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# $B_2O_3/Al_2O_3$ as a New, Highly Efficient and Reusable Heterogeneous Catalyst for the Selective Synthesis of β-Enamino Ketones and Esters under Solvent-Free Conditions

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## Description of the products

*(Z)-Ethyl 3-(phenylamino)but-2-enoate (**3a**)*[1]

Oil, IR (KBr) $\nu_{max}$/cm$^{-1}$: 3456, 3258, 2979, 1610, 1495, 1442, 1370, 1270, 1162, 1056 cm$^{-1}$. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 10.41 (br s, 1H, NH), 7.30-7.35 (m, 2H), 7.08-7.18 (m, 3H), 4.71 (s, 1H), 4.17 (q, *J* 7.2 Hz, 2H), 2.01 (s, 3H), 1.32 (t, *J* 7.2 Hz, 3H). $^{13}$C MNR (75 MHz, $CDCl_3$): $\delta$ 170.4, 158.9, 139.3, 129.0, 124.9, 124.4, 85.9, 58.7, 20.3, 14.6.

*(Z)-4-(Phenylamino)pent-3-en-2-one (**3b**)*

Solid, mp: 47-49 °C (Lit.[1] 48-49 °C); IR (KBr) $\nu_{max}$/cm$^{-1}$: 3349, 2980, 1605, 1499, 1432, 1276, 1183, 1017, 746; $^1$H NMR (300MHz, $CDCl_3$): $\delta$ 12.46 (br s, 1H, NH), 7.25-7.30 (m, 2H), 7.03-7.15 (m, 3H), 5.14 (s, 1H), 2.05 (s, 3H), 1.93 (s, 3H); $^{13}$C MNR (75MHz, $CDCl_3$): $\delta$ 196.0, 160.2, 138.6, 129.0, 125.5, 124.6, 97.6, 29.1, 19.8.

*(Z)-Ethyl 3-(naphthalen-1-ylamino)but-2-enoate (**3c**)*[2]

Oil; IR (KBr) $\nu_{max}$/cm$^{-1}$:: 3246, 3056, 2978, 1605, 1441, 1384, 1266, 1165, 785; $^1$H NMR (300MHz, $CDCl_3$): $\delta$ 10.61 (br s, 1H, NH), 8.06-8.09 (m, 1H), 7.86-7.89 (m, 1H), 7.75 (d, *J* 8.4 Hz, 1H), 7.26-7.57 (m, 4H), 4.83 (s, 1H), 4.23 (q, *J* 7.2Hz, 2H), 1.86 (s, 3H), 1.34 (q, *J* 7.2Hz, 3H); $^{13}$C MNR (75MHz, $CDCl_3$): $\delta$ 170.7, 160.5, 135.3, 134.3, 130.4, 128.2, 126.7, 126.5, 126.4, 125.3, 123.6, 122.7, 85.7, 58.8, 20.04, 14.7.

*(Z)-4-(Naphthalen-1-ylamino)pent-3-en-2-one (**3d**)*

Solid, mp: 61-63 °C (Lit.[3] 51-53 °C); IR (KBr) $\nu_{max}$/cm$^{-1}$: 3430, 2972, 1600, 1550, 1425, 1278, 1078, 1015, 774; $^1$H NMR (300MHz, $CDCl_3$): $\delta$ 12.76 (br s, 1H, NH), 8.02-8.05 (m, 1H), 7.87-7.90 (m, 1H), 7.77 (d, *J* 8.4Hz, 1H), 7.27-7.56 (m, 4H), 5.32 (s, 1H), 2.18 (s, 3H), 1.88 (s, 3H); $^{13}$C MNR (75MHz, $CDCl_3$): $\delta$ 196.6, 161.9, 134.8, 134.2, 123.0, 128.2, 126.9, 126.9, 126.5, 125.5, 123.4, 122.8, 97.4, 29.2, 19.6.

*(Z)-Ethyl 3-(p-toluidino)but-2-enoate (**3e**)*[1]

Oil; IR (KBr) $\nu_{max}$/cm$^{-1}$: 3257, 3189, 2979, 1615, 1509, 1441, 1271, 1161, 1059, 792; $^1$H NMR (300MHz, $CDCl_3$): $\delta$ 10.28 (br s, 1H, NH), 7.10-7.13 (m, 2H), 6.96-6.99 (m, 2H), 4.66 (s, 1H), 4.14 (q, *J* 7.2Hz, 2H), 2.33 (s, 3H), 1.95 (s, 3H), 1.28 (t, *J* 7.2Hz, 3H); $^{13}$C MNR (75MHz, $CDCl_3$): $\delta$ 170.5, 158.8, 136.7, 134.9, 129.6, 124.7, 85.3, 58.7, 20.9, 20.3, 14.6.

*(Z)-4-(p-Toluidino)pent-3-en-2-one (**3f**)*

Solid, mp: 66-67 °C (Lit.[4] 68-69 °C); IR (KBr) $\nu_{max}$/cm$^{-1}$: 3448, 2922, 1607, 1508, 1434, 1276, 1178, 1013, 822, 753; $^1$H NMR (300MHz, $CDCl_3$): $\delta$ 12.40 (br s, 1H, NH), 7.14 (d, *J* 8.4Hz, 2H), 7.00 (d, *J* 8.4Hz, 2H), 5.16 (s, 1H), 2.34 (s, 3H), 2.09 (s, 3H), 1.96 (s, 3H); $^{13}$C MNR (75MHz, $CDCl_3$): $\delta$ 195.9, 160.7, 136.1, 135.5, 129.6, 124.8, 97.2, 29.1, 20.9, 19.7.

*(Z)-Ethyl 3-(2-methoxyphenylamino)but-2-enoate (**3g**)*[5]

Oil; IR (KBr) $\nu_{max}$/cm$^{-1}$: 3262, 2976, 1614, 1464, 1376, 1220, 1161, 1037, 746; $^1$H NMR (300MHz, $CDCl_3$): $\delta$ 10.28 (br s, 1H, NH), 7.08-7.14 (m, 2H), 6.88-6.92 (m, 2H), 4.71 (s, 1H), 4.16 (q, *J* 7.2Hz, 2H), 3.86 (s, 3H), 2.01 (s, 3H), 1.28 (t, *J* 7.2Hz, 3H); $^{13}$C MNR (75MHz, $CDCl_3$): $\delta$ 170.2, 158.9, 152.6, 128.6, 125.3, 124.4, 120.3, 111.0, 86.3, 58.7, 55.7, 20.4, 14.6.

*(Z)-4-(2-Methoxyphenylamino)pent-3-en-2-one (**3h**)*[5]

Oil; IR (KBr) $\nu_{max}$/cm$^{-1}$: 3456, 2949, 2841, 1607, 1481, 1344, 1274, 1180, 1025, 747; $^1$H NMR (300MHz, $CDCl_3$): $\delta$ 12.32 (br s, 1H, NH), 7.01-7.18 (m, 2H), 6.87-6.93 (m, 2H), 5.20 (s, 1H), 3.86 (s, 3H), 2.10 (s, 3H), 1.99 (s, 3H); $^{13}$C MNR (75MHz, $CDCl_3$): $\delta$ 195.9, 160.4, 152.8, 128.0, 126.2, 125.0, 120.3, 111.2, 97.8, 55.7, 29.1, 20.0.

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*(Z)-Ethyl 3-(3-chlorophenylamino)but-2-enoate (**3i**)*[6]

Oil; IR (KBr) $\nu_{max}$/cm$^{-1}$: 3190, 2979, 1637, 1476, 1370, 1270, 1164, 1074, 784; $^1$H NMR (300MHz, $CDCl_3$): $\delta$ 10.42 (br s, 1H, NH), 7.10-7.22 (m, 3H), 6.94-6.96 (m, 1H), 4.72 (s, 1H), 4.15 (q, *J* 7.2Hz, 2H), 2.02 (s, 3H), 1.28 (t, *J* 7.2Hz, 3H); $^{13}$C MNR (75MHz, $CDCl_3$): $\delta$ 170.3, 158.0, 140.7, 134.6, 130.0, 124.7, 123.9, 122.1, 87.5, 59.0, 20.4, 14.6.

*(Z)-4-(3-Chlorophenylamino)pent-3-en-2-one (**3j**)*

Solid, mp: 37-39 °C (Lit.[1] 39-40 °C); IR (KBr) $\nu_{max}$/cm$^{-1}$: 3428, 2978, 1578, 1491, 1429, 1276, 1186, 1020, 937, 772; $^1$H NMR (300MHz, $CDCl_3$): $\delta$ 12.47 (br s, 1H, NH), 6.98-7.29 (m, 4H), 5.22 (s, 1H), 2.11 (s, 3H), 2.02 (s, 3H); $^{13}$C MNR (75MHz, $CDCl_3$): $\delta$ 196.4, 157.8, 140.2, 128.1, 127.5, 124.9, 118.3, 115.7, 97.0, 43.2, 19.3.

*(Z)-Ethyl 3-(4-chlorophenylamino)but-2-enoate (**3k**)*

Solid, mp: 52-54 °C (Lit.[1] 54-55 °C); IR (KBr) $\nu_{max}$/cm$^{-1}$: 3457, 2980, 1633, 1491, 1383, 1272, 1160, 787; $^1$H NMR (300MHz, $CDCl_3$): $\delta$ 10.34 (br s, 1H, NH), 7.22-7.26 (m, 2H), 6.97-6.99 (m, 2H), 4.69 (s, 1H), 4.12 (q, *J* 7.2Hz, 2H), 1.95 (s, 3H), 1.26 (t, *J* 7.2Hz, 3H); $^{13}$C MNR (75MHz, $CDCl_3$): $\delta$ 170.4, 158.3, 138.0, 130.2, 129.2, 125.5, 86.9, 58.9, 20.2, 14.6.

*(Z)-Ethyl 3-(4-bromophenylamino)but-2-enoate (**3l**)*

Solid, mp: 53-55 °C (Lit.[3] 54-55 °C); IR (KBr) $\nu_{max}$/cm$^{-1}$: 3451, 3273, 2924, 1622, 1482, 1358, 1269, 1163, 1059, 786; $^1$H NMR (300MHz, $CDCl_3$): $\delta$ 10.35 (br s, 1H, NH), 7.38-7.43 (m, 2H), 6.91-6.96 (m, 2H), 4.70 (s, 1H), 4.12 (q, *J* 7.2Hz, 2H), 1.97 (s, 3H), 1.26 (t, *J* 7.2Hz, 3H); $^{13}$C MNR (75MHz, $CDCl_3$): $\delta$ 170.3, 158.2, 138.5, 132.1, 125.7, 117.9, 87.0, 58.9, 20.3, 14.6.

*(Z)-Ethyl 3-(propylamino)but-2-enoate (**3m**)*[7]

Oil; IR (KBr) $\nu_{max}$/cm$^{-1}$: 3285, 2965, 1609, 1448, 1270, 1160, 1065, 784, 695; $^1$H NMR (300MHz, $CDCl_3$): $\delta$ 8.51 (br s, 1H, NH), 4.36 (s, 1H), 4.00-4.03 (m, 2H), 3.07-3.11 (m, 2H), 1.85 (s, 3H), 1.49-1.53 (m, 2H), 1.16-1.18 (m, 3H), 0.90-0.91 (m, 3H); $^{13}$C MNR (75MHz, $CDCl_3$): $\delta$ 170.5, 161.8, 81.6, 58.0, 44.5, 23.5, 19.2, 14.5, 11.2.

*(Z)-4-(Propylamino)pent-3-en-2-one (**3n**)*[8]

Oil; IR (KBr) $\nu_{max}$/cm$^{-1}$: 3451, 2960, 1603, 1443, 1359, 1295, 740, 647; $^1$H NMR (300MHz, $CDCl_3$): $\delta$ 10.85 (br s, 1H, NH), 4.93 (s, 1H), 3.14-3.21 (m, 2H), 1.98 (s, 3H), 1.90 (s, 3H), 1.53-1.62 (m, 2H), 0.93-0.98 (m, 3H); $^{13}$C MNR (75MHz, $CDCl_3$): $\delta$ 194.8, 163.1, 95.0, 44.8, 28.7, 23.3, 18.8, 11.3.

*(Z)-Ethyl 3-(benzylamino)but-2-enoate (**3o**)*[5]

Oil; IR (KBr) $\nu_{max}$/cm$^{-1}$: 3289, 2977, 1605, 1499, 1445, 1280, 1169, 1113, 786, 697; $^1$H NMR (300MHz, $CDCl_3$): $\delta$ 8.96 (br s, 1H, NH), 7.24-7.37 (m, 5H), 4.54 (s, 1H), 4.43 (d, *J* 6.3Hz, 2H), 4.10 (q, *J* 7.2Hz, 2H), 1.92 (s, 3H), 1.26 (t, *J* 7.2Hz, 3H); $^{13}$C MNR (75MHz, $CDCl_3$): $\delta$ 170.5, 161.7, 138.7, 128.7, 127.2, 126.6, 83.1, 58.3, 46.7, 19.3, 14.5.

*(Z)-4-(Benzylamino)pent-3-en-2-one (**3p**)*[5]

Oil; IR (KBr) $\nu_{max}$/cm$^{-1}$: 3446, 2926, 1605, 1509, 1441, 1360, 1295, 1104, 1023, 739; $^1$H NMR (300MHz, $CDCl_3$): $\delta$ 11.16 (br s, 1H, NH), 7.24-7.36 (m, 5H), 5.04 (s, 1H), 4.45 (d, *J* 6.3Hz, 2H), 2.03 (s, 3H) 1.91 (s, 3H); $^{13}$C MNR (75MHz, $CDCl_3$): $\delta$ 195.3, 163.0, 138.0, 128.7, 127.3, 126.6, 95.8, 46.6, 28.8, 18.8.

*4-(Diethylamino)pent-3-en-2-one (**3q**)*[9]

Oil; IR (KBr) $\nu_{max}$/cm$^{-1}$: 2975, 1628, 1538, 1439, 1355, 1193; $^1$H NMR (300MHz, $CDCl_3$): $\delta$ 5.07 (s, 1H), 3.25-3.32 (m, 4H), 2.51 (s, 3H), 2.05 (s, 3H), 1.13-1.18 (m, 6H); $^{13}$C MNR (75MHz, $CDCl_3$): $\delta$ 194.1, 160.0, 93.8, 43.7, 15.1, 12.4.

*4-Morpholinopent-3-en-2-one (**3r**)*[1]

Oil; IR (KBr) $\nu_{max}$/cm$^{-1}$: 2964, 2854, 1640, 1544, 1431, 1257, 1184, 1119; $^1$H NMR (300MHz, $CDCl_3$): $\delta$ 5.21 (s, 1H), 3.64-3.71 (m, 4H), 3.26-3.30 (m, 4H), 2.43 (s, 3H), 1.97 (s, 3H); $^{13}$C MNR (75MHz, $CDCl_3$): $\delta$ 195.5, 160.6, 96.9, 66.5, 45.8, 30.7, 15.1.

