Synthesis of *meta*-Alkylphenols via a Ruthenium-Catalyzed C-H Bond Functionalization of Phenol Derivatives

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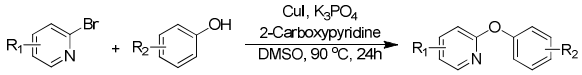
Supporting Information

1. General Information

All commercial reagents and solvents were used directly without additional purification. Column chromatography were performed on silica gel 200-300 mesh. ^{1}H NMR and ^{13}C NMR spectra were registered on a Bruker Ascend^{TM} 400 spectrometer (Germany). Chemical shifts were reported in units (ppm) referenced to 0.0 ppm of TMS in the ^{1}H spectrum and 77.0 ppm of $CDCl_3$ in the ^{13}C spectrum. All coupling constants were reported in Hertz (Hz). HRMS data were obtained on a Waters LCT Premierxe^{TM} (USA), Single-crystal X-ray crystallography was carried out on a Bruker Smart Apex II diffractometer system.

2. Experimental Section

2.1. Typical Procedure for the Synthesis of 2-Phenoxypyridines.[1]



To a 100 mL round bottomed flask, were successively added ArOH (10 mmol), 2-bromopyridine (12 mmol), CuI (1 mmol, 10 mol%), picolinic acid (2 mmol, 20 mol%.), K_3PO_4 (20 mmol) and DMSO (20 mL). The flask was then evacuated and back-filled with N_2. The mixture was heated at 90 °C for 24 h. After cooling to room temperature, ethyl acetate (20 mL) and water (10 mL) were added. The organic layer was separated and the aqueous layer was extracted twice more with ethyl acetate (10 mL). Combined organic layer was dried over Na_2SO_4 and filtered through the pad of silica gel. The filtrate was concentrated and the resulting residue was purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether = 1:5, v/v) to obtain the desired products.

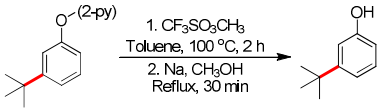
2.2. Typical Experimental Procedure of the *meta*-Selective C-H Alkylation of 2-Phenoxypyridines

2-phenoxypyridine (0.2 mmol), Alkyl bromide (0.6 mmol, 3.0 equiv.), [Ru(*p*-Cymene)Cl_2]$_2$, (0.01 mmol, 5 mol %), K_2CO_3 (0.4 mmol, 2.0 equiv), 1-AdCOOH (30 mmol %), dry benzene (1.5 mL) were charged into a pre-dried 30-mL pressure tube sealed with rubber plugs under N_2 atmosphere. The reaction mixture was stirred at 120 °C for 24 h. The reaction was cooled down to room temperature. The mixture was passed through a short pad of celite, washing with a mixture of EtOAc. The organic layer was concentrated under reduced pressure to give a crude oil, which was purified by column chromatography (PE/EtOAc as eluent) on silica gel to afford the desired products.

2.3. 1 mmol Scale Experiment for the *meta*-Selective C-H Alkylation of 2-Phenoxypyridines

2-phenoxypyridine (1 mmol), 3-bromopentane (3 mmol, 3.0 equiv.), [Ru(*p*-Cymene)Cl_2]$_2$, (0.05 mmol, 5 mol %), K_2CO_3 (2 mmol, 2.0 equiv), 1-AdCOOH (30 mol %), dry benzene (3 mL) were charged into a pre-dried 30-mL pressure tube sealed with rubber plugs under N_2 atmosphere. The reaction mixture was stirred at 120 °C for 24 h. The reaction was cooled down to room temperature. The mixture was passed through a short pad of celite, washing with a mixture of EtOAc. The organic layer was concentrated under reduced pressure to give a crude oil, which was purified by column chromatography (PE/EtOAc 8:1 as eluent) on silica gel to afford 2-(3-(pentan-3-yl)phenoxy)pyridine (125 mg, isolated yield 52%).

2.4. Synthesis of *meta*-alkylphenols via removal of DG.[2]

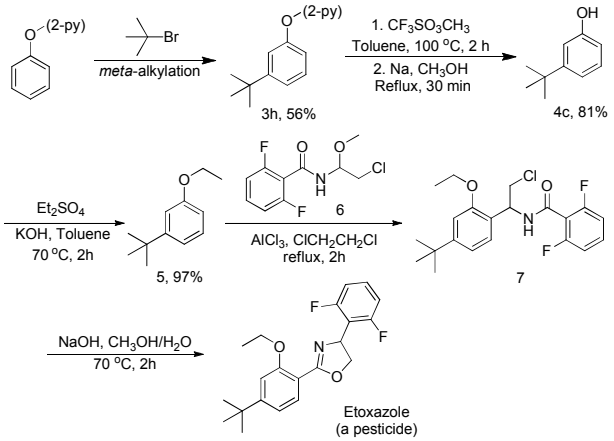


To a solution of 2-(3-(pentan-3-yl)phenoxy)pyridine in dry toluene (15 mL), MeOTf (144 mg, 0.88 mmol) was added. The solution was stirred at 100 °C under a N_2 atmosphere for 2 h. The reaction mixture was cooled to ambient temperature, and the solvent was evaporated under vacuum. The crude product was dissolved in dry

methanol (5.0 mL) and then added to a solution of Na (276 mg, 12 mmol) in dry methanol (15 mL) under a N_2 atmosphere. The reaction mixture was heated to reflux for 15 min and then cooled to room temperature. After evaporating the solvent under vacuum, water (70 mL) was added, and the aqueous solution was extracted with EtOAc (50 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4. The solution was concentrated by vacuum, and the residue was purified by column chromatography on silica gel (hexane/EtOAc: 10/1) to give the corresponding product.

2.5. Synthesis of etoxazole.[3]

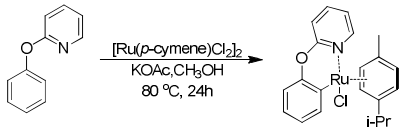
Synthesis of 1-(*tert*-butyl)-3-ethoxybenzene(6): To a 30 mL of reaction tube was added 3-(*tert*-butyl)phenol (**5c**, 750 mg, 5.0 mmol) and 10% NaOH (8 mmol) in toluene (2.0 mL) was heated at 70 ^oC for 1 h. Then, Et_2SO_4 (456 mg, 15 mmol) was slowly dropped into the system. The reaction was monitored by TLC (thin layer chromatography). After the reaction was completed, the reaction mixture was allowed to cool down to room temperature. The organic layer was separated and the aqueous layer was extracted thrice with toluene (5 mL). The organic phase were combined and washed with sparse chlorhydric acids(5 mL). The organic layer was washed with water to neutral. Then, dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure to give crude products(**6**), which were purified by column chromatography.



Synthesis of *N*-(1-(4-(*tert*-butyl)-2-ethoxyphenyl)-2-chloroethyl)-2,6-difluoro-benzamide (7): *N*-(2-chloro-1-methoxyethyl)-2,6-difluorobenzamide (**7,** 250 mg, 1 mmol) and 1-(*tert*-butyl)-3-ethoxybenzene (**6,** 356 mg, 2 mmol) dissolve in $ClCH_2CH_2Cl$. Then, the mixture was dropped into a cold solution of $AlCl_3$(480 mg, 3.6 mmol) in $ClCH_2CH_2Cl$ (2 mL). The system was heated and refluxed for 2 h. The reaction was monitored by TLC (thin layer chromatography). After the reaction was completed, the reaction mixture was poured into ice water. The aqueous layer was extracted with $ClCH_2CH_2Cl$. The organic phase was distilled by reduced pressure to give crude products(**8**), which were purified by column chromatography.

Synthesis of etoxazole: 20% NaOH (1 mL) was slowly dropped into a solution of *N*-(1-(4-(*tert*-butyl)-2-ethoxyphenyl)-2-chloroethyl)-2,6-difluorobenzamide (400 mg, 1 mmol) in MeOH. The system was stirred for 2h in 70 ^oC. The reaction was monitored by TLC (thin layer chromatography). After the reaction was completed, MeOH was removed by rotary evaporator. The reaction mixture was dissolved in EtOAc and washed by with saturated NaCl solution. The organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure to give crude products (etoxazole), which were purified by column chromatography.

2.6. Preparation of 2-Phenoxypyridines -Ruthenium Complex.[4]



$[RuCl_2(p\text{-cymene})]_2$ (1 mmol, 612 mg), KOAc (4 mmol, 392 mg), 2-Phenoxy-pyridine (2 mmol, 182mg) and dry CH_3OH (15 mL) were charged into a pre-dried 50-mL pressure tube sealed with rubber plugs under N_2 atmosphere. The reaction was stirred 80 ^oC for 24h. The reaction was then concentrated to dryness, dissolved in a minimal amount of EtOAc and then purified through neutral alumina with EtOAc as the solvent to yield the complex as a yellow solid.

3. References

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4. Data and Spectra of ^{1}H NMR and ^{13}C NMR

2-(3-(pentan-2-yl)phenoxy)pyridine (**3a**, 35 mg, colorless oil, PE/EtOAc 8:1 as eluent): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 3.4 Hz, 1H), 7.72 – 7.64 (m, 1H), 7.32 (t, J = 7.8 Hz, 1H), 7.06 – 6.94 (m, 4H), 6.88 (d, J = 8.3 Hz, 1H), 2.73 (m, 1H), 1.56 (m, 2H), 1.25 (d, J = 6.9 Hz, 3H), 0.88 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.89, 154.23, 150.04, 147.88, 139.31, 129.34, 123.38, 119.62, 118.30(d), 111.37, 40.57, 39.52, 22.04, 20.72, 14.10. HRMS (ESI) Calcd. For $C_{16}H_{20}NO$: $[M+H]^+$, 242.1545, Found: m/z 242.1545.

2-(4-chloro-3-(pentan-3-yl)phenoxy)pyridine (**3b**, 21 mg, colorless oil, PE/EtOAc 8:1 as eluent): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 – 8.18 (m, 1H), 7.74 – 7.66 (m, 1H), 7.37 (d, J = 8.6 Hz, 1H), 7.05–6.96 (m, 2H), 6.93 (m, 1H), 6.89 (d, J = 8.3 Hz, 1H), 3.13 – 3.03 (m, 1H), 1.74 – 1.67 (m, 2H), 1.56 (m, 2H), 0.84 (t, J = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.51, 152.92, 147.78, 144.73, 139.44, 130.36, 130.13, 120.42, 119.49, 118.60, 111.39, 44.23, 28.13, 11.67. HRMS (ESI) Calcd. For $C_{16}H_{19}ClNO$: $[M+H]^+$, 276.1155, Found: m/z 276.1151.

2-(4-methoxy-3-(pentan-3-yl)phenoxy)pyridine (**3c**, 44 mg, colorless oil, PE/EtOAc 8:1 as eluent): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.15 (m, 1H), 7.71 – 7.55 (m, 1H), 6.99 – 6.91 (m, 3H), 6.88 (d, J = 8.7 Hz, 1H), 6.82 (d, J = 8.4 Hz, 1H), 3.82 (s, 3H), 3.06 – 2.91 (m, 1H), 1.66 (m, 2H), 1.57 (m, 2H), 0.82 (t, J = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.45, 154.84, 147.83, 147.45, 139.19, 135.68, 120.66, 118.69, 117.94, 111.34, 110.71, 55.84, 40.75, 27.68, 11.89. HRMS (ESI) Calcd. For $C_{17}H_{22}NO_2$: $[M+H]^+$, 272.1651, Found: m/z 272.1648.

2-(2-methyl-3-(pentan-3-yl)phenoxy)pyridine (**3d**, 26 mg, colorless oil, PE/EtOAc 8:1 as eluent): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (m, 1H), 7.69 – 7.61 (m, 1H), 7.21 (t, J = 7.9 Hz, 1H), 7.06 (d, J = 7.7 Hz, 1H), 6.98 – 6.88 (m, 2H), 6.76 (d, J = 8.3 Hz, 1H), 2.82 – 2.73 (m, 1H), 2.15 (s, 3H), 1.79 – 1.67 (m, 3H), 1.65 – 1.53 (m, 3H), 0.82 (t, J = 7.4 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.08, 152.04, 148.02, 146.53, 139.26, 129.47, 126.44, 122.69, 118.68, 117.83, 110.27,

43.65, 12.03. HRMS (ESI) Calcd. For $C_{17}H_{22}NO$: $[M+H]^+$, 256.1701, Found: m/z 256.1695.

2-(3-(pentan-2-yl)phenoxy)pyridine (**3e**, 31 mg, colorless oil, PE/EtOAc 8:1 as eluent): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 3.4 Hz, 1H), 7.72 – 7.64 (m, 1H), 7.32 (t, J = 7.8 Hz, 1H), 7.06 – 6.94 (m, 4H), 6.88 (d, J = 8.3 Hz, 1H), 2.73 (m, 1H), 1.56 (m, 2H), 1.25 (d, J = 6.9 Hz, 3H), 0.88 (t, J = 7.3 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 163.89, 154.23, 150.04, 147.88, 139.31, 129.34, 123.38, 119.62, 118.30 (d), 111.37, 40.57, 39.52, 22.04, 20.72, 14.10. HRMS (ESI) Calcd. For $C_{16}H_{20}NO$: $[M+H]^+$, 242.1545, Found: m/z 242.1537.

methyl 2-(2-methoxy-5-(pyridin-2-yloxy)phenyl)propanoate (**3f**, 33.5 mg, colorless oil, PE/EtOAc 8:1 as eluent): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 – 8.13 (m, 1H), 7.72 – 7.60 (m, 1H), 7.01 – 6.92 (m, 3H), 6.86 (t, J = 8.4 Hz, 2H), 3.84 (s, 3H), 3.23 (m, 1H), 1.65 – 1.53 (m, 1H), 1.49 (m, 1H), 1.37 – 1.24 (m, 2H), 1.19 (d, J = 6.9 Hz, 3H), 0.89 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ164.41, 154.02, 147.80, 147.37, 139.23, 137.74, 120.02, 118.73, 117.94, 111.18, 110.84, 55.78, 39.27, 31.52, 20.77 (d), 14.22. HRMS (ESI) Calcd. For $C_{16}H_{18}NO_4$: $[M+H]^+$, 288.1236, Found: m/z 288.1230.

2-(3-cyclopentyl-4-methoxyphenoxy)pyridine (**3g**, 31 mg, colorless oil, PE/EtOAc 8:1 as eluent): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 3.6 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 6.97 (m, 3H), 6.86 (d, J = 8.9 Hz, 2H), 3.84 (s, 3H), 3.32 (m, 1H), 2.03 (d, J = 5.5 Hz, 2H), 1.80 – 1.73 (m, 2H), 1.67 (m, 2H), 1.55 (d, J = 6.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.85, 153.39, 147.77, 146.35, 138.14, 136.11 (d), 120.01, 118.80, 117.91, 110.98 (d,), 55.78 , 39.09 , 32.95 , 25.35 . HRMS (ESI) Calcd. For $C_{17}H_{20}NO2$: $[M+H]^+$, 270.1494, Found: m/z 270.1483.

2-(3-(*tert*-butyl)phenoxy)pyridine (**3h**, 25 mg, colorless oil, PE/EtOAc 8:1 as eluent): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 4.3 Hz, 1H), 7.68 (m, 1H), 7.34 (t, J = 7.9 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H), 7.18 (s, 1H), 7.03 – 6.94 (m, 2H), 6.89 (d, J = 8.3 Hz, 1H), 1.34 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 163.91, 153.99, 153.31, 147.87, 139.34, 129.09, 121.71, 118.31, 118.02, 111.36, 34.80, 31.29. HRMS (ESI) Calcd. For $C_{15}H_{18}NO$: $[M+H]^+$, 228.1388, Found: m/z 228.1382.

2-(3-(*tert*-butyl)-4-methoxyphenoxy)pyridine (**3i**, 32 mg, colorless oil, PE/EtOAc 8:1 as eluent): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (m, 1H), 7.73 – 7.58 (m, 1H), 7.09 (d, J = 2.8 Hz, 1H), 7.01 – 6.93 (m, 2H), 6.88 (m, 2H), 3.86 (s, 3H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.37, 155.52, 147.78, 146.97, 139.77, 139.24, 120.10, 119.05, 117.94, 112.11, 110.94, 55.35, 34.94, 29.60. HRMS (ESI) Calcd. For $C_{16}H_{20}NO_2$: $[M+H]^+$, 258.1494, Found: m/z 258.1490.

2-(4-methoxy-3-(tetrahydro-2H-pyran-4-yl)phenoxy)pyridine (**3j**, 29 mg, colorless oil, PE/EtOAc 8:1 as eluent): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 4.0 Hz, 1H), 7.73 – 7.59 (m, 1H), 6.97 (m, 3H), 6.88 (d, J = 9.0 Hz, 2H), 4.06 (d, J = 10.8 Hz, 2H), 3.84 (s, 3H), 3.57 (m, 2H),

3.26 – 3.15 (m, 1H), 1.77 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.23, 153.81, 147.70, 147.40, 139.31, 135.31, 119.99, 119.37, 118.05, 111.07, 68.55, 55.65, 34.51, 32.50. HRMS (ESI) Calcd. For $C_{17}H_{20}NO_3$: $[M+H]^+$, 286.1443, Found: m/z286.1437.

2-(3-(1-chloro-2-methylpropan-2-yl)-4-methoxyphenoxy)pyridine (**3k**, 21 mg, colorless oil, PE/EtOAc 8:1 as eluent): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 3.6 Hz, 1H), 7.62-7.52 (m, 1H), 7.01 (s, 1H), 6.90 (s, 2H), 6.75 (d, J = 8.3 Hz, 1H), 3.90 (s, 2H), 3.51 (s, 3H), 1.40 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.43, 154.61, 147.50, 144.08, 139.79, 134.00, 129.67, 122.61, 117.68, 114.11, 111.11, 25.51. HRMS (ESI) Calcd. For $C_{16}H_{19}ClNO_2$: $[M+H]^+$, 292.1104, Found: m/z292.1096.

methyl 2-(2-methyl-5-(pyridin-2-yloxy)phenyl)propanoate (**3l**, 18 mg, colorless oil, PE/EtOAc 5:1 as eluent): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 4.3 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 7.19 (d, J = 8.2 Hz, 1H), 7.06 (s, 1H), 6.98 (m, 2H), 6.89 (d, J = 8.3 Hz, 1H), 3.95 (q, J = 7.0 Hz, 1H), 3.66 (s, 3H), 2.36 (s, 3H), 1.47 (d, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 163.74, 152.43, 147.55, 140.48, 139.45, 132.05, 131.48, 119.59(d), 118.28, 111.34, 52.01, 41.43, 19.00, 17.84. HRMS (ESI) Calcd. For $C_{16}H_{18}NO_3$: $[M+H]^+$, 272.1287, Found: m/z 272.1283.

methyl 2-(4-(pyridin-2-yloxy)-[1,1'-biphenyl]-2-yl)propanoate (**3m**, 22 mg, colorless oil, PE/EtOAc 5:1 as eluent): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 3.2 Hz, 1H), 7.78 – 7.66 (m, 1H), 7.43 (d, J = 7.0 Hz, 2H), 7.38 (t, J = 6.6 Hz, 2H), 7.26 (s, 2H), 7.20 (d, J = 2.4 Hz, 1H), 7.09 (m, 1H), 7.03 (m, 1H), 6.97 (d, J = 8.3 Hz, 1H), 3.91 (q, J = 7.0 Hz, 1H), 3.64 (s, 3H), 1.37 (d, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.06, 166.08 – 163.16 (m), 153.70, 147.73, 141.06 – 140.58 (m), 140.17, 139.48, 138.68 – 137.60 (m), 131.36, 129.56, 128.21, 127.14, 119.29 (d), 118.63, 111.80, 52.01, 41.30, 19.26. HRMS (ESI) Calcd. For $C_{21}H_{20}NO_3$: $[M+H]^+$, 334.1443, Found: m/z 334.1434.

methyl 2-(2-methoxy-5-(pyridin-2-yloxy)phenyl)propanoate (**3n**, 22 mg, colorless oil, PE/EtOAc 5:1 as eluent): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 3.8 Hz, 1H), 7.74 – 7.56 (m, 1H), 7.04 (d, J = 7.0 Hz, 2H), 6.97 (m, 1H), 6.88 (t, J = 8.8 Hz, 2H), 4.06 (q, J = 7.2 Hz, 1H), 3.84 (s, 3H), 3.66 (s, 3H), 1.46 (d, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.19, 153.68, 147.68, 147.34, 139.27, 130.63, 121.28, 120.50, 118.11, 111.44, 111.07, 55.89, 51.92, 39.05, 17.30. HRMS (ESI) Calcd. For $C_{16}H_{18}NO_4$: $[M+H]^+$, 288.1236, Found: m/z 288.1228.

methyl 2-(2-methoxy-5-(pyridin-2-yloxy)phenyl)octanoate (**3o**, 25 mg, colorless oil, PE/EtOAc 5:1 as eluent): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 3.7 Hz, 1H), 7.68 (m, 1H), 7.09 (d, J = 2.7 Hz, 1H), 7.04 (m, 1H), 7.00 – 6.95 (m, 1H), 6.88 (m, 2H), 4.02 (t, J = 7.5 Hz, 1H), 3.84 (s, 3H), 3.66 (s, 3H), 1.99 (m, 2H), 1.79 – 1.59 (m, 2H), 1.28 (s, 6H), 0.87 (t, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.69 , 166.69 – 162.34 (m), 153.92, 147.50, 139.46, 129.41, 121.57,

120.40, 118.11, 111.50, 111.02, 55.99, 51.82, 43.88, 32.50, 31.61, 29.02, 27.47, 22.57, 14.04. HRMS (ESI) Calcd. For $C_{21}H_{28}NO_4$: $[M+H]^+$, 358.2018, Found: m/z 358.2012.

methyl 2-(3-(pyridin-2-yloxy)naphthalen-1-yl)propanoate (**3p**, 19 mg, colorless oil, PE/EtOAc 5:1 as eluent): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (m, 1H), 8.09 – 8.03 (m, 1H), 7.81 (m, 1H), 7.75 – 7.68 (m, 2H), 7.53 – 7.46 (m, 3H), 7.31 (d, J = 2.3 Hz, 1H), 7.04 (m, 1H), 6.98 (d, J = 8.3 Hz, 1H), 4.53 (q, J = 7.2 Hz, 1H), 3.66 (s, 3H), 1.66 (d, J = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 147.83, 139.47, 126.26, 125.58, 123.14, 116.86, 111.73, 52.16, 18.09. HRMS (ESI) Calcd. For $C_{19}H_{18}NO_3$: $[M+H]^+$, 308.1287, Found: m/z 308.1284.

methyl 2-(2-methoxy-5-(pyridin-2-yloxy)phenyl)-2-methylpropanoate (**3q**, 22 mg, colorless oil, PE/EtOAc 5:1 as eluent): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 4.0 Hz, 1H), 7.69 (t, J = 7.5 Hz, 1H), 7.09 (d, J = 2.2 Hz, 1H), 7.07 – 6.95 (m, 2H), 6.88 (d, J = 8.5 Hz, 2H), 3.79 (s, 3H), 3.64 (s, 3H), 1.51 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.69, 139.38, 119.97, 119.17, 118.14, 111.61, 111.06, 55.64, 51.87, 44.27, 25.61 . HRMS (ESI) Calcd. For $C_{17}H_{20}NO_4$: $[M+H]^+$, 302.1392, Found: m/z 302.1388.

