A Squaramide-catalysed Asymmetric Cascade Michael Addition/Acyl Transfer Reaction between Unsaturated Benzothiophenones and α-Nitroketones

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Supporting Information

Content

1. General information and starting materials

General information. Commercially available reagents were used without further purification. Column chromatography was performed with silica gel (200-300 mesh). Melting points were determined with an XT-4 melting-point apparatus and are uncorrected. ^{1}H NMR spectra were measured with Bruker Ascend 400 MHz spectrometer in $CDCl_3$, chemical shifts were reported in δ (ppm) units relative to tetramethylsilane (TMS) as the internal standard. ^{13}C NMR spectra were measured at 100 MHz (or 176 MHz) with a Bruker Ascend 400 MHz (or 700 MHz) spectrometer, chemical shifts were reported in δ (ppm) relative to tetramethylsilane and referenced to the solvent peak ($CDCl_3$ at 77.0 ppm). High resolution mass spectra were measured with an Agilent 6520 Accurate-Mass-Q-TOF MS system equipped with an electrospray ionization (ESI) source. Enantiomeric excesses were determined by chiral HPLC analysis using an Agilent 1200 LC instrument with a Daicel Chiralpak IC or AD-H column. Optical rotations were measured with a Krüss P8000 polarimeter at the indicated concentration with the units of grams per 100 mL.

Starting materials. 1a–**1l** and **3a**–**3f** were prepared according to the literature.[1] **2a**−**2m** were prepared as described in the literature.[2] The squaramide organocatalysts were prepared by following the reported procedures.[3]

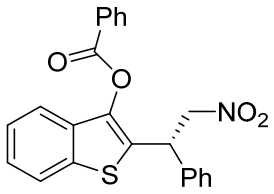
[1] Y. Zhang, A. Yu, J. Jia, S. Ma, K. Li, Y. Wei and X. Meng, *Chem. Commun. (Camb)*, 2017, **53**, 10672-10675. b) V. Dočekal, B. Formánek, I. Císařová and J. Veselý, *Org. Chem. Front.*, 2019, **6**, 3259-3263.

[2] H. H. Nguyen and M. J. Kurth, *Org. Lett.*, 2013, **15**, 362-365. b) R. Maity, C. Gharui, A. K. Sil and S. C. Pan, *Org. Lett.*, 2017, **19**, 662-665.

[3] a) Y. Zhu, J. P. Malerich and V. H. Rawal, *Angew. Chem. Int. Ed.*, 2010, **49**, 153-156. b) W. Yang, D. M. Du, *Org. Lett.* 2010, **12**, 5450−5453. c) W.Yang, D. M. Du, *Adv. Synth. Catal.*, 2011, 353, 1241−1246.

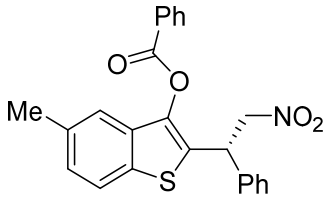
2. Enantioselective synthesis and characterization of compounds 3

Unsaturated benzothiophene **1a** (0.12 mmol), *α*-nitroketones **2** (0.10 mmol), and catalyst **C3** (0.0025 mmol) were dissolved in CH_2Cl_2 (1.0 mL), and the mixture was stirred at room temperature for 48 h. After completion of the reaction, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 to 8:1) to afford the pure products **3**. Racemates were prepared following a similar procedure with Et_3N (2.5 mol%).



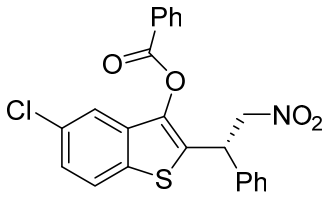
3aa

(*S*)-2-(2-Nitro-1-phenylethyl)benzo[*b*]thiophen-3-yl benzoate (3aa). White solid (42.8 mg, 95% yield), mp 87–89 °C. HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 7.2 min (major), t_R = 8.7 min (minor); 96% *ee*. $[\alpha]_D^{25}$ = +56.6° (*c* = 1.58, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 – 8.25 (m, 2H, ArH), 7.69 – 7.66 (m, 2H, ArH), 7.55 (t, *J* = 7.8 Hz, 2H, ArH), 7.47 – 7.45 (m, 1H, ArH), 7.33 – 7.24 (m, 7H, ArH), 5.28 (t, *J* = 8.0 Hz, 1H, CH), 5.04 (d, *J* = 7.8 Hz, 2H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 138.1, 137.3, 135.8, 134.2, 132.5, 130.4, 129.3, 129.1, 128.8, 128.2, 128.1, 127.4, 125.4, 124.8, 122.8, 120.7, 78.0, 41.8 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{21}N_2O_4S$ $[M + NH_4]^+$ 421.1217, found 421.1215.



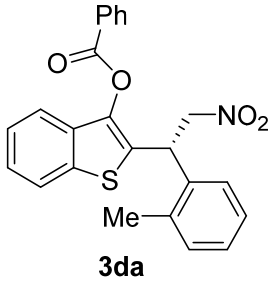
3ba

(*S*)-5-Methyl-2-(2-nitro-1-phenylethyl)benzo[b]thiophen-3-yl benzoate (3ba). Colorless oil (33.8 mg, 81% yield). HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 7.0 min (major), t_R = 7.7 min (minor); 96% *ee*. $[\alpha]_D^{25}$ = +55.4° (*c* = 1.84, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 – 8.27 (m, 2H, ArH), 7.71 (t, *J* = 7.4 Hz, 1H, ArH), 7.60 – 7.56 (m, 3H, ArH), 7.32 – 7.25 (m, 6H, ArH), 7.16 (dd, J_1 = 8.4, J_2 = 1.2 Hz, 1H, ArH), 5.26 (t, *J* = 8.0 Hz, 1H, CH), 5.05 (d, *J* = 8.0 Hz, 2H, ArH), 2.38 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3, 137.8, 137.4, 134.9, 134.2, 133.1, 132.8, 130.5, 129.3, 129.1, 128.8, 128.3, 128.1, 127.4, 127.2, 122.5, 120.5, 78.1, 41.8, 21.4 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{23}N_2O_4S$ $[M + NH_4]^+$ 435.1374, found 435.1366; calcd. for $C_{24}H_{19}NO_4SK$ $[M + K]^+$ 456.0666, found 456.0664.



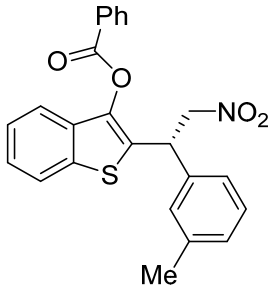
3ca

(*S*)-5-Chloro-2-(2-nitro-1-phenylethyl)benzo[*b*]thiophen-3-yl benzoate (3ca). Colorless oil (41.6 mg, 95% yield). HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 95:5, flow rate 1.0 mL/min, detection at 254 nm): t_R = 15.7 min (major), t_R = 19.7 min (minor); 97% *ee*. $[\alpha]_D^{25}$ = +62.6° (*c* = 2.13, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 – 8.25 (m, 2H, ArH), 7.72 (t, *J* = 7.4 Hz, 1H, ArH), 7.62 – 7.56 (m, 3H, ArH), 7.44 (d, *J* = 1.6 Hz, 1H, ArH), 7.32 – 7.27 (m, 6H, ArH), 5.26 (t, *J* = 8.0 Hz, 1H, CH), 5.05 (d, *J* = 8.0 Hz, 2H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 137.4, 137.1, 134.4, 133.9, 133.8, 131.6, 131.4, 130.5, 129.2, 128.9, 128.3, 127.9, 127.4, 126.0, 123.9, 120.4, 77.9, 41.9 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{20}ClN_2O_4S$ $[M + NH_4]^+$ 455.0827, found 455.0829; calcd. for $C_{23}H_{16}ClNO_4SNa$ $[M + Na]^+$ 460.0381, found 460.0384.



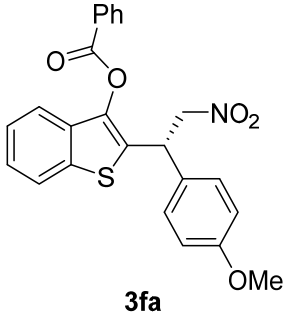
3da

(*S*)-2-(2-Nitro-1-(*o*-tolyl)ethyl)benzo[*b*]thiophen-3-yl benzoate (3da). Colorless oil (38.0 mg, 91% yield). HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 95:5, flow rate 1.0 mL/min, detection at 254 nm): t_R = 14.0 min (major), t_R = 20.6 min (minor); 94% *ee*. $[\alpha]_D^{25}$ = +68.1° (*c* = 1.10, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 – 8.26 (m, 2H, ArH), 7.74 – 7.67 (m, 2H, ArH), 7.58 (t, *J* = 7.8 Hz, 2H, ArH), 7.48 – 7.46 (m, 1H, ArH), 7.39 – 7.37 (m, 1H, ArH), 7.34 – 7.31 (m, 2H, ArH), 7.24 – 7.14 (m, 3H, ArH), 5.51 (dd, J_1 = 8.8 Hz, J_2 = 7.2 Hz, 1H, CH), 5.15 – 5.04 (m, 2H, CH_2), 2.34 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3, 138.1, 136.7, 136.0, 135.7, 134.3, 132.5, 131.3, 130.5, 129.2, 128.9, 128.2, 128.1, 126.6, 125.4, 125.1, 124.8, 122.8, 120.7, 77.6, 37.6, 19.3 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{23}N_2O_4S$ $[M + NH_4]^+$ 435.1374, found 435.1367; calcd. for $C_{24}H_{19}NO_4SK$ $[M + K]^+$ 456.0666, found 456.0663.



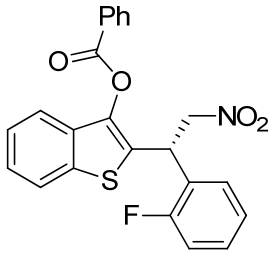
3ea

(*S*)-2-(2-Nitro-1-(*m*-tolyl)ethyl)benzo[*b*]thiophen-3-yl benzoate (3ea). Colorless oil (35.9 mg, 86% yield). HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 6.7 min (major), t_R = 8.0 min (minor); 95% *ee*. $[\alpha]_D^{25}$ = +60.1° (*c* = 0.79, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, *J* = 7.2 Hz, 2H, ArH), 7.73 – 7.70 (m, 2H, ArH), 7.58 (t, *J* = 7.8 Hz, 1H, ArH), 7.48 – 7.46 (m, 1H, ArH), 7.34 – 7.32 (m, 2H, ArH), 7.21 (t, *J* = 7.4 Hz, 1H, ArH), 7.13 (d, *J* = 8.4 Hz, 2H, ArH), 7.07 (d, *J* = 7.6 Hz, 1H, ArH), 5.24 (t, *J* = 8.0 Hz, 1H, CH), 5.06 (d, *J* = 8.0 Hz, 2H, CH_2), 2.27 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 138.9, 138.1, 137.2, 135.8, 134.2, 132.6, 130.5, 129.4, 129.01, 128.96, 128.8, 128.3, 125.4, 124.8, 124.3, 122.8, 120.7, 78.1, 41.8, 21.4 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{23}N_2O_4S$ $[M + NH_4]^+$ 435.1374, found 435.1365; calcd. for $C_{24}H_{19}NO_4SK$ $[M + K]^+$ 456.0666, found 456.0660.



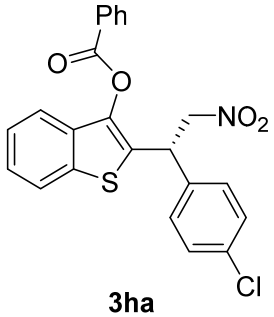
3fa

(*S*)-2-(1-(4-Methoxyphenyl)-2-nitroethyl)benzo[*b*]thiophen-3-yl benzoate (3fa). Colorless oil (36.8 mg, 86% yield). HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 9.8 min (major), t_R = 11.5 min (minor); 93% *ee*. $[\alpha]_D^{25}$ = +61.1° (*c* = 0.43, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 – 8.27 (m, 2H, ArH), 7.74 – 7.70 (m, 2H, ArH), 7.59 (t, *J* = 7.6 Hz, 2H, ArH), 7.48 – 7.46 (m, 1H, ArH), 7.35 – 7.32 (m, 2H, ArH), 7.26 (d, *J* = 8.4 Hz, 2H, ArH), 6.84 (d, *J* = 8.8 Hz, 2H, ArH), 5.25 (dd, J_1 = 8.4 Hz, J_2 = 7.6 Hz, 1H, CH), 5.05 – 5.02 (m, 2H, CH_2), 3.76 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3, 159.4, 137.9, 135.8, 134.3, 132.7, 130.5, 129.8, 129.4, 128.9, 128.6, 128.3, 125.4, 124.9, 122.9, 120.7, 114.5, 78.4, 55.3, 41.2 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{23}N_2O_5S$ $[M + NH_4]^+$ 451.1323, found 451.1322; calcd. for $C_{24}H_{19}NO_5SK$ $[M + K]^+$ 472.0616, found 472.0617.



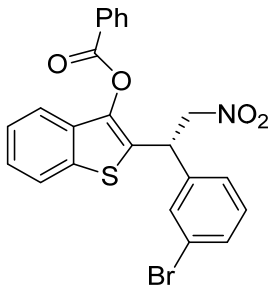
3ga

(*S*)-2-(1-(2-Fluorophenyl)-2-nitroethyl)benzo[*b*]thiophen-3-yl benzoate (3ga). Colorless oil (37.9 mg, 90% yield). HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 6.6 min (major), t_R = 8.2 min (minor); 95% *ee*. $[\alpha]_D^{25}$ = +47.7° (*c* = 1.73, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 – 8.26 (m, 2H, ArH), 7.73 – 7.69 (m, 2H, ArH), 7.57 (t, *J* = 7.8 Hz, 2H, ArH), 7.48 – 7.46 (m, 1H, ArH), 7.38 – 7.32 (m, 3H, ArH), 7.27 – 7.22 (m, 1H, ArH), 7.08 (t, *J* = 7.6 Hz, 1H, ArH), 7.06 – 7.01 (m, 1H, ArH), 5.58 (t, *J* = 7.8 Hz, 1H, CH), 5.10 (d, *J* = 8.0 Hz, 2H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2, 153.4 (d, $^1J_{C–F}$ = 245.9 Hz), 131.5, 128.7, 127.2, 125.5, 123.5, 123.0 (d, $^3J_{C–F}$ = 8.3 Hz), 121.8, 121.6 (d, $^3J_{C–F}$ = 3.5 Hz), 121.2, 120.7, 118.5, 117.9, 117.7 (d, $^4J_{C–F}$ = 3.5 Hz), 117.5 (d, $^2J_{C–F}$ = 13.8 Hz), 115.8, 113.8, 109.2 (d, $^2J_{C–F}$ = 21.8 Hz), 69.9 (d, $^4J_{C–F}$ = 2.8 Hz), 28.9 (d, $^3J_{C–F}$ = 3.0 Hz) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{16}FNO_4SNa$ $[M + Na]^+$ 444.0677, found 444.0682; calcd. for $C_{23}H_{16}FNO_4SK$ $[M + K]^+$ 460.0416, found 460.0420.



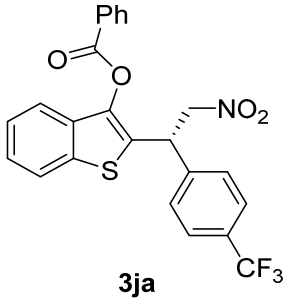
3ha

(*S*)-2-(1-(4-Chlorophenyl)-2-nitroethyl)benzo[*b*]thiophen-3-yl benzoate (3ha). Colorless oil (39.3 mg, 90% yield). HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 6.6 min (major), t_R = 8.2 min (minor); 93% *ee*. $[\alpha]_D^{25}$ = +65.4° (*c* =1.88, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 – 8.24 (m, 2H, ArH), 7.73 – 7.70 (m, 2H, ArH), 7.58 (t, *J* = 7.8 Hz, 2H, ArH), 7.49 – 7.47 (m, 1H, ArH), 7.35 – 7.33 (m, 2H, ArH), 7.27 (s, 4H, ArH), 5.25 (dd, J_1 = 8.8 Hz, J_2 = 7.2 Hz, 1H, CH), 5.08 – 4.98 (m, 2H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 138.3, 135.8, 135.7, 134.3, 134.2, 132.5, 130.5, 129.3, 128.9, 128.8, 128.5, 128.1, 125.6, 125.0, 122.8, 120.8, 77.9, 41.2 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{16}ClNO_4SNa$ $[M + Na]^+$ 460.0381, found 460.0387; calcd. for $C_{23}H_{16}ClNO_4SK$ $[M + K]^+$ 476.0120, found 476.0124.



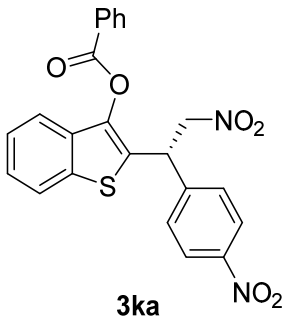
3ia

(*S*)-2-(1-(3-Bromophenyl)-2-nitroethyl)benzo[*b*]thiophen-3-yl benzoate (3ia). Colorless oil (42.8 mg, 89% yield). HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 7.9 min (major), t_R = 9.4 min (minor); 96% *ee*. $[\alpha]_D^{25}$ = +50.6° (*c* = 2.03, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (dd, *J* = 8.2, 1.0 Hz, 2H , ArH), 7.74 – 7.69 (m, 2H , ArH), 7.58 (t, *J* = 7.6 Hz, 2H , ArH), 7.49 – 7.47 (m, 2H , ArH), 7.40 – 7.38 (m, 1H , ArH), 7.35 – 7.30 (m, 2H , ArH), 7.27 (d, *J* = 7.6 Hz, 1H , ArH), 7.17 (t, *J* = 7.8 Hz, 1H , ArH), 5.23 (dd, J_1 = 8.8 Hz, J_2 = 7.2 Hz, 1H, CH), 5.08 – 4.99 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 139.5, 138.4, 135.7, 134.3, 132.5, 131.4, 130.7, 130.6, 130.5, 128.9, 128.2, 128.0, 126.0, 125.6, 125.0, 123.1, 122.8, 120.8, 77.7, 41.4 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{20}{}^{79}BrN_2O_4S$ $[M + NH_4]^+$ 499.0322, found 499.0320, $C_{23}H_{20}{}^{81}BrN_2O_4S$ $[M + NH_4]^+$ 501.0302, found 501.0304.



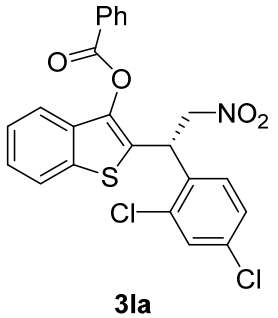
3ja

(*S*)-2-(2-Nitro-1-(4-(trifluoromethyl)phenyl)ethyl)benzo[*b*]thiophen-3-yl benzoate (3ja). White solid (44.3 mg, 94% yield), mp 130–131 °C. HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 5.5 min (major), t_R = 6.6 min (minor); 97% *ee*. $[\alpha]_D^{25}$ = +54.3° (*c* = 2.13, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 – 8.22 (m, 2H), 7.74 – 7.70 (m, 2H, ArH), 7.57 (t, *J* = 8.8 Hz, 4H ArH), 7.50 – 7.45 (m, 3H ArH), 7.36 – 7.34 (m, 2H, ArH), 5.33 (t, *J* = 7.8 Hz, 1H, CH), 5.08 (d, *J* = 8.0 Hz, 2H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 141.3, 138.5, 135.7, 134.4, 132.5, 130.438 (q, $^1J_{C–F}$ = 32.6 Hz), 130.436, 128.9, 127.99, 127.95, 127.8, 126.1 (q, $^2J_{C–F}$ = 3.7 Hz), 125.7, 125.1, 122.9, 122.4, 120.8, 77.6, 41.6 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{20}F_3N_2O_4S$ $[M + NH_4]^+$ 489.1091, found 489.1091; calcd. for $C_{24}H_{16}F_3NO_4SK$ $[M + K]^+$ 510.0384, found 510.0384.



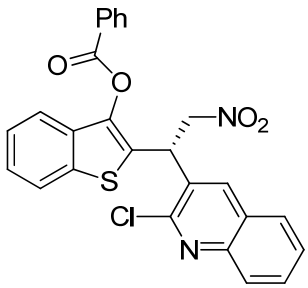
3ka

(*S*)-2-(2-Nitro-1-(4-nitrophenyl)ethyl)benzo[*b*]thiophen-3-yl benzoate (3ka). White solid (39.5 mg, 88% yield), mp 138–139 °C. HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 21.4 min (major), t_R = 25.1 min (minor); 94% *ee*. $[\alpha]_D^{25}$ = +37.8° (*c* = 2.00, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 – 8.22 (m, 2H, ArH), 8.16 (d, *J* = 8.8 Hz, 2H, ArH), 7.76 – 7.72 (m, 2H, ArH), 7.59 (t, *J* = 7.8 Hz, 1H ArH), 7.53 – 7.49 (m, 3H ArH), 7.40 – 7.35 (m, 2H, ArH), 5.38 (t, *J* = 7.8 Hz, 1H, CH), 5.11 (d, *J* =7.6 Hz, 2H, CH_2) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 164.2, 147.6, 144.4, 138.8, 135.7, 134.6, 132.4, 130.4, 129.0, 128.6, 127.8, 127.0, 125.9, 125.2, 124.3, 122.9, 120.9, 77.4, 41.5 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{20}N_2O_6S$ $[M + NH_4]^+$ 466.1068, found 466.1079; calcd. for $C_{23}H_{16}N_2O_6SNa$ $[M + Na]^+$ 471.0621, found 471.0637.



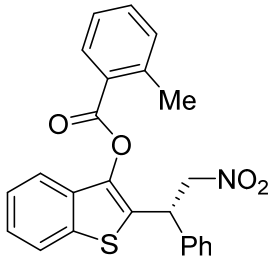
3la

(*S*)-2-(1-(2,4-Dichlorophenyl)-2-nitroethyl)benzo[*b*]thiophen-3-yl benzoate (3la). Colorless oil (39.1 mg, 83% yield). HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 6.4 min (major), t_R = 7.8 min (minor); 95% *ee*. $[\alpha]_D^{25}$ = +25.4° (*c* = 1.87, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 – 8.22 (m, 2H, ArH), 7.74 – 7.69 (m, 2H, ArH), 7.56 (t, *J* = 7.6 Hz, 2H, ArH), 7.50 – 7.46 (m, 1H, ArH), 7.39 – 7.32 (m, 4H, ArH), 7.20 (dd, J_1 = 8.4, J_2 = 2.0 Hz Hz, 1H, ArH), 5.77 (t, *J* = 8.0 Hz, 1H, CH), 5.07 – 5.04 (m, 2H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 138.9, 135.7, 134.8, 134.7, 134.3, 133.5, 132.5, 130.4, 130.2, 128.8, 128.5, 128.1, 127.8, 126.7, 125.7, 125.0, 122.8, 120.9, 76.6, 38.0 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{19}Cl_2N_2O_4S$ $[M + NH_4]^+$ 489.0438, found 489.0442; calcd. for $C_{23}H_{15}Cl_2NO_4SK$ $[M + K]^+$ 509.9730, found 509.9731.



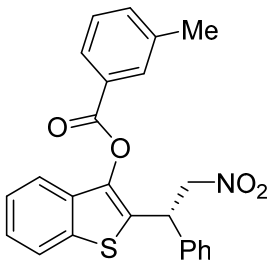
3ma

(*S*)-2-(1-(2-Chloroquinolin-3-yl)-2-nitroethyl)benzo[*b*]thiophen-3-yl benzoate (3ma). Colorless oil (32.2 mg, 89% yield). HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 13.1 min (major), t_R = 15.3 min (minor); 98% *ee*. $[\alpha]_D^{25}$ = +129.5° (*c* =1.63, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 1H, ArH), 8.17 – 8.15 (m, 2H, ArH), 7.97 (d, *J* = 8.4 Hz, 1H, ArH), 7.75 – 7.65 (m, 4H, ArH), 7.53 – 7.48 (m, 4H, ArH), 7.38 – 7.35 (m, 2H, ArH), 5.86 (t, *J* = 8.0 Hz, 1H, CH), 5.22 (qd, J_1 = 14.0, J_2 = 8.4 Hz, 2H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3, 149.9, 146.9, 139.2, 136.3, 135.8, 134.3, 132.7, 131.0, 130.4, 129.0, 128.8, 128.2, 127.8, 127.6, 126.8, 126.2, 125.8, 125.1, 122.8, 120.9, 76.3, 38.8 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{27}H_{17}Cl_2NO_4S$ $[M + H]^+$ 489.0671, found 489.0658; calcd. for $C_{27}H_{16}Cl_2NO_4SK$ $[M + K]^+$ 527.0229, found 527.0227.



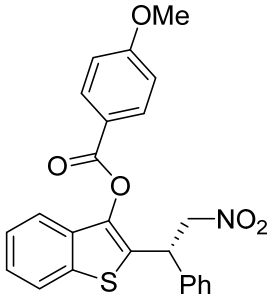
3ab

(*S*)-2-(2-Nitro-1-phenylethyl)benzo[*b*]thiophen-3-yl 2-methylbenzoate (3ab). Colorless oil (28.8 mg, 69% yield). HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 6.2 min (major), t_R = 6.9 min (minor); 97% *ee*. $[\alpha]_D^{25}$ =53.5° (*c* = 0.70, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (dd, J_1 = 7.8 Hz, J_2 = 1.0 Hz, 1H, ArH), 7.73 – 7.71 (m, 1H, ArH), 7.56 (td, J_1 = 7.4 Hz, J_2 = 1.2 Hz, 1H, ArH), 7.51 – 7.49 (m, 1H, ArH), 7.42 – 7.27 (m, 9H, ArH), 5.29 (t, *J* = 8.0 Hz, 1H, CH), 5.08 (d, *J* = 8.0 Hz, 2H, CH_2), 2.68 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6, 142.1, 138.2, 137.4, 135.8, 133.4, 132.7, 132.2, 131.4, 129.2, 129.1, 128.2, 127.4, 127.2, 126.2, 125.4, 124.9, 122.9, 120.7, 78.1, 41.8, 22.0 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{23}N_2O_4$ $[M + NH_4]^+$ 435.1363, found 435.1363.



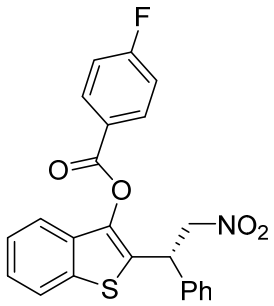
3ac

(*S*)-2-(2-Nitro-1-phenylethyl)benzo[*b*]thiophen-3-yl 3-methylbenzoate (3ac). White solid (38.0 mg, 91% yield), mp 77–78 °C. HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 7.3 min (major), t_R = 9.3 min (minor); 95% *ee*. $[\alpha]_D^{25}$ = +40.5° (*c* = 1.87, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 – 8.07 (m, 2H, ArH), 7.72 – 7.69 (m, 1H, ArH), 7.52 (d, *J* = 7.6 Hz, 1H, ArH), 7.48 – 7.44 (m, 2H, ArH), 7.33 – 7.27 (m, 7H, ArH), 5.28 (t, *J* = 8.0 Hz, 1H, CH), 5.06 (d, *J* = 8.0 Hz, 2H, CH_2), 2.48 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 138.8, 138.2, 137.4, 135.8, 135.0, 132.6, 131.0, 129.3, 129.1, 128.8, 128.2, 128.1, 127.6, 127.4, 125.4, 124.8, 122.8, 120.7, 78.1, 41.8, 21.3 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{23}N_2O_4S$ $[M + NH_4]^+$ 435.1373, found 435.1363.



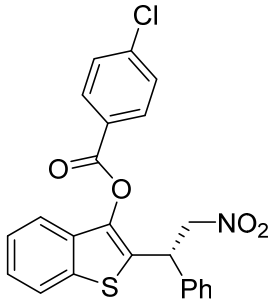
3ad

(*S*)-2-(2-Nitro-1-phenylethyl)benzo[*b*]thiophen-3-yl 4-methoxybenzoate (3ad). Colorless oil (41.1 mg, 95% yield). HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 10.0 min (major), t_R = 12.9 min (minor); 95% *ee*. $[\alpha]_D^{25}$ = +63.0° (*c* = 1.91, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 – 8.21 (m, 2H, ArH), 7.70 – 7.62 (m, 1H, ArH), 7.49 – 7.45 (m, 1H, ArH), 7.36 – 7.26 (m, 7H, ArH), 7.05 – 7.03 (m, 2H, ArH), 5.27 (t, *J* = 7.8 Hz, 1H, CH), 5.06 (d, *J* = 8.0 Hz, 2H, CH_2), 3.91 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 163.9, 138.3, 137.5, 135.8, 132.73, 132.67, 129.2, 129.1, 128.2, 127.4, 125.3, 124.8, 122.8, 120.8, 120.4, 114.1, 78.0, 55.6, 41.8 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{19}NO_5SNa$ $[M + Na]^+$ 456.0877, found 456.0877; calcd. for $C_{24}H_{19}NO_5SK$ $[M + K]^+$ 472.0616, found 472.0613.



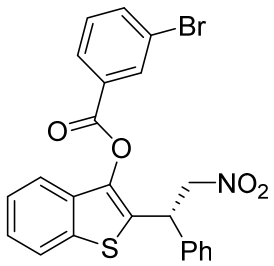
3ae

(*S*)-2-(2-Ntro-1-phenylethyl)benzo[*b*]thiophen-3-yl 4-fluorobenzoate (3ae). White solid (33.3 mg, 79% yield), mp 96–97 °C. HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 7.1 min (major), t_R = 8.5 min (minor); 95% *ee*. $[\alpha]_D^{25}$ = +64.4° (*c* = 1.28, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 – 8.26 (m, 2H, ArH), 7.73 – 7.69 (m, 1H, ArH), 7.47 – 7.43 (m, 1H, ArH), 7.35 – 7.22 (m, 9H, ArH), 5.27 (t, *J* = 8.0 Hz, 1H, CH), 5.05 (d, *J* = 7.6 Hz, 2H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5 (d, $^1J_{C–F}$ = 244.9 Hz), 163.3, 138.0, 137.3, 135.8, 133.2 (d, $^3J_{C–F}$ = 9.5 Hz), 132.5, 129.4, 129.1, 128.2, 127.4, 125.5, 124.9, 124.5 (d, $^4J_{C–F}$ = 3.0 Hz), 122.9, 120.6, 116.2 (d, $^2J_{C–F}$ = 22.2 Hz), 78.2, 41.8 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{20}FN_2O_4S$ $[M + NH_4]^+$ 439.1123, found 439.1121; calcd. for $C_{23}H_{16}FNO_4SNa$ $[M + Na]^+$ 444.0677, found 444.0672.



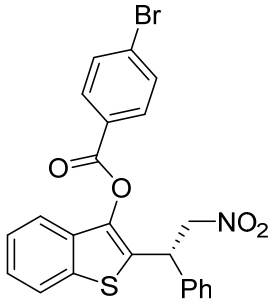
3af

(*S*)-2-(2-Nitro-1-phenylethyl)benzo[*b*]thiophen-3-yl 4-chlorobenzoate (3af). White solid (39.3 mg, 90% yield), mp 97–98 °C. HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 7.5 min (major), t_R = 9.2 min (minor); 96% *ee*. $[\alpha]_D^{25}$ = +12.1° (*c* = 4.79, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): 8.19 (d, *J* = 8.4 Hz, 2H, ArH), 7.73 – 7.71 (m, 1H, ArH), 7.55 (d, *J* = 8.4 Hz, 2H, ArH), 7.46 – 7.42 (m, 1H, ArH), 7.35 – 7.27 (m, 7H, ArH), 5.26 (t, *J* = 8.0 Hz, 1H, CH), 5.05 (d, *J* = 8.0 Hz, 2H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4, 140.9, 137.9, 137.3, 135.8, 132.4, 131.8, 129.4, 129.3, 129.2, 128.3, 127.4, 126.7, 125.5, 124.9, 122.9, 120.6, 78.2, 41.8 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{20}ClN_2O_4S$ $[M + NH_4]^+$ 455.0827, found 455.0825; calcd. for $C_{23}H_{16}ClNO_4SK$ $[M + K]^+$ 476.0120, found 476.0122.



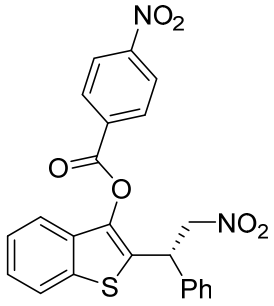
3ag

(*S*)-2-(2-Nitro-1-phenylethyl)benzo[*b*]thiophen-3-yl 3-bromobenzoate(3ag). White solid (32.2 mg, 67% yield), mp 105–107 °C. HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 7.4 min (major), t_R = 8.8 min (minor); 92% *ee*. $[\alpha]_D^{25}$ = +44.6° (*c* = 1.04, CH_2Cl_2).^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (t, *J* = 1.6 Hz, 1H, ArH), 8.19 (d, *J* = 8.0 Hz, 1H, ArH), 7.85 – 8.83 (m, 1H, ArH), 7.74 – 7.71 (m, 1H, ArH), 7.48 – 7.44 (m, 2H, ArH), 7.36 – 7.28 (m, 7H, ArH), 5.26 (t, *J* = 8.0 Hz, 1H, CH), 5.06 (d, *J* = 8.0 Hz, 2H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.0, 137.8, 137.24, 137.19, 135.8, 133.4, 132.3, 130.4, 130.1, 129.5, 129.2, 129.0, 128.3, 127.4, 125.5, 124.9, 122.92, 122.88 120.6, 78.2, 41.8 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{20}{}^{79}BrN_2O_4S$ $[M + NH_4]^+$ 499.0322, found 499.0274, $C_{23}H_{20}{}^{81}BrN_4O_4S$ $[M + NH_4]^+$ 501.0302, found 501.0257.



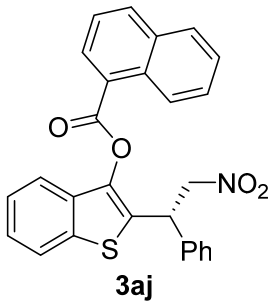
3ah

(*S*)-2-(2-Nitro-1-phenylethyl)benzo[*b*]thiophen-3-yl 4-bromobenzoate (3ah). Colorless oil (40.4 mg, 84% yield). HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 7.9 min (major), t_R = 9.8 min (minor); 96% *ee*. $[\alpha]_D^{25}$ = +64.1° (*c* = 1.69, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 – 8.09 (m, 2H, ArH), 7.73 – 7.70 (m, 3H, ArH), 7.45 – 7.42 (m, 1H, ArH), 7.35 – 7.27 (m, 7H, ArH), 5.26 (t, *J* = 7.8 Hz, 1H, CH), 5.04 (d, *J* = 8.0 Hz, 2H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.6, 137.9, 137.3, 135.8, 132.4, 132.3, 131.9, 129.6, 129.4, 129.2, 128.2, 127.4, 127.1, 125.5, 124.9, 122.9, 120.6, 78.2, 41.8 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{20}{}^{79}BrN_2O_4S$ $[M + NH_4]^+$ 499.0322, found 499.0328, $C_{23}H_{20}{}^{81}BrN_4O_4S$ $[M + NH_4]^+$ 501.0302, found 501.0309; calcd. for $C_{23}H_{16}{}^{79}BrNO_4SNa$ $[M + Na]^+$ 503.9876, found 503.9890, $C_{23}H_{16}{}^{81}BrNO_4SNa$ $[M + Na]^+$ 505.9856, found 505.9861.



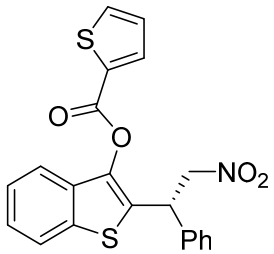
3ai

(*S*)-2-(2-Nitro-1-phenylethyl)benzo[*b*]thiophen-3-yl 4-nitrobenzoate (3ai). Colorless oil (26.9 mg, 60% yield). HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 21.4 min (major), t_R = 28.8 min (minor); 96% *ee*. $[\alpha]_D^{25}$ = +53.8° (*c* = 0.64, CH_2Cl_2).^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, 4H, ArH), 7.76 – 7.74 (m, 1H, ArH), 7.45 – 7.43 (m, 1H, ArH), 7.39 – 7.36 (m, 2H, ArH), 7.34 – 7.28 (m, 5H, ArH), 5.27 (t, *J* = 8.0 Hz, 1H, CH), 5.10 – 5.01 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 151.2, 137.6, 137.1, 135.8, 133.6, 132.1, 131.6, 129.7, 129.2, 128.4, 127.4, 125.7, 125.1, 124.0, 123.0, 120.5, 78.3, 41.9 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{20}N_3O_6S$ $[M + NH_4]^+$ 466.1068, found 466.1072; calcd. for $C_{23}H_{16}N_2O_6SK$ $[M + K]^+$ 487.0361, found 487.0358.



3aj

(*S*)-2-(2-Nitro-1-phenylethyl)benzo[*b*]thiophen-3-yl 1-naphthoate (3aj). Colorless oil (29.9 mg, 66% yield). HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 7.6 min (major), t_R = 9.2 min (minor); 96% *ee*. $[\alpha]_D^{25}$ = +91.8° (*c* = 0.52, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.00 (d, *J* = 8.4 Hz, 1H, ArH), 8.61 – 8.61 (dd, J_1 = 8.8 Hz, J_2 = 0.8 Hz, 1H, ArH), 8.18 (d, *J* = 8.4 Hz, 1H, ArH), 7.97 (d, *J* = 8.0 Hz, 1H, ArH), 7.75 – 7.73 (m, 1H, ArH), 7.69 – 7.58 (m, 3H, ArH), 7.57 – 7.55 (m, 1H, ArH), 7.37 – 7.26 (m, 7H, ArH), 5.36 (t, *J* = 8.0 Hz, 1H, CH), 5.15 – 5.05 (m, 2H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6, 138.3, 137.4, 135.9, 135.1, 134.0, 132.7, 131.84, 131.78, 129.4, 129.2, 128.8, 128.6, 128.2, 127.5, 126.7, 125.7, 125.4, 124.9, 124.6, 124.4, 122.9, 120.8, 78.2, 41.9 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{27}H_{23}N_2O_4S$ $[M + NH_4]^+$ 471.1374, found 471.1370; calcd. for $C_{27}H_{19}NO_4SK$ $[M + K]^+$ 492.0666, found 492.0664.

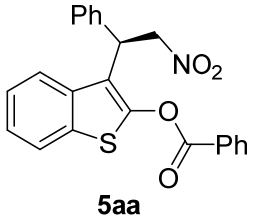


3ak

(*S*)-2-(2-nitro-1-phenylethyl)benzo[*b*]thiophen-3-yl thiophene-2-carboxylate (3ak). White solid (40.0 mg, 97% yield), mp 112-113 °C. HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 8.4 min (major), t_R = 10.4 min (minor); 91% *ee*. $[\alpha]_D^{25}$ = +55.8° (*c* = 1.55, CH_2Cl_2).^{1}H NMR (400 MHz, $CDCl_3$): 8.07 (dd, J_1 = 3.8 Hz, J_2 = 1.4 Hz, 1H, ArH), 7.74 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H, ArH), 7.71 – 7.69 (m, 1H, ArH), 7.52 – 7.50 (m, 1H, ArH), 7.37 – 7.27 (m, 7H, ArH), 7.25 – 7.23 (m, 1H, ArH), 5.29 (t, *J* = 8.0 Hz, 1H, CH), 5.07 (d, *J* = 8.0 Hz, 1H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 137.6, 137.3, 135.7, 135.6, 134.5, 132.5, 131.2, 129.6, 129.1, 128.4, 128.2, 127.4, 125.4, 124.9, 122.8, 120.8, 78.0, 41.8 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{21}H_{19}N_2O_4S_2$ $[M + NH_4]^+$ 427.0781, found 427.0784; calcd. for $C_{21}H_{15}NO_4S_2Na$ $[M + Na]^+$ 432.0335, found 432.0334.

3. Enantioselective synthesis and characterization of compounds 5

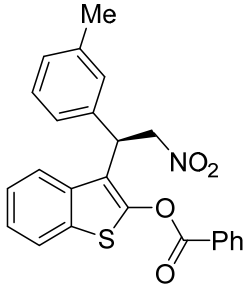
Unsaturated *α*-nitroketones **2** (0.10 mmol), benzothiophene **4** (0.12 mmol), and catalyst **C6** (5 mmol%) were dissolved in CH_2Cl_2 (1.0 mL), and the mixture was stirred at -10°C for 120 h. After completion of the reaction, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 to 8:1) to afford the pure products **5**. Racemates were prepared following a similar procedure with Et_3N (5 mol %) as achiral catalyst.



5aa

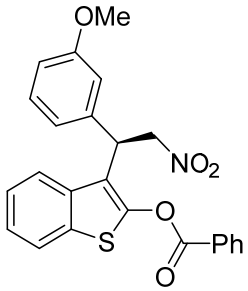
(*R*)-3-(2-Nitro-1-phenylethyl)benzo[*b*]thiophen-2-yl benzoate (5aa). Colorless oil (38.7 mg, 96% yield). HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 12.6 min (minor), t_R = 14.4 min (major); 90% *ee*. $[\alpha]_D^{25}$ = –3.1° (*c* = 1.15, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (dd, J_1 = 8.4 Hz, J_2 = 8.4 Hz, 1.2 Hz, 2H, ArH), 7.78 – 7.75 (m, 1H, ArH), 7.71 – 7.66 (m, 1H, ArH), 7.59 – 7.52 (m, 3H, ArH), 7.34 – 7.27 (m, 6H, ArH), 7.25 – 7.21 (m, 1H, ArH), 5.52 (t, *J* = 7.8 Hz, 1H, CH), 5.28 (dd, J_1 = 13.0 Hz, J_2 = 7.8 Hz, 1H, CH_2), 5.16 (dd, *J* = 12.8 Hz, J_2 = 7.6 Hz, 1H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4, 148.8, 137.5, 135.0, 134.7, 134.6, 130.4, 129.1, 129.0, 127.8, 127.7, 127.2, 124.9, 124.7, 122.6, 121.6, 118.5, 77.3, 40.7 ppm. HRMS (ESI): *m*/*z* calcd. for

$C_{23}H_{21}N_2O_4S$ $[M + NH_4]^+$ 421.1217, found 421.1208.



5ba

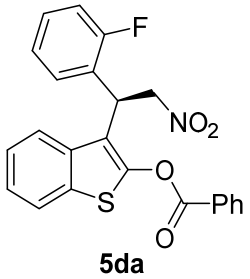
(*R*)-3-(2-Nitro-1-(m-tolyl)ethyl)benzo[*b*]thiophen-2-yl benzoate (5ba). Colorless oil (37.5 mg, 90% yield). HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 12.6 min (minor), t_R = 13.4 min (major); 94% *ee*. $[\alpha]_D^{25}$ = –5.6° (*c* = 1.70, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 – 8.11 (m, 2H, ArH), 7.76 – 7.74 (m, 1H, ArH), 7.70 – 7.65 (m, 1H, ArH), 7.62 – 7.60 (m, 1H, ArH), 7.53 (t, *J* = 7.8 Hz, 2H, ArH), 7.34 – 7.32 (m, 2H, ArH), 7.18 – 7.10 (m, 3H, ArH), 7.02 (d, *J* = 7.2 Hz, 1H, ArH), 5.48 (t, *J* = 7.8 Hz, 1H, CH), 5.26 (dd, J_1 = 13.2 Hz, J_2 = 8.0 Hz, 1H, CH_2), 5.13 (dd, J_1 = 13.2 Hz, J_2 = 7.6 Hz, 1H, CH_2), 2.22 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3, 148.6, 138.8, 137.3, 134.9, 134.7, 134.5, 130.3, 128.9, 128.4, 127.8, 127.7, 124.8, 124.6, 124.2, 122.5, 121.5, 118.6, 77.3, 40.6, 21.4 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{23}N_2O_4S$ $[M + NH_4]^+$ 435.1374, found 435.1376; calcd. for $C_{24}H_{19}NO_4SNa$ $[M + Na]^+$ 440.0927, found 440.0925.



5ca

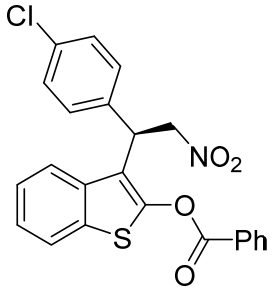
(*R*)-3-(1-(3-Methoxyphenyl)-2-nitroethyl)benzo[*b*]thiophen-2-yl benzoate (5ca). Colorless oil (37.7 mg, 87% yield). HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 18.0 min (minor), t_R = 20.9 min (major); 81% *ee*. $[\alpha]_D^{25}$ = +6.5° (*c* = 1.65, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 – 8.13 (m, 2H, ArH), 7.76 – 7.73 (m, 1H, ArH), 7.68 (t, *J* = 7.6 Hz, 1H, ArH), 7.58 – 7.52 (m, 3H, ArH), 7.34 – 7.30 (m, 2H, ArH), 7.23 (d, *J* = 8.4 Hz, 2H, ArH), 6.82 – 6.78 (m, 2H, ArH), 5.45 (t, *J* = 7.8 Hz, 1H, CH), 5.23 (dd, J_1 = 12.8 Hz, J_2 = 8.0 Hz, 1H, CH_2) 5.13 (dd, J_1 = 12.8 Hz, J_2 = 7.6 Hz, 1H, CH_2) 3.72 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4, 158.9, 148.5, 134.9, 134.7, 134.5, 130.3, 129.3, 128.9, 128.3, 127.7, 124.8, 124.6, 122.5, 121.6, 118.8, 114.4, 77.6, 55.2, 40.2 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{23}N_2O_5S$ $[M + NH_4]^+$ 451.1323, found 451.1332;

$C_{24}H_{19}NO_5SNa$ $[M + Na]^+$ 456.0876, found 456.0885.



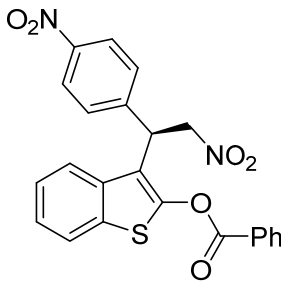
5da

(*R*)-3-(1-(2-Fluorophenyl)-2-nitroethyl)benzo[*b*]thiophen-2-yl benzoate (5da). Colorless oil (28.6 mg, 68% yield). HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 10.4 min (minor), t_R = 14.8 min (major); 82% *ee*. $[\alpha]_D^{25}$ = +3.5° (*c* = 1.31, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 – 8.08 (m, 4H, ArH), 7.81 – 7.78 (m, 1H, ArH), 7.713 – 7.70 (m, 1H, ArH), 7.57 – 7.49 (m, 5H, ArH), 7.38 – 7.36 (m, 2H, ArH), 5.59 (dd, J_1 = 8.4 Hz, J_2 = 6.8 Hz, 1H, CH), 5.34 (dd, J_1 = 13.4 Hz, J_2 = 8.6 Hz, 1H, CH_2), 5.14 (dd, *J* = 13.4 Hz, 6.8 Hz, 1H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3, 160.6 (d, $^1J_{C–F}$ = 245.8 Hz), 149.0, 134.7 (d, $^2J_{C–F}$ = 20.8 Hz), 134.5, 130.3, 129.6 (d, $^3J_{C–F}$ = 8.5 Hz), 129.0, 128.6 (d, $^4J_{C–F}$ = 3.5 Hz), 127.7, 124.9, 124.7, 124.6 (d, $^4J_{C–F}$ = 3.6 Hz), 124.2 (d, $^3J_{C–F}$ = 13.7 Hz), 122.5, 121.3, 117.0, 116.1 (d, $^2J_{C–F}$ = 21.9 Hz) , 75.9 (d, $^4J_{C–F}$ = 1.7 Hz), 35.3 (d, $^3J_{C–F}$ = 2.7 Hz) ppm. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{20}FN_2O_4S$ $[M + NH_4]^+$ 439.1123, found 439.1122; calcd. for $C_{23}H_{16}FNO_4SNa$ $[M + Na]^+$ 444.0677, found 444.0674.



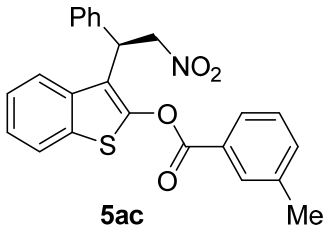
5ea

(*R*)-3-(1-(4-Chlorophenyl)-2-nitroethyl)benzo[*b*]thiophen-2-yl benzoate (5ea). Colorless oil (35.8 mg, 82% yield). HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 13.2 min (minor), t_R = 16.3 min (major); 98% *ee*. $[\alpha]_D^{25}$ = –2.9° (*c* = 1.79, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 – 8.10 (m, 2H, ArH), 7.77 – 7.75 (m, 1H, ArH), 7.70 (t, *J* = 7.6 Hz, 1H, ArH), 7.57 – 7.53 (m, 3H, ArH), 7.35 – 7.33 (m, 2H, ArH), 7.25 (s, 4H, ArH), 5.47 (t, *J* = 7.8 Hz, 1H, CH), 5.25 (dd, J_1 = 13.2 Hz, J_2 = 8.4 Hz, 1H, CH_2), 5.12 (dd, J_1 = 13.2 Hz, J_2 = 7.2 Hz, 1H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3, 149.0, 135.9, 134.9, 134.6, 134.4, 133.6, 130.3, 129.2, 129.0, 128.6, 127.5, 124.9, 124.8, 122.6, 121.4, 118.1, 77.1, 40.2 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{16}ClNO_4SK$ $[M + K]^+$ 476.0120, found 476.0127.



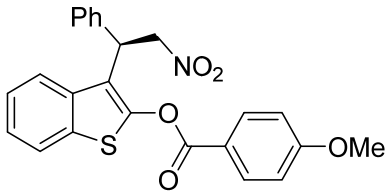
5fa

(*R*)-3-(2-Nitro-1-(4-nitrophenyl)ethyl)benzo[*b*]thiophen-2-yl benzoate (5fa). Colorless oil (20.2 mg, 45% yield). HPLC (Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 13.1 min (minor), t_R = 15.7 min (major); 93% *ee*. $[\alpha]_D^{25}$ = –13.1° (*c* = 0.31, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 – 8.16 (m, 2H, ArH), 7.76 – 7.67 (m, 3H, ArH), 7.55 (t, *J* = 7.8 Hz, 2H, ArH), 7.38 – 7.32 (m, 3H, ArH), 7.23 – 7.19 (m, 1H, ArH), 7.07 – 6.99 (m, 2H, ArH), 5.74 (t, *J* = 8.0 Hz, 1H, CH), 5.29 – 5.19 (m, 2H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3, 149.6, 147.3, 144.8, 135.0, 134.9, 134.1, 130.3, 129.1, 128.2, 127.3, 125.2, 125.1, 124.2, 122.8, 121.0, 117.5, 76.5, 40.4 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{20}N_3O_6S$ $[M + NH_4]^+$ 466.1067, found 466.1075.



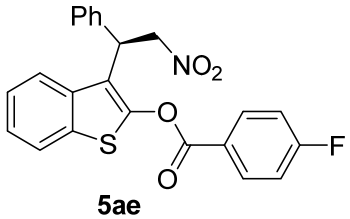
5ac

(*R*)-3-(2-Nitro-1-phenylethyl)benzo[*b*]thiophen-2-yl 3-methylbenzoate (5ac). Colorless oil (36.7 mg, 88% yield). HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 14.3 min (minor), t_R = 15.6 min (major); 91% *ee*. $[\alpha]_D^{25}$ = –13.0° (*c* = 0.95, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 – 7.92 (m, 2H, ArH), 7.78 – 7.73 (m, 1H, ArH), 7.59 – 7.55 (m, 1H, ArH),7.48 (d, *J* = 7.6 Hz, 1H, ArH), 7.42 (t, *J* = 7.8 Hz, 1H, ArH), 7.34 – 7.21 (m, 7H, ArH), 5.52 (t, *J* = 7.8 Hz, 1H, CH), 5.28 (dd, J_1 = 12.8 Hz, J_2 = 8.0 Hz, 1H, CH_2), 5.15 (dd, J_1 = 13.0 Hz, J_2 = 7.4 Hz, 1H, CH_2), 2.45 (s, 3H, CH_3) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 163.5, 148.8, 138.9, 137.5, 135.3, 135.0, 134.7, 130.9, 129.1, 128.8, 127.6, 127.5, 127.2, 124.8, 124.6, 122.5, 121.5, 118.4, 77.4, 40.7, 21.3 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{23}N_2O_4S$ $[M + NH_4]^+$ 435.1374, found 435.1373; calcd. for $C_{24}H_{19}NO_4SNa$ $[M + Na]^+$ 440.0927, found 440.0925.



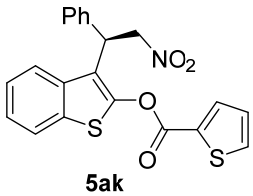
5ad

(*R*)-3-(2-Nitro-1-phenylethyl)benzo[*b*]thiophen-2-yl 4-methoxybenzoate (5ad). Colorless oil (39.9 mg, 90% yield). HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 19.9 min (minor), t_R = 22.0 min (major); 95% *ee*. $[\alpha]_D^{25}$ = –2.4° (*c* = 2.71, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 – 8.08 (m, 1H, ArH), 7.78 – 7.74 (m, 1H, ArH), 7.58 – 7.54 (m, 1H, ArH), 7.34 – 7.28 (m, 6H, ArH), 7.25 – 7.22 (m, 1H, ArH), 7.03 – 6.99 (m, 1H, ArH), 5.51 (t, J = 7.8 Hz, 1H, CH), 5.28 (dd, J_1 = 13.0 Hz, J_2 = 8.2 Hz, 1H, CH_2), 5.16 (dd, J_1 = 13.2 Hz, J_2 = 7.6 Hz, 1H, CH_2), 3.91 (s, 3H, CH_3) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 164.6, 163.0, 148.9, 137.6, 135.0, 134.7, 132.6, 129.1, 127.6, 127.2, 124.7, 124.5, 122.5, 121.5, 119.8, 118.2, 114.3, 77.5, 55.6, 40.8 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{23}N_2O_5S$ $[M + NH_4]^+$ 451.1323, found 451.1313; $C_{24}H_{19}NO_5SNa$ $[M + Na]^+$ 456.0876, found 456.0867.



5ae

(*R*)-3-(2-Nitro-1-phenylethyl)benzo[*b*]thiophen-2-yl 4-fluorobenzoate (5ae). Colorless oil (39.2 mg, 93% yield). HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 12.7 min (minor), t_R = 14.9 min (major); 90% *ee*. $[\alpha]_D^{25}$ = –16.2° (*c* = 2.02, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 – 8.12 (m, 2H, ArH), 7.76 – 7.74 (m, 1H, ArH), 7.57 – 7.55 (m, 1H, ArH), 7.35 – 7.26 (m, 6H, ArH), 7.24 – 7.18 (m, 3H, ArH), 5.52 (t, J = 8.0 Hz, 1H, CH) 5.26 (dd, J_1 = 13.0 Hz, J_2 = 7.6 Hz, 1H, CH_2), 5.13 (dd, J_1 = 13.2 Hz, J_2 = 8.0 Hz, 1H, CH_2) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 166.6 (d, $^1J_{C–F}$ = 257.0 Hz), 162.4, 148.6, 137.3, 134.9, 134.5, 133.1 (d, $^3J_{C–F}$ = 10.6 Hz), 129.1, 127.6, 127.1, 124.8, 124.7, 124.0, 123.9 (d, $^4J_{C–F}$ = 2.6 Hz), 122.5, 121.6, 118.6, 116.3 (d, $^2J_{C–F}$ = 22.2 Hz), 77.2, 40.6 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{20}FN_2O_4S$ $[M + NH_4]^+$ 439.1123, found 439.1119; calcd. for $C_{23}H_{16}FNO_4SNa$ $[M + Na]^+$ 444.0677, found 444.0673.

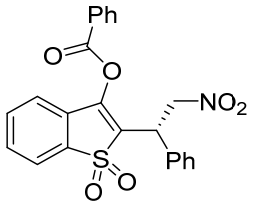


5ak

(*R*)-3-(2-Nitro-1-phenylethyl)benzo[*b*]thiophen-2-yl thiophene-2-carboxylate (5ak). Colorless oil (29.5 mg, 72% yield). HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 17.6 min (major), t_R = 19.9 min (minor); 89% *ee*. $[\alpha]_D^{25}$ = –1.6° (*c* = 1.61, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 – 8.00 (m, 1H, ArH), 7.75 – 7.73 (m, 2H, ArH), 7.62 – 7.60 (m, 1H, ArH), 7.36 – 7.26 (m, 6H, ArH), 7.24 – 7.20 (m, 2H, ArH), 5.47 (t, J = 8.0 Hz, 1H, CH), 5.32 (dd, J_1 = 13.0 Hz, J_2 = 8.2 Hz, 1H, CH_2), 5.20 (dd, J_1 = 12.8 Hz, J_2 = 7.6 Hz, 1H, CH_2) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 158.4, 148.1, 137.6, 136.1, 135.0, 134.9, 134.5, 130.5, 129.1, 128.6, 127.7, 127.3, 124.8, 124.7, 122.4, 121.5, 118.2, 77.5, 41.0 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{21}H_{19}N_2O_4S_2$ $[M + NH_4]^+$ 427.0781, found 427.0778; calcd. for $C_{21}H_{15}NO_4S_2Na$ $[M + Na]^+$ 432.0335, found 432.0331.

4. Enantioselective synthesis and characterization of compound 6

The compound **3aa** (40.3 mg, 0.1 mmol) was dissolved in $CHCl_3$ (1.0 mL) and HCO_2H (1.0 mL), H_2O_2 (35% aq, 0.5 mL) was added dropwise and the mixture was stirred at room temperature for 12 h. After completion of the reaction, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1 to 1:1) to afford the pure product **6**.



6

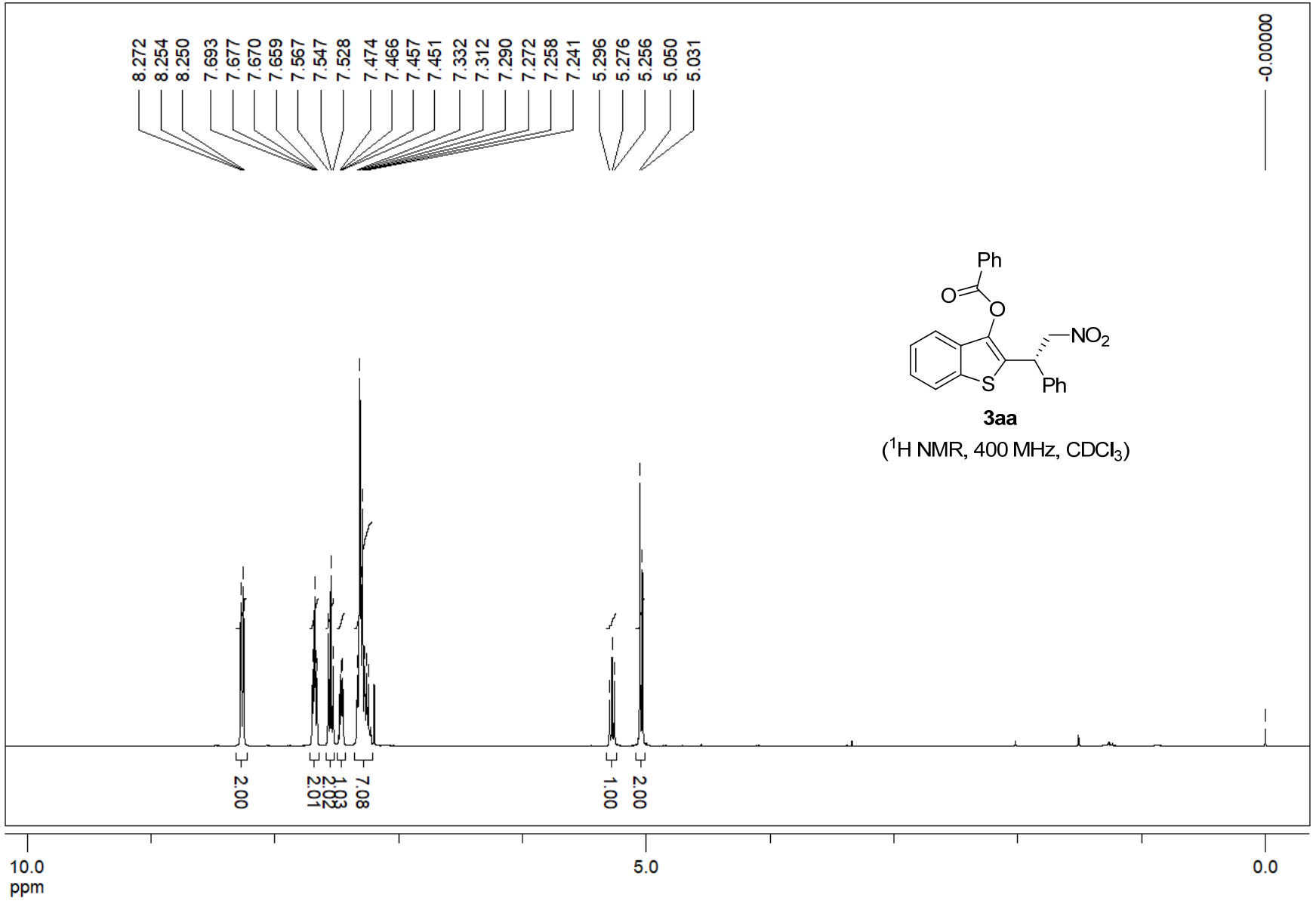
(*S*)-2-(2-Nitro-1-phenylethyl)-1,1-dioxidobenzo[*b*]thiophen-3-yl benzoate (6). Colorless oil (35.3 mg, 81% yield). HPLC (Daicel Chiralpak IC, *n*-hexane/2-propanol = 70:30, flow rate 1.0 mL/min, detection at 254 nm): t_R = 23.7 min (major), t_R = 27.1 min (minor); 96% *ee*. $[\alpha]_D^{25}$ = –5.9° (*c* = 3.66, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 – 8.00 (m, 2H, ArH), 7.77 – 7.75 (m, 1H, ArH), 7.72 (t, J = 7.4 Hz, 1H, ArH), 7.58 – 7.52 (m, 4H, ArH), 7.35 – 7.33 (m, 2H, ArH), 7.24 – 7.17 (m, 4H, ArH), 5.28 (dd, J_1 = 13.8 Hz, J_2 = 6.2 Hz, 1H, CH), 5.18 (dd, J_1 = 13.6 Hz, J_2 = 9.6 Hz, 1H, CH_2), 5.05 (dd, J_1 = 9.4 Hz, J_2 = 6.2 Hz, 1H, CH_2) ppm. ^{13}C NMR (176 MHz, $CDCl_3$): δ 162.3, 148.9, 136.9, 135.0, 134.1, 133.5, 131.0, 130.6, 129.1, 129.0, 128.5, 128.4, 128.2, 127.8, 126.7, 121.4, 121.3, 74.8, 39.2 ppm. HRMS (ESI): *m*/*z* calcd. for $C_{23}H_{21}N_2O_6S$ $[M + NH_4]^+$ 453.1115, found 453.1115.

