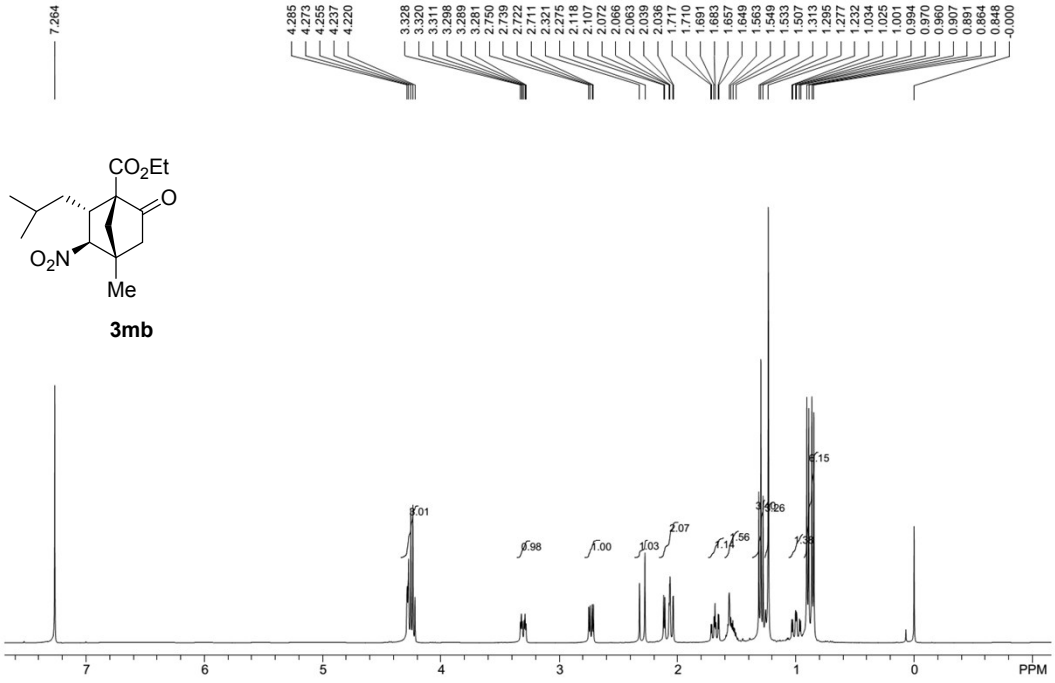
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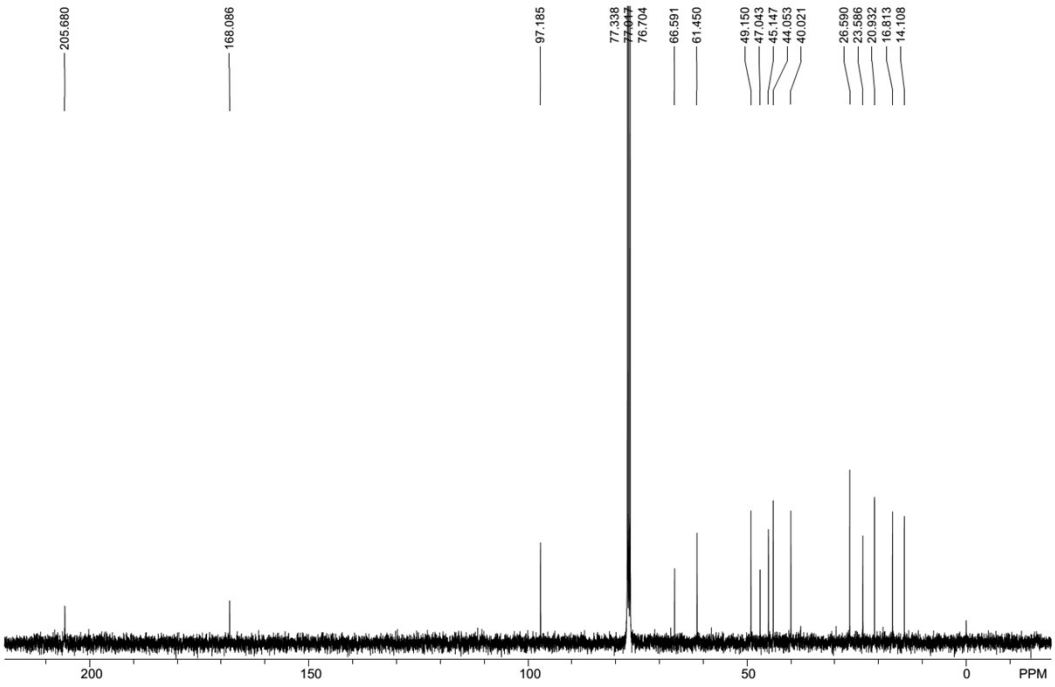
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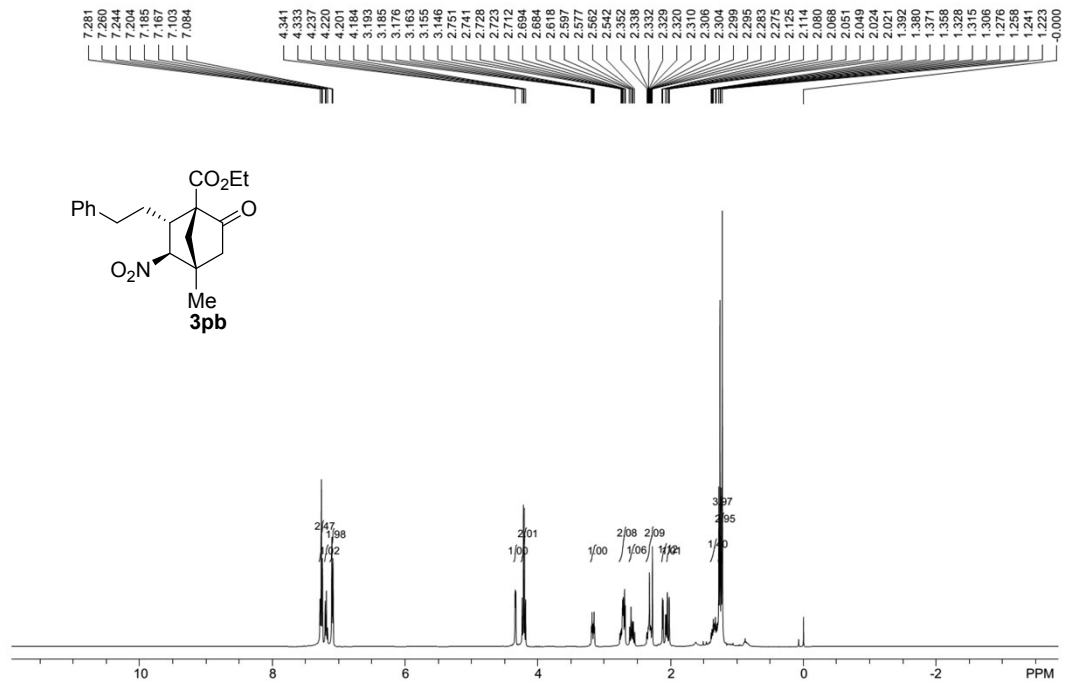
