Supporting Information

Synthesis of 4-aryl-3,4-dihydrocoumarins and 4-aryl-4*H*-chromenes *via* $Er(OTf)_3$-catalyzed cascade reactions of *p*-quinone methides with 1,3-dicarbonyl compounds

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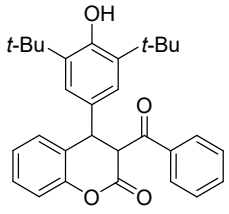
1. General methods of synthesis

All commercially available solvents and reagents were used without further purification unless otherwise specified. Reactions were monitored by thin layer chromatography (TLC) on Silica Gel 60 F254 plates. Purification was performed by flash column chromatography separations using silica gel (200-300 mesh). Melting points (mp) were measured on a X4 micro melting point apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECZS 400MHz NMR spectrometer with Me_4Si as the internal standard in DMSO-d_6 or $CDCl_3$. High resolution mass spectra (HRMS) were recorded on an Agilent 6500 Time-of-Flight (TOF) LC/MS system.

2. General procedure for preparation of 7a-7o and 8a-8o

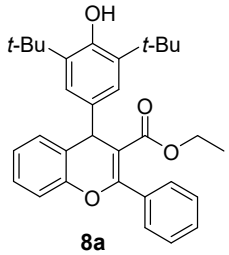
To a solution of *p*-QMs **5** (1.0 mmol) and β-ketoesters **6** (1.1 mmol) in toluene (3 mL) was added $Er(OTf)_3$ (123 mg, 0.2 mmol). The reaction was heated and stirred at 110 °C until completion (monitored by TLC). The reaction system was quenched by H_2O and extracted with ethyl acetate after removing toluene. The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by a short silica gel column filtration (petroleum ether/ethyl acetate) to give the desired products **7a-7o** and **8a-8o**.



7a

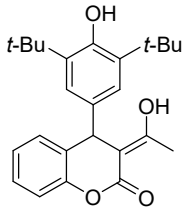
3-Benzoyl-4-(3,5-di-tert-butyl-4-hydroxyphenyl)chroman-2-one (7a). White solid (148 mg, 68% yield, mp 163-164 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.94 (d, J = 7.8 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.30 (t, J = 7.7 Hz, 1H), 7.17 (d, J = 8.0 Hz, 1H), 7.07 (t, J = 7.5 Hz, 1H), 6.91 (s, 2H), 6.88 (s, 1H), 6.81 (d, J = 7.6 Hz, 1H), 5.68 (d, J = 9.1 Hz, 1H), 4.68 (d, J = 9.1 Hz, 1H), 1.22 (s, 18H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 195.92, 166.90, 153.50, 151.05, 140.08, 136.25, 134.48, 129.78, 129.33, 129.23, 129.08, 128.72, 126.54, 125.32, 124.75, 116.85, 53.13, 43.79, 35.08, 30.77. HRMS calcd for $C_{30}H_{32}NaO_4$ $[M + Na]^+$ *m/z*

479.21928, found 479.21829.



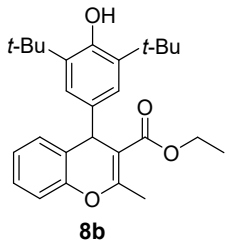
8a

Ethyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenyl-4H-chromene-3-carboxylate (8a). Yellow oil (53 mg, 22% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.46 – 7.40 (m, 3H), 7.19 (ddd, *J* = 15.1, 8.0, 1.7 Hz, 2H), 7.14 (s, 2H), 7.11 – 7.04 (m, 2H), 5.06 (s, 1H), 5.06 (s, 1H), 3.91 (q, *J* = 7.1 Hz, 2H), 1.40 (s, 18H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.21, 158.85, 152.58, 150.29, 136.74, 135.77, 135.65, 129.54, 129.19, 128.86, 128.03, 127.48, 125.76, 124.83, 124.25, 116.51, 108.23, 60.21, 42.08, 34.42, 30.43, 13.77. HRMS calcd for $C_{32}H_{36}NaO_4$ $[M + Na]^+$ *m/z* 507.25058, found 507.25010.



7b

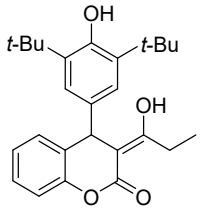
4-(3,5-Di-tert-butyl-4-hydroxyphenyl)-3-(1-hydroxyethylidene)chroman-2-one (7b). White solid (28 mg, 14% yield, mp 161-162 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (ddt, *J* = 7.5, 3.3, 1.7 Hz, 2H), 7.11 – 7.03 (m, 2H), 6.93 (s, 2H), 5.08 (s, 1H), 4.74 (s, 1H), 2.09 (s, 3H), 1.36 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.60, 169.76, 152.67, 149.47, 136.29, 135.72, 128.85, 128.10, 126.01, 124.98, 123.35, 117.15, 97.26, 43.11, 34.39, 30.28, 19.66. HRMS calcd for $C_{25}H_{30}NaO_4$ $[M + Na]^+$ *m/z* 417.20363, found 417.20425.



8b

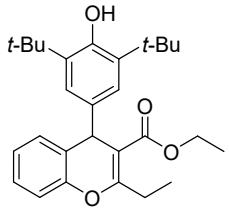
Ethyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-methyl-4H-chromene-3-carboxylate (8b). White solid (158 mg, 75% yield, mp 159-160 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.18 – 7.12 (m, 2H), 7.08 – 6.98 (m, 2H), 6.88 (s, 2H),

6.74 (s, 1H), 4.87 (s, 1H), 4.08 – 3.89 (m, 2H), 2.37 (s, 3H), 1.26 (s, 18H), 1.06 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.95, 159.47, 152.78, 149.63, 139.60, 137.96, 129.63, 128.10, 125.76, 125.14, 123.81, 116.34, 107.11, 60.29, 40.80, 34.94, 30.84, 19.34, 14.47. HRMS calcd for $C_{27}H_{34}NaO_4$ $[M + Na]^+$ *m/z* 445.23493, found 445.23522.



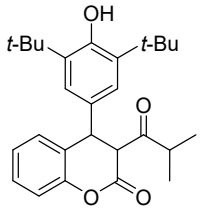
7c

4-(3,5-Di-tert-butyl-4-hydroxyphenyl)-3-(1-hydroxypropylidene)chroman-2-one (7c). White solid (76 mg, 37% yield, mp 157-158 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.16 (m, 2H), 7.06 (td, J = 7.9, 7.3, 1.3 Hz, 2H), 6.94 (s, 2H), 5.07 (s, 1H), 4.81 (s, 1H), 2.54 – 2.29 (m, 2H), 1.36 (s, 18H), 0.99 (t, J = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.78, 170.09, 152.64, 149.40, 136.31, 136.27, 128.85, 128.06, 126.07, 124.93, 123.36, 117.13, 96.25, 42.71, 34.41, 30.29, 25.92, 10.15. HRMS calcd for $C_{26}H_{32}NaO_4$ $[M + Na]^+$ *m/z* 431.21928, found 431.21910.

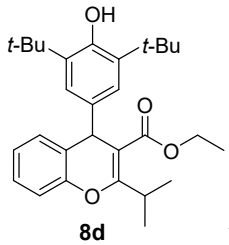


8c

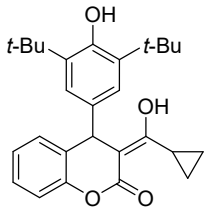
Ethyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-ethyl-4H-chromene-3-carboxylate (8c). White solid (90 mg, 41% yield, mp 168-169 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.08 (m, 2H), 7.04 – 6.96 (m, 4H), 4.99 (s, 1H), 4.91 (s, 1H), 4.18 – 4.01 (m, 2H), 2.99 (dq, J = 13.4, 7.5 Hz, 1H), 2.78 (dtd, J = 13.1, 7.8, 7.0 Hz, 1H), 1.36 (s, 18H), 1.28 (t, J = 7.5 Hz, 3H), 1.18 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.22, 164.81, 152.31, 149.91, 137.48, 135.55, 129.11, 127.23, 125.85, 124.44, 124.17, 116.12, 106.21, 60.06, 41.30, 34.36, 30.37, 26.03, 14.26, 12.13. HRMS calcd for $C_{28}H_{36}NaO_4$ $[M + Na]^+$ *m/z* 459.25058, found 459.25081.



7d **4-(3,5-Di-tert-butyl-4-hydroxyphenyl)-3-isobutyrylchroman-2-one (7d)**. White solid (46 mg, 22% yield, mp 144-145 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 1H), 7.12 – 7.05 (m, 2H), 7.01 (dt, *J* = 7.6, 1.4 Hz, 1H), 6.90 (s, 2H), 5.18 (s, 1H), 4.62 (d, *J* = 8.7 Hz, 1H), 4.13 (d, *J* = 8.7 Hz, 1H), 2.68 (hept, *J* = 6.9 Hz, 1H), 1.37 (s, 18H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.79 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.99, 165.88, 153.32, 150.92, 136.56, 129.52, 128.93, 128.76, 125.27, 125.00, 124.94, 116.78, 57.95, 43.34, 41.37, 34.46, 30.30, 17.54, 17.45. HRMS calcd for $C_{27}H_{34}NaO_4$ $[M + Na]^+$ *m/z* 445.23493, found 445.23558.

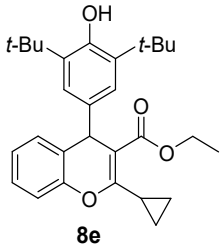


8d **Ethyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-isopropyl-4H-chromene-3-carboxylate (8d)**. White solid (131 mg, 58% yield, mp 185-186 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (dd, *J* = 8.0, 6.3 Hz, 2H), 7.05 – 6.96 (m, 4H), 5.00 (s, 1H), 4.89 (s, 1H), 4.08 (p, *J* = 7.2 Hz, 2H), 4.04 – 3.96 (m, 1H), 1.36 (s, 18H), 1.32 (d, *J* = 6.9 Hz, 3H), 1.22 – 1.15 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.32, 167.01, 152.33, 149.89, 137.52, 135.56, 128.96, 127.19, 126.08, 124.40, 124.08, 116.06, 105.46, 60.07, 41.64, 34.38, 30.39, 29.68, 20.18, 19.30, 14.25. HRMS calcd for $C_{29}H_{38}NaO_4$ $[M + Na]^+$ *m/z* 473.26623, found 473.26672.



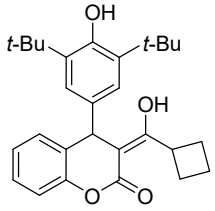
7e **3-(Cyclopropyl(hydroxy)methylene)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)chroman-2-one (7e)**. White solid (38 mg, 18% yield, mp 184-185 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 1H), 7.24 – 7.19 (m, 1H), 7.10 (ddt, *J* =

6.2, 3.0, 1.5 Hz, 2H), 6.95 (s, 2H), 5.07 (s, 1H), 5.05 (s, 1H), 1.97 (dddd, *J* = 12.7, 8.0, 4.7, 1.5 Hz, 1H), 1.35 (s, 18H), 1.27 (dddd, *J* = 9.9, 6.6, 3.9, 2.2 Hz, 1H), 1.08 (dddd, *J* = 9.8, 6.8, 4.7, 3.5 Hz, 1H), 0.98 – 0.84 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.60, 170.01, 152.54, 149.87, 136.11, 135.79, 128.96, 128.11, 125.96, 124.80, 123.41, 117.10, 96.02, 41.94, 34.44, 30.30, 13.19, 9.93, 9.22. HRMS calcd for $C_{27}H_{32}NaO_4$ [M + Na]$^+$ *m/z* 443.21928, found 443.21936.



8e

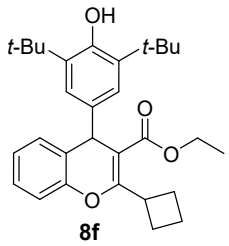
Ethyl 2-cyclopropyl-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-4H-chromene-3-carboxylate (8e). White solid (135 mg, 60% yield, mp 160-161 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (ddd, *J* = 7.5, 6.2, 1.7 Hz, 2H), 7.02 – 6.94 (m, 3H), 6.92 (dd, *J* = 8.5, 1.3 Hz, 1H), 4.99 (s, 1H), 4.94 (s, 1H), 4.14 (qd, *J* = 7.1, 1.0 Hz, 2H), 3.22 (tt, *J* = 8.4, 5.1 Hz, 1H), 1.36 (s, 18H), 1.23 (t, *J* = 7.1 Hz, 4H), 1.13 – 1.05 (m, 1H), 0.94 – 0.81 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.87, 163.31, 152.28, 149.82, 137.39, 135.49, 128.97, 127.18, 126.58, 124.51, 124.10, 115.80, 106.72, 60.10, 41.68, 34.35, 30.35, 14.38, 11.86, 6.85, 6.61. HRMS calcd for $C_{29}H_{36}NaO_4$ [M + Na]$^+$ *m/z* 471.25058, found 471.25086.



7f

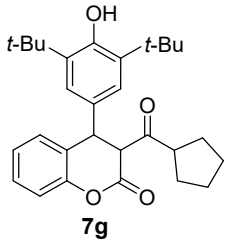
3-(Cyclobutyl(hydroxy)methylene)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)chroman-2-one (7f). White solid (61 mg, 28% yield, mp 158-159 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.15 (m, 2H), 7.09 – 7.03 (m, 2H), 6.92 (s, 2H), 5.06 (s, 1H), 4.81 (s, 1H), 3.47 (p, *J* = 8.5 Hz, 1H), 2.44 (dq, *J* = 11.0, 9.1 Hz, 1H), 2.21 – 2.00 (m, 2H), 1.96 – 1.77 (m, 2H), 1.60 (d, *J* = 3.6 Hz, 1H), 1.36 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.55, 170.14, 152.57, 149.36, 136.44, 136.27, 128.92, 128.02, 125.91, 124.84, 123.39, 117.10, 95.34, 42.28, 36.89, 34.42, 30.32, 25.96, 24.83, 18.31.

HRMS calcd for $C_{28}H_{34}NaO_4$ $[M + Na]^+$ *m/z* 457.23493, found 457.23496.



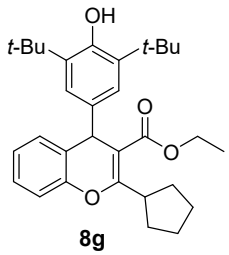
8f

Ethyl 2-cyclobutyl-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-4H-chromene-3-carboxylate (8f). White solid (136 mg, 59% yield, mp 118-119 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.08 (m, 3H), 7.01 (td, *J* = 7.3, 1.7 Hz, 1H), 6.97 (s, 2H), 4.99 (s, 1H), 4.89 (s, 1H), 4.55 – 4.44 (m, 1H), 4.09 (qd, *J* = 7.1, 3.8 Hz, 2H), 2.58 – 2.38 (m, 2H), 2.31 – 2.17 (m, 1H), 2.16 – 2.05 (m, 1H), 2.05 – 1.96 (m, 1H), 1.96 – 1.85 (m, 1H), 1.35 (s, 18H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.27, 163.55, 152.32, 150.05, 137.37, 135.52, 128.98, 127.23, 126.15, 124.49, 124.09, 116.15, 105.89, 60.07, 41.58, 36.09, 34.37, 30.36, 26.48, 25.15, 18.51, 14.29. HRMS calcd for $C_{30}H_{38}NaO_4$ $[M + Na]^+$ *m/z* 485.26623, found 485.26663.



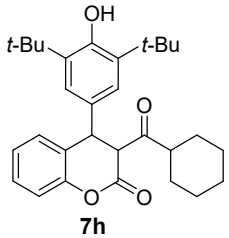
7g

3-(Cyclopentanecarbonyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)chroman-2-one (7g). White solid (56 mg, 25% yield, mp 141-142 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 1H), 7.13 – 7.02 (m, 3H), 6.89 (s, 2H), 5.17 (s, 1H), 4.66 (d, *J* = 7.8 Hz, 1H), 4.07 (d, *J* = 8.2 Hz, 1H), 3.01 (tt, *J* = 8.6, 6.9 Hz, 1H), 1.75 – 1.56 (m, 3H), 1.54 – 1.38 (m, 4H), 1.37 (s, 18H), 1.29 (dt, *J* = 12.1, 7.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.29, 165.89, 153.28, 150.91, 136.56, 129.73, 129.02, 128.74, 125.17, 125.00, 124.84, 116.78, 59.38, 51.45, 43.20, 34.45, 30.27, 28.82, 28.22, 25.90, 25.86. HRMS calcd for $C_{29}H_{36}NaO_4$ $[M + Na]^+$ *m/z* 471.25058, found 471.25104.



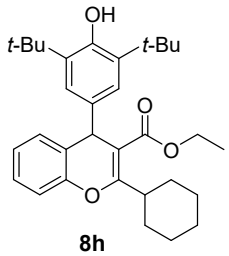
8g

Ethyl 2-cyclopentyl-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-4H-chromene-3-carboxylate (8g). White solid (119 mg, 50% yield, mp 103-104 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.09 (m, 2H), 7.00 (d, *J* = 7.3 Hz, 4H), 4.99 (s, 1H), 4.89 (s, 1H), 4.19 – 4.00 (m, 3H), 2.05 – 1.89 (m, 2H), 1.89 – 1.74 (m, 4H), 1.74 – 1.60 (m, 2H), 1.36 (s, 18H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.50, 165.69, 152.32, 150.02, 137.44, 135.54, 128.91, 127.18, 126.24, 124.36, 124.06, 116.05, 106.44, 60.05, 41.78, 40.40, 34.37, 31.03, 30.38, 30.03, 26.62, 26.58, 14.26. HRMS calcd for $C_{31}H_{40}NaO_4$ $[M + Na]^+$ *m/z* 499.28188, found 499.28216.



7h

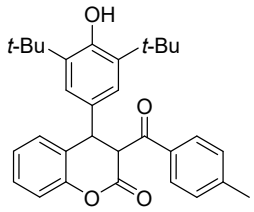
3-(Cyclohexanecarbonyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)chroman-2-one (7h). White solid (146 mg, 63% yield, mp 175-176 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (dddd, *J* = 8.0, 7.2, 1.8, 0.7 Hz, 1H), 7.12 – 7.04 (m, 2H), 7.00 (dt, *J* = 7.6, 1.4 Hz, 1H), 6.90 (s, 2H), 5.18 (s, 1H), 4.61 (d, *J* = 8.9 Hz, 1H), 4.14 (d, *J* = 8.9 Hz, 1H), 2.38 (tt, *J* = 11.0, 3.2 Hz, 1H), 1.76 – 1.64 (m, 2H), 1.58 – 1.45 (m, 3H), 1.37 (s, 18H), 1.29 – 1.02 (m, 4H), 0.97 – 0.79 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.30, 165.95, 153.31, 150.92, 136.55, 129.47, 128.88, 128.71, 125.44, 125.04, 124.96, 116.76, 57.71, 51.12, 43.36, 34.46, 30.30, 27.76, 27.60, 25.73, 25.42, 25.28. HRMS calcd for $C_{30}H_{38}NaO_4$ $[M + Na]^+$ *m/z* 485.26623, found 485.26703.



8h

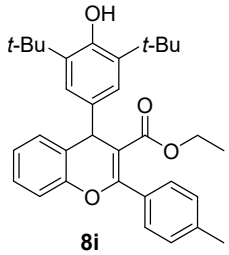
Ethyl 2-cyclohexyl-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-4H-

chromene-3-carboxylate (8h). White solid (61 mg, 25% yield, mp 124-125 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.07 (m, 2H), 7.05 – 6.94 (m, 4H), 4.98 (s, 1H), 4.89 (s, 1H), 4.17 – 3.99 (m, 2H), 3.67 (tt, *J* = 11.7, 3.5 Hz, 1H), 1.96 – 1.69 (m, 6H), 1.64 (td, *J* = 12.3, 3.6 Hz, 1H), 1.43 (d, *J* = 12.7 Hz, 1H), 1.36 (s, 18H), 1.34 – 1.21 (m, 2H), 1.18 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.37, 166.70, 152.30, 149.92, 137.56, 135.56, 128.95, 127.15, 126.10, 124.36, 124.07, 116.05, 105.60, 60.01, 41.63, 40.01, 34.37, 30.40, 30.16, 29.30, 26.48, 26.18, 26.13, 14.25. HRMS calcd for $C_{32}H_{42}NaO_4$ $[M + Na]^+$ *m/z* 513.29753, found 513.29770.



7i

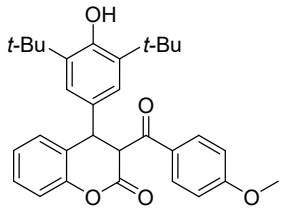
4-(3,5-Di-tert-butyl-4-hydroxyphenyl)-3-(4-methylbenzoyl)chroman-2-one (7i). White solid (73 mg, 31% yield, mp 173-174 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.74 (m, 2H), 7.32 – 7.26 (m, 1H), 7.26 – 7.24 (m, 1H), 7.23 (d, *J* = 0.9 Hz, 1H), 7.16 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.07 (td, *J* = 7.5, 1.3 Hz, 1H), 6.98 (dt, *J* = 7.5, 1.5 Hz, 1H), 6.91 (s, 2H), 5.14 (s, 1H), 4.93 (d, *J* = 6.0 Hz, 1H), 4.61 (d, *J* = 6.0 Hz, 1H), 2.40 (s, 3H), 1.34 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.58, 165.76, 153.31, 151.09, 145.03, 136.66, 133.03, 130.08, 129.62, 128.95, 128.92, 128.87, 125.00, 124.43, 124.21, 116.96, 55.54, 45.02, 34.45, 30.21, 21.79. HRMS calcd for $C_{31}H_{34}NaO_4$ $[M + Na]^+$ *m/z* 493.23493, found 493.23439.



8i

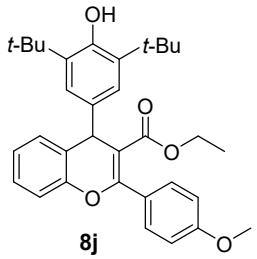
Ethyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(p-tolyl)-4H-chromene-3-carboxylate (8i). Yellow oil (72 mg, 29% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H), 7.25 (s, 1H), 7.24 – 7.22 (m, 1H), 7.18 (ddd, *J* = 15.0, 7.2, 1.6 Hz, 2H), 7.14 (s, 2H), 7.11 – 7.03 (m, 2H), 5.06 (s, 1H), 5.04 (s, 1H), 3.94 (q, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 1.40 (s, 18H), 0.95 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101

MHz, $CDCl_3$) δ 167.28, 159.10, 152.55, 150.33, 139.66, 136.85, 135.76, 132.66, 129.59, 129.15, 128.83, 128.77, 128.73, 127.44, 125.90, 124.75, 124.25, 116.51, 107.82, 60.18, 42.15, 34.41, 30.44, 21.60, 13.88. HRMS calcd for $C_{33}H_{38}NaO_4$ [M + Na]$^+$ *m/z* 521.26623, found 521.26559.



7j

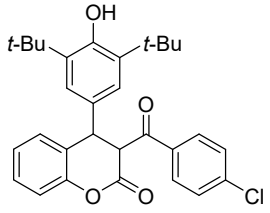
4-(3,5-Di-tert-butyl-4-hydroxyphenyl)-3-(4-methoxybenzoyl)chroman-2-one (7j). White solid (34 mg, 14% yield, mp 158-159 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 2H), 7.31 – 7.26 (m, 1H), 7.16 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.07 (td, *J* = 7.5, 1.3 Hz, 1H), 7.02 – 6.98 (m, 1H), 6.92 (s, 3H), 6.90 (d, *J* = 2.0 Hz, 1H), 5.14 (s, 1H), 4.91 (d, *J* = 5.8 Hz, 1H), 4.61 (d, *J* = 5.8 Hz, 1H), 3.86 (s, 3H), 1.34 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.24, 165.83, 164.24, 153.29, 151.05, 136.63, 131.29, 130.23, 128.88, 128.39, 125.01, 124.51, 124.18, 116.94, 114.12, 55.70, 55.32, 45.05, 34.46, 30.22. HRMS calcd for $C_{31}H_{34}NaO_5$ [M + Na]$^+$ *m/z* 509.22985, found 509.22929.



8j

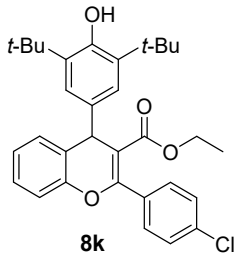
Ethyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(4-methoxyphenyl)-4H-chromene-3-carboxylate (8j). Yellow oil (154 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.19 (ddd, *J* = 15.4, 7.4, 1.7 Hz, 2H), 7.15 (s, 2H), 7.13 – 7.04 (m, 2H), 6.98 (d, *J* = 2.0 Hz, 1H), 6.96 (d, *J* = 2.1 Hz, 1H), 5.08 (s, 1H), 5.05 (s, 1H), 3.97 (q, *J* = 6.9 Hz, 2H), 3.86 (s, 3H), 1.41 (s, 18H), 0.99 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.43, 160.79, 159.00, 152.56, 150.37, 136.86, 135.76, 130.57, 129.12, 127.73, 127.46, 126.09, 124.77, 124.22, 116.49, 113.41, 107.37, 60.21, 55.44, 42.22, 34.42, 30.45, 13.99. HRMS calcd for

$C_{33}H_{38}NaO_5$ [M + Na]$^+$ *m/z* 537.26115, found 537.26105.



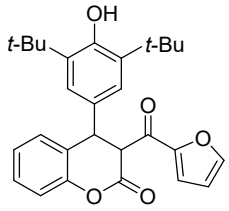
7k

3-(4-Chlorobenzoyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)chroman-2-one (7k). Brown solid (155 mg, 63% yield, mp 95-96 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 1.9 Hz, 1H), 7.78 (d, *J* = 2.0 Hz, 1H), 7.41 (d, *J* = 1.9 Hz, 1H), 7.40 (d, *J* = 2.0 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.15 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.09 (td, *J* = 7.5, 1.3 Hz, 1H), 7.00 (dt, *J* = 7.5, 1.3 Hz, 1H), 6.94 (s, 2H), 5.20 (s, 1H), 4.93 (d, *J* = 7.3 Hz, 1H), 4.66 (d, *J* = 7.3 Hz, 1H), 1.35 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.11, 165.48, 153.43, 150.96, 140.48, 136.78, 134.26, 130.13, 129.42, 129.21, 128.99, 128.79, 125.14, 124.74, 124.41, 116.96, 55.30, 44.80, 34.47, 30.24. HRMS calcd for $C_{30}H_{31}ClNaO_4$ [M + Na]$^+$ *m/z* 513.18031, found 513.18005.



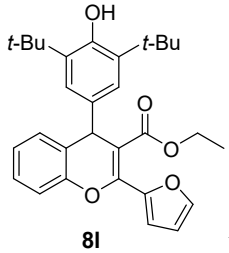
8k

Ethyl 2-(4-chlorophenyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-4H-chromene-3-carboxylate (8k). Yellow oil (49 mg, 19% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H), 7.41 – 7.36 (m, 2H), 7.17 (ddd, *J* = 7.1, 4.1, 1.4 Hz, 2H), 7.08 (s, 2H), 7.07 (d, *J* = 0.9 Hz, 1H), 7.06 – 7.03 (m, 1H), 5.04 (s, 1H), 5.02 (s, 1H), 3.92 (q, *J* = 7.1 Hz, 2H), 1.37 (s, 18H), 0.94 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.90, 157.57, 152.61, 150.14, 136.55, 135.83, 135.58, 133.96, 130.33, 129.21, 128.28, 127.55, 125.59, 124.96, 124.23, 116.43, 108.68, 60.36, 42.02, 34.39, 30.40, 13.85. HRMS calcd for $C_{32}H_{35}ClNaO_4$ [M + Na]$^+$ *m/z* 541.21161, found 541.21131.



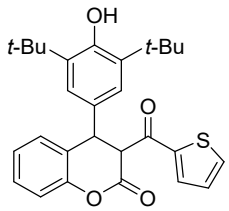
7l

4-(3,5-Di-tert-butyl-4-hydroxyphenyl)-3-(furan-2-carbonyl)chroman-2-one (7l). White solid (138 mg, 62% yield, mp 220-221 ℃). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.99 (s, 1H), 7.76 (d, J = 3.7 Hz, 1H), 7.30 (t, J = 7.9 Hz, 1H), 7.17 (d, J = 8.2 Hz, 1H), 7.08 (t, J = 7.7 Hz, 1H), 6.94 (s, 2H), 6.90 (s, 1H), 6.69 (d, J = 7.6 Hz, 2H), 5.38 (d, J = 11.2 Hz, 1H), 4.70 (d, J = 11.1 Hz, 1H), 1.24 (s, 18H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 182.44, 166.76, 153.56, 152.15, 150.90, 149.82, 140.15, 129.18, 129.03, 128.55, 127.23, 125.35, 125.06, 122.33, 116.81, 113.36, 52.88, 43.12, 35.12, 30.88. HRMS calcd for $C_{28}H_{30}NaO_5$ $[M + Na]^+$ *m/z* 469.19855, found 469.19831.



8l

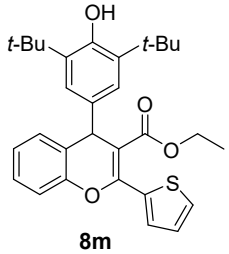
Ethyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(furan-2-yl)-4H-chromene-3-carboxylate (8l). Brown oil (62 mg, 26% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, J = 1.9, 0.8 Hz, 1H), 7.18 (ddd, J = 8.5, 6.9, 1.7 Hz, 1H), 7.13 (t, J = 2.0 Hz, 1H), 7.11 (dd, J = 2.8, 1.6 Hz, 1H), 7.08 – 7.01 (m, 3H), 6.86 (dd, J = 3.5, 0.8 Hz, 1H), 6.50 (dd, J = 3.4, 1.8 Hz, 1H), 5.06 (s, 1H), 5.01 (s, 1H), 4.15 – 3.99 (m, 2H), 1.38 (s, 18H), 1.07 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.29, 152.67, 150.06, 147.37, 146.39, 143.50, 135.72, 135.51, 129.28, 127.63, 125.30, 124.69, 116.43, 112.44, 111.33, 108.84, 60.57, 42.37, 34.38, 30.38, 14.17. HRMS calcd for $C_{30}H_{34}NaO_5$ $[M + Na]^+$ *m/z* 497.22985, found 497.22922.



7m

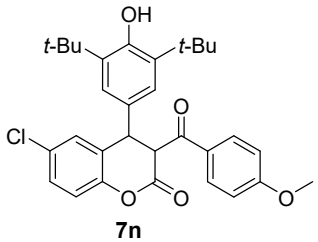
4-(3,5-Di-tert-butyl-4-hydroxyphenyl)-3-(thiophene-2-

carbonyl)chroman-2-one (7m). White solid (136 mg, 59% yield, mp 175-176 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 3.9, 1.1 Hz, 1H), 7.67 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.34 – 7.27 (m, 1H), 7.15 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.13 – 7.07 (m, 2H), 7.05 – 7.00 (m, 1H), 6.92 (s, 2H), 5.14 (s, 1H), 4.73 (d, *J* = 7.0 Hz, 1H), 4.69 (d, *J* = 7.0 Hz, 1H), 1.33 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.01, 165.15, 153.35, 151.01, 142.79, 136.64, 135.43, 133.55, 129.53, 128.94, 128.87, 128.50, 125.10, 124.68, 124.44, 116.91, 56.83, 45.01, 34.45, 30.22. HRMS calcd for $C_{28}H_{30}NaO_4S$ $[M + Na]^+$ *m/z* 485.1757, found 485.17537.



8m

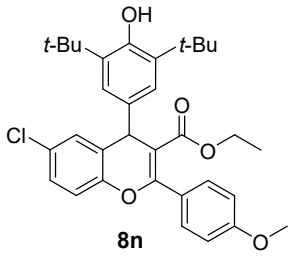
Ethyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(thiophen-2-yl)-4H-chromene-3-carboxylate (8m). Brown oil (74 mg, 30% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 1.9, 0.8 Hz, 1H), 7.18 (ddd, *J* = 8.5, 6.9, 1.7 Hz, 1H), 7.13 (t, *J* = 2.0 Hz, 1H), 7.11 (dd, *J* = 2.8, 1.6 Hz, 1H), 7.08 – 7.01 (m, 3H), 6.86 (dd, *J* = 3.5, 0.8 Hz, 1H), 6.50 (dd, *J* = 3.4, 1.8 Hz, 1H), 5.06 (s, 1H), 5.01 (s, 1H), 4.15 – 3.99 (m, 2H), 1.38 (s, 18H), 1.07 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.29, 152.67, 150.06, 147.37, 146.39, 143.50, 135.72, 135.51, 129.28, 127.63, 125.30, 124.69, 116.43, 112.44, 111.33, 108.84, 60.57, 42.37, 34.38, 30.38, 14.17. HRMS calcd for $C_{30}H_{34}NaO_4S$ $[M + Na]^+$ *m/z* 513.207, found 513.20661.



7n

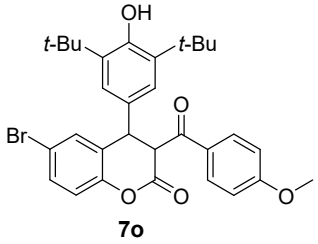
6-Chloro-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-(4-methoxybenzoyl)chroman-2-one (7n). Light yellow solid (135 mg, 52% yield, mp 105-106 ℃). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.97 – 7.92 (m, 2H), 7.38 – 7.33 (m, 1H), 7.22 (d, *J* = 8.7 Hz, 1H), 7.00 (d, *J* = 2.0 Hz, 1H), 6.98 (d, *J* = 2.0 Hz, 1H), 6.94 (s, 1H), 6.92 (s, 2H), 6.90 (dd, *J* = 2.6, 0.9 Hz, 1H), 5.59 (d, *J* = 8.1 Hz, 1H), 4.70 (d, *J*

= 8.1 Hz, 1H), 3.80 (s, 3H), 1.24 (s, 18H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 193.49, 166.40, 164.40, 153.69, 149.93, 140.26, 131.87, 129.71, 128.95, 128.90, 128.82, 128.75, 128.40, 124.60, 118.80, 114.63, 56.22, 52.85, 43.73, 35.12, 30.79. HRMS calcd for $C_{31}H_{32}ClO_5$ [M - H]$^-$ *m/z* 519.19438, found 519.19428.



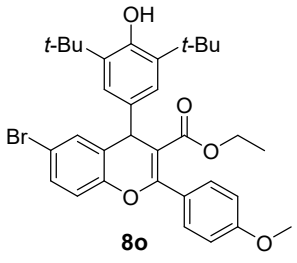
8n

Ethyl 6-chloro-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(4-methoxyphenyl)-4H-chromene-3-carboxylate (8n). Yellow oil (107 mg, 39% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 2H), 7.15 – 7.10 (m, 2H), 7.09 (s, 2H), 7.03 (d, *J* = 8.5 Hz, 1H), 6.95 (d, *J* = 2.0 Hz, 1H), 6.93 (d, *J* = 2.1 Hz, 1H), 5.09 (s, 1H), 4.96 (s, 1H), 3.94 (qd, *J* = 7.2, 1.4 Hz, 2H), 3.85 (s, 3H), 1.40 (s, 18H), 0.97 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.10, 160.88, 158.68, 152.77, 148.89, 136.25, 135.95, 130.52, 129.36, 128.82, 127.65, 127.58, 127.28, 124.21, 117.88, 113.43, 107.17, 60.32, 55.43, 42.26, 34.41, 30.39, 13.93. HRMS calcd for $C_{33}H_{36}ClO_5$ [M - H]$^-$ *m/z* 547.22568, found 547.22592.



7o

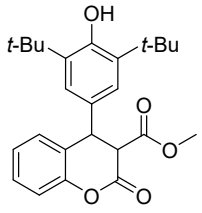
6-Bromo-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-(4-methoxybenzoyl)chroman-2-one (7o). Light yellow solid (156 mg, 55% yield, mp 132-133 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.84 (m, 2H), 7.39 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.17 (dd, *J* = 2.4, 0.8 Hz, 1H), 7.04 (d, *J* = 8.6 Hz, 1H), 6.93 (d, *J* = 2.0 Hz, 1H), 6.92 (d, *J* = 2.2 Hz, 1H), 6.90 (s, 2H), 5.19 (s, 1H), 4.87 (d, *J* = 4.8 Hz, 1H), 4.54 (d, *J* = 4.8 Hz, 1H), 3.87 (s, 3H), 1.36 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.66, 164.94, 164.44, 153.55, 150.16, 136.91, 131.89, 131.71, 131.41, 129.94, 127.91, 126.48, 123.96, 118.71, 117.60, 114.23, 55.72, 55.38, 45.09, 34.49, 30.19. HRMS calcd for $C_{31}H_{33}BrNaO_5$ [M + Na]$^+$ *m/z* 587.14036, found 589.13856.



8o **Ethyl 6-bromo-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(4-methoxyphenyl)-4H-chromene-3-carboxylate (8o)**. Pink solid (77 mg, 26% yield, mp 180-181 ℃). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.52 (d, J = 2.4 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.33 (dd, J = 8.7, 2.4 Hz, 1H), 7.10 (d, J = 8.7 Hz, 1H), 7.06 (s, 2H), 6.98 (d, J = 2.1 Hz, 1H), 6.96 (d, J = 2.1 Hz, 1H), 6.84 (s, 1H), 4.95 (s, 1H), 3.80 (qd, J = 7.1, 1.3 Hz, 2H), 3.76 (s, 3H), 1.29 (s, 18H), 0.81 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.92, 161.11, 158.43, 153.16, 149.47, 139.84, 136.74, 131.75, 130.93, 130.80, 129.08, 126.82, 123.74, 119.11, 116.64, 113.98, 107.06, 60.33, 55.83, 41.52, 35.05, 30.89, 14.07. HRMS calcd for $C_{33}H_{37}BrNaO_5$ $[M + Na]^+$ *m/z* 615.17166, found 617.16989.

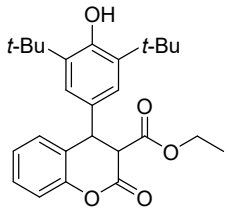
3. General procedure for preparation of 10a-10j

To a solution of *p*-QMs **5** (1.0 mmol) and malonates **9** (1.1 mmol) in toluene (3 mL) was added $Er(OTf)_3$ (123 mg, 0.2 mmol). The reaction was heated and stirred at 110 °C until completion (monitored by TLC). The reaction system was quenched by H_2O and extracted with ethyl acetate after removing toluene. The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by a short silica gel column filtration (petroleum ether/ethyl acetate) to give the desired products **10a-10j**.



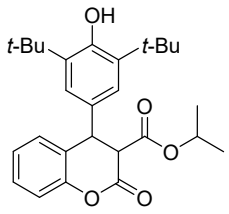
10a **Methyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-oxochromane-3-carboxylate (10a).** Light yellow solid (304 mg, 74% yield, mp 168-169 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, J = 7.9 Hz, 1H), 7.09 (dt, J = 23.8, 8.1 Hz, 3H), 6.88 (s,

2H), 5.18 (s, 1H), 4.64 (d, *J* = 6.5 Hz, 1H), 3.96 (d, *J* = 6.5 Hz, 1H), 3.64 (s, 3H), 1.36 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.58, 164.56, 153.43, 151.06, 136.58, 129.12, 129.02, 128.95, 125.16, 124.37, 124.28, 116.99, 54.34, 53.09, 44.44, 34.49, 30.27. HRMS calcd for $C_{25}H_{30}NaO_5$ $[M + Na]^+$ *m/z* 433.19855, found 433.19938.



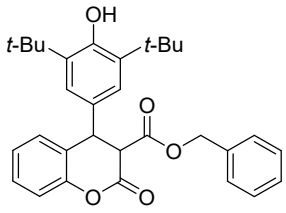
10b

Ethyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-oxochromane-3-carboxylate (10b). White solid (352 mg, 83% yield, mp 134-135 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 1H), 7.17 – 7.06 (m, 2H), 7.05 – 7.00 (m, 1H), 6.90 (s, 2H), 5.18 (s, 1H), 4.62 (d, *J* = 7.1 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.93 (d, *J* = 7.1 Hz, 1H), 1.36 (s, 18H), 1.02 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.11, 164.77, 153.43, 151.16, 136.54, 129.05, 128.91, 128.71, 125.06, 124.69, 124.42, 116.91, 62.06, 54.39, 44.60, 34.48, 30.26, 13.93. HRMS calcd for $C_{26}H_{32}NaO_5$ $[M + Na]^+$ *m/z* 447.2142, found 447.21362.



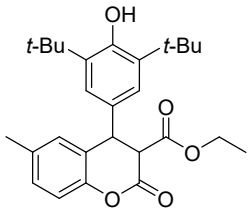
10c

Isopropyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-oxochromane-3-carboxylate (10c). Yellow solid (237 mg, 54% yield, mp 130-131 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 8.0 Hz, 1H), 7.16 – 7.05 (m, 2H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.90 (s, 2H), 5.18 (s, 1H), 4.90 (p, *J* = 6.4 Hz, 1H), 4.59 (d, *J* = 7.6 Hz, 1H), 3.90 (d, *J* = 7.5 Hz, 1H), 1.37 (s, 18H), 1.02 (d, *J* = 6.1 Hz, 3H), 0.98 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.68, 164.92, 153.43, 151.23, 136.49, 129.00, 128.83, 128.52, 124.98, 124.95, 124.53, 116.85, 69.82, 54.45, 44.73, 34.47, 30.26, 21.40, 21.37. HRMS calcd for $C_{27}H_{34}NaO_5$ $[M + Na]^+$ *m/z* 461.22985, found 461.22936.



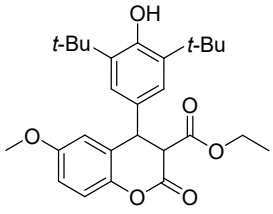
10d

Benzyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-oxochromane-3-carboxylate (10d). Yellow oil (204 mg, 42% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 1H), 7.25 (s, 1H), 7.23 (d, *J* = 1.9 Hz, 1H), 7.13 – 7.08 (m, 2H), 7.00 (td, *J* = 4.8, 4.1, 1.8 Hz, 3H), 6.97 (s, 1H), 6.91 (s, 2H), 5.21 (s, 1H), 5.08 (s, 2H), 4.65 (d, *J* = 7.2 Hz, 1H), 4.02 (d, *J* = 7.2 Hz, 1H), 1.36 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.12, 164.59, 153.49, 151.11, 136.60, 135.95, 134.98, 129.10, 128.93, 128.72, 128.60, 128.32, 127.75, 125.98, 125.09, 124.56, 124.45, 116.98, 67.60, 54.41, 44.56, 34.49, 30.28. HRMS calcd for $C_{31}H_{34}NaO_5$ $[M + Na]^+$ *m/z* 509.22985, found 509.22970.



10e

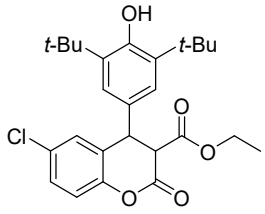
Ethyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-6-methyl-2-oxochromane-3-carboxylate (10e). White solid (360 mg, 82% yield, mp 220-221 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.3 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.89 (s, 2H), 6.85 (s, 1H), 5.18 (s, 1H), 4.57 (d, *J* = 6.0 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.89 (d, *J* = 6.2 Hz, 1H), 2.25 (s, 3H), 1.36 (s, 18H), 1.04 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.20, 164.89, 153.39, 149.12, 136.49, 134.72, 129.60, 129.28, 129.15, 124.32, 123.98, 116.63, 62.11, 54.69, 44.75, 34.48, 30.26, 20.90, 13.95. HRMS calcd for $C_{27}H_{34}NaO_5$ $[M + Na]^+$ *m/z* 461.22985, found 461.22941.



10f

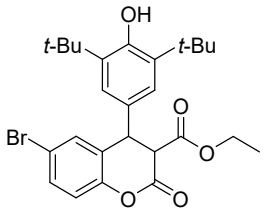
Ethyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-6-methoxy-2-oxochromane-3-carboxylate (10f). White solid (386 mg, 85% yield, mp 210-211 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.9 Hz, 1H), 6.90 (s, 2H), 6.81 (d, *J* = 8.8 Hz, 1H), 6.54 (s, 1H), 5.18 (s, 1H), 4.57 (d, *J* = 7.0 Hz, 1H), 4.08 (q, *J* = 7.4 Hz, 2H), 3.89 (d, *J* = 6.8 Hz, 1H), 3.71 (s, 3H), 1.37 (s, 18H), 1.04 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.16, 164.93, 156.56, 153.45, 145.08, 136.55, 128.62, 125.63, 124.38, 117.73, 114.27, 113.72, 62.08, 55.69, 54.40, 44.85, 34.48, 30.27, 13.96. HRMS calcd for $C_{27}H_{35}O_6$ $[M + H]^+$ *m/z* 455.24282, found 455.24176.



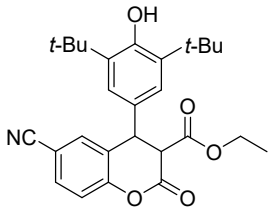
10g

Ethyl 6-chloro-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-oxochromane-3-carboxylate (10g). Light yellow solid (390 mg, 85% yield, mp 182-183 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 1H), 7.08 (d, *J* = 8.7 Hz, 1H), 7.03 (d, *J* = 2.5 Hz, 1H), 6.87 (s, 2H), 5.22 (s, 1H), 4.58 (d, *J* = 6.7 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.90 (d, *J* = 6.7 Hz, 1H), 1.37 (s, 18H), 1.06 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.76, 164.04, 153.67, 149.66, 136.75, 130.20, 129.15, 128.80, 128.12, 126.40, 124.28, 118.32, 62.30, 54.08, 44.59, 34.50, 30.24, 13.97. HRMS calcd for $C_{26}H_{31}ClNaO_5$ $[M + Na]^+$ *m/z* 481.17522, found 481.17496.



