Supplementary Information

Highly enantioselective Friedel–Crafts alkylation of *N,N*-dialkylanilines with *trans*-β-nitrostyrene catalyzed by homochiral metal-organic framework

Koichi Tanaka*, Kenji Sakuragi, Hiroto Ozaki and Yoshiki Takada

Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering, Kansai University, Suita, Osaka 564-8680, Japan. Fax: +81-06-6339-4026; Tel: +81-06-6368-0861; E-mail: ktanaka@kansai-u.ac.jp

General procedures

^{1}H and ^{13}C NMR spectra were recorded on a JEOL-ECZ400 spectrometer. Tetramethylsilane (TMS) and deuterated solvents ($CDCl_3$, δ = 77.00 ppm; DMSO-d_6, δ = 39.50 ppm) were used as internal standards in ^{1}H and ^{13}C NMR experiments, respectively. Enantiomeric excesses were determined by high-performance liquid chromatography (HPLC) on CHIRALCEL OD-H or CHIRALCEL AS columns (Daicel).

General procedure for the asymmetric Friedel–Crafts reaction

A mixture of *N,N*-dimethylaniline derivative **3** (0.25 mmol), β-nitrostyrene **4** (0.25 mmol) and evacuated (*R*)-CuMOF-**1** (25 mg, 20 mol %) was stirred at indicated temperature and for the indicated time in various solvents (0.5 mL). Then, the solid catalyst was collected by filtration, washed with MeOH, and the solvent of the filtrate were removed in vacuum to afford the desired product **5**. The enantiomeric purity of the product was determined by HPLC analysis.

N,N-Dimethyl-4-(2-nitro-1-phenylethyl)benzenamine 5a

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 7.32-7.28 (m, 2H), 7.24-7.20 (m, 3H), 7.08 (d, J = 8.8 Hz, 2H), 6.66 (d, J = 8.8 Hz, 2H), 4.97-4.88 (m, 2H), 4.80 (t, J = 8.4 Hz, 1H), 2.90 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.8, 139.9, 128.9, 128.3, 127.6, 127.3, 126.6, 112.7, 79.6, 48.2, 40.4.

N,N-Diethyl-4-(2-nitro-1-phenylethyl)aniline 5b

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm): 7.33-7.20 (m, 5H), 7.04 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 4.97-4.87 (m, 2H), 4.78 (t, J = 8.4 Hz, 1H), 3.30 (q, J = 7.2 Hz, 4H), 1.12 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0, 140.0, 128.8, 128.5, 127.6, 127.2, 125.3, 111.8, 49.6, 48.2, 44.2.

***N,N*-Dipropyl-4-(2-nitro-1-phenylethyl)aniline 5c**

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm): 7.33-7.22 (m, 5H), 7.02 (d, J = 9.0 Hz, 2H), 6.55 (d, J = 9.0 Hz, 2H), 4.97-4.87 (m, 2H), 4.78 (t, J = 8.0 Hz, 1H), 3.18 (t, J = 7.2 Hz, 4H), 1.61-1.52(m, 4H), 0.90 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 140.0, 128.8, 128.6, 128.4, 127.6, 125.1, 111.7, 79.7, 52.8, 48.2, 20.3, 11.4.

***N,N*-Dibenzyl-4-(2-nitro-1-phenylethyl)aniline 5d**

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm): 7.33-7.18 (m, 15H), 6.97 (d, J = 8.8 Hz, 2H), 6.63 (d, J = 8.8 Hz, 2H), 4.90-4.81 (m, 2H), 4.74 (t, J = 8.0 Hz, 1H), 4.59 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 139.8, 138.3, 128.8, 128.4, 127.6, 127.3, 126.9, 136.8, 126.5, 112.6, 79.5, 54.2, 48.1.

3-Methyl-*N,N*-dimethyl-4-(2-nitro-1-phenylethyl)aniline 5e

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm): 7.30-7.04 (m, 6H), 6.59-6.54 (m, 2H), 5.03-4.99 (m, 1H), 4.91-4.89 (m, 2H), 2.91 (s, 6H), 2.27 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 139.7, 137.1, 128.8, 127.9, 127.2, 126.7, 124.9, 115.1, 110.3, 79.5, 44.4, 40.4, 20.2.

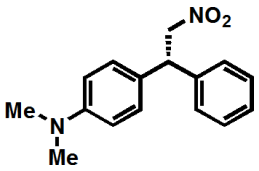
3-Chloro-*N,N*-dimethyl-4-(2-nitro-1-phenylethyl)aniline 5f

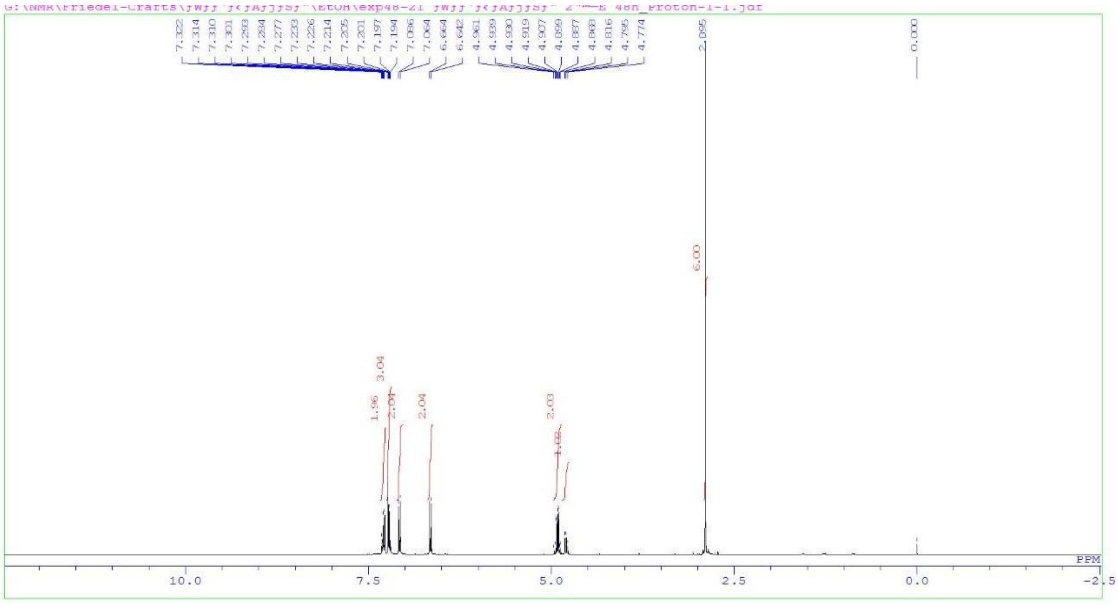
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm): 7.33-7.22 (m, 5H), 7.01 (d, J = 8.8 Hz, 1H), 6.70-6.54 (m, 2H), 5.34-5.30 (m, 1H), 4.97-4.88 (m, 2H), 2.91 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 138.7, 134.7, 128.9, 128.5, 127.8, 127.4, 123.3, 113.3, 111.1, 78.1, 44.5, 40.2

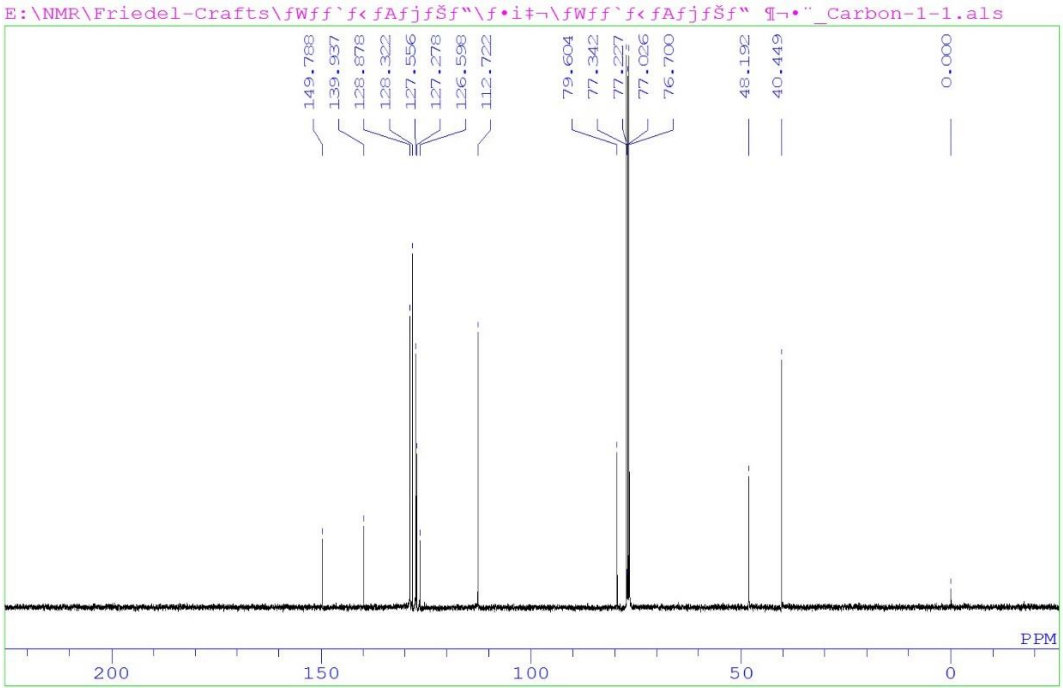
3-Methoxy-*N,N*-dimethyl-4-(2-nitro-1-phenylethyl)aniline 5g

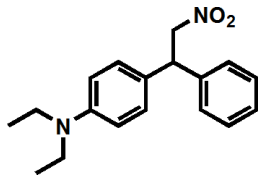
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm): 7.32-7.19 (m, 5H), 6.86 (d, J = 8.8 Hz, 1H), 6.24-6.21 (m, 2H), 5.16-5.12 (m, 1H), 5.01-4.90 (m, 2H), 3.82 (s, 3H), 2.92 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.6, 151.2, 139.6, 128.9, 128.6, 127.8, 126.9, 115.2, 104.4, 96.0, 78.1, 55.2, 42.8, 40.5.





