Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Ionic liquid grafted onto graphene oxide as a new multifunctional heterogeneous catalyst and its application for the one-pot multi-component synthesis of hexahydroquinolines

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Spectral data of HHQs

Ethyl-4-phenyl-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (4a): ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 0.86 (s, 3H), 1.02 (s, 3H), 1.14 (t, *J* = 7.2 Hz, 3H), 1.99 (d, *J* = 16.0 Hz, 1H), 2.18 (d, *J* = 16.0 Hz, 1H), 2.30 (d, J = 16.4 Hz, 1H), 2.30 (s, 1H), 2.43 (d, *J* = 16.8 Hz, 1H), 3.99 (q, *J* = 7.2 Hz, 2H), 4.87 (s, 1H), 7.06-7.10 (m, 1H), 7.15-7.21 (m, 4H), 9.08 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 14.6, 18.7, 26.9, 29.6, 32.6, 36.3, 50.7, 59.5, 104.1, 110.4, 126.1, 127.9, 128.2, 145.4, 148.1, 150.0, 167.3, 194.7.

Ethyl-4-(4-methylphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (4b): ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 0.86 (s, 3H), 1.02 (s, 3H), 1.15 (t, *J* = 7.2 Hz, 3H), 1.98 (d, *J* = 16.0 Hz, 1H), 2.15–2.21 (m, 4H), 2.29–2.31 (m, 4H), 2.43 (d, *J* = 16.8 Hz, 1H), 3.98 (q, *J* = 7.2 Hz, 2H), 4.82 (s, 1H), 6.99 (d, *J* = 7.6 Hz, 2H), 7.04 (d, *J* = 7.6 Hz, 2H), 9.04 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 14.7, 18.8, 21.1, 26.9, 29.7, 32.6, 35.9, 50.8, 59.5, 104.3, 110.6, 127.9, 128.8, 135.0, 145.3, 149.8, 167.4, 194.7.

Ethyl-4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (4c): ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 0.86 (s, 3H), 1.02 (s, 3H), 1.15 (t, *J* = 7.2 Hz, 3H), 1.98 (d, *J* = 16.0 Hz, 1H), 2.17 (d, *J* = 16.4 Hz, 1H), 2.28 (s, 3H), 2.29 (d, *J* = 16.0 Hz, 1H), 2.42 (d, *J* = 16.8 Hz, 1H), 3.68 (s, 3H), 3.98 (q, *J* = 7.2 Hz, 2H), 4.80 (s, 1H), 6.75 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 9.03 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 14.6, 18.6, 18.7, 26.9, 29.6, 32.6, 35.4, 50.7, 55.3, 59.4, 104.3, 110.6, 113.5, 128.8, 140.5, 145.1, 149.7, 157.7, 167.4, 194.7.

Ethyl-4-(4-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (4d): ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 0.84 (s, 3H), 1.02 (s, 3H), 1.13 (t, *J* = 7.2 Hz, 3H), 1.98 (d, *J* = 15.6 Hz, 1H), 2.18 (d, *J* = 14.4 Hz, 1H), 2.27 - 2.30 (m, 4H), 2.43 (d, *J* = 17.2 Hz, 1H), 3.98 (q, *J* = 6.8 Hz, 2H), 4.85 (s, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 9.13 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 14.5, 18.7, 18.8, 26.9, 29.5, 32.6, 36.0, 50.6, 59.5, 103.6, 110.1, 128.1, 129.8, 130.6, 145.9, 147.0, 150.1, 167.1, 194.7.

Ethyl-4-(4-nitrophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (4e): ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 0.83 (s, 3H), 1.02 (s, 3H), 1.12 (t, *J* = 6.8 Hz, 3H), 1.99 (d, *J* = 16.0 Hz, 1H), 2.20 (d, *J* = 16.4 Hz, 1H), 2.29 - 2.33 (m, 4H), 2.45 (d, *J* = 16.8 Hz, 1H), 3.97 (q, *J* = 7.2 Hz, 2H), 4.98 (s, 1H), 7.43 (d, *J* = 8.8 Hz, 2H), 8.11 (d, *J* = 8.8 Hz, 2H), 9.26 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 14.5, 18.8, 26.8, 29.4, 32.6, 37.1, 50.5, 59.7, 102.8, 109.5, 123.6, 129.2, 146.1, 146.6, 150.5, 155.4, 166.8, 194.7.

Ethyl-4-(4-cyanophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (4f): ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 0.82 (s, 3H), 1.01 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 3H), 1.99 (d, *J* = 16.0 Hz, 1H), 2.19 (d, *J* = 16.0 Hz, 1H), 2.28 - 2.32 (m, 4H), 2.44 (d, *J* = 17.2 Hz, 1H), 3.97 (q, *J* = 7.2 Hz, 2H), 4.92 (s, 1H), 7.35 (d, *J* = 6.8 Hz, 2H), 7.69 (d, *J* = 6.8 Hz, 2H), 9.22 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 14.5, 18.8, 26.8, 29.4, 32.6, 37.1, 50.5, 59.6, 102.9, 109.0, 109.6, 119.4, 129.0, 132.3, 146.5, 150.4, 153.4, 166.9, 194.7.

Ethyl-4-(4-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (4g): ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 0.84 (s, 3H), 1.02 (s, 3H), 1.13 (t, *J* = 7.2 Hz, 3H), 1.99 (d, *J* = 15.2 Hz, 1H), 2.13 (d, *J* = 24.8 Hz, 1H), 2.23 (d, *J* = 27.2 Hz, 1H), 2.30 (s, 3H), 2.43 (d, *J* = 16.8 Hz, 1H), 3.98 (q, *J* = 7.2 Hz, 2H), 4.83 (s, 1H), 7.12 (d, *J* = 6.8 Hz, 2H), 7.39 (d, *J* = 6.8 Hz, 2H), 9.13 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 14.6, 18.7, 26.9, 29.5, 32.6, 36.1, 50.6, 59.6, 103.5, 110.0, 119.1, 130.2, 131.0, 145.9, 147.4, 150.1, 167.1, 194.7.

