<Supporting Information>

Construction of Polyheterocyclic Benzopyran Library with Diverse Core Skeletons through Diversity-Oriented Synthesis Pathway: Part II

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S. No.	**Content**	**Page No.**

I. Synthetic procedure for all intermediates and products.

General Information. All reagents in this synthetic procedure were purchased from Sigma-Aldrich [MO, USA], TCI [Japan] and were used without further purification unless otherwise noted. The fluorous reagent and fluorous solid-phase extraction (FSPE) cartridges were purchased from Fluorous Technologies Incorporated. Polystyrene resin was purchased from Novabiochem (lot No.01-64-0415). The progress of reaction was monitored using thin-layer chromatography (TLC) (silica gel 60 F_{254} 0.25 mm), and components were visualized by observation under UV light (254 nm) or by treating the TLC plates with anisaldehyde or ninhydrin staining solution followed by heating. Silica gel 60 (0.040–0.063 mm) used in flash column chromatography was purchased from Merck [Germany]. All reactions were conducted in oven-dried glassware under argon atmosphere, unless otherwise specified. CH_2Cl_2 and THF were purified by passage through solvent purification system employing activated aluminum oxide prior to use. Toluene was distilled in the presence of sodium metal. Other solvents and organic reagents were purchased from commercial venders and used without further purification unless otherwise mentioned. ^{1}H, ^{13}C NMR and gCOSY spectra were recorded on a Varian Inova-500 [Palo Alto, USA] or Bruker Avance DPX-300 [Germany], NOESY spectra were recorded on a Bruker Avance DPX-600 [Germany]. Chemical shifts were measured in ppm relative to internal standard tetramethylsilane (TMS) or specific solvent signal. Multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet); dd (doublet of doublet); dt (doublet of triplet); td (triplet of doublet); bs (broad singlet), etc. Coupling constants were reported in Hz. Routine mass analysis were performed on LC/MS system equipped with a reverse phase column (C-18, 50 × 2.1 mm, 5 μm), PDA detector (200 nm to 600 nm) and electron spray ionization (ESI).

General Synthetic Procedure for Compound 1. *ortho*-Hydroxyacetophenone derivative (1.0 equiv.) was dissolved in EtOH (absolute), pyrrolidine (2.0 equiv.) was added to the solution, followed by the addition of acetone (10 equiv.). The reaction mixture was then heated to reflux for about 12 h. After the completion of reaction monitored by TLC, the reaction mixture was concentrated *in vacuo*. The residue was re-dissolved in ethyl acetate and washed several times with 1N HCl aqueous solution, after washing with brine, the combined organic layer was dried over anhydrous $MgSO_4$, filtrated, and evaporated *in vacuo*. The resulting mixture was purified with silica-gel flash column chromatography to provide desired products **1**{*1*–*2*} (The compounds **1**{*1*}–**3**{*1*} and **1**{*2*}–**3**{*2*} were previously reported).[1] For **1**{*3*–*4*}, bromo-substituted *ortho*-hydroxyactophenone (for **1**{*3*}: 5′-bromo-2′-hydroxyacetophenone; for **1**{*4*}: 3′-bromo-5′-chloro-2′-hydroxyacetophenone) was cyclized with acetone in the same procedure, then the resulting bromo-dimethylchromanone (**1**′{*3*–*4*}, 1.0 equiv.) was dissolved in toluene/EtOH/H_2O (2:1:2), followed by the addition of 3-hydroxyphenylboronic acid (1.2 equiv.), Na_2CO_3 (2.5 equiv.), and $Pd(PPh_3)_4$ (0.05 equiv.). The reaction mixture was refluxed under Argon atmosphere. After the completion of reaction monitored by TLC, the reaction mixture was concentrated *in vacuo* and the residue was re-dissolved in ethyl acetate and washed with brine. The combined organic layer was dried over anhydrous $MgSO_4$, filtrated, and evaporated *in vacuo*. The resulting mixture was purified with silica-gel flash column chromatography to provide desired products

6-bromo-2,2-dimethylchroman-4-one (1′{*3*}). Pale yellow oil (72%); ^{1}H NMR (500 MHz,

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[1](a)Ko, S. K.; Jang, H. J.; Kim, E.; Park, S. B. Concise and diversity-oriented synthesis of novel scaffolds embedded with privileged benzopyran motif. *Chem. Commun.* **2006,** 2962–2964
(b) Zhu, M.; Kim, M.H.; Lee, S.; Bae, S.J.; Kim, S.H.; Park, S.B. Discovery of novel benzopyranyl tetracycles that act as inhibitors of osteoclastogenesis induced by receptor activator of NF-κB ligand. *J. Med. Chem.* **2010**, *53*, 8760–8764.

$CDCl_3$): δ 7.95 (d, *J* = 2.5 Hz, 1H), 7.53 (dd, *J* = 9.0 and 2.5 Hz, 1H), 6.83 (d, *J* = 9.0 Hz, 1H), 2.71 (s, 2H), 1.45 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 191.4, 159.0 138.8, 129.1, 121.5, 120.6, 113.4, 79.9, 48.6, 26.6.

6-(3-Hydroxyphenyl)-2,2-dimethylchroman-4-one (**1{*3*}**). Colorless crystal (86%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (d, *J* = 2.0 Hz, 1H), 7.70 (dd, *J* = 8.5 and 2.5 Hz, 1H), 7.25 (dd, *J* = 15.0 and 7.0 Hz, 1H), 7.13 (t, *J* = 2.0 Hz, 1H), 7.09 (m, 1H), 6.96 (d, *J* = 8.5 Hz, 1H), 6.82 (ddd, *J* = 8.0, 2.5 and 1.0 Hz, 1H), 6.53 (br.s, 1H), 2.76 (s, 2H), 1.46 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.8, 159.8, 156.6, 141.2, 135.2, 133.5, 130.2, 124.7, 120.1, 119.0, 118.8, 114.5, 113.7, 79.6, 48.9, 26.8.

6-Chloro-8-bromo-2,2-dimethylchroman-4-one (**1′{*4*}**). Pale yellow oil (85%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, *J* = 2.5 Hz, 1H), 7.66 (d, *J* = 2.5 Hz, 1H), 2.73 (s, 2H), 1.48 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 190.7, 155.2 138.6, 126.3, 125.4, 121.6, 113.1, 81.0, 48.3, 26.6.

6-Chloro-8-(3-hydroxyphenyl)-2,2-dimethylchroman-4-one (**1{*4*}**). Colorless crystal (88%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (d, *J* = 2.5 Hz, 1H), 7.45 (d, *J* = 2.5 Hz, 1H), 7.25 (dd, *J* = 16 and 7.5 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.98 (s, 1H), 6.84 (dd, *J* = 8.0 and 2.5 Hz, 1H), 5.54 (s, 1H), 2.72 (s, 2H), 1.42 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.2, 155.6, 155.5, 137.6, 136.7, 133.2, 129.5, 126.3, 125.4, 121.9, 121.7, 116.5, 115.0, 80.0, 48.6, 26.6.

General Synthetic Procedure for Compound 2. Each compound was dissolved in a mixed solvent of EtOAc/$CHCl_3$/MeOH (5:5:1), then $CuBr_2$ (2.05 equiv.) was added and the resulting mixture was heated at 70℃ for about 4 h. After the reaction completed monitored by TLC, the resulting solid was filtered off and the filtrate was diluted by EtOAc and washed with brine for 3 times. The combined organic layer was dried over anhydrous $MgSO_4$, filtrated, and concentrated *in vacuo*. The resulting mixture was purified with silica-gel flash column chromatography (EtOAc:Hexane 1:4) to provide desired products.

3-bromo-6-(3-hydroxyphenyl)-2,2-dimethylchroman-4-one (**2{*3*}**). Pale yellow oil (89%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (d, *J* = 2.5 Hz, 1H), 7.72 (dd, *J* = 8.5 and 2.5 Hz, 1H), 7.25 (dd, *J* = 16.0 and 5.5 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 2.0 Hz, 1H), 6.99 (d, *J* = 9.0 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.03 (s, 1H), 4.39 (s, 1H), 1.62 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 187.0, 158.3, 156.4, 141.0, 135.7, 134.5, 130.3, 125.9, 119.1, 118.9, 117.8, 114.7, 113.8, 80.2, 56.0, 26.0, 23.3.

3-bromo-6-chloro-8-(3-hydroxyphenyl)-2,2-dimethylchroman-4-one (**2{*4*}**). Pale yellow oil (98%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (d, *J* = 2.5 Hz, 1H), 7.54 (d, *J* = 2.5 Hz, 1H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.07 (dt, *J* = 7.5 and 1.0 Hz, 1H), 7.01 (t, *J* = 2.5 Hz, 1H), 6.87 (dd, *J* = 8.0 and 3.0 Hz, 1H), 5.33 (br. s, 1H), 4.40 (s, 1H), 1.59 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 186.4, 155.7, 154.1, 137.4, 136.9, 133.1, 129.6, 127.0, 126.2, 121.7, 119.1, 116.4, 115.3, 80.5, 55.2, 25.5, 23.0.

General Synthetic Procedure for Compound 3. After TIPS protection of hydroxyl group, compound **2** was dissolved in EtOH and added with $NaBH_4$ (1.0 equiv.). The resulting mixture was stirred at 40℃ for 30 min. After the reaction completion monitored by TLC, the reaction was quenched by saturated NH_4Cl solution, then the aqueous mixture was extracted by EtOAc for 3 times and the combined organic extracts were washed with brine and dried over anhydrous $MgSO_4$, filtrated, and concentrated *in vacuo*. The resulting mixture was re-dissolved in toluene, treated with *p*-toluenesulfonic acid monohydrate (p-TsOH, 0.1 equiv.), and heated at 80℃ for about 2 h. After the reaction completion monitored by TLC, the reaction mixture was diluted with EtOAc and washed with saturated $NaHCO_3$ and brine. The combined organic layer was dried over anhydrous $MgSO_4$, filtrated, and concentrated *in vacuo*. The resulting mixture was purified by silica-gel flash column chromatography (100% Hexane) to provide TIPS-protected vinylbromide compound **3**. For deprotection of silyl group, TIPS-protected **3** in THF solution was slowly added with TBAF (1.0 M solution in THF, 1.0 equiv.) at 0˚C, and the reaction mixture was stirred at room temperature for 30min. After the reaction completion monitored by TLC, organic solvent was carefully removed under reduced pressure and the resulting residue was re-dissolved in EtOAc. The organic layer was washed with brine, dried over anhydrous $MgSO_4$ and condensed. The resulting mixture was purified by silica-gel flash column chromatography (EA:Hexane 1:10) to provide desired compounds **3**{*1–4*}.

3-bromo-2,2-dimethyl-*2H*-chromen-7-ol (**3{*1*}**). Colorless crystal (62% four-step yield from **2{*1*}**); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.80 (d, *J* = 8.5 Hz, 1H), 6.63 (s, 1H), 6.35 (dd, *J* = 8.0 and 2.5 Hz, 1H), 6.32 (d, *J* = 2.5 Hz, 1H), 5.21 (s, 1H), 1.54 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.8, 153.0, 126.7, 125.4, 122.0, 115.9, 108.5, 104.0, 80.4, 26.7.

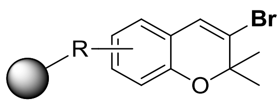
3-bromo-7-methoxy-2,2-dimethyl-*2H*-chromen-8-ol (**3{*2*}**). Colorless crystal (59% four-step yield from **2{*2*}**); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.65 (s, 1H), 6.47 (d, *J* = 8.5 Hz, 1H), 6.43 (d, *J* = 8.5 Hz, 1H), 5.38 (s, 1H), 3.86 (s, 3H), 1.58 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.1, 138.8, 134.2, 125.7, 122.9, 116.7, 116.2, 104.3, 80.7, 56.3, 26.7.

3-(3-bromo-2,2-dimethyl-*2H*-chromen-6-yl)phenol (**3{*3*}**). White solid (50% four-step yield from **2{*3*}**); ¹H NMR (500 MHz, $CDCl_3$): δ 7.35 (dd, *J* = 8.5 and 2.0 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 2.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.99 (t, *J* = 2.0 Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 1H), 6.78 (dd, *J* = 7.5 and 2.5 Hz, 1H), 6.75 (s, 1H), 5.01(br. s, 1H), 1.58 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.0, 151.4, 142.4, 134.2, 130.1, 128.2, 125.9, 125.8, 124.2, 122.4, 119.4, 116.9, 113.9, 113.7, 80.5, 26.8.

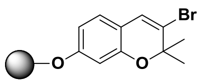
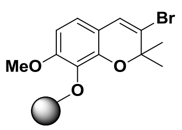
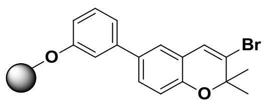
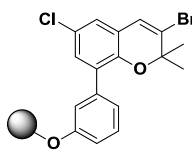
3-(3-bromo-6-chloro-2,2-dimethyl-*2H*-chromen-8-yl)phenol (**3{*4*}**). White crystal (41% four-step yield from **2{*4*}**); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (t, *J* = 7.5 Hz, 2H), 7.17 (d, *J* = 2.5 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.99 (t, *J* = 2.0 Hz, 1H), 6.90 (d, *J* = 2.0 Hz, 1H), 6.82 (dd, *J* = 8.0 and 2.5 Hz, 1H), 6.68 (s, 1H), 5.30 (br. s, 1H), 1.53 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.3, 146.9, 138.1, 131.0, 130.0, 129.4, 127.1, 126.3, 125.1, 124.5, 124,1 116.3, 114.6, 80.7, 26.4.

Loading of Compound 3 on Solid-support and Immobilized Intermediate 4{1–4}.

Table S1. Structure of immobilized vinyl bromide intermediate **4**{*1–4*} and loading level of resins.



4{*1–4*}

Structure	 **4**{*1*}	 **4**{*2*}	 **4**{*3*}	 **4**{*4*}
Loading level	0.98mmol/g	1.02mmol/g	0.96mmol/g	1.08mmol/g

[(3-bromo-2,2-dimethyl-*2H*-chromen-7-yl)oxy](3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)diisopropylsilane (**5{*1*}**). Transparent oil (85%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.80 (d, *J* = 8.0 Hz, 1H), 6.64 (s, 1H), 6.37 (d, *J* = 8.5 Hz, 1H), 6.34 (s, 1H), 2.19–2.08 (m, 2H), 1.46 (s, 6H), 1.22 (q, *J* = 7.5 Hz, 2H), 1.08 (d, *J* = 7.5 Hz, 12H), 0.90 (quintet, *J* = 4.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.5, 153.0, 126.4, 125.5, 122.7, 116.8, 112.9, 108.3, 80.3, 26.6, 17.5, 13.0.

[(3-bromo-7-methoxy-2,2-dimethyl-*2H*-chromen-8-yl)oxy](3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)diisopropylsilane (**5{*2*}**). Pale yellow oil (87%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.63 (s, 1H), 6.52 (d, *J* = 8.5 Hz, 1H), 6.40 (d, *J* = 8.5 Hz, 1H), 3.77 (s, 1H), 2.37-2.26 (m, 2H), 1.55 (s, 6H), 1.21 (q, *J* = 7.5 Hz, 2H), 1.08 (d, *J* = 7.5 Hz, 12H), 1.00 (quintet, *J* = 4.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.2, 143.2, 133.4, 125.9, 122.5, 118.1, 116.9, 104.1, 80.4, 55.3, 26.7, 17.6, 13.4.

[3-(3-bromo-2,2-dimethyl-*2H*-chromen-6-yl)phenoxy](3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)diisopropylsilane (**5{*3*}**). Transparent oil (88%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (d, *J* = 8.5 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 7.11 (s, 1H), 7.00 (s, 1H), 6.86 (d, *J* = 8.5 Hz, 1H), 6.79 (dt, *J* = 8.0 and 1.2 Hz, 1H), 6.76 (s, 1H), 2.24–2.13 (m, 2H), 1.58 (s, 6H), 1.23 (q, *J* = 7.5 Hz, 2H), 1.10 (d, *J* = 7.5 Hz, 12H), 1.04 (quintet, *J* = 4.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.7, 151.4, 142.4, 134.3, 130.0, 128.2, 125.9, 125.8, 124.2, 122.5, 120.3, 118.1, 118.0, 116.9, 80.5, 26.8, 17.5, 13.0.

[3-(3-bromo-6-chloro-2,2-dimethyl-*2H*-chromen-8-yl)phenoxy](3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)diisopropylsilane (**5{*4*}**). Pale yellow oil (80%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28–7.25 (m, 1H), 7.16 (d, *J* = 2.5 Hz, 1H), 7.09 (dt, *J* = 7.0 and 1.5

Hz, 1H), 7.03 (t, *J* = 2.0 Hz, 1H), 6.91 (d, *J* = 2.5 Hz, 1H), 6.84 (dd, *J* = 8.0 and 2.5 Hz, 1H), 6.69 (s, 1H), 2.18–2.15 (m, 2H), 1.52 (s, 6H), 1.24 (q, *J* = 7.5 Hz, 2H), 1.11 (d, *J* = 7.5 Hz, 12H), 1.04 (quintet, *J* = 4.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.9, 147.0, 138.2, 131.2, 130.1, 129.4, 127.1, 126.3, 125.2, 124.5, 124.2, 122.8, 120.8, 118.8, 80.7, 26.5, 17.6, 13.1.

[(2,2-dimethyl-3-vinyl-*2H*-chromen-7-yl)oxy](3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)diisopropylsilane (**7{*1*}**). Pale yellow oil (83%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.87 (d, *J* = 8.0 Hz, 1H), 6.41 (s, 1H), 6.37 (dd, *J* = 8.0 and 2.5 Hz, 1H), 6.34 (d, *J* = 2.0 Hz, 1H), 6.24 (ddd, *J* = 17.5, 11.0 and 1.0 Hz, 1H), 5.50 (dd, *J* = 17.5 and 1.2 Hz, 1H), 5.10 (dd, *J* = 11.0 and 1.5 Hz, 1H), 2.17–2.10 (m, 2H), 1.48 (s, 6H), 1.23 (q, *J* = 7.5 Hz, 2H), 1.09 (d, *J* = 7.5 Hz, 12H), 1.01 (quintet, *J* = 4.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.3, 153.9, 137.5, 133.8, 127.2, 118.8, 116.9, 114.8, 112.5, 108.0, 78.8, 26.6, 17.5, 13.1.

(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)(diisopropyl)[7-methoxy-2,2-dimethyl-3-vinyl-*2H*-chromen-8-yl]oxy]silane (**7{*2*}**). Yellow oil (89%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.60 (d, *J* = 8.5 Hz, 1H), 6.39 (s, 1H), 6.38 (d, *J* = 8.5 Hz, 1H), 6.24 (dd, *J* = 17.5 and 11.0 Hz, 1H), 5.50 (d, *J* = 17.5 Hz, 1H), 5.09 (d, *J* = 11.0 Hz, 1H), 3.77 (s, 1H), 2.38-2.27 (m, 2H), 1.49 (s, 6H), 1.23 (q, *J* = 7.5 Hz, 2H), 1.06 (d, *J* = 7.5 Hz, 12H), 1.00 (quintet, *J* = 4.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.1, 144.2, 137.2, 133.6, 133.1, 119.3, 119.0, 117.9, 115.6, 103.7, 79.1, 55.2, 26.8, 17.6, 13.5.

[3-(2,2-dimethyl-3-vinyl-*2H*-chromen-6-yl)phenoxy](3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)diisopropylsilane (**7{*3*}**). Transparent oil (75%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30–7.25 (m, 2H), 7.19 (d, *J* = 2.5 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 7.02 (d, *J* =

2.0 Hz, 1H), 6.83 (d, *J* = 8.5 Hz, 1H), 6.78 (dd, *J* = 8.0 and 2.5 Hz, 1H), 6.51 (s, 1H), 6.28 (dd, *J* = 17.5 and 11.0 Hz, 1H), 5.57 (d, *J* = 17.5 Hz, 1H), 5.17 (d, *J* = 11.0 Hz, 1H), 2.21-2.17 (m, 2H), 1.52 (s, 6H), 1.24 (q, *J* = 7.5 Hz, 2H), 1.10 (d, *J* = 7.5 Hz, 12H), 1.04 (quintet, *J* = 4.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.6, 152.4, 142.8, 140.2, 133.7, 133.6, 129.9, 127.7, 125.0, 122.6, 120.3, 119.0, 118.0, 117.9, 116.5, 115.8, 78.9, 26.8, 17.5, 13.1.

[3-(6-chloro-2,2-dimethyl-3-vinyl-*2H*-chromen-8-yl)phenoxy](3,3,4,4,5,5,6,6,7,7,8,8,9,9, 10,10,10-heptadecafluorodecyl)diisopropylsilane (**7{*4*}**). Pale yellow oil (88%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29–7.26 (m, 1H), 7.13–7.12 (m, 1H), 6.99–6.98 (m, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.43 (s, 1H), 6.26 (dd, *J* = 17.5 and 11.0 Hz, 1H), 5.58 (d, *J* = 17.5 Hz, 1H), 5.19 (d, *J* = 11.0 Hz, 1H), 2.21–2.13 (m, 2H), 1.46 (s, 6H), 1.23 (q, *J* = 7.5 Hz, 2H), 1.11 (d, *J* = 7.5 Hz, 12H), 1.04 (quintet, *J* = 4.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.9, 148.0, 141.2, 138.7, 133.2, 130.6, 129.6, 129.3, 125.8, 125.3, 124.5, 122.9, 121.0, 118.7, 118.4, 116.5, 76.9, 26.4, 17.5, 13.1.

[(3-ethynyl-2,2-dimethyl-*2H*-chromen-7-yl)oxy](3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-hepta-decafluorodecyl)diisopropylsilane (**11{*1*}**). Yellow oil (70%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.86 (d, *J* = 8.0 Hz, 1H), 6.68 (s, 1H), 6.37 (dd, *J* = 8.0 and 2.5 Hz, 1H), 6.33 (d, *J* = 2.5 Hz, 1H), 3.08 (s, 1H), 2.18–2.06 (m, 2H), 1.52 (s, 6H), 1.22 (q, *J* = 7.5 Hz, 2H), 1.07 (d, *J* = 7.5 Hz, 12H), 1.00 (quintet, *J* = 4.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.2, 154.0, 130.0, 127.6, 120.3, 115.8, 112.9, 108.2, 81.7, 80.2, 77.9, 26.5, 17.5, 13.0.

[(3-ethynyl-7-methoxy-2,2-dimethyl-*2H*-chromen-8-yl]oxy](3,3,4,4,5,5,6,6,7,7,8,8,9,9,10, 10,10-heptadecafluorodecyl)diisopropylsilane(**11{*2*}**). Yellow oil (89%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.67 (s, 1H), 6.59 (d, *J* = 8.5 Hz, 1H), 6.40 (d, *J* = 8.5 Hz, 1H), 3.78 (s, 3H), 3.09 (s, 1H), 2.33–2.30 (m, 2H), 1.54 (s, 6H), 1.21 (q, *J* = 7.5 Hz, 2H), 1.05 (d, *J* = 7.5 Hz, 12H), 1.00 (quintet, *J* = 4.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.8, 144.1, 133.2, 130.5, 120.1, 119.3, 115.8, 103.9, 81.8, 80.2, 78.1, 55.3, 26.7, 17.7, 13.4.

[3-(3-ethynyl-2,2-dimethyl-*2H*-chromen-6-yl)phenoxy](3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)diisopropylsilane (**11{*3*}**). Yellow oil (87%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.5 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 2.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 7.01 (s, 1H), 6.85 (d, *J* = 8.5 Hz, 1H), 6.80 (d, *J* = 1.5 Hz, 1H), 6.78 (s, 1H), 3.14 (s, 1H), 2.24–2.13 (m, 2H), 1.57 (s, 6H), 1.24 (q, *J* = 7.5 Hz, 2H), 1.11 (d, *J* = 7.5 Hz, 12H), 1.04 (quintet, *J* = 4.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.7, 152.4, 142.4, 134.1, 130.3, 130.0, 128.9, 125.1, 123.4, 121.4, 120.3, 118.1, 118.0, 117.0, 104.9, 81.4, 81.1, 78.1, 26.7, 17.6, 13.1.

[3-(6-chloro-3-ethynyl-2,2-dimethyl-*2H*-chromen-8-yl)phenoxy](3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)diisopropylsilane (**11{*4*}**). Yellow oil (85%); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28–7.25 (m, 1H), 7.15 (d, *J* = 2.5 Hz, 1H), 7.09 (dt, *J* = 8.0 and 1.5 Hz, 1H), 7.03 (t, *J* = 2.0 Hz, 1H), 6.96 (d, *J* = 2.5 Hz, 1H), 6.82 (dd, *J* = 8.0 and 2.5 Hz, 1H), 6.70 (s, 1H), 3.17 (s, 1H), 2.21–2.10 (m, 2H), 1.50 (s, 6H), 1.23 (q, *J* = 7.5 Hz, 2H), 1.10 (d, *J* = 7.5 Hz, 12H), 1.02 (quintet, *J* = 4.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.9, 150.1, 147.9, 138.2, 131.1, 129.4, 129.3, 126.0, 125.3, 124.5, 123.2, 122.8, 120.8, 118.8, 104.9, 81.9, 80.8, 78.3, 17.5, 13.1.

Compound 6{*1,23*}. Pale yellow solid, 5.0 mg, 58% yield from 31mg **4**{*1*} (loading level 0.98mmol/g); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 (t, *J* = 7.5 Hz, 1H), 6.91 (t, *J* = 9.0 Hz, 2H), 6.87–6.86 (m, 1H), 6.85 (s, 1H), 6.39–6.37 (m, 2H), 6.29 (s, 1H), 4.86 (br. s, 1H), 3.83

(s, 3H), 1.52 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.4, 156.7, 153.9, 141.2, 139.2, 129.2, 127.5, 122.1, 120.8, 116.5, 114.4, 112.6, 108.2, 103.9, 79.2, 55.4, 27.2; LRMS(ESI+) *m/z* calculated for $C_{18}H_{19}O_3$ $[M+H]^+$: 283.13; Found: 283.07.

Compound 6{*2,15*}. Pale yellow solid, 5.5 mg, 59% yield from 28mg **4**{*2*} (loading level 1.02mmol/g); ^1H NMR (500 MHz, $CDCl_3$): δ 7.20 (d, *J* = 9.0 Hz, 2H), 6.70 (d, *J* = 9.0 Hz, 2H), 6.57 (d, *J* = 8.5 Hz, 1H), 6.47 (d, *J* = 8.5 Hz, 1H), 6.26 (s, 1H), 5.40 (br. s, 1H), 3.89 (s, 3H), 2.97 (s, 6H), 1.58 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.9, 147.5, 140.3, 139.5, 134.1, 129.0, 127.7, 120.8, 117.8, 116.7, 112.0, 104.1, 79.9, 56.3, 40.6, 27.3; LRMS(ESI+) *m/z* calculated for $C_{20}H_{24}NO_3$ $[M+H]^+$: 326.17; Found: 326.21.

Compound 6{*3,11*}. white solid, 4.9 mg, 53% yield from 26mg **4**{*3*} (loading level 0.96mmol/g); ^1H NMR (500 MHz, $CDCl_3$): δ 7.93–7.92 (m, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 1H), 7.29–7.28 (m, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.03 (s, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 8.5 Hz, 1H), 6.41 (s, 1H), 2.63 (s, 3H), 1.50 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.1, 152.4, 141.7, 141.0, 137.3, 134.0, 132.9, 130.1, 128.7, 128.2, 128.1, 127.7, 125.3, 123.3, 122.8, 119.4, 116.8, 113.8, 113.7, 79.0, 27.2, 26.9; LRMS(ESI+) *m/z* calculated for $C_{25}H_{23}O_3$ $[M+H]^+$: 371.16; Found: 370.96.

Compound 6{*4,19*}. Pale yellow solid, 6.2 mg, 61% yield from 25mg **4**{*4*} (loading level 1.08mmol/g); ^1H NMR (500 MHz, $CDCl_3$): δ 7.30–7.23 (m, 3H), 7.13 (d, *J* = 9.0 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.06 (s, 1H), 7.02 (d, *J* = 2.0 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.41 (s, 1H), 1.47 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.5, 152.9, 138.6, 138.3, 131.1, 129.7, 129.6, 129.4, 126.1, 125.5, 124.7, 124.6, 124.0, 121.9, 120.3, 116.4, 116.0, 114.6, 79.8, 26.3; LRMS(ESI+) *m/z* calculated for

$C_{23}H_{18}ClO_3$ $[M-H]^-$: 377.10; Found: 377.05.

Compound 8{*1,4*}. White solid, 13.0 mg, 77% two-step yield from 0.0415mmol **7**{*1*}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.41 (t, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.16 (s, 1H), 6.96 (d, *J* = 8.5 Hz, 1H), 6.90 (d, *J* = 8.5 Hz, 1H), 6.36 (d, *J* = 9.5 Hz, 1H), 6.34 (s, 1H), 5.81 (s, 1H), 5.68 (s, 1H), 4.26 (dd, *J* = 16.5 and 4.5 Hz, 1H), 4.08 (d, *J* = 16.5 Hz, 1H), 3.84 (s, 3H), 1.57 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.0, 156.8, 124.1, 153.7, 151.3, 137.2, 131.9, 129.9, 124.5, 117.6, 115.3, 114.3, 112.5, 111.2, 108.8, 104.8, 78.7, 55.4, 50.0, 44.1, 27.4, 26.6; LRMS(ESI+) *m/z* calculated for $C_{22}H_{22}N_3O_5$ $[M+H]^+$: 408.42; Found: 408.17.

Compound 8{*2,10*}. Pale yellow solid, 10.3 mg, 51% two-step yield from 0.0445mmol **7**{*2*}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.65 (s, 1H), 8.27 (d, *J* = 8.5 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.71 (t, *J* = 8.0 Hz, 1H), 6.55 (s, 2H), 5.84 (s, 1H), 5.74 (s, 1H), 5.45 (s, 1H), 4.33 (dd, *J* = 16.5 and 4.5 Hz, 1H), 4.14 (d, *J* = 16.5 Hz, 1H), 3.86 (s, 3H), 1.66 (s, 3H), 1.65 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.7, 147.5, 140.6, 137.9, 135.3, 132.8, 130.7, 130.2, 122.9, 120.3, 117.5, 133.3, 122.9, 105.0, 80.3, 56.4, 50.6, 44.3, 27.9, 27.2; LRMS(ESI+) *m/z* calculated for $C_{20}H_{21}N_4O_7$ $[M+H]^+$: 453.13; Found: 453.15.

Compound 8{*3,7*}. White solid, 12.6 mg, 72% two-step yield from 0.0375mmol **7**{*3*}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.44 (d, *J* = 5.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.25–7.19 (m, 4H), 7.14 (s, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 6.83 (s, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 5.79-5.78 (m, 1H), 5.70 (s, 1H), 5.65 (br. s, 1H), 4.85(d, *J* = 15 Hz, 1H), 4.78 (d, *J* = 15 Hz, 1H), 4.21 (d, *J* = 16.0 Hz, 1H), 3.98 (d, *J* = 16.0 Hz, 1H), 1.58 (s, 3H), 1.57 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.2, 155.1, 152.9, 142.3, 137.6, 135.5, 134.6, 130.2, 129.0, 128.5, 128.3, 128.2, 124.2, 122.2, 119.3, 118.3, 114.0, 113.9, 113.2, 79.3, 50.3, 44.2, 43.1, 27.9, 27.0; LRMS(ESI+) *m/z* calculated for $C_{28}H_{26}N_3O_4$ $[M+H]^+$: 468.18; Found: 468.22.

Compound 8{*4,3*}. Pale yellow solid, 15.9 mg, 70% two-step yield from 0.044mmol **7**{*4*}; ^{1}H NMR (500 MHz, Acetone-d_6): δ 8.44(br. s, 1H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.30 (s, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.12–7.08 (m, 4H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.0 Hz, 1H), 6.02 (s, 1H), 5.65 (s, 1H), 4.23 (s, 2H), 3.87 (s, 3H), 1.64 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (75 MHz, Acetone-d_6): δ 159.4, 157.1, 153.5, 151.9, 149.1, 137.9, 137.7, 133.4, 129.1, 129.0, 128.9, 127.4, 126.2, 124.6, 122.4, 120.5, 116.3, 114.6, 114.3, 114.1, 81.2, 55.0, 50.8, 43.5, 27.9, 26.8; LRMS(ESI+) *m/z* calculated for $C_{28}H_{25}ClN_3O_5$ $[M+H]^+$: 518.14; Found: 518.23.

Compound 9{3,*1*}. Pale yellow solid, 11.6 mg, 69% two-step yield from 0.0375mmol **7**{*3*}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, *J* = 2.0 Hz, 1H), 7.40–7.35 (m, 4H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 3H), 7.06 (s, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 6.77 (dd, *J* = 8.0 and 2.5 Hz, 1H), 5.98 (t, *J* = 4.0 Hz, 1H), 3.74 (s, 1H), 3.70 (t, *J* = 8.5 Hz, 1H), 3.42 (t, *J* = 7.5 Hz, 1H), 3.02 (q, *J* = 7.5 Hz, 1H), 2.35–2.31 (m, 1H), 1.48 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 178.5, 175.4, 163.1, 156.5, 145.2, 143.1, 142.7, 134.3, 131.9, 130.0, 129.2, 128.6, 126.9, 126.6, 123.3, 119.0, 118.7, 113.9, 45.2, 40.4, 36.9, 35.2, 35.0, 31.8, 27.5, 27.0, 25.0; LRMS(ESI+) *m/z* calculated for $C_{29}H_{26}NO_4$ $[M+H]^+$: 452.18; Found: 452.29.

Compound 9{*4,3*}. Pale yellow solid, 19.2 mg, 85% two-step yield from 0.044mmol **7**{*4*}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31(s, 1H), 7.24–7.21 (m, 2H), 7.04 (d, *J* = 7.0 Hz, 3H), 6.96 (s, 1H), 6.88 (d, *J* = 9.0 Hz, 1H), 6.77 (d, *J* = 8.5 Hz, 1H), 5.92 (t, *J* = 2.5 Hz, 1H), 3.67 (s, 1H), 3.63 (t, *J* = 8.5 Hz, 1H), 3.41 (t, *J* = 8.0 Hz, 1H), 2.99 (q, *J* = 7.5 Hz, 1H), 2.31–2.28 (m, 1H), 1.39 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.6, 175.2, 159.6, 155.4, 150.0, 144.7, 138.8, 132.8, 129.2, 129.1, 127.6, 126.8, 126.2, 125.5, 124.5, 122.1, 118.5, 116.8, 114.5, 114.3, 55.6, 45.1, 40.2, 36.7, 35.5, 27.1, 26.8, 24.9; LRMS(ESI+) *m/z* calculated for $C_{30}H_{27}ClNO_5$ $[M+H]^+$: 516.15; Found: 516.29.

Compound 10{*1,12*}. Yellow solid, 7.6 mg, 59% three-step yield from 0.0415mmol **7**{*1*}; ^1H NMR (500 MHz, Acetone-d_6): δ 8.93 (br. s, 1H), 8.61 (d, *J* = 8.5 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 6.62 (dd, *J* = 8.5 and 2.5 Hz, 1H), 6.46 (d, *J* = 2.5 Hz, 1H), 3.12 (s, 3H), 1.62 (s, 6H); ^{13}C NMR (75 MHz, Acetone-d_6): δ 169.4, 168.2, 161.5, 156.7, 148.0, 134.6, 132.7, 130.8, 129.7, 125.8, 121.4, 112.8, 109.8, 105.2, 78.9, 55.0, 27.3, 24.2; LRMS(ESI+) *m/z* calculated for $C_{18}H_{14}NO_4$ $[M-H]^-$: 308.10; Found: 308.10.

Compound 10{*2,1*}. Yellow solid, 13.4 mg, 75% three-step yield from 0.0445mmol **7**{*2*}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.24 (d, *J* = 9.0 Hz, 1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.53–7.50 (m, 2H), 7.44-7.40 (m, 3H), 6.68 (d, *J* = 9.0 Hz, 1H), 6.26 (s, 1H), 5.47 (br. s, 1H), 3.96 (s, 3H), 2.97 (s, 6H), 1.71 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.8, 166.7, 149.5, 148.3, 141.8, 135.0, 133.3, 132.0, 131.1, 129.3, 128.4, 127.1, 125.1, 122.2, 121.7, 113.8, 104.7, 79.3, 56.3, 27.4; LRMS(ESI+) *m/z* calculated for $C_{24}H_{20}NO_5$ $[M+H]^+$: 402.13; Found: 402.17.

Compound 12{*1,1*}. Pale white solid, 9.2 mg, 72% two-step yield from 0.0375mmol **11**{*1*}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.51 (s, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.63 (s, 1H), 6.38 (s, 1H), 6.36 (s, 1H), 5.40 (br.s, 1H), 4.35 (t, *J* = 8.5 Hz, 2H), 1.92 (t, *J* = 6.0 Hz, 2H), 1.66 (s, 6H), 1.34–1.25 (m, 8H), 0.88 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.4, 154.1, 146.1, 139.5, 132.9, 128.0, 127.7, 122.1, 120.6, 115.3, 108.4, 103.9, 78.9, 50.5, 31.7, 30.4, 28.8, 27.2, 26.6, 22.7, 14.2; LRMS(ESI+) *m/z* calculated for $C_{20}H_{28}N_3O_2$ $[M+H]^+$:

342.21; Found: 341.97.

Compound 12{*1,15*}. Pale white solid, 9.2 mg, 82% two-step yield from 0.035mmol **11**{*1*}; ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.69 (s, 1H), 9.19 (s, 1H), 9.09 (s, 1H), 8.71 (s, 1H), 8.38–8.36 (m, 1H), 7.67 (br. s, 1H), 6.99 (d, *J* = 2.5 Hz, 1H), 6.90 (s, 1H), 6.35–6.32 (m, 1H), 6.24 (s, 1H), 1.63 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 159.2, 153.3, 149.7, 145.9, 141.2, 133.2, 127.8, 127.7, 126.1, 124.6, 121.8, 120.3, 113.2, 108.5, 103.0, 77.9, 26.8; LRMS(ESI+) *m/z* calculated for $C_{18}H_{17}N_4O_2$ $[M+H]^+$: 321.13; Found: 321.22.

Compound 12{*2,4*}. Yellow solid, 12.4 mg, 68% two-step yield from 0.0445mmol **11**{*2*}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (s, 1H), 7.27–7.22 (m, 4H), 6.59 (s, 1H), 6.56 (d, *J* = 8.5 Hz, 1H), 6.44 (d, *J* = 8.5 Hz, 1H), 5.49 (s, 2H), 5.40 (br. s, 1H), 3.88 (s, 3H), 2.49 (s, 3H), 1.70 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.2, 146.6, 139.9, 139.6, 133.9, 131.1, 128.9, 128.8, 126.9, 125.7, 122.1, 120.5, 117.3, 116.2, 104.1, 79.5, 56.3, 53.9, 27.2, 26.7, 15.6; LRMS(ESI+) *m/z* calculated for $C_{22}H_{24}N_3O_3S$ $[M+H]^+$: 410.15; Found: 410.24.

Compound 12{*3,2*}. Yellow solid, 14.6 mg, 81% two-step yield from 0.0435mmol **11**{*3*}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.27–7.24 (m, 1H), 7.22 (s, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 7.05 (s, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 6.81 (d, *J* = 7.5 Hz, 1H), 6.75 (s, 1H), 6.19 (br. s, 1H), 4.20 (d, *J* = 7.0 Hz, 2H), 1.92–1.89 (m, 1H), 1.76–1.64 (m, 5H), 1.70 (s, 6H), 1.29-1.16 (m, 3H) 1.06-0.99 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.5, 152.4, 145.6, 142.6, 134.1, 131.5, 130.1, 128.4, 125.4, 122.4, 121.7, 119.1, 116.7, 114.1, 113.9, 79.1, 56.8, 39.0, 30.8, 27.4, 26.3, 25.7; LRMS(ESI+) *m/z* calculated for $C_{26}H_{29}N_3O_2$ $[M+H]^+$: 416.23; Found: 416.35.

Compound 12{*4,3*}. Pale yellow solid, 14.2 mg, 73% two-step yield from 0.0425mmol

11{*4*}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30–7.28(m, 2H), 7.27–7.25 (m, 3H), 7.17–7.16 (m, 2H), 7.13–7.07(m, 3H), 6.97 (s, 1H), 6.84 (d, *J* = 6.0 Hz, 1H), 6.60 (s, 1H), 5.75 (br. s, 1H), 4.61 (t, *J* = 7.0 Hz, 2H), 3.22 (t, *J* = 7.0 Hz, 2H), 1.58 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.7, 147.9, 144.7, 138.3, 137.1, 132.4, 130.8, 130.0, 129.3, 129.0, 128.9, 127.4, 125.8, 125.4, 123.8, 121.8, 121.7, 121.4, 116.5, 114.6, 79.1, 51.9, 36.9, 27.0; LRMS(ESI+) *m/z* calculated for $C_{27}H_{25}ClN_3O_3$ $[M+H]^+$: 458.16; Found: 458.14.

Compound 13{*1,1*}. Pale yellow solid, 7.9 mg, 66% two-step yield from 0.035mmol **11**{*1*}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (s, 1H), 7.22 (br. s, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.50 (d, *J* = 2.0 Hz, 1H), 6.46 (s, 1H), 4.32 (t, *J* = 7.5 Hz, 1H), 1.96 (t, *J* = 6.5 Hz, 1H), 1.42 (s, 6H), 1.31–1.25 (m, 8H), 0.85 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1, 154.3, 134.8, 132.9,128.4, 127.8, 123.3, 114.2, 109.2, 104.4, 78.4, 48.6, 31.8, 30.6, 28.9, 26.8, 26.7, 22.7, 14.2; LRMS(ESI+) *m/z* calculated for $C_{20}H_{28}N_3O_2$ $[M+H]^+$: 342.21; Found: 342.27.

Compound 13{*2,4*}. Yellow solid, 14.9 mg, 82% two-step yield from 0.0445mmol **11**{*2*}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (s, 1H), 7.17 (d, *J* = 7.5 Hz, 2H), 7.13 (d, *J* = 7.5 Hz, 2H), 6.49 (s, 2H), 6.15 (s, 1H), 5.51 (s, 2H), 5.48 (br. s, 1H), 3.91 (s, 3H), 2.45 (s, 3H), 1.36 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.6, 139.3, 138.8, 134.1, 133.8, 133.1, 131.8, 128.0, 127.6, 126.3, 125.3. 123.9, 117.5, 115.8, 114.9, 103.9, 78.4, 55.9, 51.3, 26.2, 26.1, 15.3; LRMS(ESI+) *m/z* calculated for $C_{22}H_{24}N_3O_3S$ $[M+H]^+$: 410.15; Found: 410.16.

Compound 13{*3,3*}. Pale yellow solid, 14.2 mg, 77% two-step yield from 0.0435mmol **11**{*3*}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.5 Hz, 1H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.26–7.25 (m, 2H), 7.09–7.05 (m, 3H), 6.98 (d, *J* = 6.0 Hz, 2H), 6.88 (s, 1H), 6.87–6.85 (m, 2H), 6.27 (br. s, 1H), 5.38 (s, 1H), 4.52 (t, *J* = 6.0 Hz, 2H), 3.36 (t, *J* = 6.0 Hz, 2H), 1.33 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.6, 152.3, 142.2, 137.6, 134.6, 130.1, 129.5, 129.2, 129.0, 128.9, 128.2, 127.3, 126.6, 125.8, 120.8, 118.9, 117.1, 114.2, 113.8, 78.3, 49.7, 36.8, 26.5; LRMS(ESI+) *m/z* calculated for $C_{27}H_{25}N_3O_2$ $[M+H]^+$: 424.19; Found: 424.33.

Compound 13{*4,3*}. Pale yellow solid, 13.6 mg, 70% two-step yield from 0.0425mmol **11**{*2*}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (br. s, 1H), 7.28–7.24 (m, 6H), 7.06 (d, *J* = 8.0 Hz, 1H), 7.02 (s, 1H), 6.97 (d, *J* = 7.0 Hz, 2H), 6.85 (d, *J* = 7.5 Hz, 1H), 6.78 (s, 1H), 5.21 (s, 1H), 4.49 (t, *J* = 6.0 Hz, 2H), 3.36 (t, *J* = 6.0 Hz, 2H), 1.30 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.8, 147.9, 137.8, 137.6, 131.4, 131.2, 129.4, 129.2, 129.1, 127.8, 127.3, 126.2, 125.9, 122.6, 121.7, 116.4, 114.8, 78.6, 49.7, 36.8, 26.2; LRMS(ESI+) *m/z* calculated for $C_{27}H_{25}ClN_3O_3$ $[M+H]^+$: 458.16; Found: 458.23.

II. Principal Component Analysis (PCA) of Benzopyran Library.

PCA was performed against total 718 molecules of benzopyran library using 14 major molecular descriptors [molecular weight, number of rotatable bonds, number of H-bond acceptors, number of H-bond donors, topological PSA, 2D VDW surface, 2D VDW volume, 2D VSA hydrophobic surface, 2D VSA polar surface, 2D VSA H-bond donor, 2D VSA H-bond acceptor, AlogP98 value, charge polarization and hydrophobic SA_MPEOE]. Molecular descriptors were calculated using PreADMET 2.0 software (BMDRC, Seoul, Korea) and PCA was executed using SAS 9.1 software (SAS institute Inc., Cary, NC, USA). Three principal components (Prin1, Prin2, and Prin3) represent 99.3% of the total variance in molecular descriptors. Prin1 factor, which explains 89.9% of the total variance, is mainly constituted by molecular weight (MW), van der Waals (VDW) surface and VDW volume. Prin2 factor, which explains 7.1% of the total variance, is influenced by hydrophobic surface area by MPEOE. Prin3 factor, accounting for 2.3% of the total variance, includes polar surface area, 2D VDW surface area, and hydrophobic surface area by MPEOE. Prin1 represents the diversity by size and surface area descriptors. Prin2 and Prin3 illustrate the molecular diversity by lipophilic descriptors and polar surface area, respectively. The eigenvalues of covariance matrix and eigenvectors are presented Table S1 and S2, respectively. On the basis of this principal component analysis, we can claim that our library members containing 11 unique core skeletons possess quite diverse physicochemical properties in 3-dimensional chemical space. In Figure S1, four different benzopyranyl starting molecules **3{*1–4*}** were color-coded to demonstrate the importance of appendices diversity for the molecular diversity in library construction.

Table S1. Eigenvalues of the covariance matrix

Eigenvalues of the Covariance Matrix				
	Eigenvalue	Difference	Proportion	Cumulative
Prin1	17405.6563	16041.0425	0.8989	0.8989
Prin2	1364.6138	916.8576	0.0705	0.9694
Prin3	447.7562	333.0494	0.0231	0.9925

Table S2. Eigenvectors in principal component analysis

Eigenvectors			
	Prin1	Prin2	Prin3
Molecular_weight	0.602099	-0.46741	-0.19733
No_Rotatable_bonds	0.003876	0.020343	0.030776
No_H_bond_acceptors	0.006359	-0.00117	0.062006

No_H_bond_donors	-0.000318	-0.00223	0.003173
Topological_PSA	0.097989	-0.213	0.937102
2D_VDW_surface	0.481875	0.016227	0.167299
2D_VDW_volume	0.4719	-0.12391	-0.19725
Fraction_of_2D_VSA_hydrophobic	-0.000062	0.000838	-0.00229
Fraction_of_2D_VSA_polar	0.000003	-0.00048	0.001455
Fraction_of_2D_VSA_Hbond_donor	-0.000084	-0.00011	0.000153
Fraction_of_2D_VSA_Hbond_acceptor	0.000051	-0.0004	0.001291
AlogP98_value	0.004603	0.005108	-0.0482
Charge_polarization	0.000012	-0.00016	0.000289
Hydrophobic_SA_MPEOE	0.415819	0.848582	0.094177

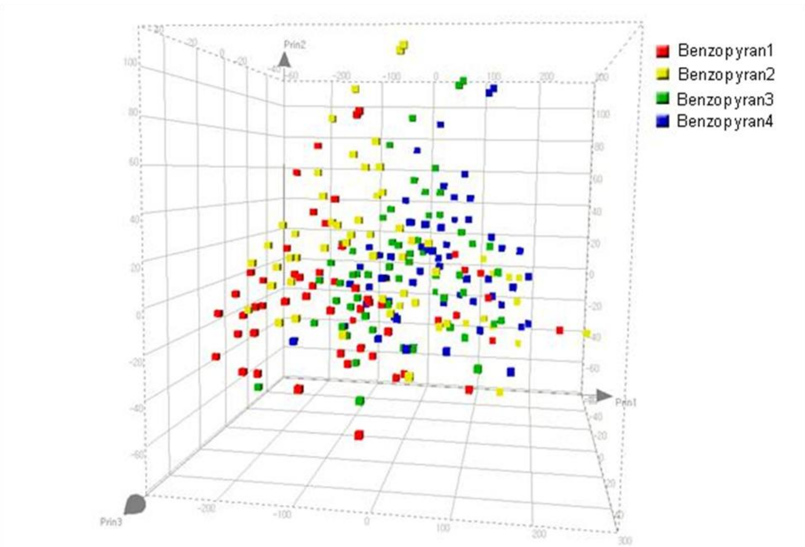


Figure S1. PCA of the combinatorial benzopyran library and color coding of library members, according to different benzopyran starting materials, which shows the contribution of appendance on benzopyran moiety to the diversity of library; red: benzopyran {1}; yellow: benzopyran {2}; green: benzopyran {3}; blue: benzopyran {4}.

III. Crystal Structure of aza Diels-Alder Product and Structural Difference of Three Distinct Benzopyrano-Tetracycle Core Skeletons.

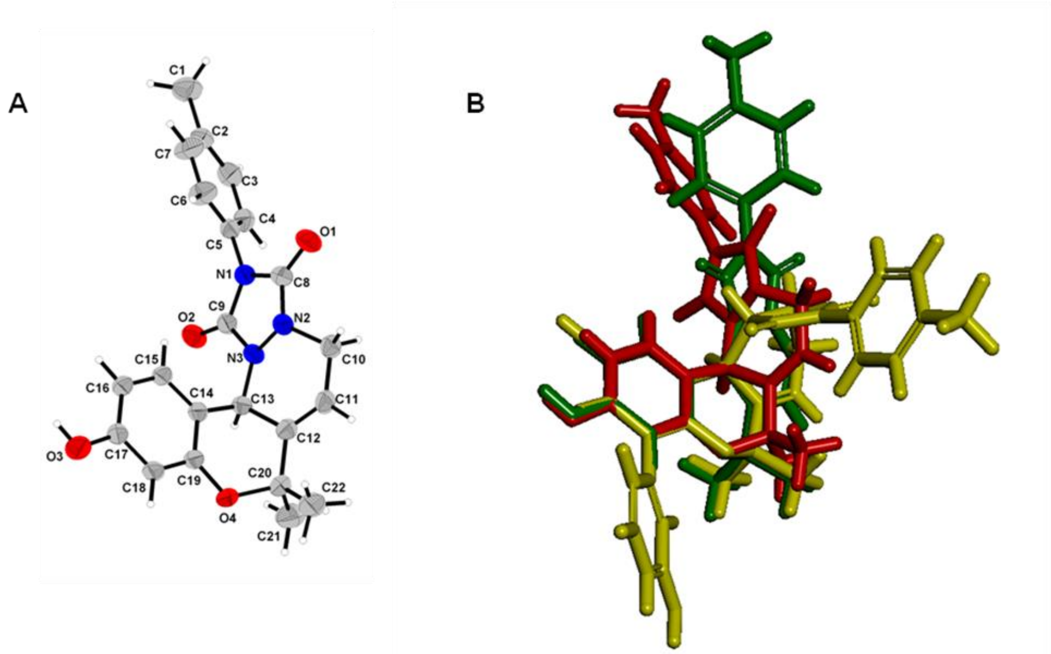
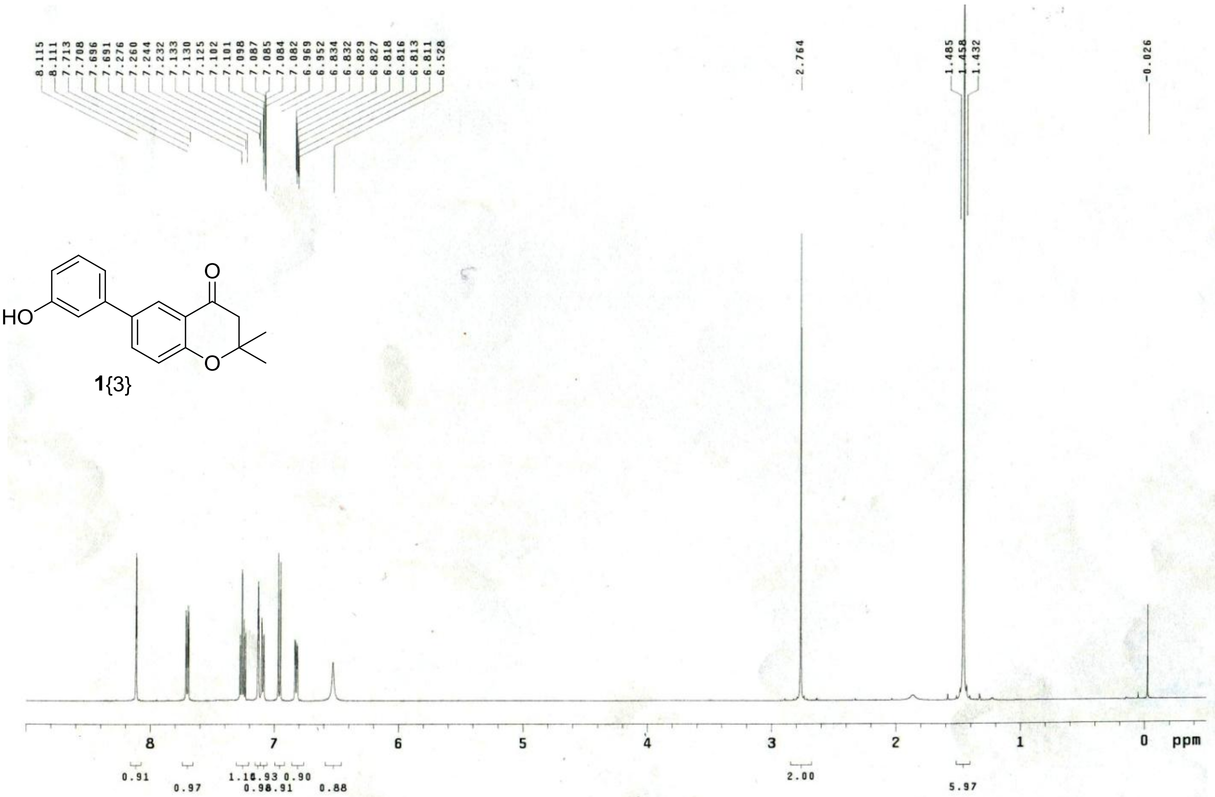
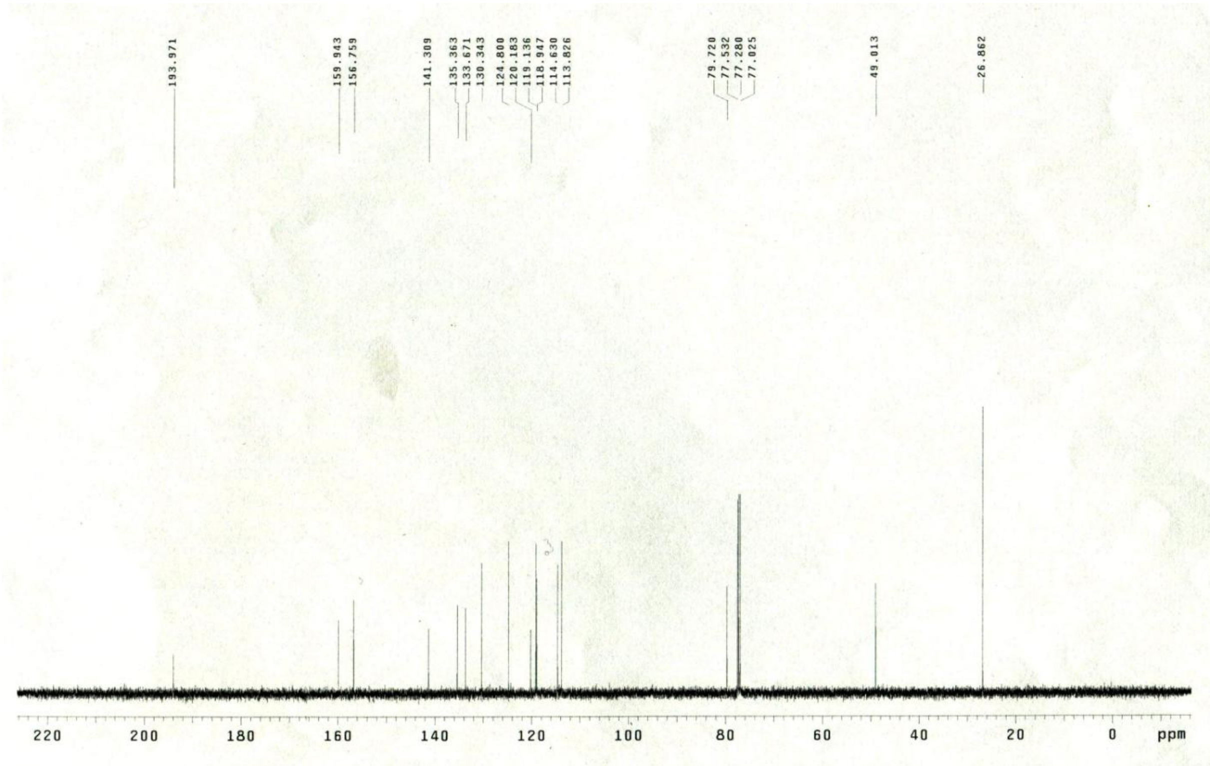
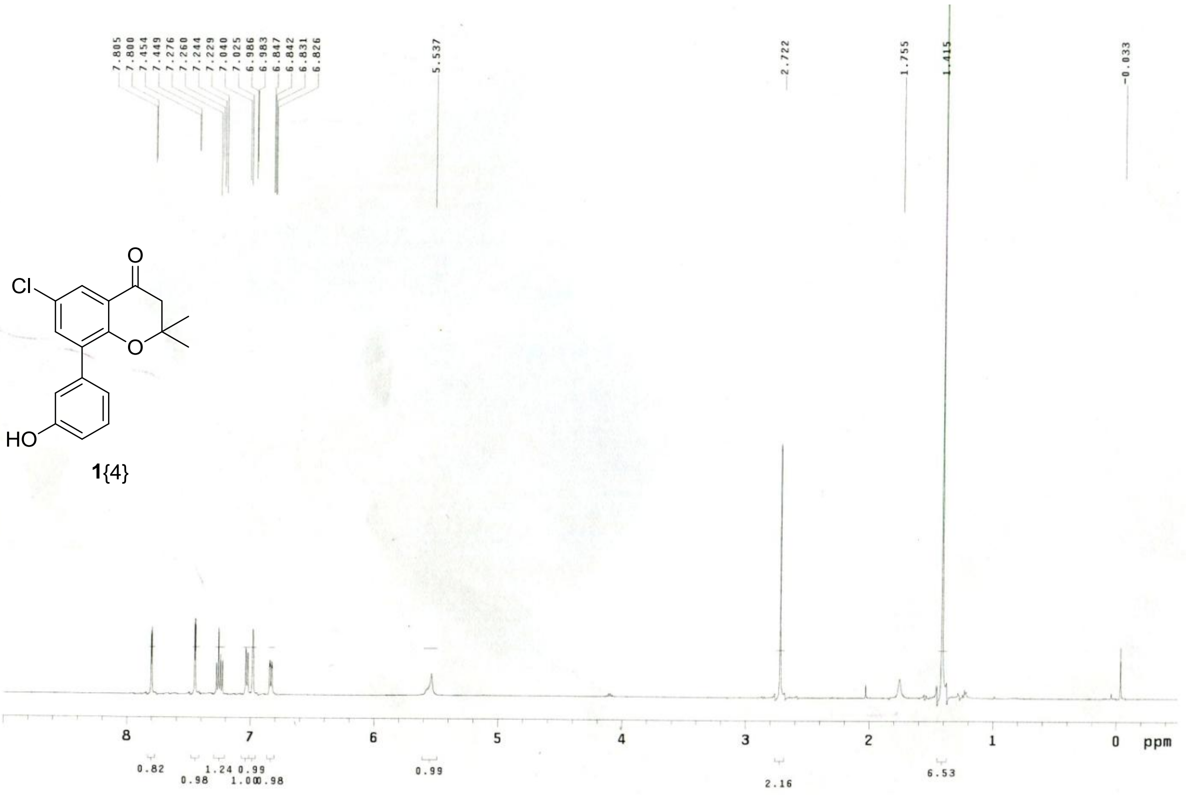


Figure S2. (A) Crystal structure of aza Diels-Alder product **8**{*1*,*2*}, which shows the unique conformation of this heterocyclic compound. (B) 3-D structure of each molecules **8**{*1*,*2*} in red, **9**{*4*,*2*} in yellow, **10**{*1*,*2*} in green were superimposed with three points of each benzopyran (C13, C17 and C19) by using Discovery Studio 1.7 software (Accelrys Software Inc.)