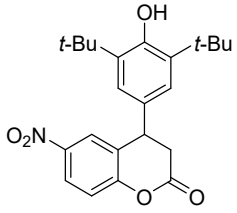
10h

Ethyl 6-bromo-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-oxochromane-3-carboxylate (10h). White solid (438 mg, 87% yield, mp 189-190 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.19 (dd, *J* = 2.4, 0.8 Hz, 1H), 7.03 (d, *J* = 8.6 Hz, 1H), 6.87 (s, 2H), 5.22 (s, 1H), 4.58 (d, *J* = 6.5 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.90 (d, *J* = 6.5 Hz, 1H), 1.37 (s, 18H), 1.06 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.74, 163.96, 153.67, 150.21, 136.74, 132.11, 131.74, 128.17, 126.73, 124.26, 118.70, 117.74, 62.34, 54.14, 44.56, 34.50, 30.23, 13.97. HRMS calcd for $C_{26}H_{31}BrKO_5$ $[M + K]^+$ *m/z* 541.09865, found 543.09688.



10i

Ethyl 6-cyano-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-oxochromane-3-carboxylate (10i). White solid (395 mg, 88% yield, mp 167-168 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.34 (d, *J* = 1.5 Hz, 1H), 7.23 (d, *J* = 8.5 Hz, 1H), 6.86 (s, 2H), 5.26 (s, 1H), 4.62 (d, *J* = 7.5 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.96 (d, *J* = 7.5 Hz, 1H), 1.38 (s, 18H), 1.06 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.33, 163.09, 153.99, 153.91, 137.05, 133.21, 127.30, 126.72, 124.22, 118.16, 118.09, 108.97, 62.44, 53.58, 44.32, 34.52, 30.21, 13.94. HRMS calcd for $C_{27}H_{31}NNaO_5$ $[M + Na]^+$ *m/z* 472.20944, found 472.20944.



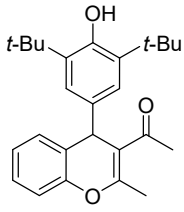
10j

4-(3,5-Di-tert-butyl-4-hydroxyphenyl)-6-nitrochroman-2-one (10j). Yellow solid (357 mg, 90% yield, mp 135-136 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.8, 2.7 Hz, 1H), 7.97 (dd, *J* = 2.7, 0.9 Hz, 1H), 7.24 (d, *J* = 9.0 Hz, 1H), 6.92 (s, 2H), 5.26 (s, 1H), 4.38 – 4.30 (m, 1H), 3.17 – 2.98 (m, 2H), 1.39 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.22, 156.09, 153.72, 144.40, 137.03, 129.42, 128.06, 124.58, 124.53, 123.91, 118.08, 40.76, 36.65, 34.55, 30.23. HRMS calcd for $C_{23}H_{27}NNaO_5$ $[M - H]^-$ *m/z* 396.46352, found 396.18073.

4. General procedure for preparation of 12a-12l

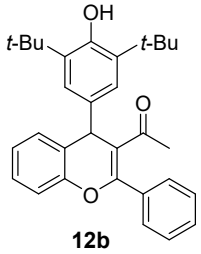
To a solution of *p*-QMs **5** (1.0 mmol) and β-diketones **11** (1.1 mmol) in toluene (3 mL) was added $Er(OTf)_3$ (123 mg, 0.2 mmol). The reaction was heated and stirred at 110 ^{o}C until completion (monitored by TLC). The reaction system was quenched by H_2O and extracted with ethyl acetate after removing toluene. The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was

purified by a short silica gel column filtration (petroleum ether/ethyl acetate) to give the desired products **12a**-**12l**.



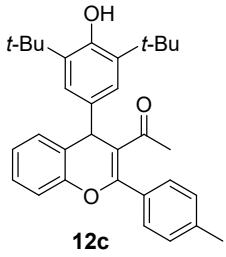
12a

1-(4-(3,5-Di-tert-butyl-4-hydroxyphenyl)-2-methyl-4H-chromen-3-yl)ethan-1-one (12a). Yellow oil (153 mg, 39% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.15 (m, 1H), 7.13 (td, *J* = 7.7, 1.7 Hz, 1H), 7.04 – 6.97 (m, 4H), 5.07 (s, 1H), 4.90 (s, 1H), 2.45 (s, 3H), 2.19 (s, 3H), 1.38 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.41, 159.35, 152.65, 149.41, 136.42, 136.08, 128.88, 127.42, 125.91, 124.56, 124.00, 116.31, 114.68, 42.17, 34.38, 30.35, 30.19, 20.13. HRMS calcd for $C_{26}H_{32}NaO_3$ $[M + Na]^+$ *m/z* 415.22437, found 415.22361.



12b

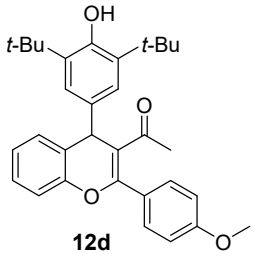
1-(4-(3,5-Di-tert-butyl-4-hydroxyphenyl)-2-phenyl-4H-chromen-3-yl)ethan-1-one (12b). Yellow oil (173 mg, 38% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 2H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.17 (ddd, *J* = 8.7, 6.9, 2.0 Hz, 1H), 7.07 – 6.96 (m, 3H), 6.78 (s, 2H), 5.06 (s, 1H), 4.97 (s, 1H), 1.92 (s, 3H), 1.28 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.16, 152.38, 152.35, 150.26, 139.53, 135.87, 135.72, 132.29, 129.73, 128.75, 128.45, 127.57, 124.75, 124.43, 124.14, 116.06, 114.63, 42.97, 34.26, 30.28, 19.20. HRMS calcd for $C_{31}H_{34}NaO_3$ $[M + Na]^+$ *m/z* 477.24002, found 477.23896.



12c

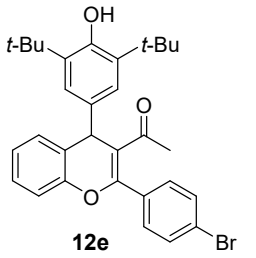
1-(4-(3,5-Di-tert-butyl-4-hydroxyphenyl)-2-(p-tolyl)-4H-chromen-3-yl)ethan-1-one (12c). Brown oil (244 mg, 52% yield). ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.49 (d, *J* = 8.2 Hz, 2H), 7.20 – 7.10 (m, 3H), 7.07 – 6.97 (m, 3H), 6.80 (s, 2H), 5.07 (s, 1H), 4.97 (s, 1H), 2.36 (s, 3H), 1.91 (s, 3H), 1.29 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.86, 152.36, 151.52, 150.36, 143.09, 136.84, 135.89, 135.69, 129.74, 129.14, 129.05, 127.53, 124.76, 124.47, 124.06, 116.05, 114.69, 43.07, 34.26, 30.29, 21.70, 19.13. HRMS calcd for $C_{32}H_{36}NaO_3$ $[M + Na]^+$ *m/z* 491.25567, found 491.25447.



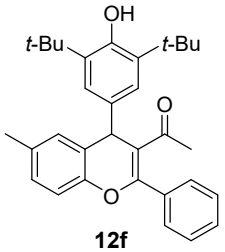
12d

1-(4-(3,5-Di-tert-butyl-4-hydroxyphenyl)-2-(4-methoxyphenyl)-4H-chromen-3-yl)ethan-1-one (12d). Yellow oil (271 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.55 (m, 2H), 7.17 (ddt, *J* = 8.3, 6.9, 1.5 Hz, 1H), 7.06 – 6.96 (m, 3H), 6.80 (dt, *J* = 6.8, 1.7 Hz, 4H), 5.05 (s, 1H), 4.96 (s, 1H), 3.81 (s, 3H), 1.88 (s, 3H), 1.27 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.86, 163.17, 152.34, 150.49, 150.13, 135.81, 135.65, 131.98, 131.38, 129.79, 127.54, 124.71, 124.30, 123.98, 116.02, 114.48, 113.62, 55.53, 43.20, 34.25, 30.28, 18.99. HRMS calcd for $C_{32}H_{36}NaO_4$ $[M + Na]^+$ *m/z* 507.25058, found 507.24946.



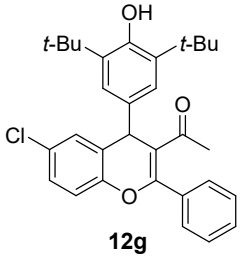
12e

1-(2-(4-Bromophenyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-4H-chromen-3-yl)ethan-1-one (12e). Yellow oil (320 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.42 – 7.36 (m, 2H), 7.17 (ddd, *J* = 8.6, 6.3, 2.7 Hz, 1H), 7.04 – 6.99 (m, 3H), 6.76 (s, 2H), 5.00 (s, 1H), 4.99 (s, 1H), 1.93 (s, 3H), 1.28 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.03, 152.72, 152.45, 150.12, 138.33, 135.85, 135.69, 131.71, 130.19, 129.67, 127.66, 127.18, 124.74, 124.25, 116.09, 114.33, 42.94, 34.26, 30.28, 19.24. HRMS calcd for $C_{31}H_{33}BrNaO_3$ $[M + Na]^+$ *m/z* 555.15053, found 557.14890.



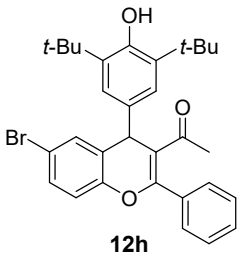
12f

1-(4-(3,5-Di-tert-butyl-4-hydroxyphenyl)-6-methyl-2-phenyl-4H-chromen-3-yl)ethan-1-one (12f). Brown oil (267 mg, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dt, *J* = 8.2, 1.2 Hz, 2H), 7.50 – 7.42 (m, 1H), 7.34 (td, *J* = 7.2, 6.8, 1.2 Hz, 2H), 7.04 – 6.92 (m, 2H), 6.88 (s, 1H), 6.83 (d, *J* = 1.1 Hz, 2H), 5.04 (s, 1H), 5.03 (s, 1H), 2.24 (s, 3H), 1.93 (s, 3H), 1.32 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.30, 152.62, 152.41, 148.34, 139.66, 136.14, 135.74, 133.57, 132.25, 129.84, 128.76, 128.47, 128.34, 124.74, 124.02, 115.85, 114.65, 43.16, 34.32, 30.33, 20.93, 19.27. HRMS calcd for $C_{32}H_{36}NaO_3$ $[M + Na]^+$ *m/z* 491.25567, found 491.25514.



12g

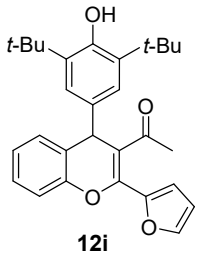
1-(6-Chloro-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenyl-4H-chromen-3-yl)ethan-1-one (12g). Yellow oil (254 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 2H), 7.48 – 7.41 (m, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.12 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.03 – 6.92 (m, 2H), 6.76 (s, 2H), 5.01 (s, 1H), 4.99 (s, 1H), 1.89 (s, 3H), 1.28 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.78, 152.63, 151.89, 148.83, 139.25, 135.92, 135.17, 132.44, 129.33, 128.76, 128.71, 128.49, 127.75, 126.07, 124.74, 117.55, 114.28, 43.01, 34.27, 30.25, 19.07. HRMS calcd for $C_{31}H_{33}ClNaO_3$ $[M + Na]^+$ *m/z* 511.20104, found 511.19987.



12h

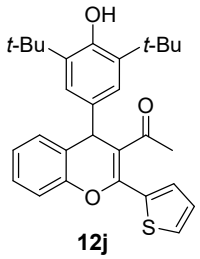
1-(6-Bromo-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenyl-4H-chromen-3-yl)ethan-1-one (12h). Yellow oil (288 mg, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.48 – 7.42 (m, 1H), 7.36 – 7.29 (m, 2H), 7.27

(dd, J = 8.7, 2.5 Hz, 1H), 7.15 (dd, J = 2.4, 0.8 Hz, 1H), 6.91 (d, J = 8.7 Hz, 1H), 6.75 (s, 2H), 5.00 (s, 1H), 4.99 (s, 1H), 1.89 (s, 3H), 1.28 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.72, 152.63, 151.73, 149.41, 139.22, 135.96, 135.15, 132.43, 132.26, 130.64, 128.71, 128.48, 126.57, 124.72, 117.95, 116.29, 114.43, 42.95, 34.27, 30.24, 19.01. HRMS calcd for $C_{31}H_{33}BrNaO_3$ [M + Na]$^+$ *m/z* 555.15053, found 557.14800.



12i

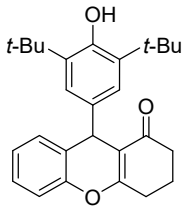
1-(4-(3,5-Di-tert-butyl-4-hydroxyphenyl)-2-(furan-2-yl)-4H-chromen-3-yl)ethan-1-one (12i). White solid (245 mg, 55% yield, mp 155-156 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, J = 1.7, 0.8 Hz, 1H), 7.15 (ddd, J = 8.5, 6.9, 1.8 Hz, 1H), 7.03 (ddd, J = 7.6, 1.8, 0.8 Hz, 1H), 7.01 – 6.95 (m, 2H), 6.89 (dd, J = 3.5, 0.8 Hz, 1H), 6.86 (s, 2H), 6.43 (dd, J = 3.5, 1.7 Hz, 1H), 5.13 (s, 1H), 4.97 (s, 1H), 2.01 (s, 3H), 1.29 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.64, 153.64, 152.44, 152.17, 150.03, 146.21, 135.74, 135.70, 129.62, 127.54, 124.75, 124.45, 124.11, 118.65, 116.09, 113.91, 112.30, 42.40, 34.30, 30.33, 18.94. HRMS calcd for $C_{29}H_{32}NaO_4$ [M + Na]$^+$ *m/z* 467.21928, found 467.21812.



12j

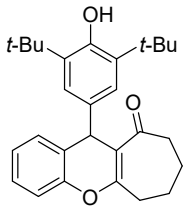
1-(4-(3,5-Di-tert-butyl-4-hydroxyphenyl)-2-(thiophen-2-yl)-4H-chromen-3-yl)ethan-1-one (12j). Brown oil (267 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 4.9, 1.2 Hz, 1H), 7.31 (dd, J = 3.8, 1.2 Hz, 1H), 7.17 (ddd, J = 8.5, 7.0, 1.9 Hz, 1H), 7.05 (dd, J = 7.7, 1.8 Hz, 1H), 7.03 – 6.97 (m, 2H), 6.95 (dd, J = 4.9, 3.8 Hz, 1H), 6.82 (s, 2H), 5.08 (s, 1H), 4.97 (s, 1H), 1.97 (s, 3H), 1.28 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.97, 152.40, 150.48, 149.21, 145.50, 135.73, 135.61, 133.96, 133.59, 129.82, 127.80, 127.67, 124.79, 124.04, 123.95, 116.05, 114.95, 43.28, 34.26, 30.28, 19.12. HRMS calcd for $C_{29}H_{32}NaO_3S$ [M + Na]$^+$ *m/z* 483.19644, found

483.19537.



12k

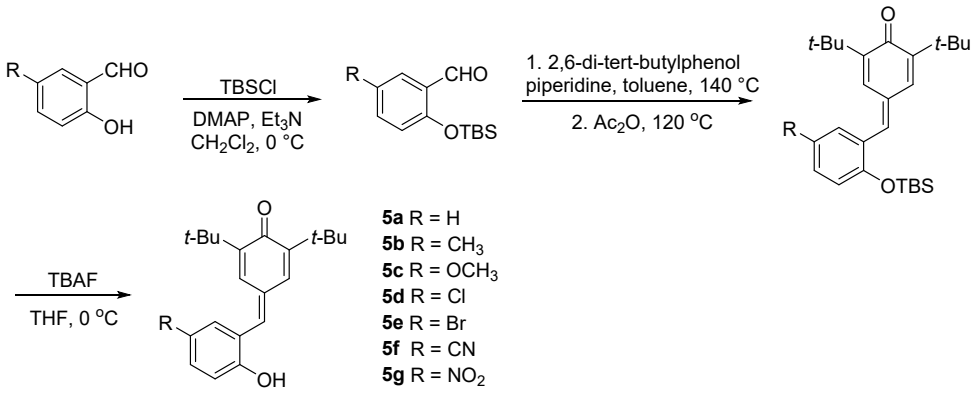
9-(3,5-Di-tert-butyl-4-hydroxyphenyl)-2,3,4,9-tetrahydro-1H-xanthen-1-one (12k). Yellow solid (332 mg, 82% yield, mp 215-216 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.12 (m, 2H), 7.04 (td, *J* = 7.6, 1.0 Hz, 2H), 6.98 (s, 2H), 5.00 (s, 1H), 5.00 (s, 1H), 2.78 – 2.56 (m, 2H), 2.51 – 2.29 (m, 2H), 2.12 – 1.97 (m, 2H), 1.35 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.21, 166.65, 152.28, 149.88, 136.71, 135.50, 129.96, 127.37, 126.37, 125.08, 124.29, 116.38, 115.39, 37.20, 37.17, 34.36, 30.37, 27.99, 20.54. HRMS calcd for $C_{27}H_{32}NaO_3$ $[M + Na]^+$ *m/z* 427.22437, found 427.22355.



12l

11-(3,5-Di-tert-butyl-4-hydroxyphenyl)-6,8,9,11-tetrahydrocyclohepta[b]chromen-10(7H)-one (12l). Light yellow solid (322 mg, 77% yield, mp 206-207 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.10 (m, 2H), 7.03 (ddd, *J* = 7.2, 3.5, 2.1 Hz, 2H), 6.98 (s, 2H), 4.98 (s, 1H), 4.98 (s, 1H), 2.93 – 2.76 (m, 2H), 2.72 – 2.51 (m, 2H), 2.06 – 1.87 (m, 2H), 1.86 – 1.74 (m, 2H), 1.35 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.64, 166.71, 152.30, 150.00, 136.97, 135.54, 129.32, 127.19, 126.52, 124.87, 123.89, 117.69, 116.24, 41.72, 39.81, 34.39, 31.64, 30.42, 23.46, 20.99. HRMS calcd for $C_{28}H_{34}NaO_3$ $[M + Na]^+$ *m/z* 441.24002, found 441.23912.

5. General procedure for preparation of 5

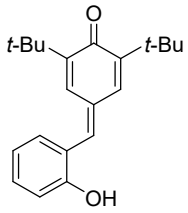


Scheme S1. Synthesis of *p*-QMs **5**.

To a solution of salicylaldehyde (50 mmol) and TBSCl (9.0 g, 60 mmol) in CH_2Cl_2 (30 mL) was added DMAP (1.2 g, 10 mmol). And then, Et_3N (6.1 g, 60 mmol) was dropwise added into the reaction vessel at 0 °C. The mixture was stirred overnight at room temperature. The reaction system was quenched by H_2O and extracted with CH_2Cl_2. The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was used directly in the next step without purification.

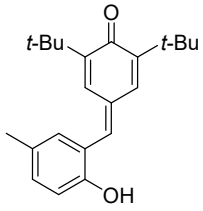
To a solution of 2-tert-butyldimethylsilyloxybenzaldehyde (4.0 mmol) and 2,6-di-tert-butylphenol (825 mg, 4.0 mmol) in toluene (5 mL) was added piperidine (681 mg, 8.0 mmol) by dropwise slowly. The mixture was heated to 140 °C and stirred for 12 h. After that, the reaction mixture was cooled to 120 °C and acetic anhydride (817 mg, 8.0 mmol) was added by dropwise. The stirring was continued for 30 min, and then the solution was poured on ice-water and extracted with ethyl acetate. The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by a short silica gel column filtration (petroleum ether/ethyl acetate) to give the corresponding products.

To a solution of the above product (1.0 mmol) in THF (3 mL) at 0 °C was added tetrabutylammonium fluoride trihydrate (307 mg, 1.1 mmol). The reaction mixture was stirred for 10 min and a saturated NH_4Cl solution was added by dropwise to quench the reaction. The resulting solution was extracted with ethyl acetate. The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by a short silica gel column filtration (petroleum ether/ethyl acetate) to give the desired products **5a**-**5g**.



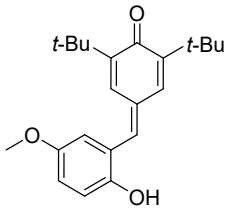
5a

2,6-Di-tert-butyl-4-(2-hydroxybenzylidene)cyclohexa-2,5-dien-1-one (5a).[1] Yellow solid (286 mg, 92% yield, mp 175-176 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 2.4 Hz, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.30 (s, 1H), 7.27 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.06 (d, *J* = 2.5 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.1 Hz, 1H), 5.19 (s, 1H), 1.32 (s, 9H), 1.27 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.90, 154.66, 149.36, 147.71, 137.91, 135.31, 132.29, 131.80, 130.99, 128.37, 123.81, 123.22, 120.98, 116.14, 35.51, 35.10, 30.30, 29.64.



5b

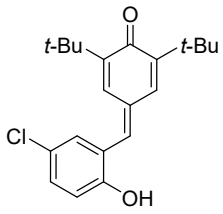
2,6-Di-tert-butyl-4-(2-hydroxy-5-methylbenzylidene)cyclohexa-2,5-dien-1-one (5b).[1] Yellow solid (302 mg, 93% yield, mp 109-110 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 2.5 Hz, 1H), 7.27 (s, 1H), 7.14 (d, *J* = 2.0 Hz, 1H), 7.08 (dd, *J* = 8.1, 2.2 Hz, 1H), 7.05 (d, *J* = 2.4 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 4.94 (s, 1H), 2.31 (s, 3H), 1.32 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.17, 159.89, 152.78, 151.55, 136.66, 136.10, 130.97, 130.50, 130.19, 129.04, 128.79, 128.66, 127.88, 125.97, 116.36, 34.49, 34.46, 30.39, 30.18, 20.85.



5c

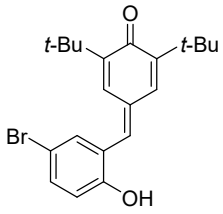
2,6-Di-tert-butyl-4-(2-hydroxy-5-methoxybenzylidene)cyclohexa-2,5-dien-1-one (5c). Yellow solid (306 mg, 90% yield, mp 106-107 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 2.5, 0.8 Hz, 1H), 7.27 (s, 1H), 7.05 (dd, *J* = 2.5, 0.7 Hz, 1H), 6.87 (s, 1H), 6.85 (d, *J* = 2.8 Hz, 1H), 6.83 (d, *J* = 1.0 Hz, 1H), 4.97 (s, 1H), 3.78 (s, 3H), 1.32 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (101

MHz, $CDCl_3$) δ 186.85, 153.46, 149.33, 149.22, 147.68, 138.21, 135.97, 135.50, 132.09, 128.36, 123.97, 123.57, 117.65, 117.10, 115.59, 55.94, 35.55, 35.10, 29.71, 29.62.



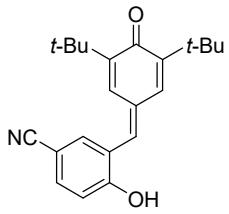
5d

2,6-Di-tert-butyl-4-(5-chloro-2-hydroxybenzylidene)cyclohexa-2,5-dien-1-one (5d).[2] Yellow solid (314 mg, 91% yield, mp 108-109 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 2.4, 0.8 Hz, 1H), 7.31 – 7.29 (m, 1H), 7.23 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.15 (s, 1H), 7.03 (d, *J* = 2.5 Hz, 1H), 6.84 (d, *J* = 8.6 Hz, 1H), 5.25 (s, 1H), 1.31 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.81, 153.52, 149.91, 148.27, 135.62, 134.83, 134.05, 133.30, 133.18, 127.79, 125.02, 123.57, 117.81, 112.90, 35.58, 35.15, 30.28, 29.59.



5e

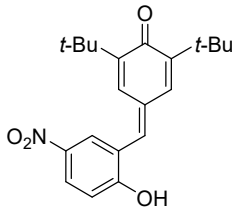
4-(5-Bromo-2-hydroxybenzylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (5e).[1] Yellow solid (370 mg, 95% yield, mp 106-107 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 2.5, 0.8 Hz, 1H), 7.36 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.31 (dd, *J* = 2.5, 0.8 Hz, 1H), 7.14 (s, 1H), 7.02 (dd, *J* = 2.5, 0.7 Hz, 1H), 6.79 (d, *J* = 8.6 Hz, 1H), 5.13 (s, 1H), 1.31 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.83, 154.44, 149.42, 147.78, 137.58, 135.18, 132.43, 131.79, 130.97, 128.24, 123.19, 121.08, 116.11, 35.52, 35.11, 29.62, 29.60.



5f

3-((3,5-Di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)-4-hydroxybenzonitrile (5f). Yellow solid (295 mg, 88% yield, mp 102-103 °C). ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 1.5 Hz, 1H), 7.46 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.32 (d, *J* = 1.6 Hz, 1H), 7.27 (s, 1H), 7.07 (d, *J* = 8.5 Hz, 1H), 7.01 (d, *J* = 2.4 Hz, 1H), 1.27 (s, 9H), 1.24 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.73, 160.92, 149.56, 147.83, 136.69, 135.48, 135.17, 134.34, 132.43, 127.67, 124.45, 119.29, 117.07, 102.43, 35.49, 35.06, 29.58, 29.55.



5g

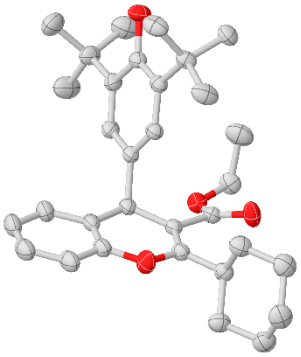
2,6-Di-tert-butyl-4-(2-hydroxy-5-nitrobenzylidene)cyclohexa-2,5-dien-1-one (5g). Yellow solid (298 mg, 84% yield, mp 105-106 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 2.7 Hz, 1H), 8.18 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.30 (d, *J* = 2.5 Hz, 1H), 7.15 (s, 1H), 7.05 (d, *J* = 2.4 Hz, 1H), 7.01 (d, *J* = 9.0 Hz, 1H), 1.32 (s, 9H), 1.27 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.86, 160.00, 150.47, 148.73, 141.47, 134.74, 134.25, 133.96, 127.56, 127.29, 126.29, 124.54, 123.53, 116.31, 35.64, 35.21, 30.17, 29.57.

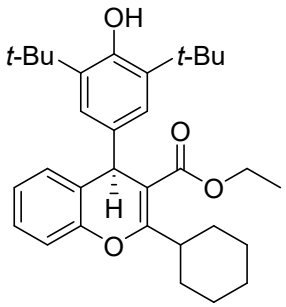
6. References for preparation of 5

1. N. Kaur, P. Kumar, S. Dutt and P. Banerjee, *J. Org. Chem.*, 2022, **87**, 7905.
2. M. Xiang, C.-Y. Li, X.-J. Song, Y. Zou, Z.-C. Huang, X. Li, F. Tian and L.-X. Wang, *Chem. Commun.*, 2020, **56**, 14825.

7. Single-crystal X-ray diffraction data of 8h and 10c

Crystal of 8h and 10c was grown by slow evaporation of methanol solution at room temperature (20 °C). X-ray diffraction data was collected at 293(2) K on a Bruker Kappa Apex Duo diffractometer with graded-multilayer focused CuK(alpha) X-rays.





(*R*)-8h

Figure S1. Crystal structure of **8h** with thermal ellipsoids at 30% probability.

Crystal data and structure refinement for 8h	
Identification code	8h
CCDC number	2248199
Empirical formula	$C_{32}H_{42}O_4$
Formula weight	490.65
Temperature/K	293(2)
Wavelength	1.54184
Crystal system	monoclinic
Space group	$C2/_C$
a/Å	18.6928(2)
b/Å	14.67570(10)
c/Å	21.8092(3)
α/°	90
β/°	99.3630(10)
γ/°	90
Volume/Å^3	5903.21(11)
Z	8
ρ_{calc}g/cm^3	1.104
μ/mm^{-1}	0.558
F(000)	2128
Crystal size/mm^3	0.05*0.05*0.04
Radiation	CuKα (λ = 1.54184)
Theta range for data collection/°	3.849 to 68.115
Index ranges	-20≤ h≤ 22, -17≤ k≤ 13, -26≤ l≤ 25
Reflections collected	28471
Independent reflections	5373 [R(int) = 0.0319, Rsigma =0.0181]

Data/restraints/parameters	5373/495/334
Goodness-of-fit on F^2	1.105
Final R indices [I >=2sigma(I)]	R_1 = 0.0530, wR_2 = 0.1516
Final R indexes [all data]	R_1 = 0.0577, wR_2 = 0.1558
Largest diff. peak/hole / e $Å^{-3}$	0.289/-0.183

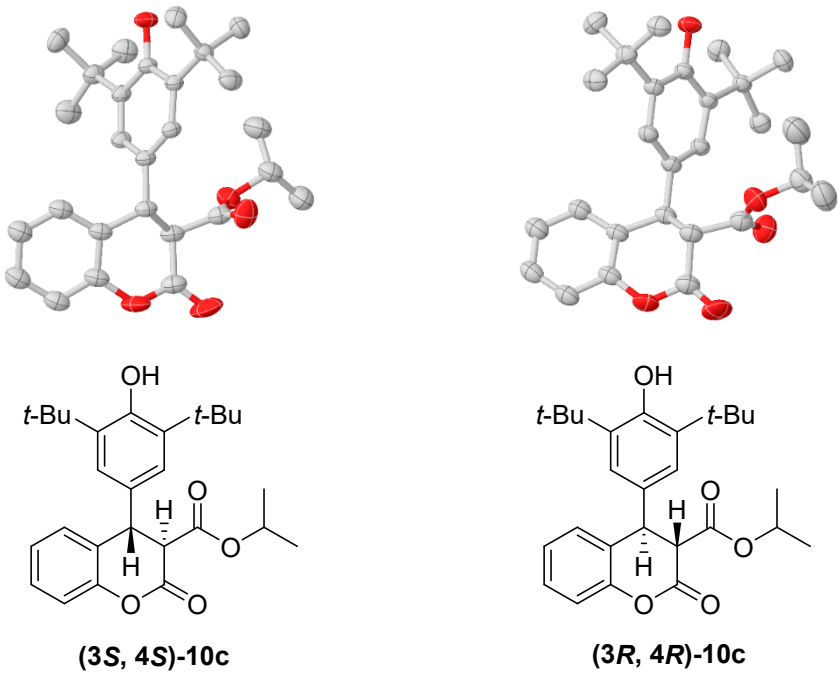
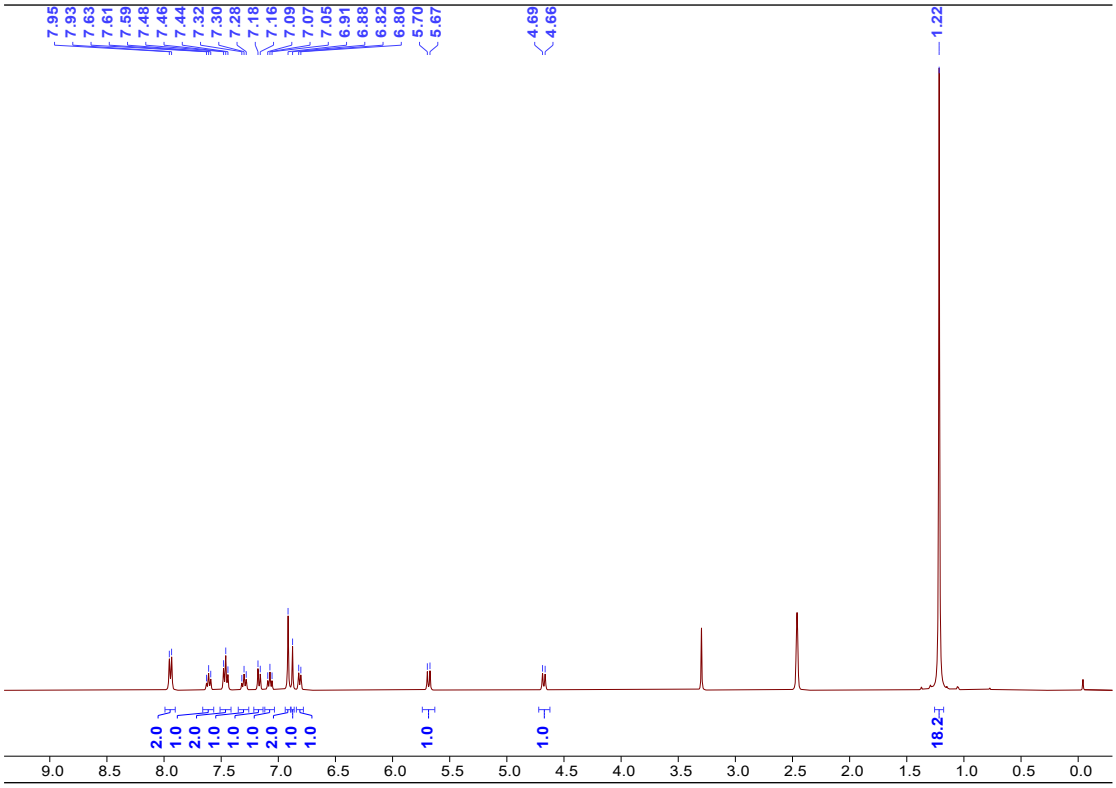


Figure S2. Crystal structure of **10c** with thermal ellipsoids at 30% probability.

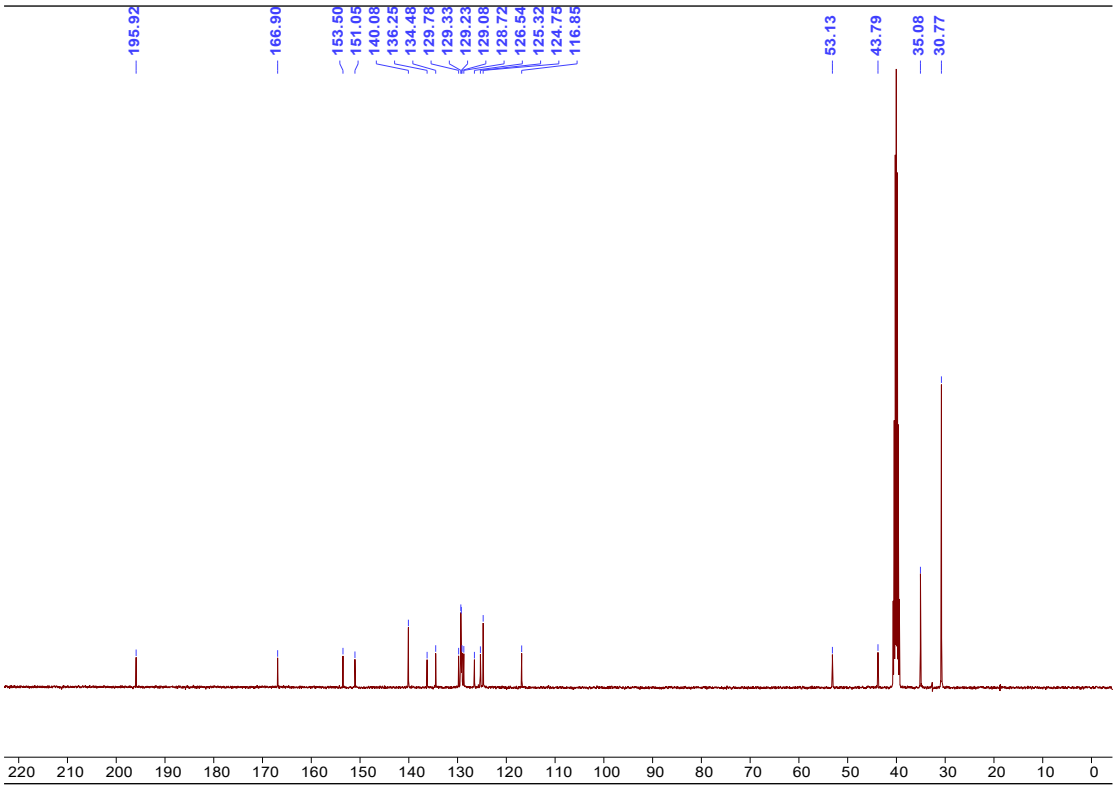
Crystal data and structure refinement for 10c	
Identification code	10c
CCDC number	2246898
Empirical formula	$C_{54}H_{68}O_{10}$
Formula weight	877.08
Temperature/K	293(2)
Wavelength	1.54184
Crystal system	monoclinic
Space group	$P2_1$
a/Å	11.4572(4)
b/Å	18.7701(7)
c/Å	11.9458(5)
α/°	90
β/°	98.041(4)
γ/°	90
Volume/$Å^3$	2543.72(17)
Z	2

ρ_{calc}g/cm^3	1.145
μ/mm^{-1}	0.624
F(000)	944
Crystal size/mm^3	0.08*0.06*0.05
Radiation	CuKα (λ = 1.54184)
Theta range for data collection/°	3.737 to 68.006
Index ranges	-13≤ h≤ 13, -22≤ k≤ 17, -14≤ l≤ 14
Reflections collected	28077
Independent reflections	7449 [R(int) = 0.0500, Rsigma =0.0487]
Data/restraints/parameters	7449/598/596
Goodness-of-fit on F^2	1.071
Final R indices [I >=2sigma(I)]	R_1 = 0.0798, wR_2 = 0.2223
Final R indexes [all data]	R_1 = 0.0875, wR_2 = 0.2385
Largest diff. peak/hole / e Å^{-3}	0.413/-0.350

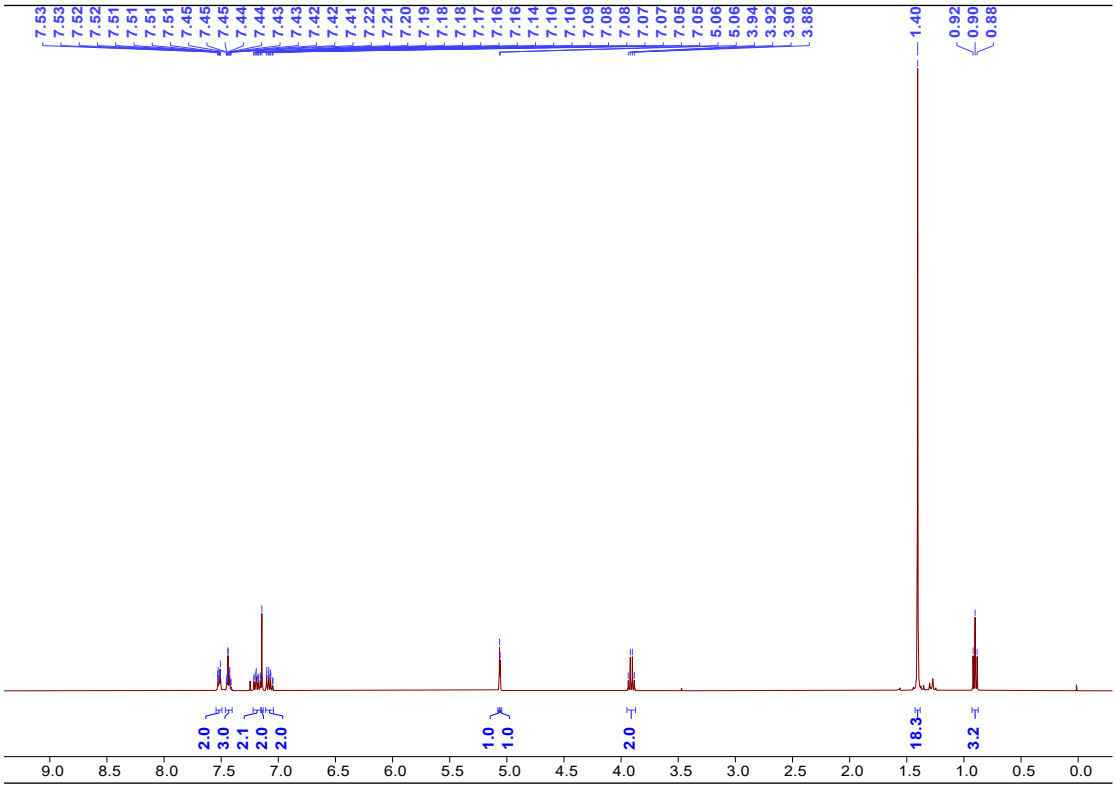
8. Copies of ^{1}H NMR and ^{13}C NMR spectra for 7, 8, 10 and 12