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Ph
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O2N
Me
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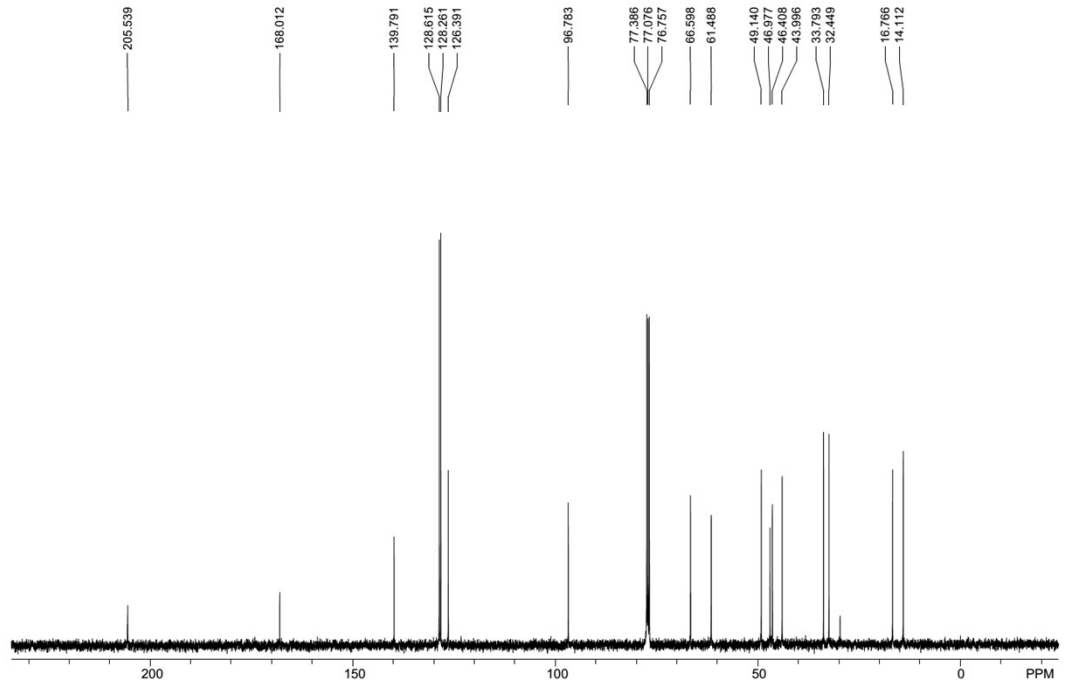
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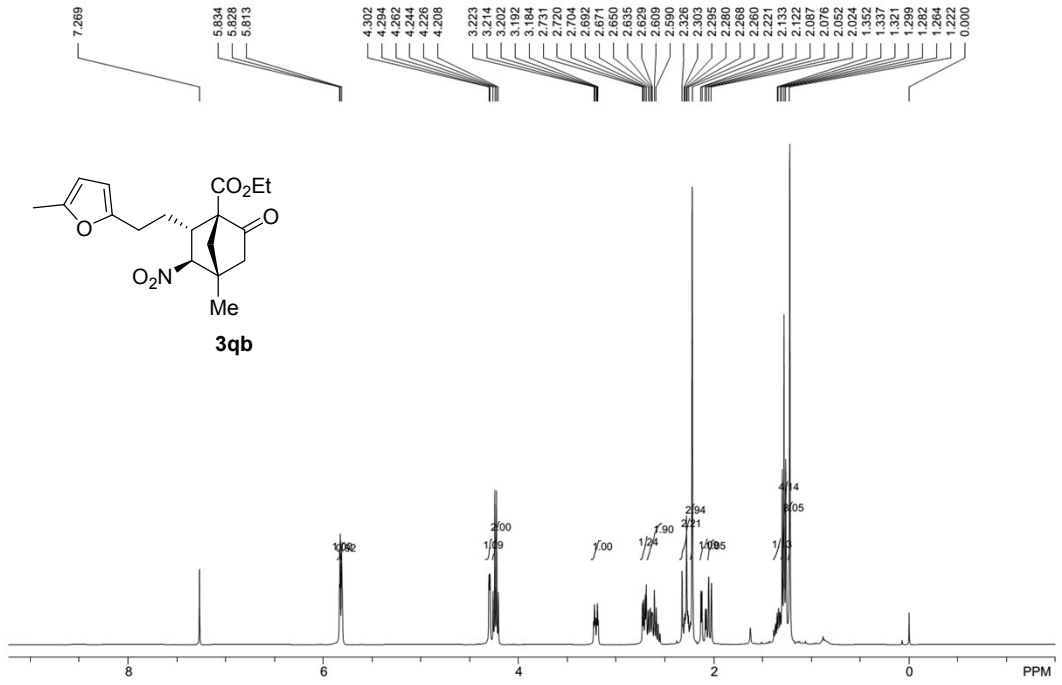
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O2N
Me