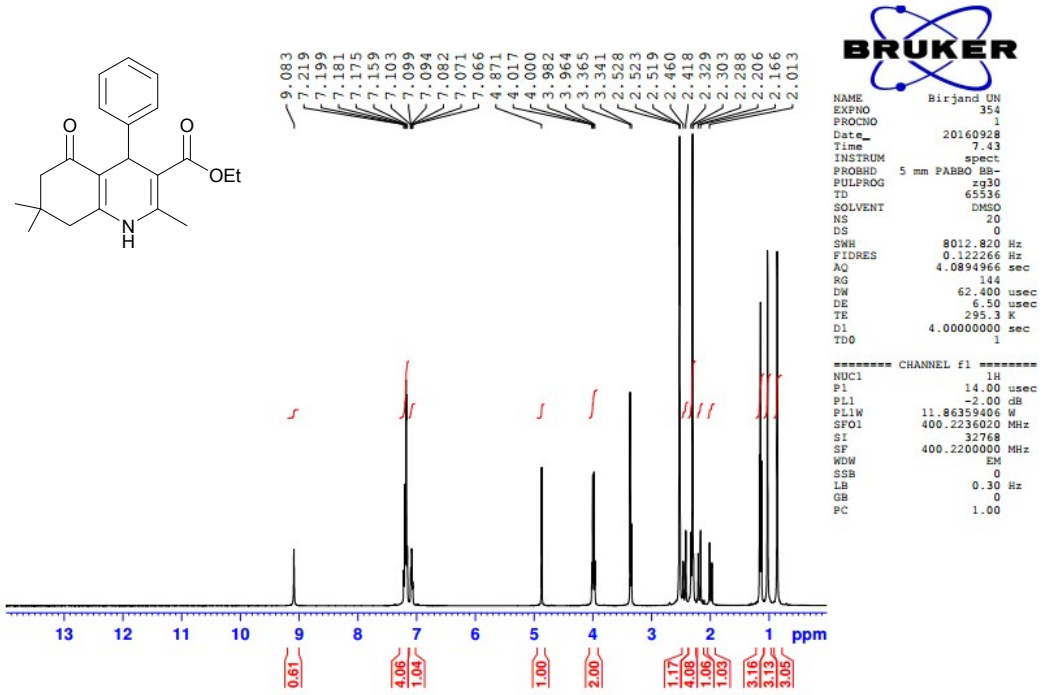
Ethyl-4-(3-hydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (4h): ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 0.88 (s, 3H), 1.02 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H), 1.99 (d, *J* = 16.0 Hz, 1H), 2.18 (d, *J* = 16.0 Hz, 1H), 2.29 (d, *J* =

16.4 Hz, 1H), 2.29 (s, 3H), 2.42 (d, *J* = 16.8 Hz, 1H), 4.00 (q, *J* =7.2 Hz, 2H), 4.80 (s, 1H), 6.47 (d, *J* = 7.2 Hz, 1H), 6.58-6.60 (m, 2H), 6.96 (t, *J* = 8.0 Hz, 1H), 9.04 (s, 1H), 9.10 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 14.6, 18.7, 27.0, 29.6, 32.6, 36.1, 50.7, 59.5, 104.1, 110.4, 113.1, 115.0, 118.6, 128.9, 145.2, 149.4, 149.9, 157.3, 167.4, 194.7.

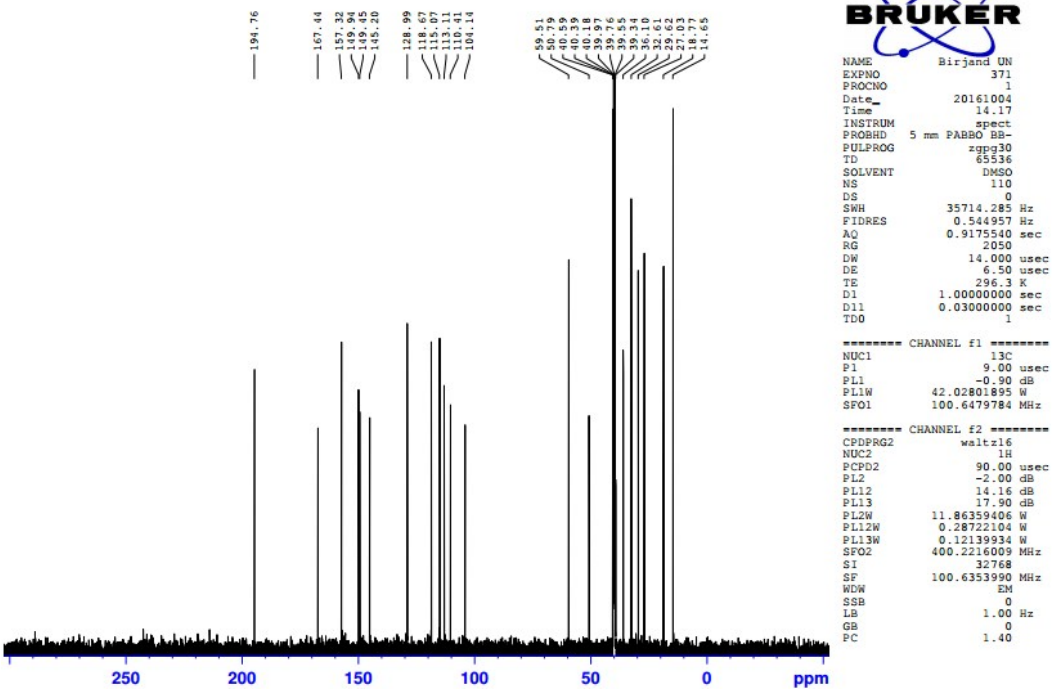
Ethyl-4-(3-nitrophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (4i): ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 0.85 (s, 3H), 1.03 (s, 3H), 1.13 (t, *J* = 7.2 Hz, 3H), 1.99 (d, *J* = 16.0 Hz, 1H), 2.21 (d, *J* = 16.0 Hz, 1H), 2.33 - 2.36 (m, 4H), 2.47 (d, *J* = 17.2 Hz, 1H), 3.95-4.01 (m, 2H), 4.98 (s, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.97-8.00 (m, 2H), 9.27 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 14.4, 18.8, 26.7, 29.5, 32.6, 36.9, 50.4, 59.7, 103.1, 109.7, 121.3, 122.5, 129.8, 134.8, 146.6, 147.8, 150.2, 150.6, 166.8, 194.8.

Ethyl-4-(4-hydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (4j): ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 0.87 (s, 3H), 1.02 (s, 3H), 1.15 (t, *J* = 7.2 Hz, 3H), 1.98 (d, *J* = 16.0 Hz, 1H), 2.17 (d, *J* = 16.0 Hz, 1H), 2.28 - 2.34 (m, 4H), 2.42 (d, *J* = 16.8 Hz, 1H), 3.99 (q, *J* = 7.2 Hz, 2H), 4.75 (s, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 8.99 (s, 1H), 9.06 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 14.6, 18.7, 26.9, 29.6, 32.6, 35.3, 50.8, 59.4, 104.6, 110.8, 114.9, 128.8, 138.9, 144.8, 149.6, 155.7, 167.5, 194.8.

