Organocatalytic Asymmetric [4+1] Cyclization of In Situ Generated *ortho*-Quinomethanes with 4-Halogen Pyrazolones in Oil-Water Phases

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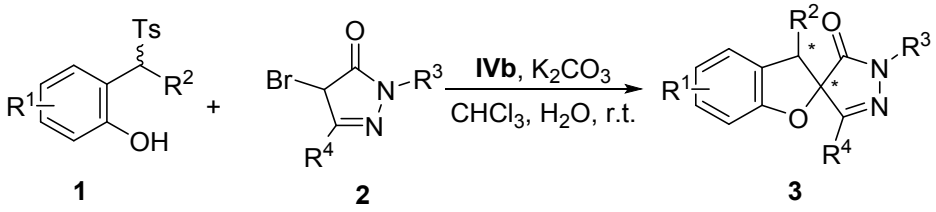
General information

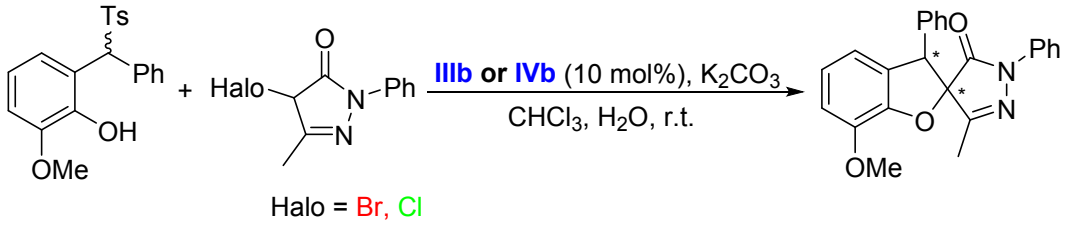
Unless otherwise stated, all reagents were purchased from commercial suppliers and used without purifications. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE Ⅲ spectrometer in $CDCl_3$ using TMS as the internal standard, operating at 500 MHz and 126 MHz, respectively. HRMS data were measured on an Agilent 6120 LC/TOF-MS with ESI source. Chiral HPLC analyses were performed using Agilent 1260 chromatography and JASCO LC-2000 Plus. Chiralpak IA, IC, AD-H and OD-H columns were purchased from Daicel Chemical Industries (Shanghai, China). Optical rotations were measured on a Rudolph Autopol IV polarimeter. Flash column chromatography experiments were conducted using silica gel GF254 (200-300 mesh) eluting with ethyl acetate (EtOAc) and petroleum ether (PE). TLC experiments were carried out on glass-backed silica plates. Starting materials 2-(phenyl(tosyl)methyl)phenols[1] and 4-halogen pyrazolones[2] were synthesized according to the known method.

Typical experimental procedure for [4+1] cyclization

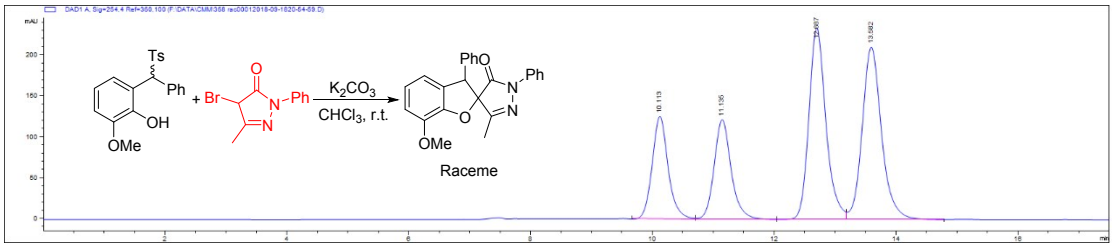


To a Schlenk tube equipped with a magnetic stir bar was charged with the catalyst **IVb** (0.010 mmol, 10 mol%), K_2CO_3 (2.6 equiv., 0.26 mmol), the substituted 2-(phenyl(tosyl)methyl)phenol **1** (0.1 mmol) and 4-halogen pyrazolones **2** (1.3 equiv., 0.13 mmol), and 1.5 mL $CHCl_3$ and 0.15 mL H_2O were then added through syringe. The resulting solution was stirred at room temperature for 24 h. The reaction mixture was extracted with CH_2Cl_2, and the organic layer was concentrated under reduced pressure. The crude product was purified by flash column chromatography eluting with ethyl acetate (EtOAc) and petroleum ether (PE) to afford the resulting product. The enantiomeric excess was determined by HPLC using a Chiralpak IA, IC, ID, AD-H or OD-H column.

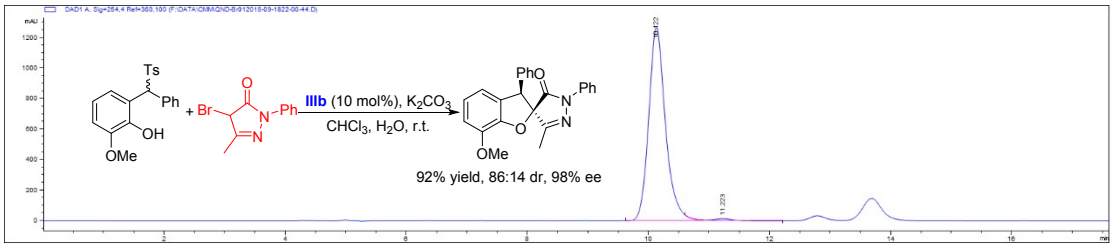
Diastereodivergent construction of the 4-spiropyrazolone



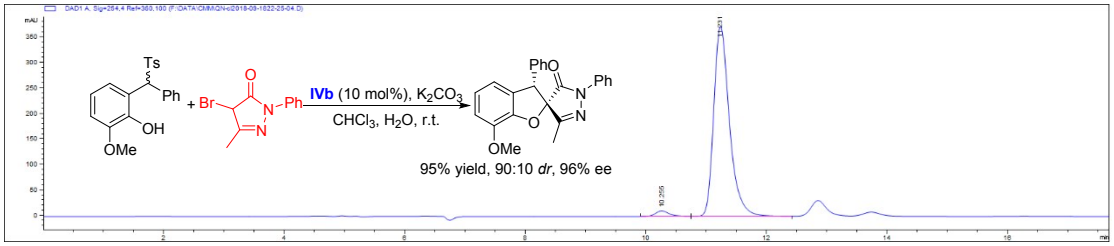
To a Schlenk tube equipped with a magnetic stir bar was charged with the catalyst **IIIb** or **IVb** (0.010 mmol, 10 mol%), K_2CO_3 (2.6 equiv., 0.26 mmol), the substituted 2-(phenyl(tosyl)methyl)phenol **1** (0.1 mmol) and 4-halogen pyrazolones **2** or **4** (1.3 equiv., 0.13 mmol), 1.5 mL $CHCl_3$ and 0.15 mL H_2O were then added through syringe. The resulting solution was stirred at room temperature for 24 h. Then it was extracted with CH_2Cl_2, and the organic layer was concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel, eluting with petroleum ether/ethyl acetate 1/10 (v/v) and the enantiomeric excess was determined by HPLC on Daicel Chiralpak IA with hexane/i-PrOH (90:10) as the eluent, flow = 1.0 mL/min, UV =254 nm.



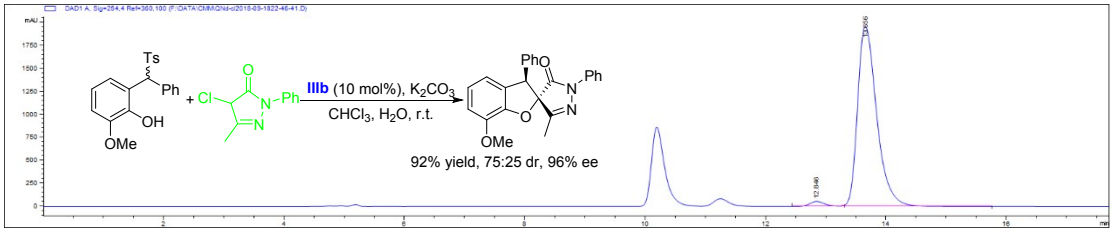
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	10.113	2296.2	126	0.2747	0.88	16.534	BV
2	11.135	2371.3	122.1	0.2945	0.846	17.075	VB
3	12.687	4562	234.6	0.2969	0.809	32.850	BV
4	13.582	4657.8	211.3	0.3372	0.836	33.540	VB



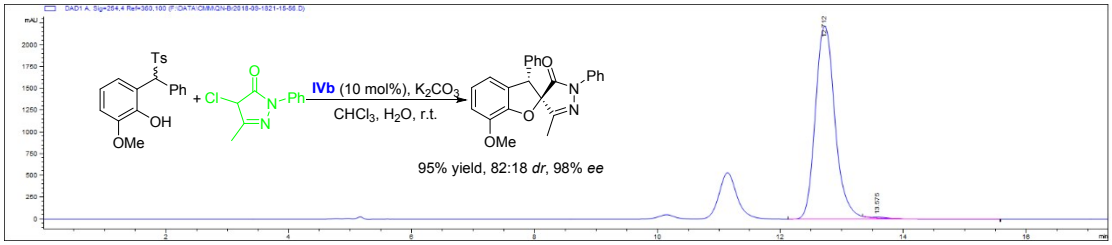
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	10.122	24392.2	1267	0.2886	0.792	98.748	BV R
2	11.223	309.1	13.4	0.3356	1.066	1.252	VB E



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	10.255	162.9	10.7	0.2314	0.8	2.360	BB
2	11.231	6739.1	372.1	0.2773	0.705	97.640	BB

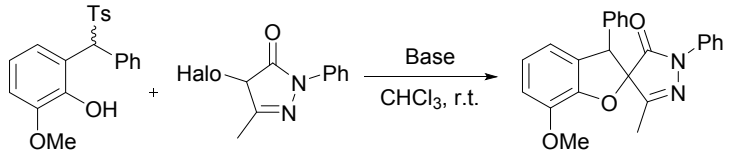


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	12.846	964.9	54.5	0.2707	0.799	2.167	BV E
2	13.656	43555	1964.1	0.3407	0.71	97.833	VB R



#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	12.712	49418.4	2214.5	0.3464	0.844	99.324	BV R
2	13.575	336.3	13.9	0.3469	0.362	0.676	VB E

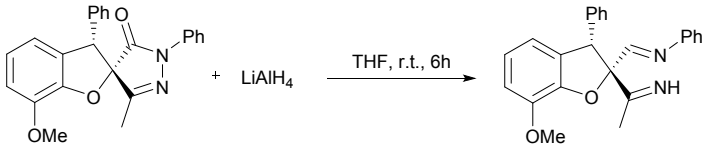
Control experiences for the racemic [4+1] cyclization



Halo = Cl	K_2CO_3 (2.6 eq)	**3aa**, 85: 15 dr
	NEt_3 (2.6 eq)	**3aa**, 76: 24 dr
Halo = Br	K_2CO_3 (2.6 eq)	**3aa**, 54: 46 dr
	NEt_3 (2.6 eq)	**3aa**, 59: 41 dr

To a Schlenk tube equipped with a magnetic stir bar was charged with organic base or inorganic base (2.6 equiv., 0.26 mmol), the substituted 2-(phenyl(tosyl)methyl)phenol **1** (0.1 mmol) and 4-halogen pyrazolones **2** or **4** (1.3 equiv., 0.13 mmol), 1.5 mL $CHCl_3$ were then added through syringe. The resulting solution was stirred at room temperature for 24 h. Then it was extracted with CH_2Cl_2, and the organic layer was concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel, eluting with petroleum ether/ethyl acetate 1/10 (v/v) and the diastereo ratio was determined by chiral HPLC (JASCO LC-2000 Plus) on Daicel Chiralpak IA with hexane/i-PrOH (90:10) as the eluent, flow = 1.0 mL/min, UV =254 nm.

The reduction of 3aa with $LiAlH_4$



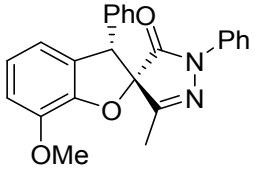
3aa
99% ee, > 95:5 dr

5
77% yield, > 95:5 dr, 99% ee

Under nitrogen atmosphere, the solution of **3aa** (0.05 mmol) in dry THF (1.0 mL) was cooled to -10 °C and $LiAlH_4$ (2.5 M solution in THF, 80ul, 0.2 mmol) were then added through syringe. The mixture was warmed to room temperature and stirred for 6 h. Saturated NH_4Cl solution (0.5 mL) was added to quench the reaction and the aqueous layer was extracted with EA. The combined organic layers was concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel, eluting with petroleum ether/ethyl acetate 1/20 (v/v). The racemate of **5** was synthesized through the reduction of the corresponding pre-isolated diastereoisomer, and the enantiomeric excess was determined by chiral HPLC (JASCO LC-2000 Plus) on Daicel Chiralpak AD-H with hexane/i-PrOH (80:20) as the eluent, flow = 1.0 mL/min, UV =254 nm.

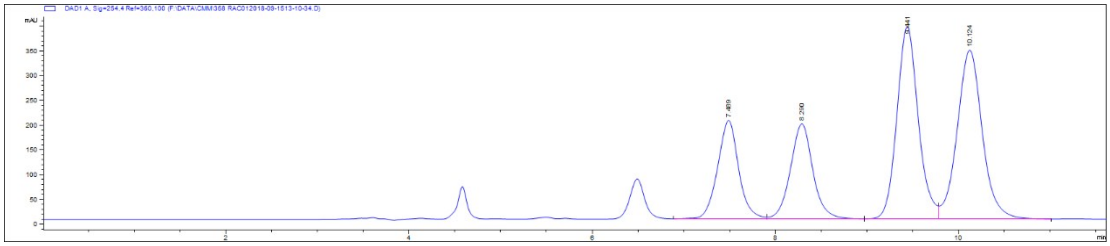
Characterization and NMR spectra of resulting products

(2*S*,3*S*)-7-methoxy-3'-methyl-1',3-diphenyl-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3aa)

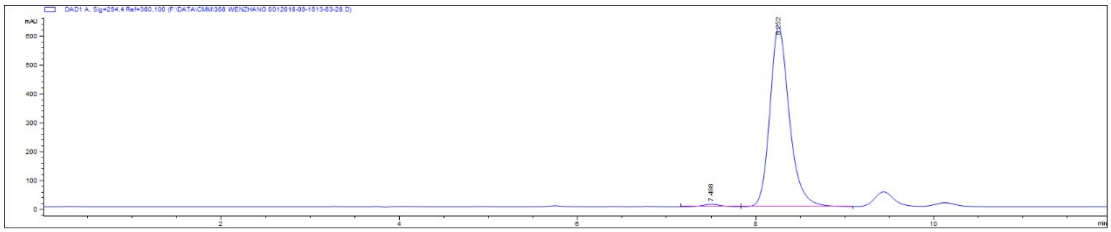


Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as white solid (95% yield, 37.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (q, *J* = 1.8 Hz, 1H), 7.33 (dd,

J = 2.1, 1.1 Hz, 1H), 7.32 -7.27 (m, 3H), 7.27 - 7.23 (m, 4H), 7.12 - 7.07 (m, 1H), 7.02 (dd, *J* = 8.1, 7.5 Hz, 1H), 6.94 (dt, *J* = 8.2, 1.0 Hz, 1H), 6.79 (dt, *J* = 7.5, 1.1 Hz, 1H), 5.16 (s, 1H), 3.96 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.04, 158.08, 148.25, 144.83, 136.98, 133.76, 129.10, 128.58, 128.48, 128.47, 127.84, 125.18, 123.00, 119.11, 117.47, 112.66, 92.32, 56.19, 55.34, 13.11. $[\alpha]_D^{30}$ = -198.4 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/*i*-PrOH = 90/10), 1.0 mL/min; Major enantiomer: t_R = 8.25 min, minor enantiomer: t_R = 7.50 min. 90:10 *dr*, 98% *ee*. HRMS (ESI) calcd for $C_{24}H_{20}N_2O_3Na$ *m/z* $[M + Na]^+$: 407.1366, found: 407.1360.

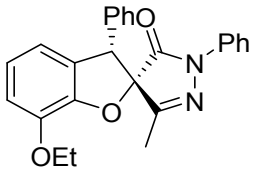


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	7.489	3171.9	198.8	0.2402	1.039	16.465	BV
2	8.29	3267.3	192.1	0.2564	0.985	16.961	VB
3	9.441	6318.1	388.3	0.2478	0.884	32.797	BV
4	10.124	6506.9	341.1	0.2905	0.944	33.777	VB



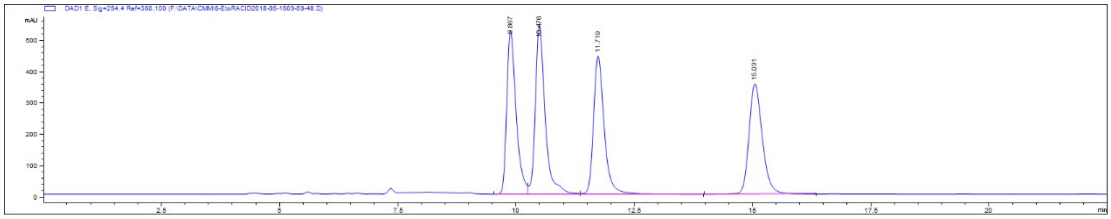
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	7.498	116.6	8.5	0.2102	0.988	1.217	BB
2	8.252	9468.7	622.2	0.2315	0.768	98.783	BV

(2*S*,3*S*)-7-ethoxy-3'-methyl-1',3-diphenyl-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3ba)

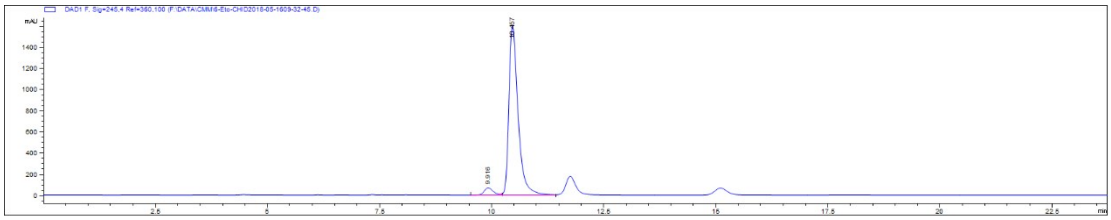


Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as white solid (93% yield, 37.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.32 (m, 1H), 7.32 (dd, *J* = 2.1, 1.1 Hz, 1H), 7.31 – 7.29 (m, 1H), 7.29 – 7.25 (m, 3H), 7.25 – 7.23 (m, 3H), 7.13 – 7.06 (m, 1H), 6.99 (dd, *J* = 8.2, 7.4 Hz, 1H), 6.97 – 6.90 (m, 1H), 6.77 (dt, *J* = 7.4, 1.2 Hz, 1H), 5.14 (s, 1H), 4.21 (q, *J* = 7.0 Hz, 2H), 2.40 (s, 3H), 1.49 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.18, 158.29, 148.52, 144.14, 137.01, 133.92, 129.13, 128.59, 128.47, 128.45, 127.94, 125.18, 122.93, 119.12, 117.44, 114.13, 92.30, 64.80, 55.41, 14.93, 13.17. $[\alpha]_D^{30}$ = -163.0 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak ID-H column at 254 nm (n-hexane/*i*-PrOH = 85/15), 0.7 mL/min; Major enantiomer: t_R = 10.45 min, minor enantiomer: t_R = 9.92 min. 86:14 *dr*, 92% *ee*. HRMS (ESI) calcd for $C_{25}H_{22}N_2O_3Na$ *m/z* $[M + Na]^+$: 421.1523,

found: 421.1522.

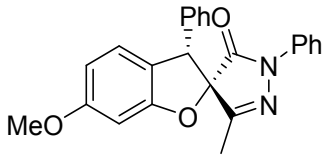


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.867	7195.6	522.3	0.2087	0.617	24.986	BV
2	10.476	7799.9	539.1	0.2168	0.628	27.084	VV
3	11.719	6915.9	441.7	0.2367	0.701	24.015	VB
4	15.031	6887.1	352.5	0.3	0.746	23.915	BB

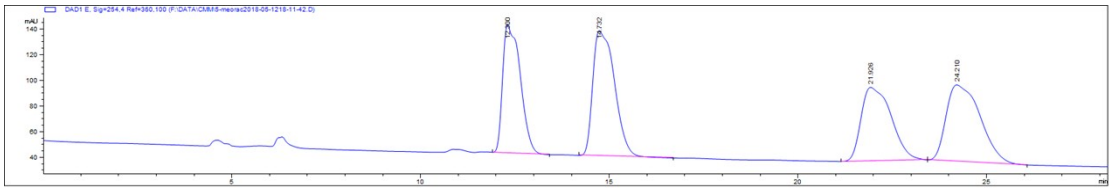


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.916	959.4	69.1	0.212	0.753	4.067	BV E
2	10.457	22634.2	1594.4	0.2136	0.714	95.933	VV R

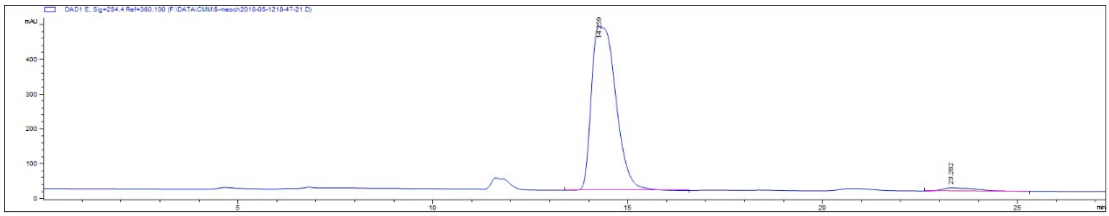
(2*S*,3*S*)-6-methoxy-3'-methyl-1',3-diphenyl-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3ca)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as white solid (95% yield, 36.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 4H), 7.30 – 7.24 (m, 4H), 7.23 (dd, *J* = 6.1, 1.8 Hz, 2H), 7.12 – 7.08 (m, 1H), 7.07 – 7.03 (m, 1H), 6.92 (dd, *J* = 1.8, 1.1 Hz, 1H), , 5.13 (s, 1H), 3.94 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.63, 157.43, 147.55, 145.20, 136.81, 132.82, 129.50, 129.00, 128.71, 128.62, 128.58, 125.29, 120.26, 119.07, 116.12, 114.42, 92.50, 56.44, 55.05, 13.06. $[\alpha]_D^{30}$ = -189.38 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak IC column at 254 nm (n-hexane/*i*-PrOH = 85/15), 0.7 mL/min; Major enantiomer: t_R = 14.26 min, minor enantiomer: t_R = 23.28 min. 94:6 *dr*, 95% *ee*. HRMS (ESI) calcd for $C_{24}H_{20}N_2O_3Na$ *m/z* $[M + Na]^+$: 407.1366, found: 407.1363.

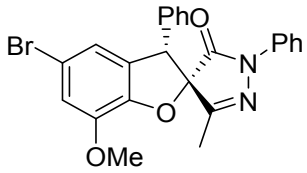


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	12.3	3234.1	99.6	0.4348	0.377	22.997	BB
2	14.732	3899	97.5	0.5404	0.417	27.725	BB
3	21.926	3174.2	57.3	0.7588	0.455	22.571	BB
4	24.21	3755.7	59.5	0.864	0.442	26.706	BBA

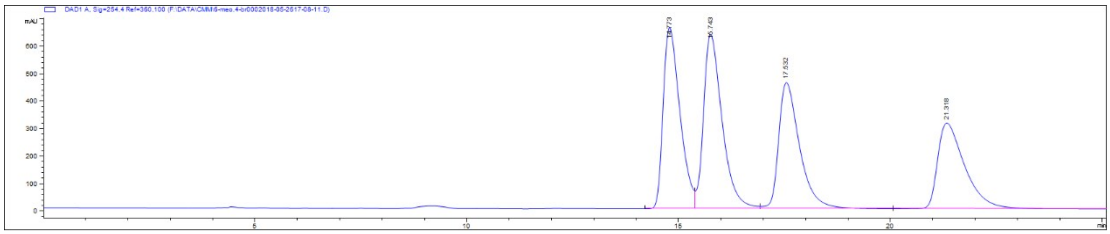


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	14.259	20509.9	471.3	0.5878	0.469	97.379	BB
2	23.282	552.1	8.9	0.8313	0.351	2.621	BBA

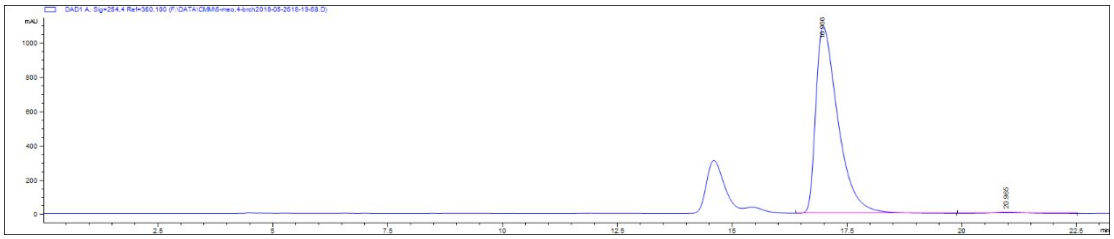
(2*S*,3*S*)-5-bromo-7-methoxy-3'-methyl-1',3-diphenyl-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3da)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as colorless oil (95% yield, 44.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 5H), 7.28 – 7.24 (m, 2H), 7.24 – 7.21 (m, 2H), 7.12 – 7.04 (m, 2H), 6.95 – 6.88 (m, 1H), 5.13 (s, 1H), 3.94 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.67, 157.47, 147.59, 145.24, 136.84, 132.85, 129.03, 128.75, 128.66, 128.62, 128.15, 125.32, 120.30, 119.11, 116.15, 114.45, 92.54, 56.47, 55.08, 13.10. $[\alpha]_D^{30}$ = -227.5 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak OD-H column at 254 nm (n-hexane/*i*-PrOH = 96/4), 0.7 mL/min; Major enantiomer: t_R = 16.97 min, minor enantiomer: t_R = 20.97 min. 80:20 *dr*, 98% *ee*. HRMS (ESI) calcd for $C_{24}H_{19}N_2O_3Na$ *m/z* $[M + Na]^+$: 485.0471, found: 485.0469.

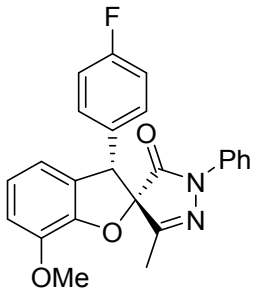


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	14.773	18213.6	661.1	0.4214	0.574	26.930	BV
2	15.743	19446.2	636.6	0.4624	0.573	28.753	VV
3	17.532	15915.2	460.9	0.5208	0.547	23.532	VB
4	21.318	14058	313.4	0.6754	0.47	20.786	BB

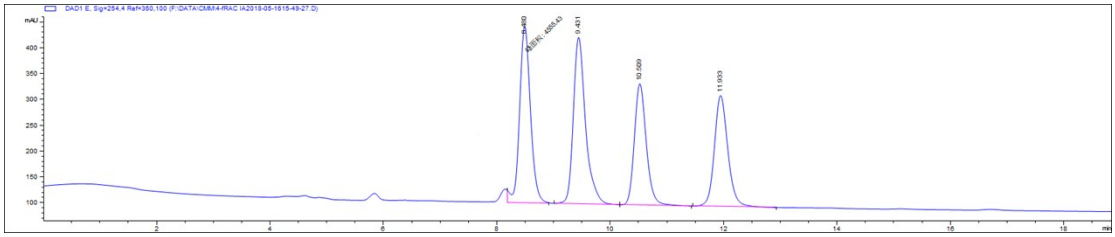


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	16.966	36434.3	1084.7	0.5079	0.474	99.111	BB
2	20.965	327	7.2	0.6878	0.757	0.889	BB

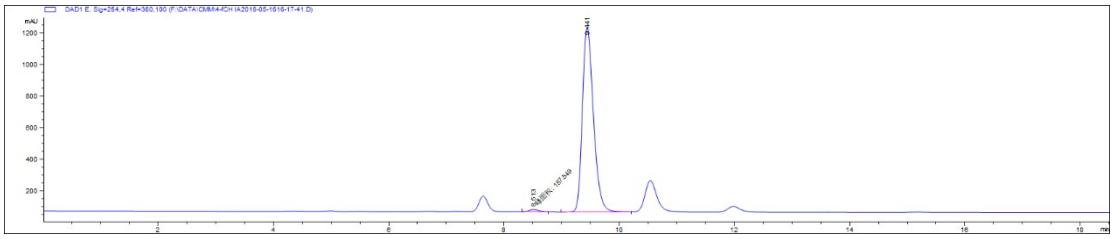
(2*S*,3*S*)-3-(4-fluorophenyl)-7-methoxy-3'-methyl-1'-phenyl-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3ea)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as white solid (95% yield, 38.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.27 (dd, *J* = 8.7, 7.3 Hz, 2H), 7.21 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.04 – 6.92 (m, 4H), 6.74 (d, *J* = 7.5 Hz, 1H), 5.13 (s, 1H), 3.95 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.96, δ 162.70 (d, *J* = 247.6 Hz), 158.13, 148.13, 144.87, 136.96, 130.86 (d, *J* = 8.3 Hz), 129.68 (d, *J* = 3.1 Hz), 128.68, 127.79, 125.30, 123.14, 118.97, 117.27, 115.47 (d, *J* = 21.6 Hz), 112.78, 92.13, 56.20, 54.61, 13.07. ^{19}F NMR (471 MHz, $CDCl_3$) δ -113.21. $[\alpha]_D^{30}$ = -150.30 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/*i*-PrOH = 85/15), 0.7 mL/min; Major enantiomer: t_R = 9.44 min, minor enantiomer: t_R = 8.51 min. 82:18 *dr*, 98% *ee*. HRMS (ESI) calcd for $C_{24}H_{19}FN_2O_3Na$ *m/z* $[M + Na]^+$: 425.1272, found: 425.1271.

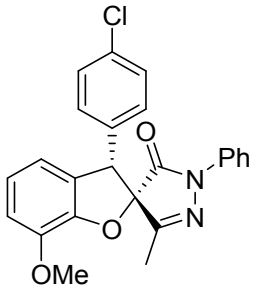


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	8.48	4555.4	342.2	0.2218	0.868	27.823	MM
2	9.431	4825.5	322.8	0.2264	0.714	29.472	BB
3	10.509	3447.6	235.2	0.223	0.795	21.057	BB
4	11.933	3544.6	215.1	0.2523	0.815	21.649	BB

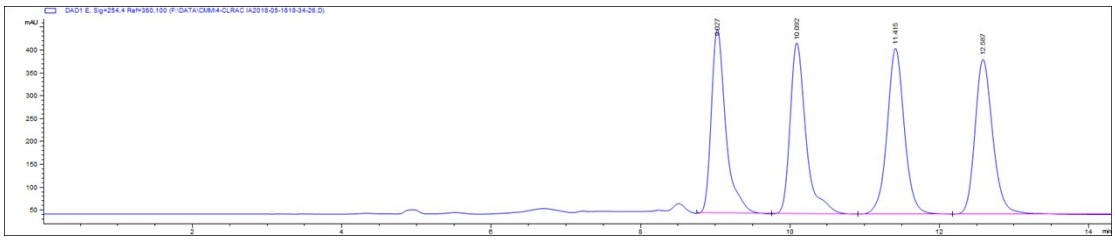


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	8.513	187.5	14.9	0.2094	0.804	1.184	MM
2	9.441	15651.5	1170.5	0.206	0.708	98.816	BV

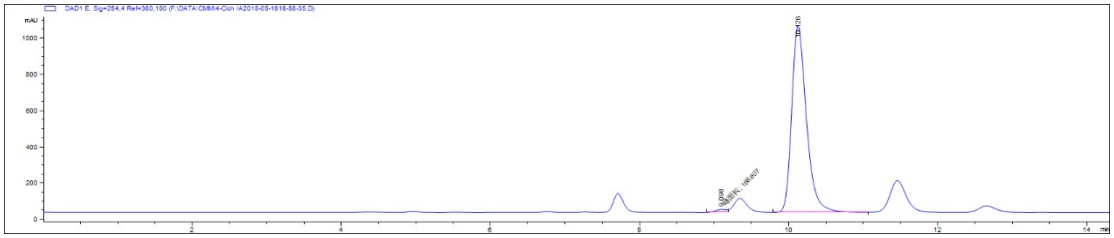
(2*S*,3*S*)-3-(4-chlorophenyl)-7-methoxy-3'-methyl-1'-phenyl-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3fa)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as white solid (93% yield, 38.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.30 – 7.27 (m, 2H), 7.27 – 7.24 (m, 2H), 7.19 – 7.16 (m, 2H), 7.14 – 7.10 (m, 1H), 7.04 – 6.99 (m, 1H), 6.94 (d, J = 8.2 Hz, 1H), 6.73 (dt, J = 7.6, 1.1 Hz, 1H), 5.11 (s, 1H), 3.96 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.83, 158.09, 148.15, 144.89, 136.93, 134.41, 132.54, 130.50, 128.68, 127.55, 125.34, 123.18, 119.00, 117.24, 112.85, 91.96, 56.19, 54.65, 13.03. $[\alpha]_D^{30}$ = -152.30 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 236 nm (n-hexane/*i*-PrOH = 85/15), 0.7 mL/min; Major enantiomer: t_R = 10.12 min, minor enantiomer: t_R = 8.10 min. 82:18 *dr*, 98% *ee*. HRMS (ESI) calcd for $C_{24}H_{19}ClN_2O_3Na$ *m/z* $[M + Na]^+$: 441.0976, found: 441.0975.

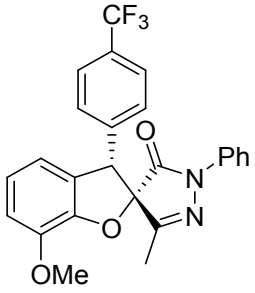


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.027	5480.6	404.9	0.2039	0.645	24.347	BB
2	10.092	5535.1	376.1	0.2217	0.67	24.589	BB
3	11.415	5840.5	364.3	0.2431	0.922	25.946	BB
4	12.587	5654.2	340.4	0.2538	0.76	25.118	BBA

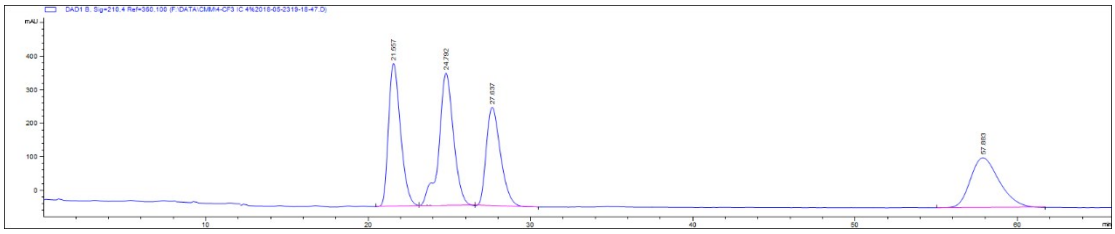


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.098	166.6	15.7	0.1765	1.058	1.163	MM
2	10.126	14154.6	1027.9	0.2087	0.686	98.837	BV

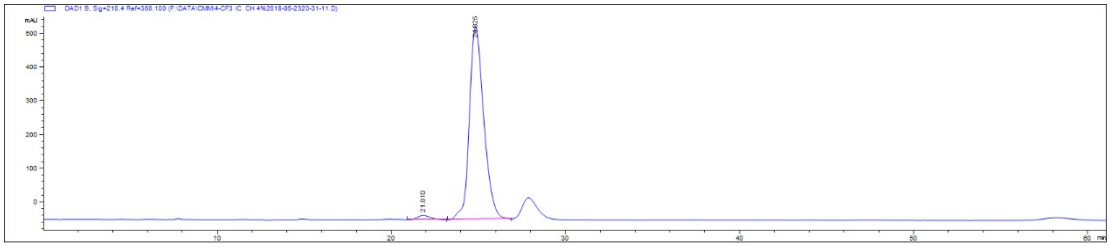
(2*S*,3*S*)-7-methoxy-3'-methyl-1'-phenyl-3-(4-(trifluoromethyl)phenyl)-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3ga)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as white solid (83% yield, 37.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.32 – 7.29 (m, 2H), 7.28 – 7.23 (m, 2H), 7.14 – 7.09 (m, 1H), 7.06 – 7.01 (m, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.74 (dt, *J* = 7.5, 1.1 Hz, 1H), 5.19 (s, 1H), 3.96 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.68, 158.05, 148.26, 144.98, 138.25, 136.75, 130.68 (q, *J* = 32.6 Hz), 129.64, 128.69, 127.09, 125.49, 125.41 (q, *J* = 3.6 Hz), 123.86 (q, *J*=272.8 Hz), 123.32, 119.07, 117.21, 112.97, 91.95, 56.21, 54.98, 13.07. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.73. $[\alpha]_D^{30}$ = -113.24 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak IC column at 254 nm (n-hexane/*i*-PrOH = 96/4), 0.7 mL/min; Major enantiomer: t_R = 24.82 min, minor enantiomer: t_R = 21.81 min. 88:12 *dr*, 96% *ee*. HRMS (ESI) calcd for $C_{25}H_{19}F_3N_2O_3Na$ *m/z* $[M + Na]^+$: 475.1240, found: 475.1239.

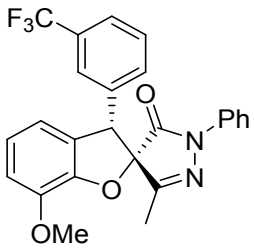


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	21.557	22019.4	425.7	0.7975	0.682	26.381	BV
2	24.792	25027.1	395.5	0.9289	1.029	29.985	VB R
3	27.637	18040.5	293.7	0.9506	0.671	21.614	BB
4	57.883	18379.3	148.2	1.879	0.723	22.020	BB

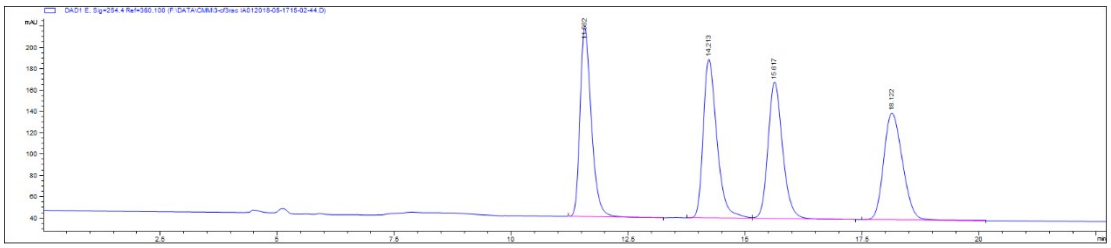


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	21.81	635.3	12.4	0.7979	0.728	1.901	BB
2	24.825	32791.1	571.5	0.8735	0.732	98.099	BB

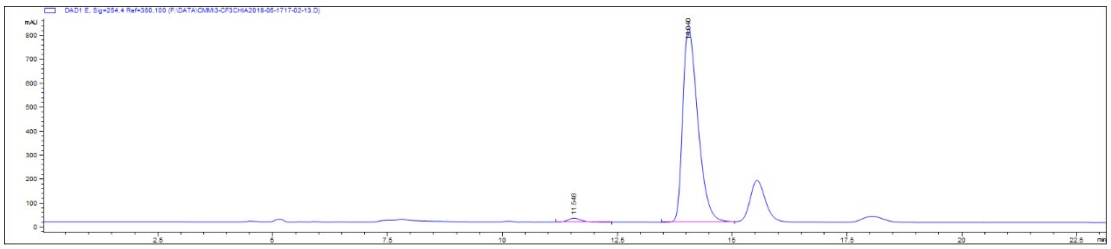
(2*S*,3*S*)-7-methoxy-3'-methyl-1'-phenyl-3-(3-(trifluoromethyl)phenyl)-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3ha)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as white solid (95% yield, 42.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.44 – 7.40 (m, 2H), 7.38 – 7.33 (m, 2H), 7.28 – 7.23 (m, 2H), 7.12 – 7.09 (m, 1H), 7.04 (dd, *J* = 8.2, 7.5 Hz, 1H), 6.96 (dt, *J* = 8.2, 1.0 Hz, 1H), 6.74 (dt, *J* = 7.4, 1.1 Hz, 1H), 5.19 (s, 1H), 3.96 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.72, 158.06, 148.27, 144.98, 136.83, 135.26, 132.64, δ 130.90 (q, *J* = 32.6 Hz), 128.65, 127.02, 125.81 (q, *J* = 3.7 Hz), 125.37 (q, *J* = 3.5), 125.35, 123.79 (q, *J* = 271), 123.38, 118.91, 117.16, 113.01, 92.02, 56.21, 55.05, 13.07. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.63. $[\alpha]_D^{30}$ = -148.30 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak IC column at 254 nm (n-hexane/*i*-PrOH = 95/5), 0.7 mL/min; Major enantiomer: t_R = 14.04 min, minor enantiomer: t_R = 11.55 min. 81:19 *dr*, 96% *ee*. HRMS (ESI) calcd for $C_{25}H_{19}F_3N_2O_3Na$ *m/z* $[M + Na]^+$: 475.1240, found: 475.1236.

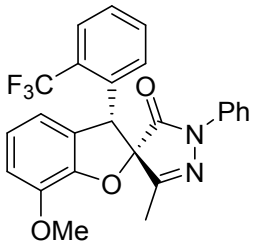


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	11.562	2981.4	176.7	0.2568	0.667	25.808	VB
2	14.213	3022.7	148.3	0.3097	0.647	26.166	BV
3	15.617	2770.6	127.7	0.3311	0.779	23.983	VB
4	18.122	2777.5	99.7	0.437	0.744	24.043	BBA

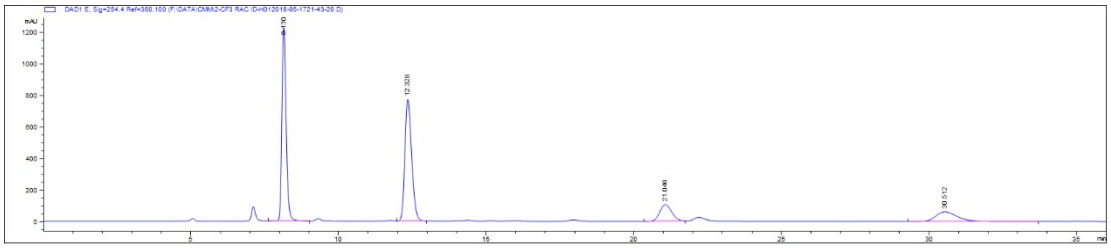


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	11.548	312.3	15.9	0.3031	0.788	1.655	BB
2	14.04	18560.4	808.5	0.3538	0.59	98.345	BV

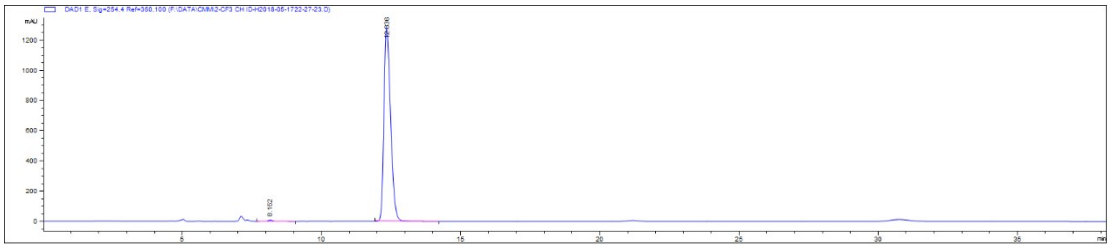
(2*S*,3*S*)-7-methoxy-3'-methyl-1'-phenyl-3-(2-(trifluoromethyl)phenyl)-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3ia)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as white solid (84% yield, 38 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.59 – 7.48 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.33 – 7.24 (m, 3H), 7.16 – 7.11 (m, 1H), 7.04 – 6.91 (m, 2H), 6.64 (d, *J* = 7.5 Hz, 1H), 5.39 (s, 1H), 4.12 (s, 3H), 3.98 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.98, 158.36, 147.54, 144.86, 137.30, 134.10, 133.63, 131.52, 129.37, 128.67, δ 128.39 (q, *J* = 29.2 Hz), 128.19, 125.43 (q, *J* = 5.7 Hz), 125.24, 124.23 (q, *J*=272.08), 123.60, 119.15, 117.30, 112.69, 90.12, 56.19, 49.81, 12.71. ^{19}F NMR (471 MHz, $CDCl_3$) δ -58.04. $[\alpha]_D^{30}$ = 21.04 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak ID column at 254 nm (n-hexane/*i*-PrOH = 85/15), 0.7 mL/min; Major enantiomer: t_R =12.33 min, minor enantiomer: t_R = 8.15 min. 96:4 *dr*, 99% *ee*. HRMS (ESI) calcd for $C_{25}H_{19}F_3N_2O_3Na$ *m/z* $[M + Na]^+$: 475.1240, found: 475.1239.