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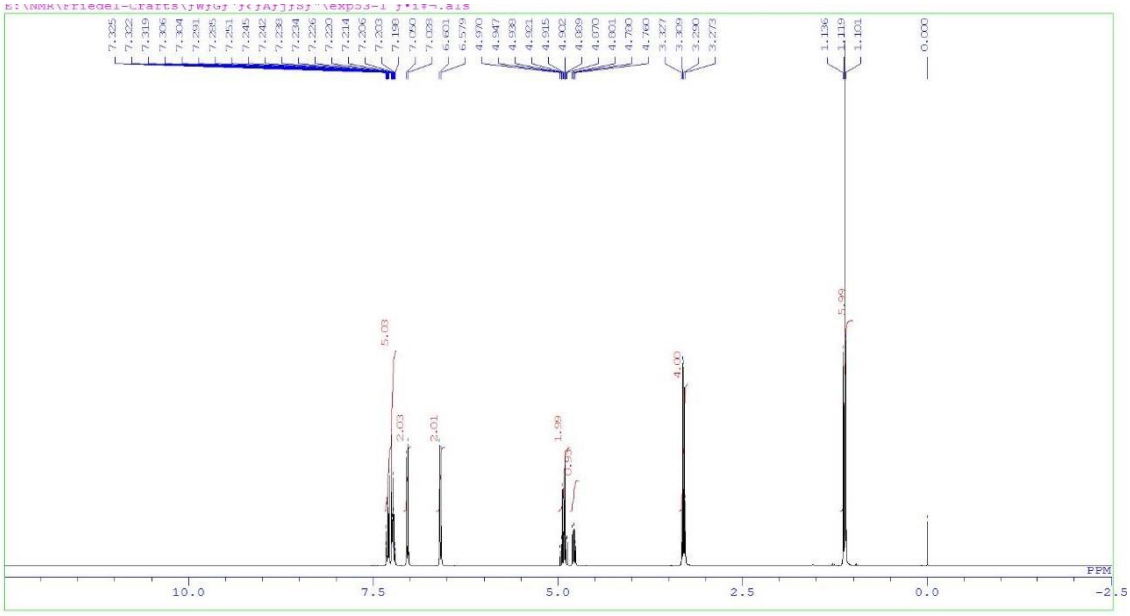
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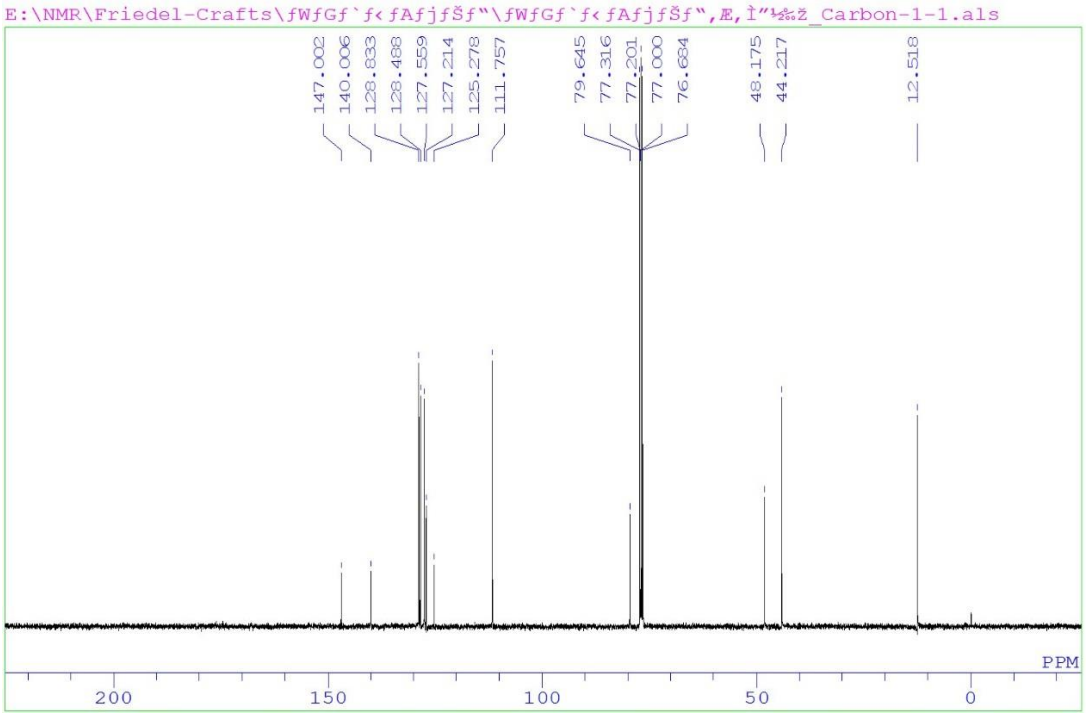
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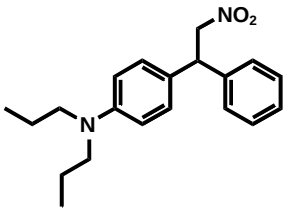
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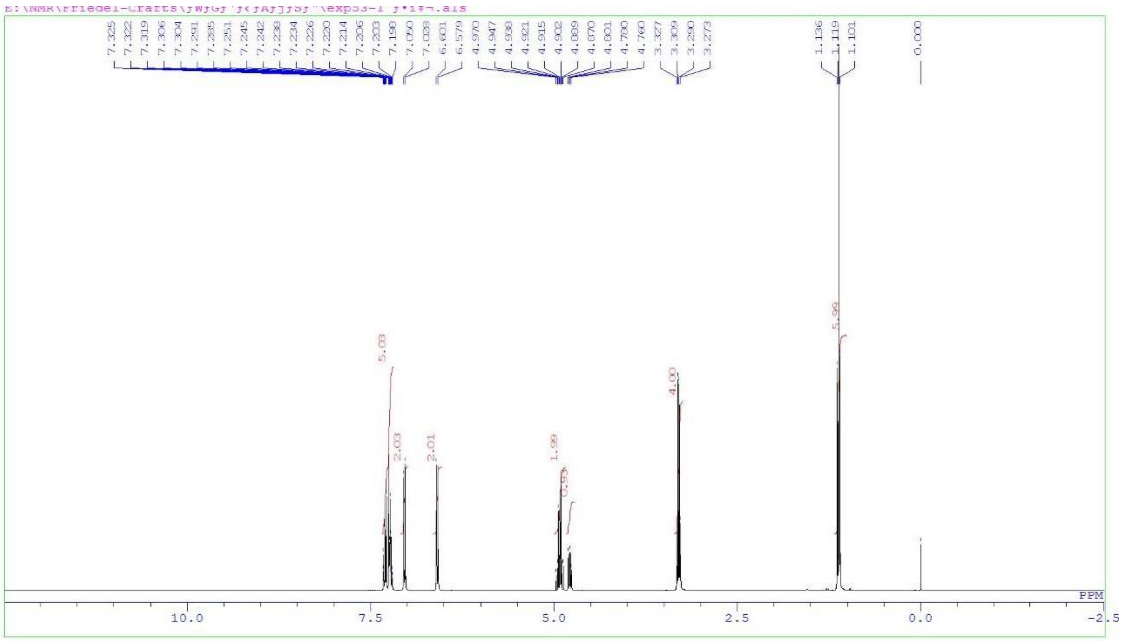
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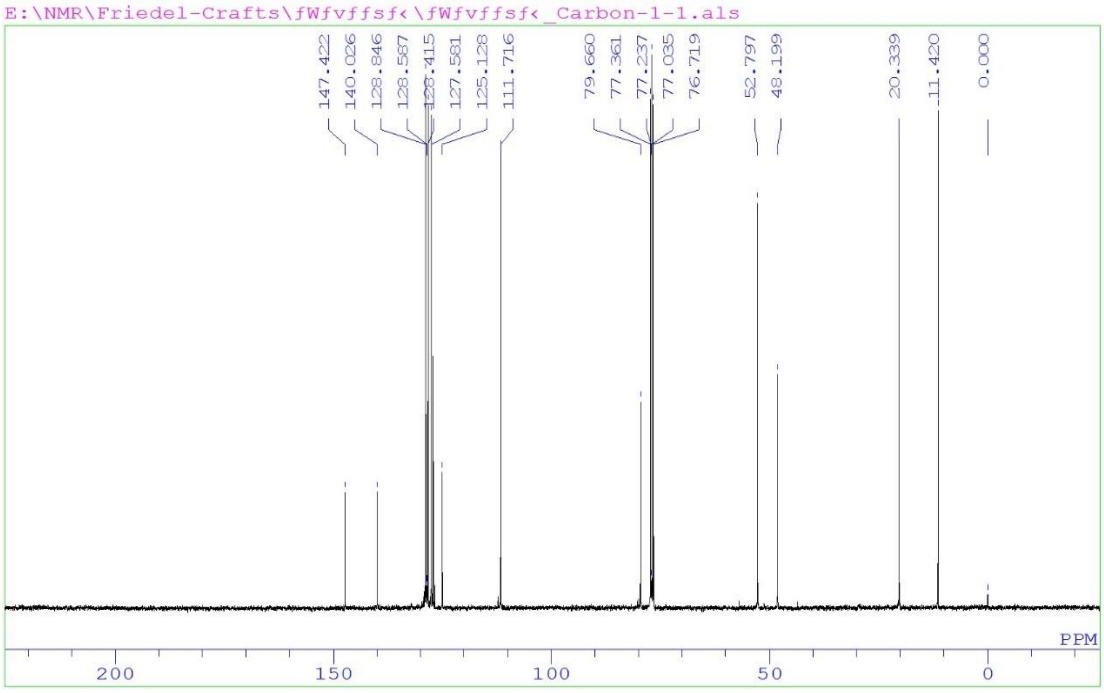
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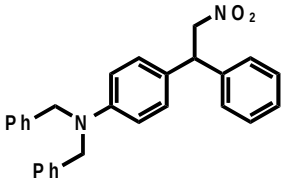
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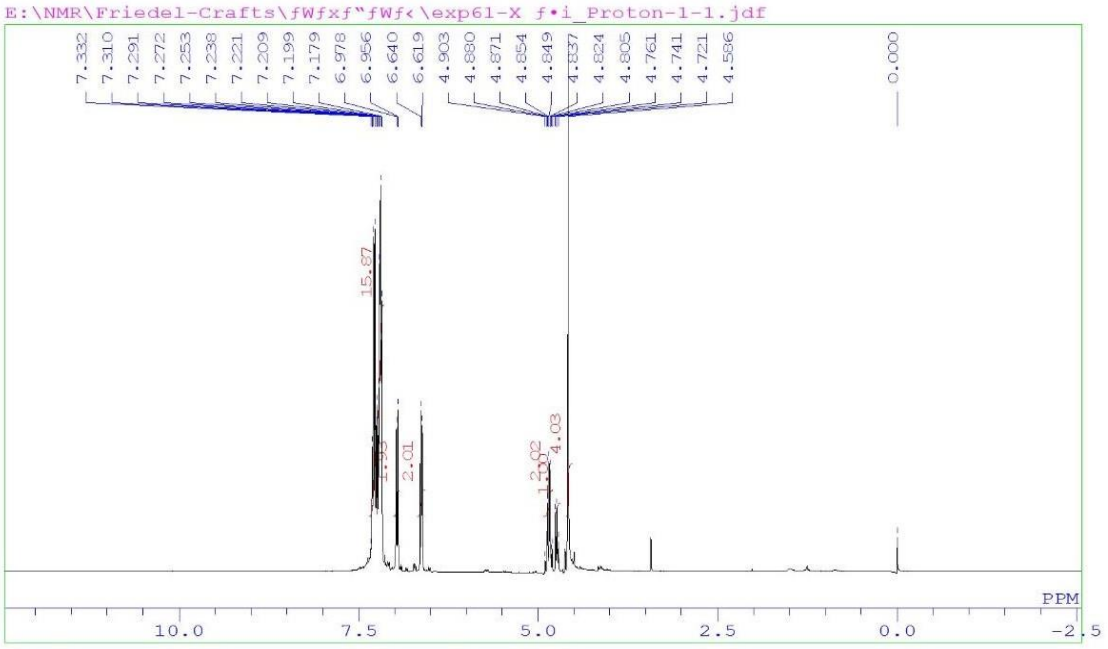
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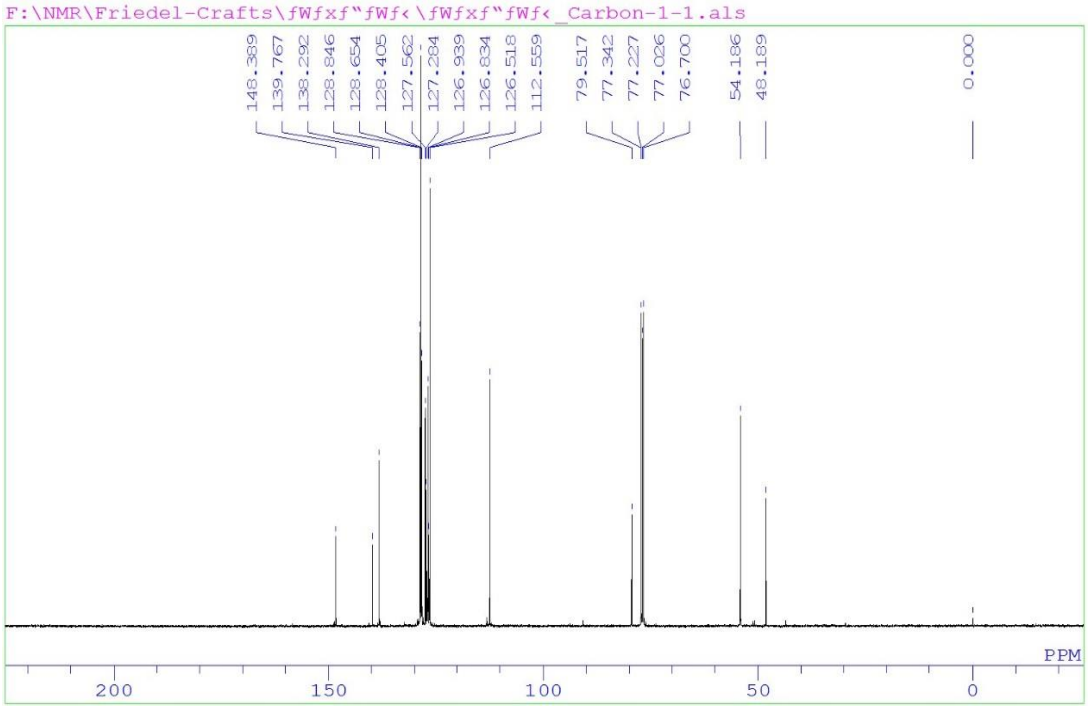
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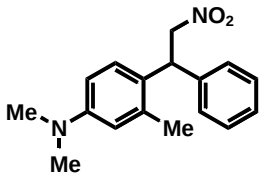
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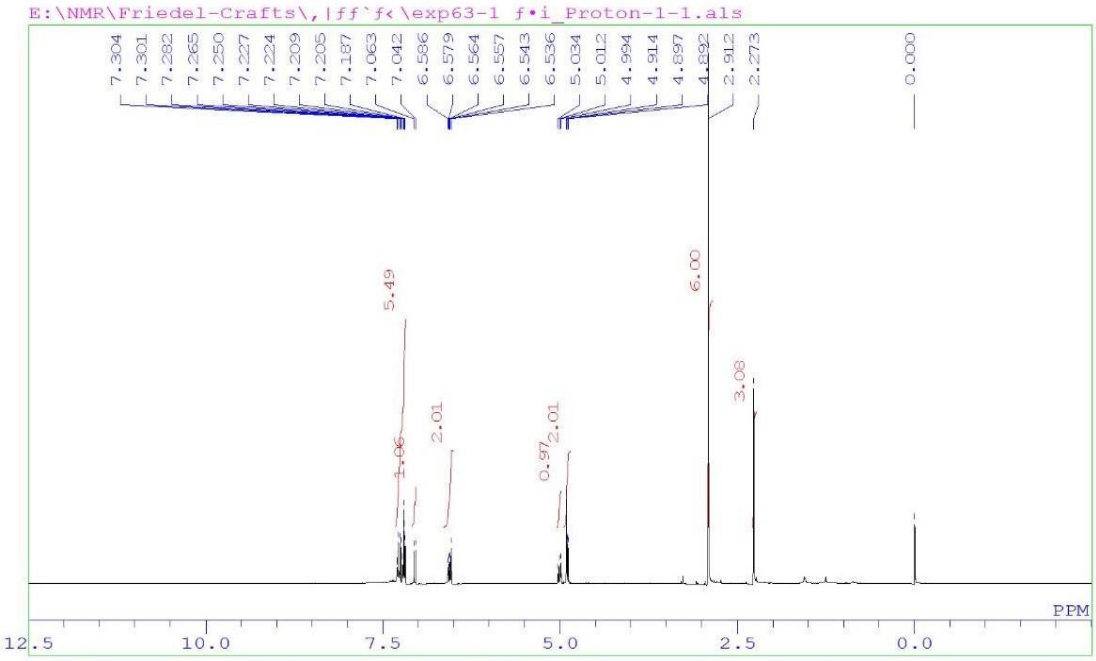
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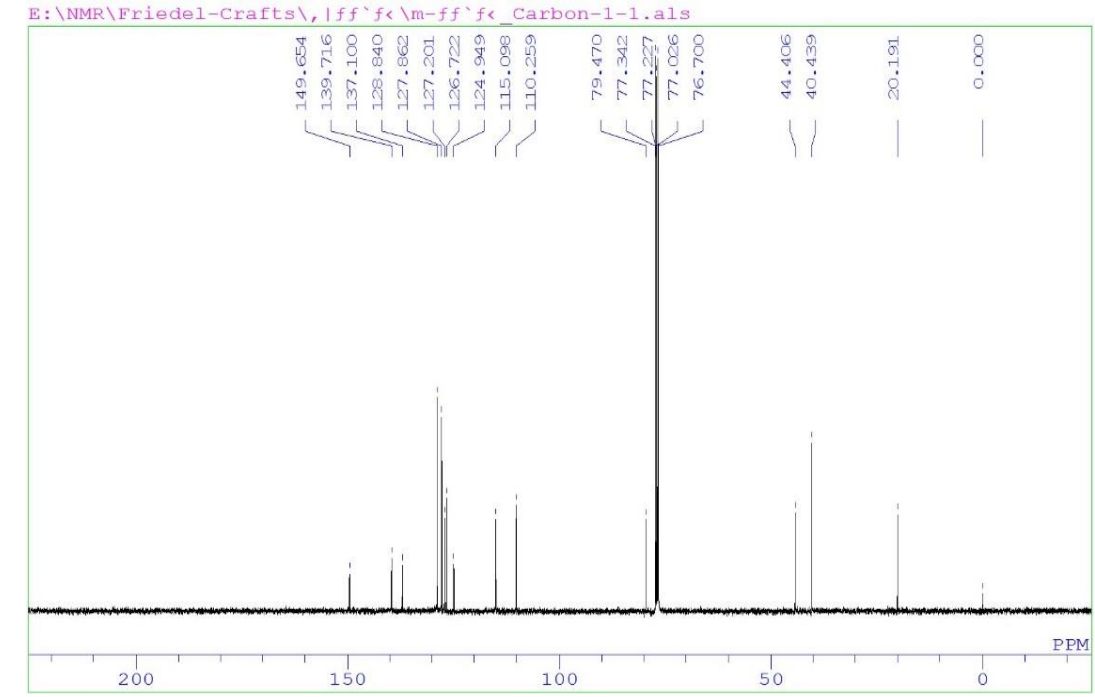
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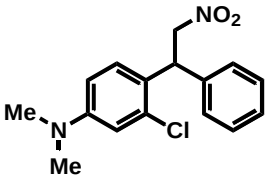
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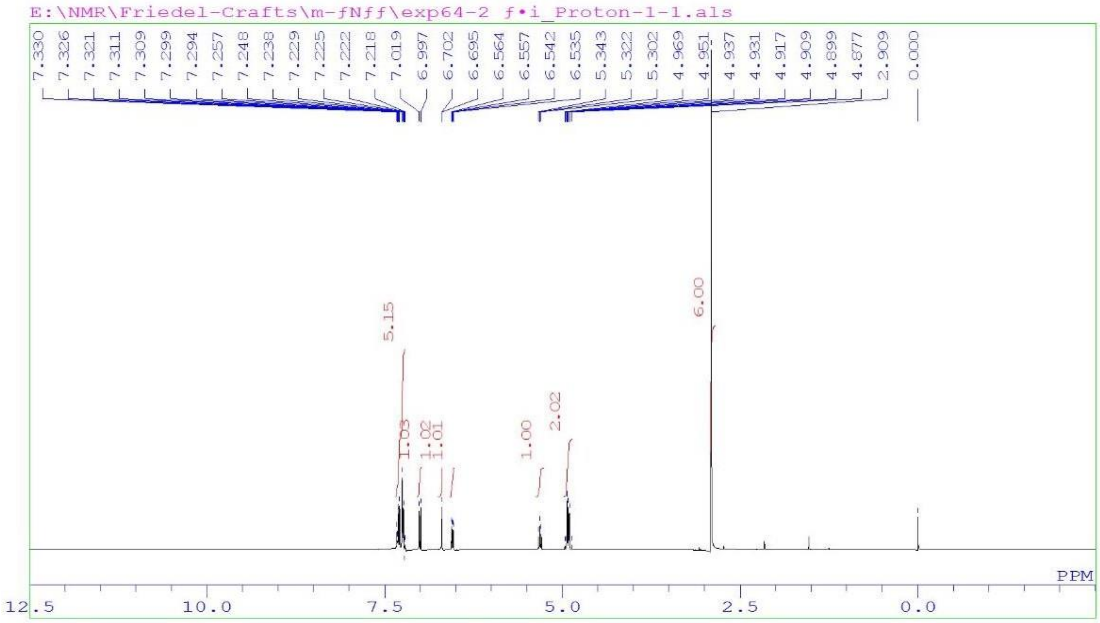
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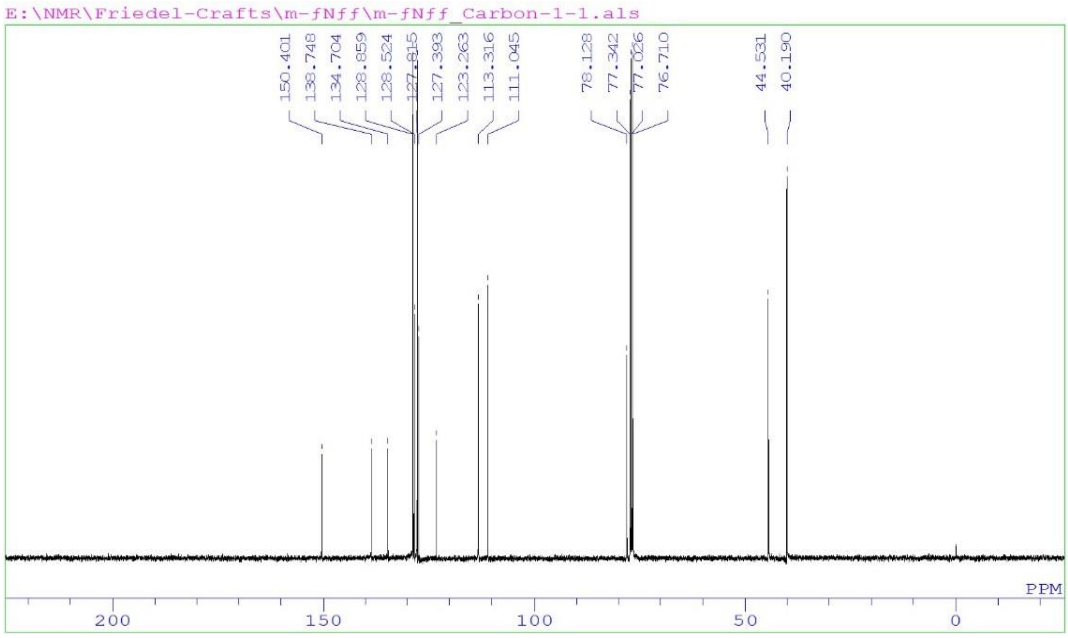
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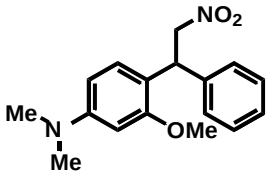
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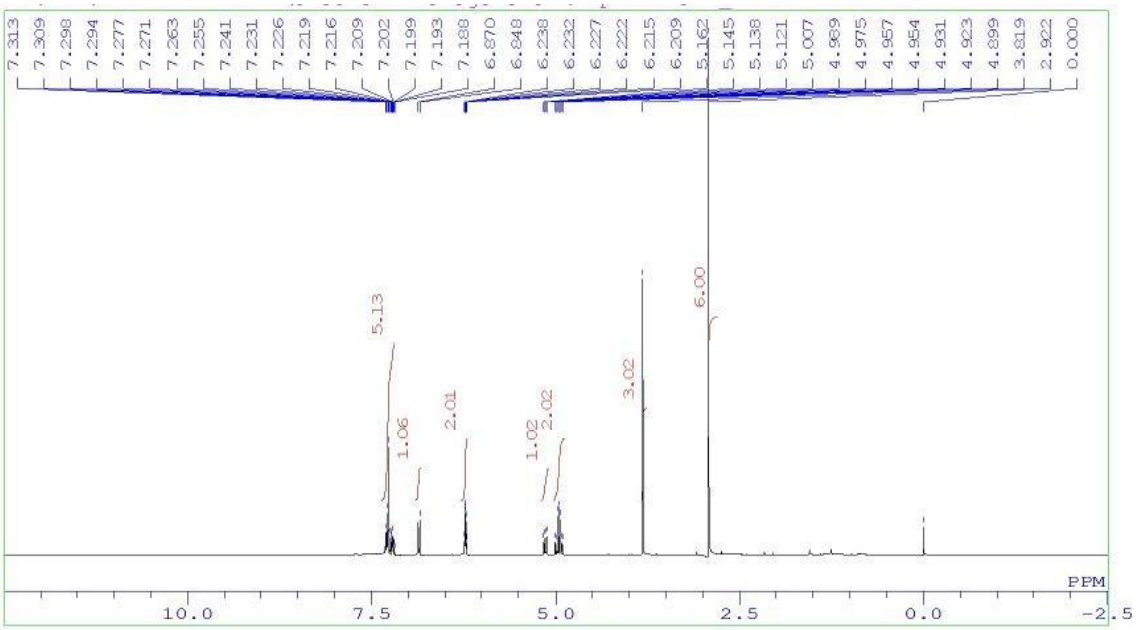
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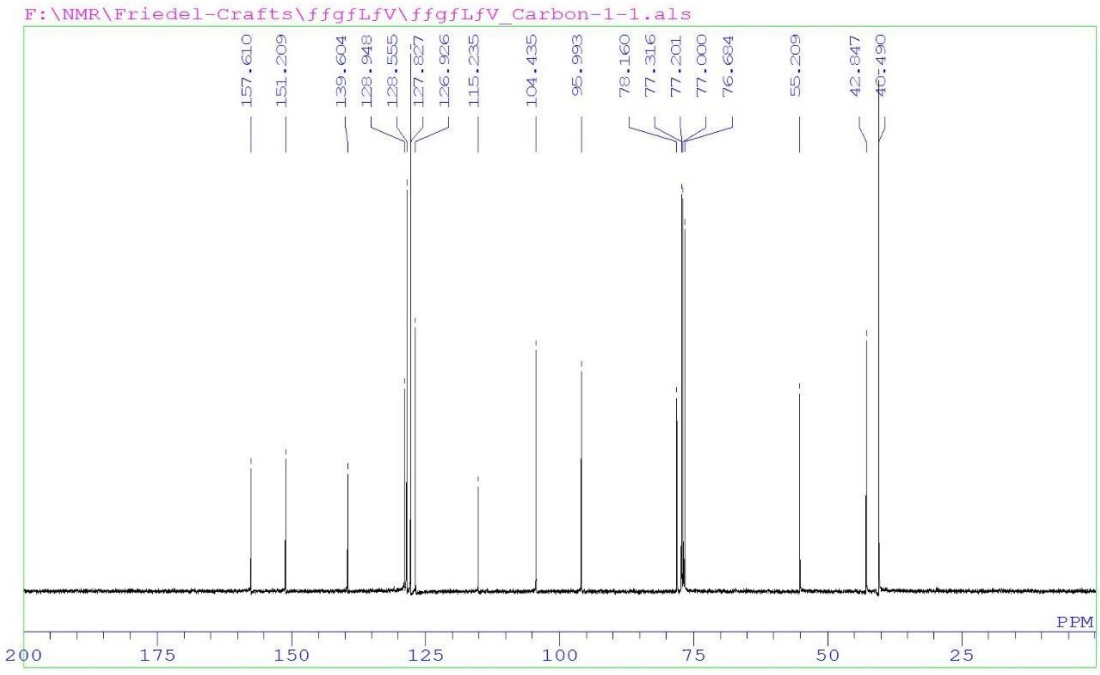
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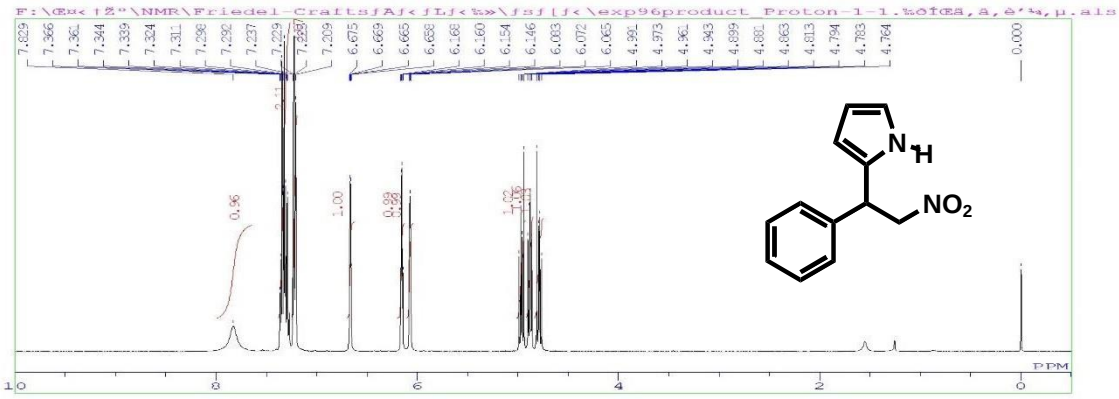
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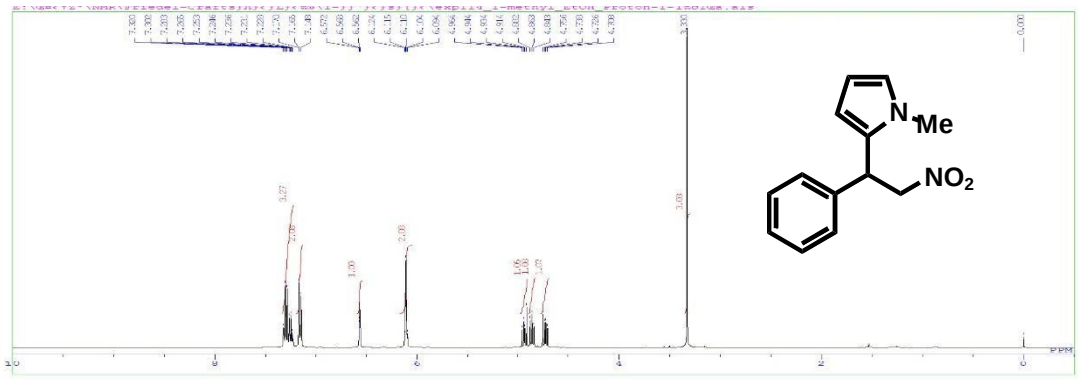
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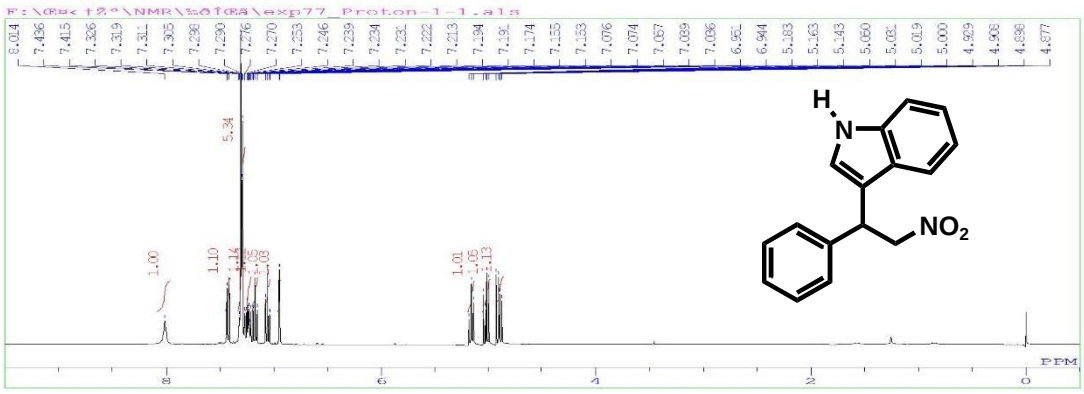
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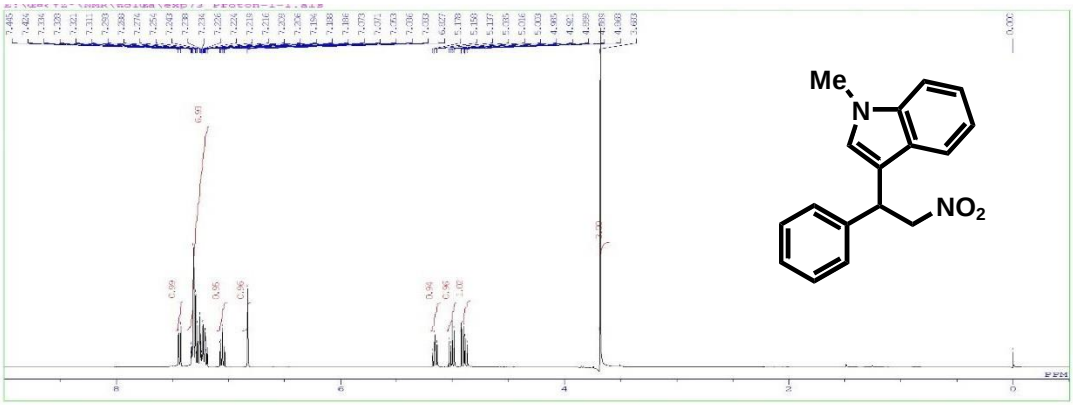
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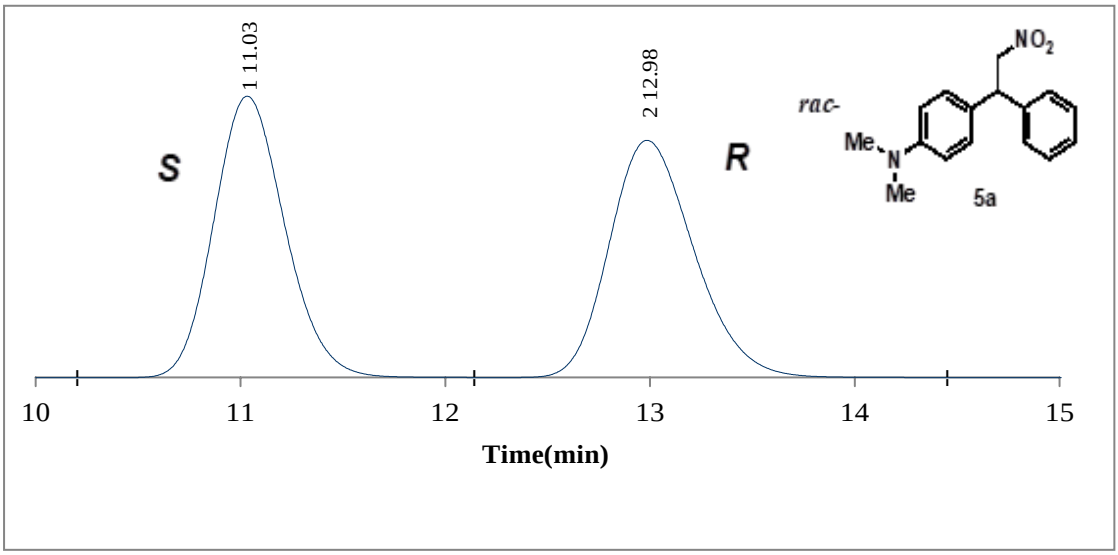

