Supporting Information

Squaramide-Catalyzed Enantioselective Michael Additions of Pyrazol-3-ones to ortho-Quinone Methides

Laura Carceller-Ferrer, Gonzalo Blay,* José R. Pedro* and Carlos Vila

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1. General Experimental Methods

Reactions were carried out in 5 mL vials under air unless otherwise indicated. Commercial reagents were used as purchased. Reactions were monitored by TLC analysis using Merck Silica Gel 60 F-254 thin layer plates and these are visualized using both an UV lamp (254 nm) and then a CAM solution (an aqueous solution of ceric ammonium molybdate). Flash column chromatography was performed on Merck Silica Gel 60, 0.040-0.063 mm. NMR spectra were run at 300 MHz for ^{1}H and 75 MHz for ^{13}C using residual nondeuterated solvent as internal standard ($CHCl_3$: δ 7.26 and δ 77.00 ppm respectively, MeOH: δ 3.34 ppm and δ 49.87 ppm respectively, Acetone: δ 2.05 ppm and δ 29.84 ppm respectively). Chemical shifts are given in ppm. The carbon multiplicity was established by DEPT experiments. High resolution mass spectra (HRMS-ESI) were recorded on a AB SCIEX Triple TOF^{TM} spectrometer equipped with an electrospray source with a capillary voltage of 4.5 kV (ESI).

Quinine (**Cat-1**), 5-methyl-2-phenol-2,4-dihydro-3H-pyrazol-3-one (**2a**) and 5-trifluoromethylpyrazolone (**2g**) were commercially available. Thiourea catalyst **Cat-2** was synthetized as described in the literature from quinine,[1a] and squaramide catalyst Cat-3 and Cat-4 synthetized as described in the literature from quinine and dihydroquinine, respectively.[1b] 2-(1-tosylalkyl)phenols **1** were prepared as described in the literature.[2] 2 4-Substituted pyrazolones were prepared according to the literature and references therein.[3]

2. General procedures

General Procedure for the Enantioselective Michael addition of pirazolones to *ortho*-quinone methines

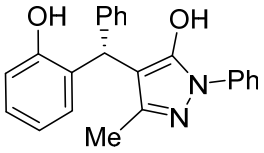
In a 5 mL vial, 2-(1-tosylalkyl)phenol **1** (0.1 mmol, 1 eq.), pyrazol-3-one **2** (0.12 mmol, 1.2 eq.), K_2CO_3 (0.15 mmols, 1.5 eq.), and the **Cat-3** (3.10 mg, 0.005 mmol, 5 mol%) were added. After $ClCH_2CH_2Cl$ (1 mL) and H_2O (0.5 mL) were added. The mixture was stirred at room temperature until TLC analysis indicated full conversion of the starting material. Finally, purification by flash chromatography (CH_2Cl_2:EtOAc, 95:5) on silica gel afforded compound **3**.

General Procedure for the non-enantioselective Michael addition of pirazolones to *ortho*-quinone methines

In a 5 mL vial, 2-(1-tosylalkyl)phenol **1** (0.1 mmol, 1 eq.), pyrazol-3-one **2** (0.12 mmol, 1.2 eq.), K_2CO_3 (0.15 mmols, 1.5 eq.), and the achiral catalyst 1-(3-(dimethylamino)propyl)-3-phenylthiourea (3.70 mg, 0.01 mmol, 10 mol%) were added. After CH_2Cl_2 (1 mL) and H_2O (0.5 mL) were added. The mixture was stirred at room temperature until TLC analysis indicated full conversion of the starting material. Finally, purification by flash chromatography (CH_2Cl_2:EtOAc, 95:5) on silica gel afforded compound **3**.

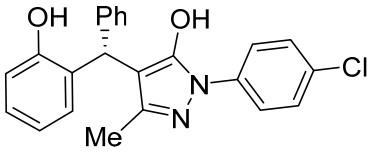
3. Characterization of products 3

(*S*)-4-((2-hydroxyphenyl)(phenyl)methyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-ol (3aa)



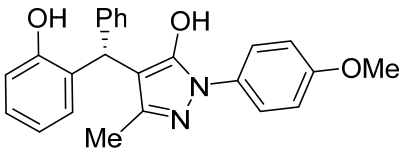
White solid, M. p.= 91-92 °C; $[\alpha]_D^{20}$ = +56.8 (c 0.83, $CHCl_3$). The enantiomeric excess (91%) was determined by chiral HPLC (Chiralpak ADH), hexane-iPrOH 90:10, 1 mL/min, major enantiomer t_r = 27.15 min, minor enantiomer t_r = 31.97 min. **^{1}H NMR (300 MHz, CD_3OD)** δ 7.71–7.64 (m, 2H), 7.51–7.43 (m, 2H), 7.33–7.25 (m, 3H), 7.24–7.16 (m, 3H), 7.11 (ddd, *J* = 8.2, 7.3, 1.8 Hz, 1H), 7.01 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.80 (ddd, *J* = 14.9, 7.7, 1.1 Hz, 2H), 5.70 (s, 1H), 1.89 (s, 3H) ppm. **^{13}C NMR (100 MHz, CD_3OD)** δ 157.31 (C), 149.98 (C), 144.64 (C), 138.71 (C), 132.14 (CH), 131.19 (C), 131.02 (CH), 130.58 (CH), 129.93 (CH), 129.87 (C), 129.56 (CH), 128.04 (CH), 127.85 (CH), 122.92 (CH), 121.11 (CH), 117.32 (CH), 110.25 (C), 41.82 (CH), 12.81 (CH_3) ppm. **HRMS (ESI)** m/z 357.1584 $[M + H]^+$, $C_{23}H_{21}N_2O_2$ requires 357.1598.

(*S*)-1-(4-chlorophenyl)-4-((2-hydroxyphenyl)(phenyl)methyl)-3-methyl-1*H*-pyrazol-5-ol (3ab)



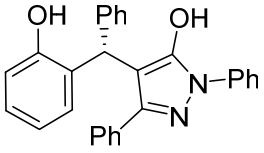
White solid, M. p.= 145-147 °C; $[\alpha]_D^{20}$ = +16.98 (c 0.76, MeOH). The enantiomeric excess (91%) was determined by chiral HPLC (Chiralpak ADH), hexane-iPrOH 90:10, 1 mL/min, major enantiomer t_r = 21.11 min, minor enantiomer t_r = 27.78 min. **^{1}H NMR (300 MHz, CD_3OD)** δ 7.69 (d, *J* = 9.0 Hz, 2H), 7.46 (d, *J* = 8.9 Hz, 2H), 7.29 (tt, *J* = 6.7, 1.1 Hz, 2H), 7.24–7.15 (m, 3H), 7.14–7.07 (m, 1H), 6.99 (dd, J = 7.6, 1.7 Hz, 1H), 6.82 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.81–6.75 (m, 1H), 5.69 (s, 1H), 1.88 (s, 3H) ppm. **^{13}C NMR (100 MHz, CD_3OD)** δ 157.27 (C), 150.86 (C), 144.55 (C), 137.61 (C), 133.09 (C), 132.11 (CH), 131.08 (C), 131.02 (CH), 130.60 (CH), 129.95(CH), 129.57 (CH), 127.89 (CH), 123.90 (CH), 121.09 (CH), 117.22 (CH), 41.73 (CH), 12,86 (CH_3) ppm. **HRMS (ESI)** m/z 391.1210 $[M + H]^+$, $C_{23}H_{20}ClN_2O_2$ requires 391,1208.

(*S*)-4-((2-hydroxyphenyl)(phenyl)methyl)-1-(4-methoxyphenyl)-3-methyl-1*H*-pyrazol-5-ol (3a)



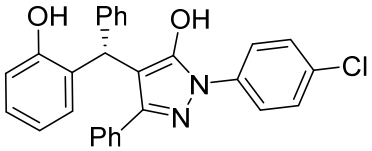
Oil; $[\alpha]_D^{20}$ = +12.9 (c 1.7, MeOH). The enantiomeric excess (88%) was determined by chiral HPLC (Chiralpak ADH), hexane-iPrOH 80:20, 1 mL/min, major enantiomer t_r = 11.75 min, minor enantiomer t_r = 19.61 min. **^{1}H NMR (300 MHz, CD_3OD)** δ 7.53 (d, J = 9.2 Hz, 2H), 7.29 (ddd, J = 7.5, 4.4, 1.4 Hz, 2H), 7.23–7.16 (m, 3H), 7.14–7.08 (m, 1H), 7.06–6.99 (m, 3H), 6.83 (dd, J = 6.6, 1.2 Hz, 1H), 6.82–6.76 (m, 1H), 5.69 (s, 1H), 3.84 (s, 3H), 1.88 (s, 3H) ppm. **^{13}C NMR (100 MHz, CD_3OD)** δ 157.14 (C), 155.49 (C), 147.26 (C), 141.31 (C), 130.98 (CH), 130.25 (C), 129.30 (CH), 127.67 (CH), 127.52 (CH), 125.44 (CH), 121.18 (CH), 119.03 (CH), 117.34 (C), 113.70 (CH), 113.63 (C), 107.85 (C), 54.62 (CH_3), 41.78 (CH), 10.61 (CH_3) ppm. **HRMS (ESI)** m/z 387.1708 $[M + H]^+$, $C_{23}H_{23}N_2O_3$ requires 387.1703.

(*S*)-4-((2-hydroxyphenyl)(phenyl)methyl)-1,3-diphenyl-1*H*-pyrazol-5-ol (3ad)



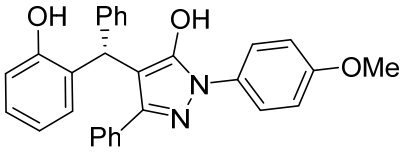
White solid, M. p.= 126-127 °C; $[\alpha]_D^{20}$ = +2.4 (c 1.37, MeOH). The enantiomeric excess (70%) was determined by chiral HPLC (Chiralpak IC), hexane-iPrOH 80:20, 1 mL/min, major enantiomer t_r = 7.31 min, minor enantiomer t_r = 22.17 min. **^{1}H NMR (300 MHz, CD_3OD)** δ 7.75 (dd, *J* = 8.7, 1.2 Hz, 2H), 7.55–7.49 (m, 4H), 7.45 (ddd, *J* = 5.9, 4.1, 1.4 Hz, 4H), 7.36–7.29 (m, 1H), 7.27–7.14 (m, 7H), 7.10 (ddd, *J* = 8.0, 7.4, 1.7 Hz, 1H), 6.81 (dd, *J* = 4.8, 1.1 Hz, 1H), 6.80–6.75 (m, 1H), 5.67 (s, 1H) ppm. **^{13}C NMR (100 MHz, CD_3OD)** δ 156.84 (C), 152.90 (C), 144.47 (C), 133.24 (CH), 131.46 (C), 131.37 (C), 131.04 (CH), 130.70 (CH), 130.49 (CH), 130.28 (CH), 129.82 (CH), 129.71 (CH), 128.42 (CH), 127.73 (CH), 123.74 (CH), 123.70 (CH), 121.44 (CH), 117.79 (CH), 43.03 (CH) ppm. **HRMS (ESI)** m/z 419.1759 $[M + H]^+$, $C_{28}H_{23}N_2O_2$ requires 419.1754.

(*S*)-1-(4-chlorophenyl)-4-((2-hydroxyphenyl)(phenyl)methyl)-3-phenyl-1*H*-pyrazol-5-ol (3ae)



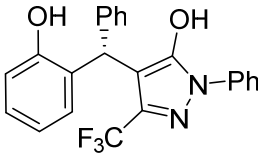
White solid, M. p.= 119-120 °C; $[\alpha]_D^{20}$ = +5.79 (c 1.88, MeOH). The enantiomeric excess (82%) was determined by chiral HPLC (Chiralpak ADH), hexane-iPrOH 90:10, 1 mL/min, major enantiomer t_r = 10.51 min, minor enantiomer t_r = 31.40 min. **^{1}H NMR (300 MHz, CD_3OD)** δ 7.77 (d, *J* = 8.9 Hz, 2H), 7.55–7.43 (m, 7H), 7.27–7.14 (m, 6H), 7.09 (ddd, *J* = 8.0, 7.3, 1.7 Hz, 1H), 6.83–6.73 (m, 2H), 5.67 (s, 1H) ppm. **^{13}C NMR (126 MHz, CD_3OD)** δ 163.66 (C), 156.77 (C), 153.51 (C), 144.44 (C), 137.81 (C), 133.50 (C), 133.18 (CH), 131.24 (C), 131.05 (CH), 130.67 (CH), 130.63 (CH), 130.50 (CH), 130.33 (CH), 129.84 (CH), 129.71 (CH), 129.04 (C), 127.77 (CH), 124.61 (CH), 122.64 (C), 121.43 (CH), 117.62 (CH), 42.85 (CH) ppm. **HRMS (ESI)** m/z 453.1339 $[M + H]^+$, $C_{28}H_{22}ClN_2O_2$ requires 453.1364.

(*S*)-4-((2-hydroxyphenyl)(phenyl)methyl)-1-(4-methoxyphenyl)-3-phenyl-1*H*-pyrazol-5-ol (3af)



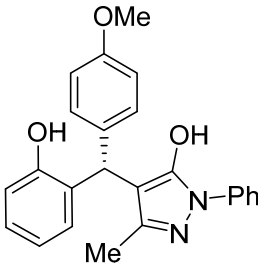
White solid; $[\alpha]_D^{20}$ = +11.4 (c 2.04, MeOH). The enantiomeric excess (99%) was determined by chiral HPLC (Chiralpak IC), hexane-iPrOH 80:20, 1 mL/min, major enantiomer t_r = 16.17 min, minor enantiomer t_r = 8.26 min. **^{1}H NMR (300 MHz, CD_3OD)** *δ* 7.61 (d, *J* = 9.1 Hz, 2H), 7.53–7.49 (m, 2H), 7.44 (dd, *J* = 5.2, 2.1 Hz, 3H), 7.25–7.09 (m, 7H), 7.05 (d, *J* = 9.1 Hz, 2H), 6.86–6.72 (m, 2H), 5.65 (s, 1H), 3.85 (s, 3H) ppm. **^{13}C NMR (100 MHz, CD_3OD)** *δ* 160.90 (C), 156.83 (C), 151.86 (C), 144.45 (C), 133.31 (CH), 131.50 (C), 131.34 (CH), 130.64 (CH), 130.48 (CH), 130.19 (CH), 129.79 (CH), 129.74 (CH), 128.9 (C), 127.69 (CH), 126.25 (CH), 124.0 (C), 121.50 (CH), 118.06 (CH), 116.19 (CH), 115.7 (C), 56.83 (CH_3), 43.31 (CH) ppm. **HRMS (ESI)** m/z 449.1866 $[M + H]^+$, $C_{29}H_{25}N_2O_3$ requires 449.1860.

(*S*)-4-((2-hydroxyphenyl)(phenyl)methyl)-1-phenyl-3-(trifluoromethyl)-1*H*-pyrazol-5-ol (3ag)



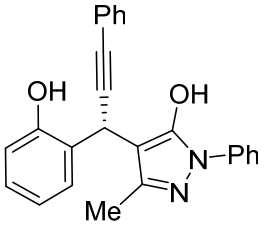
Oil; $[\alpha]_D^{20}$ = -3.72 (c 0.83, MeOH). The enantiomeric excess (14%) was determined by chiral HPLC (Chiralpak ADH), hexane-iPrOH 80:20, 1 mL/min, major enantiomer t_r = 13.65 min, minor enantiomer t_r = 17.89 min. **^{1}H NMR (300 MHz, CD_3OD)** *δ* 7.98 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.61–7.51 (m, 4H), 7.37–7.31 (m, 3H), 7.27 (dd, *J* = 8.6, 0.6 Hz, 2H), 7.13 (ddd, *J* = 8.1, 7.4, 1.7 Hz, 1H), 6.91 (td, *J* = 7.6, 1.2 Hz, 1H), 6.69 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.13 (s, 1H) ppm. **^{13}C NMR (100 MHz, CD_3OD)** *δ* 157.44 (C), 146.81 (C), 138.03 (C), 135.67 (C), 132.35 (CH), 131.65 (CH), 131.47 (CH), 131.15 (CH), 130.80 (CH), 130.28 (CH), 130.23 (CH), 129.87 (C), 122.19 (C), 121.25 (CH), 116.97 (CH), 68.91 (CH) ppm. **^{19}F NMR (282 MHz, CD_3OD)** *δ* 61.38 (s, 3F). **HRMS (ESI)** m/z 411.1319 $[M + H]^+$, $C_{23}H_{18}F_3N_2O_2$ requires 411.1315.