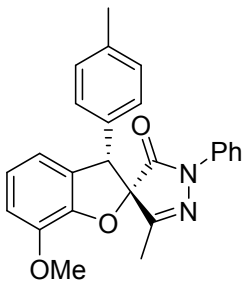


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	8.13	12311.7	1224.5	0.1533	0.739	39.900	BB
2	12.328	12327.2	770	0.2488	0.717	39.950	BB
3	21.046	3065.5	106.6	0.4475	0.814	9.935	BV
4	30.512	3152	61.7	0.784	0.685	10.215	BB

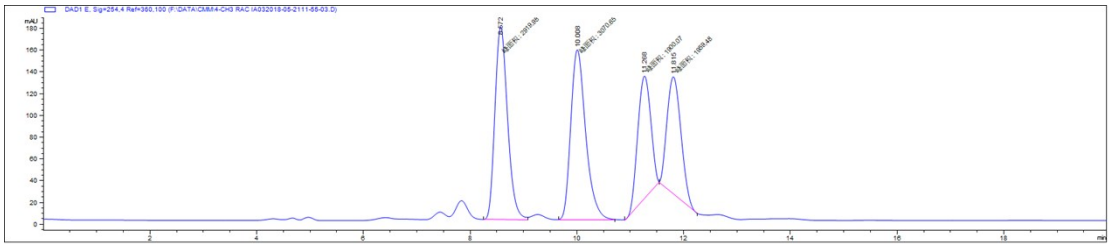


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	8.152	124.9	9.2	0.1962	0.859	0.579	BB
2	12.336	21444.7	1281.3	0.2573	0.636	99.421	BB

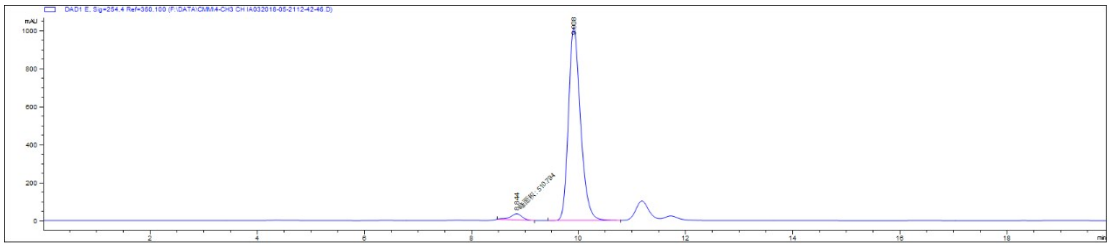
(2*S*,3*S*)-7-methoxy-3'-methyl-1'-phenyl-3-(p-tolyl)-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3ja)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as white solid (93% yield, 37.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (ddd, *J* = 8.7, 2.0, 1.1 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.15 – 7.08 (m, 5H), 7.04 – 6.98 (m, 1H), 6.93 (dt, *J* = 8.3, 1.0 Hz, 1H), 6.78 (dt, *J* = 7.6, 1.1 Hz, 1H), 5.13 (s, 1H), 3.96 (s, 3H), 2.39 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.12, 158.15, 148.16, 144.79, 138.19, 137.09, 130.66, 129.17, 128.98, 128.55, 128.15, 125.12, 122.94, 119.13, 117.46, 112.59, 92.31, 56.18, 55.02, 21.07, 13.09. $[\alpha]_D^{30}$ = -213.43 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/*i*-PrOH = 85/15), 0.7 mL/min; Major enantiomer: t_R = 8.84 min, minor enantiomer: t_R = 9.91 min. 85:15 *dr*, 94% *ee*. HRMS (ESI) calcd for $C_{25}H_{22}N_2O_3Na$ *m/z* $[M + Na]^+$: 421.1523, found: 421.1520.

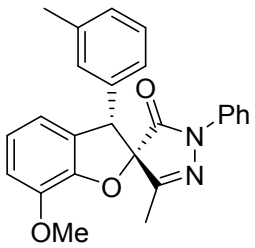


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	8.572	2920	176.8	0.2752	0.802	29.644	MM
2	10.008	3070.7	156.4	0.3272	0.745	31.174	MM
3	11.268	1900.1	112.2	0.2821	1.104	19.290	MM
4	11.815	1959.5	107.6	0.3036	0.785	19.893	MM



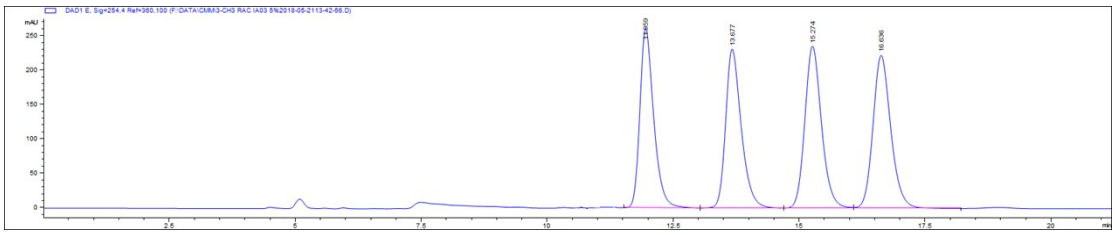
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	8.844	510.8	32.5	0.2618	1.131	3.103	MM
2	9.908	15951.1	1015.8	0.2392	0.731	96.897	BV

(2*S*,3*S*)-7-methoxy-3'-methyl-1'-phenyl-3-(m-tolyl)-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3ka)

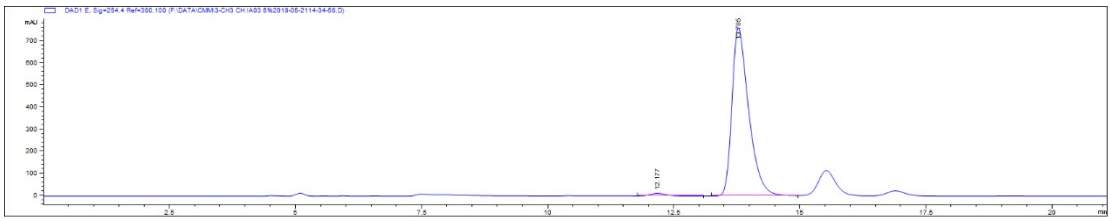


Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as white solid (95% yield, 38.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.28 – 7.24 (m, 2H), 7.20 – 7.15 (m, 1H), 7.11 – 7.00 (m, 5H), 6.93 (d, *J* = 7.9 Hz, 1H), 6.79 (dd, *J* = 7.3, 0.9 Hz, 1H), 5.13 (s, 1H), 3.96 (s, 3H), 2.40 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.11, 158.16, 148.21, 144.80, 138.12, 137.05, 133.71, 129.62, 129.20, 128.56, 128.35, 127.91, 126.16, 125.13, 122.96, 119.08, 117.55, 112.61, 92.34, 56.18, 55.29, 21.26, 13.09. $[\alpha]_D^{30}$ = -176.35 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/*i*-PrOH = 95/5), 0.7 mL/min; Major enantiomer: t_R = 13.79 min, minor enantiomer: t_R =

12.18 min. 85:15 *dr*, 94% *ee*. HRMS (ESI) calcd for $C_{25}H_{22}N_2O_3Na$ *m/z* $[M + Na]^+$: 421.1523, found: 421.1520.

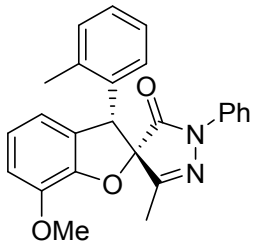


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	11.959	4986.4	261.4	0.2865	0.673	23.889	BB
2	13.677	4982.6	231.2	0.3235	0.678	23.871	BB
3	15.274	5423.3	235.6	0.3506	0.815	25.982	BV
4	16.636	5480.7	222.5	0.3754	0.8	26.257	VB

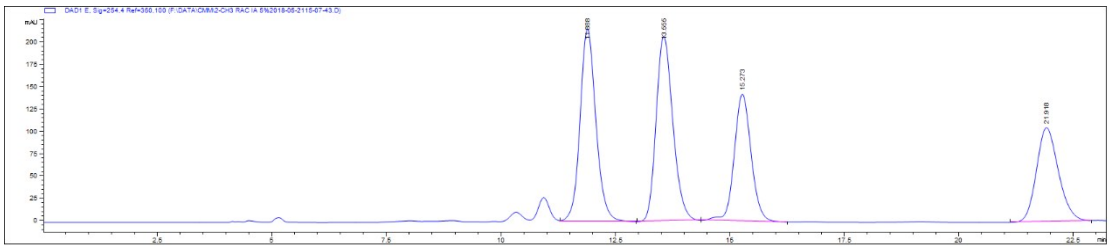


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	12.177	247.7	12	0.3147	0.779	1.390	BB
2	13.785	17567.9	761.8	0.3451	0.578	98.610	BB

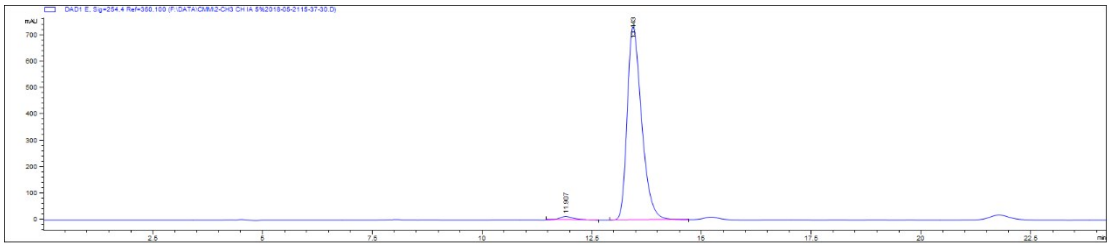
(2*S*,3*S*)-7-methoxy-3'-methyl-1'-phenyl-3-(o-tolyl)-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3la)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as white solid(92% yield, 36.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.8 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.19 – 7.10 (m, 5H), 7.01 (t, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.70 (d, *J* = 7.5 Hz, 1H), 5.44 (s, 1H), 3.97 (s, 3H), 2.36 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.00, 159.14, 148.09, 144.77, 137.16, 136.34, 133.25, 130.77, 130.05, 129.09, 128.67, 128.05, 125.98, 125.20, 123.05, 119.13, 117.58, 112.39, 91.09, 56.18, 51.38, 19.45, 13.14. $[\alpha]_D^{30}$ = -212.42 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/*i*-PrOH = 95/5), 0.7 mL/min; Major enantiomer: t_R = 13.44 min, minor enantiomer: t_R = 11.91 min. 95:5 *dr*, 96% *ee*. HRMS (ESI) calcd for $C_{25}H_{22}N_2O_3Na$ *m/z* $[M + Na]^+$: 421.1523, found: 421.1521.

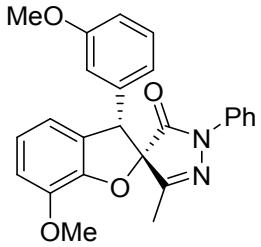


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	11.888	5232.9	216.2	0.3704	0.838	29.568	VB
2	13.555	5286.2	207.6	0.393	0.786	29.869	BB
3	15.273	3668.9	142.6	0.3962	0.912	20.731	BB
4	21.918	3510	105.4	0.5105	0.809	19.833	BB

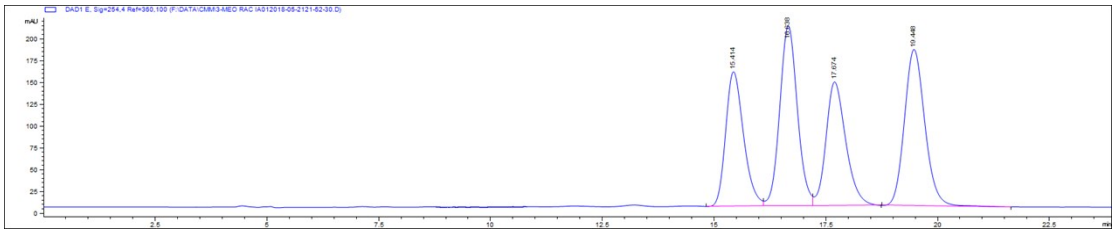


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	11.907	280.6	12.6	0.3327	0.693	1.656	BB
2	13.443	16660.5	729.4	0.3485	0.642	98.344	BB

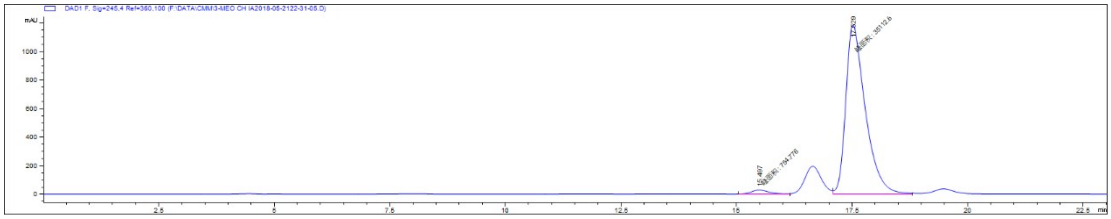
(2*S*,3*S*)-7-methoxy-3-(3-methoxyphenyl)-3'-methyl-1'-phenyl-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3ma)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as colorless oil(90% yield, 37.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.7, 1.2 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.23 (ddd, *J* = 7.7, 6.1, 1.7 Hz, 2H), 7.11 (ddt, *J* = 8.6, 7.2, 1.2 Hz, 1H), 7.03 (t, *J* = 7.8 Hz, 1H), 6.96 – 6.91 (m, 2H), 6.84 – 6.74 (m, 2H), 5.53 (s, 1H), 3.95 (s, 3H), 3.65 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.78, 158.88, 157.26, 148.13, 144.84, 137.51, 130.00, 129.18, 128.60, 127.64, 124.79, 123.43, 122.68, 120.52, 118.71, 117.82, 112.35, 109.53, 91.15, 56.13, 55.08, 48.11, 12.95. $[\alpha]_D^{30}$ = -116.23 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/*i*-PrOH = 93/7), 0.7 mL/min; Major enantiomer: t_R = 17.53 min, minor enantiomer: t_R = 15.50 min. 87:13 *dr*, 96% *ee*. HRMS (ESI) calcd for $C_{25}H_{22}N_2O_3Na$ *m/z* $[M + Na]^+$: 437.1472, found: 437.1471.

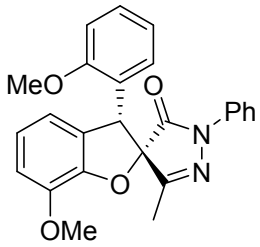


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	15.414	4280.2	153.4	0.4276	0.735	21.462	BV
2	16.638	5648.4	205.3	0.423	0.902	28.323	VV
3	17.674	4347.4	141.1	0.4674	0.734	21.799	VB
4	19.448	5667	178.3	0.4909	0.833	28.416	BB

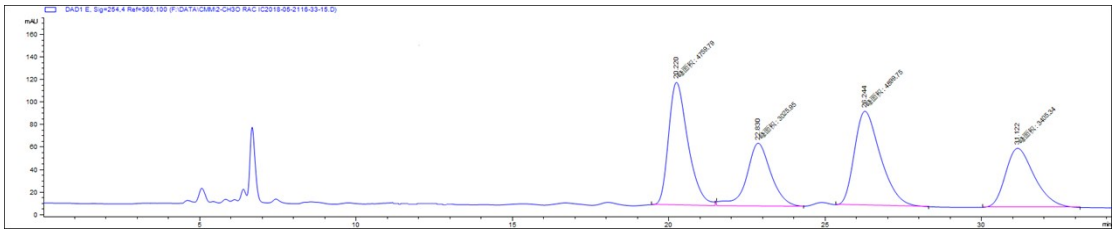


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	15.498	507.5	20.5	0.3832	0.808	1.988	BV
2	17.529	25017.4	848.3	0.4915	0.569	98.012	MM

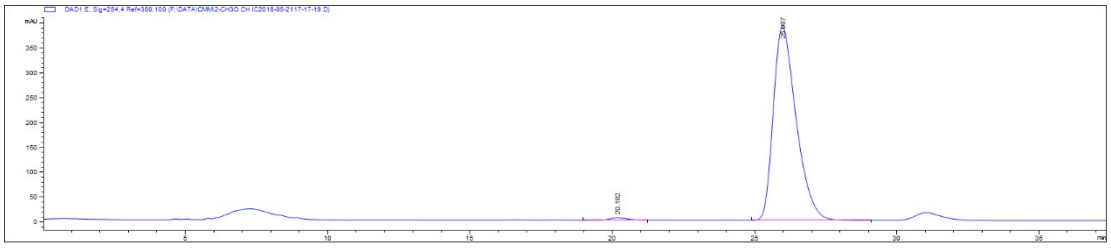
(2*S*,3*S*)-7-methoxy-3-(2-methoxyphenyl)-3'-methyl-1'-phenyl-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3na)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as white solid (92% yield, 38.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 2H), 7.28 – 7.18 (m, 4H), 7.10 – 7.06 (m, 1H), 7.00 (dd, *J* = 8.1, 7.5 Hz, 1H), 6.93 – 6.88 (m, 2H), 6.79 (dt, *J* = 7.6, 1.1 Hz, 1H), 6.74 (dd, *J* = 8.2, 1.1 Hz, 1H), 5.50 (s, 1H), 3.92 (s, 3H), 3.62 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.81, 158.92, 157.29, 148.17, 144.87, 137.54, 130.05, 129.22, 128.64, 127.67, 124.83, 123.46, 122.71, 120.56, 118.75, 117.86, 112.37, 109.56, 91.19, 56.16, 55.11, 48.14, 12.99. $[\alpha]_D^{30}$ = -215.43 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak IC column at 254 nm (n-hexane/*i*-PrOH = 85/15), 0.7 mL/min; Major enantiomer: t_R = 25.99 min, minor enantiomer: t_R = 20.18 min. 95:15 *dr*, 98% *ee*. HRMS (ESI) calcd for $C_{25}H_{22}N_2O_3Na$ *m/z* $[M + Na]^+$: 437.1472, found: 437.1470.

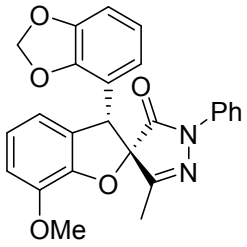


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	20.22	4759.8	109.7	0.7233	0.664	29.581	MM
2	22.83	3026	56.1	0.8997	0.896	18.805	MM
3	26.244	4899.8	84	0.9717	0.65	30.451	MM
4	31.122	3405.3	52.7	1.0764	0.697	21.163	MM

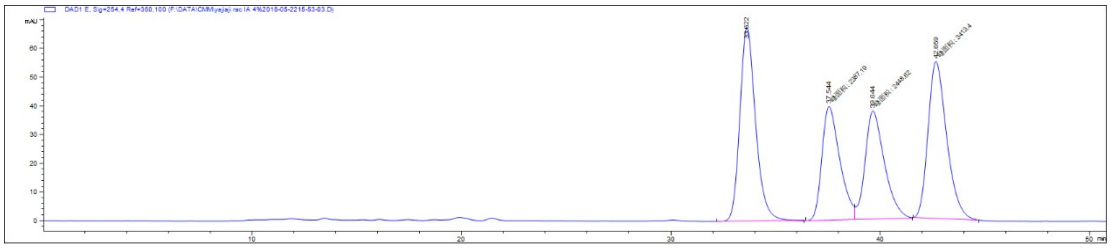


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	20.182	197.5	4.7	0.6393	0.744	0.900	BB
2	25.987	21738.7	387.7	0.8582	0.633	99.100	BB

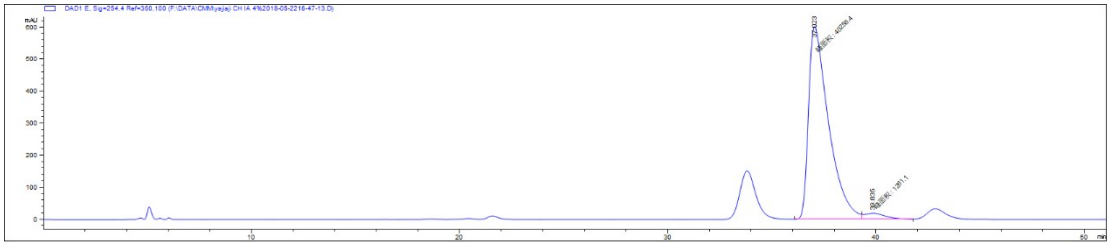
(2*S*,3*R*)-3-(benzo[d][1,3]dioxol-4-yl)-7-methoxy-3'-methyl-1'-phenyl-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3oa)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as white solid (89% yield, 36.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (dt, *J* = 8.7, 1.6 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.14 – 7.10 (m, 1H), 7.01 (t, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.79 – 6.68 (m, 4H), 5.89 (dd, *J* = 9.9, 1.4 Hz, 2H), 5.07 (s, 1H), 3.95 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.07, 158.13, 148.04, 147.75, 147.66, 144.80, 137.18, 128.63, 128.03, 127.42, 125.14, 123.02, 122.68, 118.97, 117.42, 112.69, 109.49, 108.13, 101.11, 92.18, 56.16, 55.10, 13.05. $[\alpha]_D^{30}$ = -100.50 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/*i*-PrOH = 96/4), 0.7 mL/min; Major enantiomer: t_R = 37.02 min, minor enantiomer: t_R = 39.83 min. 80:20 *dr*, 94% *ee*. HRMS (ESI) calcd for $C_{25}H_{20}N_2O_5Na$ *m/z* $[M + Na]^+$: 451.1264, found: 451.1267.

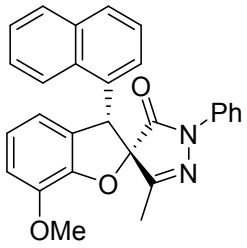


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	33.622	3552.7	67.5	0.802	0.762	30.103	BB
2	37.544	2387.2	39.7	1.0024	0.634	20.227	MF
3	39.644	2448.6	37.8	1.0784	0.658	20.748	FM
4	42.659	3413.4	54.8	1.0384	0.718	28.923	MM

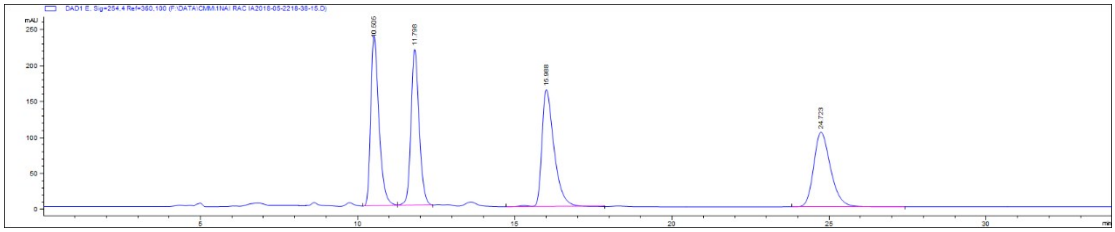


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	37.023	40256.4	601.8	1.1149	0.419	96.962	MF
2	39.835	1261.1	18.6	1.1274	0.661	3.038	FM

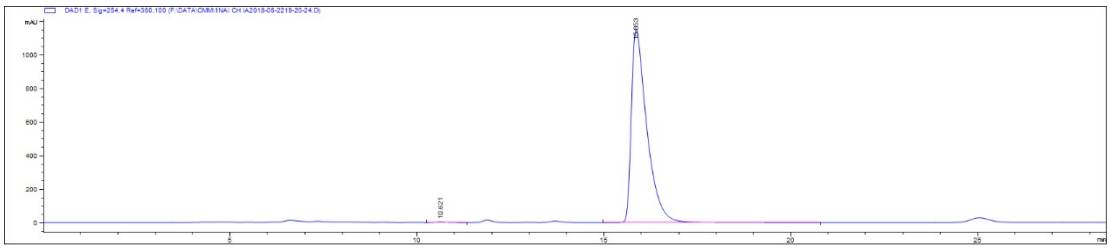
(2*S*,3*S*)-7-methoxy-3'-methyl-3-(naphthalen-1-yl)-1'-phenyl-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3pa)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as colorless oil (90% yield, 39.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.73 (m, 3H), 7.43 – 7.35 (m, 3H), 7.26 – 7.22 (m, 1H), 7.14 – 7.08 (m, 2H), 7.06 – 6.97 (m, 4H), 6.93 (d, *J* = 8.1 Hz, 1H), 6.78 (d, *J* = 7.5 Hz, 1H), 5.89 (s, 1H), 3.95 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.46, 158.71, 148.16, 144.95, 136.81, 133.54, 131.88, 131.62, 129.12, 128.72, 128.49, 128.38, 128.18, 126.48, 125.63, 125.25, 125.13, 123.16, 121.40, 119.25, 118.06, 112.51, 90.88, 56.14, 50.36, 13.13. $[\alpha]_D^{30}$ = -449.90 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/*i*-PrOH = 85/15), 0.7 mL/min; Major enantiomer: t_R = 15.85 min, minor enantiomer: t_R = 10.62 min. 96:4 *dr*, 99% *ee*. HRMS (ESI) calcd for $C_{28}H_{22}N_2O_3Na$ *m/z* $[M + Na]^+$: 457.1523, found: 457.1519.

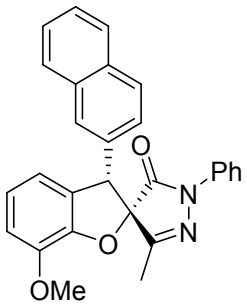


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	10.505	4318.3	237	0.2765	0.625	26.174	BV
2	11.798	3918.1	216.8	0.2748	0.802	23.749	VB
3	15.988	4392.2	162.7	0.4005	0.56	26.622	VB R
4	24.723	3869.6	103.8	0.5669	0.725	23.455	BB

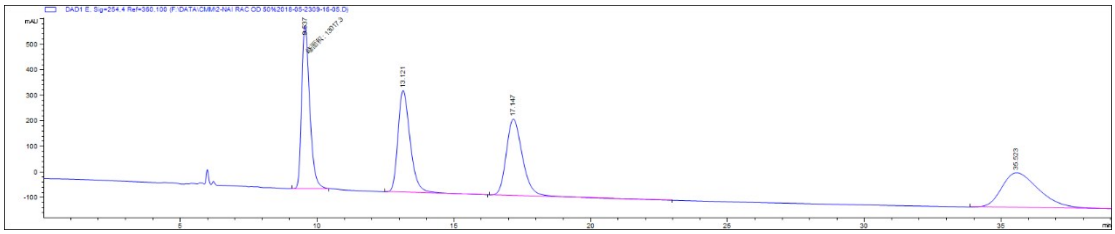


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	10.621	67.6	3.4	0.3041	0.779	0.203	BB
2	15.853	33277.9	1155.3	0.4241	0.412	99.797	BB

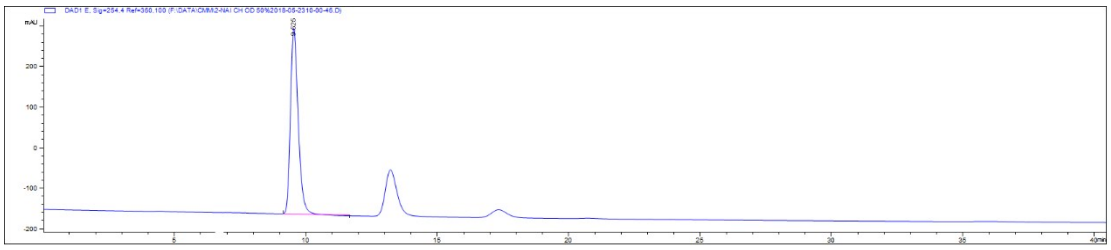
(2*S*,3*S*)-7-methoxy-3'-methyl-3-(naphthalen-2-yl)-1'-phenyl-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3qa)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) colorless oil (75% yield, 32.6 mg) after flash column chromatography on silica-gel. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.73 (m, 3H), 7.43 – 7.35 (m, 3H), 7.26 – 7.22 (m, 1H), 7.14 – 7.08 (m, 2H), 7.06 – 6.97 (m, 4H), 6.93 (d, *J* = 8.1 Hz, 1H), 6.78 (d, *J* = 7.5 Hz, 1H), 5.89 (s, 1H), 3.95 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.04, 158.41, 147.67, 145.05, 137.65, 133.20, 132.46, 128.95, 127.93, 127.75, 127.39, 127.19, 126.65, 126.55, 125.99, 125.50, 123.19, 119.06, 117.91, 91.82, 56.87, 56.20, 14.57. $[\alpha]_D^{30}$ = -28.07 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak OD-H column at 254 nm (n-hexane/i-PrOH = 50/50), 0.7 mL/min; Major enantiomer: t_R = 9.54 min, minor enantiomer: t_R = 35.52 min. 68:32 *dr*, 99% *ee*. HRMS (ESI) calcd for $C_{28}H_{22}N_2O_3Na$ *m/z* $[M + Na]^+$: 457.1523, found: 457.1520.

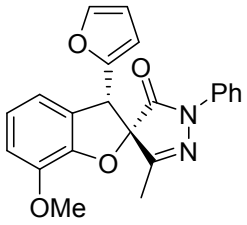


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.537	13406.7	635.2	0.3222	0.62	26.365	BB
2	13.121	12402.6	396.6	0.4788	0.674	24.390	BB
3	17.147	12302.4	297.6	0.6343	0.721	24.193	BB
4	35.523	12738.8	135	1.4449	0.638	25.051	BBA

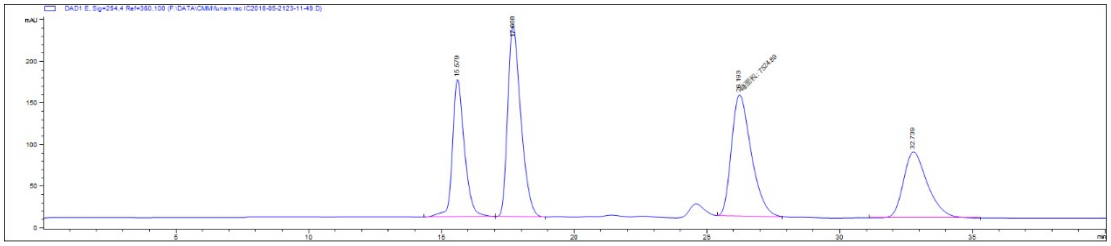


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.525	9543.1	458.9	0.3146	0.698	100.000	VB

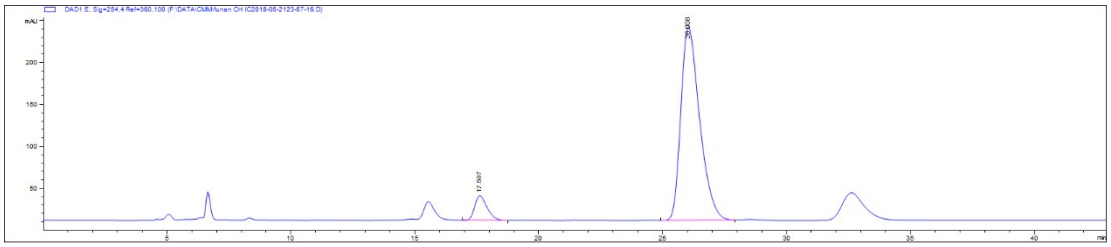
(2*S*,3*R*)-3-(furan-2-yl)-7-methoxy-3'-methyl-1'-phenyl-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3ra)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) colorless oil (92% yield, 34.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (dt, *J* = 8.8, 1.6 Hz, 2H), 7.36 – 7.29 (m, 3H), 7.19 – 7.13 (m, 1H), 7.05 – 7.00 (m, 1H), 6.92 (t, *J* = 7.4 Hz, 2H), 6.34 – 6.28 (m, 2H), 5.23 (s, 1H), 3.94 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.53, 157.88, 148.91, 144.85, 142.92, 137.40, 128.87, 128.70, 125.74, 125.16, 123.10, 118.94, 117.30, 113.05, 110.74, 109.58, 90.42, 56.19, 48.56, 12.97. $[\alpha]_D^{30}$ = -160.32 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak IC column at 254 nm (n-hexane/*i*-PrOH = 85/15), 0.7 mL/min; Major enantiomer: t_R =26.01 min, minor enantiomer: t_R = 17.60 min. 83:17 *dr*, 85% *ee.* HRMS (ESI) calcd for $C_{22}H_{18}N_2O_4Na$ *m/z* $[M + Na]^+$: 397.1159, found: 397.1156.

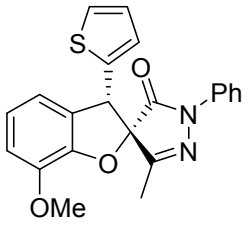


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	15.579	5162.4	164.4	0.4703	0.71	20.191	BB
2	17.668	7889.5	228.5	0.5228	0.646	30.856	BB
3	26.193	7524.9	145.1	0.8641	0.67	29.430	MM
4	32.739	4991.6	79.1	0.9545	0.678	19.523	BB

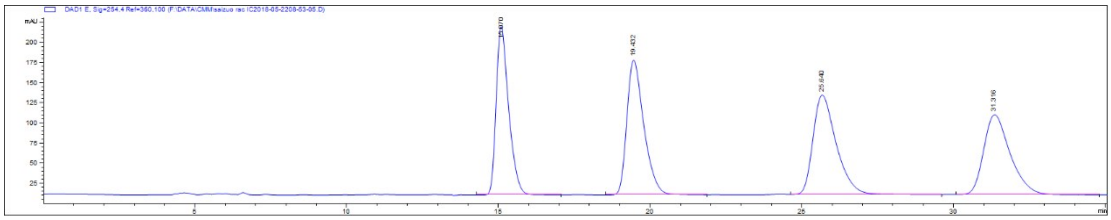


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	17.597	1020.9	29.5	0.524	0.682	7.759	BB
2	26.008	12136	230.2	0.8009	0.64	92.241	BB

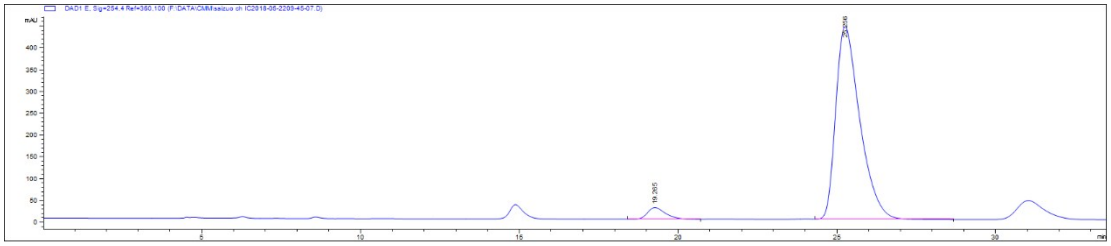
(2*S*,3*S*)-7-methoxy-3'-methyl-1'-phenyl-3-(thiophen-2-yl)-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3sa)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as solid (91% yield, 35.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (dt, *J* = 8.8, 1.6 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.21 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.15 – 7.11 (m, 1H), 7.04 – 7.00 (m, 2H), 6.98 – 6.89 (m, 3H), 5.42 (s, 1H), 3.95 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.62, 157.72, 147.70, 144.77, 137.11, 135.90, 128.64, 127.79, 127.61, 127.16, 125.83, 125.20, 123.09, 119.03, 117.32, 113.05, 91.90, 56.19, 50.14, 13.05. $[\alpha]_D^{30}$ = -241.48 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak IC column at 254 nm (n-hexane/*i*-PrOH = 85/15), 0.7 mL/min; Major enantiomer: t_R = 25.26 min, minor enantiomer: t_R = 19.26 min. 87:13 *dr*, 92% *ee*. HRMS (ESI) calcd for $C_{22}H_{18}N_2O_3SNa$ *m/z* $[M + Na]^+$: 413.0930, found: 413.0930.

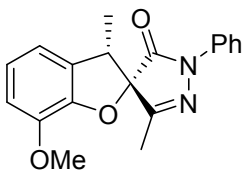


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	15.07	6011.3	209.6	0.4327	0.634	23.917	BB
2	19.432	6530.2	167.7	0.5883	0.633	25.981	BB
3	25.64	6570.8	123.7	0.8059	0.617	26.143	BB
4	31.316	6021.9	99.5	0.9162	0.665	23.959	BB



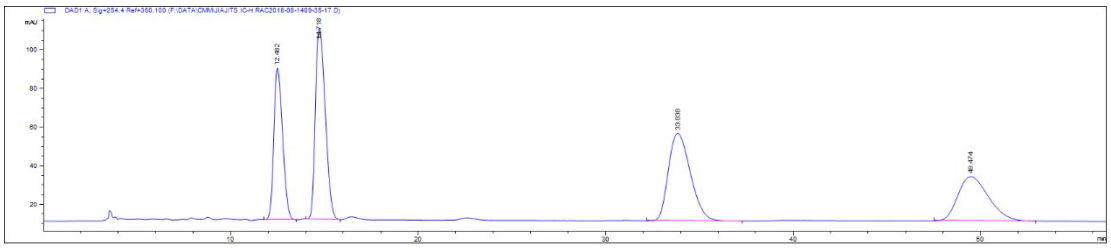
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	19.265	1034.4	26.7	0.5886	0.669	4.244	BB
2	25.256	23335.3	442.1	0.7998	0.589	95.756	BB

(2*S*,3*S*)-7-methoxy-3,3'-dimethyl-1'-phenyl-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3ta)

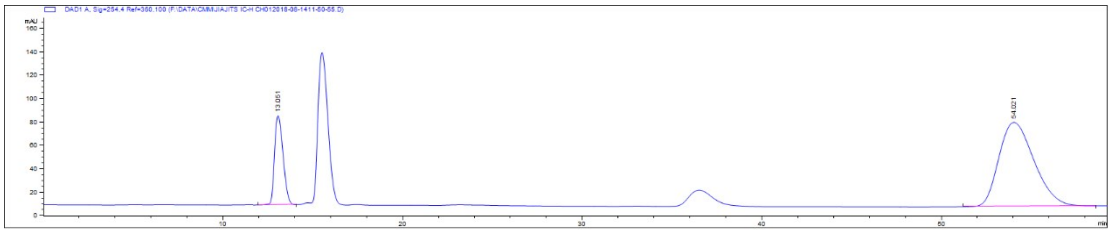


Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) colorless oil (56% yield, 18.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.82 (m, 2H), 7.45 – 7.36 (m,

2H), 7.24 – 7.16 (m, 1H), 6.96 (td, *J* = 7.8, 5.9 Hz, 1H), 6.87 – 6.75 (m, 2H), 3.90 (s, 3H), 3.87 (q, *J* = 7.5 Hz, 1H), 2.20 (s, 3H), 1.43 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.52, 158.98, 146.64, 144.57, 137.64, 130.66, 128.87, 125.22, 122.94, 118.73, 115.83, 112.26, 91.35, 56.12, 43.15, 14.09, 12.94. $[\alpha]_D^{30}$ = -15.03 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak IC column at 254 nm (n-hexane/*i*-PrOH = 90/10), 1.0 mL/min; Major enantiomer: t_R = 54.02 min, minor enantiomer: t_R = 13.05 min. 66:34 *dr*, 60% *ee*. HRMS (ESI) calcd for $C_{19}H_{18}N_2O_3Na$ *m/z* [M + Na]$^+$: 345.1221, found: 345.1217.

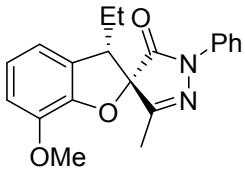


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	12.482	2546.5	78.5	0.5145	0.673	20.459	BB
2	14.718	3631.7	98.8	0.5887	0.643	29.178	BB
3	33.838	3676.2	45.2	1.2788	0.705	29.535	BB
4	49.474	2592.5	22.9	1.7132	0.7	20.829	BB

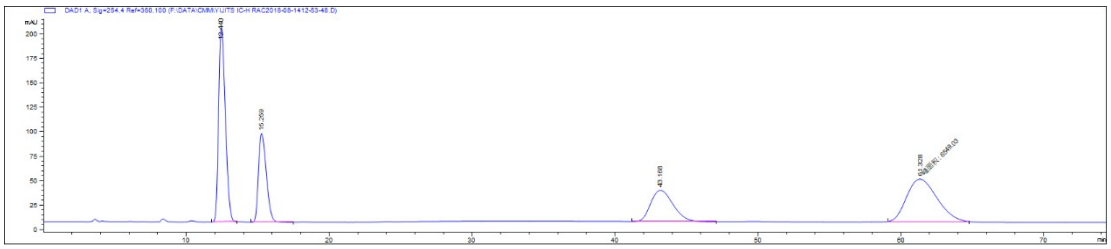


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	13.051	2529	76.4	0.5282	0.682	20.493	BB
2	54.021	9811.6	72.1	2.1377	0.723	79.507	BB

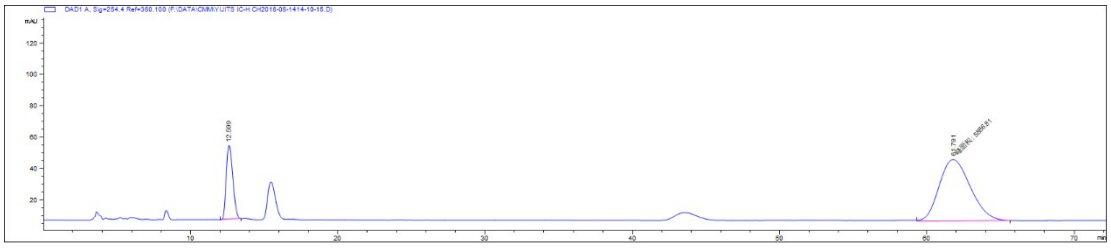
(2*S*,3*S*)-3-ethyl-7-methoxy-3'-methyl-1'-phenyl-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3ua)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) colorless oil (65% yield, 21.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.83 (m, 2H), 7.42 – 7.37 (m, 2H), 7.21 – 7.17 (m, 1H), 6.94 (dd, *J* = 8.6, 7.1 Hz, 1H), 6.83 (d, *J* = 8.1 Hz, 2H), 3.89 (s, 3H), 3.75 – 3.66 (m, 1H), 2.20 (s, 3H), 2.04 – 1.96 (m, 2H), 0.99 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.37, 159.41, 146.54, 144.65, 137.63, 130.17, 128.90, 125.27, 122.72, 118.82, 116.30, 112.18, 90.55, 56.09, 50.37, 23.37, 12.97, 12.38. $[\alpha]_D^{30}$ = -37.07 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak IC column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: t_R = 61.79 min, minor enantiomer: t_R = 12.60 min. 83:17 *dr*, 60% *ee*. HRMS (ESI) calcd for $C_{20}H_{20}N_2O_3Na$ m/z [M + Na]$^+$: 359.1377, found: 359.1367.

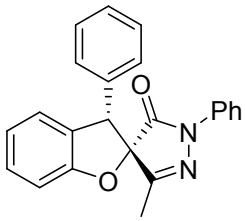


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	12.44	6509.5	197.7	0.5221	0.652	32.577	BB
2	15.259	3477.4	90.6	0.6079	0.63	17.403	BB
3	43.168	3445.9	31.8	1.6258	0.74	17.245	BB
4	61.328	6549	43.9	2.488	0.757	32.775	MM

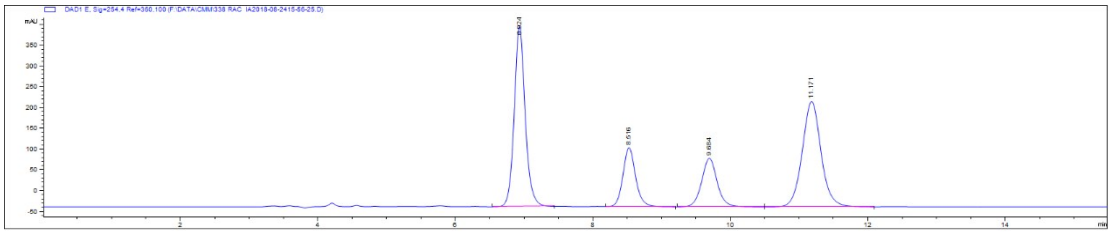


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	12.599	1472.9	47.2	0.4977	0.712	20.014	BB
2	61.791	5886.8	39.5	2.482	0.796	79.986	MM

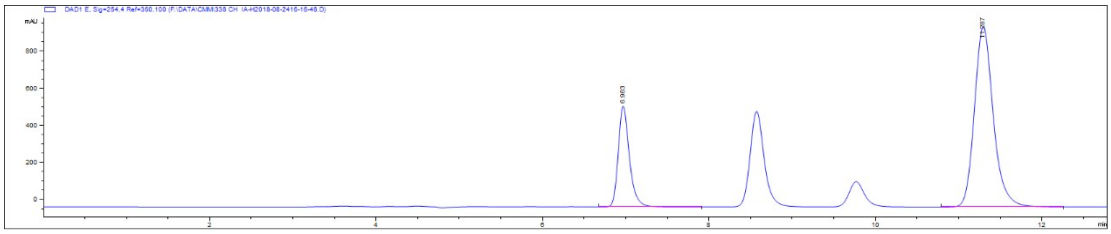
(2*S*,3*S*)-3'-methyl-1',3-diphenyl-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3va)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) colorless oil (94% yield, 33.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.23 (m, 3H), 7.20 – 7.11 (m, 8H), 6.99 – 6.94 (m, 3H), 5.01 (s, 1H), 2.26 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.44, 160.01, 158.56, 136.99, 134.06, 129.46, 129.07, 128.60, 128.51, 128.48, 128.15, 126.62, 125.62, 125.19, 122.21, 119.01, 110.51, 92.02, 55.15, 13.05. $[\alpha]_D^{30}$ = -81.162 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: t_R = 11.29 min, minor enantiomer: t_R = 6.96 min. 72:18 *dr*, 50% *ee*. HRMS (ESI) calcd for $C_{23}H_{18}N_2O_2Na$ m/z $[M + Na]^+$: 377.1260, found: 377.1263.

