Appendix. Supporting Information

New o-substituted diphenylphosphinic amides ligands: synthesis, characterization and complexation with Zn^{2+}, Cu^{2+} and Y^{3+}

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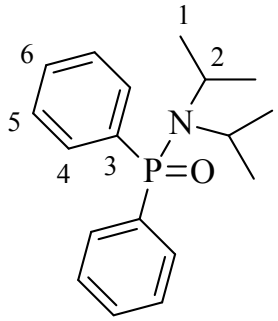
Contents

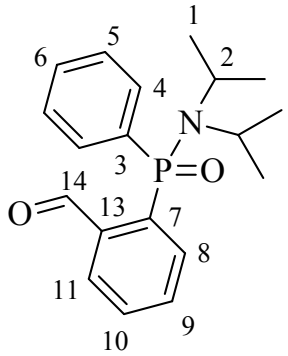
Structural characterization of compounds 1-13

1



White solid. Yield: 80%. Empirical formula: $C_{18}H_{24}NOP$. MW: 301.36 g/mol. Mp: 115 °C. ^{1}H-NMR (499.84 MHz, $CDCl_3$, ppm): δ 1.15 (d, 12 H, $^{3}J_{HH}$ = 6.8 Hz, H-1) 3.39 (dhep, 2H, $^{3}J_{HH}$ = 6.7 Hz and $^{3}J_{PH}$ = 5.9 Hz, H-2), 7.32-7.44 (m, 6H, H-5, H-6), 7.73-7.81 (m, 4 H, H-4). ^{31}P-NMR (202.34 MHz, $CDCl_3$, ppm): δ 30,44. IR: 2970 cm^{-1} (νC-H), 1435 (νP-Ph), 1173 (νP=O), 1021 (νP N-C).

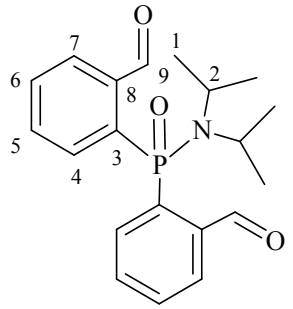
2



White solid. Yield: 88%. Empirical formula: $C_{19}H_{24}NO_2P$. MW: 329.37 g/mol. Mp = 116-117 °C. ^{1}H-NMR (299,95 MHz, $CDCl_3$, ppm): δ 1.31 and 1.22 (2d, 12H, $^{3}J_{HH}$ = 6,0 Hz, H-1), 3.48 (dhep, 2H, $^{3}J_{HH}$ = 6.5 Hz and $^{3}J_{PH}$= 7.5 Hz, H-2), 7.54 to 7.44 (m, 3H), 7.70 to 7.58 (m, 3H), 7.76-7.72 (m, 2H, H-4), 8.11 to 8.09 (m, 1H, H-8), 10.95 (s, 1H,

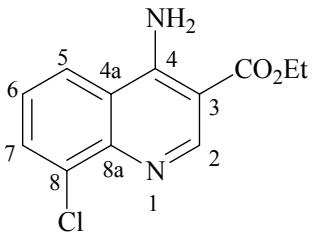
H-13). ^{31}P-NMR (202.34 MHz, $CDCl_3$, ppm): δ 32.49. IR: 2970 cm^{-1} (νC-H), 1689 (νC=O), 1404 (νP-Ph), 1190 (νP=O), 984 (νP N-C).

3



Yellow solid. Yield: 65%. Empirical formula: $C_{20}H_{24}NO_3P$. MW: 357.38 g/mol. Mp = 123 °C. ^{1}H-NMR (299.95 MHz, $CDCl_3$, ppm): δ 1.24 (12H, H-1), 3.45 (2H, H-2), 7.64 to 7.37 (m, 6H, H-5, H-6, H-7), 8.10-8.05 (m, 2H, H-4), 10.94 (s, 2H, H-9). ^{13}C-NMR (75.43 MHz, $CDCl_3$, ppm): δ 23.67 and 23.45 (C-1), 48.28 (C-2), 129.12 (C-4), 132.48 (C-5), 132.72 (C-6), 132.89 (C-7), 136.95 (d, $^1J_{PC}$ = 116.9 Hz, C-3), 139.84 (C-8), 192.49 (C-9). ^{31}P-NMR (121.42 MHz, $CDCl_3$, ppm): δ 34.94. IR: 2969 (νC-H), 1688 (νC=O), 1398 (νP-Ph), 1190 (νP=O), 976 (νP-N-C). HRMS (ESI) *m/z,* calc. for $C_{20}H_{24}NO_3P$: 358.1572 $[M+H]^+$; found: 358.1561.

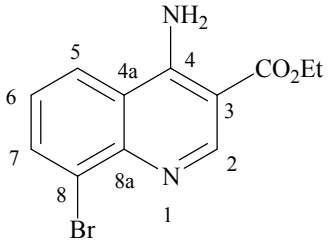
5a



White solid. Yield: 65%. Empirical Formula: $C_{12}H_{11}ClN_2O_2$. MW: 250.68 g/mol. Mp = 291 °C. ^{1}H-NMR (500 MHz, DMSO-d_6, ppm): δ 1.36 (t, 3H, $^3J_{HH}$ = 7.1 Hz, CH_3), 4.35

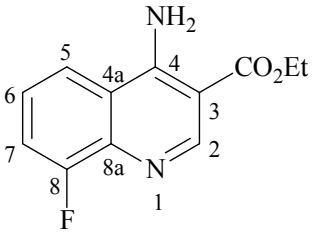
(q, 2H, $^3J_{HH}$ = 7.1 Hz, CH_2), 7.48 (t, 1H, $^3J_{HH}$ = 7.1 Hz, H-6), 7.91 (d, 1H, $^3J_{HH}$ = 6.5 Hz, H-7), 8.36 (d, 1H, $^3J_{HH}$ = 8.4 Hz, H-5), 8.42 (s, 2H, NH_2), 8.98 (s, 1H, H-2). ^{13}C-NMR (125.69 MHz, DMSO-d_6, ppm): δ 14.61 (CH_3), 61.09 (CH_2), 100.89 (C-3), 120.12 (C-4a), 122.77 (C-5), 125.84 (C-6), 132.22 (C-7), 132.98 (C-4), 145.16 (C-8), 152.30 (C-2), 154.73 (C-8a), 167.74 (C=O). IR: 3374 (νN-H), 3159 (νC-H), 1687 (νC=O), 753 (νC-Cl).

5b



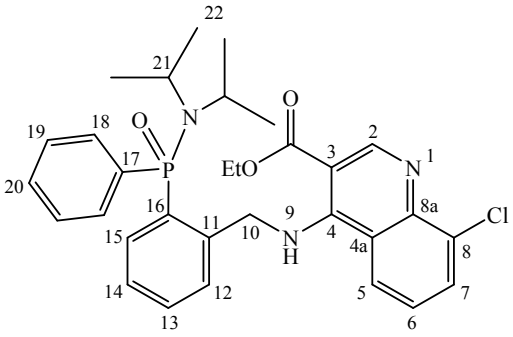
White solid. Yield: 62%. Empirical Formula: $C_{12}H_{11}BrN_2O_2$. MW: 295.13 g/mol. Mp = 265 °C. ^{1}H-NMR (500 MHz, DMSO-d_6, ppm): δ 1.36 (t, 3H, $^3J_{HH}$ = 7.1 Hz, CH_3), 4.36 (q, 2H, $^3J_{HH}$ = 7.1 Hz, CH_2), 7.41 (t, 1H, $^3J_{HH}$ = 7.1 Hz, H-6), 8.10 (d, 1H, $^3J_{HH}$ = 10.0 Hz, H-7), 8.37 (s, 2H, NH_2), 8.39 (m, 1H, H-5), 8.98 (s, 1H, H-2). ^{13}C-NMR (125.69 MHz, DMSO-d_6, ppm): δ 14.46 (CH_3), 62.34 (CH_2), 101.13 (C-3), 101.37 (C-4), 119.23 (C-8), 125.08 (C-5), 128.05 (C-6), 138.16 (C-7), 148.24 (C-2), 165.83 (C=O). IR: 3368 (νN-H), 3139 (νC-H), 1688 (νC=O), 558 (νC-Br).

5c



White solid. Yield: 70%. Empirical Formula: $C_{12}H_{11}FN_2O_2$. MW: 234.23 g/mol. Mp = 289 °C. ^{1}H-NMR (300 MHz, DMSO-d_6, ppm): δ 1.28 (t, 3H, $^3J_{HH}$ = 7.1 Hz, CH_3), 4.22 (q, 2H, $^3J_{HH}$ = 7.1 Hz, CH_2), 7.25 (1H, H-6), 7.37 (1H, H-7), 8.22 (m, 1H, H-5), 8.55 (s, 1H, H-2). ^{13}C-NMR (75.43 MHz, DMSO-d_6, ppm): δ 14.11 (CH_3), 59.47 (CH_2), 104.04 (C-6), 110.33 (C-4), 113.00 (C-7), 124.10 (C-8), 128.81 (C-5), 140.38 (C-8a), 145.19 (C-2), 162.27 (C-4a), 164.44 (C-3), 165.58 (C=O). IR: 3106 (νN-H), 2988 (νC-H), 1692 (νC=O), 1194 (νC-F).

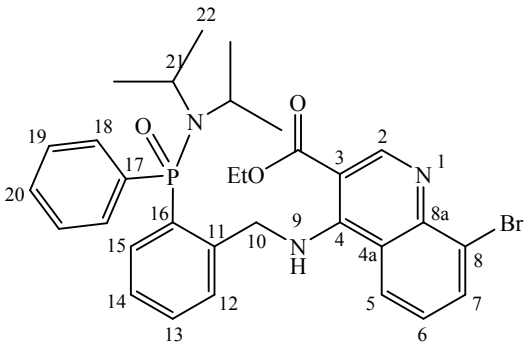
6a



White solid. Yield: 62%. Empirical formula: $C_{31}H_{35}ClN_3O_3P$. MW: 564.05 g/mol. Mp = 211 °C. ^{1}H-NMR (499.84 MHz, $CDCl_3$, ppm): δ 1.15 and 1.22 (12H, H-22), 1.36 (t, 3H, $^3J_{HH}$ = 7.1 Hz, $OCH_2\underline{CH_3}$), 3.45 (2H, H-21), 4.35 (q, 2H, $^3J_{HH}$ = 7.1 Hz, $O\underline{CH_2}$), 4.45 (d, 1H, $^2J_{HH}$ = 9.9 Hz, H-10), 4.71 (d, 1H, $^2J_{HH}$ = 9.9 Hz, H-10'), 6.05 (s, 1H, H-9), 7.23-7.27 (m, 1H, H-6), 7.31-7.46 (m, 7H), 7.66-7.78 (m, 4H), 9.17 (s, 1H, H-2). ^{13}C-NMR (125.69 MHz, $CDCl_3$, ppm): δ 14.61 (s, $OCH_2\underline{CH_3}$), 23.41-23.43 (C-22), 47.63 (d, $^2J_{PC}$

= 5.0 Hz, C-21), 60.80 (O<u>CH$_2$</u>CH$_3$), 64.69 (d, $^3J_{PC}$ = 5.0 Hz, C-10), 101.68 (C-3), 119.44 (C-4a), 119.84 (C-5), 125.06 (C-6), 126.96 (d, $^3J_{PC}$ = 12.5 Hz, C-19 or C-14), 128.24 (d, $^3J_{PC}$ = 12.5 Hz, C-19 or C-14), 131.46 (C-13), 131.63 (C-18 or C-15), 131.68 (C-18 or C-15), 132,14, 132.22, 133.46, (C-17 or C-16), 133.47 (C-17 or C-16), 134.50, 152.43 (C-2), 153.74 (C-8), 167.99 (C=O). ^{31}P-NMR (202.34 MHz, $CDCl_3$, ppm): δ 35.77. IR: 3378 (νNH), 3165 (νCH), 1687 (νC=O), 1626 (νC=N), 1495 (νP-Ph), 1254 (νC-O), 1167 (νP=O), 781 (νC-Cl).

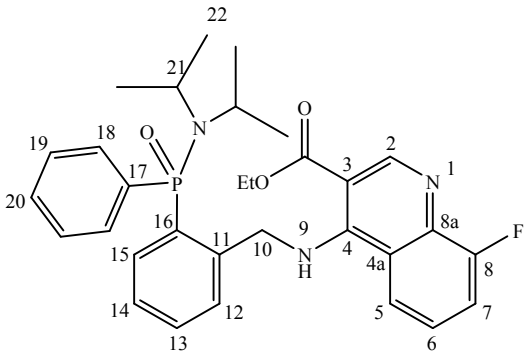
6b



White solid. Yield: 59%. Empirical formula: $C_{31}H_{35}BrN_3O_3P$. MW: 608.51 g/mol. Mp = 249 °C. ^{1}H-NMR (499.84 MHz, DMSO-d_6, ppm): δ 1.12 and 1.22 (12H, H-22), 1.36 (t, 3H, $^3J_{HH}$ = 7.1 Hz, OCH$_2$<u>CH$_3$</u>), 3.45 (2H, H-21), 4.36 (q, 2H, $^3J_{HH}$ = 7.1 Hz, O<u>CH$_2$</u>), 4.61 (d, 1H, $^2J_{HH}$ = 9.9 Hz, H-10), 4.63 (d, 1H, $^2J_{HH}$ = 9.9 Hz, H-10'), 5.52 (1H, H-9), 7.40-7.66 (m, 9H), 8,10 (H-7 or H-5), 8.11 (H-7 or H-5), 8.40 to 8.43 (m, 2H), 8.98 (s, 1H, H-2). ^{13}C-NMR (125.69 MHz, DMSO-d_6, ppm): δ 14.32 (OCH$_2$<u>CH$_3$</u>), 23.09 and 23.14 (C-22), 46.97 (C-21), 60.67 (O<u>CH$_2$</u>CH$_3$), 61.95 (d, $^3J_{PC}$ = 5.0 Hz, C-10), 100.57 (C-3), 119.82 (C-4a), 123.30 (C-5), 124.53 (C-4), 125.96 (C-6), 126.58 (d, $^2J_{PC}$ = 12.5 Hz, C-18), 128.56 (d, $^2J_{PC}$ = 11.3 Hz, C-15), 128.85 (C-12), 130.92 (C-11), 131.62 (C-19 or C-14), 131.79 (C-19 or C-14), 132.03 (C-18 or C-15), 132.66 (C-18 or C-15), 134.91 (d, $^1J_{PC}$ = 120.6 Hz, C-17 or C-16), 135.32 (C-7), 146.27 (d, $^1J_{PC}$ = 118.1 Hz, C-

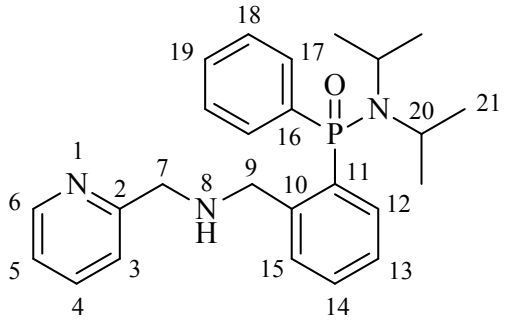
17 or C-16), 152.19 (C-2), 154.43 (C-8), 167.41 (C=O). ^{31}P-NMR (202.34 MHz, DMSO-d_6, ppm): δ 34.18. IR: 3370 (νNH), 2961 (νCH), 1687 (νC=O), 1628 (νC=N), 1442 (νP-Ph), 1258 (νC-O), 1175 (νP=O), 980 (νP-N-C), 760 (νC-Br).

6c



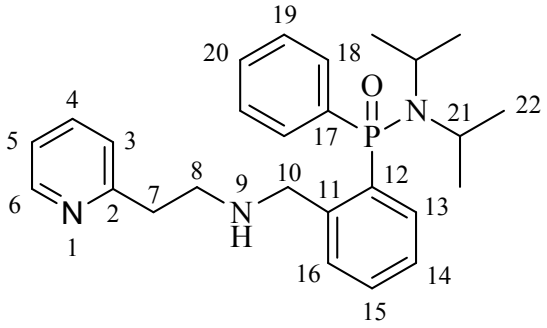
White solid. Yield: 69%. Empirical formula: $C_{31}H_{35}FN_3O_3P$. MW: 547.60 g/mol. Mp = 228 °C. ^{1}H-NMR (499.84 MHz, DMSO-d_6, ppm): δ 1.16 and 1.22 (12H, $^3J_{HH}$ = 4.9 Hz, H-22), 1.55 (m, 3H, $OCH_2\underline{CH_3}$) 3.44 (2H, $^3J_{HH}$ = 4.9 Hz and $^3J_{PH}$ = 9.9 Hz, H-21), 4.05 (q, 2H, $^3J_{HH}$ = 7.1 Hz, $O\underline{CH_2}$), 4.45 (d, 1H, $^2J_{HH}$ = 9.9 Hz, H-10), 4.71 (d, 1H, $^2J_{HH}$ = 9.9 Hz, H-10'), 6.05 (1H, H-9), 6.72 (H-5), 7.02 (m, 1H, H-7), 7.23-7.27 (m, 1H, H-6), 7.33-7.46 (m, 6H), 7.55 (m, 1H), 7.66-7.70 (m, 2H), 8.29 (s, 1H, H-2). ^{13}C-NMR (125.69 MHz, DMSO-d_6, ppm): δ 14.47 ($OCH_2\underline{CH_3}$), 23.18 and 23.21 (C-22), 47.08 (C-21), 60.12 ($O\underline{CH_2}CH_3$), 62.01 (d, $^3J_{PC}$ = 3.8 Hz, C-10), 126.68 (d, $^2J_{PC}$ = 12.6 Hz, C-18), 128.65 (d, $^2J_{PC}$ = 12.6 Hz, C-15), 128.93 (d, $^3J_{PC}$ = 11.3 Hz, C-12), 130.94 (C-11), 131.72 (C-19 or C-14), 131.90 (C-19 or C-14), 132.14 (C-6), 132.77 (d, $^2J_{FC}$ = 11.3 Hz, C-7), 134.91 (d, $^1J_{PC}$ = 122.2 Hz, C-17 or C-16), 146,73 (C-8), 162.02 (C=O). ^{31}P-NMR (202.34 MHz, DMSO-d_6, ppm): δ 34.20. IR: 3380 (νNH), 2960 (νCH), 1683 (νC=O), 1627 (νC=N), 1435 (νP-Ph), 1180 (νP=O), 980 (νP-N-C), 1181 (νCF).

8a



Yellow oil. Yield: 71%. Empirical formula: $C_{25}H_{32}N_3OP$. MW: 421.51 g/mol. ^{1}H-NMR (499.84 MHz, $CDCl_3$, ppm): δ 1.15 and 1.22 (H-21), 3.44 (2H, H-20), 3.78-4.07 (m, 2H, H-7), 4.45 (d, 1H, $^2J_{HH}$ = 9.9 Hz, H-9), 4.71 (d, 1H, $^2J_{HH}$ = 9.9 Hz, H-9'), 5.73 (1H, H-8), 7.23-7.27 (m, 1H, H-4), 7.33-7.46 (m, 6H), 7.48-7.64 (m, 1H), 7.64-7.70 (m, 2H, H-17), 7.74-7.86 (m, 1H), 8.01-8.04 (m, 1H, H-6). ^{31}P-NMR (202.34 MHz, $CDCl_3$, ppm): δ 33.69. IR: 3298 (νN-H), 2968 (νC-H), 1591 (νC=N), 1435 (νP -Ph), 1176 (νP=O), 978 (νP-N-C).

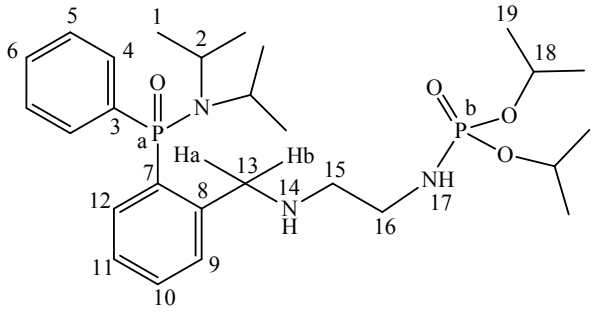
8b



Yellow oil. Yield: 69%. Empirical formula: $C_{26}H_{34}N_3OP$. MW: 435.54 g/mol. ^{1}H-NMR (499.84 MHz, $CDCl_3$, ppm): δ 1.10 and 1.22 (2d, 12H, H-22), 2.82-2.92 (m, 4H, H-7, H-8), 3.38 (2H, H-21), 3.79 (d, 1H, $^2J_{HH}$ = 14.9 Hz, H-10), 4.03 (d, 1H, $^2J_{HH}$ = 14.9 Hz, H-10'), 7.00 (1H, H-5), 7.08 (d, 1H, $^3J_{HH}$ = 9.9 Hz, H-3), 7.19-7.22 (m, 1H, H-4), 7.50-7.31 (m, 6H), 7.62 (d, 2H, $^3J_{HH}$ = 9.9 Hz, H-18), 8.41 (d, 1H, $^3J_{HH}$ = 9.9 Hz, H-6). ^{31}P-

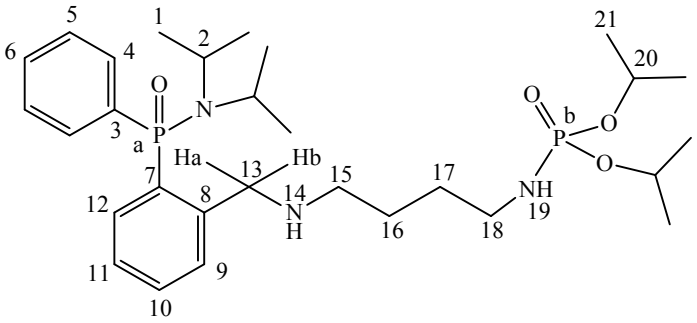
NMR (202.34 MHz, $CDCl_3$, ppm): δ 34.20. IR: 3298 (νN-H), 2968 (νC-H), 1591 (νC=N), 1435 (νP -Ph), 1176 (νP=O), 978 (νP-N-C).

11a



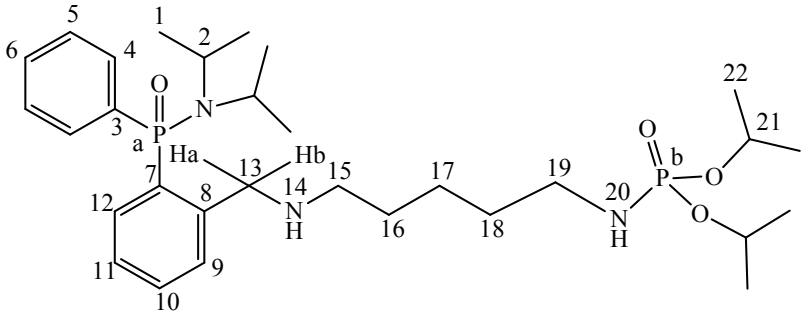
Yellow oil. Yield: 68%. Empirical formula: $C_{27}H_{45}N_3O_4P_2$ MW: 537.61 g/mol. ^{1}H-NMR (299.95 MHz, $CDCl_3$, ppm): δ 1.21-1.31 (m, 24H, H-1, H-19), 2.51 (1H, H-14), 2.64 (m, 2H, H-15), 2.89-3.03 (m, 2H, H-16), 3.46 (dhep, 2H, $^3J_{HH}$ = 5.9 Hz, $^3J_{PH}$ = 8.9 Hz, H-2), 3.70 (d, 1H, $^2J_{HH}$ = 11.9 Hz, H-13b), 3.91 (d, 1H, $^2J_{HH}$ = 11.9 Hz, H-13a), 4.48-4.62 (m, 2H, H-18), 6.12 (1H, H-17), 7.36-7.53 (m, 7H, H-5, H-6, H-9, H-10, H-11), 7.63-7.77 (m, 3H, H-4, H-12). ^{31}P-NMR (121.42 MHz, $CDCl_3$, ppm): δ 8.83 (Pb), 34.29 (Pa). IR: 3361 and 3254 (νN-H), 2978 (νC-H), 1214 (νP=O phosphoramidate), 1178 (νP=O phosphinic amide) 979 (νP-O).

11b



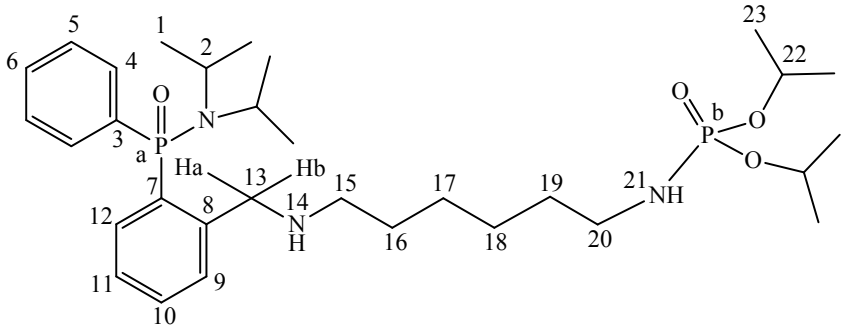
Yellow oil. Yield: 65%.Empirical formula: $C_{29}H_{49}N_3O_4P_2$ MW: 565.66 g/mol. ^{1}H-NMR (499.84 MHz, $CDCl_3$, ppm): δ 1.15-1.25 (m, 24H, H-1, H-21), 1.44 (m, 4H, H-16, H-17), 2.48 (m, 2H, H-15), 2.79 (m, 2H, H-18), 3.17 (1H, H-14), 3.41 (2H, H-2), 3.68 (d, 1H, $^2J_{HH}$ = 14.9 Hz, H-13b), 4.02 (d, 1H, $^2J_{HH}$ = 14.9 Hz, H-13a), 4.43-4.54 (m, 2H, H-20), 7.33-7.47 (m, 7H, H-5, H-6, H-9, H-10, H-11, H-12), 7.61-7.69 (m, 2H, H-4). ^{13}C-NMR (125.69 MHz,$CDCl_3$, ppm): δ 23.23 (d, $^3J_{PC}$ = 8.8 Hz, C-1), 23.64 (d, $^3J_{PC}$ = 8.8 Hz, C-21), 26.40 (C-16), 29.13 (d, $^3J_{PC}$ = 11.3 Hz, C-17), 41.05 (C-18), 47.28 (d, $^2J_{PC}$ = 7.5 Hz, C-2) 48.17 (C-15), 52.15 (d, $^3J_{PC}$ = 6.3 Hz, C-13), 70.27 (d, $^2J_{PC}$ = 8.8 Hz, C-20), 126.51, 128.05 (C-5), 131.69, 131.99 (C-4), 132.88 (C-9), 133.67 (d, $^1J_{PC}$ = 109.3 Hz, C-3), 135.31 (d, $^1J_{PC}$ = 101.8 Hz, C-7). ^{31}P-NMR (202.34 MHz, $CDCl_3$, ppm): δ 8.11 (Pb), 34.46 (Pa). IR: 3340 and 3227 (νN-H), 2976 (νC-H), 1228 (νP=O phosphoramidate), 1176 (νP=O phosphinic amide) 976 (νP-O). HRMS (ESI) *m/z,* calc. for $C_{29}H_{49}N_3O_4P_2$: 566.3263 $[M+H]^+$; found: 566.3276.

11c



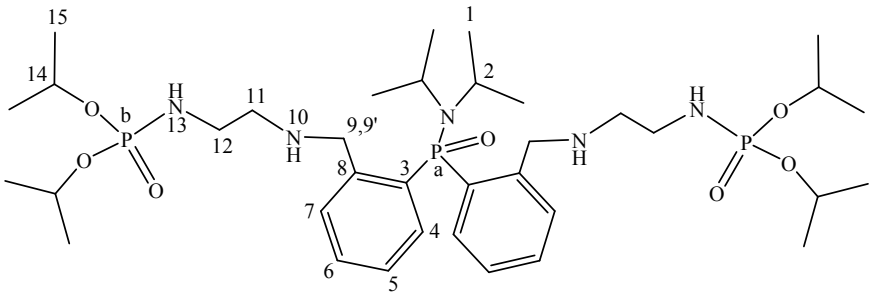
Yellow oil. Yield: 68%. Empirical formula: $C_{30}H_{51}N_3O_4P_2$ MW: 579.69 g/mol. ^{1}H-NMR (499.84 MHz, $CDCl_3$, ppm): δ 0.82 (m, 2H, H-17), 1.11-1.25 (m, 24H, H-1, H-22), 1.34-1.48 (m, 4H, H-16, H-18), 2.47 (H-15), 2.75-2.84 (m, 2H, H-19), 3.35-3.45 (m, 3H, H-2, H-14), 3.70 (d, 1H, $^2J_{HH}$ = 14.9 Hz, H-13b), 4.04 (d, 1H, $^2J_{HH}$ = 14.9 Hz, H-13a), 4.45-4.54 (m, 2H, H-21), 7.36-7.47 (m, 7H, H-5 H-6, H-9, H-10, H-11, H-12), 7.60-7.65 (m, 2H, H-4). ^{13}C-NMR (125.69 MHz, $CDCl_3$, ppm,): δ 23.25 (C-1), 23.67 (C-22), 24.09 (C-17), 28.75 (C-16), 31.24 (C-18), 41.20 (C-19), 47.34 (C-2), 48.50 (C-15), 52.23 (d, $^3J_{PC}$ = 5.0 Hz, C-13), 70.36 (d, $^2J_{PC}$ = 6.3 Hz, C-21), 126.63, 128.10 (C-5), 131.36, 131.73 (C-4), 132.92 (C-9), 132.55 (d, $^1J_{PC}$ = 123.2 Hz, C-3), 134.72 (d, $^1J_{PC}$ = 121.9 Hz, C-7), 134.88 (C-8). ^{31}P-NMR (202.34 MHz, $CDCl_3$, ppm): δ 7.66 (Pb) and 34.82 (Pa). IR: 3371 and 3203 (νN-H), 2927 (νC-H), 1205 (νP=O phosphoramidate), 1177 (νP=O phosphinic amide) 978 (νP-O). HRMS (ESI) *m/z,* calc. for $C_{30}H_{51}N_3O_4P_2$: 580.3433 $[M+H]^+$; found: 580.3428.

11d



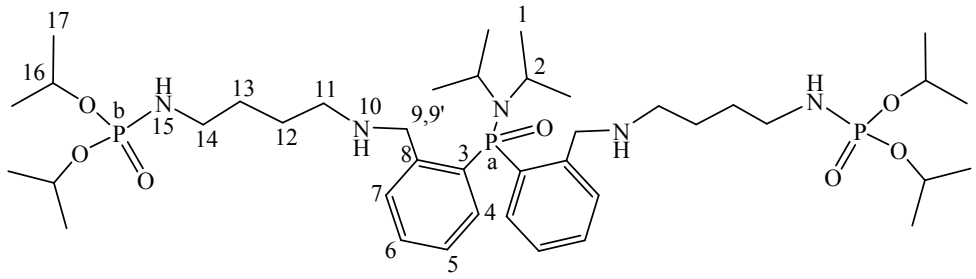
Yellow oil. Yield: 69%. Empirical formula: $C_{31}H_{53}N_3O_4P_2$ MW: 593.72 g/mol. ^{1}H-NMR (299.95 MHz, $CDCl_3$, ppm): δ 1.11-1.13 (m, 4H, H-17, H-18), 1.23-1.25 (m, 24H, H-1, H-23), 1.33-1.43 (m, 4H, H-16, H-19), 2.32-2.44 (m, 3H, H-14, H-15), 2,76-2.84 (m, 2H, H-20), 3.33-3.48 (m, 2H, H-2), 3.69 (d, 1H, $^2J_{HH}$ = 11,9 Hz, H-13b), 4.03 (d, 1H, $^2J_{HH}$ = 11,9 Hz, H-13a), 4.46-4.57 (m, 2H, H-22), 7.34-7.49 (m, 7H, H-5, H-6, H-9, H-10, H 11, H-12), 7.61-7.68 (m, 2H, H-4). ^{13}C-NMR (75.43 MHz, $CDCl_3$, ppm): δ 23.13 (C-1), 23.57 (C-23), 26.17 (C-18), 26.58 (C-17), 28.88 (C-16), 31.27 ($^3J_{PC}$ = 6.8 Hz, C-19), 41.13 (C-20), 47.22 (C-2), 48.38 (C-15), 51.99 (d, $^3J_{PC}$ = 3.8 Hz, C-13), 70.25 (d, $^2J_{PC}$ = 6.0 Hz, C-22), 126.54, 127.99 (C-5), 131.26, 131.60 (C-4), 132.50 (C-9), 132.83, 134.70 (d, $^1J_{PC}$ = 121.4 Hz, C-3), 132.21 (d, $^1J_{PC}$ = 123.7 Hz, C-7), 142.54 (C-8). ^{31}P-NMR (121.42 MHz, $CDCl_3$, ppm): δ 7.66 (Pb), 34.87 (Pa). IR: 3405 and 3251 (νN-H), 2931 (νC-H), 1205 (νP=O phosphoramidate), 1176 (νP=O phosphinic amide) 976 (νP-O). HRMS (ESI) *m/z,* calc. for $C_{31}H_{53}N_3O_4P_2$: 594.3589 $[M+H]^+$; found: 594.3584.

13a



Yellow oil. Yield: 68%. Empirical formula: $C_{36}H_{66}N_5O_7P_3$ MW: 773.85 g/mol. ^{1}H-NMR (299.95 MHz, $CDCl_3$, ppm): δ 0.84 (m, 4H, H-12), 1.12-1.22 (m, 36H, H-1, H-15), 1.49-1.98(m, 4H, H-11), 2.73-2.79 (2H, H-10), 3.42-3.51 (m, 2H, H-9/9'), 3.64 (1H, H-9), 3.92 (1H, H-9'), 4.38 (dhep, 4H, $^3J_{HH}$ = 5.9, $^3J_{PH}$ = 8.9 Hz, H-14), 4.70-4.79 (2H, H-13), 7.51-7.80 (m, 8H, H-4, H-5, H-6, H-7). ^{13}C-NMR (75.43 MHz, $CDCl_3$, ppm): δ 23.69 (C-15), 29.36 (C-1), 39.33 (C-11), 42.59 (d, $^3J_{PC}$ = 5.3 Hz, C-9), 47.73 (d, $^2J_{PC}$ = 5.3 Hz, C-12), 70.76 (d, $^2J_{PC}$ = 5.3 Hz, C-14), 70,43 (C-2), 127.21-133,54 (C-3, C-4, C-5, C-6, C-7, C-8). ^{31}P-NMR (121.42 MHz, $CDCl_3$, ppm): δ 8.62 (2P, Pb), 28.90 (1P, Pa). IR: 3386 and 3233 (νN-H), 2976 (νC-H), 1205 (νP=O phosphoramidate), 1177 (νP=O phosphinic amide) 979 (νP-O).

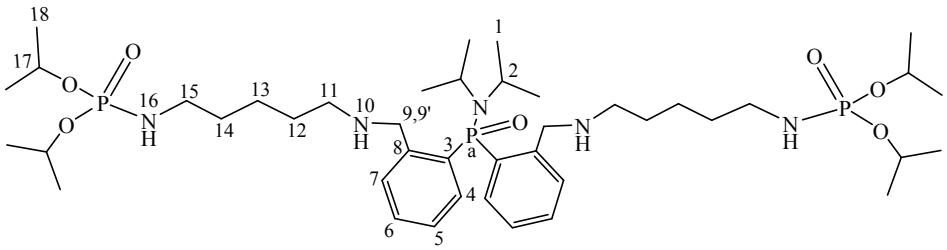
13b



Yellow oil. Yield: 58%. Empirical formula: $C_{40}H_{74}N_5O_7P_3$ MW: 829.96 g/mol. ^{1}H-NMR (299.95 MHz, $CDCl_3$, ppm): δ 1.14-1.27 (m, 36H, H-1, H-17), 1.41-1.49 (m, 4H, H-13), 2.43-2.57 (m, 4H, H-12), 2.72-2.87 (m, 4H, H-14), 3.13-3.22 (2H, H-10), 3.39

(dhep, 2H, $^{3}J_{HH}$ = 5.9 Hz, $^{3}J_{PH}$ = 8.9 Hz, H-2), 3.70 (d, 2H, $^{2}J_{HH}$ = 14.9 Hz, H-9/9'), 4.09 (d, 2H, $^{2}J_{HH}$ = 14.9 Hz, H-9/9'), 4.49 (4H, H-16), 7.19-7.20 (m, 2H, H-6), 7.23 (m, 4H, H-4, H-5), 7.73-7.80 (m, 1H, H-7). ^{13}C-NMR (75.43 MHz, $CDCl_3$, ppm): δ 22.82 and 22.88 (C-17), 25.64 (C-12), 28.38 (C-1), 40.21 (C-13), 46.07 (d, $^{3}J_{PC}$ = 4.5 Hz, C-9), 46.67 (d, $^{2}J_{PC}$ = 5.3 Hz, C-14), 47.23 (C-11), 69.39 (d, $^{2}J_{PC}$ = 5.3 Hz, C-2), 69.64 (d, $^{2}J_{PC}$ = 5.3 Hz, C-16), 125.62-132.90 (C-3, C-4, C-5, C-6, C-7, C-8). ^{31}P-NMR (121.42 MHz, $CDCl_3$, ppm): δ 8.23 (2P, Pb), 38.84 (1P, Pa). IR: 3409 and 3265 (νN-H), 2918 (νC-H), 1229 (νP=O phosphoramidate), 1179 (νP=O phosphinic amide), 979 (νP-O). HRMS (ESI) *m/z,* calc. for $C_{40}H_{74}N_5O_7P_3$: 830.4879 $[M+H]^+$; found: 830.4883.

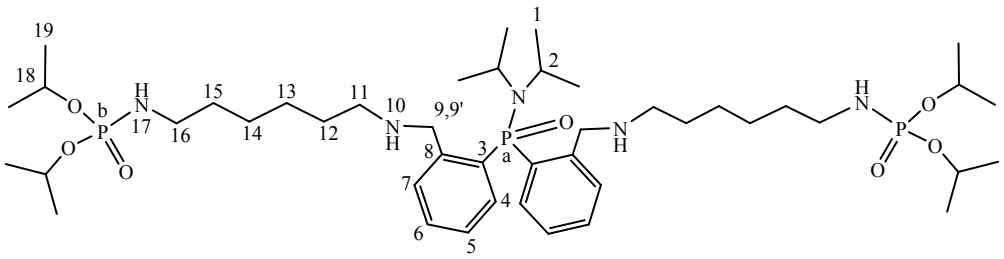
13c



Yellow oil. Yield: 62%. Empirical formula: $C_{42}H_{78}N_5O_7P_3$ MW: 858,01 g/mol. ^{1}H-NMR (499.84 MHz, $CDCl_3$, ppm): δ 1.12-1.26 (m, 36H, H-1, H-18), 1.30-1.61 (m, 12H, H-12, H-13, H-14), 2.41-2.55 (m, 4H, H-11), 2.74-2.84 (m, 4H, H-15), 3.35-3.43 (m, 2H, H-2), 3.72 (d, 2H, $^{2}J_{HH}$ = 14.9 Hz, H-9/9'), 4.10 (d, 2H, $^{2}J_{HH}$ = 14.9 Hz, H-9/9'), 4.43-4.56 (m, 4H, H-17), 7.20 (m, 2H, H-6), 7.34-7.76 (m, 6H, H-4, H-5, H-7). ^{13}C-NMR (125.69 MHz, $CDCl_3$, ppm): δ 15.08 (C-13), 23.66 and 23.67 (C-18), 24.17 (C-13), 28.91 (C-12), 31.18 (d, $^{3}J_{PC}$ = 6.3 Hz, C-14), 41.15 (d, $^{3}J_{PC}$ = 1.3 Hz, C-9), 47.54 (C-11), 48.50 (C-15), 70.26 (d, $^{2}J_{PC}$ = 5.0 Hz, C-2), 70.41 (d, $^{2}J_{PC}$ = 5.0 Hz, C-17), 126.60-133,33 (C-3, C-4, C-5, C-6, C-7, C-8). ^{31}P-NMR (202.34 MHz, $CDCl_3$, ppm): δ 8.15 (2P, Pb), 38.62 (1P, Pa). IR: 3420 and 3251 (νN-H), 2930 (νC-H), 1205 (νP=O

phosphoramidate), 1177 (νP=O phosphinic amide), 978 (νP-O). HRMS (ESI) *m/z,* calc. for $C_{42}H_{78}N_5O_7P_3$: 858.5192 $[M+H]^+$; found: 858.5159.

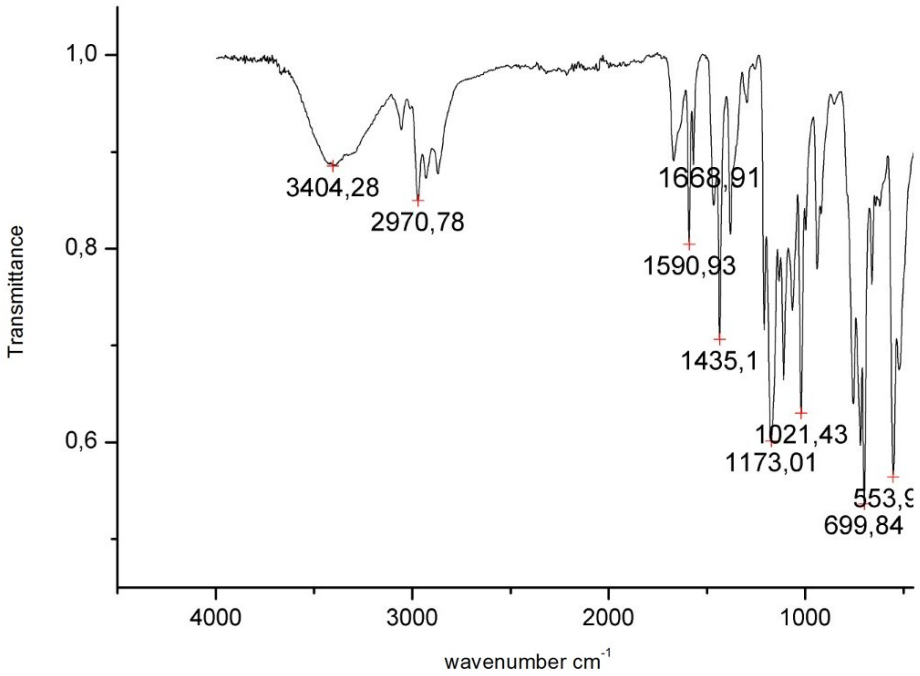
13d



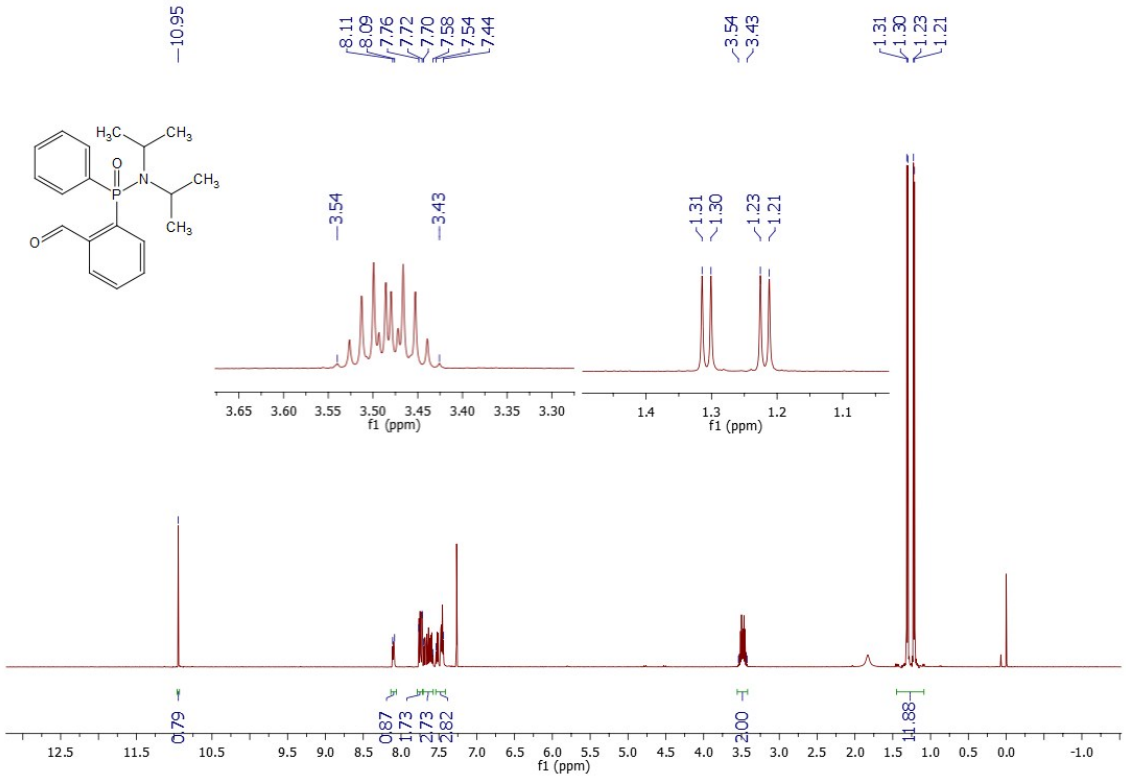
Yellow. Yield: 69%. Empirical formula: $C_{44}H_{82}N_5O_7P_3$ MW: 886.07 g/mol. ^{1}H-NMR (299.95 MHz, $CDCl_3$, ppm): δ 0.91-1.12 (m, 4H, H-14), 1.14-1.27 (m, 36H, H-1, H-19), 1.28-1.61 (m, 8H, H-12, H-13), 2.51 (m, 4H, H-15 or H-16), 2.72-2.85 (m, 4H, H-11), 3.32-3.46 (m, 2H, H-2), 3.73 (d, 2H, $^2J_{HH}$= 11.9 Hz, H-9/9'), 4.10 (d, 2H, $^2J_{HH}$ = 11.9 Hz, H-9,9'), 4.45-4.57 (m, 4H, H-18), 7.19 (m, 2H, H-6), 7.24-7.77 (m, 6H, H-4, H-5, H-7). ^{13}C-NMR (75.43 MHz, $CDCl_3$, ppm): δ 23.45-23.68 (C-19), 26.17 (C-14), 26.79 (C-13), 31.48 (d, $^3J_{PC}$ = 6,8 Hz, C-15), 41.23 (C-12), 47.55 (C-11), 48.67 (C-16), 51.97 (d, $^3J_{PC}$ = 4.5 Hz, C-9), 70.33 (d, $^2J_{PC}$ = 5.3 Hz, C-2), 70.41 (d, $^2J_{PC}$ = 6.0 Hz, C-18), 126.66-133.59 (C-3, C-4, C-5, C-6, C-7, C-8). ^{31}P-NMR (121.42 MHz, $CDCl_3$, ppm): δ 4.75 (2P, Pb), 5.76 (1P, Pa). IR: 3409 and 3244 (νN-H), 2928 (νC-H), 1205 (νP=O phosphoramidate), 1182 (νP=O phosphinic amide), 979 (νP-O). HRMS (ESI) *m/z,* calc. for $C_{44}H_{82}N_5O_7P_3$: 886.5505 $[M+H]^+$; found: 886.5535.