(*S*)-4-((2-hydroxyphenyl)(4-methoxyphenyl)methyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-ol (3ba)



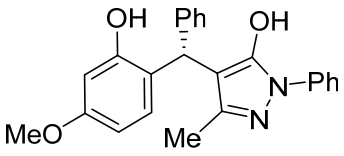
White solid, M. p.= 129-130 °C; $[\alpha]_D^{20}$ = +5.39 (c 1.58, MeOH). The enantiomeric excess (86%) was determined by chiral HPLC (Chiralpak IC), hexane-iPrOH 80:20, 1 mL/min, major enantiomer t_r = 18.57 min, minor enantiomer t_r = 35.11 min. **^{1}H NMR (300 MHz, CD_3OD)** *δ* 7.66 (dd, J = 8.7, 1.1 Hz, 2H), 7.46 (t, J = 7.9 Hz, 2H), 7.32–7.24 (m, 1H), 7.08 (d, J = 8.3 Hz, 3H), 7.01 (dd, J = 7.6, 1.6 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.80 (ddd, J = 14.5, 7.8, 1.1 Hz, 2H), 5.64 (s, 1H), 3.78 (s, 3H), 1.89 (s, 3H) ppm. **^{13}C NMR (100 MHz, CD_3OD)** *δ* 160.33 (C), 157.28 (C), 149.90 (C), 138.72 (C), 136.49 (C), 132.08 (CH), 131.54 (C), 131.50 (CH), 131.02 (CH), 130.28 (C), 129.48 (CH), 128.02 (CH), 122.89 (CH), 121.09 (CH), 117.31 (CH), 115.36 (CH), 110.49 (C), 56.52 (CH_3), 41.05 (CH), 12.77 (CH_3) ppm. **HRMS (ESI)** m/z 387.1710 $[M + H]^+$, $C_{24}H_{23}N_2O_3$ requires 387.1703.

(*S*)-4-(1-(2-hydroxyphenyl)-3-phenylprop-2-yn-1-yl)-3-methyl-1-phenyl-1*H*-pyrazol-5-ol (3ca)



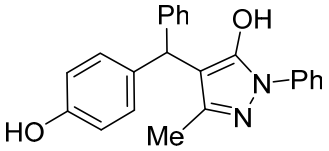
White solid, M. p.= 110-111 °C; $[\alpha]_D^{20}$ = -27.86 (c 0.39, MeOH). The enantiomeric excess (91%) was determined by chiral HPLC (Lux-Amilosa-1), hexane-iPrOH 90:10, 1 mL/min, major enantiomer t_r = 25.97 min, minor enantiomer t_r = 20.20 min. **^{1}H NMR (300 MHz, CD_3OD)** *δ* 7.73 (dd, *J* =7.6, 1.7 Hz, 1H), 7.68–7.63 (m, 2H), 7.53–7.44 (m, 4H), 7.37–7.26 (m, 4H), 7.13 (td, *J* = 7.7, 1.7 Hz, 1H), 6.90 (td, *J* = 7.5, 1.2 Hz, 1H), 6.83 (dd, *J* = 8.0, 1.1 Hz, 1H), 5.45 (s, 1H), 2.32 (s, 3H) ppm. **^{13}C NMR (100 MHz, CD_3OD)** *δ* 156.58 (C), 148.74 (C), 138.53 (C), 133.45 (CH), 131.07 (CH), 130.55 (CH), 130.28 (CH), 130.06 (CH), 129.88 (CH), 128.89 (C), 128.32 (CH), 125.85 (C), 123.22 (CH), 121.42 (CH), 121.29 (C), 117.90 (CH), 107.64 (C), 90.74 (C), 84.69 (C), 28.85 (CH), 12.68 (CH_3) ppm. **HRMS (ESI)** m/z 381.1590 $[M + H]^+$, $C_{25}H_{21}N_2O_2$ requires 381.1598.

(*S*)-4-((2-hydroxy-4-methoxyphenyl)(phenyl)methyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-ol (3da)



White solid, M. p.= 189-191 °C; $[\alpha]_D^{20}$ = +39.4 (c 0.25, $CHCl_3$). The enantiomeric excess (87%) was determined by chiral HPLC (Chiralpak ADH), hexane-iPrOH 80:20, 1 mL/min, major enantiomer t_r = 31.11 min, minor enantiomer t_r = 35.17 min. **^{1}H NMR (300 MHz, CD_3OD)** *δ* 7.66 (dd, *J* = 8.7, 1.2 Hz, 2H), 7.49–7.42 (m, 2H), 7.32–7.17 (m, 7H), 6.77 (d, *J* = 8.6 Hz, 1H), 6.70 (dd, *J* = 8.7, 3.0 Hz, 1H), 6.63 (d, *J* = 3.0 Hz, 1H), 5.67 (s, 1H), 3.67 (s, 3H), 1.92 (s, 3H) ppm. **^{13}C NMR (100 MHz, CD_3OD)** *δ* 155.08 (C), 151.15 (C), 149.88 (C), 144.42 (C), 138.68 (C), 132.38 (C), 131.01 (CH), 130.53 (CH), 129.96 (CH), 128.06 (CH), 127.92 (CH), 122.95 (CH), 118.48 (CH), 117.98 (CH), 114.19 (CH), 109.99 (C), 56.96 (CH_3), 42.08 (CH), 12.74 (CH_3) ppm. **HRMS (ESI)** m/z 387.1711 [M + H]+, $C_{24}H_{23}N_2O_3$ requires 387.1703.

4-((4-hydroxyphenyl)(phenyl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol (3ea)

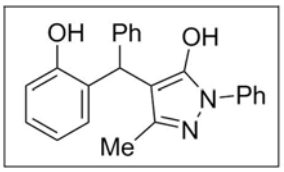


White solid, M. p.= 198-200 °C. The enantiomeric excess (0%) was determined by chiral HPLC (Chiralpak IC), hexane-iPrOH 80:20, 1 mL/min, major enantiomer t_r = 13.03 min, minor enantiomer t_r = 9.86 min. **^{1}H NMR (300 MHz, CD_3OD)** *δ* 7.66 (d, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.33–7.26 (m, 3H), 7.21 (dd, *J* = 12.0, 7.3 Hz, 3H), 7.01 (d, J = 8.4 Hz, 2H), 6.76 (d, *J* = 8.6 Hz, 2H), 5.42 (s, 1H), 1.82 (s, 3H) ppm. **^{13}C NMR (100 MHz, CD_3OD)** *δ* 155.56 (C), 147.38 (C), 147.35 (C), 143.11 (C), 136.39 (C), 133.26 (C), 129.65 (CH), 128.81 (CH), 128.63 (CH), 127.85 (CH), 125.89 (C), 125.86 (CH), 120.71 (CH), 114.66 (CH), 108.92 (CH), 44.22 (CH), 10.85 (CH_3) ppm. **HRMS (ESI)** m/z 357.1605 $[M + H]^+$, $C_{23}H_{21}N_2O_2$ requires 357.1598.

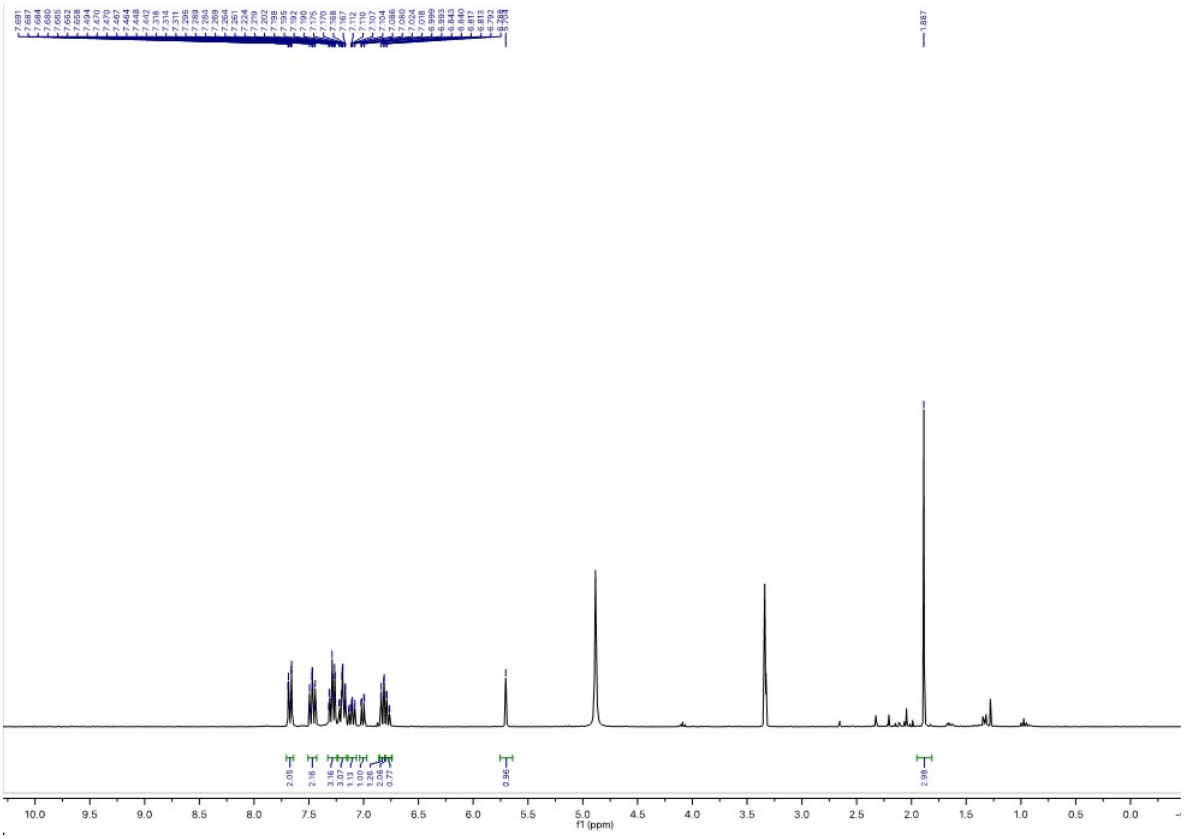
4. References

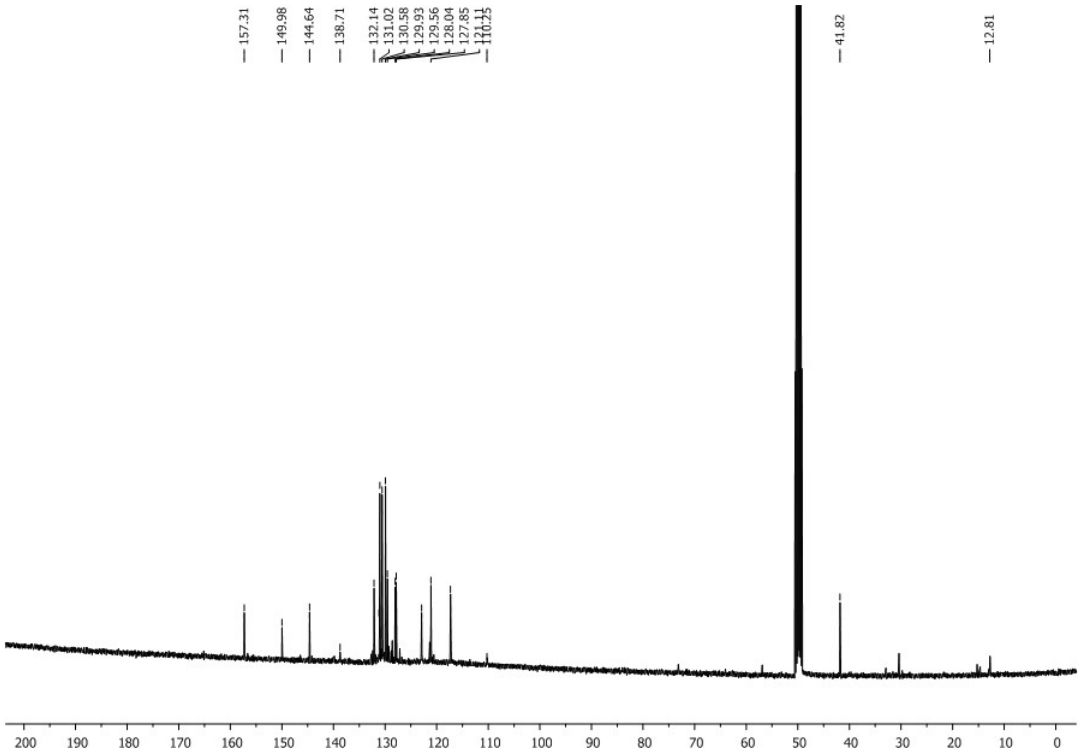
1. (a) B. Vakulya, S. Varga, A. Csámpai, T. Soós, *Org. Lett.* **2005**, *7*, 1967-1969. (b) Yang, W. & Du, D.-M. *Org. Lett*., **2010**, *12*, 5450-5453.
2. (a) M. W. Chen, L. L. Cao, Z. S. Ye, G. F. Jiang, Y. G. Zhou, *Chem. Commun*., **2013**, *49*, 1660-1662; (b) N. Gagey, P. Neveu, C. Benbrahim, B. Goetz, I. Aujard, J. B. Baudin, L. Jullien, *J. Am. Chem. Soc*. **2007**, *129*, 9986-9998.
3. (a) L. Carpino, *J. Am. Chem. Soc.* **1958**, *80*, 599-601; (b) J. Sun, C. –G. Yan, Y.Han, *Synthetic Commun.*, **2001**, *31*, 151; (c) A. Mazzanti, T. Calbet, M.Font-Bardia, A. Moyano, R. Rios; *Org. Biomol. Chem*., **2012**, *10*, 1645-1652; (d) S. Mao, X. Geng, Y. Yang, X. Qian, S. Wu, J. Han; L. Wang; *RSC Adv*., **2015**, *5*, 36390-36393; (e) Z. Yang, Z. Wang, S. Bai, X. Liu, L. Lin, X. Feng; *Org. Lett*., **2011**, *13*,596–599.