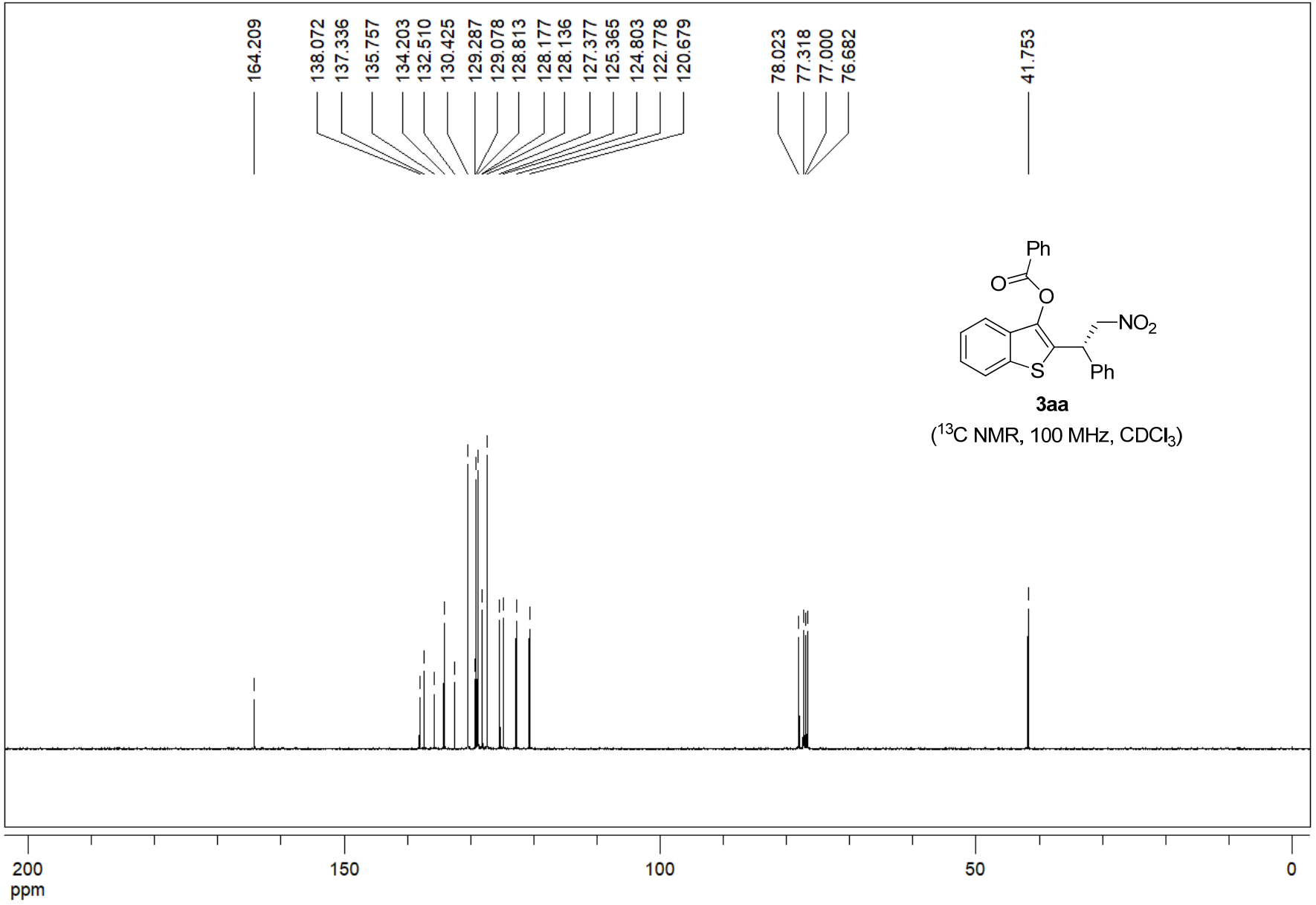
5. Crystal data and structure refinement for 3ka

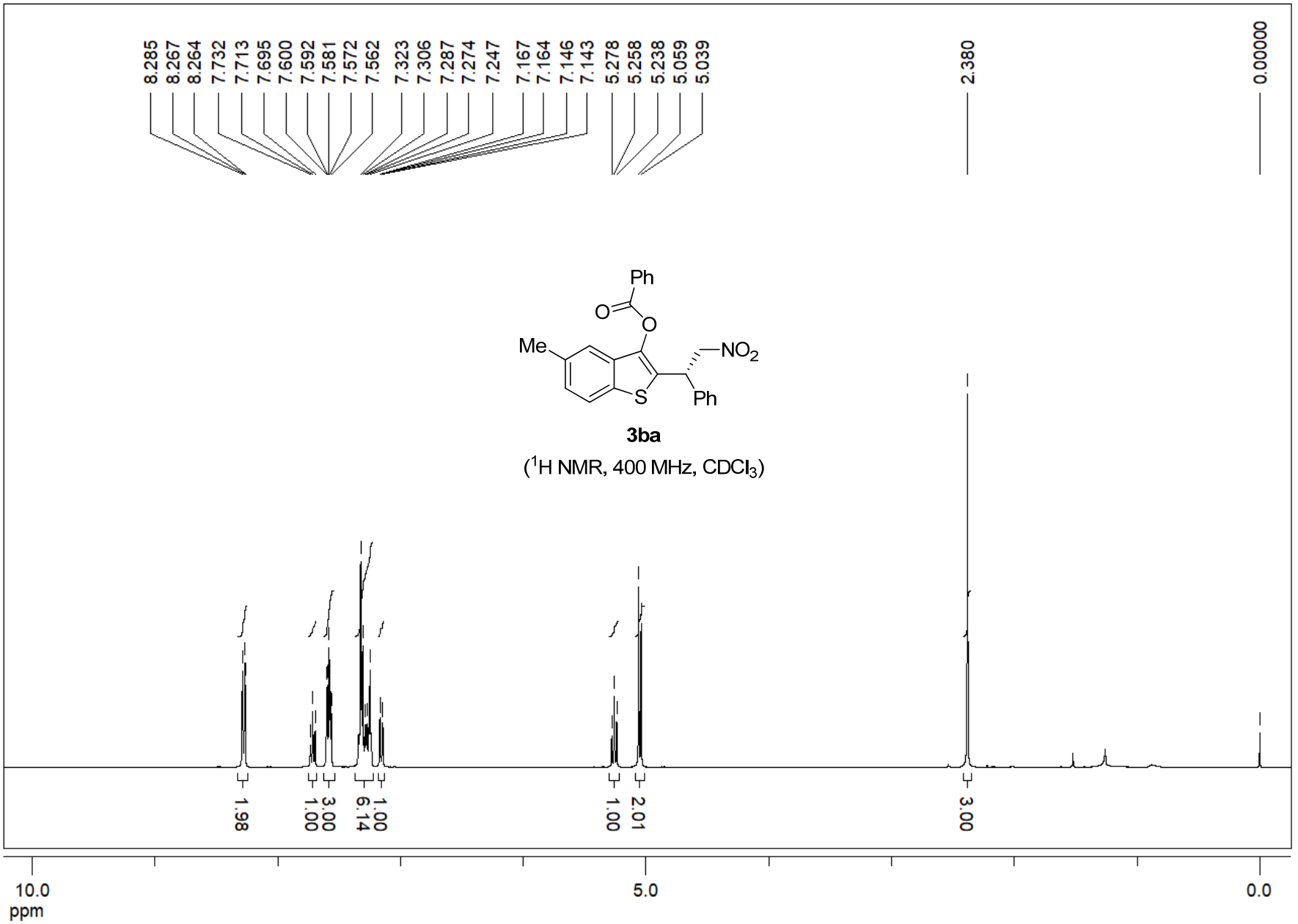
Table S1. Crystal data and structure refinement for **3ka** (CCDC 2120491)

Identification code	mo_210929_NC_1784_0m
Empirical formula	$C_{23}H_{16}N_2O_6S$
Formula weight	448.44
Temperature/K	170.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	14.8028(7)
b/Å	8.2847(3)
c/Å	17.6240(7)
α/°	90
β/°	108.031(2)
γ/°	90
Volume/Å^3	2055.20(15)
Z	4
ρ_{calc}g/cm^3	1.449
μ/mm^{-1}	0.203
F(000)	928.0
Crystal size/mm^3	0.49 × 0.2 × 0.16
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.316 to 54.296
Index ranges	$-18 \le h \le 18$, $-10 \le k \le 10$, $-22 \le l \le 22$
Reflections collected	40374
Independent reflections	9048 [R_{int} = 0.0388, R_{sigma} = 0.0318]
Data/restraints/parameters	9048/1/577
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0357, wR_2 = 0.0885
Final R indexes [all data]	R_1 = 0.0416, wR_2 = 0.0929
Largest diff. peak/hole / e Å^{-3}	0.30/-0.22
Flack parameter	-0.01(2)

6. Copies of ^{1}H and ^{13}C NMR spectra of new compounds

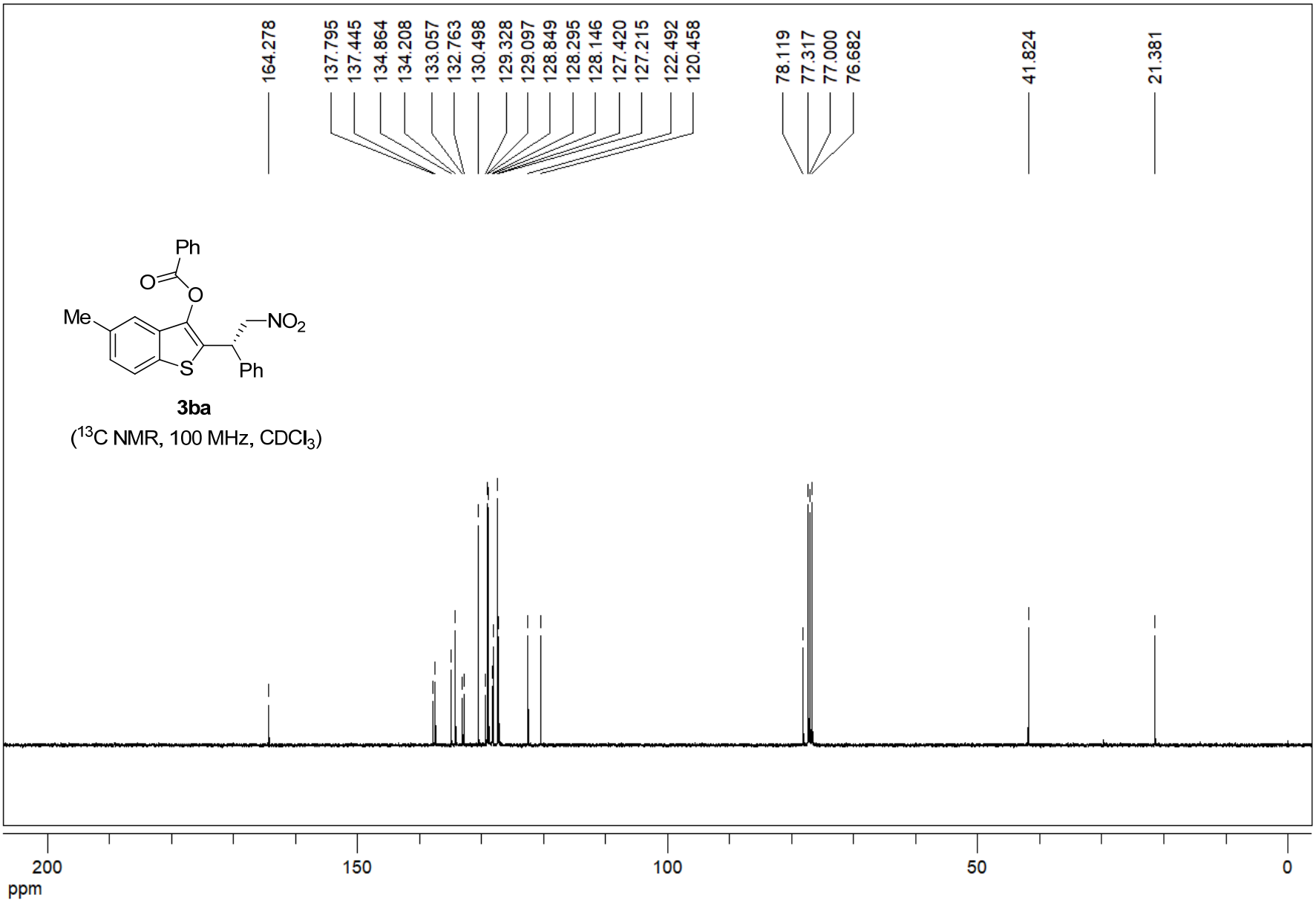


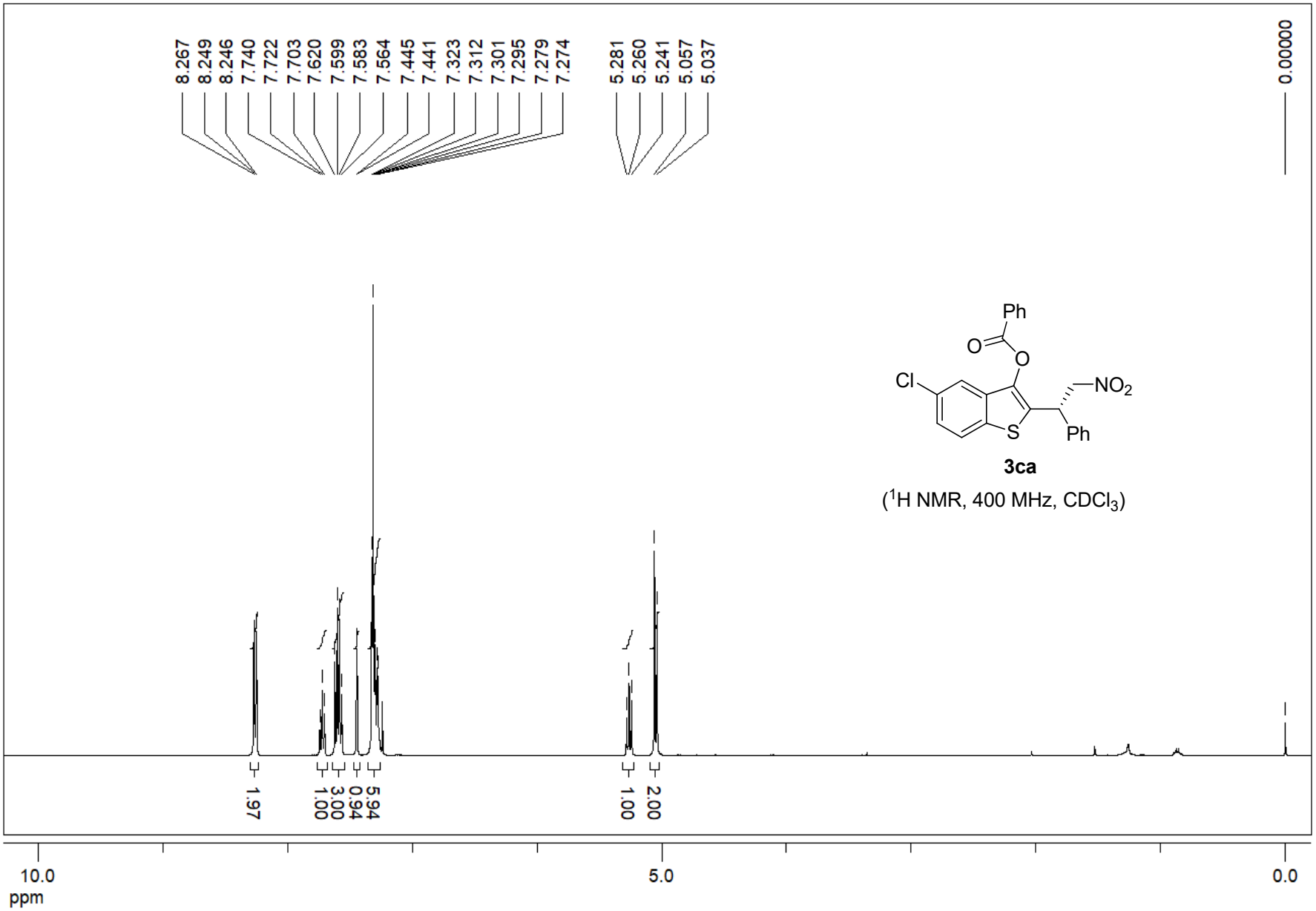

164.209
138.072
137.336
135.757
134.203
132.510
130.425
129.287
129.078
128.813
128.177
128.136
127.377
125.365
124.803
122.778
120.679
78.023
77.318
77.000
76.682
41.753
Ph
O
O
NO2
S
Ph
3aa
(13C NMR, 100 MHz, CDCl3)
200
ppm
150
100
50
0



3ba

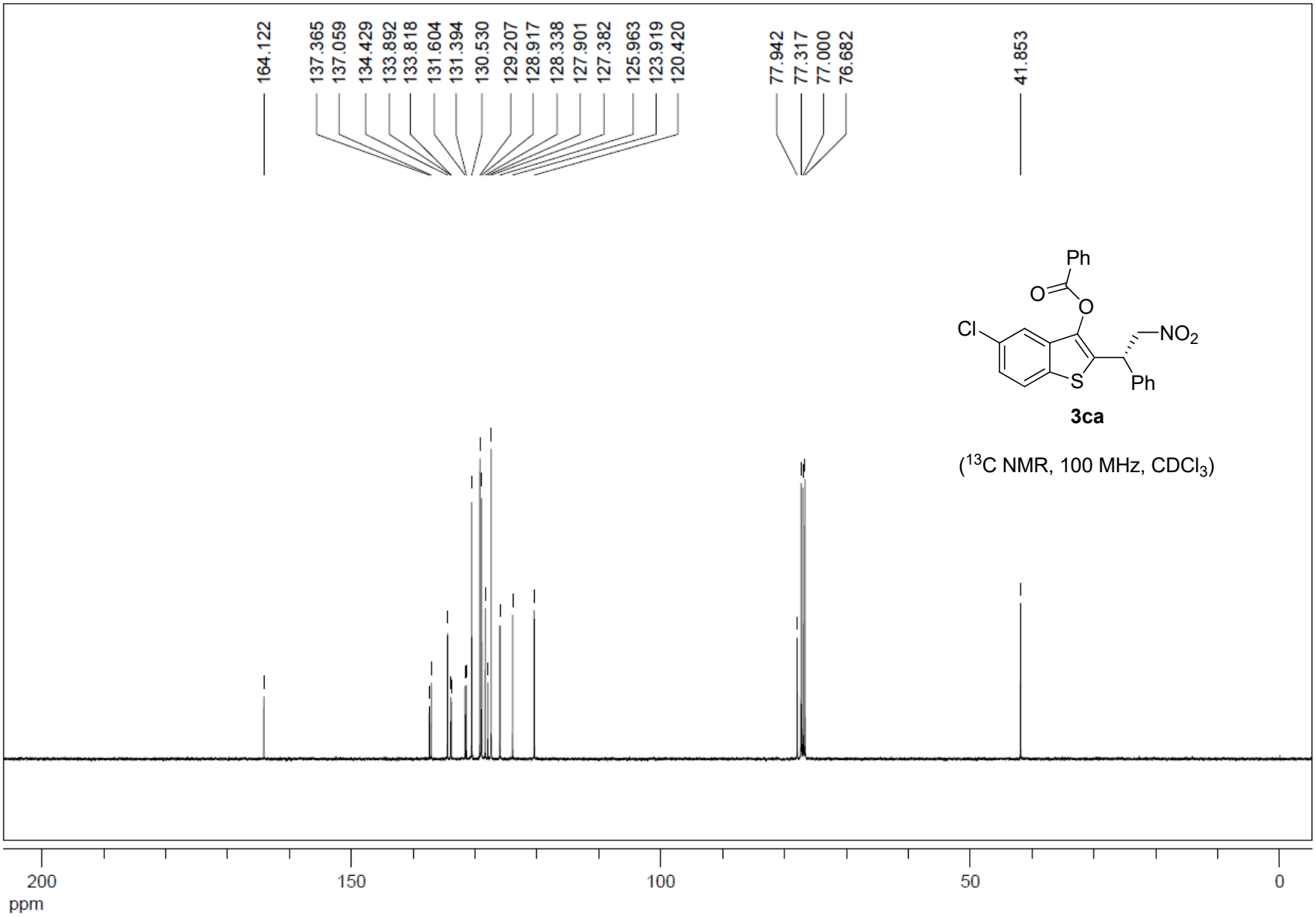
(^{1}H NMR, 400 MHz, $CDCl_3$)


164.278
137.795
137.445
134.864
134.208
133.057
132.763
130.498
129.328
129.097
128.849
128.295
128.146
127.420
127.215
122.492
120.458
78.119
77.317
77.000
76.682
41.824
21.381
Ph
O
O
Me
NO2
S
Ph
3ba
(13C NMR, 100 MHz, CDCl3)
200
150
100
50
0
ppm



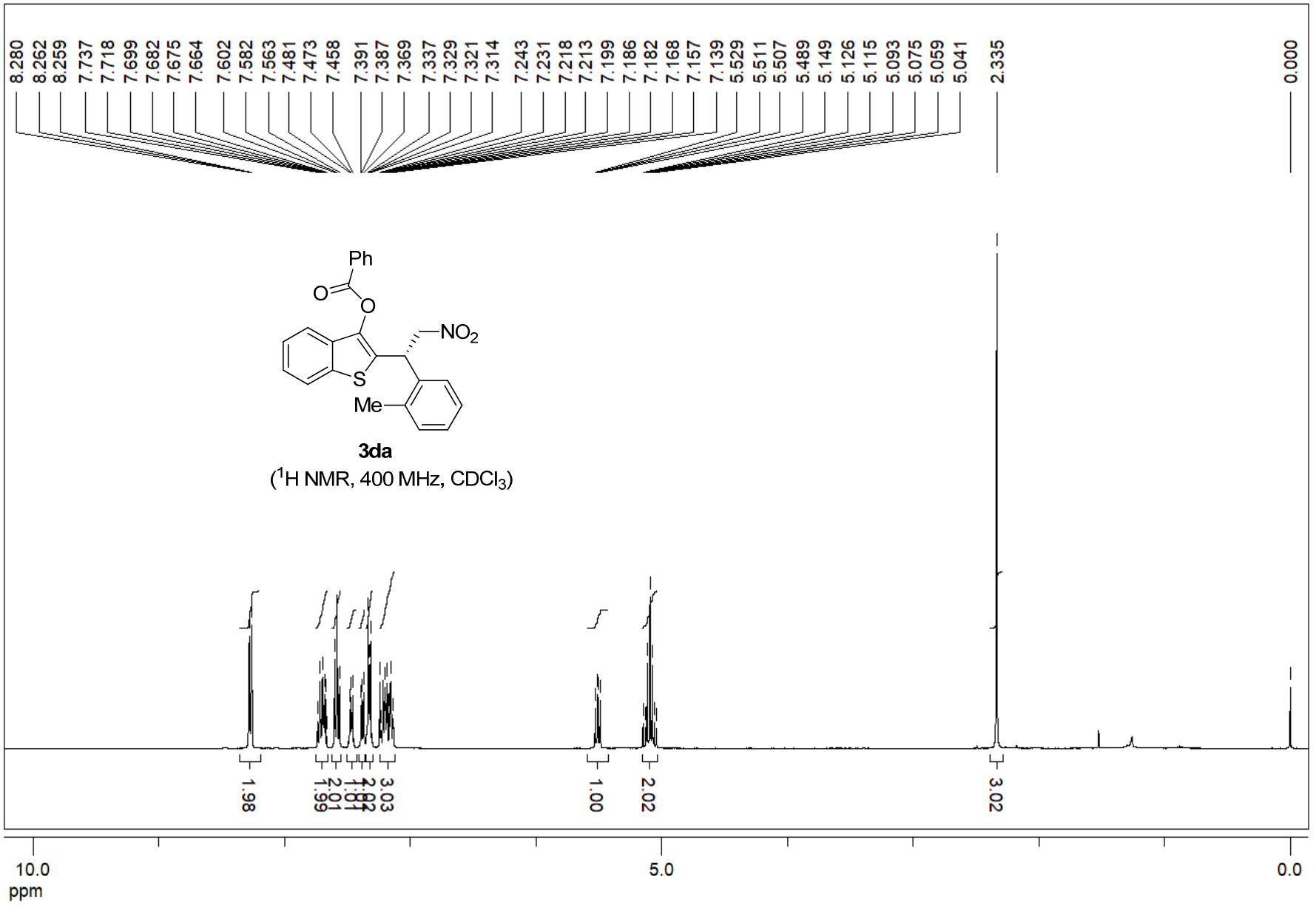
3ca

(^{1}H NMR, 400 MHz, $CDCl_3$)



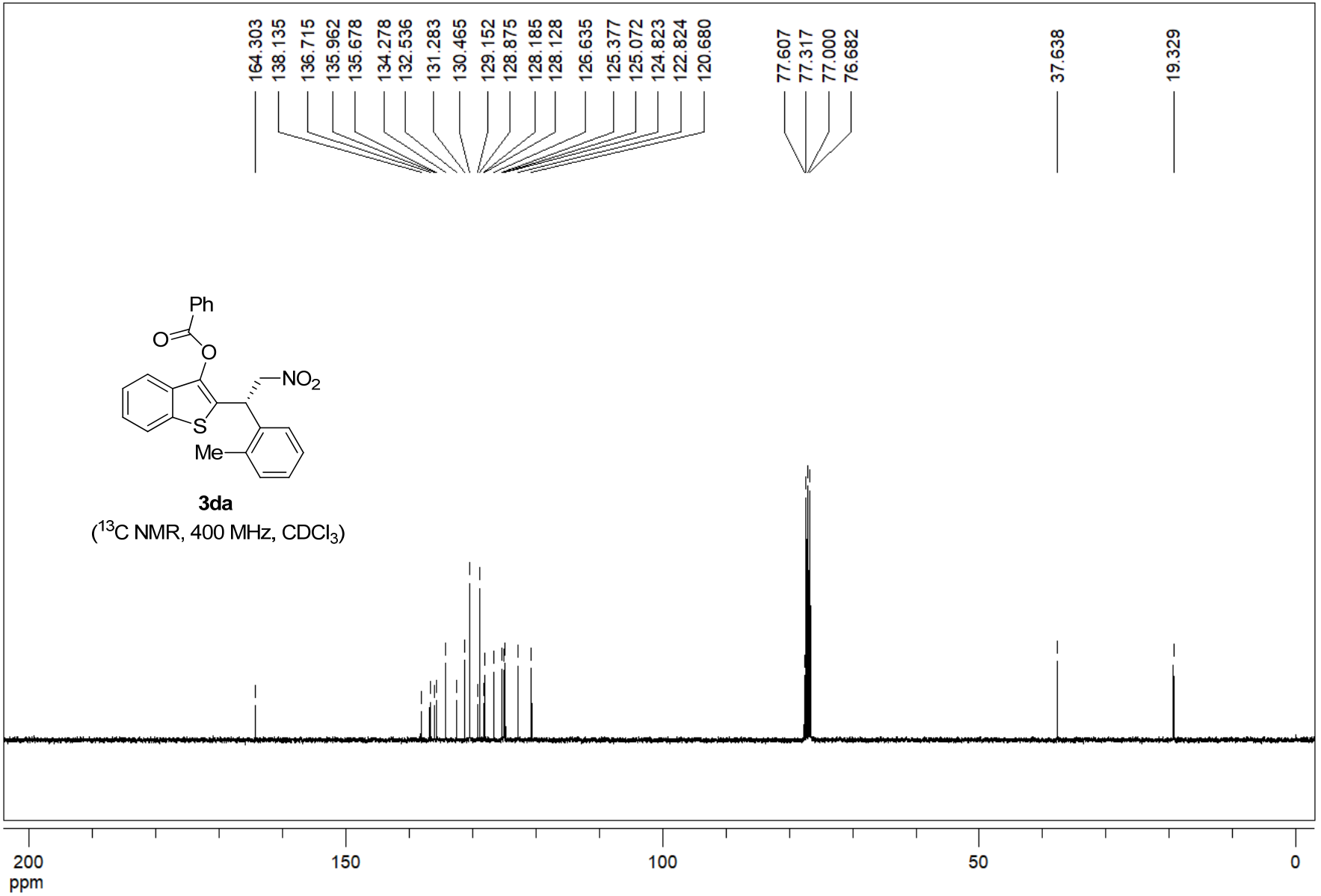
3ca

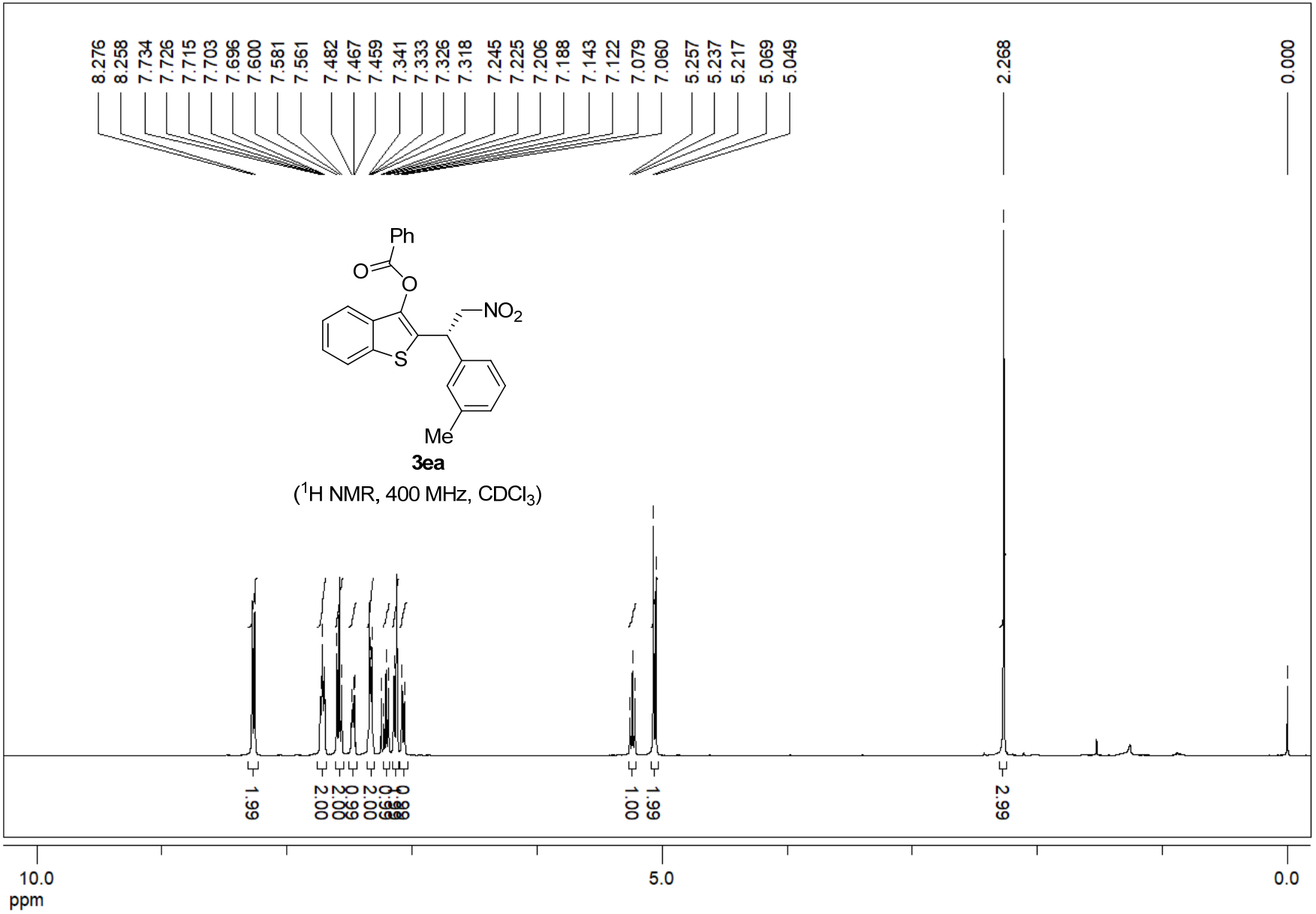
(^{13}C NMR, 100 MHz, $CDCl_3$)

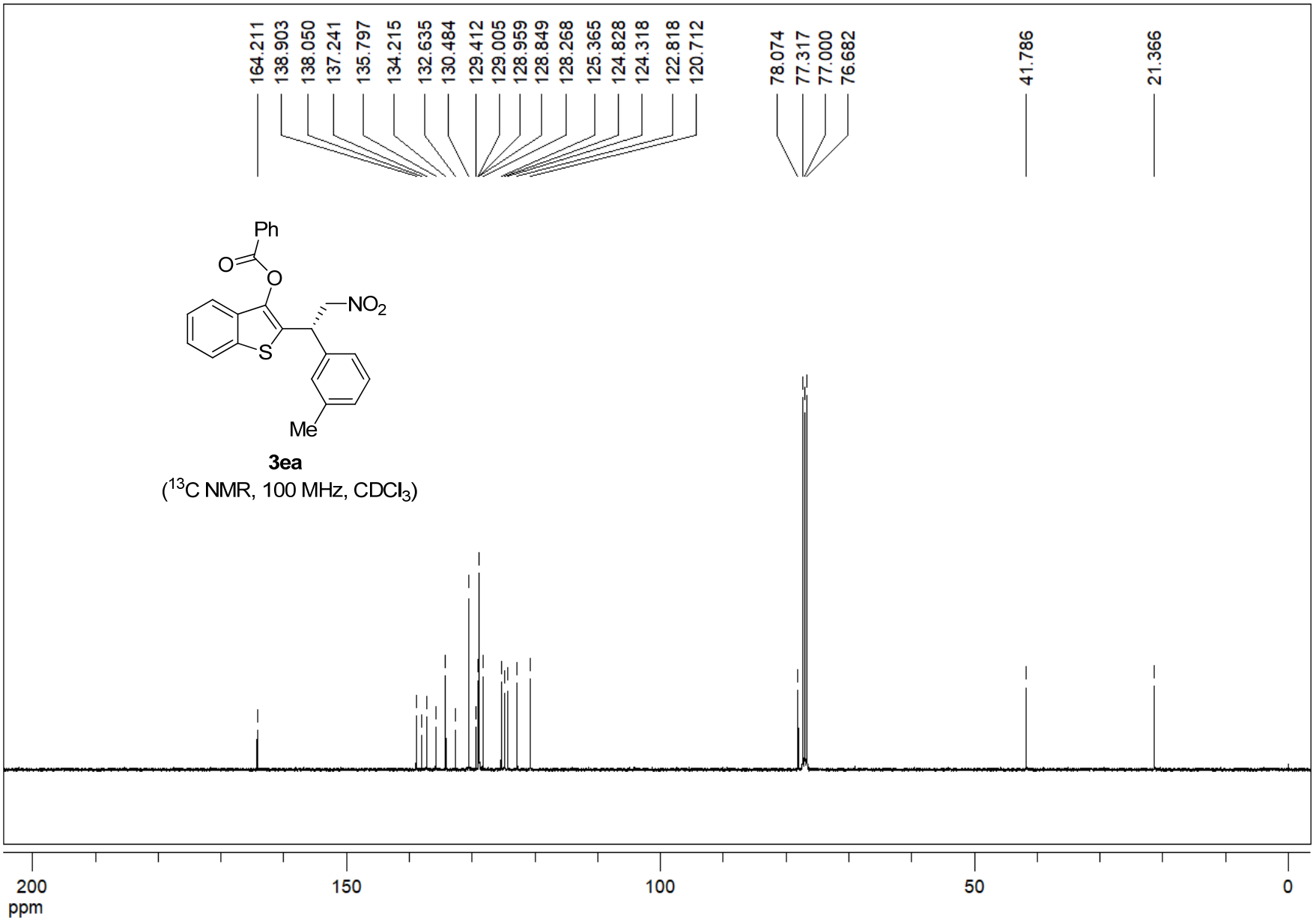


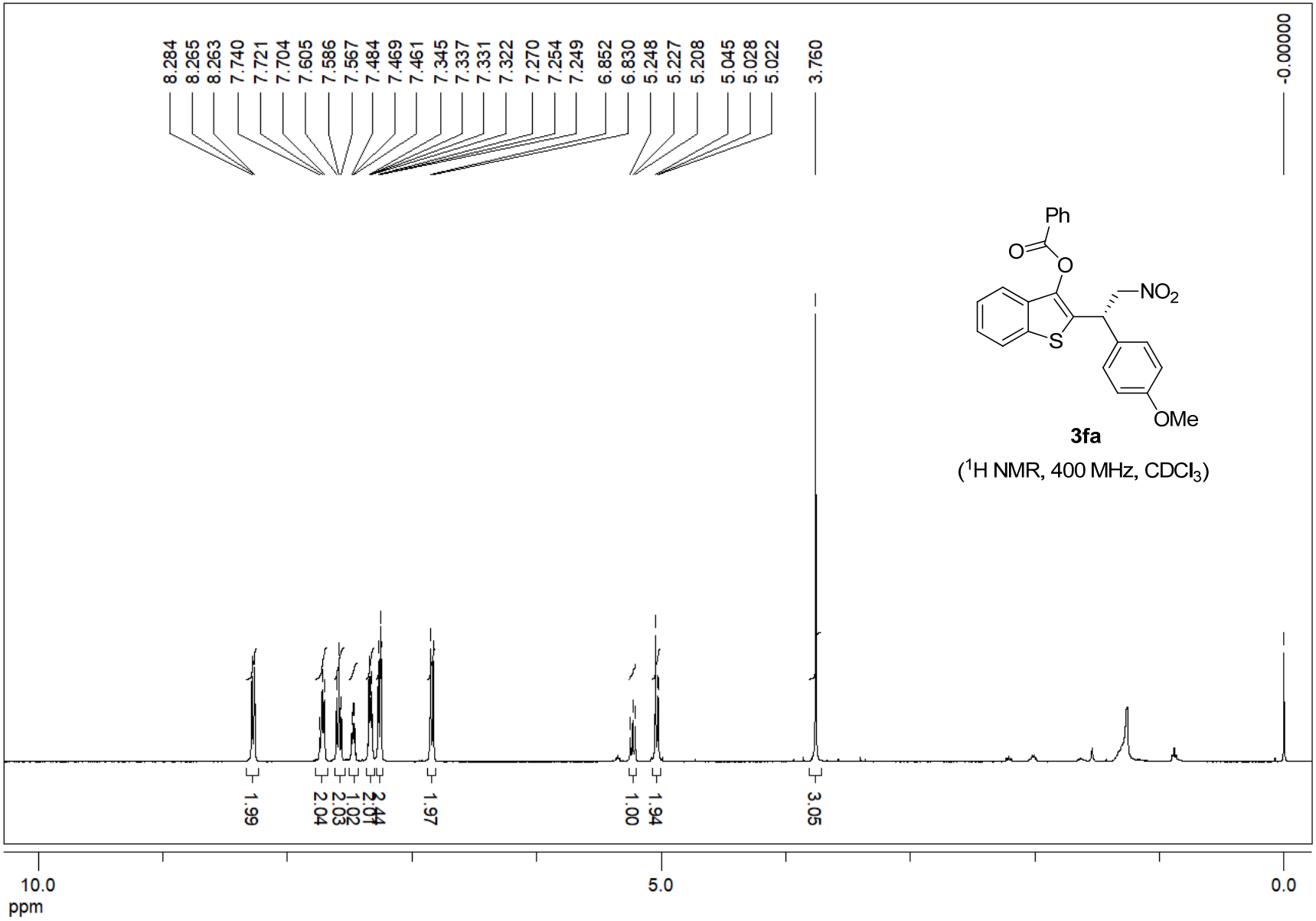
3da

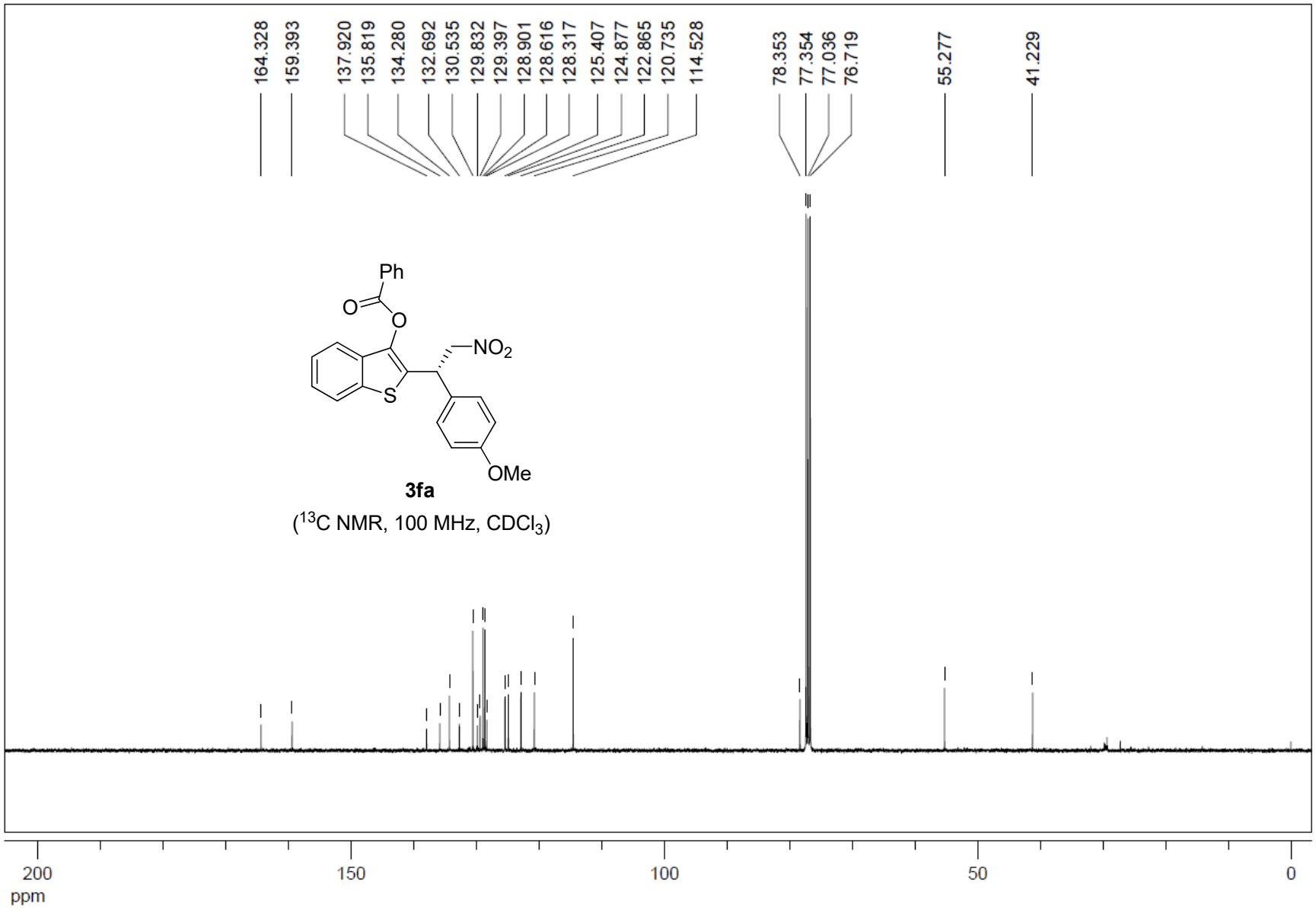
(^{1}H NMR, 400 MHz, $CDCl_3$)

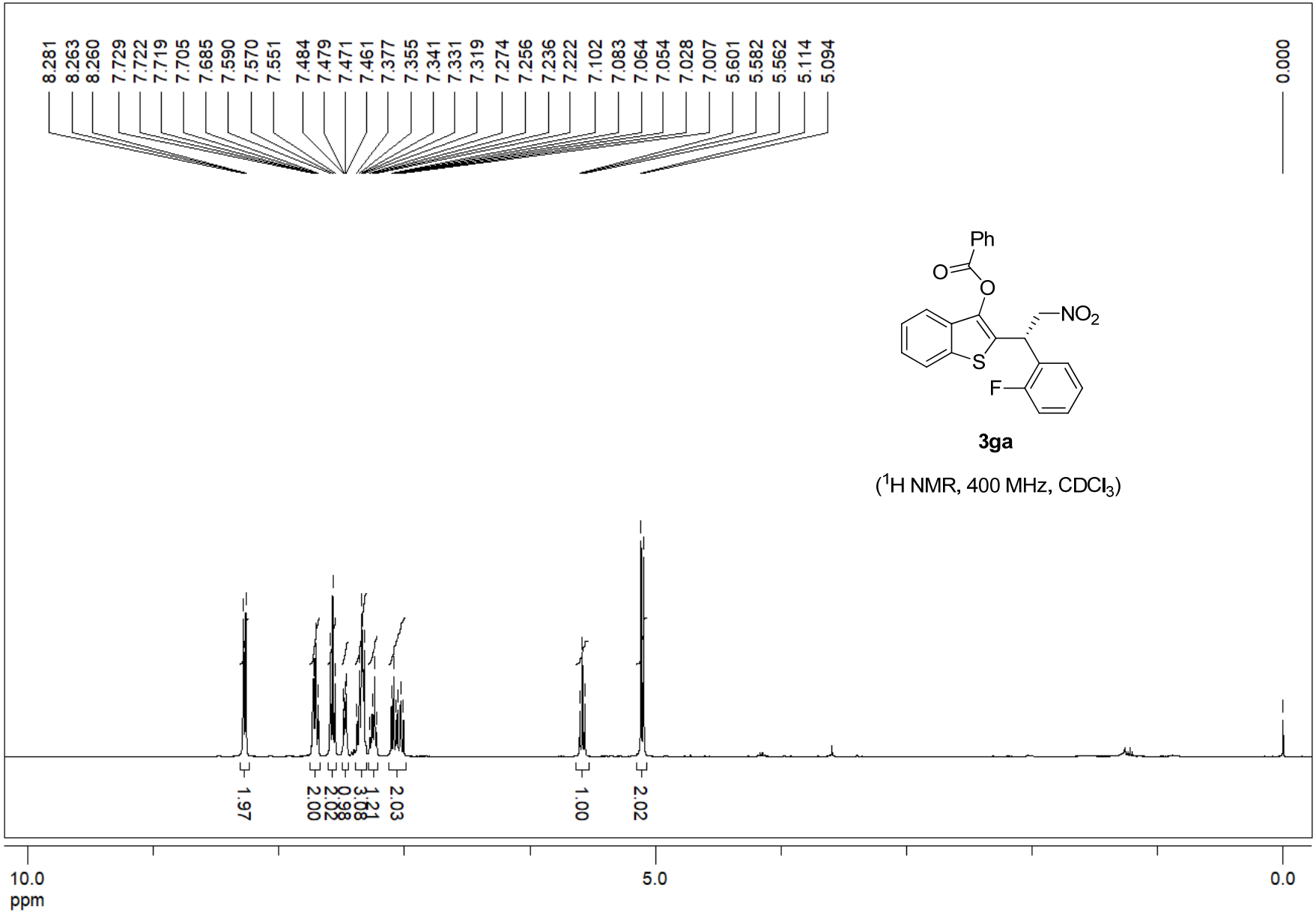

164.303
138.135
136.715
135.962
135.678
134.278
132.536
131.283
130.465
129.152
128.875
128.185
128.128
126.635
125.377
125.072
124.823
122.824
120.680
77.607
77.317
77.000
76.682
37.638
19.329
Ph
O
O
NO2
S
Me
3da
(13C NMR, 400 MHz, CDCl3)
200
ppm
150
100
50
0


8.276
8.258
7.734
7.726
7.715
7.703
7.696
7.600
7.581
7.561
7.482
7.467
7.459
7.341
7.333
7.326
7.318
7.245
7.225
7.206
7.188
7.143
7.122
7.079
7.060
5.257
5.237
5.217
5.069
5.049
2.268
0.000
Ph
O
O
NO2
S
Me
3ea
(1H NMR, 400 MHz, CDCl3)
1.99
2.00
2.09
2.00
1.00
1.99
2.99
10.0
ppm
5.0
0.0


164.211
138.903
138.050
137.241
135.797
134.215
132.635
130.484
129.412
129.005
128.959
128.849
128.268
125.365
124.828
124.318
122.818
120.712
78.074
77.317
77.000
76.682
41.786
21.366
Ph
O
O
NO2
S
Me
3ea
(13C NMR, 100 MHz, CDCl3)
200
150
100
50
0
ppm

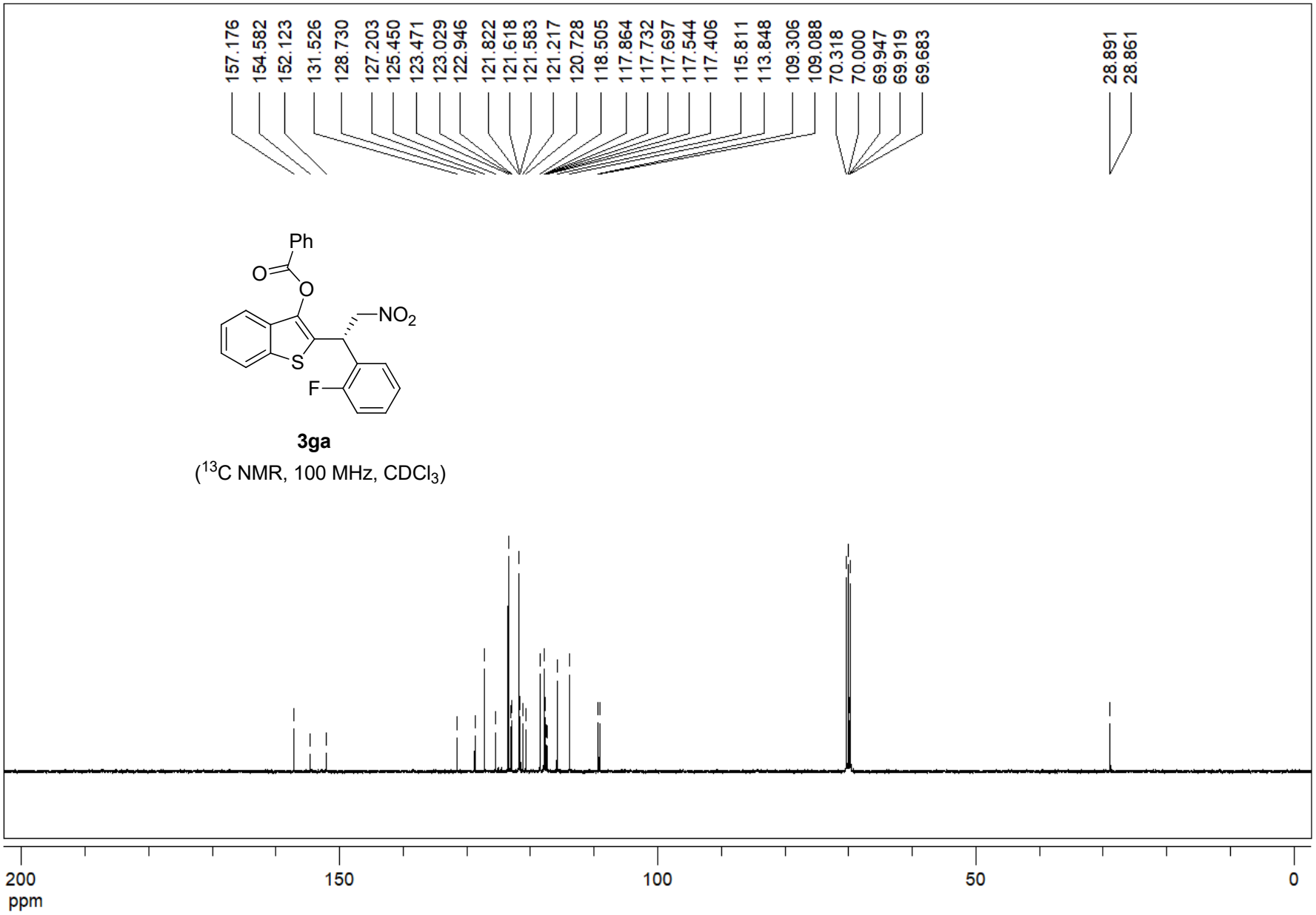

8.284
8.265
8.263
7.740
7.721
7.704
7.605
7.586
7.567
7.484
7.469
7.461
7.345
7.337
7.331
7.322
7.270
7.254
7.249
6.852
6.830
5.248
5.227
5.208
5.045
5.028
5.022
3.760
-0.00000
Ph
O
O
NO2
S
OMe
3fa
(1H NMR, 400 MHz, CDCl3)
1.99
2.04
2.03
1.02
2.01
2.44
1.97
1.00
1.94
3.05
10.0
ppm
5.0
0.0


164.328
159.393
137.920
135.819
134.280
132.692
130.535
129.832
129.397
128.901
128.616
128.317
125.407
124.877
122.865
120.735
114.528
78.353
77.354
77.036
76.719
55.277
41.229
Ph
O
O
NO2
S
OMe
3fa
(13C NMR, 100 MHz, CDCl3)
200
150
100
50
0
ppm



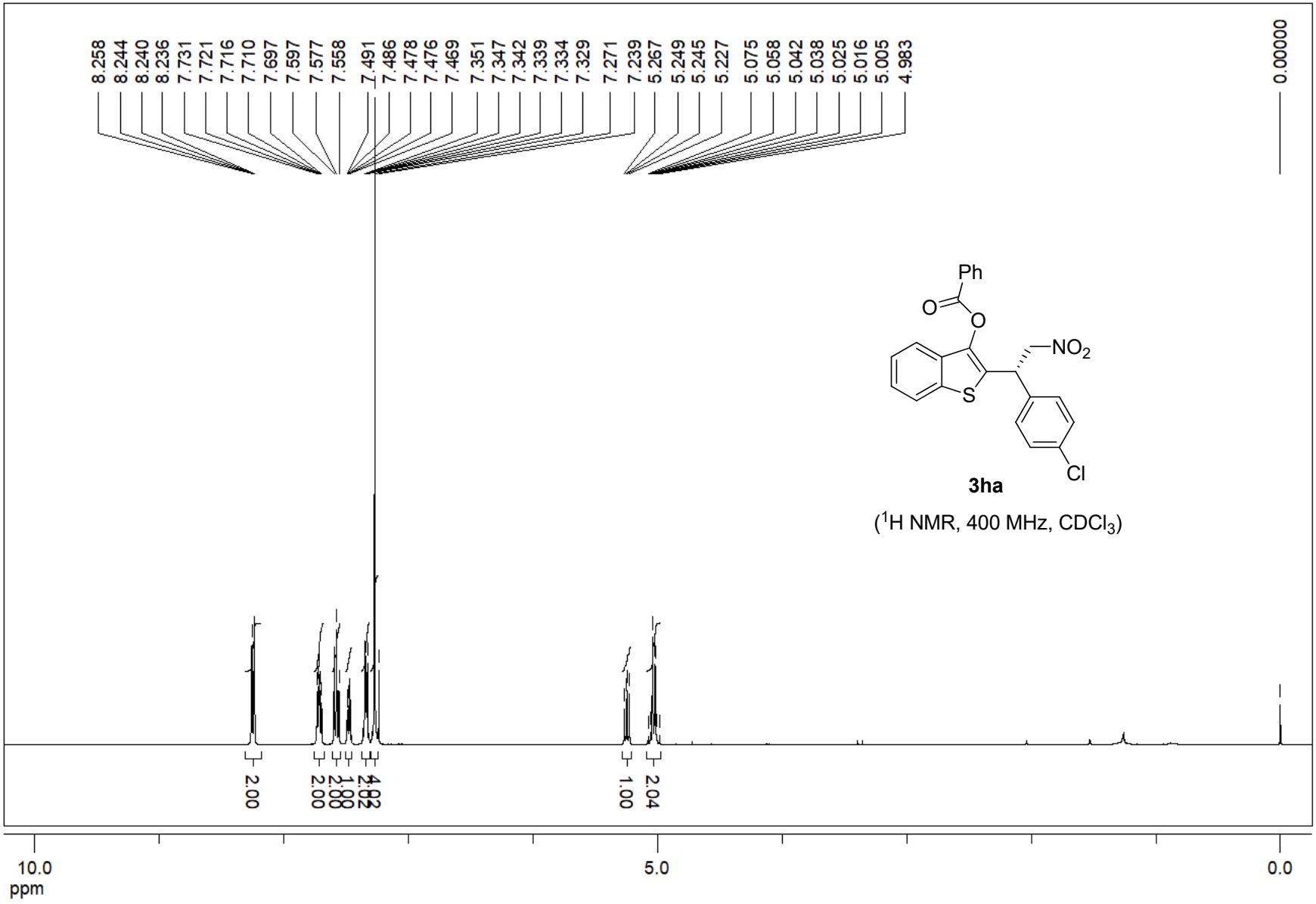
3ga

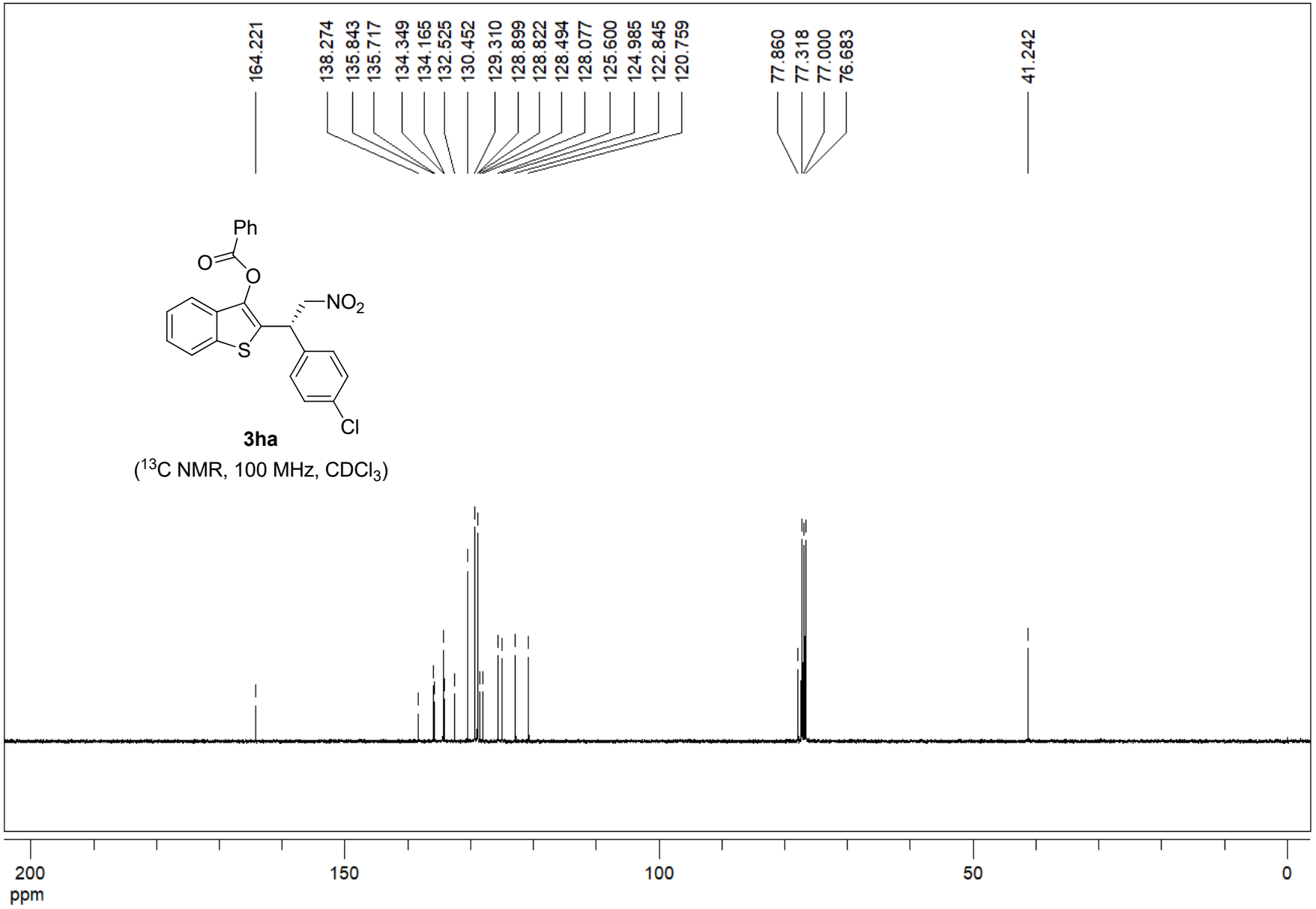
(^{1}H NMR, 400 MHz, $CDCl_3$)



3ga

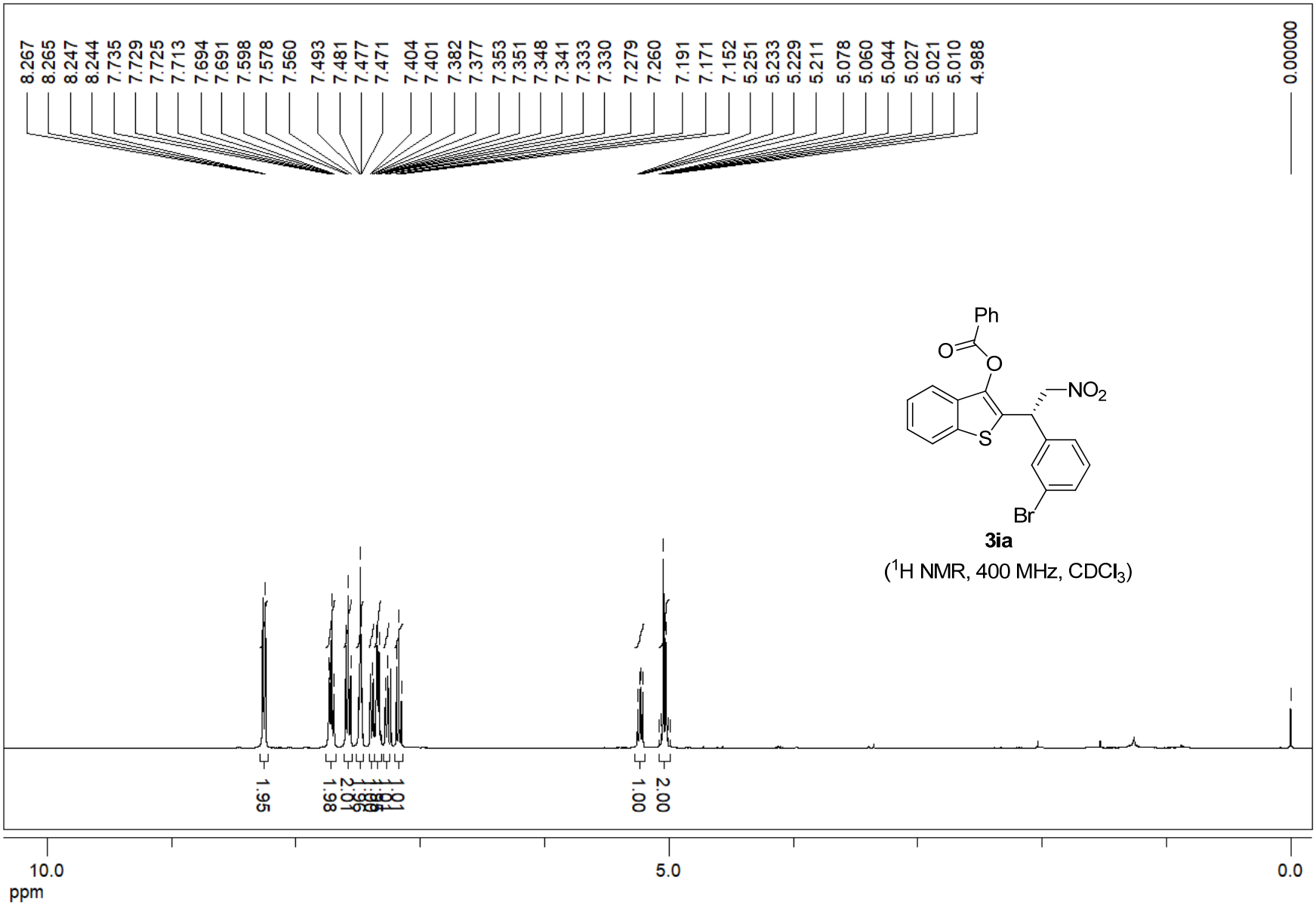
(^{13}C NMR, 100 MHz, $CDCl_3$)