*Ethyl 3-morpholinobut-2-enoate (**3s**)*[9]

Oil; IR (KBr) $\nu_{max}$/cm$^{-1}$: 2970, 2854, 1688, 1584, 1435, 1259, 1144, 998, 805; $^1$H NMR (300MHz, $CDCl_3$): $\delta$ 4.78 (s, 1H), 4.06-4.12 (m, 2H), 3.69-3.73 (m, 4H), 3.19-3.23 (m, 4H), 2.40 (s, 3H), 1.22-1.27 (m, 3H); $^{13}$C MNR (75MHz, $CDCl_3$): $\delta$ 168.6, 160.9, 88.1, 66.0, 58.4, 46.1, 15.0, 14.2.

*(2Z, 2'Z)-Diethyl 3, 3'-(propane-1, 3-diylbis(azanediyl)) dibut-2-enoate (**5a**)*[1]

Oil; IR (KBr) $\nu_{max}$/cm$^{-1}$: 3283, 3193, 2977, 2248, 1604, 1270, 913, 787, 726, 554; $^1$H NMR (300MHz, $CDCl_3$): $\delta$ 8.47 (br s, 2H, NH), 4.37 (s, 2H), 3.98 (q, *J* 7.2Hz, 4H), 3.22 (q, *J* 6.3Hz, 4H), 1.82 (s, 6H), 1.74-1.76 (m, 2H), 1.15 (t, *J* 7.2Hz, 6H); $^{13}$C MNR (75MHz, $CDCl_3$): $\delta$ 170.5, 161.7, 82.6, 58.2, 39.7, 30.9, 19.2, 14.5.

*(3Z, 3'Z)-4, 4'-(Propane-1, 3-diylbis(azanediyl))dipent-3-en-2-one (**5b**)*

Solid, mp: 43-45 °C (Lit.[10] 50-52 °C); IR (KBr) $\nu_{max}$/cm$^{-1}$: 3442, 2940, 1606, 1438, 1363, 1294, 1123, 1016, 742; $^1$H NMR (300MHz, $CDCl_3$): $\delta$ 10.87 (br s, 1H, NH), 4.98 (s,

1H), 3.32-3.38 (m, 2H), 1.99 (s, 3H), 1.92 (s, 3H), 1.85-1.89 (m, 1H); $^{13}$C MNR (75MHz, $CDCl_3$): $\delta$ 195.2, 163.2 95.6, 39.6, 30.2, 28.8, 18.8.

*(2Z,2'Z)-Diethyl 3,3'-(1,4-phenylenebis(azanediyl))dibut-2-enoate (**5c**)*[27]

Solid, mp: 135-137 °C (Lit.[11] 135 °C); IR (KBr) $\nu_{max}$/cm$^{-1}$: 2450, 2979, 2929, 1617, 1484, 1385, 1256, 1056, 780, 679; $^1$H NMR (300MHz, $CDCl_3$): $\delta$ 10.34 (br s, 2H, NH), 7.04 (s, 4H), 4.70 (s, 2H), 4.15 (q, *J* 7.2Hz, 4H), 2.00 (s, 6H), 1.29 (d, *J* 7.2Hz, 6H); $^{13}$C MNR (75MHz, $CDCl_3$): $\delta$ 170.3, 158.7, 136.2, 124.9, 86.2, 58.7, 20.2, 14.5.

*(3Z,3'Z)-4,4'-(1,4-Phenylenebis(azanediyl))dipent-3-en-2-one (**5d**)*[28]

Solid, mp: 185-187 °C (Lit.[12] 172 °C); IR (KBr) $\nu_{max}$/cm$^{-1}$: 3442, 2926, 1614, 1568, 1492, 1430, 1267, 1177, 1008, 865, 737; $^1$H NMR (300MHz, $CDCl_3$): $\delta$ 11.96 (br s, 2H, NH), 7.07 (s, 4H), 5.19 (s, 2H), 2.10 (s, 6H), 2.00 (s, 6H); $^{13}$C MNR (75MHz, $CDCl_3$): $\delta$ 196.3, 159.8, 136.1, 125.1, 97.8, 29.1, 19.8.

*(Z)-Ethyl 3-(2-aminophenylamino)but-2-enoate (**6a**)*[29]

Solid, mp: 77-79 °C (Lit.[13] 85 °C); IR (KBr) $\nu_{max}$/cm$^{-1}$: 3408, 3285, 2965, 1609, 1448, 1270, 1159, 1065, 784, 695; $^1$H NMR (300MHz, $CDCl_3$): $\delta$ 9.70 (br s, 1H, NH), 7.04-7.10 (m, 2H), 6.68-6.76 (m, 2H), 4.72 (s, 1H), 4.15 (q, *J* 7.2Hz, 2H), 3.84 (br s, 2H, NH), 1.80 (s, 3H), 1.28 (t, *J* 7.2Hz, 3H); $^{13}$C MNR (75MHz, $CDCl_3$): $\delta$ 170.6, 161.5, 143.5, 128.6, 128.0, 124.7, 118.3, 115.6, 85.1, 58.7, 19.7, 14.6.

*(Z)-4-(2-Aminophenylamino)pent-3-en-2-one (**6b**)*

Solid, mp: 129-131 °C (Lit.[6] not reported); IR (KBr) $\nu_{max}$/cm$^{-1}$: 3759, 3445, 2931, 1624, 1426, 1256, 1255, 1114, 765; $^1$H NMR (300MHz, $CDCl_3$): $\delta$ 12.47 (br s, 1H, NH), 6.98-7.28 (m, 4H), 5.21 (s, 1H), 2.10 (s, 3H), 2.02 (s, 3H); $^{13}$C MNR (75MHz, $CDCl_3$): $\delta$ 196.7, 159.3, 140.1, 134.6, 130.1, 125.4, 124.5, 122.6, 98.4, 29.3, 19.9.

## References


1. Zhang, Z. H.; Yin, L.; Wang, Y. M.; *Adv. Synth. Catal.* **2006**, *348*, 184.
2. Khodaei, M. M.; Khosropour, A. R.; Kookhazadeh, M.; *Synlett* **2004**, 1980.
3. Xu, F.; Lv, H.-X.; Wang, J.-P.; Tian, Y.-P.; Wang, J.-J.; *J. Chem. Res.* **2008**, 707.
4. Roberts, E.; Turnur, E. E.; *J. Chem. Soc.* **1927**, 1832.
5. Chen, X.; She, J.; Shang, Z. C.; Wu, J.; Wu, H. F.; Zhang, P. Z.; *Synthesis* **2008**, 3478.
6. Song, Z. Y.; Bai, D. R.; Yu, H. T.; Xu, L. L.; Zhang, W. X.; Meng, J. B.; Matsuura, T.; *Chin. Chem. Lett.* **2004**, *15*, 127.
7. Jacobs, J.; Kesteleyn, B.; De Kimpe, N.; *Tetrahedron* **2008**, *64*, 7545.
8. Zhang, Y.; Raines, A. J.; Flowers, R. A.; *J. Org. Chem.* **2004**, *69*, 6267.
9. Vohra, R. K.; Renaud, J. L.; Bruneau, C.; *Synthesis* **2007**, 731.
10. Zhang, Z. H.; Hu, J.-Y; *J. Braz. Chem. Soc.* **2006**, *17*, 1447.
11. Bangdiwala, B. P.; Desai, C. M.; *J. Indian Chem. Soc.* **1954**, *31*, 688.
12. Kudryavtsev, A. S.; Savich, I. A.; Khimiya **1962**, *17*, 57.
13. Sexton, W. A.; *J. Chem. Soc.* **1942**, 303.