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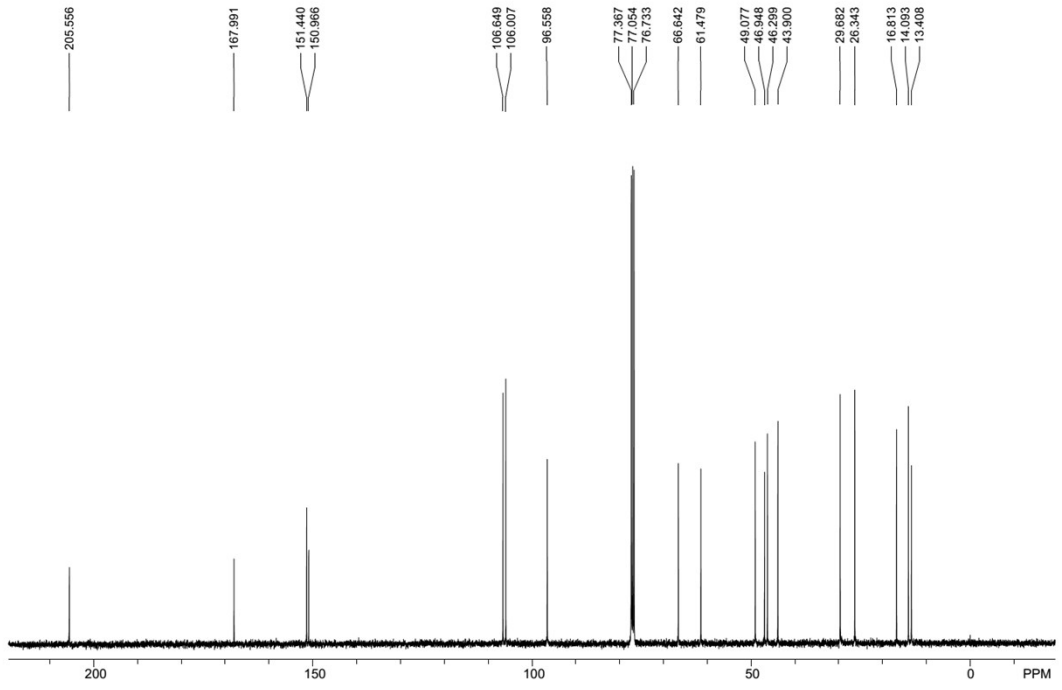
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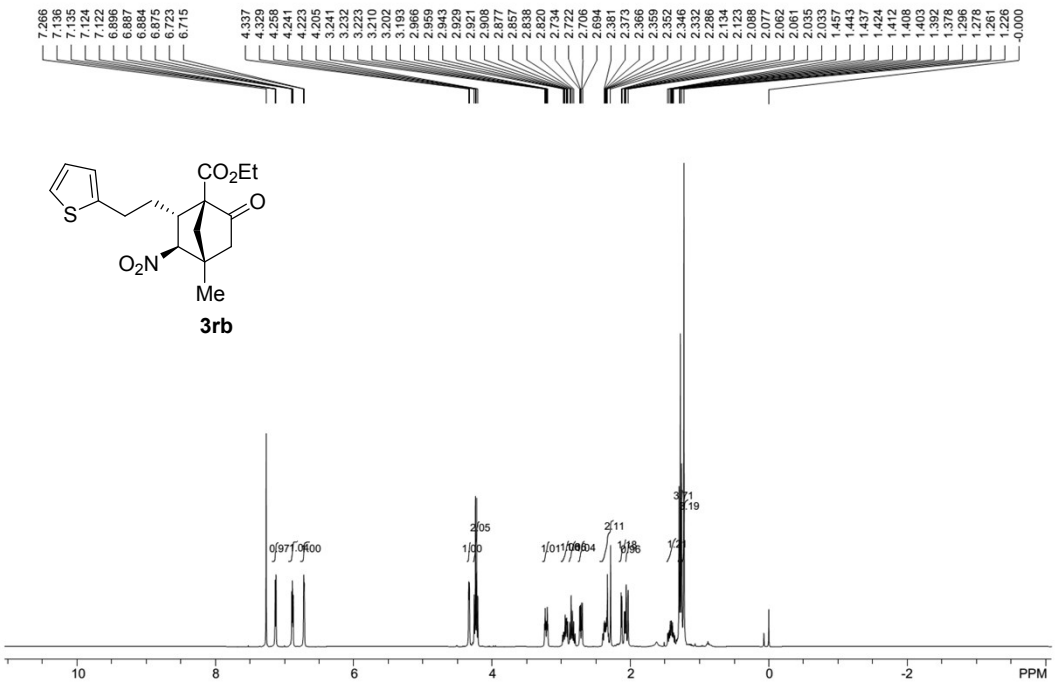
