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V-Shaped Fluorophores with a 1-Methyl-4,5-bis(arylethynyl)imidazole Skeleton Displaying Solid-state Fluorescence, Acid Responsiveness, and Remarkable Fluorescence Solvatochromism

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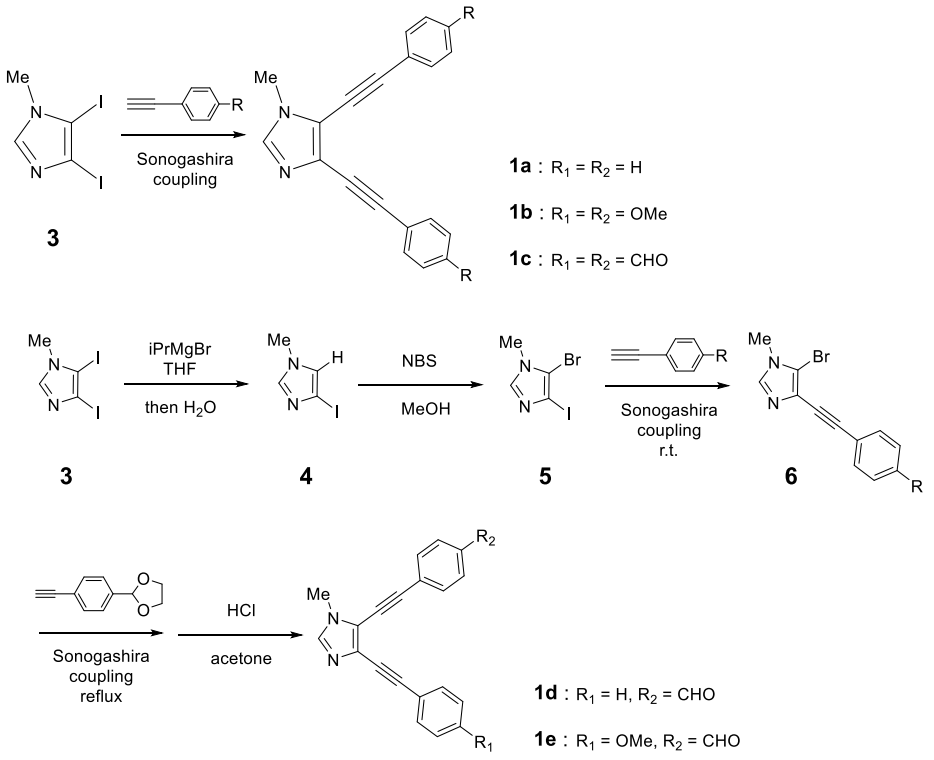
Synthetic methods



• Preparation of 4-iodo-1-methylimidazole (**4**)

To a solution of **3** (334 mg, 1.0 mmol) in dry THF (5 mL) was added slowly isopropylmagnesium bromide (1.5mL, 1 M in dry THF, 1.5 mmol) at 0 °C. The solution was stirred at room temperature for 1 h, then saturated ammonium chloride solution was added. The aqueous phase was extracted with CH_2Cl_2. The combined organic phase extracts were dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography over silica gel (eluent: ethyl acetate) to give **4** as a yellow oil.

Compound data

4 (184 mg, 0.88 mmol, 88%) : ^{1}H-NMR ($CHCl_3$, TMS, 300 MHz) 7.34 (s, 1H), 6.98 (s, 1H), 3.69 (s, 3H) ; HRMS(ESI) calcd. for $C_4H_7IN_2^{2+}$ 209.9643, found 209.9651 [*M*+2H]$^{2+}$

• Preparation of 5-bromo-4-iodo-1-methylimidazole (**5**)

To a solution of **4** (184 mg, 0.88 mmol) in MeOH was added NBS (203 mg, 1.1 mmol). The mixture was stirred at room temperature for 15 h, then quenched with sodium sulfite solution. The aqueous phase was extracted with ethyl acetate. The combined organic phase extracts ware dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography over silica gel (eluent: ethyl acetate/*n*-hexane = 1 / 1) to give **5** as a white solid.

Compound data

5 (132 mg, 0.46 mmol, 52%) : ^{1}H-NMR ($CHCl_3$, TMS, 300 MHz) 7.53 (s, 1H), 3.68 (s, 3H) ; ^{13}C-NMR ($CHCl_3$, TMS, 75 MHz) 139.75, 111.27, 86.33, 34.33 ; IR 3094, 1488, 1237, 945, 658 ; HRMS(ESI) calcd. for $C_4H_5BrIN_2^+$ 286.8675, found 286.8681 [*M*+H]$^+$; Melting point 108-109 °C

• Preparation of 5-bromo-4-(phenylethynyl)-1-methylimidazole (**6d**)

To a mixture of **5** (574 mg, 2.0 mmol), $PdCl_2(PPh_3)_2$ (35 mg, 0.050 mmol) and CuI (19 mg, 0.10 mmol) in THF (4 mL) and Et_3N (1.5 mL) was added dropwise ethynylbenzene (347 µL, 3.0 mmol) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 16 h. THF and Et_3N were then evaporated under reduced pressure. The residue was purified by column chromatography over silica gel (eluent: ethyl acetate / *n*-hexane = 2 / 1) to give **6d** as a brown solid.