IV. NMR and LC-MS spectra for representative compounds



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7.449
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7.260
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6.847
6.842
6.831
6.826
5.537
2.722
1.755
1.415
-0.033
Cl
O
O
HO
8
7
6
5
4
3
2
1
0
ppm
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0.98
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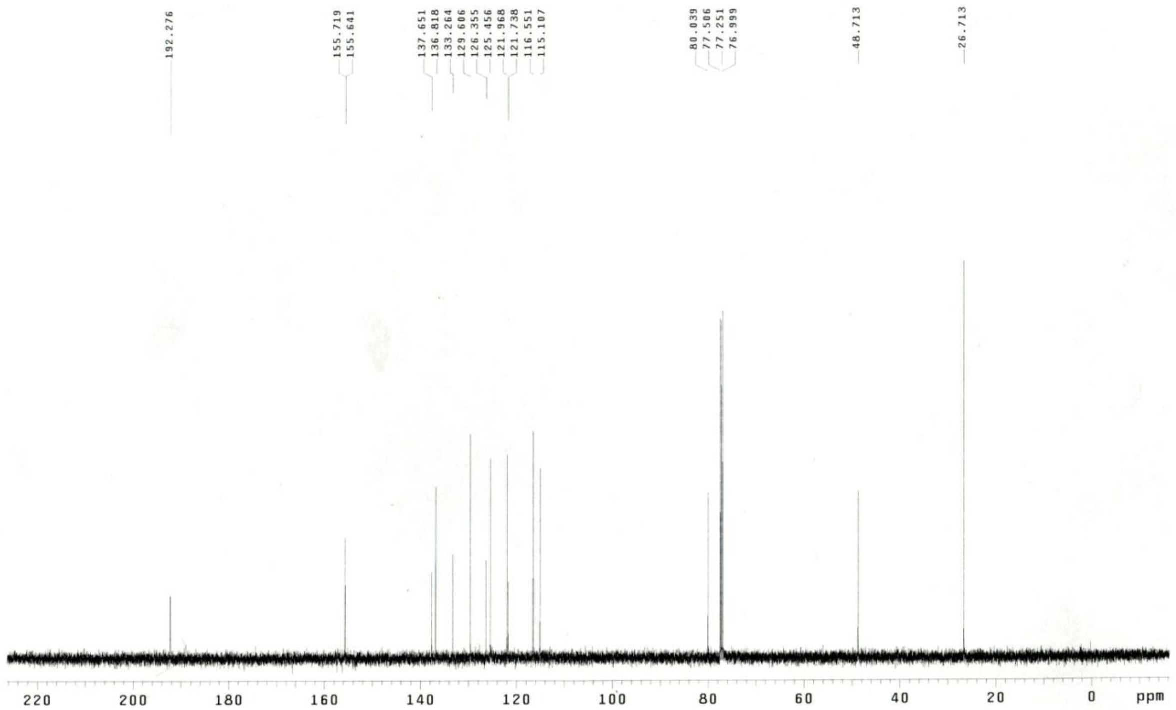
1.00
0.99
0.98
0.99
2.16
6.53

1{4}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155.641
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136.818
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129.606
126.355
125.456
121.968
121.738
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115.107
80.039
77.506
77.251
76.999
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26.713
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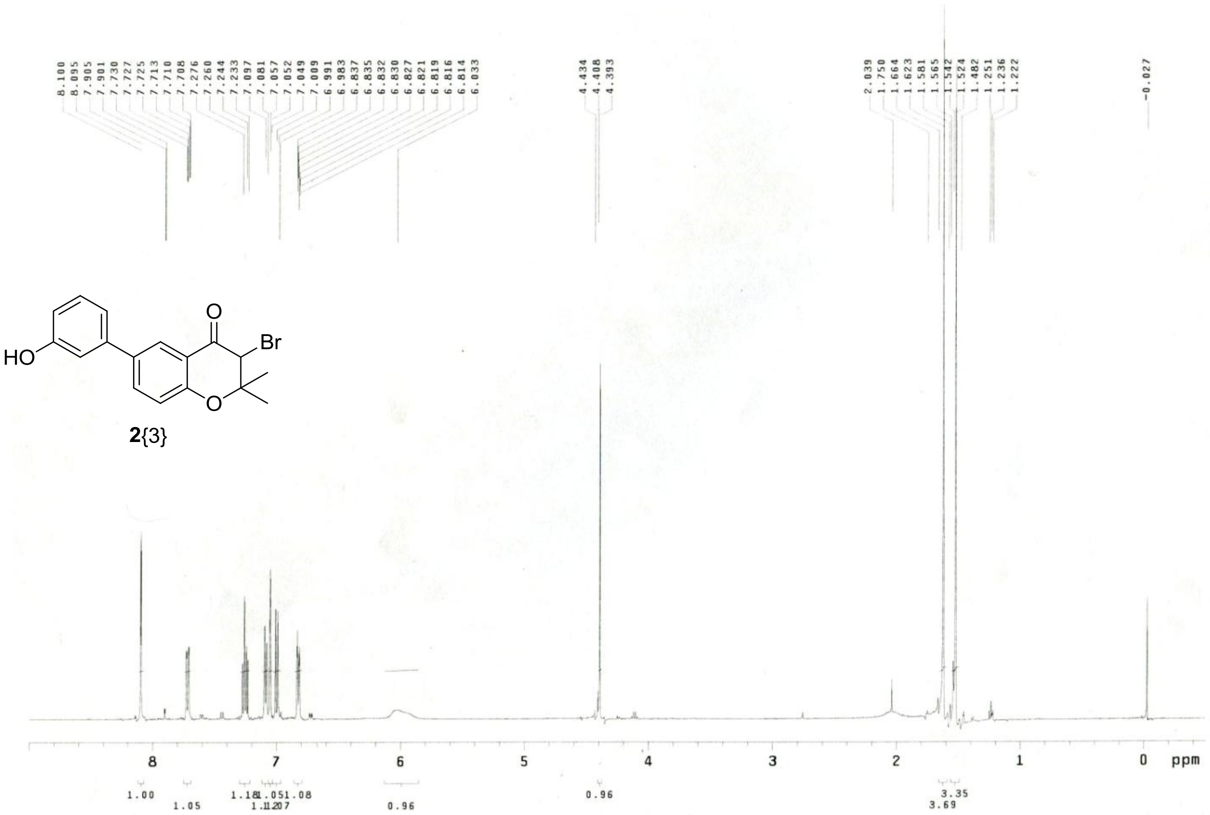
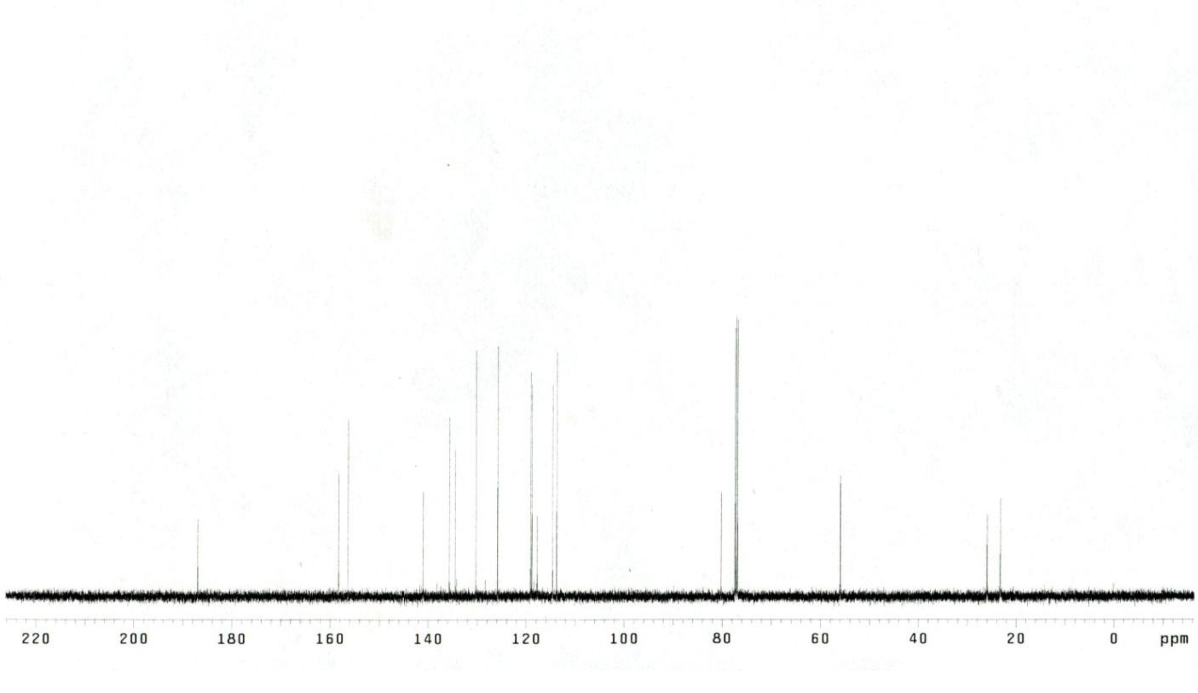
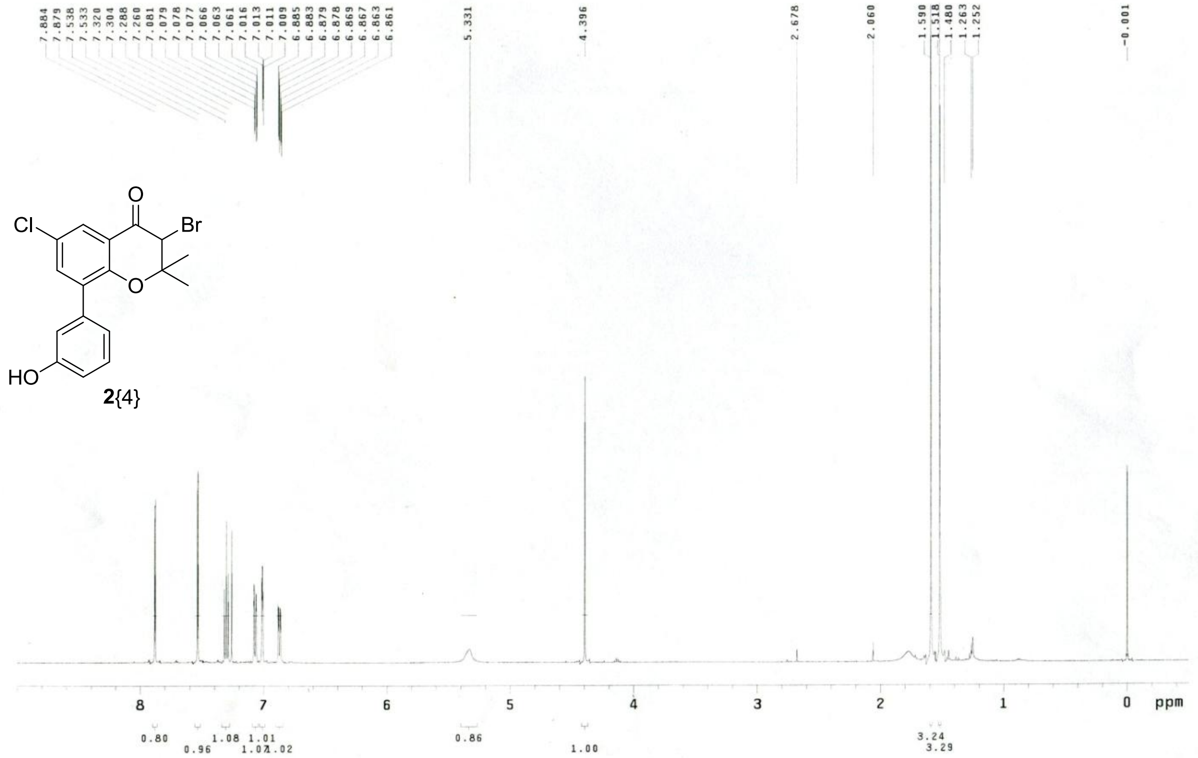
120
100
80
60
40
20
0
ppm



2{3}

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5.331
4.396
2.678
2.060
1.590 1.518 1.480 1.263 1.252
-0.001
Cl
O
Br
O
HO
2{4}
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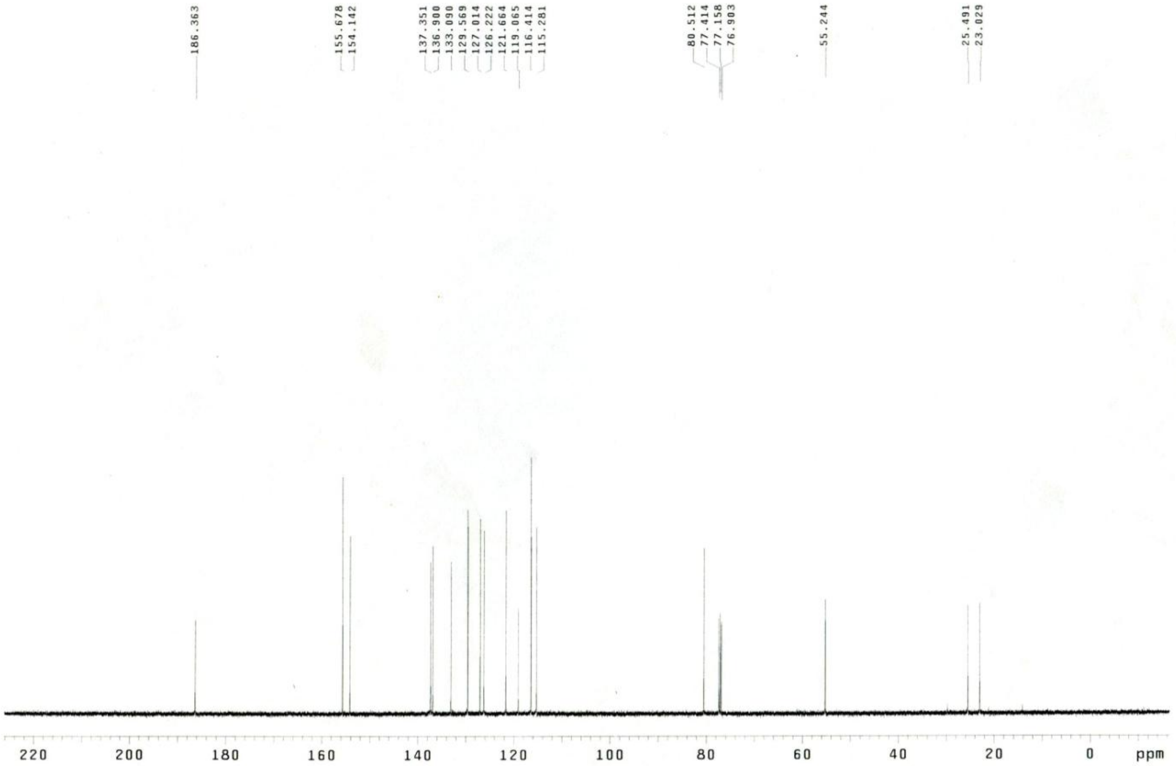
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155.678 154.142
137.351 136.900 133.090 129.569 127.014 126.222 121.664 119.065 116.414 115.281
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55.244
25.491 23.029
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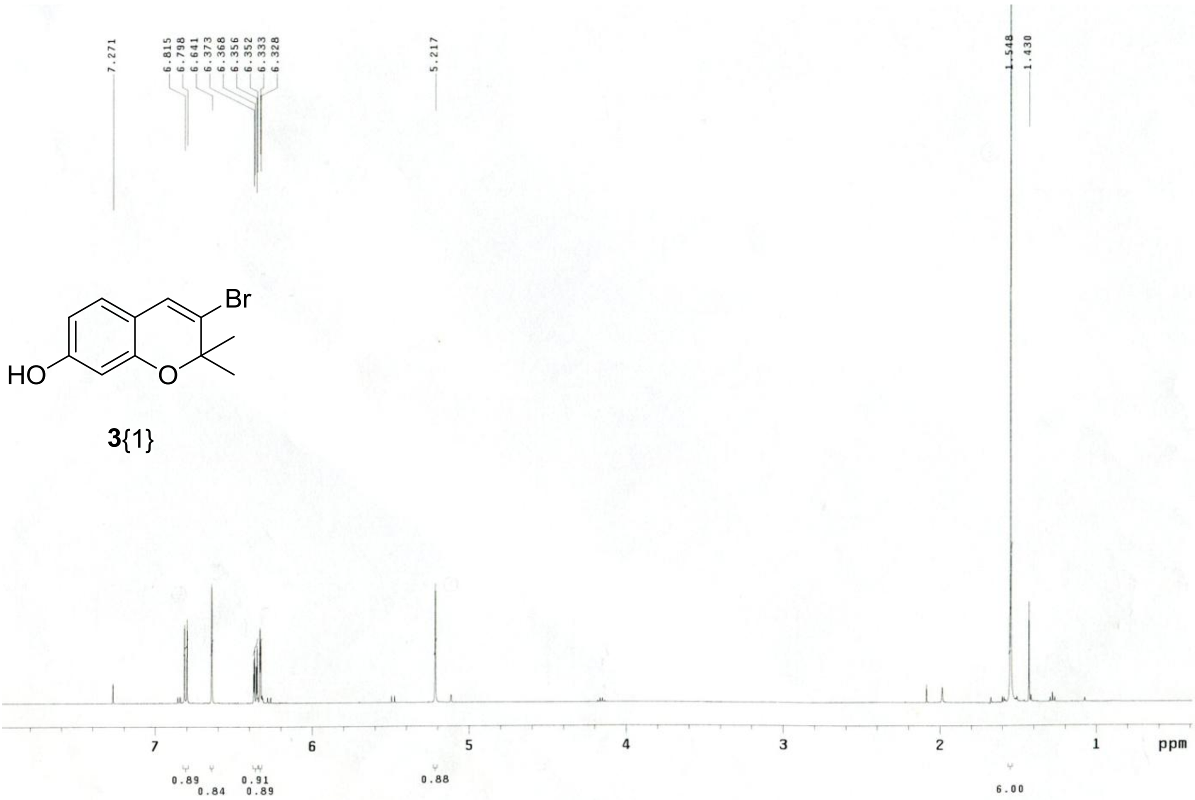
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HO
O
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6.373
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1.430
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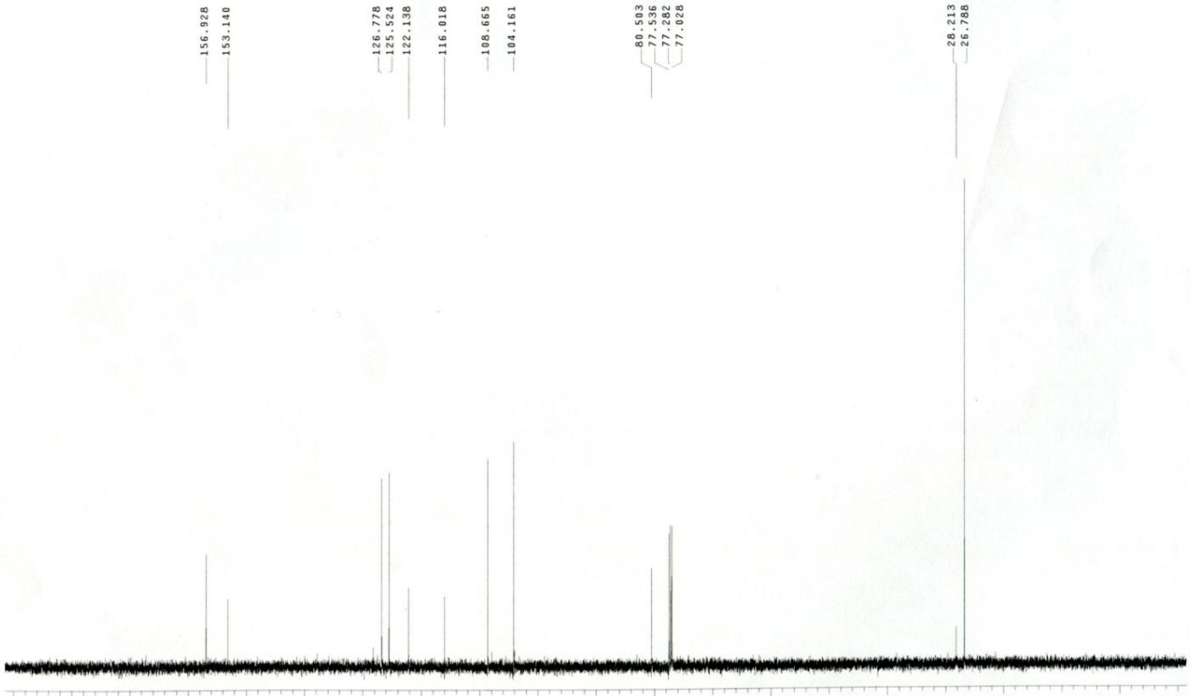
0.89
0.88
6.00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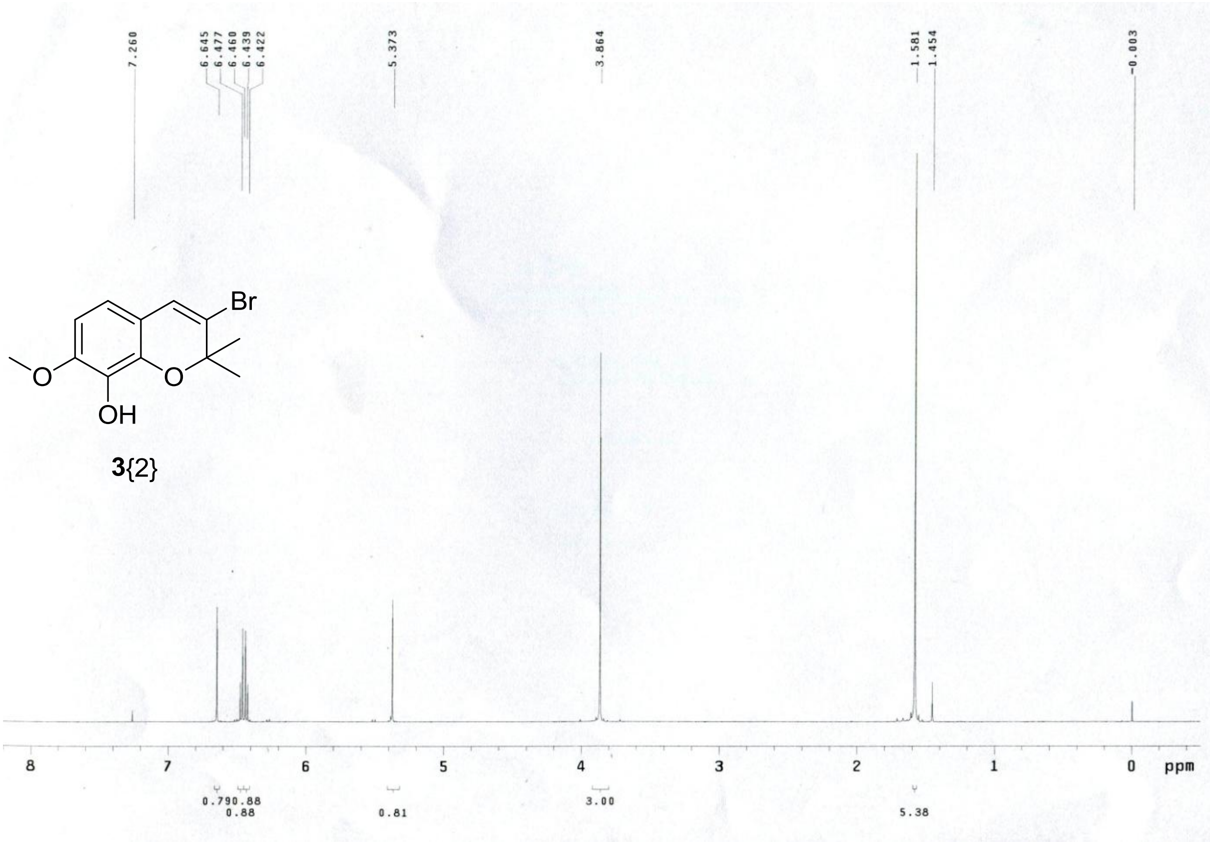
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O
OH
3{2}
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4
3
2
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0
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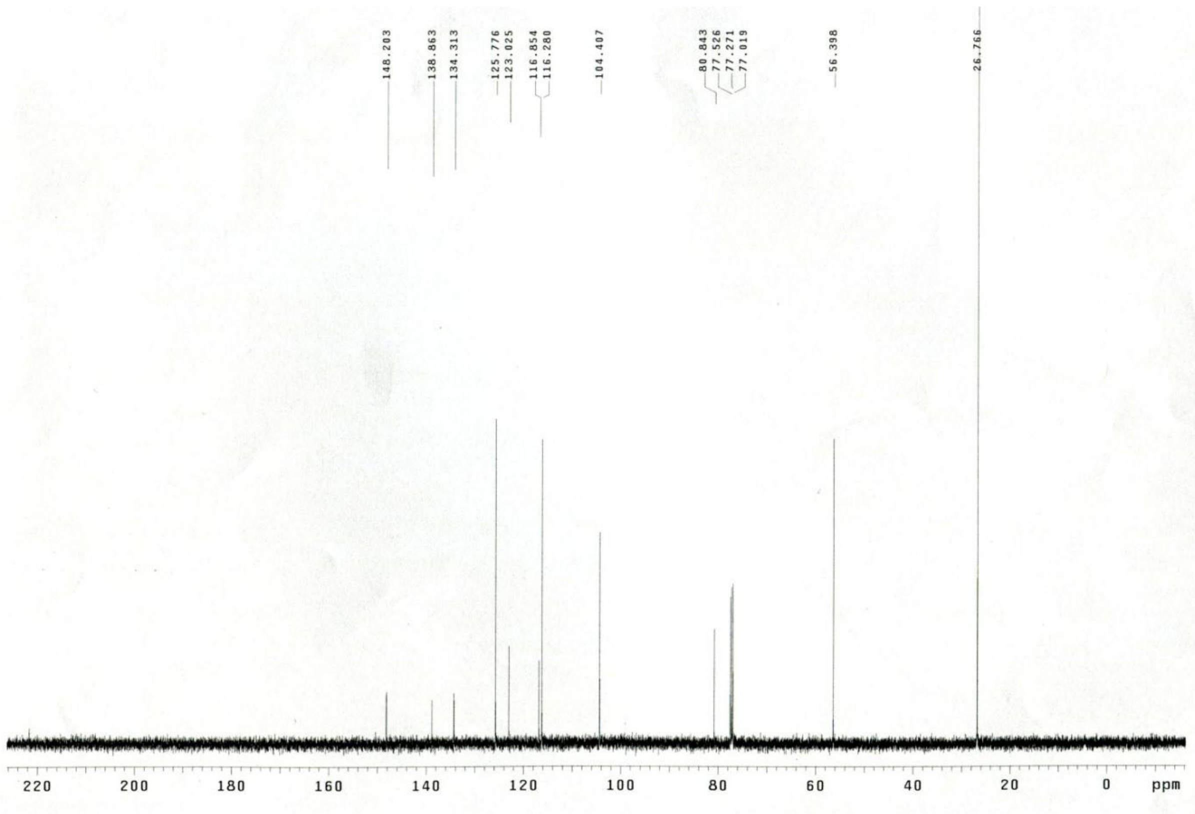
5.38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0
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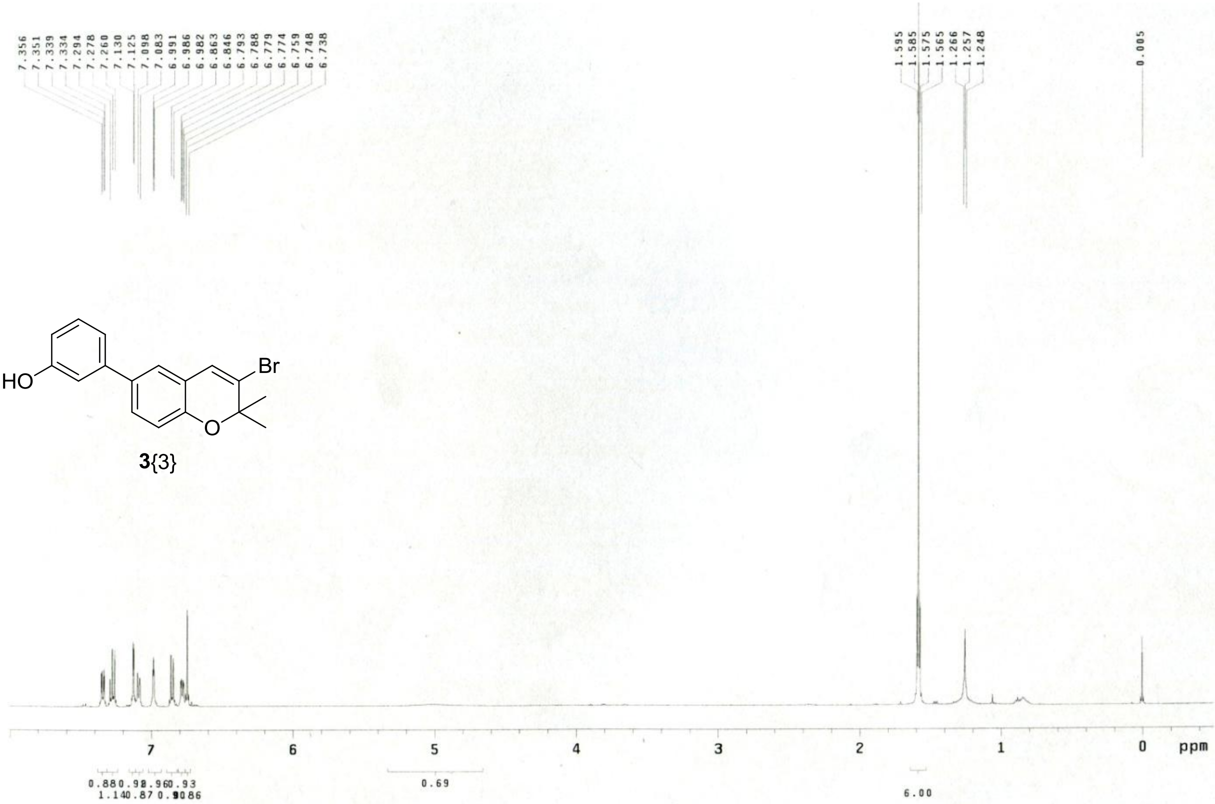
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1.595 1.585 1.575 1.565 1.266 1.257 1.248
0.005
HO
Br
O
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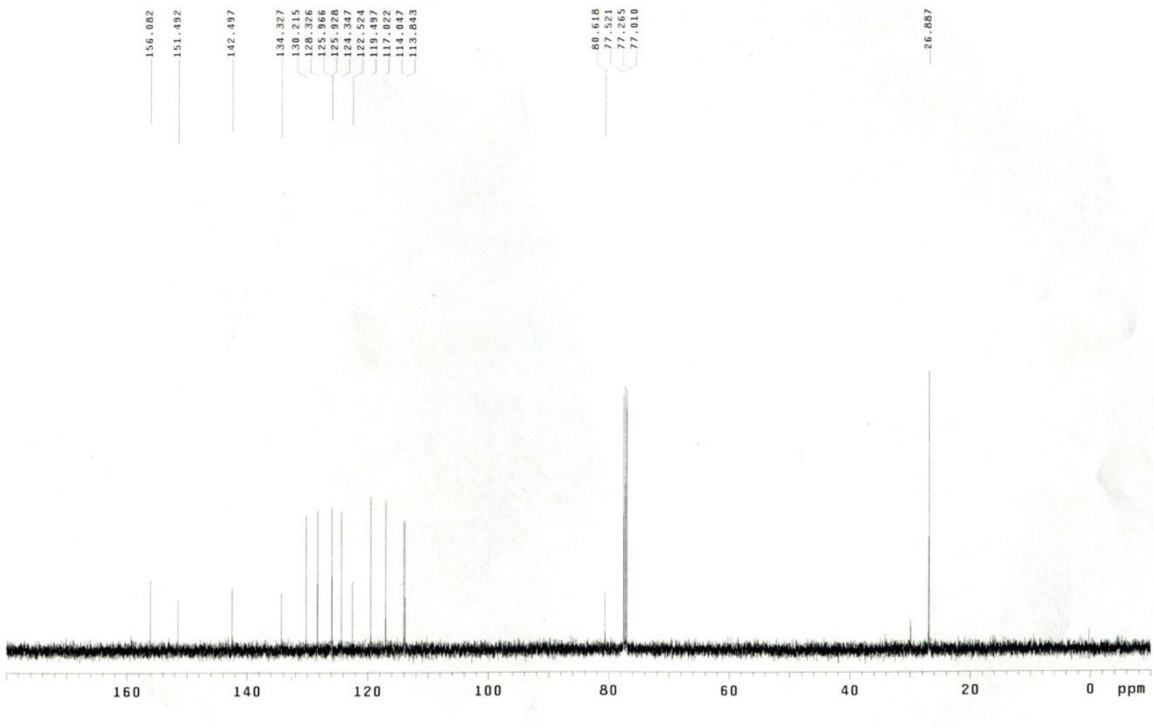
0.69
6.00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80.618 77.521 77.265 77.010
26.887
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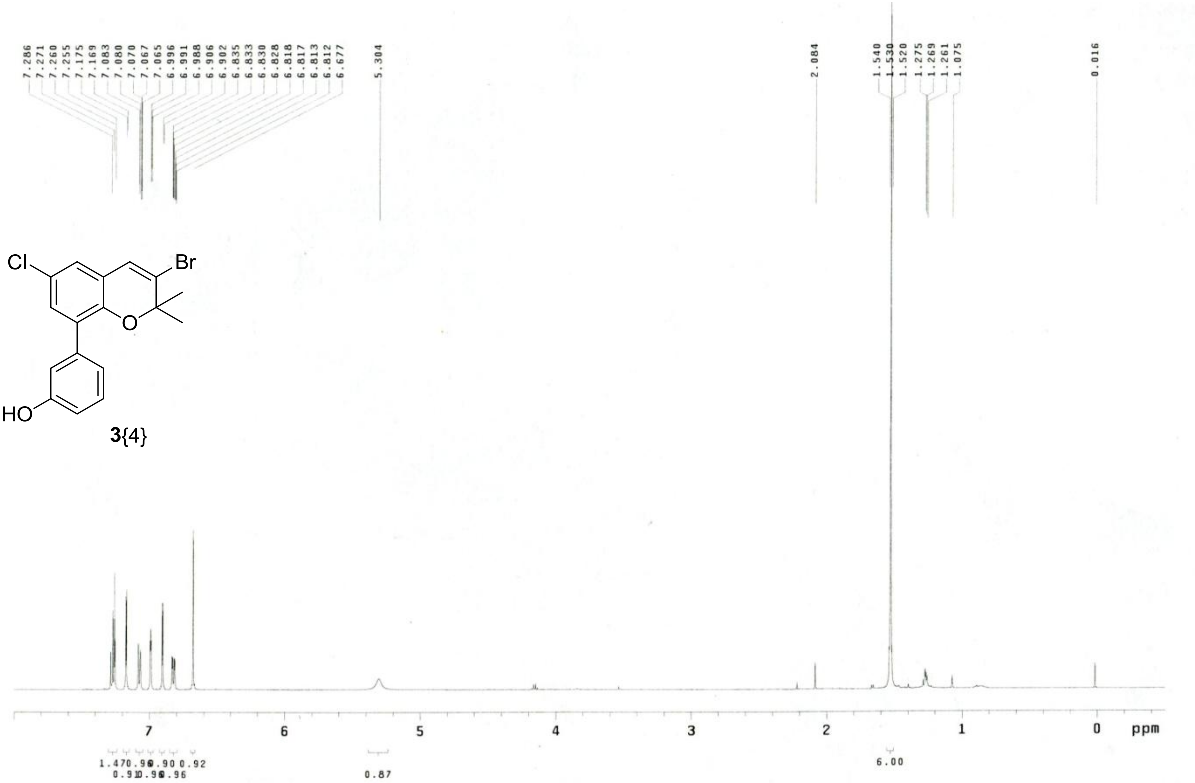
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Br
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6.991
6.988
6.906
6.902
6.835
6.833
6.830
6.828
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6.813
6.812
6.677
5.304
2.084
1.540
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1.520
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1.269
1.261
1.075
0.016
7
6
5
4
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2
1
0
ppm
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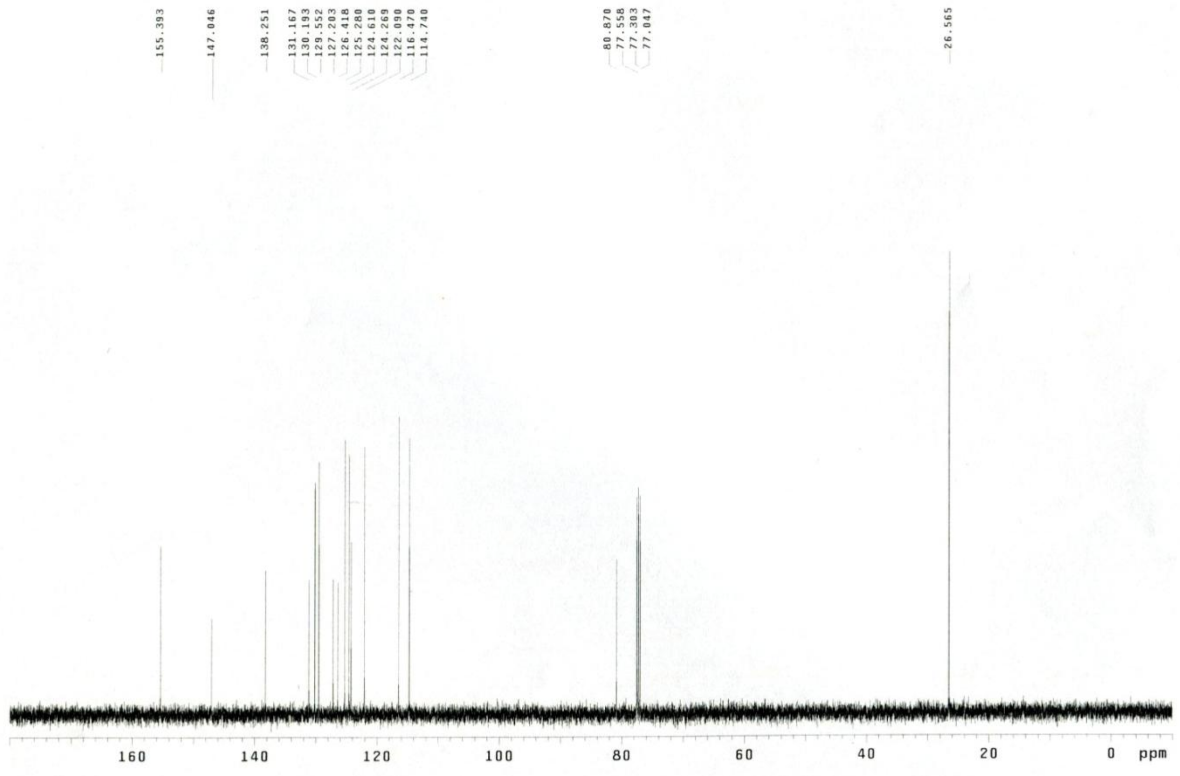
0.87
6.00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20
0
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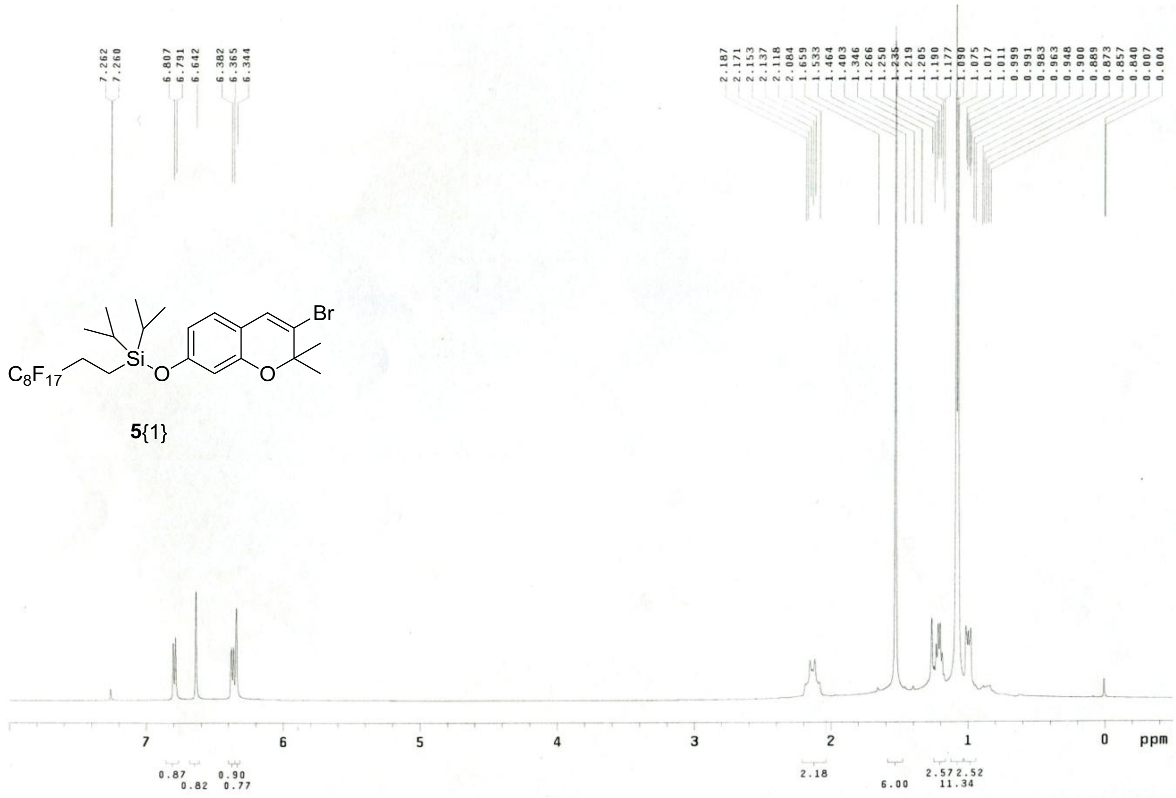
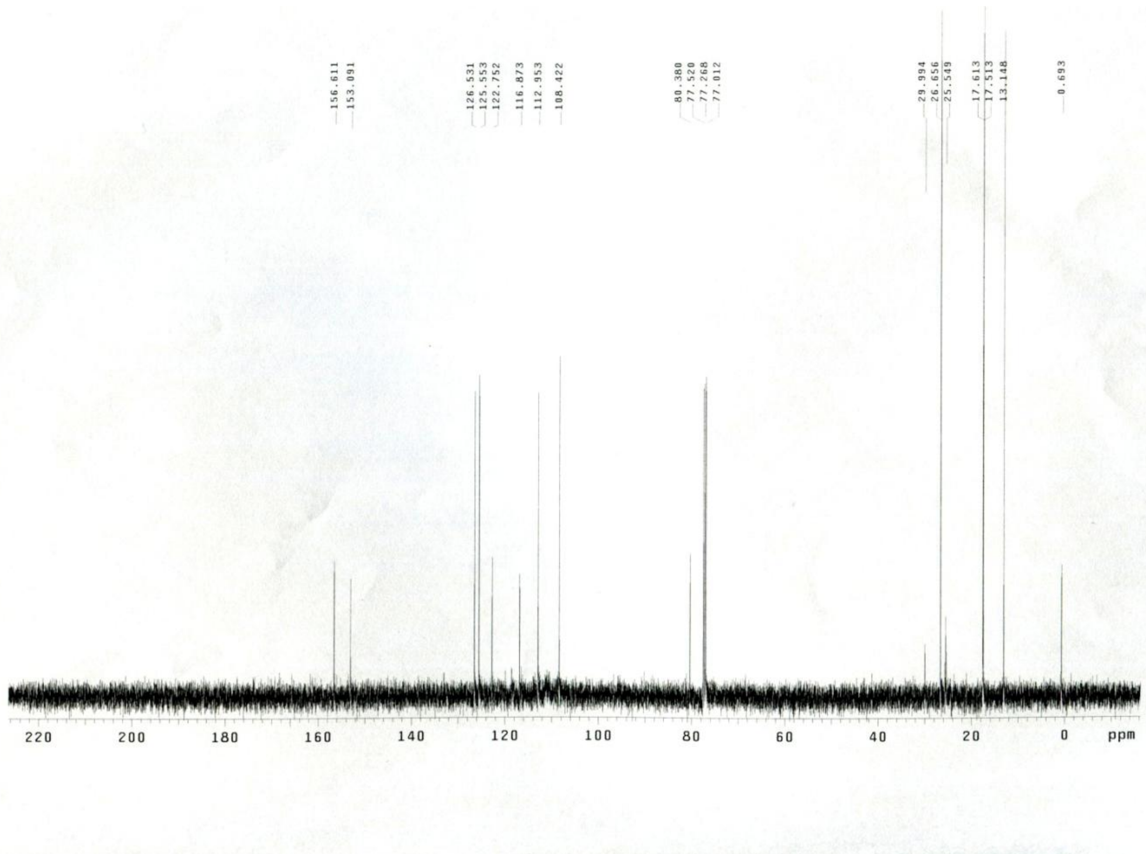
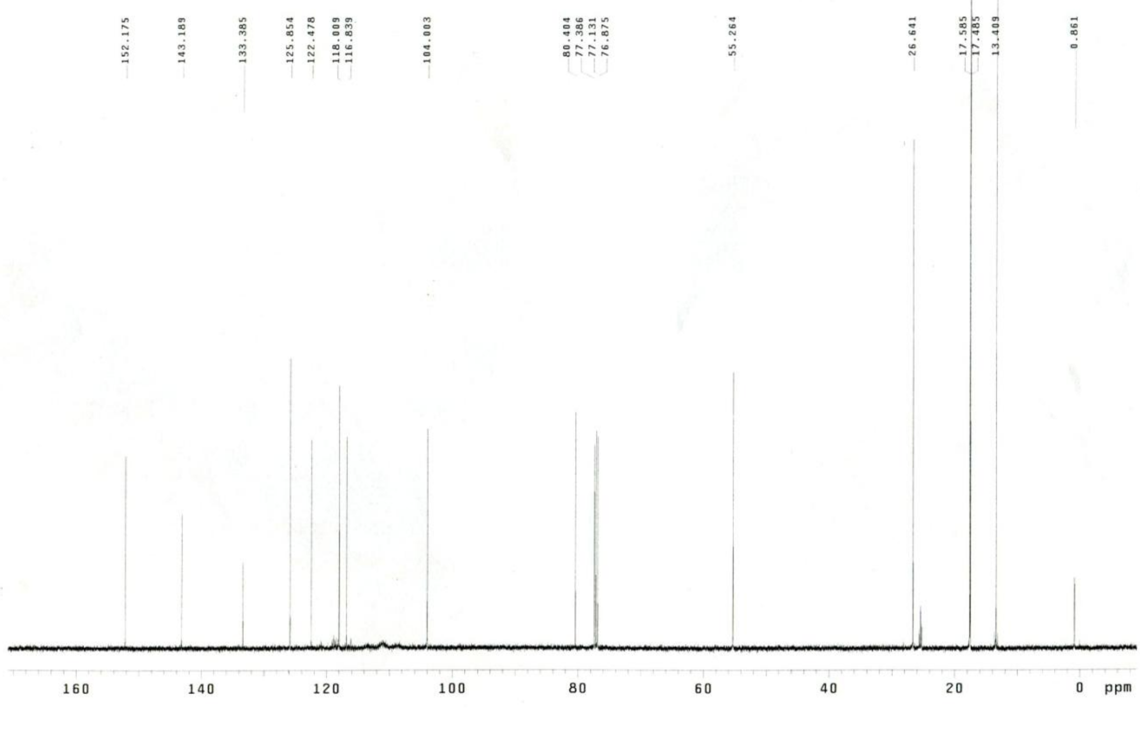
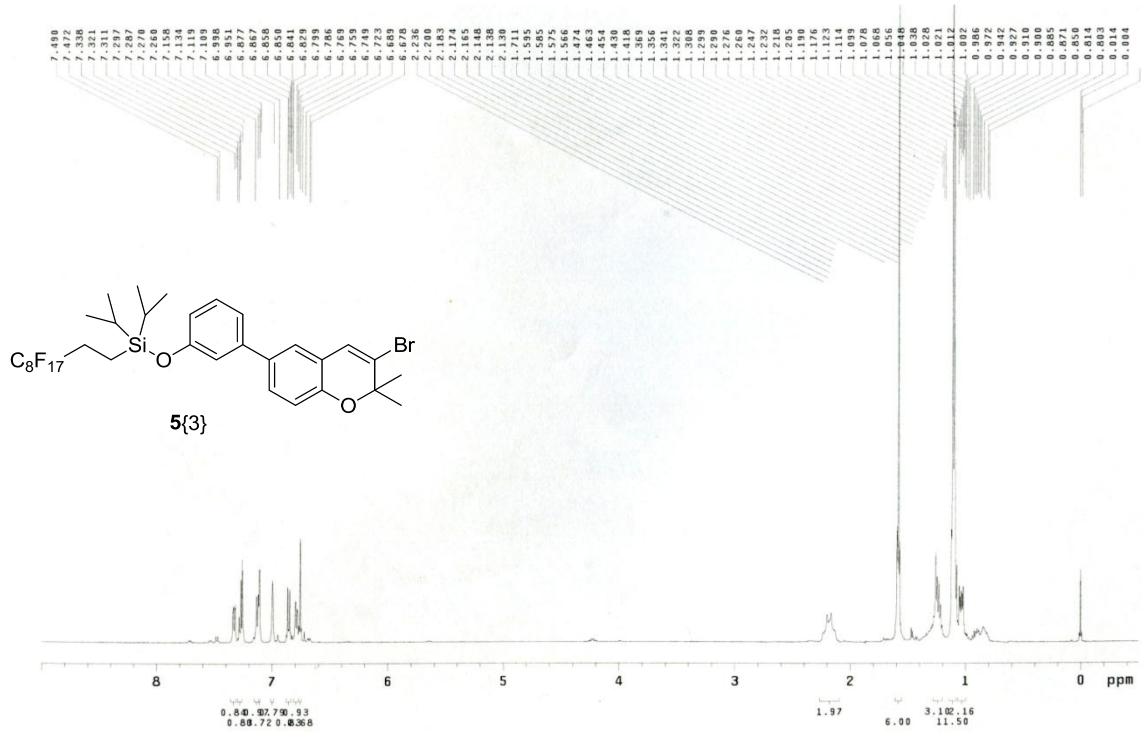


5{1}



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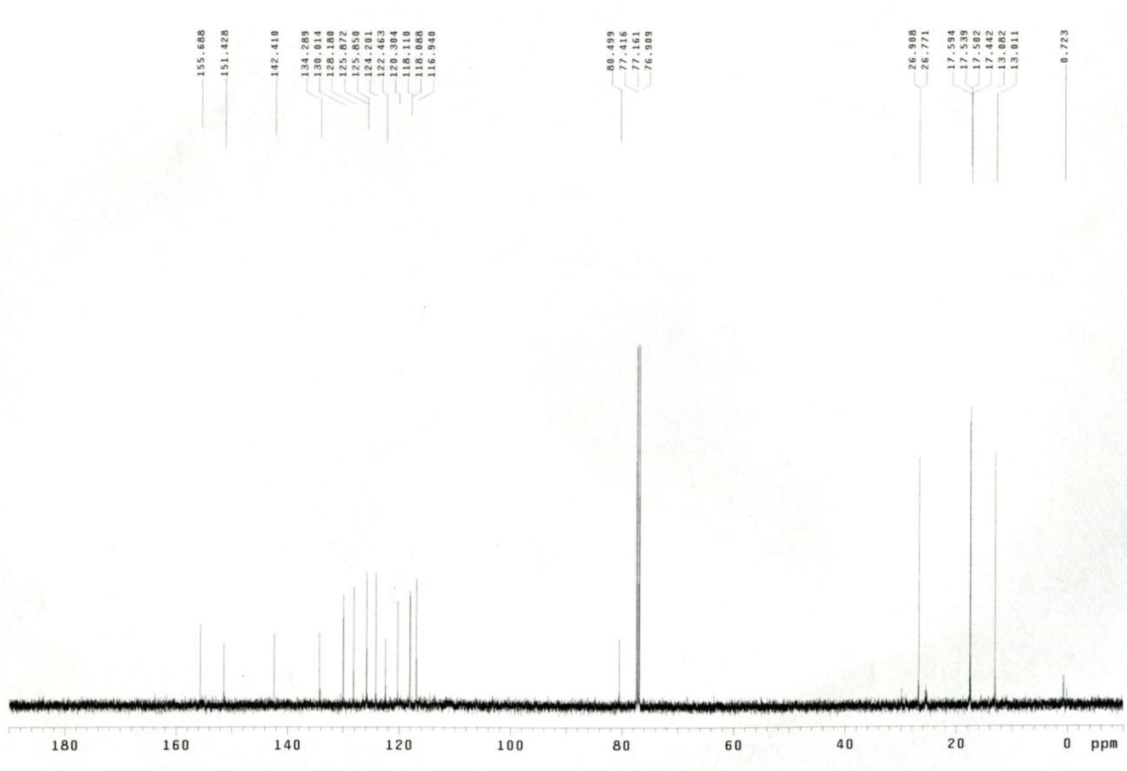
Si
O
Br
O
5{3}
ppm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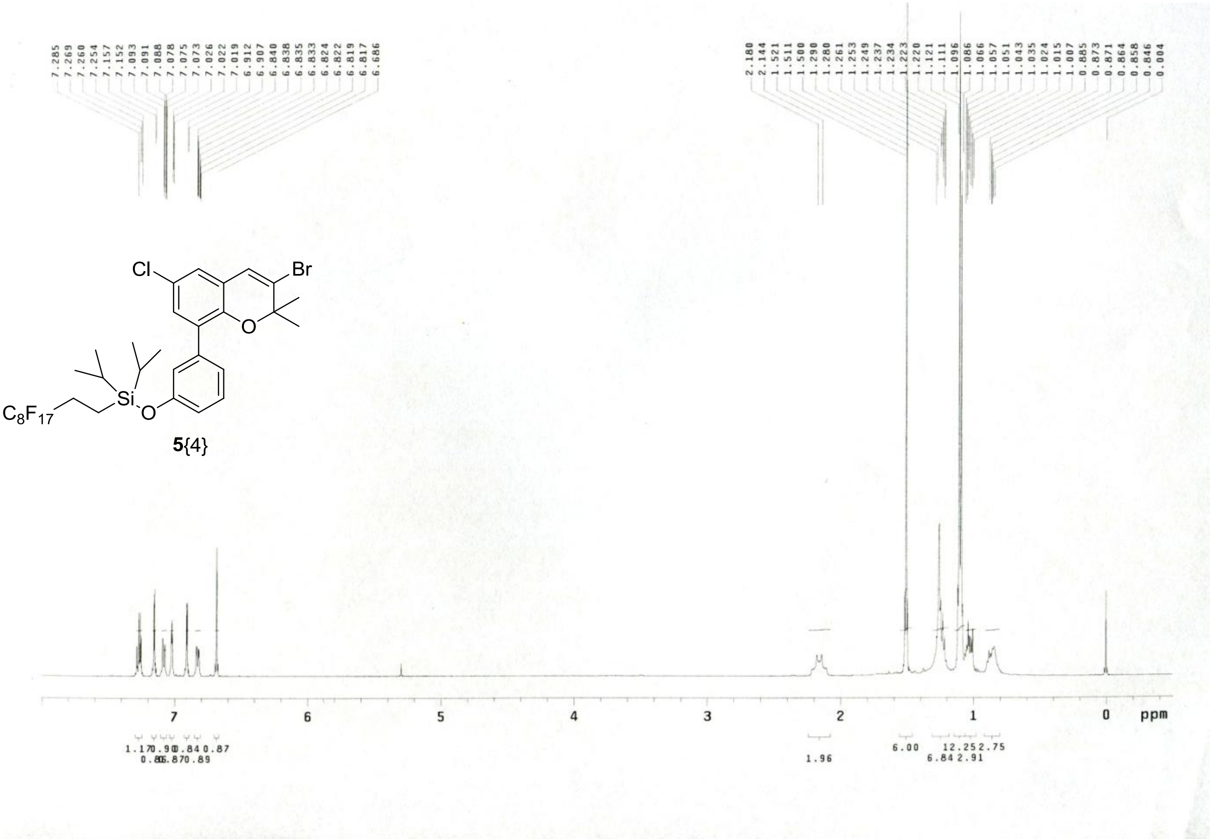
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2.180 2.144 1.521 1.511 1.500 1.290 1.280 1.261 1.253 1.249 1.237 1.234 1.223 1.220 1.121 1.111 1.096 1.086 1.066 1.057 1.051 1.043 1.035 1.024 1.015 1.007 0.885 0.873 0.871 0.864 0.858 0.846 0.004
Cl
Br
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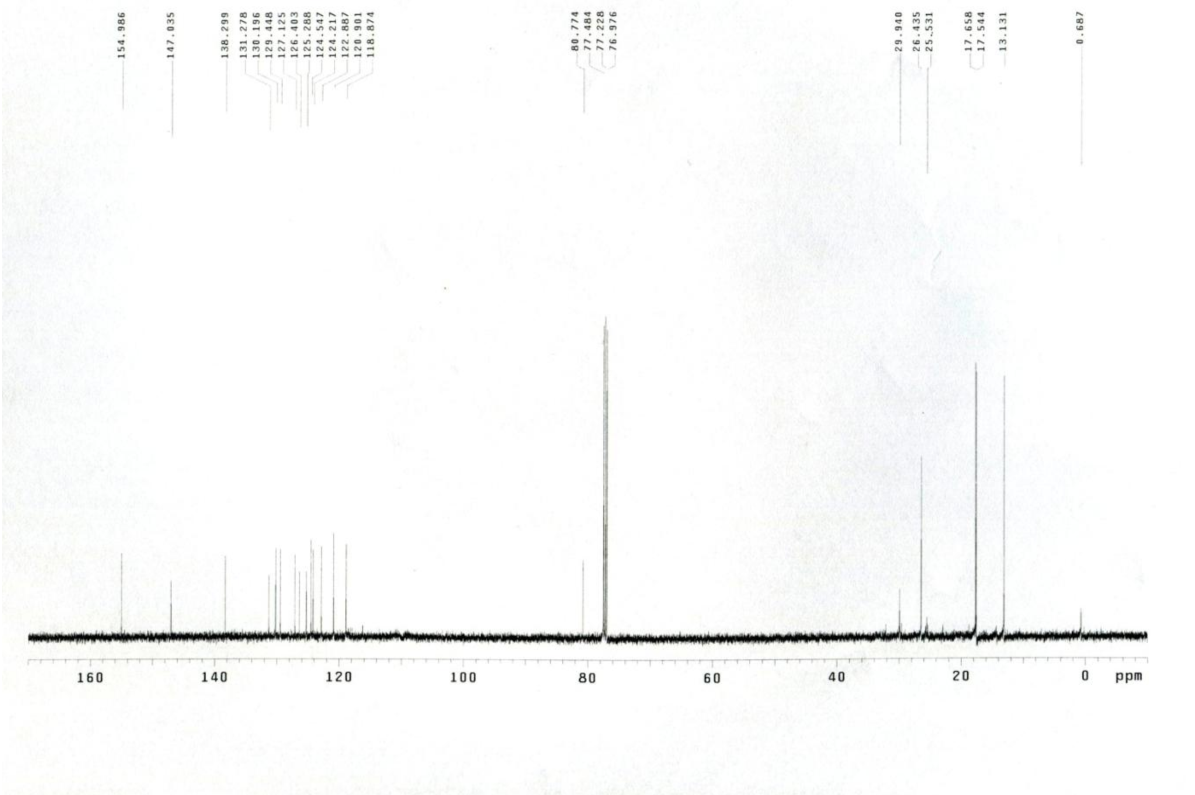
Si
O
C8F17
5{4}
ppm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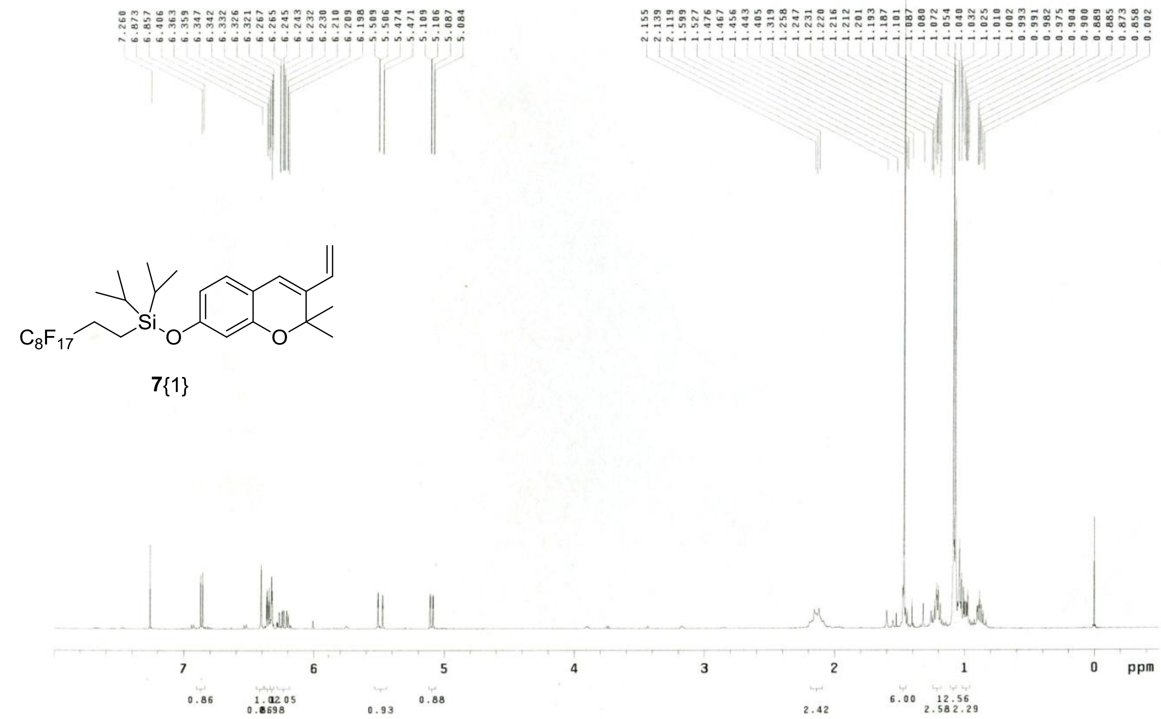
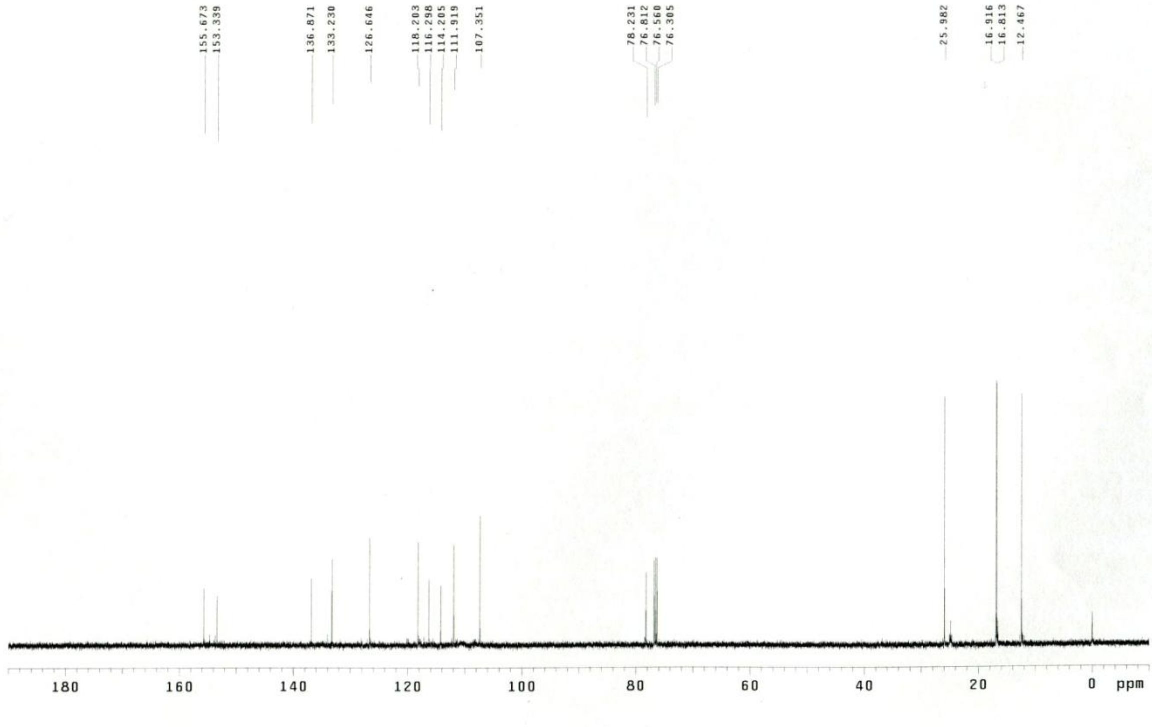
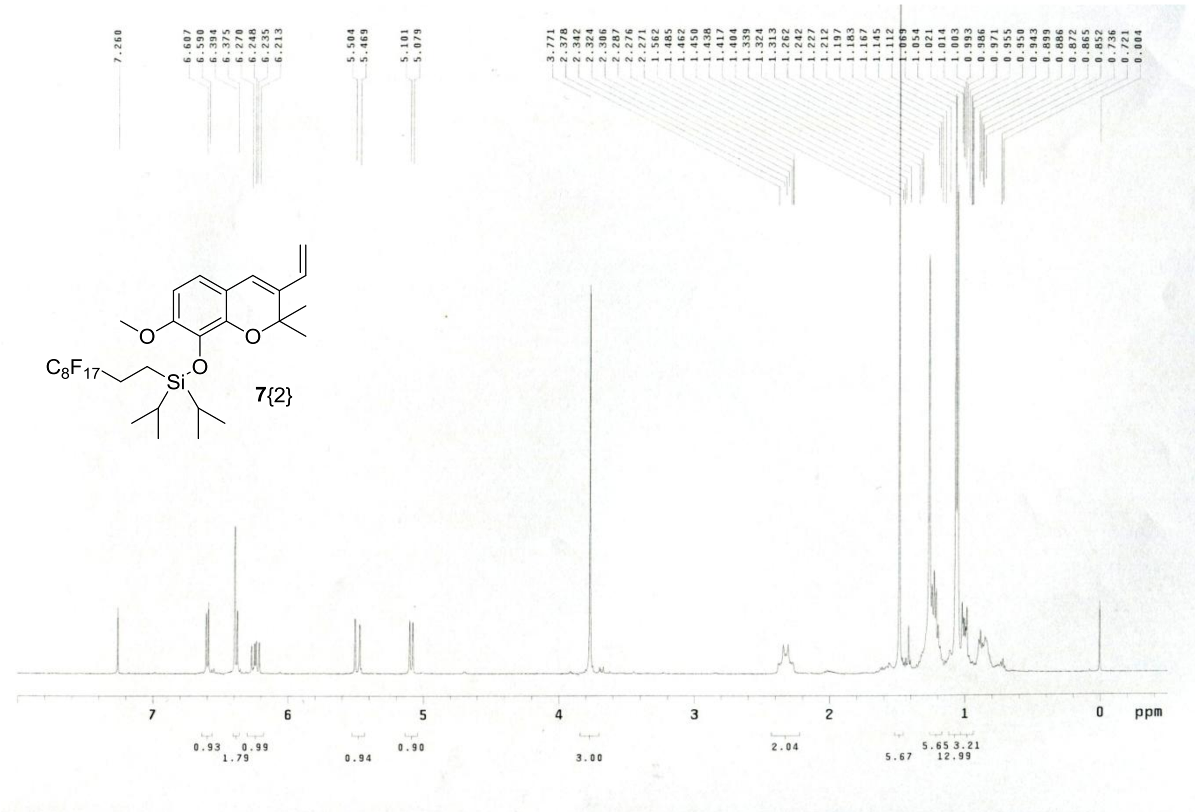
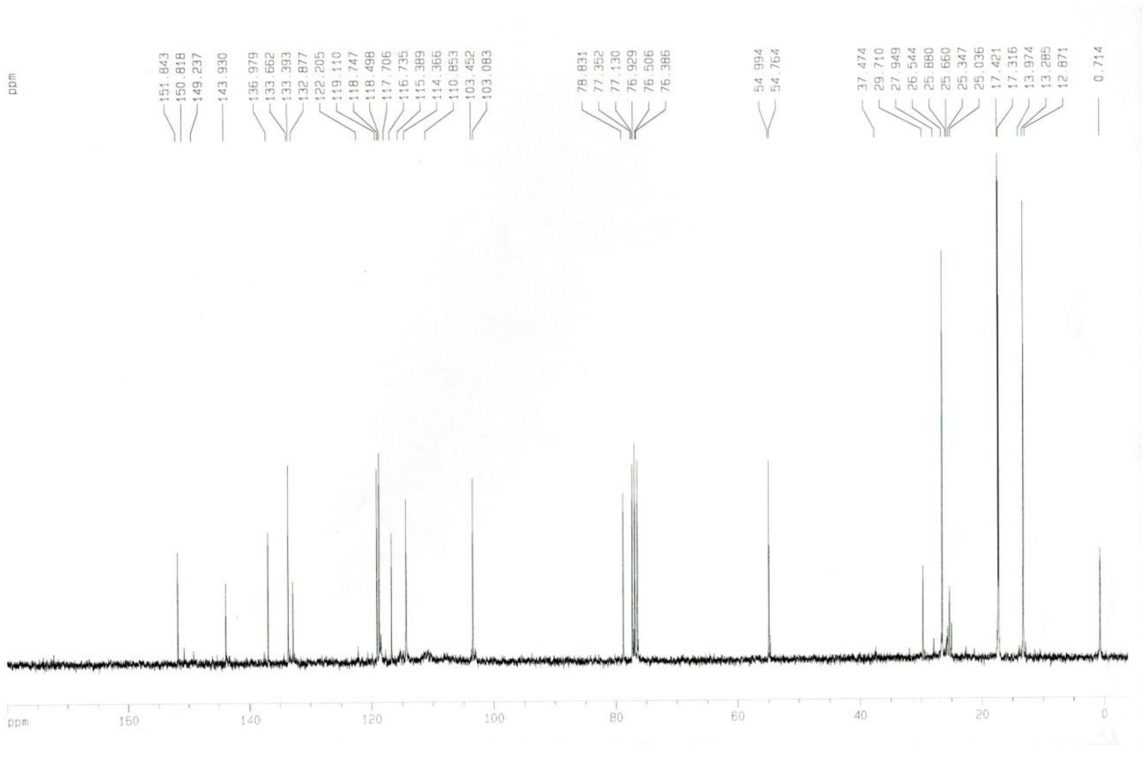
80.774 77.484 77.228 76.976
29.940 26.435 25.531 17.658 17.544 13.131 0.687
160 140 120 100 80 60 40 20 0 ppm

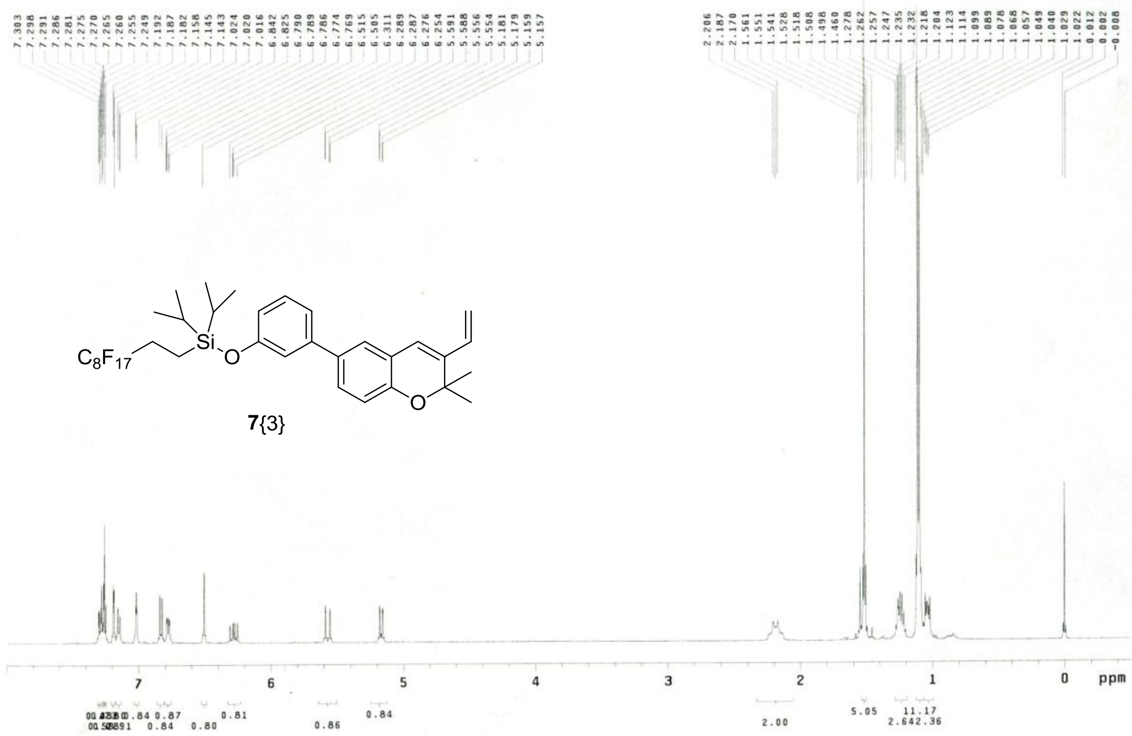

7.260
6.873
6.857
6.406
6.363
6.359
6.347
6.342
6.332
6.326
6.321
6.267
6.265
6.245
6.243
6.232
6.230
6.210
6.198
5.509
5.506
5.474
5.471
5.109
5.106
5.087
5.084
2.155
2.139
1.599
1.527
1.476
1.467
1.456
1.443
1.405
1.319
1.258
1.247
1.231
1.220
1.216
1.212
1.201
1.193
1.187
1.101
1.087
1.080
1.072
1.054
1.040
1.032
1.025
1.010
1.002
0.993
0.991
0.982
0.975
0.904
0.900
0.889
0.885
0.873
0.858
0.002
7
6
5
4
3
2
1
0
ppm
0.86
0.93
0.88
2.42
6.00
12.56
2.58
2.29

7{1}


155.673
153.339
136.871
133.230
126.646
118.203
116.298
114.205
111.919
107.351
78.231
76.812
76.560
76.305
25.982
16.916
16.813
12.467
180
160
140
120
100
80
60
40
20
0
ppm