8.258
8.244
8.240
8.236
7.731
7.721
7.716
7.710
7.697
7.597
7.577
7.558
7.491
7.486
7.478
7.476
7.469
7.351
7.347
7.342
7.339
7.334
7.329
7.271
7.239
5.267
5.249
5.245
5.227
5.075
5.058
5.042
5.038
5.025
5.016
5.005
4.983
0.00000
Ph
O
O
NO2
S
Cl
3ha
(1H NMR, 400 MHz, CDCl3)
2.00
2.00
1.00
2.04
10.0
ppm
5.0
0.0



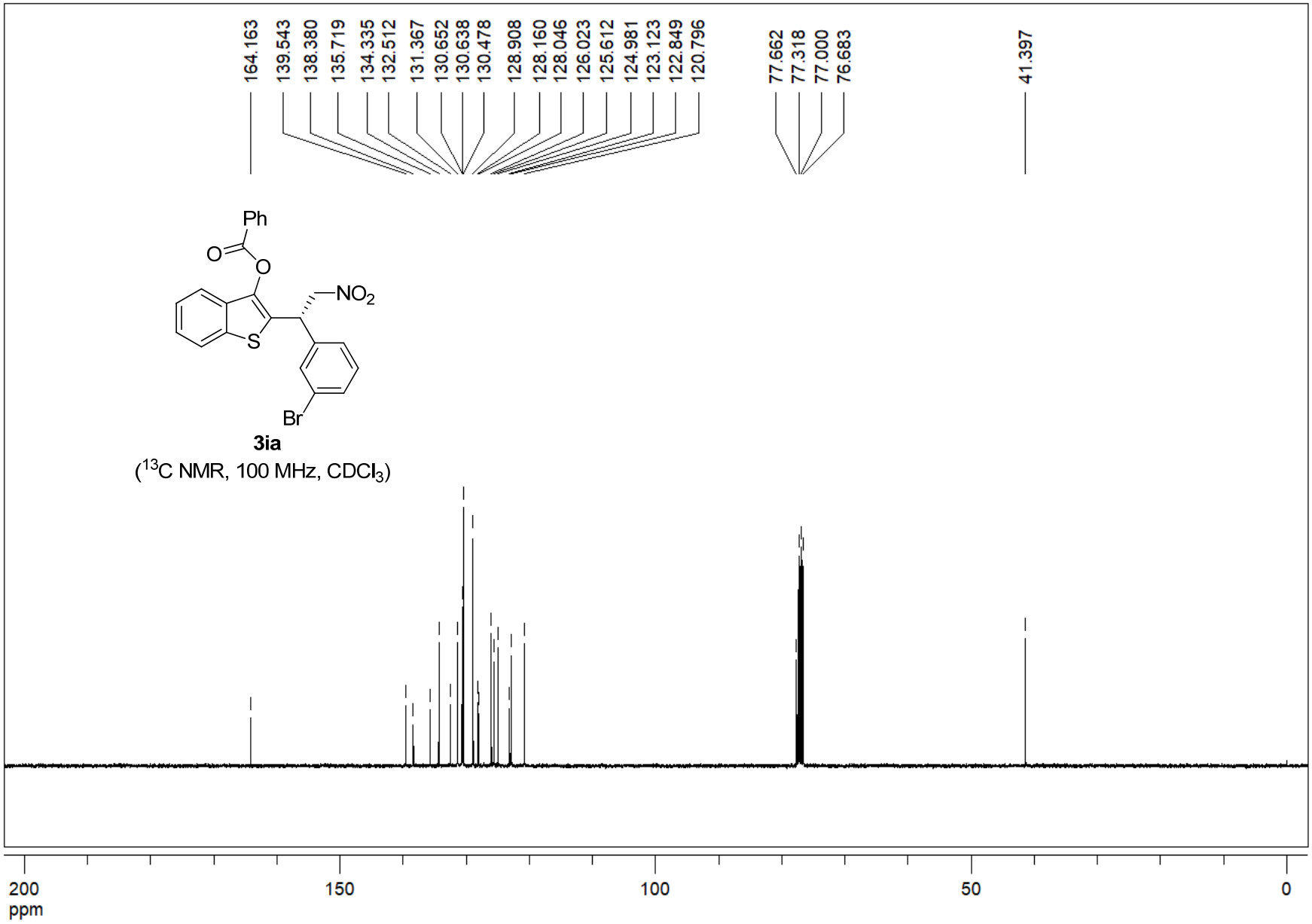
3ha

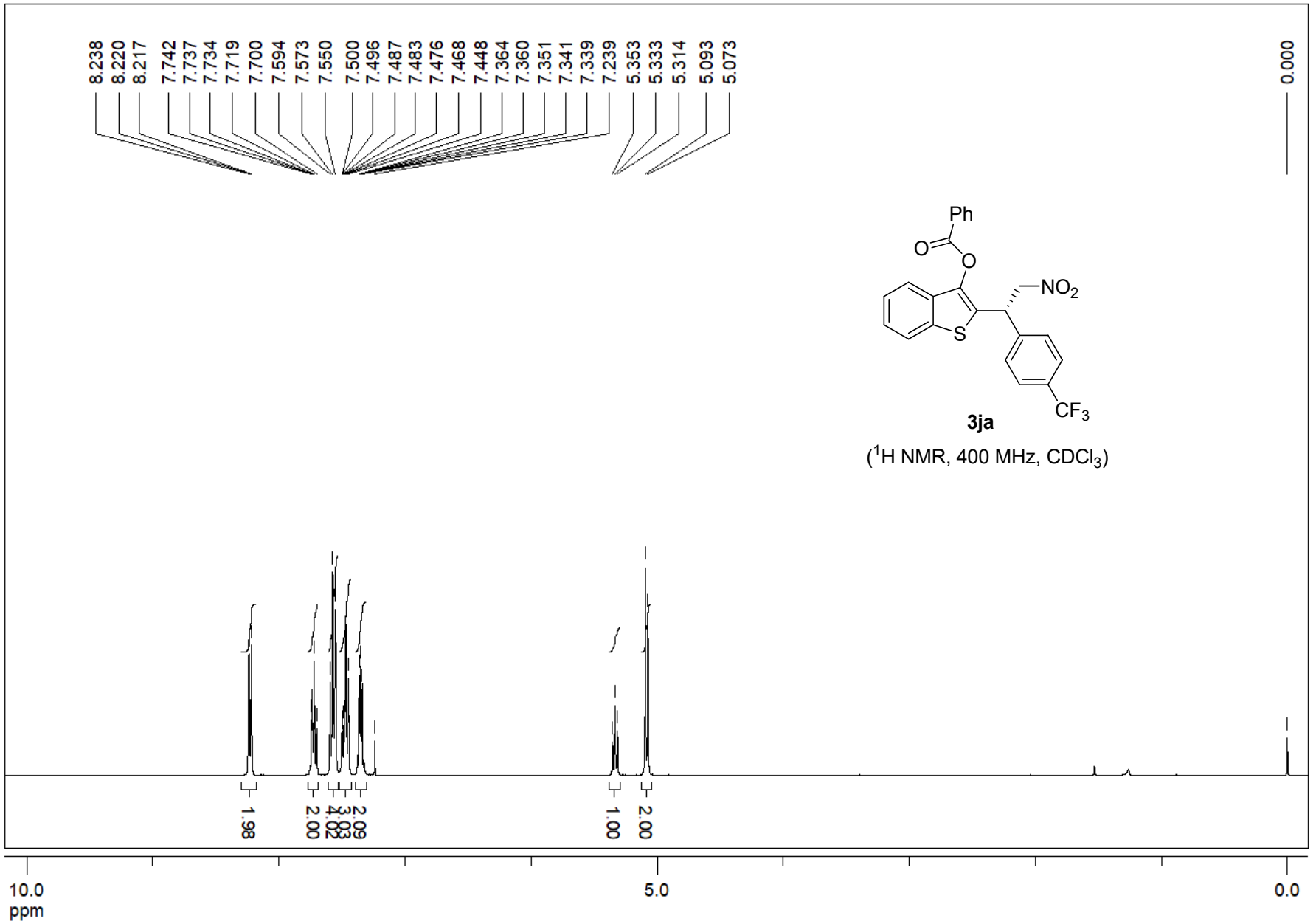
(^{13}C NMR, 100 MHz, $CDCl_3$)



3ia

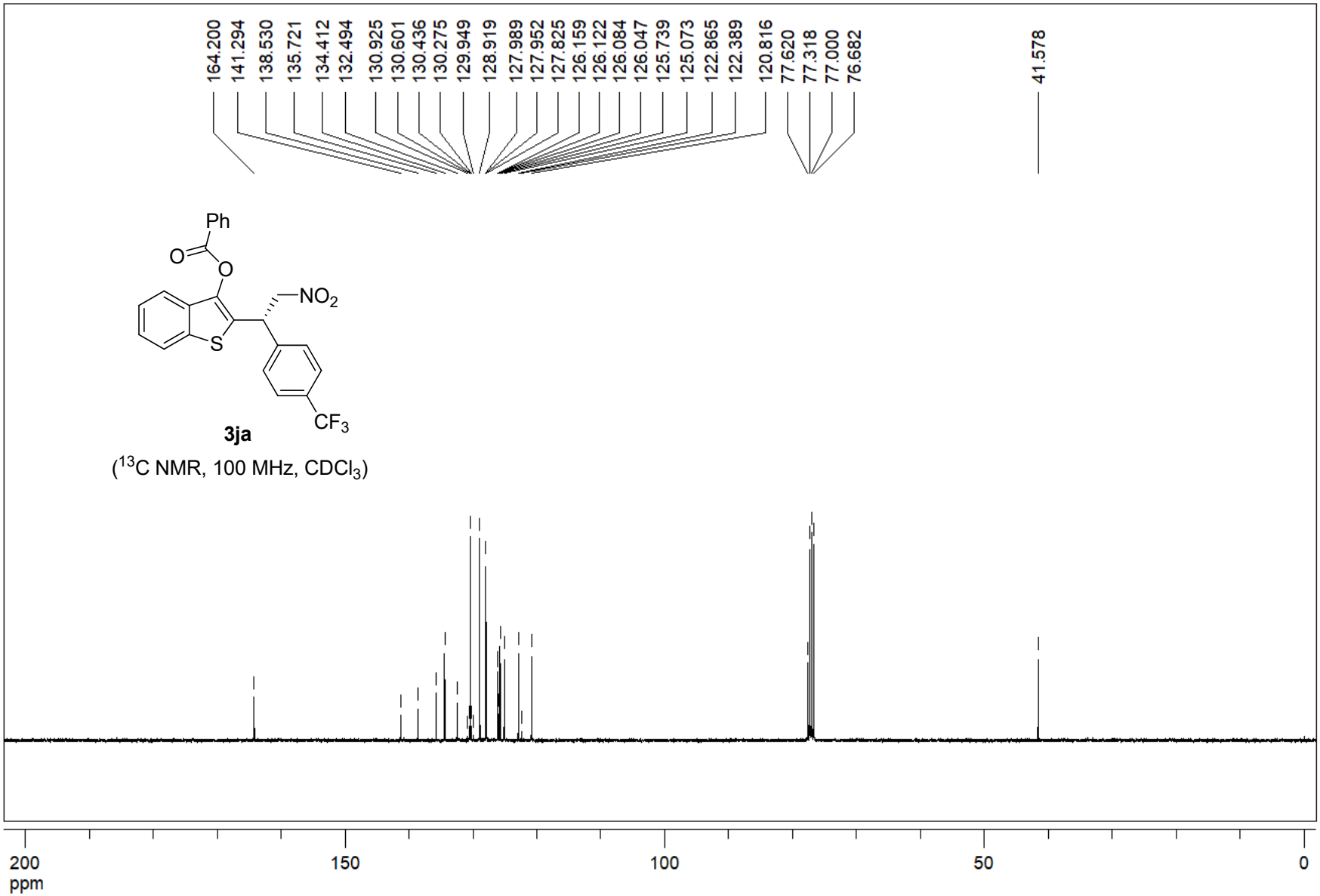
(^{1}H NMR, 400 MHz, $CDCl_3$)


164.163
139.543
138.380
135.719
134.335
132.512
131.367
130.652
130.638
130.478
128.908
128.160
128.046
126.023
125.612
124.981
123.123
122.849
120.796
77.662
77.318
77.000
76.683
41.397
Ph
O
O
NO2
S
Br
3ia
(13C NMR, 100 MHz, CDCl3)
200
ppm
150
100
50
0



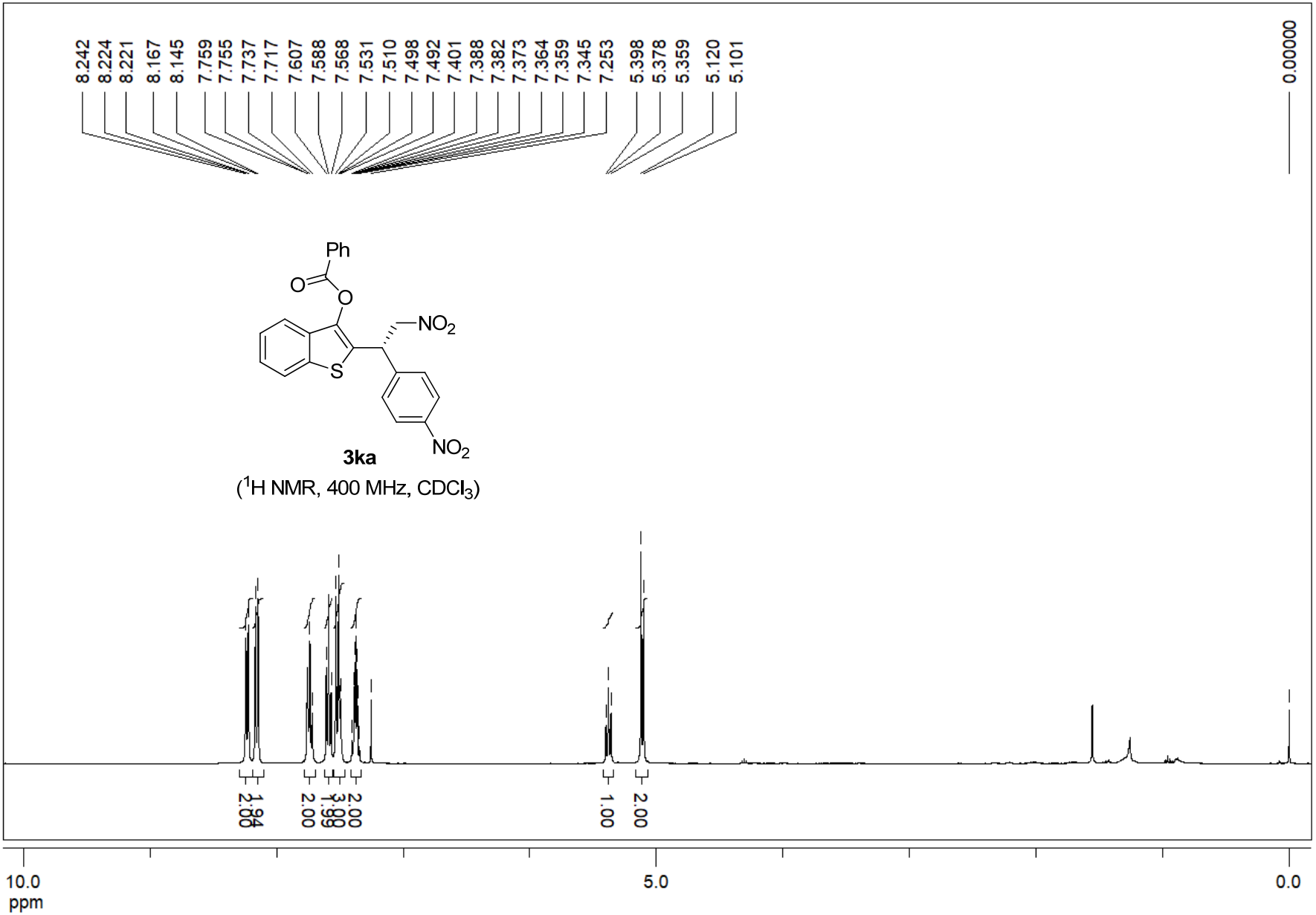
3ja

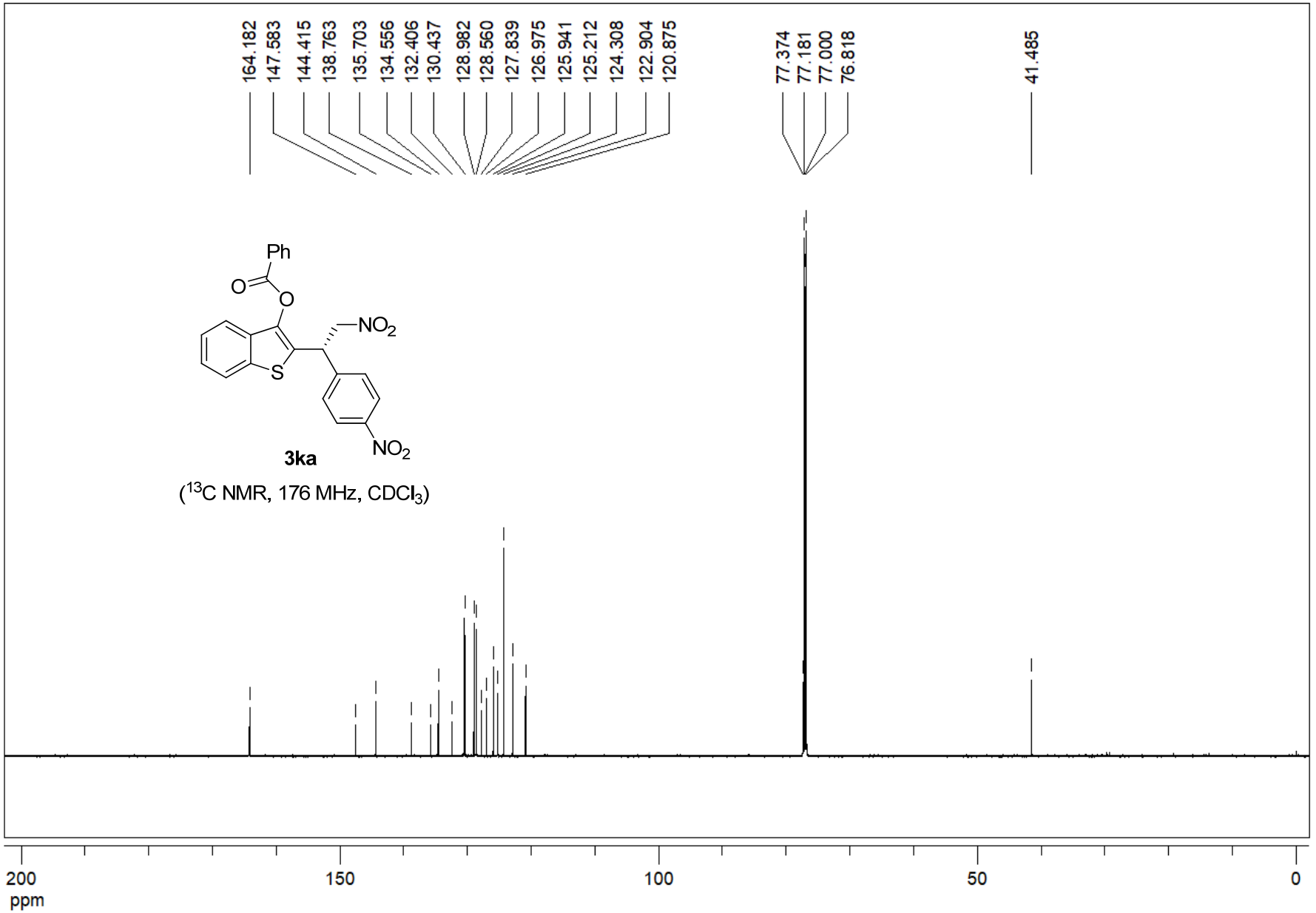
(^{1}H NMR, 400 MHz, $CDCl_3$)

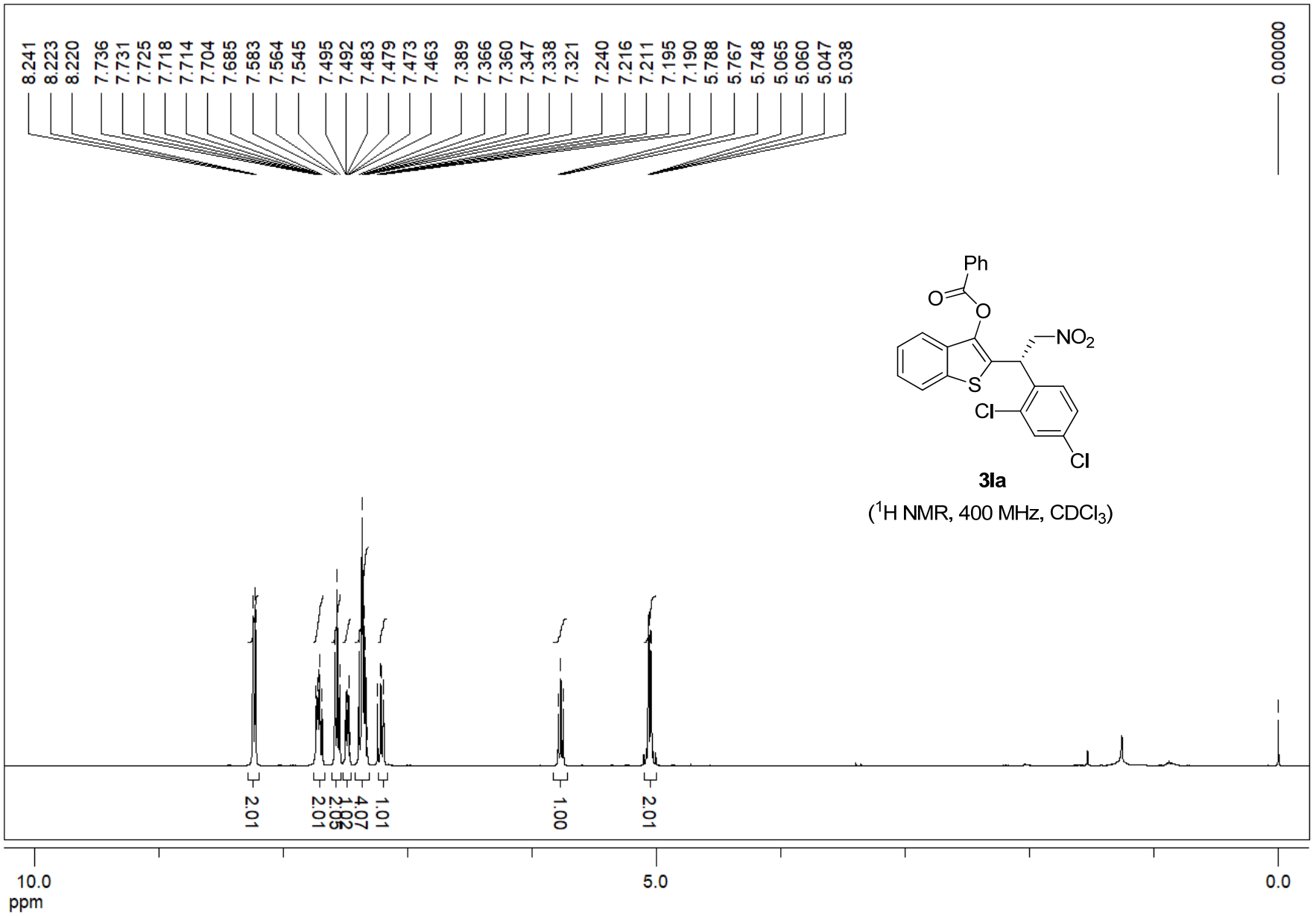


3ja

(^{13}C NMR, 100 MHz, $CDCl_3$)

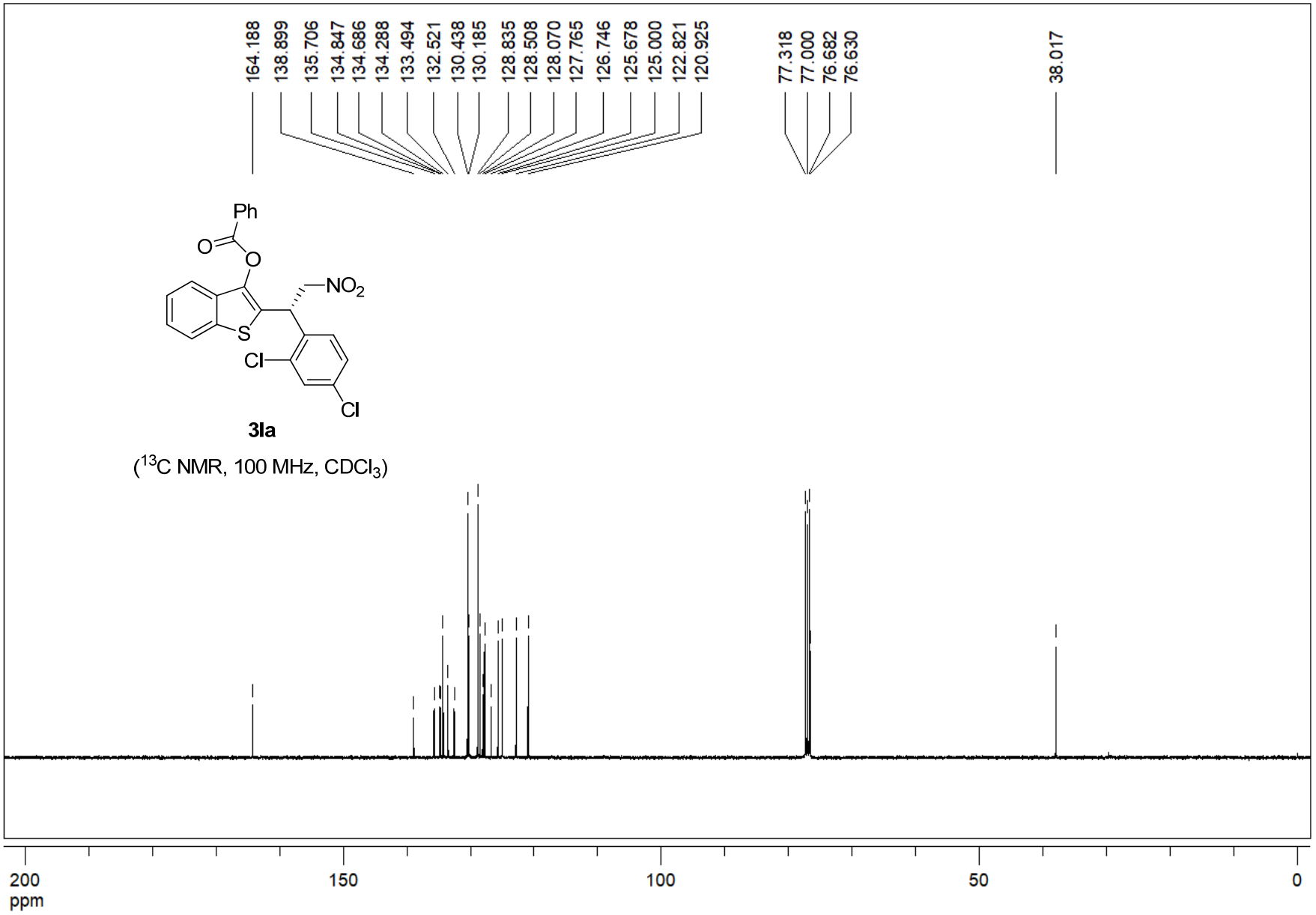

8.242
8.224
8.221
8.167
8.145
7.759
7.755
7.737
7.717
7.607
7.588
7.568
7.531
7.510
7.498
7.492
7.401
7.388
7.382
7.373
7.364
7.359
7.345
7.253
5.398
5.378
5.359
5.120
5.101
0.00000
Ph
O
O
NO2
S
NO2
3ka
(1H NMR, 400 MHz, CDCl3)
2.00
1.94
2.00
1.00
2.00
10.0
ppm
5.0
0.0


164.182
147.583
144.415
138.763
135.703
134.556
132.406
130.437
128.982
128.560
127.839
126.975
125.941
125.212
124.308
122.904
120.875
77.374
77.181
77.000
76.818
41.485
Ph
O
O
NO2
S
NO2
3ka
(13C NMR, 176 MHz, CDCl3)
200
150
100
50
0
ppm



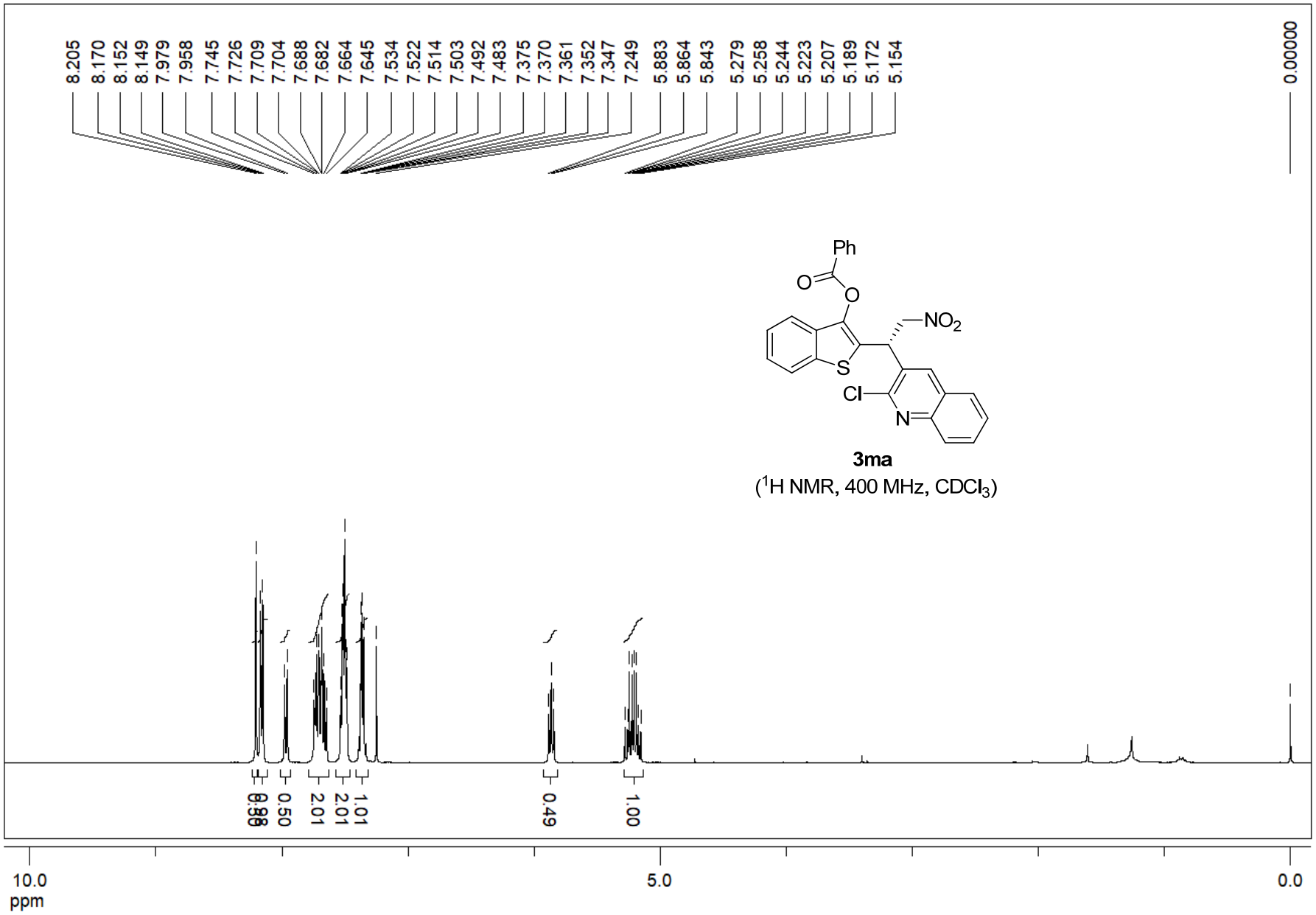
3la

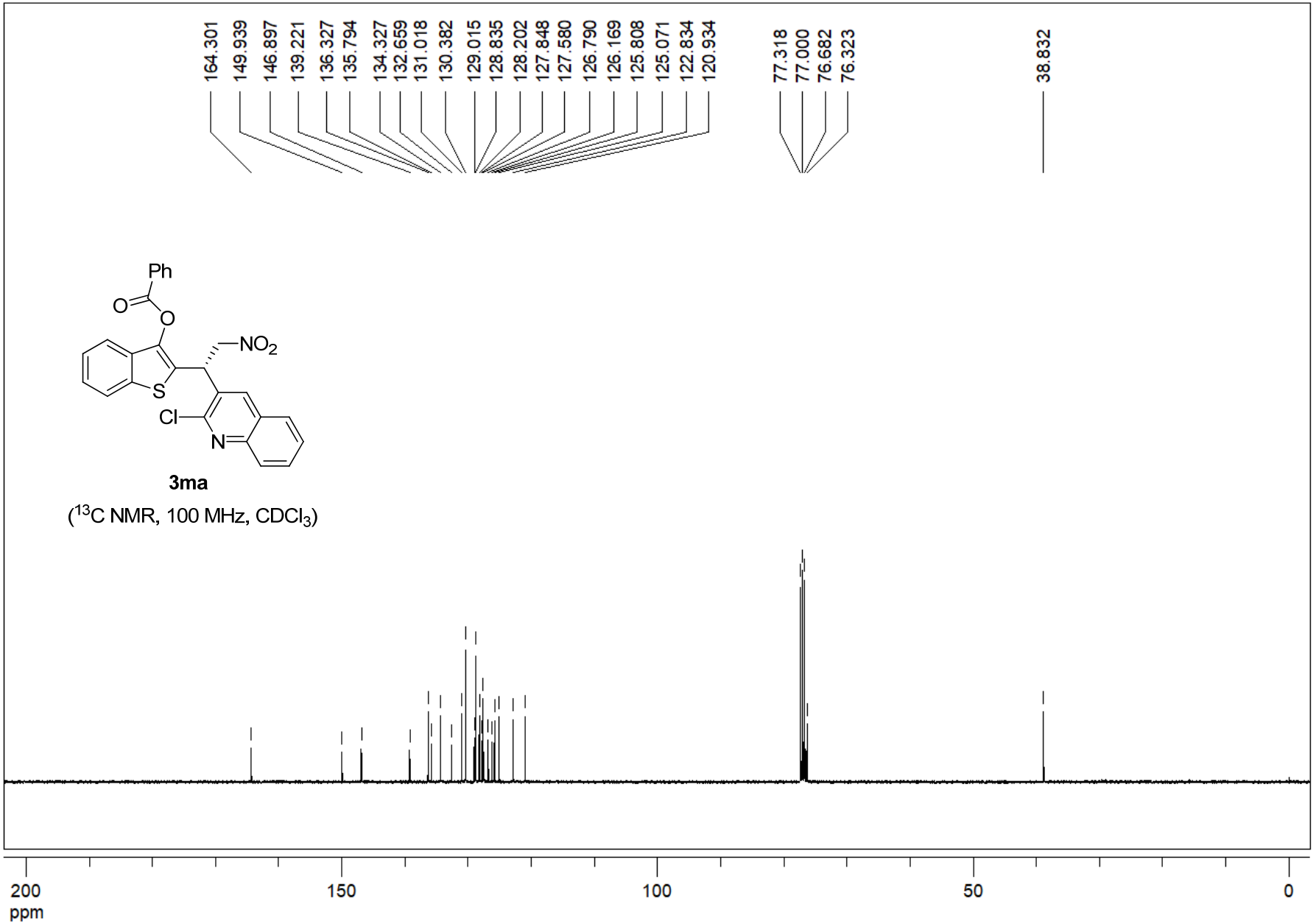
(^{1}H NMR, 400 MHz, $CDCl_3$)



3la

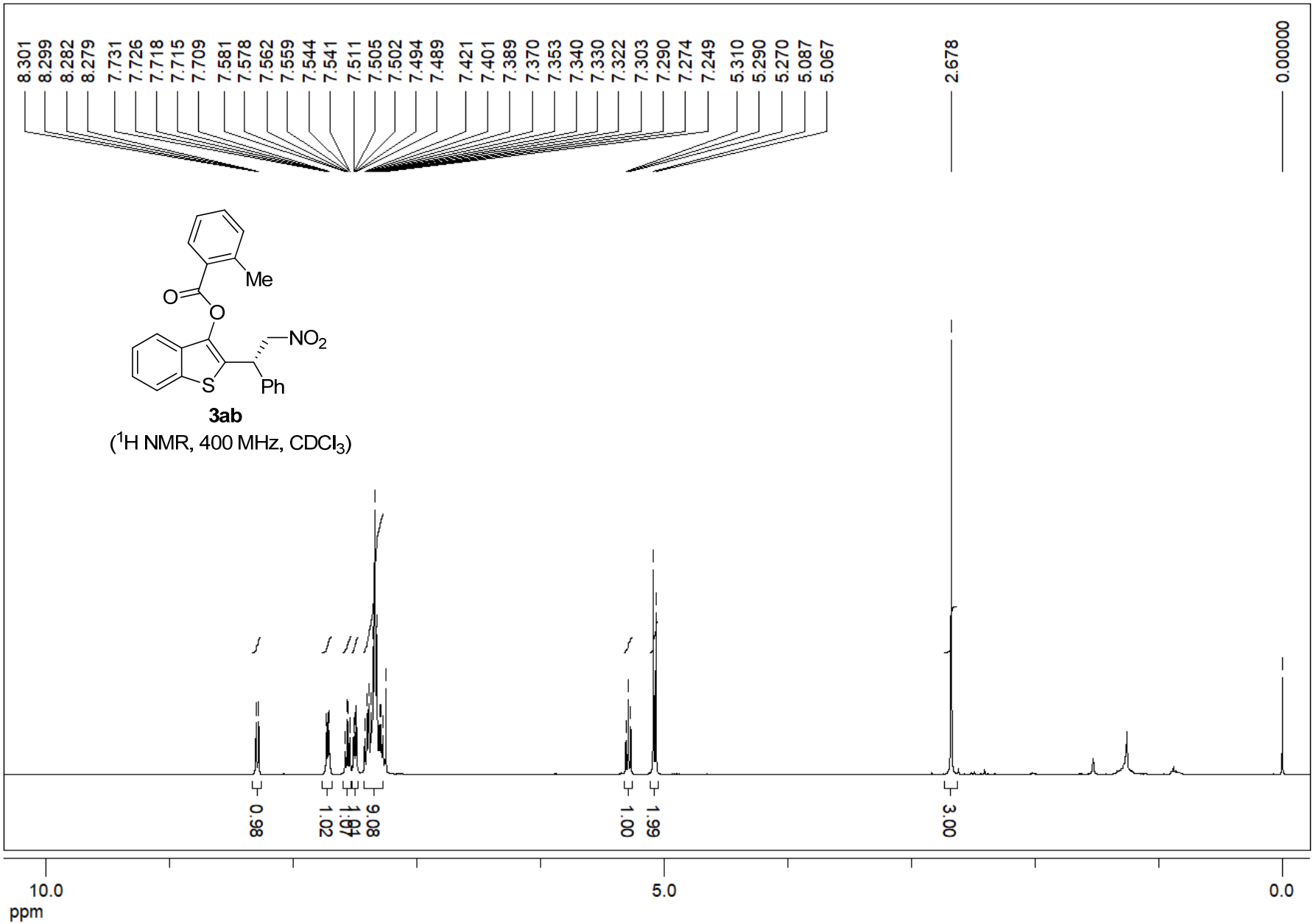
(^{13}C NMR, 100 MHz, $CDCl_3$)


8.205
8.170
8.152
8.149
7.979
7.958
7.745
7.726
7.709
7.704
7.688
7.682
7.664
7.645
7.534
7.522
7.514
7.503
7.492
7.483
7.375
7.370
7.361
7.352
7.347
7.249
5.883
5.864
5.843
5.279
5.258
5.244
5.223
5.207
5.189
5.172
5.154
0.00000
Ph
O
O
NO2
S
Cl
N
3ma
(1H NMR, 400 MHz, CDCl3)
0.50
2.01
2.01
1.01
0.49
1.00
10.0
ppm
5.0
0.0



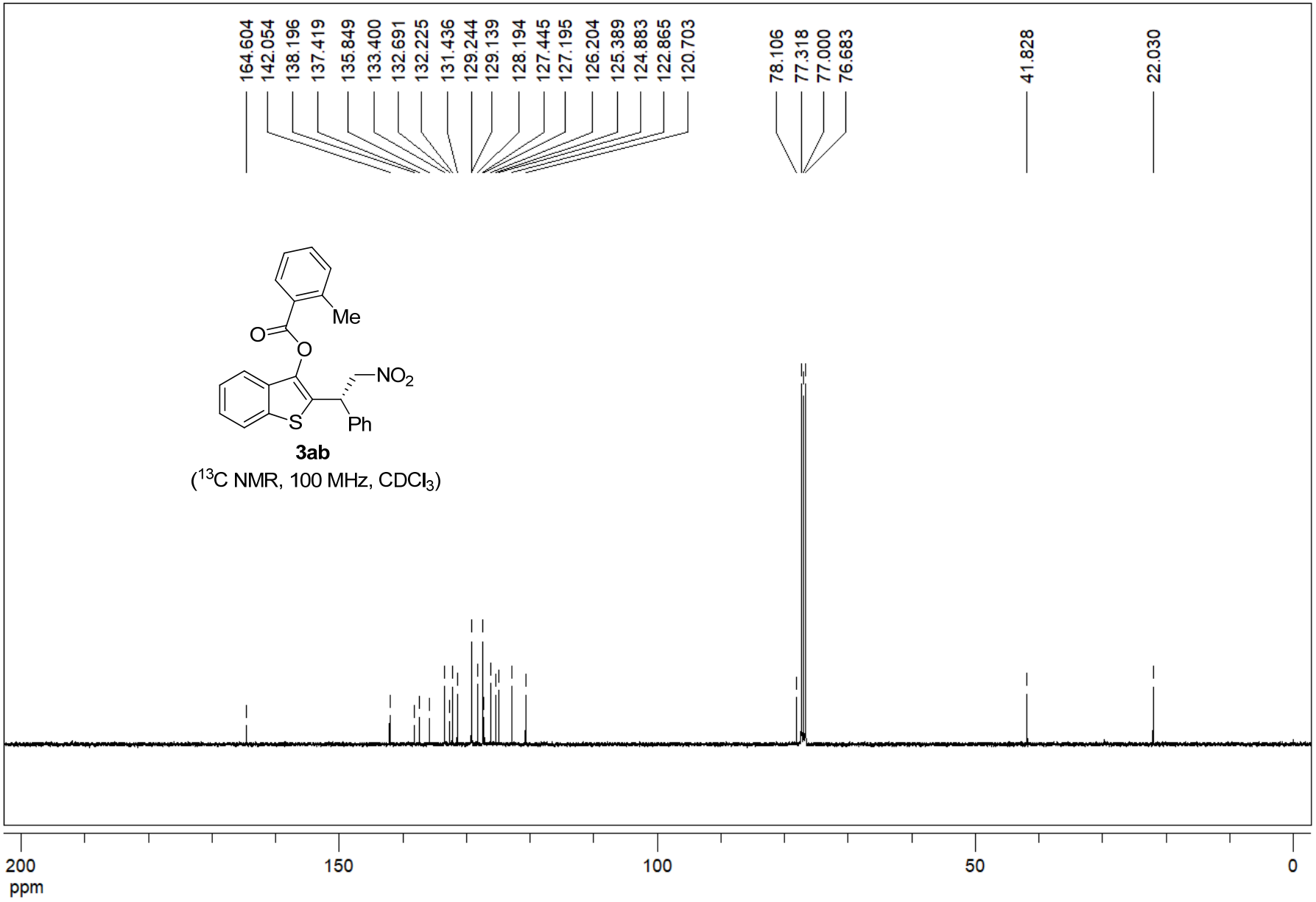
3ma

(^{13}C NMR, 100 MHz, $CDCl_3$)



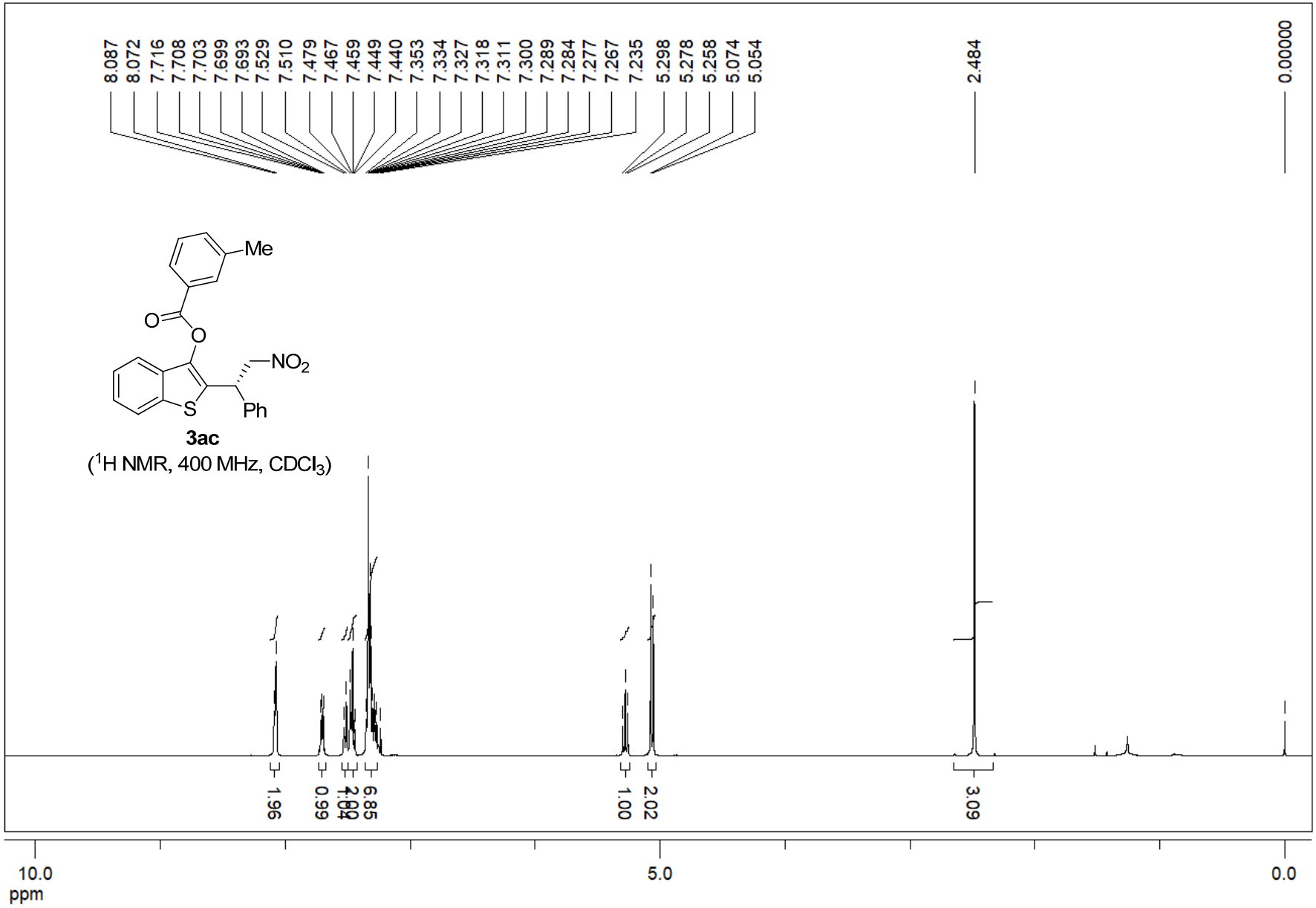
3ab

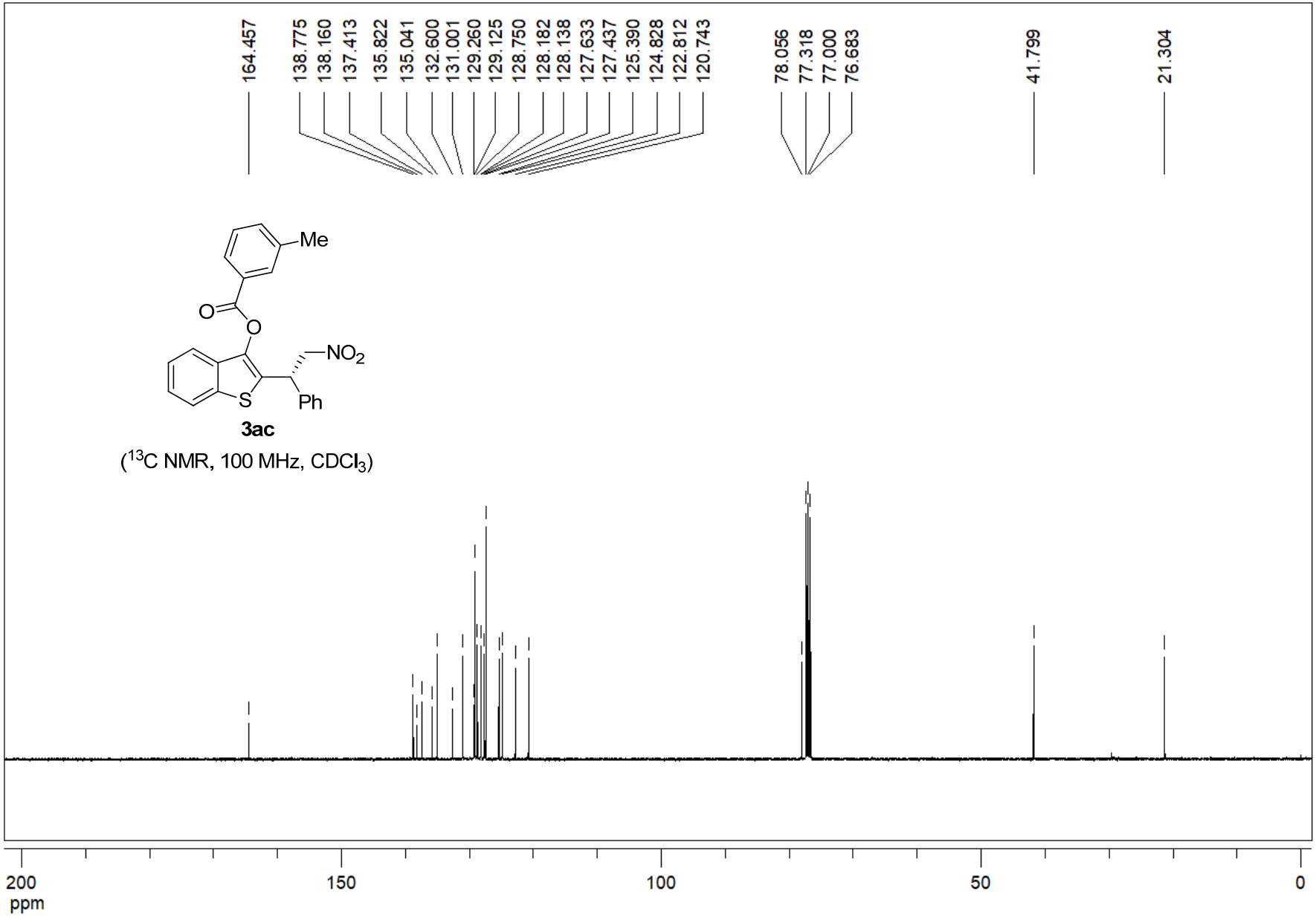
(^{1}H NMR, 400 MHz, $CDCl_3$)

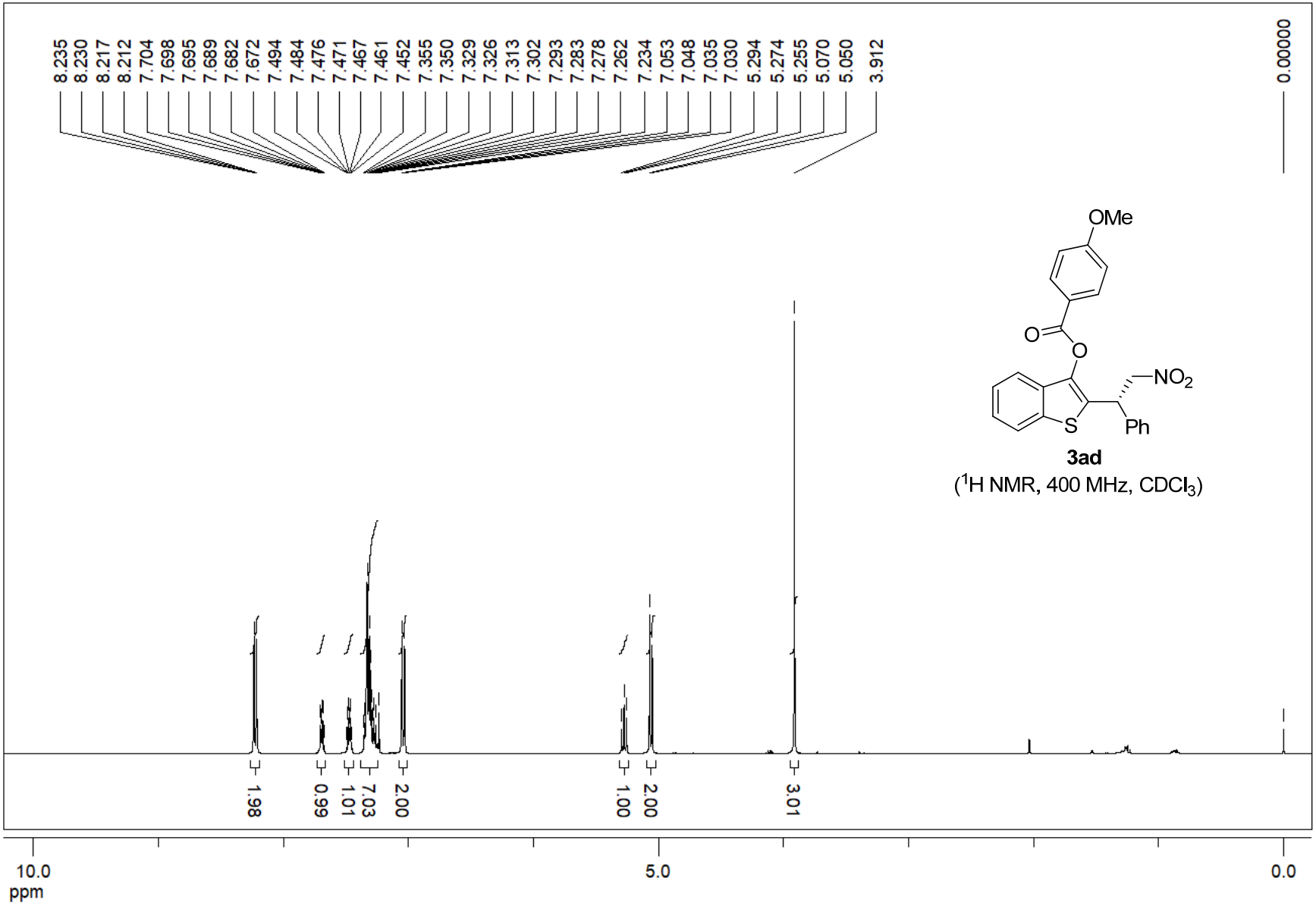


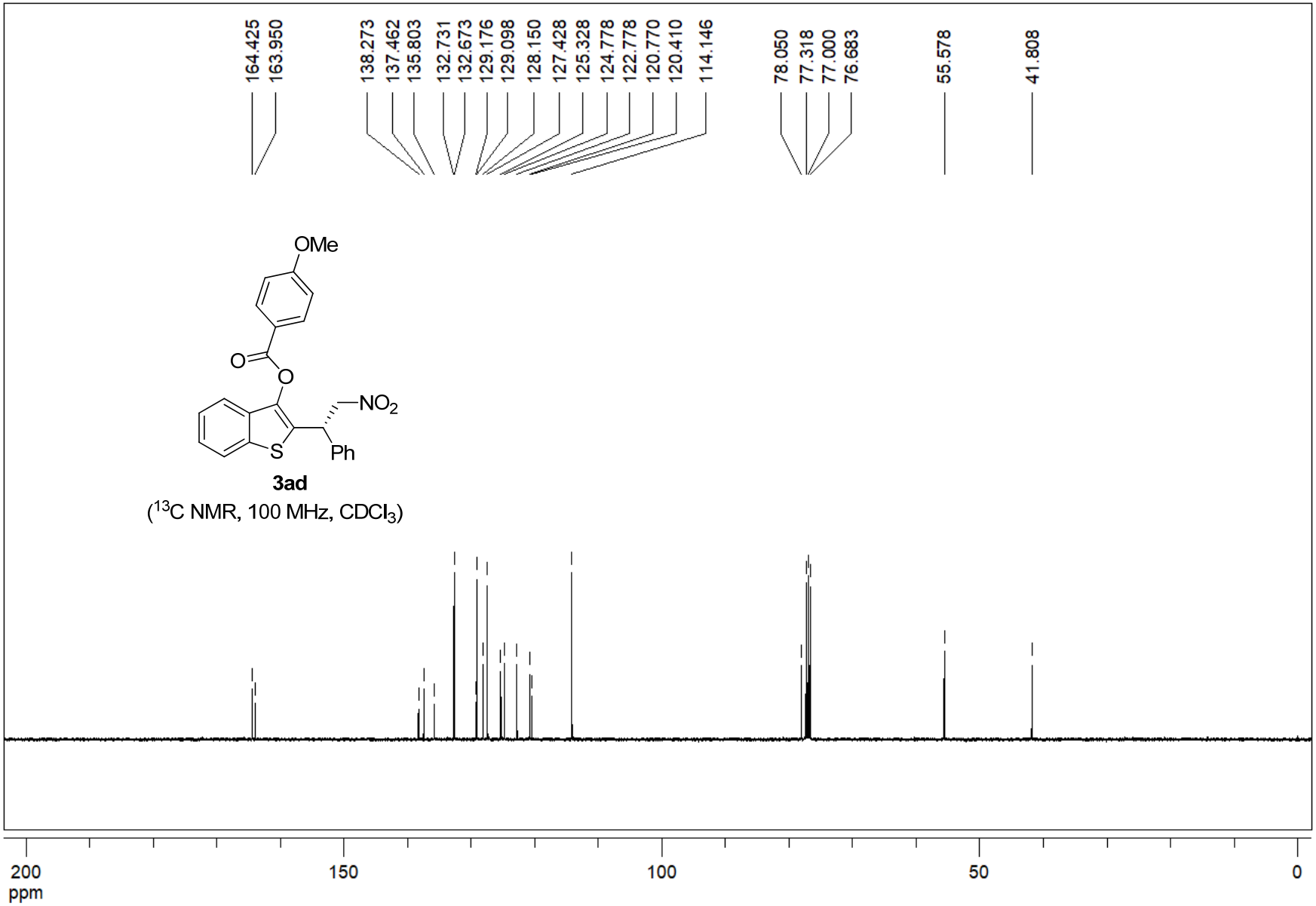
3ab

(^{13}C NMR, 100 MHz, $CDCl_3$)


8.087
8.072
7.716
7.708
7.703
7.699
7.693
7.529
7.510
7.479
7.467
7.459
7.449
7.440
7.353
7.334
7.327
7.318
7.311
7.300
7.289
7.284
7.277
7.267
7.235
5.298
5.278
5.258
5.074
5.054
2.484
0.00000
Me
O
O
NO2
S
Ph
3ac
(1H NMR, 400 MHz, CDCl3)
1.96
0.99
2.04
6.86
1.00
2.02
3.09
10.0
ppm
5.0
0.0

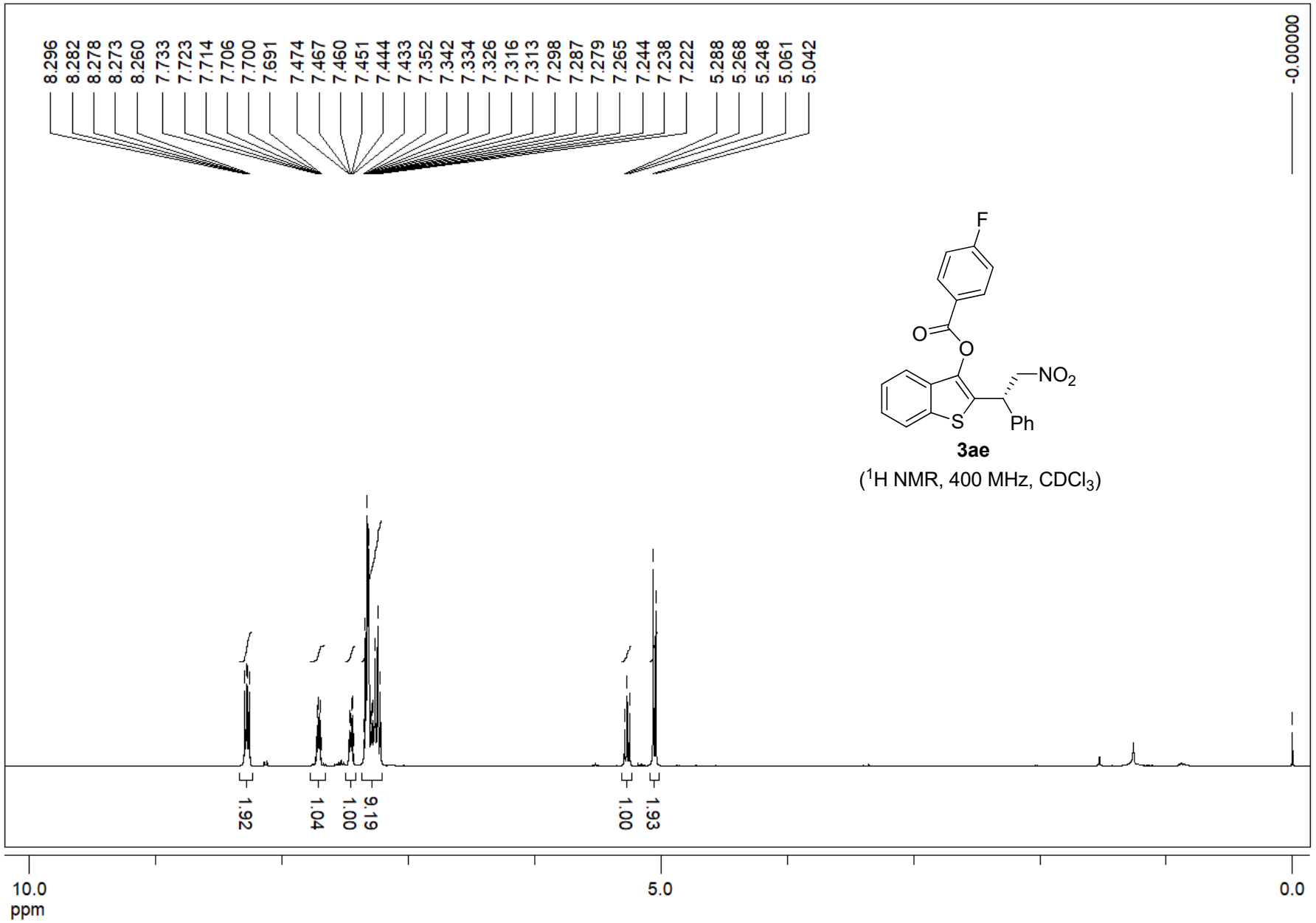

164.457
138.775
138.160
137.413
135.822
135.041
132.600
131.001
129.260
129.125
128.750
128.182
128.138
127.633
127.437
125.390
124.828
122.812
120.743
78.056
77.318
77.000
76.683
41.799
21.304
Me
O
O
NO2
S
Ph
3ac
(13C NMR, 100 MHz, CDCl3)
200
ppm
150
100
50
0