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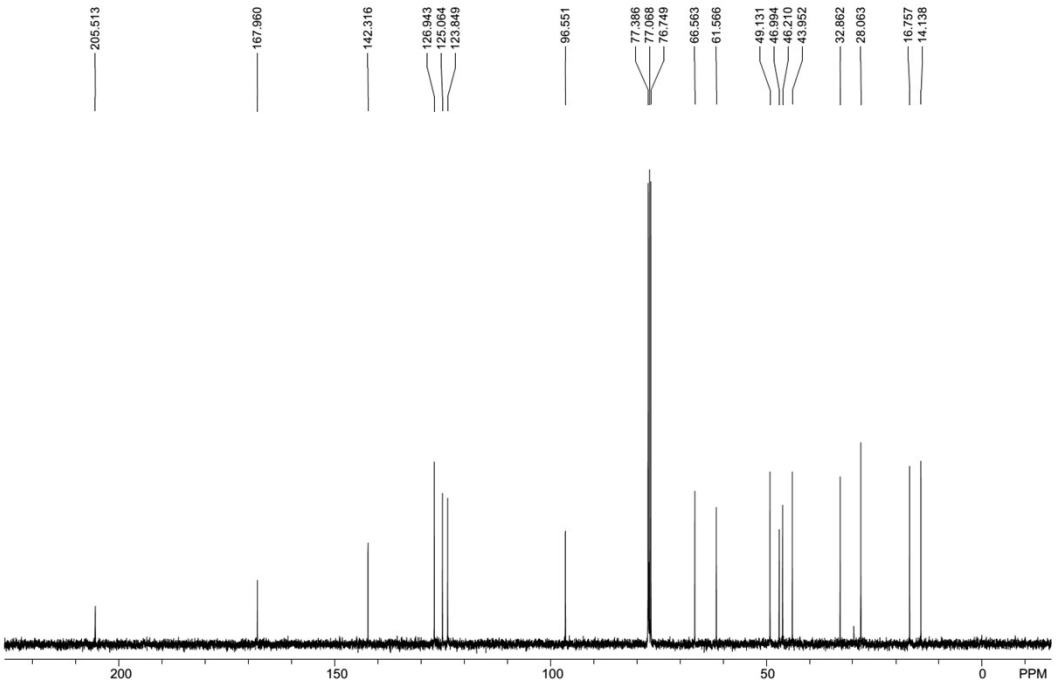
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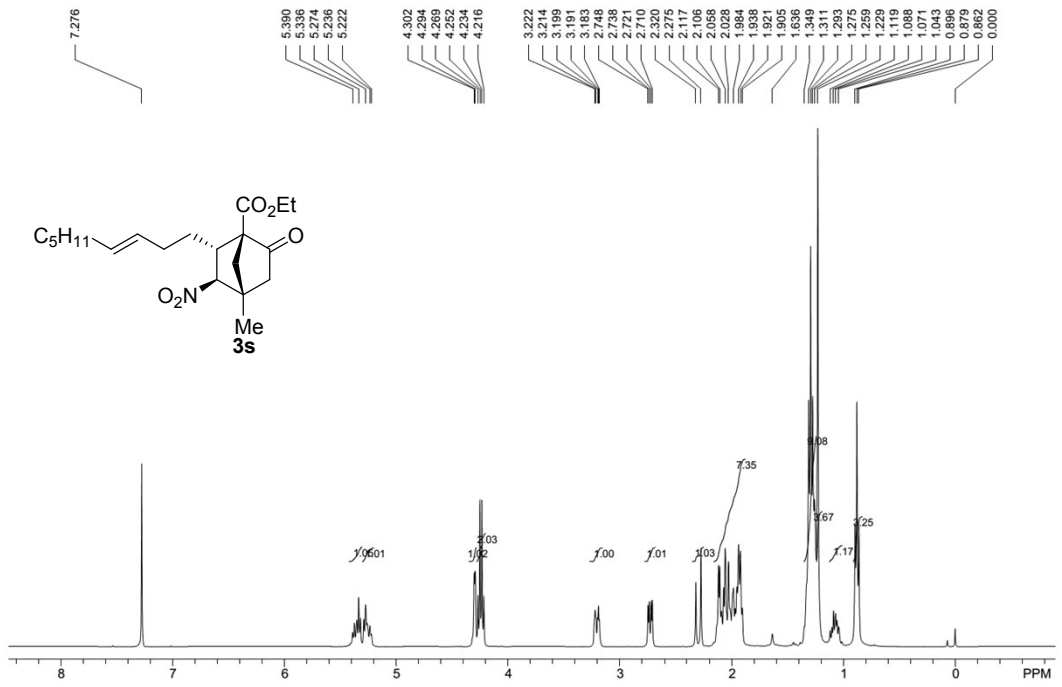
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C5H11