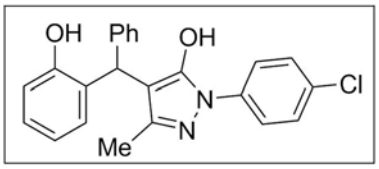
5. NMR spectra and HPLC traces



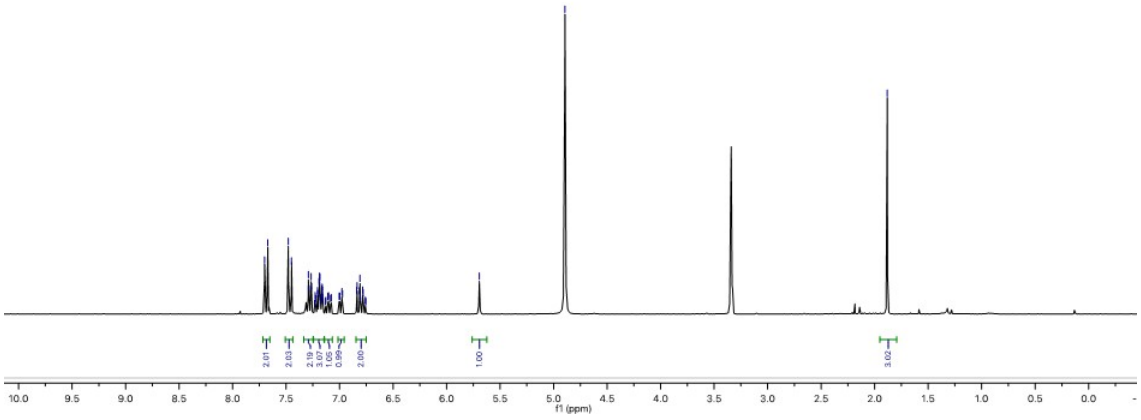
3aa






OH
Ph
OH
N
N
Cl
Me

3ab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2.03
2.19
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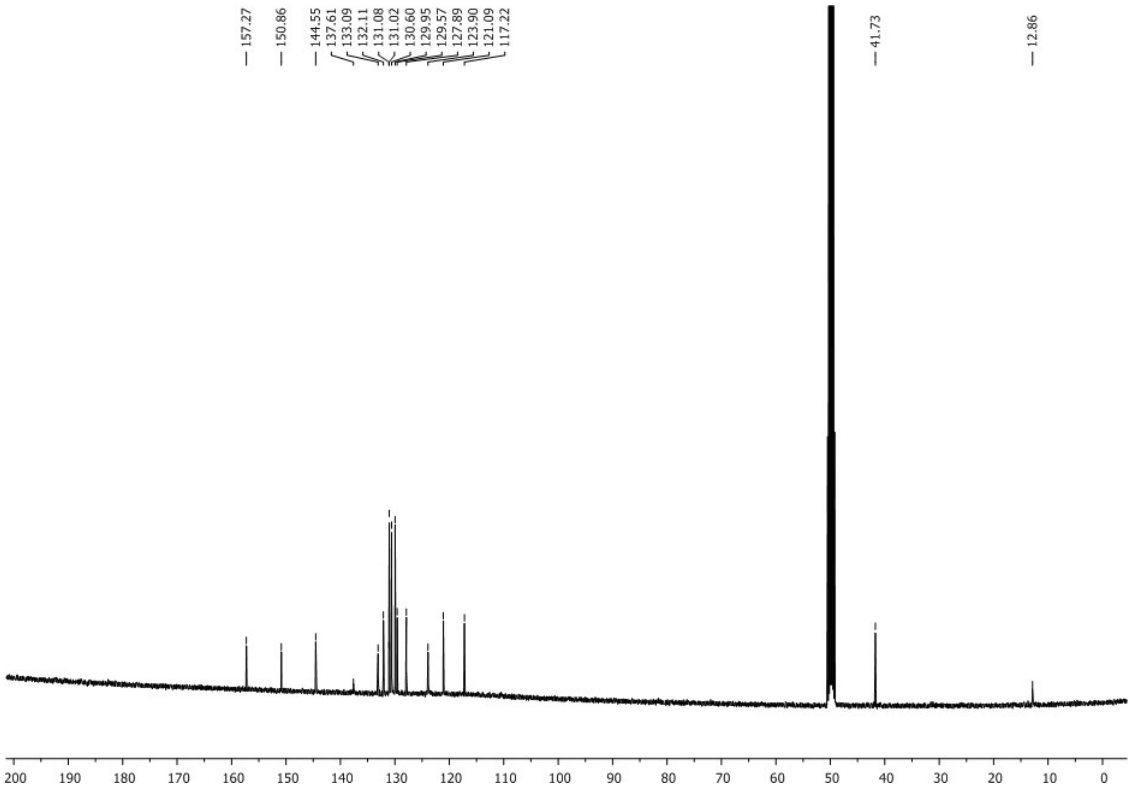
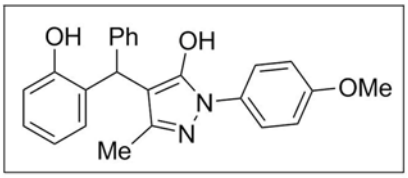
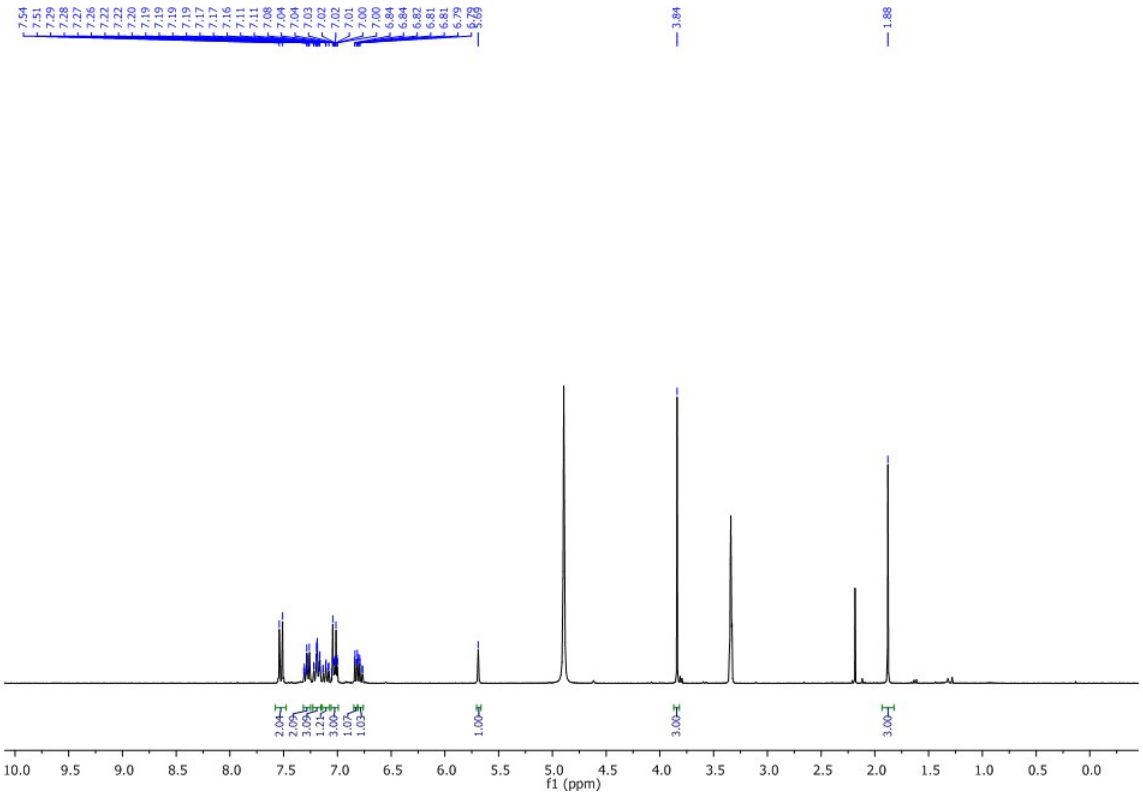
1.05
0.99
2.00
1.00
3.02
f1 (ppm)


157.27
150.86
144.55
137.61
133.09
132.11
131.08
131.02
130.60
129.95
129.57
127.89
123.90
121.09
117.22
41.73
12.86


OH
Ph
OH
N
N
OMe
Me

3ac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7.22
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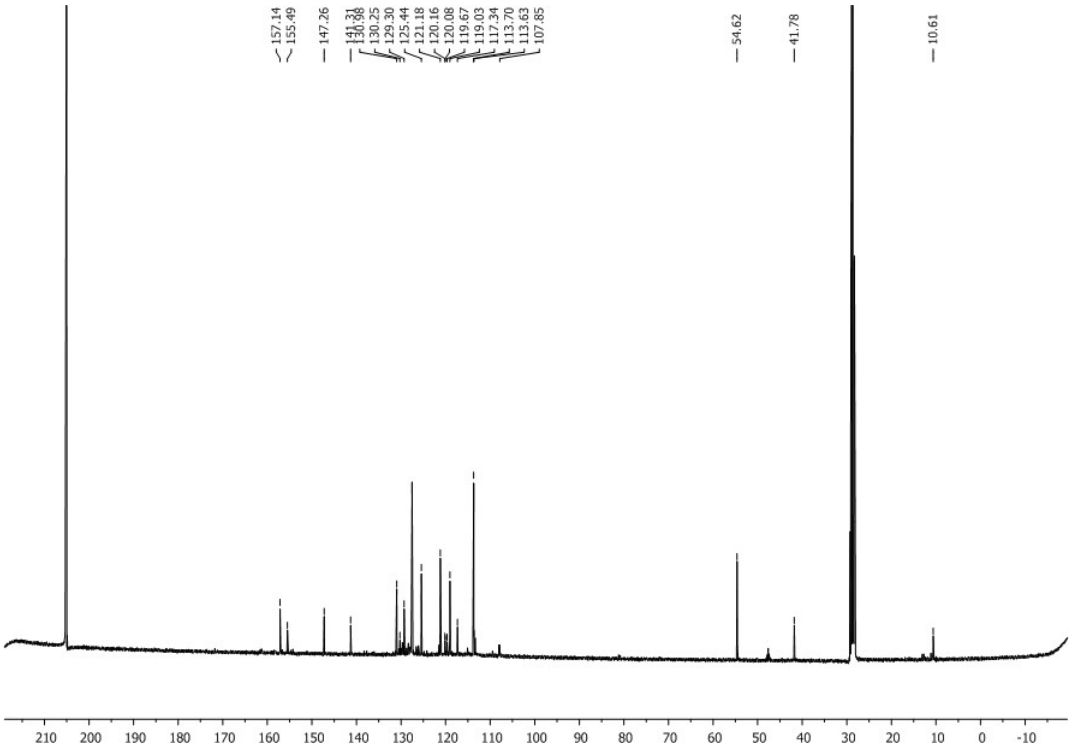
7.19
7.19
7.19
7.19
7.17
7.17
7.16
7.11
7.11
7.08
7.04
7.04
7.03
7.02
7.02
7.01
7.00
7.00
6.84
6.84
6.82
6.81
6.81
6.79
6.78
5.69
3.84
1.88
2.04
2.09
3.09
1.21
3.00
1.07
1.03
1.00
3.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


157.14
155.49
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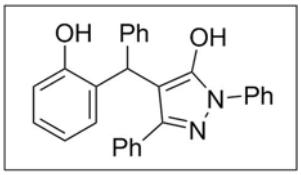
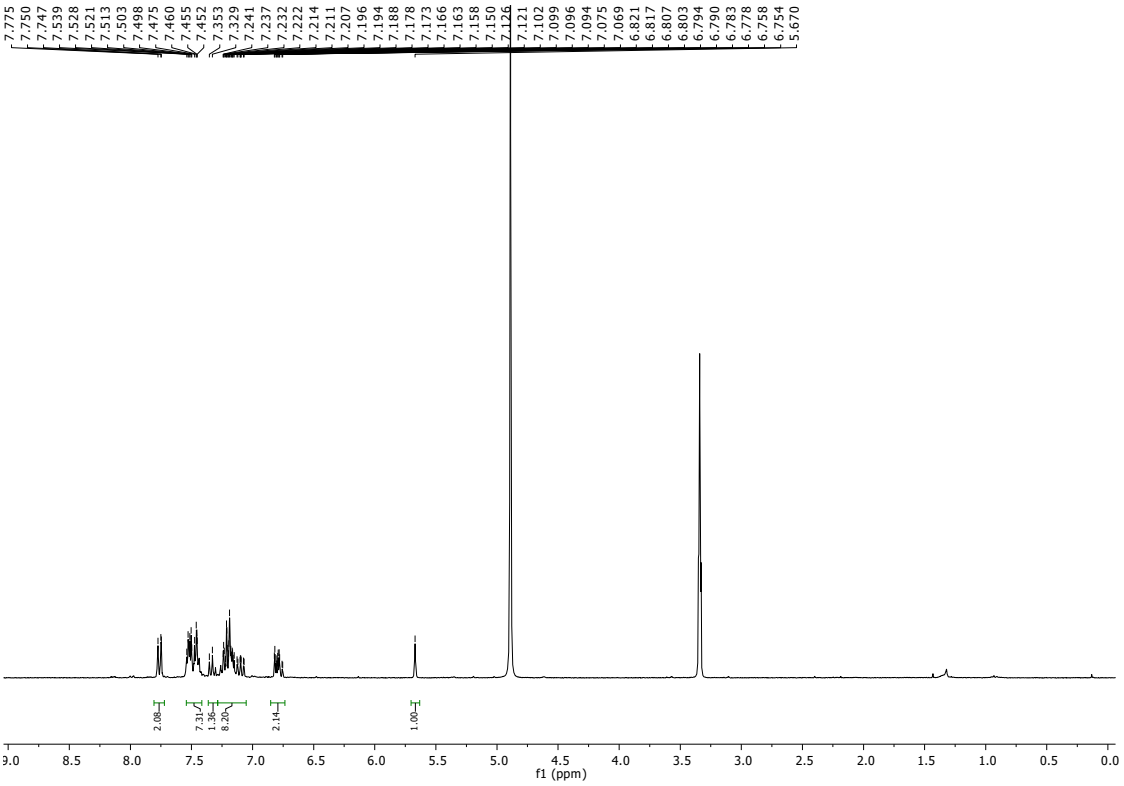
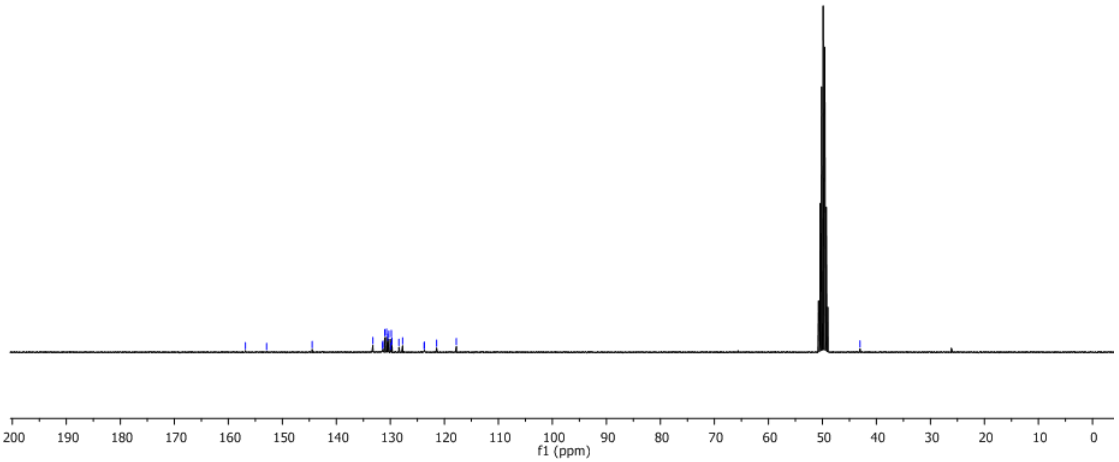
129.30
125.44
121.18
120.16
120.08
119.67
119.03
117.34
113.70
113.63
107.85
54.62
41.78
10.61
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

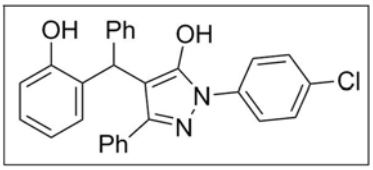

OH
Ph
OH
N–Ph
N
Ph

3ad


7.775
7.750
7.747
7.539
7.528
7.521
7.513
7.503
7.498
7.475
7.460
7.455
7.452
7.353
7.329
7.241
7.237
7.232
7.222
7.214
7.211
7.207
7.196
7.194
7.188
7.178
7.173
7.166
7.163
7.158
7.150
7.126
7.121
7.102
7.099
7.096
7.094
7.075
7.069
6.821
6.817
6.807
6.803
6.794
6.790
6.783
6.778
6.758
6.754
5.670
2.08
7.31
1.36
8.20
2.14
1.00
f1 (ppm)

