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Supporting Information

for

Stereoselective Biginelli-like reaction catalyzed by a chiral phosphoric acid bearing two hydroxy groups

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Experimental data and copies of ^{1}H NMR and ^{13}C NMR spectra

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I Experimental data

(*R*)-1-Benzyl-4-phenyl-3,4,5,6,7,8-hexahydroquinazoline-2(1*H*)-thione (5a)

Yield: 85%, m.p.: 183-185 ℃, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (t, *J* = 6.4 Hz, 5H), 7.28 (t, *J* = 7.8 Hz, 5H), 7.03 (s, 1H), 5.87 (d, *J* = 15.5 Hz, 1H), 5.31 (d, *J* = 9.3 Hz, 1H), 4.76 (s, 1H), 2.30–2.17 (m, 2H), 1.89–1.72 (m, 2H), 1.71–1.46 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.4, 141.4, 138.1, 130.1, 128.9, 128.6, 128.3, 127.2, 127.1, 126.4, 113.5, 59.3, 51.0, 26.7, 25.6, 22.8, 21.2. Enantiomeric excess: 95%, determined by HPLC (Daicel Chirapak AD-H, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min): T_R = 9.617 min (minor), T_R = 18.415 min (major).

(*R*)-1-Benzyl-4-(2-bromophenyl)-3,4,5,6,7,8-hexahydroquinazoline-2(1*H*)-thione (5b)

Yield: 86%, m.p.: 179-180 ℃, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.34–7.26 (m, 4H), 7.25–7.22 (m, 2H), 7.20–7.13 (m, 2H), 7.05 (s, 1H), 6.05 (d, *J* = 14.2 Hz, 1H), 5.18 (s, 1H), 5.08 (d, *J* = 16.1 Hz, 1H),

2.28 (t, *J* = 5.7 Hz, 2H), 1.98–1.74 (m, 2H), 1.70–1.54 (m, 3H), 1.47–1.37 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.7, 139.0, 137.9, 133.3, 131.9, 130.0, 129.2, 128.6, 128.3, 127.2, 126.7, 123.8, 112.6, 57.4, 51.0, 26.6, 25.7, 22.8, 21.2. Enantiomeric excess: 77%, determined by HPLC (Daicel Chirapak AD-H, hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min): T_R = 9.265 min (minor), T_R = 15.480 min (major).

(*R*)-1-Benzyl-4-(3-bromophenyl)-3,4,5,6,7,8-hexahydroquinazoline-2(1*H*)-thione (5c)

Yield: 83%, m.p.: 108-110 ℃, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.37 (m, 5H), 7.31 (t, *J* = 6.4 Hz, 3H), 7.23 (d, *J* = 6.4 Hz, 2H), 6.00 (d, *J* = 7.6 Hz, 1H), 5.22 (d, *J* = 8.3 Hz, 1H), 4.74 (s, 1H), 2.26 (s, 2H), 1.94–1.73 (m, 2H), 1.71–1.38 (m, 4H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 176.0, 142.7, 136.8, 130.4, 129.5, 129.0, 127.7, 126.1, 125.3, 124.9, 122.0, 111.8, 57.6, 49.8, 25.6, 24.5, 21.6, 20.1. Enantiomeric excess: 91%, determined by HPLC (Daicel Chirapak AD-H, hexane/*i*-PrOH = 70/ 30, flow rate 1.5 mL/min): T_R = 6.823 min (minor), T_R = 16.628 min (major).

(*R*)-1-Benzyl-4-(4-bromophenyl)-3,4,5,6,7,8-hexahydroquinazoline-2(1*H*)-thione (5d)

Yield: 90%, m.p.: 175-176 ℃, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.39 (s, 1H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.30–7.22 (m, 3H), 7.13 (s, 1H), 7.11 (s, 1H), 5.87 (d, *J* = 17.0 Hz, 1H), 5.23 (d, *J* = 17.8 Hz, 1H), 4.70 (s, 1H), 2.58–2.10 (m, 2H), 1.83–1.69 (m, 2H), 1.65–1.43 (m, 4H). ^{13}C NMR (101

MHz, Chloroform-*d*) δ 177.3, 140.5, 137.9, 132.0, 130.5, 128.9, 128.6, 127.2, 126.4, 122.3, 113.1, 77.4, 77.1, 76.7, 58.5, 50.9, 26.6, 25.6, 22.7, 21.2. Enantiomeric excess: 87%, determined by HPLC (Daicel Chirapak AD-H, hexane/*i*-PrOH = 70/ 30, flow rate 1.0 mL/min): T_R = 10.002 min (minor), T_R = 14.087 min (major).

(*R*)-1-Benzyl-4-(4-tolyl)-3,4,5,6,7,8-hexahydroquinazoline-2(1*H*)-thione (5e)

Yield: 88%, m.p.: 130-131 ℃, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37–7.31 (m, 2H), 7.31–7.24 (m, 4H), 7.14 (s, 4H), 5.86 (d, *J* = 14.5 Hz, 1H), 5.27 (d, *J* = 8.6 Hz, 1H), 4.71 (s, 1H), 2.35 (s, 3H), 2.21 (s, 2H), 1.89–1.72 (m, 2H), 1.66–1.38 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.3, 138.6, 138.1, 129.9, 129.5, 128.6, 127.1, 127.0, 126.4, 113.6, 59.0, 51.0, 26.6, 25.6, 22.8, 21.2. Enantiomeric excess: 80%, determined by HPLC (Daicel Chirapak AD-H, hexane/*i*-PrOH = 70/ 30, flow rate 1.5 mL/min): T_R = 3.278 min (minor), T_R = 7.154 min (major).

(*R*)-1-Benzyl-4-(4-methoxyphenyl)-3,4,5,6,7,8-hexahydroquinazoline-2(1*H*)-thione (5f)

Yield: 85%, m.p.: 142-145 ℃, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.31 (m, 2H), 7.29–7.24 (m, 3H), 7.21–7.12 (m, 2H), 7.02 (s, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.83 (d, *J* = 8.5 Hz, 1H), 5.31 (d, *J* = 10.0 Hz, 1H), 4.70 (s, 1H), 3.80 (s, 3H), 2.21 (d, *J* = 5.9 Hz, 2H), 1.83–1.71 (m, 2H), 1.63–1.37 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.3, 159.6, 138.1, 133.7, 129.9, 128.6,

128.4, 127.1, 126.4, 58.6, 55.4, 50.9, 26.6, 25.6, 22.8, 21.2. Enantiomeric excess: 83%, determined by HPLC (Daicel Chirapak AD-H, hexane/*i*-PrOH = 70/ 30, flow rate 1.0 mL/min): T_R = 8.528 min (minor), T_R = 9.287 min (major).

(*R*)-1-Benzyl-4-(4-fluorophenyl)-3,4,5,6,7,8-hexahydroquinazoline-2(1*H*)-thione (5g)

Yield: 89%, m.p.: 172-175 ℃, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (s, 1H), 7.39–7.31 (m, 2H), 7.32–7.24 (m, 3H), 7.26–7.17 (m, 2H), 7.01 (t, *J* = 8.6 Hz, 2H), 5.89 (d, *J* = 9.3 Hz, 1H), 5.25 (d, *J* = 8.5 Hz, 1H), 4.73 (s, 1H), 2.35–2.13 (m, 2H), 1.93–1.70 (m, 2H), 1.68–1.40 (m, 4H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 175.9, 162.3, 160.7, 136.9, 136.2, 129.3, 127.9, 127.6, 126.1, 125.4, 114.8, 112.3, 57.3, 49.8, 25.6, 24.5, 21.7, 20.1. Anal. calc. for $C_{21}H_{21}N_2FS$: C 71.56, H 6.01; found: C 71.48, H 5.96. Enantiomeric excess: 73%, determined by HPLC (Daicel Chirapak AD-H, hexane/*i*-PrOH = 70/ 30, flow rate 1.5 mL/min): T_R = 6.904 min (minor), T_R = 13.005 min (major).

(*R*)-1-Benzyl-4-(4-nitrophenyl)-3,4,5,6,7,8-hexahydroquinazoline-2(1*H*)-thione (5h)

Yield: 79%, m.p.: 170-175 ℃, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 8.5 Hz, 2H), 7.72 (s, 1H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.32 (dd, *J* = 13.1, 7.1 Hz, 3H), 7.28–7.23 (m, 2H), 5.88 (d, *J* = 12.0 Hz, 1H), 5.21 (d, *J* = 17.6 Hz, 1H), 4.83 (s, 1H), 2.37–2.18 (m, 2H), 1.96–1.71 (m, 2H), 1.69–1.41 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.6, 148.3, 147.8, 137.7, 131.2, 128.7, 128.0, 127.3, 126.5, 124.2, 123.5, 112.5, 58.5, 50.9, 26.8, 25.7, 22.6, 21.1.

Enantiomeric excess: 42%, determined by HPLC (Daicel Chirapak AD-H, hexane/*i*-PrOH = 70/ 30, flow rate 1.0 mL/min): T_R = 12.190 min (minor), T_R = 23.253 min (major).

(*R*)-1-Benzyl-4-(2-nitrophenyl)-3,4,5,6,7,8-hexahydroquinazoline-2(1*H*)-thione (5i)

Yield: 76%, m.p.: 182-185 ℃, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.0 Hz, 1H), 7.60–7.49 (m, 2H), 7.45 (s, 1H), 7.34–7.26 (m, 6H), 6.19 (d, *J* = 6.5 Hz, 1H), 5.18 (s, 1H), 5.01 (d, *J* = 18.5 Hz, 1H), 2.36 (s, 2H), 1.93–1.78 (m, 1H), 1.75–1.58 (m, 4H), 1.47–1.36 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.6, 149.0, 137.8, 134.4, 133.4, 129.7, 129.5, 128.6, 127.4, 126.9, 125.4, 111.5, 53.6, 50.9, 26.8, 25.8, 22.7, 21.1. Anal. calc. for $C_{21}H_{21}N_3O_2S$: C 66.47, H 5.58; found: C 66.36, H 5.49. Enantiomeric excess: 23%, determined by HPLC (Daicel Chirapak AD-H, hexane/*i*-PrOH = 70/ 30, flow rate 1.5 mL/min): T_R = 5.086 min (minor), T_R= 6.648 min (major).

(*R*)-1-Benzyl-4-(2-chlorophenyl)-3,4,5,6,7,8-hexahydroquinazoline-2(1*H*)-thione (5j)

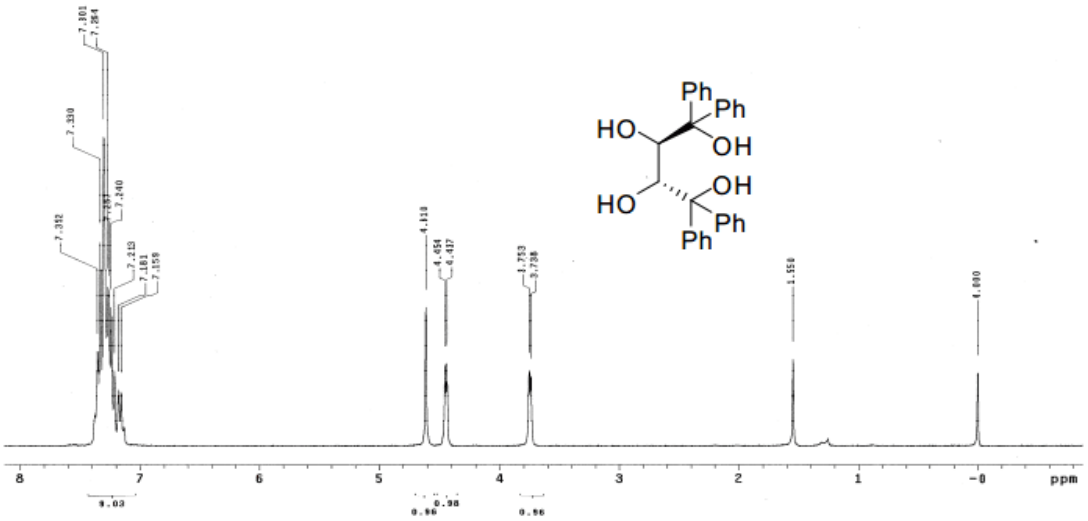
Yield: 72%, m.p.: 190-191 ℃, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.36–7.27 (m, 5H), 7.25–7.21 (m, 2H), 7.17 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.05 (s, 1H), 6.07 (d, *J* = 11.3 Hz, 1H), 5.23 (s, 1H), 5.10 (d, *J* = 13.7 Hz, 1H), 2.35–2.25 (m, 2H), 2.00–1.75 (m, 2H), 1.73–1.55 (m, 3H), 1.52–1.40 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.7, 137.8, 137.3, 133.5, 132.0, 130.0, 129.8, 128.9, 128.6, 127.6, 127.2, 126.6, 112.4, 54.9, 51.0, 26.6, 25.7,

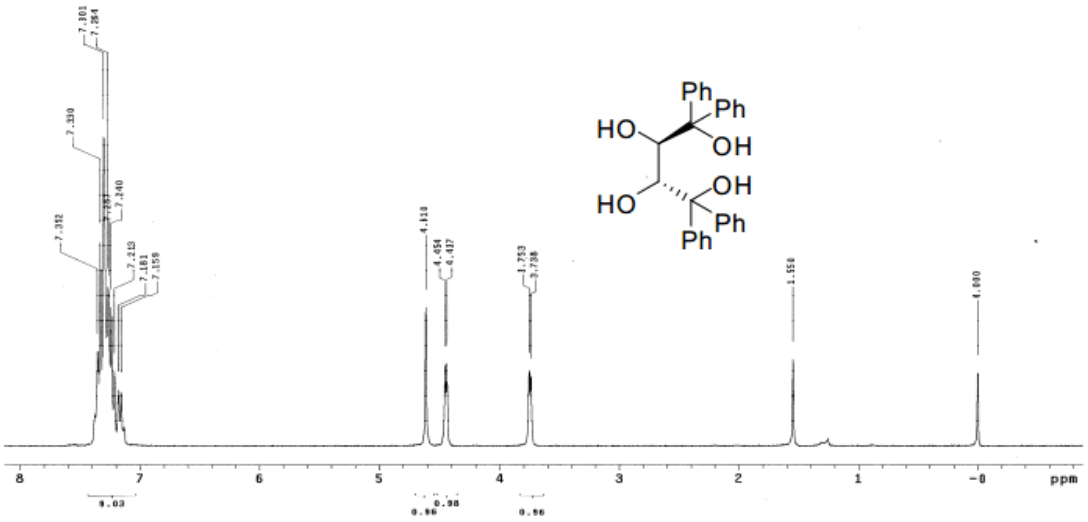
22.8, 21.2. Anal. calc. for $C_{21}H_{21}ClN_2S$: C 68.37, H 5.74; found: C 68.28, H 5.69. Enantiomeric excess: 53%, determined by HPLC (Daicel Chirapak AD-H, hexane/*i*-PrOH = 70/ 30, flow rate 1.5 mL/min): T_R = 6.389 min (minor), T_R= 11.041 min (major).