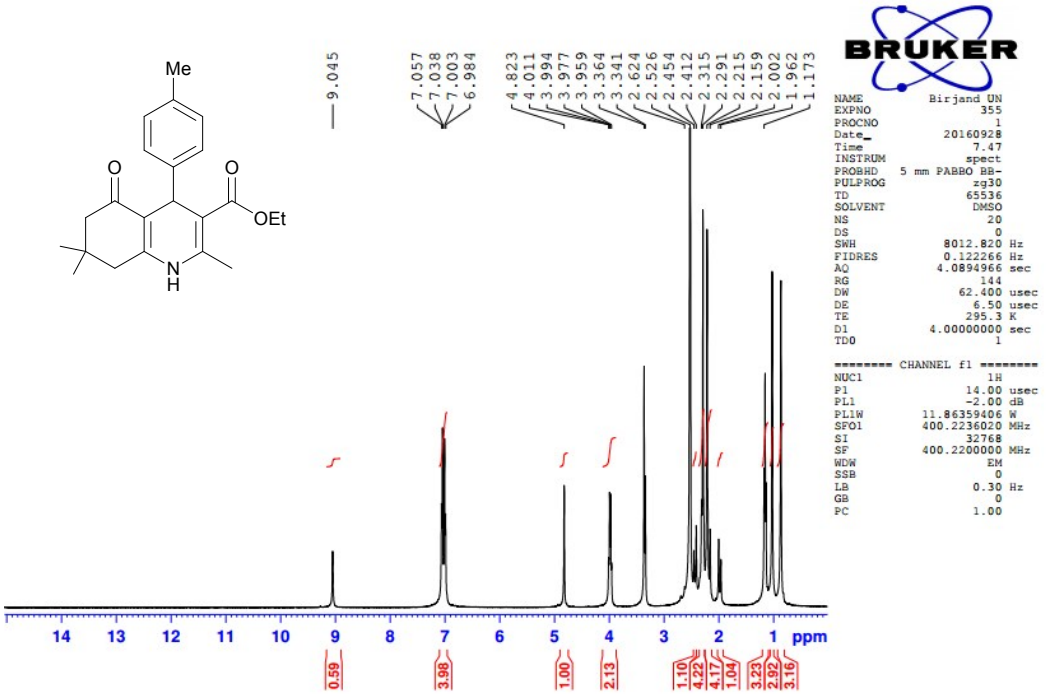
^{1}H NMR spectra of Compound 4a



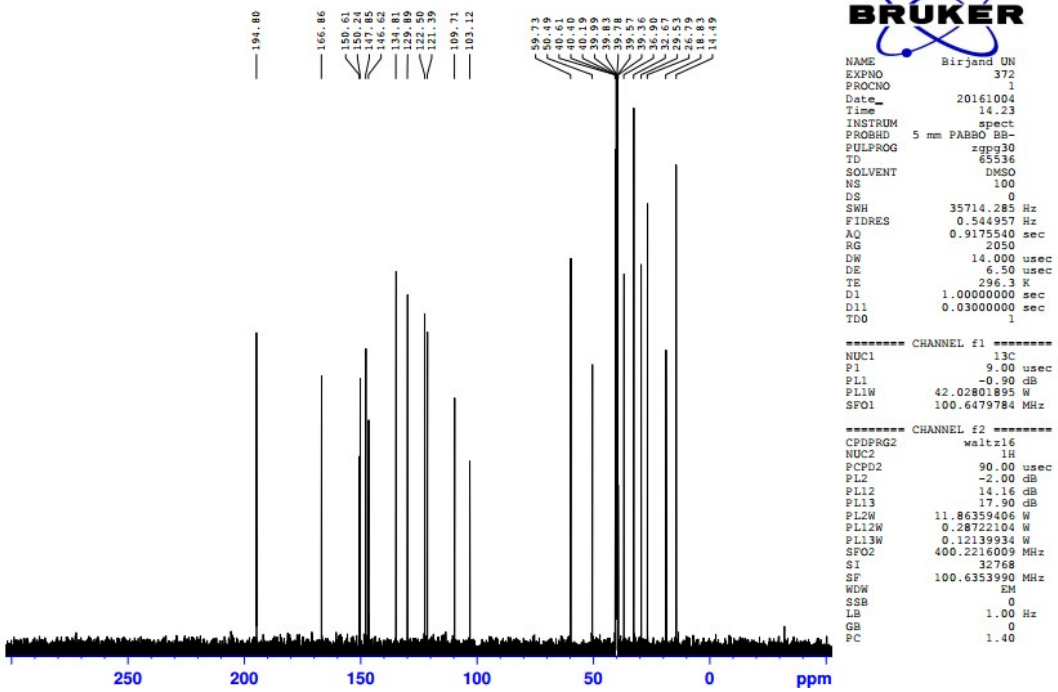
^{13}C NMR spectra of Compound 4a



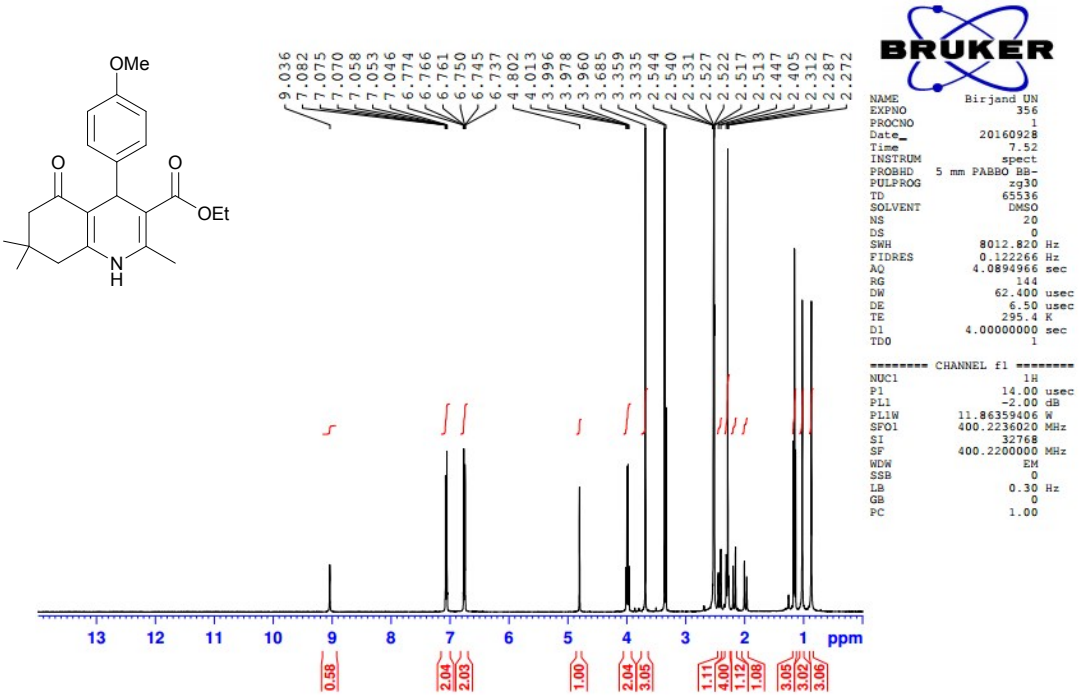
^{1}H NMR spectra of Compound 4b