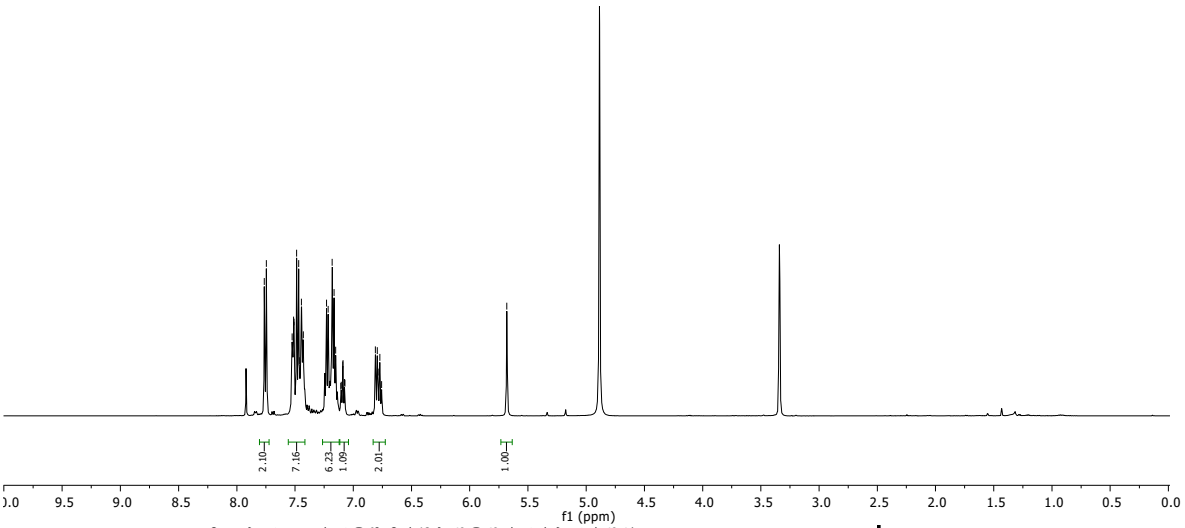

156.84
152.90
144.47
133.24
131.46
131.37
131.04
130.70
130.49
130.28
129.96
129.82
129.71
128.42
127.73
123.74
123.70
121.44
117.79
43.03

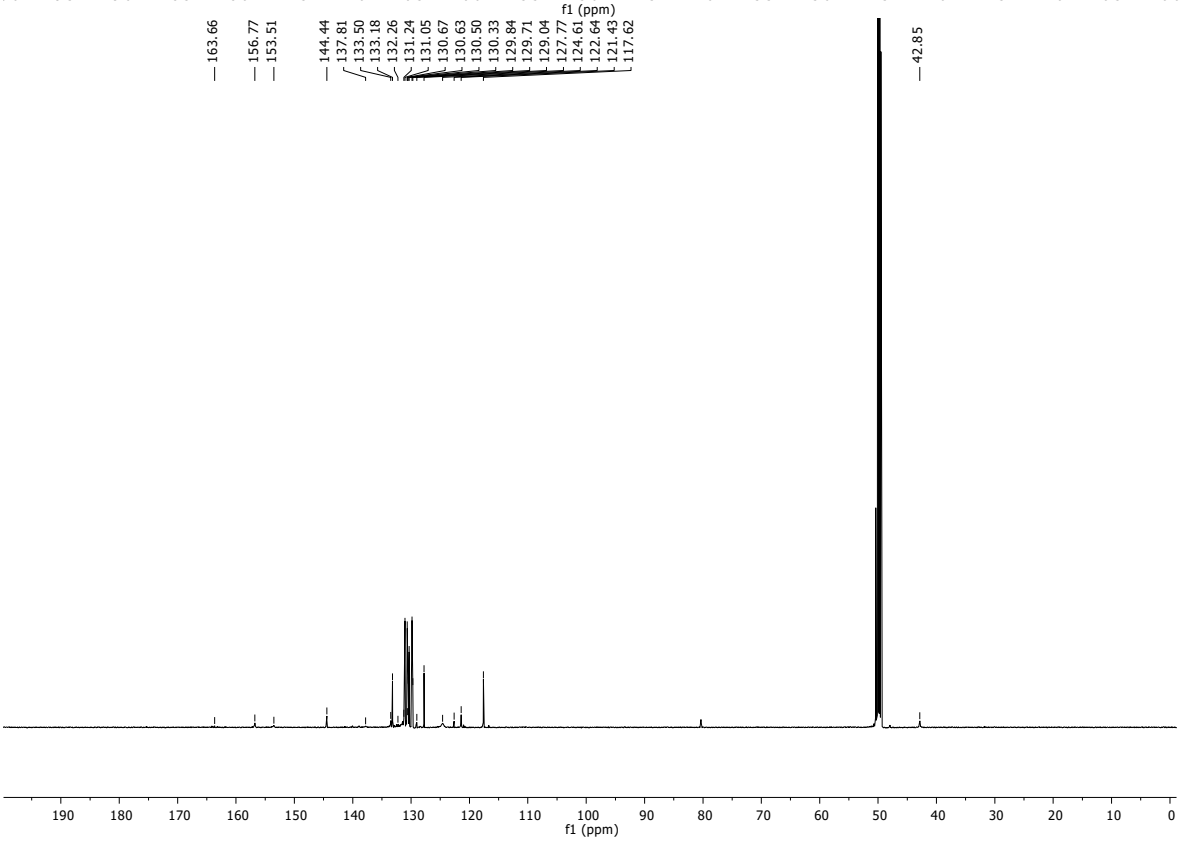

f1 (ppm)


OH
Ph
OH
N
N
Cl
Ph

3ae


7.764
7.746
7.525
7.513
7.509
7.487
7.483
7.474
7.470
7.463
7.445
7.430
7.230
7.215
7.181
7.165
7.151
7.107
7.103
7.091
7.088
7.076
7.072
6.810
6.793
6.787
6.772
6.757
5.681


2.10
7.16
6.23
1.09
2.01
1.00
f1 (ppm)


163.66
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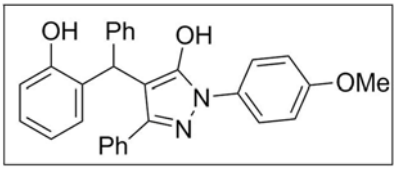
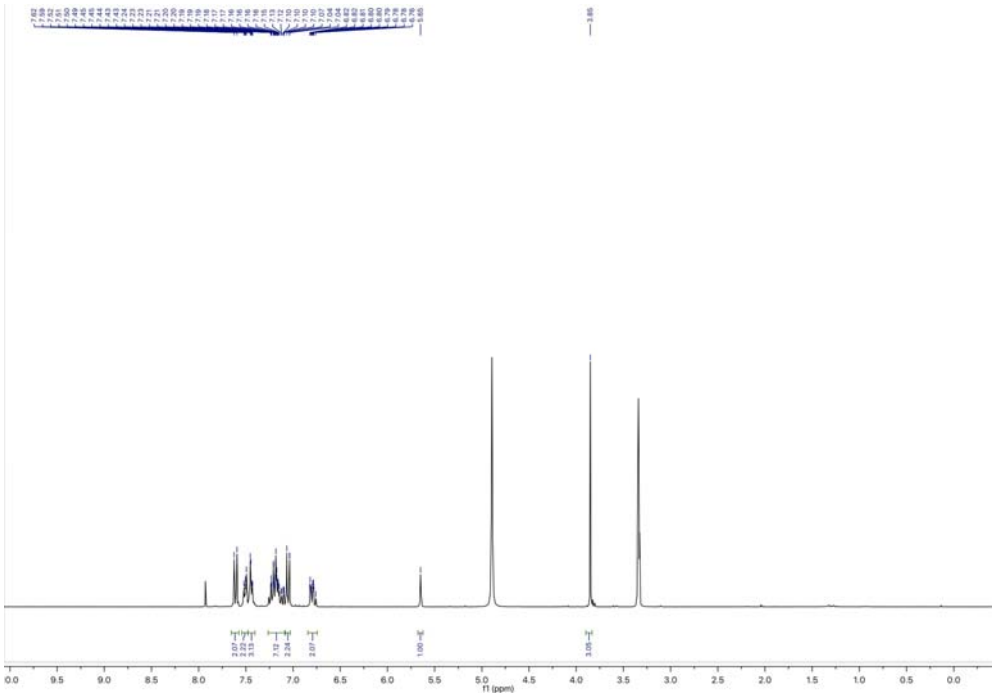
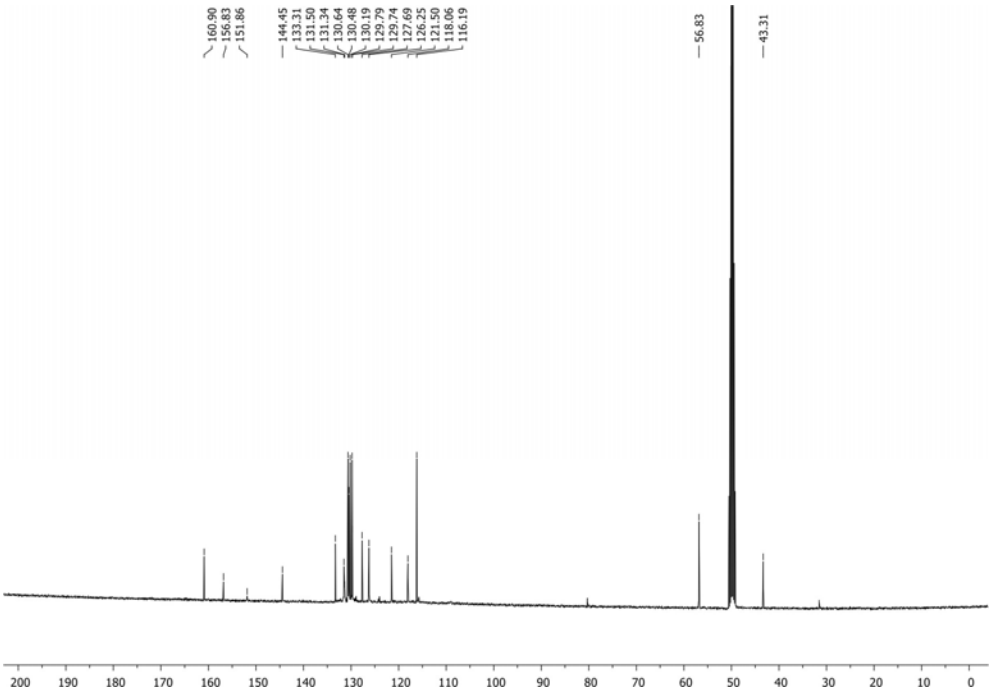
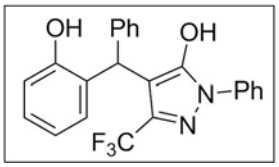
153.51
144.44
137.81
133.50
133.18
132.26
131.24
131.05
130.67
130.63
130.50
130.33
129.84
129.71
129.04
127.77
124.61
122.64
121.43
117.62
42.85
f1 (ppm)


OH
Ph
OH
N
N
OMe
Ph

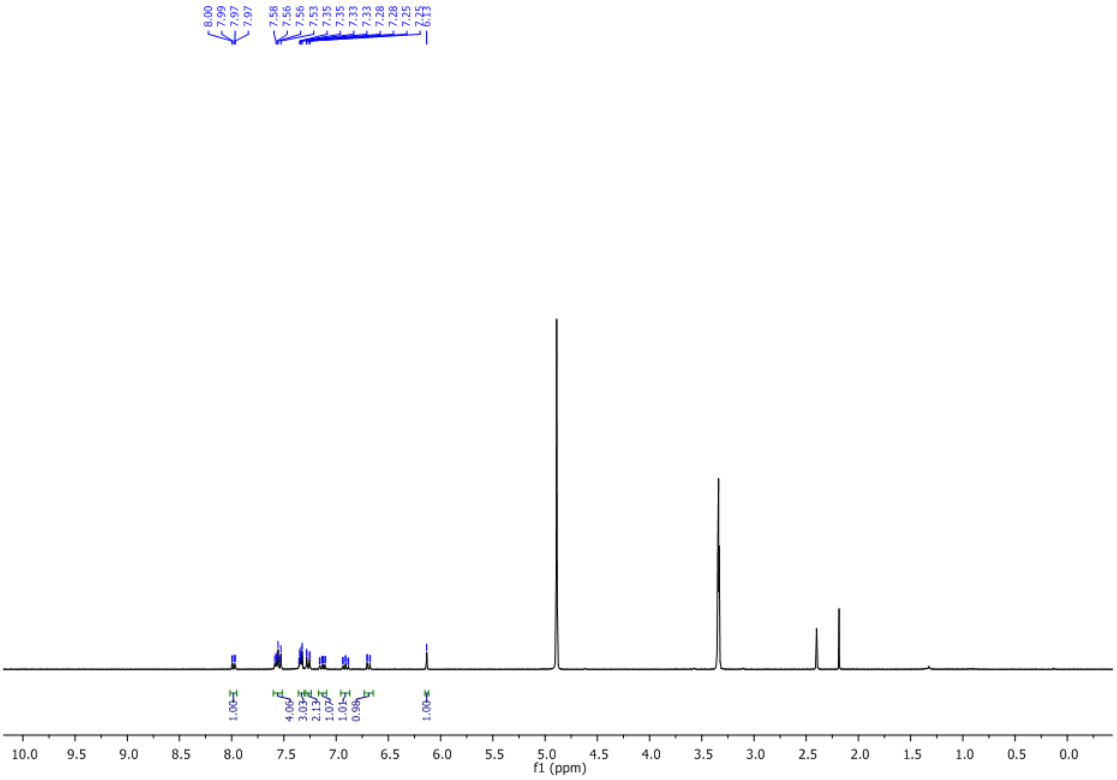
3af




160.90
156.83
151.86
144.45
133.31
131.50
131.34
130.64
130.48
130.19
129.79
129.74
127.69
126.25
121.50
118.06
116.19
56.83
43.31


OH
Ph
OH
N–Ph
N
F3C

3ag


8.00
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7.97
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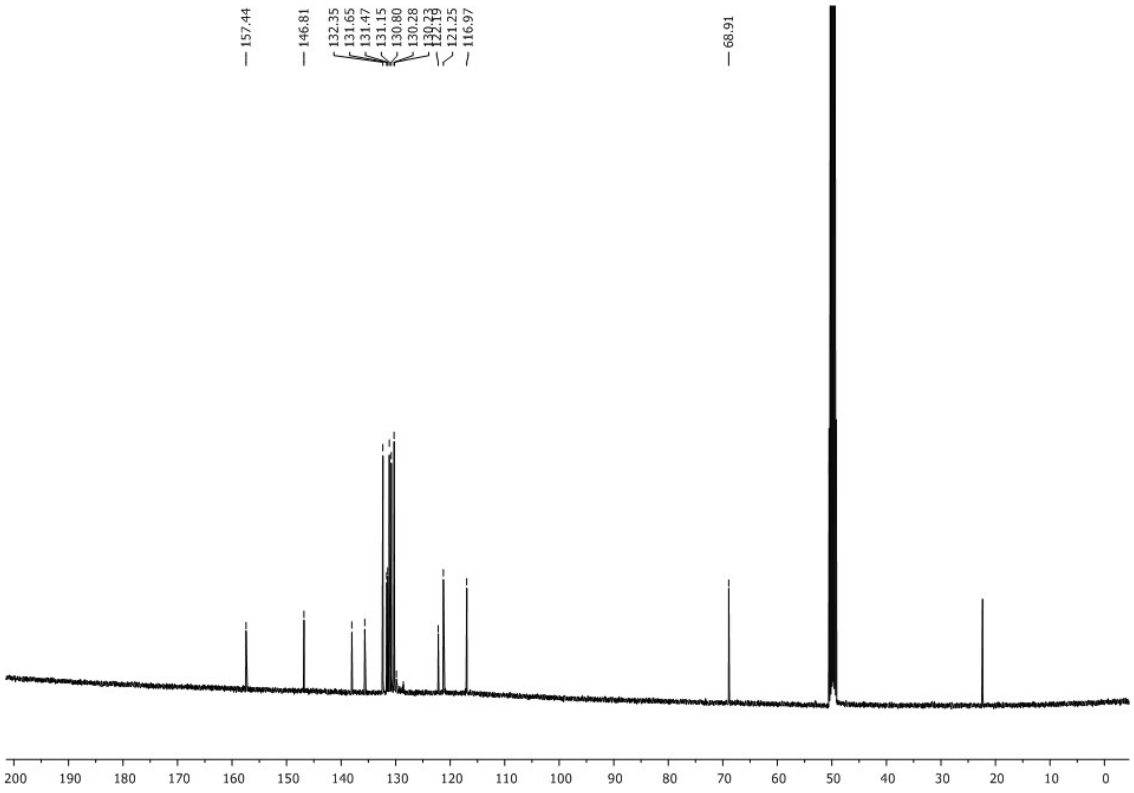
7.56
7.56
7.53
7.35
7.35
7.33
7.33
7.28
7.25
6.13
1.00
4.06
3.03
2.13
1.07
1.01
0.98
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