^{1}H NMR,^{13}C NMR, ^{31}P NMR, IR and HRMS (ESI) spectra

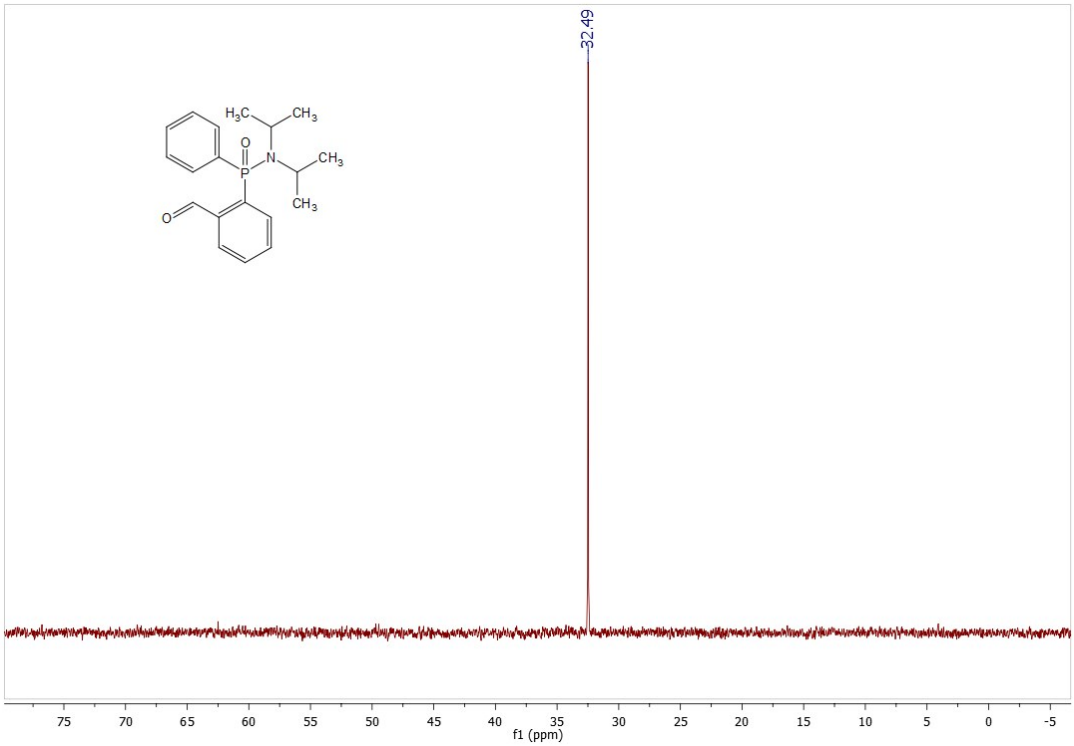
IR spectrum of **1**



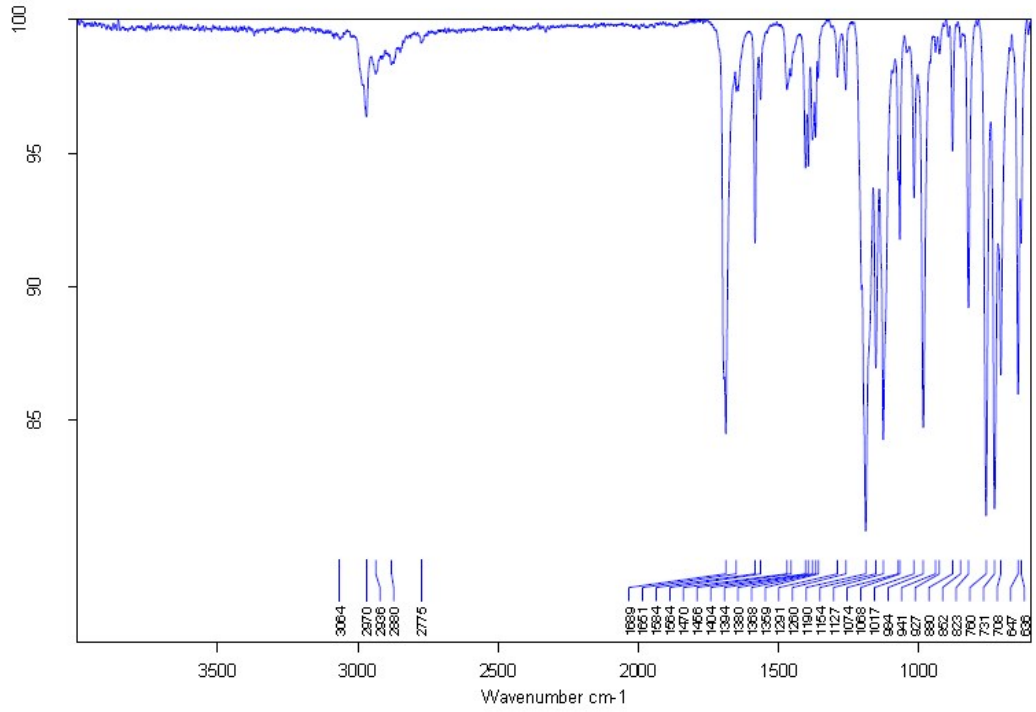
^{1}H NMR spectrum of **2**



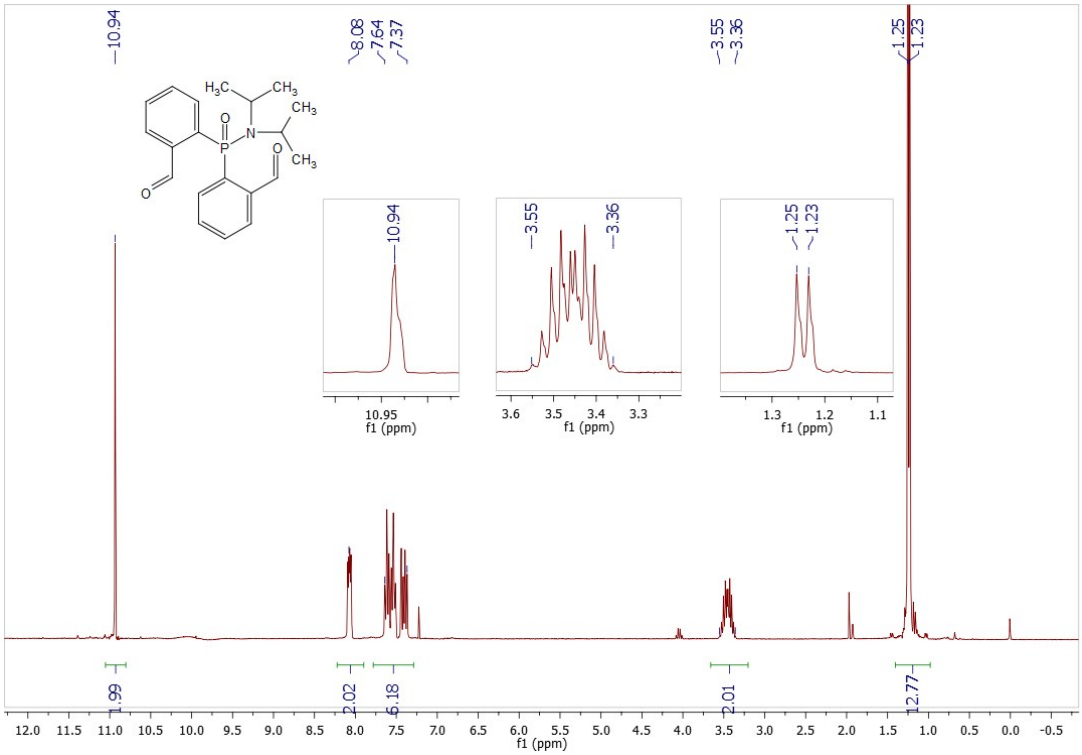
^{31}P NMR spectrum of **2**



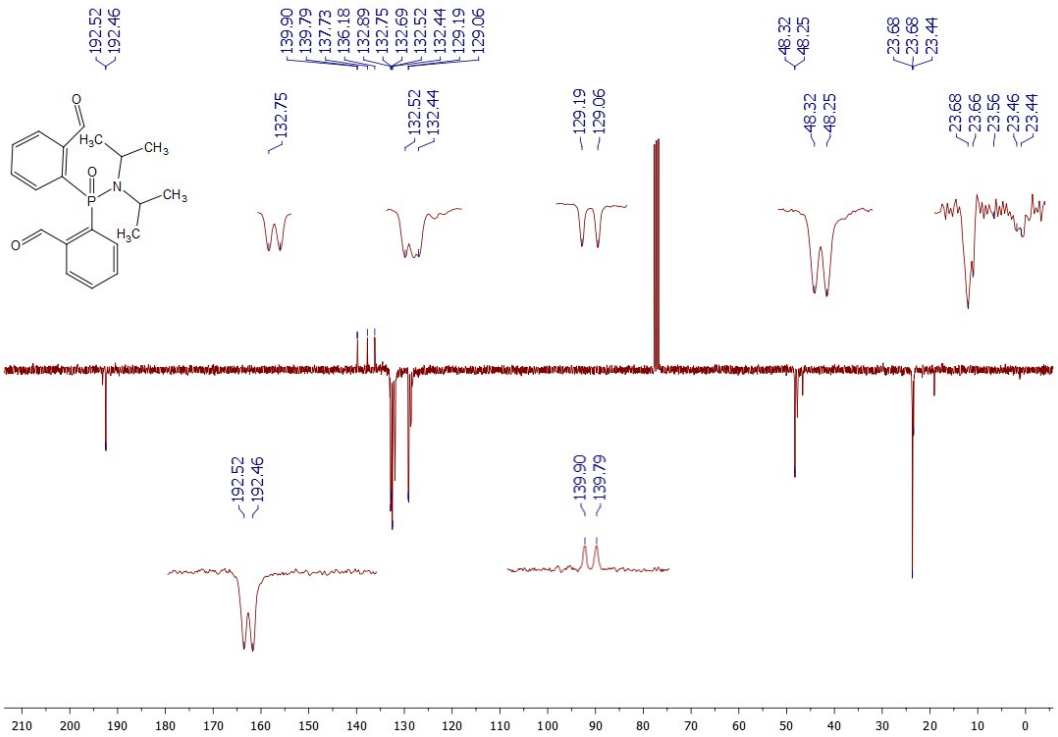
IR spectrum of **2**



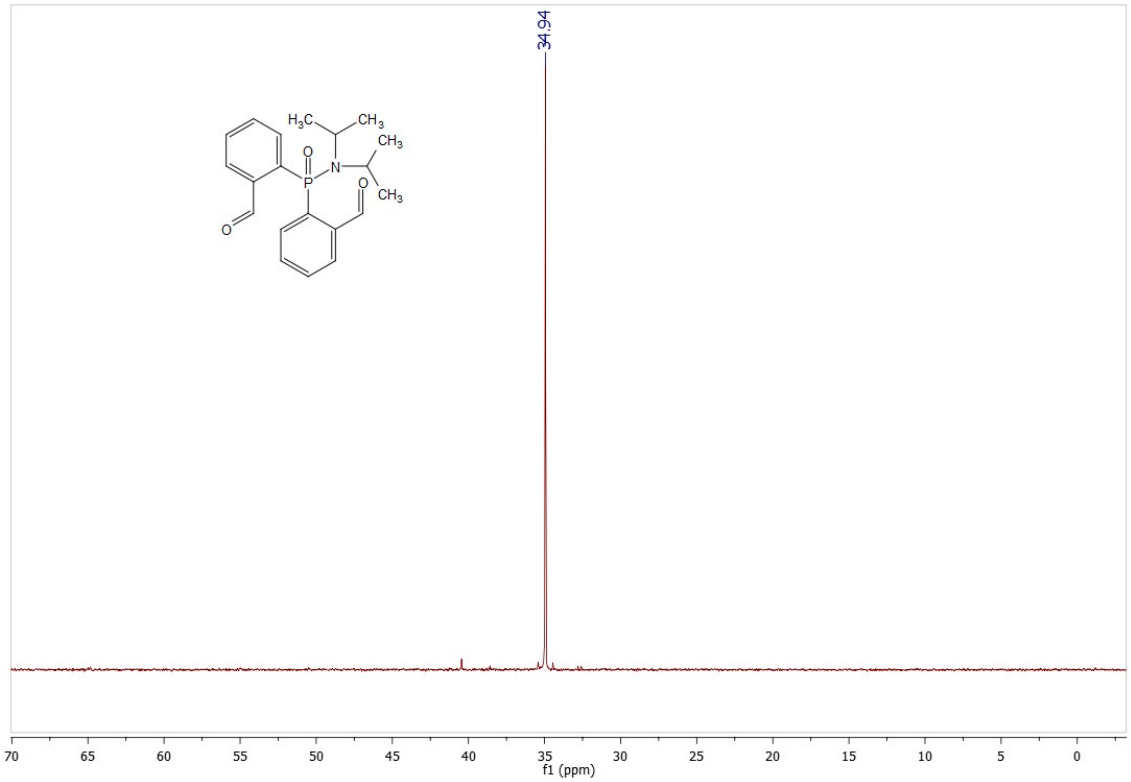
^{1}H NMR spectrum of **3**



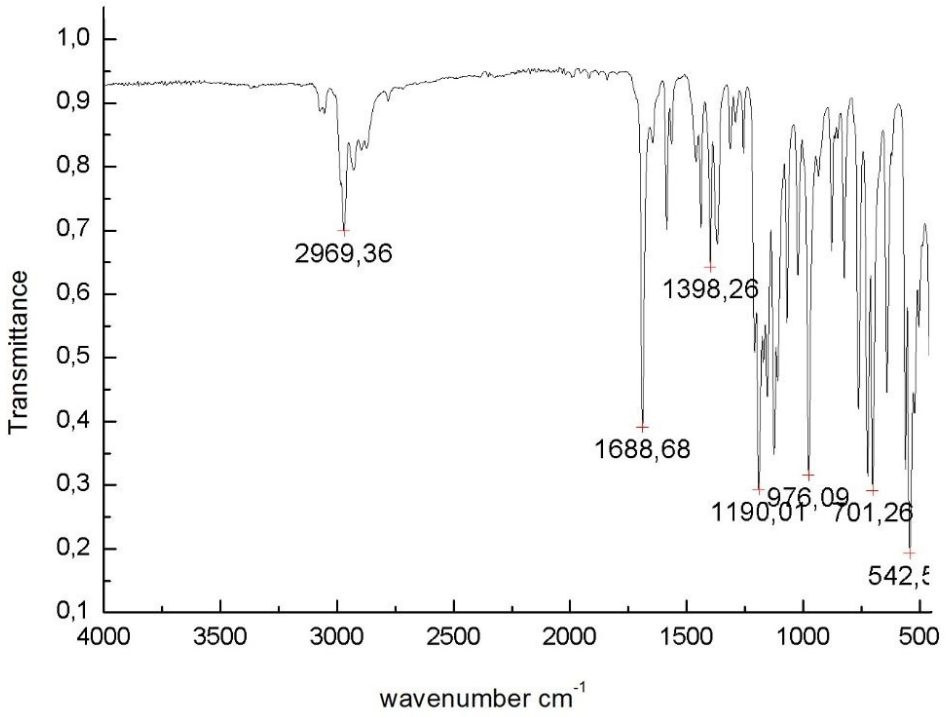
APT ^{13}C NMR spectrum of **3**



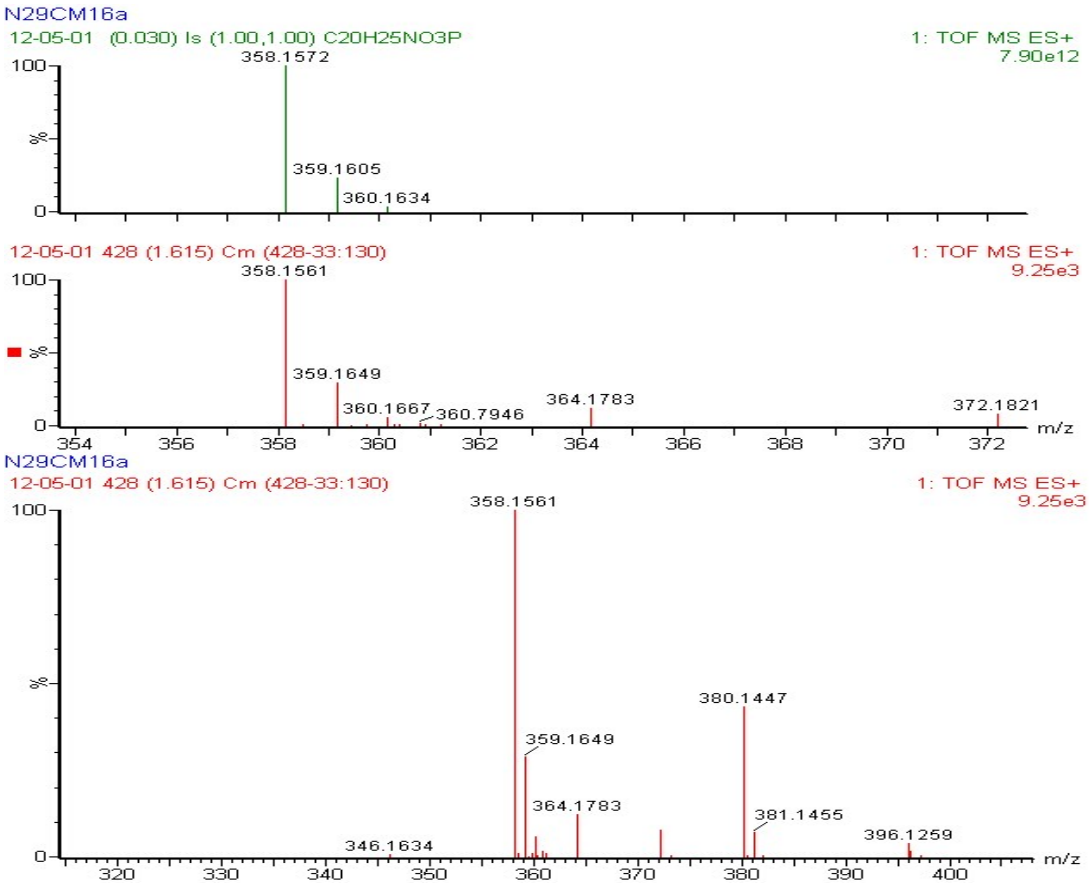
^{31}P NMR spectrum of **3**



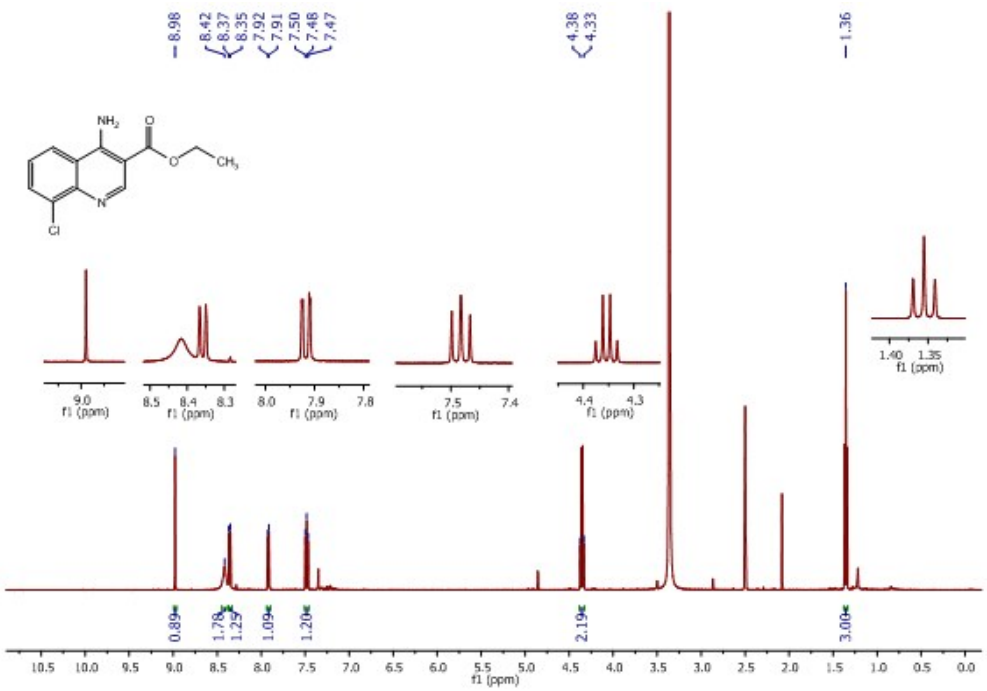
IR spectrum of **3**



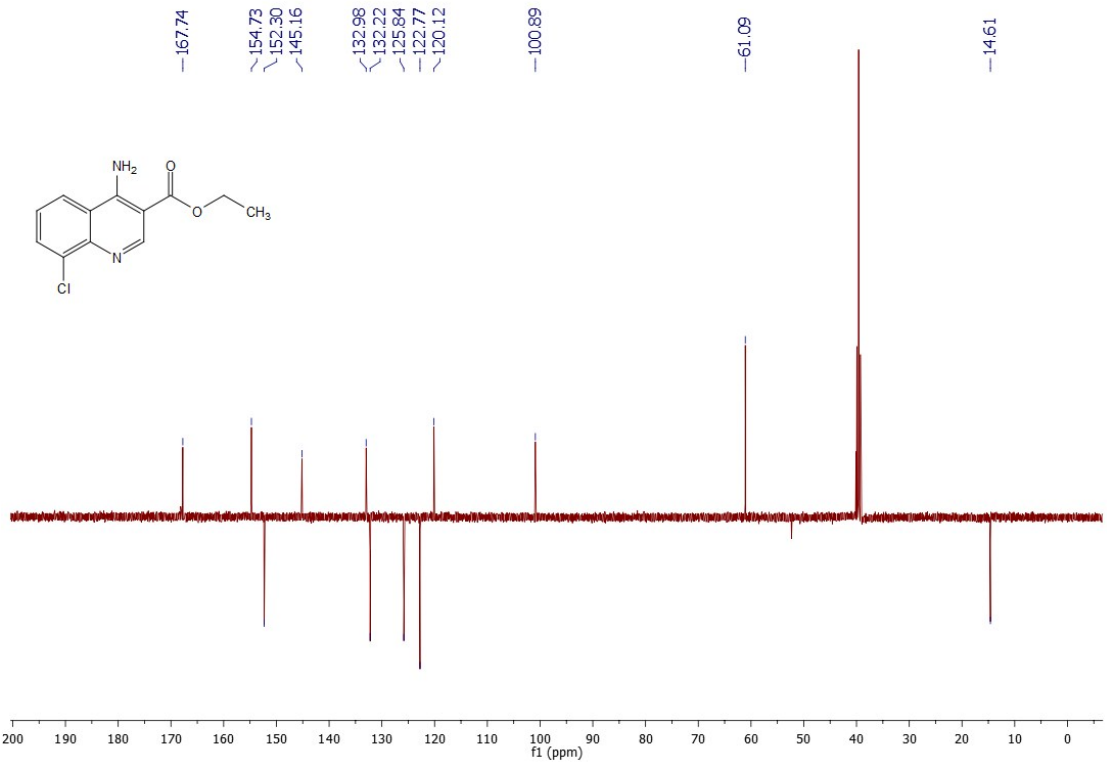
HRMS (ESI) spectrum of **3**



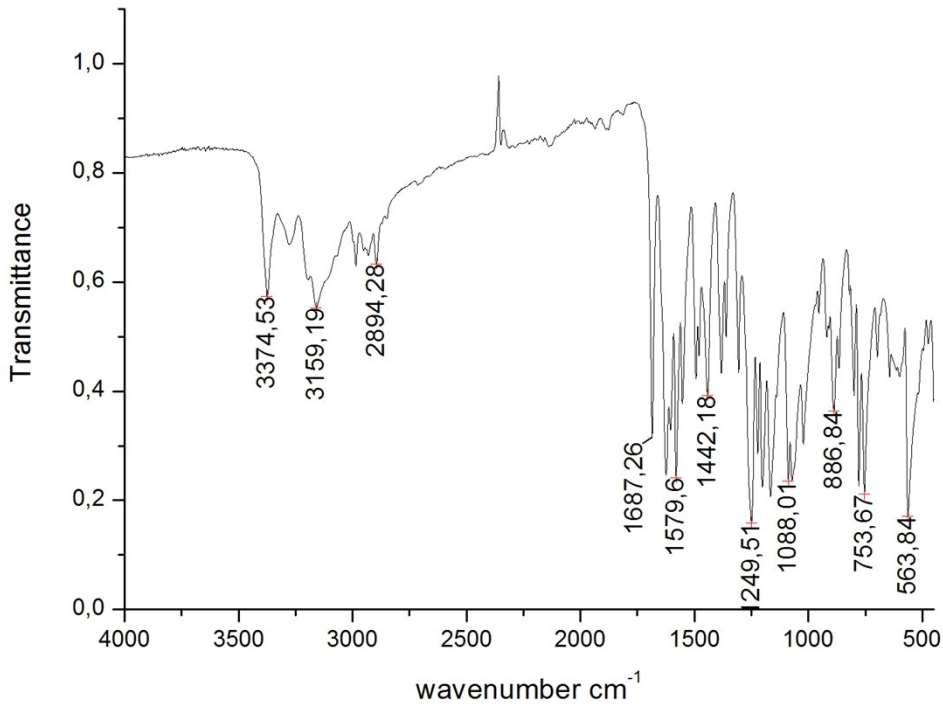
^{1}H NMR spectrum of **5a**



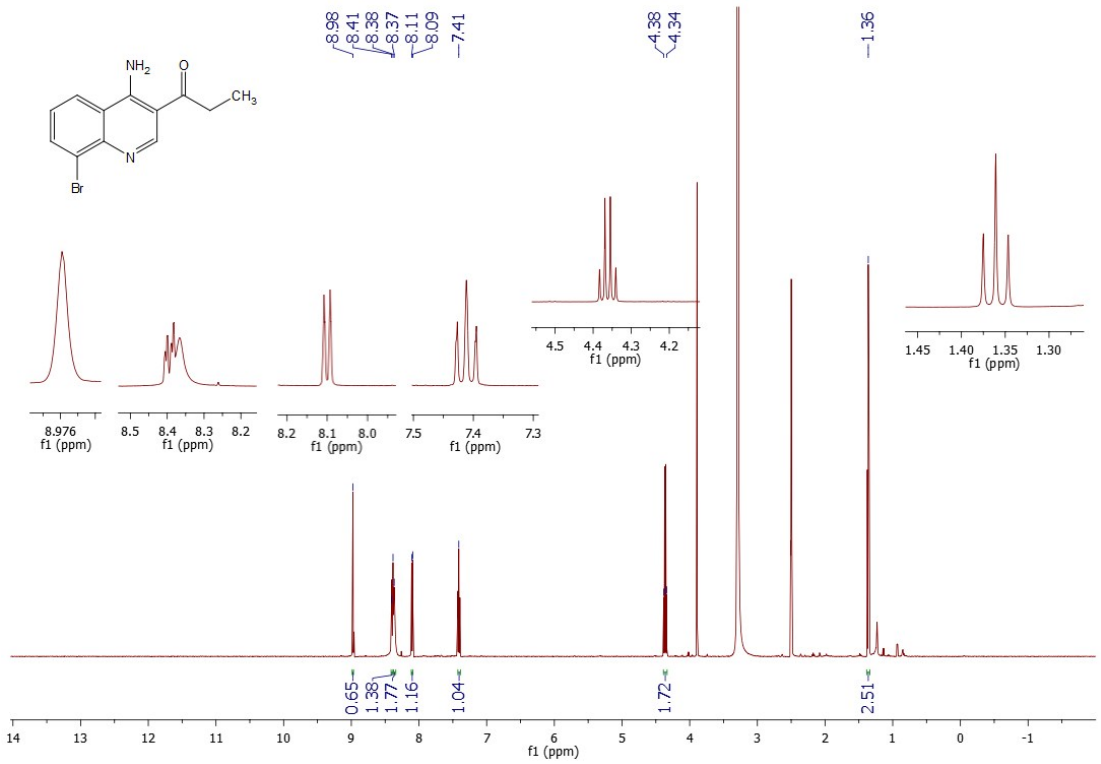
APT ^{13}C NMR spectrum of **5a**



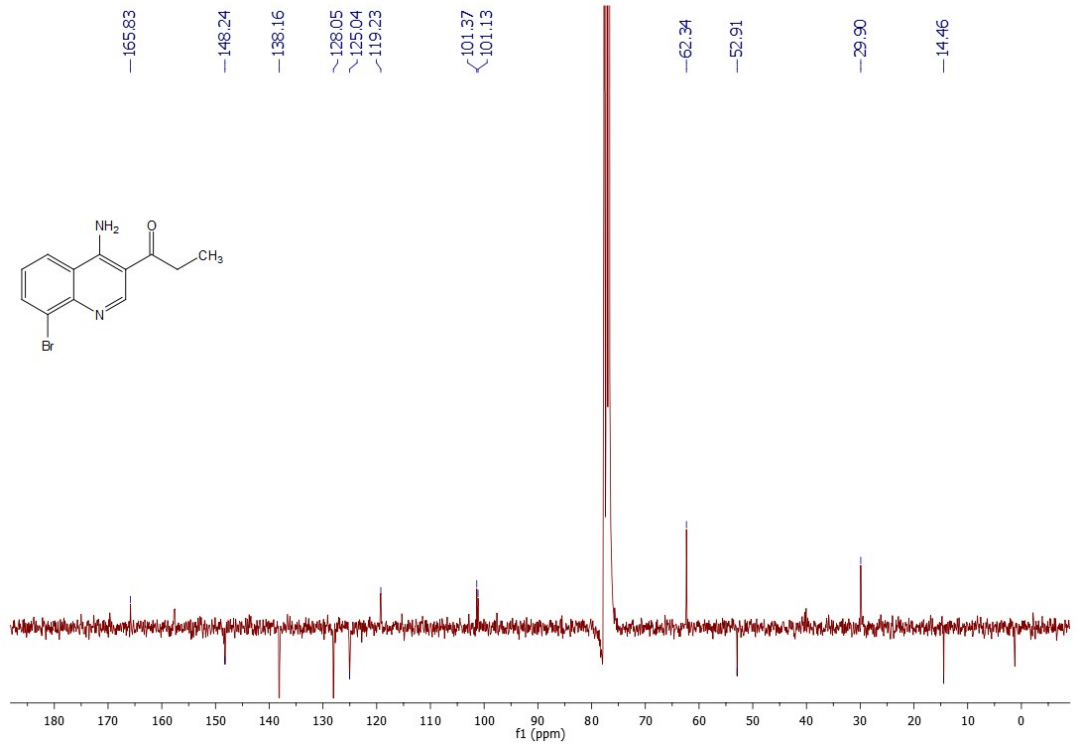
IR spectrum of **5a**



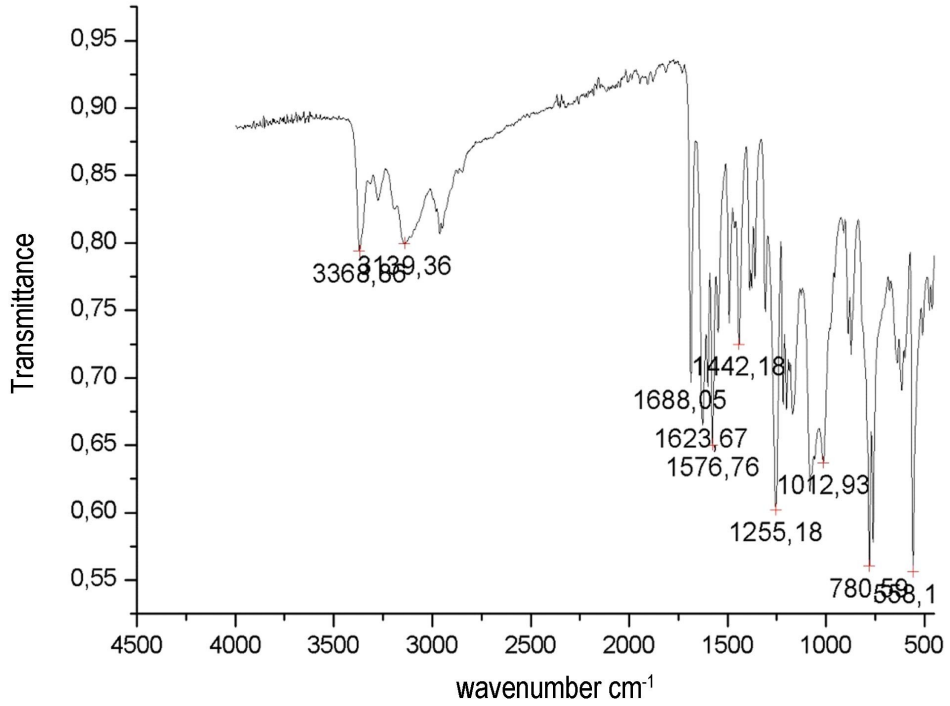
^{1}H NMR spectrum of **5b**



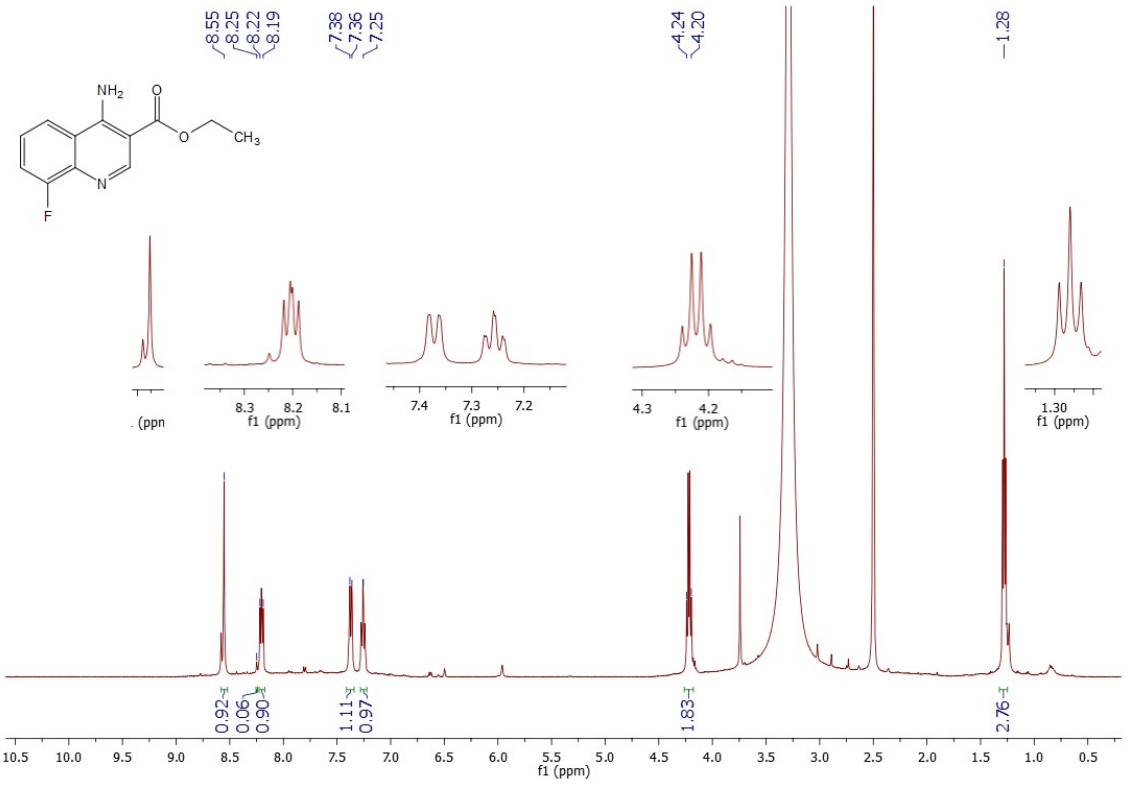
APT ^{13}C NMR spectrum of **5b**



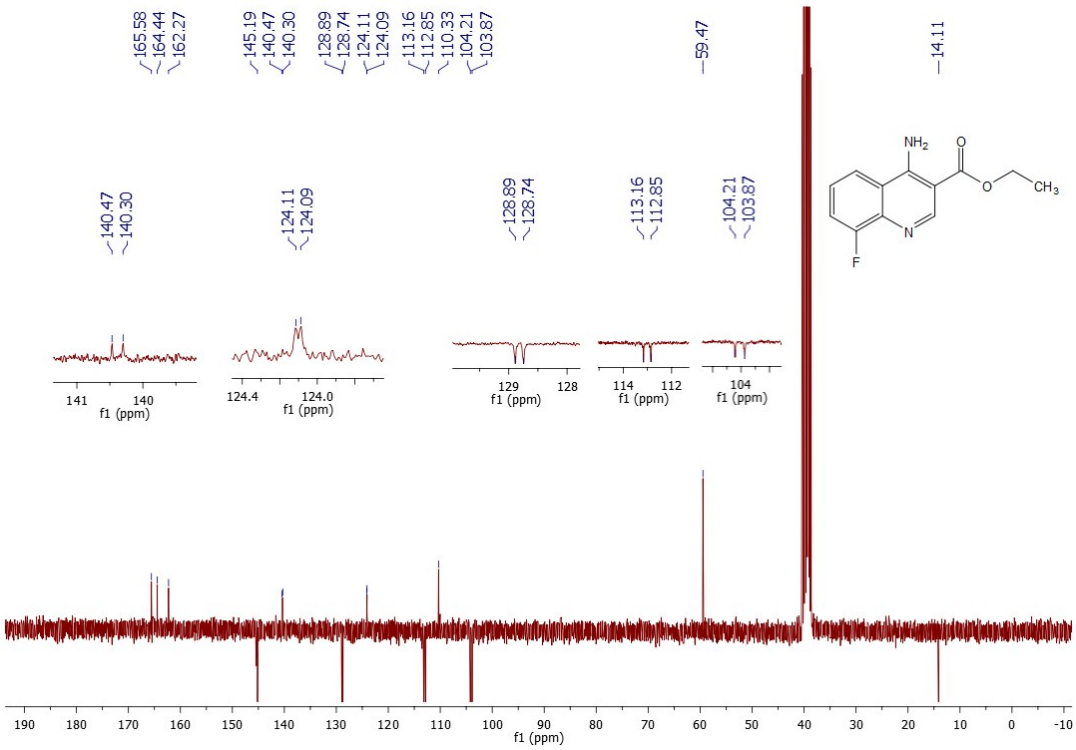
IR spectrum of **5b**



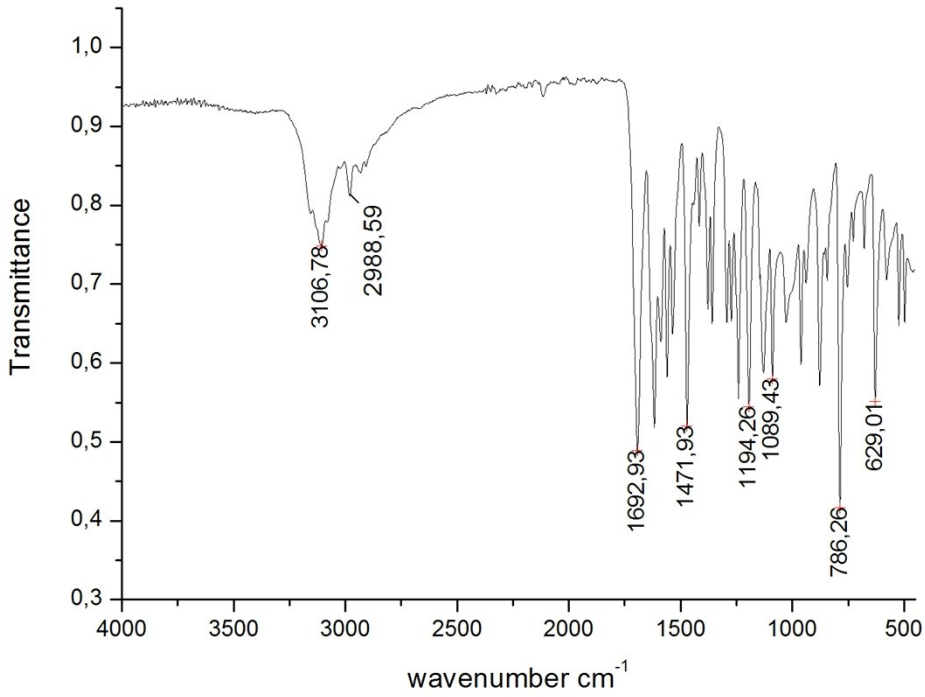
^{1}H NMR spectrum of **5c**



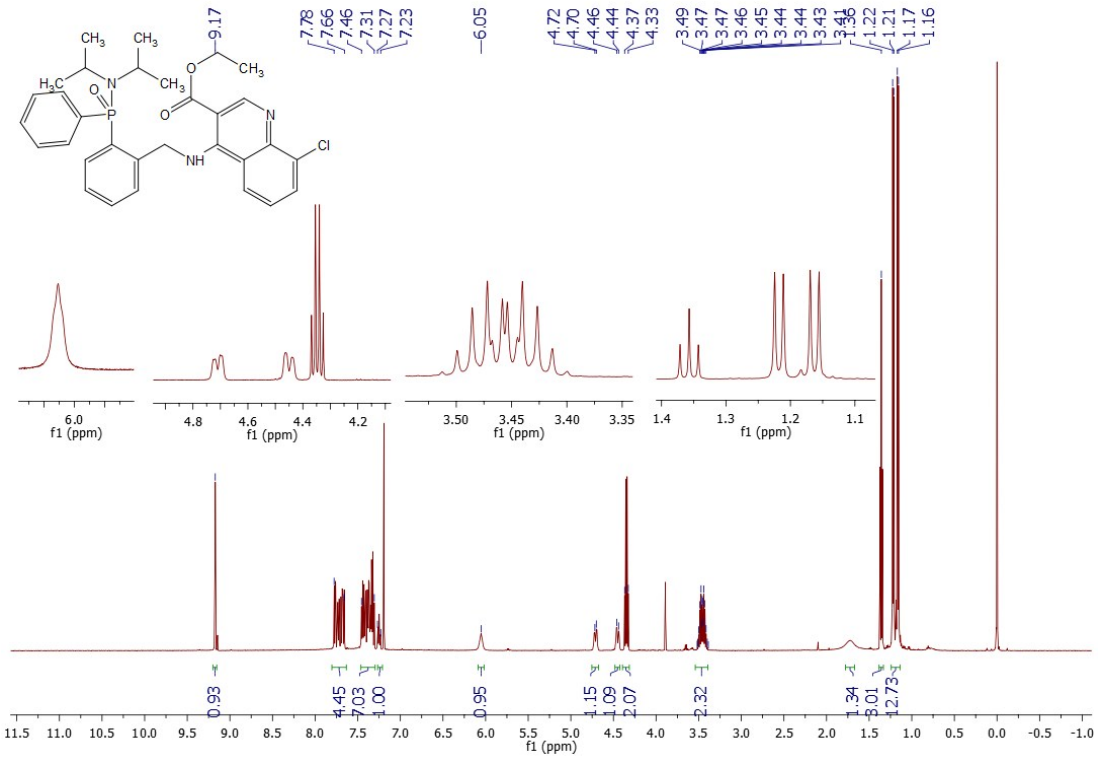
APT ^{13}C NMR spectrum of **5c**



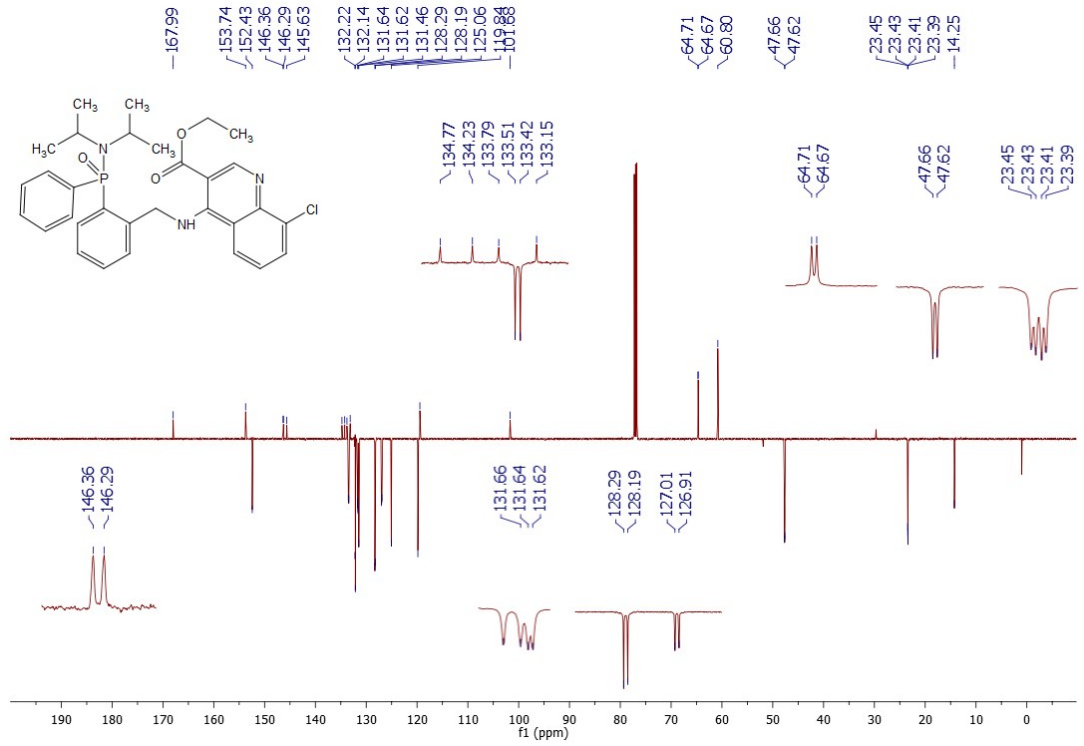
IR spectrum of **5c**



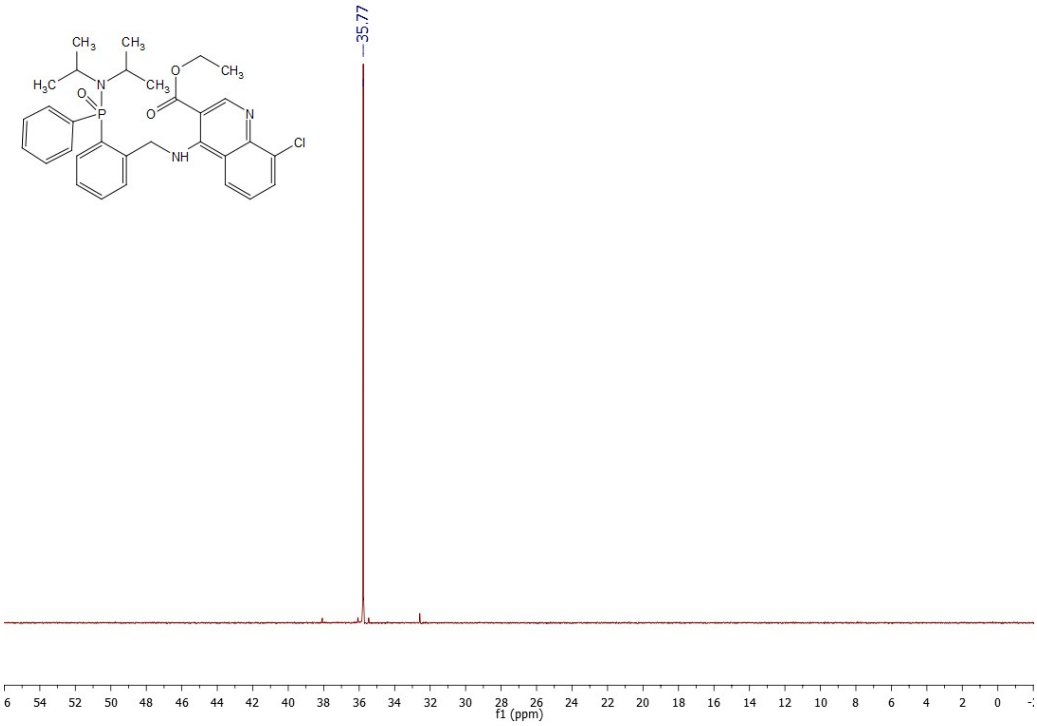