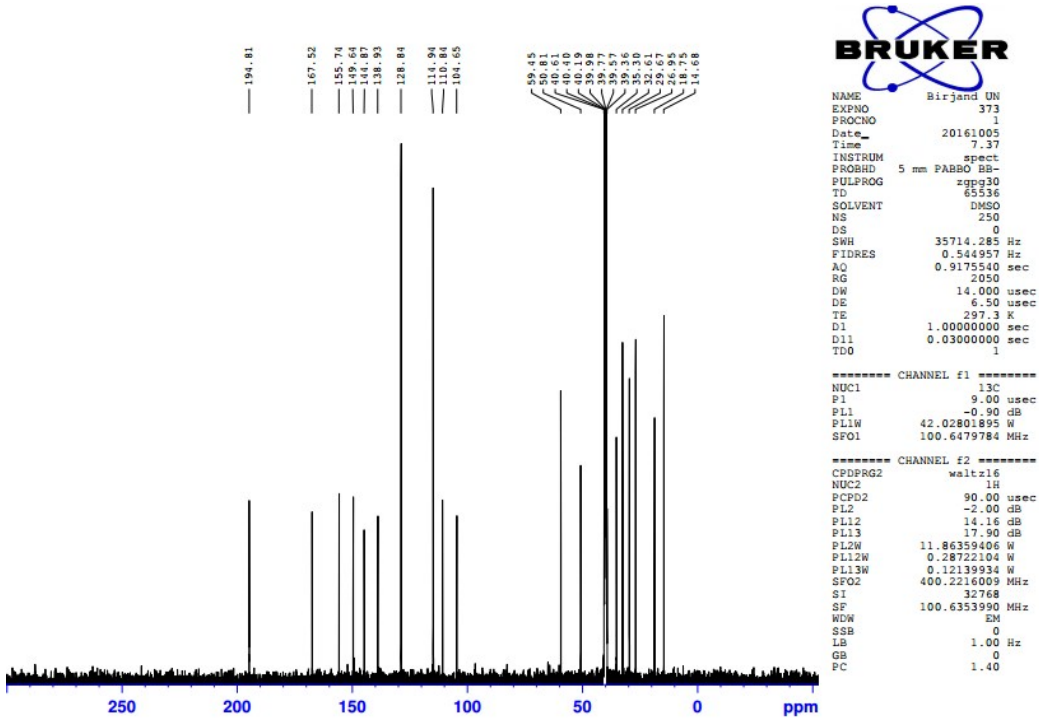
^{13}C NMR spectra of Compound 4b



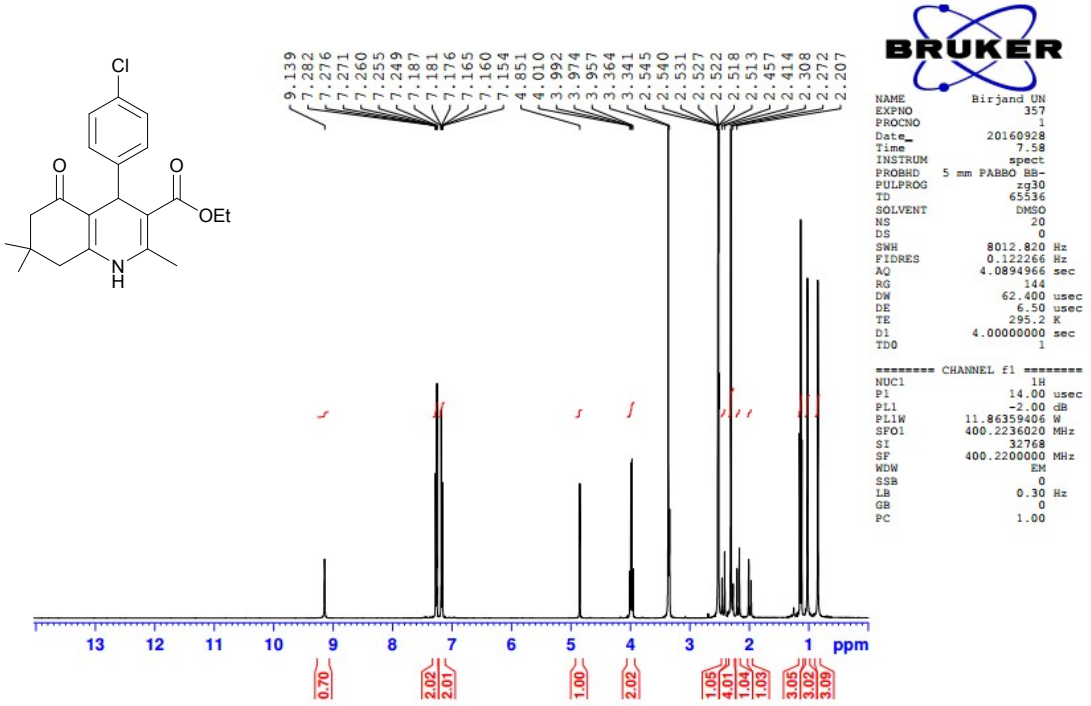
^{1}H NMR spectra of Compound 4c



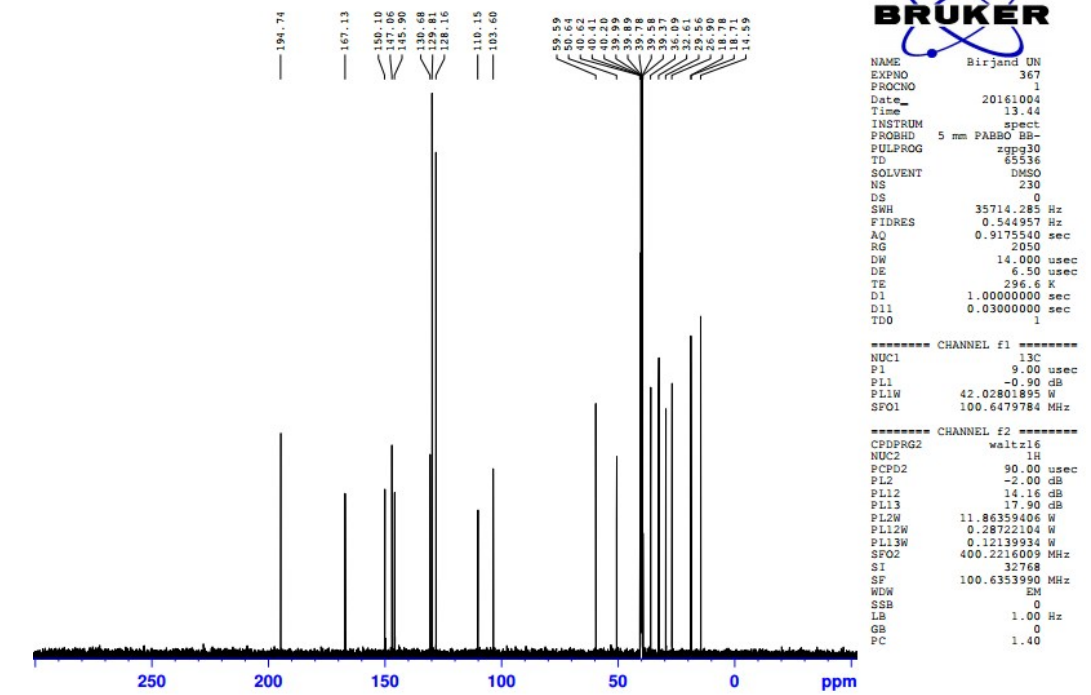
^{13}C NMR spectra of Compound 4c



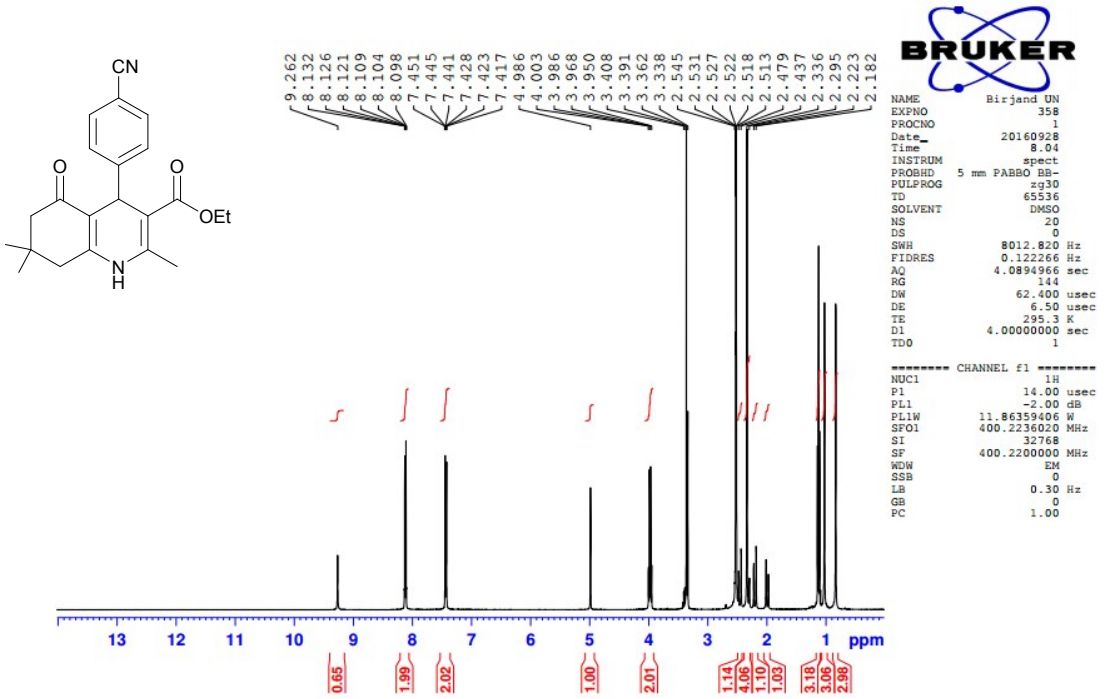