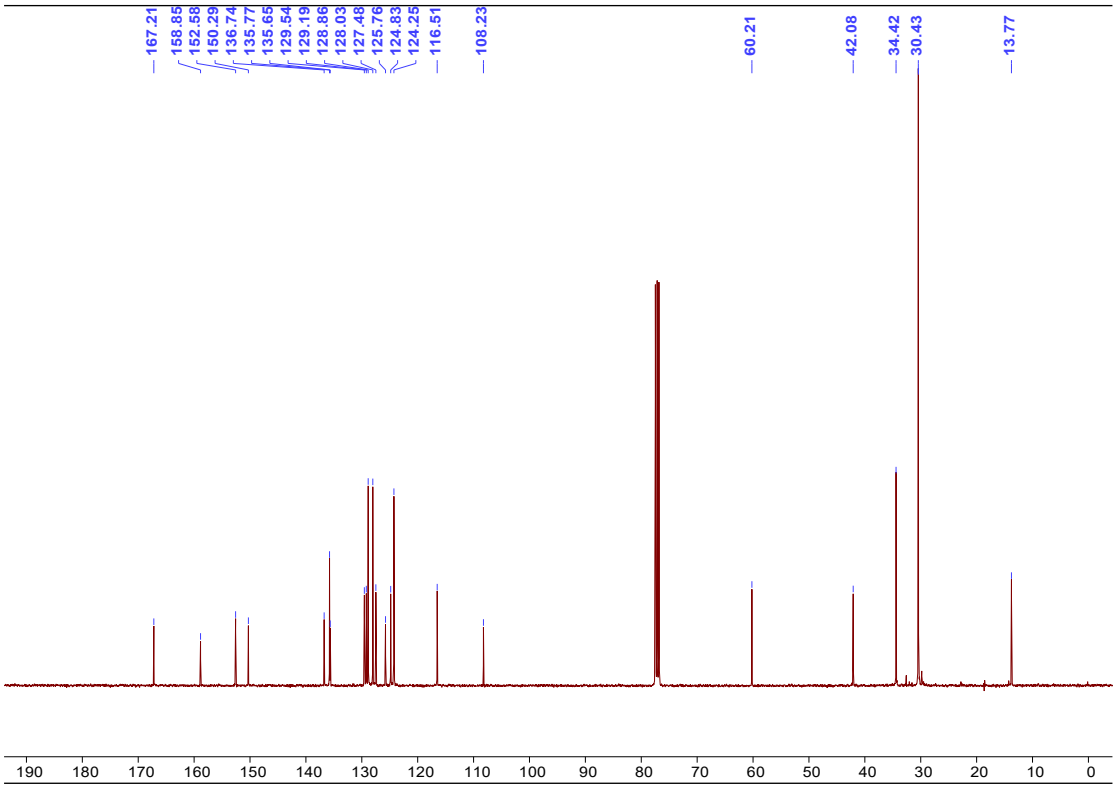
^{1}H NMR spectrum of 7a



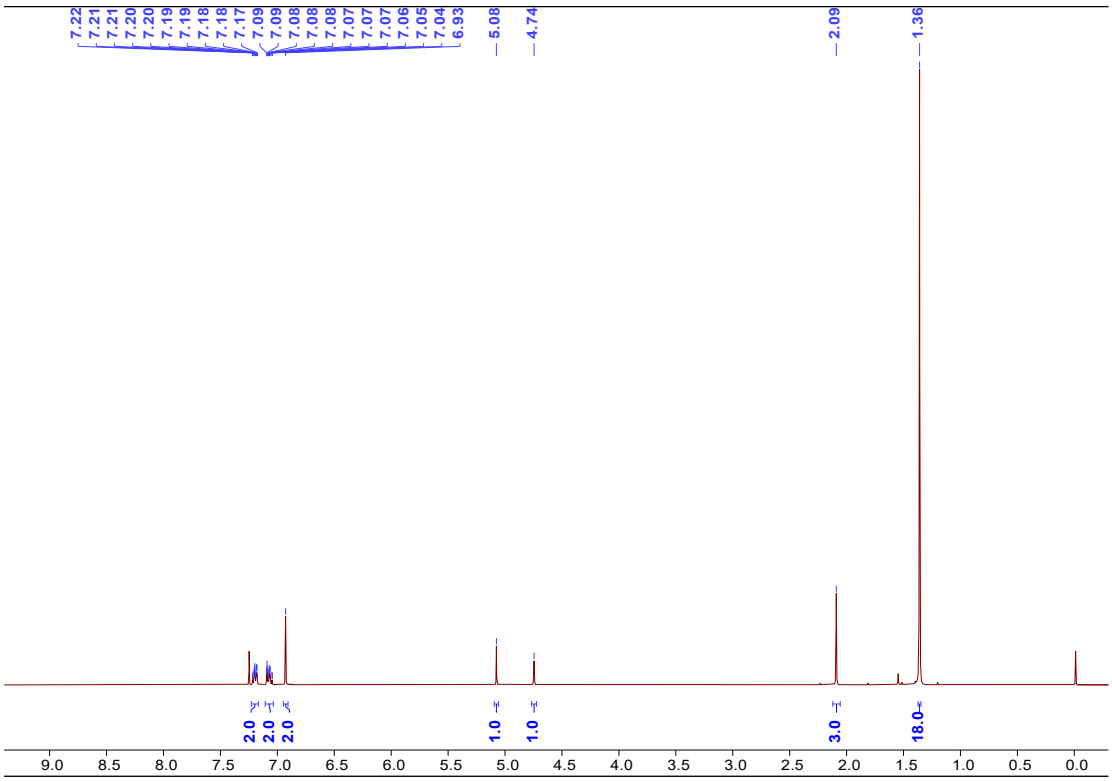
^{13}C NMR spectrum of 7a



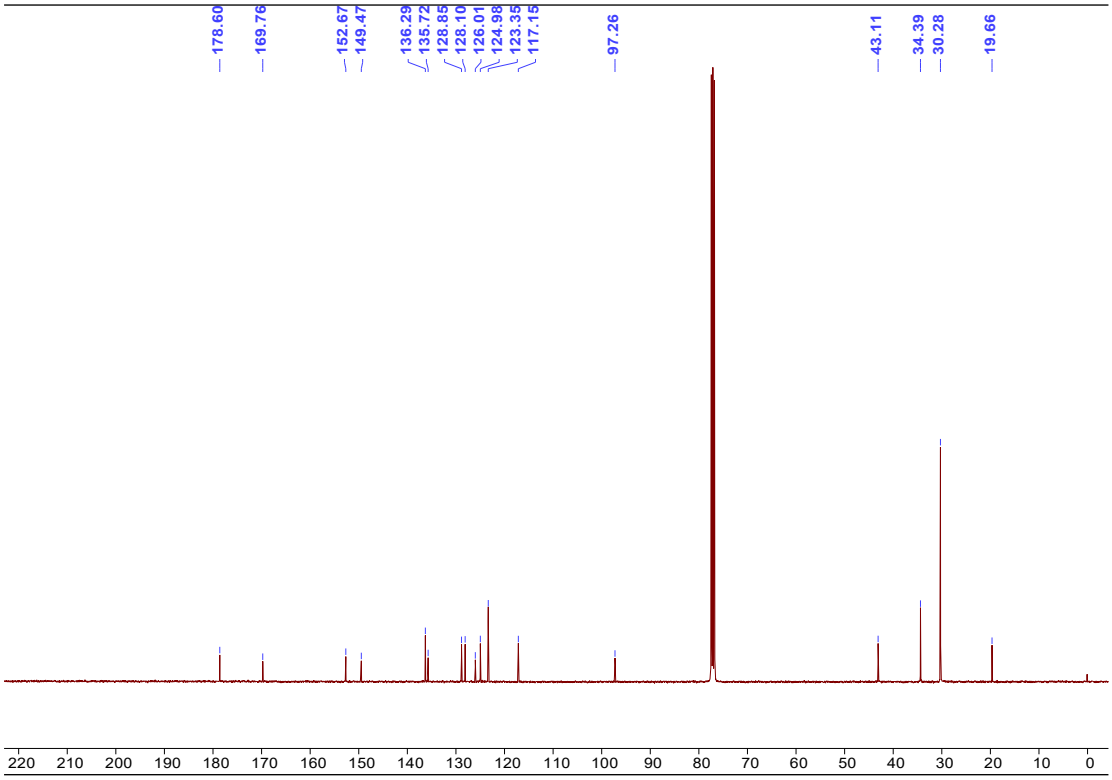
^{1}H NMR spectrum of 8a



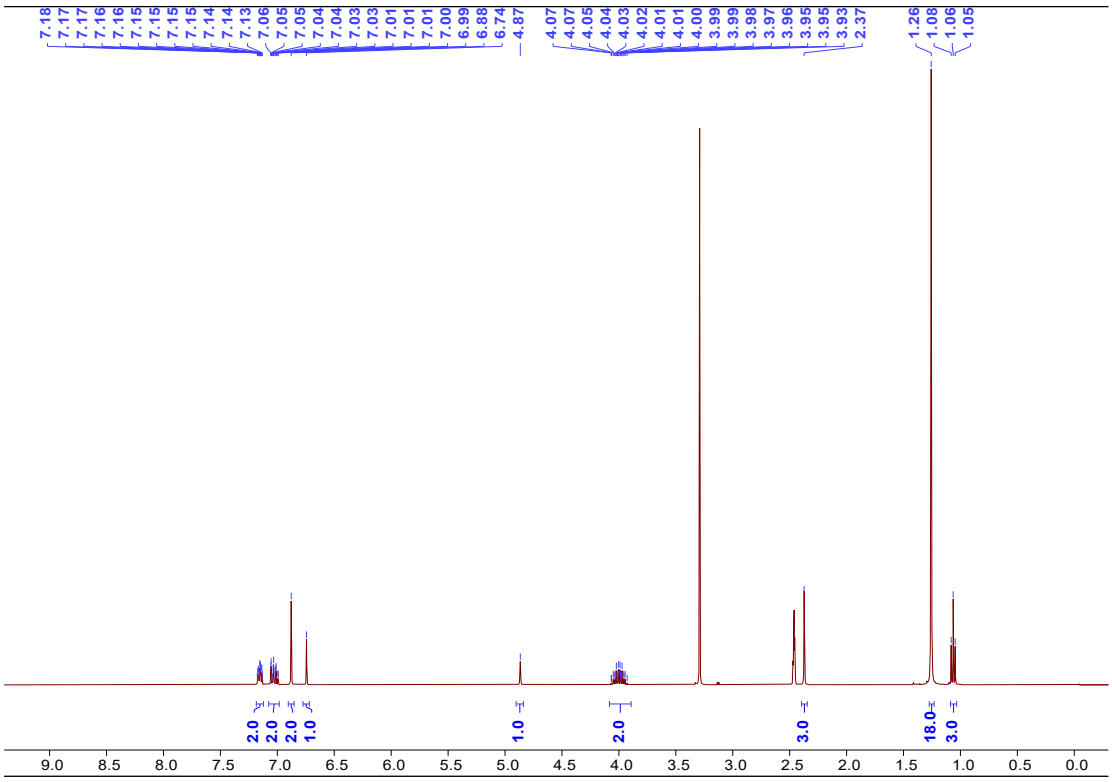
^{13}C NMR spectrum of 8a



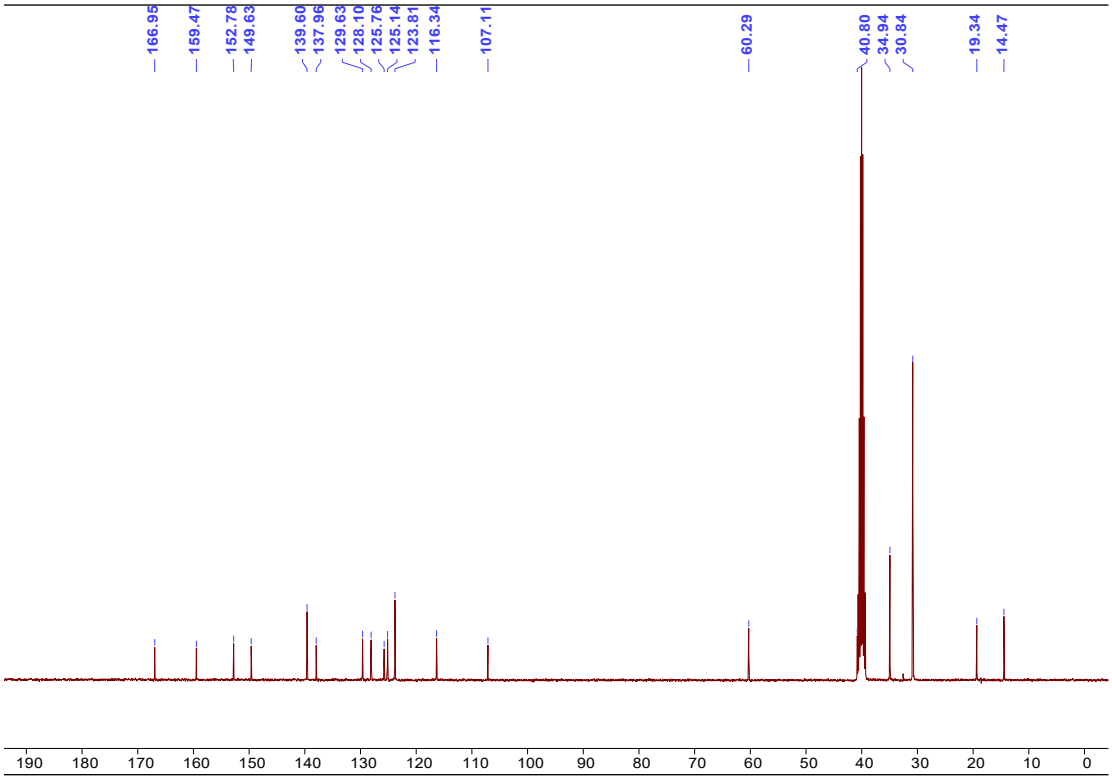
^{1}H NMR spectrum of 7b



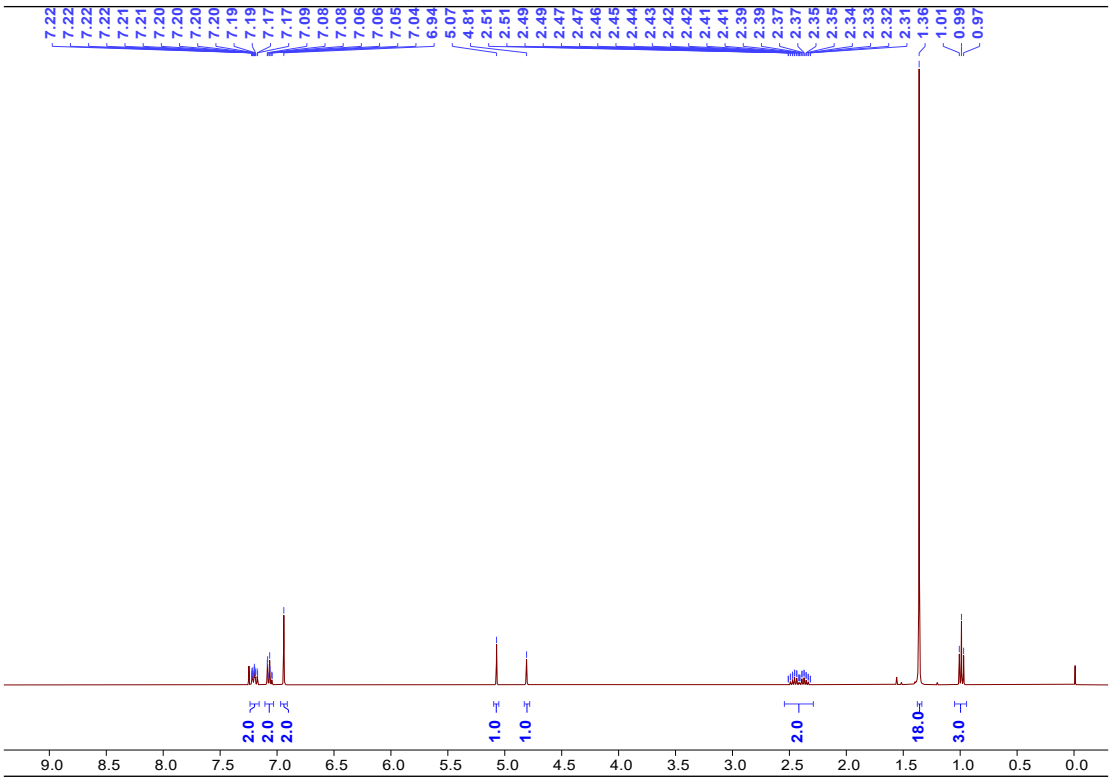
^{13}C NMR spectrum of 7b



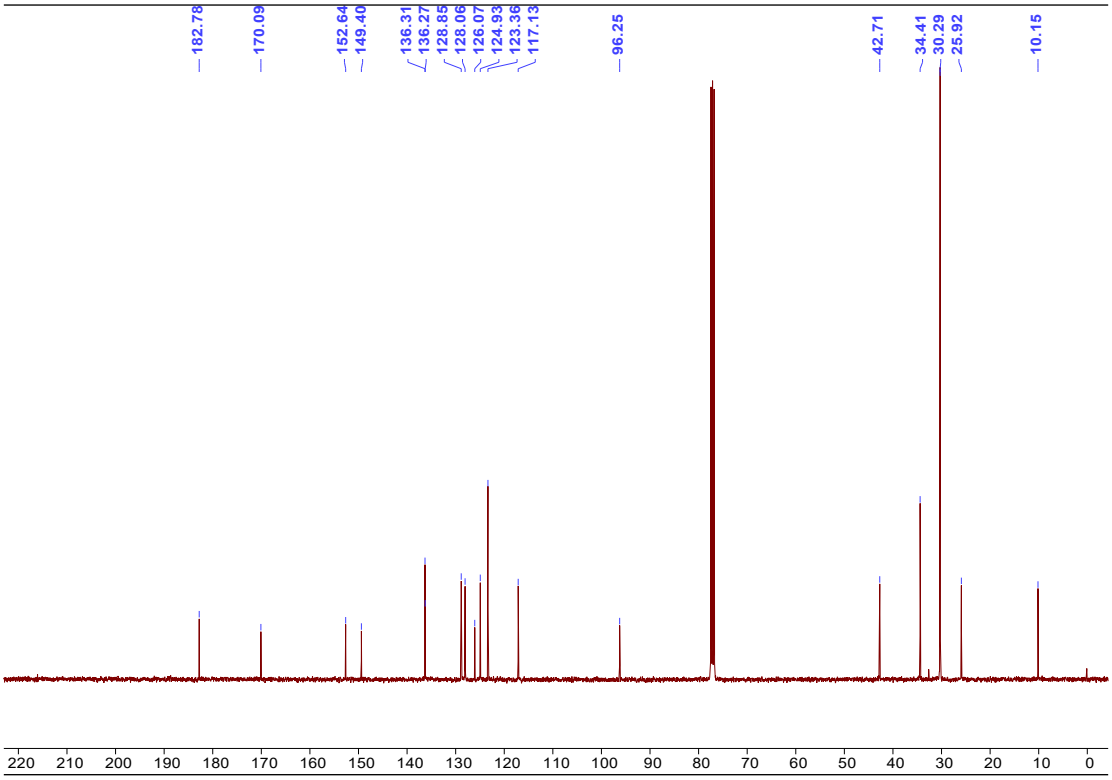
^{1}H NMR spectrum of 8b



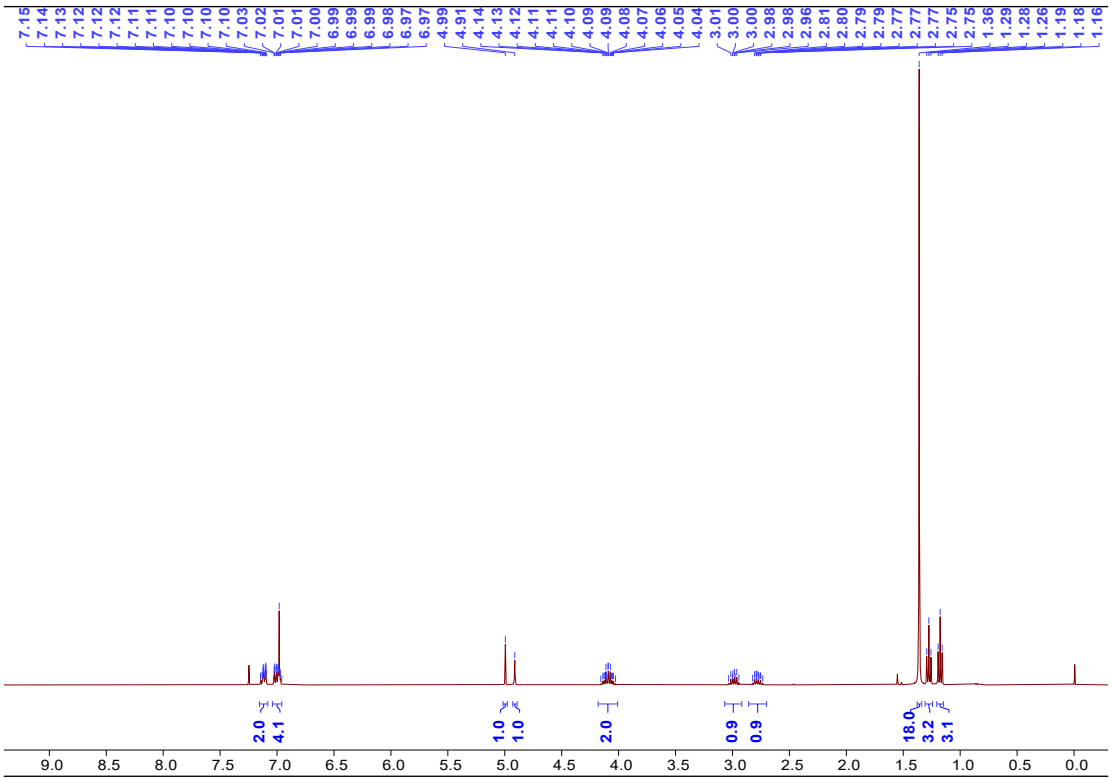
^{13}C NMR spectrum of 8b



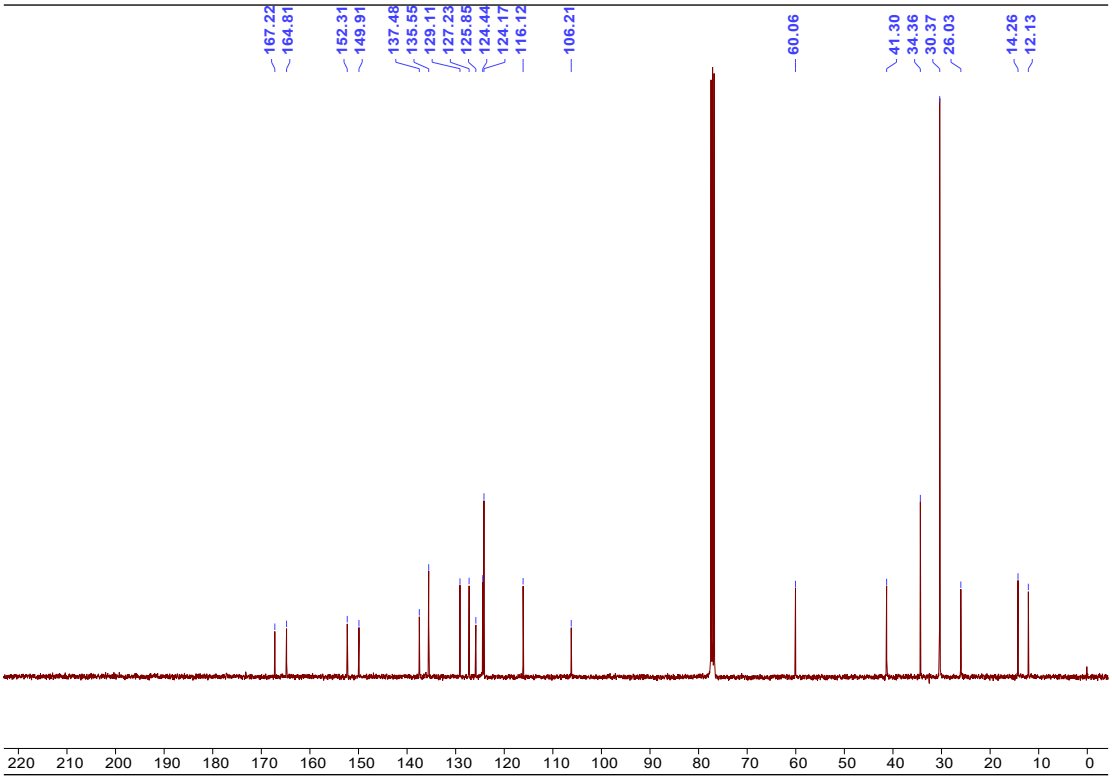
^{1}H NMR spectrum of 7c



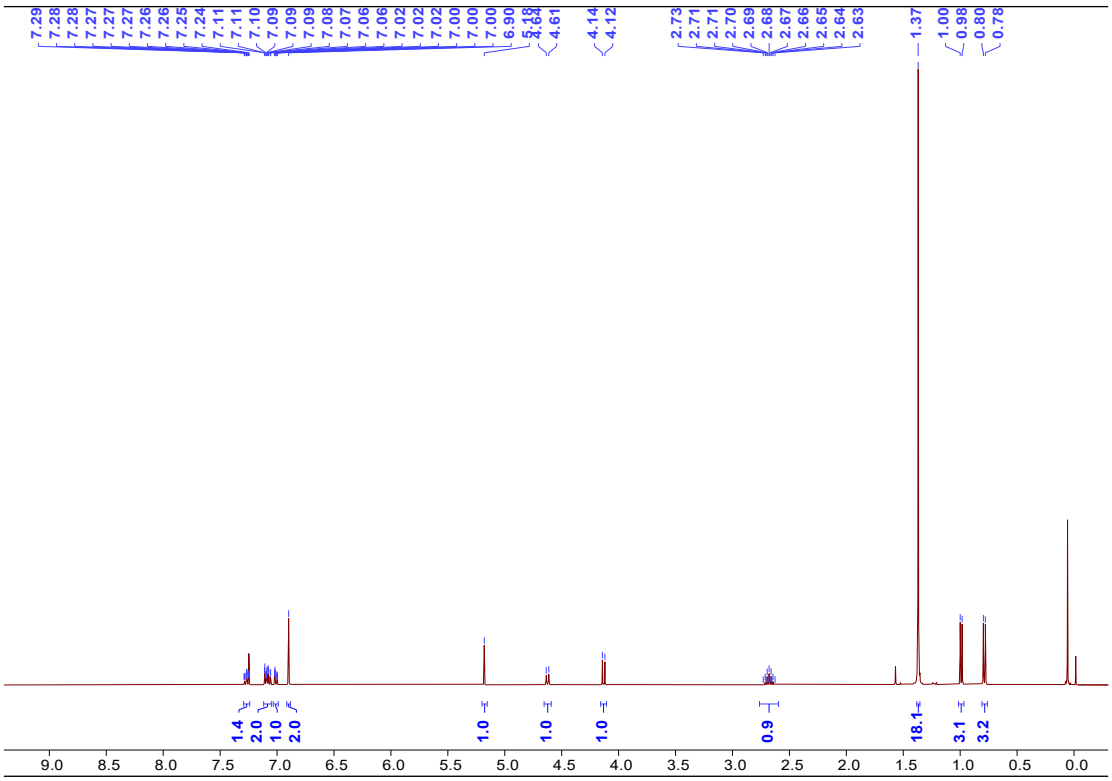
^{13}C NMR spectrum of 7c



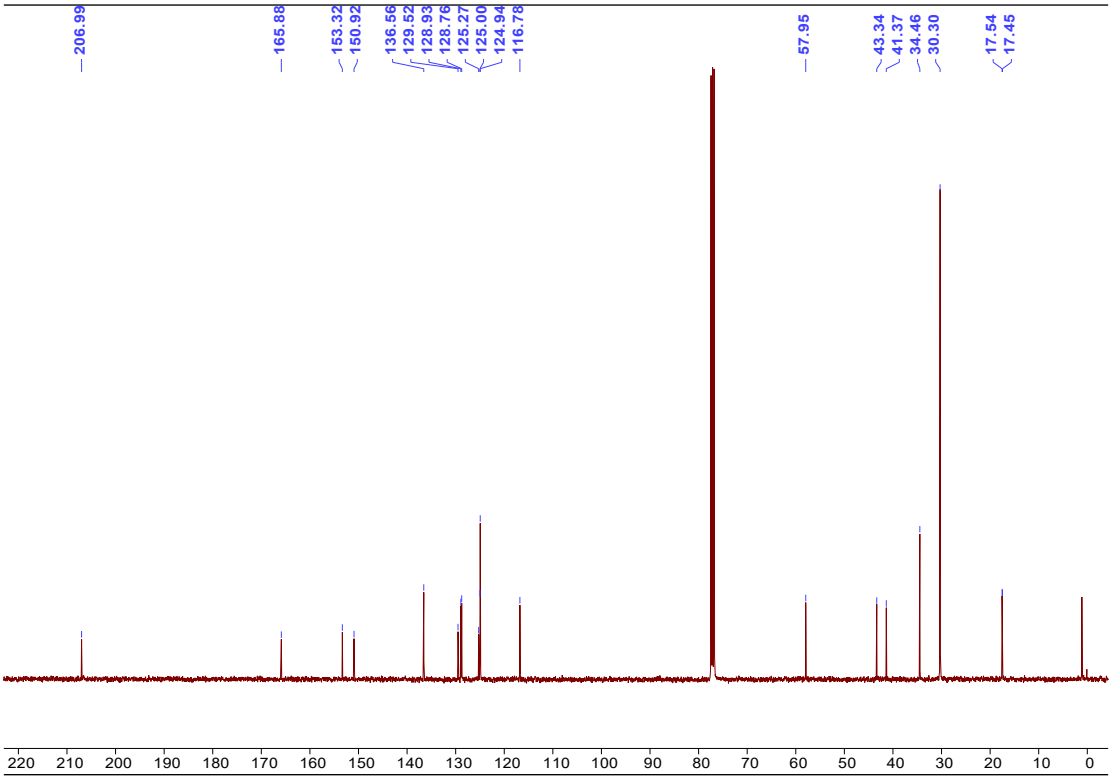
^{1}H NMR spectrum of 8c



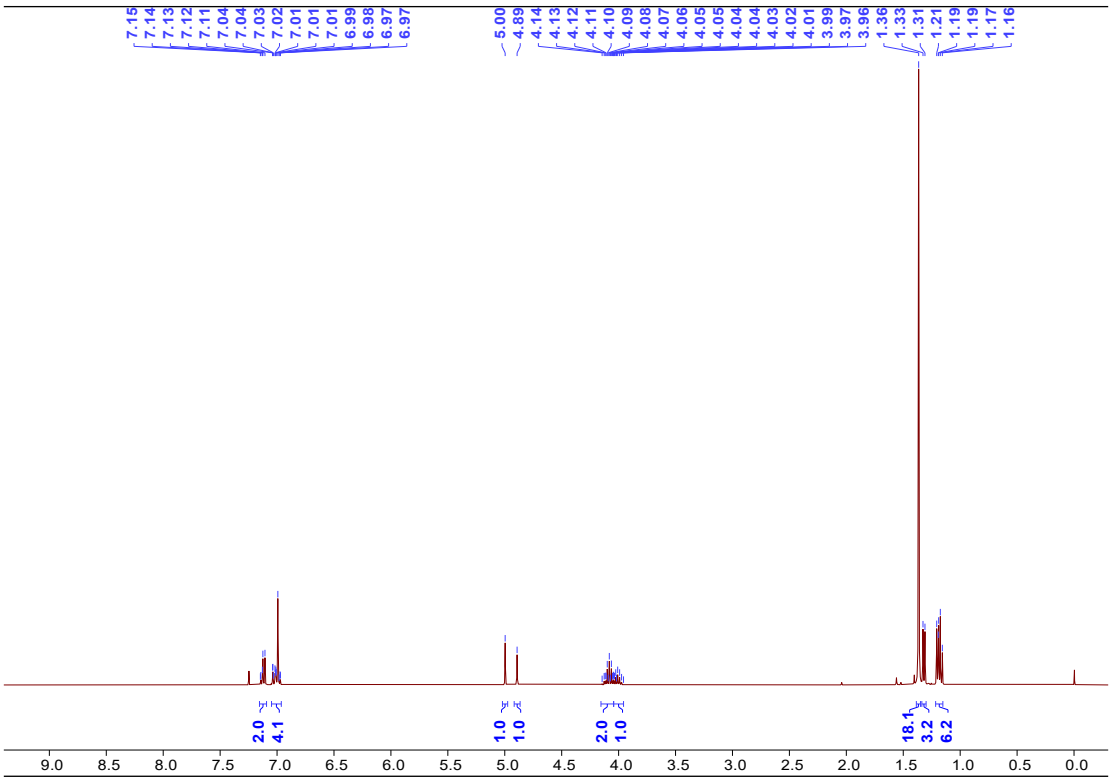
^{13}C NMR spectrum of 8c



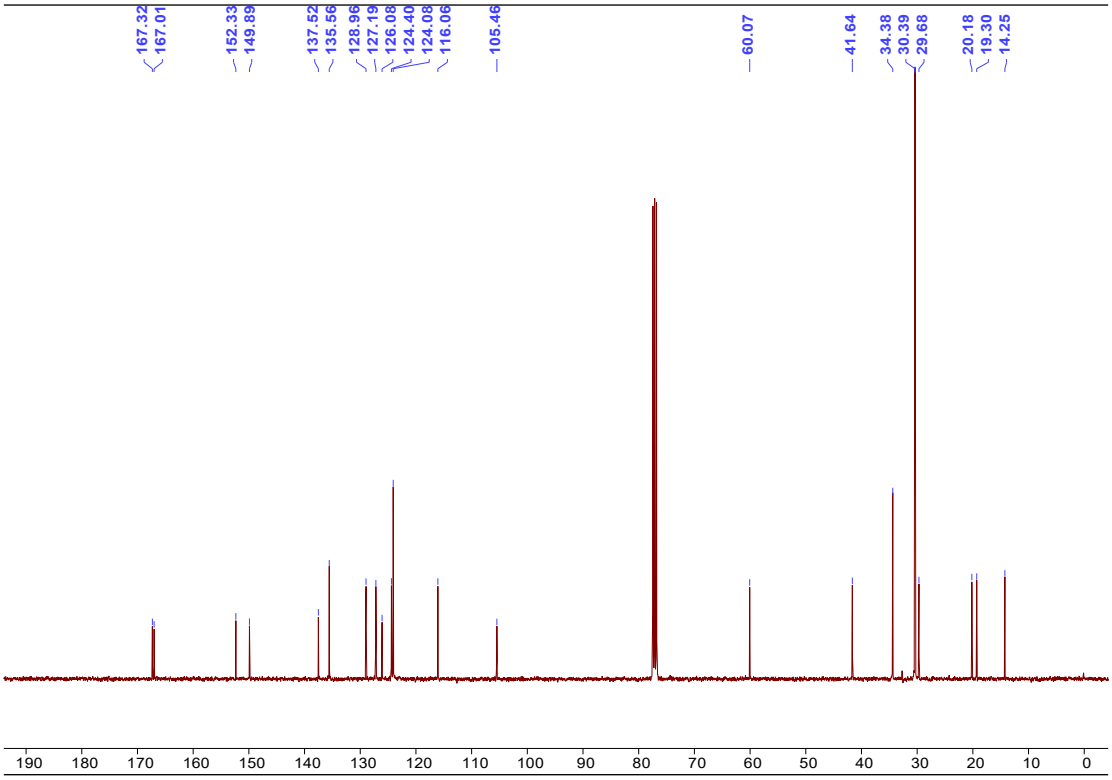
^{1}H NMR spectrum of 7d



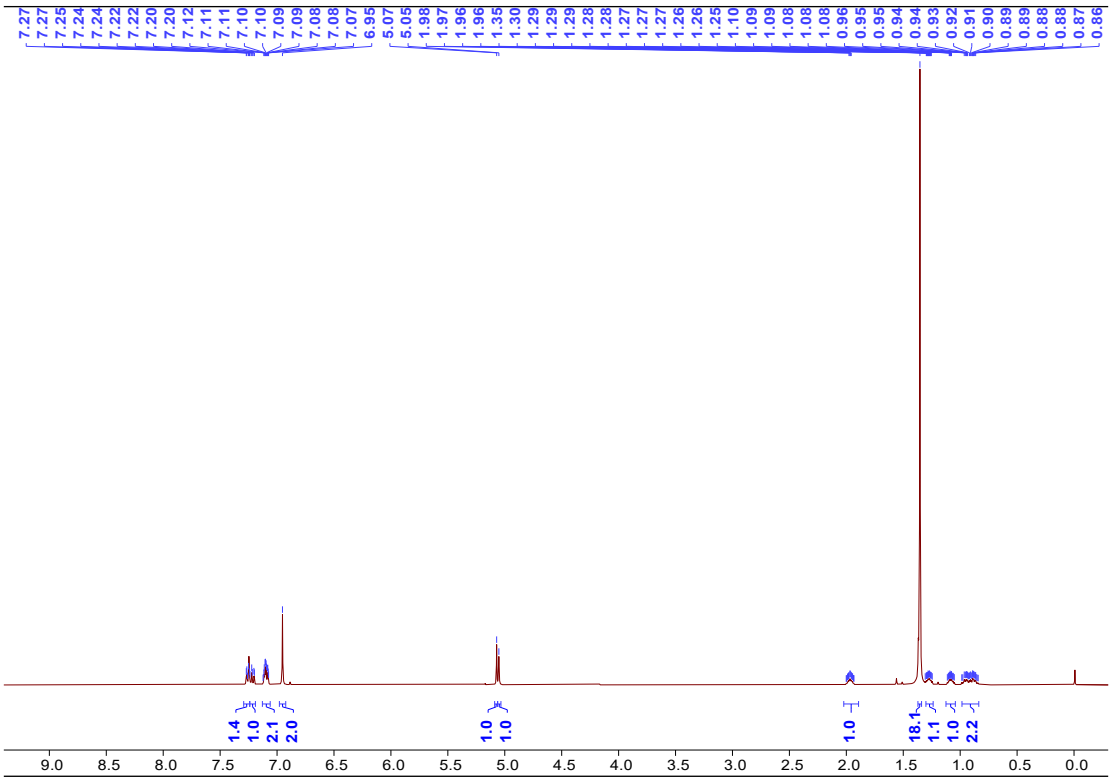
^{13}C NMR spectrum of 7d



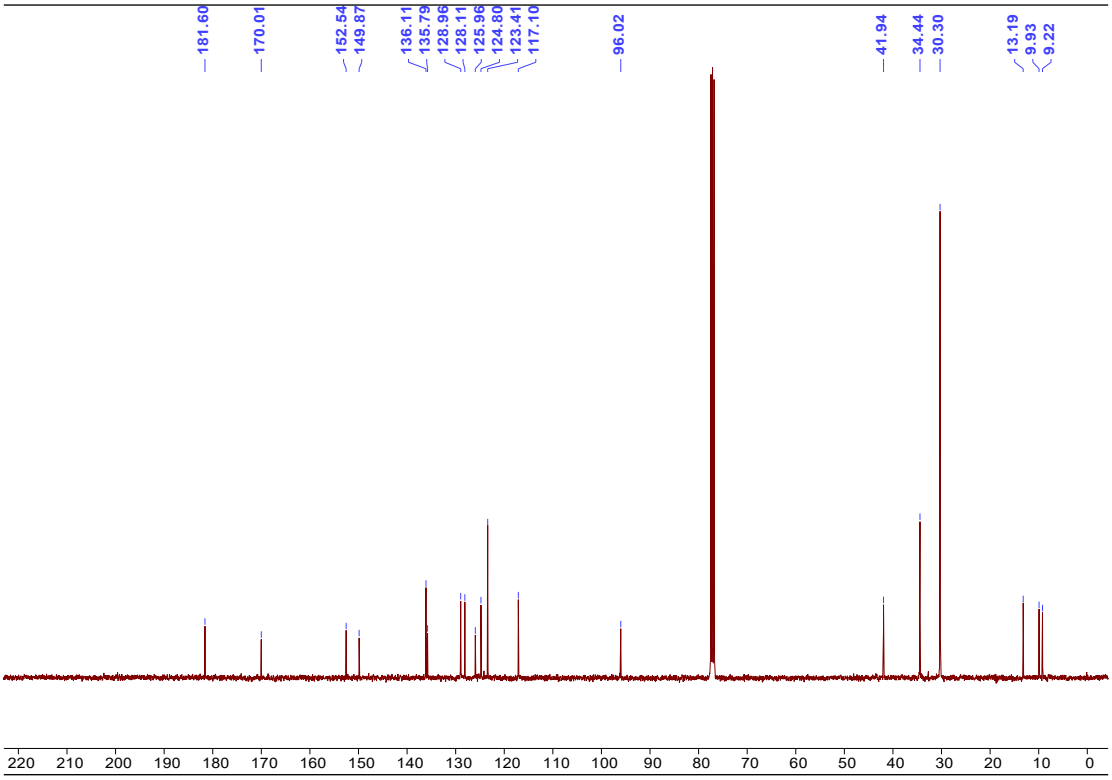
^{1}H NMR spectrum of 8d



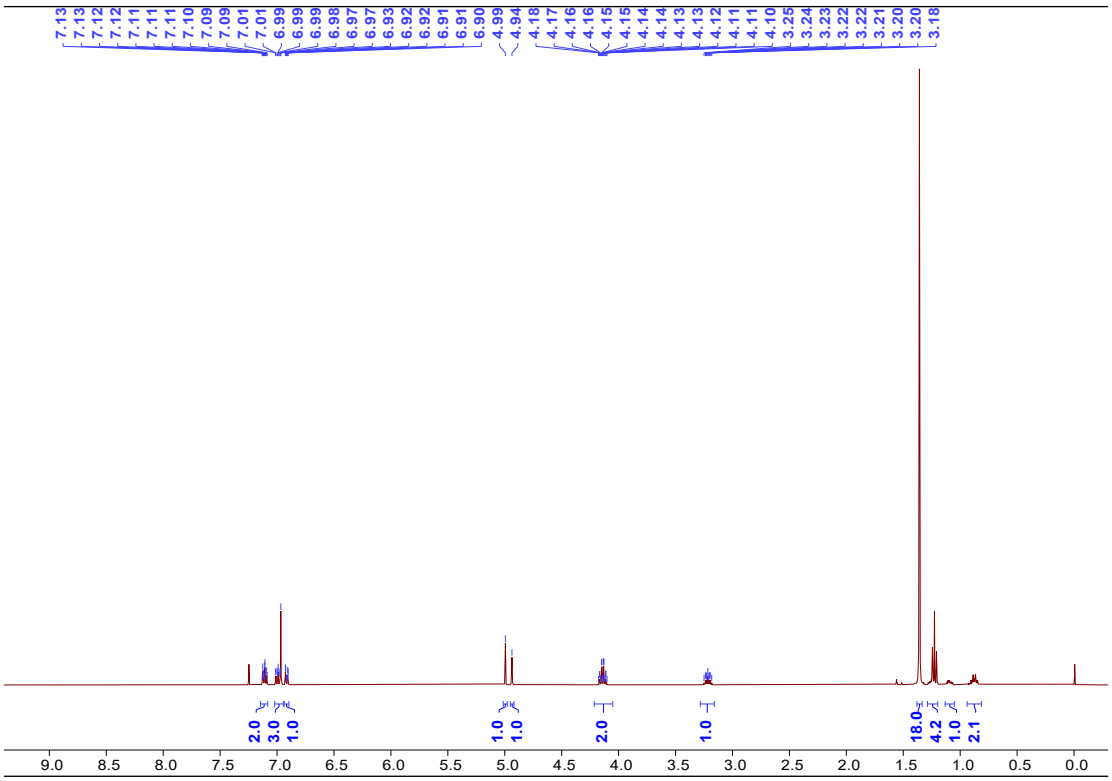
^{13}C NMR spectrum of 8d