5-methyl-2-(3-(pentan-3-yl)phenoxy)pyridine (**3r**, 35 mg, colorless oil, PE/EtOAc 8:1 as eluent): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 5.1 Hz, 1H), 7.30 (m, 1H), 6.96 (m, 2H), 6.83 (d, J = 5.0 Hz, 1H), 6.67 (s, 1H), 2.33 (s, 3H), 1.74 – 1.66 (m, 2H), 1.60 – 1.50 (m, 2H), 0.81 (t, J = 7.4 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.18, 154.39, 150.83, 147.94, 147.46, 129.19, 124.06, 120.26, 119.76, 118.15, 111.56, 49.49, 29.05, 21.00, 12.11. HRMS (ESI) Calcd. For $C_{17}H_{22}NO$: $[M+H]^+$, 256.1701, Found: m/z 256.1700.

methyl 2-(3-((5-methylpyridin-2-yl)oxy)phenyl)propanoate (**3s**, 25 mg, colorless oil, PE/EtOAc 5:1 as eluent): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 1.6 Hz, 1H), 7.50 (m, 1H), 7.32 (t, J = 7.9 Hz, 1H), 7.15 – 6.96 (m, 3H), 6.81 (d, J = 8.3 Hz, 1H), 3.66 (s, 3H), 2.29 (s, 3H), 1.50 (d, J = 7.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 174.65, 161.64, 154.89, 147.44, 142.19, 140.27, 129.67, 127.96, 123.37, 119.85, 119.31, 111.27, 52.03, 45.24, 18.42, 17.48. HRMS (ESI) Calcd. For $C_{16}H_{18}NO_3$: $[M+H]^+$, 272.1287, Found: m/z 272.1288.

methyl 2-(3-(pyrimidin-2-yloxy)phenyl)propanoate (**3t**, 19 mg, colorless oil, PE/EtOAc 5:1 as eluent): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 4.8 Hz, 2H), 7.39 (t, J = 7.9 Hz, 1H), 7.21 (d, J = 7.8 Hz, 1H), 7.17 (s, 1H), 7.12 (d, J = 8.1 Hz, 1H), 7.05 (t, J = 4.8 Hz, 1H), 3.75 (d, J = 7.1 Hz, 1H), 3.68 (s, 3H), 1.53 (d, J = 7.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 174.29 (d), 164.46 , 159.24 (d), 152.74 (d), 141.71 (d), 129.64, 124.61, 120.84, 120.36, 52.06, 45.20, 18.43. HRMS (ESI) Calcd. For $C_{14}H_{15}N_2O_3$: $[M+H]^+$, 259.1083, Found: m/z 259.1076.

3-(pentan-3-yl)phenol (**4a**, 27 mg, colorless oil, PE/EtOAc 6:1 as eluent): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, J = 7.7 Hz, 1H), 6.76 (d, J = 7.6 Hz, 1H), 6.73 – 6.66 (m, 2H), 5.50 (d, J = 4.8 Hz, 1H), 2.35 – 2.20 (m, 1H), 1.69 (m, 2H), 1.59 – 1.47 (m, 2H), 0.80 (t, J = 7.4 Hz, 6H). ^{13}C

NMR (101 MHz, $CDCl_3$) δ 155.30, 148.06, 129.26, 120.60, 114.68, 112.77, 49.64, 29.21, 12.20. HRMS (ESI) Calcd. For $C_{11}H_{17}O$: $[M+H]^+$,165.1279, Found: m/z 165.1268.

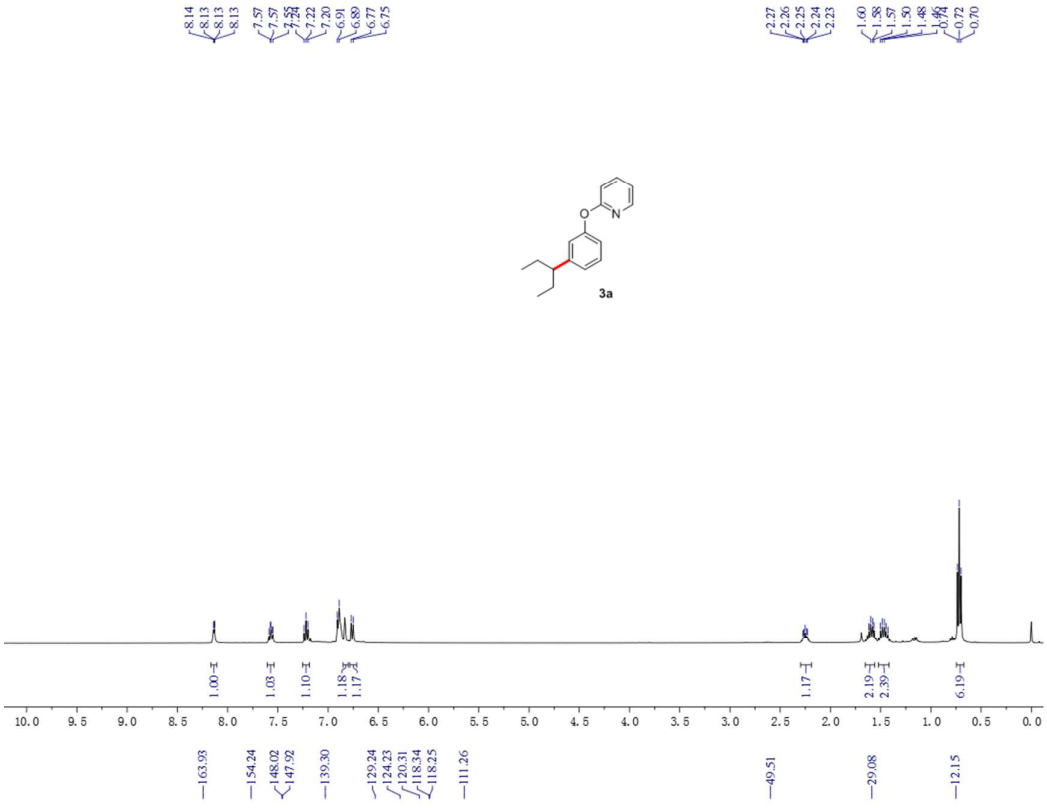
3-(pentan-2-yl)phenol (**4b**, 26 mg, colorless oil, PE/EtOAc 6:1 as eluent): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, J = 7.7 Hz, 1H), 6.78 (d, J = 7.6 Hz, 1H), 6.72 – 6.62 (m, 2H), 4.80 (s, 1H), 2.67 (m, 1H), 1.62 – 1.48 (m, 2H), 1.23 (d, J = 6.9 Hz, 3H), 0.88 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.42, 150.10, 129.38, 119.67, 113.85, 112.62, 40.57, 39.57, 22.20, 20.78, 14.13. HRMS (ESI) Calcd. For $C_{11}H_{17}O$: $[M+H]^+$, 165.1279, Found: m/z 165.1276.

3-(*tert*-butyl)phenol (**4c**, 24 mg, colorless oil, PE/EtOAc 6:1 as eluent): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, J = 7.9 Hz, 1H), 6.99 (m, 1H), 6.94 – 6.84 (m, 1H), 6.67 (m, 1H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.23, 153.37, 129.18, 117.88, 112.59, 112.26, 34.66, 31.27. HRMS (ESI) Calcd. For $C_{10}H_{15}O$: $[M+H]^+$, 151.1123, Found: m/z151.1118.

4-methoxy-3-(pentan-3-yl)phenol (**4d**, 29 mg, colorless oil, PE/EtOAc 6:1 as eluent): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (d, J = 8.7 Hz, 1H), 6.67 – 6.56 (m, 2H), 4.84 (s, 1H), 3.77 (s, 3H), 2.90 (m, 1H), 1.73 – 1.60 (m, 2H), 1.51 (m, 2H), 0.79 (t, J = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.27, 149.45, 135.97, 114.60, 112.37 (d, J = 13.8 Hz), 56.52, 40.79, 28.07, 11.99. HRMS (ESI) Calcd. For $C_{12}H_{19}O_2$: $[M+H]^+$, 195.1385, Found: m/z 195.1376.

4-methoxy-3-(pentan-2-yl)phenol (**4e**, 29 mg, colorless oil, PE/EtOAc 6:1 as eluent)**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (d, J = 8.6 Hz, 1H), 6.70 (d, J = 2.9 Hz, 1H), 6.62 (m, 1H), 4.47 (s, 1H), 3.78 (s, 3H), 3.18 (m, 1H), 1.60 – 1.41 (m, 2H), 1.27 (m, 2H), 1.17 (d, J = 6.9 Hz, 3H), 0.89 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.34, 149.44, 137.95, 114.10, 112.33, 112.05, 56.34, 39.50, 31.44, 21.06, 20.74, 14.20. HRMS (ESI) Calcd. For $C_{12}H_{19}O_2$: $[M+H]^+$, 195.1385, Found: m/z 195.1377.

1-(*tert*-butyl)-3-ethoxybenzene (**5,** 34 mg, colorless oil, PE/EtOAc 12:1 as eluent): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, J = 7.9 Hz, 1H), 7.08 (m, 2H), 6.82 (m, 1H), 4.13 (q, J = 7.0 Hz, 2H), 1.52 (t, J = 7.0 Hz, 3H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.87, 152.95, 129.02, 117.80, 112.71, 110.49, 63.27, 34.79, 31.42, 15.02. HRMS (ESI) Calcd. For $C_{12}H_{19}O$: $[M+H]^+$, 179.1436, Found: m/z 179.1433.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1.17
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2.39
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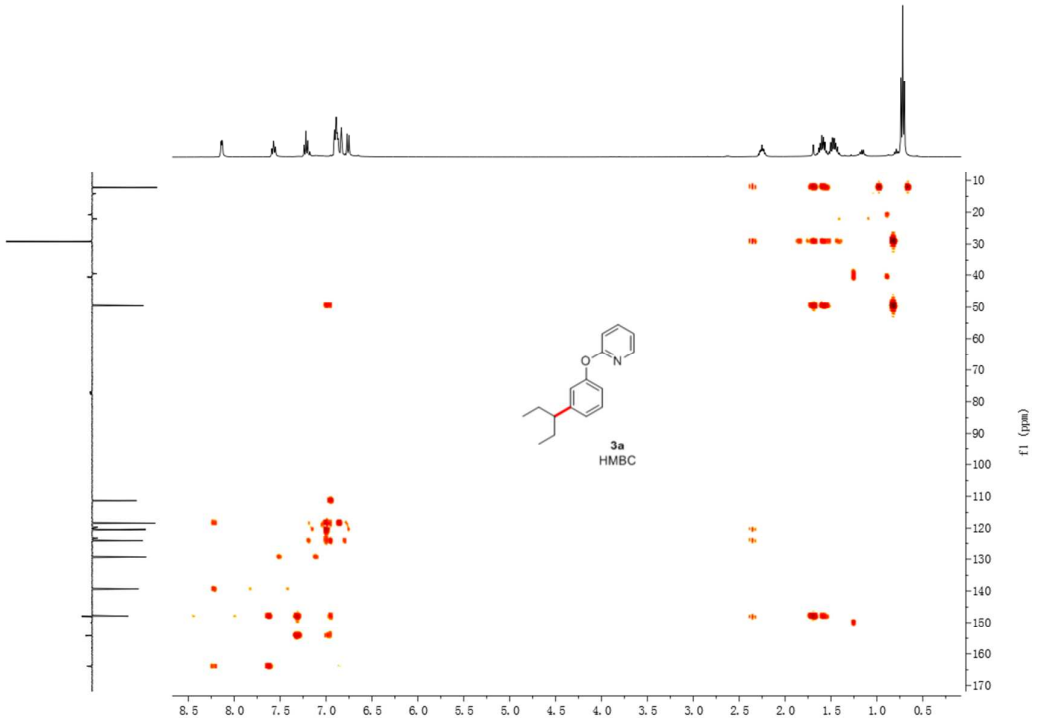
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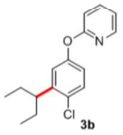
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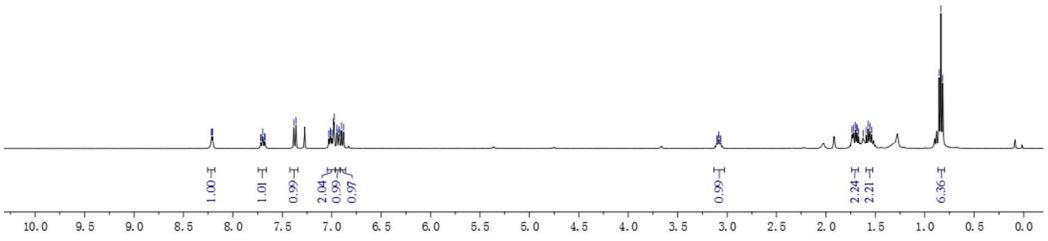

