Quaternary Carbon Center Forming Formal [3 + 3] Cycloaddition Reaction *via* Bifunctional Catalysis: Asymmetric Synthesis of Spirocyclohexene Pyrazolones

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Contents

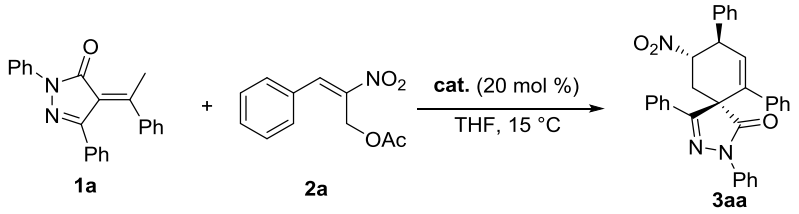
1. General Information

Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Analytical thin-layer chromatography (TLC) was performed on silicycle silica gel plates with F-254 indicator and compounds were visualized by irradiation with UV light. Flash chromatography was carried out utilizing silica gel 200-300 mesh. ^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer (400 MHz ^{1}H, 100 MHz ^{13}C). The spectra were recorded in $CDCl_3$ as the solvent at room temperature, ^{1}H and ^{13}CNMR chemical shifts are reported in ppm relative to either the residual solvent peak (^{13}C) (δ = 77.00 ppm) or TMS (^{1}H) (δ = 0 ppm) as an internal standard. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = double doublet, br = broad), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported as chemical shift. IR spectra were recorded using Nicolet NEXUS 670 FT-IR instrument and are reported in wavenumbers (cm^{-1}). HRMS were performed on Bruker Apex II mass instrument (ESI). Enantiomeric excess values were determined by HPLC with a Daicel Chirapak AD-H/IA column on Agilent 1260 series with *i*-PrOH and *n*-hexane. Optical rotation was measured on the Perkin Elmer 341 polarimeter with $[\alpha]_D$ values reported in degrees. Concentration (c) is in g/100 mL. α-Arylidene pyrazolinones substrates **1** were prepared according to the literature procedures.[1] (*E*)-2-Nitroallylic acetates **2** were also prepared according to the literature procedures.[2]

(1) Yetra, S. R.; Mondal, S.; Mukherjee, S.; Gonnade, R. G.; Biju, A. T. *Angew. Chem., Int. Ed.* **2016**, *55*, 268.

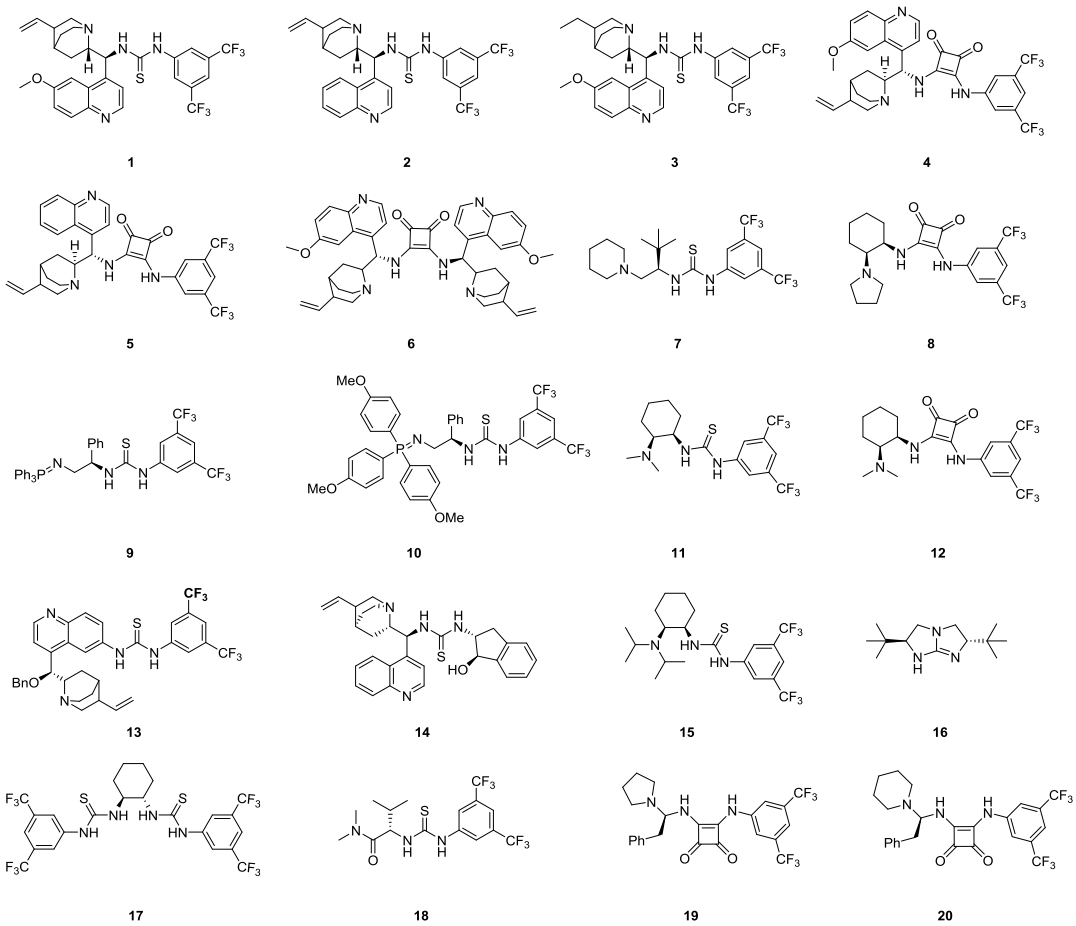
(2) Cao, C.-L.; Zhou, Y.-Y.; Zhou, J.; Sun, X.-L.; Tang, Y.; Li, Y.-X.; Li, G.-Y.; Sun, J. *Chem. - Eur. J.* **2009**, *15*, 11384

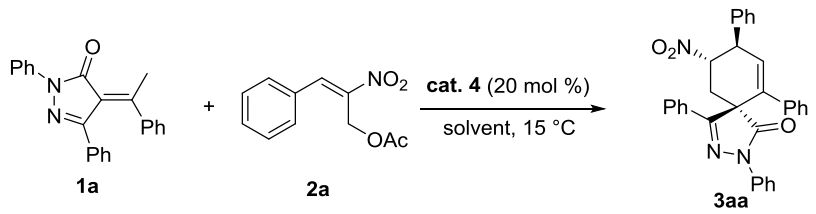
2. Preliminary condition optimization for [3 + 3] cycloaddition reaction



entry[a]	catalyst	T/h	Yield (%)[d]	dr[e]	*ee* (%)[f]
1	**1**	24	46	17:1	67
2[b]	**1**	6	70	10:1	9
3	**2**	24	46	9:1	31
4	**3**	20	69	10:1	52
5	**4**	20	60	16:1	91
6	**5**	30	40	15:1	79
7	**6**	20	57	14:1	57
8	**7**	20	50	14:1	75
9	**8**	20	63	16:1	72
10	**9**	20	50	10:1	40
11	**10**	7	72	16:1	44
12	**11**	20	62	16:1	50
13	**12**	24	53	15:1	68
14	**13**	20	60	10:1	0
15	**14**	24	47	9:1	37
16	**15**	-	NR	-	-
17	**16**	-	NR	-	-
18	**17**	-	NR	-	-
19	**18**	-	NR	-	-
20	**19**	36	40	7:1	69
21	**20**	36	38	8:1	72
22[c]	**4**	20	60	10:1	85

[a]Conditions: Reactions performed with **1a** (0.1 mmol), **2a** (0.1 mmol), **cat.** (20 mol %) in THF (1 mL) at 15 °C. [b]0.1 mmol K_2CO_3 was added. [c]50 mg 4 Å MS was added. [d]Isolated yield. [e]Determined by ^{1}H NMR analysis of the crude products. [f]Determined by chiral-phase HPLC analysis.

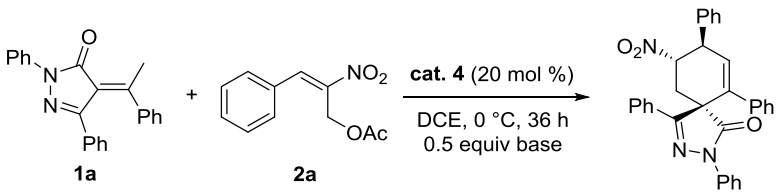




entry[a]	solvent	T/h	Yield (%)[f]	dr[g]	*ee* (%)[h]
1	THF	20	60	16:1	91
2	toulene	48	50	15:1	92
3	CH_2Cl_2	24	53	>20:1	94
4	CH_3CN	24	70	>20:1	84
5	dioxane	6	52	14:1	73
6	DCE	24	54	>20:1	94
7	$CHCl_3$	24	60	>20:1	78
8	mesitylene	48	56	16:1	92
9	CH_3OH	12	62	>20:1	35
10	ethyl acetate	24	60	17:1	87

11	acetone	24	62	>20:1	80
12	chlorobenzene	24	50	>20:1	84
13	CCl_4	24	52	>20:1	78
14[b]	DCE	36	70	>20:1	93
15[b,c]	DCE	36	62	>20:1	94
16[b,c,d]	DCE	36	72	>20:1	94
17[b,c,e]	DCE	36	80	>20:1	94

[a]Conditions: Reactions performed with **1a** (0.1 mmol), **2a** (0.1 mmol), **cat. 4** (20 mol %) in solvent (1 mL) at 15 °C. [b]0.5 equiv K_2CO_3 was added after the reaction had been stirred for 18 h. [c]under 0 °C. [d]0.5 mL DCE was used. [e]0.25 mL DCE was used. [f]Isolated yield. [g]Determined by ^{1}H NMR analysis of the crude products. [h]Determined by chiral-phase HPLC analysis.

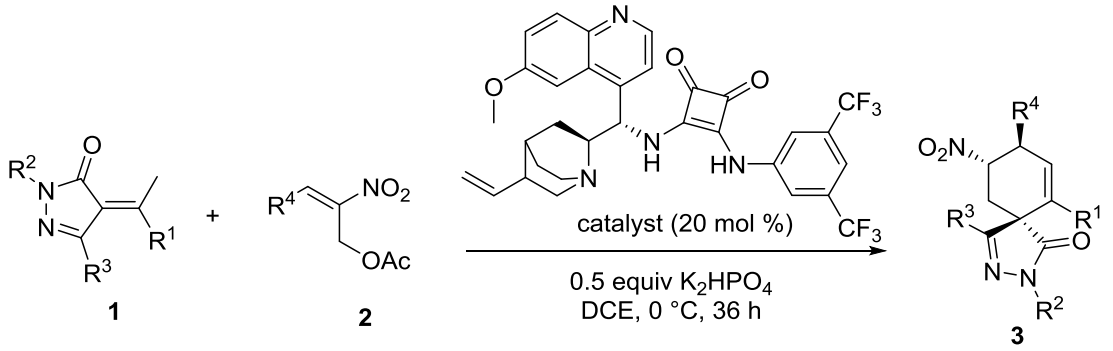


entry[a]	base	Yield (%)[d]	dr[e]	*ee* (%)[f]
1	K_2CO_3	80	>20:1	94
2	Na_2CO_3	76	>20:1	92
3	Cs_2CO_3	84	>20:1	76
4	K_3PO_4	82	>20:1	92
5	K_2HPO_4	86	>20:1	94
6	Na_2HPO_4	70	>20:1	88
7	triethylamine	70	>20:1	75
8[b]	K_2HPO_4	76	>20:1	92
9[c]	K_2HPO_4	80	>20:1	92
10		complex	-	-

[a]Conditions: Reactions performed with **1a** (0.1 mmol), **2a** (0.1 mmol), **cat. 4** (20 mol %) in 0.25 mL DCE at 0 °C, and 0.5 equiv base was added after the reation had had been stirred for 18 h. [b]10 mol% **cat. 4** was added. [c]15 mol% **cat. 4** was added. [d]Isolated yield. [e]Determined by ^{1}H NMR analysis of the crude products. [f]Determined by chiral-phase HPLC analysis.

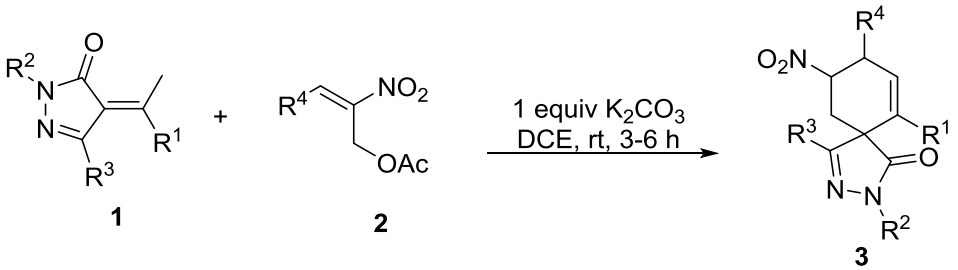
3. General Procedure and Spectral Data of Products

3.1 General Procedure for the Synthesis of Compounds 3



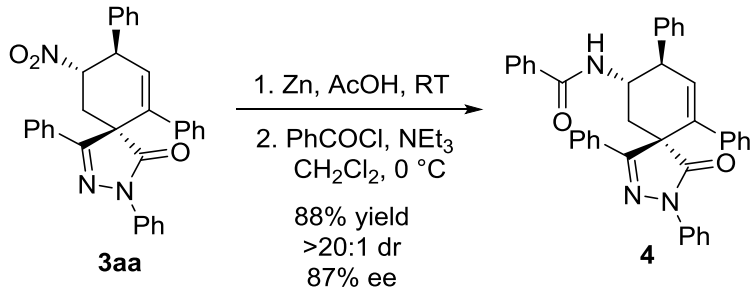
To a flame dried vessel were successively added α-arylidene pyrazolinone **1a** (33.8 mg, 0.1 mmol), (*E*)-2-nitroallylic acetates **2a** (22.1 mg, 0.1 mmol), catalyst (12.6 mg, 0.02 mmol) and dried DCE (0.25 mL) at 0 ^{o}C. After the reaction was stirred for 18 h at the same temperature, 0.5 equiv K_2HPO_4 (8.7 mg, 0.05 mmol) was added to the mixture. The reaction proceeded at 0 ^{o}C for another 18 h. When the reaction was completed, the solvent was evaporated under reduced pressure and the residue was purified by silica gel flash column chromatography (petroleumether/EtOAc = 20:1) to give the corresponding compound **3aa** (43 mg, 86% yield) as white solid. The procedures of the asymmetric synthesis of compounds **3ba-3ah** and the gram-scale synthesis of **3aa** (1.30 g, 87% yield) were in common.

3.2 General Procedure for the Synthesis of Racemic Products 3



To a flame dried vessel were successively added α-arylidene pyrazolinone **1a** (33.8 mg, 0.1 mmol), (*E*)-2-nitroallylic acetates **2a** (22.1 mg, 0.1 mmol), K_2CO_3 (13.8 mg, 0.1 mmol) and dried DCE (1 mL) at room temperature. When the reaction was completed (6 h), the solvent was evaporated under reduced pressure and the residue was purified by silica gel flash column chromatography (petroleumether/EtOAc = 20:1) to give the racemic product **3aa (**25 mg, 51% yield) as white solid. The procedures of racemic products **3ba-3ah** were in common.

3.3 General Procedure for the Synthesis of Compounds 4

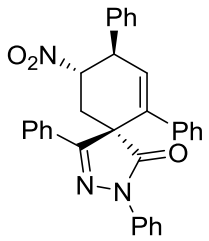


To a stirred solution of **3aa** (49.9 mg, 0.1 mmol) in 1 mL of acetic acid was added zinc powder (131 mg, 2 mmol) in one portion at room temperature. After the reaction proceeded at room temperature for 3 h, the mixture was filtered through a pad of Celite and concentrated under reduced pressure. The residue was dissolved in aqueous sodium carbonate (7.5 mL) and extracted twice (3 × 5 mL) with CH_2Cl_2. The combined organic phase was dried over anhydrous sodium sulfate and filtered. Removal of the solvent under the reduced pressure afforded the crude amine as a pale yellow solid, which was used directly in the next step without further purification.

To a solution of the crude amine and triethylamine (10.1 mg, 0.1 mmol) in 0.5 mL of dichloromethane was added benzoyl chloride (14.1 mg, 0.1 mmol) at 0 °C. The resulting mixture was stirred at the same temperature until the reaction was complete (5 h). The reaction mixture was purified directly by column chromatography (petroleumether/EtOAc = 8:1) on silica gel to afford compound **4** (50 mg, 88% yield).

3.4 Analytical Data of Compounds 3 and 4

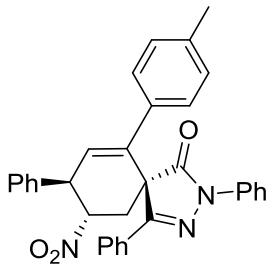
(5*R*, 8*R*, 9*S*)-9-nitro-2,4,6,8-tetraphenyl-2,3-diazaspiro[4.5]deca-3,6-dien-1-one (3aa)



White solid. 86% yield (43 mg). m. p.: 176–180 °C. $[\alpha]_D^{20}$ = 157 (*c* 1.0, CH_2Cl_2, 94% ee); IR (KBr): 698, 737, 758, 805, 1029, 1077, 1120, 1264, 1287, 1303, 1320, 1379, 1445, 1492, 1554, 1596, 1719, 2856, 2924, 2959, 3034, 3060, 3417 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.93-8.03 (m, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.51-7.63 (m, 3H), 7.27-7.44 (m, 7H), 7.18-7.25 (m, 6H), 6.40 (d, *J* = 2.0 Hz, 1H), 4.70-4.81 (m, 1H), 4.46 (dd, *J* = 10.4 Hz, *J* = 2.0 Hz, 1H), 3.09 (t, *J* = 13.2 Hz, 1H), 2.49 (dd, *J* = 13.2 Hz, *J* = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.0, 160.3, 138.8, 137.8, 137.4, 134.0, 133.7, 131.6, 131.3, 129.2, 129.0, 128.7, 128.2, 128.0, 127.7, 126.6, 125.9, 119.4, 84.4, 58.8, 46.6, 37.0. The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane:*i*-PrOH

= 80:20), 1 mL/min; minor enantiomer t_R = 14.13 min, major enantiomer t_R = 35.19 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{32}H_{26}N_3O_3]$: 500.1969, found: 500.1960.

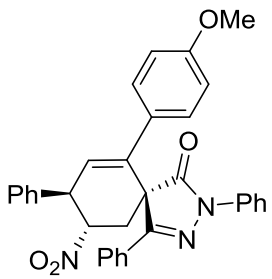
(5*R*, 8*R*, 9*S*)-9-nitro-2,4,8-triphenyl-6-(p-tolyl)-2,3-diazaspiro[4.5]deca-3,6-dien-1-one (3ba)



3ba

White solid. 90% yield (46 mg). m. p.: 100–108 °C. $[\alpha]_D^{20}$ = 141 (*c* 1.0, CH_2Cl_2, 93% ee); IR (KBr): 511, 699, 738, 759, 805, 827, 873, 1029, 1078, 1120, 1184, 1264, 1287, 1303, 1320, 1378, 1447, 1492, 1512, 1555, 1596, 1719, 2855, 2925, 2961, 3031, 3061, 3419 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.92-8.02 (m, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.49-7.62 (m, 3H), 7.27-7.44 (m, 5H), 7.15-7.24 (m, 5H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.38 (d, *J* = 2.0 Hz, 1H), 4.67-4.79 (m, 1H), 4.44 (dd, *J* = 10.4 Hz, *J* = 2.0 Hz, 1H), 3.08 (t, *J* = 13.2 Hz, 1H), 2.48 (dd, *J* = 13.2 Hz, *J* = 3.2 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.2, 160.5, 138.9, 138.6, 137.5, 135.0, 133.5, 133.4, 131.6, 131.3, 129.6, 129.2, 128.9, 128.2, 128.0, 127.7, 126.3, 125.8, 119.4, 84.5, 58.9, 46.7, 37.2, 21.0. The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane:*i*-PrOH = 80:20), 1 mL/min; minor enantiomer t_R = 16.87 min, major enantiomer t_R = 33.68 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{33}H_{28}N_3O_3]$: 514.2125, found: 514.2109.

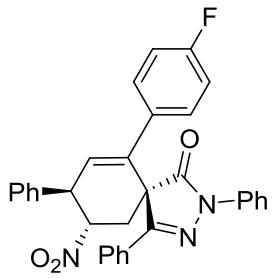
(5*R*, 8*R*, 9*S*)-6-(4-methoxyphenyl)-9-nitro-2,4,8-triphenyl-2,3-diazaspiro[4.5]deca-3,6-dien-1-one (3ca)



3ca

White solid. 90% yield (48 mg). m. p.: 160–166 °C. $[\alpha]_D^{20}$ = 141 (*c* 1.0, CH_2Cl_2, 92% ee); IR (KBr): 698, 738, 759, 779, 802, 835, 1030, 1078, 1191, 1182, 1259, 1288, 1302, 1378, 1492, 1512, 1554, 1597, 1606, 1719, 2847, 2926, 2960, 3060, 3406 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.91-8.01 (m, 2H), 7.82-7.90 (m, 2H), 7.51-7.61 (m, 3H), 7.27-7.44 (m, 5H), 7.15-7.27 (m, 5H), 6.69-6.79 (m, 2H), 6.32 (d, *J* = 2.4 Hz, 1H), 4.67-4.79 (m, 1H), 4.43 (dd, *J* = 10.4 Hz, *J* = 2.4 Hz, 1H), 3.68 (s, 3H), 3.07 (t, *J* = 13.2 Hz, 1H), 2.46 (dd, *J* = 13.2 Hz, *J* = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.2, 160.5, 159.8, 139.0, 137.5, 133.1, 132.9, 131.6, 131.3, 130.2, 129.2, 128.9, 128.2, 128.0, 127.7, 127.7, 125.8, 119.3, 114.3, 84.5, 58.9, 55.1, 46.7, 37.1. The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane:*i*-PrOH = 80:20), 1 mL/min; minor enantiomer t_R = 24.40 min, major enantiomer t_R = 43.20 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{33}H_{28}N_3O_4]$: 530.2074, found: 530.2067.

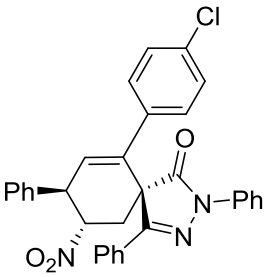
(5*R*, 8*R*, 9*S*)-6-(4-fluorophenyl)-9-nitro-2,4,8-triphenyl-2,3-diazaspiro[4.5]deca-3,6-dien-1-one (3da)



3da

White solid. 79% yield (41 mg). m. p.: 84-90 °C. $[\alpha]_D^{20}$ = 49 (*c* 1.0, CH_2Cl_2, 93% ee); IR (KBr): 515, 540, 662, 699, 738, 759, 840, 909, 940, 1008, 1029, 1122, 1163, 1185, 1236, 1287, 1265, 1303, 1320, 1378, 1447, 1493, 1509, 1555, 1597, 1718, 2854, 2926, 2956, 3032, 3063, 3420 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.90-8.02 (m, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.51-7.65 (m, 3H), 7.29-7.45 (m, 5H), 7.17-7.29 (m, 5H), 6.91 (t, *J* = 8.0 Hz, 2H), 6.34 (d, *J* = 2.0 Hz, 1H), 4.69-4.85 (m, 1H), 4.45 (dd, *J* = 10.4 Hz, *J* = 2.0 Hz, 1H), 3.08 (t, *J* = 13.2 Hz, 1H), 2.49 (dd, *J* = 13.2 Hz, *J* = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.9, 162.7 (J_{C-F} = 250 Hz), 160.0, 138.6, 137.3, 134.2, 133.9, 133.8, 132.8, 131.4, 131.4, 129.3, 129.0, 128.6, 125.5, 128.3, 127.9, 127.7, 126.0, 119.3, 116.0, 115.8, 84.3, 58.8, 46.5, 36.7. The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane:*i*-PrOH = 80:20), 1 mL/min; minor enantiomer t_R = 14.15 min, major enantiomer t_R = 21.23 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{32}H_{25}FN_3O_3]$: 518.1874, found: 518.1865.

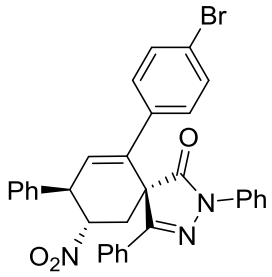
(5*R*, 8*R*, 9*S*)-6-(4-chlorophenyl)-9-nitro-2,4,8-triphenyl-2,3-diazaspiro[4.5]deca-3,6-dien-1-one (3ea)



3ea

White solid. 78% yield (42 mg). m. p.: 184–188 °C. $[\alpha]_D^{20}$ = 116 (*c* 1.0, CH_2Cl_2, 91% ee); IR (KBr): 507, 662, 698, 739, 761, 834, 1014, 1029, 1.96, 1184, 1264, 1288, 1303, 1320, 1378, 1446, 1493, 1555, 1596, 1720, 2855, 2926, 2961, 3032, 3063, 3419 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.90-8.00 (m, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.50-7.62 (m, 3H), 7.28-7.44 (m, 5H), 7.14-7.26 (m, 7H), 6.37 (d, *J* = 2.0 Hz, 1H), 4.69-4.83 (m, 1H), 4.44 (dd, *J* = 10.4 Hz, *J* = 2.0 Hz, 1H), 3.07 (t, *J* = 13.2 Hz, 1H), 2.49 (dd, *J* = 13.2 Hz, *J* = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.8, 160.0, 138.5, 137.3, 136.2, 134.7, 134.5, 132.6, 131.4, 131.3, 129.2, 129.1, 129.0, 128.3, 127.9, 127.8, 127.7, 126.0 119.2, 84.2, 58.6, 46.5, 36.8. The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane:*i*-PrOH = 80:20), 1 mL/min; minor enantiomer t_R = 17.80 min, major enantiomer t_R = 28.86 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{32}H_{25}ClN_3O_3]$: 534.1579, found: 534.1570.

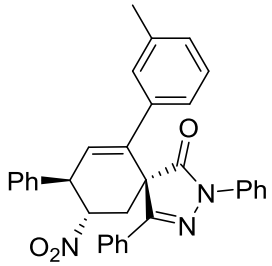
(5*R*, 8*R*, 9*S*)-6-(4-bromophenyl)-9-nitro-2,4,8-triphenyl-2,3-diazaspiro[4.5]deca-3,6-dien-1-one (3fa)



3fa

White solid. 80% yield (46 mg). m. p.: 194–198 °C. $[\alpha]_D^{20}$ = 115 (*c* 1.0, CH_2Cl_2, 91% ee); IR (KBr): 507, 662, 699, 738, 760, 802, 832, 909, 1009, 1029, 1078, 1121, 1184, 1264, 1288, 1303, 1320, 1378, 1446, 1491, 1555, 1596, 1719, 2854, 2926, 2961, 3032, 3063, 3416 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.90-8.00 (m, 2H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.51-7.62 (m, 3H), 7.28-7.44 (m, 7H), 7.18-7.27 (m, 3H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.38 (d, *J* = 2.0 Hz, 1H), 4.70-4.81 (m, 1H), 4.44 (dd, *J* = 10.4 Hz, *J* = 2.0 Hz, 1H), 3.06 (t, *J* = 12.8 Hz, 1H), 2.49 (dd, *J* = 12.8 Hz, *J* = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.8, 160.0, 138.5, 137.3, 136.7, 134.6, 132.7, 132.1, 131.5, 131.4, 129.3, 129.0, 128.3, 128.2, 127.9, 127.7, 126.0, 126.0 122.9, 84.2, 58.6, 46.6, 36.9. The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane:*i*-PrOH = 80:20), 1 mL/min; minor enantiomer t_R = 18.91 min, major enantiomer t_R = 33.59 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{32}H_{25}BrN_3O_3]$: 578.1074, found: 578.1061.

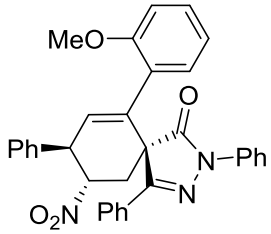
(5R, 8R, 9S)-9-nitro-2,4,8-triphenyl-6-(m-tolyl)-2,3-diazaspiro[4.5]deca-3,6-dien-1-one (3ga)



3ga

White solid. 96% yield (49 mg). m. p.: 162–166 °C. $[\alpha]_D^{20}$ = 128 (*c* 1.0, CH_2Cl_2, 95% ee); IR (KBr): 700, 738, 758, 774, 789, 805, 822, 865, 1029, 1120, 1183, 1264, 1286, 1303, 1320, 1379, 1446, 1492, 1555, 1596, 1719, 2855, 2924, 2959, 3032, 3060, 3419 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.92-7.98 (m, 2H), 7.79-7.87 (m, 2H), 7.50-7.60 (m, 3H), 7.26-7.43 (m, 5H), 7.18-7.24 (m, 3H), 7.14 (s, 1H), 7.06-7.10 (m, 2H), 7.00-7.05 (m, 1H), 6.40 (d, *J* = 2.4 Hz, 1H), 4.66-4.78 (m, 1H), 4.43 (dd, *J* = 10.4 Hz, *J* = 2.4 Hz, 1H), 3.07 (t, *J* = 12.8 Hz, 1H), 2.47 (dd, *J* = 12.8 Hz, *J* = 3.6 Hz, 1H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.1, 160.6, 138.8, 138.6, 137.7, 137.4, 133.7, 133.5, 131.5, 131.2, 129.4, 129.1, 128.9, 128.7, 128.2, 128.0, 127.7, 127.4, 125.9, 123.1, 119.4, 84.4, 58.8, 46.6, 37.1, 21.4. The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane:*i*-PrOH = 80:20), 1 mL/min; minor enantiomer t_R = 10.62 min, major enantiomer t_R = 24.68 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{33}H_{28}N_3O_3]$: 514.2125, found: 514.2109.

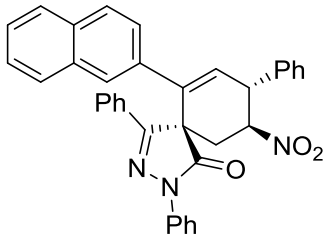
(5R, 8R, 9S)-6-(2-methoxyphenyl)-9-nitro-2,4,8-triphenyl-2,3-diazaspiro[4.5]deca-3,6-dien-1-one (3ha)



3ha

White solid. 91% yield (48 mg). m. p.: 190-192 ^{o}C. $[\alpha]_D^{20}$ = 110 (*c* 1.0, CH_2Cl_2, 93% ee); IR (KBr): 704, 741, 803, 863, 1010, 1029, 1079, 1098, 1263, 1379, 1422, 1447, 1492, 1555, 1579, 1597, 1720, 2854, 2927, 2962, 3054, 3409 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91-8.00 (m, 2H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.50-7.61 (m, 3H), 7.27-7.44 (m, 5H), 7.18-7.26 (m, 3H), 7.12 (t, *J* = 8.0 Hz,1H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.85 (t, *J* = 2.0 Hz,1H), 6.77 (dd, *J* = 8.4 Hz, *J* = 2.0 Hz, 1H), 6.43 (d, J = 2.0 Hz, 1H), 4.66-4.78 (m, 1H), 4.45 (dd, *J* = 10.4 Hz, *J* = 2.0 Hz, 1H), 3.60 (s, 3H), 3.08 (t, *J* = 13.2 Hz, 1H), 2.48 (dd, *J* = 13.2 Hz, *J* = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.1, 160.5, 159.8, 139.2, 138.7, 137.5, 134.0, 133.4, 131.5, 131.3, 130.0, 129.2, 128.9, 128.2, 128.0, 127.7, 125.9, 119.3, 118.6, 114.5, 111.9, 84.4, 58.8, 55.1, 46.6, 37.1. The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane:*i*-PrOH = 80:20), 1 mL/min; minor enantiomer t_R = 13.34 min, major enantiomer t_R = 34.75 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{33}H_{28}N_3O_4]$: 530.2074, found: 530.2072.

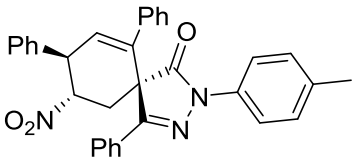
(5R, 8R, 9S)-6-(naphthalen-2-yl)-9-nitro-2,4,8-triphenyl-2,3-diazaspiro[4.5]deca-3,6-dien -1-one (3ia)



3ia

White solid. 83% yield (46 mg). m. p.: 176-184 ^{o}C. $[\alpha]_D^{20}$ = 113 (*c* 1.0, CH_2Cl_2, 90% ee); IR (KBr): 702, 740, 823, 859, 1009, 1030, 1119, 1184, 1226, 1265, 1303, 1320, 1378, 1447, 1493, 1556, 1596, 1719, 2927, 2962, 3057 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94-8.03 (m, 2H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.74 (br, 1H), 7.65-7.72 (m, 2H), 7.58-7.64 (m, 1H), 7.50-7.57 (m, 3H), 7.44 (dd, *J* = 8.4 Hz, *J* = 2.0 Hz, 1H), 7.26-7.41 (m, 7H), 7.14-7.25 (m, 3H), 6.55 (d, J = 2.0 Hz, 1H), 4.69-4.83 (m, 1H), 4.50 (dd, *J* = 10.4 Hz, *J* = 2.0 Hz, 1H), 3.13 (t, *J* = 13.2 Hz, 1H), 2.52 (dd, *J* = 13.2 Hz, *J* = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.2, 160.7, 138.8, 137.4, 135.1, 134.4, 133.2, 133.0, 131.5, 131.3, 129.2, 128.9, 128.8, 128.3, 128.0, 127.7, 127.4, 126.5, 125.9, 125.5, 124.2, 119.4, 84.4, 58.9, 46.8, 37.3. The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane:*i*-PrOH = 80:20), 1 mL/min; minor enantiomer t_R = 27.77 min, major enantiomer t_R = 49.93 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{36}H_{28}N_3O_3]$: 550.2125, found: 550.2122.

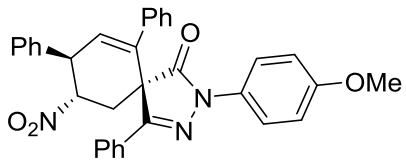
(5R, 8R, 9S)-9-nitro-4,6,8-triphenyl-2-(p-tolyl)-2,3-diazaspiro[4.5]deca-3,6-dien-1-one (3ja)



3ja

White solid. 92% yield (47 mg). m. p.: 136–142 ^{o}C. $[\alpha]_D^{20}$ = 89 (*c* 1.0, CH_2Cl_2, 95% ee); IR (KBr): 702, 739, 779, 819, 873, 1009, 1029, 1077, 1103, 1126, 1265, 1378, 1446, 1495, 1512, 1556, 1718, 2855, 2926, 2960, 3034, 3056, 3408 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 7.2 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.49-7.60 (m, 3H), 7.26-7.38 (m, 5H), 7.13-7.25 (m, 7H), 6.38 (d, *J* = 1.6 Hz, 1H), 4.69-4.81 (m, 1H), 4.45 (dd, *J* = 10.4 Hz, *J* = 1.6 Hz, 1H), 3.08 (t, *J* = 13.6 Hz, 1H), 2.47 (dd, *J* = 13.6 Hz, *J* = 3.2 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.9, 160.1, 138.8, 137.8, 135.7, 135.0, 133.9, 133.7, 131.6, 131.2, 129.4, 129.2, 128.9, 128.6, 128.2, 128.0, 127.7, 126.5, 119.4, 84.5, 58.7, 46.6, 36.9, 21.0. The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane:*i*-PrOH = 80:20), 1 mL/min; minor enantiomer t_R = 18.29 min, major enantiomer t_R = 37.00 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{33}H_{28}N_3O_3]$: 514.2125, found: 514.2111.

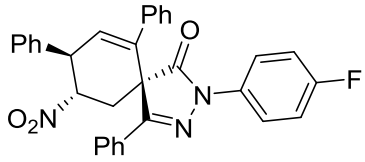
(5R, 8R, 9S)-2-(4-methoxyphenyl)-9-nitro-4,6,8-triphenyl-2,3-diazaspiro[4.5]deca-3,6-dien-1-one (3ka)



3ka

White solid. 92% yield (49 mg). m. p.: 170–174 ^{o}C. $[\alpha]_D^{20}$ = 173 (*c* 1.0, CH_2Cl_2, 93% ee); IR (KBr): 702, 741, 804, 833, 874, 1030, 1078, 1102, 1122, 1265, 1299, 1376, 1444, 1511, 1556, 1717, 2854, 2928, 2962, 3056, 3403 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89-8.02 (m, 2H), 7.62-7.71 (m, 2H), 7.50-7.60 (m, 3H), 7.27-7.39 (m, 5H), 7.20-7.26 (m, 5H), 6.83-6.96 (m, 2H), 6.38 (d, *J* = 2.4 Hz, 1H), 4.70-4.80 (m, 1H), 4.45 (dd, *J* = 10.4 Hz, *J* = 2.4 Hz, 1H), 3.79 (s, 3H), 3.08 (t, *J* = 13.2 Hz, 1H), 2.48 (dd, *J* = 13.2 Hz, *J* = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.7, 160.1, 157.6, 138.8, 137.8, 133.9, 133.7, 131.6, 131.2, 130.6, 129.2, 128.9, 128.6, 128.2, 127.9, 127.7, 126.6, 121.3, 114.0, 84.4, 58.5, 55.4, 46.6, 36.8. The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane:*i*-PrOH = 80:20), 1 mL/min; minor enantiomer t_R = 23.96 min, major enantiomer t_R = 68.16 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{33}H_{28}N_3O_4]$: 530.2074, found: 530.2072.

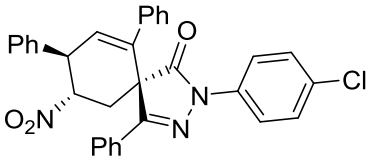
(5R, 8R, 9S)-2-(4-fluorophenyl)-9-nitro-4,6,8-triphenyl-2,3-diazaspiro[4.5]deca-3,6-dien-1-one (3la)



3la

White solid. 87% yield (45 mg). m. p.: 124–132 ^{o}C. $[\alpha]_D^{20}$ = 158 (*c* 1.0, CH_2Cl_2, 92% ee); IR (KBr): 700, 739, 759, 837, 874, 1029, 1078, 1120, 1156, 1228, 1265, 1377, 1446, 1508, 1555, 1719, 2854, 2926, 2959, 3032, 3060 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87-8.04 (m, 2H), 7.69-7.84 (m, 2H), 7.49-7.66 (m, 3H), 7.16-7.41 (m, 10H), 6.99-7.13 (m, 2H), 6.40 (d, *J* = 2.0 Hz, 1H), 4.64-4.84 (m, 1H), 4.46 (dd, *J* = 10.4 Hz, *J* = 2.0 Hz, 1H), 3.08 (t, *J* = 13.6 Hz, 1H), 2.49 (dd, *J* = 13.6 Hz, *J* = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.9, 160.5, 160.4 ($J_{C\text{-}F}$ = 250 Hz), 138.7, 137.7, 134.1, 133.5, 131.4, 129.2, 129.2, 128.9, 128.7, 128.3, 128.0, 127.7, 126.5, 121.2, 121.2, 115.8, 115.6, 84.4, 58.7, 46.6, 36.8. The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane:*i*-PrOH = 80:20), 1 mL/min; minor enantiomer t_R = 12.90 min, major enantiomer t_R = 43.57 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{32}H_{25}FN_3O_3]$: 518.1874, found: 518.1867.