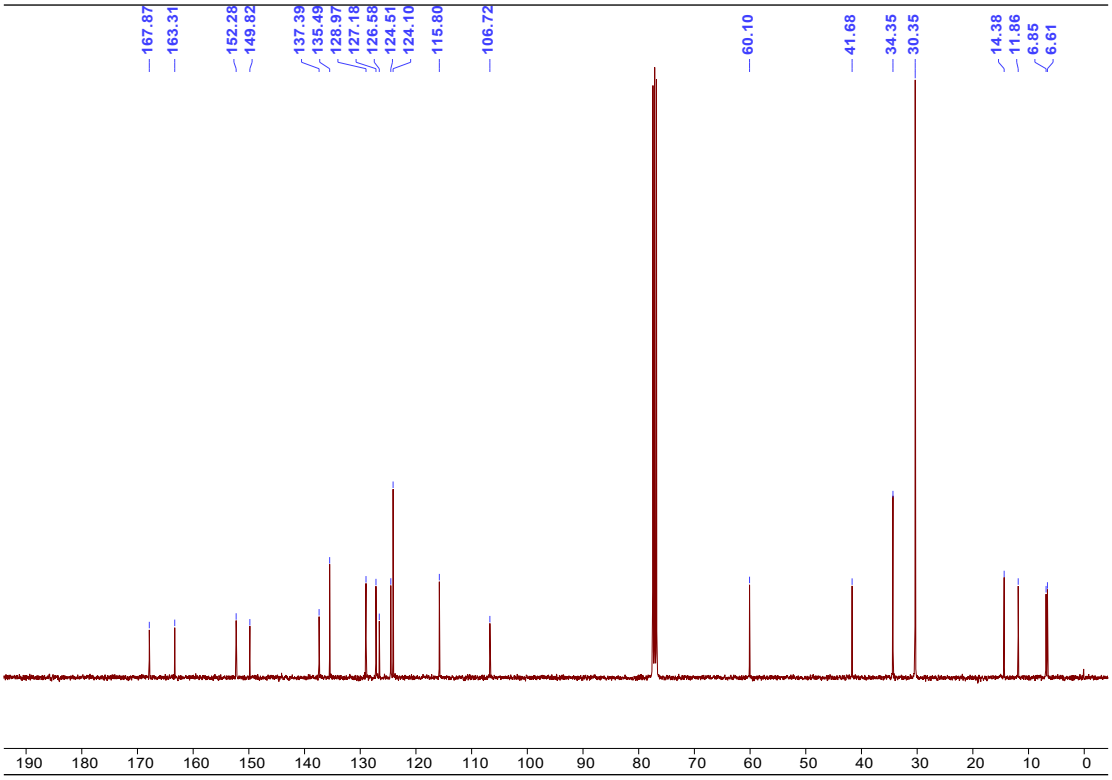
^{1}H NMR spectrum of 7e



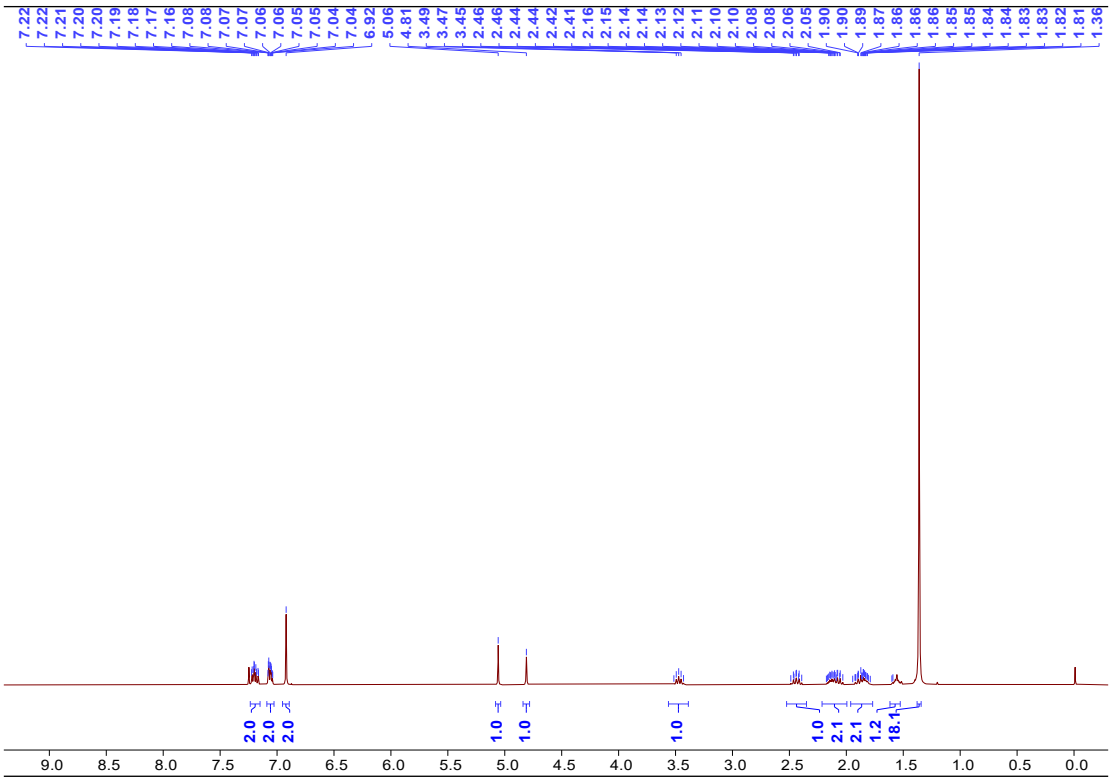
^{13}C NMR spectrum of 7e



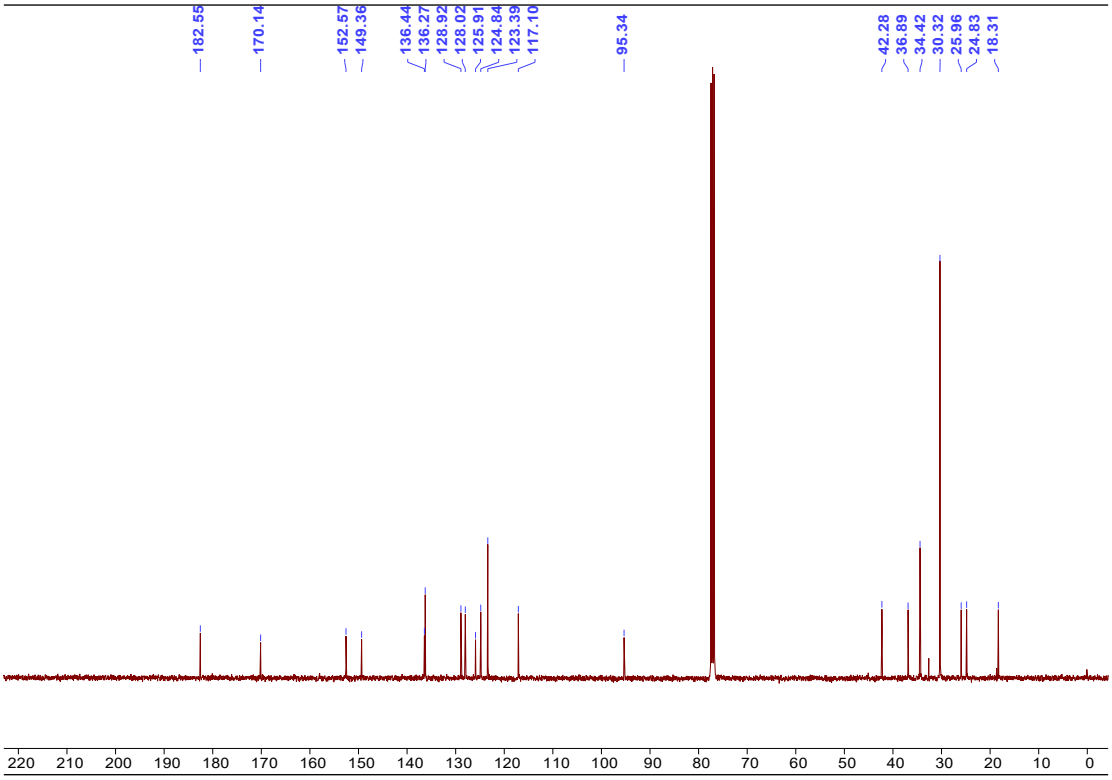
^{1}H NMR spectrum of 8e



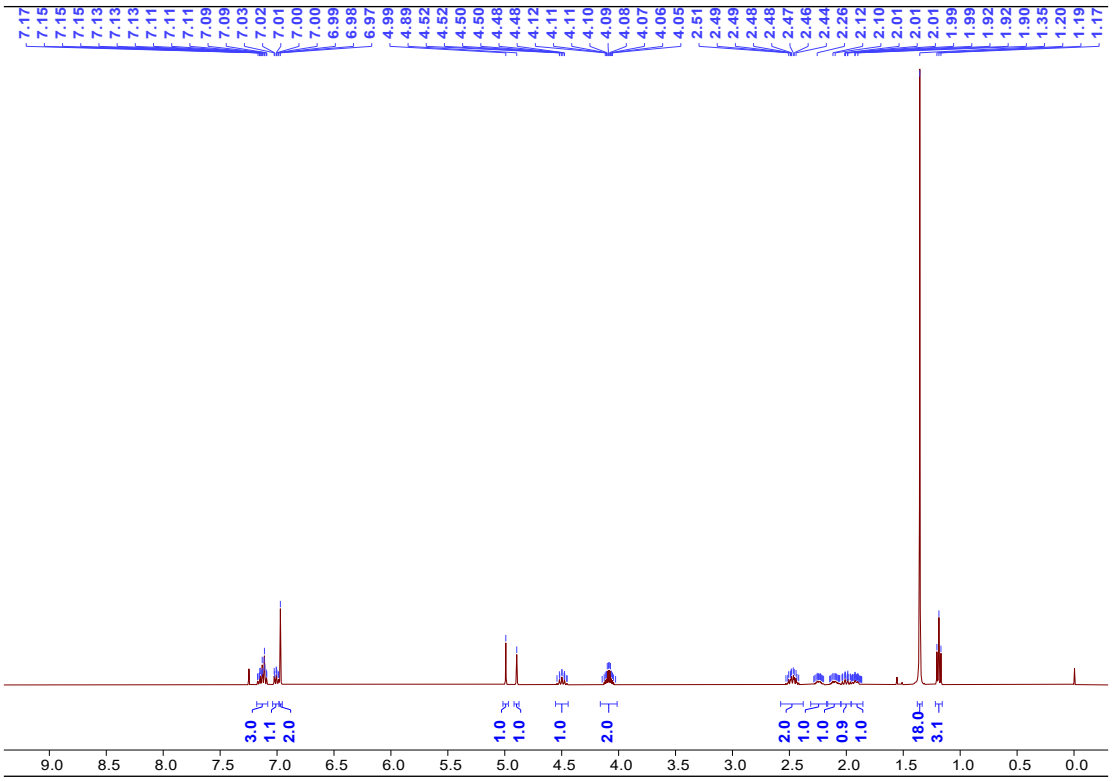
^{13}C NMR spectrum of 8e



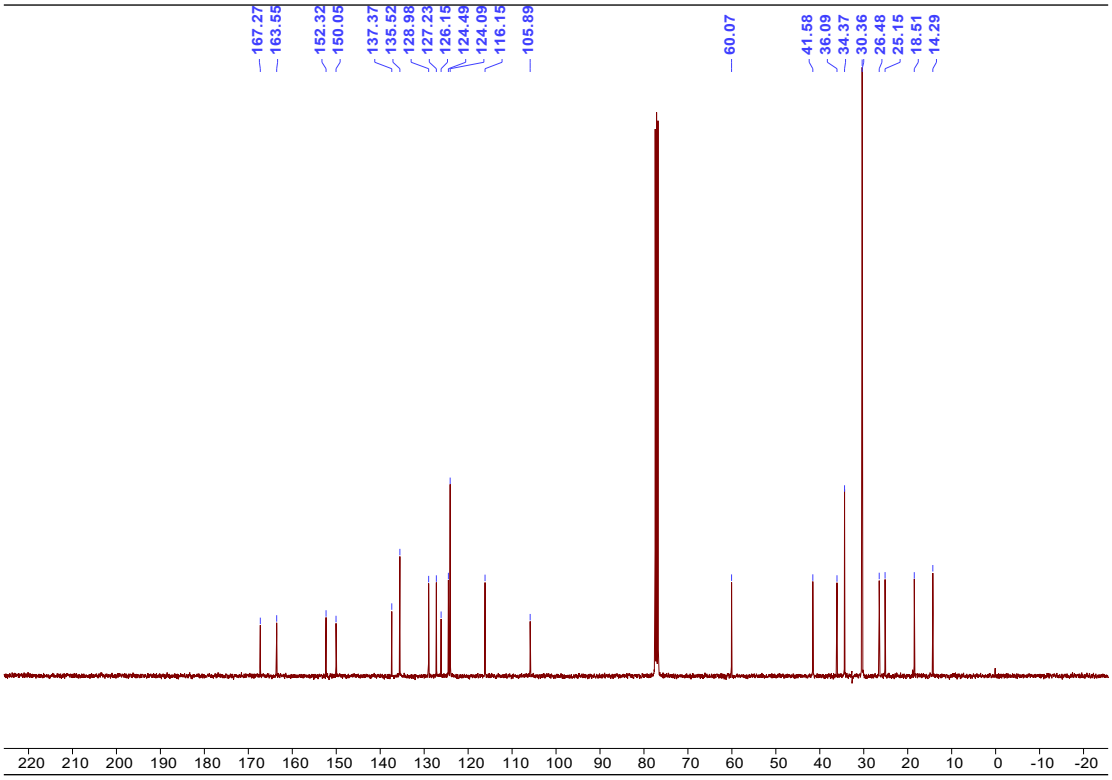
^{1}H NMR spectrum of 7f



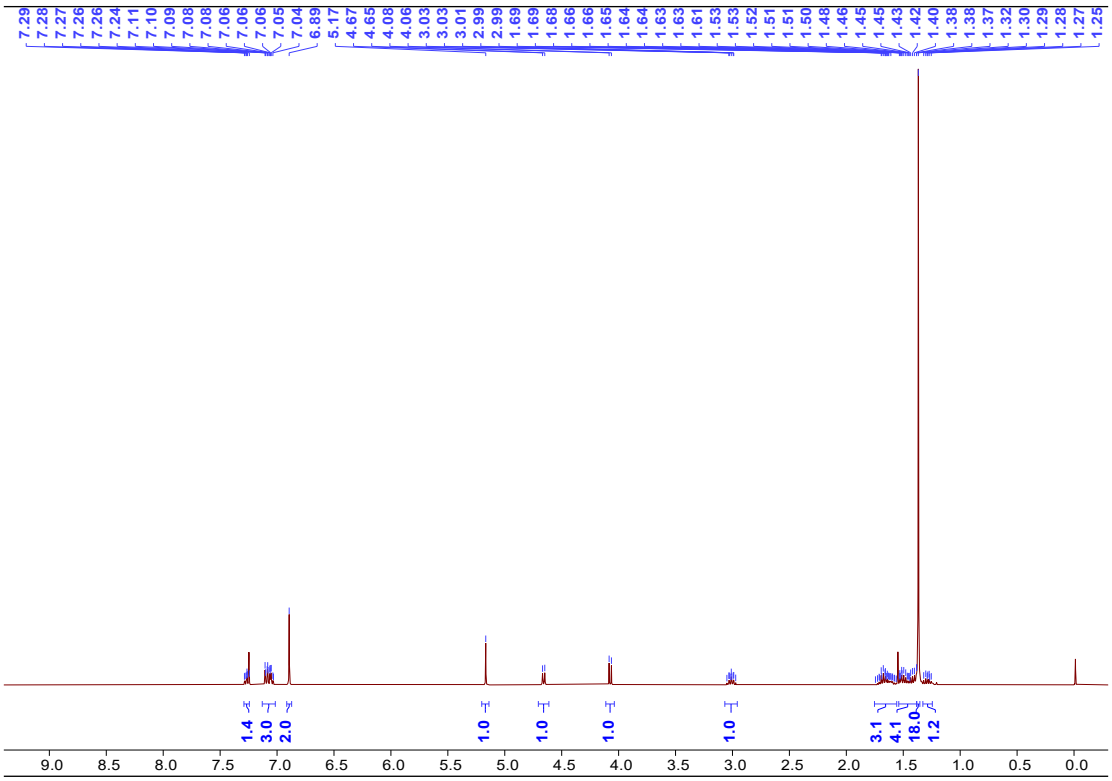
^{13}C NMR spectrum of 7f



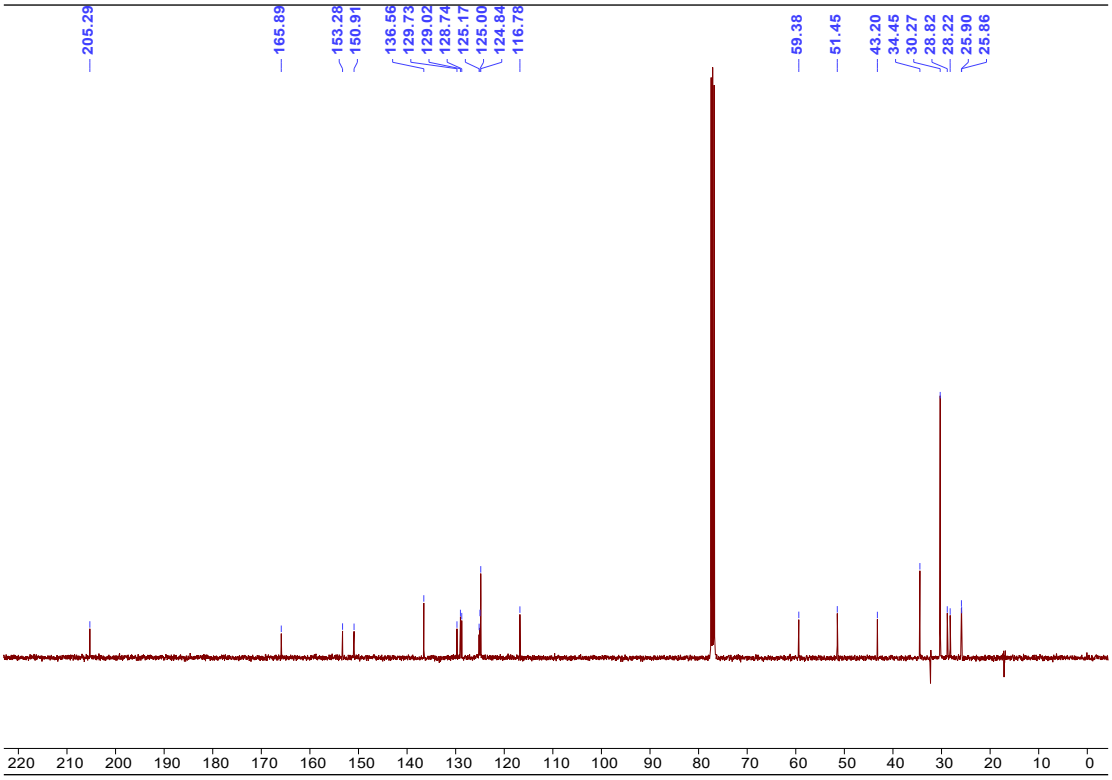
^{1}H NMR spectrum of 8f



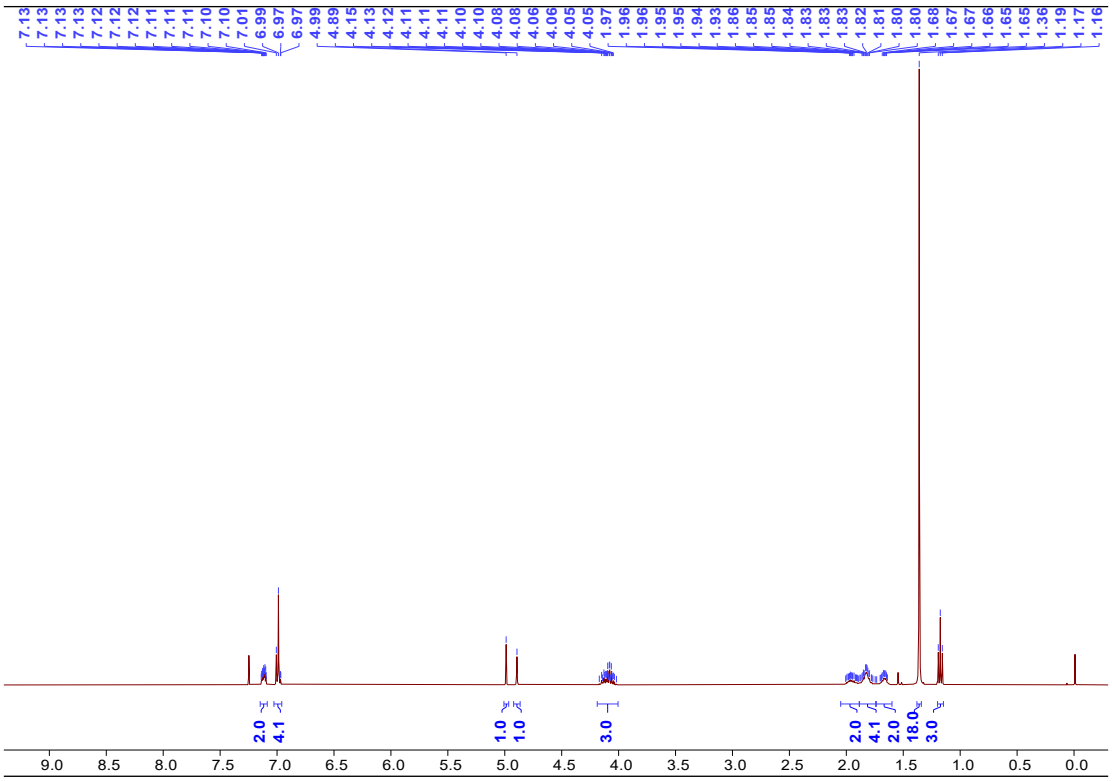
^{13}C NMR spectrum of 8f



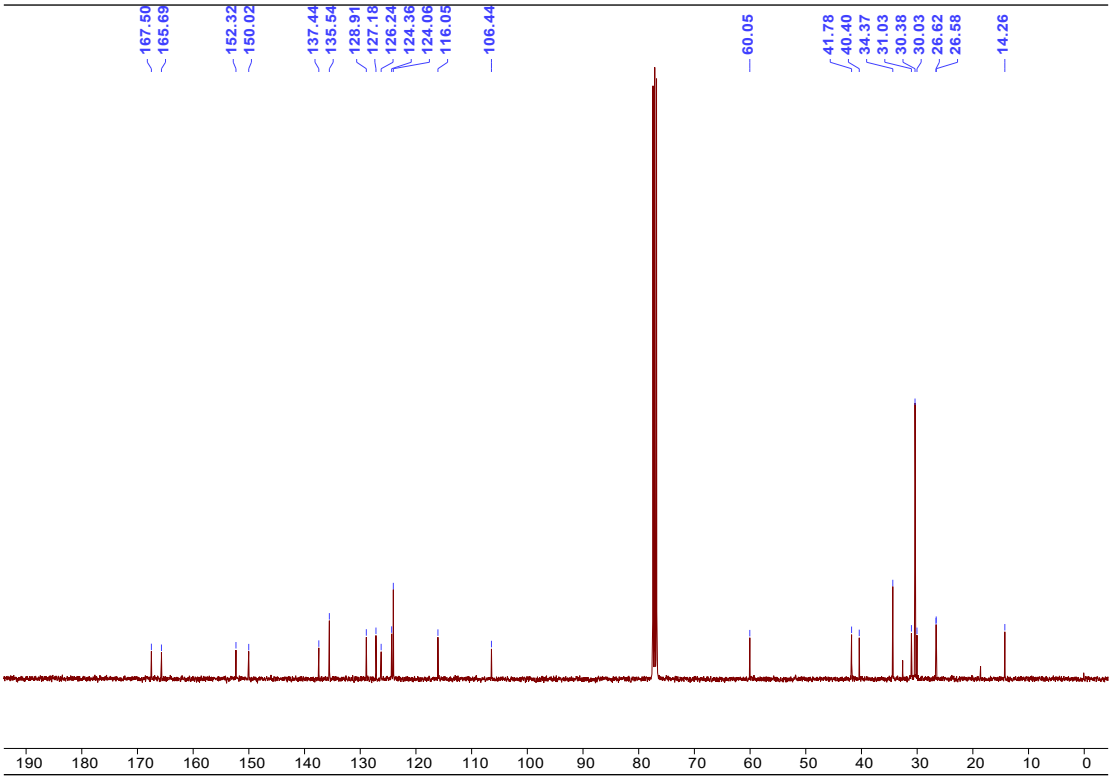
^{1}H NMR spectrum of 7g



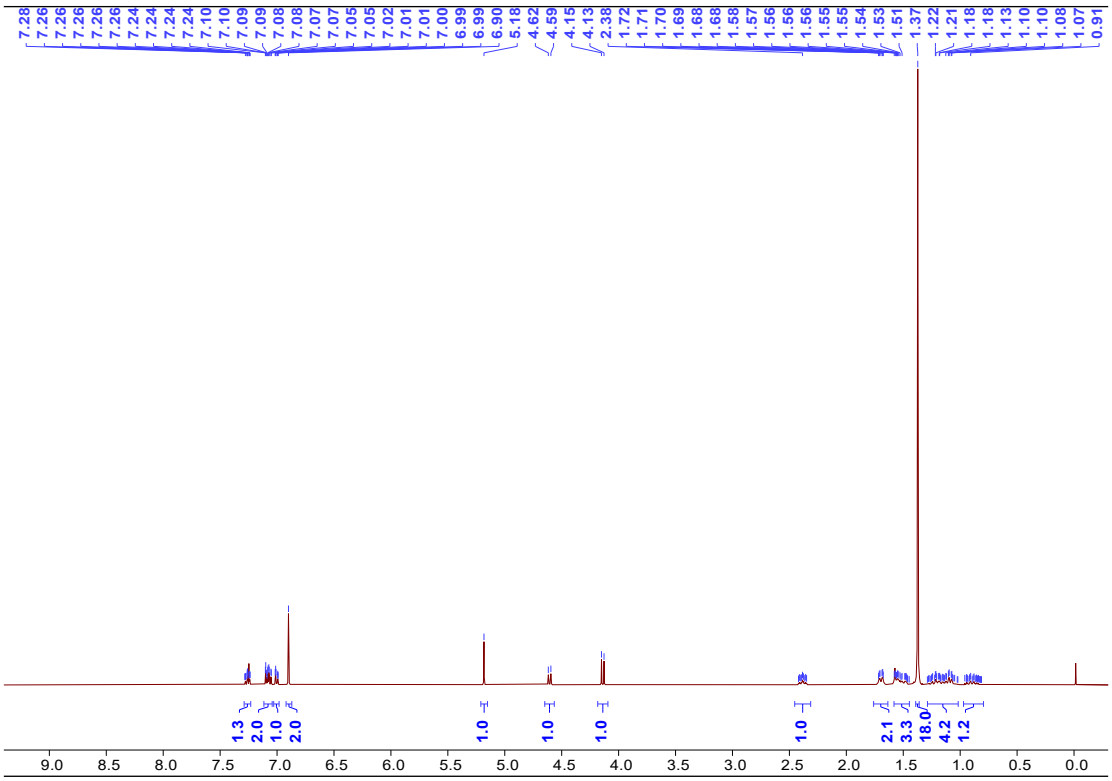
^{13}C NMR spectrum of 7g



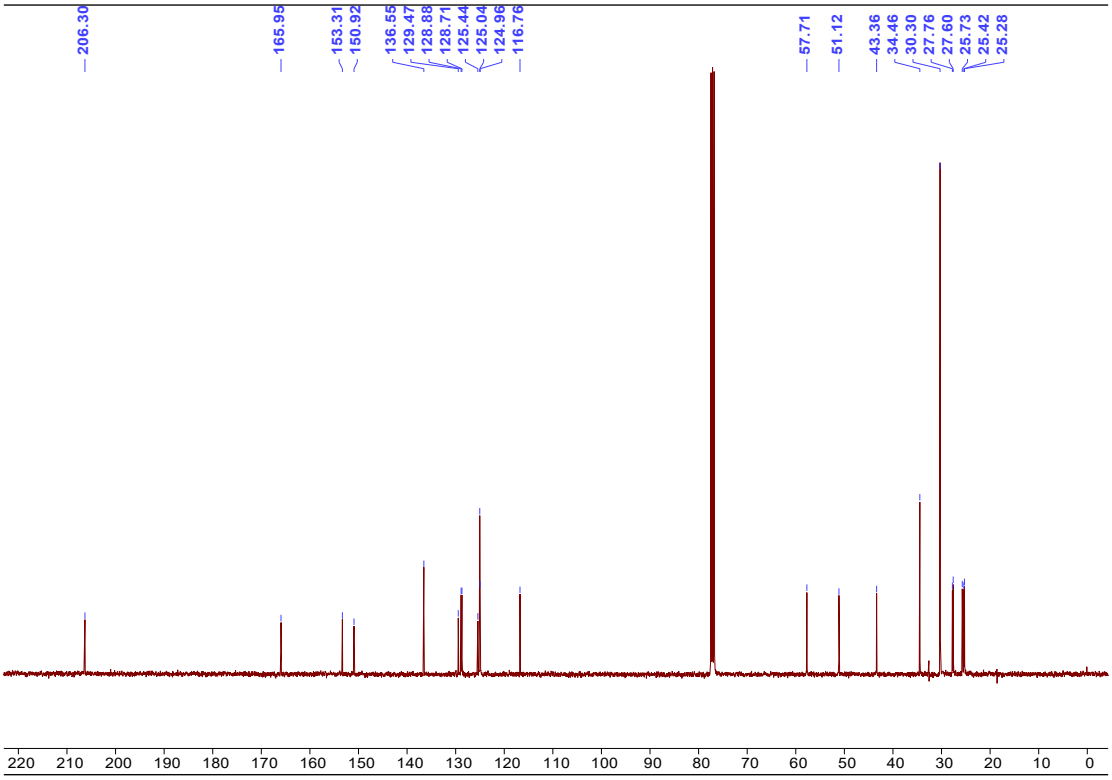
^{1}H NMR spectrum of 8g



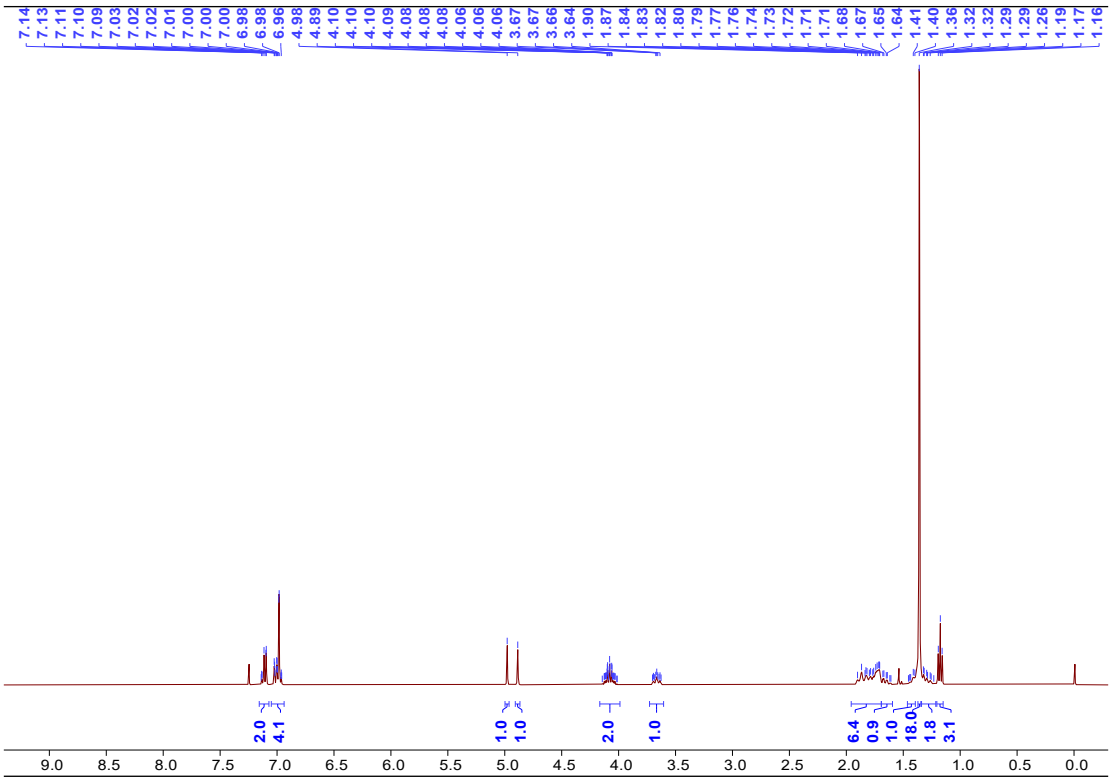
^{13}C NMR spectrum of 8g



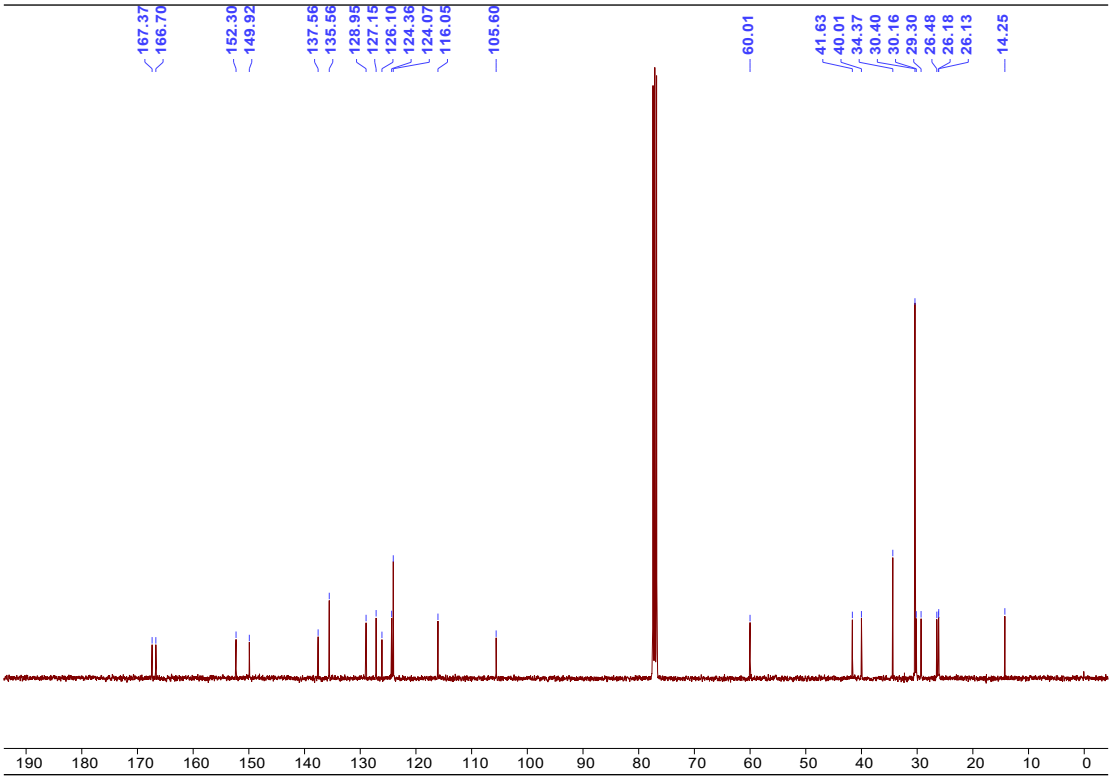
^{1}H NMR spectrum of 7h



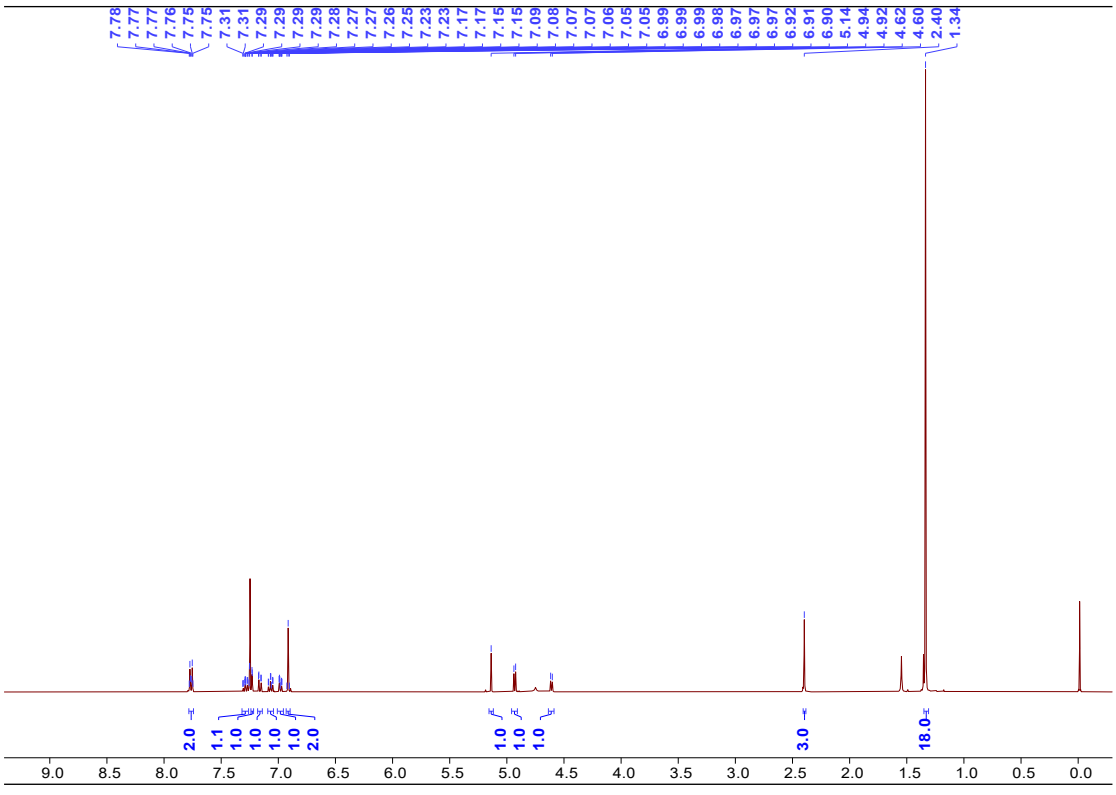
^{13}C NMR spectrum of 7h



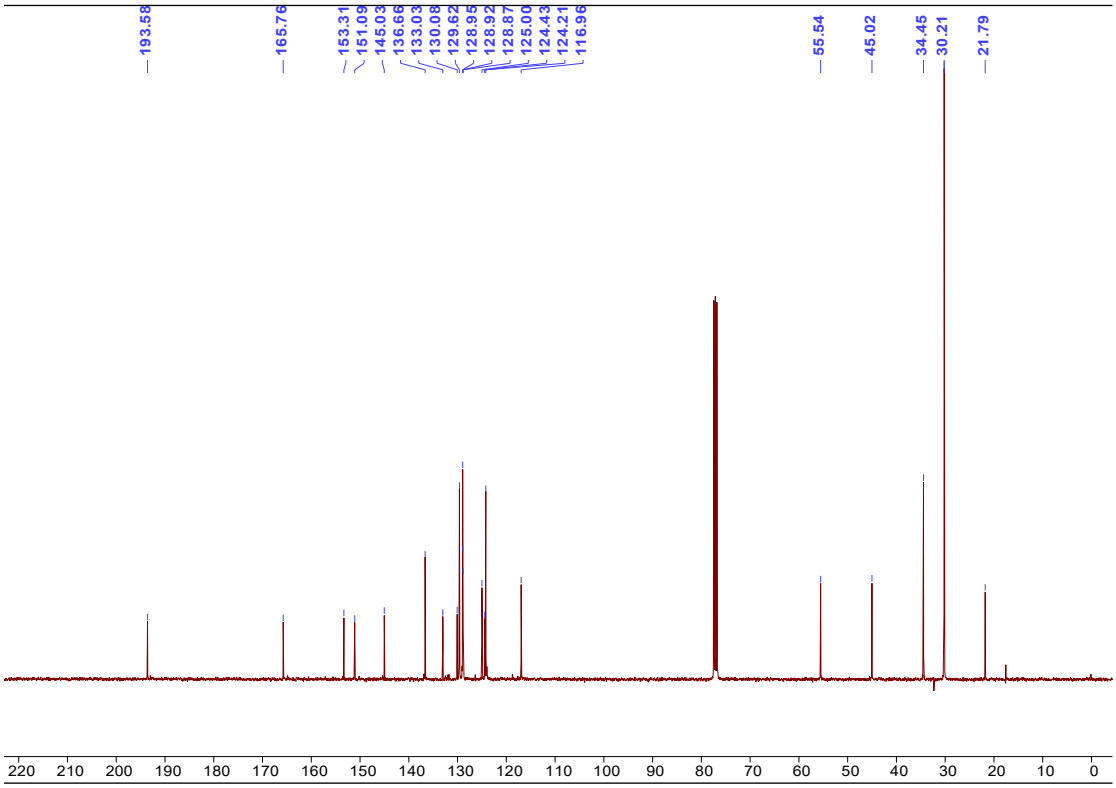
^{1}H NMR spectrum of 8h



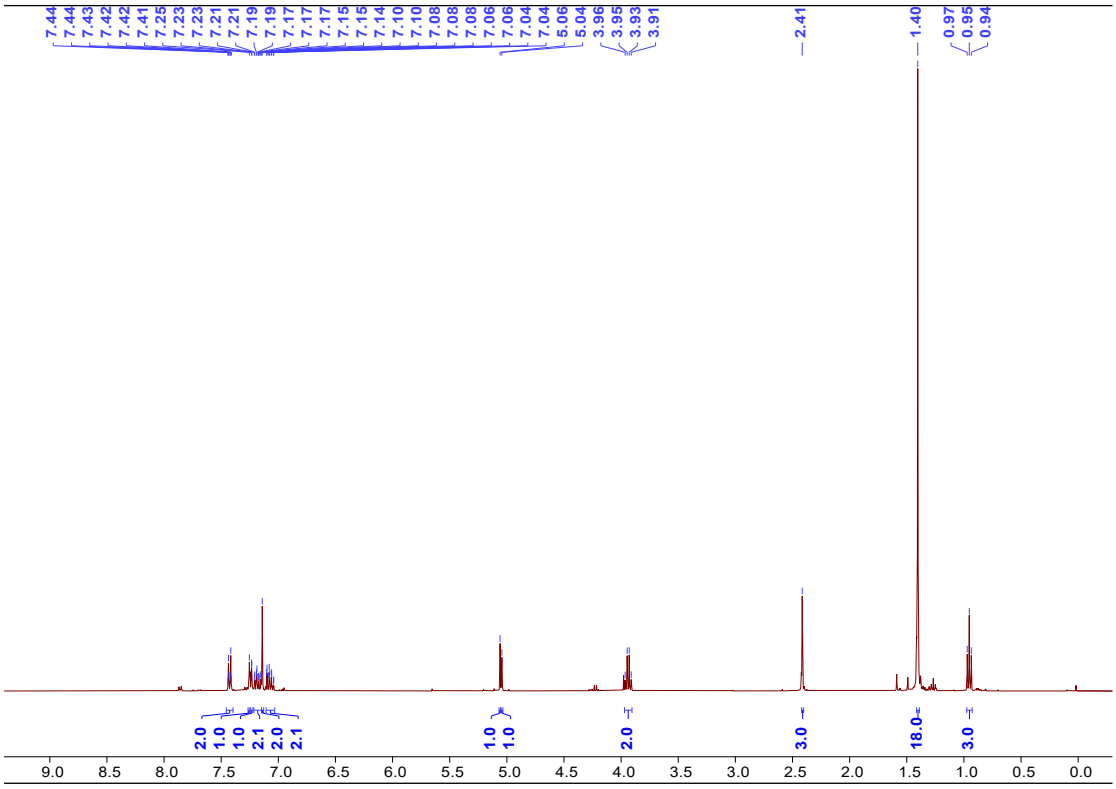
^{13}C NMR spectrum of 8h