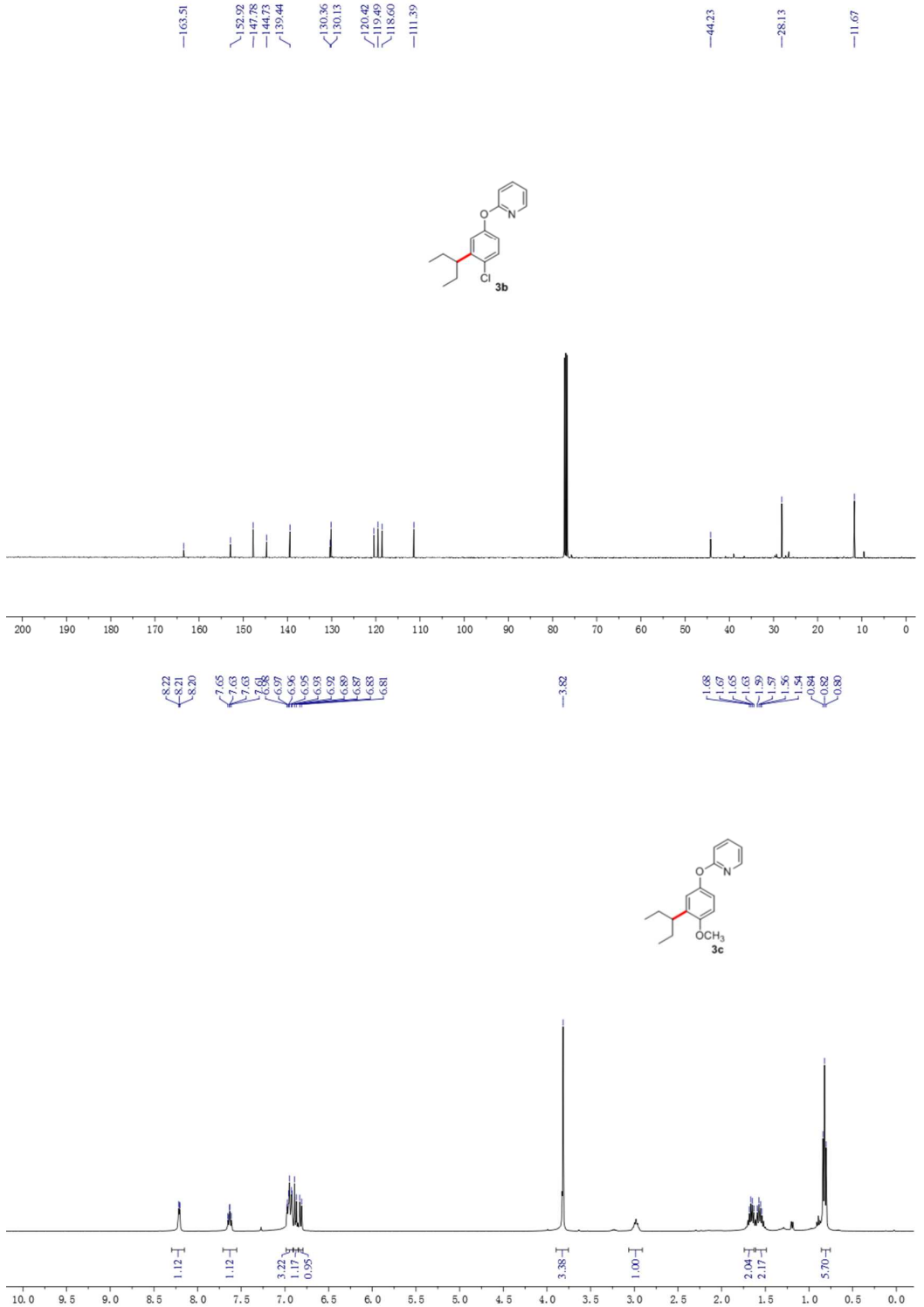
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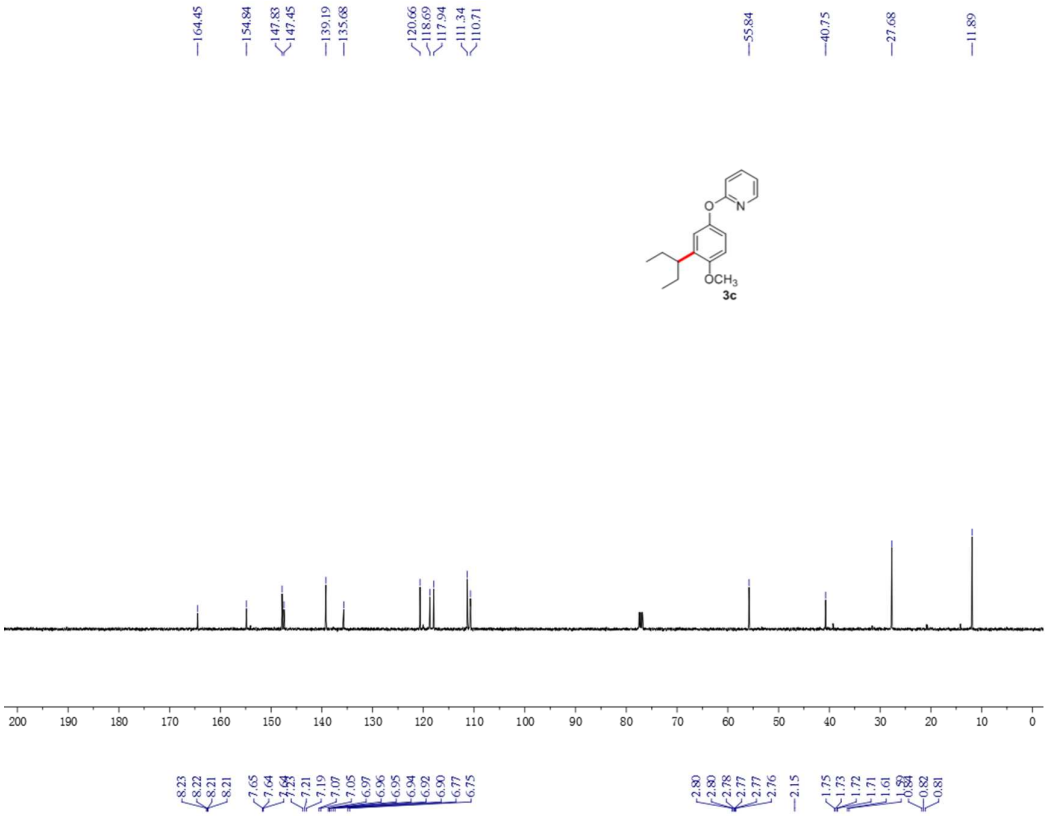
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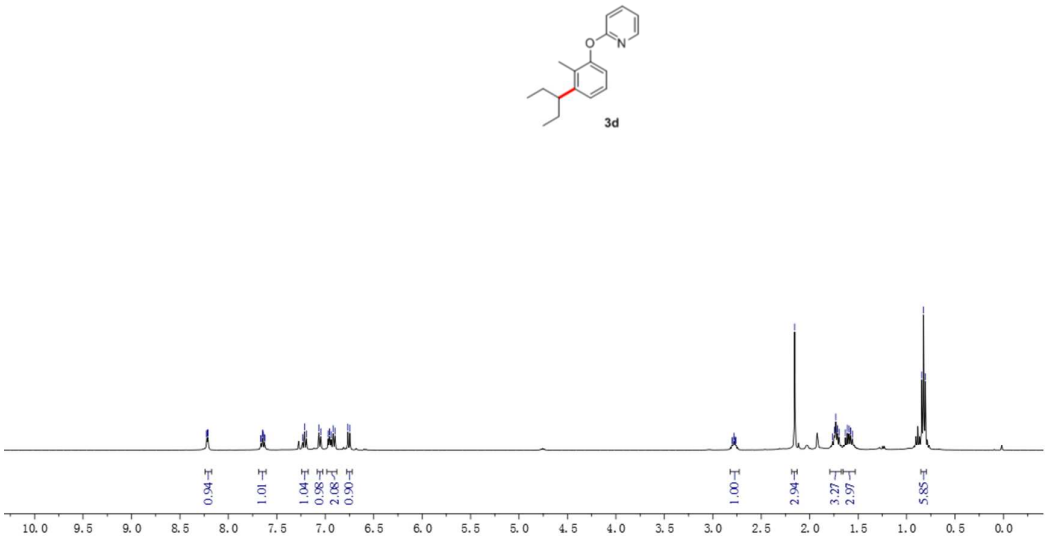
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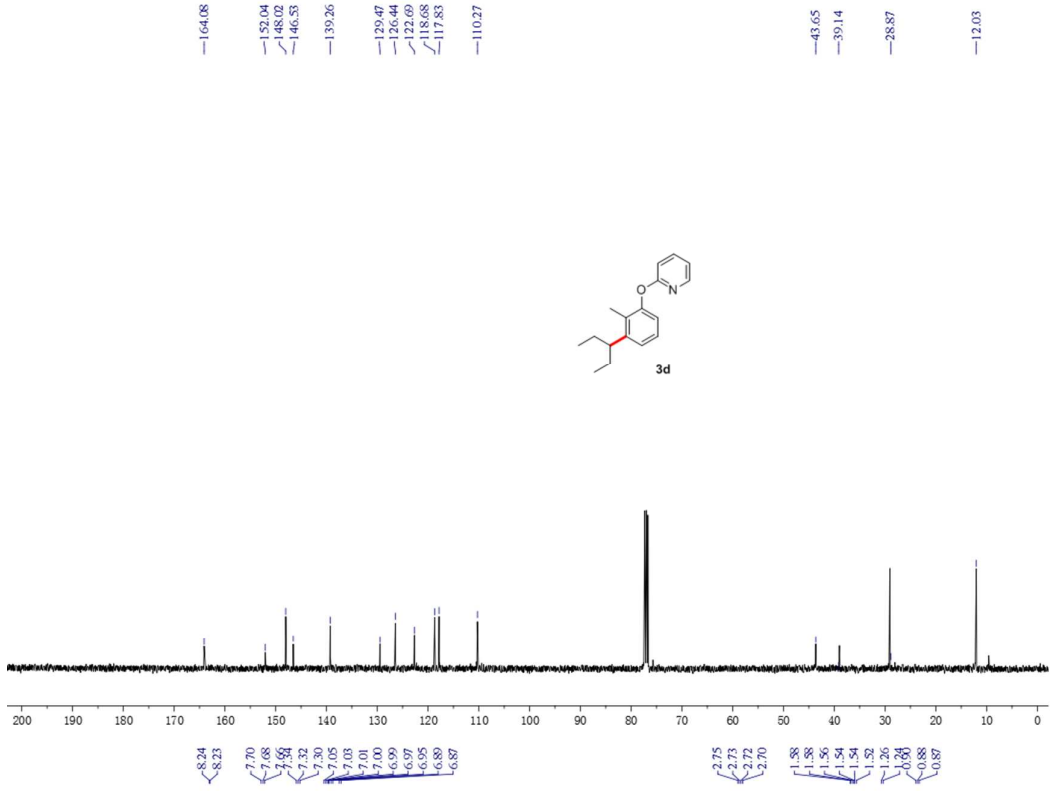
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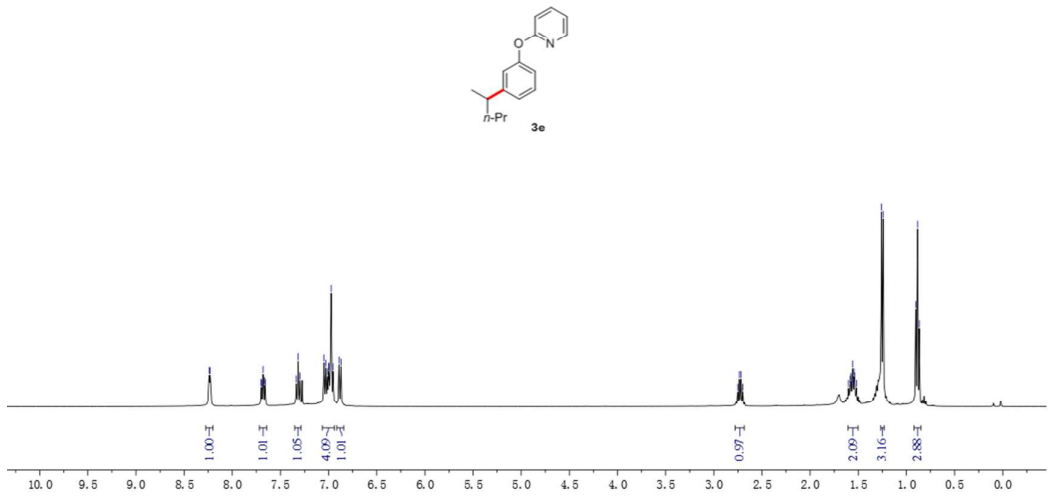
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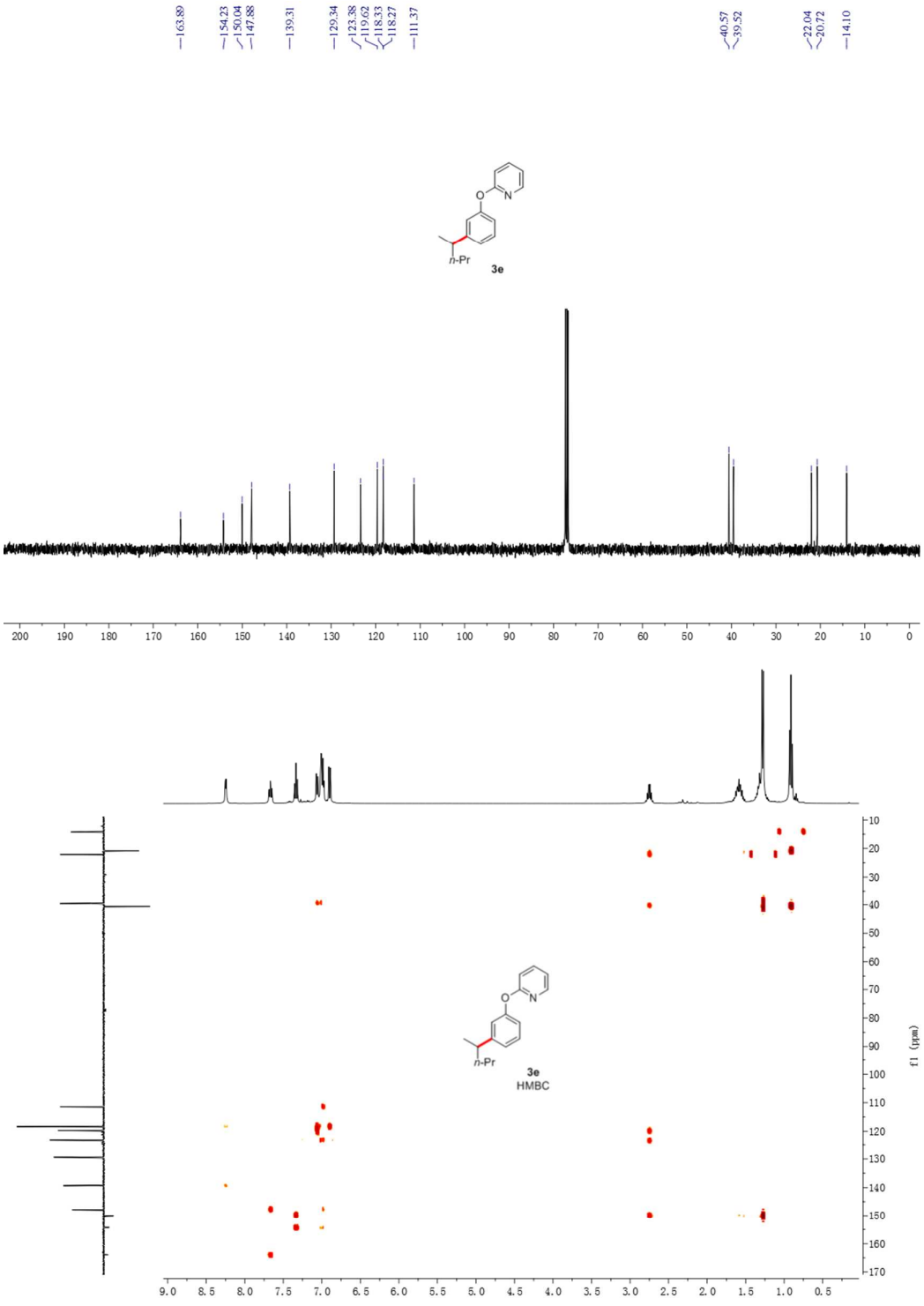
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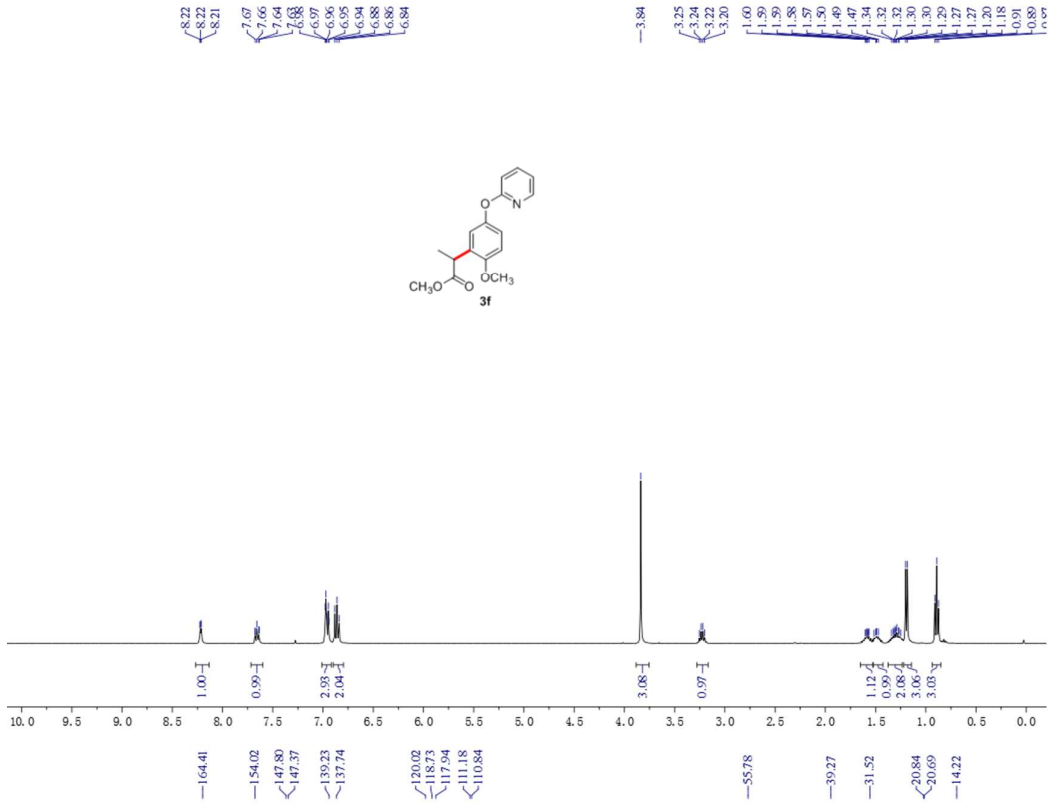
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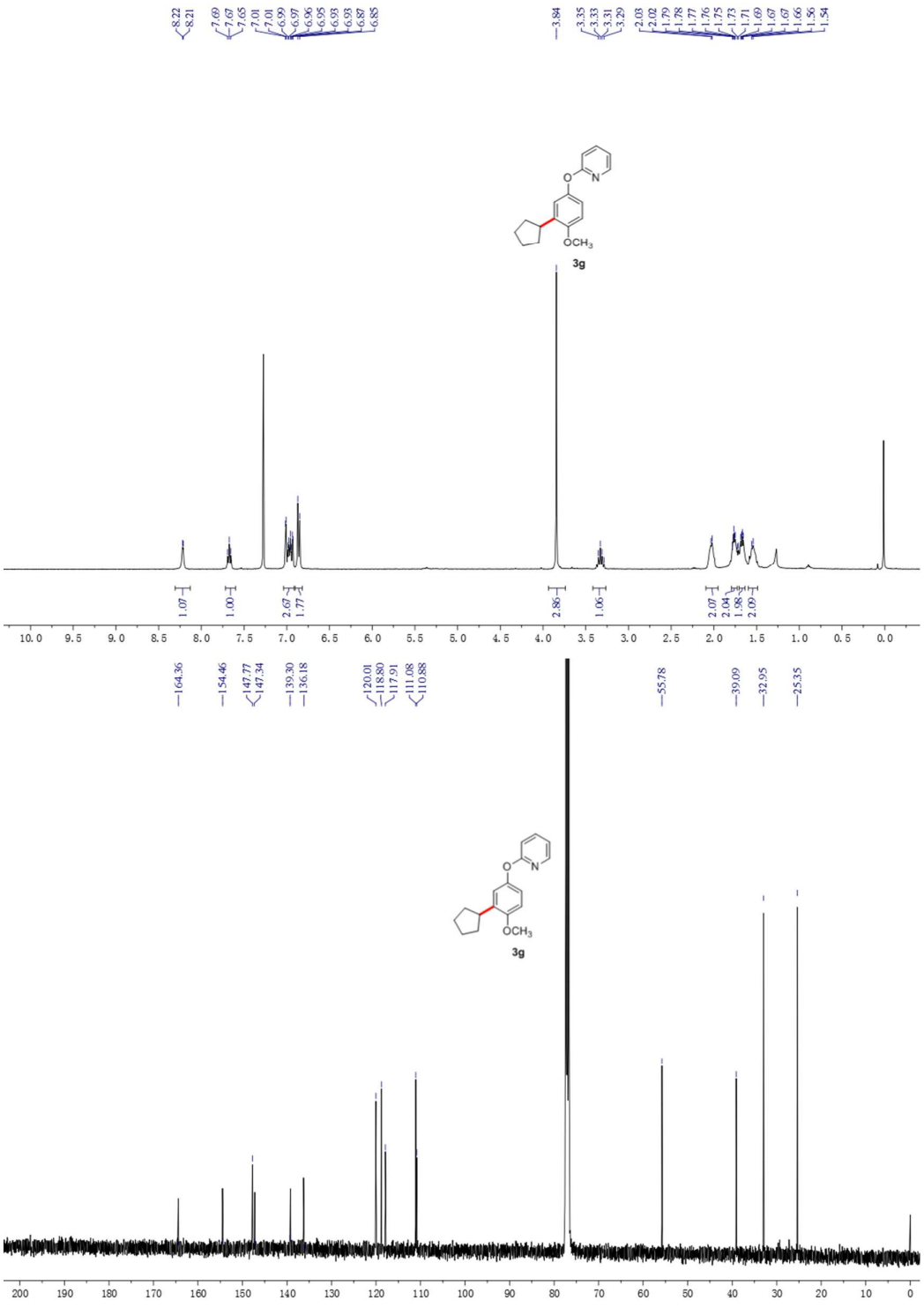
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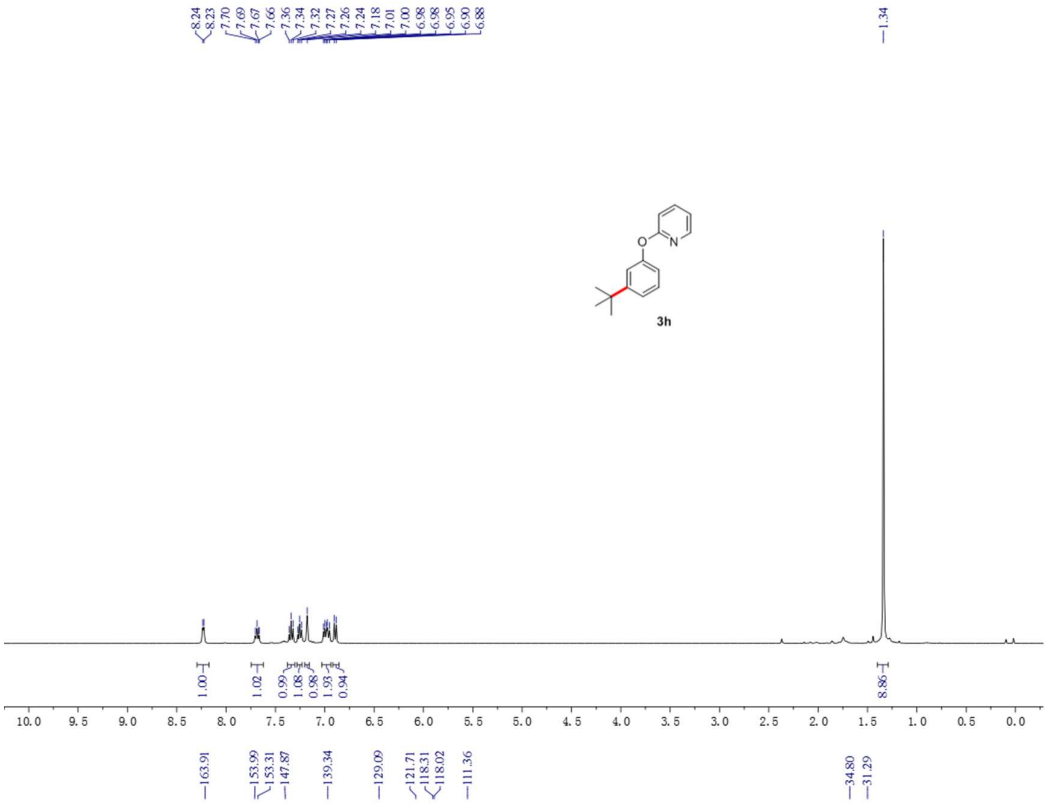
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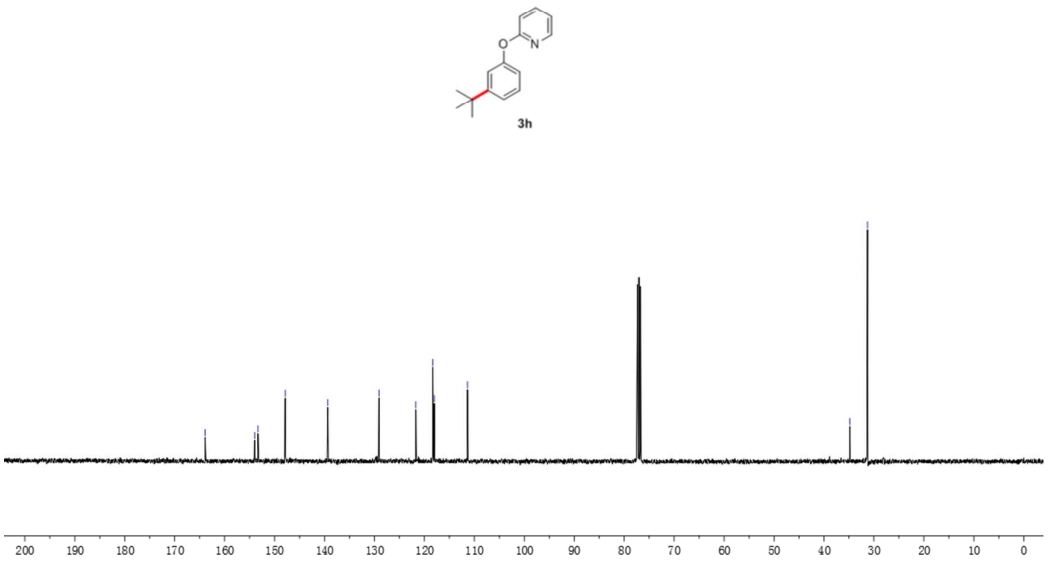
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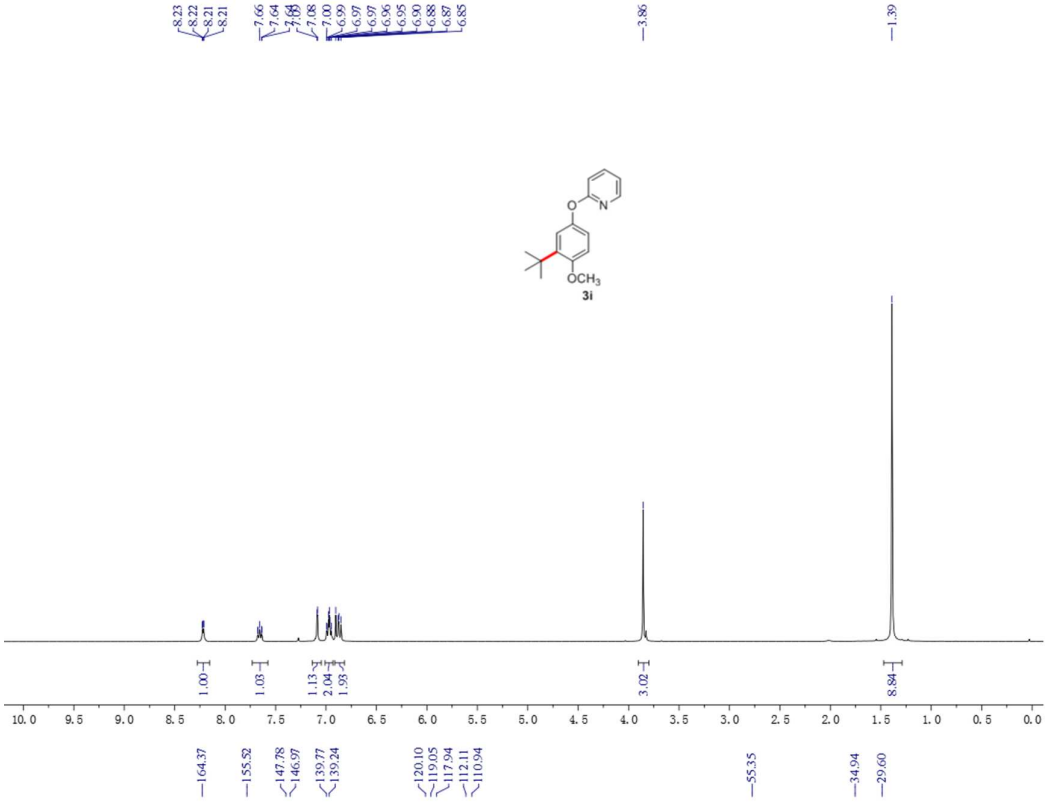
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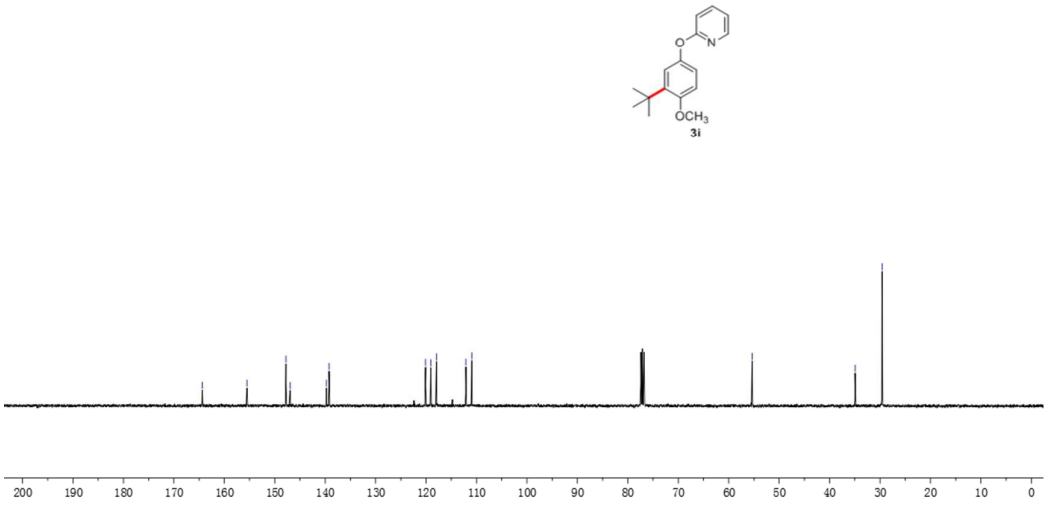
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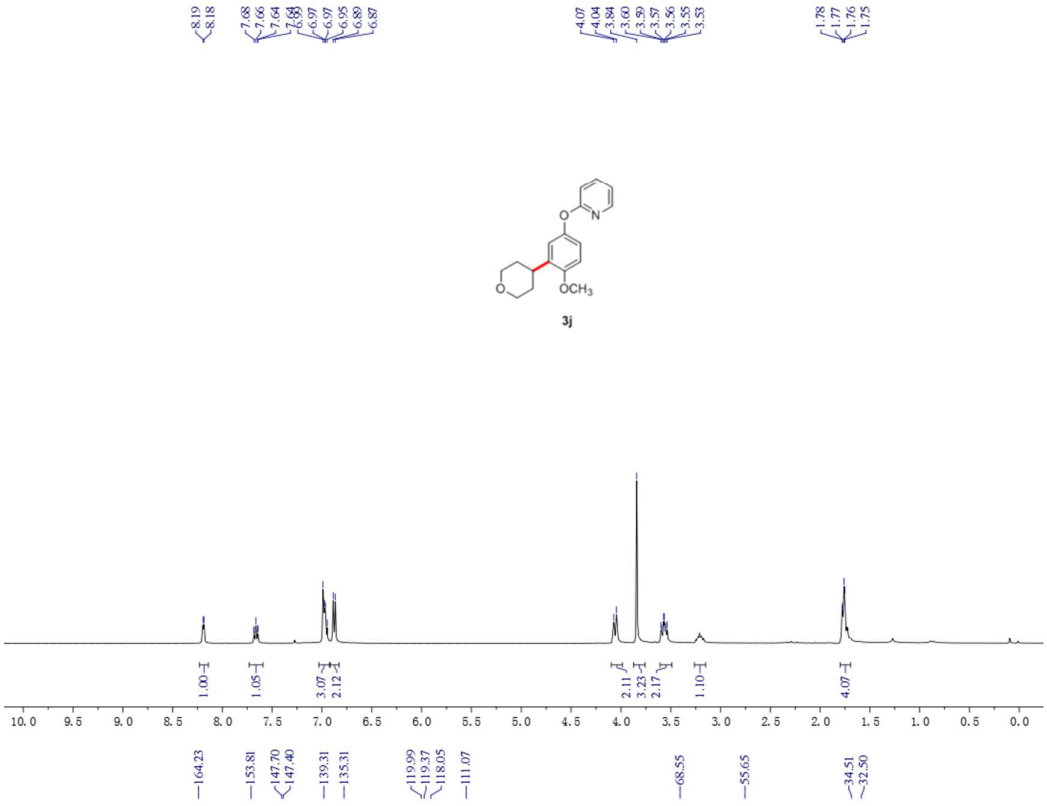
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6.97
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6.89
6.87
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4.04
3.84
3.60
3.59
3.57
3.56
3.55
3.53
1.78
1.77
1.76
1.75
OCH3
3j
1.00
1.05
3.07
2.12
2.11
3.23
2.17
1.10
4.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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153.81
147.70
147.40
139.31
135.31
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119.37
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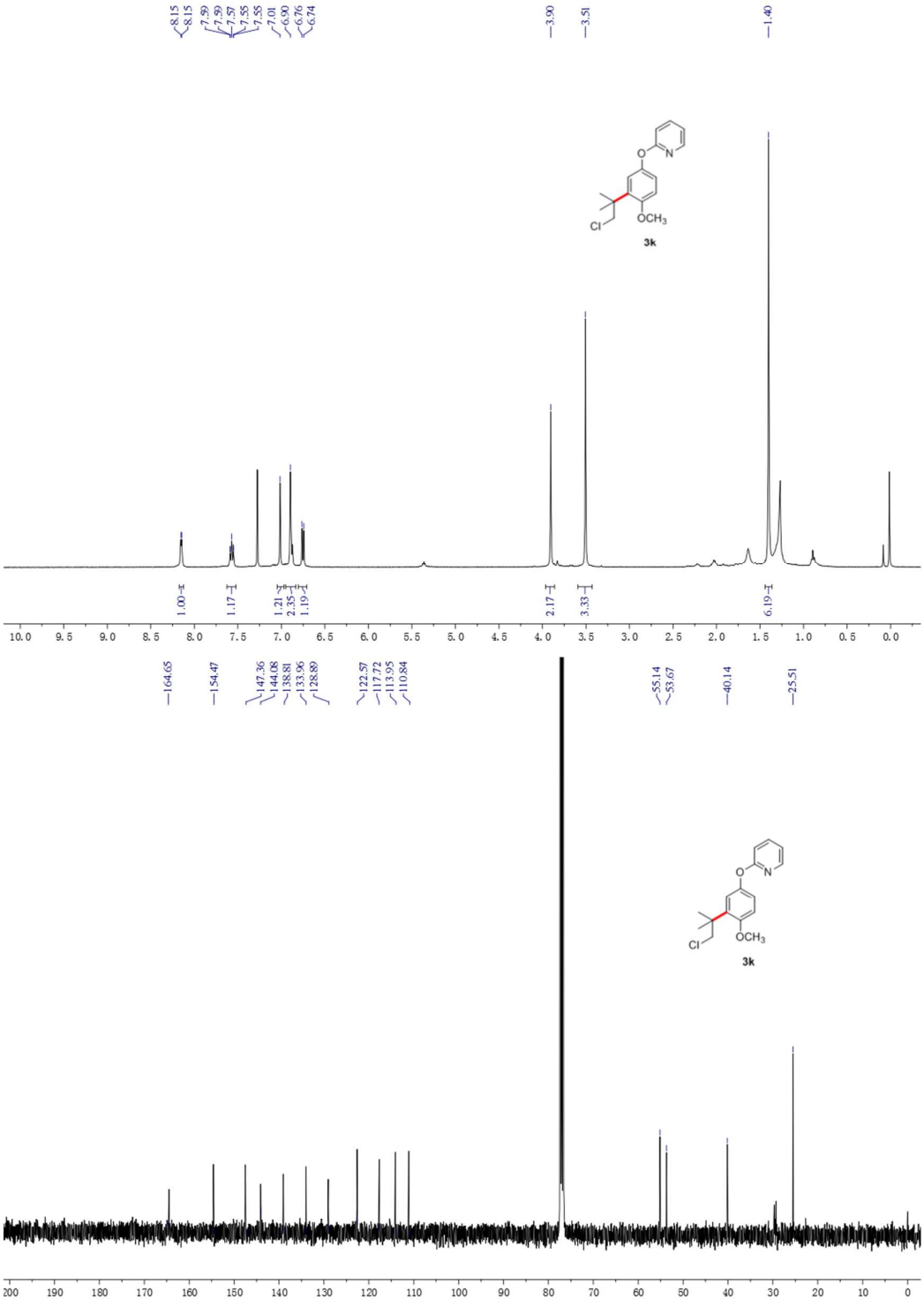
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3.51
1.40
3k
1.00
1.17
1.21
2.35
1.19
2.17
3.33
6.19
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154.47
147.36
144.08
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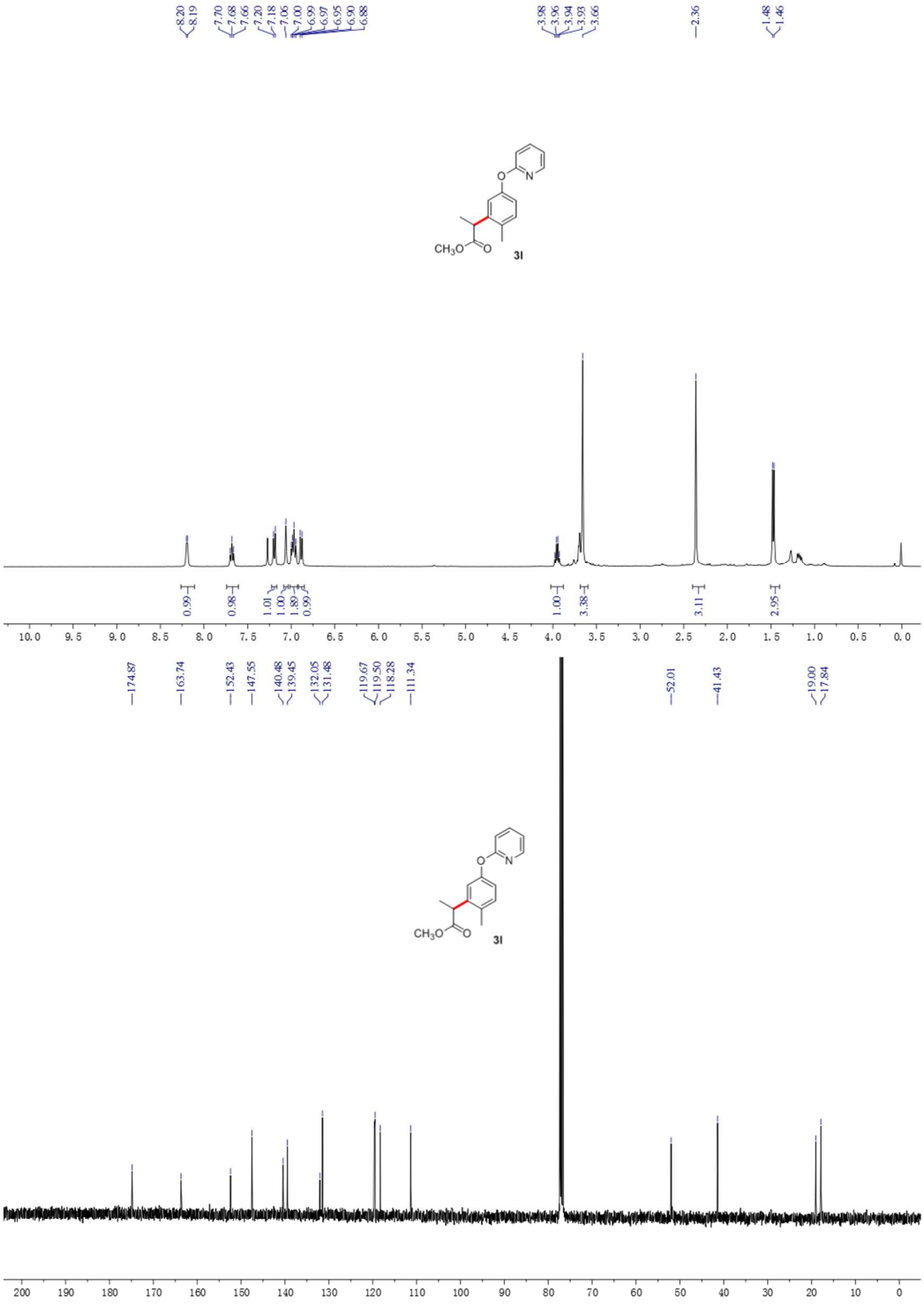
3k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6.88
3.98
3.96
3.94
3.93
3.66
2.36
1.48
1.46
3l
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0.98
1.01
1.00
1.89
0.99
1.00
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3.11
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174.87
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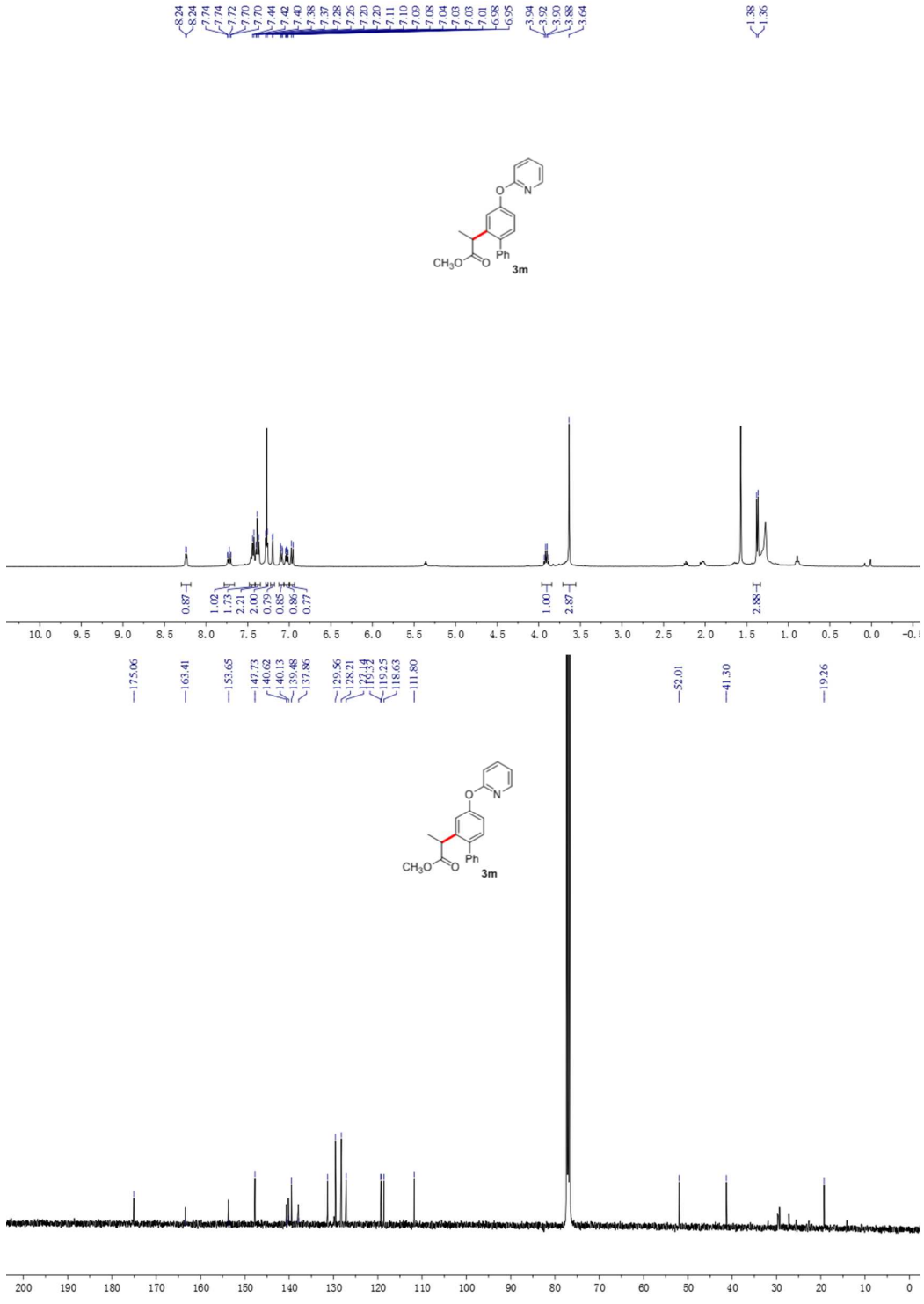
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7.20
7.20
7.11
7.10
7.09
7.08
7.04
7.03
7.03
7.01
6.98
6.95
3.94
3.92
3.90
3.88
3.64
1.38
1.36
O
N
Ph
CH3O
O
3m
0.87
1.02
1.73
2.21
2.00
0.79
0.85
0.86
0.77
1.00
2.87
2.88
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
175.06
163.41
153.65
147.73
140.62
140.13
139.48
137.86
129.56
128.21
119.25
118.63
111.80
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Ph
CH3O
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3m
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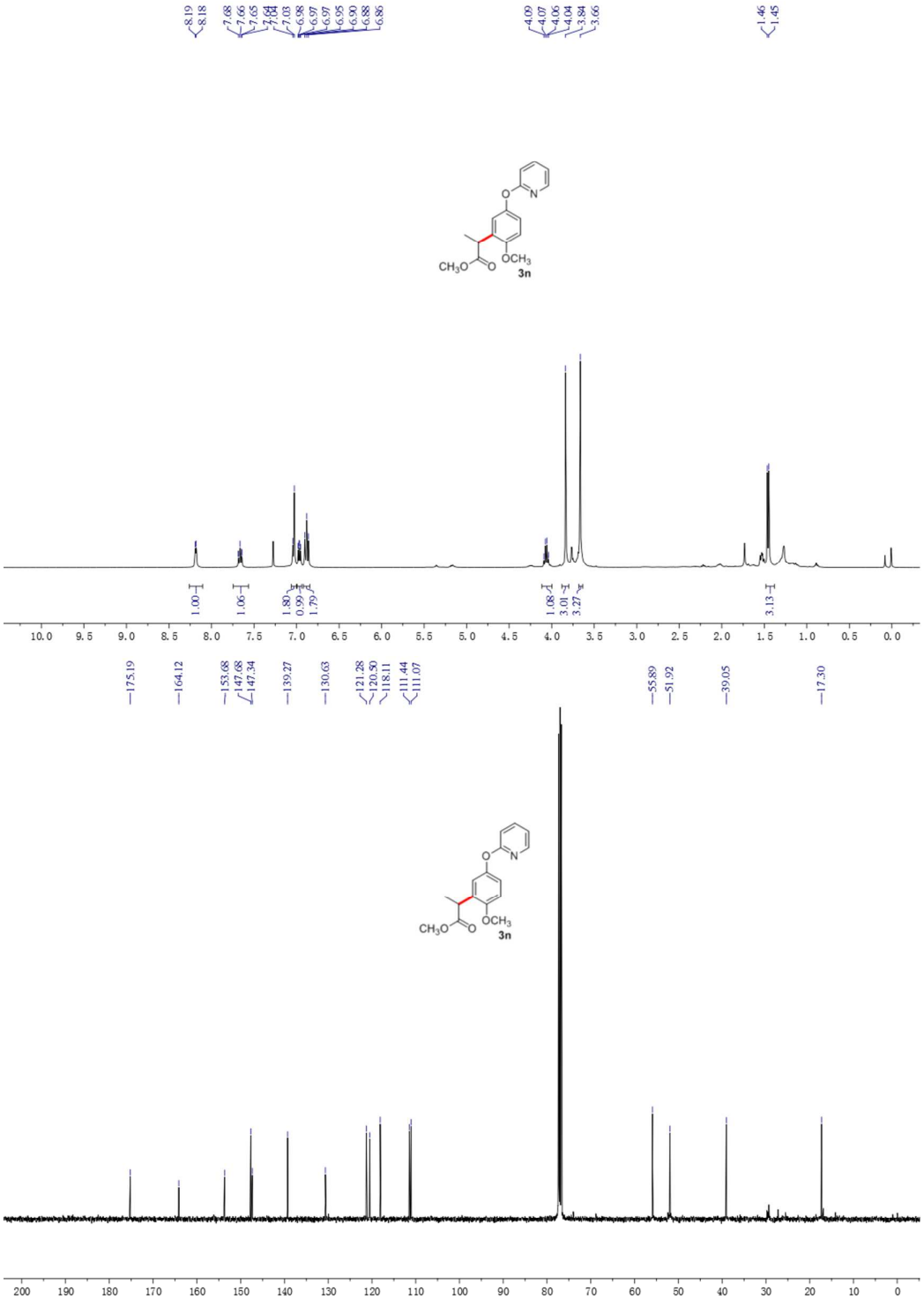
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6.86
4.09
4.07
4.06
4.04
3.84
3.66
1.46
1.45
3n
1.00
1.06
1.80
0.99
1.79
1.08
3.01
3.27
3.13
175.19
164.12
153.68
147.68
147.34
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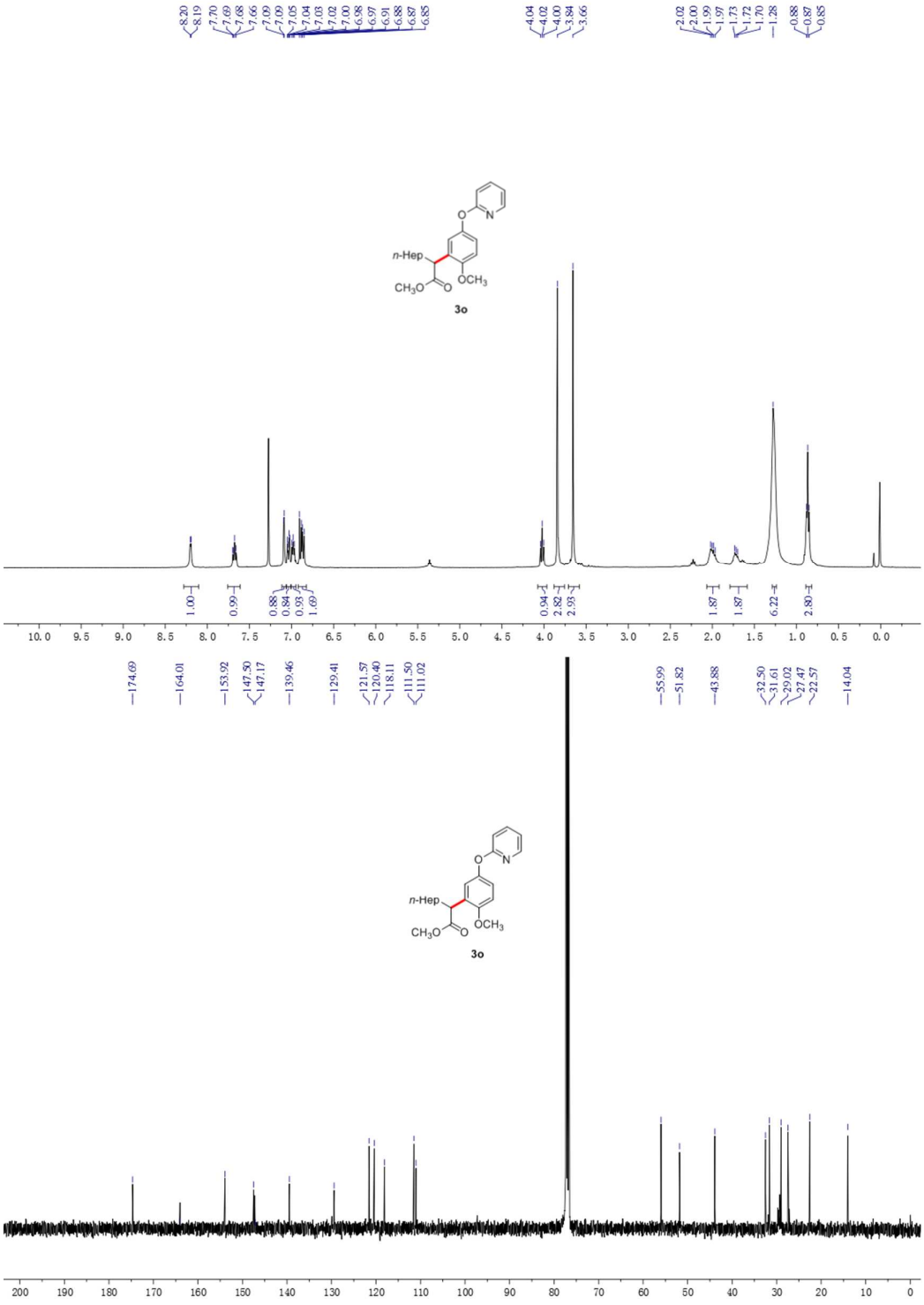
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7.04
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7.02
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6.98
6.97
6.91
6.88
6.87
6.85
4.04
4.02
4.00
3.84
3.66
2.02
2.00
1.99
1.97
1.73
1.72
1.70
1.28
0.88
0.87
0.85
n-Hep
CH3O
O
OCH3
3o
1.00
0.99
0.88
0.84
0.93
1.69
0.94
2.82
2.93
1.87
1.87
6.22
2.80
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
174.69
164.01
153.92
147.50
147.17
139.46
129.41
121.57
120.40
118.11
111.50
111.02
55.99
51.82
43.88
32.50
31.61
29.02
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14.04
n-Hep
CH3O
O
OCH3
3o
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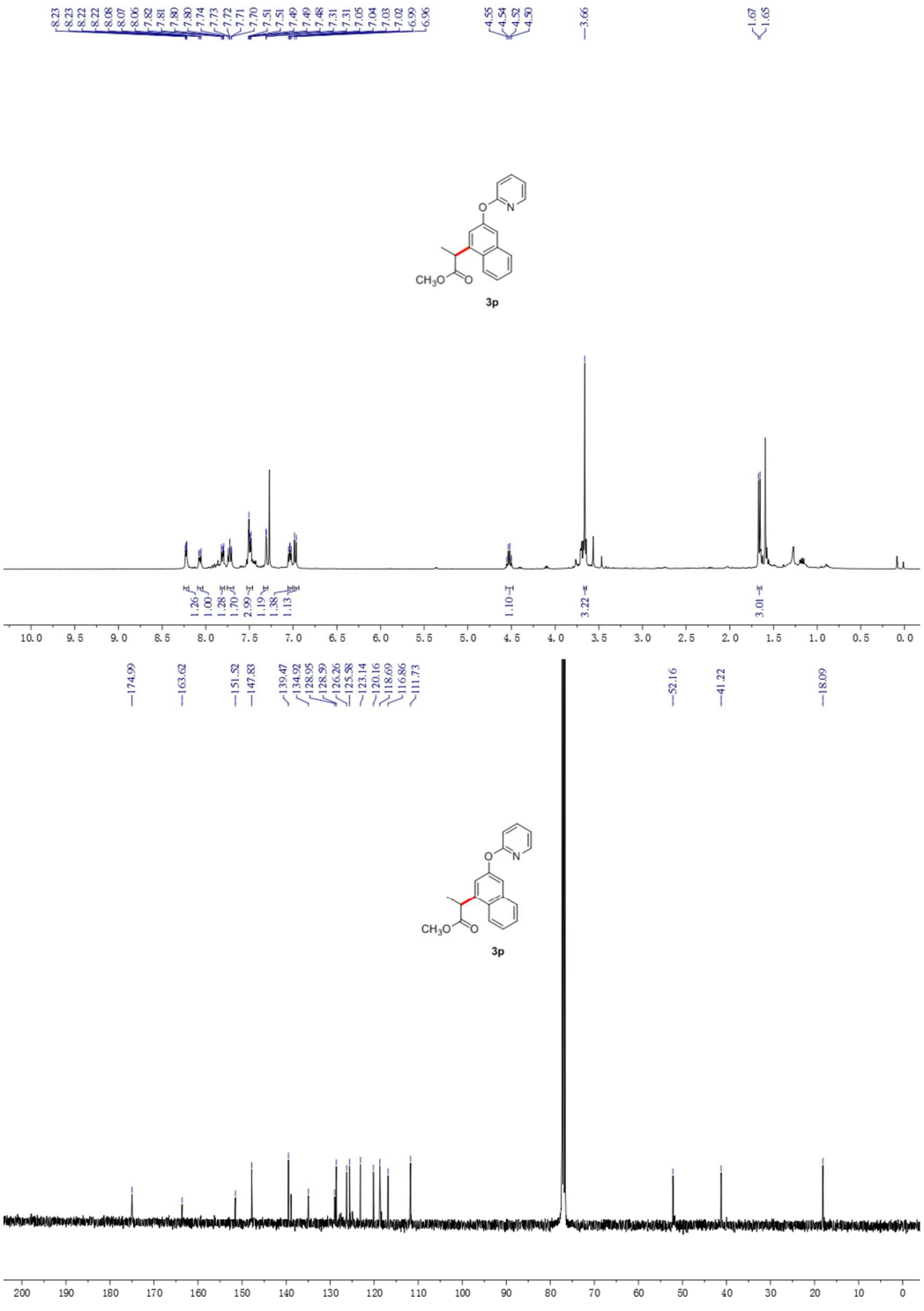
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7.72
7.71
7.70
7.51
7.51
7.49
7.49
7.48
7.31
7.05
7.04
7.03
7.02
6.99
6.96
4.55
4.54
4.52
4.50
3.66
1.67
1.65
O
N
CH3O
O
3p
1.26
1.00
1.28
1.70
2.99
1.19
1.38
1.13
1.10
3.22
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
174.99
163.62
151.52
147.83
139.47
134.92
128.95
128.89
126.26
125.88
123.14
120.16
118.69
116.86
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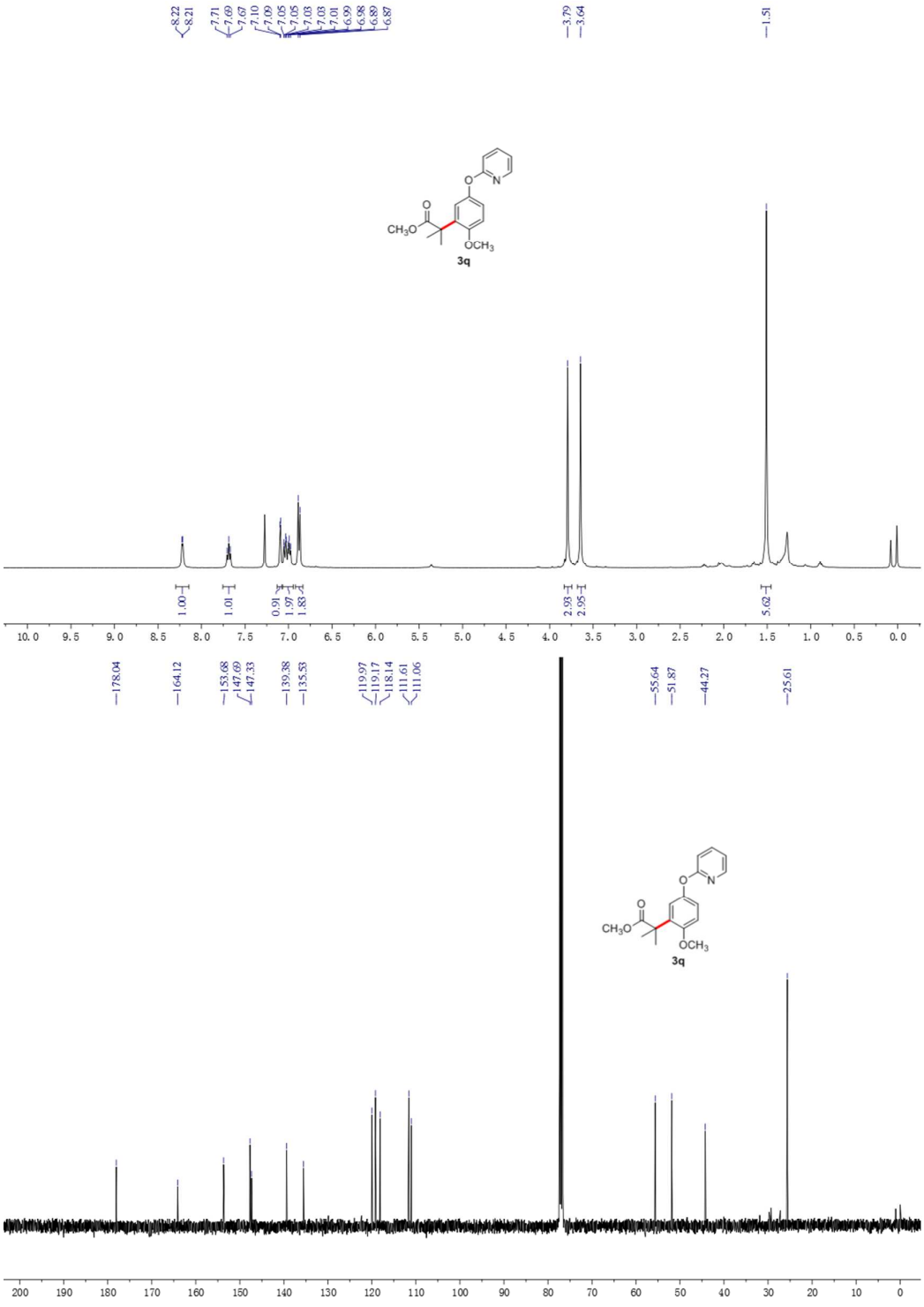
18.09
O
N
CH3O
O
3p
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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7.05
7.05
7.03
7.03
7.01
6.99
6.98
6.89
6.87
3.79
3.64
1.51
3q
1.00
1.01
0.91
1.97
1.83
2.93
2.95
5.62
178.04
164.12
153.68
147.69
147.33
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111.61
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55.64
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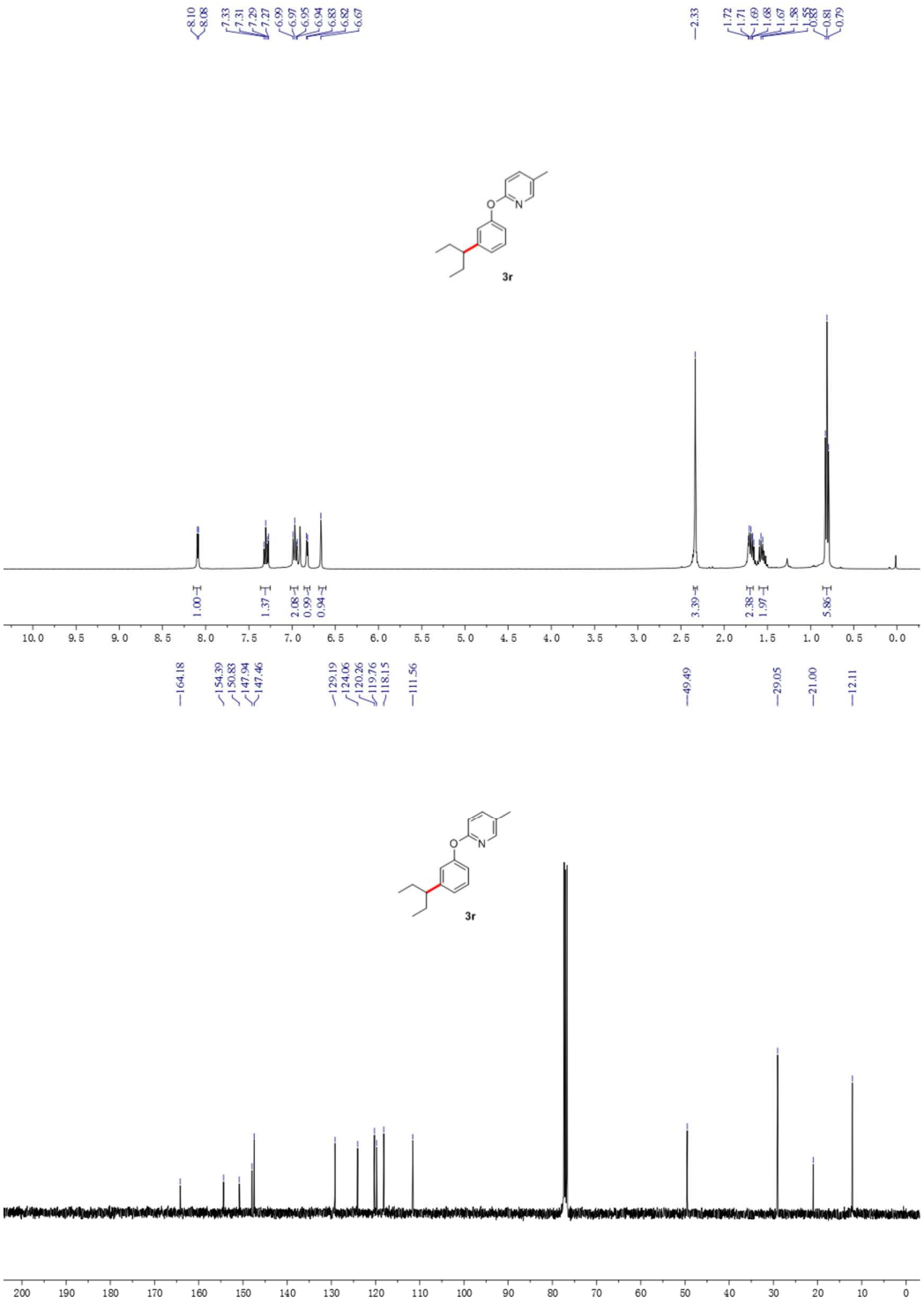
44.27
25.61
3q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6.94
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6.82
6.67
2.33
1.72
1.71
1.69
1.68
1.67
1.38
1.55
0.83
0.81
0.79
3r
1.00
1.37
2.08
0.99
0.94
3.39
2.38
1.97
5.86
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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150.83
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147.46
129.19
124.06
120.26
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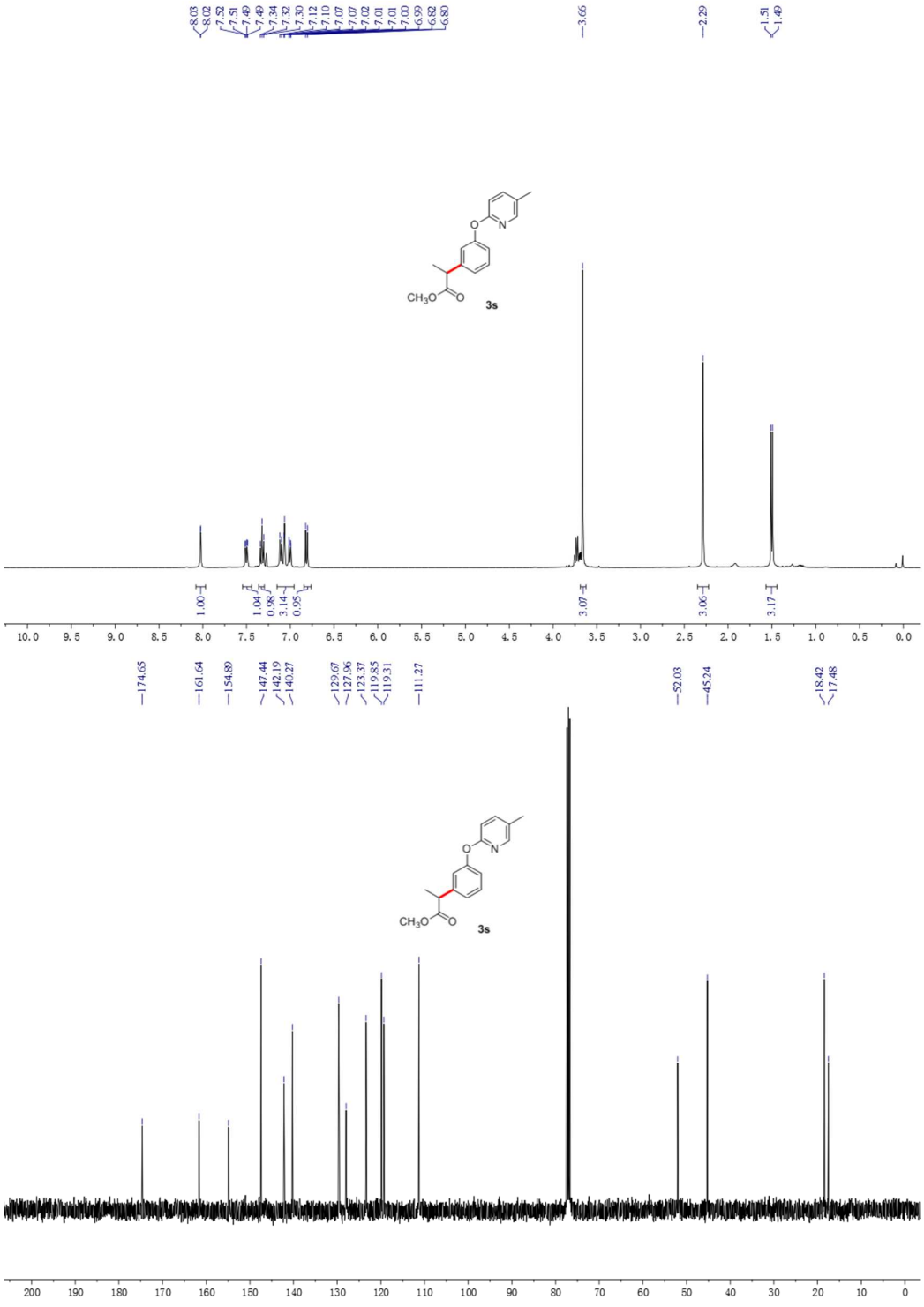
21.00
12.11
3r
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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7.12
7.10
7.07
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7.01
7.00
6.99
6.82
6.80
3.66
2.29
1.51
1.49
3s
1.00
1.04
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3.14
0.95
3.07
3.06
3.17
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
174.65
161.64
154.89
147.44
142.19
140.27
129.67
127.96
123.37
119.85
119.31
111.27
52.03
45.24
18.42
17.48
3s
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180
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150
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100
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10
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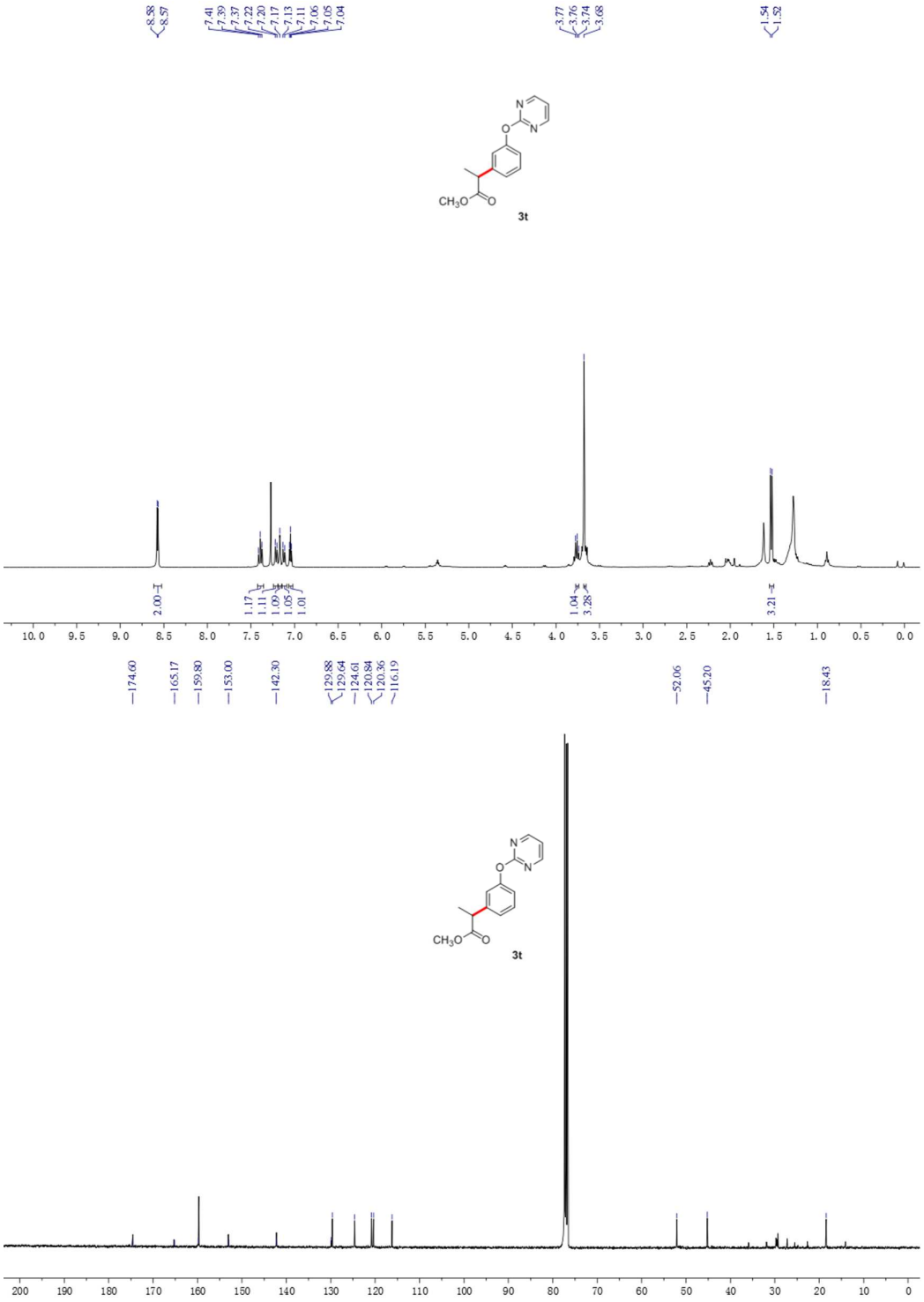
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7.04
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3.76
3.74
3.68
1.54
1.52
3t
2.00
1.17
1.11
1.09
1.05
1.01
1.04
3.28
3.21
174.60
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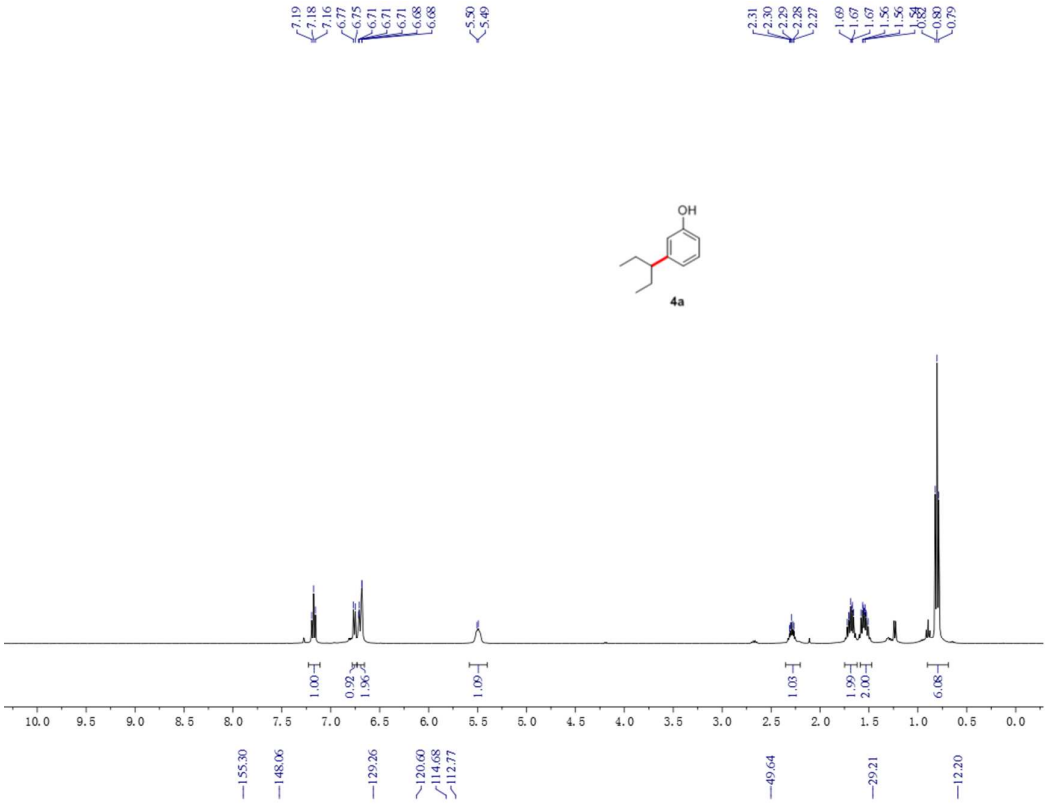
45.20
18.43
3t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6.68
5.50
5.49
2.31
2.30
2.29
2.28
2.27
1.69
1.67
1.67
1.56
1.56
1.54
0.82
0.80
0.79
OH
4a
1.00
0.92
1.96
1.09
1.03
1.99
2.00
6.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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129.26
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114.68
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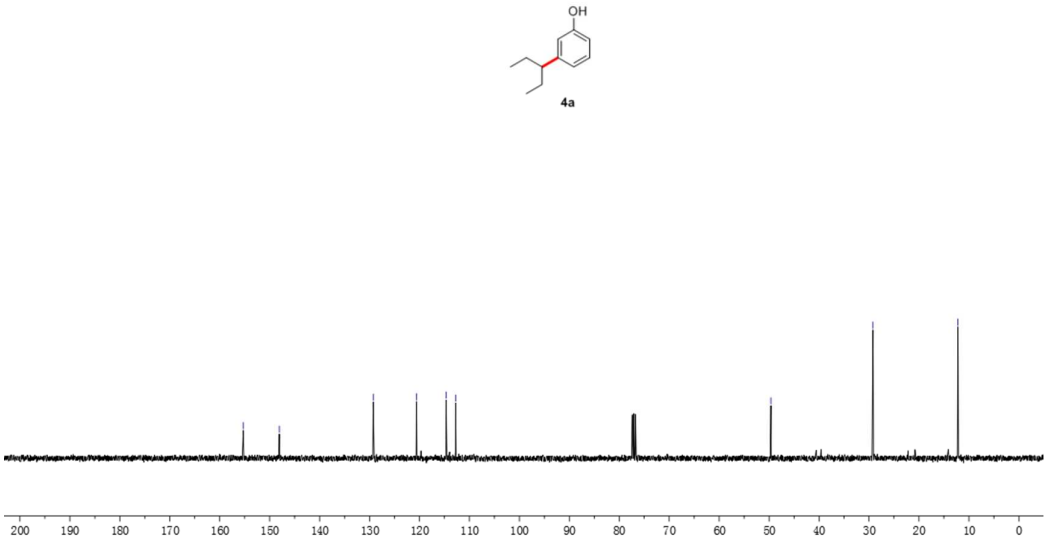
49.64
29.21
12.20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4a
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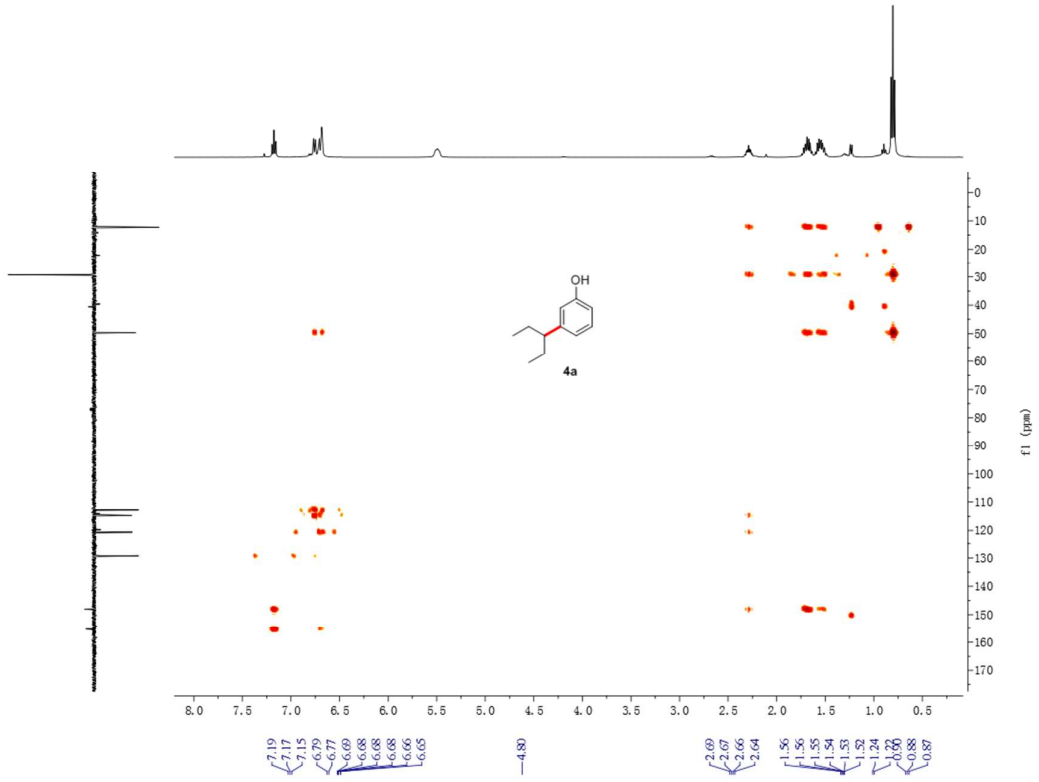
OH
4a
f1 (ppm)
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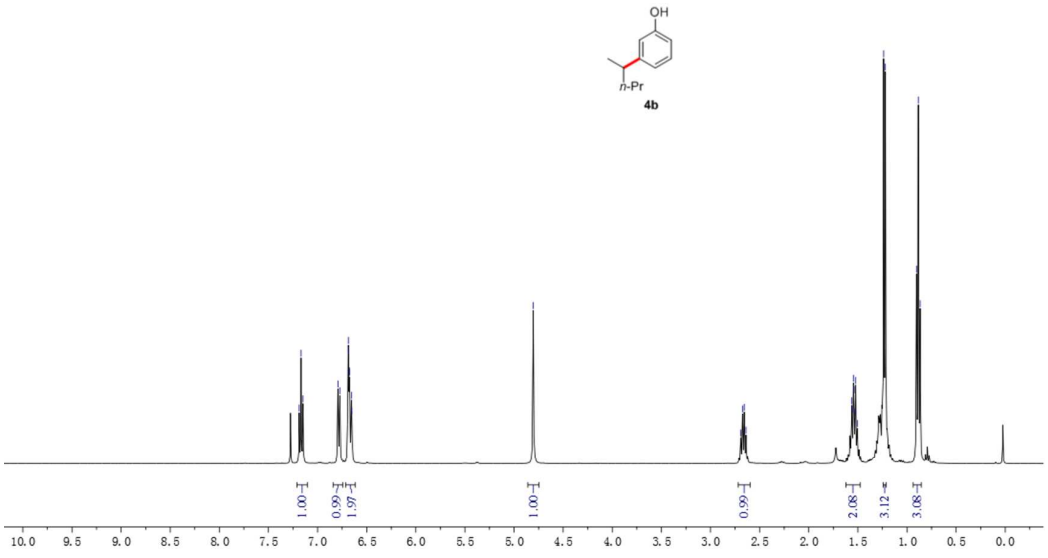
7.17
7.15
6.79
6.77
6.69
6.68
6.68
6.68
6.66
6.65
4.80
2.69
2.67
2.66
2.64
1.56
1.56
1.55
1.54
1.53
1.52
1.24
0.92
0.88
0.87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n-Pr
4b
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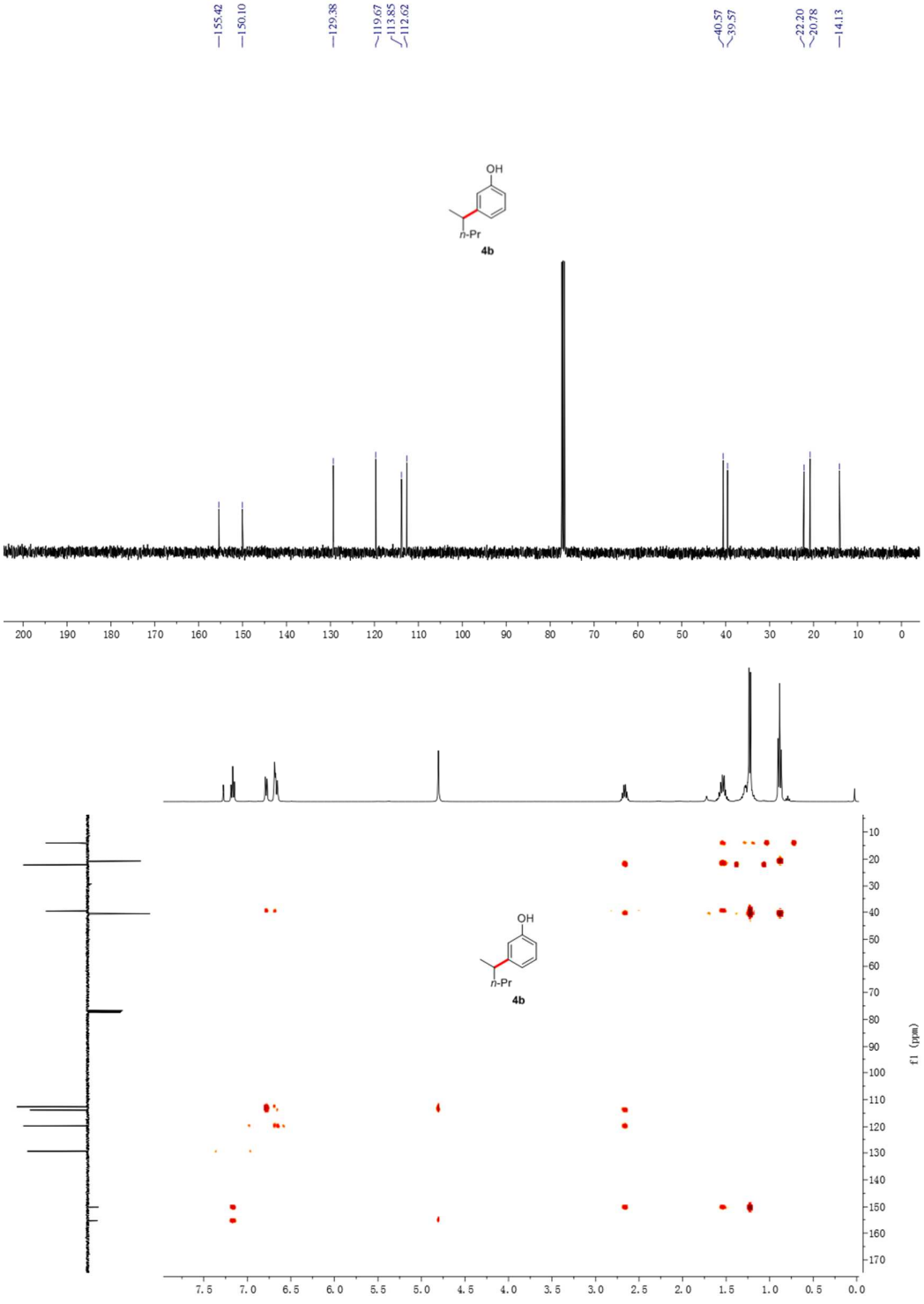
0.99
1.97
1.00
0.99
2.08
3.12
3.08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129.38
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40.57
39.57
22.20
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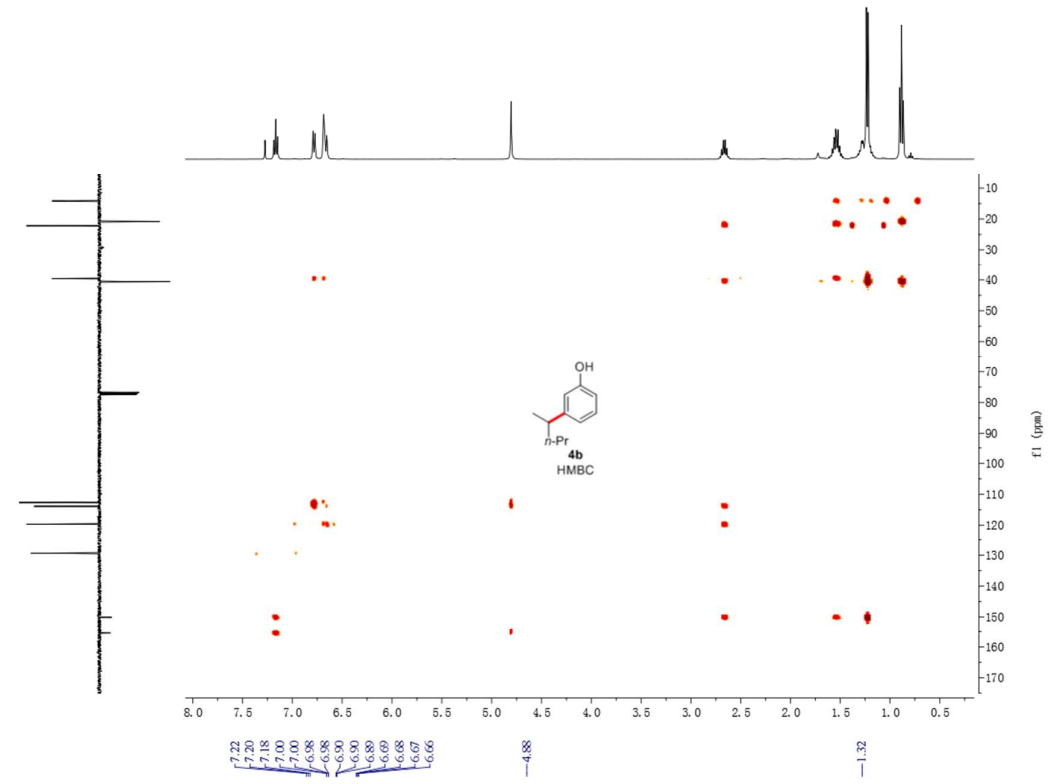
14.13
OH
n-Pr
4b
f1 (ppm)