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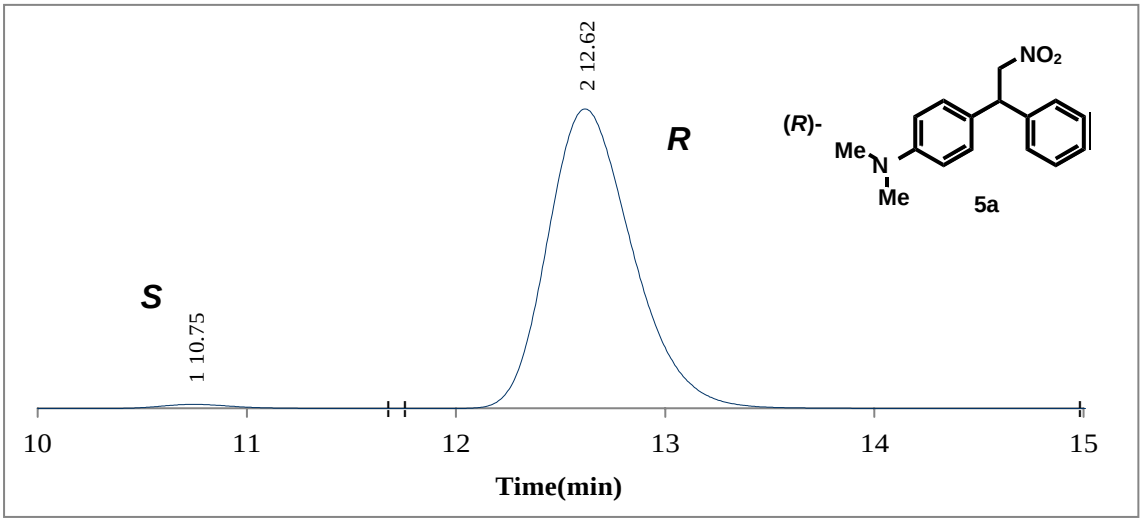
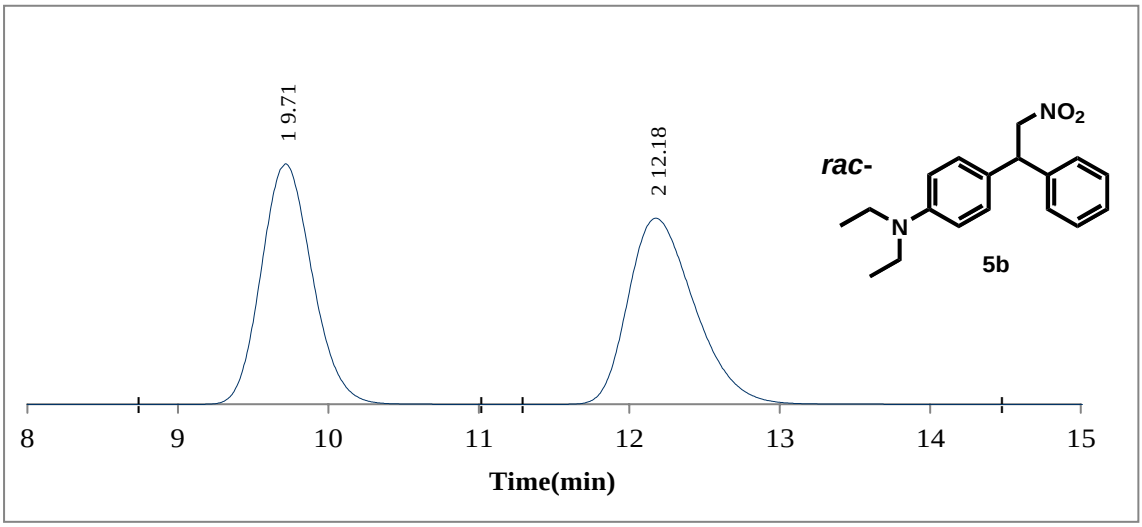