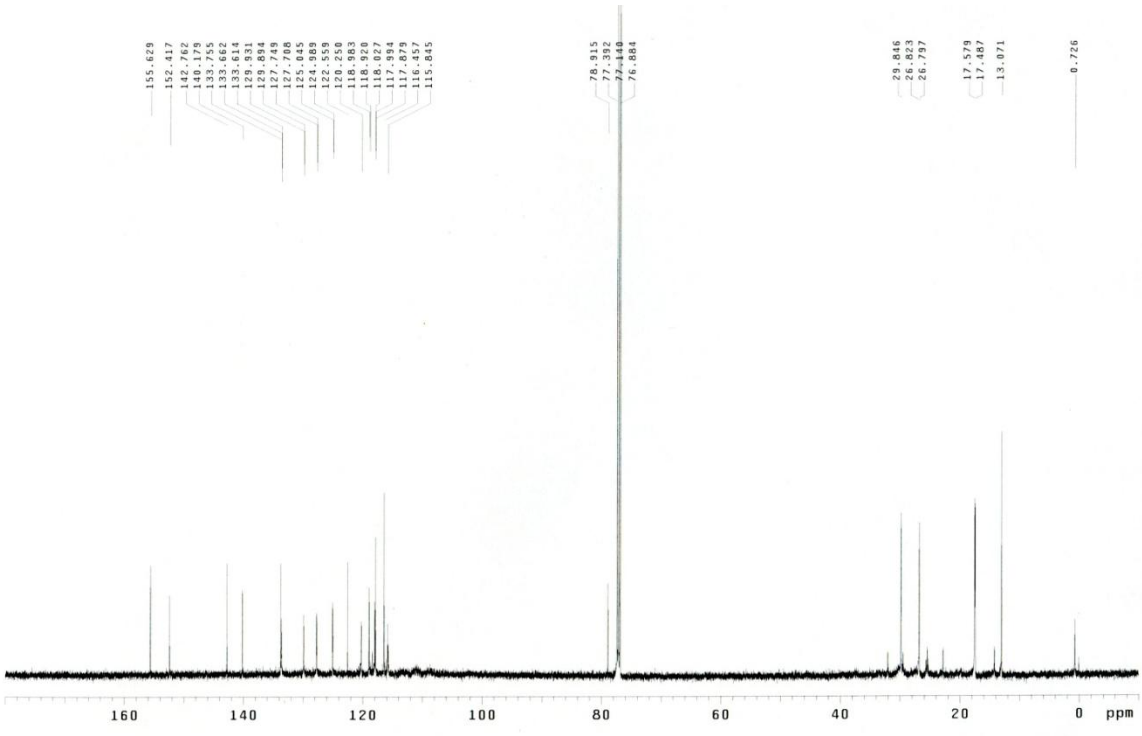

7.260
6.607
6.590
6.394
6.375
6.270
6.248
6.235
6.213
5.504
5.469
5.101
5.079
3.771
2.378
2.342
2.324
2.306
2.287
2.276
2.271
1.562
1.485
1.462
1.450
1.438
1.417
1.404
1.339
1.324
1.313
1.262
1.242
1.227
1.212
1.197
1.183
1.167
1.145
1.112
1.069
1.054
1.021
1.014
1.003
0.993
0.986
0.971
0.955
0.950
0.943
0.899
0.886
0.872
0.865
0.852
0.736
0.721
0.004
C_8F_{17}
Si
O
7{2}
ppm
0.93
1.79
0.99
0.94
0.90
3.00
2.04
5.67
5.65
3.21
12.99


ppm
151.843
150.818
149.237
143.930
136.979
133.662
133.393
132.877
122.205
119.110
118.747
118.498
117.706
116.735
115.389
114.366
110.853
103.452
103.083
78.831
77.352
77.130
76.929
76.506
76.386
54.994
54.764
37.474
29.710
27.949
26.544
25.880
25.660
25.347
25.036
17.421
17.316
13.974
13.285
12.871
0.714

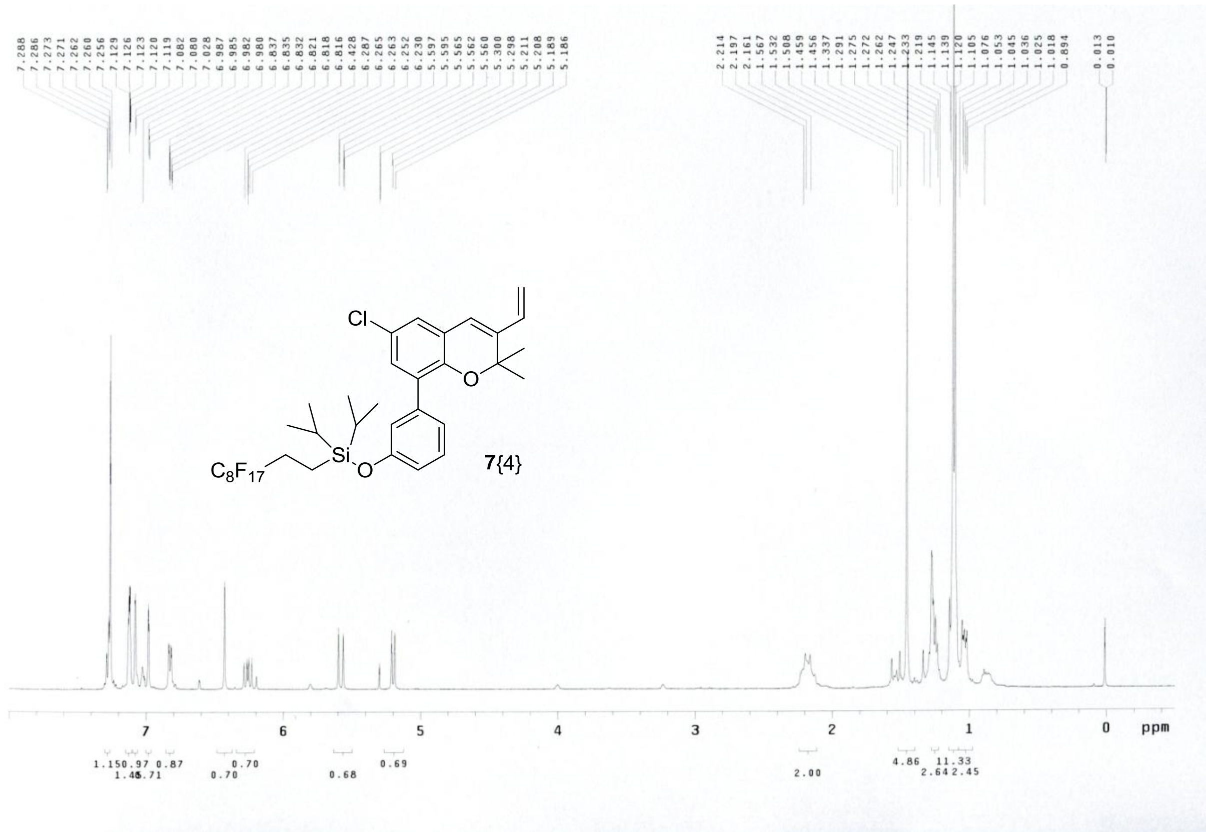


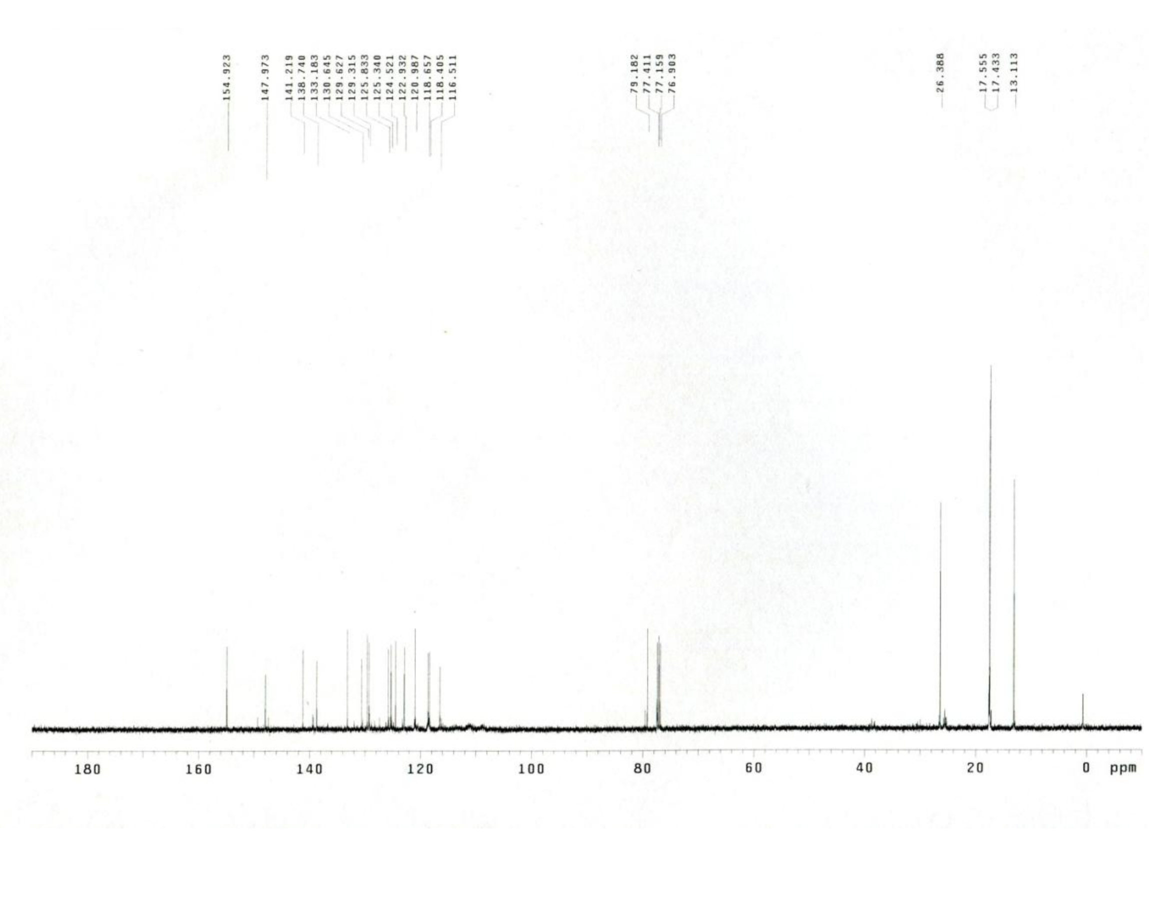
7.303 7.298 7.291 7.286 7.281 7.275 7.270 7.265 7.260 7.255 7.249 7.192 7.187 7.182 7.158 7.145 7.143 7.024 7.020 7.016 6.842 6.825 6.790 6.789 6.786 6.774 6.769 6.515 6.505 6.311 6.289 6.287 6.276 6.254 5.591 5.588 5.556 5.554 5.181 5.179 5.159 5.157
2.206 2.187 2.170 1.561 1.551 1.541 1.526 1.518 1.508 1.498 1.460 1.278 1.262 1.257 1.247 1.235 1.232 1.218 1.204 1.123 1.114 1.099 1.089 1.078 1.068 1.057 1.049 1.040 1.029 1.022 0.012 0.002 -0.008
C8F17
Si
O
7 6 5 4 3 2 1 0 ppm
0.84 0.87 0.81 0.84 0.80 0.86 0.84 2.00 5.05 11.17 2.64 2.36

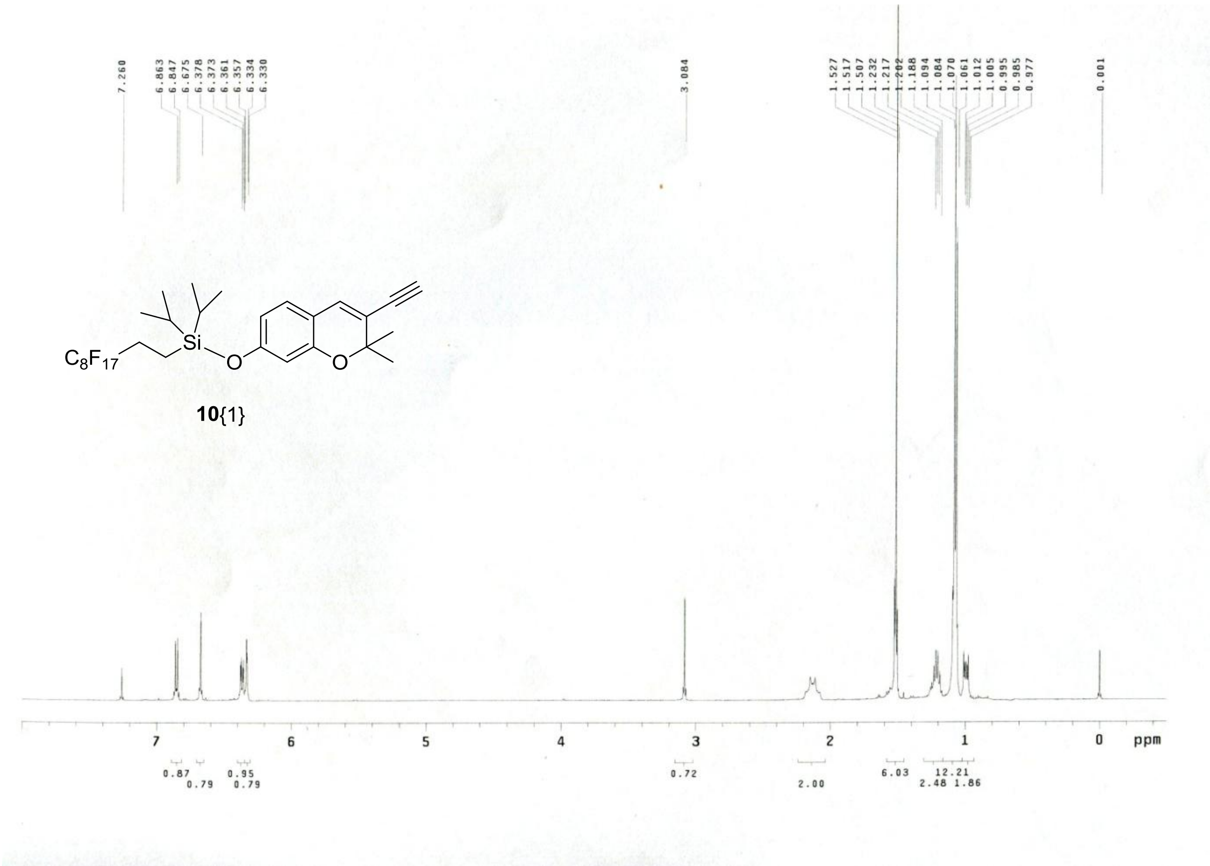
7{3}

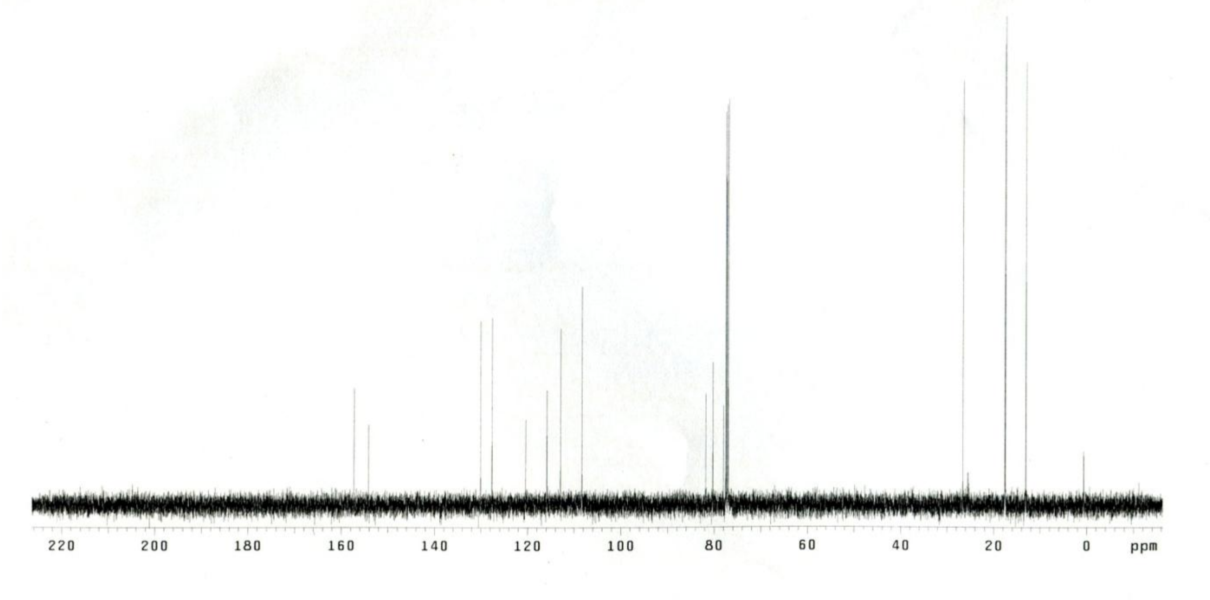


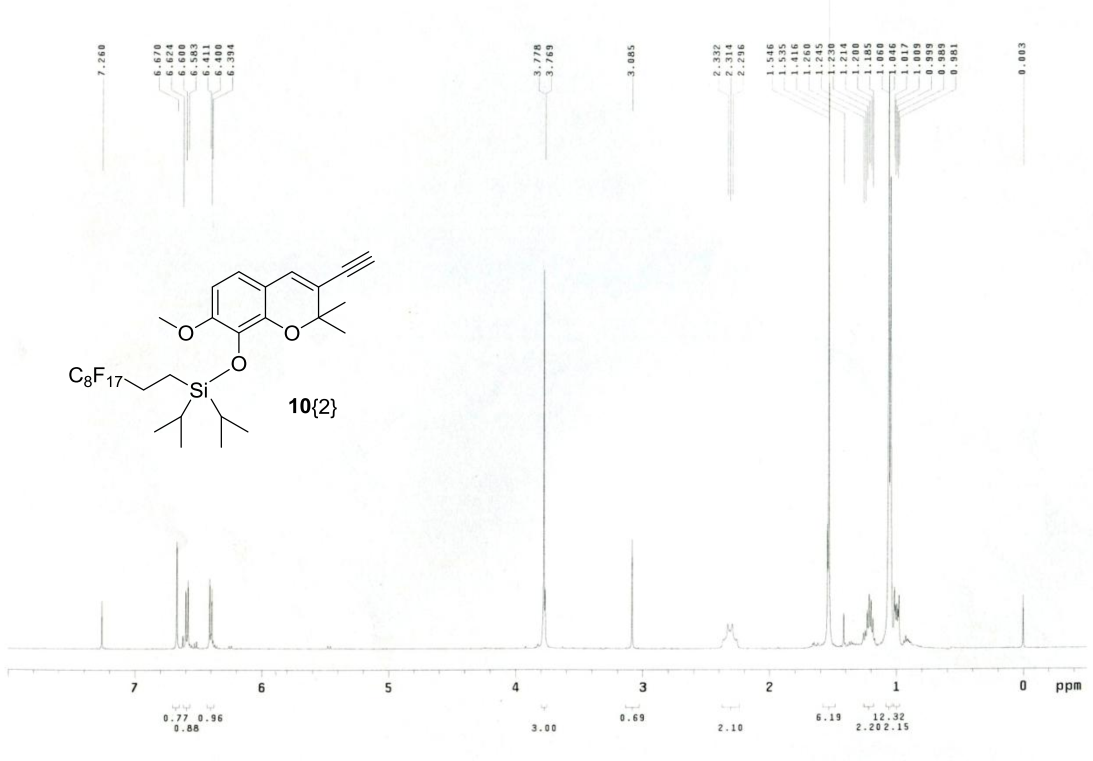
155.629 152.417 142.762 140.179 133.755 133.662 133.614 129.931 129.894 127.749 127.708 125.045 124.989 122.559 120.250 118.983 118.920 118.027 117.994 117.879 116.457 115.845
78.915 77.392 77.140 76.884
29.846 26.823 26.797 17.579 17.487 13.071 0.726
160 140 120 100 80 60 40 20 0 ppm


7.288 7.286 7.273 7.271 7.262 7.260 7.256 7.129 7.126 7.123 7.120 7.119 7.082 7.080 7.028 6.987 6.985 6.982 6.980 6.837 6.835 6.832 6.821 6.818 6.816 6.428 6.287 6.265 6.263 6.252 6.230 5.597 5.595 5.565 5.562 5.560 5.300 5.298 5.211 5.208 5.189 5.186
2.214 2.197 2.161 1.567 1.532 1.508 1.459 1.456 1.337 1.291 1.275 1.272 1.262 1.247 1.233 1.219 1.145 1.139 1.120 1.105 1.076 1.053 1.045 1.036 1.025 1.018 0.894
0.013 0.010
Cl
O
Si
O
C_8F_{17}
7{4}
7 6 5 4 3 2 1 0 ppm
1.15 0.97 0.87 1.45 0.71 0.70 0.70 0.68 0.69 2.00 4.86 2.64 11.33 2.45

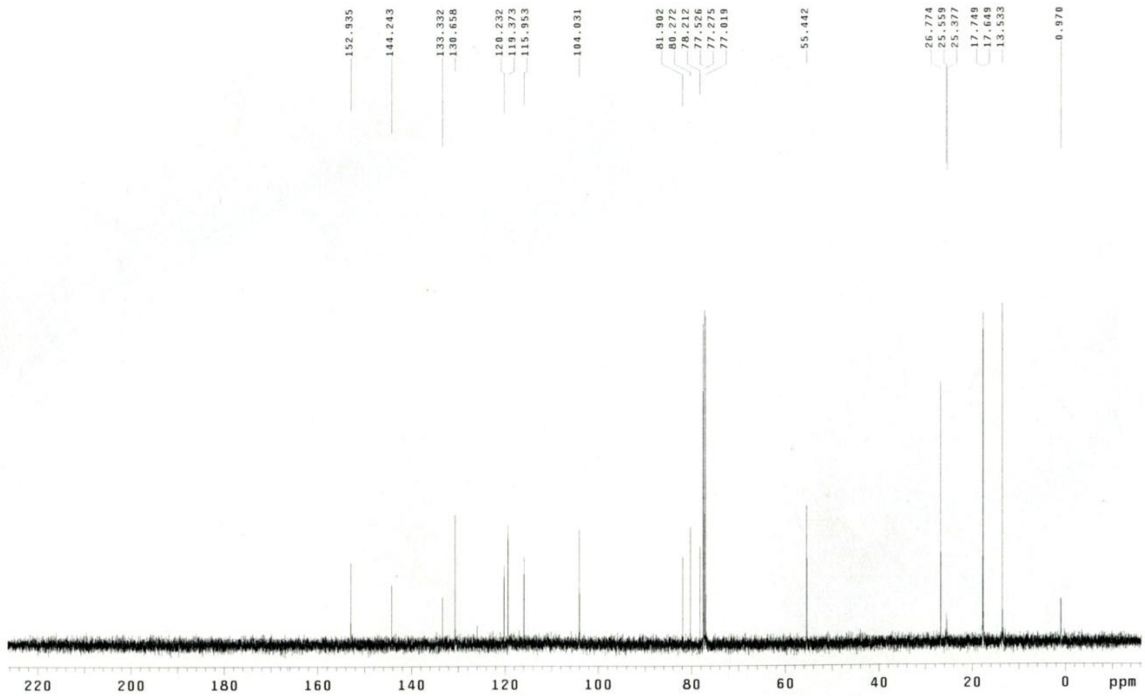

154.923
147.973
141.219 138.740 133.183 130.645 129.627 129.315 125.833 125.340 124.521 122.932 120.987 118.657 118.405 116.511
79.182 77.411 77.159 76.903
26.388
17.555 17.433
13.113
180 160 140 120 100 80 60 40 20 0 ppm


7.260
6.863
6.847
6.675
6.378
6.373
6.361
6.357
6.334
6.330
3.084
1.527
1.517
1.507
1.232
1.217
1.202
1.188
1.094
1.084
1.070
1.061
1.012
1.005
0.995
0.985
0.977
0.001
C_8F_{17}
Si
O
O
10{1}
7
6
5
4
3
2
1
0
ppm
0.87
0.79
0.95
0.79
0.72
2.00
6.03
12.21
2.48
1.86

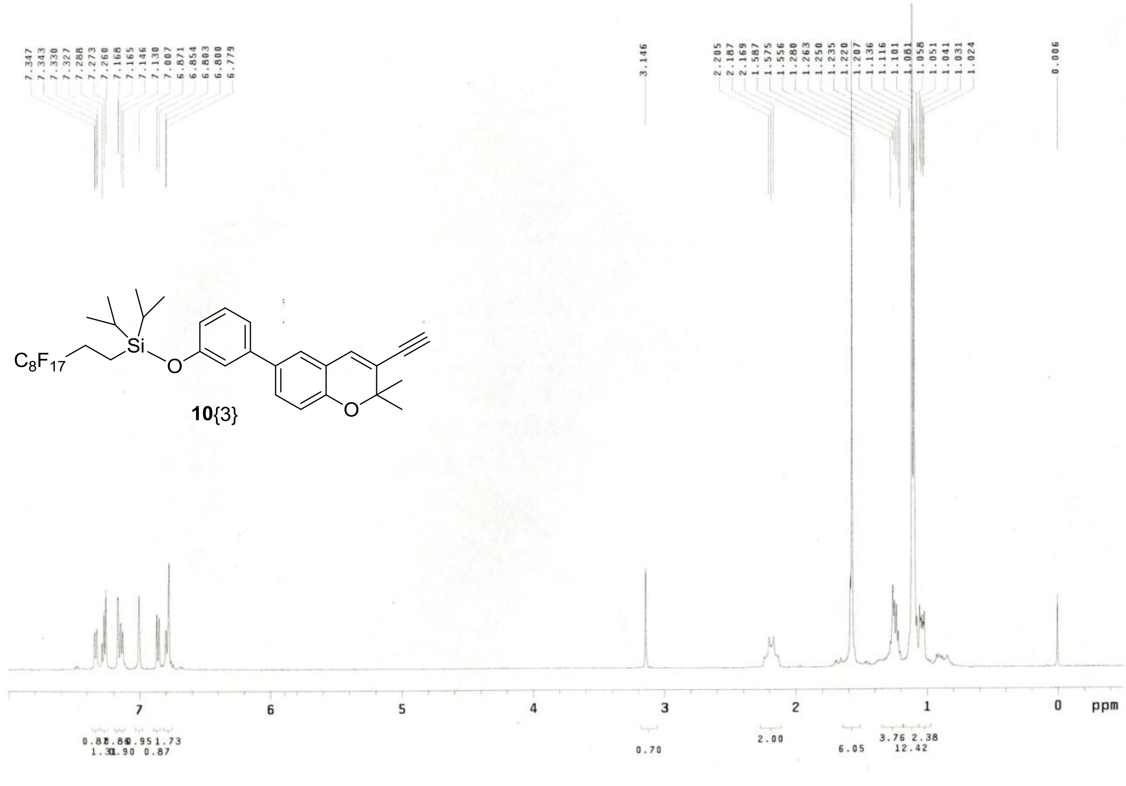

157.263
154.132
130.103
127.661
120.433
115.898
112.972
108.341
81.807
80.306
78.028
77.520
77.268
77.012
26.608
17.620
17.520
13.137
0.682
220
200
180
160
140
120
100
80
60
40
20
0
ppm

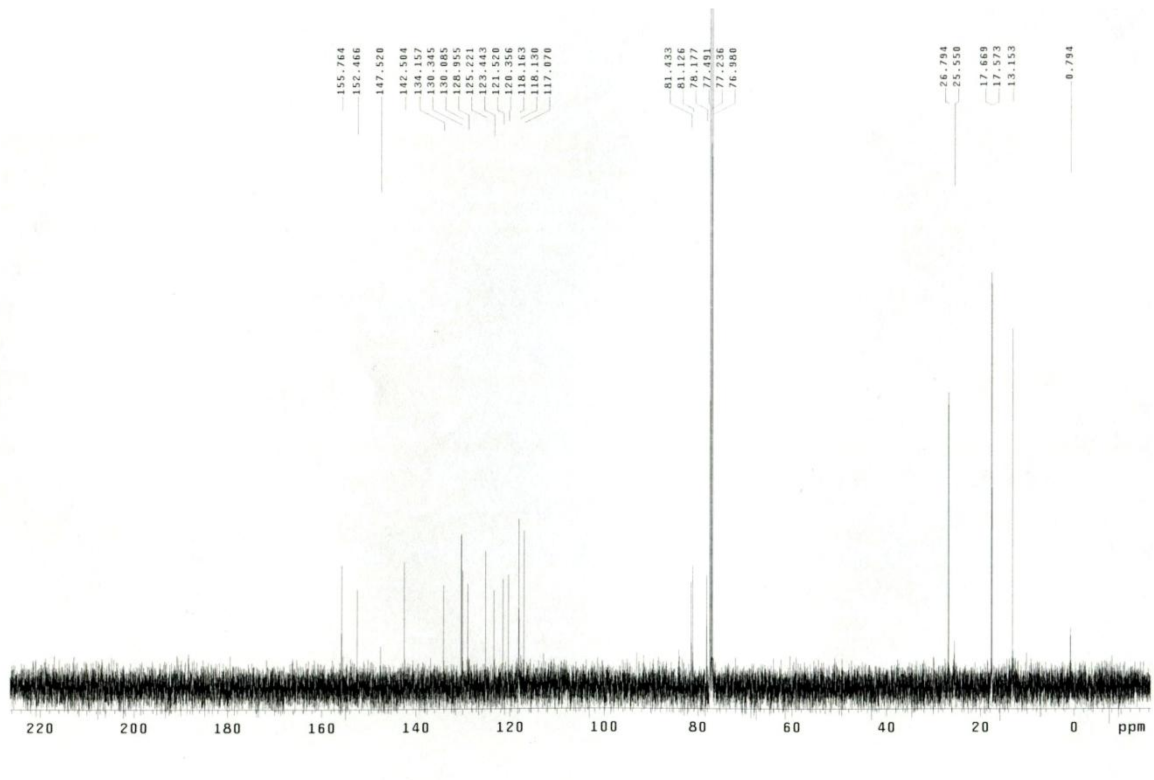


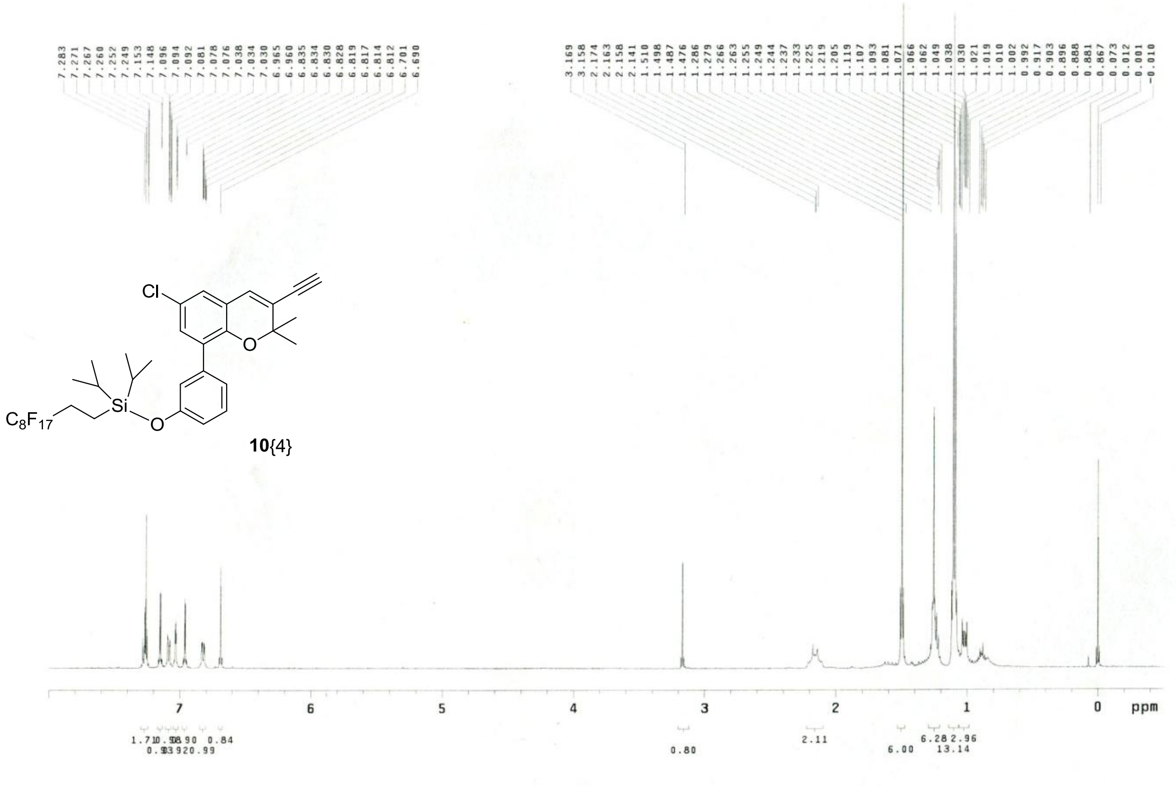
10{2}
ppm

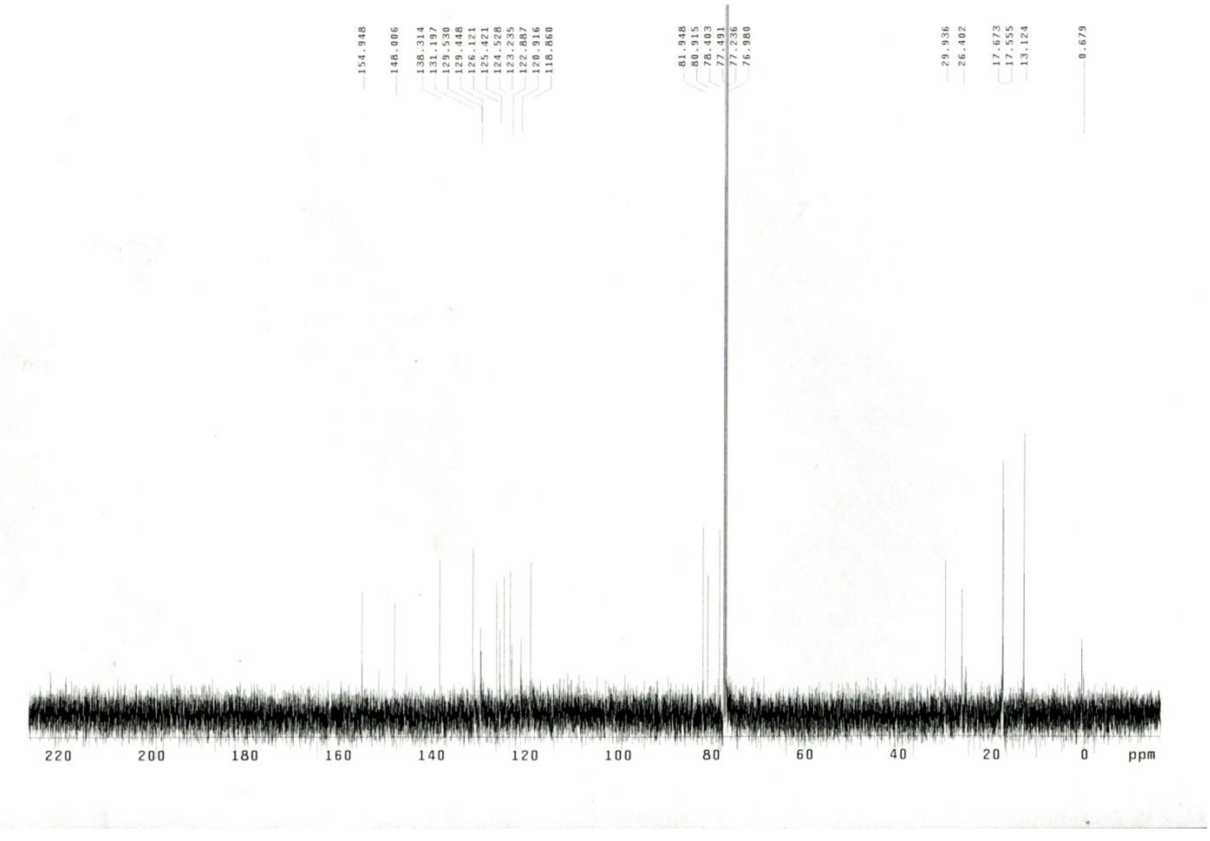


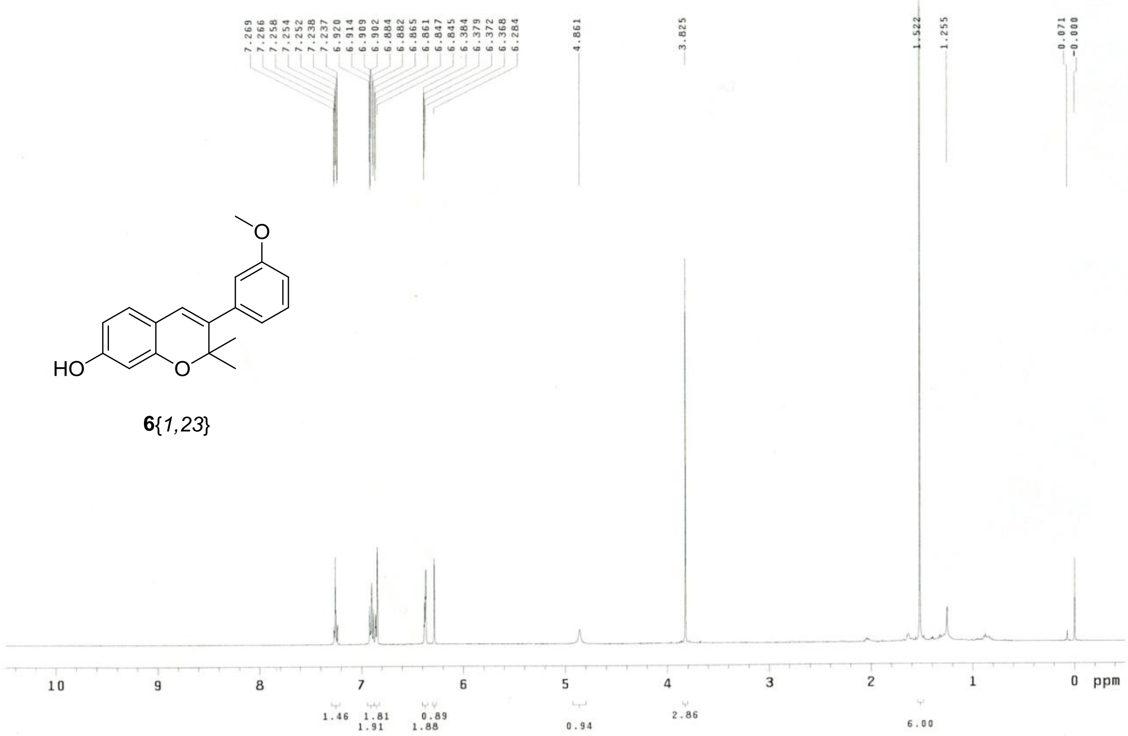
ppm


C8F17
Si
O
O
10{3}
7.347 7.343 7.330 7.327 7.288 7.273 7.260 7.168 7.165 7.146 7.130 7.007 6.871 6.854 6.803 6.800 6.779
3.146
2.205 2.187 2.169 1.587 1.575 1.556 1.280 1.263 1.250 1.235 1.220 1.207 1.136 1.116 1.101 1.081 1.058 1.051 1.041 1.031 1.024
0.006
ppm
2.00
6.05
12.42
0.70

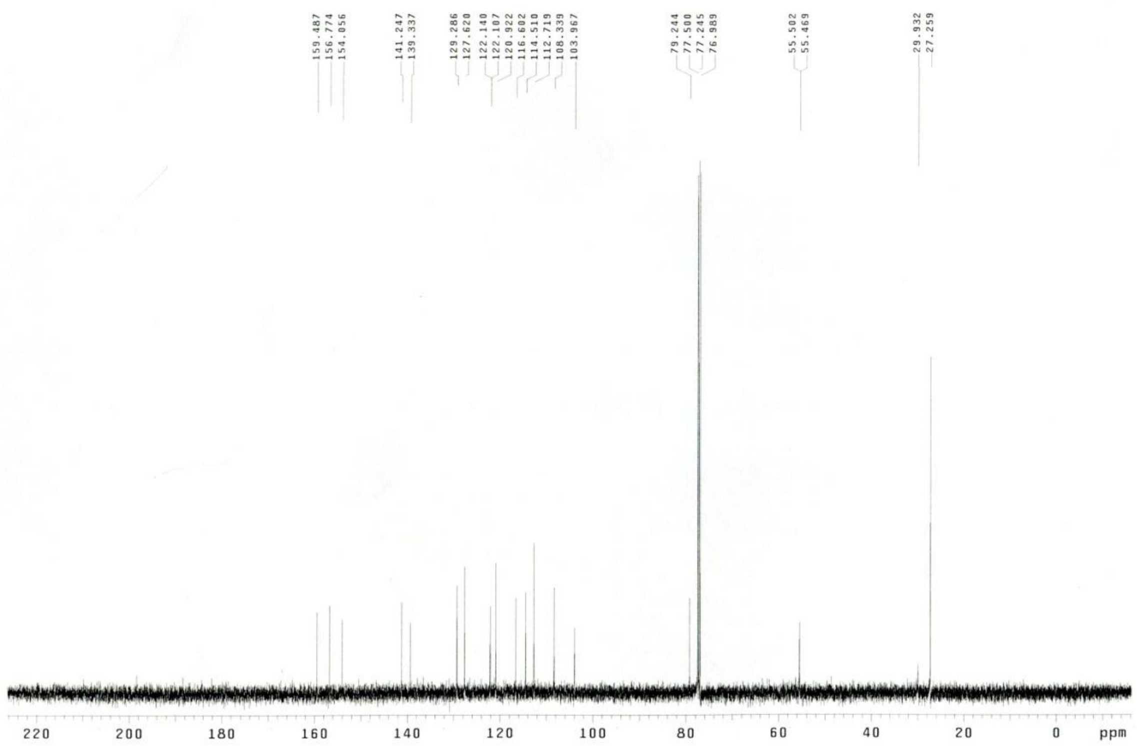

155.764 152.466 147.520 142.504 134.157 130.345 130.085 128.955 125.221 123.443 121.520 120.356 118.163 118.130 117.070
81.433 81.126 78.177 77.491 77.236 76.980
26.794 25.550 17.669 17.573 13.153
0.794
220 200 180 160 140 120 100 80 60 40 20 0 ppm

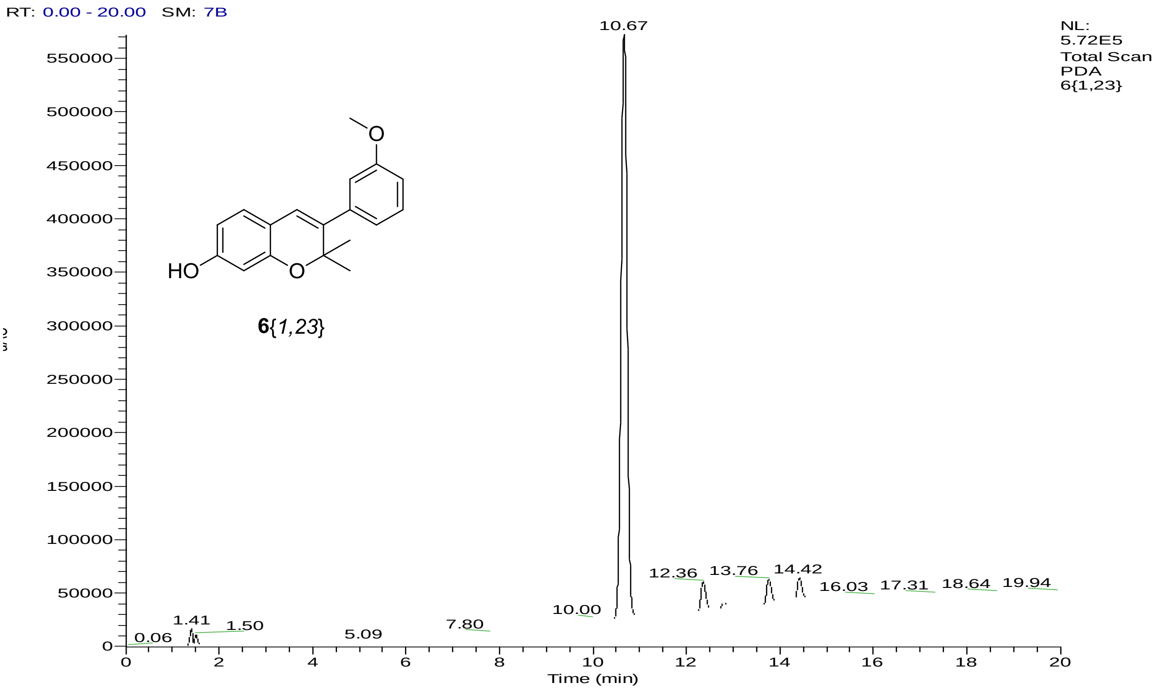

7.283 7.271 7.267 7.260 7.252 7.249 7.153 7.148 7.096 7.094 7.092 7.081 7.078 7.076 7.038 7.034 7.030 6.965 6.960 6.835 6.834 6.830 6.828 6.819 6.817 6.814 6.812 6.701 6.690
3.169 3.158 2.174 2.163 2.158 2.141 1.510 1.498 1.487 1.476 1.286 1.279 1.266 1.263 1.255 1.249 1.244 1.237 1.233 1.225 1.219 1.205 1.119 1.107 1.093 1.081 1.071 1.066 1.062 1.049 1.038 1.030 1.021 1.019 1.010 1.002 0.992 0.917 0.903 0.896 0.888 0.881 0.873 0.867 0.012 0.001 -0.010
Cl
O
Si
O
C_8F_{17}
10{4}
ppm


154.948 148.006 138.314 131.197 129.530 129.448 126.121 125.421 124.528 123.235 122.887 120.916 118.860
81.948 80.915 78.403 77.491 77.236 76.980
29.936 26.402 17.673 17.555 13.124 0.679
220 200 180 160 140 120 100 80 60 40 20 0 ppm


7.269 7.266 7.258 7.254 7.252 7.238 7.237 6.920 6.914 6.909 6.902 6.884 6.882 6.865 6.861 6.847 6.845 6.384 6.379 6.372 6.368 6.284
4.861
3.825
1.522
1.255
0.071
-0.000
HO
O
10 9 8 7 6 5 4 3 2 1 0 ppm
1.46 1.81 1.91 0.89 1.88 0.94 2.86 6.00

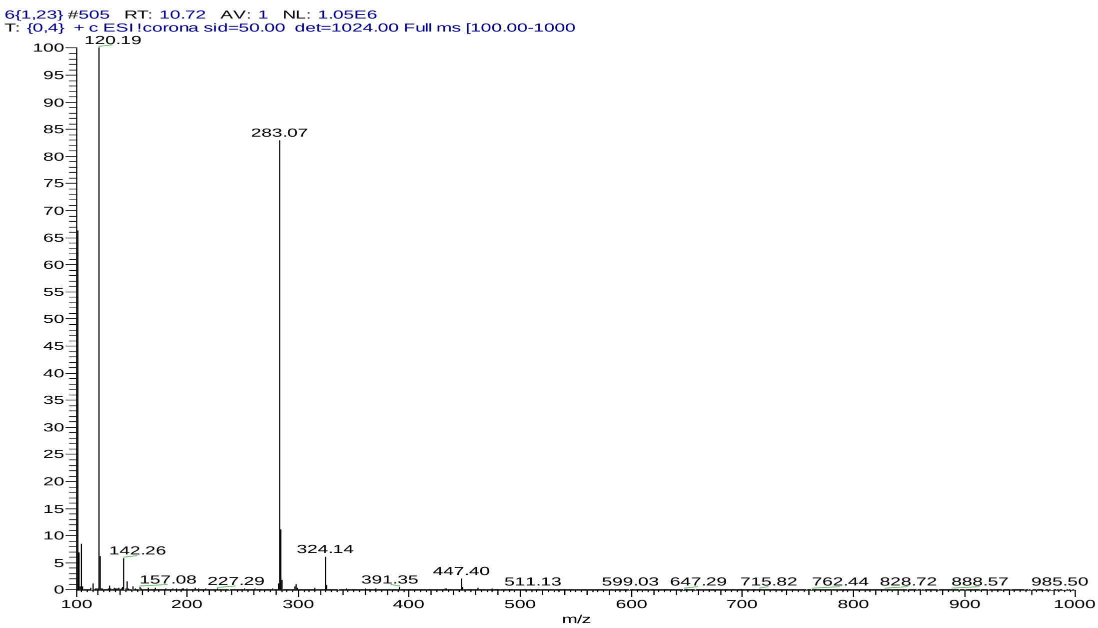
6{*1,23*}

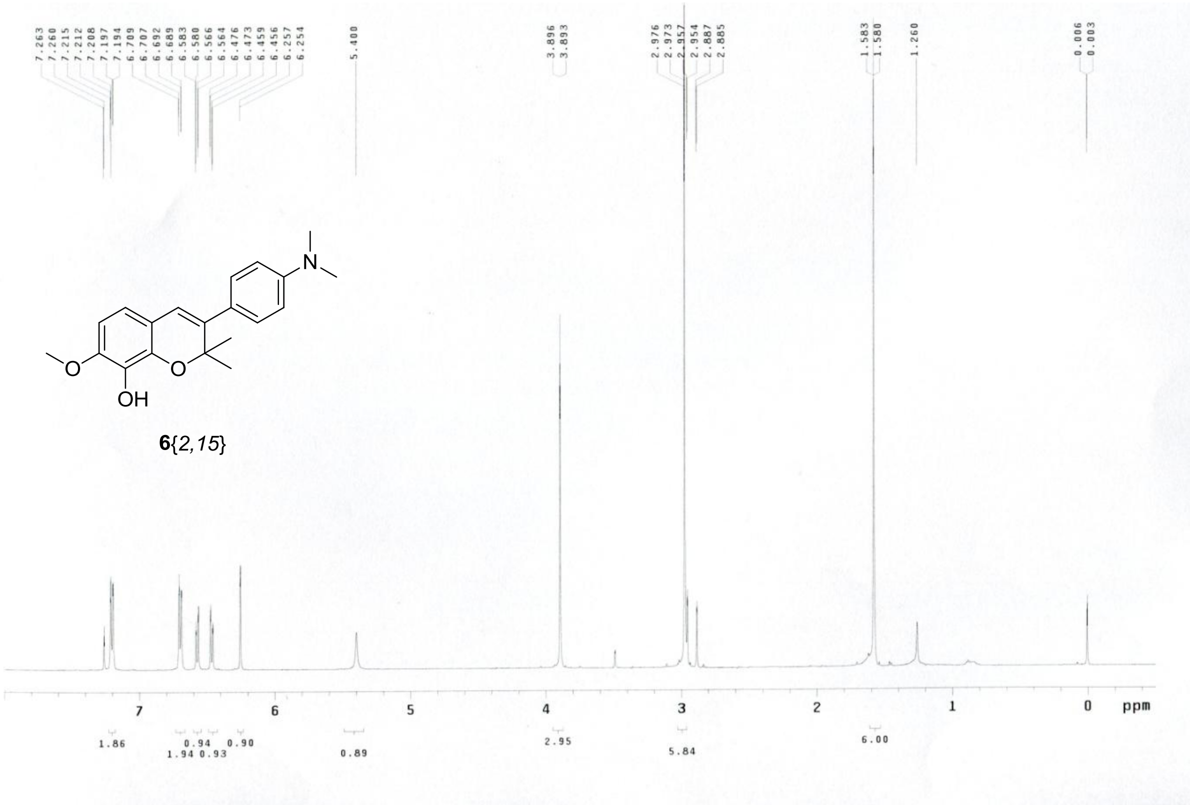

159.487 156.774 154.056
141.247 139.337
129.286 127.620 122.140 122.107 120.922 116.602 114.510 112.719 108.339 103.967
79.244 77.500 77.245 76.989
55.502 55.469
29.932 27.259
220 200 180 160 140 120 100 80 60 40 20 0 ppm



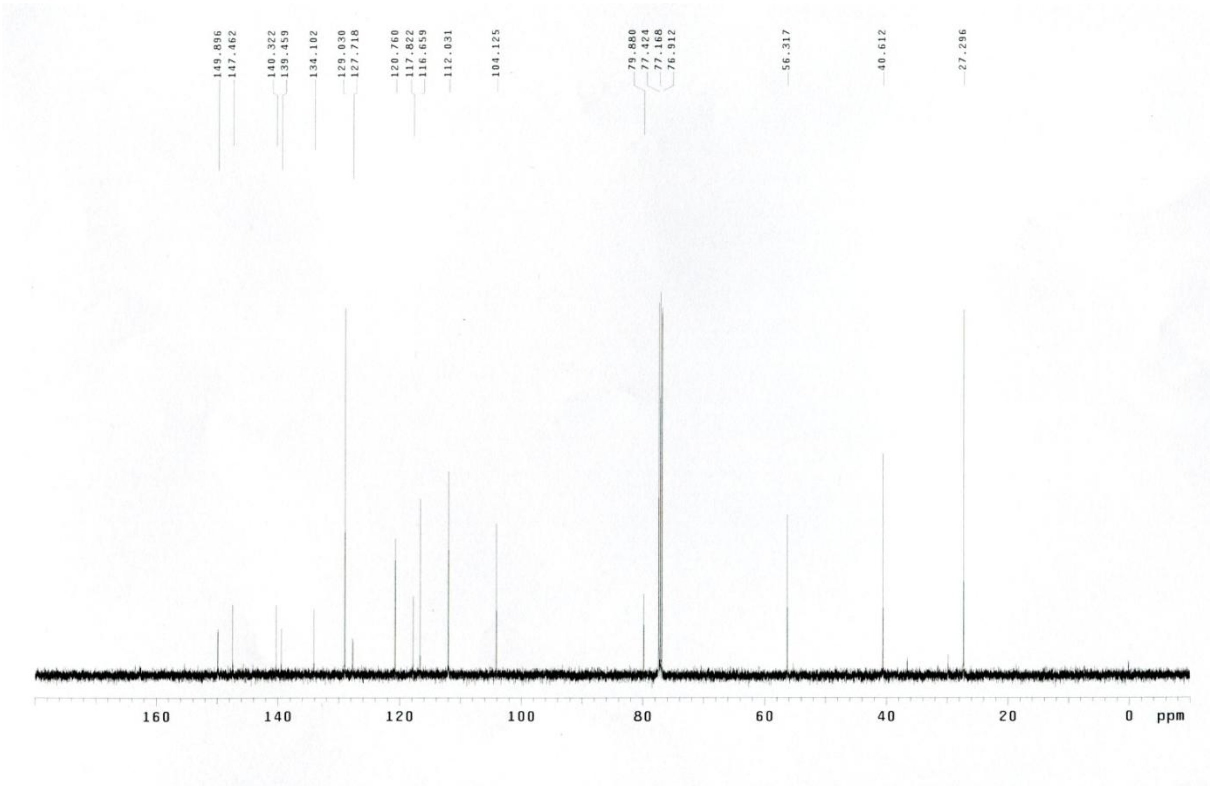
PEAK LIST
6{1,23}.RAW
RT: 0.00 - 20.00
Number of detected peaks: 4

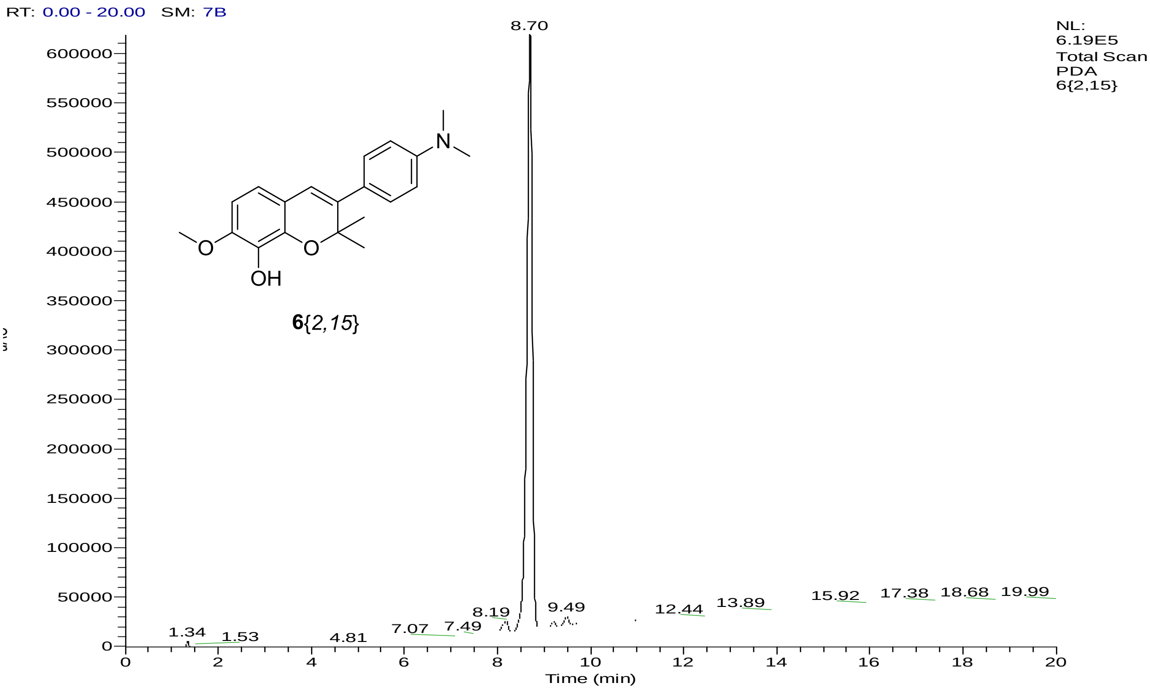
Apex RT	Start RT	End RT	Area	%Area	Height	%Height
10.67	10.44	10.92	4895228	91.19	545197.1	88.85
12.36	12.24	12.51	189212.5	3.52	26543.71	4.33
13.76	13.65	13.91	155370.8	2.89	22402.35	3.65
14.42	14.32	14.56	128145.5	2.39	19489.47	3.18




7.263
7.260
7.215
7.212
7.208
7.197
7.194
6.709
6.707
6.692
6.689
6.583
6.580
6.566
6.564
6.476
6.473
6.459
6.456
6.257
6.254
5.400
3.896
3.893
2.976
2.973
2.957
2.954
2.887
2.885
1.583
1.580
1.260
0.006
0.003
OH
7
6
5
4
3
2
1
0
ppm
1.86
1.94
0.94
0.93
0.90
0.89
2.95
5.84
6.00

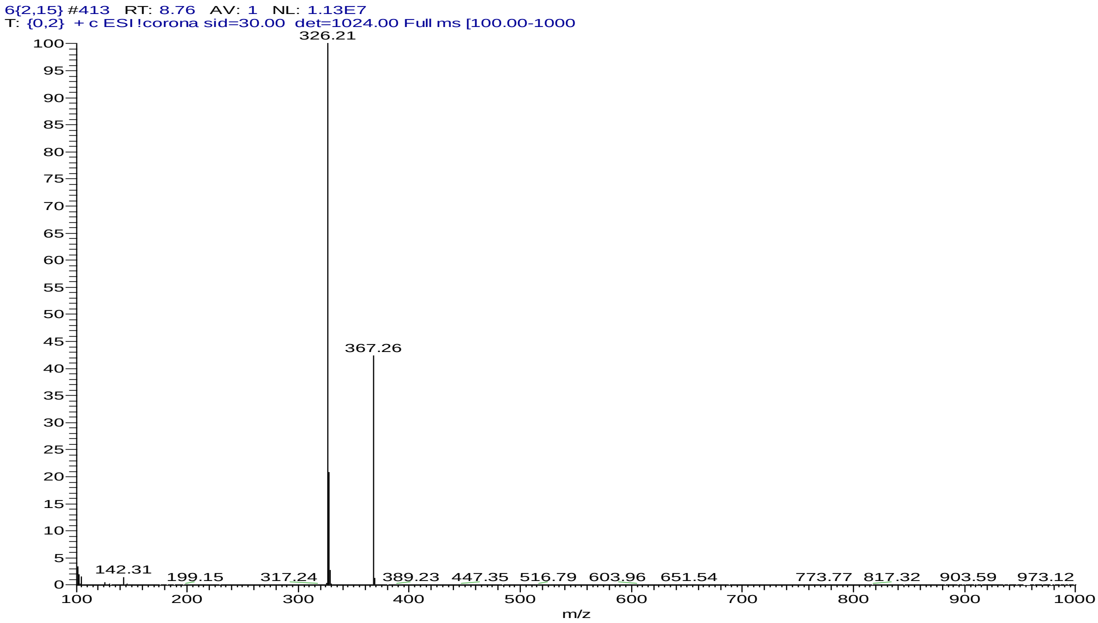
6{*2,15*}

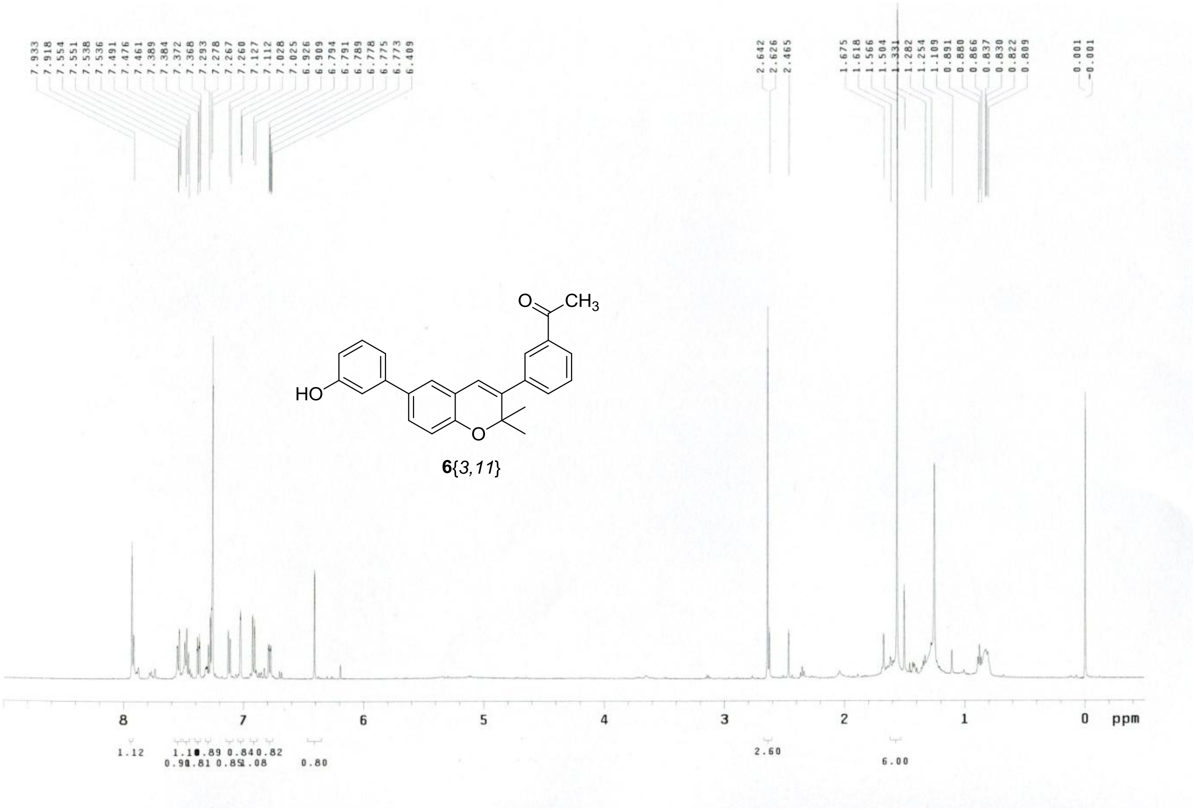

149.896
147.462
140.322
139.459
134.102
129.030
127.718
120.760
117.822
116.659
112.031
104.125
79.880
77.424
77.168
76.912
56.317
40.612
27.296
160
140
120
100
80
60
40
20
0
ppm

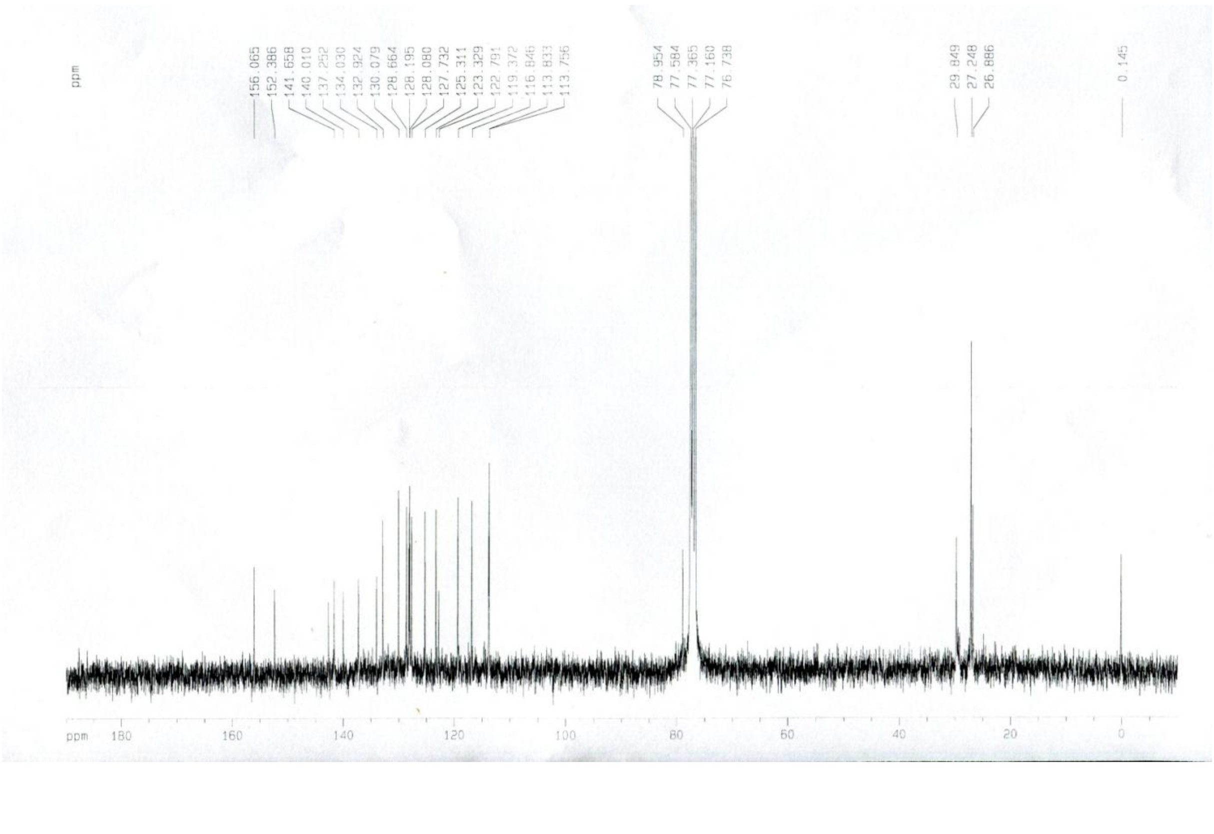


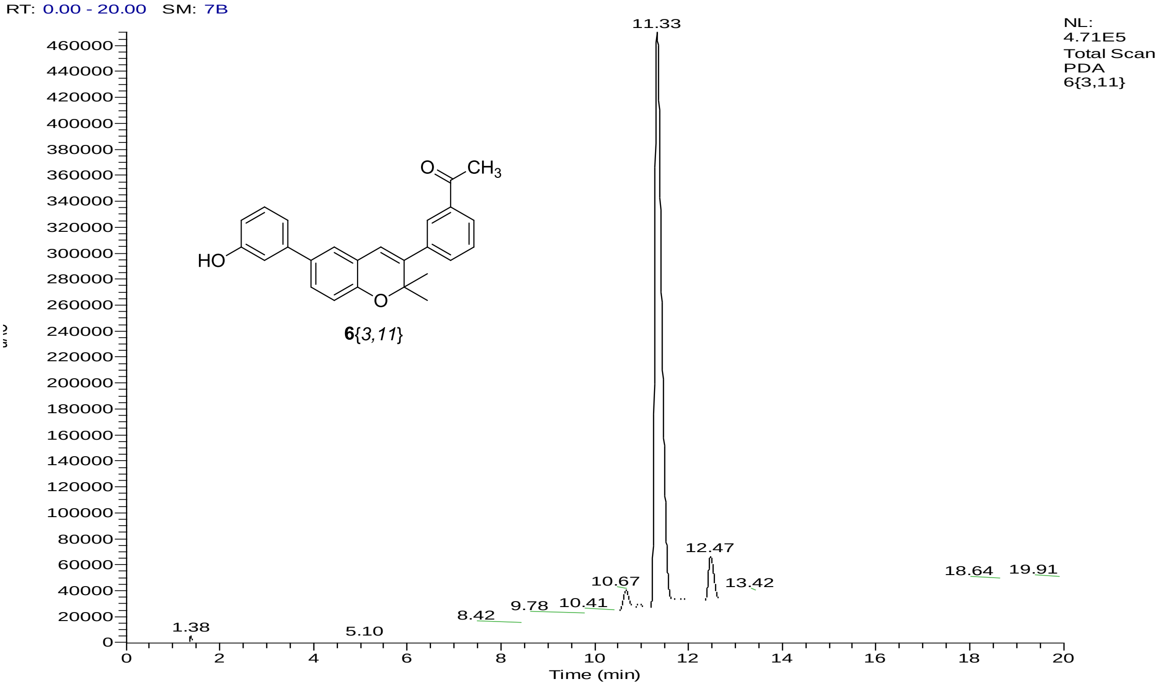
PEAK LIST
6{2,15}.RAW
RT: 0.00 - 20.00
Number of detected peaks: 2