8.235
8.230
8.217
8.212
7.704
7.698
7.695
7.689
7.682
7.672
7.494
7.484
7.476
7.471
7.467
7.461
7.452
7.355
7.350
7.329
7.326
7.313
7.302
7.293
7.283
7.278
7.262
7.234
7.053
7.048
7.035
7.030
5.294
5.274
5.255
5.070
5.050
3.912
0.00000
OMe
O
O
NO2
S
Ph
3ad
(1H NMR, 400 MHz, CDCl3)
1.98
0.99
1.01
7.03
2.00
1.00
2.00
3.01
10.0
ppm
5.0
0.0



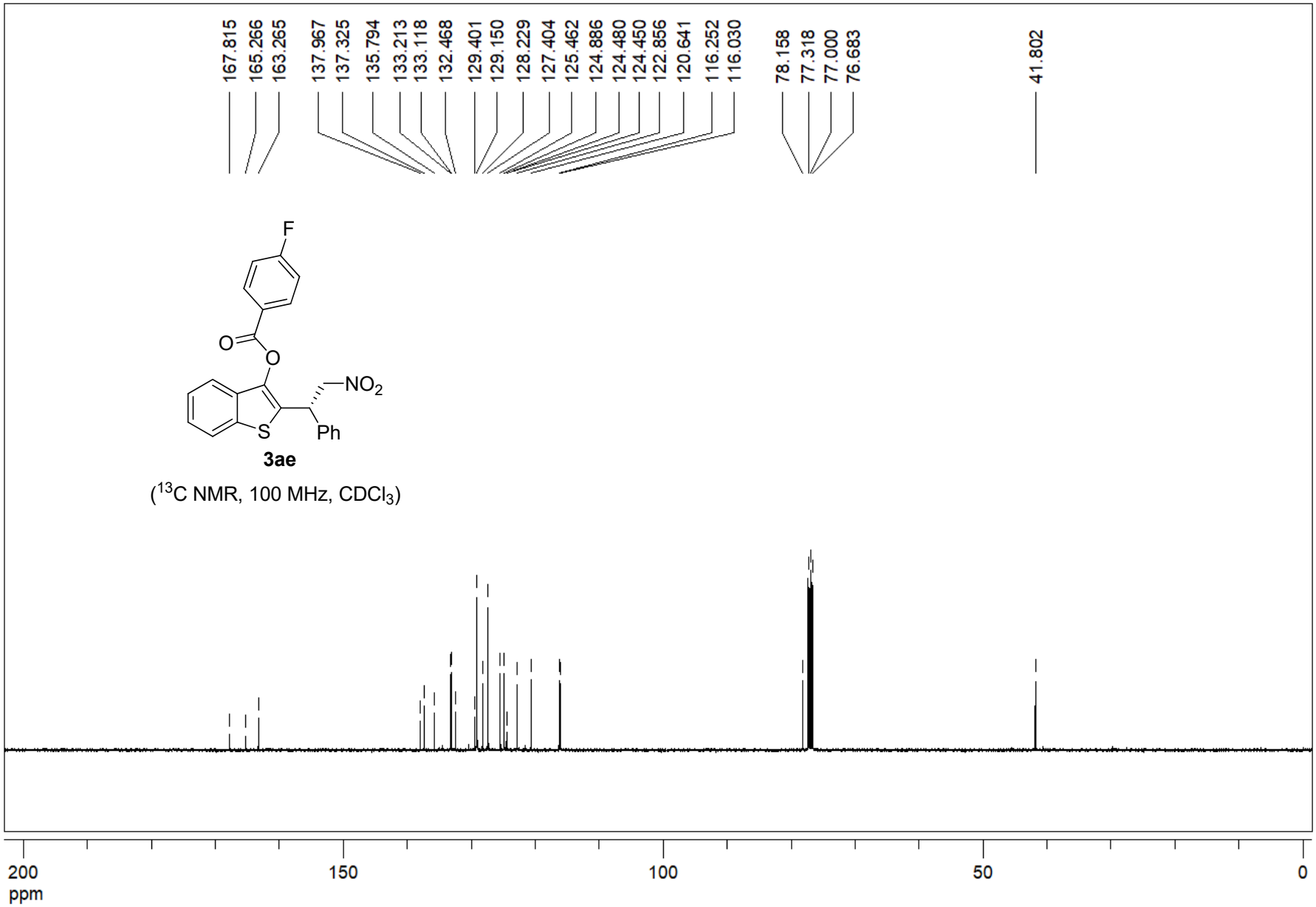
3ad

(^{13}C NMR, 100 MHz, $CDCl_3$)



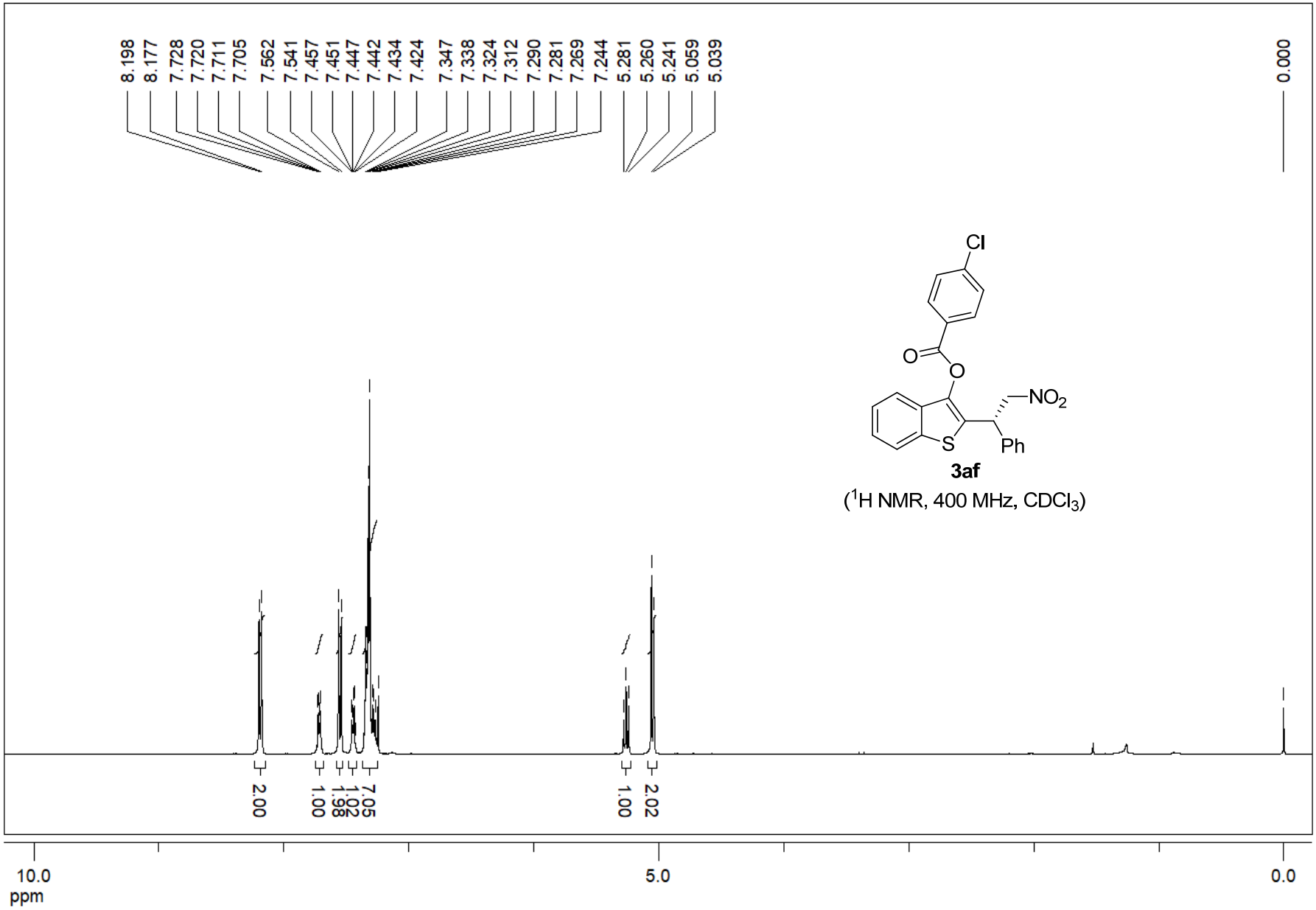
3ae

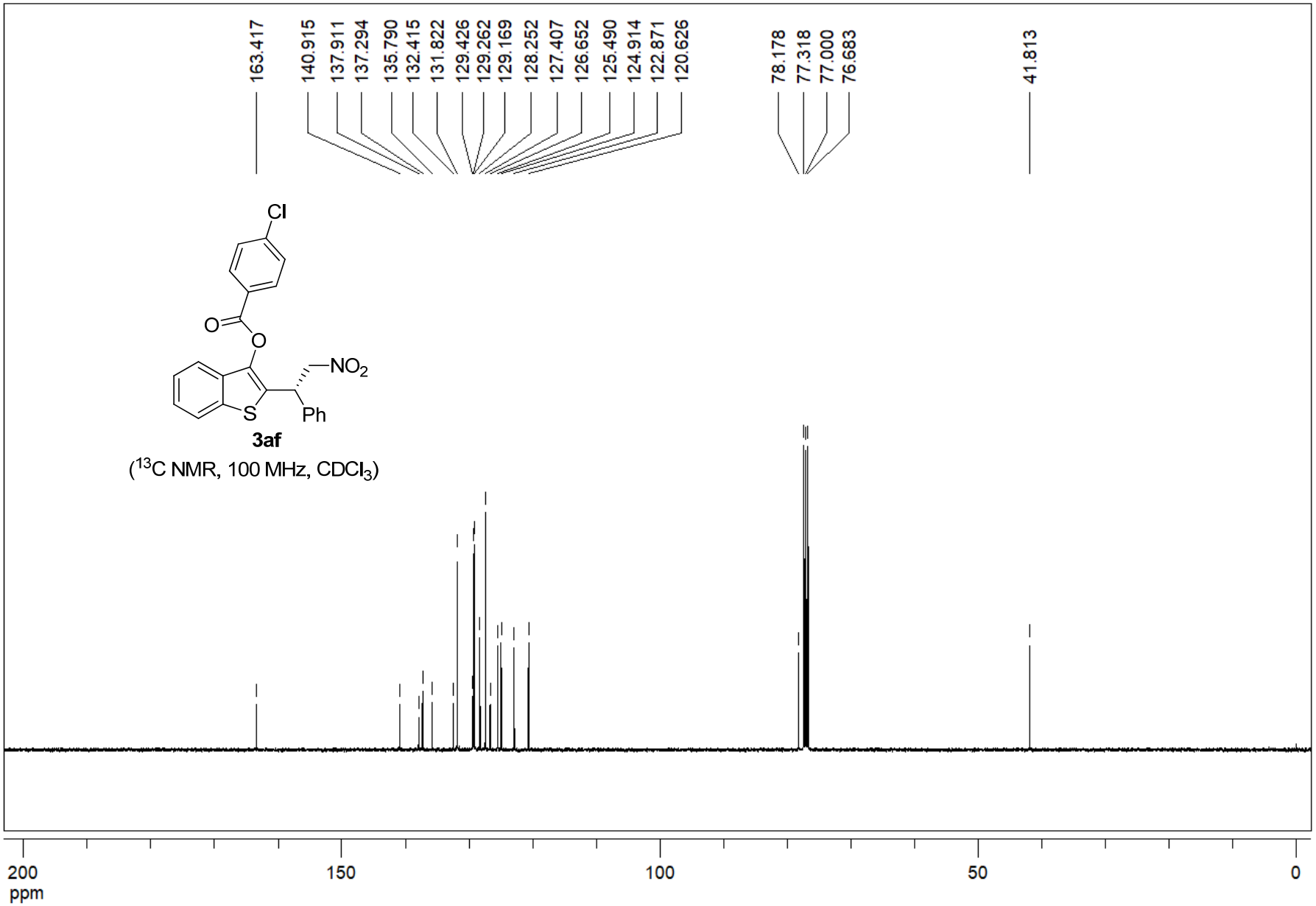
(^{1}H NMR, 400 MHz, $CDCl_3$)

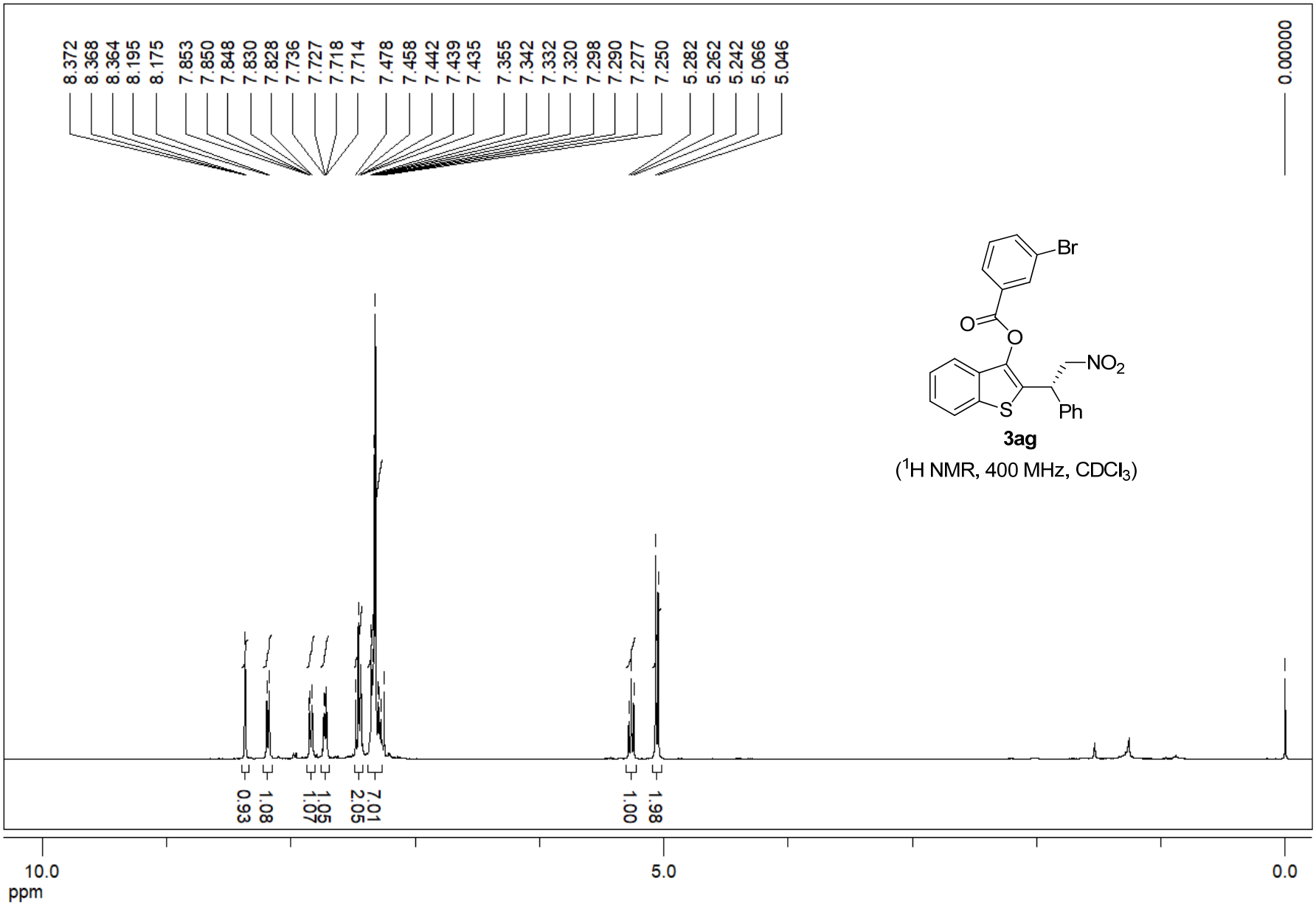


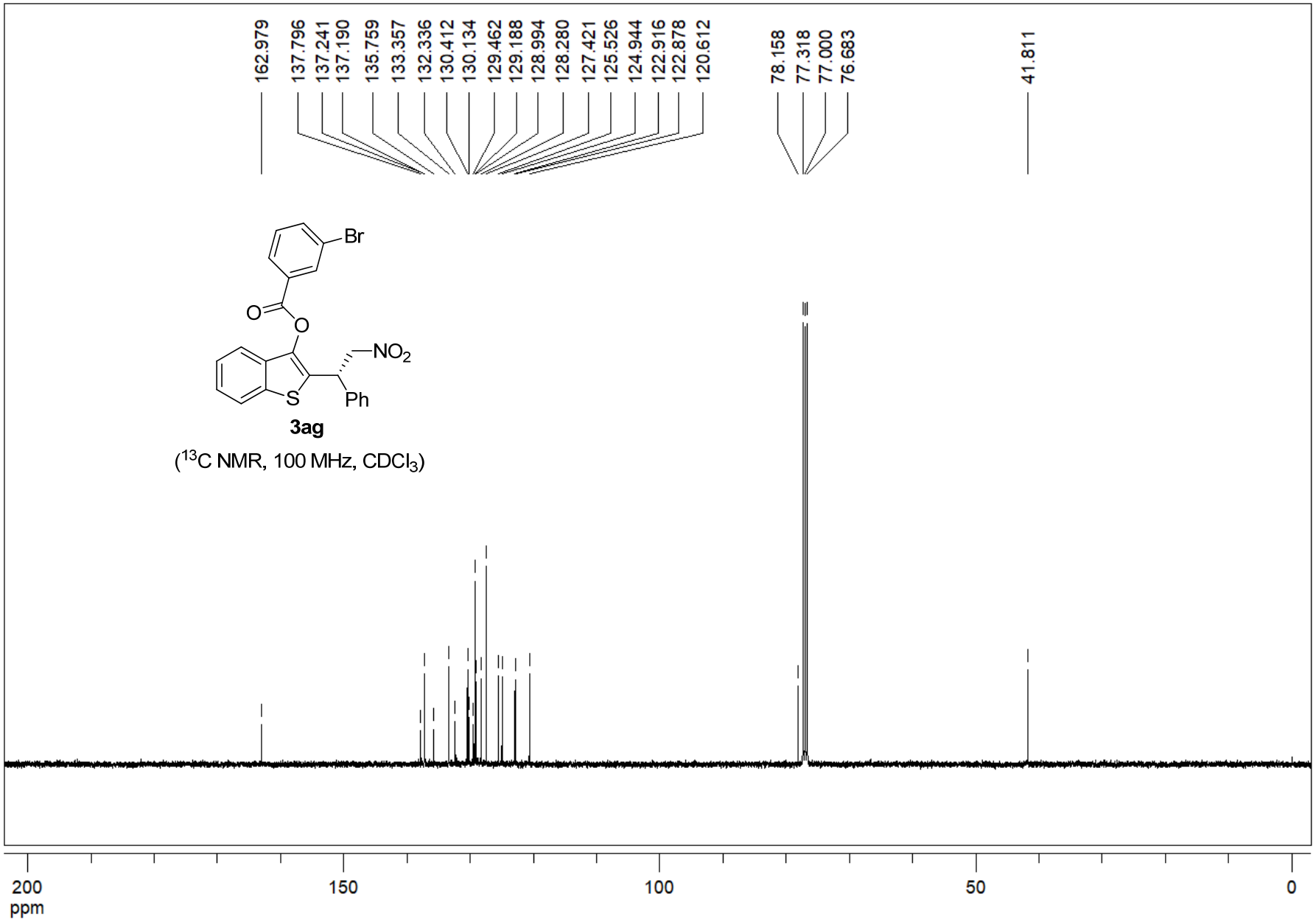
3ae

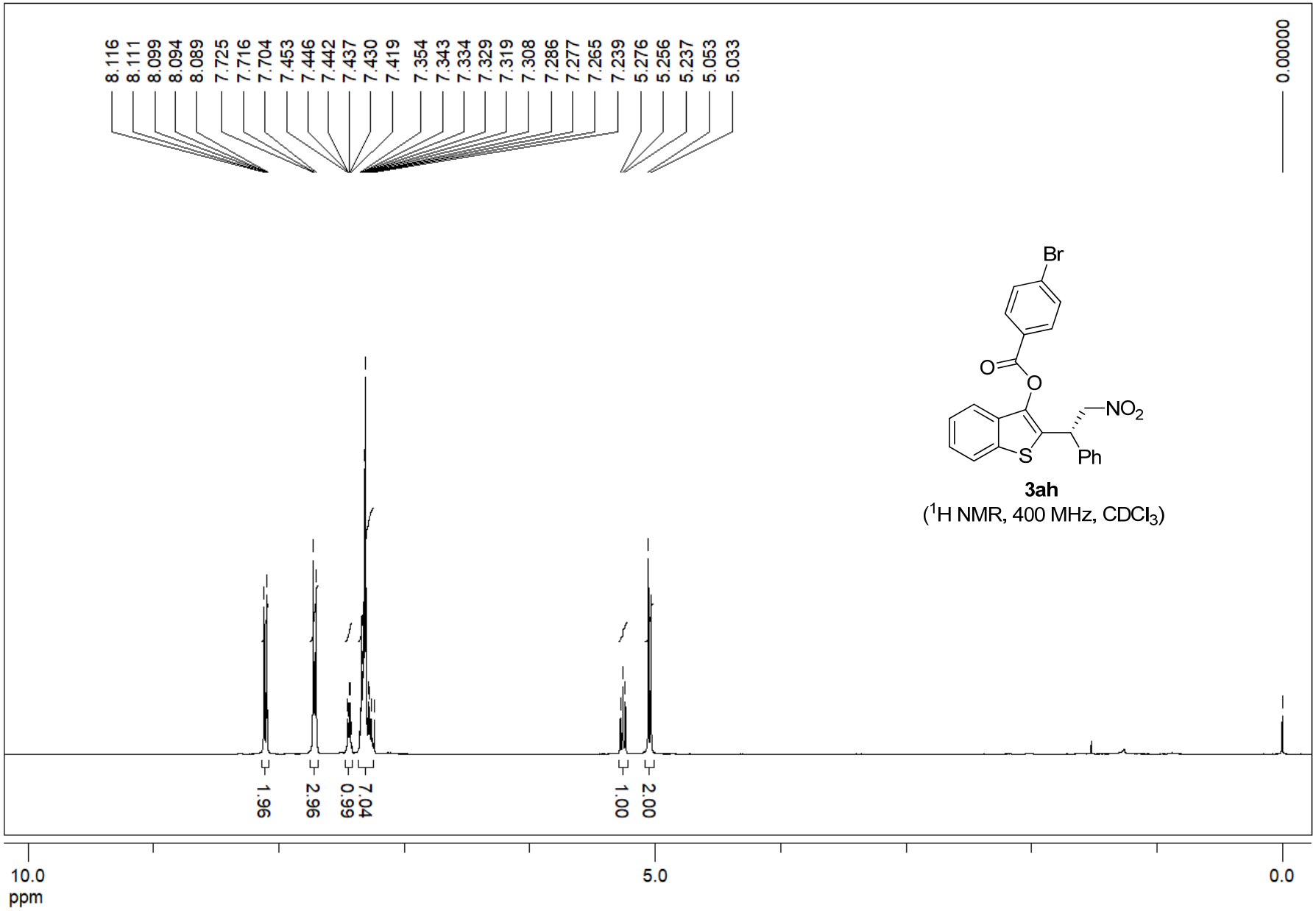
(^{13}C NMR, 100 MHz, $CDCl_3$)


8.198
8.177
7.728
7.720
7.711
7.705
7.562
7.541
7.457
7.451
7.447
7.442
7.434
7.424
7.347
7.338
7.324
7.312
7.290
7.281
7.269
7.244
5.281
5.260
5.241
5.059
5.039
0.000
Cl
O
O
NO2
S
Ph
3af
(1H NMR, 400 MHz, CDCl3)
2.00
1.00
1.98
1.02
7.05
1.00
2.02
10.0
ppm
5.0
0.0


163.417
140.915
137.911
137.294
135.790
132.415
131.822
129.426
129.262
129.169
128.252
127.407
126.652
125.490
124.914
122.871
120.626
78.178
77.318
77.000
76.683
41.813
Cl
O
O
NO2
S
Ph
3af
(13C NMR, 100 MHz, CDCl3)
200
ppm
150
100
50
0

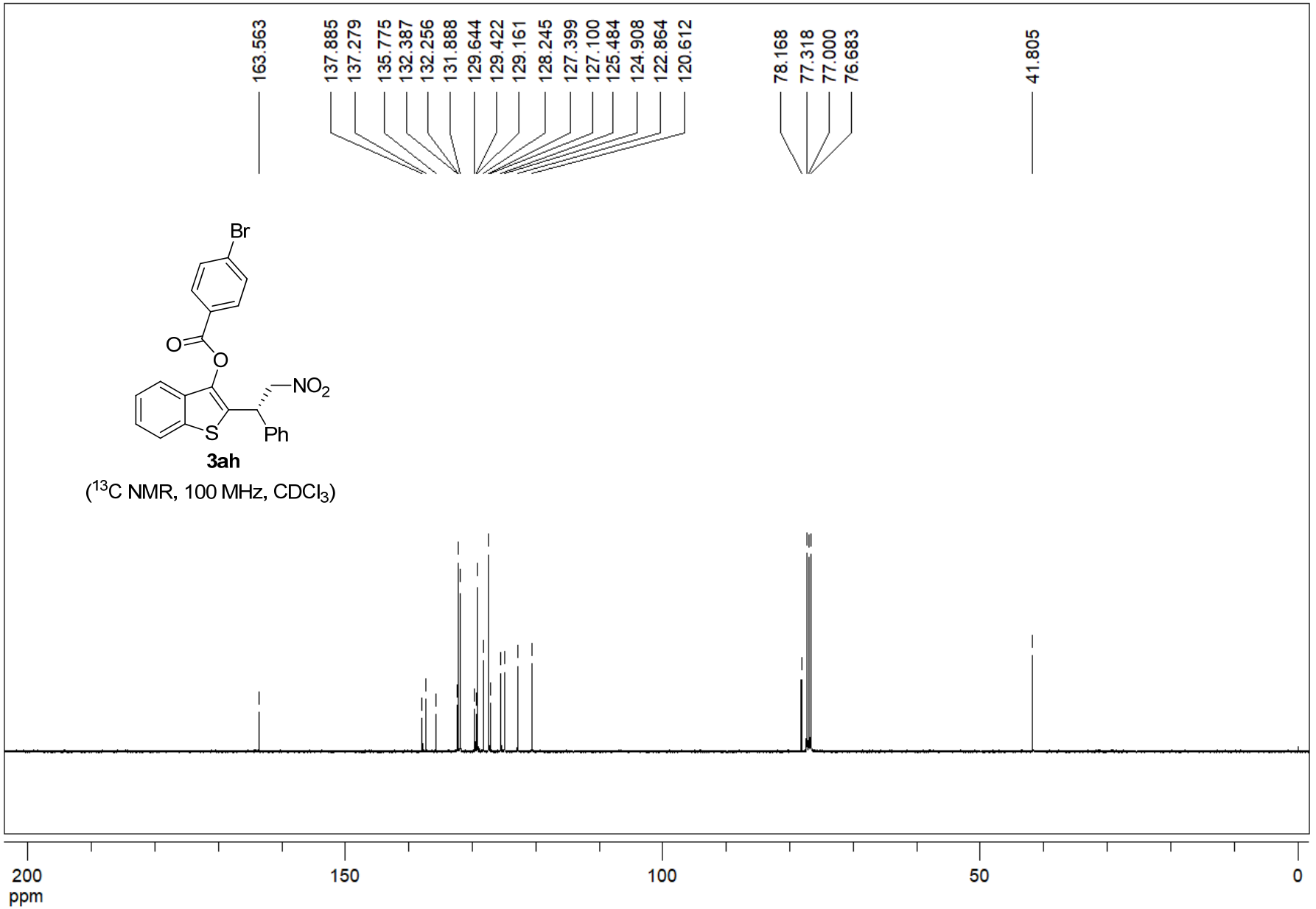

8.372
8.368
8.364
8.195
8.175
7.853
7.850
7.848
7.830
7.828
7.736
7.727
7.718
7.714
7.478
7.458
7.442
7.439
7.435
7.355
7.342
7.332
7.320
7.298
7.290
7.277
7.250
5.282
5.262
5.242
5.066
5.046
0.00000
0.93
1.08
1.07
1.05
2.05
7.01
1.00
1.98
10.0
5.0
0.0
ppm
Br
O
O
NO2
S
Ph
3ag
(1H NMR, 400 MHz, CDCl3)

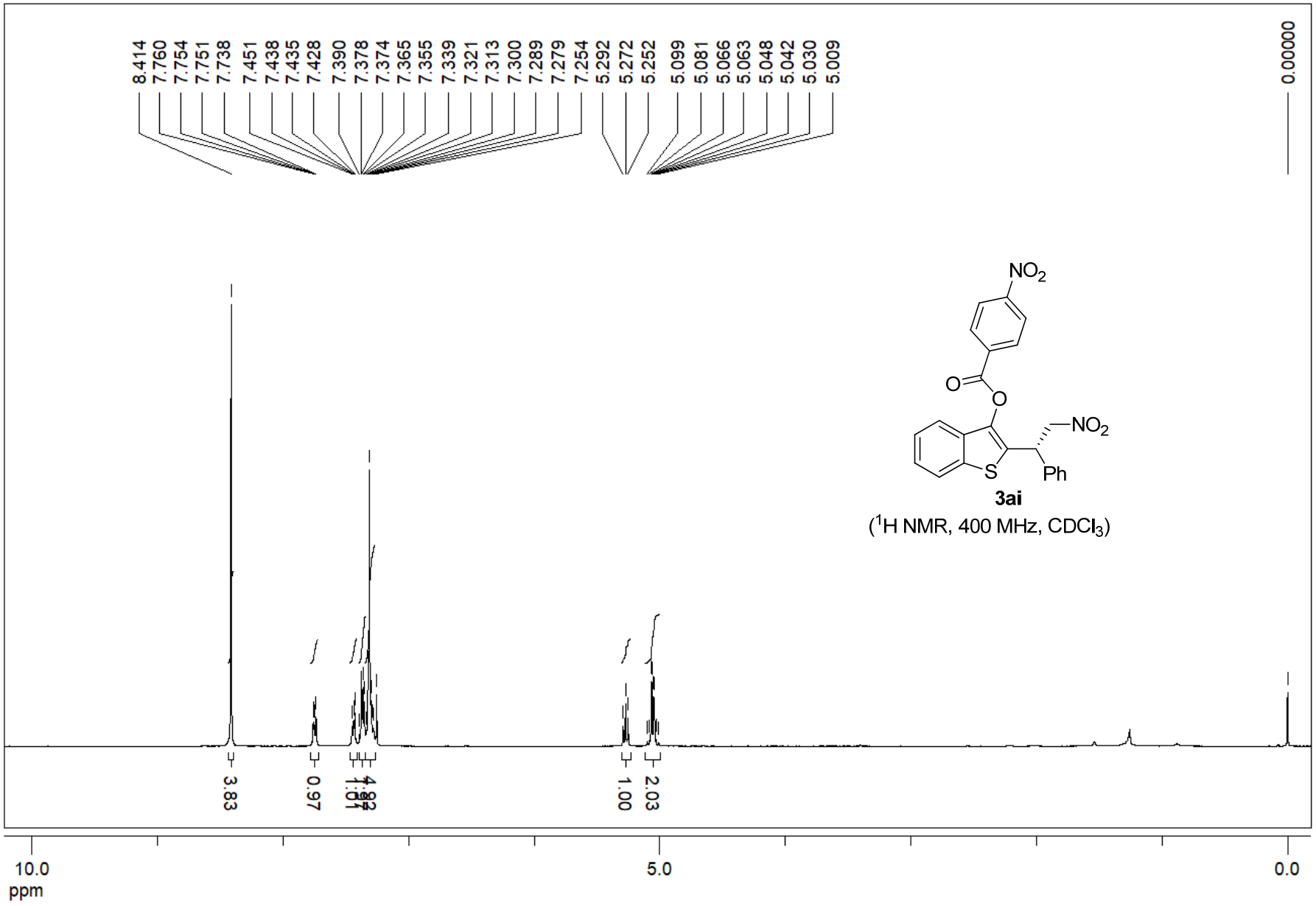

162.979
137.796
137.241
137.190
135.759
133.357
132.336
130.412
130.134
129.462
129.188
128.994
128.280
127.421
125.526
124.944
122.916
122.878
120.612
78.158
77.318
77.000
76.683
41.811
Br
O
O
NO2
S
Ph
3ag
(13C NMR, 100 MHz, CDCl3)
200
ppm
150
100
50
0



3ah

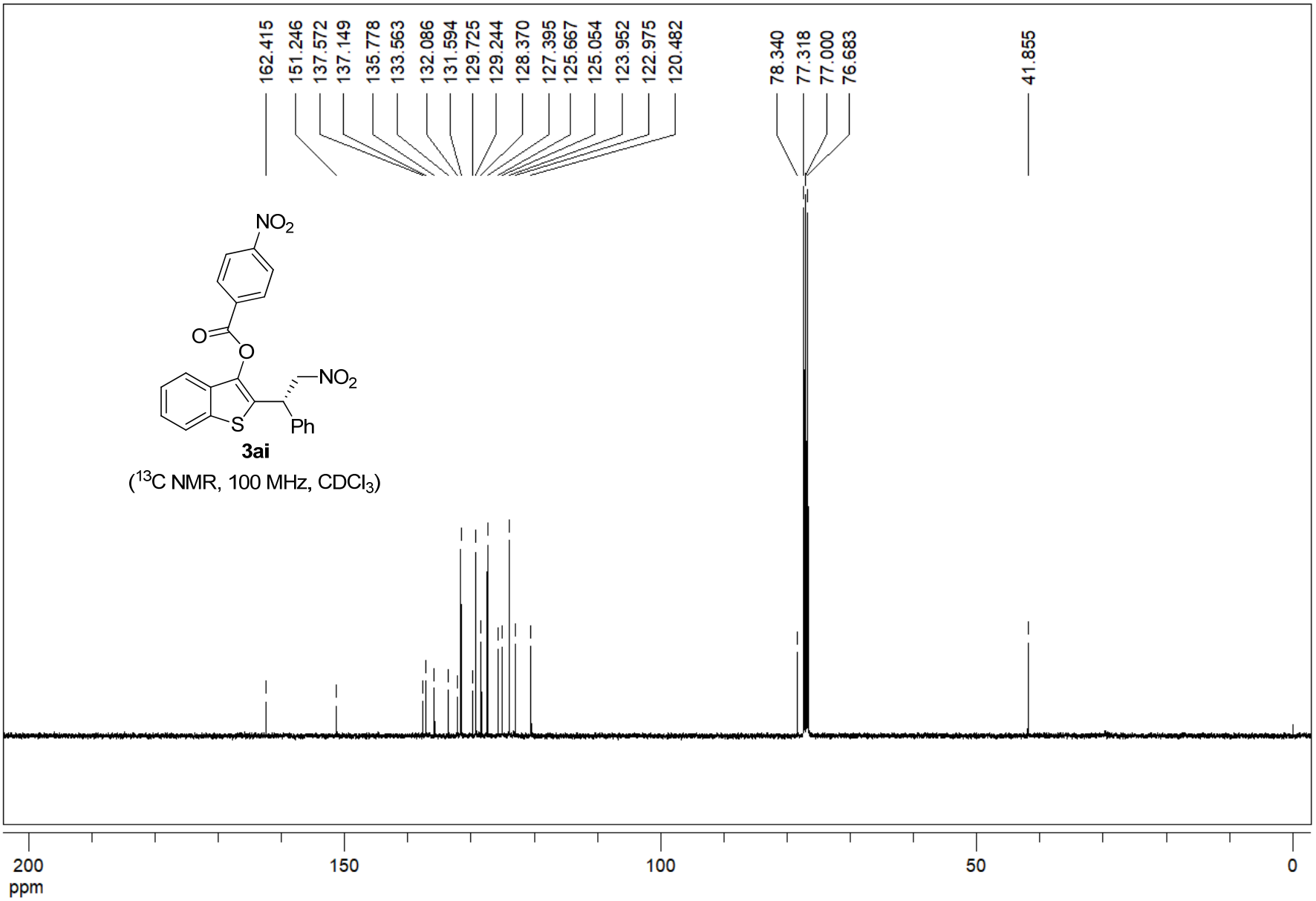
(^{1}H NMR, 400 MHz, $CDCl_3$)

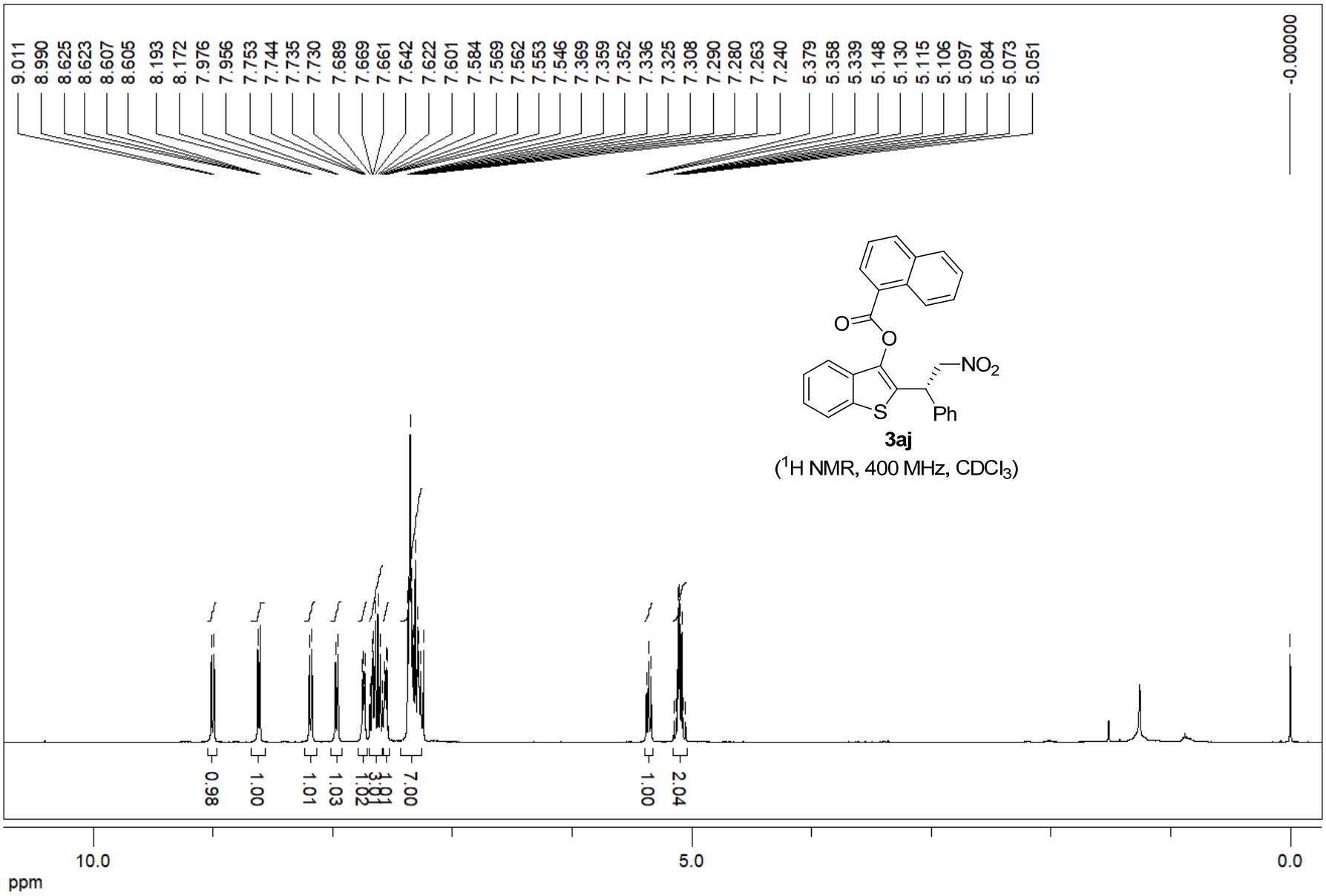

163.563
137.885
137.279
135.775
132.387
132.256
131.888
129.644
129.422
129.161
128.245
127.399
127.100
125.484
124.908
122.864
120.612
78.168
77.318
77.000
76.683
41.805
Br
O
O
NO2
S
Ph
3ah
(13C NMR, 100 MHz, CDCl3)
200
ppm
150
100
50
0



3ai

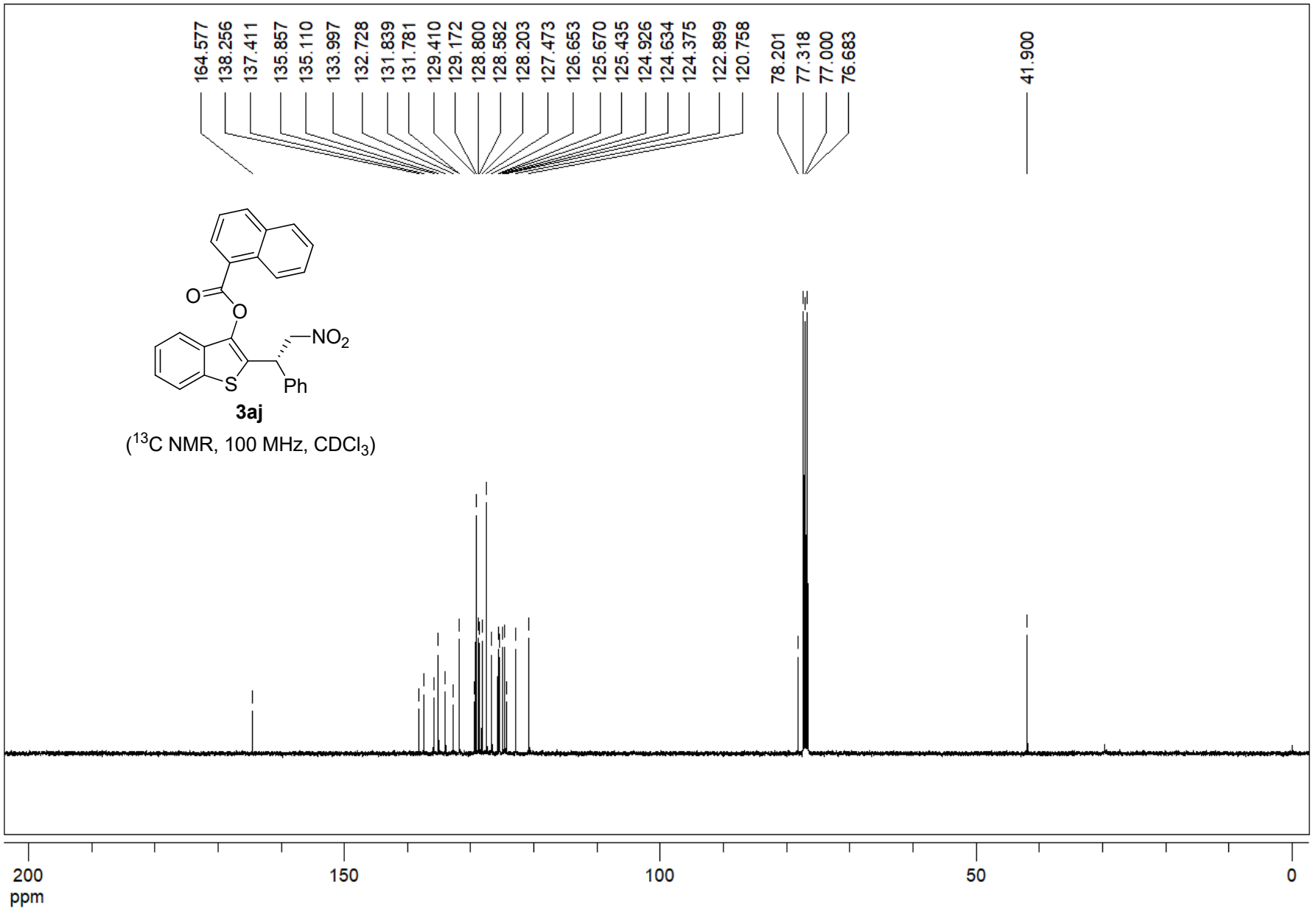
(^{1}H NMR, 400 MHz, $CDCl_3$)


162.415
151.246
137.572
137.149
135.778
133.563
132.086
131.594
129.725
129.244
128.370
127.395
125.667
125.054
123.952
122.975
120.482
78.340
77.318
77.000
76.683
41.855
NO2
O
O
NO2
S
Ph
3ai
(13C NMR, 100 MHz, CDCl3)
200
ppm
150
100
50
0



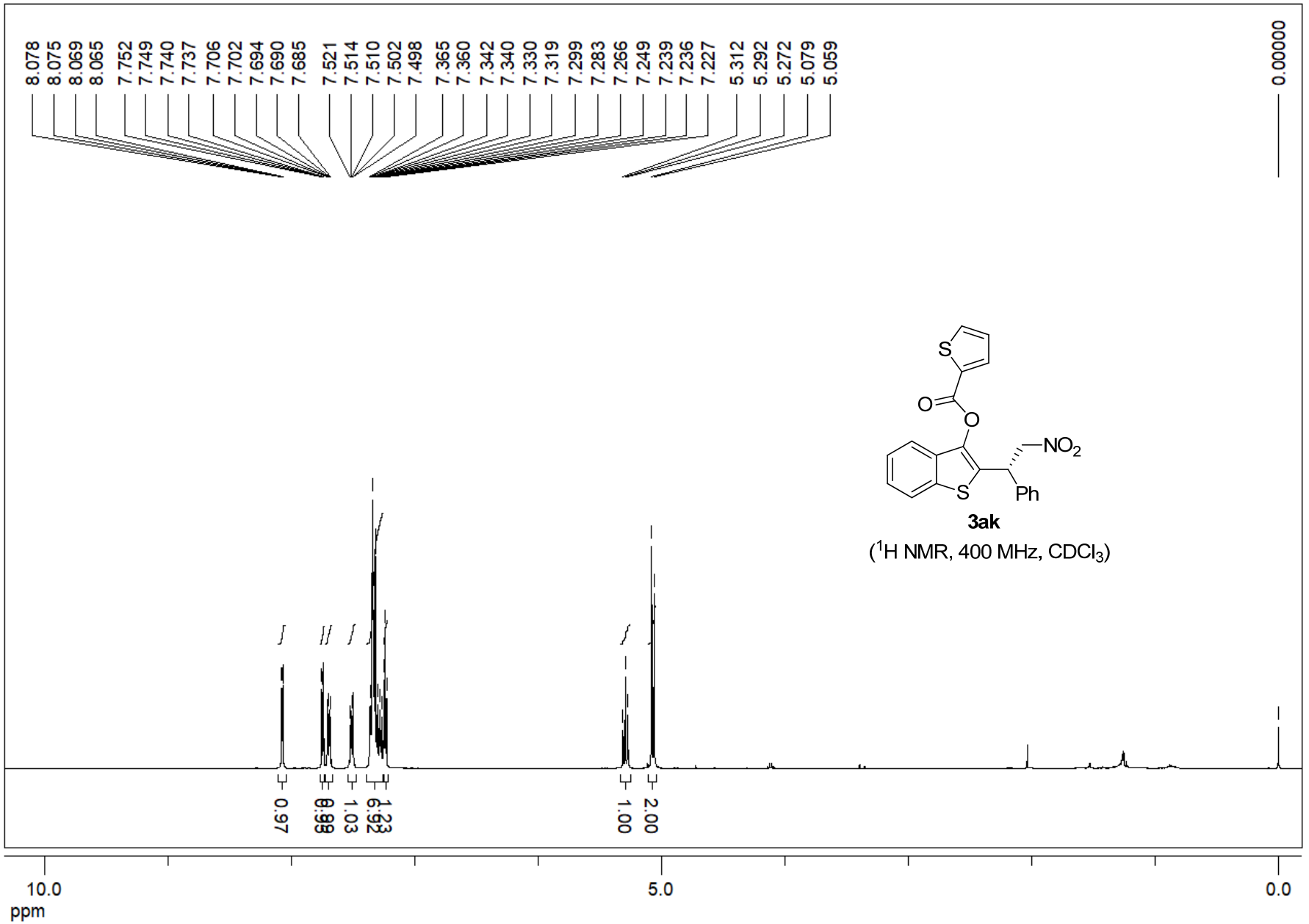
3aj

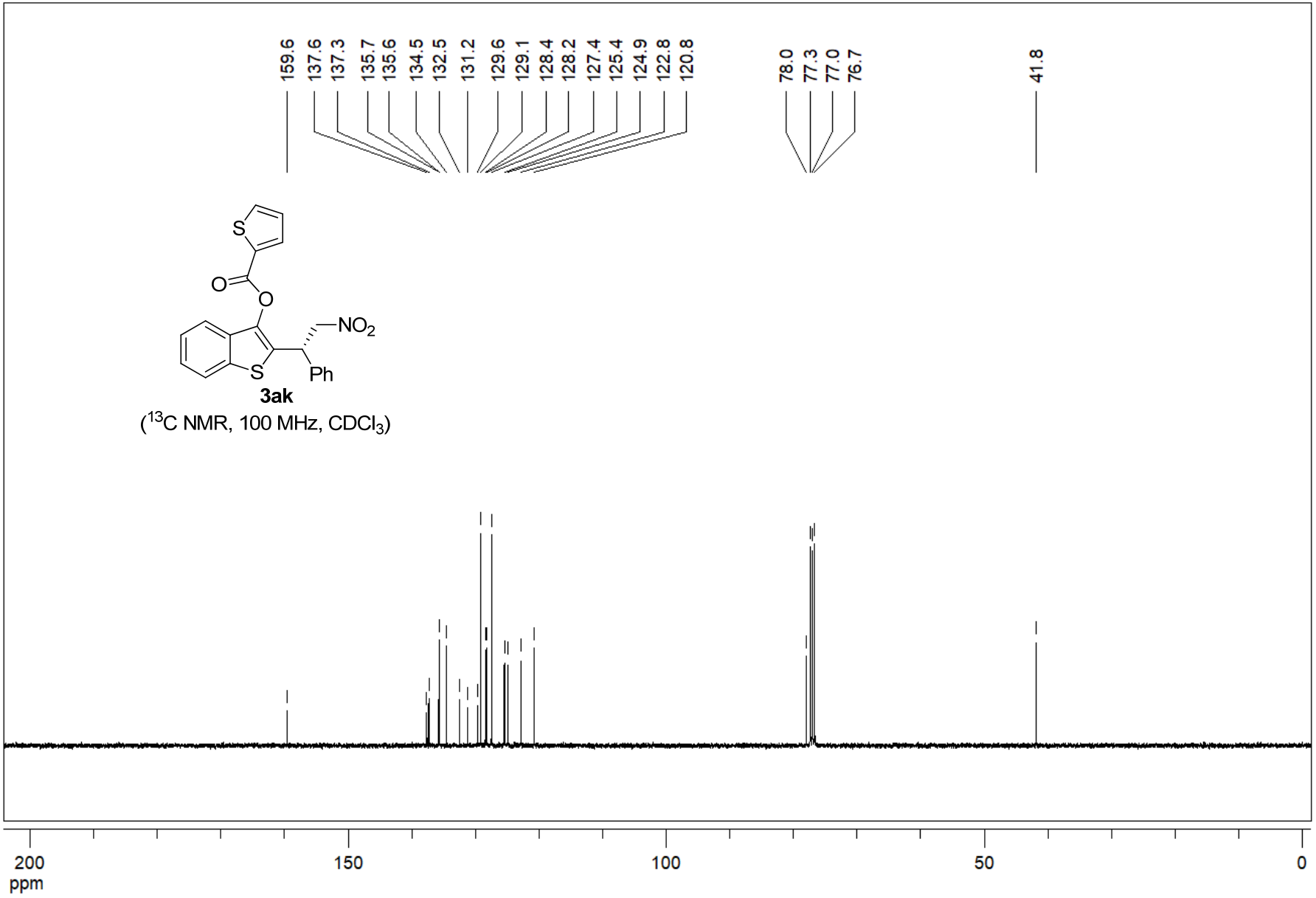
(^{1}H NMR, 400 MHz, $CDCl_3$)

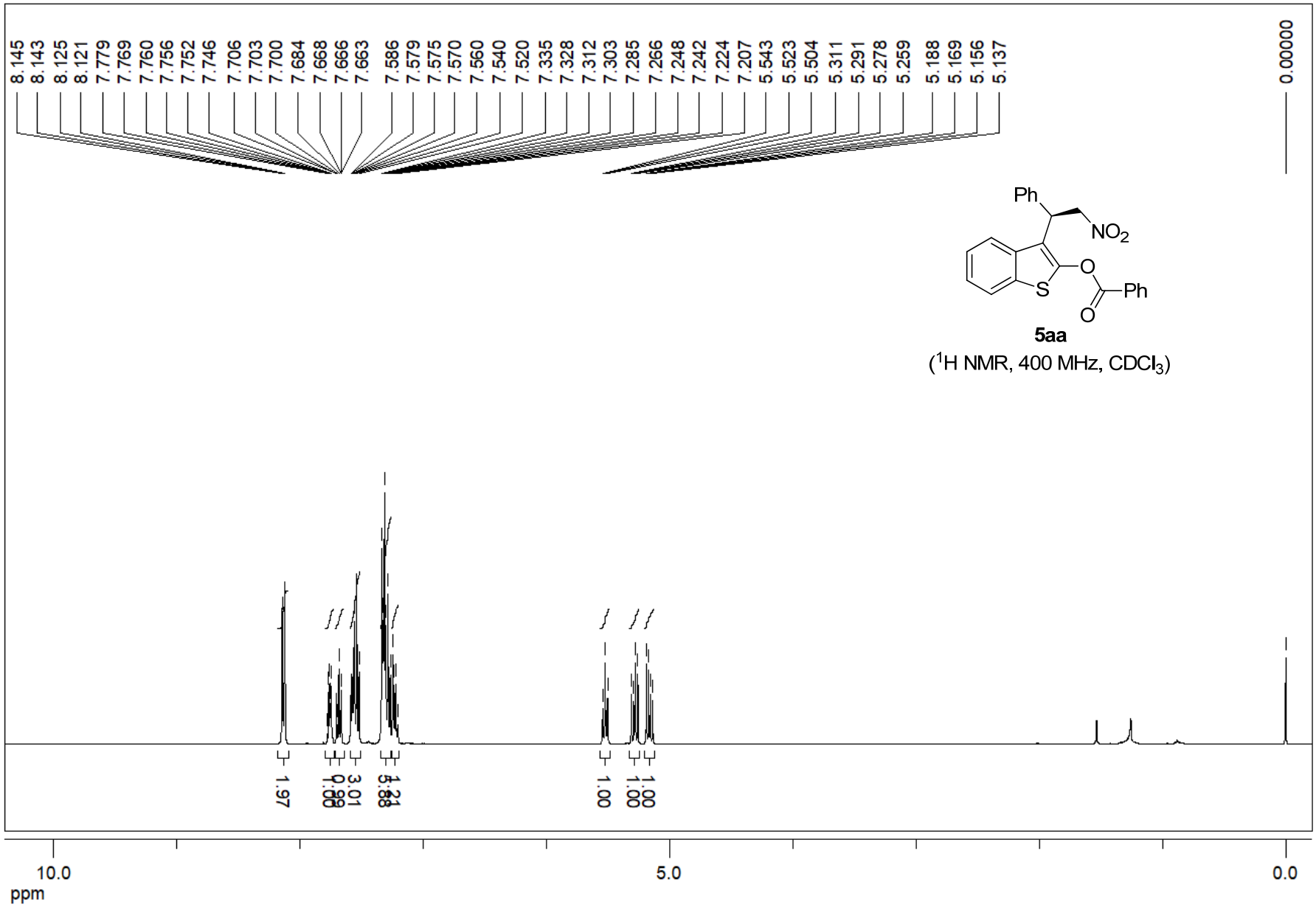


3aj

(^{13}C NMR, 100 MHz, $CDCl_3$)

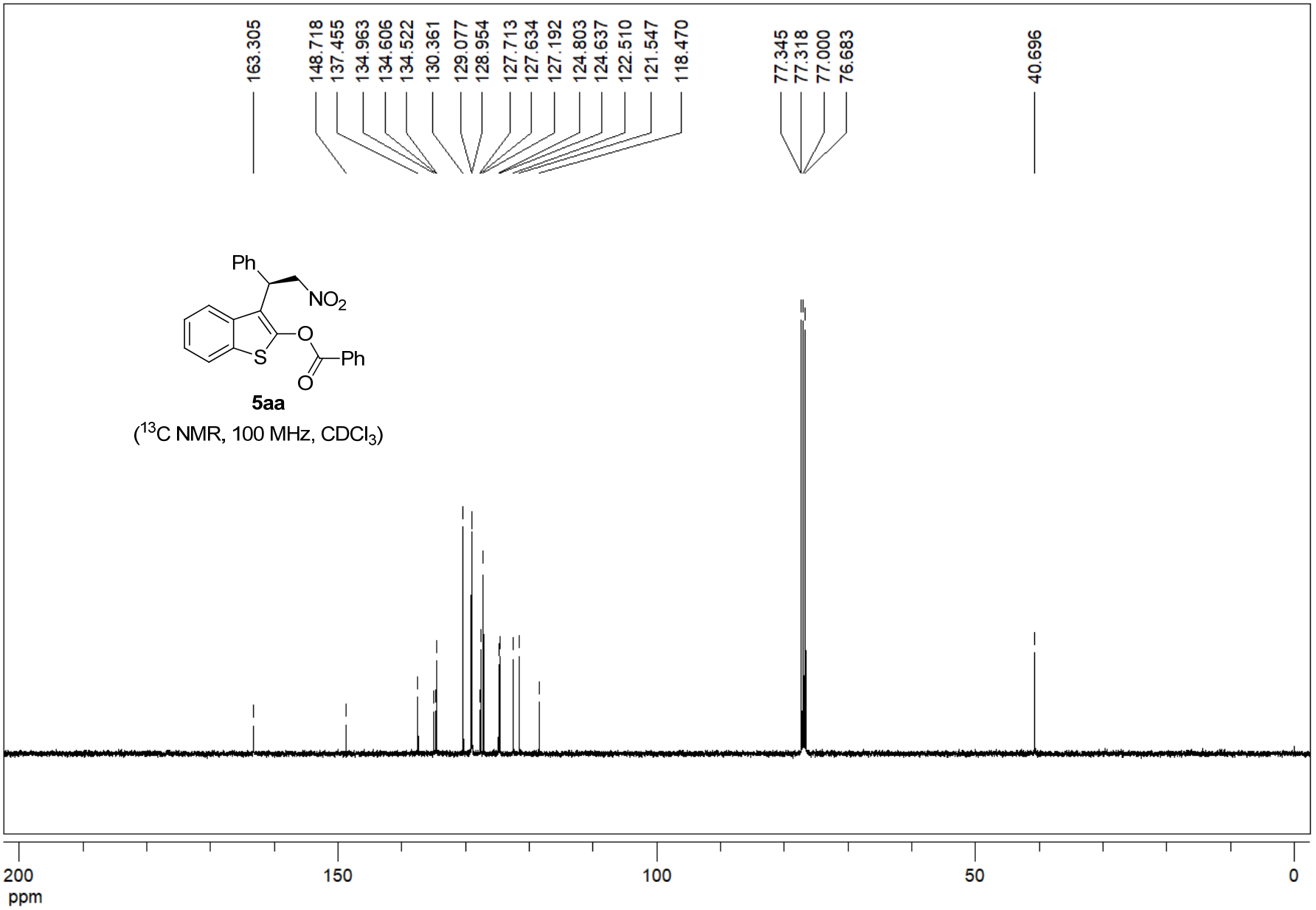

8.078
8.075
8.069
8.065
7.752
7.749
7.740
7.737
7.706
7.702
7.694
7.690
7.685
7.521
7.514
7.510
7.502
7.498
7.365
7.360
7.342
7.340
7.330
7.319
7.299
7.283
7.266
7.249
7.239
7.236
7.227
5.312
5.292
5.272
5.079
5.059
0.00000
0.97
0.99
0.99
1.03
6.92
1.23
1.00
2.00
10.0
5.0
0.0
ppm
S
O
O
NO2
S
Ph
3ak
(1H NMR, 400 MHz, CDCl3)


159.6
137.6
137.3
135.7
135.6
134.5
132.5
131.2
129.6
129.1
128.4
128.2
127.4
125.4
124.9
122.8
120.8
78.0
77.3
77.0
76.7
41.8
S
O
O
NO2
S
Ph
3ak
(13C NMR, 100 MHz, CDCl3)
200
ppm
150
100
50
0



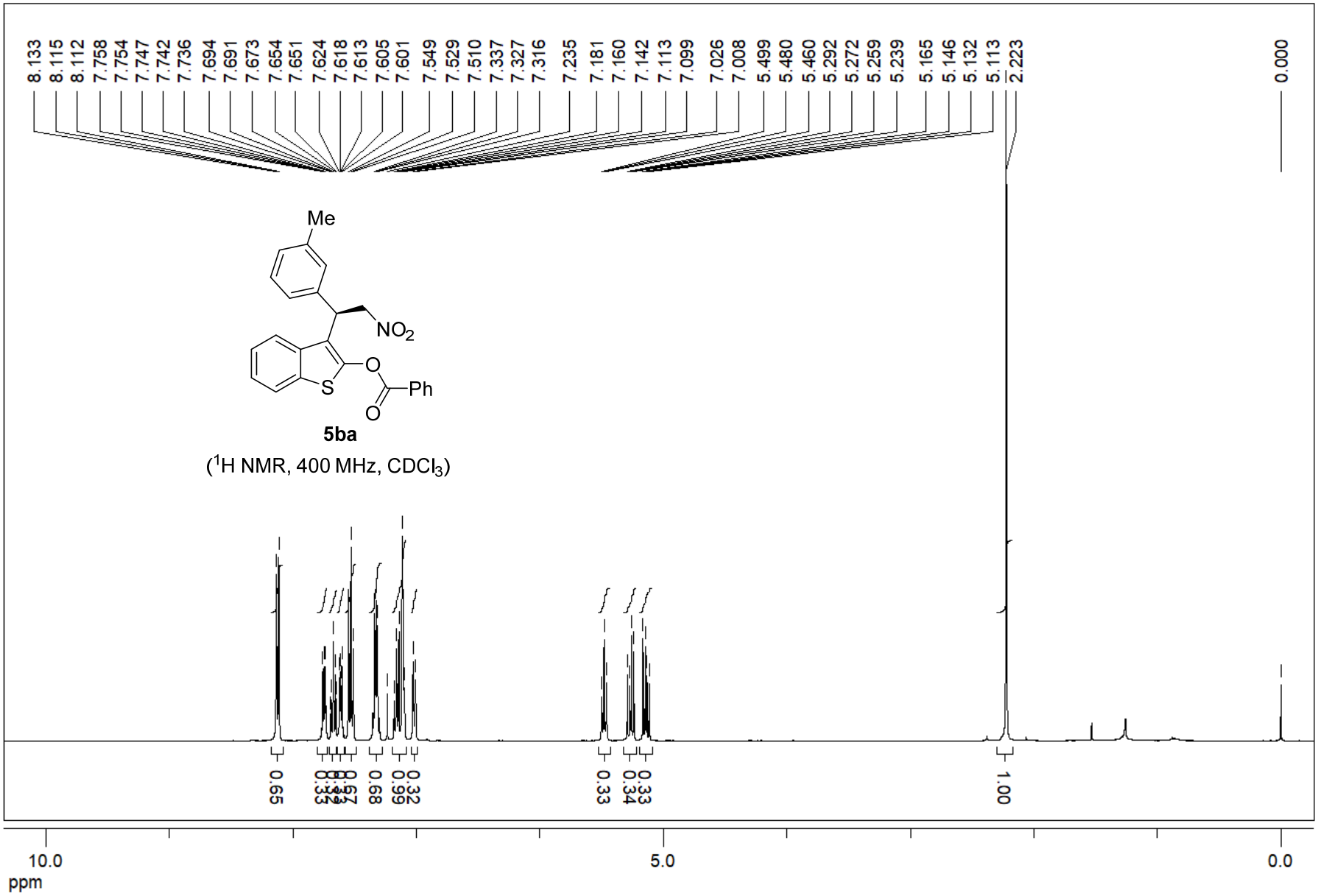
5aa

(^{1}H NMR, 400 MHz, $CDCl_3$)