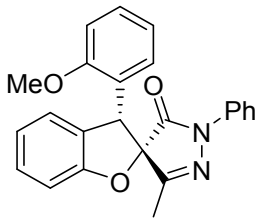


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	6.924	4801.9	432.3	0.1676	0.872	36.269	BB
2	8.516	1812.6	141.4	0.1955	0.871	13.691	BB
3	9.684	1819.5	116.4	0.2384	0.942	13.743	BB
4	11.171	4805.5	252.7	0.2898	0.948	36.297	BB

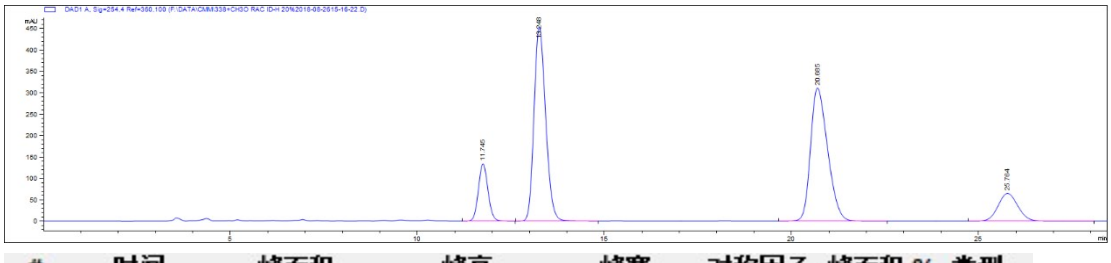


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	6.963	5046.4	541.2	0.1428	0.733	24.829	BB
2	11.287	15278.3	970.8	0.2396	0.817	75.171	BB

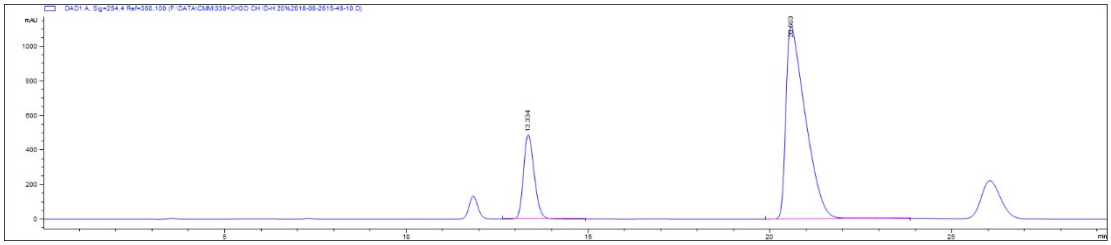
(2*S*,3*S*)-3-(2-methoxyphenyl)-3'-methyl-1'-phenyl-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3wa)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as white solid (90% yield, 34.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.22 – 7.16 (m, 4H), 7.12 – 7.06 (m, 2H), 7.03 – 6.92 (m, 3H), 6.84 (td, *J* = 7.5, 1.1 Hz, 1H), 6.67 (d, *J* = 8.2 Hz, 1H), 5.38 (s, 1H), 3.53 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.16, 159.88, 159.27, 157.27, 137.57, 129.88, 129.24, 129.20, 128.66, 126.40, 125.97, 124.79, 123.71, 121.94, 120.58, 118.61, 110.48, 109.55, 90.87, 55.11, 47.84, 12.94. $[\alpha]_D^{30}$ = -173.35 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak ID column at 254 nm (n-hexane/i-PrOH = 80/20), 1.0 mL/min; Major enantiomer: t_R = 20.56 min, minor enantiomer: t_R = 13.33 min. 83:17 *dr*, 61% *ee*. HRMS (ESI) calcd for $C_{24}H_{20}N_2O_3Na$ m/z $[M + Na]^+$: 407.1366, found: 407.1368.

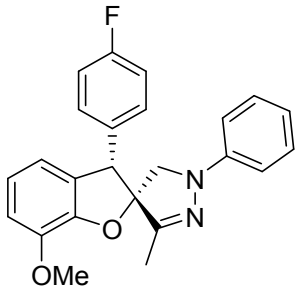


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	11.745	2381.5	133.5	0.2762	0.892	9.749	BB
2	13.248	9784.2	452.4	0.3363	0.776	40.051	BB
3	20.685	9872.8	310.4	0.491	0.661	40.413	BB
4	25.764	2391	64.9	0.572	0.885	9.787	BB

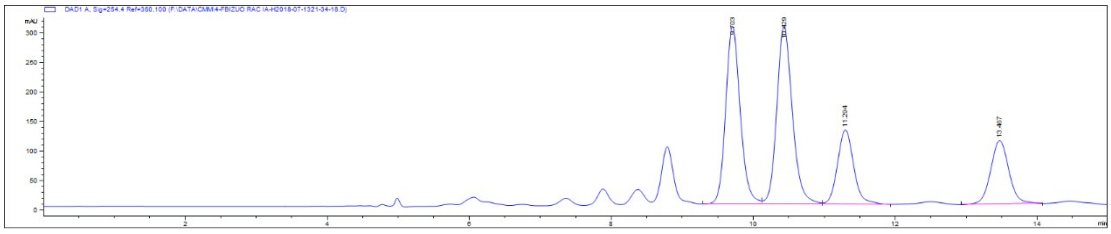


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	13.334	10009.8	487.6	0.3175	0.753	19.350	BB
2	20.563	41721.1	1114.9	0.5546	0.335	80.650	BB

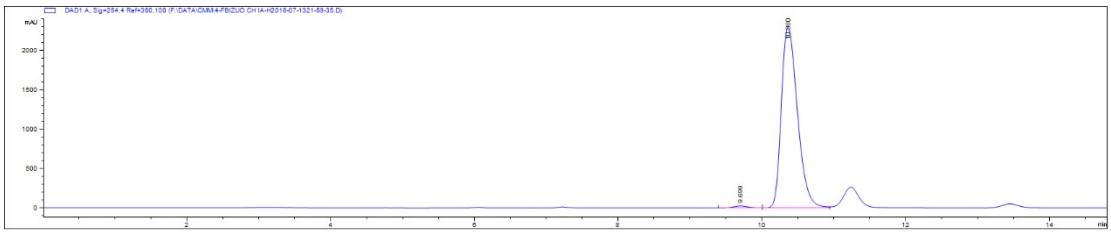
(2*S*,3*S*)-1'-(4-fluorophenyl)-7-methoxy-3'-methyl-3-phenyl-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3ab)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as white solid (83% yield, 33.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 7H), 7.05 – 6.99 (m, 1H), 6.93 (t, *J* = 8.7 Hz, 3H), 6.78 (d, *J* = 7.5 Hz, 1H), 5.16 (s, 1H), 3.96 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.00, 160.01 (d, *J* = 244.6 Hz), 158.29, 148.25, 144.86, 133.72, 133.07 (d, *J* = 2.7 Hz), 129.10, 128.53, 128.51, 127.73, 123.09, 120.96 (d, *J* = 8.1 Hz), 117.49, 115.36 (d, *J* = 22.7 Hz), 112.71, 92.35, 56.21, 55.42, 13.10. ^{19}F NMR (471 MHz, $CDCl_3$) δ -58.04. $[\alpha]_D^{30}$ = -225.45 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/i-PrOH = 90/10), 0.7 mL/min; Major enantiomer: t_R = 10.36 min, minor enantiomer: t_R = 9.70 min. 89:11 *dr*, 98% *ee*. HRMS (ESI) calcd for $C_{24}H_{19}FN_2O_3Na$ m/z [M + Na]$^+$: 425.1272, found: 425.1273.



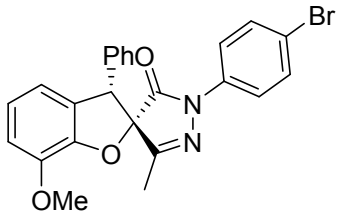
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.703	4266.9	299.2	0.2184	0.827	33.428	BV
2	10.429	4586.3	299.5	0.2326	0.805	35.931	VV
3	11.294	1988.2	125.1	0.2453	0.891	15.576	VB
4	13.467	1922.9	107.2	0.2772	0.941	15.065	BB



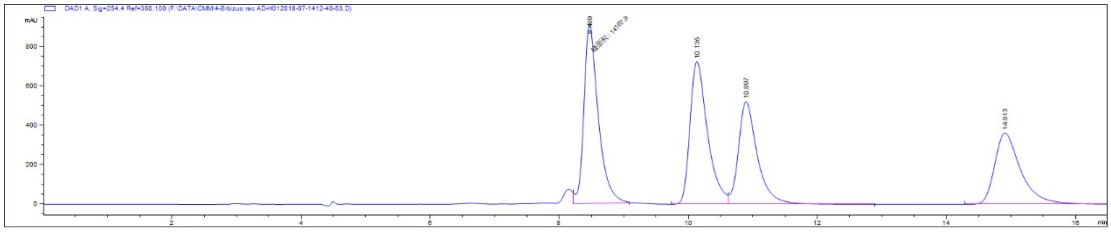
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.699	332.5	24.5	0.2105	0.88	0.922	BV
2	10.36	35724.9	2285	0.2424	0.653	99.078	VV

(2*S*,3*S*)-1'-(4-bromophenyl)-7-methoxy-3'-methyl-3-phenyl-3H-spiro[benzofuran-2,4'-pyrazol]-

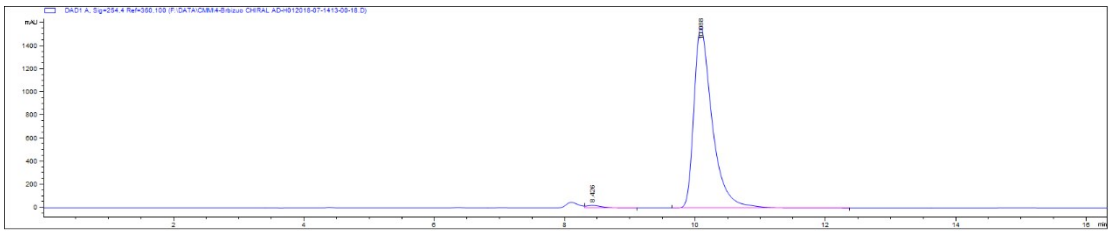
5'(1'H)-one (3ac)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as white solid (79% yield, 36.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.30 – 7.25 (m, 5H), 7.22 (dd, *J* = 7.5, 1.9 Hz, 2H), 7.02 (t, *J* = 7.8 Hz, 1H), 6.94 (s, 1H), 6.78 (d, *J* = 7.5 Hz, 1H), 5.15 (s, 1H), 3.96 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.01, 158.50, 148.17, 144.83, 136.05, 133.60, 131.61, 129.02, 128.55, 128.50, 127.64, 123.12, 120.25, 117.99, 117.46, 112.70, 92.34, 56.18, 55.43, 13.11. $[\alpha]_D^{30}$ = -242.48 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak AD-H column at 254 nm (n-hexane/*i*-PrOH = 90/10), 1.0 mL/min; Major enantiomer: t_R = 10.09 min, minor enantiomer: t_R = 8.43 min. 99:1 *dr*, 98% *ee*. HRMS (ESI) calcd for Chemical Formula: $C_{24}H_{19}BrN_2O_3Na$ *m/z* $[M + Na]^+$: 485.0482, found: 485.0480.

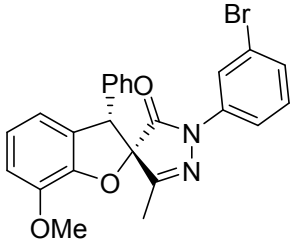


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	8.469	14167.9	906.8	0.2604	0.623	29.032	MM
2	10.135	13730.8	725.3	0.2849	0.61	28.136	BV
3	10.897	10688.4	521.3	0.3032	0.628	21.902	VB
4	14.913	10213.7	361.9	0.4193	0.607	20.929	BBA

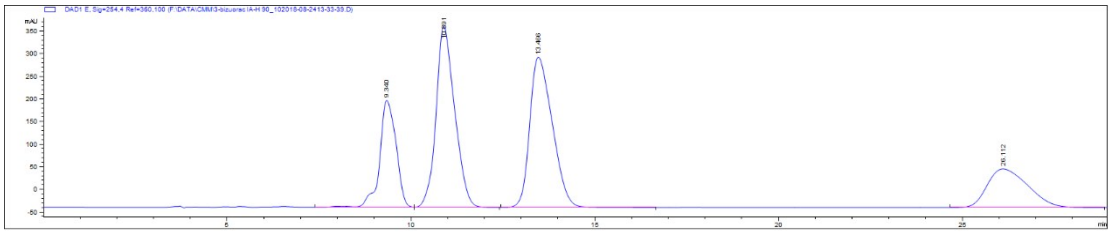


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	8.426	362.8	22.1	0.2398	0.564	1.176	VB
2	10.088	30473.6	1558.7	0.2921	0.56	98.824	BB

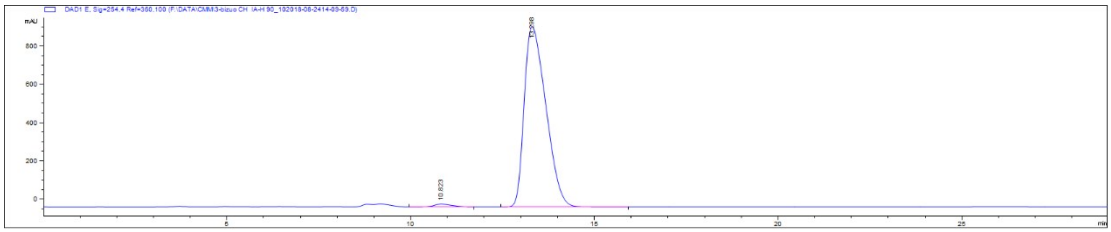
(2*S*,3*S*)-1'-(3-bromophenyl)-7-methoxy-3'-methyl-3-phenyl-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3ad)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as colorless oil (93% yield, 43.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (t, *J* = 2.0 Hz, 1H), 7.33 (ddd, *J* = 8.2, 2.1, 1.0 Hz, 1H), 7.28 – 7.24 (m, 3H), 7.21 – 7.16 (m, 3H), 7.07 (t, *J* = 8.1 Hz, 1H), 7.02 – 6.98 (m, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.76 (dt, *J* = 7.6, 1.1 Hz, 1H), 5.13 (s, 1H), 3.94 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.09, 158.58, 148.15, 144.84, 138.12, 133.52, 129.94, 129.04, 128.61, 128.56, 127.99, 127.67, 123.15, 122.26, 121.59, 117.47, 117.11, 112.71, 92.40, 56.21, 55.47, 13.14. $[\alpha]_D^{30}$ = -244.49 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak IC column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: t_R = 13.30 min, minor enantiomer: t_R = 10.82 min. 98:2 *dr*, 98% *ee*. HRMS (ESI) calcd for $C_{24}H_{19}BrN_2O_3Na$ *m/z* $[M + Na]^+$: 485.0482, found: 485.0479.

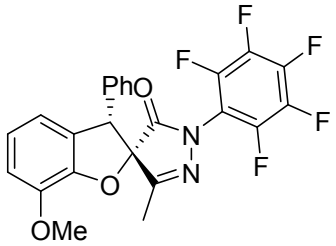


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.34	7306.2	235.5	0.4988	0.828	17.387	VV R
2	10.891	14095.8	398.7	0.5204	0.698	33.544	VB
3	13.466	14121.7	331.3	0.6873	0.596	33.605	BB
4	26.112	6498.5	84.9	1.2447	0.616	15.465	BBA



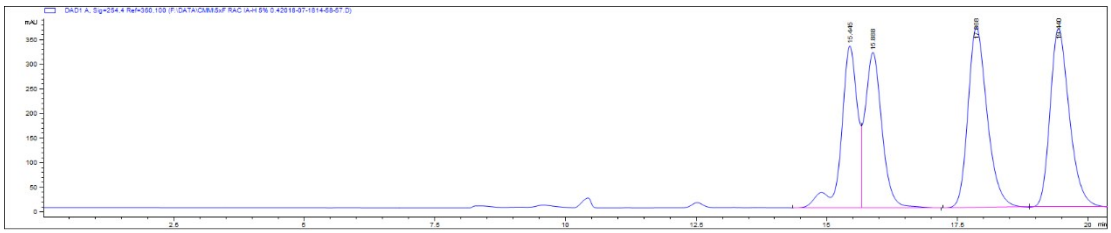
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	10.823	501.3	15.1	0.4863	0.667	1.283	BB
2	13.298	38559.1	941	0.6601	0.553	98.717	BB

(2*S*,3*S*)-7-methoxy-3'-methyl-1'-(perfluorophenyl)-3-phenyl-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3ae)

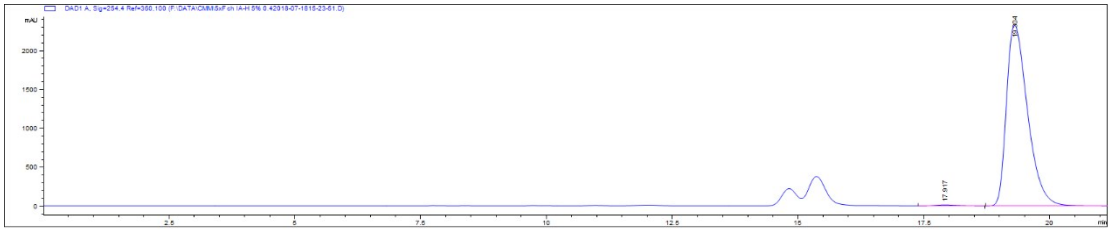


Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as white solid (91% yield, 42.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 3H), 7.26 – 7.21 (m, 2H), 7.03 (t, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.77 (dt, *J* = 7.6, 1.1 Hz, 1H), 5.20 (s, 1H), 3.98 (s, 3H), 2.38 (s, 3H), 1.30 (d, *J* = 14.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.69, 159.88, 147.81, 144.89, 144.81-144.63(m), 142.76-142.57(m), 140.67-140.40(m), 138.81-138.51(m), 136.79-136.51(m), 133.21, 129.18, 128.74, 128.73, 127.70, 123.34, 117.41, 112.60, 111.50-111.24(m), 90.51, 56.14, 55.50, 13.13. ^{19}F NMR (471 MHz, $CDCl_3$) δ -161.58 – (-161.69) (m, 2F), -152.92 (t, *J* =21.2, 2F),

-142.82 – (-142.65) (m, 1F). $[\alpha]_D^{30}$ = -254.51 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak IC column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: t_R = 19.30 min, minor enantiomer: t_R = 17.92 min. 90:10 *dr*, 99% *ee*. HRMS (ESI) calcd for $C_{24}H_{15}F_5N_2O_3Na$ *m/z* $[M + Na]^+$: 497.0906, found: 497.0900.

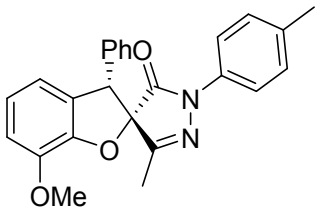


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	15.445	7056.3	328	0.2995	1.528	21.571	VV R
2	15.888	7055	314.7	0.3335	0.79	21.567	VB
3	17.868	9340.7	365.5	0.3861	0.729	28.554	BB
4	19.44	9260.1	361.2	0.3911	0.721	28.308	BBA

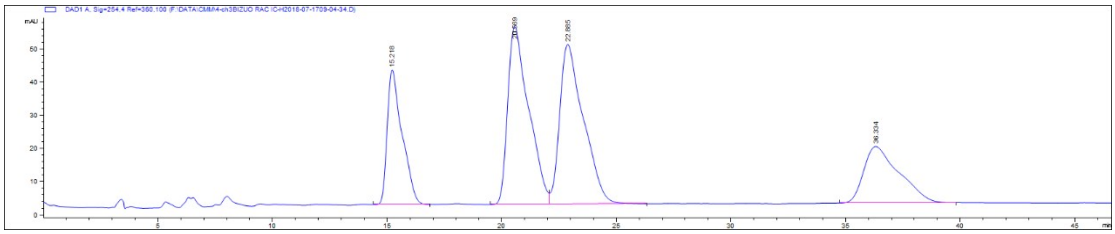


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	17.917	391.9	12.7	0.4688	0.696	0.576	BB
2	19.304	67632.2	2315.2	0.4488	0.581	99.424	BB

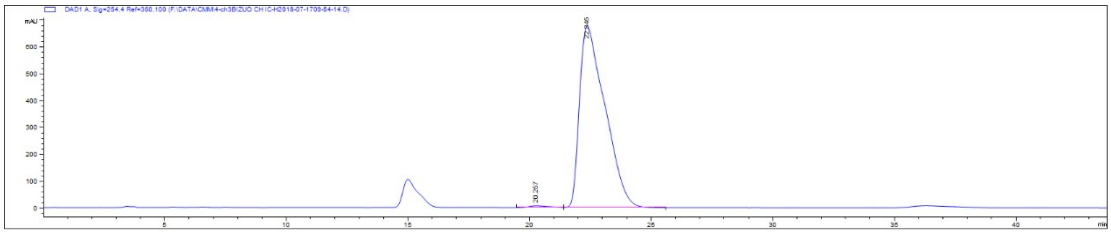
(2*S*,3*S*)-7-methoxy-3'-methyl-3-phenyl-1'-(p-tolyl)-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3af)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as white solid (84% yield, 33.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 5H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.03 (dd, *J* = 20.3, 8.1 Hz, 3H), 6.93 (d, *J* = 8.1 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 1H), 5.15 (s, 1H), 3.96 (s, 3H), 2.39 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.90, 157.89, 148.29, 144.82, 134.94, 134.53, 133.81, 129.12, 128.46, 128.43, 127.89, 122.95, 119.26, 117.48, 112.66, 92.31, 56.19, 55.30, 20.88, 13.08. $[\alpha]_D^{30}$ = -228.46 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak IC column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: t_R = 22.36 min, minor enantiomer: t_R =20.26. 92:8 *dr*, 98% *ee*. HRMS (ESI) calcd for $C_{25}H_{22}N_2O_3Na$ m/z $[M + Na]^+$: 421.1523, found: 421.1526.

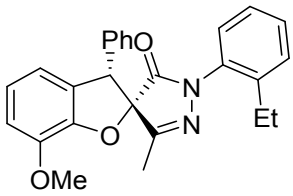


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	15.218	1828.5	40.5	0.647	0.471	17.395	BB
2	20.569	3399.5	53.5	0.9119	0.472	32.341	BV
3	22.885	3467.5	48	1.0322	0.482	32.988	VB
4	36.334	1815.9	17	1.4906	0.488	17.276	BB

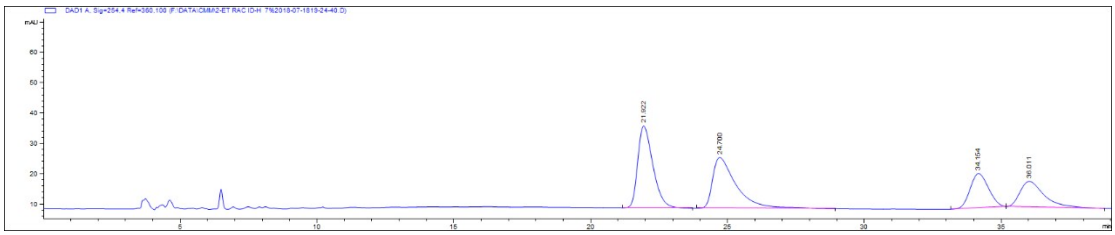


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	20.257	326.3	6.2	0.7677	0.605	0.661	BB
2	22.345	49001.6	671.7	1.0391	0.412	99.339	BB

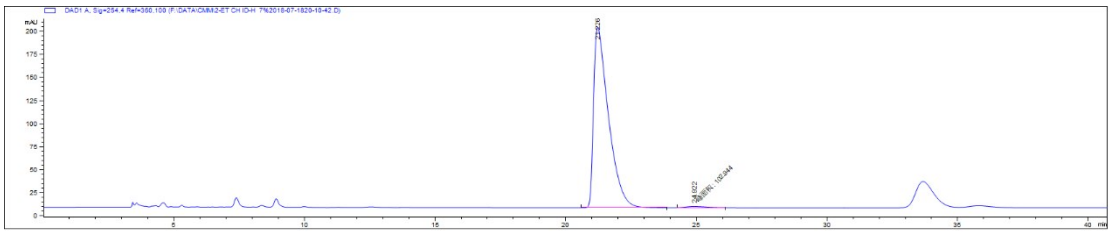
(2*S*,3*S*)-1'-(2-ethylphenyl)-7-methoxy-3'-methyl-3-phenyl-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3ag)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as colorless oil (81% yield, 33.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (ddd, *J* = 19.4, 5.0, 2.5 Hz, 5H), 7.21 (td, *J* = 7.6, 1.2 Hz, 1H), 7.16 (d, *J* = 6.6 Hz, 1H), 7.10 (td, *J* = 7.7, 1.6 Hz, 1H), 7.02 – 6.97 (m, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.73 (ddd, *J* = 19.4, 7.7, 1.0 Hz, 2H), 5.20 (s, 1H), 3.97 (s, 3H), 2.39 (s, 3H), 1.91 (dd, *J* = 19.8, 7.6 Hz, 2H), 0.95 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.15, 157.62, 148.13, 144.80, 141.02, 134.72, 133.79, 129.73, 128.70, 128.60, 128.59, 128.52, 128.35, 126.26, 126.21, 122.93, 117.31, 112.45, 91.58, 56.14, 55.16, 23.35, 14.07, 13.16. $[\alpha]_D^{30}$ = -13.03 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak ID column at 254 nm (n-hexane/i-PrOH = 93/7), 1.0 mL/min; Major enantiomer: t_R = 21.23 min, minor enantiomer: t_R = 24.92 min. 85:15 *dr*, 95% *ee*. HRMS (ESI) calcd for $C_{26}H_{24}N_2O_3Na$ m/z $[M + Na]^+$: 435.1679, found: 435.1682.

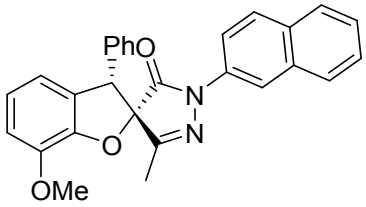


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	21.922	1042.9	27	0.5922	0.612	33.600	BB
2	24.7	1009.9	16.8	0.8728	0.394	32.536	BB
3	34.154	529.6	11.3	0.7319	0.82	17.063	BB
4	36.011	521.5	8.4	0.9172	0.582	16.800	BBA

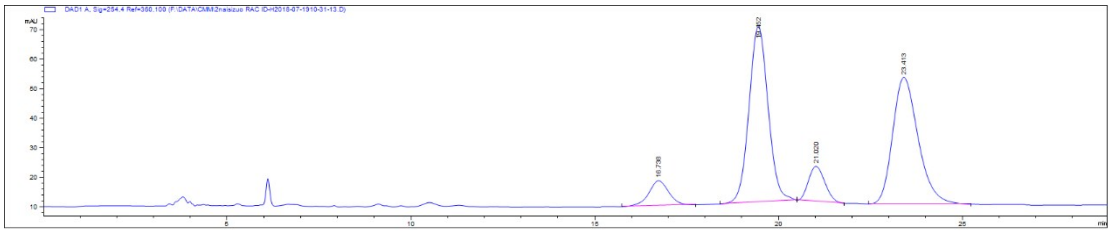


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	21.226	7730.2	195.4	0.5796	0.355	98.686	BB
2	24.922	102.9	1.6	1.0442	0.617	1.314	MM

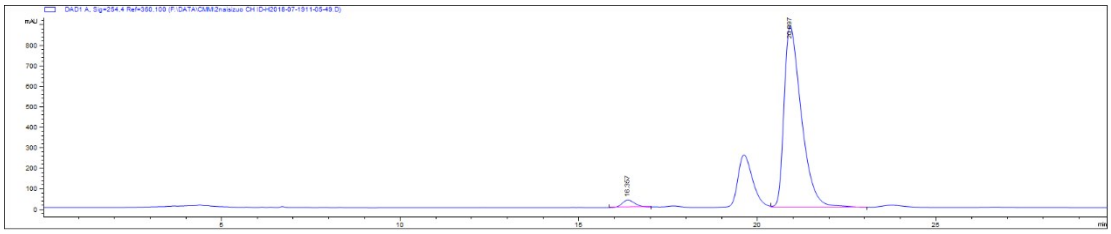
(2*S*,3*S*)-7-methoxy-3'-methyl-1'-(naphthalen-2-yl)-3-phenyl-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3ah)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as white solid (95% yield, 41.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, *J* = 1.9 Hz, 1H), 8.11 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.94 – 7.84 (m, 3H), 7.50 (dddd, *J* = 20.9, 8.1, 6.9, 1.3 Hz, 2H), 7.38 – 7.33 (m, 3H), 7.24 – 7.20 (m, 2H), 7.10 – 7.06 (m, 1H), 6.99 – 6.89 (m, 2H), 5.40 (t, *J* = 0.9 Hz, 1H), 3.97 (s, 3H), 1.65 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.12, 158.61, 147.58, 144.95, 135.19, 134.99, 133.42, 131.16, 128.99, 128.79, 128.47, 128.21, 127.98, 127.60, 127.28, 126.53, 125.50, 123.10, 118.23, 117.80, 116.15, 112.61, 91.83, 56.71, 56.13, 14.43. $[\alpha]_D^{30}$ = 214.43 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak ID column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: t_R = 20.90 min, minor enantiomer: t_R = 16.36 min. 80:20 *dr*, 94% *ee*. HRMS (ESI) calcd for $C_{28}H_{22}N_2O_3Na$ m/z $[M + Na]^+$: 457.1523, found: 457.1521.

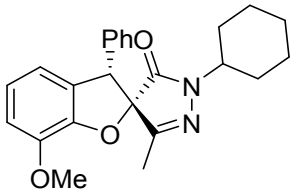


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	16.738	321.9	8.4	0.5793	0.967	6.562	BB
2	19.452	2151.8	59.3	0.5614	0.924	43.859	BB
3	21.02	366.9	11.8	0.4919	0.805	7.478	BB
4	23.413	2065.5	42.8	0.7394	0.74	42.101	BB

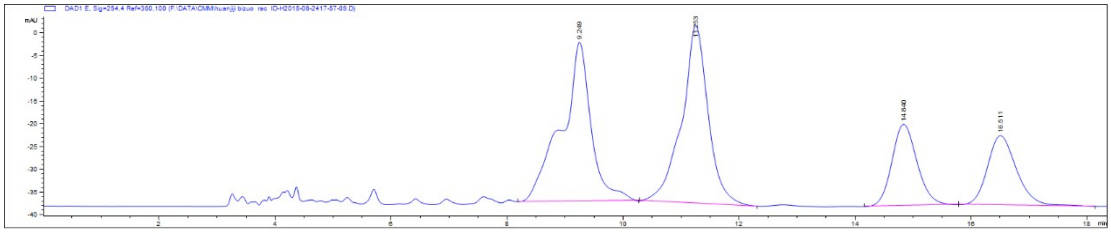


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	16.357	863.7	34.6	0.3868	0.805	2.829	BB
2	20.897	29670	879.9	0.5114	0.511	97.171	VB

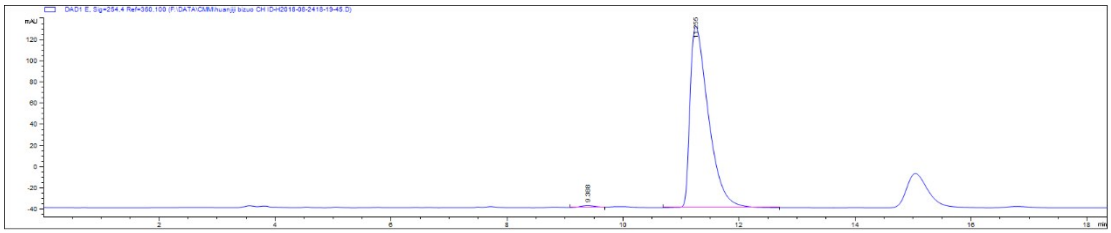
(2*S*,3*S*)-1'-cyclohexyl-7-methoxy-3'-methyl-3-phenyl-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3ai)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as white solid (76% yield, 29.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 3H), 7.18 (dd, *J* = 6.6, 2.9 Hz, 2H), 6.96 (dd, *J* = 8.1, 7.5 Hz, 1H), 6.88 (d, *J* = 8.1 Hz, 1H), 6.73 (dt, *J* = 7.5, 1.1 Hz, 1H), , 5.03 (s, 1H), 3.93 (s, 3H), 3.52 – 3.44 (m, 1H), 2.27 (s, 3H), 1.75 – 1.65 (m, 2H), 1.62 – 1.51 (m, 3H), 1.27 – 1.00 (m, 5H), 0.88 – 0.81 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.59, 156.35, 148.35, 144.75, 133.82, 129.20, 128.35, 128.23, 128.12, 122.69, 117.34, 112.33, 92.45, 56.06, 54.88, 51.98, 30.32, 29.73, 25.21, 25.19, 25.09, 12.97. $[\alpha]_D^{30}$ = -160.3 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak ID column at 254 nm (n-hexane/i-PrOH = 90/10), 1.0 mL/min; Major enantiomer: t_R = 11.26min, minor enantiomer: t_R = 9.39 min. 82:18 *dr*, 98% *ee*. HRMS (ESI) calcd for $C_{24}H_{26}N_2O_3Na$ m/z $[M + Na]^+$: 413.1836, found: 413.1839.

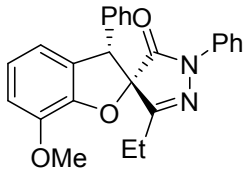


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.249	1245.5	34.9	0.4863	1.537	34.932	BB
2	11.253	1243.3	39	0.456	1.113	34.871	BB
3	14.84	542.5	17.9	0.4655	0.83	15.216	BB
4	16.511	534.1	15.3	0.5319	0.762	14.981	BB

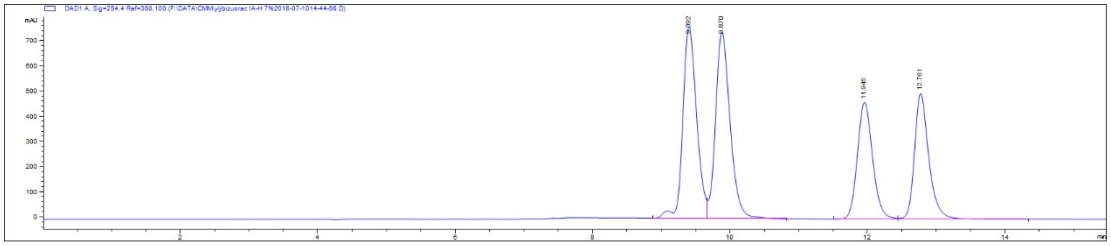


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.388	24.5	1.5	0.2642	1.002	0.649	BB
2	11.255	3753.4	170.3	0.3351	0.418	99.351	BB

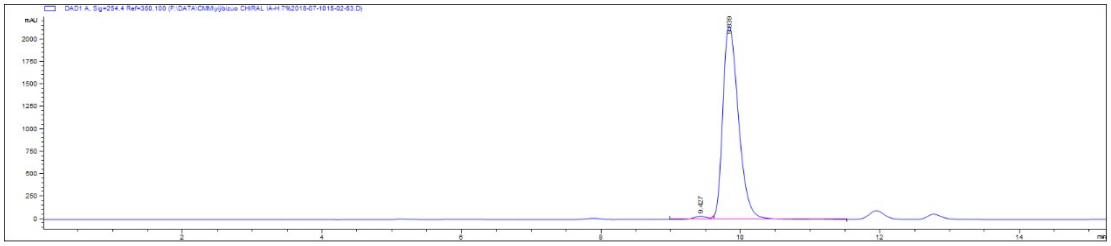
(2*S*,3*S*)-3'-ethyl-7-methoxy-1',3-diphenyl-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3aj)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as white solid (92% yield, 36.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.30 – 7.21 (m, 7H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.01 (t, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 8.1 Hz, 1H), 6.78 (d, *J* = 7.5 Hz, 1H), 5.17 (s, 1H), 3.96 (s, 3H), 2.77 (dd, *J* = 7.4, 3.7 Hz, 2H), 1.44 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.29, 161.96, 148.29, 144.85, 137.16, 133.96, 129.11, 128.56, 128.47, 128.43, 127.93, 125.11, 122.94, 119.12, 117.51, 112.74, 92.51, 56.24, 55.55, 20.74, 9.41. $[\alpha]_D^{30}$ = -179.36 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/i-PrOH = 93/7), 0.7 mL/min; Major enantiomer: t_R = 9.84 min, minor enantiomer: t_R = 9.43 min. 94:6 *dr*, 97% *ee*. HRMS (ESI) calcd for $C_{25}H_{22}N_2O_3Na$ m/z $[M + Na]^+$: 421.1523, found: 421.1521.

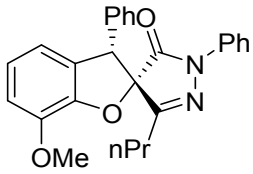


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.392	10649.2	761.8	0.211	0.843	29.734	VV R
2	9.87	10852.1	739.8	0.2231	0.724	30.301	VB
3	11.945	7130.9	463.5	0.2375	0.843	19.911	BV
4	12.761	7182.5	498.3	0.2162	0.703	20.055	VB



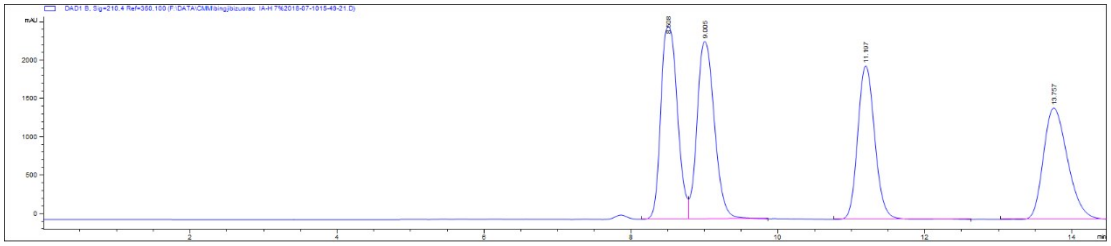
#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.427	451.2	34	0.2068	1.072	1.319	BV E
2	9.839	33741.6	2148.5	0.2428	0.683	98.681	VV R

(2*S*,3*S*)-7-methoxy-1',3-diphenyl-3'-propyl-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3ak)

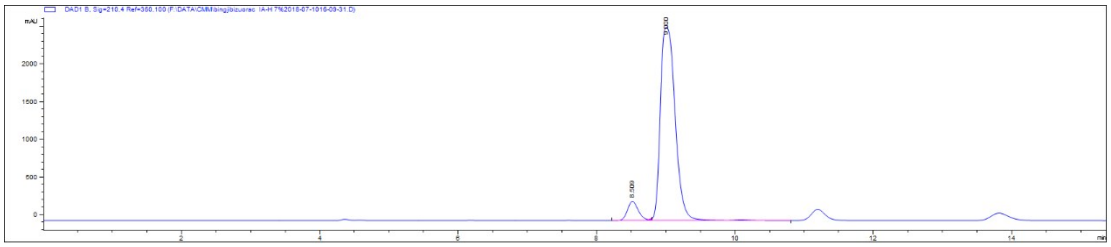


Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as white solid (91% yield, 37.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (dt, *J* = 8.9, 1.8 Hz, 2H), 7.29 – 7.23 (m, 7H), 7.12 – 7.07 (m, 1H), 7.01 (t, *J* = 7.8 Hz, 1H), 6.93 (dt, *J* = 8.1, 1.0 Hz, 1H), 6.78 (dt, *J* = 7.6, 1.1 Hz, 1H), 5.18 (s, 1H), 3.96 (s, 3H), 2.76 – 2.64 (m, 2H), 1.95 (t, *J* = 7.4 Hz, 2H), 1.14 (t, *J* = 7.4

Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.23, 160.95, 148.30, 144.83, 137.11, 133.93, 129.11, 128.54, 128.45, 128.41, 127.91, 125.09, 123.10, 119.09, 117.49, 112.75, 92.60, 56.19, 55.48, 29.29, 18.64, 14.05. $[\alpha]_D^{30}$ = -131.26 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak IA column at 254 nm (n-hexane/*i*-PrOH = 93/7), 1.0 mL/min; Major enantiomer: t_R = 9.00 min, minor enantiomer: t_R = 8.51 min. 91:9 *dr*, 87% *ee*. HRMS (ESI) calcd for $C_{26}H_{24}N_2O_3Na$ *m/z* [M + Na]$^+$: 435.1679, found: 435.1675.

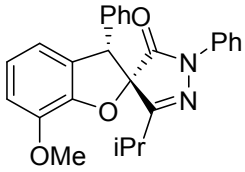


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	8.508	39352.3	2512	0.2488	0.786	27.542	BV
2	9.005	38123.4	2313.8	0.2562	0.765	26.682	VB
3	11.197	32323.7	1998.6	0.2494	0.849	22.622	BV R
4	13.757	33084	1449.2	0.3563	0.723	23.155	VBAR

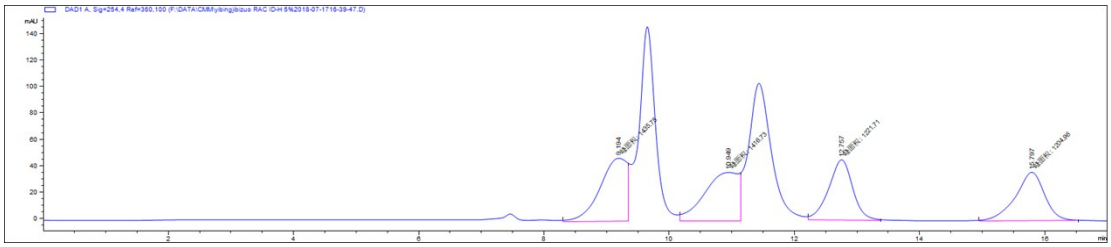


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	8.509	2810.4	256.5	0.1678	0.804	6.868	BV E
2	9	38112.4	2563.5	0.2327	0.928	93.132	VV R

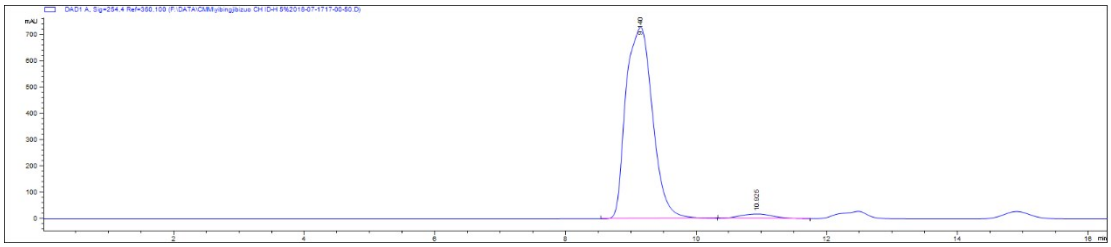
(2*S*,3*S*)-3'-isopropyl-7-methoxy-1',3-diphenyl-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3al)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as white solid (90% yield, 37.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.30 (m, 2H), 7.26 – 7.19 (m, 7H), 7.08 – 7.04 (m, 1H), 7.00 – 6.95 (m, 1H), 6.90 (d, *J* = 8.1 Hz, 1H), 6.75 (dt, *J* = 7.5, 1.1 Hz, 1H), 5.22 (s, 1H), 3.93 (s, 3H), 3.08 (hept, *J* = 7.0 Hz, 1H), 1.49 (d, *J* = 6.8 Hz, 3H), 1.41 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.26, 164.80, 148.36, 144.91, 137.13, 134.01, 129.12, 128.53, 128.43, 128.40, 127.93, 125.07, 122.85, 119.12, 117.55, 112.94, 93.13, 56.31, 55.53, 28.18, 21.30, 20.06. $[\alpha]_D^{30}$ = -191,38 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak ID column at 254nm (n-hexane/*i*-PrOH = 95/5), 1.0 mL/min; Major enantiomer: t_R = 10.93 min, minor enantiomer: t_R = 9.14 min. 93:7 *dr*, 95% *ee*. HRMS (ESI) calcd for $C_{26}H_{24}N_2O_3Na$ *m/z* [M+Na]$^+$: 435.1679, found: 435.1679.