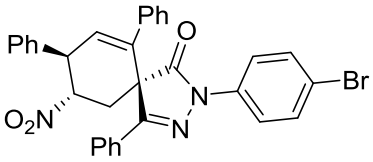
(5R, 8R, 9S)-2-(4-chlorophenyl)-9-nitro-4,6,8-triphenyl-2,3-diazaspiro[4.5]deca-3,6-dien-1-one (3ma)



3ma

White solid. 80% yield (43 mg). m. p.: 158–162 ^{o}C. $[\alpha]_D^{20}$ = 173 (*c* 1.0, CH_2Cl_2, 93% ee); IR (KBr): 510, 700, 737, 760, 830, 874, 941, 1011, 1029, 1093, 1124, 1184, 1264, 1303, 1378, 1445, 1492, 1555, 1720, 2854, 2926, 2963, 3032, 3060, 3424 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91-8.02 (m, 2H), 7.75-7.86 (m, 2H), 7.51-7.62 (m, 3H), 7.24-7.38 (m, 7H), 7.17-7.24 (m, 5H), 6.39 (d, *J* = 2.0 Hz, 1H), 4.67-4.82 (m, 1H), 4.45 (dd, *J* = 10.4 Hz, *J* = 2.0 Hz, 1H), 3.06 (t, *J* = 13.6 Hz, 1H), 2.48 (dd, *J* = 13.2 Hz, *J* = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.9, 160.6, 138.6, 137.7, 135.9, 134.1, 133.4, 131.4, 131.3, 131.0, 129.2, 129.2, 128.9, 128.9, 128.7, 128.2, 128.0, 127.7, 126.5, 120.3, 84.3, 58.8, 46.5, 36.8. The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane:*i*-PrOH = 80:20), 1 mL/min; minor enantiomer t_R = 14.74 min, major enantiomer t_R = 35.10 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{32}H_{25}ClN_3O_3]$: 534.1579, found: 534.1566.

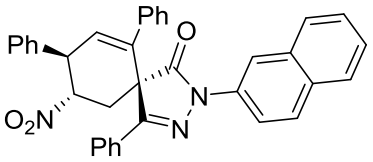
(5R, 8R, 9S)-2-(4-bromophenyl)-9-nitro-4,6,8-triphenyl-2,3-diazaspiro[4.5]deca-3,6-dien-1-one (3na)



3na

White solid. 81% yield (47 mg). m. p.: 168–170 ^{o}C. $[\alpha]_D^{20}$ = 190 (*c* 1.0, CH_2Cl_2, 93% ee); IR (KBr): 510, 699, 738, 760, 828, 942, 1010, 1030, 1074, 1123, 1185, 1265, 1303, 1320, 1378, 1446, 1490, 1554, 1721, 2854, 2926, 2962, 3032, 3059, 3429 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 6.4 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.52-7.64 (m, 3H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.18-7.39 (m, 10H), 6.40 (d, *J* = 2.0 Hz, 1H), 4.68-4.81 (m, 1H), 4.45 (dd, *J* = 10.4 Hz, *J* = 2.0 Hz, 1H), 3.07 (t, *J* = 12.8 Hz, 1H), 2.48 (dd, *J* = 12.8 Hz, *J* = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.9, 160.5, 138.6, 137.6, 136.4, 134.1, 133.3, 131.8, 131.4, 131.2, 129.2, 129.1, 128.9, 128.6, 128.2, 127.9, 127.6, 126.4, 120.5, 118.7, 84.2, 58.8, 46.5, 36.7. The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane:*i*-PrOH = 80:20), 1 mL/min; minor enantiomer t_R = 16.37 min, major enantiomer t_R = 37.10 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{32}H_{25}BrN_3O_3]$: 578.1074, found: 578.1057.

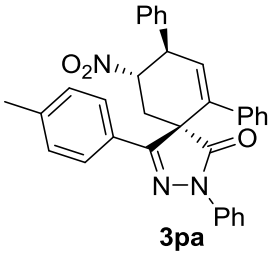
(5R, 8R, 9S)-2-(naphthalen-2-yl)-9-nitro-4,6,8-triphenyl-2,3-diazaspiro[4.5]deca-3,6-dien-1-one (3oa)



3oa

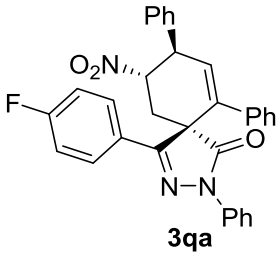
White solid. 80% yield (44 mg). m. p.: 150–157 ^{o}C. $[\alpha]_D^{20}$ = 105 (*c* 1.0, CH_2Cl_2, 90% ee); IR (KBr): 475, 701, 740, 779, 817, 859, 887, 1029, 1077, 1112, 1129, 1240, 1265, 1302, 1320, 1379, 1391, 1446, 1470, 1495, 1511, 1556, 1600, 1631, 1719, 2855, 2927, 2961, 2984, 3034, 3058, 3416 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (br, 1H), 7.95-8.07 (m, 3H), 7.74-7.89 (m, 3H), 7.50-7.64 (m, 3H), 7.38-7.50 (m, 2H), 7.26-7.38 (m, 5H), 7.16-7.25 (m, 5H), 6.41 (d, *J* = 2.0 Hz, 1H), 4.69-4.85 (m, 1H), 4.47 (dd, *J* = 10.2 Hz, *J* = 2.0 Hz, 1H), 3.12 (t, *J* = 12.8 Hz, 1H), 2.52 (dd, *J* = 12.8 Hz, *J* = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.2, 160.4, 138.7, 137.8, 135.0, 134.0, 133.6, 133.3, 131.5, 131.3, 131.3, 129.2, 129.2, 128.9, 128.8, 128.7, 128.2, 128.0, 127.7, 127.6, 126.6, 126.5, 125.7, 118.4, 116.7, 84.4, 58.9, 46.6, 37.0. The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane:*i*-PrOH = 80:20), 1 mL/min; minor enantiomer t_R = 19.53 min, major enantiomer t_R = 57.96 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{36}H_{28}N_3O_3]$: 550.2125, found: 550.2117.

(5R, 8R, 9S)-9-nitro-2,6,8-triphenyl-4-(p-tolyl)-2,3-diazaspiro[4.5]deca-3,6-dien-1-one (3pa)



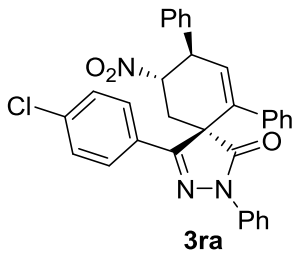
White solid. 92% yield (47 mg). m. p.: 184–188 ^{o}C. $[\alpha]_D^{20}$ = 167 (*c* 1.0, CH_2Cl_2, 94% ee); IR (KBr): 703, 739, 787, 824, 873, 1010, 1029, 1078, 1115, 1184, 1265, 1302, 1317, 1379, 1446, 1496, 1512, 1556, 1597, 1719, 2855, 2926, 2962, 3034, 3056, 3415 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.0 Hz, 2H), 7.78-7.85 (m, 2H), 7.26-7.42 (m, 9H), 7.17-7.26 (m, 6H), 6.38 (d, *J* = 2.0 Hz, 1H), 4.76-4.87 (m, 1H), 4.46 (dd, *J* = 10.2 Hz, *J* = 2.0 Hz, 1H), 3.08 (t, *J* = 13.2 Hz, 1H), 2.4-2.52 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.0, 160.2, 141.8, 138.8, 137.8, 137.4, 133.8, 133.8, 129.9, 129.2, 128.9, 128.8, 128.7, 128.6, 128.2, 127.8, 127.7, 126.6, 125.8, 119.3, 84.5, 58.8, 46.6, 36.9, 21.5. The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane:*i*-PrOH = 80:20), 1 mL/min; minor enantiomer t_R = 16.58 min, major enantiomer t_R = 24.51 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{33}H_{28}N_3O_3]$: 514.2125, found: 514.2114.

(5R, 8R, 9S)-4-(4-fluorophenyl)-9-nitro-2,6,8-triphenyl-2,3-diazaspiro[4.5]deca-3,6-dien -1-one (3qa)



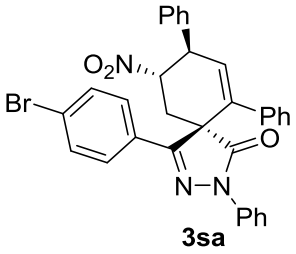
White solid. 76% yield (39 mg). m. p.: 144–156 ^{o}C. $[\alpha]_D^{20}$ = 246 (*c* 1.0, CH_2Cl_2, 94% ee); IR (KBr): 704, 741, 766, 844, 874, 1015, 1030, 1078, 1099, 1120, 1159, 1239, 1265, 1311, 1379, 1447, 1498, 1511, 1557, 1598, 1720, 2854, 2927, 2961, 3056, 3403 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94-8.04 (m, 2H), 7.81 (d, *J* = 7.6 Hz, 2H), 7.30-7.42 (m, 5H), 7.16-7.29 (m, 10H), 6.41 (d, *J* = 2.4 Hz, 1H), 4.69-4.79 (m, 1H), 4.47 (dd, *J* = 10.4 Hz, *J* = 2.0 Hz, 1H), 3.08 (t, *J* = 12.8 Hz, 1H), 2.47 (dd, *J* = 12.8 Hz, *J* = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.9, 164.3 (J_{C-F} = 250 Hz), 159.1, 138.6, 137.6, 137.3, 134.1, 133.5, 130.0, 129.9, 129.2, 128.9, 128.9, 128.7, 128.3, 127.7, 127.7, 127.6, 126.4, 125.9, 119.3, 116.6, 116.4, 84.4, 58.6, 46.4, 36.9. The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane:*i*-PrOH = 80:20), 1 mL/min; minor enantiomer t_R = 21.06 min, major enantiomer t_R = 26.73 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{32}H_{25}FN_3O_3]$: 518.1874, found: 518.1863.

(5R, 8R, 9S)-4-(4-chlorophenyl)-9-nitro-2,6,8-triphenyl-2,3-diazaspiro[4.5]deca-3,6-dien-1-one (3ra)



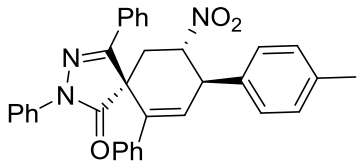
White solid. 74% yield (39 mg). m. p.: 88-94 ^{o}C. $[\alpha]_D^{20}$ = 306 (*c* 1.0, CH_2Cl_2, 94% ee); IR (KBr): 502, 700, 738, 758, 805, 835, 874, 909, 940, 1016, 1030, 1094, 1122, 1183, 1263, 1296, 1310, 1379, 1445, 1492, 1555, 1720, 2853, 2925, 2962, 3033, 3062, 3422 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89-7.97 (m, 2H), 7.76-7.84 (m, 2H), 7.48-7.56 (m, 2H), 7.31-7.44 (m, 5H), 7.17-7.25 (m, 8H), 6.41 (d, *J* = 2.4 Hz, 1H), 4.74-4.83 (m, 1H), 4.50 (dd, *J* = 10.4 Hz, *J* = 2.4 Hz, 1H), 3.10 (t, *J* = 13.2 Hz, 1H), 2.50 (dd, *J* = 13.2 Hz, *J* = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.9, 158.9, 138.6, 137.5, 137.5, 137.3, 134.0, 133.7, 129.9, 129.5, 129.3, 129.0, 128.9, 128.7, 128.3, 127.6, 126.4, 126.0, 119.3, 84.4, 58.5, 46.4, 36.8. The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane:*i*-PrOH = 80:20), 1 mL/min; minor enantiomer t_R = 18.79 min, major enantiomer t_R = 26.38 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{32}H_{25}ClN_3O_3]$: 534.1579, found: 534.1566.

(5R, 8R, 9S)-4-(4-bromophenyl)-9-nitro-2,6,8-triphenyl-2,3-diazaspiro[4.5]deca-3,6-dien-1-one (3sa)



White solid. 72% yield (42 mg). m. p.: 190-192 ^{o}C. $[\alpha]_D^{20}$ = 129 (*c* 1.0, CH_2Cl_2, 93% ee); IR (KBr): 508, 537, 600, 701, 737, 758, 804, 873, 909, 939, 1013, 1023, 1073, 1099, 1182, 1263, 1296, 1310, 1377, 1445, 1491, 1555, 1596, 1720, 2852, 2925, 2962, 3032, 3062, 3422 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84-7.90 (m, 2H), 7.76-7.83 (m, 2H), 7.64-7.71 (m, 2H), 7.31-7.44 (m, 5H), 7.17-7.25 (m, 8H), 6.41 (d, *J* = 2.4 Hz, 1H), 4.71-4.85 (m, 1H), 4.50 (dd, *J* = 10.0 Hz, *J* = 2.4 Hz, 1H), 3.10 (t, *J* = 13.2 Hz, 1H), 2.50 (dd, *J* = 13.2 Hz, *J* = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.9, 158.9, 138.6, 137.5, 137.2, 134.0, 133.7, 132.4, 130.3, 129.3, 129.2, 128.9, 128.7, 128.3, 127.6, 126.5, 126.0, 125.9, 119.4, 84.4, 58.4, 46.4, 36.7. The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane:*i*-PrOH = 80:20), 1 mL/min; minor enantiomer t_R = 17.51 min, major enantiomer t_R = 28.41 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{32}H_{25}BrN_3O_3]$: 578.1074, found: 578.1059.

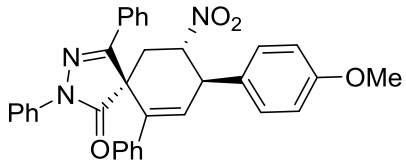
(5R, 8R, 9S)-9-nitro-2,4,6-triphenyl-8-(p-tolyl)-2,3-diazaspiro[4.5]deca-3,6-dien-1-one (3ab)



3ab

White solid. 90% yield (46 mg). m. p.: 80-88 ^{o}C. $[\alpha]_D^{20}$ = 312 (*c* 1.0, CH_2Cl_2, 92% ee); IR (KBr): 704, 742, 817, 875, 1010, 1028, 1052, 1068, 1078, 1120, 1146, 1184, 1264, 1303, 1320, 1379, 1446, 1492, 1514, 1556, 1720, 2855, 2926, 2961, 3053, 3414 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91-8.05 (m, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.47-7.61 (m, 3H), 7.25-7.33 (m, 2H), 7.19-7.25 (m, 4H), 7.05-7.17 (m, 4H), 6.39 (d, *J* = 2.0 Hz, 1H), 4.63-4.80 (m, 1H), 4.41 (dd, *J* = 10.0 Hz, *J* = 2.0 Hz, 1H), 3.07 (t, *J* = 13.2 Hz, 1H), 2.46 (dd, *J* = 13.2 Hz, *J* = 3.2 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.0, 160.3, 138.0, 137.8, 137.4, 135.7, 134.2, 133.4, 131.5, 131.3, 129.8, 129.2, 128.9, 128.6, 128.0, 127.5, 126.5, 125.8, 119.3, 84.5, 58.8, 46.3, 37.0, 21.0. The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane:*i*-PrOH = 80:20), 1 mL/min; minor enantiomer t_R = 12.76 min, major enantiomer t_R = 20.43 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{33}H_{28}N_3O_3]$: 514.2125, found: 514.2109.

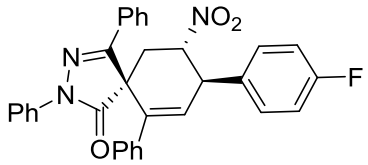
(5R, 8R, 9S)-8-(4-methoxyphenyl)-9-nitro-2,4,6-triphenyl-2,3-diazaspiro[4.5]deca-3,6-dien-1-one (3ac)



3ac

White solid. 94% yield (50 mg). m. p.: 88–94 ^{o}C. $[\alpha]_D^{20}$ = 129 (*c* 1.0, CH_2Cl_2, 92% ee); IR (KBr): 704, 742, 808, 833, 875, 1010, 1031, 1068, 1077, 1151, 1179, 1262, 1304, 1321, 1379, 1445, 1460, 1493, 1513, 1555, 1596, 1612, 1720, 2854, 2927, 2961, 3054, 3416 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 6.8 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.49-7.61 (m, 3H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.26-7.33 (m, 2H), 7.16-7.25 (m, 4H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.38 (s, 1H), 4.62-4.78 (m, 1H), 4.39 (d, *J* = 10.0 Hz, 1H), 3.76 (s, 3H), 3.06 (t, *J* = 12.8 Hz, 1H), 2.45 (dd, *J* = 12.8 Hz, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.0, 160.2, 159.3, 137.8, 137.3, 134.3, 133.3, 131.5, 131.2, 130.5, 129.1, 128.8, 128.7, 128.5, 127.9, 126.4, 125.8, 119.3, 114.4, 84.6, 58.7, 55.2, 46.9, 36.9. The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane:*i*-PrOH = 80:20), 1 mL/min; minor enantiomer t_R = 22.82 min, major enantiomer t_R = 33.41 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{33}H_{28}N_3O_4]$: 530.2074, found: 530.2070.

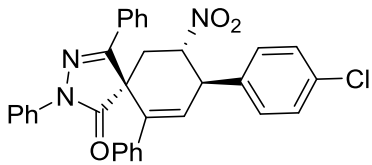
(5R, 8R, 9S)-8-(4-fluorophenyl)-9-nitro-2,4,6-triphenyl-2,3-diazaspiro[4.5]deca-3,6-dien-1-one (3ad)



3ad

White solid. 71% yield (37 mg). m. p.: 92-98 ^{o}C. $[\alpha]_D^{20}$ = 152 (*c* 1.0, CH_2Cl_2, 93% ee); IR (KBr): 704, 741, 806, 838, 875, 1012, 1028, 1079, 1100, 1119, 1160, 1227, 1264, 1303, 1321, 1378, 1445, 1501, 1510, 1555, 1596, 1716, 2855, 2927, 2962, 3056, 3410 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89-8.01 (m, 2H), 7.81 (d, *J* = 7.6 Hz, 2H), 7.48-7.64 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.26-7.34 (m, 2H), 7.13-7.26 (m, 6H), 7.03 (t, *J* = 8.4 Hz, 2H), 6.35 (d, *J* = 2.0 Hz, 1H), 4.62-4.73 (m, 1H), 4.44 (dd, *J* = 10.4 Hz, *J* = 2.0 Hz, 1H), 3.07 (t, *J* = 12.8 Hz, 1H), 2.48 (dd, *J* = 13.2 Hz, *J* = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.9, 162.4 (J_{C-F} = 250 Hz), 160.2, 137.7, 137.4, 134.6, 134.5, 133.9, 133.6, 131.5, 131.4, 129.4, 129.4, 129.2, 129.0, 128.9, 128.8, 128.0, 126.5, 125.9, 119.4, 116.3, 116.1, 84.5, 58.8, 45.9, 37.0. The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane:*i*-PrOH = 80:20), 1 mL/min; minor enantiomer t_R = 24.96 min, major enantiomer t_R = 48.58 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{32}H_{25}FN_3O_3]$: 518.1874, found: 518.1864.

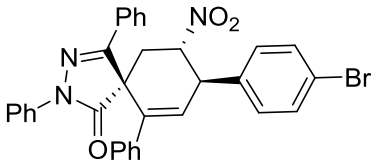
(5R, 8R, 9S)-8-(4-chlorophenyl)-9-nitro-2,4,6-triphenyl-2,3-diazaspiro[4.5]deca-3,6-dien-1-one (3ae)



3ae

White solid. 80% yield (43 mg). m. p.: 101-104 ^{o}C. $[\alpha]_D^{20}$ = 198 (*c* 1.0, CH_2Cl_2, 92% ee); IR (KBr): 508, 537, 701, 739, 762, 810, 831, 874, 909, 938, 1015, 1028, 1093, 1121, 1185, 1265, 1286, 1304, 1321, 1379, 1446, 1493, 1556, 1296, 1719, 2854, 2927, 2962, 3056, 3419 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 6.8 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.47-7.63 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.26-7.34 (m, 4H), 7.17-7.26 (m, 4H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.33 (d, *J* = 1.6 Hz, 1H), 4.61-4.73 (m, 1H), 4.42 (dd, *J* = 10.0 Hz, *J* = 1.6 Hz, 1H), 3.06 (t, *J* = 13.2 Hz, 1H), 2.48 (dd, *J* = 13.2 Hz, *J* = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.8, 160.2, 137.6, 137.3, 137.2, 134.2, 134.1, 133.2, 131.5, 131.4, 129.4, 129.2, 129.1, 129.0, 128.9, 128.8, 128.0, 126.5, 125.9, 119.3, 84.3, 58.7, 46.0, 36.9. The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane:*i*-PrOH = 80:20), 1 mL/min; minor enantiomer t_R = 28.88 min, major enantiomer t_R = 40.76 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{32}H_{25}ClN_3O_3]$: 534.1579, found: 534.1569.

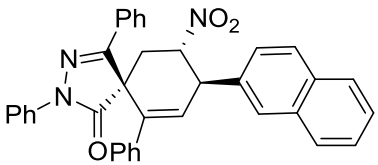
(5R, 8R, 9S)-8-(4-bromophenyl)-9-nitro-2,4,6-triphenyl-2,3-diazaspiro[4.5]deca-3,6-dien-1-one (3af)



3af

White solid. 81% yield (47 mg). m. p.: 86-90 ^{o}C. $[\alpha]_D^{20}$ = 155 (*c* 1.0, CH_2Cl_2, 92% ee); IR (KBr): 703, 742, 805, 873, 1011, 1028, 1075, 1103, 1120, 1264, 1303, 1320, 1379, 1446, 1491, 1556, 1595, 1720, 2854, 2926, 2961, 3056, 3412 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89-7.99 (m, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.52-7.64 (m, 3H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.27-7.34 (m, 2H), 7.18-7.25 (m, 4H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.33 (d, *J* = 2.0 Hz, 1H), 4.61-4.73 (m, 1H), 4.42 (dd, *J* = 10.4 Hz, *J* = 2.0 Hz, 1H), 3.06 (t, *J* = 13.2 Hz, 1H), 2.49 (dd, *J* = 13.2 Hz, *J* = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.9, 160.2, 137.8, 137.6, 137.3, 134.1, 133.2, 132.4, 131.5, 131.4, 129.4, 129.2, 129.0, 128.9, 128.8, 128.0, 126.5, 126.0, 122.3, 119.4, 84.4, 58.8, 46.1, 37.0. The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane:*i*-PrOH = 80:20), 1 mL/min; minor enantiomer t_R = 29.98 min, major enantiomer t_R = 36.05 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{32}H_{25}BrN_3O_3]$: 578.1074, found: 578.1063.

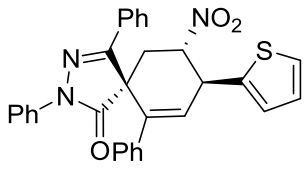
(5R, 8R, 9S)-8-(naphthalen-2-yl)-9-nitro-2,4,6-triphenyl-2,3-diazaspiro[4.5]deca-3,6-dien-1-one (3ag)



3ag

White solid. 86% yield (47 mg). m. p.: 198–208 ^{o}C. $[\alpha]_D^{20}$ = 105 (*c* 1.0, CH_2Cl_2, 94% ee); IR (KBr): 479, 509, 700, 760, 814, 859, 1028, 1101, 1119, 1184, 1222, 1262, 1303, 1320, 1378, 1445, 1492, 1529, 1554, 1596, 1720, 2854, 2925, 2962, 3057, 3418 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96-8.08 (m, 2H), 7.75-7.89 (m, 5H), 7.66 (s, 1H), 7.53-7.62 (m, 3H), 7.43-7.53 (m, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.27-7.36 (m, 3H), 7.16-7.26 (m, 4H), 6.47 (br, 1H), 4.77-4.96 (m, 1H), 4.62 (d, *J* = 10.0 Hz, 1H), 3.13 (t, *J* = 12.8 Hz, 1H), 2.51 (dd, *J* = 13.2 Hz, *J* = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.0, 160.3, 137.8, 137.4, 136.0, 133.9, 133.6, 133.3, 132.9, 131.6, 131.3, 129.2, 129.1, 128.9, 128.9, 128.7, 128.0, 127.7, 127.7, 127.0, 126.6, 126.5, 126.4, 125.9, 125.1, 119.3, 84.2, 58.8, 46.7, 37.0. The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane:*i*-PrOH = 80:20), 1 mL/min; minor enantiomer t_R = 19.20 min, major enantiomer t_R = 26.73 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{36}H_{28}N_3O_3]$: 550.2125, found: 550.2119.

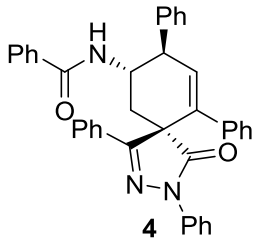
(5R, 8S, 9S)-9-nitro-2,4,6-triphenyl-8-(thiophen-2-yl)-2,3-diazaspiro[4.5]deca-3,6-dien-1-one (3ah)



3ah

White solid. 79% yield (40 mg). m. p.: 156-160 ^{o}C. $[\alpha]_D^{20}$ = 86 (*c* 1.0, CH_2Cl_2, 93% ee); IR (KBr): 701, 742, 804, 1027, 1095, 1121, 1264, 1303, 1321, 1380, 1445, 1492, 1555, 1596, 1720, 2856, 2925, 2959, 3057, 3381 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96-8.08 (m, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.47-7.63 (m, 3H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.25-7.32 (m, 3H), 7.14-7.25 (m, 4H), 6.88-6.99 (m, 2H), 6.42 (d, *J* = 2.0 Hz, 1H), 4.75-4.92 (m, 2H), 3.04 (t, *J* = 12.8 Hz, 1H), 2.49 (dd, *J* = 13.2 Hz, *J* = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.8, 159.7, 141.2, 137.5, 137.3, 133.9, 133.0, 131.4, 131.3, 129.3, 128.9, 128.7, 127.8, 127.2, 126.7, 126.6, 125.9, 125.5, 119.3, 84.7, 58.5, 46.6, 36.6. The enantiomeric excess was determined by HPLC with an AD-H column. (*n*-hexane:*i*-PrOH = 80:20), 1 mL/min; minor enantiomer t_R = 16.49 min, major enantiomer t_R = 27.78 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{30}H_{24}N_3O_3S]$: 506.1533, found: 506.1529.

N-((5R, 7S, 8R)-4-oxo-1,3,8,10-tetraphenyl-2,3-diazaspiro[4.5]deca-1,9-dien-7-yl) benzamide (4)

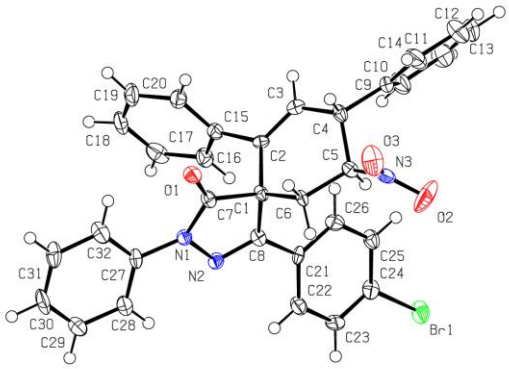


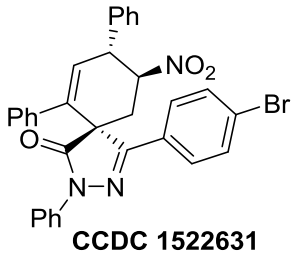
4

White solid. 88% yield (50 mg). m. p.: 110-116 ^{o}C. $[\alpha]_D^{20}$ = -653 (*c* 1.0, CH_2Cl_2, 87% ee); IR (KBr): 634, 664, 698, 757, 764, 1028, 1123, 1240, 1302, 1319, 1379, 1444, 1494, 1561, 1596, 1714, 2855, 2924, 2949, 3029, 3060, 3420 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.83 (d, *J* = 7.4Hz, 1H), 8.04-8.16 (m, 2H), 7.83-7.98 (m, 4H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.47-7.55 (m, 3H), 7.38-7.46 (m, 5H), 7.22-7.37 (m, 6H), 7.13-7.21 (m, 3H), 6.61 (d, *J* = 5.2 Hz, 1H), 4.96 (br, 1H), 4.15 (d, *J* = 5.2 Hz, 1H), 2.49 (dd, *J* = 15.2 Hz, *J* = 2.8Hz, 1H), 2.12 (d, *J* = 15.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.1, 160.9, 141.0, 138.9, 137.3, 135.7, 134.2, 132.5, 131.3, 130.8, 129.7, 128.9, 128.6, 128.6, 128.5, 128.2, 127.3, 127.3, 127.1, 127.0, 126.1, 119.9, 58.6, 49.5, 46.5, 29.3. The enantiomeric excess was determined by HPLC with an IA column. (*n*-hexane:*i*-PrOH = 95:5), 1 mL/min; minor enantiomer t_R = 19.70 min, major enantiomer t_R = 23.02 min. HRMS (ESI): $[M+H]^+$ calcd for $[C_{39}H_{32}N_3O_2]$: 574.2489, found: 574.2482.

4. X-ray Crystallographic Data

X-ray Crystallographic Data of Compound 3sa





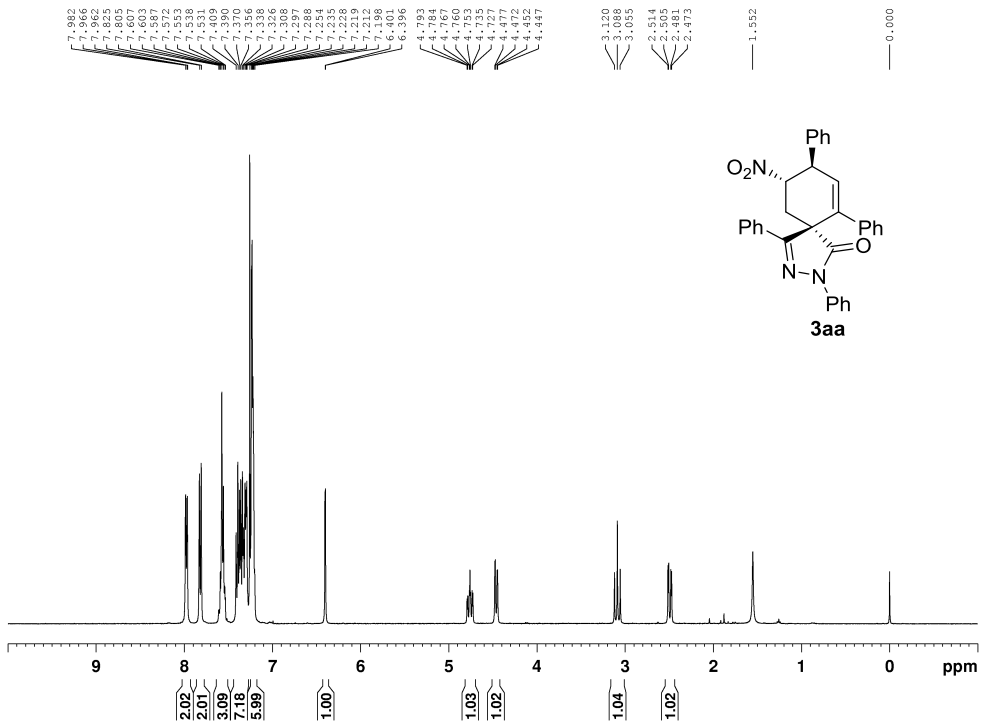
Bond precision:	C-C = 0.0062 A	Wavelength=0.71070	
Cell:	a = 7.6027(3)	b = 16.7807(6)	c = 21.1178(5)
	Alpha = 90	Beta = 90	Gamma = 90
Temperature:	173 K		
	Calculated	Reported	
Volume	2694.18(16)	2694.18(16)	
Space group	P 21 21 21	P 21 21 21	
Hall group	P 2ac 2ab	P 2ac 2ab	
Moiety formula	$C_{32}H_{24}BrN_3O_3$	$C_{32}H_{24}BrN_3O_3$	
Sum formula	$C_{32}H_{24}BrN_3O_3$	$C_{32}H_{24}BrN_3O_3$	
Mr	578.44	578.45	
Dx,g cm^{-3}	1.426	1.426	
Z	4	4	
Mu (mm^{-1})	1.565	1.565	
F000	1184.0	1184.0	
F000’	1183.30		
h, k, lmax	9, 20, 26	9, 20, 26	
Nref	5314[3027]	4624	
Tmin,Tmax	0.734, 0.939	0.864, 1.000	
Tmin’	0.702		

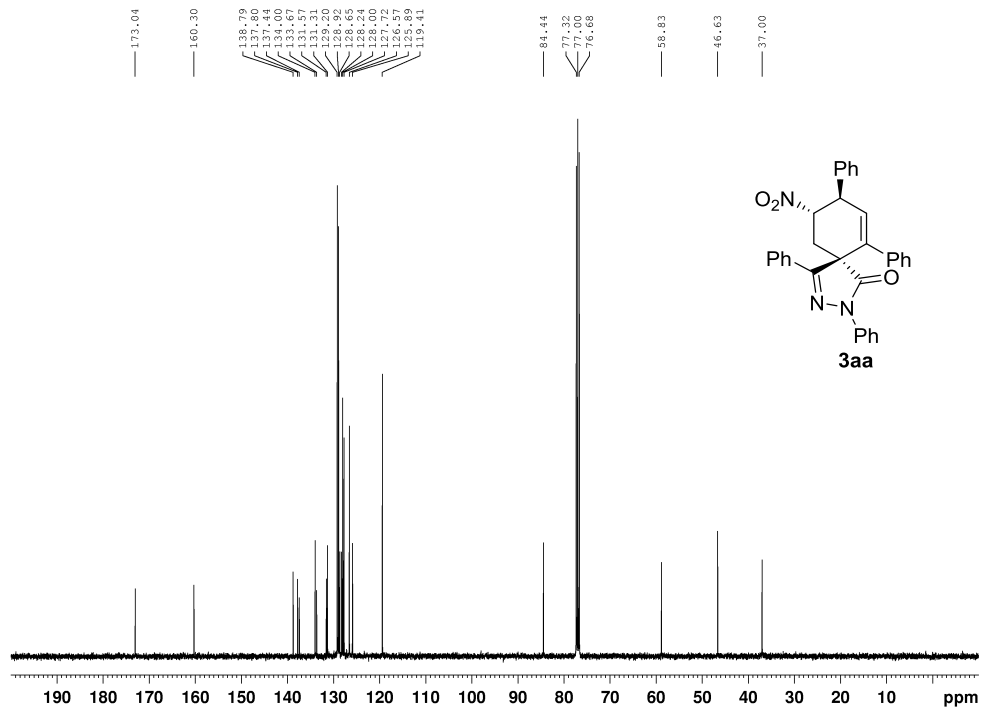
Correction method = # Reported T Limits: Tmin = 0.864 Tmax = 1.000
AbsCorr = MULTI-SCAN

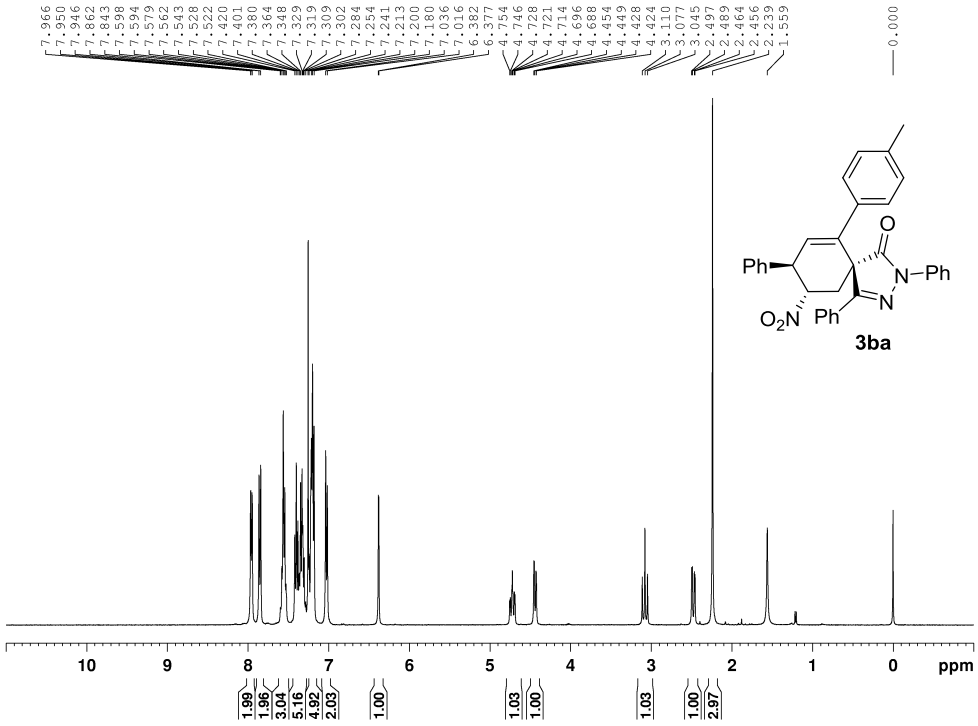
Data completeness = 1.53/0.87	Theta(max) = 26.020
R(reflections) = 0.0457(3777)	wR2(reflections) = 0.0857(4624)
S = 1.014	Npar= 352