Compound data

6d (384 mg, 1.5 mmol, 70%) : ^{1}H-NMR ($CHCl_3$, TMS, 300 MHz) 7.57-7.55 (m, 3H), 7.36-7.32 (m, 3H), 3.65 (s, 3H) ; ^{13}C-NMR ($CHCl_3$, TMS, 100 MHz) 139.72, 138.30, 131.48, 128.30, 128.27, 124.87, 122.86, 109.04, 91.85, 81.64, 33.42 ; IR (KBr) 3399, 3107, 3056, 2947, 2217, 1492, 757, 690 ; HRMS(ESI) calcd. for $C_{12}H_{10}BrN_2^+$ 261.0022, found 260.9999 [*M*+H]$^+$; Melting point 106-107 °C

• Preparation of 5-bromo-4-(4-methoxyphenylethynyl)-1-methylimidazole (**6e**)

Using the procedure described above for the synthesis of **6d**. A mixture of **5** (287 mg, 1.0 mmol), $PdCl_2(PPh_3)_2$ (35 mg, 0.050 mmol), CuI (19 mg, 0.10 mmol), 1-ethynyl-4-methoxybenzene (198 mg, 1.5 mmol) in DMF (2 mL) and Et_3N (1.5 mL) was stirred at room temperature for 16 h under nitrogen atmosphere. Purification by column chromatography over silica gel (eluent: ethyl acetate / *n*-hexane = 2 / 1) gave **6e** as a pale yellow solid.

Compound data

6e (106 mg, 0.36 mmol, 36%) : ^{1}H-NMR ($CHCl_3$, TMS, 300 MHz) 7.53 (s, 1H), 7.49 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 9.0 Hz, 2H), 3.82 (s, 3H), 3.64 (s, 3H) ; ^{13}C-NMR ($CHCl_3$, TMS, 100 MHz) 159.78, 133.17, 132.23, 132.13, 128.66, 128.54, 115.21, 114.05, 92.02, 55.41 ; IR (KBr) 3133, 3007, 2947, 2840, 2536, 2210, 1604, 1502, 1285, 1170, 1027, 835, 690 ; HRMS(ESI) calcd. for $C_{13}H_{12}BrN_2O^+$ 291.0128, found 291.0120 [*M*+H]$^+$; Melting point 113-115 °C

• Preparation of 4,5-bis(phenylethynyl)-1-methylimidazole (**1a**)

To a mixture of **3** (167 mg, 0.50 mmol), $PdCl_2(PPh_3)_2$ (17.5 mg, 0.025 mmol) and CuI (9.5 mg, 0.050 mmol) in DMF (2 mL) and Et_3N (750 µL) was dropwise added ethynylbenzene (165 µL, 1.5 mmol) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 16 h. DMF and Et_3N were then evaporated under reduced pressure. The residue was purified by column chromatography over silica gel (eluent: ethyl acetate / *n*-hexane = 1 / 1) to give brown solid. The white plate crystal of **1a** was prepared by recrystallization from CH_2Cl_2 / *n*-hexane.

Compound data

1a (88.4 mg, 0.31 mmol, 61%) : ^{1}H-NMR ($CHCl_3$, TMS, 300 MHz) 7.58-7.55 (m, 4H), 7.46 (s, 1H), 7.40-7.32 (m, 6H), 3.75 (s, 3H) ; IR (KBr) 3400, 3109, 2948, 2194, 2211, 1490, 756, 688, 631 ; HRMS(ESI) calcd. for $C_{20}H_{15}N_2^+$ 283.1230, found 283.1254 [*M*+H]$^+$; elemental analysis calcd. for C : 85.08, H : 5.00, N : 9.92, found C : 85.26, H : 5.02, N : 9.83 ; Melting point 110-111 °C

• Preparation of 4,5-bis(4-methoxyphenylethynyl)-1-methylimidazole (**1b**)

Using the procedure described above for the synthesis of **1a**. A mixture of **3** (167 mg, 0.50 mmol), $PdCl_2(PPh_3)_2$ (17.5 mg, 0.025 mmol), CuI (9.5 mg, 0.050 mmol), 1-ethynyl-4-methoxybenzene (198 mg, 1.5 mmol) in DMF (2 mL) and Et_3N (750 µL) was stirred at room temperature for 18 h under nitrogen atmosphere. Purification by column chromatography over silica gel (eluent: ethyl acetate / *n*-hexane = 4 / 1) gave brown solid. The white needle crystal of **1b** was prepared by recrystallization from CH_2Cl_2 / *n*-hexane.