^{1}H NMR spectrum of **6a**



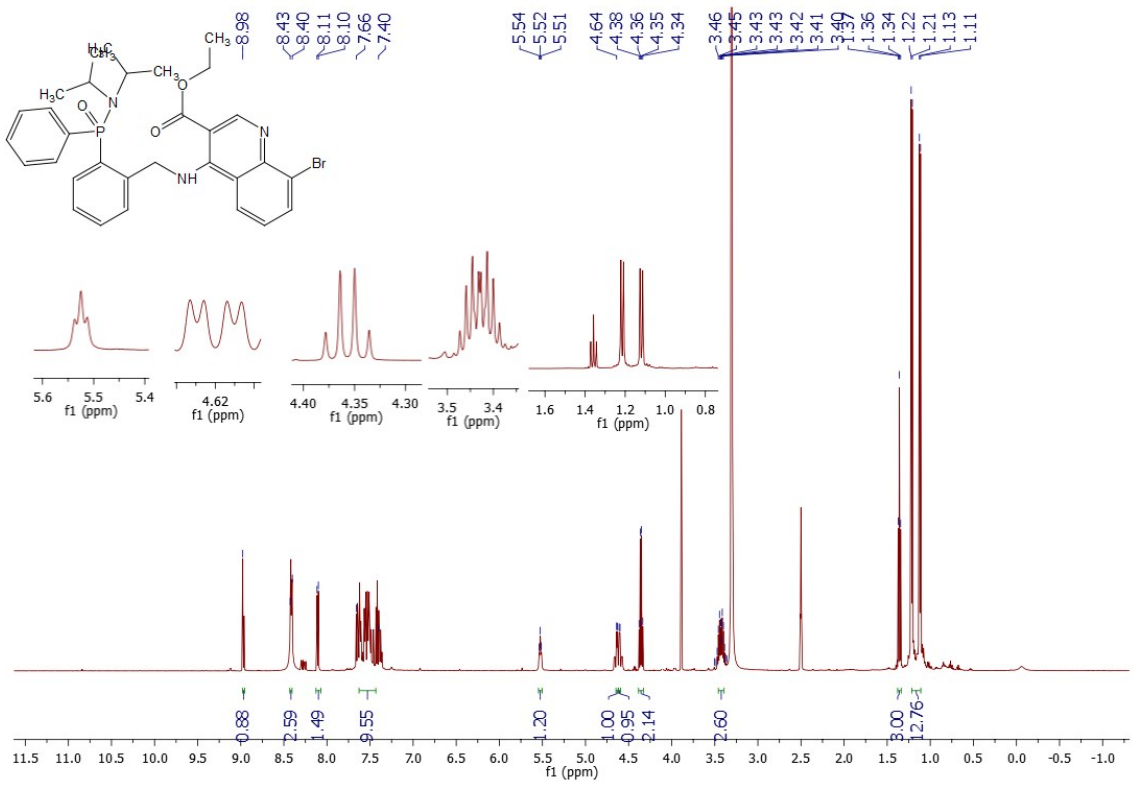
APT ^{13}C NMR spectrum of **6a**



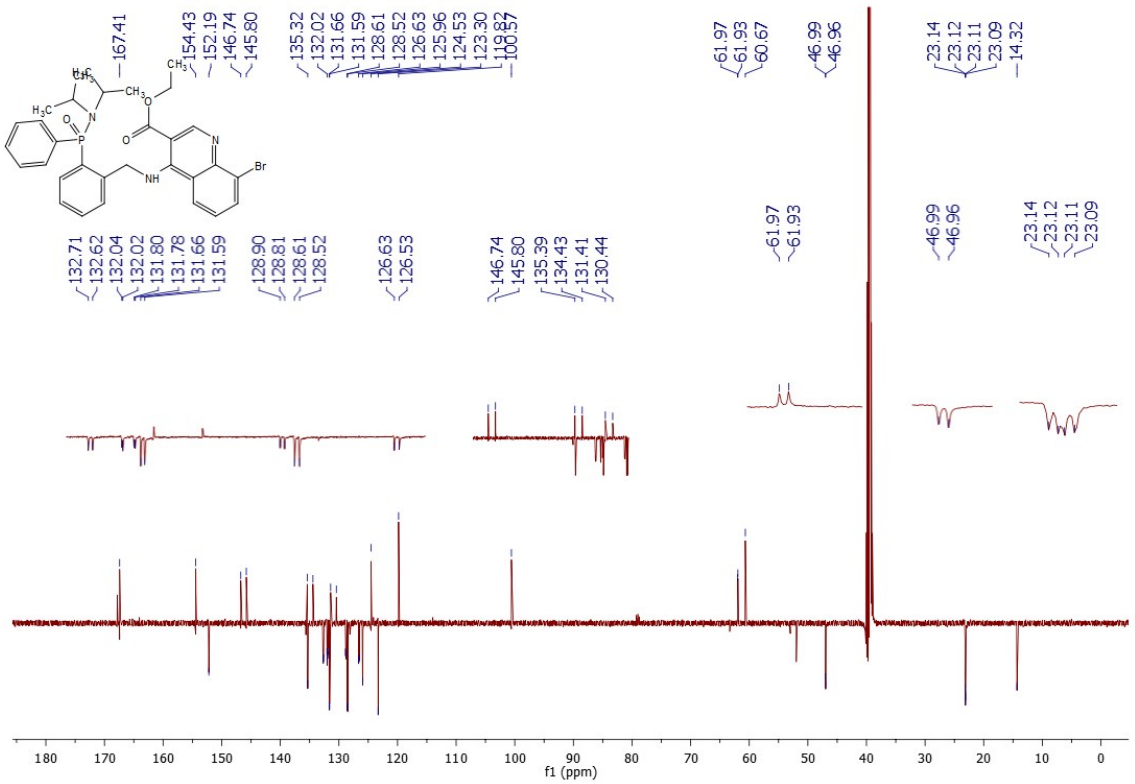
^{31}P NMR spectrum of **6a**



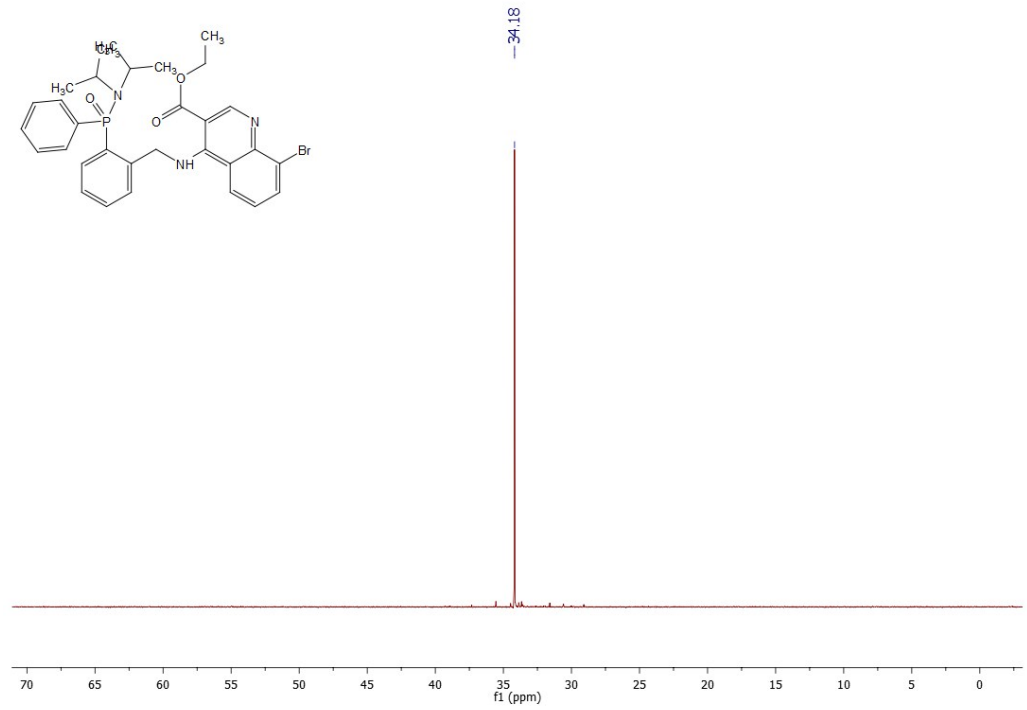
^{1}H NMR spectrum of **6b**



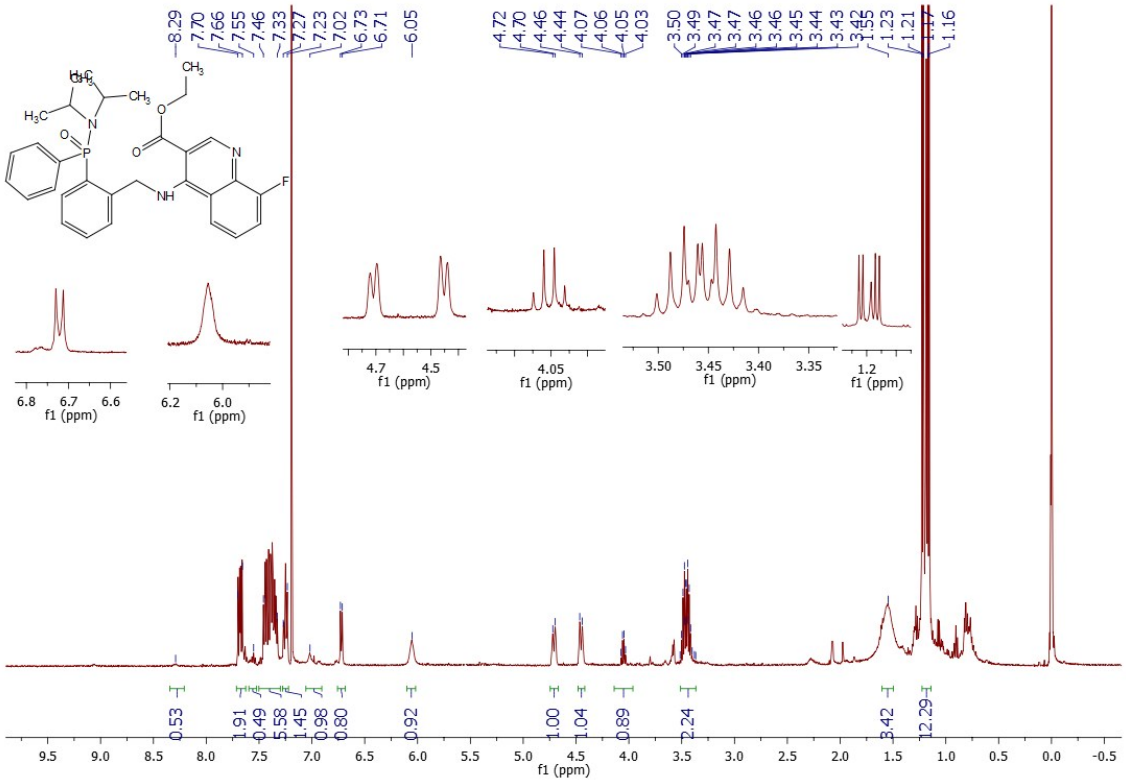
APT ^{13}C NMR spectrum of **6b**



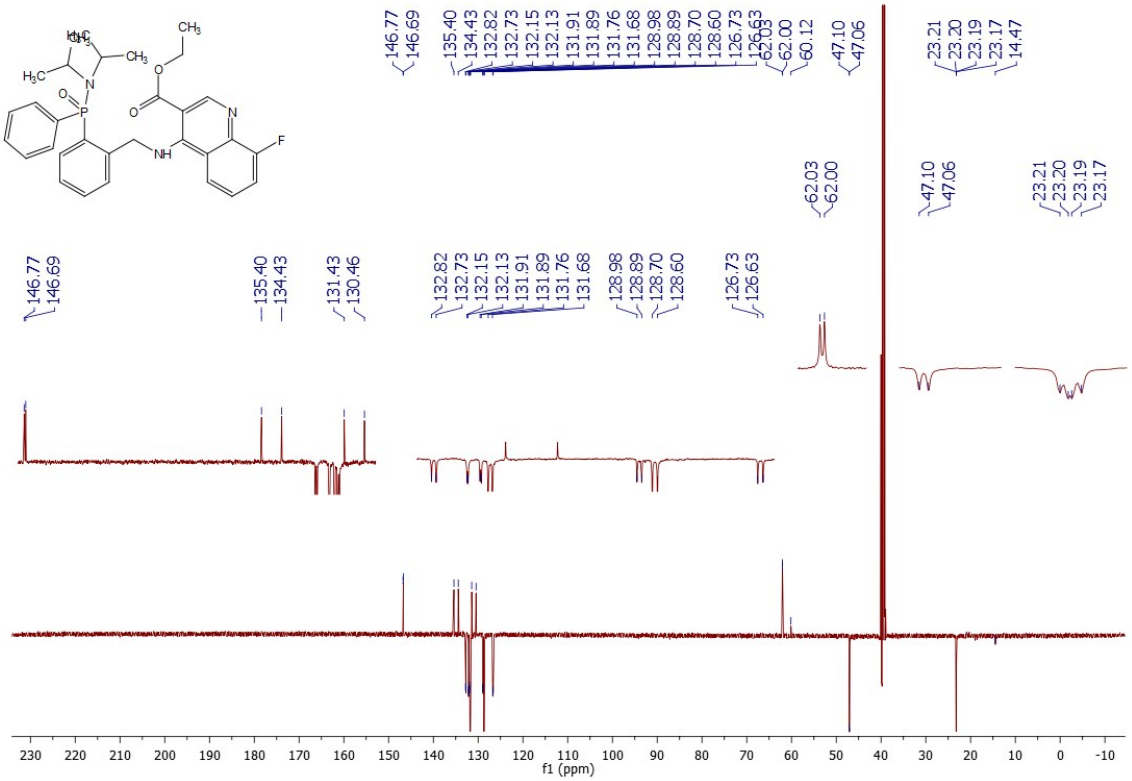
^{31}P NMR spectrum of **6b**



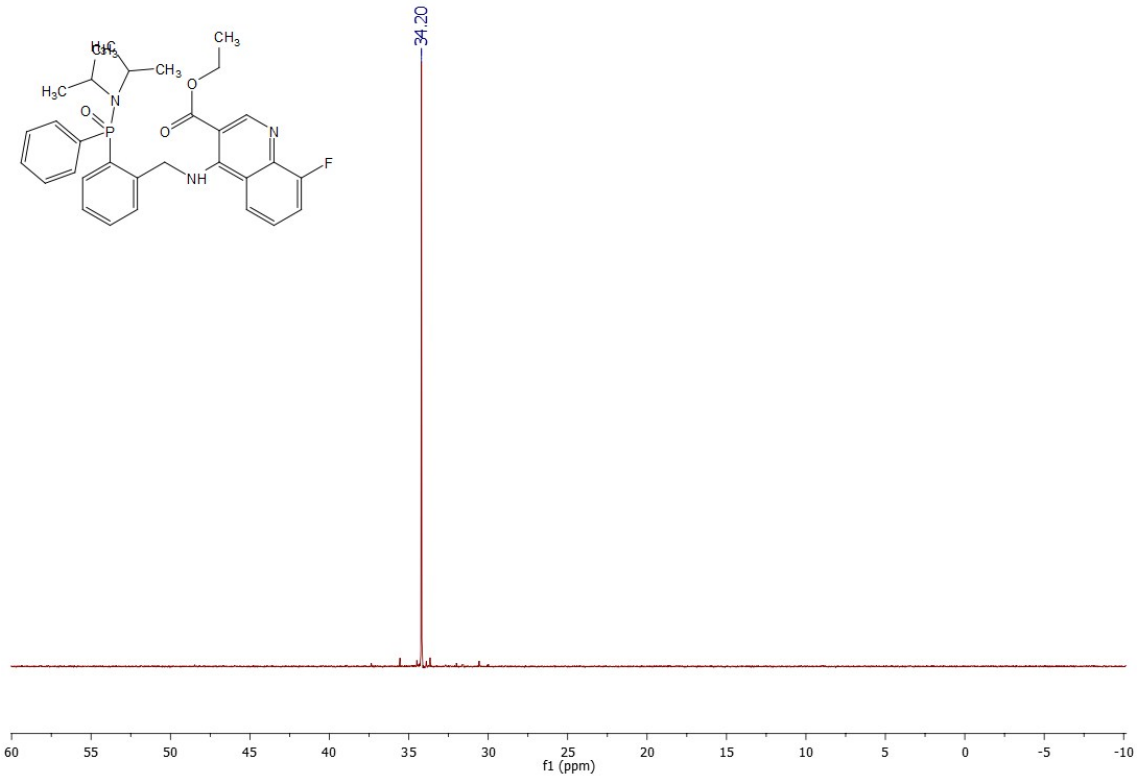
^{1}H NMR spectrum of **6c**



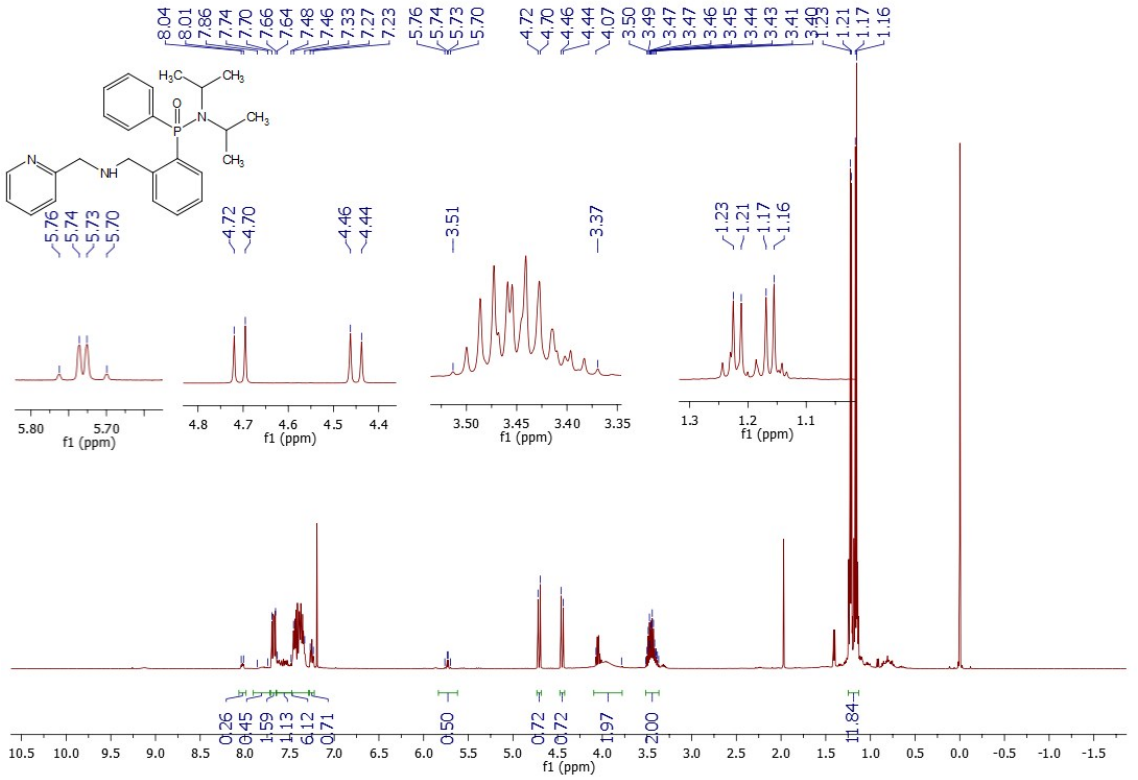
APT ^{13}C NMR spectrum of **6c**



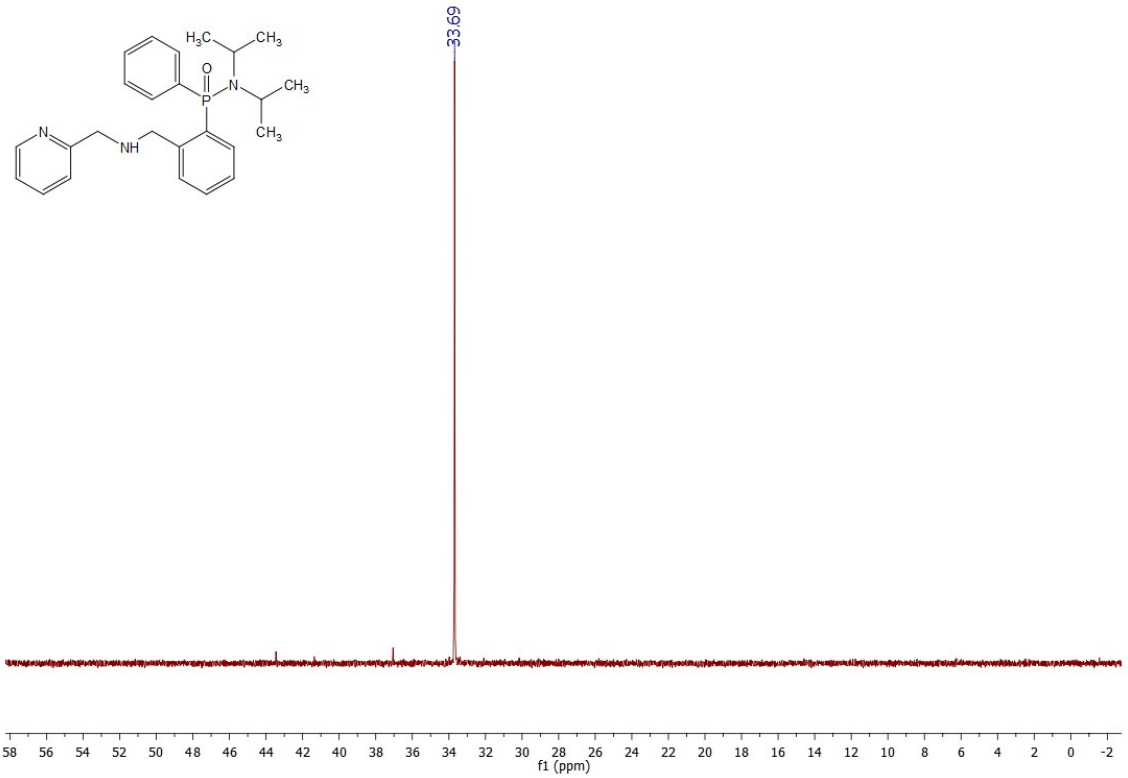
^{31}P NMR spectrum of **6c**



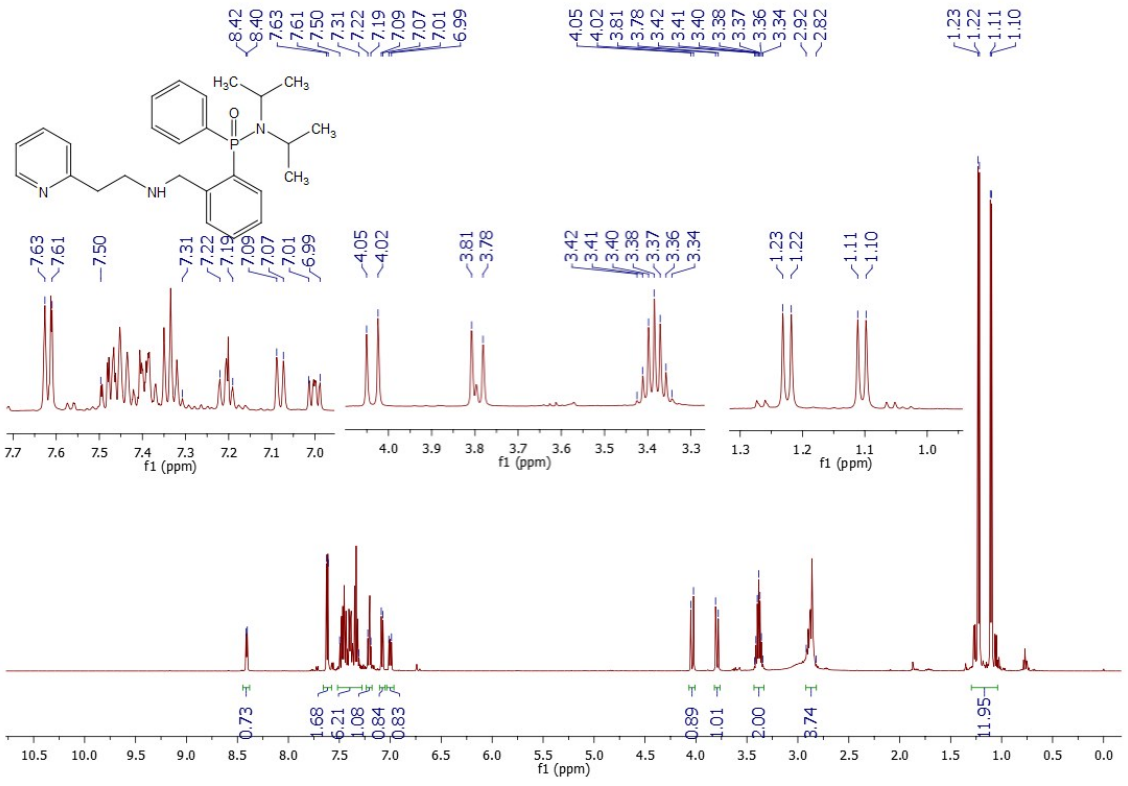
^{1}H NMR spectrum of **8a**



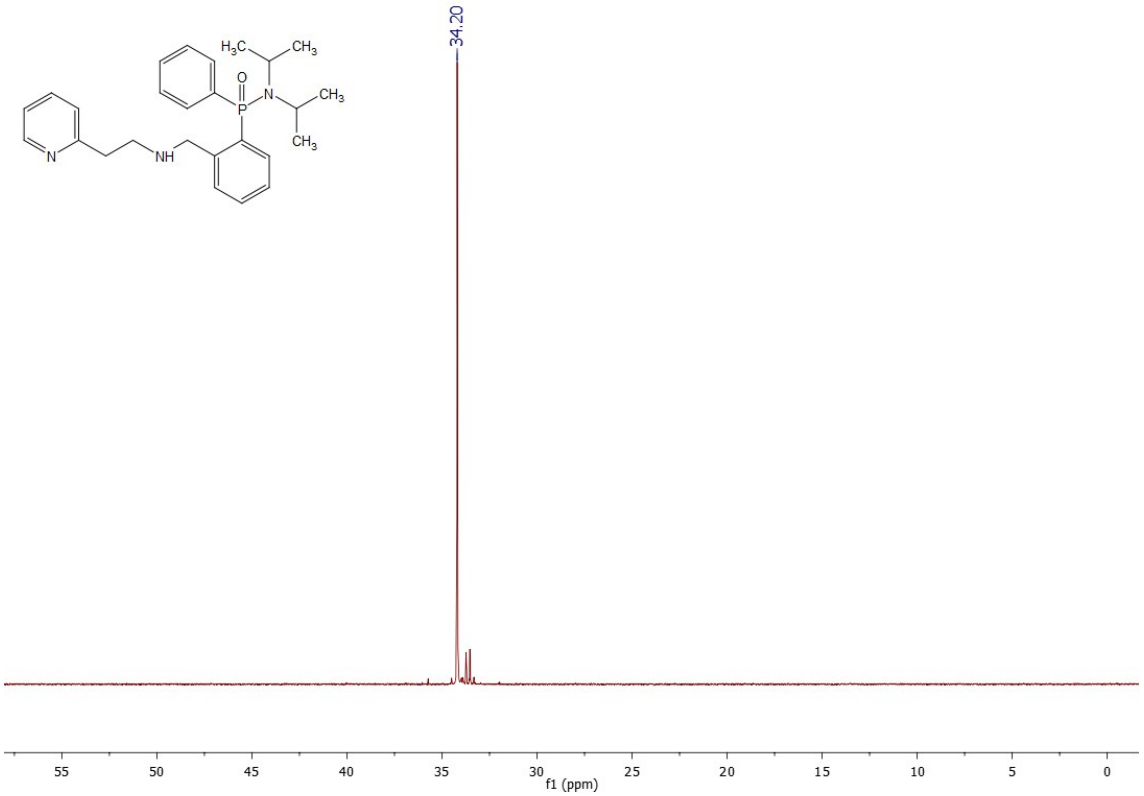
^{31}P NMR spectrum of **8a**



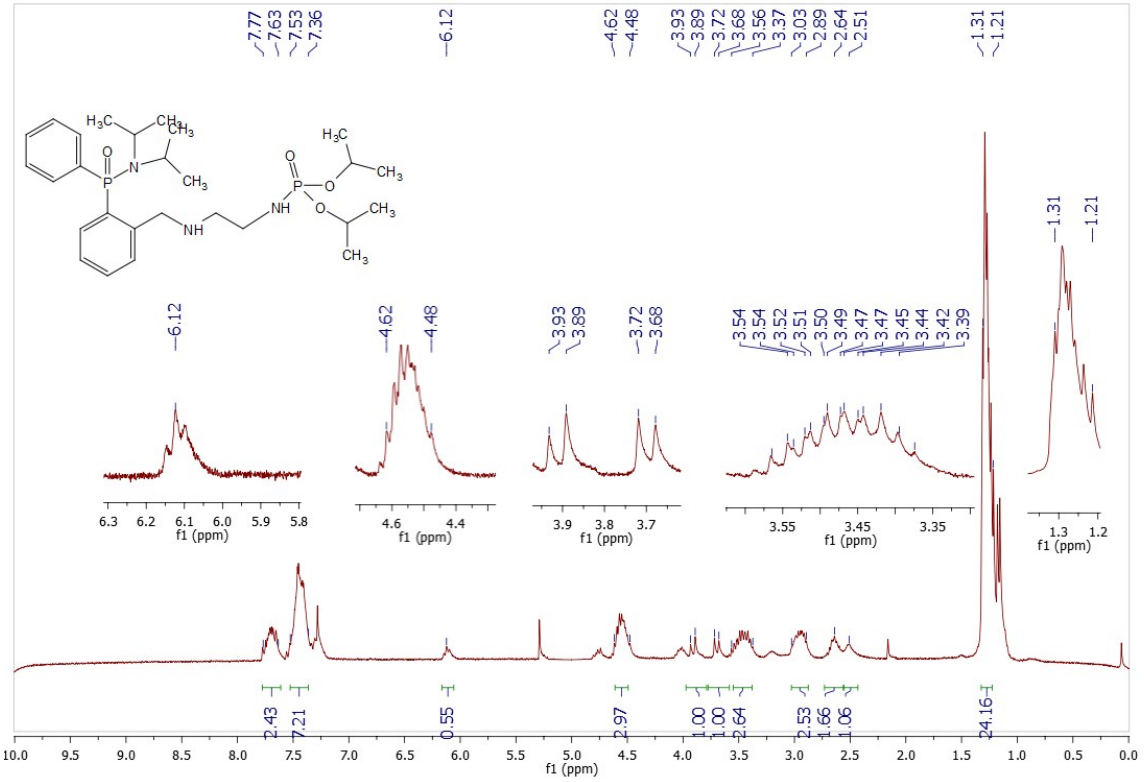
^{1}H NMR spectrum of **8b**



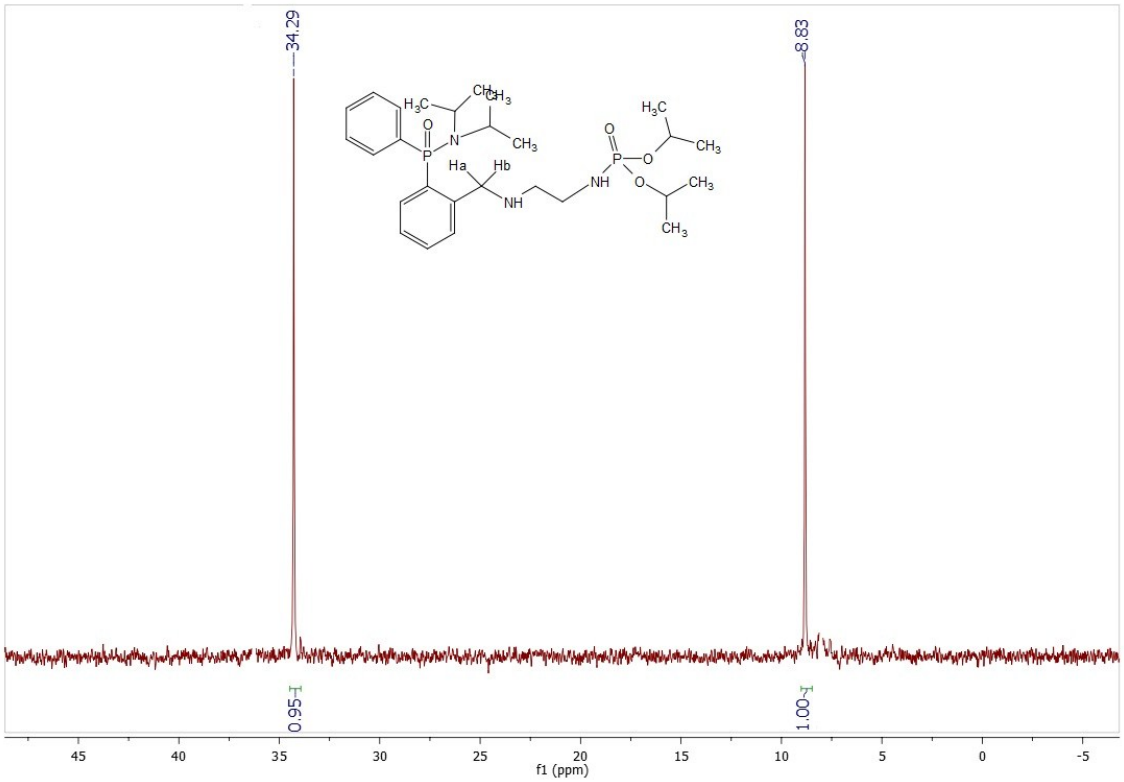
^{31}P NMR spectrum of **8b**



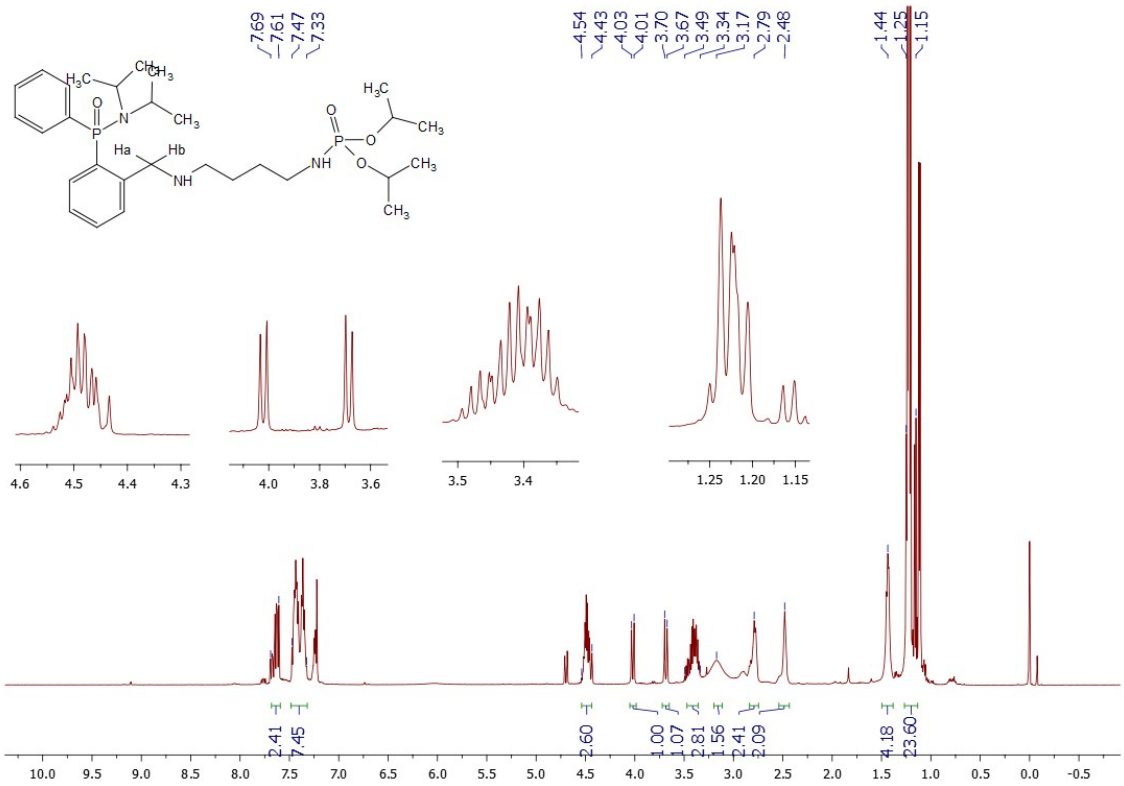
^{1}H NMR spectrum of **11a**



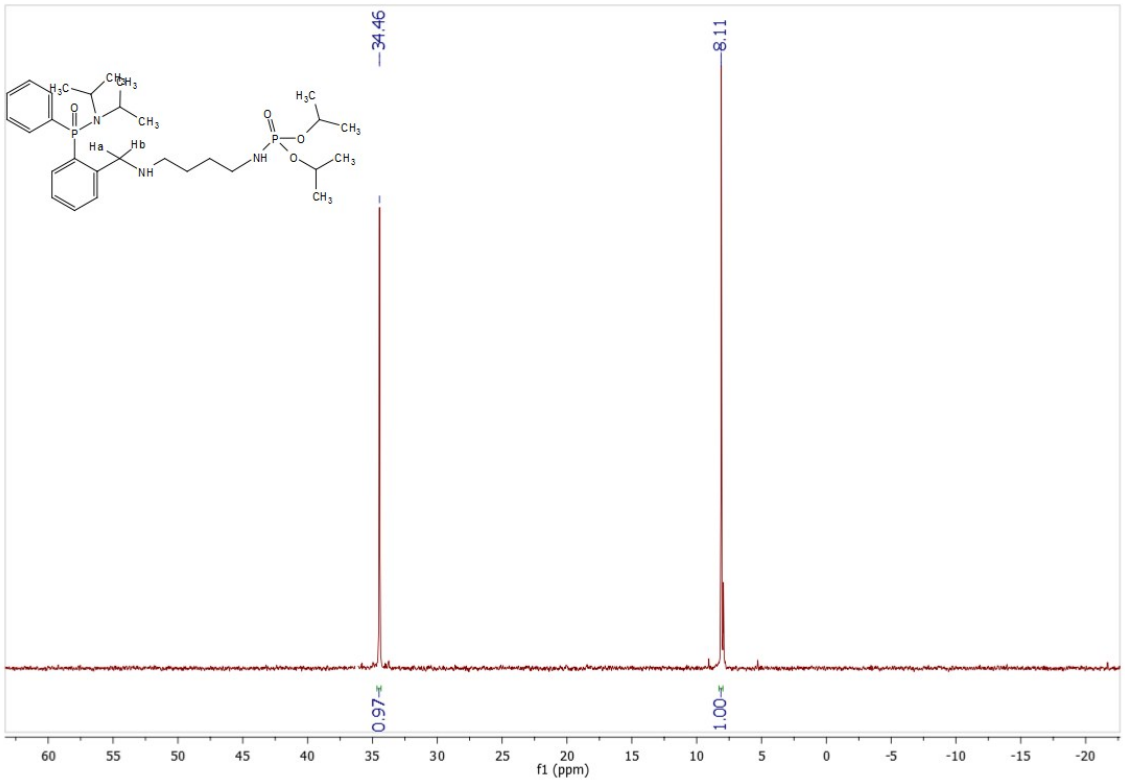
^{31}P NMR spectrum of **11a**



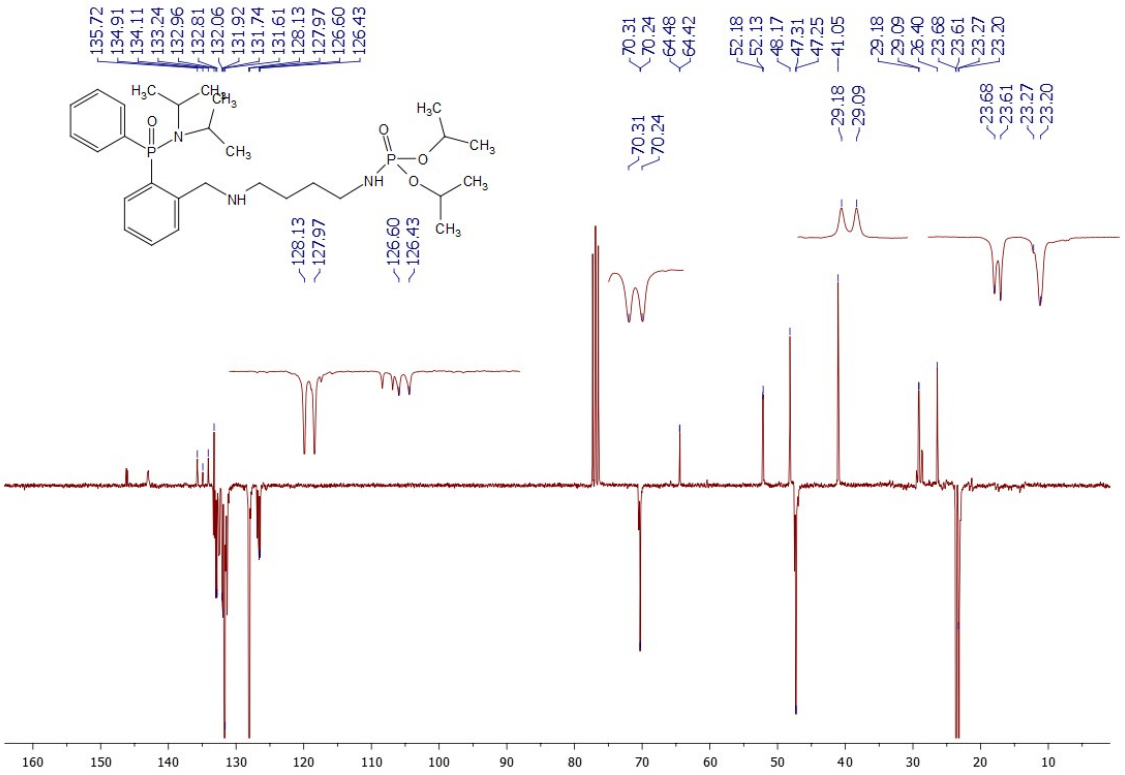
^{1}H NMR spectrum of **11b**



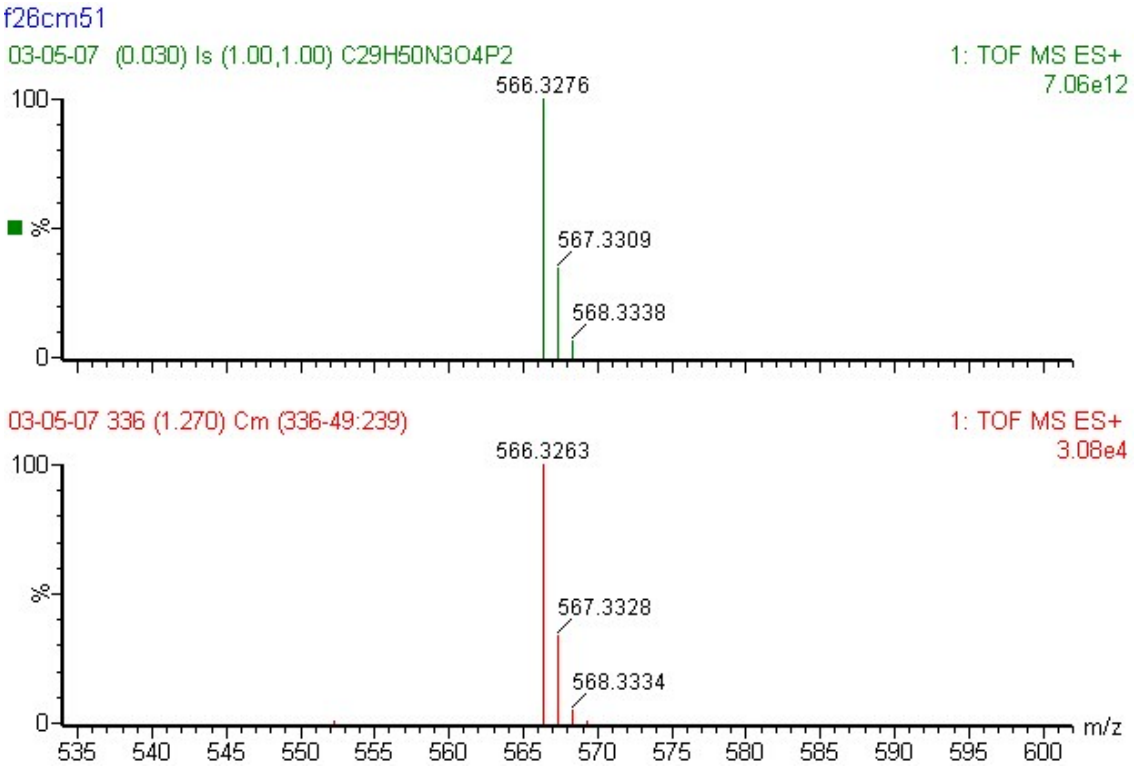
^{31}P NMR spectrum of **11b**



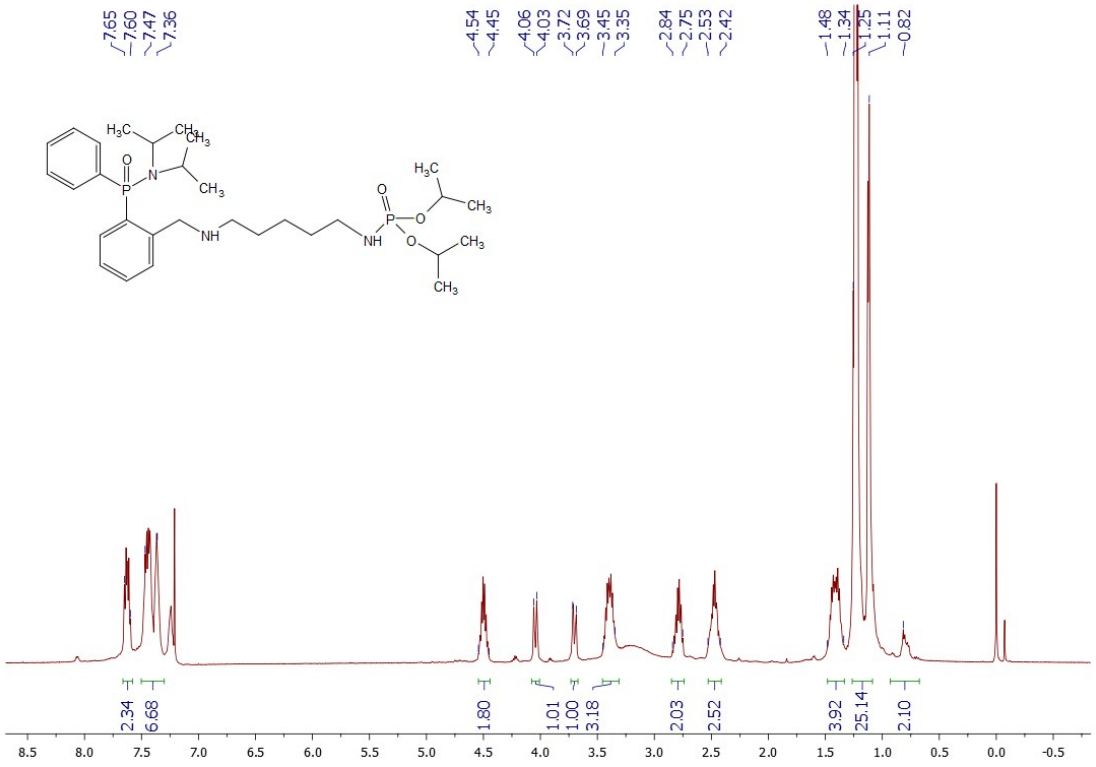
APT ^{13}C NMR spectrum of **11b**



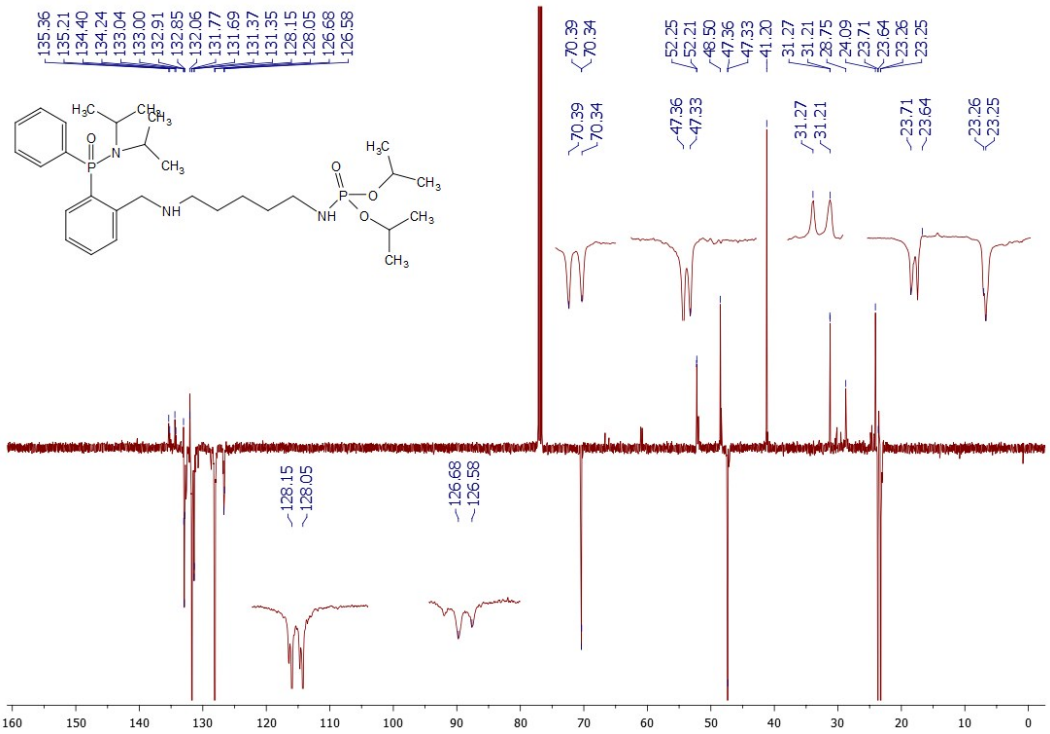
HRMS (ESI) spectrum of **11b**