Displacement ellipsoids are drawn at 30% probability level

5. Copies of NMR and HPLC spectrogram



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7.543
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7.522
7.420
7.401
7.380
7.364
7.348
7.329
7.319
7.309
7.302
7.284
7.254
7.241
7.213
7.200
7.180
7.036
7.016
6.382
6.377
4.754
4.746
4.728
4.721
4.714
4.696
4.688
4.454
4.449
4.428
4.424
3.110
3.077
3.045
2.497
2.489
2.464
2.456
2.239
1.559
0.000
Ph
O
N–Ph
N
O2N
Ph
3ba
10
9
8
7
6
5
4
3
2
1
0
ppm
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5.16
4.92
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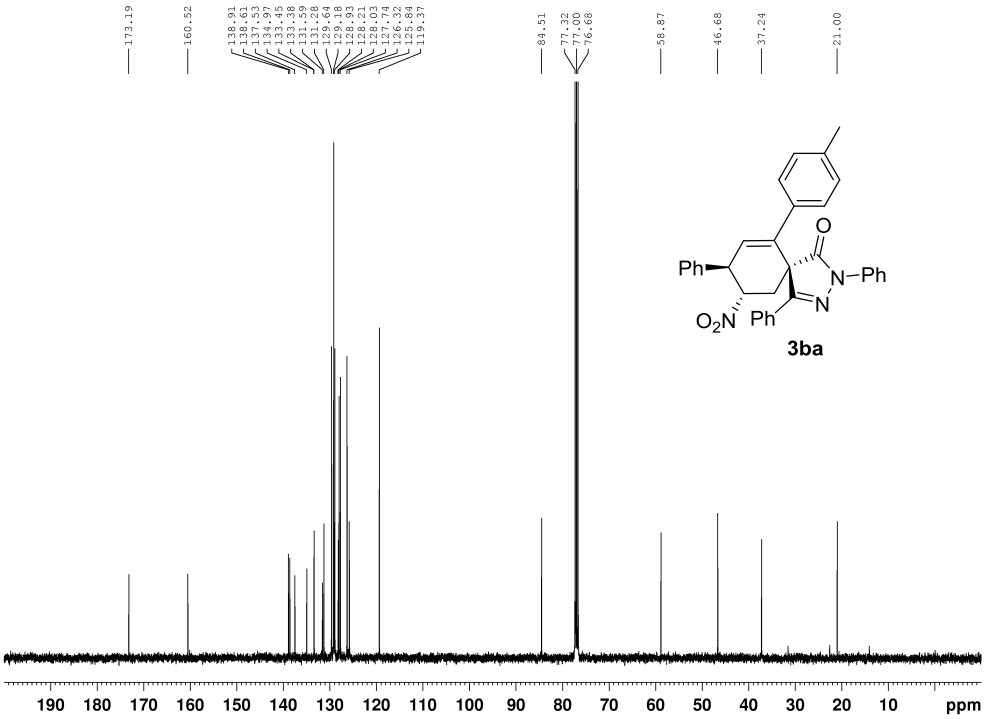
1.03
1.00
1.03
1.00
2.97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134.97
133.45
133.38
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131.28
129.64
129.18
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128.21
128.03
127.74
126.32
125.84
119.37
84.51
77.32
77.00
76.68
58.87
46.68
37.24
21.00
Ph
O
N–Ph
N
O2N
Ph
3ba
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180
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150
140
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110
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70
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30
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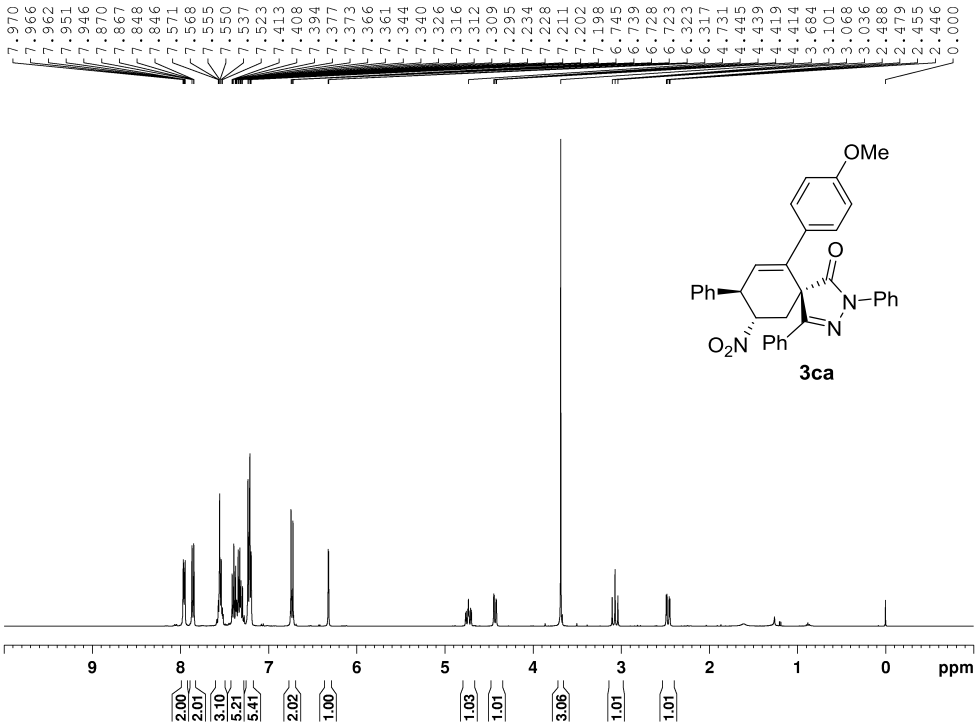
10
ppm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OMe
O
Ph
N–Ph
N
O_2N Ph
3ca
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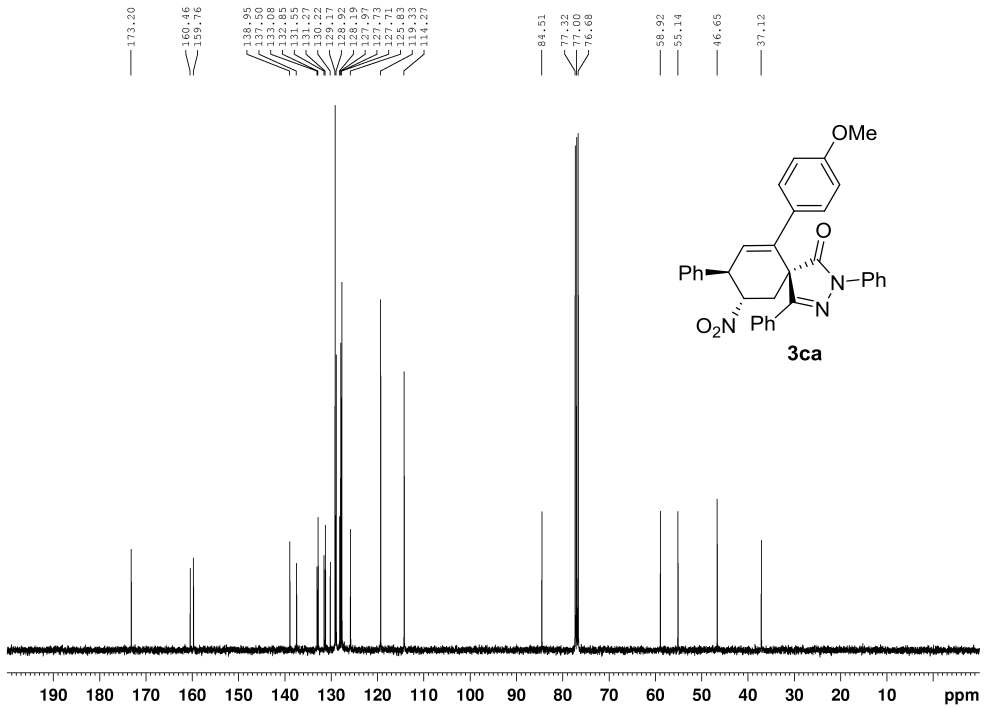
2.00 2.01 3.10 5.21 5.41 2.02 1.00 1.03 1.01 3.06 1.01 1.01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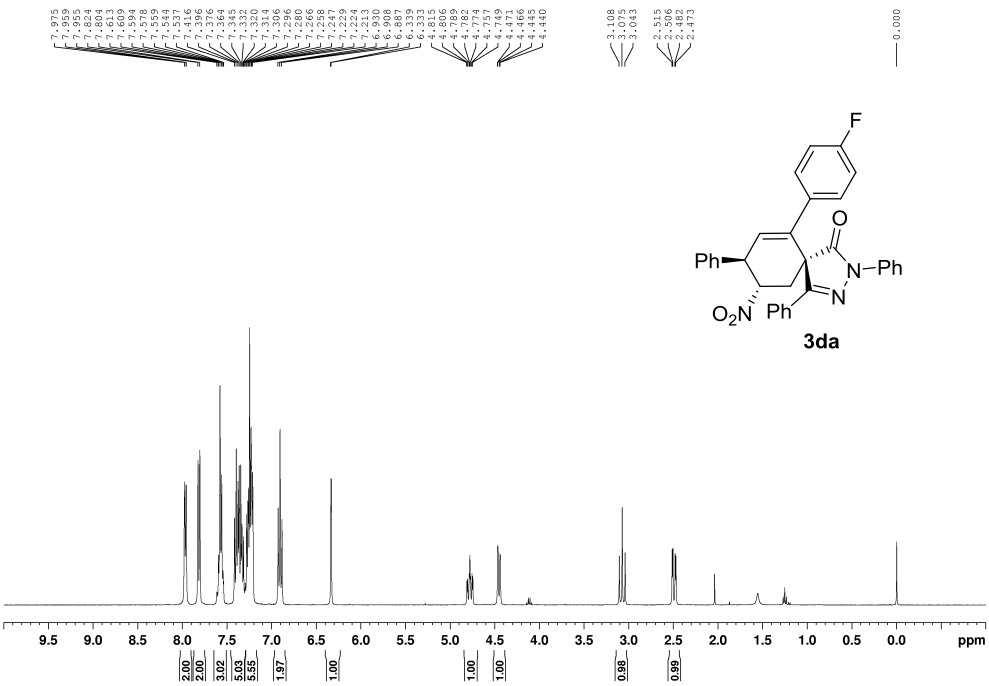
160.46 159.76
138.95 137.50 137.08 132.85 131.55 131.27 130.22 129.17 128.92 128.79 127.97 127.73 127.71 125.83 119.33 114.27
84.51
77.32 77.00 76.68
58.92
55.14
46.65
37.12
OMe
O
Ph
N–Ph
N
O_2N Ph
3ca
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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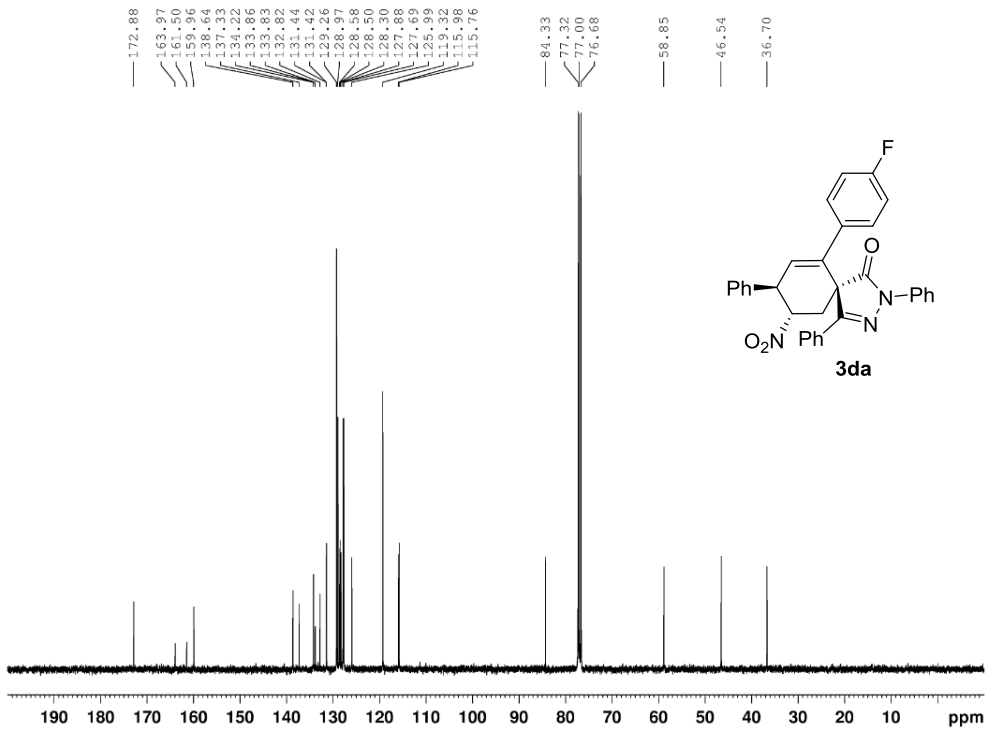
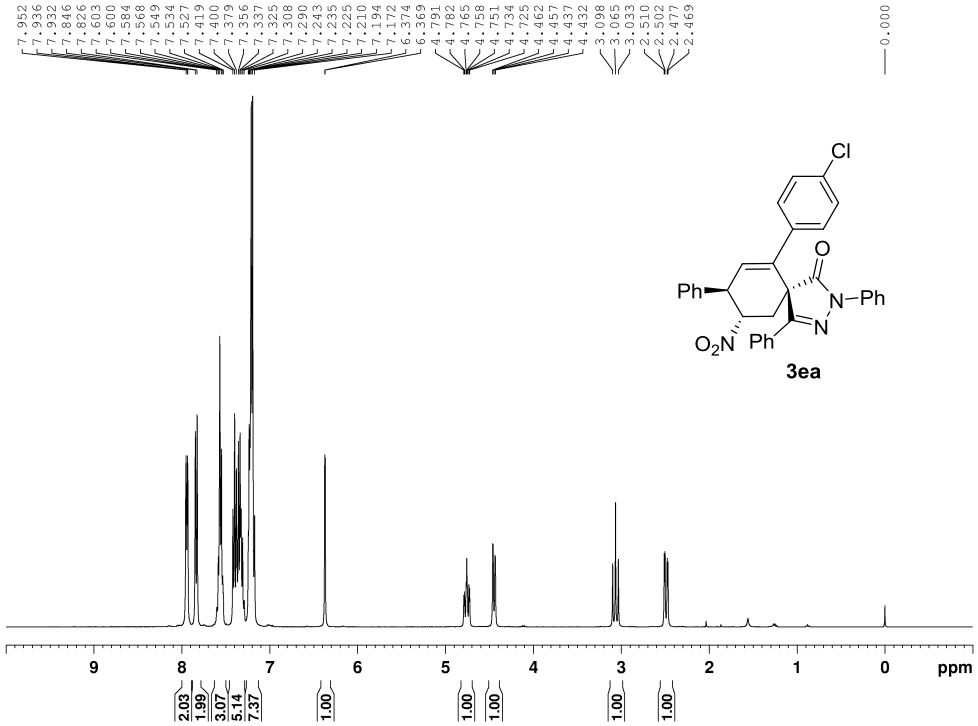
ppm


3da
ppm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7.325
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7.290
7.243
7.235
7.225
7.210
7.194
7.172
6.369
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4.782
4.765
4.758
4.751
4.734
4.725
4.462
4.457
4.437
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3.065
3.033
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2.477
2.469
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Cl
O
Ph
N–Ph
N
O2N
Ph
3ea
9
8
7
6
5
4
3
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7.37
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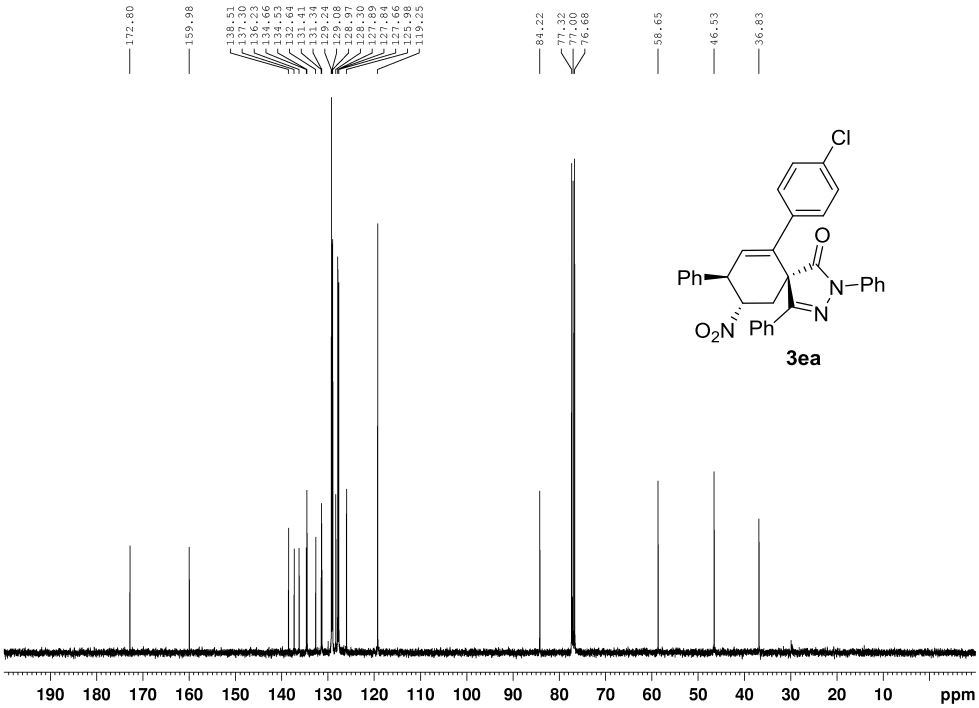
1.00
1.00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132.64
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128.97
128.30
127.89
127.84
127.66
125.98
119.25
84.22
77.32
77.00
76.68
58.65
46.53
36.83
Cl
O
Ph
N–Ph
N
O2N
Ph
3ea
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180
170
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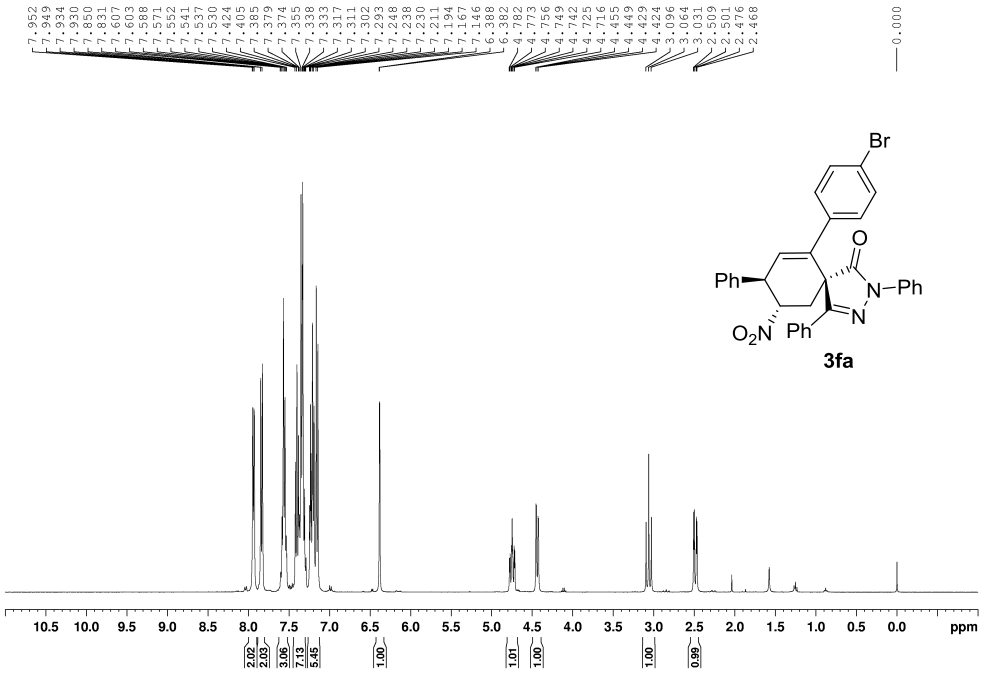
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.541
7.537
7.530
7.424
7.405
7.385
7.379
7.374
7.355
7.338
7.333
7.317
7.311
7.302
7.293
7.248
7.238
7.230
7.211
7.194
7.167
7.146
6.388
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4.773
4.756
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4.716
4.455
4.449
4.429
4.424
3.096
3.064
3.031
2.509
2.501
2.476
2.468
0.000
Br
O
Ph
N–Ph
N
O_2N
Ph
3fa
10.5 10.0 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 ppm
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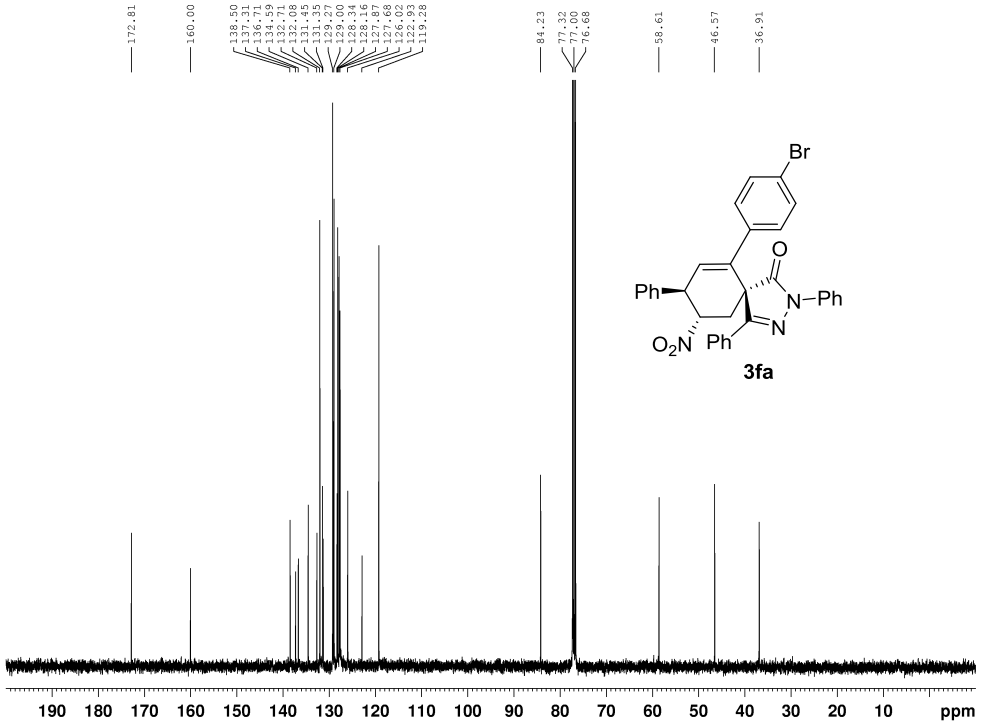
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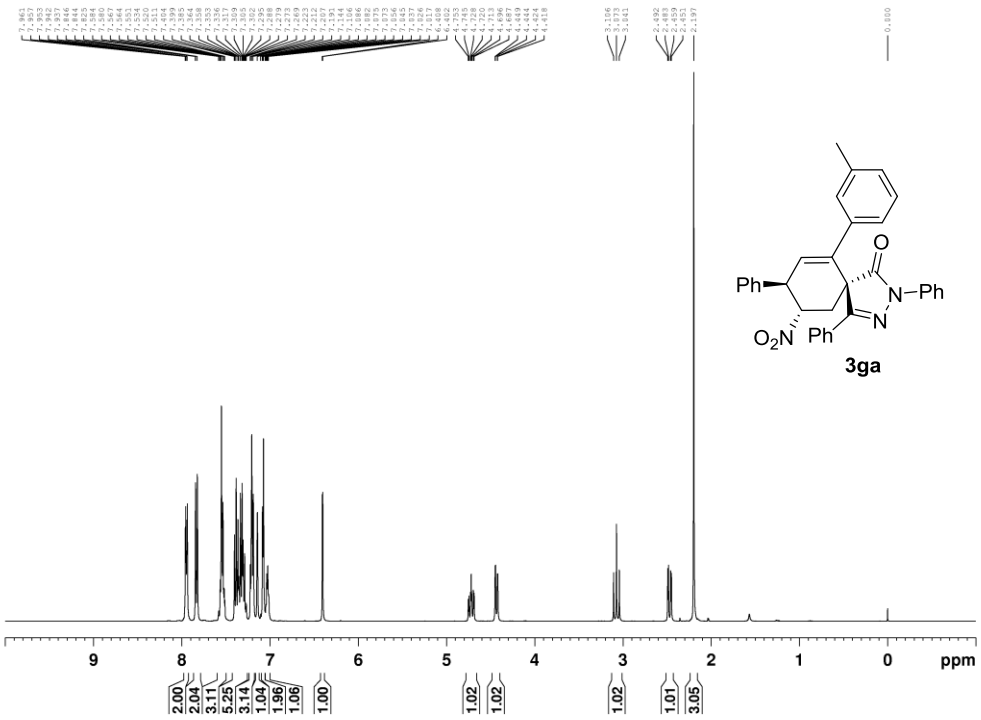
127.68
126.02
122.93
119.28
84.23
77.32
77.00
76.68
58.61
46.57
36.91
Br
O
Ph
N–Ph
N
O_2N
Ph
3fa
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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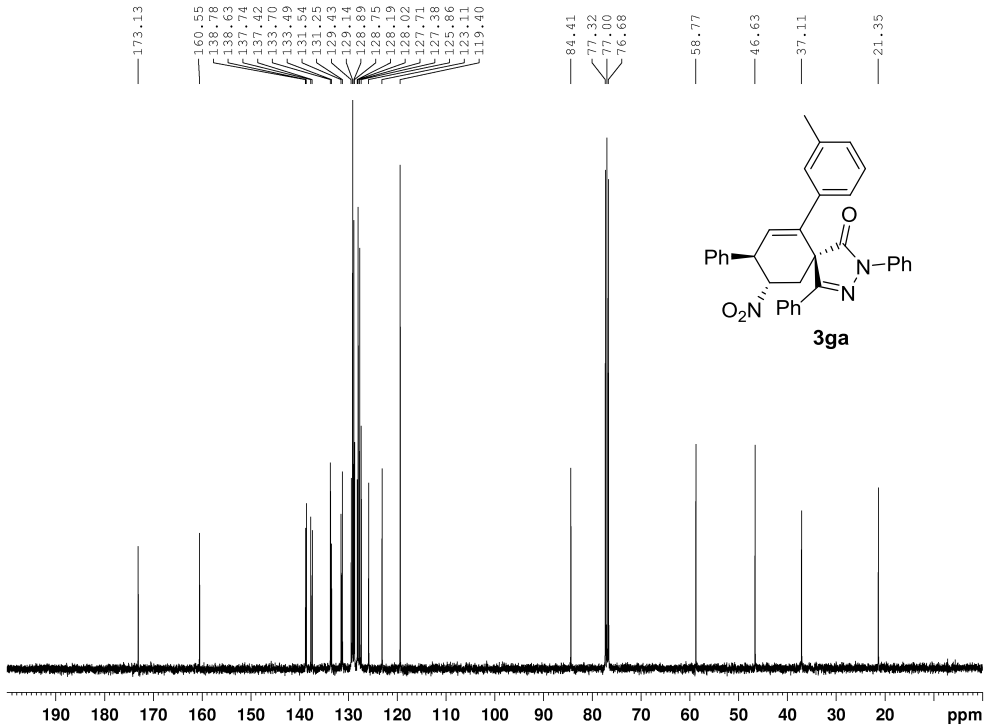
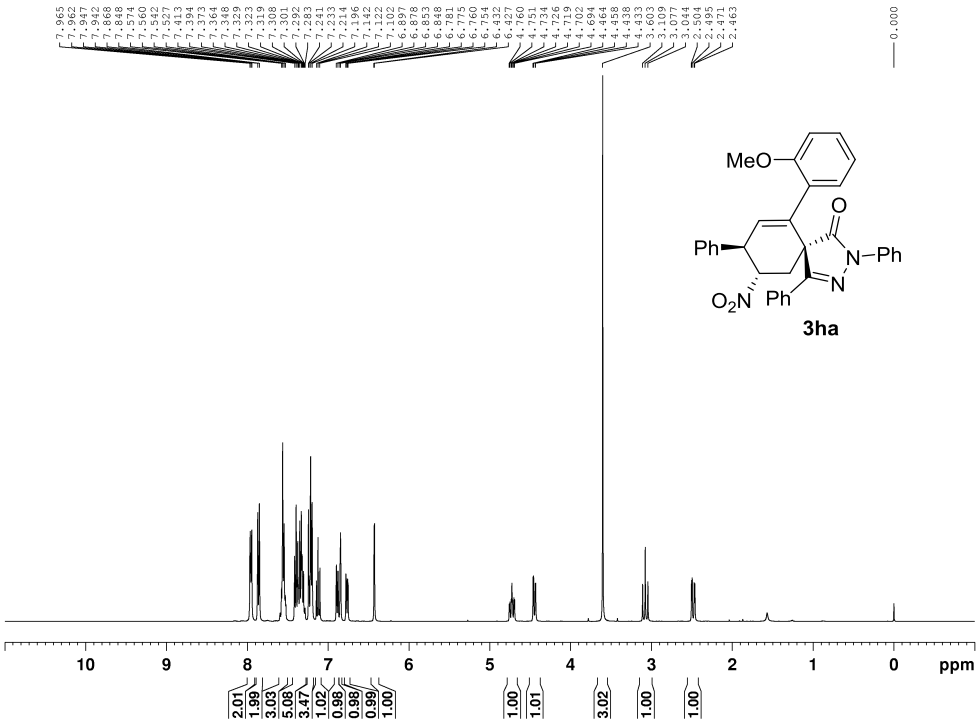
ppm