Compound data

1b (136 mg, 0.40 mmol, 80%) : ^{1}H-NMR ($CHCl_3$, TMS, 300 MHz) 7.52-7.48 (m, 4H), 7.43 (s, 1H), 6.91-6.85 (m, 4H), 3.85 (s, 3H), 3.82 (s, 3H), 3.72 (s, 3H) ; IR (KBr) 2941, 2840,

2202, 1604, 1497, 1248, 835 ; HRMS(ESI) calcd. for $C_{22}H_{19}N_2O_2^+$ 343.1441, found 343.1414 [*M*+H]$^+$; elemental analysis calcd. for C : 77.17, H : 5.30, N : 8.18, found C : 77.17, H : 5.28, N : 8.17 ; Melting point 102-104 °C

• Preparation of 4,5-bis(4-formylphenylethynyl)-1-methylimidazole (**1c**)

Using the procedure described above for the synthesis of **1a**. A mixture of **3** (60 mg, 0.18 mmol), $PdCl_2(PPh_3)_2$ (6.3 mg, 0.0090 mmol), CuI (3.4 mg, 0.018 mmol), 4-ethynylbenzaldehyde (70 mg, 0.54 mmol) in THF (1 mL) and Et_3N (300 µL) was stirred at room temperature for 16 h under nitrogen atmosphere. Purification by column chromatography over silica gel (eluent: ethyl acetate / *n*-hexane = 2 / 1) gave **1c** as a yellow solid.

Compound data

1c (25 mg, 0.075 mmol, 42%) : ^{1}H-NMR ($CHCl_3$, TMS, 300 MHz) 10.05 (s, 1H), 10.03 (s, 1H), 7.93-7.86 (m, 4H), 7.73-7.70 (m, 4H), 7.53 (s, 1H), 3.79 (s, 3H) ; ^{13}C-NMR ($CHCl_3$, TMS, 100 MHz) 191.54, 191.34, 139.10, 136.01, 135.58, 132.23, 132.13, 131.95, 129.83, 129.70, 129.57, 129.28, 128.69, 128.56, 128.25, 120.24, 99.39, 92.17, 86.57, 80.19, 32.89 ; IR (KBr) 3124, 2848, 2746, 2205, 1691, 1599, 1206, 1160, 806, 788 ; HRMS(ESI) calcd. for $C_{22}H_{15}N_2O_2^+$ 339.1128, found 339.1112 [*M*+H]$^+$; elemental analysis calcd. for C : 78.09, H : 4.17, N : 8.28, found C : 77.74, H : 4.14, N : 8.15 ; Melting point 203-206 °C

• Preparation of 4-phenylethynyl-5-(4-formylphenylethynyl)-1-methylimidazole (**1d**)

To a mixture of **6d** (157 mg, 0.60 mmol), $PdCl_2(PPh_3)_2$ (21 mg, 0.030 mmol) and CuI (11 mg, 0.060 mmol) in DMF (2.4 mL) and Et_3N (900 µL) was added 2-(4-ethynylphenyl)-1,3-dioxolane (157 mg, 0.90 mmol) under nitrogen atmosphere. The reaction mixture was stirred at 90 °C for 16 h. After the reaction, DMF and Et_3N were then evaporated under reduced pressure. The residue was purified by column chromatography over silica gel (eluent: toluene / acetone = 4 / 1) to give yellow solid. Further purification was performed by column chromatography over silica gel (eluent: CH_2Cl_2). The obtained solid was dissolved in acetone and hydrochloric acid (1*N*) was added. The mixture was stirred at room temperature for 30 minutes. The aqueous phase was extracted with CH_2Cl_2. The combined organic phase extracts ware dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography over silica gel (eluent: ethyl acetate / *n*-hexane = 2 / 1) to give **1d** as yellow solid. The yellow plate crystal of **1d** was prepared by recrystallization from CH_2Cl_2 / *n*-hexane.

Compound data

1d (38 mg, 0.12 mmol, 20%) : ^{1}H-NMR ($CHCl_3$, TMS, 300 MHz) 10.04 (s, 1H), 7.90 (d, *J* = 8.7 Hz, 2H), 7.70 (d, *J* = 8.7 Hz, 2H), 7.60-7.57 (m, 2H), 7.50 (s, 1H), 7.37-7.35 (m, 3H), 3.78 (s, 3H) ; IR (KBr) 3093, 2824, 2728, 2206, 2189, 1698, 1600, 1205, 825, 755 ; HRMS(ESI) calcd. for $C_{21}H_{15}N_2O^+$ 311.1179, found 311.1166 [*M*+H]$^+$; elemental analysis calcd. for C : 81.27, H : 4.55, N : 9.03, found C : 81.21, H : 4.51, N : 8.84 ; Melting point 162-163 °C