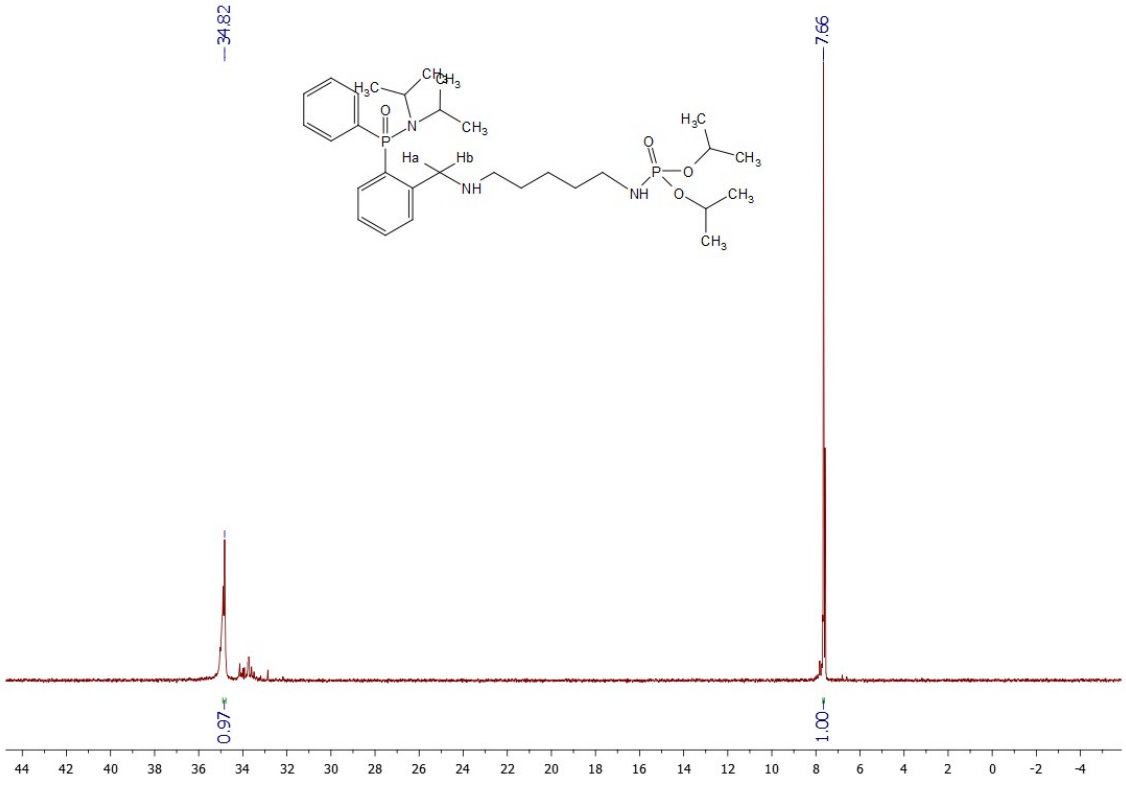
^{1}H NMR spectrum of **11c**



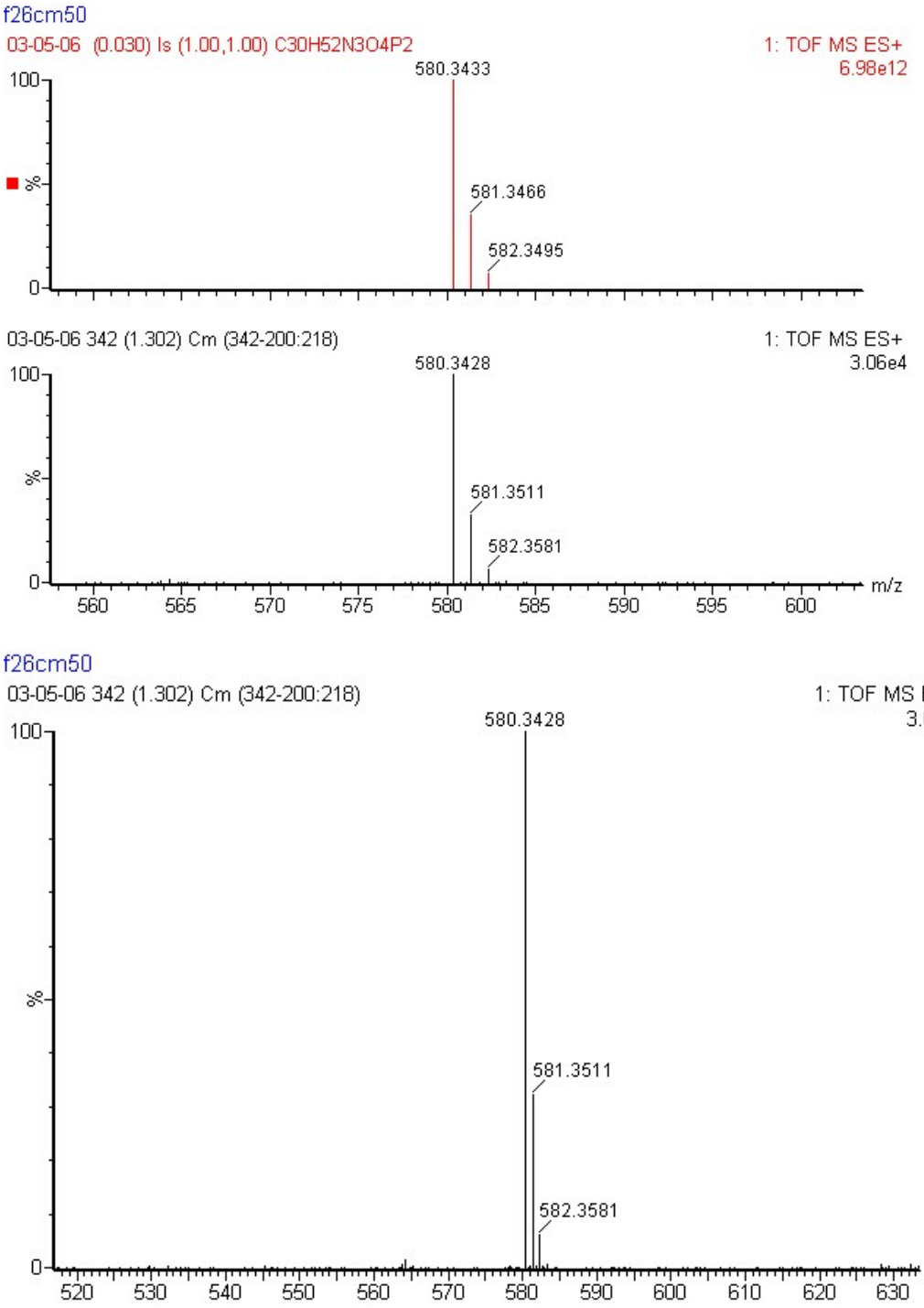
APT ^{13}C NMR spectrum of **11c**



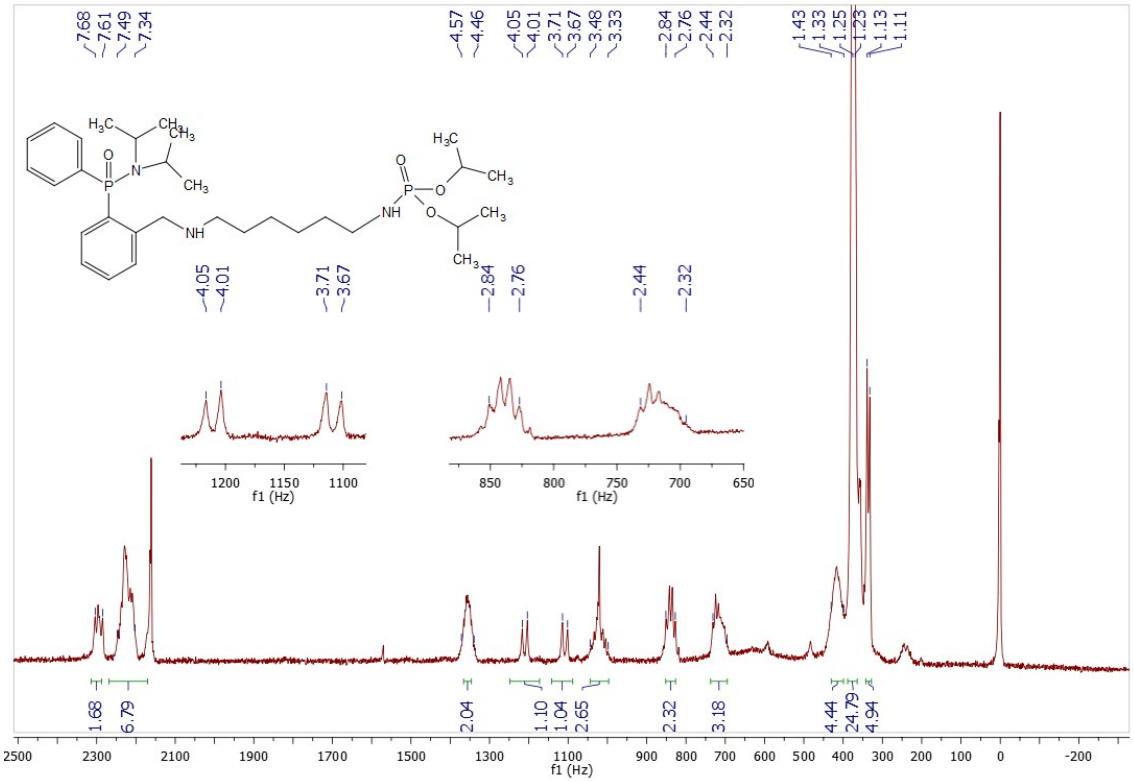
^{31}P NMR spectrum of **11c**



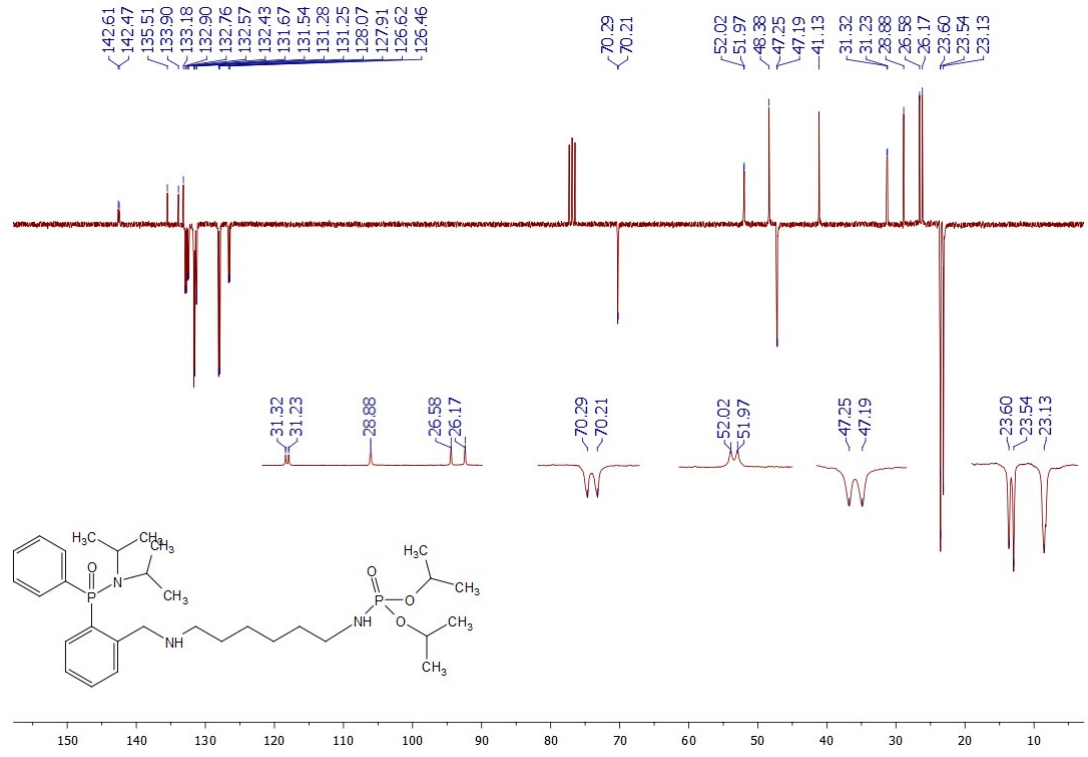
HRMS (ESI) spectrum of **11c**



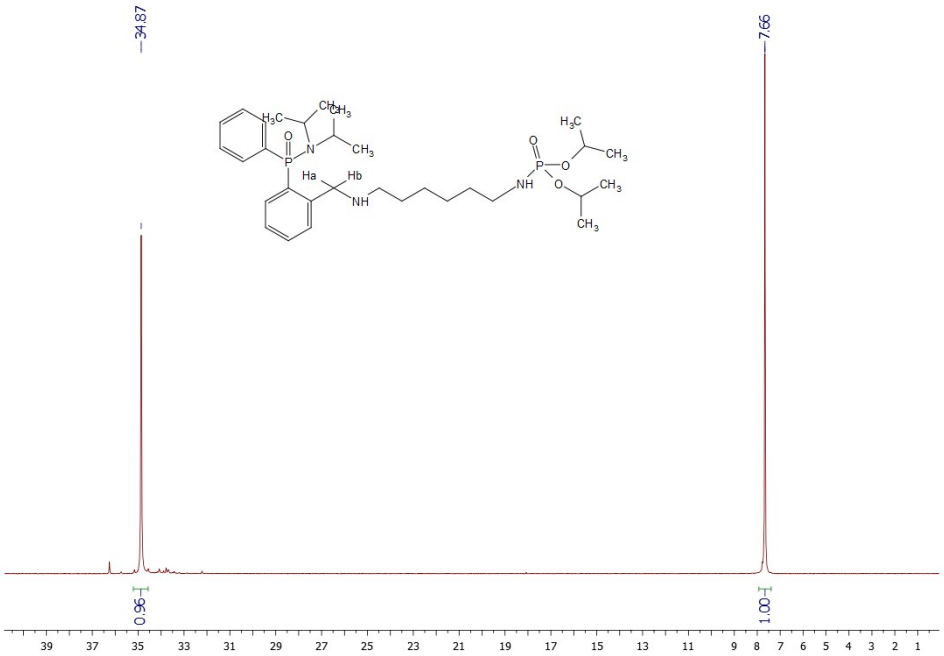
^{1}H NMR spectrum of **11d**



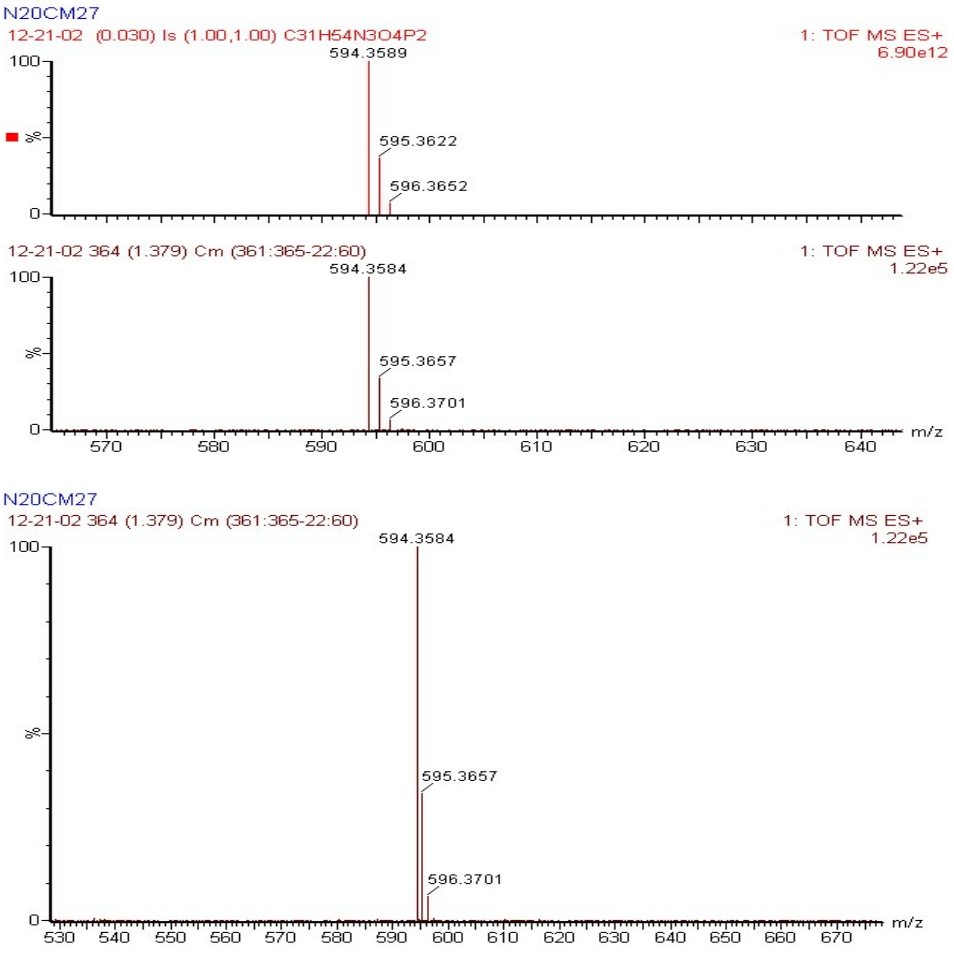
APT ^{13}C NMR spectrum of **11d**



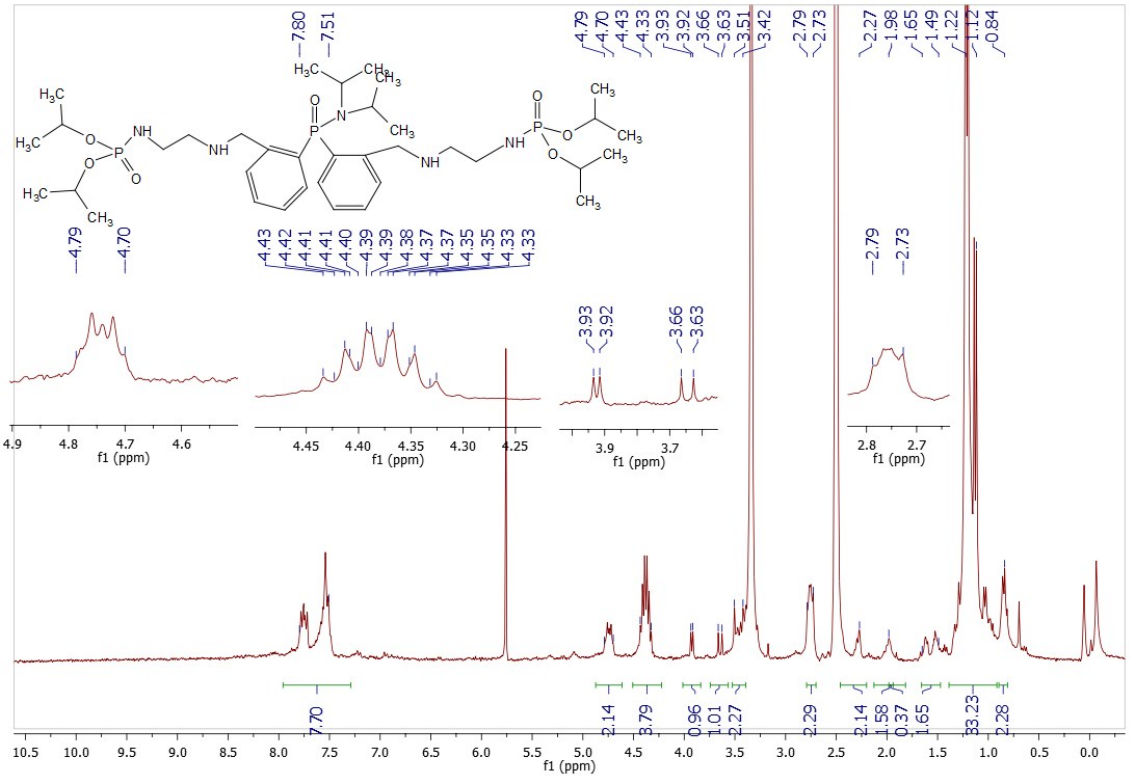
^{31}P NMR spectrum of **11d**



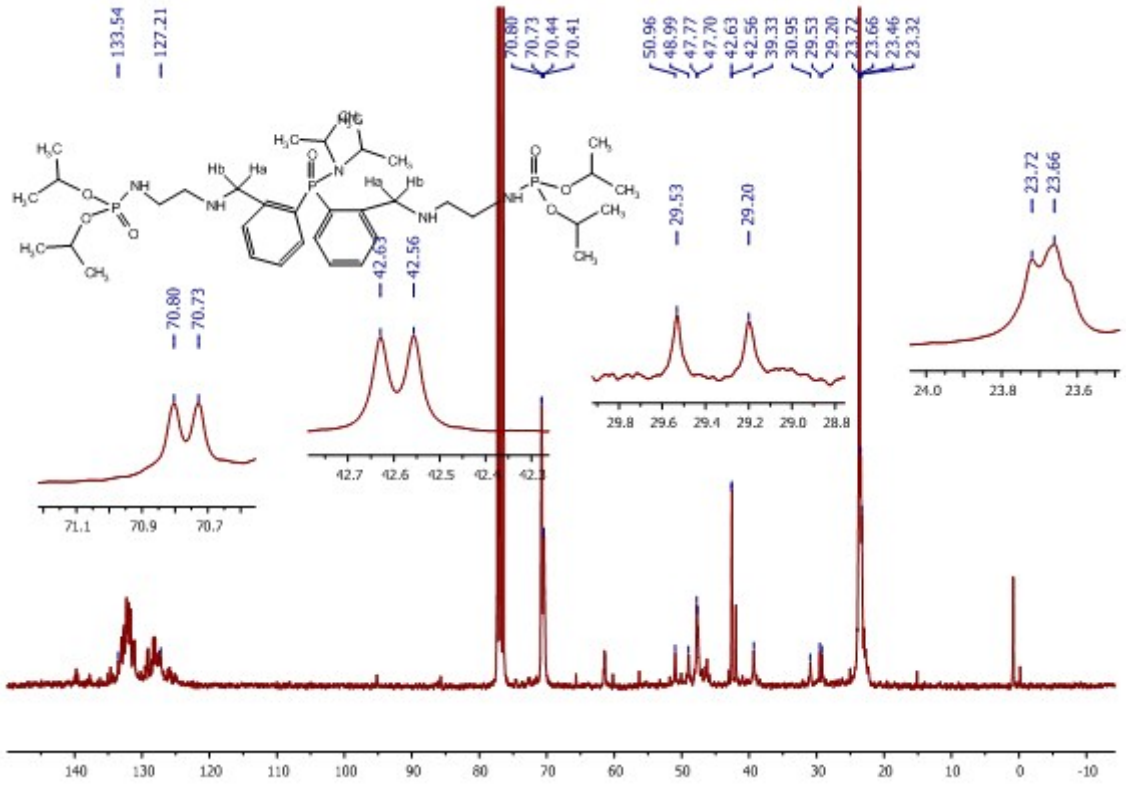
HRMS (ESI) spectrum of **11d**



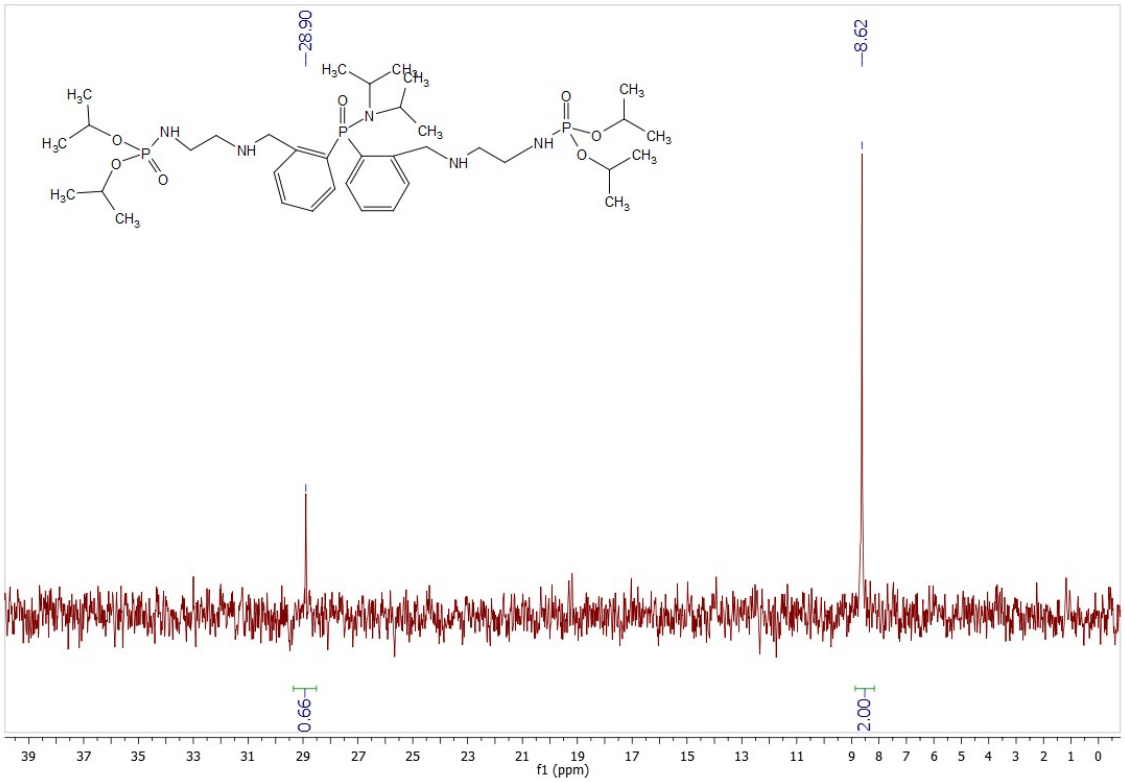
^{1}H NMR spectrum of **13a**



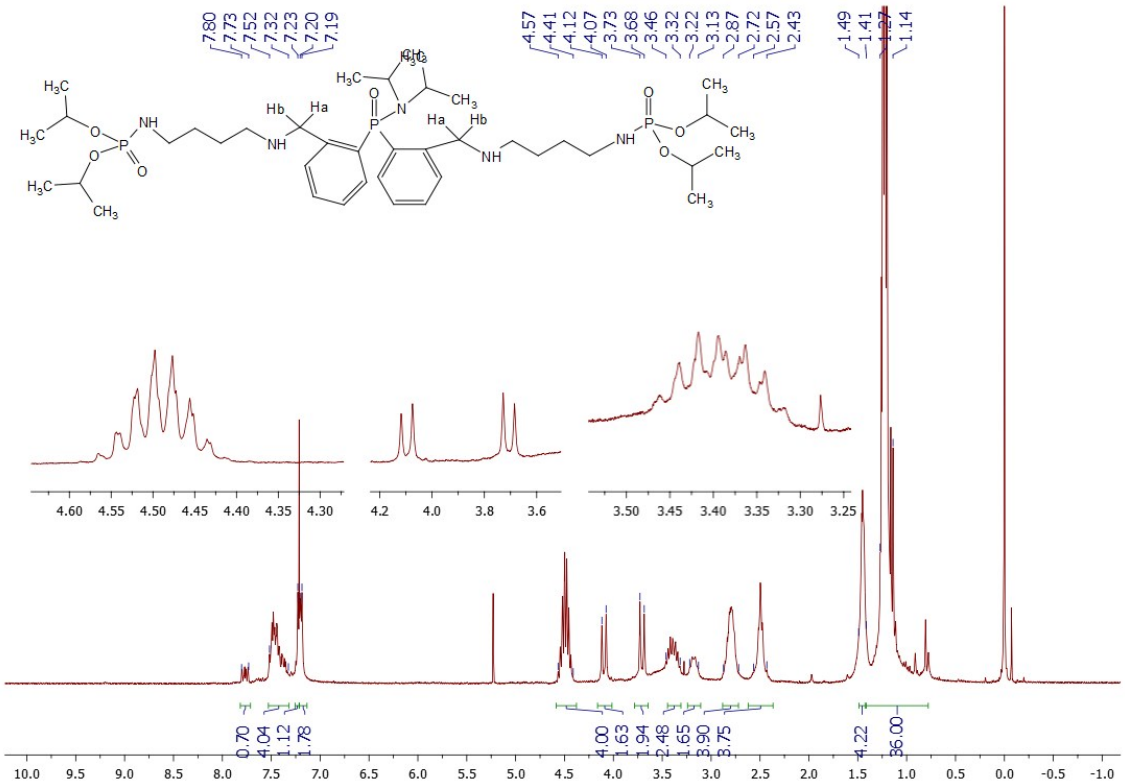
^{13}C NMR spectrum of **13a**



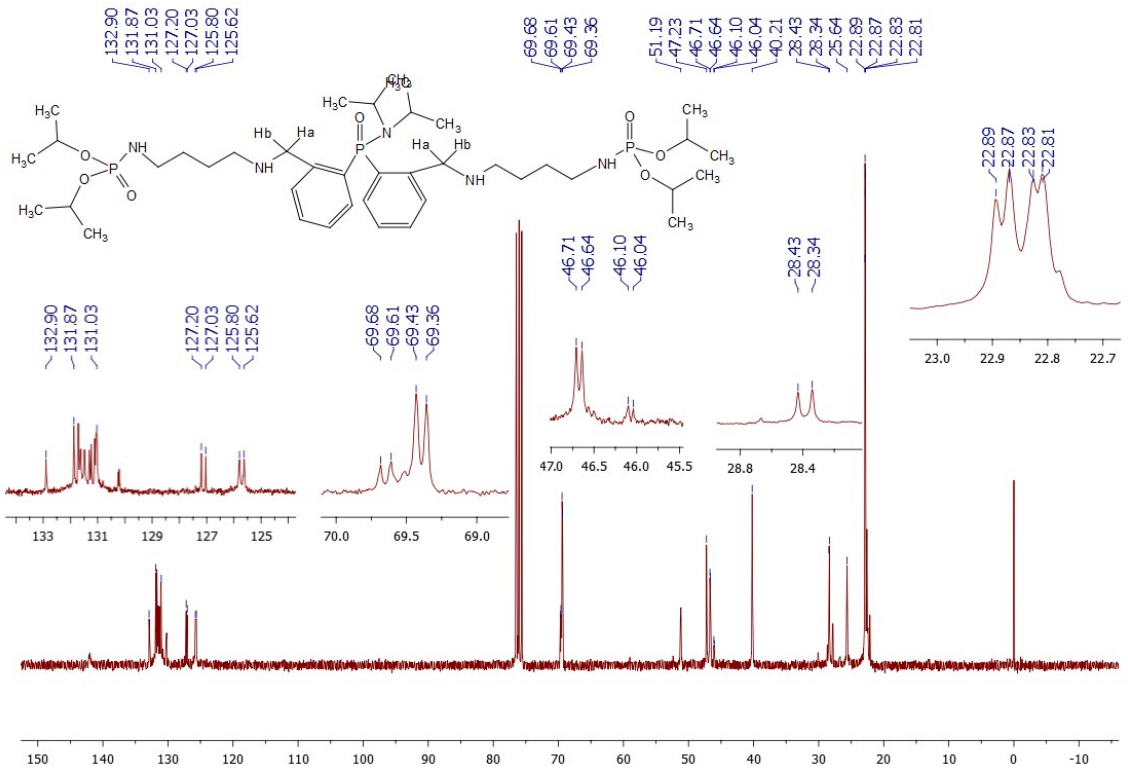
^{31}P NMR spectrum of **13a**



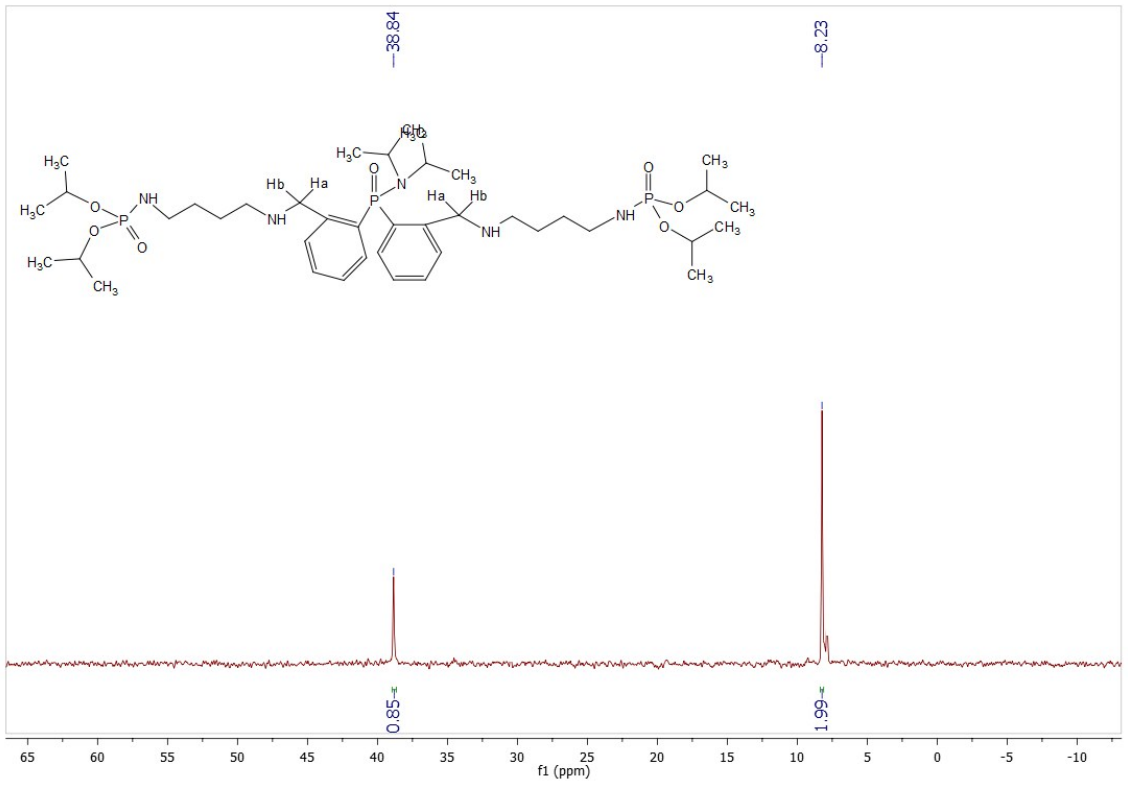
^{1}H NMR spectrum of **13b**



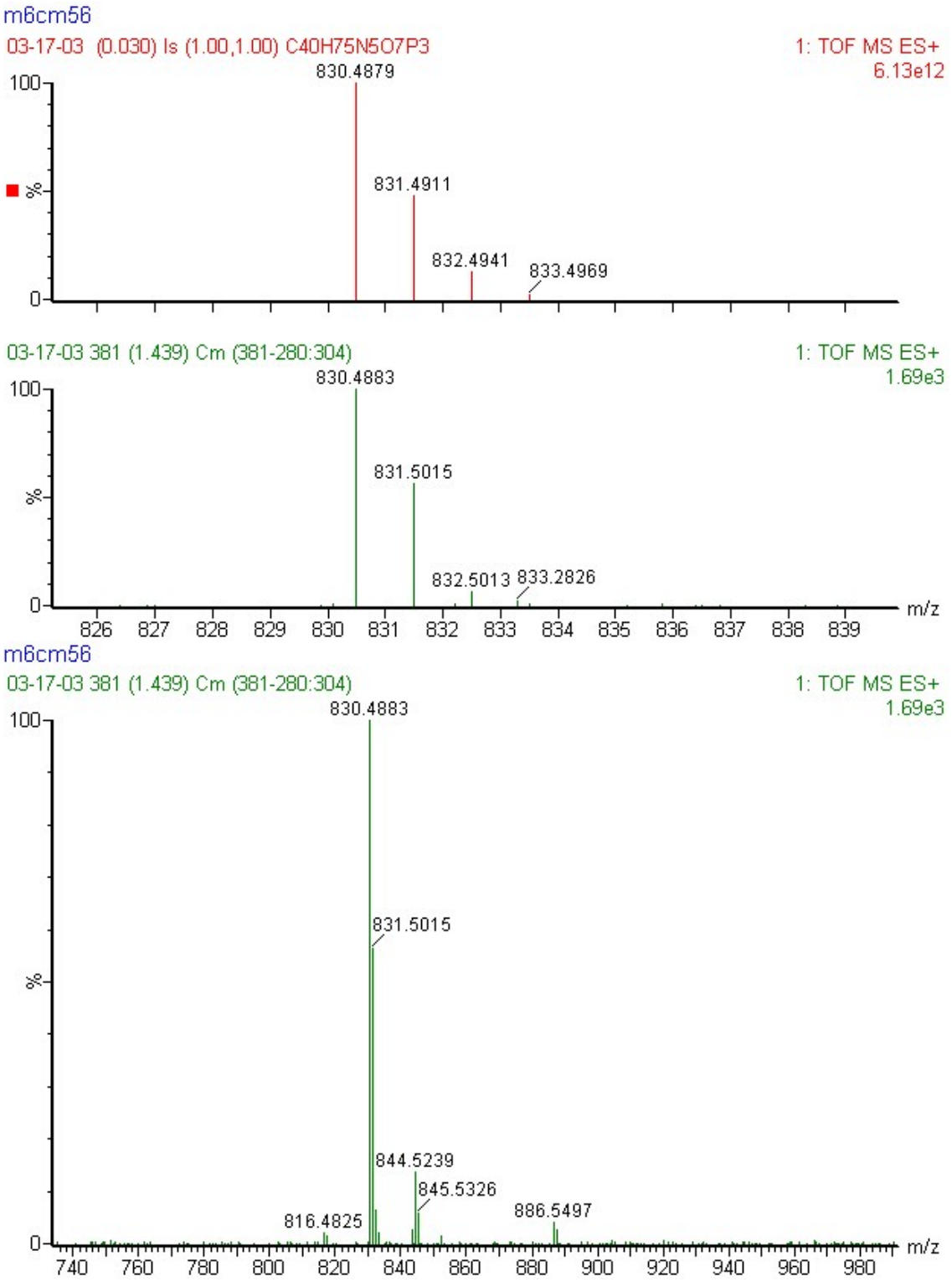
^{13}C NMR spectrum of **13b**



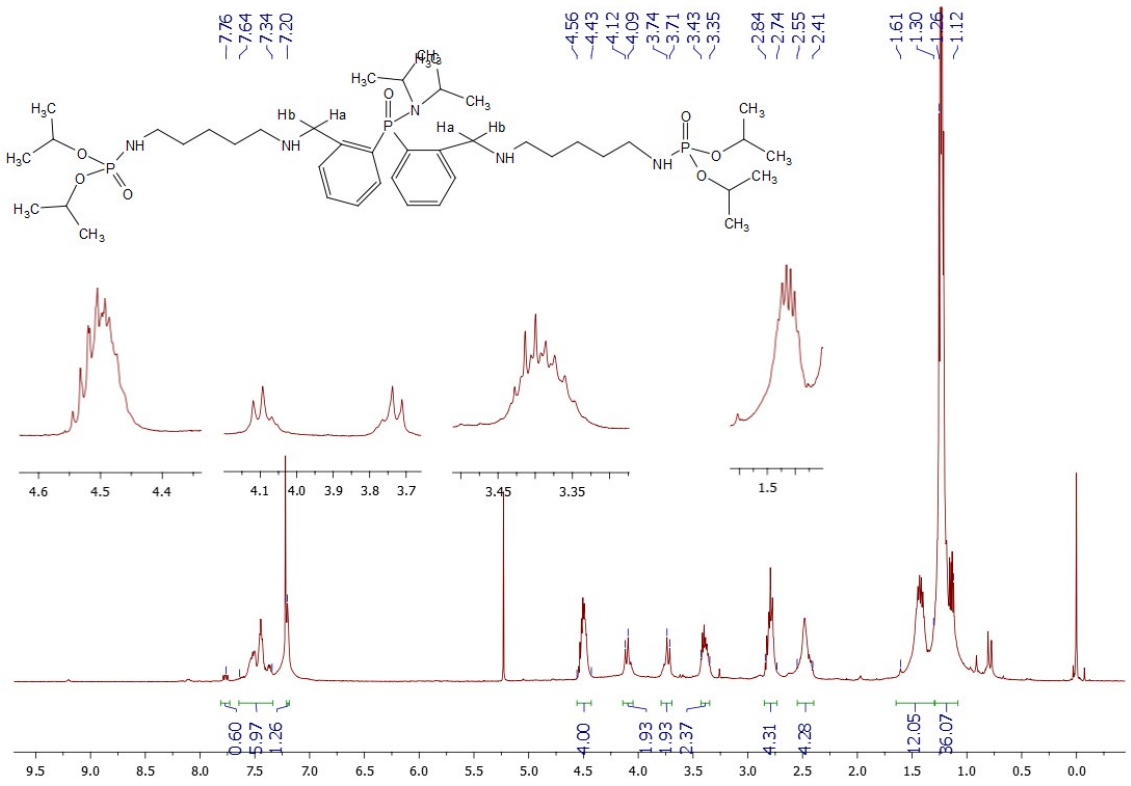
^{31}P NMR spectrum of **13b**



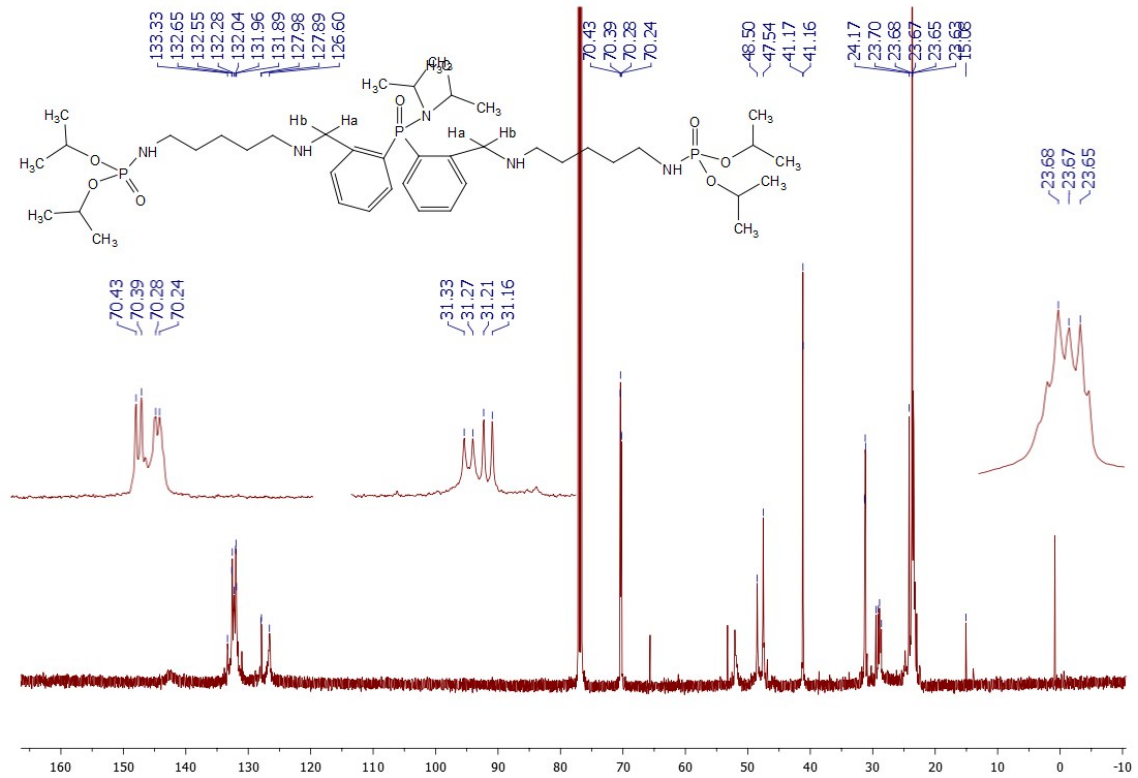
HRMS (ESI) spectrum of **13b**



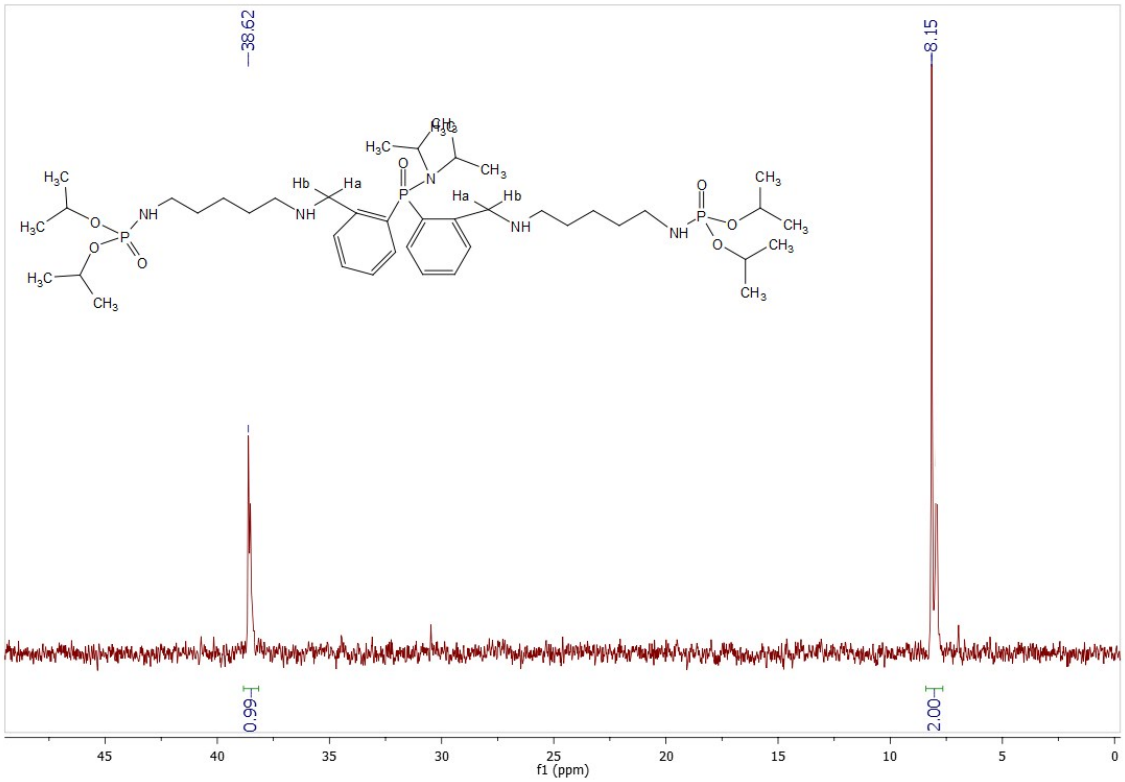
^{1}H NMR spectrum of **13c**



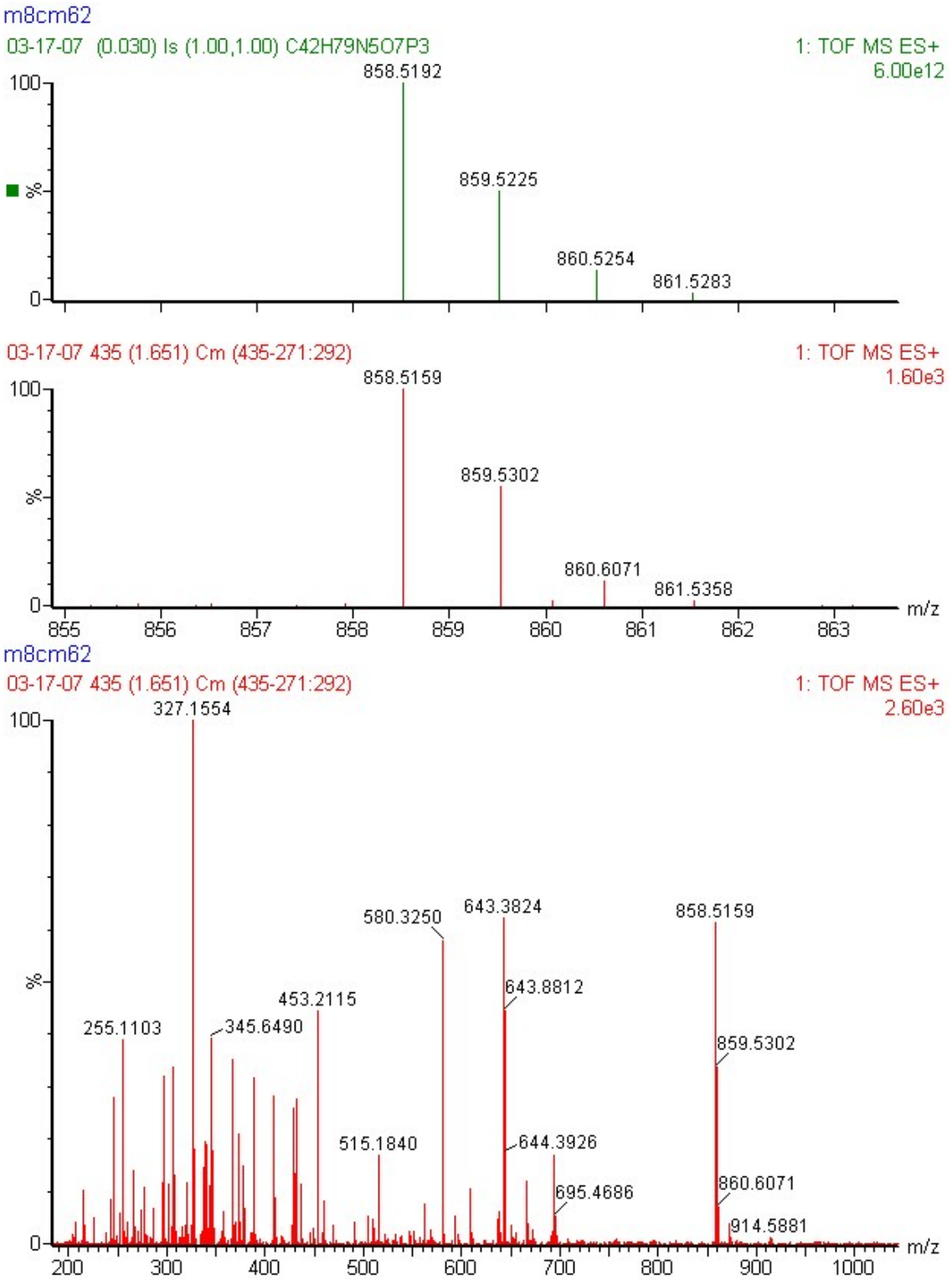
^{13}C NMR spectrum of **13c**



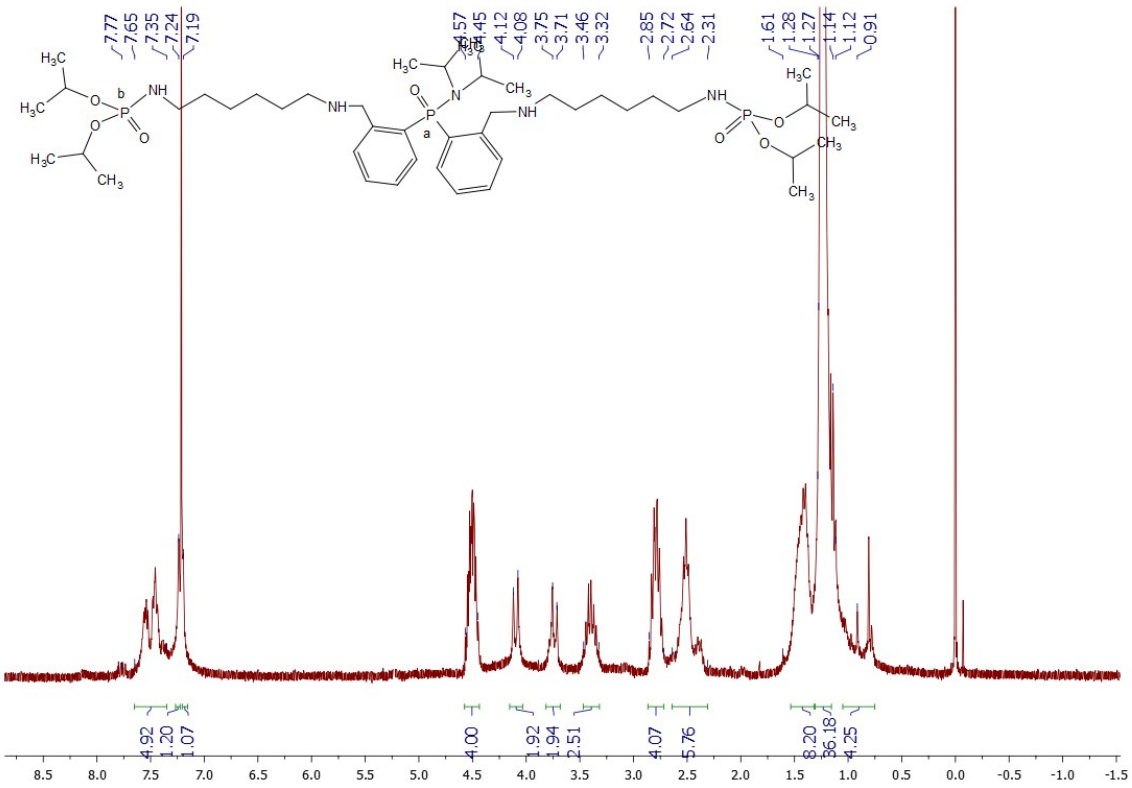
^{31}P NMR spectrum of **13c**