OH
n-Pr
4b
HMBC
f1 (ppm)
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7.20
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7.00
7.00
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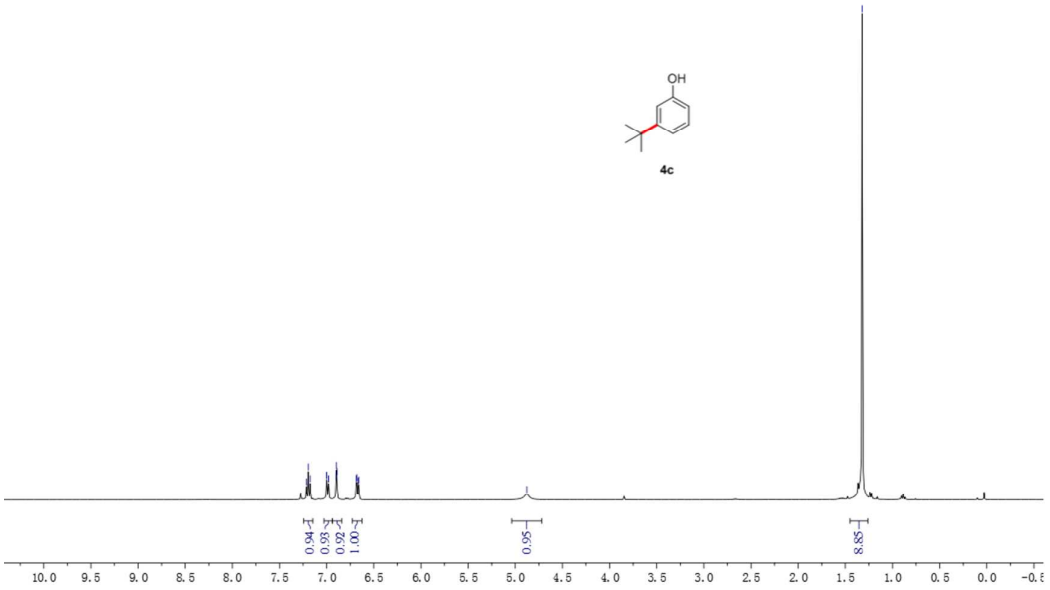
6.89
6.68
6.67
6.66
4.88
1.32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4c
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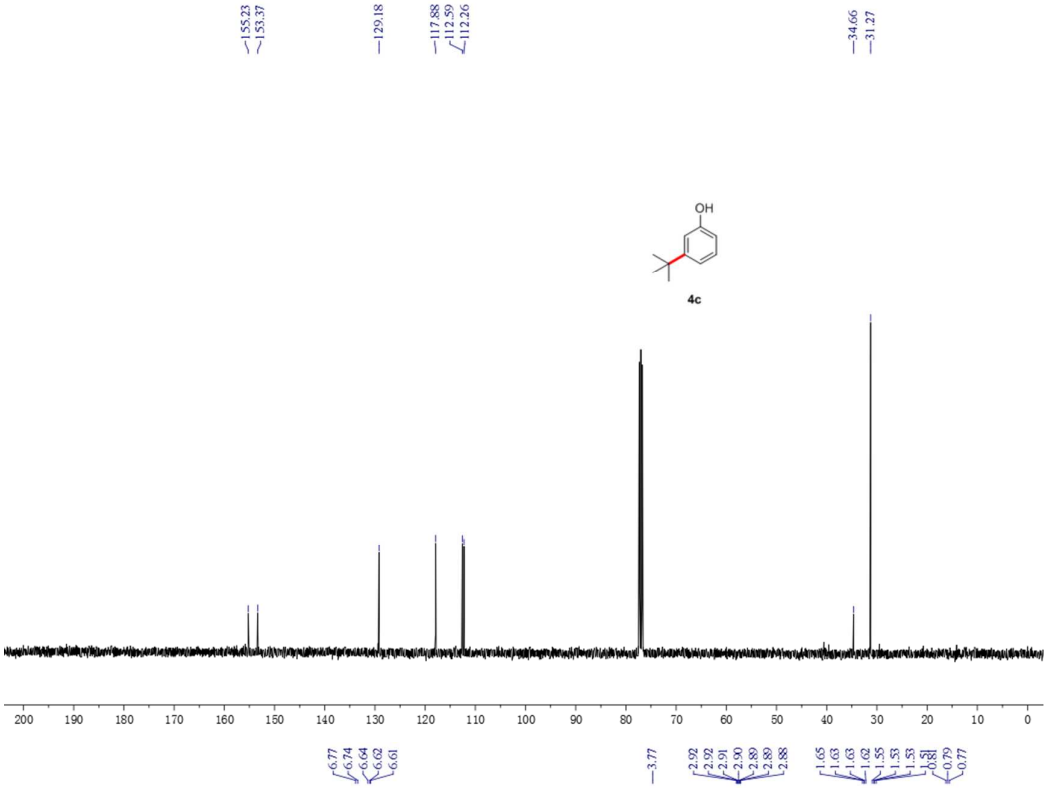
0.93
0.92
1.00
0.95
8.85