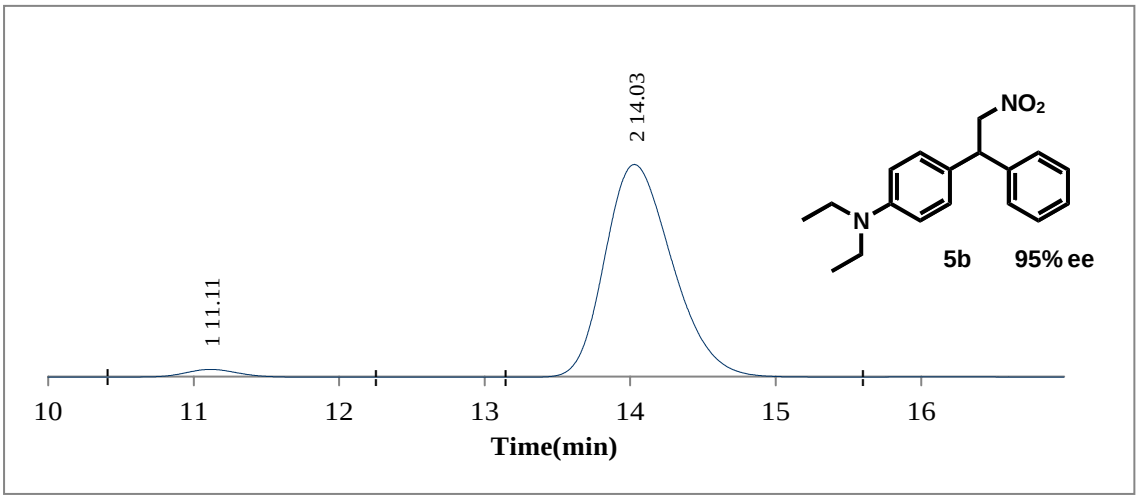
Column: CHIRALCEL OD-H, Eluent: n-hexane:2-PrOH = 50:50, Flow rate: 0.8 mL/min , Detection: UV 254 nm, t(S) = 10.8 min, t(R) =12.6 min.