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Me
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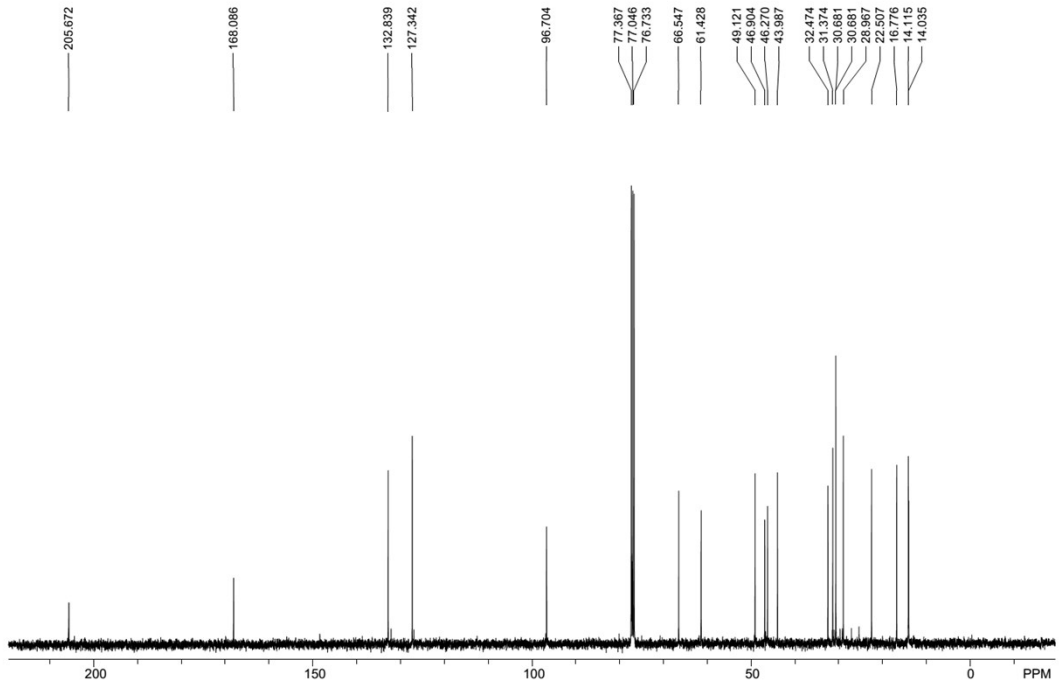