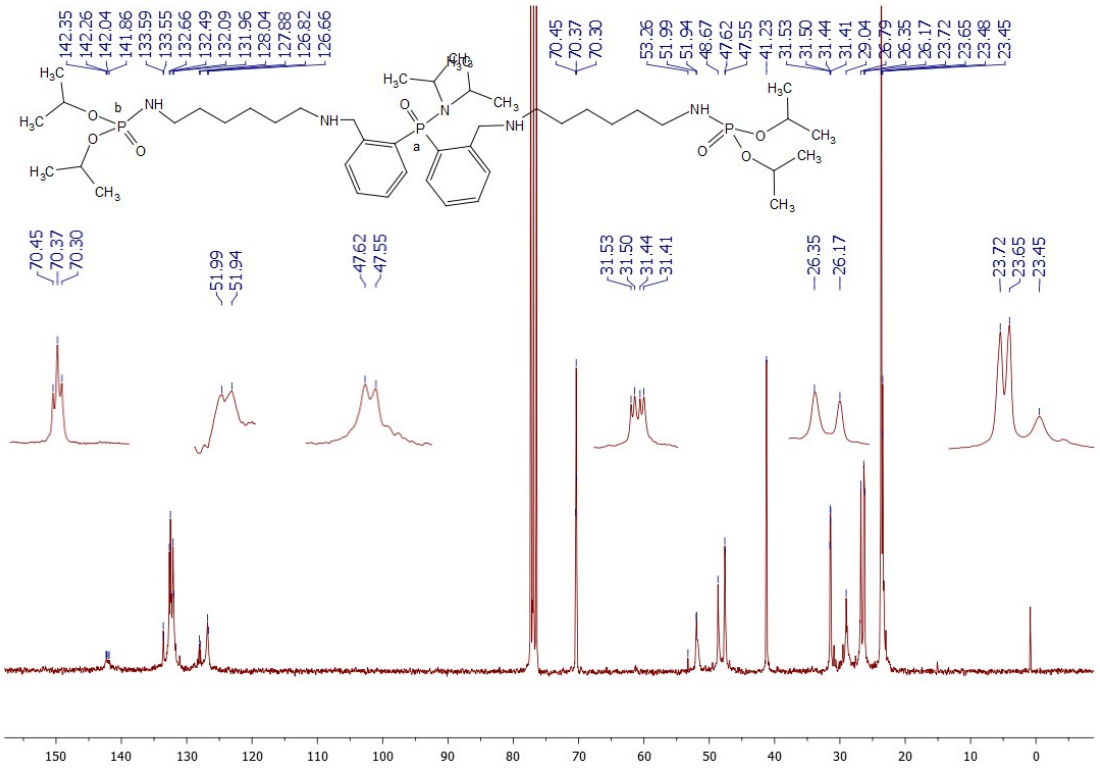
HRMS (ESI) spectrum of **13c**



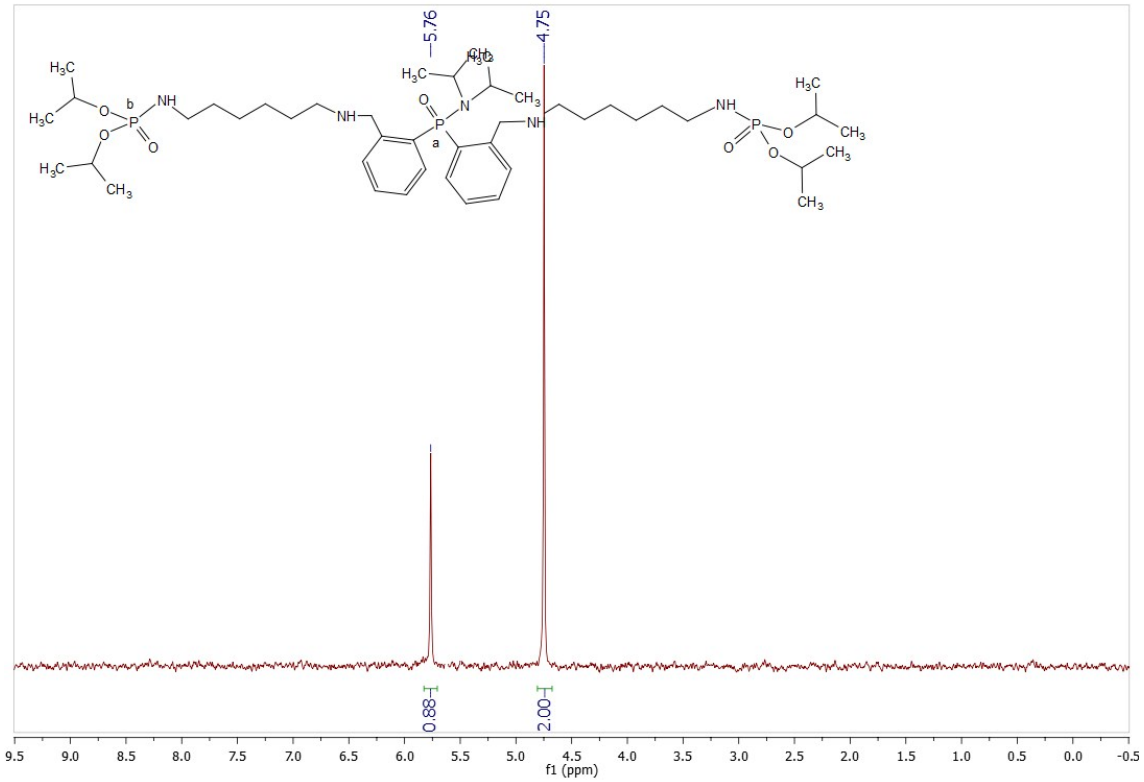
^{1}H NMR spectrum of **13d**



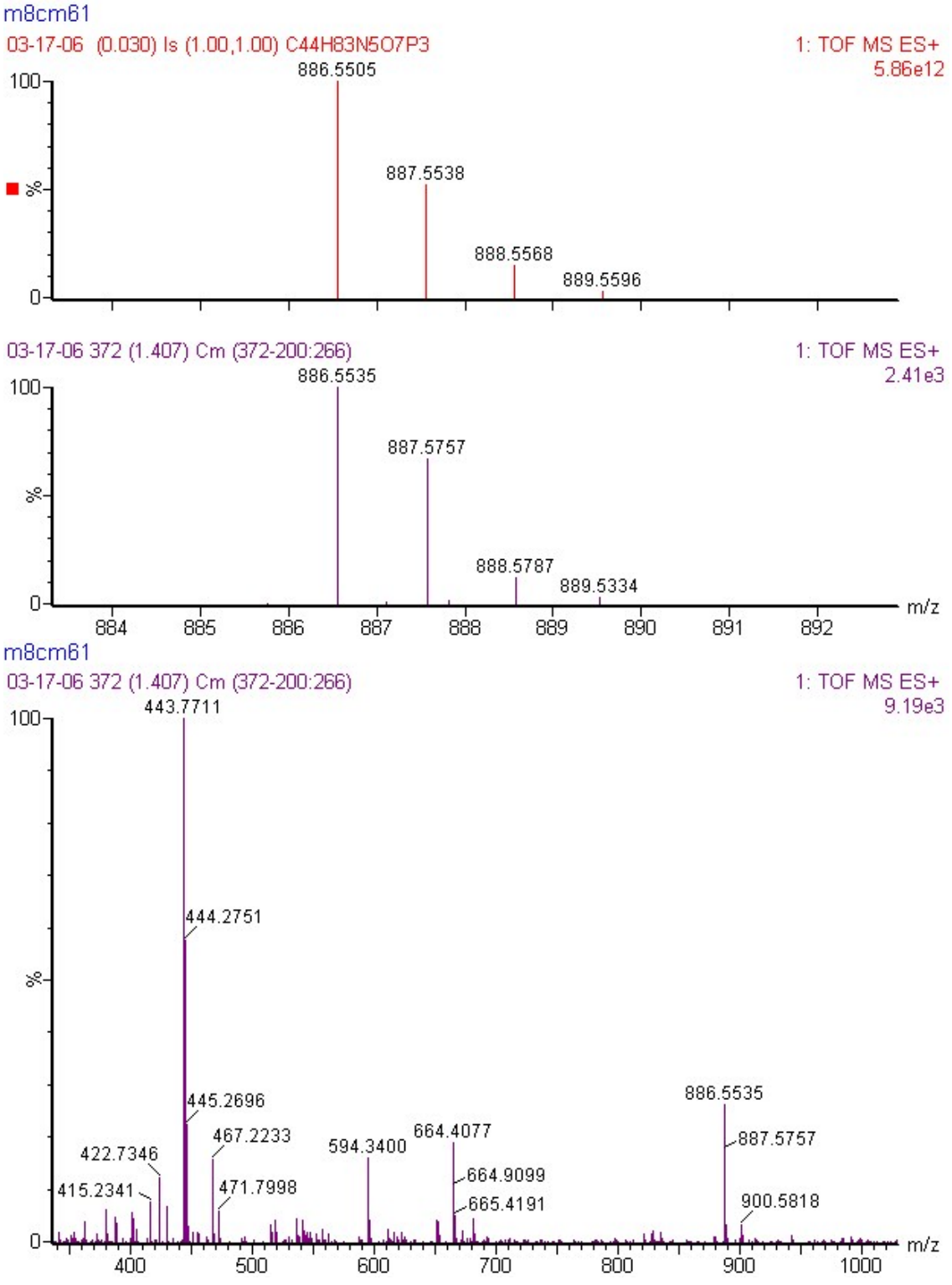
^{13}C NMR spectrum of **13d**



^{31}P NMR spectrum of **13d**

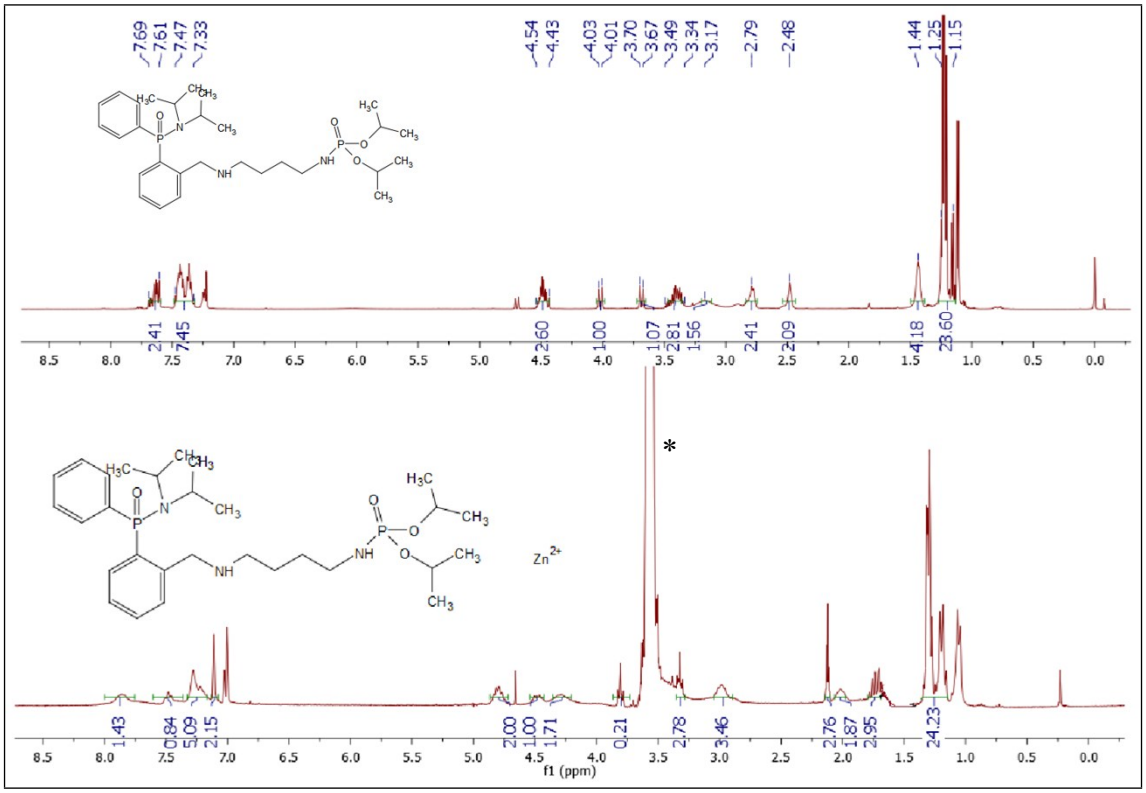


HRMS (ESI) spectrum of **13d**



Complexation data

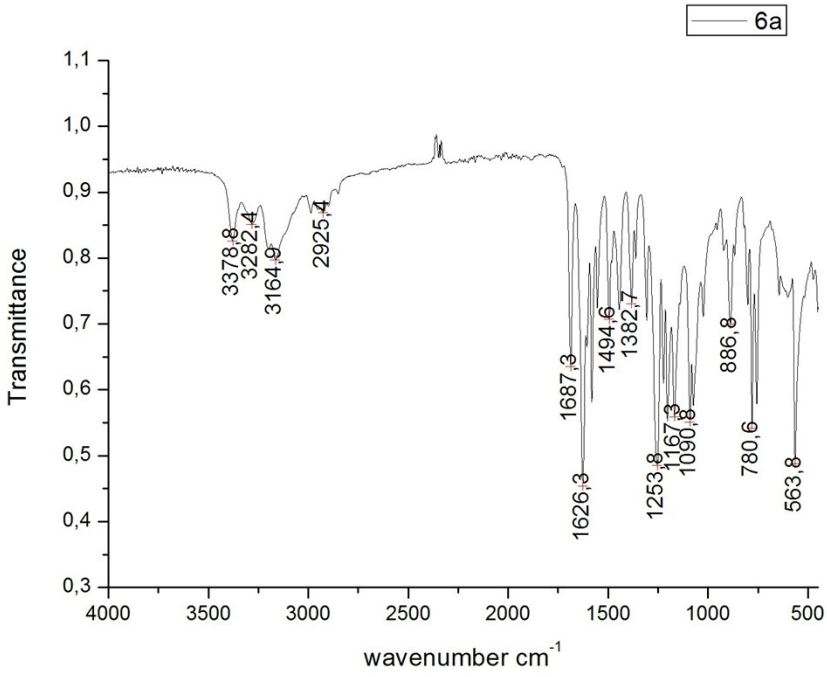
1) ^{1}H NMR spectra of **11b** and **11b**/$ZnCl_2$



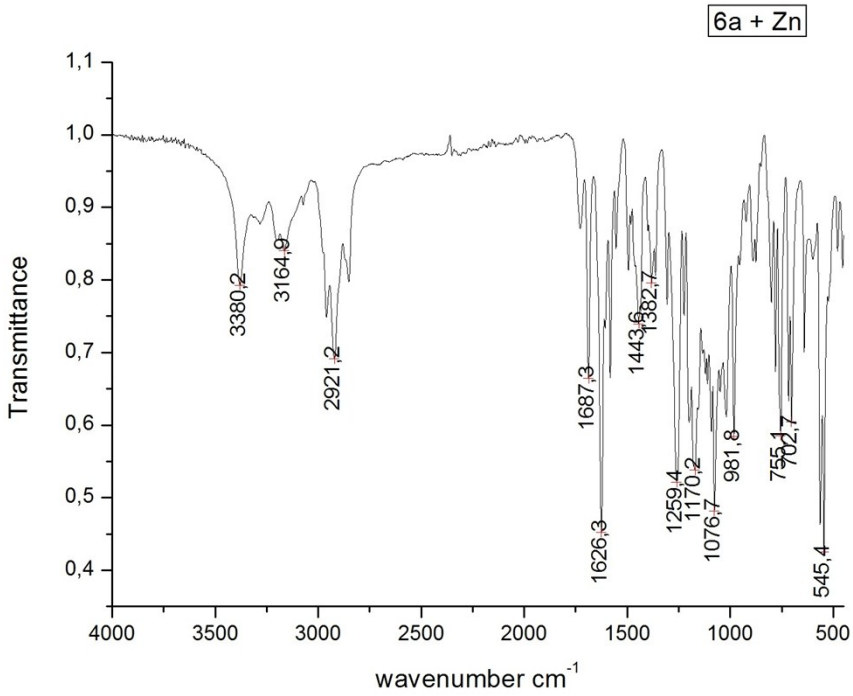
***from methanol**

2) IR spectra

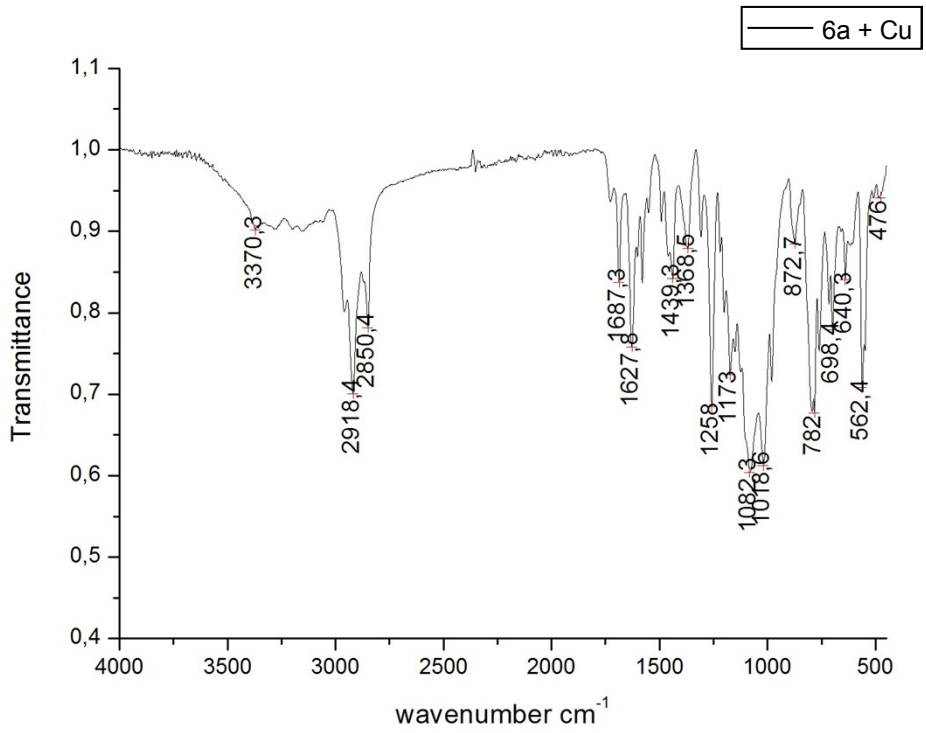
IR spectrum of **6a**



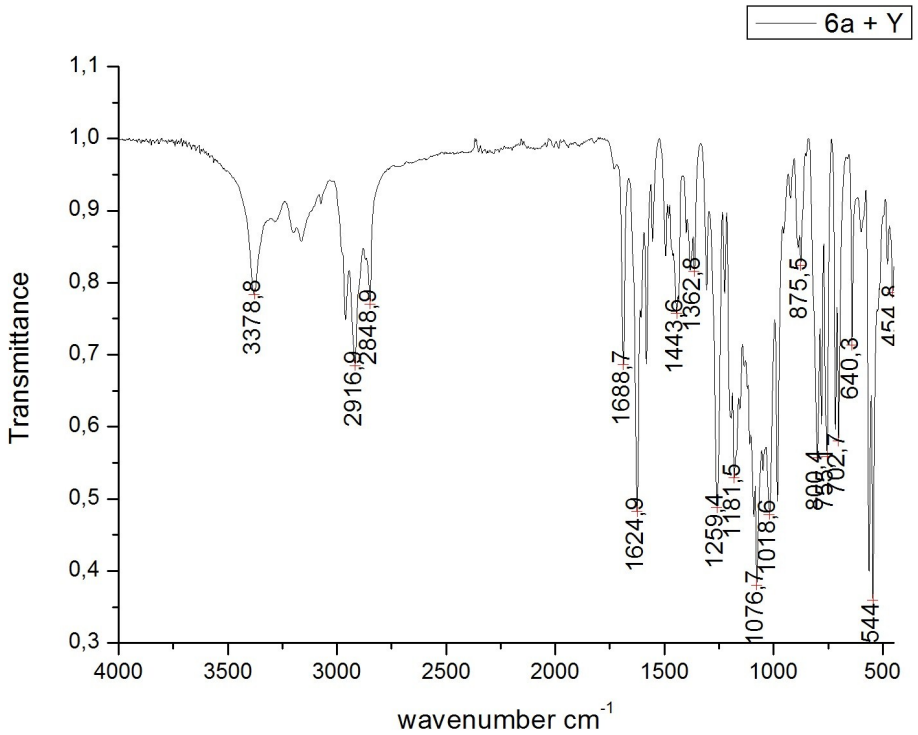
IR spectrum of **6a** in the presence of $ZnCl_2$



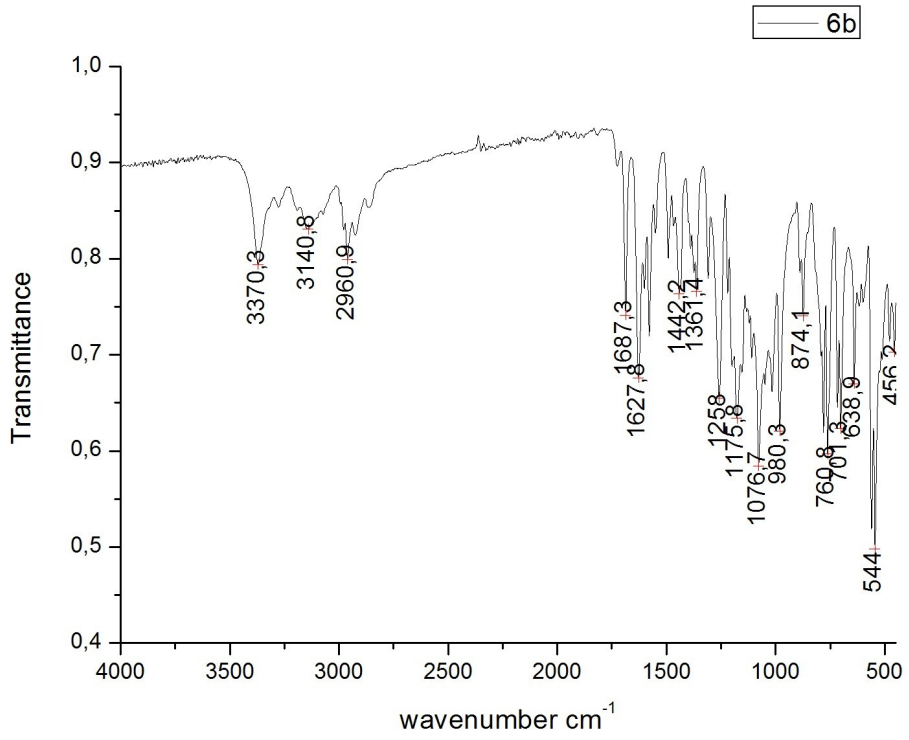
IR spectrum of **6a** in the presence of $CuSO_4$



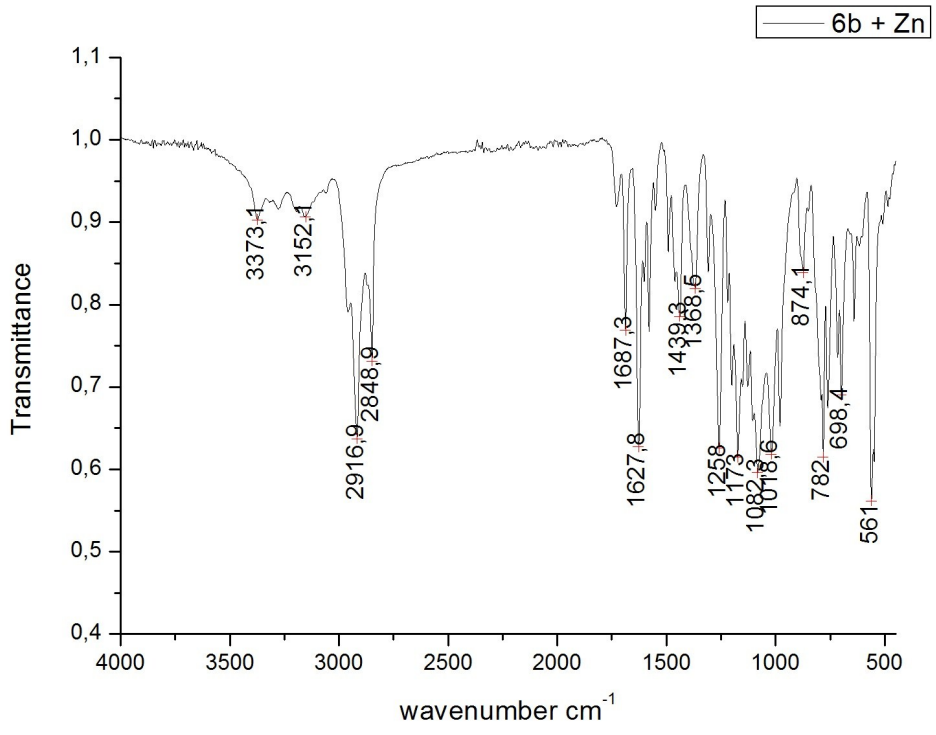
IR spectrum of **6a** in the presence of $Y(NO_3)_3$



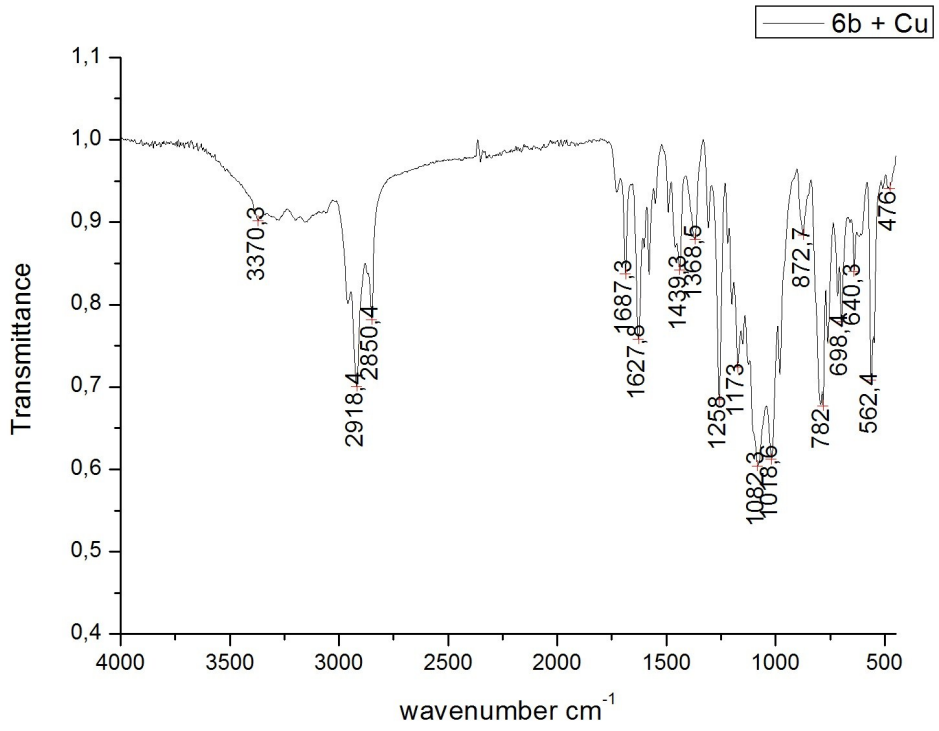
IR spectrum of **6b**



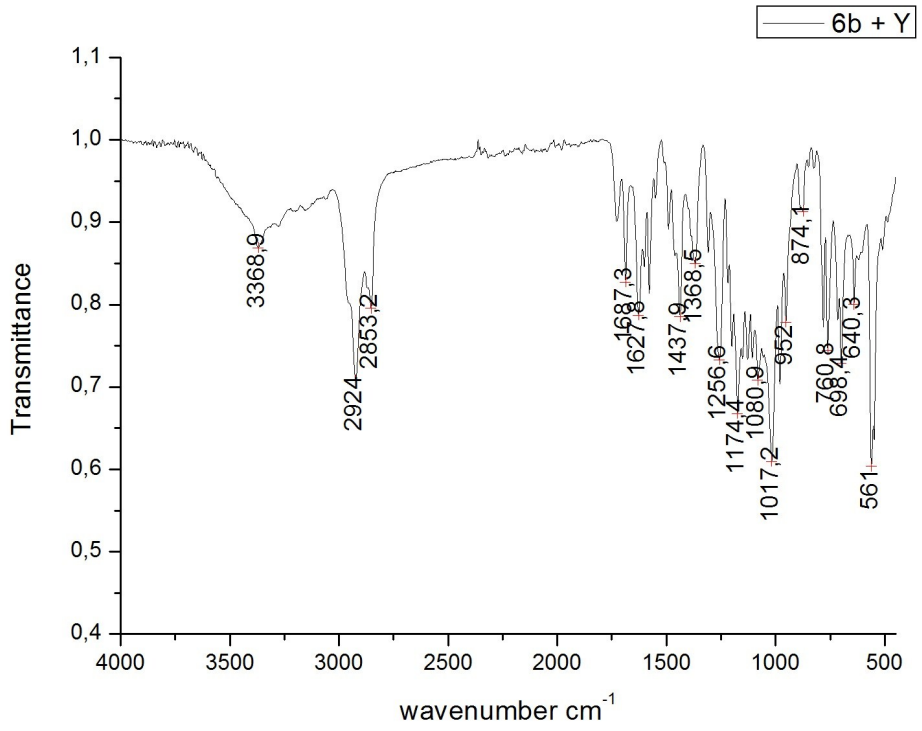
IR spectrum of **6b** in the presence of $ZnCl_2$



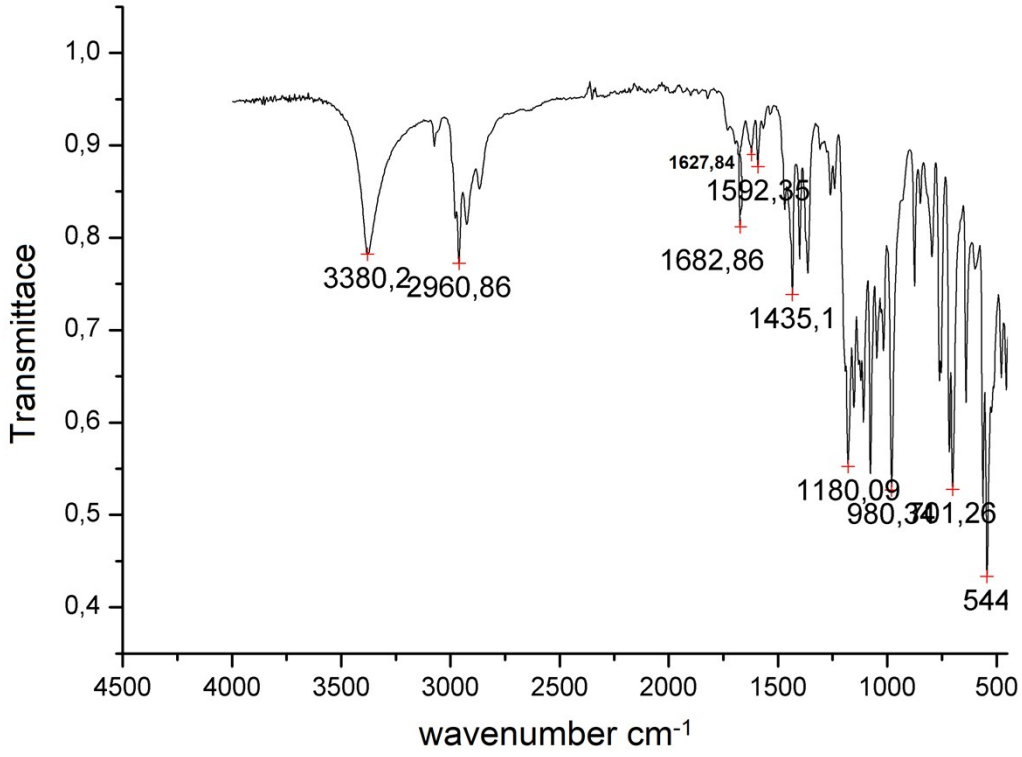
IR spectrum of **6b** in the presence of $CuSO_4$



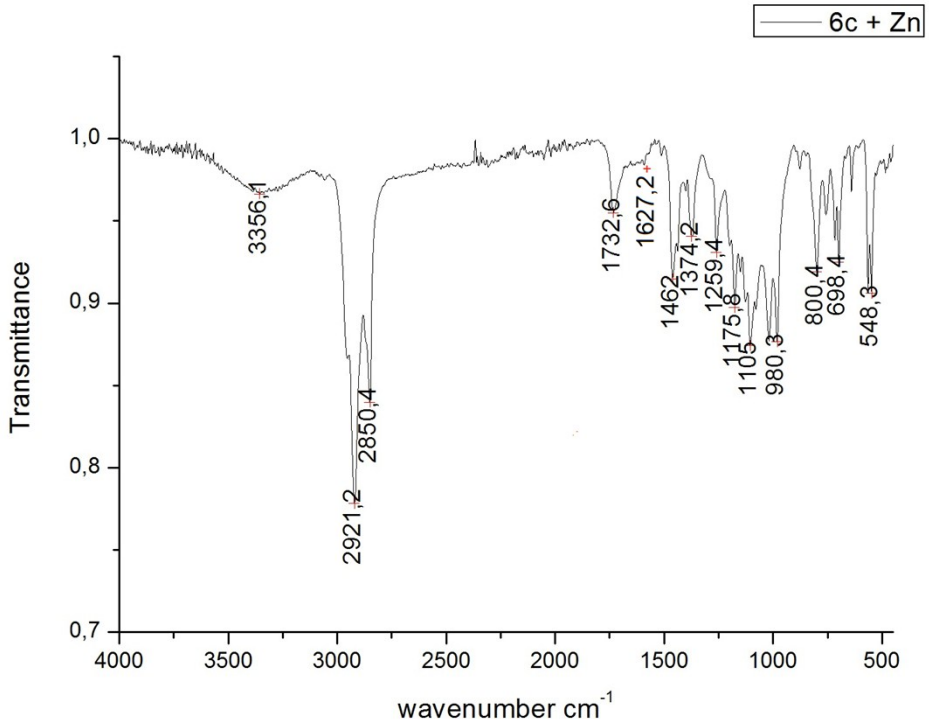
IR spectrum of **6b** in the presence of $Y(NO_3)_3$



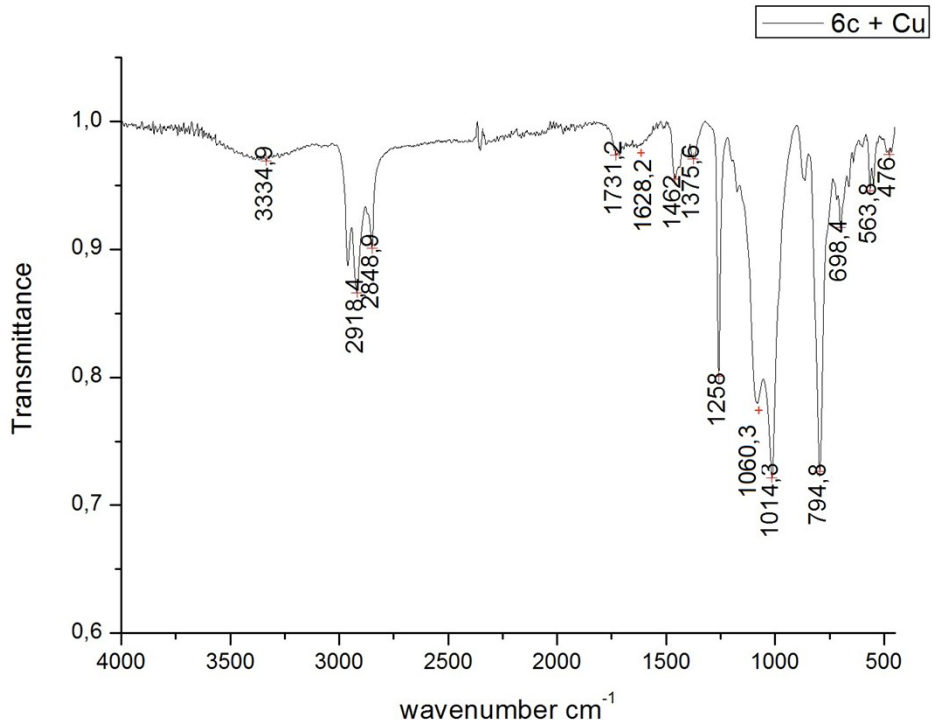
IR spectrum of **6c**



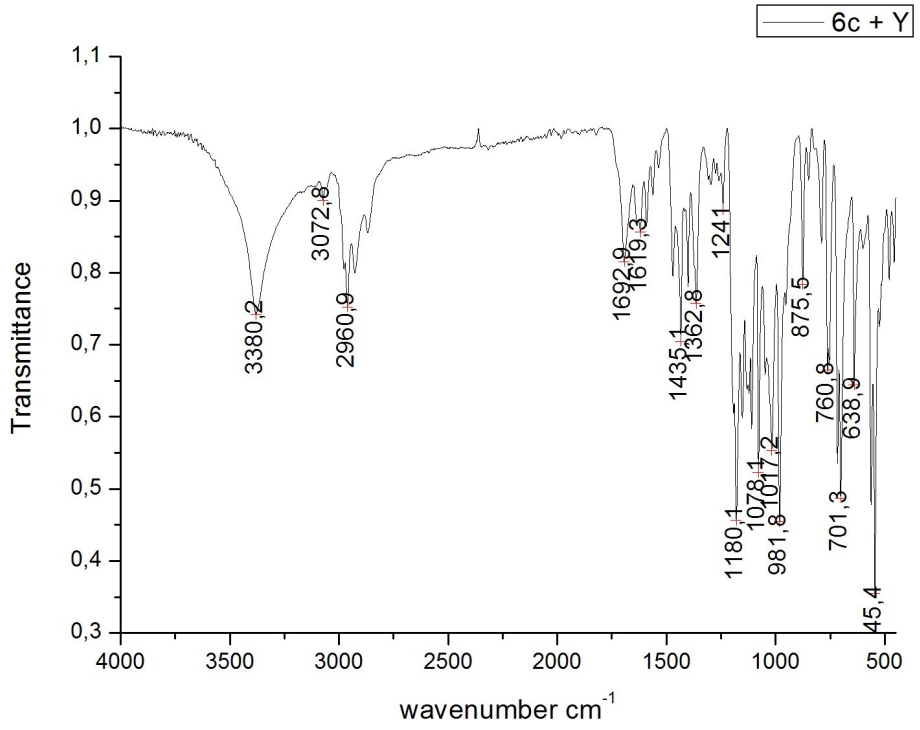
IR spectrum of **6c** in the presence of $ZnCl_2$



