

Supporting Information

Rh(III)-Catalyzed Cascade C–H Activation/Amination Enables the Synthesis of 1,2-Disubstituted Benzimidazoles from Amidines and Arynes

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1. General Information

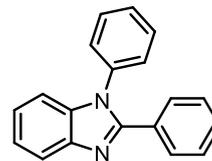
Unless otherwise noted, all the rhodium-catalyzed reactions were carried out under air condition. The commercially available chemicals and solvents were used as received without further purification. Amidines were obtained from corresponding nitriles and amines.^{S1} The reactions were monitored by TLC using UV-light or by staining with iodine. Column chromatography was performed on silica gel (200-300 mesh). Single-crystal X-ray data in this work were collected on an Agilent Technologies SuperNova Single Crystal Diffractometer at different temperatures equipped with graphite-monochromatic Mo K α or Cu K α radiation ($\lambda = 0.71073 \text{ \AA}$ or 1.54184 \AA). The structures were solved by SHELXS (direct methods) and refined by SHELXL (full matrix least-squares techniques) in the Olex2 package.^{S2} All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. ¹H, ¹³C, and ¹⁹F NMR were recorded on a 600 or 400 MHz Bruker NMR spectrometer in CDCl₃ (7.26 ppm for ¹H and 77.16 ppm for ¹³C) using tetramethylsilane (TMS) as the internal standard (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet).

2. Procedure for Rh(III)-Catalyzed Cascade Reactions

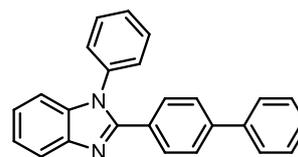
A mixture of amidines **1a-1u** (0.125 mmol), 2-(trimethylsilyl)phenyltrifluoromethanesulfonate **2a** (0.376 mmol), [Cp* RhCl_2]₂ (2.5 mol%), CsF (2 equiv, 38 mg), Cu(OAc)₂ (0.25 mmol, 45.4 mmol), Cs₂CO₃ (20 mol%, 8.2 mg), DMF (4 mL) was stirred at 110 °C for 48 h. After cooling the reaction to room temperature, the solvent was removed under vacuum and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate = 10:1-4:1 to afford desired products.

3. Characterization of Products

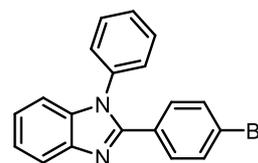
1,2-diphenyl-1H-benzo[d]imidazole (3aa). ^1H NMR (400 MHz, CDCl_3) δ = 7.94 – 7.86 (m, 1H), 7.60 – 7.54 (m, 2H), 7.53 – 7.44 (m, 3H), 7.39 – 7.29 (m, 6H), 7.29 – 7.23 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ = 152.34, 150.60, 142.84, 137.15, 136.94, 129.86, 129.46, 128.57, 128.50, 128.30, 127.40, 123.37, 123.03, 119.81, 110.47.



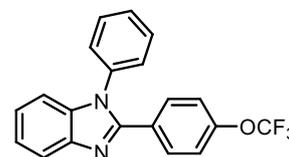
2-([1,1'-biphenyl]-4-yl)-1-phenyl-1H-benzo[d]imidazole (3ab). ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.2 Hz, 2H), 7.61 – 7.46 (m, 7H), 7.42 (t, J = 7.5 Hz, 2H), 7.35 (t, J = 7.6 Hz, 4H), 7.30 – 7.22 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 152.12, 143.08, 142.04, 140.12, 137.36, 137.09, 129.97, 129.84, 128.86, 128.79, 128.66, 127.77, 127.51, 127.07, 126.94, 123.39, 123.06, 119.85, 110.48.



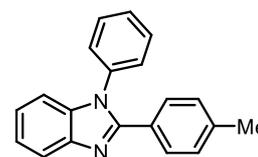
2-(4-bromophenyl)-1-phenyl-1H-benzo[d]imidazole (3ac). ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, J = 8.0 Hz, 1H), 7.51 (t, J = 7.0 Hz, 3H), 7.44 (s, 4H), 7.38 – 7.20 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.26, 142.92, 137.26, 136.76, 131.60, 130.88, 130.06, 128.91, 128.82, 127.40, 124.09, 123.63, 123.21, 119.93, 110.53.



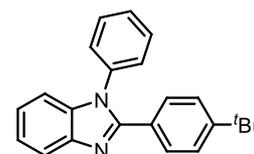
1-phenyl-2-(4-(trifluoromethoxy)phenyl)-1H-benzo[d]imidazole (3ad). ^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, J = 7.9 Hz, 1H), 7.61 (d, J = 8.5 Hz, 2H), 7.52 (t, J = 7.0 Hz, 3H), 7.40 – 7.20 (m, 5H), 7.15 (d, J = 8.3 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.92, 149.97, 142.90, 137.29, 136.73, 130.96, 130.09, 128.89, 128.57, 127.42, 123.67, 123.23, 120.53, 120.34 (d, J = 258.1 Hz), 119.95, 110.56.



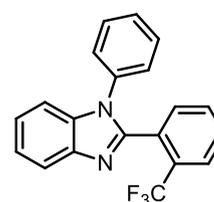
1-phenyl-2-(p-tolyl)-1H-benzo[d]imidazole (3ae). ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, J = 8.0 Hz, 1H), 7.54 – 7.42 (m, 5H), 7.36 – 7.29 (m, 3H), 7.28 – 7.20 (m, 2H), 7.11 (d, J = 8.0 Hz, 2H), 2.34 (s, 3H), 1.69 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 152.59, 143.02, 139.59, 137.24, 137.16, 129.84, 129.35, 129.04, 128.49, 127.47, 127.06, 123.15, 122.90, 119.73, 110.37, 21.38.



2-(4-(tert-butyl)phenyl)-1-phenyl-1H-benzo[d]imidazole (3af). ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, J = 8.0 Hz, 1H), 7.61 – 7.45 (m, 5H), 7.41 – 7.31 (m, 5H), 7.30 – 7.21 (m, 2H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 152.69, 152.46, 143.05, 137.36, 137.22, 129.87, 129.07, 128.54, 127.55, 126.98, 125.28, 123.12, 122.87, 119.72, 110.38, 34.76, 31.17. HRMS Calculated for $\text{C}_{23}\text{H}_{23}\text{N}_2^+$, 327.1861, found 327.1874.

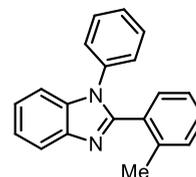


1-phenyl-2-(2-(trifluoromethyl)phenyl)-1H-benzo[d]imidazole (3ag). ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, J = 7.8 Hz, 1H), 7.72 (d, J = 7.5

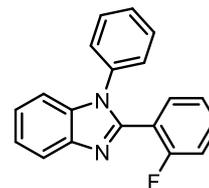


Hz, 1H), 7.56 – 7.43 (m, 2H), 7.42 – 7.28 (m, 7H), 7.24 (t, $J = 6.7$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.00, 142.86, 135.99, 135.83, 132.59, 131.14, 130.37 (q, $J = 31.1$ Hz), 129.78, 129.55, 129.25 (dd, $J = 4.1, 2.0$ Hz), 128.33, 126.96, 126.75 (q, $J = 4.8$ Hz), 123.71, 123.58 (q, $J = 274.0$ Hz), 123.00, 120.36, 110.60, 77.40, 77.08, 76.76. ^{19}F NMR (376 MHz, CDCl_3) δ -63.10.

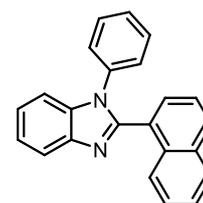
1-phenyl-2-(*o*-tolyl)-1H-benzo[d]imidazole (3ah). ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, $J = 8.0$ Hz, 1H), 7.43 – 7.24 (m, 8), 7.23 – 7.09 (m, 4H), 2.18 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 152.97, 143.07, 137.82, 136.38, 135.71, 130.94, 130.33, 130.16, 129.54, 129.46, 127.93, 126.55, 125.46, 123.28, 122.86, 120.04, 110.49, 20.06. HRMS Calculated for $\text{C}_{20}\text{H}_{17}\text{N}_2^+$, 285.1392, found 285.1402.



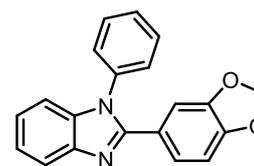
2-(2-fluorophenyl)-1-phenyl-1H-benzo[d]imidazole (3ai). ^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, $J = 8.0$ Hz, 1H), 7.53 (dtd, $J = 7.2, 5.0, 2.1$ Hz, 3H), 7.43 – 7.21 (m, 8H), 7.11 – 7.00 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.79, 162.39 (d, $J = 250.0$ Hz), 150.96, 142.85, 136.98 (d, $J = 60.8$ Hz), 132.05 (d, $J = 8.3$ Hz), 130.03, 129.92 (d, $J = 8.3$ Hz), 128.88, 127.39, 125.13, 125.10, 123.71, 123.22, 120.02, 116.44 (dd, $J = 22.4, 5.9$ Hz), 110.57.



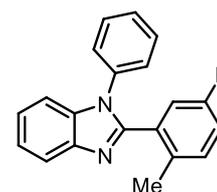
2-(naphthalen-1-yl)-1-phenyl-1H-benzo[d]imidazole (3aj). ^1H NMR (400 MHz, CDCl_3) δ 8.22 – 8.07 (m, 1H), 7.97 (d, $J = 7.5$ Hz, 1H), 7.85 (t, $J = 7.3$ Hz, 2H), 7.47 (p, $J = 6.4$ Hz, 2H), 7.40 (t, $J = 7.4$ Hz, 3H), 7.34 (dd, $J = 8.6, 6.5$ Hz, 2H), 7.28 (dt, $J = 15.0, 5.1$ Hz, 3H), 7.23 – 7.13 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.87, 149.98, 143.24, 136.46, 136.11, 133.55, 132.18, 129.99, 129.45, 128.24, 128.03, 127.71, 127.03, 126.65, 126.23, 125.87, 124.61, 123.48, 123.01, 120.18, 110.63. HRMS Calculated for $\text{C}_{23}\text{H}_{17}\text{N}_2^+$, 321.1392, found 321.1402.



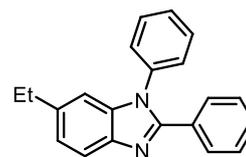
2-(benzo[d][1,3]dioxol-5-yl)-1-phenyl-1H-benzo[d]imidazole (3ak). ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, $J = 8.0$ Hz, 1H), 7.53 (ddd, $J = 8.4, 6.8, 2.2$ Hz, 3H), 7.42 – 7.19 (m, 5H), 7.16 – 7.02 (m, 2H), 6.75 (d, $J = 8.0$ Hz, 1H), 5.99 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 152.15, 148.71, 147.60, 142.87, 137.22, 137.03, 129.93, 128.62, 127.43, 124.12, 123.79, 123.18, 122.97, 119.64, 110.37, 109.69, 108.24, 101.39. HRMS Calculated for $\text{C}_{20}\text{H}_{15}\text{N}_2\text{O}_2^+$, 315.1134, found 315.1146.



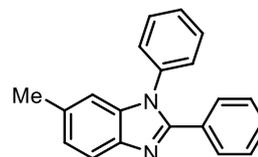
2-(5-fluoro-2-methylphenyl)-1-phenyl-1H-benzo[d]imidazole (3al). ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, $J = 7.9$ Hz, 1H), 7.45 – 7.29 (m, 6H), 7.22 (dd, $J = 5.3, 3.2$ Hz, 2H), 7.13 (dd, $J = 8.4, 5.7$ Hz, 1H), 7.07 – 6.92 (m, 2H), 2.13 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 160.41 (d, $J = 244.8$ Hz), 151.61, 151.59, 142.98, 136.08, 135.68, 133.61 (d, $J = 3.3$ Hz), 131.86, 131.78, 131.68 (d, $J = 8.0$ Hz), 129.61, 128.19, 126.47, 123.31 (d, $J = 53.1$ Hz), 120.17, 117.10 (dd, $J = 105.7, 21.7$ Hz), 110.56, 19.30. ^{19}F NMR (376 MHz, CDCl_3) δ -117.44. HRMS Calculated for $\text{C}_{20}\text{H}_{16}\text{FN}_2^+$, 303.1298, found 303.1306.



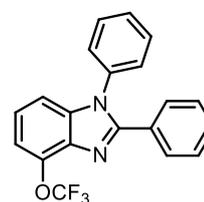
6-ethyl-1,2-diphenyl-1H-benzo[d]imidazole (4am). ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.58 (dd, *J* = 5.7, 2.4 Hz, 2H), 7.46 – 7.13 (m, 10H), 2.73 (q, *J* = 7.6 Hz, 2H), 1.30 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 152.43, 144.80, 142.95, 137.40, 134.50, 130.08, 129.47, 129.39, 129.24, 128.28, 127.23, 123.25, 122.91, 119.79, 110.60, 28.55, 15.35.



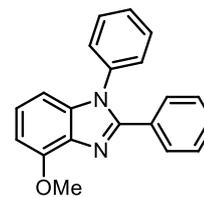
6-methyl-1,2-diphenyl-1H-benzo[d]imidazole (4an). ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.62 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.46 – 7.17 (m, 8H), 7.11 – 6.94 (m, 2H), 3.90 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 159.49, 152.51, 142.89, 137.62, 130.07, 129.64, 129.43, 129.38, 128.59, 128.31, 123.23, 122.87, 119.78, 115.01, 110.50, 55.57.



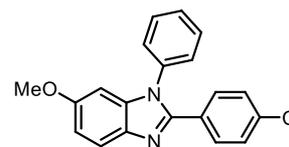
1,2-diphenyl-4-(trifluoromethoxy)-1H-benzo[d]imidazole (4ao). ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.42 – 7.22 (m, 10H). ¹³C NMR (101 MHz, CDCl₃) δ = 152.36, 148.80, 143.01, 136.94, 135.42, 129.69, 129.60, 129.45, 128.86, 128.47, 125.66, 123.62, 123.28, 122.21, 121.06, 120.38 (d, *J* = 258.3 Hz), 120.07, 110.18. ¹⁹F NMR (376 MHz, CDCl₃) δ -57.88. HRMS Calculated for C₂₀H₁₄F₃N₂O⁺, 355.1058, found 355.1072.



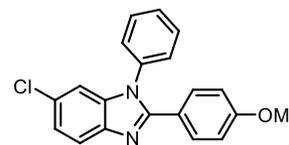
4-methoxy-1,2-diphenyl-1H-benzo[d]imidazole (4ap). ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 7.2 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.38 – 7.19 (m, 6H), 7.09 (dd, *J* = 13.5, 7.4 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 1H), 3.52 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 154.91, 153.28, 143.07, 137.27, 130.70, 130.37, 129.25, 129.16, 128.60, 128.13, 125.76, 123.04, 122.63, 121.18, 119.70, 112.63, 110.57, 55.47.



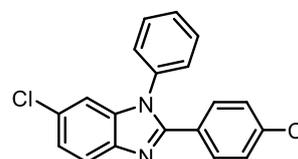
2-(4-chlorophenyl)-6-methoxy-1-phenyl-1H-benzo[d]imidazole (4aq). ¹H NMR (400 MHz, CDCl₃) δ = 7.87 (d, *J* = 7.9, 1H), 7.54 (d, *J* = 8.2, 2H), 7.38 – 7.12 (m, 8H), 7.02 (d, *J* = 8.4, 2H), 3.89 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 159.66, 153.70, 151.34, 142.80, 137.64, 135.60, 130.62, 129.35, 128.64, 128.57, 123.48, 123.05, 119.83, 115.16, 110.54, 55.60.



6-chloro-2-(4-methoxyphenyl)-1-phenyl-1H-benzo[d]imidazole (4ar). ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.49 (dd, *J* = 8.4, 2.5 Hz, 4H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.29 – 7.16 (m, 4H), 6.85 (d, *J* = 8.5 Hz, 2H), 3.82 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 160.67, 152.33, 143.06, 136.95, 135.74, 134.35, 130.93, 130.16, 128.72, 123.23, 123.10, 122.00, 119.74, 113.93, 110.05, 55.32.

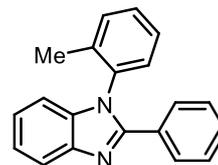


6-chloro-2-(4-chlorophenyl)-1-phenyl-1H-benzo[d]imidazole (4as). ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 4H), 7.40 – 7.14 (m, 7H). ¹³C NMR (101 MHz, CDCl₃) δ 151.13,

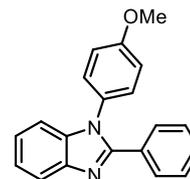


142.94, 136.99, 135.93, 135.29, 134.72, 130.66, 130.32, 128.82, 128.62, 128.15, 123.83, 123.41, 120.08, 110.26. HRMS Calculated for $C_{19}H_{13}Cl_2N_2^+$, 339.0456, found 339.0467.

2-phenyl-1-(o-tolyl)-1H-benzo[d]imidazole (4at). 1H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 2H), 7.54 – 7.44 (m, 3H), 7.39 – 7.29 (m, 5H), 7.22 – 7.14 (m, 2H), 7.12 (dd, $J = 7.6, 1.0$ Hz, 1H), 2.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.83, 142.37, 139.01, 137.19, 136.84, 134.63, 130.27, 130.03, 129.76, 129.60, 129.25, 128.38, 128.29, 127.41, 123.26, 123.23, 107.96, 16.87. HRMS Calculated for $C_{20}H_{17}N_2^+$, 285.1392, found 285.1399.



1-(4-methoxyphenyl)-2-phenyl-1H-benzo[d]imidazole (4au). 1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, $J = 8.8$ Hz, 1H), 7.51 (dd, $J = 15.6, 8.0$ Hz, 5H), 7.37 – 7.27 (m, 5H), 6.97 (dd, $J = 8.8, 2.3$ Hz, 1H), 6.70 (d, $J = 2.0$ Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.13, 151.69, 137.86, 137.52, 137.11, 130.11, 129.94, 129.22, 129.15, 128.56, 128.26, 127.41, 120.39, 112.24, 93.95, 55.91. HRMS Calculated for $C_{20}H_{17}N_2O^+$, 301.1341, found 301.1348.



4. References

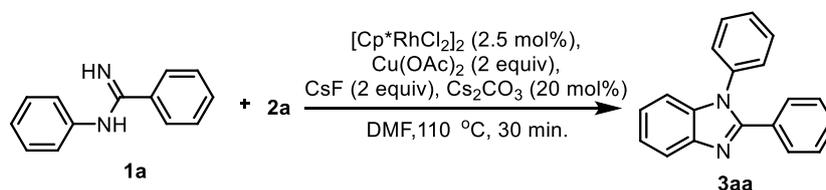
(S1) Brasche, G.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 1932–1934.

(S2) Sheldrick, G. M. *SHELXTL-97, Program for X-ray Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, **1997**.

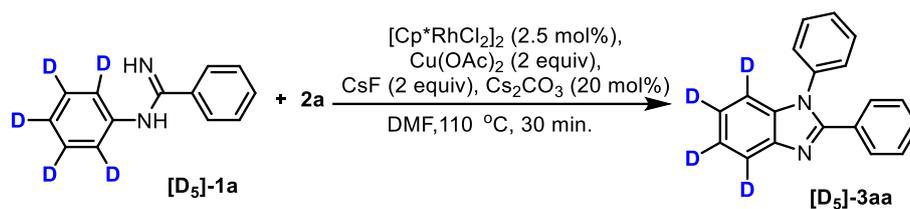
5. Procedures of mechanistic studies

5.1 Kinetic Isotope Study

5.1.1 In parallel experiments



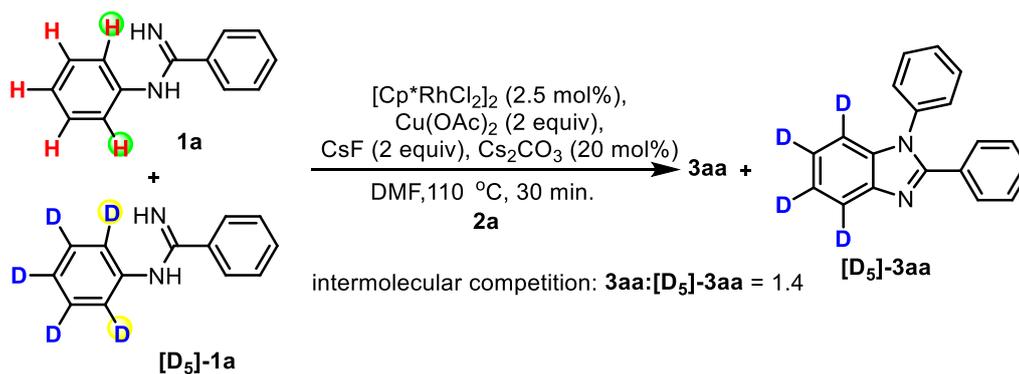
A mixture of amidines **1a** (0.125 mmol), 2-(trimethylsilyl)phenyltrifluoromethanesulfonate **2a** (0.376 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (2.5 mol%), CsF (2 equiv, 38 mg), $\text{Cu}(\text{OAc})_2$ (0.25 mmol, 45.4 mmol), Cs_2CO_3 (20 mol%, 8.2 mg), DMF (4 mL) was stirred at 110 °C for 30 min. After cooling the reaction to room temperature, the solvent was removed under vacuum and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate = 10:1-4:1 to afford desired product **3aa** (10.5 mg, 29.7% yield).



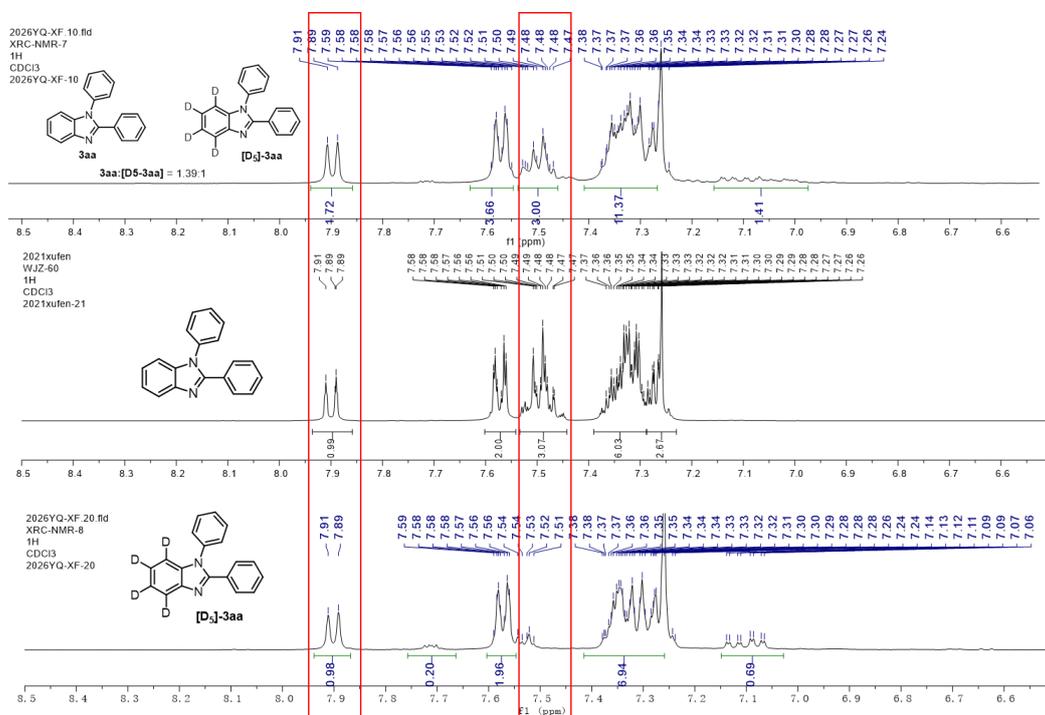
A mixture of amidines $[\text{D}_5]\text{-1a}$ (0.125 mmol), 2-(trimethylsilyl)phenyltrifluoromethanesulfonate **2a** (0.376 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (2.5 mol%), CsF (2 equiv, 38 mg), $\text{Cu}(\text{OAc})_2$ (0.25 mmol, 45.4 mmol), Cs_2CO_3 (20 mol%, 8.2 mg), DMF (4 mL) was stirred at 110 °C for 30 min. After cooling the reaction to room temperature, the solvent was removed under vacuum and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate = 10:1-4:1 to afford desired product $[\text{D}_5]\text{-3aa}$ (6.6 mg, 18.4% yield).

These two reactions were conducted at the same time in the same bath oil. Parallel competition:
 $\text{KIE} = \text{3aa}:[\text{D}_5]\text{-3aa} = 1.6$

5.1.2 In one-pot reactions

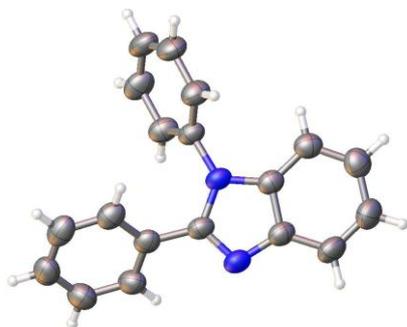


Without any particular precautions to extrude oxygen or moisture, a mixture of **1a** and **[D₅]-1a** (1:1 ratio), 2-(trimethylsilyl)phenyltrifluoromethane -sulfonate **2a** (0.376 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol%), CsF (2 equiv, 38 mg), $Cu(OAc)_2$ (0.25 mmol, 45.4 mmol), Cs_2CO_3 (20 mol%, 8.2 mg), DMF (4 mL) was stirred at 110 °C for 30 min. After cooling the reaction to room temperature, the solvent was removed under vacuum and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate = 10:1-4:1. KIE value ($k_H/k_D=1.4$) was determined by 1H NMR using CH_3I as the internal standard.

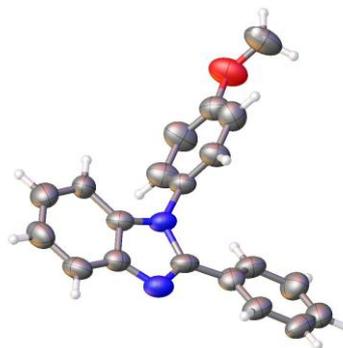


6. Single-Crystal X-Ray Crystallography

6.1 Crystal structures of targeted products (3aa and 4au) (C: black; H: gray; N: light blue). The displacement ellipsoids are drawn at the 30% probability.



3aa, CCDC: 2521462



4au, CCDC: 2522618

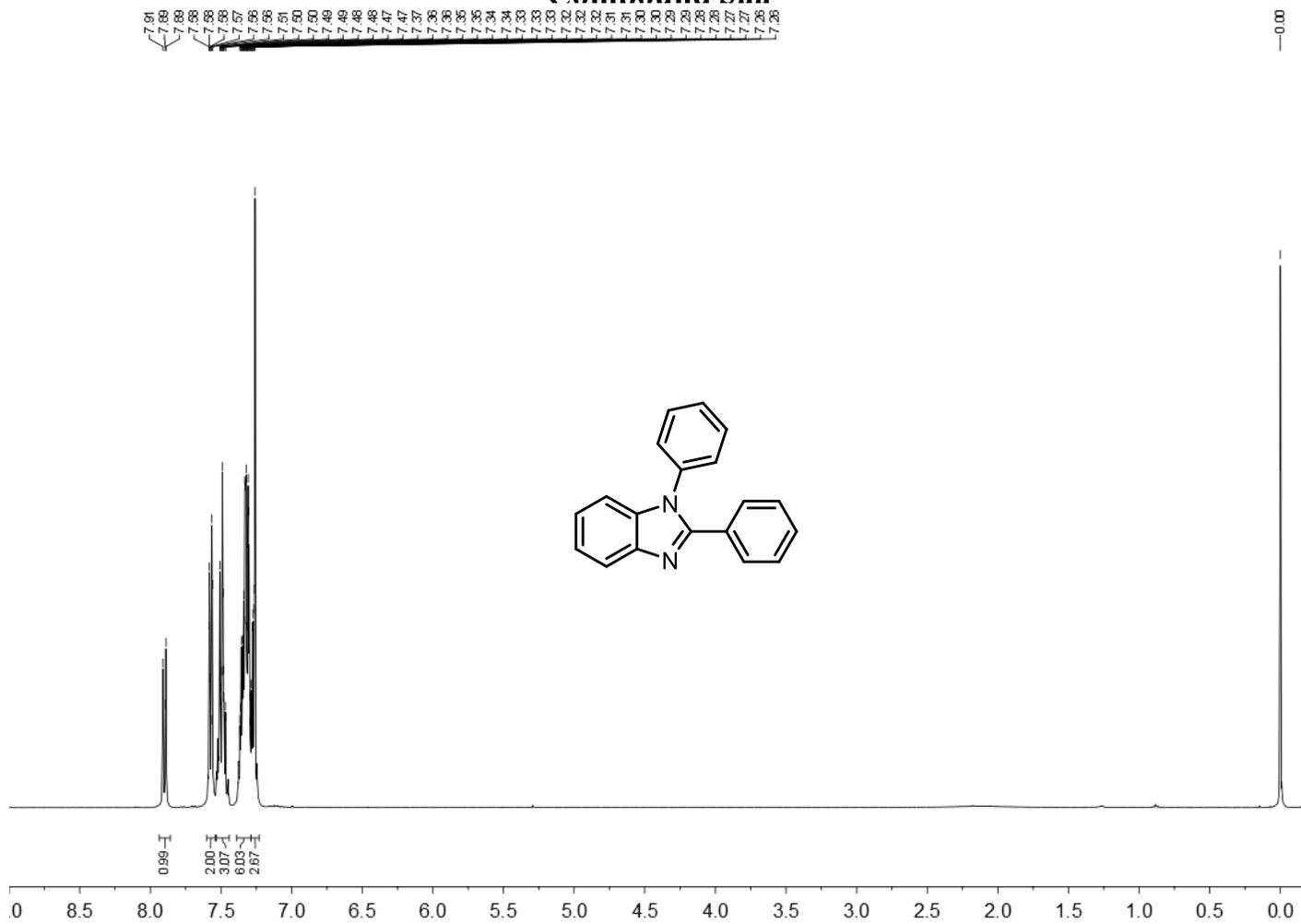
Table S1. Crystal data and structure refinement details for targeted product.