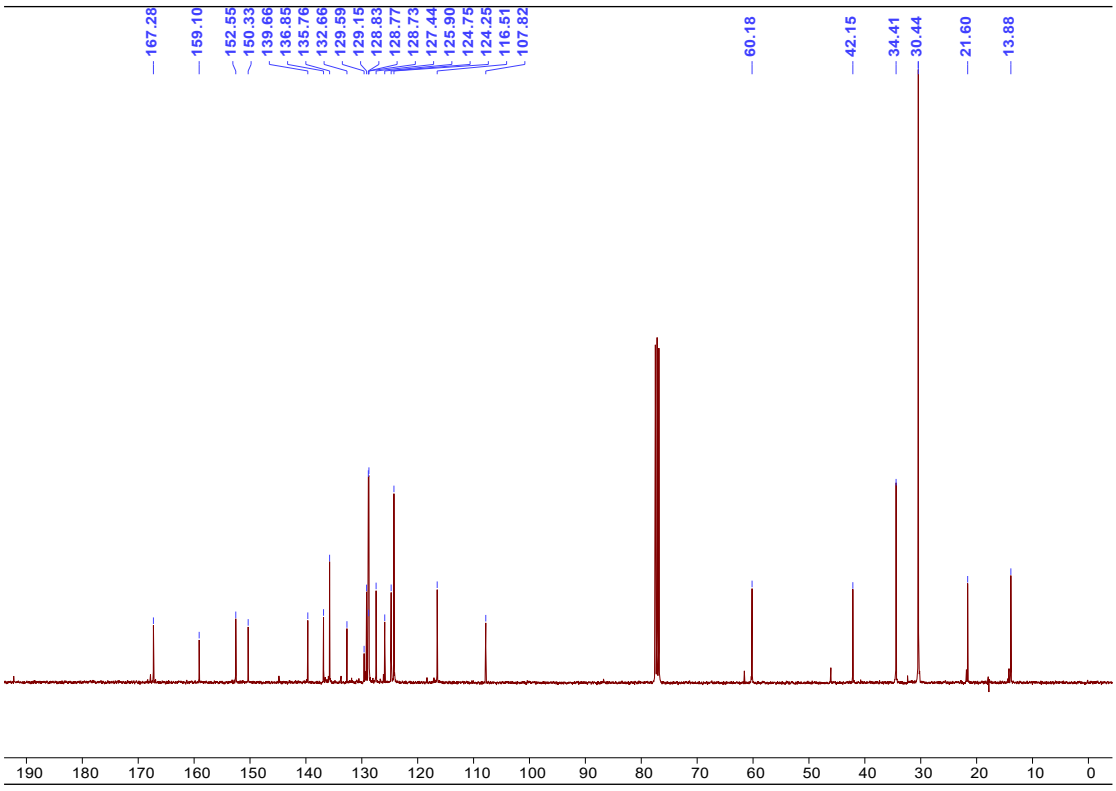
^{1}H NMR spectrum of 7i



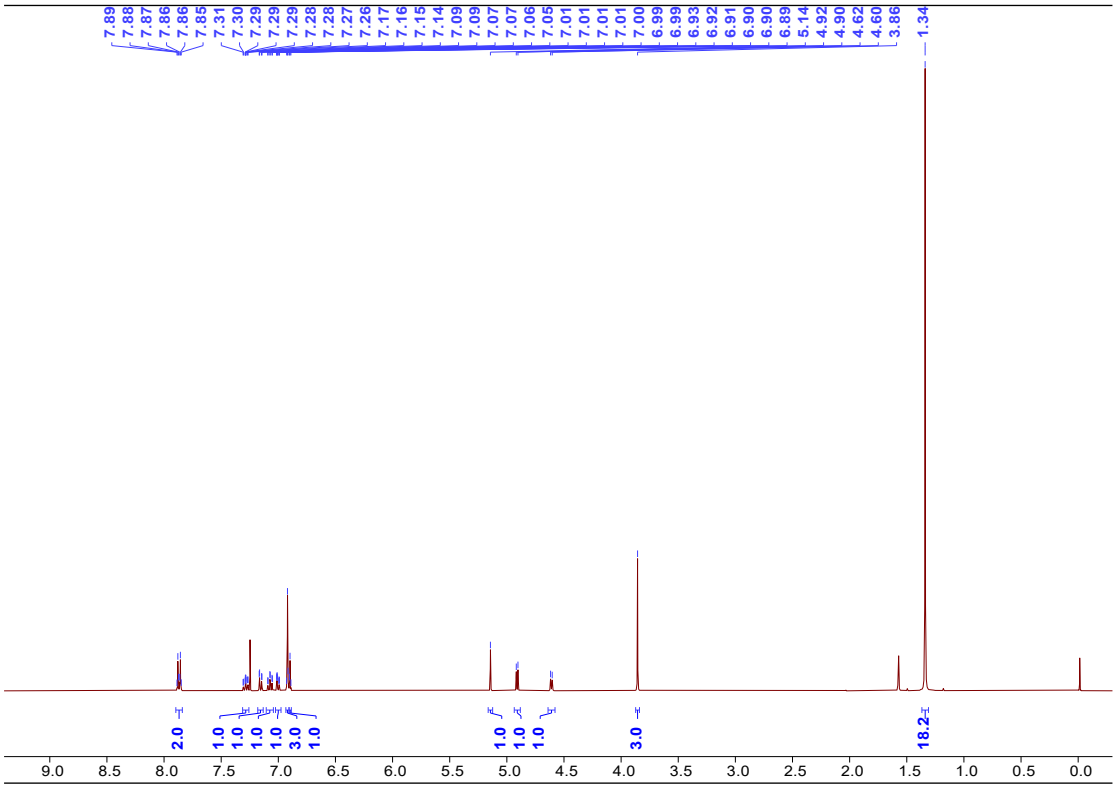
^{13}C NMR spectrum of 7i



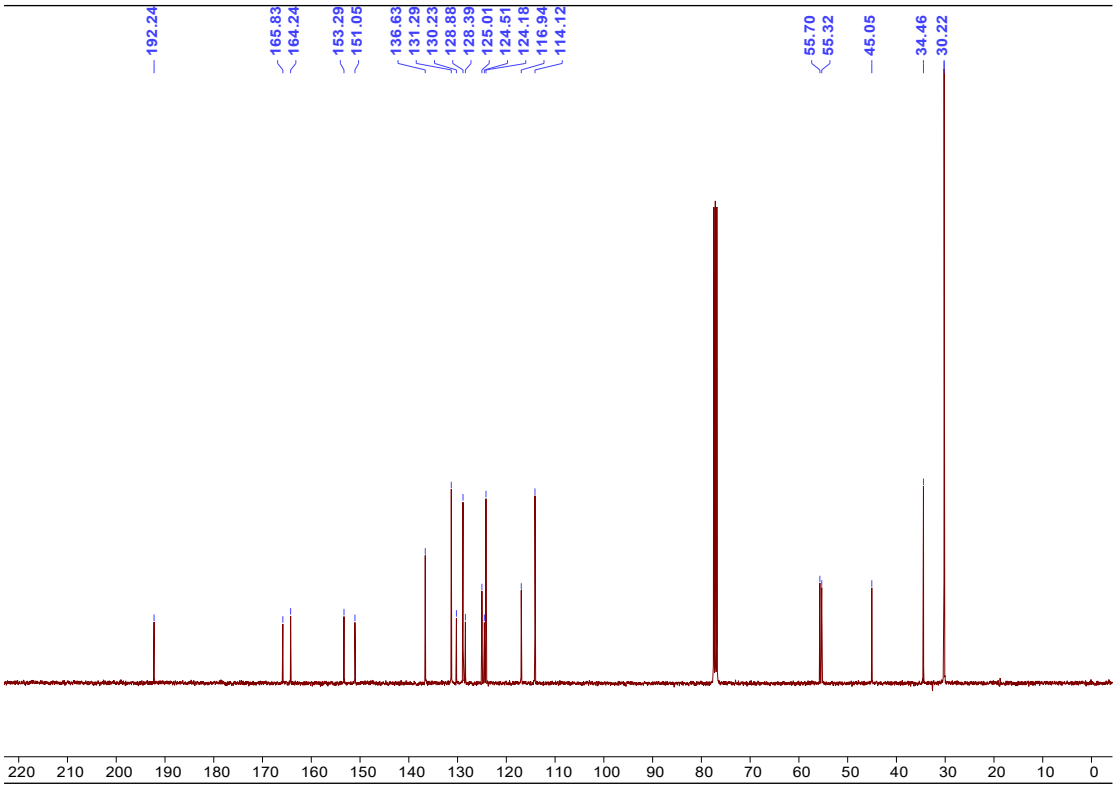
^{1}H NMR spectrum of 8i



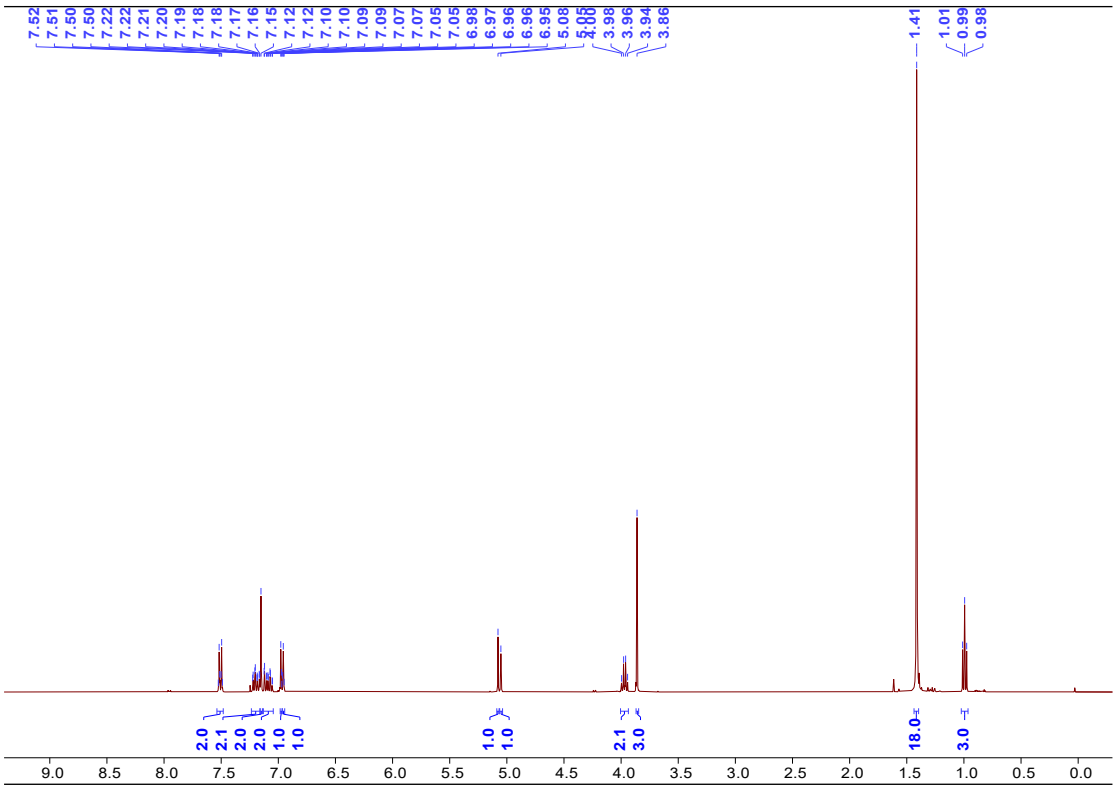
^{13}C NMR spectrum of 8i



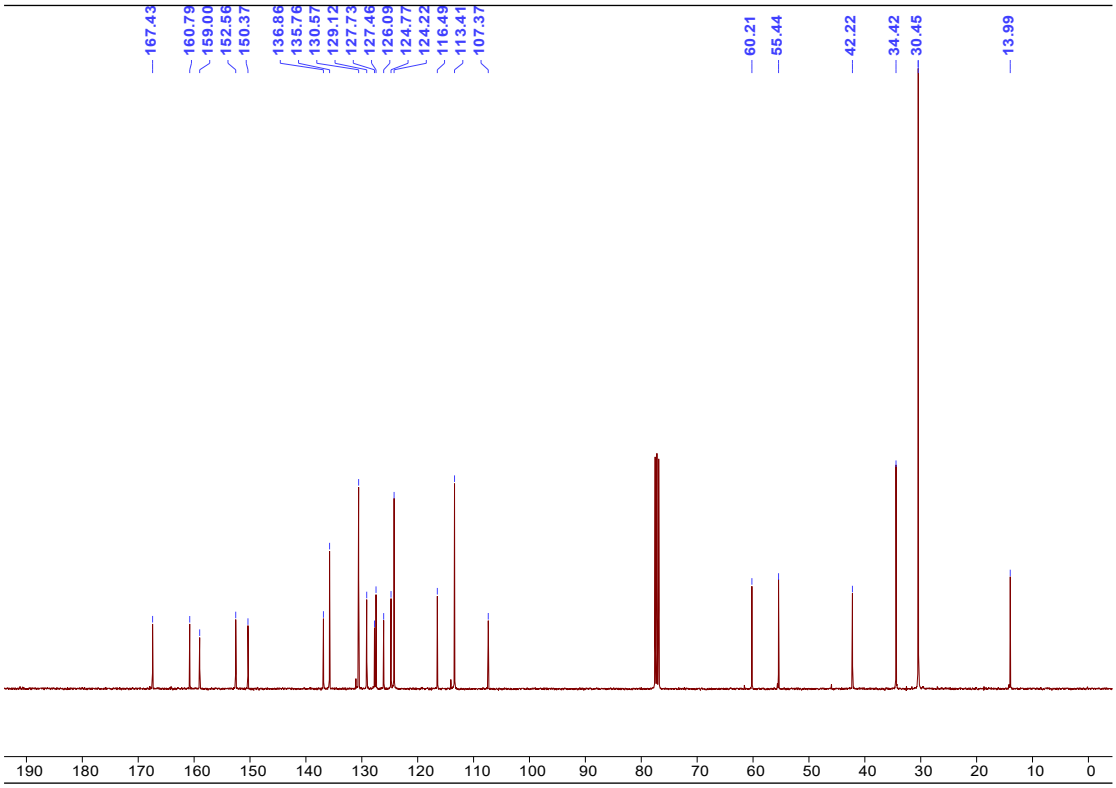
^{1}H NMR spectrum of 7j



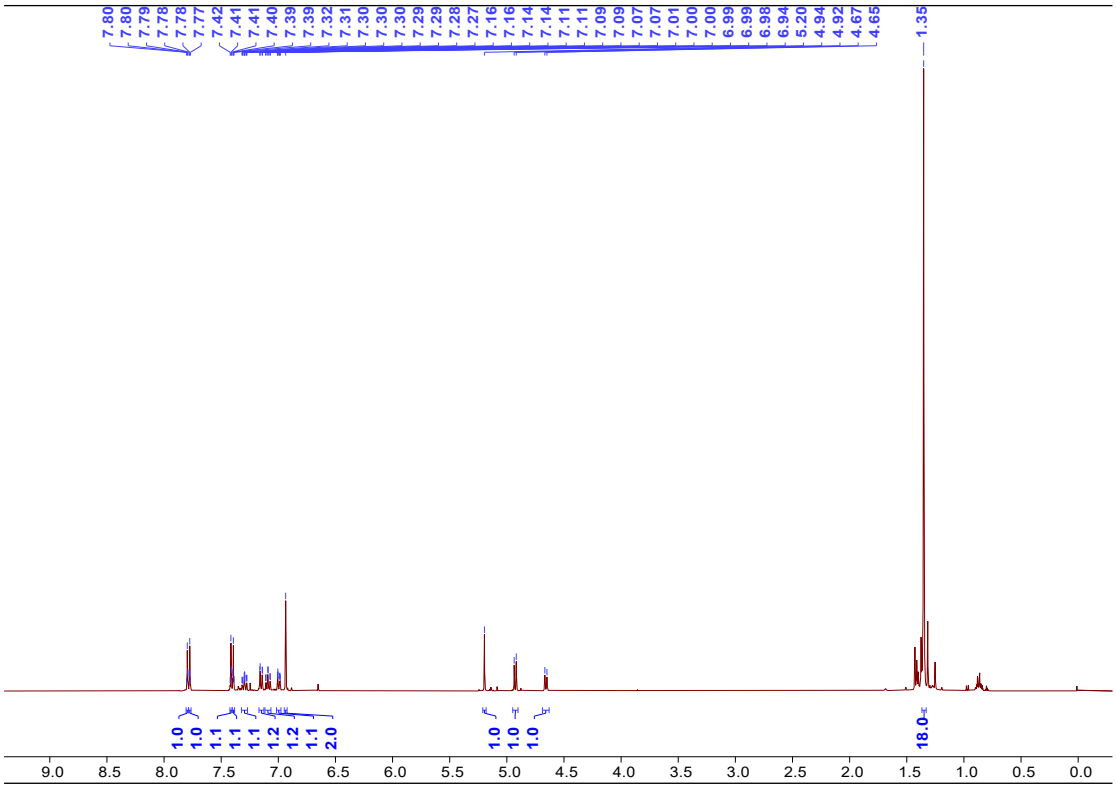
^{13}C NMR spectrum of 7j



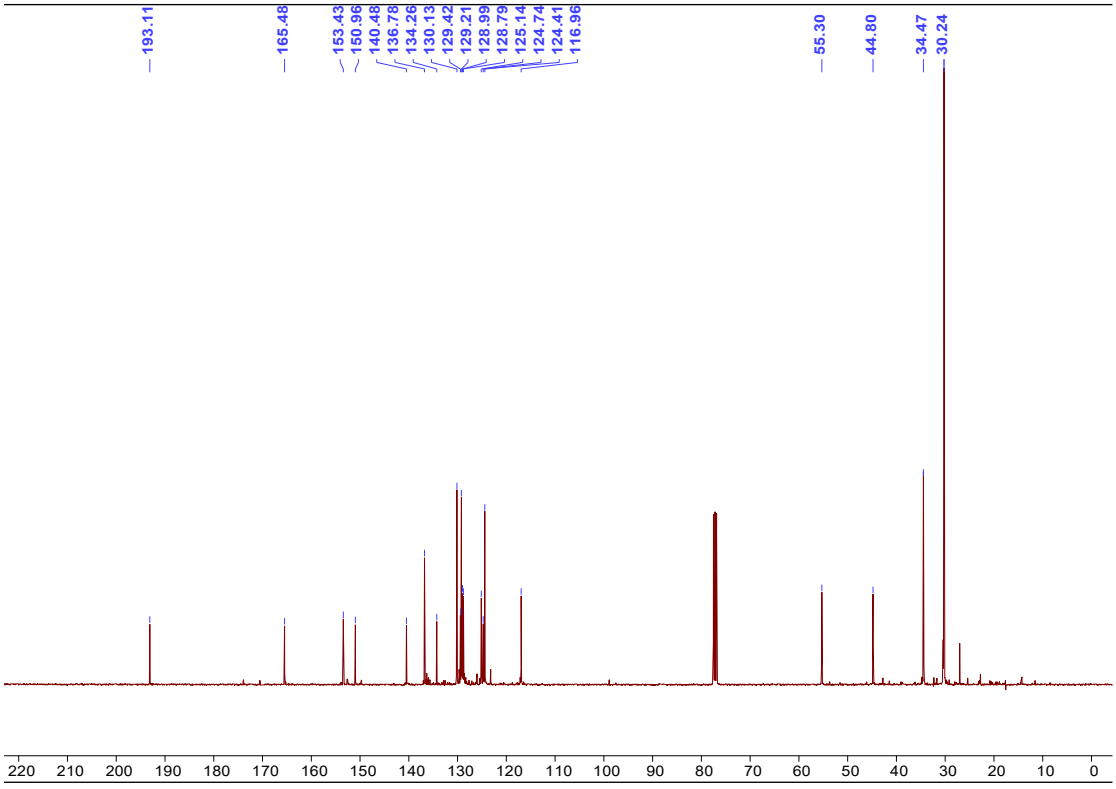
^{1}H NMR spectrum of 8j



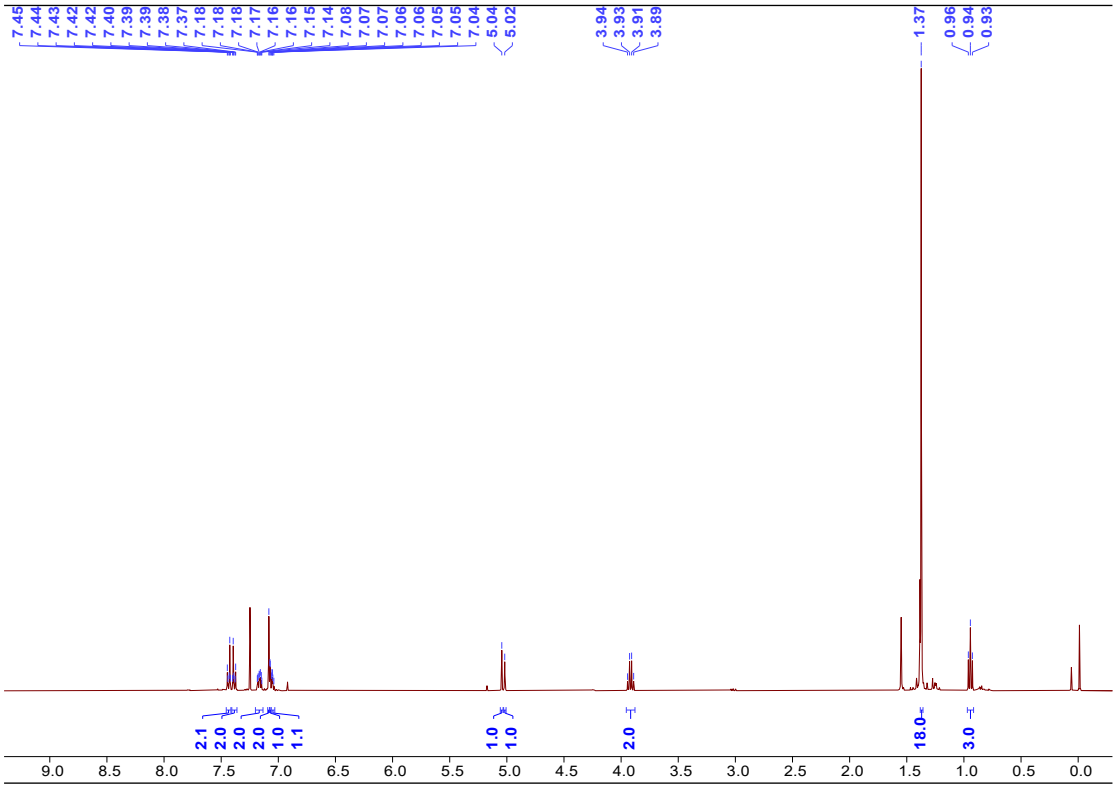
^{13}C NMR spectrum of 8j



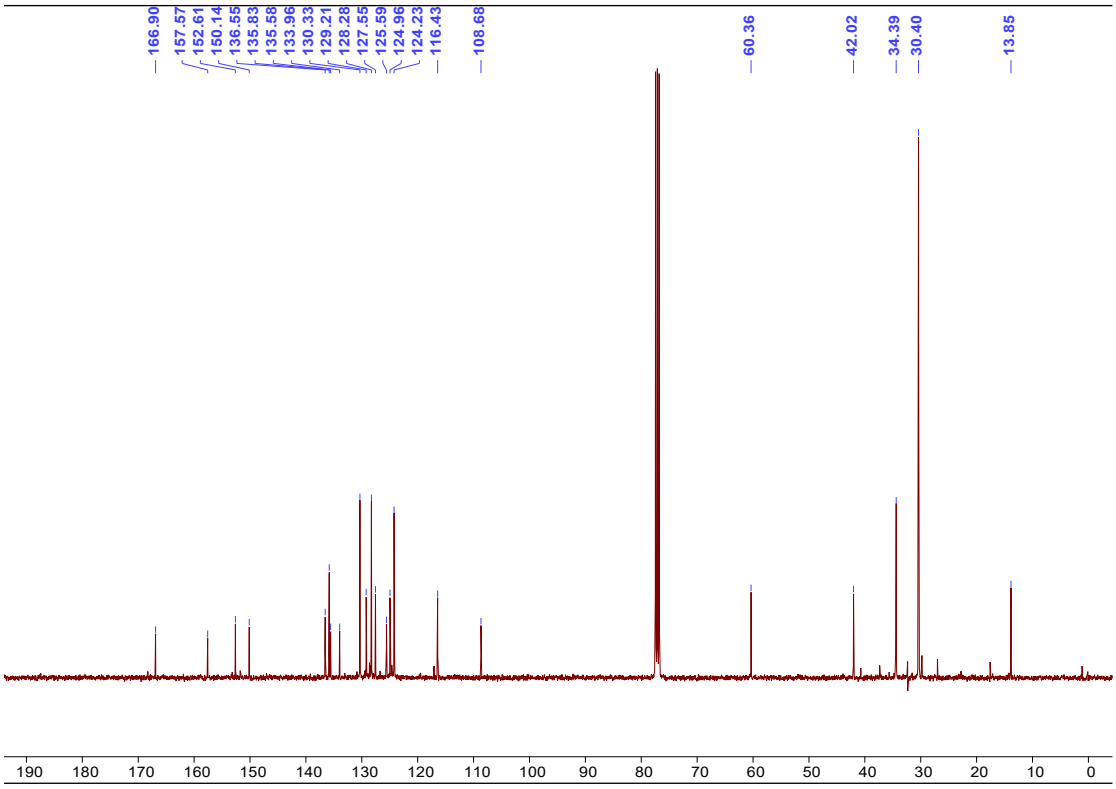
^{1}H NMR spectrum of 7k



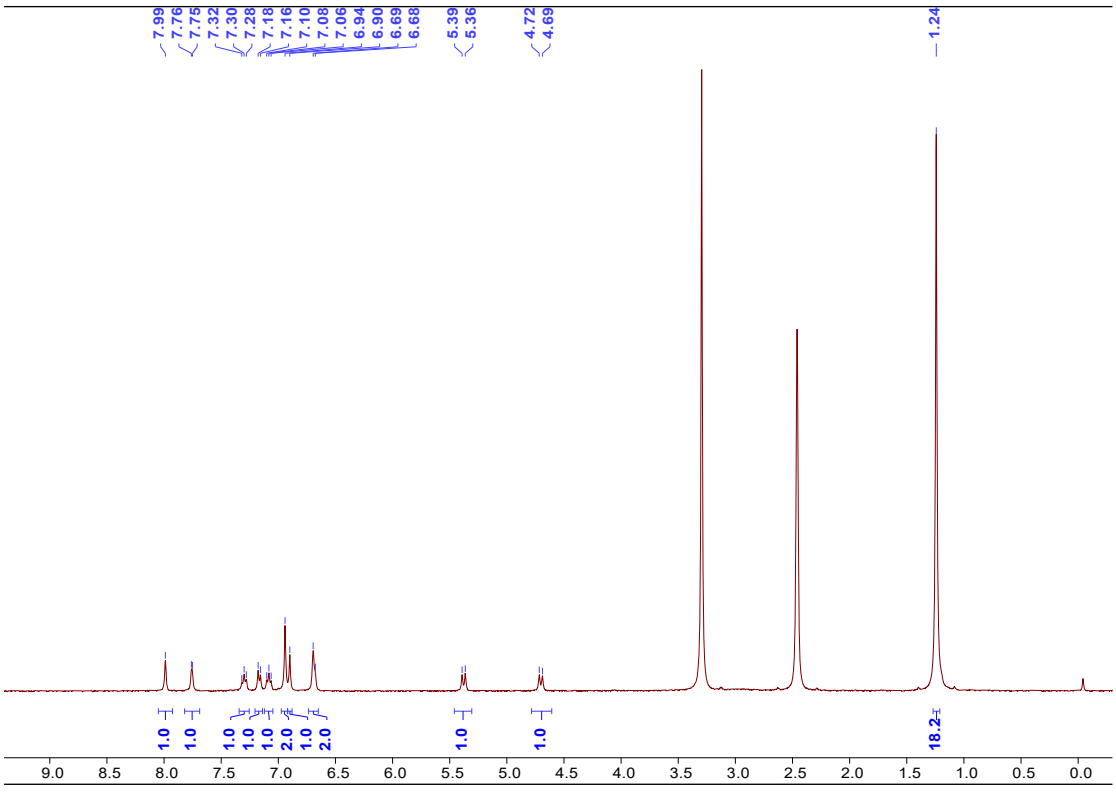
^{13}C NMR spectrum of 7k



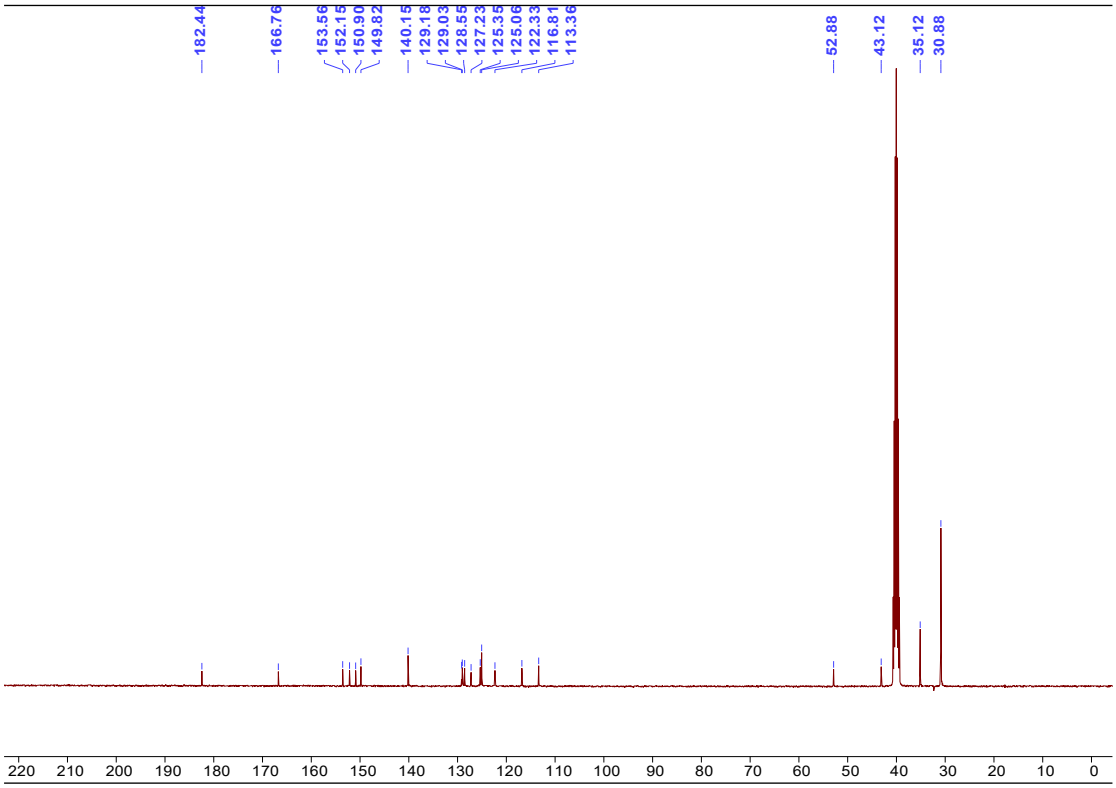
^{1}H NMR spectrum of 8k



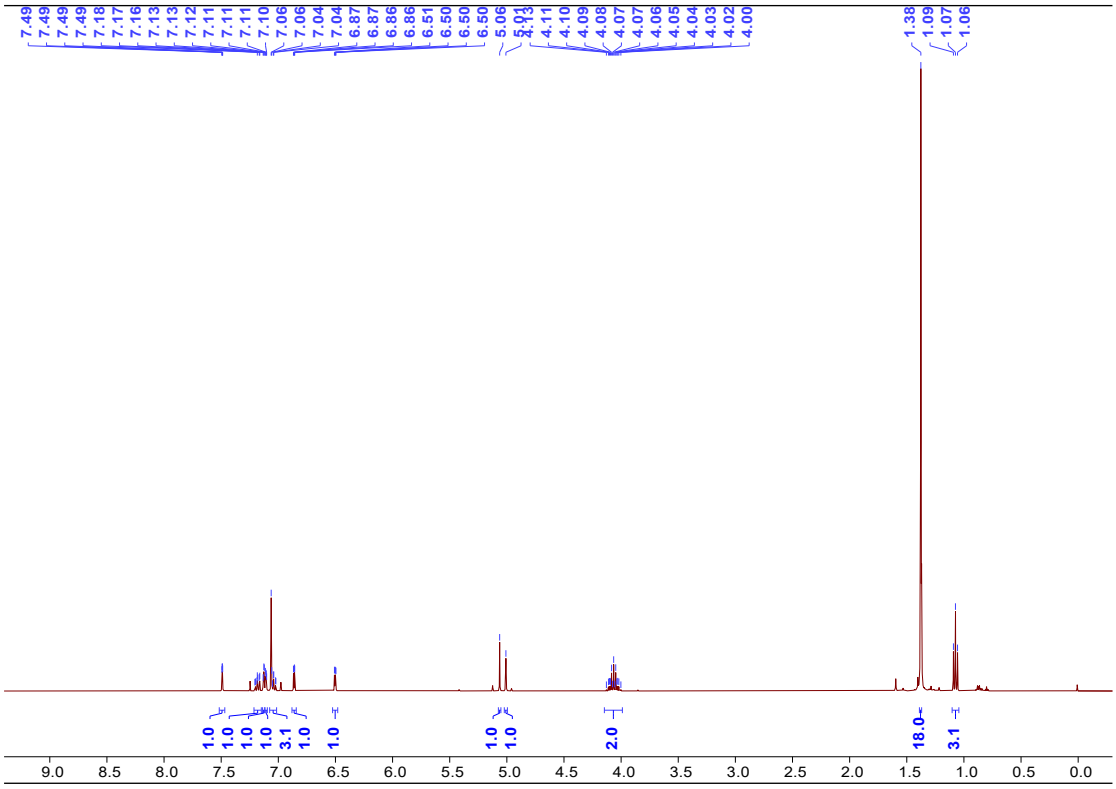
^{13}C NMR spectrum of 8k



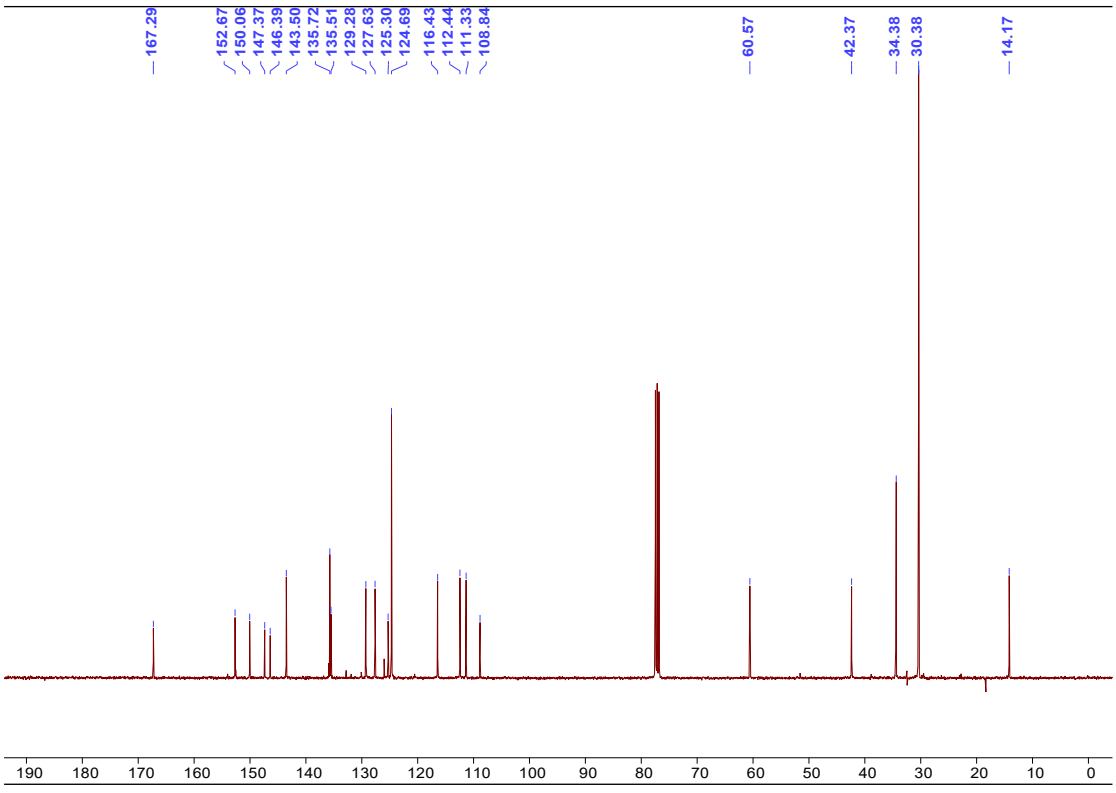
^{1}H NMR spectrum of 7l



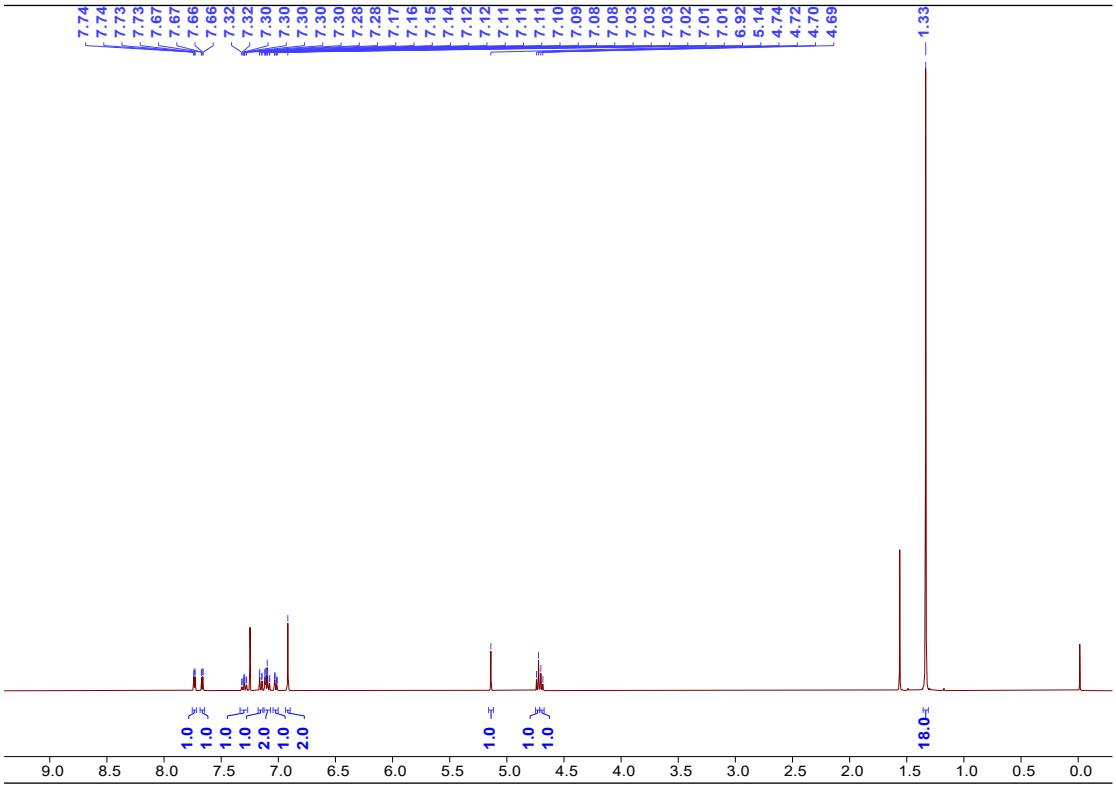
^{13}C NMR spectrum of 7l



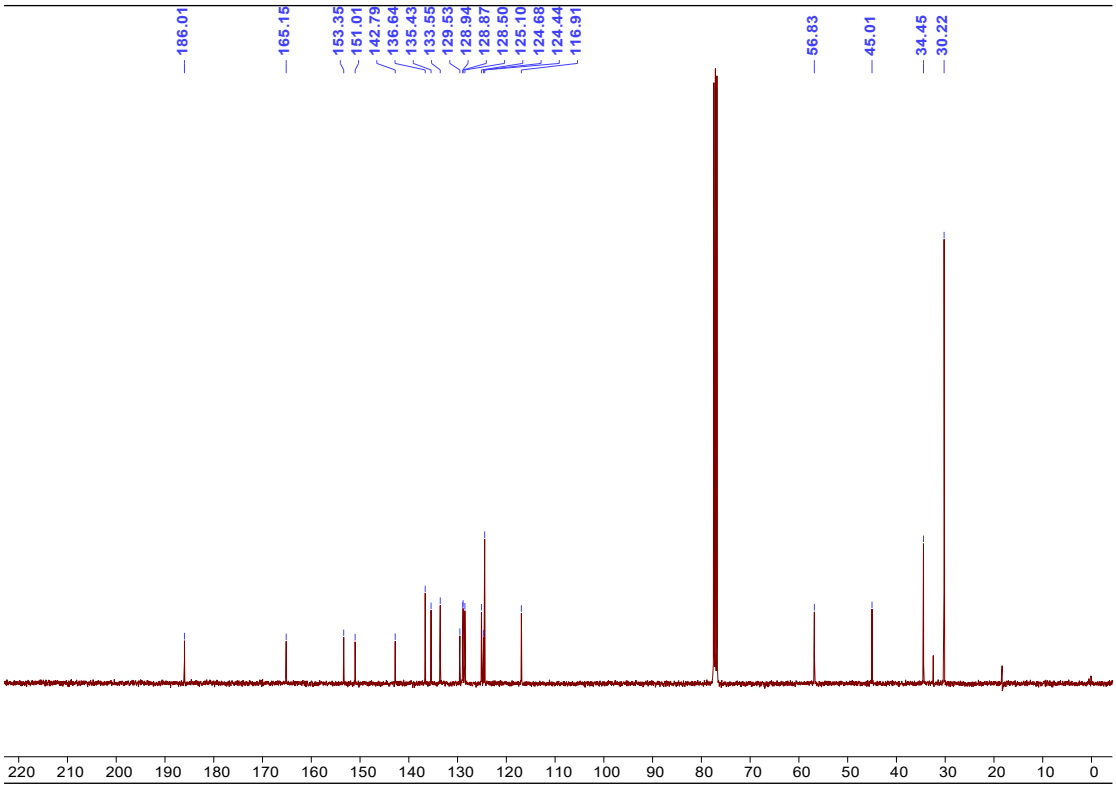
^{1}H NMR spectrum of 8l



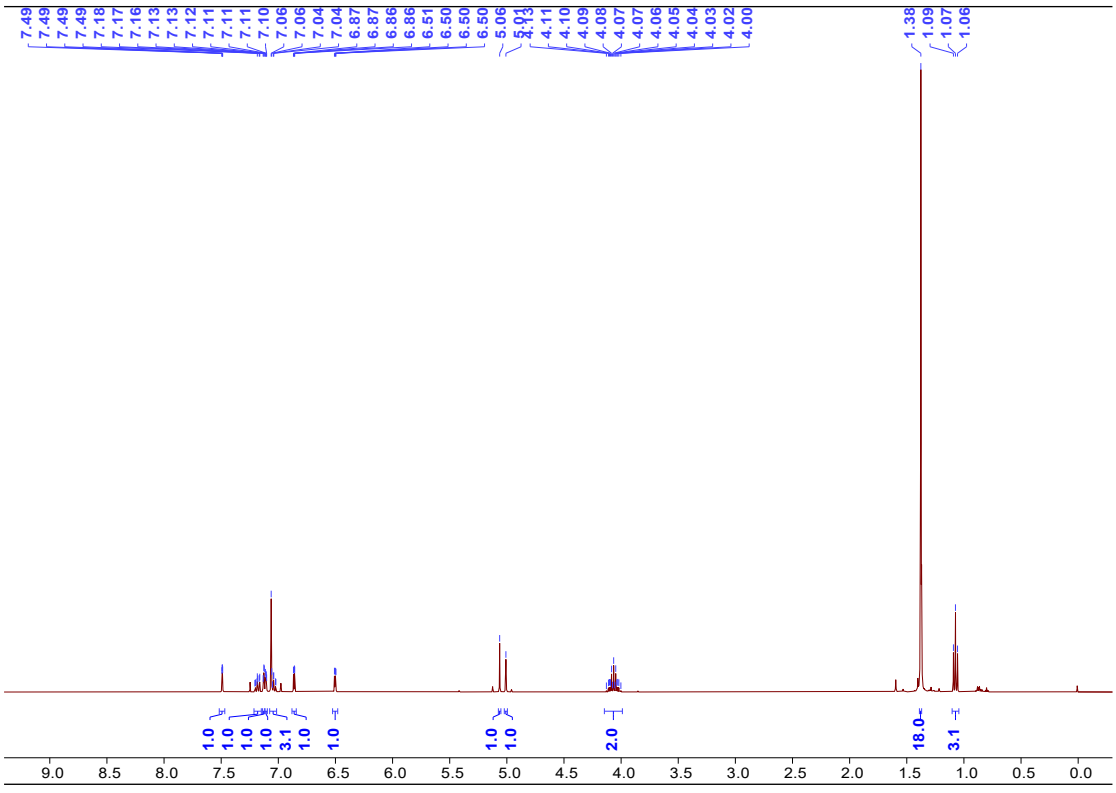