1H NMR spectra of Compound 4d



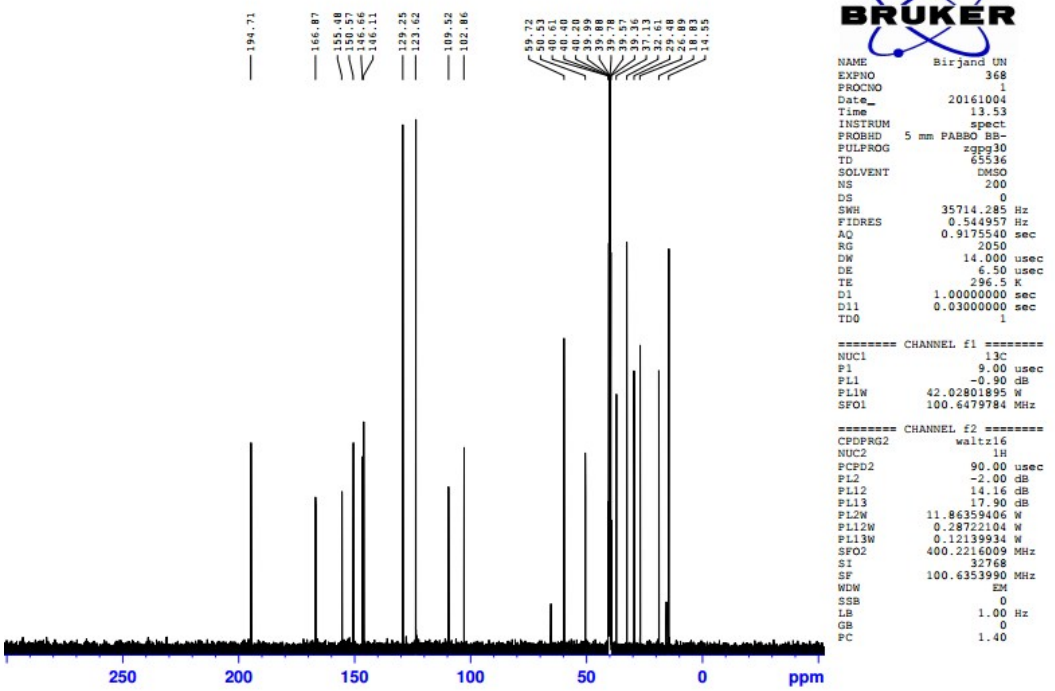
^{13}C NMR spectra of Compound 4d



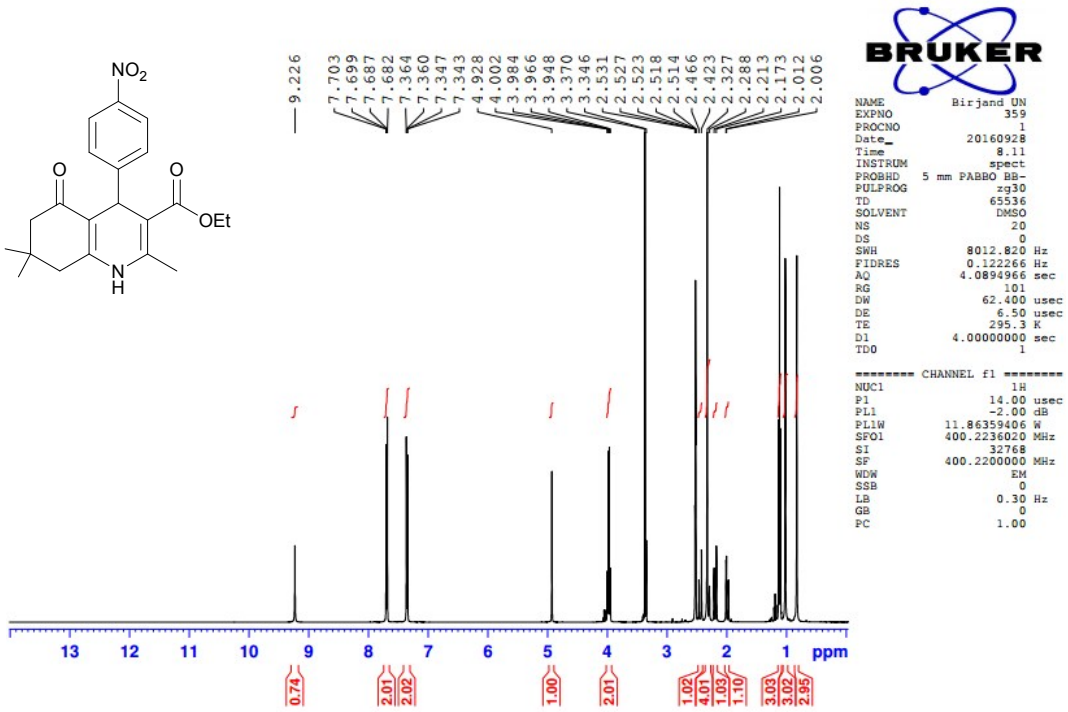
^{1}H NMR spectra of Compound 4e



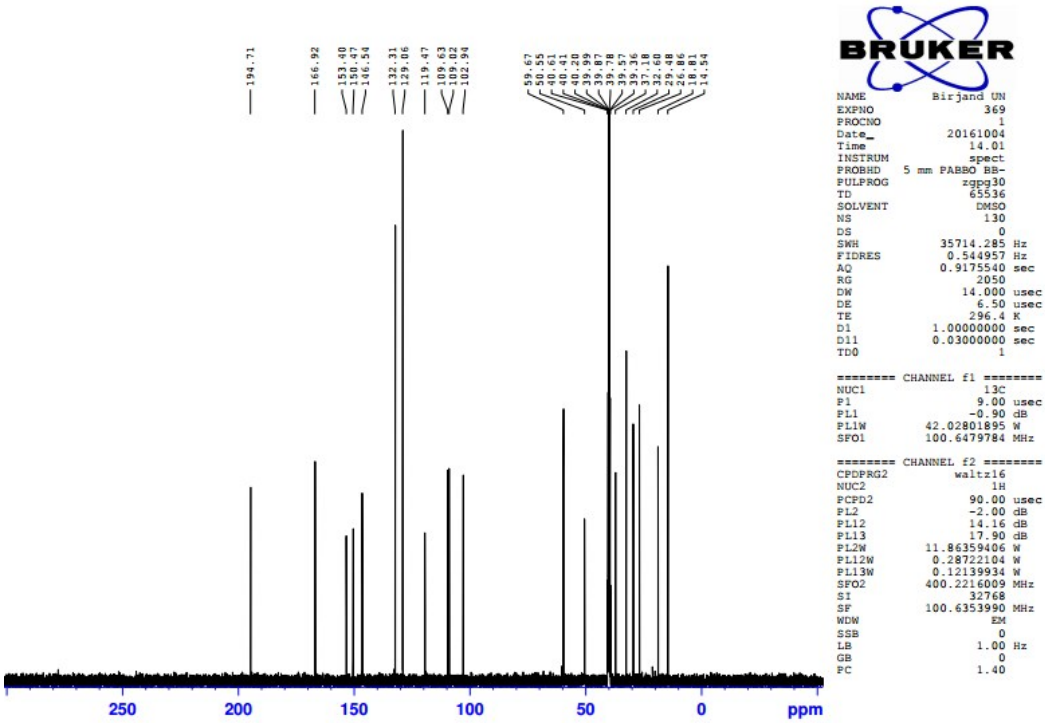