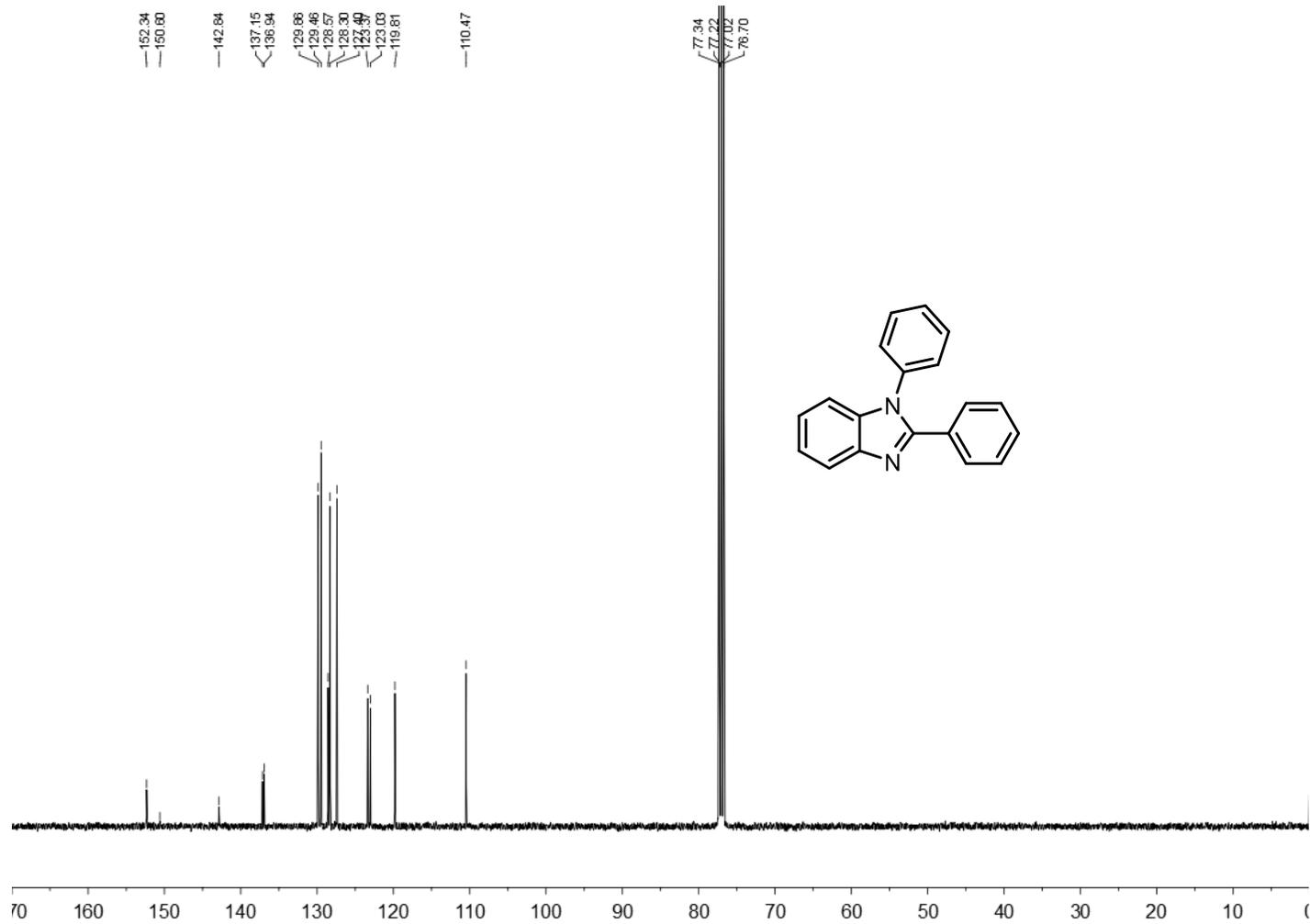
	3aa	4au
Empirical formula	C _{11.69} H _{8.62} N _{1.23}	CHNO
Formula weight	166.35	600.72
Crystal system	monoclinic	triclinic
Space group	C2/c	P-1
<i>a</i> / Å	10.2133(6)	6.2779(13)
<i>b</i> / Å	16.6796(9))	11.148(2)
<i>c</i> / Å	17.8803(12)	22.875(5)
α / °	90	90
β / °	105.687(7)	97.504(5)
γ / °	90	90
Volume / Å ³	2932.5(3)	1587.2(6)
<i>Z</i>	13	2
<i>D</i> / g cm ⁻³	1.225	1.257
μ / mm ⁻¹	0.073	0.077
F (000)	1136.0	634.0
<i>R</i> _{int}	0.0143	0.0392
Goodness-of-fit on <i>F</i> ²	1.181	1.116
<i>R</i> ₁ ^{<i>a</i>} / <i>wR</i> ₂ ^{<i>b</i>} [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0466, <i>wR</i> ₂ = 0.1636	<i>R</i> ₁ = 0.1327, <i>wR</i> ₂ = 0.3759
<i>R</i> ₁ ^{<i>a</i>} / <i>wR</i> ₂ ^{<i>b</i>} (all data)	<i>R</i> ₁ = 0.0633, <i>wR</i> ₂ = 0.1766	<i>R</i> ₁ = 0.1706, <i>wR</i> ₂ = 0.4017
CCDC number	2521462	2522618

^a $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^b $wR_2 = |\sum w(|F_o|^2 - |F_c|^2)|/\sum w(F_o^2)^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$. $P = (F_o^2 + 2F_c^2)/3$.

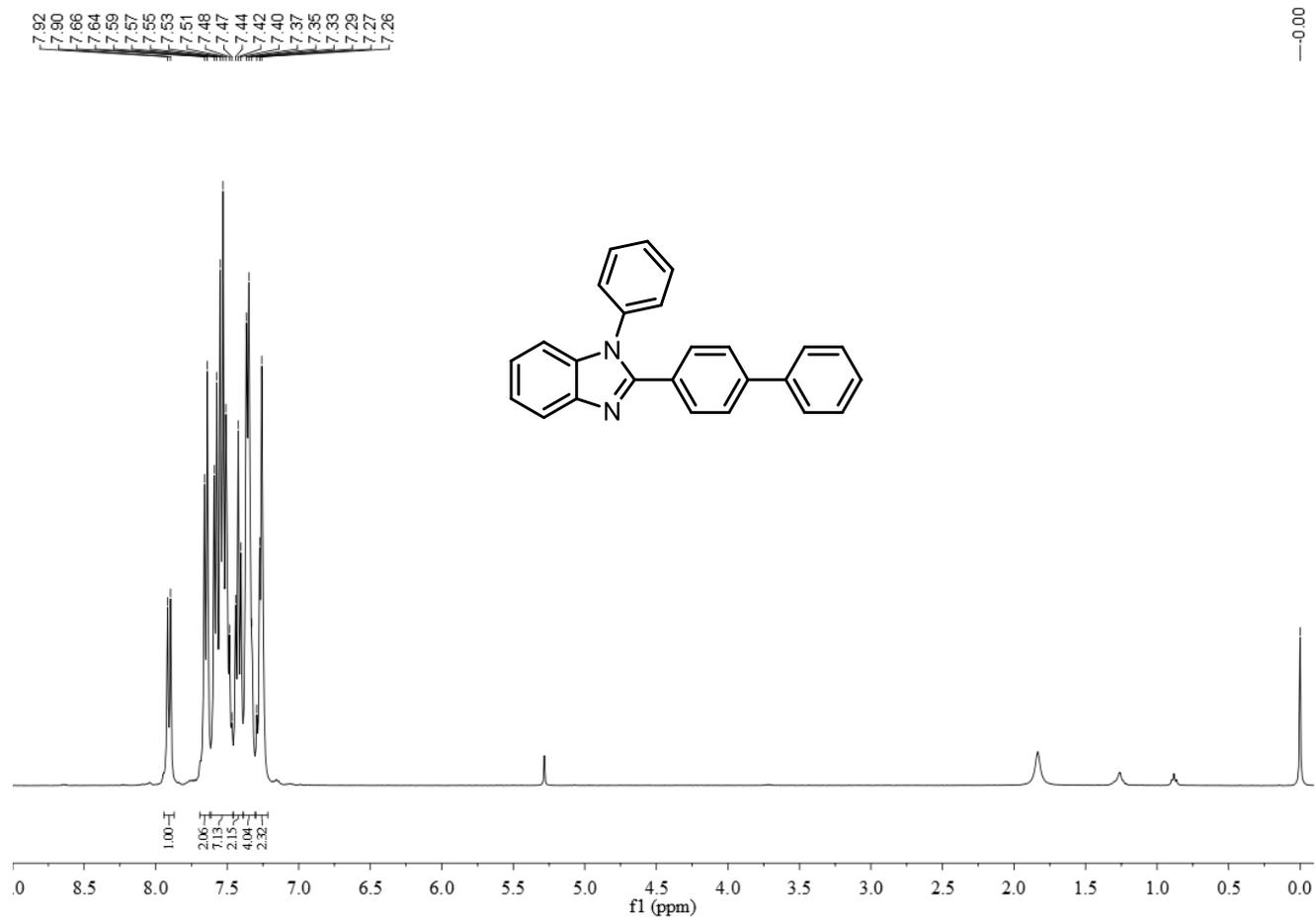
7. Copy of NMR (^1H , ^{13}C , ^{19}F) Spectra