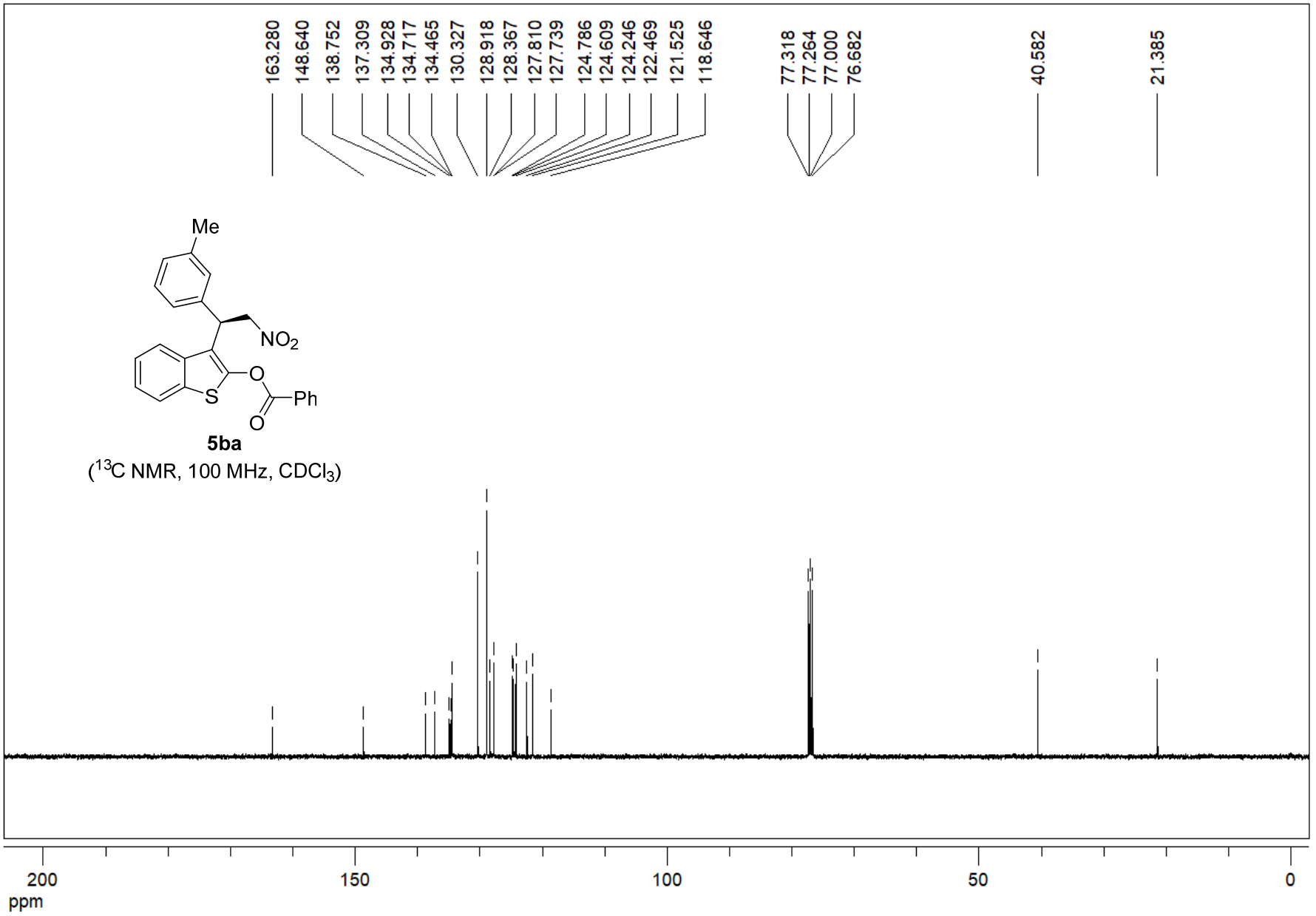
5aa

(^{13}C NMR, 100 MHz, $CDCl_3$)



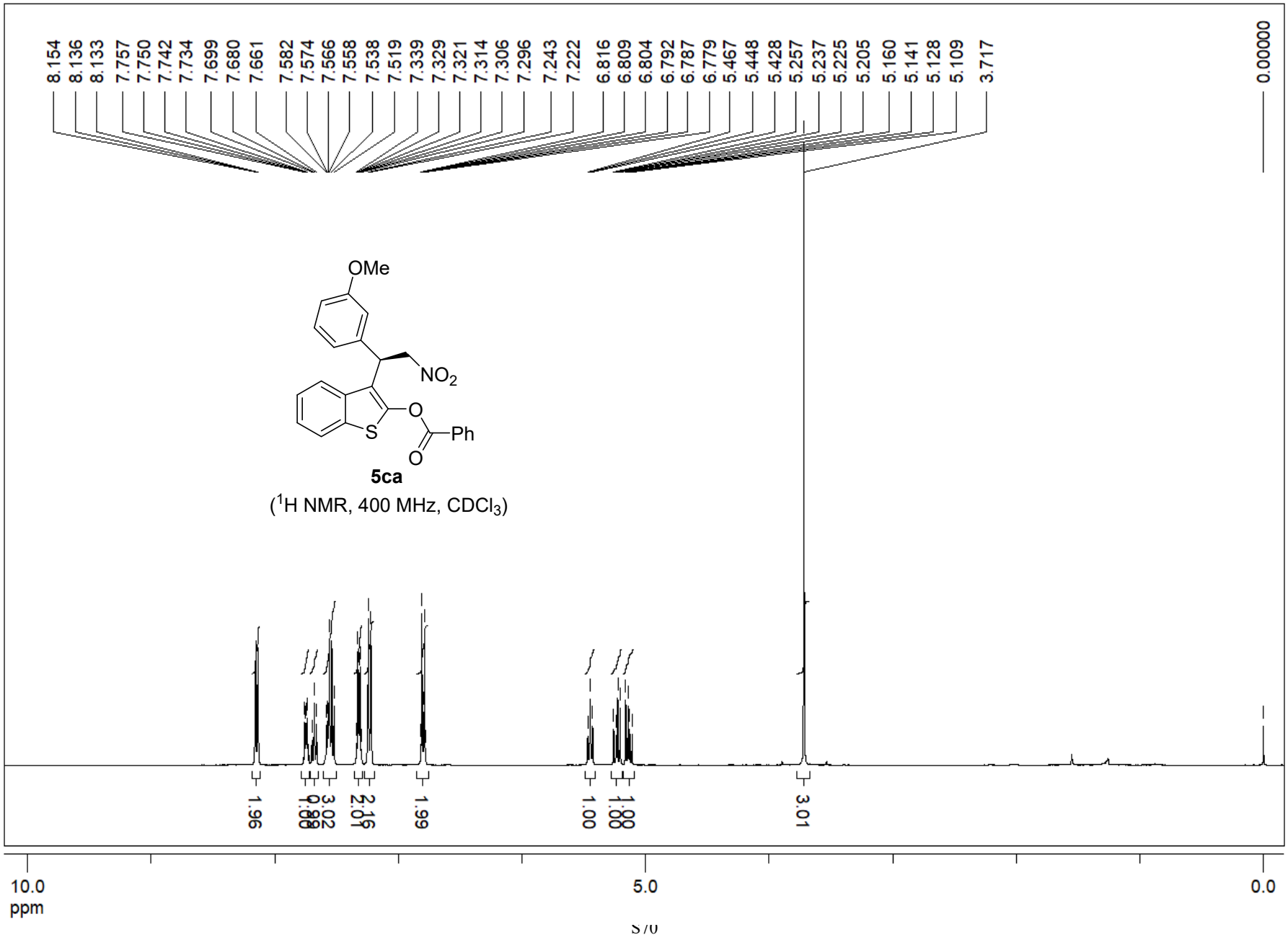
5ba

(^{1}H NMR, 400 MHz, $CDCl_3$)



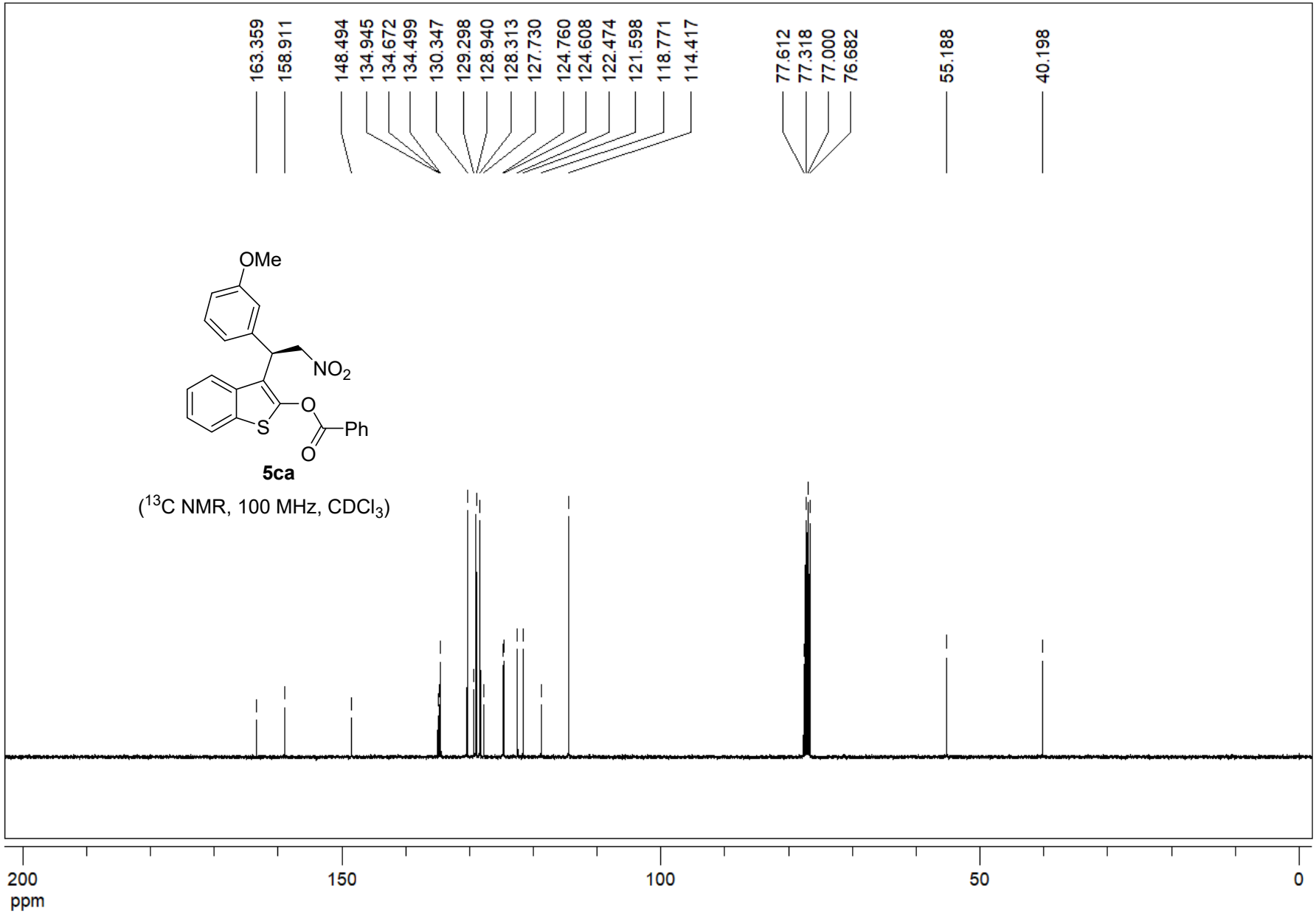
5ba

(^{13}C NMR, 100 MHz, $CDCl_3$)



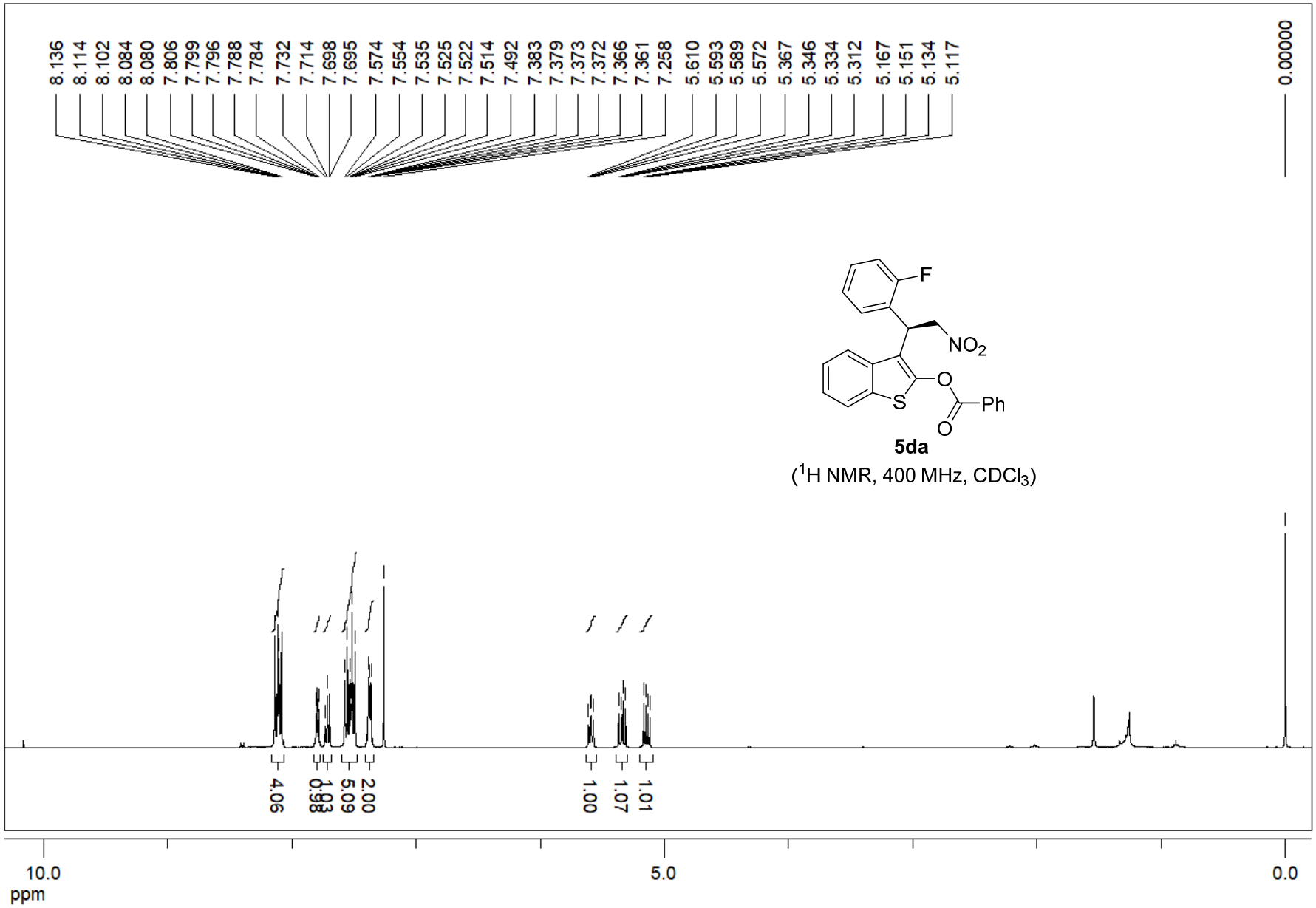
5ca

(^{1}H NMR, 400 MHz, $CDCl_3$)



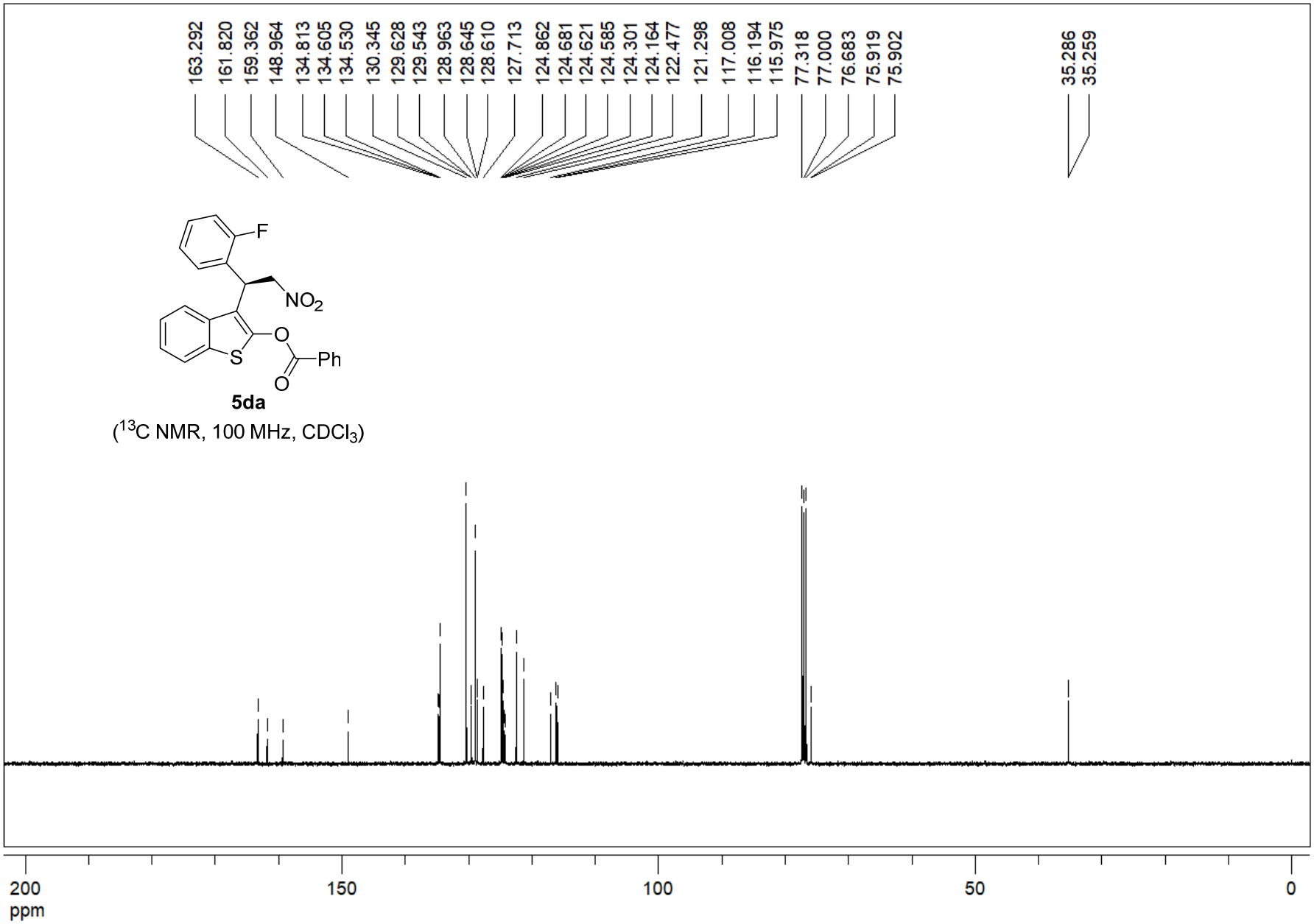
5ca

(^{13}C NMR, 100 MHz, $CDCl_3$)



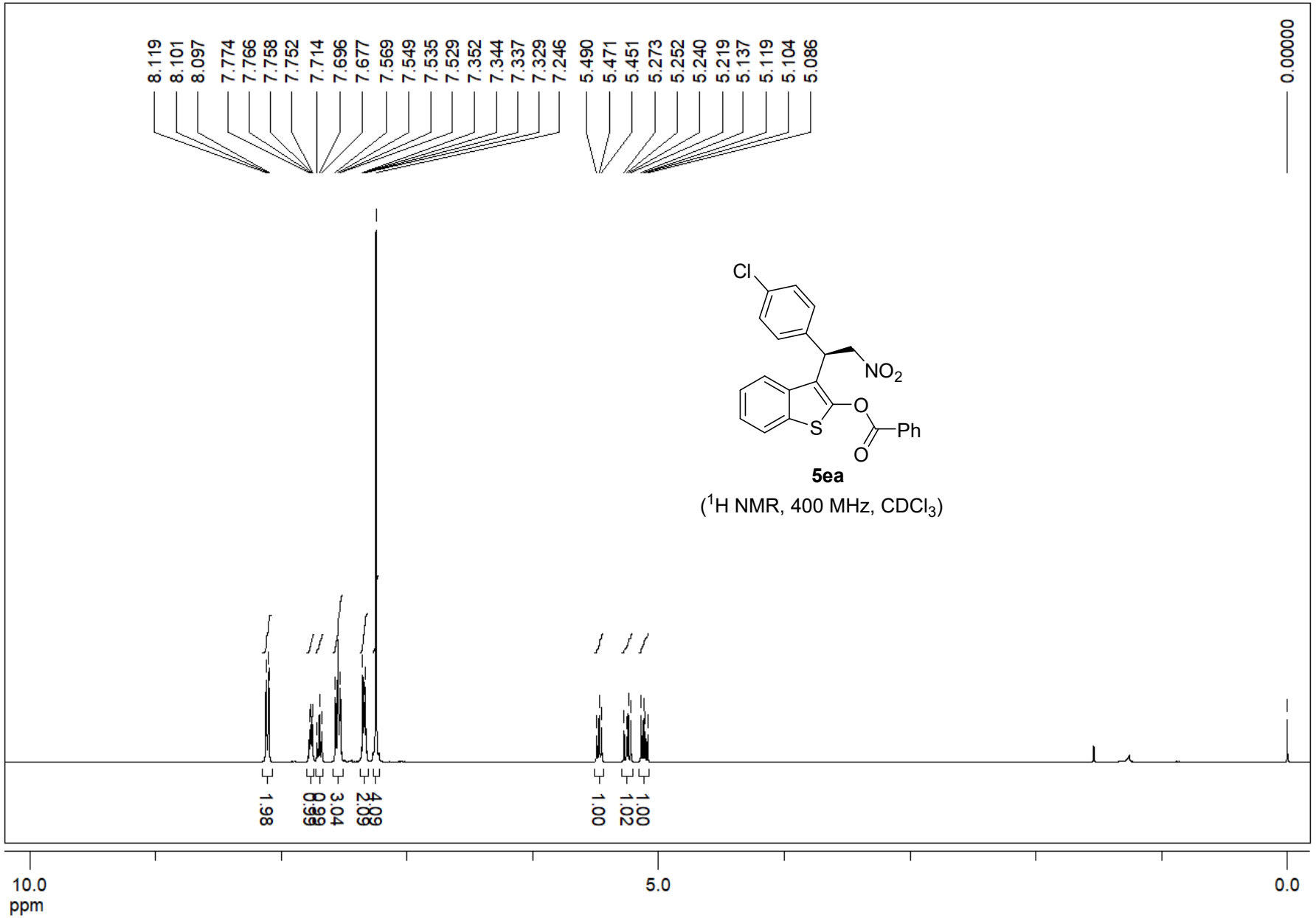
5da

(^{1}H NMR, 400 MHz, $CDCl_3$)



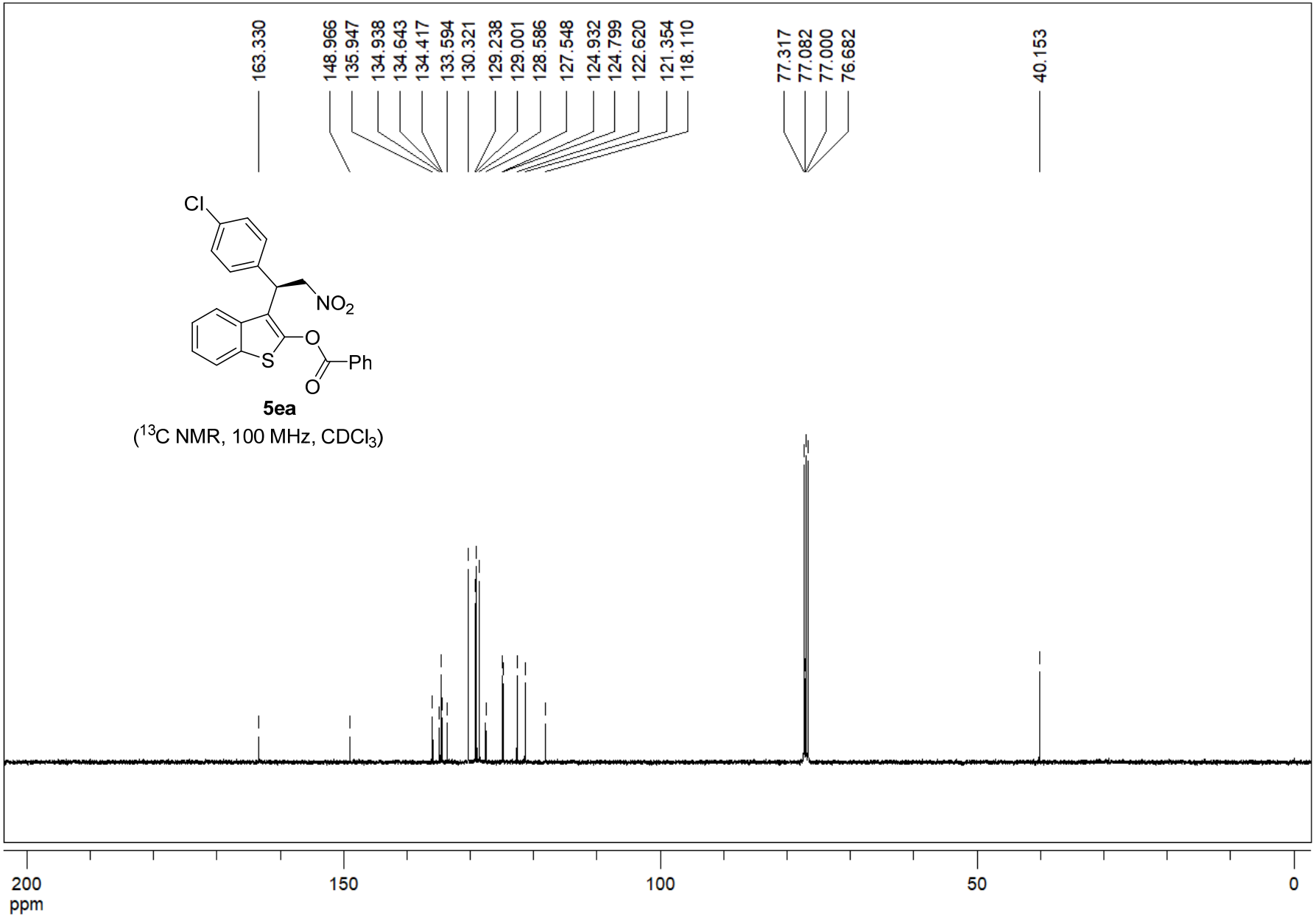
5da

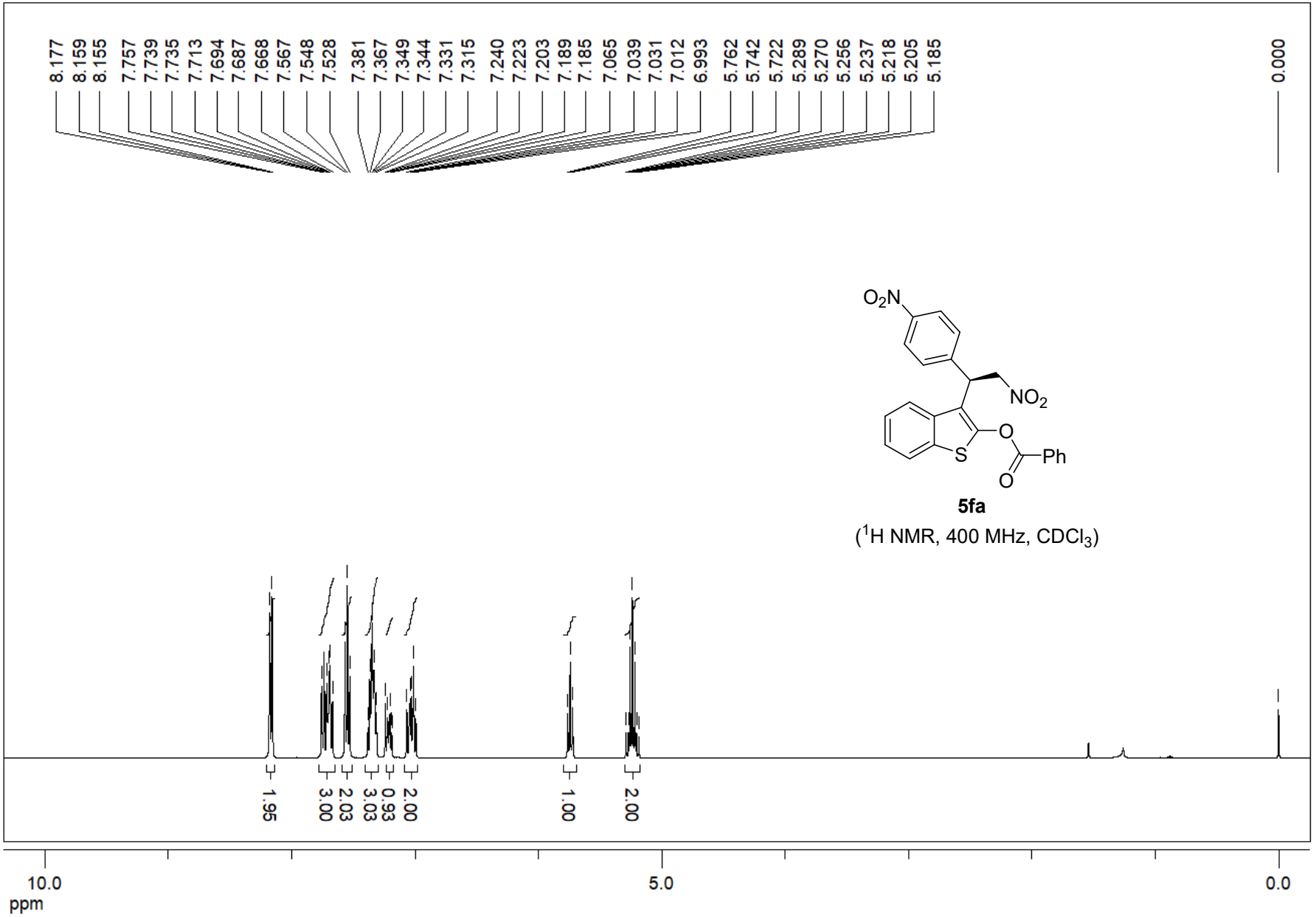
(^{13}C NMR, 100 MHz, $CDCl_3$)



5ea

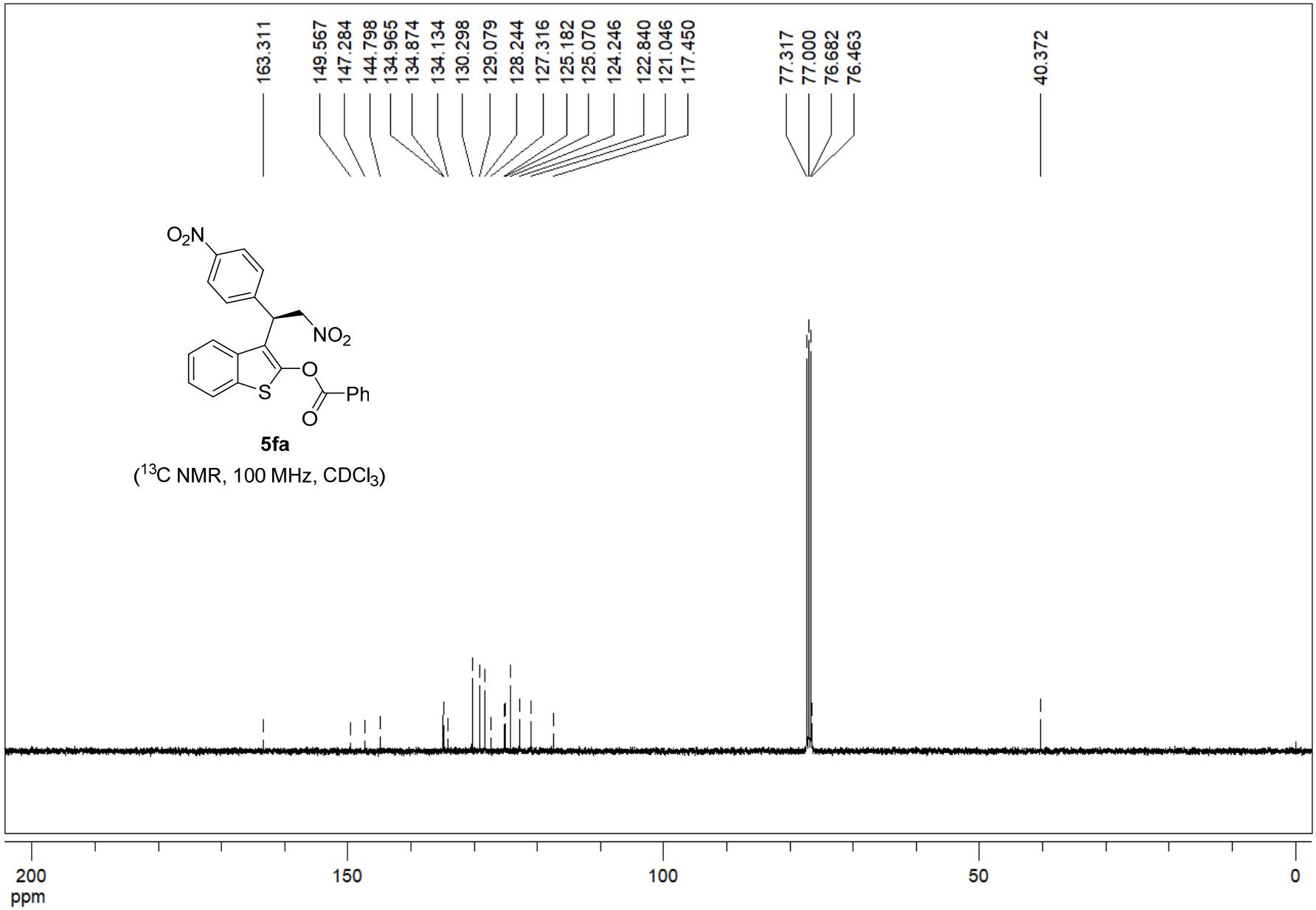
(^{1}H NMR, 400 MHz, $CDCl_3$)


163.330
148.966
135.947
134.938
134.643
134.417
133.594
130.321
129.238
129.001
128.586
127.548
124.932
124.799
122.620
121.354
118.110
77.317
77.082
77.000
76.682
40.153
Cl
NO2
O
S
O
Ph
5ea
(13C NMR, 100 MHz, CDCl3)
200
150
100
50
0
ppm



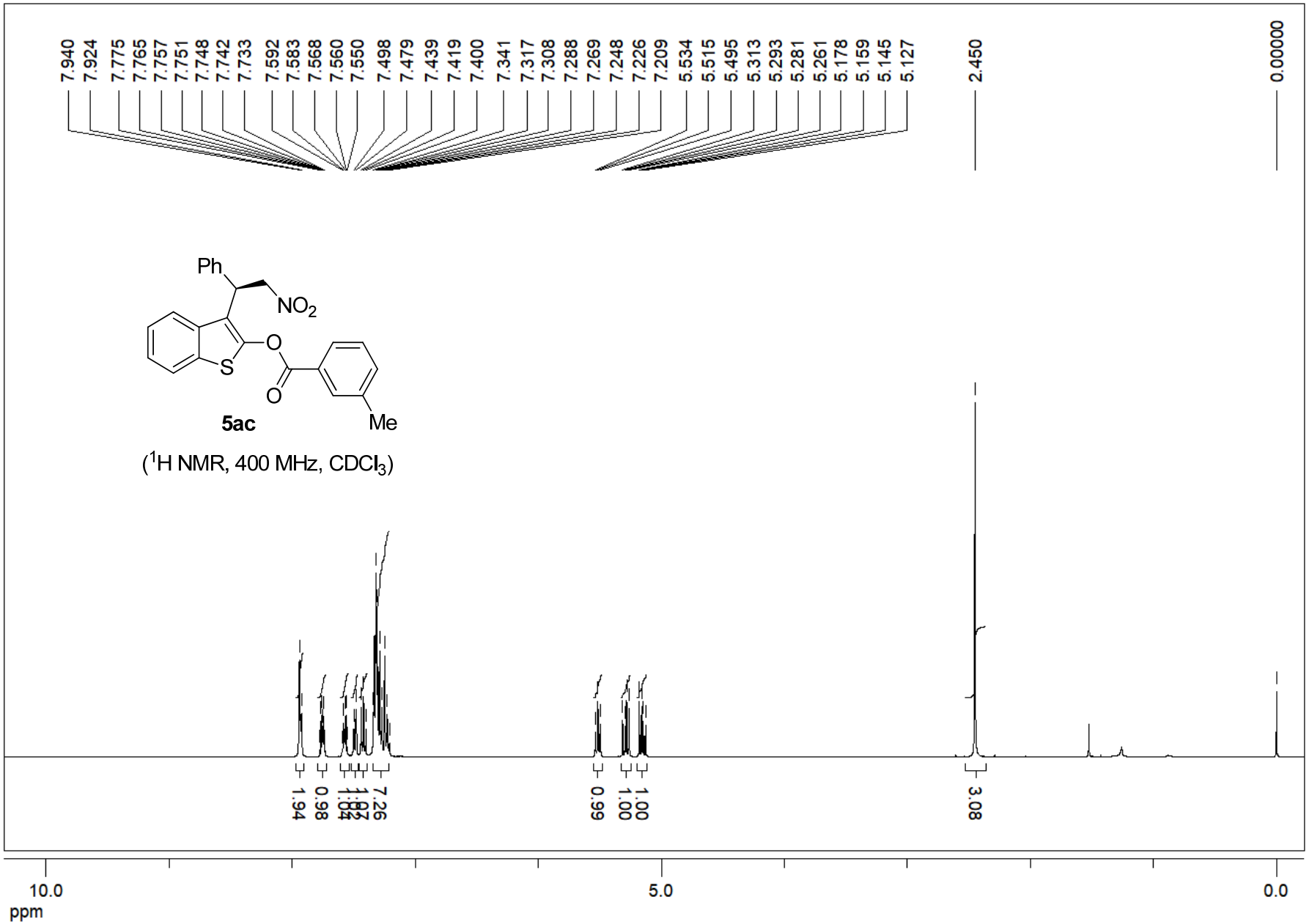
5fa

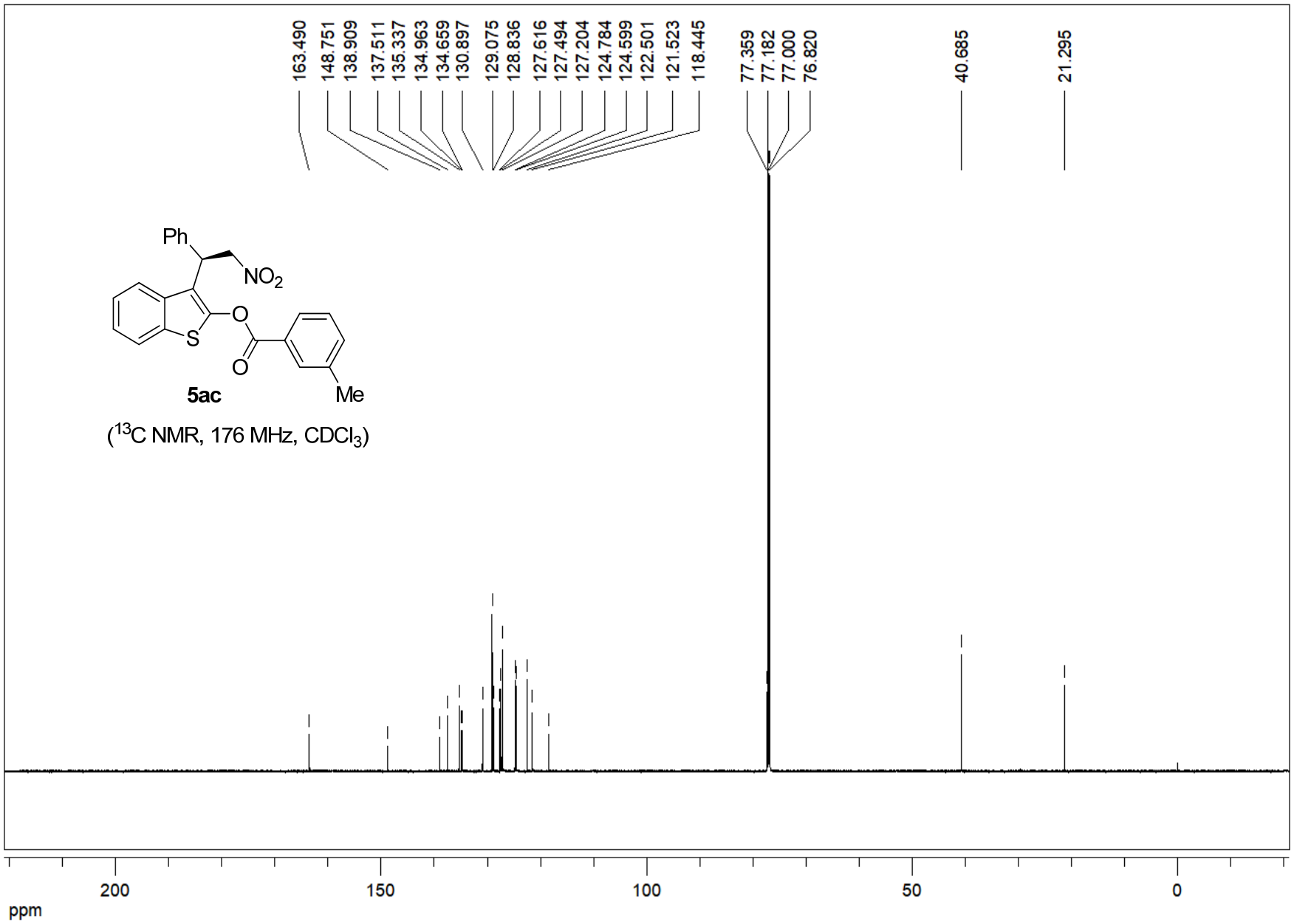
(^{1}H NMR, 400 MHz, $CDCl_3$)

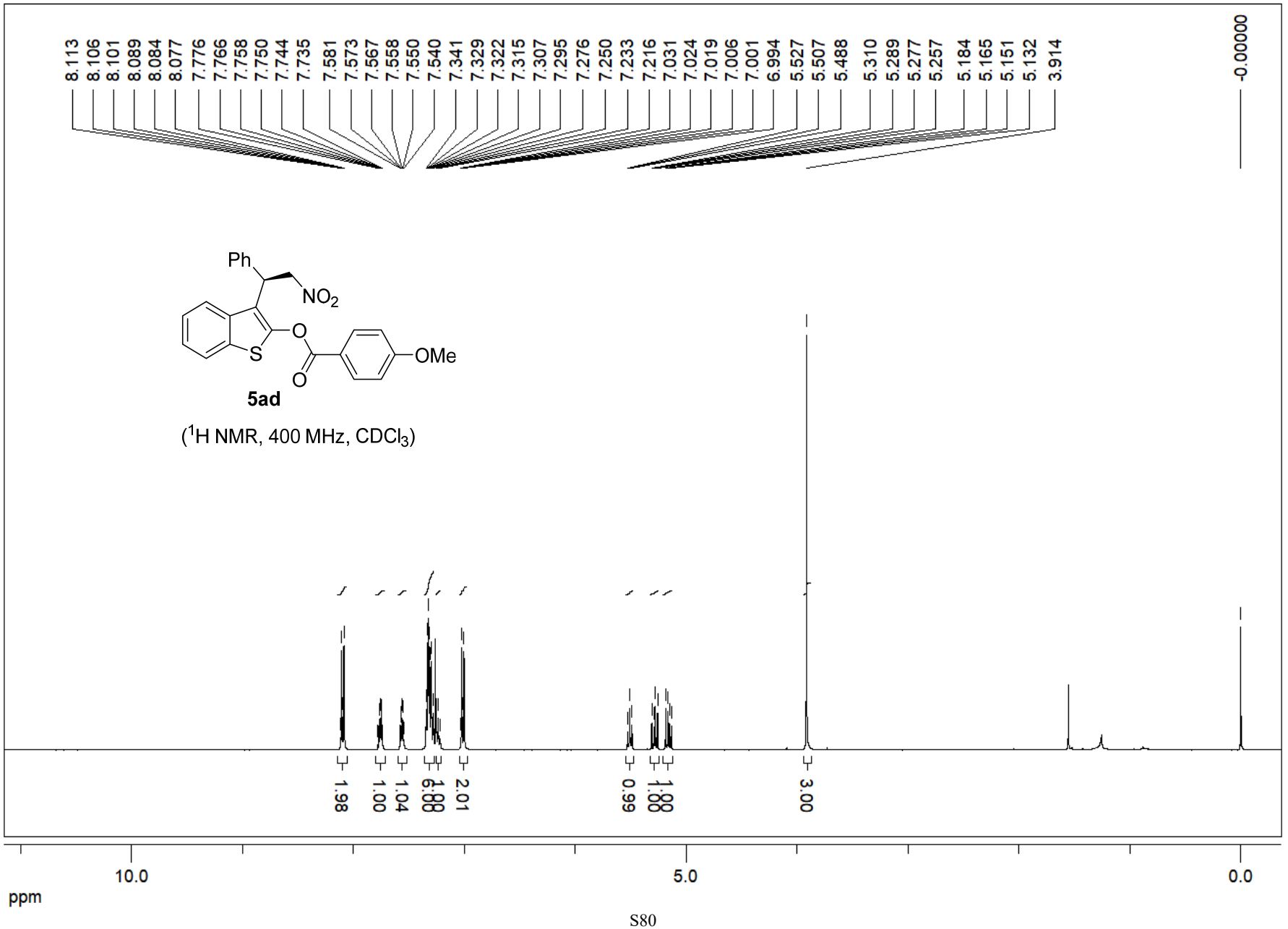


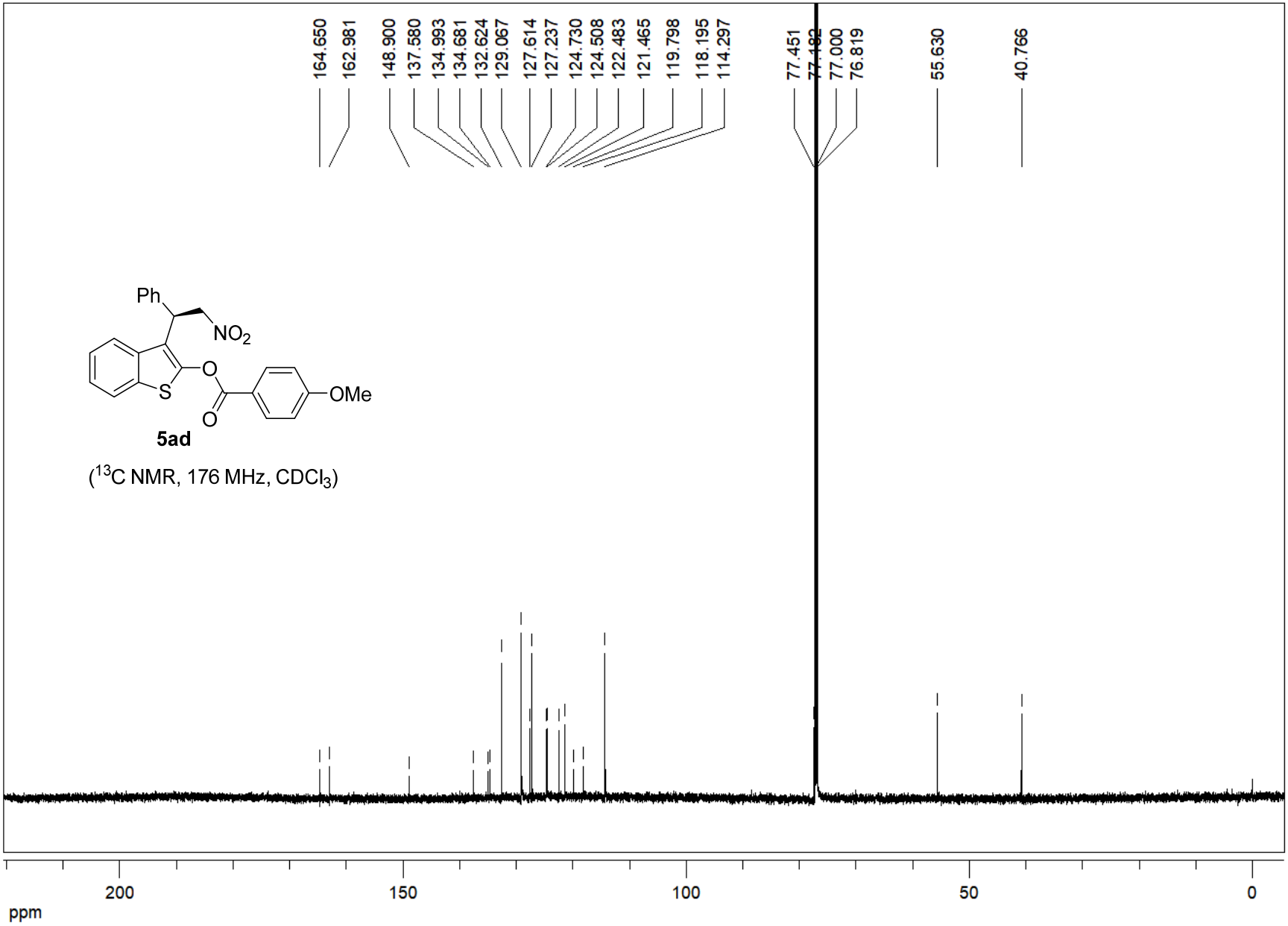
5fa

(^{13}C NMR, 100 MHz, $CDCl_3$)


7.940
7.924
7.775
7.765
7.757
7.751
7.748
7.742
7.733
7.592
7.583
7.568
7.560
7.550
7.498
7.479
7.439
7.419
7.400
7.341
7.317
7.308
7.288
7.269
7.248
7.226
7.209
5.534
5.515
5.495
5.313
5.293
5.281
5.261
5.178
5.159
5.145
5.127
2.450
0.00000
Ph
NO2
O
S
O
5ac
Me
(1H NMR, 400 MHz, CDCl3)
1.94
0.98
7.26
0.99
1.00
1.00
3.08
10.0
5.0
0.0
ppm

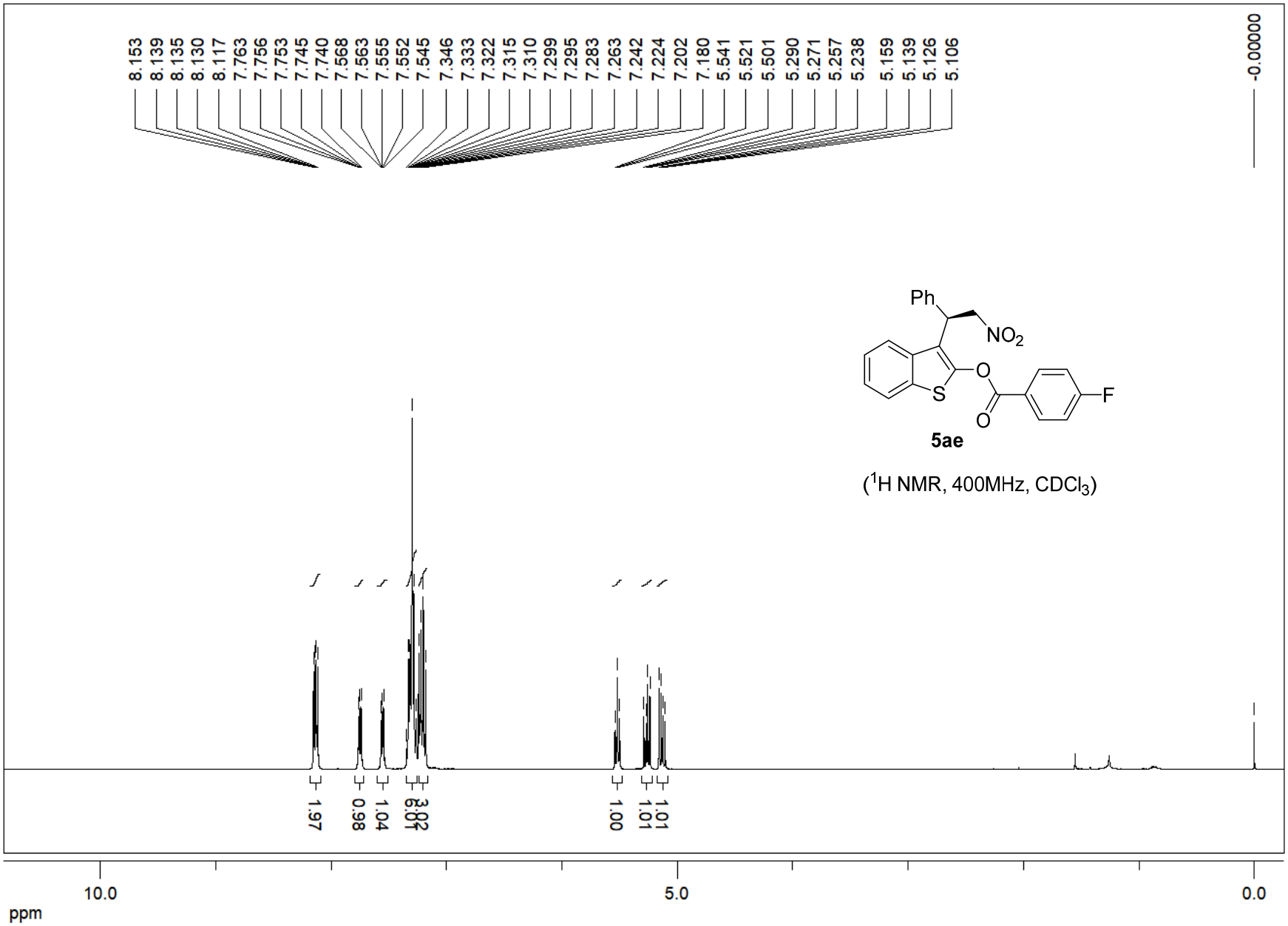

163.490
148.751
138.909
137.511
135.337
134.963
134.659
130.897
129.075
128.836
127.616
127.494
127.204
124.784
124.599
122.501
121.523
118.445
77.359
77.182
77.000
76.820
40.685
21.295
Ph
NO2
O
S
O
Me
5ac
(13C NMR, 176 MHz, CDCl3)
200
150
100
50
0
ppm

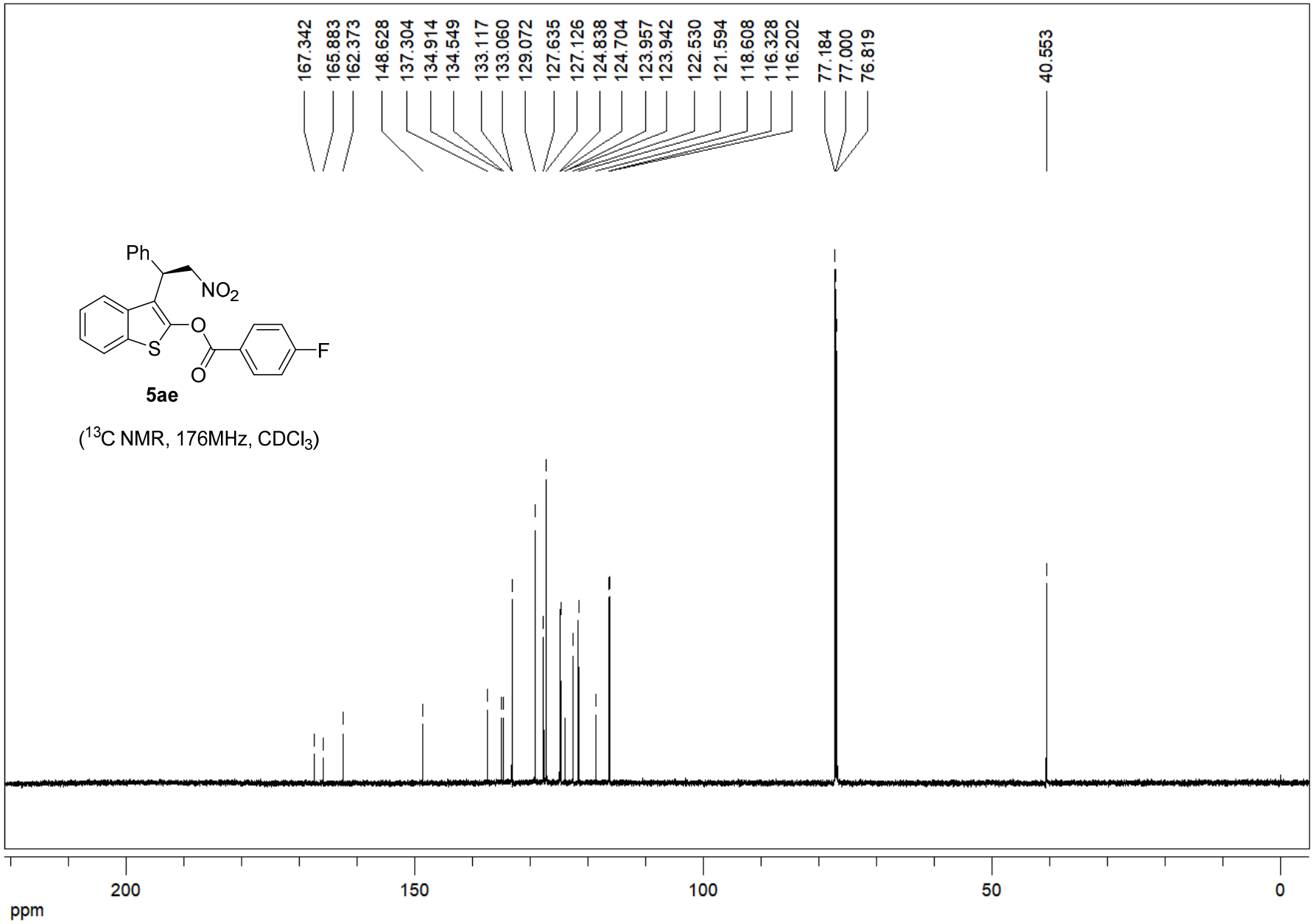

8.113
8.106
8.101
8.089
8.084
8.077
7.776
7.766
7.758
7.750
7.744
7.735
7.581
7.573
7.567
7.558
7.550
7.540
7.341
7.329
7.322
7.315
7.307
7.295
7.276
7.250
7.233
7.216
7.031
7.024
7.019
7.006
7.001
6.994
5.527
5.507
5.488
5.310
5.289
5.277
5.257
5.184
5.165
5.151
5.132
3.914
-0.00000
Ph
NO2
O
S
O
OMe
5ad
(1H NMR, 400 MHz, CDCl3)
1.98
1.00
1.04
3.88
2.01
0.99
1.88
3.00
10.0
5.0
0.0
ppm

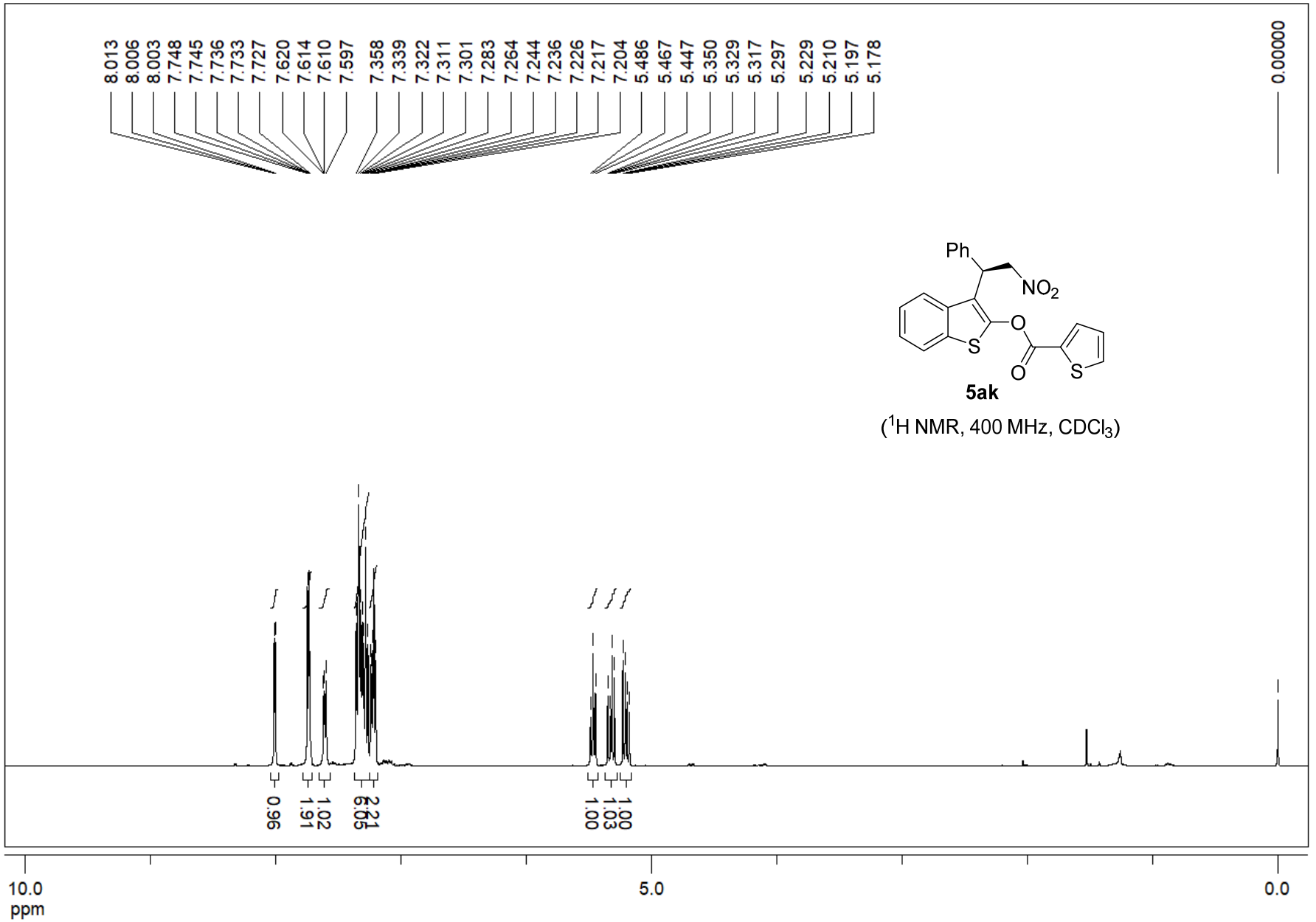


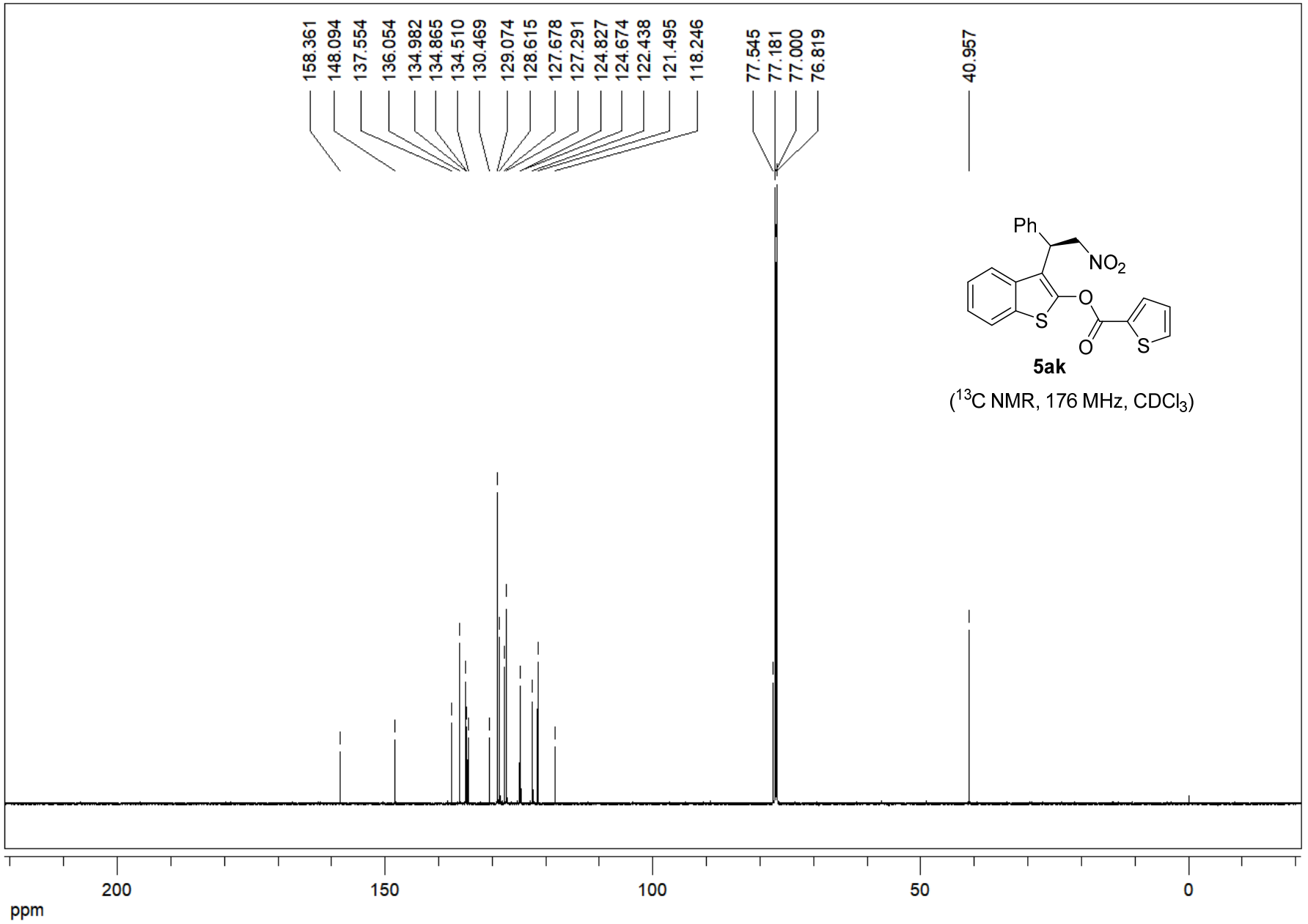
5ad

(^{13}C NMR, 176 MHz, $CDCl_3$)