157.44
146.81
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131.65
131.47
131.15
130.80
130.28
121.25
116.97
68.91
200
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180
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150
140
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120
110
100
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70
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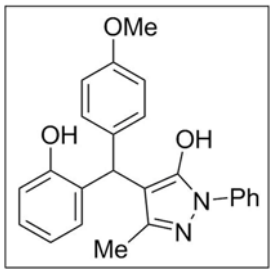
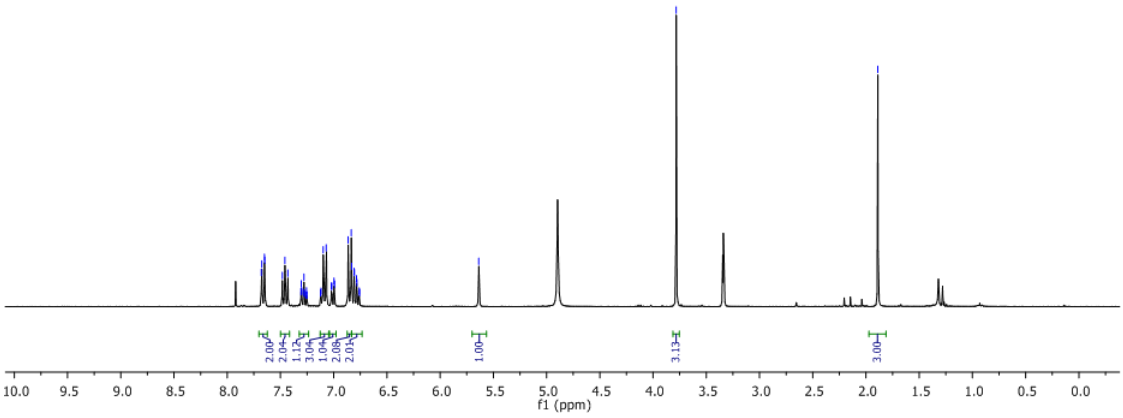
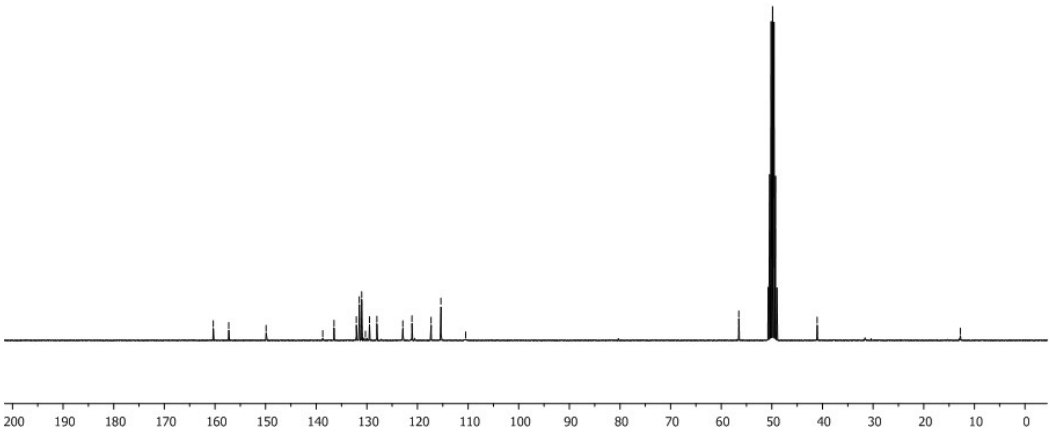
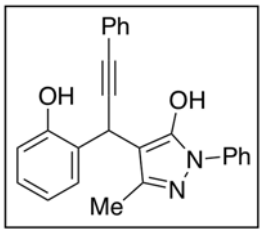
30
20
10
0



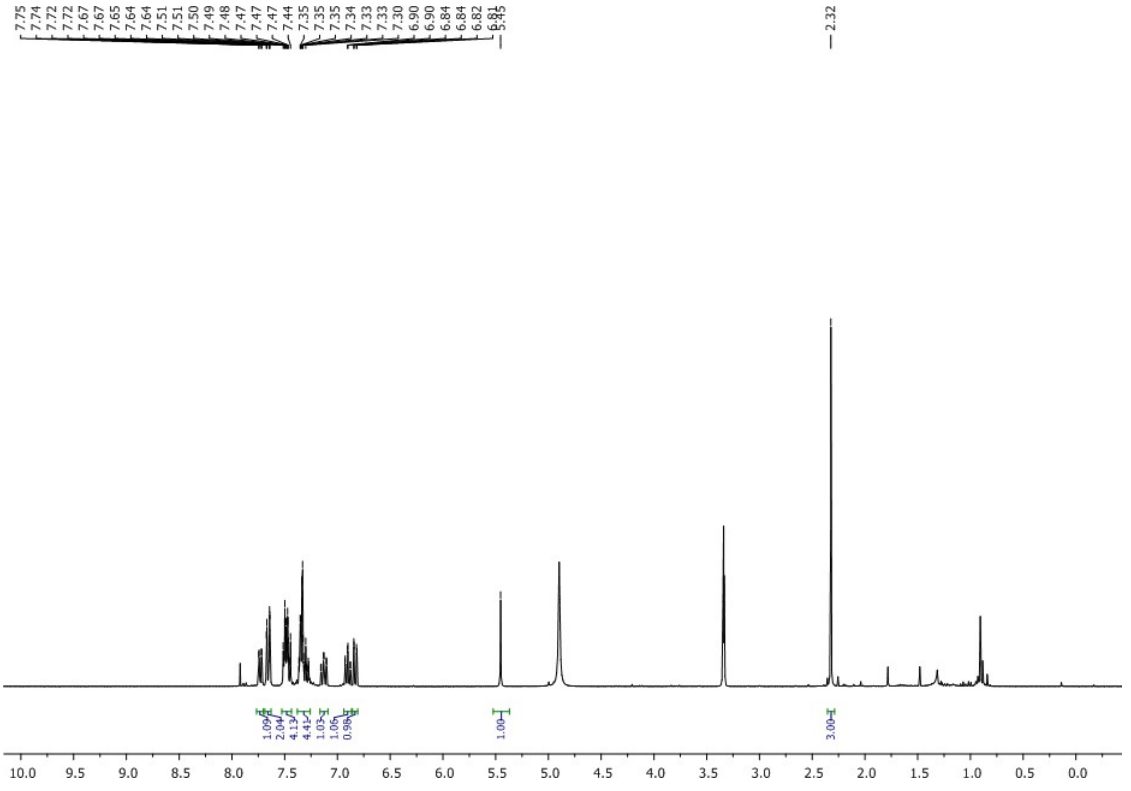
3ba






Ph
OH
OH
N–Ph
N
Me

3ca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7.72
7.67
7.67
7.65
7.64
7.64
7.51
7.51
7.50
7.49
7.48
7.47
7.47
7.47
7.44
7.35
7.35
7.35
7.34
7.33
7.33
7.30
6.90
6.90
6.84
6.84
6.82
6.81
5.45
2.32
1.09
2.04
4.13
4.41
1.03
1.06
0.96
1.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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3.0
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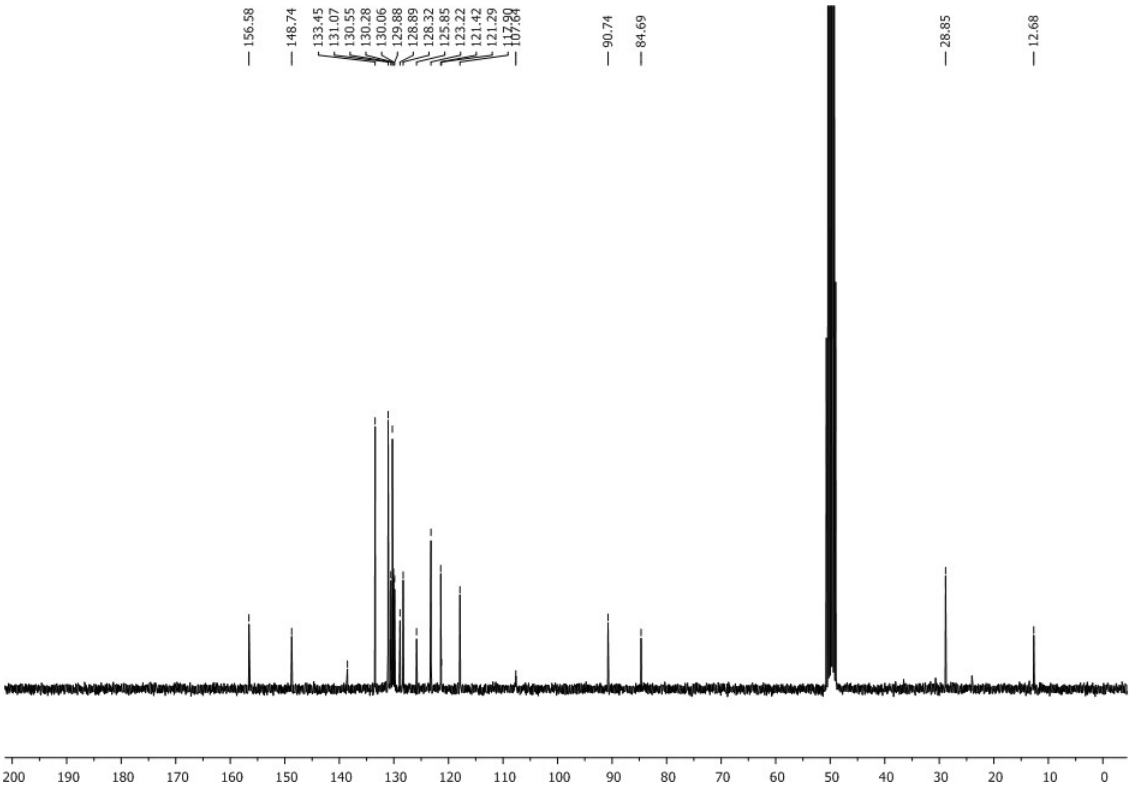
2.0
1.5
1.0
0.5
0.0


156.58
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130.55
130.28
130.06
129.88
128.89
128.32
125.85
123.22
121.42
121.29
117.80
107.84
90.74
84.69
28.85
12.68
200
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180
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150
140
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110
100
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70
60
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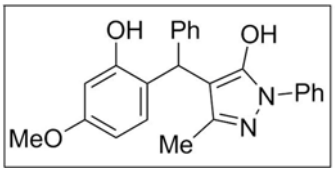
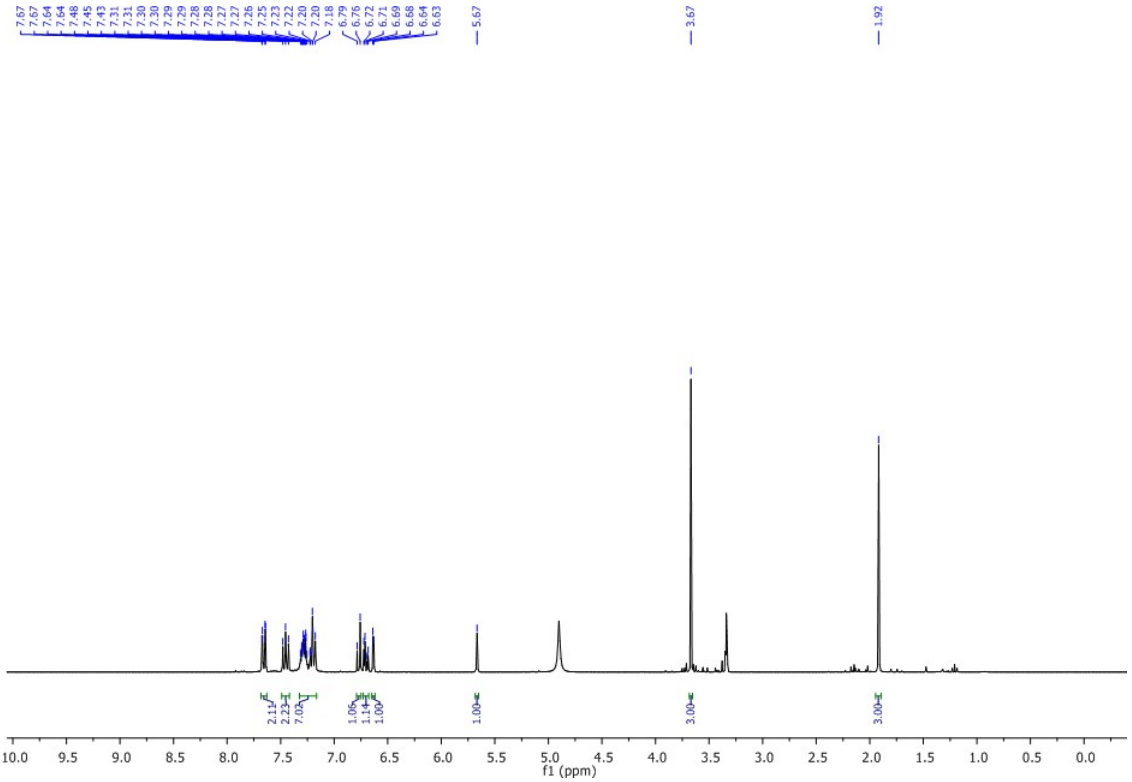
30
20
10
0