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
8.19	7.67	8.3	180381.6	3.46	14874.12	2.4
8.7	8.3	8.91	5032943	96.54	605182.8	97.6



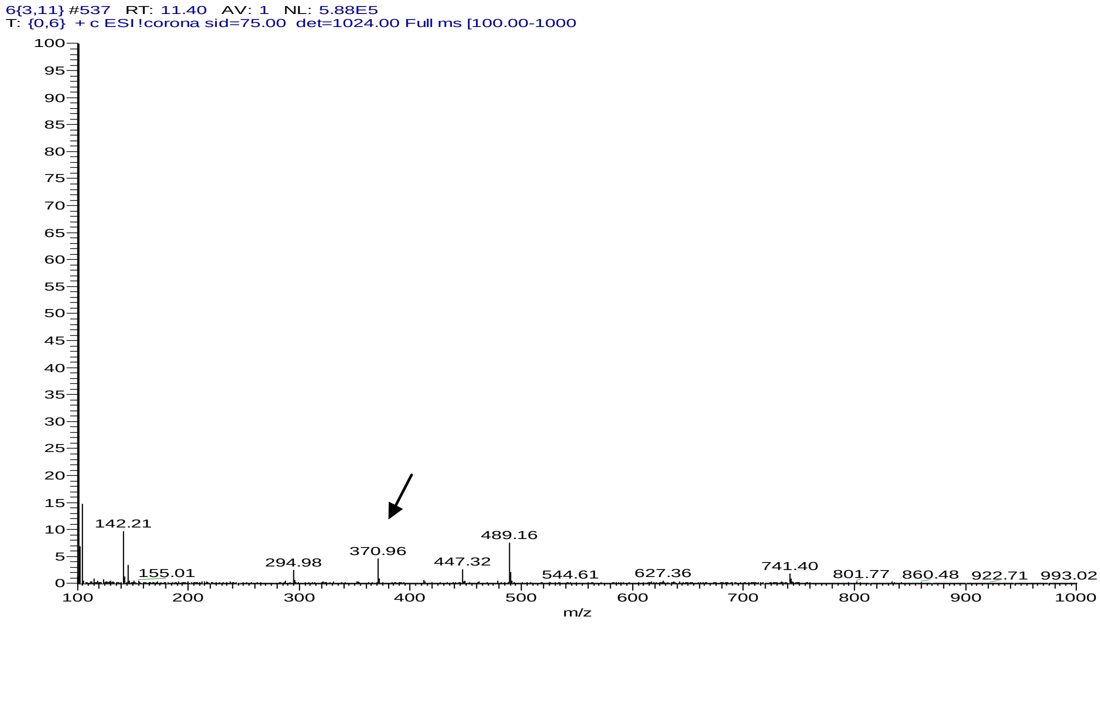


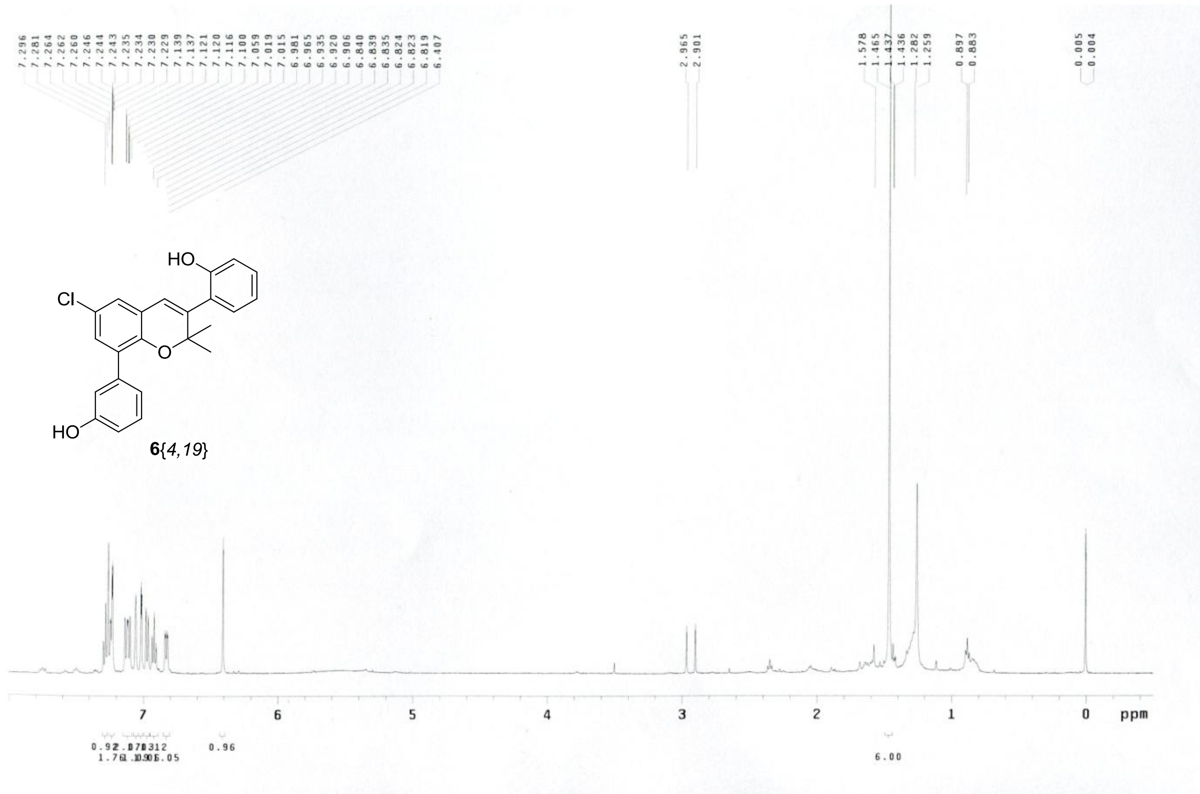


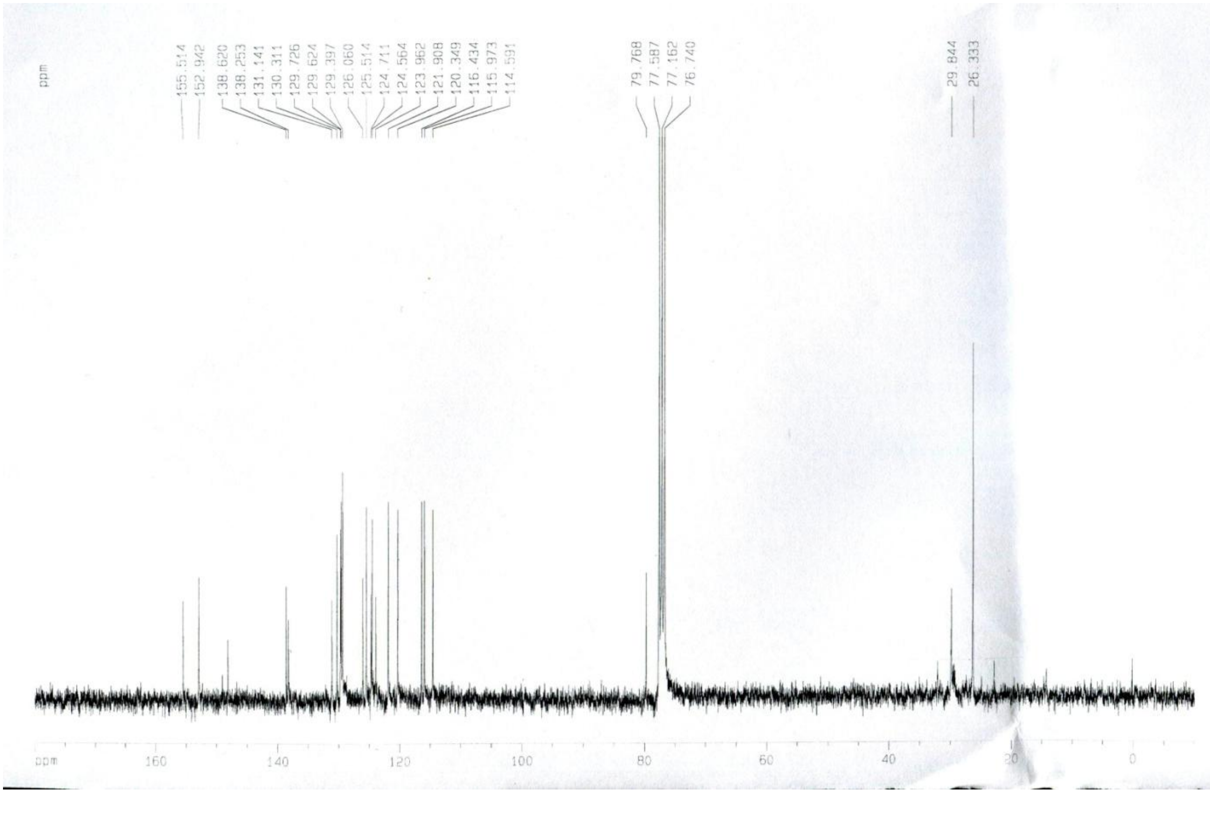


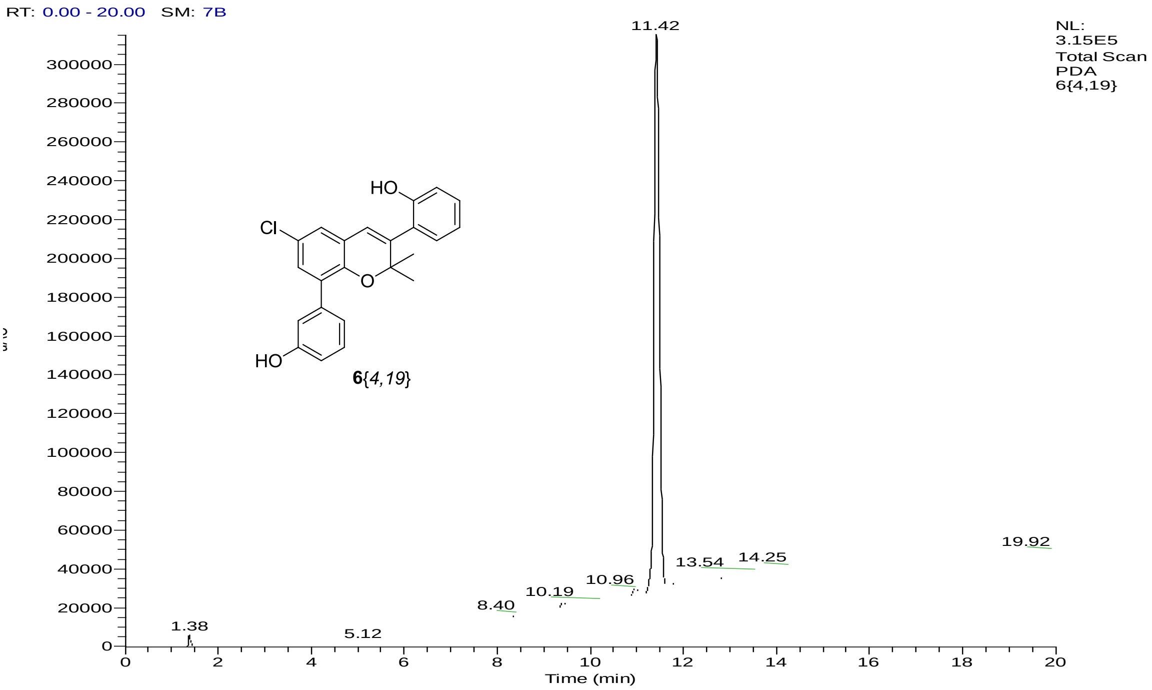
PEAK LIST
6{3,11}.RAW
RT: 0.00 - 20.00
Number of detected peaks: 2

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
11.33	11.13	11.67	4553290	94.46	443537.1	92.94
12.47	12.35	12.67	266913	5.54	33706.22	7.06




7.296 7.281 7.264 7.262 7.260 7.246 7.244 7.243 7.235 7.234 7.230 7.229 7.139 7.137 7.121 7.120 7.116 7.100 7.059 7.019 7.015 6.981 6.965 6.935 6.920 6.906 6.840 6.839 6.835 6.824 6.823 6.819 6.407
2.965 2.901
1.578 1.465 1.437 1.436 1.282 1.259
0.897 0.883
0.005 0.004
HO
Cl
O
HO
6{4,19}
0.96
6.00
ppm


ppm
155.514 152.942 138.620 138.253 131.141 130.311 129.726 129.624 129.397 126.060 125.514 124.711 124.564 123.962 121.908 120.349 116.434 115.973 114.591
79.768 77.587 77.162 76.740
29.844 26.333
160 140 120 100 80 60 40 20 0



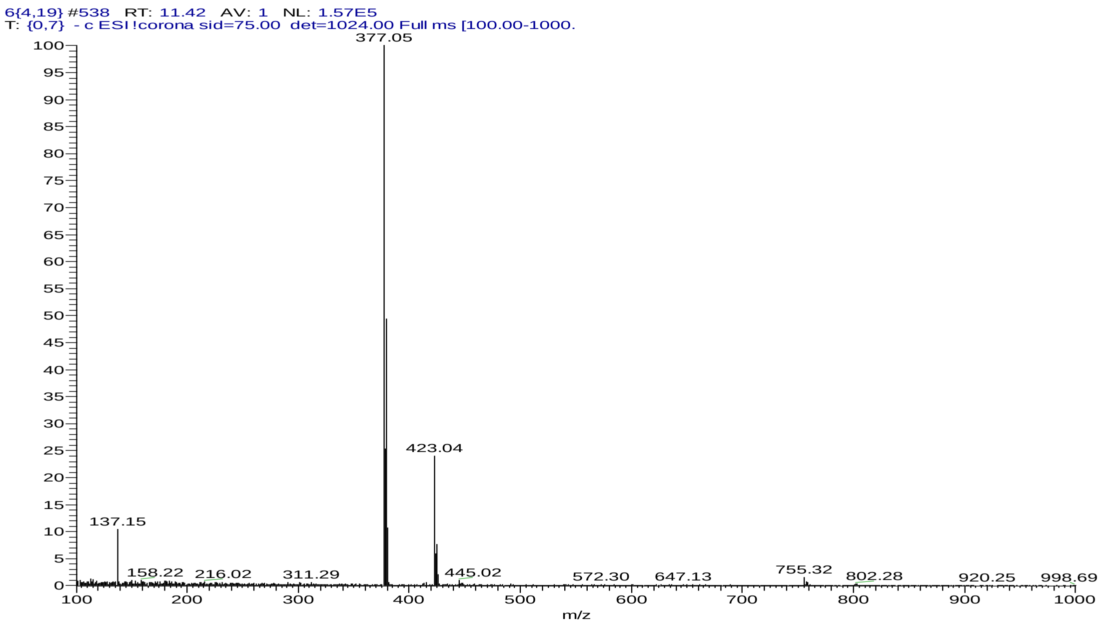
PEAK LIST

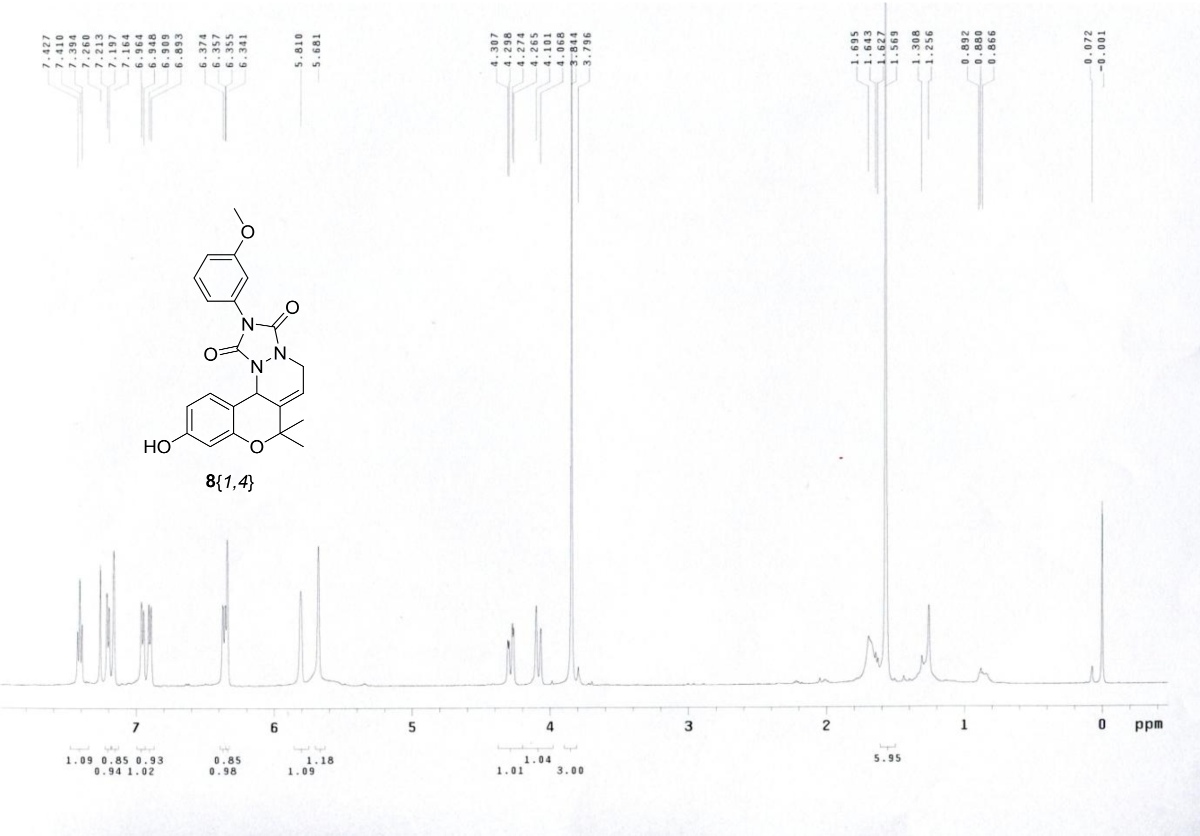
6{4,19}.RAW

RT: 0.00 - 20.00

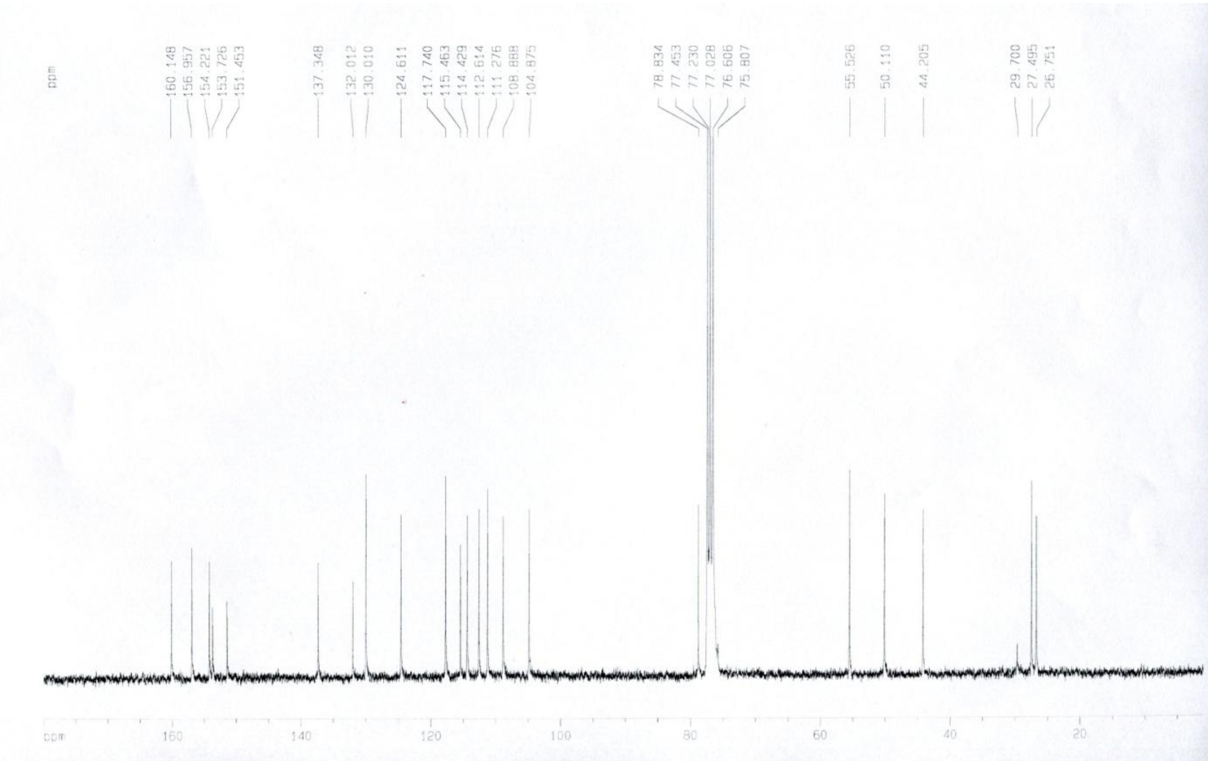
Number of detected peaks: 1

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
11.42	11.12	11.64	2420943	100	287890.6	100

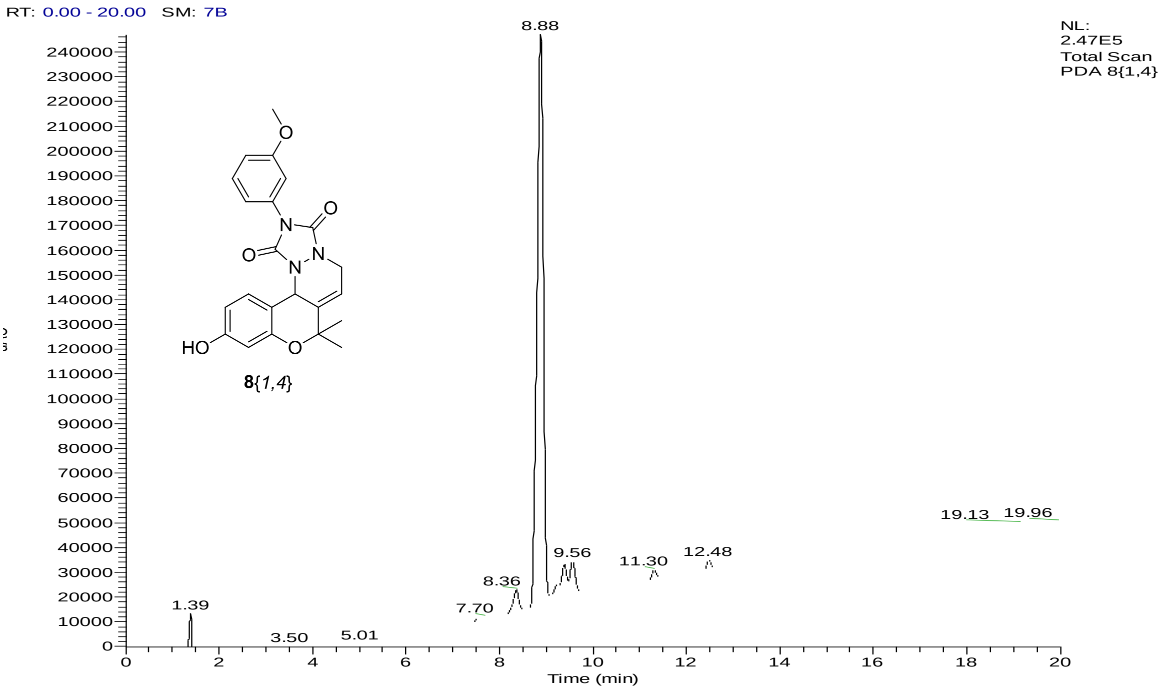




7.427 7.410 7.394 7.260 7.213 7.197 7.164 6.964 6.948 6.909 6.893 6.374 6.357 6.355 6.341 5.810 5.681 4.307 4.298 4.274 4.265 4.101 4.068 3.844 3.796 1.695 1.643 1.627 1.569 1.308 1.256 0.892 0.880 0.866 0.072 -0.001
8{1,4}
7 6 5 4 3 2 1 0 ppm
1.09 0.85 0.93 0.94 1.02 0.85 0.98 1.18 1.09 1.04 1.01 3.00 5.95



ppm
160.148 156.957 154.221 153.726 151.453 137.348 132.012 130.010 124.611 117.740 115.463 114.429 112.614 111.276 108.888 104.875 78.834 77.453 77.230 77.028 76.606 75.807 55.526 50.110 44.205 29.700 27.495 26.751
ppm 160 140 120 100 80 60 40 20



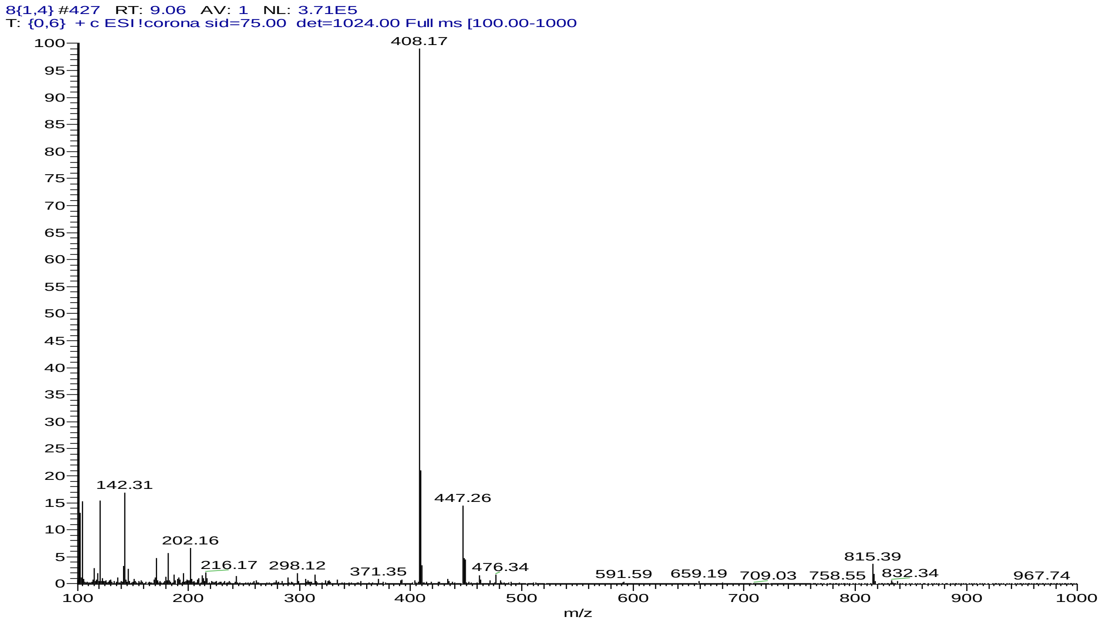
PEAK LIST

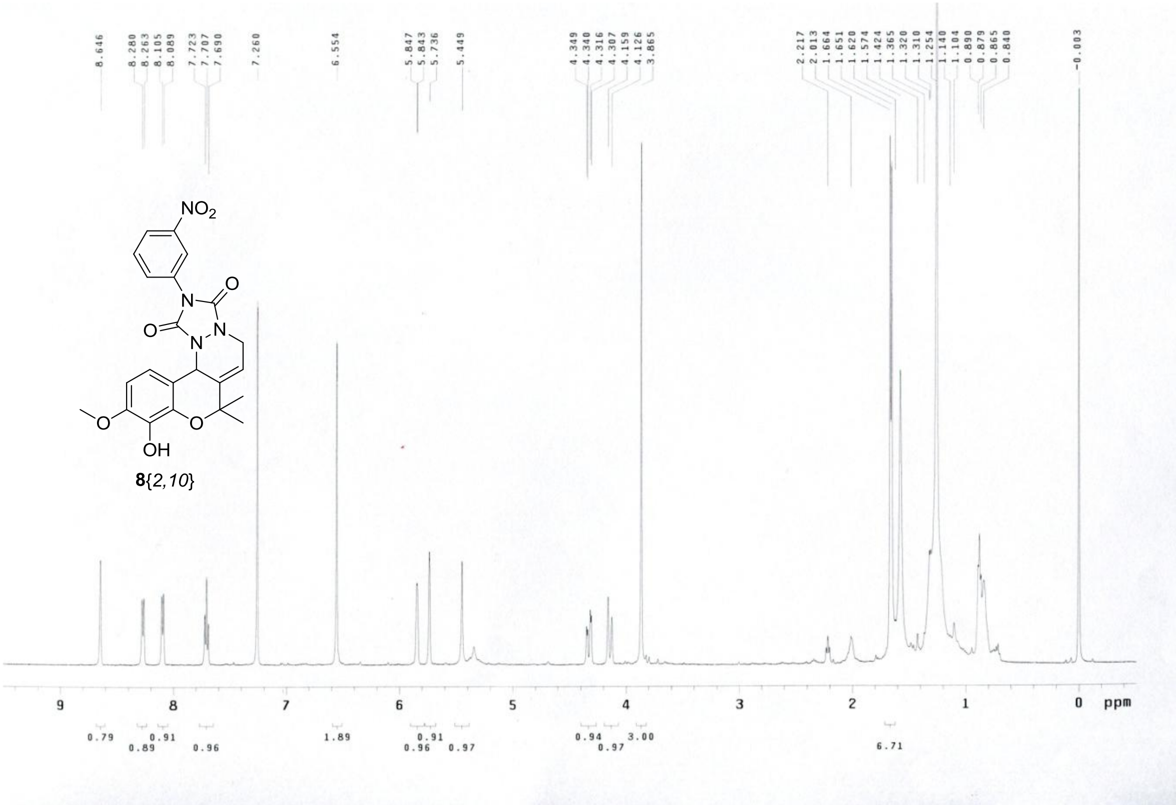
8{1,4}.RAW

RT: 0.00 - 20.00

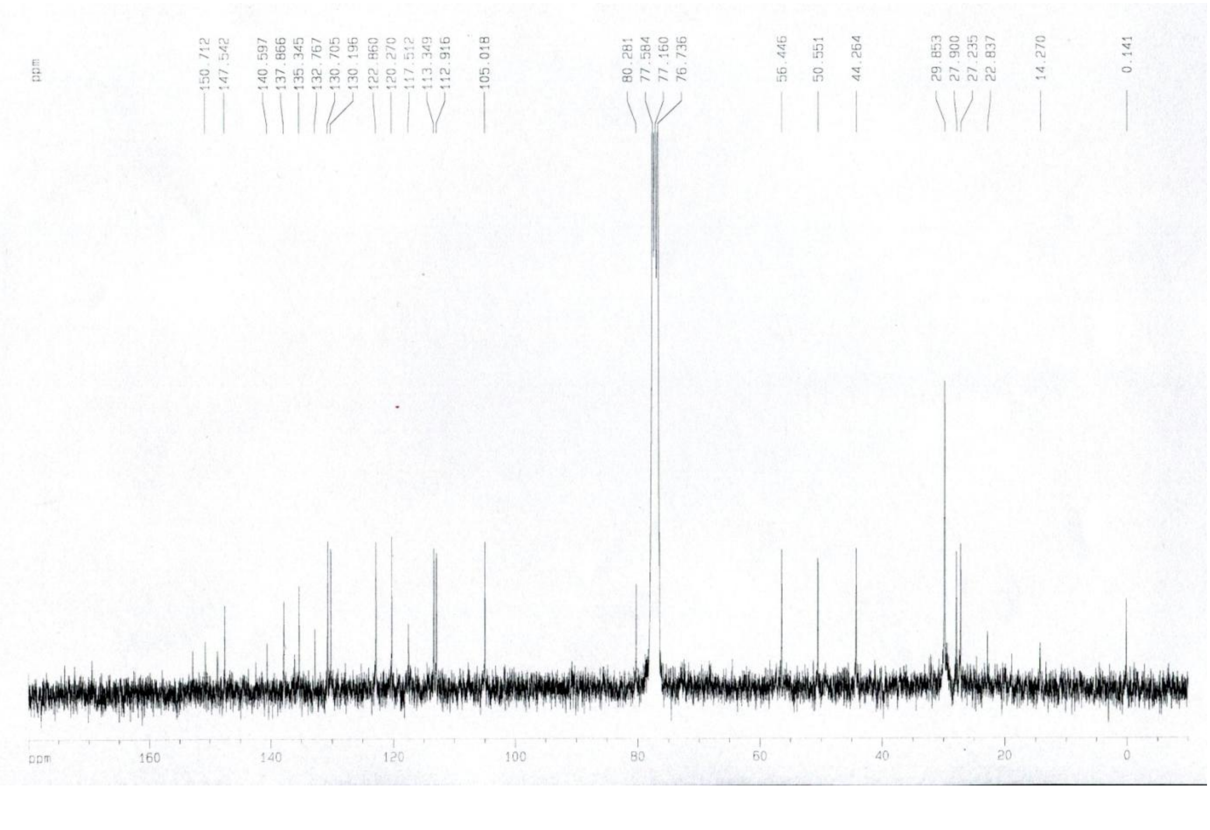
Number of detected peaks: 4

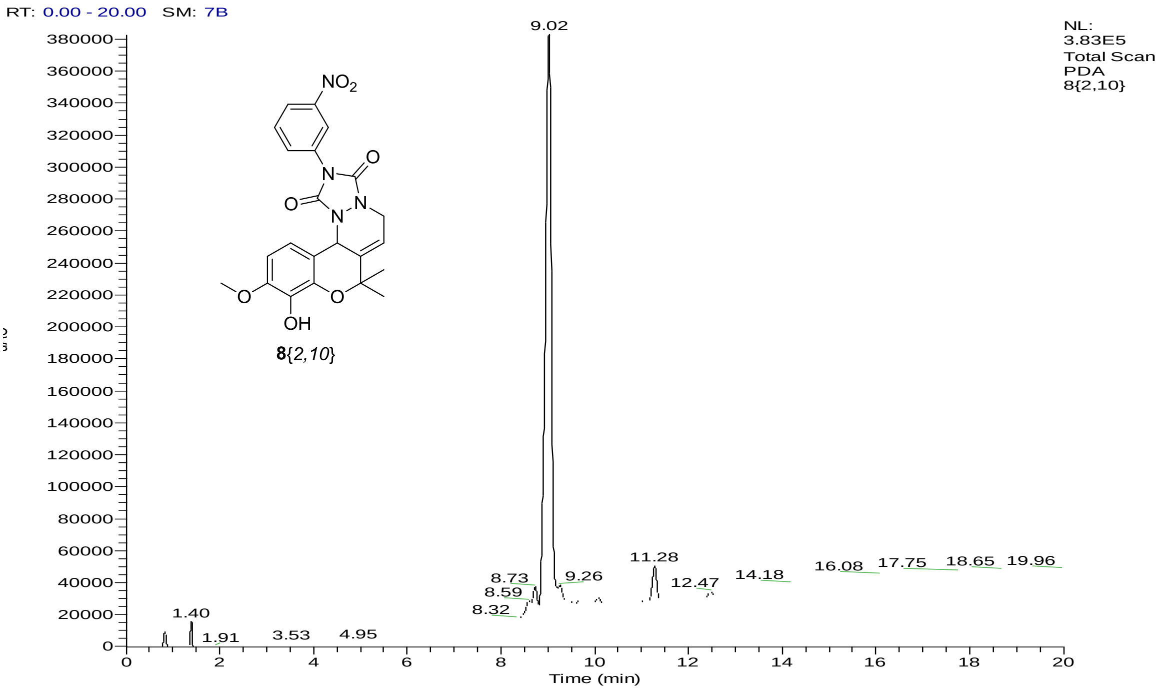
Apex RT	Start RT	End RT	Area	%Area	Height	%Height
8.36	8.16	8.49	81506.11	3.21	9328.174	3.48
8.88	8.64	9.08	2225751	87.73	230646.8	86.13
9.39	9.27	9.48	116959.5	4.61	13678.05	5.11
9.56	9.48	9.72	112759.4	4.44	14130.49	5.28




8.646
8.280
8.263
8.105
8.089
7.723
7.707
7.690
7.260
6.554
5.847
5.843
5.736
5.449
4.349
4.340
4.316
4.307
4.159
4.126
3.865
2.217
2.013
1.664
1.651
1.620
1.574
1.424
1.365
1.320
1.310
1.254
1.140
1.104
0.890
0.879
0.865
0.840
-0.003
NO2
N
O
OH
9 8 7 6 5 4 3 2 1 0 ppm
0.79
0.89
0.91
0.96
1.89
0.96
0.91
0.97
0.94
0.97
3.00
6.71

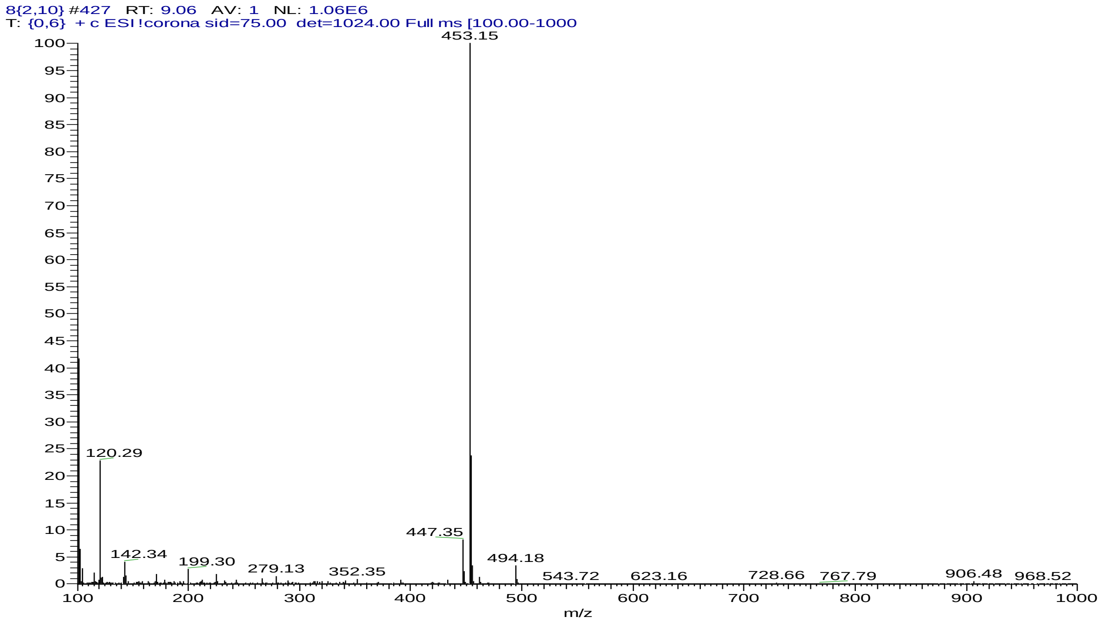
8{*2,10*}

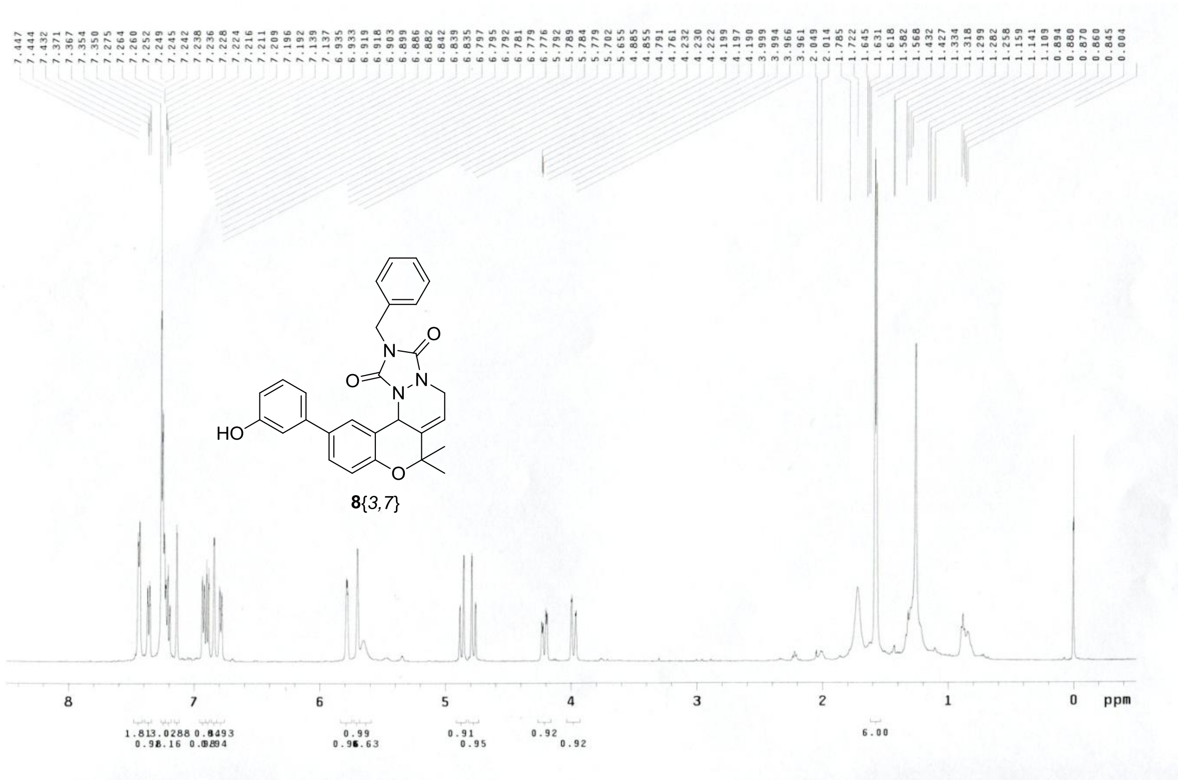

ppm
150.712
147.542
140.597
137.866
135.345
132.767
130.705
130.196
122.860
120.270
117.512
113.349
112.916
105.018
80.281
77.584
77.160
76.736
56.446
50.551
44.264
29.853
27.900
27.235
22.837
14.270
0.141
ppm 160 140 120 100 80 60 40 20 0



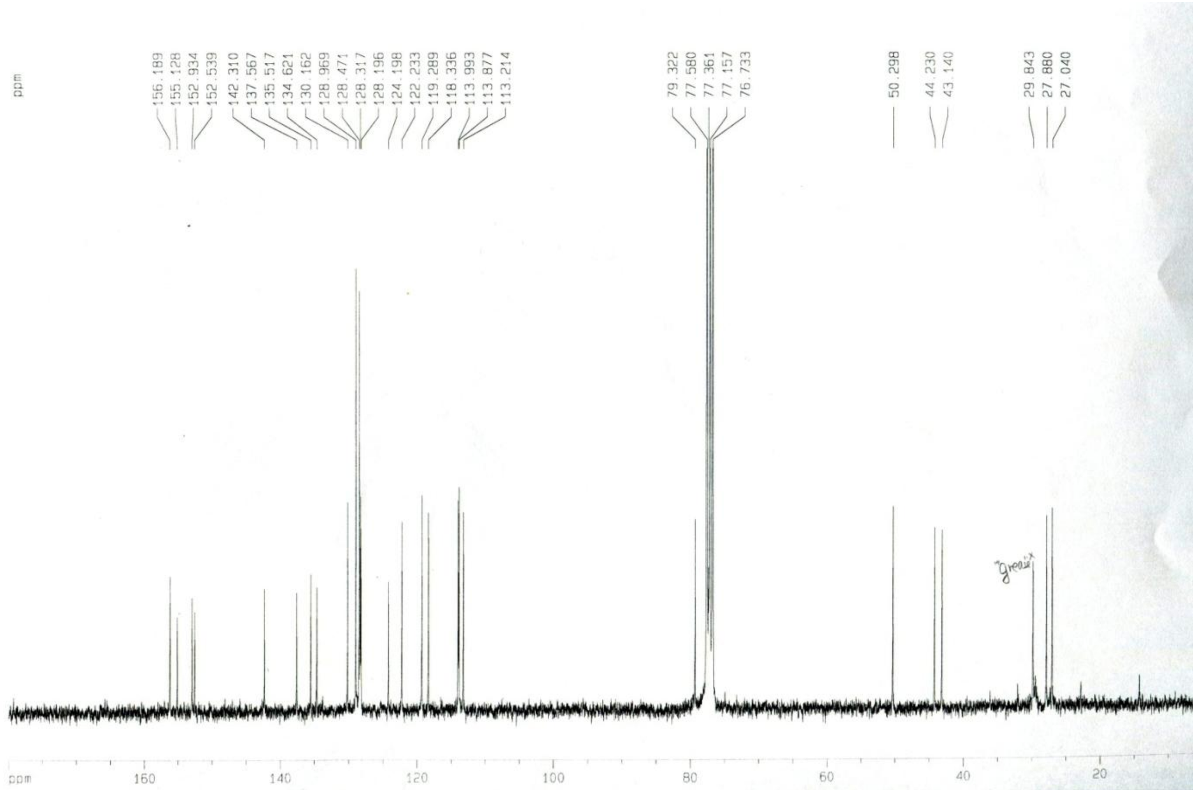
PEAK LIST
8{2,10}.RAW
RT: 0.00 - 20.00
Number of detected peaks: 2

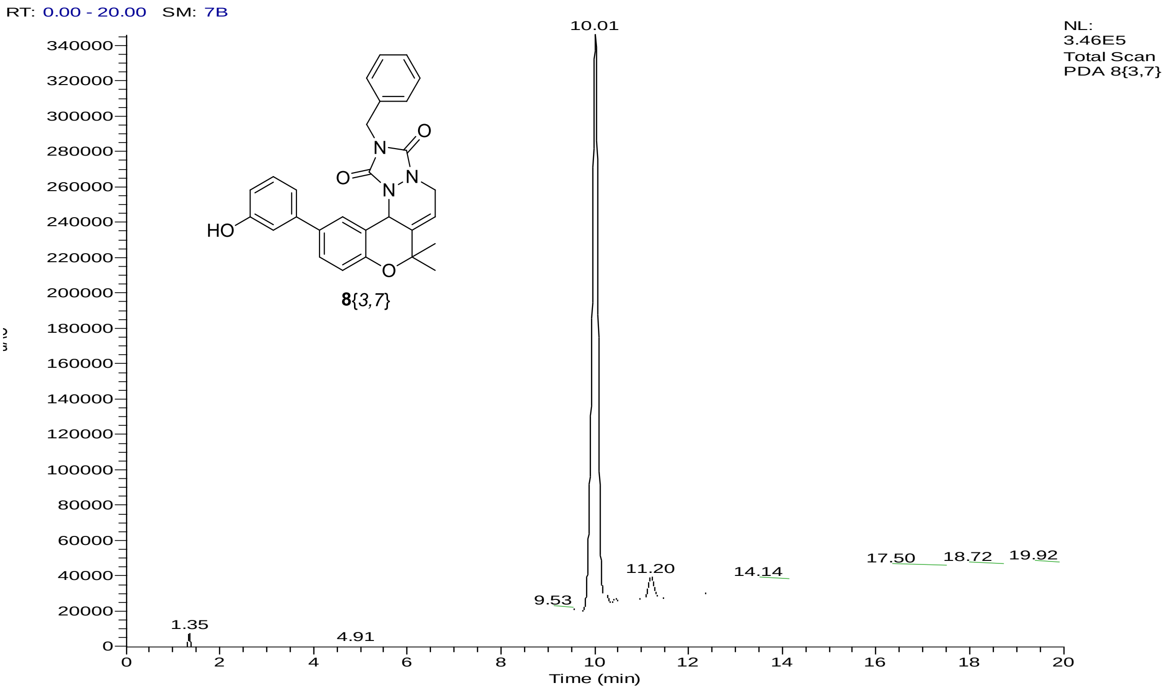
Apex RT	Start RT	End RT	Area	%Area	Height	%Height
9.02	8.81	9.2	3284740	96.05	359821.2	94.33
11.28	11.15	11.41	134990.9	3.95	21609.16	5.67





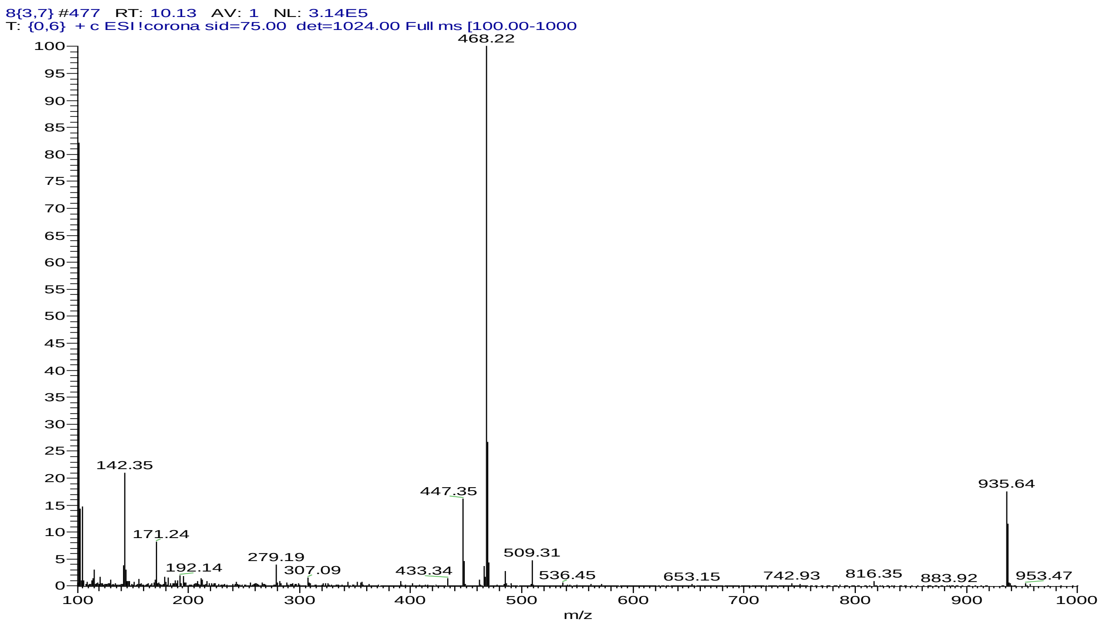
8{*3,7*}

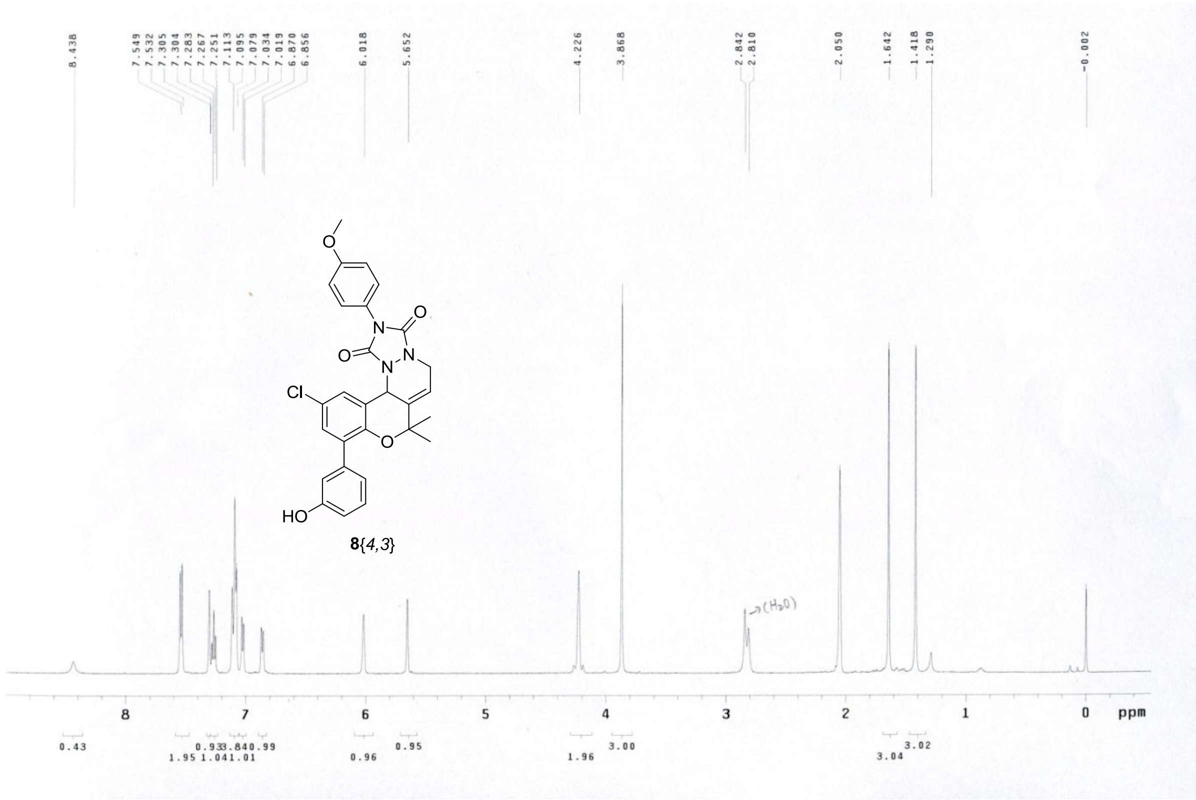


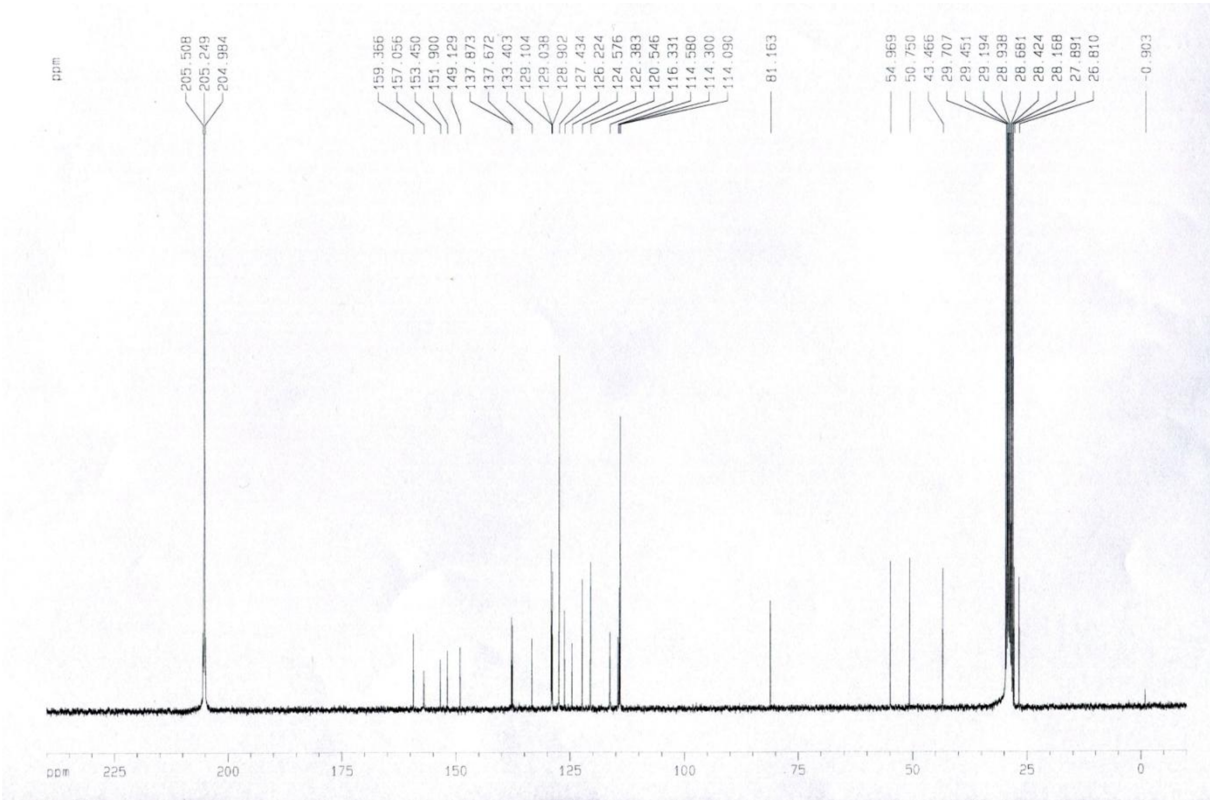


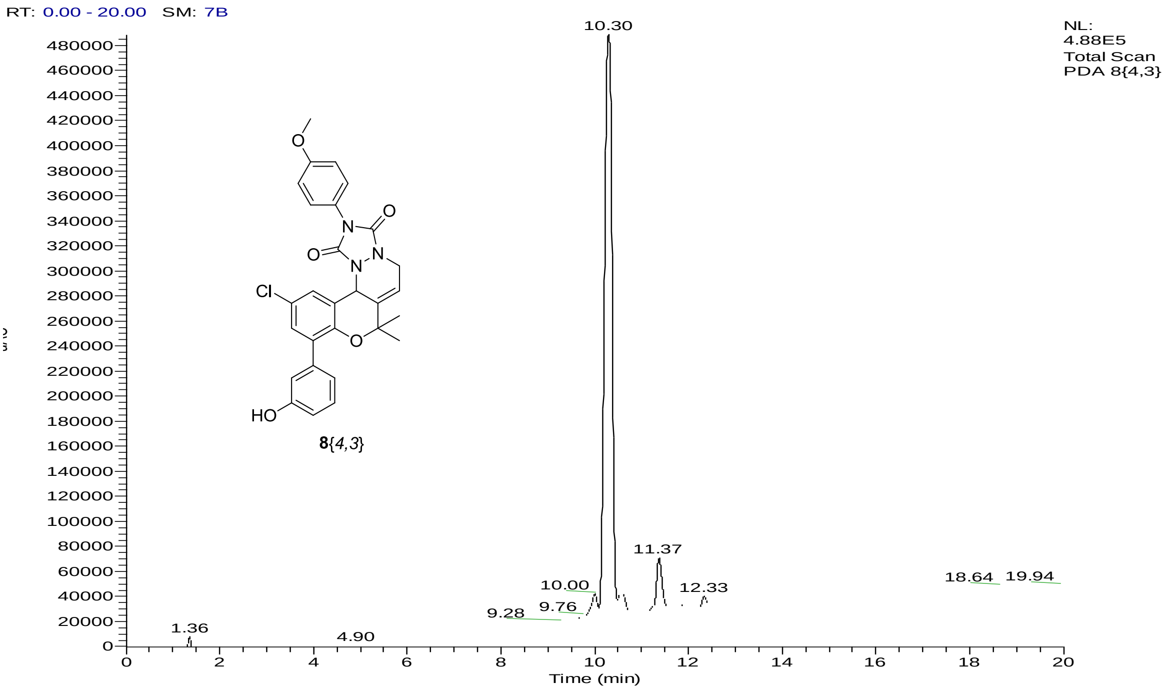
PEAK LIST
8{3,7}.RAW
RT: 0.00 - 20.00
Number of detected peaks: 2

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
10.01	9.73	10.21	2883191	95.89	323382.1	96.05
11.2	11.06	11.42	123661.7	4.11	13282.26	3.95



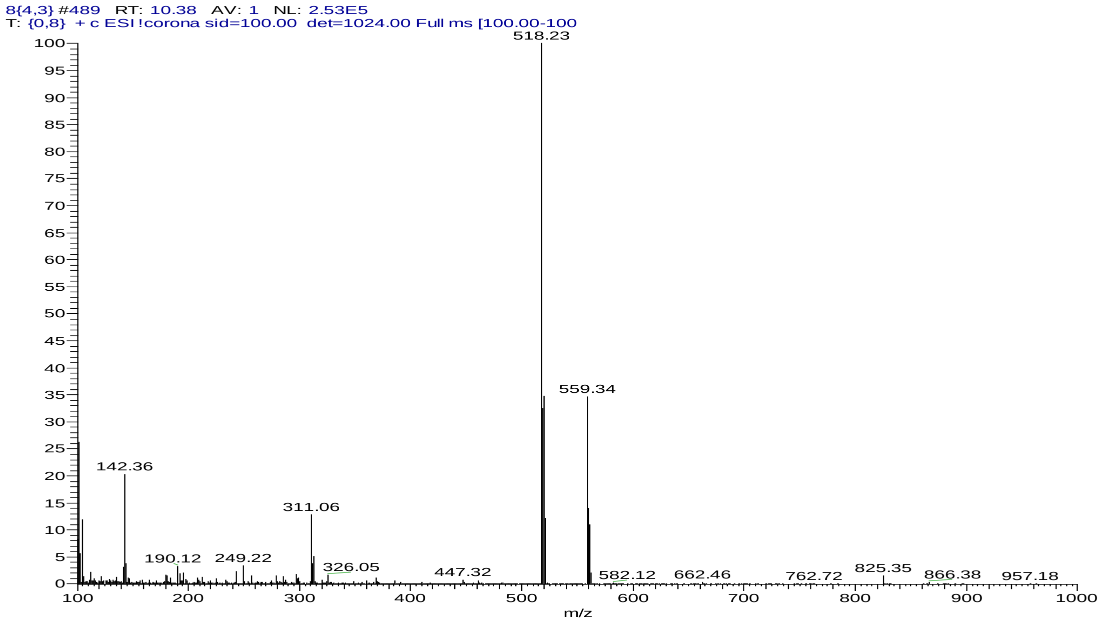

8.438
7.549
7.532
7.305
7.304
7.283
7.267
7.251
7.113
7.095
7.079
7.034
7.019
6.870
6.856
6.018
5.652
4.226
3.868
2.842
2.810
2.050
1.642
1.418
1.290
-0.002
Cl
HO
O
N
8{4,3}
→(H₂O)
8
7
6
5
4
3
2
1
0
ppm
0.43
1.95
0.93
1.04
3.84
1.01
0.99
0.96
0.95
1.96
3.00
3.04
3.02

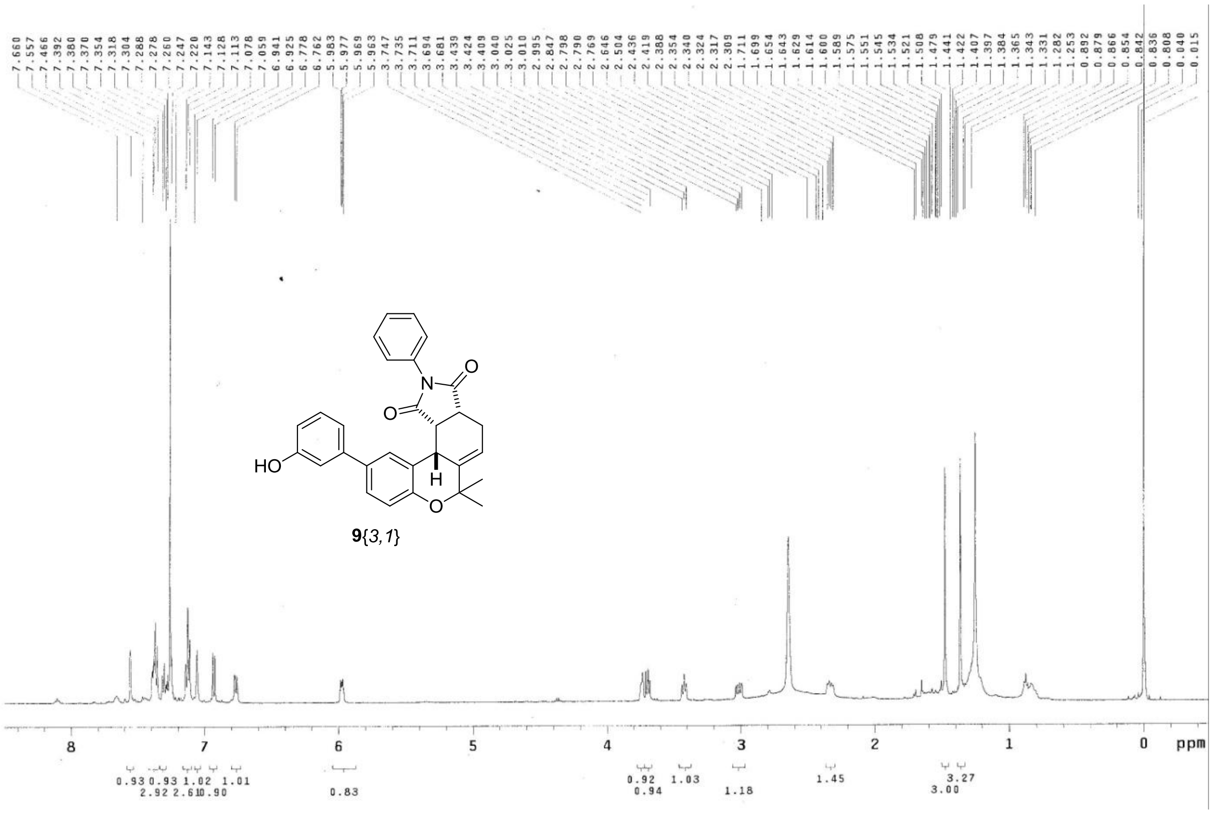

ppm
205.508
205.249
204.984
159.366
157.056
153.450
151.900
149.129
137.873
137.672
133.403
129.104
129.038
128.902
127.434
126.224
124.576
122.383
120.546
116.331
114.580
114.300
114.090
81.163
54.969
50.750
43.466
29.707
29.451
29.194
28.938
28.681
28.424
28.168
27.891
26.810
-0.903
ppm
225
200
175
150
125
100
75
50
25
0

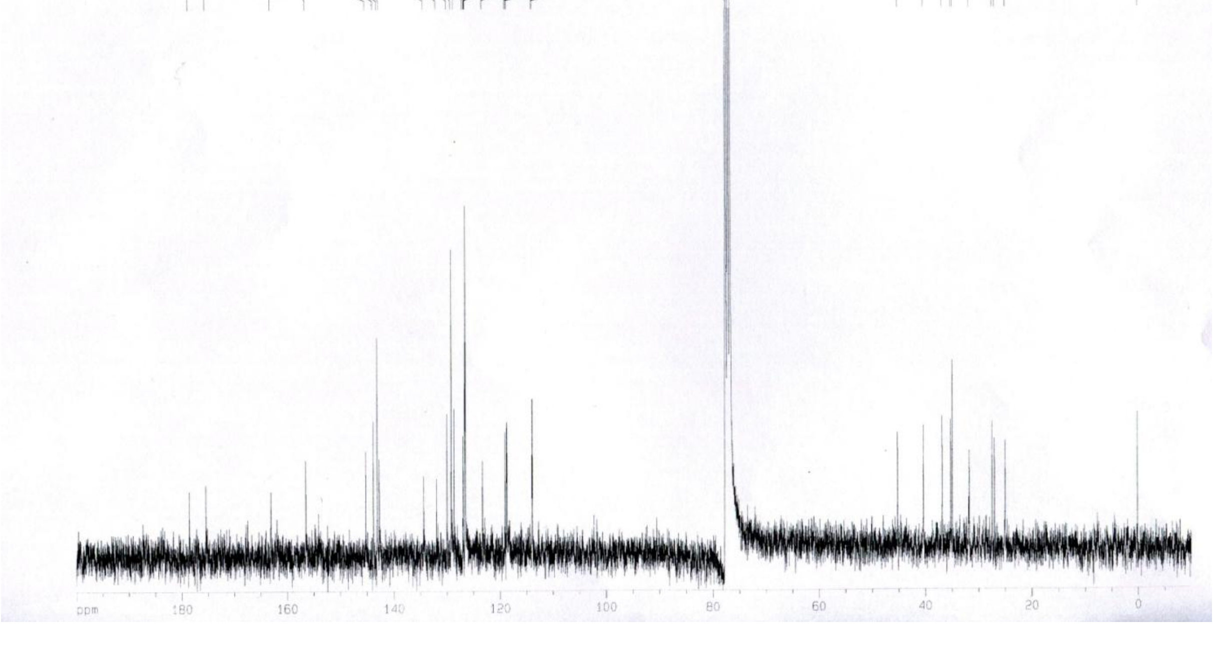


PEAK LIST
8{4,3}.RAW
RT: 0.00 - 20.00
Number of detected peaks: 2

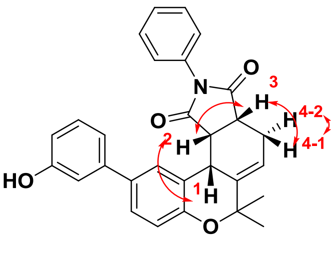
Apex RT	Start RT	End RT	Area	%Area	Height	%Height
10.3	10.09	10.48	5027606	93.66	455867.9	91.69
11.37	11.16	11.56	340172.9	6.34	41290.67	8.31