^{13}C NMR spectrum of 8l



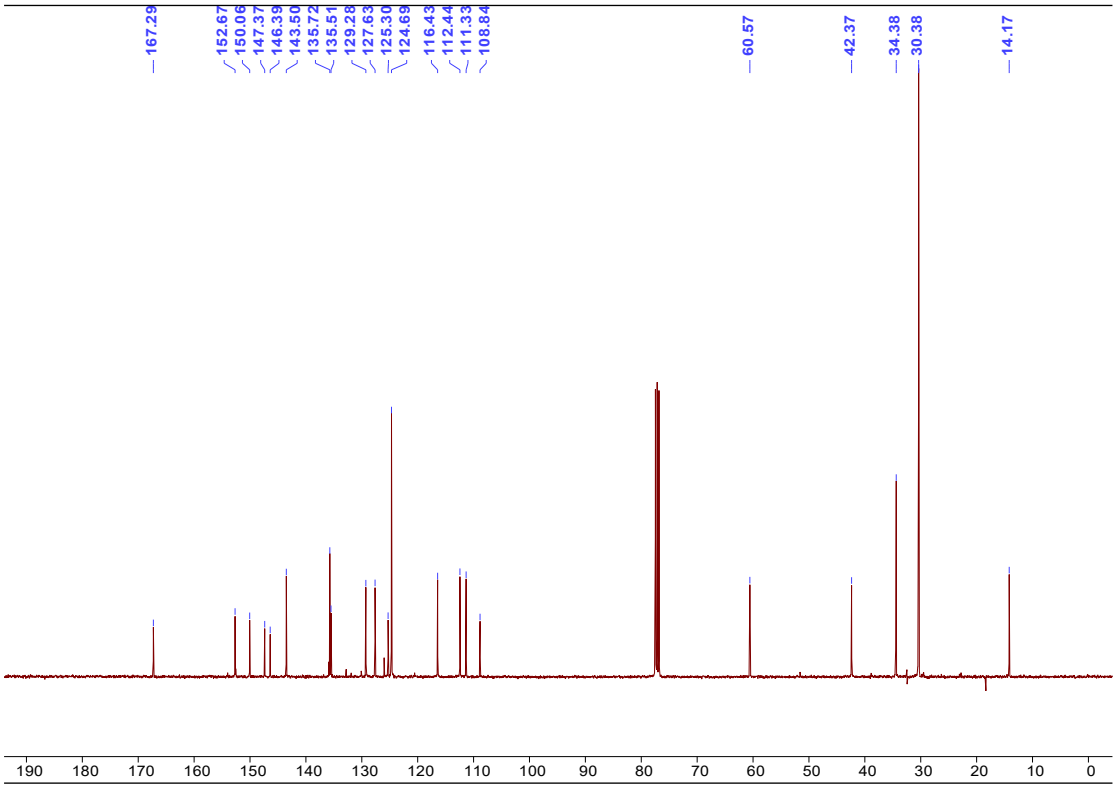
^{1}H NMR spectrum of 7m



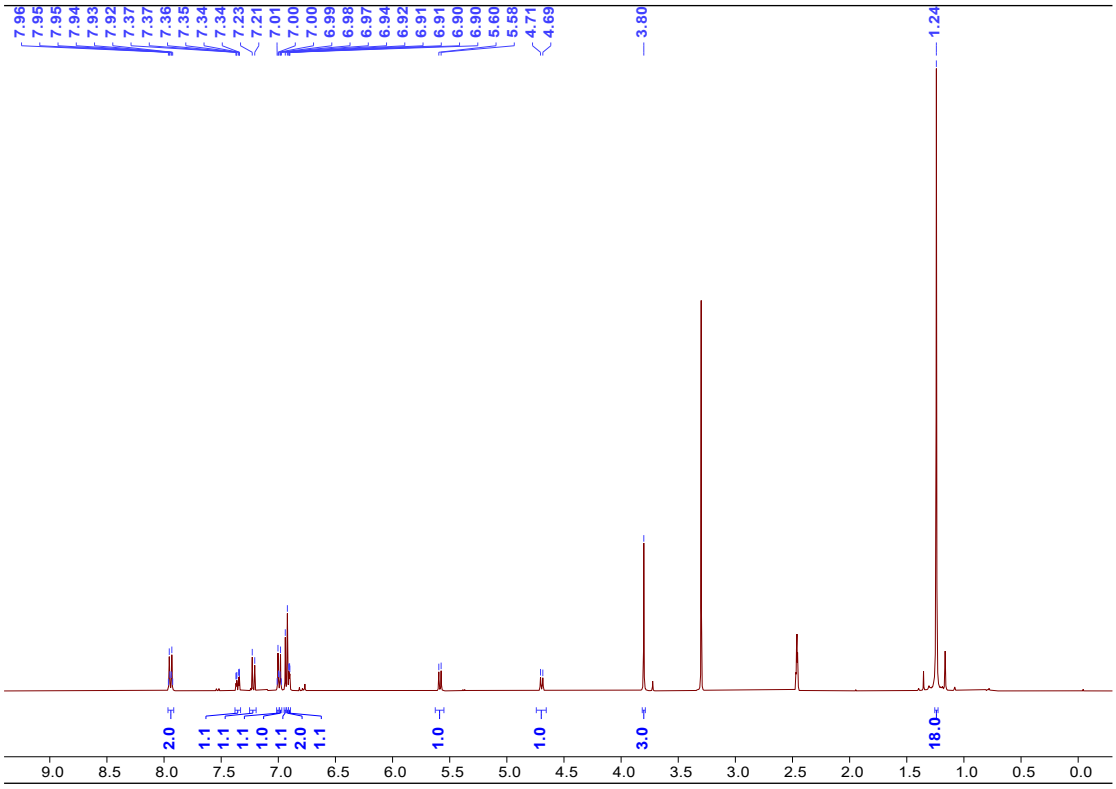
^{13}C NMR spectrum of 7m



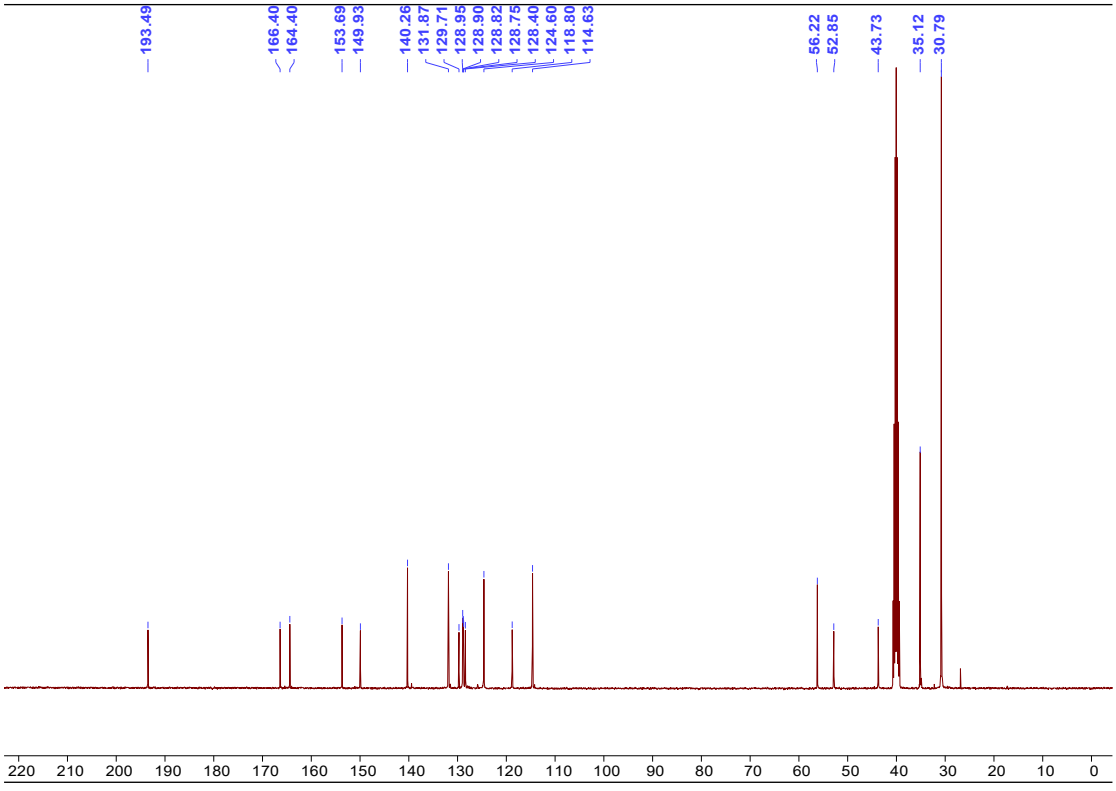
^{1}H NMR spectrum of 8m



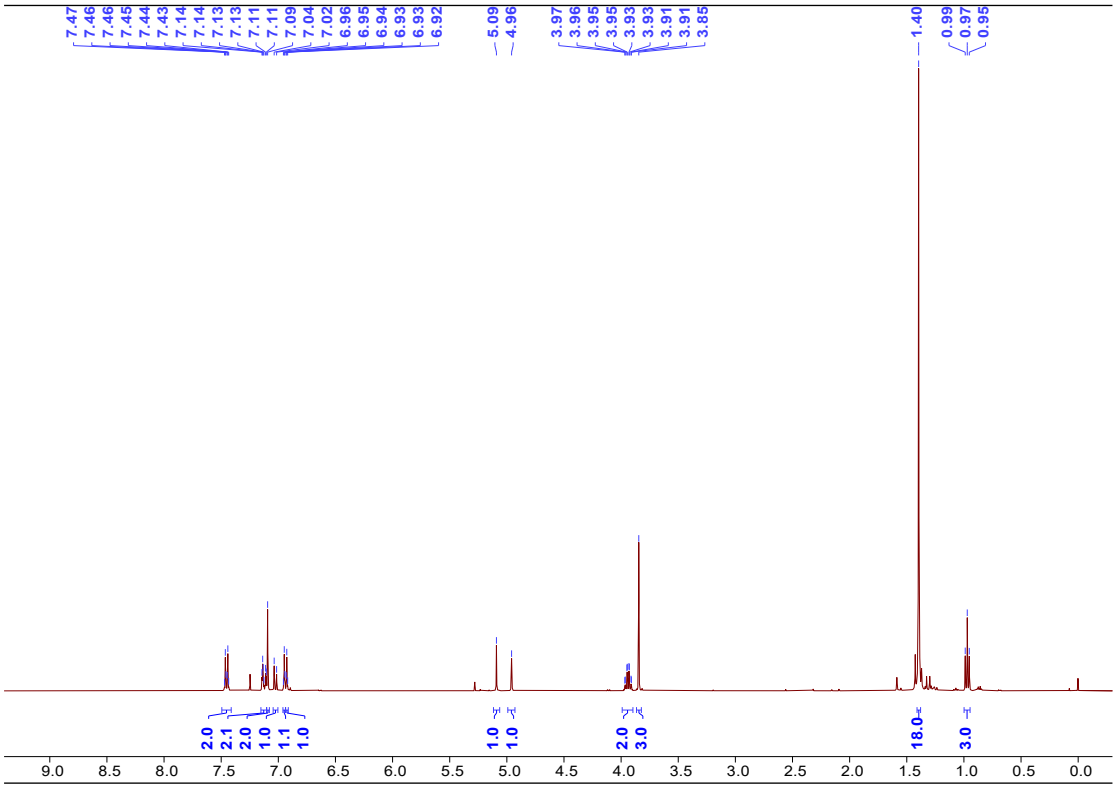
^{13}C NMR spectrum of 8m



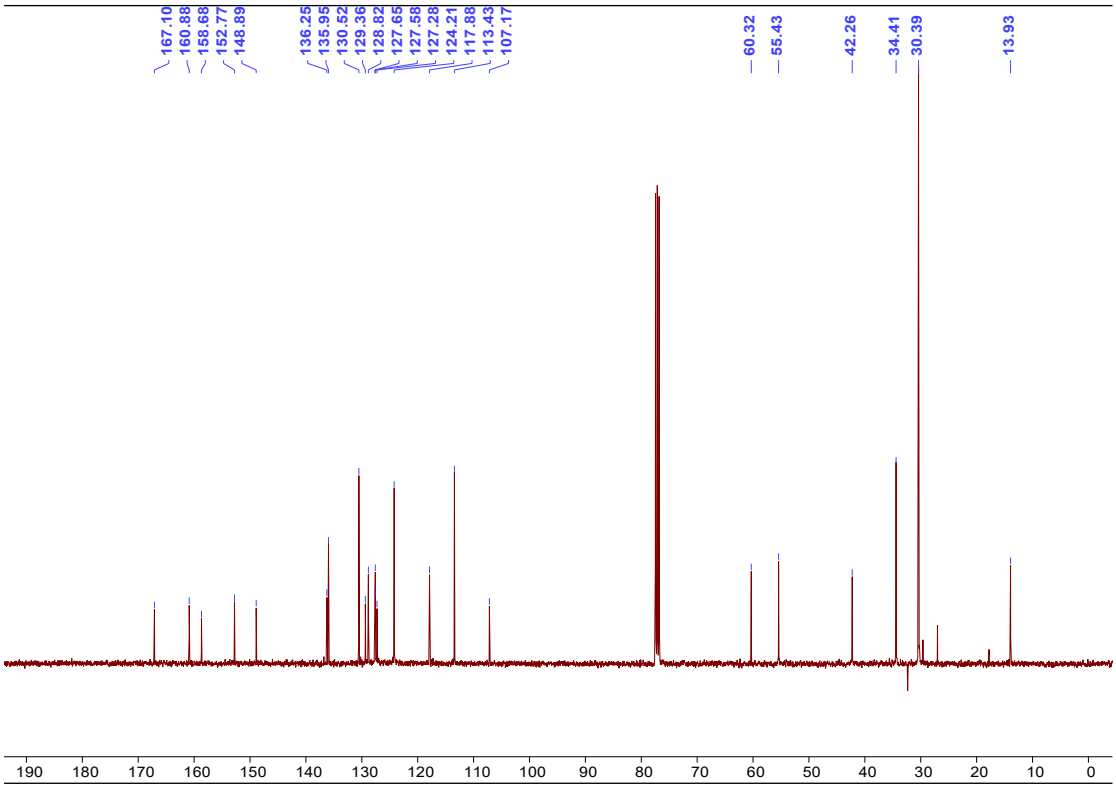
^{1}H NMR spectrum of 7n



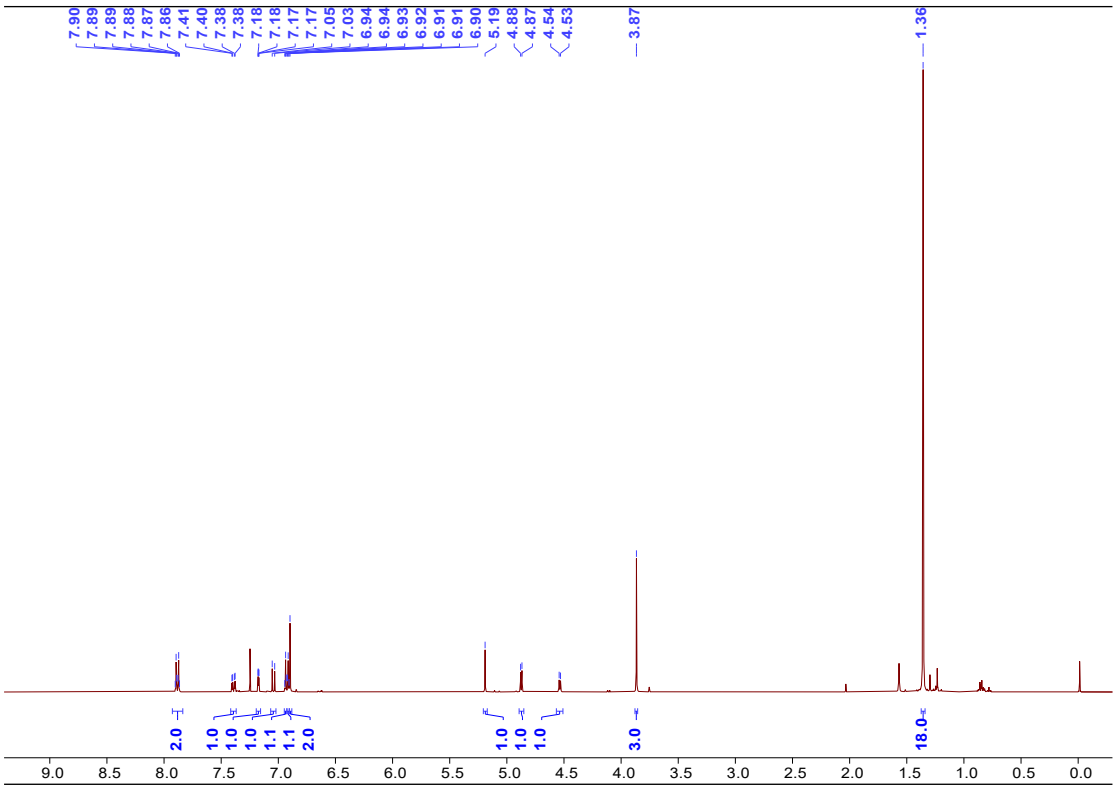
^{13}C NMR spectrum of 7n



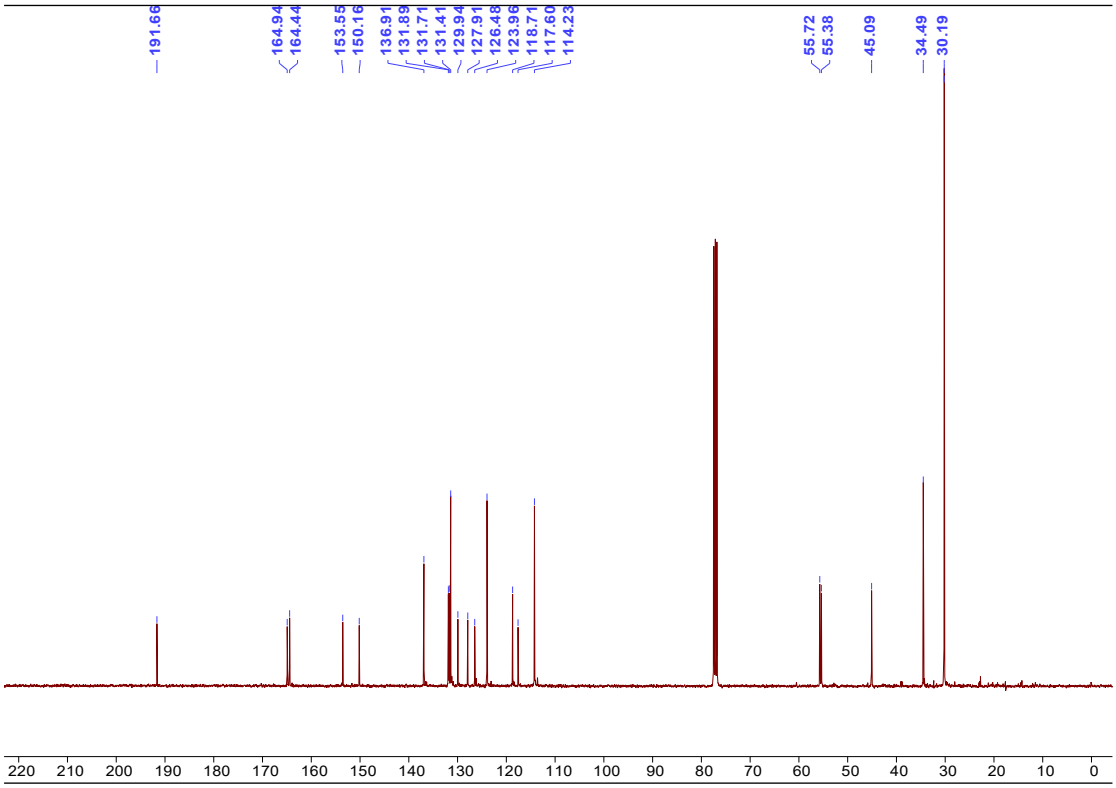
^{1}H NMR spectrum of 8n



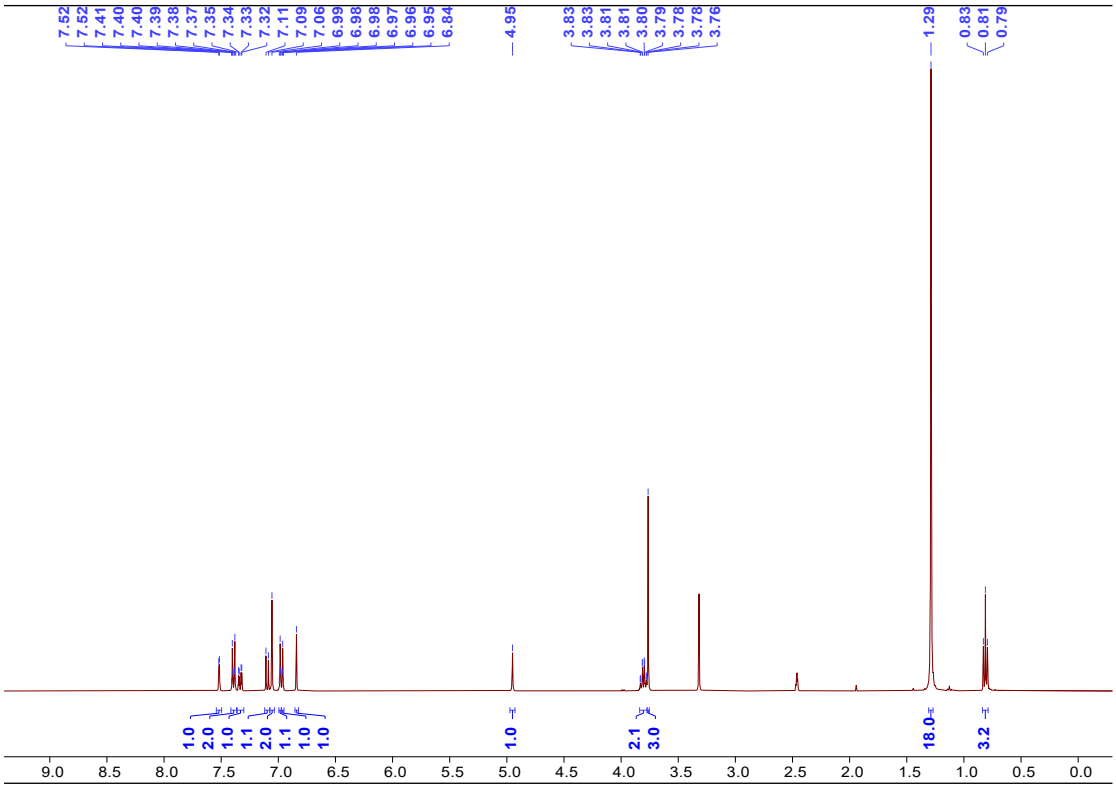
^{13}C NMR spectrum of 8n



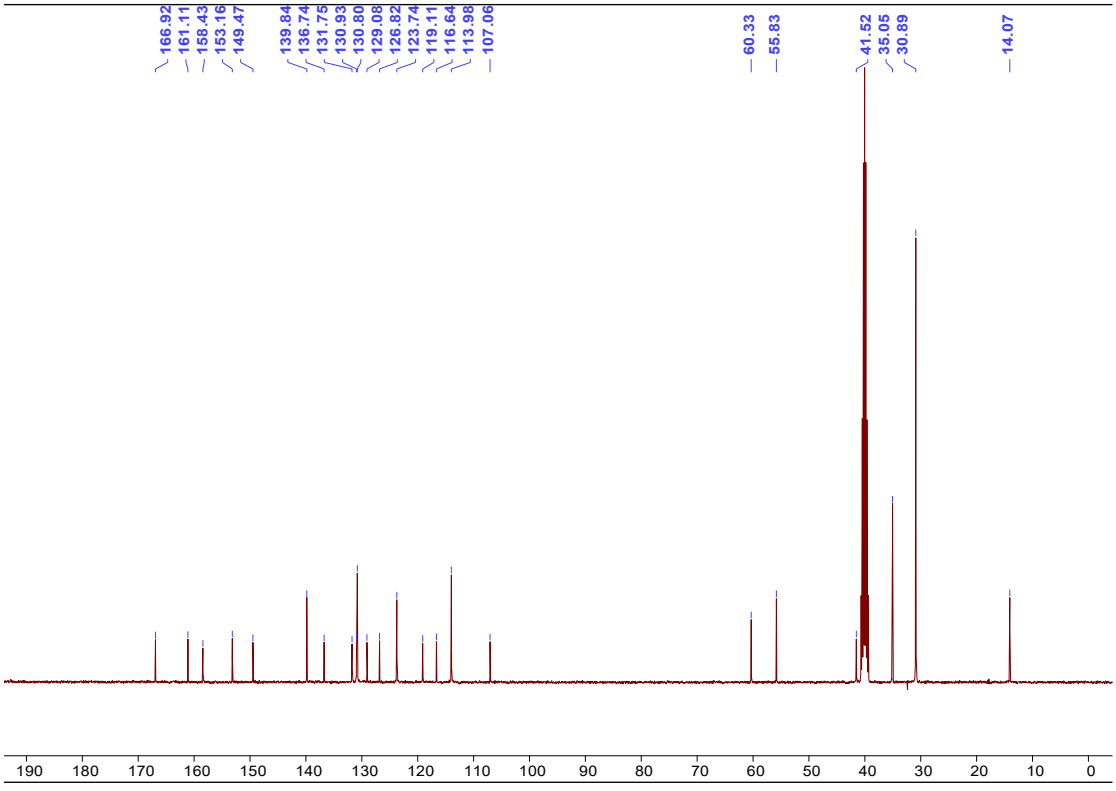
^{1}H NMR spectrum of 7o



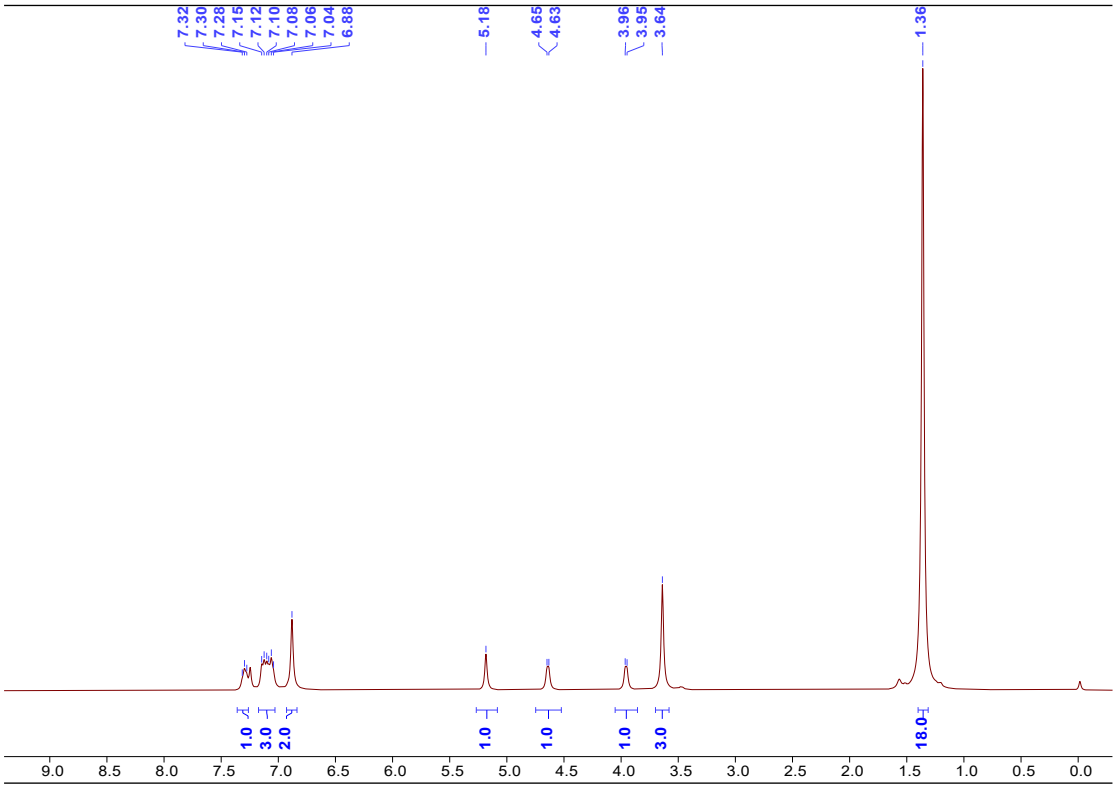
^{13}C NMR spectrum of 7o



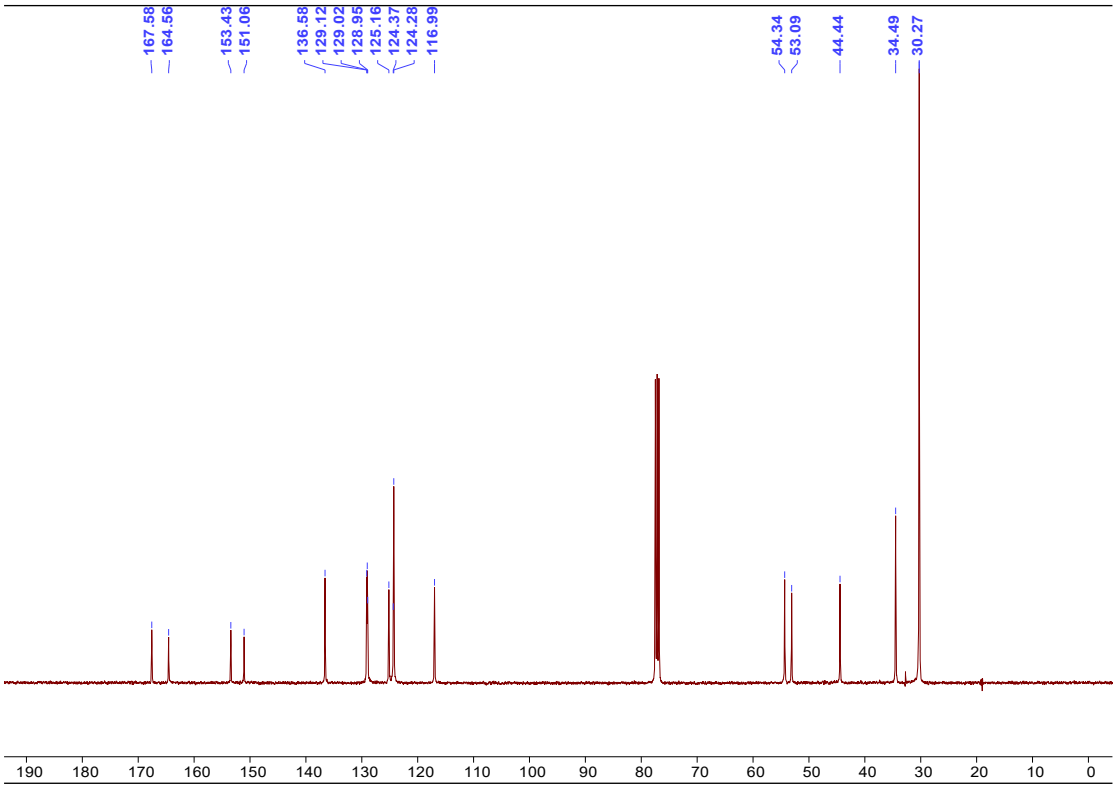
^{1}H NMR spectrum of 8o



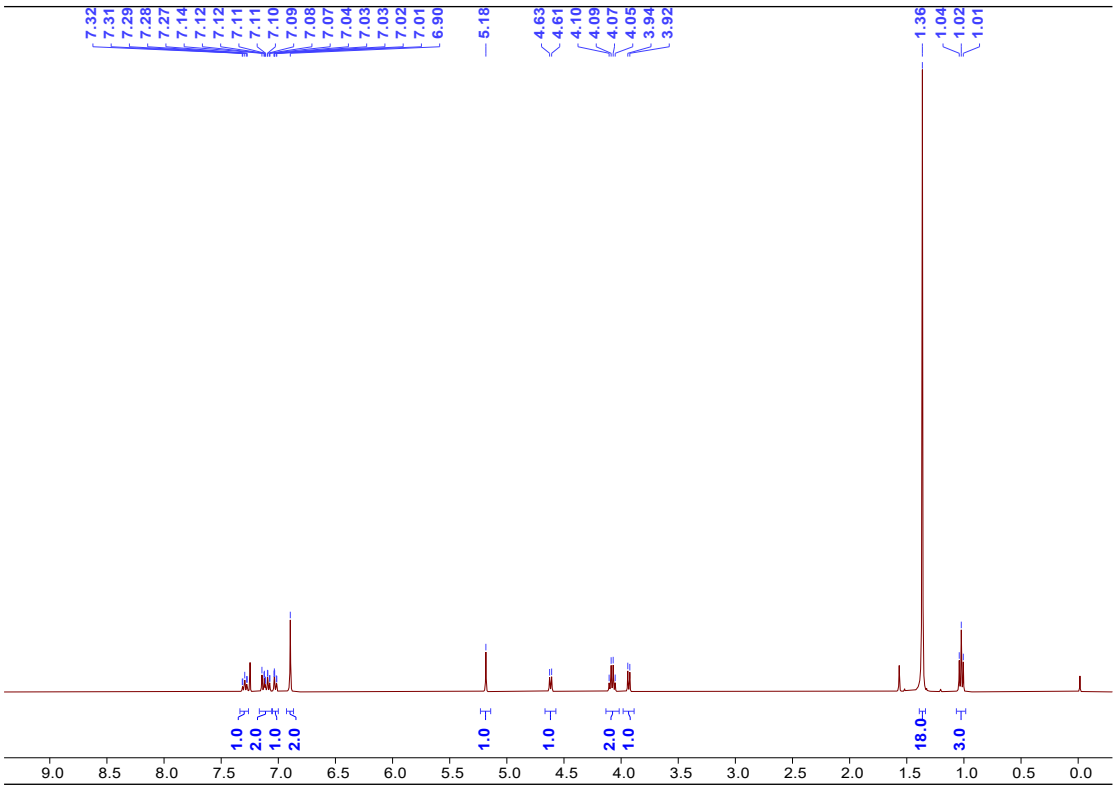
^{13}C NMR spectrum of 8o



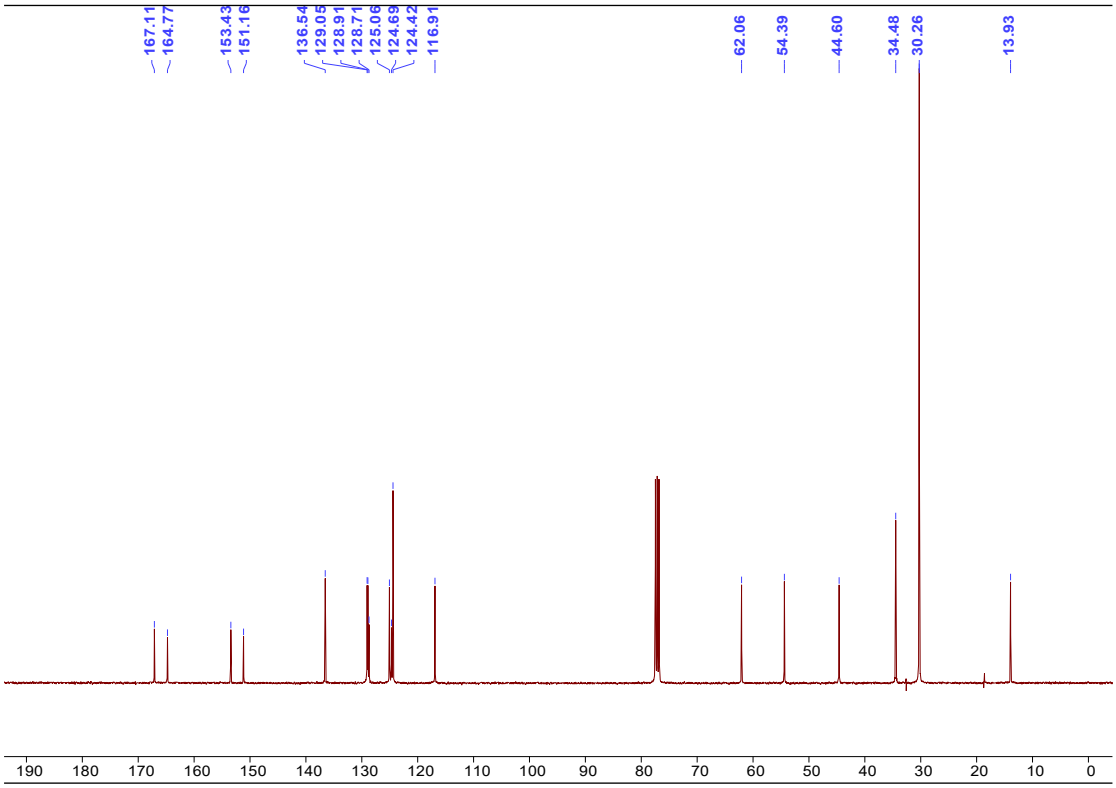
^{1}H NMR spectrum of 10a



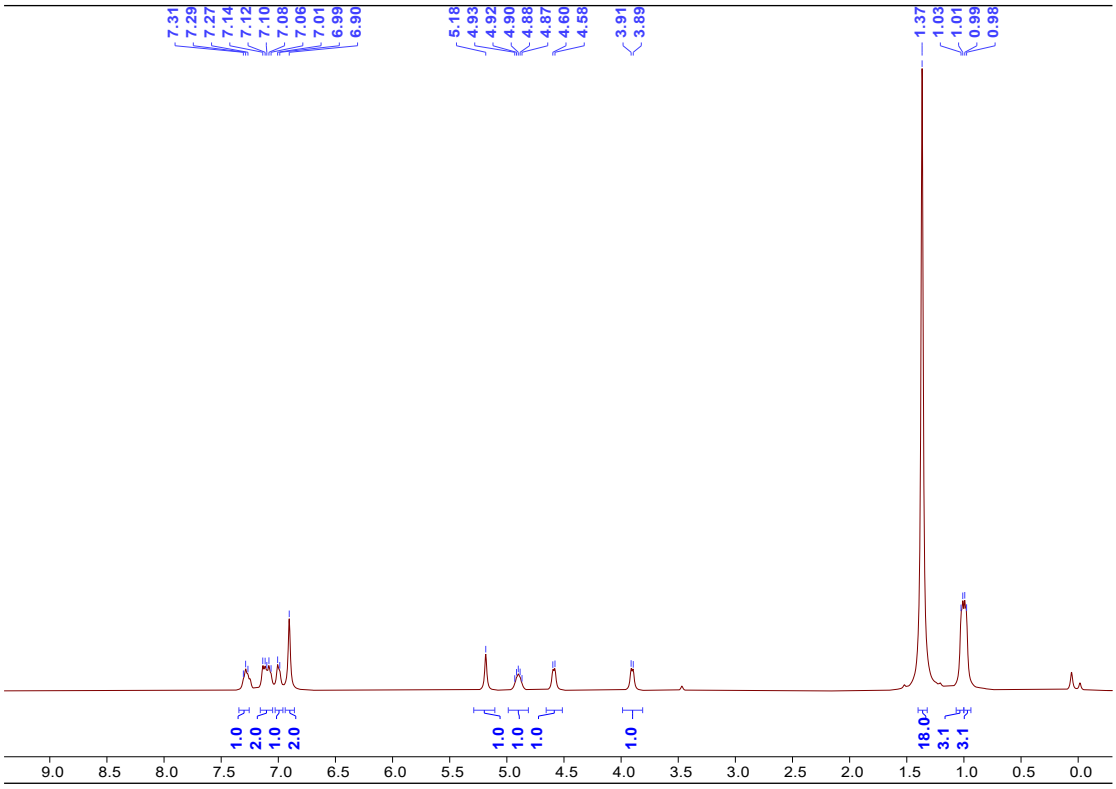
^{13}C NMR spectrum of 10a



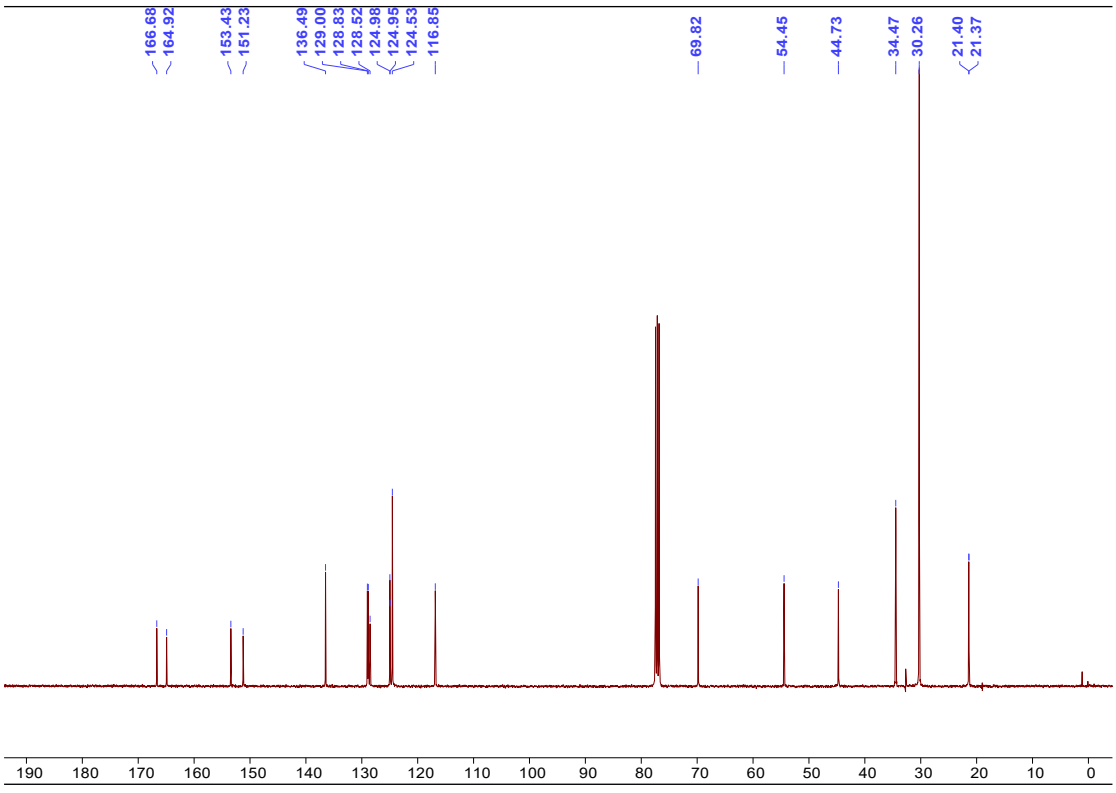
^{1}H NMR spectrum of 10b



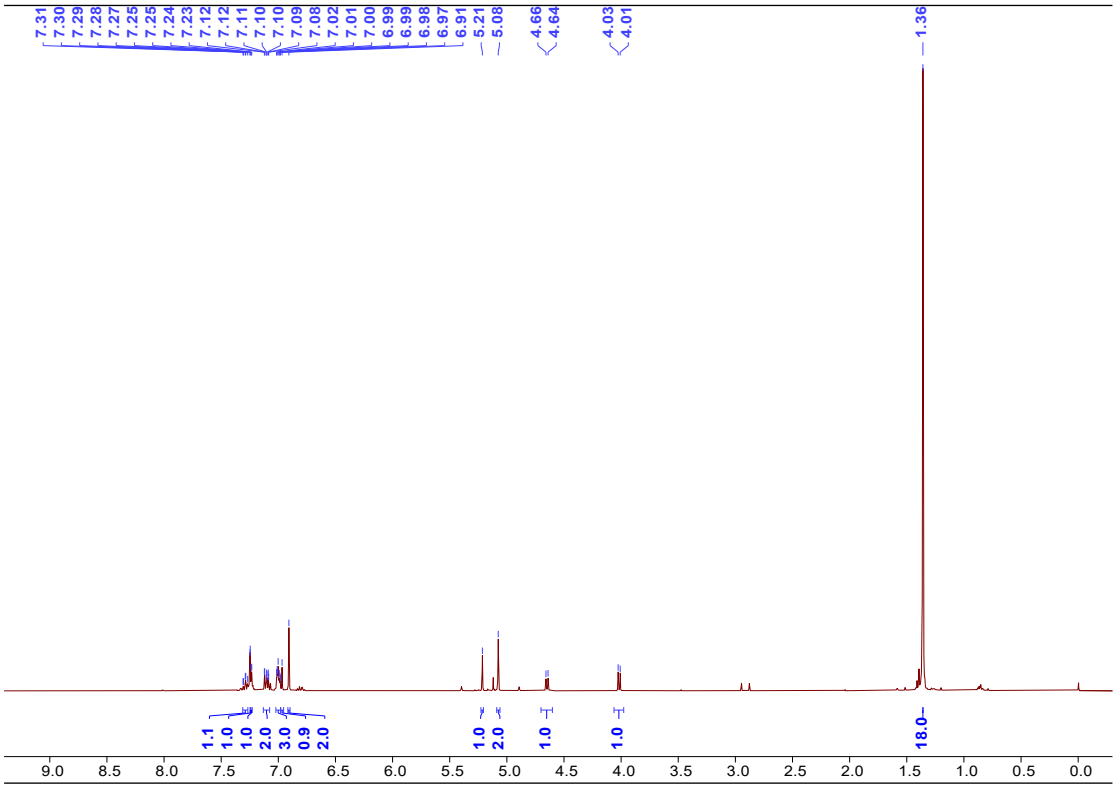