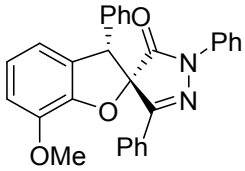


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.194	1435.8	47.7	0.5016	2.265	27.197	MM
2	10.949	1416.7	36.9	0.6399	2.275	26.836	MM
3	12.757	1221.7	45.6	0.447	1.128	23.142	MM
4	15.797	1205	36.7	0.5467	1.267	22.825	MM

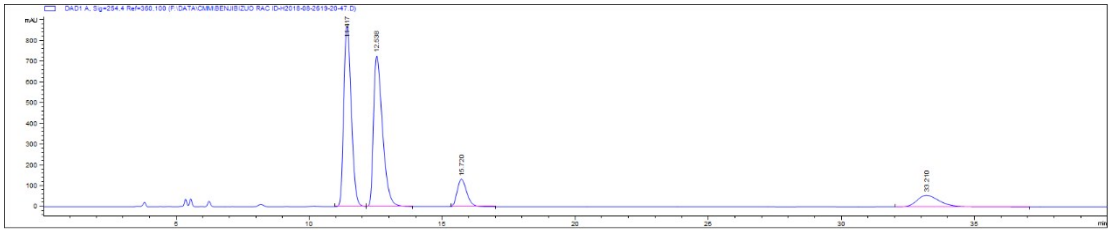


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	9.14	20606.8	727.5	0.3985	1.11	97.235	BB
2	10.925	586	17	0.5606	0.992	2.765	BB

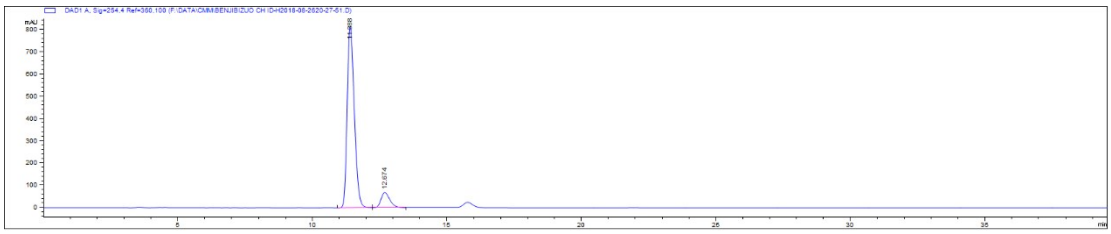
(2*S*,3*S*)-7-methoxy-1',3,3'-triphenyl-3H-spiro[benzofuran-2,4'-pyrazol]-5'(1'H)-one (3am)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/10 (v/v) as white solid (86% yield, 38.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 8.04 (m, 2H), 7.54 – 7.47 (m, 3H), 7.41 – 7.36 (m, 2H), 7.30 – 7.25 (m, 5H), 7.22 (dd, *J* = 7.5, 2.0 Hz, 2H), 7.16 – 7.11 (m, 1H), 7.09 – 7.03 (m, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 6.80 (dt, *J* = 7.4, 1.2 Hz, 1H), 5.42 (s, 1H), 4.00 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.53, 155.48, 148.20, 145.16, 136.91, 133.68, 130.97, 129.19, 129.17, 129.15, 128.61, 128.48, 127.85, 126.81, 125.52, 123.12, 119.50, 117.69, 113.12, 92.89, 57.12, 56.40. $[\alpha]_D^{30}$ = -182.1 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by HPLC using Daicel Chiralpak ID column at 254 nm (n-hexane/*i*-PrOH = 90/10), 1.0 mL/min; Major enantiomer: t_R = 11.39 min, minor enantiomer: t_R = 12.67 min. 93:7 *dr*, 95% *ee*. HRMS (ESI) calcd for $C_{29}H_{22}N_2O_3Na$ *m/z* $[M+Na]^+$: 469.1523, found: 469.1513.

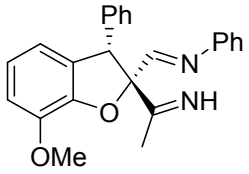


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	11.417	17172.4	871.7	0.3098	0.718	41.929	BV
2	12.538	17102.2	727.3	0.3603	0.538	41.757	VB
3	15.72	3372.6	132.7	0.3906	0.777	8.235	VB
4	33.21	3308.9	55.8	0.8995	0.677	8.079	BB

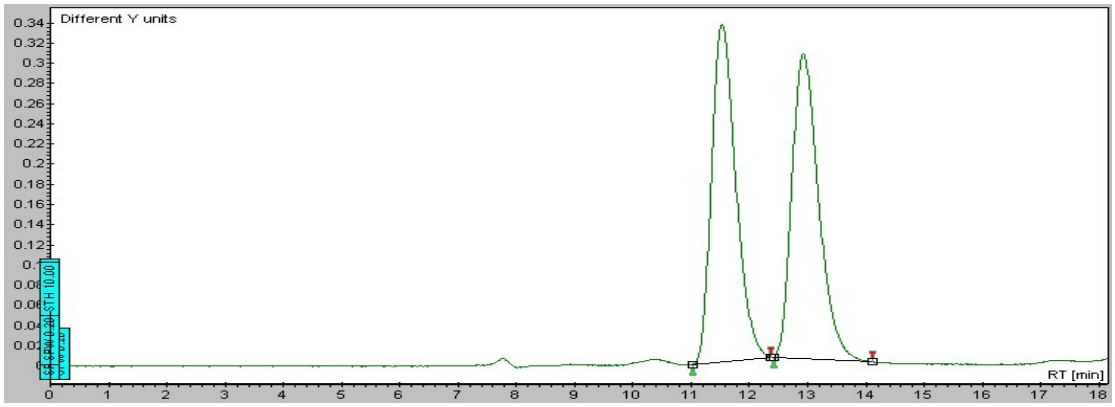


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %	类型
1	11.388	14960.8	809.4	0.2876	0.69	90.521	BV
2	12.674	1566.7	68.2	0.3518	0.711	9.479	VB

1-((2*R*,3*S*)-7-methoxy-3-phenyl-2-((E)-(phenylimino)methyl)-2,3-dihydrobenzofuran-2-yl)ethan-1-imine (5)



Purified by flash chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1/20 (v/v) as white solid (77% yield, 15.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.9 Hz, 2H), 7.35 – 7.29 (m, 3H), 7.28 – 7.23 (m, 3H), 7.20 (t, *J* = 7.4 Hz, 1H), 6.83 – 6.78 (m, 2H), 6.66 (dd, *J* = 6.3, 3.1 Hz, 1H), 5.80 (s, 1H), 5.72 (s, 1H), 3.90 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.35, 146.44, 143.16, 142.97, 140.15, 129.23, 129.15, 128.67, 128.34, 127.24, 126.33, 125.52, 124.63, 121.73, 119.32, 118.41, 108.90, 56.02, 40.11, 12.25. $[\alpha]_D^{30}$ = 3.9 (c = 1.0 in CH_2Cl_2). The enantiomers were analyzed by chiral HPLC (JASCO LC-2000 Plus) using Daicel Chiralpak AD-H column at 254 nm (n-hexane/*i*-PrOH = 80/20), 1.0 mL/min; Major enantiomer: t_R = 11.02 min, minor enantiomer: t_R = 12.42 min. > 95:5 *dr*, 99% *ee*. HRMS (ESI) calcd for $C_{24}H_{22}N_2O_2Na$ *m/z* $[M+Na]^+$: 393.1573, found: 393.1582.



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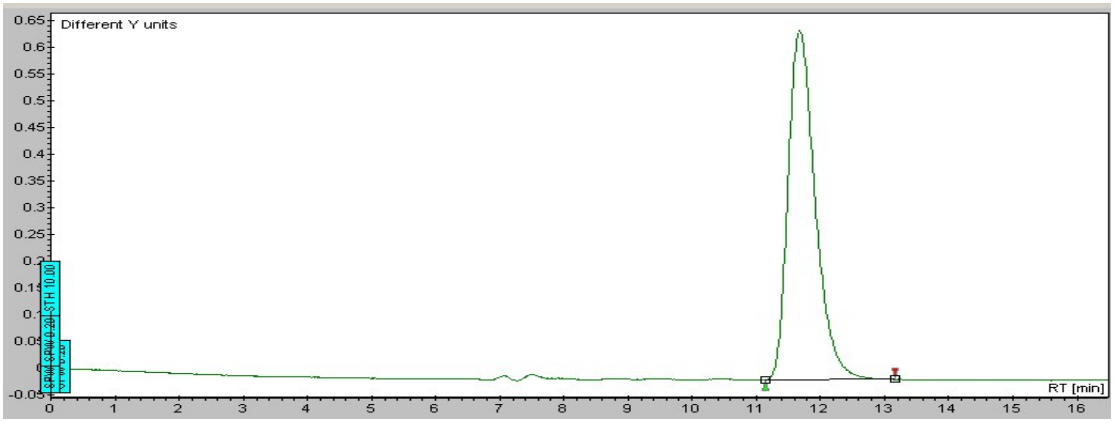
2	UNKNOWN	12.417	12.919	14.105	0.000	49.88	0.3	0.2	49.883



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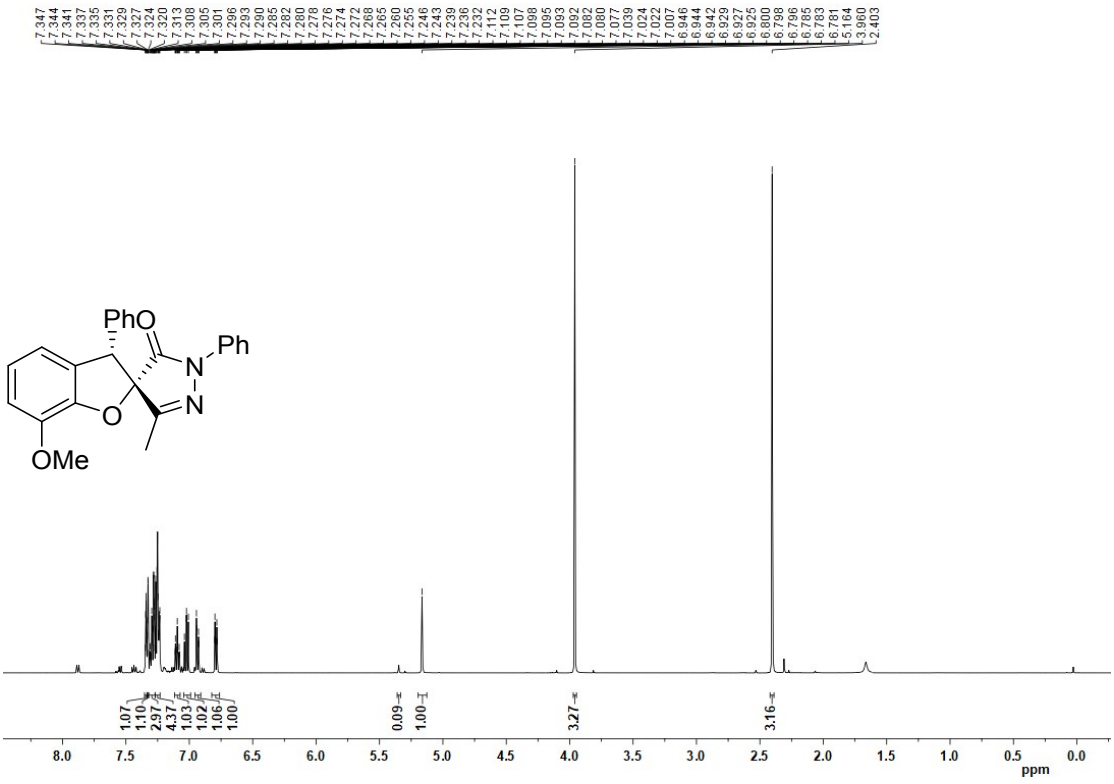

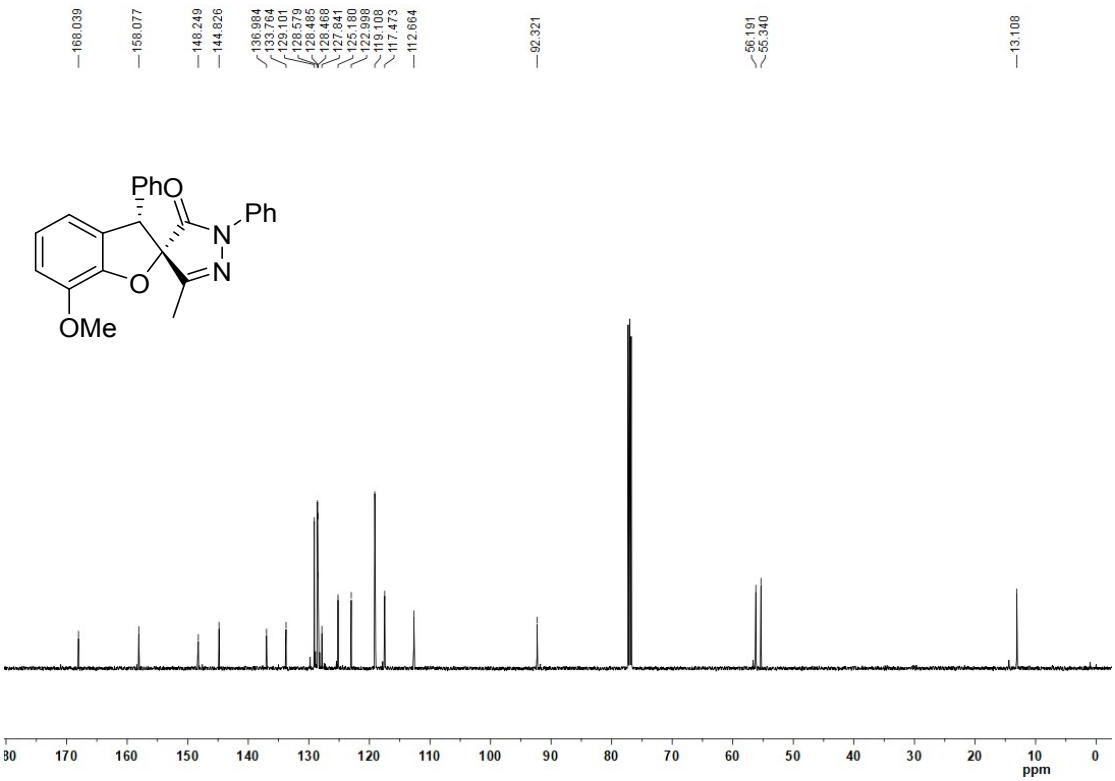
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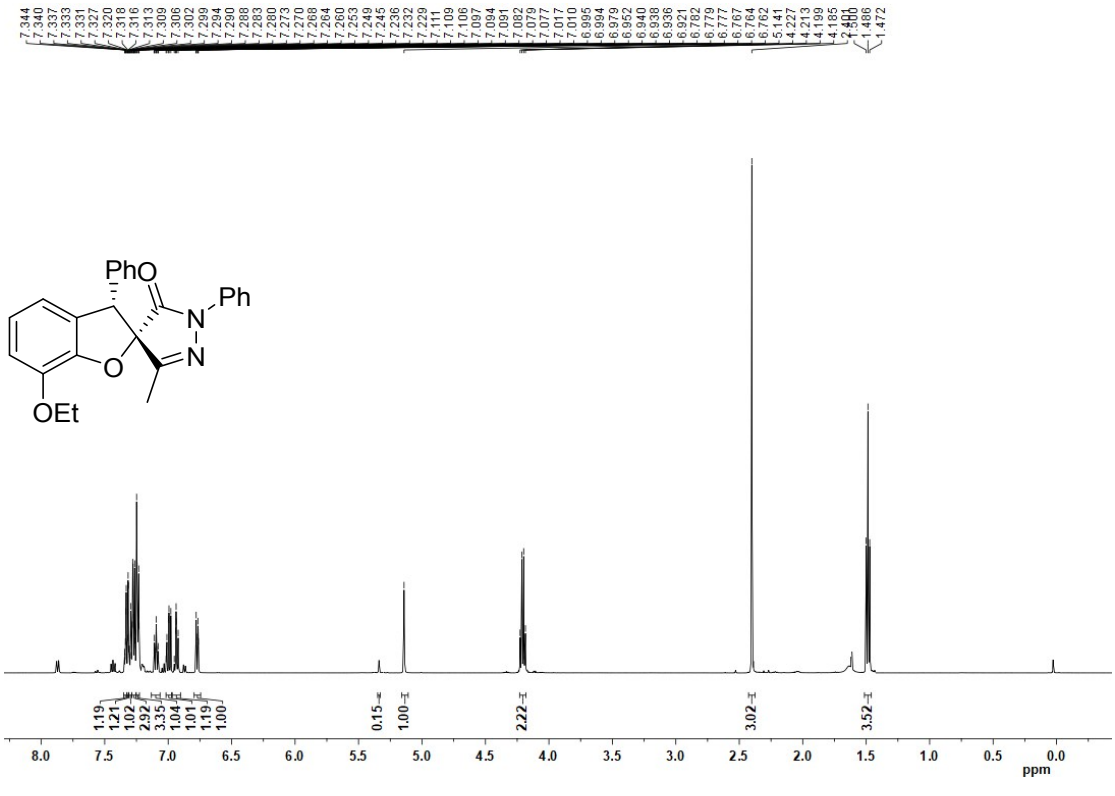
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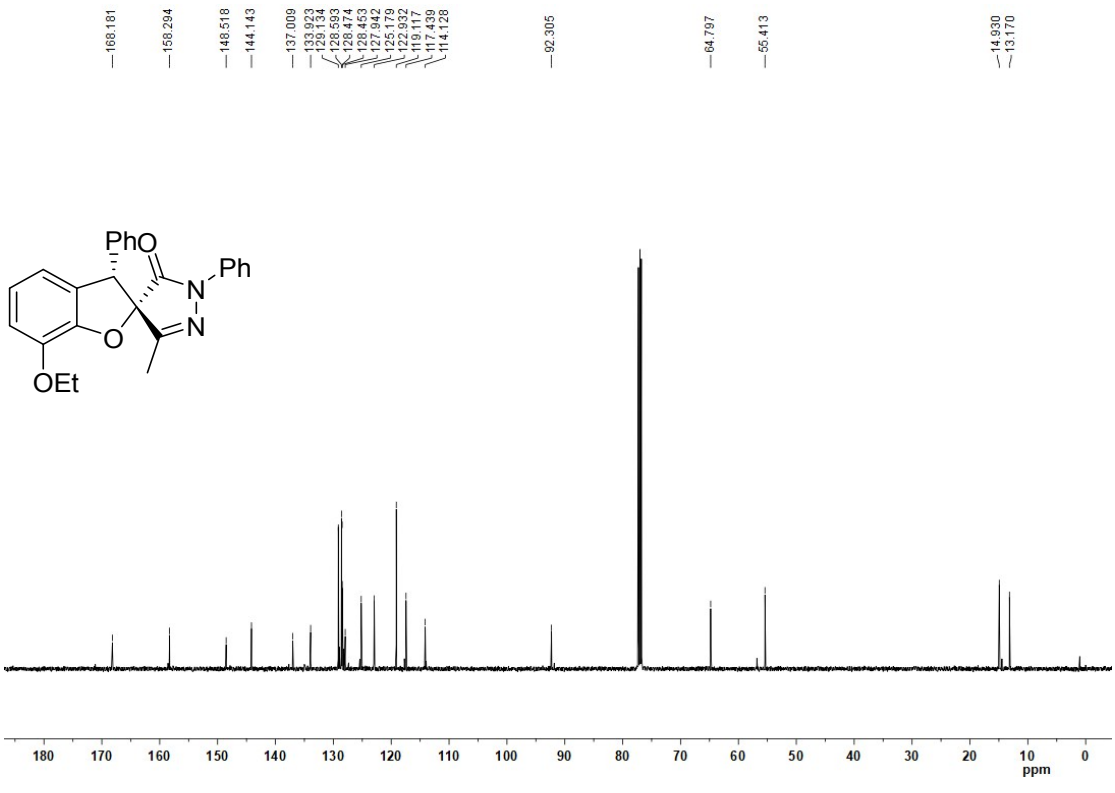
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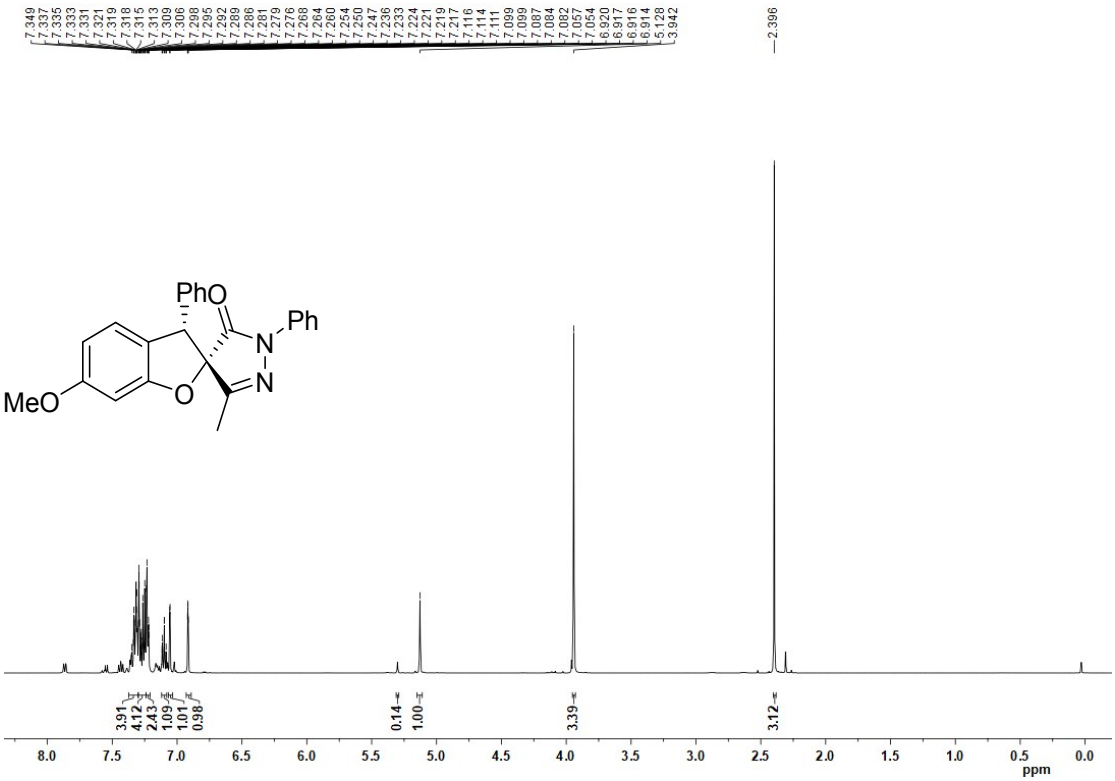
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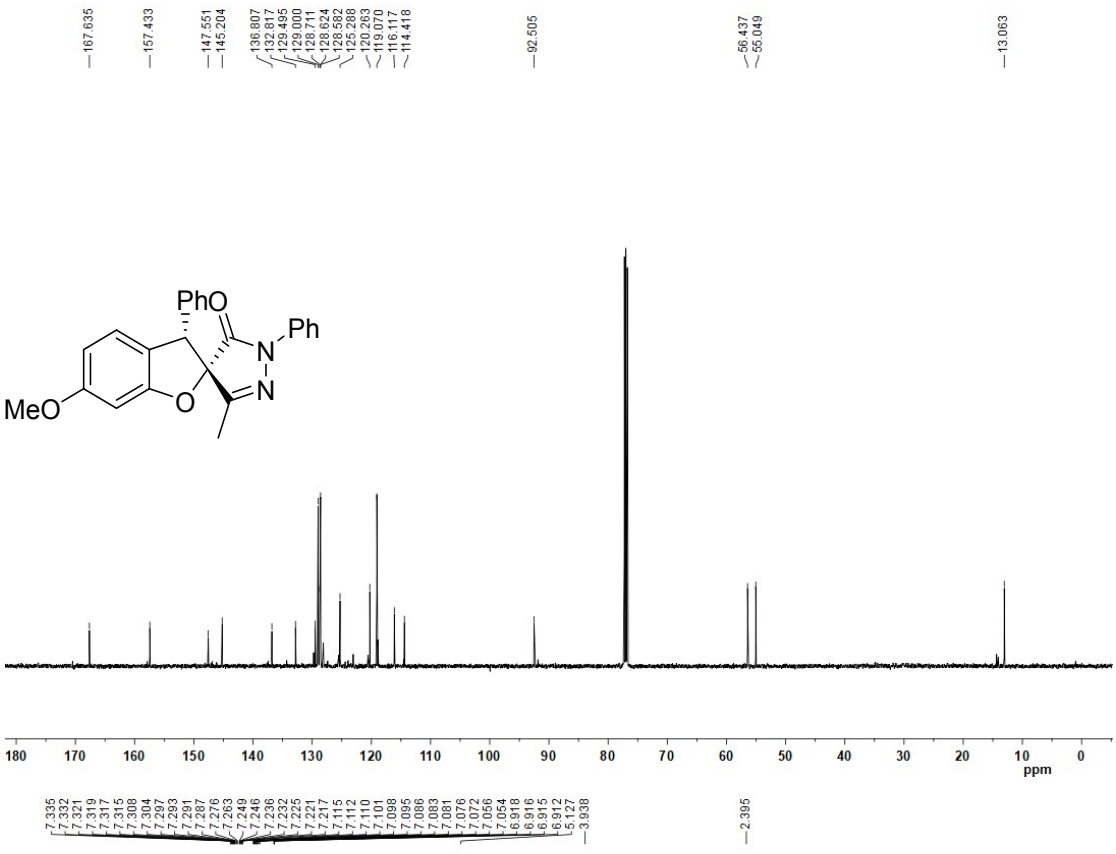
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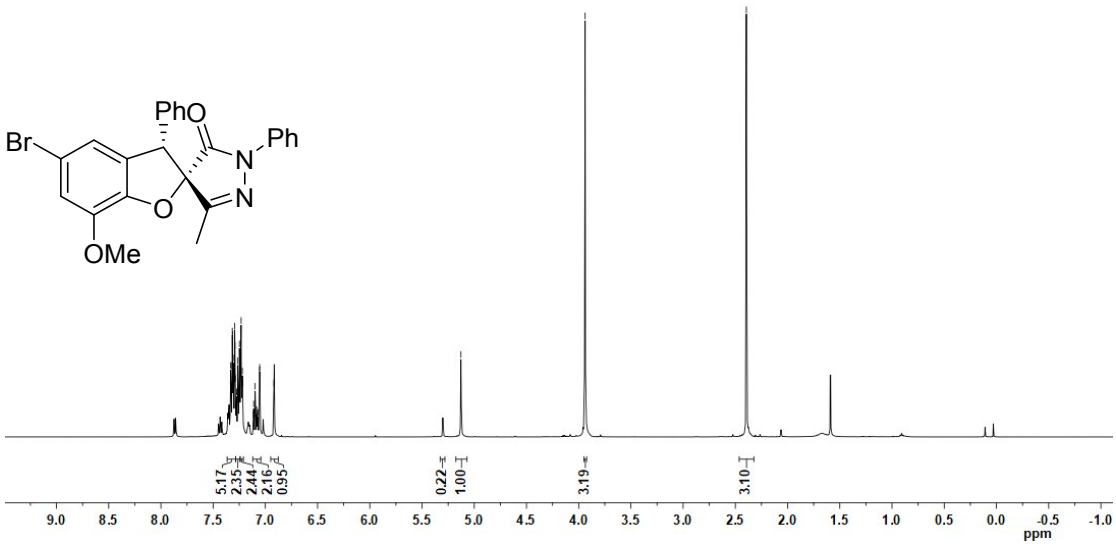
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Ph
Br
N
N
O
OMe
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2.44
2.16
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0.22
1.00
3.19
3.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
1.0
0.5
0.0
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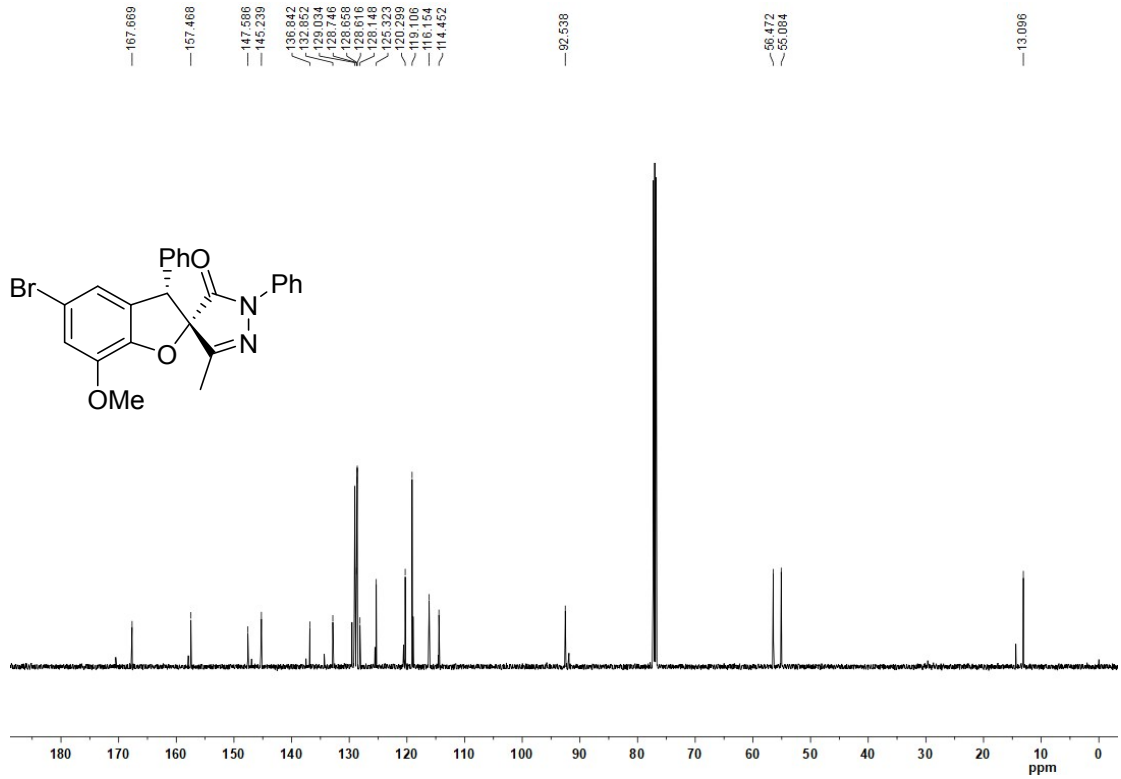
-1.0
ppm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128.746
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128.616
128.148
125.323
120.299
119.106
116.154
114.452
92.538
56.472
55.084
13.096
Br
PhO
Ph
N
N
O
OMe
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140
130
120
110
100
90
80
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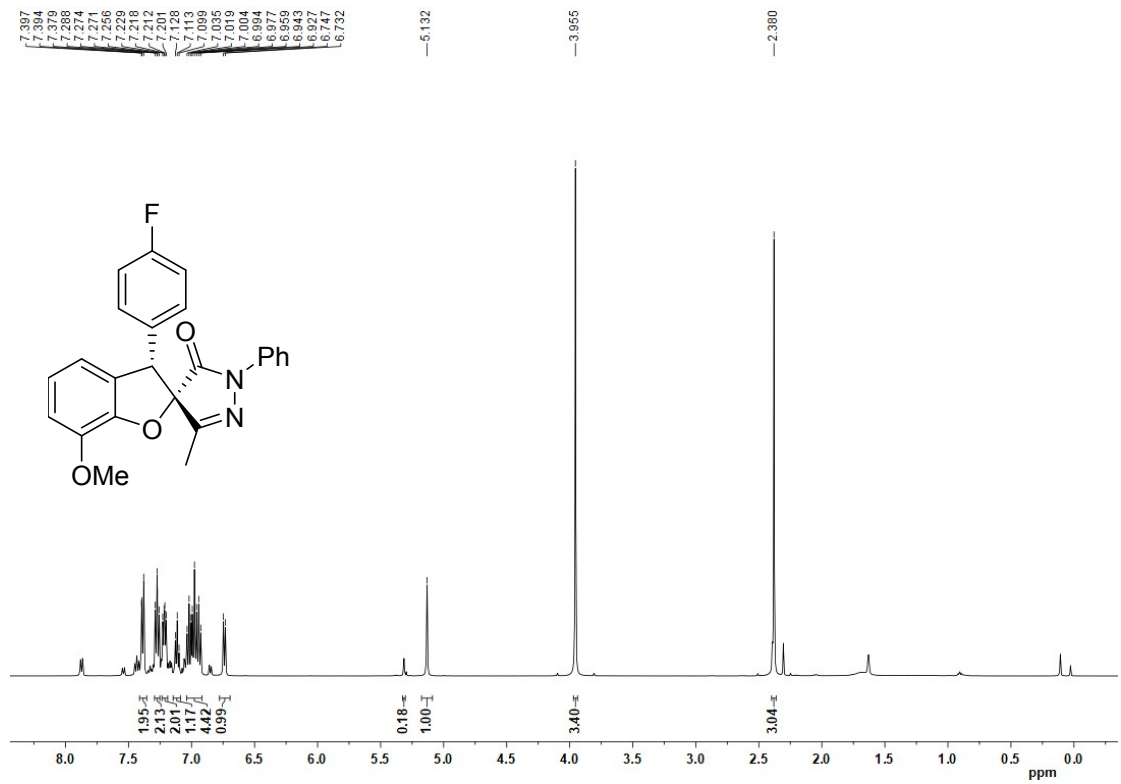
60
50
40
30
20
10
0
ppm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7.394
7.379
7.288
7.274
7.271
7.256
7.229
7.218
7.212
7.201
7.128
7.113
7.099
7.035
7.019
7.004
6.994
6.977
6.959
6.943
6.927
6.747
6.732
5.132
3.955
2.380
F
O
Ph
N
N
O
OMe
1.95
2.13
2.01
1.17
4.42
0.99
0.18
1.00
3.40
3.04
8.0
7.5
7.0
6.5
6.0
5.5
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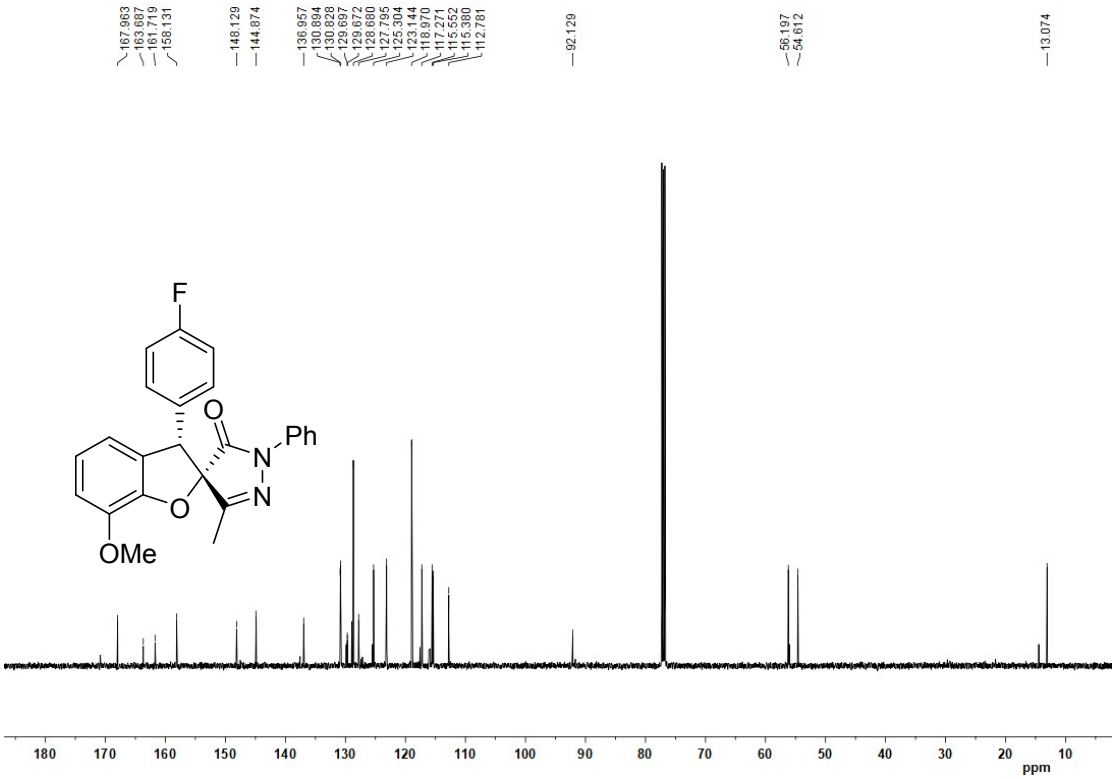
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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130.894
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129.697
129.672
128.680
127.795
125.304
123.144
118.970
117.271
115.552
115.380
112.781
92.129
56.197
54.612
13.074
F
O
Ph
N
N
O
OMe
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150
140
130
120
110
100
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70
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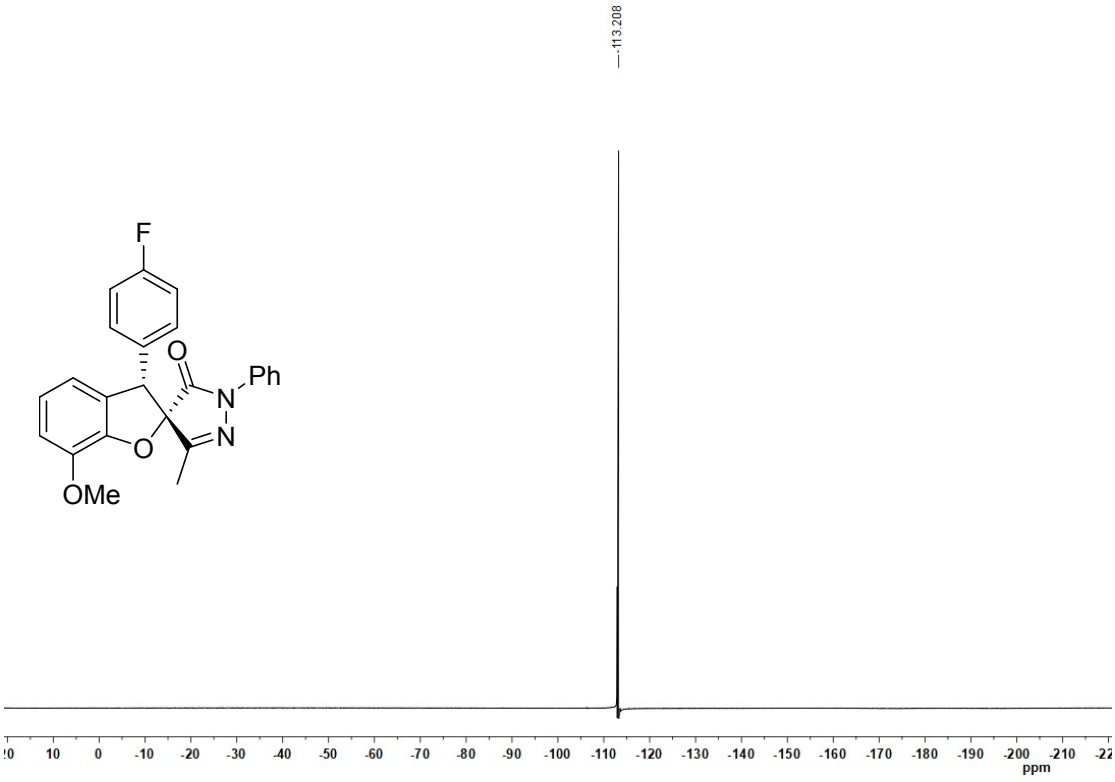
40
30
20
10
ppm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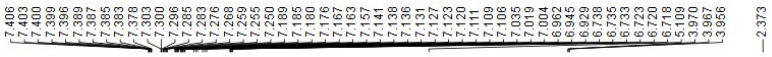
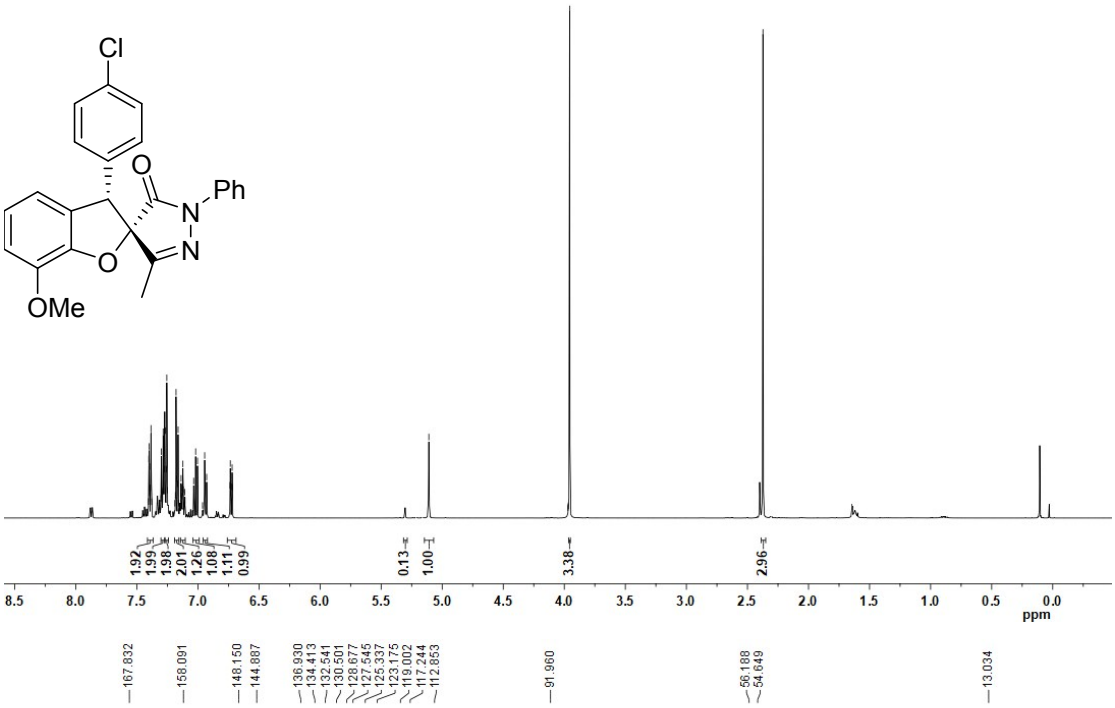
O
Ph
N
N
O
OMe
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm

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O
N
Ph
N
O
OMe
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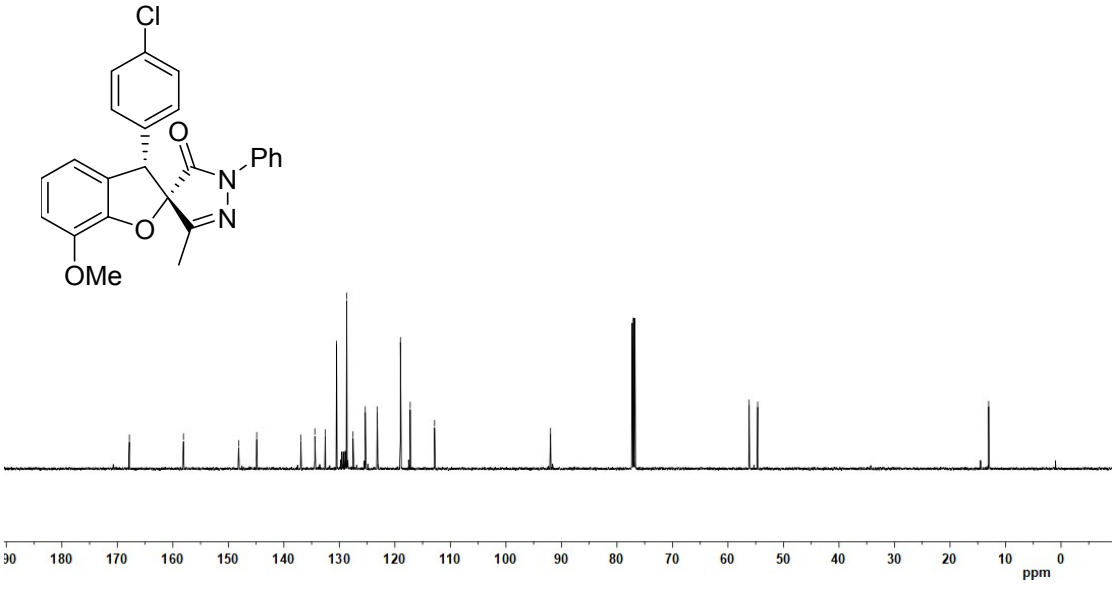
1.99
1.98
2.01
1.26
1.08
1.11
0.99
0.13
1.00
3.38
2.96
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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N
Ph
N
O
OMe
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144.887
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134.413
132.541
130.501
128.677
127.545
125.337
123.175
119.002
117.244
112.853
91.960
56.188
54.649
13.034
90
180
170
160
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140
130
120
110
100
90
80
70
60
50
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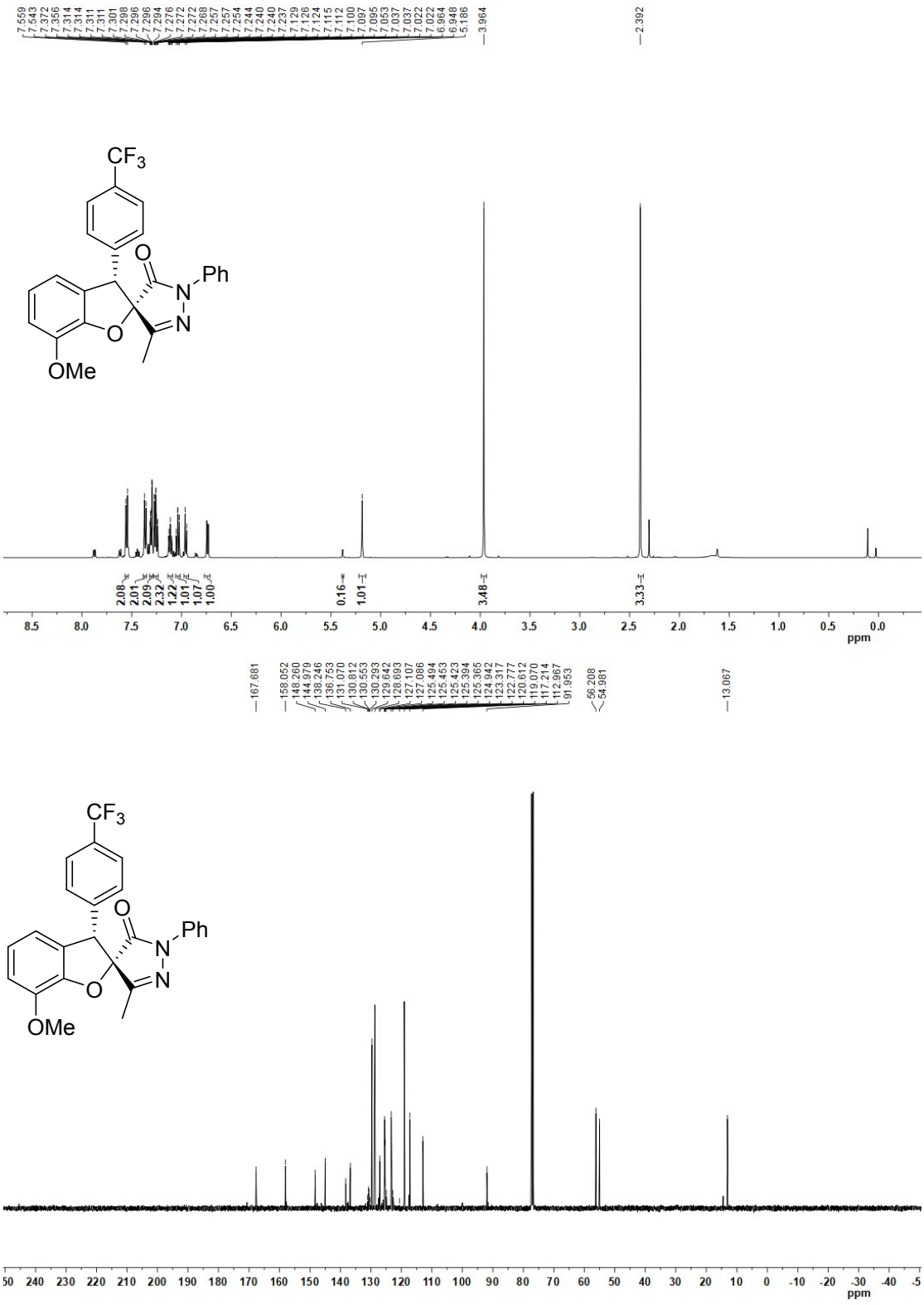
30
20
10
0
ppm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7.356
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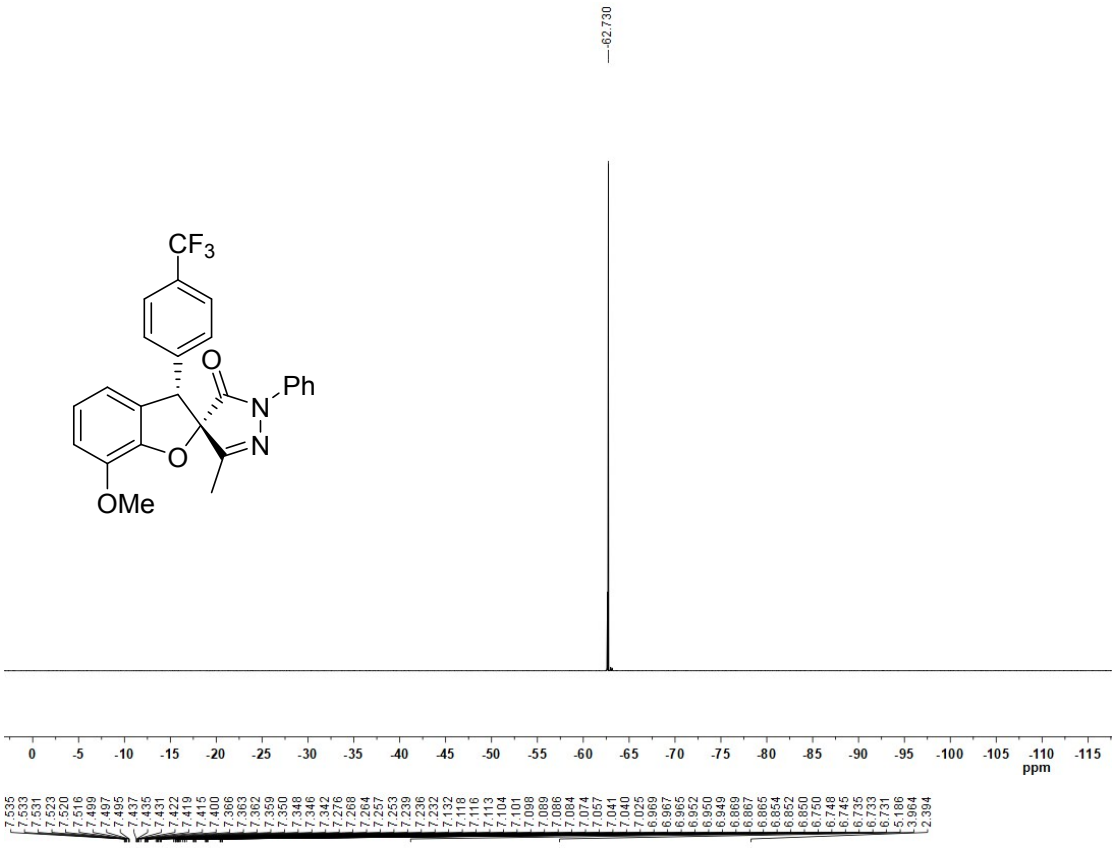
7.311
7.301
7.298
7.296
7.296
7.294
7.276
7.272
7.272
7.268
7.257
7.257
7.254
7.244
7.240
7.240
7.237
7.129
7.126
7.124
7.115
7.112
7.100
7.097
7.095
7.053
7.037
7.037
7.022
7.022
6.964
6.948
5.186
3.964
2.392
CF3
O
N
Ph
N
O
OMe
2.08
2.01
2.09
2.32
1.22
1.01
1.07
1.00
0.16
1.01
3.48
3.33
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
167.681
158.052
148.260
144.979
138.246
136.753
131.070
130.812
130.553
130.293
129.642
128.693
127.107
127.086
125.494
125.453
125.423
125.384
125.365
124.942
123.317
122.777
120.612
119.070
117.214
112.967
91.953
56.208
54.981
13.067
CF3
O
N
Ph
N
O
OMe
50
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-5
ppm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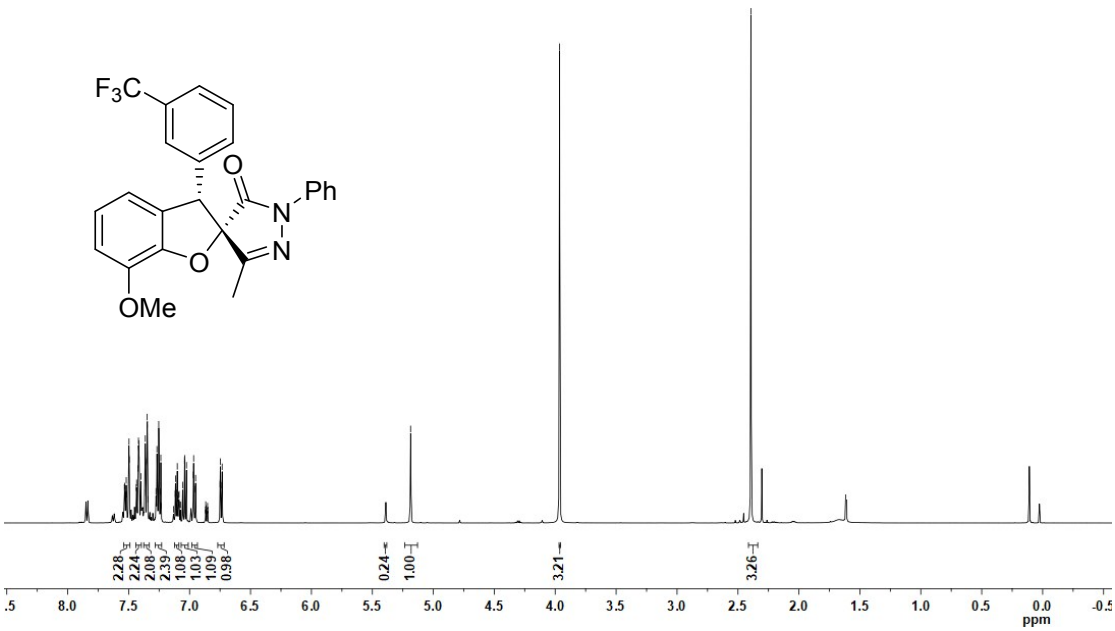
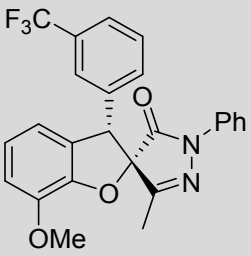
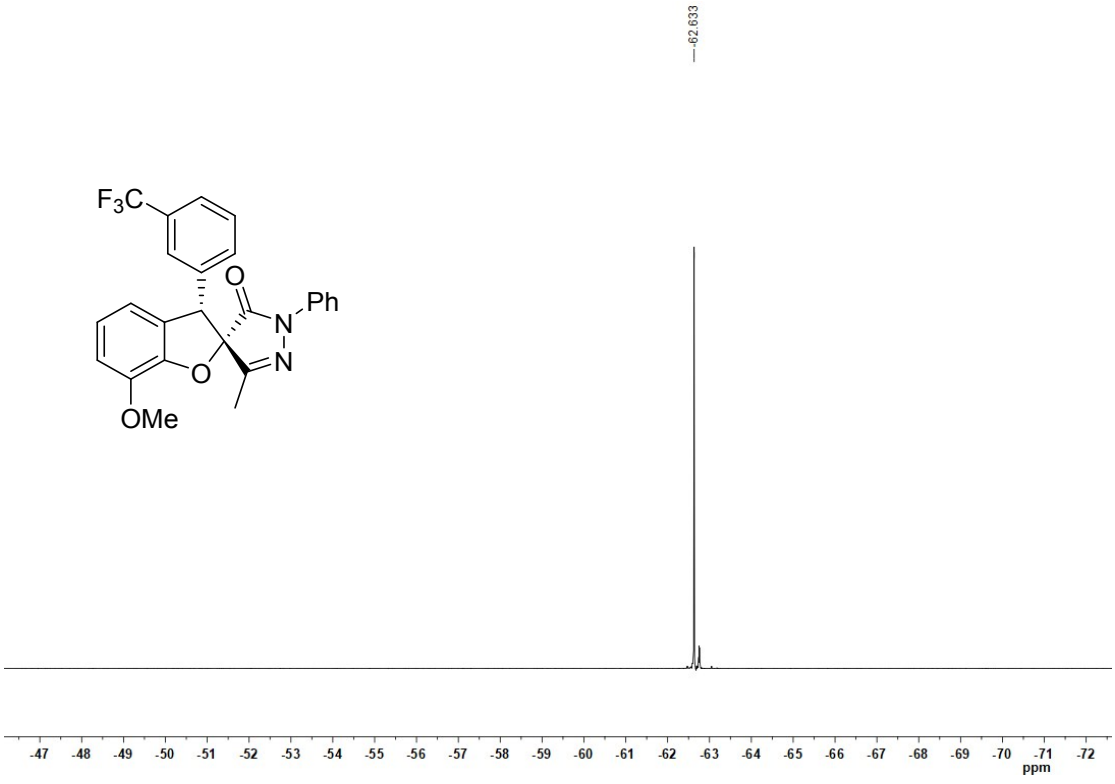
CF3
O
N
Ph
N
O
OMe
0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115
ppm


F3C
O
N
Ph
N
O
OMe
2.28
2.24
2.08
2.39
1.08
1.03
1.09
0.98
0.24
1.00
3.21
3.26
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


F3C
O
Ph
N
N
O
OMe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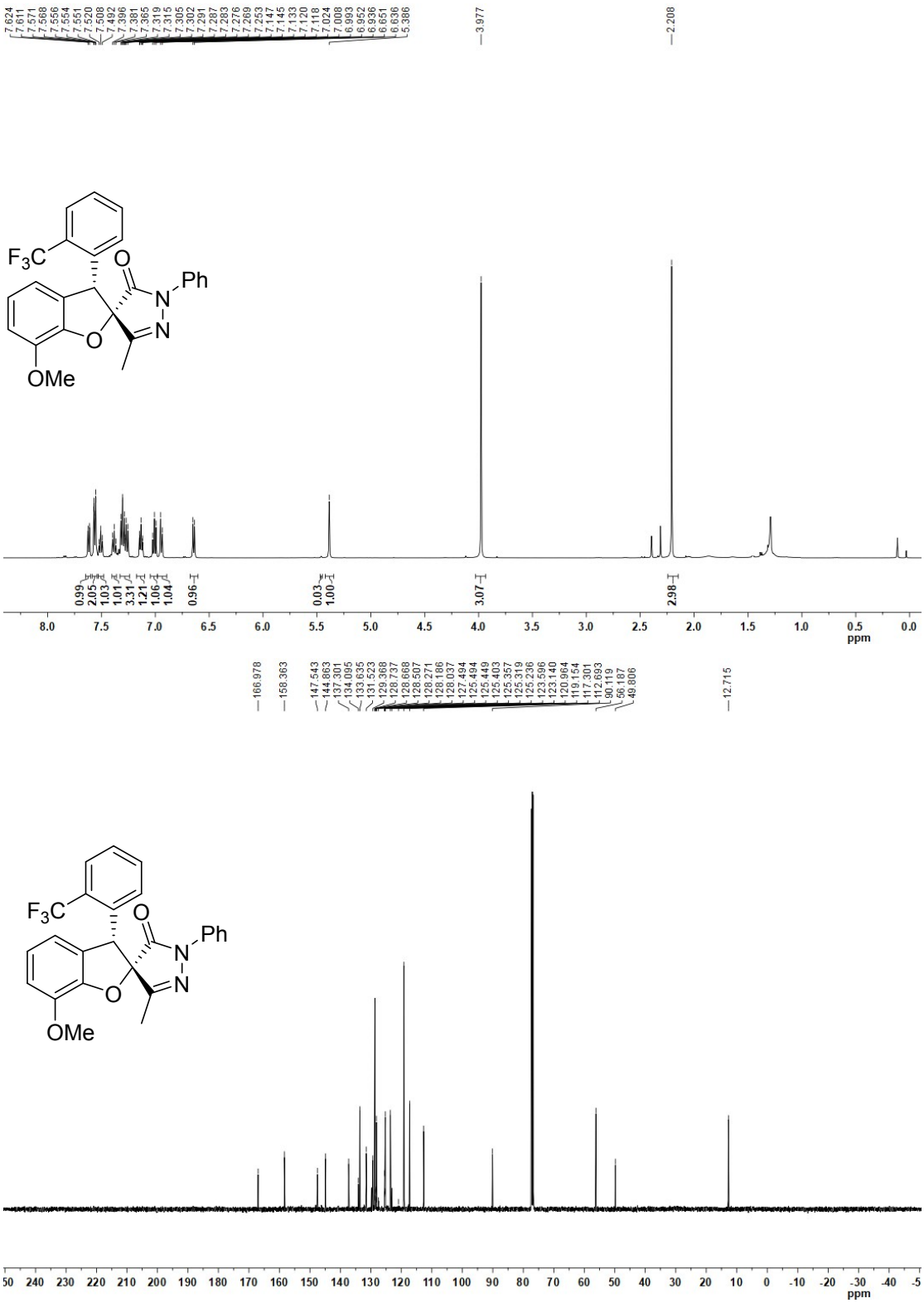
F3C
O
Ph
N
N
O
OMe
-47 -48 -49 -50 -51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72
ppm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7.492
7.396
7.381
7.365
7.319
7.315
7.305
7.302
7.291
7.287
7.283
7.276
7.269
7.253
7.147
7.145
7.133
7.120
7.118
7.024
7.008
6.993
6.952
6.936
6.651
6.636
5.386
3.977
2.208
F3C
O
Ph
N
N
O
OMe
0.99
2.05
1.03
1.01
3.31
1.21
1.06
1.04
0.96
0.03
1.00
3.07
2.98
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
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147.543
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137.301
134.095
133.635
131.523
129.368
128.737
128.668
128.507
128.271
128.186
128.037
127.494
125.494
125.449
125.403
125.357
125.319
125.236
123.596
123.140
120.964
119.154
117.301
112.693
90.119
56.187
49.806
12.715
F3C
O
Ph
N
N
O
OMe
250
240
230
220
210
200
190
180
170
160
150
140
130
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100
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80
70
60
50
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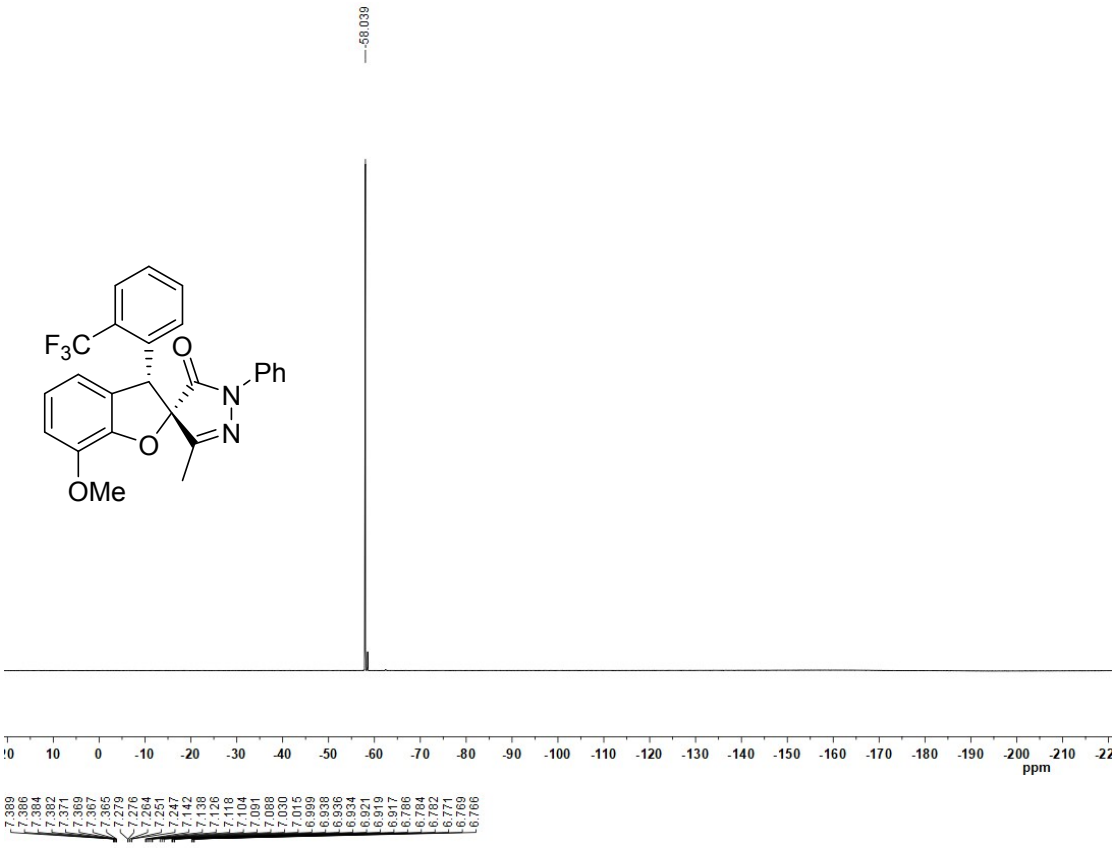
0
-10
-20
-30
-40
-50
ppm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Ph
N
N
O
OMe
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
ppm
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7.384
7.382
7.371
7.369
7.367
7.365
7.279
7.276
7.264
7.251
7.247
7.142
7.138
7.126
7.118
7.104
7.091
7.088
7.030
7.015
6.999
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6.936
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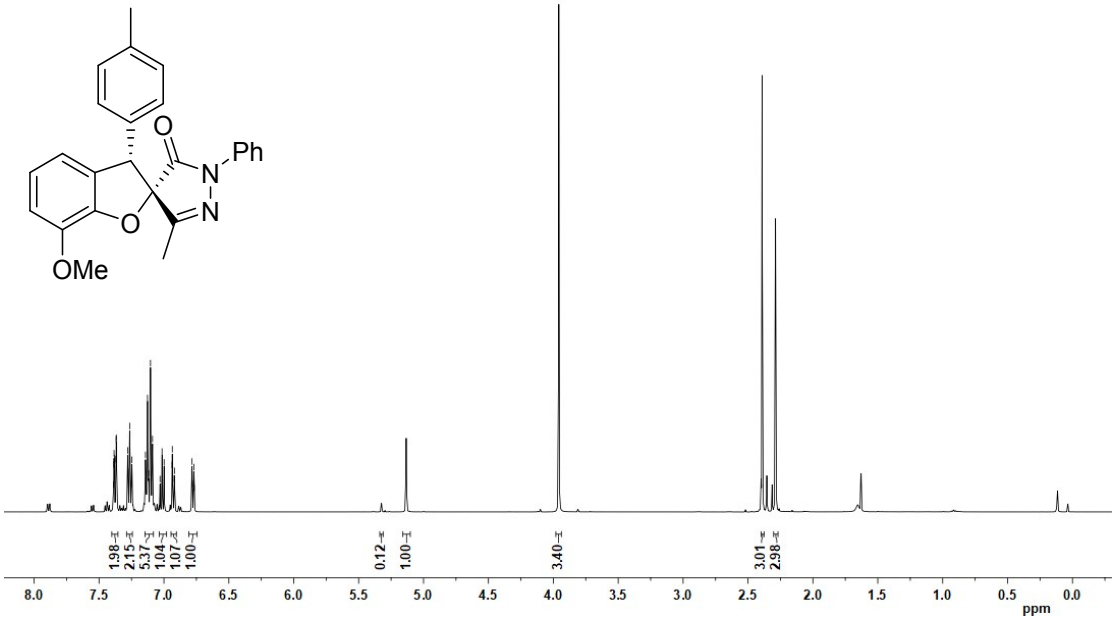
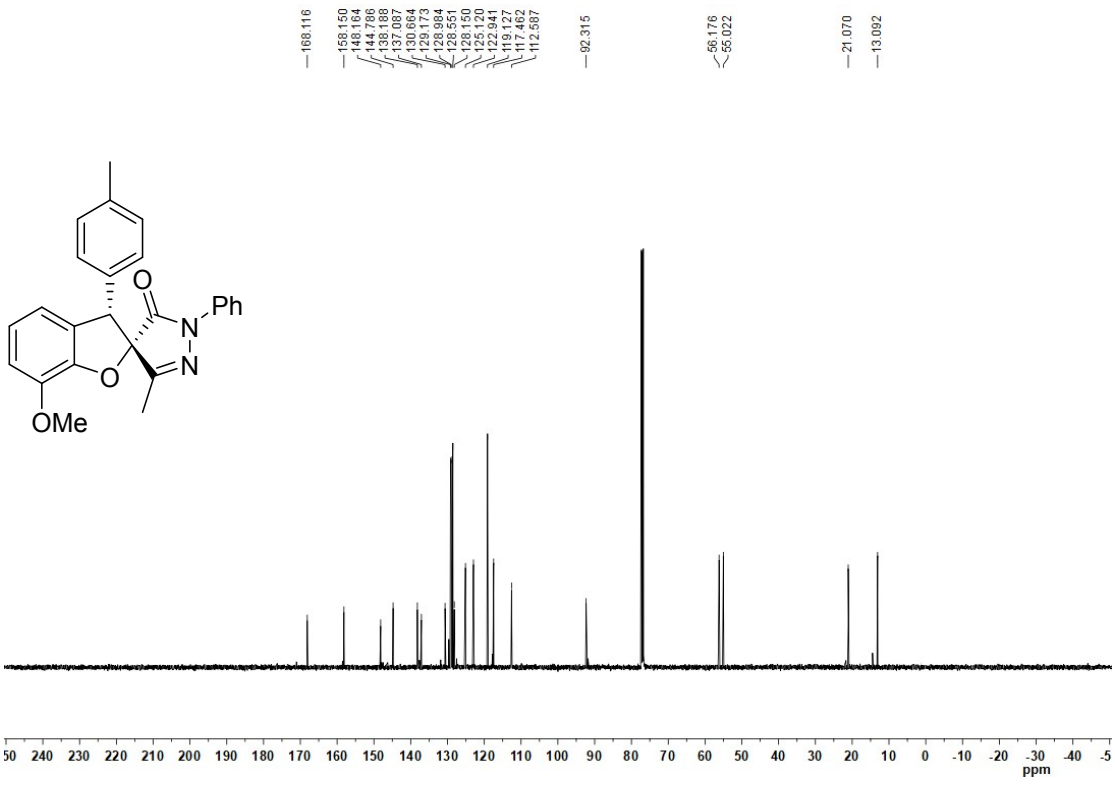
6.782
6.771
6.769
6.766


O
Ph
N
N
O
OMe
1.98
2.15
5.37
1.04
1.07
1.00
0.12
1.00
3.40
3.01
2.98
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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144.786
138.188
137.087
130.664
129.173
128.984
128.551
128.150
125.120
122.941
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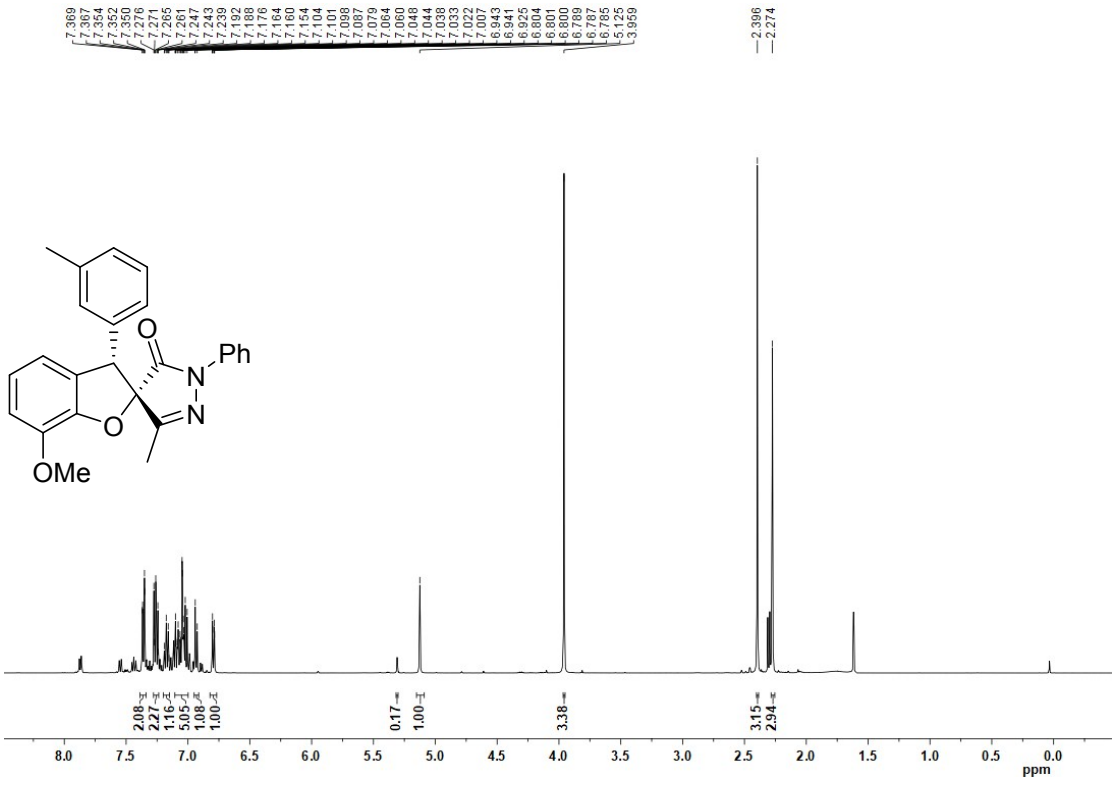
92.315
56.176
55.022
21.070
13.092
O
N
Ph
N
O
OMe
ppm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7.276
7.271
7.265
7.261
7.247
7.243
7.239
7.192
7.188
7.176
7.164
7.160
7.154
7.104
7.101
7.098
7.087
7.079
7.064
7.060
7.048
7.044
7.038
7.033
7.022
7.007
6.943
6.941
6.925
6.804
6.801
6.800
6.789
6.787
6.785
5.125
3.959
2.396
2.274
O
N
Ph
N
O
OMe
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1.16
5.05
1.08
1.00
0.17
1.00
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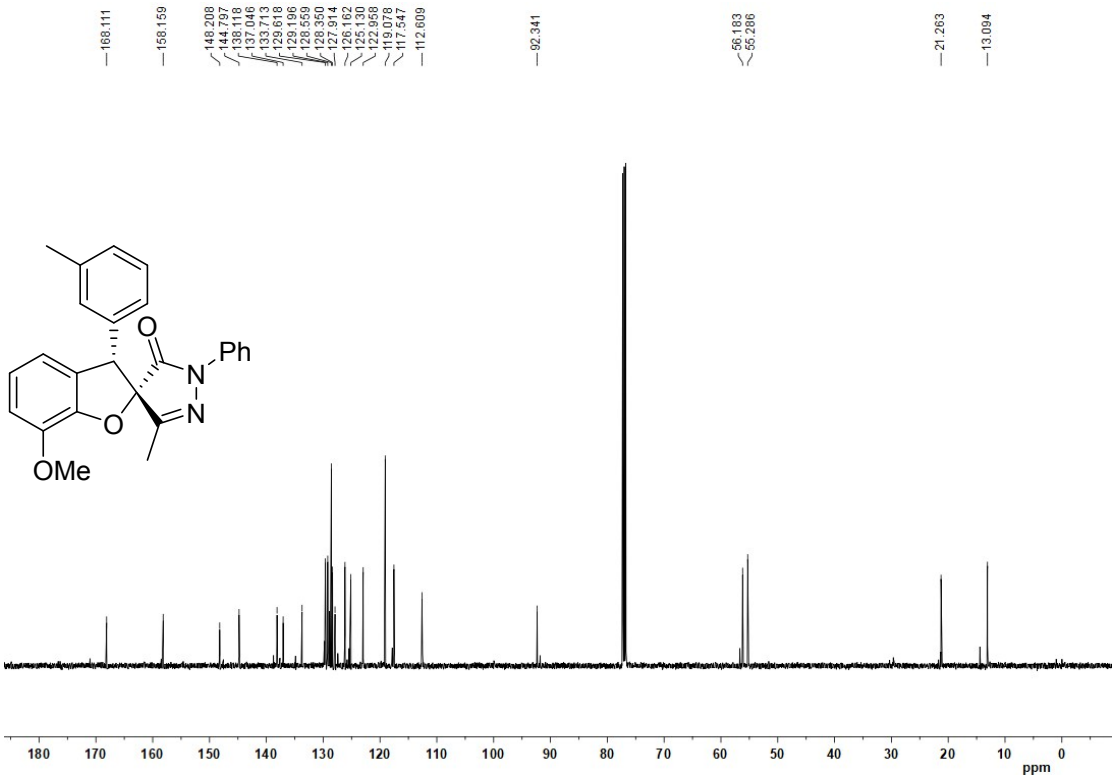
2.94
ppm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137.046
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129.618
129.196
128.559
128.350
127.914
126.162
125.130
122.958
119.078
117.547
112.609
92.341
56.183
55.286
21.263
13.094
O
Ph
N
N
O
OMe
180
170
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140
130
120
110
100
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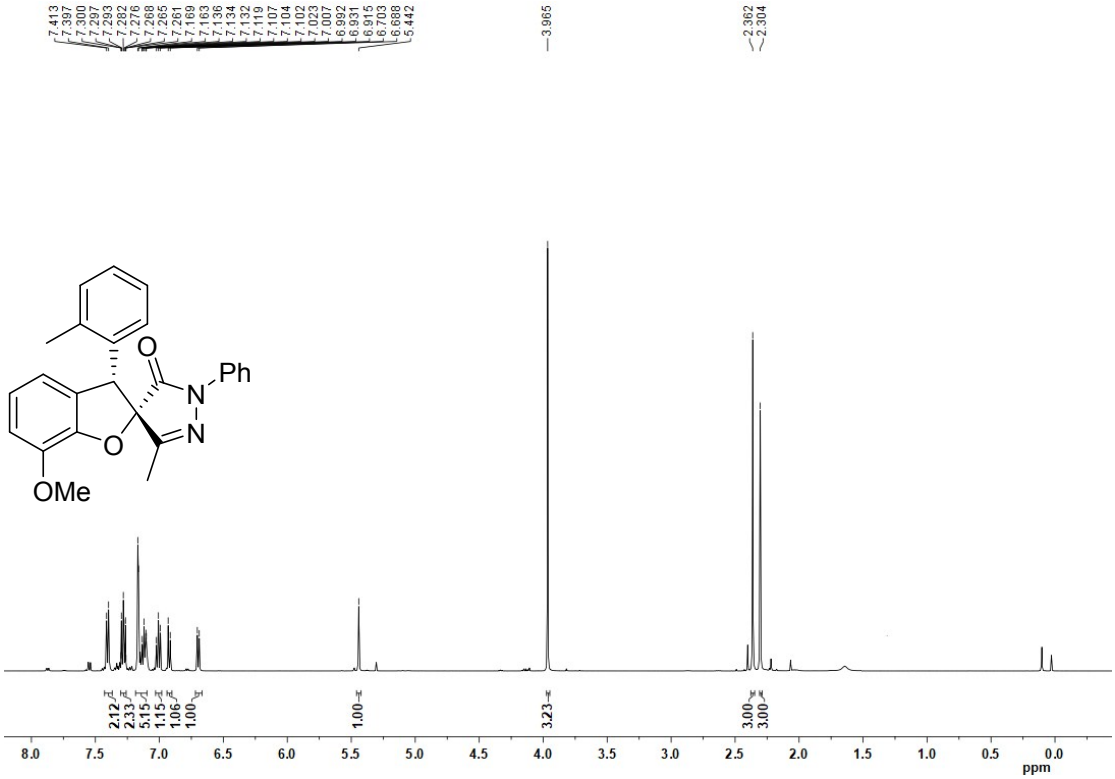
80
70
60
50
40
30
20
10
0
ppm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7.261
7.169
7.163
7.136
7.134
7.132
7.119
7.107
7.104
7.102
7.023
7.007
6.992
6.931
6.915
6.703
6.688
5.442
3.965
2.362
2.304
O
Ph
N
N
O
OMe
2.12
2.33
5.15
1.15
1.06
1.00
1.00
3.23
3.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
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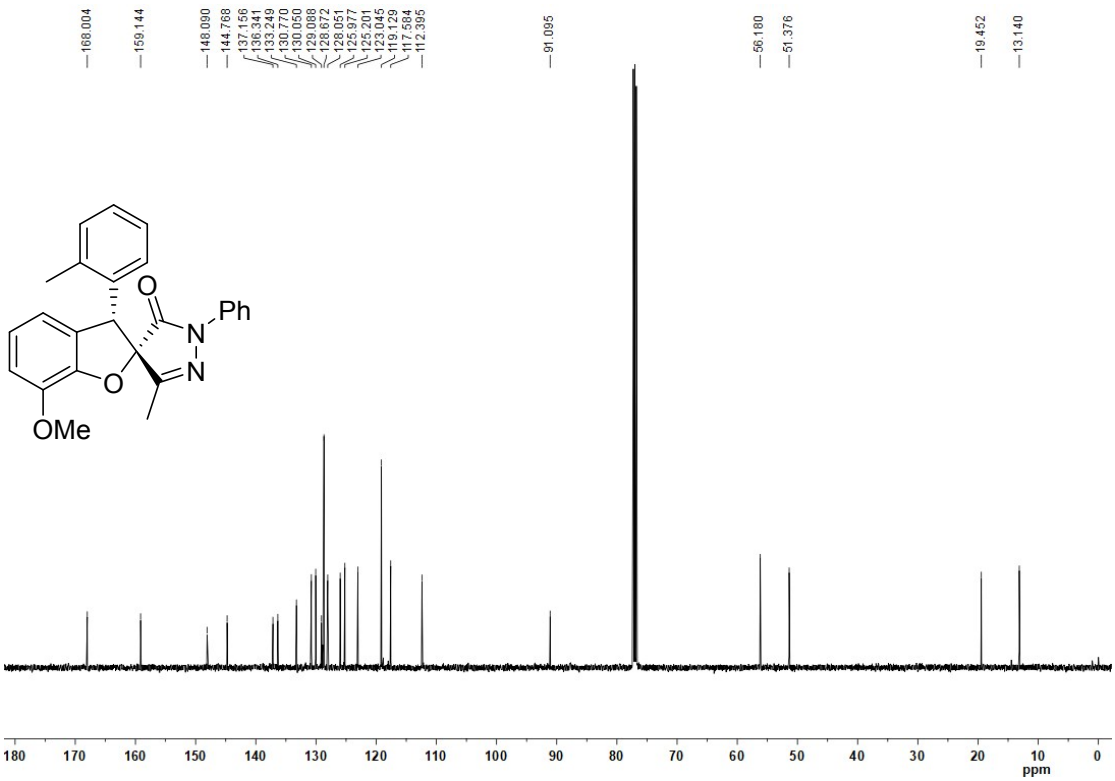
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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136.341
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130.770
130.050
129.088
128.672
128.651
125.977
125.701
123.045
119.129
117.584
112.395
91.095
56.180
51.376
19.452
13.140
O
N
Ph
N
O
OMe
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140
130
120
110
100
90
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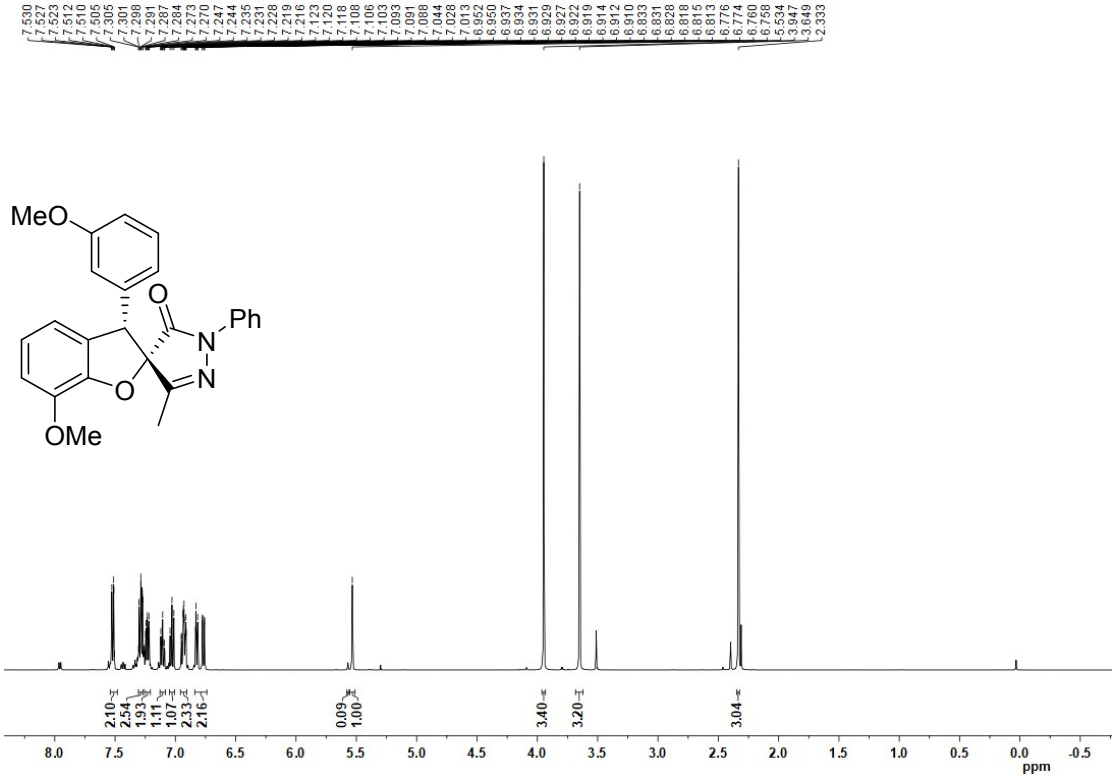
70
60
50
40
30
20
10
0
ppm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7.291
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7.273
7.270
7.247
7.244
7.235
7.231
7.228
7.219
7.216
7.123
7.120
7.118
7.108
7.106
7.103
7.093
7.091
7.088
7.044
7.028
7.013
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6.950
6.937
6.934
6.931
6.929
6.927
6.922
6.919
6.914
6.912
6.910
6.833
6.831
6.828
6.818
6.815
6.813
6.776
6.774
6.760
6.758
5.534
3.947
3.649
2.333
MeO
O
N
Ph
N
O
OMe
2.10
2.54
1.93
1.11
1.07
2.33
2.16
0.09
1.00
3.40
3.20
3.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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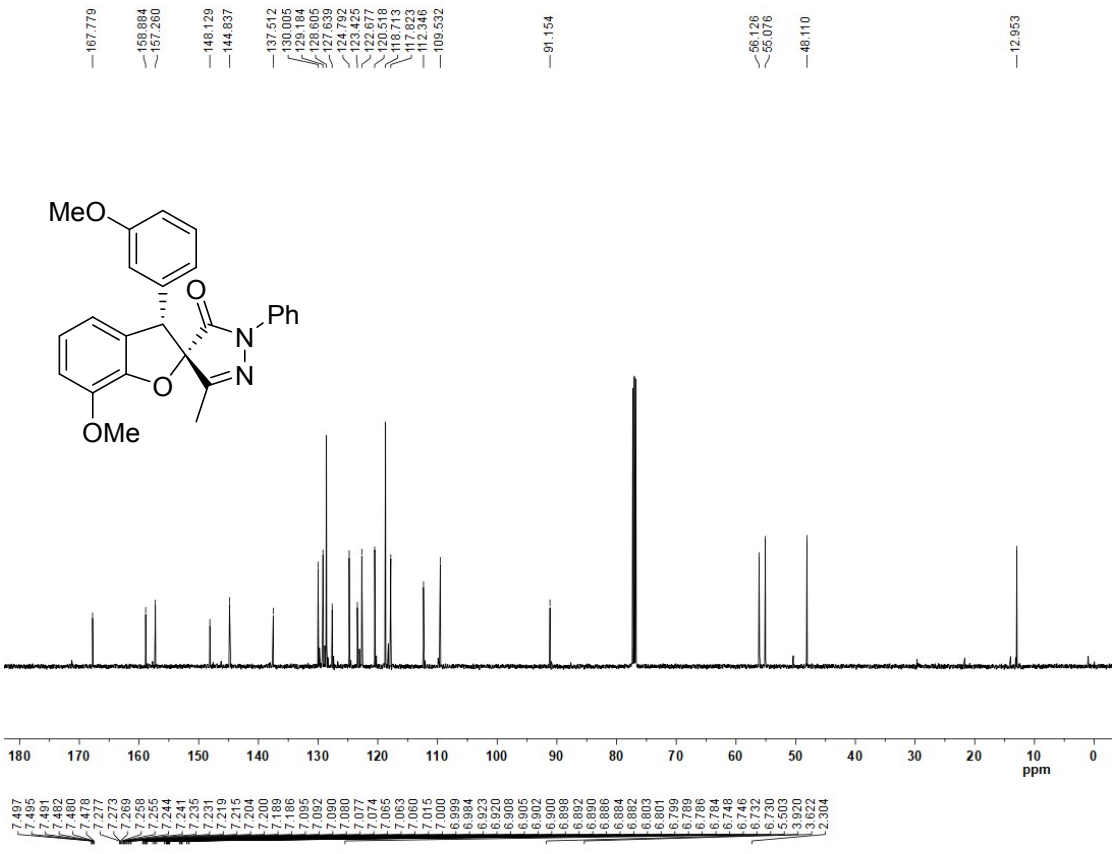
0.0
-0.5
ppm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129.184
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127.639
124.792
123.425
122.677
120.518
118.713
117.823
112.346
109.532
91.154
56.126
55.076
48.110
12.953
MeO
O
Ph
N
N
O
OMe
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
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7.495
7.491
7.482
7.480
7.478
7.277
7.273
7.269
7.258
7.255
7.244
7.241
7.235
7.231
7.219
7.215
7.204
7.200
7.189
7.186
7.095
7.092
7.090
7.080
7.077
7.074
7.065
7.063
7.060
7.015
7.000
6.999
6.984
6.923
6.920
6.908
6.905
6.902
6.900
6.898
6.892
6.890
6.886
6.884
6.882
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6.801
6.799
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6.730
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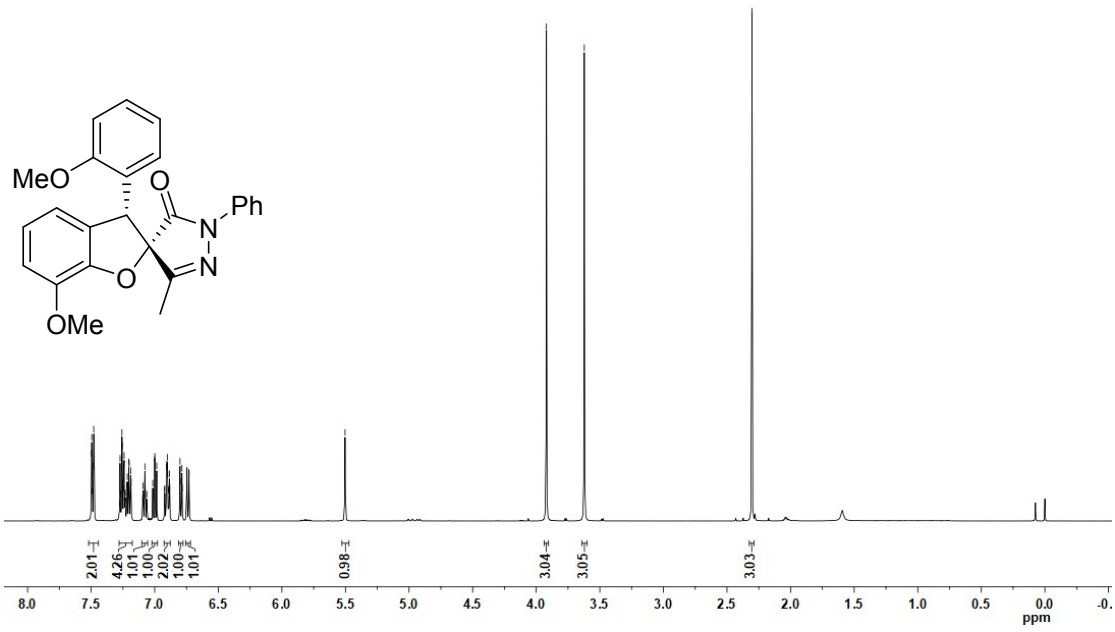
2.304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OMe
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3.05
3.03
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7.0
6.5
6.0
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3.0
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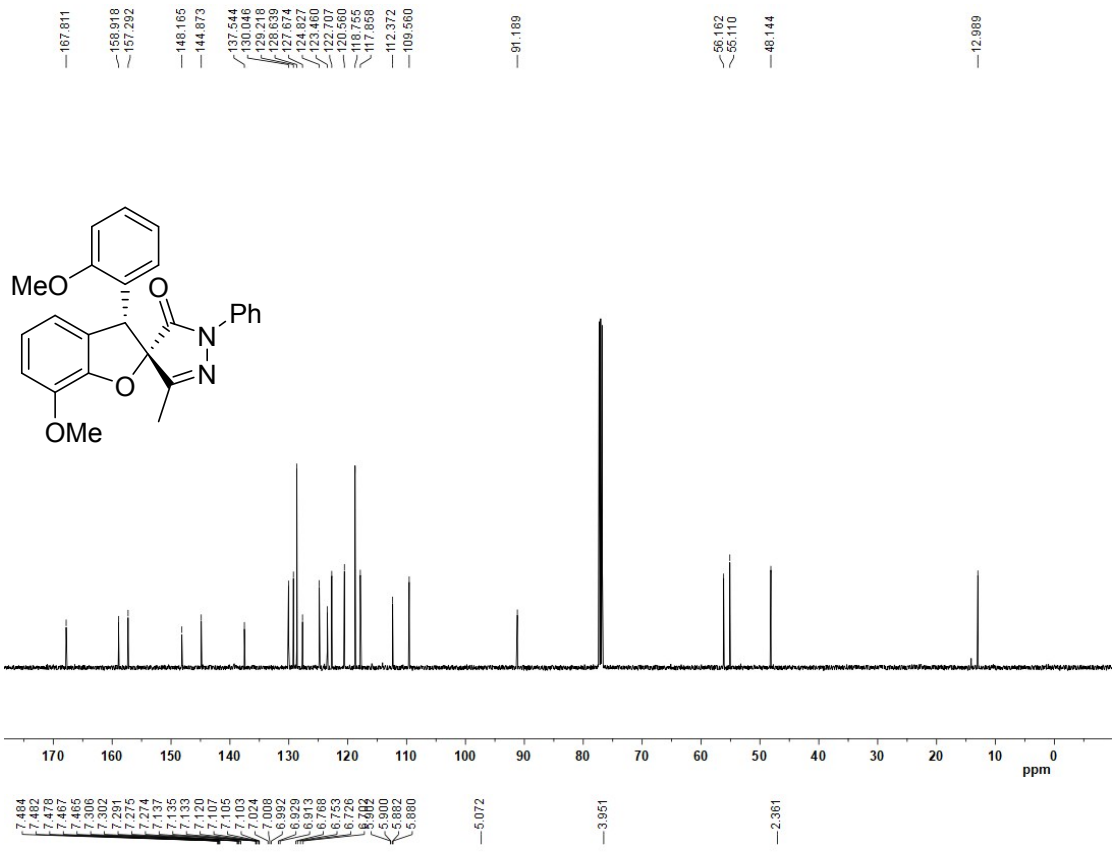
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117.858
112.372
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91.189
56.162
55.110
48.144
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MeO
O
Ph
N
N
O
OMe
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100
90
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70
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50
40
30
20
10
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7.135
7.133
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7.105
7.103
7.024
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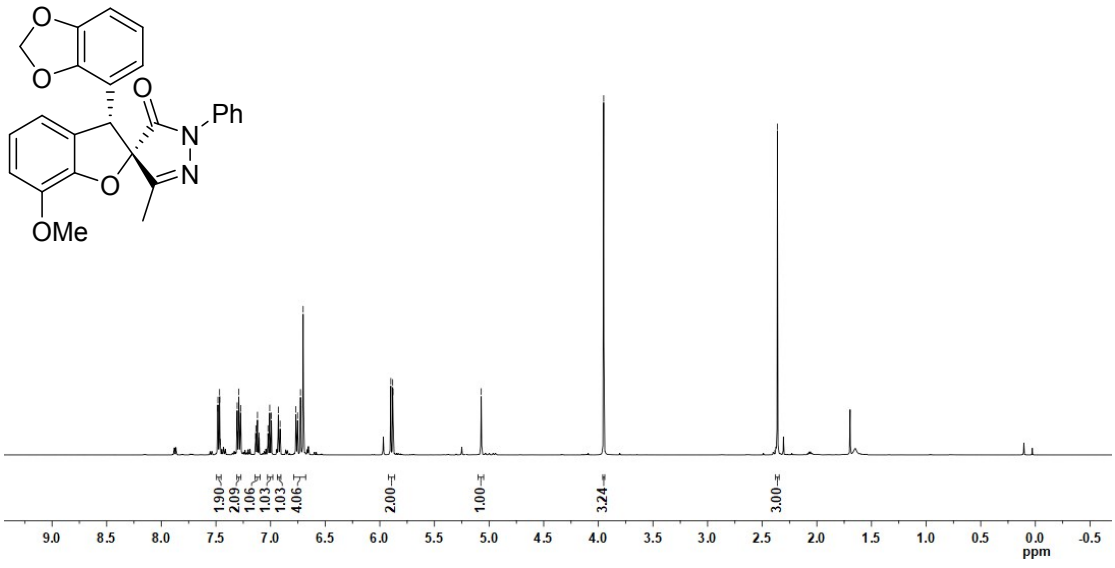
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Ph
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N
O
OMe
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1.03
4.06
2.00
1.00
3.24
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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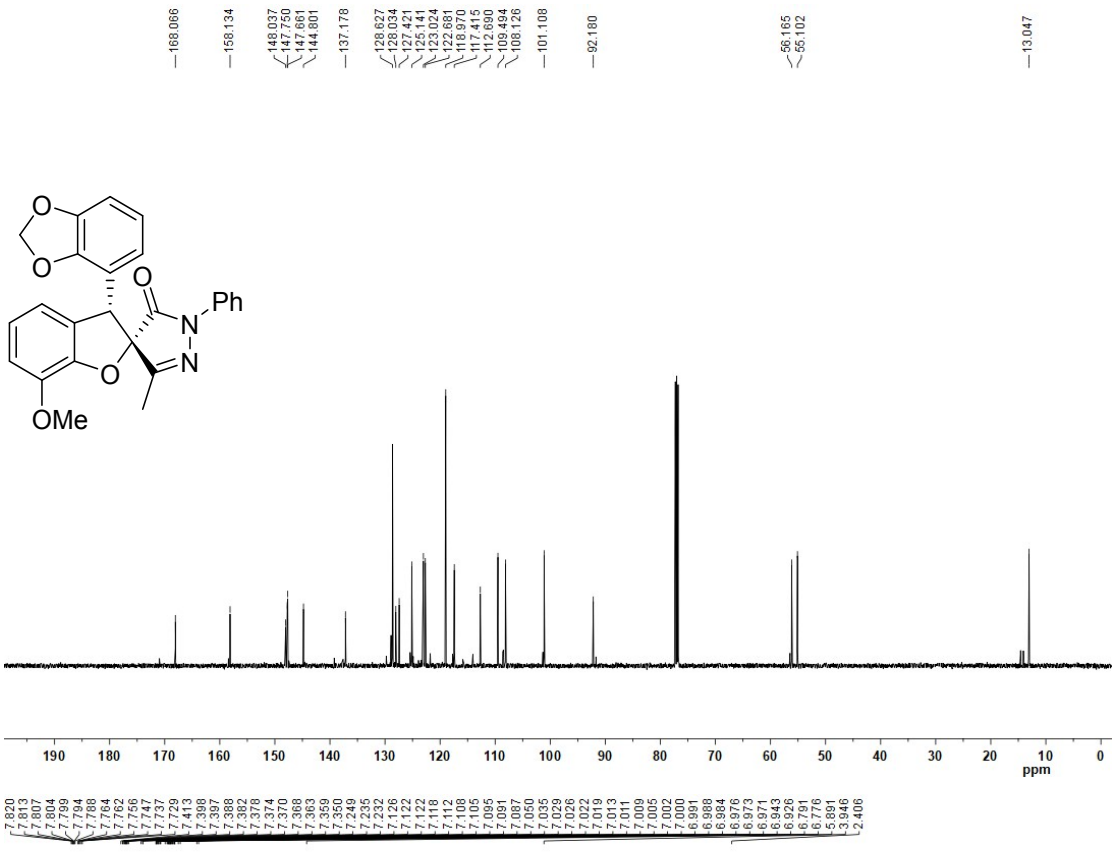
ppm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127.421
125.141
123.024
122.681
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117.415
112.690
109.494
108.126
101.108
92.180
56.165
55.102
13.047
O
O
O
N
Ph
N
O
OMe
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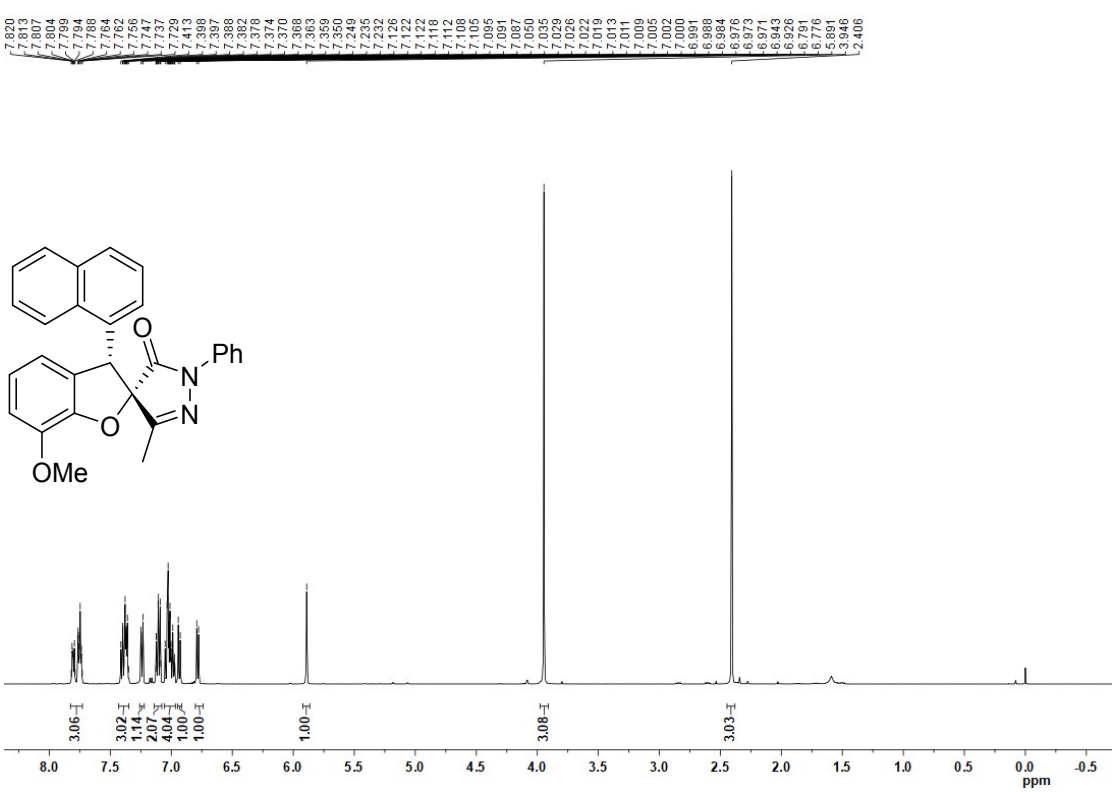
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7.398
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7.388
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7.374
7.370
7.368
7.363
7.359
7.249
7.235
7.232
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7.122
7.122
7.118
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7.108
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7.095
7.091
7.087
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7.035
7.029
7.026
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7.011
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7.002
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6.776
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2.406