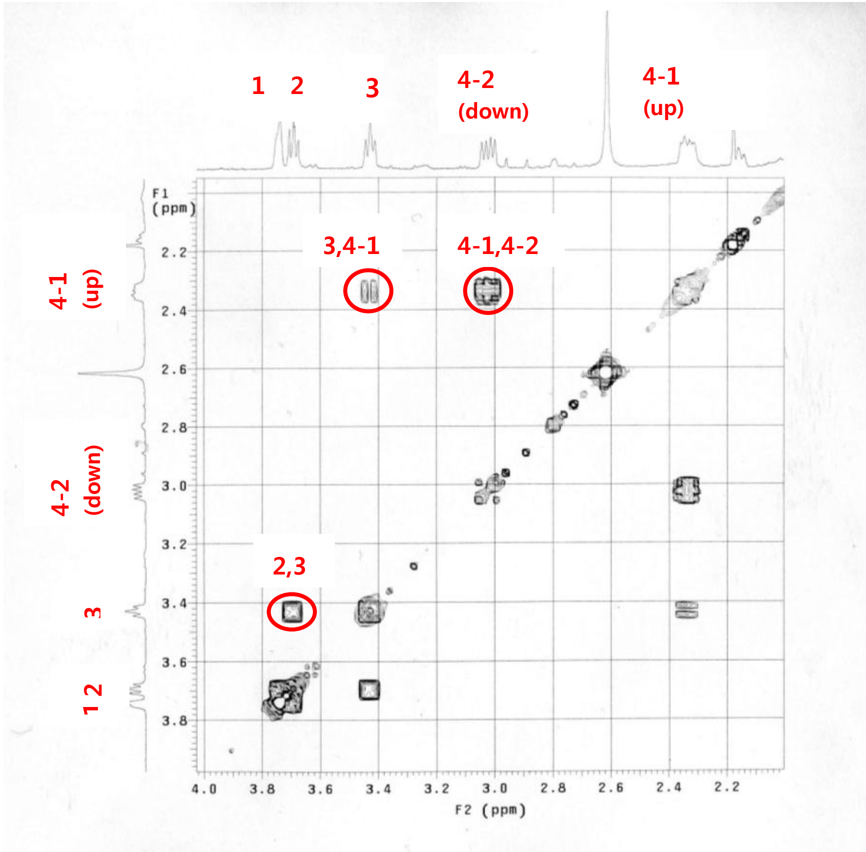




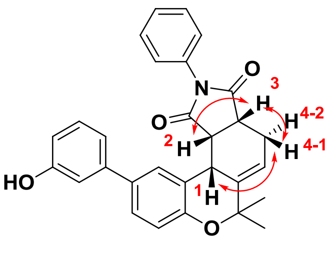
gCOSY correlations



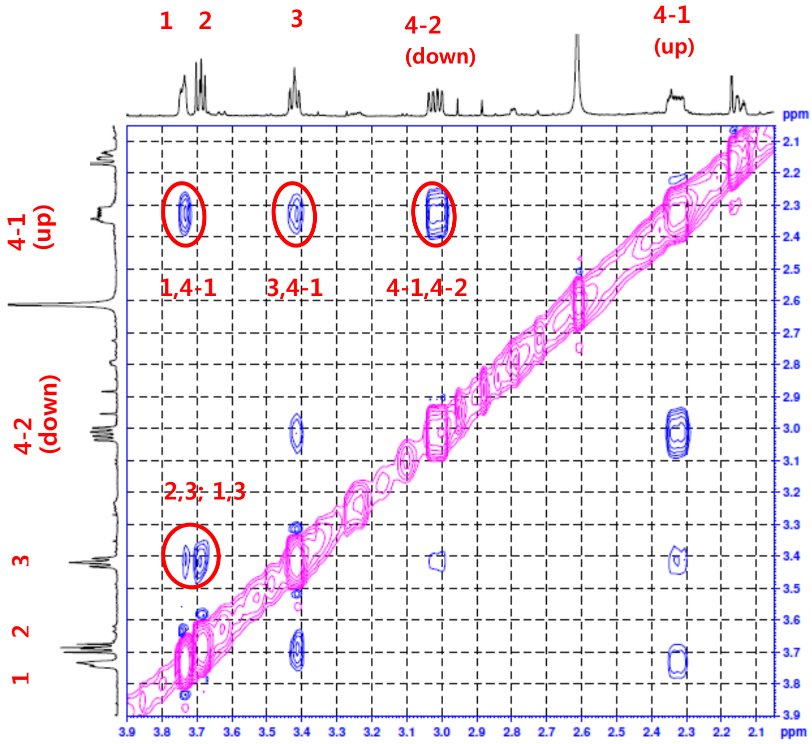
9{*3,1*}

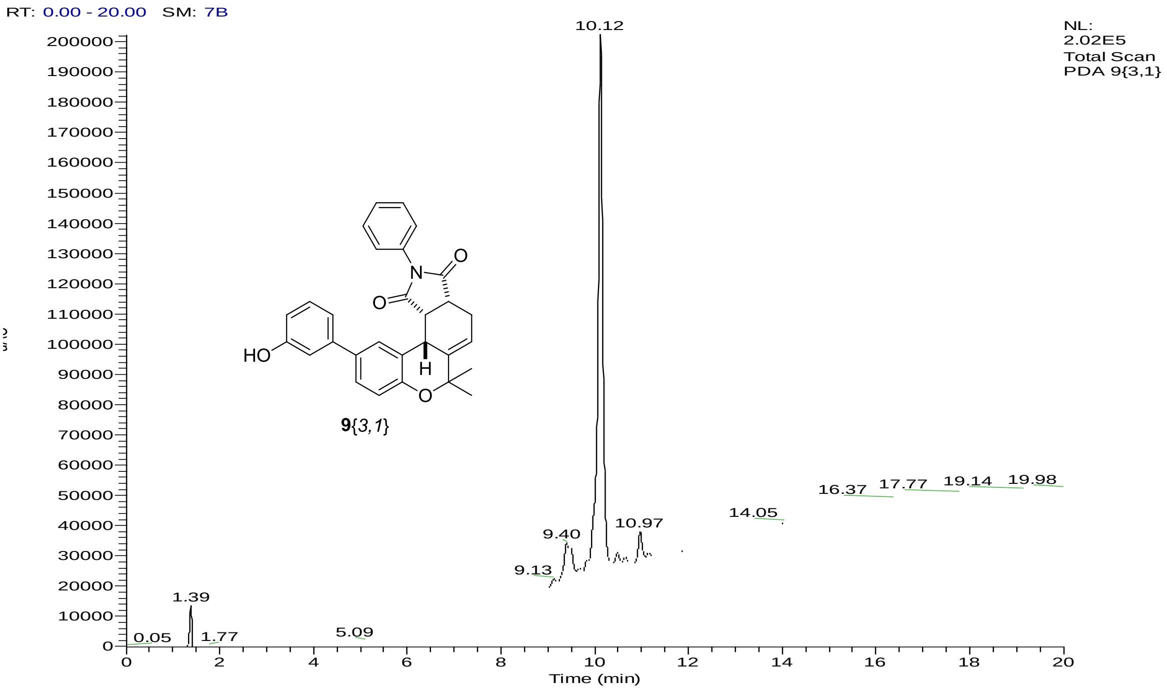


NOE correlations



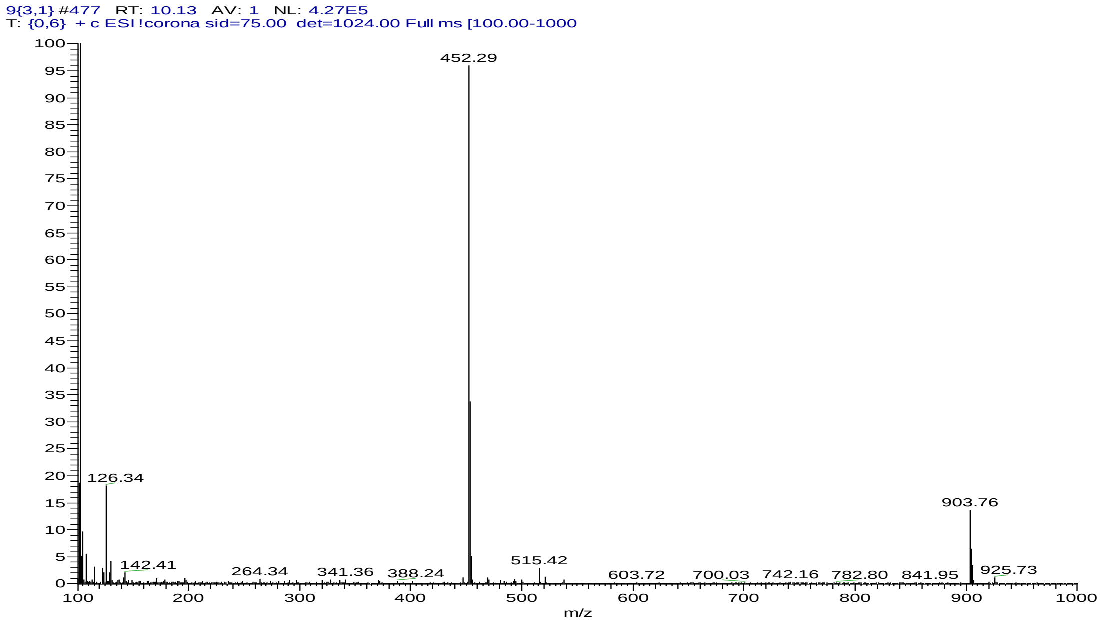
9{*3,1*}

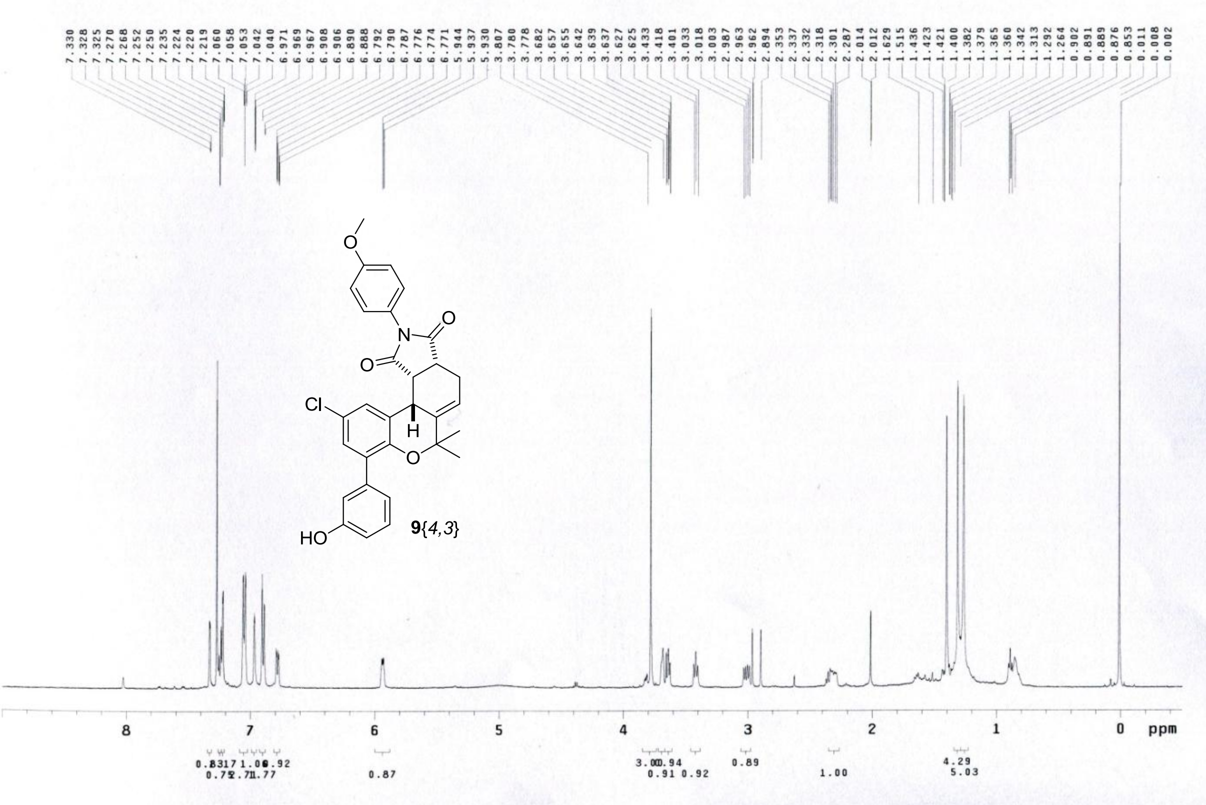


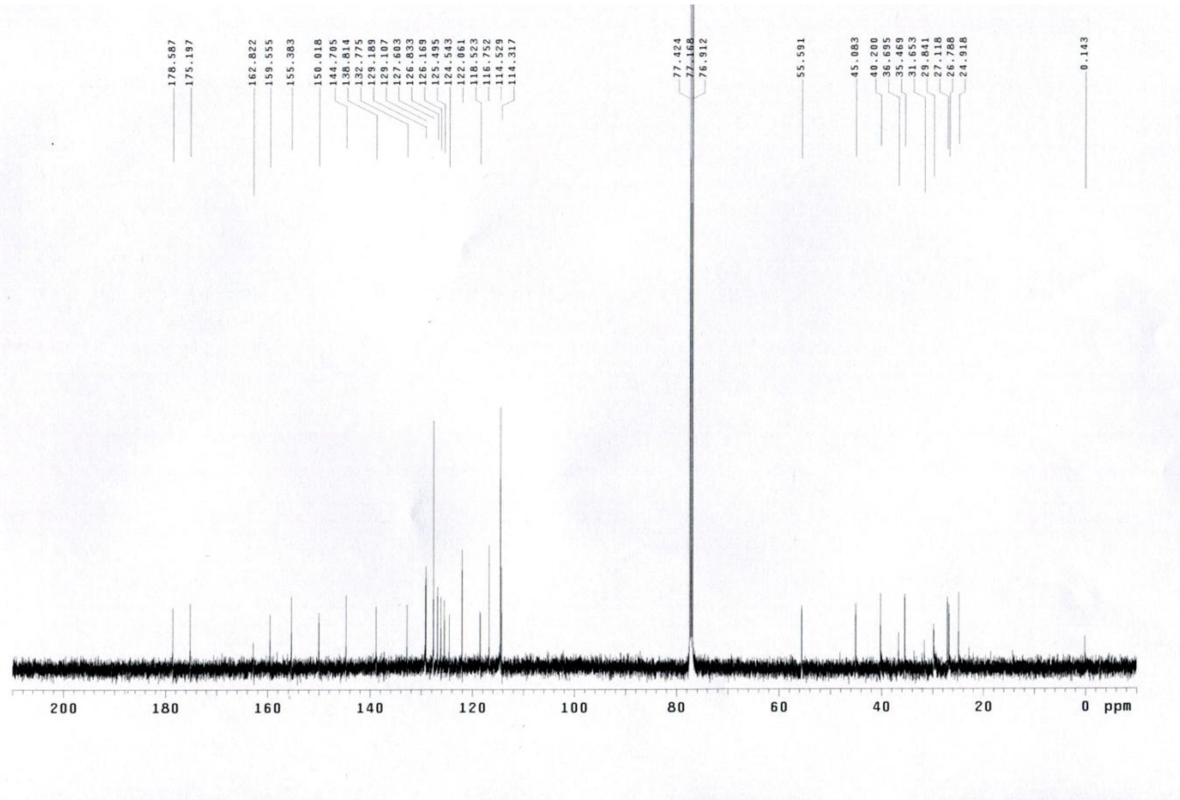


PEAK LIST
9{3,1}.RAW
RT: 0.00 - 20.00
Number of detected peaks: 2

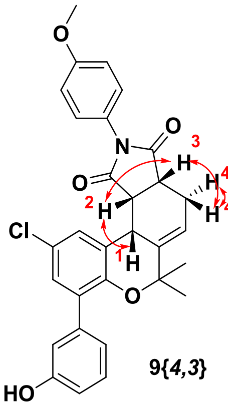
Apex RT	Start RT	End RT	Area	%Area	Height	%Height
9.4	9.2	9.45	121510.9	8.16	14181.61	7.35
10.12	9.87	10.39	1366999	91.84	178731	92.65



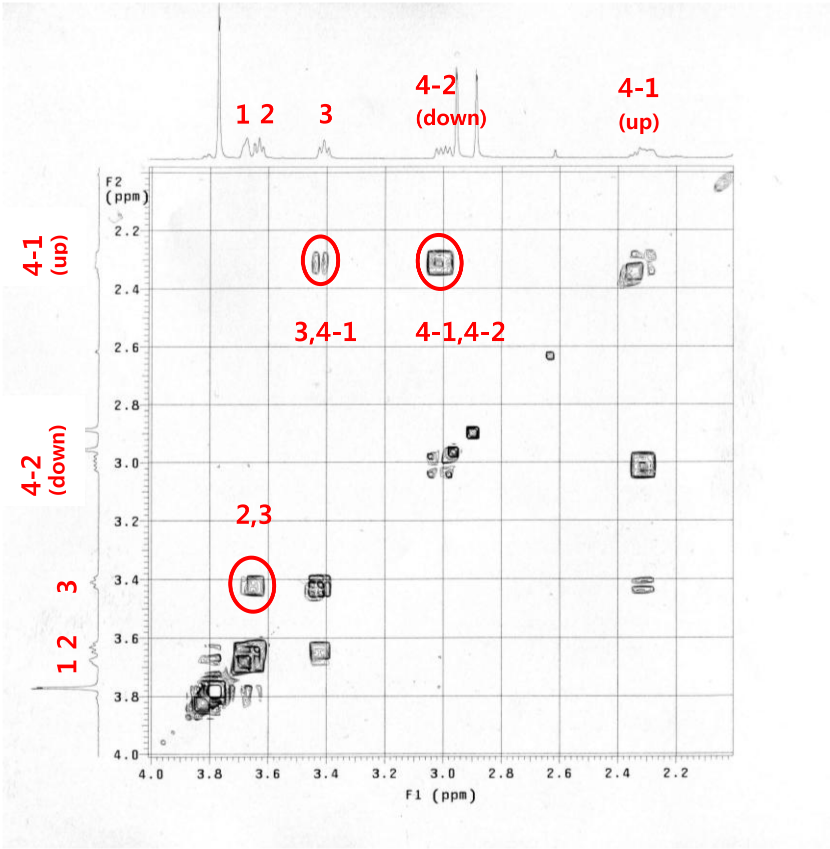




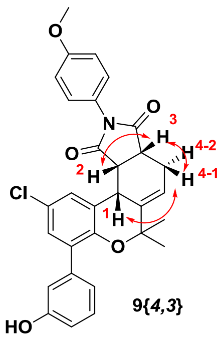
gCOSY correlations



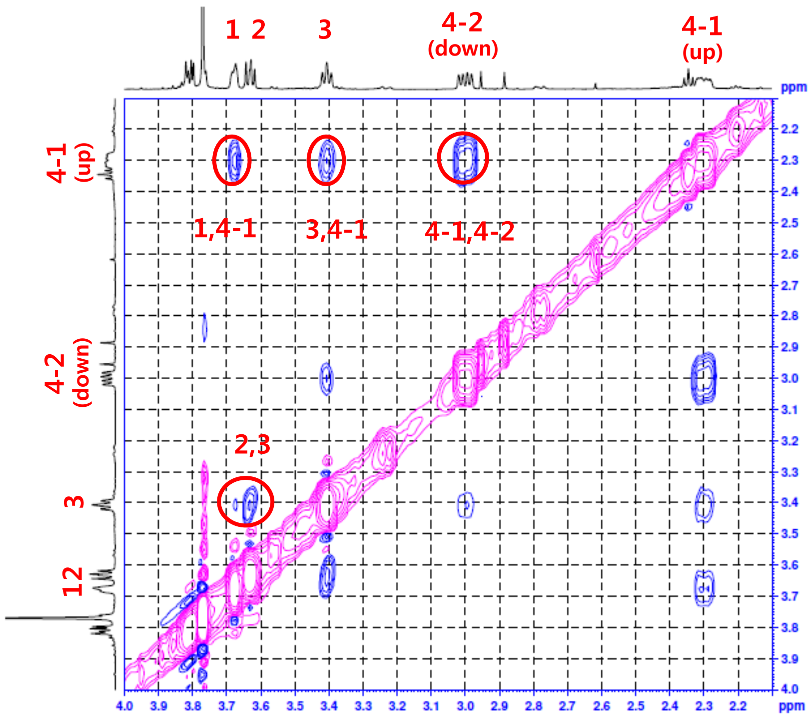
9{4,3}

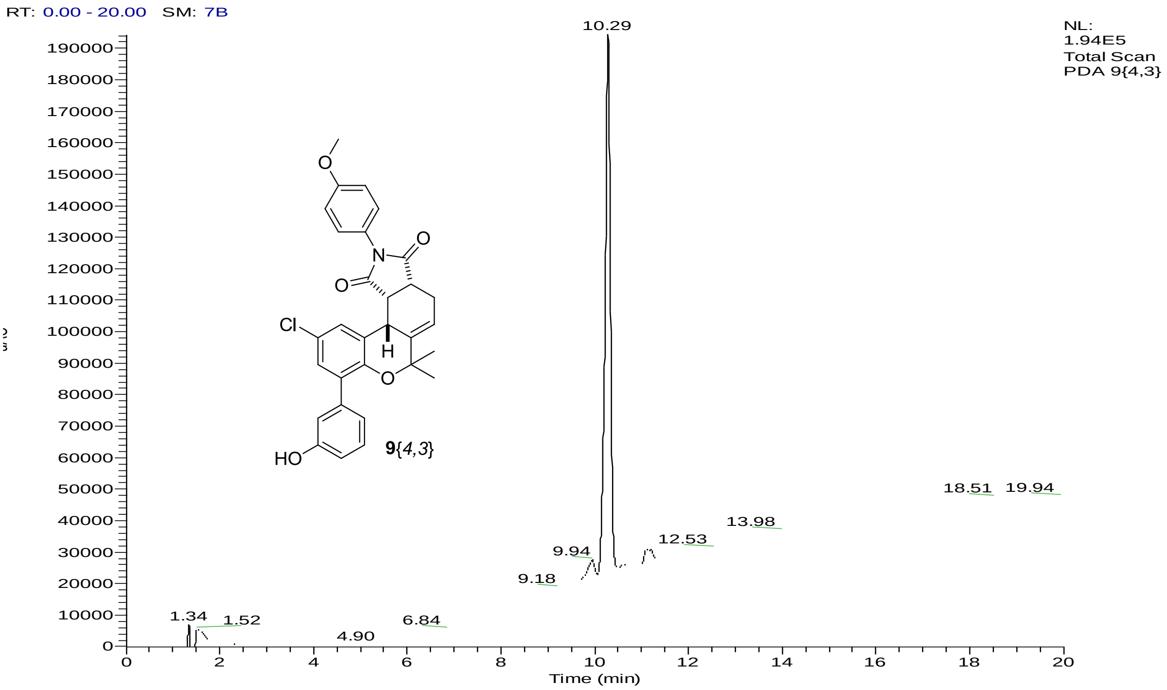


NOE correlations



9{4,3}





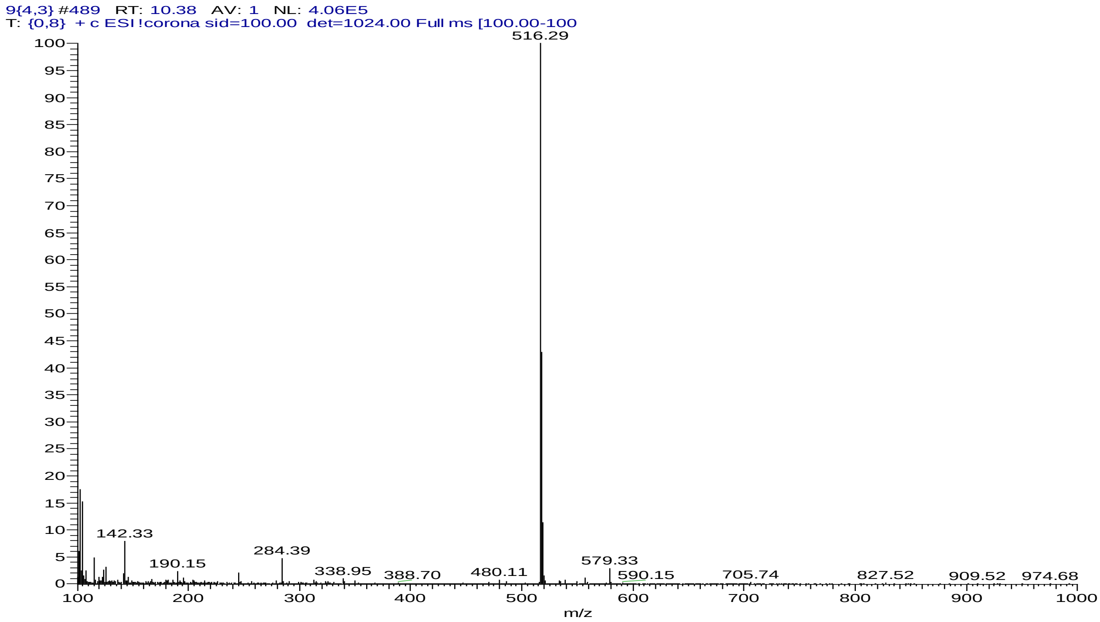
PEAK LIST

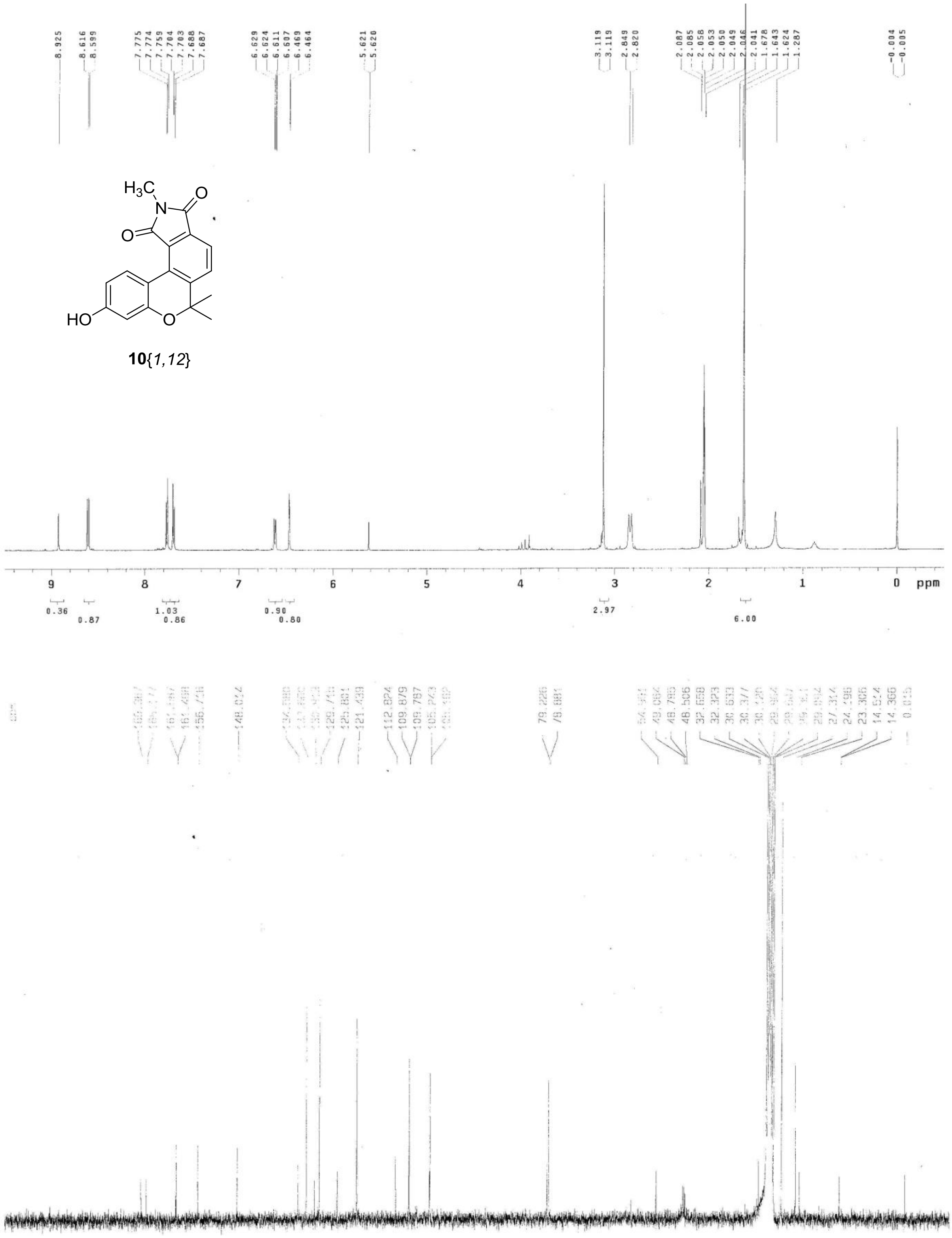
9{4,3}.RAW

RT: 0.00 - 20.00

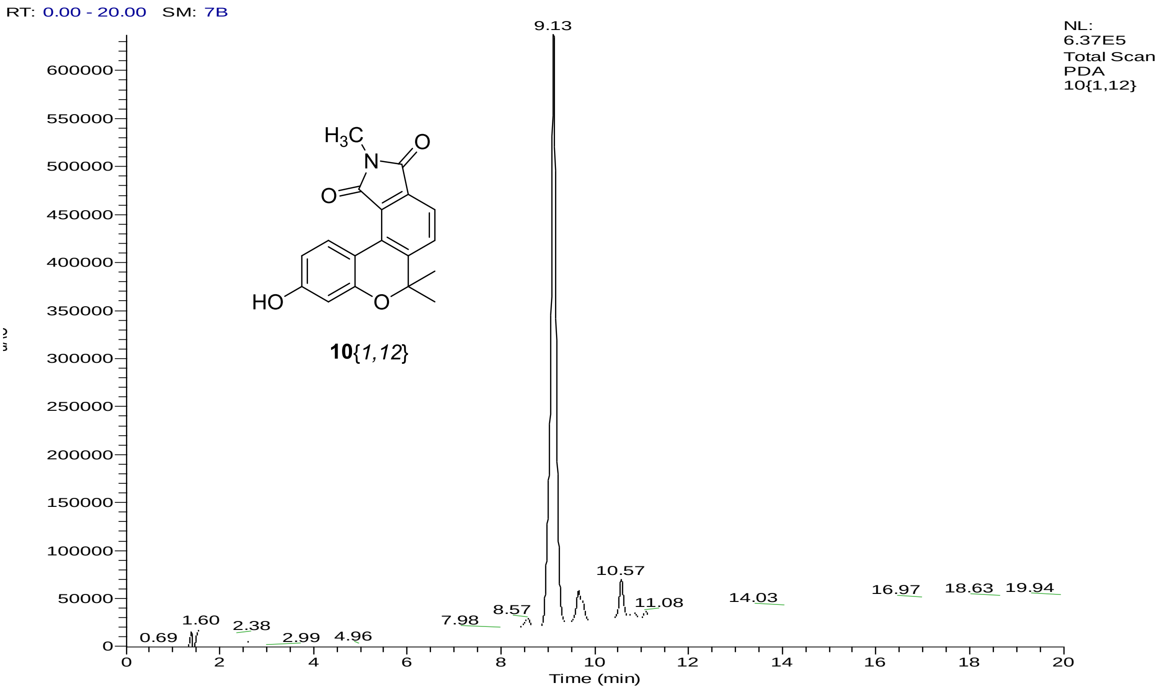
Number of detected peaks: 2

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
9.94	9.83	10.03	42196.05	2.97	5241.609	2.96
10.29	10.05	10.49	1376293	97.03	171621.5	97.04





10{*1,12*}



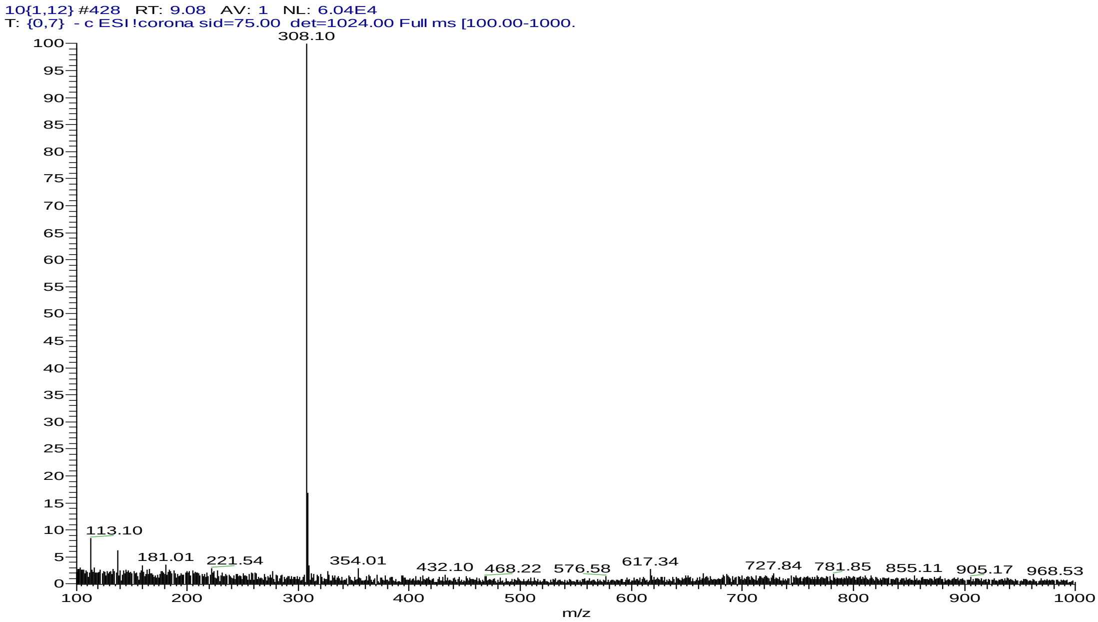
PEAK LIST

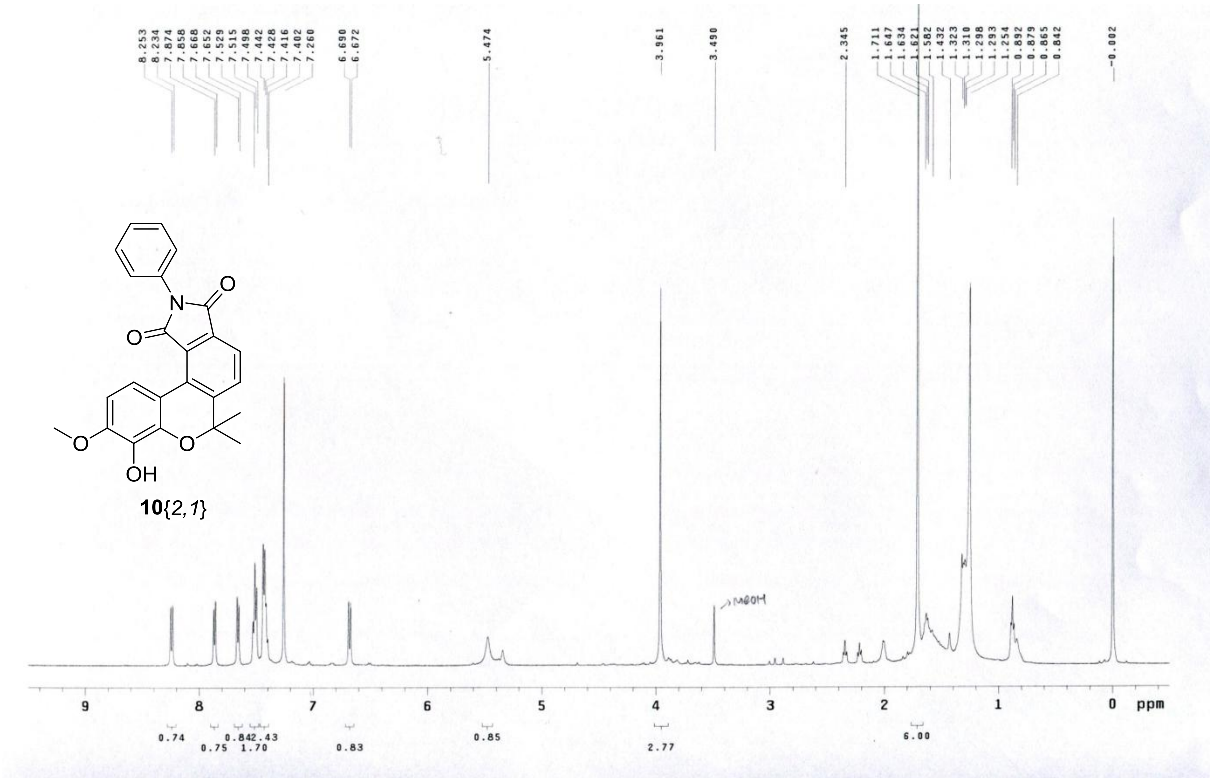
10{1,12}.RAW

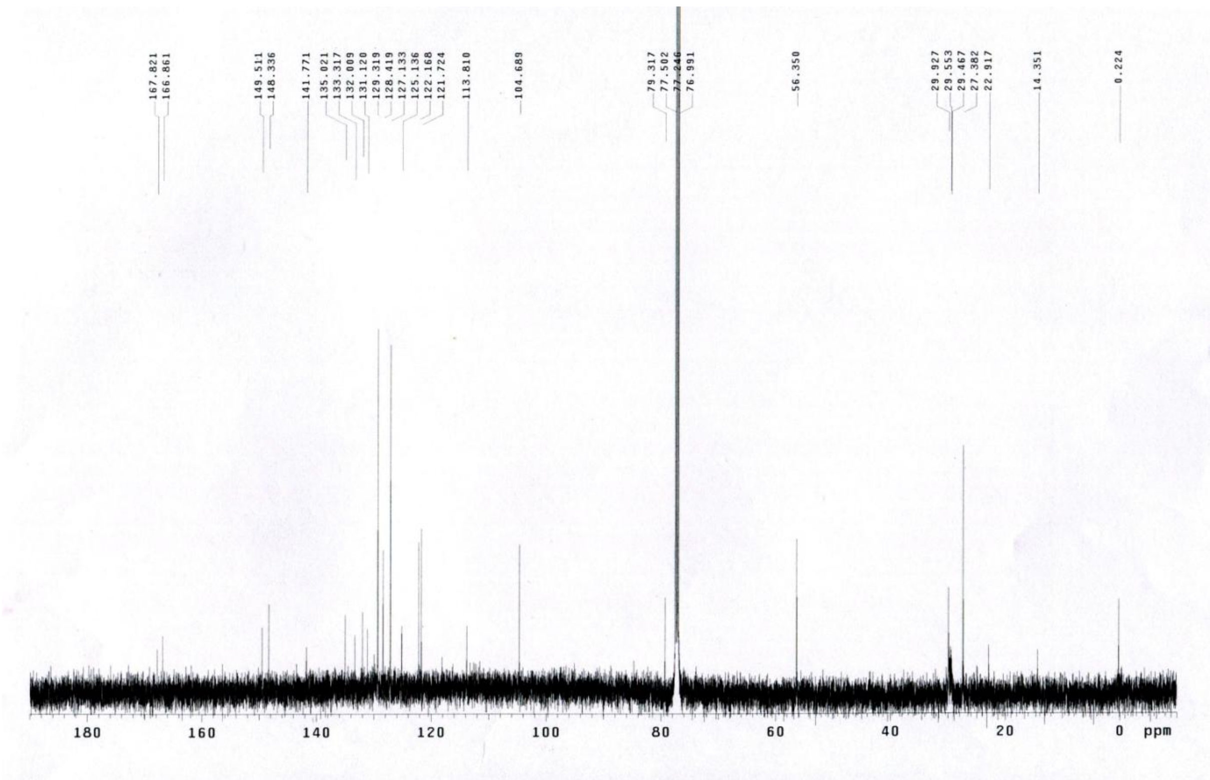
RT: 0.00 - 20.00

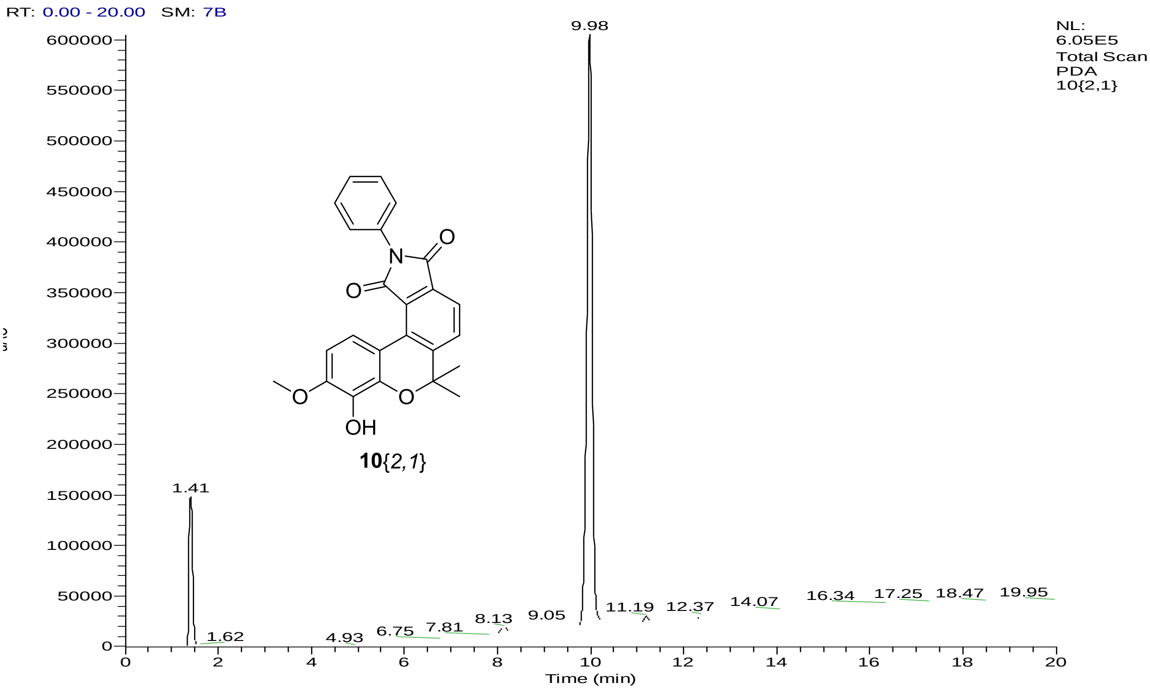
Number of detected peaks: 2

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
9.13	8.84	9.42	4985863	94.9	614509.3	93.72
10.57	10.39	10.71	268049.1	5.1	41211.42	6.28



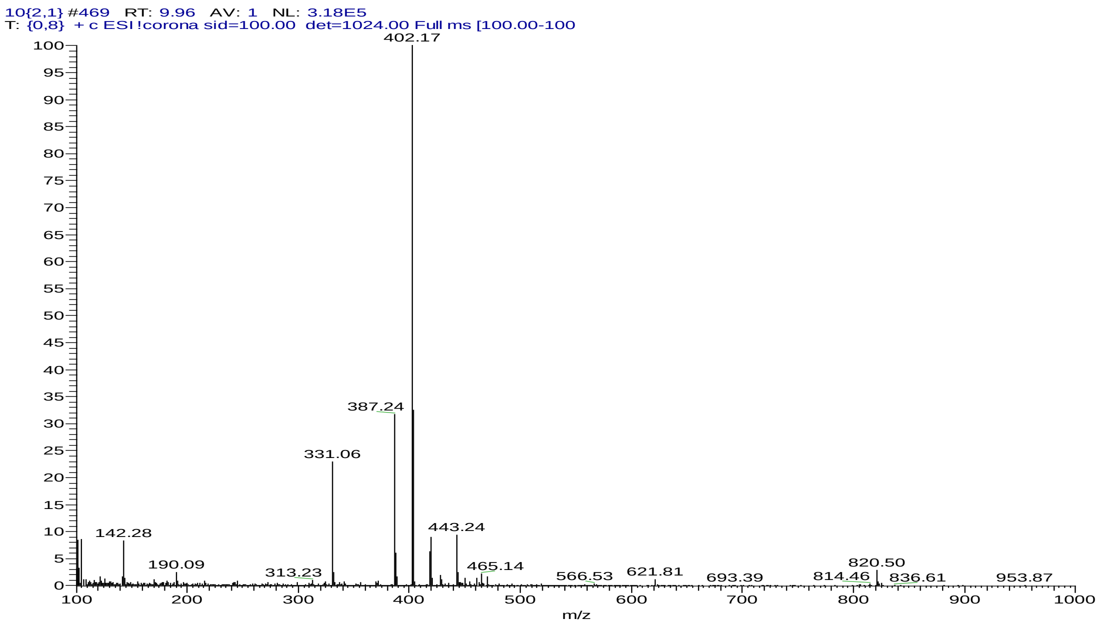

8.253 8.234 7.874 7.858 7.668 7.652 7.529 7.515 7.498 7.442 7.428 7.416 7.402 7.260
6.690 6.672
5.474
3.961
3.490
2.345
1.711 1.647 1.634 1.621 1.582 1.432 1.323 1.310 1.298 1.293 1.254 0.892 0.879 0.865 0.842
-0.002
O
N
O
O
OH
10{2,1}
MeOH
9 8 7 6 5 4 3 2 1 0 ppm
0.74 0.75 0.84 2.43 1.70 0.83 0.85 2.77 6.00

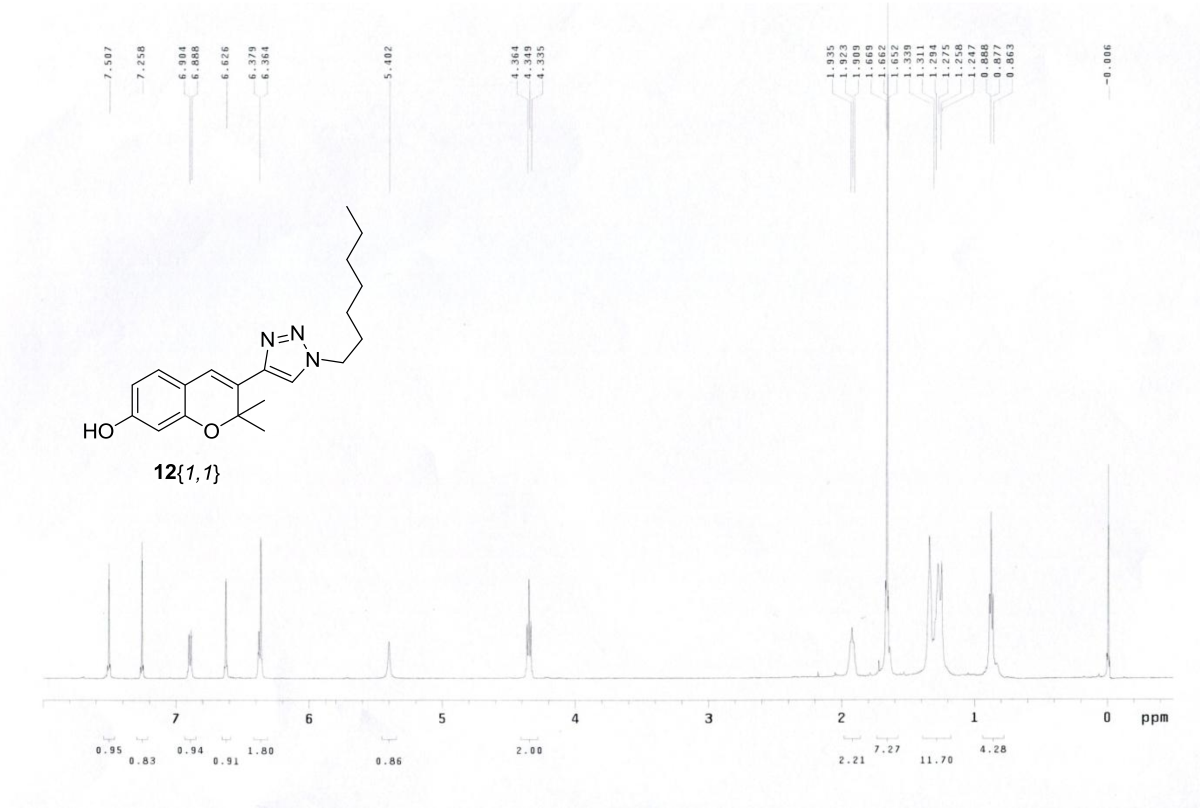

167.821 166.861
149.511 148.336
141.771 135.021 133.317 132.009 131.120 129.319 128.419 127.133 125.136 122.168 121.724
113.810
104.689
79.317 77.502 77.246 76.991
56.350
29.927 29.553 29.467 27.382 22.917
14.351
0.224
180 160 140 120 100 80 60 40 20 0 ppm

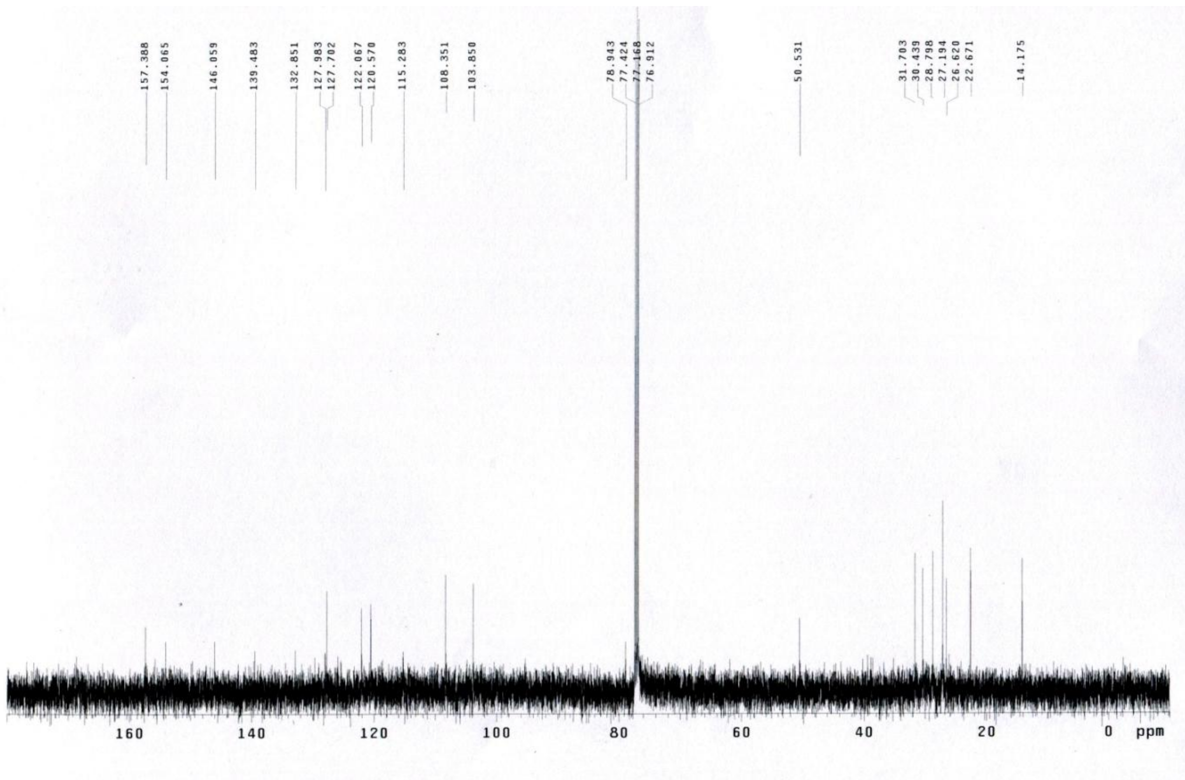


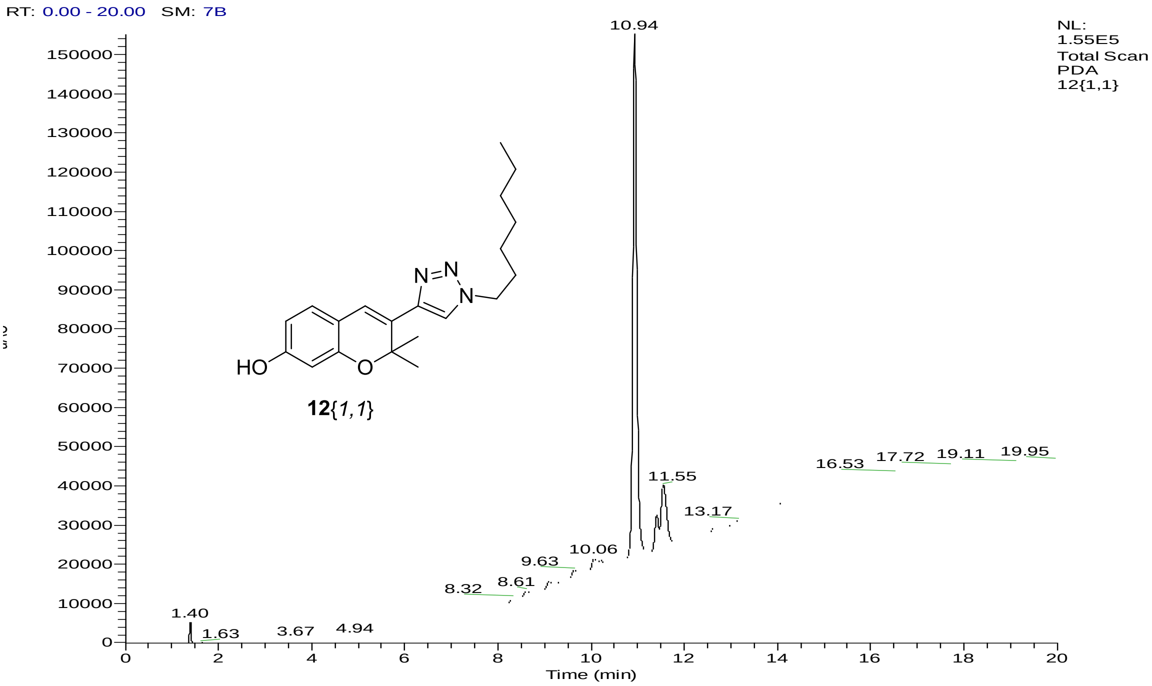
PEAK LIST
10{2,1}.RAW
RT: 0.00 - 20.00
Number of detected peaks: 1

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
9.98	9.7	10.4	4688538	100	584314.4	100



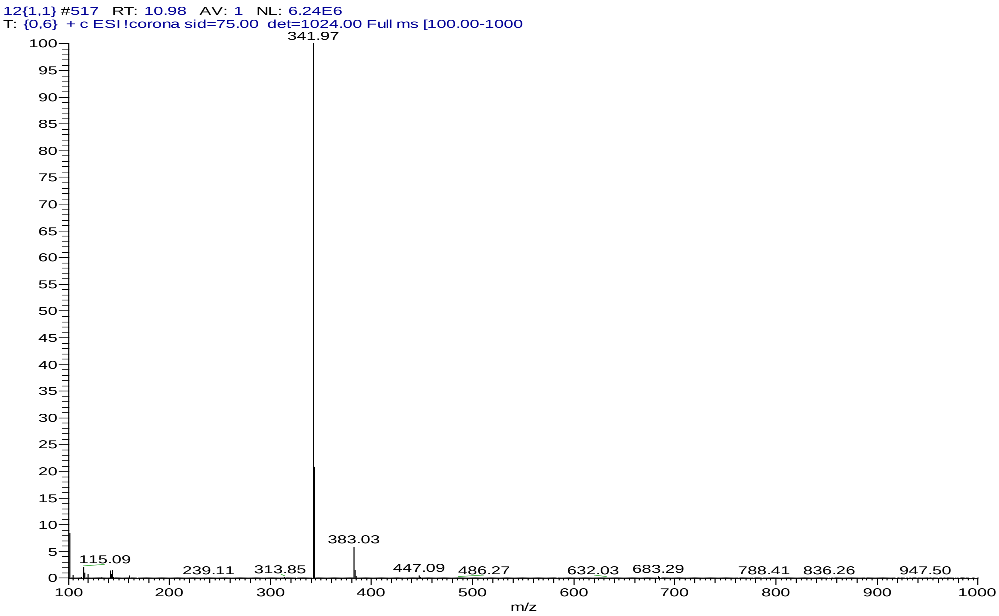

HO
O
N
12{1,1}
ppm

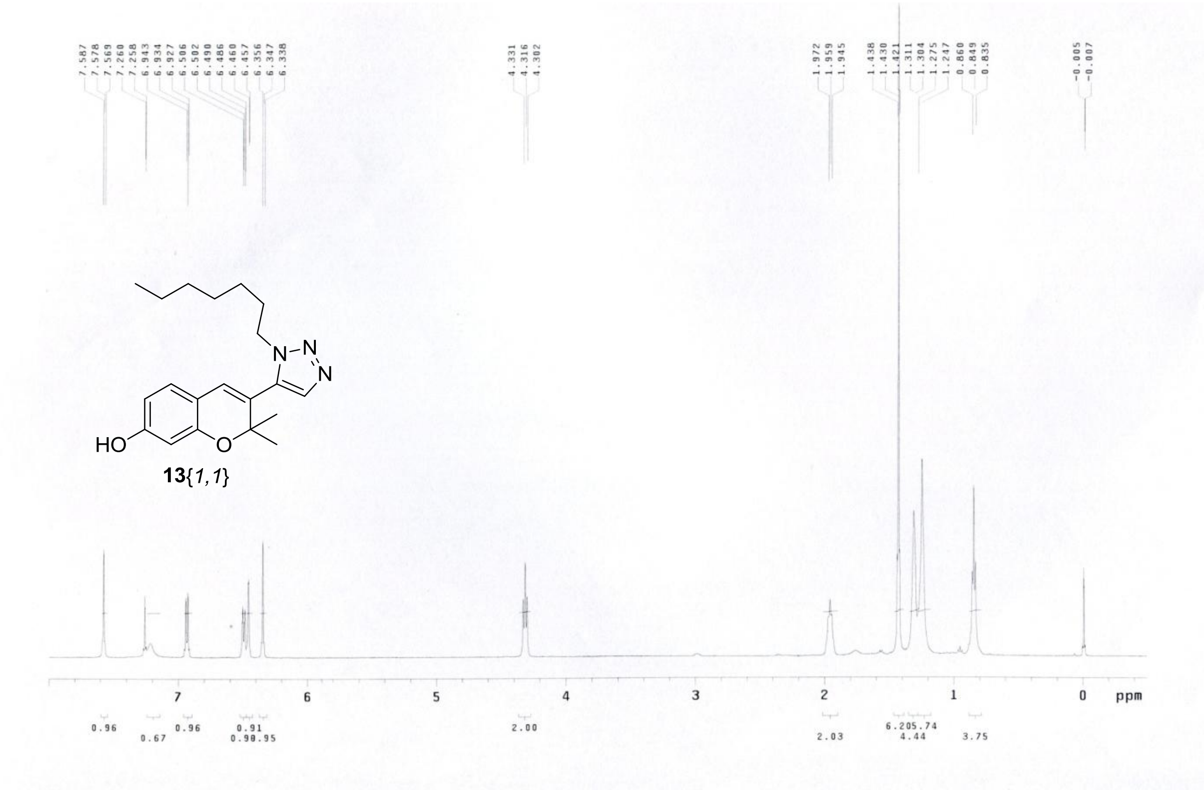

ppm

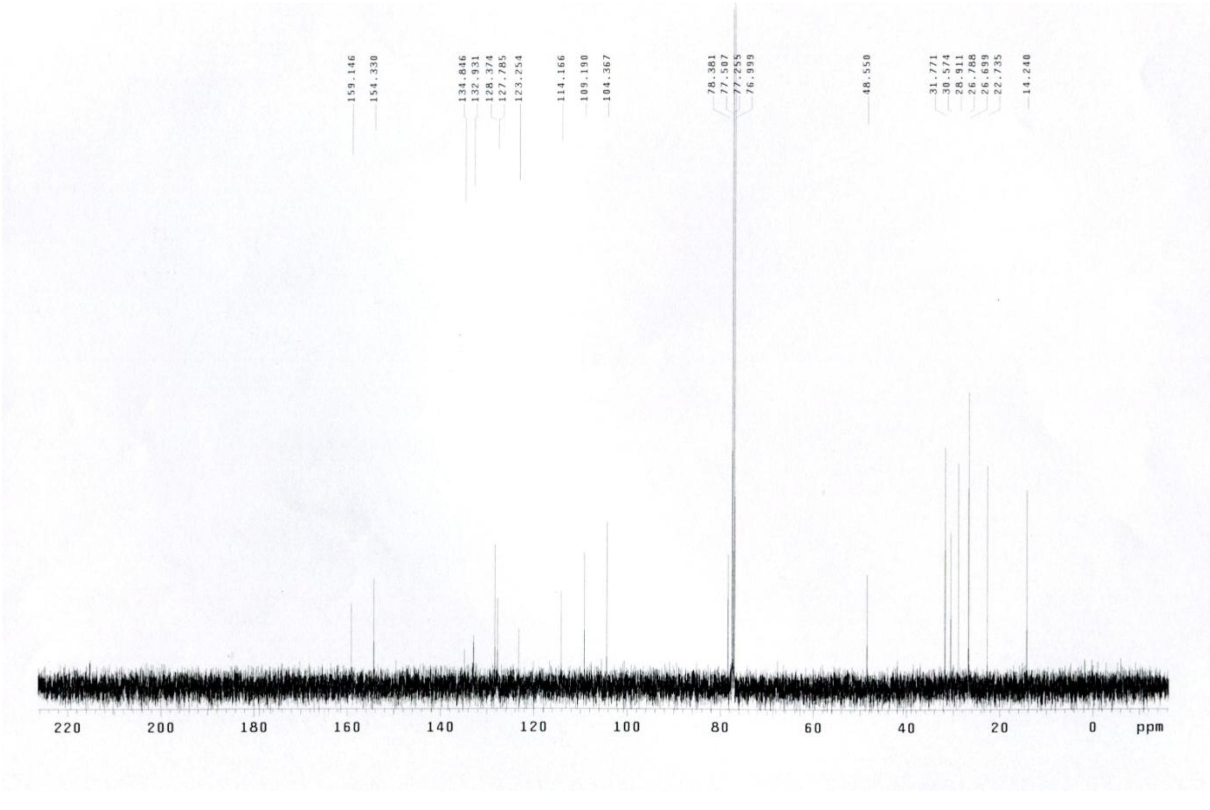


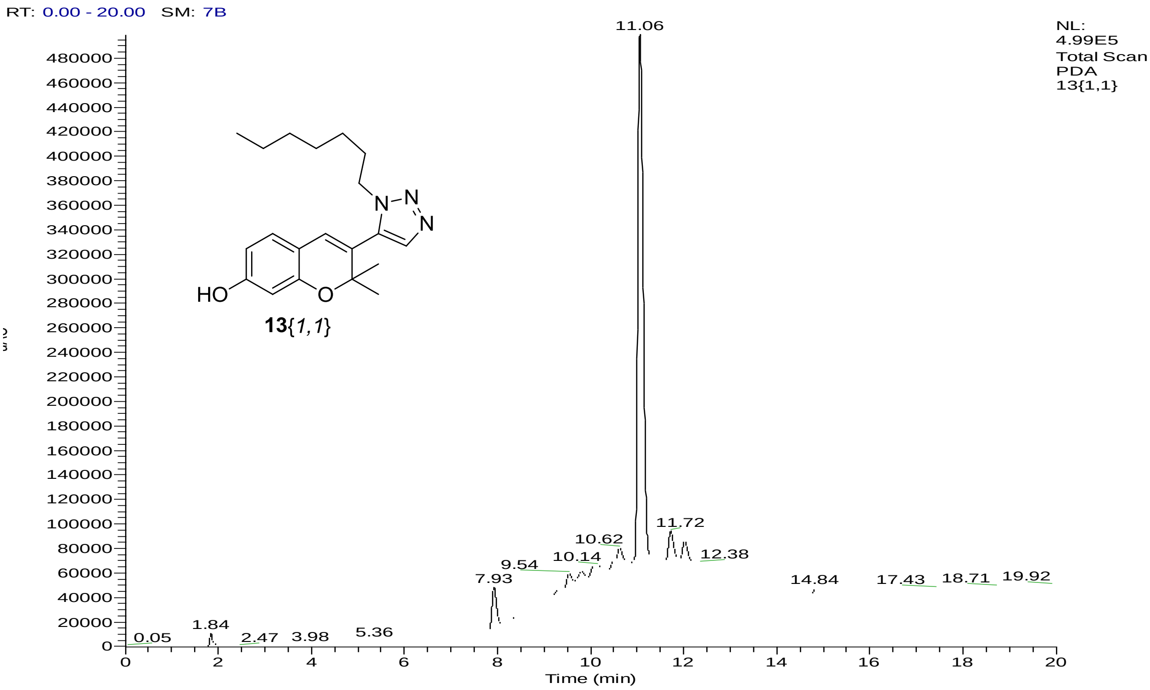
PEAK LIST
12{1,1}.RAW
RT: 0.00 - 20.00
Number of detected peaks: 2

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
10.94	10.76	11.17	798486.3	85.29	133259.3	89.29
11.55	11.47	11.75	137695.2	14.71	15975.99	10.71