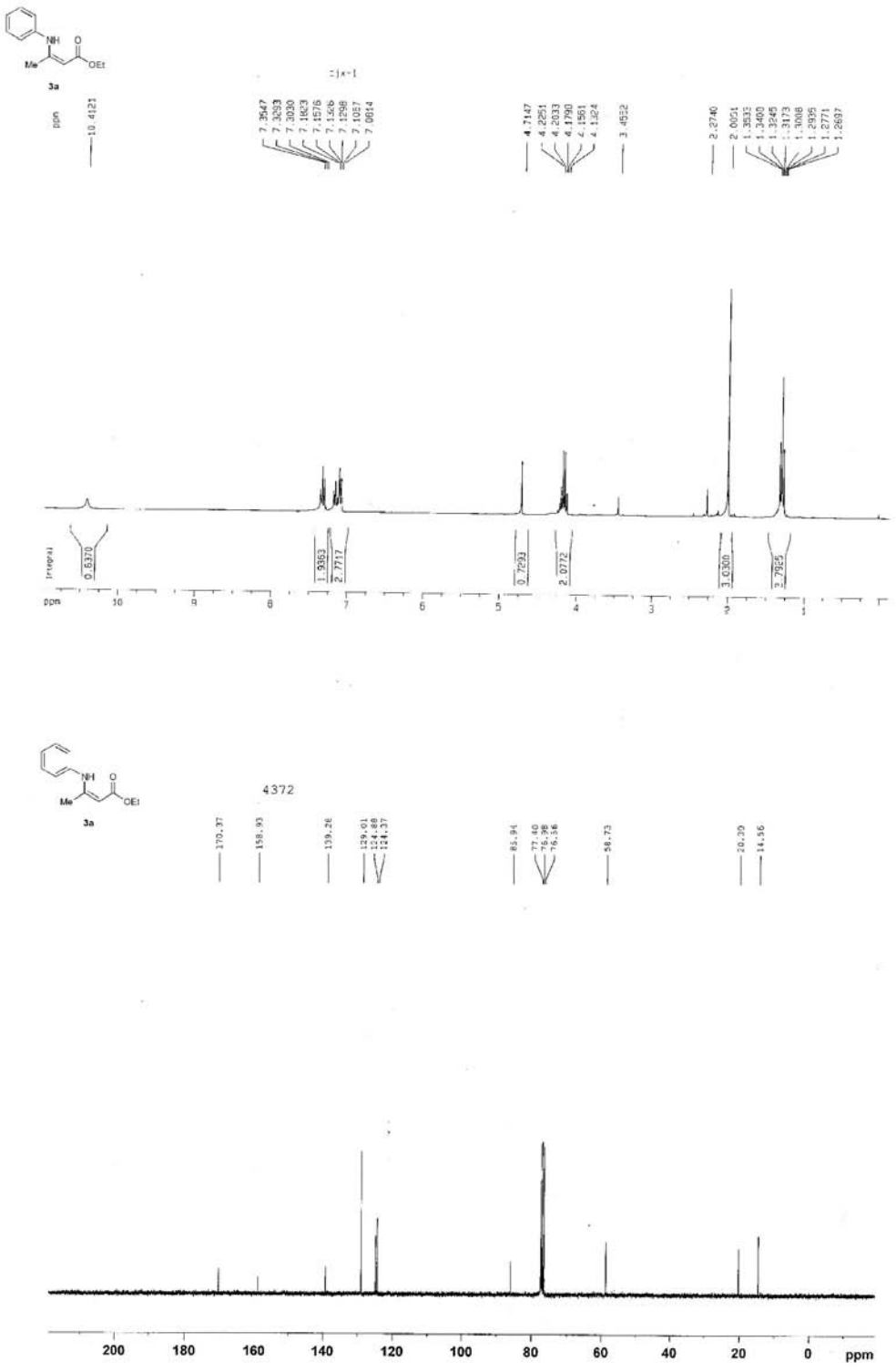


**Figure S1.** $^{1}H$ NMR of **3a** (300 MHz, $CDCl_3$) and $^{13}C$ NMR of **3a** (75 MHz, $CDCl_3$).

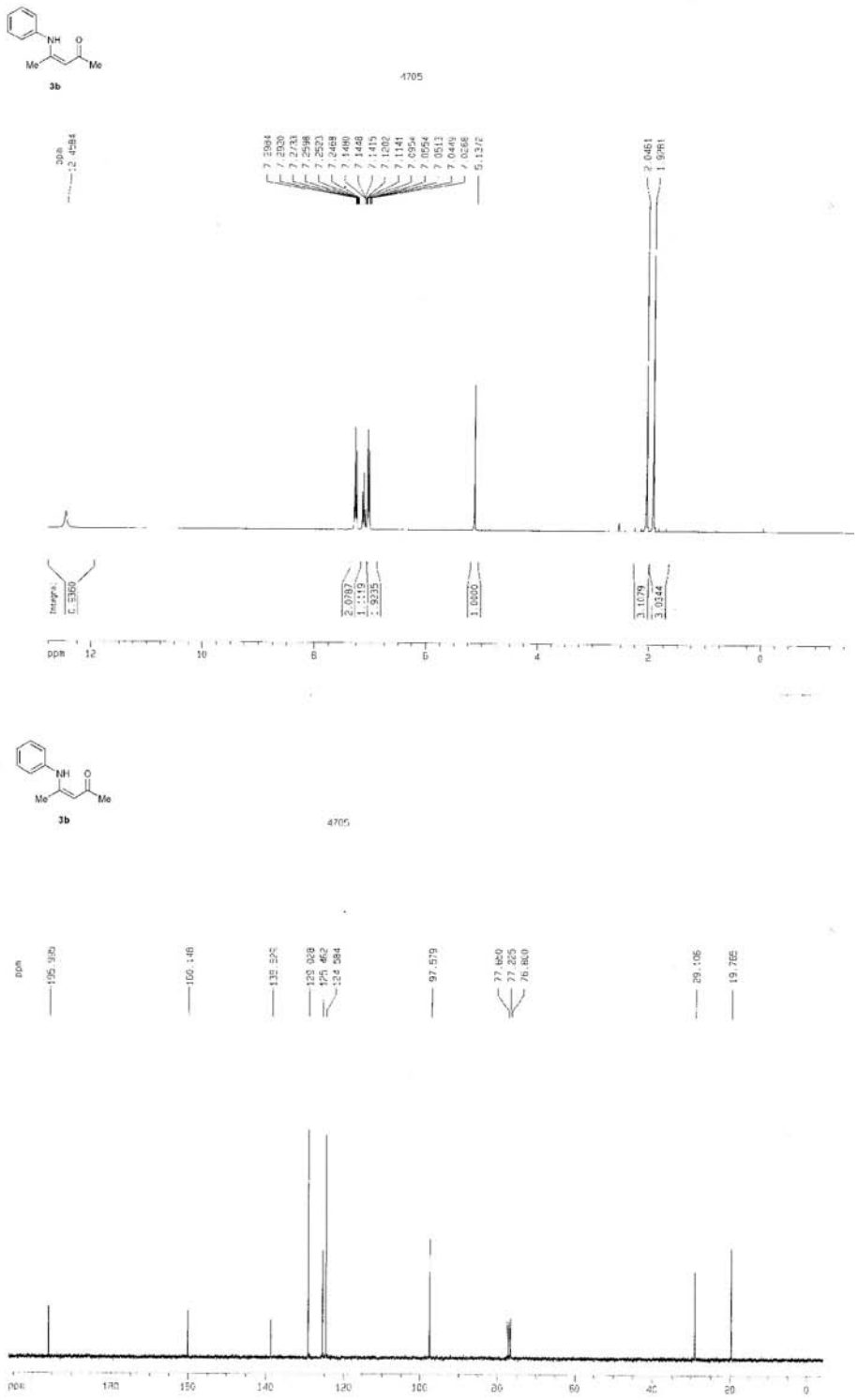

**Figure S2.** $^{1}$H NMR of **3b** (300 MHz, $CDCl_3$) and $^{13}$C NMR of **3b** (75 MHz, $CDCl_3$).

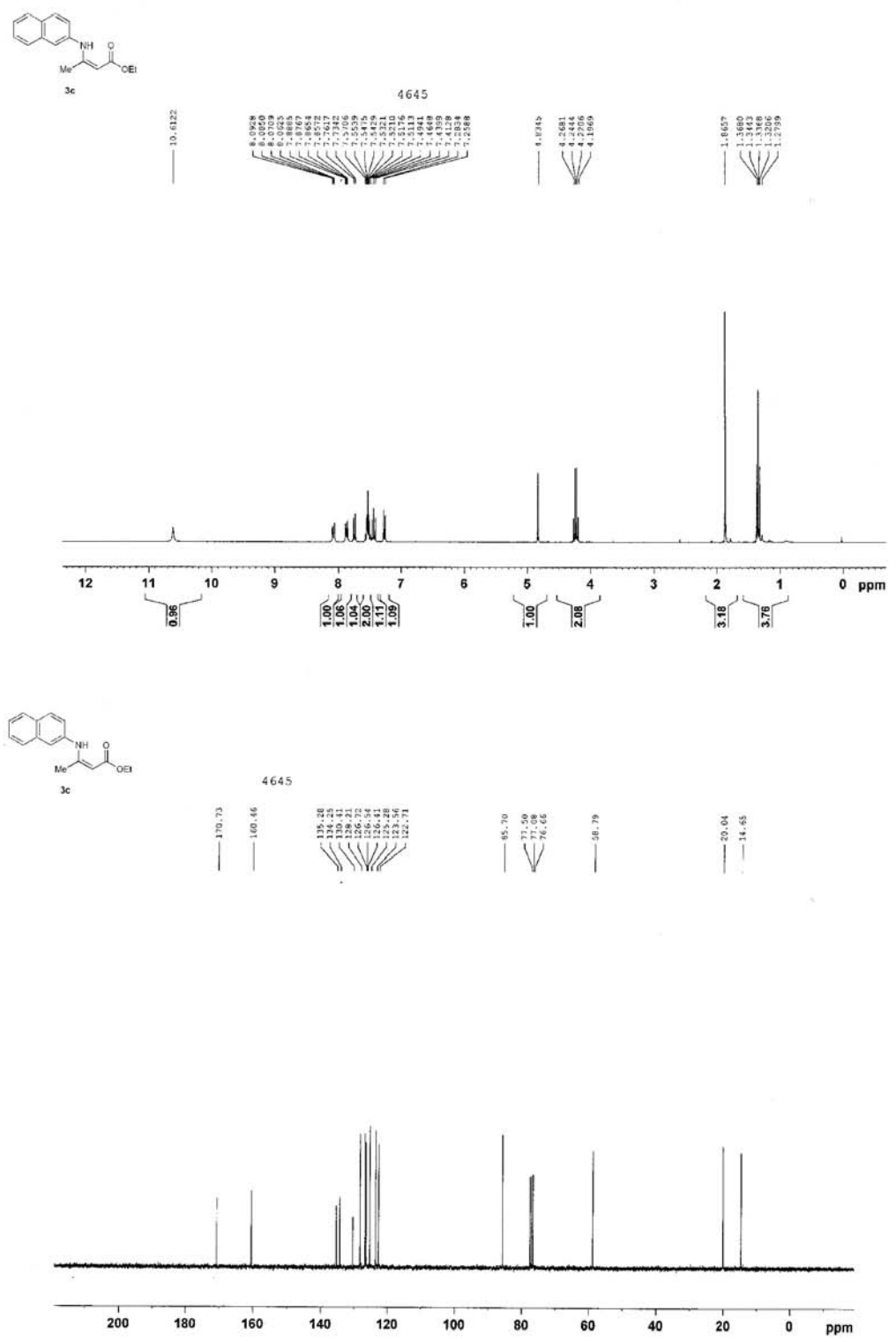


**Figure S3.** $^{1}H$ NMR of **3c** (300 MHz, $CDCl_3$) and $^{13}C$ NMR of **3c** (75 MHz, $CDCl_3$).

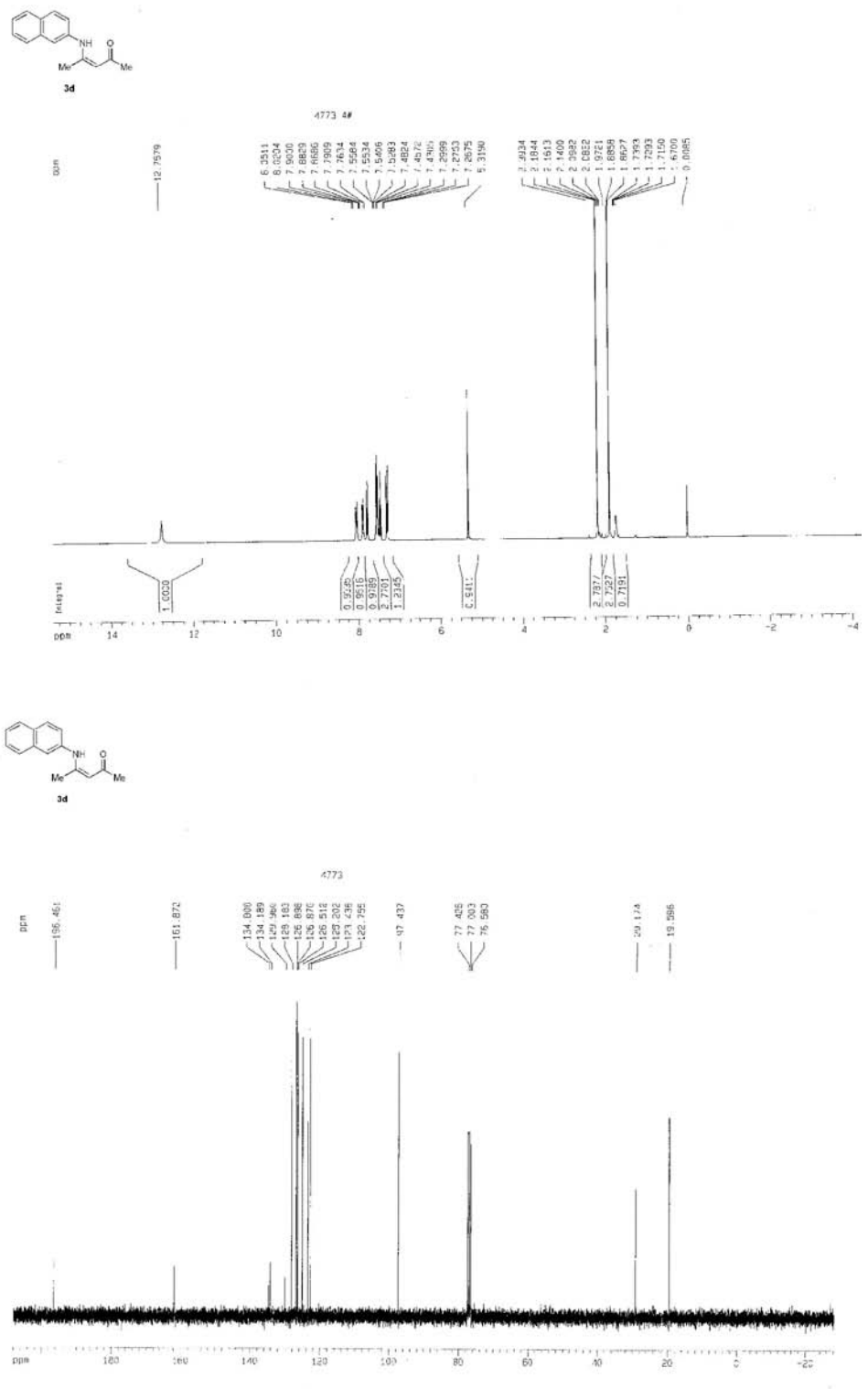


**Figure S4.** $^{1}$H NMR of **3d** (300 MHz, $CDCl_3$) and $^{13}$C NMR of **3d** (75 MHz, $CDCl_3$).

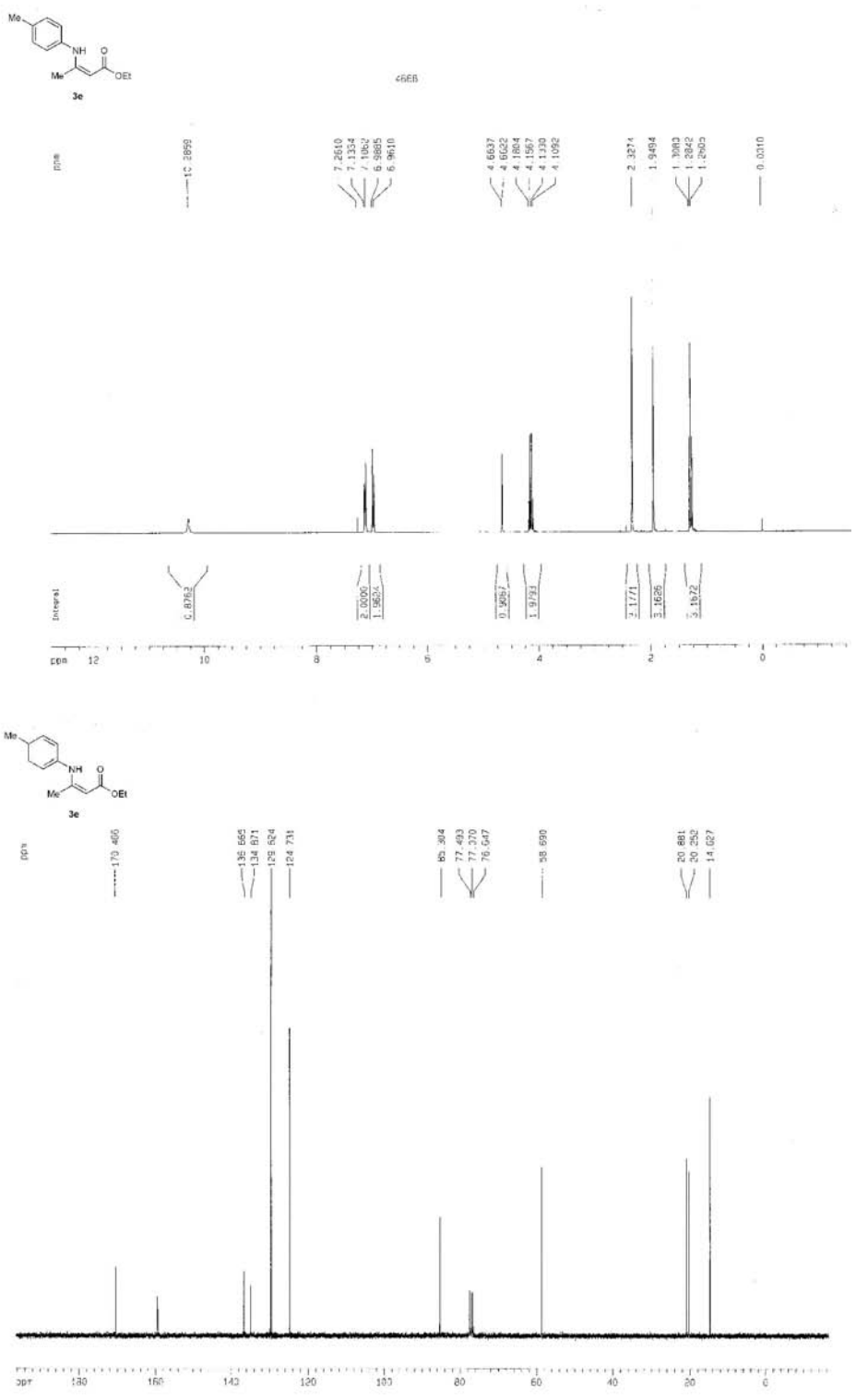