OH
Ph
OH
N–Ph
N
MeO
Me

3da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7.67
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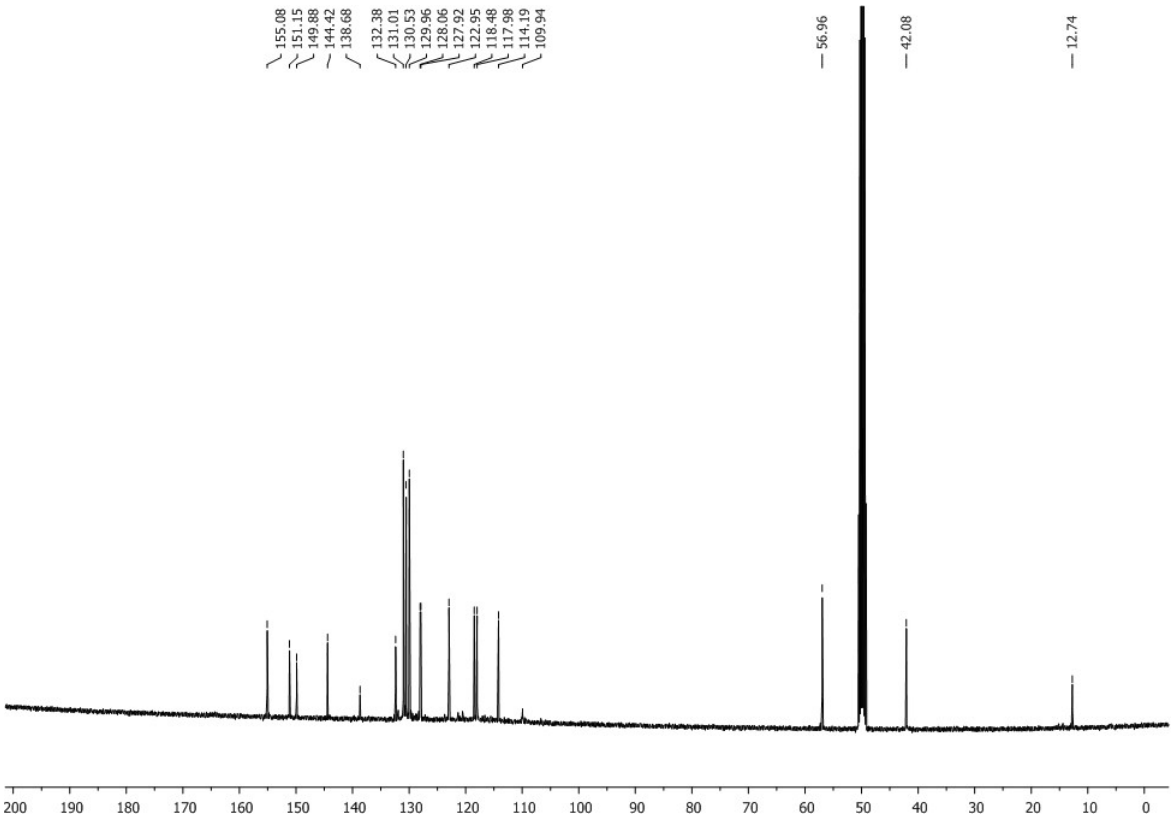
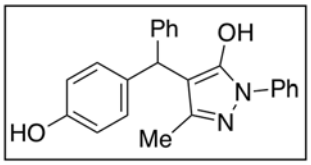
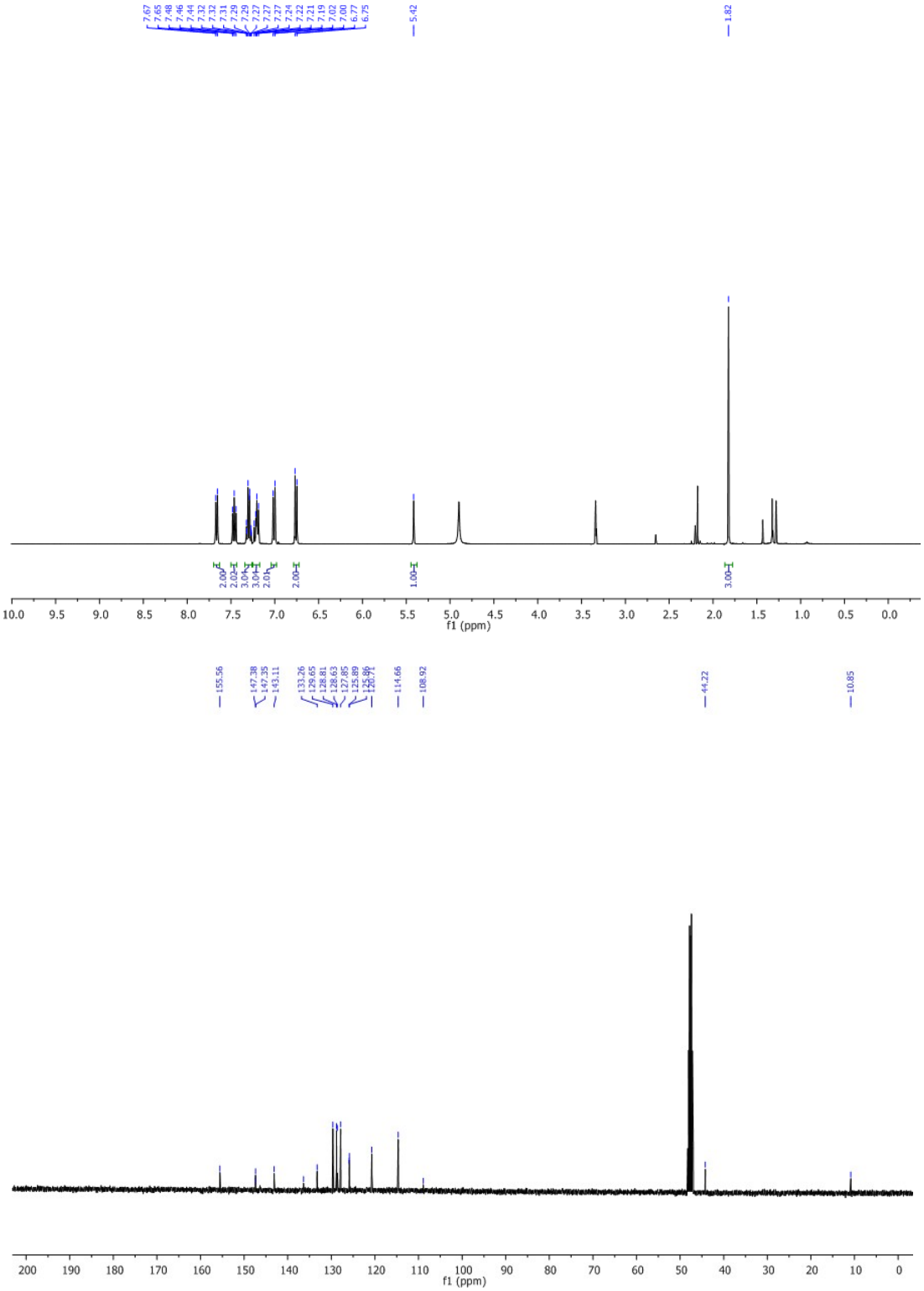
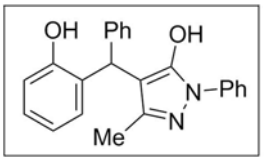
7.64
7.48
7.45
7.43
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.25
7.23
7.22
7.20
7.20
7.18
6.79
6.76
6.72
6.71
6.69
6.68
6.64
6.63
5.67
3.67
1.92
2.11
2.23
7.02
1.06
1.14
1.00
1.00
3.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


155.08
151.15
149.88
144.42
138.68
132.38
131.01
130.53
129.96
128.06
127.92
122.95
118.48
117.98
114.19
109.94
56.96
42.08
12.74
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

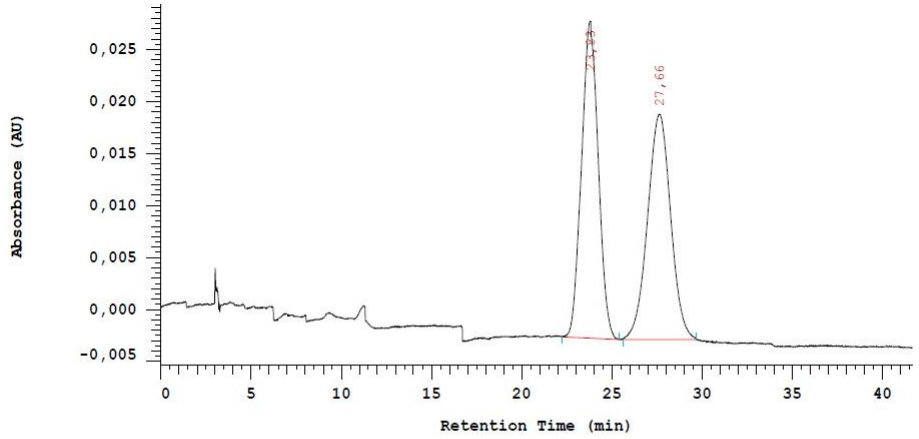

Ph
OH
N–Ph
N
HO
Me

3ea

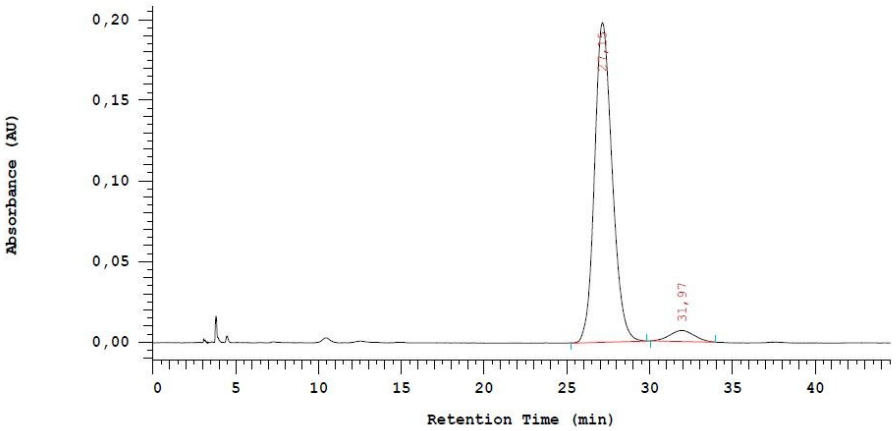

7.67
7.65
7.48
7.46
7.44
7.32
7.31
7.29
7.29
7.27
7.27
7.27
7.24
7.22
7.21
7.19
7.02
7.00
6.77
6.75
5.42
1.82
2.00
2.02
3.04
3.04
2.04
2.00
1.00
3.00
f1 (ppm)
155.56
147.38
147.35
143.11
133.26
129.65
128.61
128.43
127.85
125.89
125.86
120.71
114.66
108.92
44.22
10.85
f1 (ppm)



3aa



No.	RT	Area	Area %	Name
1	23,83	975775	50,306	enant. (+)
2	27,66	963900	49,694	enanti (-)
		1939675	100,000	



No.	RT	Area	Area %	Name
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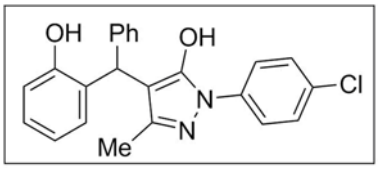
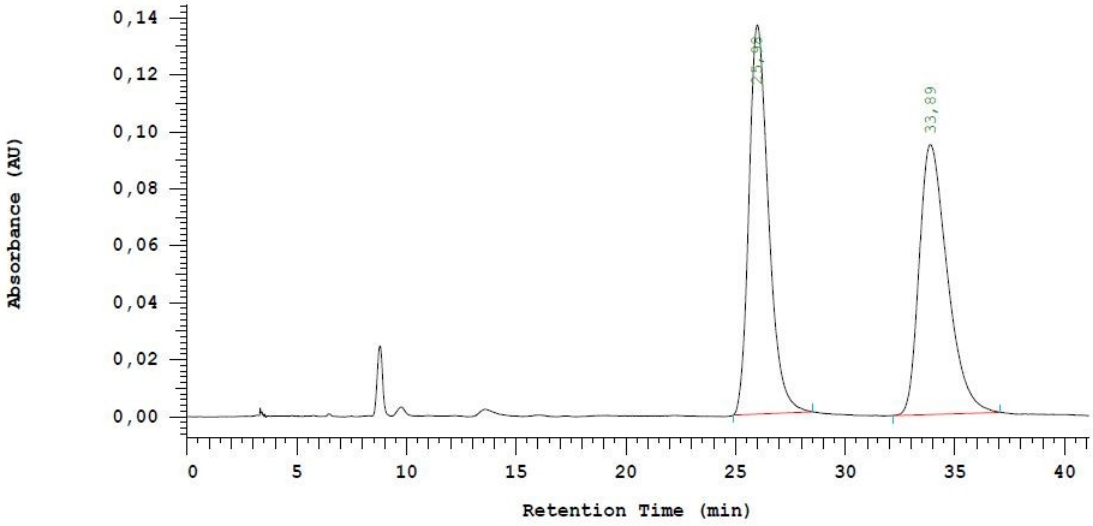
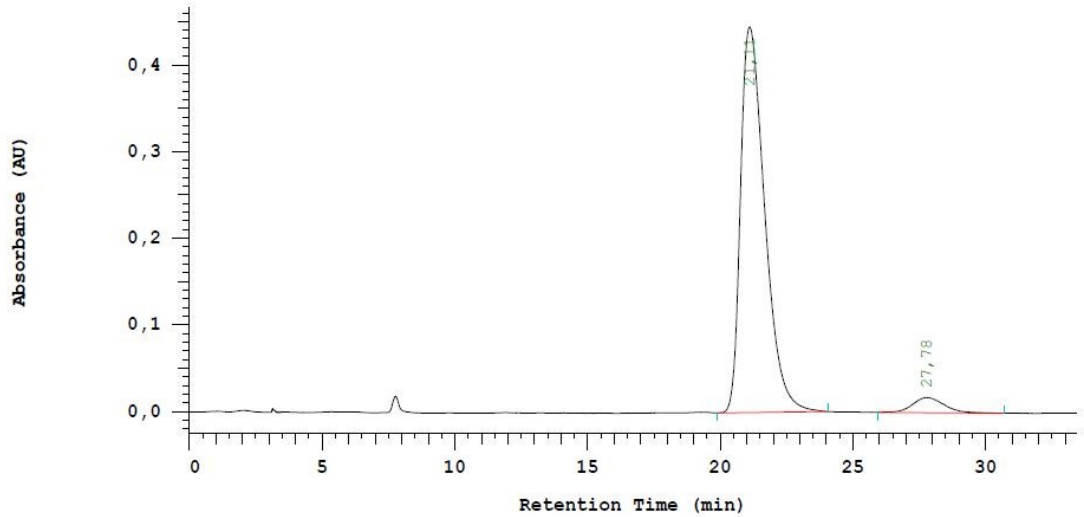
2	31,97	351670	4,580	
		7678479	100,000	



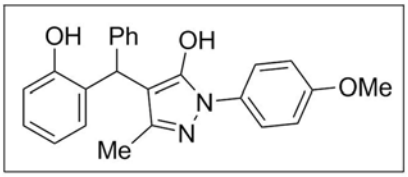
3ab



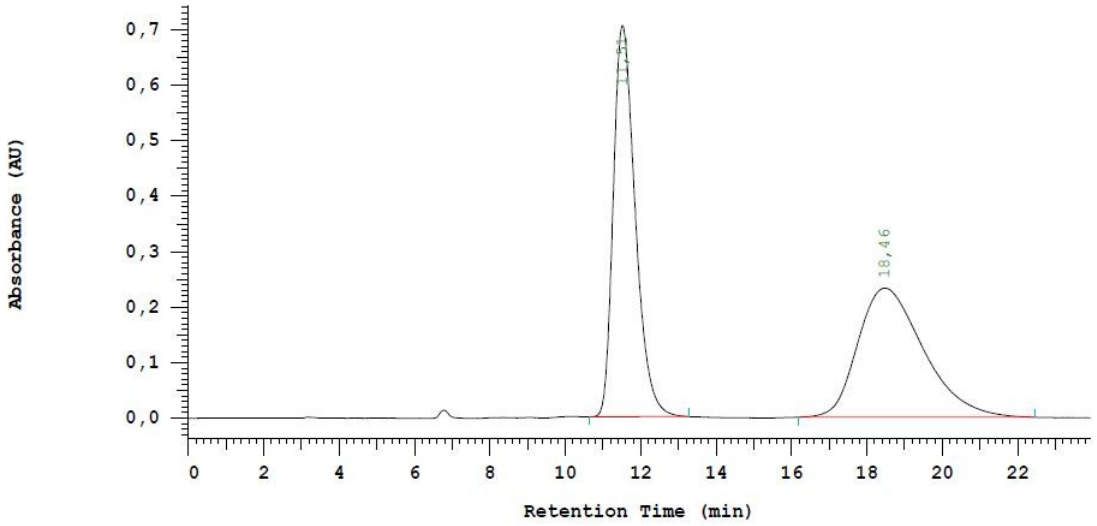
No.	RT	Area	Area %	Name
1	25,98	4210390	49,988	enant. (+)
2	33,89	4212490	50,012	
		8422880	100,000	