3ga
ppm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Ph
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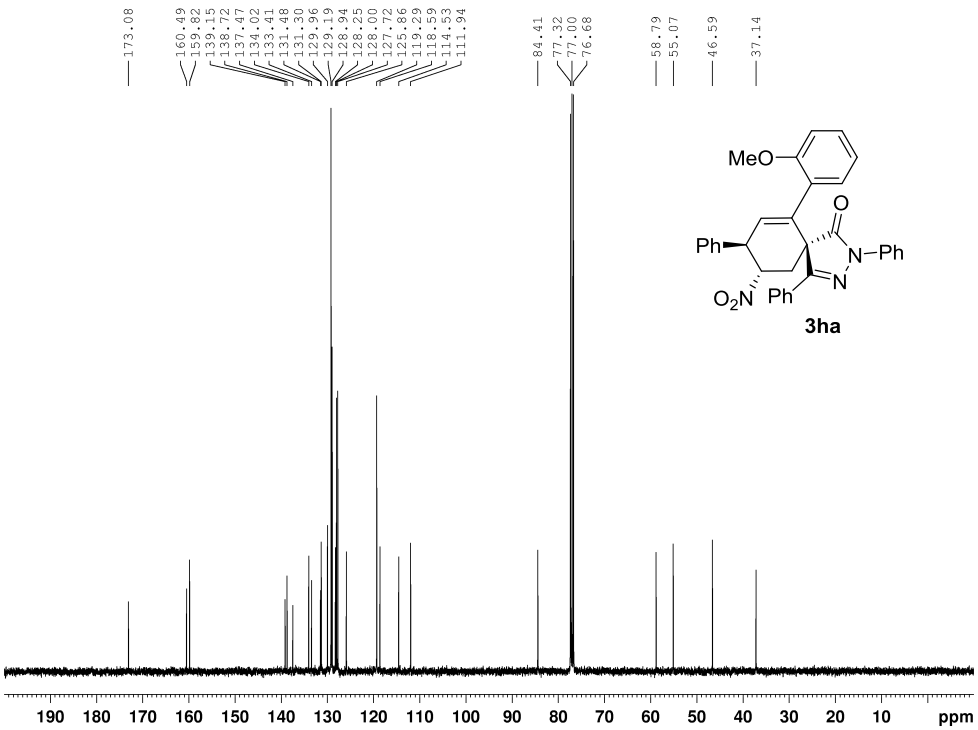
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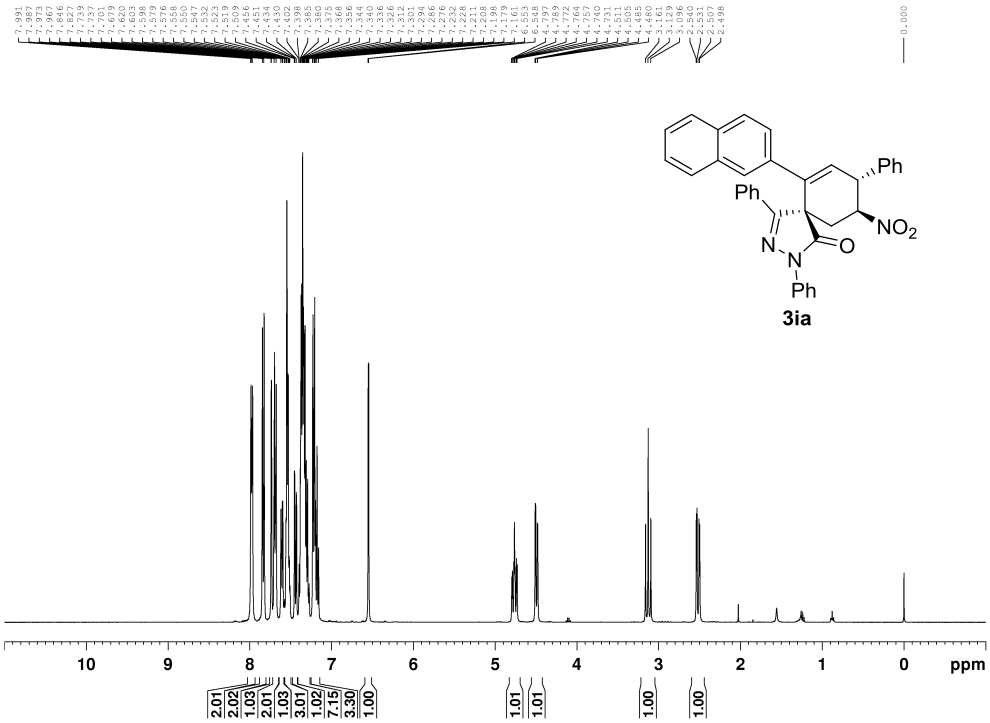
O
Ph
N–Ph
N
O2N
Ph
3ha
ppm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Ph
NO2
N
N
O
Ph
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10 9 8 7 6 5 4 3 2 1 0 ppm
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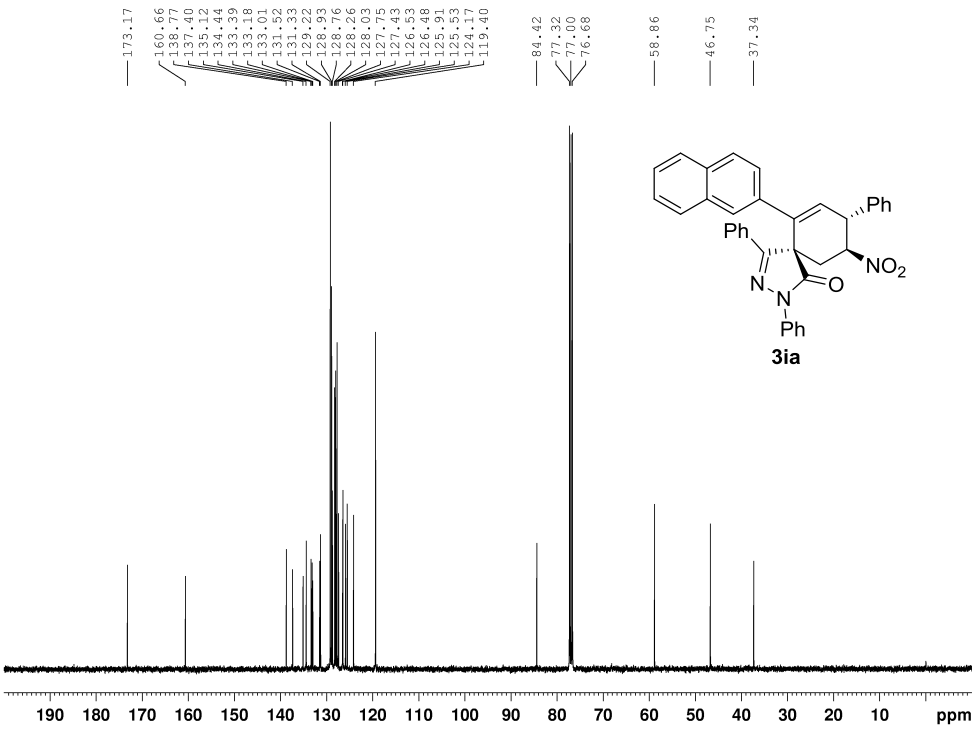
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128.26
128.03
127.75
127.43
126.53
126.48
125.91
125.53
124.17
119.40
84.42
77.32
77.00
76.68
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37.34
Ph
Ph
NO2
N
N
O
Ph
3ia
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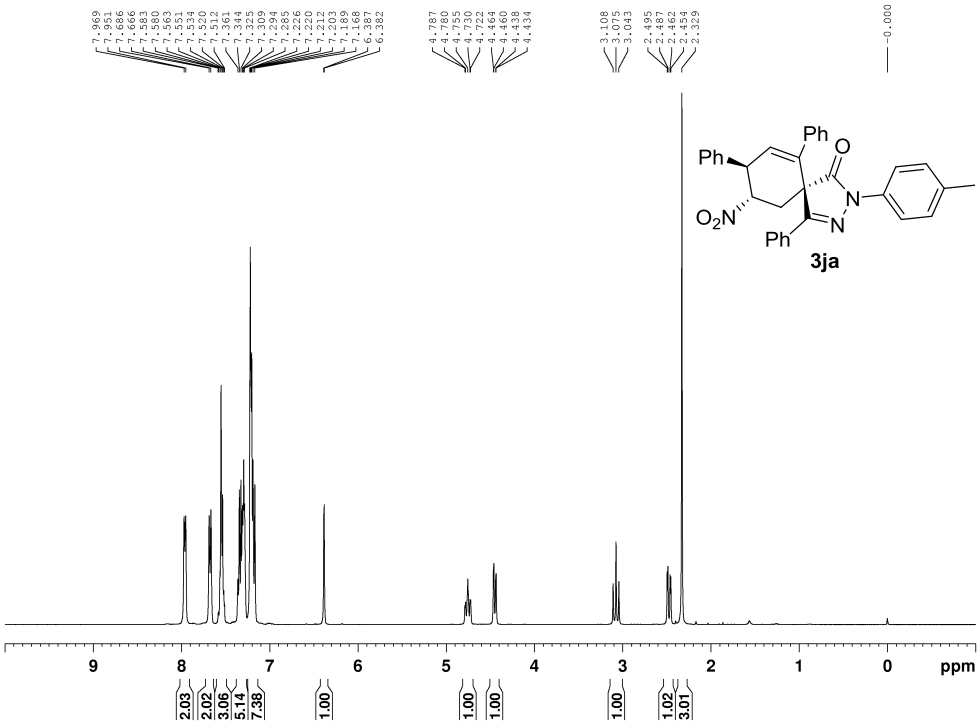
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Ph
O
Ph
N
O_2N
N
Ph
3ja
9
8
7
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5
4
3
2
1
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3.06
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1.00
1.00
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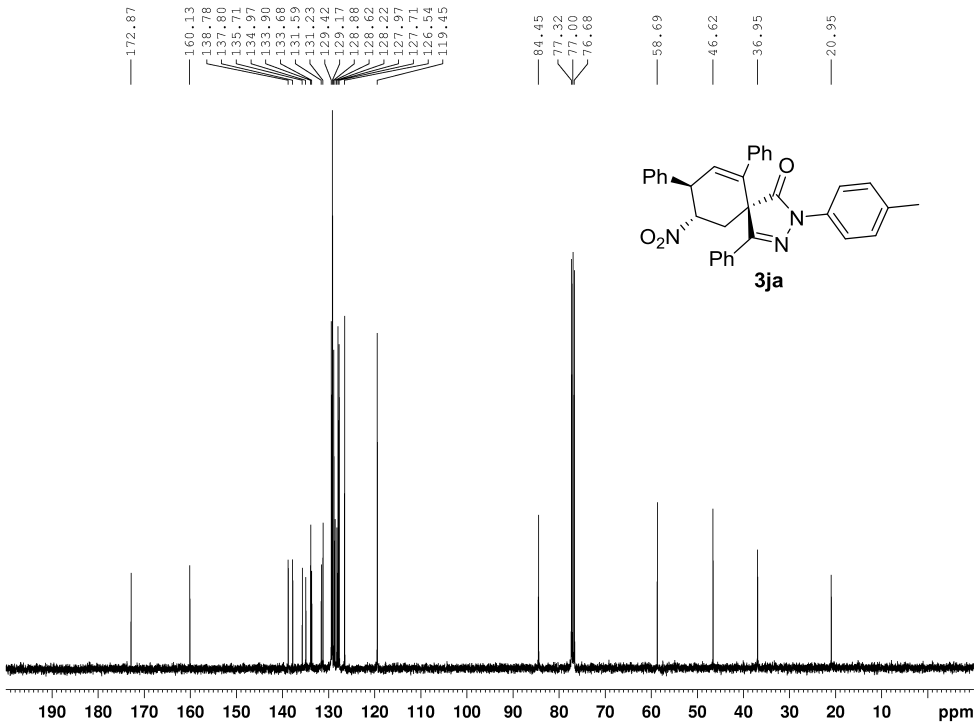
1.02
3.01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128.22
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127.71
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119.45
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77.00
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Ph
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10
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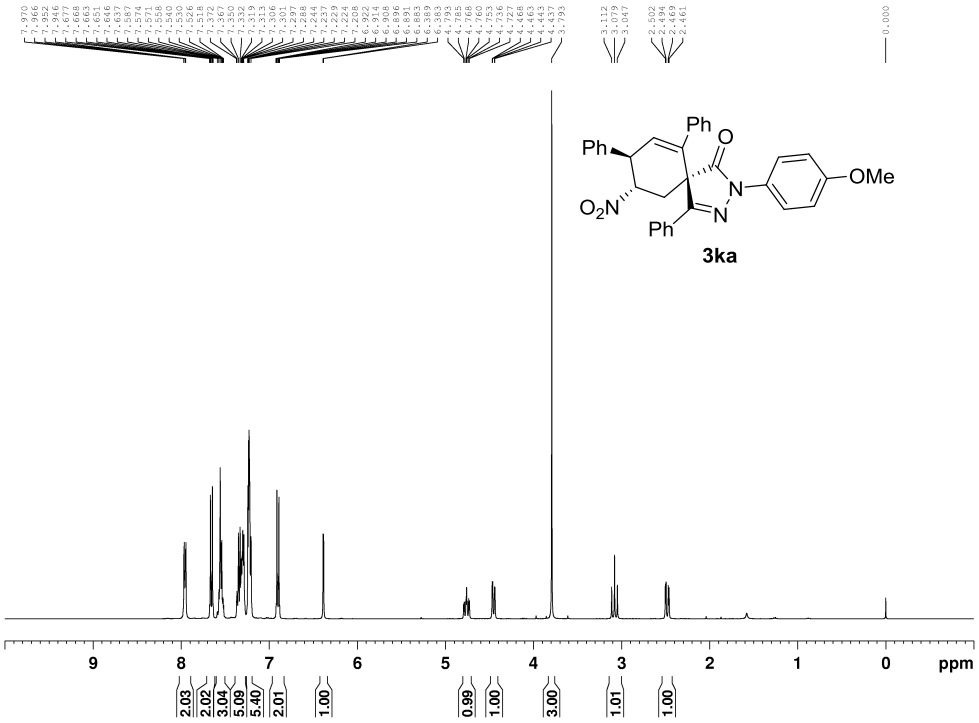
Ph
O
Ph
OMe
N
O_2N
N
Ph
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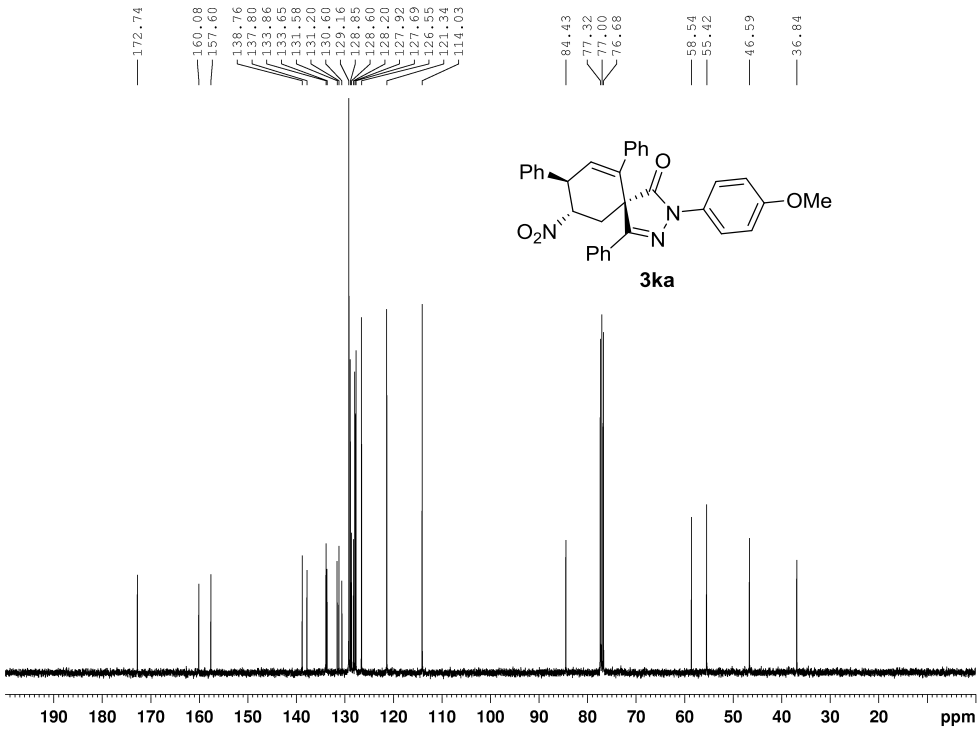
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Ph
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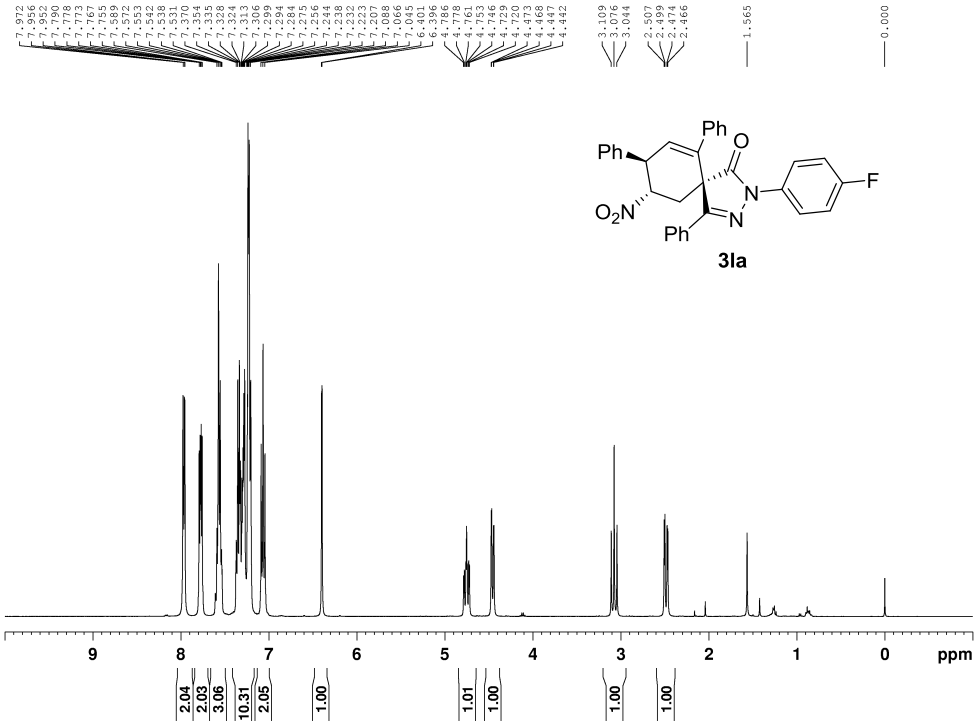
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2.466
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Ph
O
N
N
F
O2N
Ph
3Ia
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3
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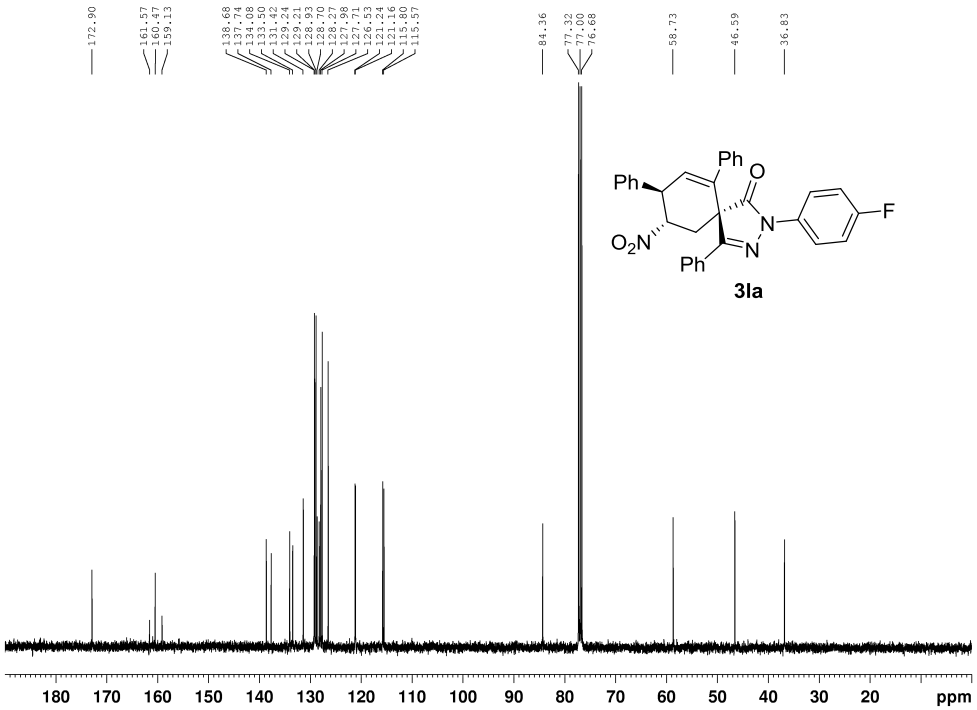
1.00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77.32
77.00
76.68
58.73
46.59
36.83
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Ph
O
N
N
F
O2N
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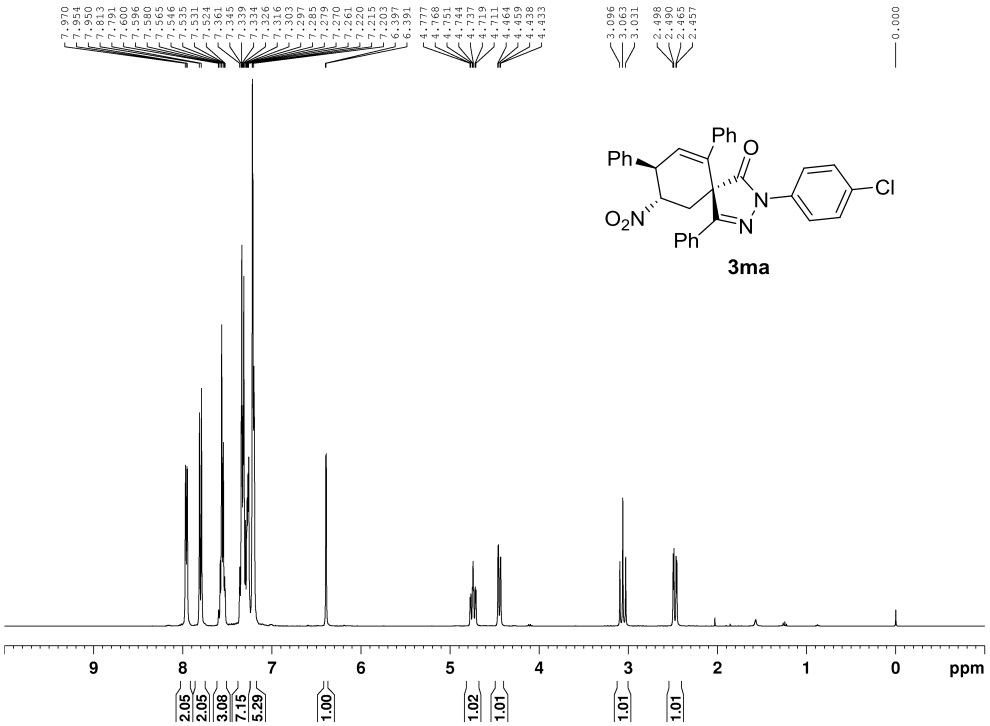
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Ph
N
Cl
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N
Ph
3ma
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8
7
6
5
4
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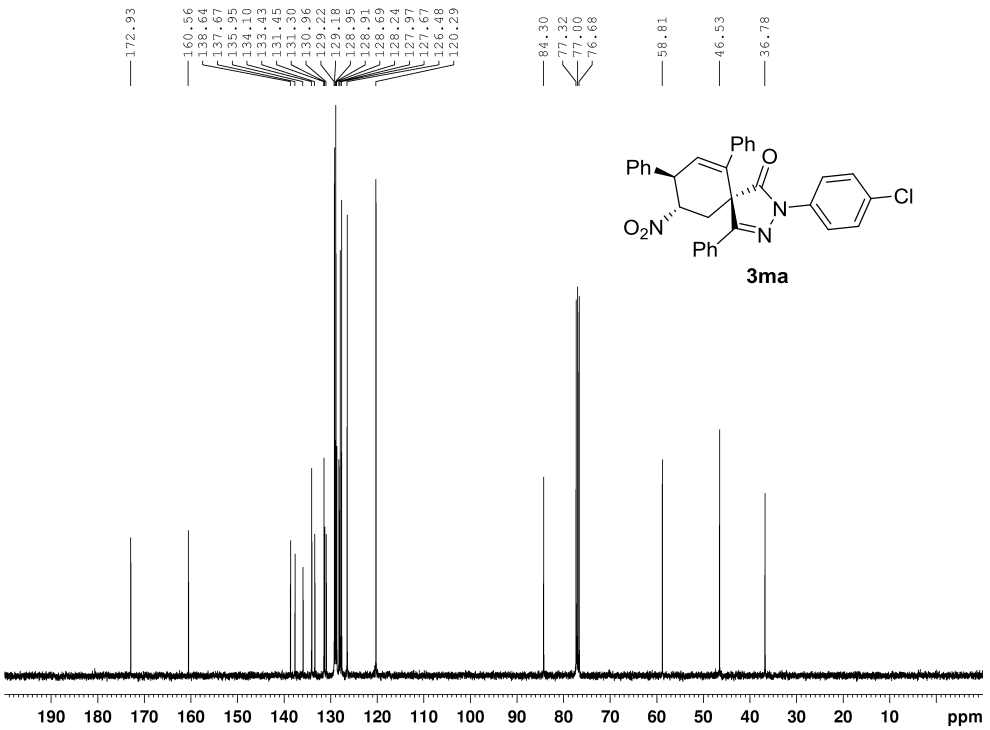
1.01
1.01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Ph
N
Cl
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N
Ph
3ma
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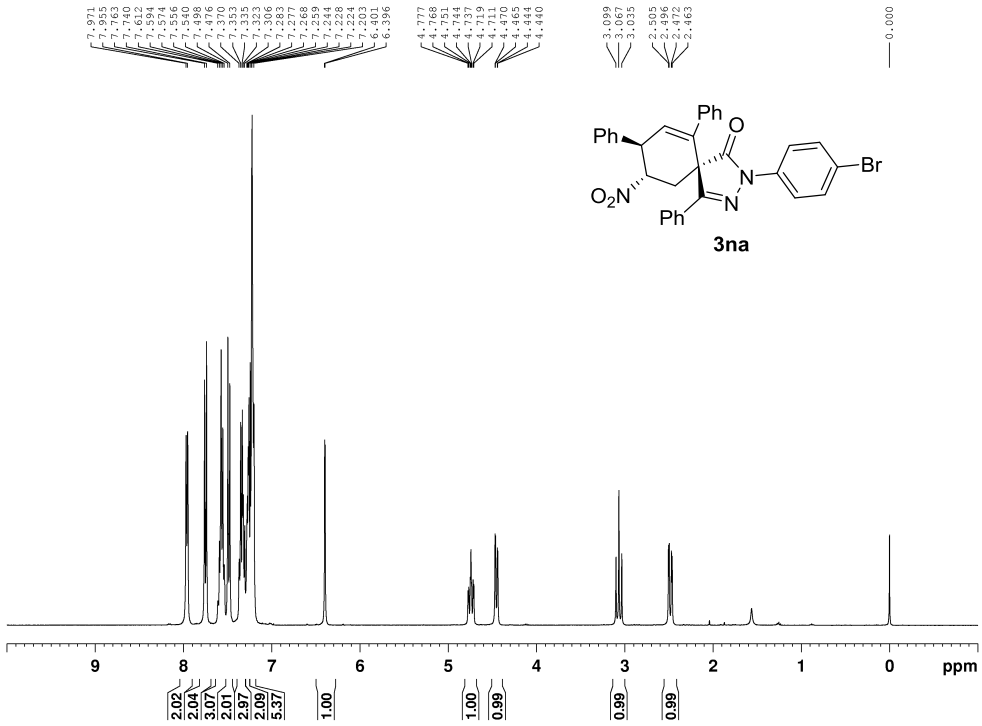
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Ph
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Br
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Ph
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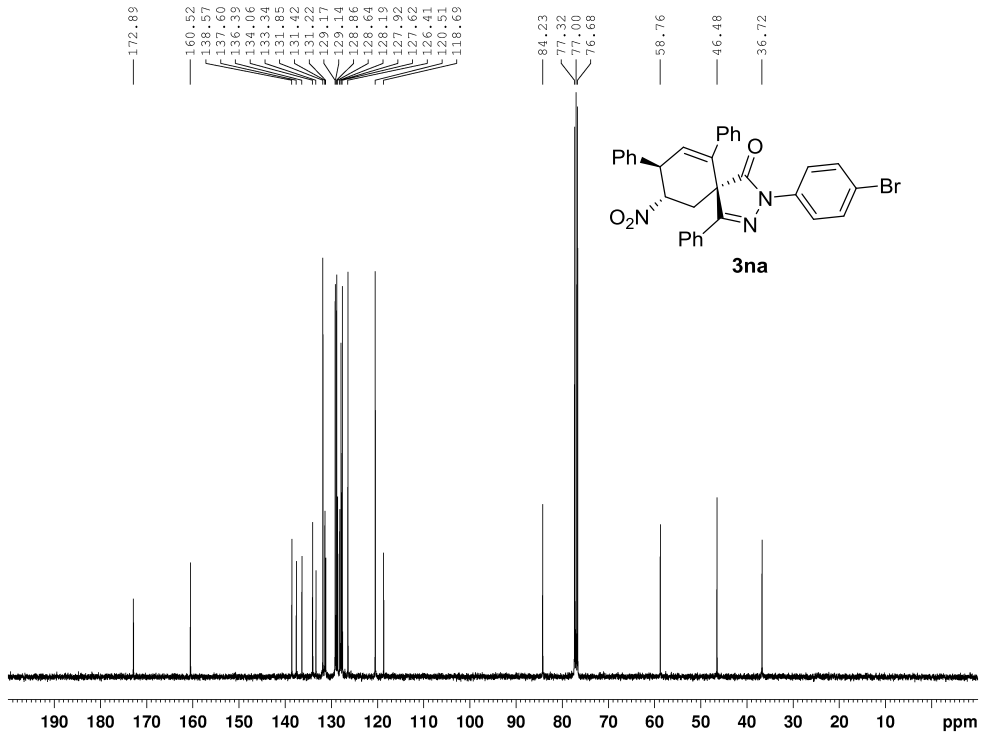
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O
Ph
N
Br
O2N
N
Ph
3na