**Figure S5.** $^1$H NMR of **3e** (300 MHz, $CDCl_3$) and $^{13}$C NMR of **3e** (75 MHz, $CDCl_3$).

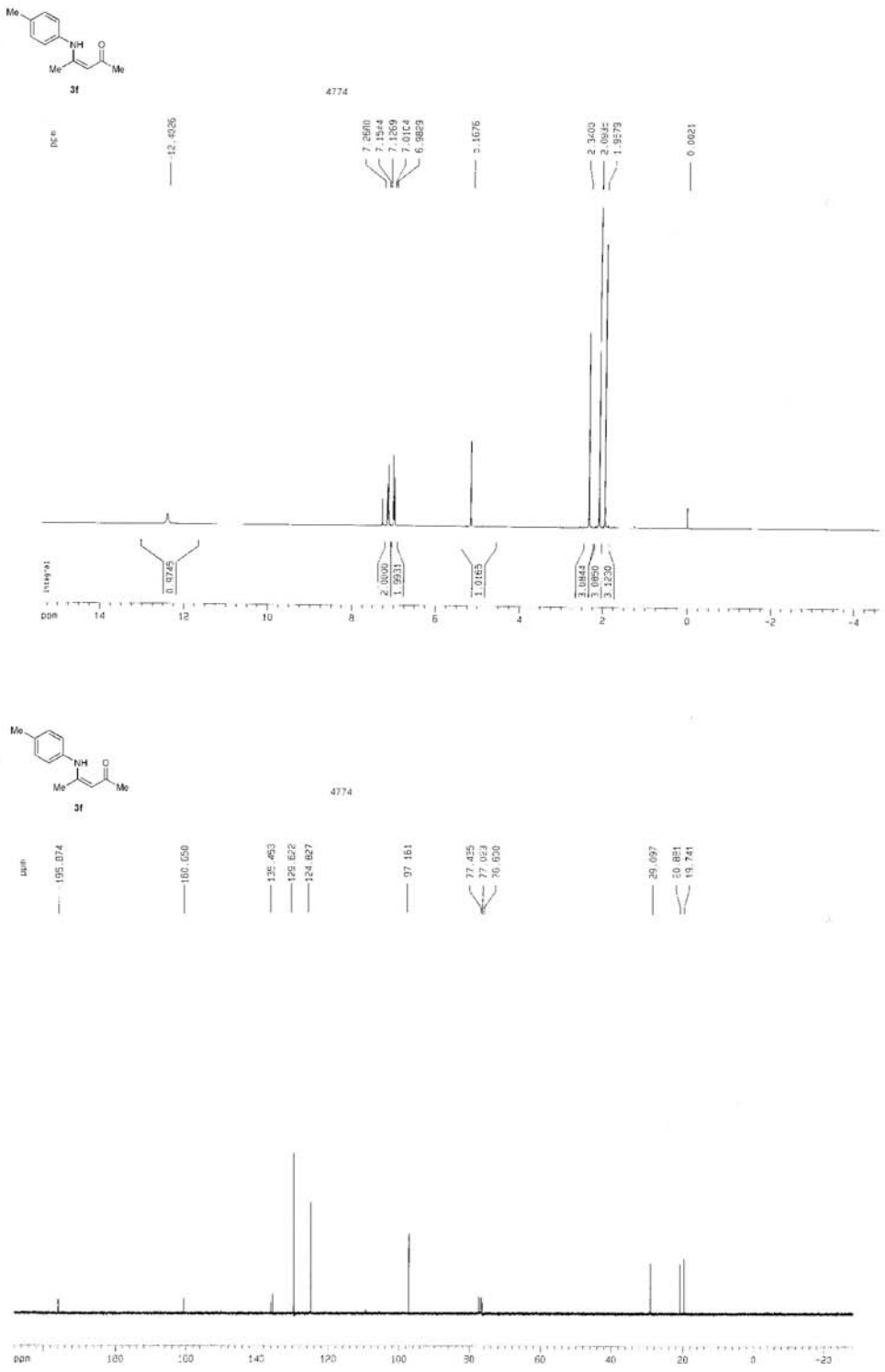


**Figure S6.** $^{1}$H NMR of **3f** (300 MHz, $CDCl_3$) and $^{13}$C NMR of **3f** (75 MHz, $CDCl_3$).

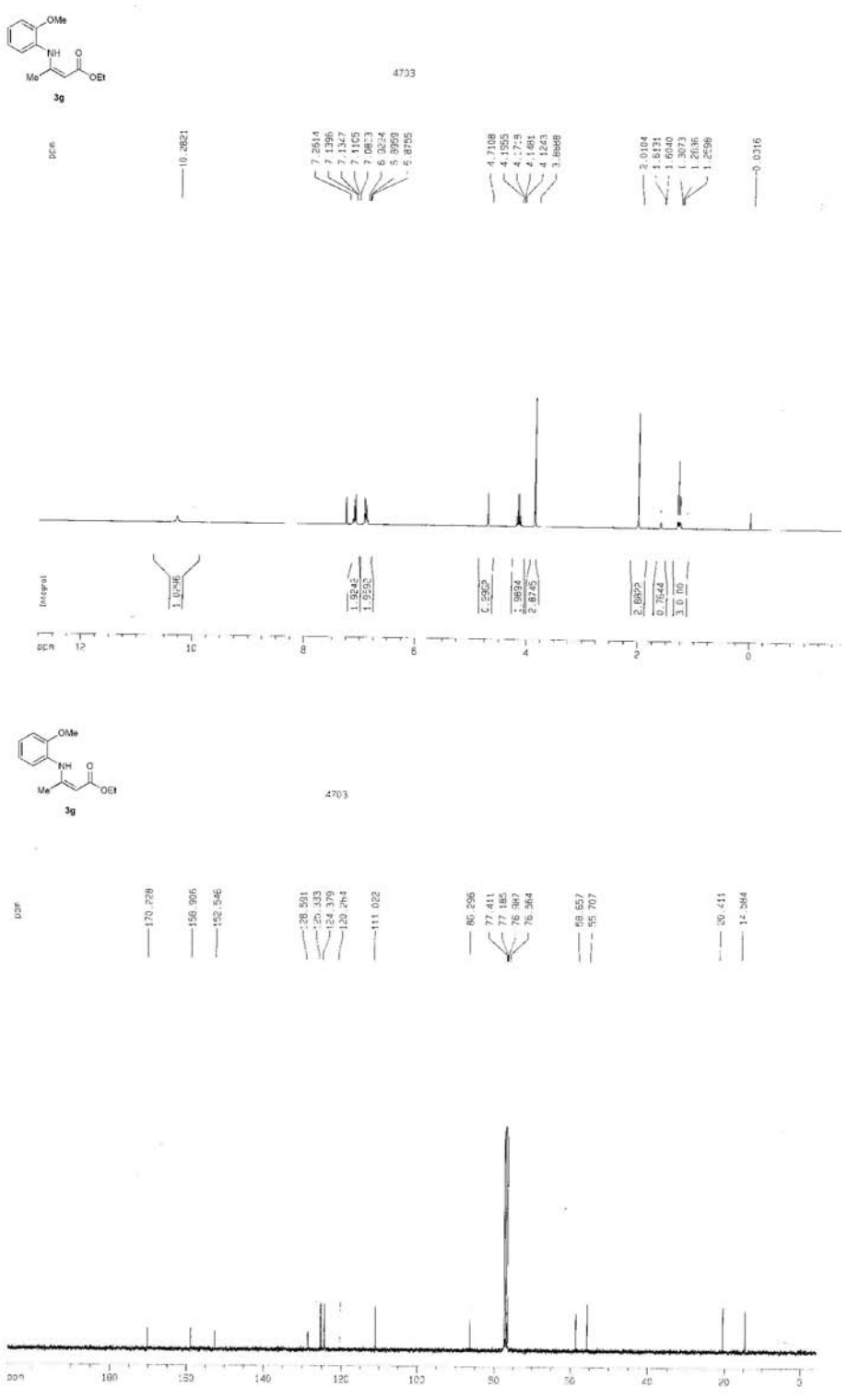

**Figure S7.** $^{1}H$ NMR of **3g** (300 MHz, $CDCl_3$) and $^{13}C$ NMR of **3g** (75 MHz, $CDCl_3$).

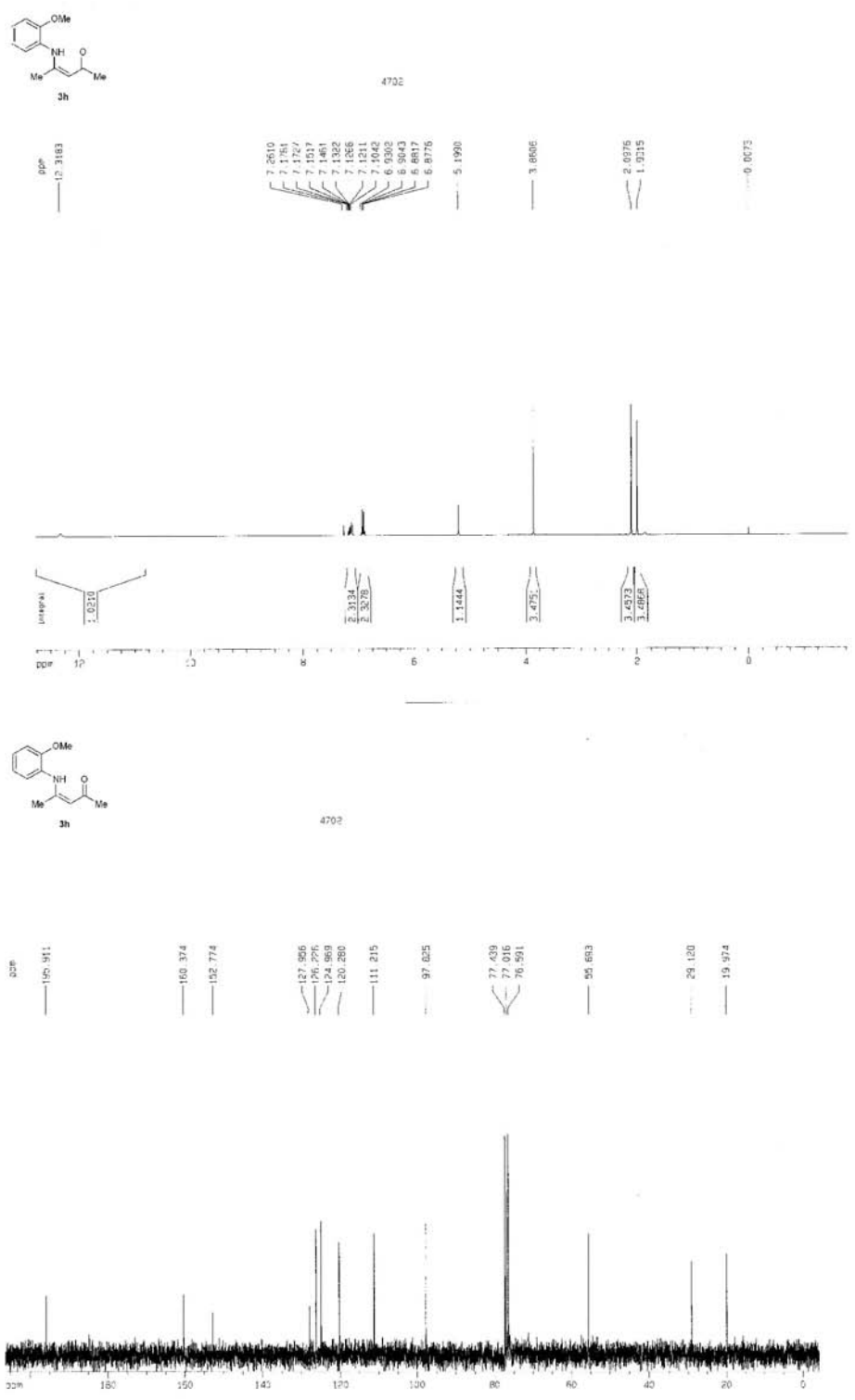


**Figure S8.** $^{1}H$ NMR of **3h** (300 MHz, $CDCl_3$) and $^{13}C$ NMR of **3h** (75 MHz, $CDCl_3$).

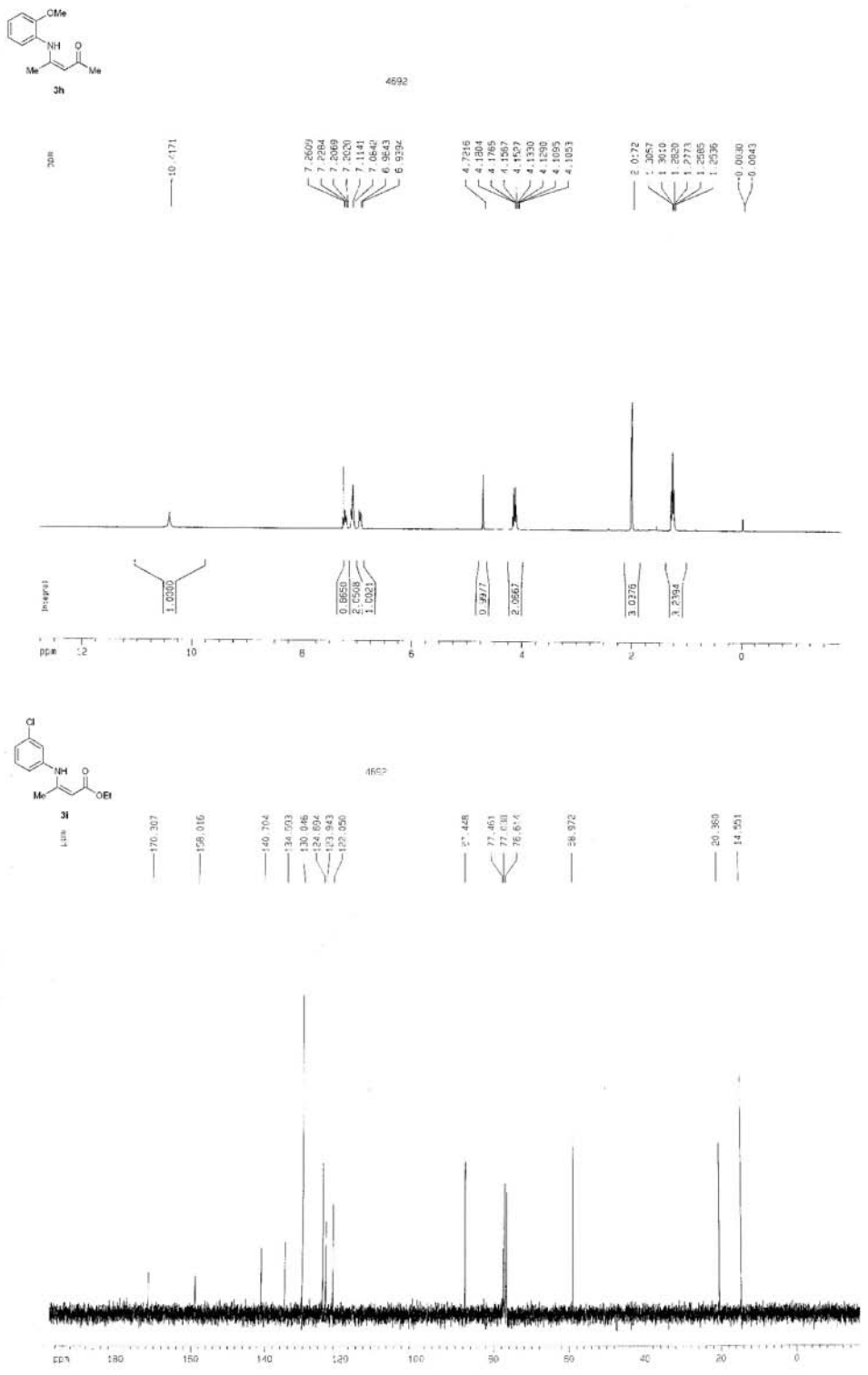