No.	Rt	Area	Area(%)
1	10.75	147892.1	1.1833
2	12.62	12350435	98.8167



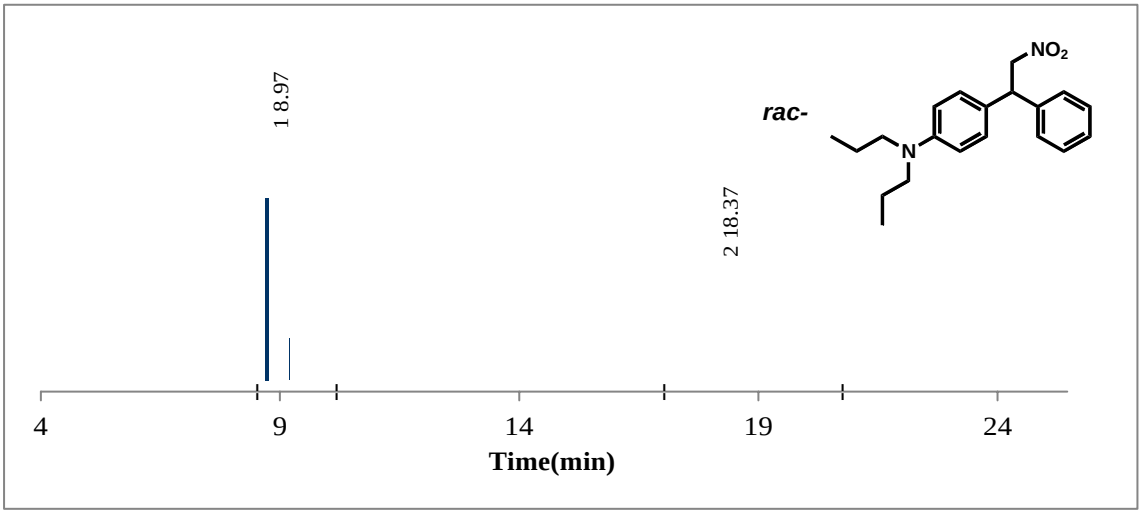
Column: CHIRALCEL OD-H, Eluent: *n*-hexane:2-PrOH = 80:20, Flow rate: 1.0 mL/min , Detection: UV 254 nm, Rt = 9.7 min,12.2 min.

No.	Rt	Area	Area(%)
1	9.71	9991159	49.8187
2	12.18	10063882	50.1813



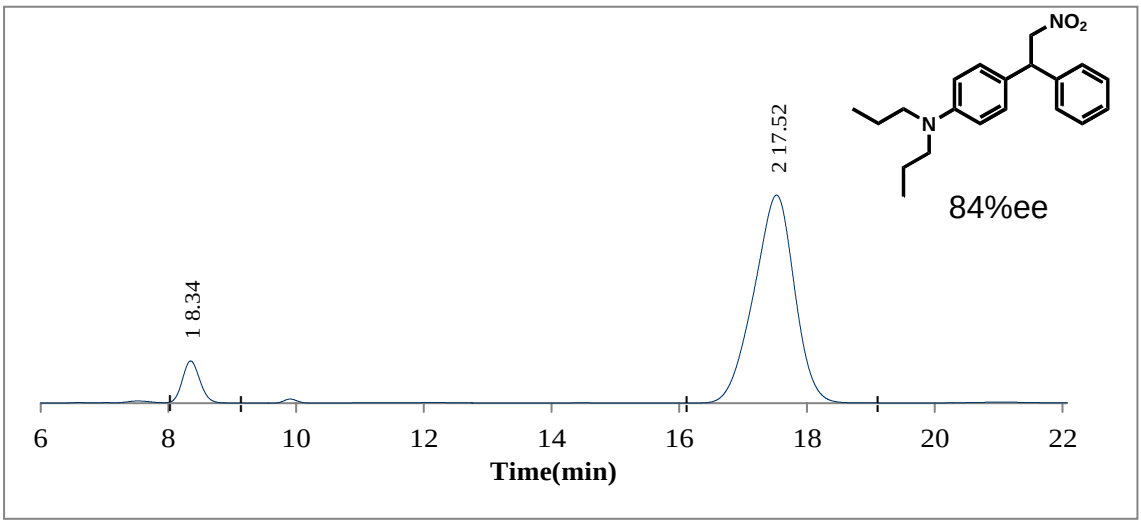
Column: CHIRALCEL OD-H, Eluent: *n*-hexane:2-PrOH = 80:20, Flow rate: 1.0 mL/min , Detection: UV 254 nm, t_{minor} = 11.1 min, t_{major} =14.0 min.

No.	Rt	Area	Area(%)
1	11.11	139533.6	2.7101
2	14.03	5009200	97.2899



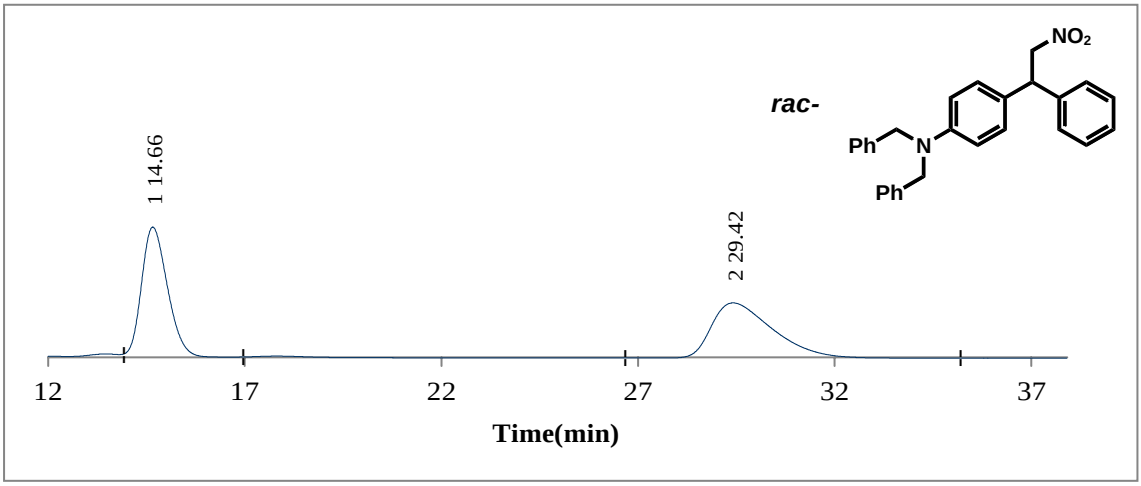
Column: CHIRALCEL OD-H, Eluent : Hex:IPA = 95:5 , Flow rate : 1.0 mL/min , Detection : UV 254 nm

No.	Rt	Area	Area (%)
1	8.97	6163243	49.7328
2	18.37	6229475	50.2672



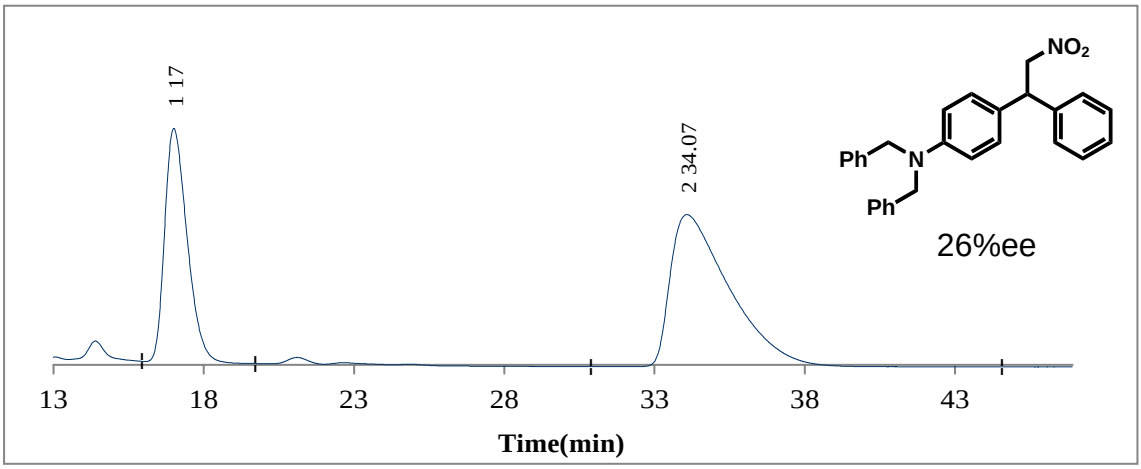
Column: CHIRALCEL OD-H, Eluent : Hex:IPA = 95:5 , Flow rate : 1.0 mL/min , Detection : UV 254 nm

No.	Rt	Area	Area (%)
1	8.34	1103327	7.8925
2	17.52	12876121	92.1075



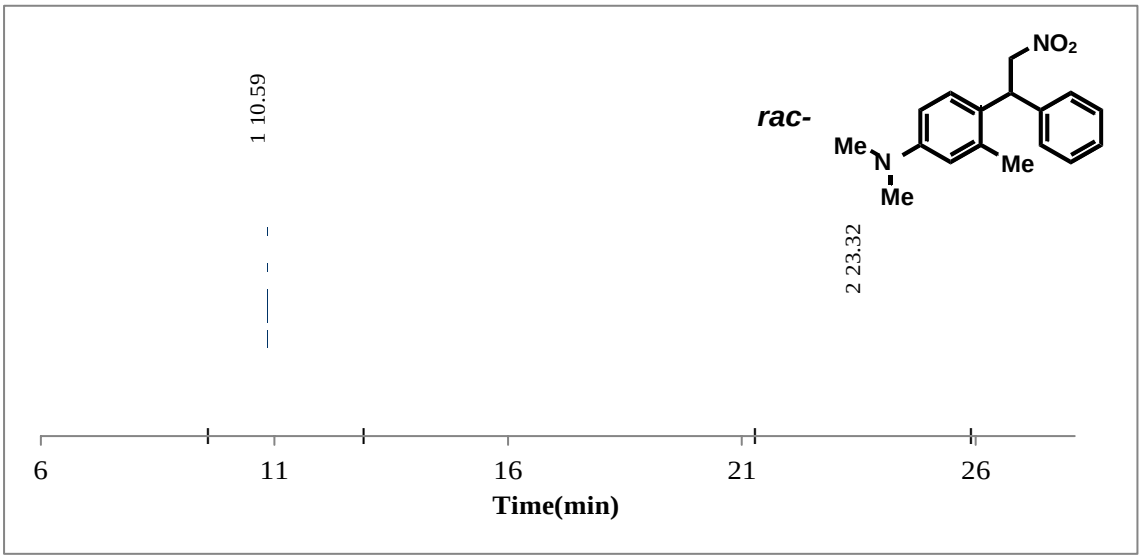
Column: CHIRALCEL OD-H, Eluent: *n*-hexane:2-PrOH = 70:30, Flow rate: 1.0 mL/min, Detection: UV 254 nm, Rt = 17.0 min, 34.3 min