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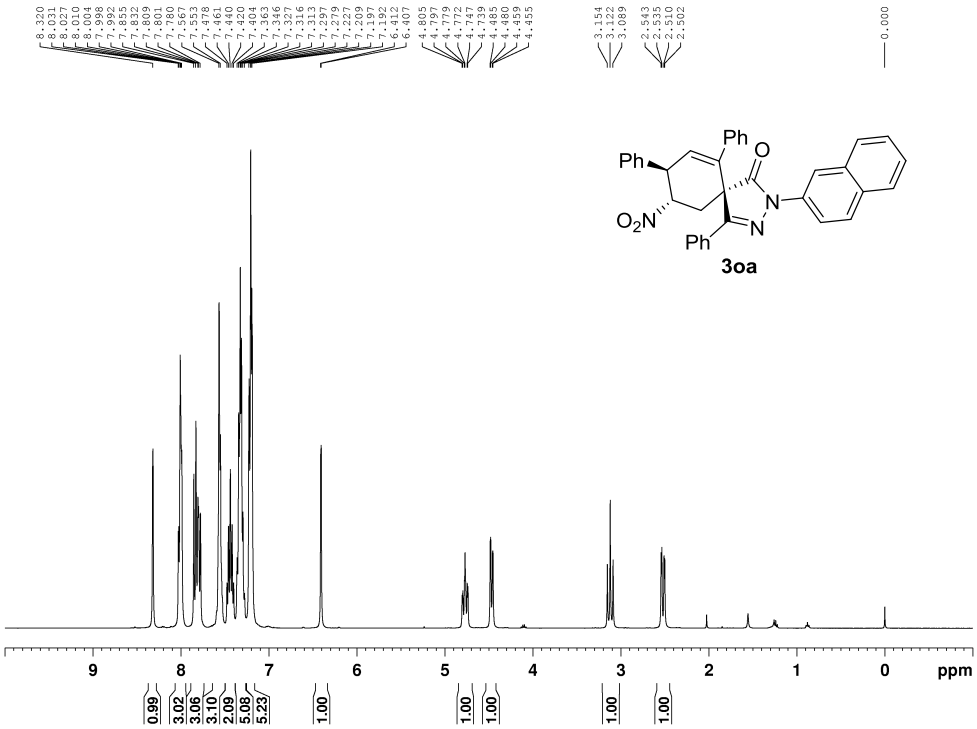
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Ph
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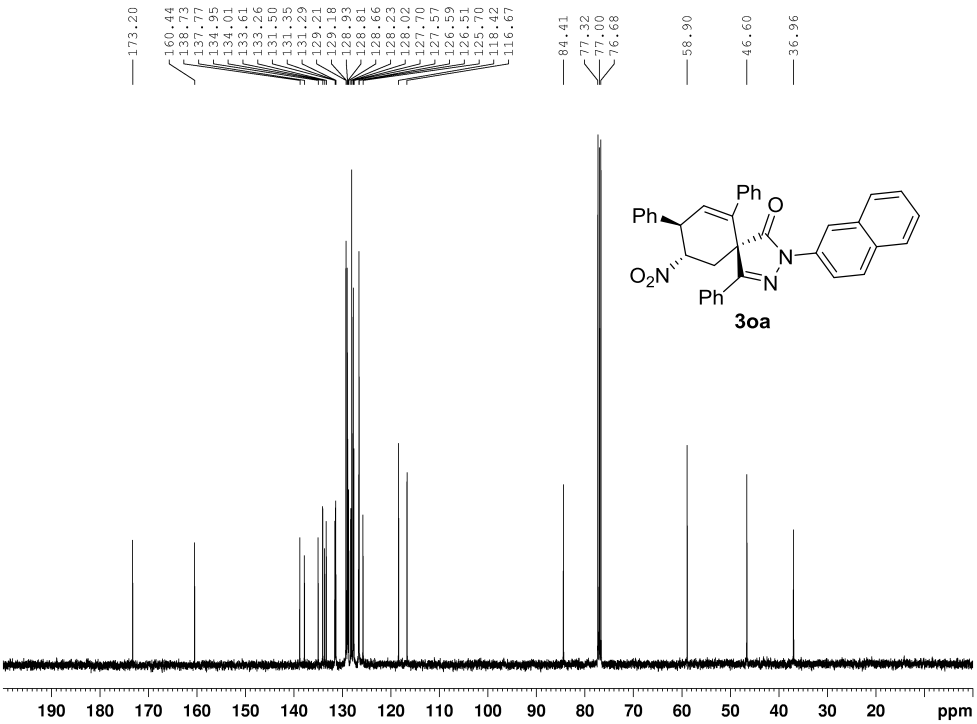
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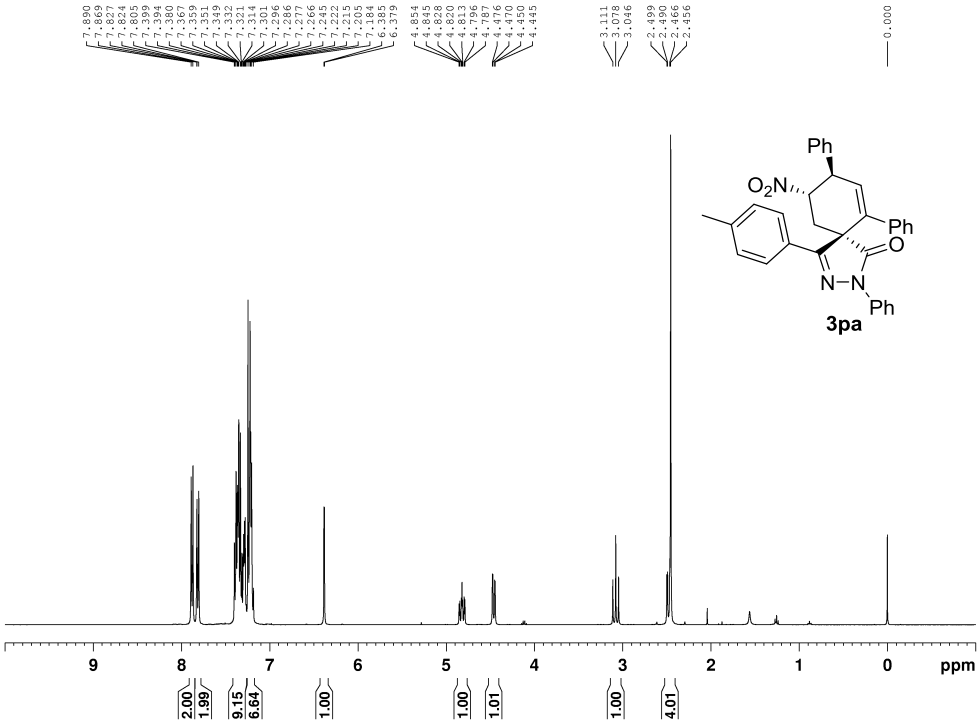
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Ph
O
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Ph
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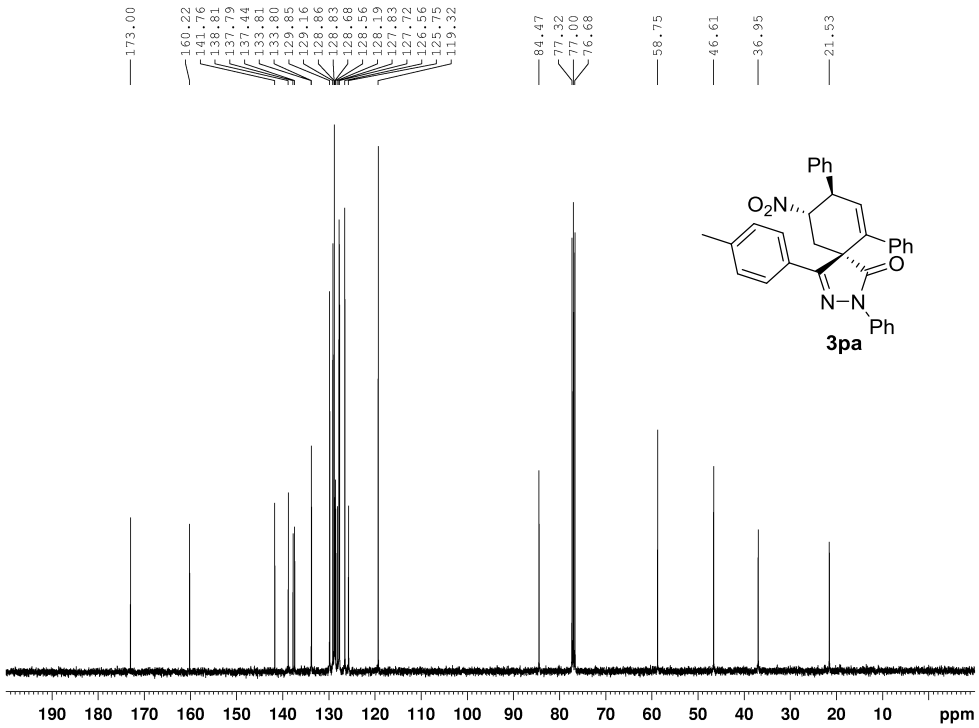
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Ph
O
N–N
Ph
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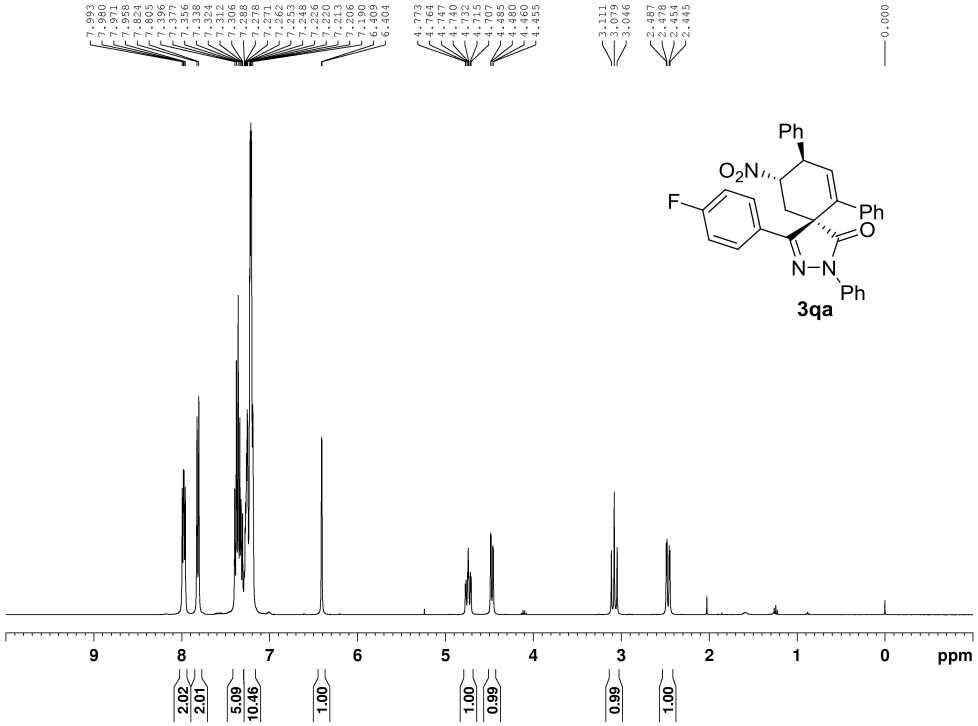
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6.404
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Ph
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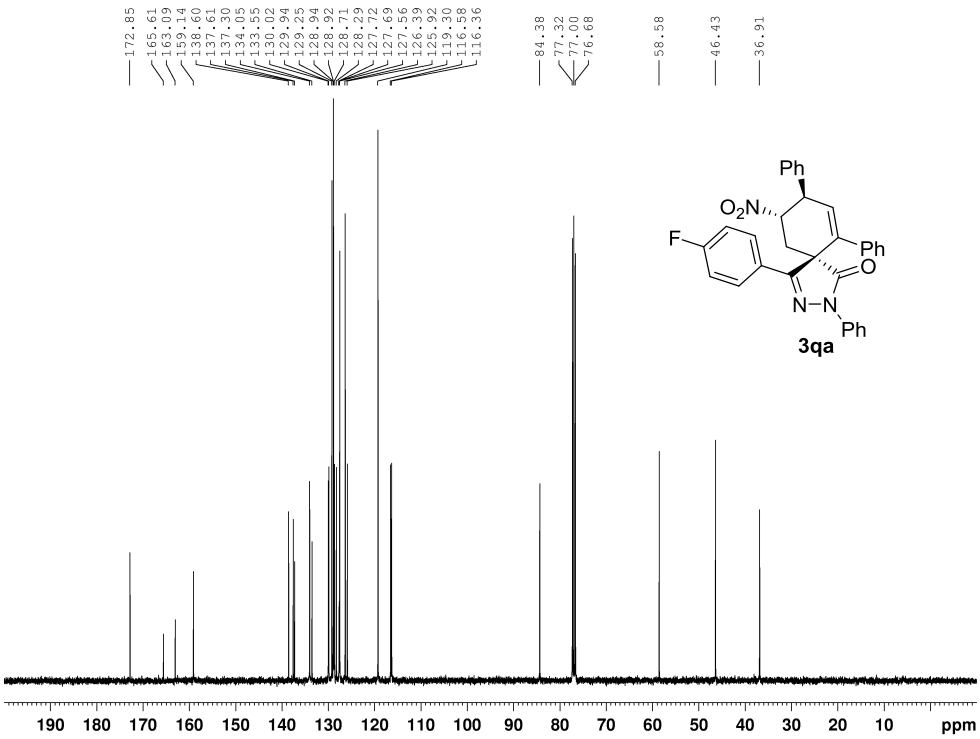
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Ph
O2N
F
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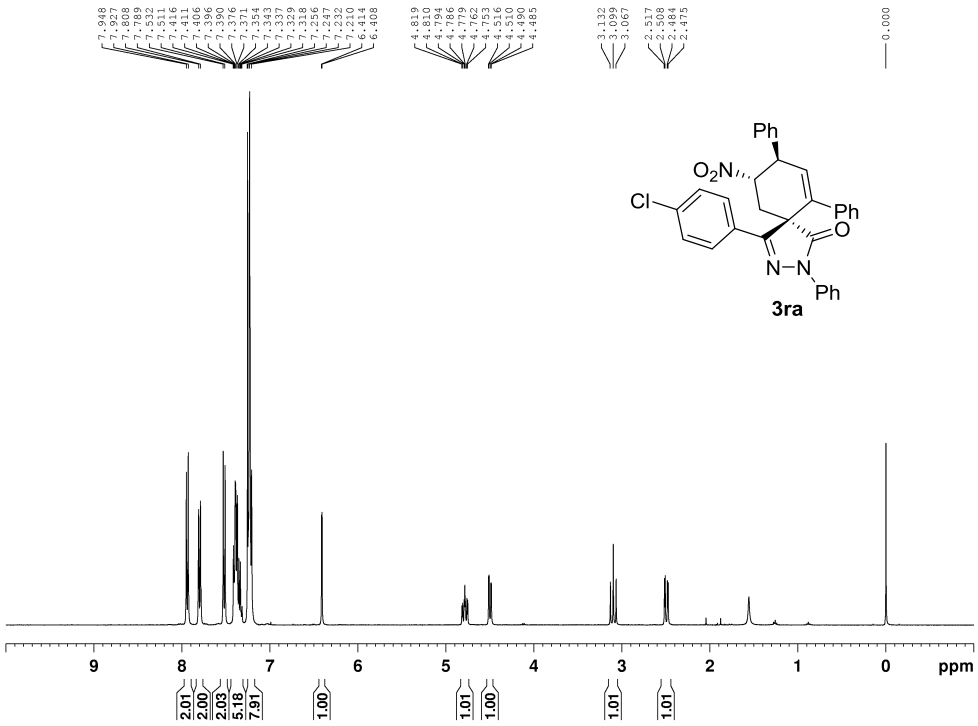
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O
N–N
Ph
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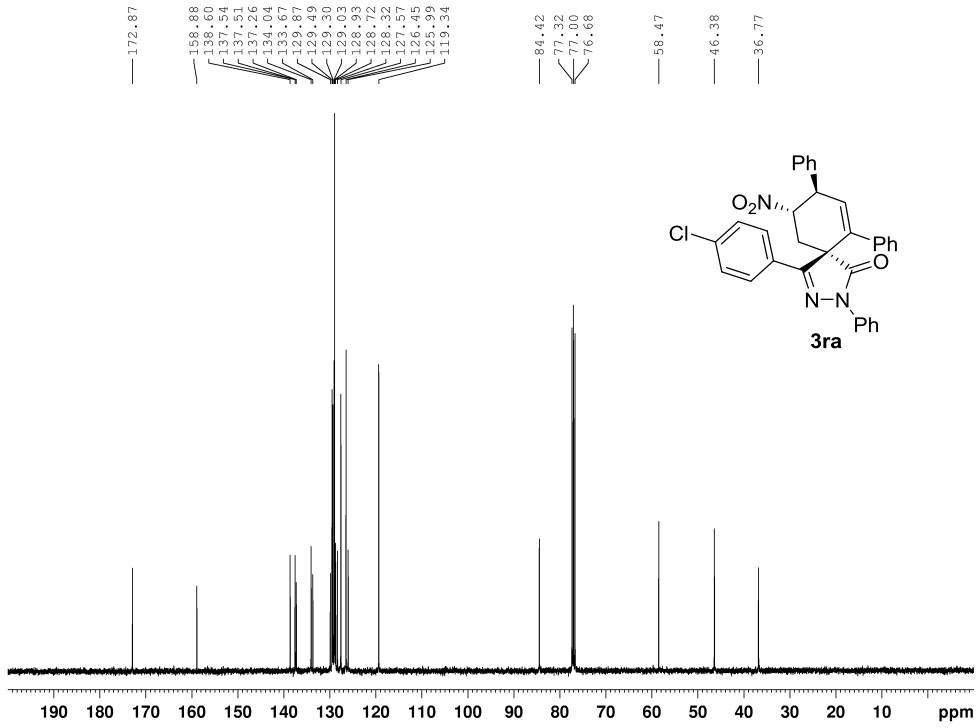
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77.00
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Cl
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Ph
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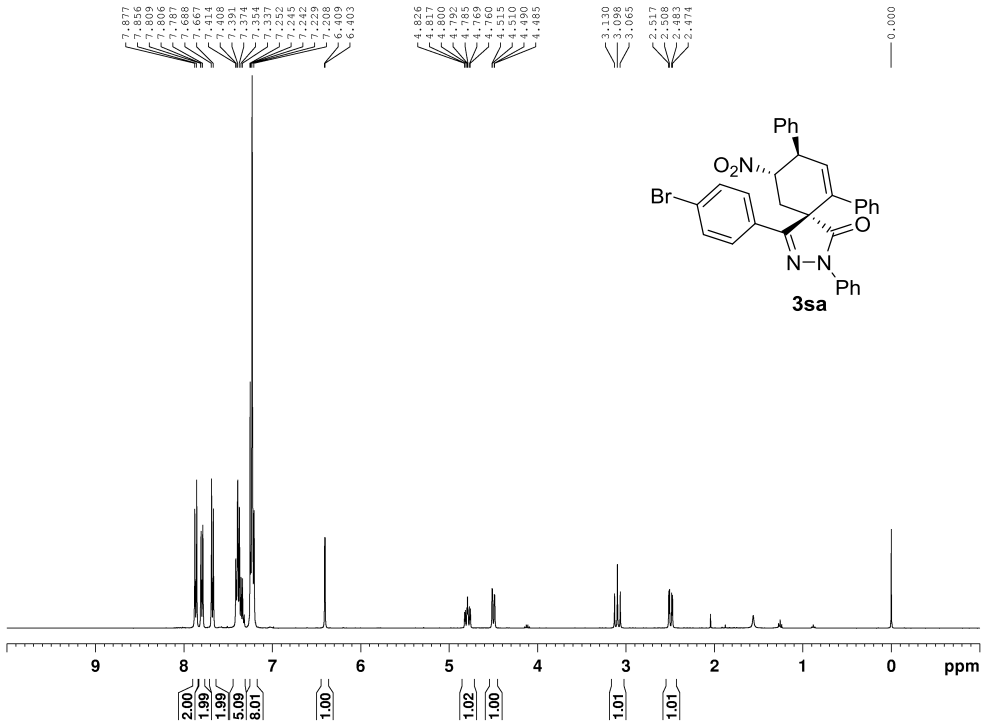
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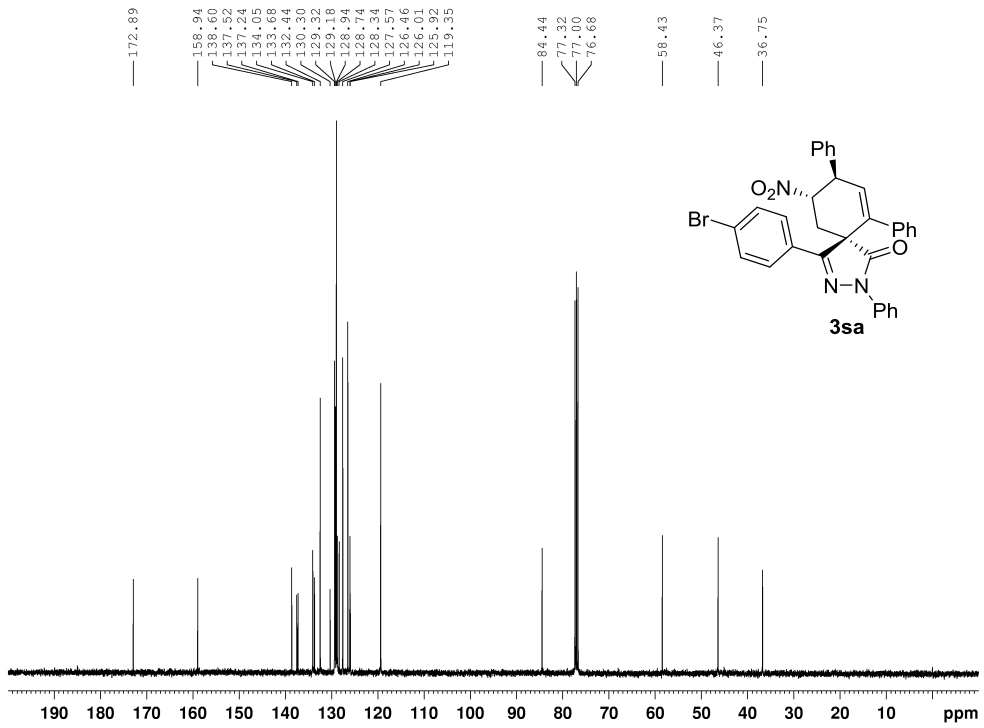
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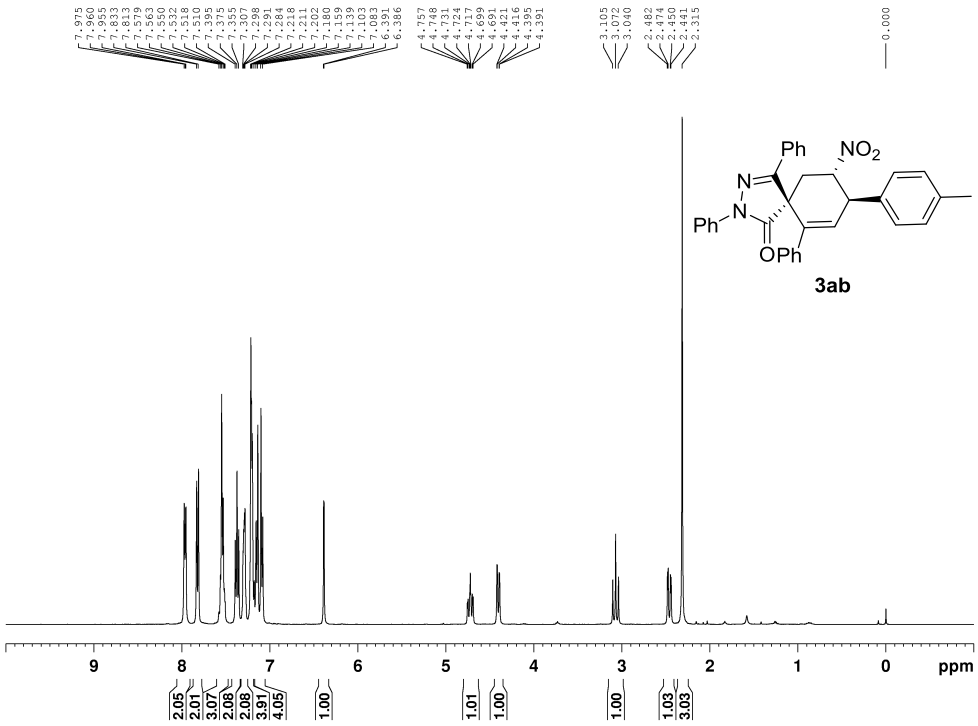
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N
Ph
OPh
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ppm
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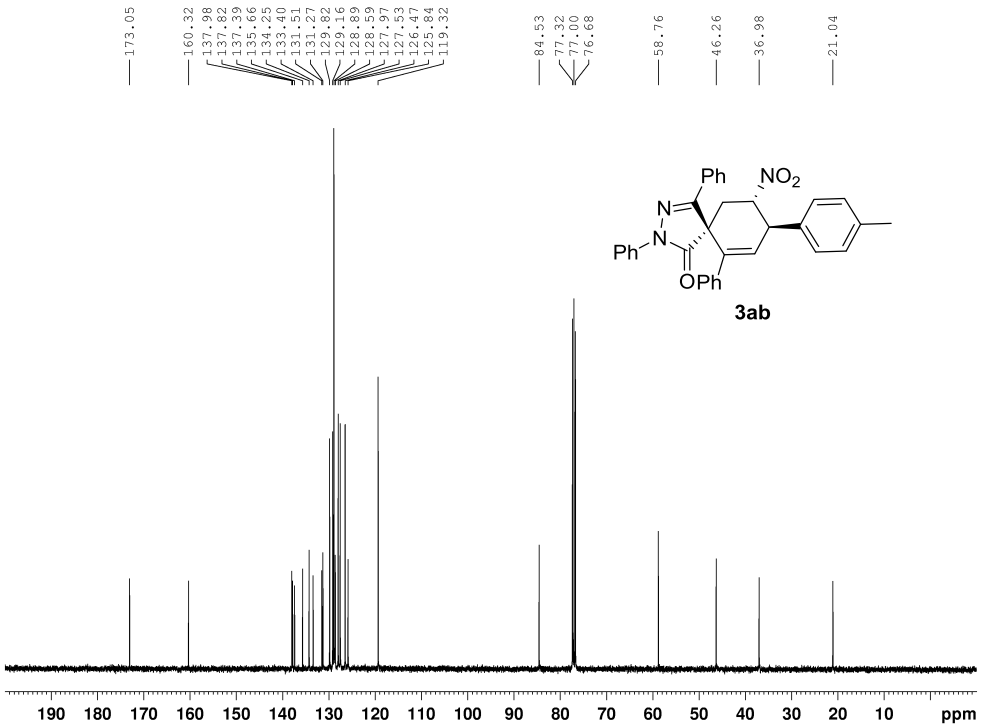
3.03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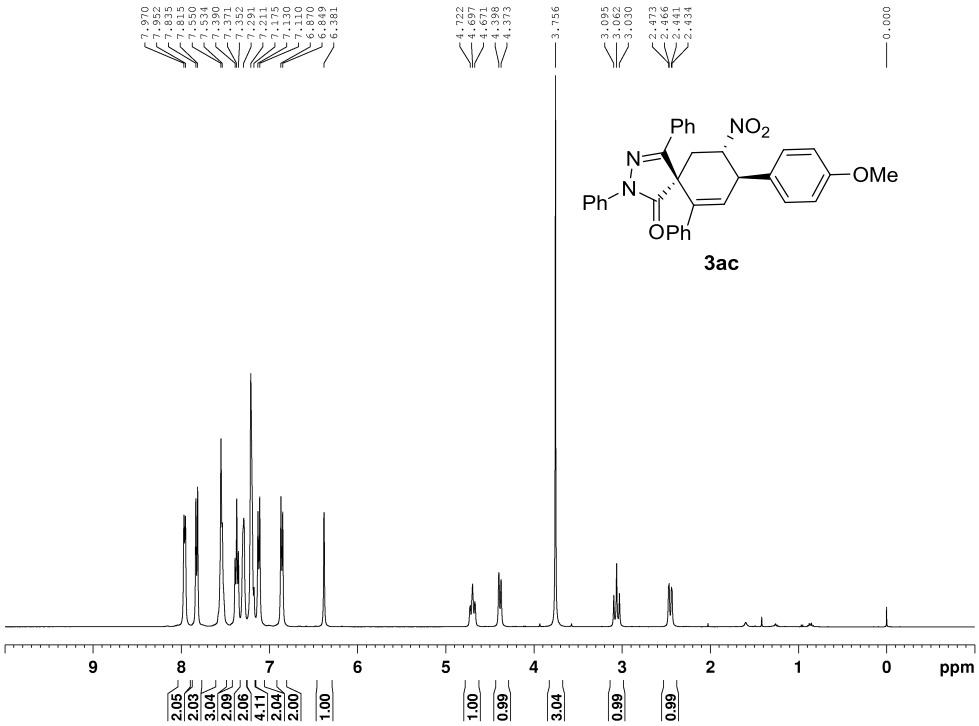
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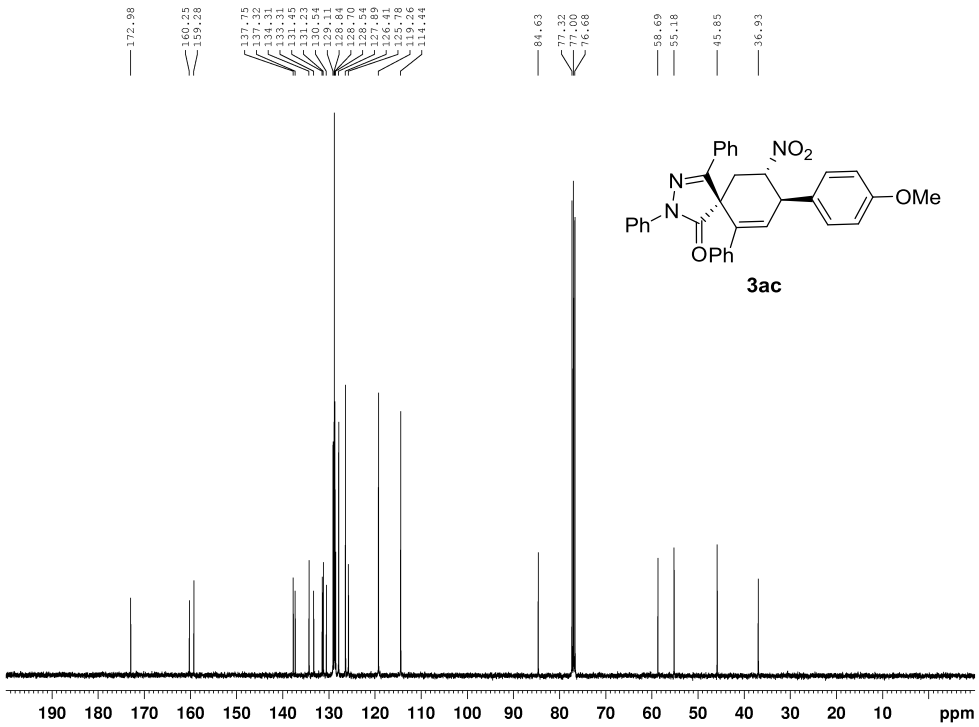
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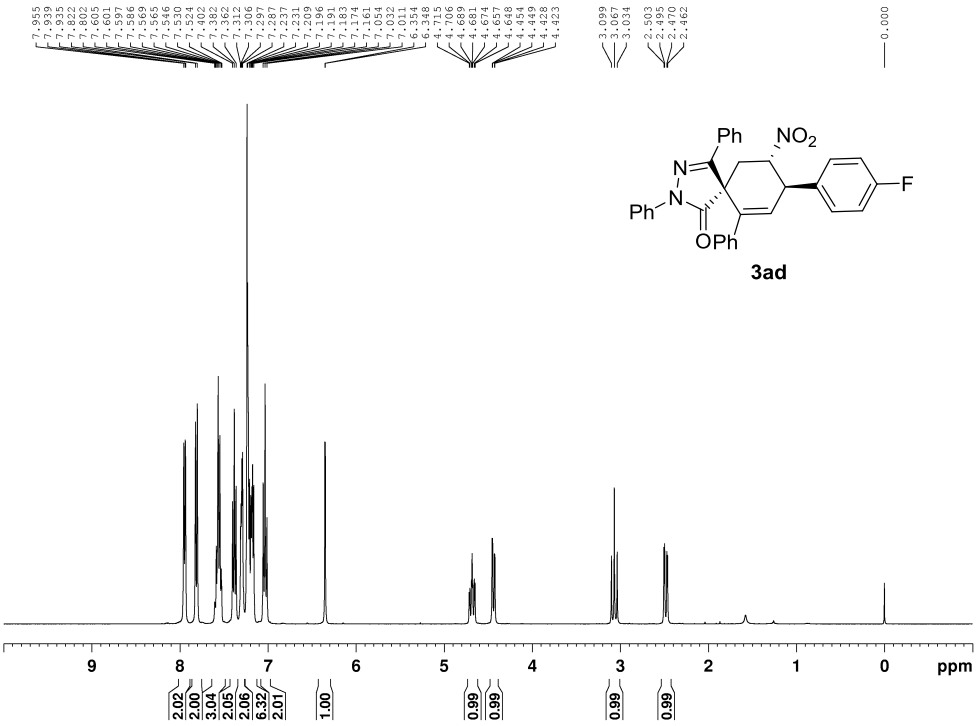
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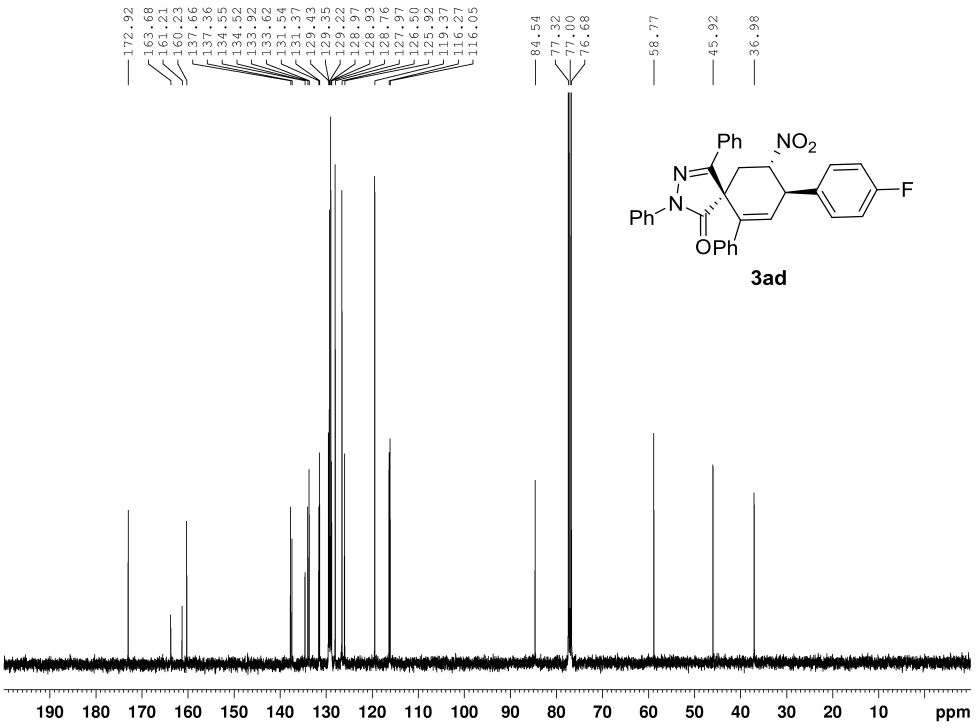
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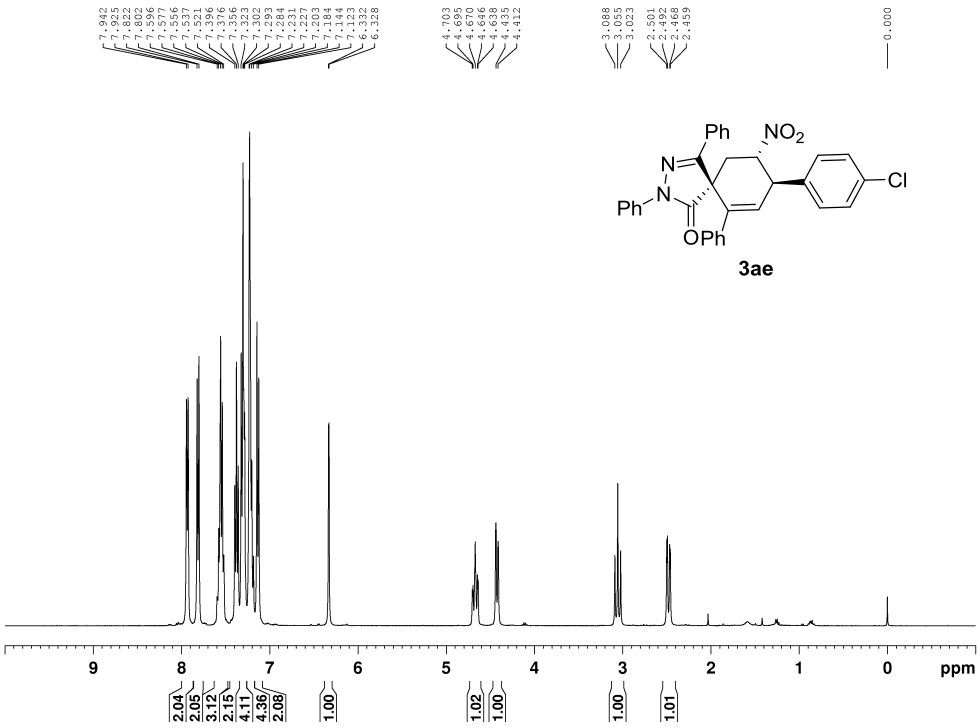
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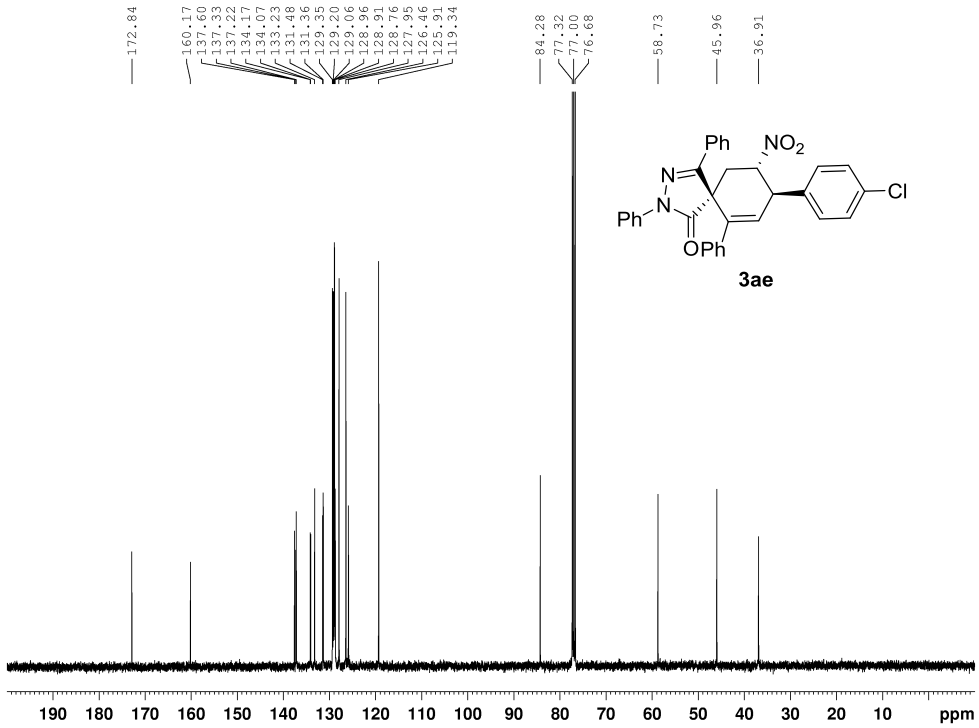
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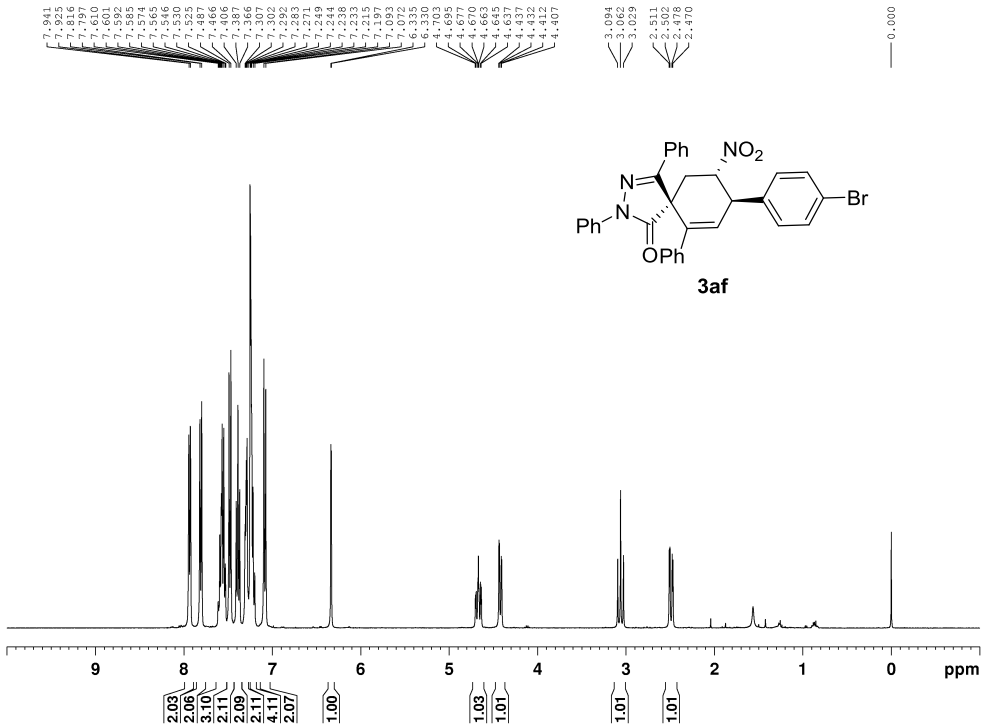
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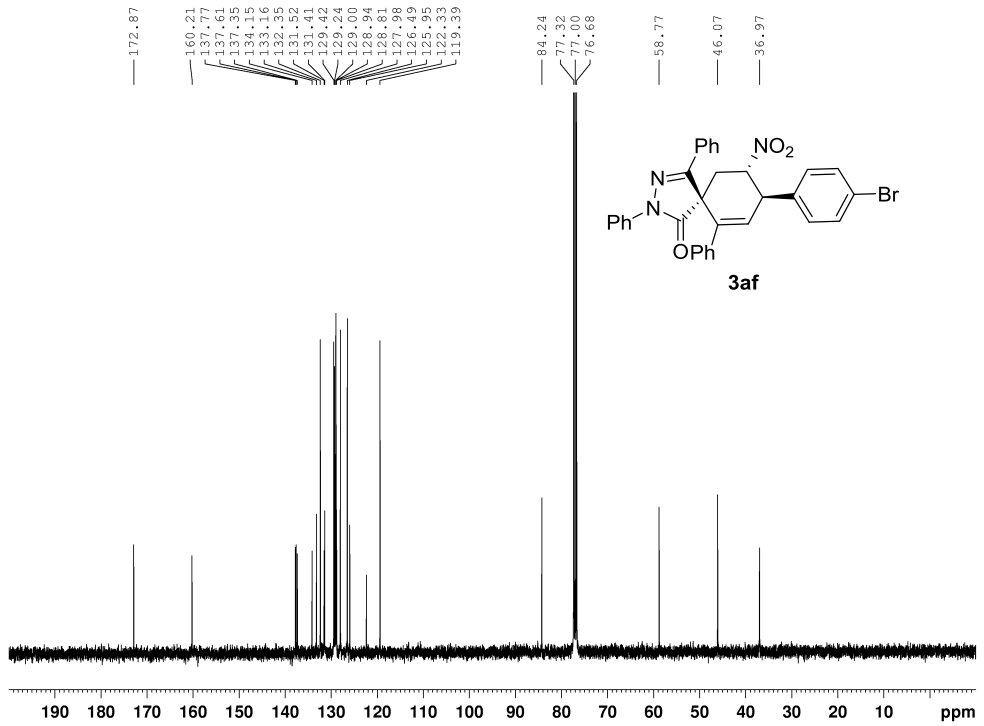
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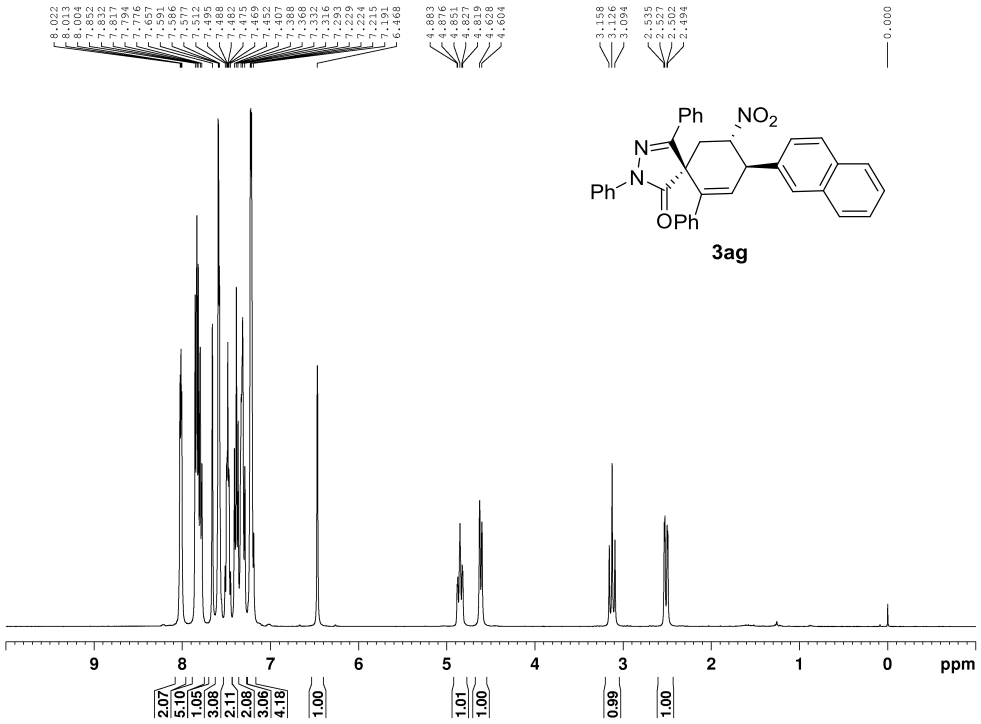
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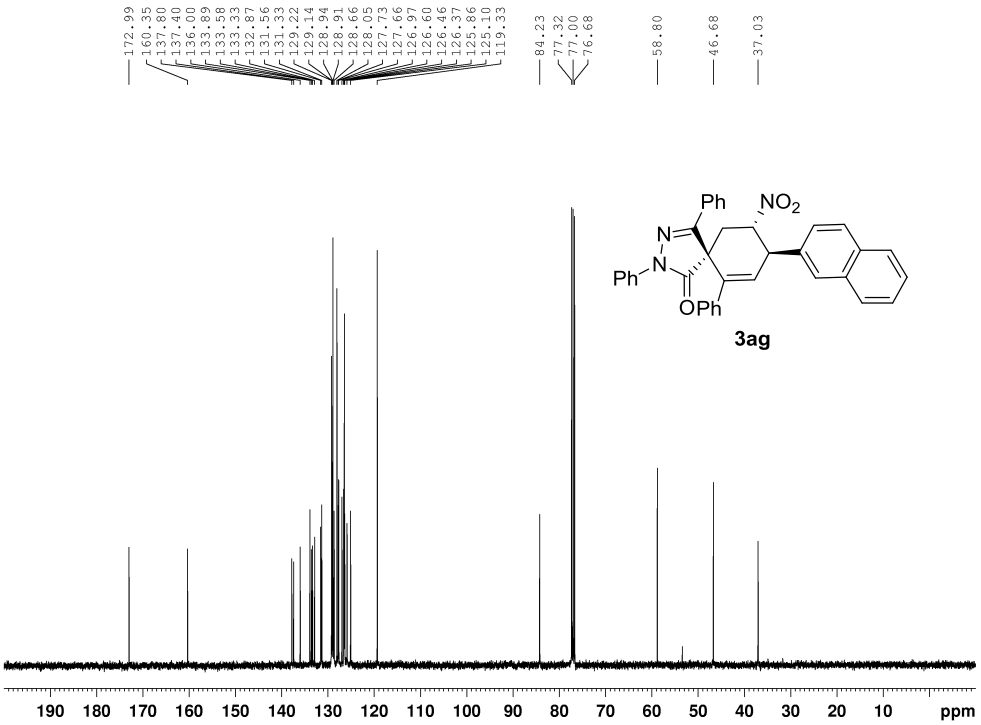
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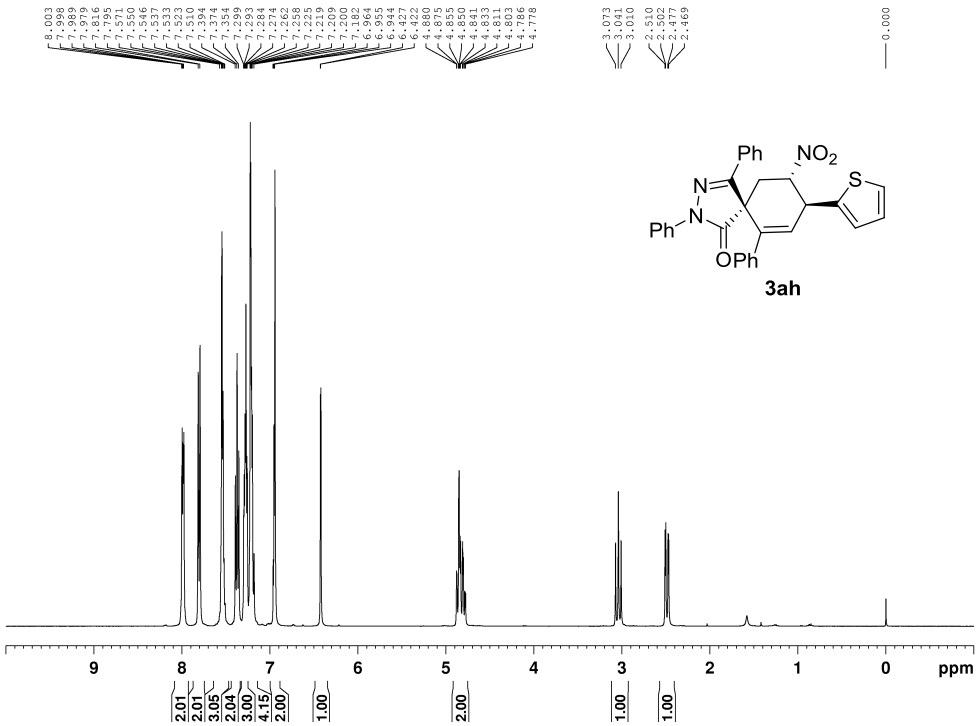
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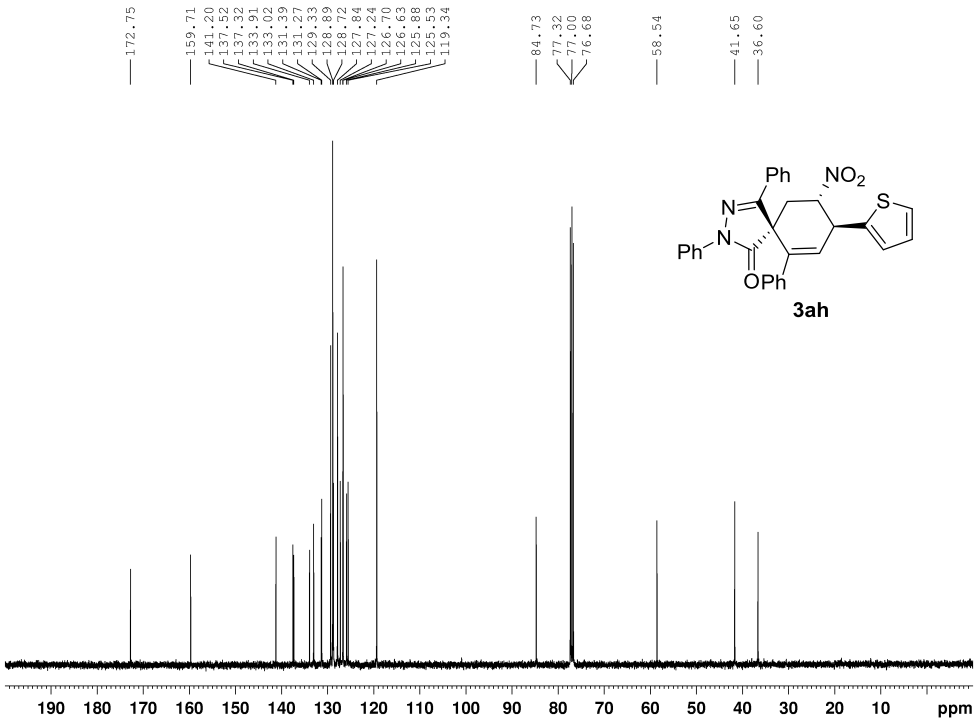
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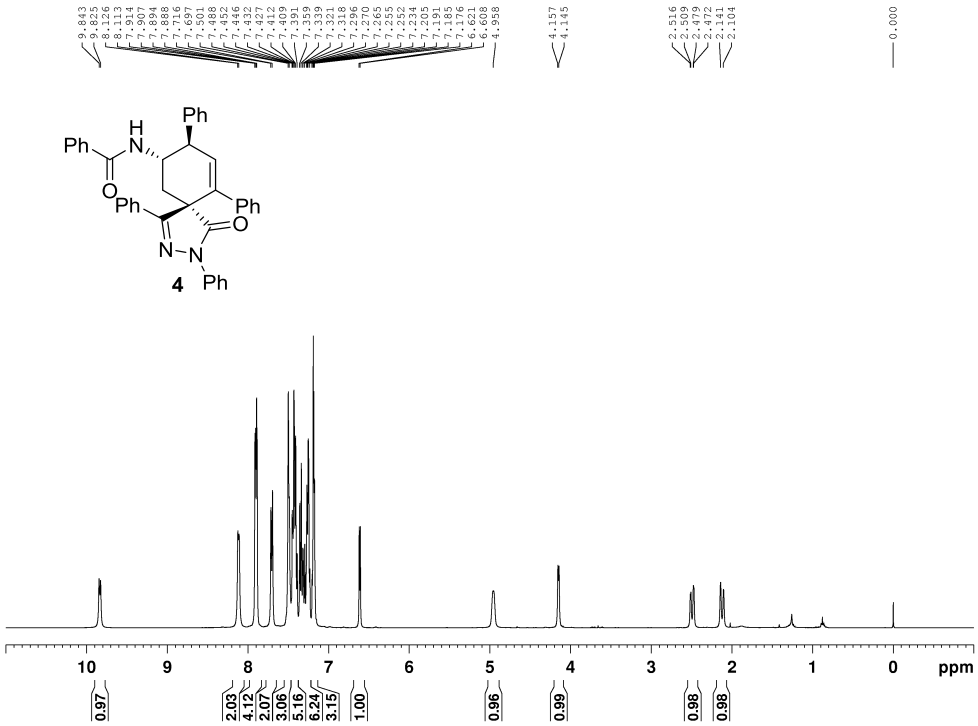
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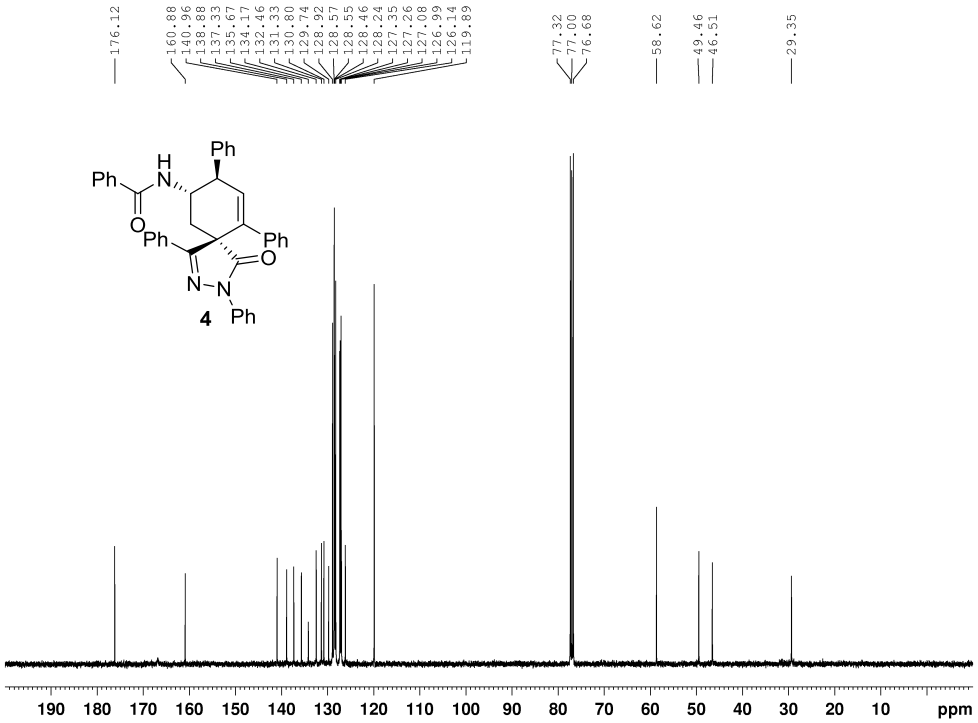
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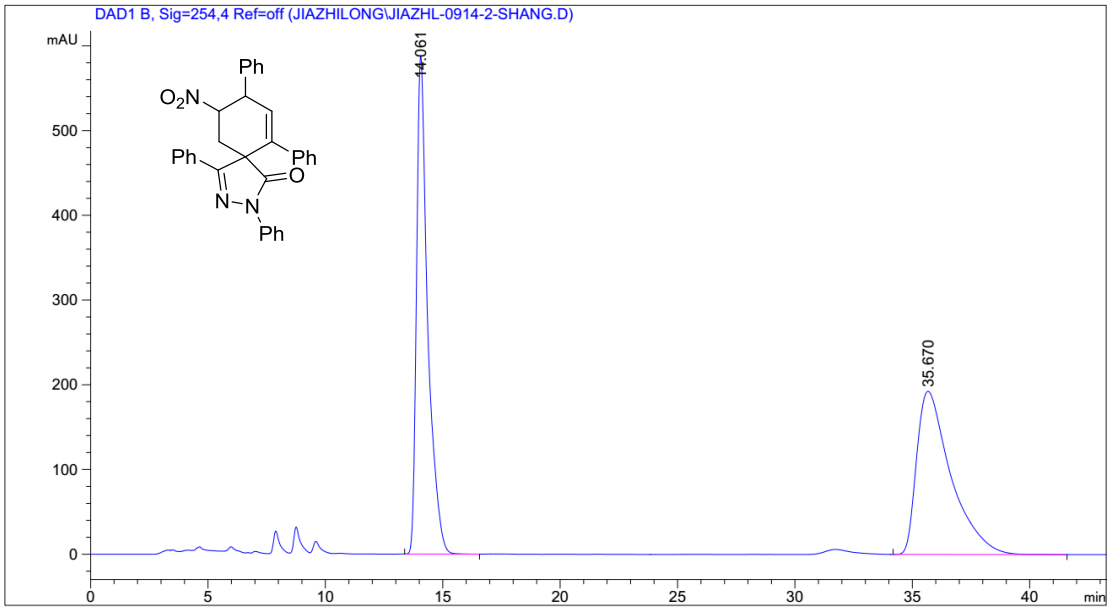
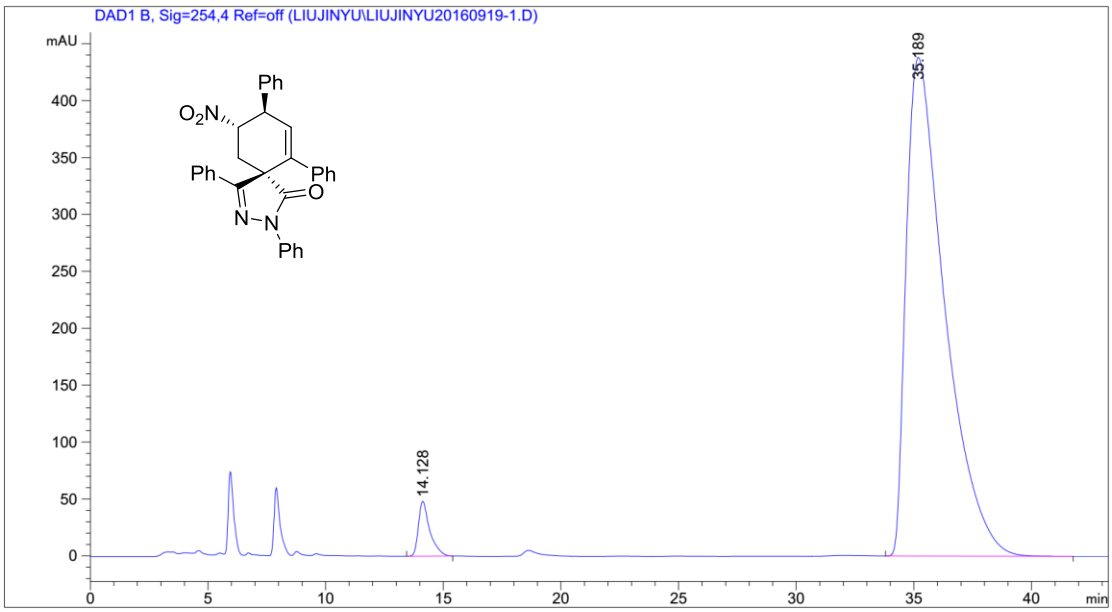
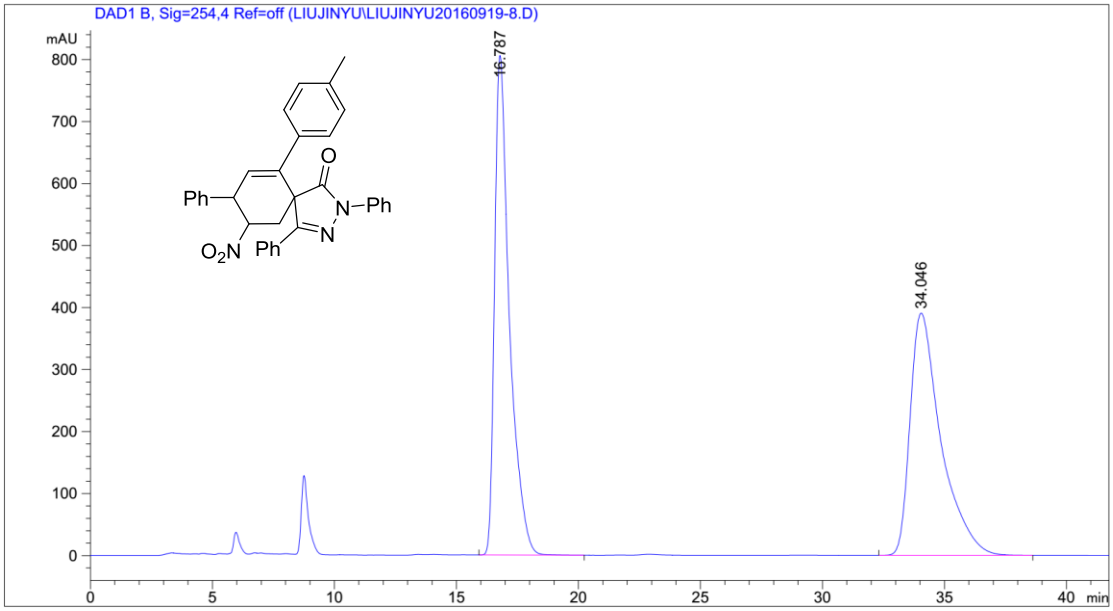