^{13}C NMR spectra of Compound 4e



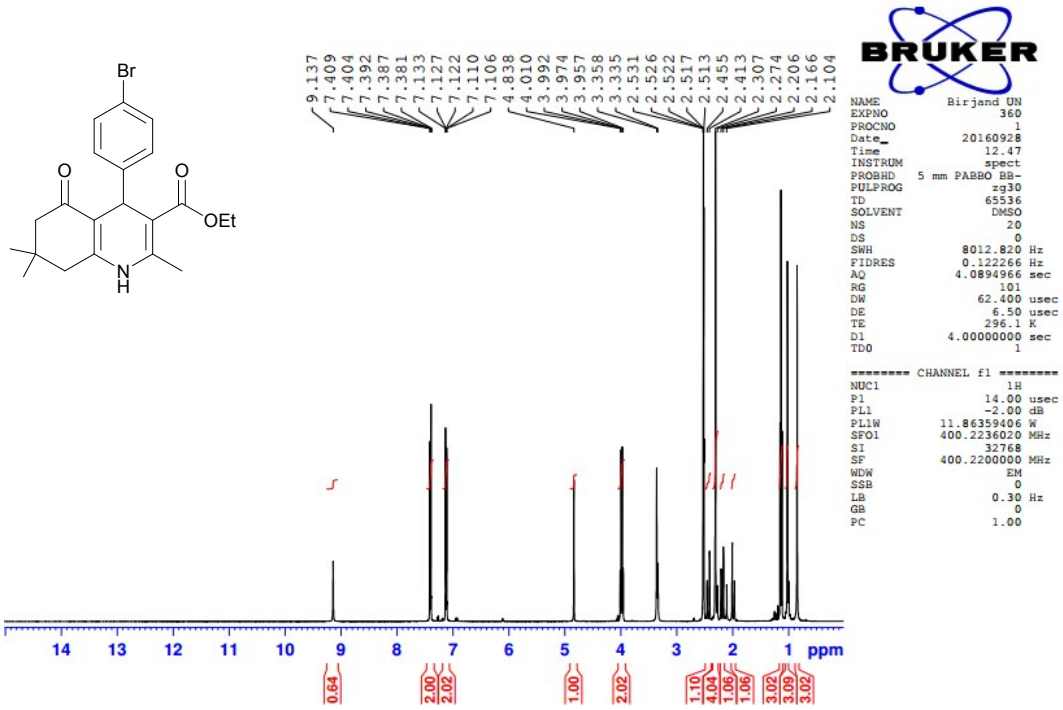
1H NMR spectra of Compound 4f



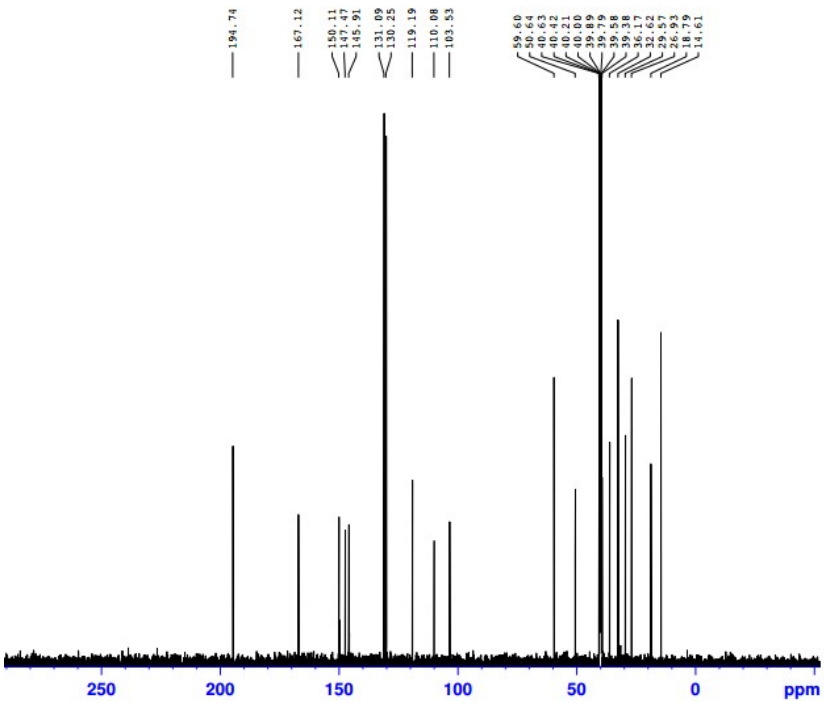
^{13}C NMR spectra of Compound 4f



^{1}H NMR spectra of Compound 4g