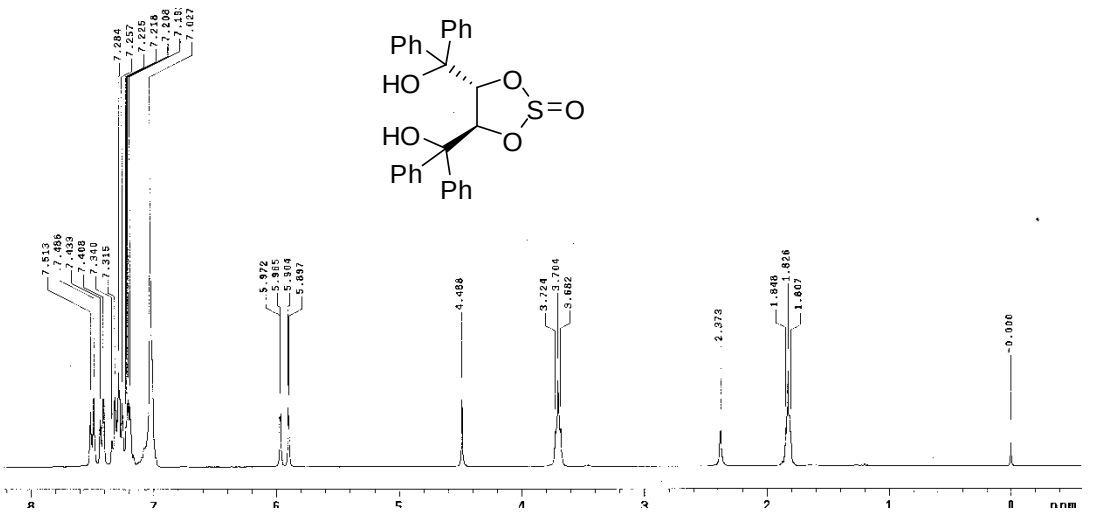
(*R*)-1-Benzyl-4-(4-(*tert*-butyl)phenyl)-3,4,5,6,7,8-hexahydroquinazo-line-2(1*H*)-thione (5k)

Yield: 73%, m.p.: 179-180 ℃, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39–7.29 (m, 4H), 7.28–7.24 (m, 3H), 7.22–7.15 (m, 2H), 6.94 (s, 1H), 5.86 (d, *J* = 9.6 Hz, 1H), 5.30 (d, *J* = 14.3 Hz, 1H), 4.72 (s, 1H), 2.21 (d, *J* = 4.5 Hz, 2H), 1.81 (q, *J* = 6.1 Hz, 2H), 1.64–1.41 (m, 4H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.4, 151.3, 138.4, 138.1, 130.0, 128.6, 127.0, 126.9, 126.4, 125.8, 113.6, 58.9, 51.0, 34.6, 31.3, 26.7, 25.6, 22.8, 21.2. Enantiomeric excess: 20%, determined by HPLC (Daicel Chirapak AD-H, hexane/*i*-PrOH = 70/ 30, flow rate 1.0 mL/min): T_R = 6,262 min (minor), T_R = 10.247 min (major).