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	14.061	1.94587e4	587.71625	49.9851
2	DAD 254, 4 nm	35.670	1.94703e4	192.57596	50.0149

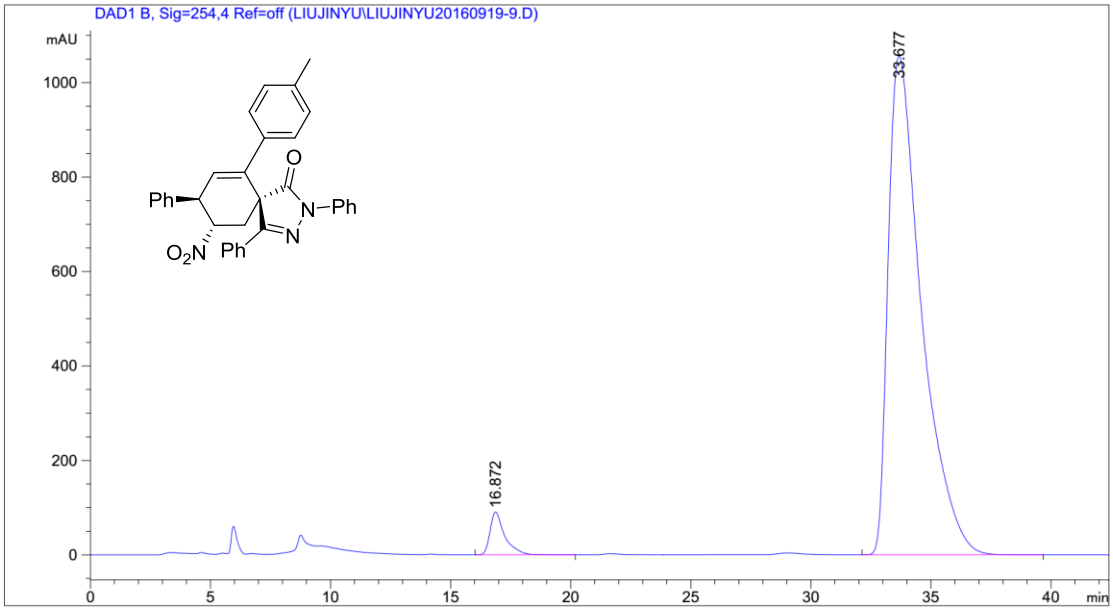


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	14.128	1613.55200	48.19073	3.1438
2	DAD 254, 4 nm	35.189	4.97111e4	438.17099	96.8562

3ba

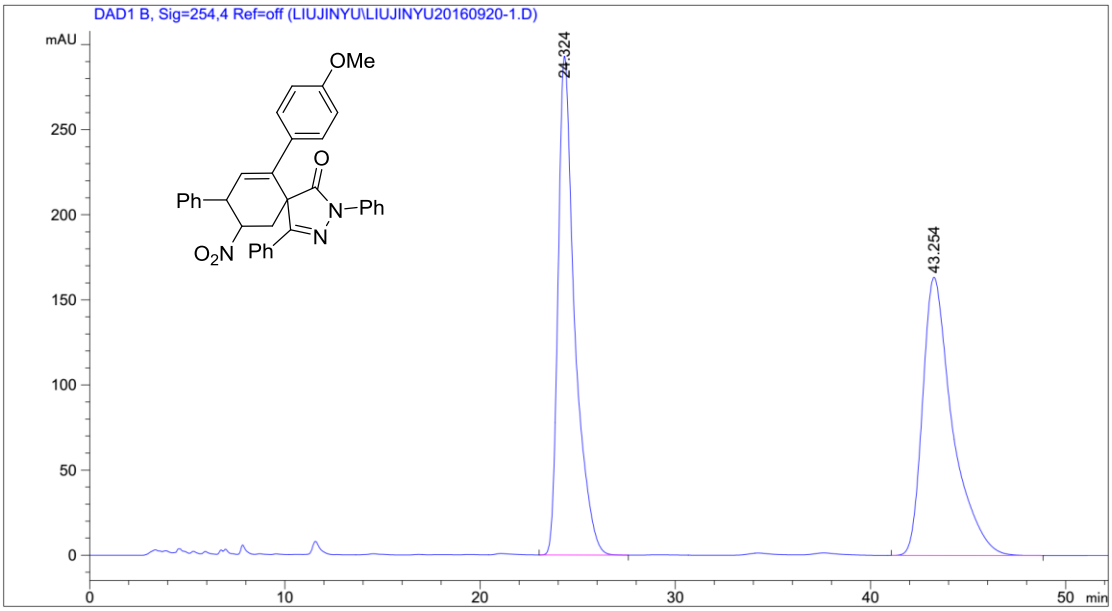


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	16.787	3.39976e4	805.60706	49.8460
2	DAD 254, 4 nm	34.046	3.42076e4	390.50558	50.1540

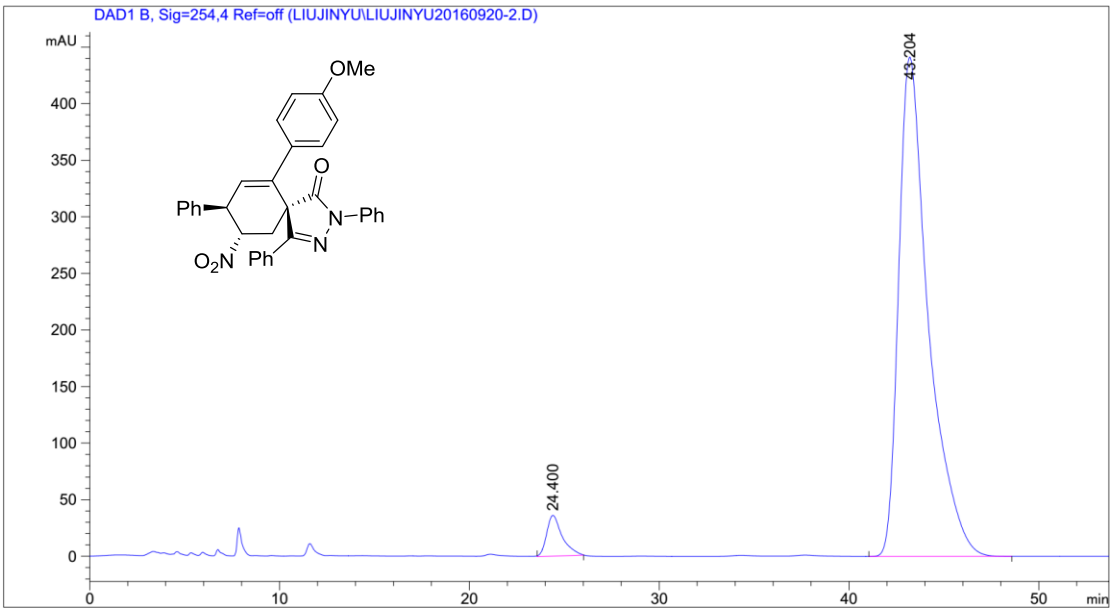


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	16.872	3813.70190	90.57460	3.6179
2	DAD 254, 4 nm	33.677	1.01599e5	1056.64990	96.3821

3ca

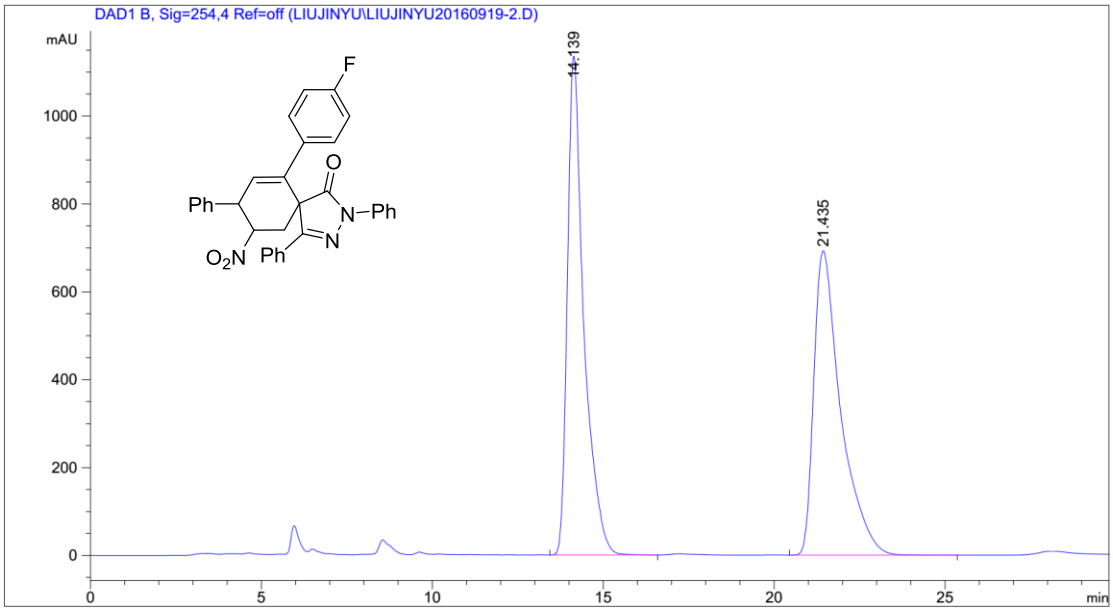


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	24.324	1.73093e4	293.10913	49. 9792
2	DAD 254, 4 nm	43.254	1.73237e4	163.34779	50. 0208

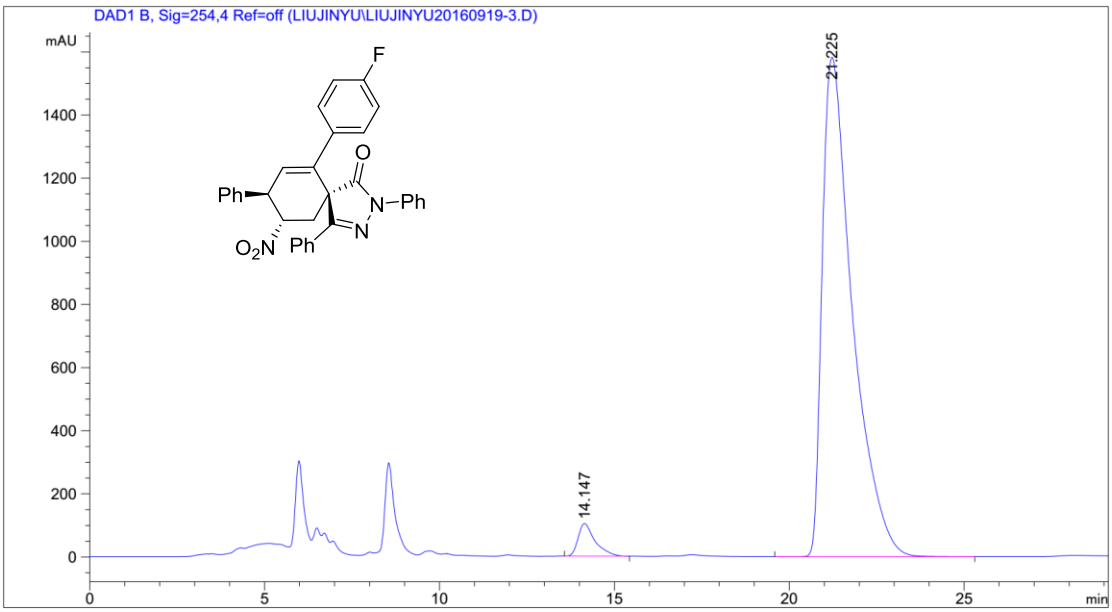


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	24.400	2047.32947	36.03970	4.0935
2	DAD 254, 4 nm	43.204	4.79672e4	441.26877	95.9065

3da

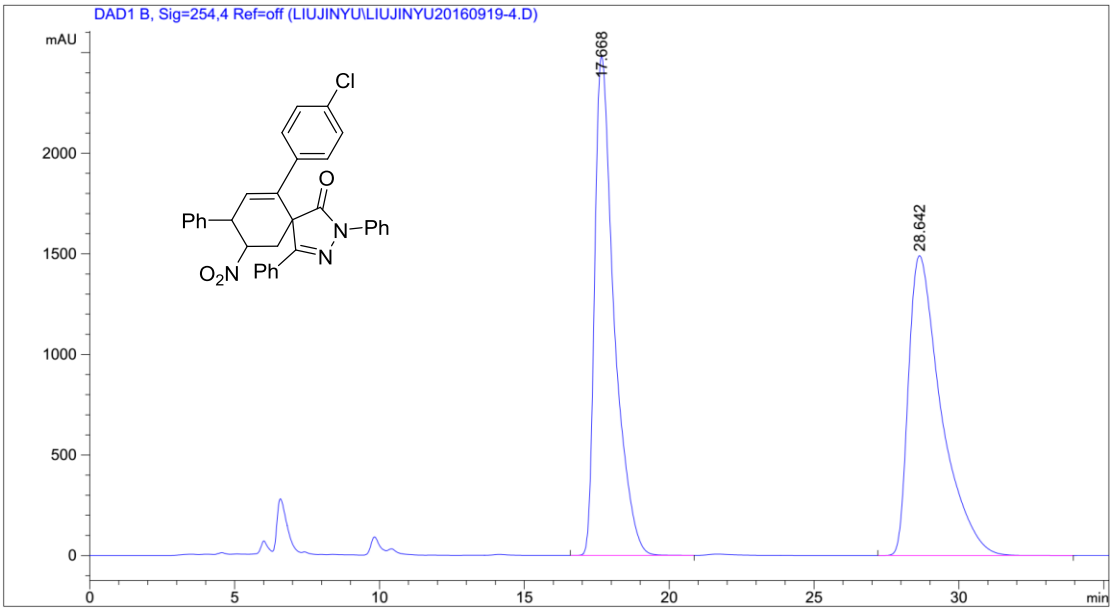


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	14.139	3.78930e4	1135.22058	50.0516
2	DAD 254, 4 nm	21.435	3.78148e4	692.26935	49.9484

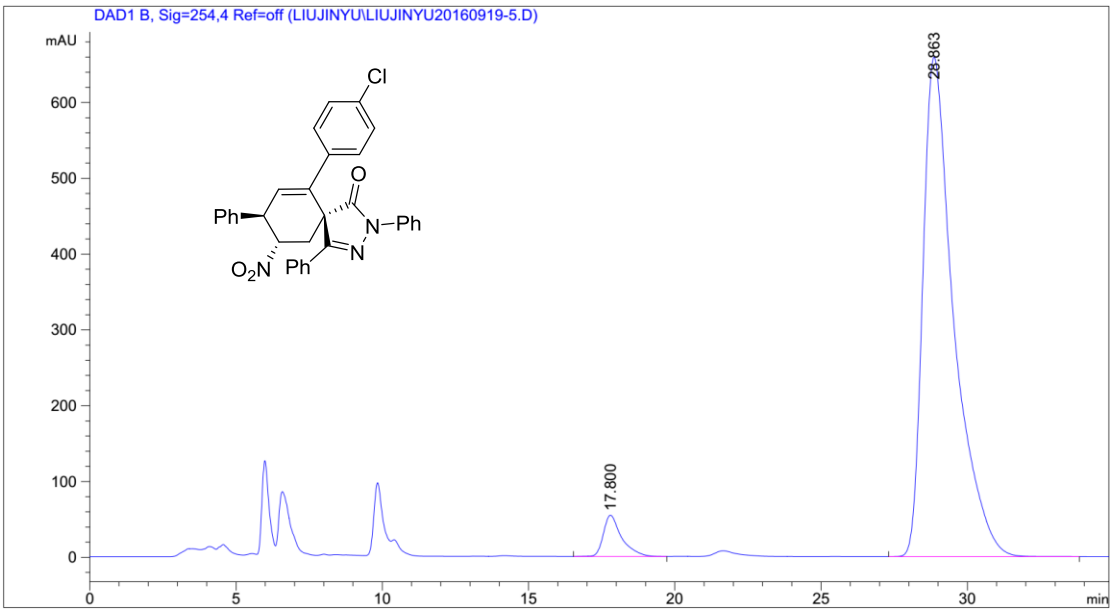


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	14.147	2047.32947	103.08821	3.5045
2	DAD 254, 4 nm	21.225	4.79672e4	1581.55688	96.4955

3ea

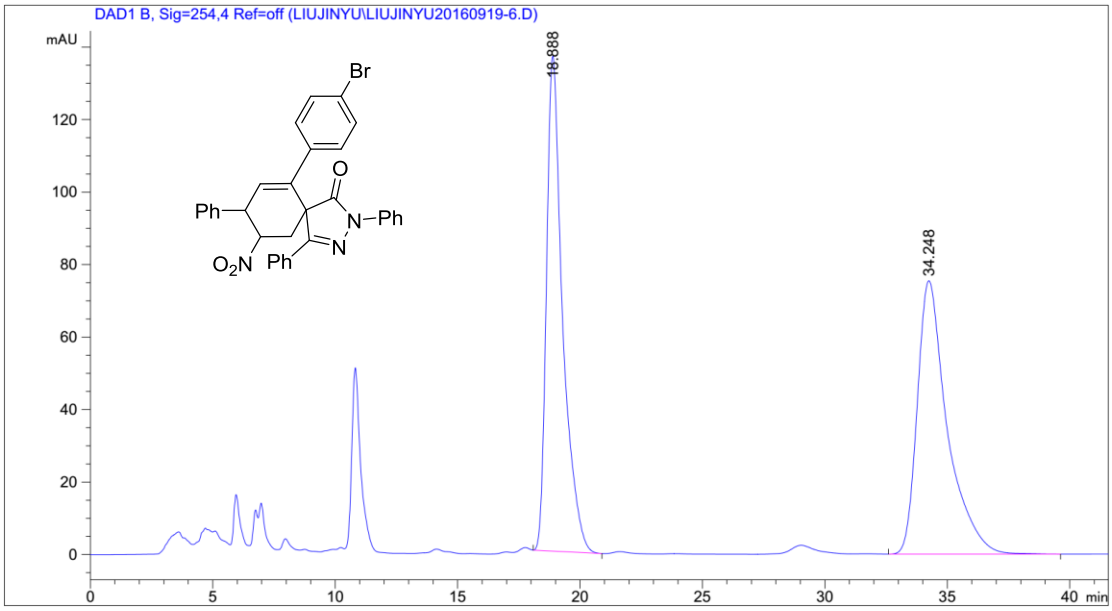


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	17.668	1.15194e5	2481.37842	49.6608
2	DAD 254, 4 nm	28.642	1.16768e5	1489.74304	50.3392

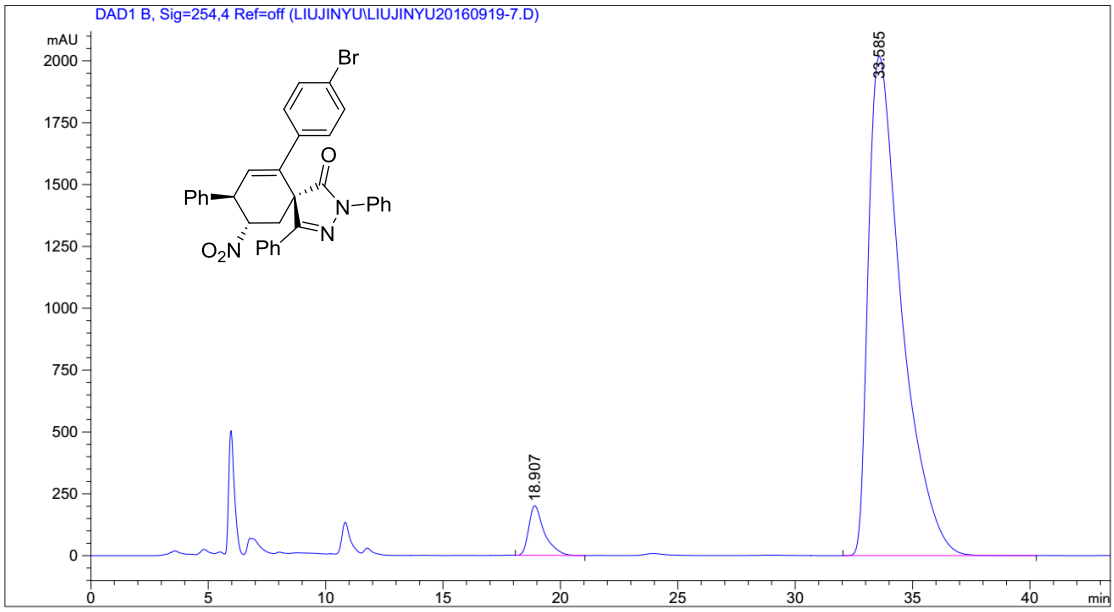


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	17.800	2353.36279	54.45732	4.6529
2	DAD 254, 4 nm	28.863	4.82251e4	658.91144	95.3471

3fa

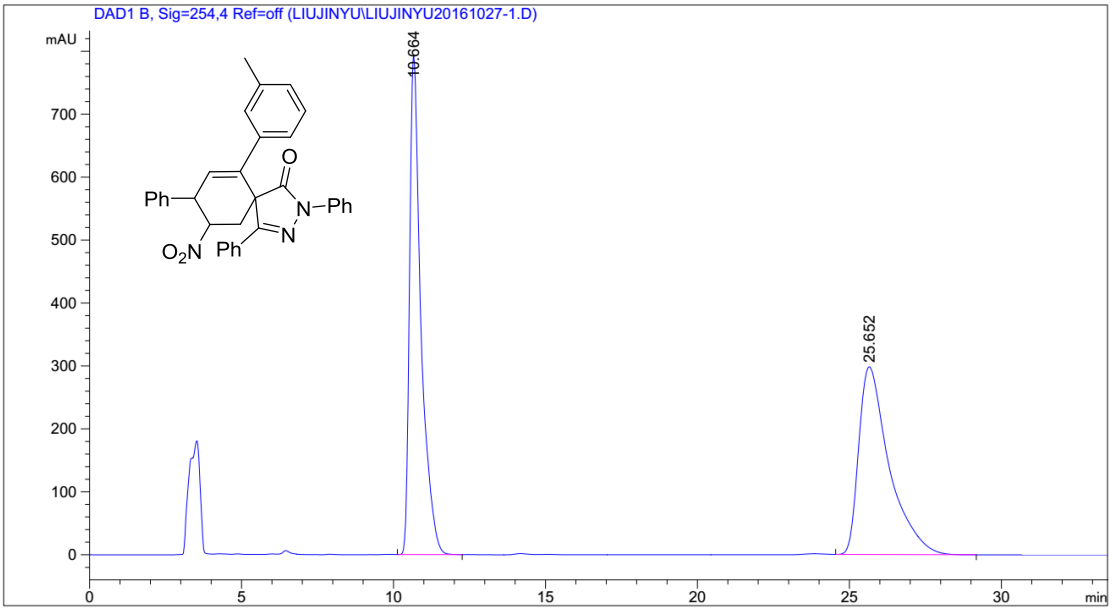


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	18.888	6237.25244	136.55716	49.3588
2	DAD 254, 4 nm	34.248	6399.29834	75.40398	50.6412

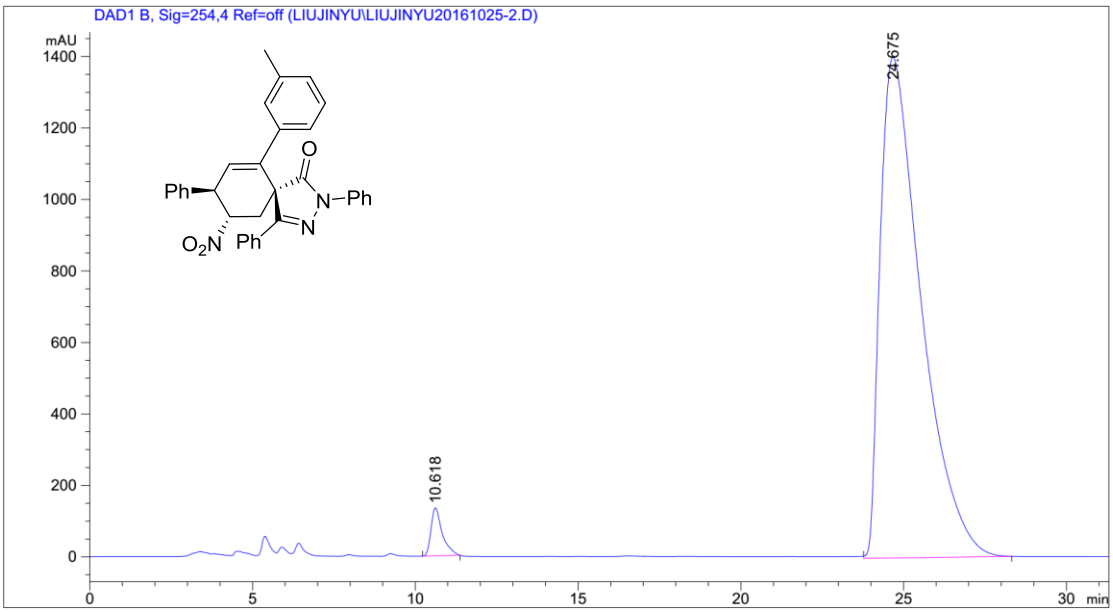


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	18.907	9228.79785	200.43303	4.4431
2	DAD 254, 4 nm	33.585	1.98480e5	2018.09277	95.5569

3ga

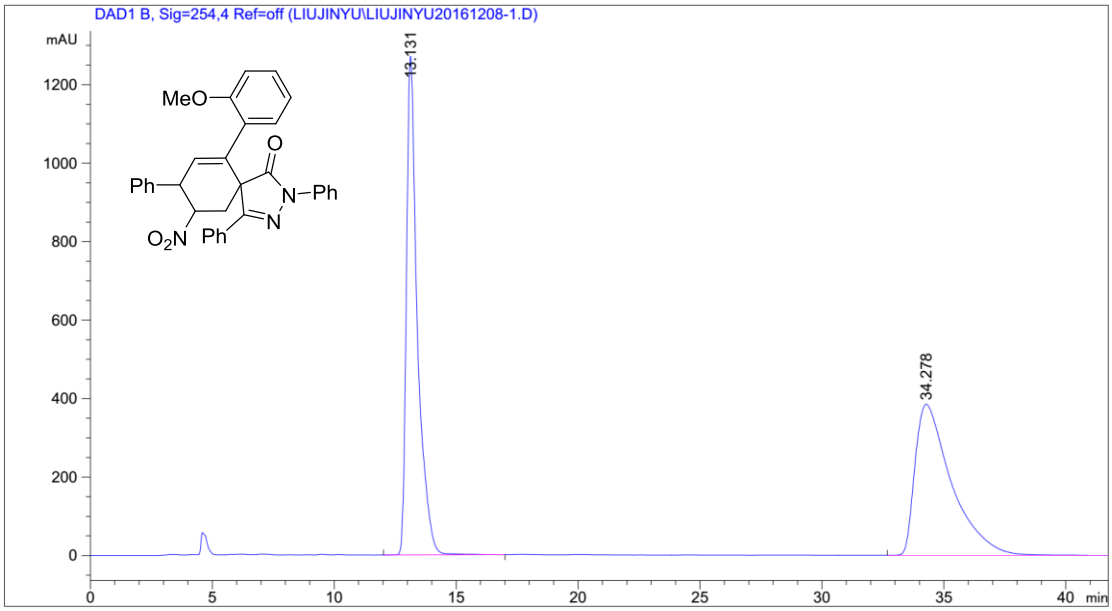


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	10.664	2.07157e4	792.48541	50.0233
2	DAD 254, 4 nm	25.652	2.06964e4	298.07260	49.9767

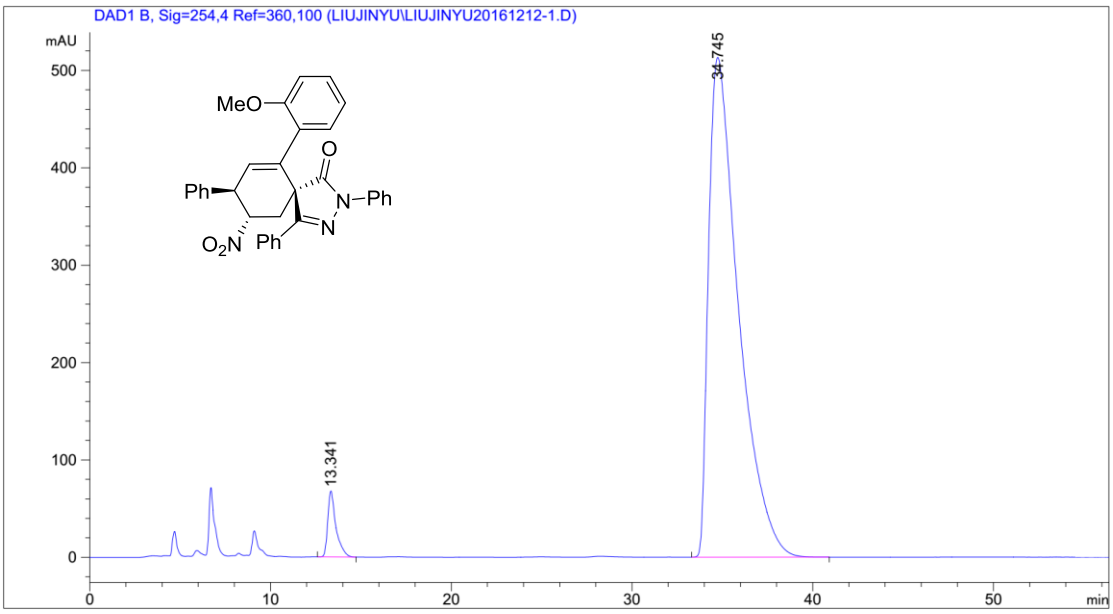


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	10.618	3207.32373	134.42850	2.5585
2	DAD 254, 4 nm	24.675	1.22154e5	1401.31506	97.4415

3ha

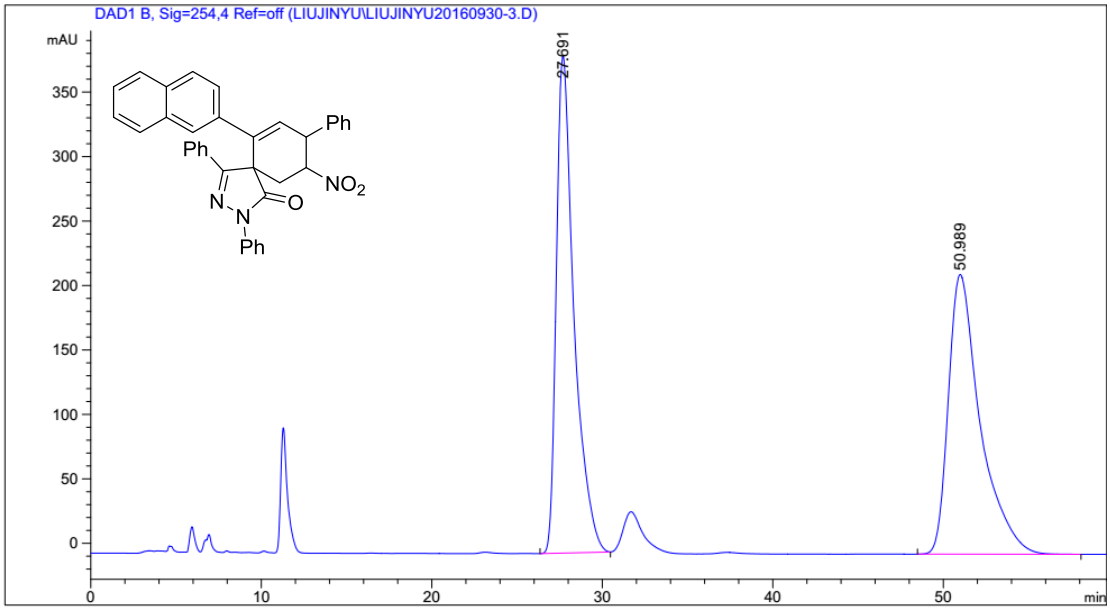


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	13.131	3.97403e4	1271.35876	49.9233
2	DAD 254, 4 nm	34.278	3.98624e4	384.80548	50.0767

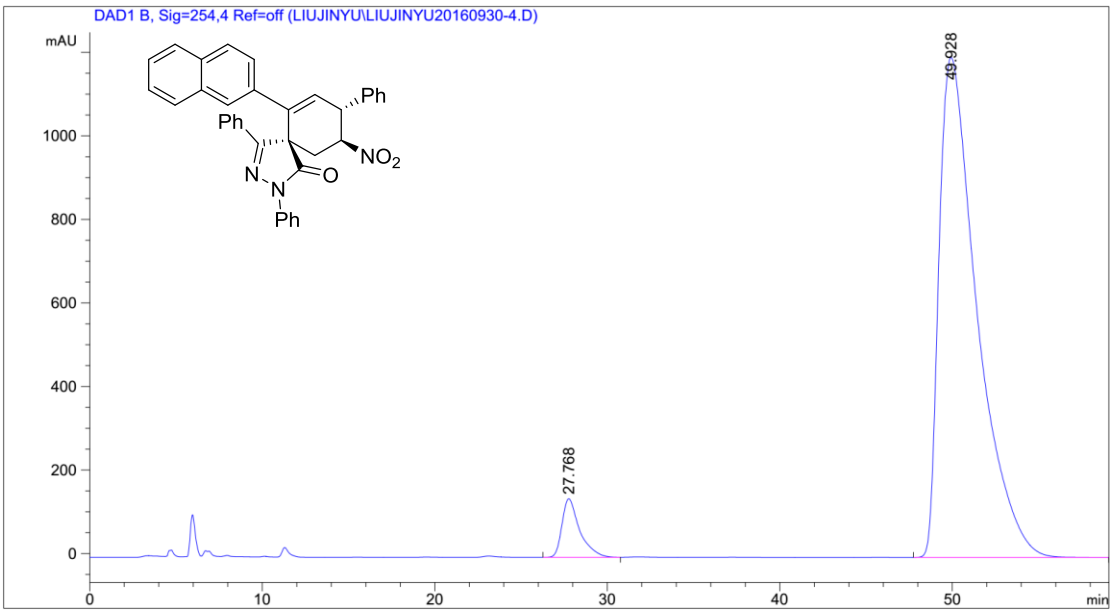


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	13.341	2132.37256	67.68431	3.4981
2	DAD 254, 4 nm	34.745	5.88261e4	513.09235	96.5019

3ia

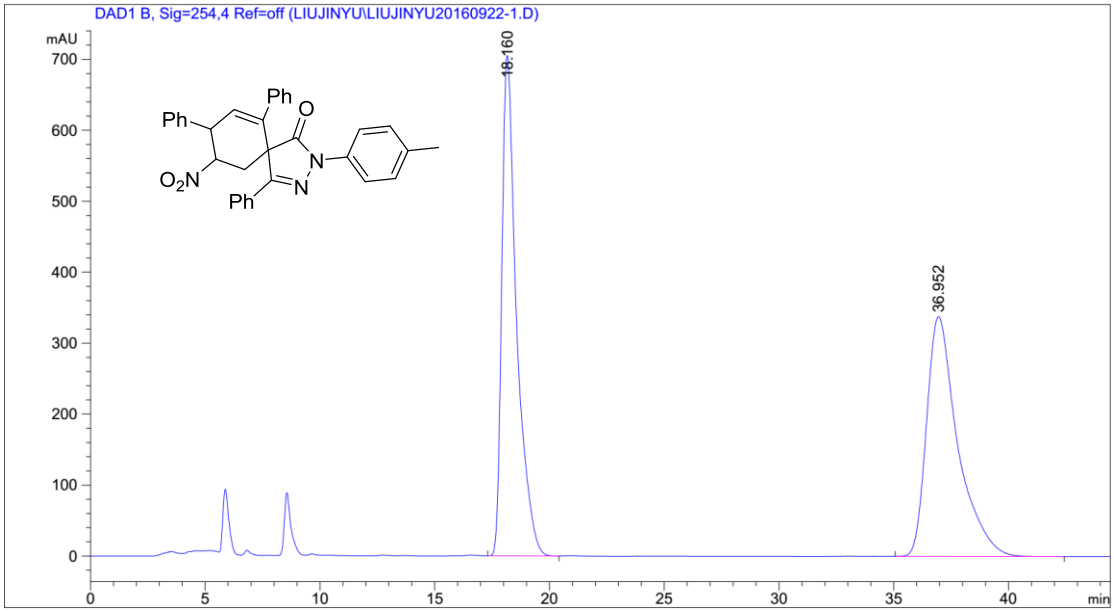


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	27.691	2.77887e4	385.68631	49.7314
2	DAD 254, 4 nm	50.989	2.80889e4	216.88777	50.2686