155.23
153.37
129.18
117.88
112.59
112.26
34.66
31.27
OH
4c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
6.77
6.74
6.64
6.62
6.61
3.77
2.92
2.92
2.91
2.90
2.89
2.89
2.88
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1.63
1.62
1.55
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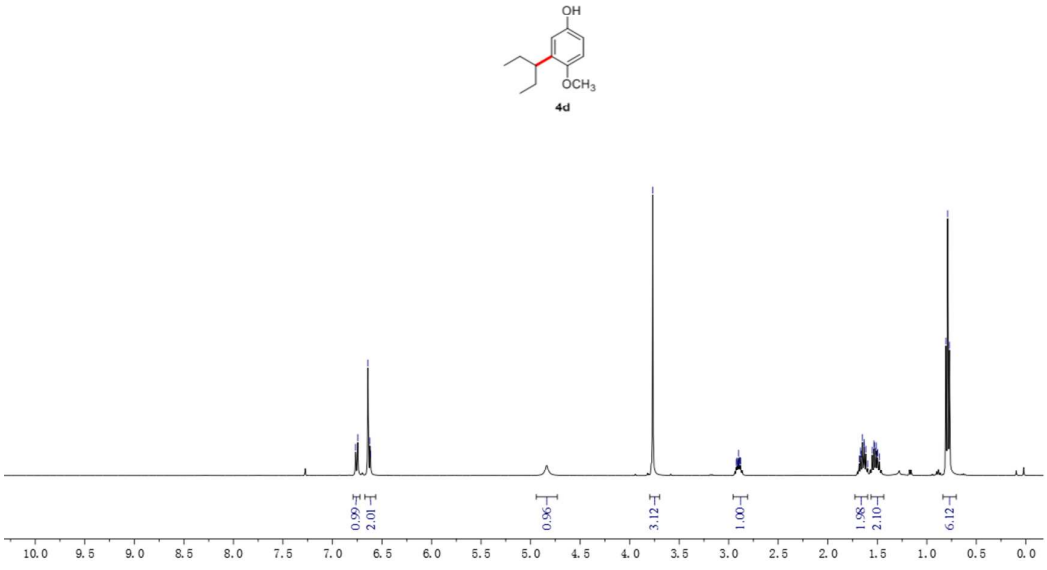
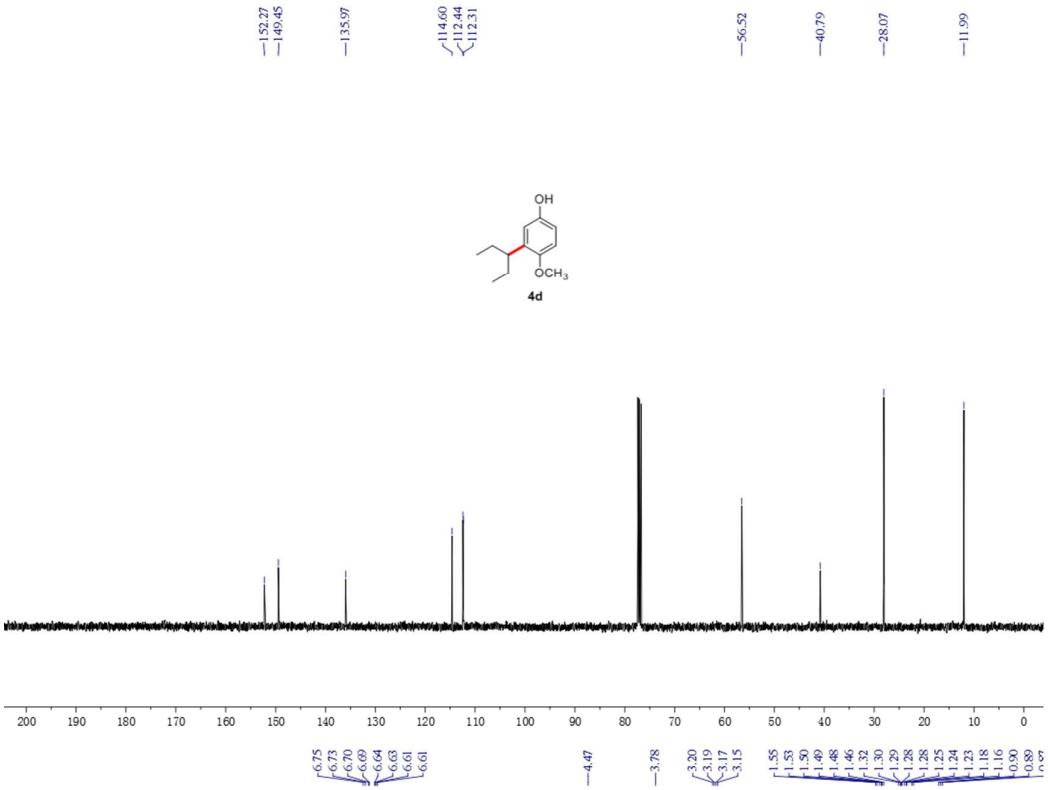
1.53
1.51
0.81
0.79
0.77