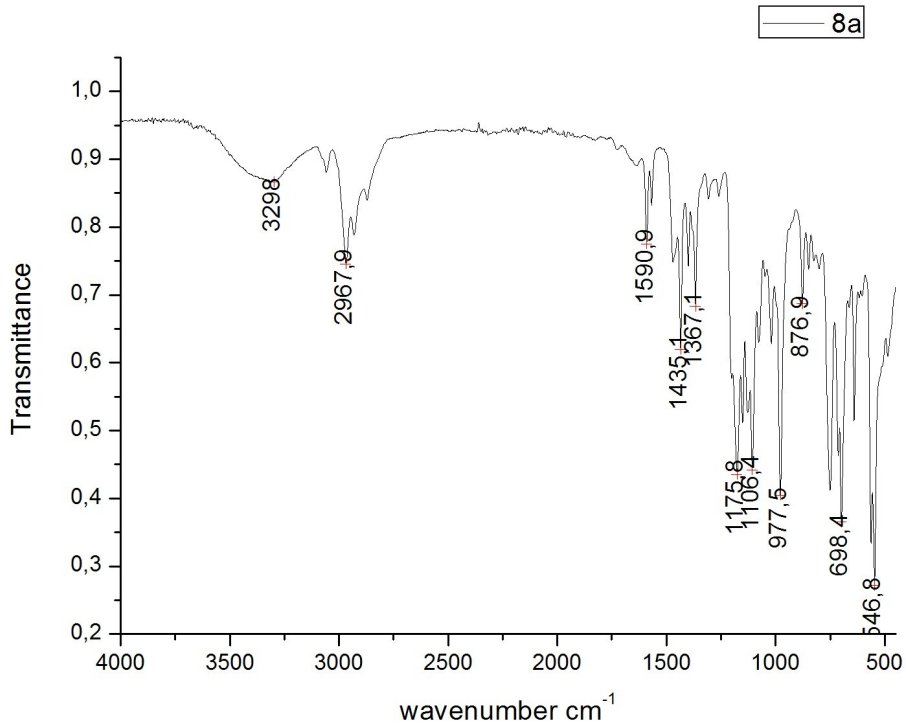
IR spectrum of **6c** in the presence of $CuSO_4$



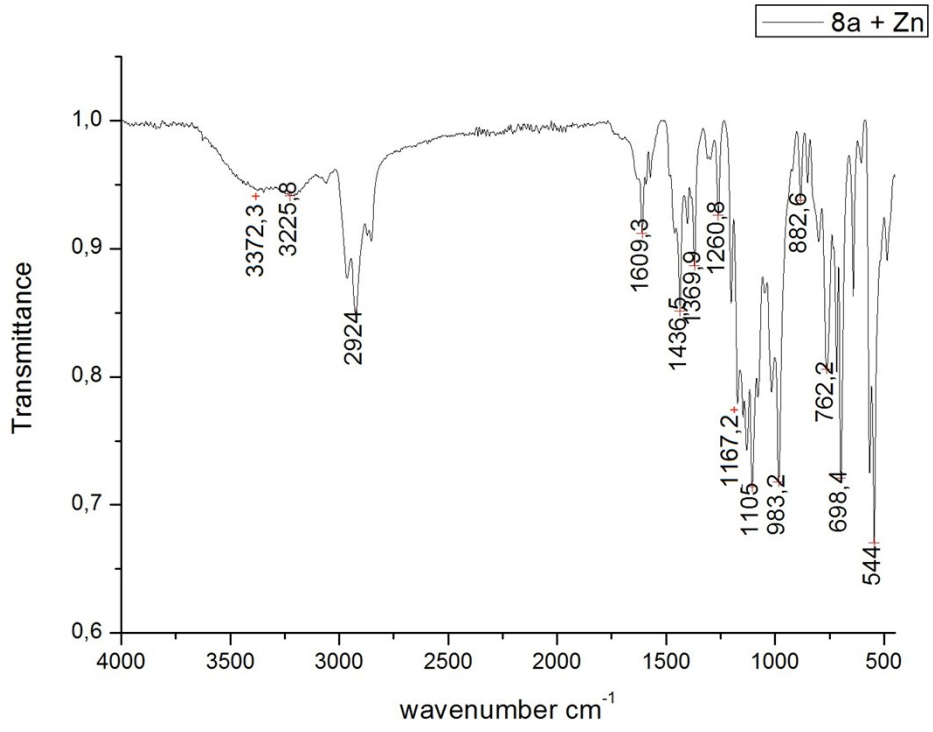
IR spectrum of **6c** in the presence of $Y(NO_3)_3$



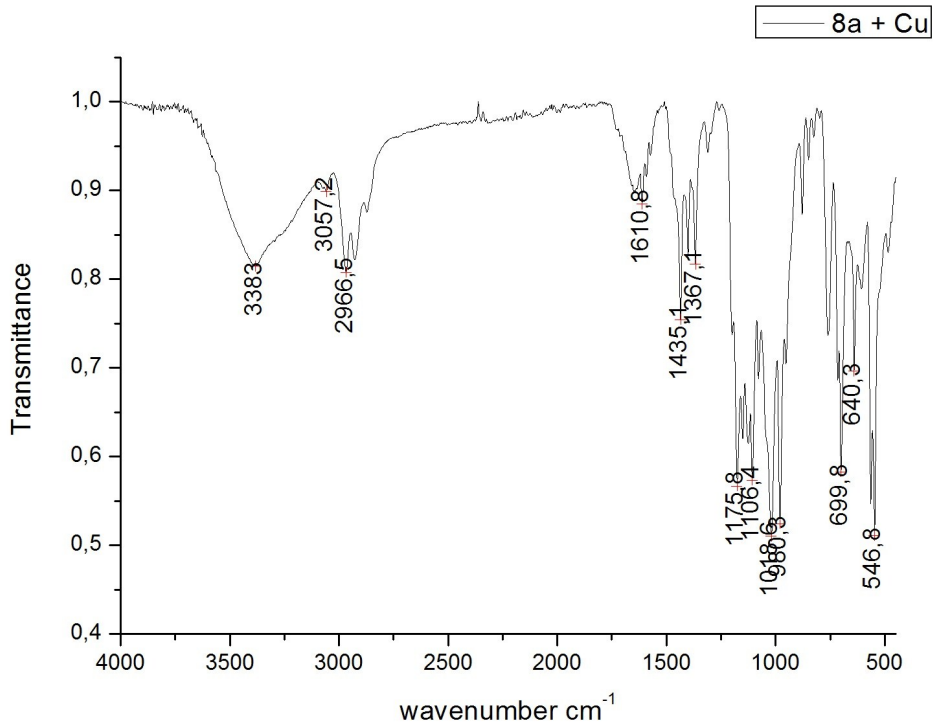
IR spectrum of **8a**



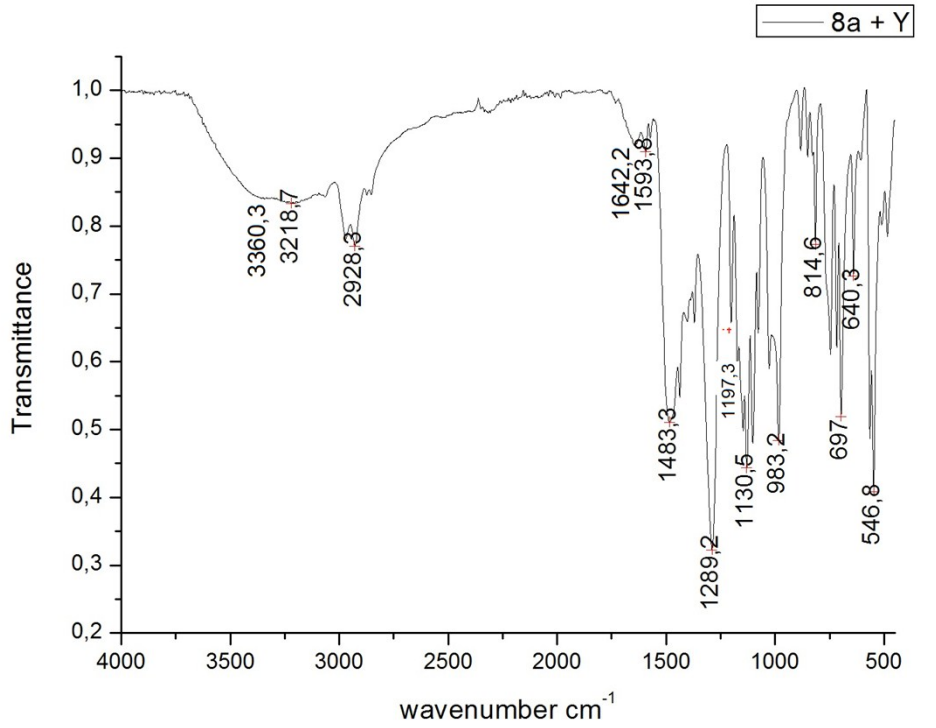
IR spectrum of **8a** in the presence of $ZnCl_2$



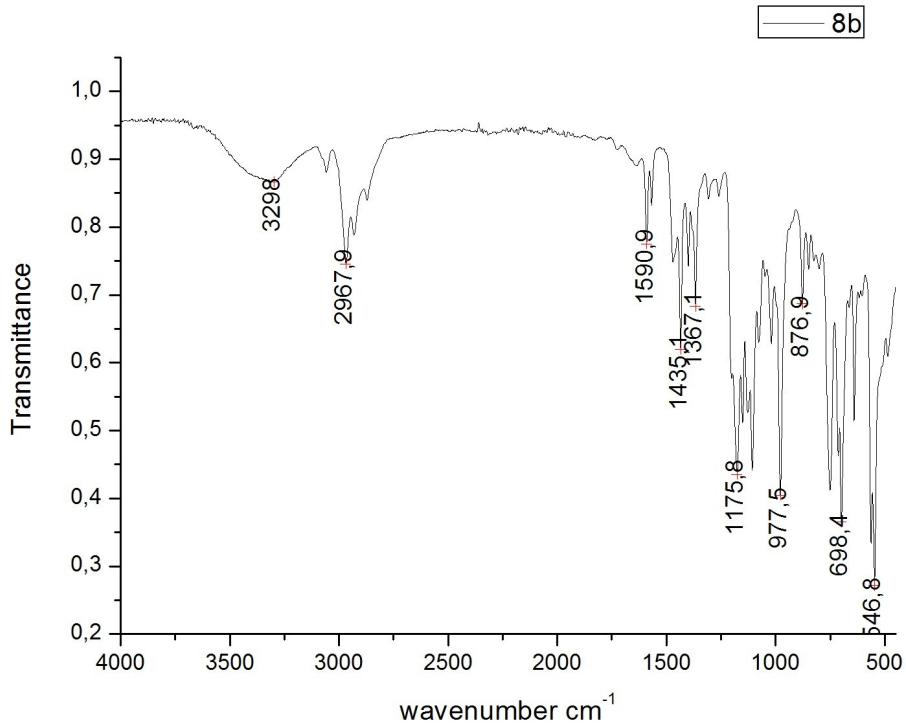
IR spectrum of **8a** in the presence of $CuSO_4$



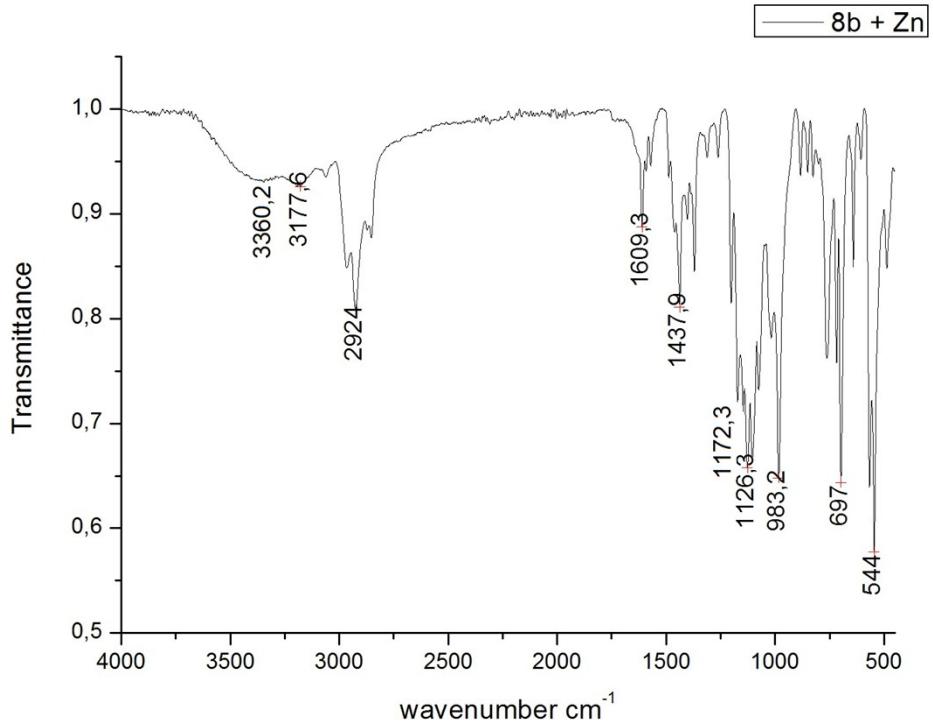
IR spectrum of **8a** in the presence of $Y(NO_3)_3$



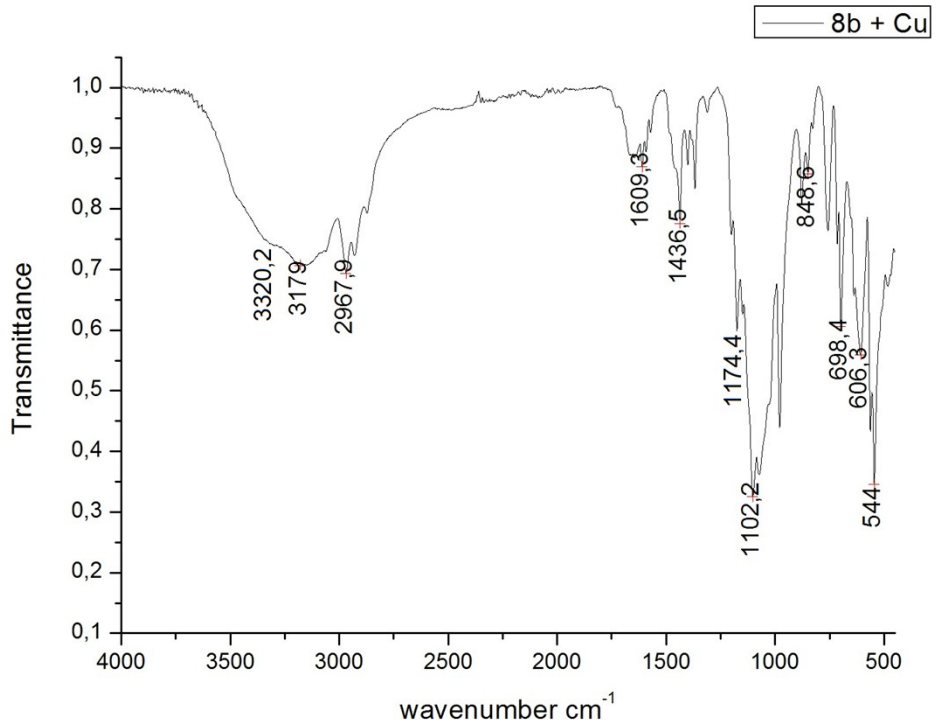
IR spectrum of **8b**



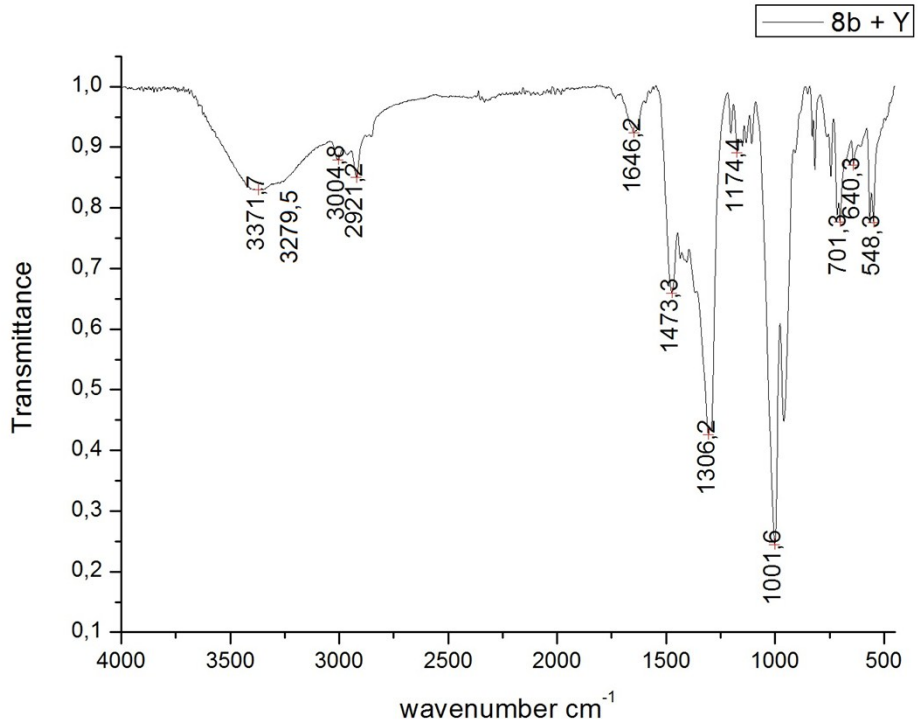
IR spectrum of **8b** in the presence of $ZnCl_2$



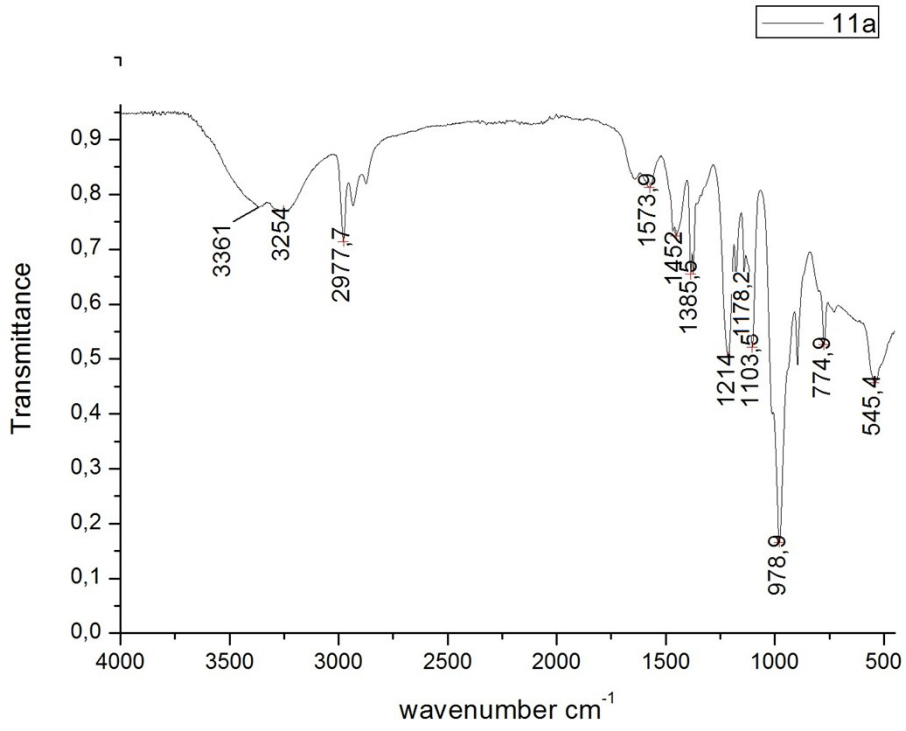
IR spectrum of **8b** in the presence of $CuSO_4$



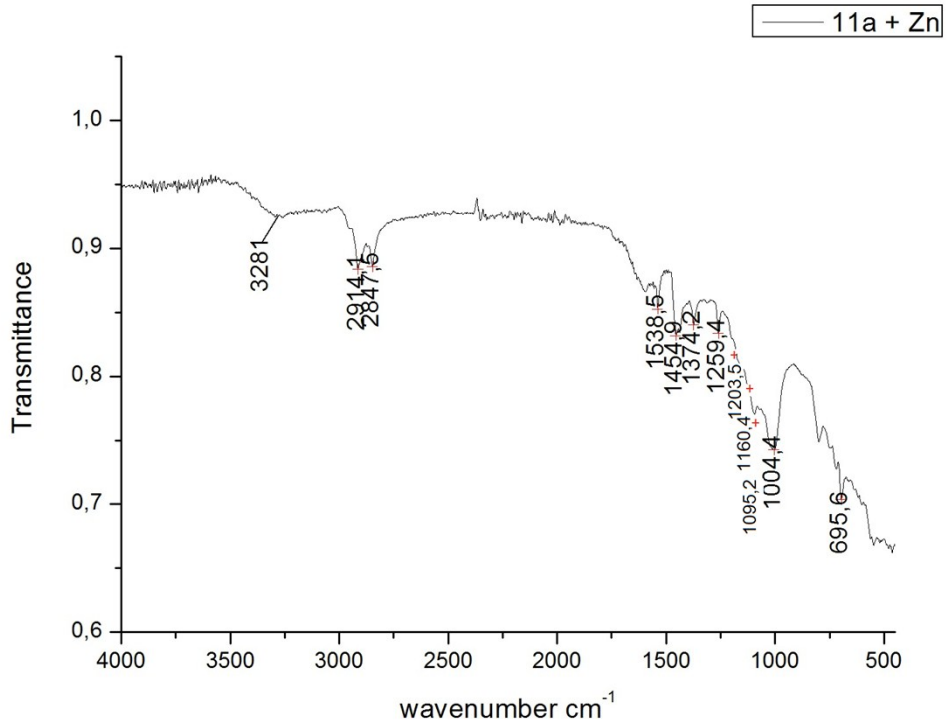
IR spectrum of **8b** in the presence of $Y(NO_3)_3$



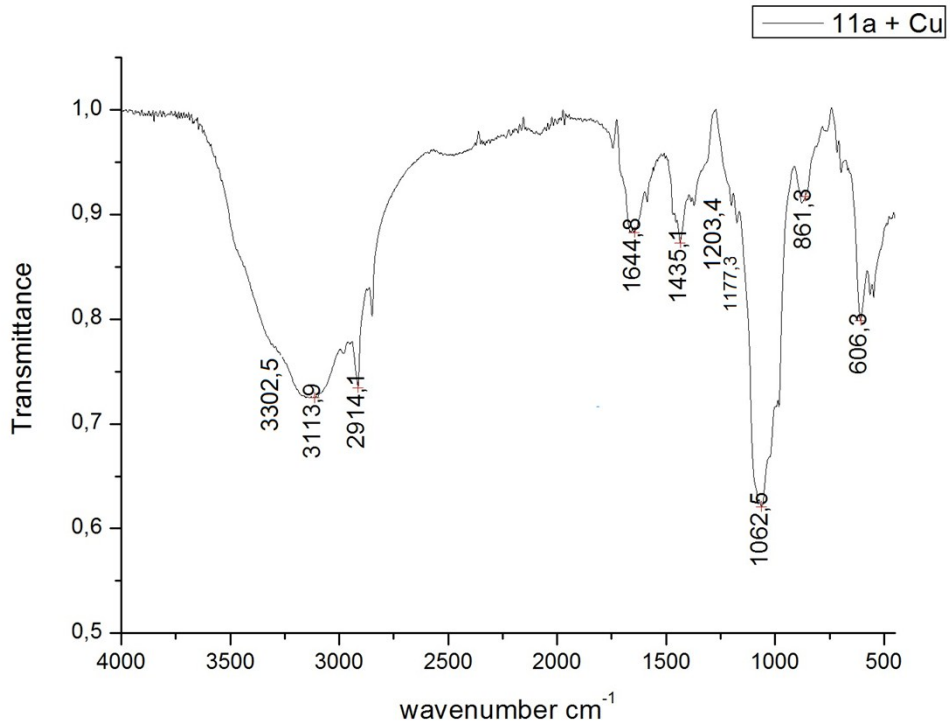
IR spectrum of **11a**



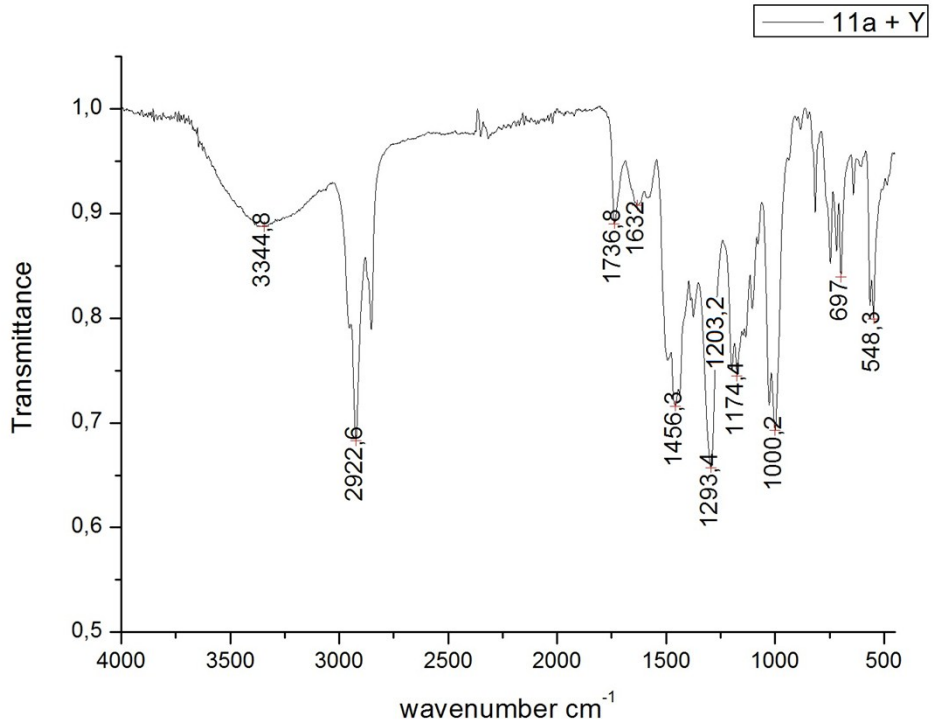
IR spectrum of **11a** in the presence of $ZnCl_2$



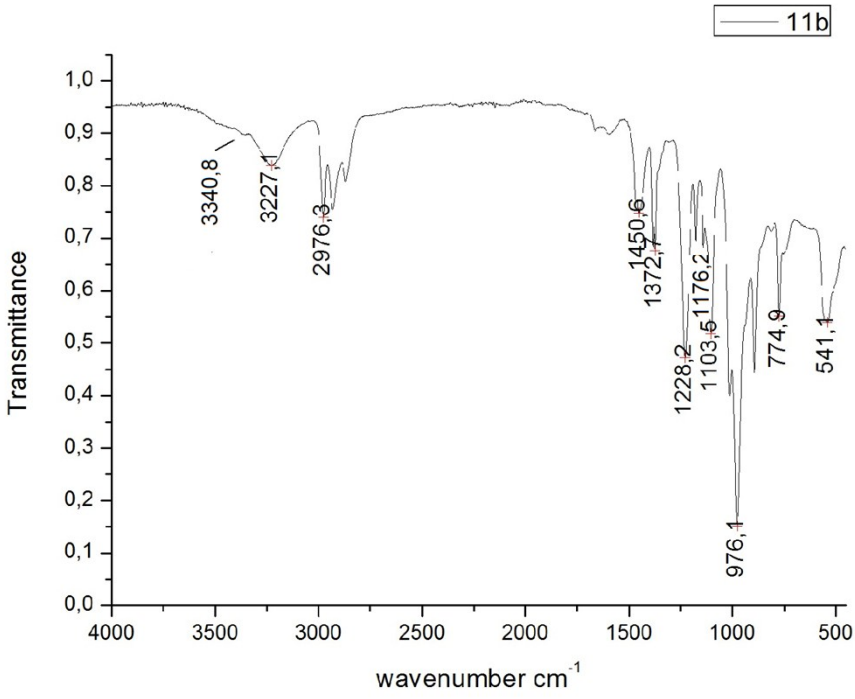
IR spectrum of **11a** in the presence of $CuSO_4$



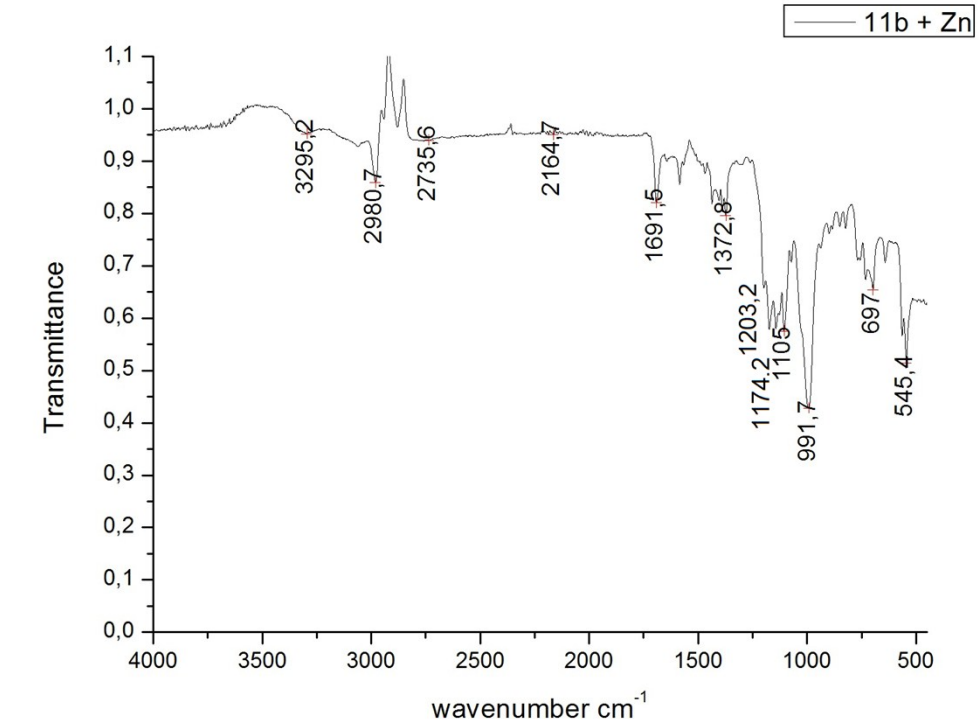
IR spectrum of **11a** in the presence of $Y(NO_3)_3$



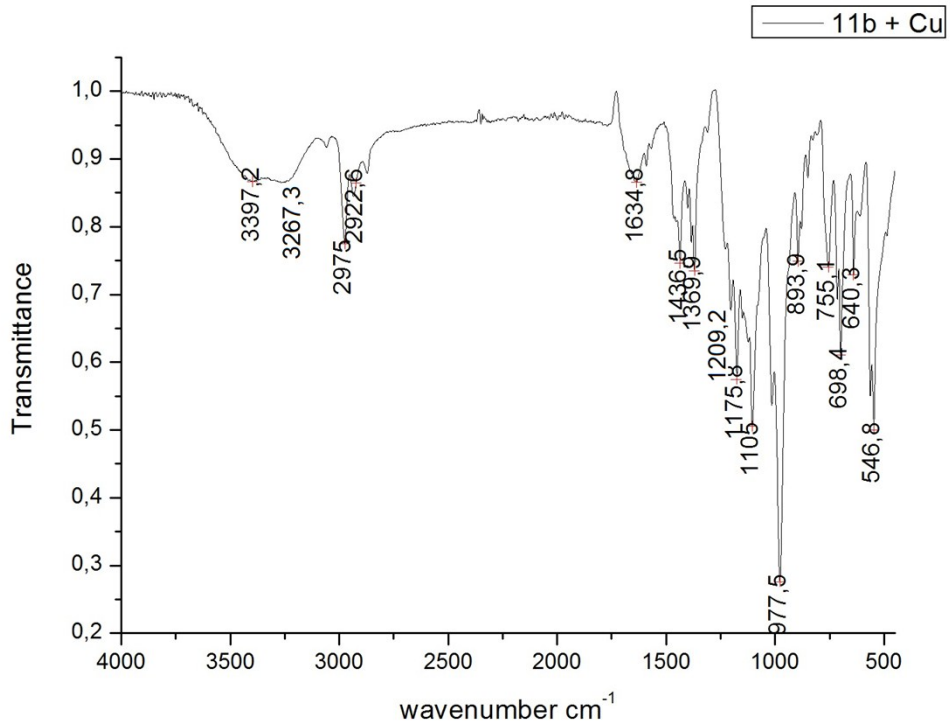
IR spectrum of **11b**



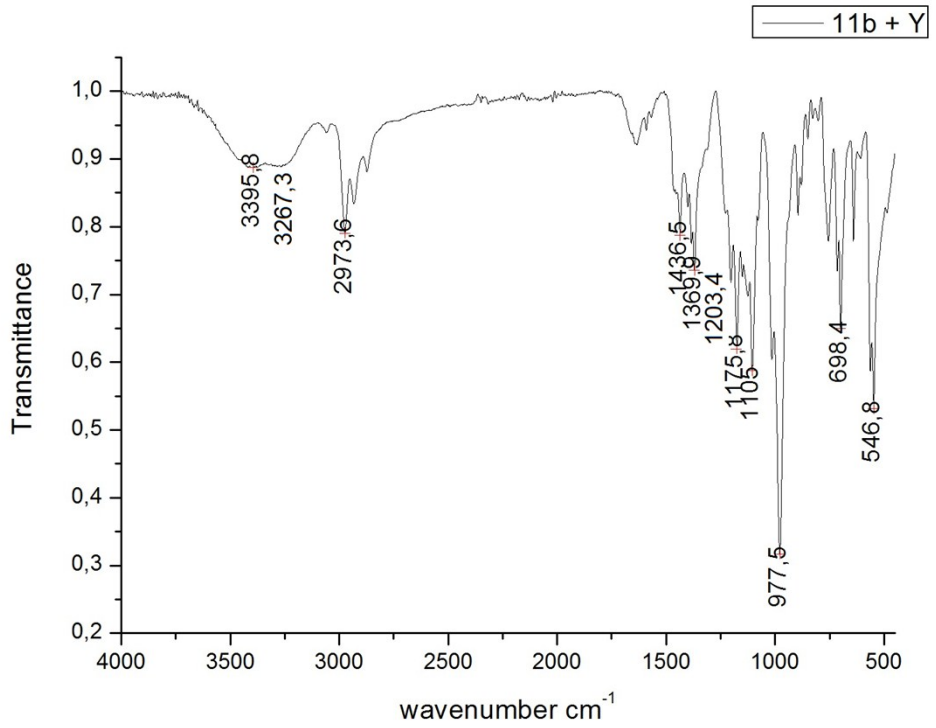
IR spectrum of **11b** in the presence of $ZnCl_2$



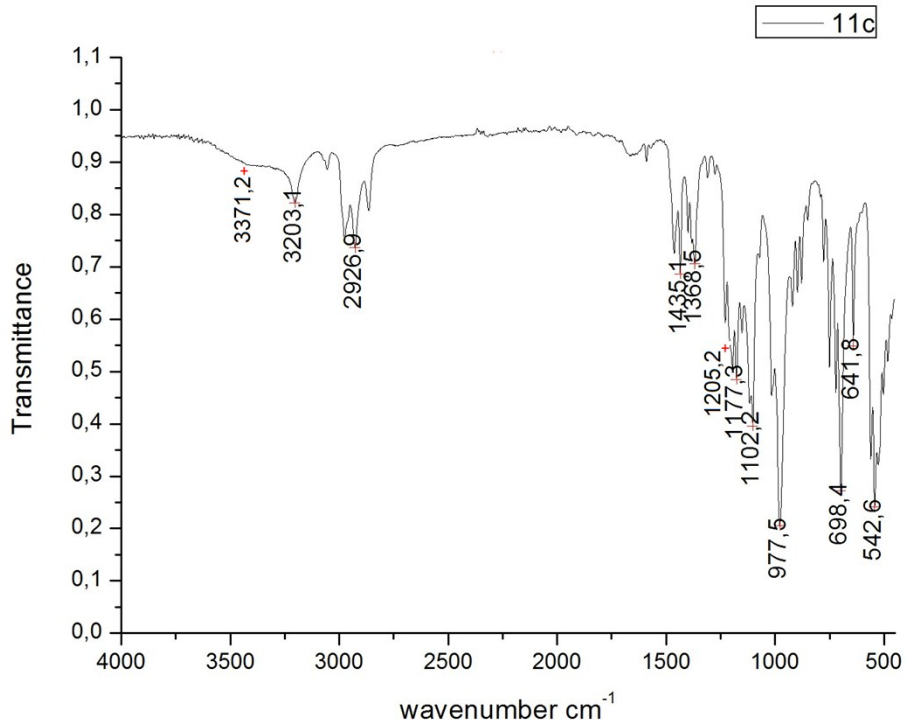
IR spectrum of **11b** in the presence of $CuSO_4$



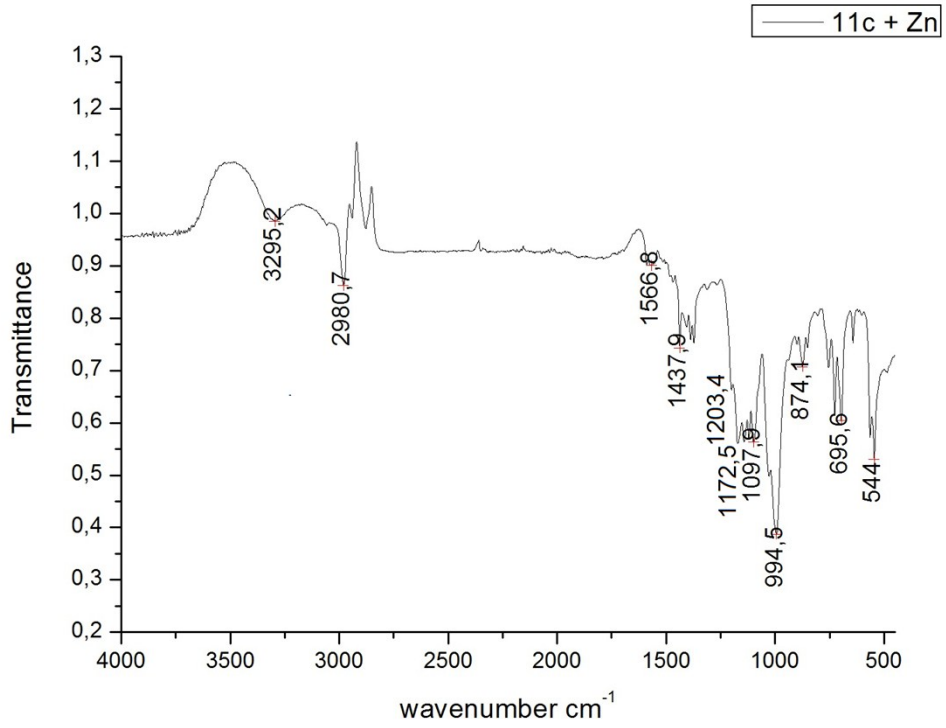
IR spectrum of **11b** in the presence of $Y(NO_3)_3$



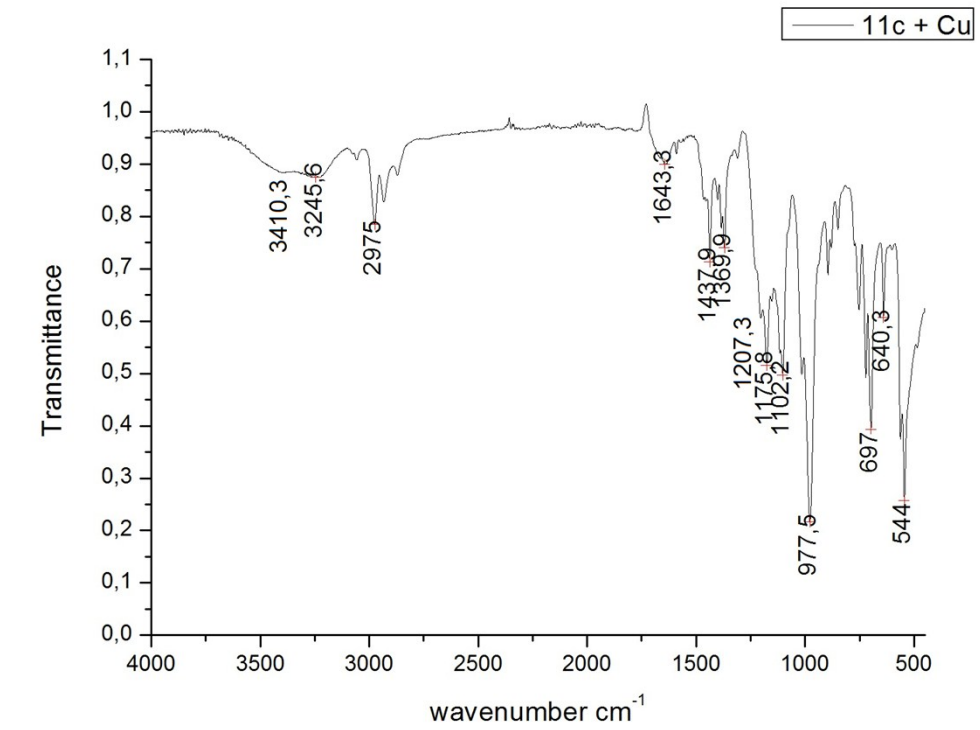
IR spectrum of **11c**



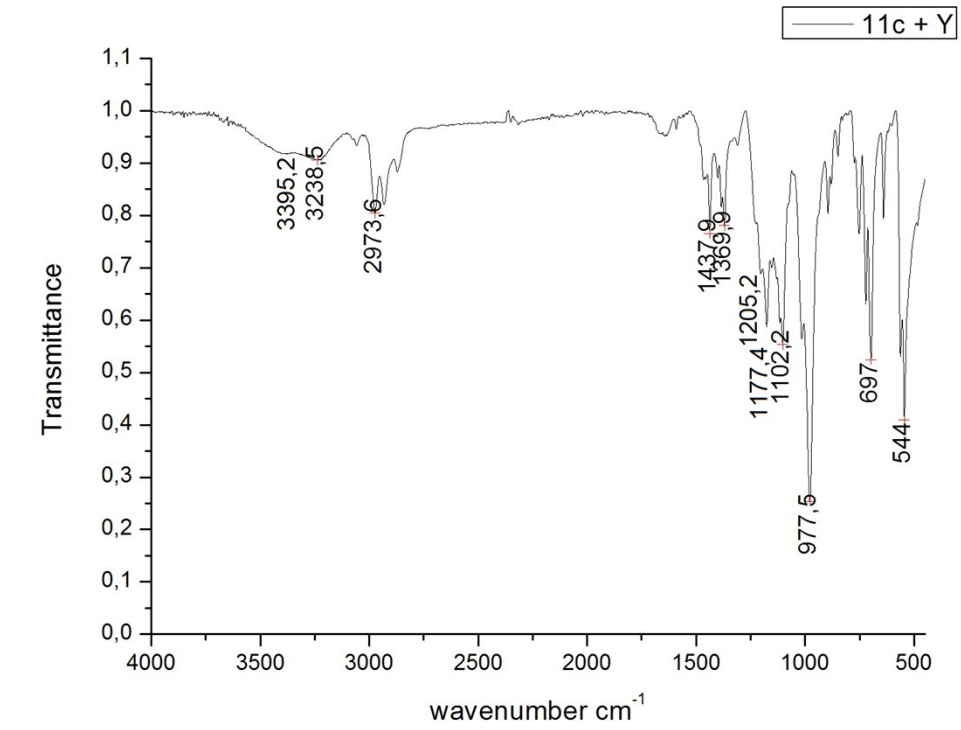
IR spectrum of **11c** in the presence of $ZnCl_2$



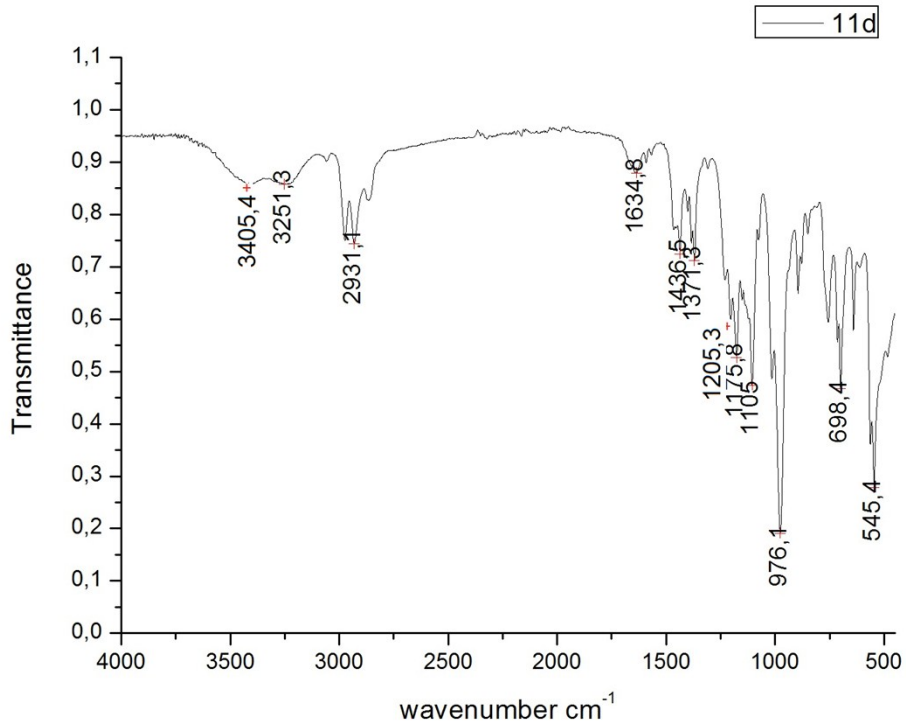
IR spectrum of **11c** in the presence of $CuSO_4$



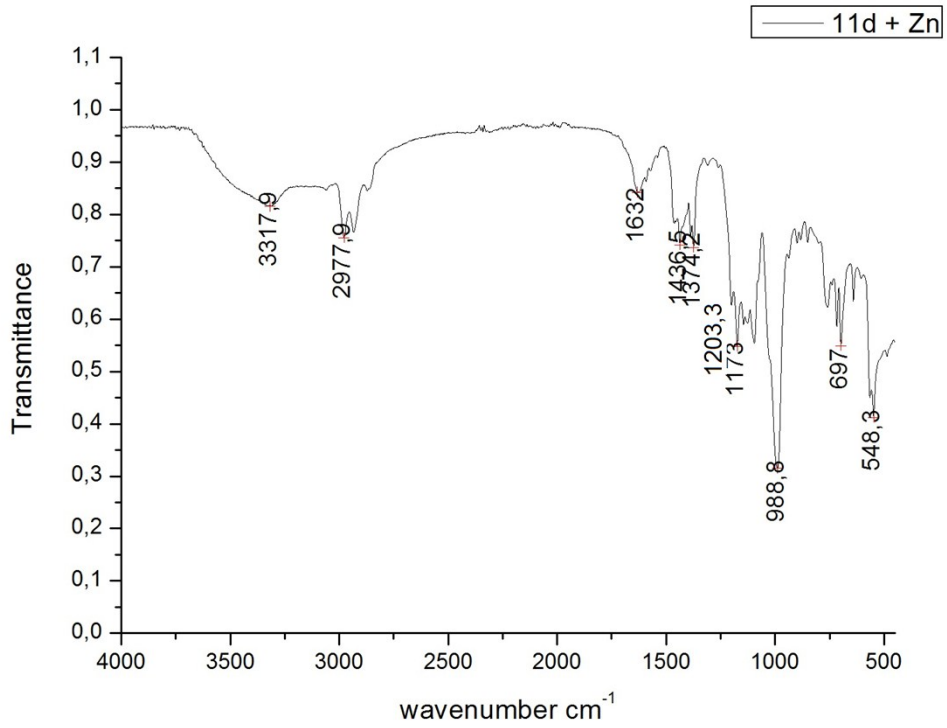
IR spectrum of **11c** in the presence of $Y(NO_3)_3$