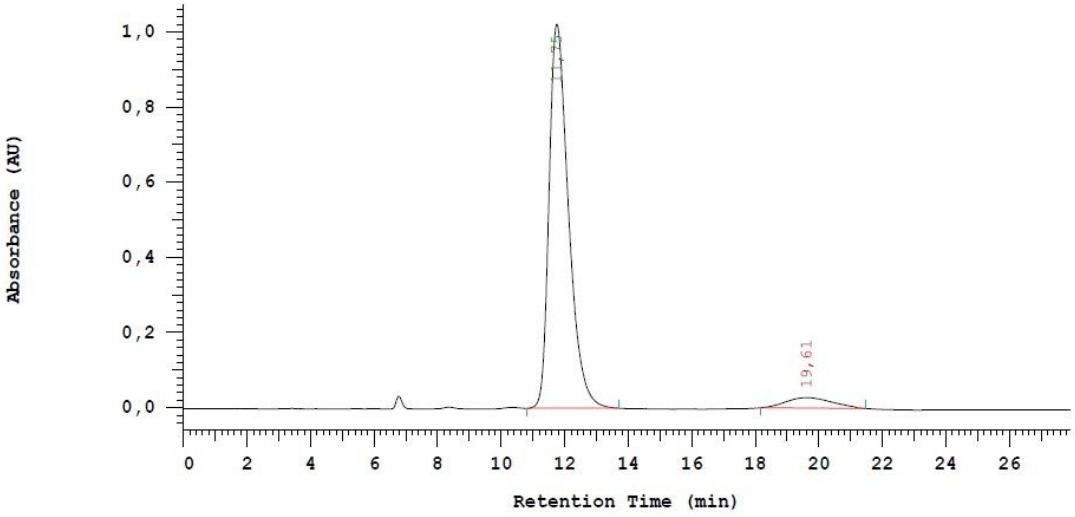
No.	RT	Area	Area %	Name
1	21,11	13998489	95,085	
2	27,78	723590	4,915	enanti (-)
		14722079	100,000	



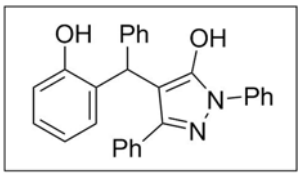
3ac



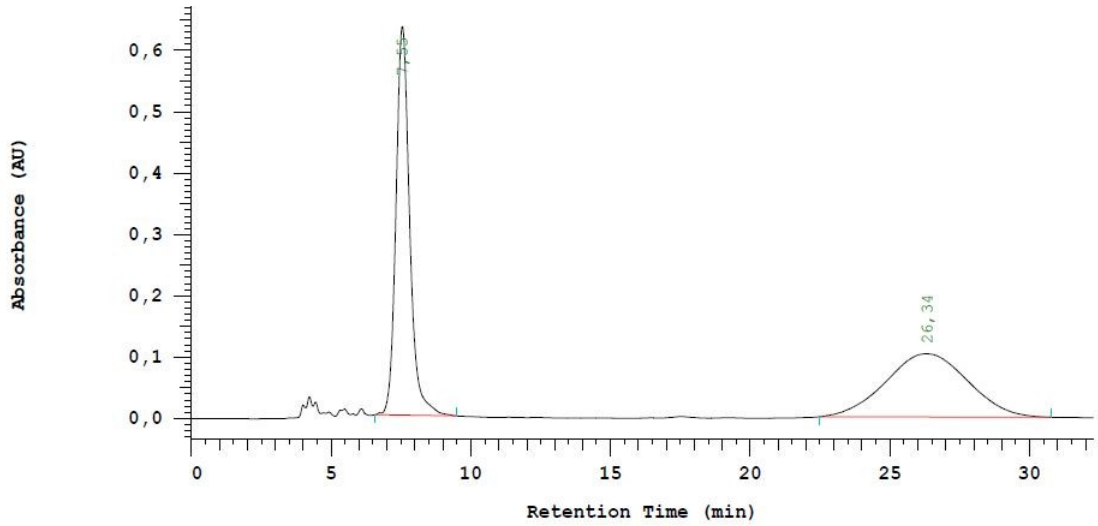
No.	RT	Area	Area %	Name
1	11,51	14214620	50,270	
2	18,46	14061710	49,730	
		28276330	100,000	



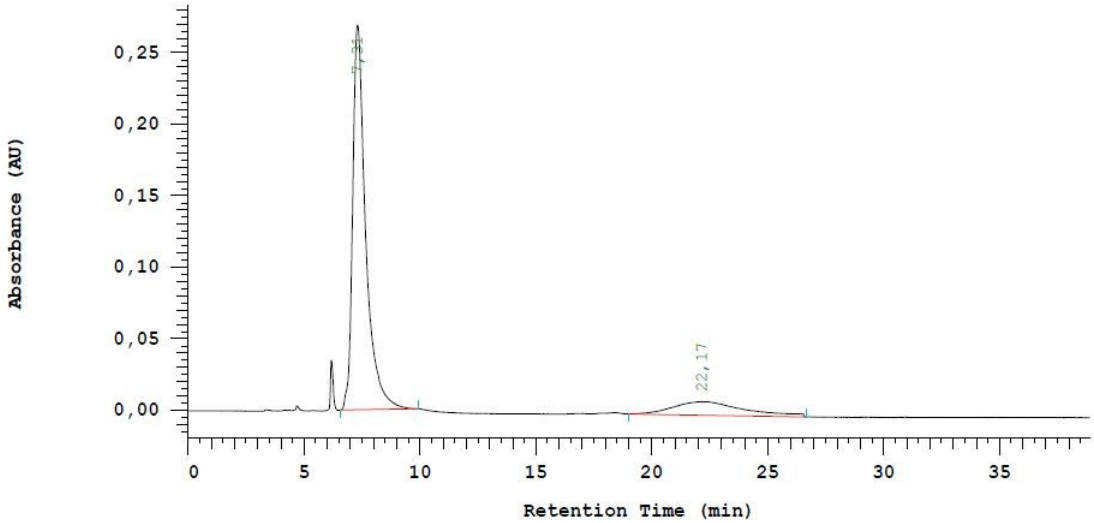
No.	RT	Area	Area %	Name
1	11,75	21609249	93,907	
2	19,61	1402200	6,093	
		23011449	100,000	



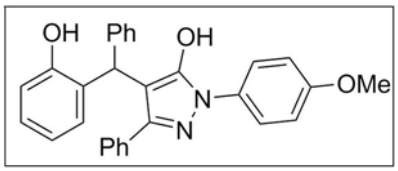
3ad



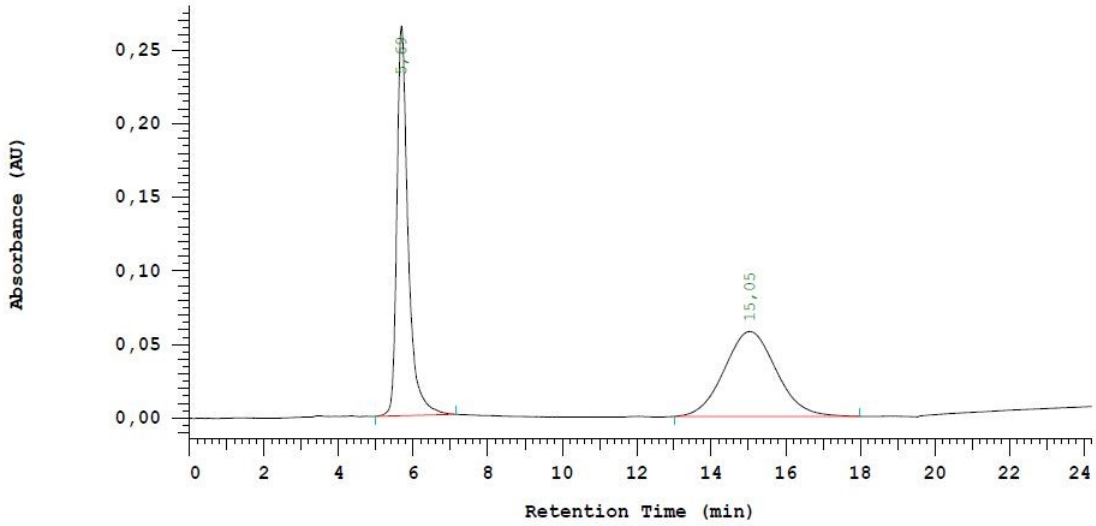
No.	RT	Area	Area %	Name
1	7,55	10727769	50,536	
2	26,34	10500364	49,464	enant. (+)
		21228133	100,000	



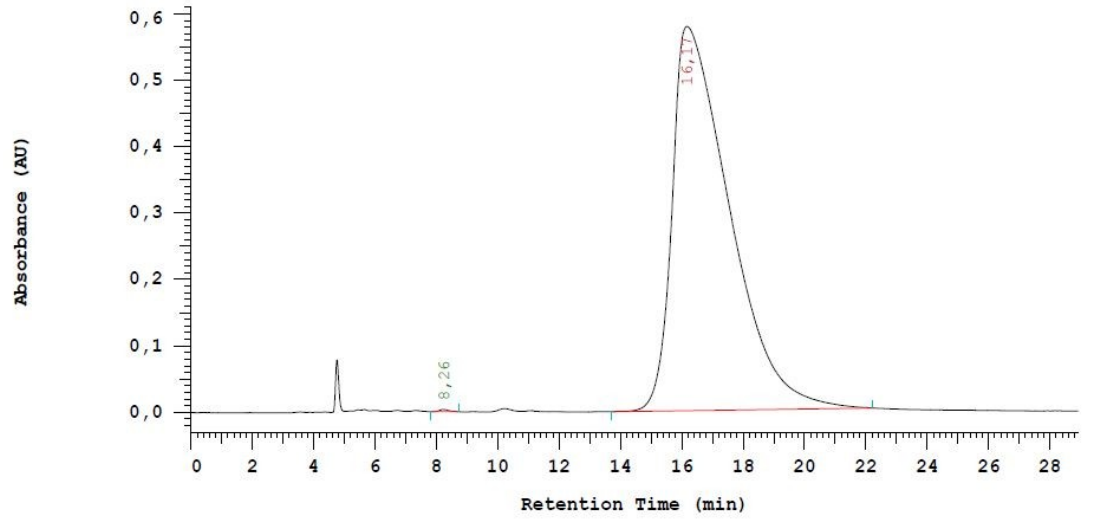
No.	RT	Area	Area %	Name
1	7,31	5195170	83,708	
2	22,17	1011105	16,292	enant. (+)
		6206275	100,000	



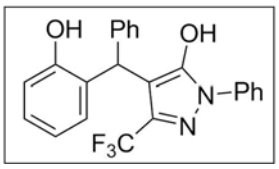
3ae



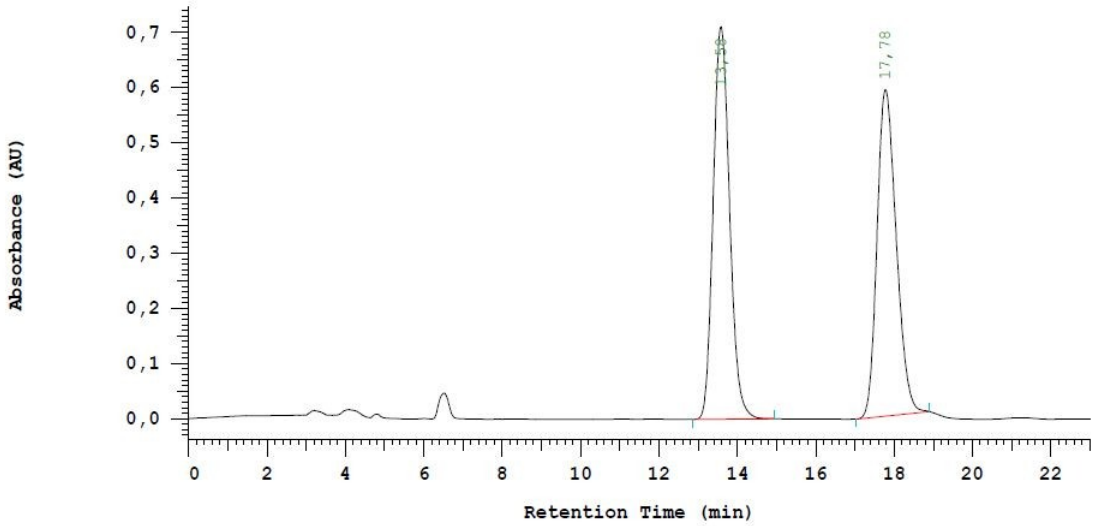
No.	RT	Area	Area %	Name
1	5,69	2766240	49,796	
2	15,05	2788890	50,204	
		5555130	100,000	



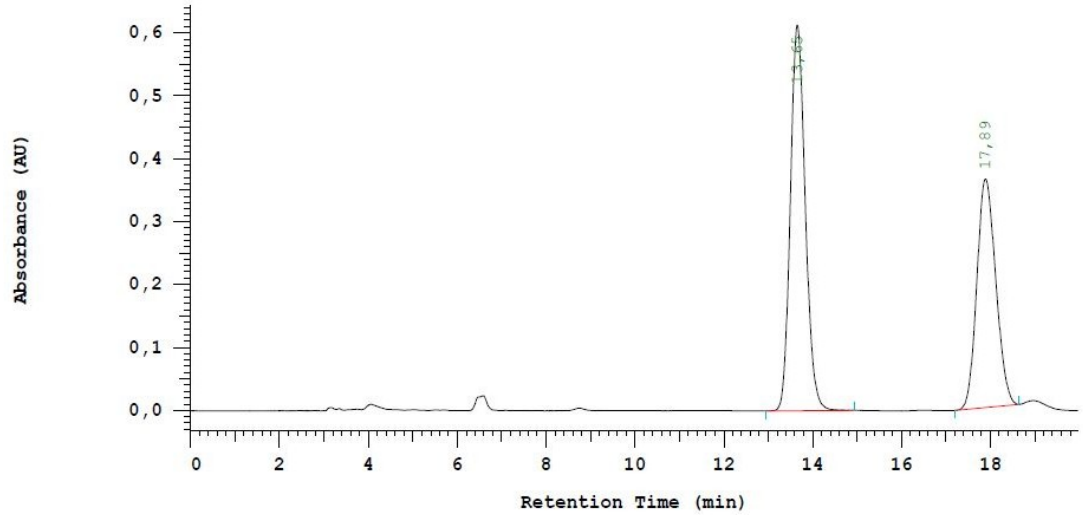
No.	RT	Area	Area %	Name
1	8,26	41020	0,109	
2	16,17	37535030	99,891	
		37576050	100,000	



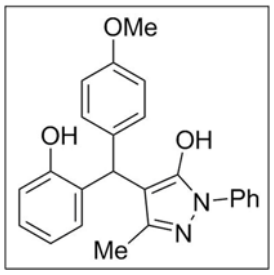
3af



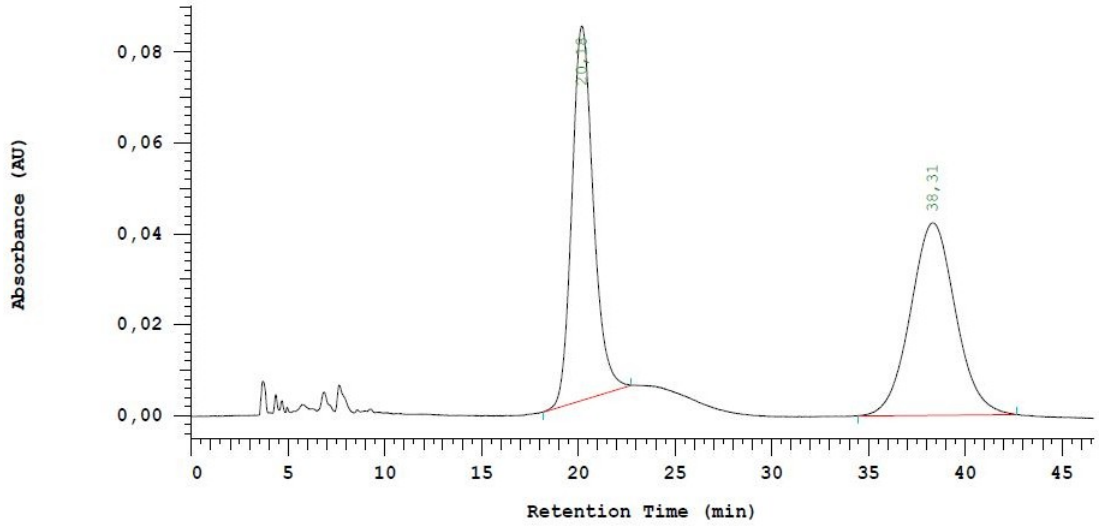
No.	RT	Area	Area %	Name
1	13,58	10314115	50,618	
2	17,78	10062449	49,382	
		20376564	100,000	