II NMR Spectra



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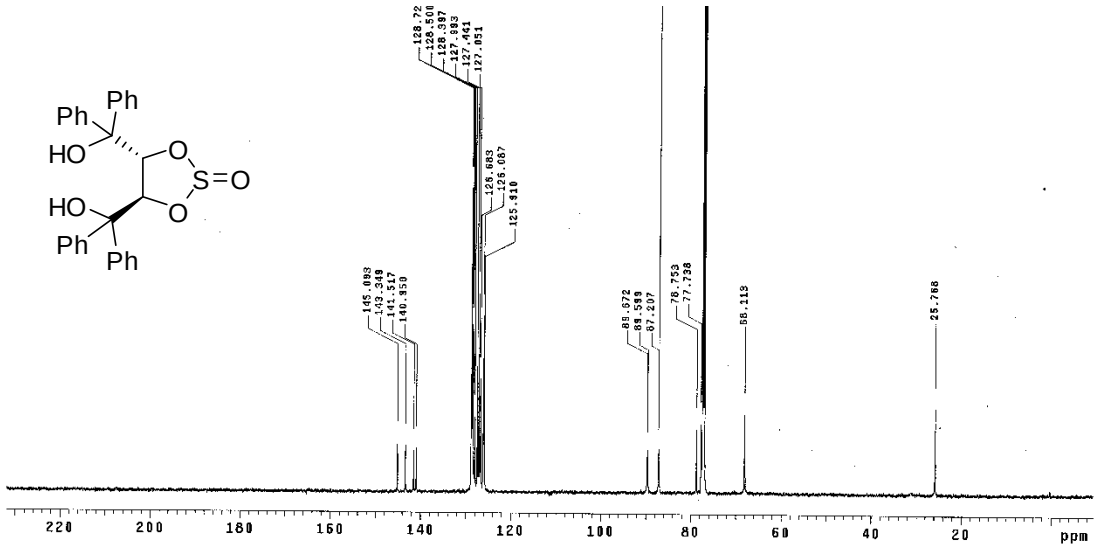
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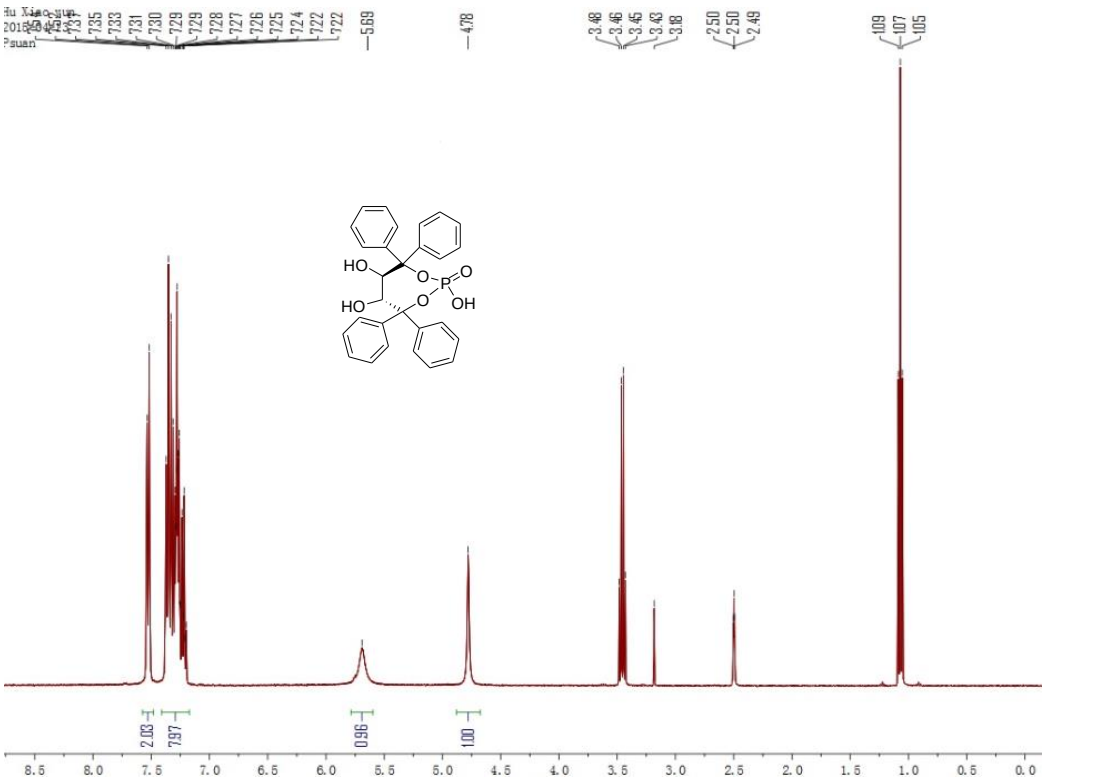
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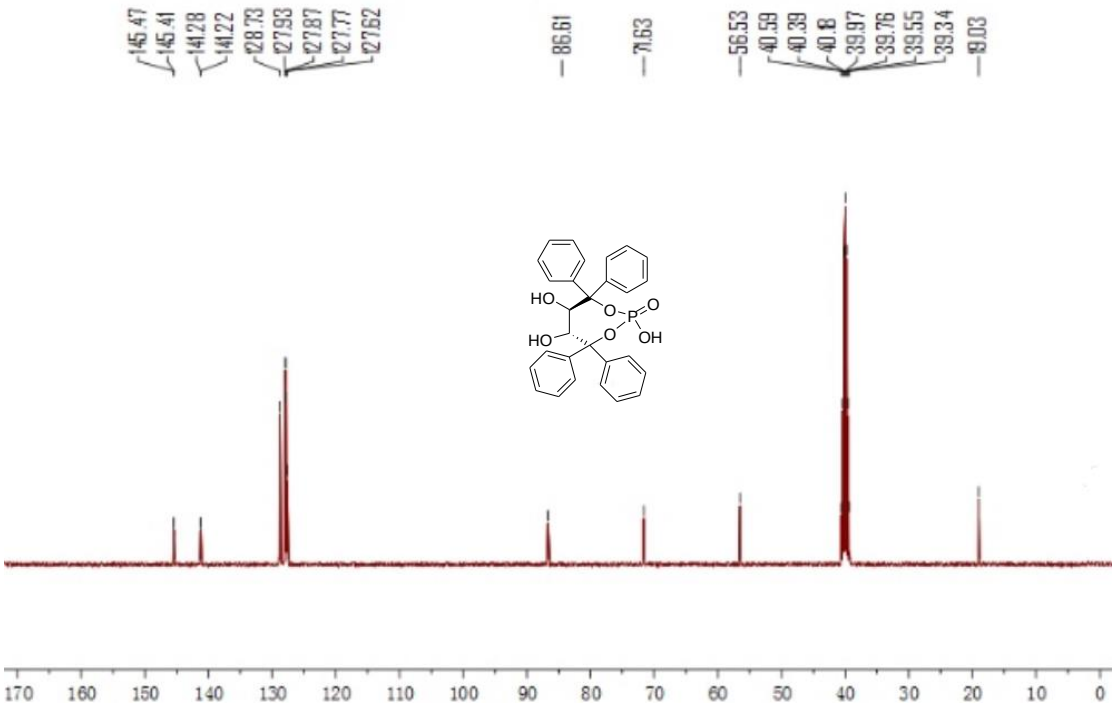
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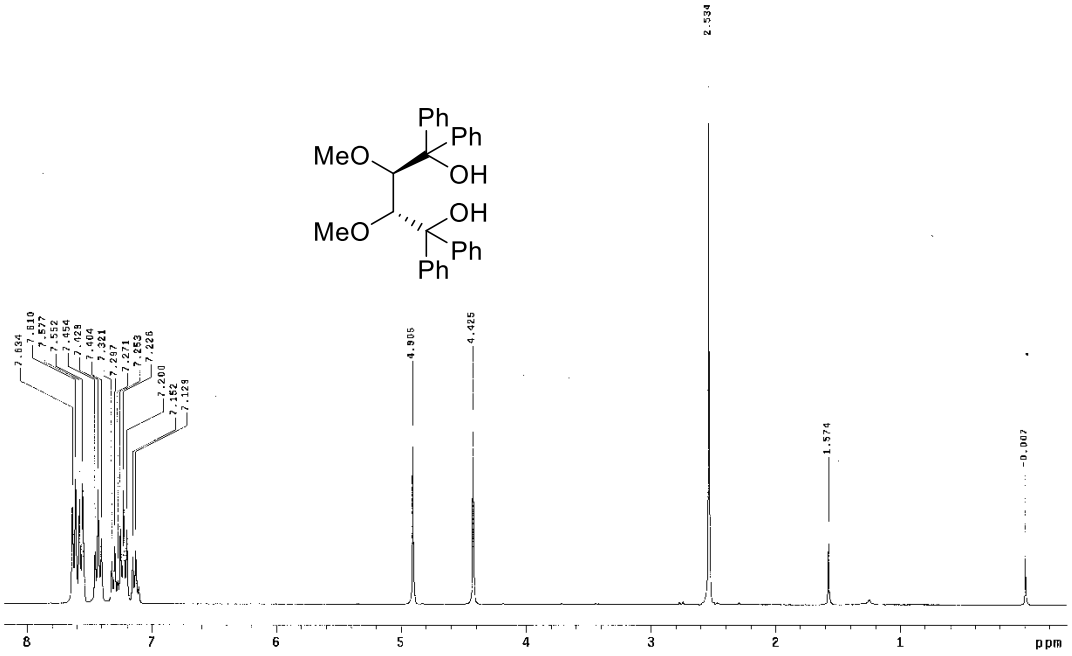
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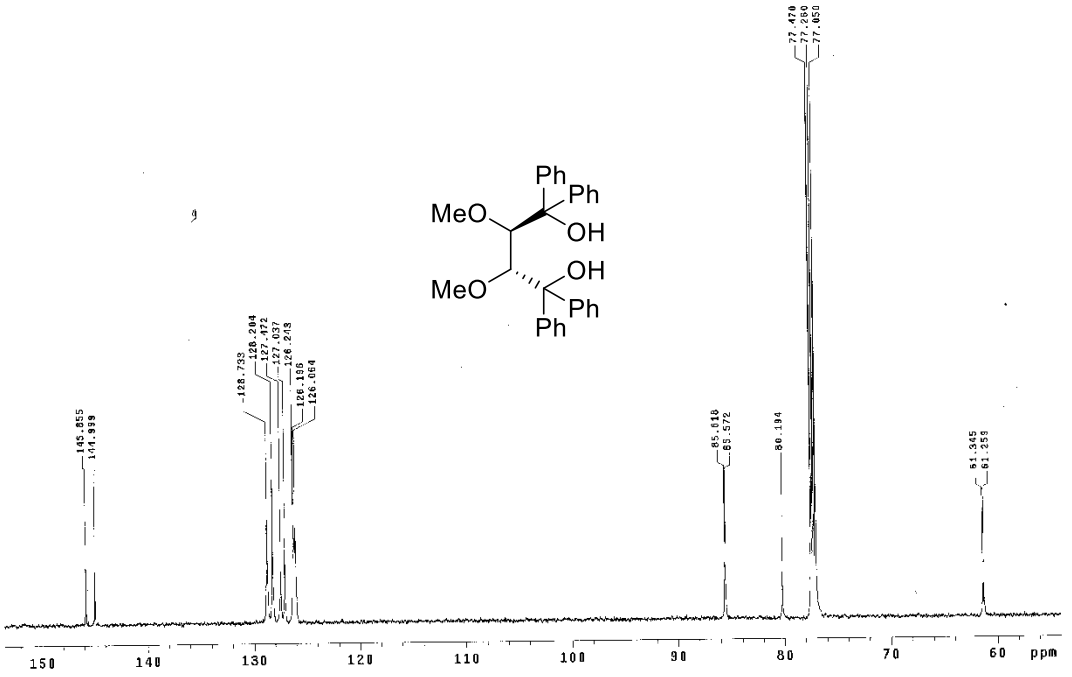
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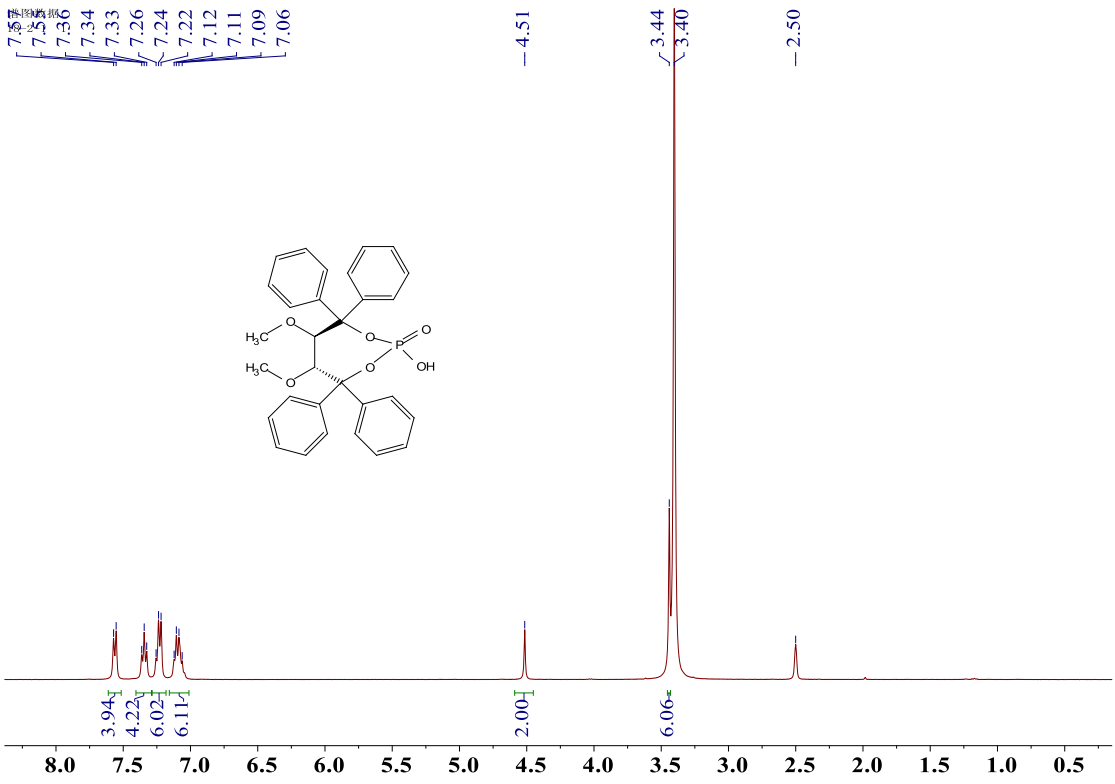
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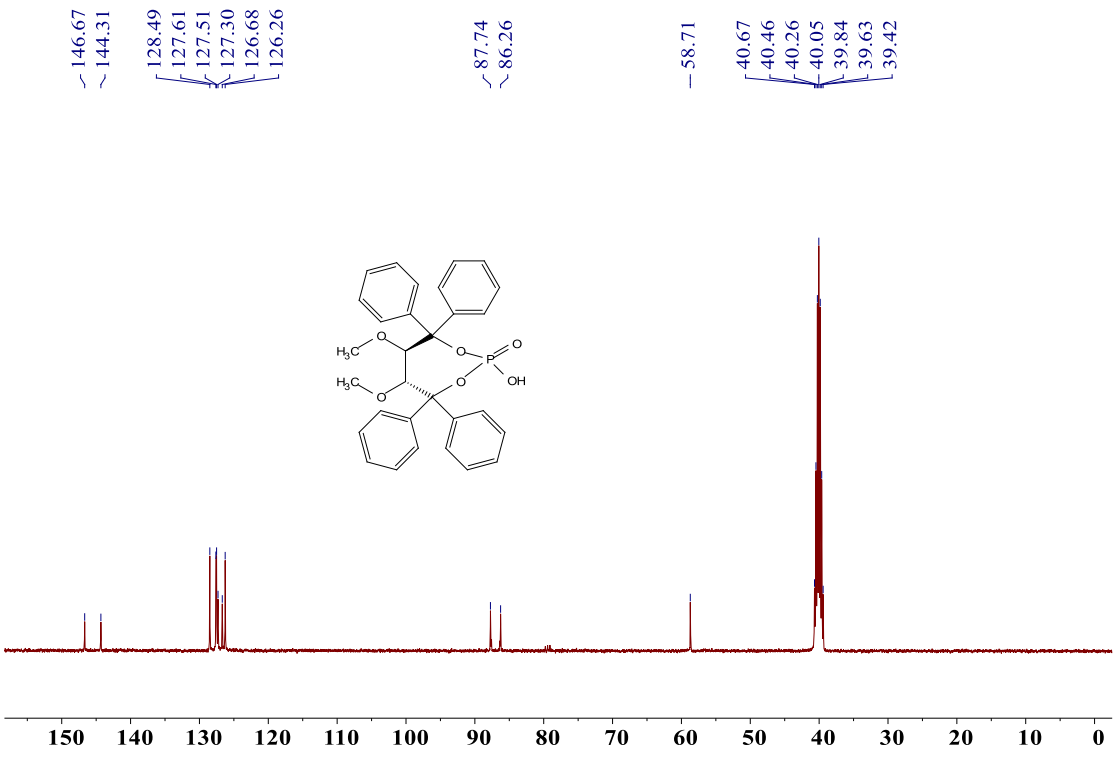
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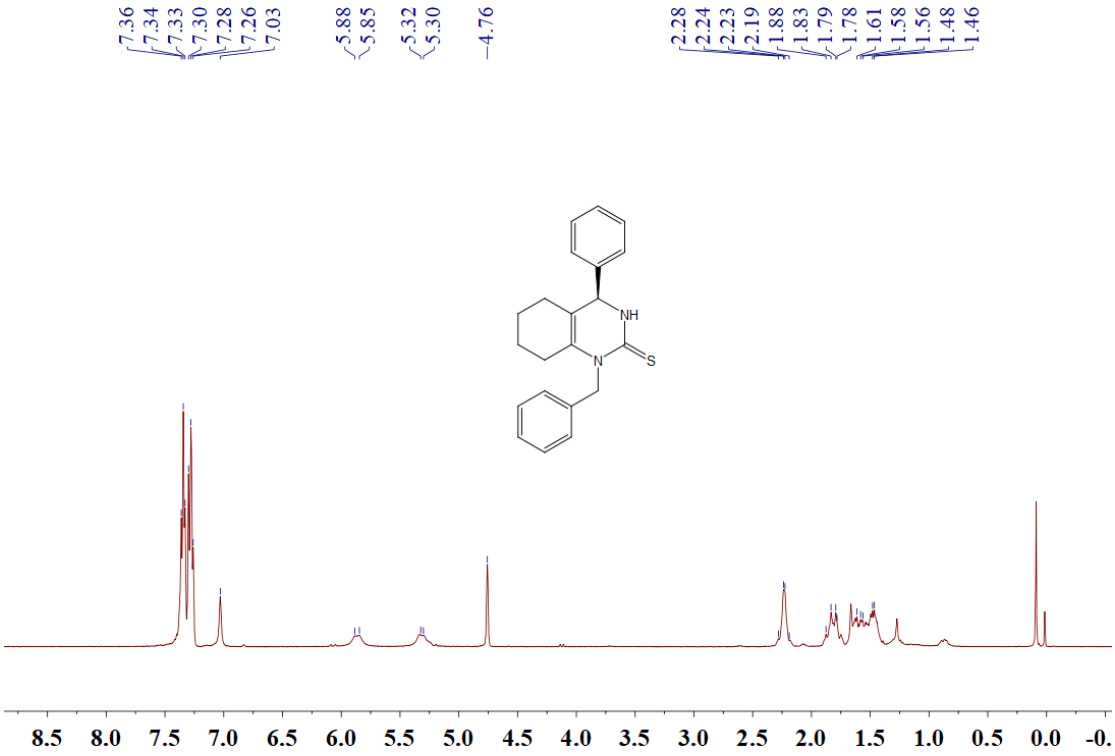
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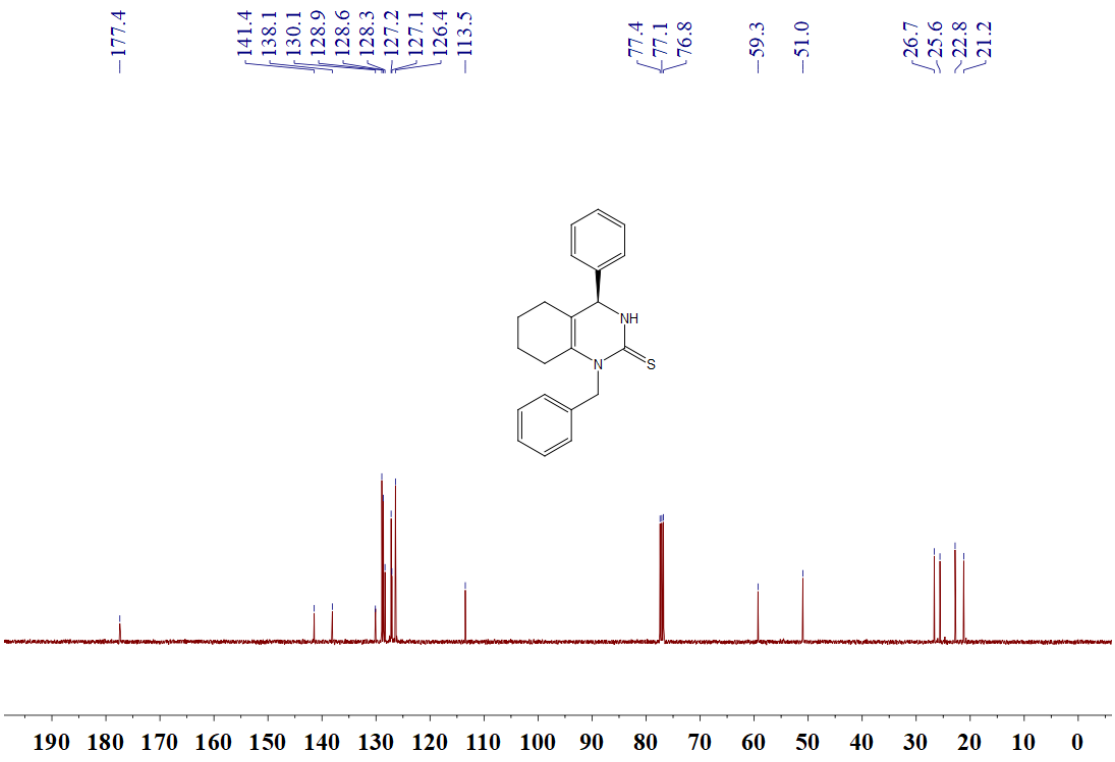
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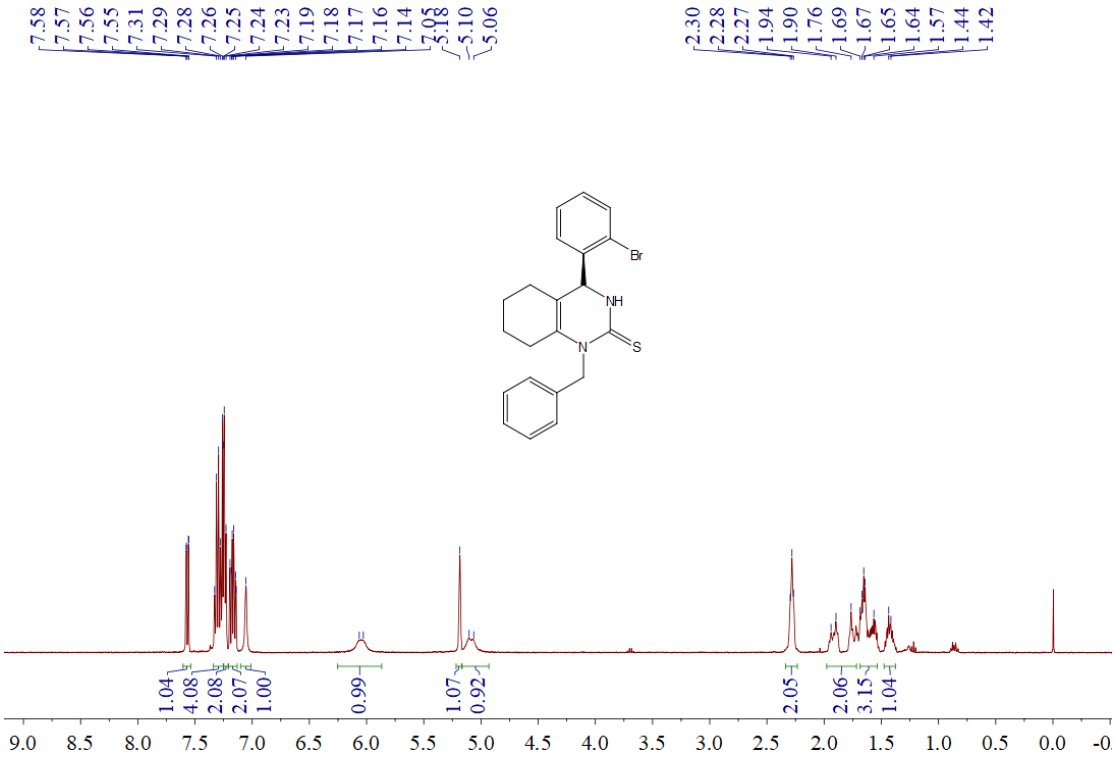
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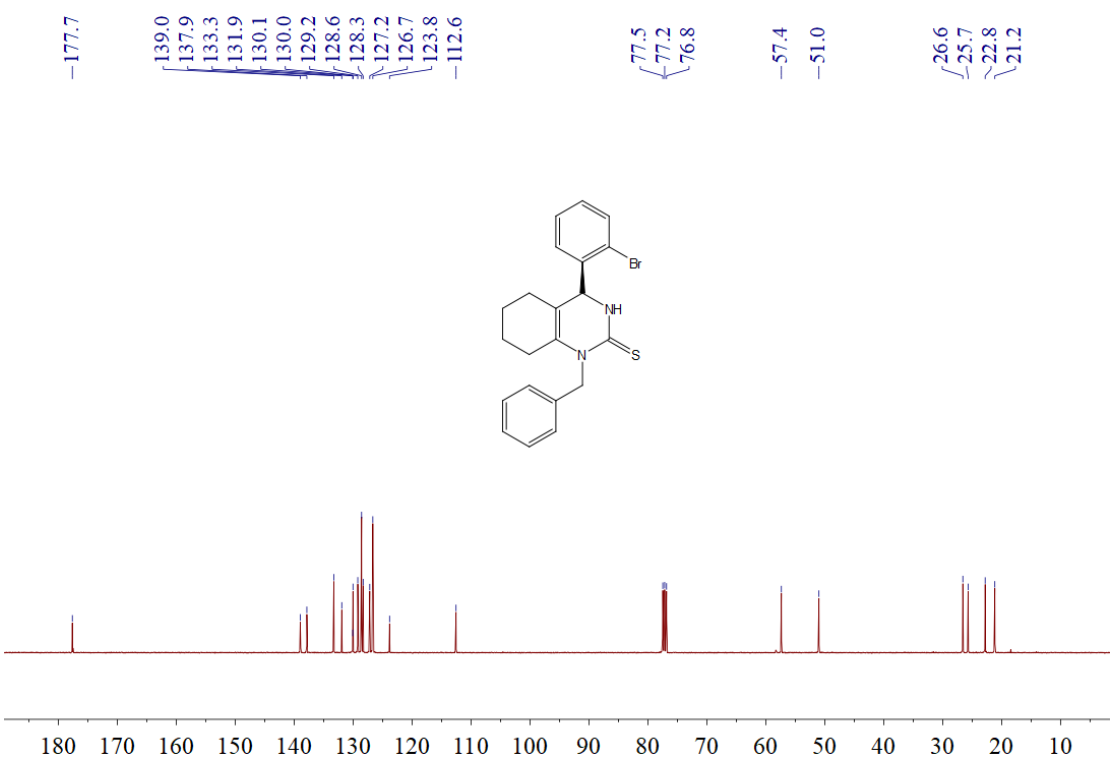
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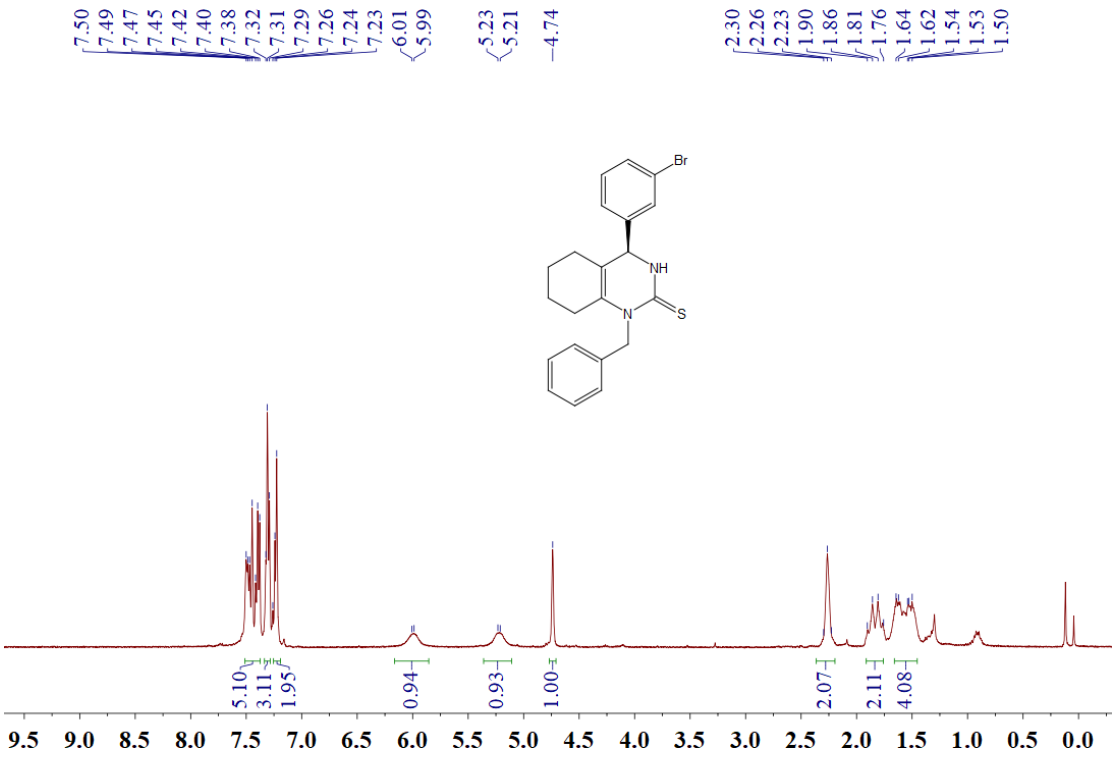
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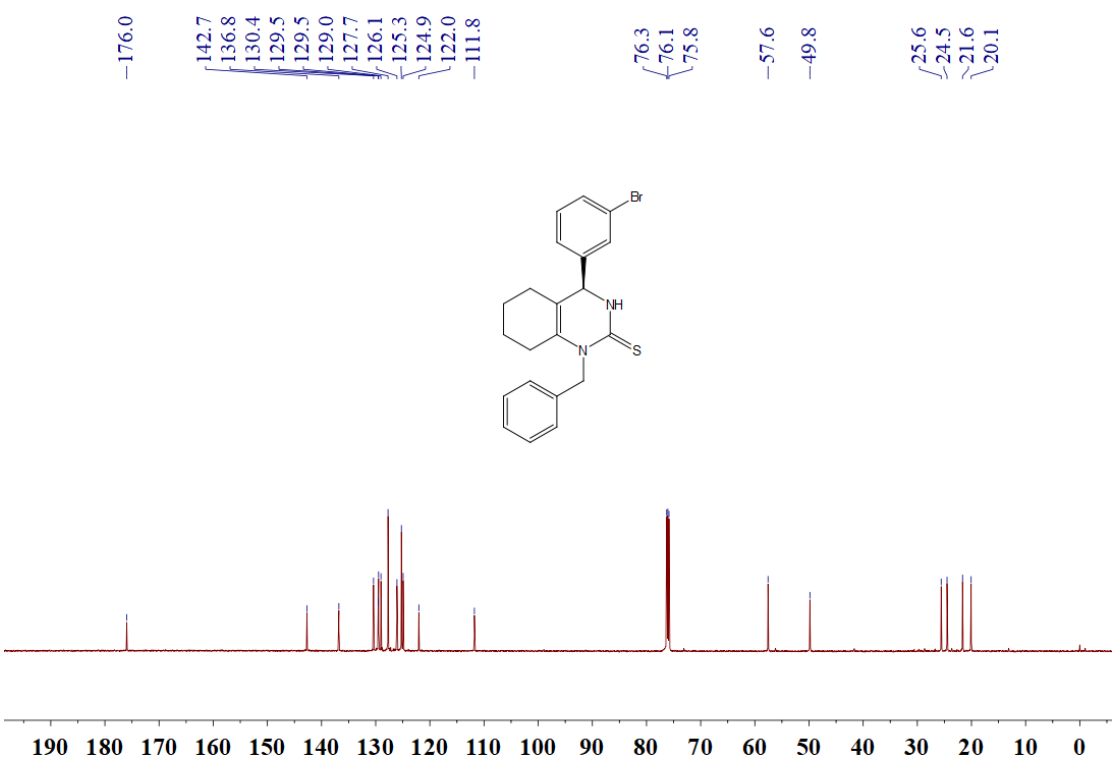
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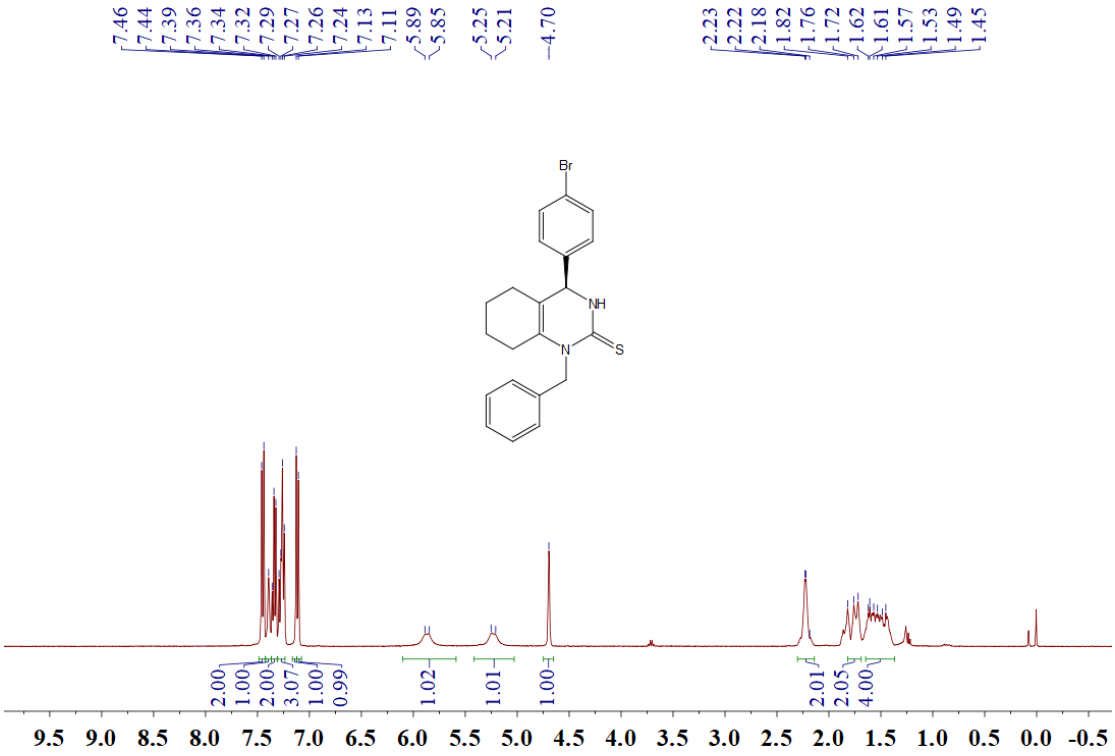
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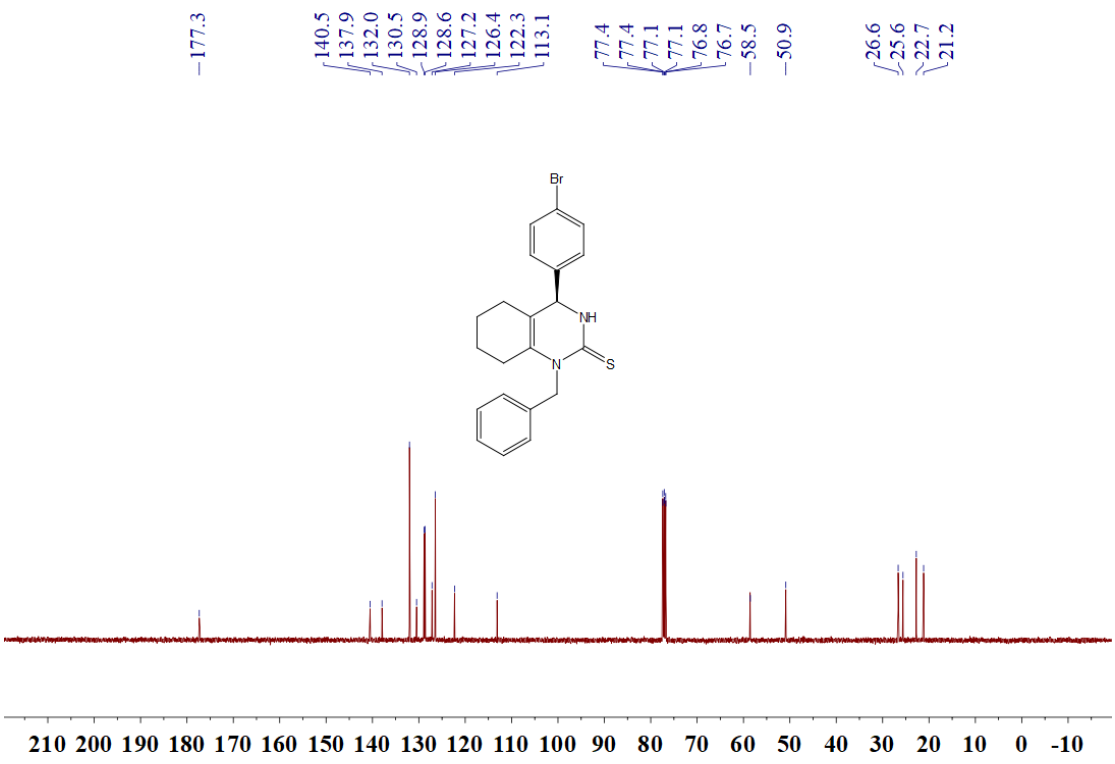
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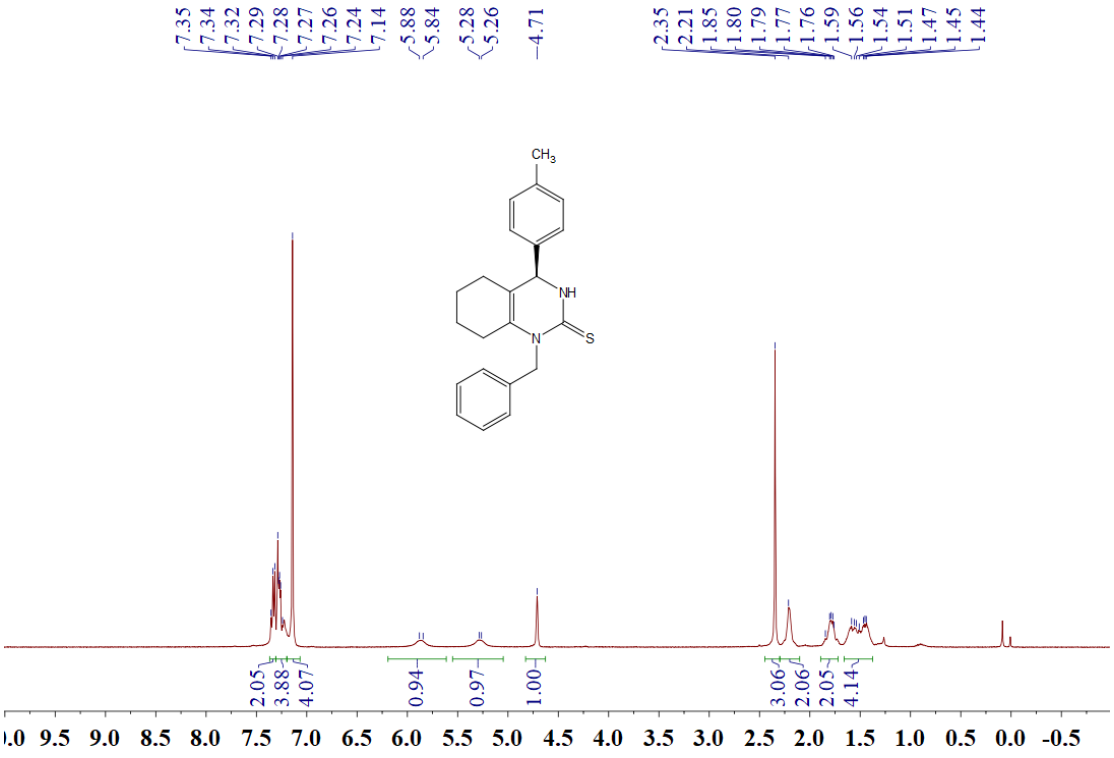
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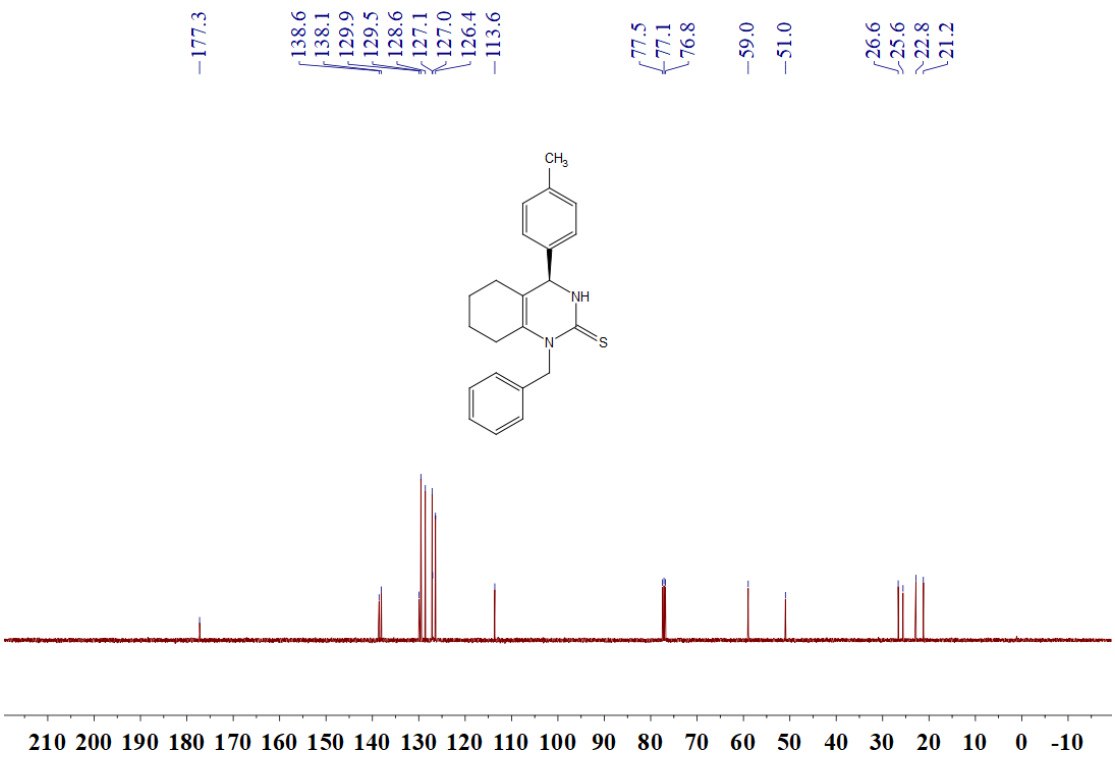