O
O
N
Ph
N
O
OMe
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3.02
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2.07
4.04
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1.00
1.00
3.08
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6.0
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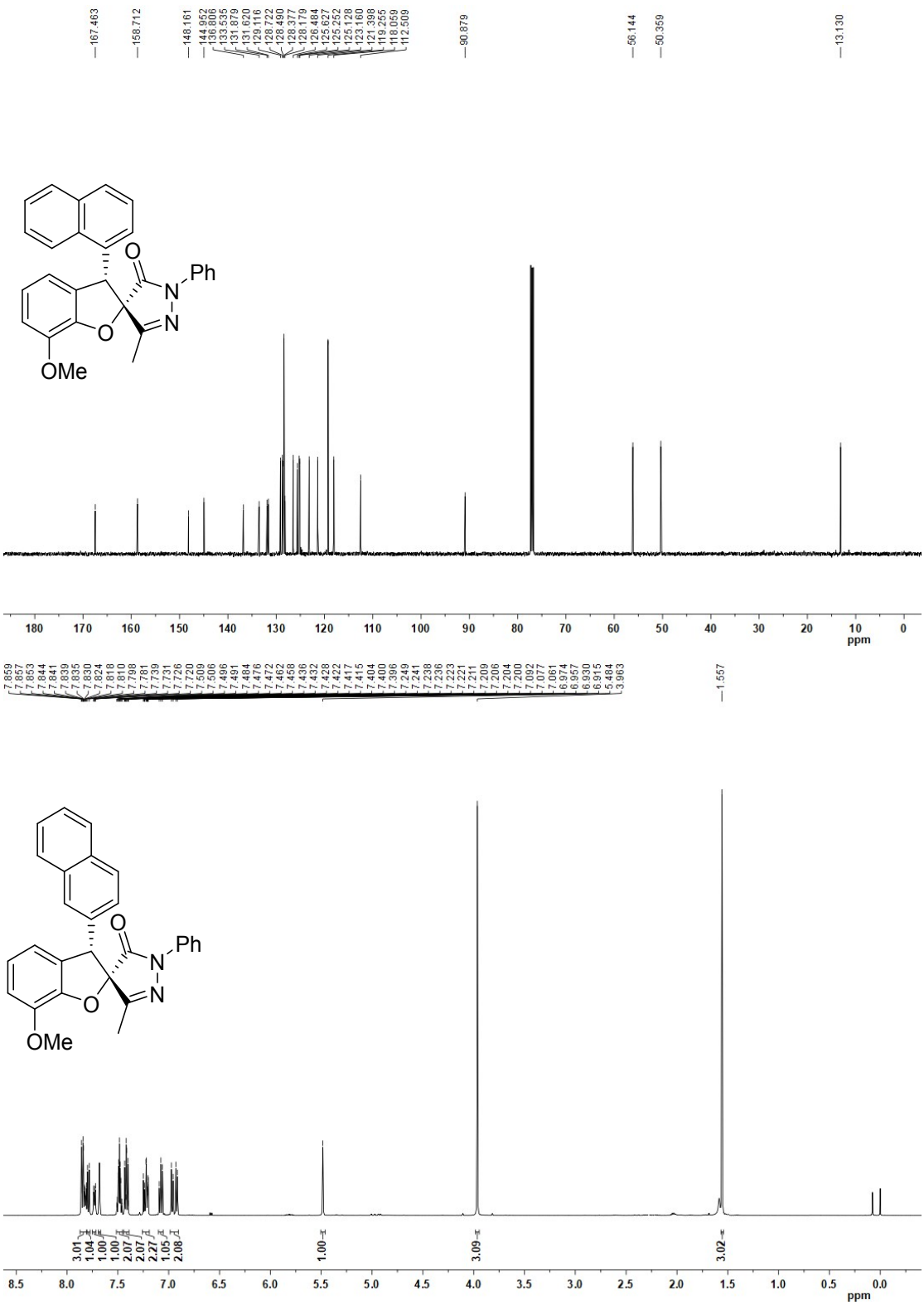
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128.377
128.179
126.484
125.827
125.252
125.128
123.160
121.398
119.255
118.059
112.509
90.879
56.144
50.359
13.130
O
N
Ph
N
O
OMe
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
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7.857
7.853
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7.841
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7.835
7.830
7.824
7.818
7.810
7.798
7.781
7.739
7.731
7.726
7.720
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7.472
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7.432
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7.422
7.417
7.415
7.404
7.400
7.396
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7.238
7.236
7.223
7.221
7.211
7.209
7.206
7.204
7.200
7.092
7.077
7.061
6.974
6.957
6.930
6.915
5.484
3.963
1.557
O
N
Ph
N
O
OMe
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1.04
1.00
1.00
2.07
2.07
2.27
1.05
2.08
1.00
3.09
3.02
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
3.5
3.0
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0.5
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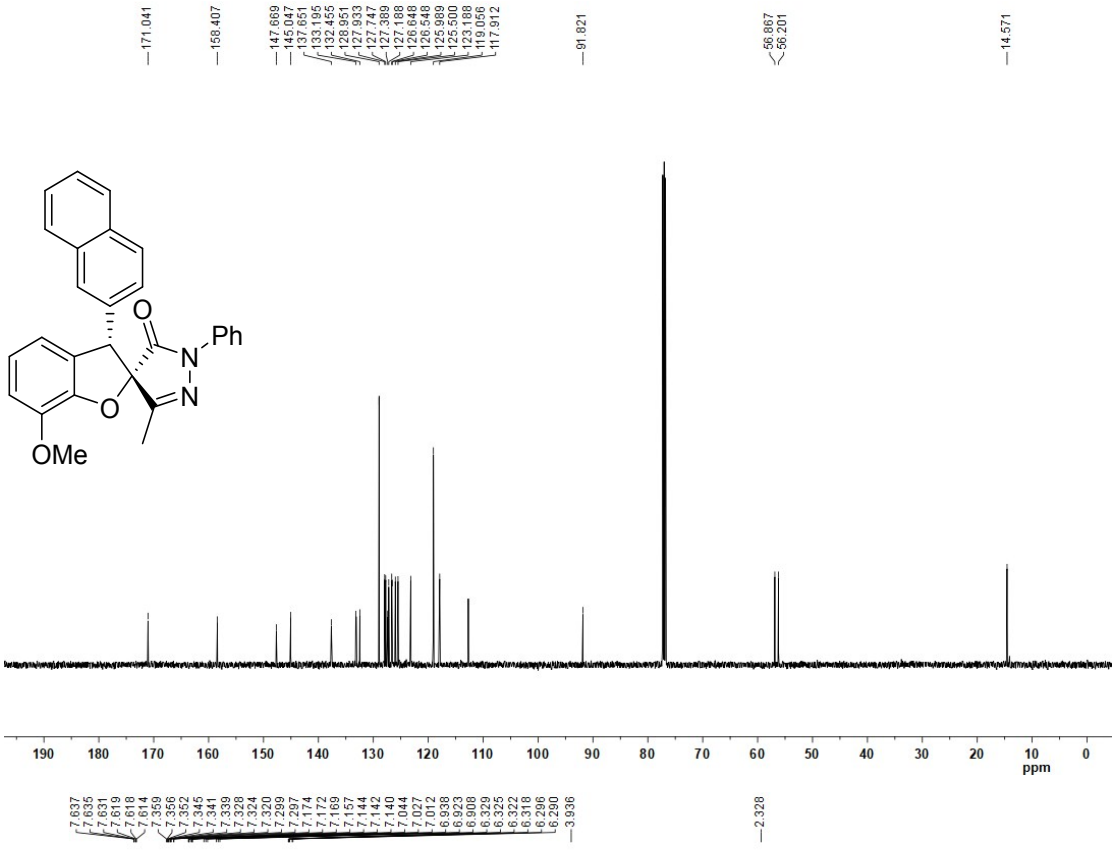
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127.188
126.648
126.548
125.989
125.500
123.188
119.056
117.912
91.821
56.867
56.201
14.571
O
N
Ph
N
O
OMe
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140
130
120
110
100
90
80
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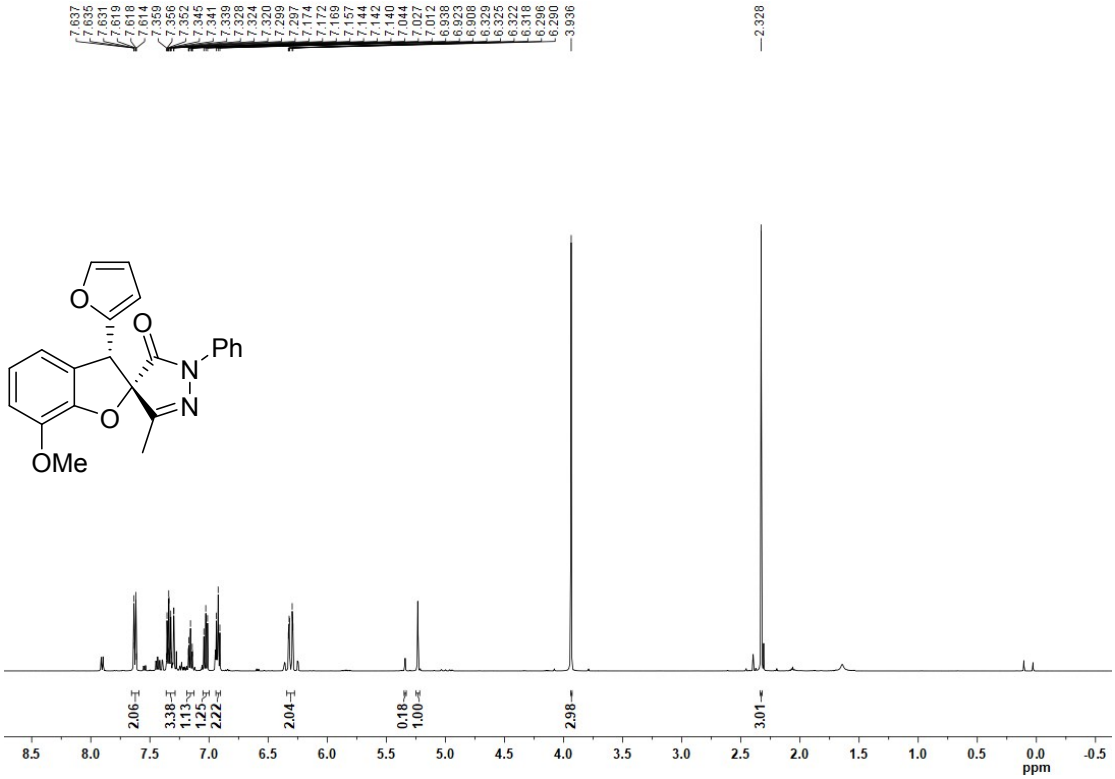
60
50
40
30
20
10
0
ppm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7.356
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7.328
7.324
7.320
7.299
7.297
7.174
7.172
7.169
7.157
7.144
7.142
7.140
7.044
7.027
7.012
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6.923
6.908
6.329
6.325
6.322
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6.296
6.290
3.936
2.328
O
O
N
Ph
N
O
OMe
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3.38
1.13
1.25
2.22
2.04
0.18
1.00
2.98
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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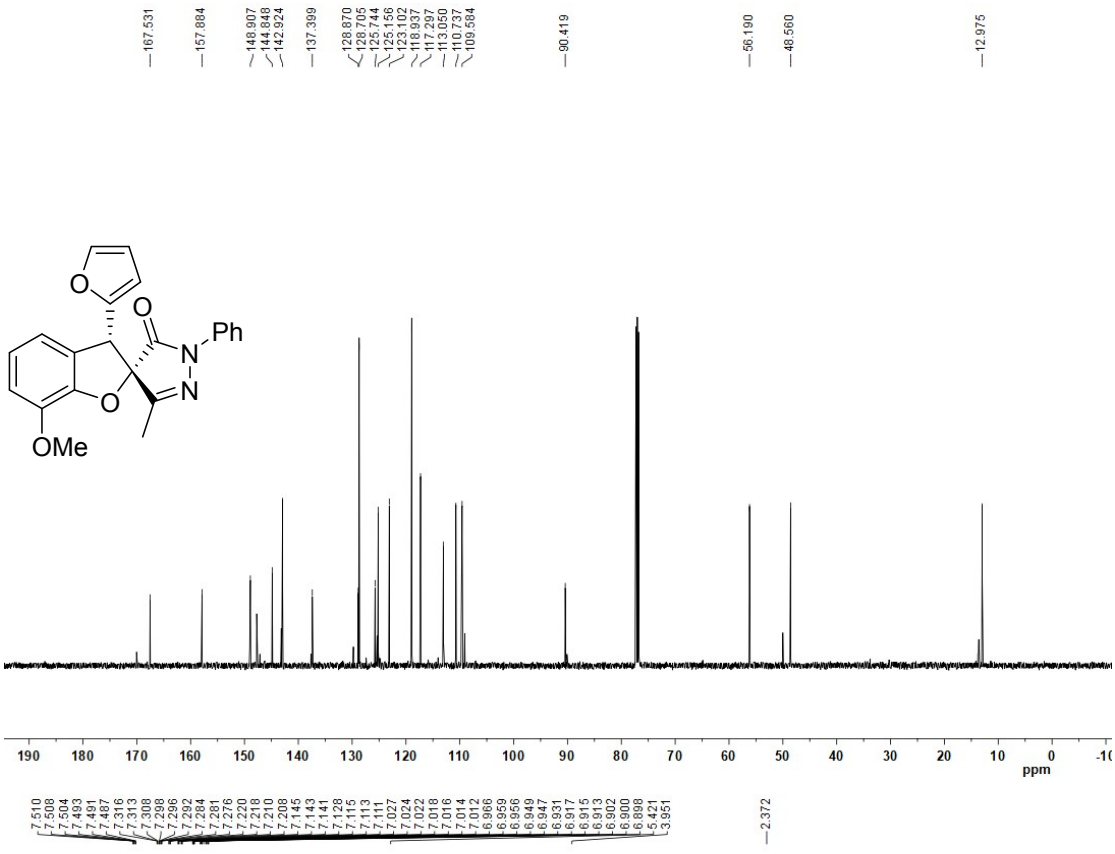
ppm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113.050
110.737
109.584
90.419
56.190
48.560
12.975
O
O
Ph
N
N
O
OMe
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm
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7.508
7.504
7.493
7.491
7.487
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7.313
7.308
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7.296
7.292
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7.281
7.276
7.220
7.218
7.210
7.208
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7.143
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7.128
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7.111
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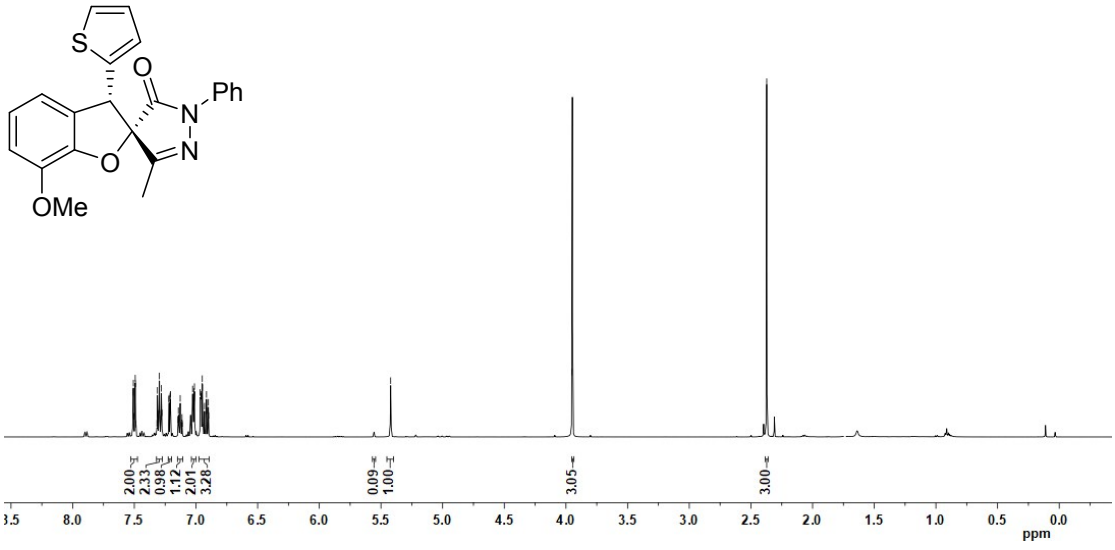
2.372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Ph
N
N
O
OMe
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0.98
1.12
2.01
3.28
0.09
1.00
3.05
3.00
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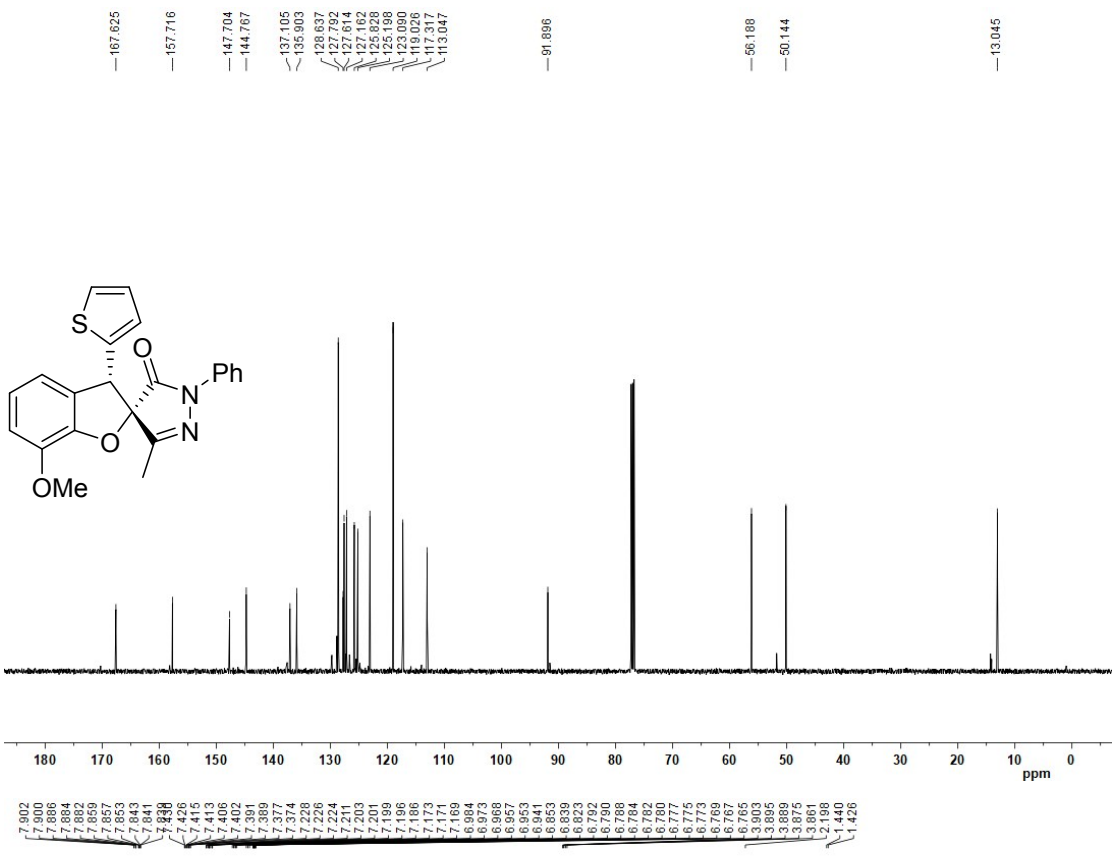
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127.162
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123.090
119.026
117.317
113.047
91.896
56.188
50.144
13.045
S
O
Ph
N
N
O
OMe
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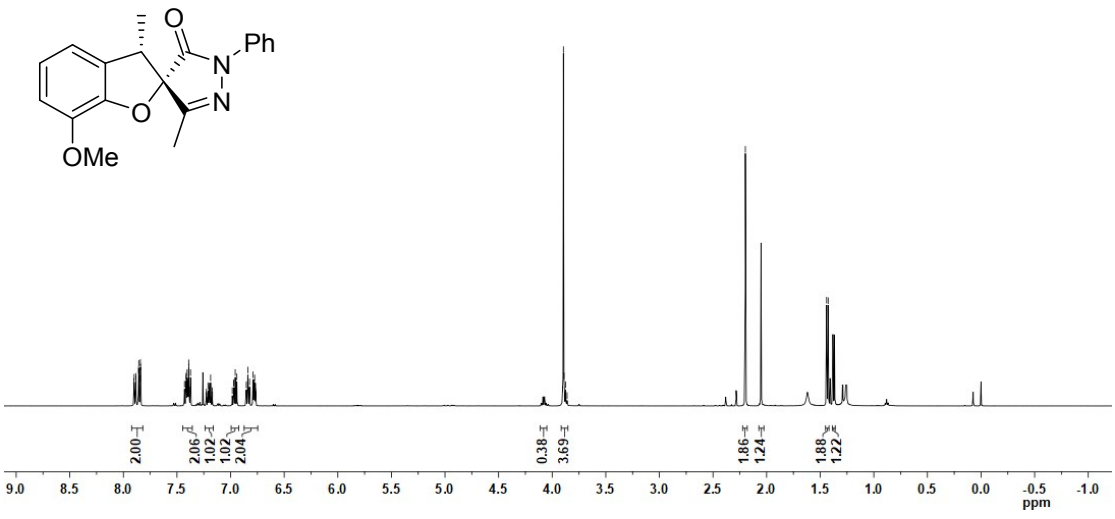
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N
O
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1.02
2.04
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1.24
1.88
1.22
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.5
2.0
1.5
1.0
0.5
0.0
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-1.0
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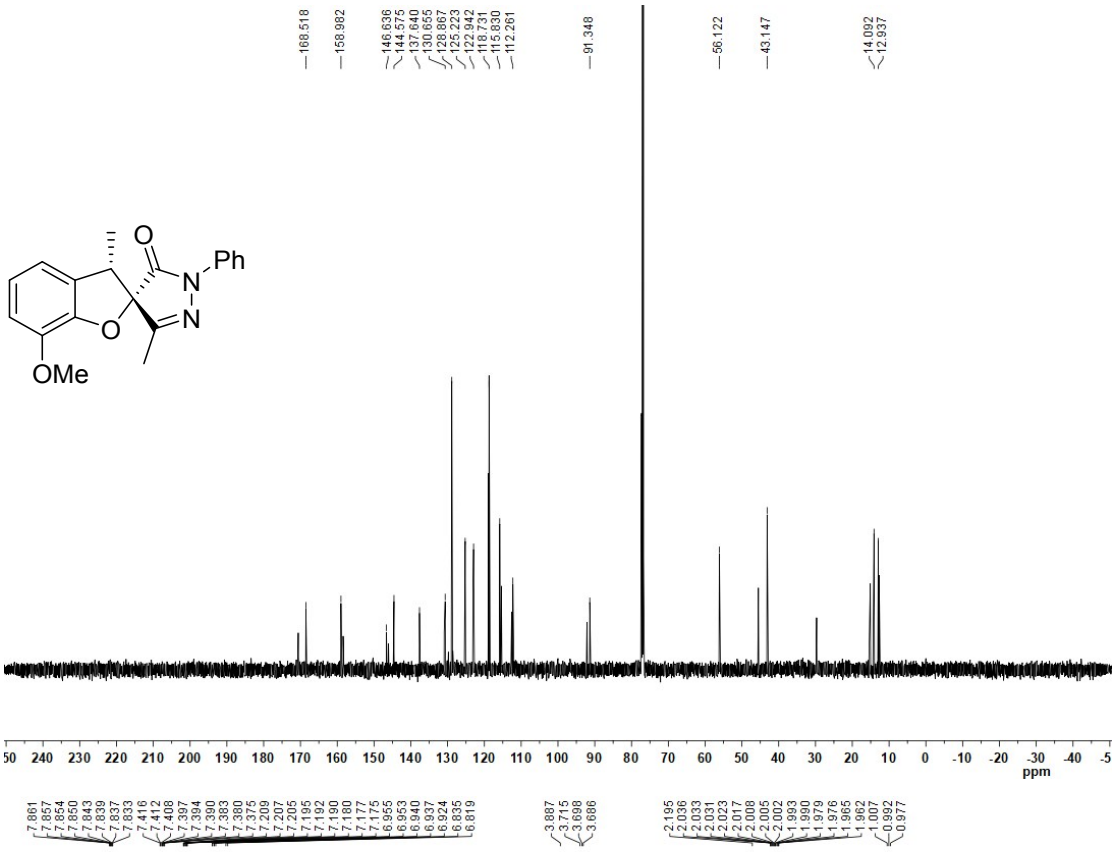
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43.147
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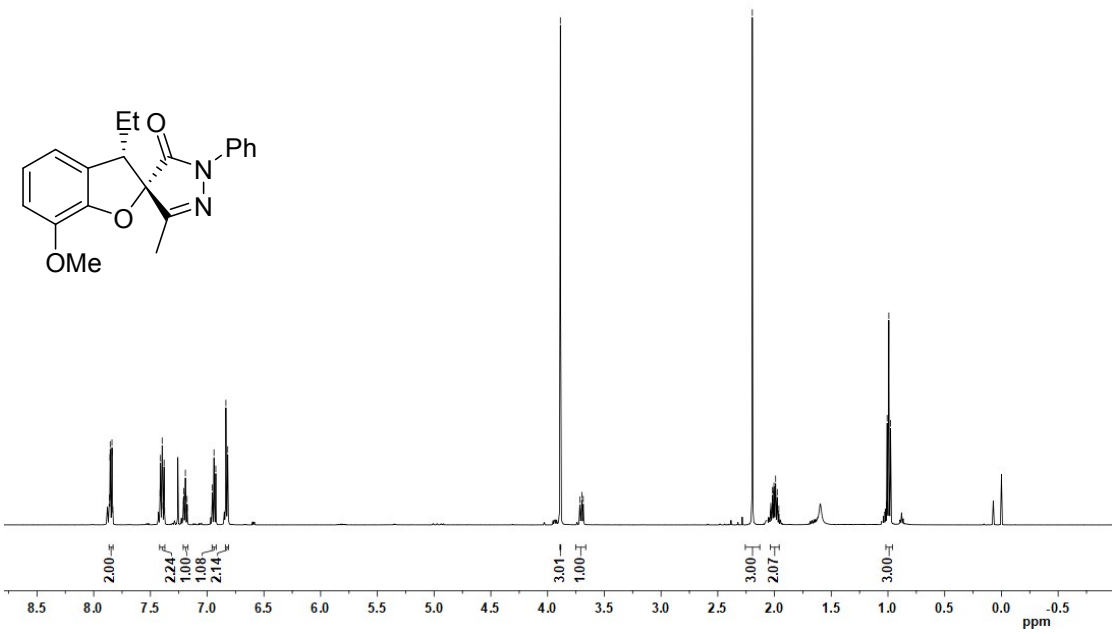
Ph
N
N
O
OMe
ppm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OMe
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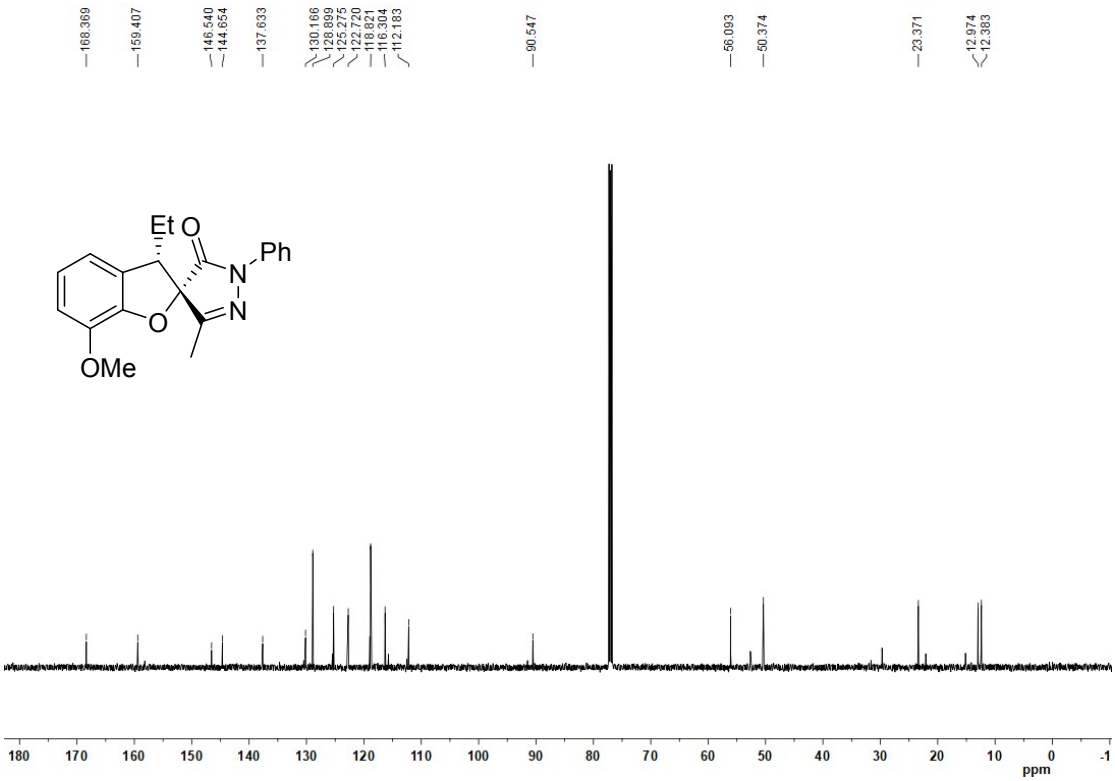
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112.183
90.547
56.093
50.374
23.371
12.974
12.383
Et
O
N
Ph
N
O
OMe
180
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130
120
110
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90
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50
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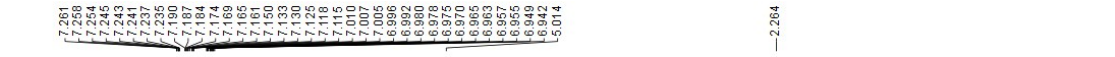
ppm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7.165
7.161
7.150
7.133
7.130
7.125
7.118
7.115
7.010
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7.005
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6.992
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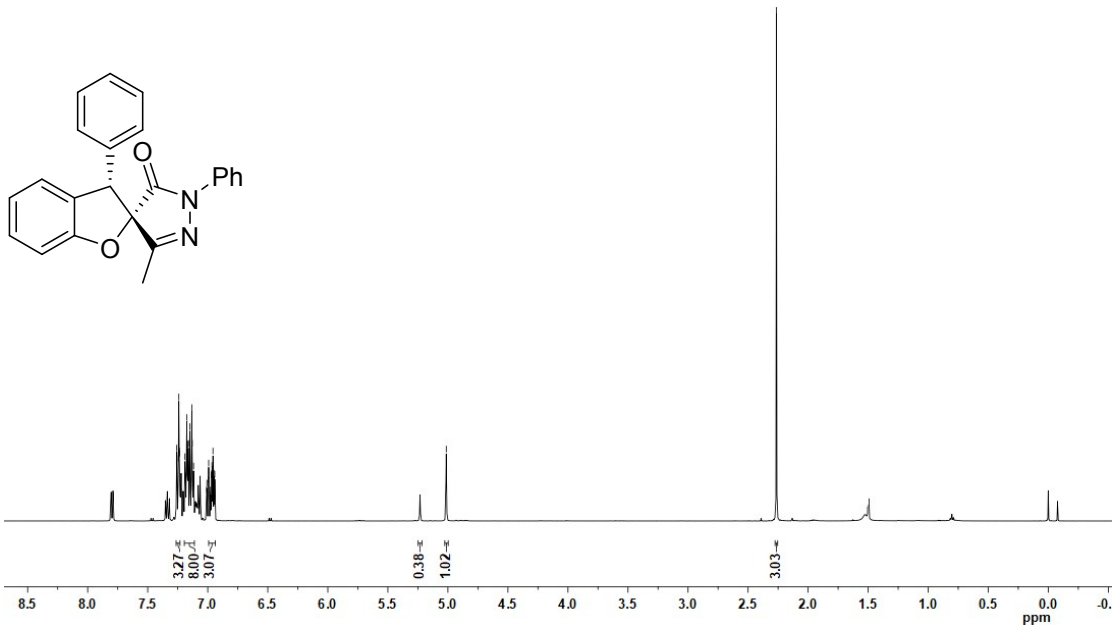
2.264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Ph
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7.0
6.5
6.0
5.5
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3.5
3.0
2.5
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1.0
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0.0
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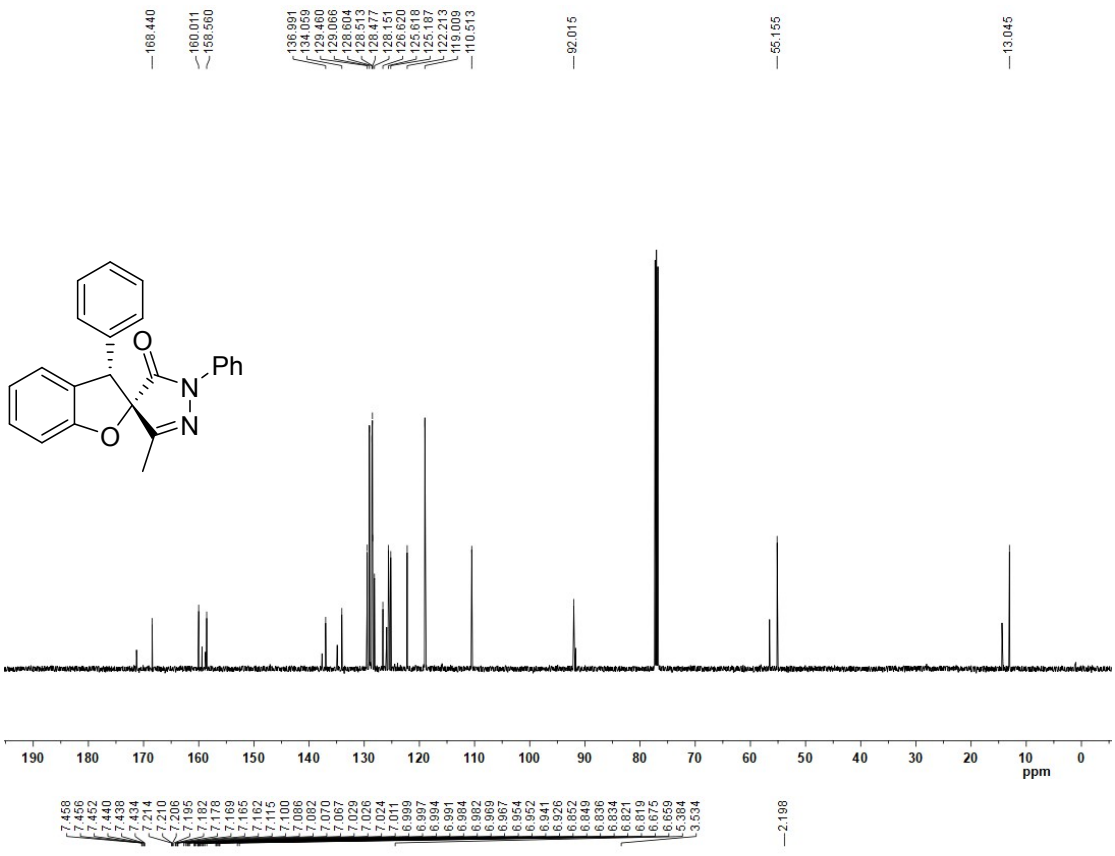
ppm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122.213
119.009
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13.045
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N
Ph
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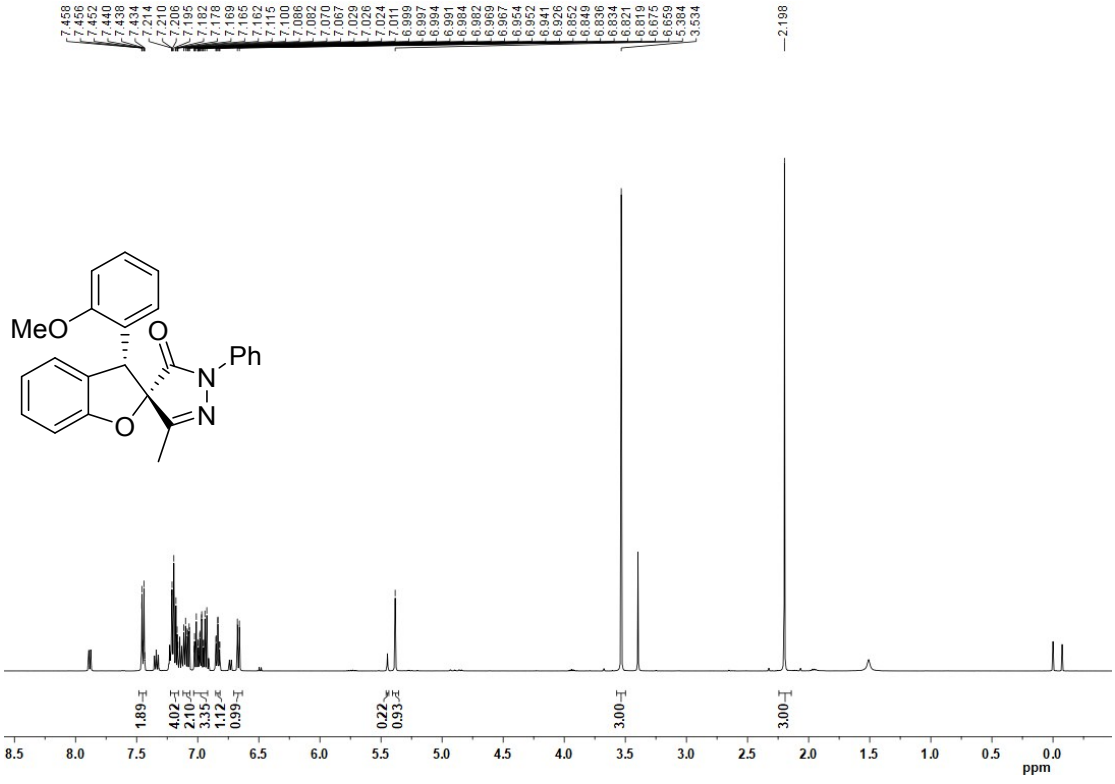
ppm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7.162
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7.100
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7.070
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7.024
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O
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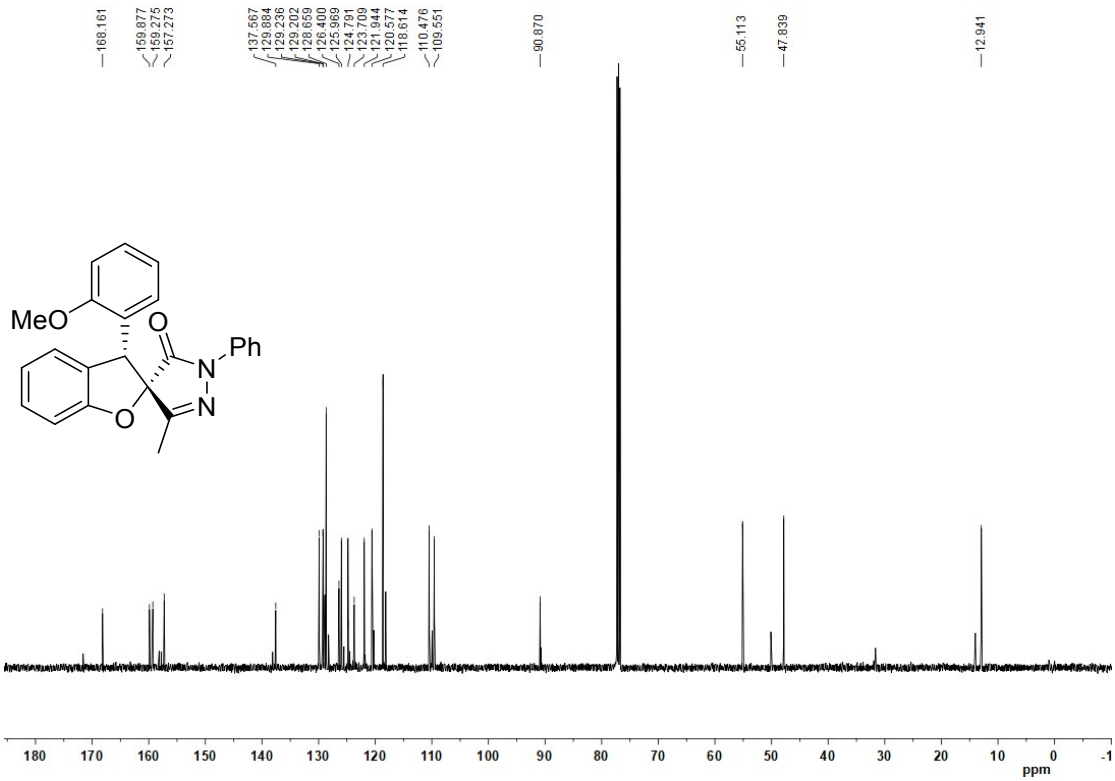
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120.577
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110.476
109.551
90.870
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MeO
O
Ph
N
N
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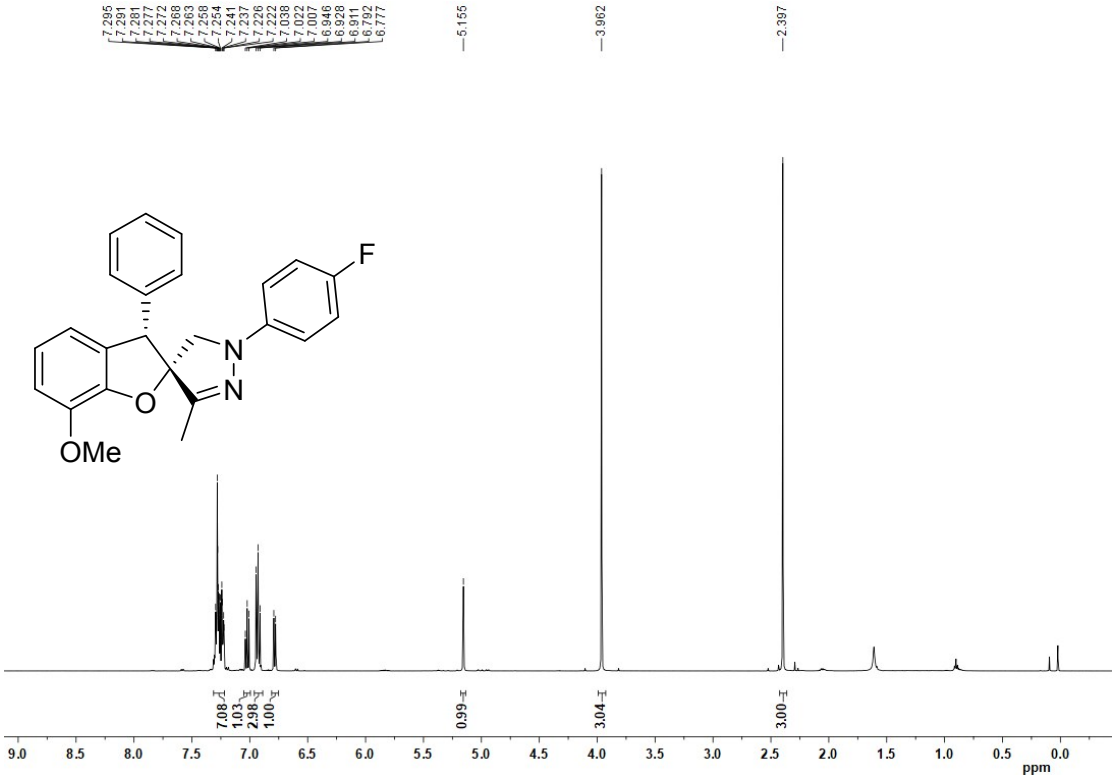
ppm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7.237
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7.222
7.038
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7.007
6.946
6.928
6.911
6.792
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5.155
3.962
2.397
F
N
N
O
OMe
7.08
1.03
2.98
1.00
0.99
3.04
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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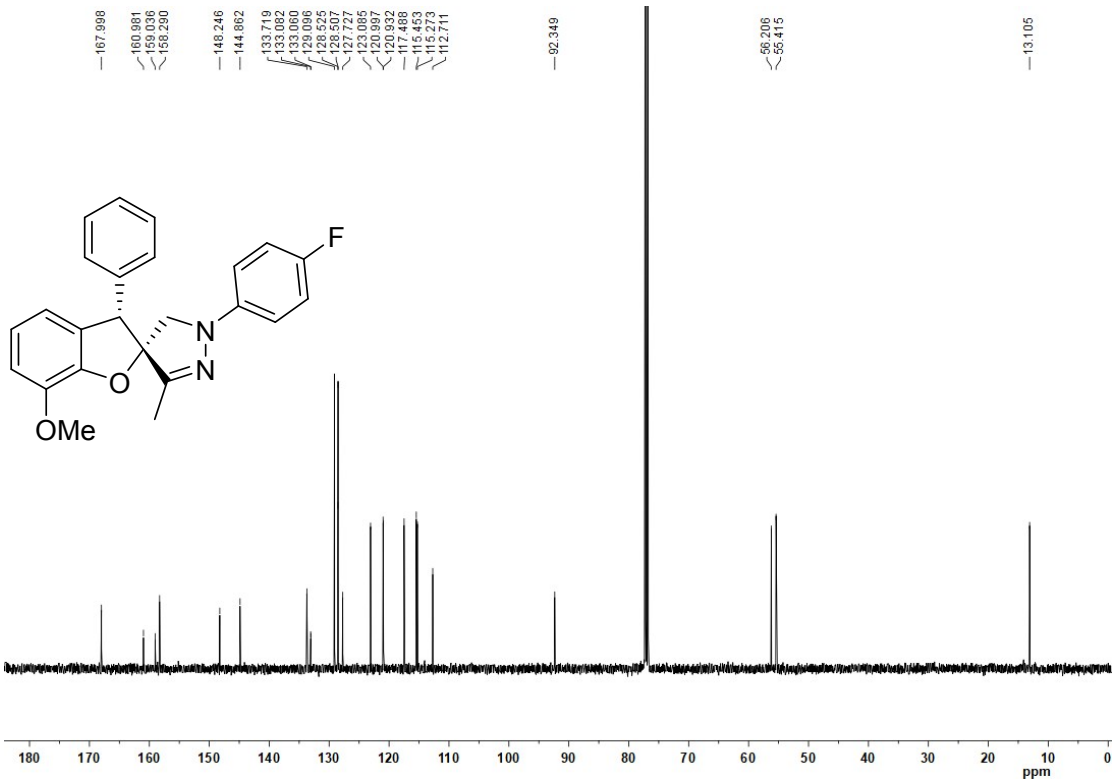
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128.525
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123.085
120.997
120.932
117.488
115.453
115.273
112.711
92.349
56.206
55.415
13.105
F
N
N
O
OMe
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140
130
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20
10
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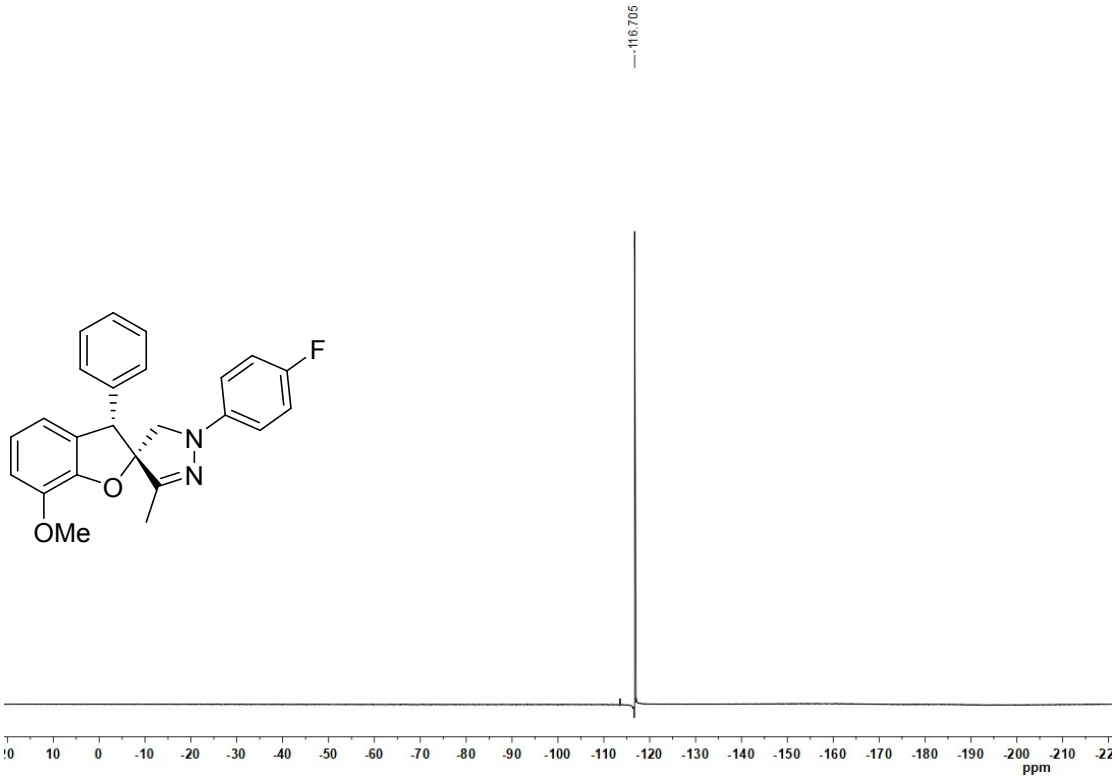
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N
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-20
-30
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-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm


7.367
7.362
7.358
7.348
7.344
7.338
7.291
7.285
7.281
7.276
7.271
7.267
7.264
7.256
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7.210
7.207
7.040
7.024
7.008
6.945
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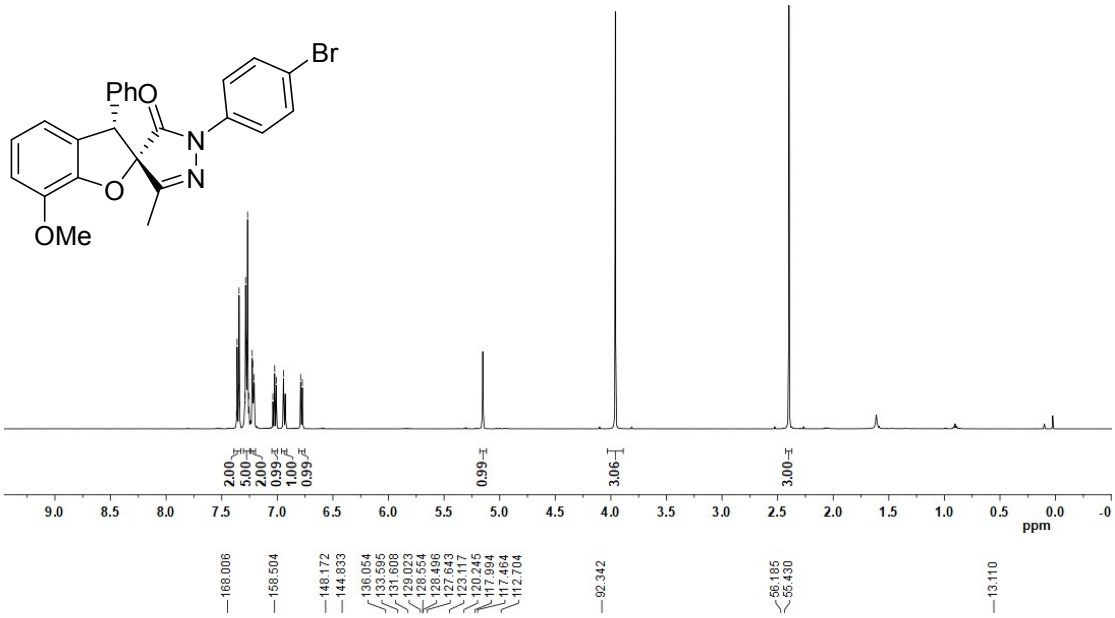
6.775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N
O
OMe
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5.00
2.00
0.99
1.00
0.99
0.99
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3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

168.006
158.504
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144.833
136.054
133.595
131.698
129.023
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127.643
123.117
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112.704
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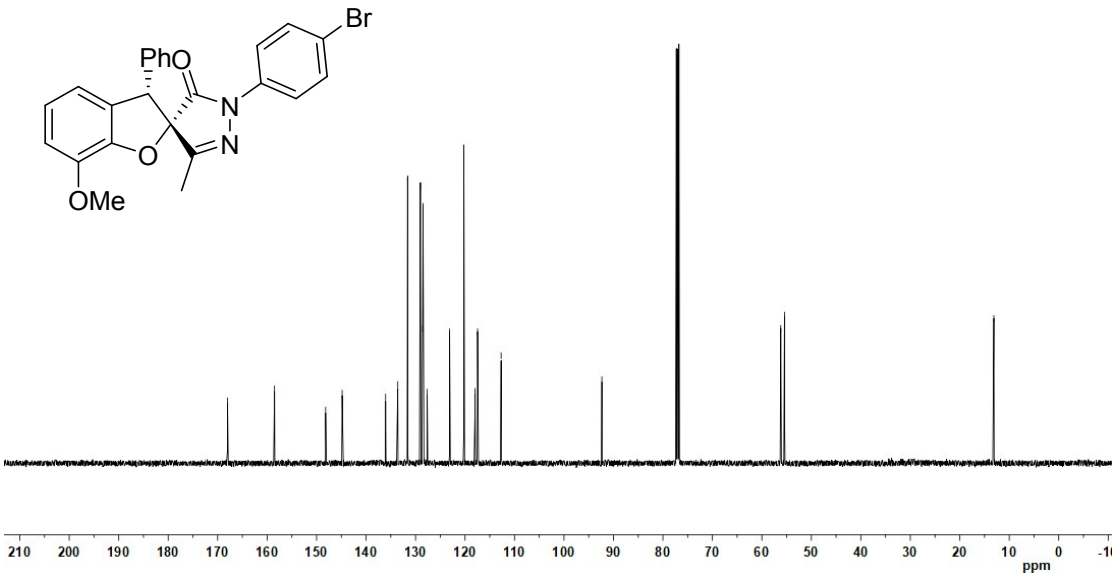
13.110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N
O
OMe
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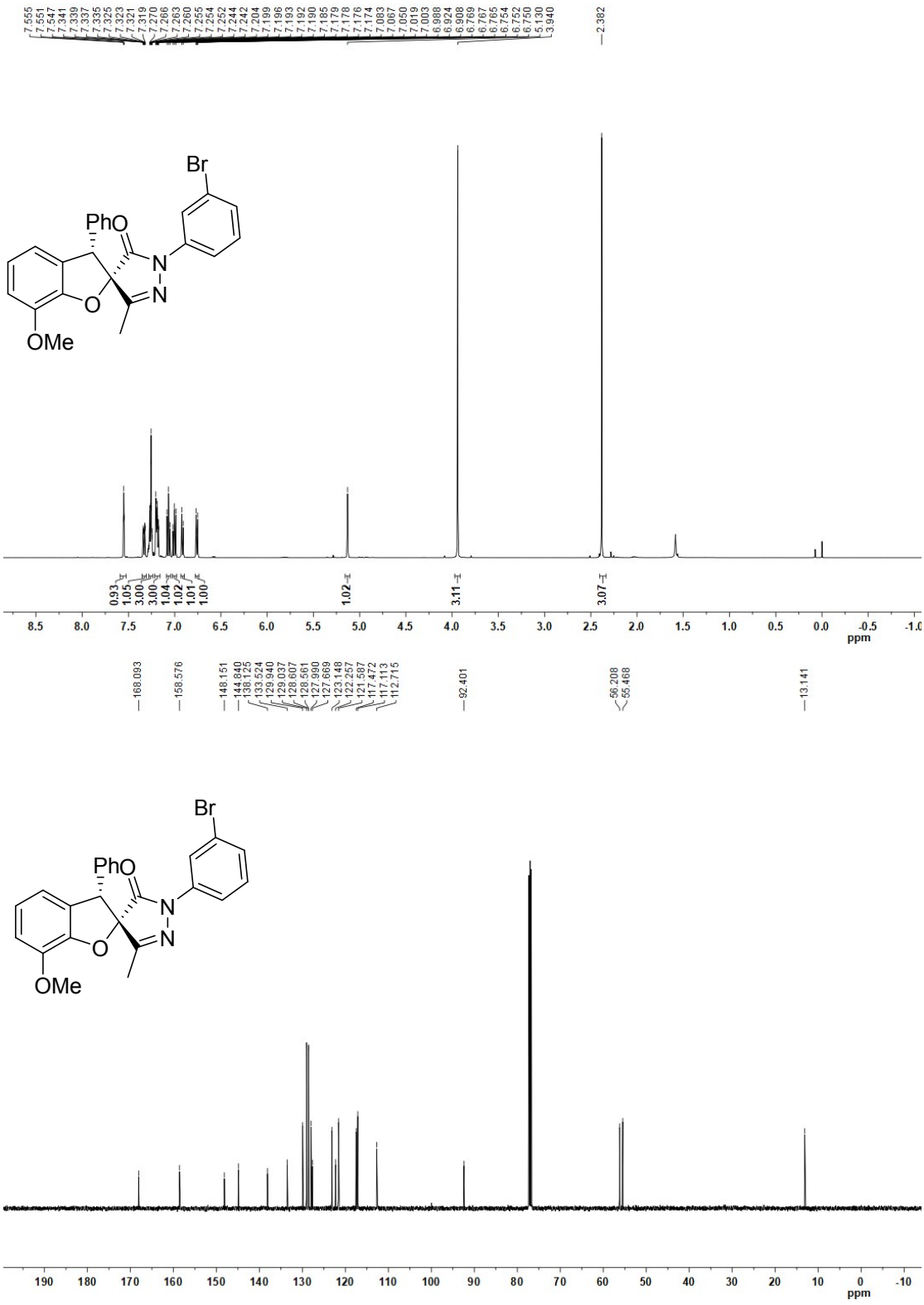
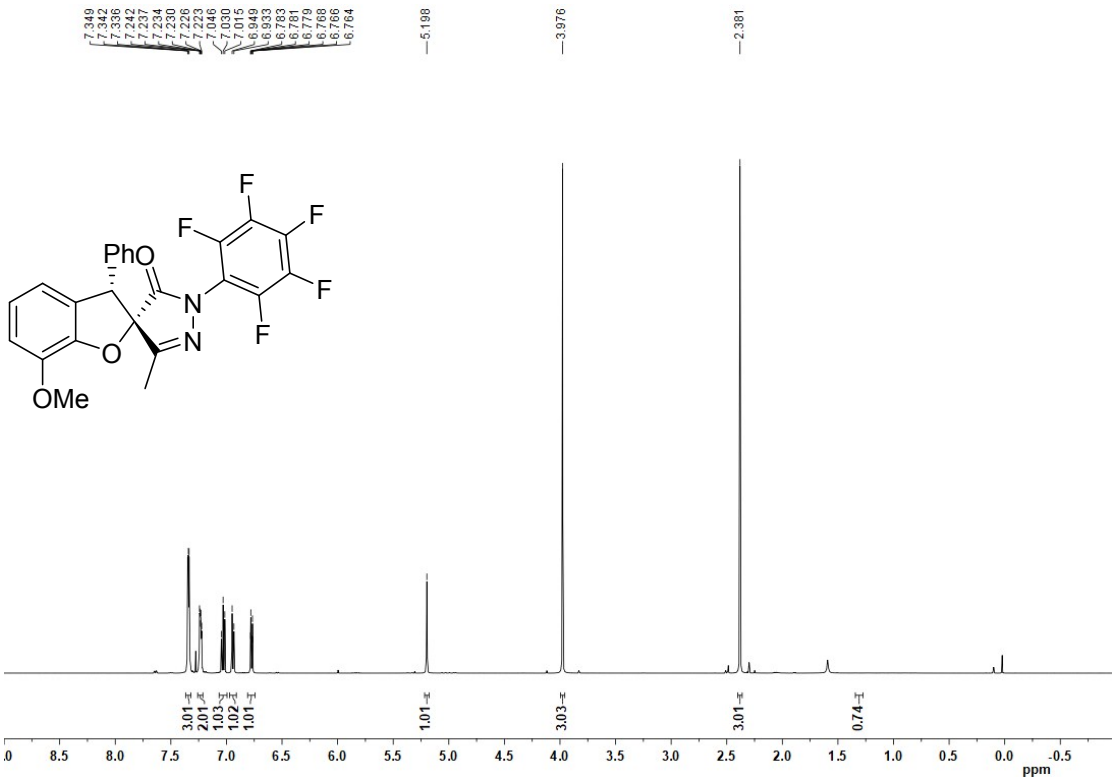
ppm


Br
PhO
N
N
O
OMe
ppm
ppm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7.226
7.223
7.046
7.016
7.010
6.949
6.933
6.783
6.781
6.779
6.768
6.766
6.764
5.198
3.976
2.381
F
F
F
F
F
PhO
N
N
O
OMe
3.01
2.01
1.03
1.02
1.01
1.01
3.03
3.01
0.74
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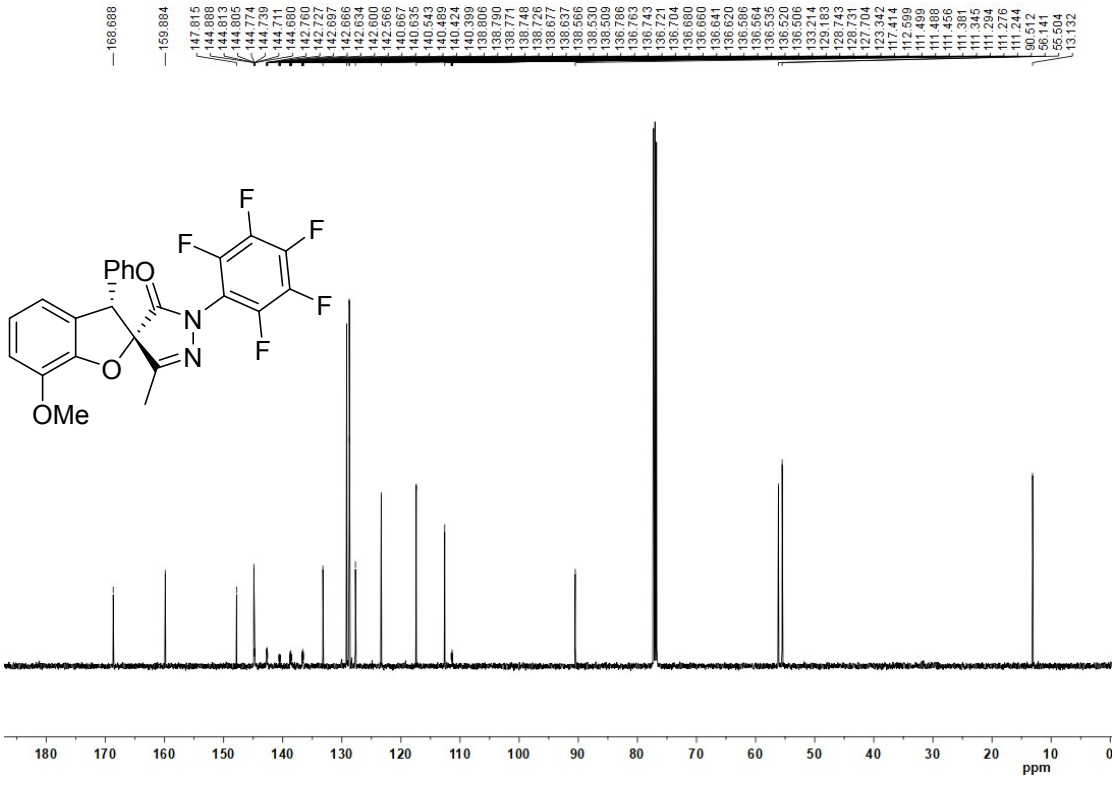
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144.739
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142.727
142.697
142.666
142.634
142.600
142.566
140.667
140.635
140.543
140.489
140.424
140.399
138.806
138.790
138.771
138.748
138.726
138.677
138.637
138.566
138.530
138.509
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136.763
136.743
136.721
136.704
136.680
136.641
136.620
136.566
136.564
136.535
136.520
136.506
133.214
129.183
128.743
128.731
127.704
123.342
117.414
112.599
111.499
111.488
111.456
111.381
111.345
111.294
111.276
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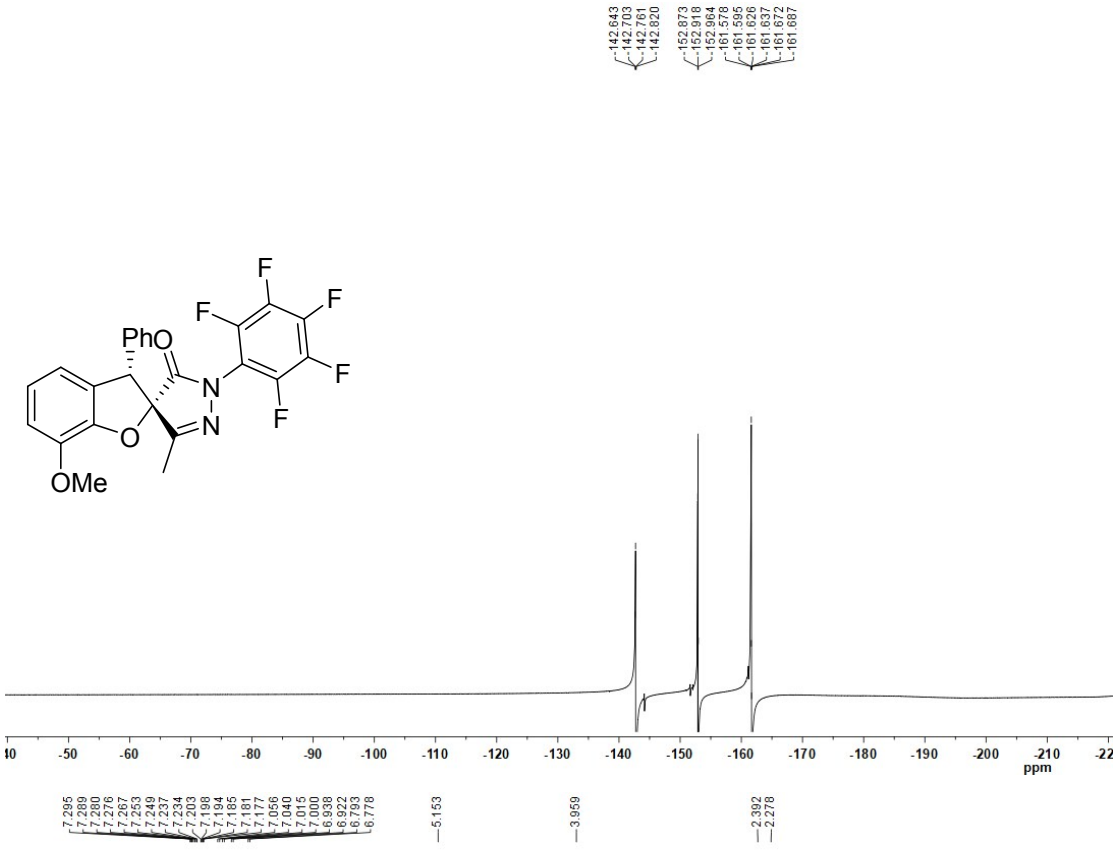
56.141
55.504
13.132
F
F
F
F
F
PhO
N
N
O
OMe
ppm


142.643
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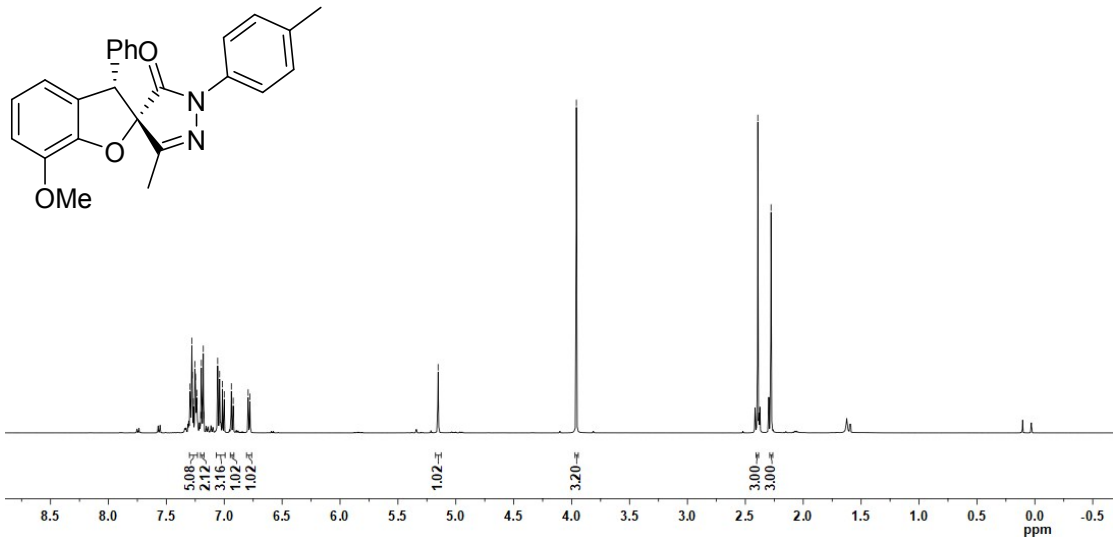
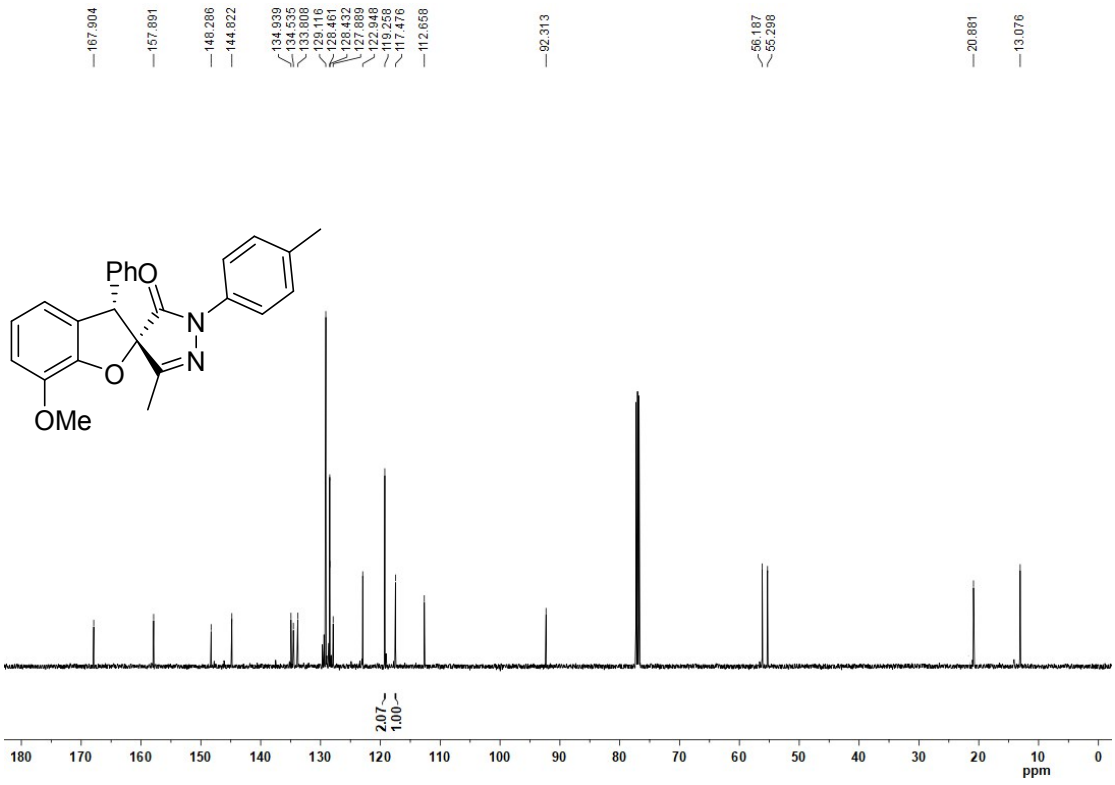
142.761
142.820
152.873
152.918
152.964
161.578
161.595
161.626
161.637
161.672
161.687
F
F
F
F
F
PhO
N
N
O
OMe
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
ppm
7.295
7.289
7.280
7.276
7.267
7.253
7.249
7.237
7.234
7.203
7.198
7.194
7.185
7.181
7.177
7.056
7.040
7.015
7.000
6.938
6.922
6.793
6.778
5.153
3.959
2.392
2.278


PhO
N
N
O
OMe
5.08
2.12
3.16
1.02
1.02
1.02
3.20
3.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm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134.535
133.808
129.116
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128.432
127.889
122.948
119.258
117.476
112.658
92.313
56.187
55.298
20.881
13.076
PhO
N
N
O
OMe
2.07
1.00
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.392
7.376
7.369
7.363
7.336
7.331
7.327
7.324
7.317
7.315
7.213
7.201
7.198
7.171
7.157
7.112
7.109
7.097
7.094
7.016
7.000
6.985
6.928
6.912
6.759
6.757
6.755
6.744
6.742
6.740
6.722
6.719
6.706
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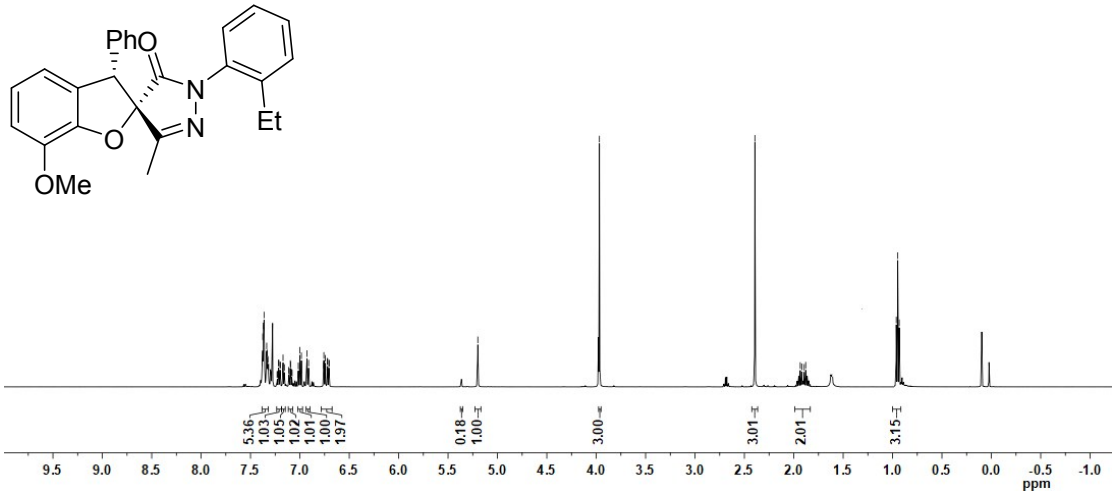
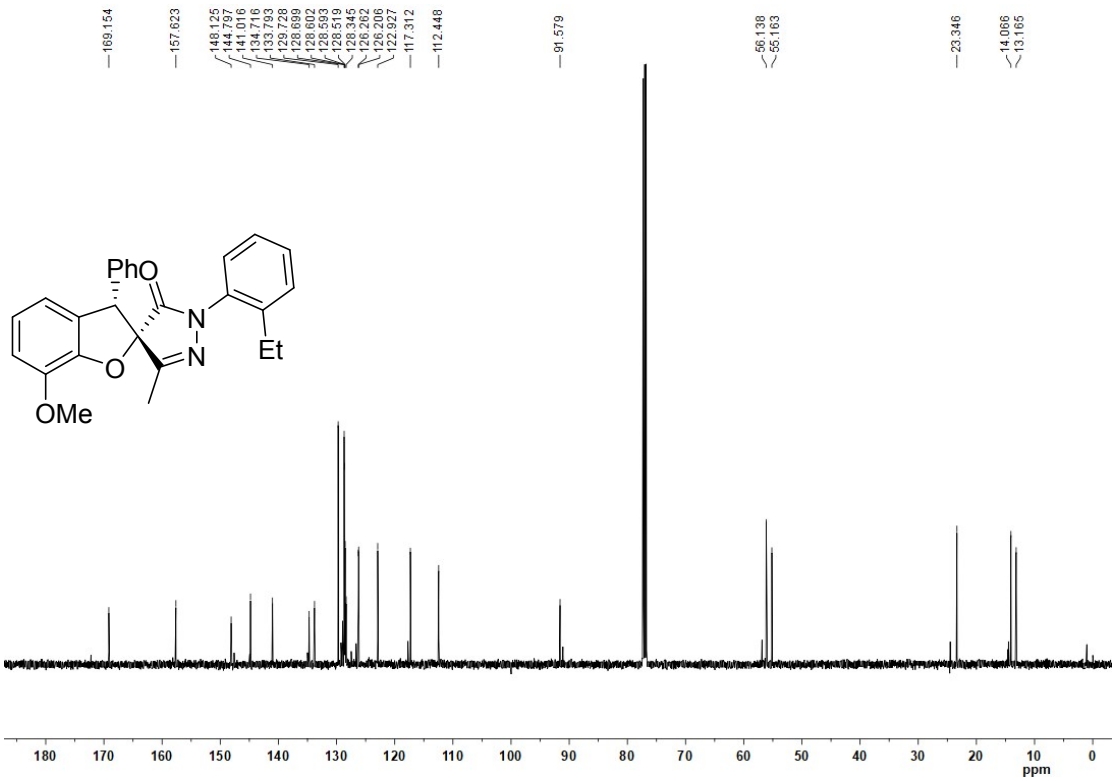
2.394
1.934
1.919
1.895
1.880
0.962
0.947
0.932