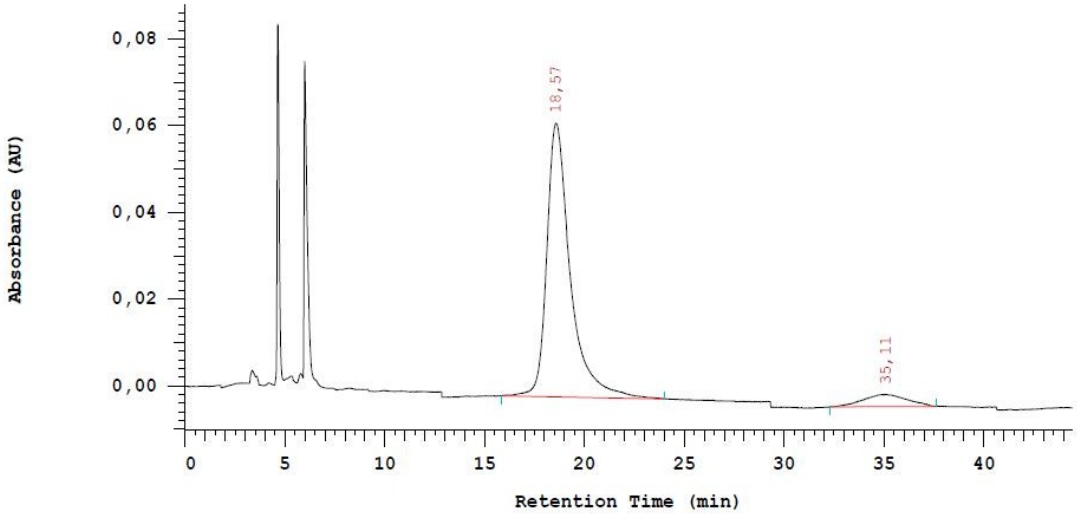
No.	RT	Area	Area %	Name
1	13,65	7128440	56,967	
2	17,89	5384930	43,033	
		12513370	100,000	



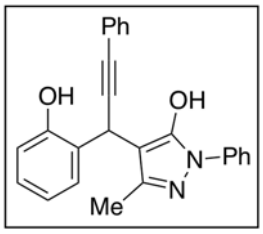
3ba



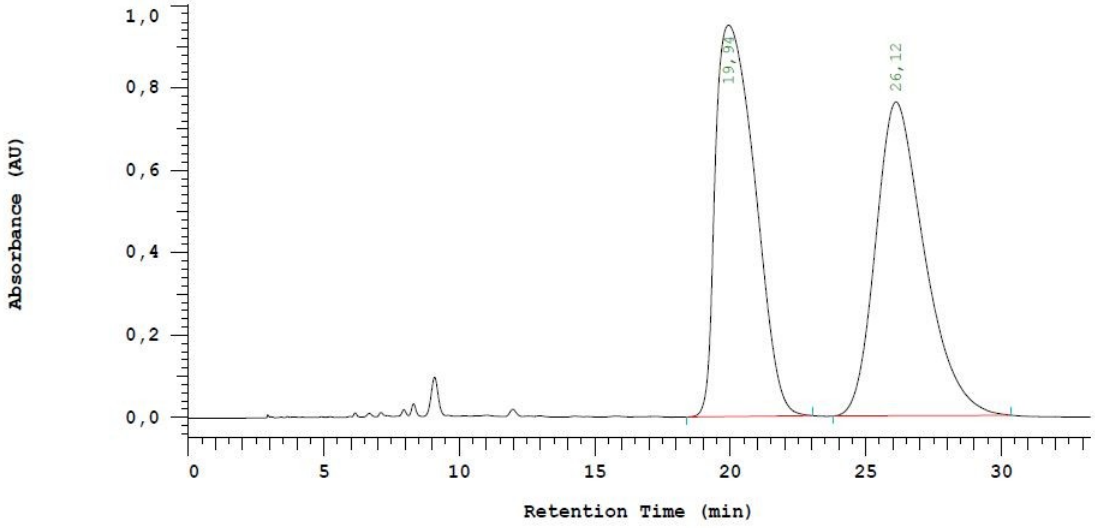
No.	RT	Area	Area %	Name
1	20,18	3165040	48,035	
2	38,31	3423950	51,965	
		6588990	100,000	



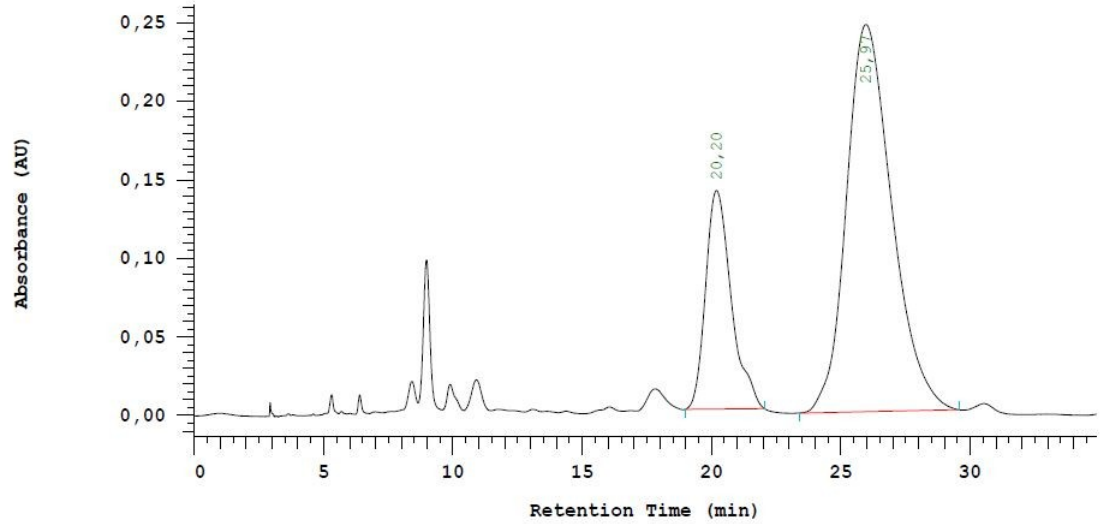
No.	RT	Area	Area %	Name
1	18,57	2570800	92,404	
2	35,11	211320	7,596	
		2782120	100,000	



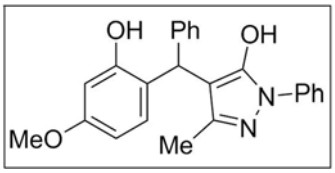
3ca



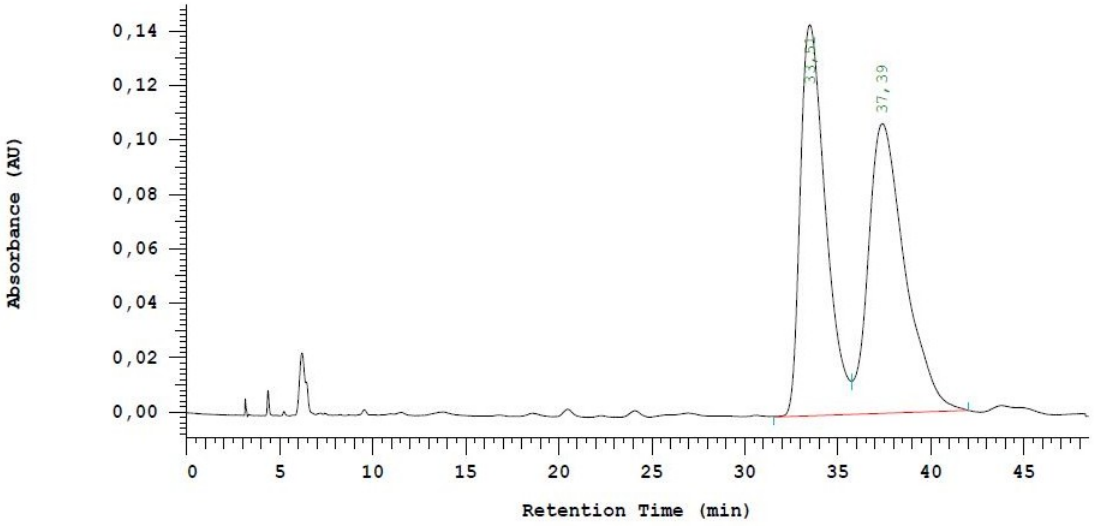
No.	RT	Area	Area %	Name
1	19,94	47956518	50,160	
2	26,12	47650499	49,840	enant. (+)
		95607017	100,000	



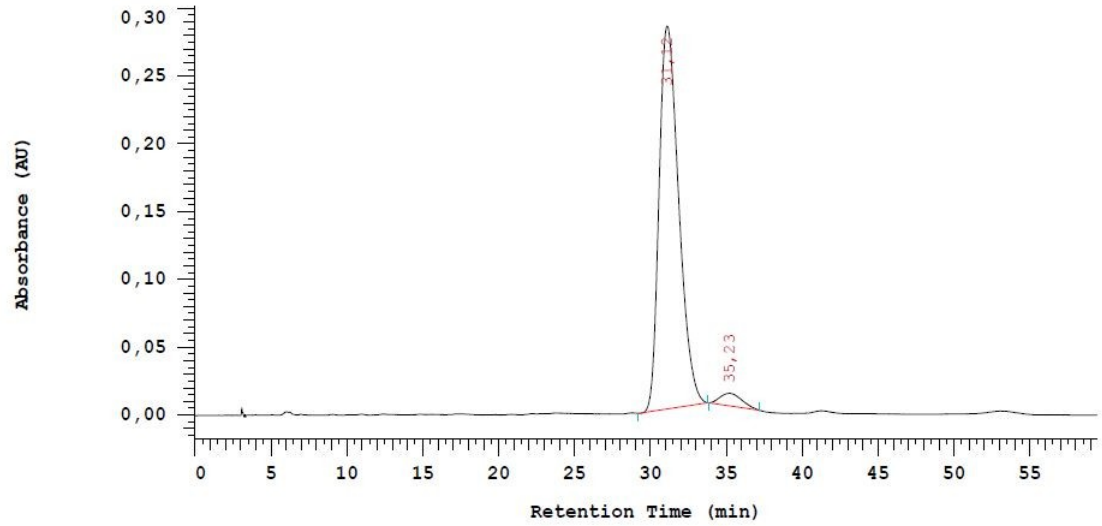
No.	RT	Area	Area %	Name
1	20,20	4791360	24,156	
2	25,97	15043649	75,844	enant. (+)
		19835009	100,000	



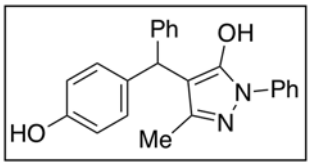
3da



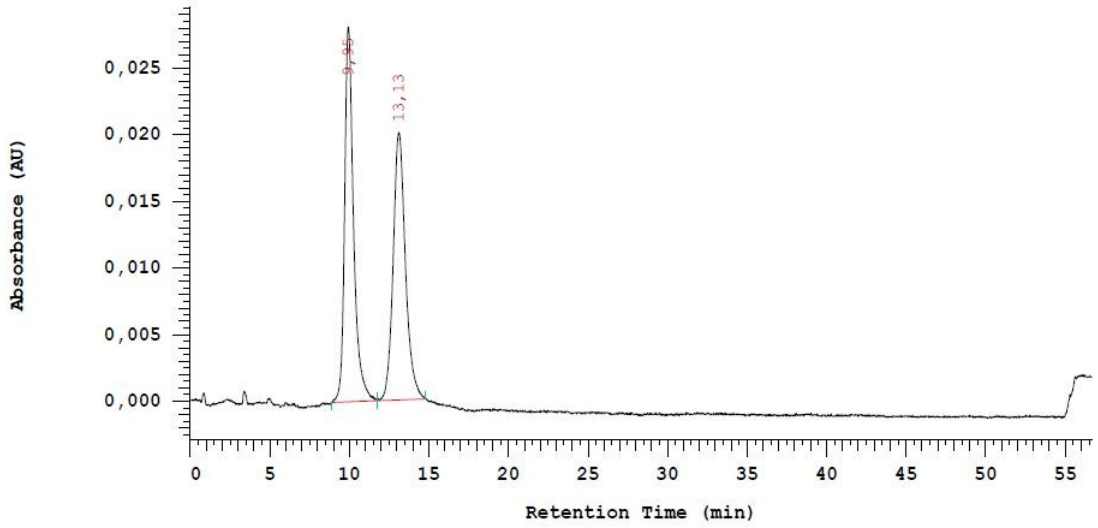
No.	RT	Area	Area %	Name
1	33,51	6746879	48,157	
2	37,39	7263396	51,843	
		14010275	100,000	



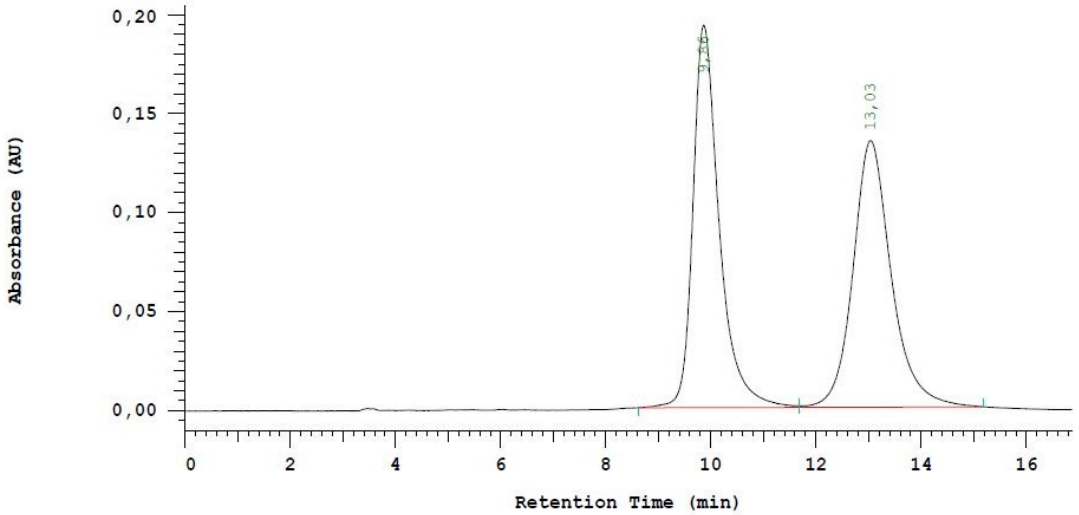
No.	RT	Area	Area %	Name
1	31,12	12574649	96,361	
2	35,23	474860	3,639	
		13049509	100,000	



3ea



No.	RT	Area	Area %	Name
1	9,95	538536	50,453	
2	13,13	528858	49,547	
		1067394	100,000	



No.	RT	Area	Area %	Name
1	9,86	3356715	49,590	
2	13,03	3412234	50,410	
		6768949	100,000	