**Figure S9.** $^{1}H$ NMR of **3i** (300 MHz, $CDCl_3$) and $^{13}C$ NMR of **3i** (75 MHz, $CDCl_3$).

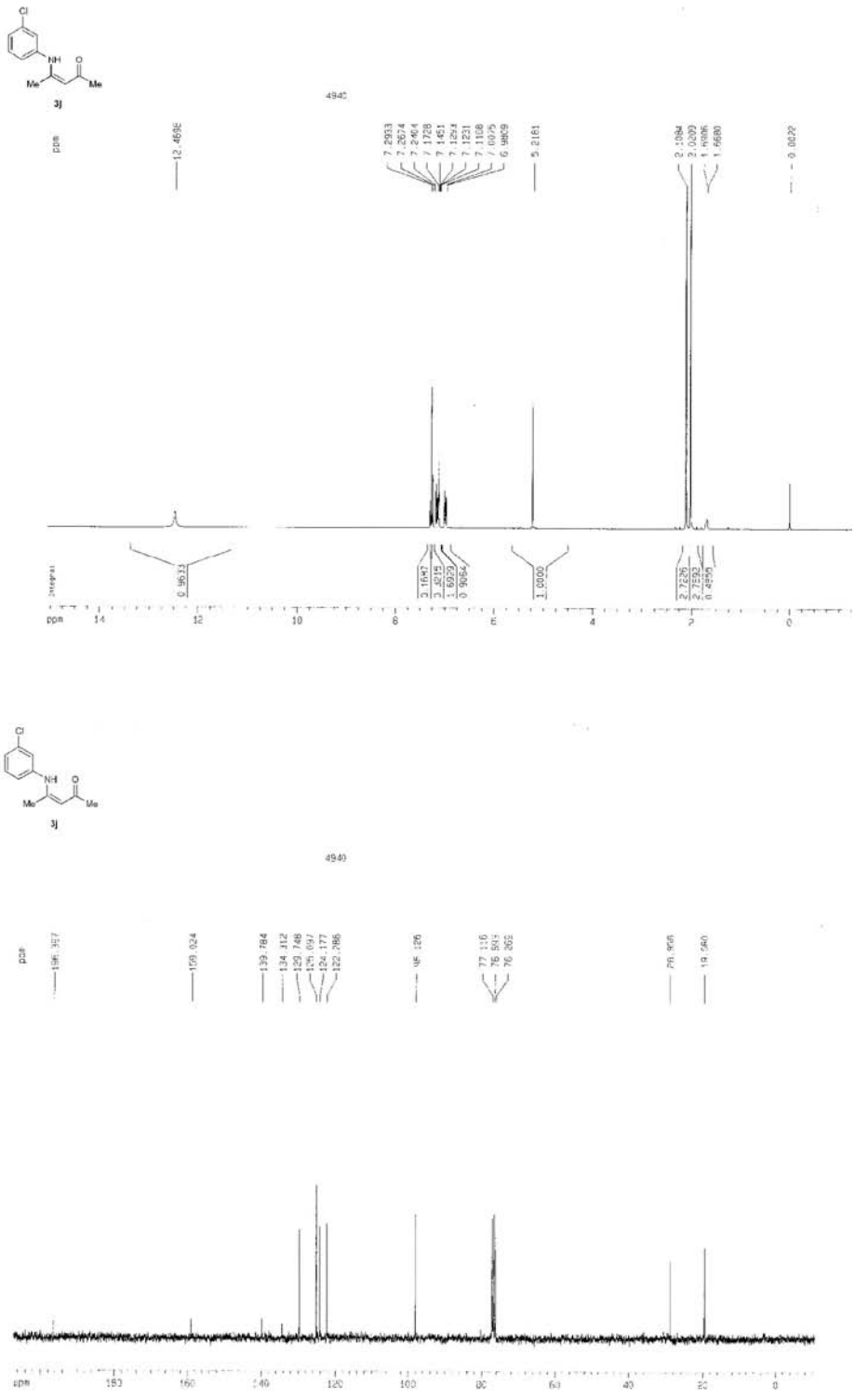

**Figure S10.** $^{1}$H NMR of **3j** (300 MHz, $CDCl_3$) and $^{13}$C NMR of **3j** (75 MHz, $CDCl_3$).

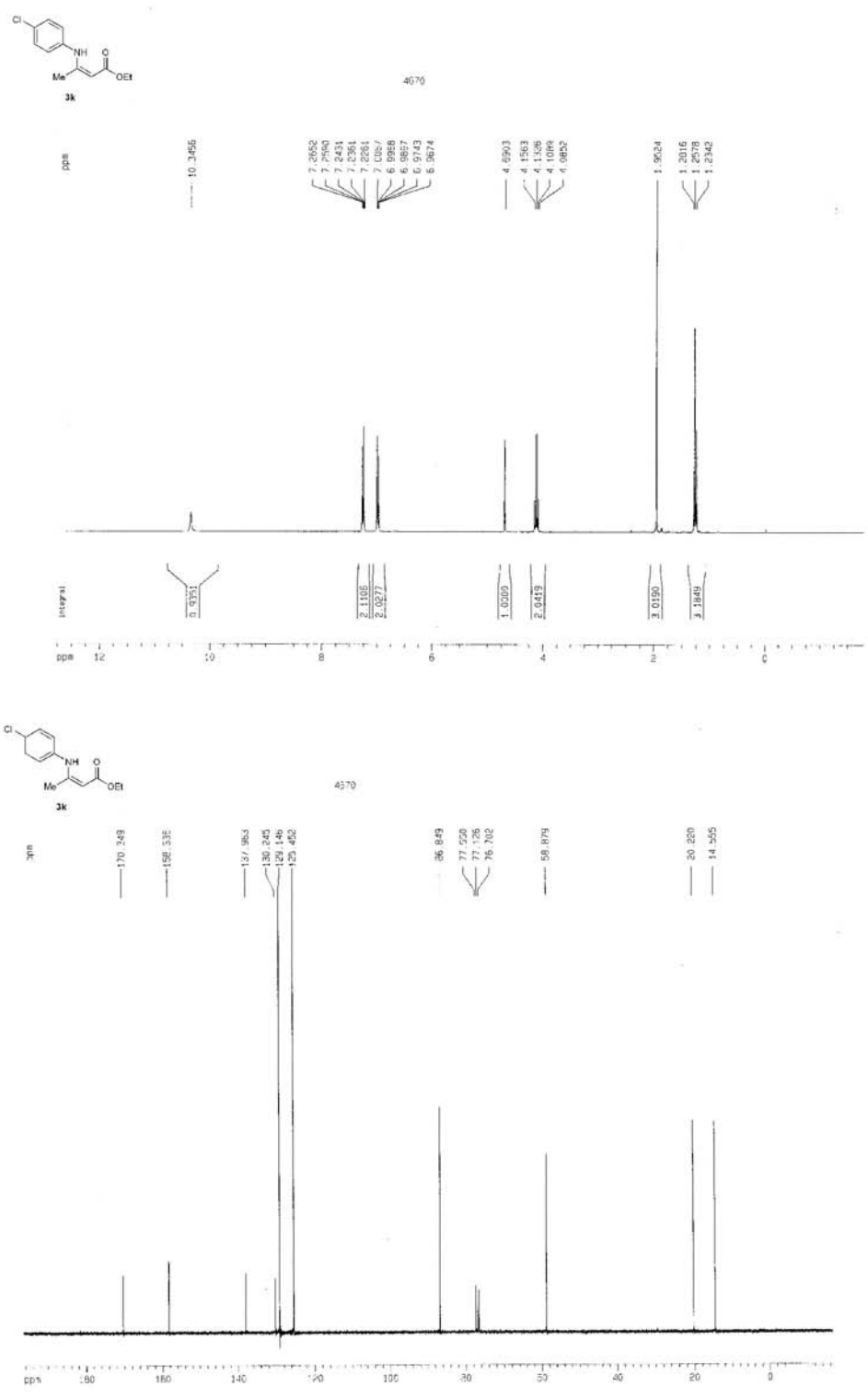


**Figure S11.** $^1$H NMR of **3k** (300 MHz, $CDCl_3$) and $^{13}$C NMR of **3k** (75 MHz, $CDCl_3$).

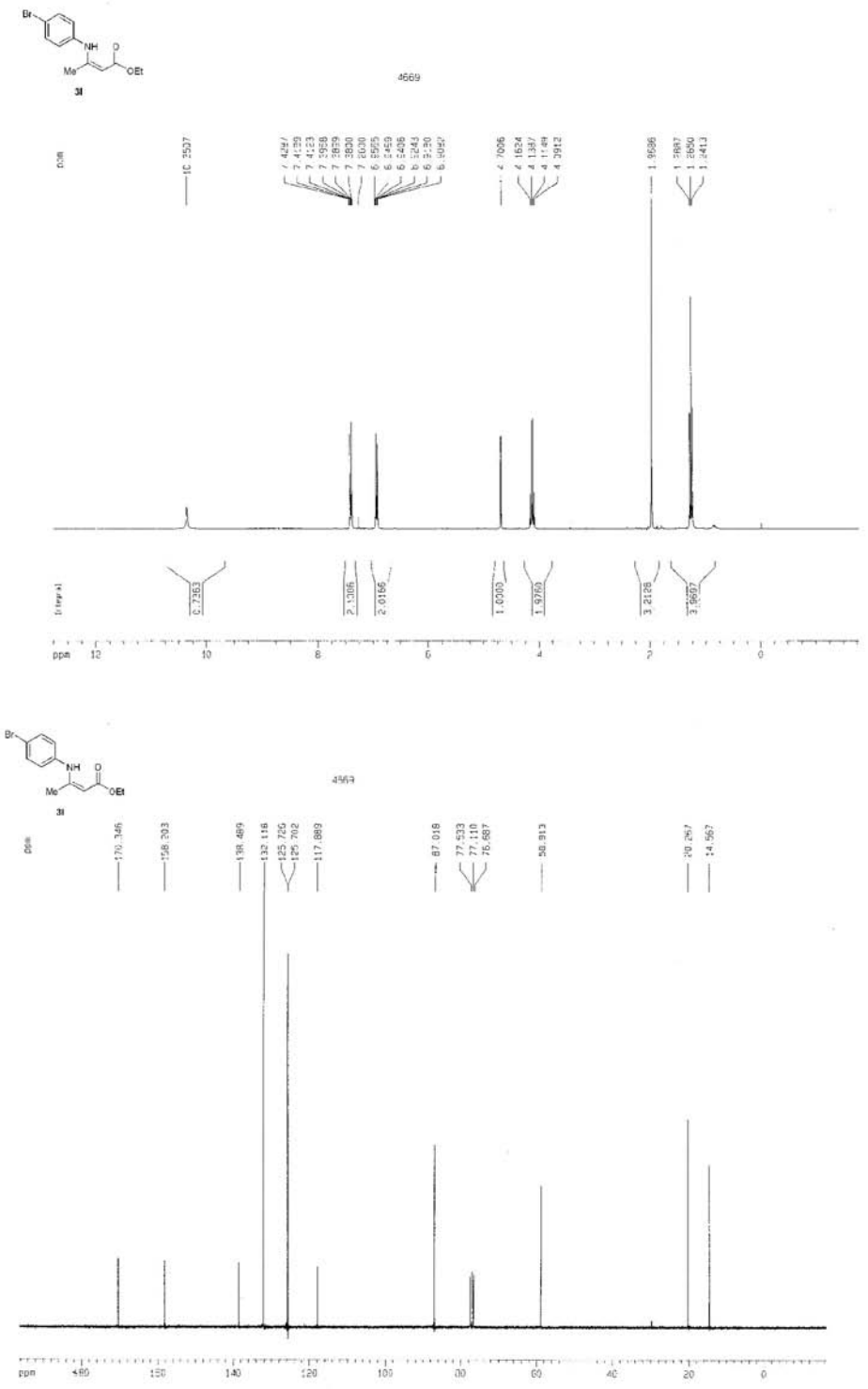


**Figure S12.** $^{1}$H NMR of **3l** (300 MHz, $CDCl_3$) and $^{13}$C NMR of **3l** (75 MHz, $CDCl_3$).

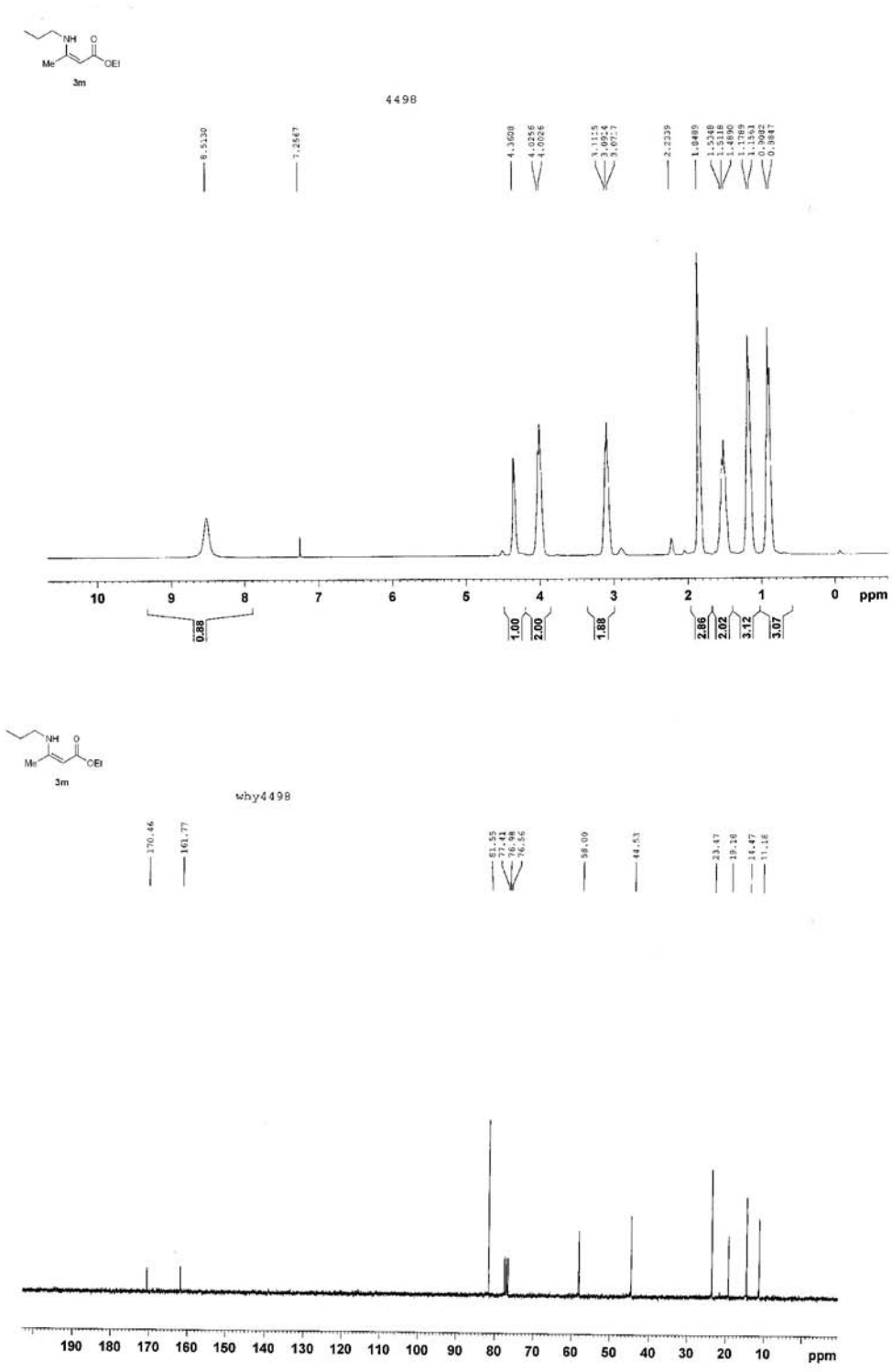