No.	Rt	Area	Area(%)
1	17.03	24446063	50.1816
2	34.26	24269139	49.8184



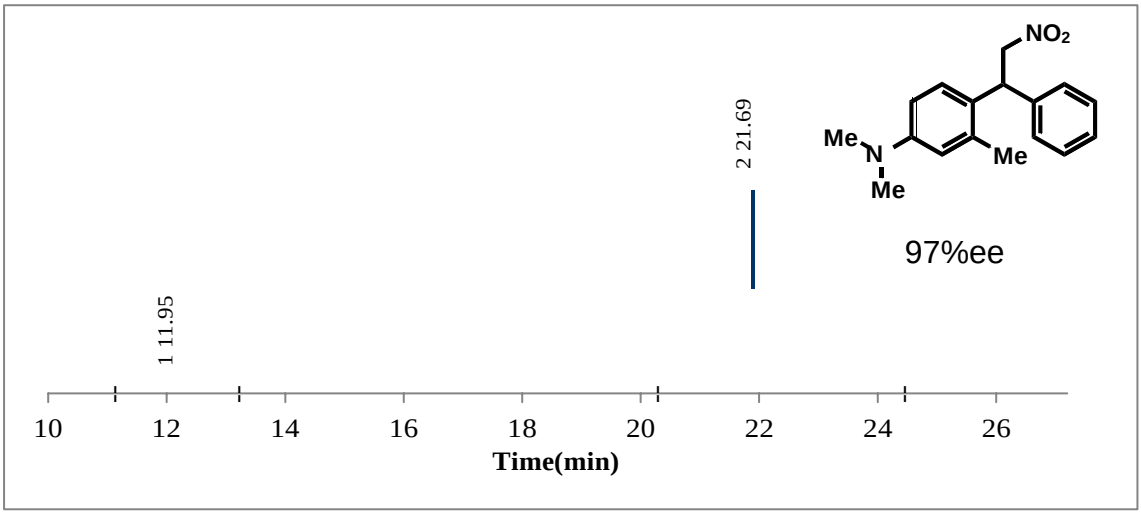
Column: CHIRALCEL OD-H, Eluent : Hex:IPA = 70:30 , Flow rate : 1.0 mL/min , Detection : UV 254 nm

No.	Rt	Area	Area (%)
1	17	5811734	36.7634
2	34.07	9996761	63.2366



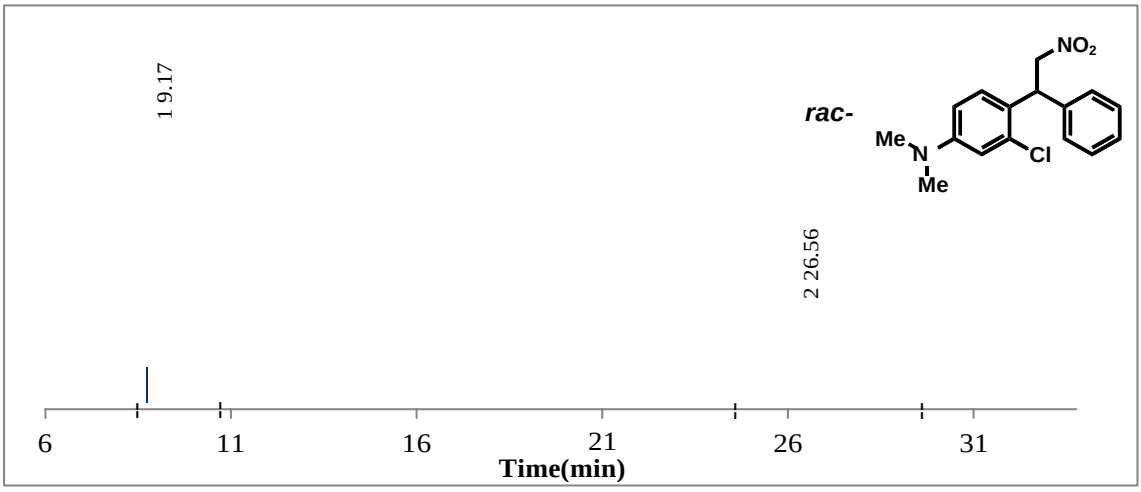
Column: CHIRALCEL OD-H, Eluent: *n*-hexane:2-PrOH = 80:20, Flow rate: 1.0 mL/min, Detection: UV 254 nm, Rt = 10.6 min, 23.3 min

No.	Rt	Area	Area(%)
1	10.59	19012489	49.9216
2	23.32	19072221	50.0784



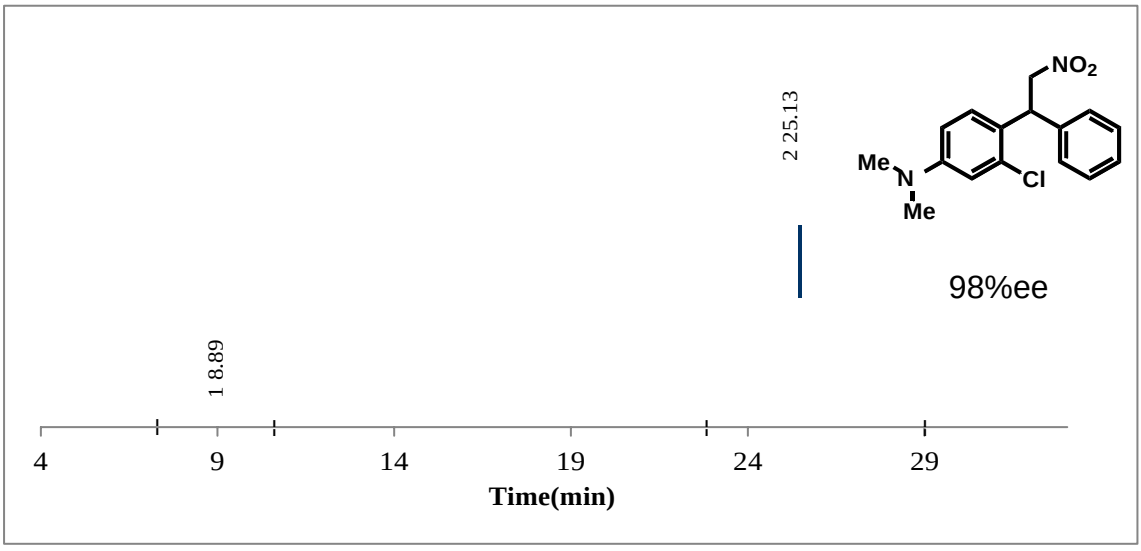
Column: CHIRALCEL OD-H, Eluent: *n*-hexane:2-PrOH = 80:20, Flow rate: 1.0 mL/min, Detection: UV 254 nm, t_{minor} = 12.0 min, t_{major} = 21.7 min

No.	Rt	Area	Area(%)
1	11.95	482966.4	1.5388
2	21.69	30903864	98.4612



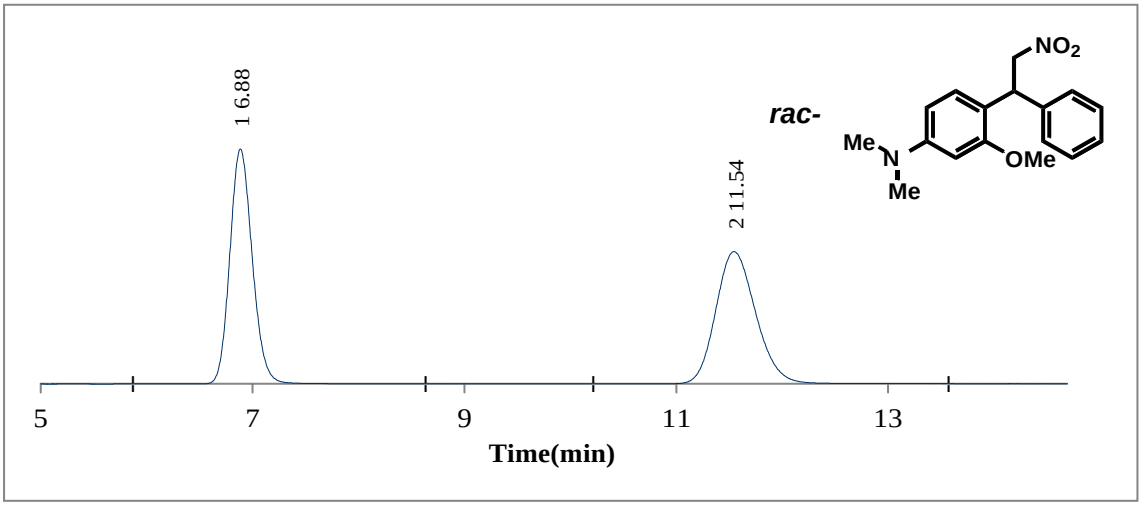
Column: CHIRALCEL OD-H, Eluent: *n*-hexane:2-PrOH = 80:20, Flow rate: 1.0 mL/min, Detection: UV 254 nm, Rt = 9.2 min, 26.6 min

No.	Rt	Area	Area(%)
1	9.17	6100699	49.8666
2	26.56	6133342	50.1334



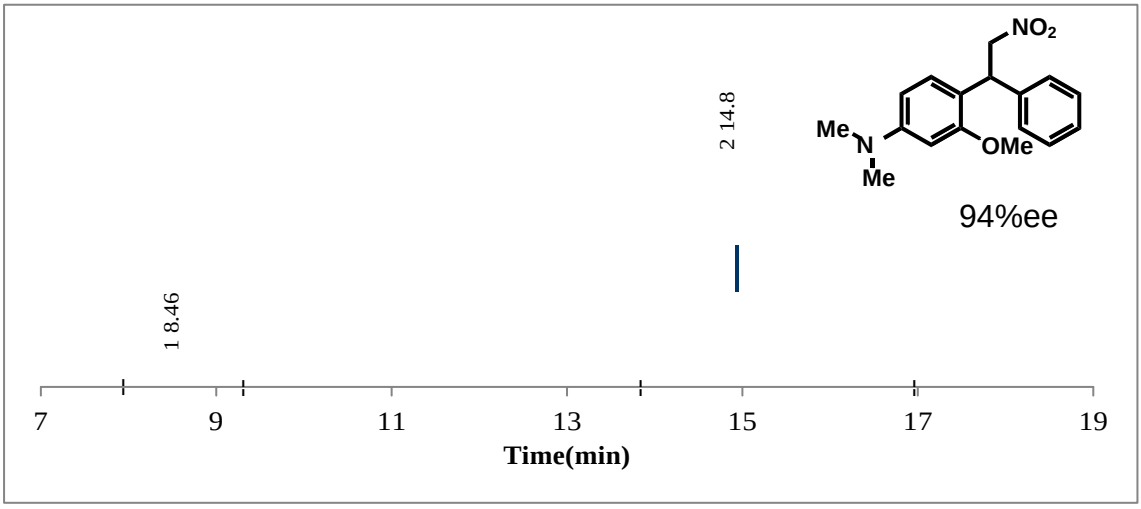
Column: CHIRALCEL OD-H, Eluent: *n*-hexane:2-PrOH = 80:20, Flow rate: 1.0 mL/min, Detection: UV 254 nm, t_{minor} = 12.0 min, t_{major} = 21.7 min