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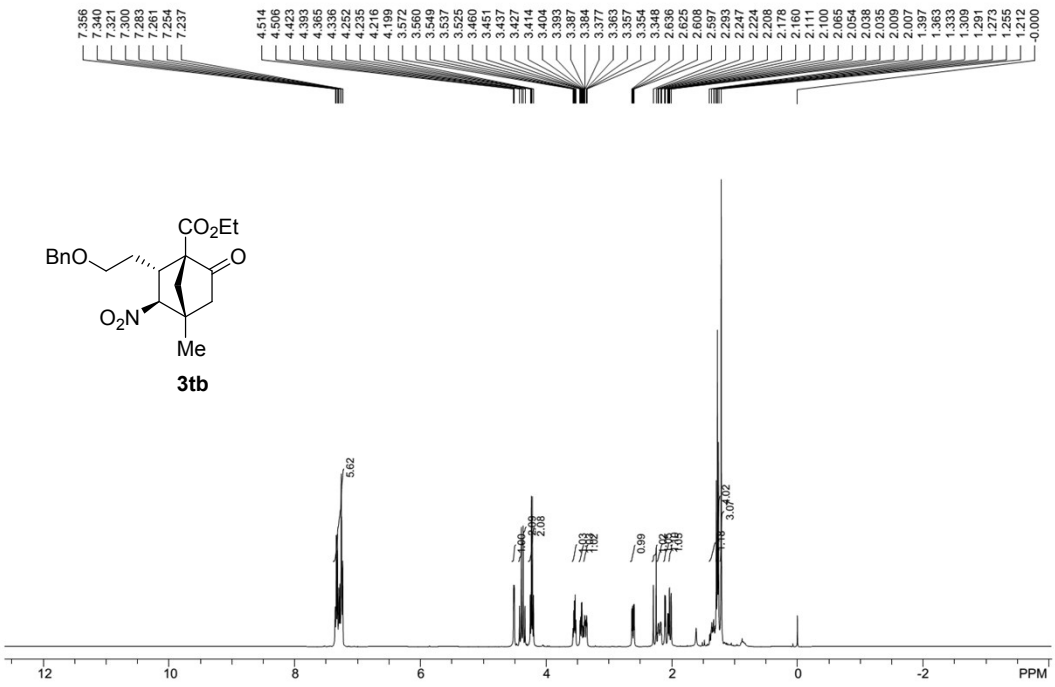
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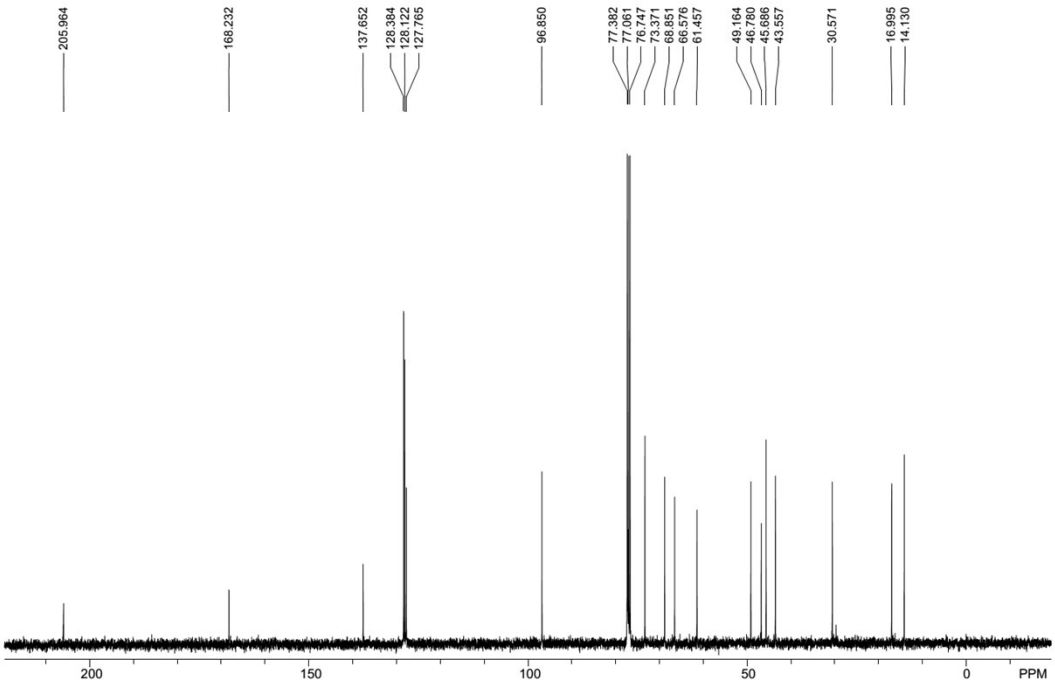
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