**Figure S13.** $^{1}H$ NMR of **3m** (300 MHz, $CDCl_3$) and $^{13}C$ NMR of **3m** (75 MHz, $CDCl_3$).

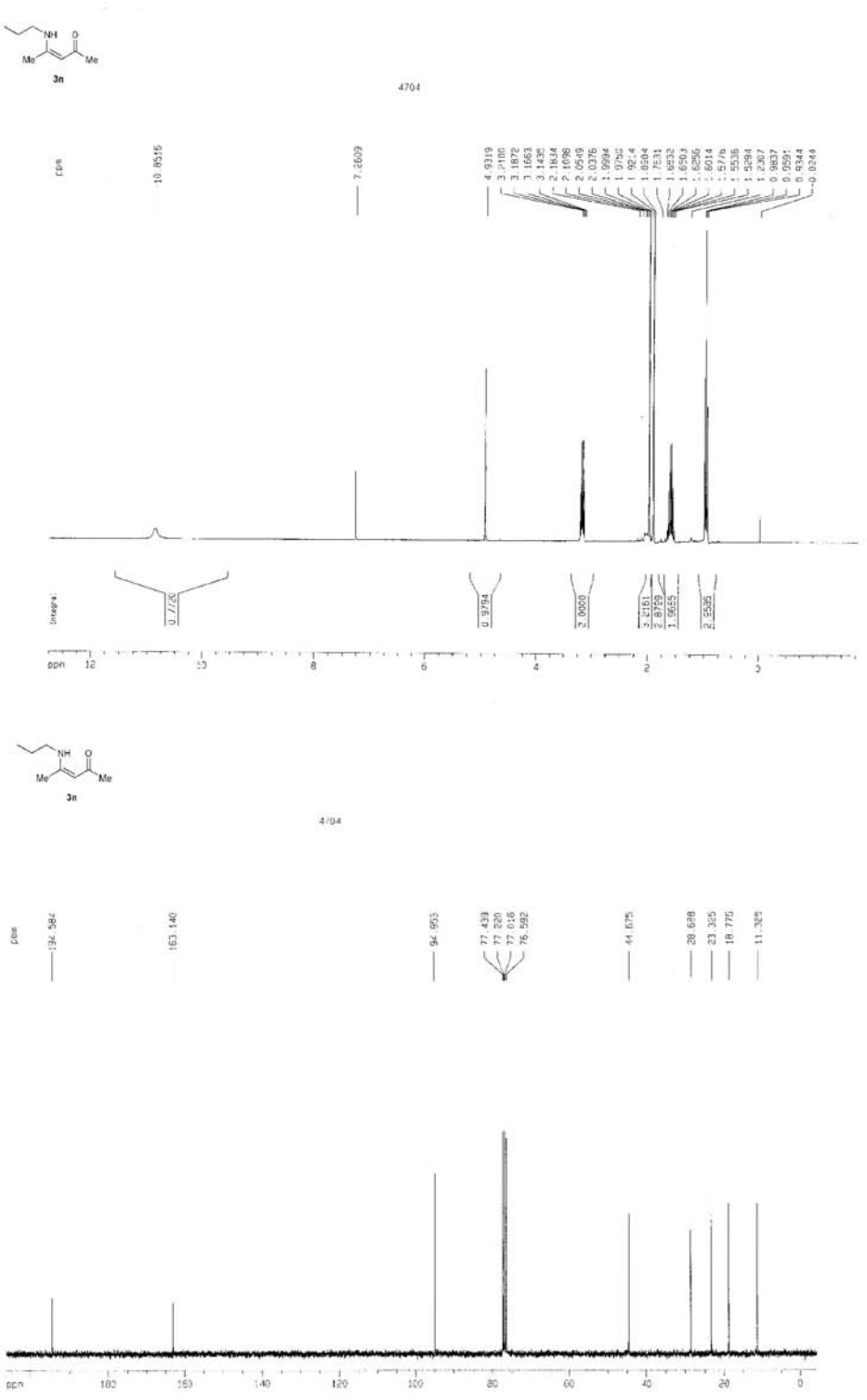


**Figure S14.** $^{1}$H NMR of **3n** (300 MHz, $CDCl_3$) and $^{13}$C NMR of **3n** (75 MHz, $CDCl_3$).

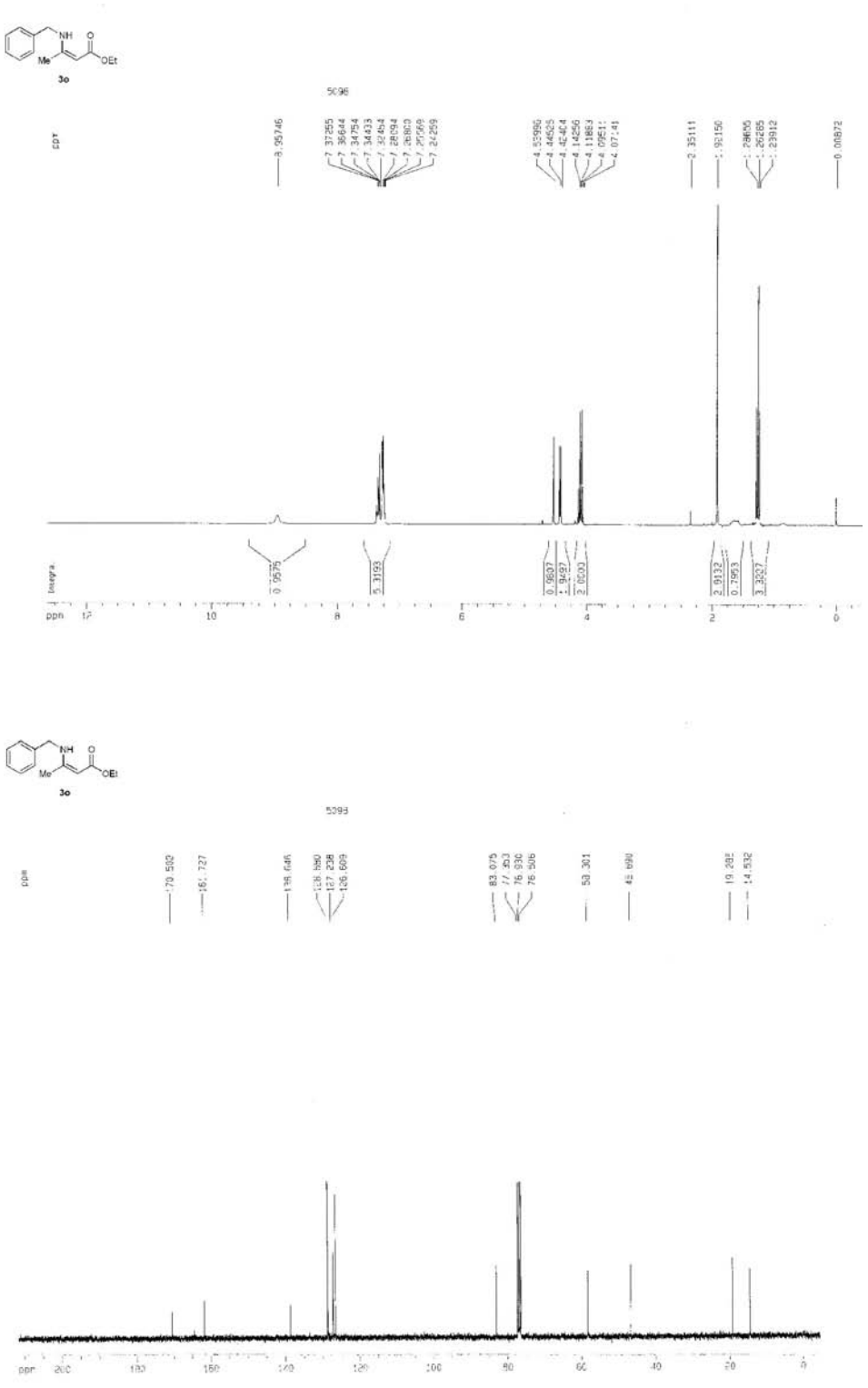


**Figure S15.** $^1$H NMR of **3o** (300 MHz, $CDCl_3$) and $^{13}$C NMR of **3o** (75 MHz, $CDCl_3$).

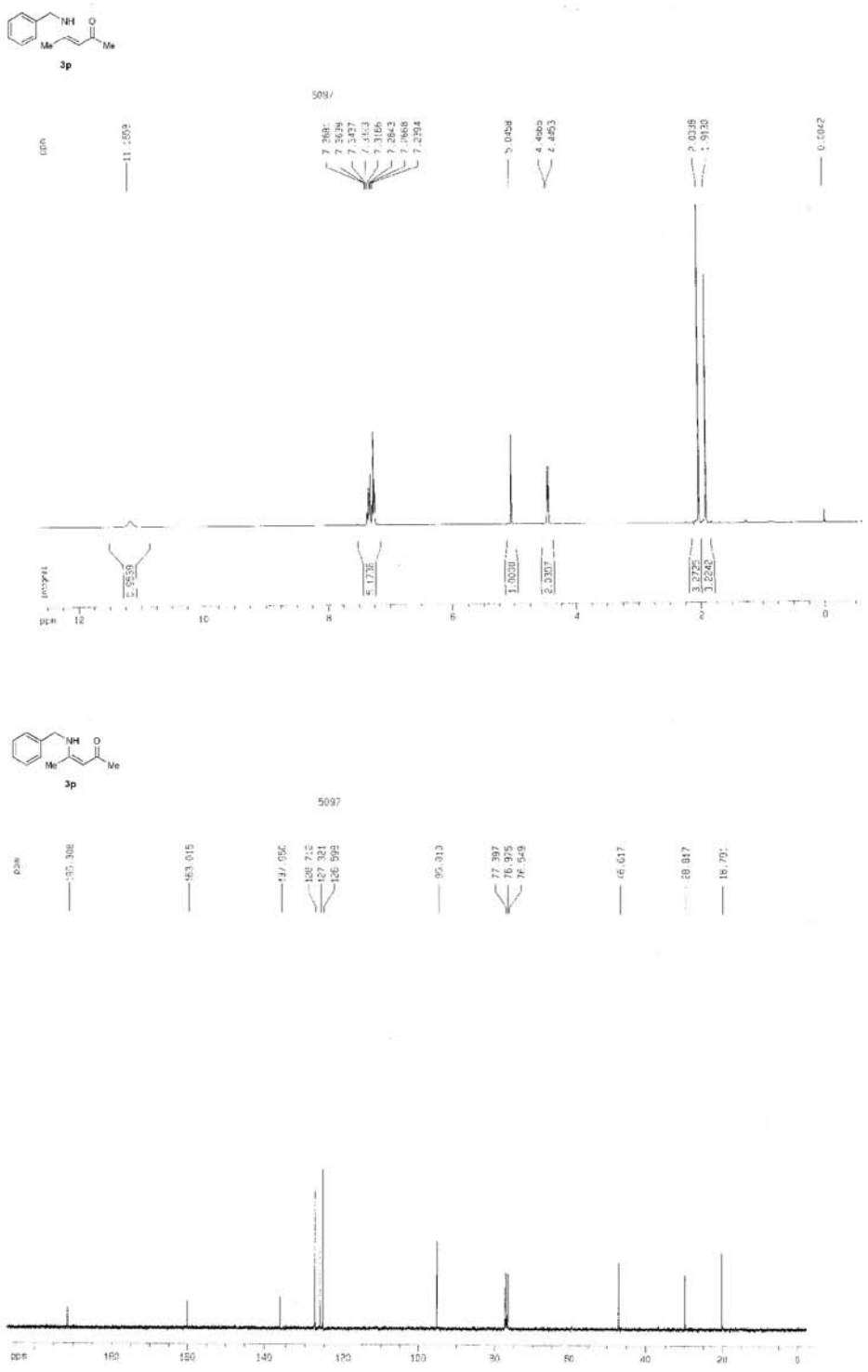


**Figure S16.** $^{1}$H NMR of **3p** (300 MHz, $CDCl_3$) and $^{13}$C NMR of **3p** (75 MHz, $CDCl_3$).

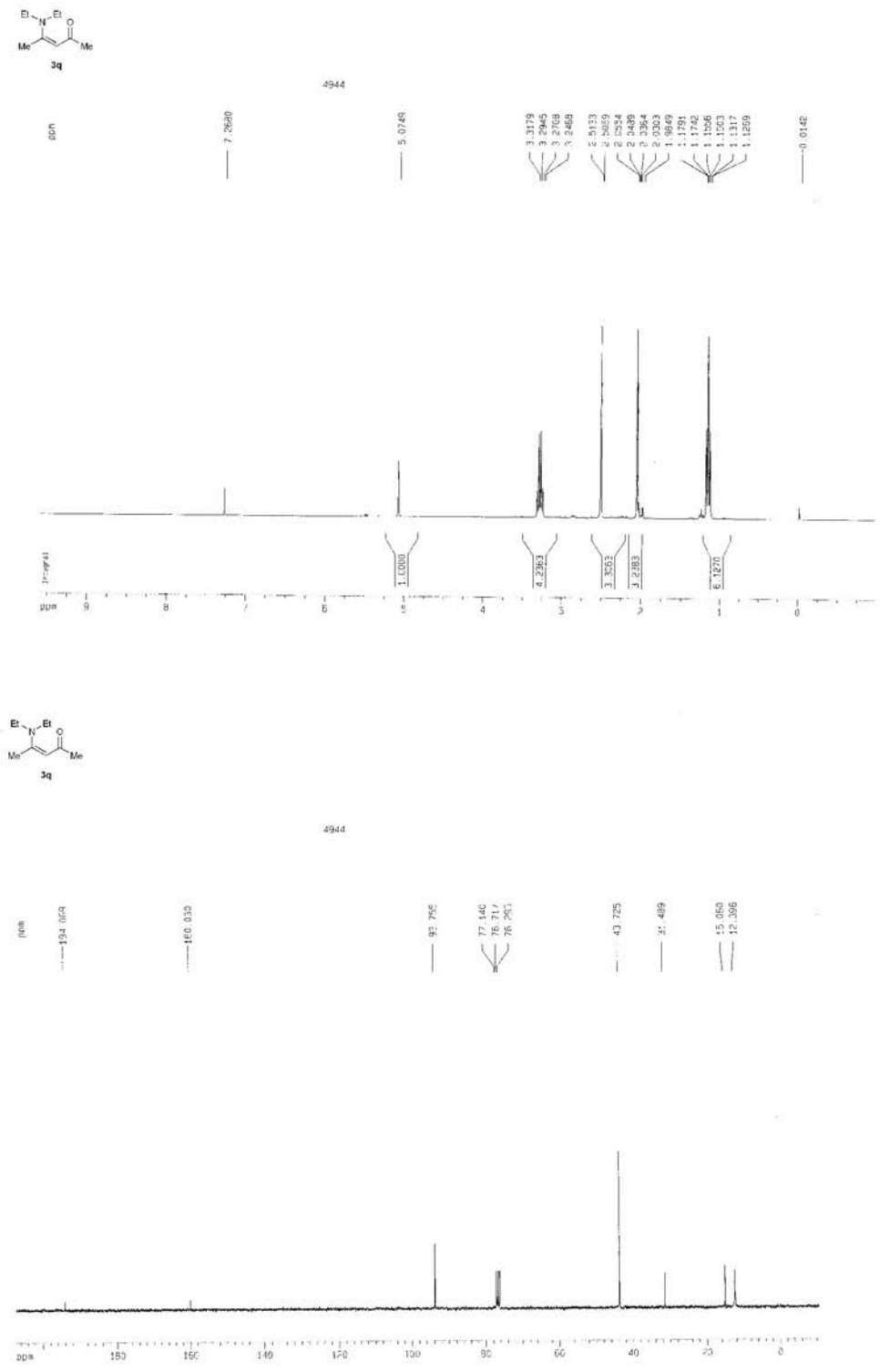