No.	Rt	Area	Area(%)
1	8.89	271734.8	0.9498
2	25.13	28338316	99.0502



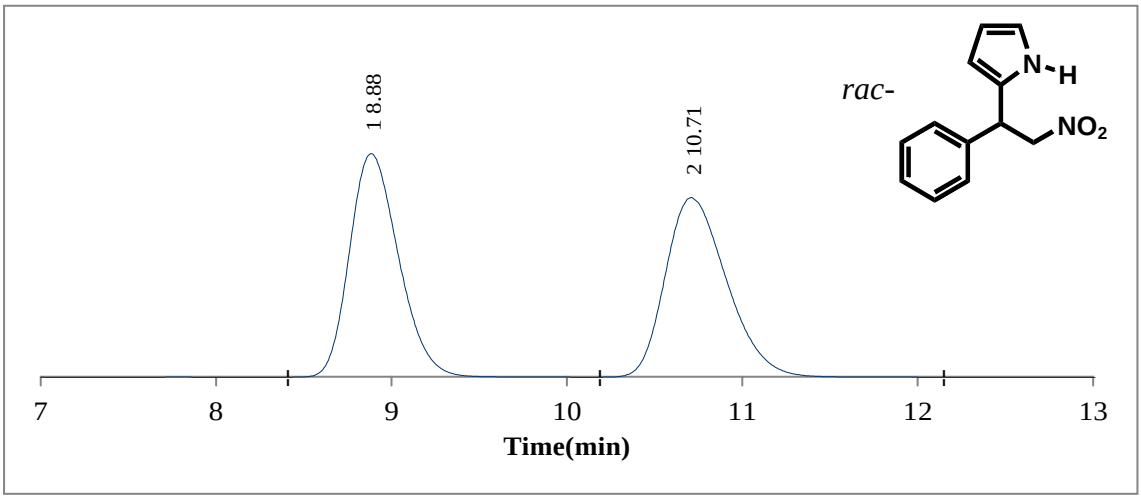
Column: CHIRALCEL OD-H, Eluent : Hex:IPA = 80:20 , Flow rate : 1.0 mL/min , Detection : UV 254 nm

No.	Rt	Area	Area (%)
1	6.88	3776798	50.0094
2	11.54	3775373	49.9906



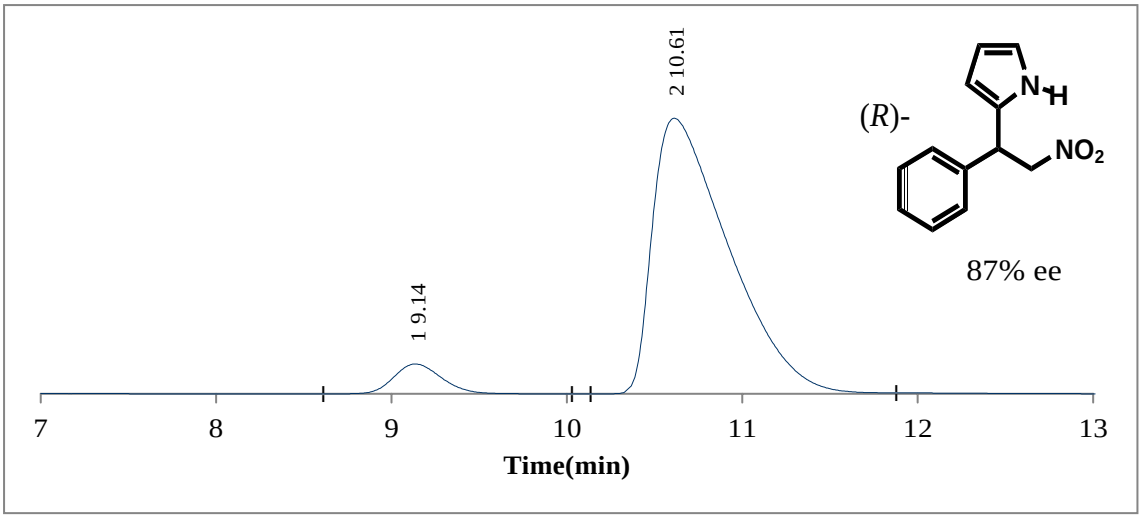
Column: CHIRALCEL OD-H, Eluent : Hex:IPA = 80:20 , Flow rate : 1.0 mL/min , Detection : UV 254 nm

No.	Rt	Area	Area (%)
1	8.46	371519.8	3.2472
2	14.8	11069823	96.7528



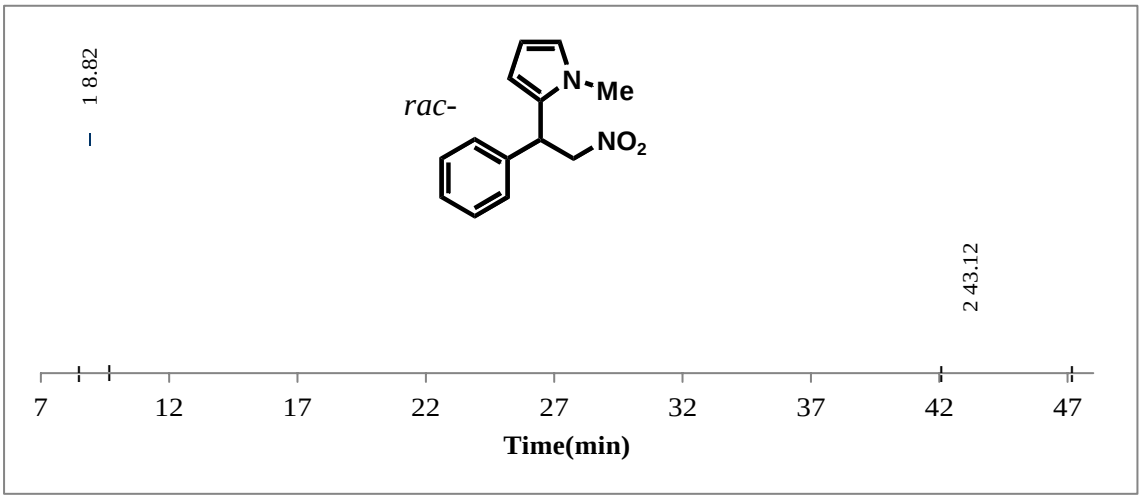
Column: CHIRALCEL OD-H, Eluent: *n*-Hexane : IPA = 80 : 20, Flow rate: 1.0 mL/min, Detection: UV254 nm, t(*R*) = 7.27min, t(*S*) = 8.75min

No.	Rt	Area	Area(%)
1	8.88	3363122	49.8882
2	10.71	3378197	50.1118



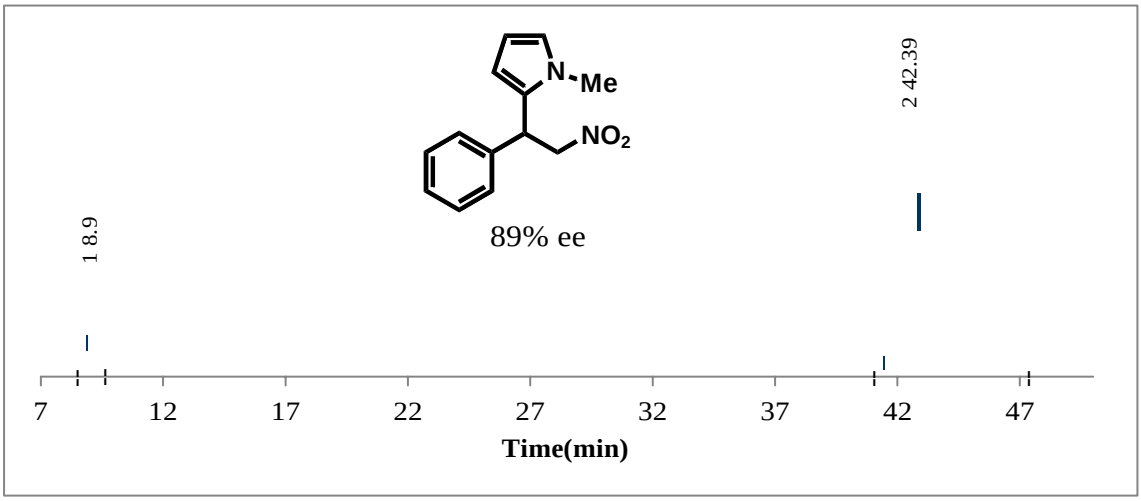
Column: CHIRALCEL OD-H, Eluent: *n*-Hexane : IPA = 80 : 20, Flow rate: 1.0 mL/min, Detection: UV254 nm, t(*R*) = 7.27min, t(*S*) = 8.75min

No.	Rt	Area	Area (%)
1	9.14	2136400	6.3633
2	10.61	31437331	93.6367



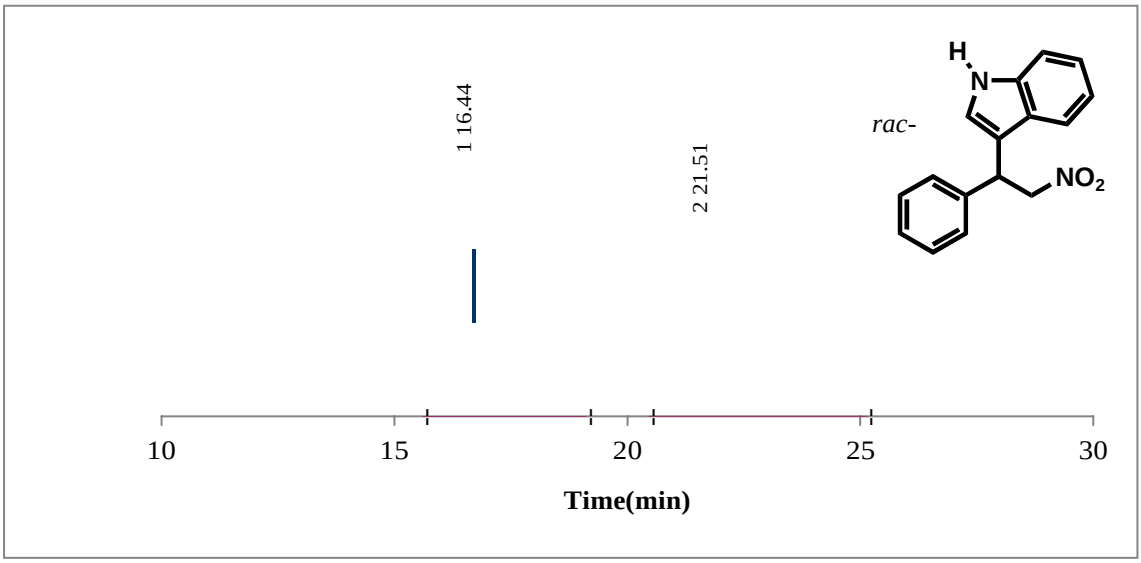
Column: CHIRALCEL OD-H, Eluent: *n*-Hexane : IPA = 80 : 20, Flow rate: 1.0 mL/min, Detection: UV254 nm, t(minor) = 8.39min, t(major) = 38.11min

No.	Rt	Area	Area(%)
1	8.82	7268956	49.7362
2	43.12	7346066	50.2638

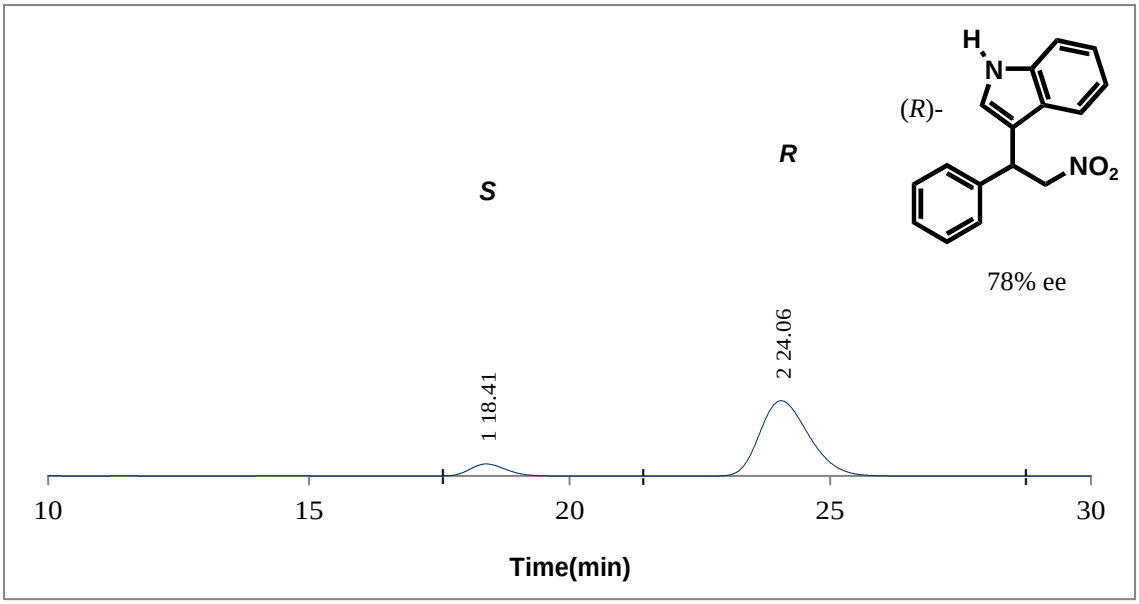


Column: CHIRALCEL OD-H, Eluent: *n*-Hexane : IPA = 80 : 20, Flow rate: 1.0 mL/min, Detection: UV254 nm, t(minor) = 8.9min, t(major) = 42.39min