HO
13{1,1}
ppm


ppm



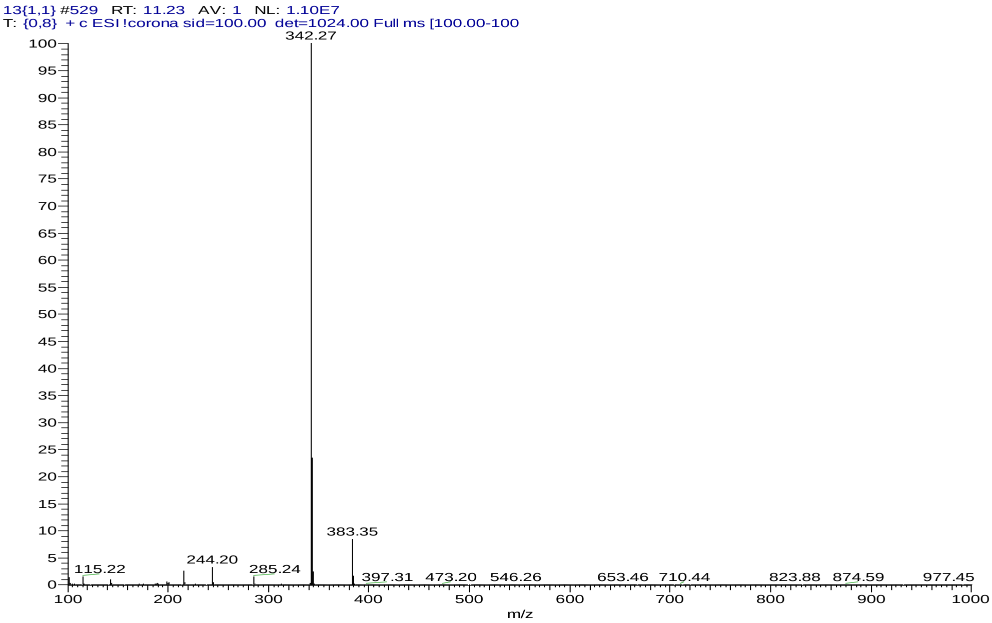
PEAK LIST

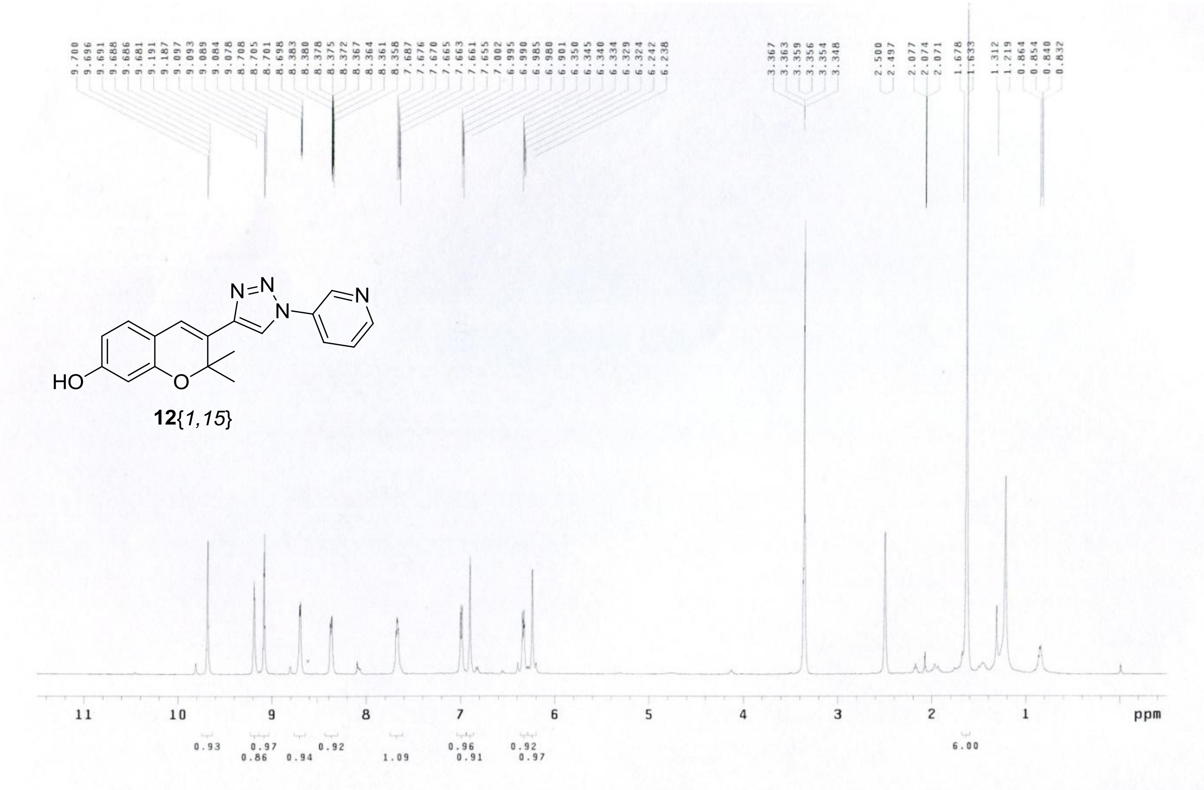
13{1,1}.RAW

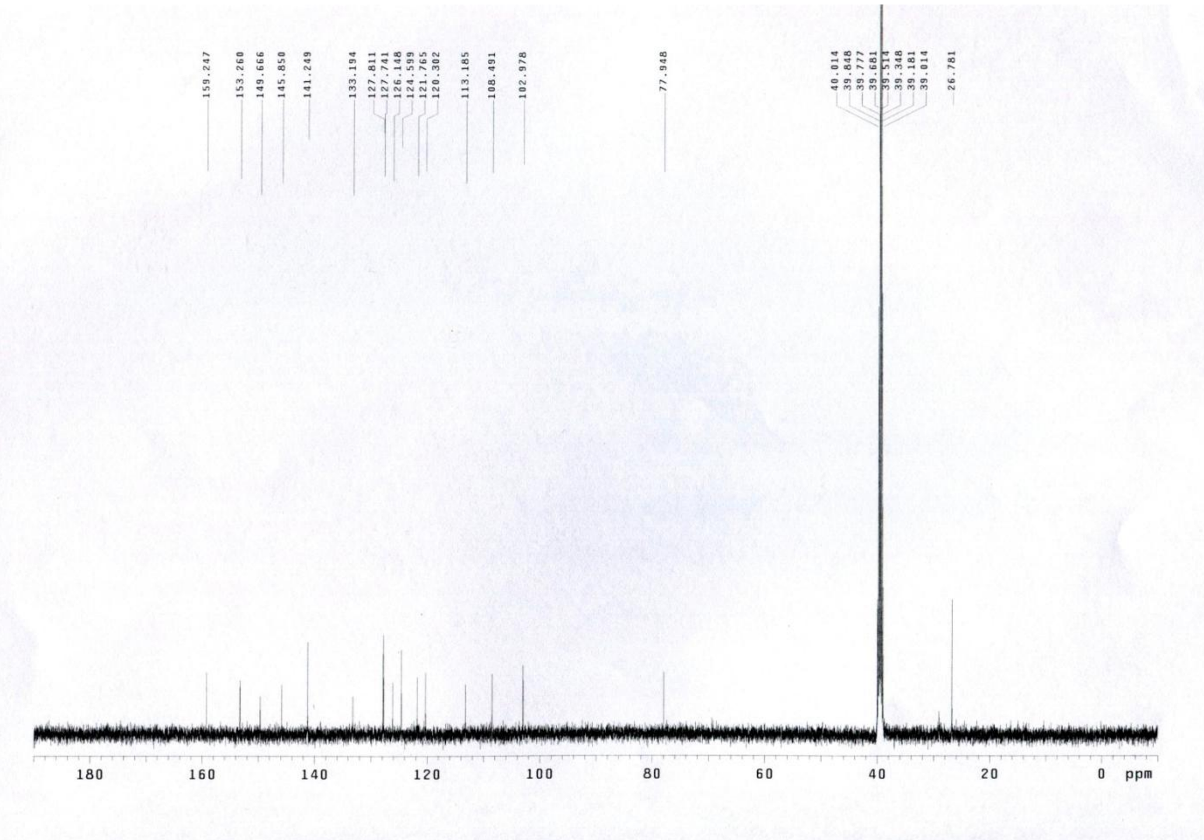
RT: 0.00 - 20.00

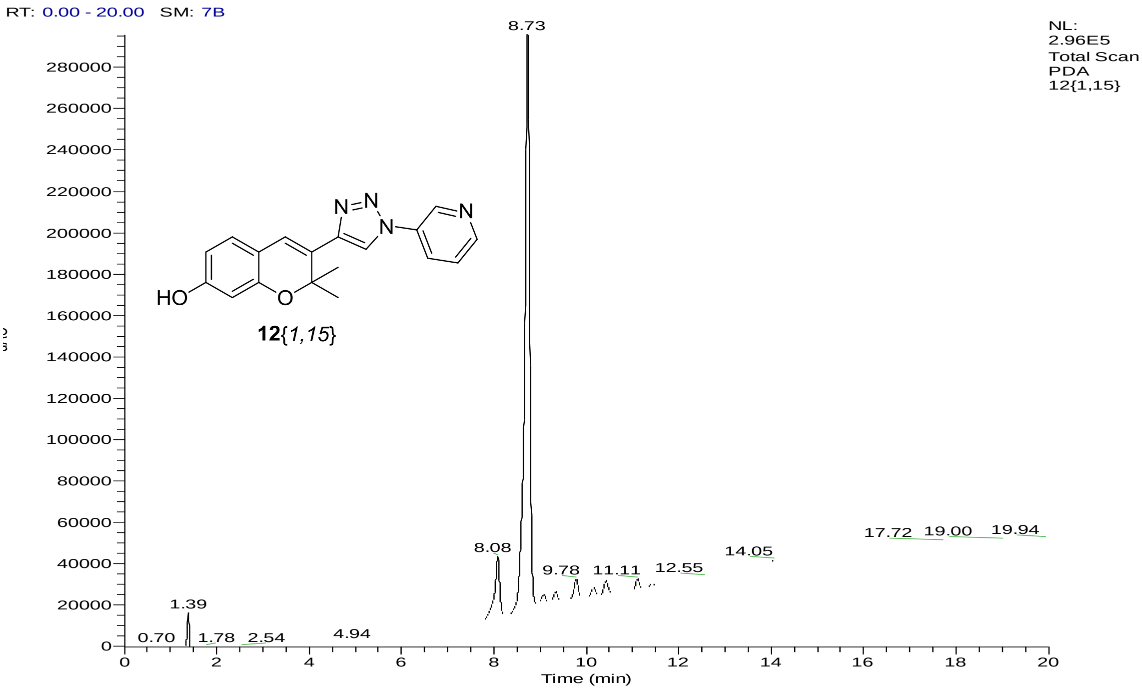
Number of detected peaks: 2

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
7.93	7.84	8.09	200856.8	5.42	32049.83	6.92
11.06	10.83	11.3	3503898	94.58	431053.6	93.08




HO
O
N
N
N
N
12{1,15}
ppm


ppm



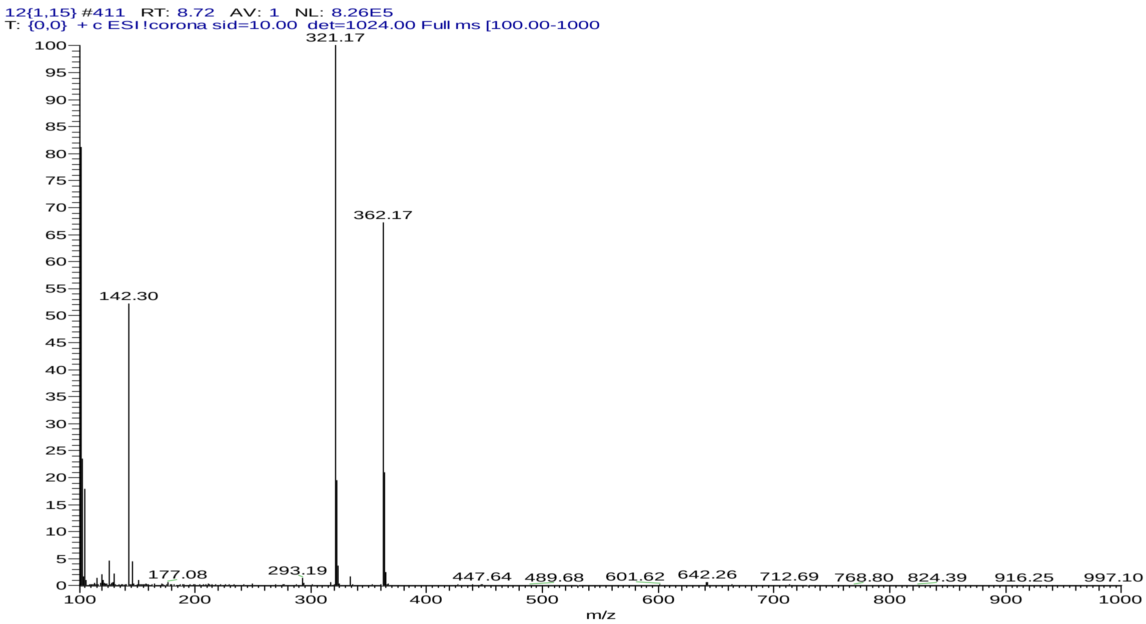
PEAK LIST

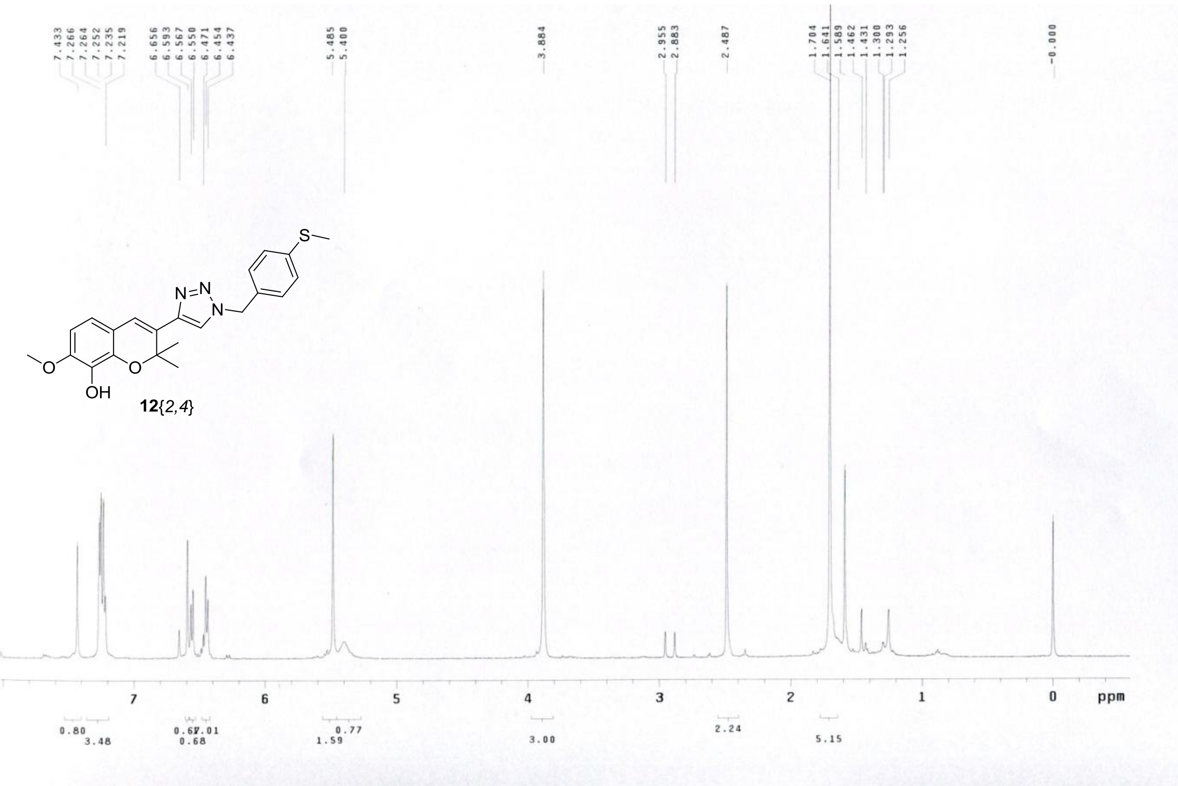
12{1,15}.RAW

RT: 0.00 - 20.00

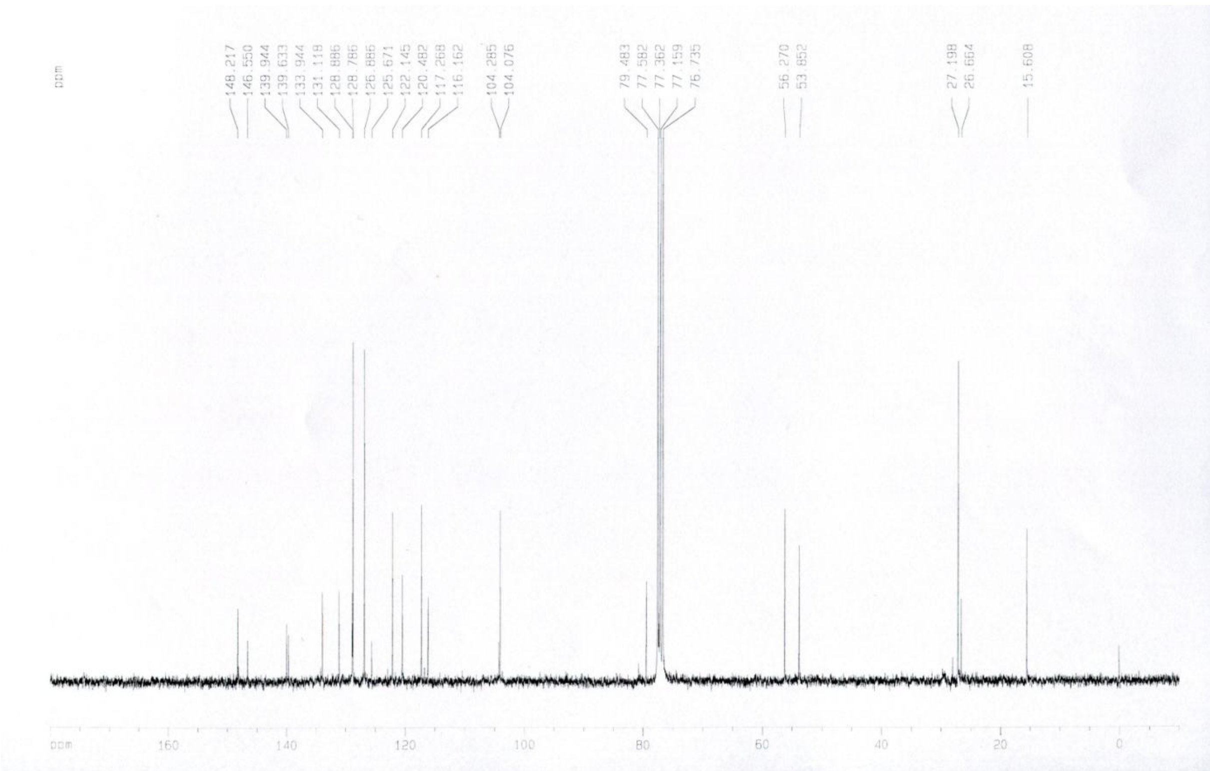
Number of detected peaks: 2

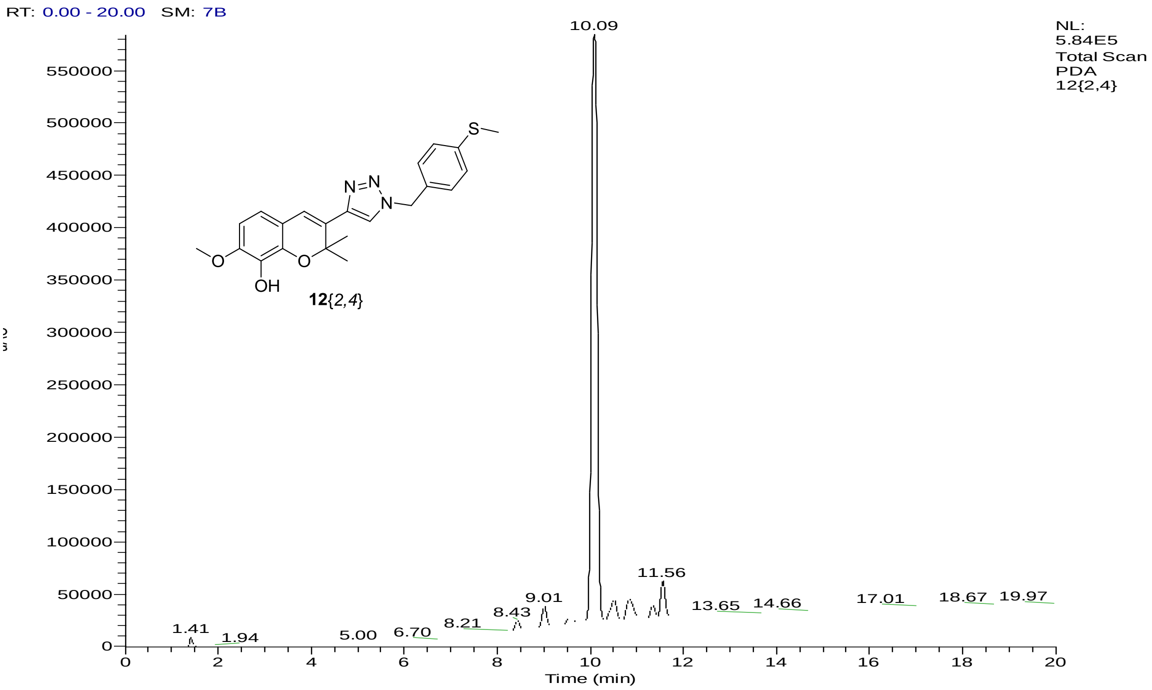
Apex RT	Start RT	End RT	Area	%Area	Height	%Height
8.08	7.8	8.22	232260.4	9.9	29514.63	9.58
8.73	8.35	8.92	2112863	90.1	278433.2	90.42





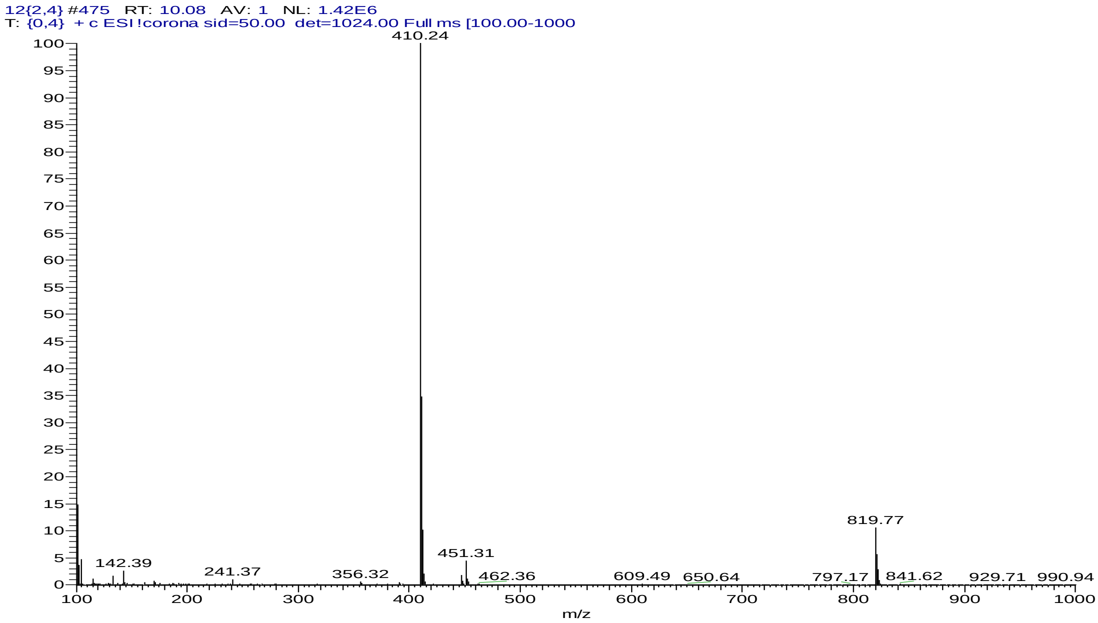
12{*2,4*}

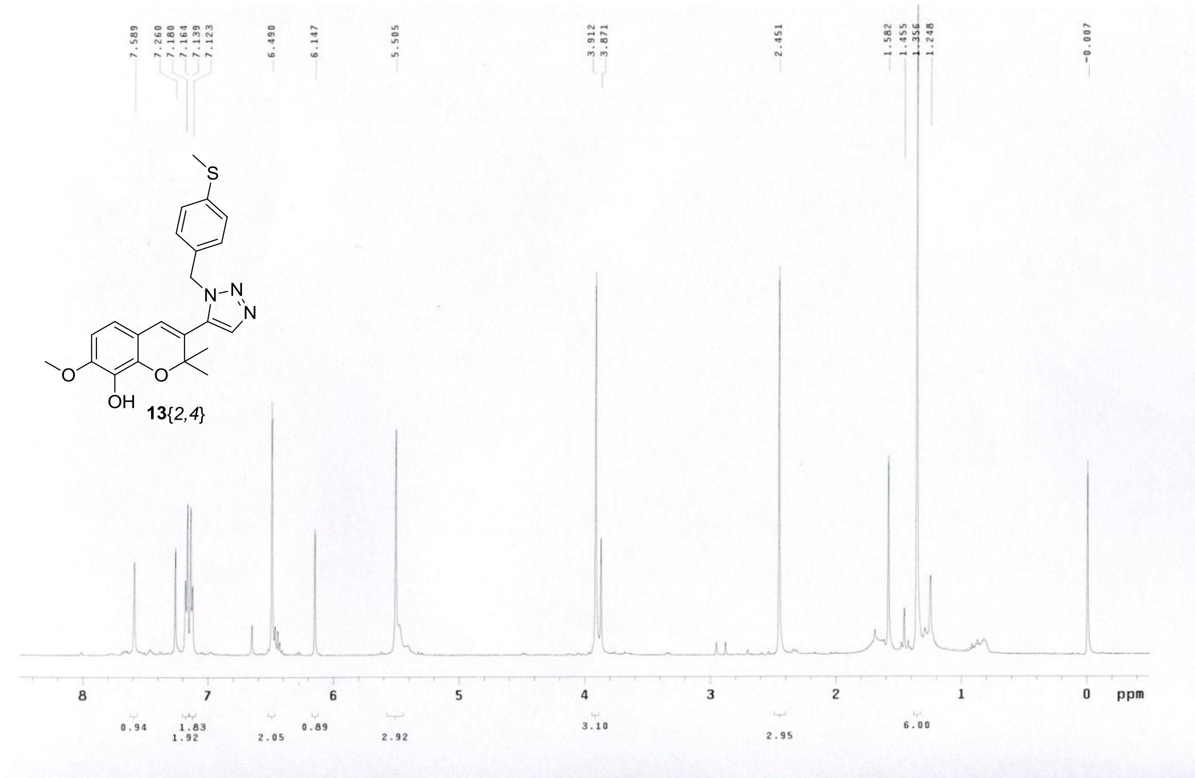


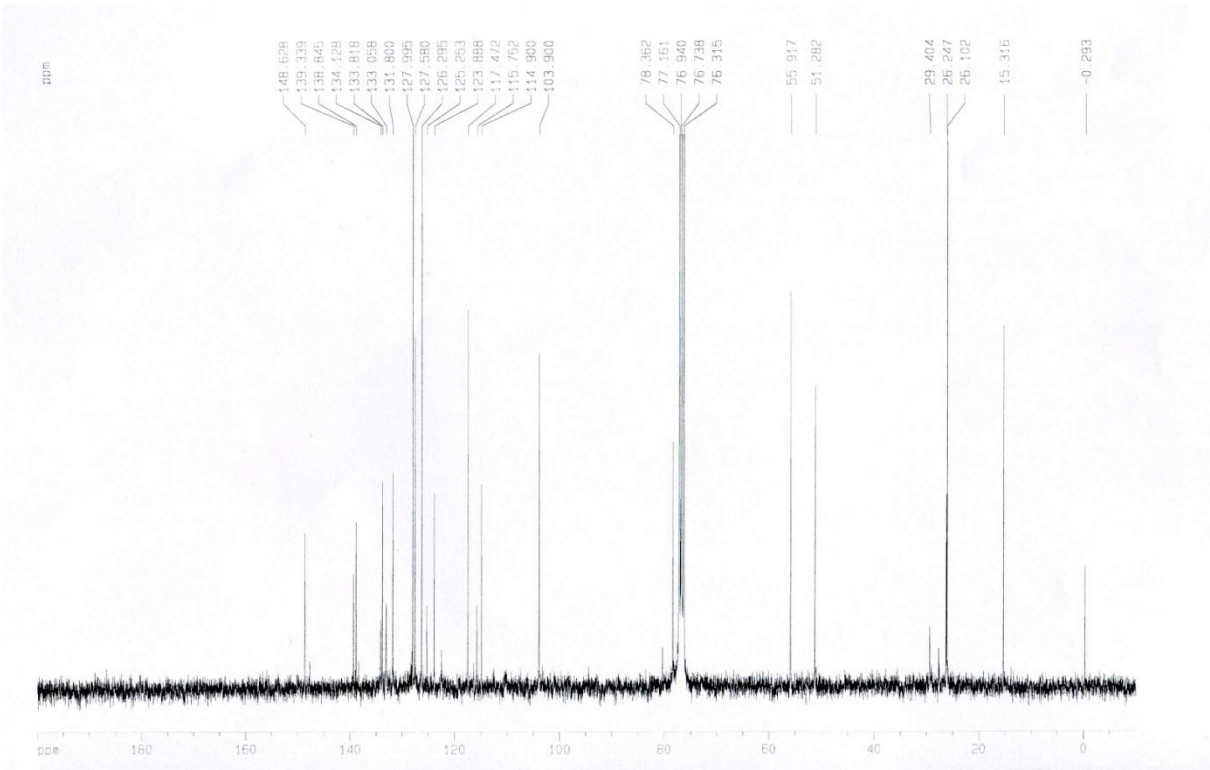


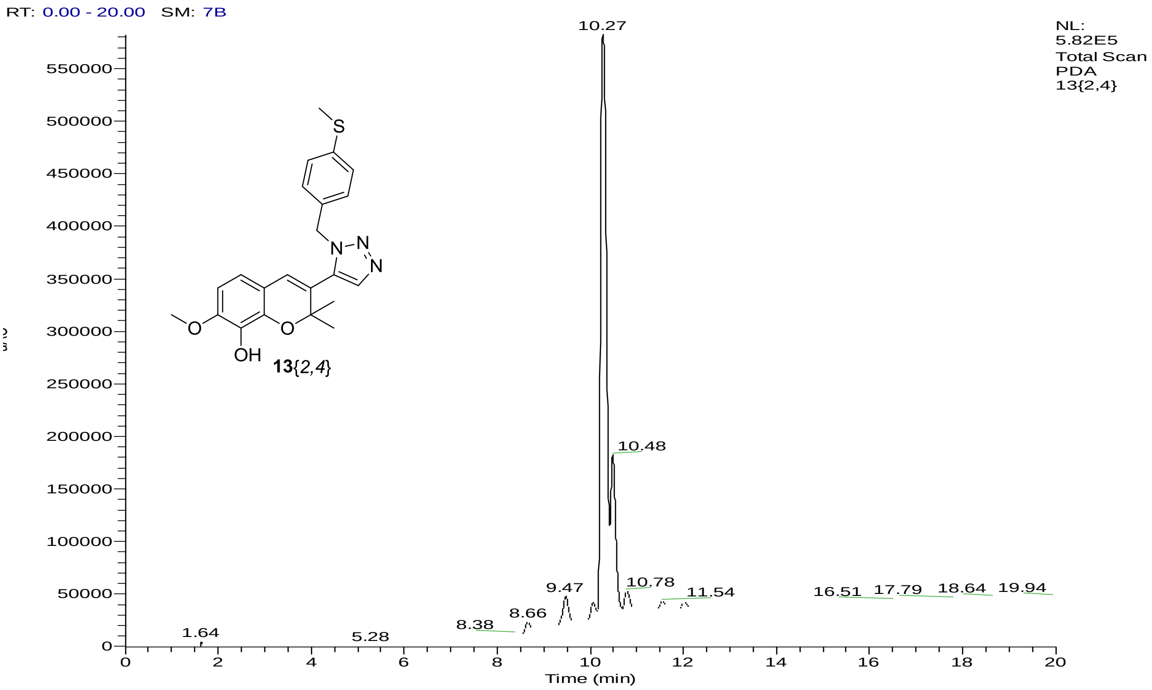
PEAK LIST
12{2,4}.RAW
RT: 0.00 - 20.00
Number of detected peaks: 2

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
10.09	9.88	10.32	4930991	95.42	559318.5	94.17
11.56	11.45	11.71	236743.4	4.58	34595.62	5.83



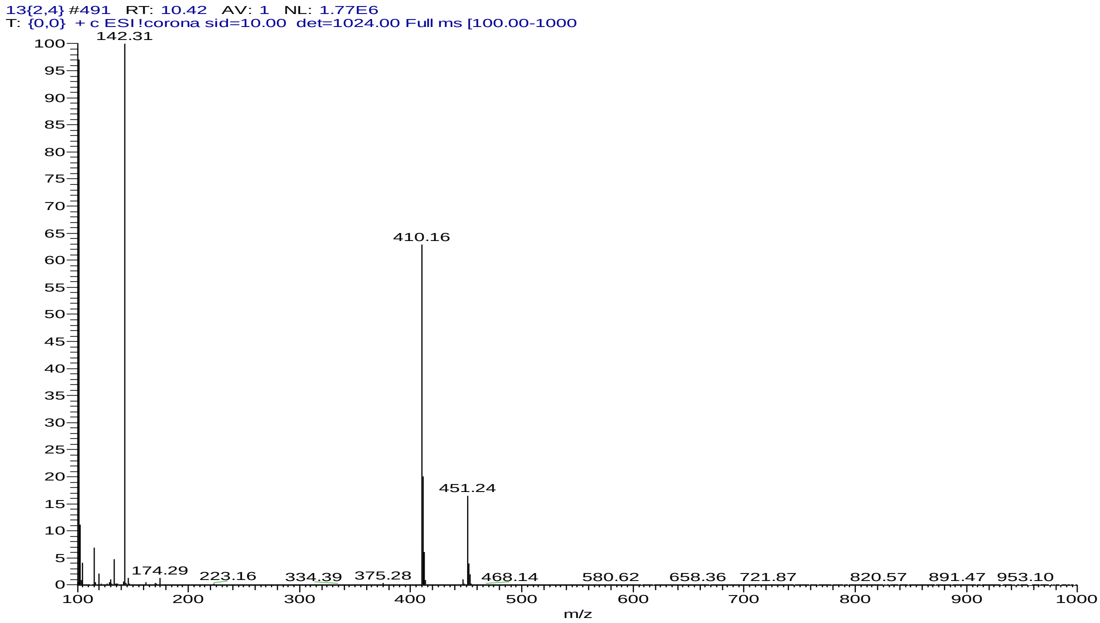

7.589
7.260
7.180
7.164
7.139
7.123
6.490
6.147
5.505
3.912
3.871
2.451
1.582
1.455
1.356
1.248
-0.007
S
N
N
N
O
OH
13{2,4}
ppm
0.94
1.83
1.92
2.05
0.89
2.92
3.10
2.95
6.00

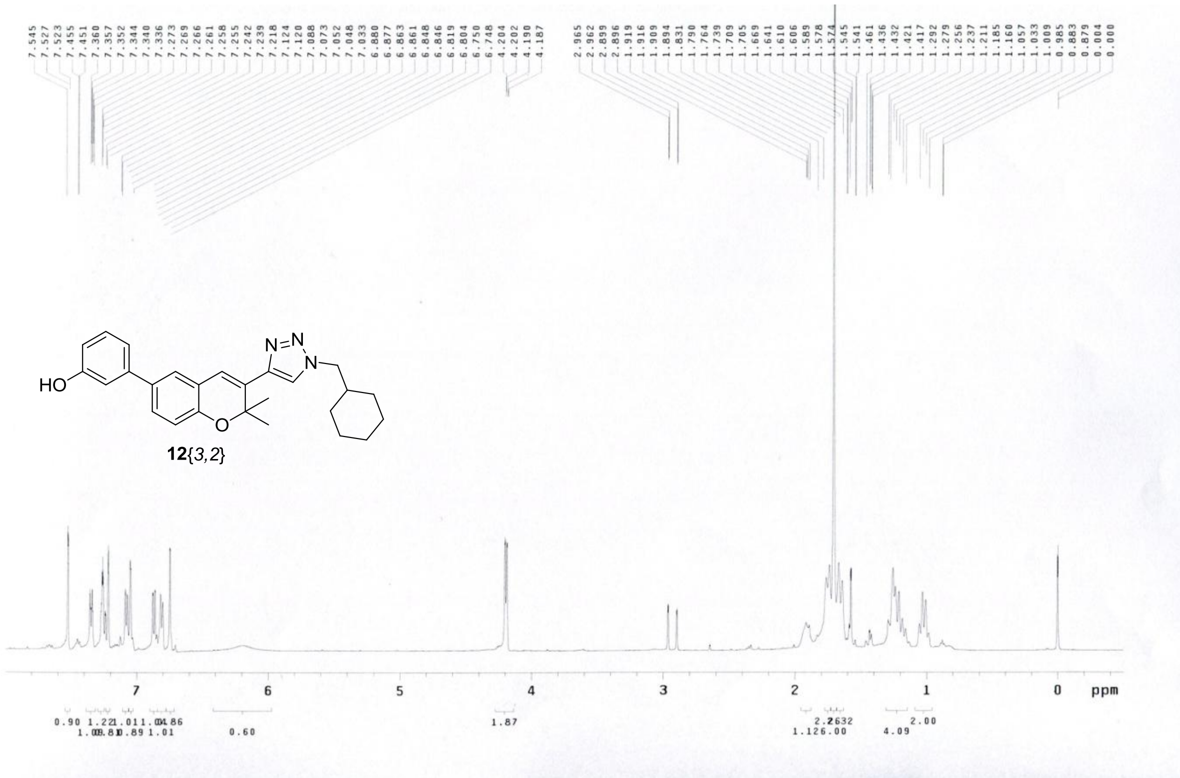

148.628
139.339
138.845
134.128
133.818
133.058
131.800
127.995
127.580
126.295
125.253
123.888
117.472
115.752
114.900
103.900
78.362
77.161
76.940
76.738
76.315
55.917
51.282
29.404
26.247
26.102
15.316
-0.293
ppm

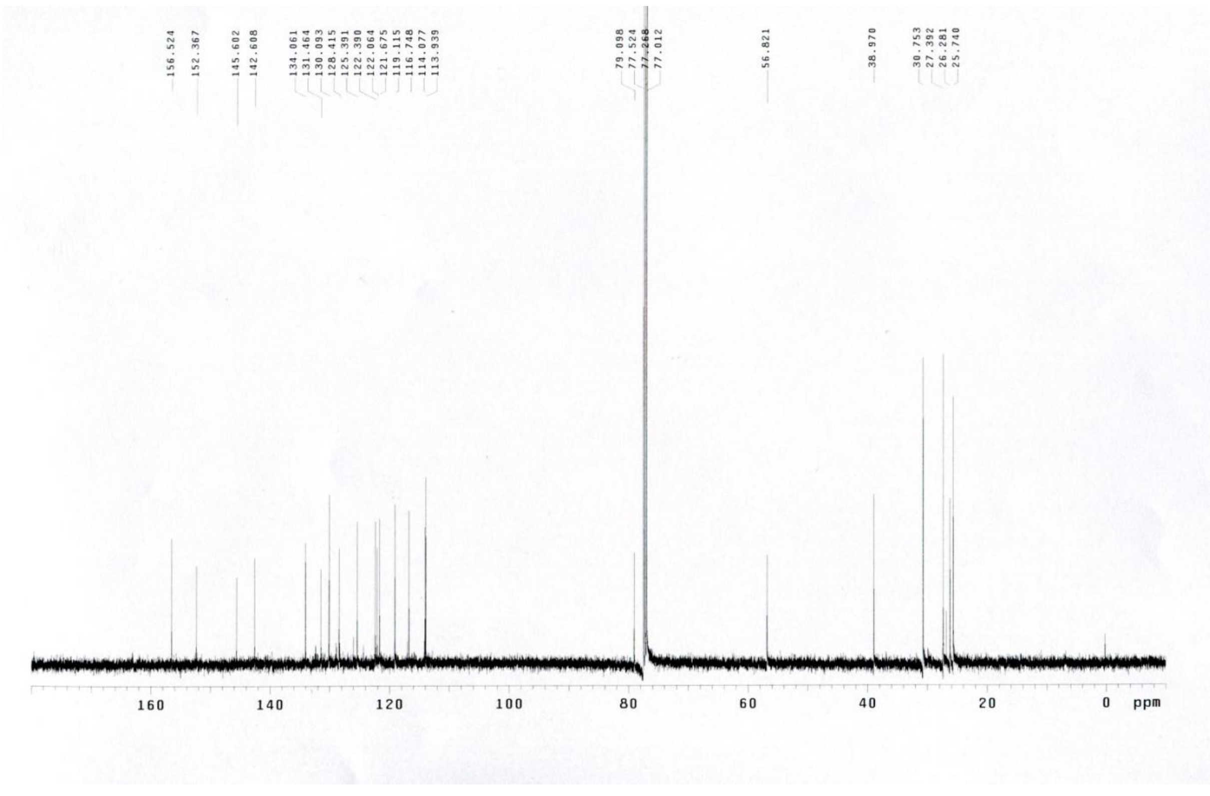


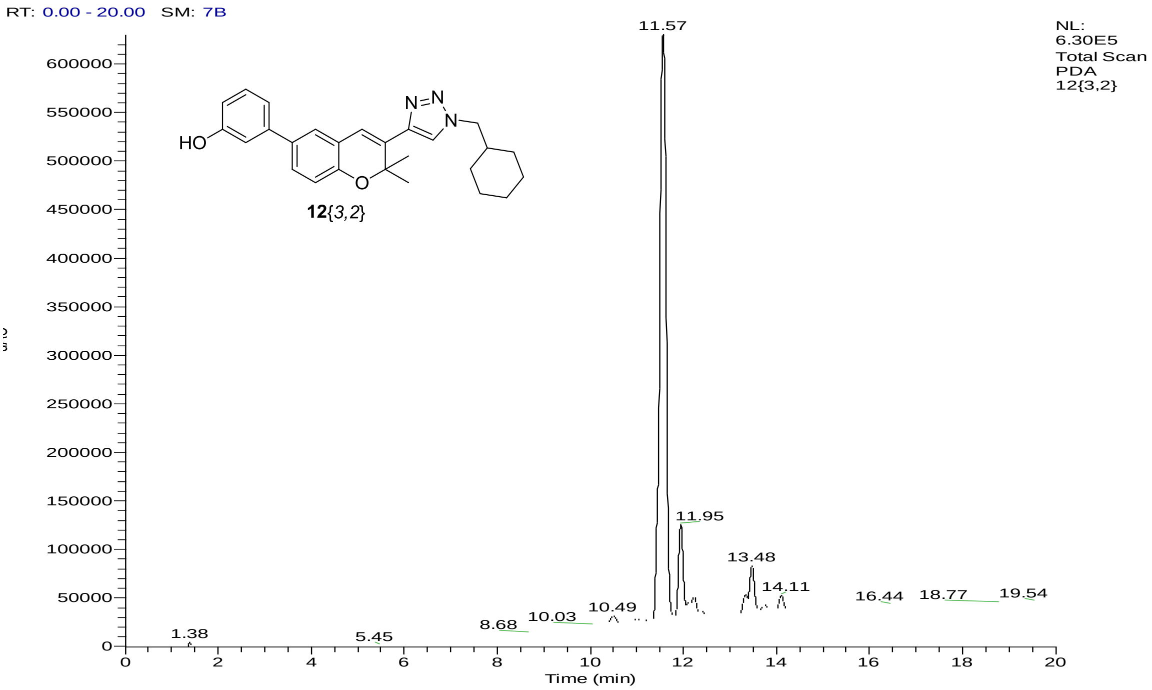
PEAK LIST
13{2,4}.RAW
RT: 0.00 - 20.00
Number of detected peaks: 2

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
10.27	10.14	10.42	4899844	80.73	554164.7	78.43
10.48	10.42	10.69	1169900	19.27	152426	21.57



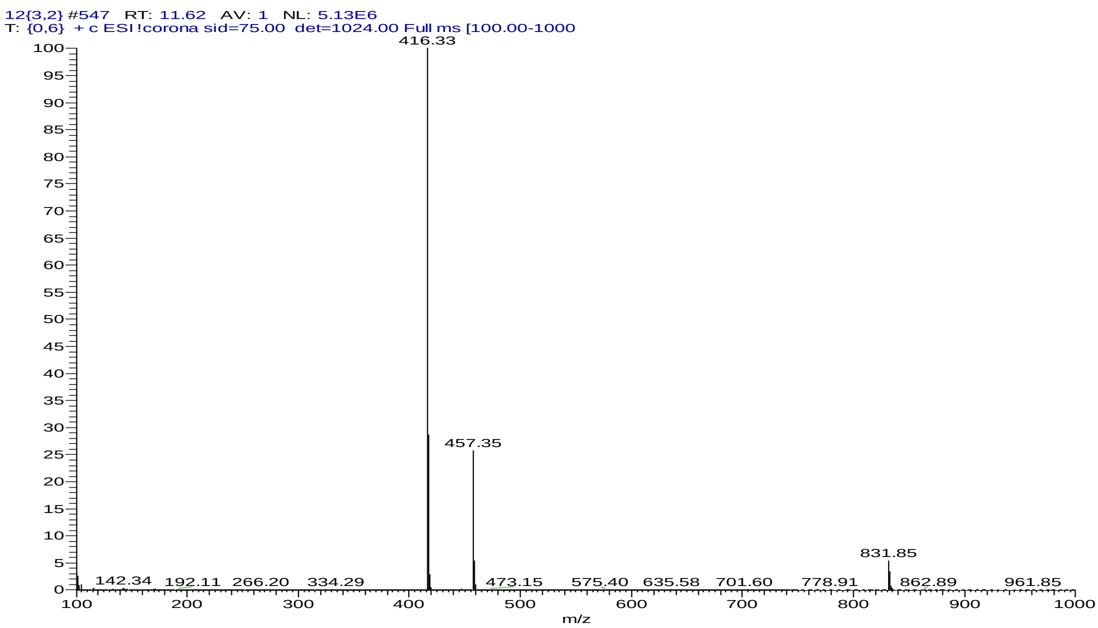


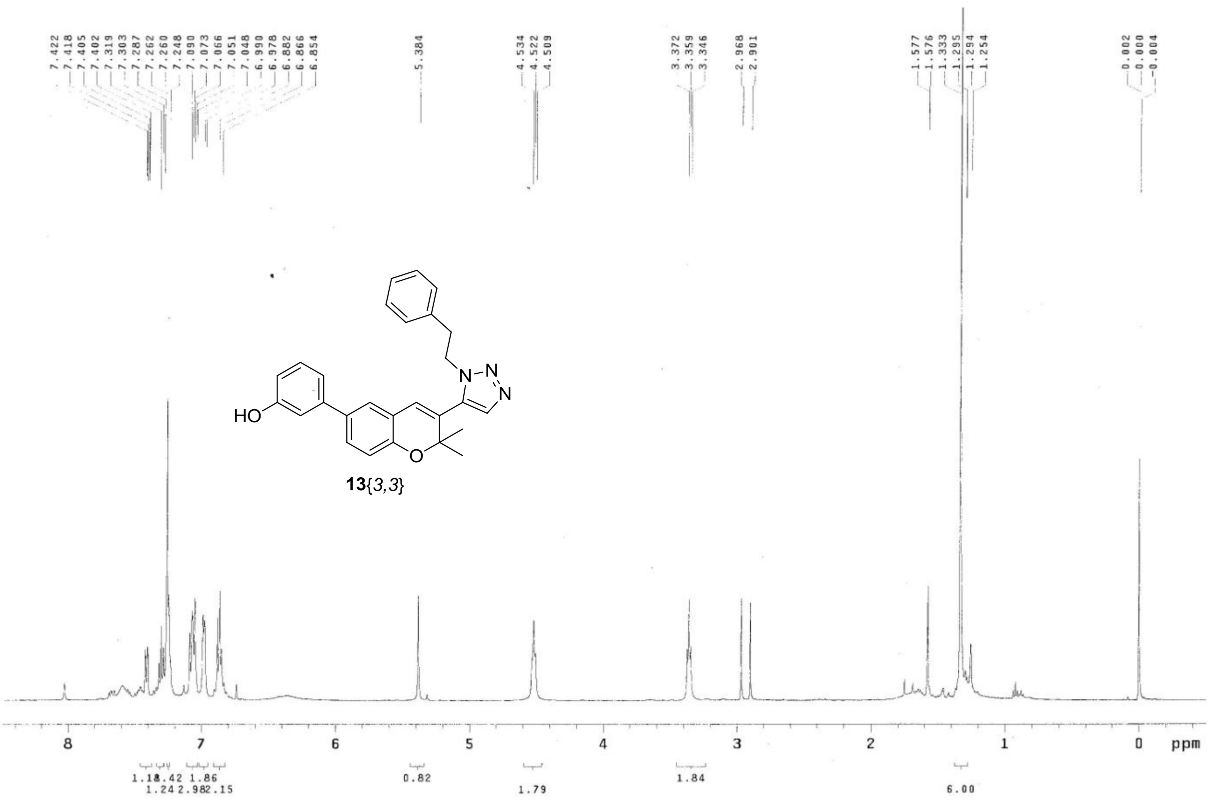


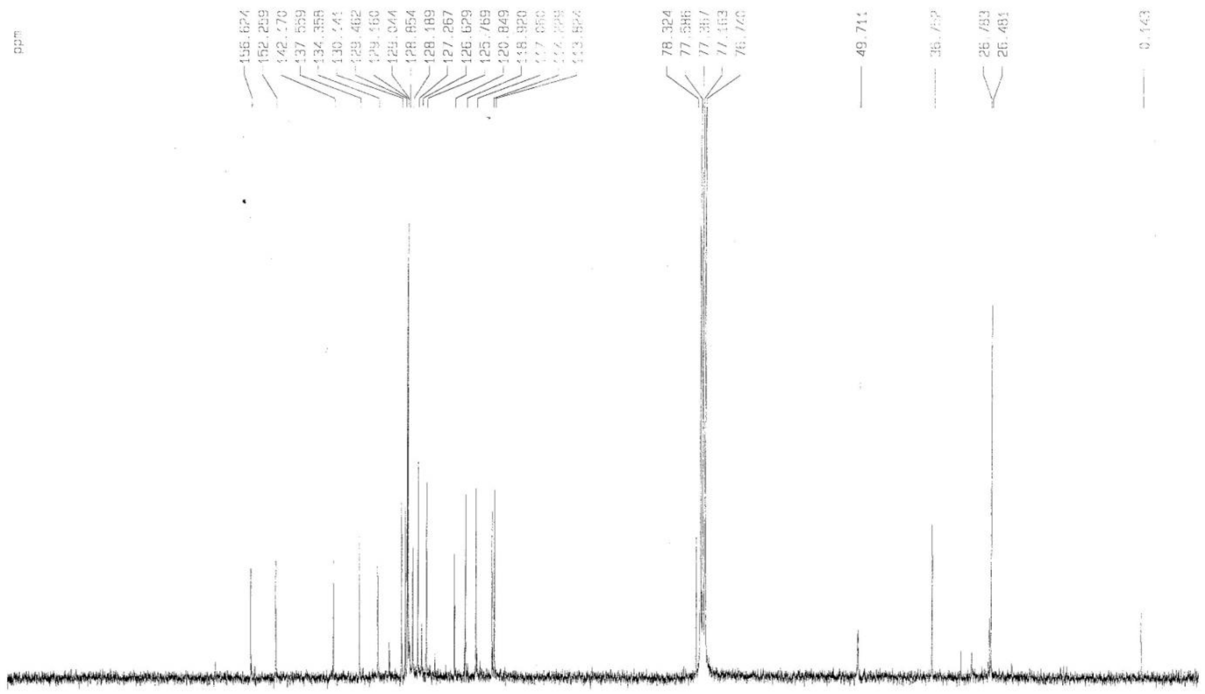


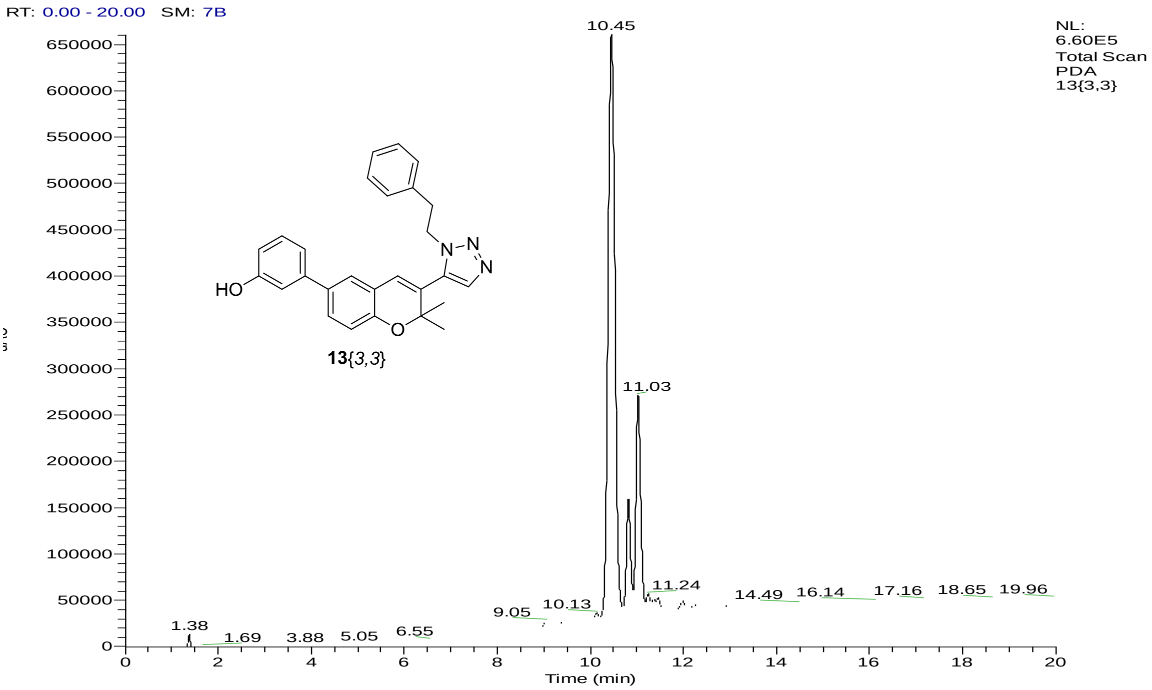
PEAK LIST
12{3,2}.RAW
RT: 0.00 - 20.00
Number of detected peaks: 3

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
11.57	11.32	11.8	5871389	85.23	602193.1	80.8
11.95	11.8	12.06	657881.2	9.55	94342.47	12.66
13.48	13.38	13.64	359531.4	5.22	48738.81	6.54



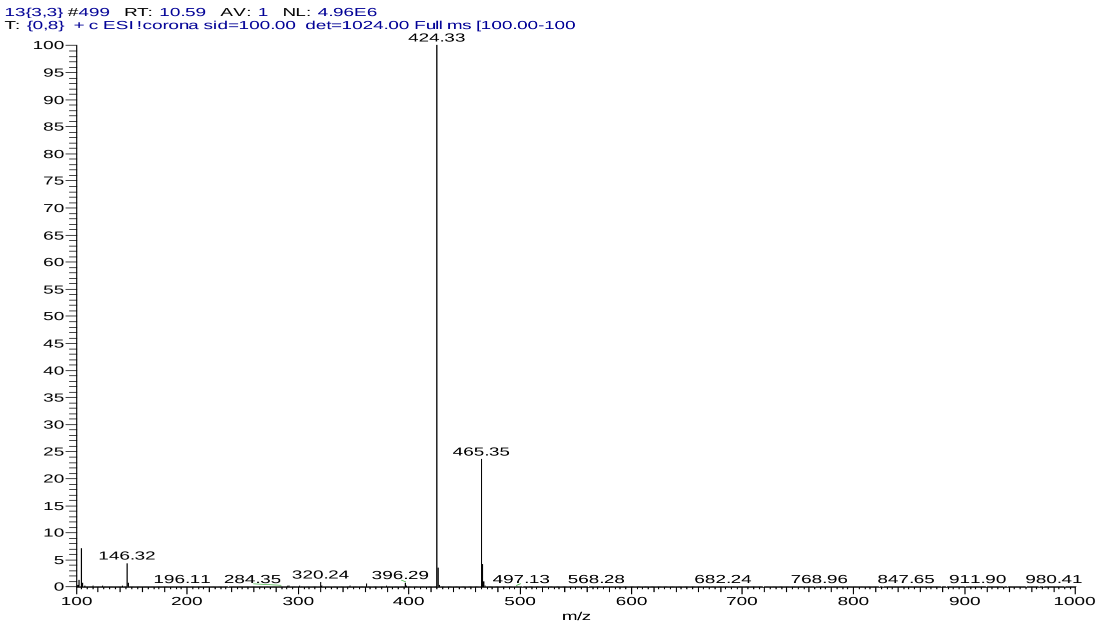

7.422 7.418 7.405 7.402 7.319 7.303 7.287 7.262 7.260 7.248 7.090 7.073 7.066 7.051 7.048 6.990 6.978 6.882 6.866 6.854
5.384
4.534 4.522 4.509
3.372 3.359 3.346
2.968 2.901
1.577 1.576 1.333 1.295 1.294 1.254
0.002 0.000 -0.004
HO
13{3,3}
ppm
0.82
1.79
1.84
6.00

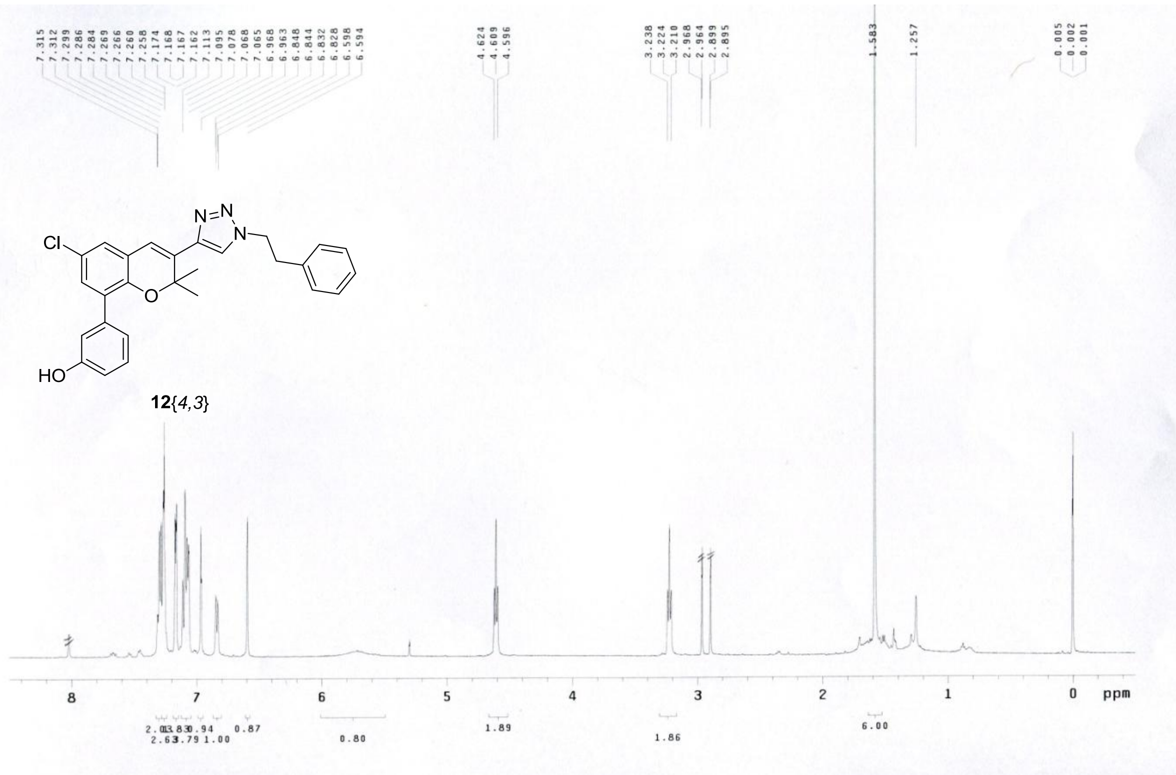

ppm
49.711

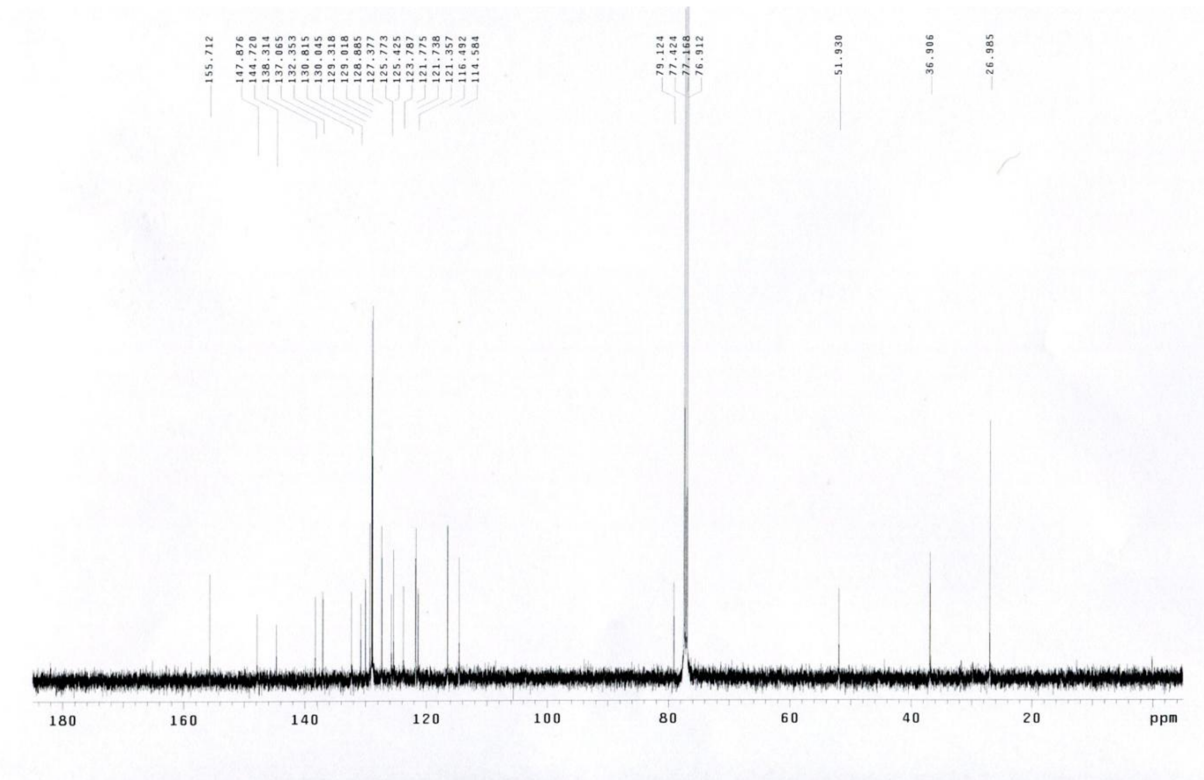


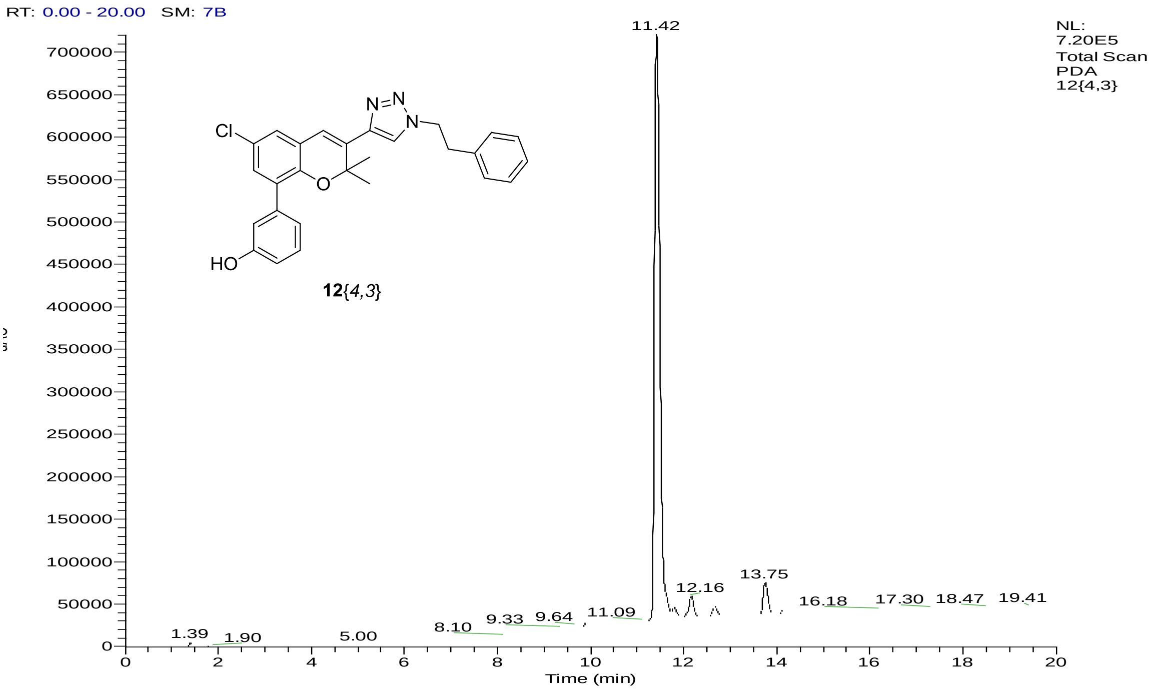
PEAK LIST
13{3,3}.RAW
RT: 0.00 - 20.00
Number of detected peaks: 3

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
10.45	10.21	10.7	6412794	72.55	627309	63.71
10.82	10.7	10.92	767356	8.68	123804.2	12.57
11.03	10.92	11.19	1659413	18.77	233484	23.71



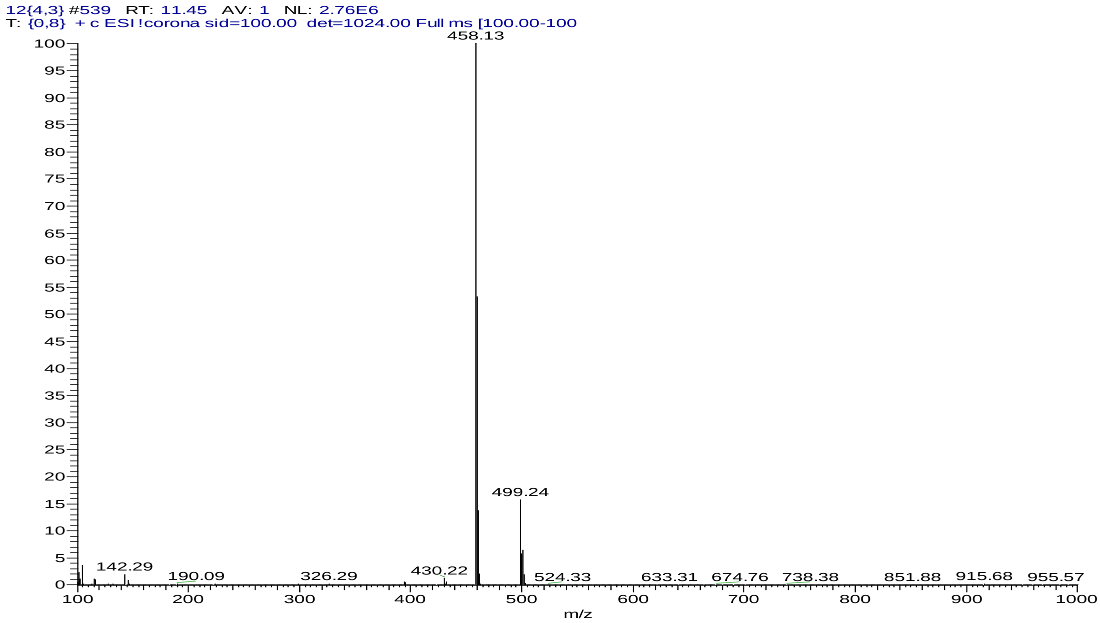

7.315
7.312
7.299
7.286
7.284
7.280
7.266
7.260
7.258
7.174
7.168
7.167
7.162
7.113
7.095
7.078
7.068
7.065
6.968
6.963
6.848
6.844
6.832
6.828
6.598
6.594
4.624
4.609
4.596
3.238
3.224
3.210
2.968
2.964
2.899
2.895
1.583
1.257
0.005
0.002
0.001
Cl
N
N
N
O
HO
12{4,3}
8
7
6
5
4
3
2
1
0
ppm
2.01
3.83
0.94
0.87
2.63
3.79
1.00
0.80
1.89
1.86
6.00