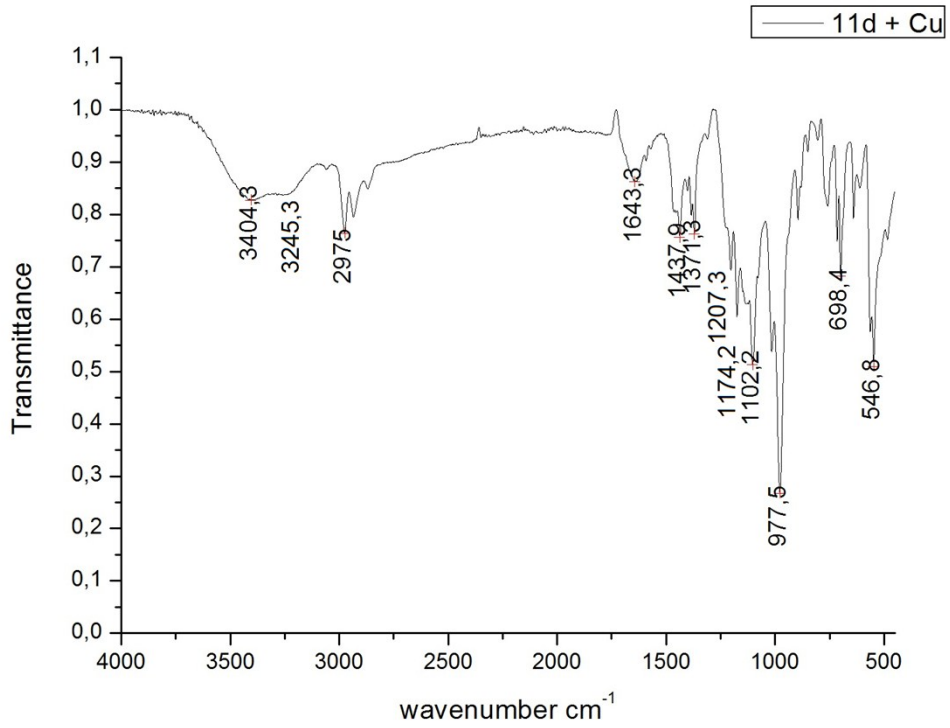
IR spectrum of **11d**



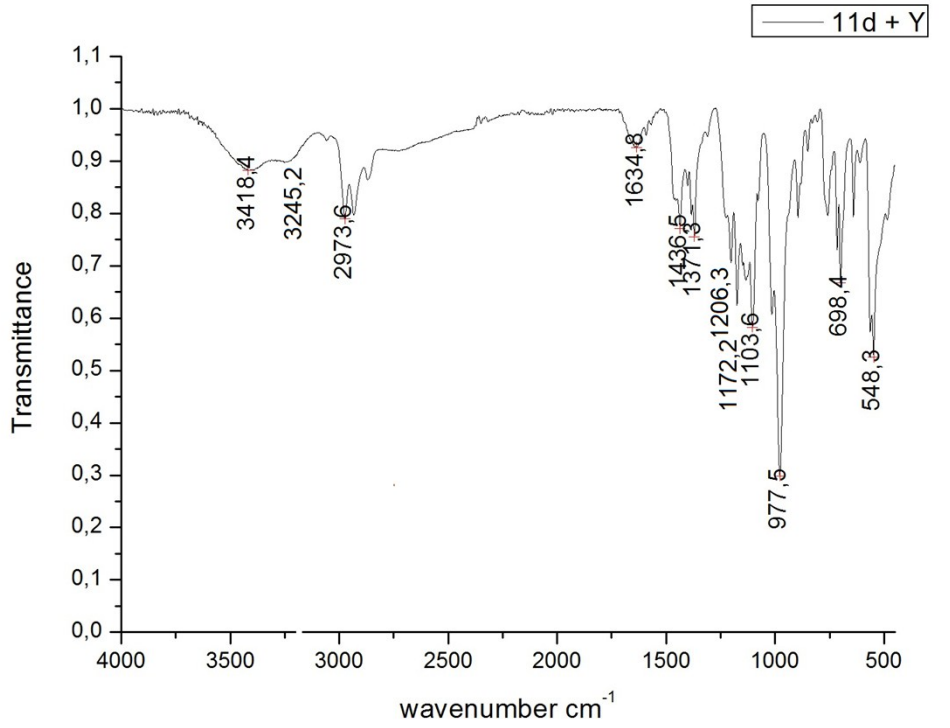
IR spectrum of **11d** in the presence of $ZnCl_2$



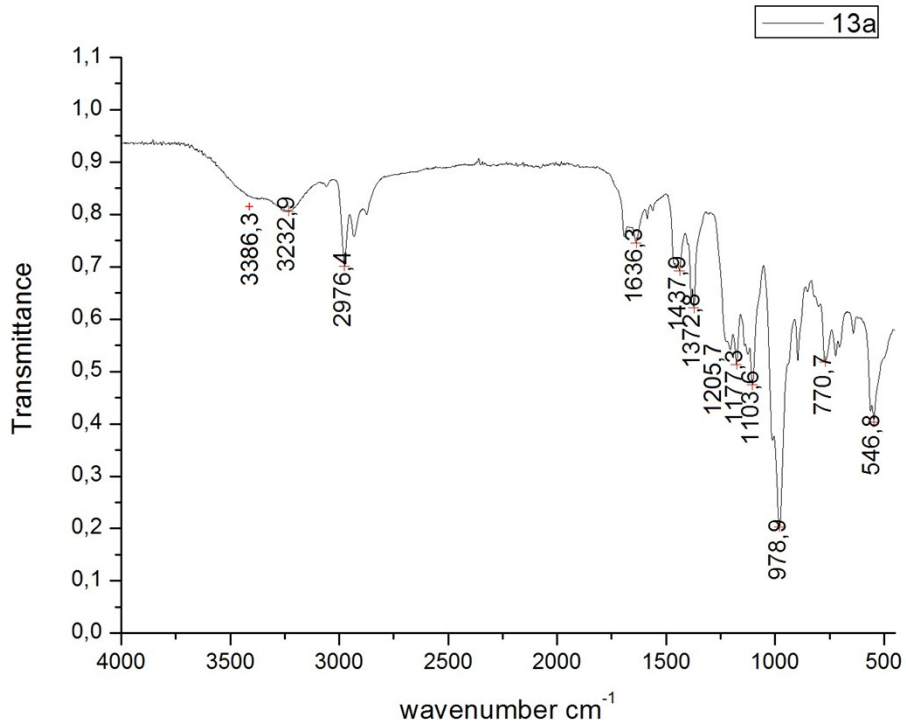
IR spectrum of **11d** in the presence of $CuSO_4$



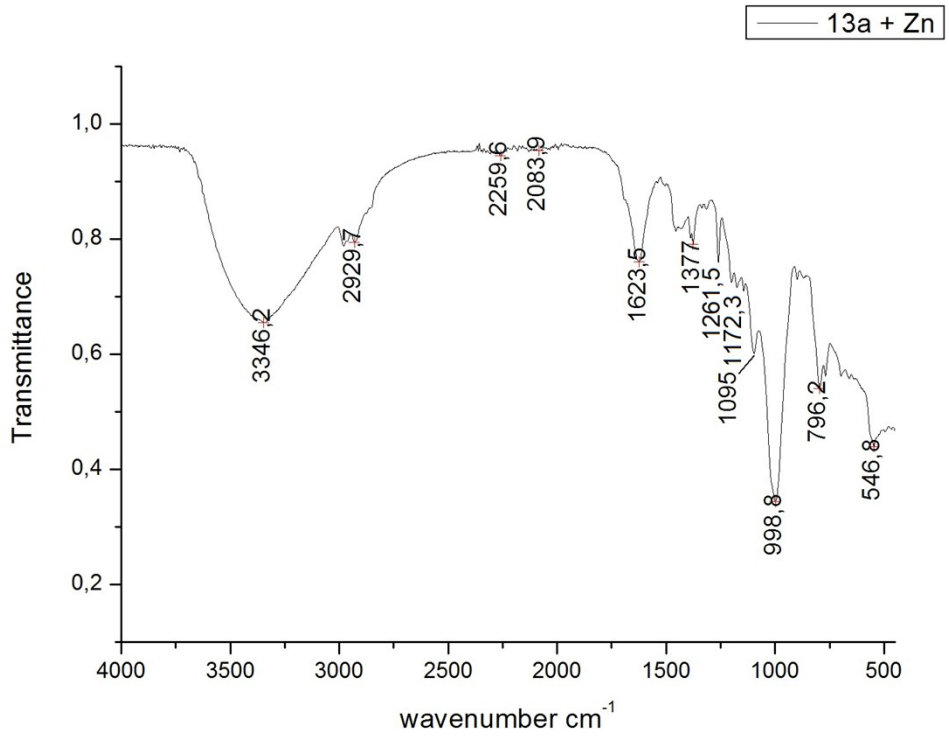
IR spectrum of **11d** in the presence of $Y(NO_3)_3$



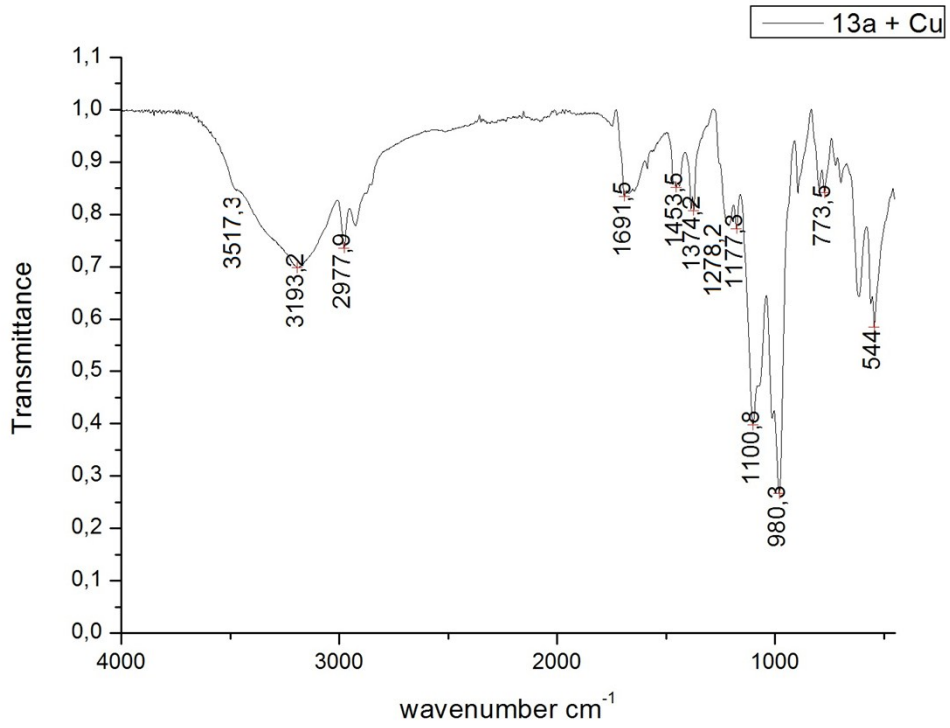
IR spectrum of **13a**



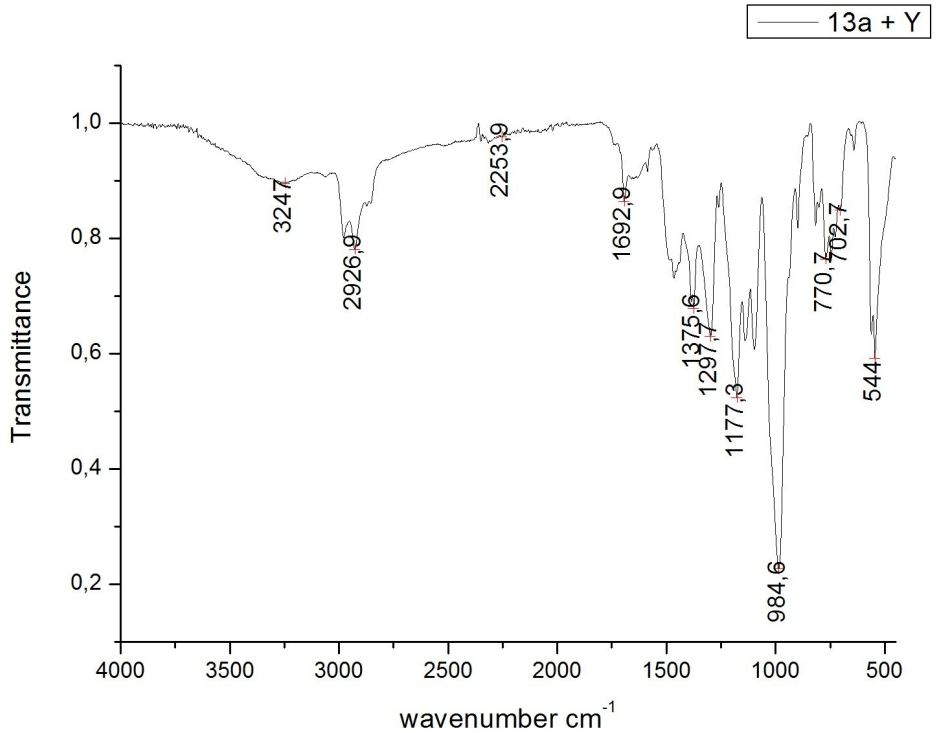
IR spectrum of **13a** in the presence of $ZnCl_2$



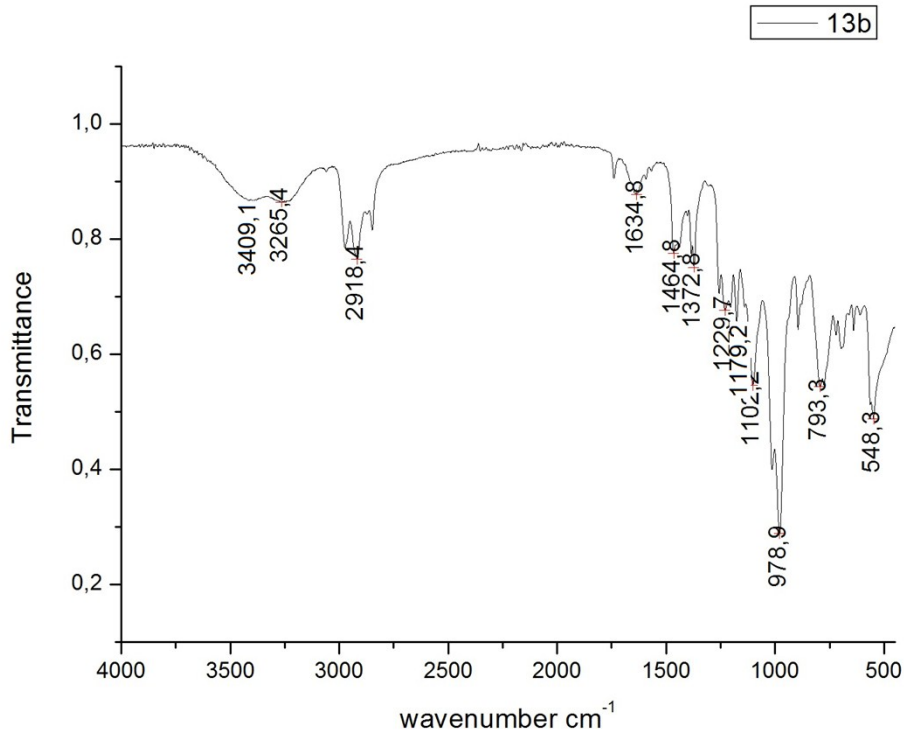
IR spectrum of **13a** in the presence of $CuSO_4$



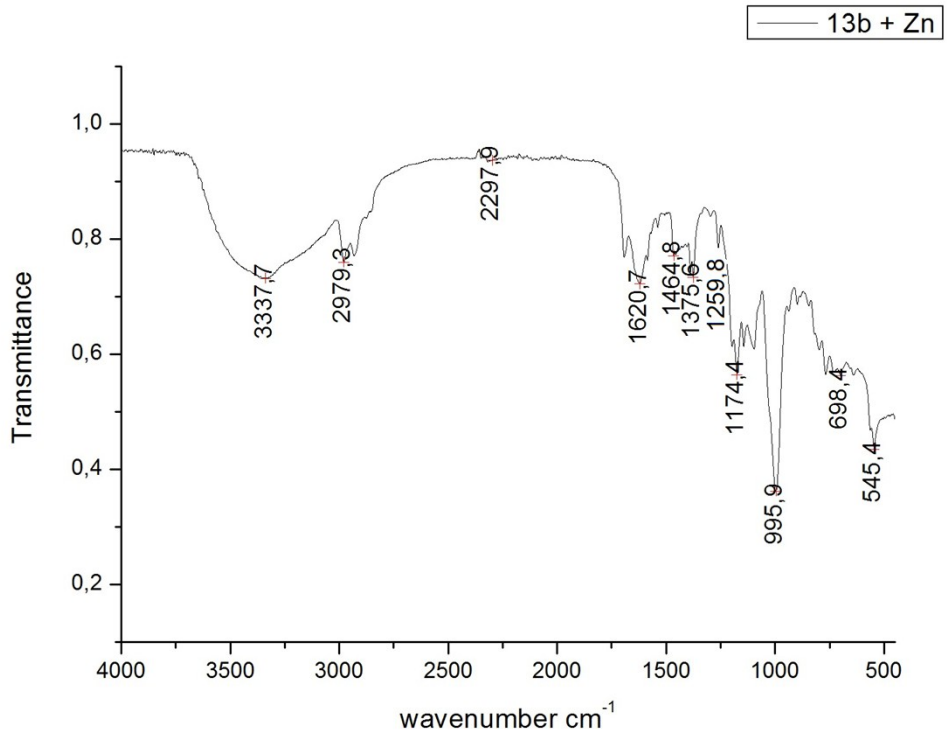
IR spectrum of **13a** in the presence of $Y(NO_3)_3$



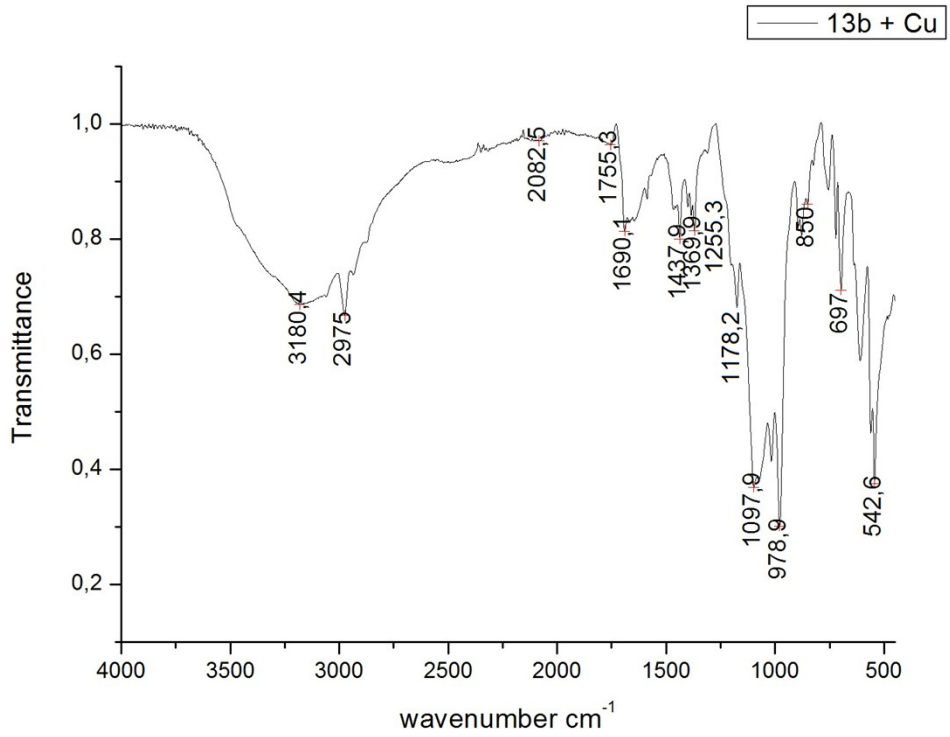
IR spectrum of **13b**



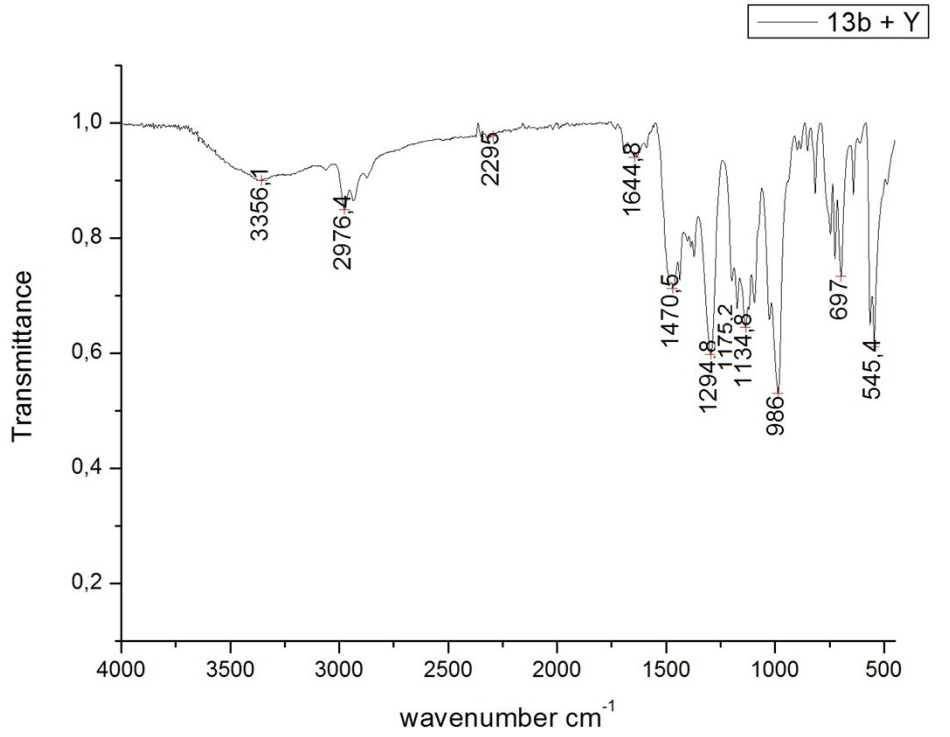
IR spectrum of **13b** in the presence of $ZnCl_2$



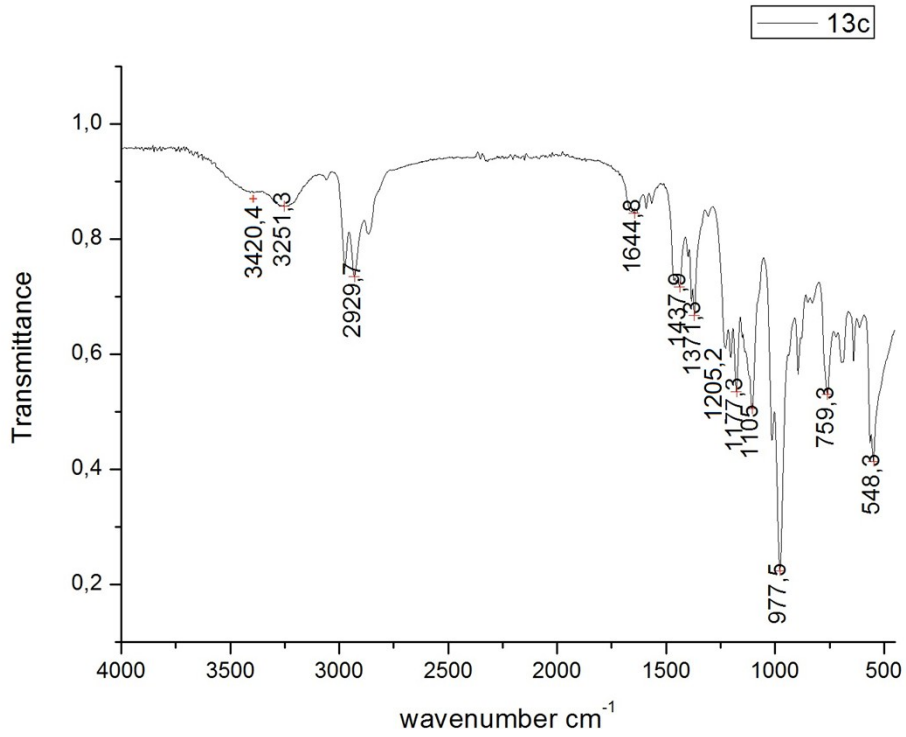
IR spectrum of **13b** in the presence of $CuSO_4$



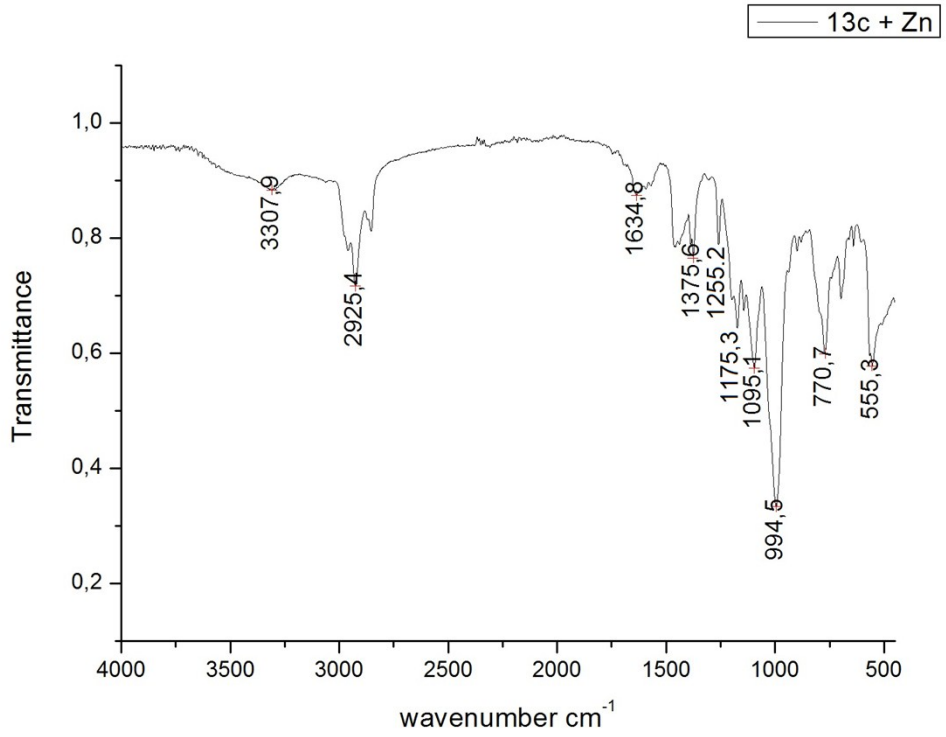
IR spectrum of **13b** in the presence of $Y(NO_3)_3$



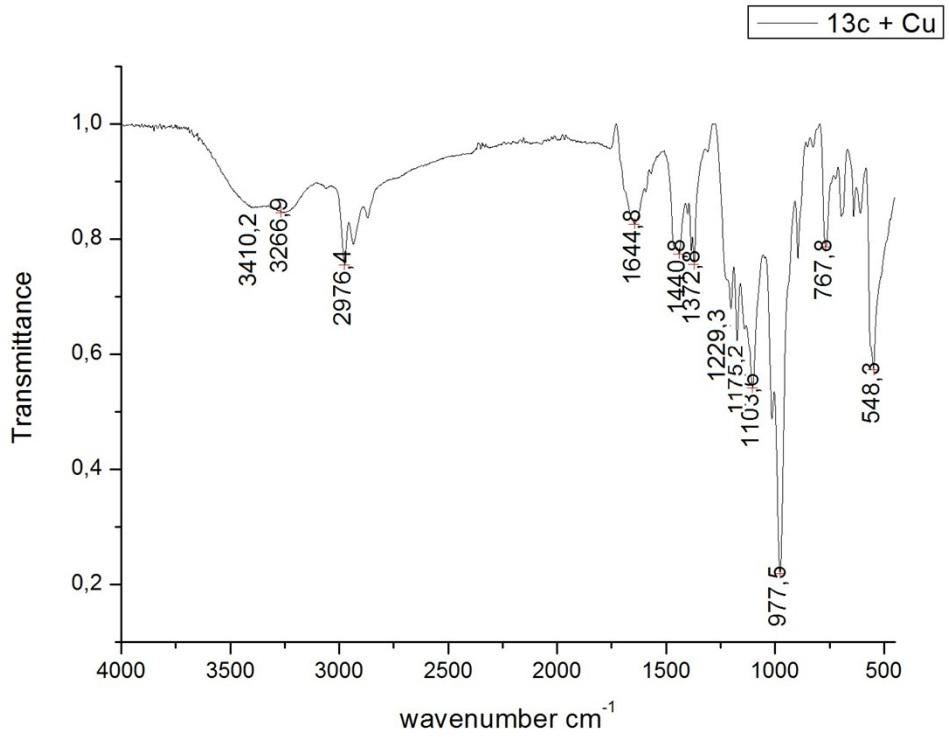
IR spectrum of **13c**



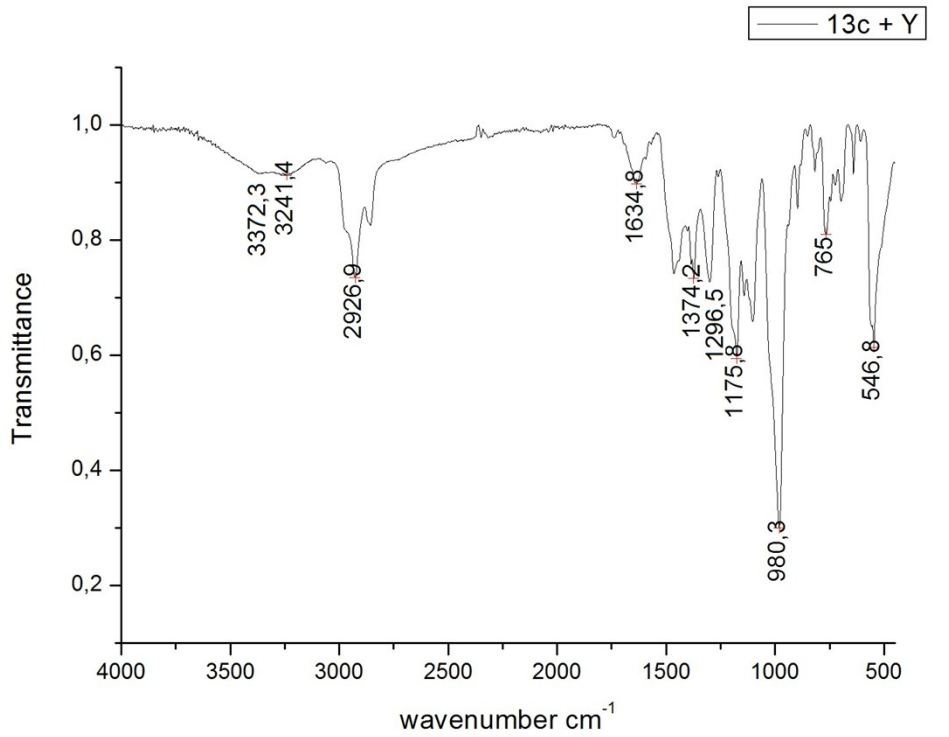
IR spectrum of **13c** in the presence of $ZnCl_2$



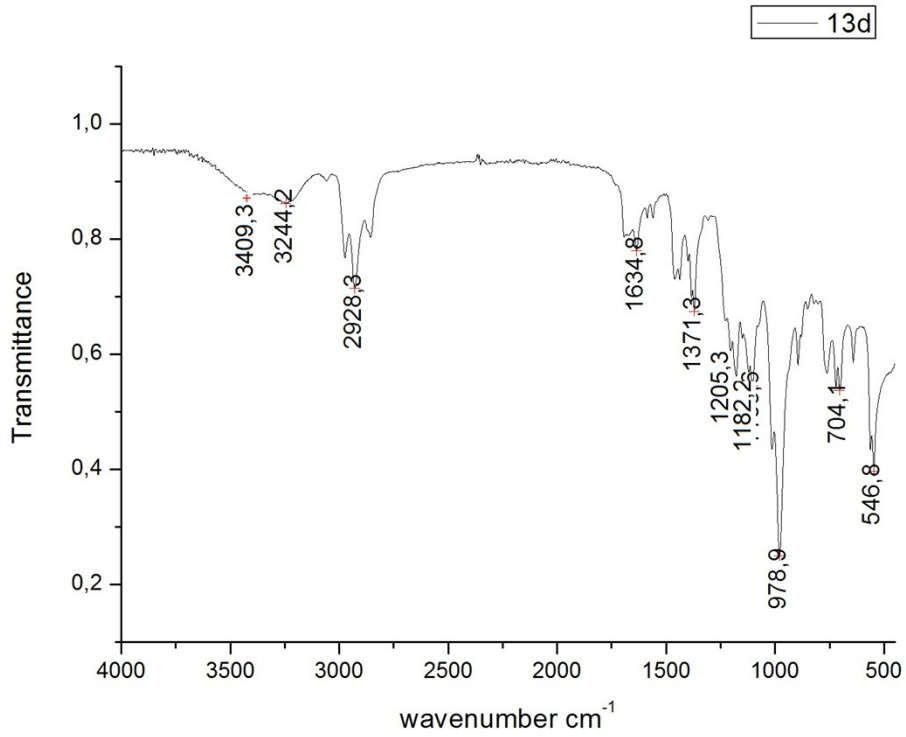
IR spectrum of **13c** in the presence of $CuSO_4$



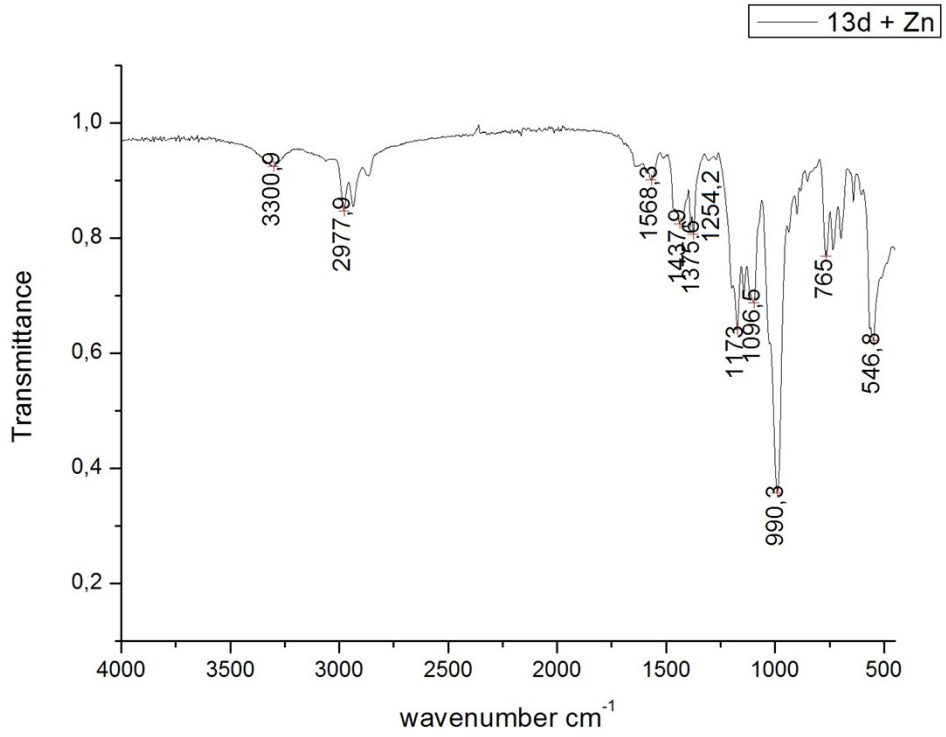
IR spectrum of **13c** in the presence of $Y(NO_3)_3$



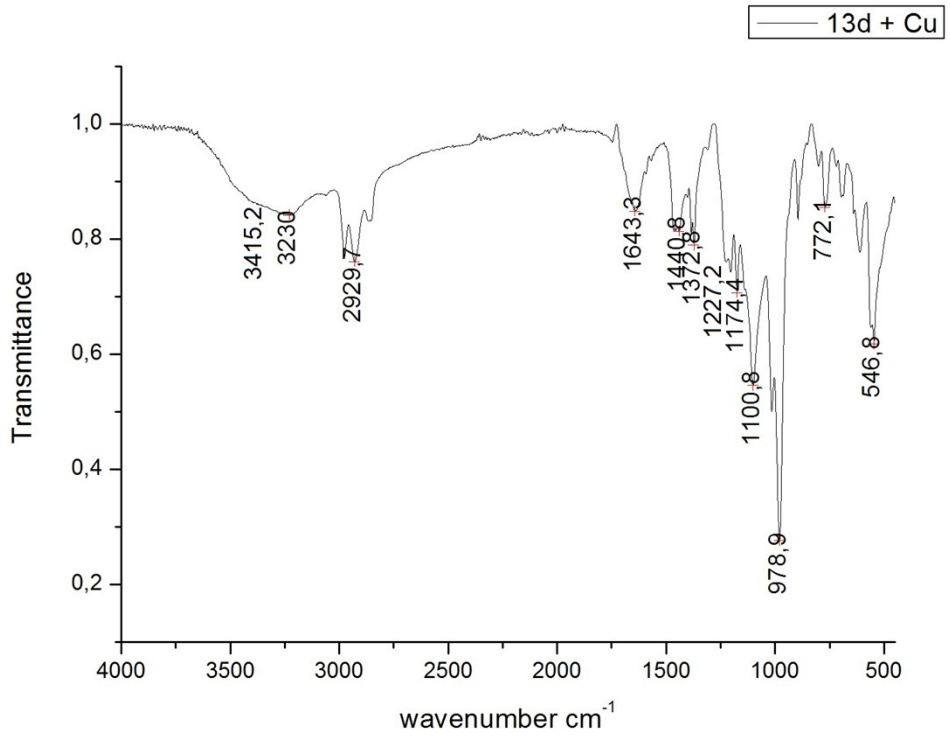
IR spectrum of **13d**



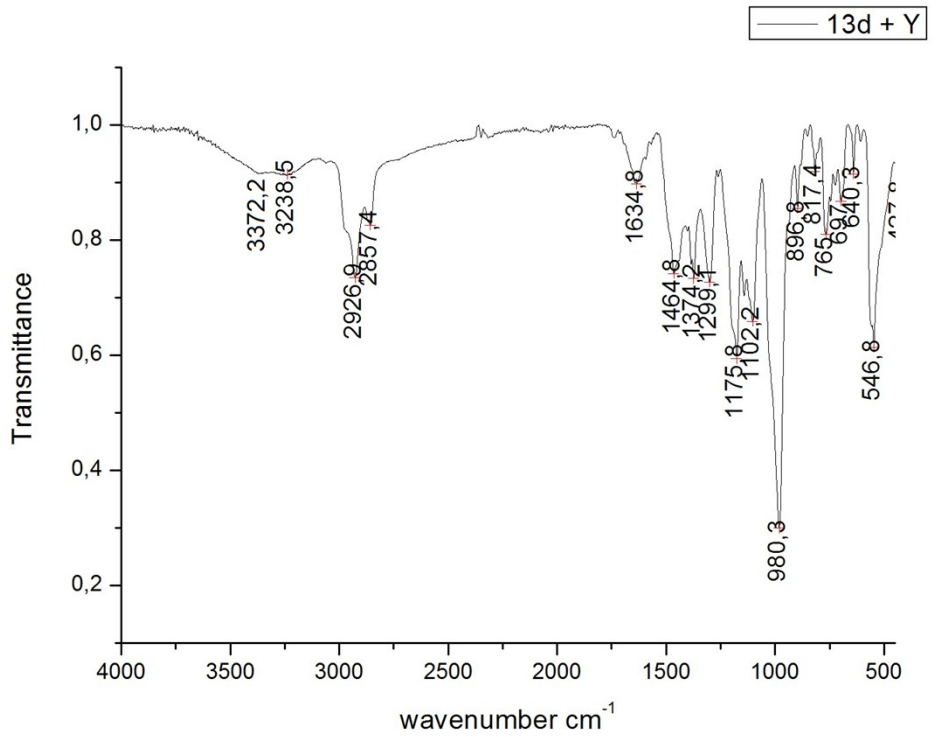
IR spectrum of **13d** in the presence of $ZnCl_2$