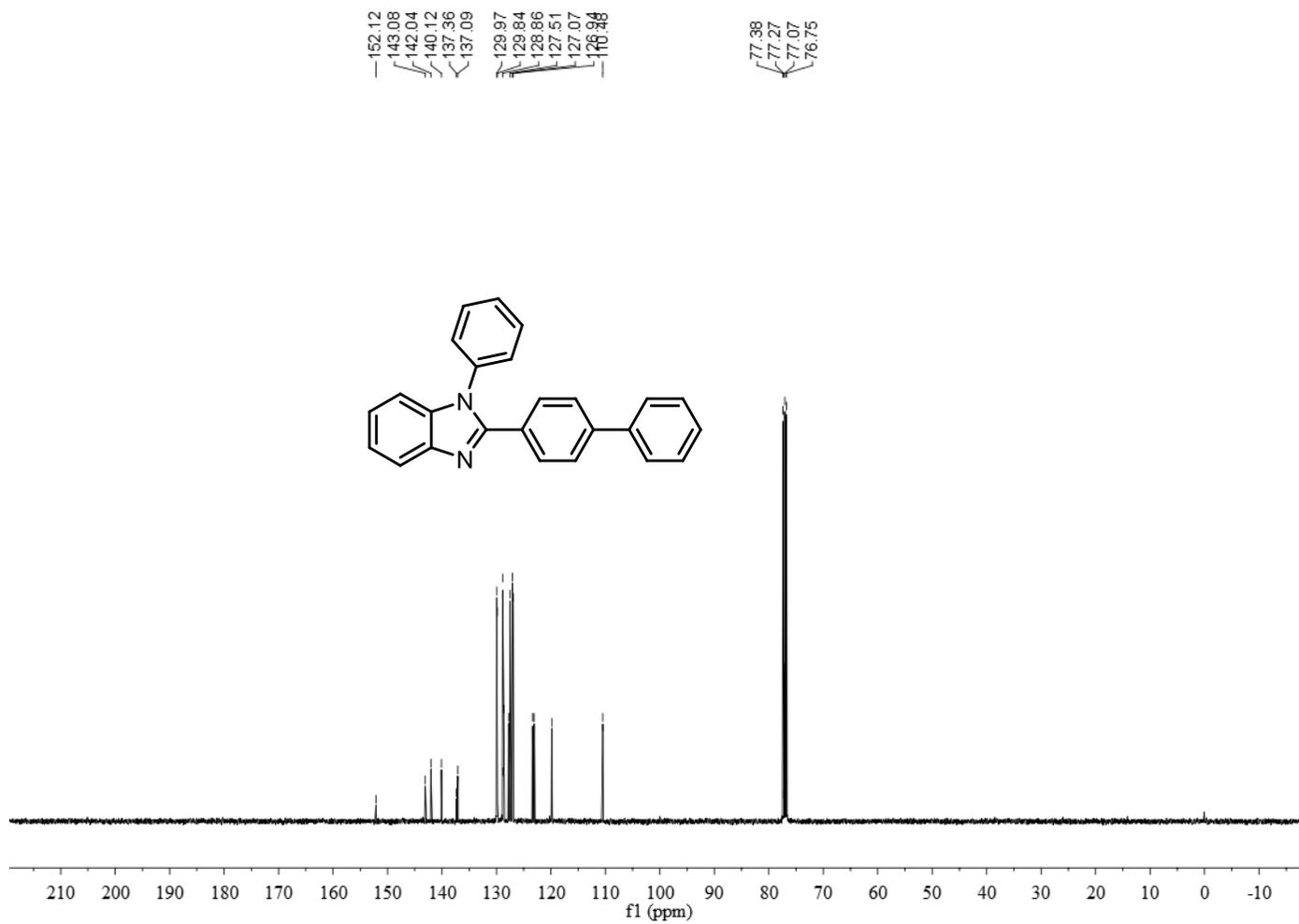
Compound 3aa



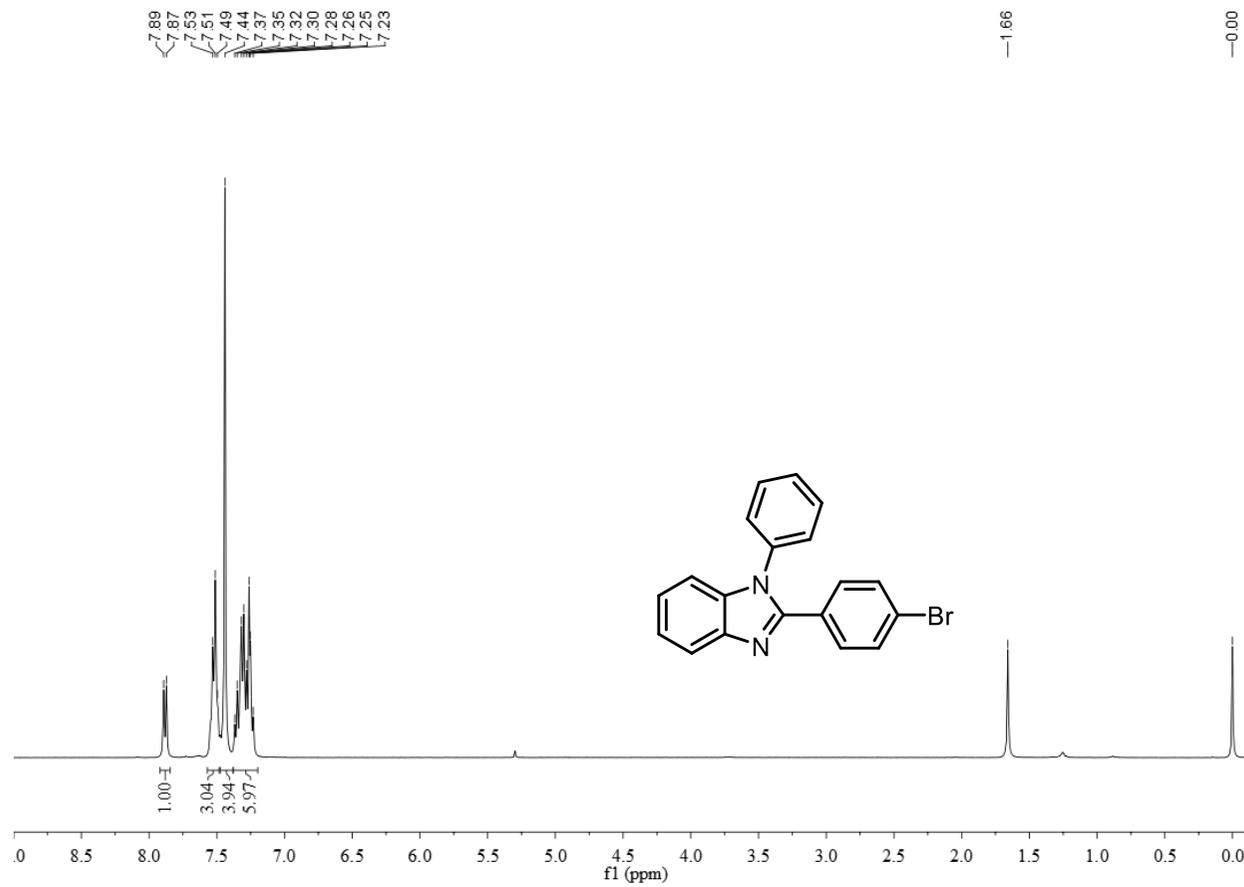


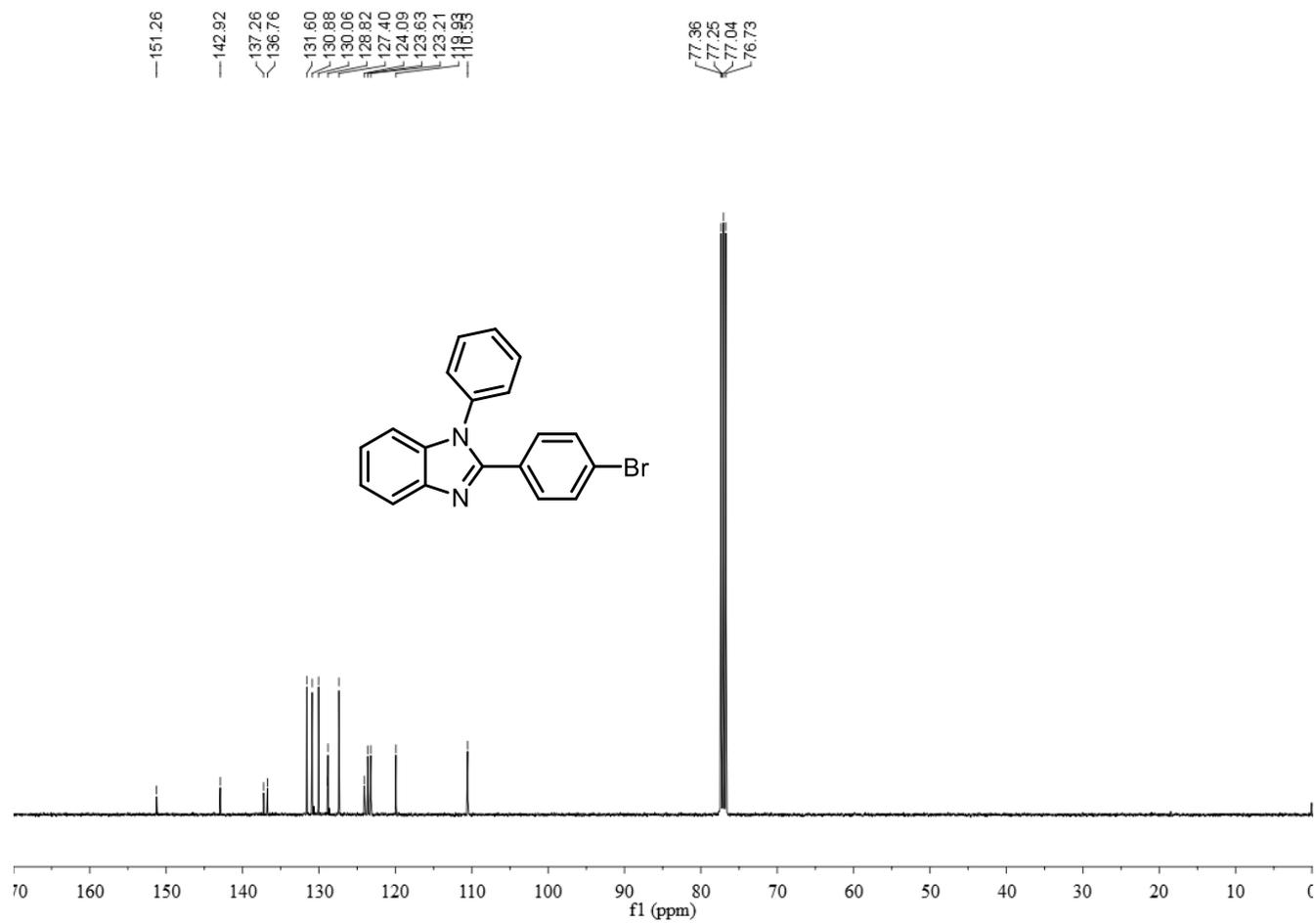
Compound 3ab



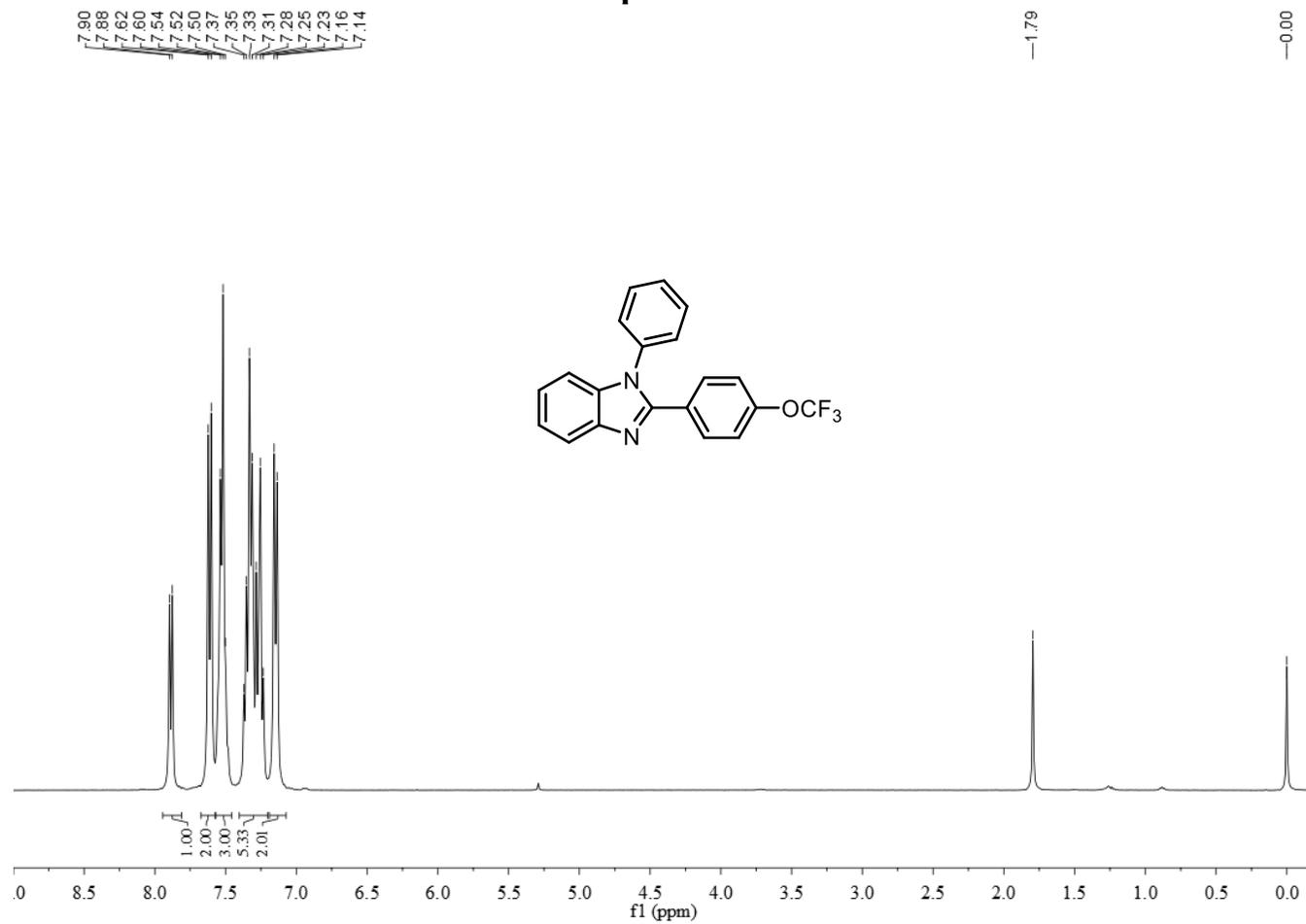


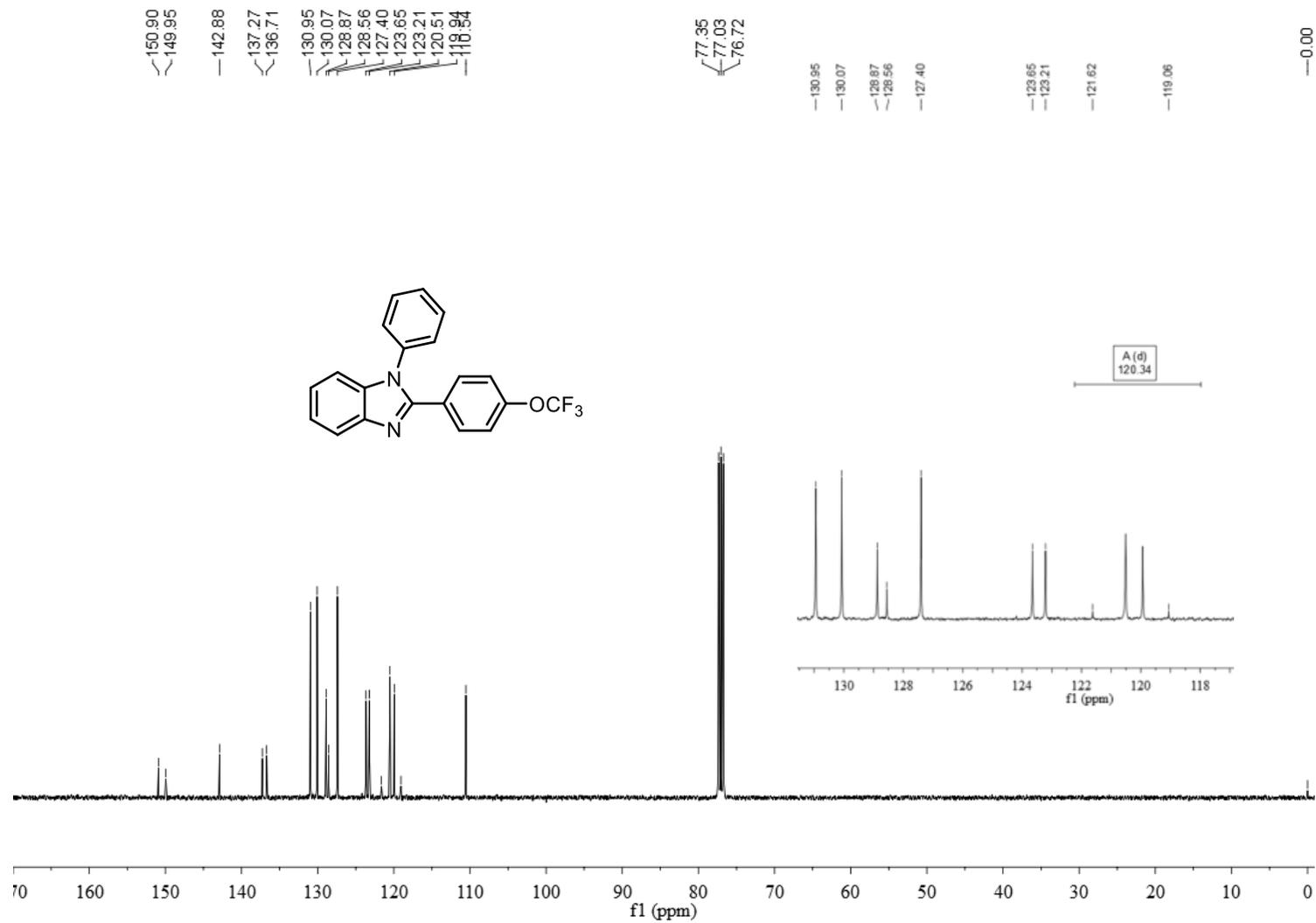
Compound 3ac



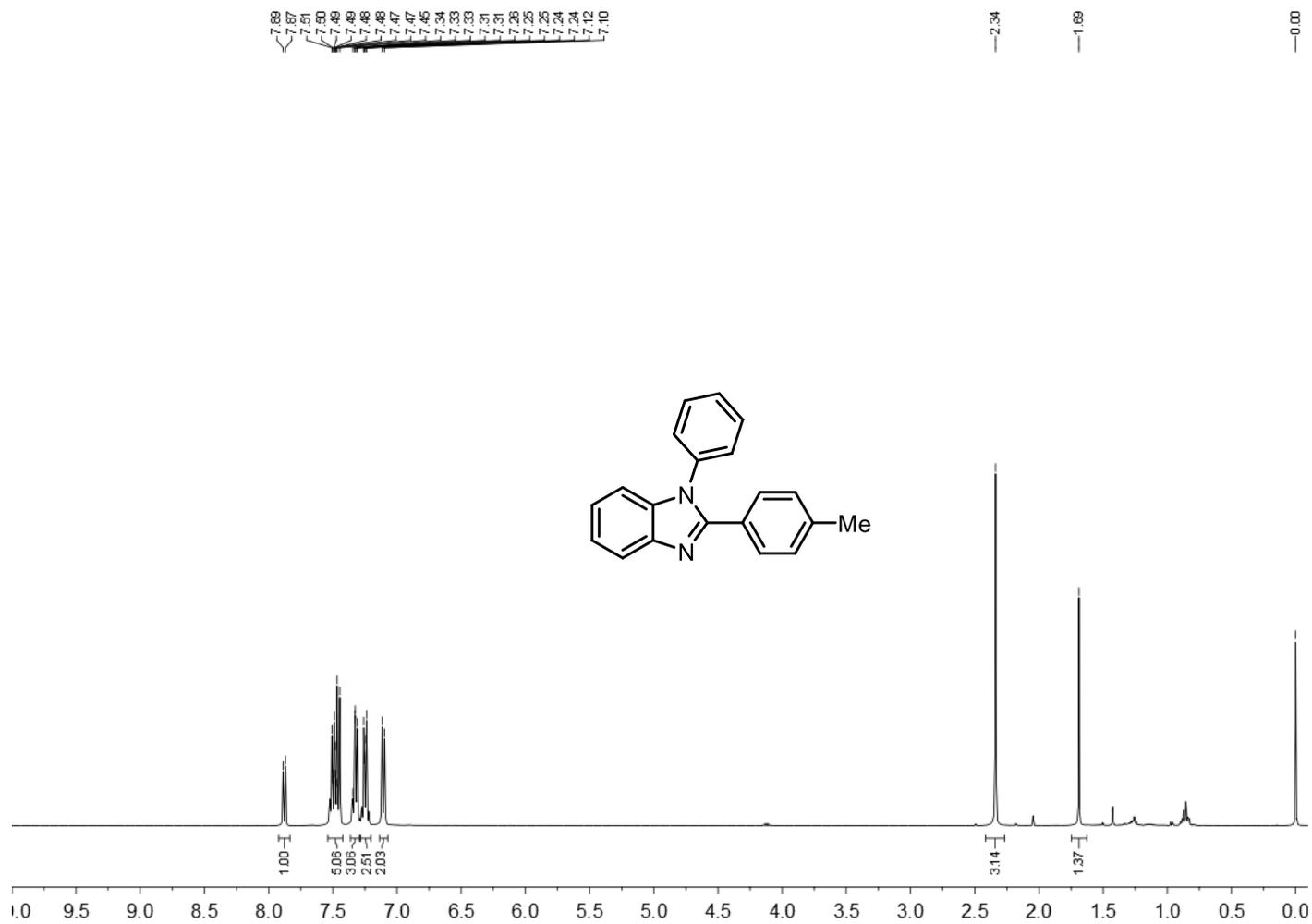


Compound 3ad





Compound 3ae

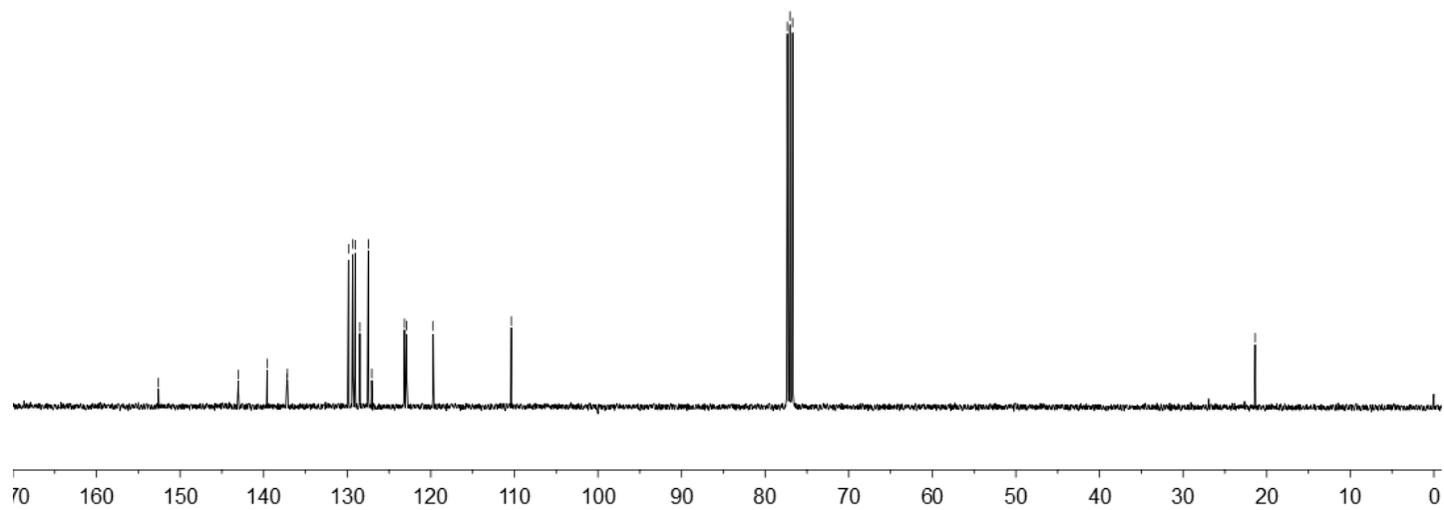
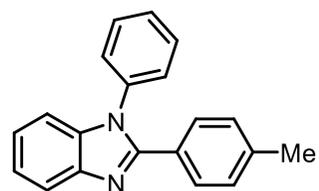


KX-25061225046 (9G)
20250612-CDC13-XR6-62

143.02
139.59
137.24
137.16
129.84
129.35
129.04
128.49
127.47
123.16
122.00
119.73
110.37

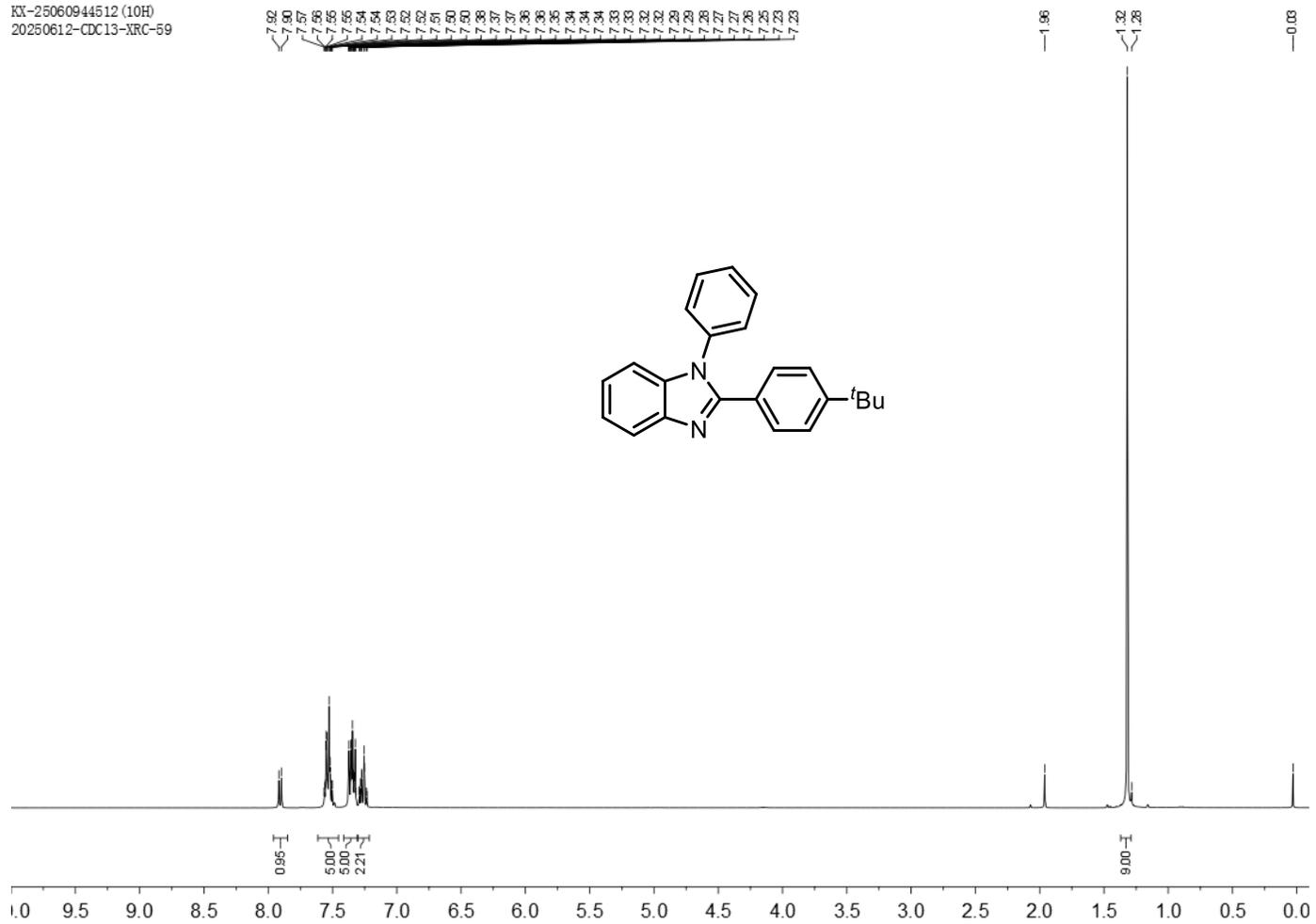
77.35
77.03
76.72

21.38



Compound 3af

KX-25060944512 (10H)
20250612-CDC13-XRC-59



KX-25061225046
20250612-CDC13

158.98
157.44
156.59

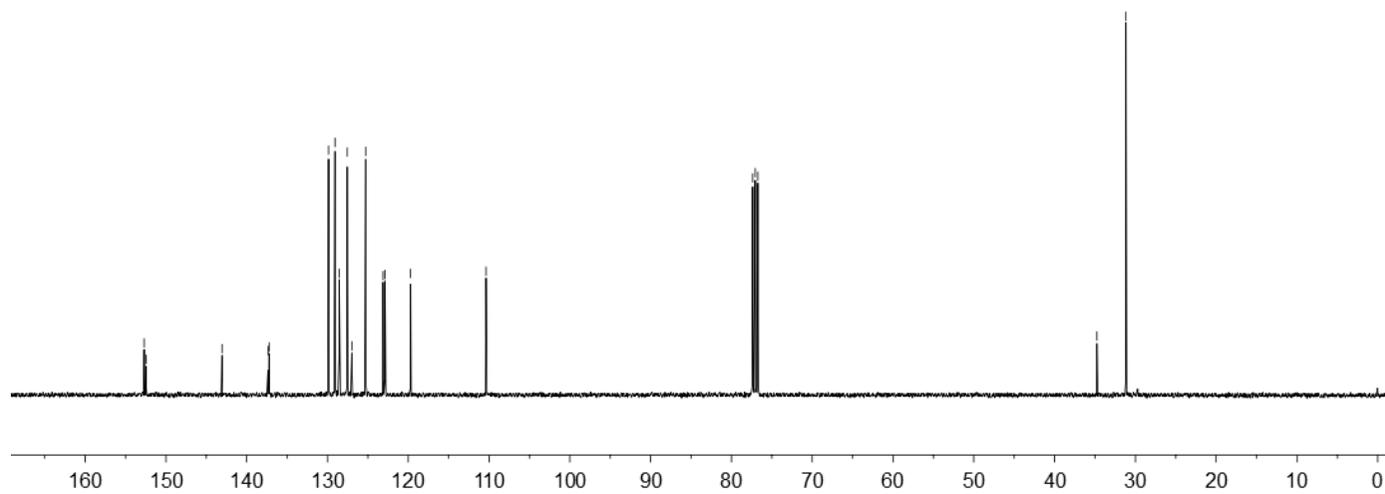
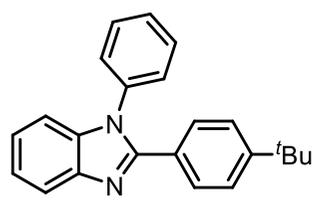
143.05
137.36
137.22

129.87
129.07
128.54
127.55
126.98
125.28
123.12
122.87
119.72

110.38

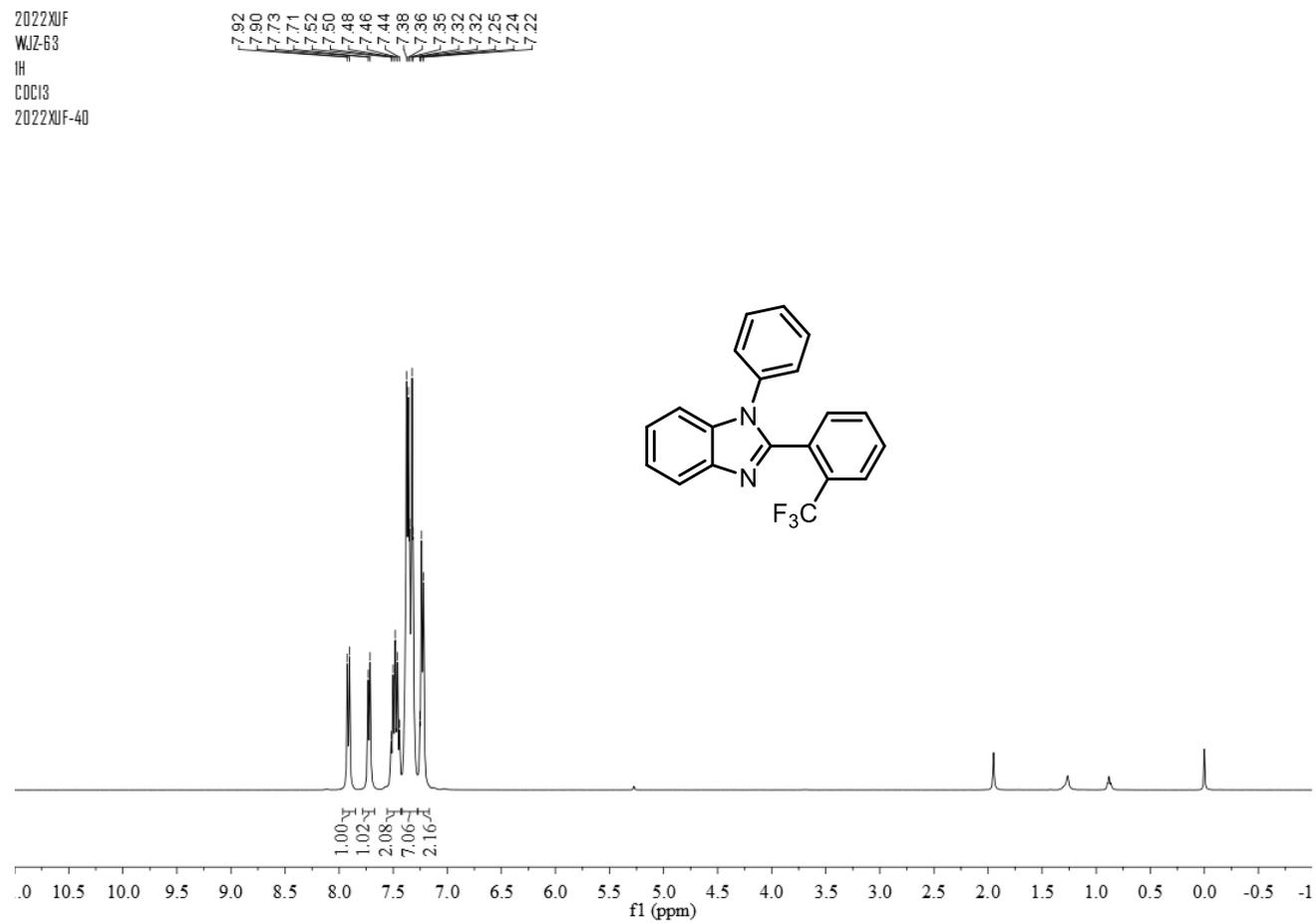
77.37
77.05
76.74

34.76
31.17

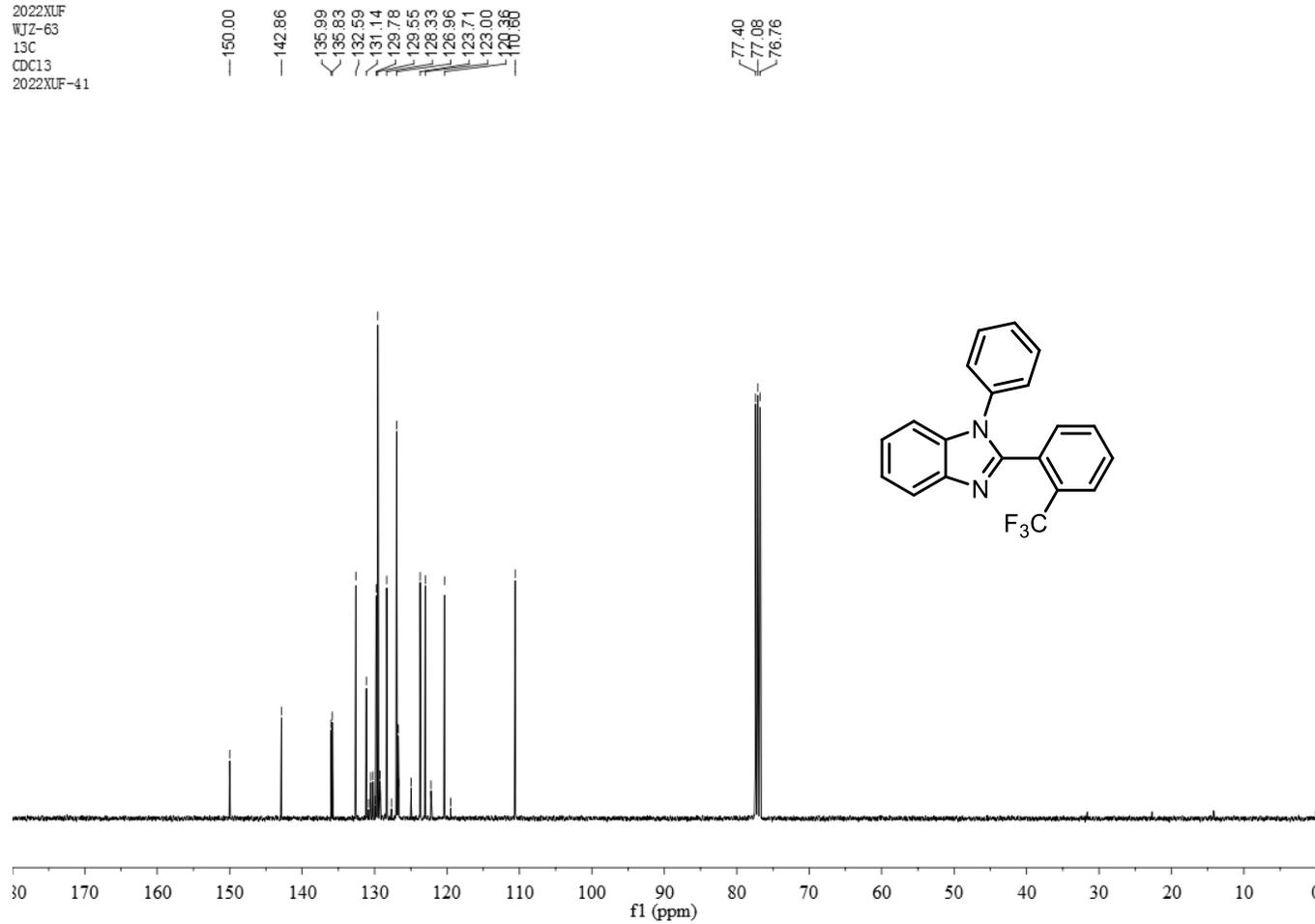


Compound 3ag

2022XUF
WJZ-63
H
CDCl3
2022XUF-40

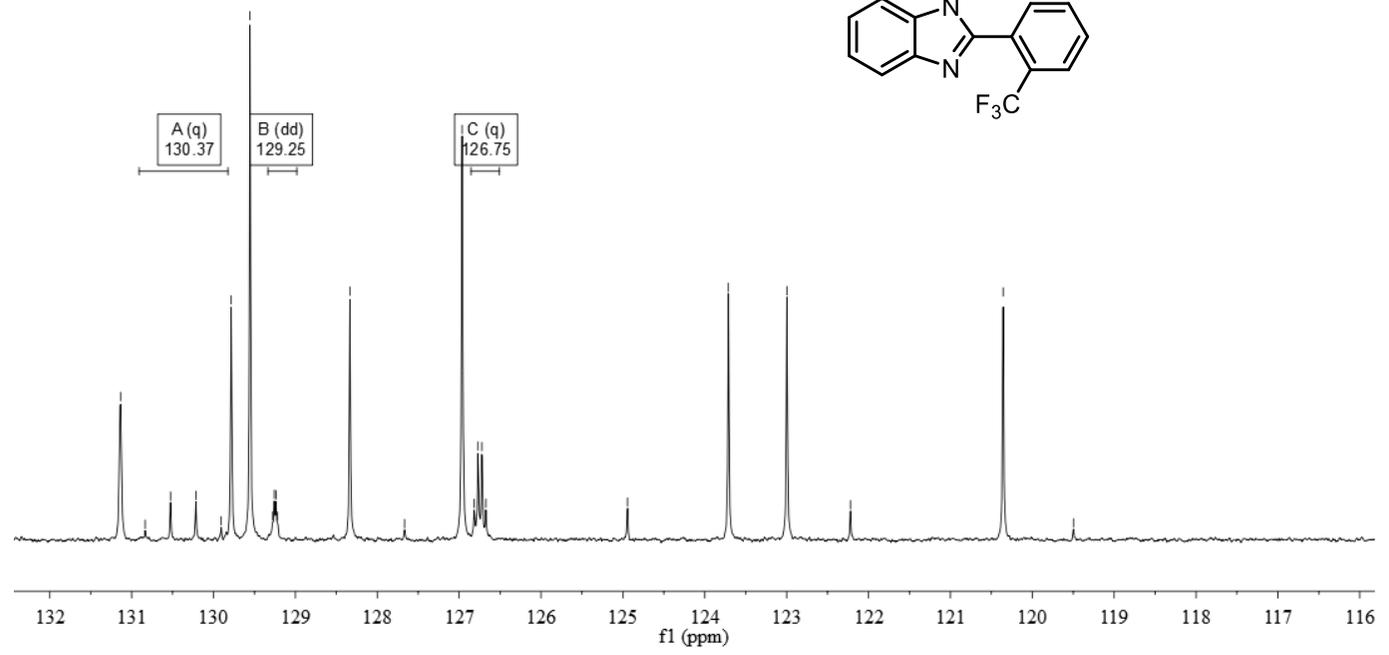
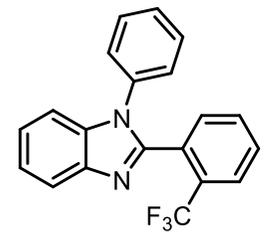


2022XUF
WJZ-63
13C
CDC13
2022XUF-41



2022XUF
WJZ-63
13C
CDC13
2022XUF-41

131.14
130.83
130.62
130.22
129.91
129.78
129.55
129.28
129.26
129.24
129.22
— 128.33
— 127.67
126.96
126.82
126.77
126.72
126.67
— 124.94
— 123.71
— 123.00
— 122.22
— 120.36
— 119.50



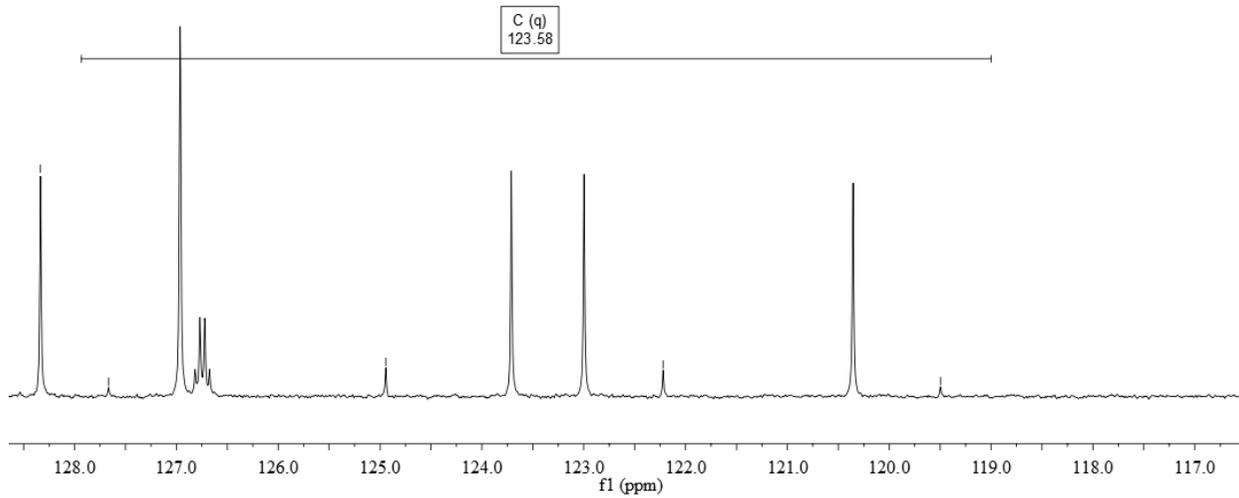
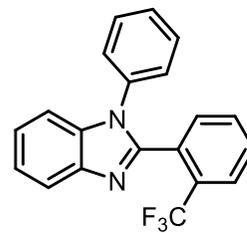
2022XUF
WJZ-83
13C NMR
CDCl₃
2022XUF-41

—127.67

—124.94

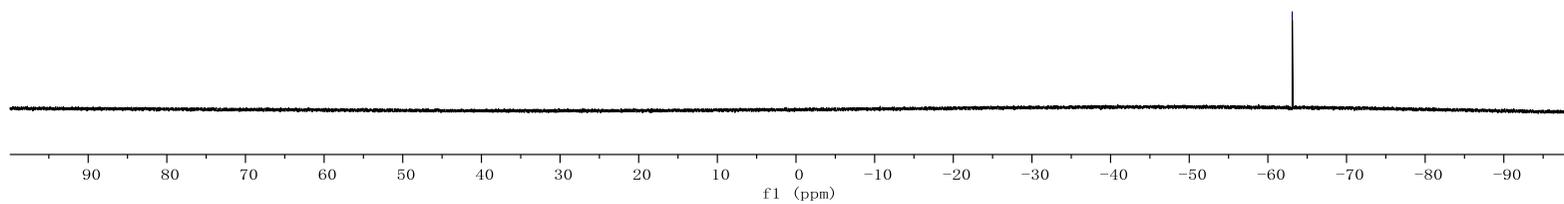
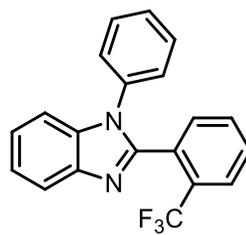
—122.22