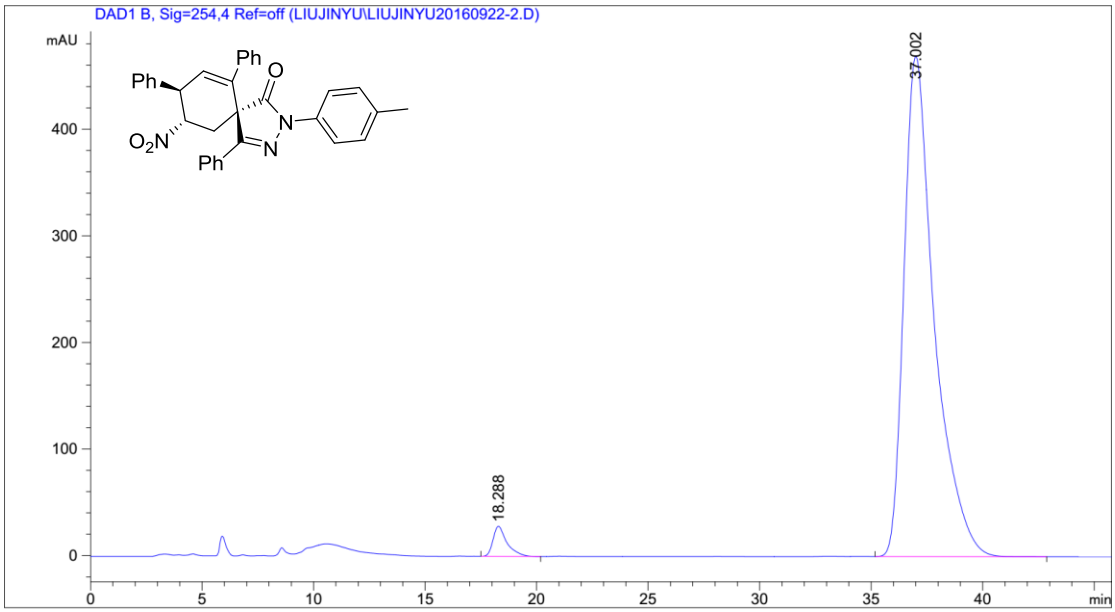


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	27.768	9921.38477	140.19441	5.1639
2	DAD 254, 4 nm	49.928	1.82208e5	1196.53003	94.8361

3ja

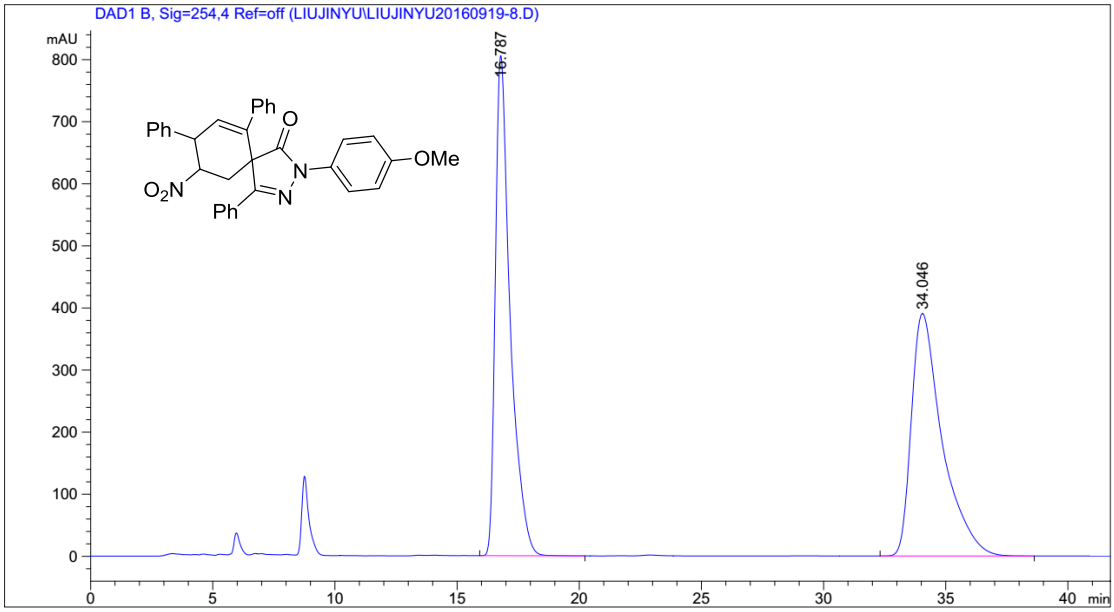


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	18.160	3.16177e4	705.08154	49.9459
2	DAD 254, 4 nm	36.952	3.16862e4	337.75668	50.0541

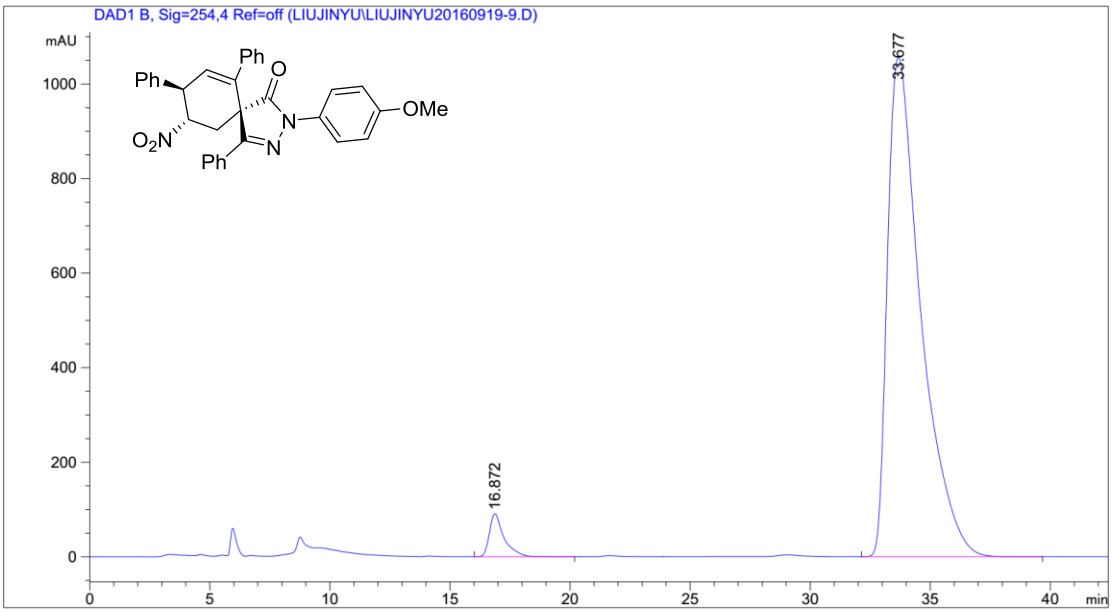


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	18.288	1215.54248	28.18168	2.6693
2	DAD 254, 4 nm	37.002	4.43222e4	469.08536	97.3307

3ka

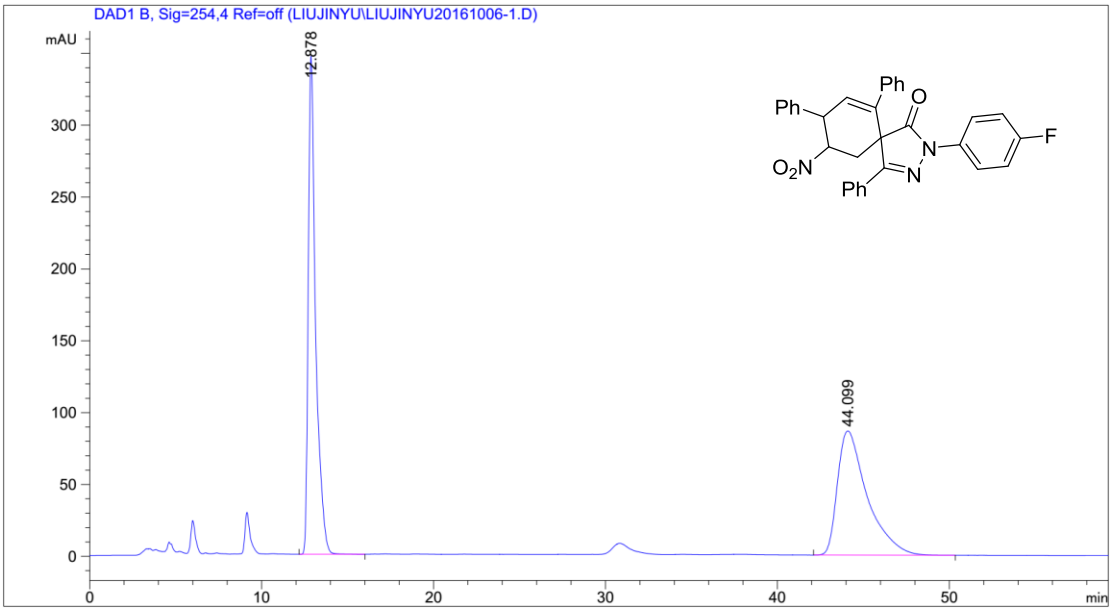


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	16.787	3.39976e4	805.60706	49.8460
2	DAD 254, 4 nm	34.046	3.42076e4	390.50558	50.1540

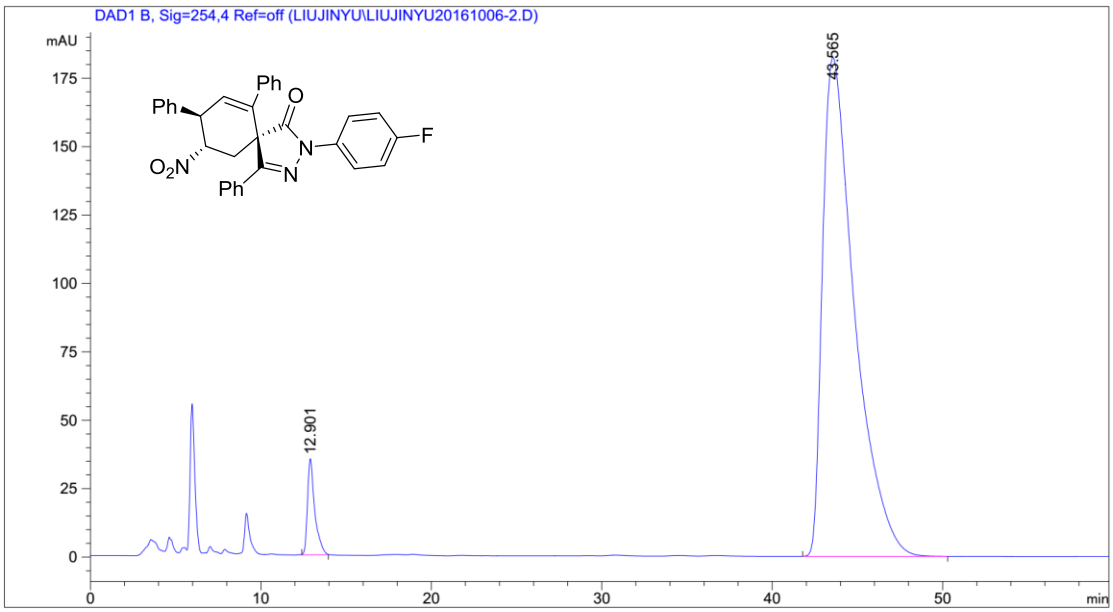


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	16.872	3813.70190	90.57460	3.6179
2	DAD 254, 4 nm	33.677	1.01599e5	1056.64990	96.3821

3la

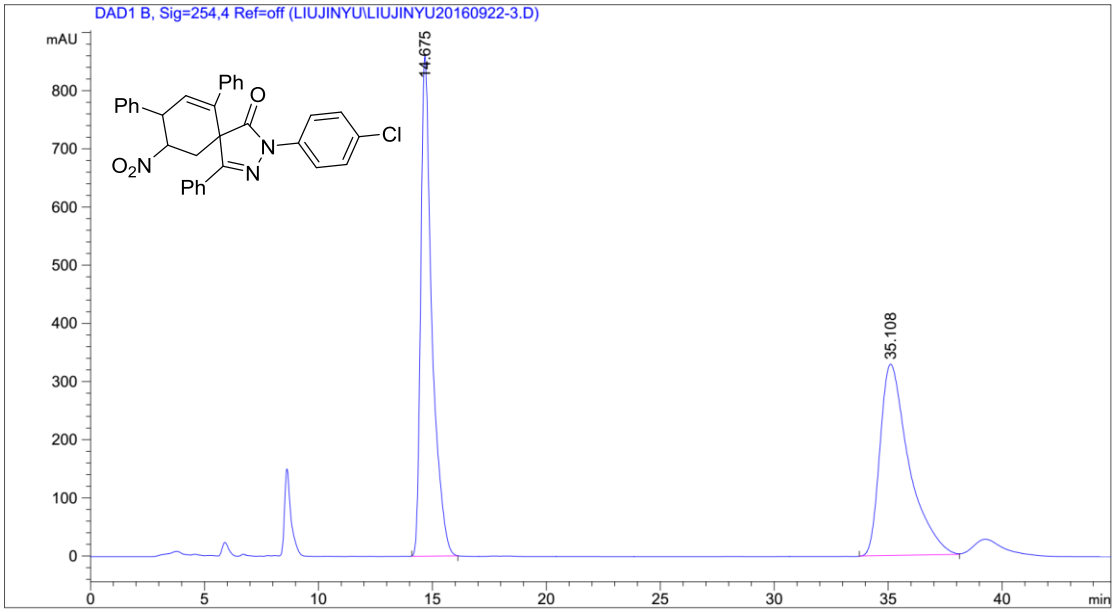


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	12.878	1.03456e4	346.72775	49.9739
2	DAD 254, 4 nm	44.099	1.03565e4	86.37258	50.0261

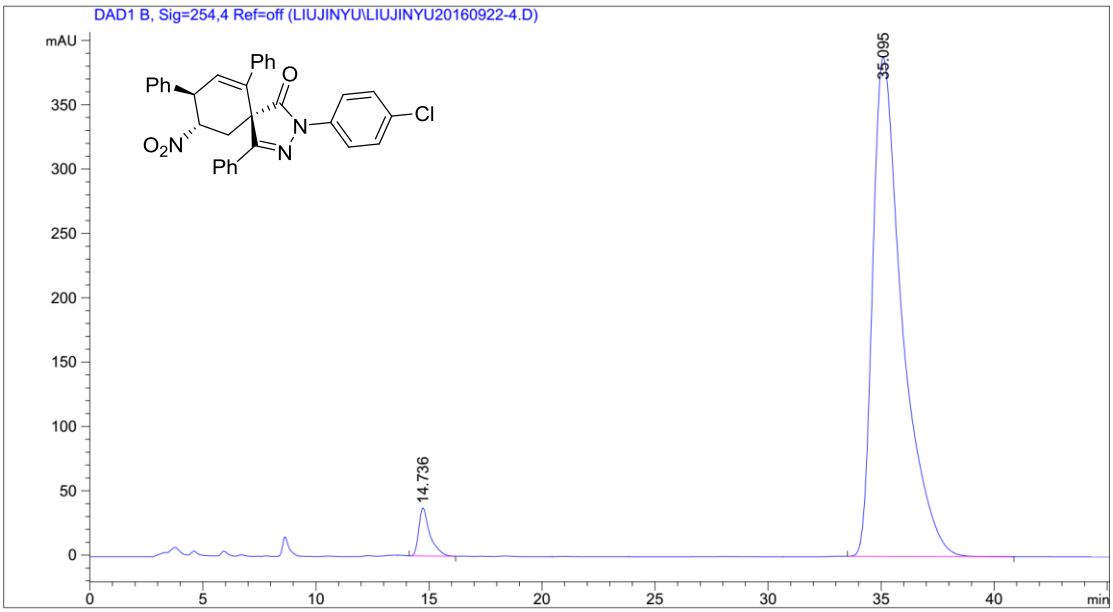


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	12.901	1040.60632	35.18246	4.1935
2	DAD 254, 4 nm	43.555	2.37744e4	182.36853	95.8065

3ma

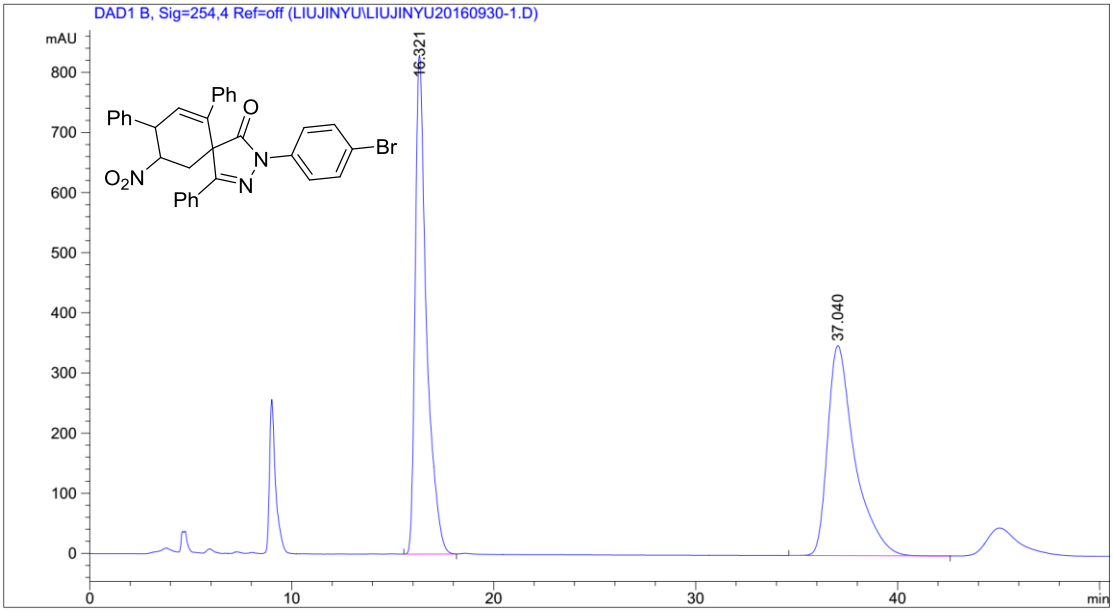


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	14.675	2.93669e4	860.56207	50.3432
2	DAD 254, 4 nm	35.108	2.89665e4	328.81561	49.6568

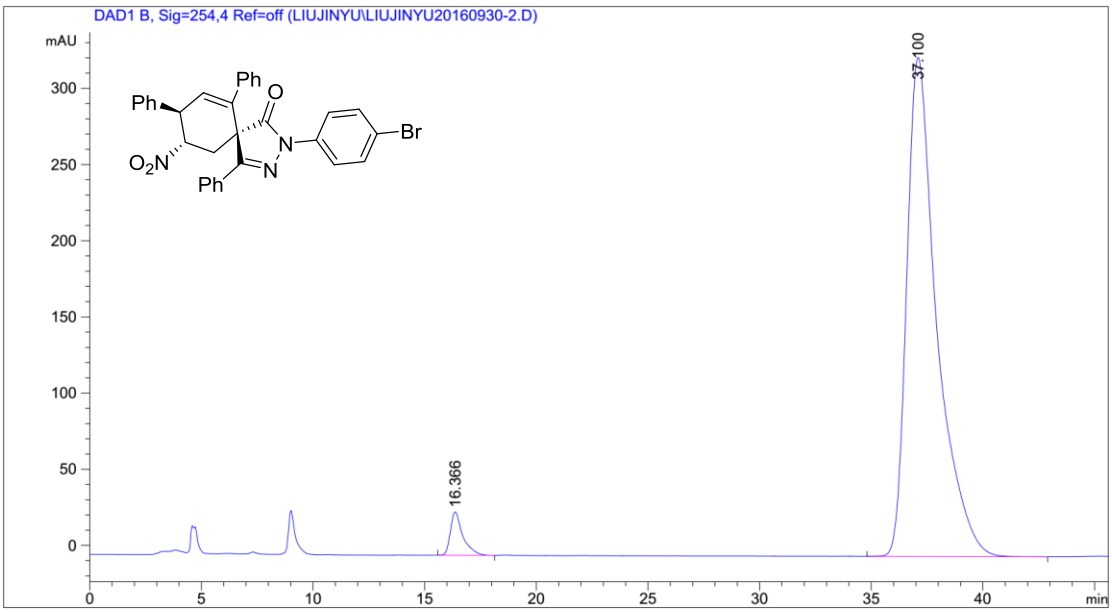


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	14.736	1274.39758	37.28904	3.5041
2	DAD 254, 4 nm	35.095	3.50943e4	387.85580	96.4959

3na

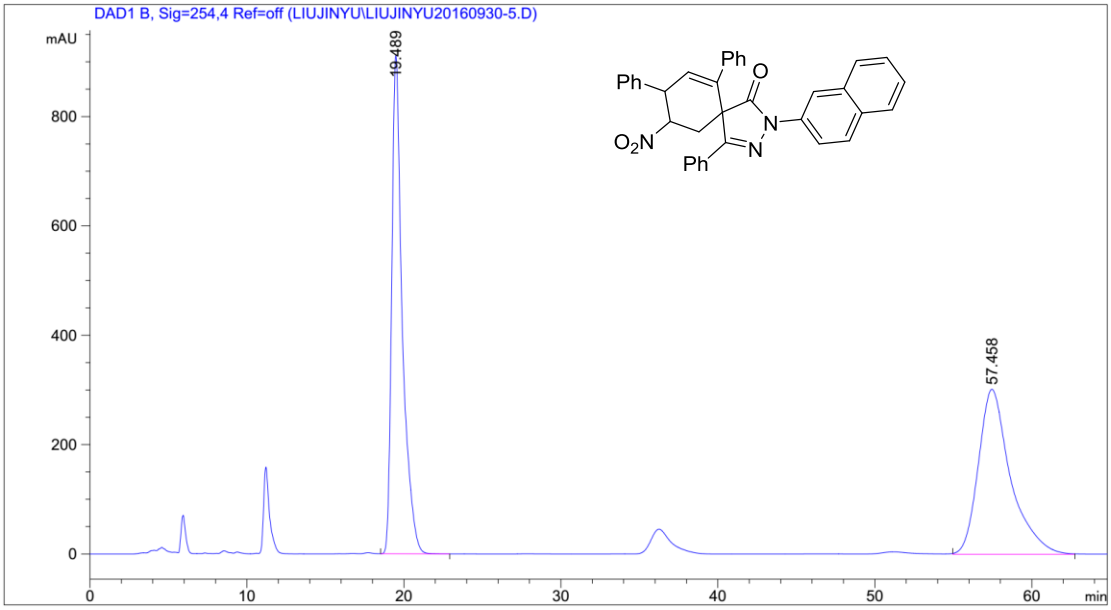


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	16.321	3.23320e4	829.49323	49.8378
2	DAD 254, 4 nm	37.040	3.25425e4	349.03583	50.1622

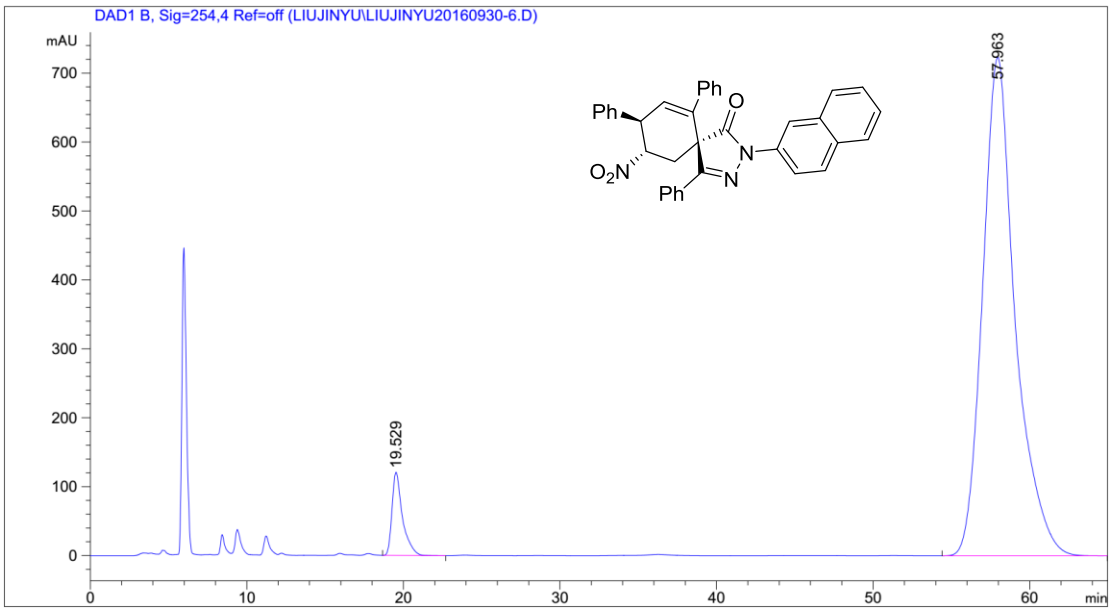


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	16.336	1090.99475	28.45909	3.4554
2	DAD 254, 4 nm	37.100	3.04828e4	327.57755	96.5446

3oa

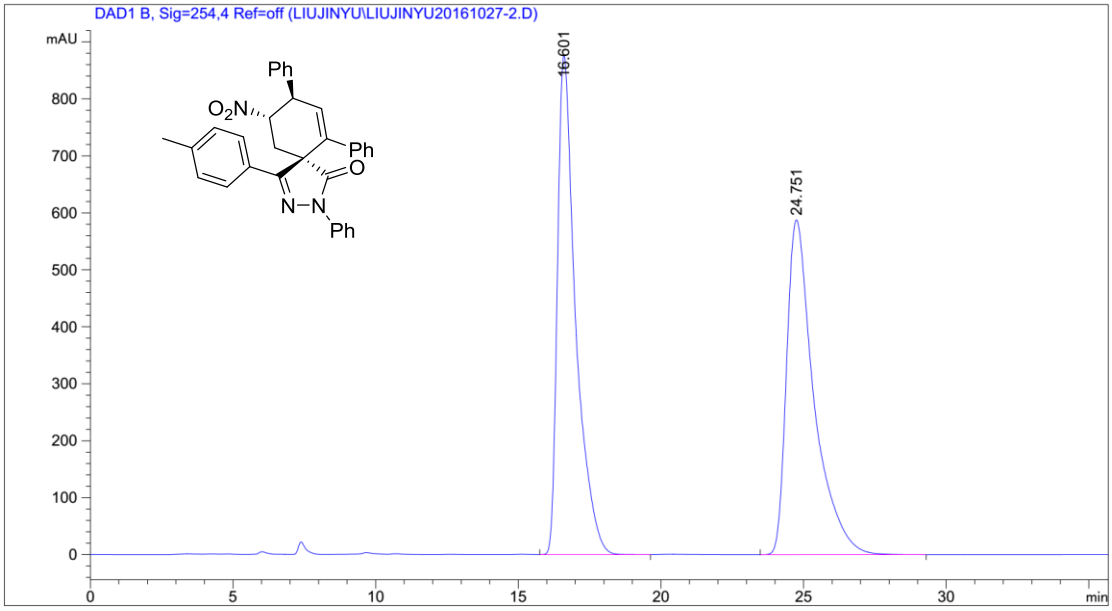


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	19.489	4.27190e4	911.46130	49.8603
2	DAD 254, 4 nm	57.458	4.29584e4	301.80850	50.1397

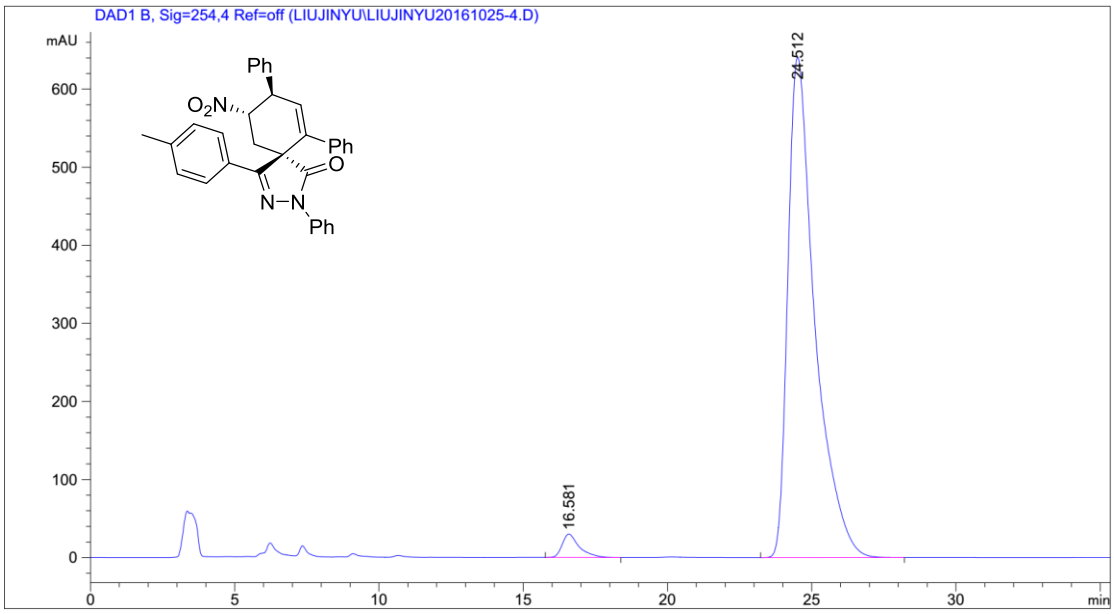


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	19.529	5634.22363	120.66306	5.1173
2	DAD 254, 4 nm	57.963	1.04467e5	723.27502	94.8827

3pa

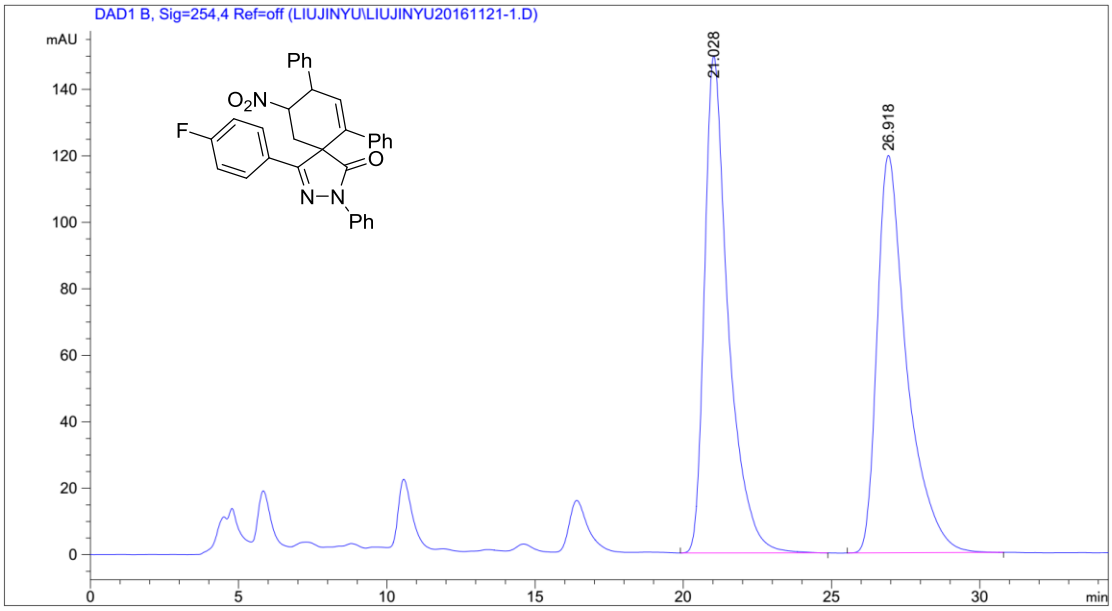


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	16.601	3.87132e4	876.29370	49.6992
2	DAD 254, 4 nm	24.751	3.91819e4	587.80853	50.3008

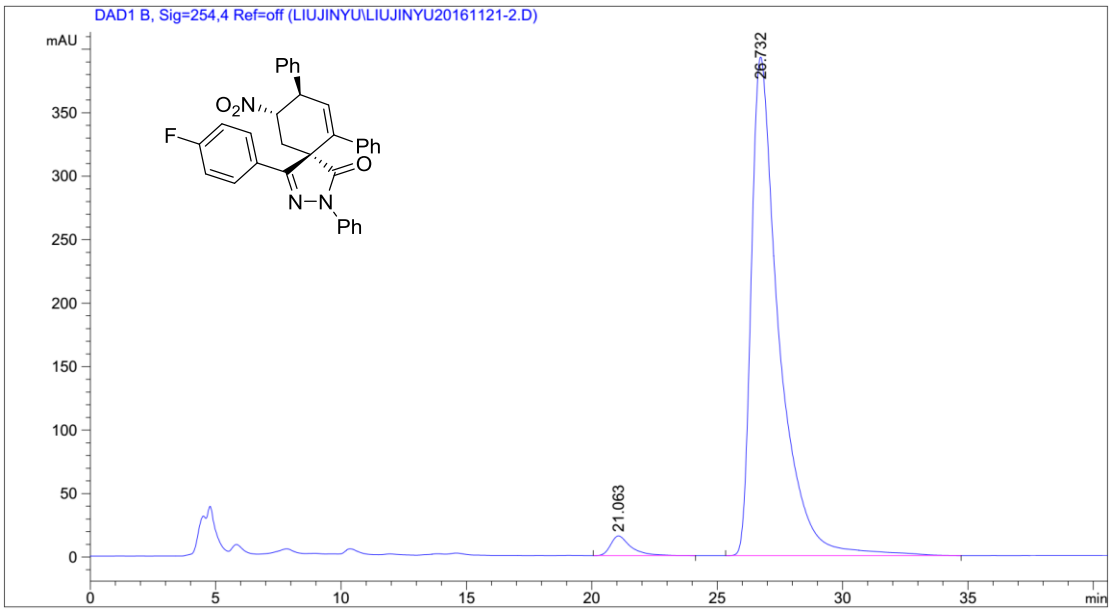


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	16.581	1229.10620	29.93784	2.8670
2	DAD 254, 4 nm	24.512	4.16424e4	640.73468	97.1330

3qa

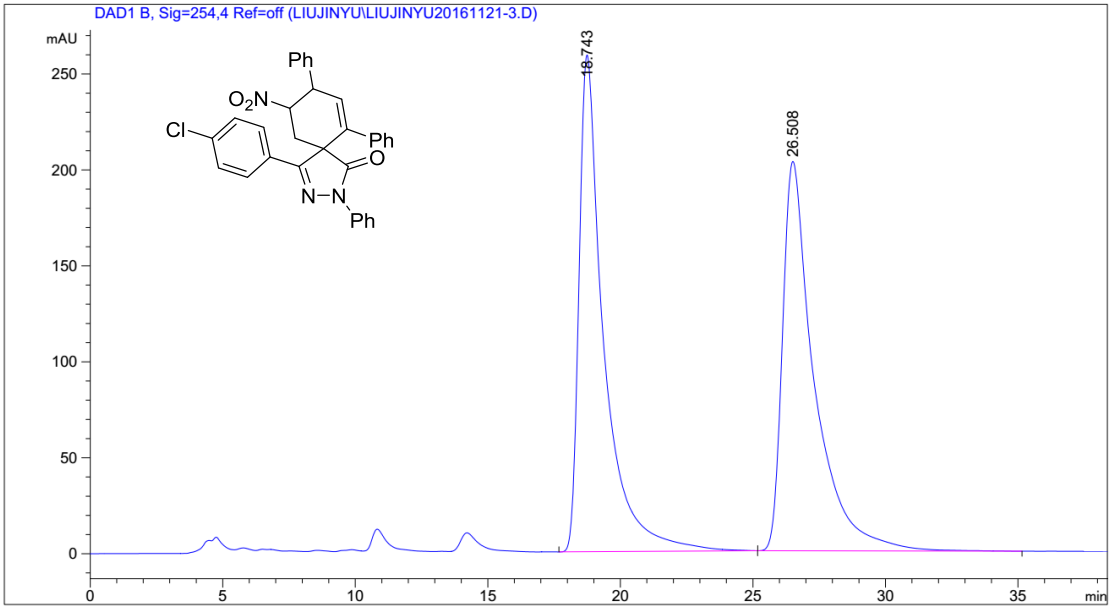


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	21.028	8328.39648	149.47665	50.0088
2	DAD 254, 4 nm	26.918	8325.45410	119.56281	49.9912

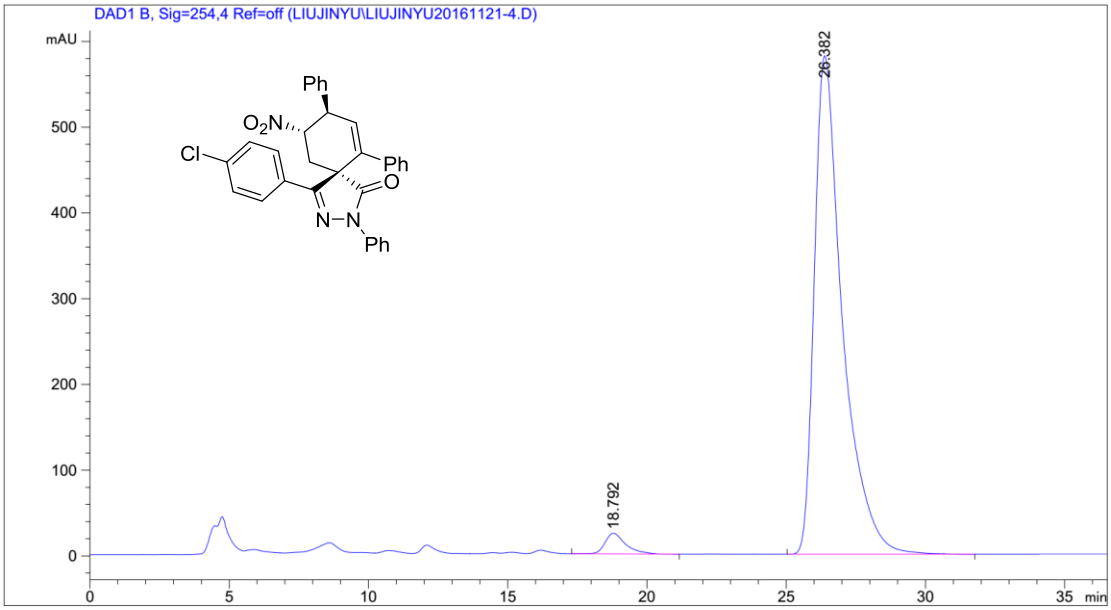


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	21.063	862.00897	15.41220	2.7941
2	DAD 254, 4 nm	26.732	2.99886e4	392.66519	97.2059

3ra

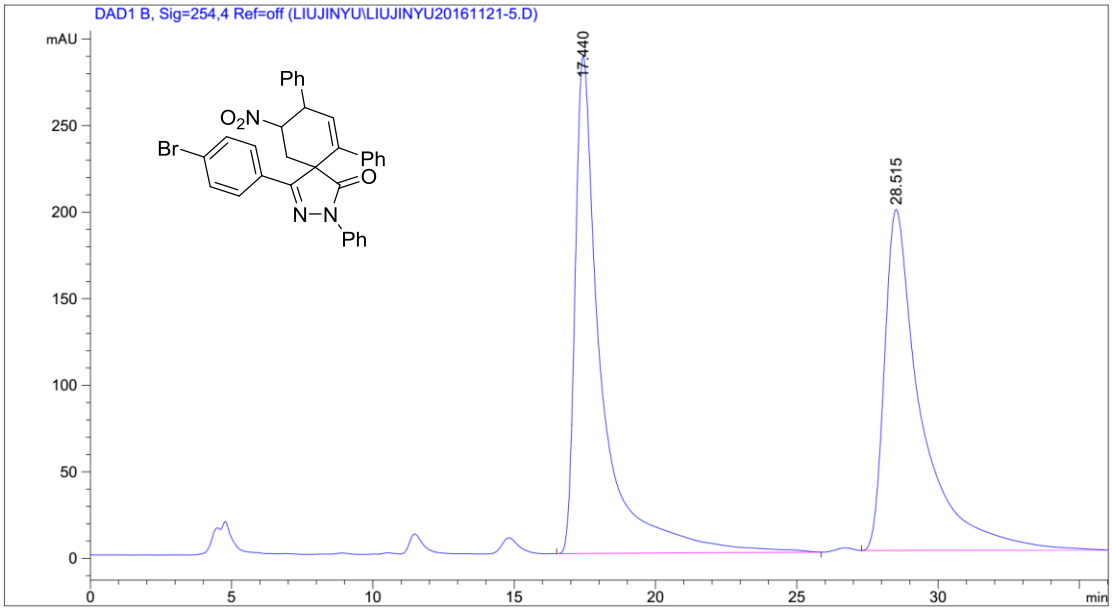


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	18.743	1.68064e4	258.82602	49.8825
2	DAD 254, 4 nm	26.508	1.68855e4	202.83923	50.1175