IR spectrum of **13d** in the presence of $CuSO_4$

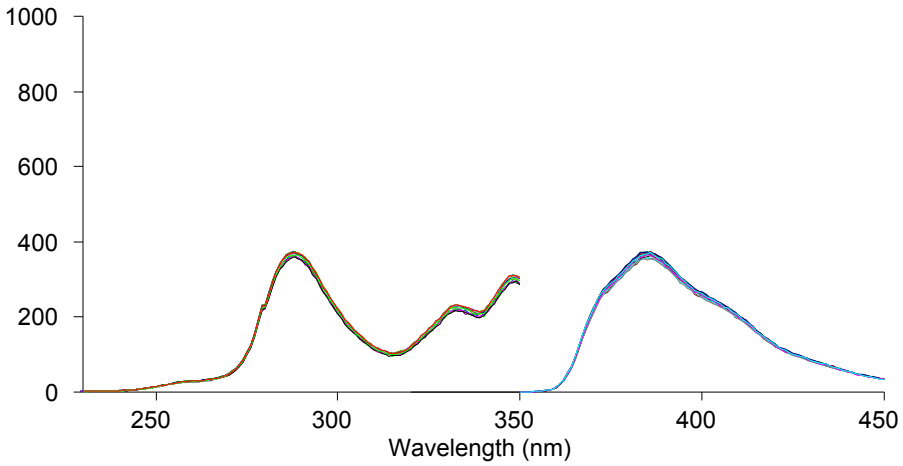


IR spectrum of **13d** in the presence of $Y(NO_3)_3$

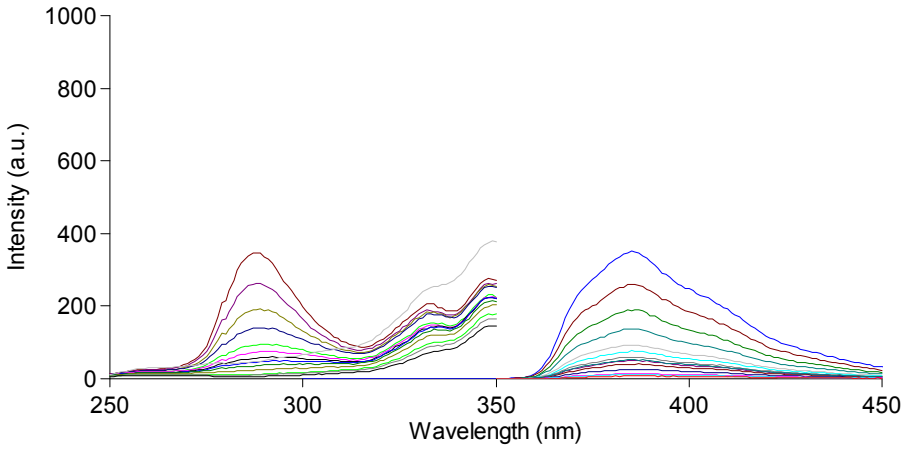


3) Spectrofluorimetric spectra

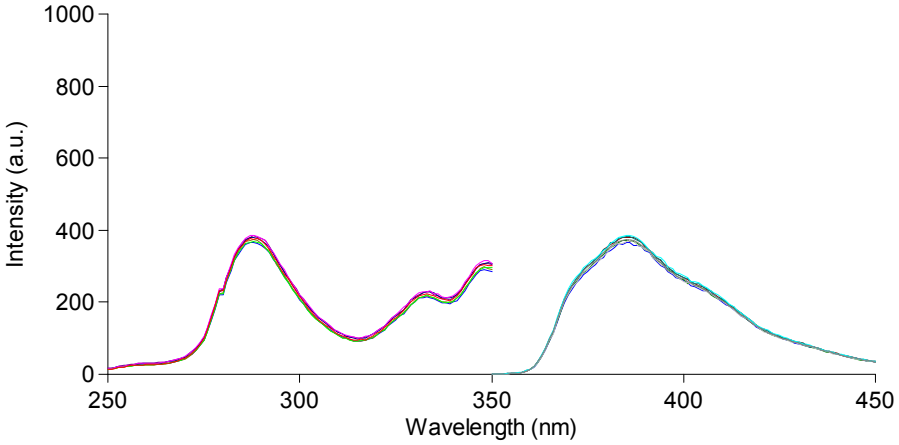
6a in the presence of $ZnCl_2$



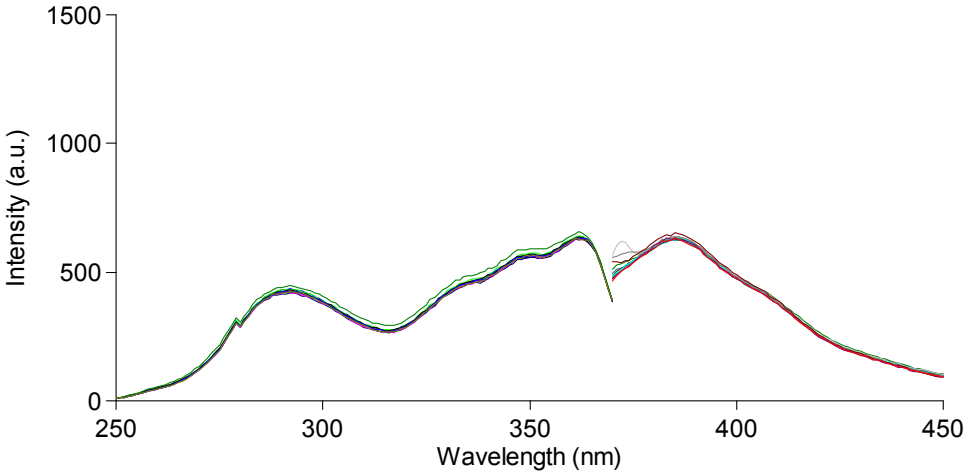
6a in the presence of $CuSO_4$



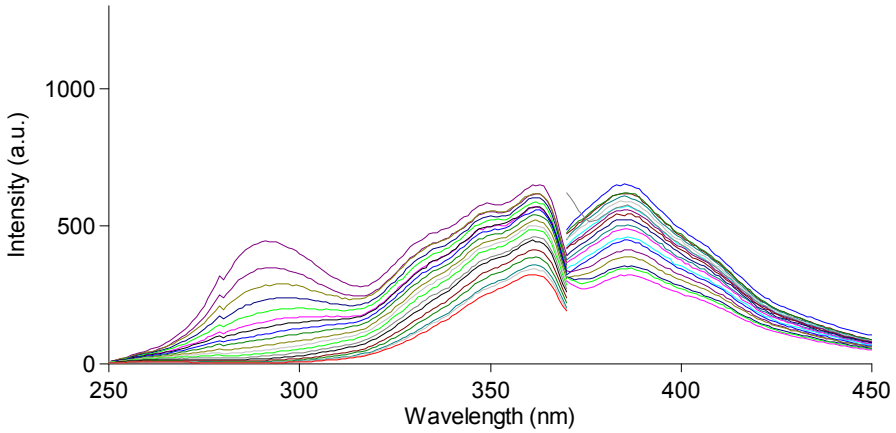
6a in the presence of $Y(NO_3)_3$



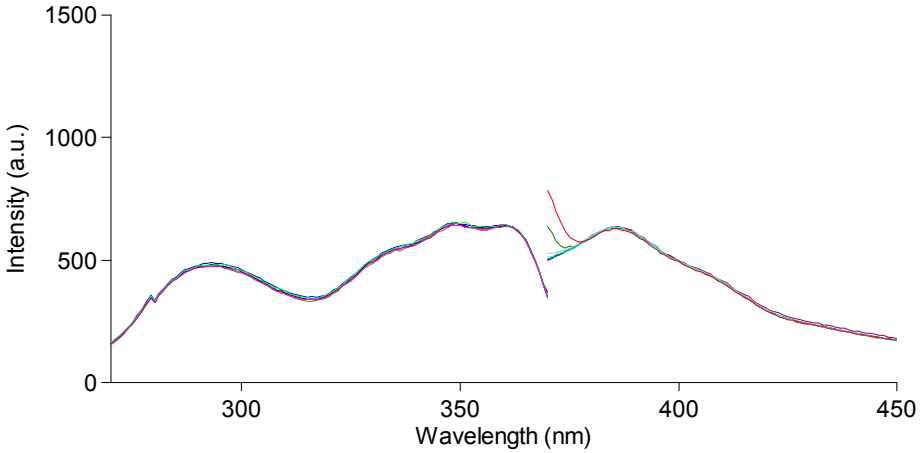
6b in the presence of $ZnCl_2$



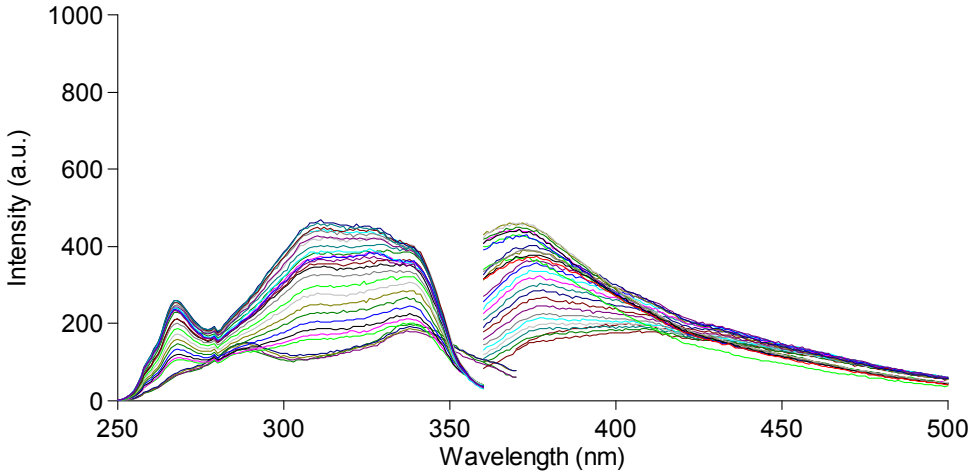
6b in the presence of $CuSO_4$



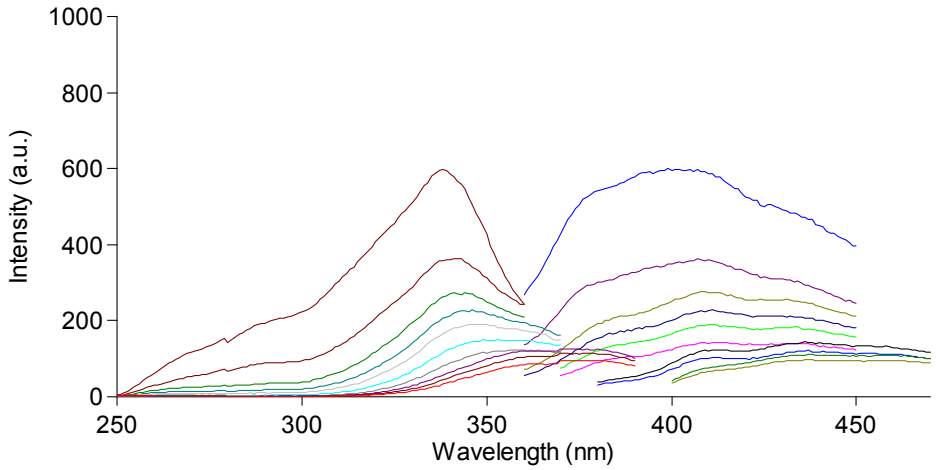
6b in the presence of $Y(NO_3)_3$



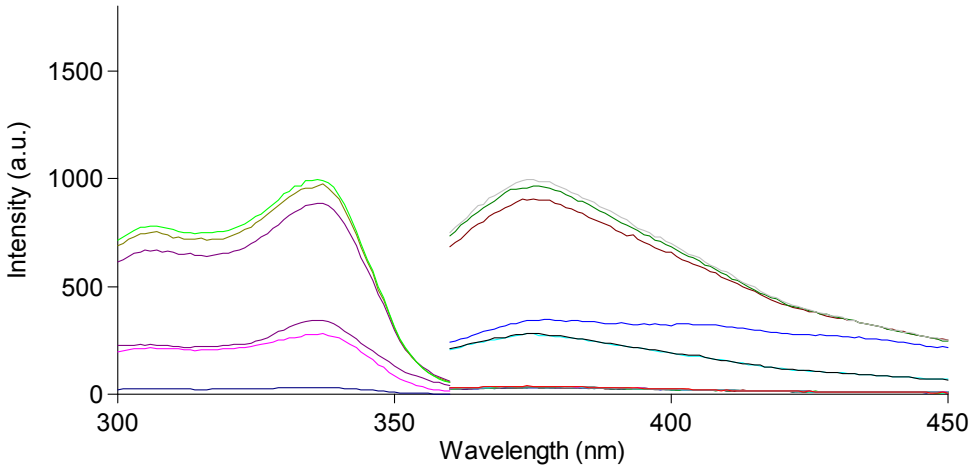
6c in the presence of $ZnCl_2$



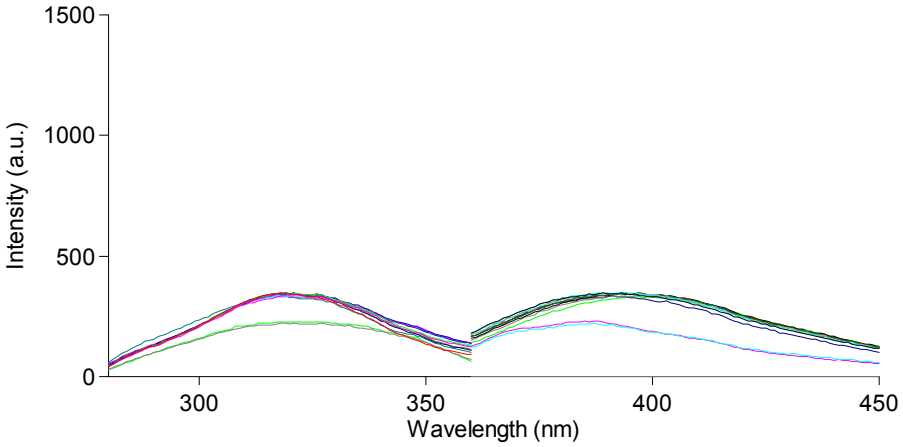
6c in the presence of $CuSO_4$



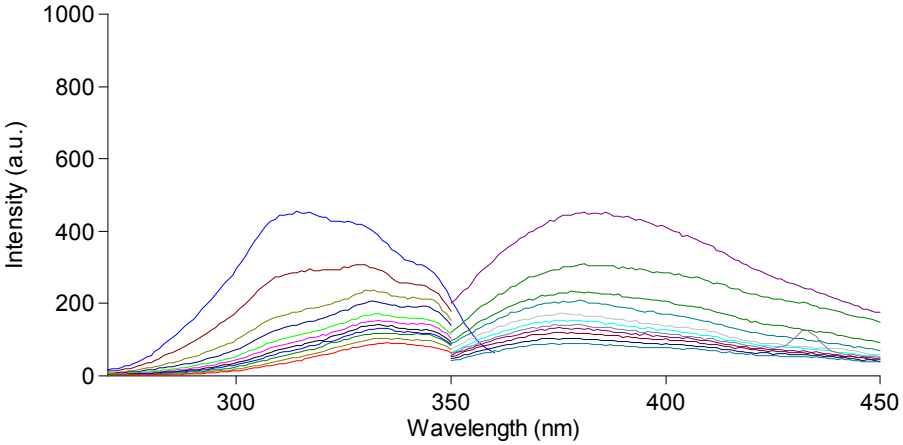
6c in the presence of $Y(NO_3)_3$



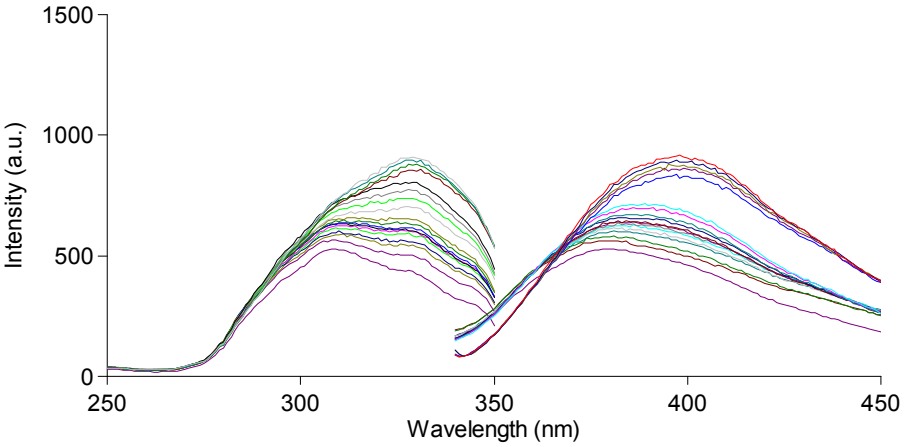
8a in the presence of $ZnCl_2$



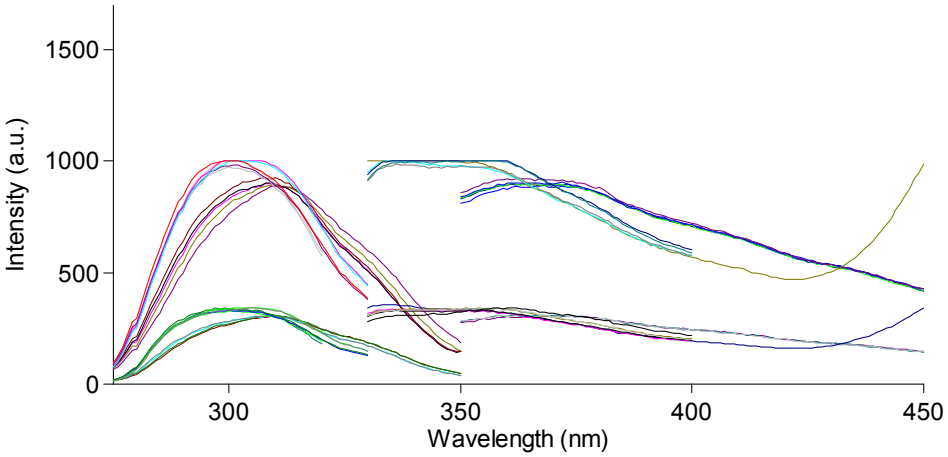
8a in the presence of $CuSO_4$



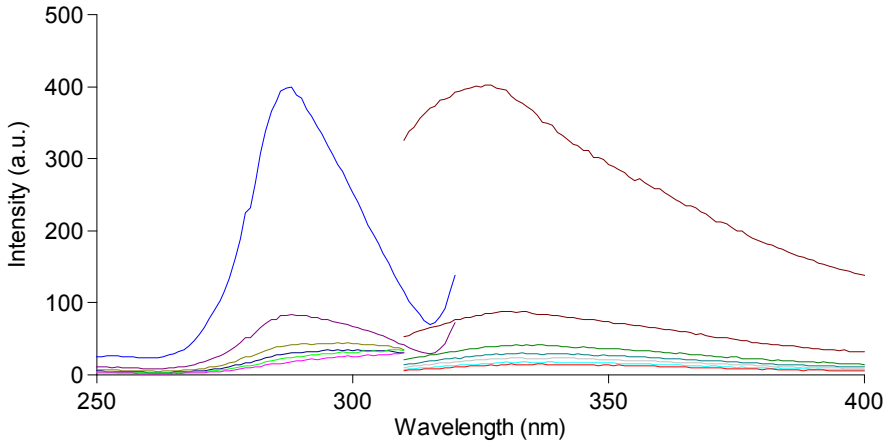
8a in the presence of $Y(NO_3)_3$



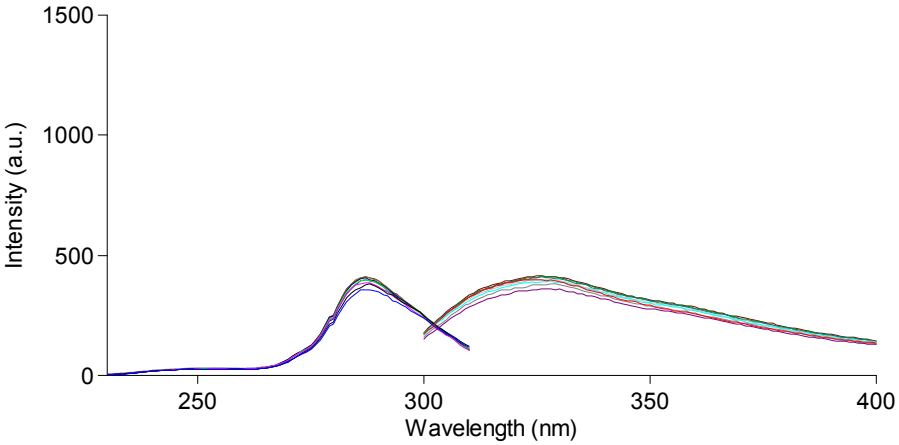
8b in the presence of $ZnCl_2$



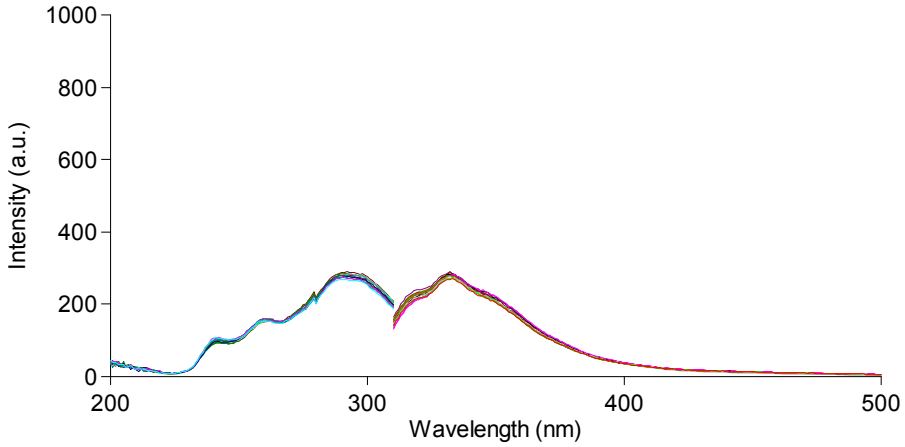
8b in the presence of $CuSO_4$



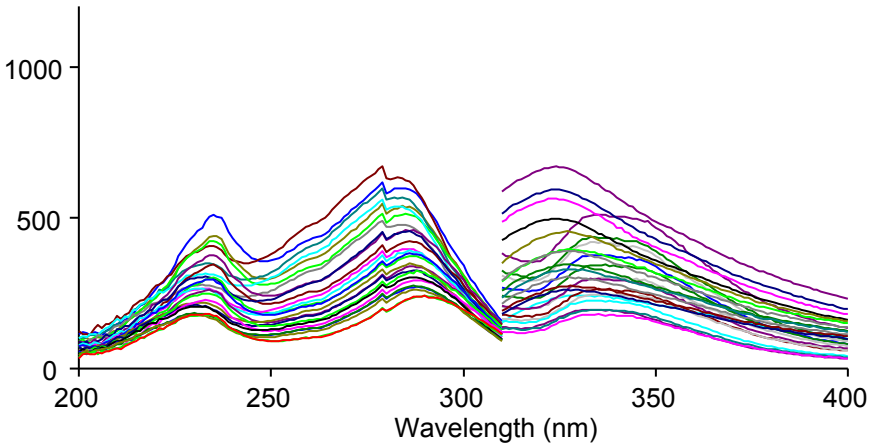
8b in the presence of $Y(NO_3)_3$



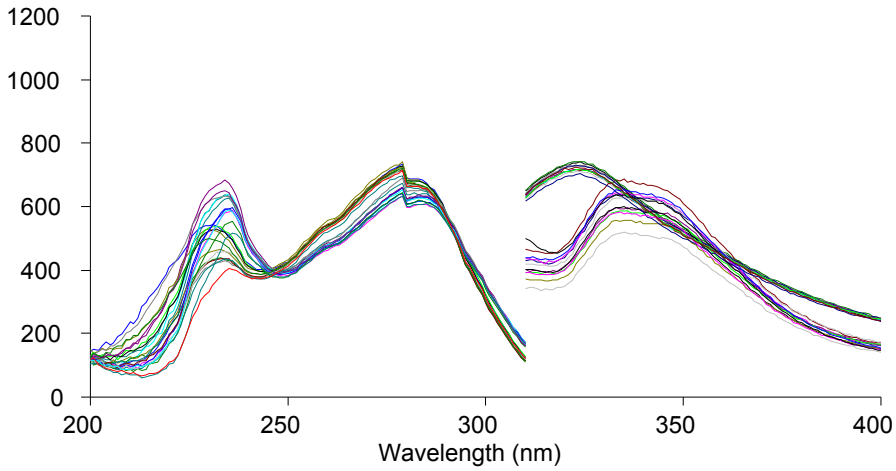
11a in the presence of $ZnCl_2$



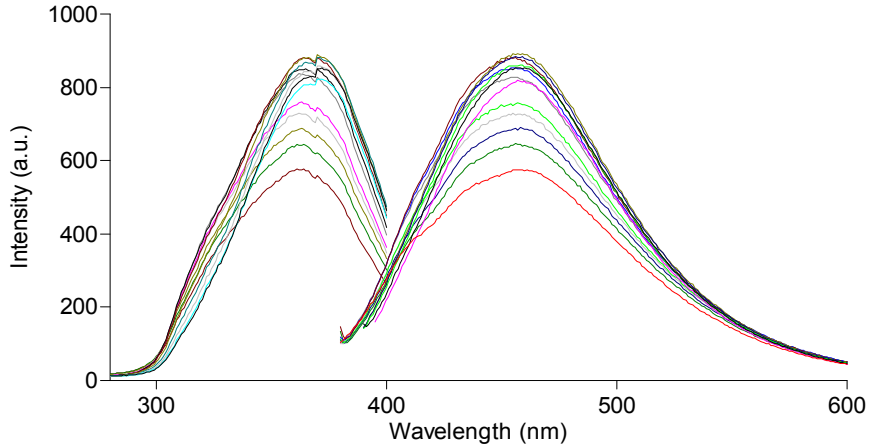
11a in the presence of $CuSO_4$



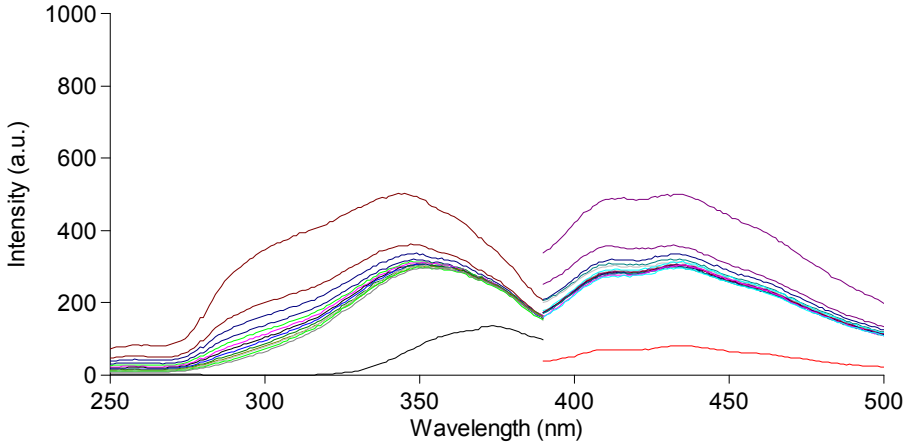
11a in the presence of $Y(NO_3)_3$



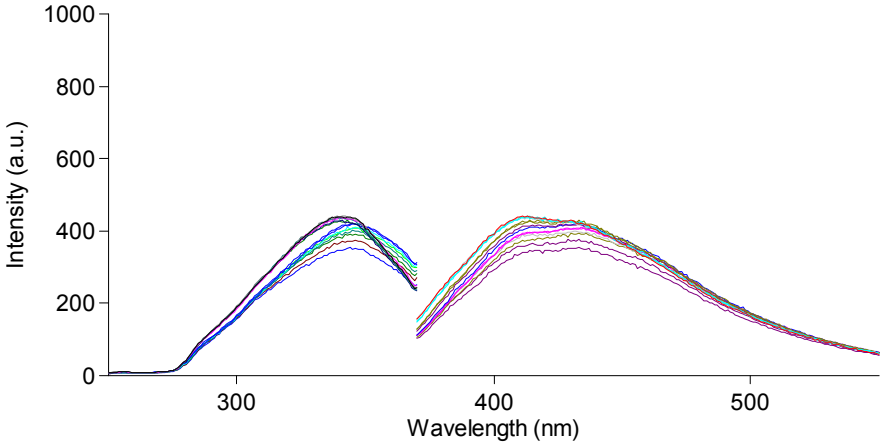
11b in the presence of $ZnCl_2$



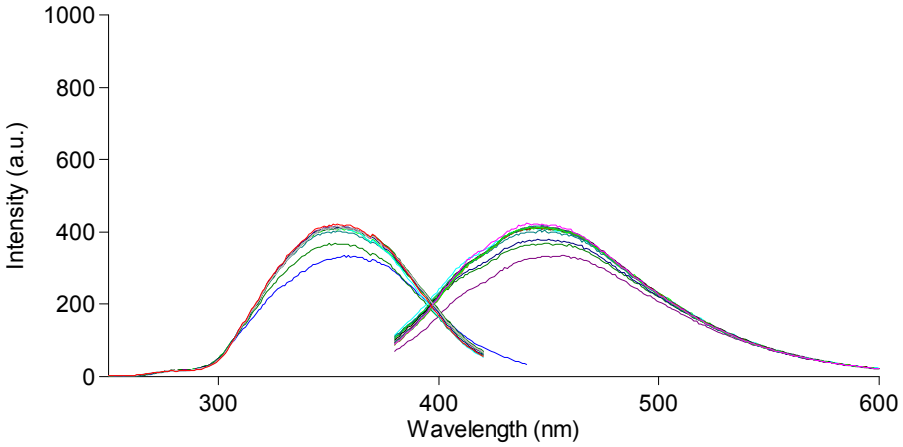
11b in the presence of $CuSO_4$



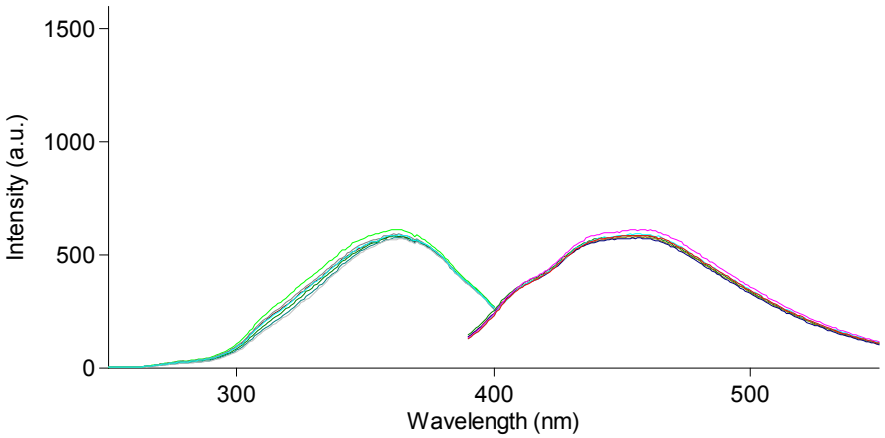
11b in the presence of $Y(NO_3)_3$



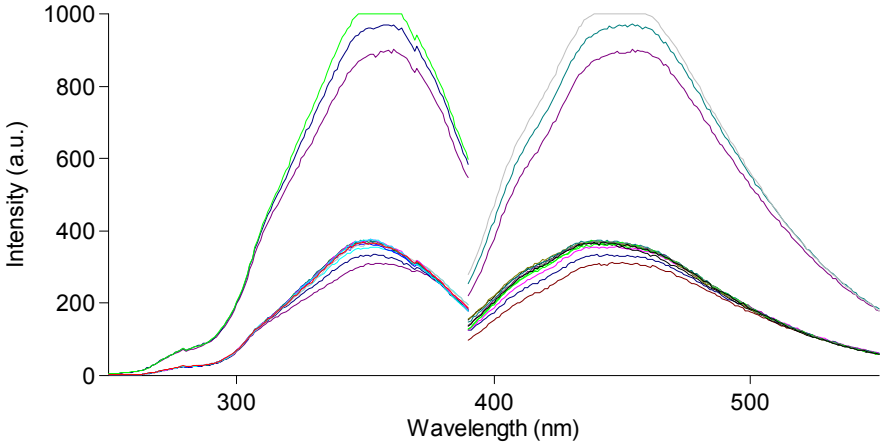
11c in the presence of $ZnCl_2$



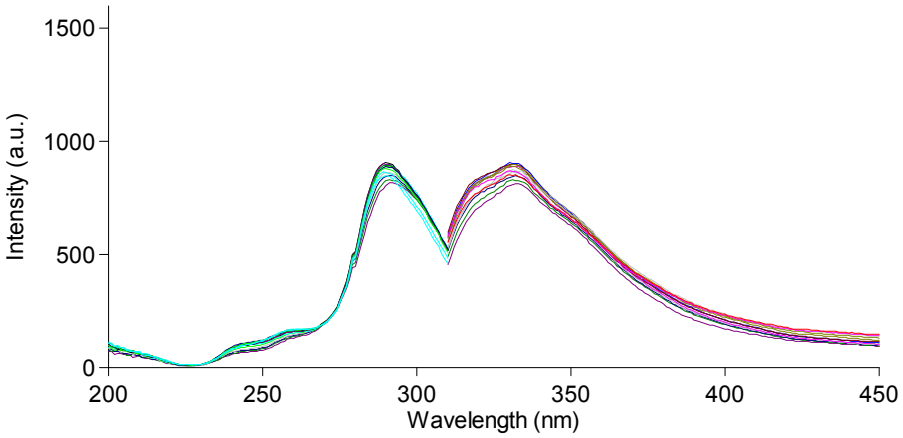
11c in the presence of $CuSO_4$



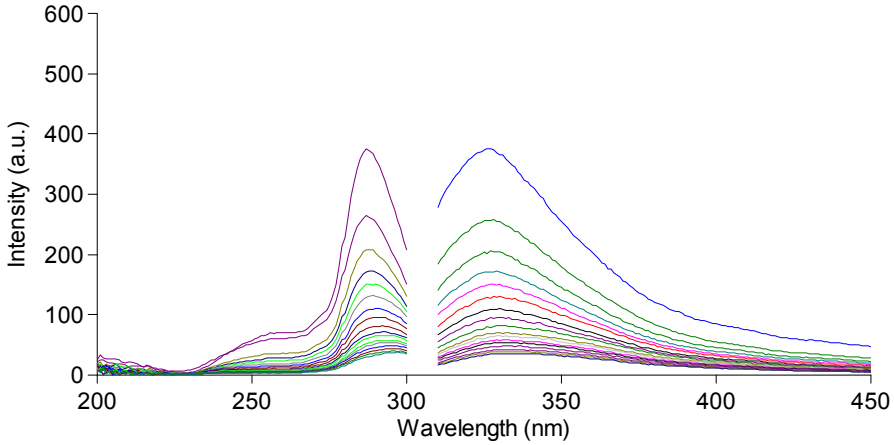
11c in the presence of $Y(NO_3)_3$



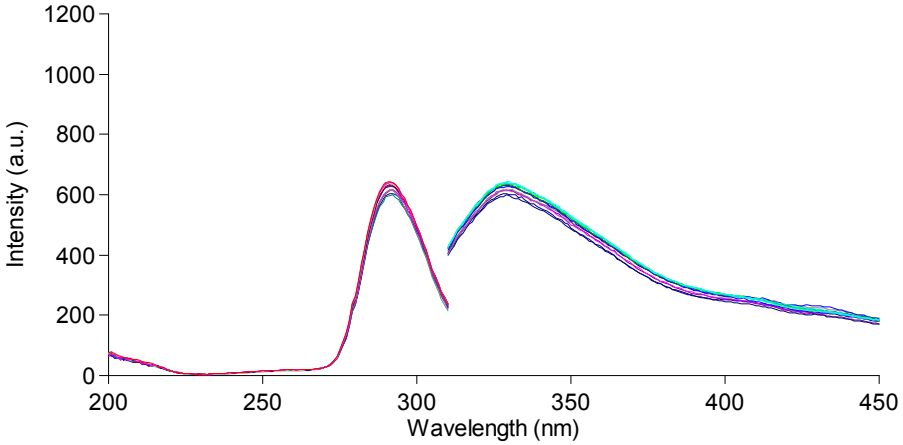
11d in the presence of $ZnCl_2$



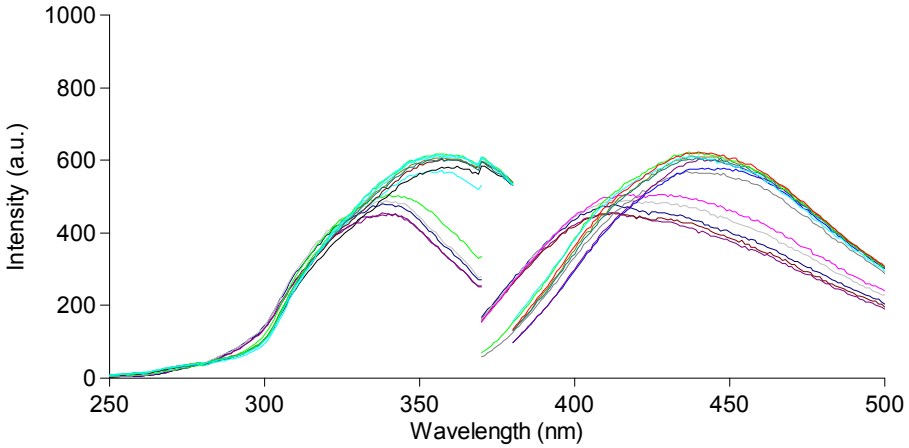
11d in the presence of $CuSO_4$



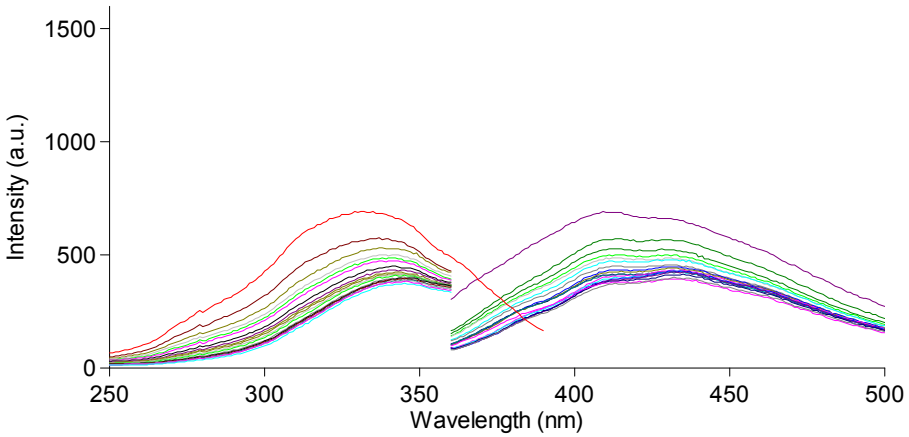
11d in the presence of $Y(NO_3)_3$



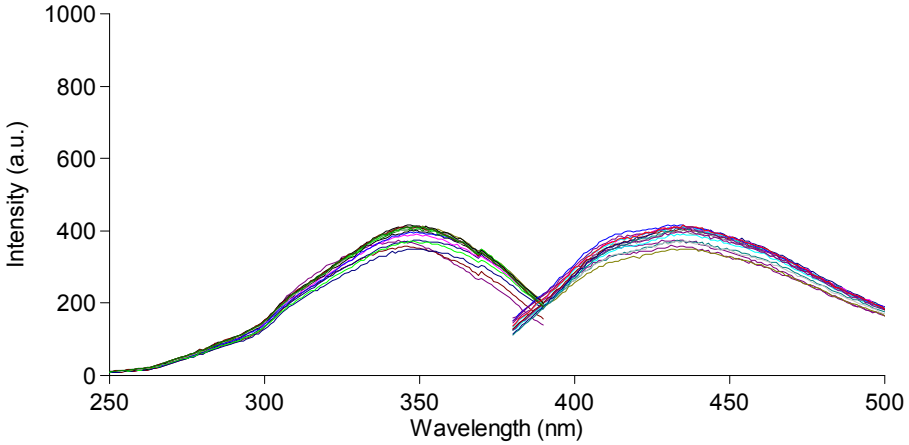
13a in the presence of $ZnCl_2$



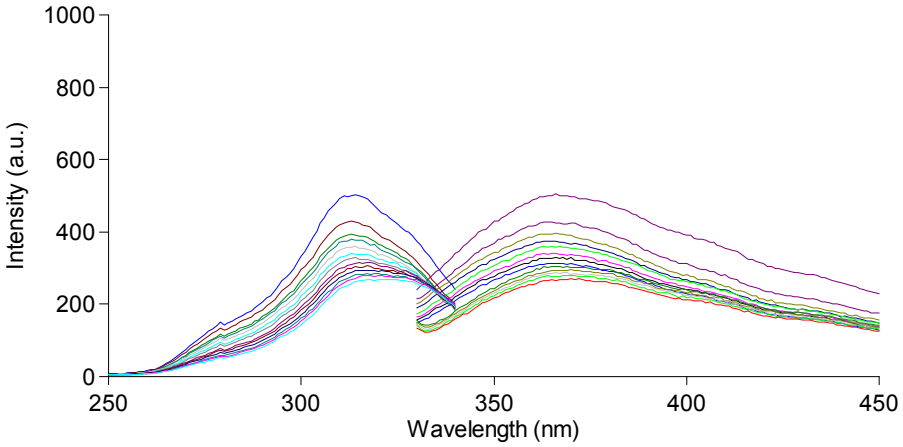
13a in the presence of $CuSO_4$



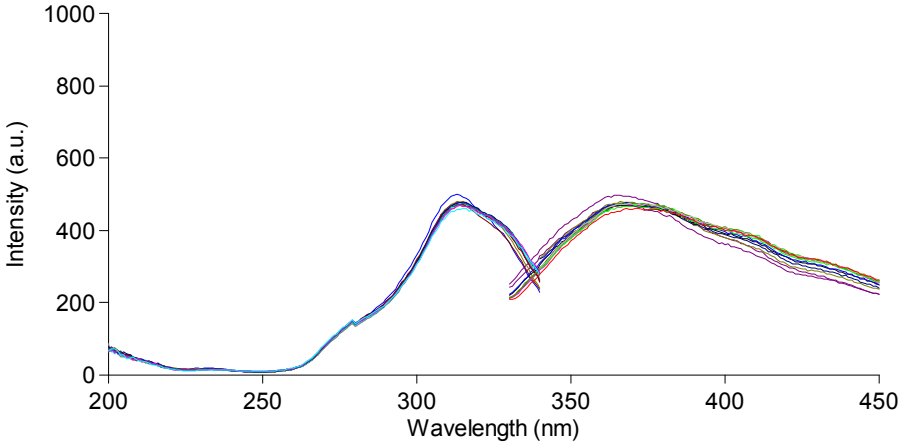
13a in the presence of $Y(NO_3)_3$



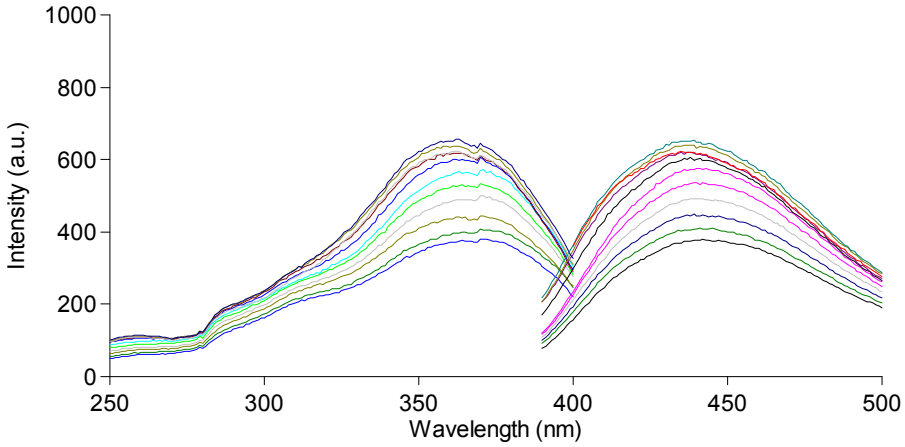
13b in the presence of $CuSO_4$



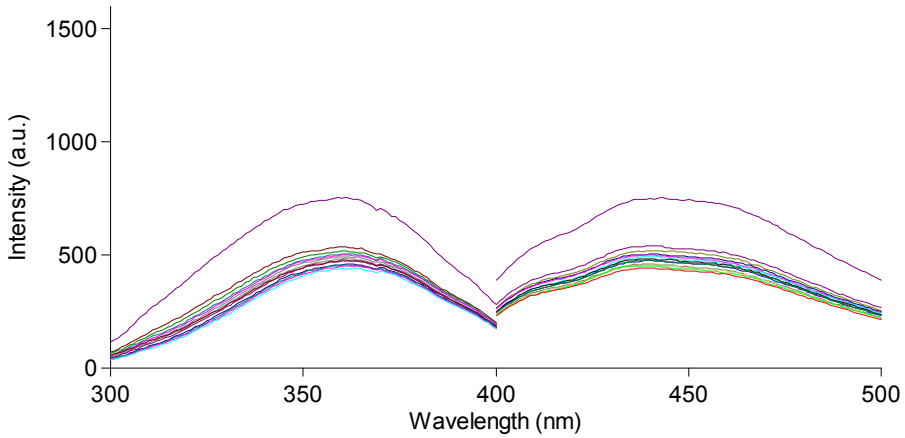
13b in the presence of $Y(NO_3)_3$



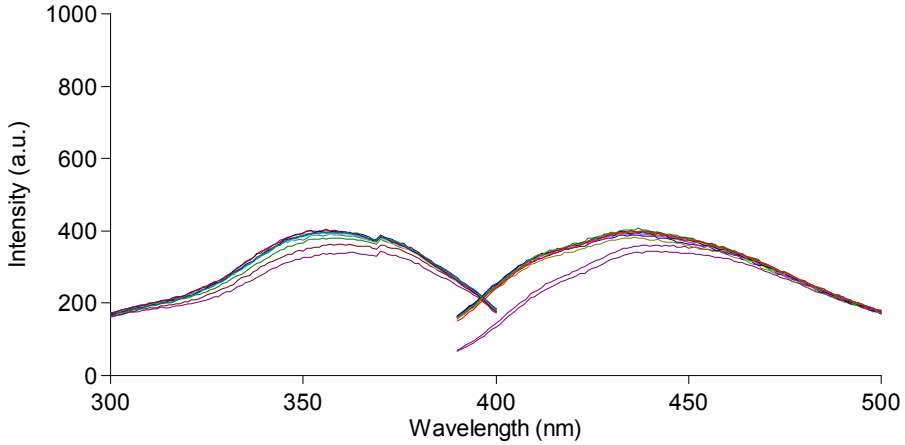
13c in the presence of $ZnCl_2$



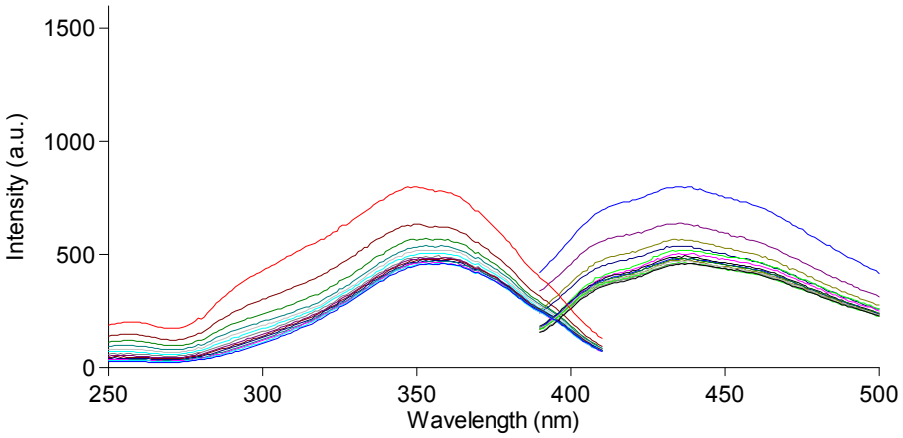
13c in the presence of $CuSO_4$



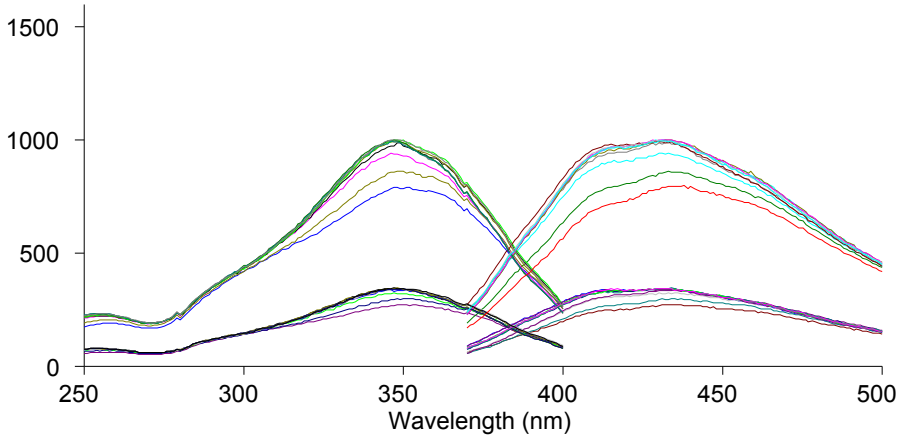
13c in the presence of $Y(NO_3)_3$



13d in the presence of $CuSO_4$

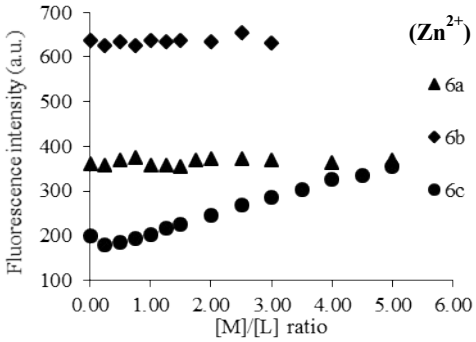


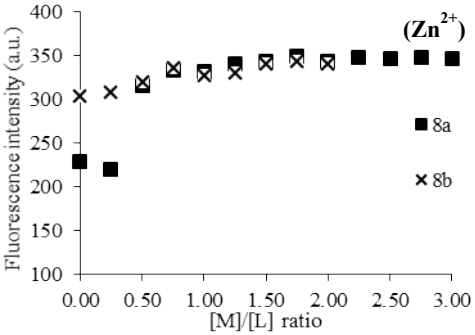
13d in the presence of $Y(NO_3)_3$



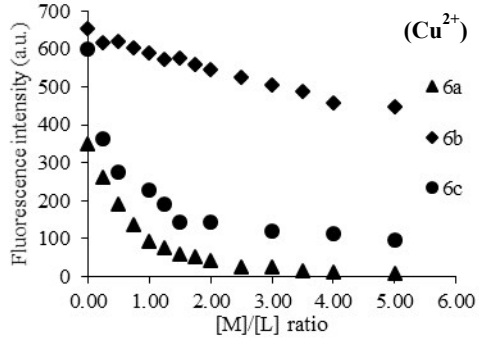
4) Titration curves

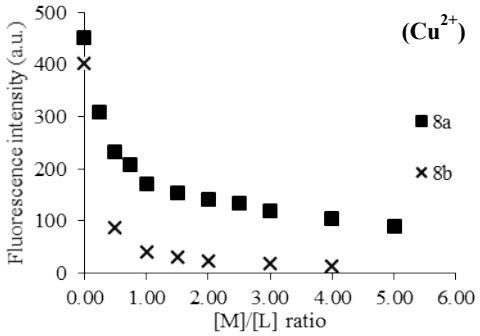
Titration curves of ligands 6a-c and 8a-b with Zn^{2+}.



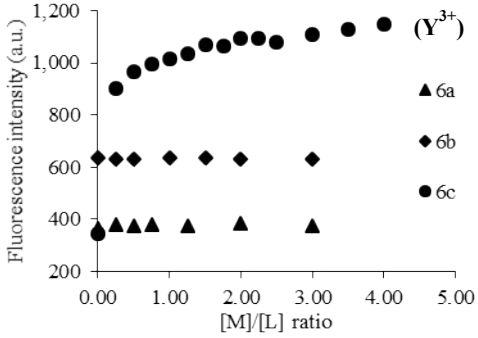


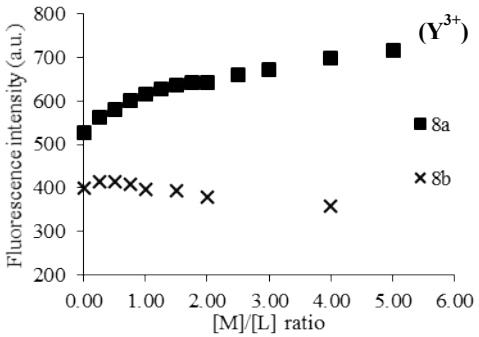
Titration curves of ligands 6a-c and 8a-b with Cu^{2+}.



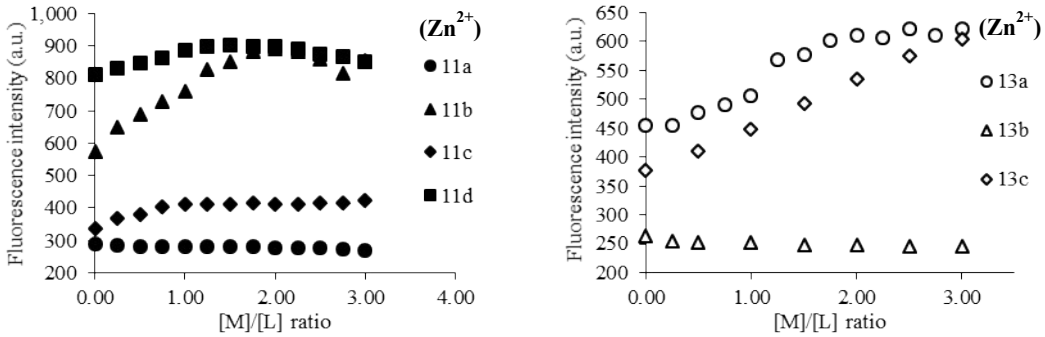


Titration curves of ligands 6a-c and 8a-b with Y^{3+}.

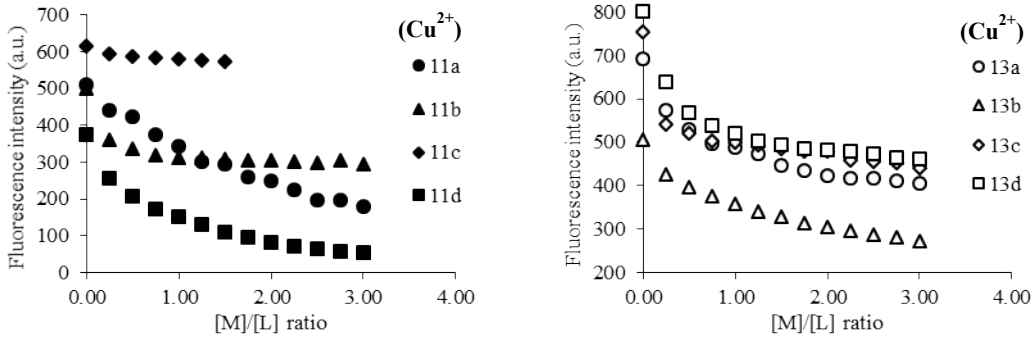




Titration curves of ligands 11a-d and 13a-c with Zn^{2+}.



Titration curves of ligands 11a-d and 13a-d with Cu^{2+}.



Titration curves of ligands 11a-d and 13a-d with Y^{3+}.