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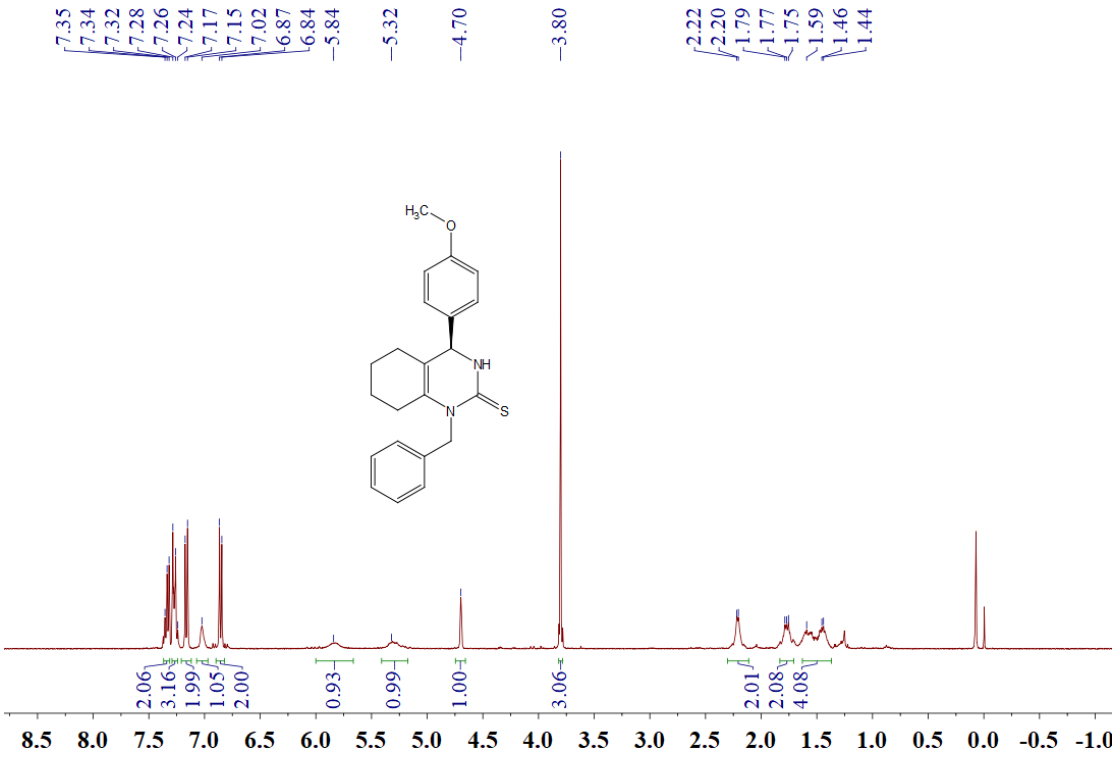
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2.08
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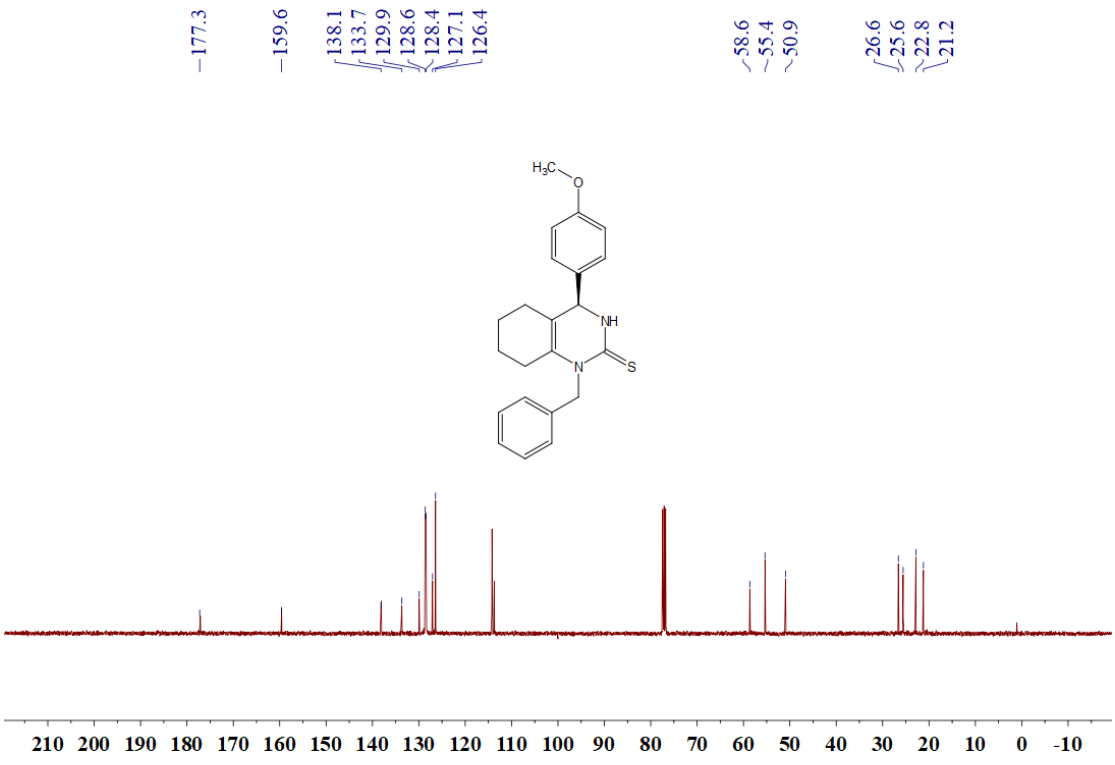
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O
NH
N
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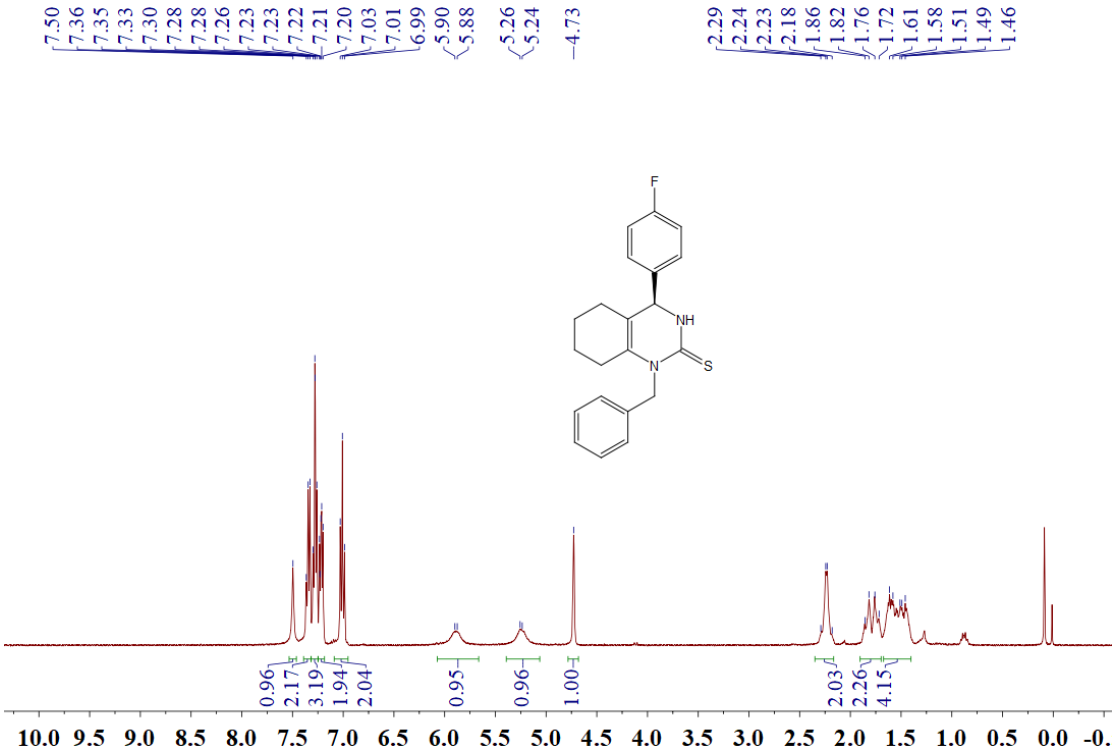
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S
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3.19
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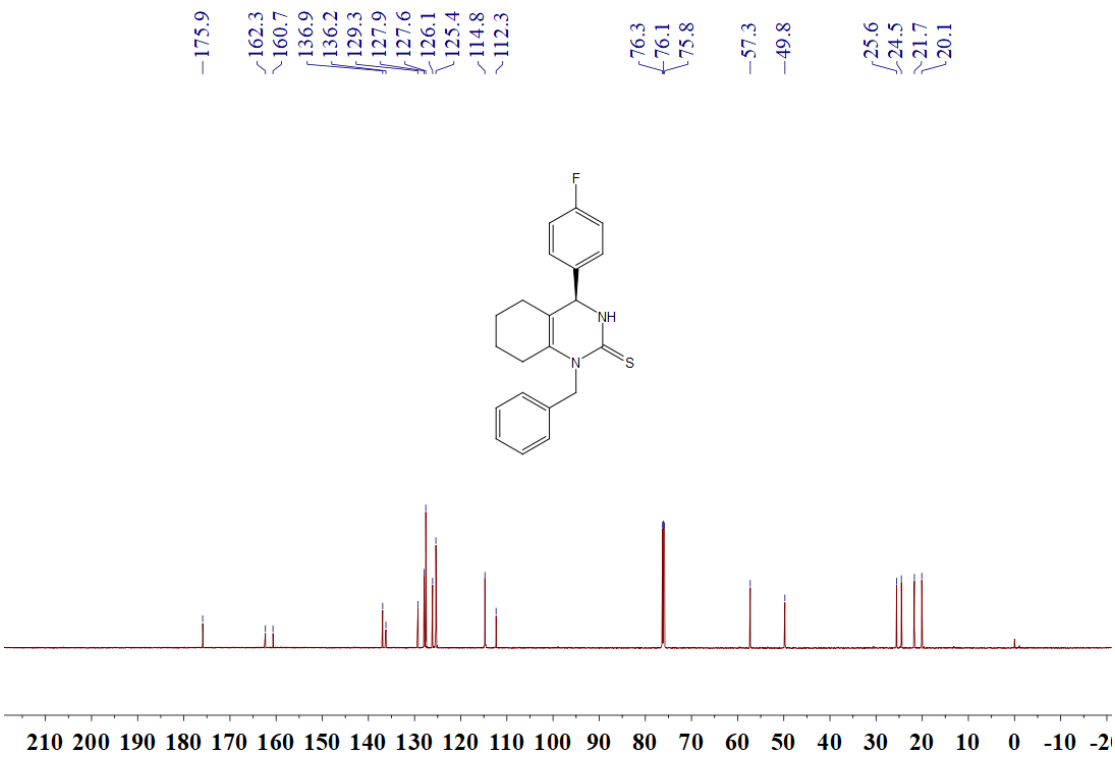
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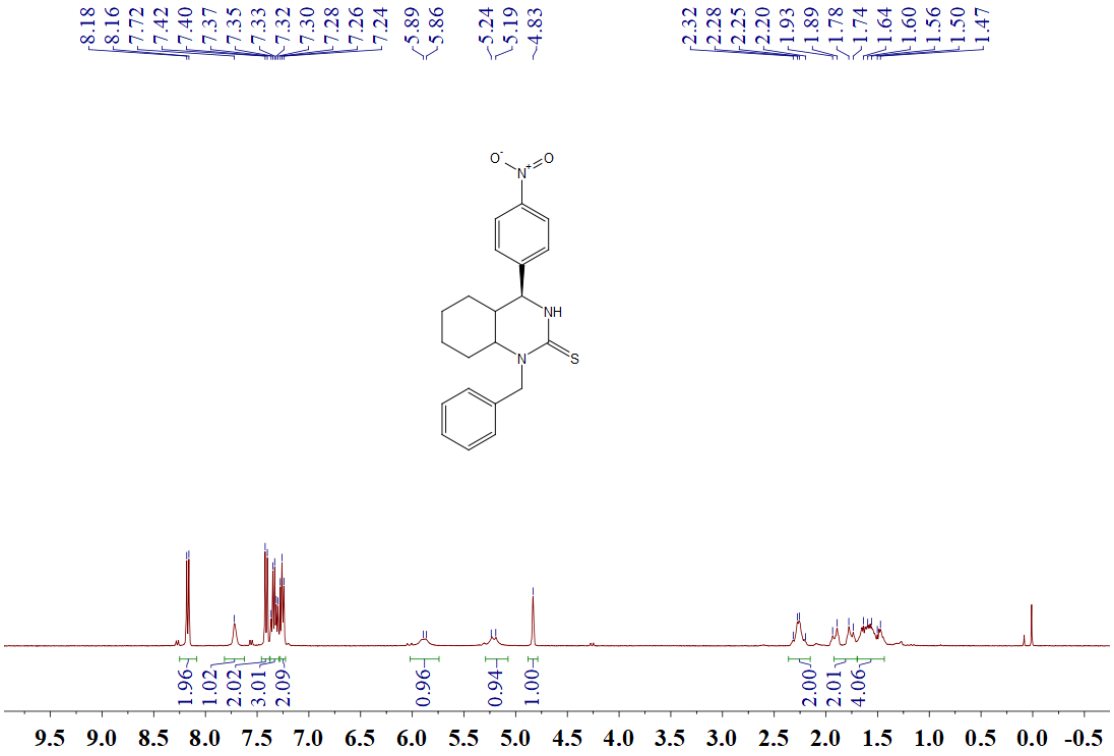
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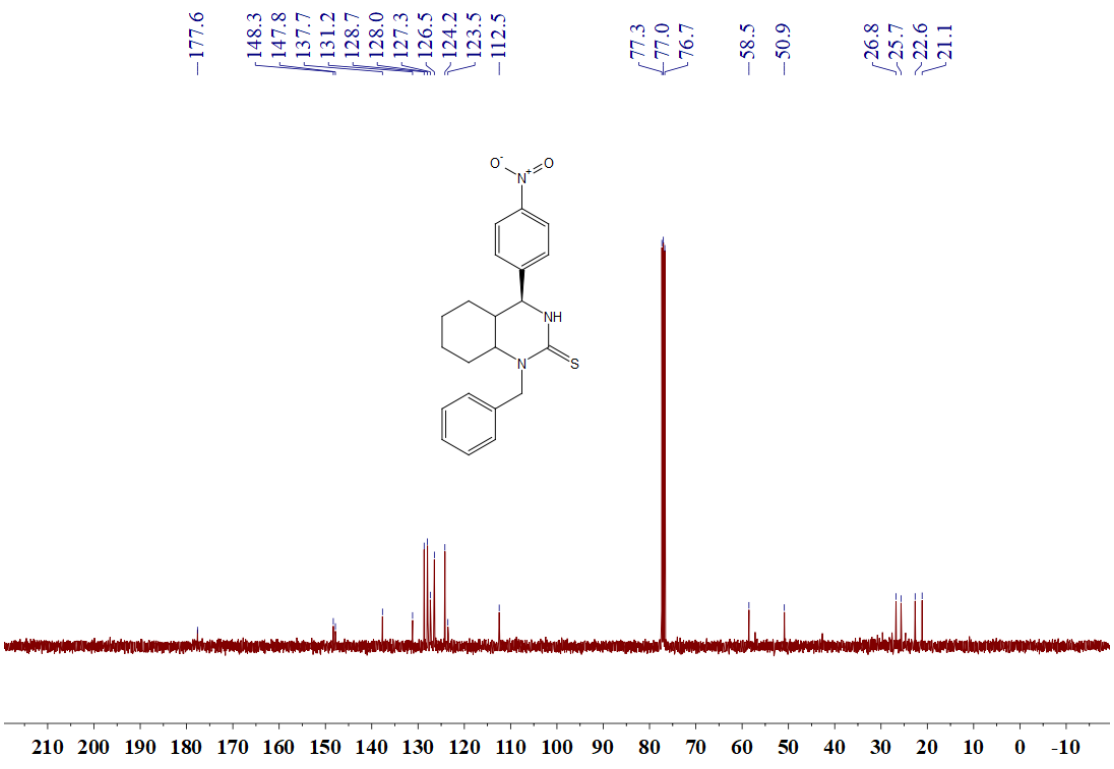
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NH
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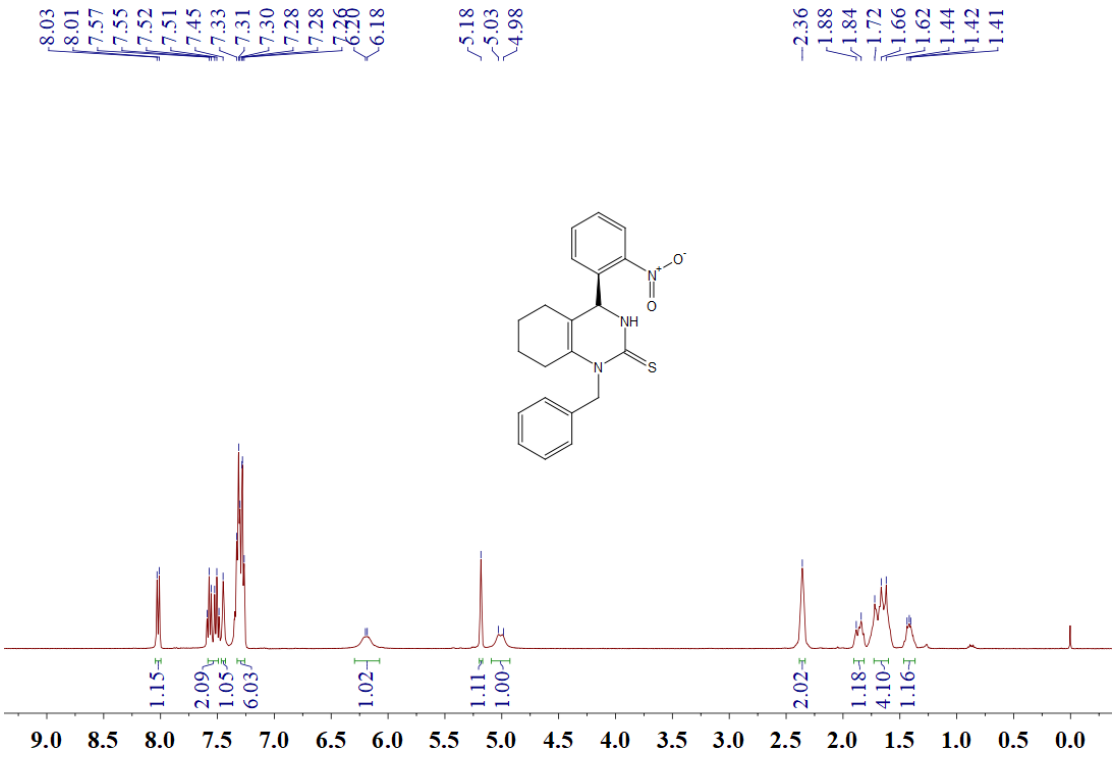
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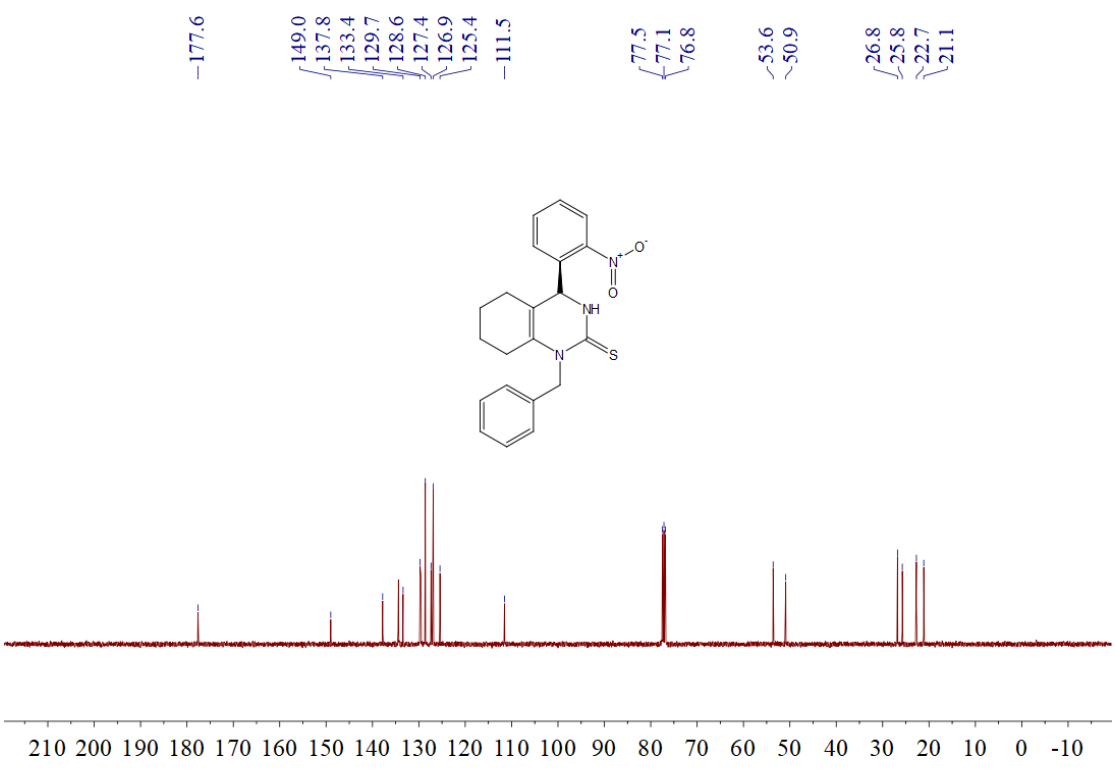
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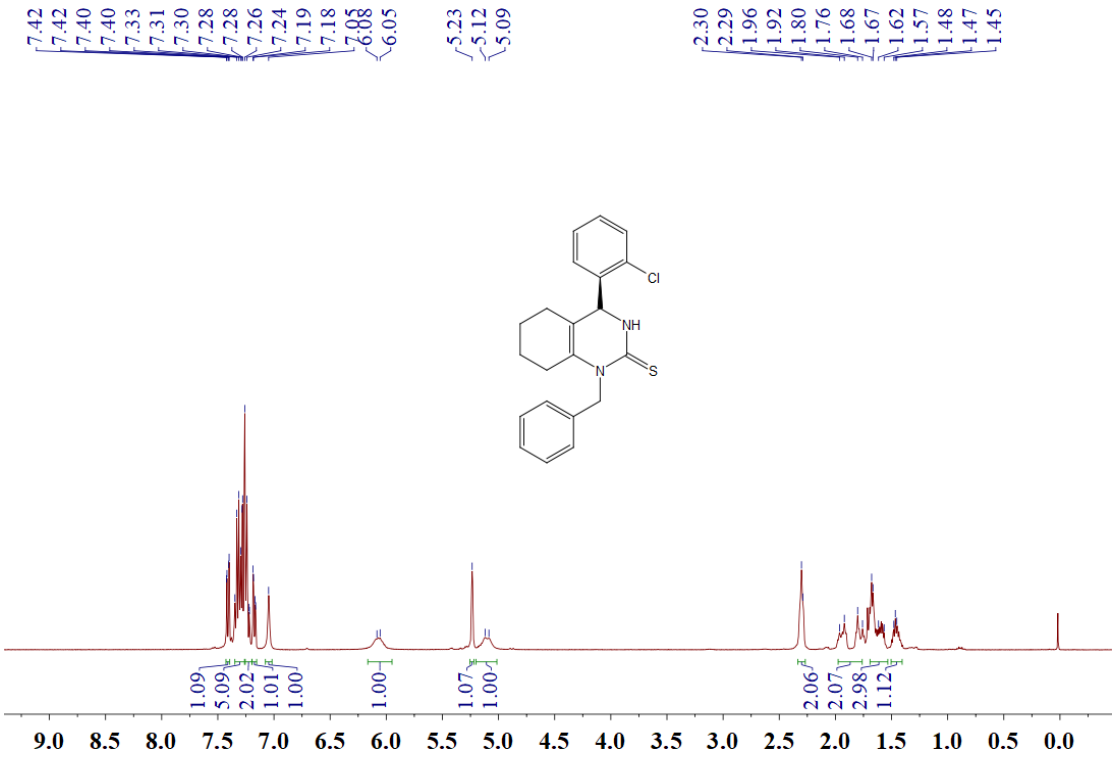
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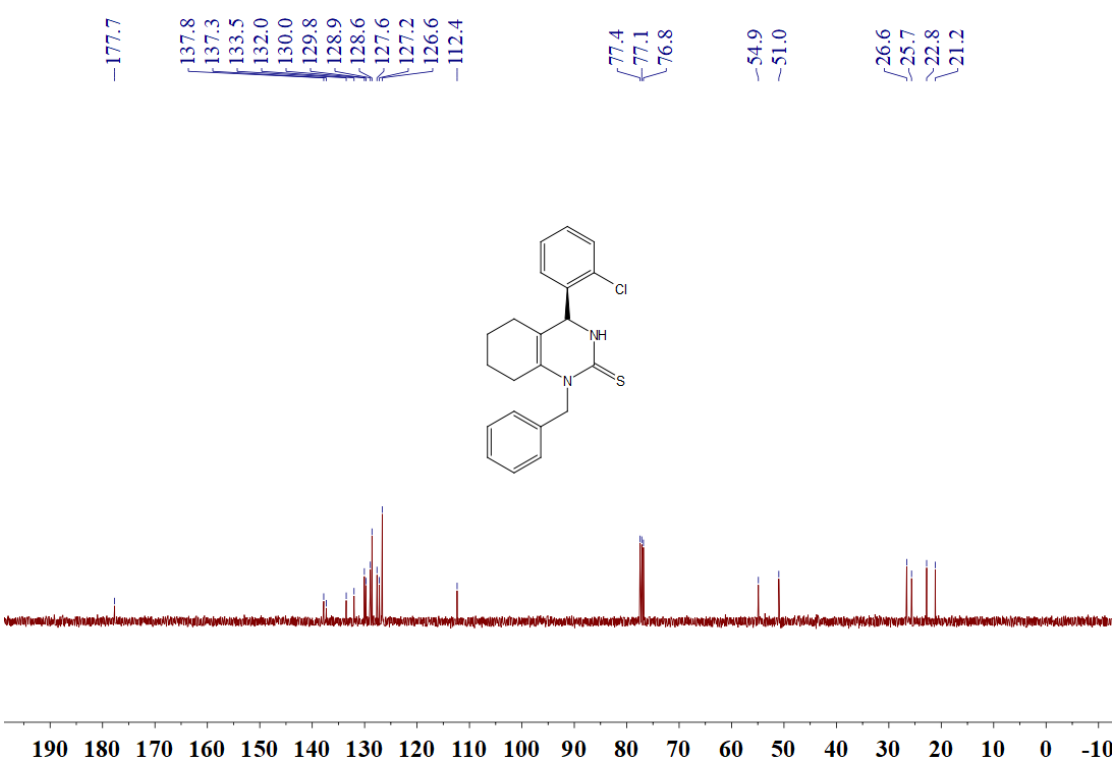
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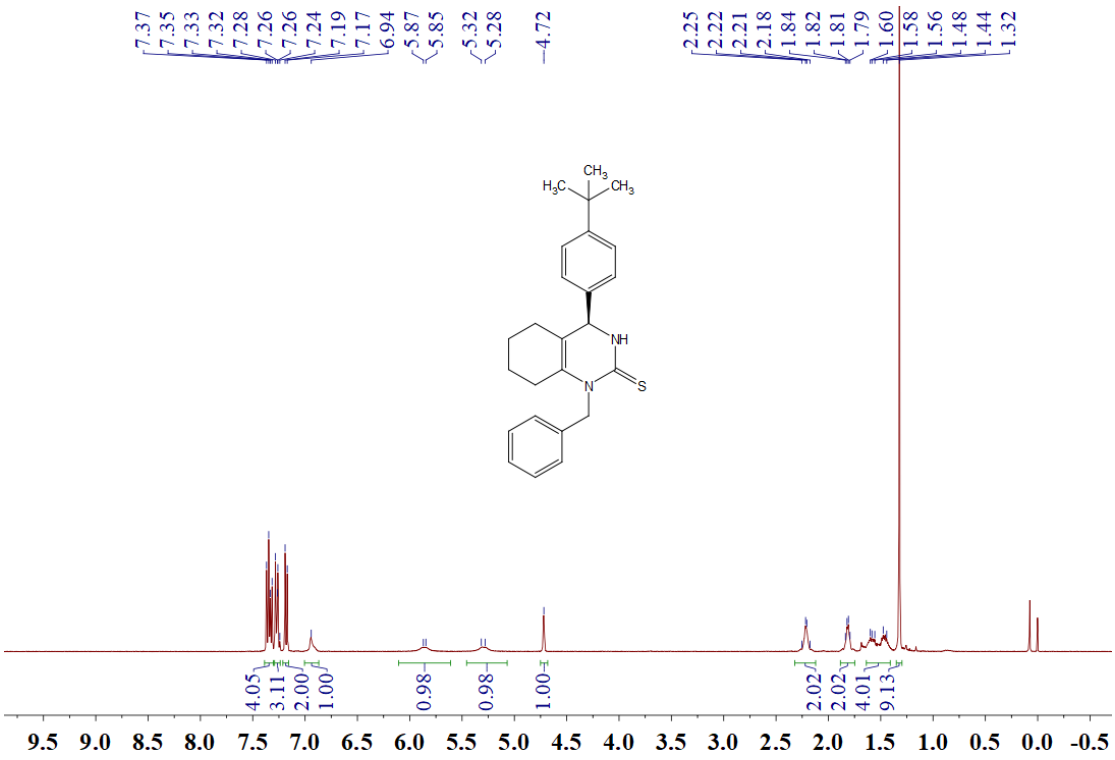
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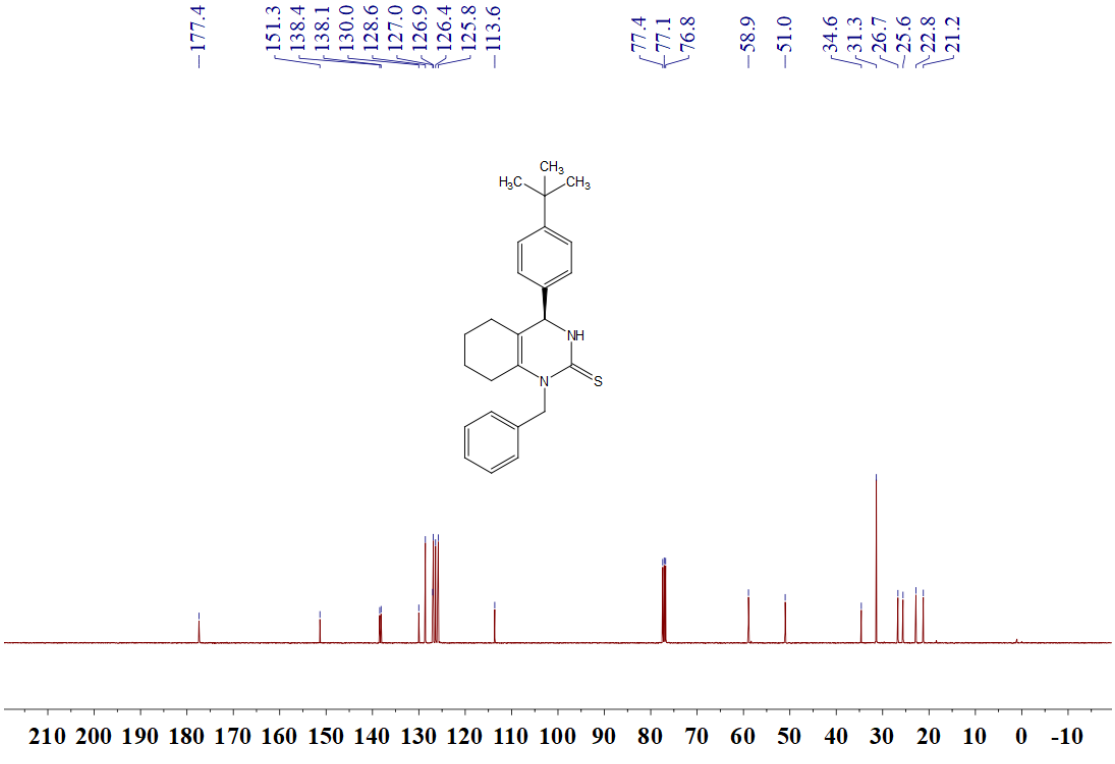
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CH3
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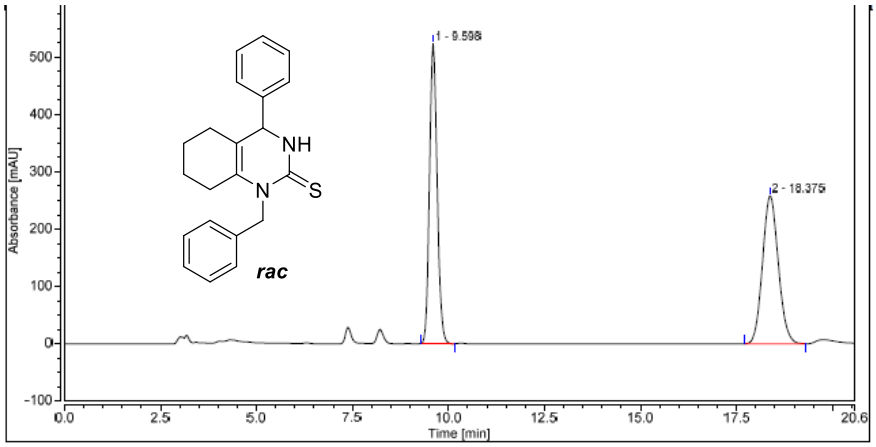
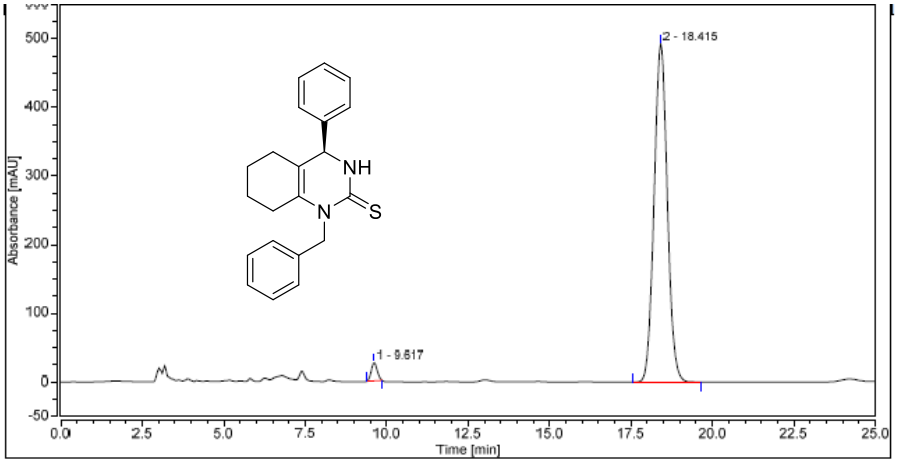
III HPLC analysis