8.153
8.139
8.135
8.130
8.117
7.763
7.756
7.753
7.745
7.740
7.568
7.563
7.555
7.552
7.545
7.346
7.333
7.322
7.315
7.310
7.299
7.295
7.283
7.263
7.242
7.224
7.202
7.180
5.541
5.521
5.501
5.290
5.271
5.257
5.238
5.159
5.139
5.126
5.106
-0.00000
Ph
NO2
O
S
O
F
5ae
(1H NMR, 400MHz, CDCl3)
1.97
0.98
1.04
6.84
3.02
1.00
1.01
1.01
10.0
5.0
0.0
ppm

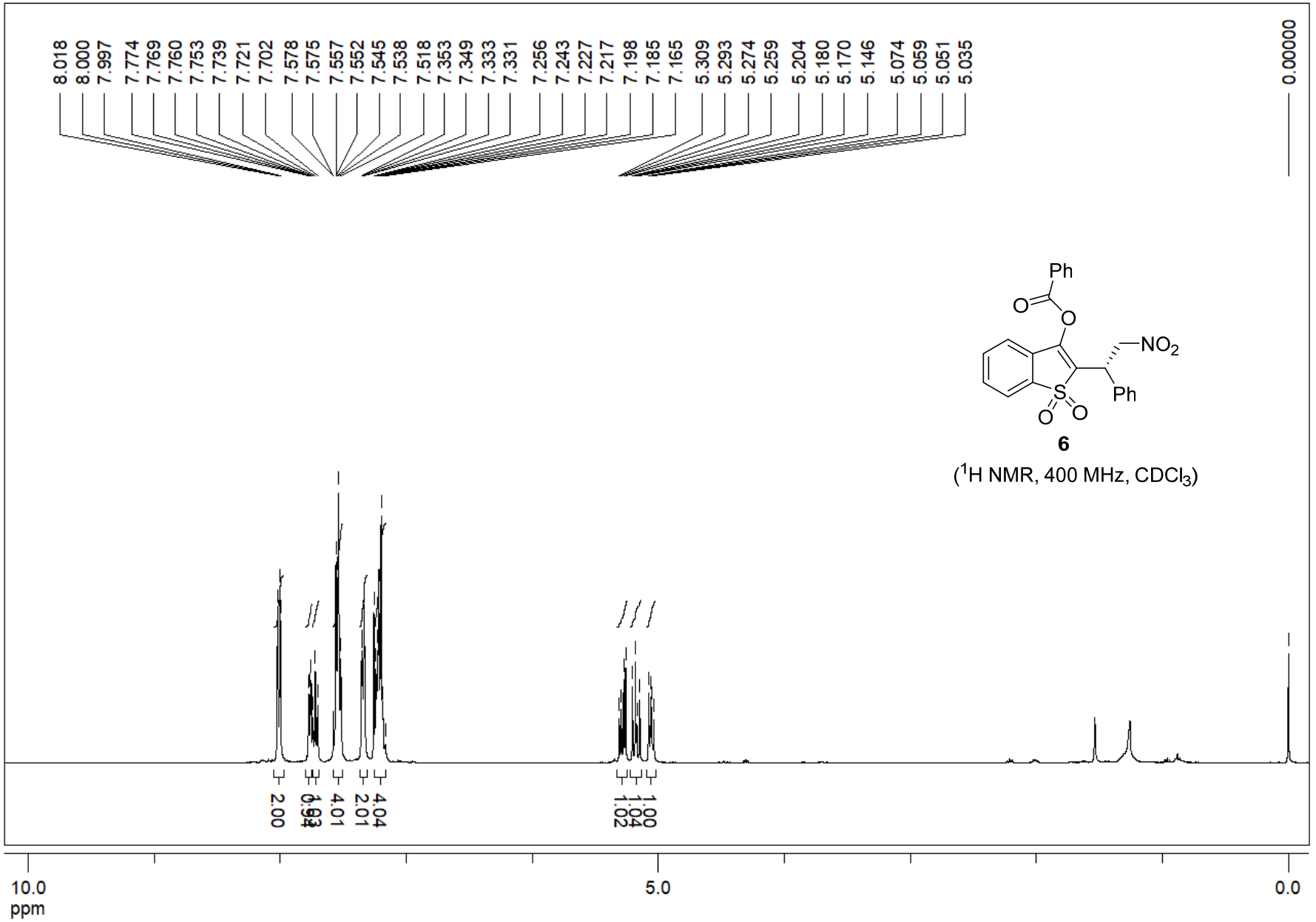

167.342
165.883
162.373
148.628
137.304
134.914
134.549
133.117
133.060
129.072
127.635
127.126
124.838
124.704
123.957
123.942
122.530
121.594
118.608
116.328
116.202
77.184
77.000
76.819
40.553
Ph
NO2
O
S
O
F
5ae
(13C NMR, 176MHz, CDCl3)
200
150
100
50
0
ppm


8.013
8.006
8.003
7.748
7.745
7.736
7.733
7.727
7.620
7.614
7.610
7.597
7.358
7.339
7.322
7.311
7.301
7.283
7.264
7.244
7.236
7.226
7.217
7.204
5.486
5.467
5.447
5.350
5.329
5.317
5.297
5.229
5.210
5.197
5.178
0.00000
Ph
NO2
O
S
O
S
5ak
(1H NMR, 400 MHz, CDCl3)
0.96
1.91
1.02
6.05
2.21
1.00
1.03
1.00
10.0
ppm
5.0
0.0



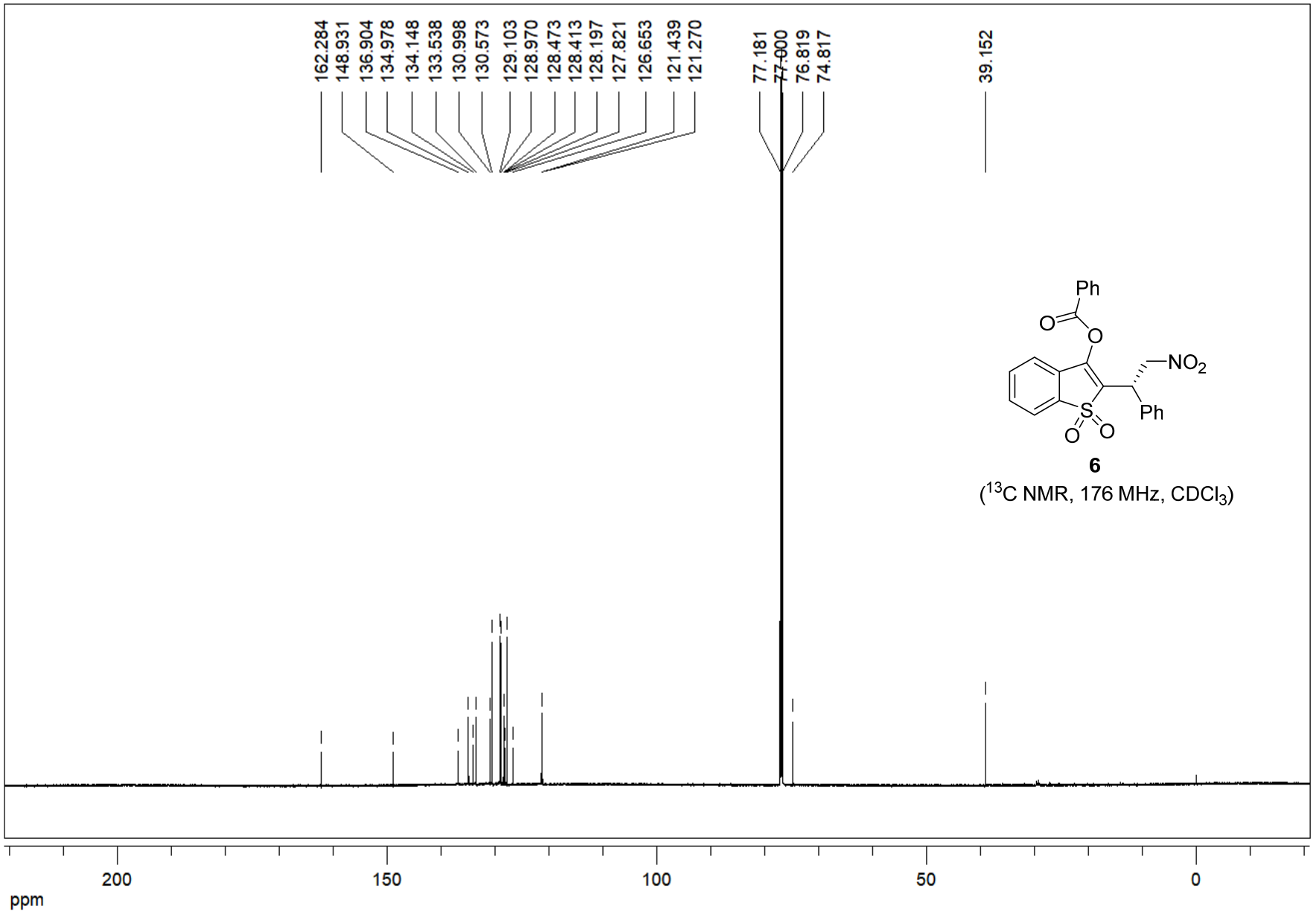
5ak

(^{13}C NMR, 176 MHz, $CDCl_3$)



6

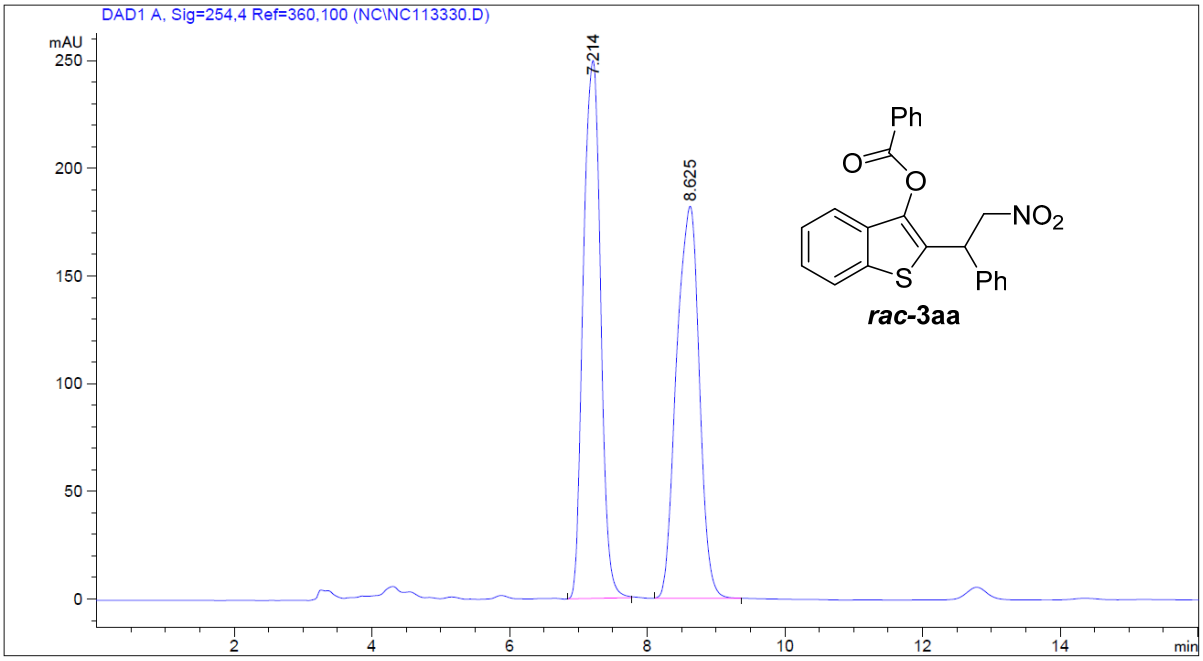
(^{1}H NMR, 400 MHz, $CDCl_3$)



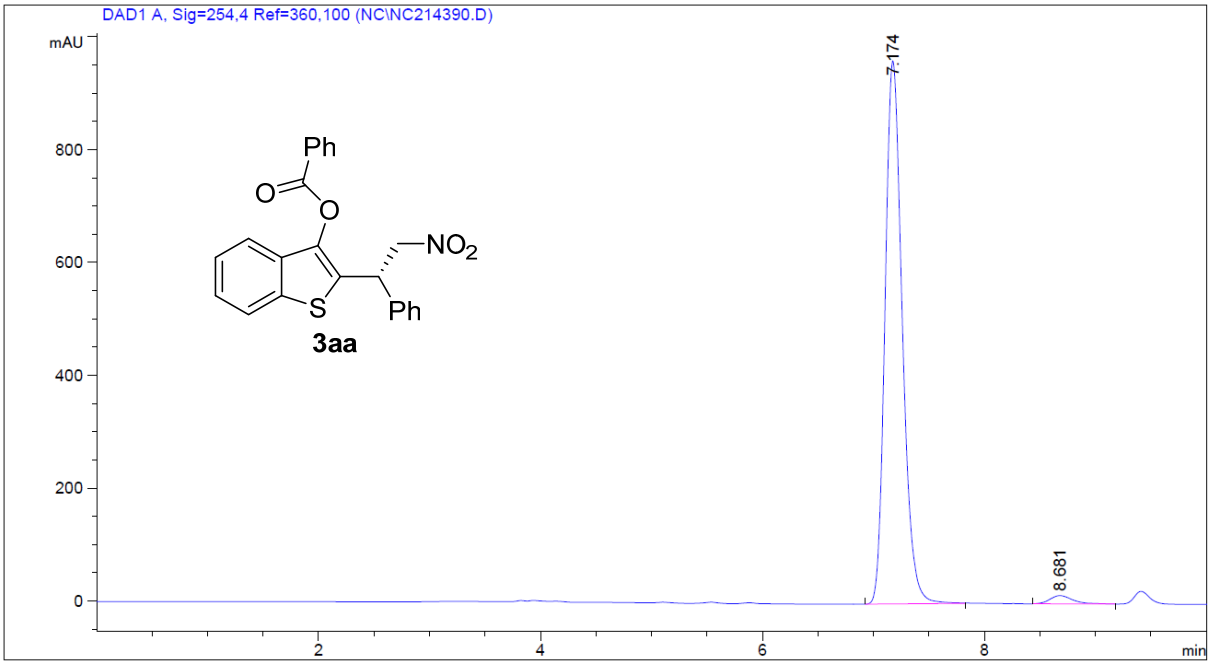
6

(^{13}C NMR, 176 MHz, $CDCl_3$)

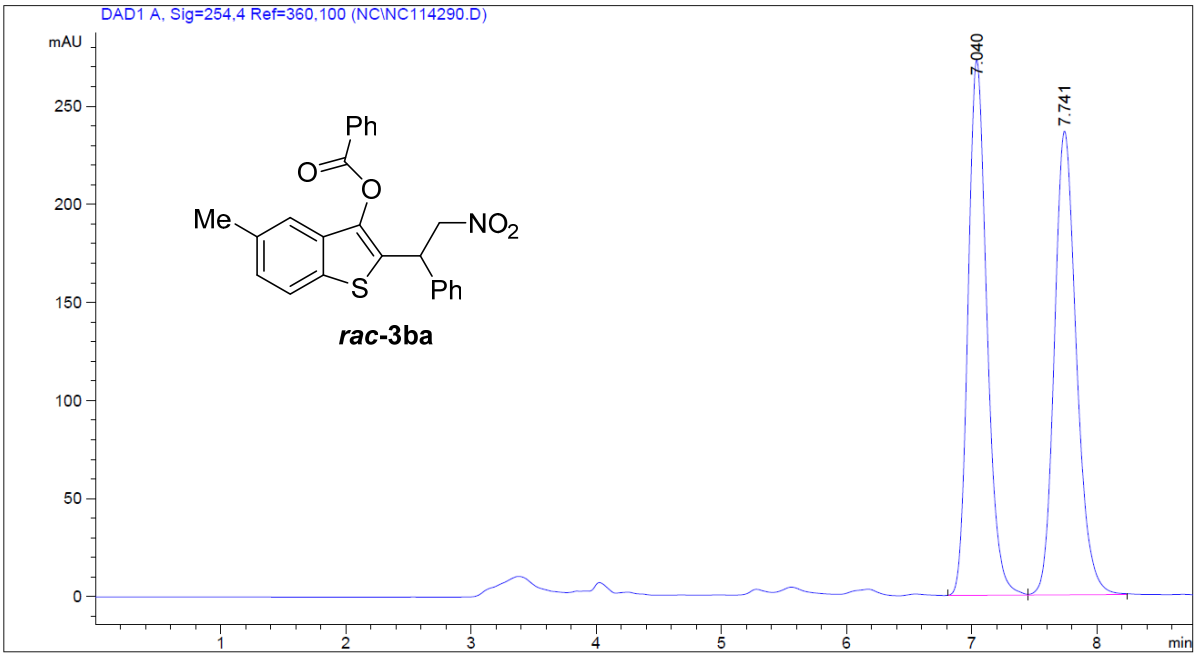
7. Copies of HPLC chromatograms of new products



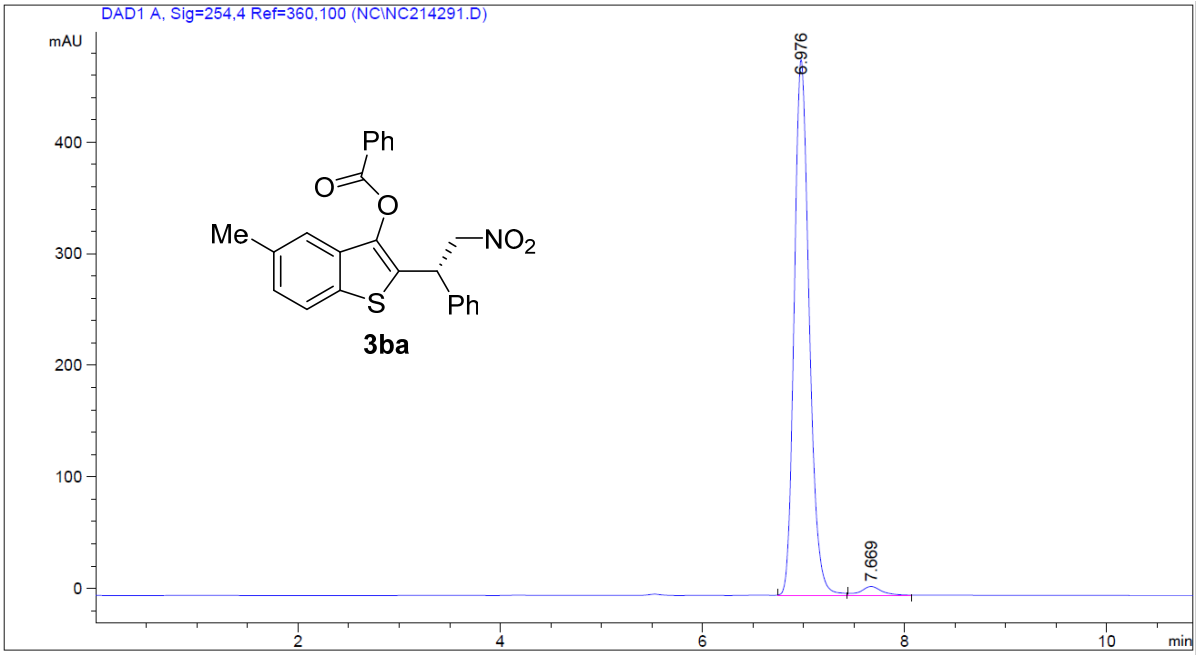
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.214	BB	0.2860	4367.04932	249.77336	51.0444
2	8.625	BB	0.3785	4188.34473	182.00984	48.9556



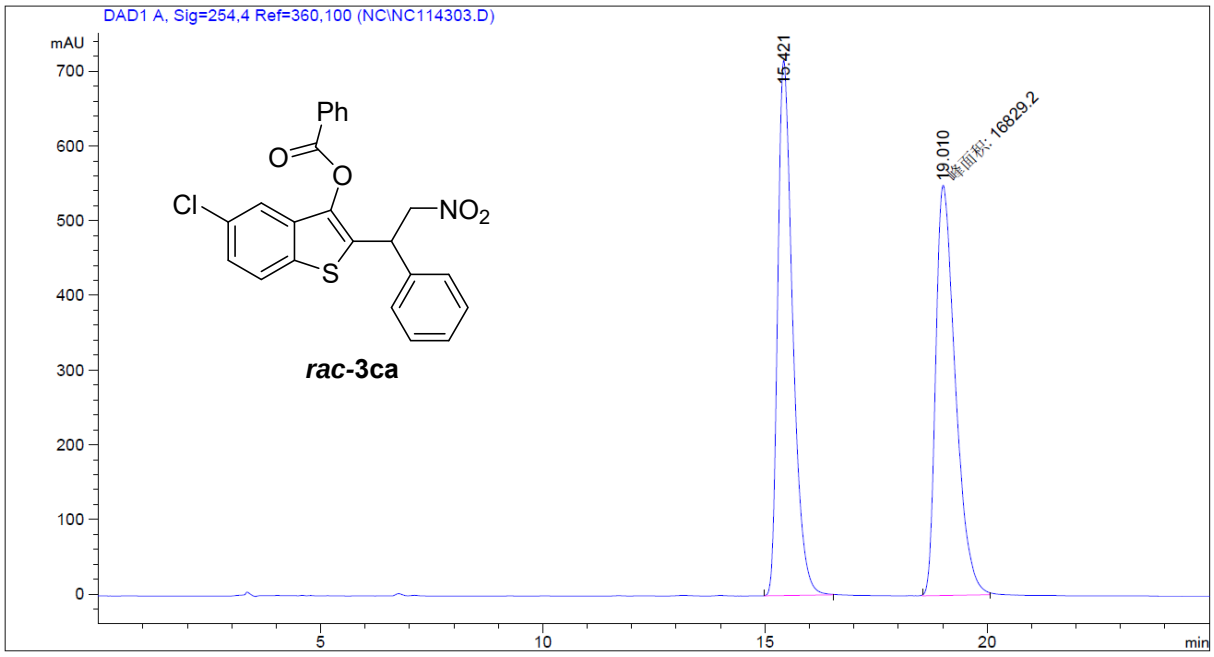
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.174	BB	0.1654	1.03468e4	962.86420	98.0134
2	8.681	BB	0.2181	209.71652	14.55237	1.9866



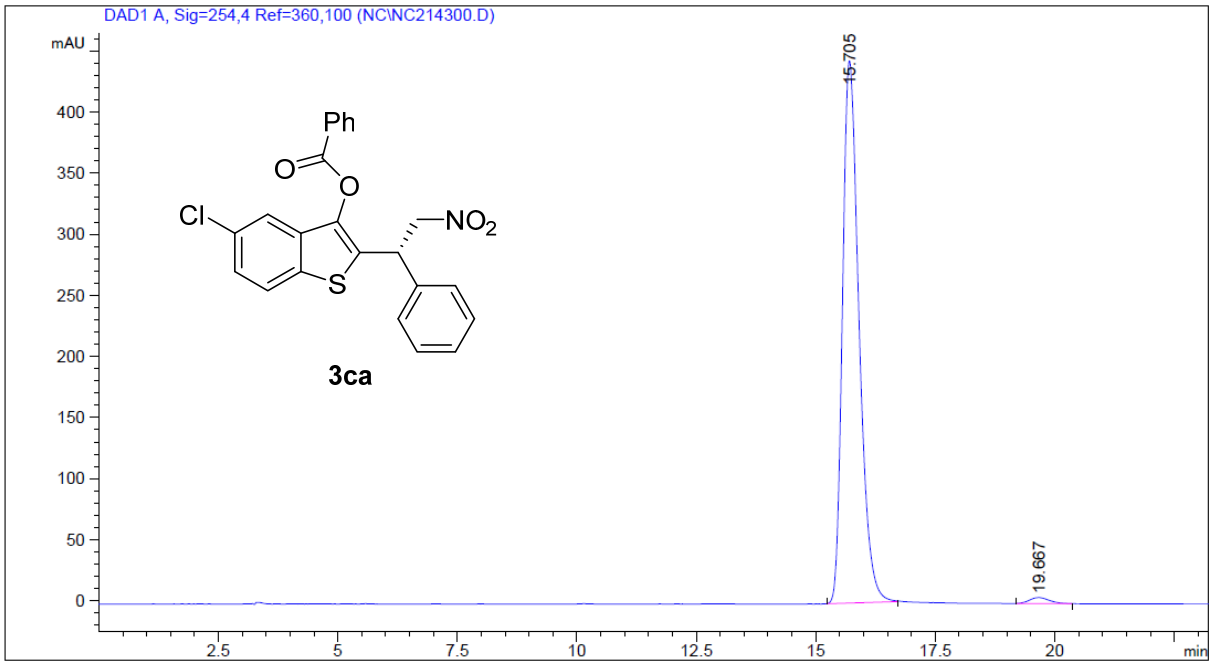
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.040	BV	0.1597	2848.92212	273.09830	49.6155
2	7.741	VB	0.1867	2893.08374	236.46387	50.3845



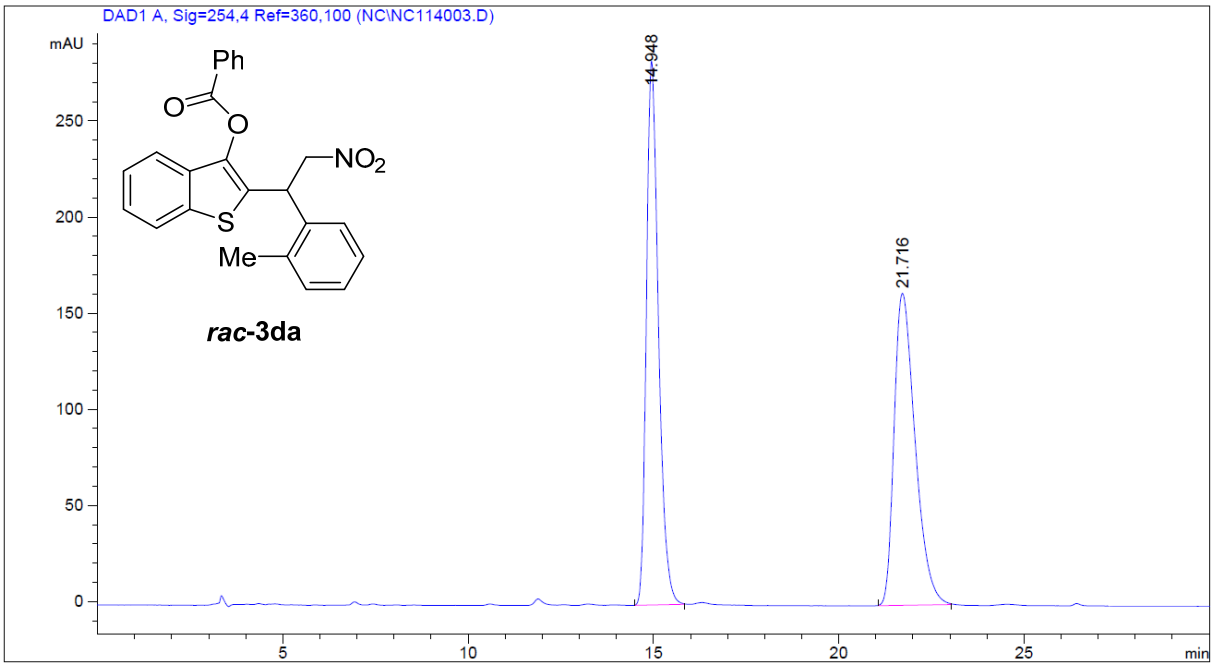
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.976	BB	0.1584	4955.16650	480.35056	97.8154
2	7.669	BB	0.2053	110.66930	7.81213	2.1846



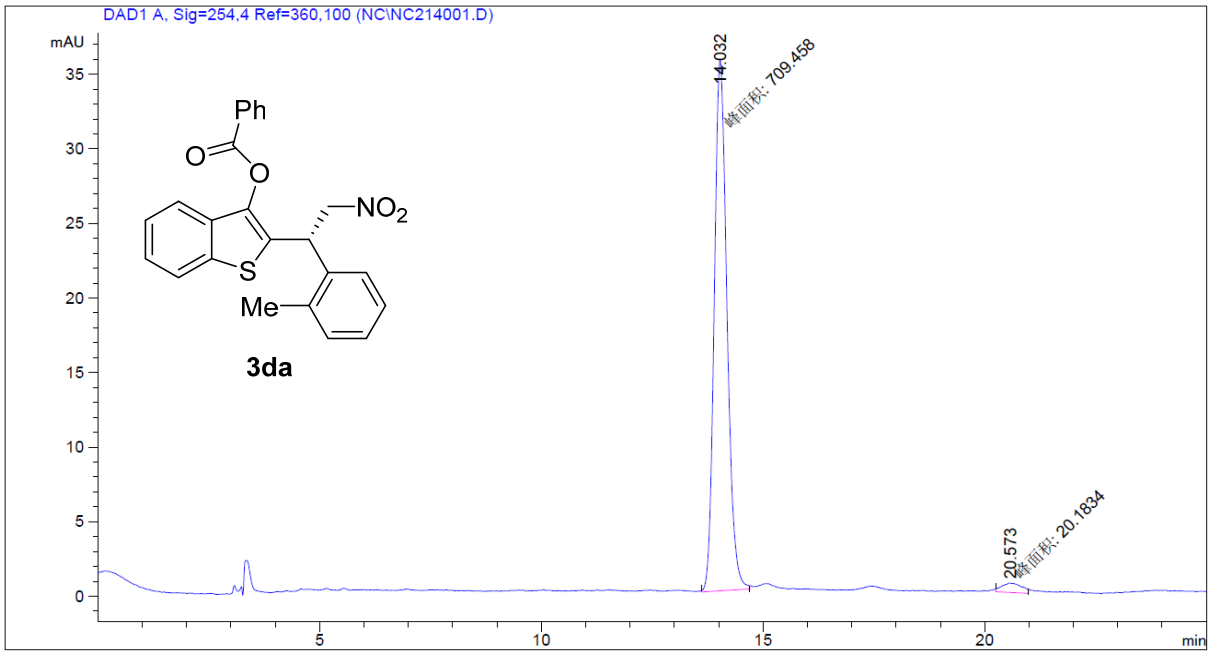
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.421	BB	0.3580	1.68209e4	716.27917	49.9876
2	19.010	MM	0.5108	1.68292e4	549.06543	50.0124



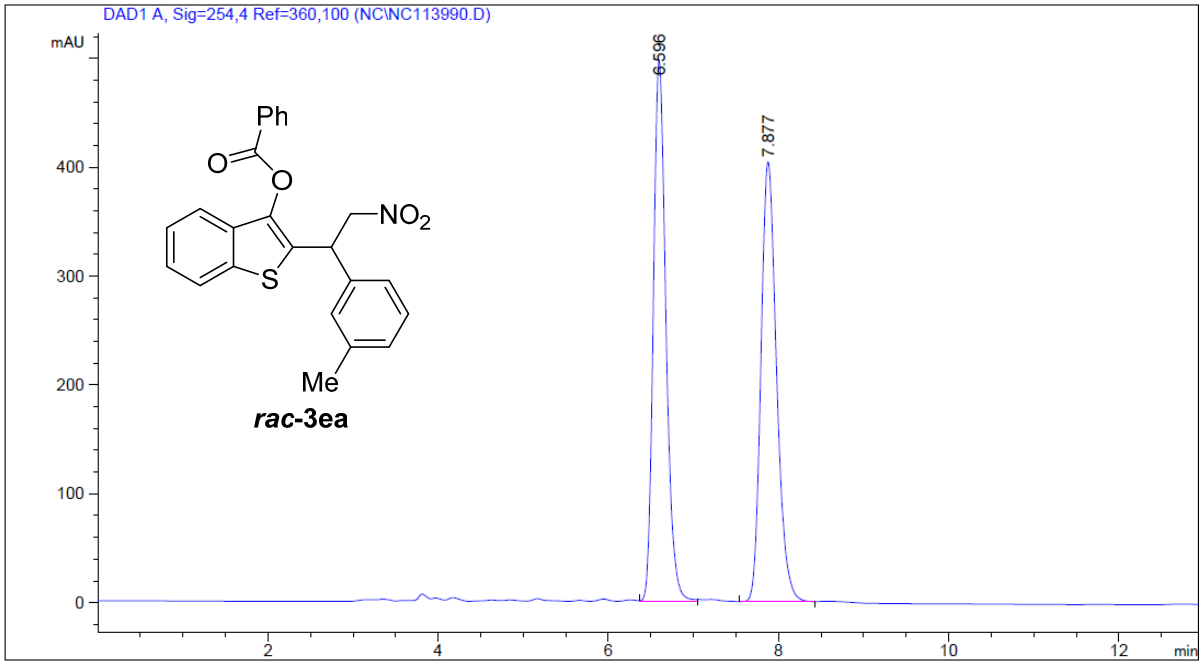
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.705	BB	0.3675	1.06305e4	443.65585	98.6974
2	19.667	BB	0.4176	140.29895	4.93617	1.3026



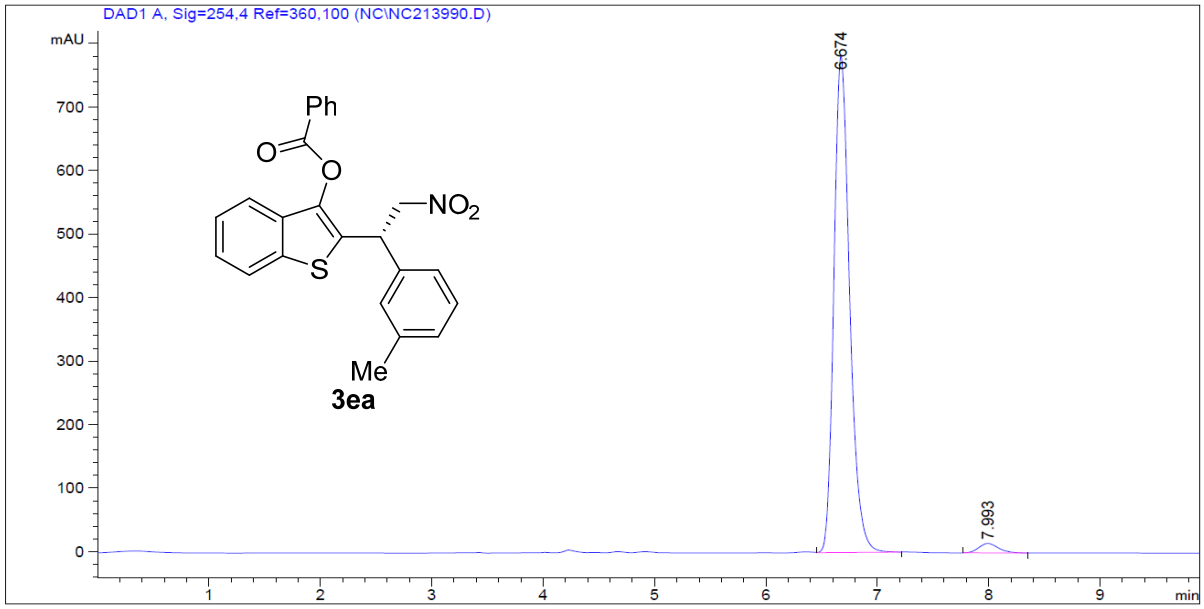
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.948	BB	0.3456	6391.13818	282.87219	50.0238
2	21.716	BB	0.6067	6385.06689	162.39990	49.9762



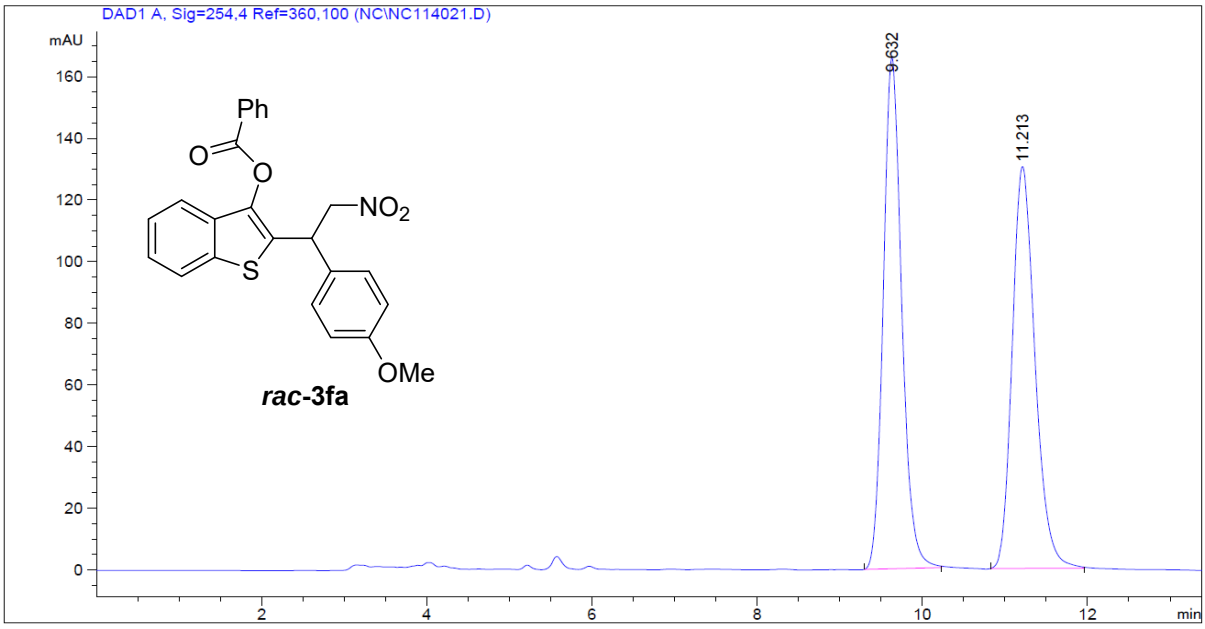
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.032	MM	0.3322	709.45825	35.59032	97.2338
2	20.573	MM	0.5379	20.18344	6.25347e-1	2.7662



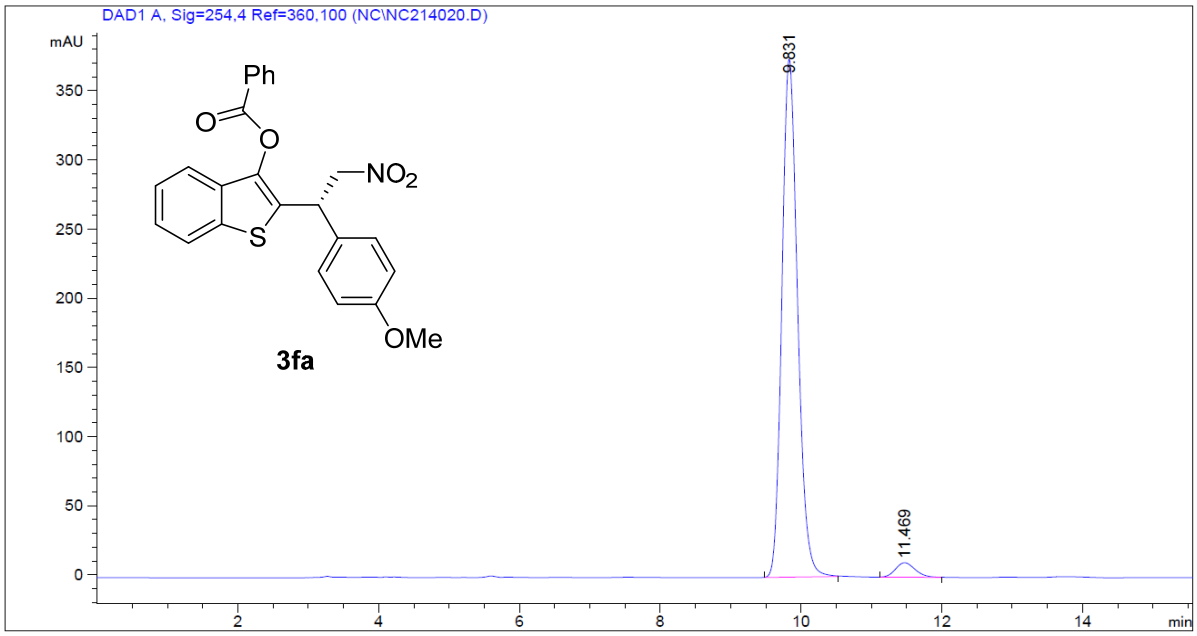
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.596	VB	0.1601	5123.11719	497.59024	49.9048
2	7.877	VB	0.1964	5142.66650	404.24677	50.0952



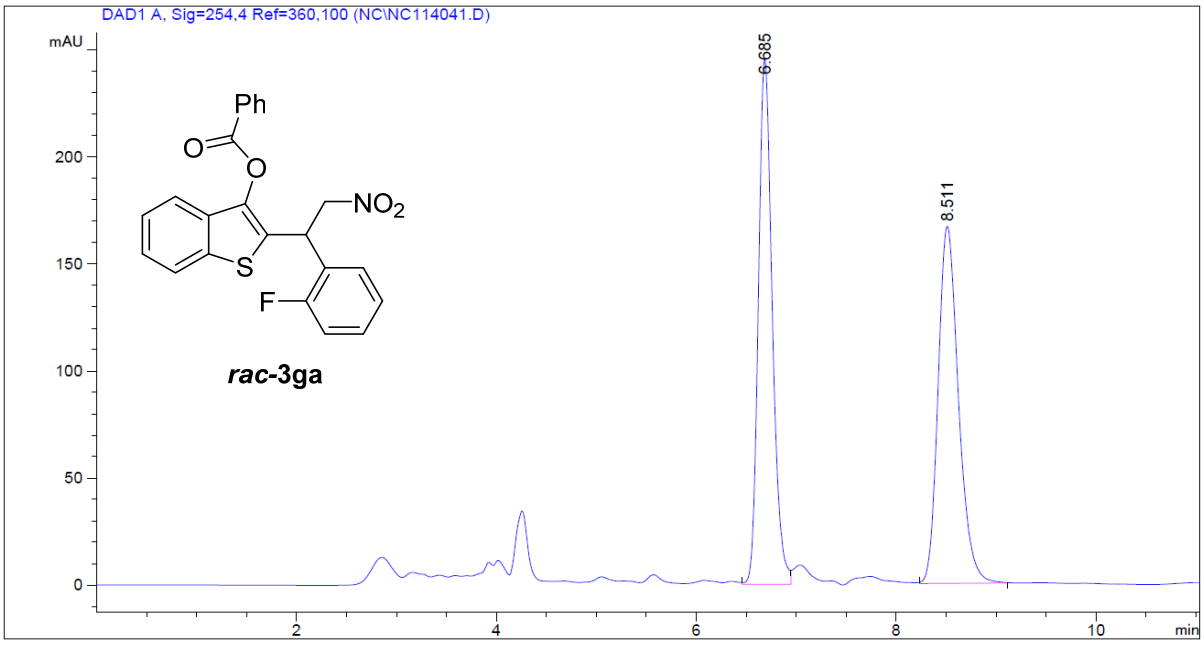
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.674	VB	0.1506	7681.10156	782.06195	97.6904
2	7.993	BB	0.1883	181.60081	14.88413	2.3096



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.632	BB	0.2368	2569.92822	165.79570	50.6702
2	11.213	BB	0.2939	2501.94385	130.37758	49.3298

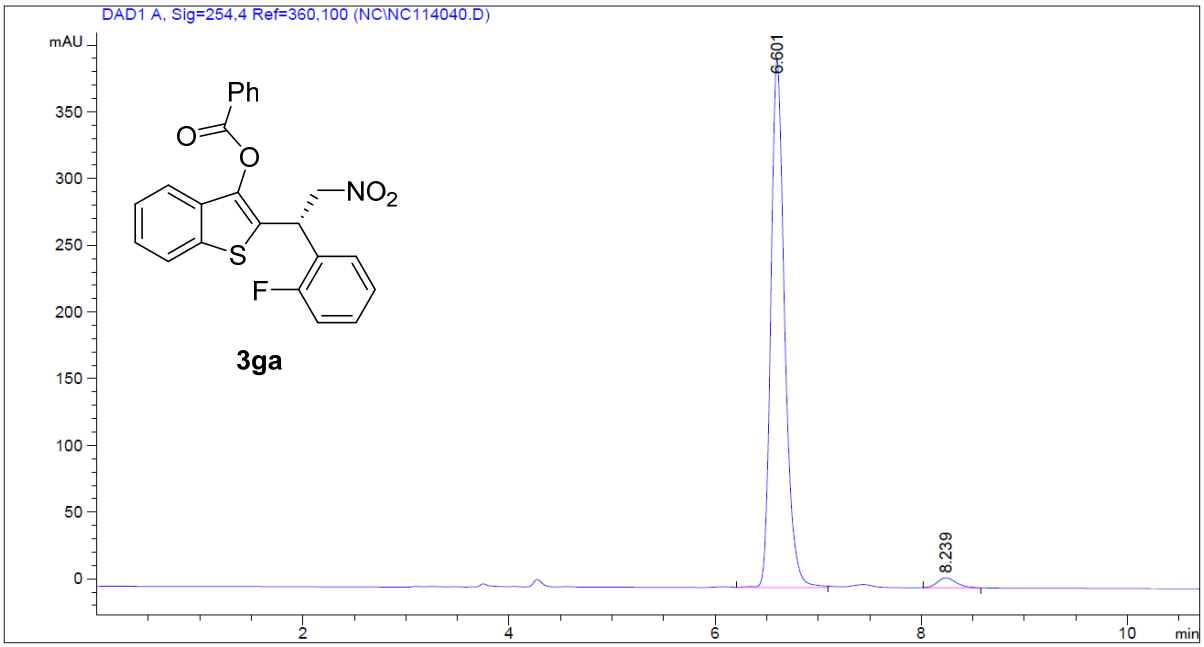


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.831	BB	0.2382	5785.66406	374.49673	96.6033
2	11.469	BB	0.2981	203.43109	10.49881	3.3967



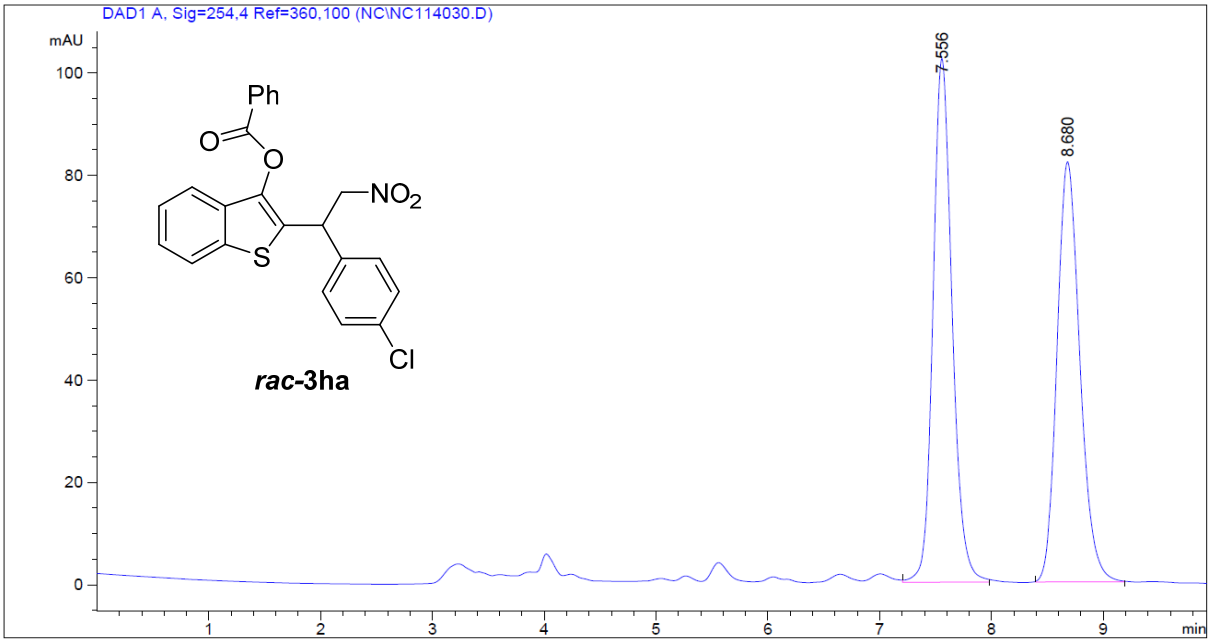
***rac*-3ga**

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.685	VV	0.1485	2368.26709	245.65640	50.0822
2	8.511	BB	0.2169	2360.49341	166.97946	49.9178

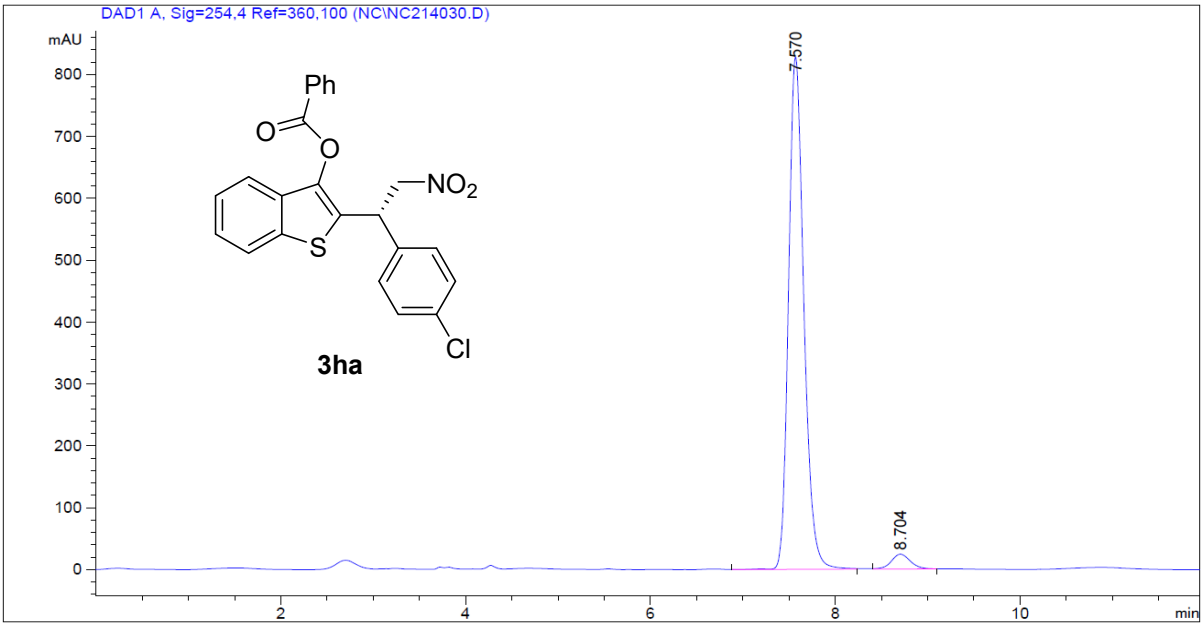


3ga

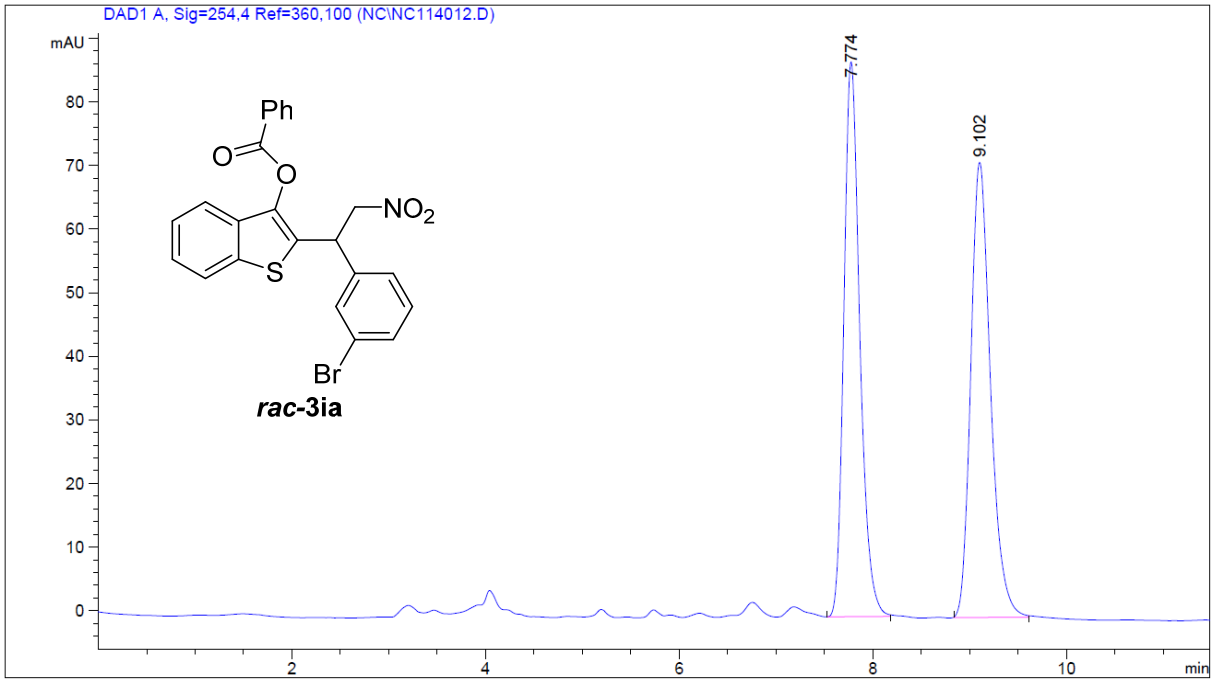
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.601	VB	0.1427	3688.06616	395.81784	97.4121
2	8.239	BB	0.1978	97.97725	7.53078	2.5879



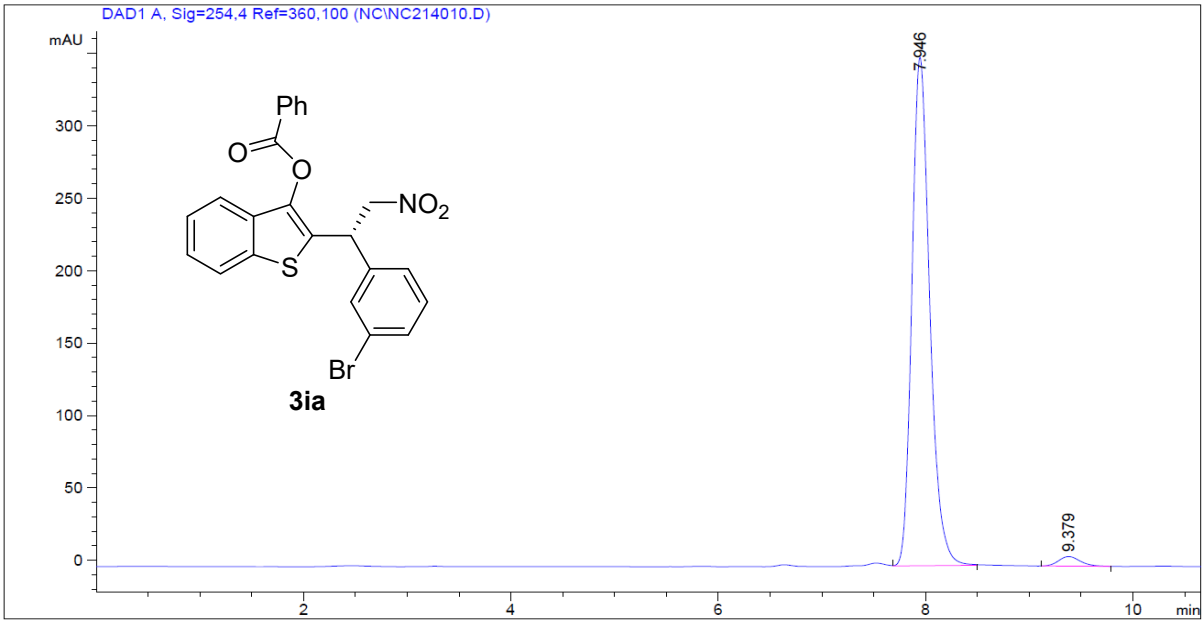
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.556	VB	0.1803	1213.95190	102.38133	50.9580
2	8.680	BB	0.2180	1168.30591	82.11063	49.0420



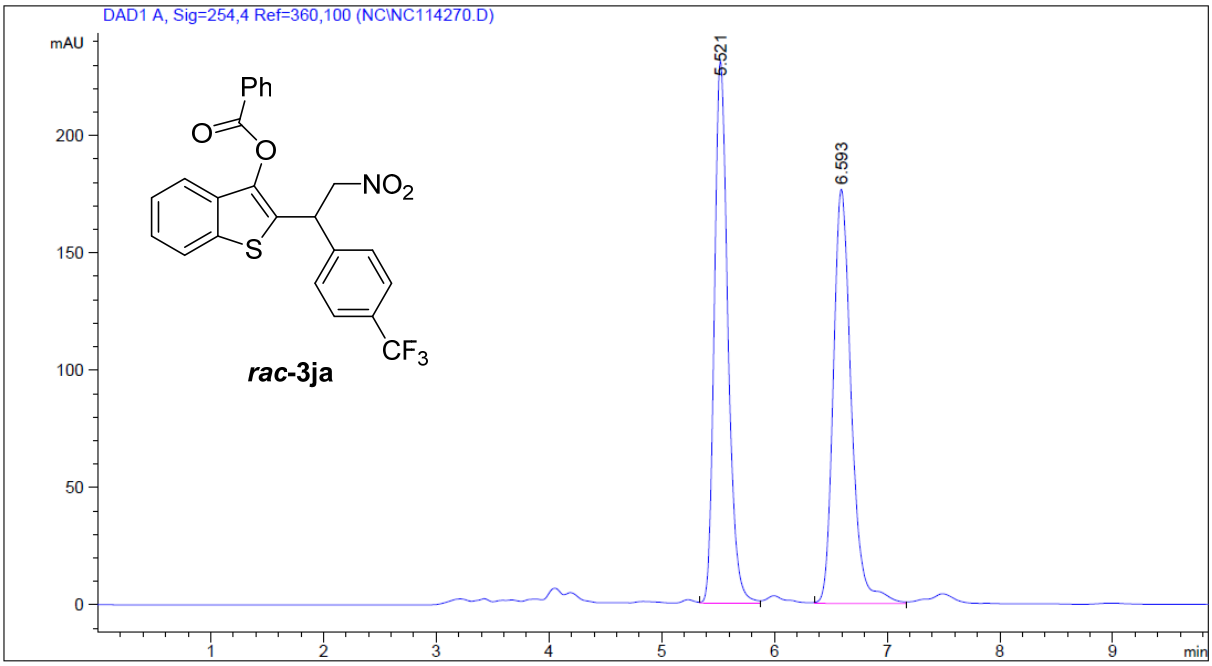
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.570	VB	0.1760	9517.87793	828.49286	96.4911
2	8.704	BB	0.2200	346.11508	24.03698	3.5089



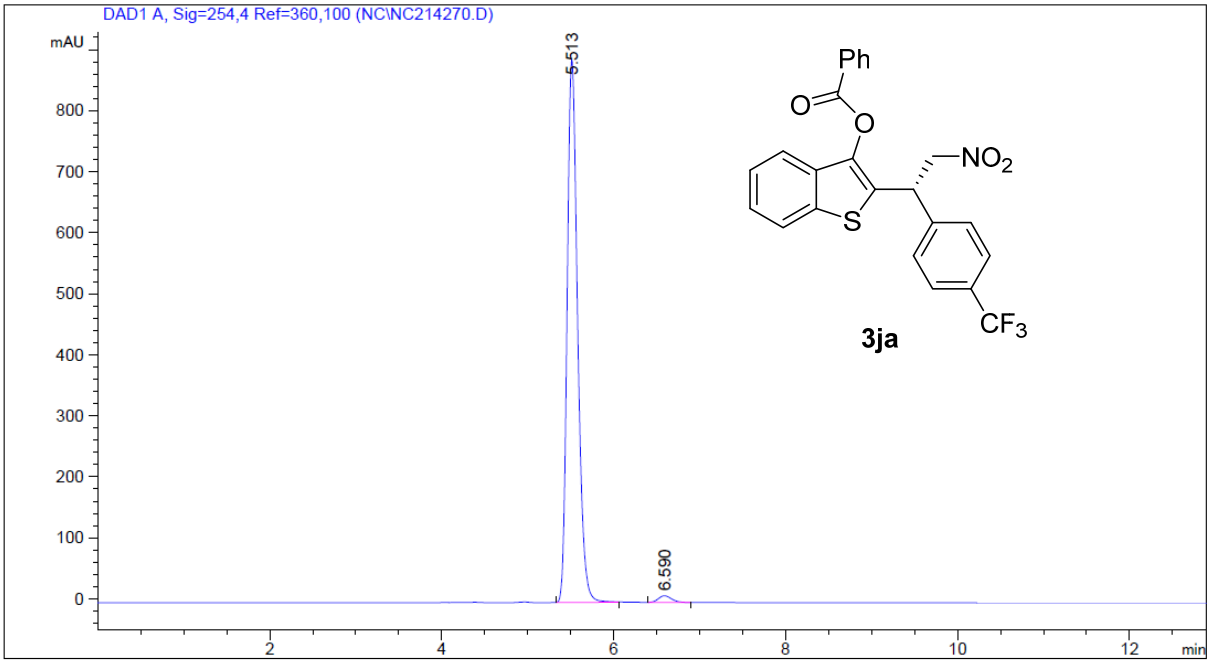
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.774	VB	0.1733	997.03558	87.24976	49.6544
2	9.102	BB	0.2148	1010.91632	71.56730	50.3456