^{13}C NMR spectrum of 10b



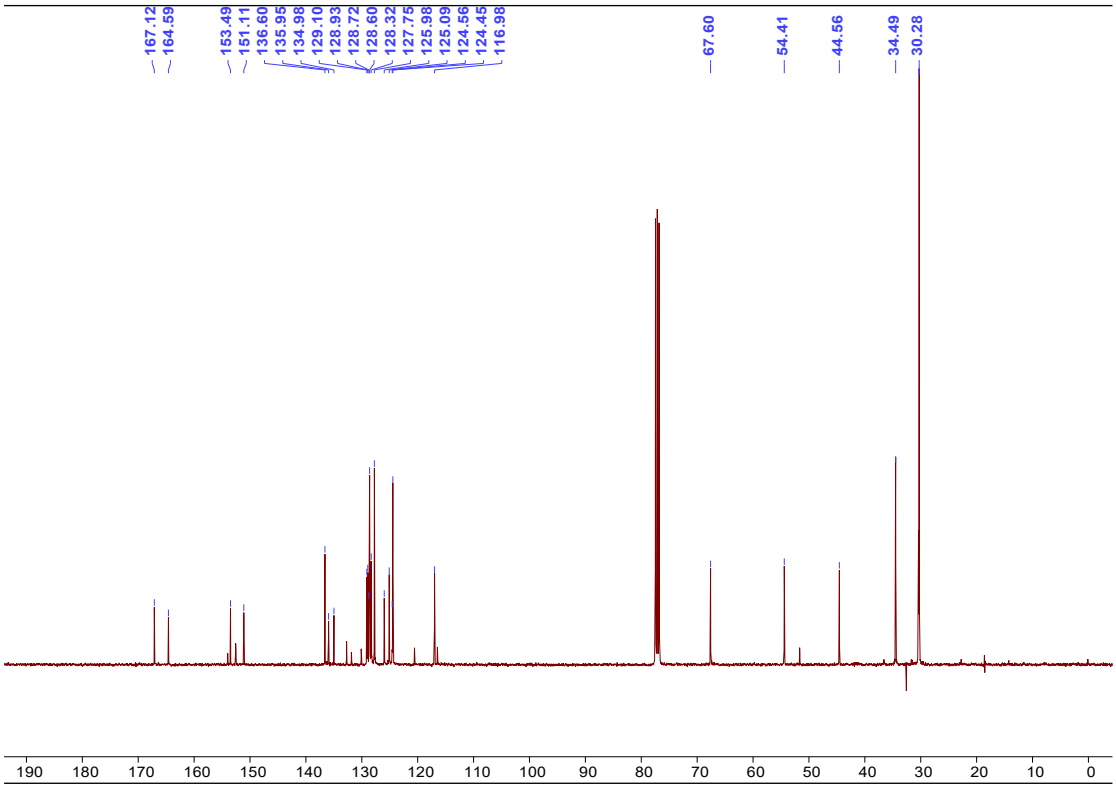
^{1}H NMR spectrum of 10c



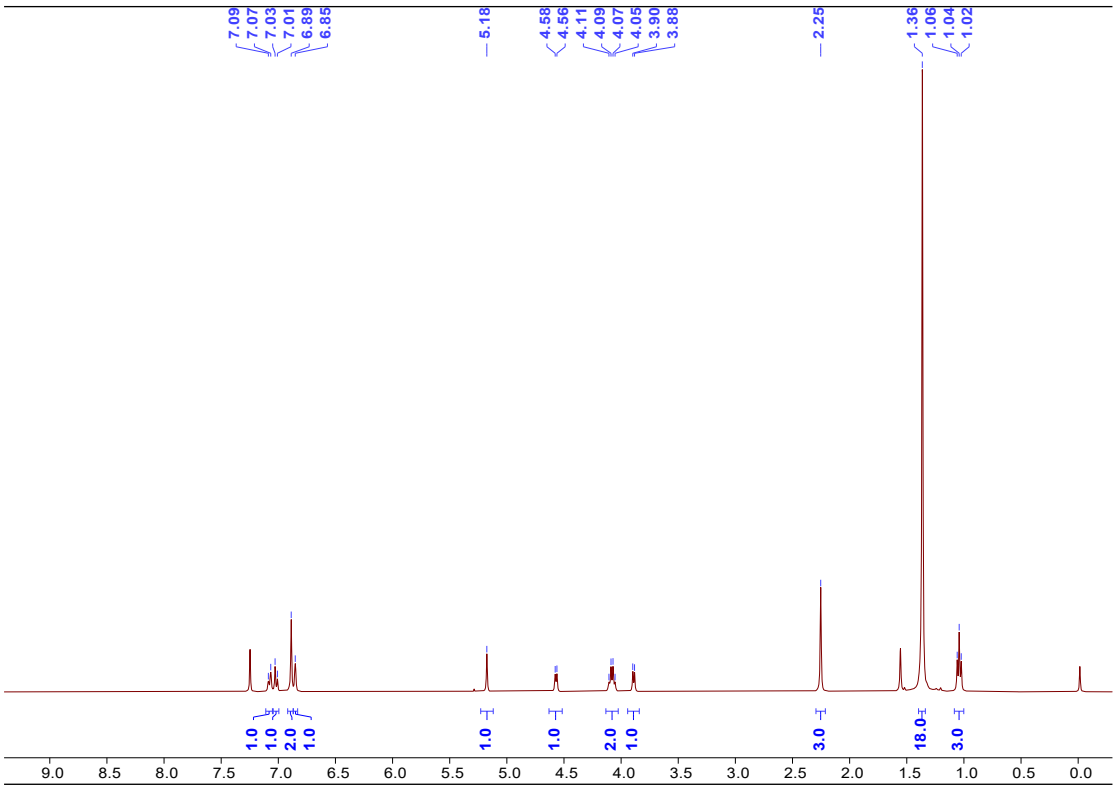
^{13}C NMR spectrum of 10c



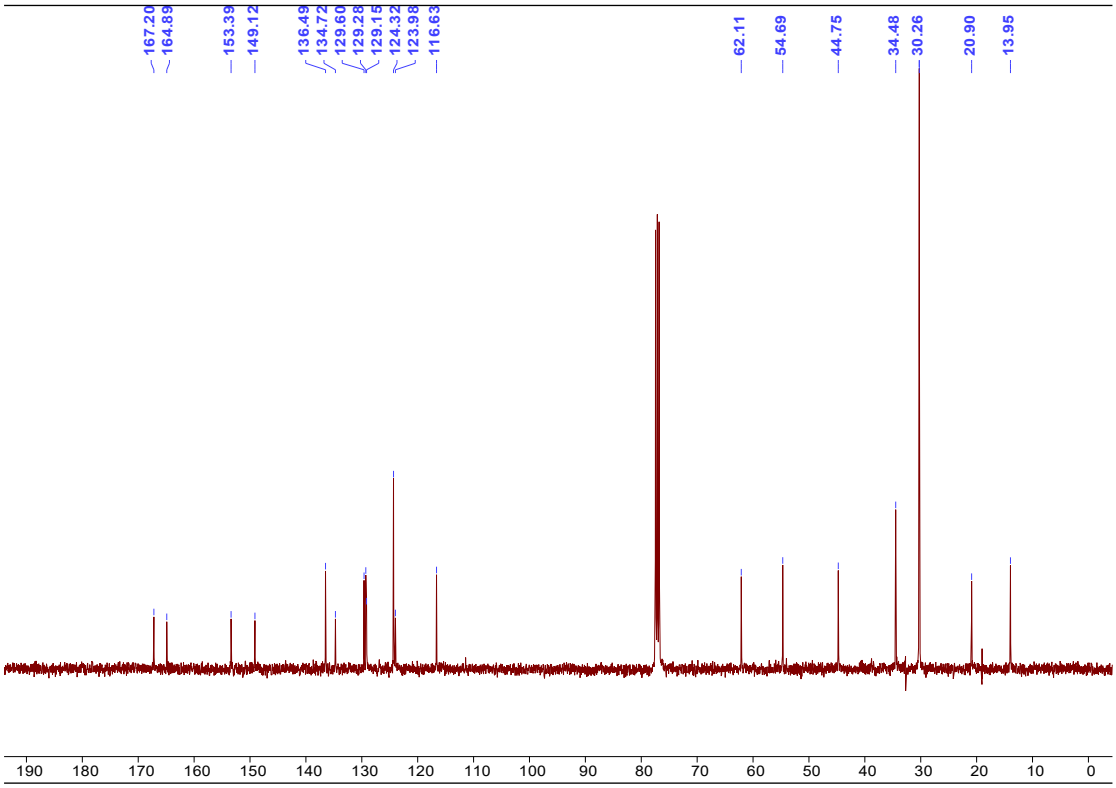
^{1}H NMR spectrum of 10d



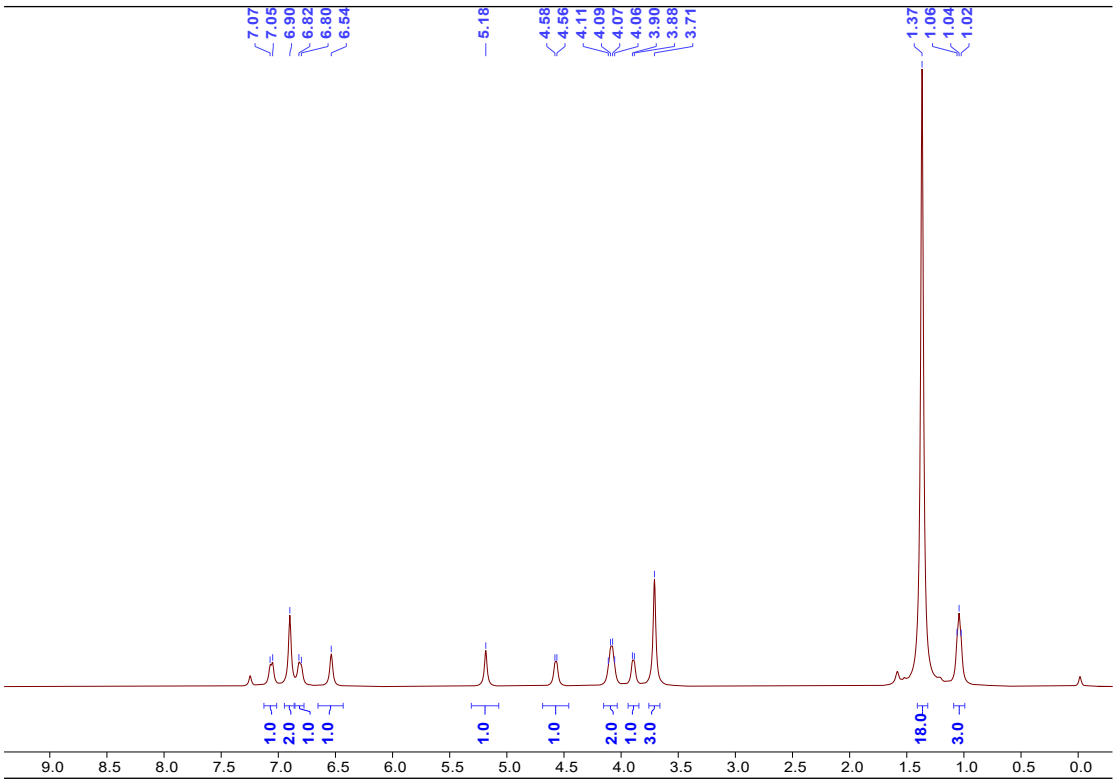
^{13}C NMR spectrum of 10d



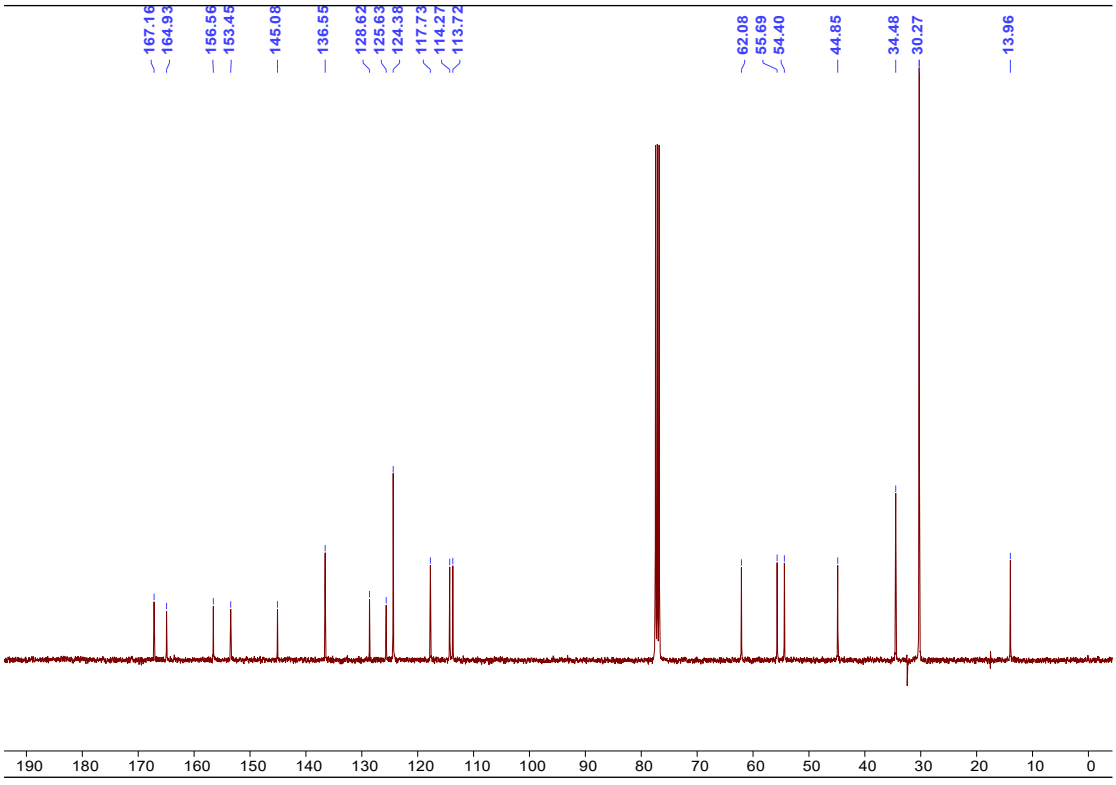
^{1}H NMR spectrum of 10e



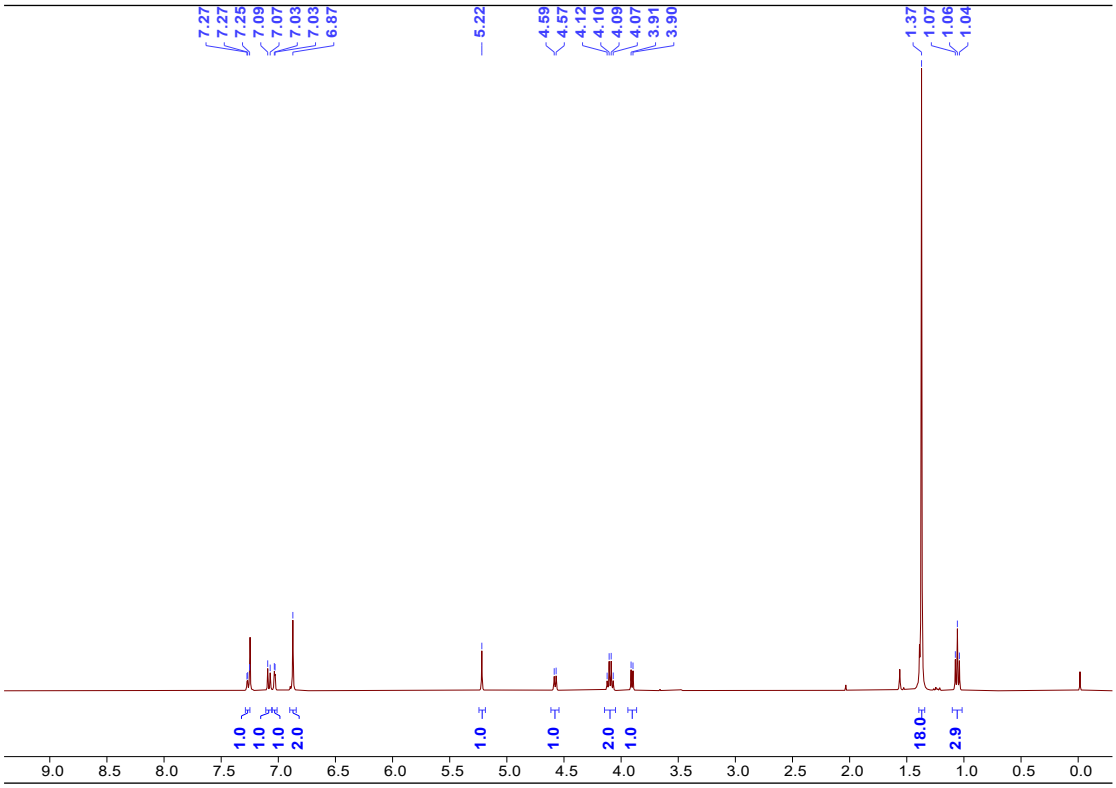
^{13}C NMR spectrum of 10e



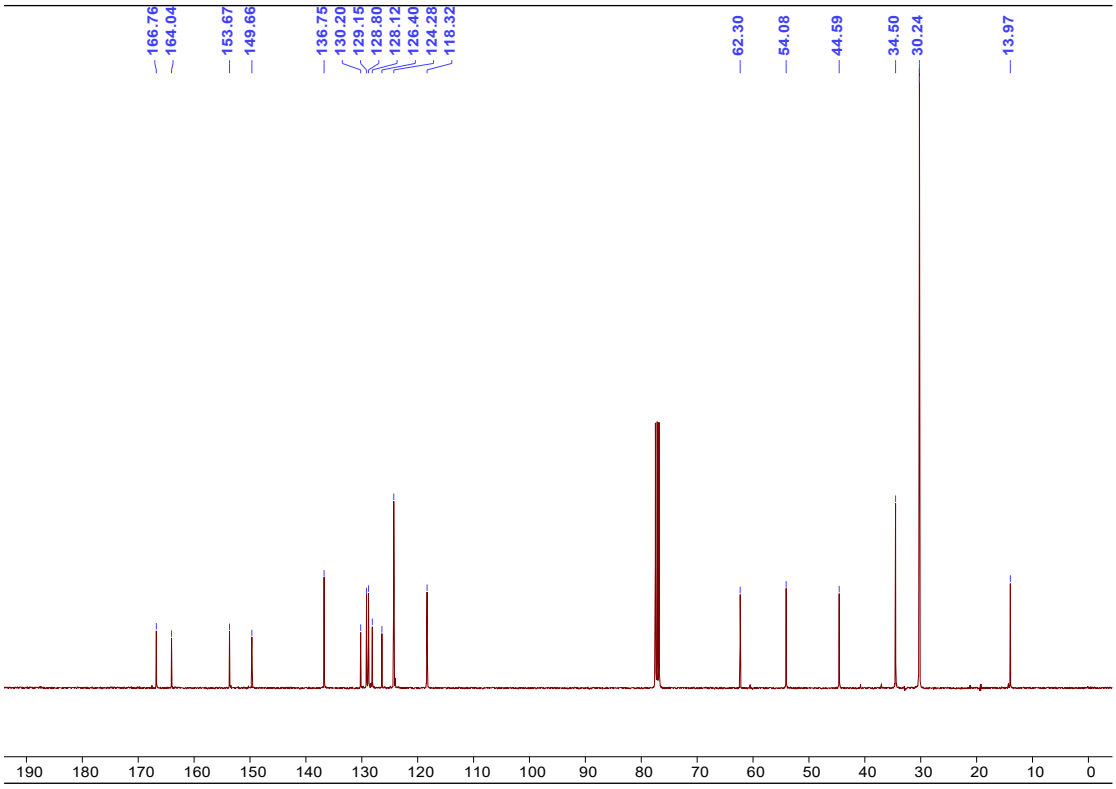
^{1}H NMR spectrum of 10f



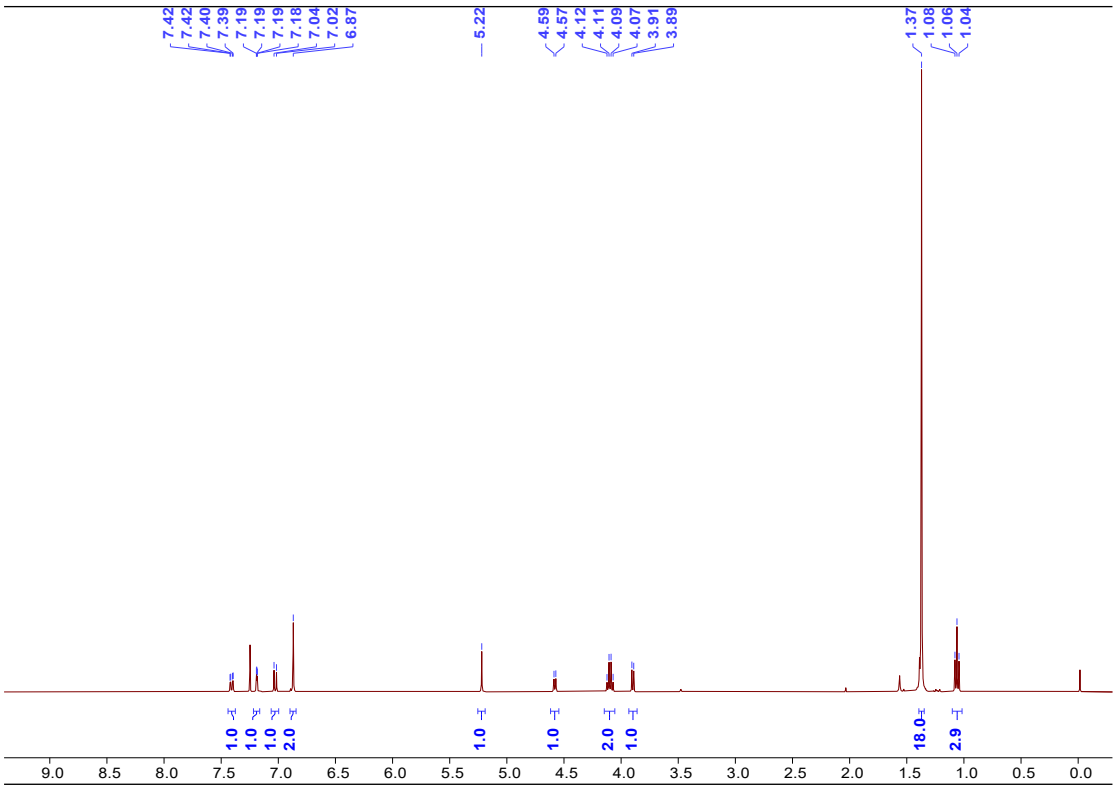
^{13}C NMR spectrum of 10f



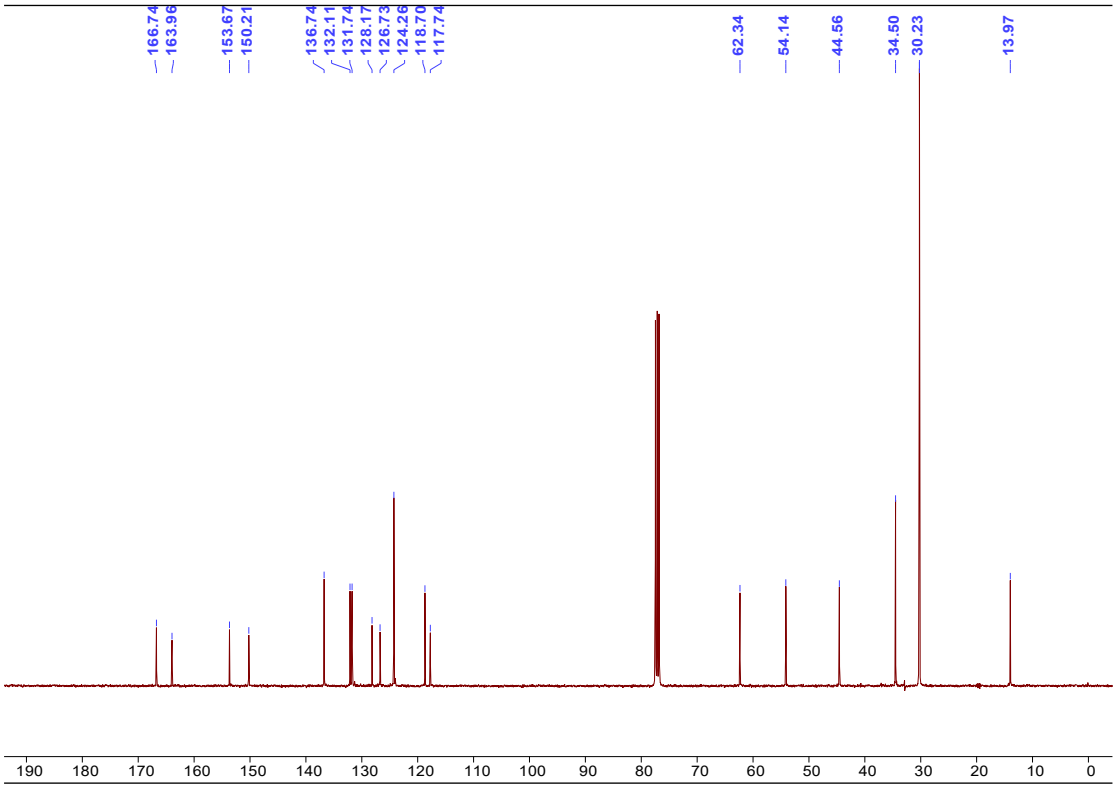
^{1}H NMR spectrum of 10g



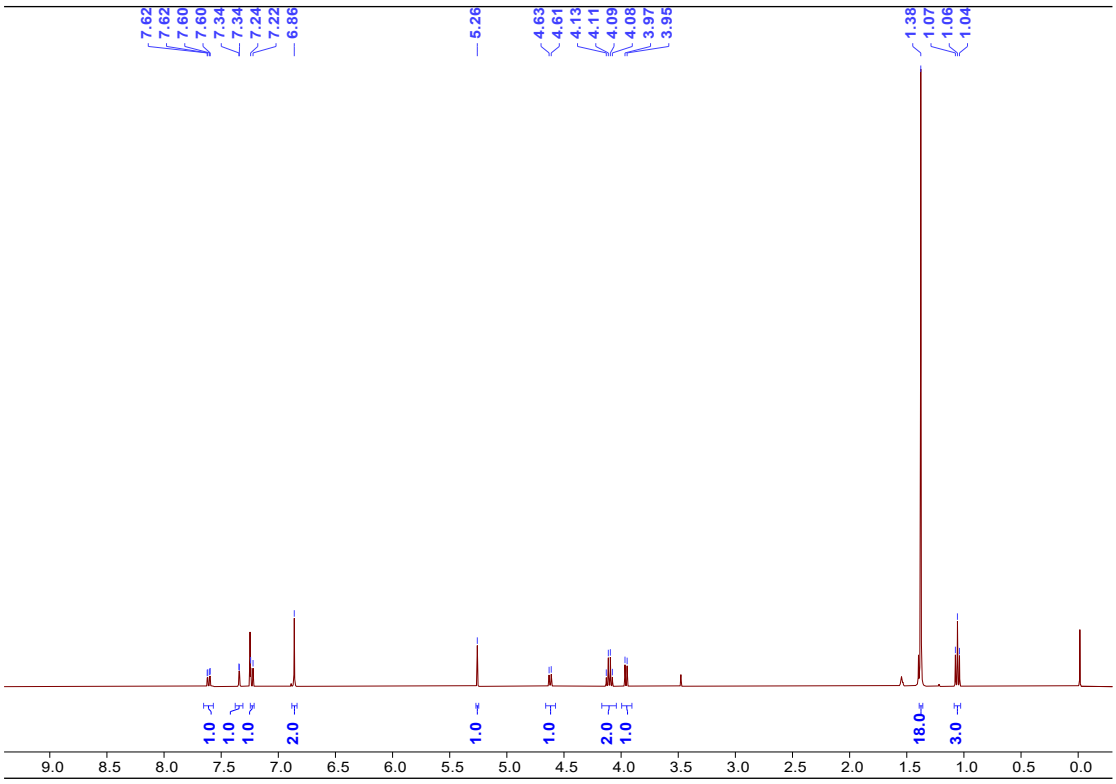
^{13}C NMR spectrum of 10g



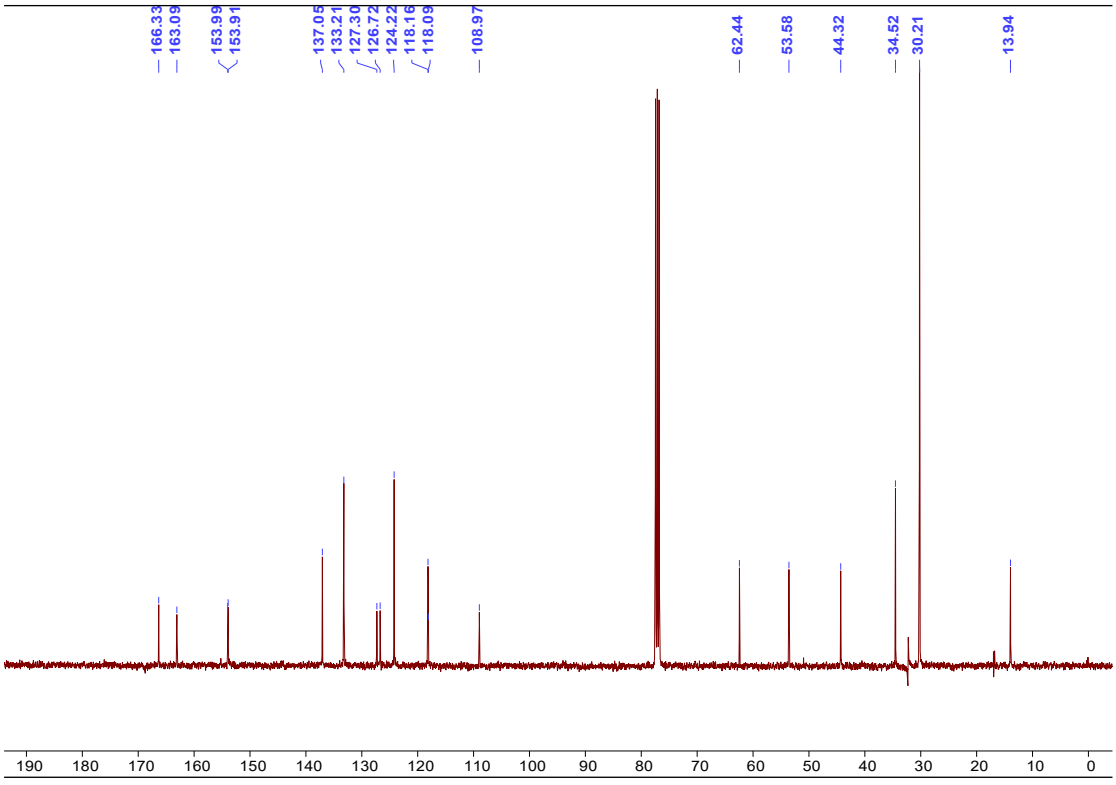
^{1}H NMR spectrum of 10h



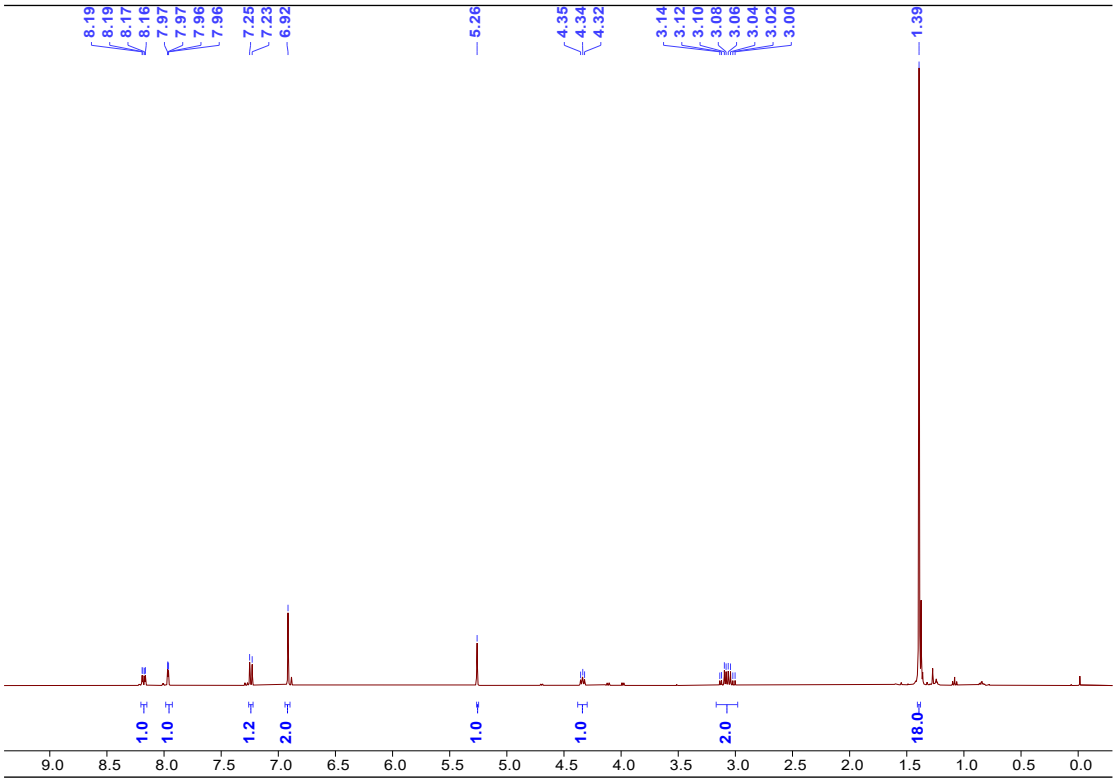
^{13}C NMR spectrum of 10h



^{1}H NMR spectrum of 10i



^{13}C NMR spectrum of 10i



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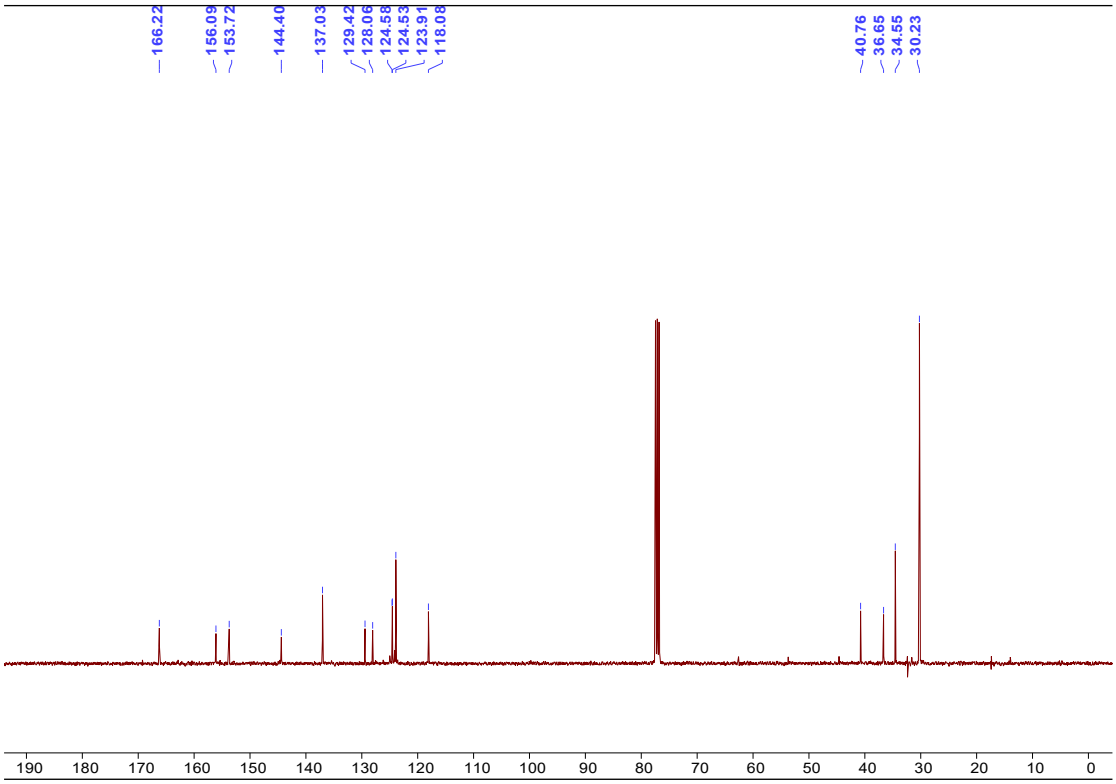
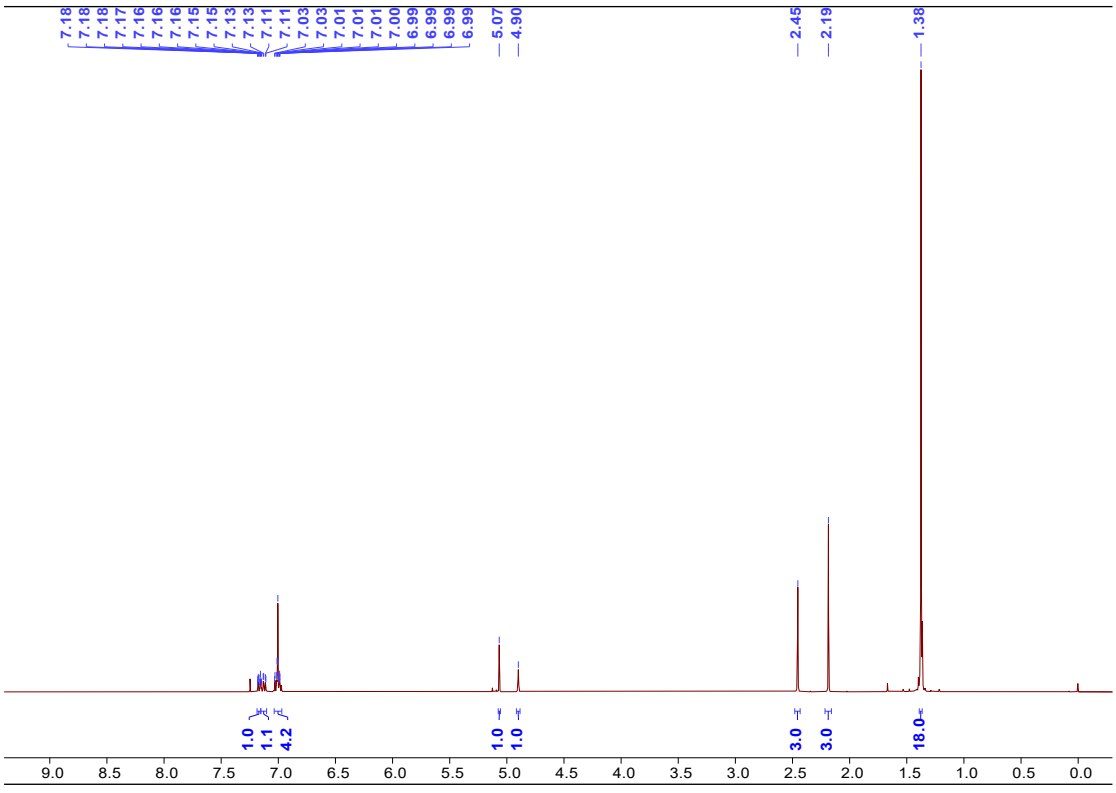
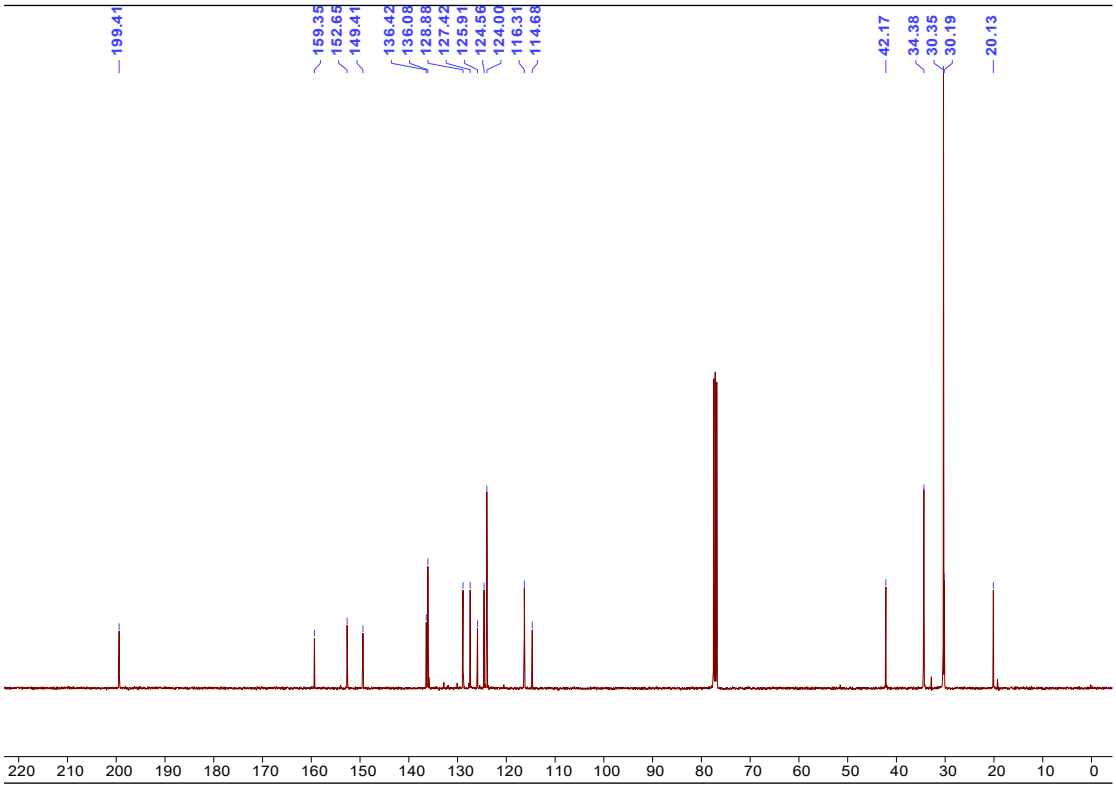