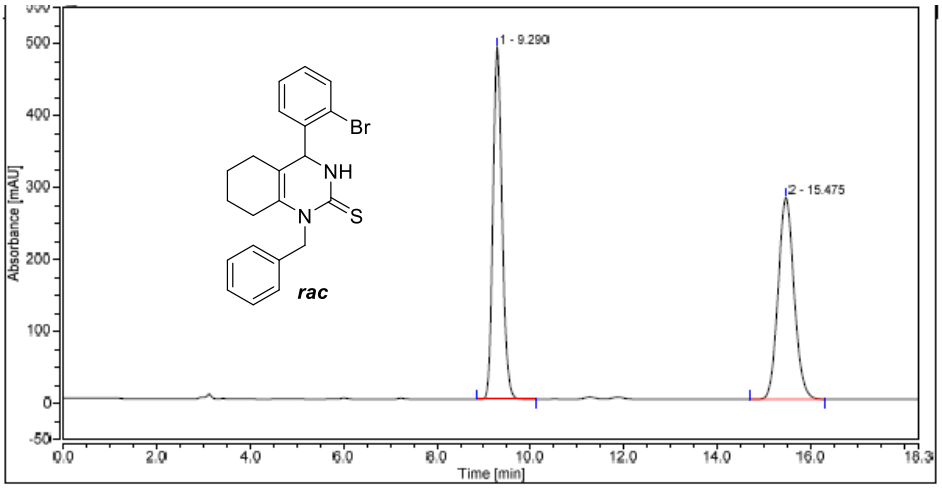
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.598	121.033	523.676	49.63	66.97	n.a.
2		18.375	122.849	258.316	50.37	33.03	n.a.
Total:			**243.881**	**781.992**	**100.00**	**100.00**	