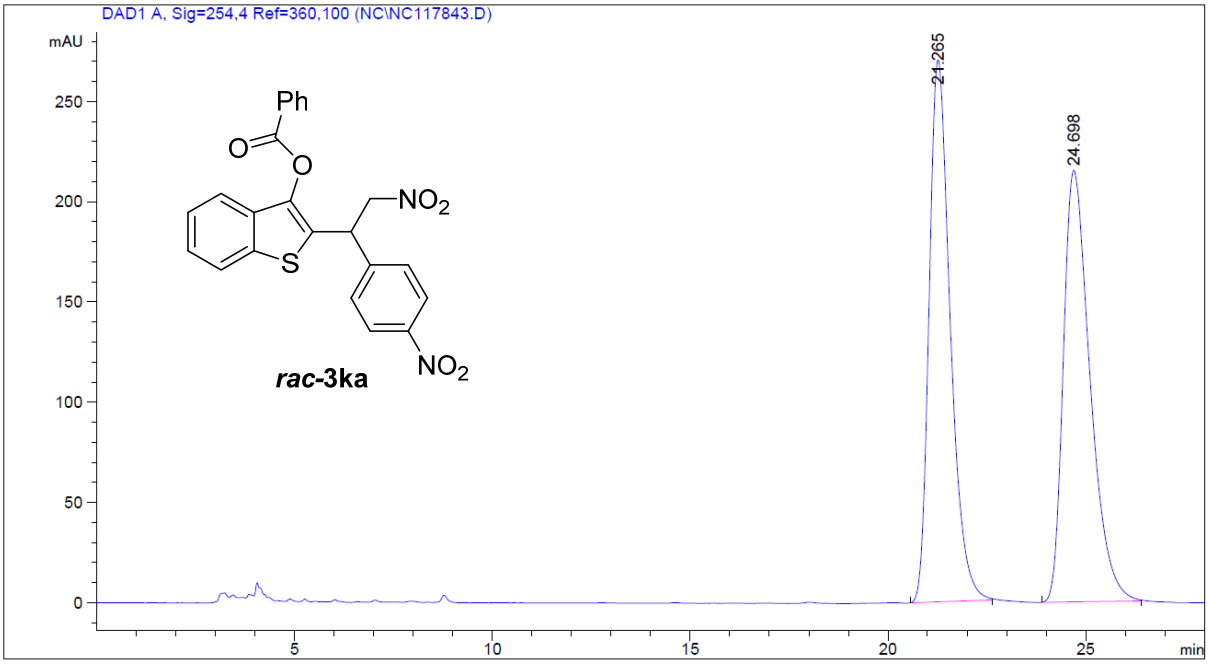
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.946	VB	0.1814	4196.32666	351.23386	97.7510
2	9.379	BB	0.2257	96.54776	6.63807	2.2490



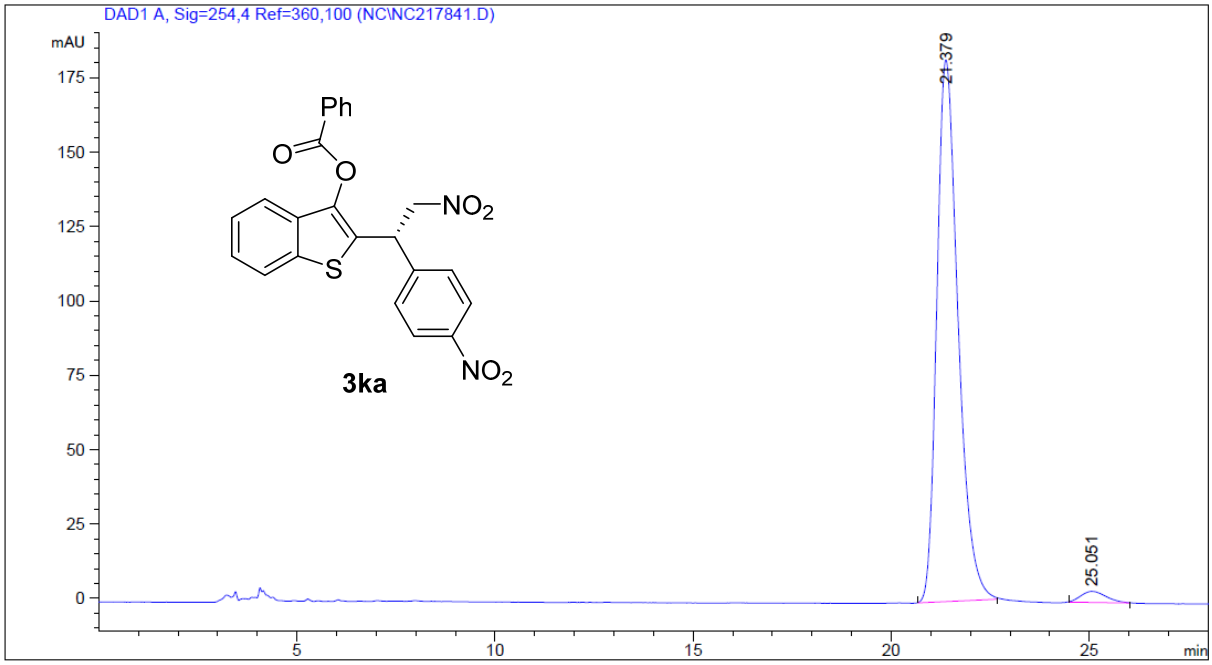
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.521	VV	0.1276	1933.99011	231.15701	49.7180
2	6.593	BB	0.1692	1955.93030	176.57790	50.2820



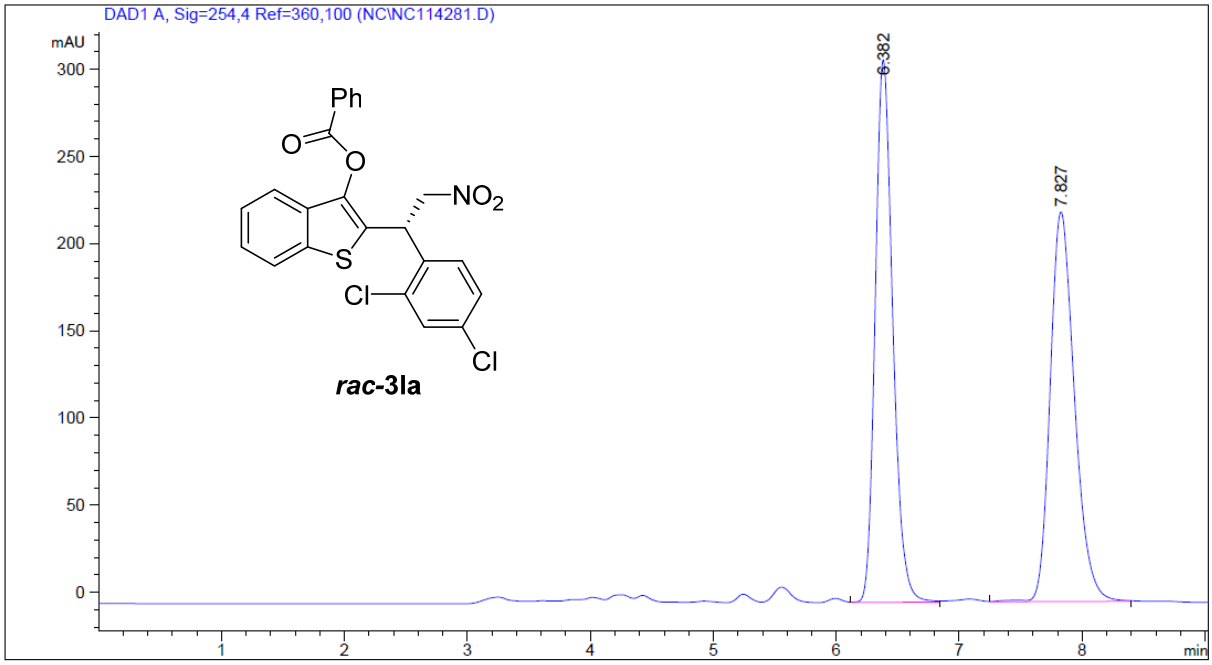
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.513	BB	0.1306	7520.27344	890.19879	98.4565
2	6.590	BB	0.1631	117.89263	10.99617	1.5435



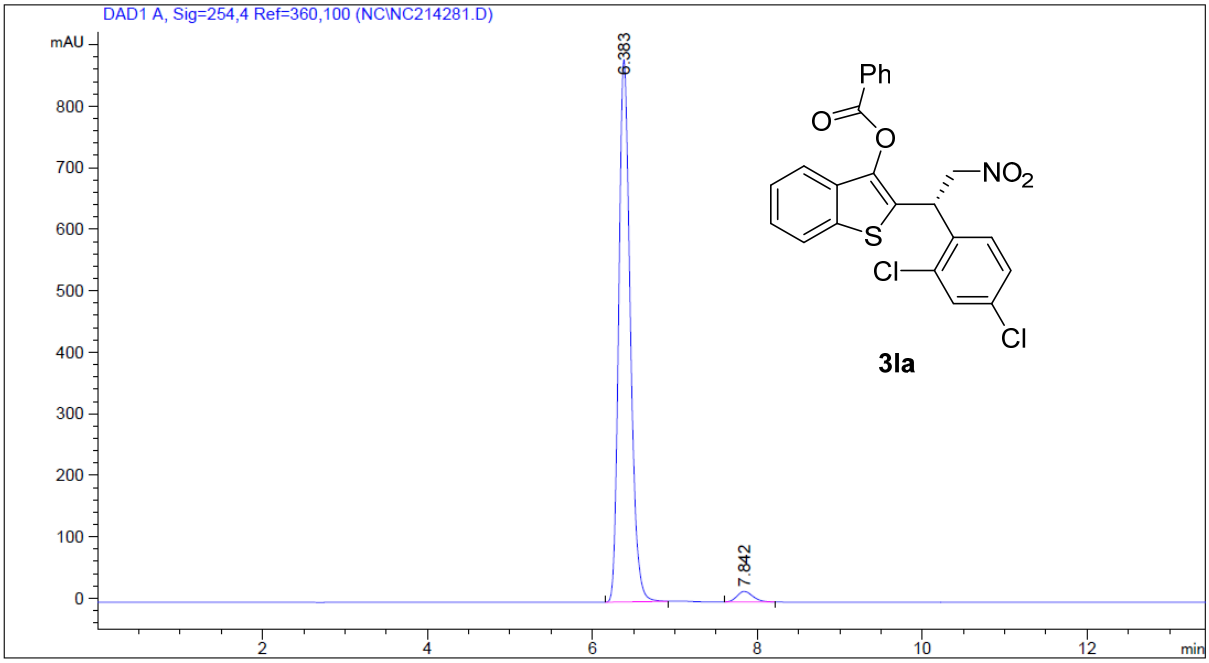
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.265	BB	0.5637	1.00019e4	270.31033	49.7862
2	24.698	BB	0.7127	1.00878e4	215.28685	50.2138



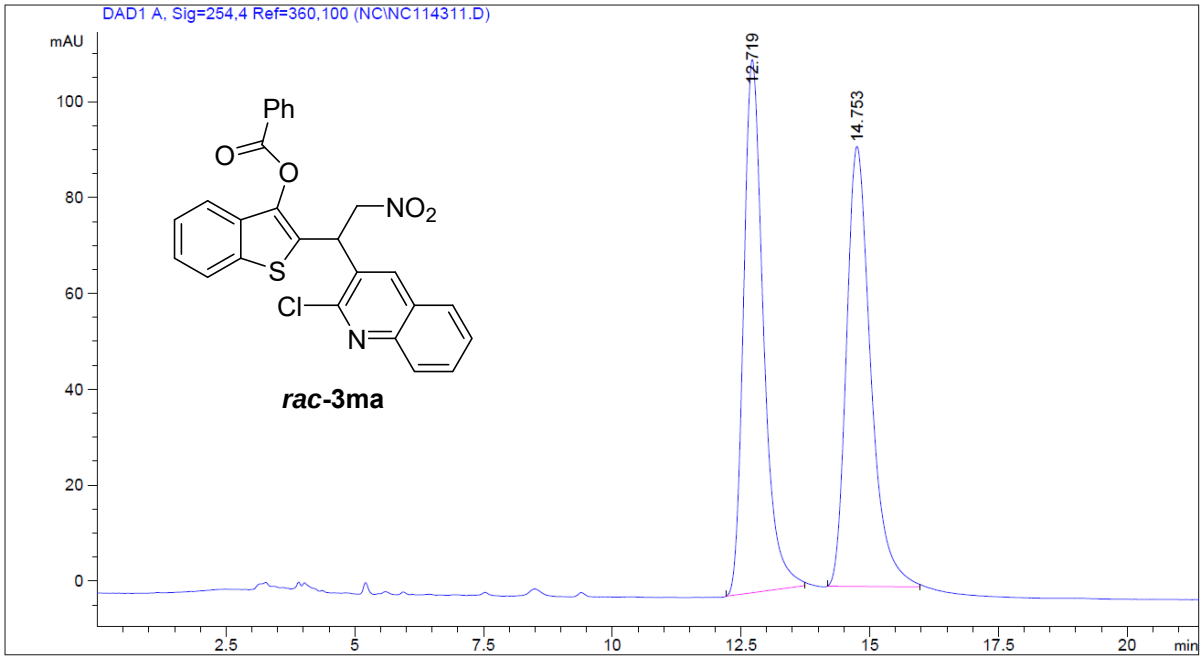
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.379	BB	0.5695	6796.57227	182.06740	97.6213
2	25.051	BB	0.5350	165.61130	3.73715	2.3787



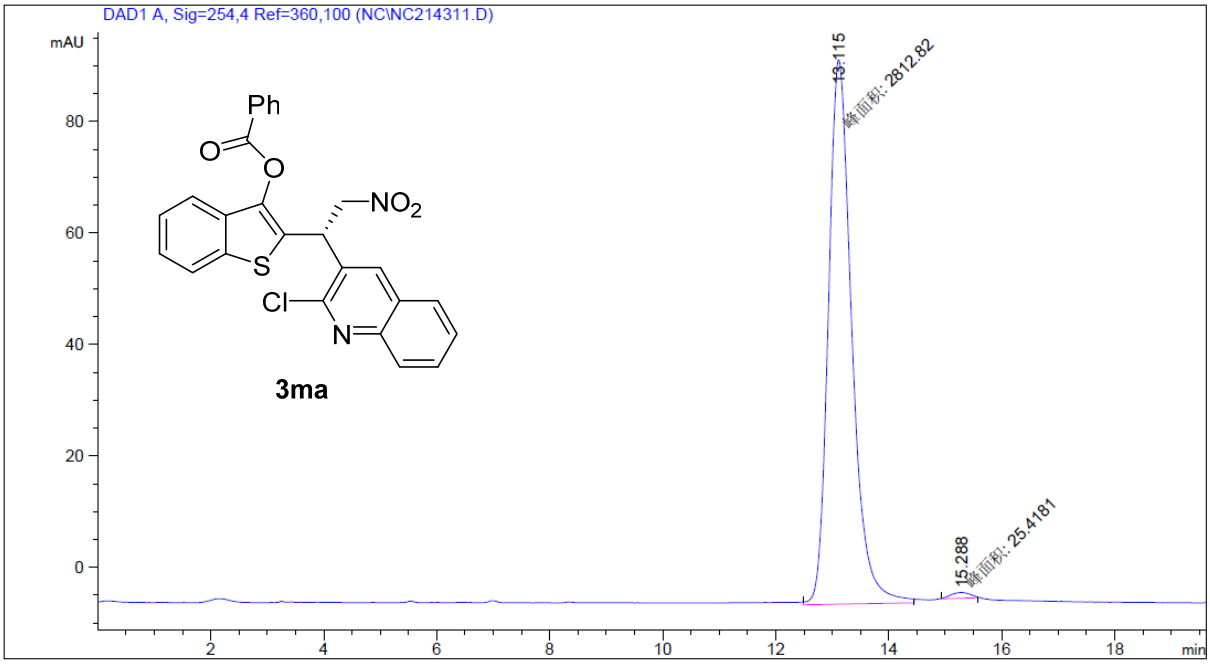
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.382	VB	0.1517	3089.39502	311.40234	50.0999
2	7.827	VB	0.2125	3077.07324	223.62166	49.9001



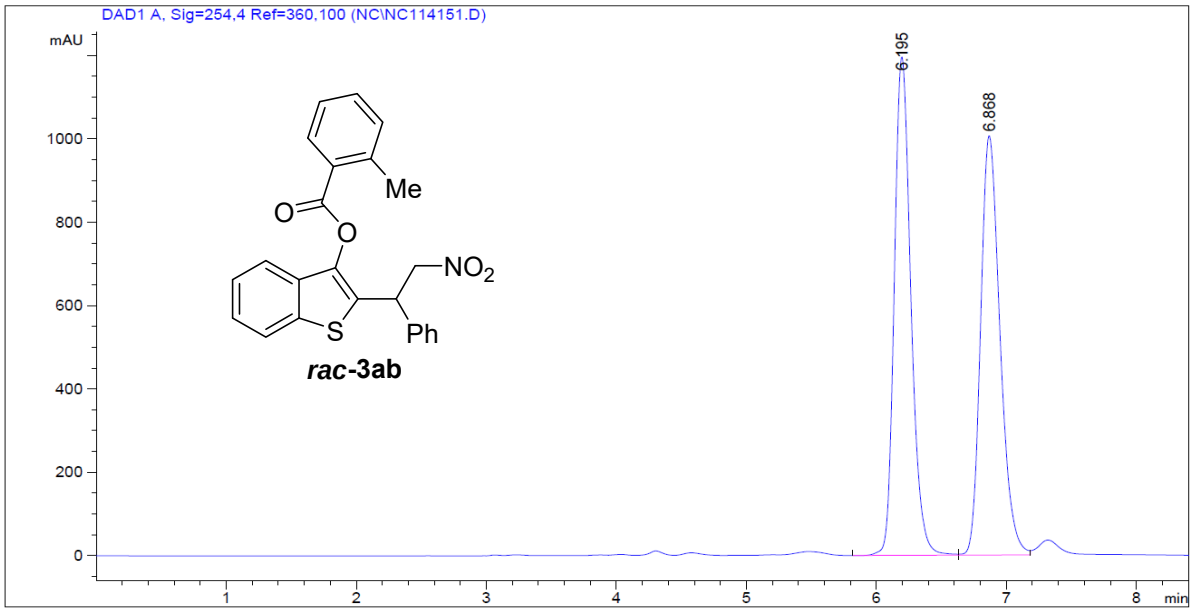
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.383	BB	0.1495	8582.33496	882.13019	97.3677
2	7.842	BB	0.2044	232.02133	17.30632	2.6323



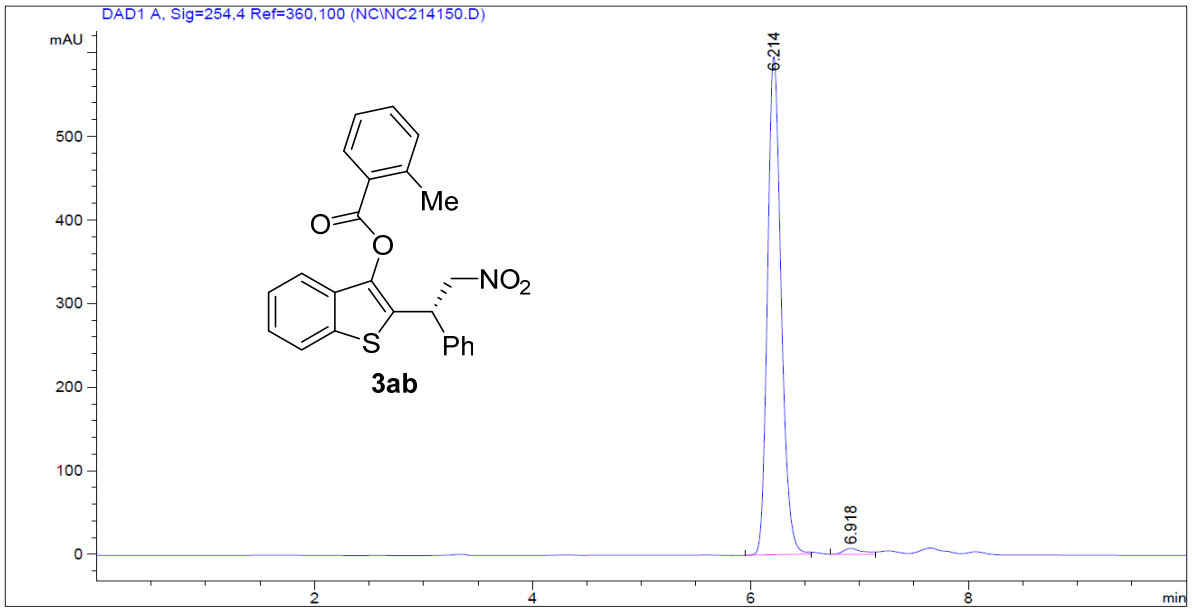
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.719	BB	0.4045	2979.63916	111.23364	49.8586
2	14.753	BB	0.4968	2996.53516	91.80228	50.1414



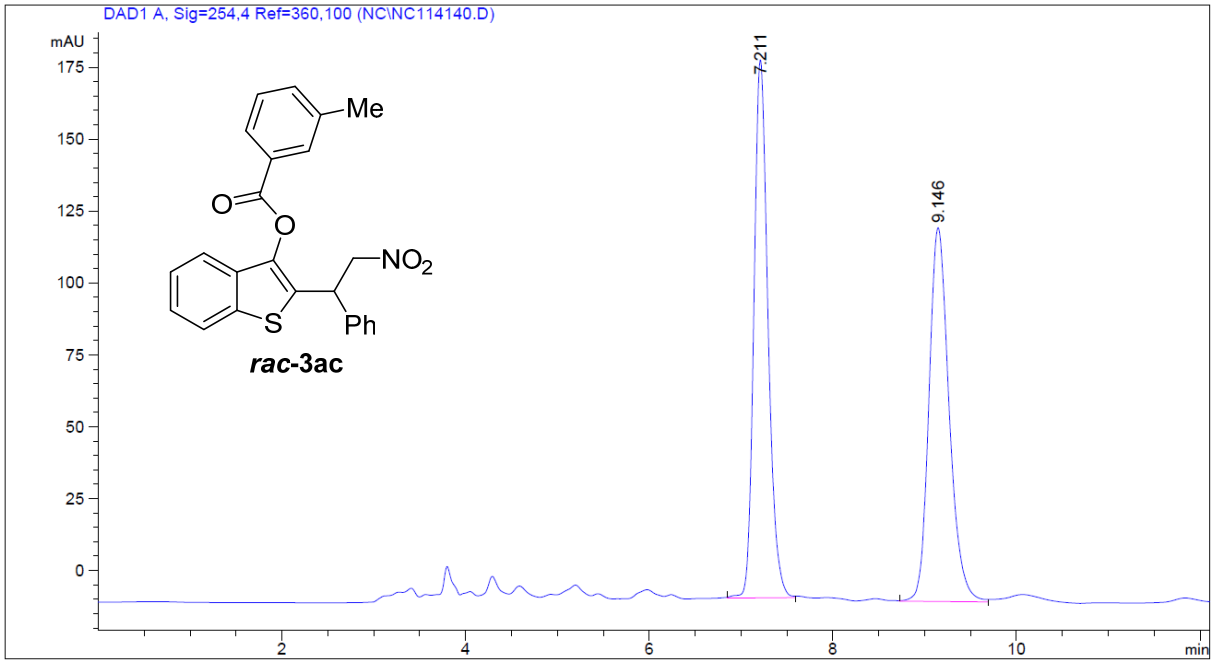
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.115	MM	0.4800	2812.82251	97.67286	99.1044
2	15.288	MM	0.3969	25.41809	1.06735	0.8956



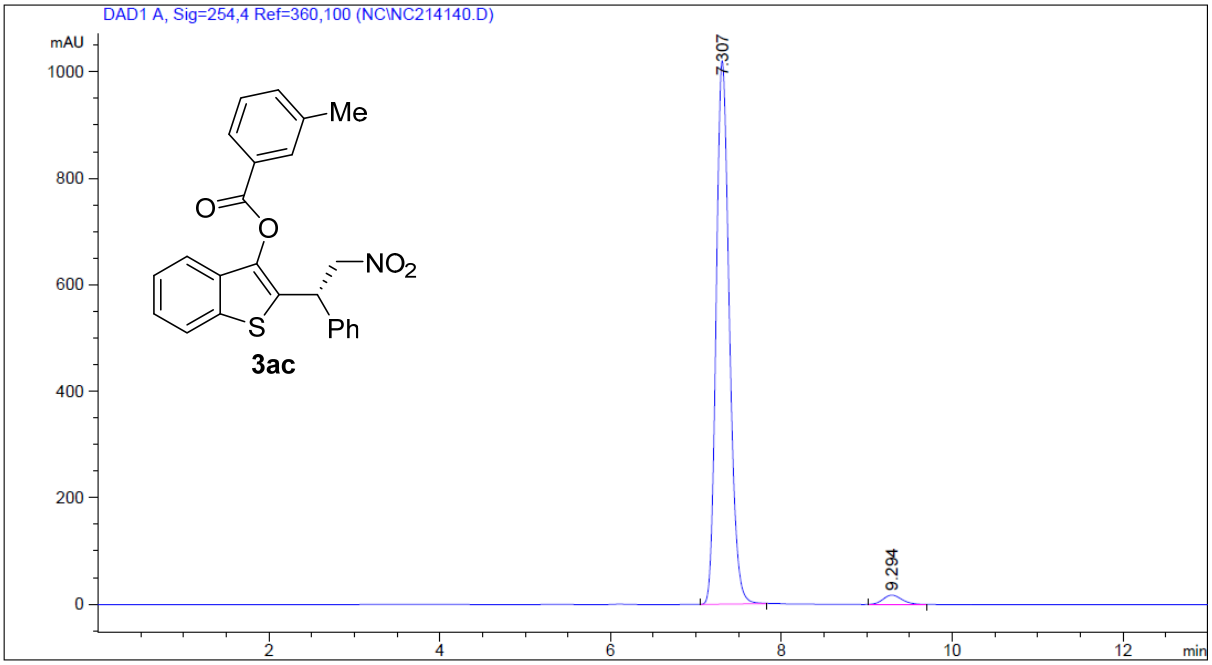
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.195	VV	0.1353	1.05991e4	1197.06946	50.4280
2	6.868	VV	0.1607	1.04192e4	1006.82849	49.5720



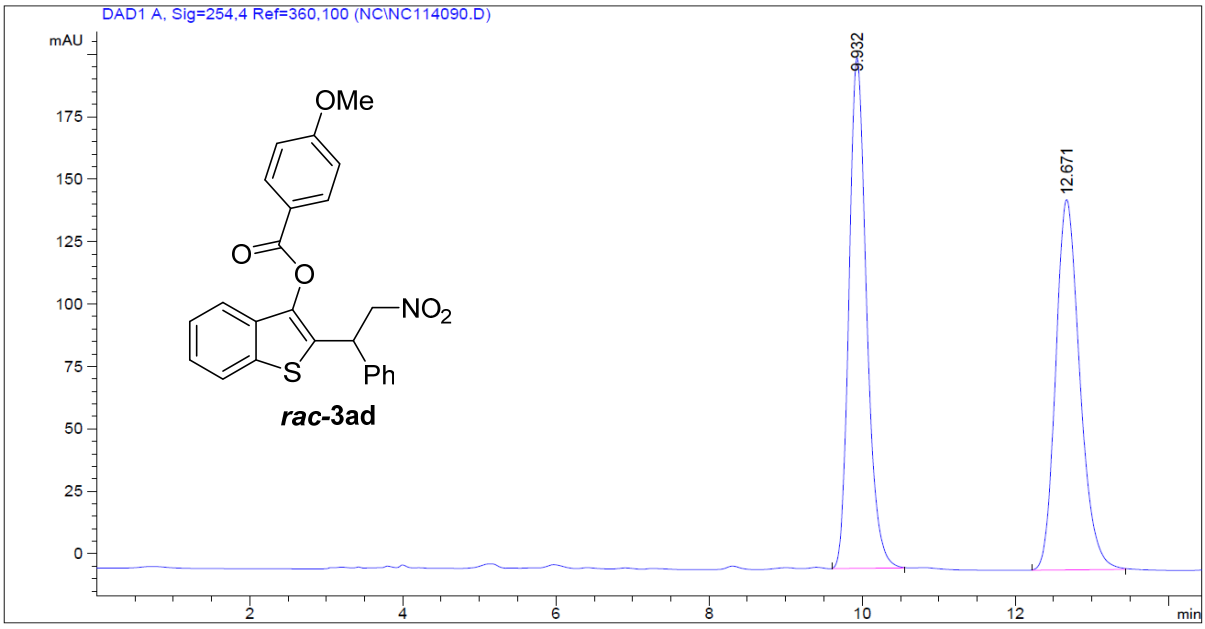
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.214	BB	0.1334	5181.00488	596.25702	98.3553
2	6.918	BV	0.1797	86.63465	7.03153	1.6447



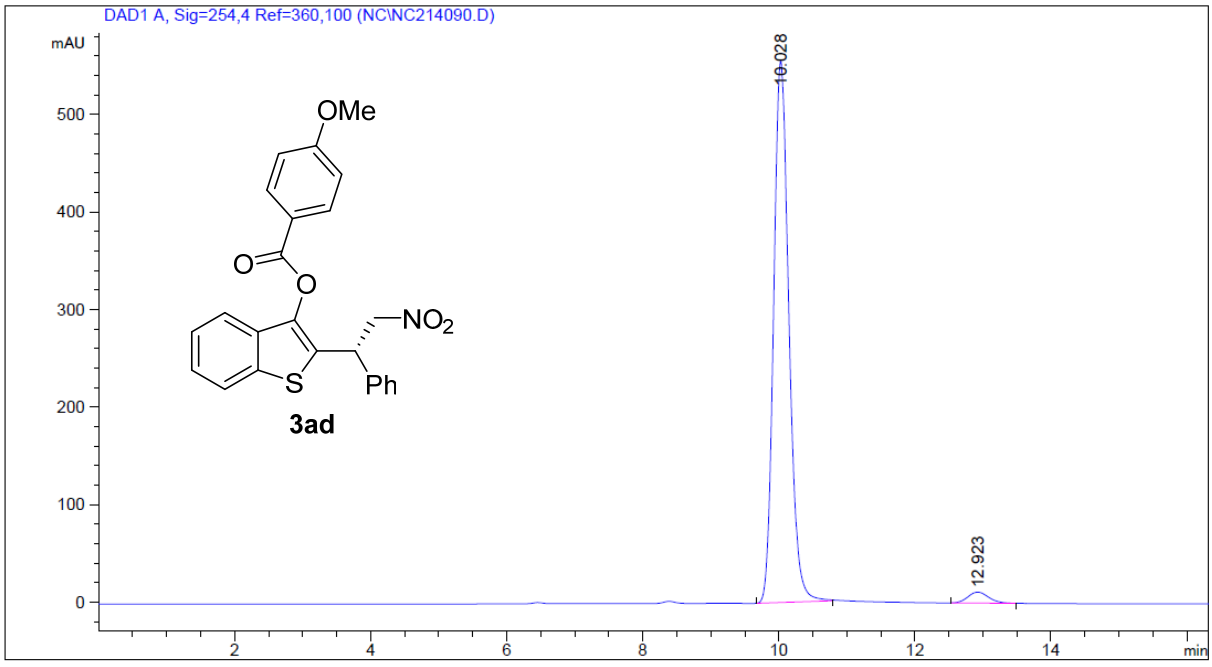
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.211	BB	0.1623	1995.43591	187.23297	50.1304
2	9.146	VB	0.2341	1985.05090	130.04665	49.8696



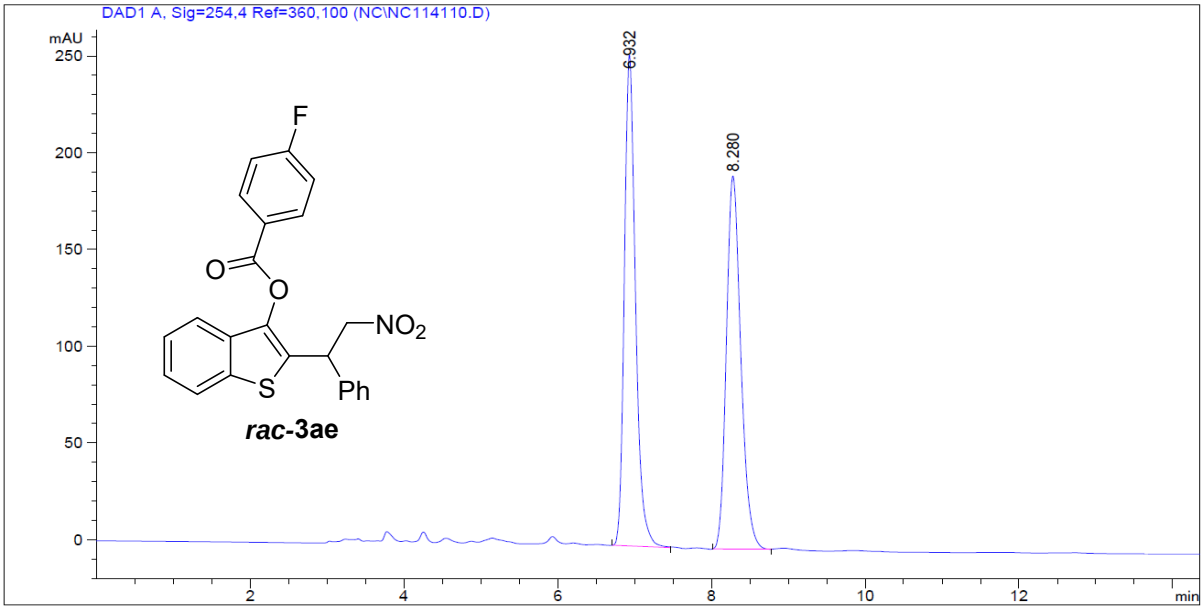
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.307	BB	0.1668	1.09246e4	1021.22949	97.6004
2	9.294	BB	0.2346	268.58734	17.54549	2.3996



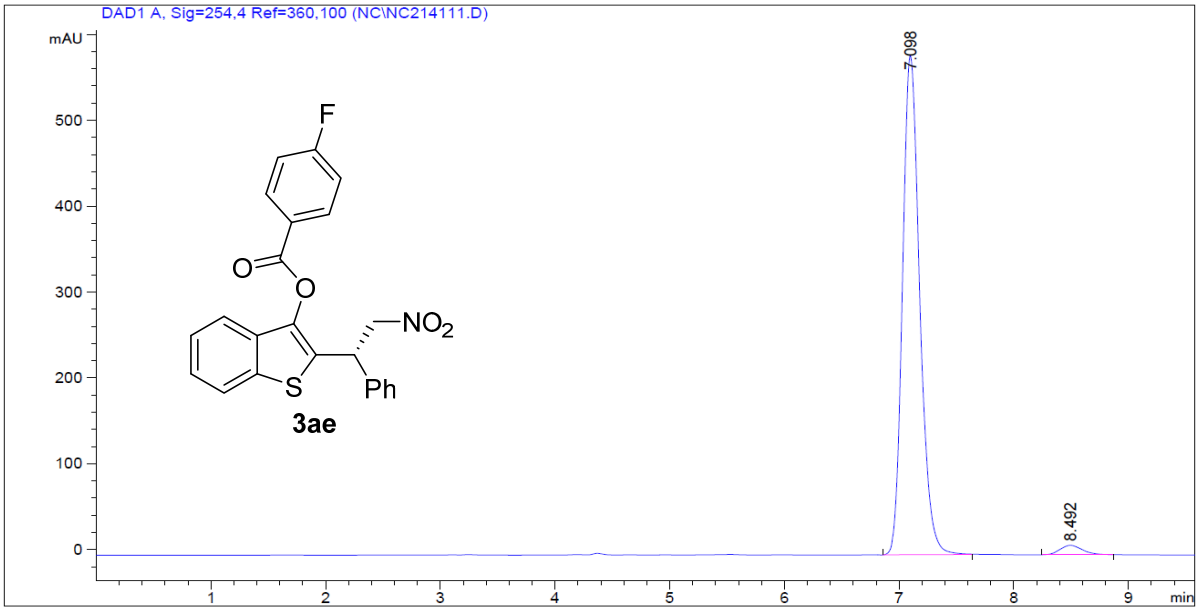
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.932	BB	0.2439	3258.43774	204.49390	50.0689
2	12.671	BB	0.3357	3249.46899	148.27846	49.9311



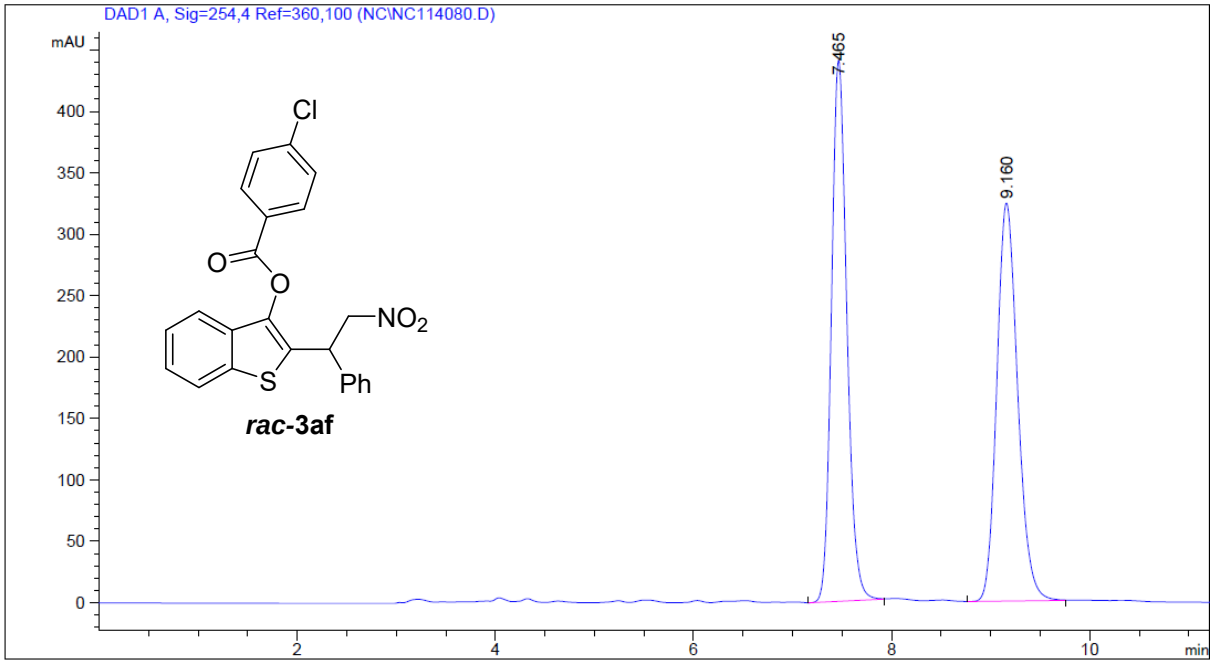
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.028	BB	0.2398	8656.08984	555.54346	97.2930
2	12.923	BB	0.3267	240.83736	11.29877	2.7070



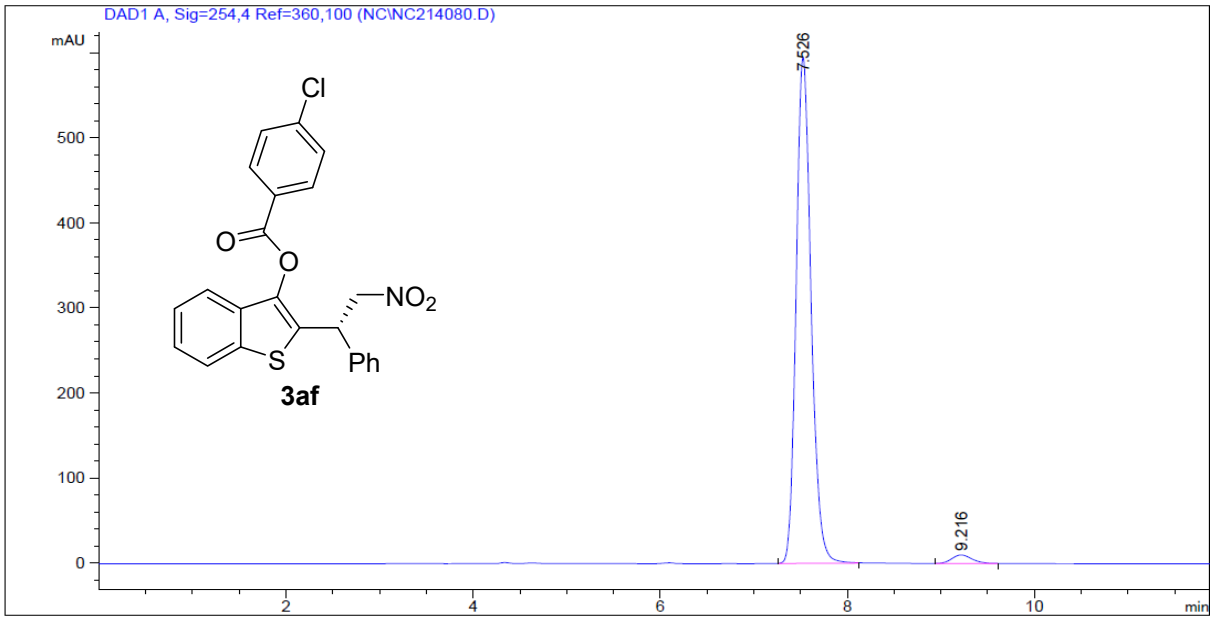
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.932	BB	0.1535	2558.28174	254.01802	50.4478
2	8.280	BB	0.2000	2512.86572	192.92363	49.5522



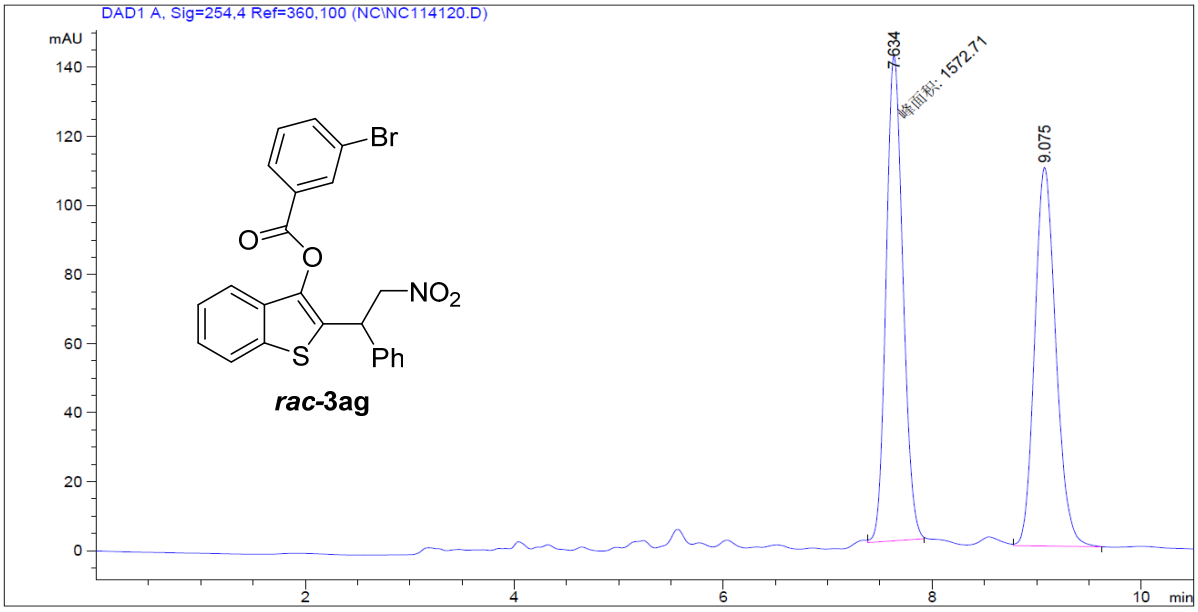
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.098	BB	0.1613	6046.92676	581.67004	97.5587
2	8.492	BB	0.2120	151.32031	11.03185	2.4413



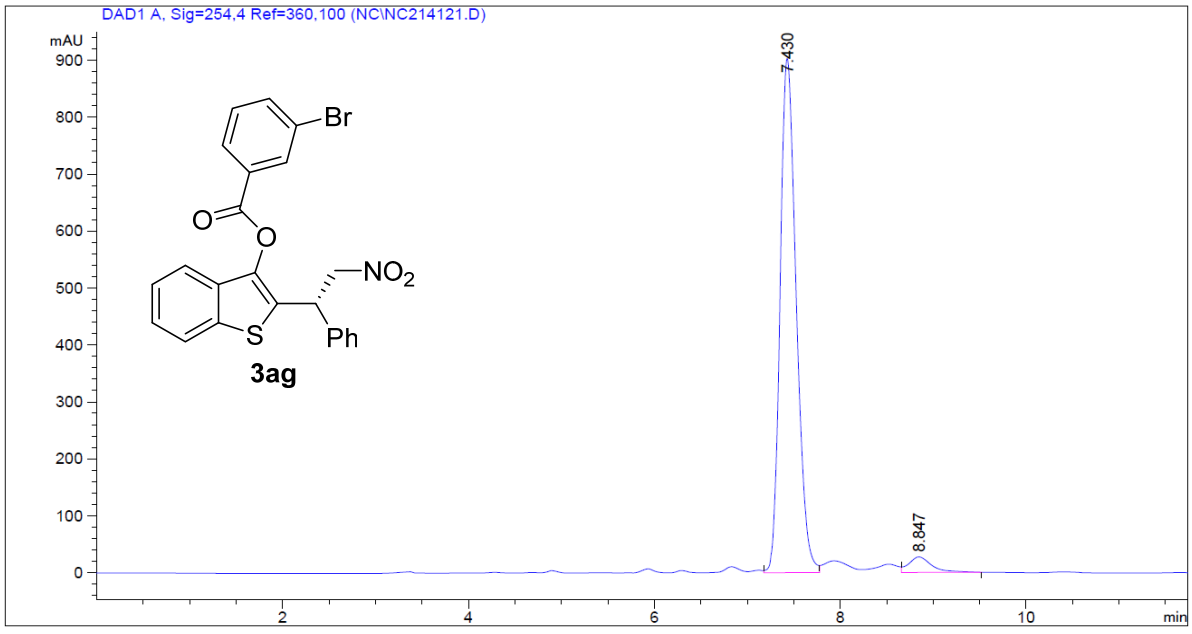
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.465	VB	0.1658	4755.33740	440.87869	50.0642
2	9.160	VB	0.2247	4743.14551	324.11017	49.9358



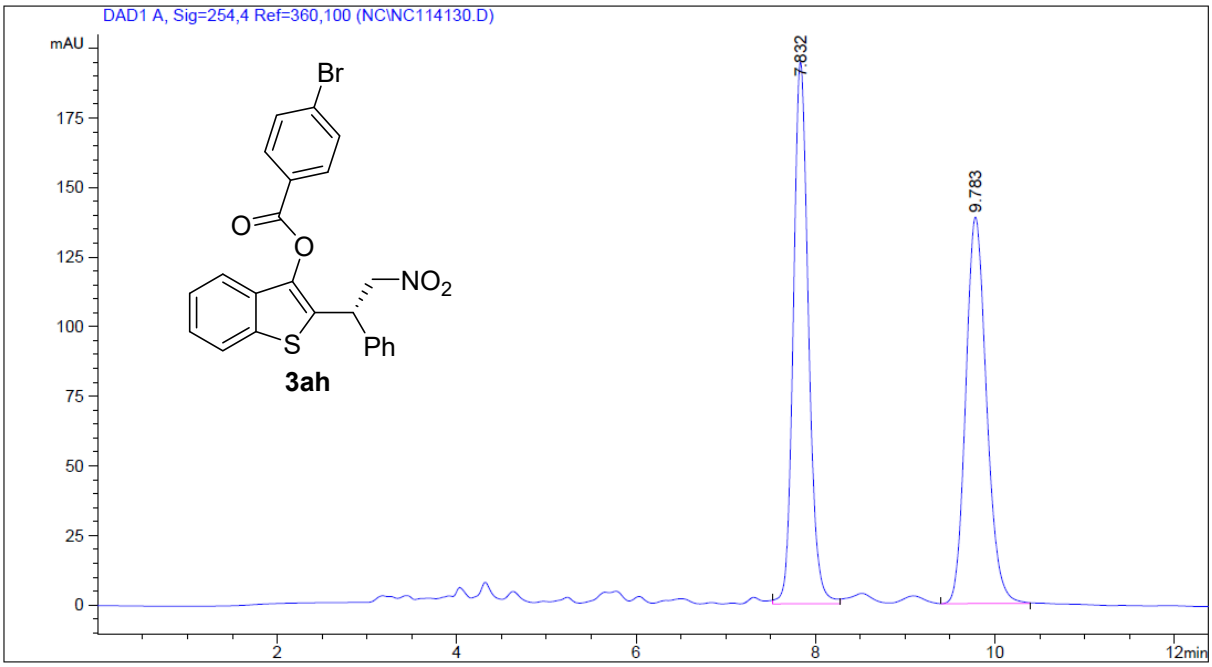
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.526	BB	0.1692	6601.14551	595.90704	97.7625
2	9.216	BB	0.2329	151.08098	10.07567	2.2375



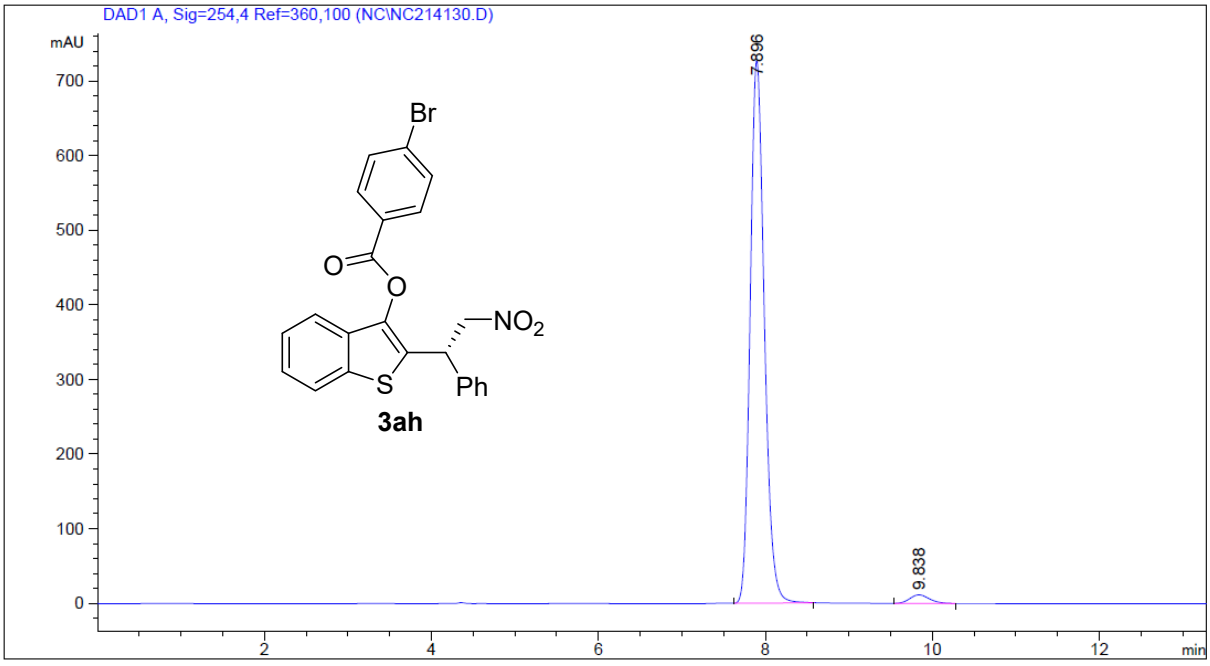
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.634	MM	0.1864	1572.70789	140.60677	50.3994
2	9.075	VB	0.2186	1547.78149	109.67541	49.6006



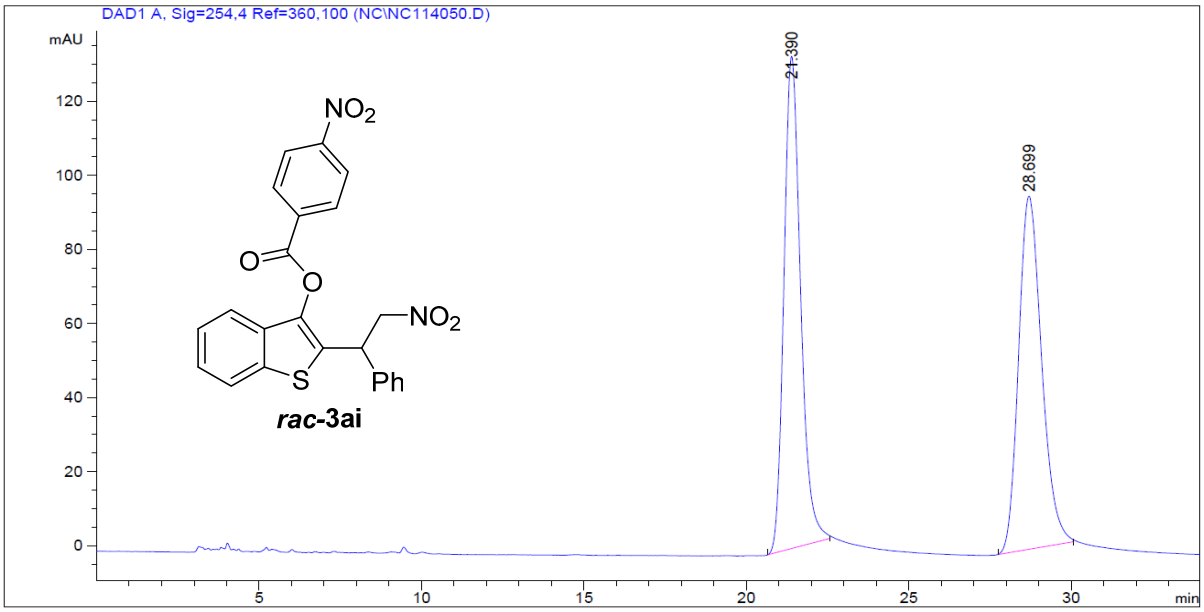
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.430	VV	0.1843	1.08644e4	903.56592	95.7850
2	8.847	VB	0.2561	478.08435	27.32607	4.2150



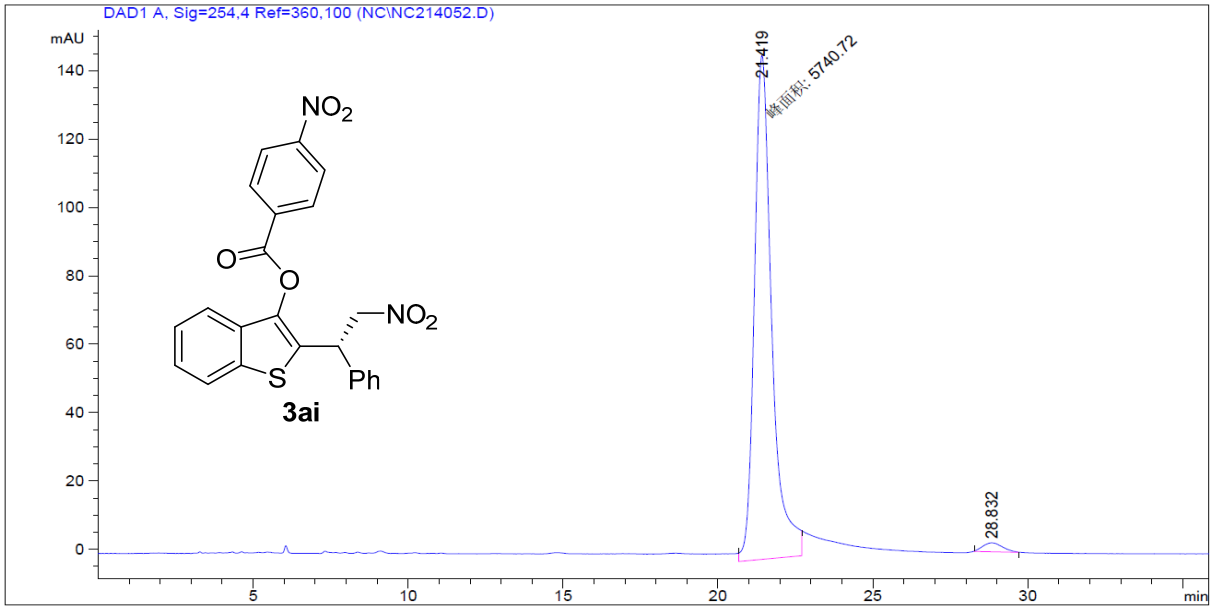
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.832	BB	0.1809	2287.29297	194.85368	50.5429
2	9.783	VB	0.2501	2238.15771	138.85237	49.4571



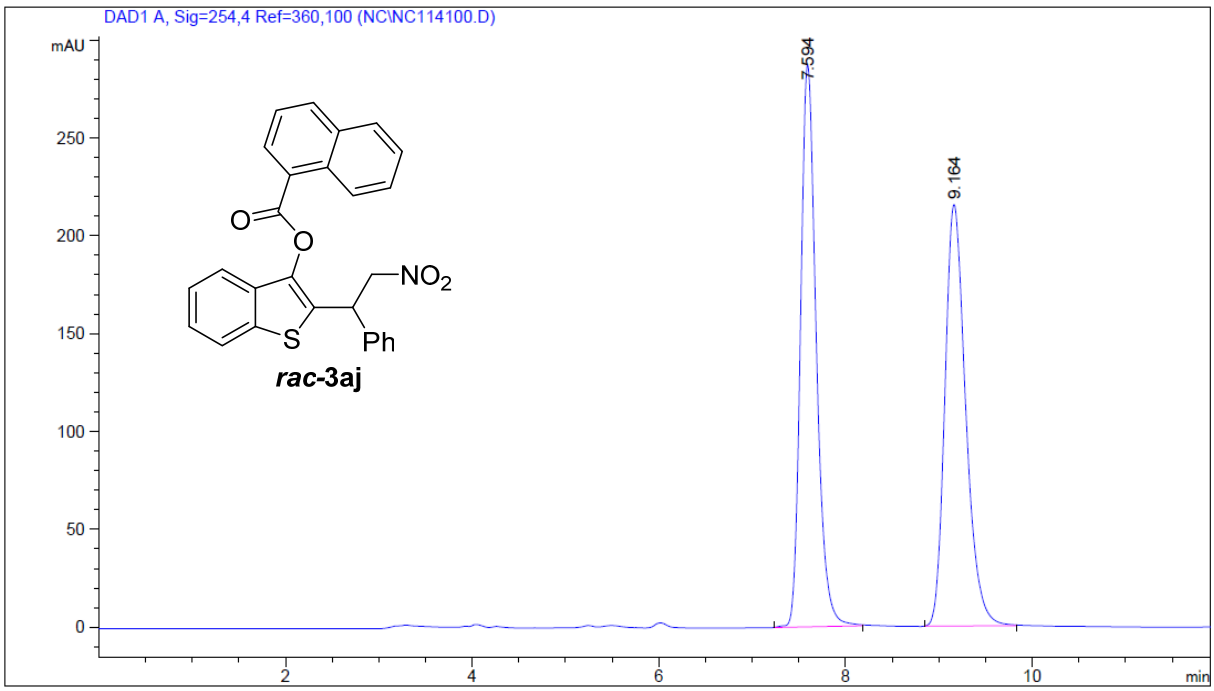
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.896	BB	0.1814	8571.41895	727.74701	97.8421
2	9.838	BB	0.2513	189.03802	11.52719	2.1579



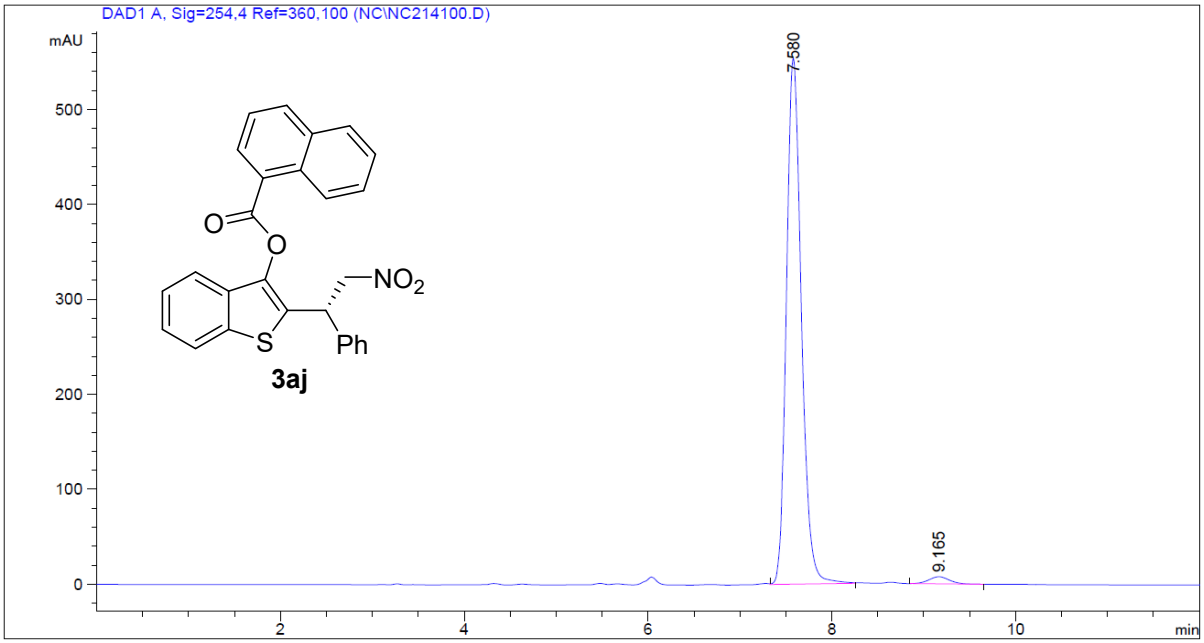
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.390	BB	0.5436	4736.08594	132.94809	50.1661
2	28.699	BB	0.7635	4704.71729	95.36868	49.8339



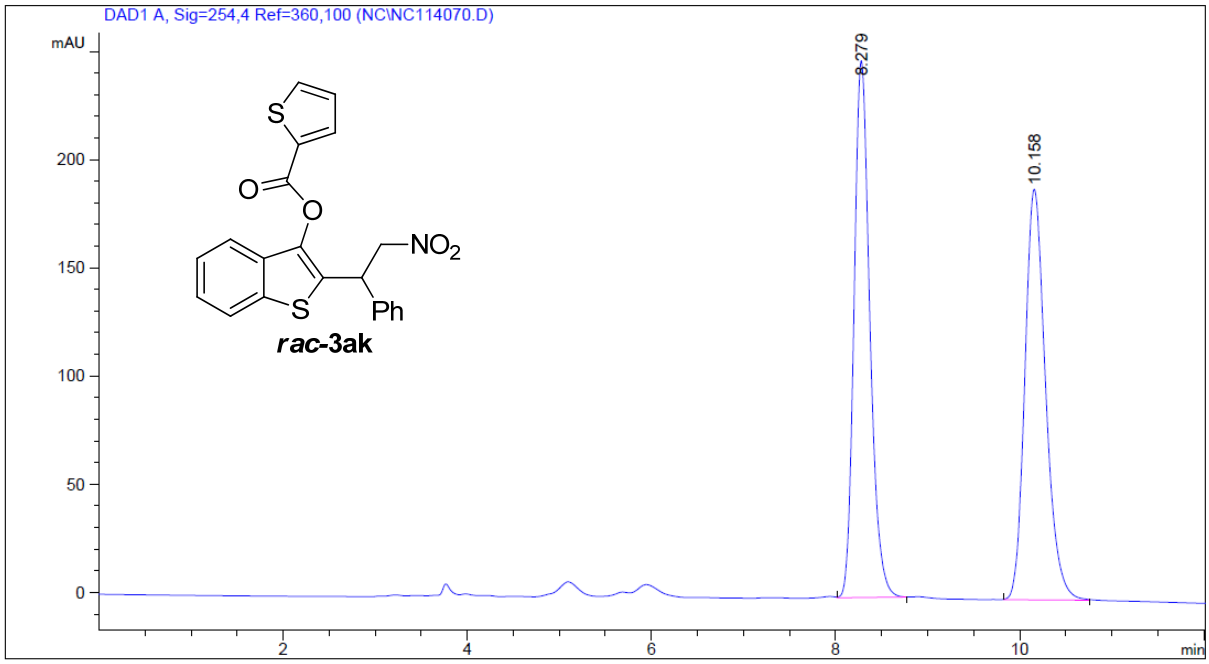
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.419	MM	0.6490	5740.71582	147.42224	98.0358
2	28.832	BB	0.5285	115.02074	2.61831	1.9642



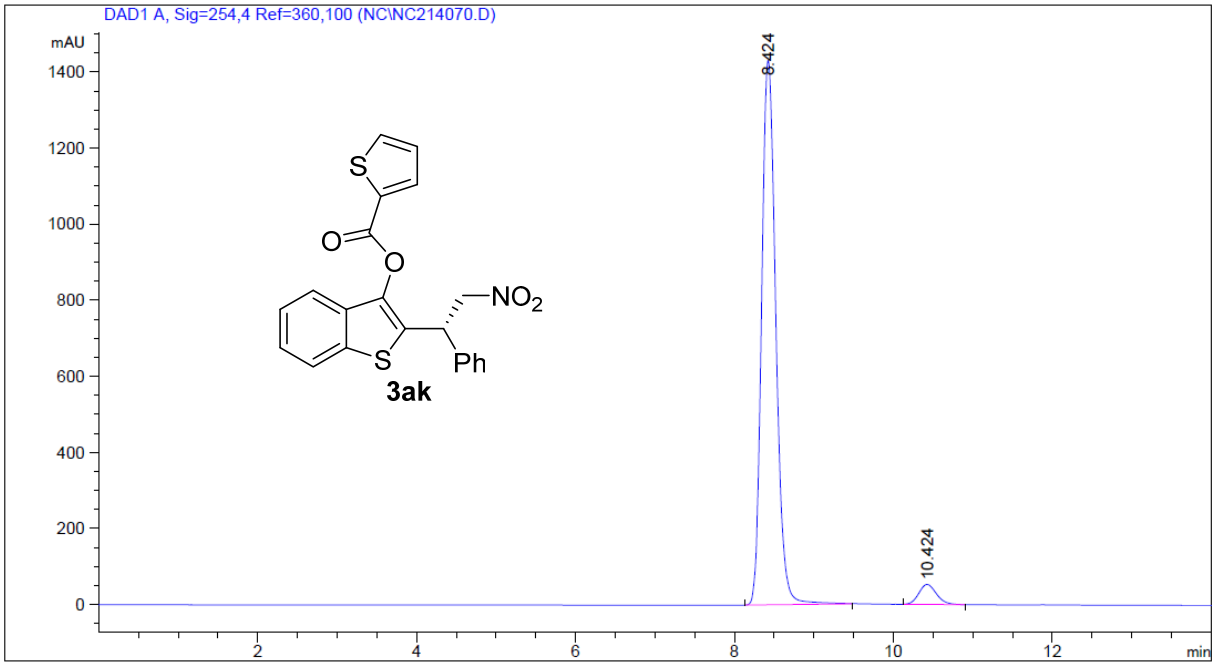
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.594	BB	0.1782	3352.94067	287.15662	50.0913
2	9.164	BB	0.2370	3340.72070	215.37683	49.9087



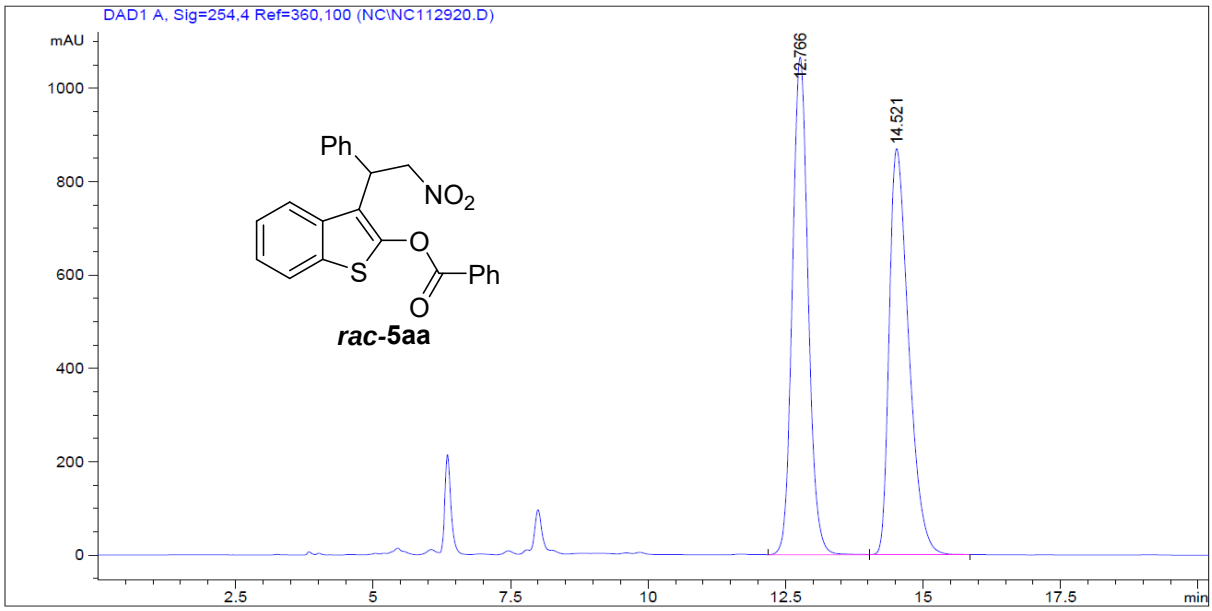
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.580	VB	0.1736	6247.54297	553.93451	98.1700
2	9.165	VB	0.2419	116.46260	7.47081	1.8300



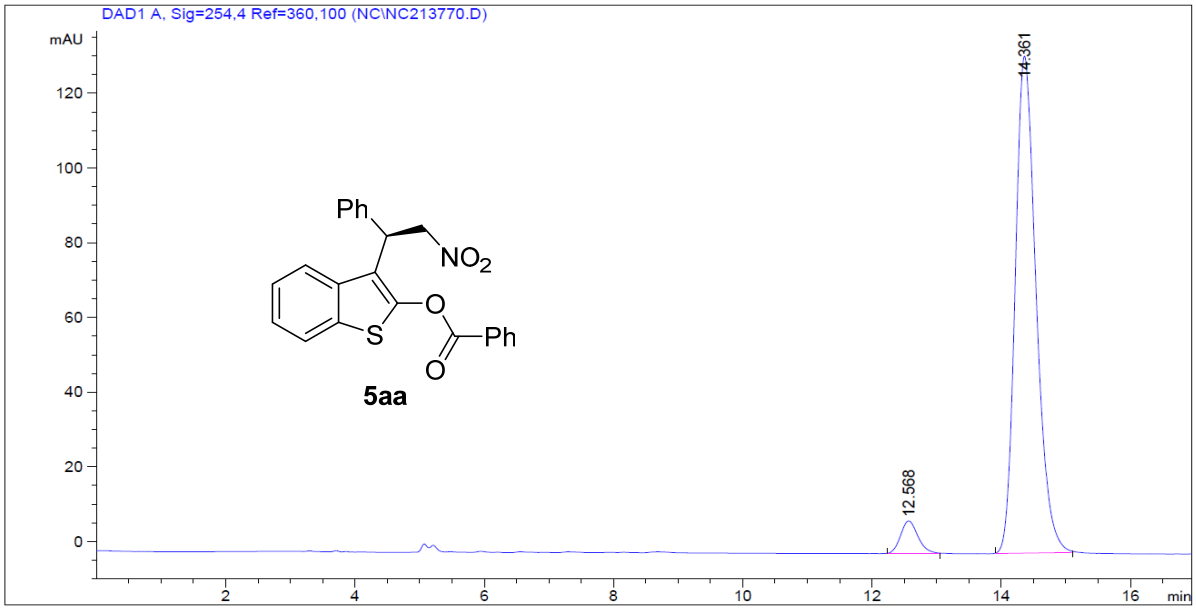
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.279	VB	0.1830	2955.59180	248.13443	49.8969
2	10.158	BB	0.2385	2967.80151	189.76013	50.1031



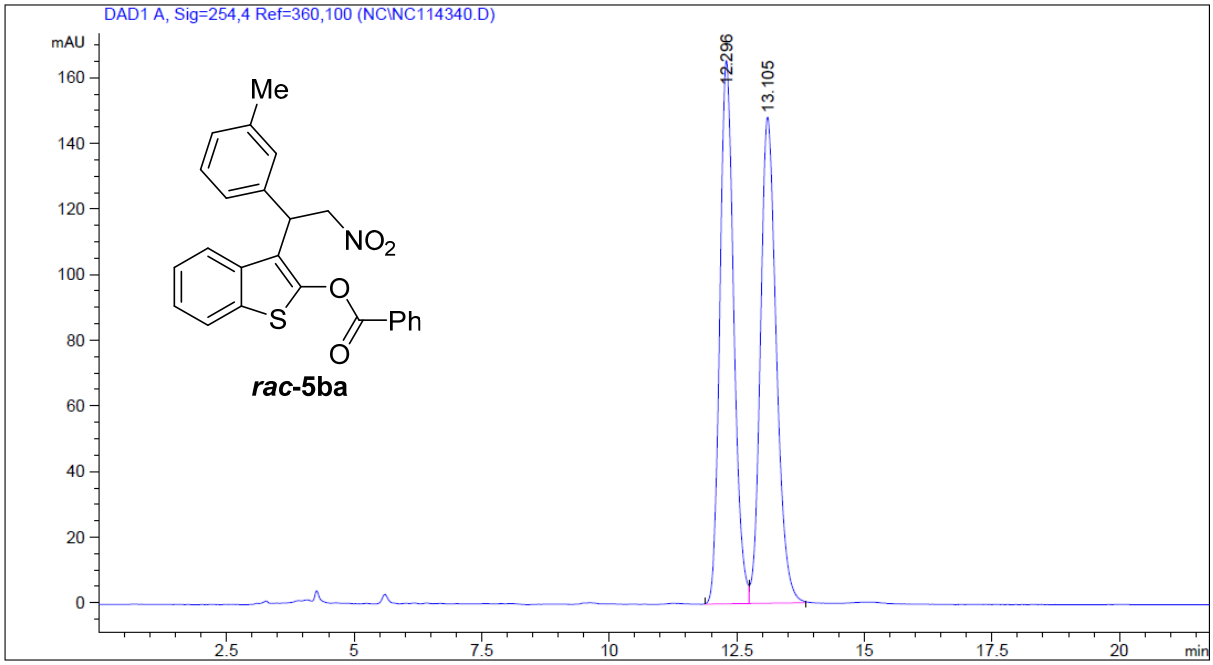
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.424	BB	0.1929	1.77729e4	1431.04163	95.6292
2	10.424	BB	0.2380	812.31348	52.65337	4.3708



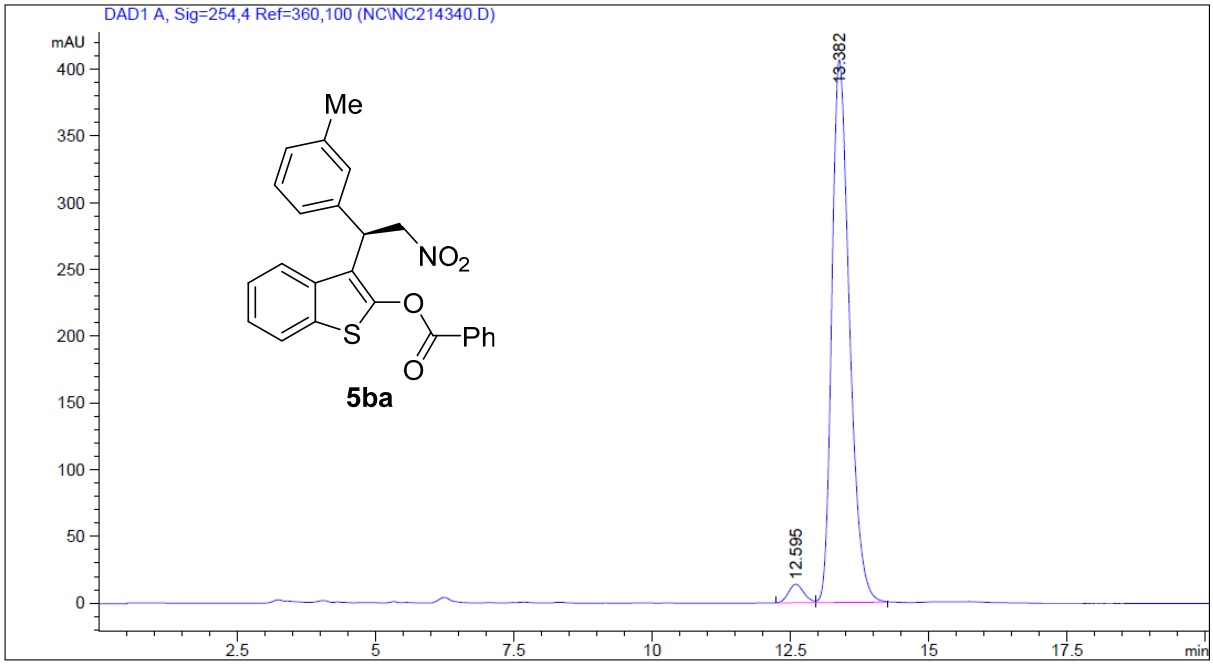
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.766	VV	0.3098	2.13660e4	1066.23230	49.9150
2	14.521	VB	0.3795	2.14388e4	869.98230	50.0850



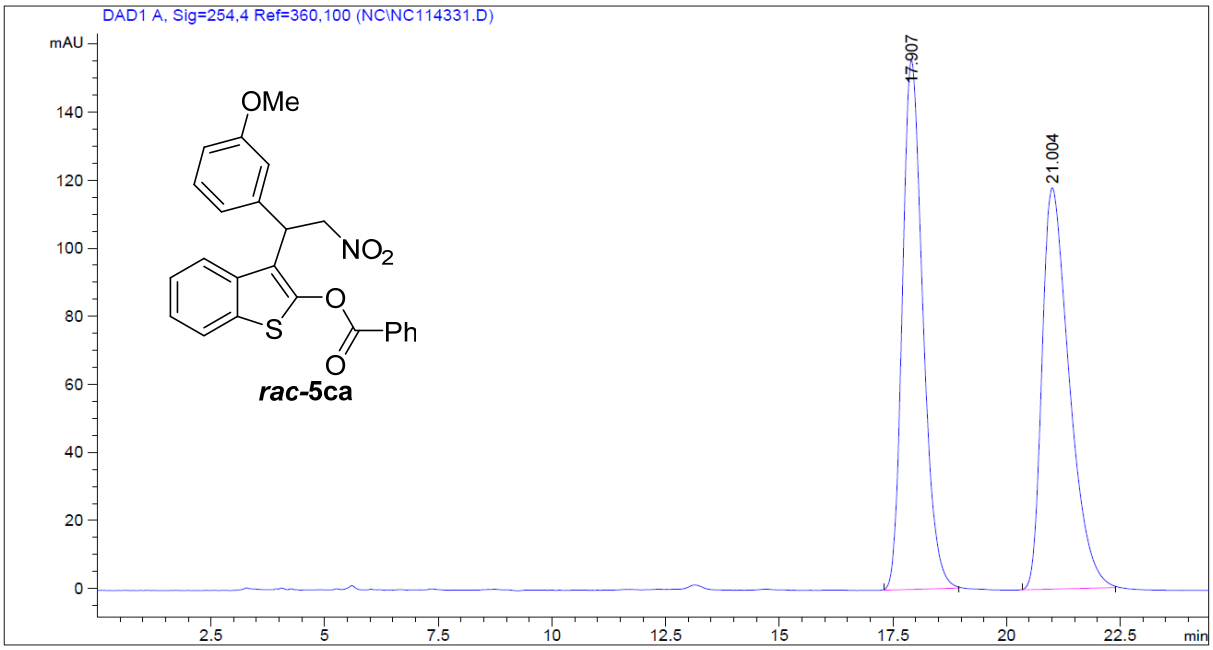
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.568	BB	0.2817	162.31677	8.69752	5.1589
2	14.361	BB	0.3456	2984.01538	133.06688	94.8411



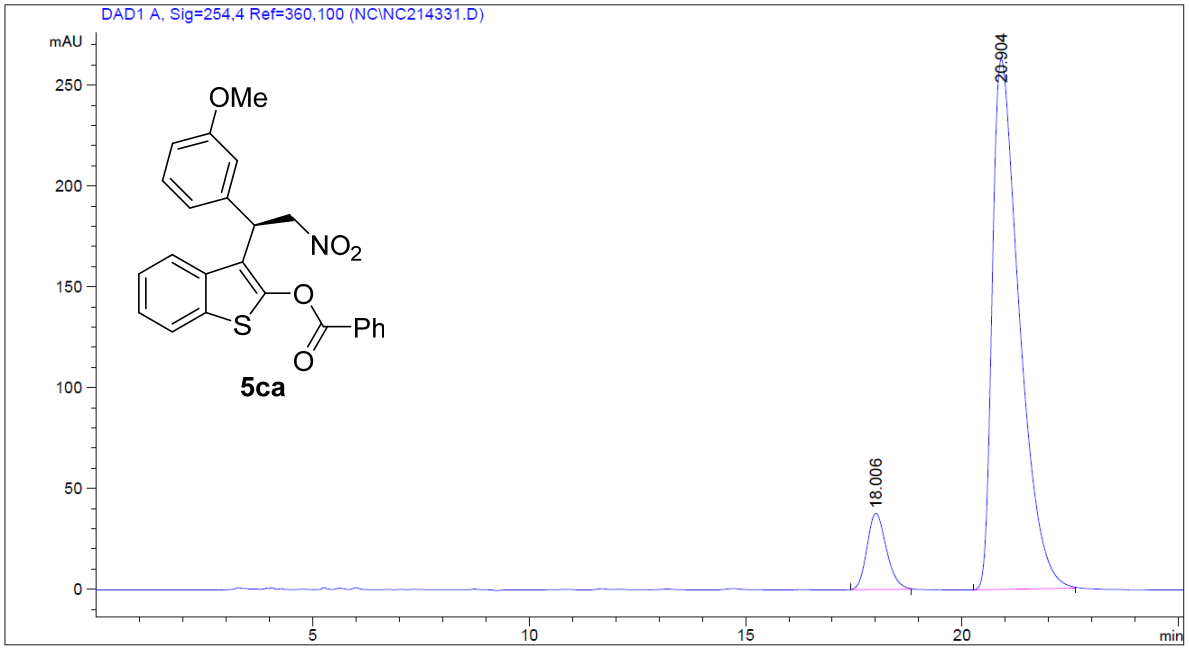
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.296	BV	0.2944	3156.19897	165.57129	49.5230
2	13.105	VB	0.3314	3217.00293	148.12973	50.4770



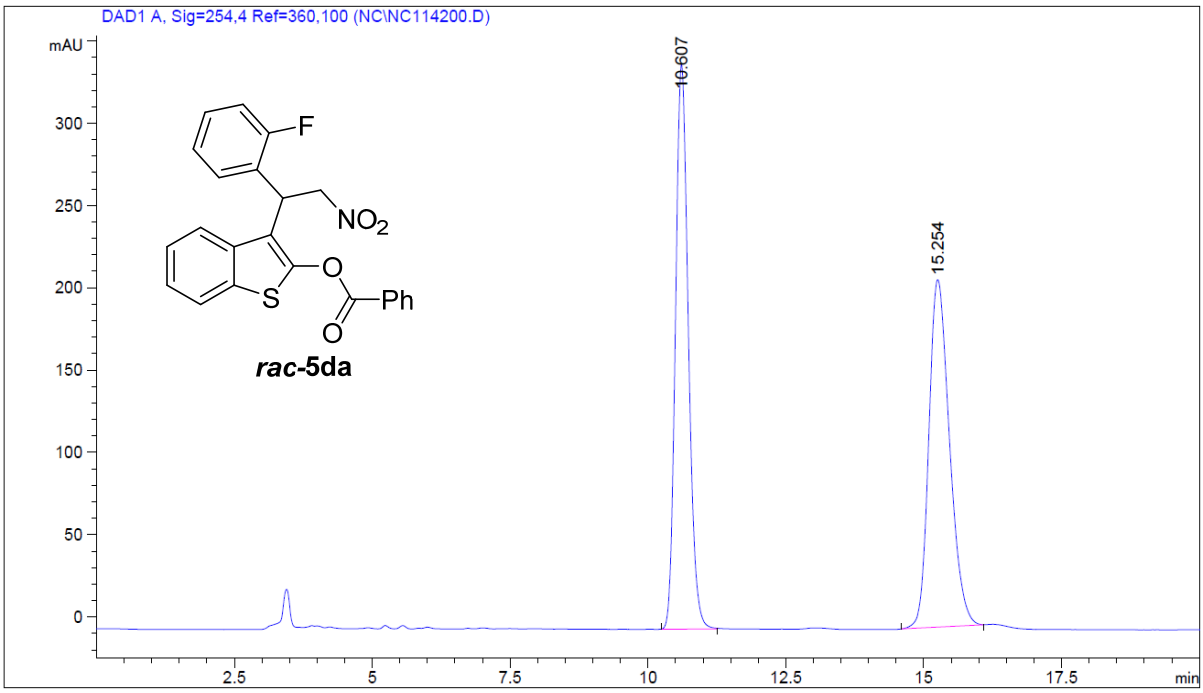
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.595	BV	0.2945	268.10394	13.93276	2.8893
2	13.382	VB	0.3405	9011.01953	406.72440	97.1107



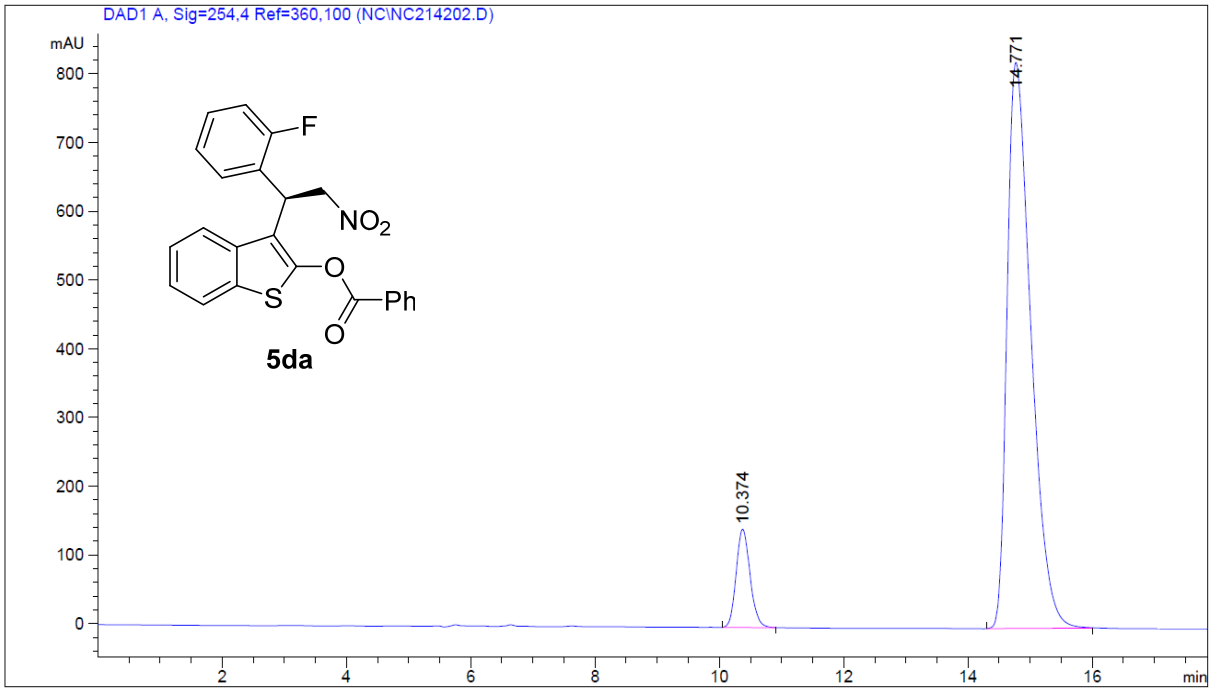
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.907	BB	0.4836	4872.92871	155.48630	49.7604
2	21.004	BB	0.6266	4919.86230	117.96192	50.2396



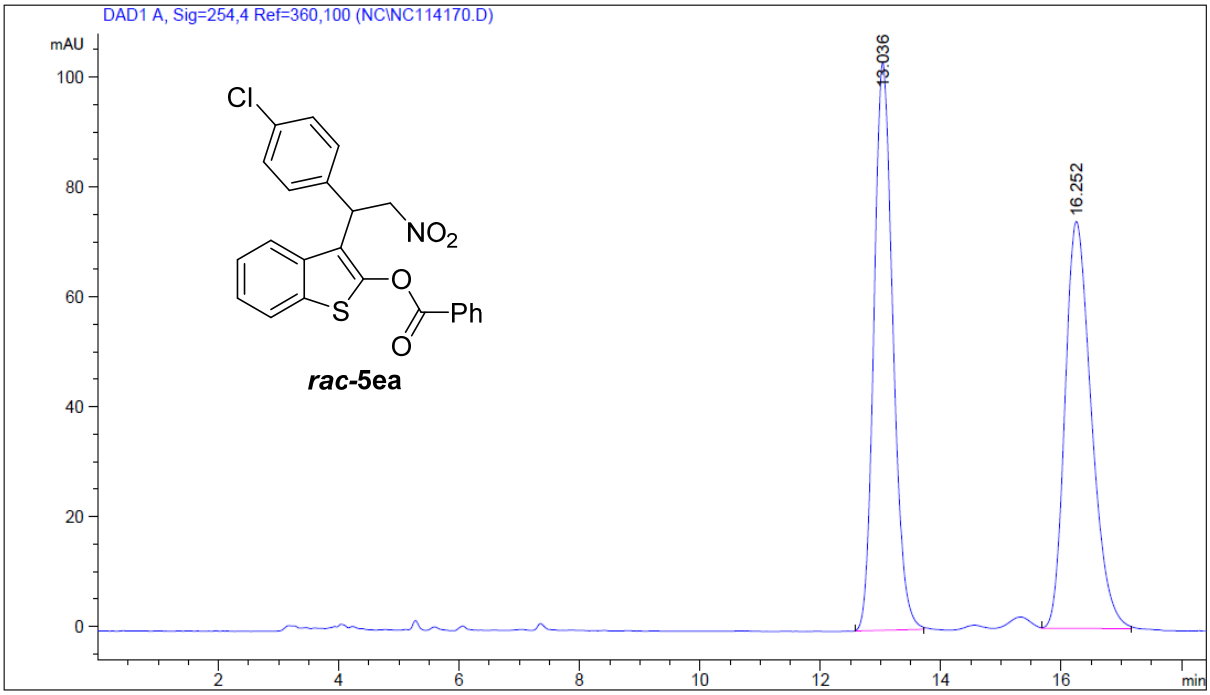
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.006	BB	0.4772	1178.54932	37.85860	9.3380
2	20.904	BB	0.6538	1.14425e4	262.89716	90.6620



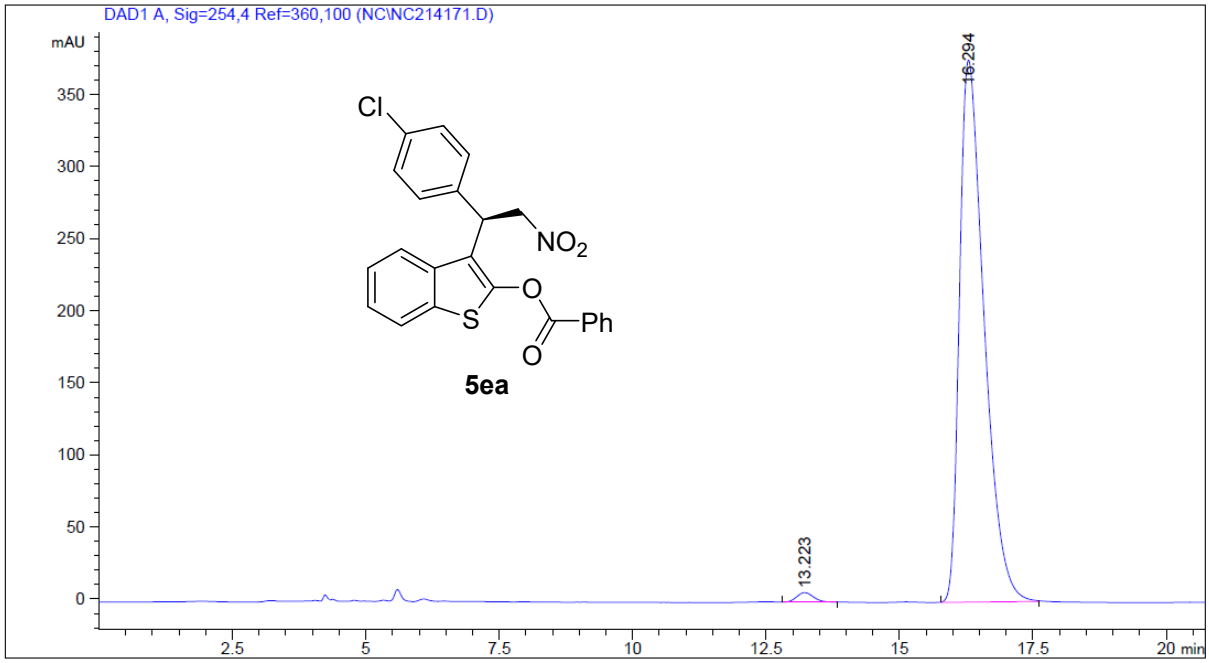
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.607	BB	0.2487	5552.13770	343.34833	50.2172
2	15.254	BB	0.4021	5504.11621	211.15509	49.7828



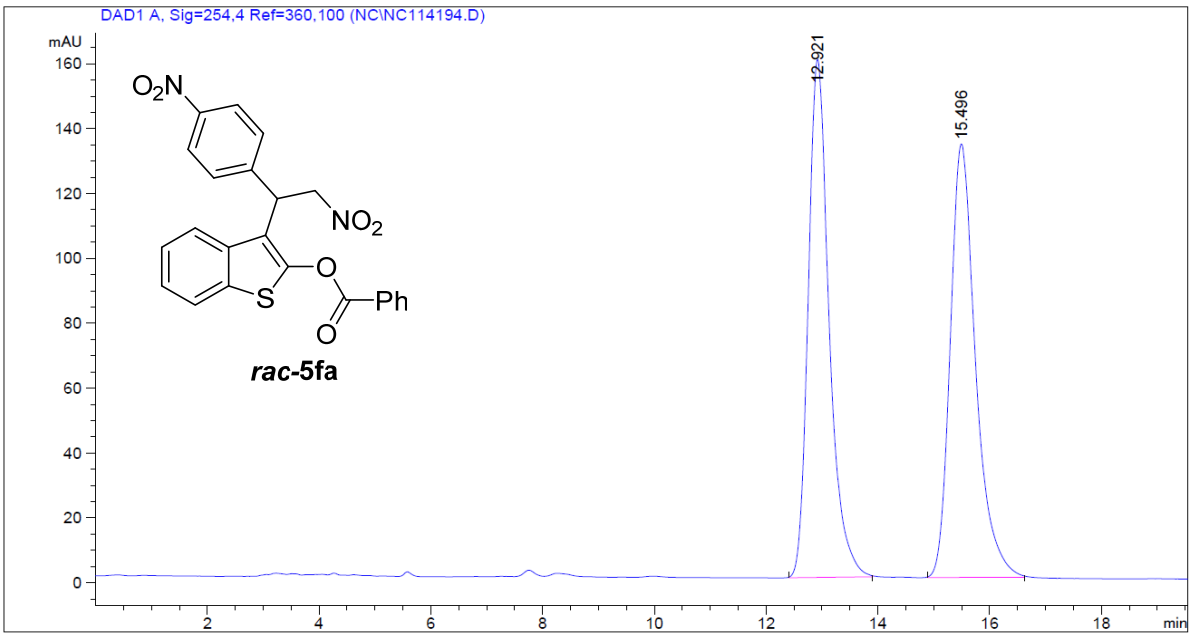
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.374	BB	0.2396	2226.78979	143.02846	9.2339
2	14.771	BB	0.4102	2.18885e4	823.33795	90.7661



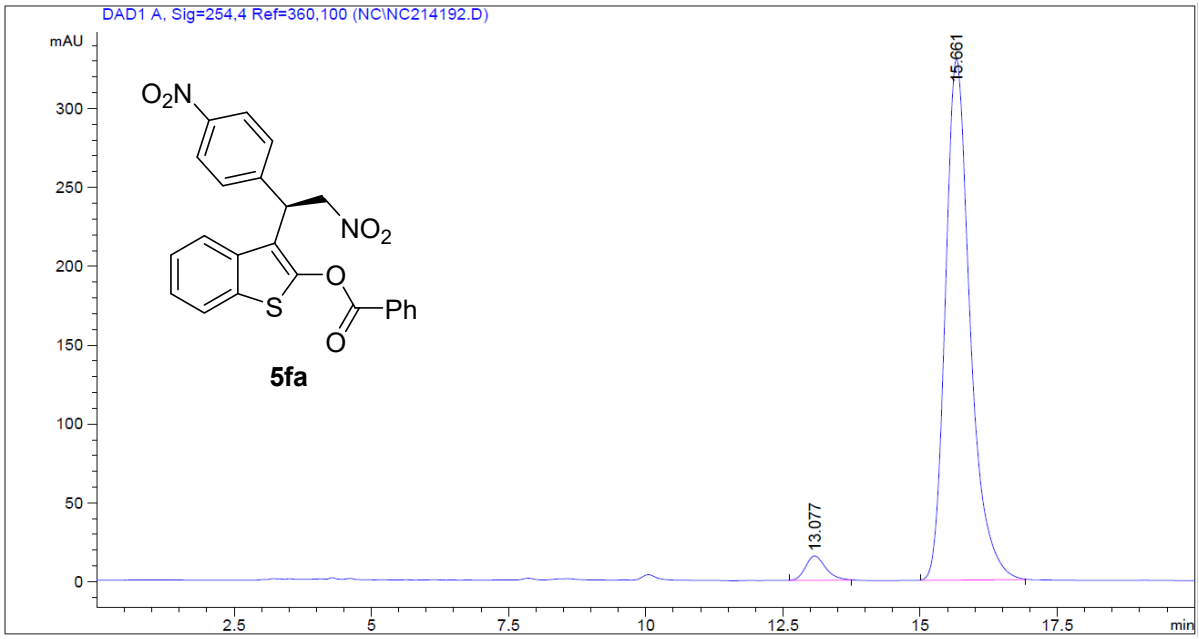
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.036	BB	0.3379	2267.42236	103.36366	50.0996
2	16.252	VB	0.4716	2258.40601	74.09304	49.9004



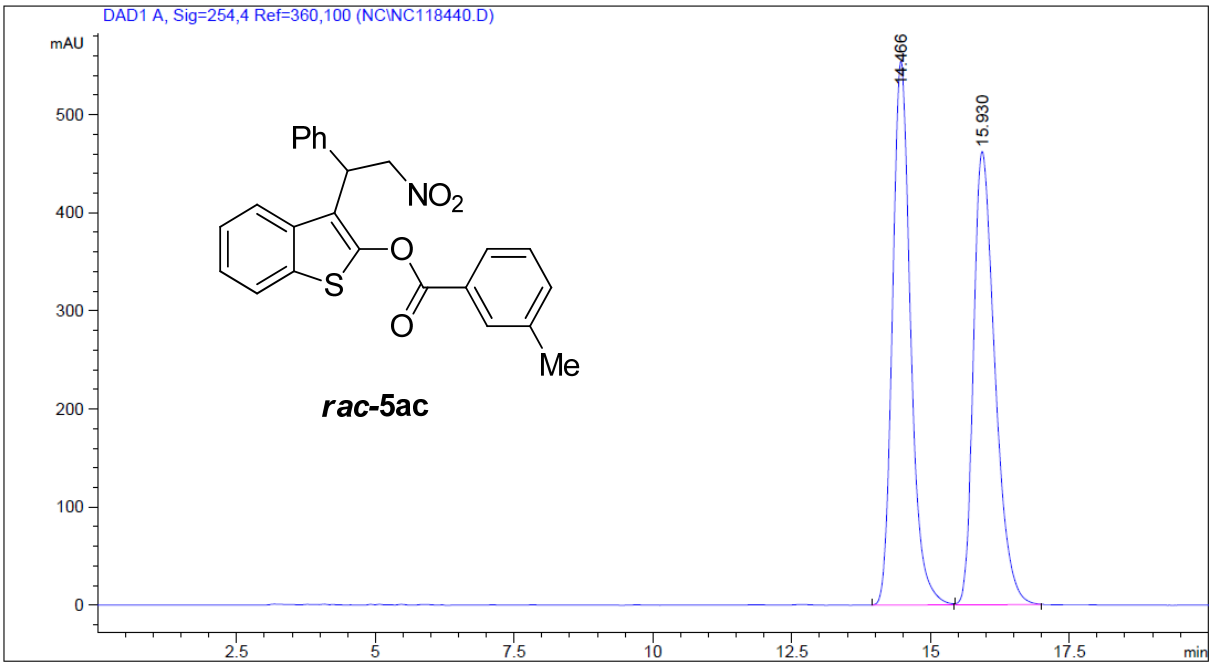
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.223	BB	0.3307	143.27058	6.56272	1.1771
2	16.294	BB	0.4894	1.20281e4	375.82846	98.8229



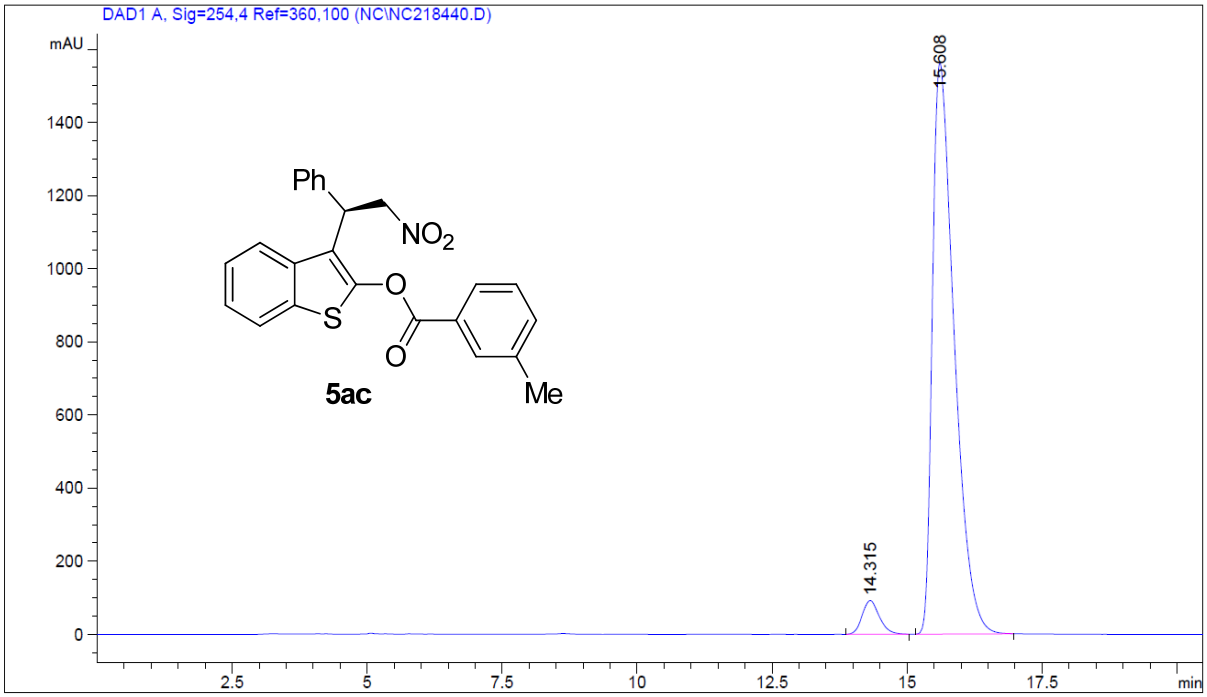
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.921	BB	0.3926	4141.35938	159.69089	49.6135
2	15.496	BB	0.4772	4205.88281	133.61923	50.3865



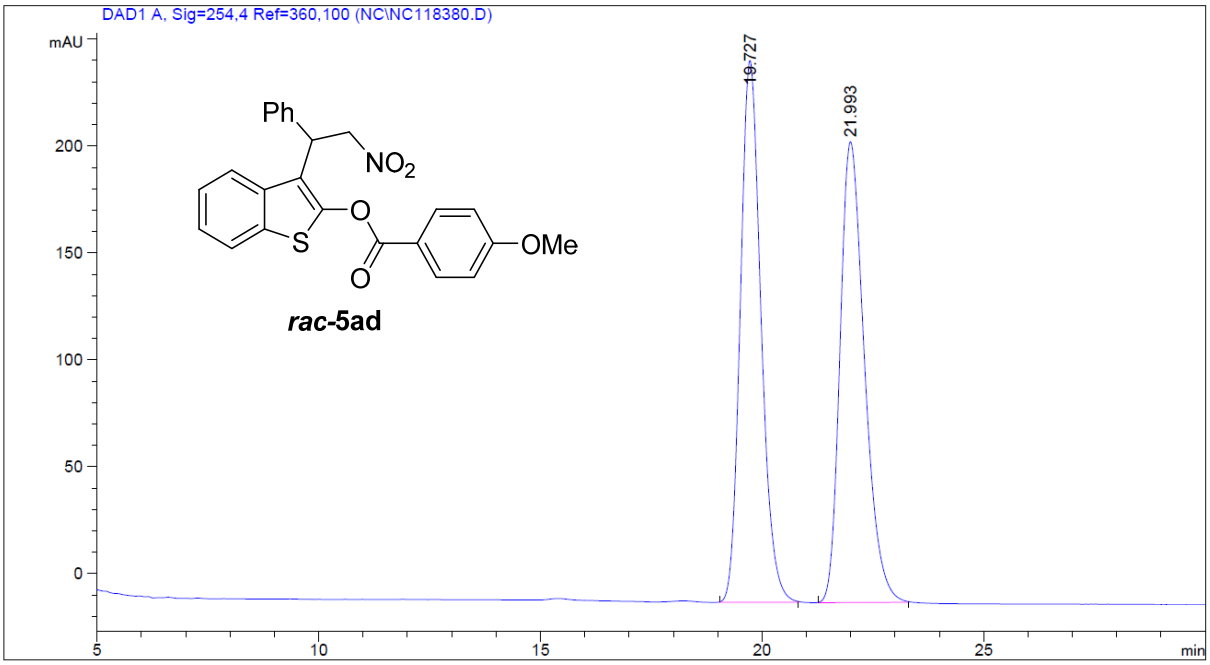
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.077	BB	0.3907	395.05270	15.43247	3.6705
2	15.661	BB	0.4759	1.03678e4	330.57544	96.3295



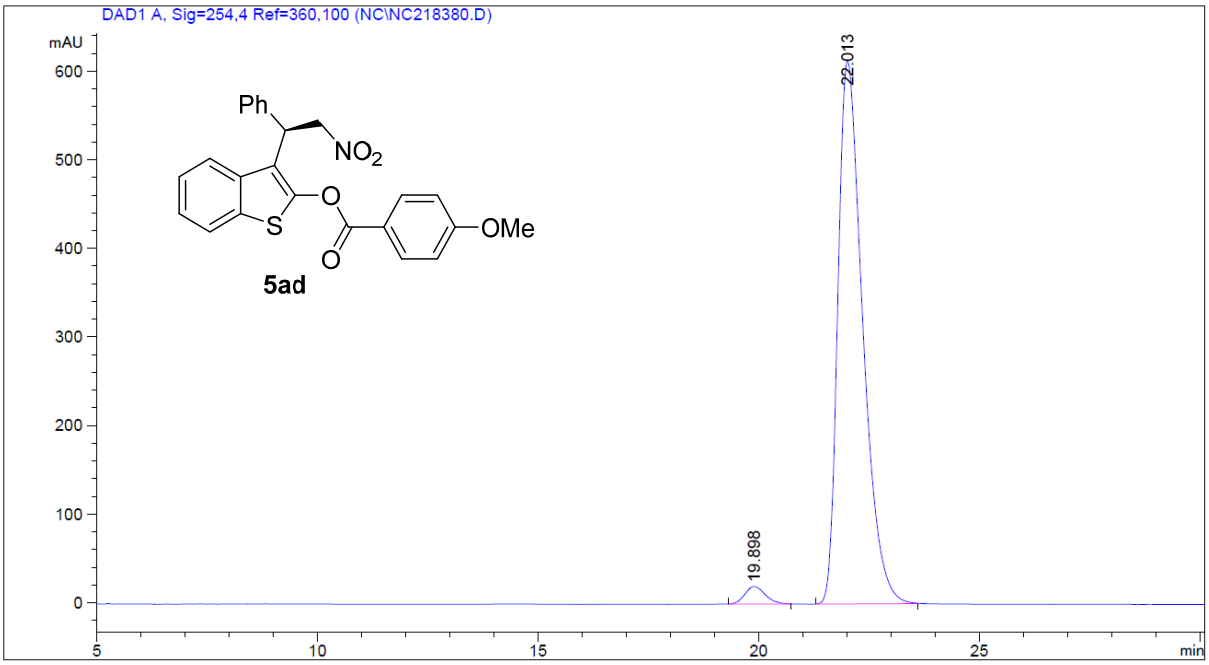
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.466	BB	0.3494	1.26167e4	554.54083	50.3829
2	15.930	BB	0.4117	1.24249e4	462.11707	49.6171



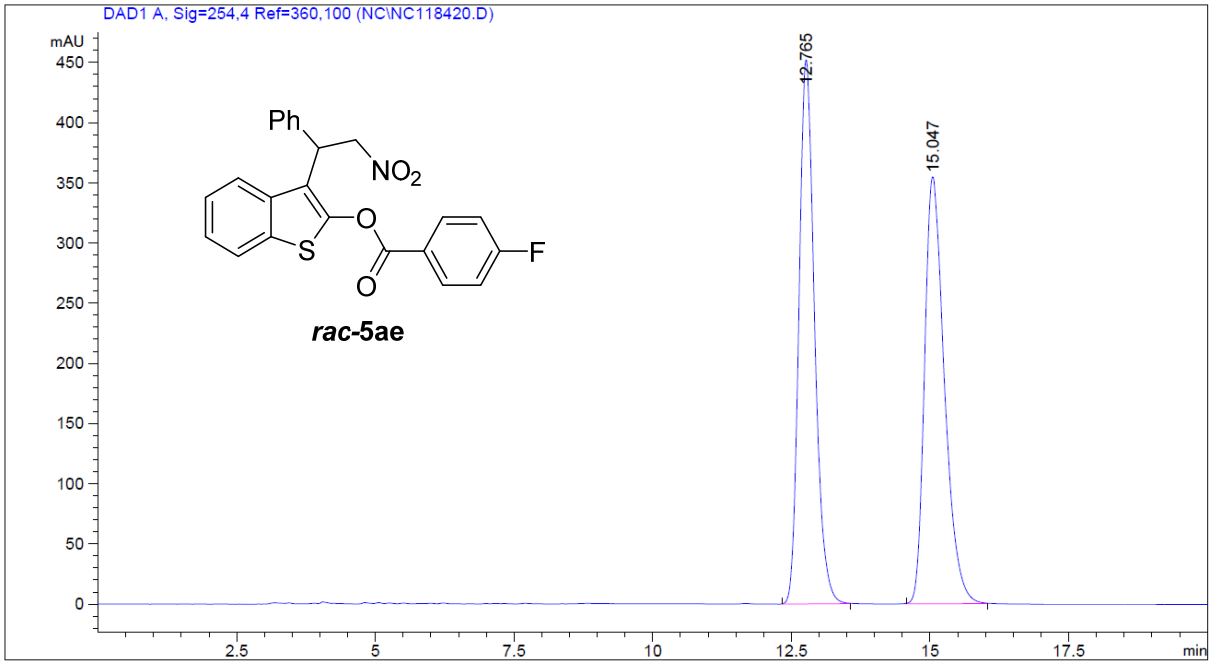
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.315	BB	0.3409	2043.06250	92.06934	4.4538
2	15.608	BB	0.4273	4.38290e4	1562.18201	95.5462



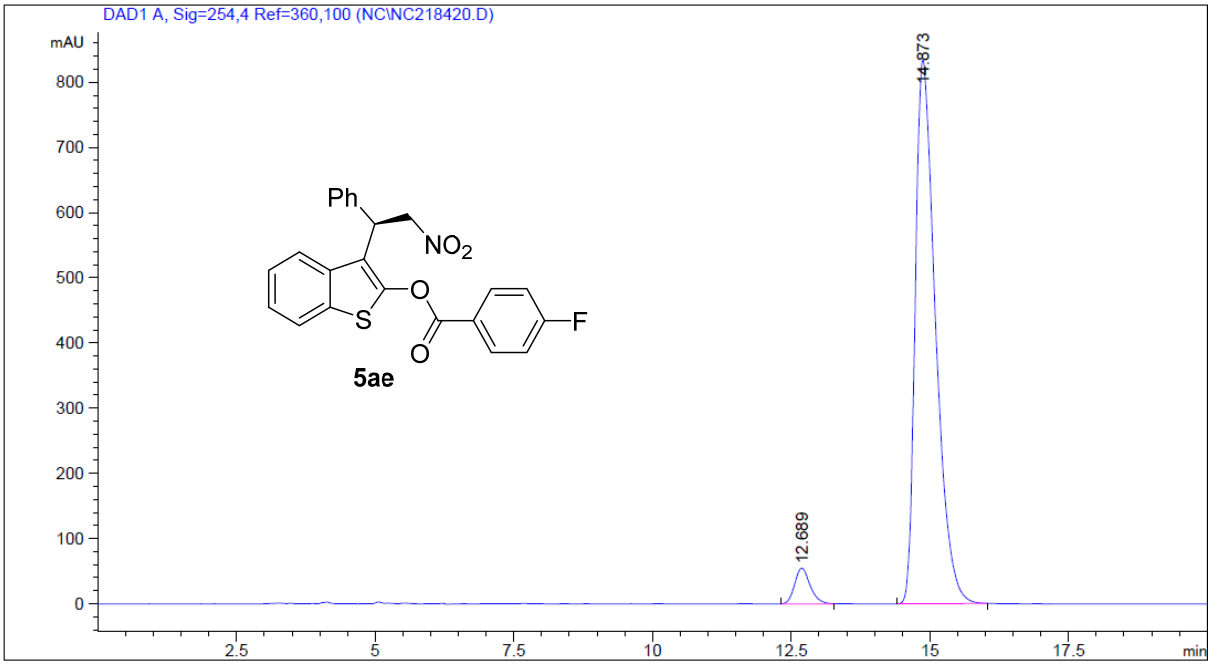
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.727	BB	0.4986	8220.27734	253.33257	49.9674
2	21.993	BB	0.5876	8231.01367	215.50906	50.0326



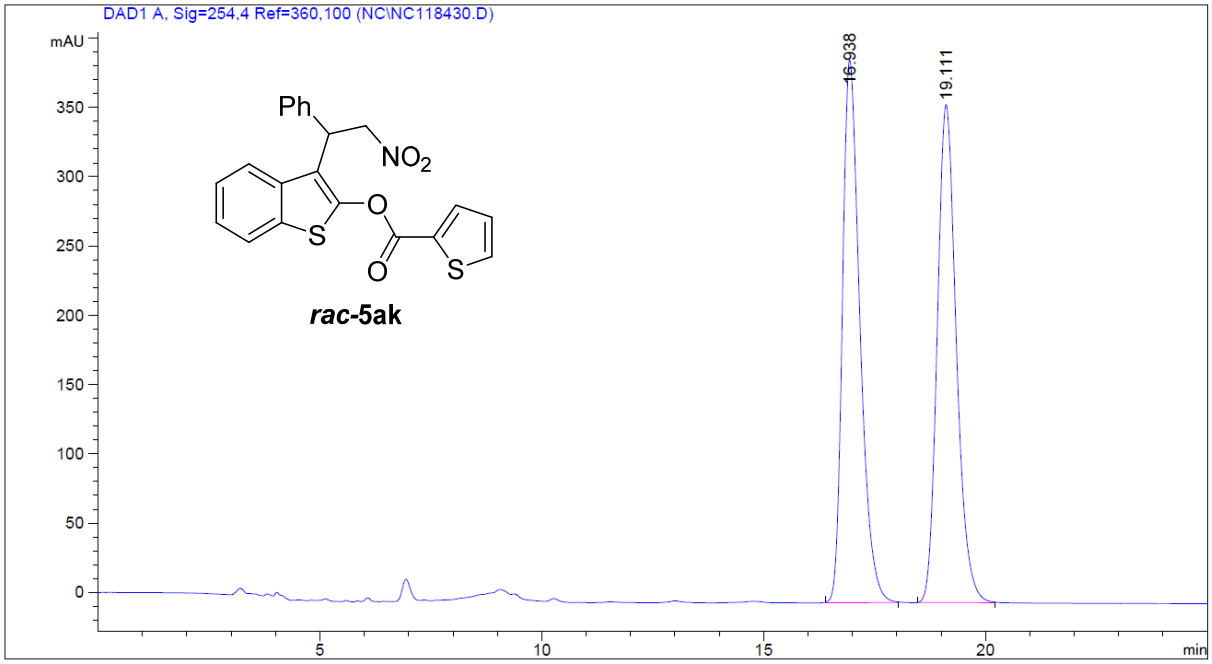
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.898	BB	0.4886	642.18207	19.89437	2.6186
2	22.013	BB	0.5945	2.38818e4	613.01630	97.3814



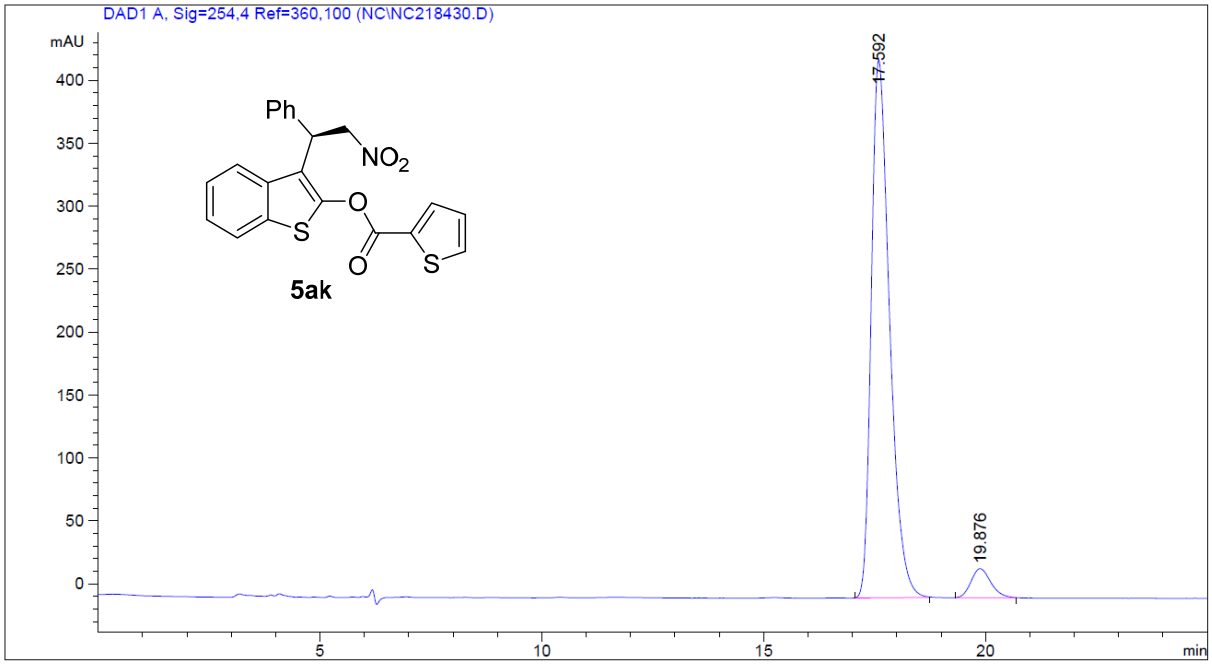
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.765	BB	0.3004	8848.68652	452.02194	50.0444
2	15.047	BB	0.3825	8832.97852	354.75439	49.9556



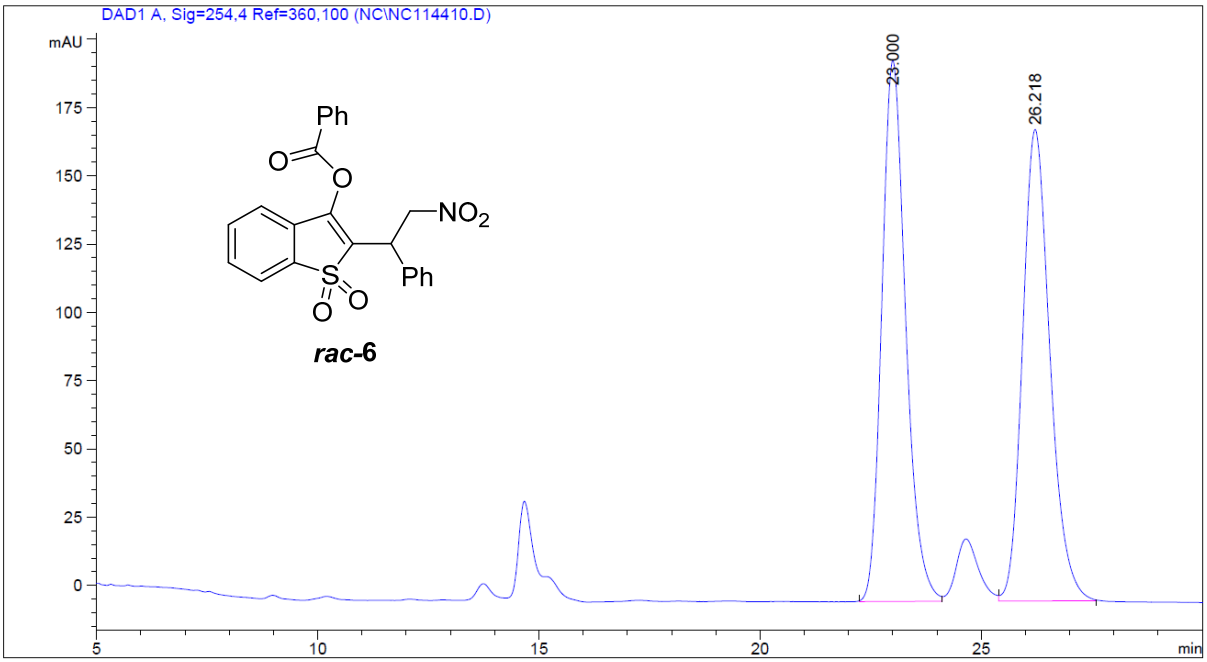
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.689	BB	0.2968	1065.35730	54.80965	4.8004
2	14.873	BB	0.3875	2.11278e4	834.24036	95.1996



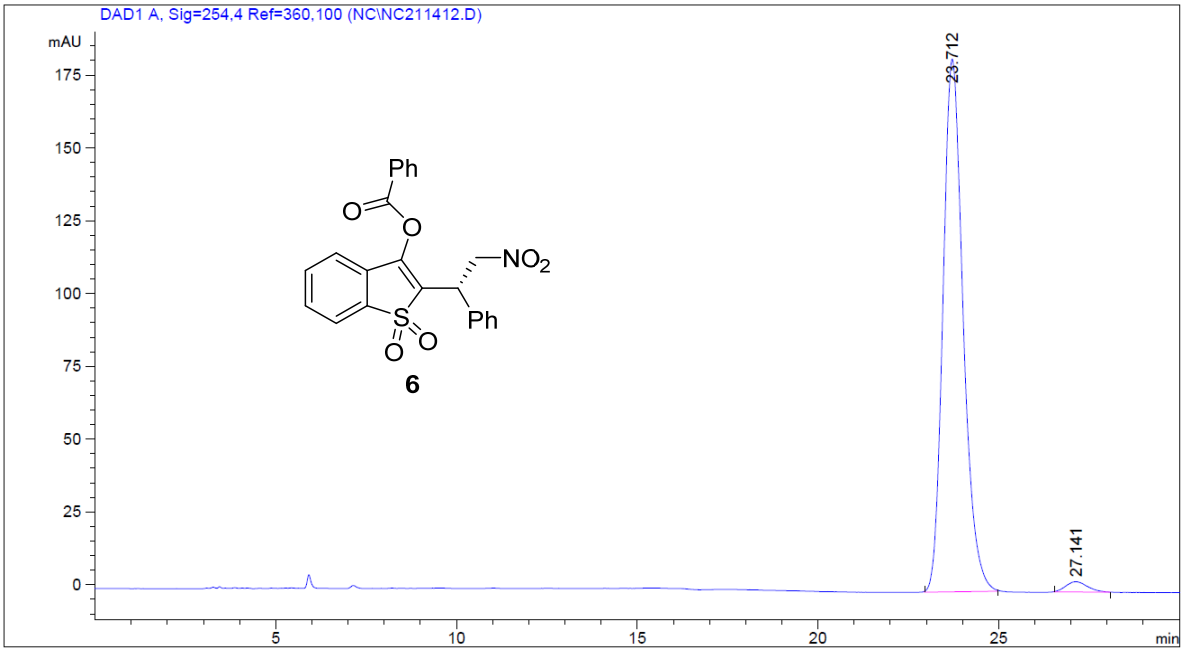
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.938	BB	0.4196	1.07286e4	391.67914	50.0232
2	19.111	BB	0.4580	1.07187e4	359.29184	49.9768



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.592	BB	0.4380	1.22330e4	427.26935	94.4253
2	19.876	BB	0.4773	722.21545	23.19302	5.5747



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.000	BB	0.5775	7427.56445	198.06184	49.9833
2	26.218	VB	0.6623	7432.52393	172.64172	50.0167



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.712	BB	0.5886	7066.24463	182.96451	97.9581
2	27.141	BB	0.5126	147.29483	3.53126	2.0419