OH
OCH3
4d
0.99
2.01
0.96
3.12
1.00
1.98
2.10
6.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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114.60
112.44
112.31
56.52
40.79
28.07
11.99
OH
OCH3
4d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
6.75
6.73
6.70
6.69
6.64
6.63
6.61
6.61
4.47
3.78
3.20
3.19
3.17
3.15
1.55
1.53
1.50
1.49
1.48
1.46
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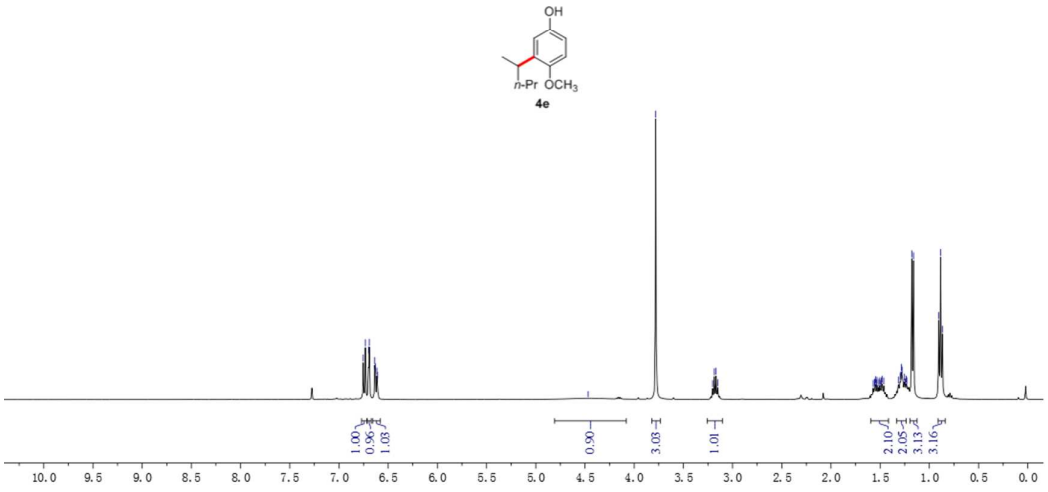
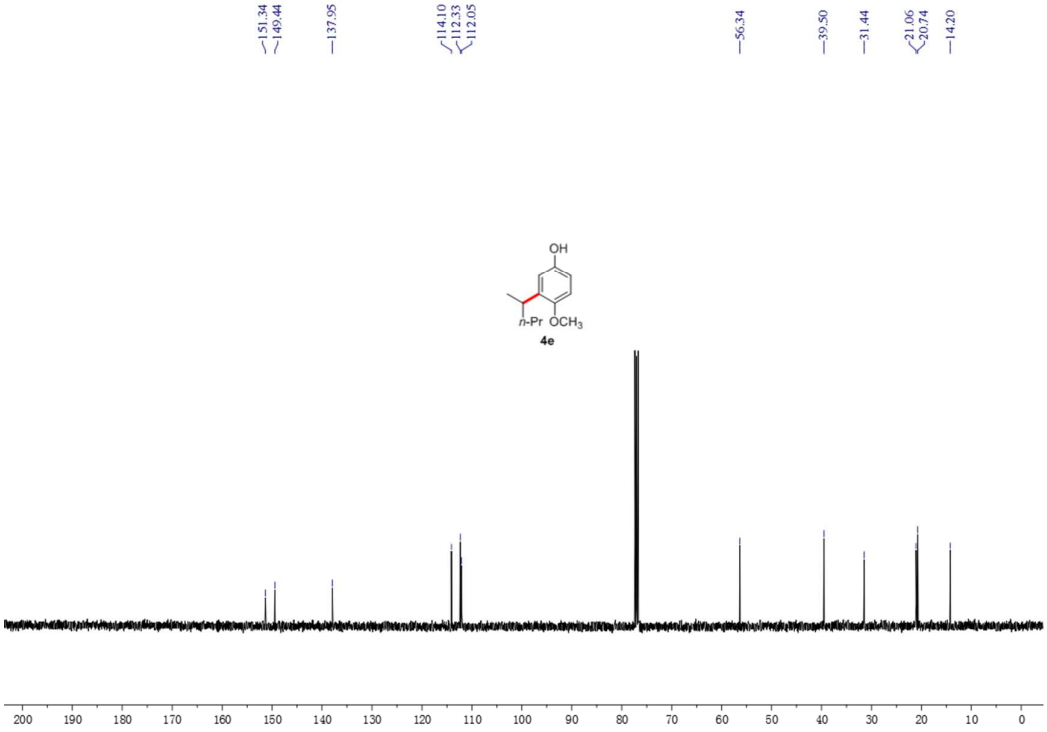
1.29
1.28
1.28
1.25
1.24
1.23
1.18
1.16
0.90
0.89