^{13}C NMR spectra of Compound 4g



BRUKER

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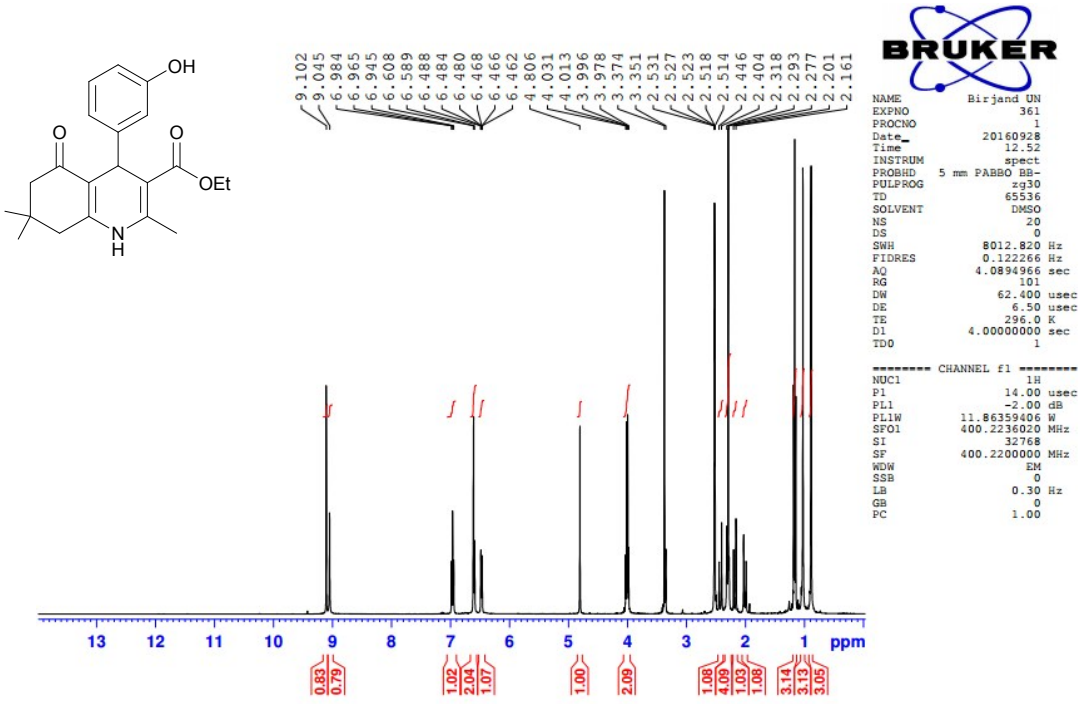
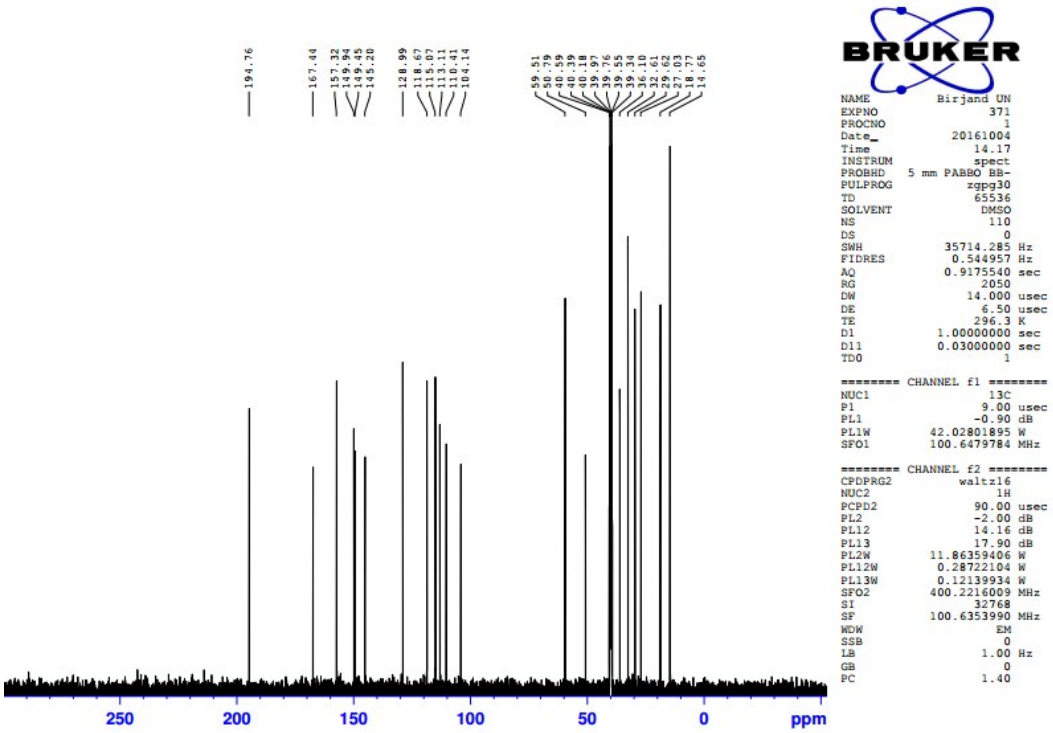
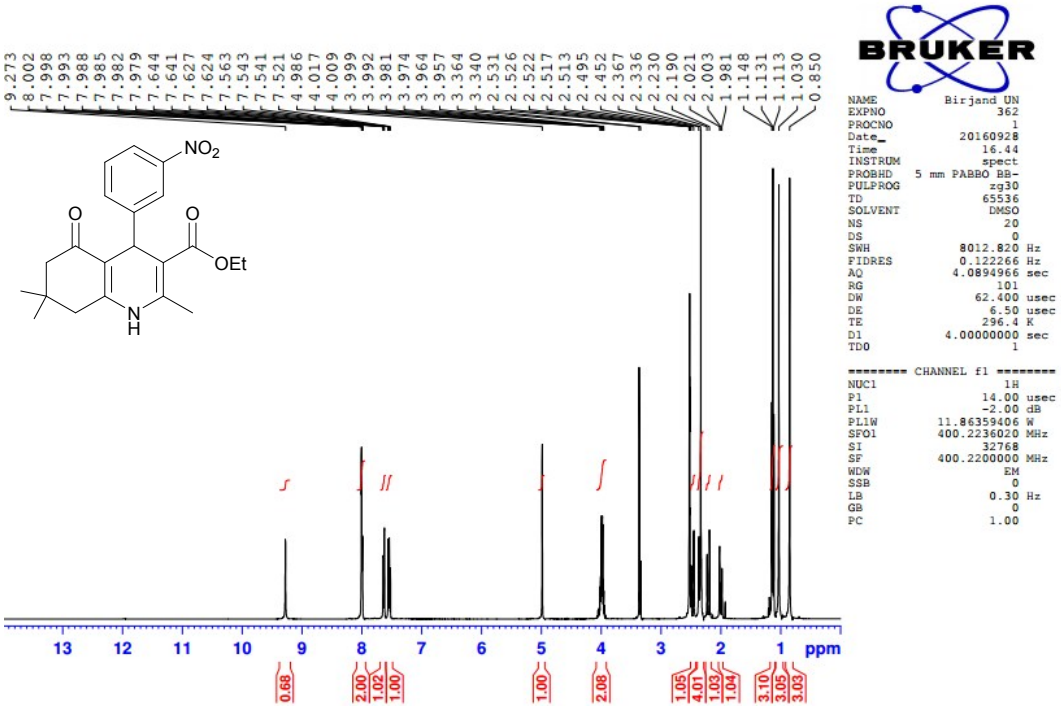
^{1}H NMR spectra of Compound 4h