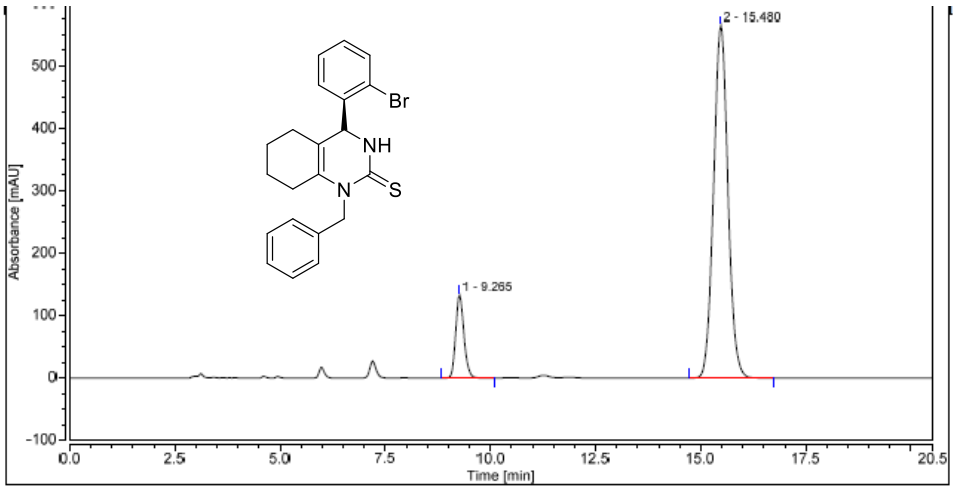
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.617	5.584	26.324	2.35	5.08	n.a.
2		18.415	231.823	492.353	97.65	94.92	n.a.
Total:			**237.407**	**518.676**	**100.00**	**100.00**	