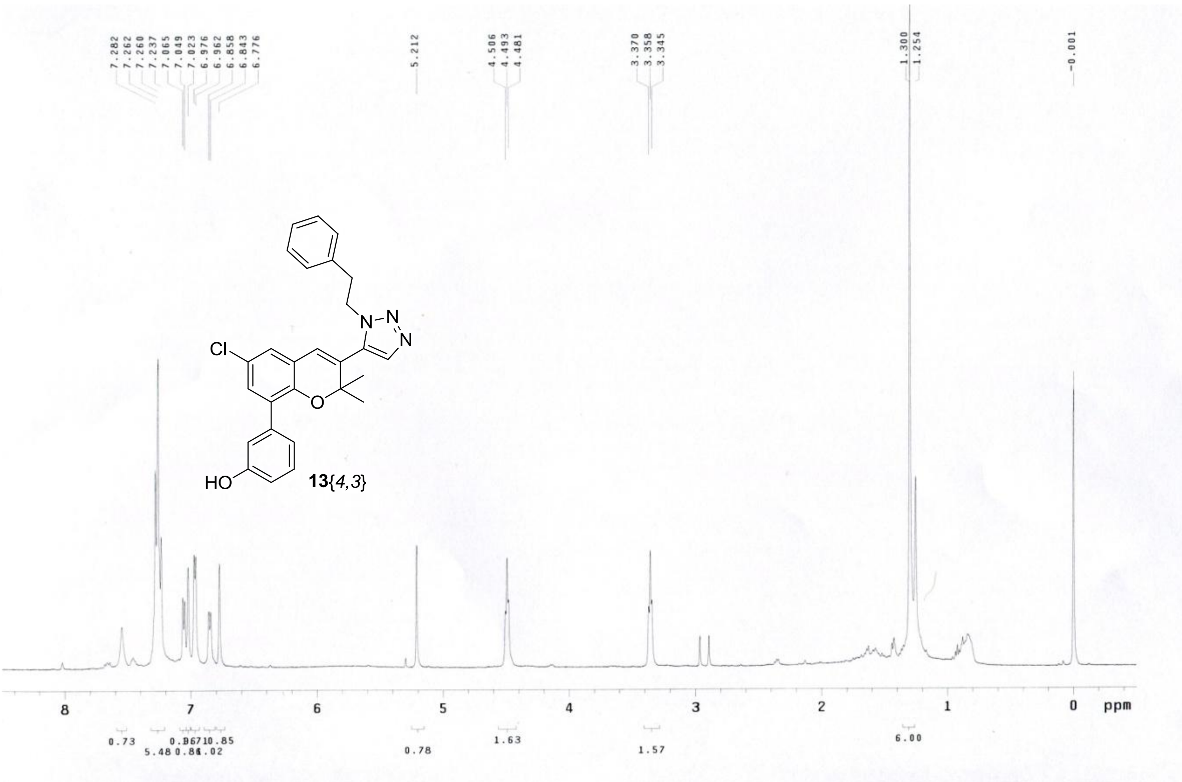

155.712
147.876
144.720
138.314
137.065
132.353
130.815
130.045
129.318
129.018
128.885
127.377
125.773
125.425
123.787
121.775
121.738
121.357
116.492
114.584
79.124
77.424
77.168
76.912
51.930
36.906
26.985
180
160
140
120
100
80
60
40
20
ppm

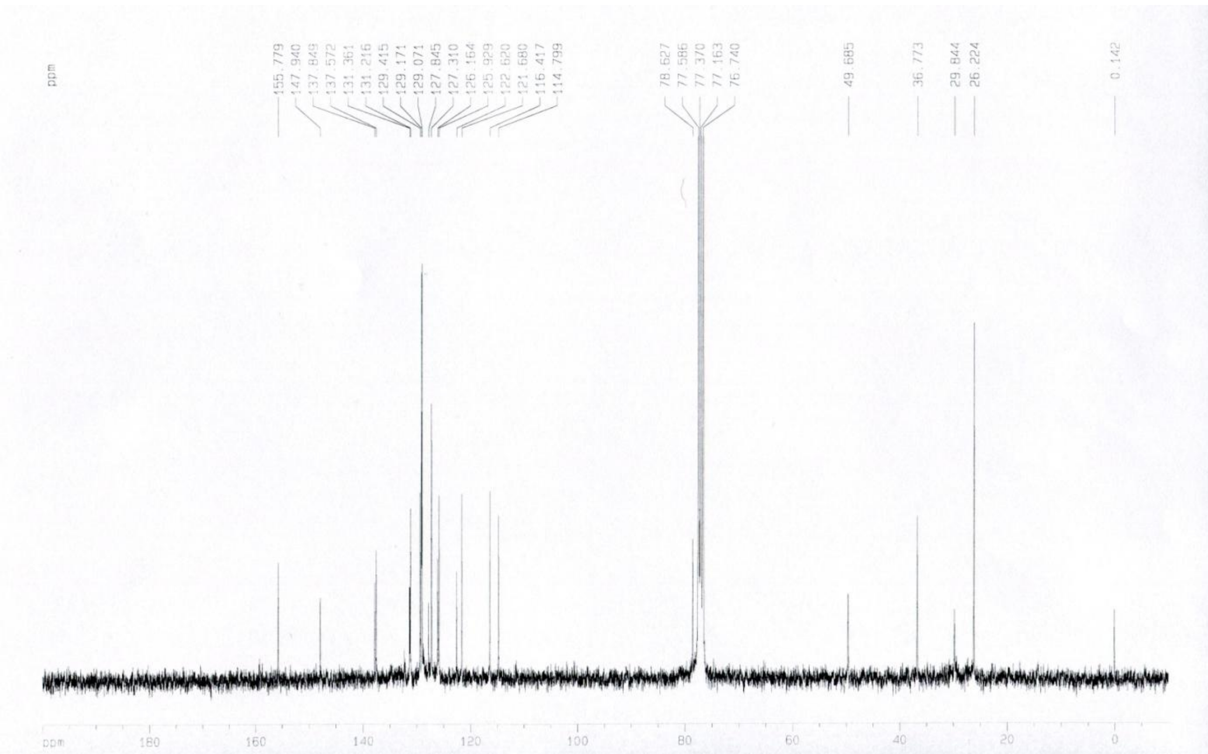


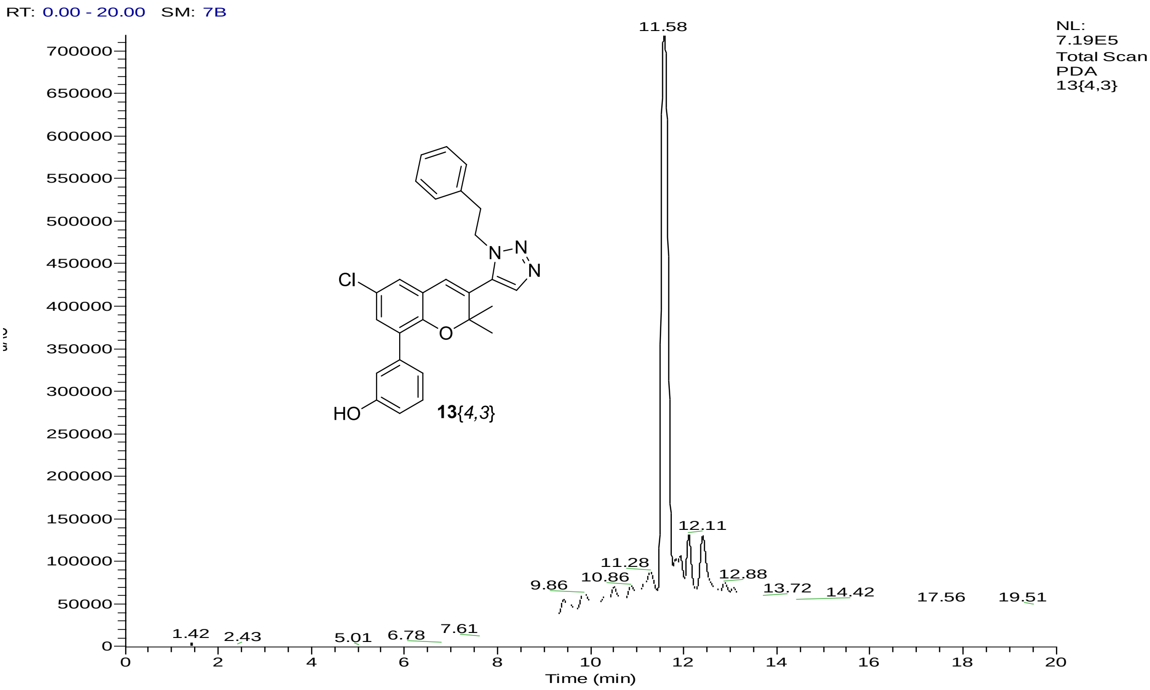
PEAK LIST
12{4,3}.RAW
RT: 0.00 - 20.00
Number of detected peaks: 2

Apex RT	Start RT	End RT	Area	%Area	Height	%Height
11.42	11.19	11.73	5781118	95.29	690462.2	94.7
13.75	13.64	13.99	285760.5	4.71	38637.9	5.3




7.282 7.262 7.260 7.237 7.065 7.049 7.023 6.976 6.962 6.858 6.843 6.776
5.212
4.506 4.493 4.481
3.370 3.358 3.345
1.300 1.254
-0.001
Cl
N
N
N
O
HO
13{4,3}
8 7 6 5 4 3 2 1 0 ppm
0.73 5.48 0.84 1.02 0.85 0.78 1.63 1.57 6.00


155.779 147.940 137.849 137.572 131.361 131.216 129.415 129.171 129.071 127.845 127.310 126.164 125.929 122.620 121.680 115.417 114.799
78.627 77.586 77.370 77.163 76.740
49.685
36.773
29.844
26.224
0.142
ppm 180 160 140 120 100 80 60 40 20 0



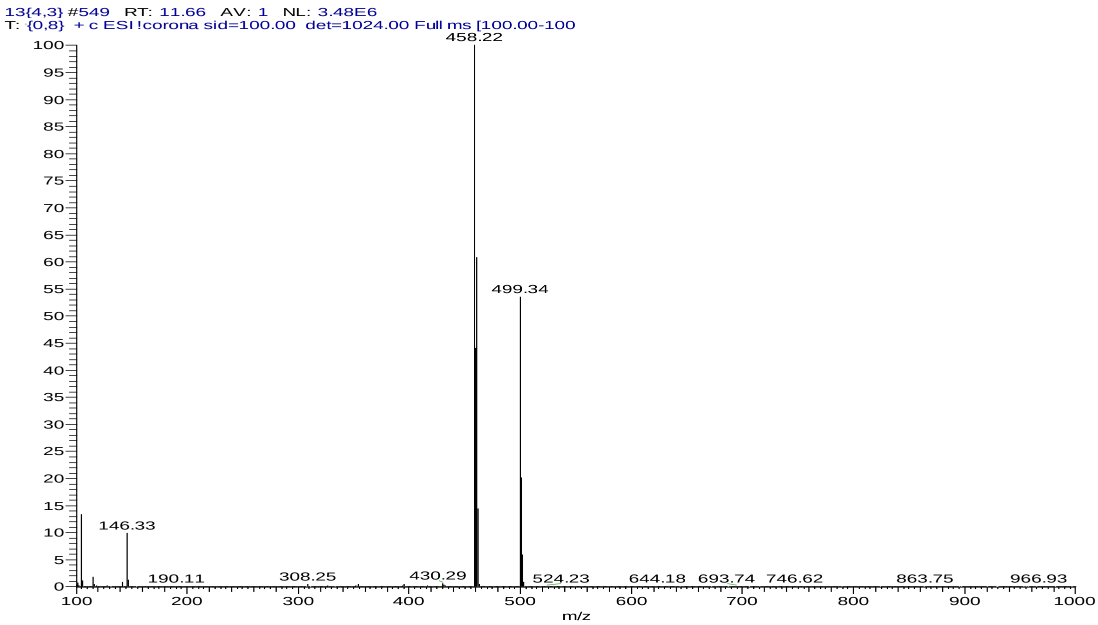
PEAK LIST

13{4,3}.RAW

RT: 0.00 - 20.00

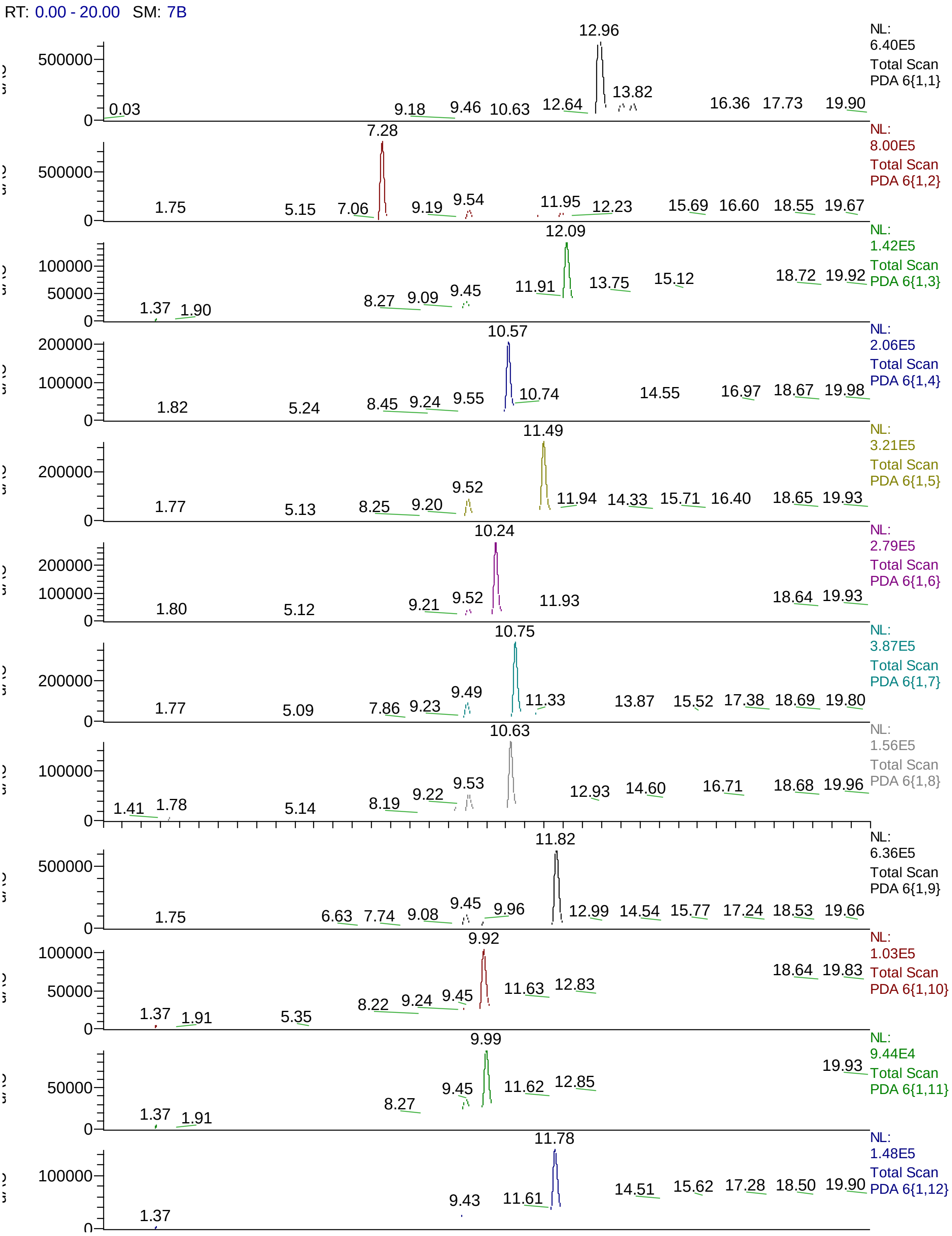
Number of detected peaks: 2

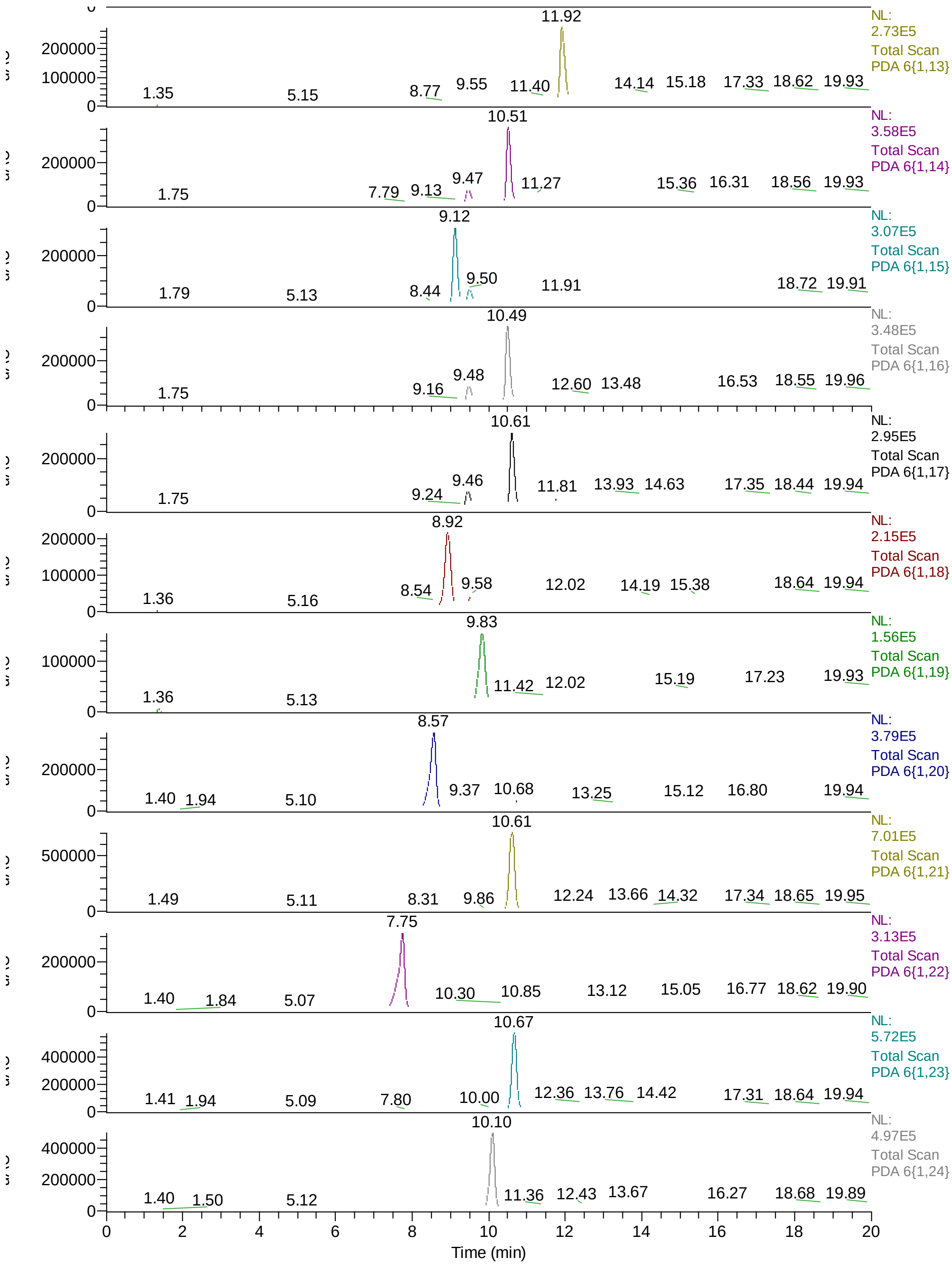
Apex RT	Start RT	End RT	Area	%Area	Height	%Height
11.58	11.43	11.77	6844245	89.54	660620.8	90.27
12.41	12.26	12.78	799547.8	10.46	71180.45	9.73

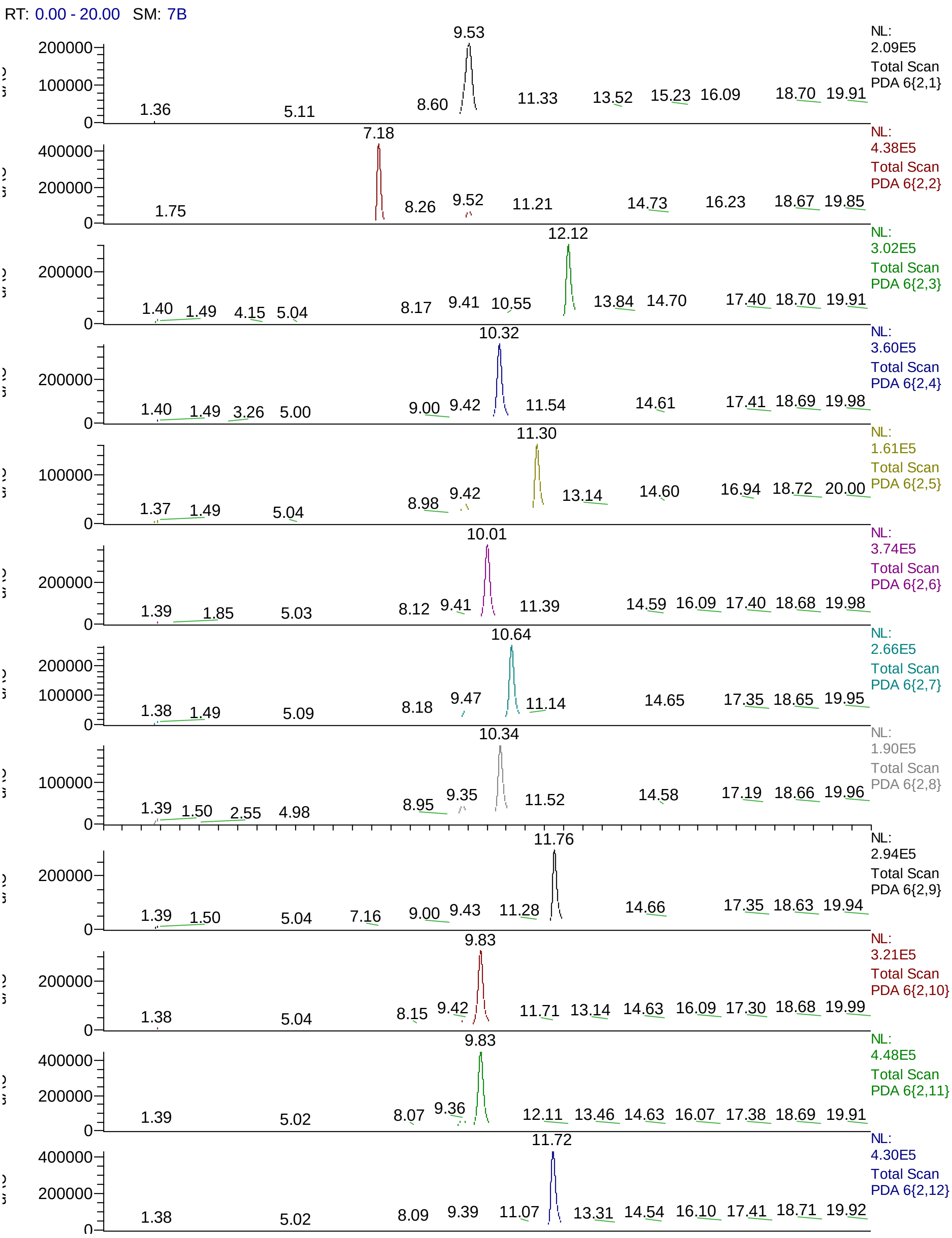


V. PDA data of final compounds

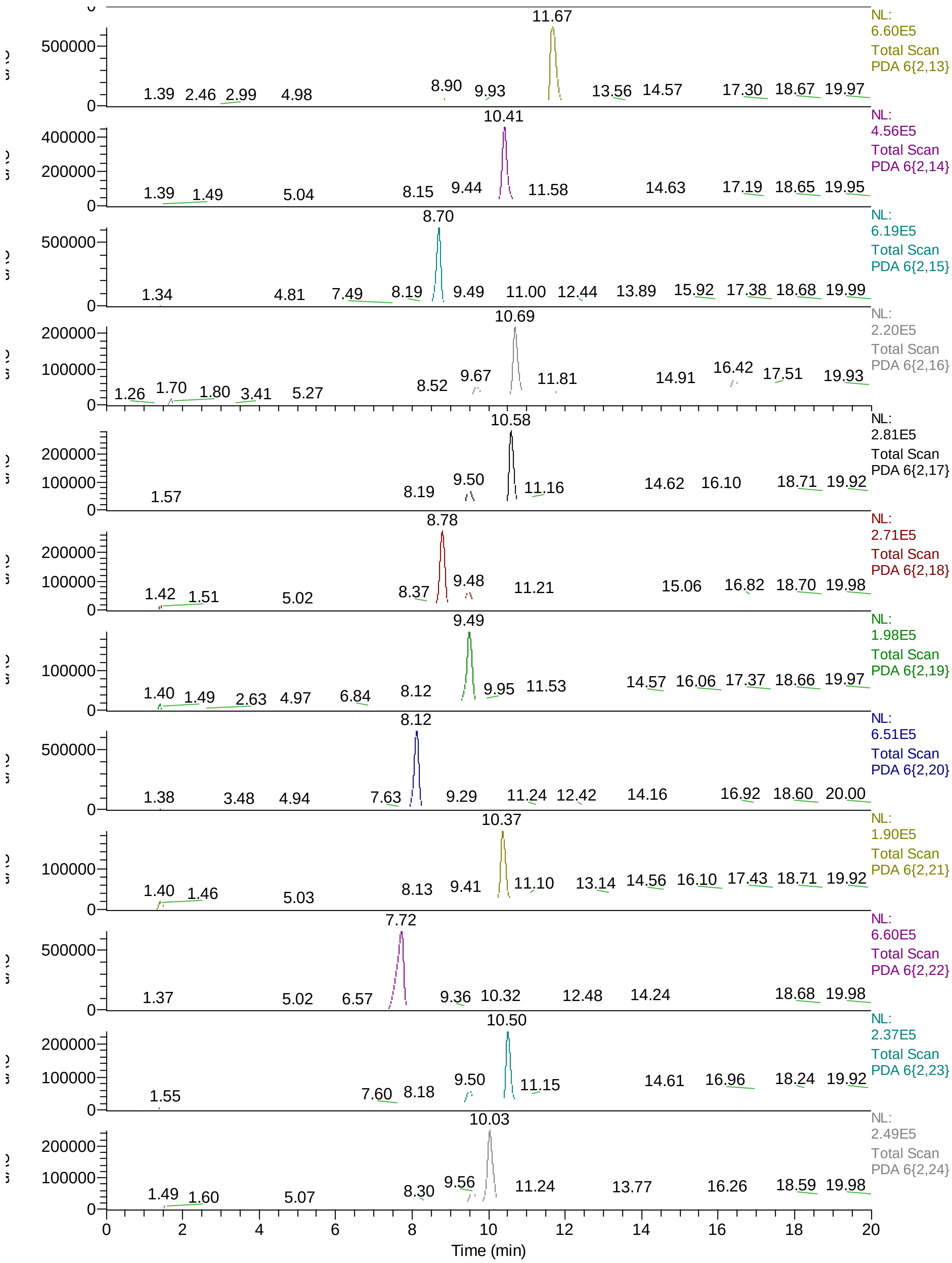
Path I: Suzuki coupling

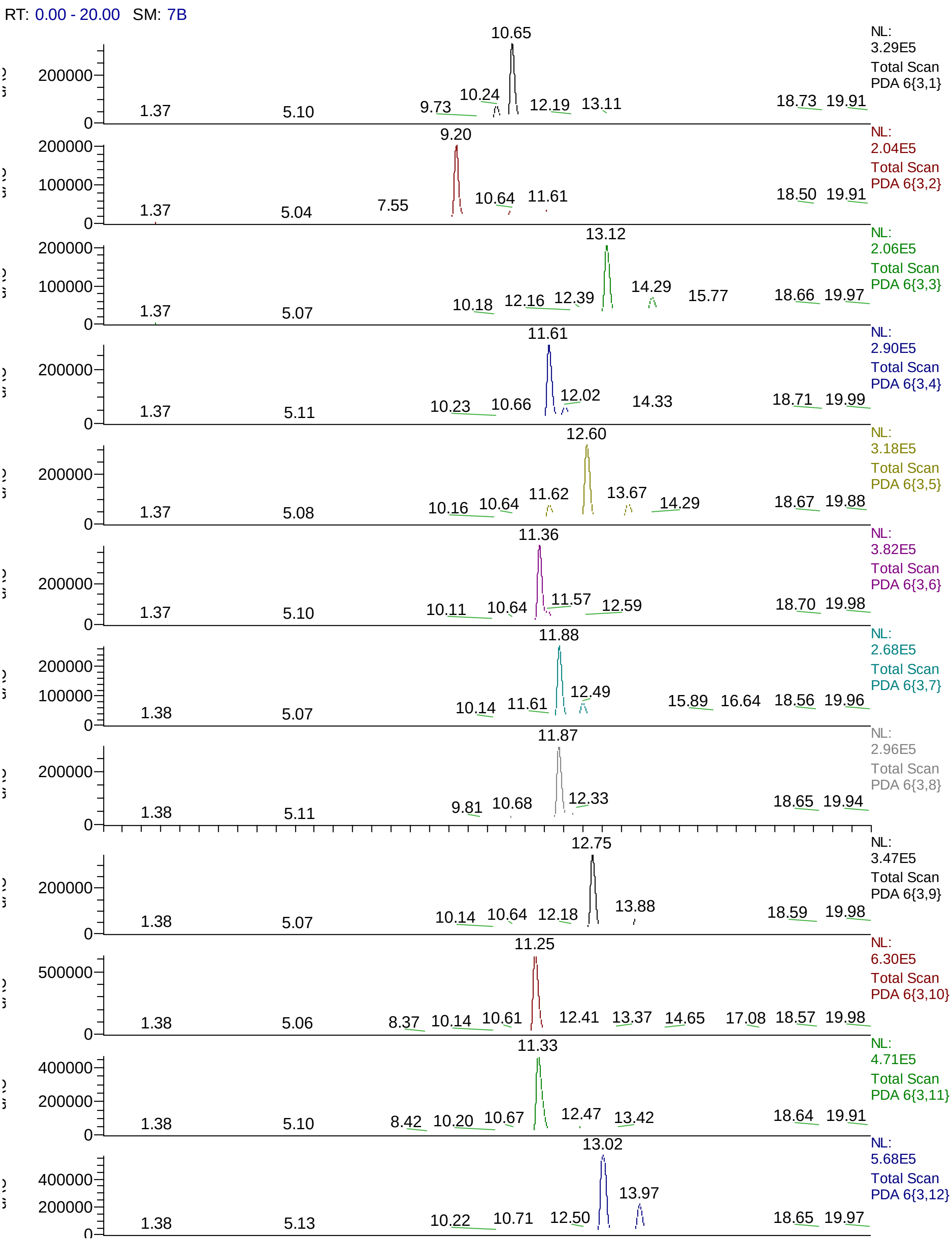



NL: 2.73E5 Total Scan PDA 6{1,13}
NL: 3.58E5 Total Scan PDA 6{1,14}
NL: 3.07E5 Total Scan PDA 6{1,15}
NL: 3.48E5 Total Scan PDA 6{1,16}
NL: 2.95E5 Total Scan PDA 6{1,17}
NL: 2.15E5 Total Scan PDA 6{1,18}
NL: 1.56E5 Total Scan PDA 6{1,19}
NL: 3.79E5 Total Scan PDA 6{1,20}
NL: 7.01E5 Total Scan PDA 6{1,21}
NL: 3.13E5 Total Scan PDA 6{1,22}
NL: 5.72E5 Total Scan PDA 6{1,23}
NL: 4.97E5 Total Scan PDA 6{1,24}
Time (min)

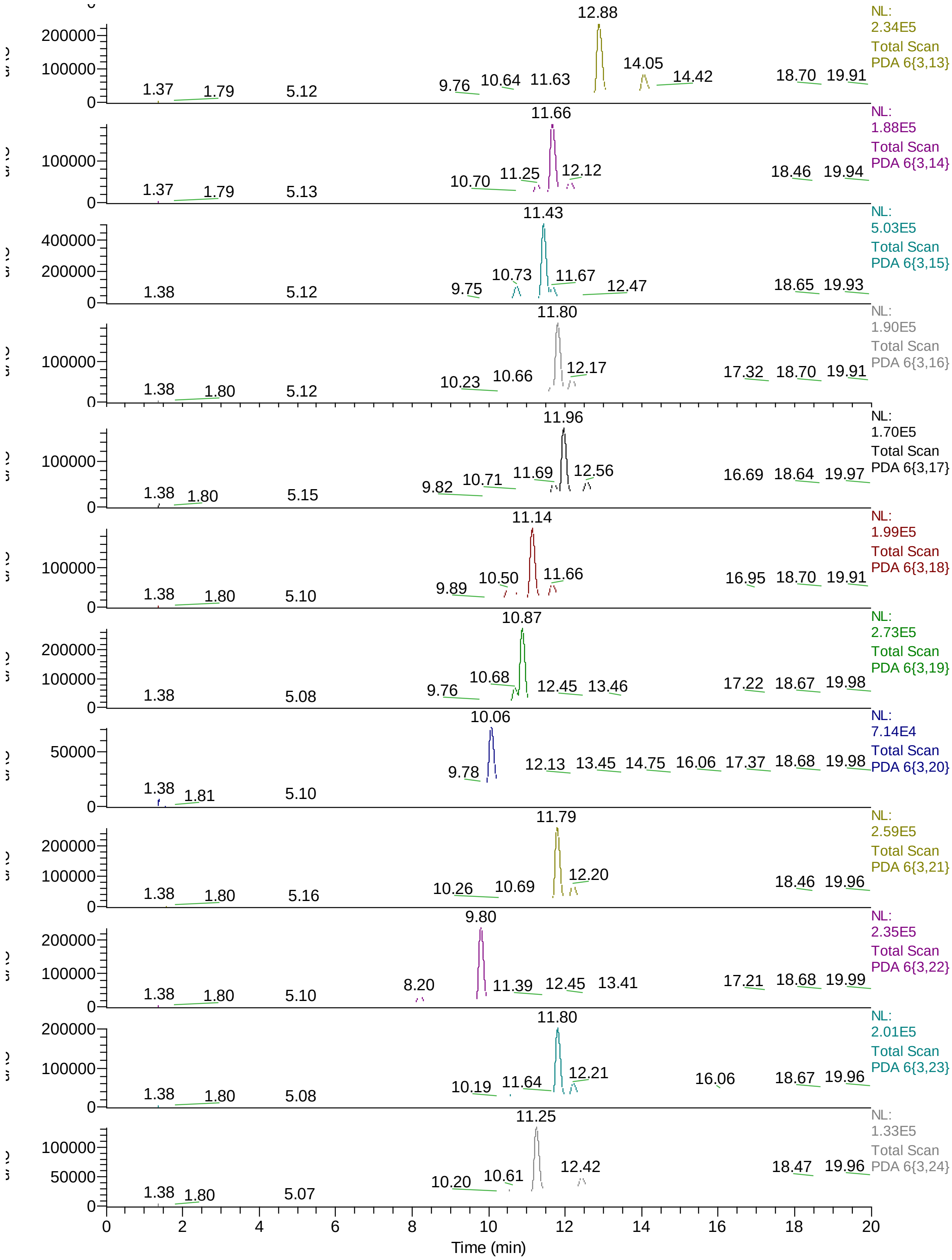


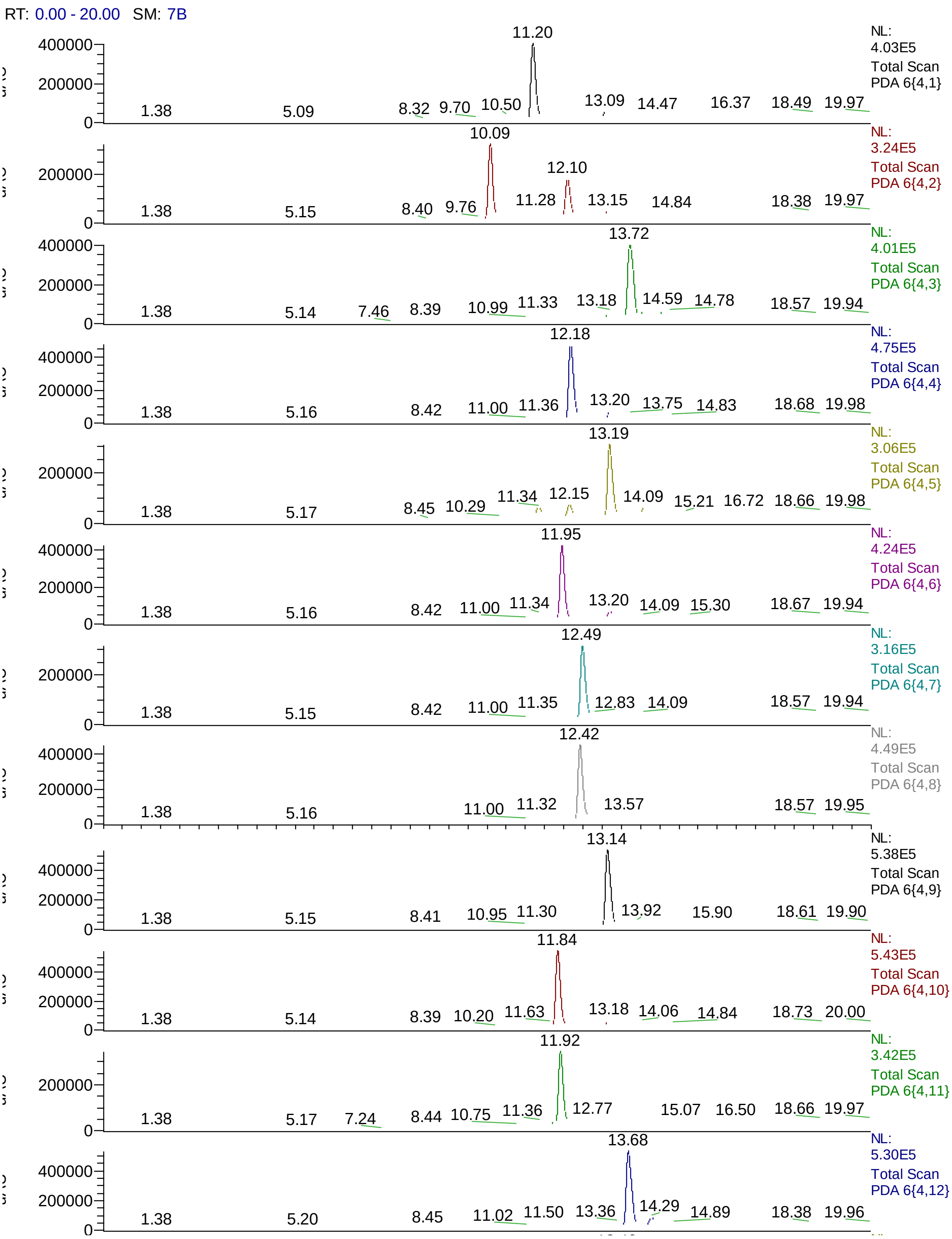
RT: 0.00 - 20.00 SM: 7B
NL: 2.09E5 Total Scan PDA 6{2,1}
NL: 4.38E5 Total Scan PDA 6{2,2}
NL: 3.02E5 Total Scan PDA 6{2,3}
NL: 3.60E5 Total Scan PDA 6{2,4}
NL: 1.61E5 Total Scan PDA 6{2,5}
NL: 3.74E5 Total Scan PDA 6{2,6}
NL: 2.66E5 Total Scan PDA 6{2,7}
NL: 1.90E5 Total Scan PDA 6{2,8}
NL: 2.94E5 Total Scan PDA 6{2,9}
NL: 3.21E5 Total Scan PDA 6{2,10}
NL: 4.48E5 Total Scan PDA 6{2,11}
NL: 4.30E5 Total Scan PDA 6{2,12}

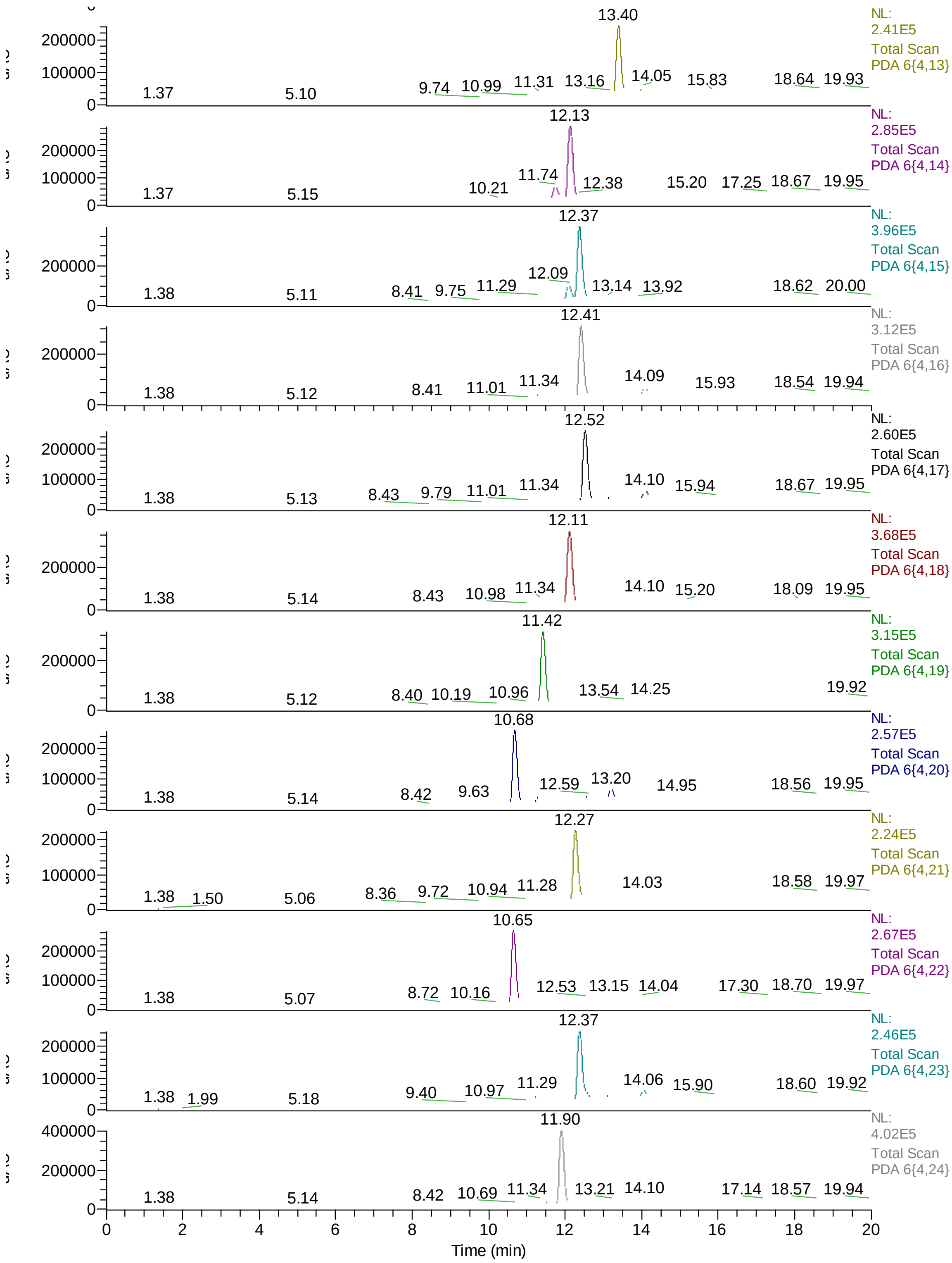

NL: 6.60E5 Total Scan PDA 6{2,13}
11.67
1.39 2.46 2.99 4.98 8.90 9.93 13.56 14.57 17.30 18.67 19.97
NL: 4.56E5 Total Scan PDA 6{2,14}
10.41
1.39 1.49 5.04 8.15 9.44 11.58 14.63 17.19 18.65 19.95
NL: 6.19E5 Total Scan PDA 6{2,15}
8.70
1.34 4.81 7.49 8.19 9.49 11.00 12.44 13.89 15.92 17.38 18.68 19.99
NL: 2.20E5 Total Scan PDA 6{2,16}
10.69
1.26 1.70 1.80 3.41 5.27 8.52 9.67 11.81 14.91 16.42 17.51 19.93
NL: 2.81E5 Total Scan PDA 6{2,17}
10.58
1.57 8.19 9.50 11.16 14.62 16.10 18.71 19.92
NL: 2.71E5 Total Scan PDA 6{2,18}
8.78
1.42 1.51 5.02 8.37 9.48 11.21 15.06 16.82 18.70 19.98
NL: 1.98E5 Total Scan PDA 6{2,19}
9.49
1.40 1.49 2.63 4.97 6.84 8.12 9.95 11.53 14.57 16.06 17.37 18.66 19.97
NL: 6.51E5 Total Scan PDA 6{2,20}
8.12
1.38 3.48 4.94 7.63 9.29 11.24 12.42 14.16 16.92 18.60 20.00
NL: 1.90E5 Total Scan PDA 6{2,21}
10.37
1.40 1.46 5.03 8.13 9.41 11.10 13.14 14.56 16.10 17.43 18.71 19.92
NL: 6.60E5 Total Scan PDA 6{2,22}
7.72
1.37 5.02 6.57 9.36 10.32 12.48 14.24 18.68 19.98
NL: 2.37E5 Total Scan PDA 6{2,23}
10.50
1.55 7.60 8.18 9.50 11.15 14.61 16.96 18.24 19.92
NL: 2.49E5 Total Scan PDA 6{2,24}
10.03
1.49 1.60 5.07 8.30 9.56 11.24 13.77 16.26 18.59 19.98
0 2 4 6 8 10 12 14 16 18 20
Time (min)



RT: 0.00 - 20.00 SM: 7B
10.65
200000
0
1.37 5.10 9.73 10.24 12.19 13.11 18.73 19.91
NL: 3.29E5 Total Scan PDA 6{3,1}
9.20
200000
100000
0
1.37 5.04 7.55 10.64 11.61 18.50 19.91
NL: 2.04E5 Total Scan PDA 6{3,2}
13.12
200000
100000
0
1.37 5.07 10.18 12.16 12.39 14.29 15.77 18.66 19.97
NL: 2.06E5 Total Scan PDA 6{3,3}
11.61
200000
0
1.37 5.11 10.23 10.66 12.02 14.33 18.71 19.99
NL: 2.90E5 Total Scan PDA 6{3,4}
12.60
200000
0
1.37 5.08 10.16 10.64 11.62 13.67 14.29 18.67 19.88
NL: 3.18E5 Total Scan PDA 6{3,5}
11.36
200000
0
1.37 5.10 10.11 10.64 11.57 12.59 18.70 19.98
NL: 3.82E5 Total Scan PDA 6{3,6}
11.88
200000
100000
0
1.38 5.07 10.14 11.61 12.49 15.89 16.64 18.56 19.96
NL: 2.68E5 Total Scan PDA 6{3,7}
11.87
200000
0
1.38 5.11 9.81 10.68 12.33 18.65 19.94
NL: 2.96E5 Total Scan PDA 6{3,8}
12.75
200000
0
1.38 5.07 10.14 10.64 12.18 13.88 18.59 19.98
NL: 3.47E5 Total Scan PDA 6{3,9}
11.25
500000
0
1.38 5.06 8.37 10.14 10.61 12.41 13.37 14.65 17.08 18.57 19.98
NL: 6.30E5 Total Scan PDA 6{3,10}
11.33
400000
200000
0
1.38 5.10 8.42 10.20 10.67 12.47 13.42 18.64 19.91
NL: 4.71E5 Total Scan PDA 6{3,11}
13.02
400000
200000
0
1.38 5.13 10.22 10.71 12.50 13.97 18.65 19.97
NL: 5.68E5 Total Scan PDA 6{3,12}

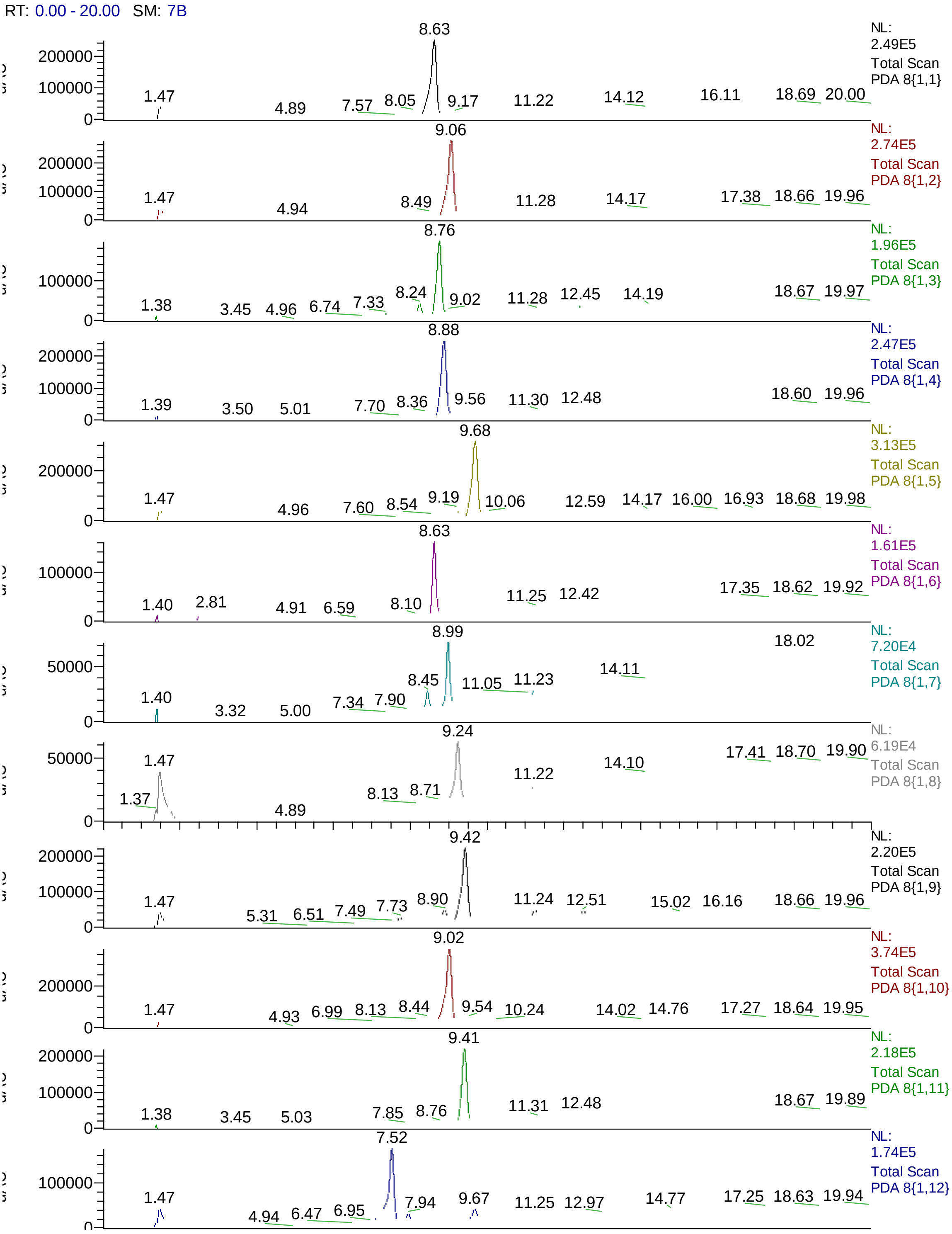

NL: 2.34E5
Total Scan PDA 6{3,13}
NL: 1.88E5
Total Scan PDA 6{3,14}
NL: 5.03E5
Total Scan PDA 6{3,15}
NL: 1.90E5
Total Scan PDA 6{3,16}
NL: 1.70E5
Total Scan PDA 6{3,17}
NL: 1.99E5
Total Scan PDA 6{3,18}
NL: 2.73E5
Total Scan PDA 6{3,19}
NL: 7.14E4
Total Scan PDA 6{3,20}
NL: 2.59E5
Total Scan PDA 6{3,21}
NL: 2.35E5
Total Scan PDA 6{3,22}
NL: 2.01E5
Total Scan PDA 6{3,23}
NL: 1.33E5
Total Scan PDA 6{3,24}
Time (min)

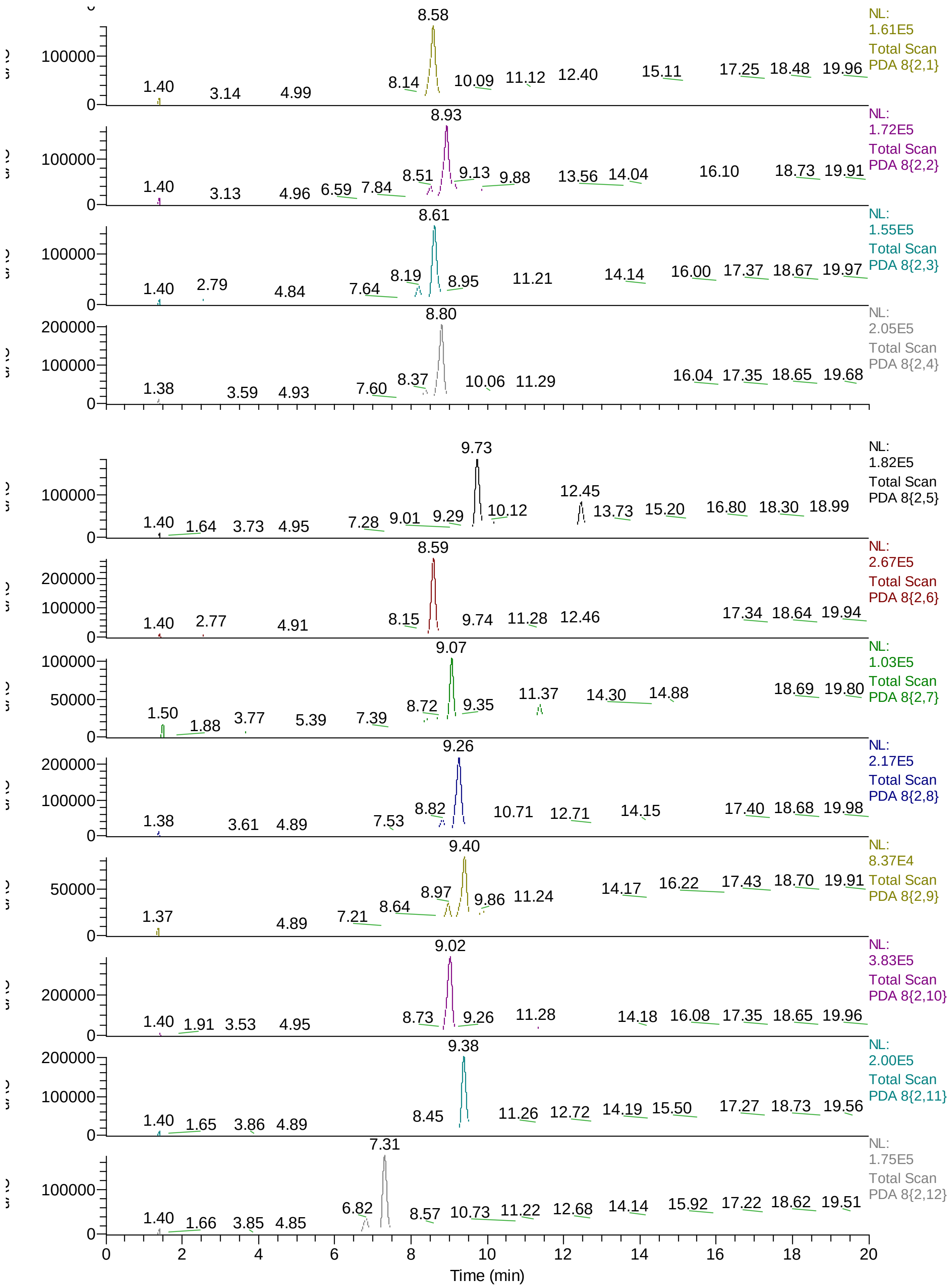

RT: 0.00 - 20.00 SM: 7B
NL: 4.03E5 Total Scan PDA 6{4,1}
NL: 3.24E5 Total Scan PDA 6{4,2}
NL: 4.01E5 Total Scan PDA 6{4,3}
NL: 4.75E5 Total Scan PDA 6{4,4}
NL: 3.06E5 Total Scan PDA 6{4,5}
NL: 4.24E5 Total Scan PDA 6{4,6}
NL: 3.16E5 Total Scan PDA 6{4,7}
NL: 4.49E5 Total Scan PDA 6{4,8}
NL: 5.38E5 Total Scan PDA 6{4,9}
NL: 5.43E5 Total Scan PDA 6{4,10}
NL: 3.42E5 Total Scan PDA 6{4,11}
NL: 5.30E5 Total Scan PDA 6{4,12}

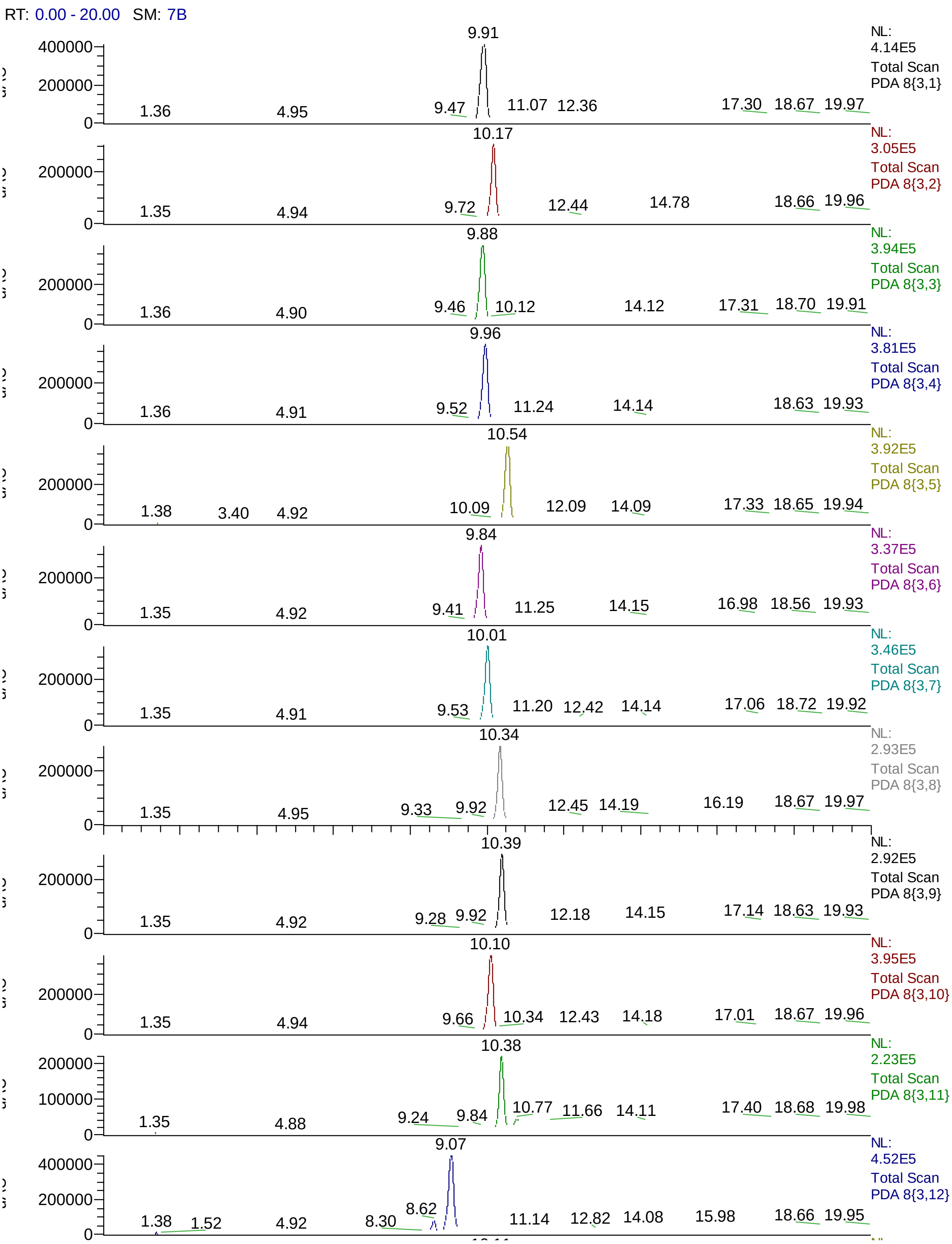


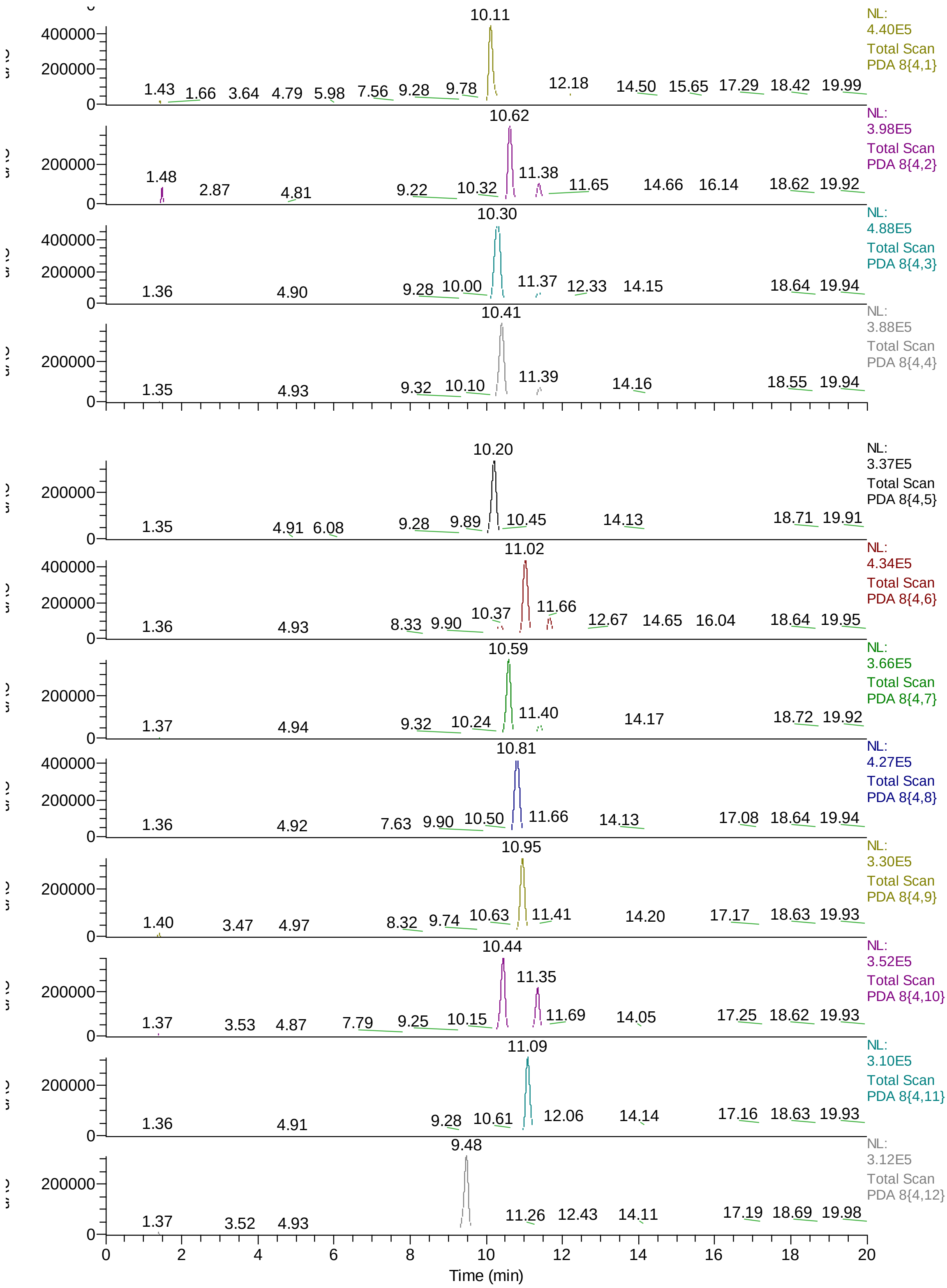
13.40
1.37 5.10 9.74 10.99 11.31 13.16 14.05 15.83 18.64 19.93
NL: 2.41E5 Total Scan PDA 6{4,13}
12.13
1.37 5.15 10.21 11.74 12.38 15.20 17.25 18.67 19.95
NL: 2.85E5 Total Scan PDA 6{4,14}
12.37
1.38 5.11 8.41 9.75 11.29 12.09 13.14 13.92 18.62 20.00
NL: 3.96E5 Total Scan PDA 6{4,15}
12.41
1.38 5.12 8.41 11.01 11.34 14.09 15.93 18.54 19.94
NL: 3.12E5 Total Scan PDA 6{4,16}
12.52
1.38 5.13 8.43 9.79 11.01 11.34 14.10 15.94 18.67 19.95
NL: 2.60E5 Total Scan PDA 6{4,17}
12.11
1.38 5.14 8.43 10.98 11.34 14.10 15.20 18.09 19.95
NL: 3.68E5 Total Scan PDA 6{4,18}
11.42
1.38 5.12 8.40 10.19 10.96 13.54 14.25 19.92
NL: 3.15E5 Total Scan PDA 6{4,19}
10.68
1.38 5.14 8.42 9.63 12.59 13.20 14.95 18.56 19.95
NL: 2.57E5 Total Scan PDA 6{4,20}
12.27
1.38 1.50 5.06 8.36 9.72 10.94 11.28 14.03 18.58 19.97
NL: 2.24E5 Total Scan PDA 6{4,21}
10.65
1.38 5.07 8.72 10.16 12.53 13.15 14.04 17.30 18.70 19.97
NL: 2.67E5 Total Scan PDA 6{4,22}
12.37
1.38 1.99 5.18 9.40 10.97 11.29 14.06 15.90 18.60 19.92
NL: 2.46E5 Total Scan PDA 6{4,23}
11.90
1.38 5.14 8.42 10.69 11.34 13.21 14.10 17.14 18.57 19.94
NL: 4.02E5 Total Scan PDA 6{4,24}
Time (min)

Path II: aza Diels-Alder reaction



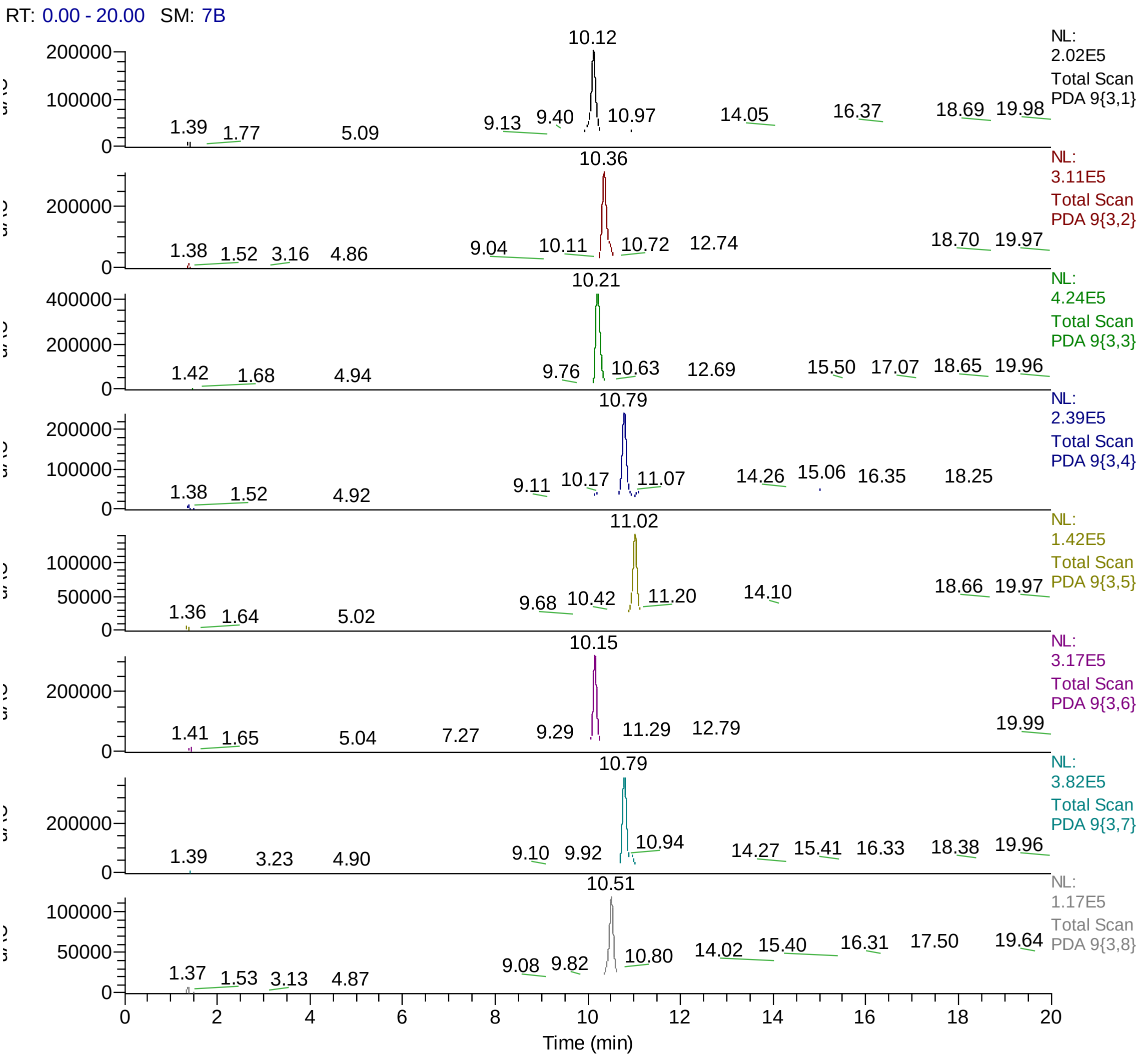

NL: 1.61E5 Total Scan PDA 8{2,1}
NL: 1.72E5 Total Scan PDA 8{2,2}
NL: 1.55E5 Total Scan PDA 8{2,3}
NL: 2.05E5 Total Scan PDA 8{2,4}
NL: 1.82E5 Total Scan PDA 8{2,5}
NL: 2.67E5 Total Scan PDA 8{2,6}
NL: 1.03E5 Total Scan PDA 8{2,7}
NL: 2.17E5 Total Scan PDA 8{2,8}
NL: 8.37E4 Total Scan PDA 8{2,9}
NL: 3.83E5 Total Scan PDA 8{2,10}
NL: 2.00E5 Total Scan PDA 8{2,11}
NL: 1.75E5 Total Scan PDA 8{2,12}
Time (min)