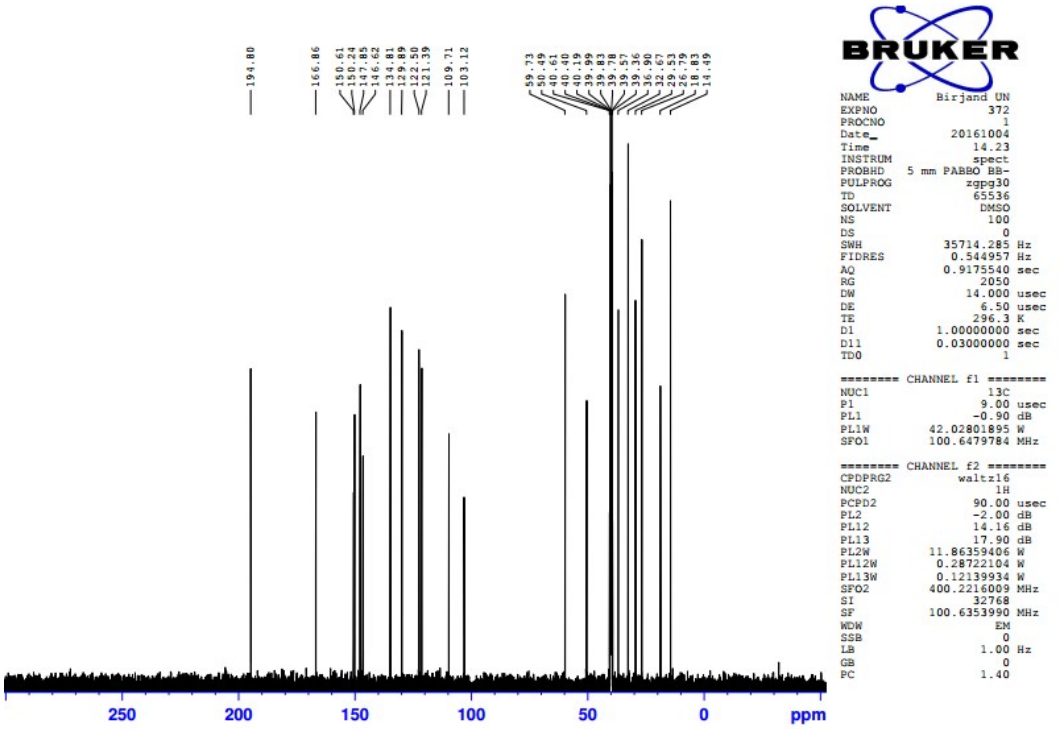
^{13}C NMR spectra of Compound 4h



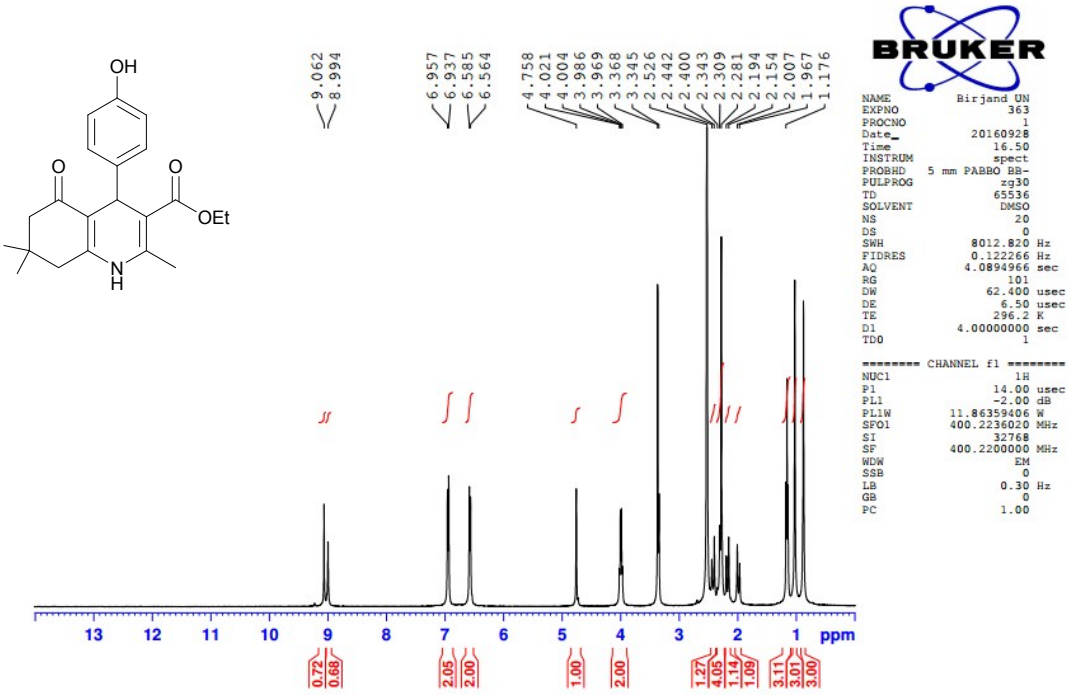
^{1}H NMR spectra of Compound 4i



^{13}C NMR spectra of Compound 4i



^{1}H NMR spectra of Compound 4j



^{13}C NMR spectra of Compound 4j