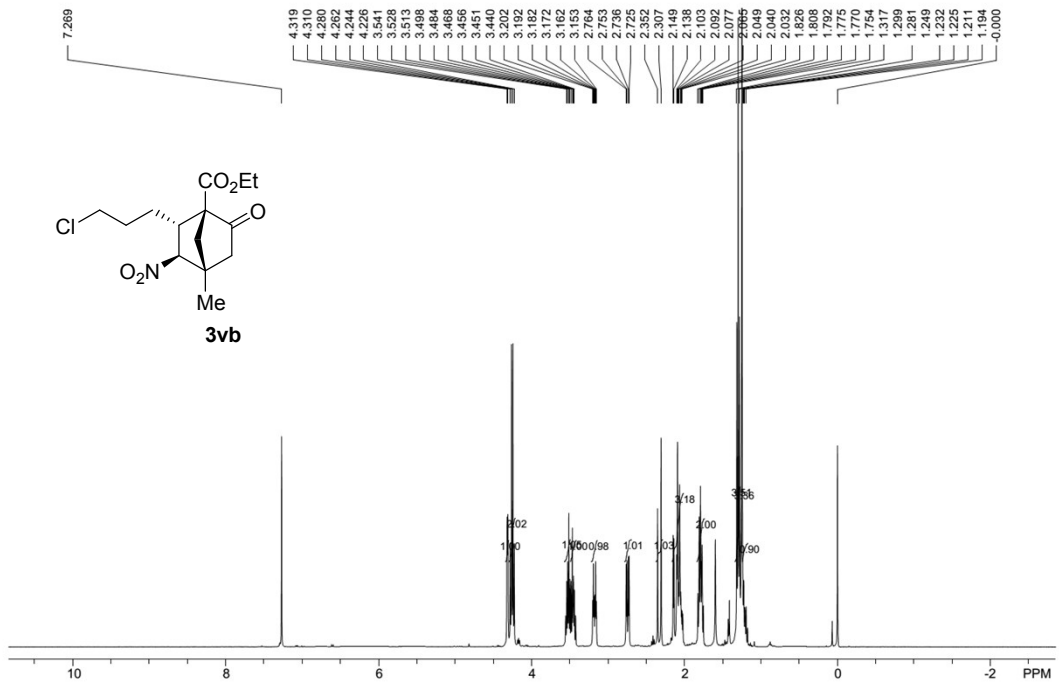
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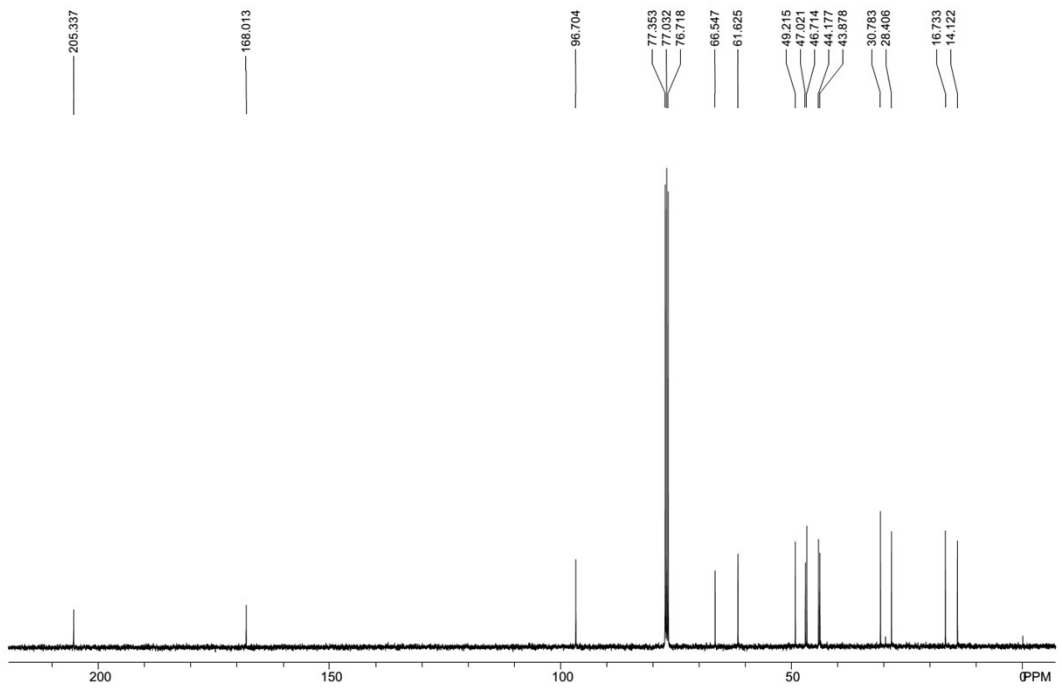
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