PhO
N
N
O
Et
OMe
5.36
1.03
1.05
1.02
1.01
1.00
1.97
0.18
1.00
3.00
3.01
2.01
3.15
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm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129.728
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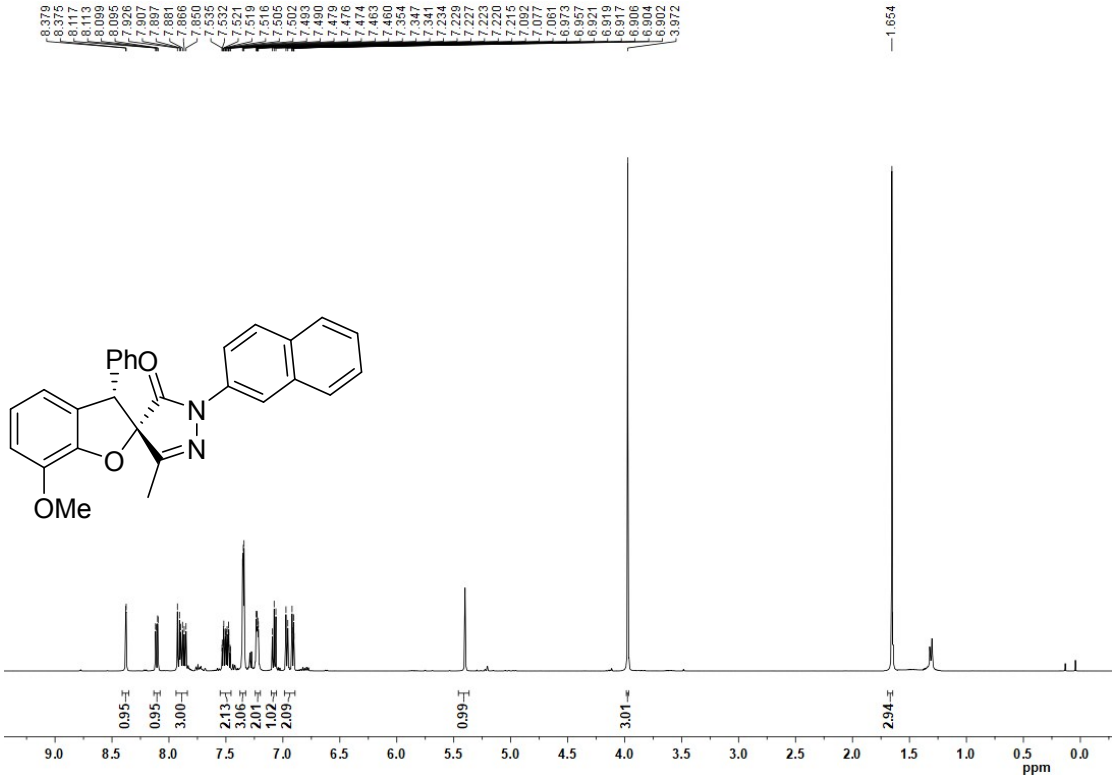
128.503
128.519
128.345
126.282
126.206
122.927
117.312
112.448
91.579
56.138
55.163
23.346
14.066
13.165
PhO
N
N
O
Et
OMe
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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8.113
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8.095
7.926
7.907
7.897
7.881
7.866
7.850
7.535
7.532
7.521
7.519
7.516
7.505
7.502
7.493
7.490
7.479
7.476
7.474
7.463
7.460
7.354
7.347
7.341
7.234
7.229
7.227
7.223
7.220
7.215
7.092
7.077
7.061
6.973
6.957
6.921
6.919
6.917
6.906
6.904
6.902
3.972
1.654
PhO
N
N
O
OMe
0.95
0.95
3.00
2.13
3.06
2.01
1.02
2.09
0.99
3.01
2.94
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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2.0
1.5
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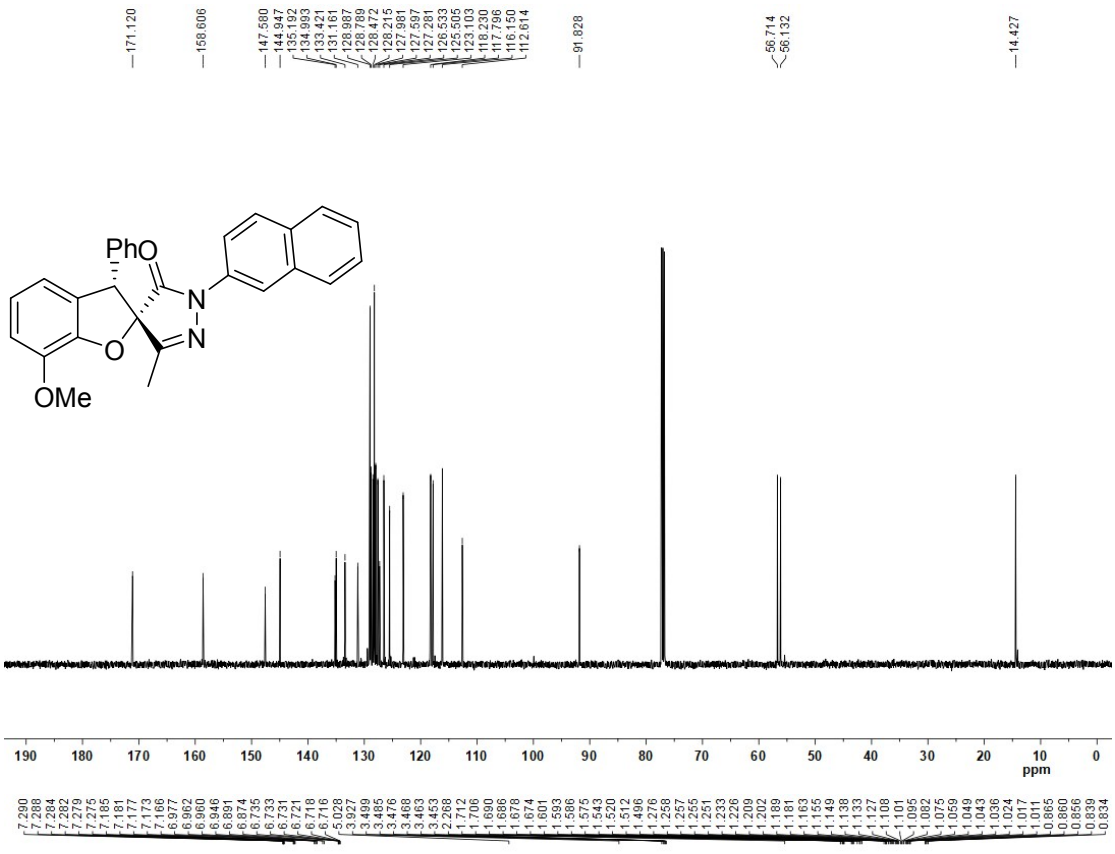
0.5
0.0
ppm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128.789
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128.215
127.981
127.597
127.281
126.533
125.505
123.103
118.230
117.796
116.150
112.614
91.828
56.714
56.132
14.427
PhO
N
N
O
OMe
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm
7.290
7.288
7.284
7.282
7.279
7.275
7.185
7.181
7.177
7.173
7.166
6.977
6.962
6.960
6.946
6.891
6.874
6.735
6.733
6.731
6.721
6.718
6.716
6.028
3.927
3.499
3.485
3.476
3.468
3.463
3.453
2.268
1.712
1.706
1.690
1.686
1.678
1.674
1.601
1.593
1.586
1.575
1.543
1.520
1.512
1.496
1.276
1.258
1.257
1.255
1.251
1.233
1.226
1.209
1.202
1.189
1.181
1.163
1.155
1.149
1.138
1.133
1.127
1.108
1.101
1.095
1.092
1.075
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1.036
1.024
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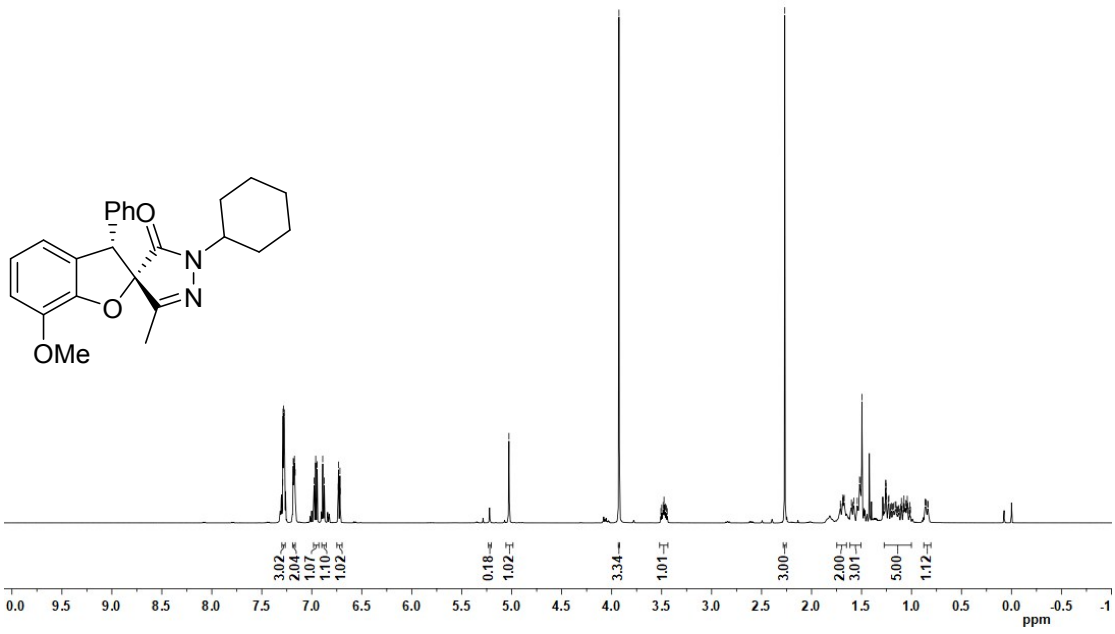
0.834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N
O
OMe
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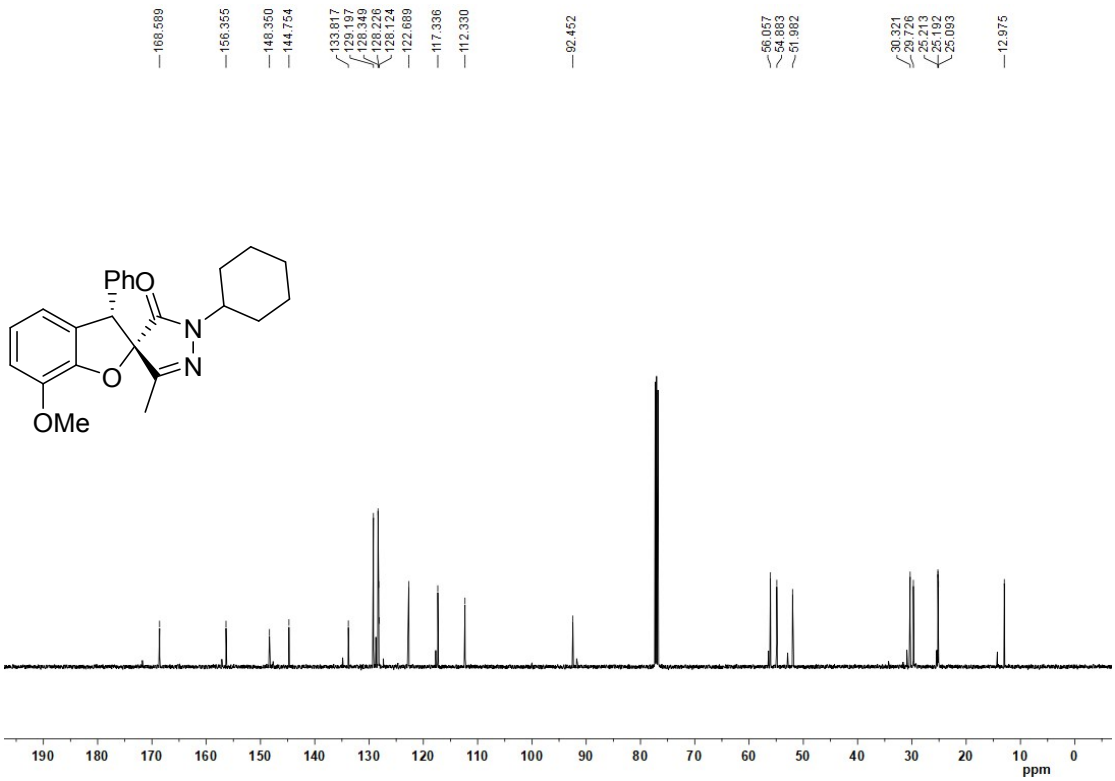
1.07
1.10
1.02
0.18
1.02
3.34
1.01
3.00
2.00
3.01
5.00
1.12
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
ppm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56.057
54.883
51.982
30.321
29.726
25.213
25.192
25.093
12.975
PhO
N
N
O
OMe
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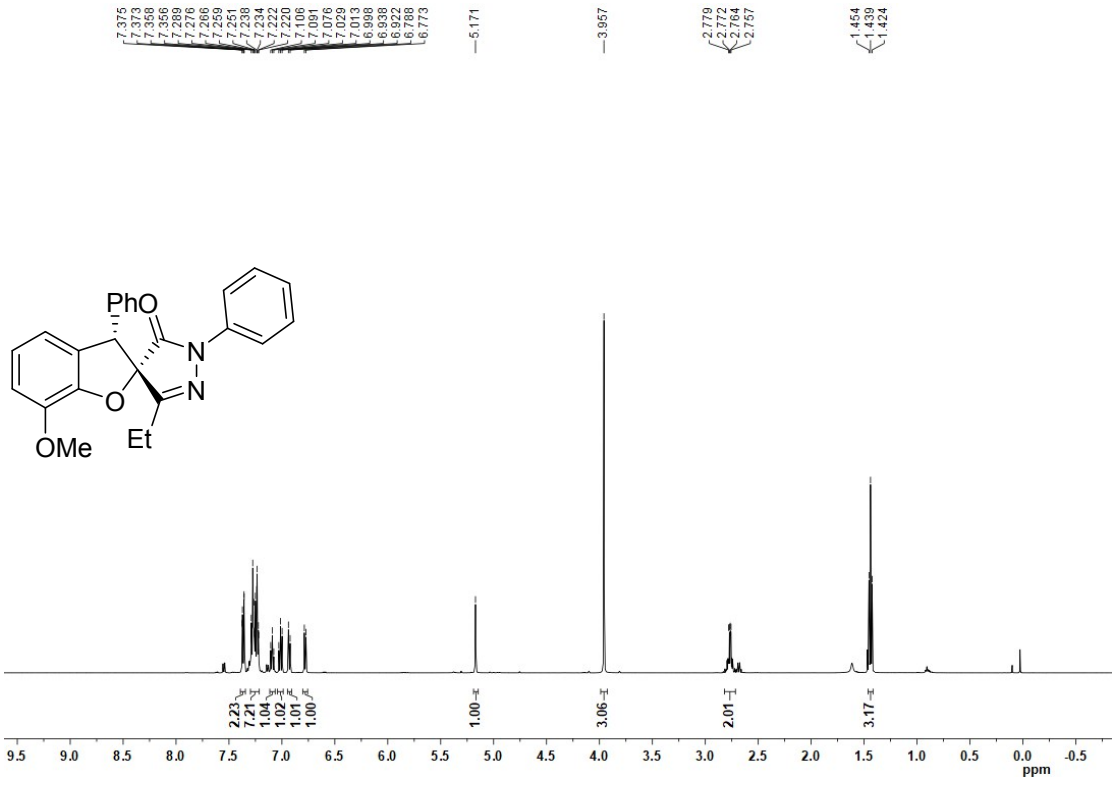
ppm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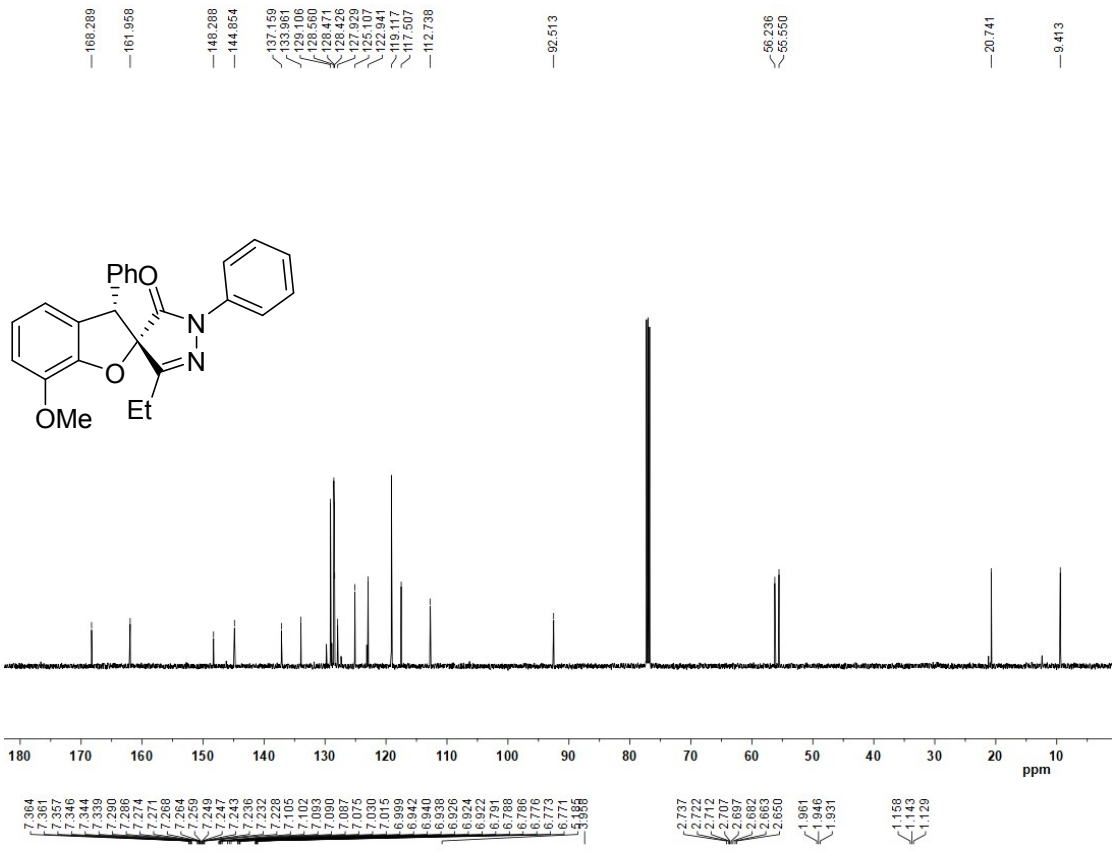
7.259
7.251
7.238
7.234
7.222
7.220
7.106
7.091
7.076
7.029
7.013
6.998
6.938
6.922
6.788
6.773
5.171
3.957
2.779
2.772
2.764
2.757
1.454
1.439
1.424
PhO
N
N
O
OMe
Et
2.23
7.21
1.04
1.02
1.01
1.00
1.00
3.06
2.01
3.17
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm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128.560
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128.426
127.929
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122.941
119.117
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92.513
56.236
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20.741
9.413
PhO
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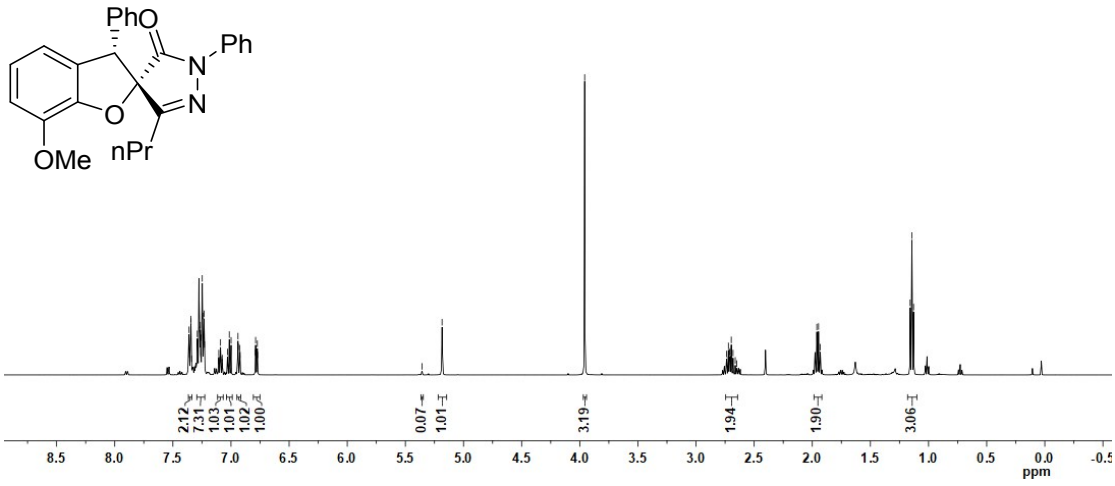
N
O
OMe
Et
ppm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Ph
N
N
O
OMe
nPr
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7.31
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1.01
1.02
1.00
0.07
1.01
3.19
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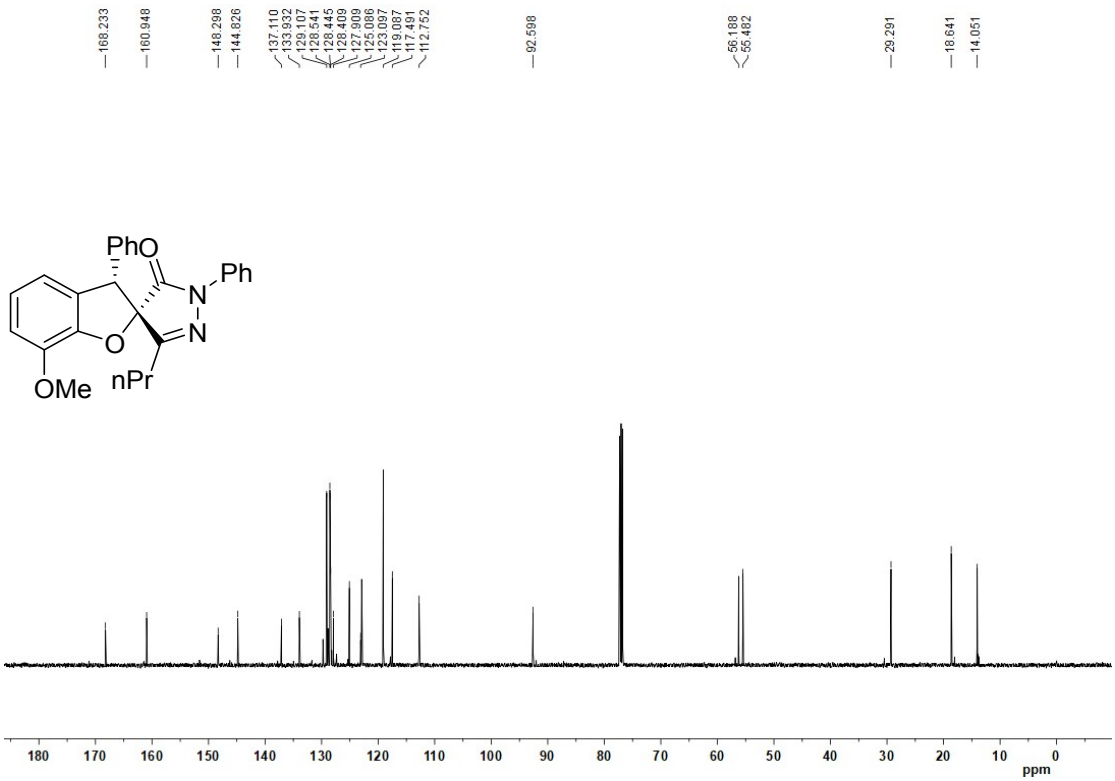
1.90
3.06
ppm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128.541
128.445
128.409
127.909
125.086
123.097
119.087
117.491
112.752
92.598
56.188
55.482
29.291
18.641
14.051
PhO
Ph
N
N
O
OMe
nPr
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140
130
120
110
100
90
80
70
60
50
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20
10
0
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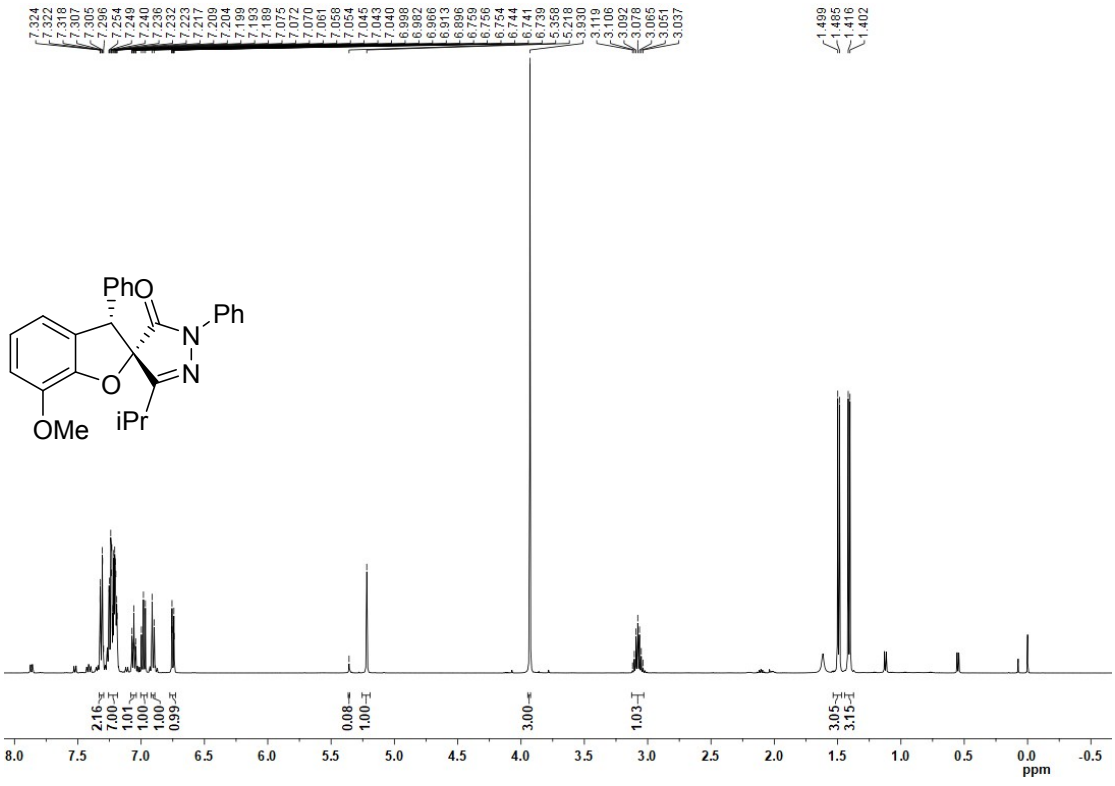
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7.296
7.254
7.249
7.240
7.236
7.232
7.223
7.217
7.209
7.204
7.199
7.193
7.189
7.075
7.072
7.070
7.061
7.058
7.054
7.045
7.043
7.040
6.998
6.982
6.966
6.913
6.896
6.759
6.756
6.754
6.744
6.741
6.739
5.358
5.218
3.930
3.119
3.106
3.092
3.078
3.065
3.051
3.037
1.499
1.485
1.416
1.402
PhO
Ph
N
N
O
OMe
iPr
2.16
7.00
1.01
1.00
1.00
0.99
0.08
1.00
3.00
1.03
3.05
3.15
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
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2.0
1.5
1.0
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0.0
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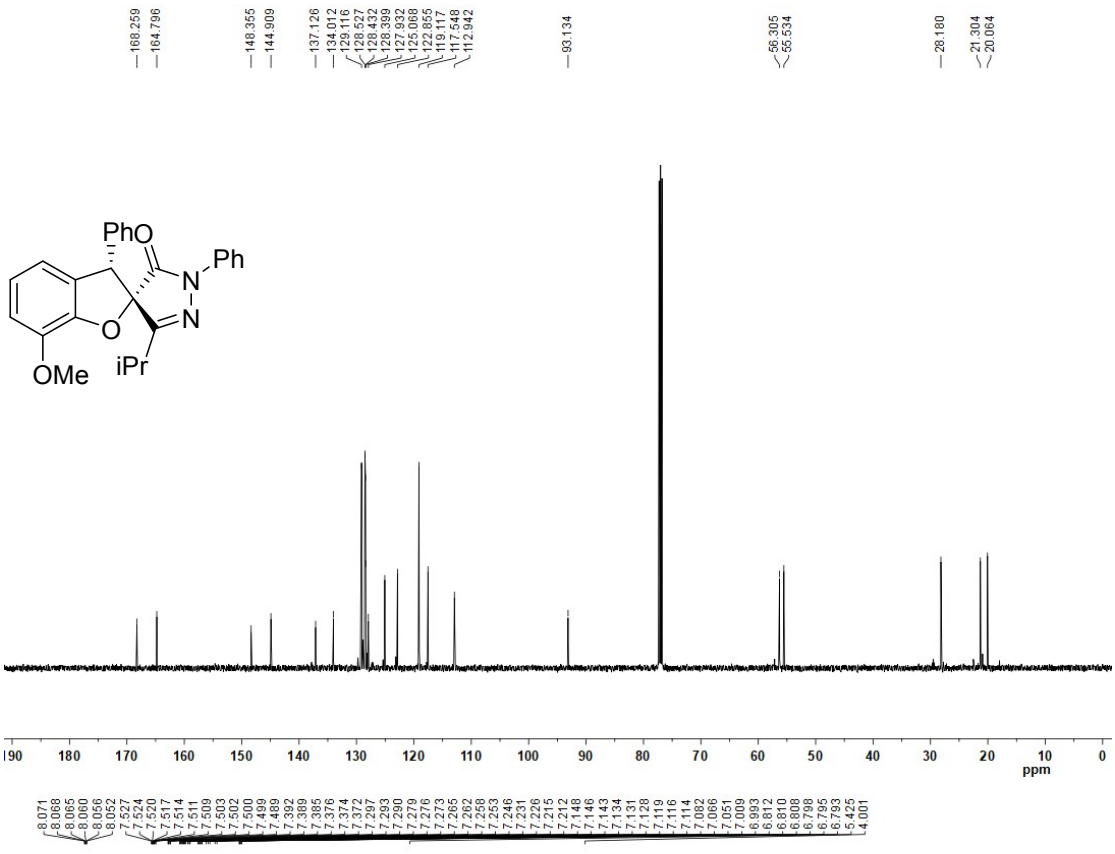
ppm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128.432
128.399
127.932
125.068
122.855
119.117
117.548
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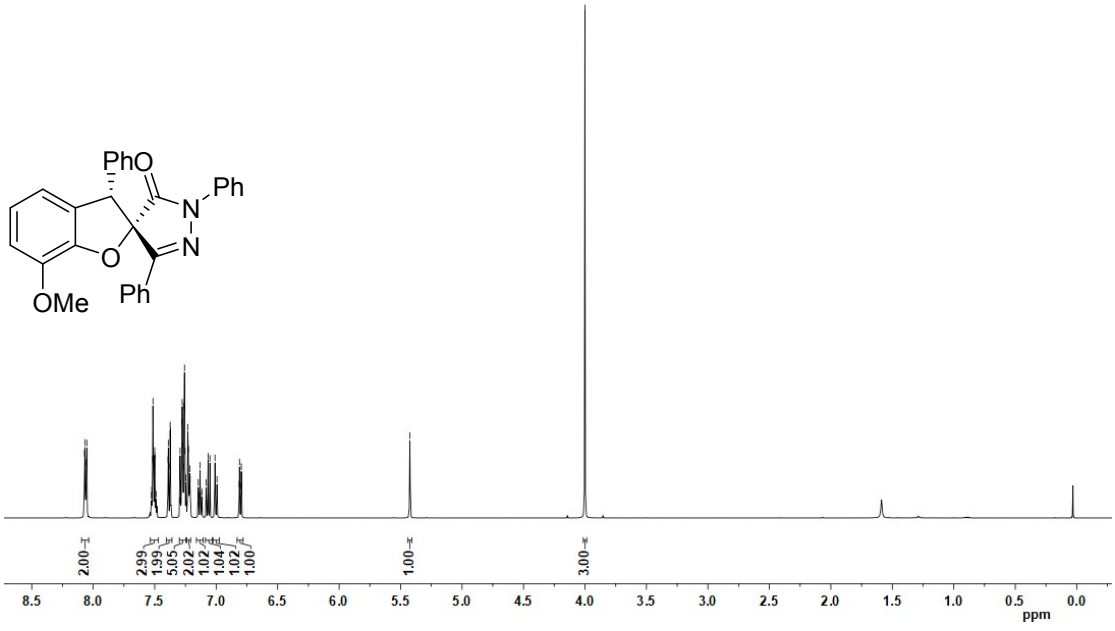
55.534
28.180
21.304
20.064
PhO
Ph
N
N
O
iPr
OMe
ppm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Ph
N
N
O
Ph
OMe
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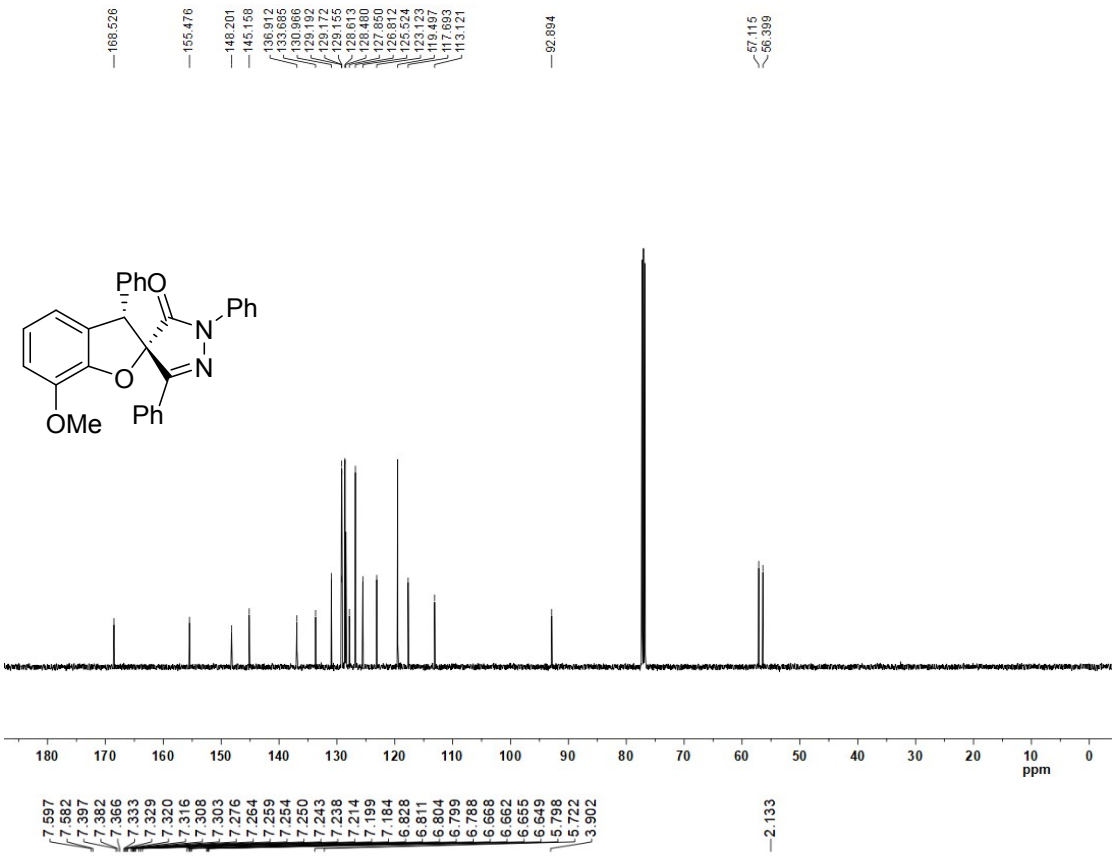
1.99
5.05
2.02
1.02
1.04
1.02
1.00
1.00
3.00
ppm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155.476
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145.158
136.912
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129.192
129.172
129.155
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125.524
123.123
119.497
117.693
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92.894
57.115
56.399
PhO
Ph
N
N
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OMe
Ph
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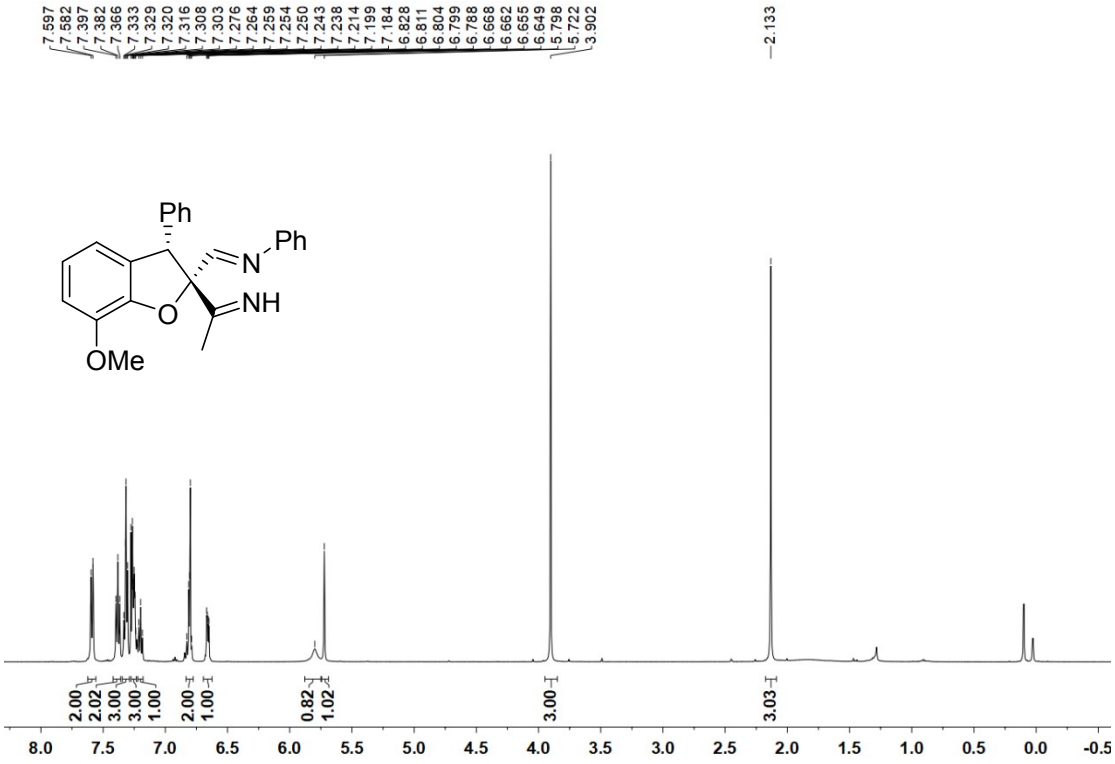
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7.259
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Ph
N
Ph
NH
O
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2.02
3.00
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1.00
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1.00
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8.0
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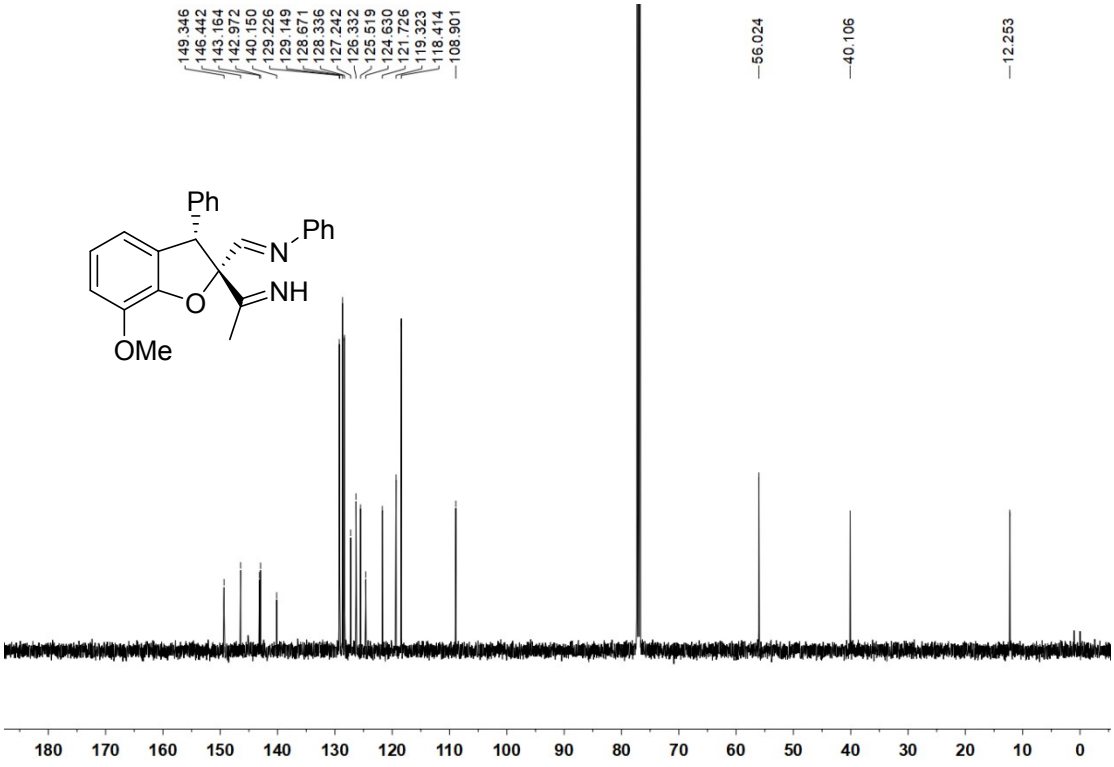

References

[1] M-W.Chen, L-L. Cao, Z-S. Ye, G-F. Jiang, Y-G. Zhou, *Chem. Commun*. **2013**, *49*, 1660-1662.

[2] A. Akbarzadeh, R. Soleymani, M. Taheri, M. Karimi-Cheshmeh Ali, *Orient. J. Chem*. **2012**, *28*, 153-164.

X-ray crystal structure of compound 3fa

Crystals of enantiopure **3fa** suitable for X-ray analysis were obtained from crystallization in a solution of dichloromethane and *iso*-propyl alcohol.

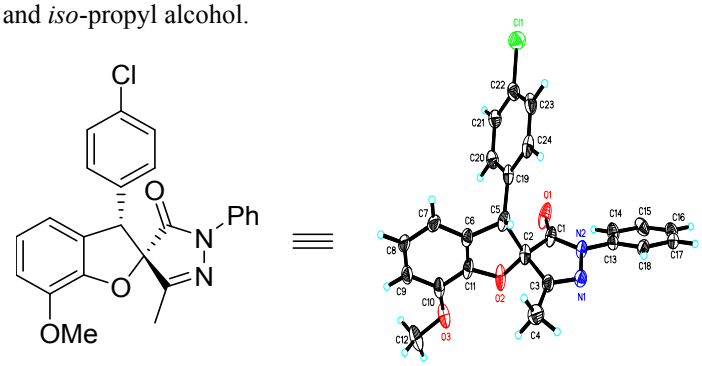

Table 1. Crystal data and structure refinement parameters of the compound **3fa**

Parameter	Value
CCDC deposition number	1867064
Empirical formula	$C_{24}H_{19}ClN_2O_3$
Formula weight	418.86
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic

Space group	P 21 21 21
Unit cell dimensions	a = 5.9309(6) Å α = 90°.
	b = 17.470(2) Å β = 90°.
	c = 19.675(3) Å γ= 90°.
Volume	2038.6(4) $Å^3$
Z	4
Density (calculated)	1.365 Mg/m^3
Absorption coefficient	0.216 mm^{-1}
F_{000}	872
Crystal size	0.180 x 0.160 x 0.110 mm^3
Theta range for data collection	2.376 to 25.493°.
Index ranges	$-6 \leq h \leq 7$, $-21 \leq k \leq 2$, $-23 \leq l \leq 23$
Reflections collected	19157
Independent reflections	3774 [R(int) = 0.0808]
Completeness to theta = 25.242°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5341
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3774/0/274
Goodness-of-fit on F^2	1.085
Final R indices [$I>2\sigma$ (I)]	$R_1 = 0.0585$, $wR_2 = 0.1544$
R indices (all data)	$R_1 = 0.0663$, $wR_2 = 0.1624$
Absolute structure parameter	0.10(4)
Extinction coefficient	0.019(6)
Largest diff. peak and hole	0.399 and -0.590 $e.Å^{-3}$