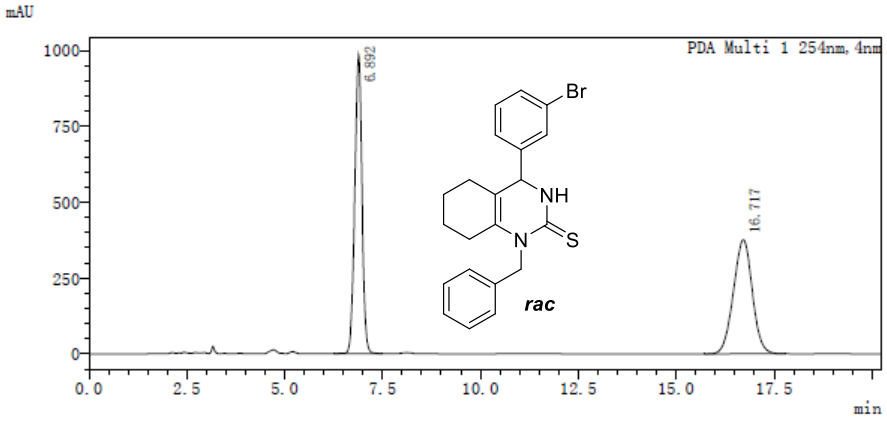
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.290	110.609	488.672	49.94	63.54	n.a.
2		15.475	110.871	280.360	50.06	36.46	n.a.
Total:			**221.480**	**769.032**	**100.00**	**100.00**	



Integration Results

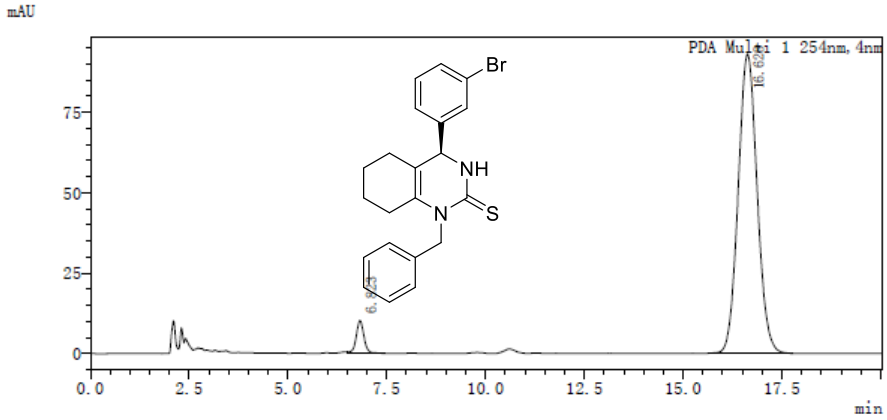
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.265	30.185	133.170	11.90	19.07	n.a.
2		15.480	223.485	565.043	88.10	80.93	n.a.
Total:			**253.669**	**698.212**	**100.00**	**100.00**	



〈峰表〉

PDA Ch1 254nm

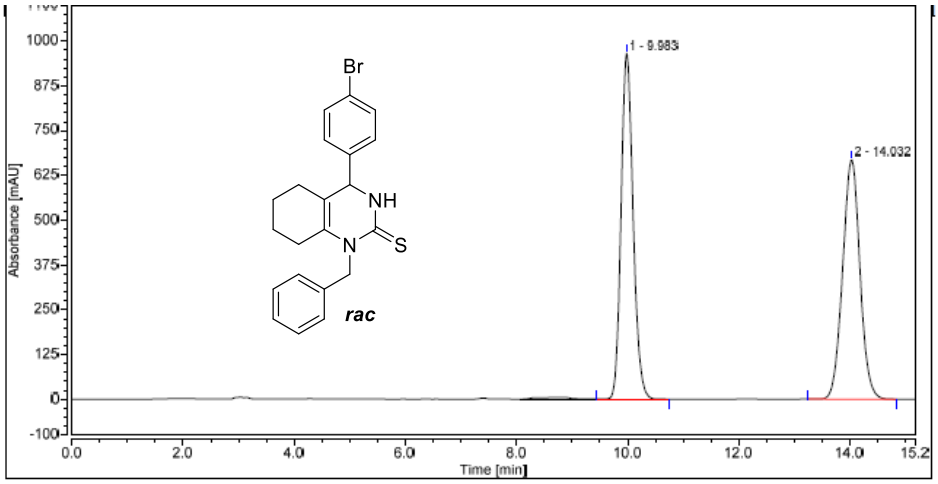
峰号	保留时间	面积	高度	面积%	高度%
1	6.892	12652770	985980	50.067	72.400
2	16.717	12618913	375878	49.933	27.600
总计		25271683	1361858	100.000	100.000



〈峰表〉

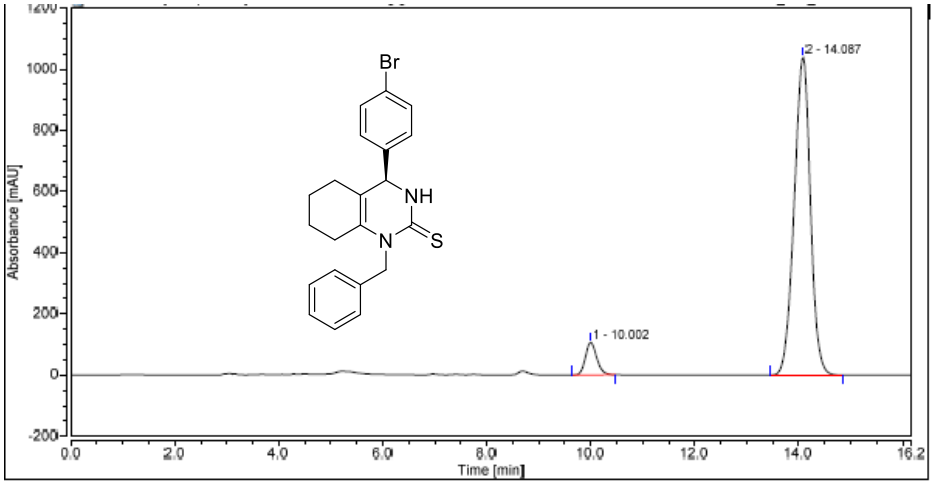
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	6.823	137950	10155	4.268	9.852
2	16.628	3094121	92923	95.732	90.148
总计		3232072	103078	100.000	100.000



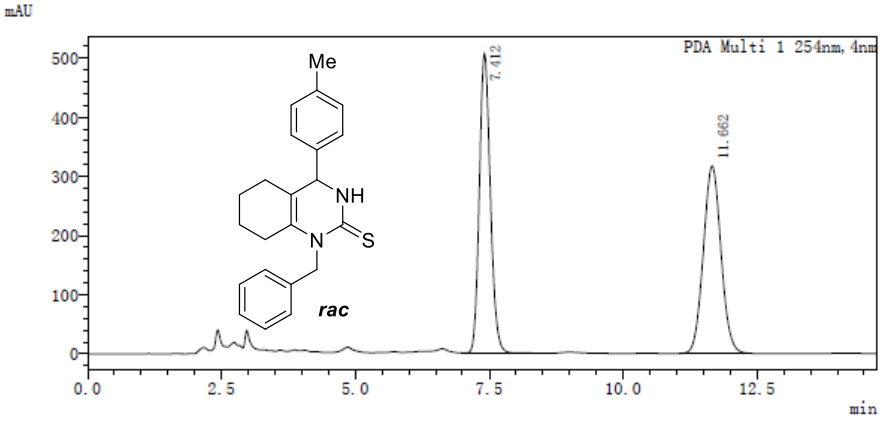
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.983	242.184	964.838	50.07	59.06	n.a.
2		14.032	241.482	668.843	49.93	40.94	n.a.
Total:			**483.666**	**1633.681**	**100.00**	**100.00**	



Integration Results

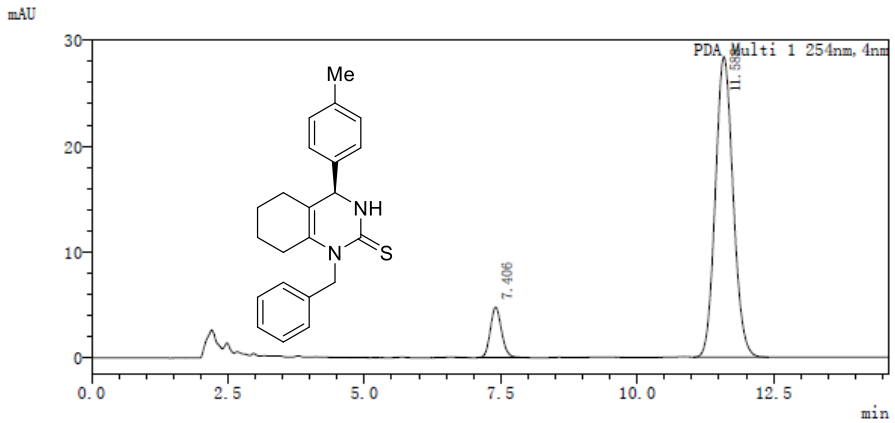
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.002	26.509	106.201	6.58	9.27	n.a.
2		14.087	376.576	1039.589	93.42	90.73	n.a.
Total:			**403.085**	**1145.790**	**100.00**	**100.00**	



〈峰表〉

PDA Ch1 254nm

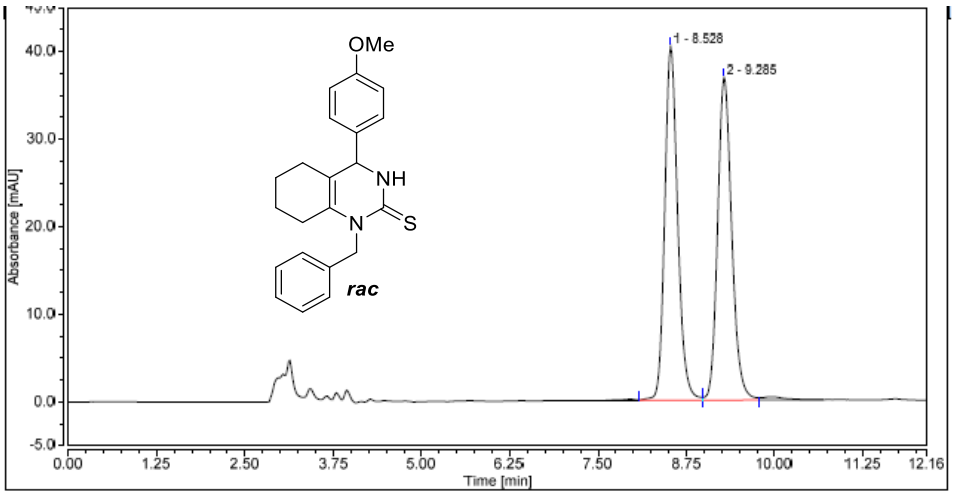
峰号	保留时间	面积	高度	面积%	高度%
1	7.412	7210578	506040	49.876	61.521
2	11.662	7246523	316505	50.124	38.479
总计		14457101	822546	100.000	100.000