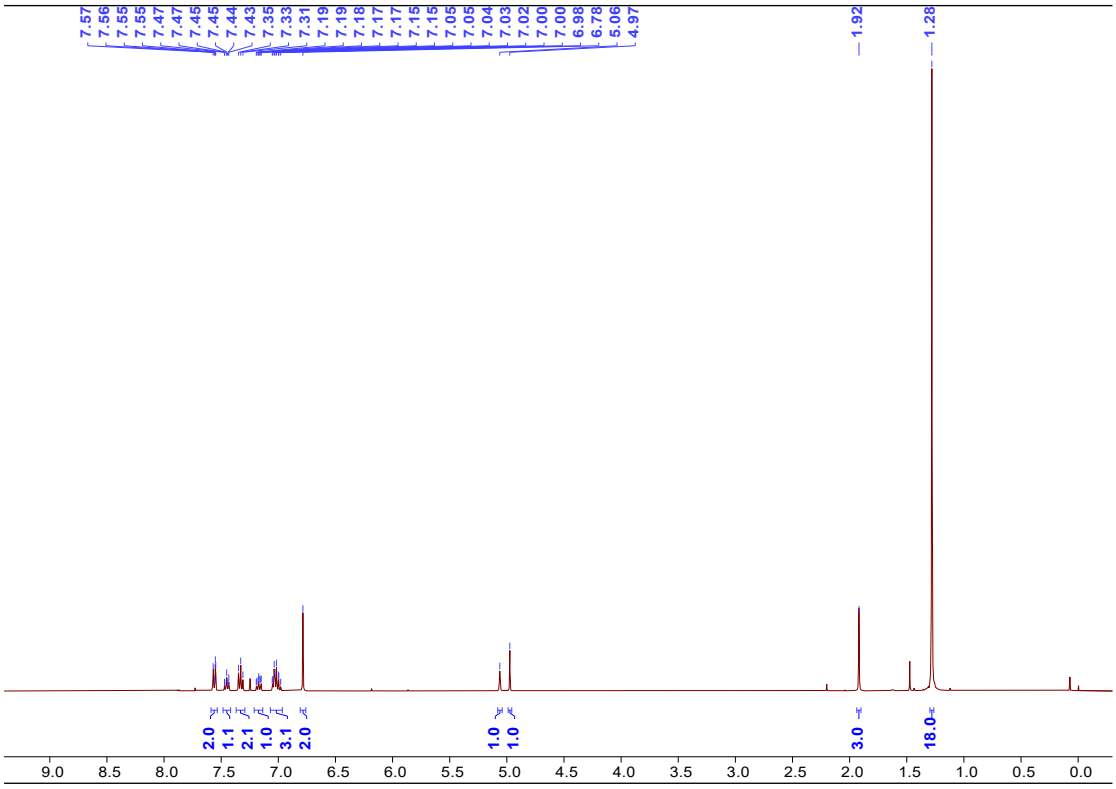
^{13}C NMR spectrum of 10j



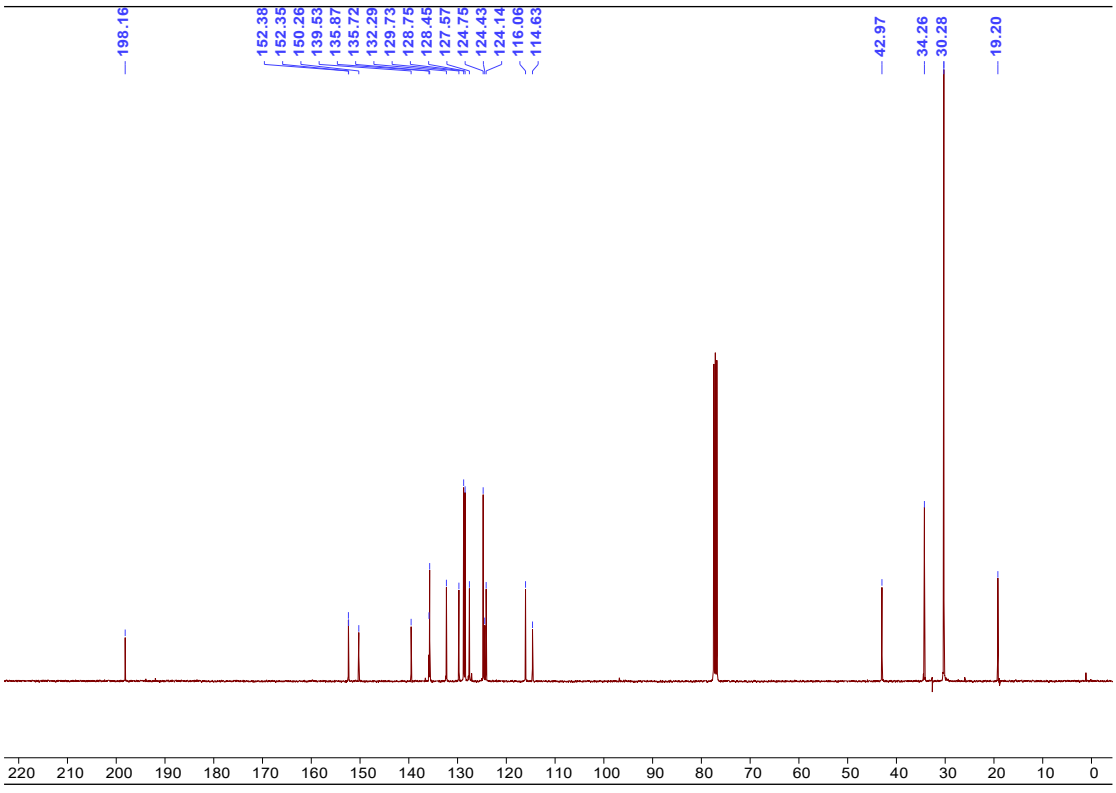
^{1}H NMR spectrum of 12a



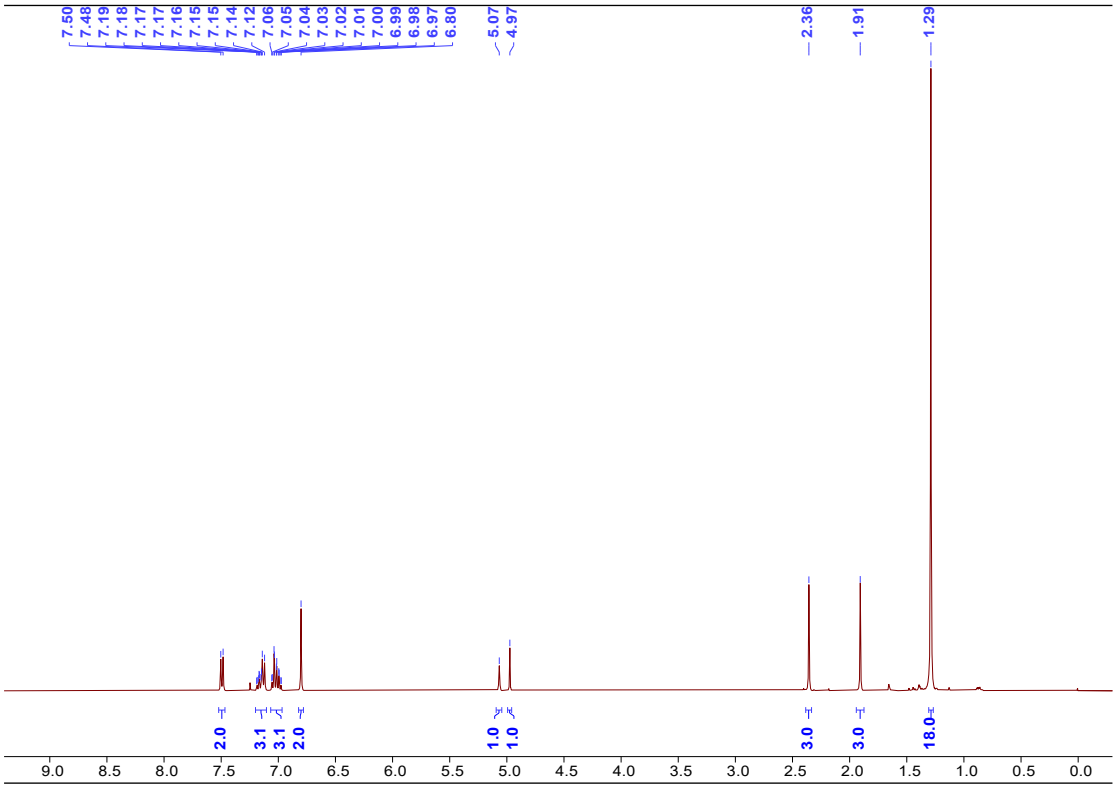
^{13}C NMR spectrum of 12a



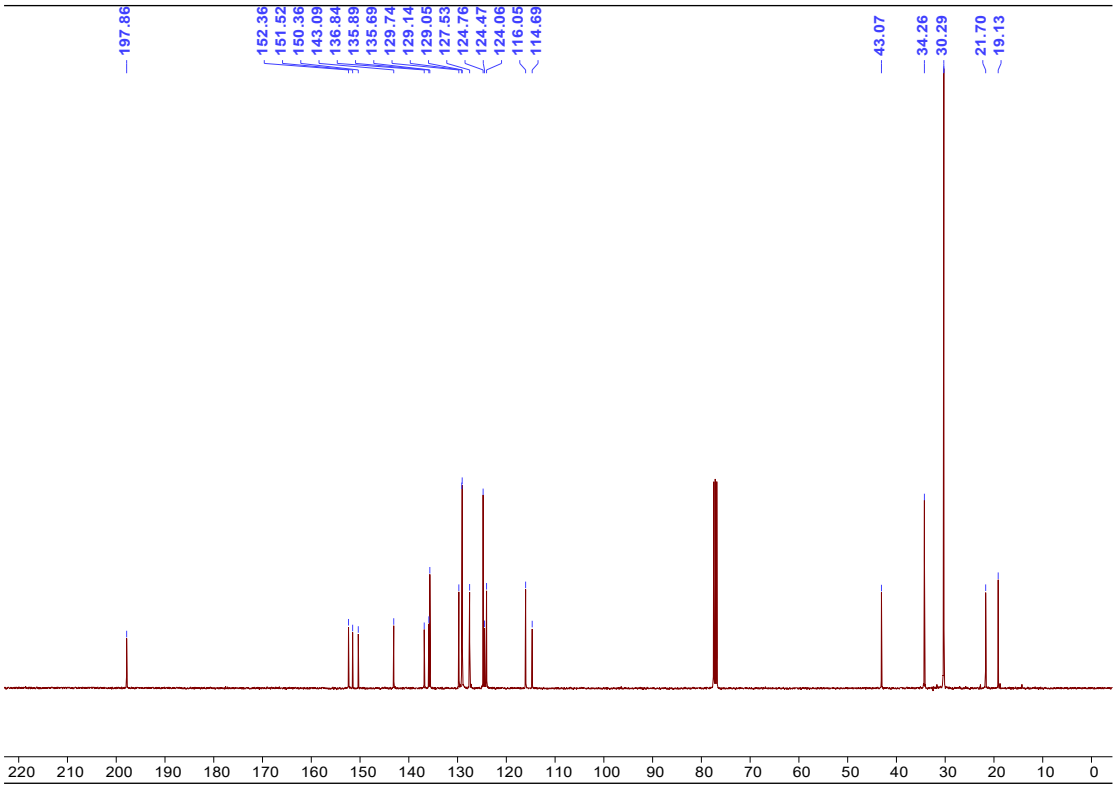
^{1}H NMR spectrum of 12b



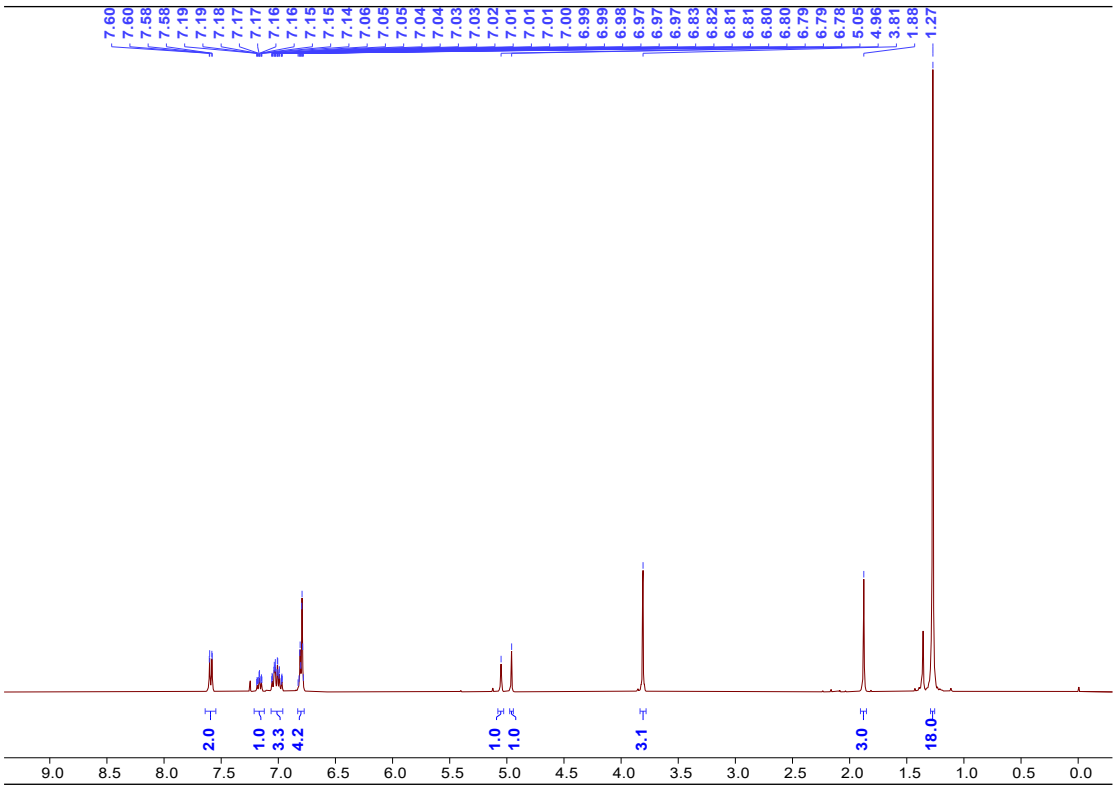
^{13}C NMR spectrum of 12b



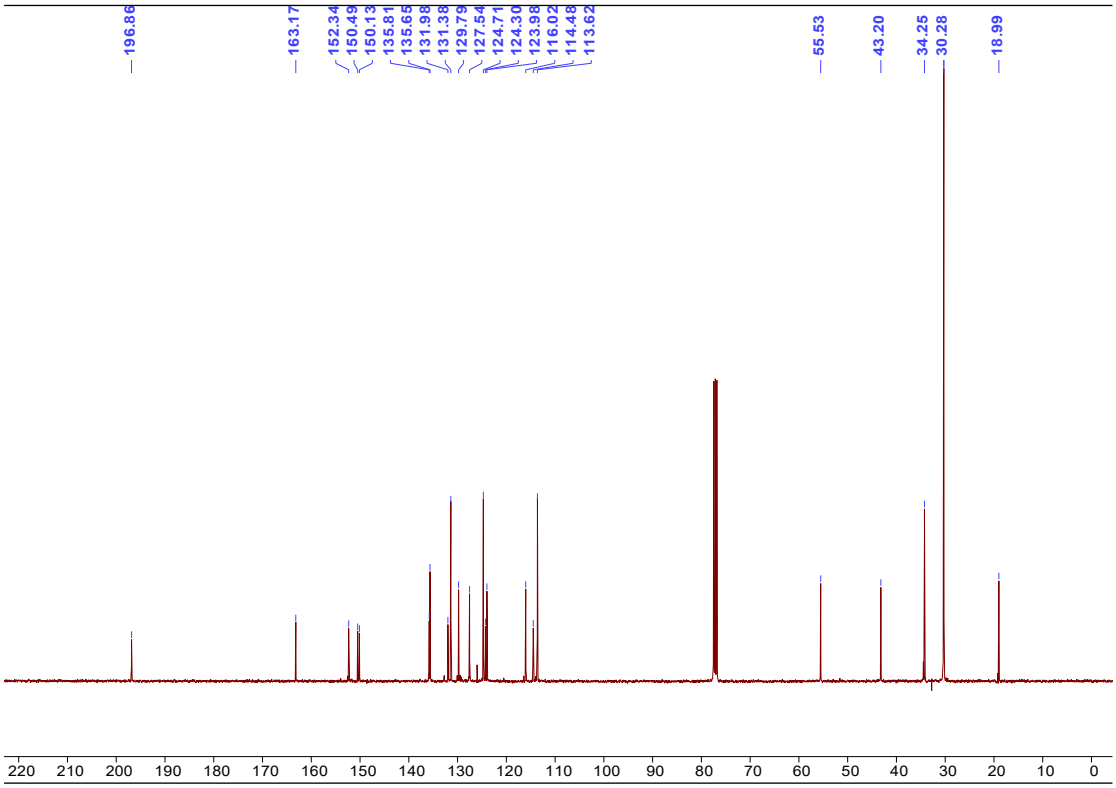
^{1}H NMR spectrum of 12c



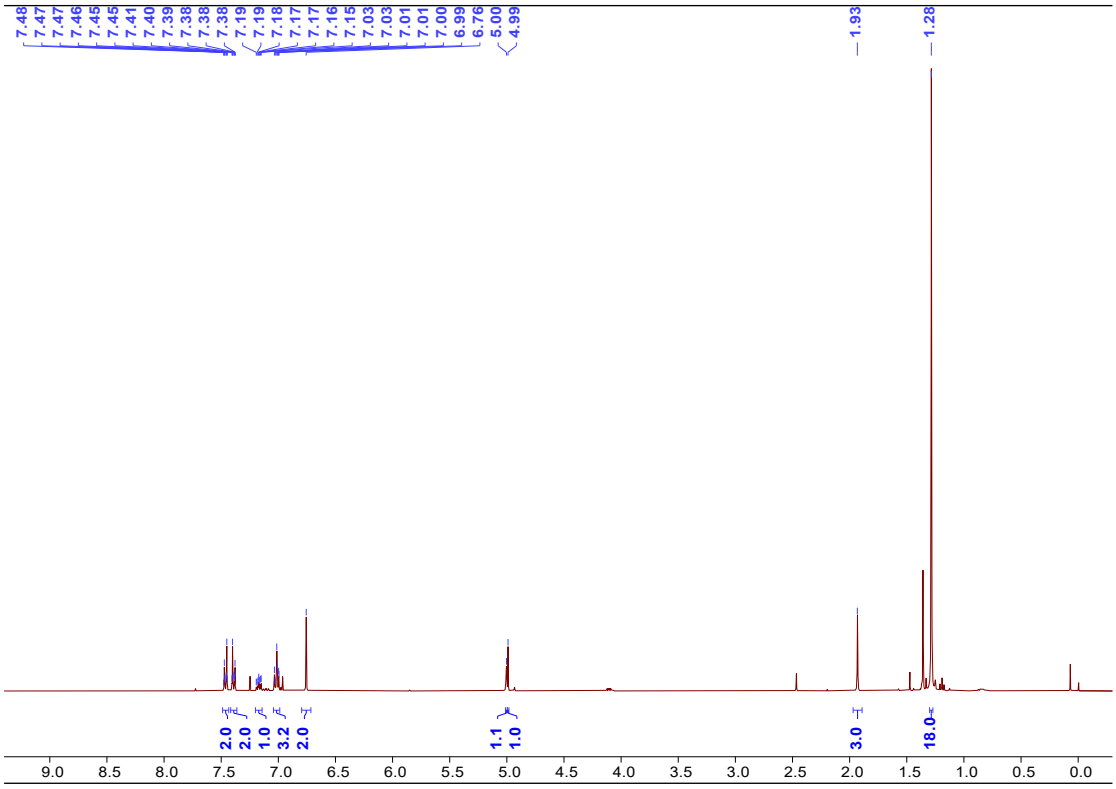
^{13}C NMR spectrum of 12c



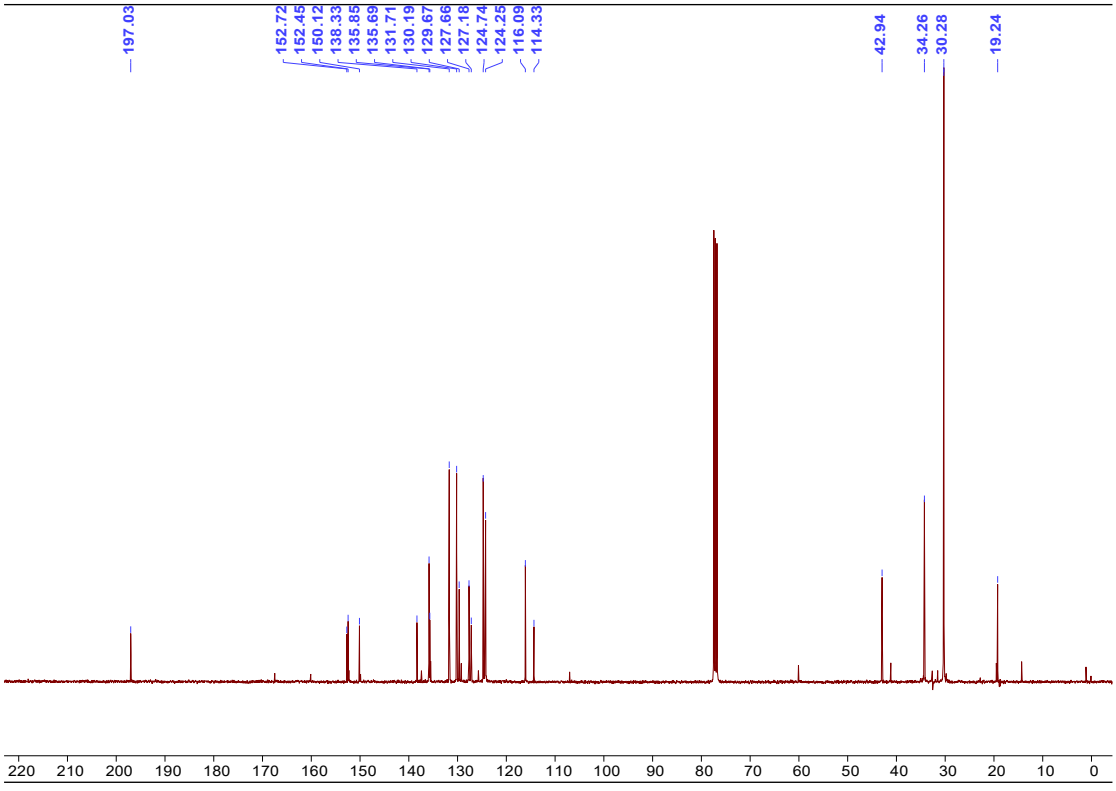
^{1}H NMR spectrum of 12d



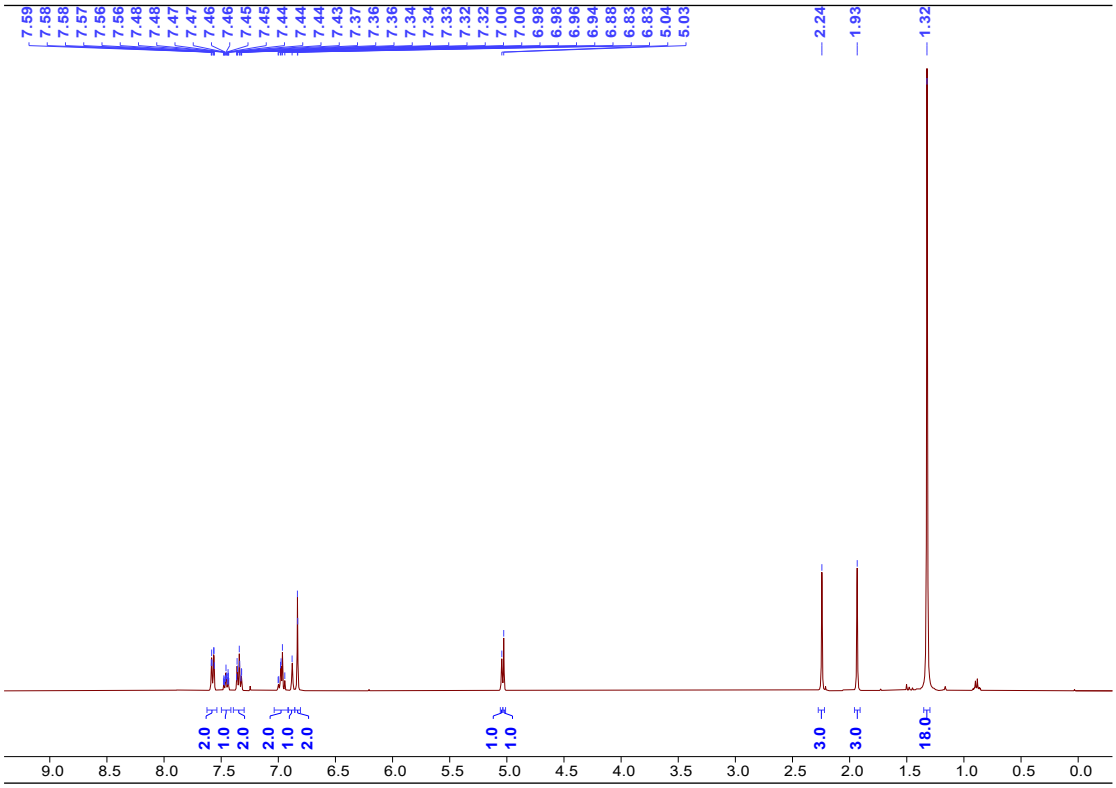
^{13}C NMR spectrum of 12d



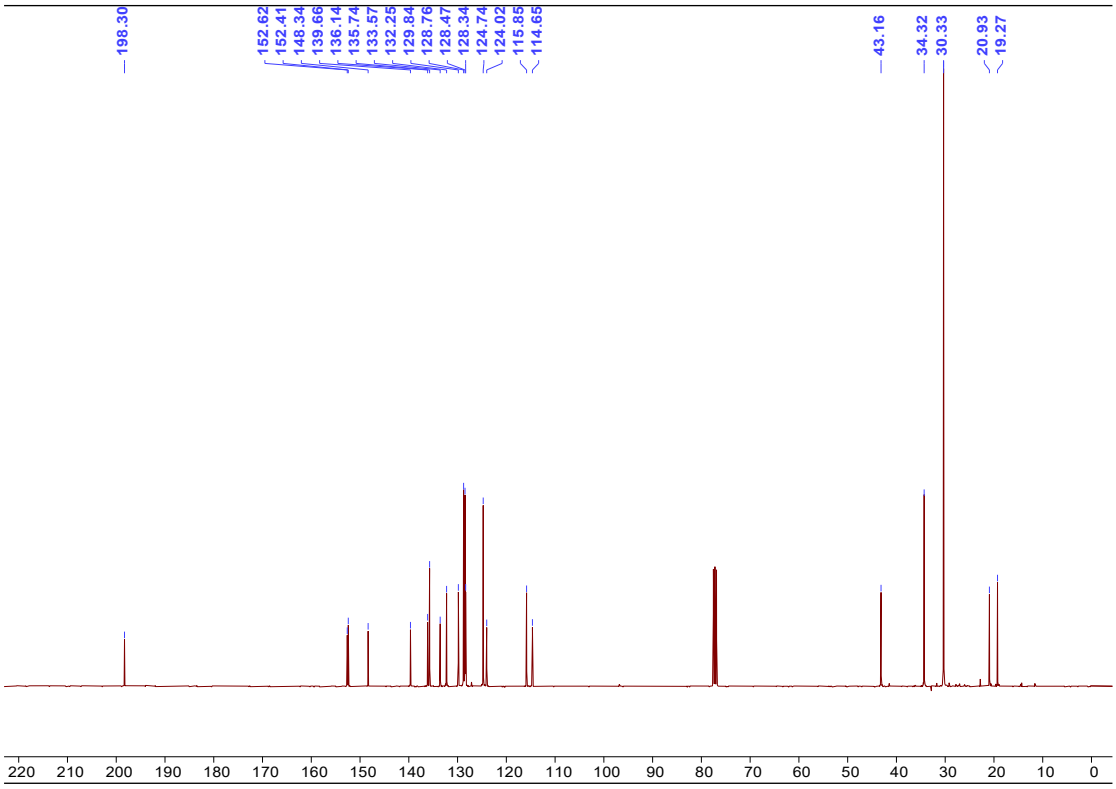
^{1}H NMR spectrum of 12e



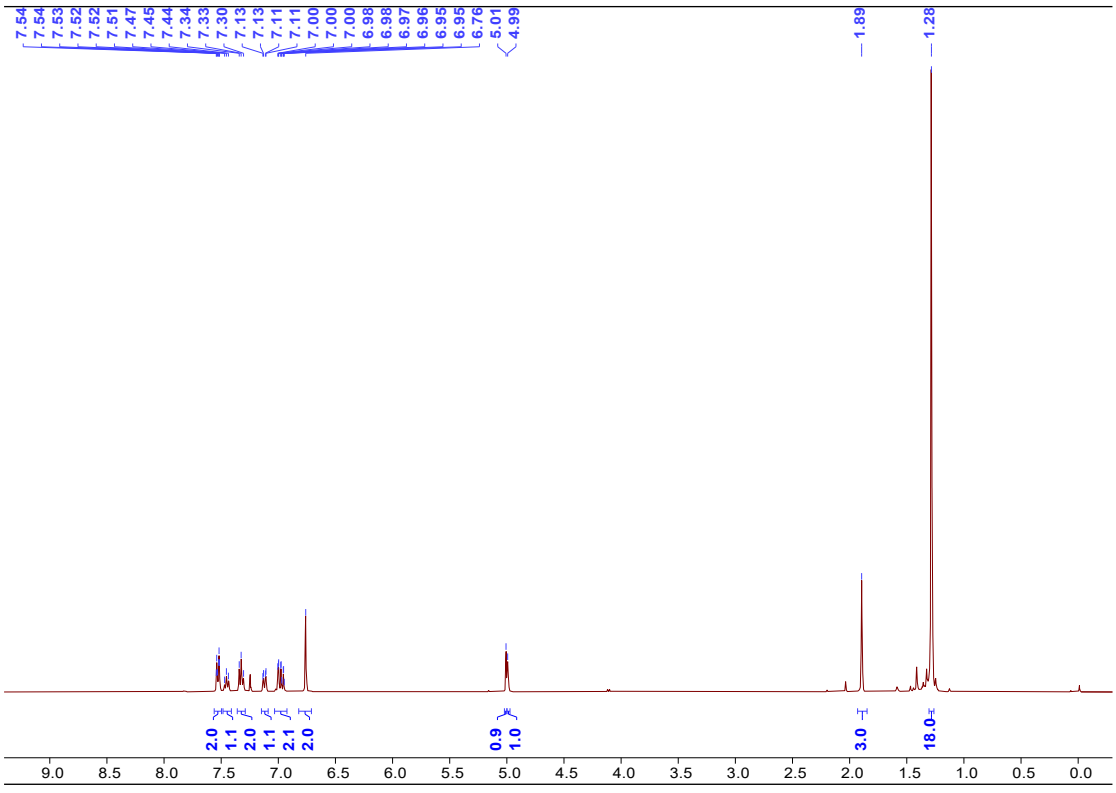
^{13}C NMR spectrum of 12e



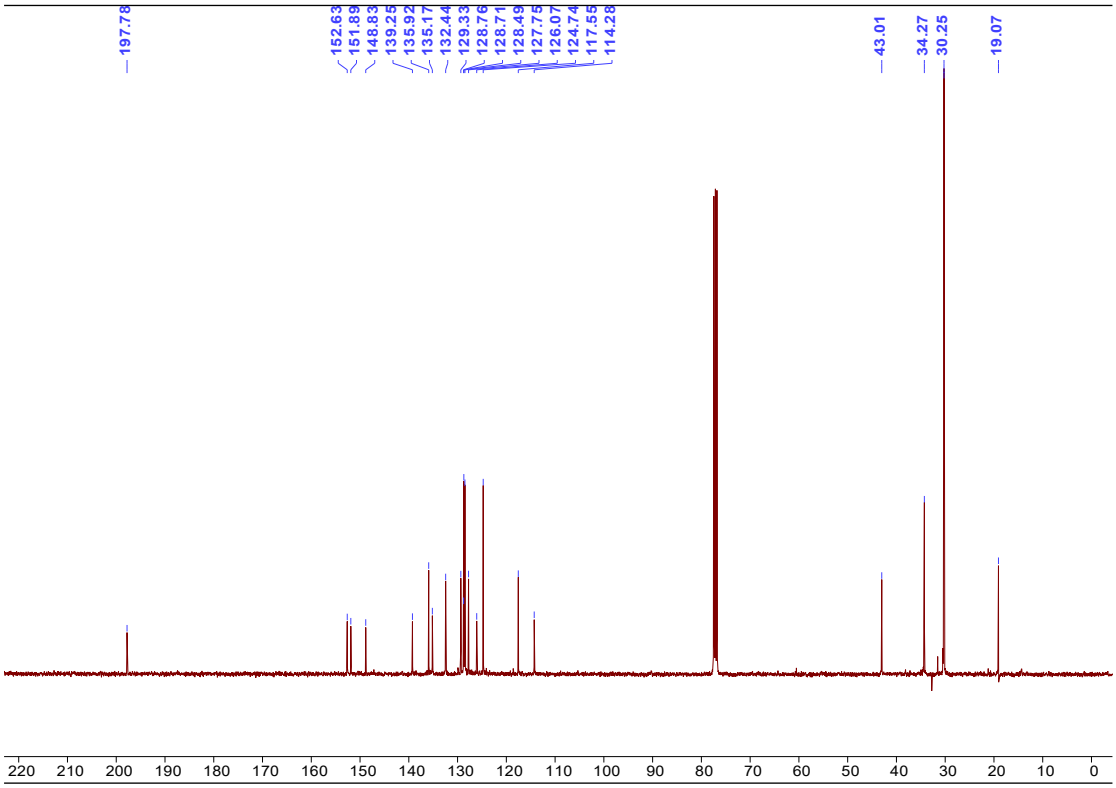
^{1}H NMR spectrum of 12f



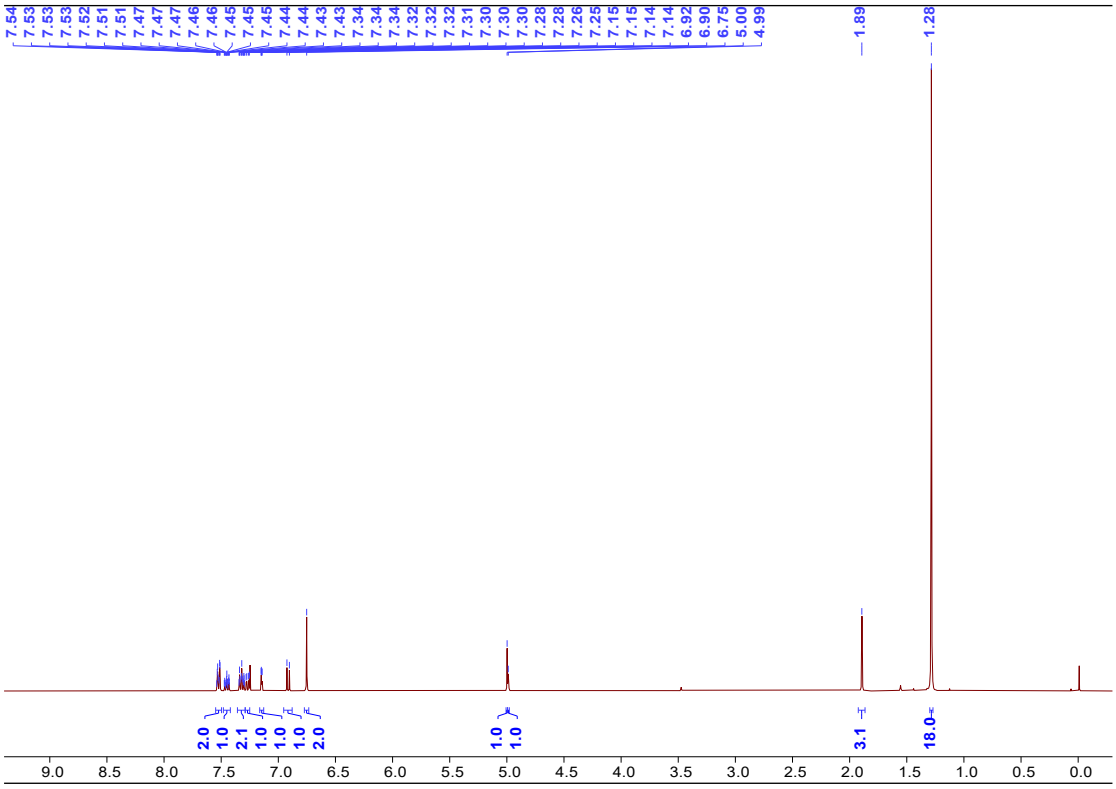
^{13}C NMR spectrum of 12f



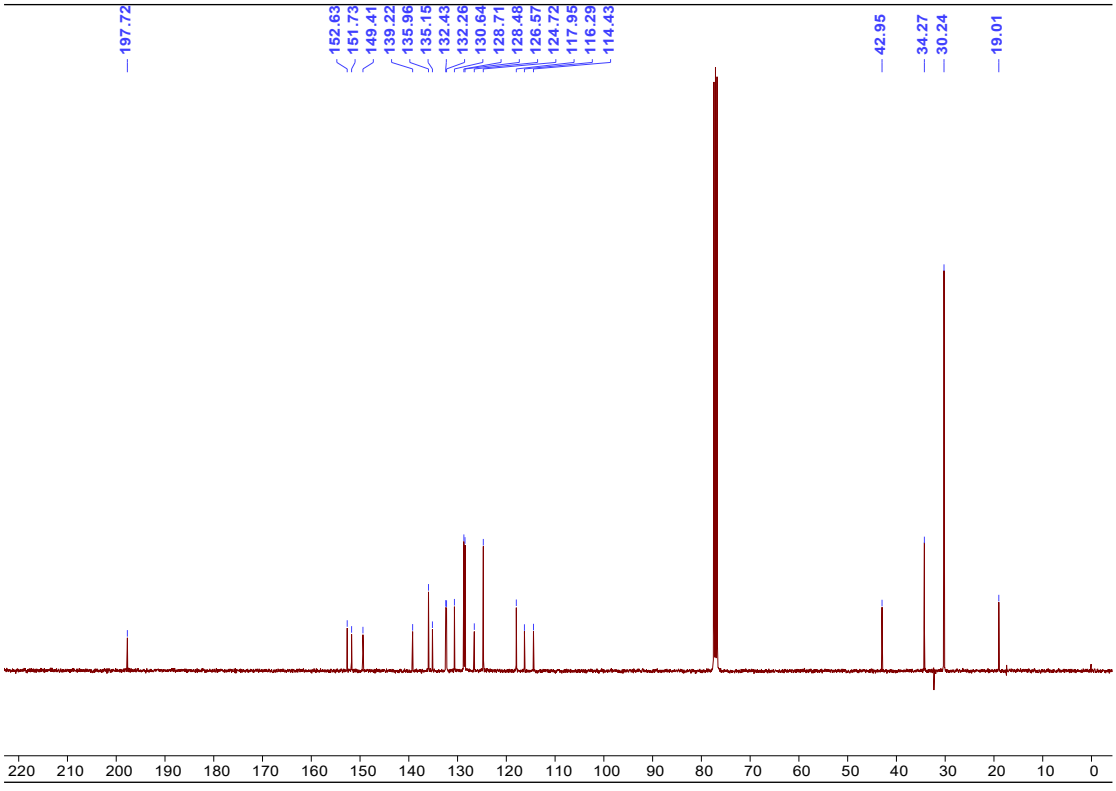
^{1}H NMR spectrum of 12g



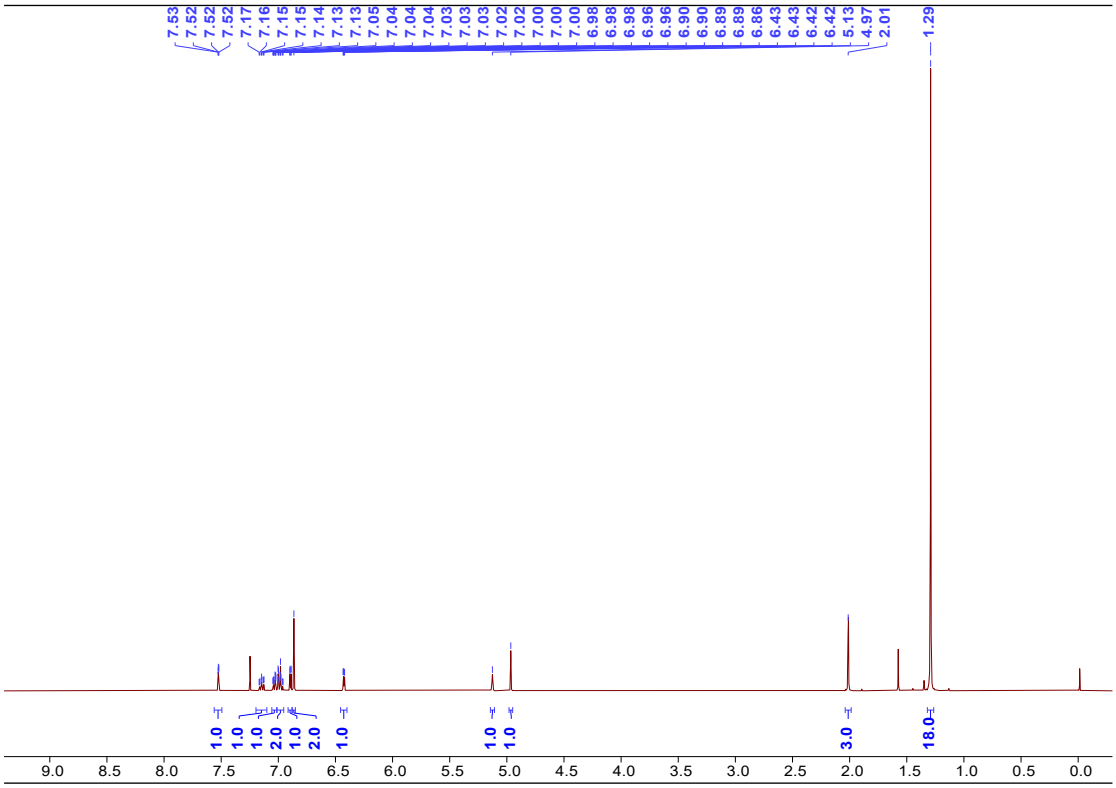
^{13}C NMR spectrum of 12g



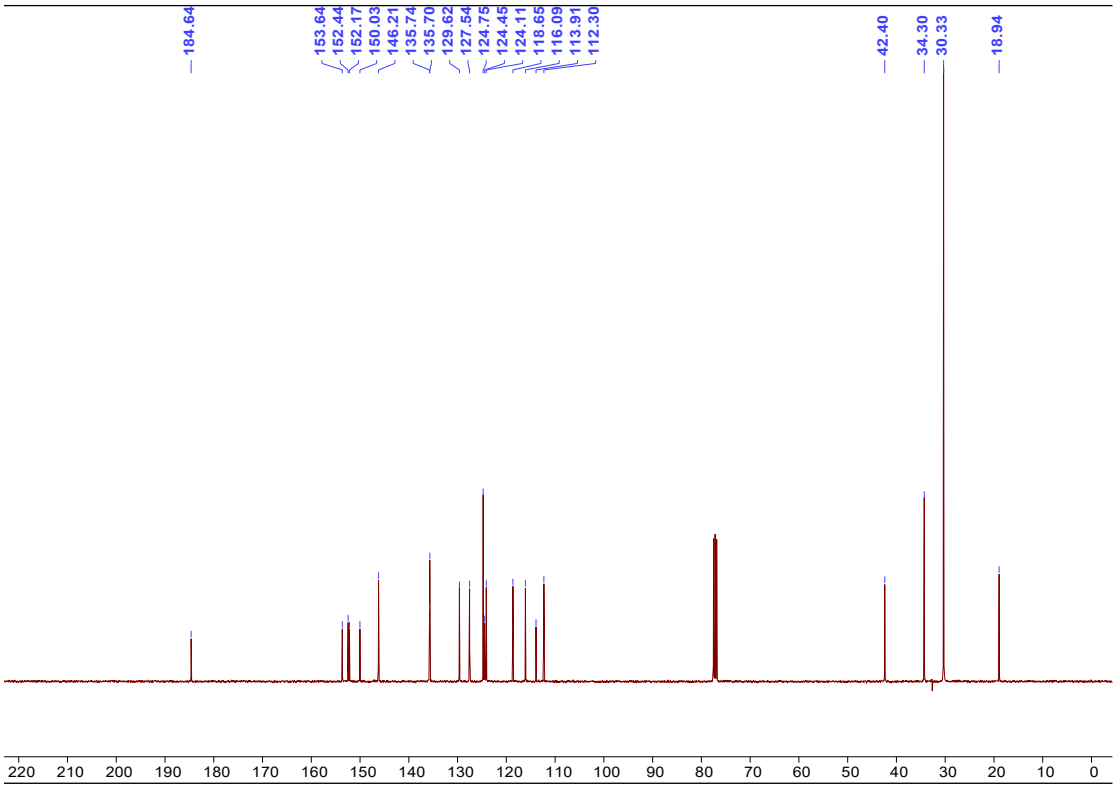
^{1}H NMR spectrum of 12h



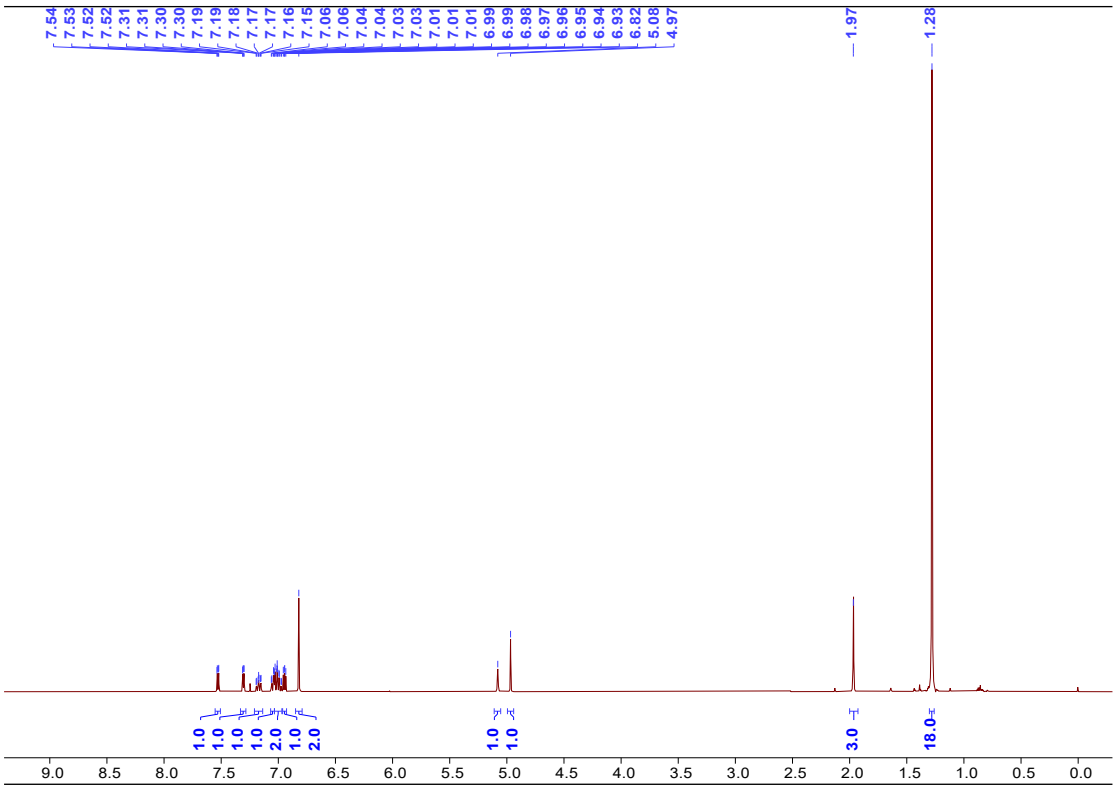
^{13}C NMR spectrum of 12h



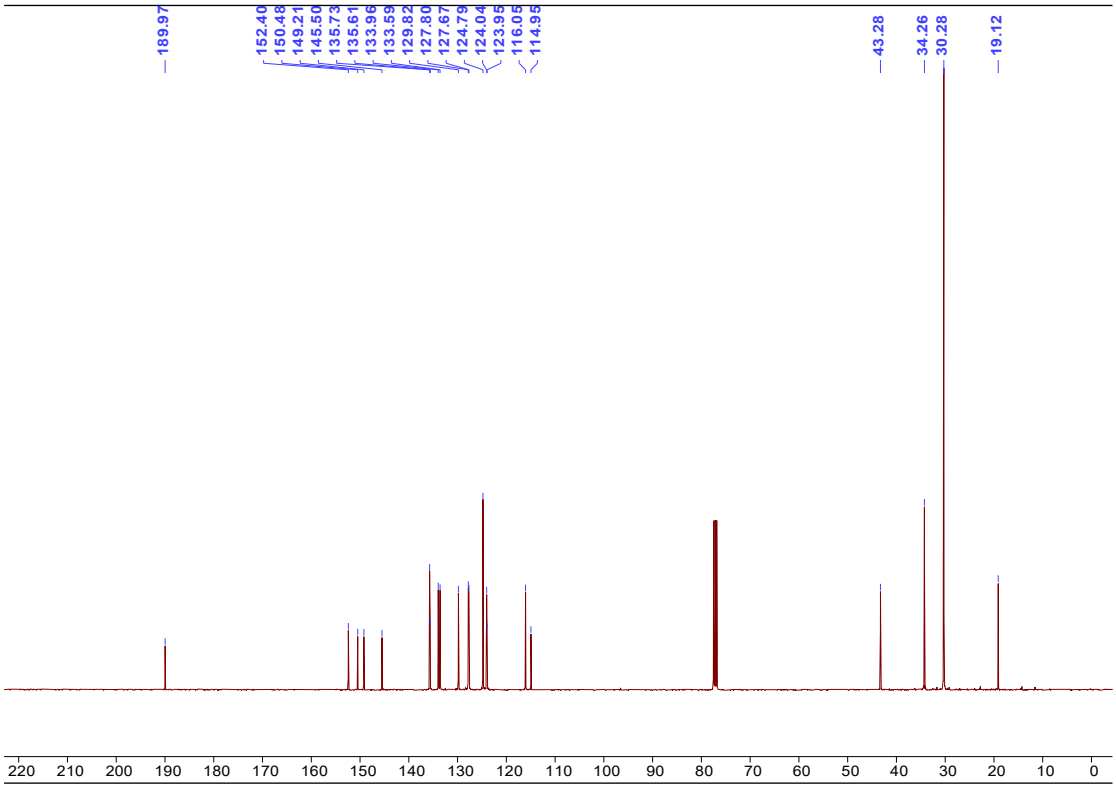
^{1}H NMR spectrum of 12i



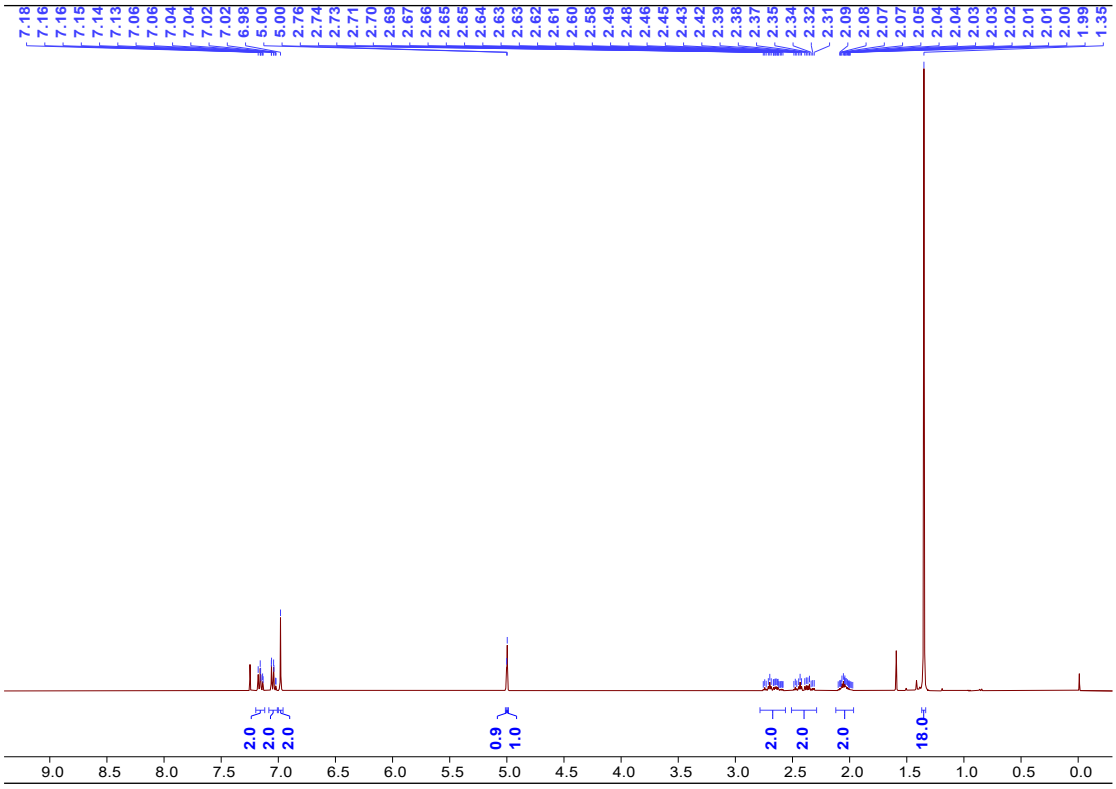
^{13}C NMR spectrum of 12i



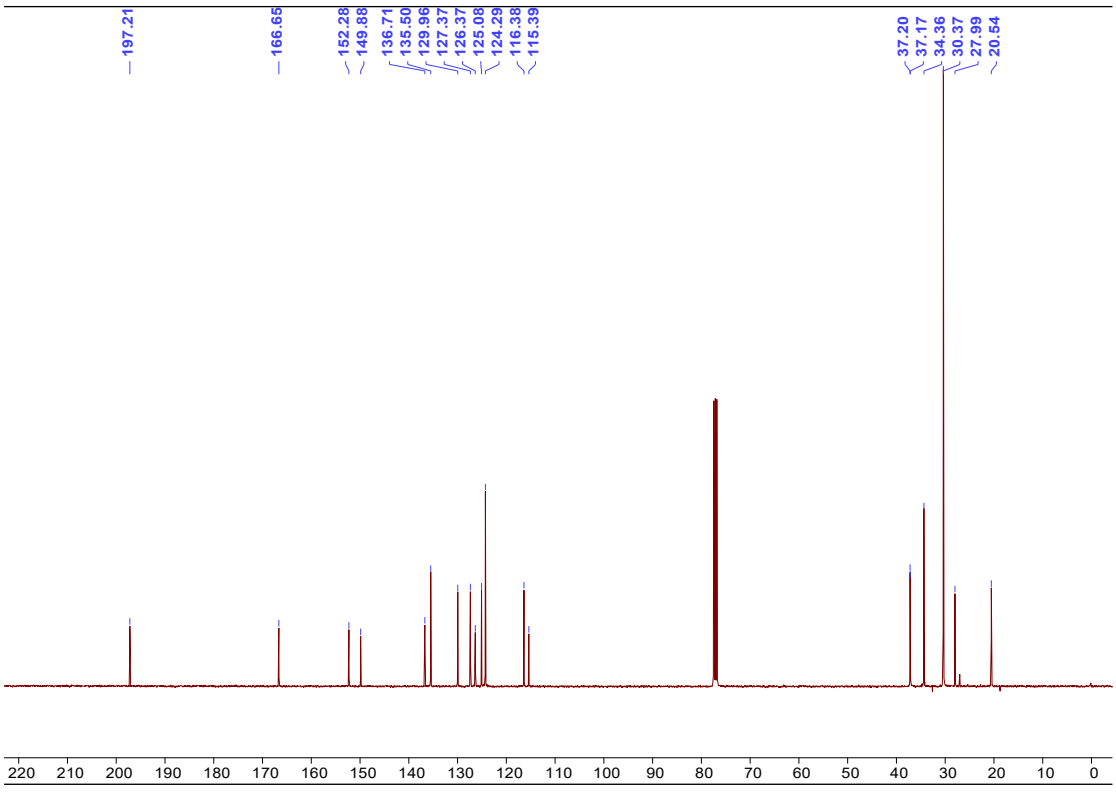
^{1}H NMR spectrum of 12j



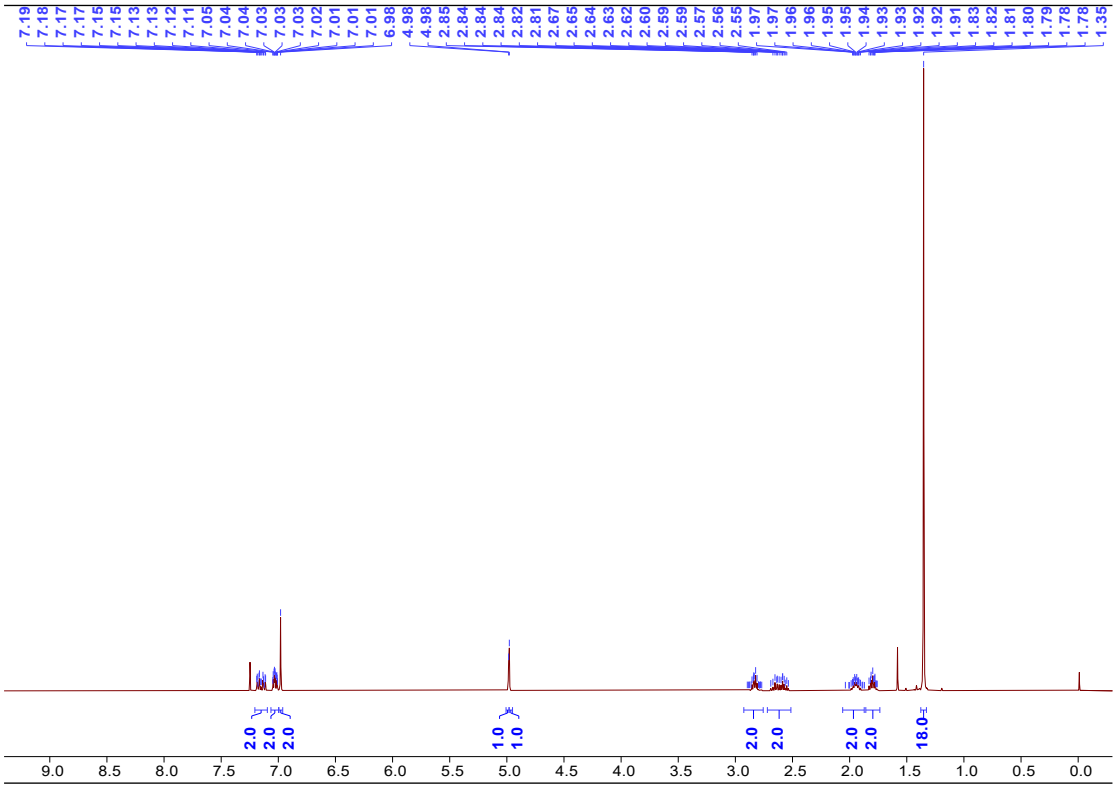
^{13}C NMR spectrum of 12j



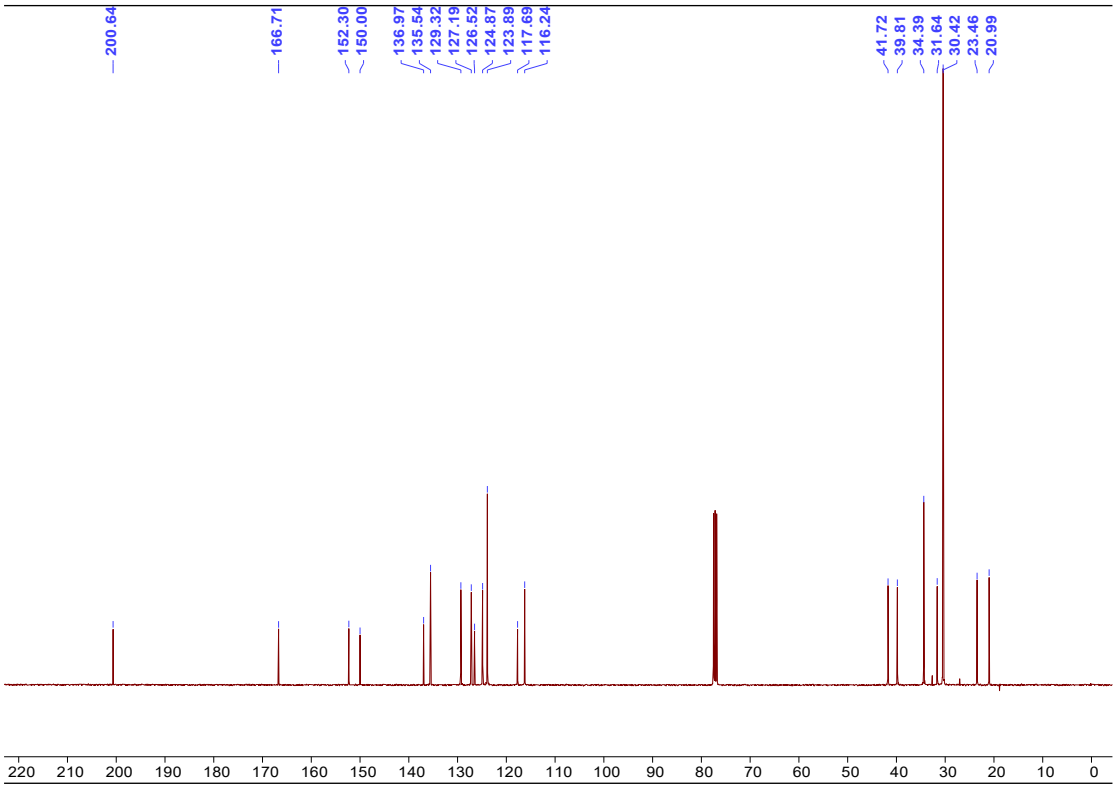
^{1}H NMR spectrum of 12k



^{13}C NMR spectrum of 12k



^{1}H NMR spectrum of 12l



^{13}C NMR spectrum of 12l