OH
n-Pr
OCH3
4e
1.00
0.96
1.03
0.90
3.03
1.01
2.10
2.05
3.13
3.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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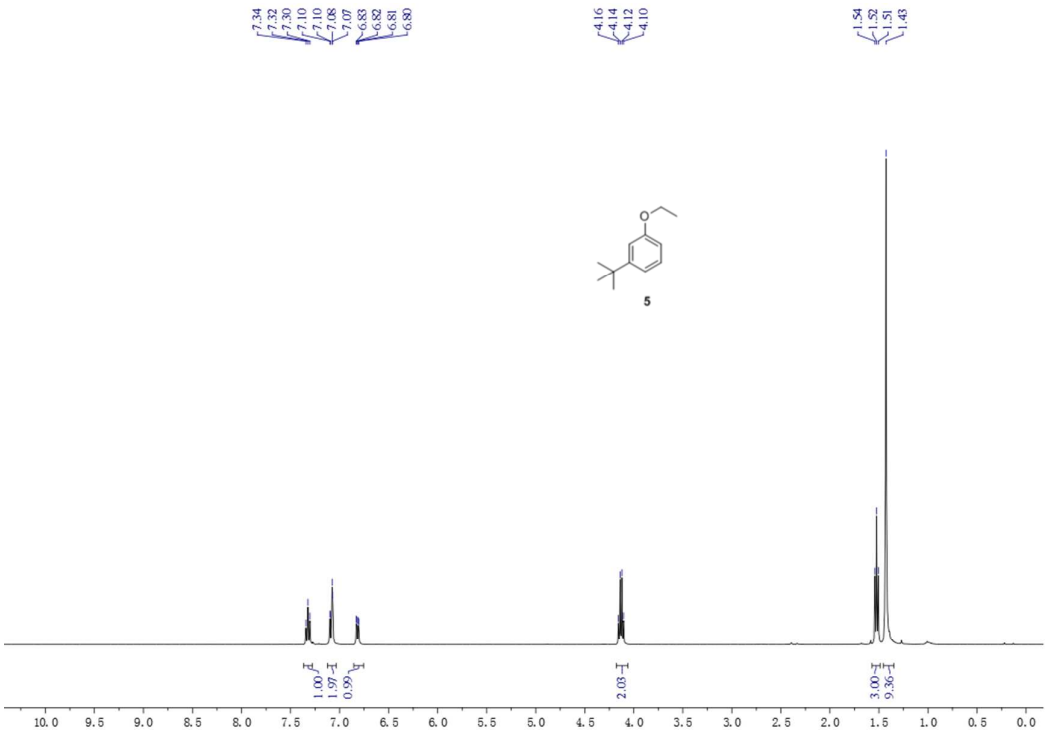
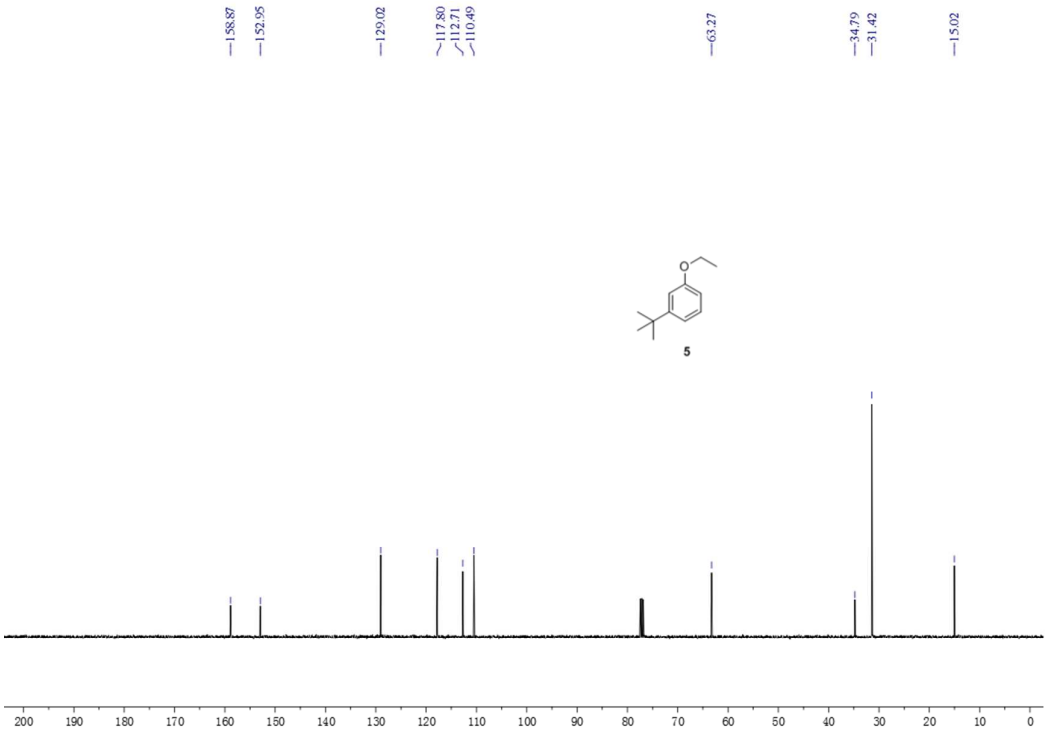
149.44
137.95
114.10
112.33
112.05
56.34
39.50
31.44
21.06
20.74
14.20
OH
n-Pr
OCH3
4e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.34
7.32
7.30
7.10
7.10
7.08
7.07
6.83
6.82
6.81
6.80
4.16
4.14
4.12
4.10
1.54
1.52
1.51
1.43
O
5
1.00
1.97
0.99
2.03
3.00
9.36
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0



5. X-ray crystal structure and data for six-membered ruthenacycle intermediate

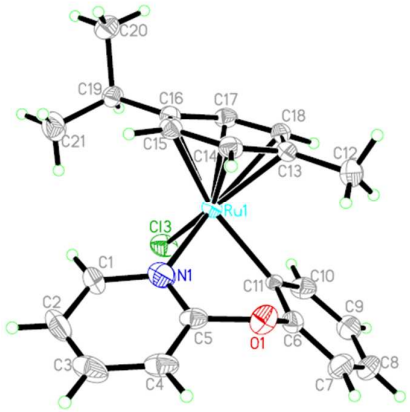


Table 1. Crystal data and structure refinement for 1503850.

Identification code	1503850
Empirical formula	C21 H22 Cl N O Ru
Formula weight	440.92
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 11.622(2) A alpha = 90 deg.
	b = 8.3594(17) A beta = 102.80(3) deg.
	c = 19.416(4) A gamma = 90 deg.
Volume	1839.4(6) A^3
Z, Calculated density	4, 1.592 Mg/m^3
Absorption coefficient	1.006 mm^-1
F(000)	896
Crystal size	0.20 x 0.20 x 0.20 mm
Theta range for data collection	2.29 to 28.33 deg.
Limiting indices	-15<=h<=14, -11<=k<=9, -25<=l<=25
Reflections collected / unique	16665 / 4556 [R(int) = 0.0582]
Completeness to theta = 28.33	99.6 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4556 / 0 / 226

Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0435, wR2 = 0.0978
R indices (all data)	R1 = 0.0757, wR2 = 0.1113
Largest diff. peak and hole	0.774 and -0.616 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 1503850. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ru(1)	7272(1)	1997(1)	792(1)	30(1)
Cl(3)	7333(1)	-855(1)	1004(1)	51(1)
N(1)	8905(3)	2197(5)	1473(2)	53(1)
C(5)	9811(4)	2995(5)	1263(2)	40(1)
C(17)	5279(3)	1994(5)	517(2)	37(1)
O(1)	9683(3)	3534(4)	565(2)	50(1)
C(2)	10241(5)	2008(6)	2627(3)	65(2)
C(11)	8318(3)	1591(4)	56(2)	22(1)
C(15)	6475(3)	3624(5)	1435(2)	37(1)
C(13)	6500(3)	4092(5)	187(2)	40(1)
C(18)	5645(4)	2844(5)	3(2)	41(1)

C(16)	5693(3)	2339(5)	1247(2)	36(1)
C(1)	9165(4)	1685(5)	2177(2)	50(1)
C(6)	9277(4)	2459(5)	44(2)	41(1)
C(10)	7963(4)	566(5)	-484(2)	49(1)
C(9)	8510(4)	415(6)	-1038(2)	53(1)
C(7)	9878(4)	2355(6)	-492(3)	53(1)
C(8)	9492(4)	1315(6)	-1038(2)	55(1)
C(4)	10878(4)	3338(6)	1705(3)	54(1)
C(3)	11099(4)	2844(6)	2397(3)	65(2)
C(19)	5224(3)	1388(5)	1797(2)	39(1)
C(14)	6889(4)	4506(5)	905(2)	39(1)
C(20)	4108(4)	2189(6)	1907(3)	61(1)
C(12)	6946(4)	4974(6)	-370(2)	60(1)
C(21)	6100(4)	1165(8)	2491(3)	73(2)

Table 3. Bond lengths [A] and angles [deg] for 1503850.