—119.50

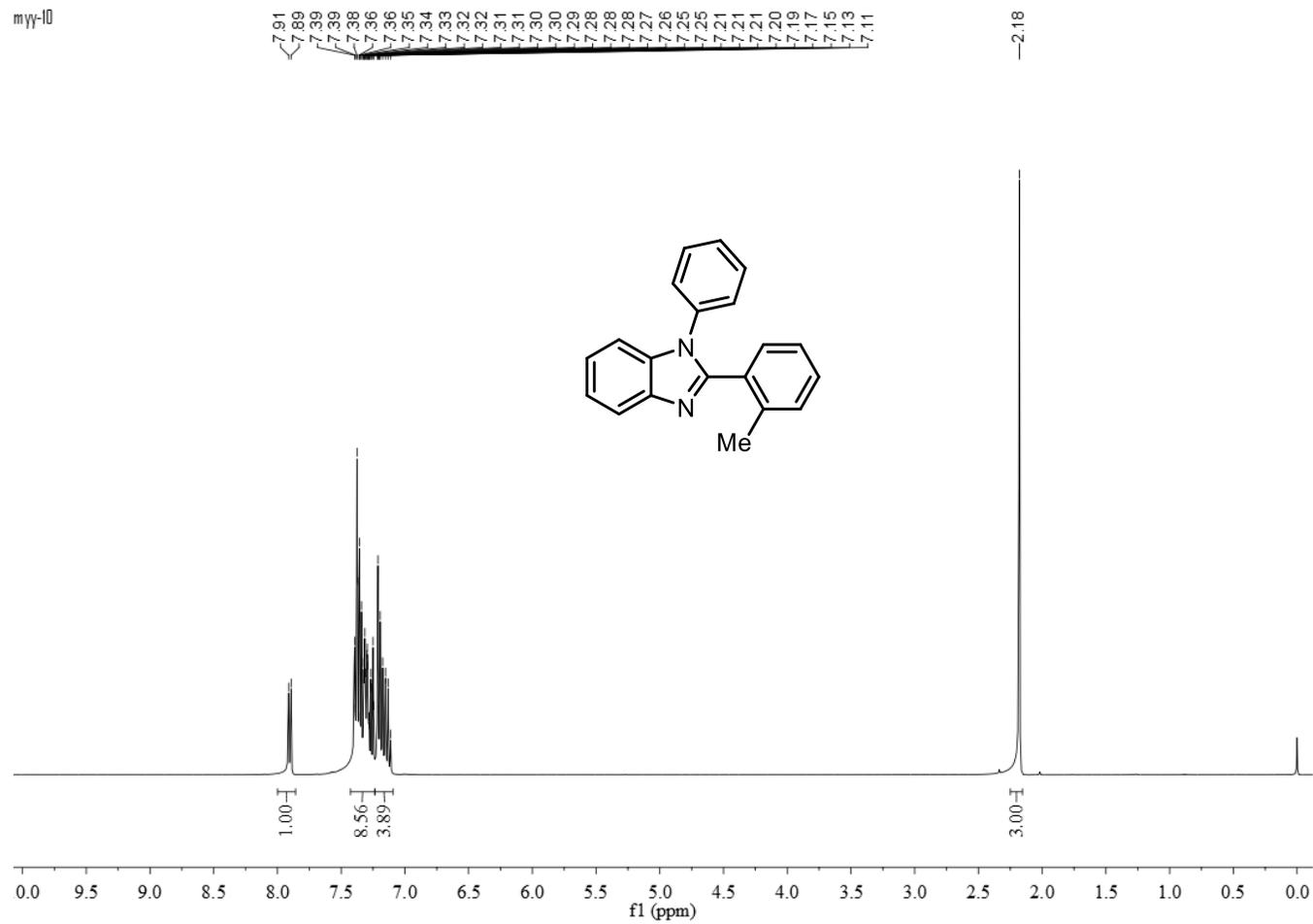


26031104166(3F)/XRC-NRM-1
20260314-CDCl3-XRC-NRM-1

— 63.10



Compound 3ah

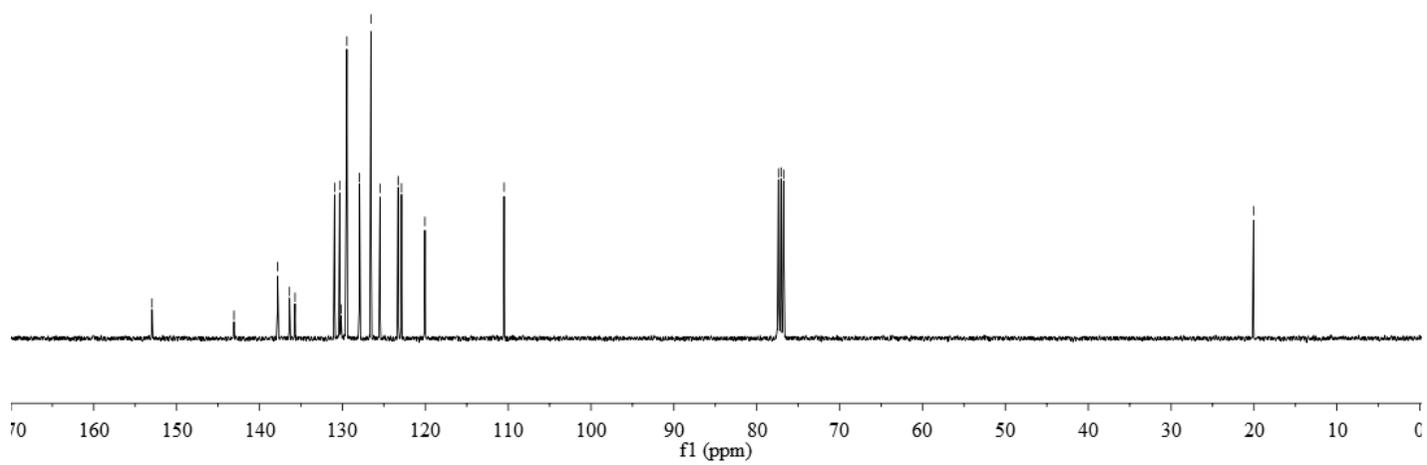
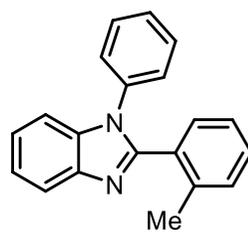


myy-10

152.97
143.07
137.82
136.38
130.94
130.33
129.54
129.46
127.93
126.55
125.46
123.28
122.86
120.99

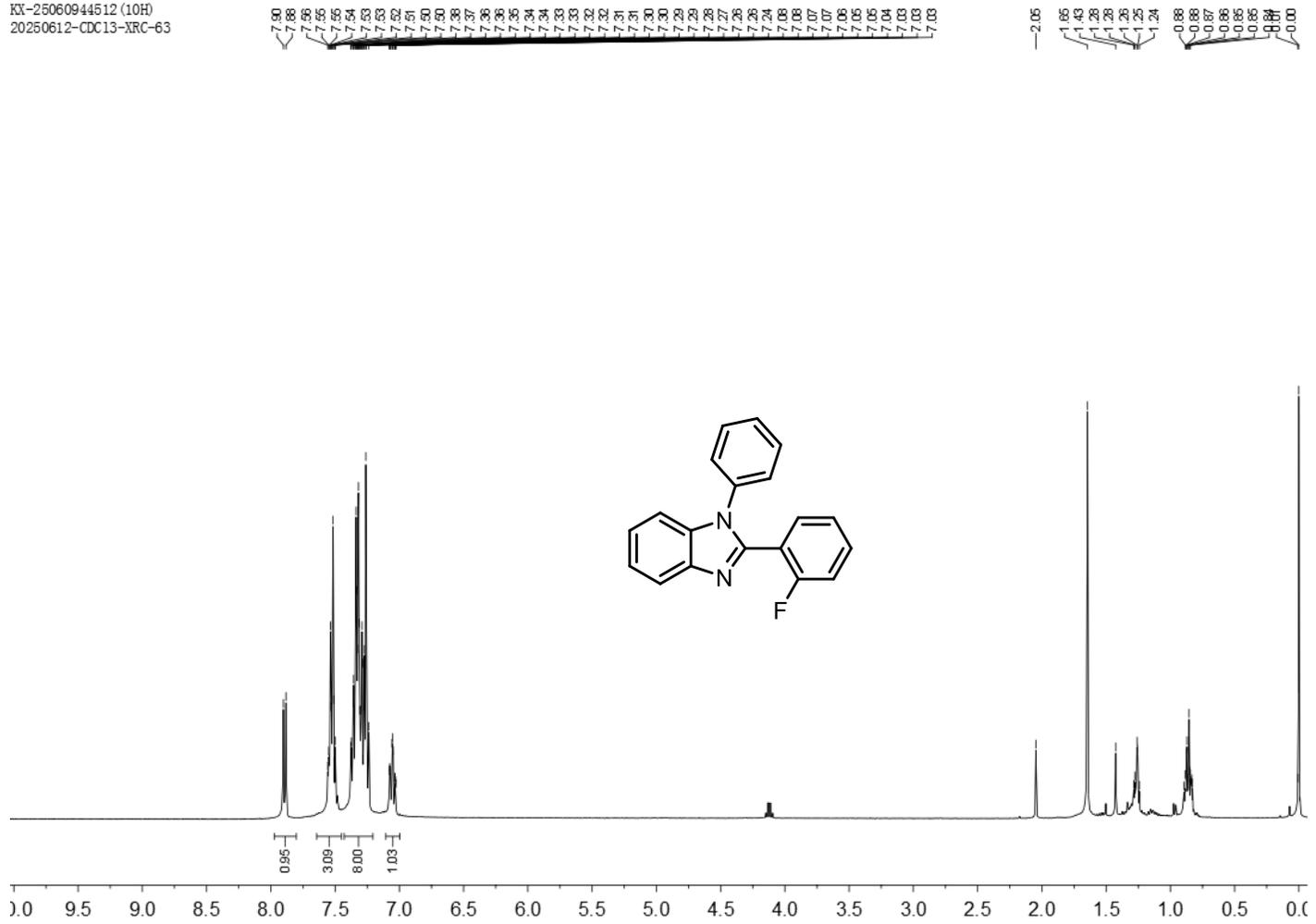
77.39
77.07
76.75

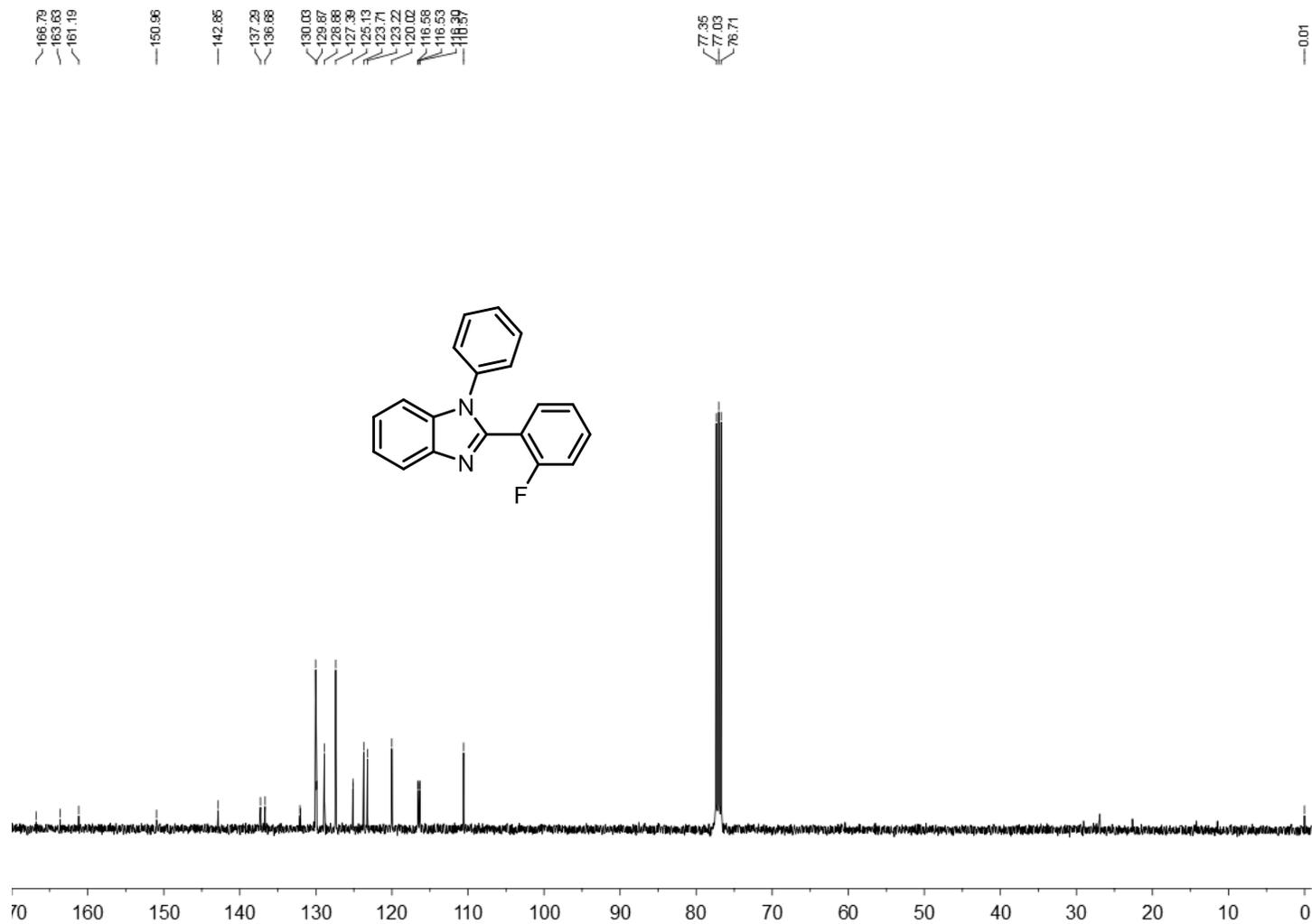
20.06

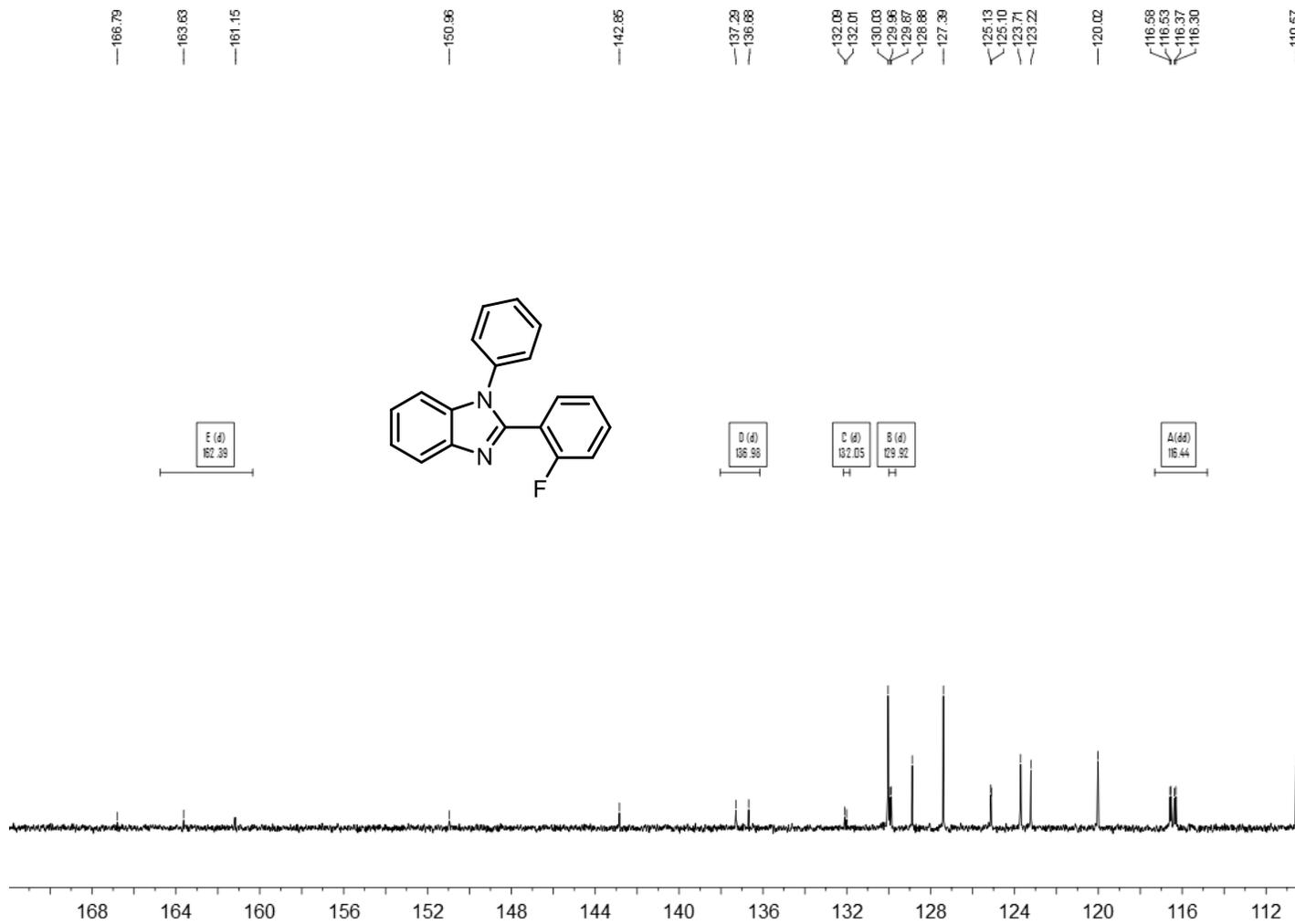


Compound 3ai

KX-25060944512 (10H)
20250612-CDC13-XRC-63

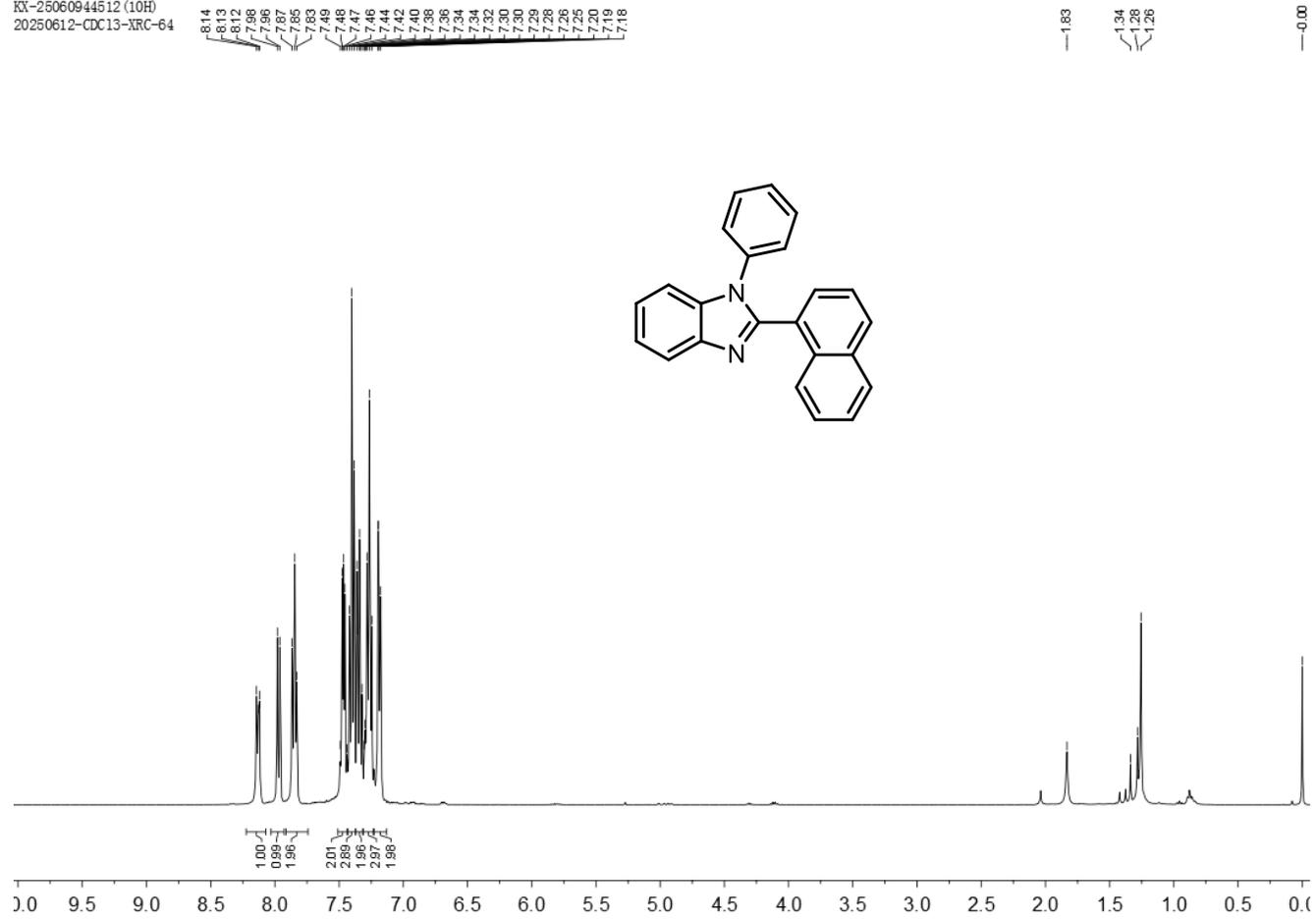


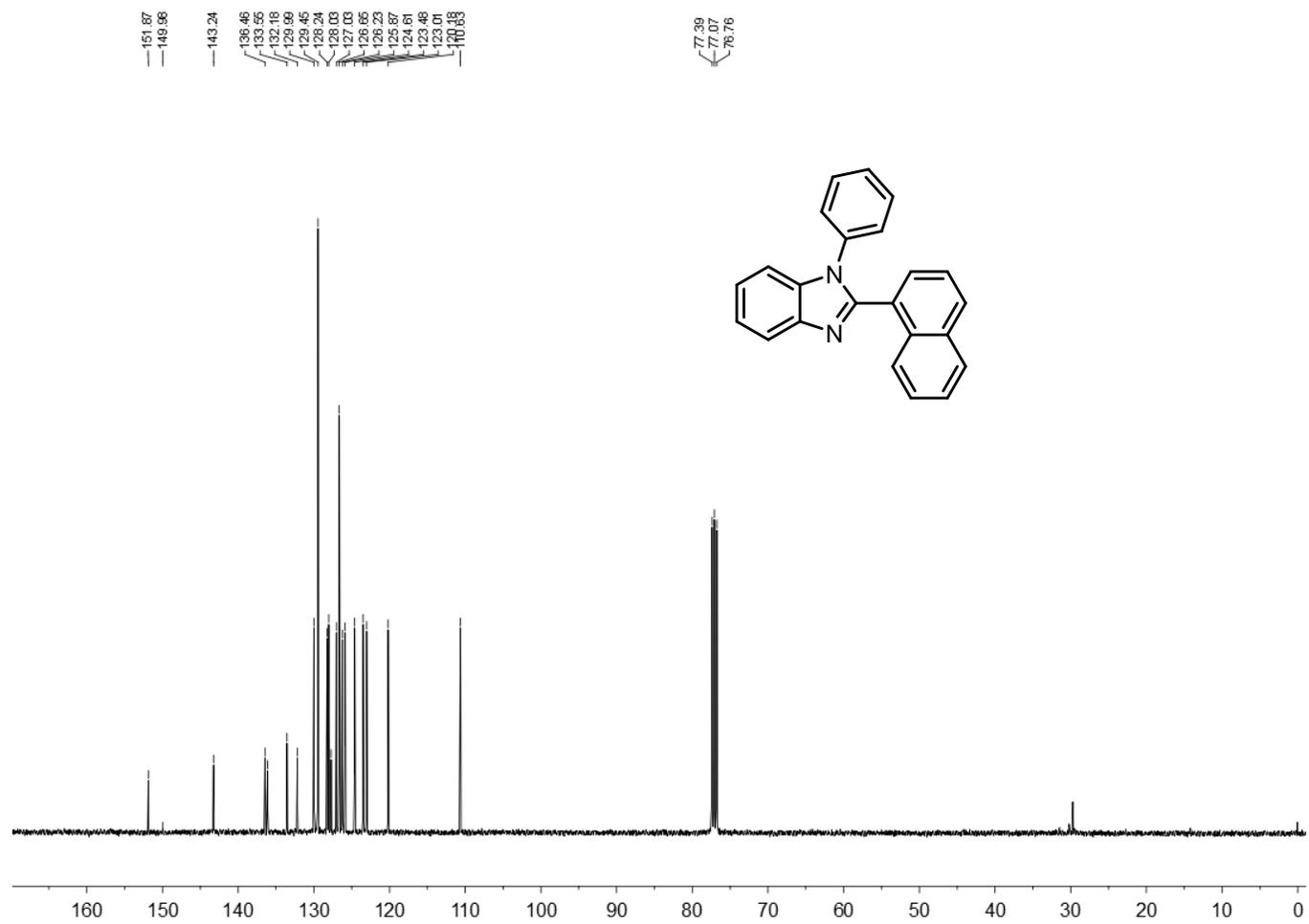




Compound 3aj

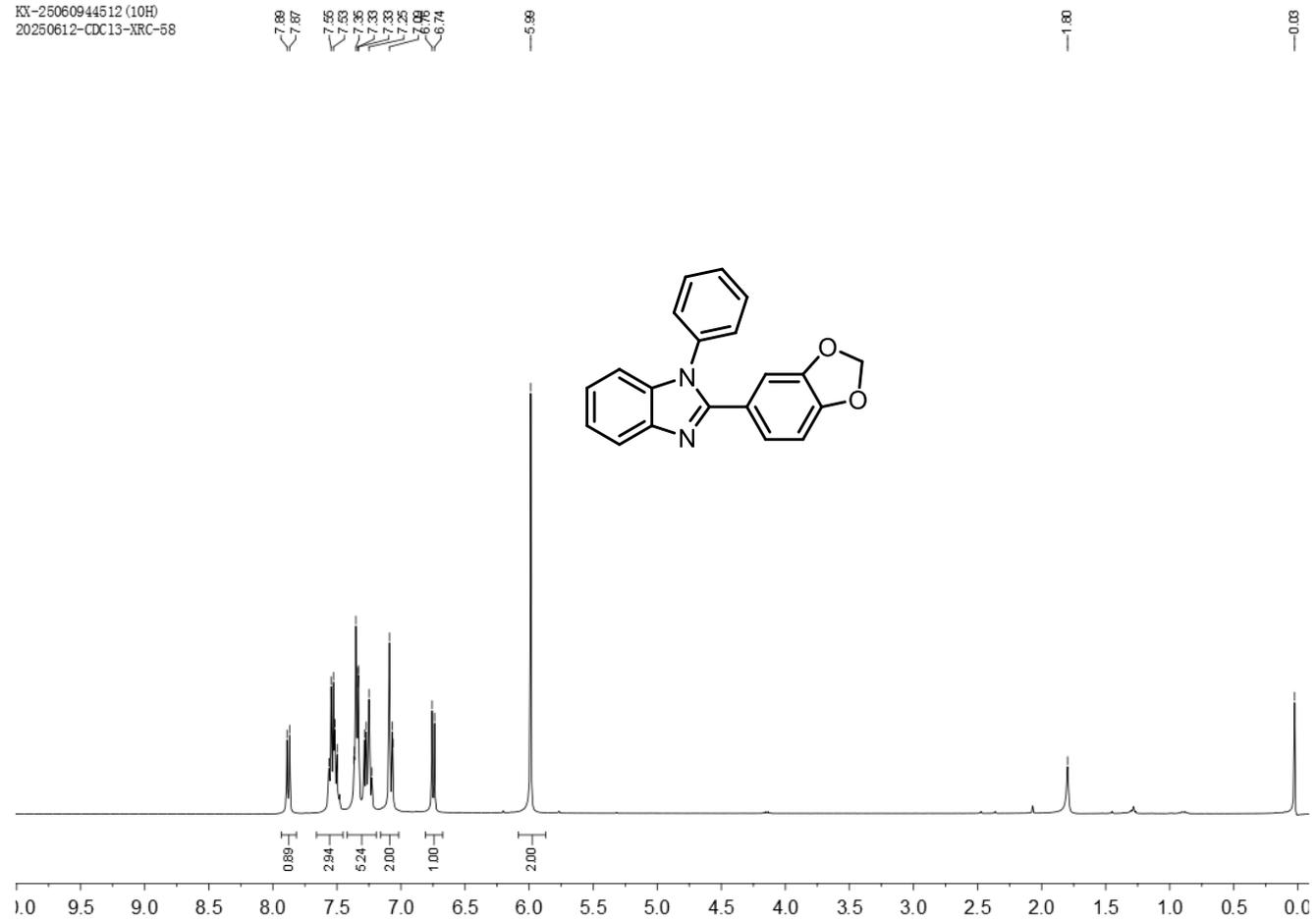
KX-25060944512 (10H)
20250612-CDC13-XRC-64



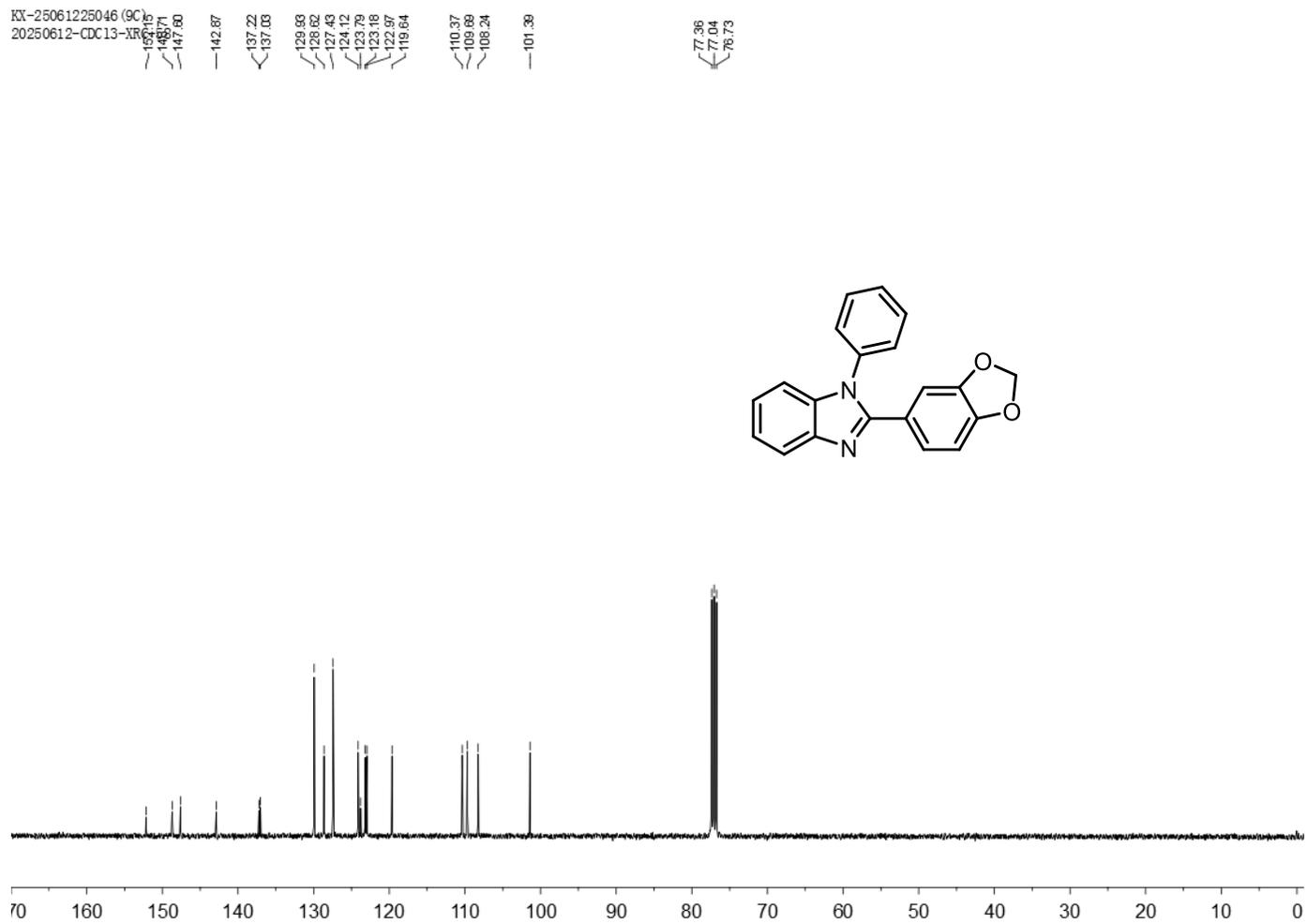


Compound 3ak

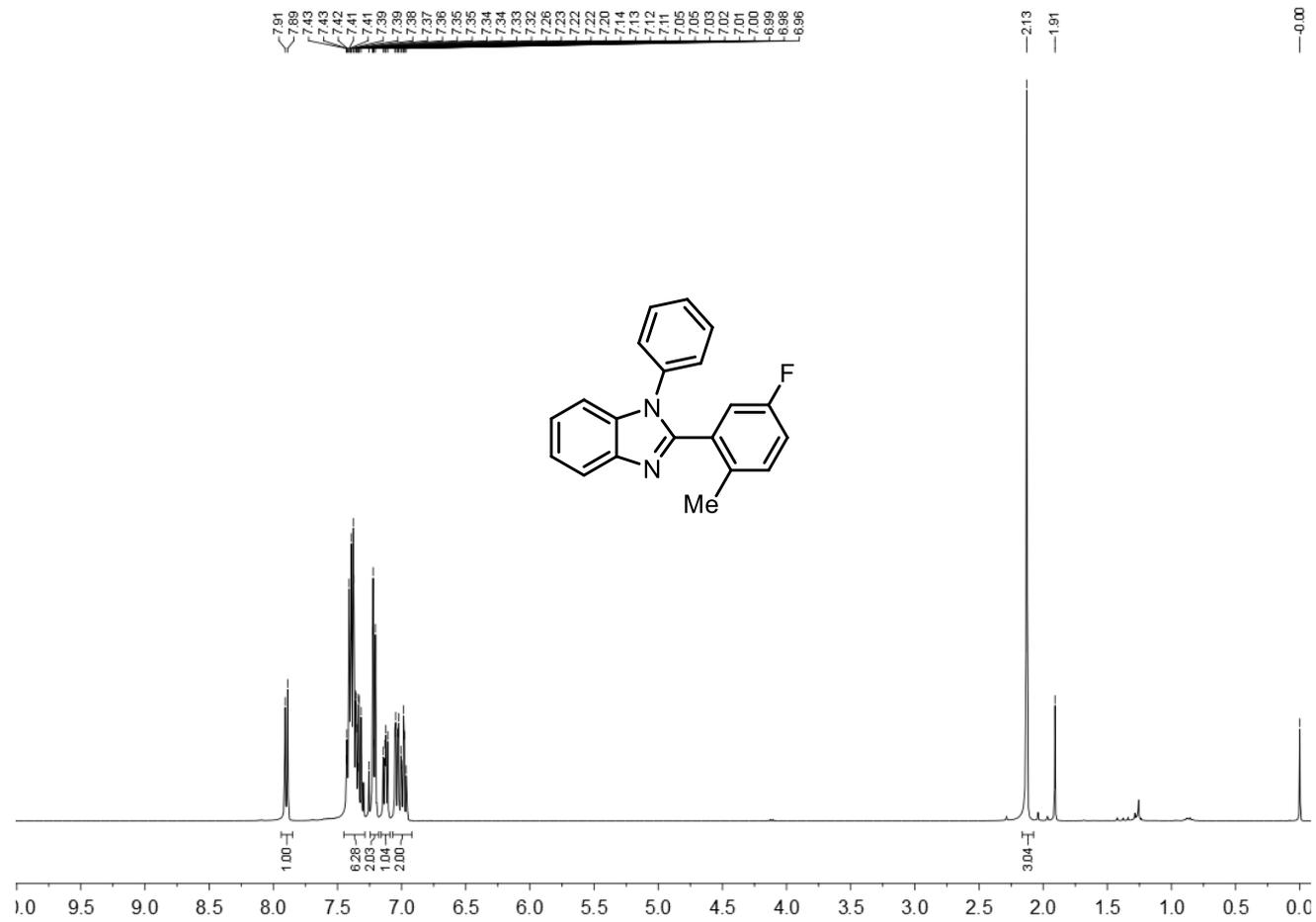
KX-25060944512 (10H)
20250612-CDC13-XRC-58



KX-25061225046 (9C)
20250612-CDC13-XR



Compound 3al

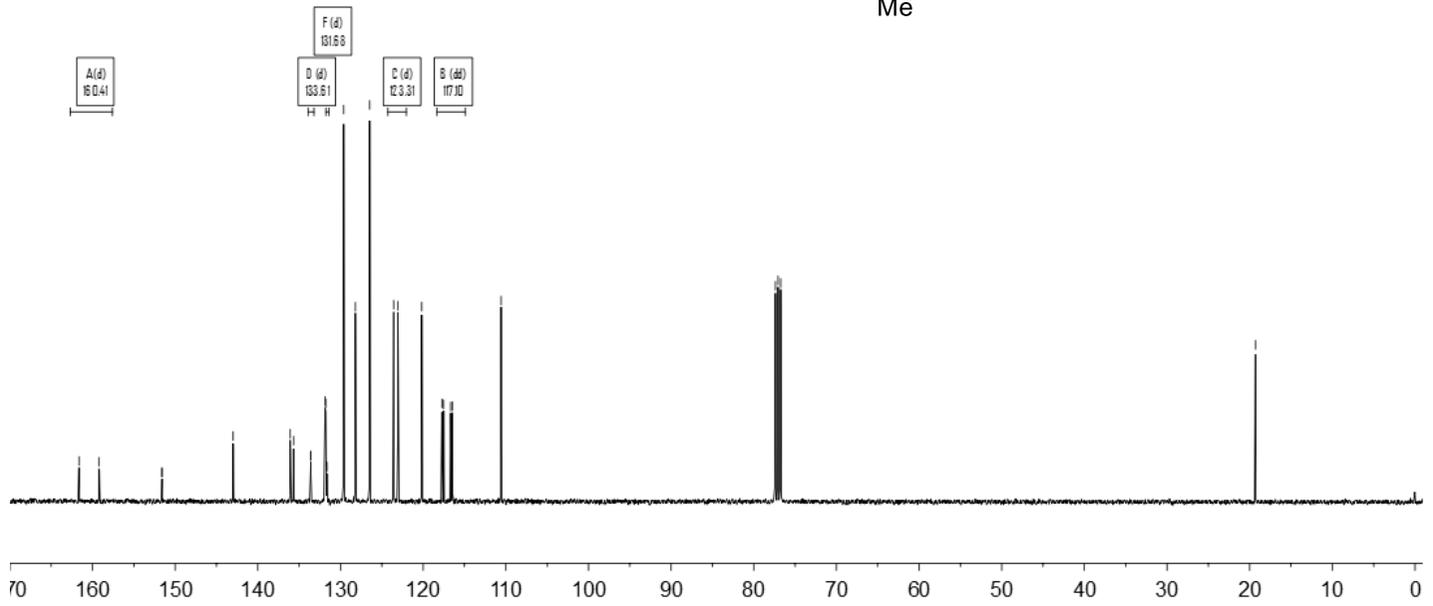
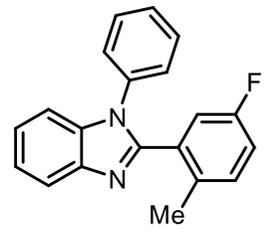


KX-25061826046 (QC)
20250613-XS

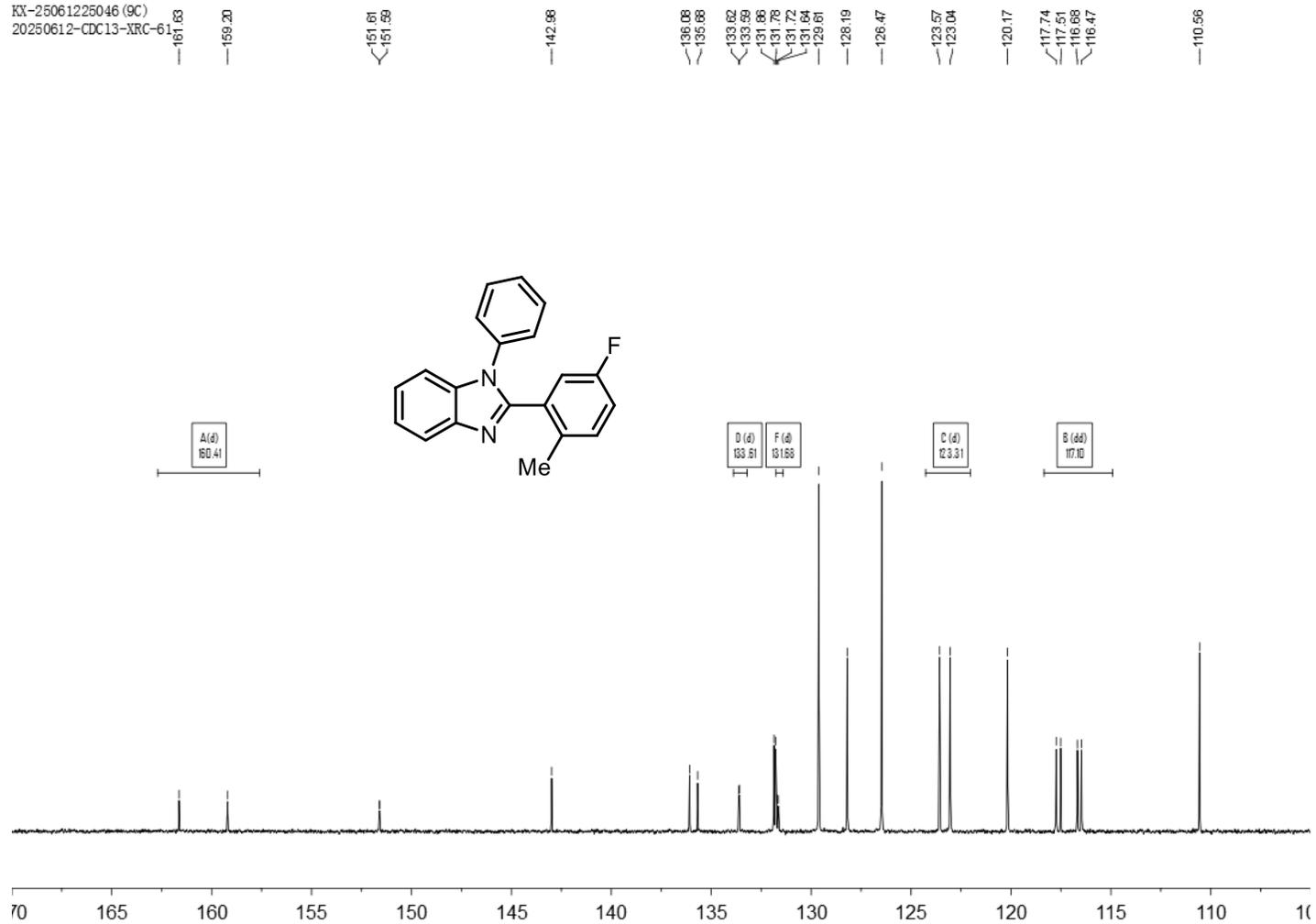
162.38
159.13
156.65
154.51
142.98
136.08
135.88
133.59
131.88
131.78
129.81
126.47
123.57
123.04
120.17
117.74
116.68
116.36

77.38
77.06
76.75

19.30

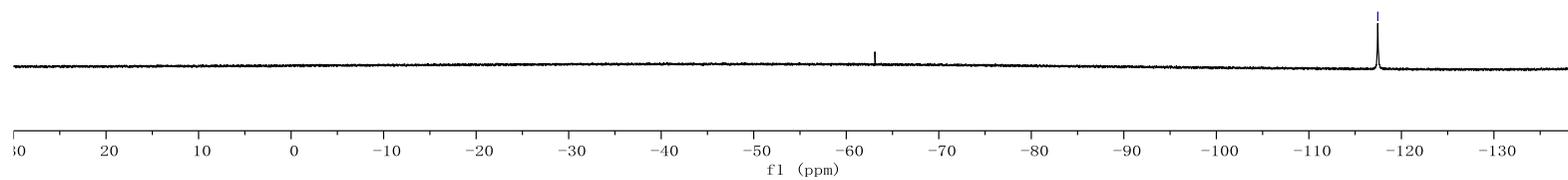
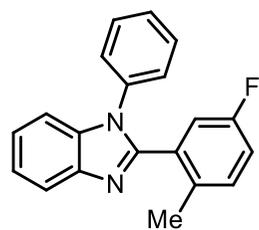


KX-25061225046 (9C)
20250612-CDC13-XRC-61

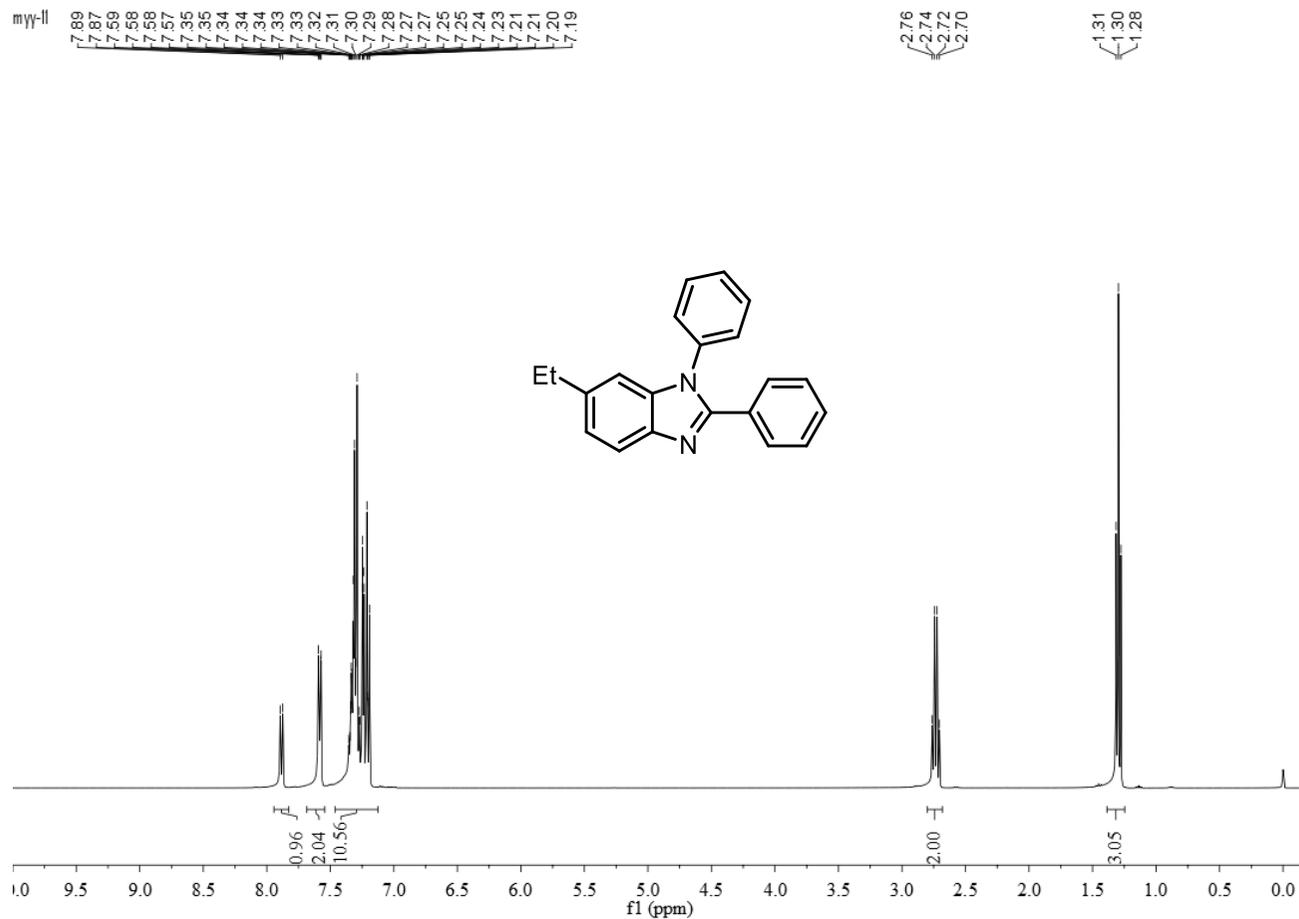


26031104166(3F)/XRC-NRM-2
20260314-CDCl3-XRC-NRM-2

— -117.44



Compound 4am



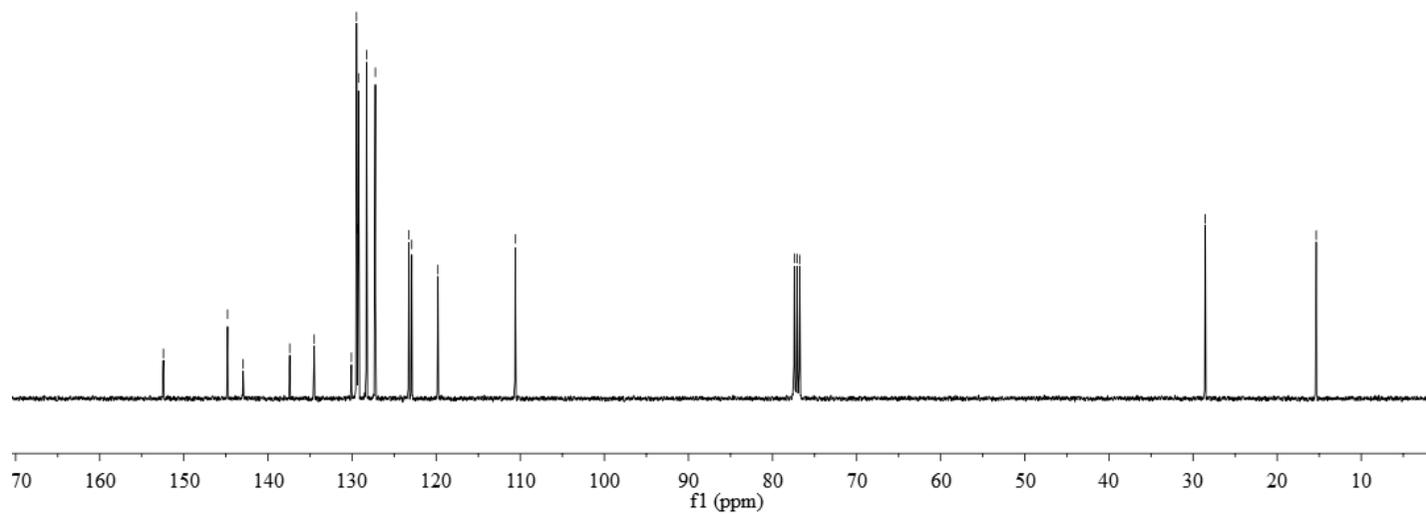
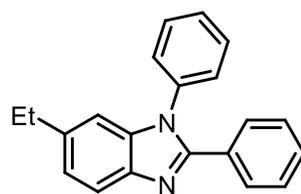
myy-II

152.43
144.80
142.95
137.40
134.50
130.08
129.47
129.39
129.24
128.28
127.23
123.25
122.91
119.79
110.60

77.41
77.09
76.77

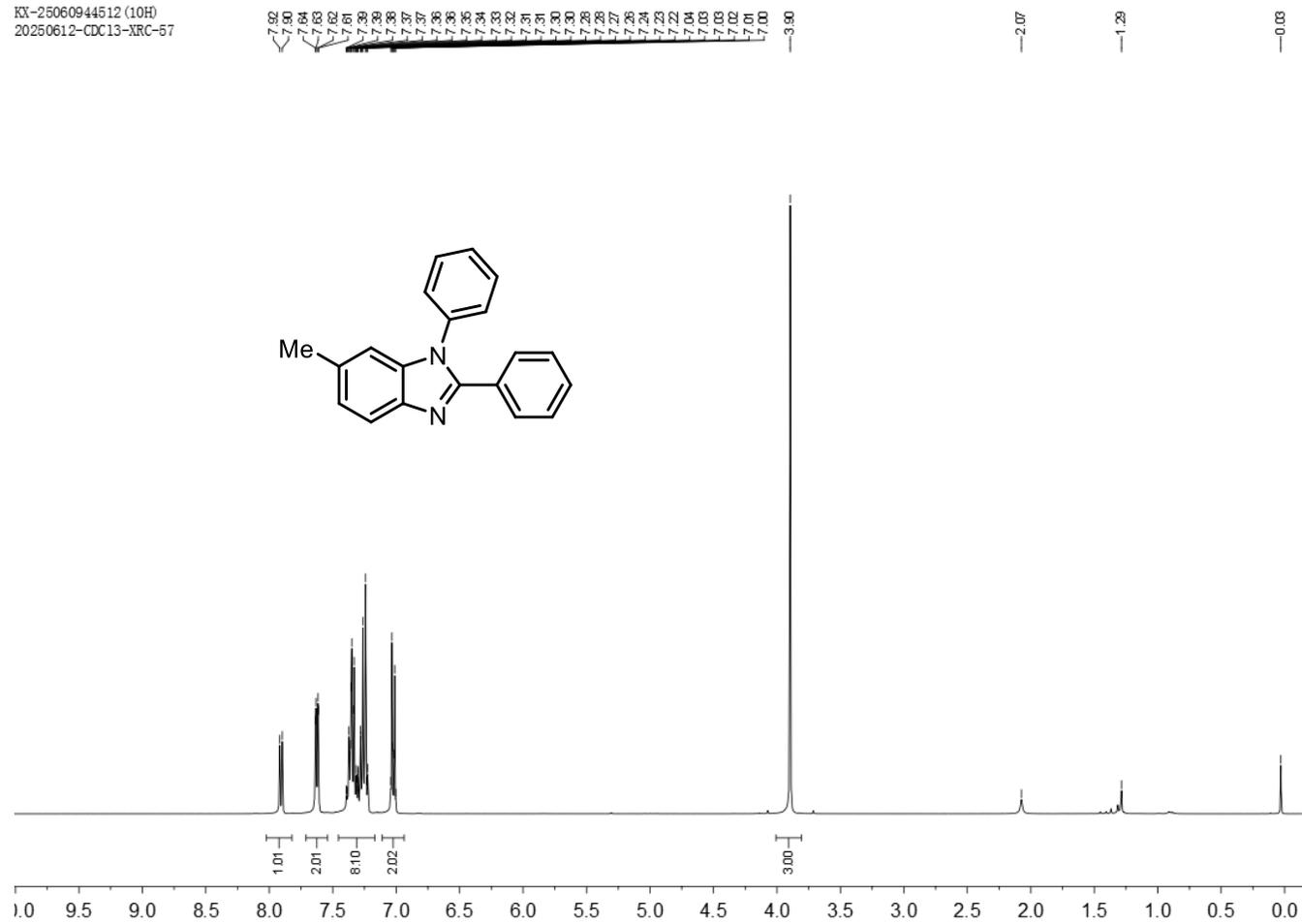
28.55

15.35

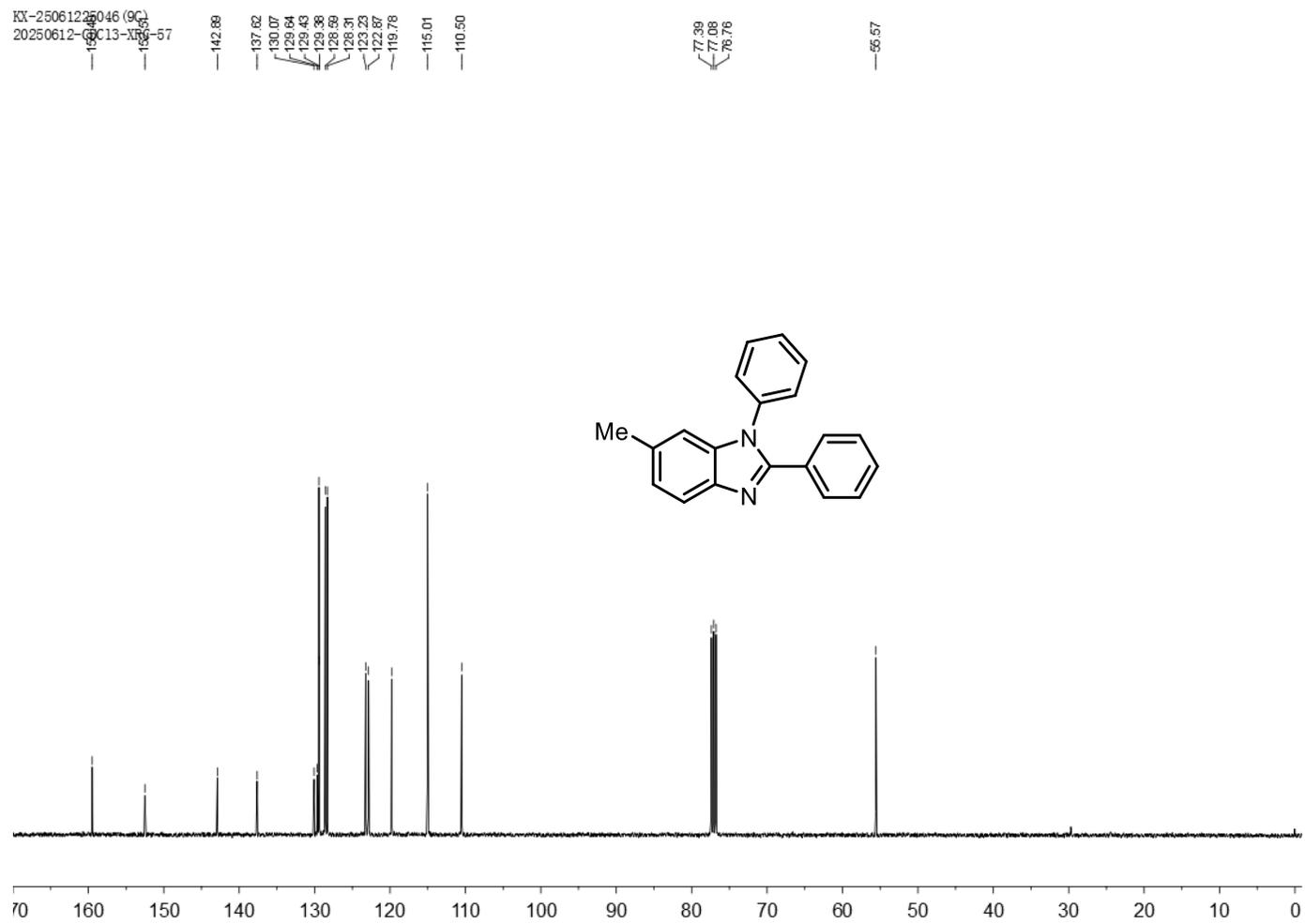


Compound 4an

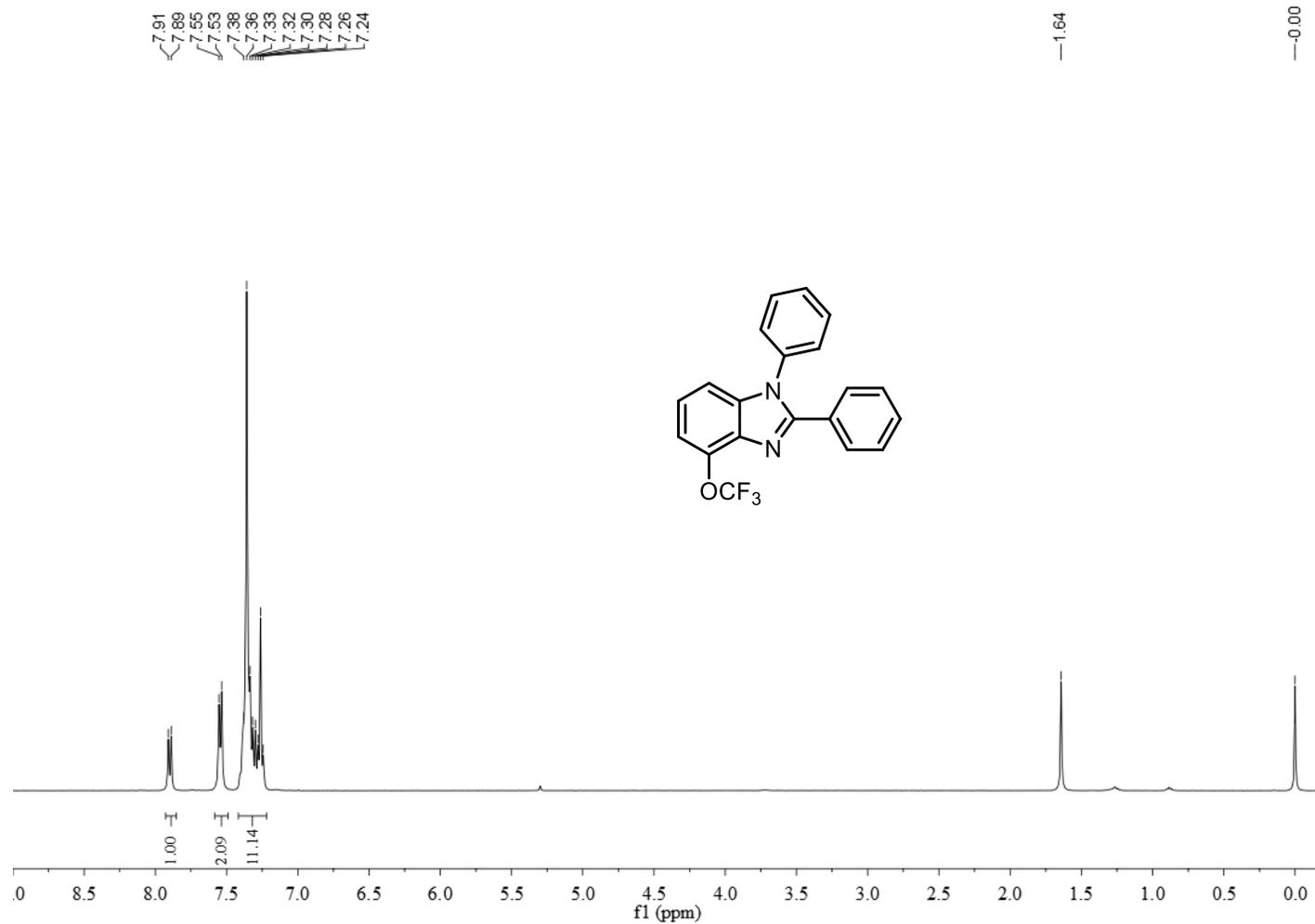
KX-25060944512 (10H)
20250612-CDC13-XRC-57

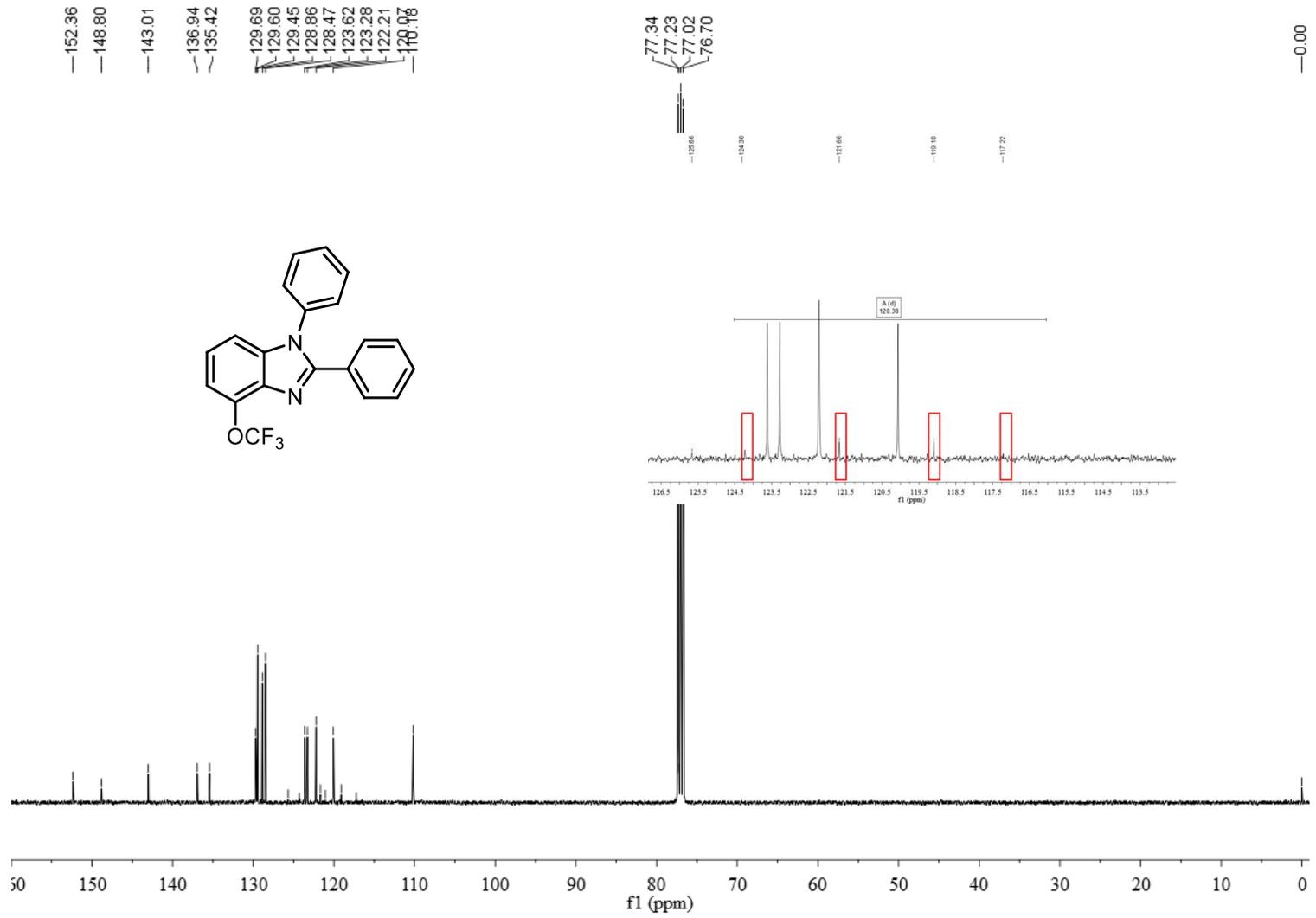


KX-2506122-046 (9C)
20250612-0013-XR6-57



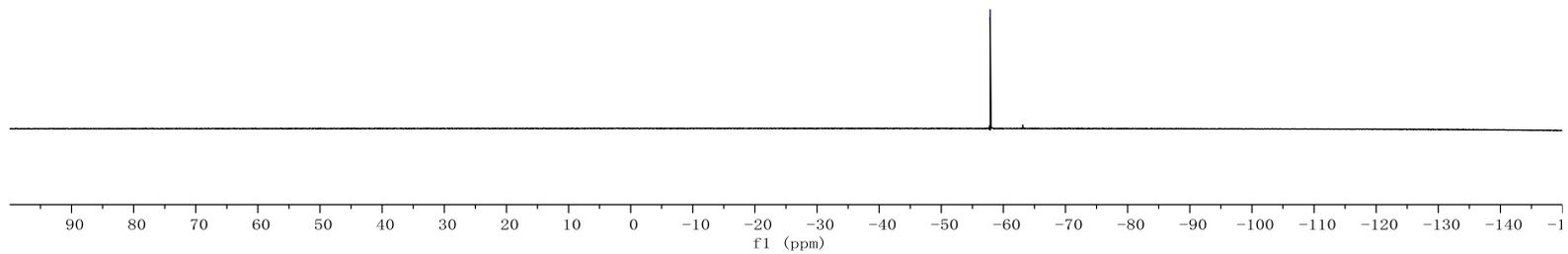
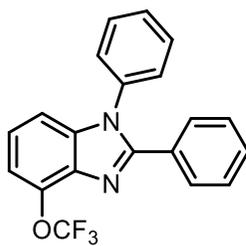
Compound 4ao



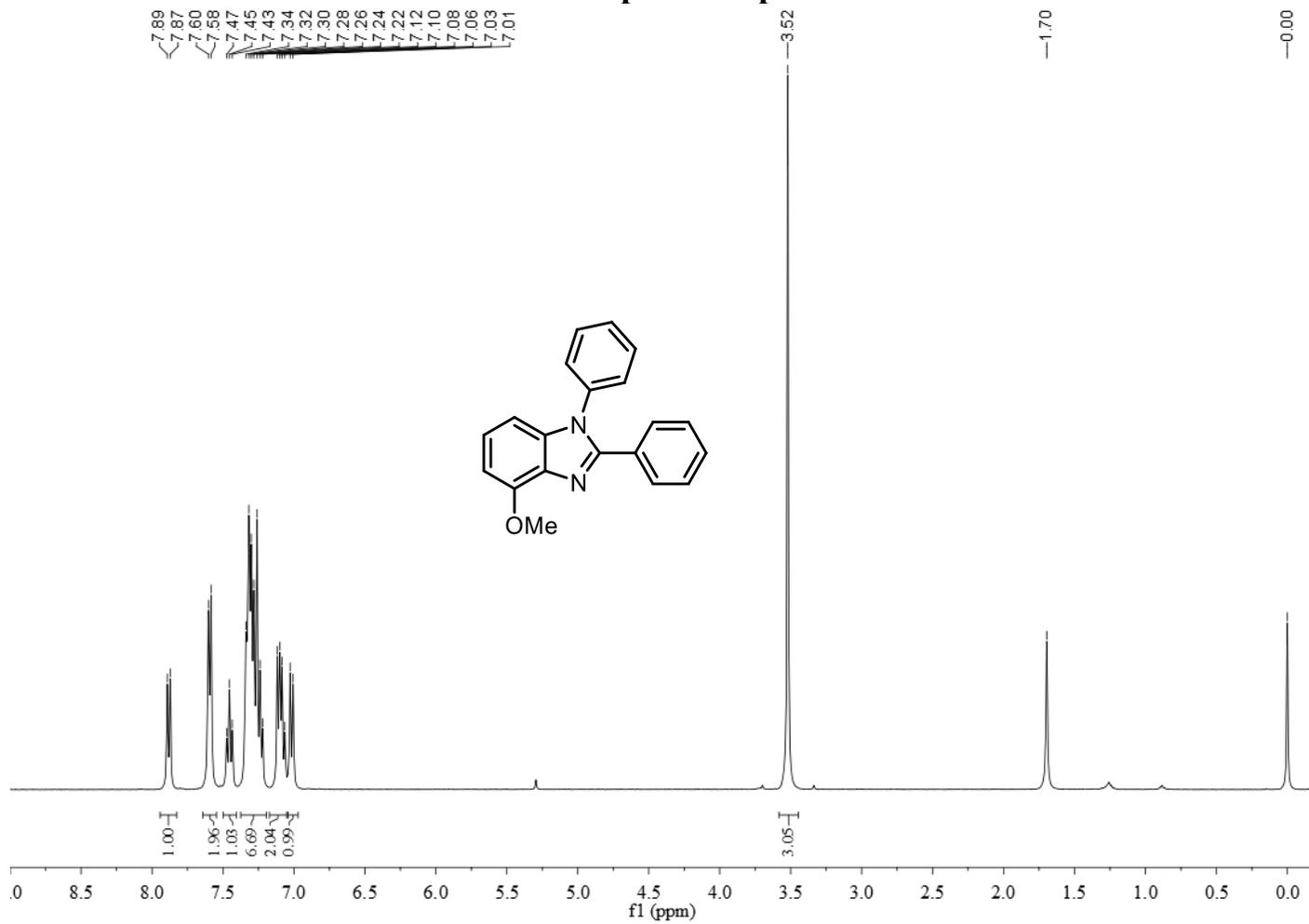


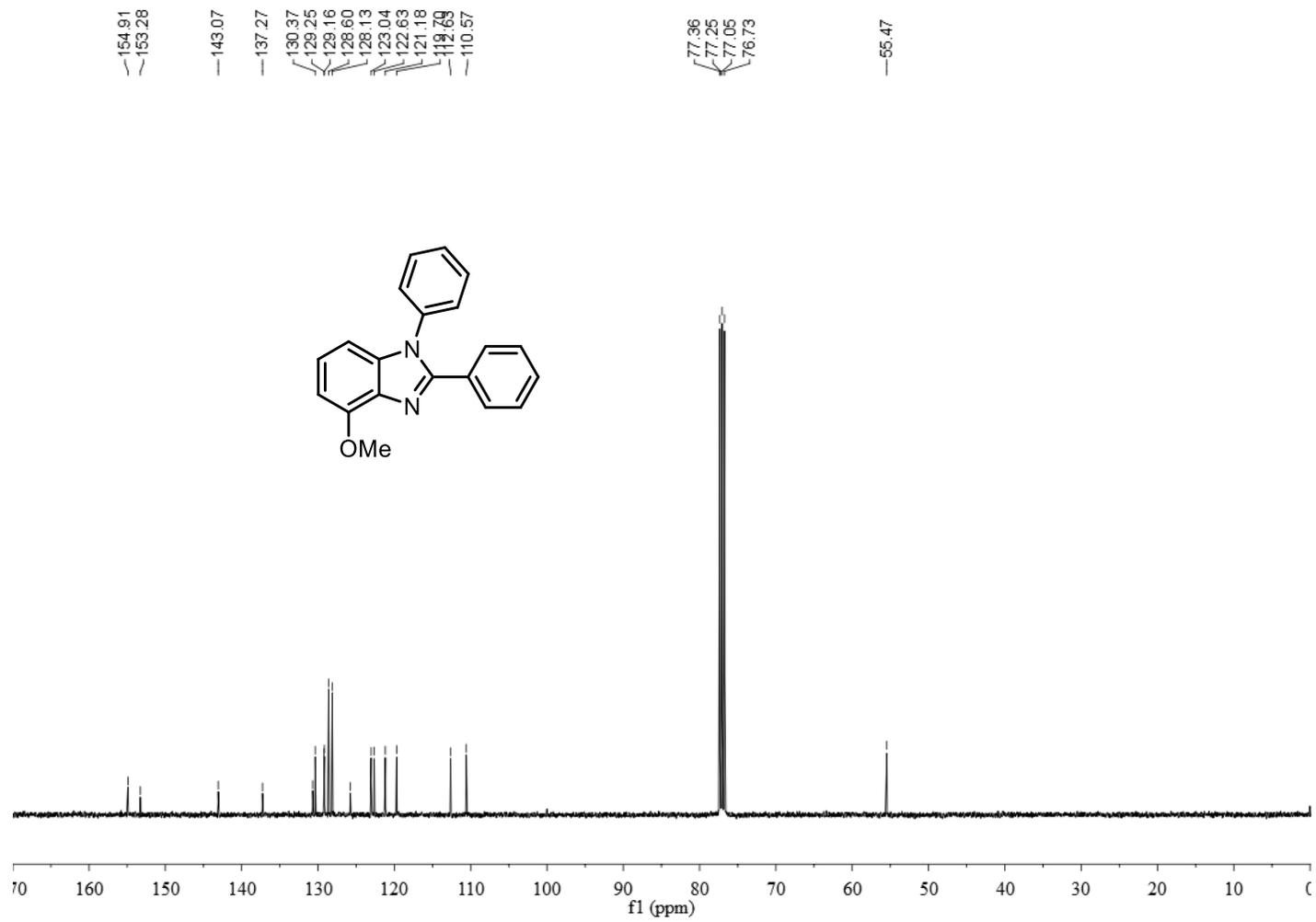
26031104166(3F)/XRC-NRM-3
20260314-CDCl3-XRC-NRM-3

— -57.88

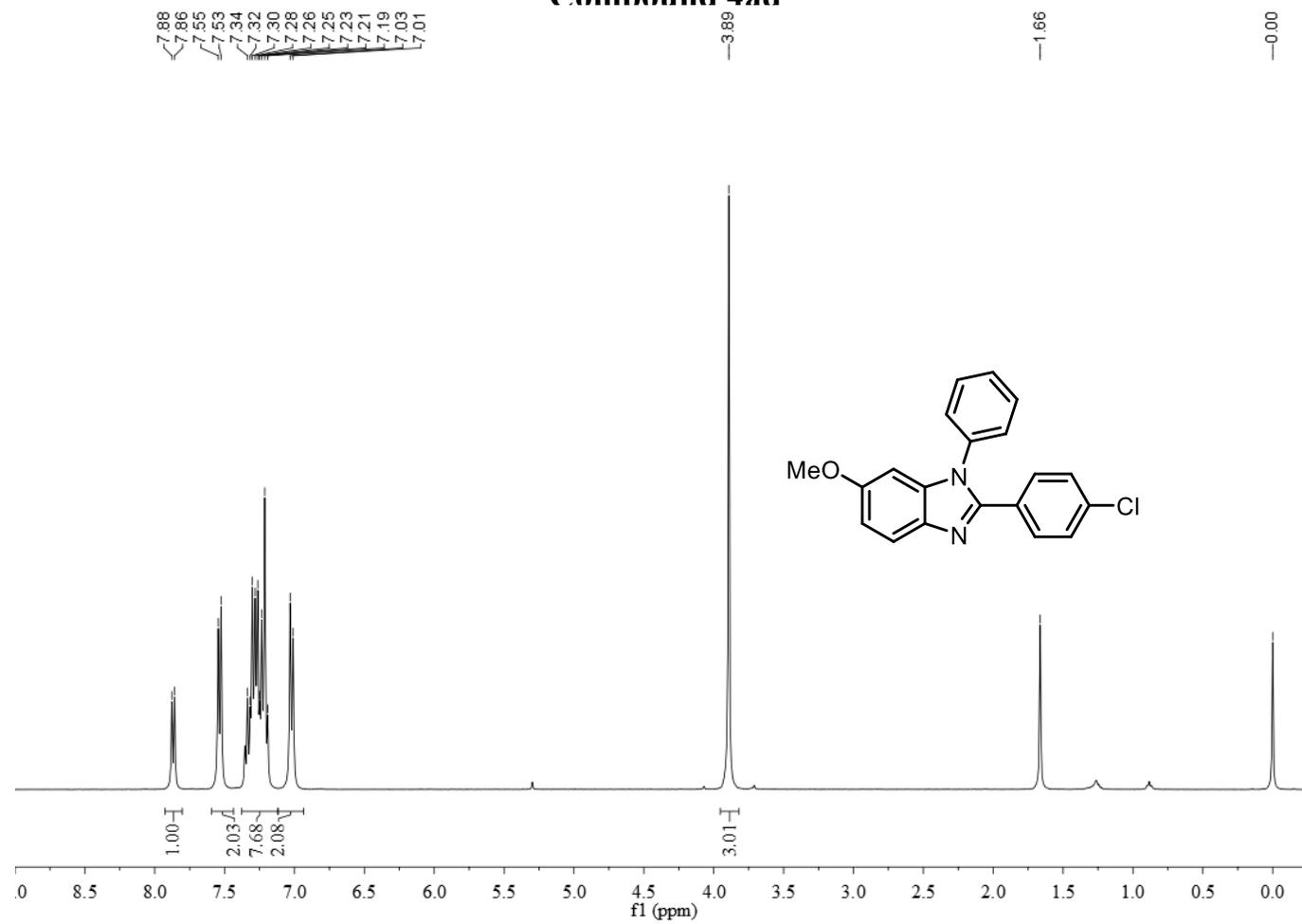


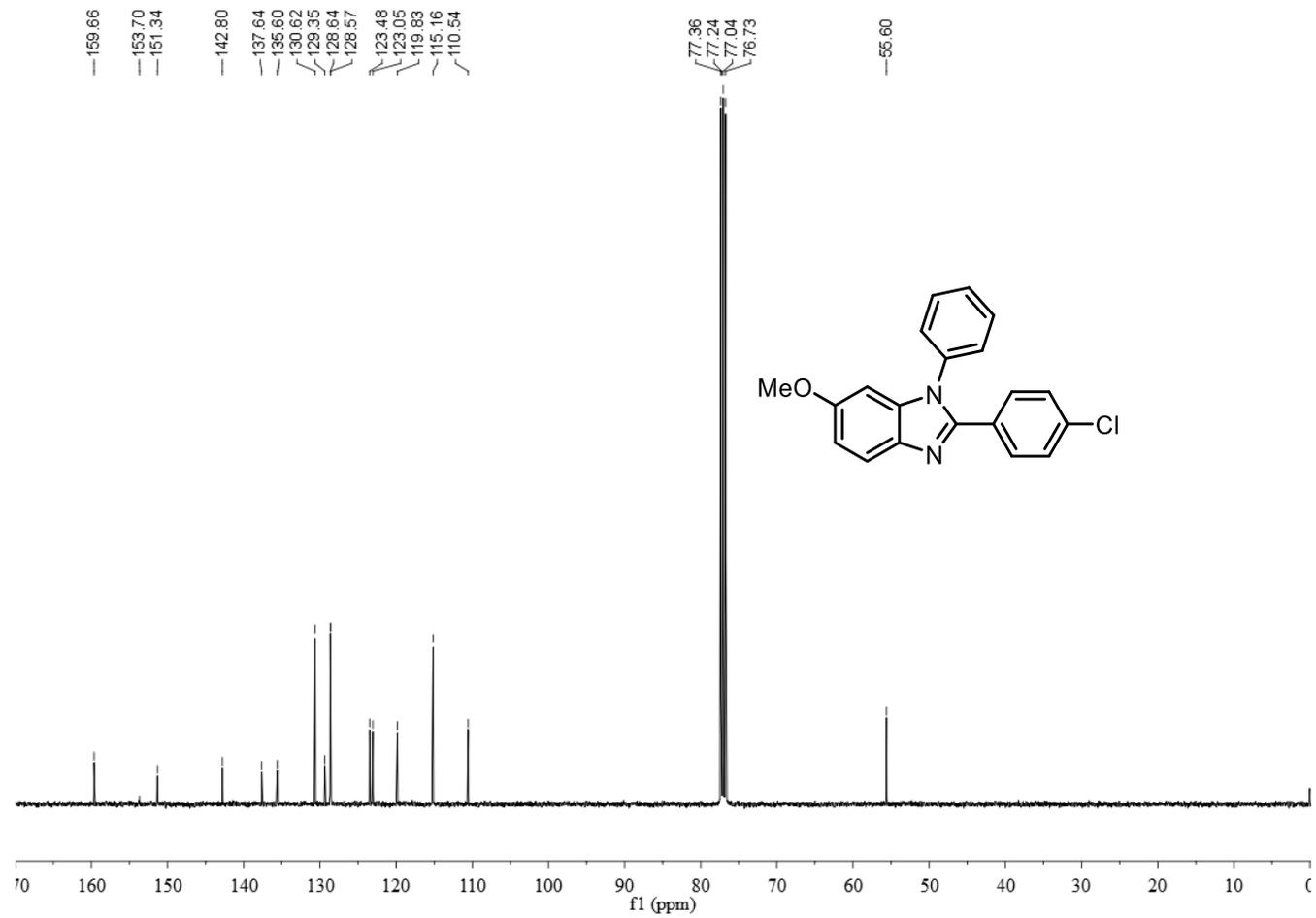
Compound 4ap



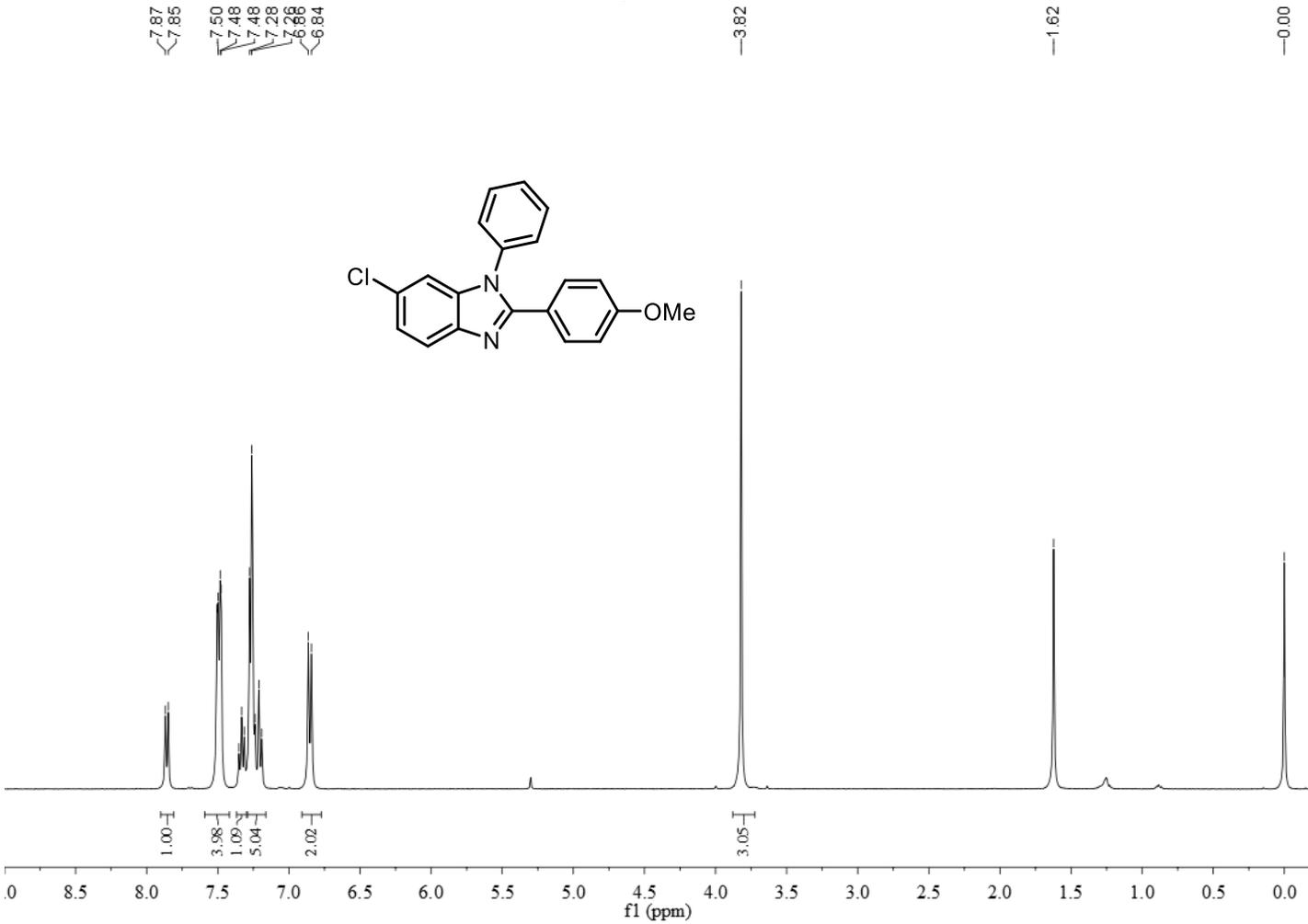


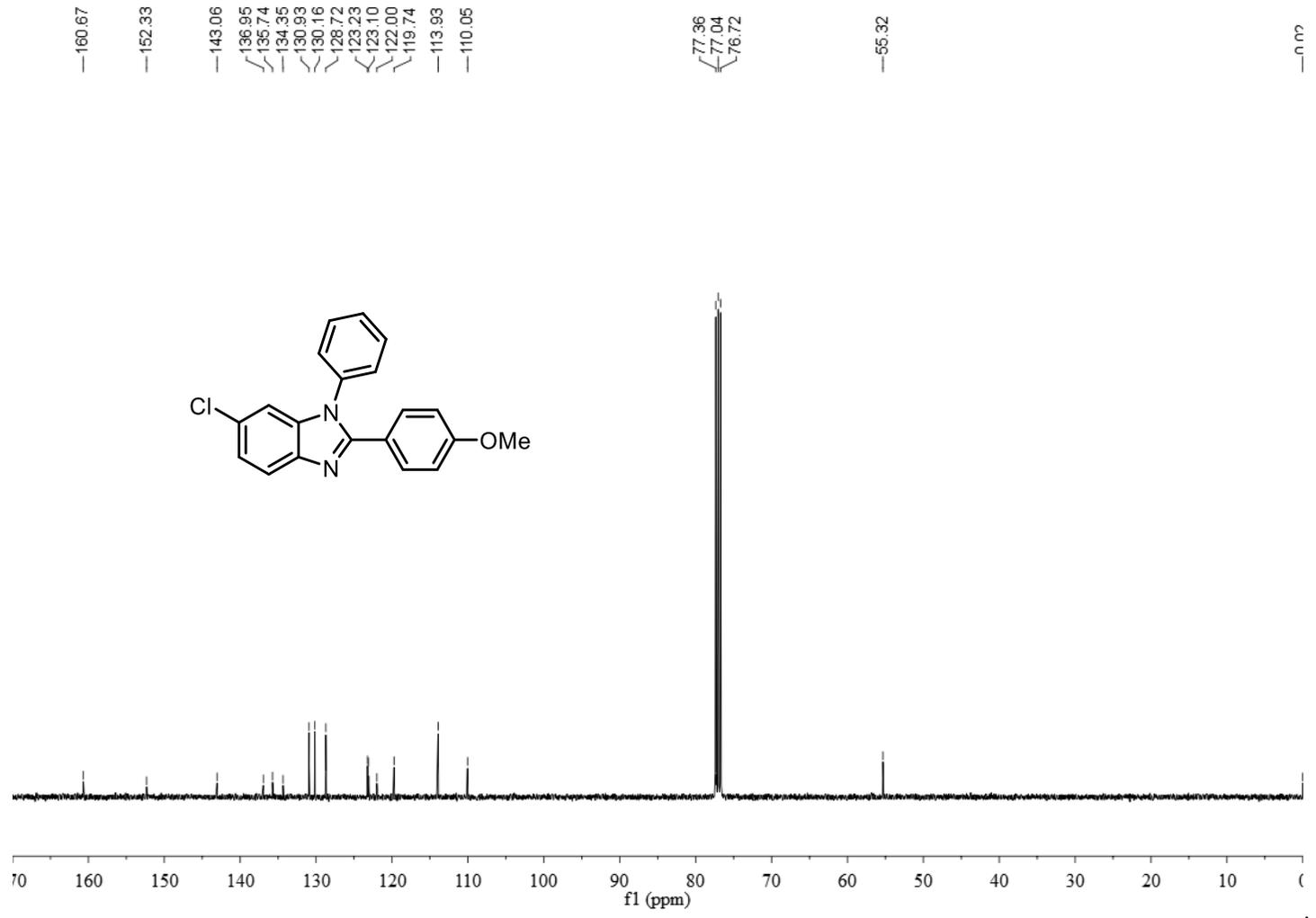
Compound 4aa





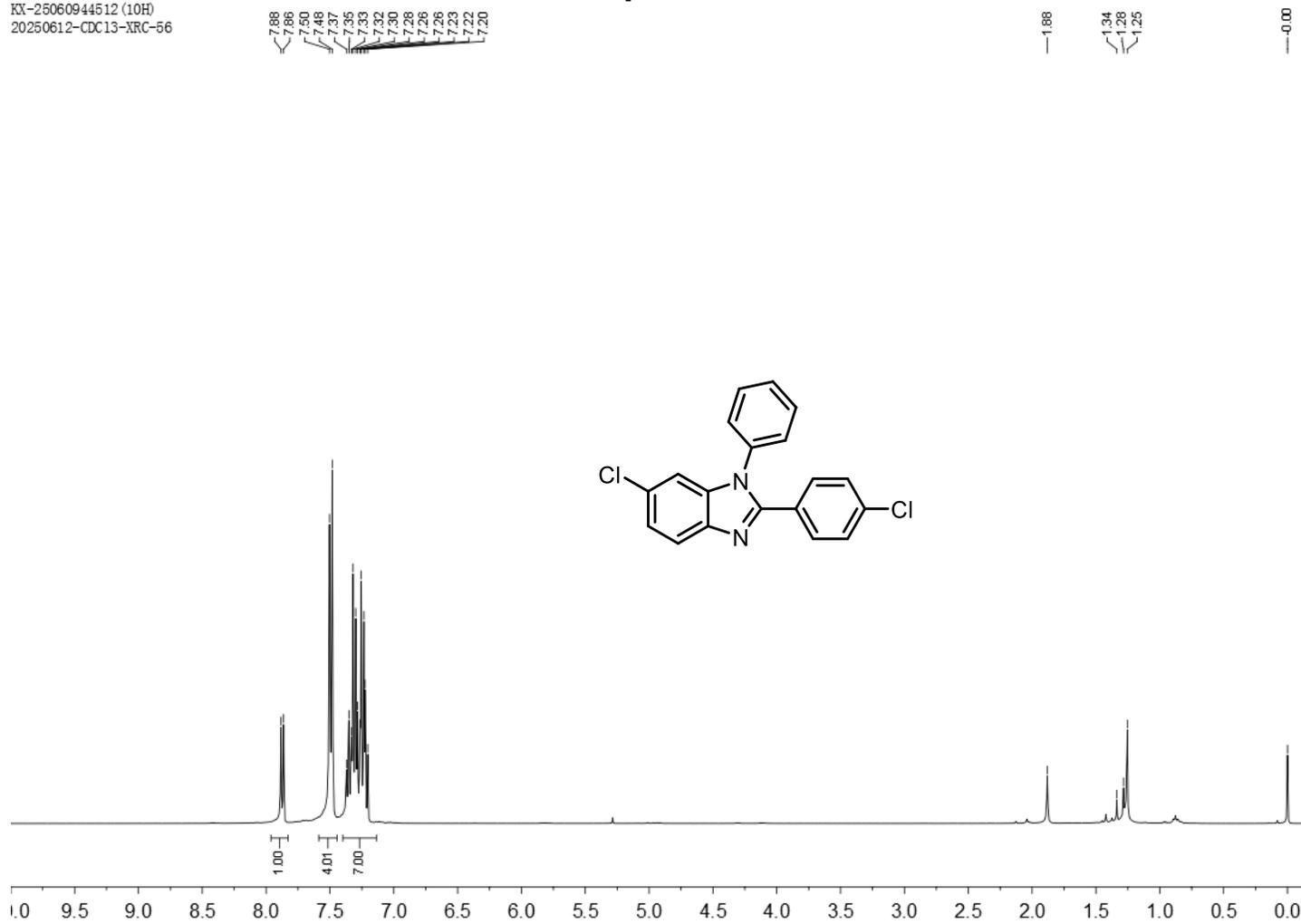
Compound 4ar



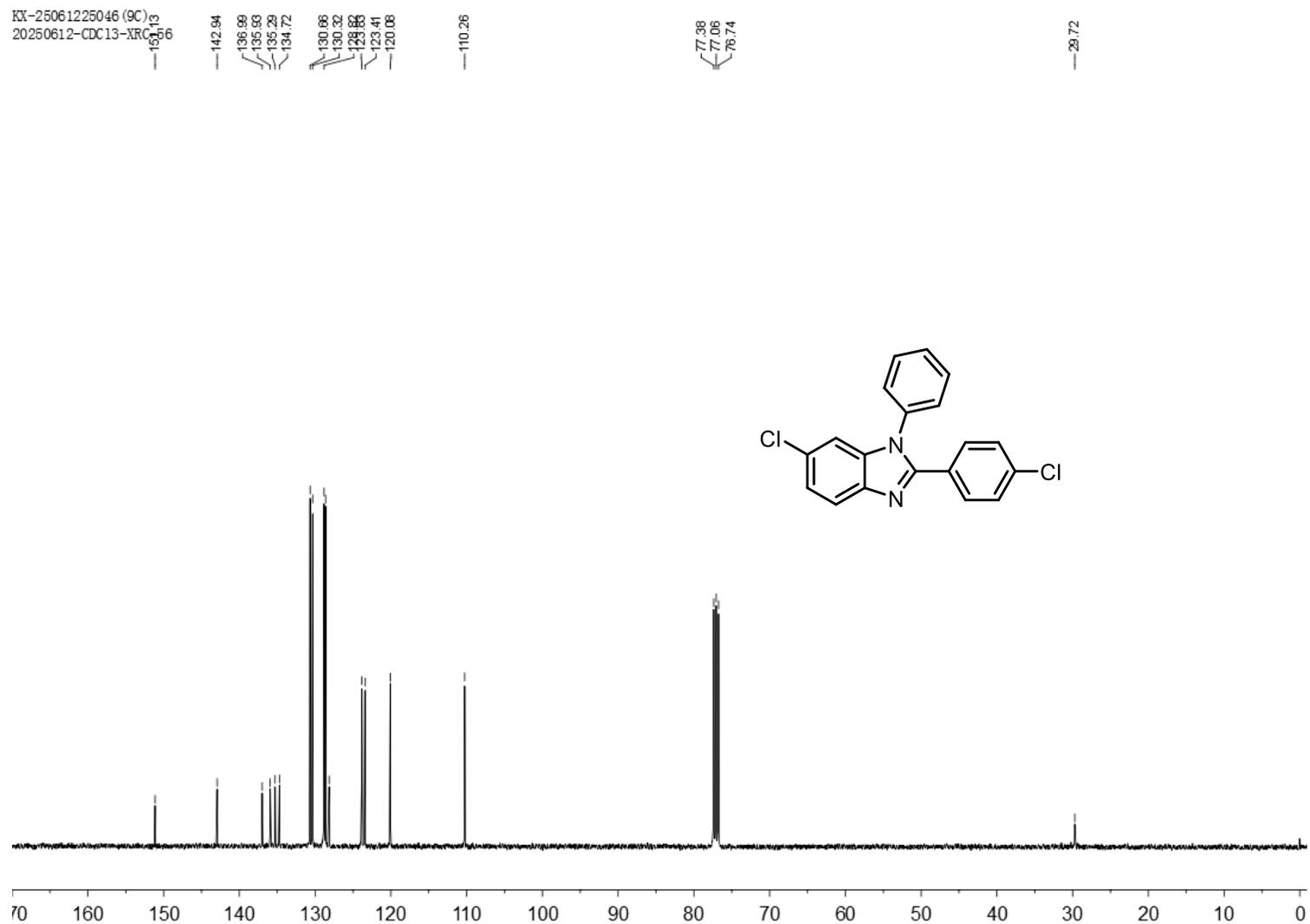


KX-25060944512 (10H)
20250612-CDC13-XRC-56

Compound 4as

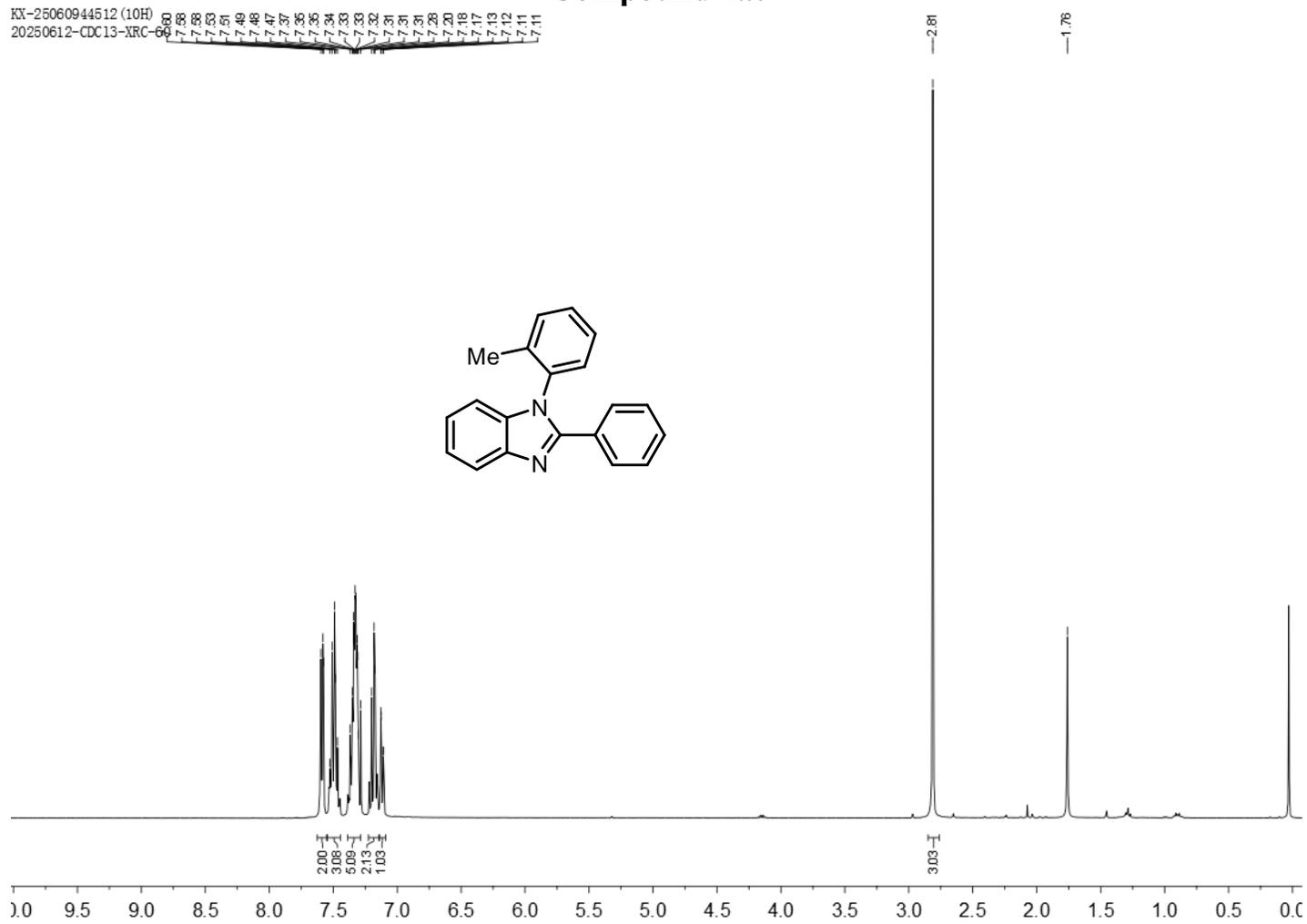


KX-25061225046 (9C)
20250612-CDC13-XRQ



Compound 4at

KX-25060944512 (10H)
20250612-CDC13-XRC-66



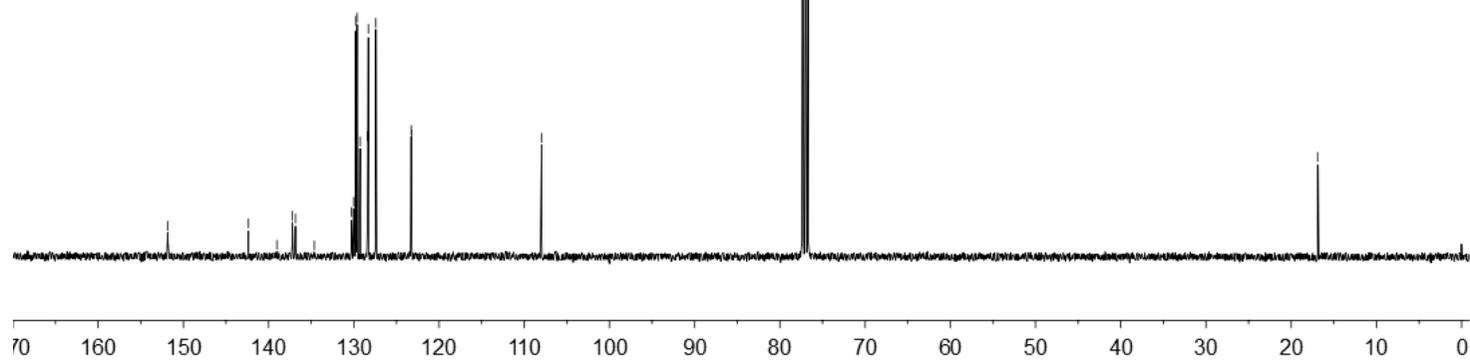
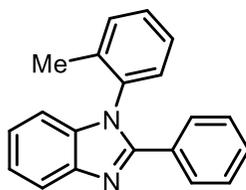
KX-25061225046 (QC)
20250612-CDC13-XR-60

142.37
139.01
137.19
136.84
134.63
129.76
129.60
128.29
127.56
123.23

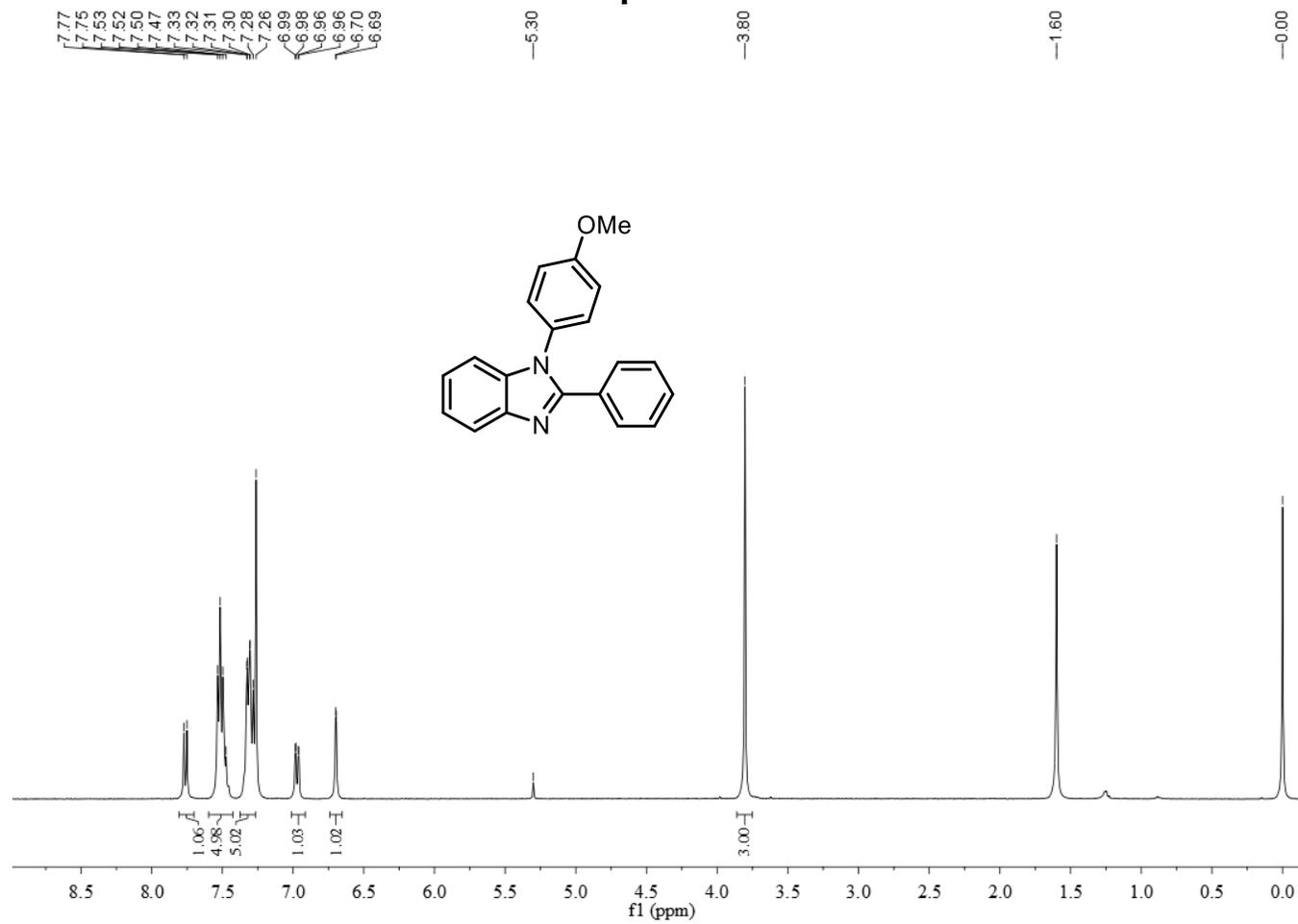
107.96

77.36
77.04
76.72

16.87

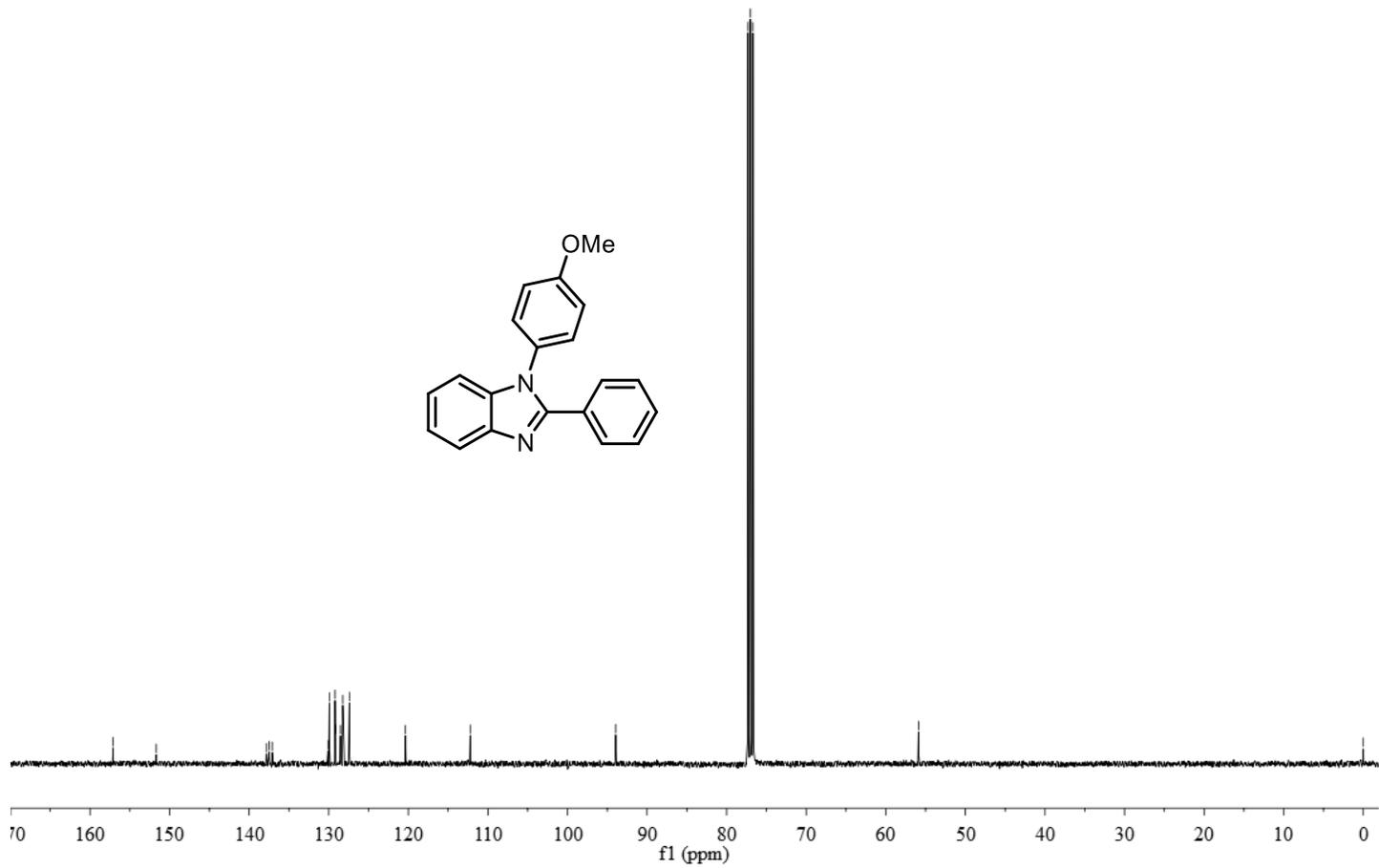
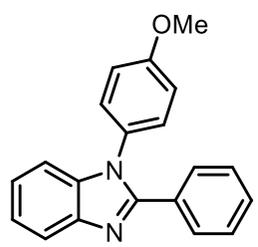


Compound 4au



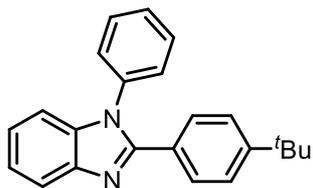
2022XUF
WJZ-72
13C
CDCl3
2022XUF-121

—157.11 —151.67
137.84 137.50 137.09
129.92 129.20 129.13 128.24 127.39
—112.22 —93.93
77.33 77.22 77.02 76.70
—55.89 —0.00



8. Copy of HRMS Spectra

Compound 3af

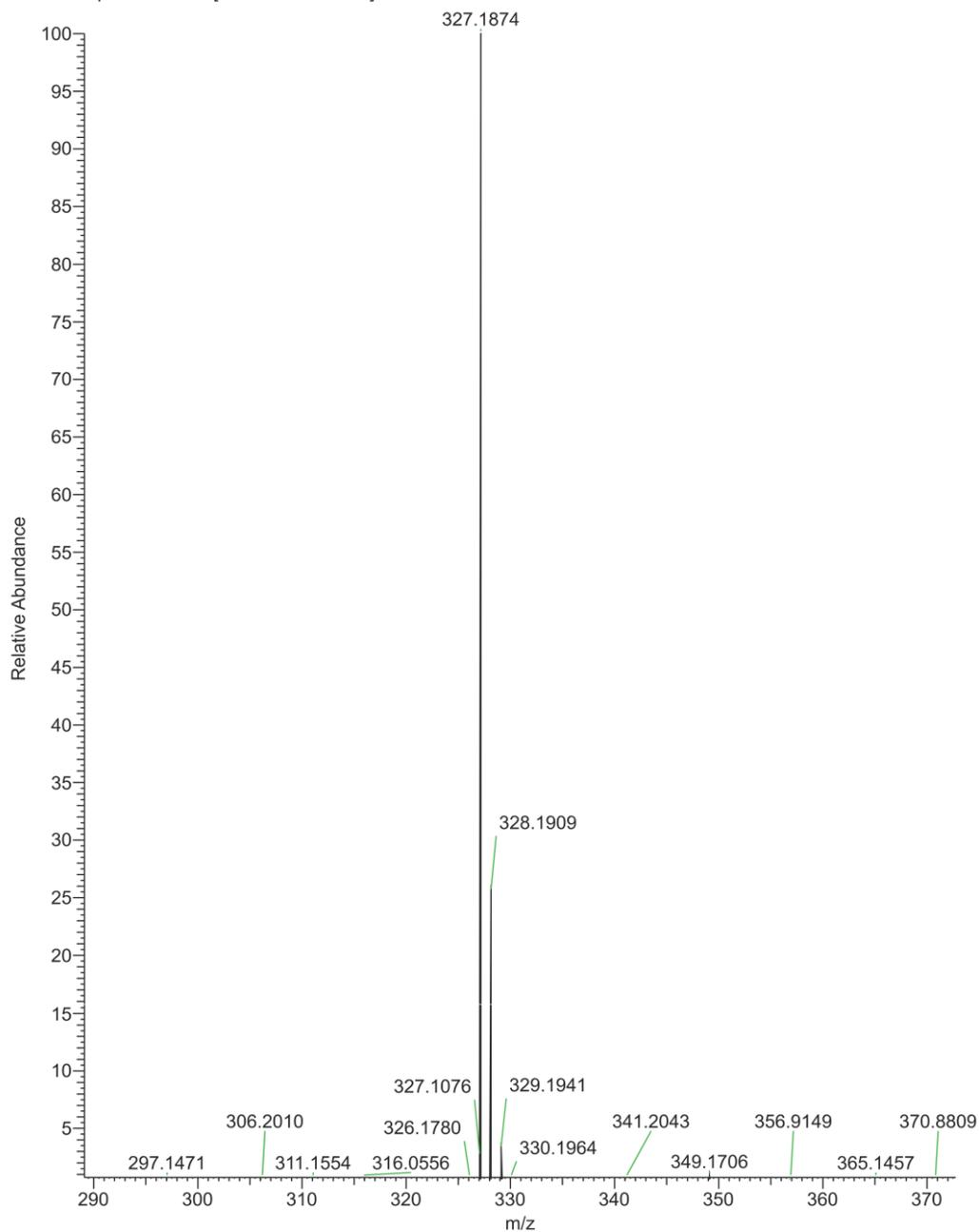


D:\DATA\2026\26030901284\XRC-HRMS-1\50-500.raw

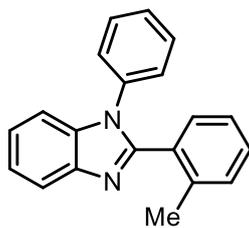
3/16/2026 15:16:30

50-500 #1013-1077 RT: 0.62-0.66 AV: 65 NL: 4.74E9

T: FTMS + p ESI Full ms [50.0000-500.0000]



Compound 3ah

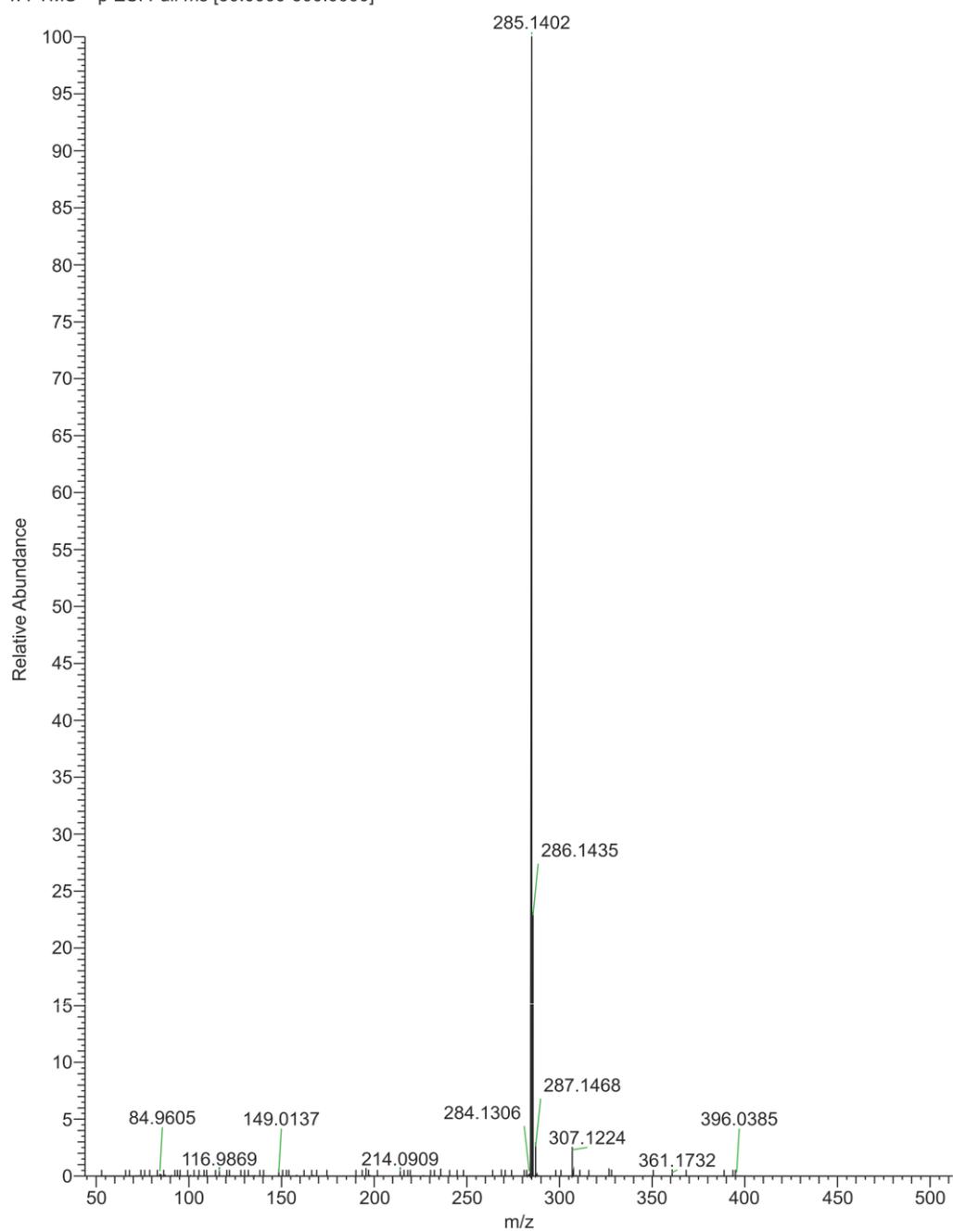


D:\DATA\2026\26030901284\XRC-HRMS-2\50-500.raw

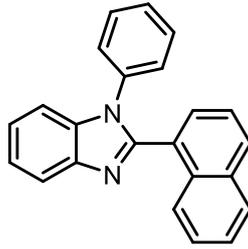
3/16/2026 15:21:19

50-500 #1014-1044 RT: 0.62-0.64 AV: 31 NL: 3.68E9

T: FTMS + p ESI Full ms [50.0000-500.0000]



Compound 3aj

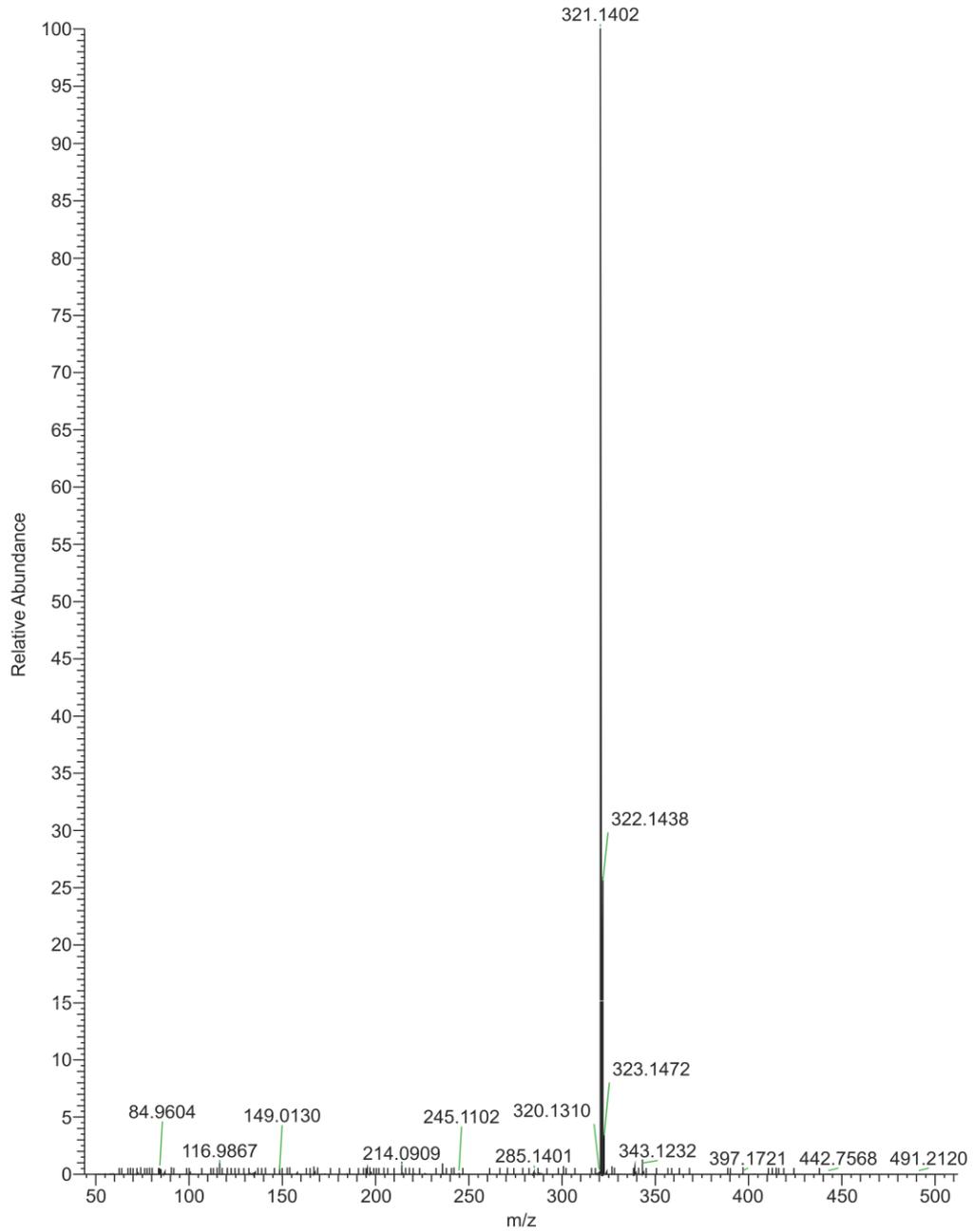


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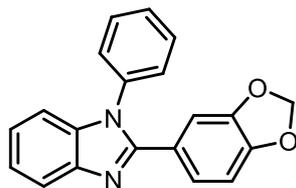
3/16/2026 15:22:59

50-500 #1000-1016 RT: 0.61-0.62 AV: 17 NL: 1.95E9

T: FTMS + p ESI Full ms [50.0000-500.0000]



Compound 3ak

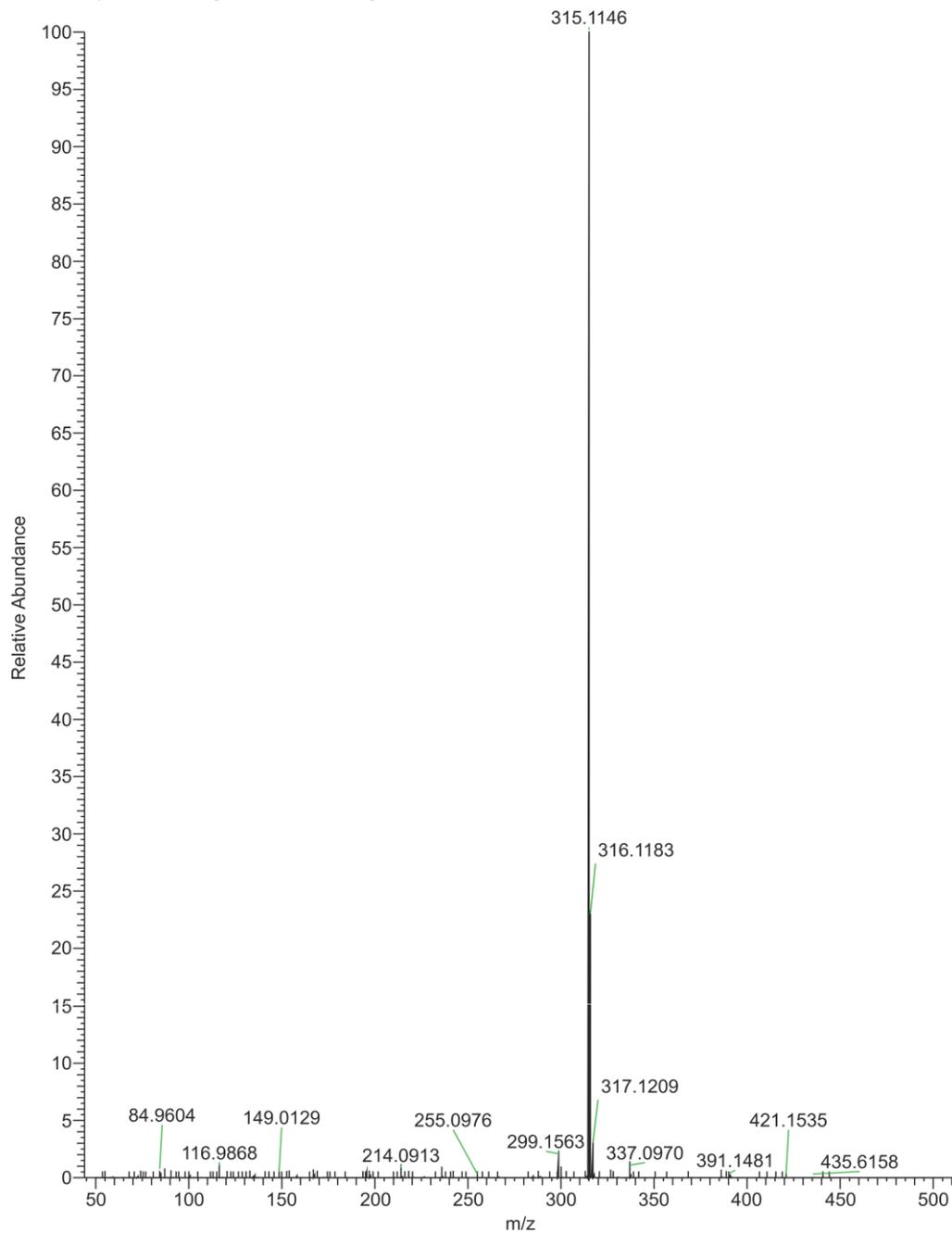


D:\DATA\2026\26030901284\XRC-HRMS-4\50-500.raw

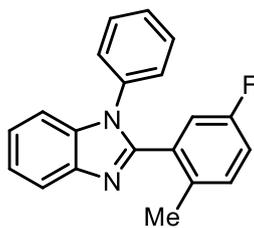
3/16/2026 15:24:42

50-500 #1002-1028 RT: 0.61-0.63 AV: 27 NL: 1.86E9

T: FTMS + p ESI Full ms [50.0000-500.0000]

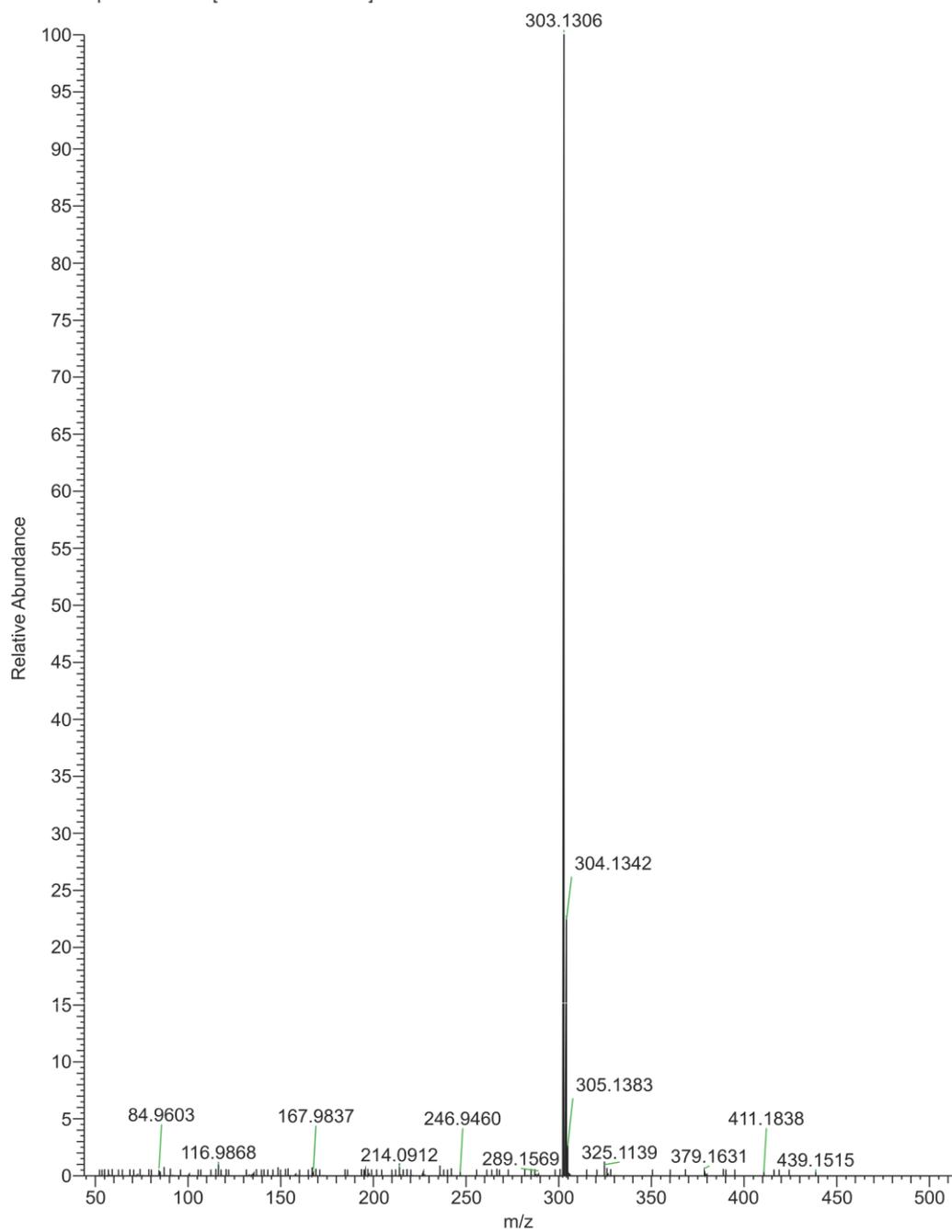


Compound 3al

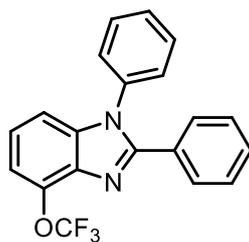


D:\DATA\2026\26030901284\XRC-HRMS-5\50-500.raw
50-500 #996-1011 RT: 0.61-0.62 AV: 16 NL: 2.00E9
T: FTMS + p ESI Full ms [50.0000-500.0000]

3/16/2026 15:26:23



Compound 4ao

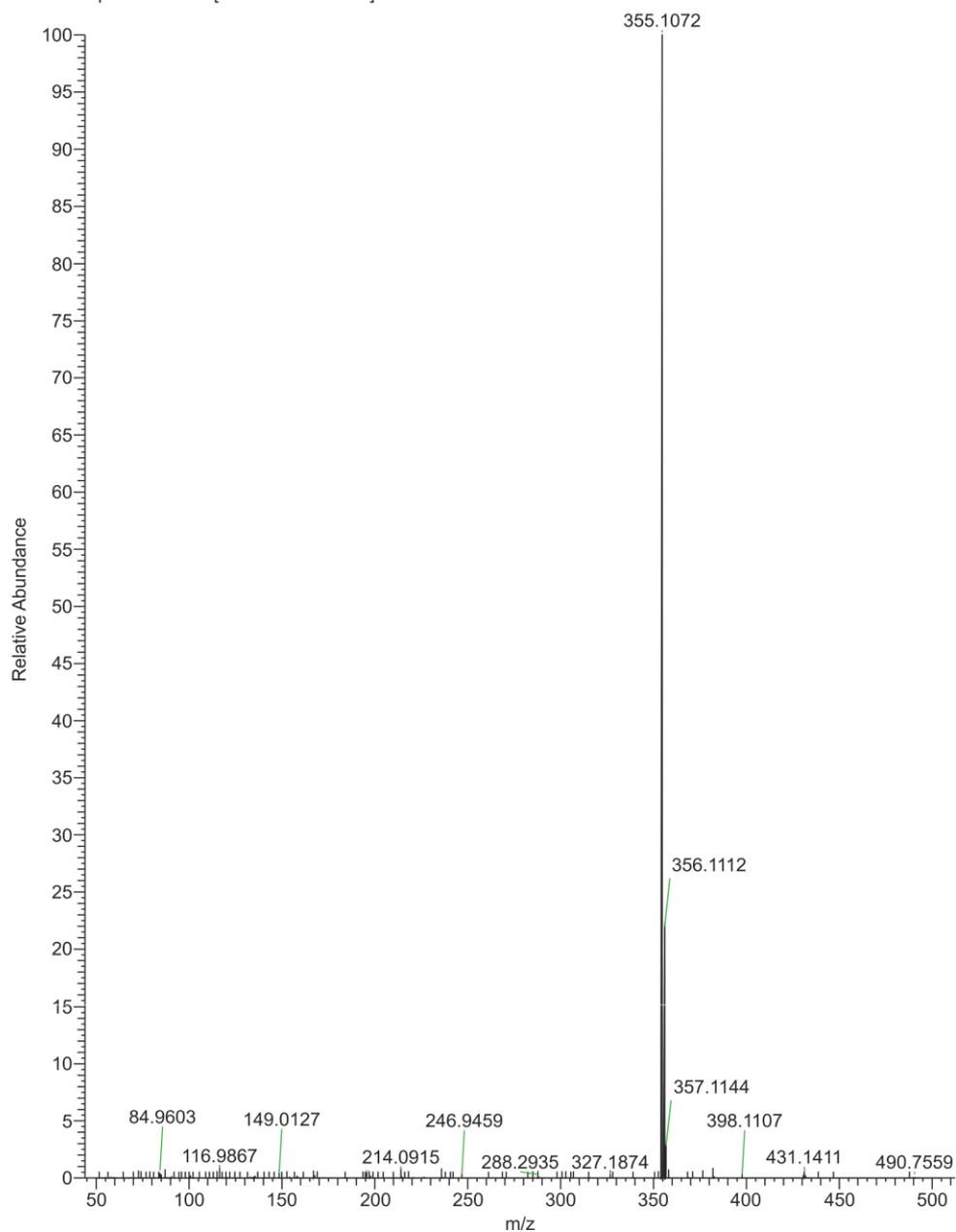


D:\DATA\2026\26030901284\XRC-HRMS-6\50-500.raw

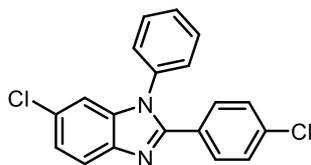
3/16/2026 15:28:12

50-500 #1012-1032 RT: 0.62-0.63 AV: 21 NL: 2.27E9

T: FTMS + p ESI Full ms [50.0000-500.0000]

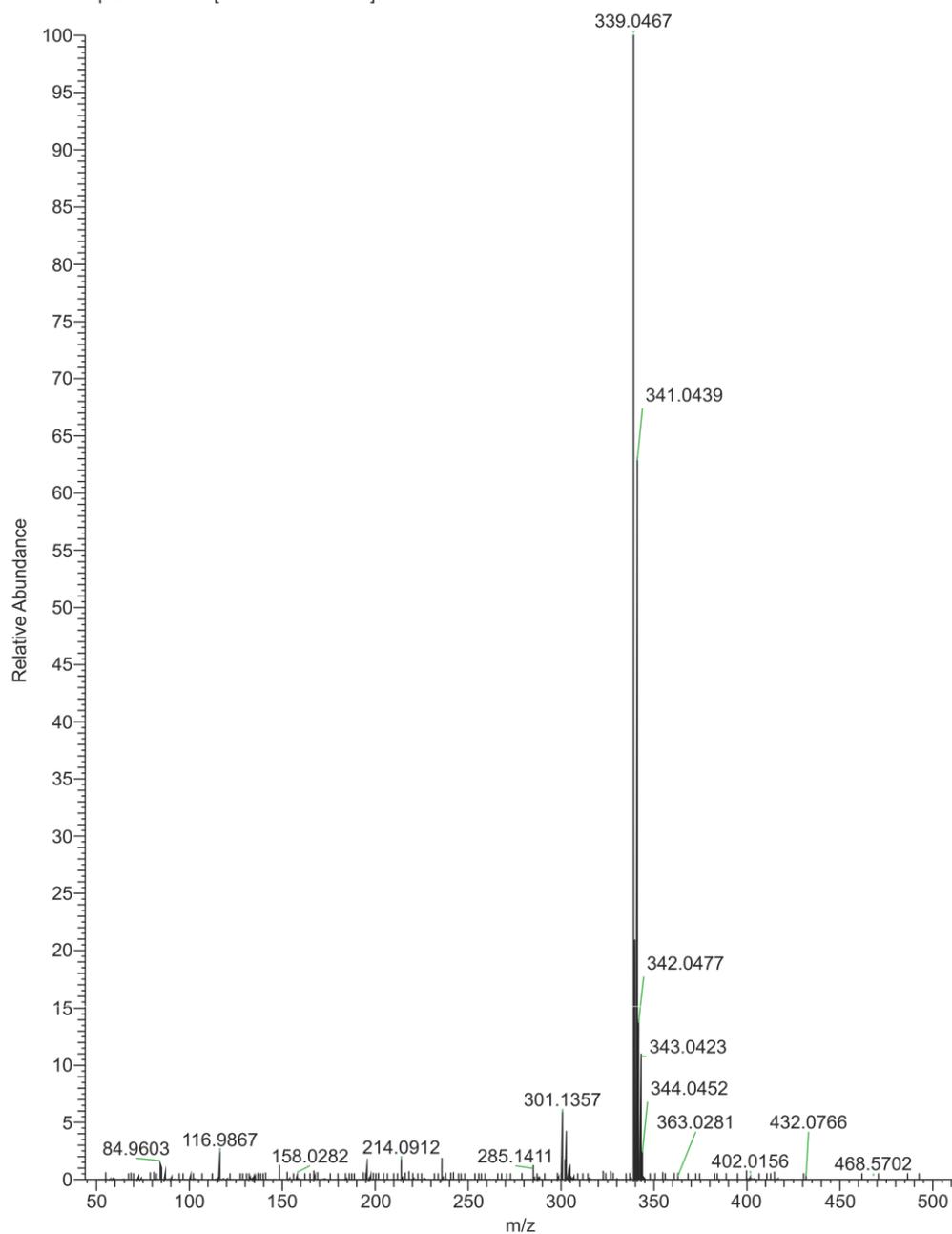


Compound 4as

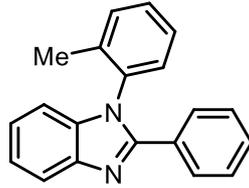


D:\DATA\2026\26030901284\XRC-HRMS-7\50-500.raw
50-500 #1013-1049 RT: 0.62-0.64 AV: 37 NL: 8.05E8
T: FTMS + p ESI Full ms [50.0000-500.0000]

3/16/2026 15:29:57



Compound 4at

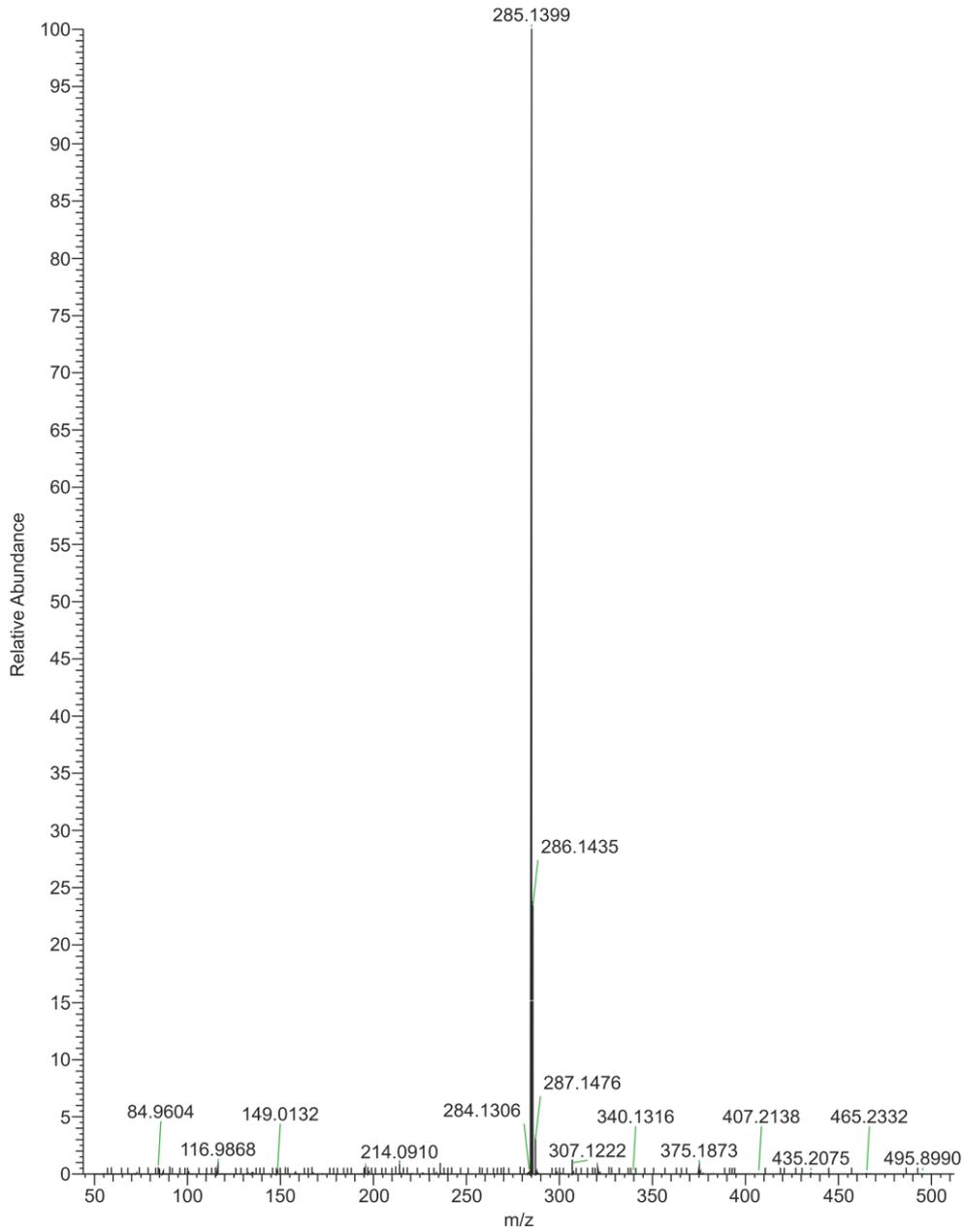


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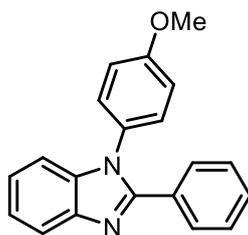
3/16/2026 15:31:33

50-500 #1006-1044 RT: 0.62-0.64 AV: 39 NL: 1.80E9

T: FTMS + p ESI Full ms [50.0000-500.0000]



Compound 4au



D:\DATA\2026\26030901284\XRC-HRMS-9\50-500.raw

3/16/2026 15:33:26

50-500 #1010-1044 RT: 0.62-0.64 AV: 35 NL: 9.32E8

T: FTMS + p ESI Full ms [50.0000-500.0000]