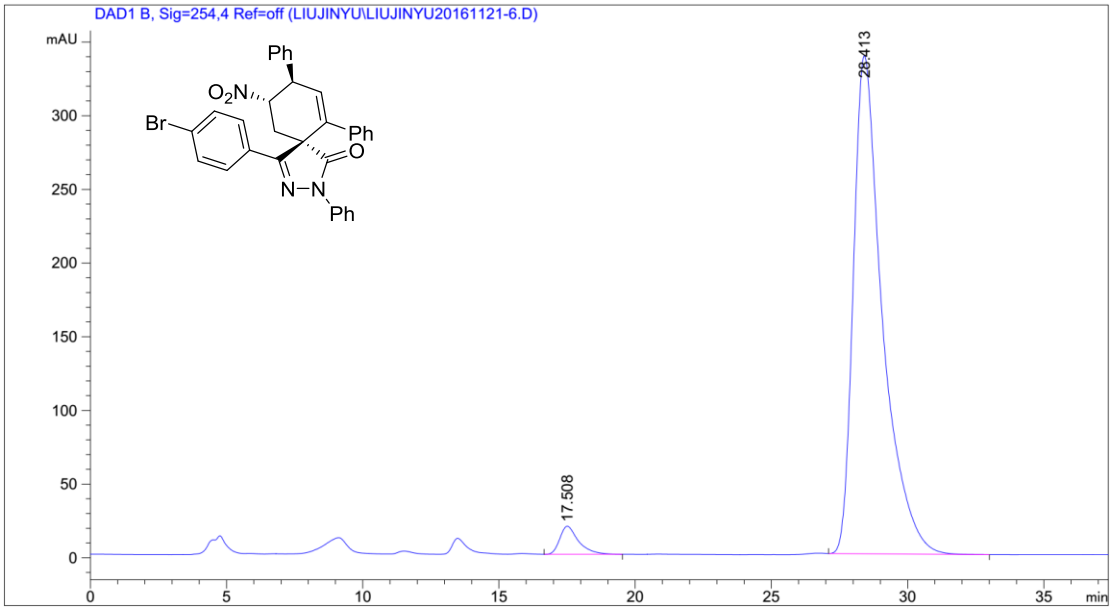


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	18.792	1236.64307	24.03218	2.9414
2	DAD 254, 4 nm	26.382	4.08066e4	581.39117	97.0586

3sa

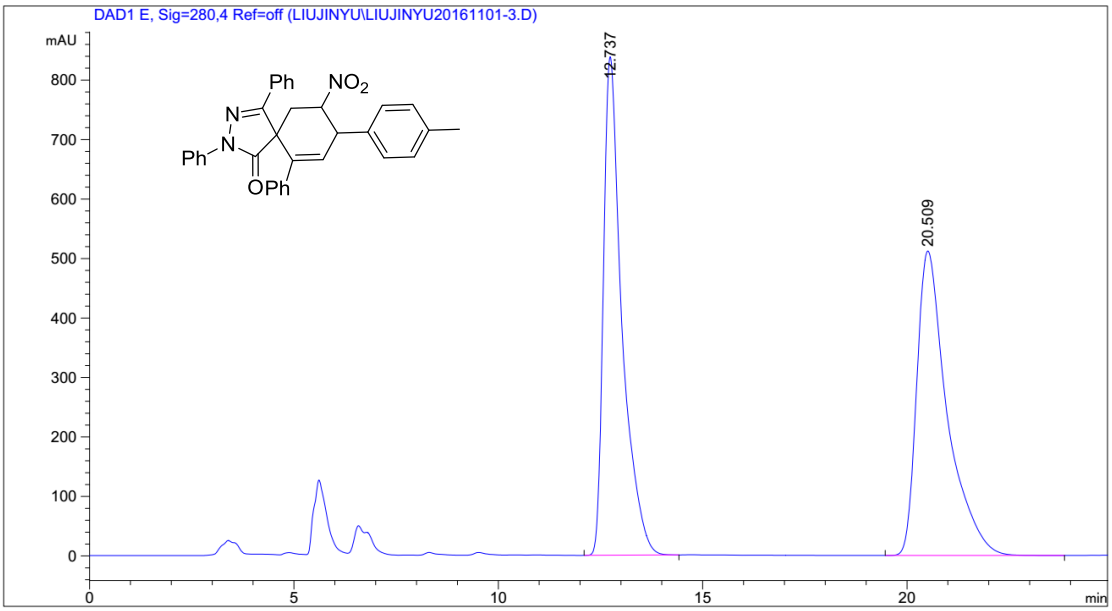


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	17.440	1.85640e4	287.48639	51.1169
2	DAD 254, 4 nm	28.515	1.77528e4	196.98853	48.8831

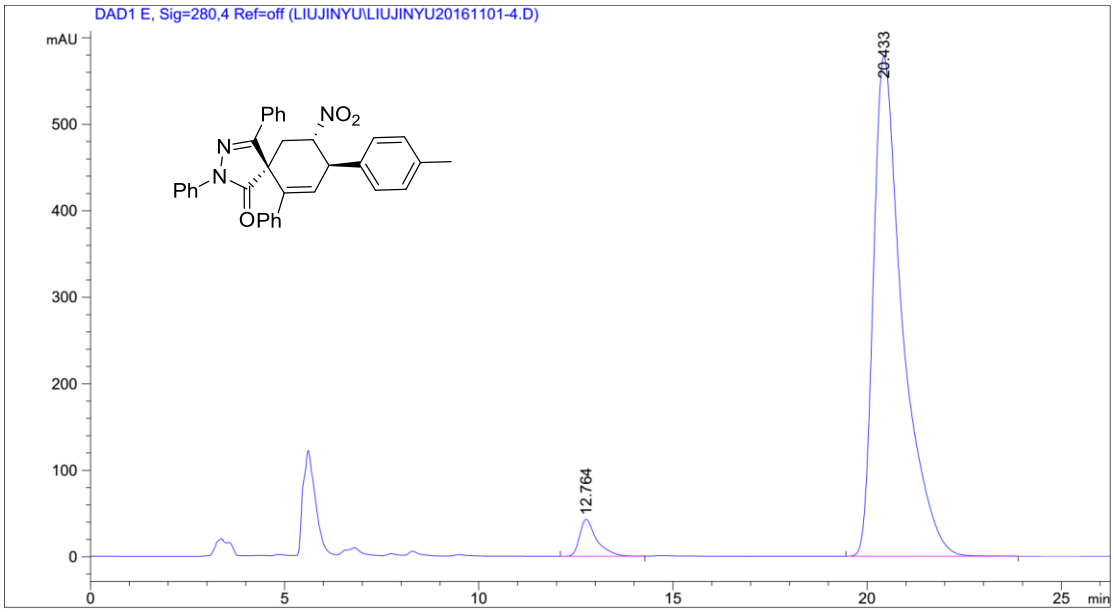


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	17.508	908.96301	19.04605	3.5089
2	DAD 254, 4 nm	28.413	2.49956e4	337.98816	96.4911

3ab

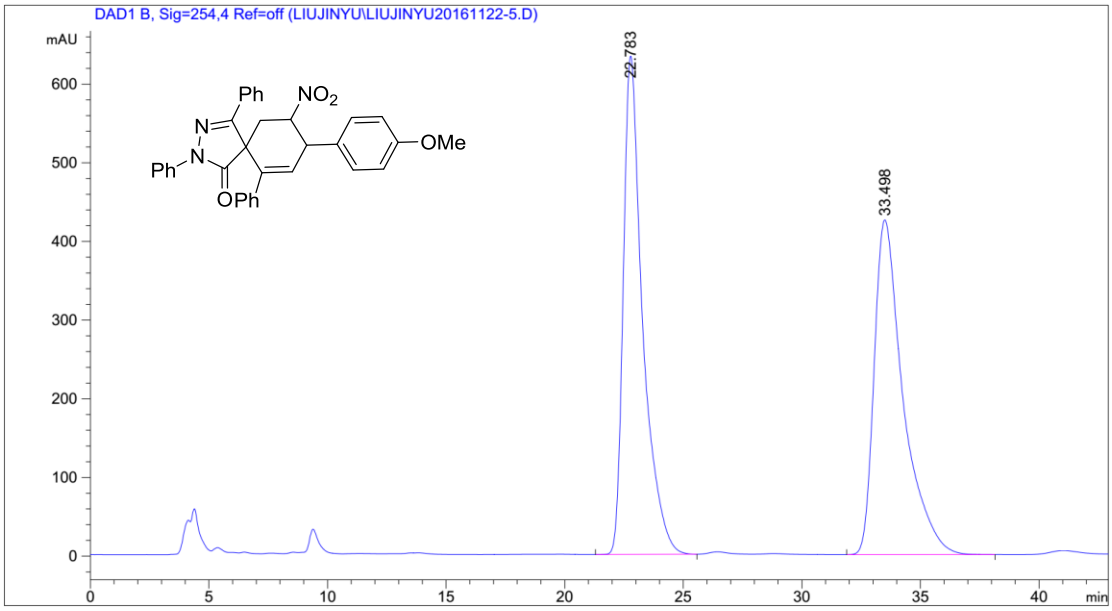


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	12.737	2.63476e4	838.08875	49.8749
2	DAD 254, 4 nm	20.509	2.64798e4	511.81802	50.1251

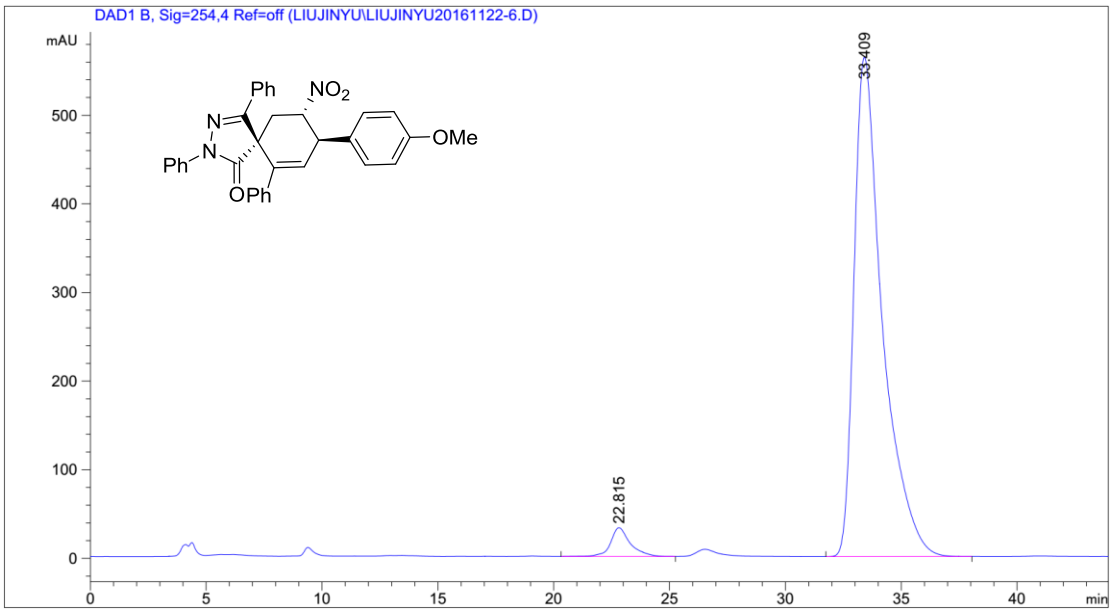


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	12.764	1289.20605	42.71472	4.1222
2	DAD 254, 4 nm	20.433	2.99857e4	577.98523	95.8778

3ac

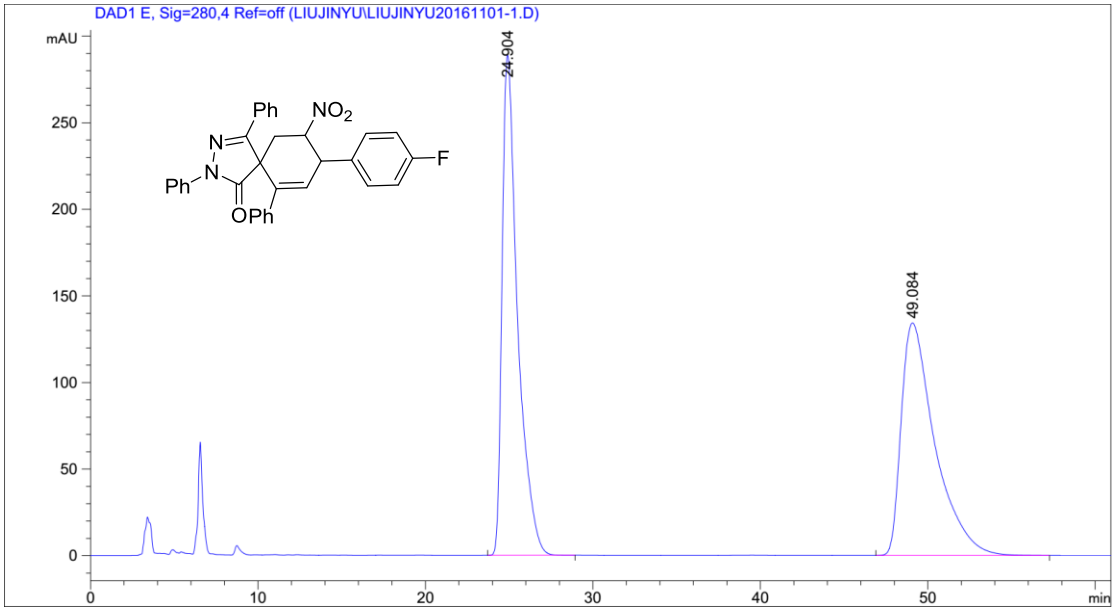


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	22.783	3.58477e4	633.56256	49.8960
2	DAD 254, 4 nm	33.498	3.59972e4	425.44238	50.1040

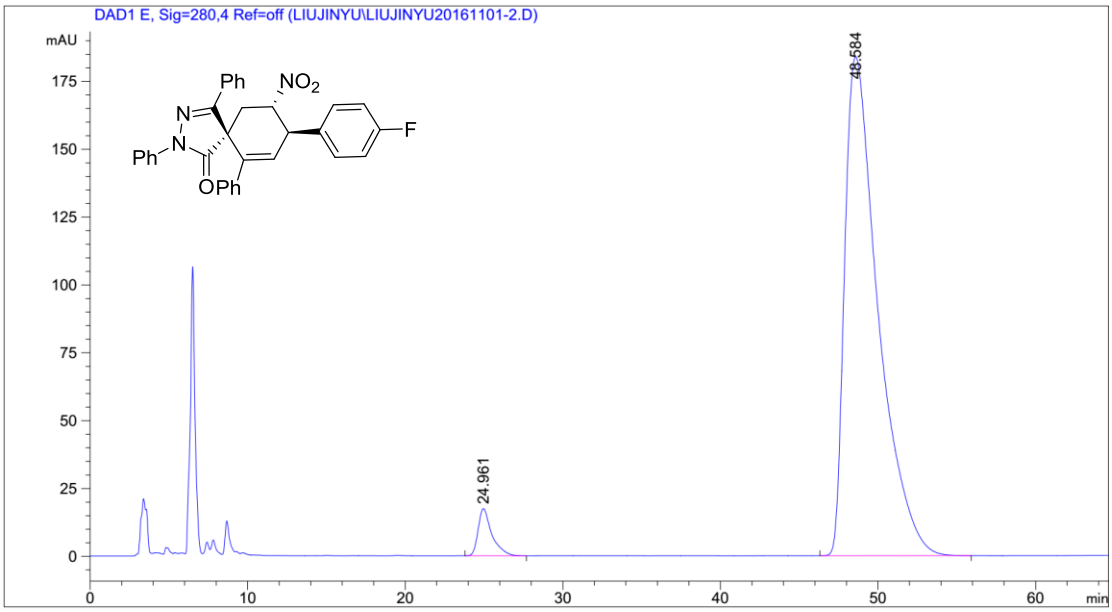


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	22.783	1921.73425	2.45596	3.8521
2	DAD 254, 4 nm	33.498	4.79663e4	563.61072	96.1479

3ad

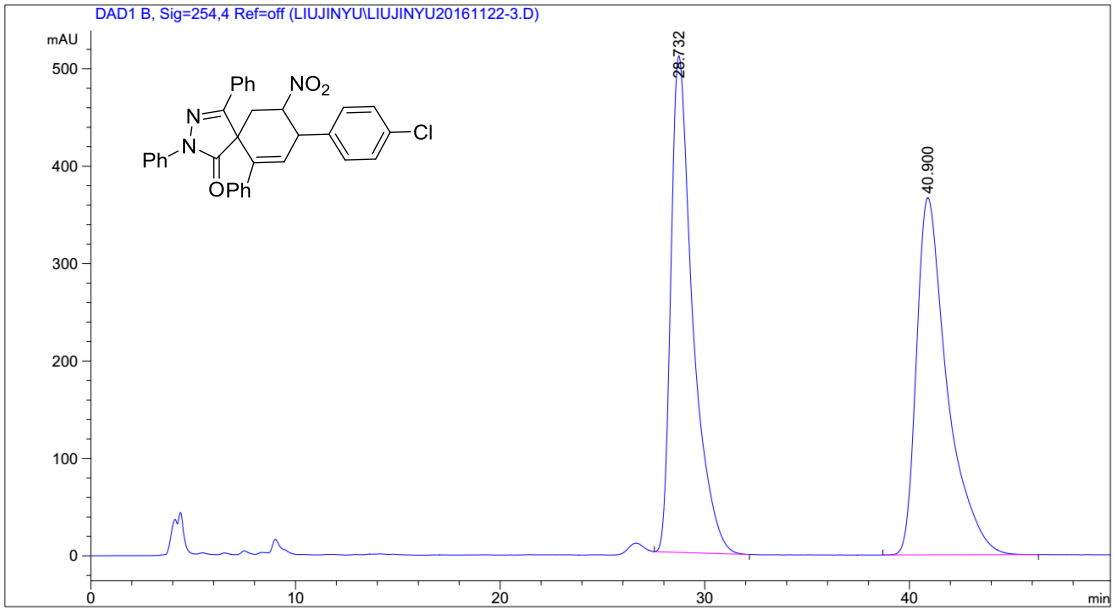


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	24.904	1.86040e4	288.79440	49.8225
2	DAD 254, 4 nm	49.084	1.87365e4	134.24454	50.1775

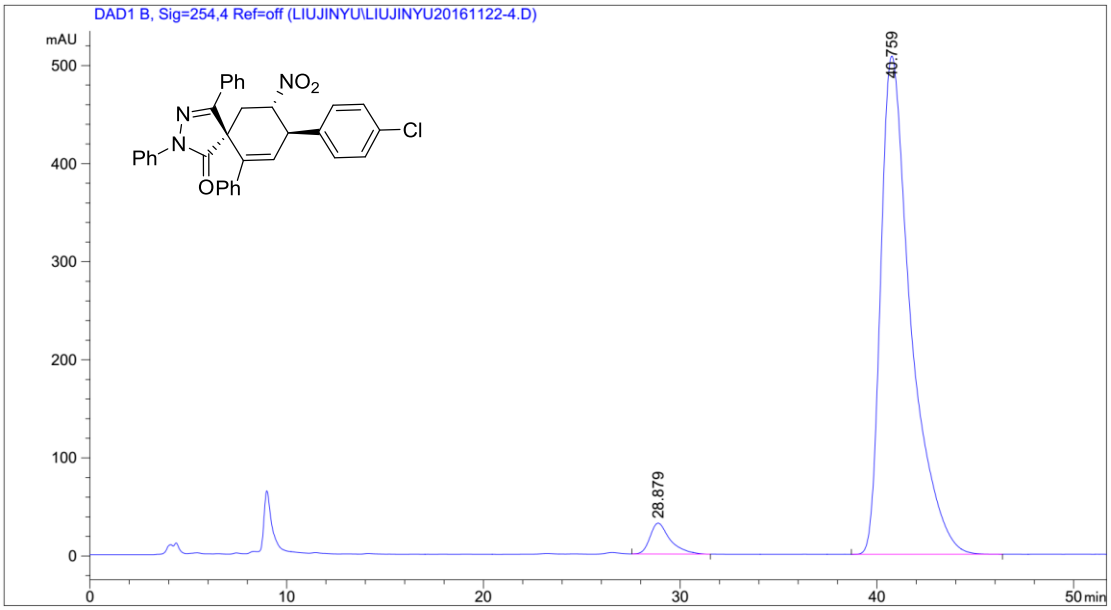


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	24.961	1047.53381	17.35882	3.7444
2	DAD 254, 4 nm	48.584	2.69283e4	183.82857	96.2556

3ae

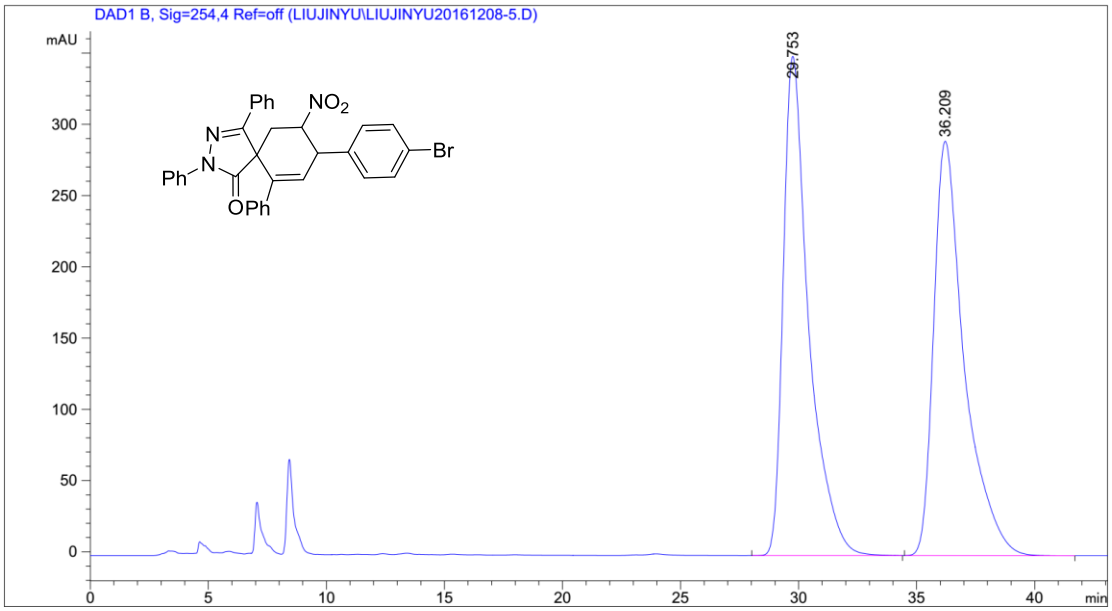


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	28.732	3.77228e4	509.60559	49.6882
2	DAD 254, 4 nm	40.900	3.81962e4	366.62033	50.3118

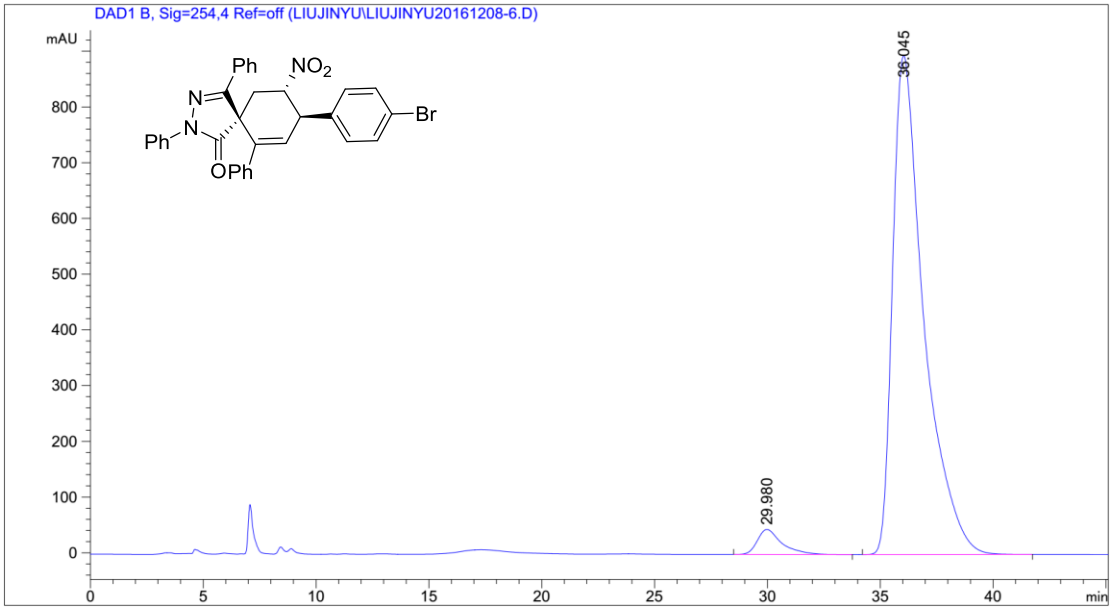


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	28.879	2227.50537	31.45564	3.9762
2	DAD 254, 4 nm	40.759	5.37928e4	507.87689	96.0238

3af

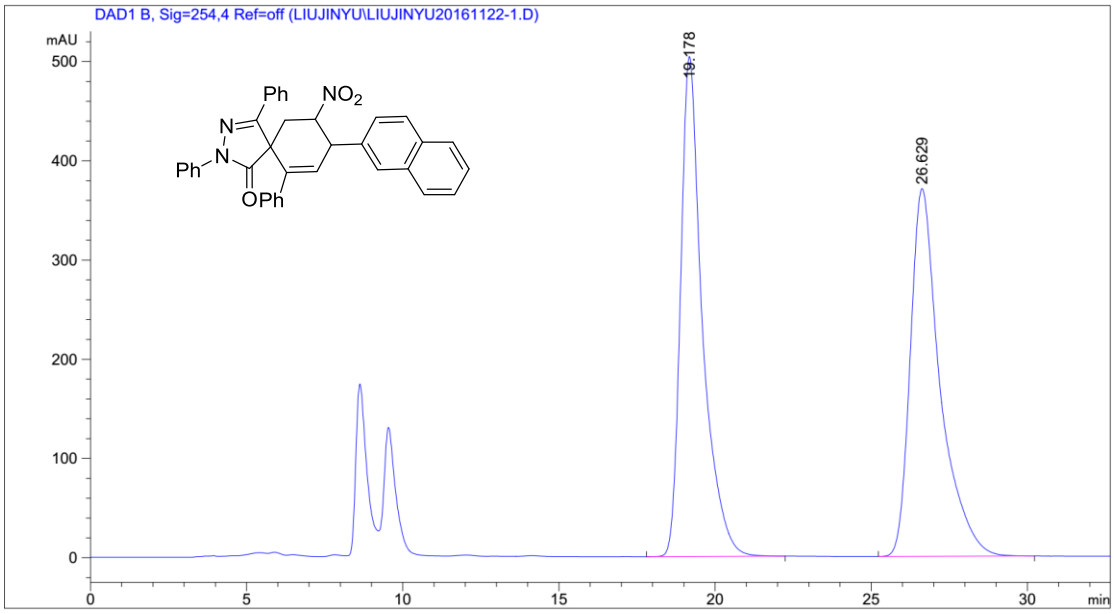


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	29.753	2.62718e4	350.22101	50.0532
2	DAD 254, 4 nm	36.209	2.62159e4	290.71719	49.9468

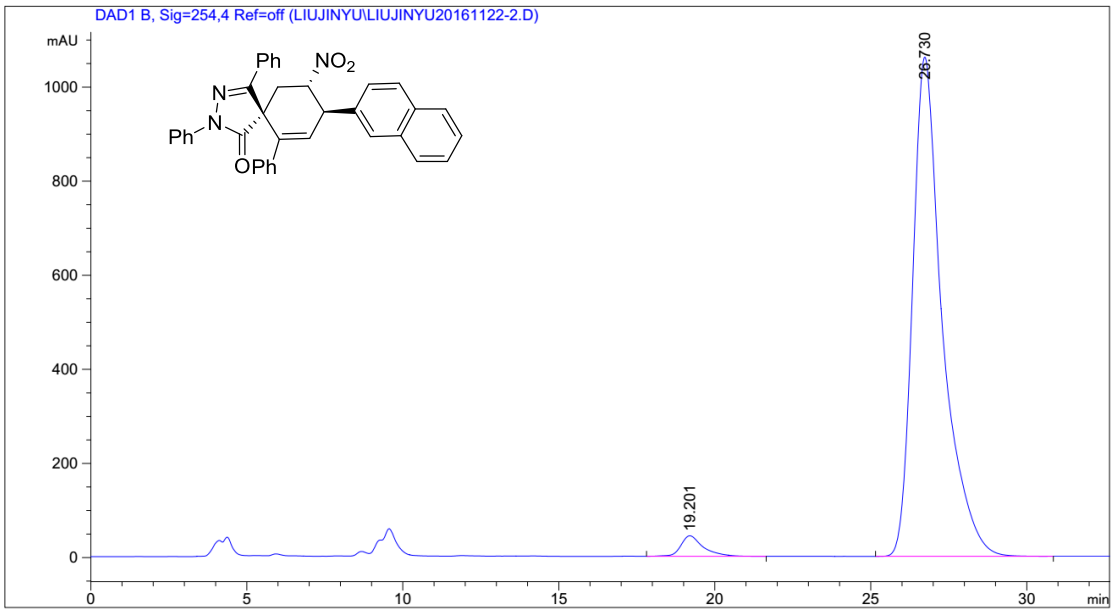


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	29.980	3351.31641	44.77388	3.7592
2	DAD 254, 4 nm	36.045	8.57994e4	895.43872	96.2408

3ag

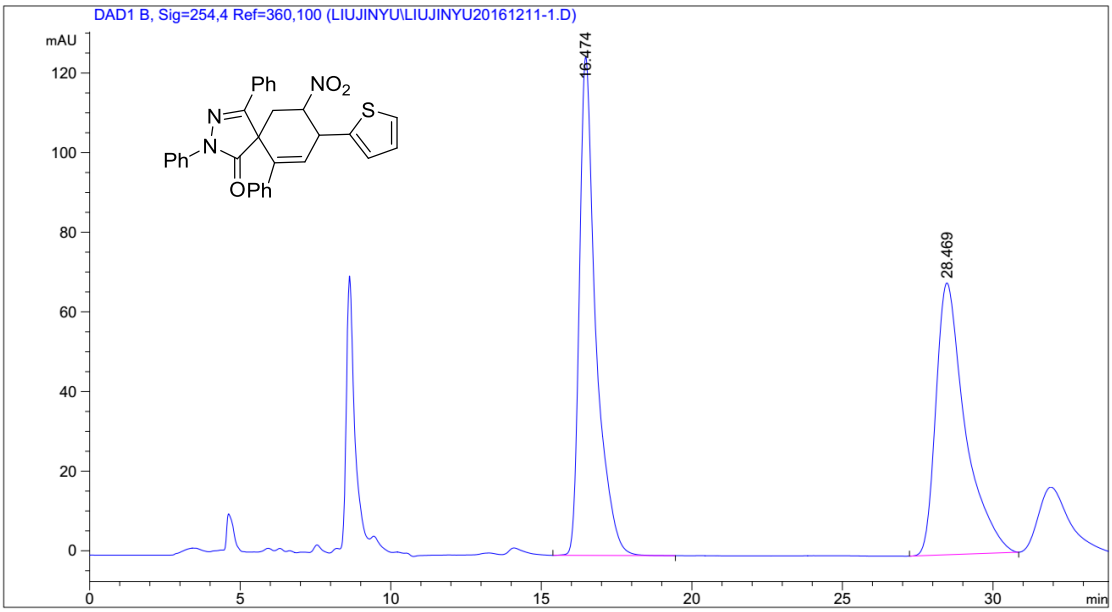


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	19.178	2.44057e4	503.78705	49.8587
2	DAD 254, 4 nm	26.629	2.45441e4	370.62308	50.1413

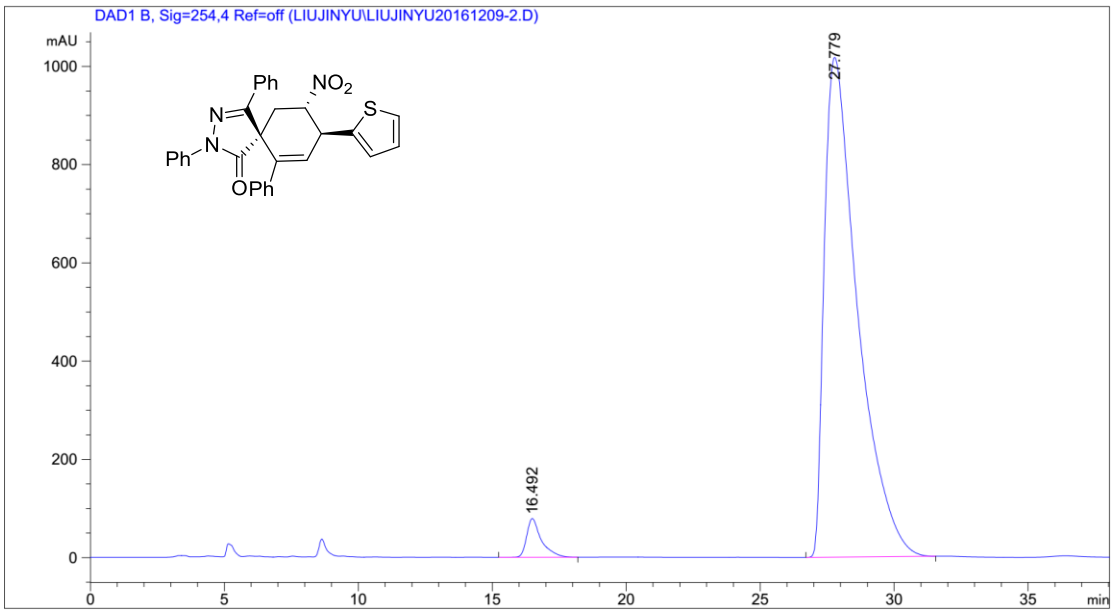


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	19.201	2163.66235	43.60474	2.9913
2	DAD 254, 4 nm	26.730	7.01681e4	1061.10620	97.0087

3ah

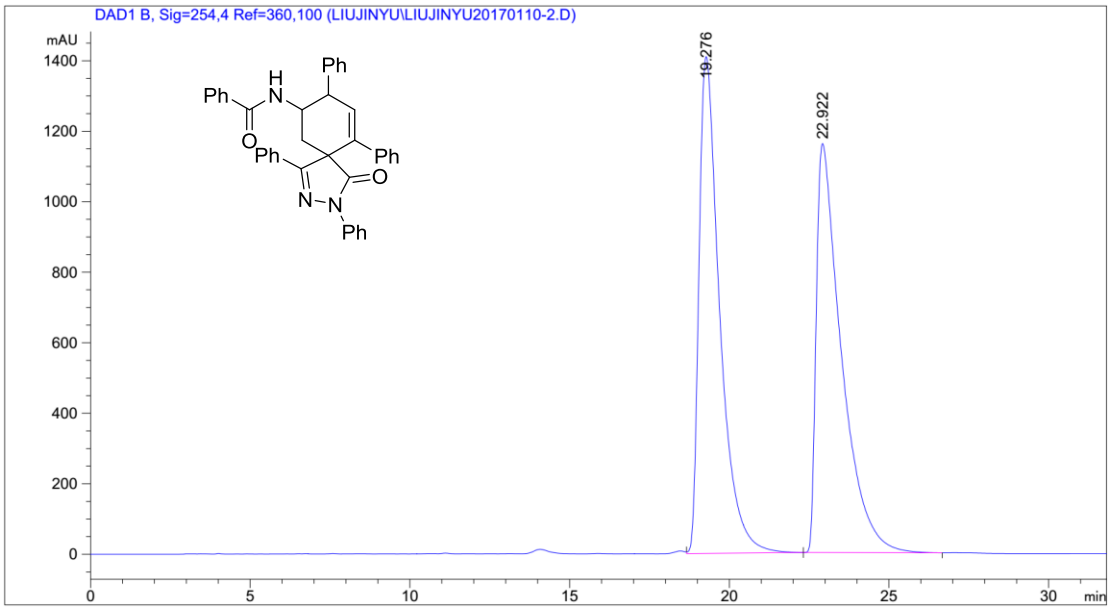


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	16.474	4739.23975	125.21667	50.7580
2	DAD 254, 4 nm	28.469	4597.69531	68.26379	49.2420

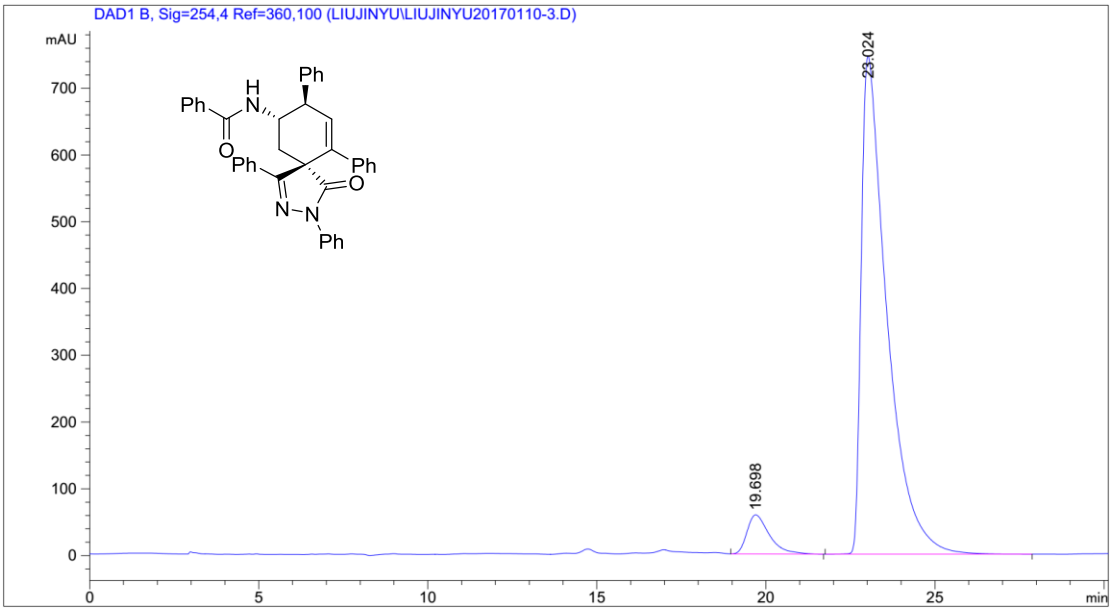


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	16.492	2985.45190	78.77143	3.2951
2	DAD 254, 4 nm	27.779	8.76183e4	1017.05627	96.7049

4



Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	19.276	6.35554e4	1409.23083	50.1449
2	DAD 254, 4 nm	22.922	6.31881e4	1160.25952	49.8551



Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254, 4 nm	19.698	2686.29712	58.53596	6.3791
2	DAD 254, 4 nm	23.024	3.94246e4	746.24164	93.6209