No.	Rt	Area	Area(%)
1	8.9	518726	5.5081
2	42.39	8898742	94.4919

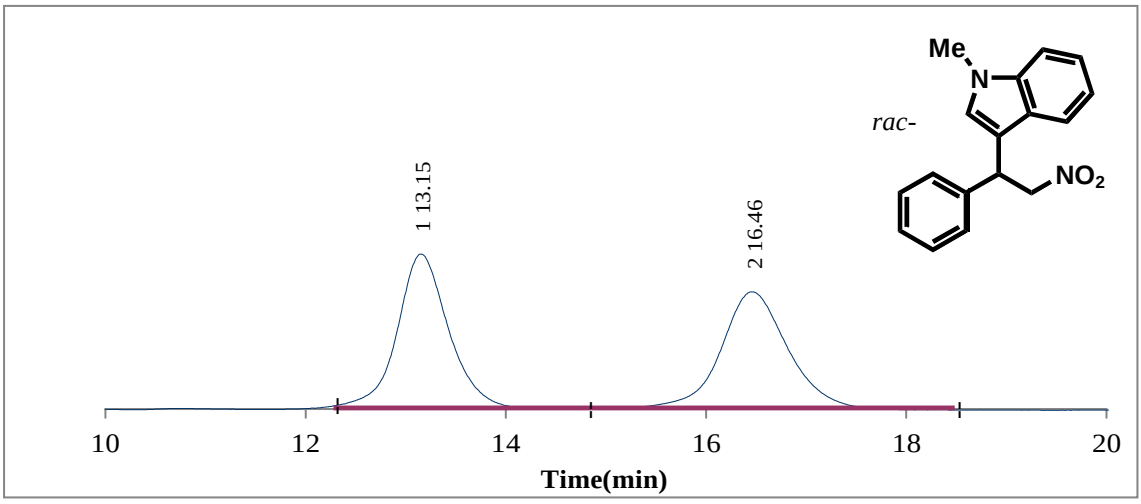


Column : Chiralcel OD-H, Eluent : Hexane /IPA = 70 : 30, Flow rate : 0.8 mL/min, Detection : UV 254 nm

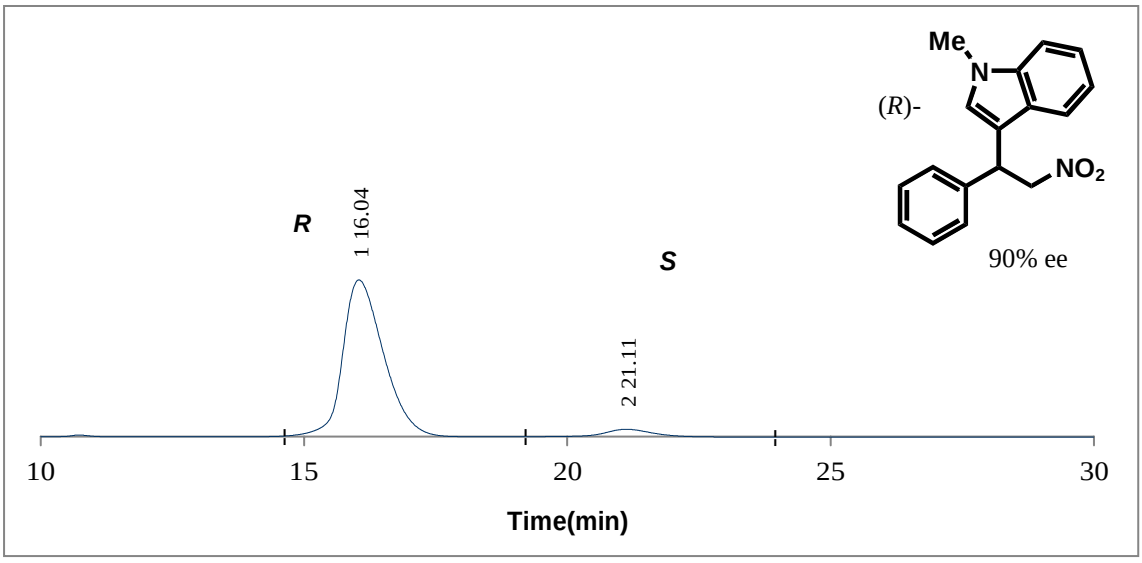


Column : Chiralcel OD-H, Eluent : Hexane /IPA = 70 : 30, Flow rate : 0.8 mL/min, Detection : UV 254 nm

No.	Rt	Area	Area (%)
1	18.41	1638397	10.5916
2	24.06	13830447	89.4084



Column : Chiralpak AS, Eluent : *n*-Hexane /IPA = 90 : 10, Flow rate : 1.0 mL/min, Detection : UV 254 nm.



Column : Chiralpak AS, Eluent : *n*-Hexane /IPA = 90 : 10, Flow rate : 1.0 mL/min, Detection : UV 254 nm.

No.	Rt	Area	Area (%)
1	16.04	25793240	94.6846
2	21.11	1447977	5.3154

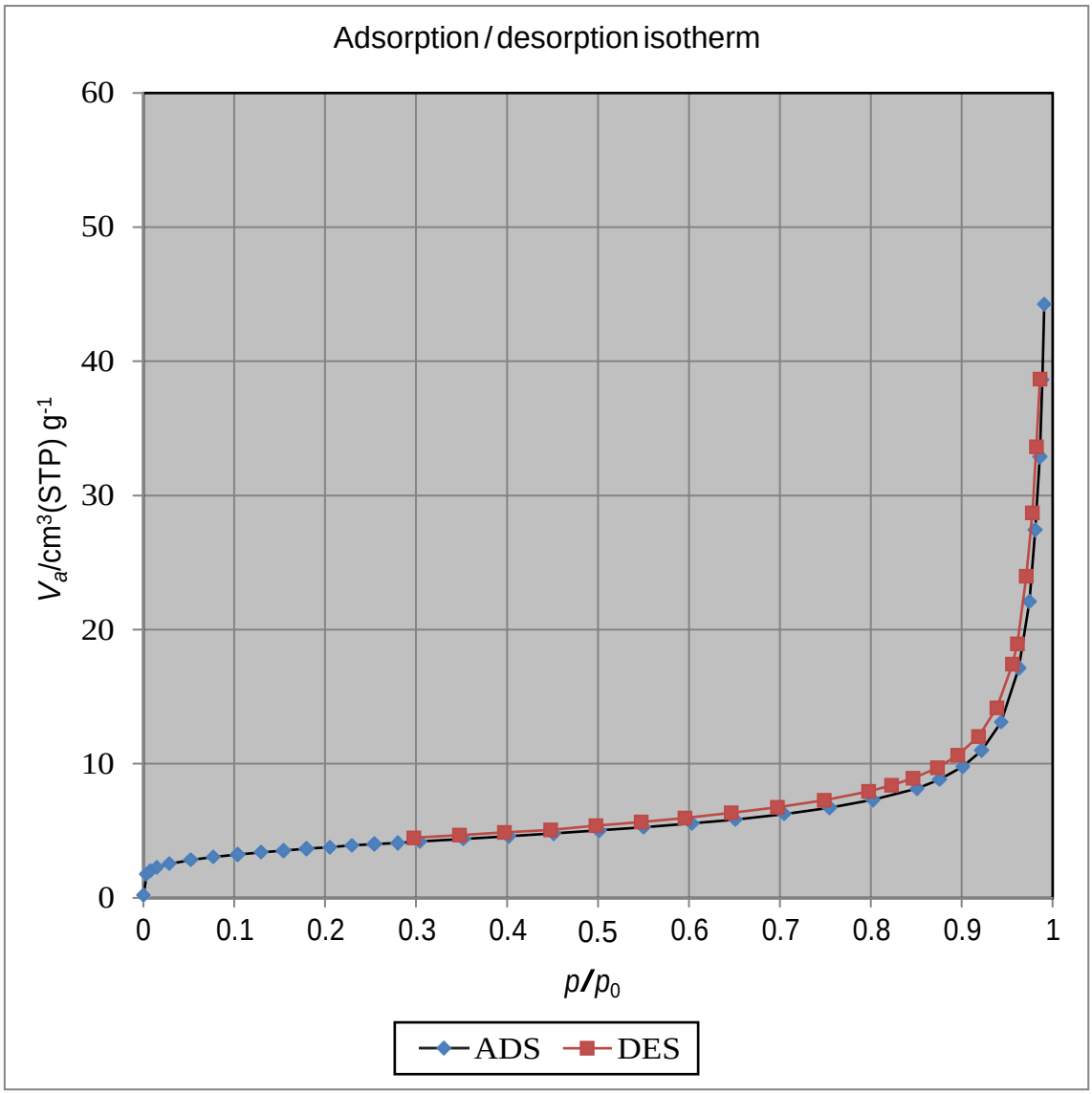


Figure S1. N_2 adsorption isotherms (77K) of (*R*)-CuMOF-**1**.

BET surface area: 13.5 m^2/g

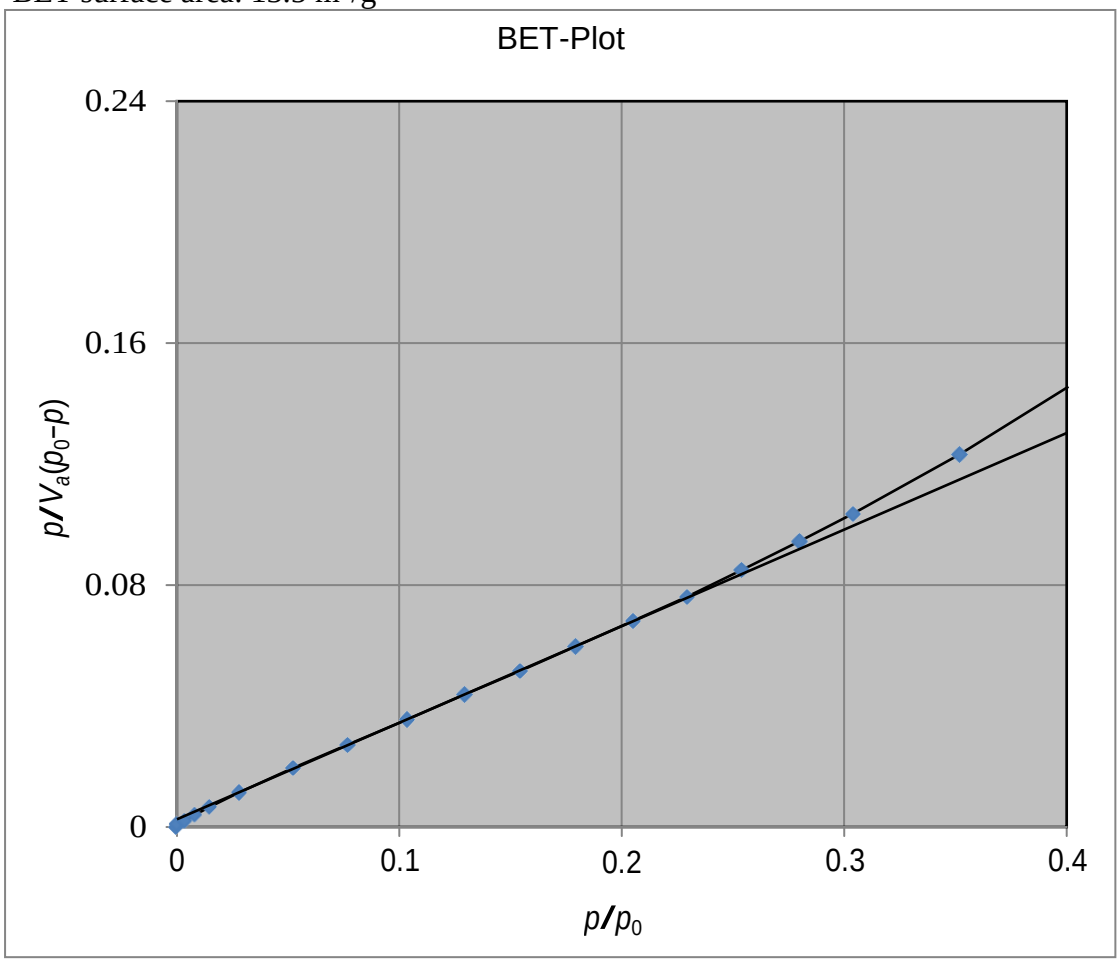


Figure S2. BET plot of (*R*)-CuMOF-**1**.