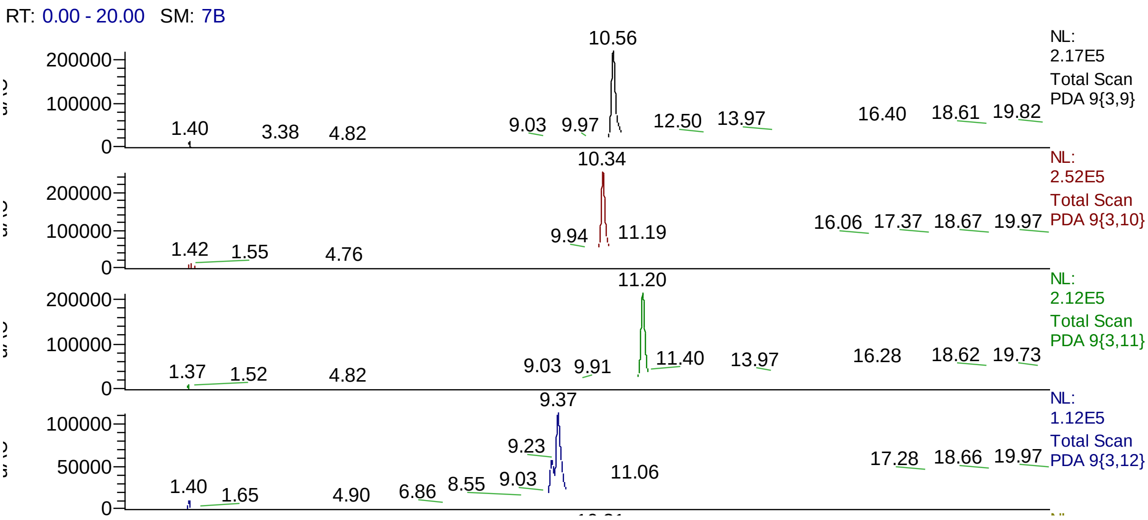

RT: 0.00 - 20.00 SM: 7B
NL: 4.14E5 Total Scan PDA 8{3,1}
NL: 3.05E5 Total Scan PDA 8{3,2}
NL: 3.94E5 Total Scan PDA 8{3,3}
NL: 3.81E5 Total Scan PDA 8{3,4}
NL: 3.92E5 Total Scan PDA 8{3,5}
NL: 3.37E5 Total Scan PDA 8{3,6}
NL: 3.46E5 Total Scan PDA 8{3,7}
NL: 2.93E5 Total Scan PDA 8{3,8}
NL: 2.92E5 Total Scan PDA 8{3,9}
NL: 3.95E5 Total Scan PDA 8{3,10}
NL: 2.23E5 Total Scan PDA 8{3,11}
NL: 4.52E5 Total Scan PDA 8{3,12}

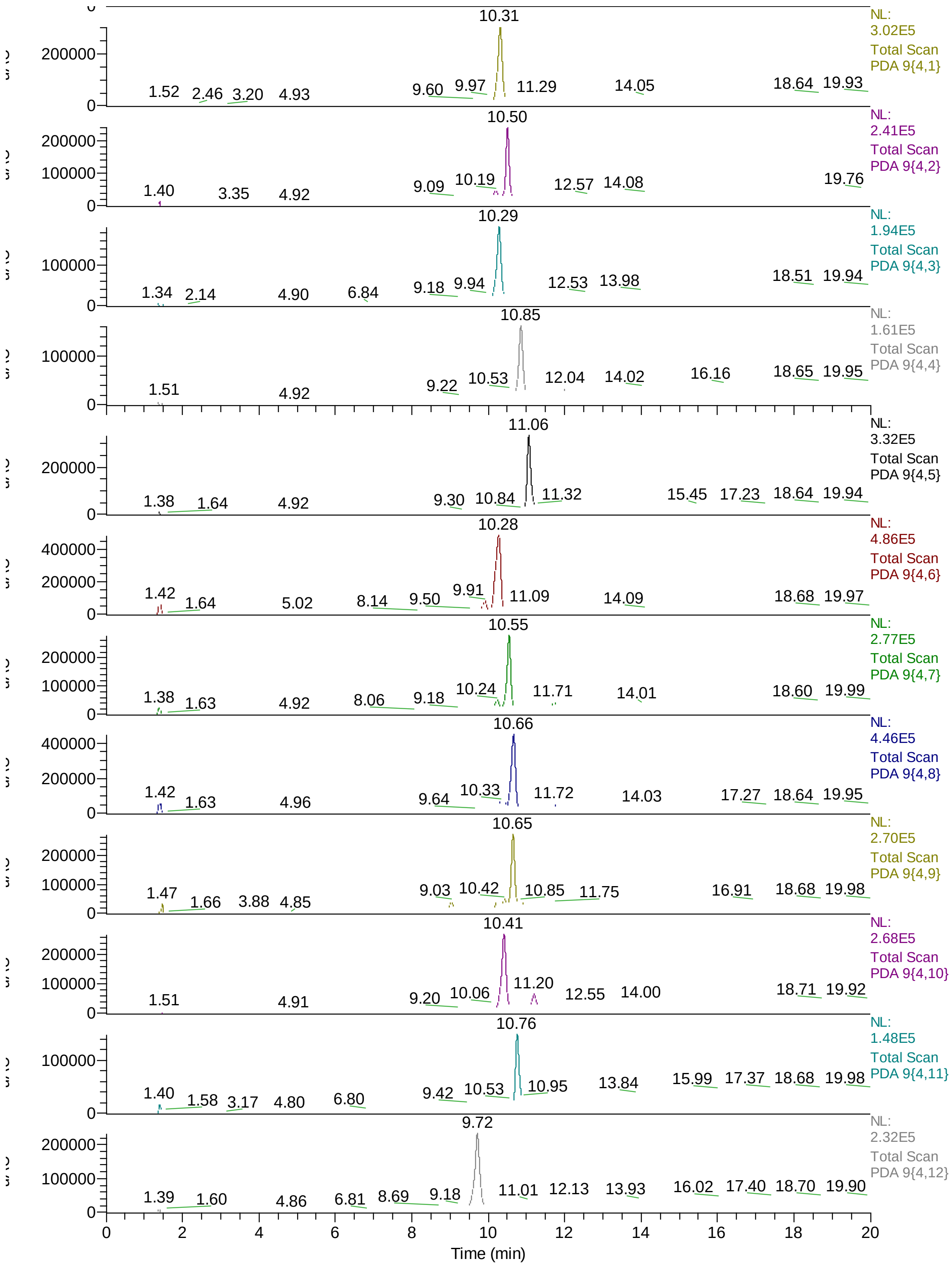


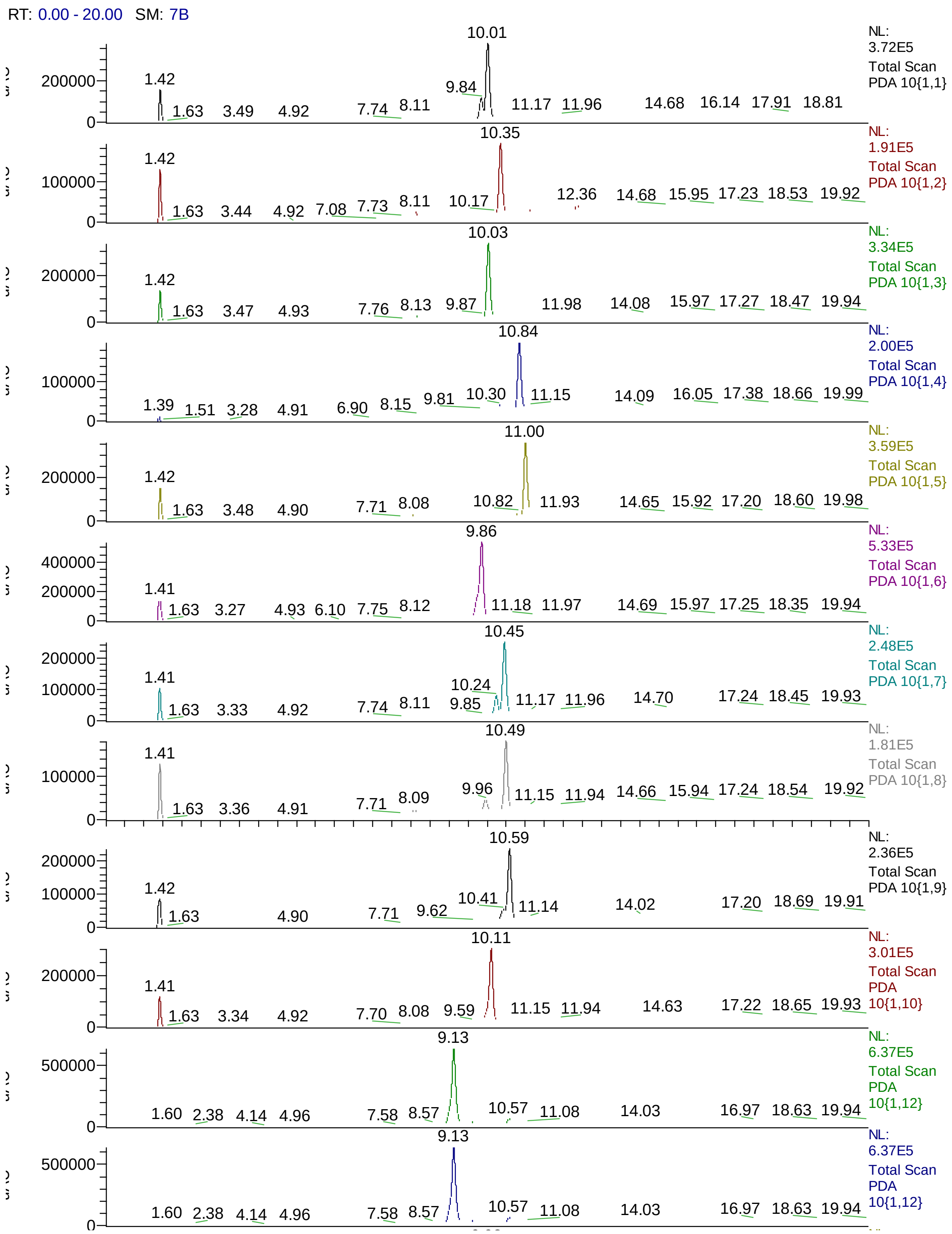
NL: 4.40E5 Total Scan PDA 8{4,1}
NL: 3.98E5 Total Scan PDA 8{4,2}
NL: 4.88E5 Total Scan PDA 8{4,3}
NL: 3.88E5 Total Scan PDA 8{4,4}
NL: 3.37E5 Total Scan PDA 8{4,5}
NL: 4.34E5 Total Scan PDA 8{4,6}
NL: 3.66E5 Total Scan PDA 8{4,7}
NL: 4.27E5 Total Scan PDA 8{4,8}
NL: 3.30E5 Total Scan PDA 8{4,9}
NL: 3.52E5 Total Scan PDA 8{4,10}
NL: 3.10E5 Total Scan PDA 8{4,11}
NL: 3.12E5 Total Scan PDA 8{4,12}
10.11
10.62
10.30
10.41
10.20
11.02
10.59
10.81
10.95
10.44
11.09
9.48
Time (min)

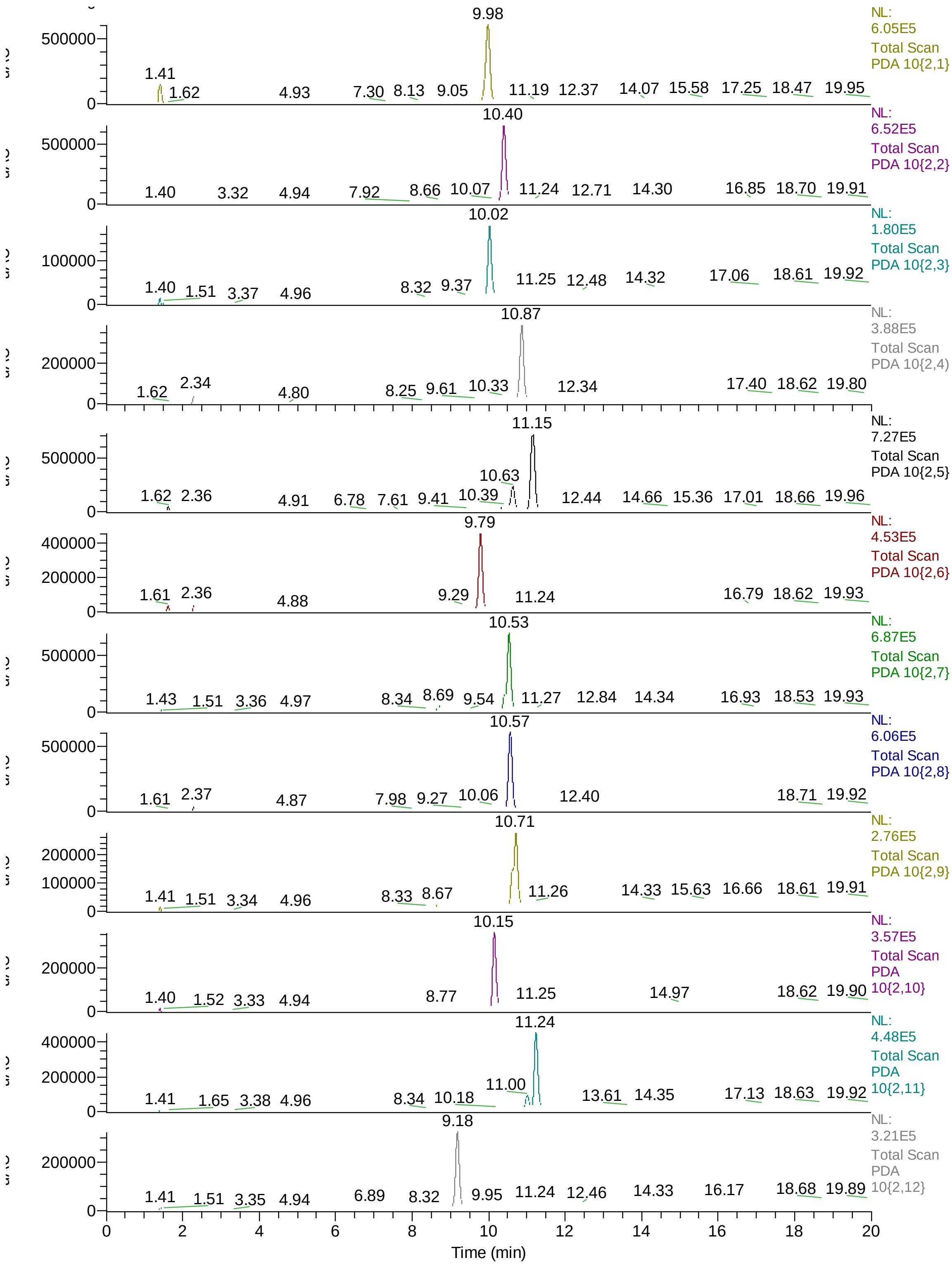
Path III and IV: Diels-Alder reaction and aromatization of Diels-Alder product



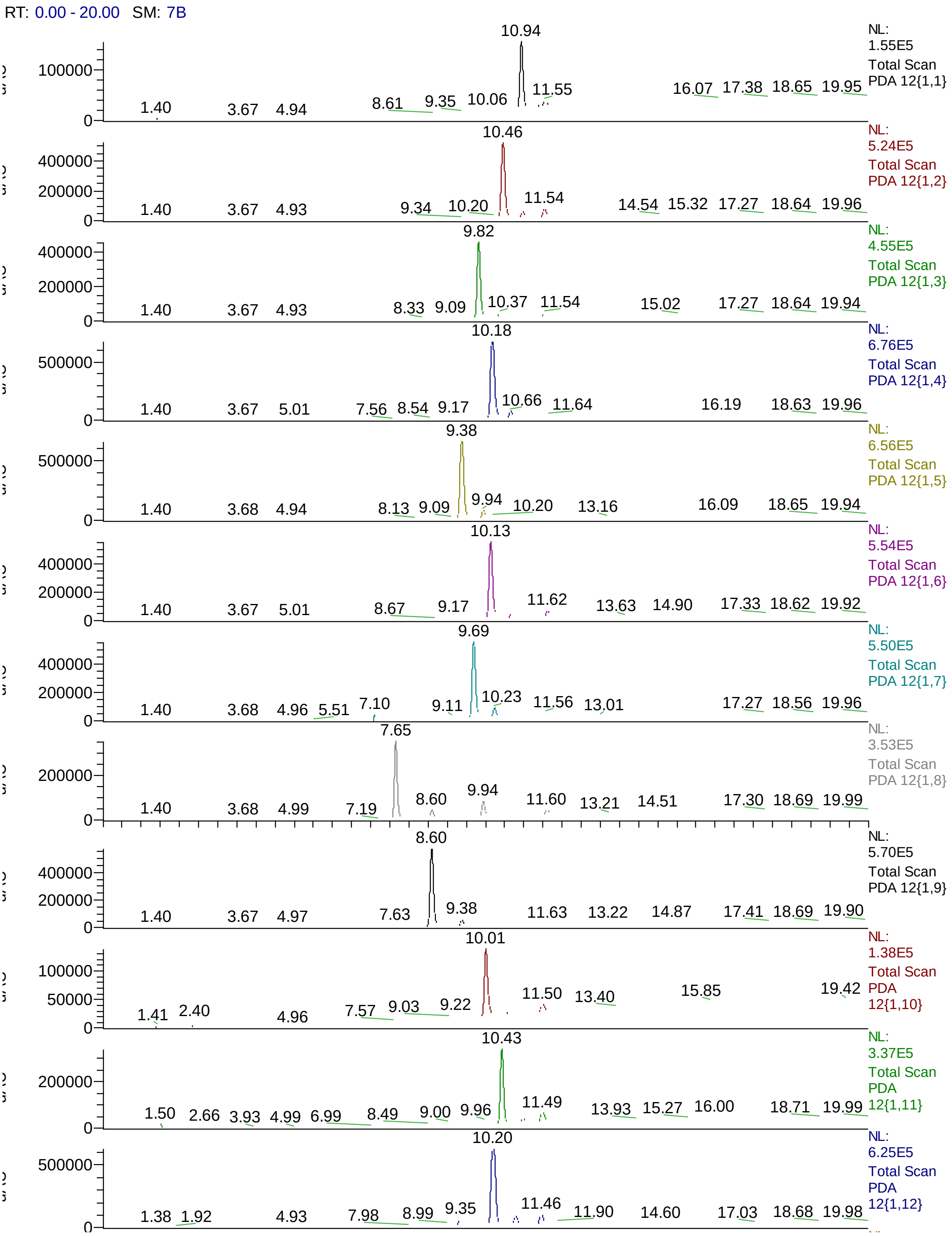


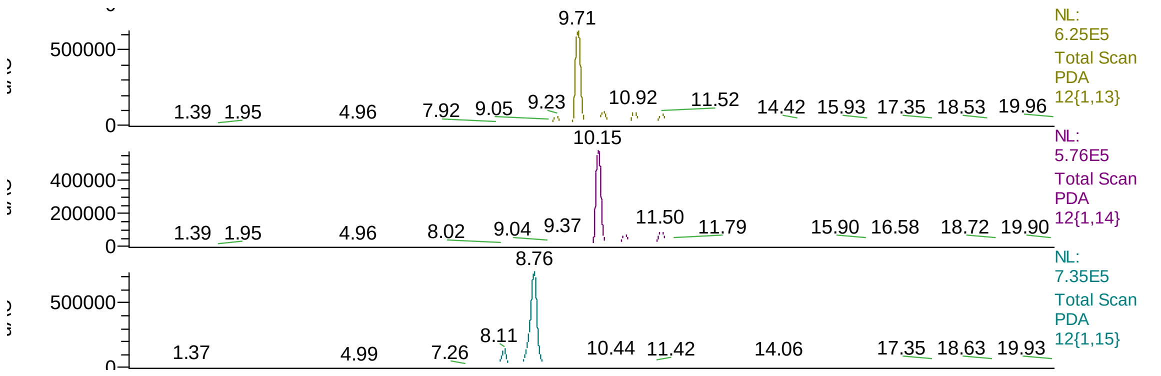

NL: 3.02E5 Total Scan PDA 9{4,1}
10.31
1.52 2.46 3.20 4.93 9.60 9.97 11.29 14.05 18.64 19.93
NL: 2.41E5 Total Scan PDA 9{4,2}
10.50
1.40 3.35 4.92 9.09 10.19 12.57 14.08 19.76
NL: 1.94E5 Total Scan PDA 9{4,3}
10.29
1.34 2.14 4.90 6.84 9.18 9.94 12.53 13.98 18.51 19.94
NL: 1.61E5 Total Scan PDA 9{4,4}
10.85
1.51 4.92 9.22 10.53 12.04 14.02 16.16 18.65 19.95
NL: 3.32E5 Total Scan PDA 9{4,5}
11.06
1.38 1.64 4.92 9.30 10.84 11.32 15.45 17.23 18.64 19.94
NL: 4.86E5 Total Scan PDA 9{4,6}
10.28
1.42 1.64 5.02 8.14 9.50 9.91 11.09 14.09 18.68 19.97
NL: 2.77E5 Total Scan PDA 9{4,7}
10.55
1.38 1.63 4.92 8.06 9.18 10.24 11.71 14.01 18.60 19.99
NL: 4.46E5 Total Scan PDA 9{4,8}
10.66
1.42 1.63 4.96 9.64 10.33 11.72 14.03 17.27 18.64 19.95
NL: 2.70E5 Total Scan PDA 9{4,9}
10.65
1.47 1.66 3.88 4.85 9.03 10.42 10.85 11.75 16.91 18.68 19.98
NL: 2.68E5 Total Scan PDA 9{4,10}
10.41
1.51 4.91 9.20 10.06 11.20 12.55 14.00 18.71 19.92
NL: 1.48E5 Total Scan PDA 9{4,11}
10.76
1.40 1.58 3.17 4.80 6.80 9.42 10.53 10.95 13.84 15.99 17.37 18.68 19.98
NL: 2.32E5 Total Scan PDA 9{4,12}
9.72
1.39 1.60 4.86 6.81 8.69 9.18 11.01 12.13 13.93 16.02 17.40 18.70 19.90
0 2 4 6 8 10 12 14 16 18 20
Time (min)


RT: 0.00 - 20.00 SM: 7B
NL: 3.72E5 Total Scan PDA 10{1,1}
NL: 1.91E5 Total Scan PDA 10{1,2}
NL: 3.34E5 Total Scan PDA 10{1,3}
NL: 2.00E5 Total Scan PDA 10{1,4}
NL: 3.59E5 Total Scan PDA 10{1,5}
NL: 5.33E5 Total Scan PDA 10{1,6}
NL: 2.48E5 Total Scan PDA 10{1,7}
NL: 1.81E5 Total Scan PDA 10{1,8}
NL: 2.36E5 Total Scan PDA 10{1,9}
NL: 3.01E5 Total Scan PDA 10{1,10}
NL: 6.37E5 Total Scan PDA 10{1,12}
NL: 6.37E5 Total Scan PDA 10{1,12}

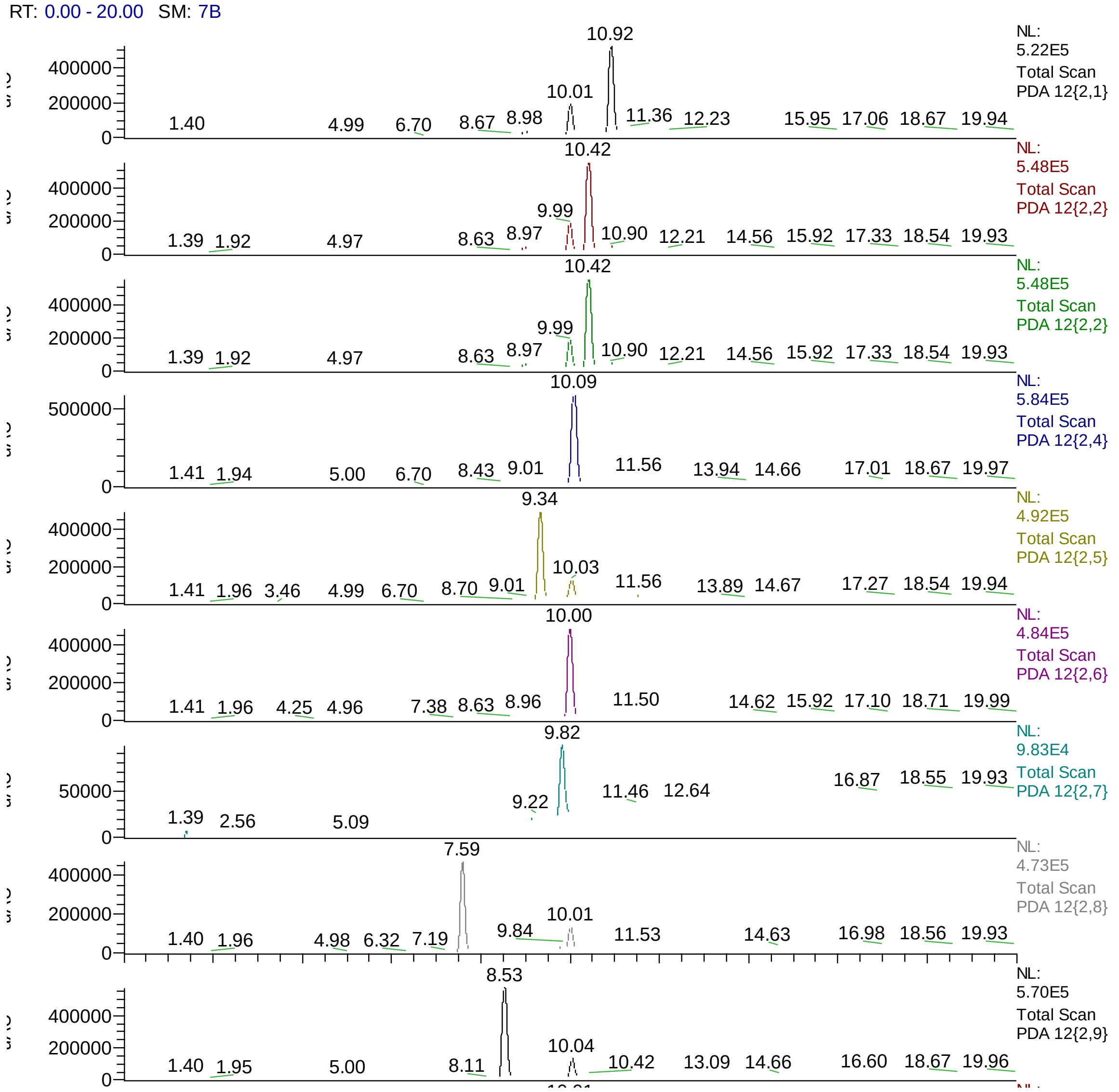

NL: 6.05E5 Total Scan PDA 10{2,1}
NL: 6.52E5 Total Scan PDA 10{2,2}
NL: 1.80E5 Total Scan PDA 10{2,3}
NL: 3.88E5 Total Scan PDA 10{2,4}
NL: 7.27E5 Total Scan PDA 10{2,5}
NL: 4.53E5 Total Scan PDA 10{2,6}
NL: 6.87E5 Total Scan PDA 10{2,7}
NL: 6.06E5 Total Scan PDA 10{2,8}
NL: 2.76E5 Total Scan PDA 10{2,9}
NL: 3.57E5 Total Scan PDA 10{2,10}
NL: 4.48E5 Total Scan PDA 10{2,11}
NL: 3.21E5 Total Scan PDA 10{2,12}
Time (min)

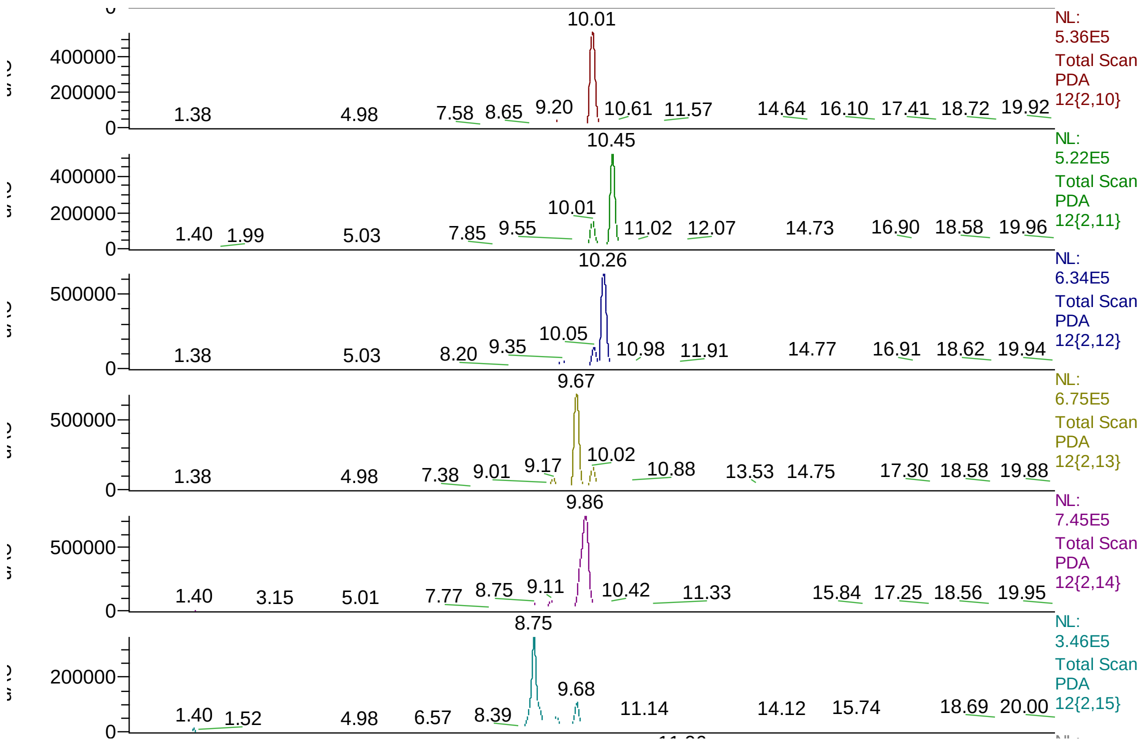
Path V: Copper(I) catalyzed alkyne-azide cycloaddition(CuAAC).



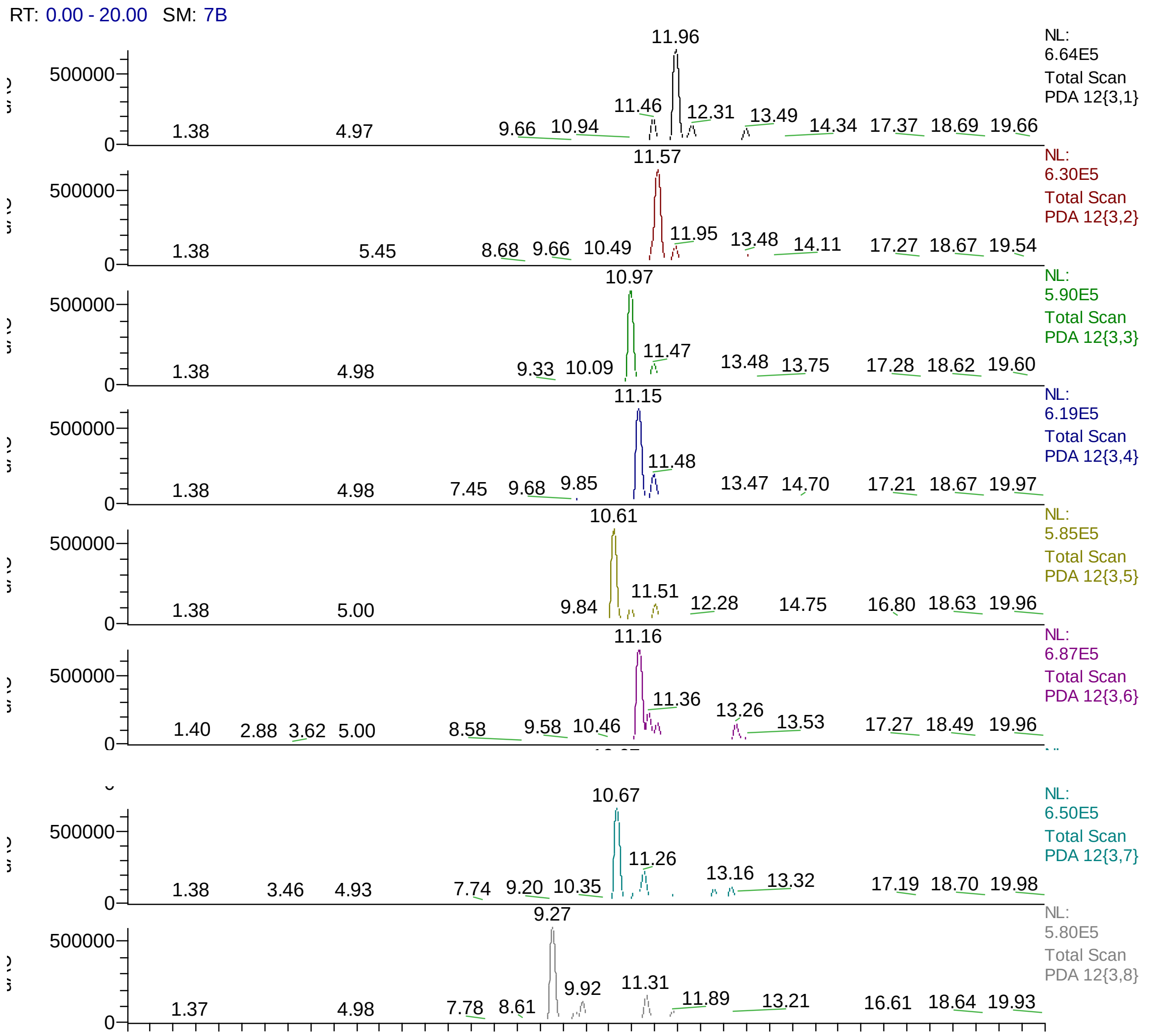


RT: 0.00 - 20.00 SM: 7B

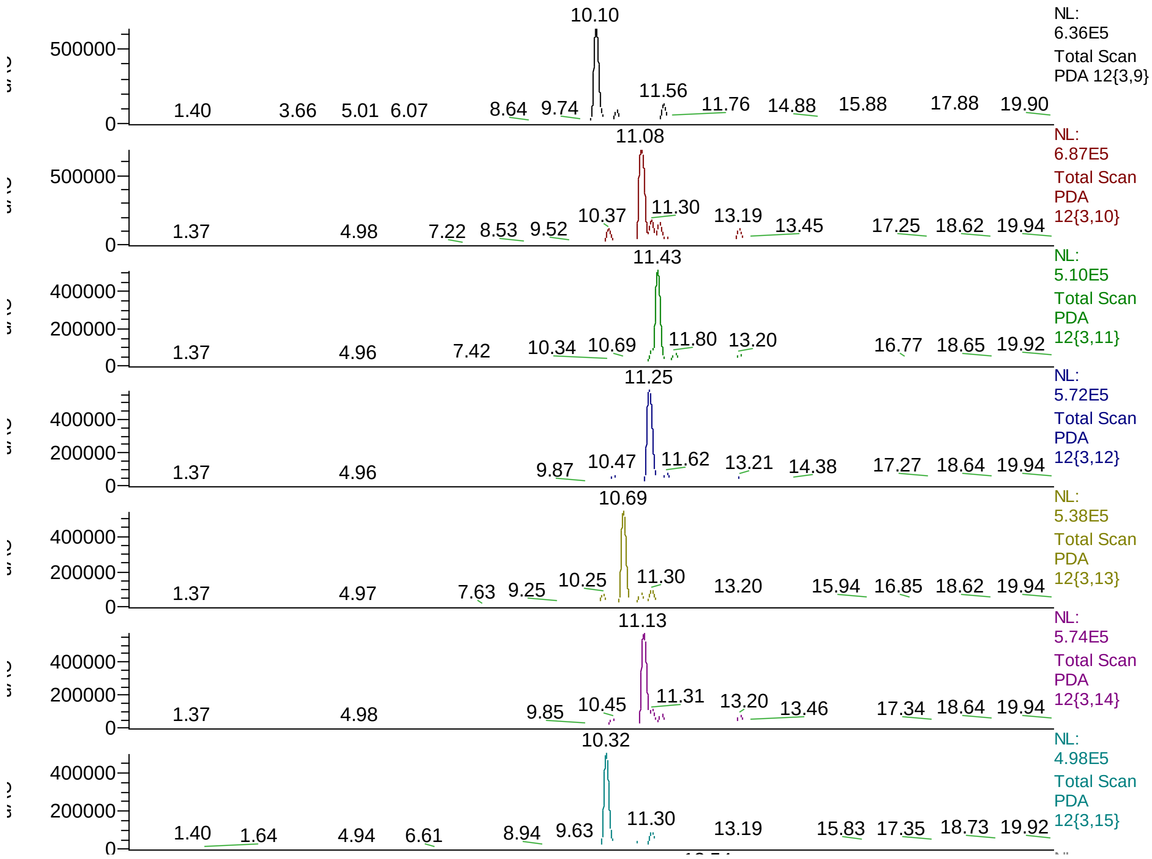


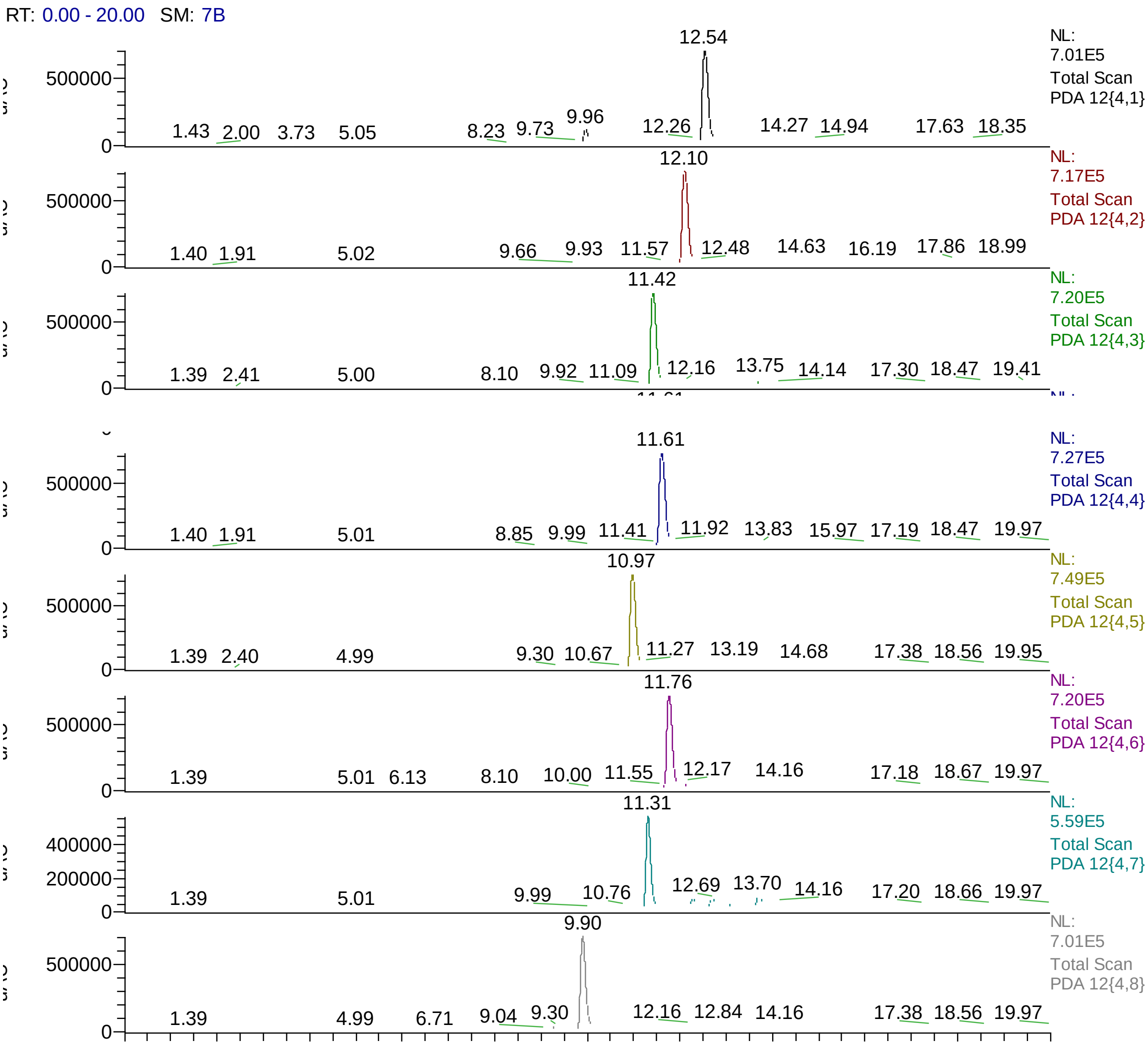


10.01
400000
200000
0
1.38
4.98
7.58
8.65
9.20
10.61
11.57
14.64
16.10
17.41
18.72
19.92
NL: 5.36E5
Total Scan PDA
12{2,10}
10.45
1.40
1.99
5.03
7.85
9.55
10.01
11.02
12.07
14.73
16.90
18.58
19.96
NL: 5.22E5
Total Scan PDA
12{2,11}
10.26
500000
8.20
9.35
10.05
10.98
11.91
14.77
16.91
18.62
19.94
NL: 6.34E5
Total Scan PDA
12{2,12}
9.67
7.38
9.01
9.17
10.02
10.88
13.53
14.75
17.30
19.88
NL: 6.75E5
Total Scan PDA
12{2,13}
9.86
3.15
5.01
7.77
8.75
9.11
10.42
11.33
15.84
17.25
18.56
19.95
NL: 7.45E5
Total Scan PDA
12{2,14}
8.75
1.52
6.57
8.39
9.68
11.14
14.12
15.74
18.69
20.00
NL: 3.46E5
Total Scan PDA
12{2,15}

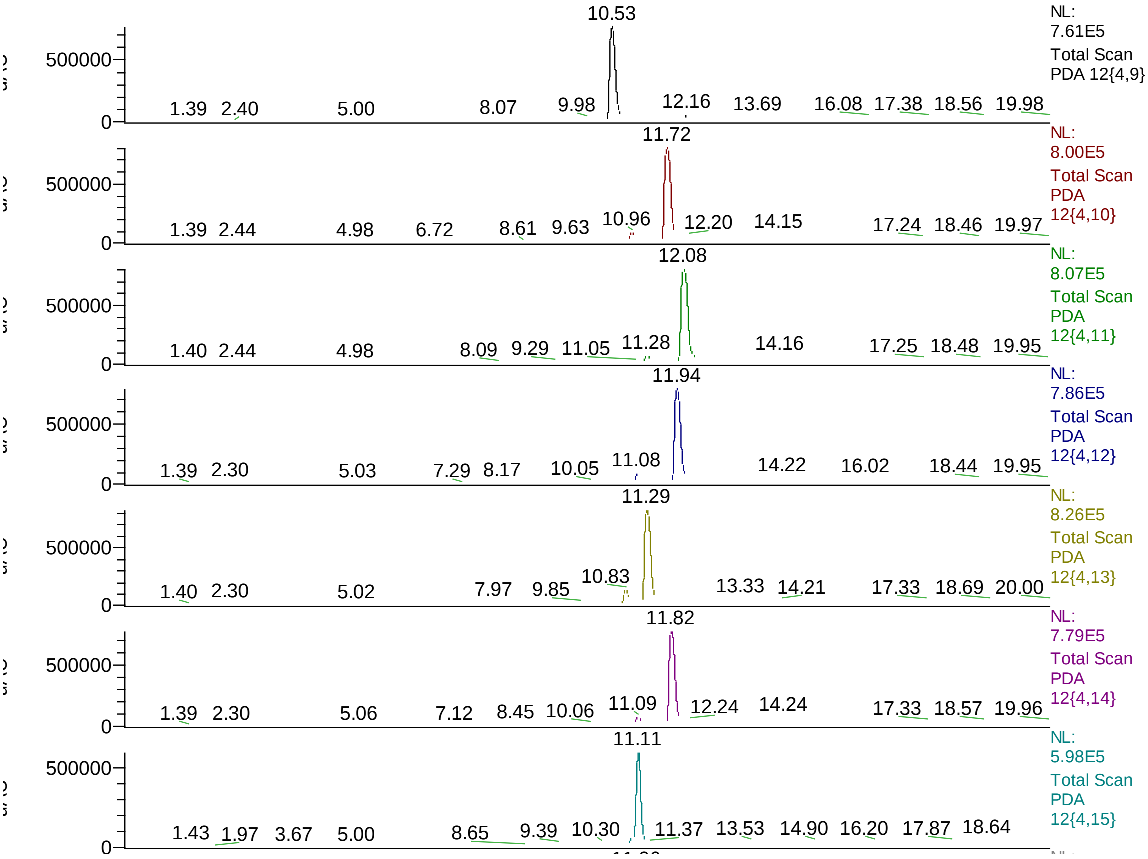


RT: 0.00 - 20.00 SM: 7B
NL: 6.64E5 Total Scan PDA 12{3,1}
11.96
11.46
12.31
13.49
1.38
4.97
9.66
10.94
14.34
17.37
18.69
19.66
NL: 6.30E5 Total Scan PDA 12{3,2}
11.57
1.38
5.45
8.68
9.66
10.49
11.95
13.48
14.11
17.27
18.67
19.54
NL: 5.90E5 Total Scan PDA 12{3,3}
10.97
1.38
4.98
9.33
10.09
11.47
13.48
13.75
17.28
18.62
19.60
NL: 6.19E5 Total Scan PDA 12{3,4}
11.15
1.38
4.98
7.45
9.68
9.85
11.48
13.47
14.70
17.21
18.67
19.97
NL: 5.85E5 Total Scan PDA 12{3,5}
10.61
1.38
5.00
9.84
11.51
12.28
14.75
16.80
18.63
19.96
NL: 6.87E5 Total Scan PDA 12{3,6}
11.16
1.40
2.88
3.62
5.00
8.58
9.58
10.46
11.36
13.26
13.53
17.27
18.49
19.96
NL: 6.50E5 Total Scan PDA 12{3,7}
10.67
1.38
3.46
4.93
7.74
9.20
10.35
11.26
13.16
13.32
17.19
18.70
19.98
NL: 5.80E5 Total Scan PDA 12{3,8}
9.27
1.37
4.98
7.78
8.61
9.92
11.31
11.89
13.21
16.61
18.64
19.93
500000
0


NL: 6.36E5
Total Scan PDA 12{3,9}
NL: 6.87E5
Total Scan PDA 12{3,10}
NL: 5.10E5
Total Scan PDA 12{3,11}
NL: 5.72E5
Total Scan PDA 12{3,12}
NL: 5.38E5
Total Scan PDA 12{3,13}
NL: 5.74E5
Total Scan PDA 12{3,14}
NL: 4.98E5
Total Scan PDA 12{3,15}

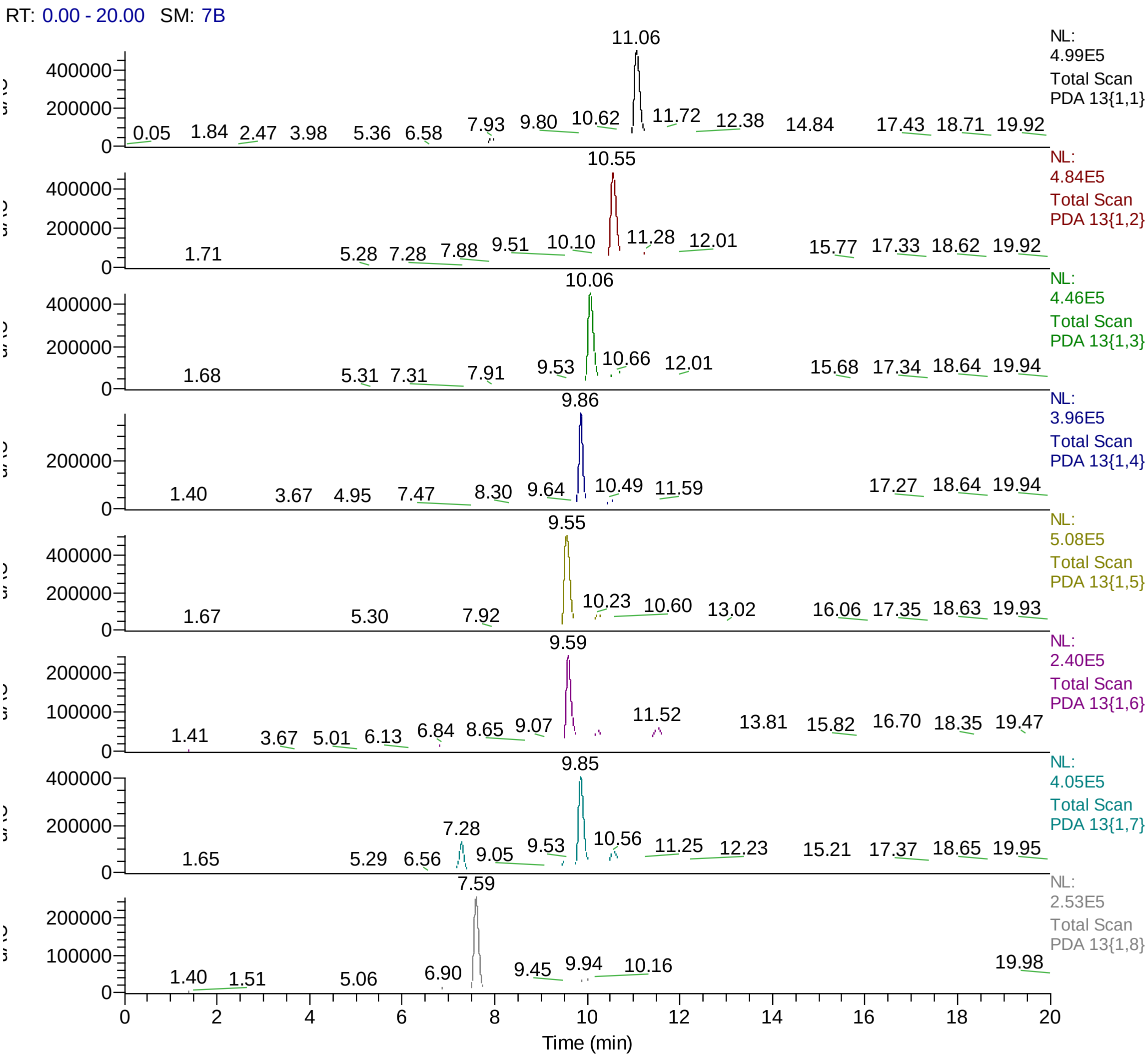


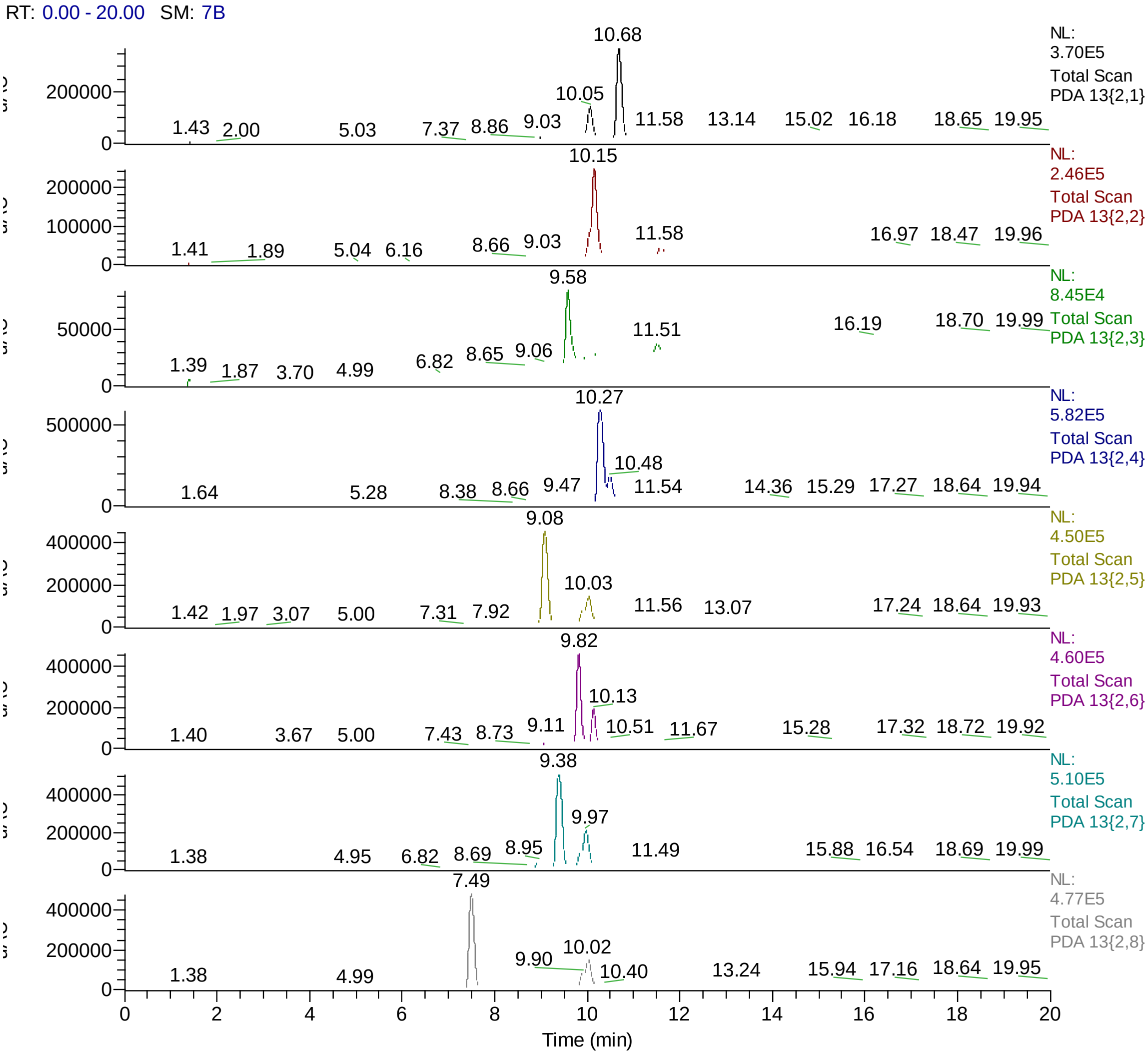
RT: 0.00 - 20.00 SM: 7B
NL: 7.01E5 Total Scan PDA 12{4,1}
NL: 7.17E5 Total Scan PDA 12{4,2}
NL: 7.20E5 Total Scan PDA 12{4,3}
NL: 7.27E5 Total Scan PDA 12{4,4}
NL: 7.49E5 Total Scan PDA 12{4,5}
NL: 7.20E5 Total Scan PDA 12{4,6}
NL: 5.59E5 Total Scan PDA 12{4,7}
NL: 7.01E5 Total Scan PDA 12{4,8}
12.54
12.10
11.42
11.61
10.97
11.76
11.31
9.90

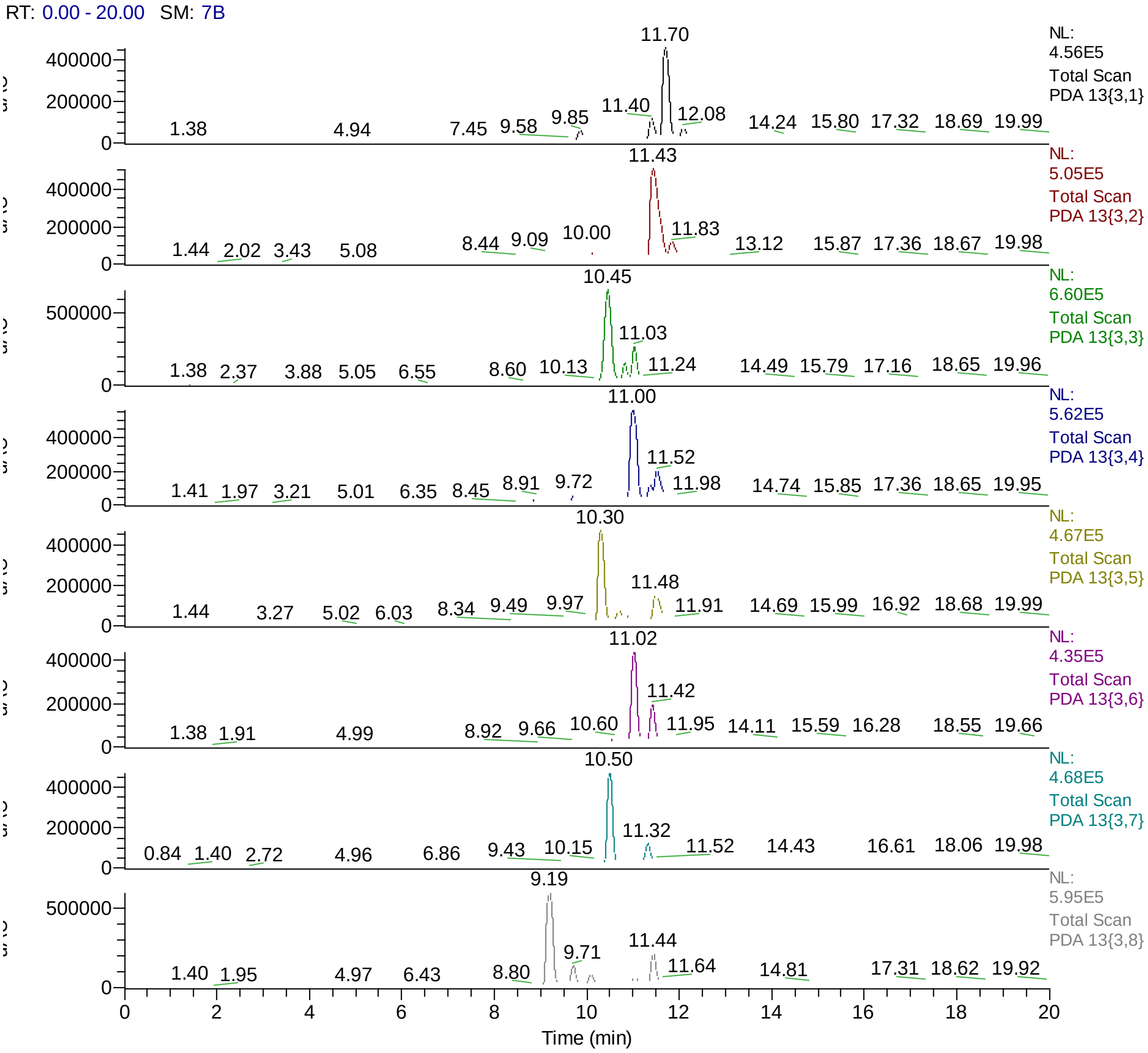


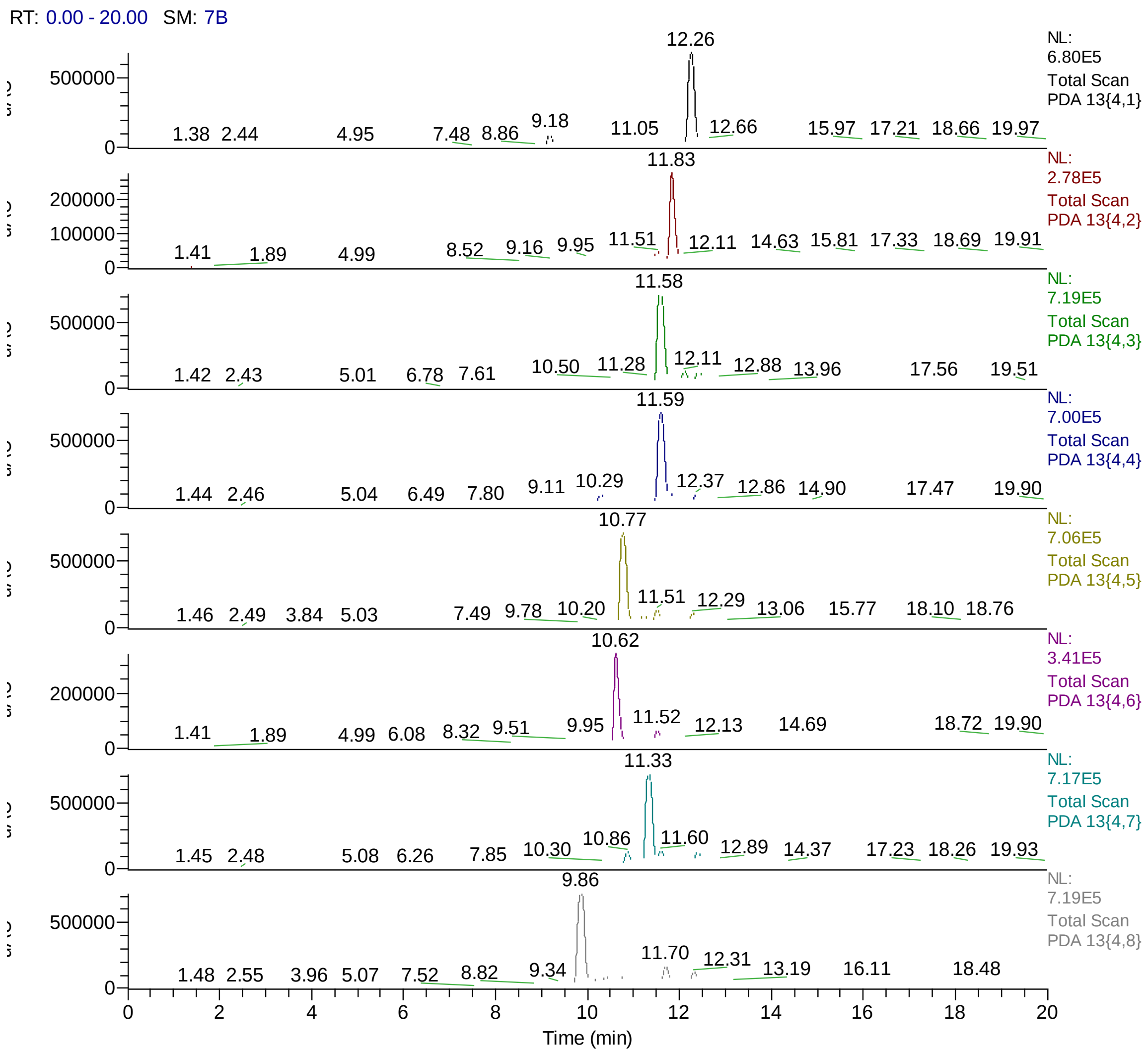
NL: 7.61E5 Total Scan PDA 12{4,9}
NL: 8.00E5 Total Scan PDA 12{4,10}
NL: 8.07E5 Total Scan PDA 12{4,11}
NL: 7.86E5 Total Scan PDA 12{4,12}
NL: 8.26E5 Total Scan PDA 12{4,13}
NL: 7.79E5 Total Scan PDA 12{4,14}
NL: 5.98E5 Total Scan PDA 12{4,15}

Path VI: Ruthenium(II) catalyzed alkyne-azide cycloaddition(RuAAC).




RT: 0.00 - 20.00 SM: 7B
NL: 3.70E5
Total Scan
PDA 13{2,1}
NL: 2.46E5
Total Scan
PDA 13{2,2}
NL: 8.45E4
Total Scan
PDA 13{2,3}
NL: 5.82E5
Total Scan
PDA 13{2,4}
NL: 4.50E5
Total Scan
PDA 13{2,5}
NL: 4.60E5
Total Scan
PDA 13{2,6}
NL: 5.10E5
Total Scan
PDA 13{2,7}
NL: 4.77E5
Total Scan
PDA 13{2,8}
Time (min)


RT: 0.00 - 20.00 SM: 7B
NL: 4.56E5 Total Scan PDA 13{3,1}
11.70
1.38 4.94 7.45 9.58 9.85 11.40 12.08 14.24 15.80 17.32 18.69 19.99
NL: 5.05E5 Total Scan PDA 13{3,2}
11.43
1.44 2.02 3.43 5.08 8.44 9.09 10.00 11.83 13.12 15.87 17.36 18.67 19.98
NL: 6.60E5 Total Scan PDA 13{3,3}
10.45
1.38 2.37 3.88 5.05 6.55 8.60 10.13 11.03 11.24 14.49 15.79 17.16 18.65 19.96
NL: 5.62E5 Total Scan PDA 13{3,4}
11.00
1.41 1.97 3.21 5.01 6.35 8.45 8.91 9.72 11.52 11.98 14.74 15.85 17.36 18.65 19.95
NL: 4.67E5 Total Scan PDA 13{3,5}
10.30
1.44 3.27 5.02 6.03 8.34 9.49 9.97 11.48 11.91 14.69 15.99 16.92 18.68 19.99
NL: 4.35E5 Total Scan PDA 13{3,6}
11.02
1.38 1.91 4.99 8.92 9.66 10.60 11.42 11.95 14.11 15.59 16.28 18.55 19.66
NL: 4.68E5 Total Scan PDA 13{3,7}
10.50
0.84 1.40 2.72 4.96 6.86 9.43 10.15 11.32 11.52 14.43 16.61 18.06 19.98
NL: 5.95E5 Total Scan PDA 13{3,8}
9.19
1.40 1.95 4.97 6.43 8.80 9.71 11.44 11.64 14.81 17.31 18.62 19.92
400000
200000
500000
0
0 2 4 6 8 10 12 14 16 18 20
Time (min)


RT: 0.00 - 20.00 SM: 7B
NL: 6.80E5
Total Scan PDA 13{4,1}
NL: 2.78E5
Total Scan PDA 13{4,2}
NL: 7.19E5
Total Scan PDA 13{4,3}
NL: 7.00E5
Total Scan PDA 13{4,4}
NL: 7.06E5
Total Scan PDA 13{4,5}
NL: 3.41E5
Total Scan PDA 13{4,6}
NL: 7.17E5
Total Scan PDA 13{4,7}
NL: 7.19E5
Total Scan PDA 13{4,8}
Time (min)