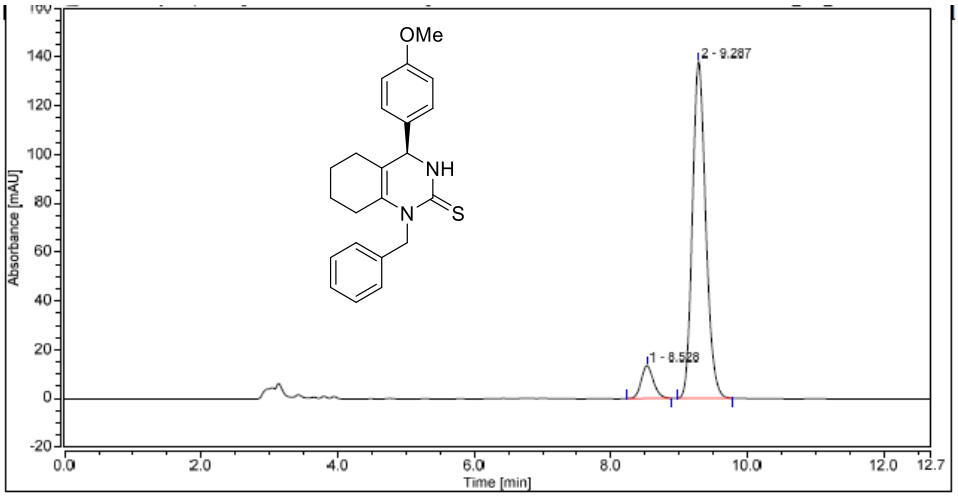
〈峰表〉

PDA Ch1 254nm

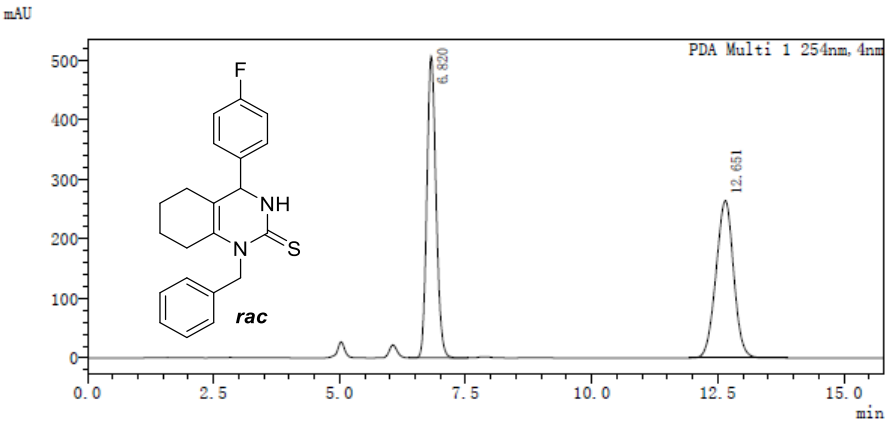
峰号	保留时间	面积	高度	面积%	高度%
1	7.406	68164	4771	9.593	14.395
2	11.588	642420	28370	90.407	85.605
总计		710584	33141	100.000	100.000



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.528	8.544	40.406	50.13	52.31	n.a.
2		9.285	8.499	36.834	49.87	47.69	n.a.
Total:			**17.042**	**77.240**	**100.00**	**100.00**	



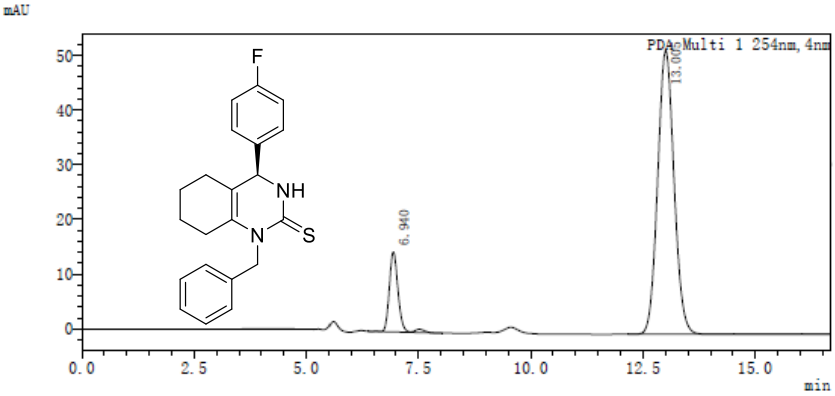
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.528	2.800	13.500	8.21	8.90	n.a.
2		9.287	31.288	138.100	91.79	91.10	n.a.
Total:			**34.088**	**151.599**	**100.00**	**100.00**	



〈峰表〉

PDA Ch1 254nm

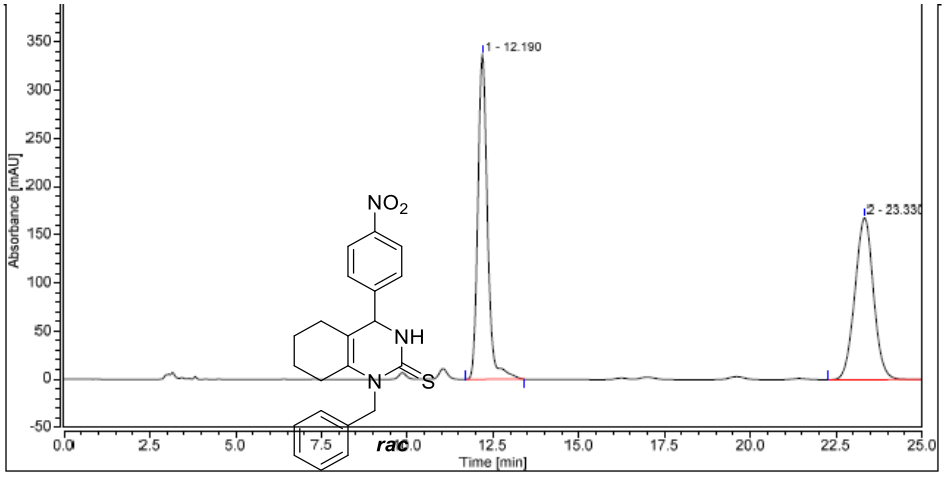
峰号	保留时间	面积	高度	面积%	高度%
1	6.820	6423215	506471	49.986	65.713
2	12.651	6426730	264264	50.014	34.287
总计		12849945	770735	100.000	100.000



〈峰表〉

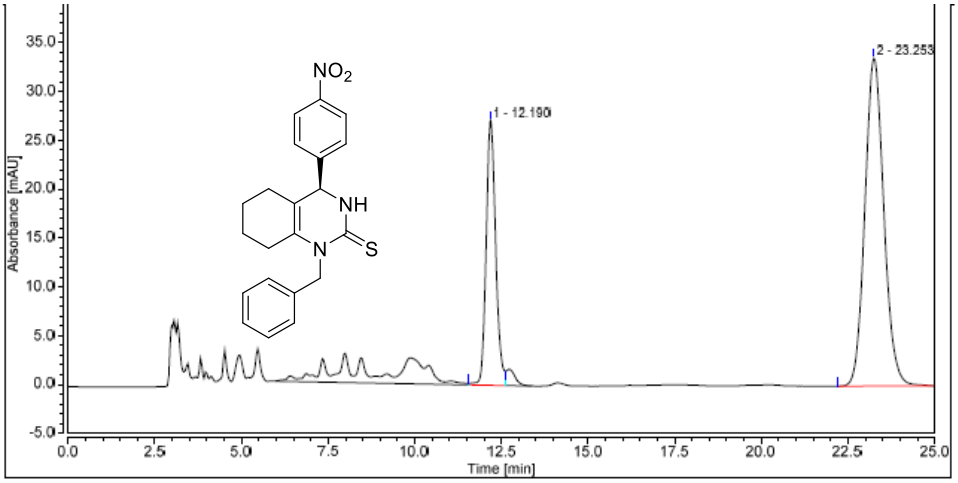
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	6.940	203650	14641	13.434	22.031
2	13.005	1312267	51816	86.566	77.969
总计		1515917	66457	100.000	100.000



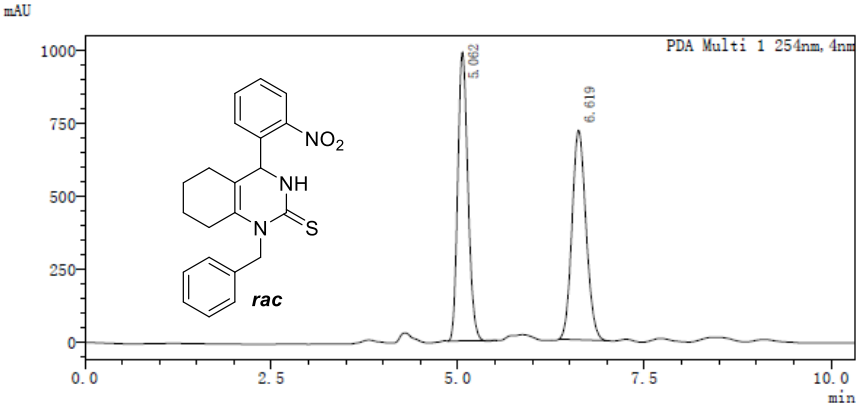
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.190	110.006	337.164	50.99	66.71	n.a.
2		23.330	105.717	168.237	49.01	33.29	n.a.
Total:			**215.723**	**505.400**	**100.00**	**100.00**	



Integration Results

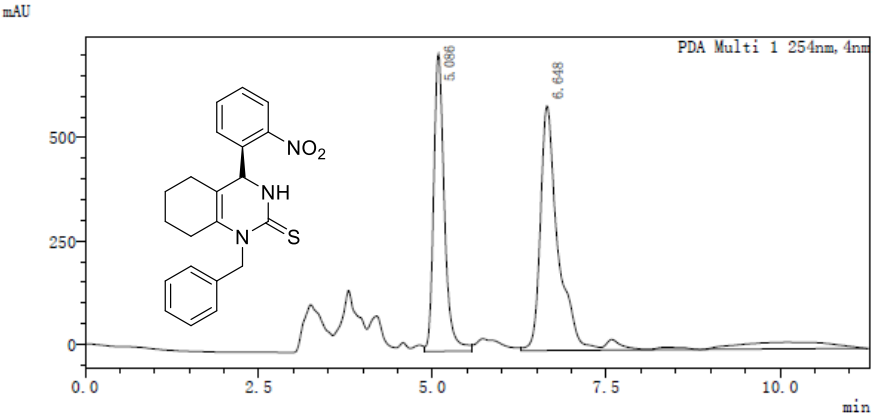
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.190	8.622	27.114	28.83	44.67	n.a.
2		23.253	21.284	33.581	71.17	55.33	n.a.
Total:			**29.907**	**60.695**	**100.00**	**100.00**	



〈峰表〉

PDA Ch1 254nm

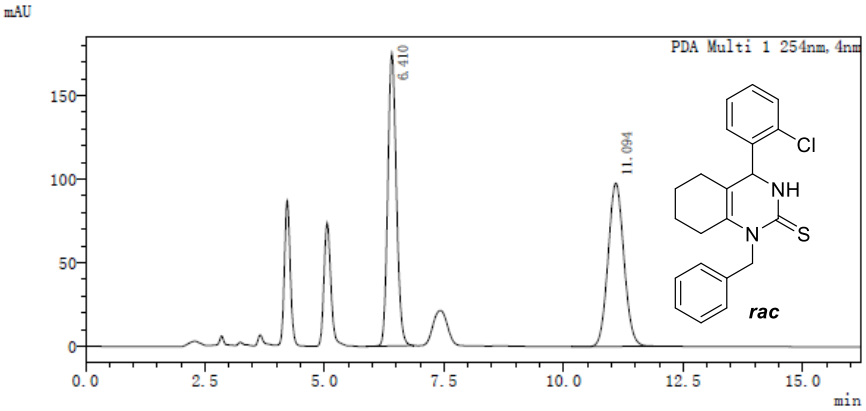
峰号	保留时间	面积	高度	面积%	高度%
1	5.062	9311879	986257	49.855	57.989
2	6.619	9365977	714519	50.145	42.011
总计		18677855	1700776	100.000	100.000



〈峰表〉

PDA Ch1 254nm

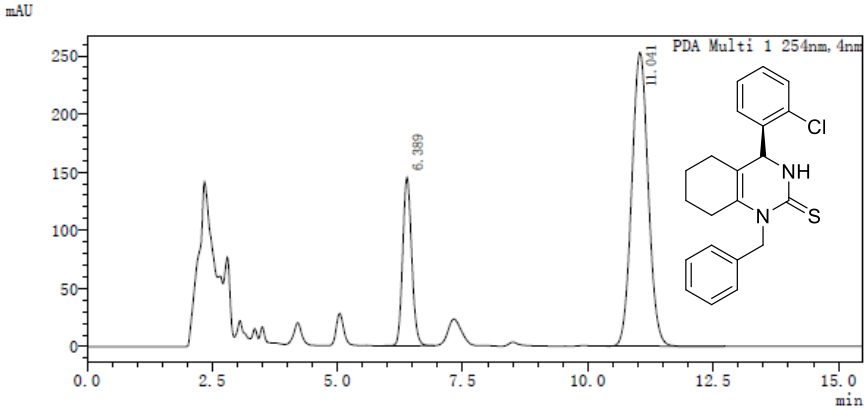
峰号	保留时间	面积	高度	面积%	高度%
1	5.086	7733980	720440	38.215	54.880
2	6.648	12503996	592312	61.785	45.120
总计		20237976	1312752	100.000	100.000



〈峰表〉

PDA Ch1 254nm

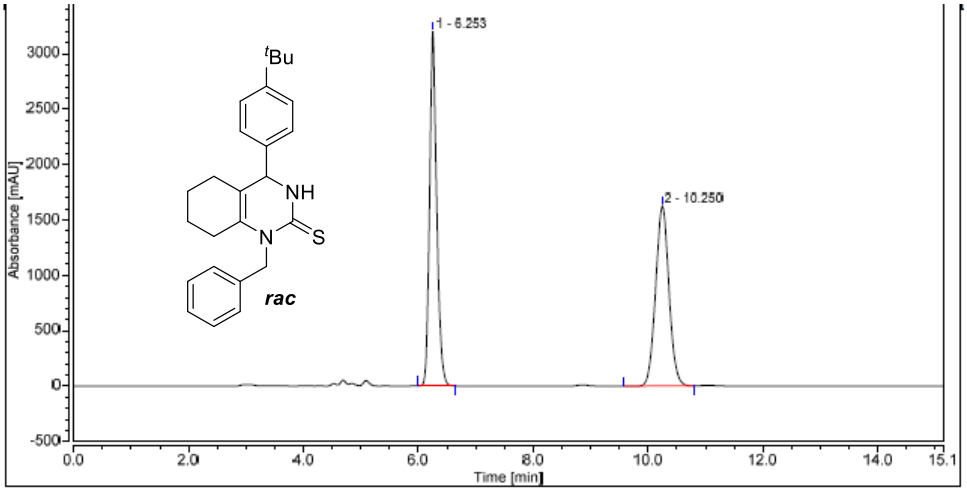
峰号	保留时间	面积	高度	面积%	高度%
1	6.410	2188387	174931	49.328	64.172
2	11.094	2248010	97667	50.672	35.828
总计		4436397	272599	100.000	100.000



〈峰表〉

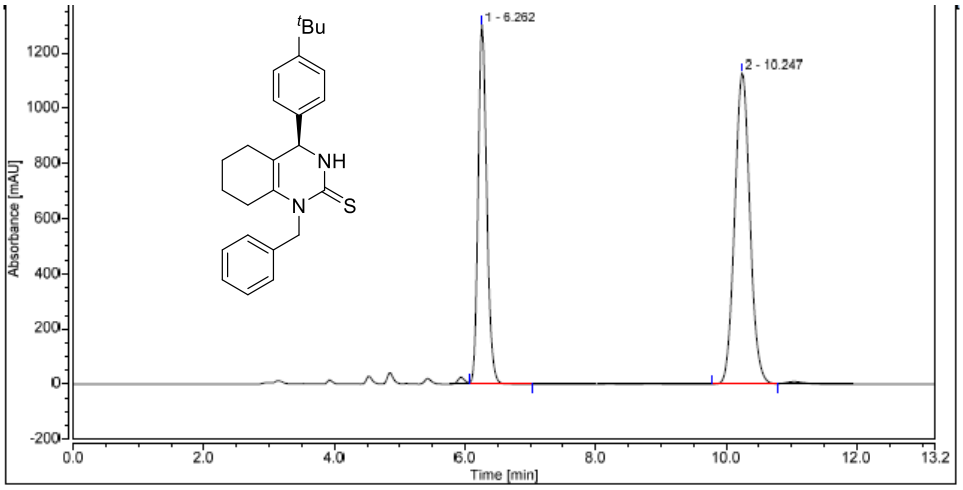
PDA Ch1 254nm

峰号	保留时间	面积	高度	面积%	高度%
1	6.389	1815045	144681	23.971	36.427
2	11.041	5756637	252501	76.029	63.573
总计		7571682	397182	100.000	100.000



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.253	455.216	3200.057	50.97	66.32	n.a.
2		10.250	437.818	1624.997	49.03	33.68	n.a.



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.262	199.200	1300.164	39.52	53.55	n.a.
2		10.247	304.877	1127.859	60.48	46.45	n.a.
Total:			**504.077**	**2428.023**	**100.00**	**100.00**	