**Figure S17.** $^{1}H$ NMR of **3q** (300 MHz, $CDCl_3$) and $^{13}C$ NMR of **3q** (75 MHz, $CDCl_3$).

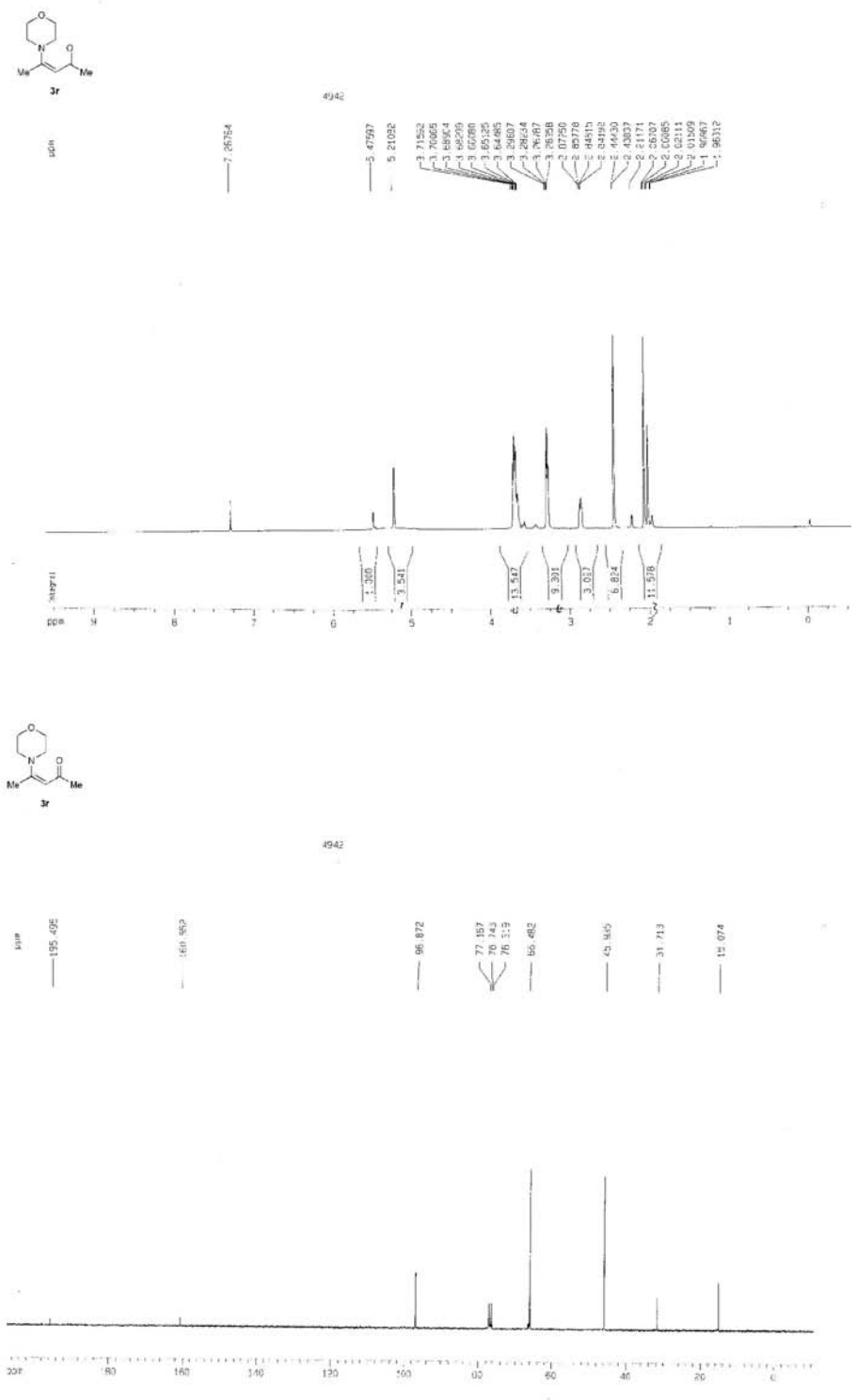

**Figure S18.** $^{1}$H NMR of **3r** (300 MHz, $CDCl_3$) and $^{13}$C NMR of **3r** (75 MHz, $CDCl_3$).

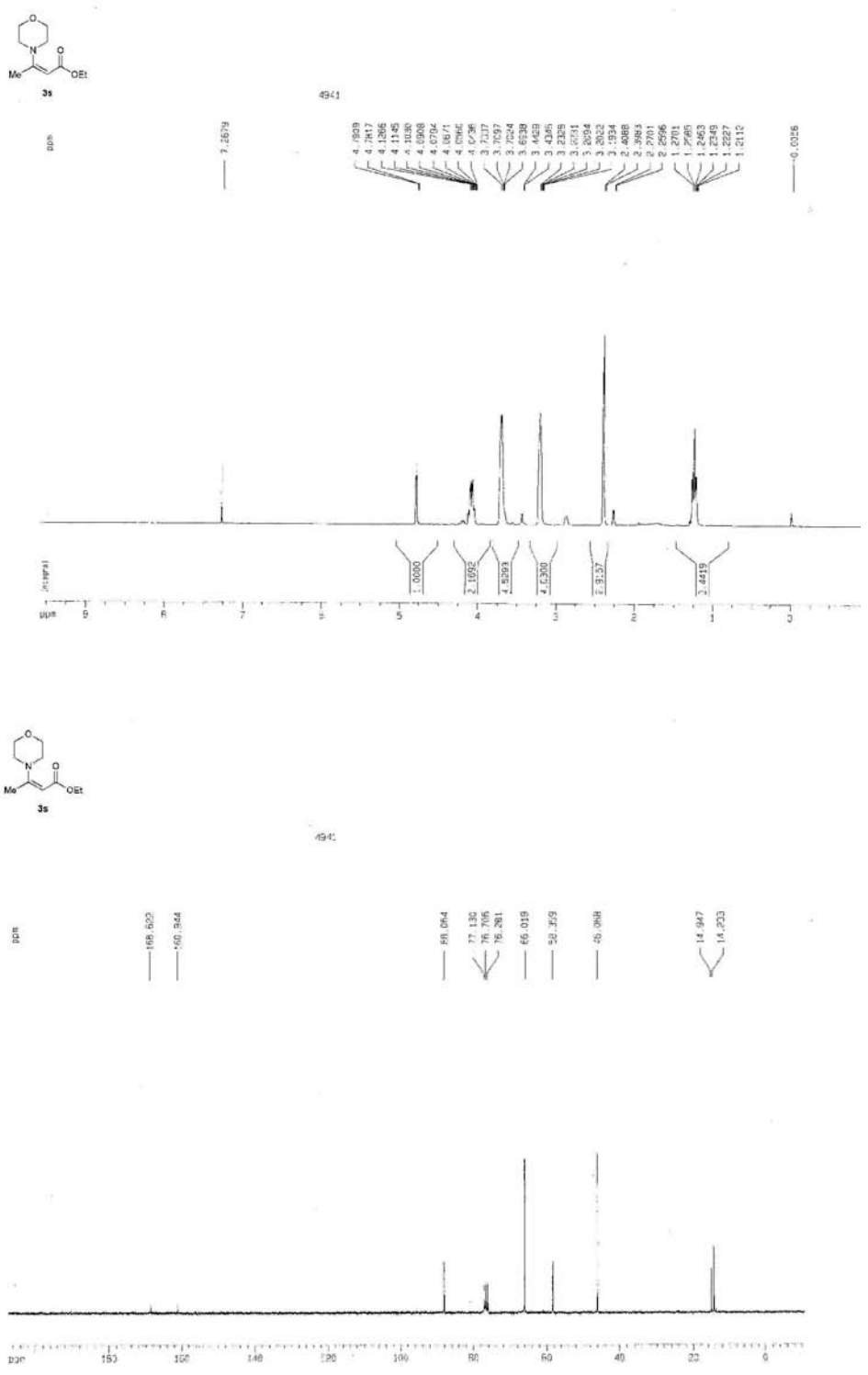


**Figure S19.** $^{1}H$ NMR of **3s** (300 MHz, $CDCl_3$) and $^{13}C$ NMR of **3s** (75 MHz, $CDCl_3$).

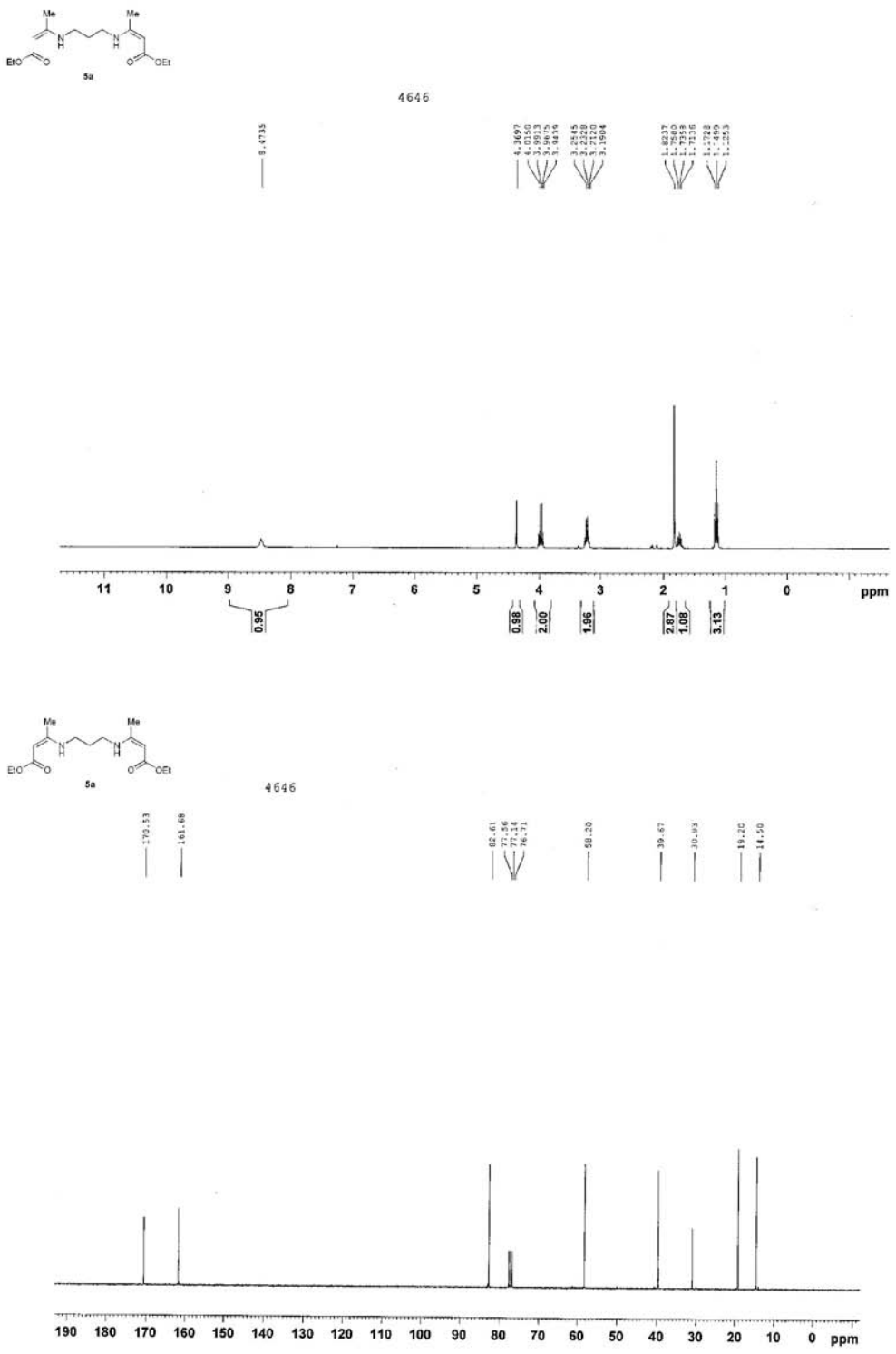


**Figure S20.** $^{1}$H NMR of **5a** (300 MHz, $CDCl_3$) and $^{13}$C NMR of **5a** (75 MHz, $CDCl_3$).

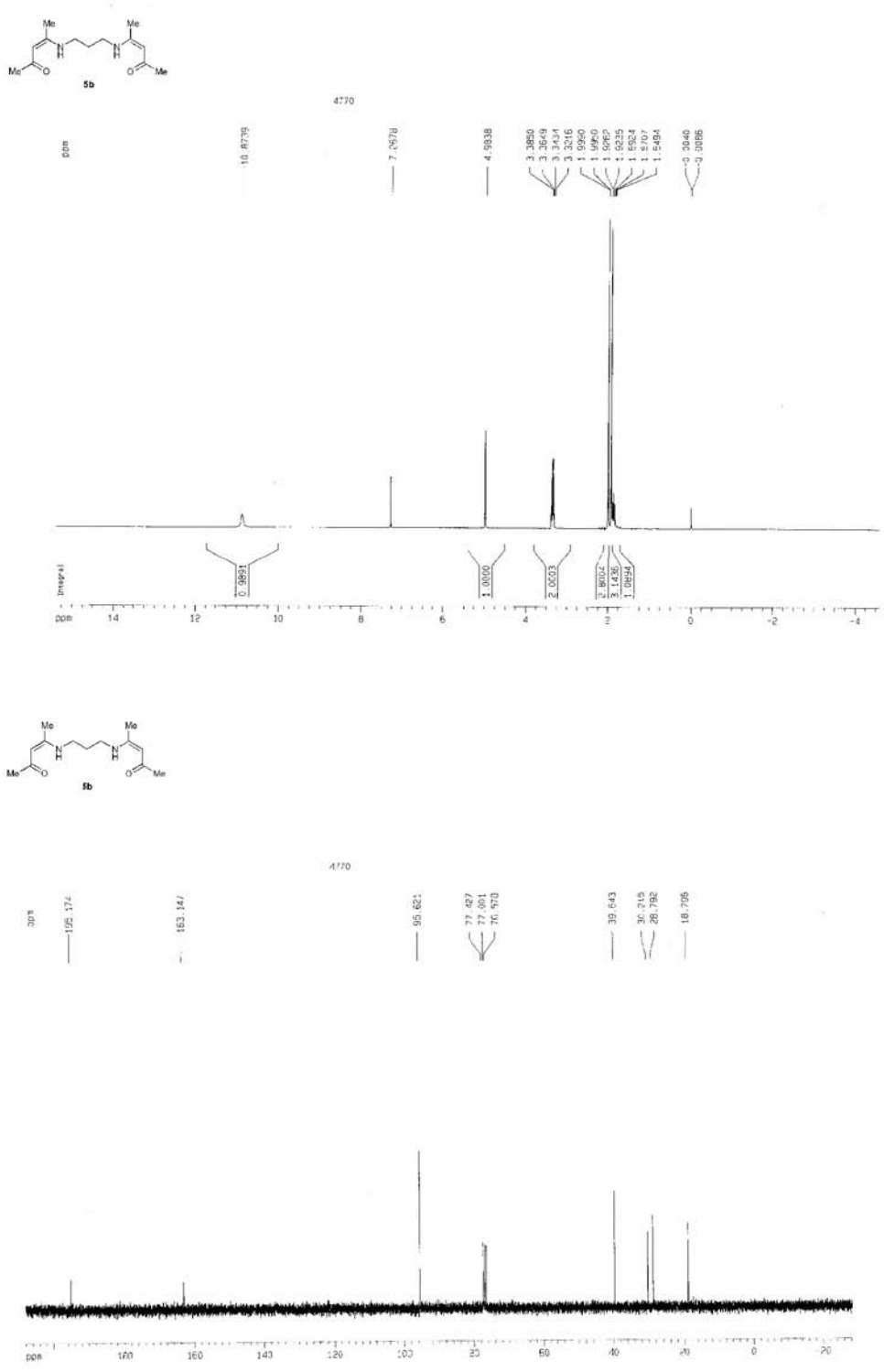


**Figure S21.** $^1$H NMR of **5b** (300 MHz, $CDCl_3$) and $^{13}$C NMR of **5b** (75 MHz, $CDCl_3$).

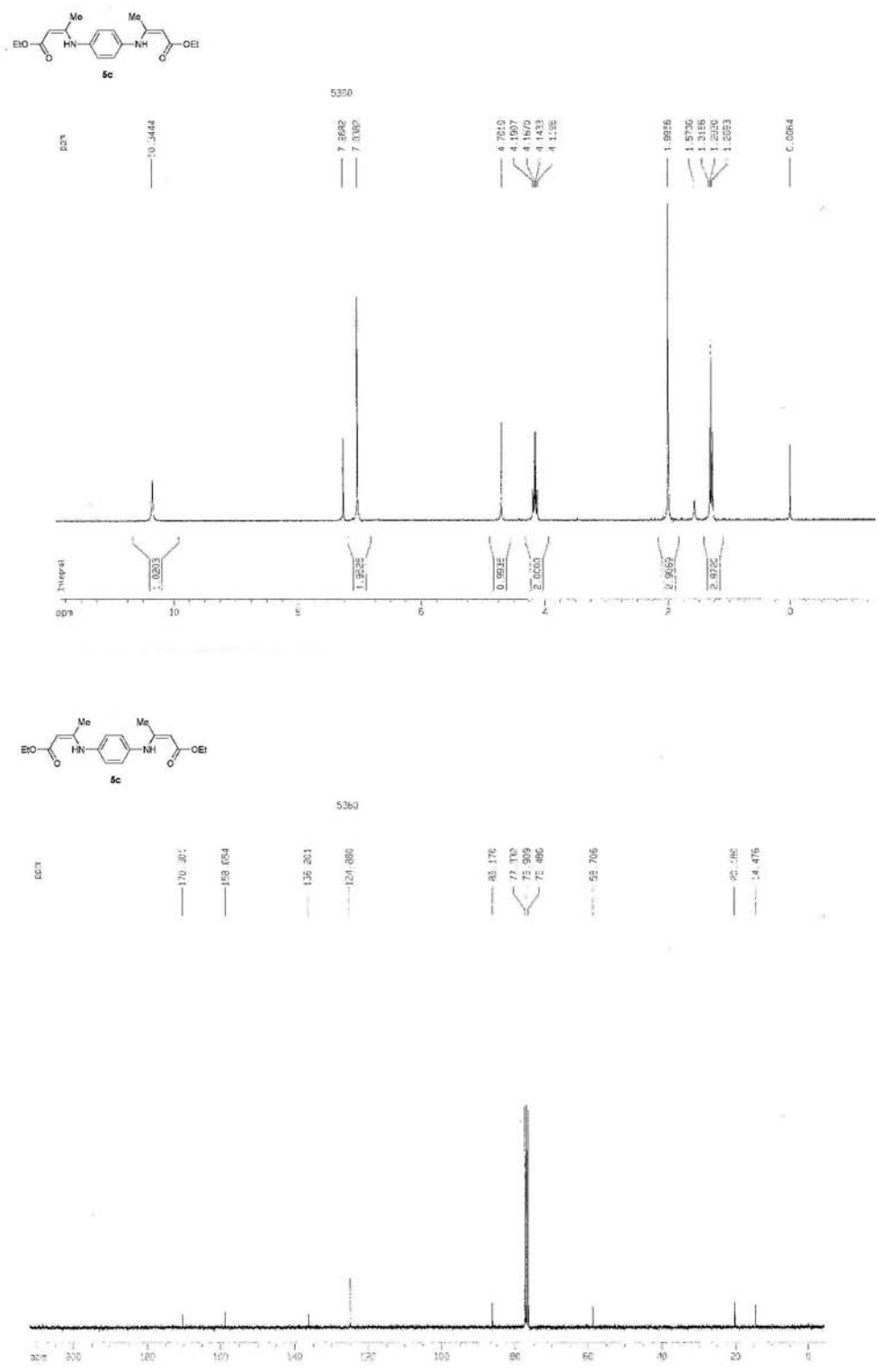