Ru(1)-N(1)	2.067(4)
Ru(1)-C(11)	2.099(3)
Ru(1)-C(14)	2.165(4)
Ru(1)-C(15)	2.185(4)

Ru(1)-C(13)	2.187(4)
Ru(1)-C(16)	2.224(4)
Ru(1)-C(17)	2.258(4)
Ru(1)-C(18)	2.266(4)
Ru(1)-Cl(3)	2.4174(12)
N(1)-C(5)	1.382(6)
N(1)-C(1)	1.398(6)
C(5)-C(4)	1.373(6)
C(5)-O(1)	1.405(5)
C(17)-C(18)	1.367(6)
C(17)-C(16)	1.420(5)
C(17)-H(17A)	0.9800
O(1)-C(6)	1.356(5)
C(2)-C(3)	1.371(8)
C(2)-C(1)	1.385(6)
C(2)-H(2A)	0.9300
C(11)-C(6)	1.335(5)
C(11)-C(10)	1.346(5)
C(15)-C(16)	1.402(5)
C(15)-C(14)	1.433(5)
C(15)-H(15A)	0.9800

C(13)-C(14)	1.410(5)
C(13)-C(18)	1.431(6)
C(13)-C(12)	1.493(6)
C(18)-H(18A)	0.9800
C(16)-C(19)	1.525(5)
C(1)-H(1A)	0.9300
C(6)-C(7)	1.379(6)
C(10)-C(9)	1.371(6)
C(10)-H(10A)	0.9300
C(9)-C(8)	1.367(7)
C(9)-H(9A)	0.9300
C(7)-C(8)	1.367(7)
C(7)-H(7A)	0.9300
C(8)-H(8A)	0.9300
C(4)-C(3)	1.373(7)
C(4)-H(4A)	0.9300
C(3)-H(3A)	0.9300
C(19)-C(20)	1.516(6)
C(19)-C(21)	1.511(6)
C(19)-H(19A)	0.9800
C(14)-H(14A)	0.9800

C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600

N(1)-Ru(1)-C(11)	81.96(14)
N(1)-Ru(1)-C(14)	92.13(15)
C(11)-Ru(1)-C(14)	112.87(14)
N(1)-Ru(1)-C(15)	91.68(15)
C(11)-Ru(1)-C(15)	150.70(14)
C(14)-Ru(1)-C(15)	38.46(14)
N(1)-Ru(1)-C(13)	119.23(16)
C(11)-Ru(1)-C(13)	89.68(14)
C(14)-Ru(1)-C(13)	37.80(14)
C(15)-Ru(1)-C(13)	68.50(15)
N(1)-Ru(1)-C(16)	117.20(15)

C(11)-Ru(1)-C(16)	160.83(14)
C(14)-Ru(1)-C(16)	68.24(15)
C(15)-Ru(1)-C(16)	37.08(14)
C(13)-Ru(1)-C(16)	80.47(15)
N(1)-Ru(1)-C(17)	154.14(16)
C(11)-Ru(1)-C(17)	123.90(13)
C(14)-Ru(1)-C(17)	78.59(15)
C(15)-Ru(1)-C(17)	66.02(14)
C(13)-Ru(1)-C(17)	66.26(15)
C(16)-Ru(1)-C(17)	36.94(14)
N(1)-Ru(1)-C(18)	156.63(17)
C(11)-Ru(1)-C(18)	96.49(14)
C(14)-Ru(1)-C(18)	66.84(15)
C(15)-Ru(1)-C(18)	78.24(15)
C(13)-Ru(1)-C(18)	37.43(15)
C(16)-Ru(1)-C(18)	65.80(15)
C(17)-Ru(1)-C(18)	35.18(15)
N(1)-Ru(1)-Cl(3)	88.98(11)
C(11)-Ru(1)-Cl(3)	87.50(9)
C(14)-Ru(1)-Cl(3)	159.56(12)
C(15)-Ru(1)-Cl(3)	121.11(11)

C(13)-Ru(1)-Cl(3)	150.95(12)
C(16)-Ru(1)-Cl(3)	93.16(11)
C(17)-Ru(1)-Cl(3)	91.68(11)
C(18)-Ru(1)-Cl(3)	114.32(12)
C(5)-N(1)-C(1)	115.0(4)
C(5)-N(1)-Ru(1)	120.1(3)
C(1)-N(1)-Ru(1)	124.7(3)
C(4)-C(5)-N(1)	123.9(4)
C(4)-C(5)-O(1)	115.1(4)
N(1)-C(5)-O(1)	121.0(4)
C(18)-C(17)-C(16)	122.1(4)
C(18)-C(17)-Ru(1)	72.7(2)
C(16)-C(17)-Ru(1)	70.2(2)
C(18)-C(17)-H(17A)	118.2
C(16)-C(17)-H(17A)	118.2
Ru(1)-C(17)-H(17A)	118.2
C(6)-O(1)-C(5)	116.9(3)
C(3)-C(2)-C(1)	120.9(5)
C(3)-C(2)-H(2A)	119.5
C(1)-C(2)-H(2A)	119.5
C(6)-C(11)-C(10)	116.5(4)

C(6)-C(11)-Ru(1)	122.4(3)
C(10)-C(11)-Ru(1)	120.6(3)
C(16)-C(15)-C(14)	120.6(4)
C(16)-C(15)-Ru(1)	73.0(2)
C(14)-C(15)-Ru(1)	70.0(2)
C(16)-C(15)-H(15A)	119.1
C(14)-C(15)-H(15A)	119.1
Ru(1)-C(15)-H(15A)	119.1
C(14)-C(13)-C(18)	118.6(4)
C(14)-C(13)-C(12)	120.5(4)
C(18)-C(13)-C(12)	120.9(4)
C(14)-C(13)-Ru(1)	70.3(2)
C(18)-C(13)-Ru(1)	74.3(2)
C(12)-C(13)-Ru(1)	128.1(3)
C(17)-C(18)-C(13)	120.5(4)
C(17)-C(18)-Ru(1)	72.1(2)
C(13)-C(18)-Ru(1)	68.3(2)
C(17)-C(18)-H(18A)	118.7
C(13)-C(18)-H(18A)	118.7
Ru(1)-C(18)-H(18A)	118.7
C(15)-C(16)-C(17)	118.1(4)

C(15)-C(16)-C(19)	121.9(4)
C(17)-C(16)-C(19)	119.8(4)
C(15)-C(16)-Ru(1)	70.0(2)
C(17)-C(16)-Ru(1)	72.8(2)
C(19)-C(16)-Ru(1)	131.7(3)
C(2)-C(1)-N(1)	121.8(5)
C(2)-C(1)-H(1A)	119.1
N(1)-C(1)-H(1A)	119.1
C(11)-C(6)-O(1)	120.1(4)
C(11)-C(6)-C(7)	122.9(4)
O(1)-C(6)-C(7)	117.0(4)
C(11)-C(10)-C(9)	123.7(4)
C(11)-C(10)-H(10A)	118.2
C(9)-C(10)-H(10A)	118.2
C(8)-C(9)-C(10)	118.8(4)
C(8)-C(9)-H(9A)	120.6
C(10)-C(9)-H(9A)	120.6
C(8)-C(7)-C(6)	119.5(5)
C(8)-C(7)-H(7A)	120.3
C(6)-C(7)-H(7A)	120.3
C(9)-C(8)-C(7)	118.7(4)

C(9)-C(8)-H(8A)	120.7
C(7)-C(8)-H(8A)	120.7
C(3)-C(4)-C(5)	119.7(5)
C(3)-C(4)-H(4A)	120.1
C(5)-C(4)-H(4A)	120.1
C(4)-C(3)-C(2)	118.7(4)
C(4)-C(3)-H(3A)	120.7
C(2)-C(3)-H(3A)	120.7
C(20)-C(19)-C(21)	110.9(4)
C(20)-C(19)-C(16)	108.6(3)
C(21)-C(19)-C(16)	114.5(4)
C(20)-C(19)-H(19A)	107.5
C(21)-C(19)-H(19A)	107.5
C(16)-C(19)-H(19A)	107.5
C(13)-C(14)-C(15)	119.9(4)
C(13)-C(14)-Ru(1)	71.9(2)
C(15)-C(14)-Ru(1)	71.5(2)
C(13)-C(14)-H(14A)	119.6
C(15)-C(14)-H(14A)	119.6
Ru(1)-C(14)-H(14A)	119.6
C(19)-C(20)-H(20A)	109.5

C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(13)-C(12)-H(12A)	109.5
C(13)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(13)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(19)-C(21)-H(21A)	109.5
C(19)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(19)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 1503850. The anisotropic

displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Ru(1)	27(1)	30(1)	32(1)	0(1)	4(1)	1(1)
Cl(3)	48(1)	32(1)	73(1)	6(1)	14(1)	3(1)
N(1)	49(2)	54(3)	52(2)	-6(2)	4(2)	7(2)
C(5)	32(2)	39(2)	49(3)	-14(2)	8(2)	2(2)
C(17)	28(2)	42(2)	41(2)	-9(2)	4(2)	-2(2)
O(1)	52(2)	48(2)	51(2)	-9(2)	16(2)	-19(2)
C(2)	69(4)	70(4)	43(3)	-4(3)	-16(3)	21(3)
C(11)	21(2)	24(2)	21(2)	-5(1)	4(1)	3(1)
C(15)	38(2)	33(2)	38(2)	-3(2)	6(2)	4(2)
C(13)	38(2)	45(3)	40(2)	12(2)	12(2)	13(2)
C(18)	35(2)	60(3)	26(2)	-2(2)	1(2)	10(2)
C(16)	31(2)	37(2)	39(2)	2(2)	7(2)	4(2)
C(1)	50(3)	54(3)	40(3)	10(2)	-1(2)	6(2)
C(6)	41(2)	46(2)	34(2)	0(2)	7(2)	7(2)
C(10)	44(3)	47(3)	56(3)	-7(2)	10(2)	4(2)
C(9)	59(3)	55(3)	42(3)	-11(2)	8(2)	10(2)
C(7)	50(3)	61(3)	54(3)	0(2)	21(2)	-1(2)

C(8)	59(3)	69(3)	43(3)	-3(2)	23(2)	11(3)
C(4)	33(2)	58(3)	70(3)	-24(3)	8(2)	-4(2)
C(3)	42(3)	72(4)	69(4)	-30(3)	-14(3)	7(3)
C(19)	38(2)	39(2)	41(2)	5(2)	14(2)	-2(2)
C(14)	37(2)	31(2)	50(3)	7(2)	12(2)	3(2)
C(20)	51(3)	73(4)	65(3)	17(3)	29(3)	7(3)
C(12)	63(3)	63(3)	59(3)	25(3)	23(2)	11(3)
C(21)	53(3)	105(5)	61(3)	36(3)	13(3)	-3(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 1503850.

	x	y	z	U(eq)
H(17A)	4873	975	387	45
H(2A)	10384	1654	3092	78
H(15A)	6861	3779	1932	44
H(18A)	5487	2410	-478	50
H(1A)	8600	1112	2346	60
H(10A)	7310	-75	-481	59
H(9A)	8218	-287	-1407	63

H(7A)	10540	2986	-483	64
H(8A)	9889	1222	-1403	66
H(4A)	11449	3902	1537	65
H(3A)	11817	3072	2703	78
H(19A)	5006	323	1599	46
H(14A)	7540	5268	1046	47
H(20A)	3565	2320	1459	91
H(20B)	4299	3217	2122	91
H(20C)	3752	1535	2209	91
H(12A)	6424	5846	-542	90
H(12B)	6979	4260	-753	90
H(12C)	7721	5382	-174	90
H(21A)	6801	665	2409	109
H(21B)	5759	502	2797	109
H(21C)	6299	2189	2710	109

Table 6. Torsion angles [deg] for 1503850.

C(11)-Ru(1)-N(1)-C(5)	41.0(3)
C(14)-Ru(1)-N(1)-C(5)	-71.8(3)
C(15)-Ru(1)-N(1)-C(5)	-110.3(3)
C(13)-Ru(1)-N(1)-C(5)	-44.1(4)
C(16)-Ru(1)-N(1)-C(5)	-138.4(3)
C(17)-Ru(1)-N(1)-C(5)	-139.7(4)
C(18)-Ru(1)-N(1)-C(5)	-46.8(6)
Cl(3)-Ru(1)-N(1)-C(5)	128.6(3)
C(11)-Ru(1)-N(1)-C(1)	-144.5(4)
C(14)-Ru(1)-N(1)-C(1)	102.7(4)
C(15)-Ru(1)-N(1)-C(1)	64.3(4)
C(13)-Ru(1)-N(1)-C(1)	130.4(4)
C(16)-Ru(1)-N(1)-C(1)	36.2(4)
C(17)-Ru(1)-N(1)-C(1)	34.9(6)
C(18)-Ru(1)-N(1)-C(1)	127.8(4)
Cl(3)-Ru(1)-N(1)-C(1)	-56.8(4)
C(1)-N(1)-C(5)-C(4)	-2.6(6)
Ru(1)-N(1)-C(5)-C(4)	172.5(3)
C(1)-N(1)-C(5)-O(1)	178.1(4)
Ru(1)-N(1)-C(5)-O(1)	-6.8(5)

N(1)-Ru(1)-C(17)-C(18)	136.6(4)
C(11)-Ru(1)-C(17)-C(18)	-44.2(3)
C(14)-Ru(1)-C(17)-C(18)	65.8(3)
C(15)-Ru(1)-C(17)-C(18)	104.1(3)
C(13)-Ru(1)-C(17)-C(18)	28.2(2)
C(16)-Ru(1)-C(17)-C(18)	134.6(4)
Cl(3)-Ru(1)-C(17)-C(18)	-132.3(2)
N(1)-Ru(1)-C(17)-C(16)	1.9(5)
C(11)-Ru(1)-C(17)-C(16)	-178.9(2)
C(14)-Ru(1)-C(17)-C(16)	-68.9(2)
C(15)-Ru(1)-C(17)-C(16)	-30.5(2)
C(13)-Ru(1)-C(17)-C(16)	-106.5(3)
C(18)-Ru(1)-C(17)-C(16)	-134.6(4)
Cl(3)-Ru(1)-C(17)-C(16)	93.0(2)
C(4)-C(5)-O(1)-C(6)	130.9(4)
N(1)-C(5)-O(1)-C(6)	-49.7(5)
N(1)-Ru(1)-C(11)-C(6)	-43.1(3)
C(14)-Ru(1)-C(11)-C(6)	45.8(3)
C(15)-Ru(1)-C(11)-C(6)	35.8(5)
C(13)-Ru(1)-C(11)-C(6)	76.5(3)
C(16)-Ru(1)-C(11)-C(6)	135.1(4)

C(17)-Ru(1)-C(11)-C(6)	137.2(3)
C(18)-Ru(1)-C(11)-C(6)	113.4(3)
Cl(3)-Ru(1)-C(11)-C(6)	-132.4(3)
N(1)-Ru(1)-C(11)-C(10)	145.4(3)
C(14)-Ru(1)-C(11)-C(10)	-125.7(3)
C(15)-Ru(1)-C(11)-C(10)	-135.7(3)
C(13)-Ru(1)-C(11)-C(10)	-95.0(3)
C(16)-Ru(1)-C(11)-C(10)	-36.4(6)
C(17)-Ru(1)-C(11)-C(10)	-34.3(4)
C(18)-Ru(1)-C(11)-C(10)	-58.2(3)
Cl(3)-Ru(1)-C(11)-C(10)	56.0(3)
N(1)-Ru(1)-C(15)-C(16)	-136.0(2)
C(11)-Ru(1)-C(15)-C(16)	147.5(3)
C(14)-Ru(1)-C(15)-C(16)	132.7(3)
C(13)-Ru(1)-C(15)-C(16)	103.1(3)
C(17)-Ru(1)-C(15)-C(16)	30.4(2)
C(18)-Ru(1)-C(15)-C(16)	65.2(2)
Cl(3)-Ru(1)-C(15)-C(16)	-46.2(3)
N(1)-Ru(1)-C(15)-C(14)	91.3(2)
C(11)-Ru(1)-C(15)-C(14)	14.8(4)
C(13)-Ru(1)-C(15)-C(14)	-29.6(2)

C(16)-Ru(1)-C(15)-C(14)	-132.7(3)
C(17)-Ru(1)-C(15)-C(14)	-102.2(3)
C(18)-Ru(1)-C(15)-C(14)	-67.4(2)
Cl(3)-Ru(1)-C(15)-C(14)	-178.87(19)
N(1)-Ru(1)-C(13)-C(14)	-49.3(3)
C(11)-Ru(1)-C(13)-C(14)	-129.9(2)
C(15)-Ru(1)-C(13)-C(14)	30.1(2)
C(16)-Ru(1)-C(13)-C(14)	66.6(2)
C(17)-Ru(1)-C(13)-C(14)	102.4(3)
C(18)-Ru(1)-C(13)-C(14)	129.0(4)
Cl(3)-Ru(1)-C(13)-C(14)	145.8(2)
N(1)-Ru(1)-C(13)-C(18)	-178.3(2)
C(11)-Ru(1)-C(13)-C(18)	101.1(2)
C(14)-Ru(1)-C(13)-C(18)	-129.0(4)
C(15)-Ru(1)-C(13)-C(18)	-98.9(3)
C(16)-Ru(1)-C(13)-C(18)	-62.3(2)
C(17)-Ru(1)-C(13)-C(18)	-26.6(2)
Cl(3)-Ru(1)-C(13)-C(18)	16.9(4)
N(1)-Ru(1)-C(13)-C(12)	64.6(4)
C(11)-Ru(1)-C(13)-C(12)	-16.0(4)
C(14)-Ru(1)-C(13)-C(12)	113.9(5)

C(15)-Ru(1)-C(13)-C(12)	143.9(4)
C(16)-Ru(1)-C(13)-C(12)	-179.5(4)
C(17)-Ru(1)-C(13)-C(12)	-143.7(4)
C(18)-Ru(1)-C(13)-C(12)	-117.2(5)
Cl(3)-Ru(1)-C(13)-C(12)	-100.3(4)
C(16)-C(17)-C(18)-C(13)	2.2(6)
Ru(1)-C(17)-C(18)-C(13)	-50.0(3)
C(16)-C(17)-C(18)-Ru(1)	52.2(4)
C(14)-C(13)-C(18)-C(17)	-4.8(6)
C(12)-C(13)-C(18)-C(17)	177.1(4)
Ru(1)-C(13)-C(18)-C(17)	51.7(4)
C(14)-C(13)-C(18)-Ru(1)	-56.5(3)
C(12)-C(13)-C(18)-Ru(1)	125.4(4)
N(1)-Ru(1)-C(18)-C(17)	-130.9(4)
C(11)-Ru(1)-C(18)-C(17)	144.4(2)
C(14)-Ru(1)-C(18)-C(17)	-103.5(3)
C(15)-Ru(1)-C(18)-C(17)	-64.8(3)
C(13)-Ru(1)-C(18)-C(17)	-134.7(4)
C(16)-Ru(1)-C(18)-C(17)	-28.0(2)
Cl(3)-Ru(1)-C(18)-C(17)	54.2(3)
N(1)-Ru(1)-C(18)-C(13)	3.8(5)

C(11)-Ru(1)-C(18)-C(13)	-80.9(2)
C(14)-Ru(1)-C(18)-C(13)	31.2(2)
C(15)-Ru(1)-C(18)-C(13)	69.9(3)
C(16)-Ru(1)-C(18)-C(13)	106.8(3)
C(17)-Ru(1)-C(18)-C(13)	134.7(4)
Cl(3)-Ru(1)-C(18)-C(13)	-171.1(2)
C(14)-C(15)-C(16)-C(17)	-3.1(6)
Ru(1)-C(15)-C(16)-C(17)	-56.5(3)
C(14)-C(15)-C(16)-C(19)	-179.2(4)
Ru(1)-C(15)-C(16)-C(19)	127.4(4)
C(14)-C(15)-C(16)-Ru(1)	53.4(3)
C(18)-C(17)-C(16)-C(15)	1.8(6)
Ru(1)-C(17)-C(16)-C(15)	55.1(3)
C(18)-C(17)-C(16)-C(19)	178.0(4)
Ru(1)-C(17)-C(16)-C(19)	-128.7(4)
C(18)-C(17)-C(16)-Ru(1)	-53.3(4)
N(1)-Ru(1)-C(16)-C(15)	51.3(3)
C(11)-Ru(1)-C(16)-C(15)	-126.8(4)
C(14)-Ru(1)-C(16)-C(15)	-29.5(2)
C(13)-Ru(1)-C(16)-C(15)	-66.8(2)
C(17)-Ru(1)-C(16)-C(15)	-129.7(4)

C(18)-Ru(1)-C(16)-C(15)	-103.0(3)
Cl(3)-Ru(1)-C(16)-C(15)	141.8(2)
N(1)-Ru(1)-C(16)-C(17)	-179.1(2)
C(11)-Ru(1)-C(16)-C(17)	2.9(6)
C(14)-Ru(1)-C(16)-C(17)	100.2(3)
C(15)-Ru(1)-C(16)-C(17)	129.7(4)
C(13)-Ru(1)-C(16)-C(17)	62.9(3)
C(18)-Ru(1)-C(16)-C(17)	26.7(2)
Cl(3)-Ru(1)-C(16)-C(17)	-88.6(2)
N(1)-Ru(1)-C(16)-C(19)	-64.1(4)
C(11)-Ru(1)-C(16)-C(19)	117.9(5)
C(14)-Ru(1)-C(16)-C(19)	-144.9(4)
C(15)-Ru(1)-C(16)-C(19)	-115.4(5)
C(13)-Ru(1)-C(16)-C(19)	177.8(4)
C(17)-Ru(1)-C(16)-C(19)	115.0(5)
C(18)-Ru(1)-C(16)-C(19)	141.7(4)
Cl(3)-Ru(1)-C(16)-C(19)	26.4(4)
C(3)-C(2)-C(1)-N(1)	-0.2(7)
C(5)-N(1)-C(1)-C(2)	1.9(6)
Ru(1)-N(1)-C(1)-C(2)	-172.9(4)
C(10)-C(11)-C(6)-O(1)	179.2(4)

Ru(1)-C(11)-C(6)-O(1)	7.3(5)
C(10)-C(11)-C(6)-C(7)	1.0(6)
Ru(1)-C(11)-C(6)-C(7)	-170.8(3)
C(5)-O(1)-C(6)-C(11)	48.9(5)
C(5)-O(1)-C(6)-C(7)	-132.8(4)
C(6)-C(11)-C(10)-C(9)	-1.8(6)
Ru(1)-C(11)-C(10)-C(9)	170.2(3)
C(11)-C(10)-C(9)-C(8)	2.0(7)
C(11)-C(6)-C(7)-C(8)	-0.4(7)
O(1)-C(6)-C(7)-C(8)	-178.6(4)
C(10)-C(9)-C(8)-C(7)	-1.2(7)
C(6)-C(7)-C(8)-C(9)	0.5(7)
N(1)-C(5)-C(4)-C(3)	1.6(7)
O(1)-C(5)-C(4)-C(3)	-179.1(4)
C(5)-C(4)-C(3)-C(2)	0.3(7)
C(1)-C(2)-C(3)-C(4)	-0.9(8)
C(15)-C(16)-C(19)-C(20)	88.8(5)
C(17)-C(16)-C(19)-C(20)	-87.3(5)
Ru(1)-C(16)-C(19)-C(20)	179.6(3)
C(15)-C(16)-C(19)-C(21)	-35.7(6)
C(17)-C(16)-C(19)-C(21)	148.2(4)

Ru(1)-C(16)-C(19)-C(21)	55.1(6)
C(18)-C(13)-C(14)-C(15)	3.4(6)
C(12)-C(13)-C(14)-C(15)	-178.5(4)
Ru(1)-C(13)-C(14)-C(15)	-55.1(3)
C(18)-C(13)-C(14)-Ru(1)	58.5(3)
C(12)-C(13)-C(14)-Ru(1)	-123.4(4)
C(16)-C(15)-C(14)-C(13)	0.5(6)
Ru(1)-C(15)-C(14)-C(13)	55.3(3)
C(16)-C(15)-C(14)-Ru(1)	-54.8(3)
N(1)-Ru(1)-C(14)-C(13)	138.5(3)
C(11)-Ru(1)-C(14)-C(13)	56.4(3)
C(15)-Ru(1)-C(14)-C(13)	-131.4(4)
C(16)-Ru(1)-C(14)-C(13)	-102.9(3)
C(17)-Ru(1)-C(14)-C(13)	-65.8(2)
C(18)-Ru(1)-C(14)-C(13)	-30.9(2)
Cl(3)-Ru(1)-C(14)-C(13)	-128.7(3)
N(1)-Ru(1)-C(14)-C(15)	-90.0(2)
C(11)-Ru(1)-C(14)-C(15)	-172.2(2)
C(13)-Ru(1)-C(14)-C(15)	131.4(4)
C(16)-Ru(1)-C(14)-C(15)	28.5(2)
C(17)-Ru(1)-C(14)-C(15)	65.6(2)

C(18)-Ru(1)-C(14)-C(15)	100.5(3)
Cl(3)-Ru(1)-C(14)-C(15)	2.8(5)

Symmetry transformations used to generate equivalent atoms: