Supplementary Information

One-shot Indole-to-Carbazole π-Extension by Pd-Cu-Ag Trimetallic System

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1. Experimental Section

General

Unless otherwise noted, all materials including the dry solvent (dimethyl sulfoxide (DMSO)) were obtained from commercial suppliers and used as received. Toluene and 1,4-dioxane were purified by passing through a solvent purification system (Glass Contour). 1-Benzyl-1*H*-indole (**1b**)[1], 1,5-dimethyl-1*H*-indole (**1d**)[2], 5-methoxy-1-methyl-1*H*-indole (**1e**)[3], 5-fluoro-1-methyl-1*H*-indole (**1f**)[1], 5-chloro-1-methyl-1*H*-indole (**1g**)[2], 7-methoxy-1-methyl-1*H*-indole (**1h**)[4], 1-methyl-1*H*-pyrrolo[2,3-*b*]pyridine (**1i**)[5], 1-propyl-1*H*-indole (**1j**)[6],1-phenylprop-2-en-1-one (**2b**)[7], 1-(4-fluorophenyl)prop-2-en-1-one (**2c**)[8], 1-(4-chlorophenyl)prop-2-en-1-one (**2d**)[9], 1-(4-methoxyphenyl)prop-2-en-1-one (**2e**)[10], 1-(4-cyclohexyl-phenyl)prop-2-en-1-one (**2f**)[7], (*E*)-4-(1-methyl-1*H*-indol-3-yl)but-3-en-2-one (**4**)[11], 4-(1-methyl-1*H*-indol-3-yl)butan-2-one (**5**)[12] were synthesized according to procedures reported in the literature. Unless otherwise noted, all reactions were performed with dry solvents under air in flame-dried glassware. All π-extension reactions were performed in screw cap 7-mL glass vessel tubes and heated in a 10-well reaction block (heater + magnetic stirrer) unless otherwise noted. All work-up and purification procedures were carried out with reagent-grade solvents in air.

Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F_{254} precoated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm). Flash column chromatography was performed with E. Merck silica gel 60 (230–400 mesh). Gas chromatography (GC) analysis was conducted on a Shimadzu GC-2010 instrument equipped with a HP-5 column (30 m × 0.25 mm, Hewlett-Packard). GC yields are expressed vs. *n*-dodecane as an internal standard. High-resolution mass spectra (HRMS) were obtained from JMS-T100TD (DART) or JMS-700 (FAB) instruments. Nuclear magnetic resonance (NMR) spectra were recorded on JEOL ECS-400 (^{1}H 400 MHz, ^{13}C 100 MHz), JEOL ECA-500 (^{1}H 500 MHz, ^{13}C 125 MHz), or JEOL ECA-600 (^{1}H 600 MHz, ^{13}C 150 MHz) spectrometer. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm) or DMSO (δ 2.50 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.16 ppm) or DMSO (δ 39.52 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, td = triplet of doublets, m = multiplet, br = broad signal), coupling constant (Hz), and integration.

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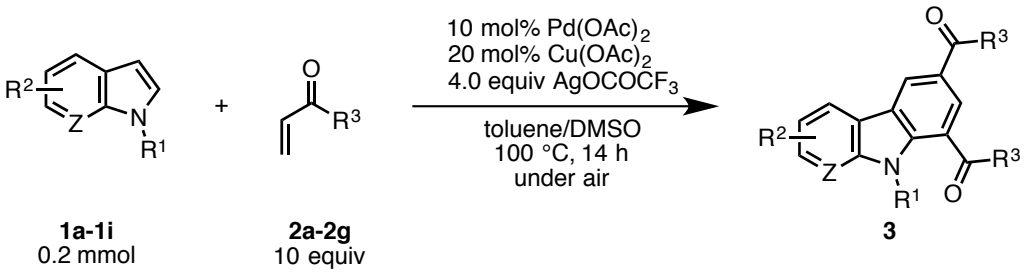
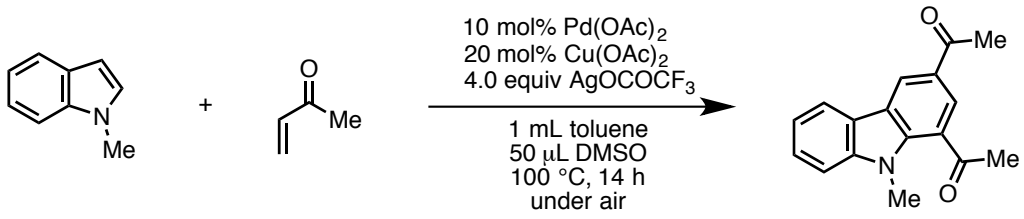
General Procedure for Direct Indole-to-Carbazole π-Extension



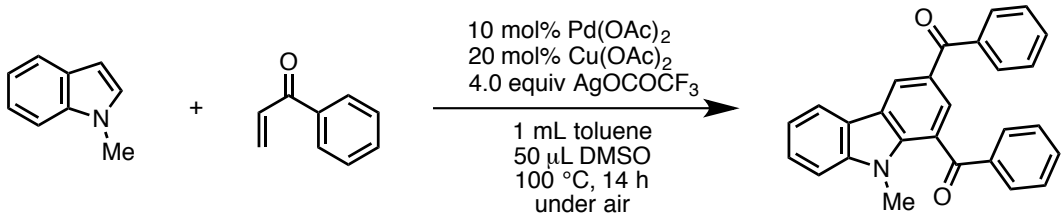
A 7-mL screw test tube containing a magnetic stirring bar was dried *in vacuo* with heating by heat-gun. After cooling, $Pd(OAc)_2$ (4.5 mg, 20 μmol), $Cu(OAc)_2$ (7.3 mg, 40 μmol), $AgOCOCF_3$ (176 mg, 0.80 mmol), alkene **2** (2.0 mmol), indole **1** (0.20 mmol), toluene and DMSO were added under air. The vessel was sealed with a cap and then the mixture was heated at 100 °C for 14 h with stirring. After cooling to room temperature, the reaction mixture was passed through a pad of Celite® and washed with EtOAc, then the filtrate was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford carbazole **3**.

Compound Data of Coupling Products



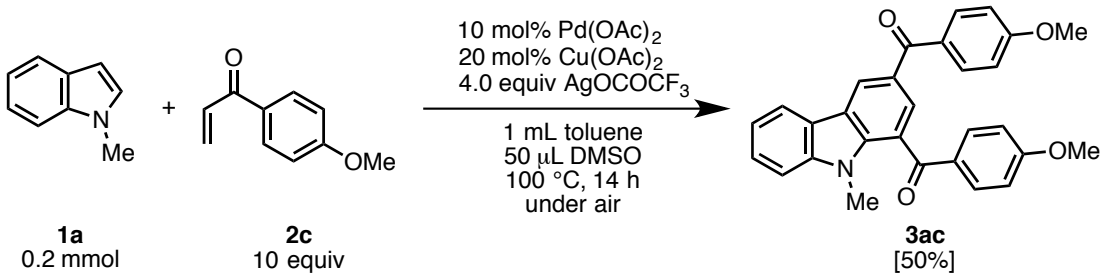
1a 0.2 mmol **2a** 10 equiv **3aa** [70%]

1,3-Diacetyl-9-methyl-9*H*-carbazole (3aa): Following the general procedure with 1-methylindole (**1a**: 26 mg) and methyl vinyl ketone (**2a**: 140 mg) in toluene (1 mL) and DMSO (50 μL), the crude product was purified by flash column chromatography (hexane/EtOAc = 3:1) to give **3aa** (37 mg, 70%) as a pale yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.77 (d, *J* = 1.8 Hz, 1H), 8.41 (d, *J* = 1.6 Hz, 1H), 8.12 (dd, *J* = 7.1, 0.8 Hz, 1H), 7.55 (td, *J* = 6.2, 1.1 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.34 (td, *J* = 7.1, 1.1 Hz, 1H), 3.78 (s, 3H), 2.83 (s, 3H), 2.74 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 200.1, 196.8, 143.1, 140.6, 127.6, 127.3, 127.2, 125.4, 124.6, 124.3, 122.6, 121.0, 120.2, 110.0, 34.1, 29.7, 26.6; HRMS (DART) *m/z* calcd for $C_{17}H_{16}NO_2$ $[M+H]^+$: 266.1181, found: 266.1180.

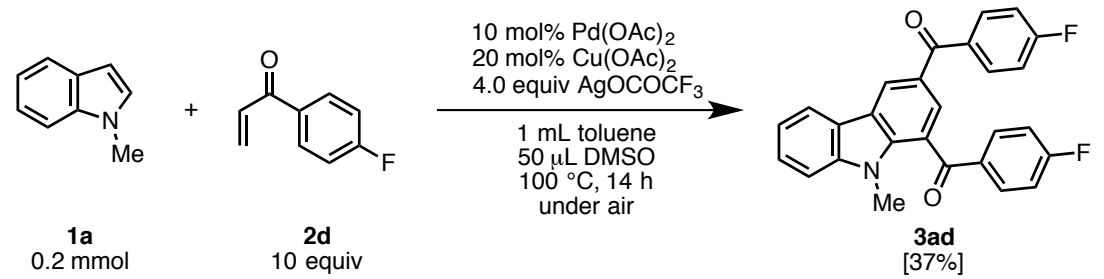


1a 0.2 mmol **2b** 10 equiv **3ab** [53%]

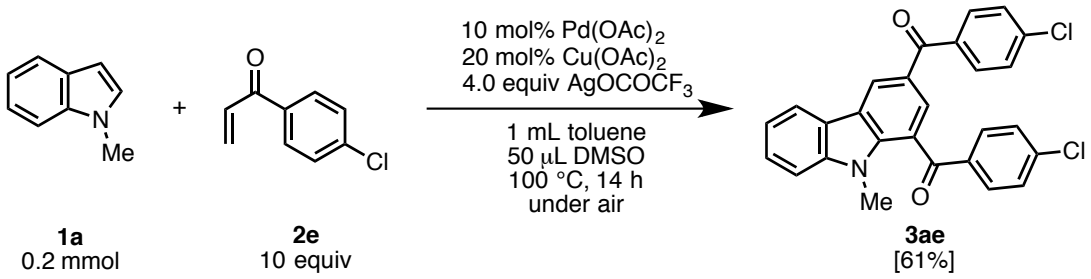
1,3-Dibenzoyl-9-methyl-9*H*-carbazole (3ab): Following the general procedure with 1-methylindole (**1a**: 26 mg) and 1-phenyl-2-propen-1-one (**2b**: 264 mg) in toluene (1 mL) and DMSO (50 μL), the crude product was purified by flash column chromatography (hexane/EtOAc = 15:1) to give **3ab** (41 mg, 53%) as a pale yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.75 (d, *J* = 1.6 Hz, 1H), 8.16 (d, *J* = 7.7 Hz, 1H), 8.04 (d, *J* = 1.8 Hz, 1H), 7.98–7.96 (m, 2H), 7.84–7.82 (m, 2H), 7.65 (m, 8H), 7.34 (td, *J* = 7.6, 0.9 Hz, 1H), 3.68 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 195.93, 195.91, 142.7, 141.2, 138.4, 137.7, 133.9, 132.1, 130.8, 130.0, 129.9, 128.8, 128.4, 127.5, 127.3, 125.7, 124.8, 122.8, 122.4, 120.9, 120.7, 109.7, 33.3; HRMS (DART) *m/z* calcd for $C_{27}H_{20}NO_2$ $[M+H]^+$: 390.1494, found: 390.1495.



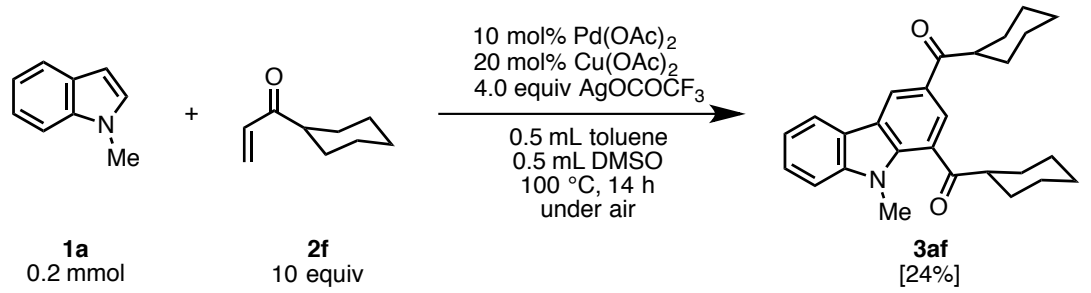
1,3-Di(4-methoxybenzoyl)-9-methyl-9*H*-carbazole (3ac): Following the general procedure with 1-methylindole (**1a**: 26 mg) and 1-(4-methoxyphenyl)prop-2-en-1-one (**2c**: 324 mg) in toluene (1 mL) and DMSO (50 μL), the crude product was purified by flash column chromatography (hexane/EtOAc = 3:1) to give **3ac** (45 mg, 50%) as a pale yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.70 (d, *J* = 1.6 Hz, 1H), 8.15 (d, *J* = 7.8 Hz, 1H), 7.97–7.91 (m, 3H), 7.87–7.85 (m, 2H), 7.54 (td, *J* = 7.6, 1.1 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.33 (td, *J* = 7.6, 0.9 Hz, 1H), 6.99–6.94 (m, 4H), 3.88 (s, 3H), 3.87 (s, 3H), 3.67 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.9, 194.8, 164.3, 163.0, 142.6, 140.7, 133.2, 132.5, 131.0, 129.2, 128.2, 127.2, 124.9, 124.6, 122.8, 122.7, 120.69, 120.67, 120.63, 114.1, 113.7, 109.5, 55.7, 55.6, 33.0; HRMS (DART) *m/z* calcd for $C_{29}H_{24}NO_4$ $[M+H]^+$: 450.1705, found: 450.1709.



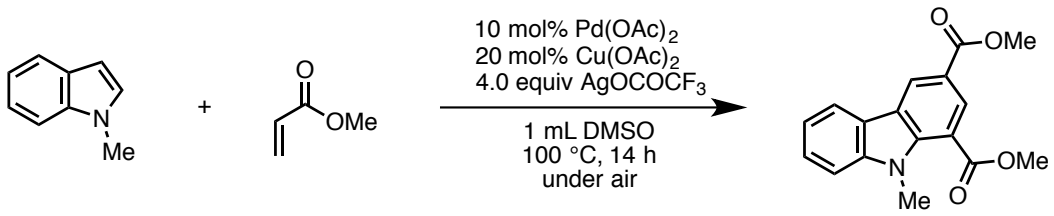
1,3-Di(4-fluorobenzoyl)-9-methyl-9*H*-carbazole (3ad): Following the general procedure with 1-methylindole (**1a**: 26 mg) and 1-(4-fluorophenyl)-2-propen-1-one (**2d**: 300 mg) in toluene (1 mL) and DMSO (50 μL), the crude product was purified by flash column chromatography (hexane/EtOAc = 15:1) to give **3ad** (32 mg, 37%) as a pale yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.71 (d, *J* = 1.6 Hz, 1H), 8.16 (d, *J* = 7.7 Hz, 1H), 8.02–7.97 (m, 3H), 7.89–7.85 (m, 2H), 7.58 (td, *J* = 7.9, 1.1 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.36 (td, *J* = 7.5, 0.9 Hz, 1H), 7.21–7.16 (m, 4H), 3.68 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ194.3, 194.2, 166.3 (d, *J* = 255 Hz), 165.3 (d, *J* = 253 Hz), 142.7, 141.0, 134.6 (d, *J* = 2.8 Hz), 134.1 (d, *J* = 2.8 Hz), 133.4 (d, *J* = 8.5 Hz), 132.5 (d, *J* = 8.7 Hz), 129.4, 127.5, 127.4, 125.5, 124.9, 122.7, 122.2, 121.0, 120.6, 116.1 (d, *J* = 25 Hz), 115.6 (d, *J* = 21 Hz), 109.7, 33.2; HRMS (DART) *m/z* calcd for $C_{27}H_{18}F_2NO_2$ $[M+H]^+$: 426.1306, found: 426.1306.



1,3-Di(4-chlorobenzoyl)-9-methyl-9*H*-carbazole (3ae): Following the general procedure with 1-methylindole (**1a**: 26 mg) and 1-(4-chlorophenyl)-2-propen-1-one (**2e**: 333 mg) in toluene (1 mL) and DMSO (50 μL), the crude product was purified by flash column chromatography (hexane/EtOAc = 30:1) to give **3ae** (56 mg, 61%) as a pale yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.70 (d, *J* = 1.6 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 1.6 Hz, 1H), 7.92–7.89 (m, 2H), 7.79–7.76 (m, 2H), 7.59 (td, *J* = 7.6, 1.1 Hz, 1H), 7.56–7.47 (m, 5H), 7.36 (td, *J* = 7.6, 0.9 Hz, 1H), 3.68 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.5, 194.4, 142.7, 141.1, 140.6, 138.6, 136.6, 136.0, 132.0, 131.4, 129.4, 129.2, 128.7, 127.5, 127.2, 125.7, 124.9, 122.6, 122.0, 121.0, 120.6, 109.7, 33.3; HRMS (DART) *m/z* calcd for $C_{27}H_{18}Cl_2NO_2$ $[M+H]^+$: 458.0715, found: 458.0716.

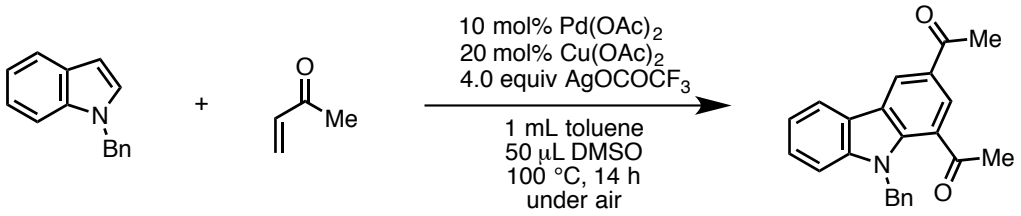


1,3-Dicyclohexanecarbonyl-9-methyl-9*H*-carbazole (3af): Following the general procedure with 1-methylindole (**1a**: 26 mg) and 1-(4-cyclohexylphenyl)prop-2-en-1-one (**2f**: 276 mg) in toluene (0.5 mL) and DMSO (0.5 mL), the crude product was purified by flash column chromatography (hexane/EtOAc = 25:1) to give **3af** (19 mg, 24%) as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.77 (d, *J* = 1.8 Hz, 1H), 8.34 (d, *J* = 1.2 Hz, 1H), 8.17 (d, *J* = 7.8 Hz, 1H), 7.55 (td, *J* = 7.2, 1.2 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 1H), 3.72 (s, 3H), 3.46 (tt, *J* = 11.4, 3.6 Hz, 1H), 3.40 (tt, *J* = 11.4, 3.6 Hz, 1H), 2.06–1.75 (m, 10H), 1.65–1.25 (m, 10H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 206.7, 202.8, 142.9, 140.7, 127.2, 126.7, 126.4, 125.1, 124.5, 123.6, 122.7, 120.8, 120.3, 109.8, 49.2, 45.6, 33.5, 29.9, 29.5, 26.1, 26.09, 26.06, 25.9; HRMS (DART) *m/z* calcd for $C_{27}H_{32}NO_2$ $[M+H]^+$: 402.2433, found: 402.2432.



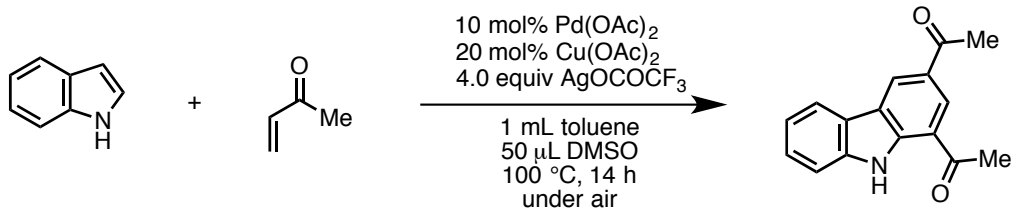
1a 0.2 mmol + **2g** 10 equiv → **3ag** [44%]

Dimethyl 9-methyl-9*H*-carbazole-1,3-dicarboxylate (3ag): Following the general procedure with 1-methylindole (**1a**: 26 mg) and methyl acrylate (**2g**: 172 mg) in DMSO (1 mL), the crude product was purified by flash column chromatography (hexane/EtOAc = 3:1) to give **3ag** (26 mg, 44%) as a pale yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.91 (d, *J* = 1.6 Hz, 1H), 8.58 (d, *J* = 1.8 Hz, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 6.0 Hz, 1H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.34 (t, *J* = 7.1 Hz, 1H), 4.04 (s, 3H), 3.99 (s, 3H), 3.93 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.5, 167.1, 143.1, 141.4, 130.1, 127.3, 125.6, 125.5, 122.6, 120.9, 120.4, 120.2, 115.0, 109.8, 52.6, 52.2, 33.6; HRMS (DART) *m/z* calcd for $C_{17}H_{16}NO_4$ $[M+H]^+$: 298.1079, found: 298.1080.



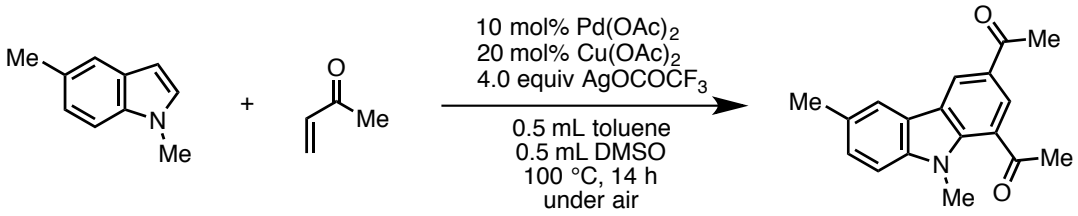
1b 0.2 mmol + **2a** 10 equiv → **3ba** [53%]

9-Benzyl-1,3-diacetyl-9*H*-carbazole (3ba): Following the general procedure with 1-benzyl-1*H*-indole (**1b**: 41 mg) and methyl vinyl ketone (**2a**: 140 mg) in toluene (1 mL) and DMSO (50 μL), the crude product was purified by flash column chromatography (hexane/EtOAc = 3:1) to give **3ba** (36 mg, 53%) as a pale yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.85 (d, *J* = 1.6 Hz, 1H), 8.22 (d, *J* = 1.6 Hz, 1H), 8.22 (d, *J* = 7.3 Hz, 1H), 7.56–7.55 (m, 2H), 7.42–7.40 (m, 1H), 7.177–7.171 (m, 3H), 6.75–6.74 (m, 2H), 5.66 (s, 2H), 2.76 (s, 3H), 2.23 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 200.7, 196.8, 143.2, 138.7, 136.4, 128.8, 128.0, 127.54, 127.52, 126.8, 126.3, 125.9 (2C), 124.3, 122.7, 121.2, 120.4, 110.1, 48.5, 29.1, 26.6.; HRMS (DART) *m/z* calcd for $C_{23}H_{20}NO_2$ $[M+H]^+$: 342.1494, found: 342.1496.



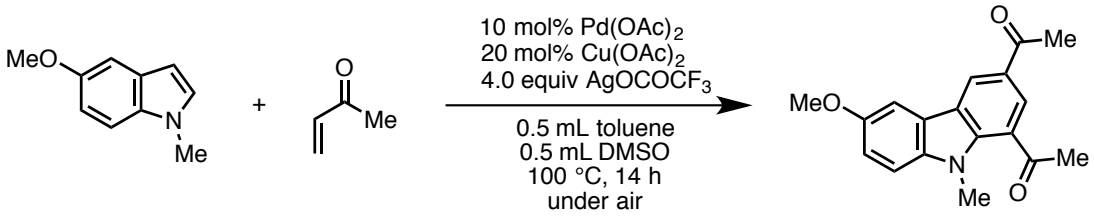
1c 0.2 mmol + **2a** 10 equiv → **3ca** [42%]

1,3-Diacetyl-9*H*-carbazole (3ca): Following the general procedure with 1*H*-indole (**1c**: 23 mg) and methyl vinyl ketone (**2a**: 140 mg) in toluene (1 mL) and DMSO (50 μL), the crude product was purified by flash column chromatography (hexane/EtOAc = 3:1) to give **3ca** (21 mg, 42%) as a pale yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.7 (br, 1H), 8.86 (d, *J* = 1.6 Hz, 1H), 8.64 (d, *J* = 1.6 Hz, 1H), 8.15 (dd, *J* = 7.6, 0.8 Hz, 1H),7.55 (t, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.37 (td, *J* = 7.1, 1.6 Hz, 1H), 2.82 (s, 3H), 2.77 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 200.4, 197.0, 141.6, 140.6, 128.5, 128.4, 127.5, 126.5, 125.0, 122.4, 121.3, 120.7, 118.9, 111.9, 26.9, 26.7; HRMS (DART) *m/z* calcd for $C_{16}H_{14}NO_2$ $[M+H]^+$: 252.1024, found: 252.1023.



1d 0.2 mmol + **2a** 10 equiv → **3da** [52%]

1,3-Diacetyl-6,9-dimethyl-9*H*-carbazole (3da): Following the general procedure with 1,5-dimethyl-1*H*-indole (**1d**: 29 mg) and methyl vinyl ketone (**2a**: 140 mg) in toluene (0.5 mL) and DMSO (0.5 mL), the crude product was purified by flash column chromatography (hexane/EtOAc = 3:1) to give **3da** (29 mg, 52%) as a pale yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.76 (d, *J* = 1.6 Hz, 1H), 8.42 (d, *J* = 1.6 Hz, 1H), 7.93 (d, *J* = 0.7 Hz, 1H), 7.377 (d, *J* = 8.7 Hz, 1H) , 7.371 (d, *J* = 7.2 Hz, 1H), 3.77 (s, 3H), 2.83 (s, 3H), 2.74 (s, 3H), 2.55 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 200.0, 196.8, 141.5, 140.8, 130.5, 128.6, 127.4, 127.1, 125.3, 124.6, 124.2, 122.8, 120.2, 109.7, 34.1, 29.6, 26.5, 21.4; HRMS (DART) *m/z* calcd for $C_{18}H_{18}NO_2$ $[M+H]^+$: 280.1338, found: 280.1336.

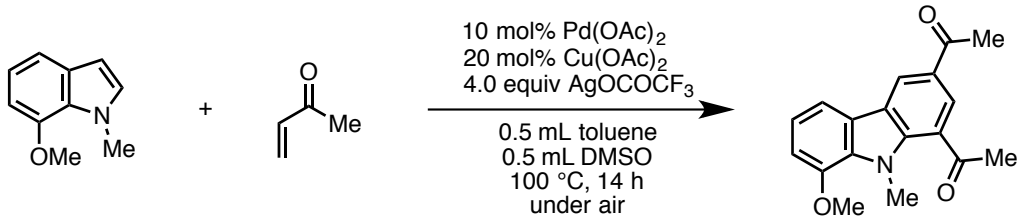


1e
0.2 mmol

2a
10 equiv

3ea
[47%]

1,3-Diacetyl-6-methoxy-9-methyl-9*H*-carbazole (3ea): Following the general procedure with 5-methoxy-1-methyl-1*H*-indole (**1e**: 32 mg) and methyl vinyl ketone (**2a**: 140 mg) in toluene (0.5 mL) and DMSO (0.5 mL), the crude product was purified by flash column chromatography (hexane/EtOAc = 3:1) to give **3ea** (28 mg, 47%) as a pale yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.74 (d, *J* = 1.6 Hz, 1H), 8.40 (d, *J* = 1.8 Hz, 1H), 7.58 (d, *J* = 2.5 Hz, 1H), 7.37 (d, *J* = 9.1 Hz, 1H), 7.17 (dd, *J* = 9.1, 2.5 Hz, 1H), 3.94 (s, 3H), 3,75 (s, 3H), 2.83 (s, 3H), 2.74 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 199.9, 196.7, 155.1, 140.9, 138.0, 127.3, 127.2, 125.3, 124.7, 124.3, 123.2, 116.5, 110.8, 102.9, 56.1, 34.2, 29.6, 26.6; HRMS (DART) *m/z* calcd for $C_{18}H_{18}NO_3$ $[M+H]^+$: 296.1286, found: 296.1285.

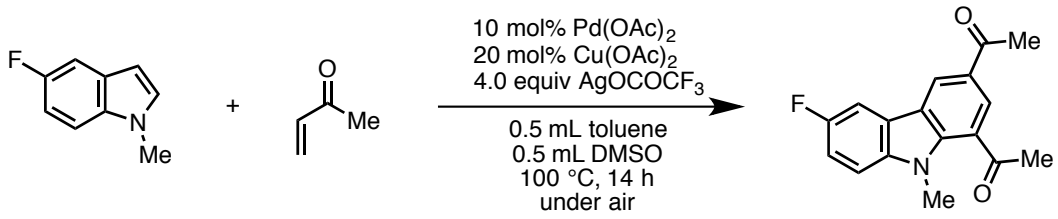


1f
0.2 mmol

2a
10 equiv

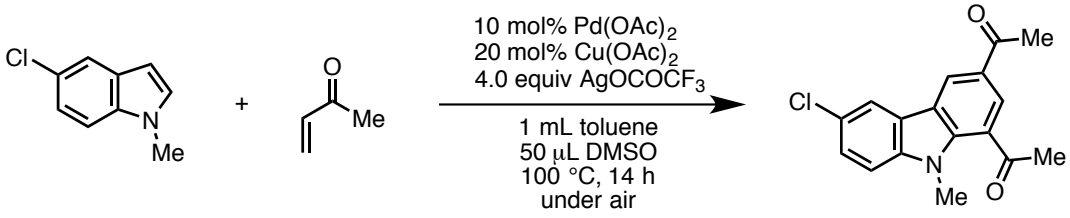
3fa
[40%]

1,3-Diacetyl-8-methoxy-9-methyl-9*H*-carbazole (3fa): Following the general procedure with 7-methoxy-1-methyl-1*H*-indole (**1f**: 32 mg) and methyl vinyl ketone (**2a**: 140 mg) in toluene (0.5 mL) and DMSO (0.5 mL), the crude product was purified by flash column chromatography (hexane/EtOAc = 3:1) to give **3fa** (24 mg, 40%) as a pale yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.75 (d, *J* = 1.6 Hz, 1H), 8.38 (d, *J* = 7.8, 0.7 Hz, 1H), 7.72 (dd, *J* = 2.5 Hz, 1H), 7.37 (d, *J* = 9.1 Hz, 1H), 7.17 (dd, *J* = 9.1, 2.5 Hz, 1H), 3.94 (s, 3H), 3,75 (s, 3H), 2.83 (s, 3H), 2.74 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 200.0, 196.8, 147.7, 141.5, 132.6, 127.8, 127.0, 125.7, 125.0, 124.8, 124.6, 121.7, 112.7, 109.0, 56.0, 37.3, 29.8, 26.6; HRMS (DART) *m/z* calcd for $C_{18}H_{18}NO_3$ $[M+H]^+$: 296.1286, found: 296.1286.



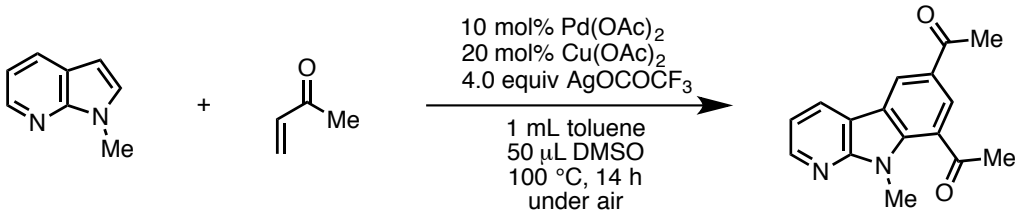
1h 0.2 mmol — **2a** 10 equiv — **3ha** [57%]

6-Chloro-1,3-diacetyl-9-methyl-9*H*-carbazole (3ga): Following the general procedure with 5-chloro-1-methyl-1*H*-indole (**1g**: 33 mg) and methyl vinyl ketone (**2a**: 140 mg) in toluene (1 mL) and DMSO (50 μL), the crude product was purified by flash column chromatography (hexane/EtOAc = 3:1) to give **3ga** (29 mg, 49%) as a pale yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.69 (d, *J* = 1.6 Hz, 1H), 8.43 (d, *J* = 1.8 Hz, 1H), 8.05 (d, *J* = 2.0 Hz, 1H), 7.48 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.37 (d, *J* = 8.9 Hz, 1H), 3.75 (s, 3H), 2.83 (s, 3H), 2.74 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 199.8, 196.5, 141.4, 140.8, 128.0, 127.7, 127.3, 126.6, 124.8, 124.6, 124.3, 123.6, 119.9, 111.0, 34.2, 29.6, 26.5; HRMS (DART) *m/z* calcd for $C_{17}H_{15}ClNO_2$ $[M+H]^+$: 300.0791, found: 300.0792.



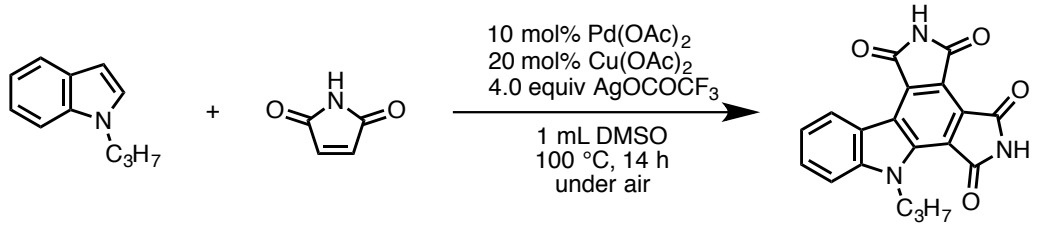
1g 0.2 mmol — **2a** 10 equiv — **3ga** [49%]

6-Fluoro-1,3-diacetyl-9-methyl-9*H*-carbazole (3ha): Following the general procedure with 5-fluoro-1-methyl-1*H*-indole (**1h**: 30 mg) and methyl vinyl ketone (**2a**: 140 mg) in toluene (0.5 mL) and DMSO (0.5 mL), the crude product was purified by flash column chromatography (hexane/EtOAc = 3:1) to give **3ha** (32 mg, 57%) as a pale yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.69 (d, *J* = 1.8 Hz, 1H), 8.43 (d, *J* = 1.8 Hz, 1H), 7.75 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.38 (dd, *J* = 9.1, 4.1 Hz, 1H), 7.26 (td, *J* = 8.9, 2.5 Hz, 1H), 3.76 (s, 3H), 2.83 (s, 3H), 2.73 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 199.8, 196.6, 158.3 (d, *J* = 237 Hz), 141.3, 139.4, 127.74, 127.71, 125.0, 124.9 (d, *J* = 4.3 Hz), 124.6, 123.2 (d, *J* = 10 Hz), 115.2 (d, *J* = 24 Hz), 110.8 (d, *J* = 8.5 Hz), 106.1 (d, *J* = 24 Hz), 34.3, 29.6, 26.6; HRMS (DART) *m/z* calcd for $C_{17}H_{15}FNO_2$ $[M+H]^+$: 284.1087, found: 284.1087.



1i 0.2 mmol + **2a** 10 equiv → **3ia** [45%]

1,3-Diacetyl-9-methyl-9*H*-8-azacarbazole (3ia): Following the general procedure with 1-methyl-1*H*-pyrrolo[2,3-*b*]pyridine (**1i**: 26 mg) and methyl vinyl ketone (**2a**: 140 mg) in toluene (1 mL) and DMSO (50 μL), the crude product was purified by flash column chromatography (hexane/EtOAc = 3:1) to give **3ia** (24 mg, 45%) as a pale yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.71 (d, *J* = 1.6 Hz, 1H), 8.58 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.39 (d, *J* = 1.6 Hz, 1H), 8.34 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.27 (dd, *J* = 7.8, 4.8 Hz, 1H), 3.89 (s, 3H), 2.83 (s, 3H), 2.73 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.7, 196.5, 153.3, 147.4, 139.7, 128.4, 128.2, 127.4, 125.0, 124.8, 122.6, 116.8, 115.4, 32.2, 29.8, 26.6; HRMS (DART) *m/z* calcd for $C_{16}H_{15}N_2O_2$ $[M+H]^+$: 267.1133, found: 267.1133.



1j 0.2 mmol + **2h** 4.0 equiv → **3jh** [24%]

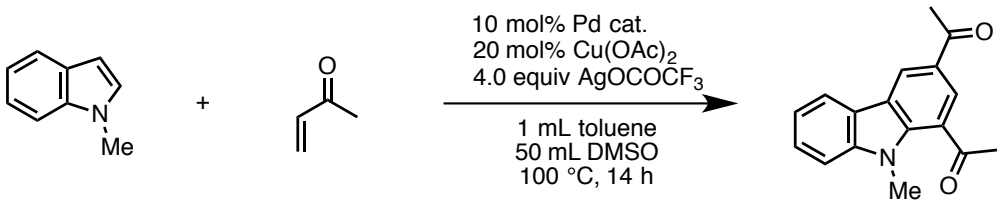
7-Propyl-1*H*-dipyrrolo[3,4-*a*:3',4'-*c*]carbazole-1,3,4,6(2*H*,5*H*,7*H*)-tetraone (3jh): A 7-mL screw test tube containing a magnetic stirrindg bar was dried under in vacuum with heating by heat-gun. After cooling, $Pd(OAc)_2$ (4.5 mg, 20 μmol), $Cu(OAc)_2$ (7.3 mg, 40 μmol), $AgOCOCF_3$ (176 mg, 0.80 mmol), maleimide (**2h**: 77 mg, 0.80 mmol), *N*-propylindole (**1j**, 31 mg, 0.20 mmol) and DMSO (1 mL) were added under air. The vessel was sealed with a cap under air and then the mixture was heated at 100 °C for 14 h with stirring. After cooling to room temperature, the reaction mixture was directly purified by flash column chromatography on silica gel ($CHCl_3$/MeOH = 20:1), and the solvent was evaporated under reduced pressure. To this residue, water and EtOAc were added. The resulting solid at the interface between a organic and an aqueous phases was separated by filtration and washed with water then EtOAc to give pure compound **3jh** (17 mg, 24%) as an orange solid. ^{1}H NMR (DMSO-d_6, 600 MHz) δ 11.56 (br, 2H), 9.05–8.98 (m, 1H), 7.79–7.66 (m, 2H), 7.41–7.38 (m, 1H), 4.94–4.89 (m, 2H), 1.74–1.73 (br, 2H), 0.91–0.88 (br, 3H). ^{13}C NMR (DMSO–*d6*, 150 MHz) δ 168.7, 167.8, 165.7, 165.6, 143.3, 138.6, 131.4, 130.0, 127.3, 125.7, 124.4, 121.7, 119.5, 119.3, 118.0,

110.8, 47.5, 22.7, 10.6.; HRMS (FAB) *m/z* calcd for $C_{19}H_{13}N_3O_4Na$ $[M+Na]^+$: 370.0804, found: 370.0805.

2. Effect of Reaction Parameters

The effects of reaction parameters (palladium, copper, silver, solvent, temperature) were investigated. The π-extension reaction of 1-methylindole (**1a**) with methyl vinyl ketone (**2a**) was used as the model reaction.

Table S1. Effect of Palladium Catalysts.[a]



1a 0.2 mmol

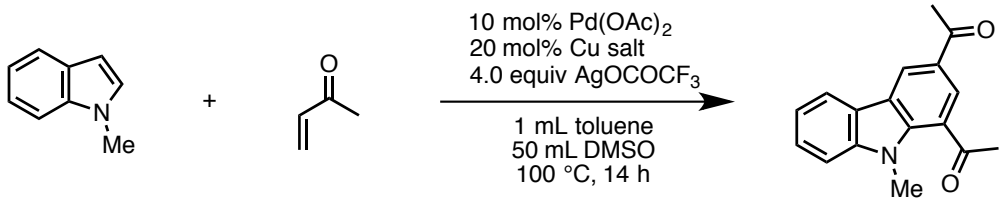
2a 10 equiv

3aa

entry	Pd cat.	yield[b]
1	$Pd(OAc)_2$	70%[c]
2	$Pd(OCOCF_3)_2$	47%
3	$PdCl_2$	39%
4	$Pd_2(dba)_3{\cdot}CHCl_3$	40%
5	none	30%

a: Conditions: **1a** (0.2 mmol), **2a** (2.0 mmol), Pd cat. (0.020 mmol), $Cu(OAc)_2$ (0.040 mmol), $AgOCOCF_3$ (0.8 mmol), toluene (1 mL), DMSO (50 μL), 100 °C, 14 h, under air.
b: Determined by GC analysis using *n*-dodecane as an internal standard.
c: Isolated yield.

Table S2. Effect of Copper Salts.[a]

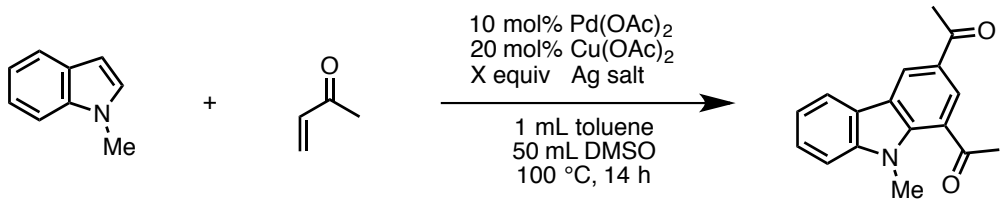


1a 0.2 mmol + **2a** 10 equiv → **3aa**

entry	Cu salt	yield[b]
1	$Cu(OAc)_2$	70%[c]
2[d]	$Cu(OAc)_2$	46%
3	$Cu(OCOCF_3)_2{\cdot}H_2O$	36%
4	$CuCl_2$	31%
5	$CuBr_2$	37%
6	CuF_2	36%
7	CuO	32%
8	$Cu(OTf)_2$	25%
9	$Cu(acac)_2$	39%
10	none	27%

a: Conditions: **1a** (0.2 mmol), **2a** (2.0 mmol), $Pd(OAc)_2$ (0.020 mmol), Cu salt (0.040 mmol), $AgOCOCF_3$ (0.8 mmol), toluene (1 mL), DMSO (50 μL), 100 °C, 14 h, under air.
b: Determined by GC analysis using *n*-dodecane as an internal standard.
c: Isolated yield.
d; $Cu(OAc)_2$ (1.0 equiv)

Table S3. Effect of Silver Salts.[a]



1a 0.2 mmol

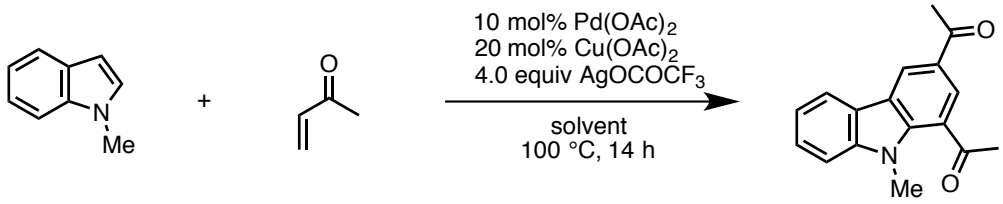
2a 10 equiv

3aa

entry	Ag salt	X equiv	yield[b]
1	$AgOCOCF_3$	(2.0 eq.)	31%
2	$AgOCOCF_3$	(4.0 eq.)	70%[c]
3	$AgOCOCF_3$	(5.0 eq.)	41%
4	AgOAc	(4.0 eq.)	35%
5	Ag_2CO_3	(4.0 eq.)	6%
6	$AgBF_4$	(4.0 eq.)	3%
7	$AgPF_6$	(4.0 eq.)	2%
8	$AgSbF_6$	(4.0 eq.)	1%
9	AgOTf	(4.0 eq.)	0%

a: Conditions: **1a** (0.2 mmol), **2a** (2.0 mmol), $Pd(OAc)_2$ (0.020 mmol), $Cu(OAc)_2$ (0.040 mmol), Ag salt (X equiv), toluene (1 mL), DMSO (50 μL), 100 °C, 14 h, under air.
b: Determined by GC analysis using *n*-dodecane as an internal standard.
c: Isolated yield.

Table S4. Effect of Solvents.[a]

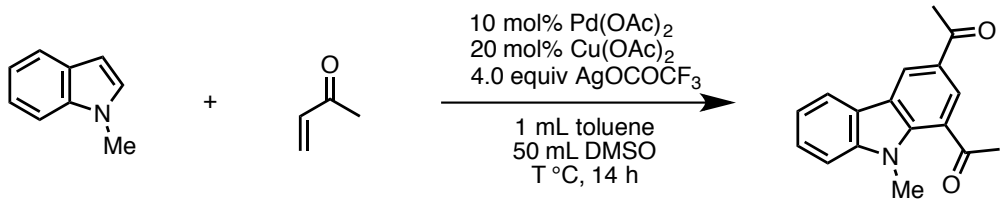


1a 0.2 mmol + **2a** 10 equiv → **3aa**

entry	solvent	yield[b]
1	toluene/DMSO (v/v = 100:5)	70%[c]
2	toluene	30%
3	DMSO	46%
4	DMF	18%
5	DCE	17%
6	1,4-dioxane	50%
7	1,4-dioxane/DMSO (v/v = 100:5)	49%

a: Conditions: **1a** (0.2 mmol), **2a** (2.0 mmol), $Pd(OAc)_2$ (0.020 mmol), $Cu(OAc)_2$ (0.040 mmol), $AgOCOCF_3$ (0.8 mmol), solvent (1 mL), 100 °C, 14 h, under air.
b: Determined by GC analysis using *n*-dodecane as an internal standard.
c: Isolated yield.

Table S5. Effect of Reaction Temperature.[a]



1a
0.2 mmol

2a
10 equiv

3aa

entry	T °C	yield[b]
1	80 °C	33%
2	100 °C	70%[c]
3	120 °C	40%

a: Conditions: **1a** (0.2 mmol), **2a** (2.0 mmol), $Pd(OAc)_2$ (0.020 mmol), $Cu(OAc)_2$ (0.040 mmol), $AgOCOCF_3$ (0.8 mmol), toluene (1 mL), DMSO (50 μL), T °C, 14 h, under air.
b: Determined by GC analysis using *n*-dodecane as an internal standard.
c: Isolated yield.

3. X-ray Crystal Structure Analysis of 3aa

Details of the crystal data and a summary of the intensity data collection parameters for **3aa** are listed in Table S6. A suitable crystal was mounted with mineral oil on a glass fiber and transferred to the goniometer of a Rigaku Saturn CCD diffractometer. Graphite-monochromated Mo Kα radiation (λ = 0.71070 Å) was used. The structures were solved by direct methods with (SIR-97)[13] or (SHELXS-97)[14] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97)[14]. The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions.

Table S6. Crystallographic data and structure refinement details for **3aa**

	3aa
formula	$C_{17}H_{15}NO_2$
fw	265.30
T (K)	103(2)
λ (Å)	0.71070
cryst syst	orthorhombic
space group	$P2_12_12_1$
a, (Å)	6.4112(19)
b, (Å)	12.077(4)
c, (Å)	16.676(5)
α, (deg)	90
β, (deg)	90
γ, (deg)	90
V, (Å^3)	1291.4(7)
Z	4
D_{calc}, (g / cm^3)	1.365
m (mm^{-1})	0.090
F(000)	560
cryst size (mm)	0.20 × 0.10 × 0.10
2θ range, (deg)	3.37–24.99
reflns collected	8665
indep reflns/R_{int}	2272/0.0487
params	184
GOF on F^2	1.113
R_1, wR_2 [I>2σ(I)]	0.0477, 0.0909
R_1, wR_2 (all data)	0.0538, 0.0942

[13] Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32,* 115.
[14] Sheldrick, G. M. University of Göttingen: Göttingen, Germany, **1997**.

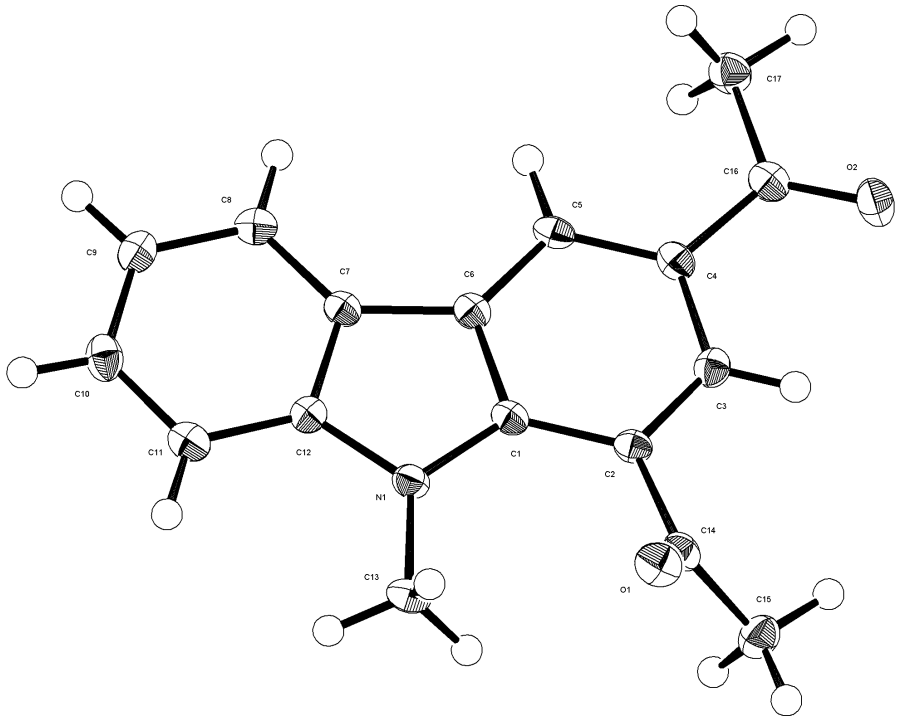
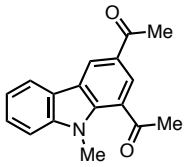


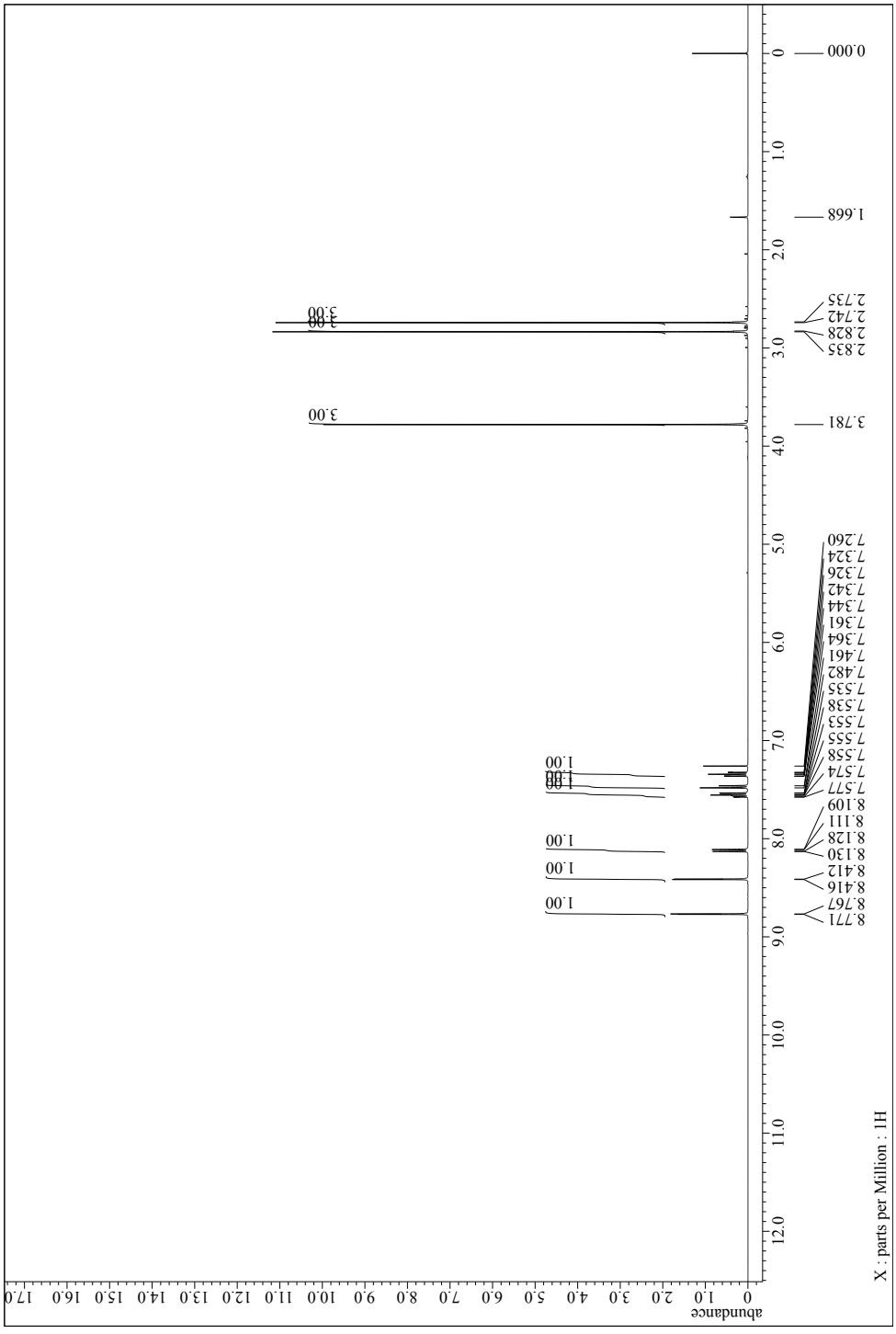
Figure S1. ORTEP drawing of **3aa** with 50% thermal ellipsoid

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

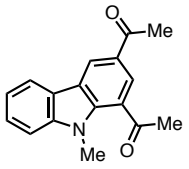
^{1}H NMR (400 MHz, $CDCl_3$) of **3aa**



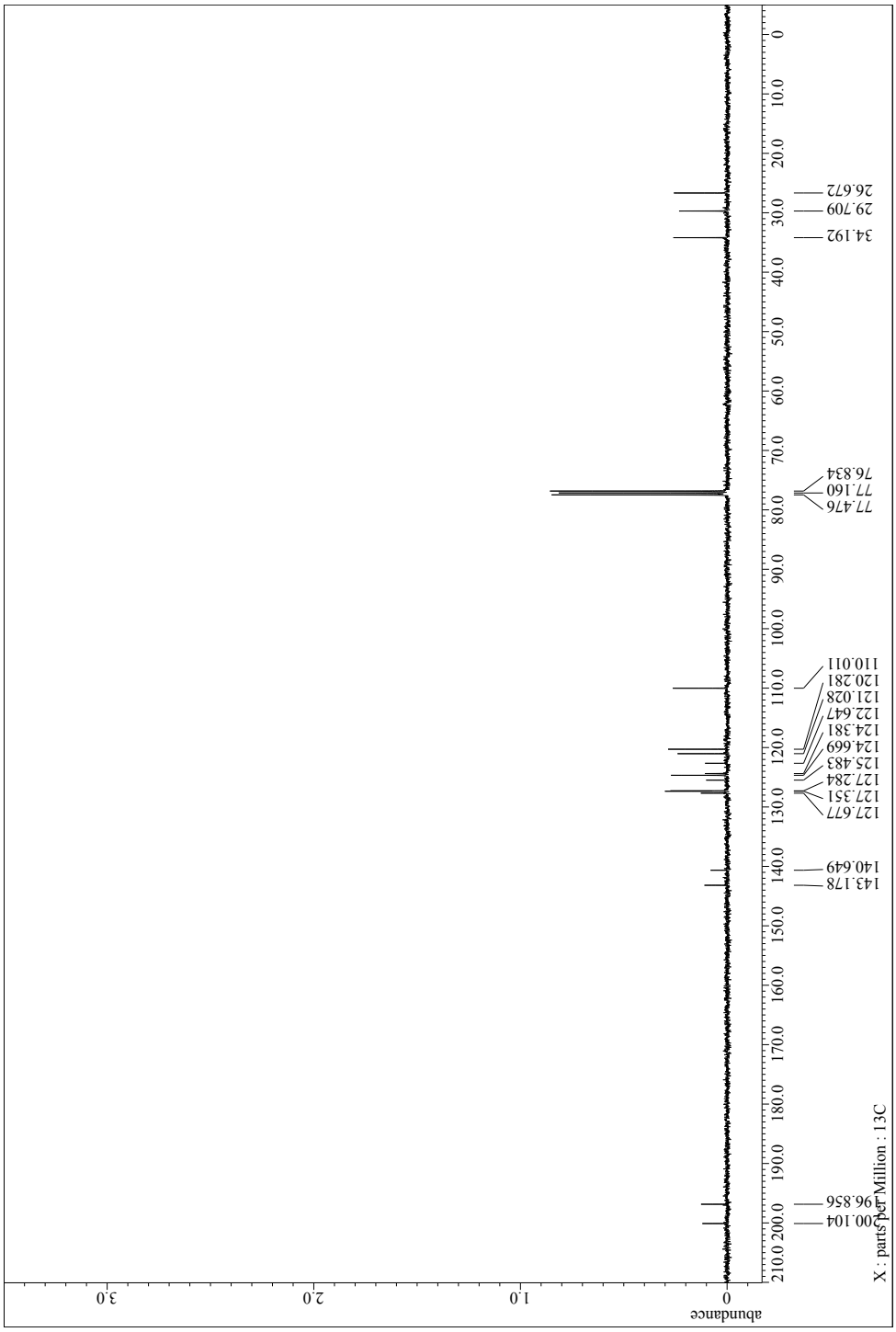
3aa



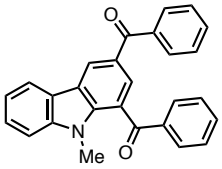
^{13}C NMR (150 MHz, $CDCl_3$) of **3aa**



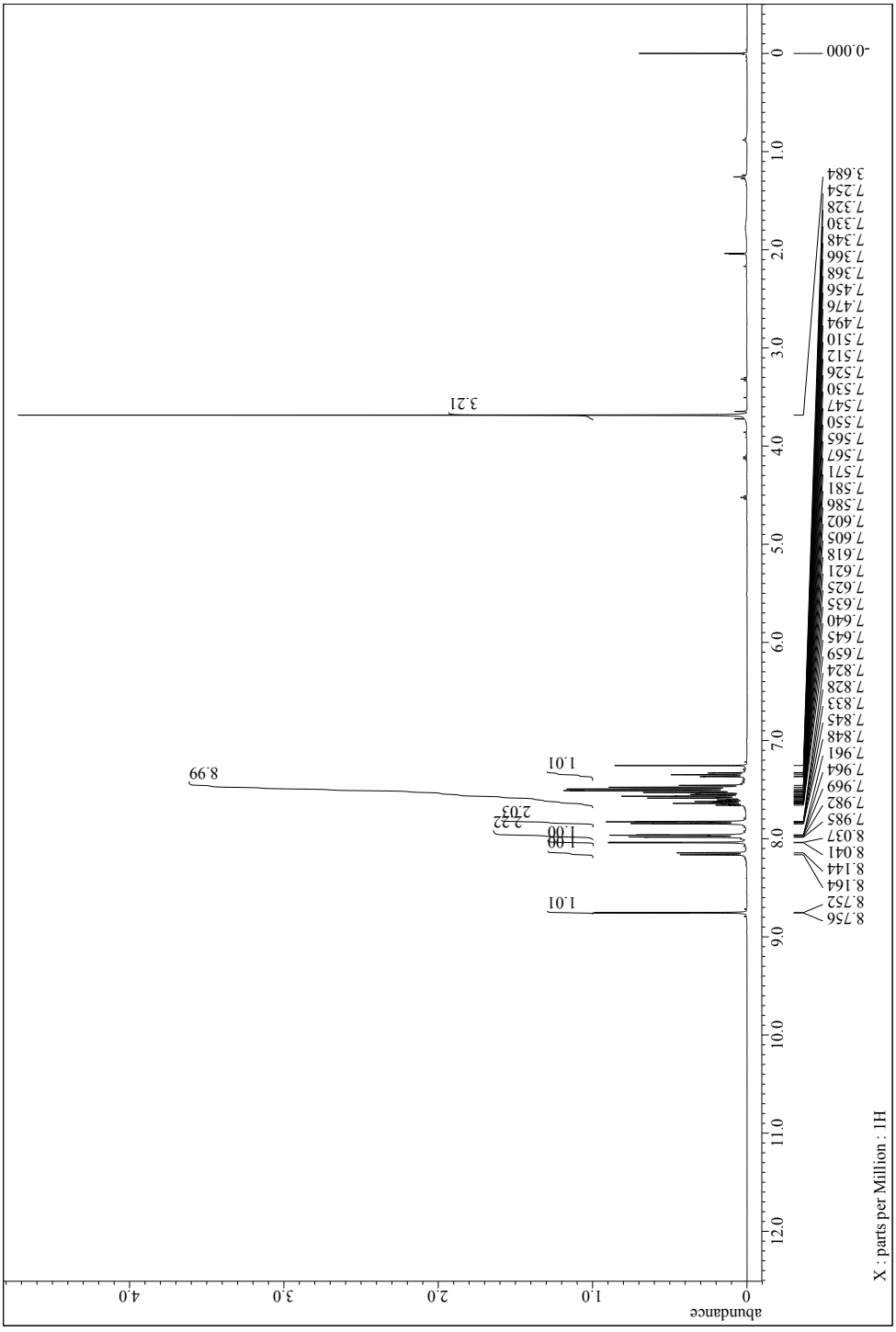
3aa



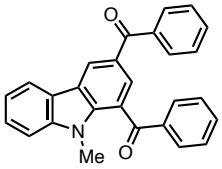
^{1}H NMR (400 MHz, $CDCl_3$) of **3ab**



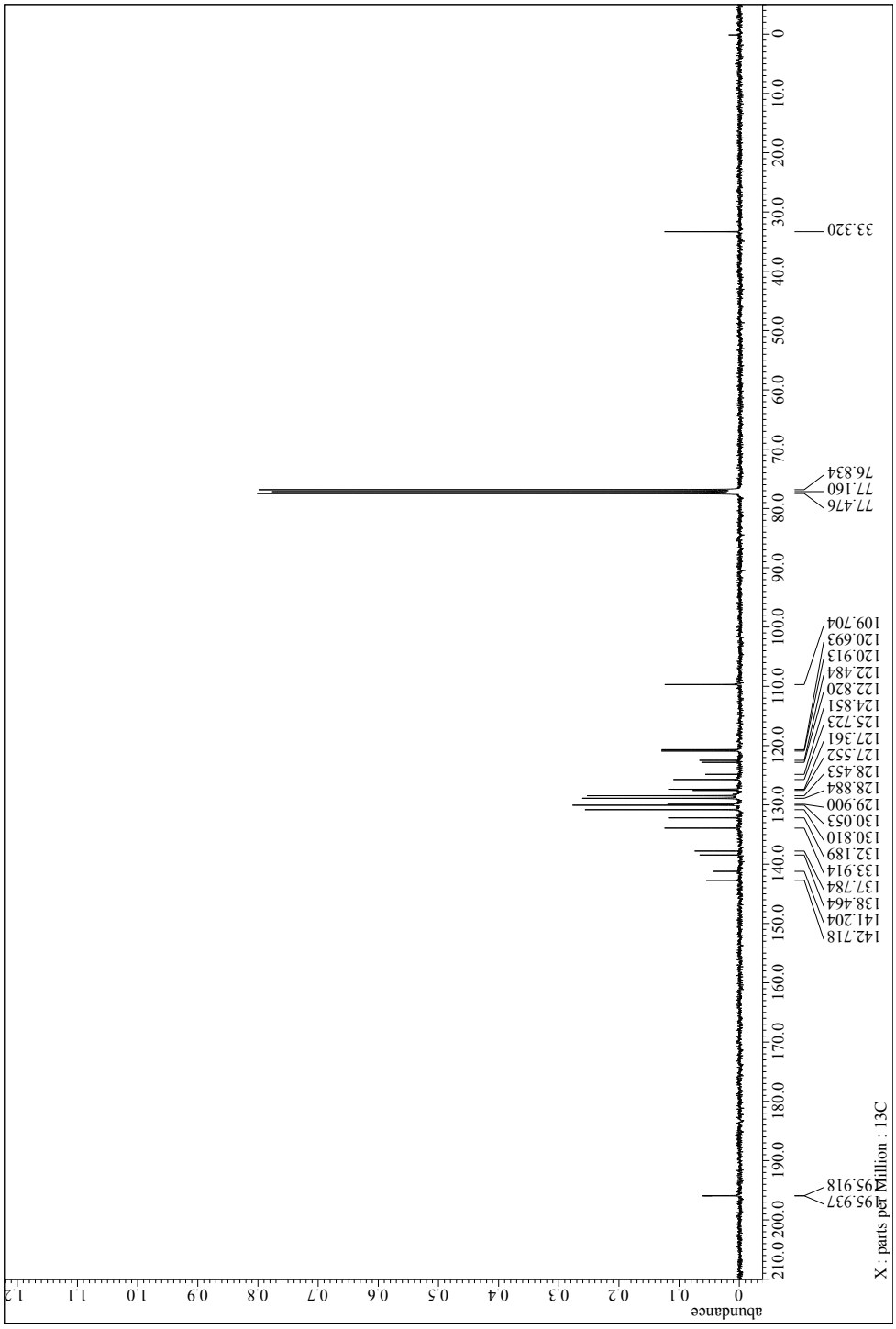
3ab



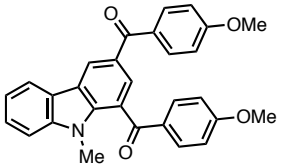
^{13}C NMR (100 MHz, $CDCl_3$) of **3ab**



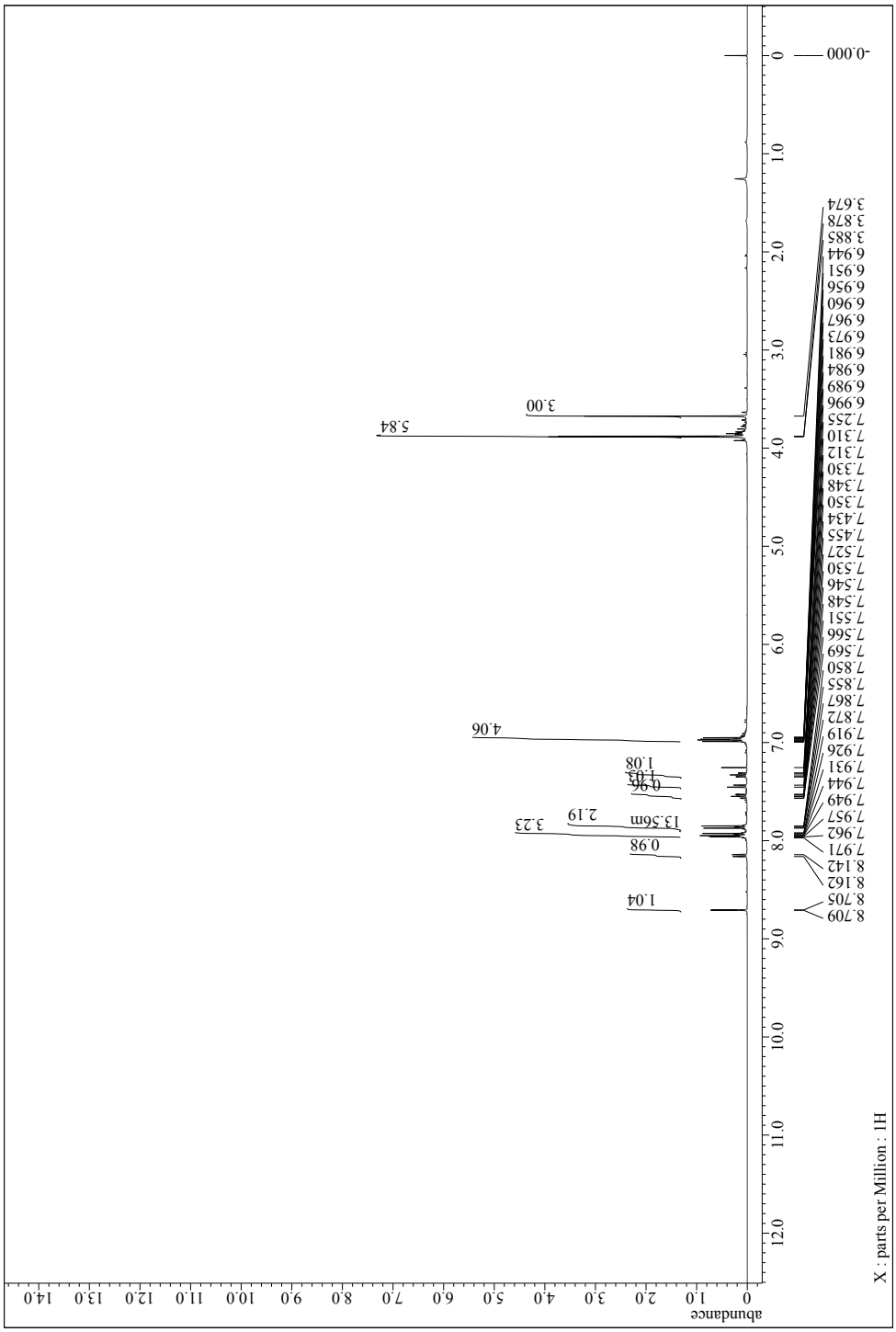
3ab



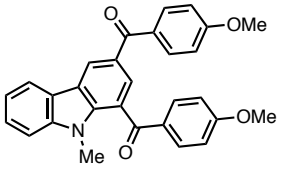
^{1}H NMR (400 MHz, $CDCl_3$) of **3ac**



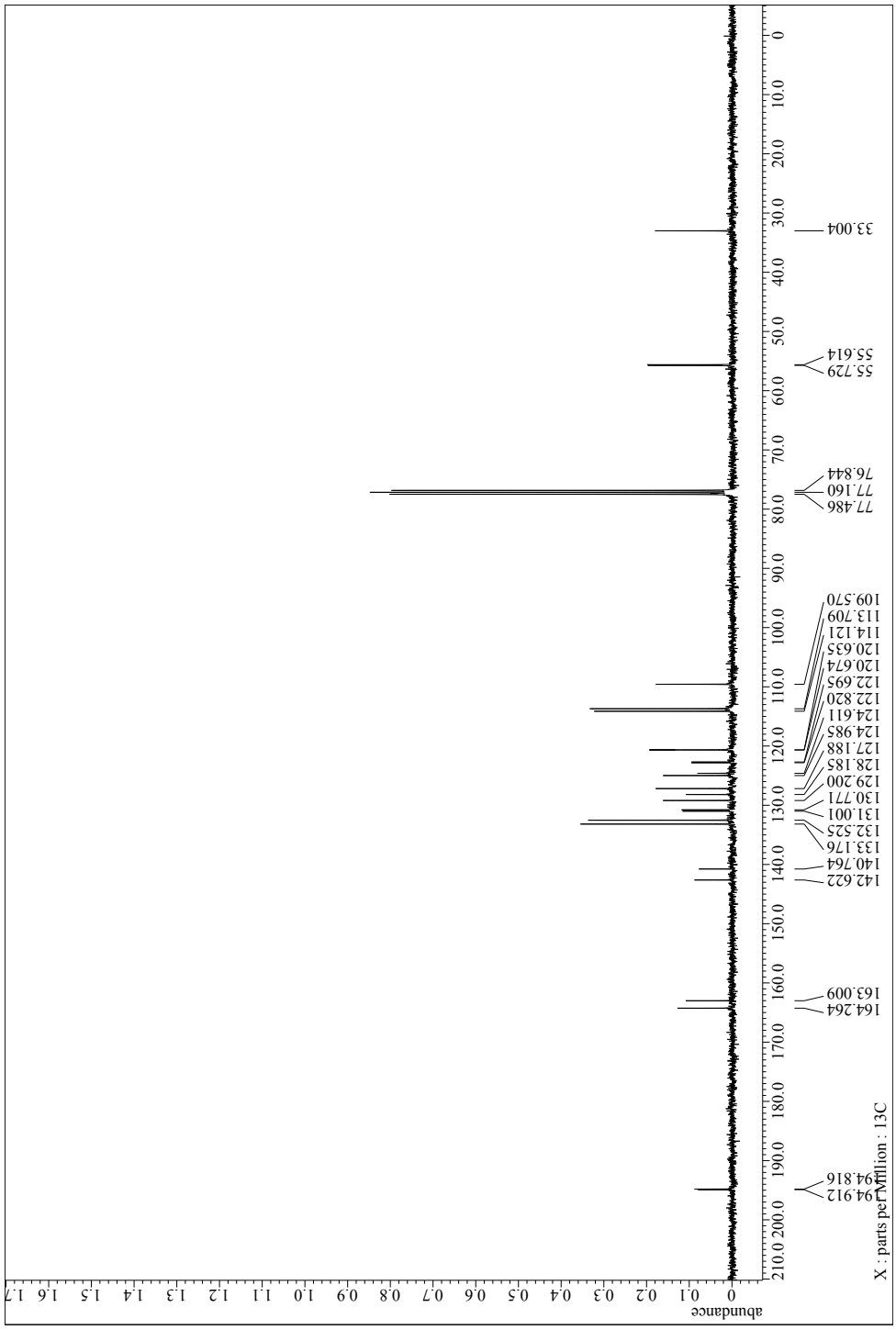
3ac



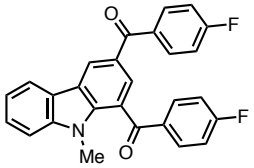
^{13}C NMR (100 MHz, $CDCl_3$) of **3ac**



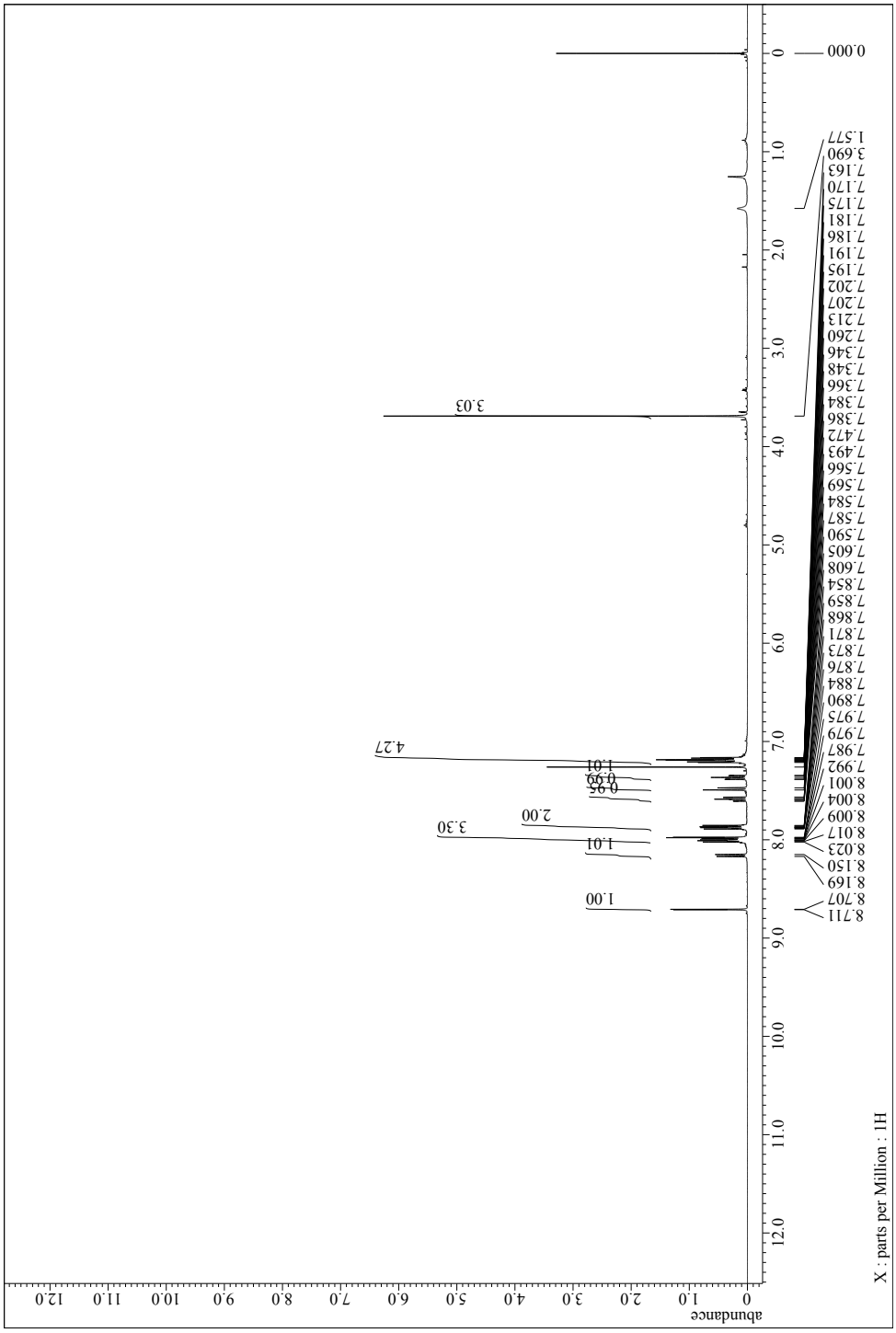
3ac



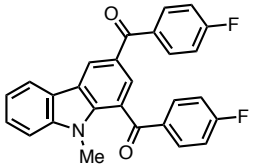
^{1}H NMR (400 MHz, $CDCl_3$) of **3ad**



3ad



^{13}C NMR (150 MHz, $CDCl_3$) of **3ad**



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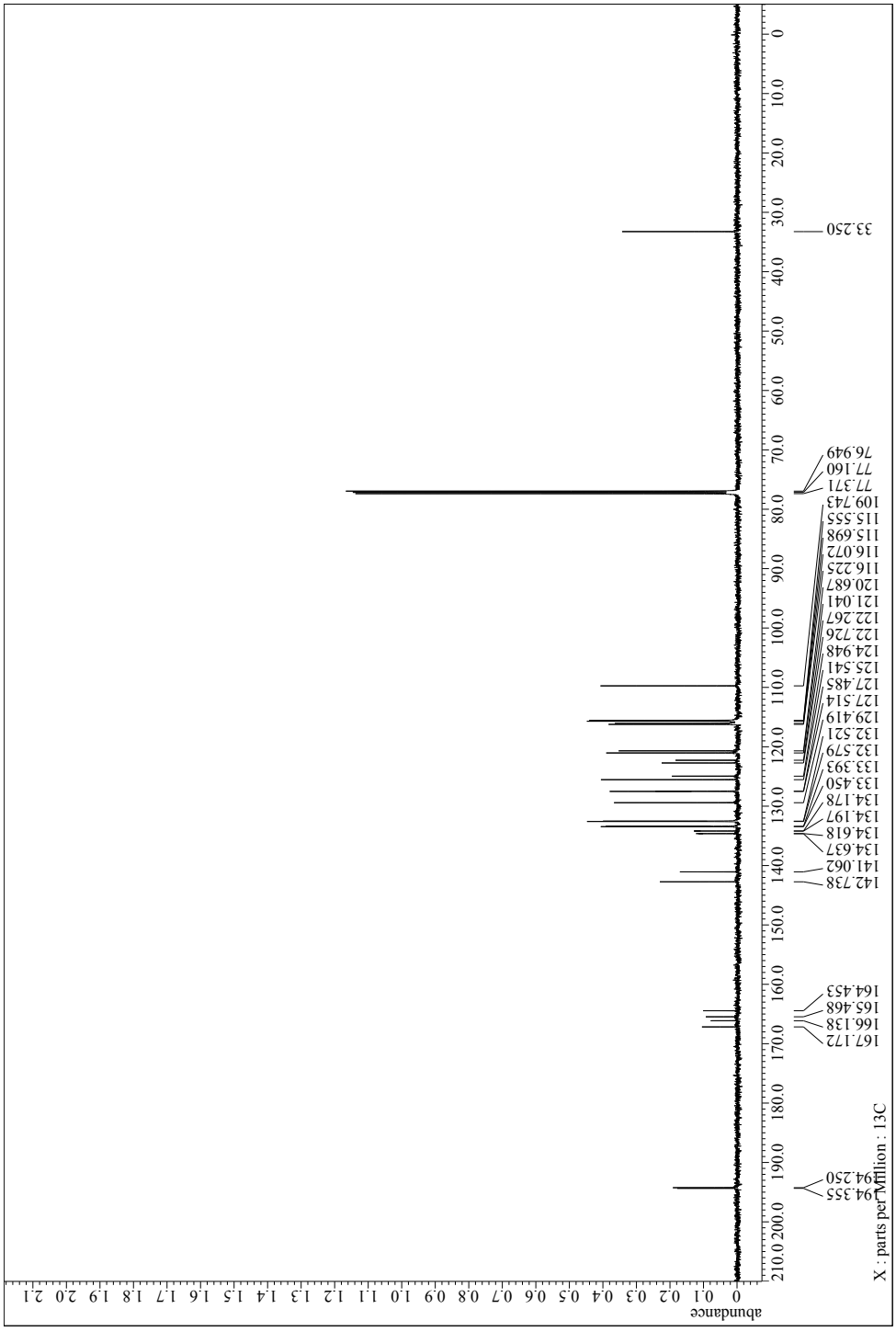
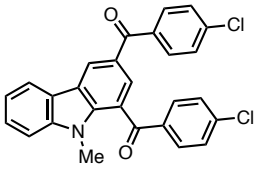
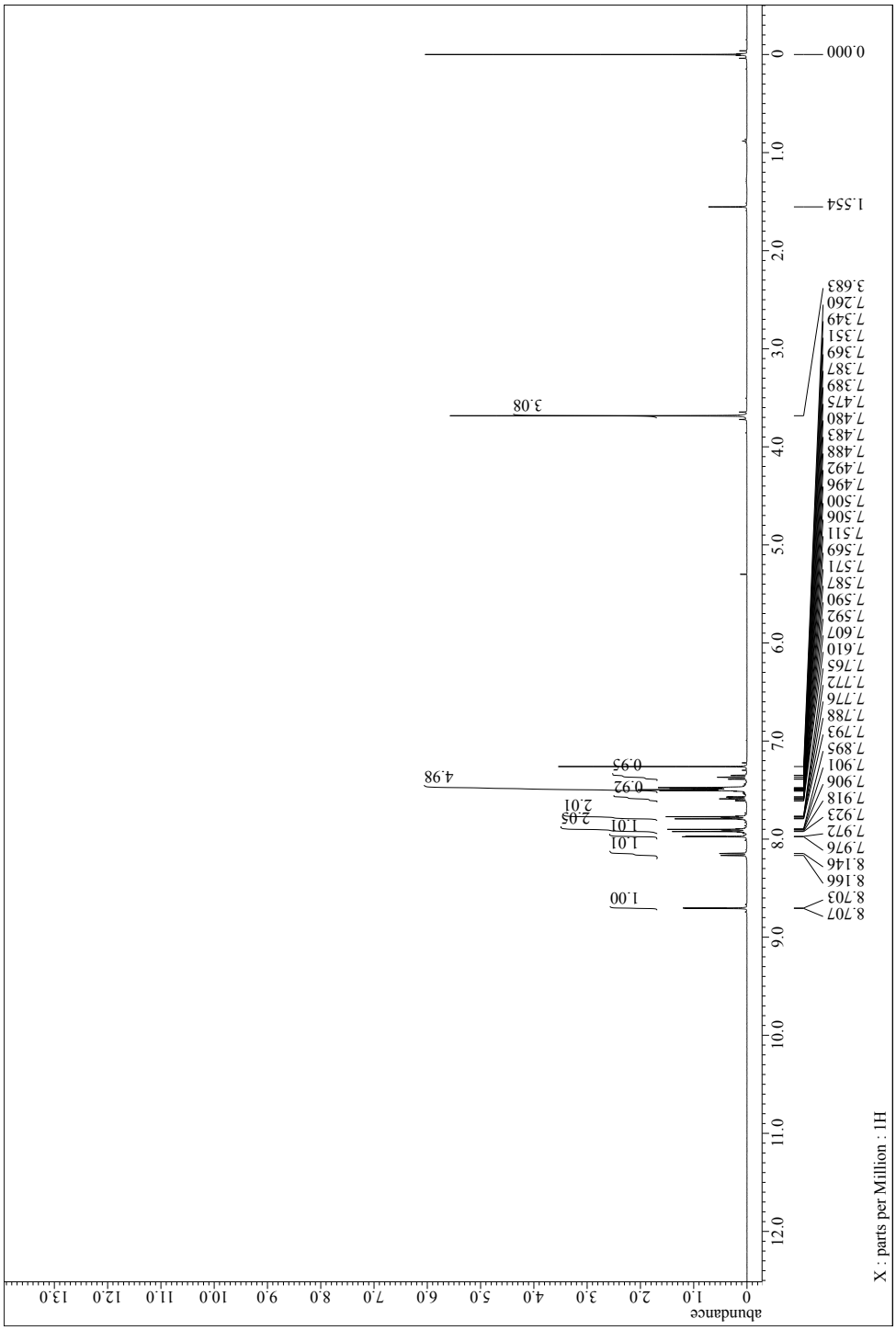


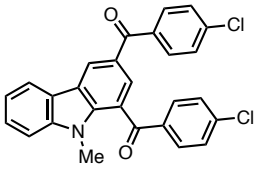
^{1}H NMR (400 MHz, $CDCl_3$) of **3ae**



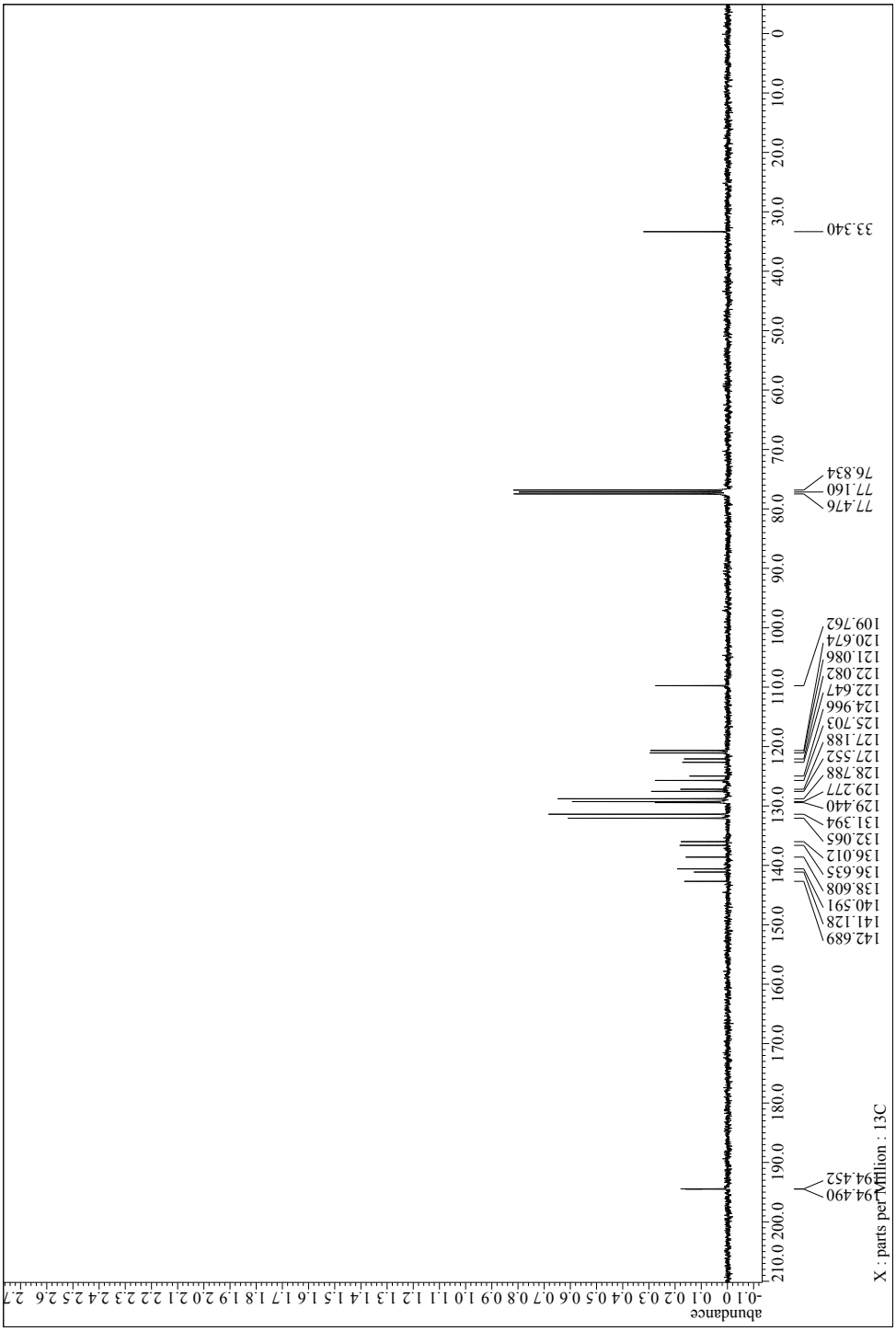
3ae



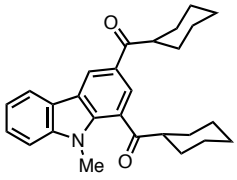
^{13}C NMR (100 MHz, $CDCl_3$) of **3ae**



3ae



^{1}H NMR (600 MHz, $CDCl_3$) of **3af**



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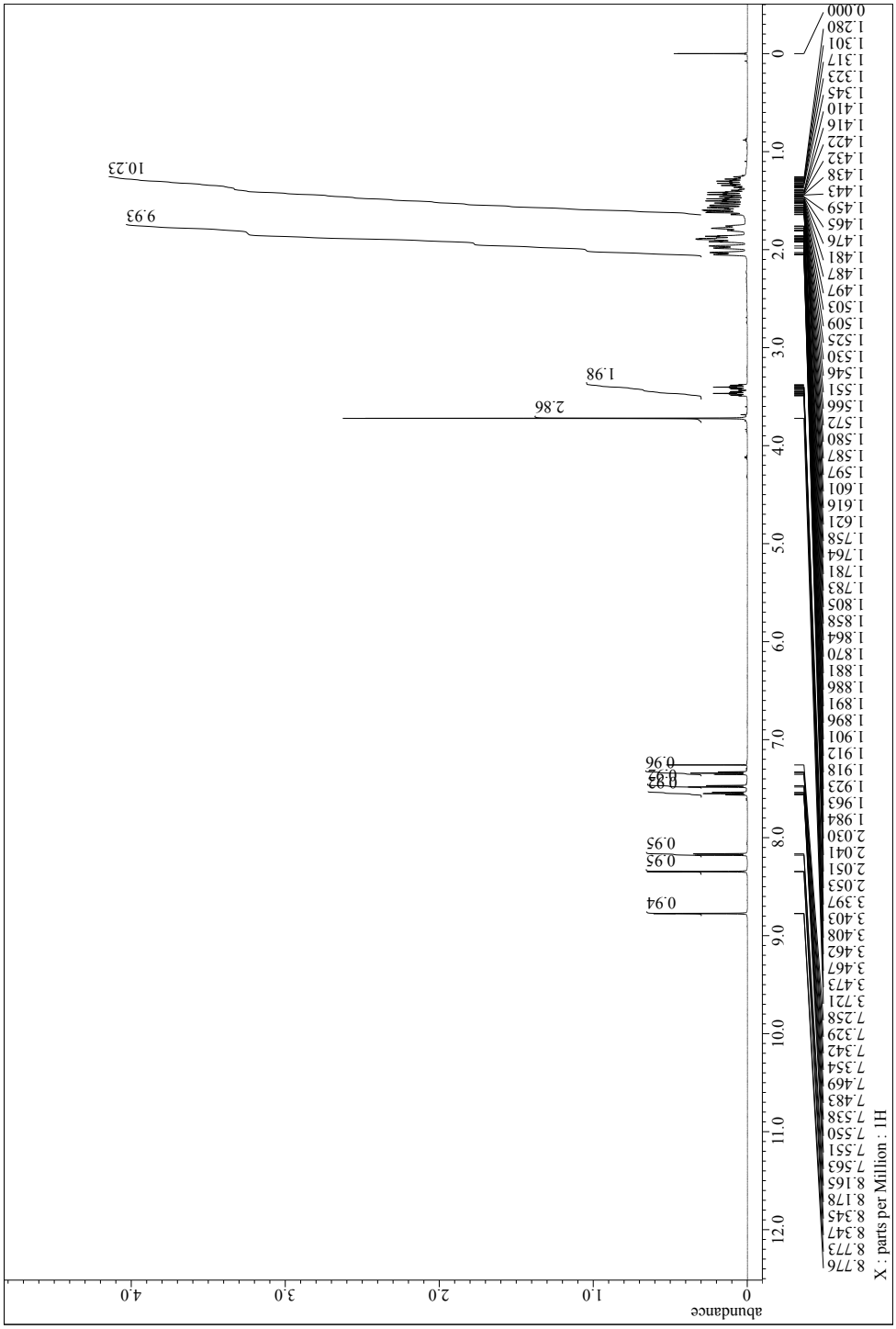
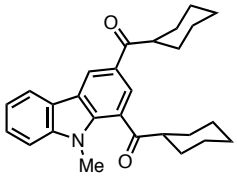


^{13}C NMR (150 MHz, $CDCl_3$) of **3af**



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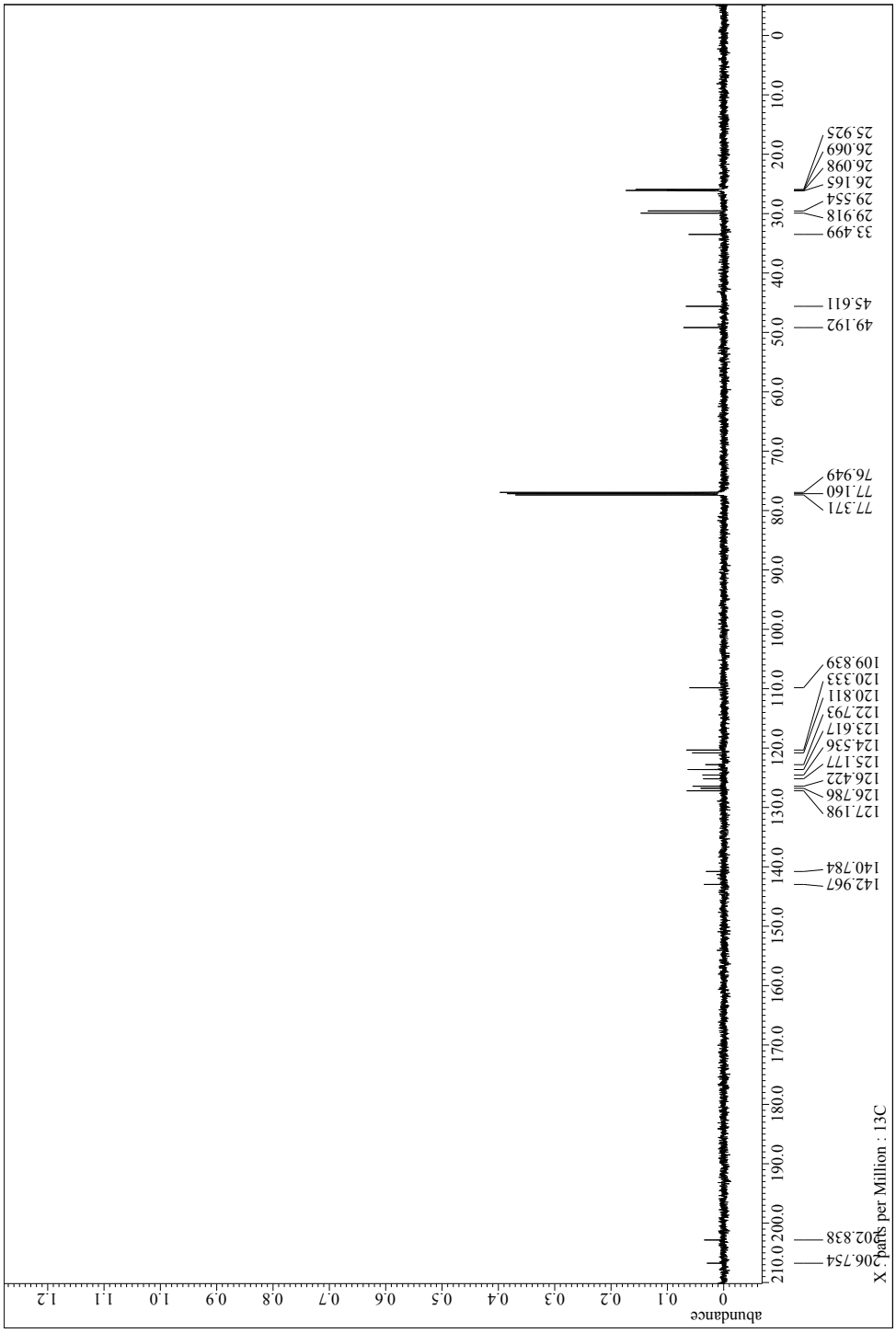
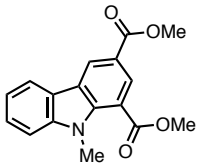
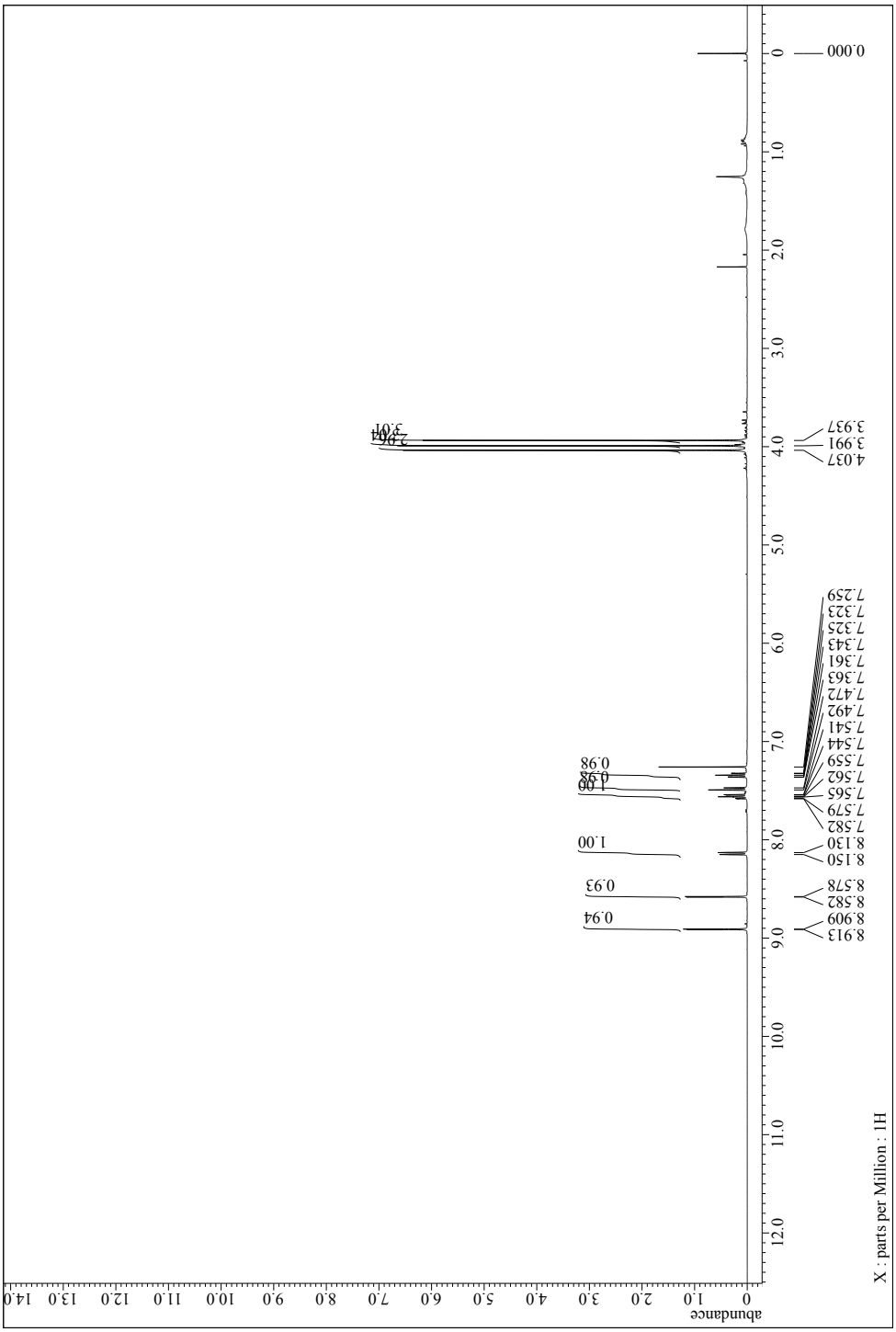


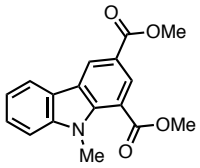
^{1}H NMR (400 MHz, $CDCl_3$) of **3ag**



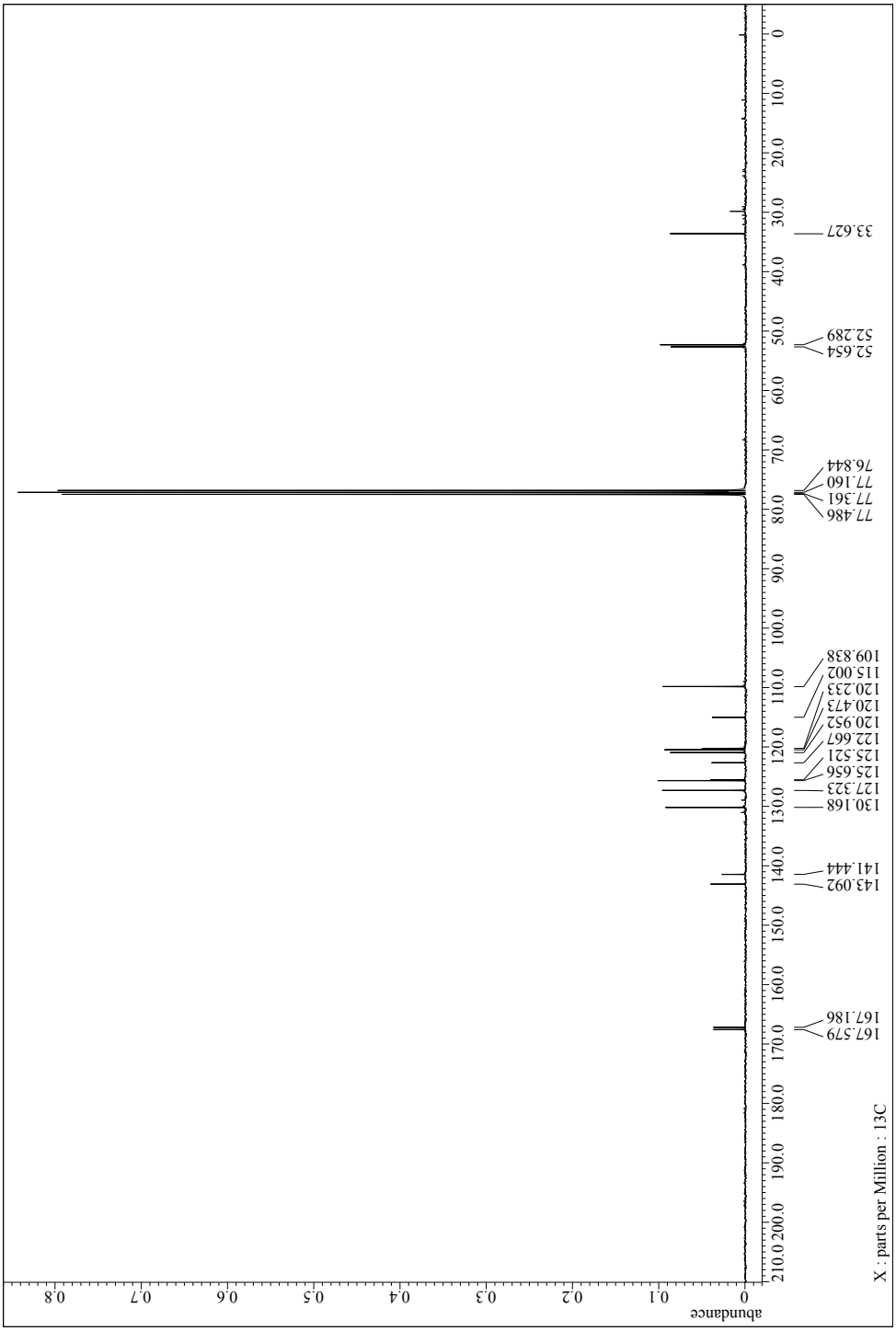
3ag



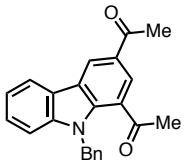
^{13}C NMR (100 MHz, $CDCl_3$) of **3ag**



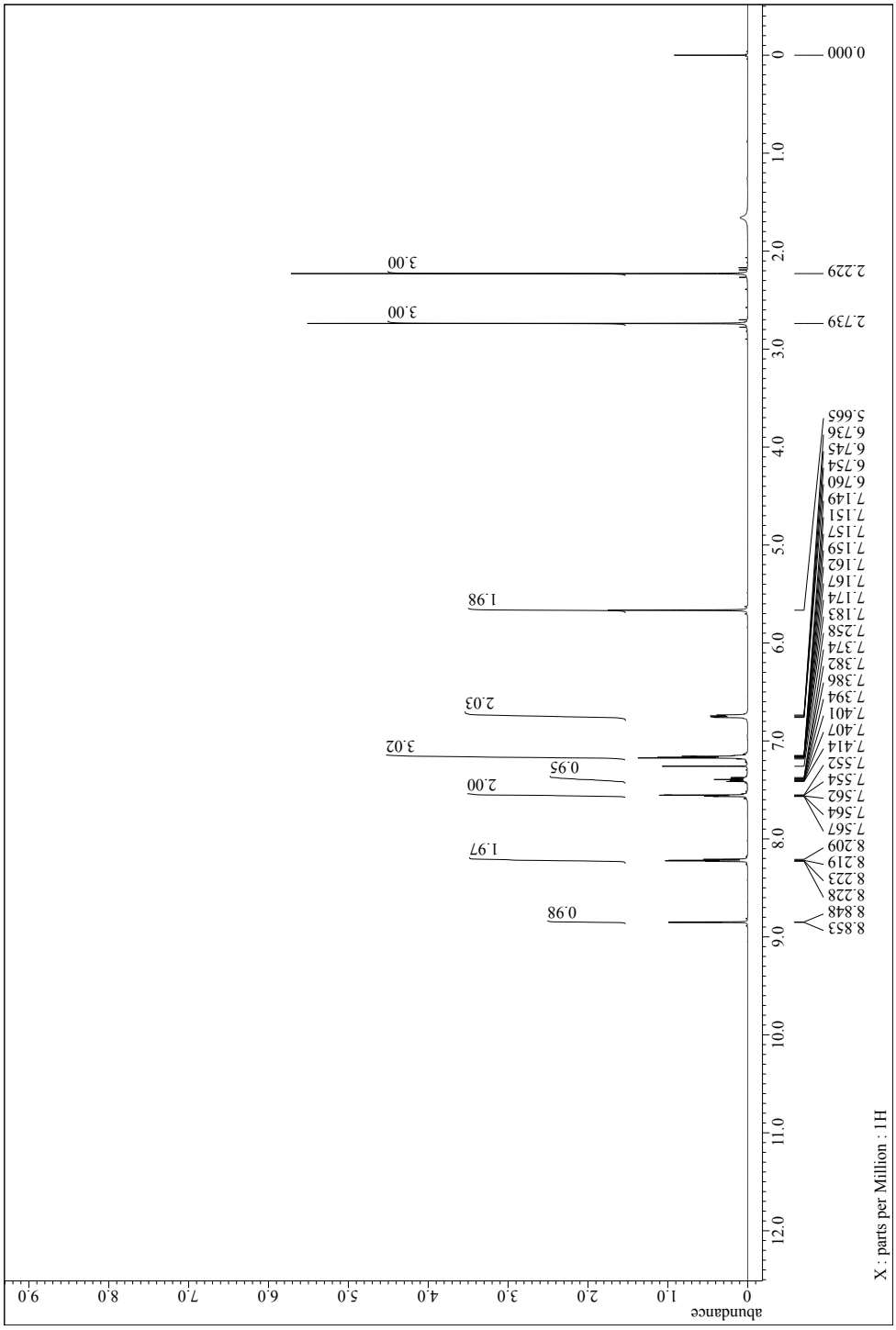
3ag



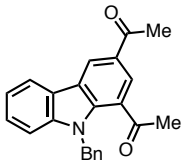
^{1}H NMR (400 MHz, $CDCl_3$) of **3ba**



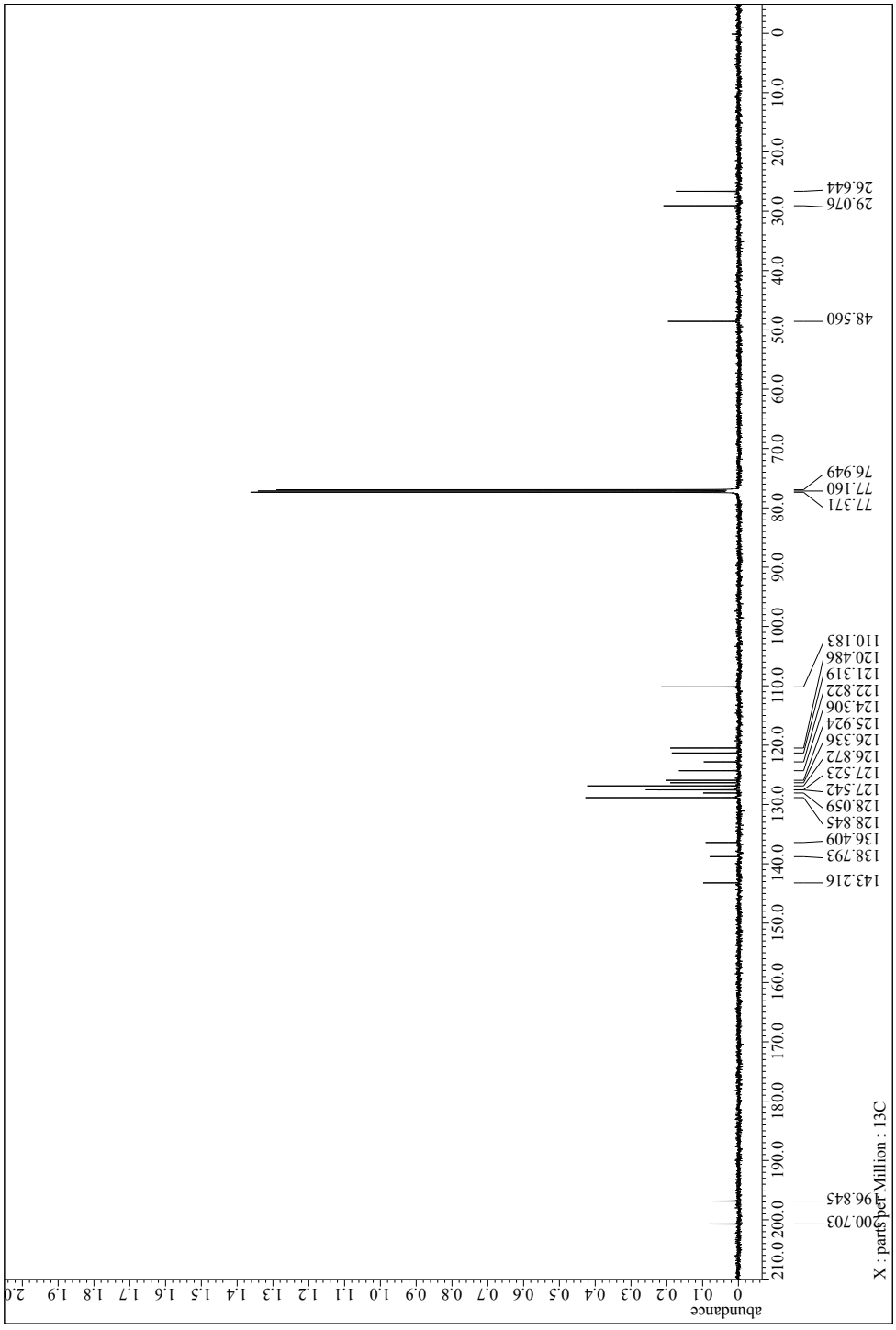
3ba



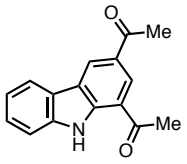
^{13}C NMR (150 MHz, $CDCl_3$) of **3ba**



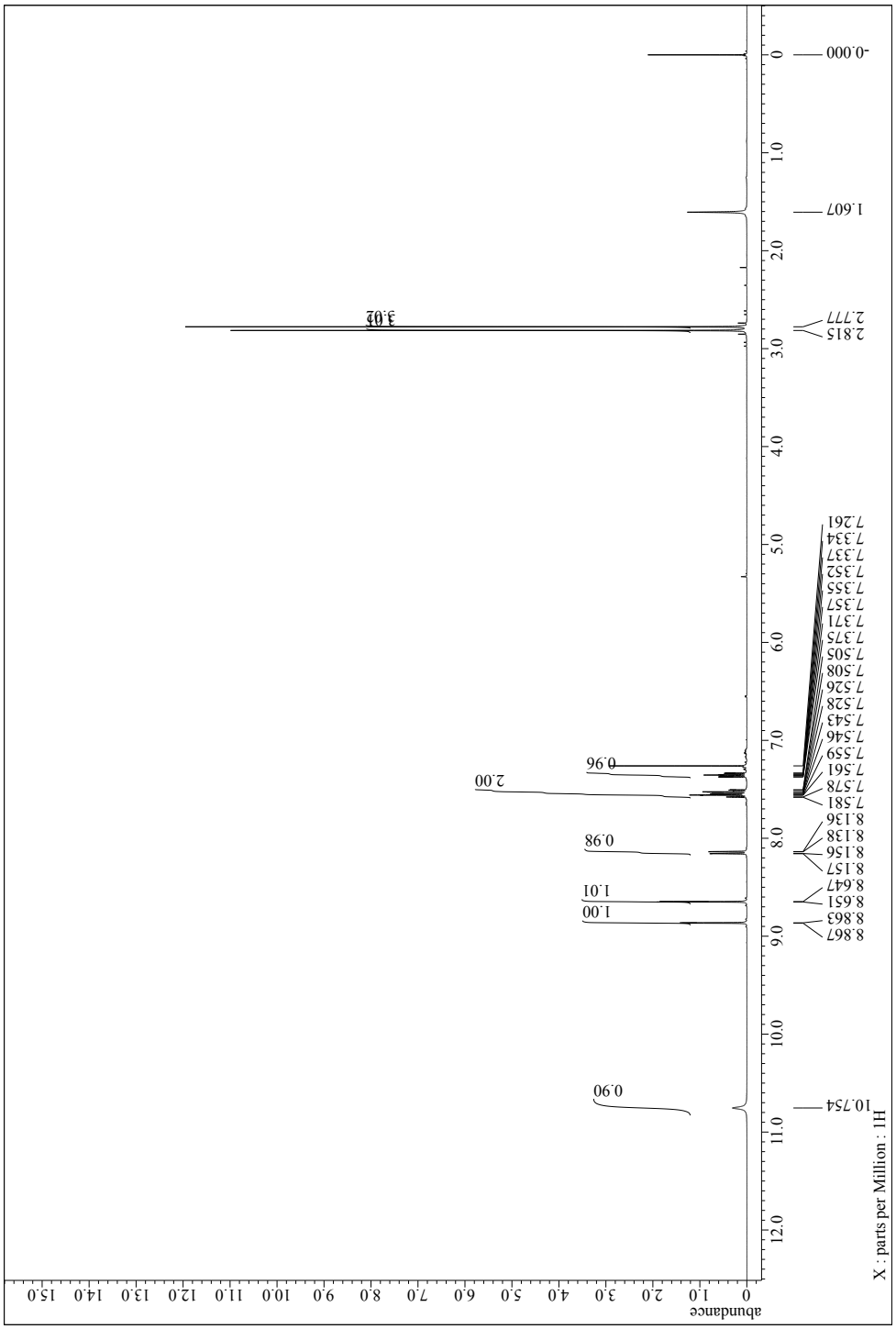
3ba



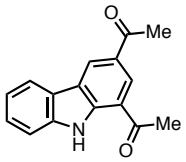
^{1}H NMR (400 MHz, $CDCl_3$) of **3ca**



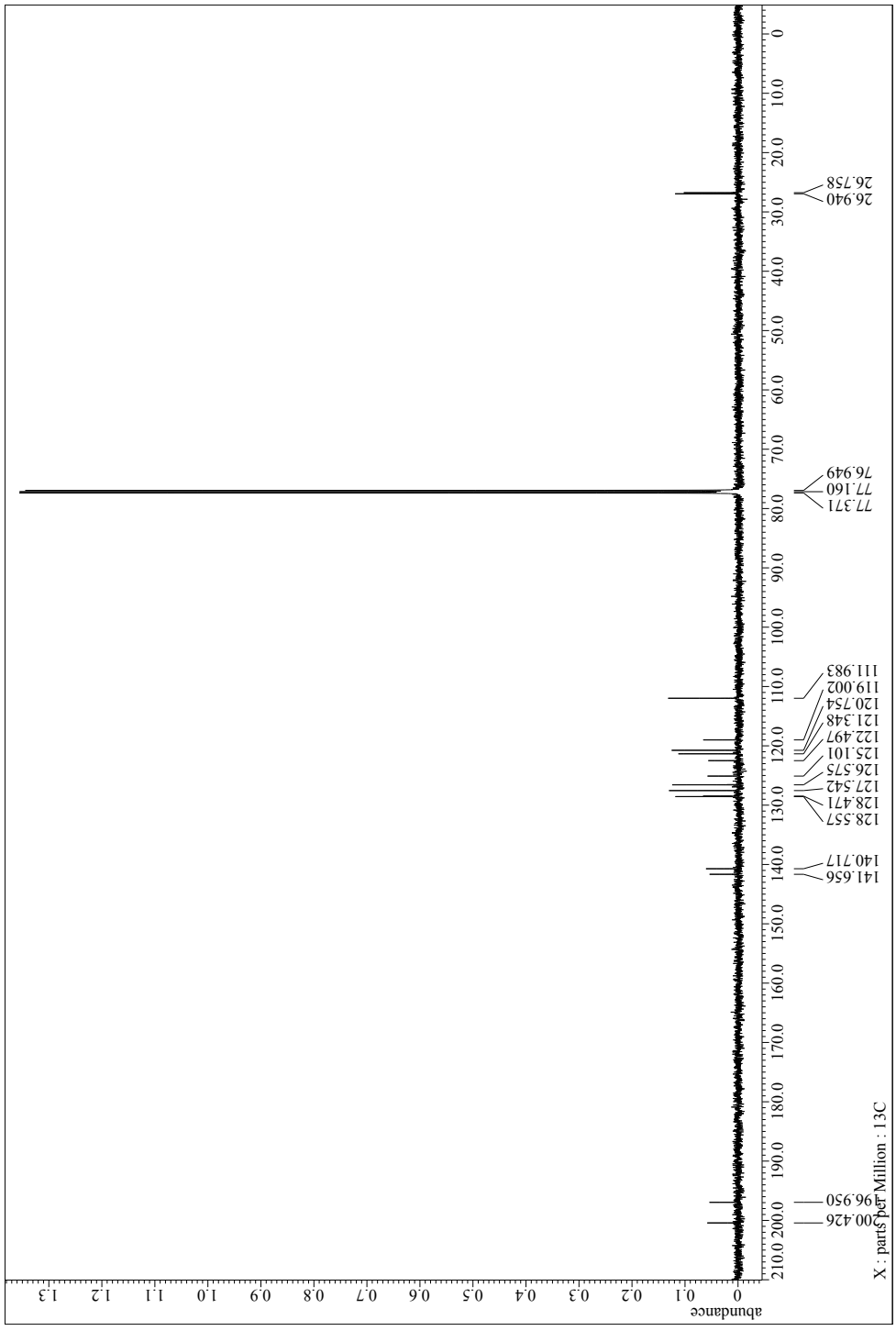
3ca



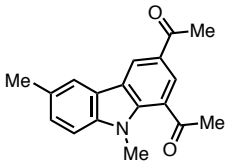
^{13}C NMR (150 MHz, $CDCl_3$) of **3ca**



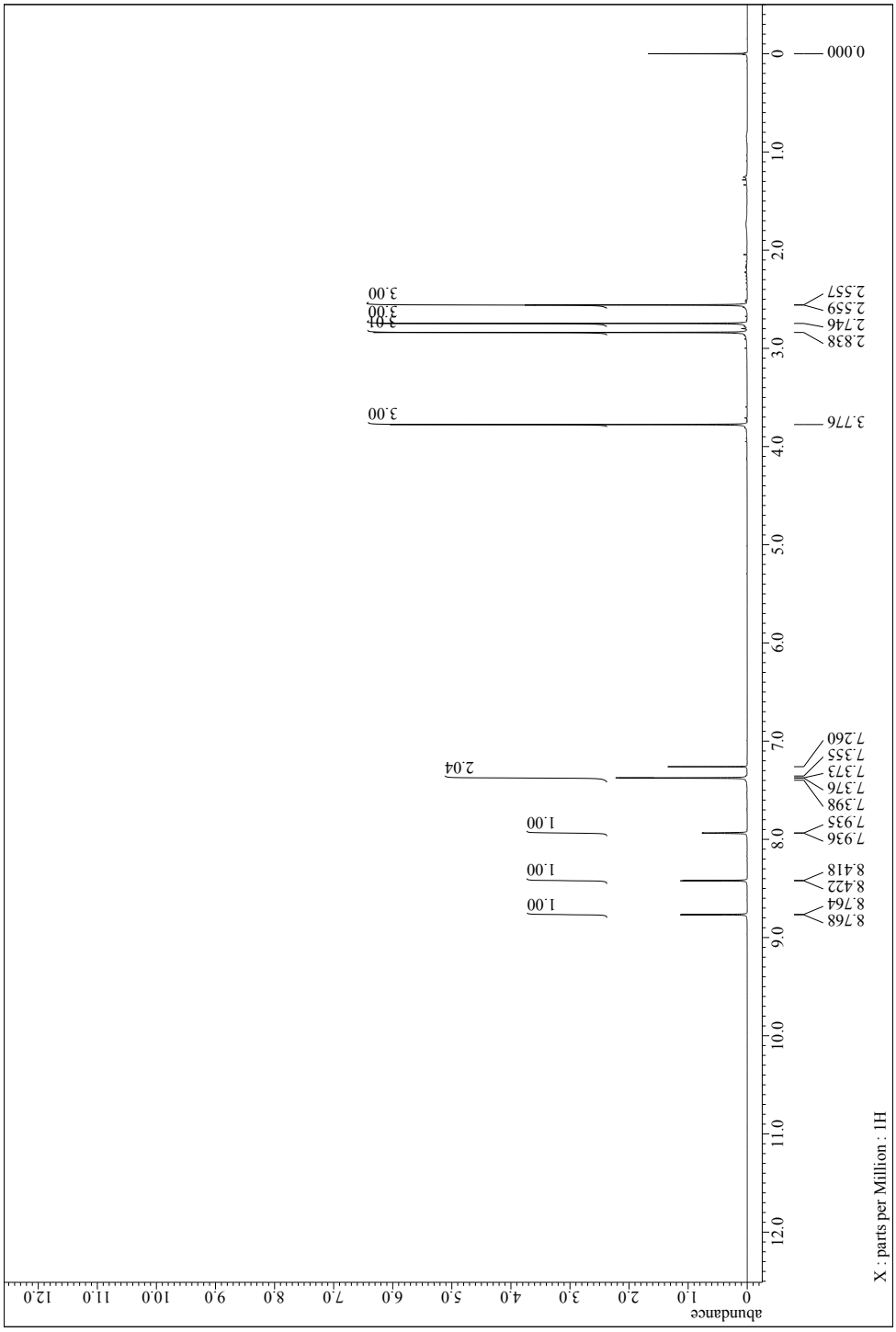
3ca



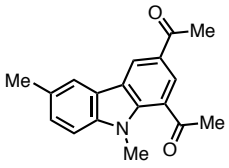
^{1}H NMR (400 MHz, $CDCl_3$) of **3da**



3da



^{13}C NMR (125 MHz, $CDCl_3$) of **3da**



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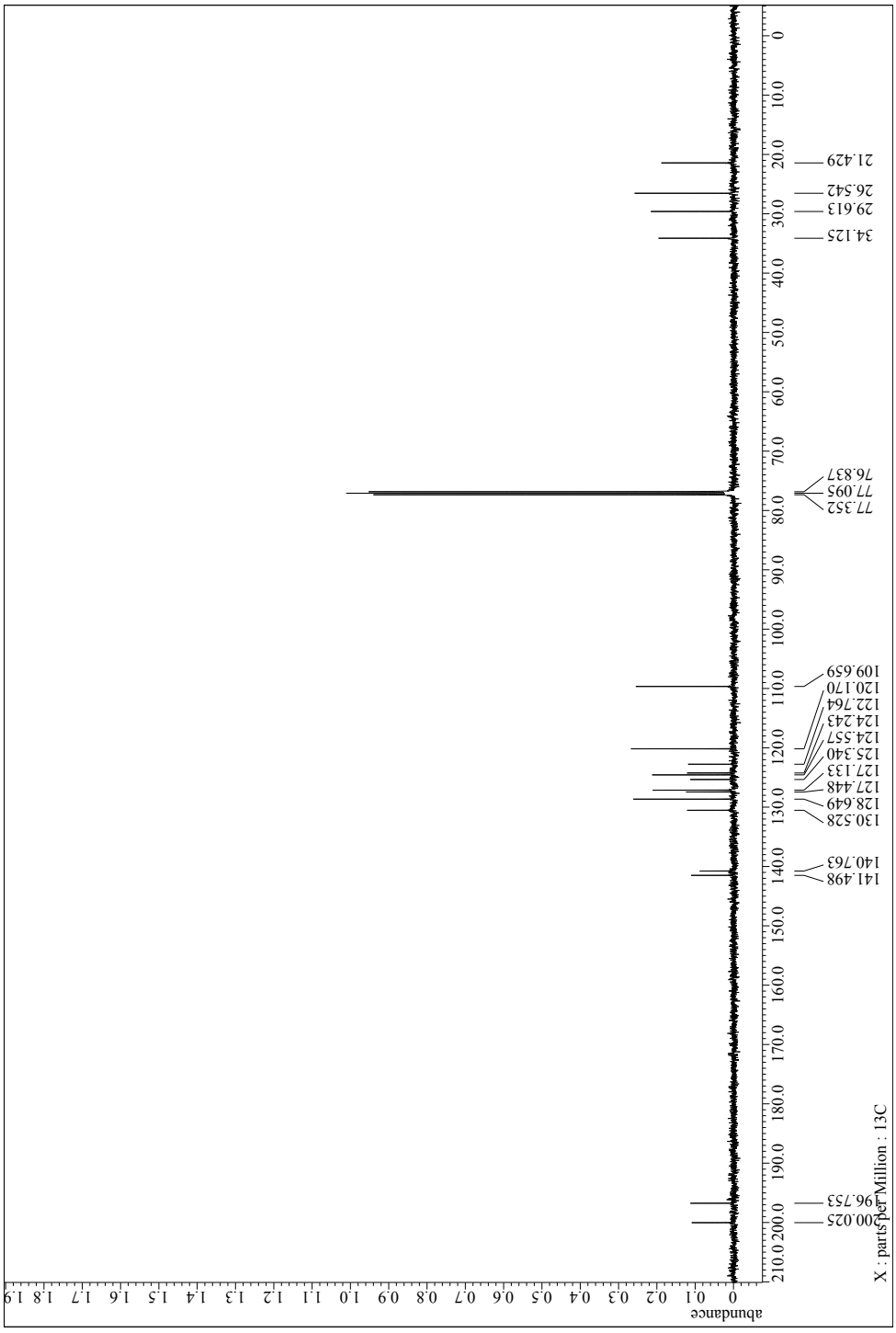
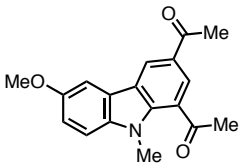


^{1}H NMR (400 MHz, $CDCl_3$) of **3ea**



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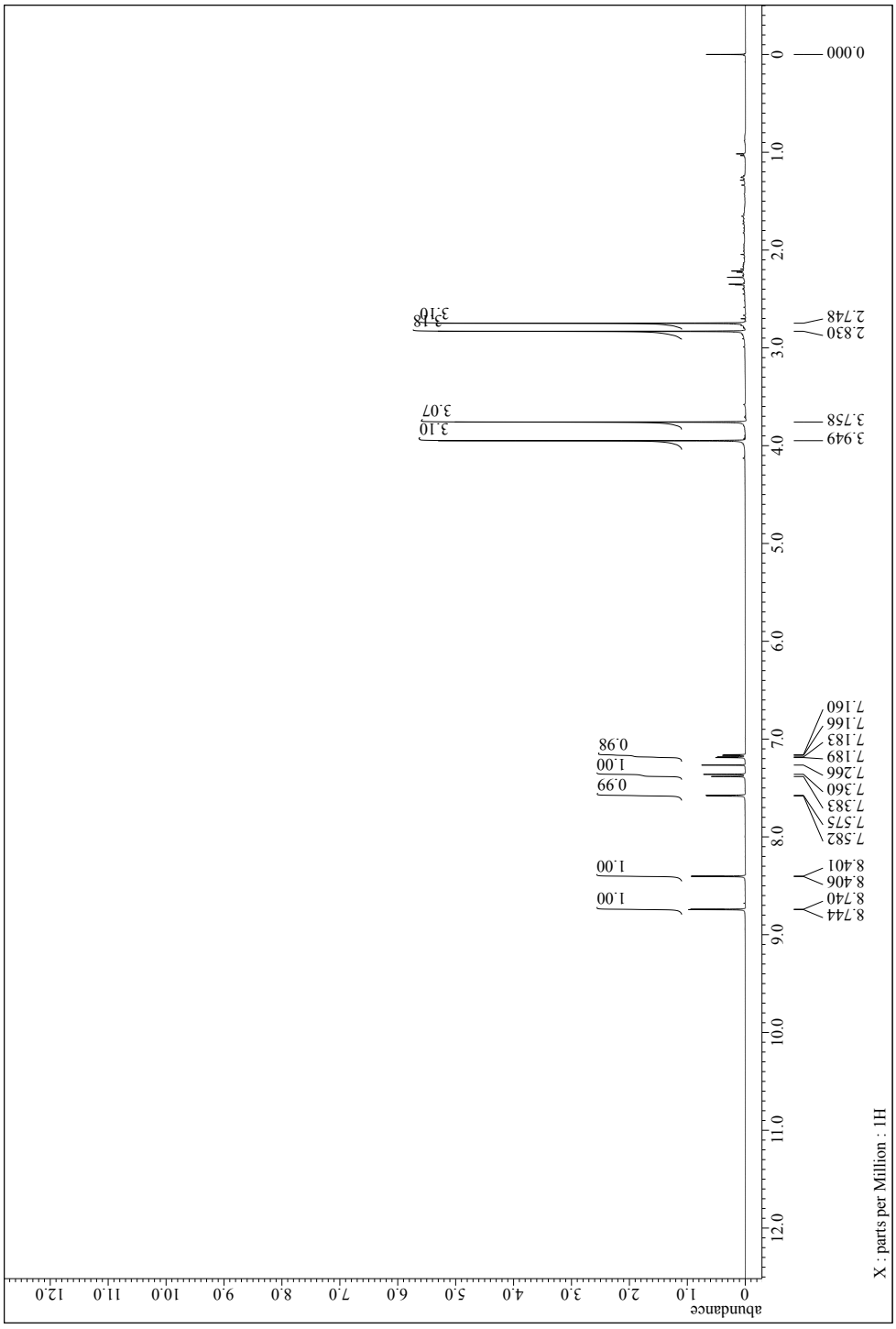
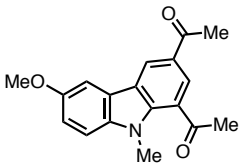


^{13}C NMR (125 MHz, $CDCl_3$) of **3ea**



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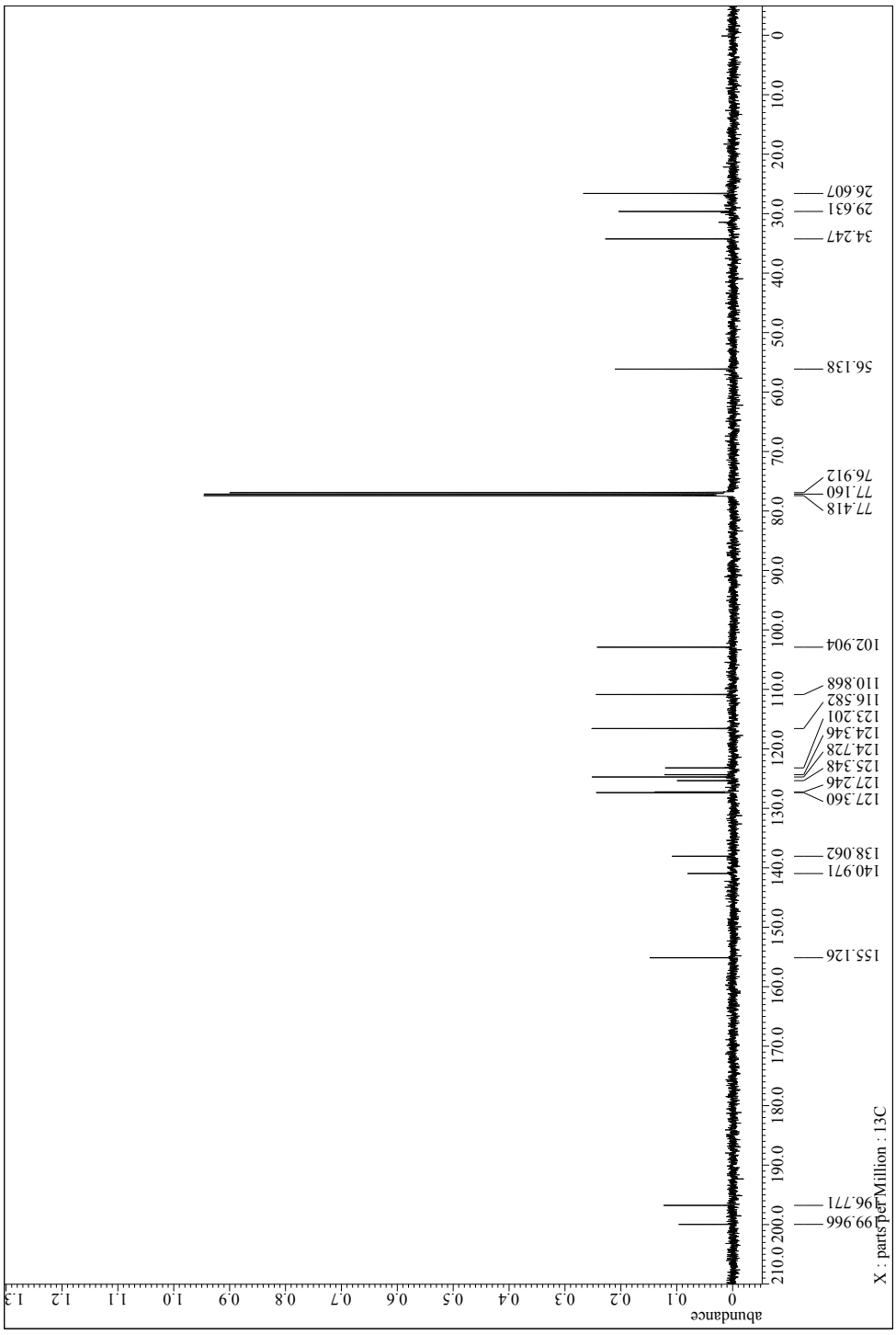
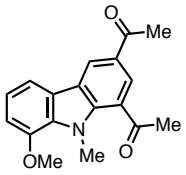


^{1}H NMR (400 MHz, $CDCl_3$) of **3fa**



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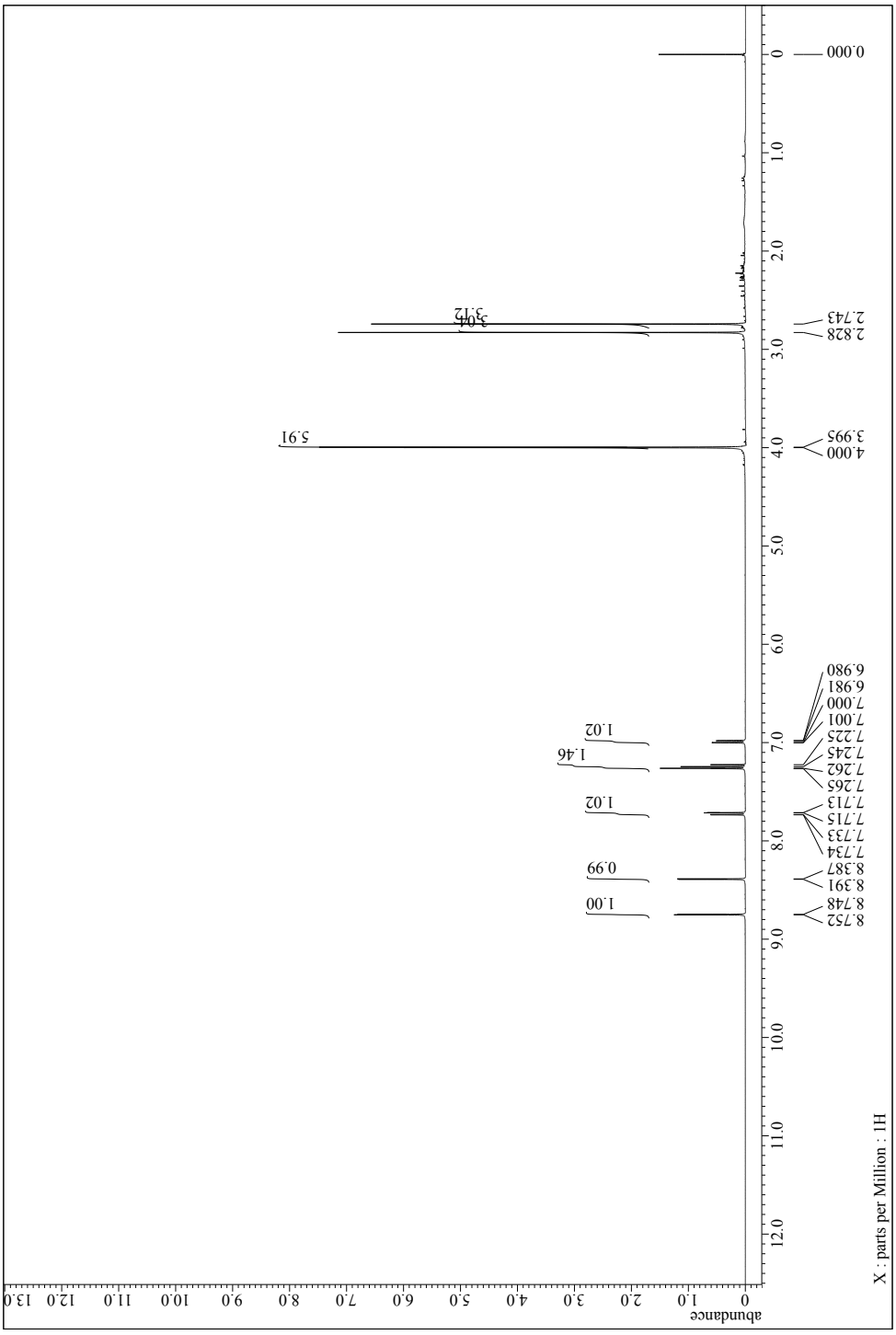
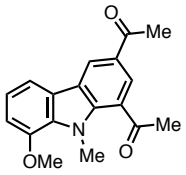


^{13}C NMR (125 MHz, $CDCl_3$) of **3fa**



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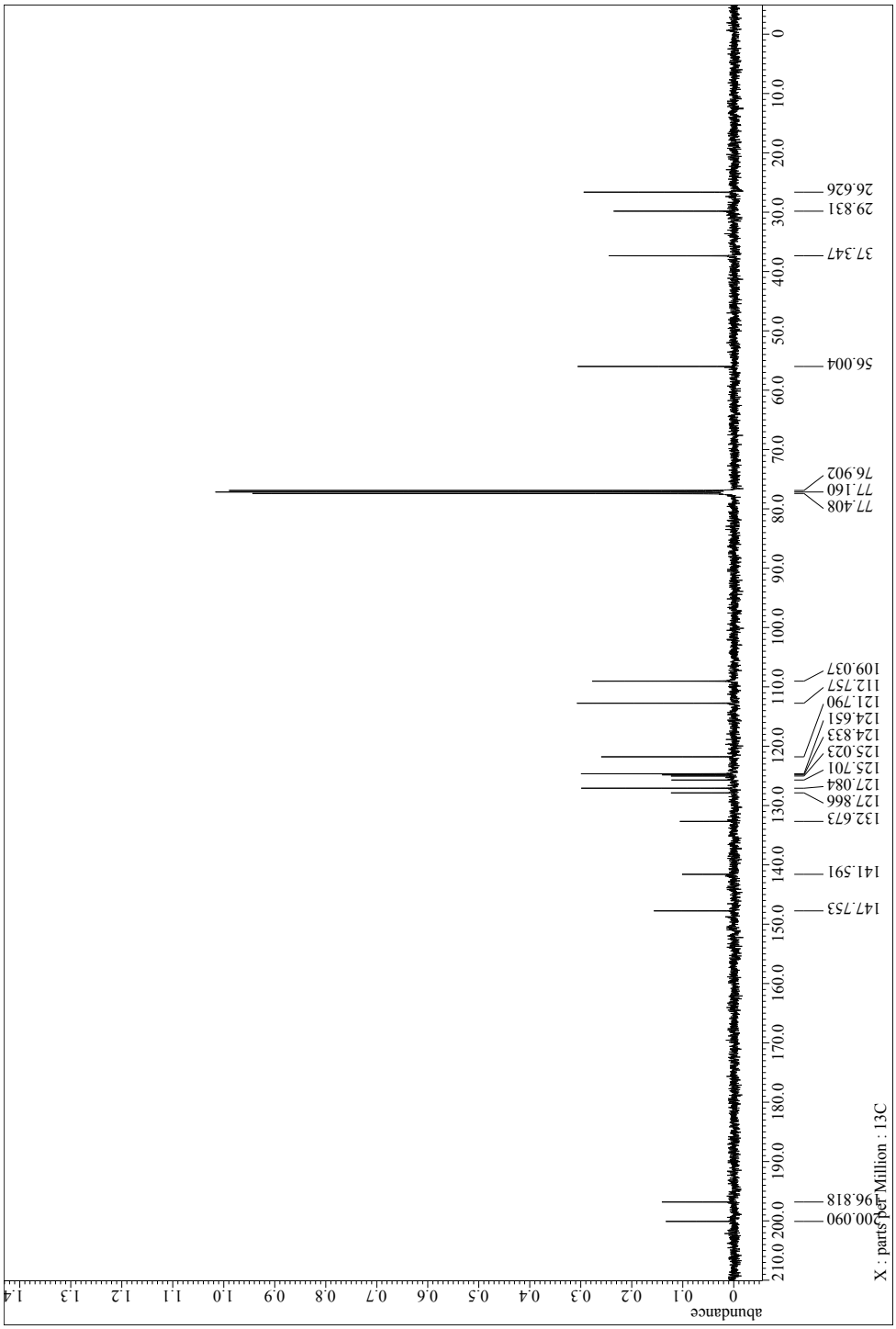
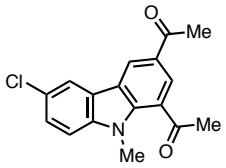
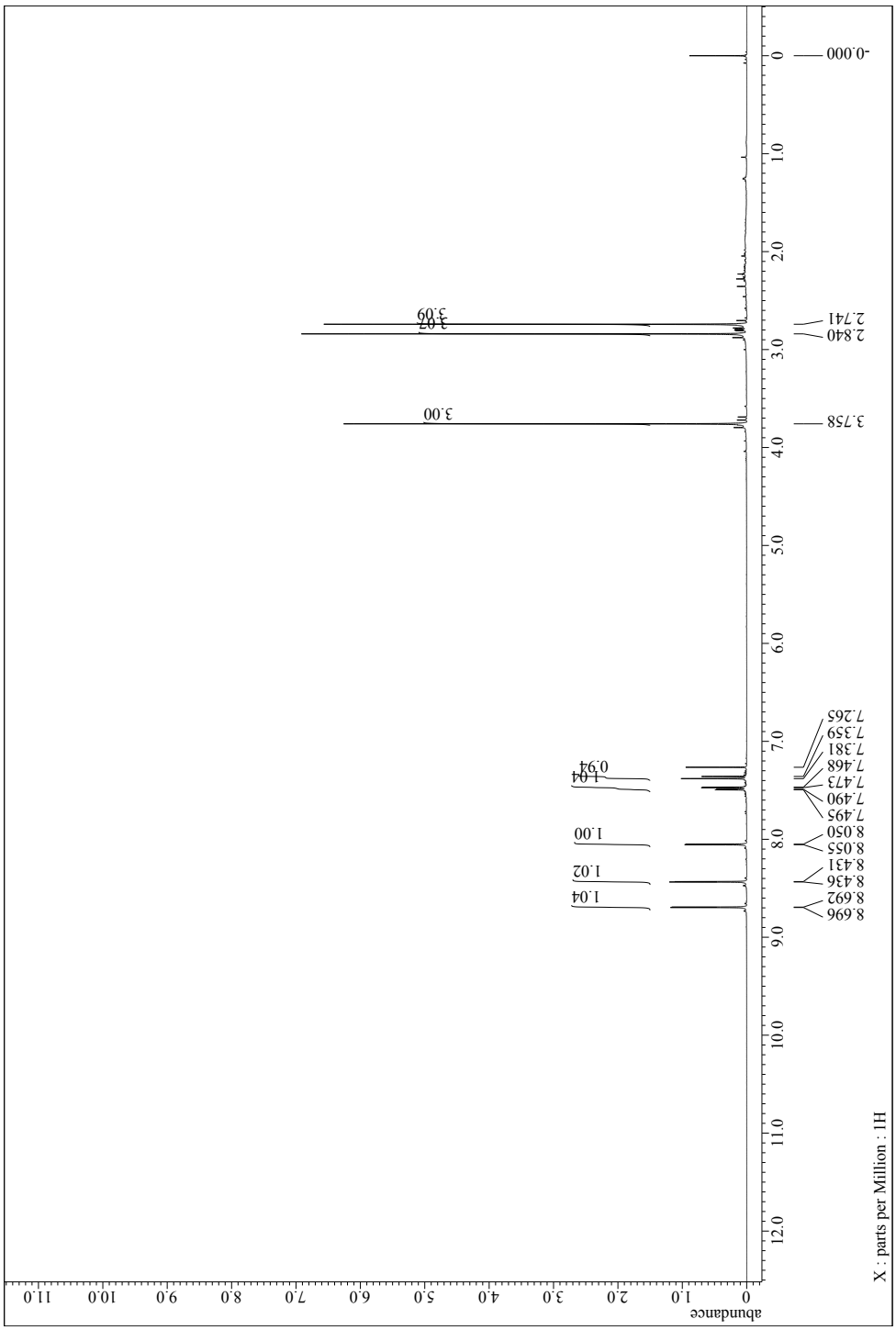


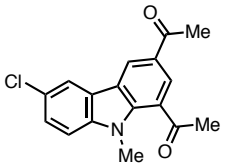
^{1}H NMR (400 MHz, $CDCl_3$) of **3ga**



3ga



^{13}C NMR (125 MHz, $CDCl_3$) of **3ga**



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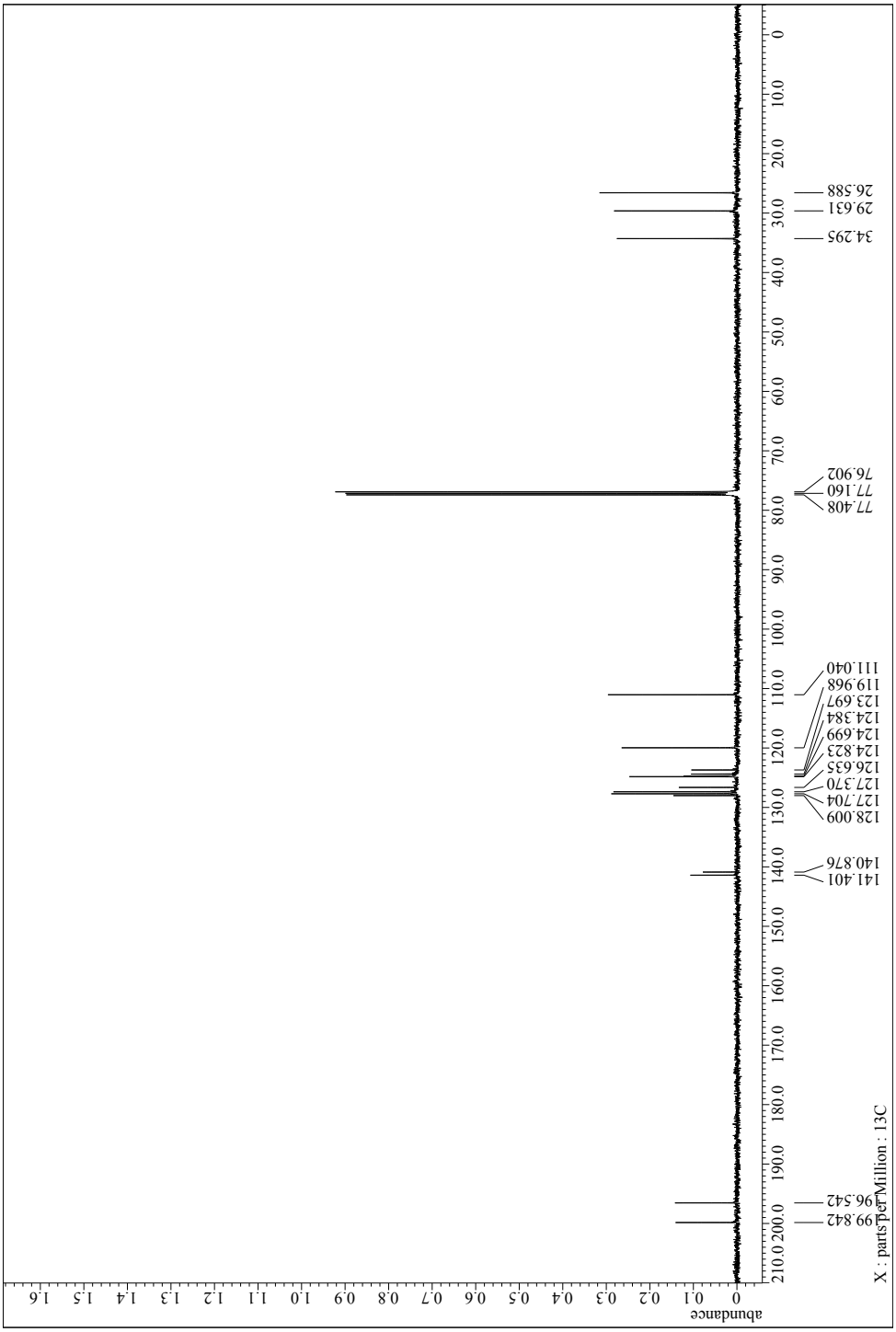
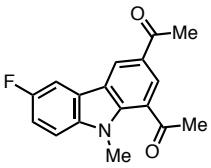
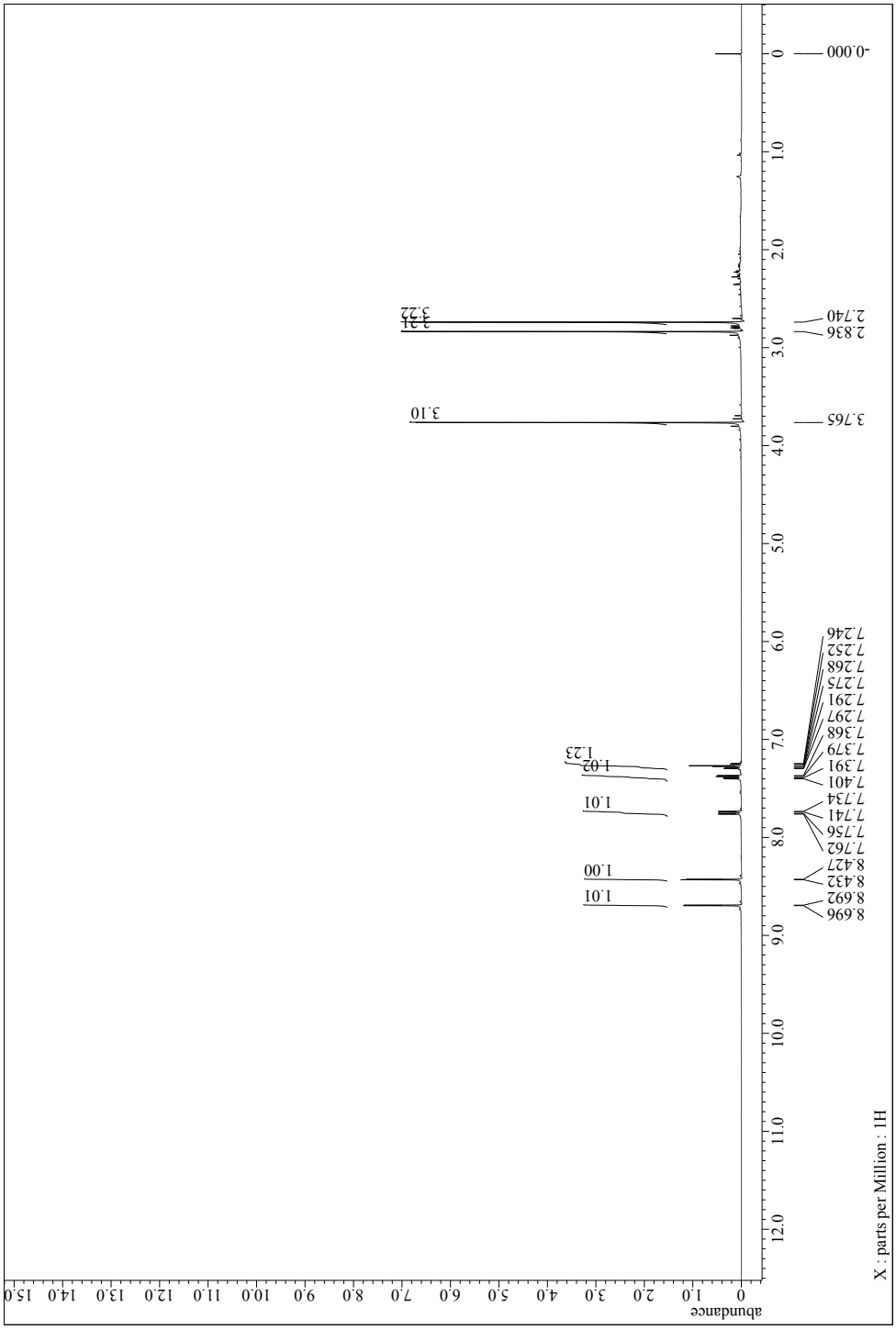


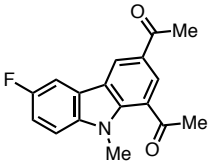
^{1}H NMR (400 MHz, $CDCl_3$) of **3ha**



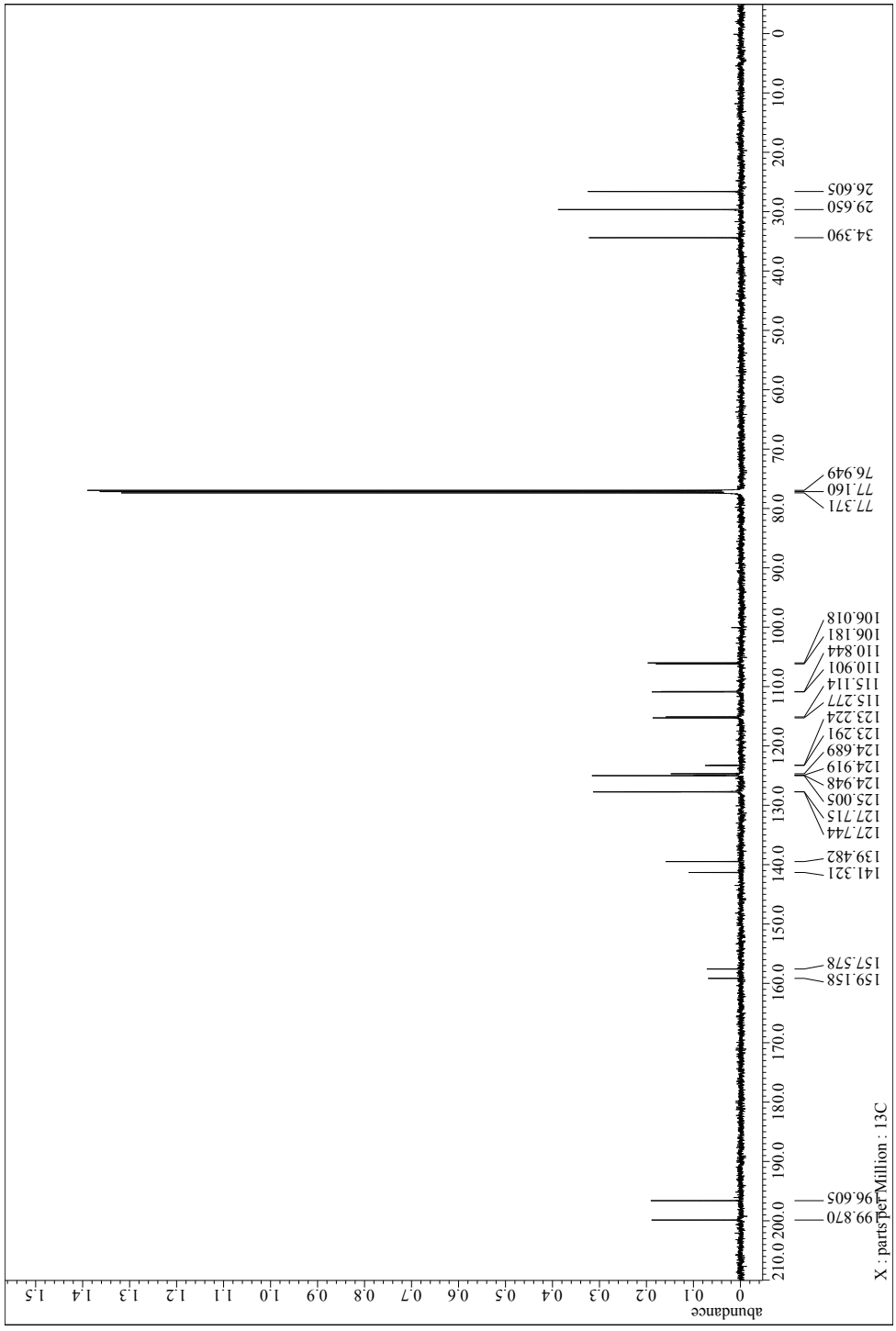
3ha



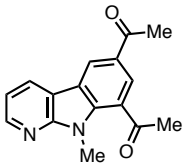
^{13}C NMR (150 MHz, $CDCl_3$) of **3ha**



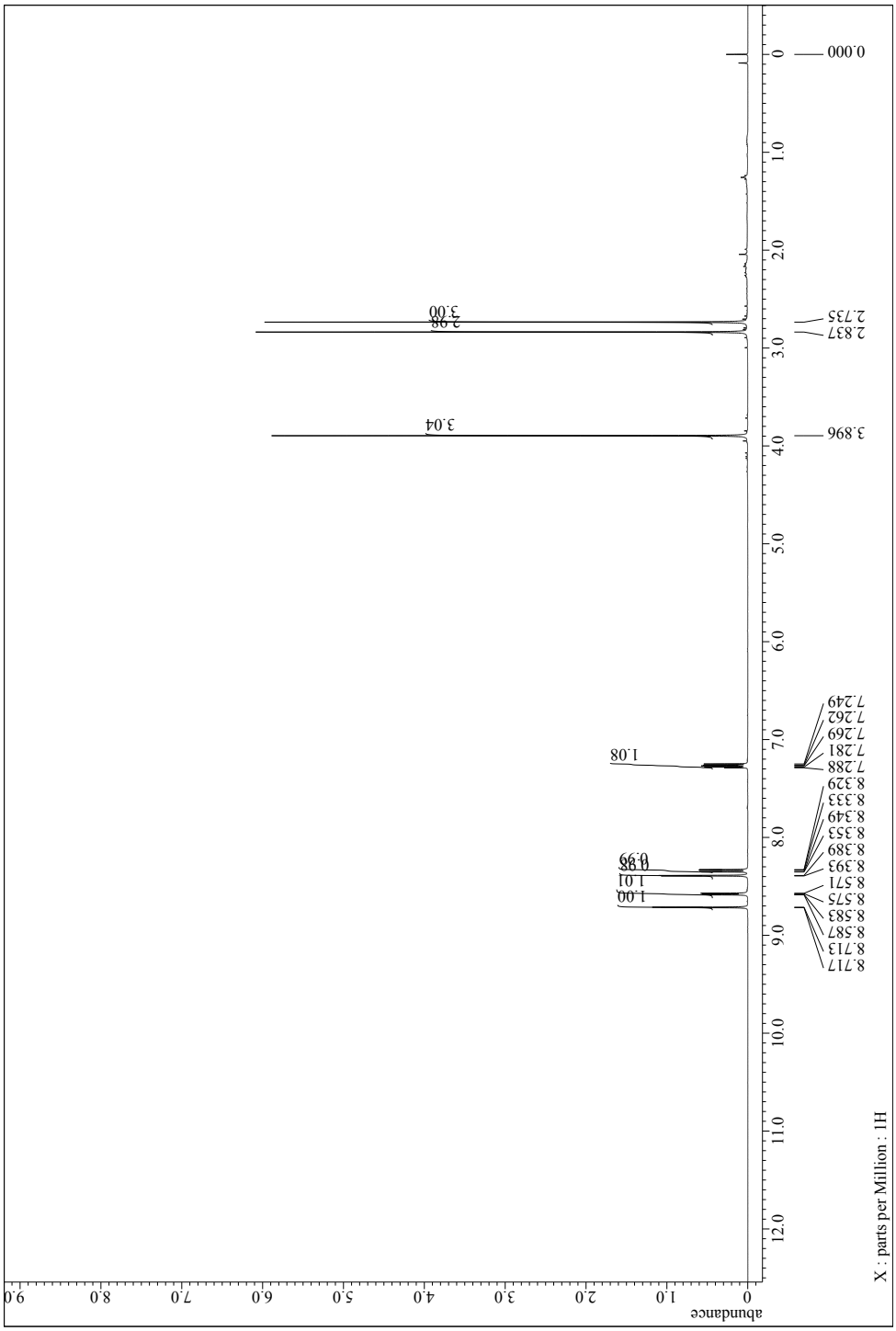
3ha



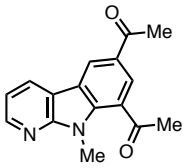
^{1}H NMR (400 MHz, $CDCl_3$) of **3ia**



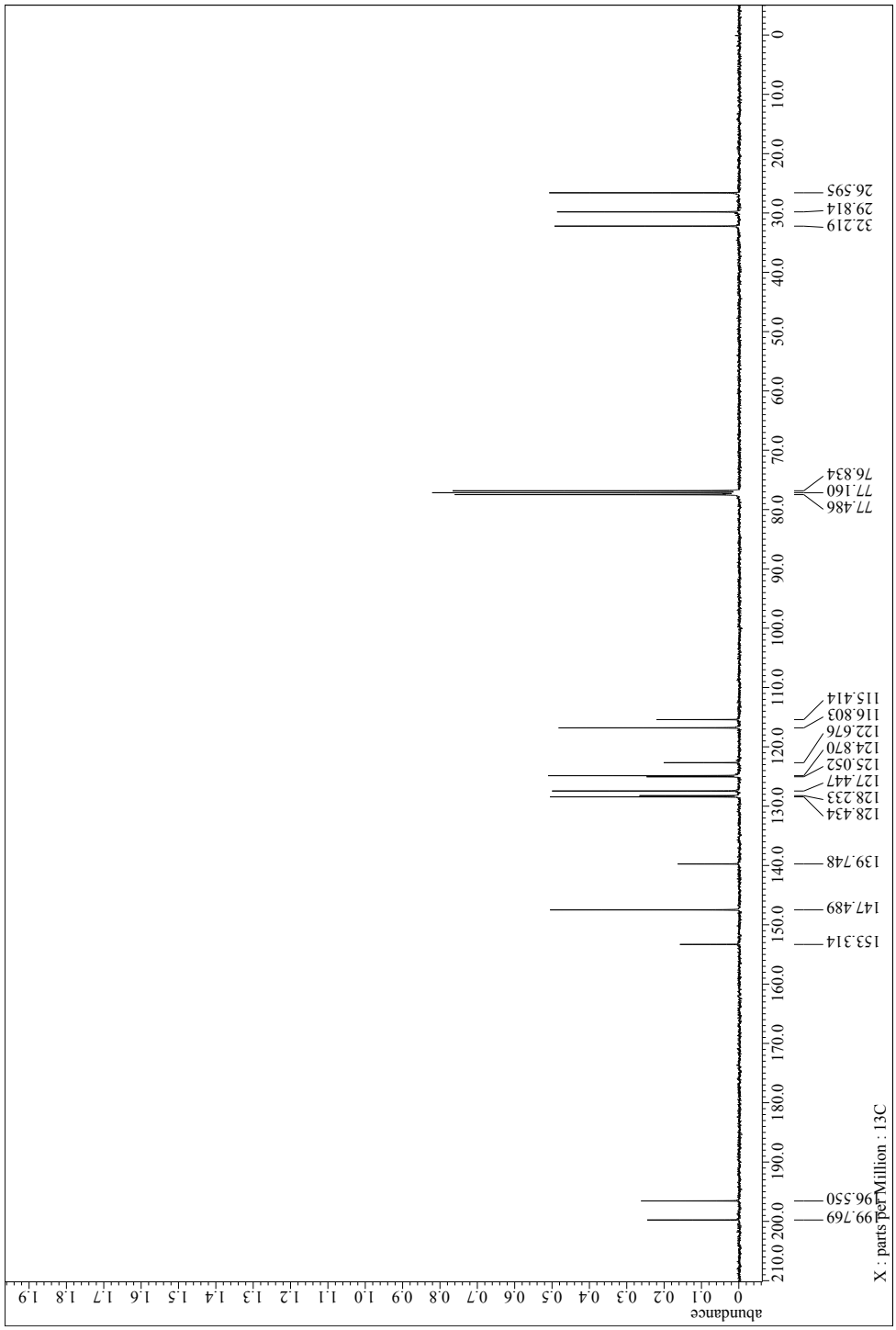
3ia



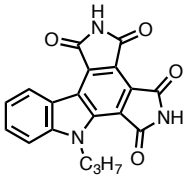
^{13}C NMR (100 MHz, $CDCl_3$) of **3ia**



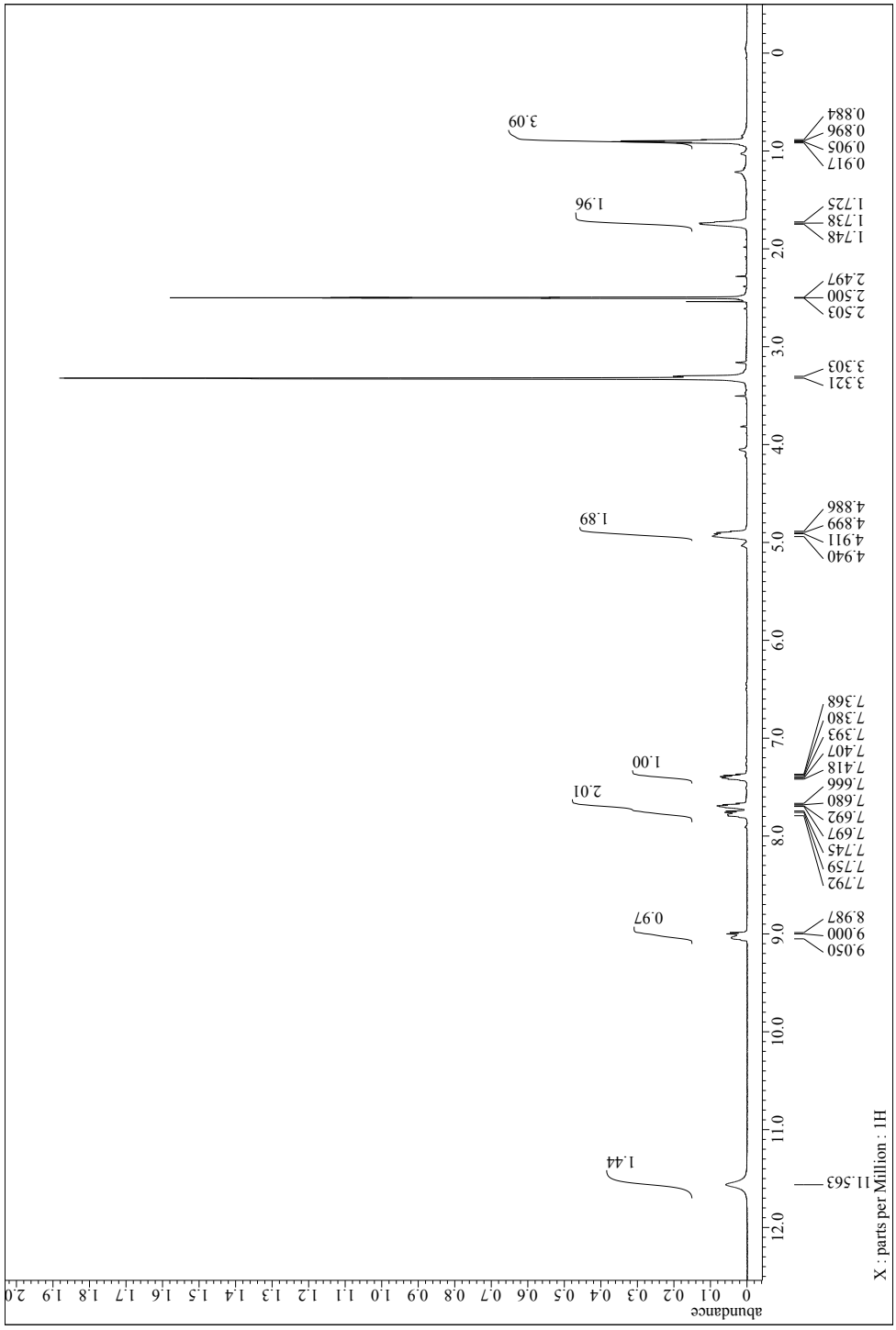
3ia



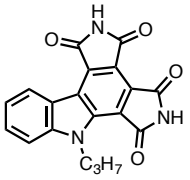
^{1}H NMR (600 MHz, DMSO-*d6*) of **3jh**



3jh



^{13}C NMR (150 MHz, DMSO-*d6*) of **3jh**



3jh