**Figure S22.** $^{1}$H NMR of **5c** (300 MHz, $CDCl_3$) and $^{13}$C NMR of **5c** (75 MHz, $CDCl_3$).

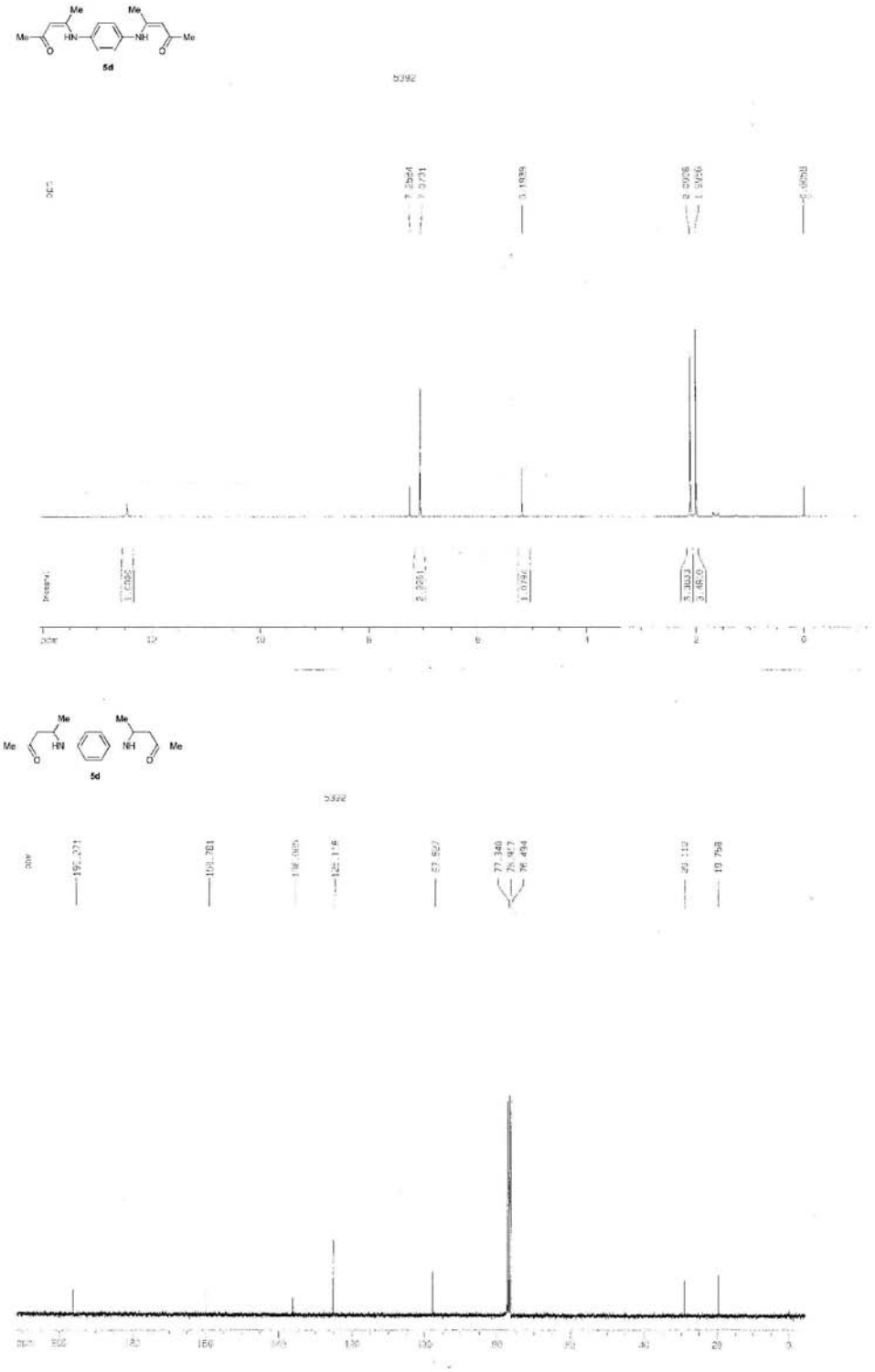

**Figure S23.** $^{1}H$ NMR of **5d** (300 MHz, $CDCl_3$) and $^{13}C$ NMR of **5d** (75 MHz, $CDCl_3$).

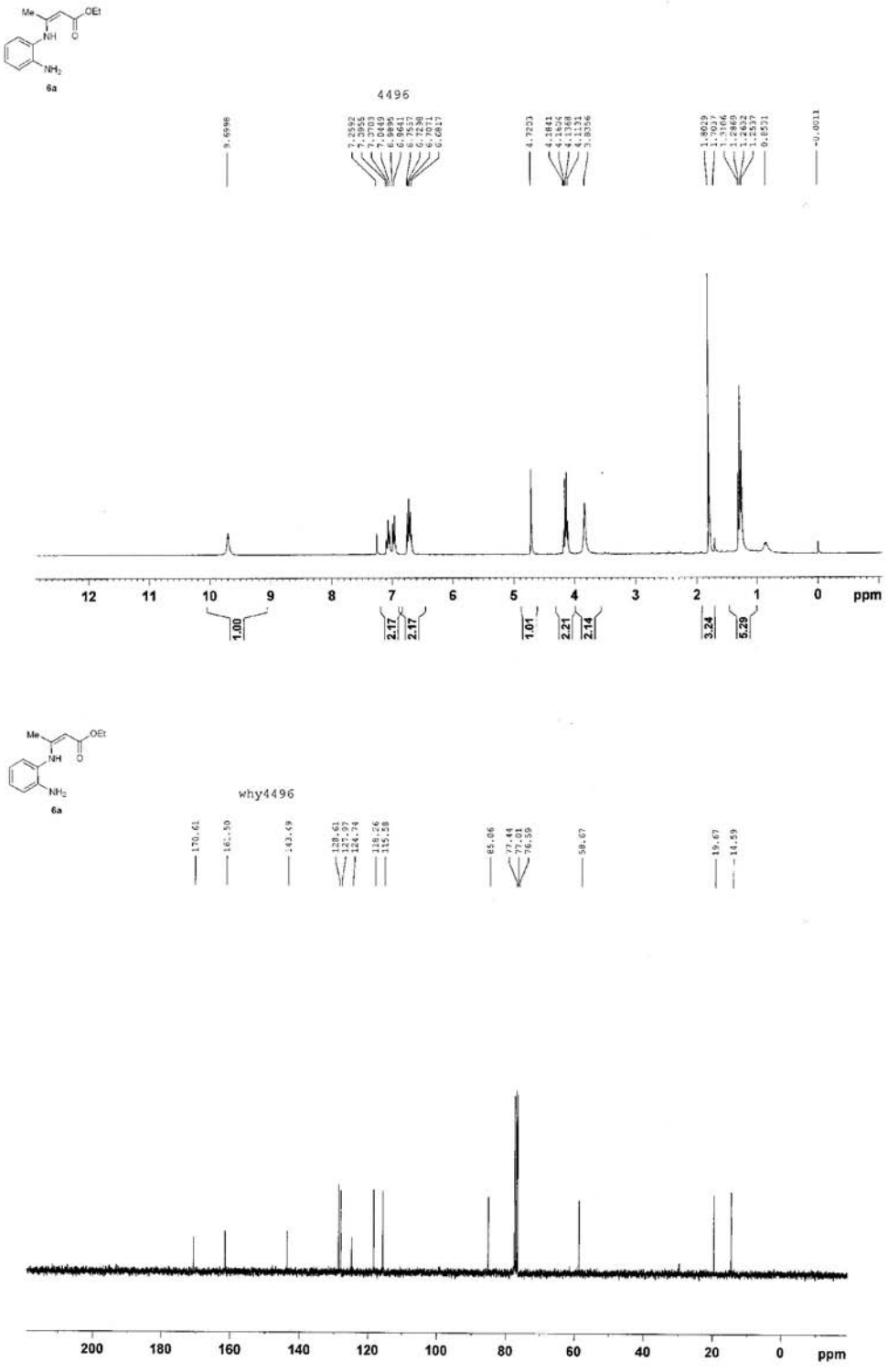


**Figure S24.** $^{1}$H NMR of **6a** (300 MHz, $CDCl_3$) and $^{13}$C NMR of **6a** (75 MHz, $CDCl_3$).

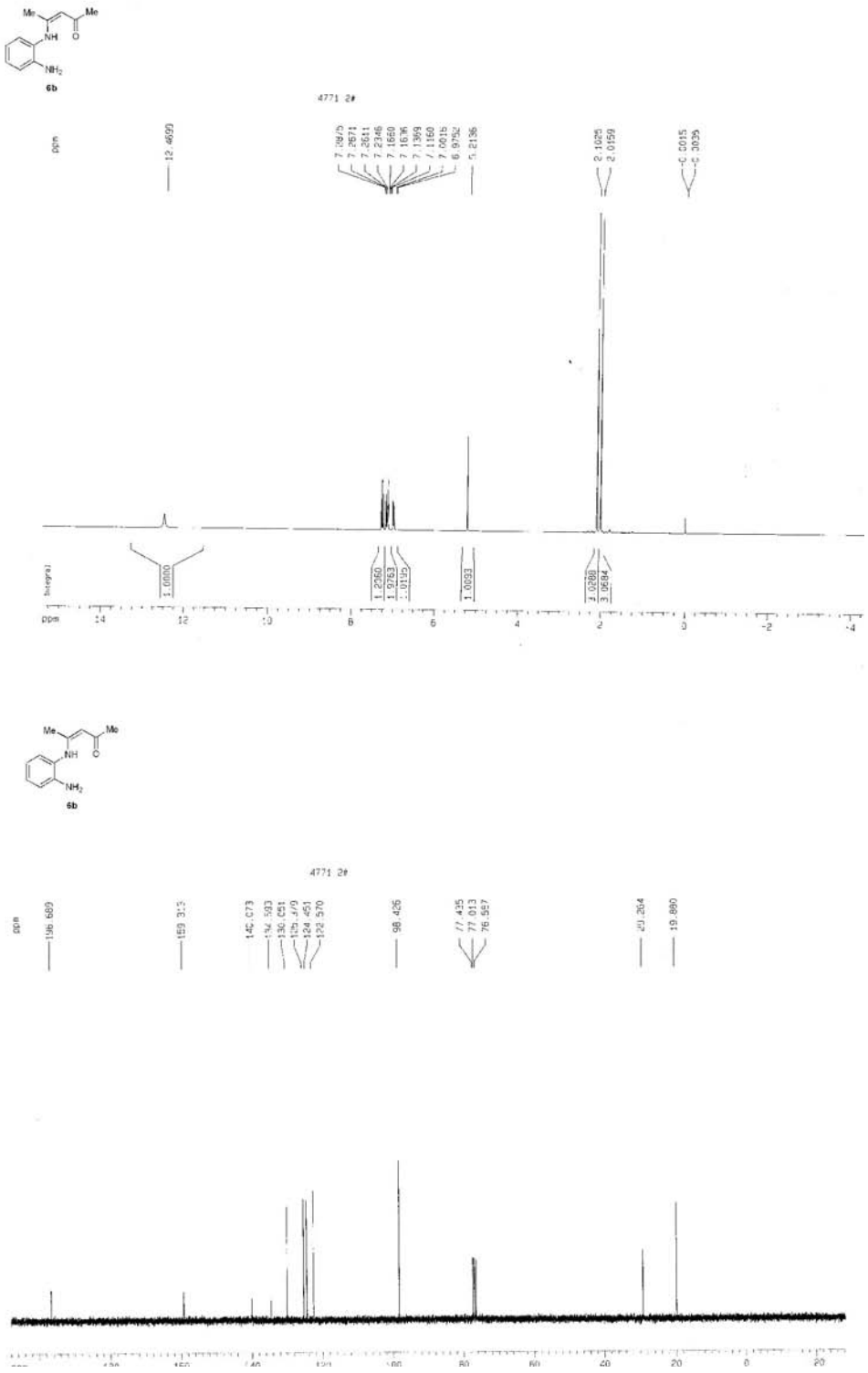

**Figure S25.** $^{1}H$ NMR of **6b** (300 MHz, $CDCl_3$) and $^{13}C$ NMR of **6b** (75 MHz, $CDCl_3$).