• Preparation of 4-(4-methoxyphenylethynyl)-5-(4-formylphenylethynyl)-1-methylimidazole (**1e**)

Using the procedure described above for the synthesis of **1d**. A mixture of **6e** (85 mg, 0.29 mmol), $PdCl_2(PPh_3)_2$ (10 mg, 0.015 mmol), CuI (5.5 mg, 0.029 mmol), 2-(4-ethynylphenyl)-1,3-dioxolane (76 mg, 0.15 mmol) in DMF (2 mL) and Et_3N (750 μL) was stirred at 90 °C for 18 h under nitrogen atmosphere. Purification by column chromatography over silica gel (eluent: ethyl acetate / *n*-hexane = 4 / 1) gave brown oil. After reaction using hydrochloric acid, purification by column chromatography over silica gel (eluent: ethyl acetate / *n*-hexane = 2 / 1) gave **1e** as a yellow solid. The yellow plate crystal of **1e** was prepared by recrystallization from CH_2Cl_2 / *n*-hexane.

Compound data

1e (62 mg, 0.18 mmol, 63%) : ^{1}H-NMR ($CHCl_3$, TMS, 300 MHz) 10.04 (s, 1H), 7.90 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.7), 7.49 (s, 1H), 6.89 (d, *J* = 8.7 Hz, 2H), 3.84 (s, 3H), 3.77 (s, 3H); IR (KBr) 3121, 2839, 2215, 2196, 1693, 1601, 1248, 1207, 1164, 1031, 794 ; HRMS(ESI) calcd. for $C_{22}H_{17}N_2O_2^+$ 341.1285, found 341.1255 [*M*+H]$^+$; elemental analysis calcd. for C : 77.63, H : 4.74, N : 8.23, found C : 77.60, H : 4.70, N : 8.10 ; Melting point 146-148 °C

General procedure of **1**-TFA salt

To a solution of **1** in dichloromethane was added dropwise excess amount of TFA. Slow evaporation gave solid of 1-TFA after 1 day. A single crystal was prepared by recrystallization from CH_2Cl_2 / *n*-hexane.

Compound data

1a-TFA : ^{1}H-NMR ($CHCl_3$, TMS, 400 MHz) 8.14 (s, 1H), 7.60-7.57 (m, 4H), 7.44-7.41 (m, 3H), 7.40-7.35 (m, 3H), 3.85 (s, 3H) ; ^{13}C-NMR ($CHCl_3$, TMS, 100 MHz) 161.96, 161.59, 137.02, 131.97, 131.87, 129.97, 129.47, 128.77, 128.56, 123.31, 121.68, 121.14, 120.67,

101.60, 96.96, 74.25, 33.98 ; IR (KBr) 3113, 3047, 2359, 2218, 1683, 1193, 1132, 753, 687 ; HRMS(ESI) calcd. for $C_{20}H_{15}N_2^+$ 283.1230, found 283.1227 [*M*] ; Melting point 105-107 °C

Compound data

1d-TFA : ^{1}H-NMR ($CHCl_3$, TMS, 400 MHz) 10.1 (s, 1H), 8.13 (s, 1H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.40-7.37 (m, 2H), 7.61-7.58 (m, 2H), 3.87 (s, 3H) ; ^{13}C-NMR ($CHCl_3$, TMS, 100 MHz) 191.24, 160.66, 136.41, 133.61, 132.62, 132.29, 132.27, 132.20, 131.36, 129.81, 128.87, 128.76, 127.26, 114.28, 113.60, 97.48, 55.47 ; IR (KBr) 3422, 3129, 2362, 1702, 1604, 1193, 1127 ; HRMS(ESI) calcd. for $C_{21}H_{15}N_2O^+$ 311.1179, found 311.1181 [*M*] ; Melting point 155-157 °C

Compound data

1e-TFA : ^{1}H-NMR ($CHCl_3$, TMS, 400 MHz) 10.1(s, 1H), 8.28 (s, 1H), 7.93 (d, *J* = 7.8 Hz, 2H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 6.91 (d, *J* = 8.2 Hz, 2H), 3.87 (s, 3H) ; ^{13}C-NMR ($CHCl_3$, TMS, 100 MHz) 191.23, 160.72, 136.46, 133.66, 132.66, 132.27, 132.20, 129.82, 128.89, 128.77, 127.19, 114.29, 113.45, 97.83, 55.47, 53.53 ; IR (KBr) 3127, 2212, 1694, 1602, 1514, 1255, 1207, 1167 ; HRMS(ESI) calcd. for $C_{22}H_{17}N_2O_2^+$ 341.1285, found 341.1283 [*M*] ; Melting point 133-135 °C

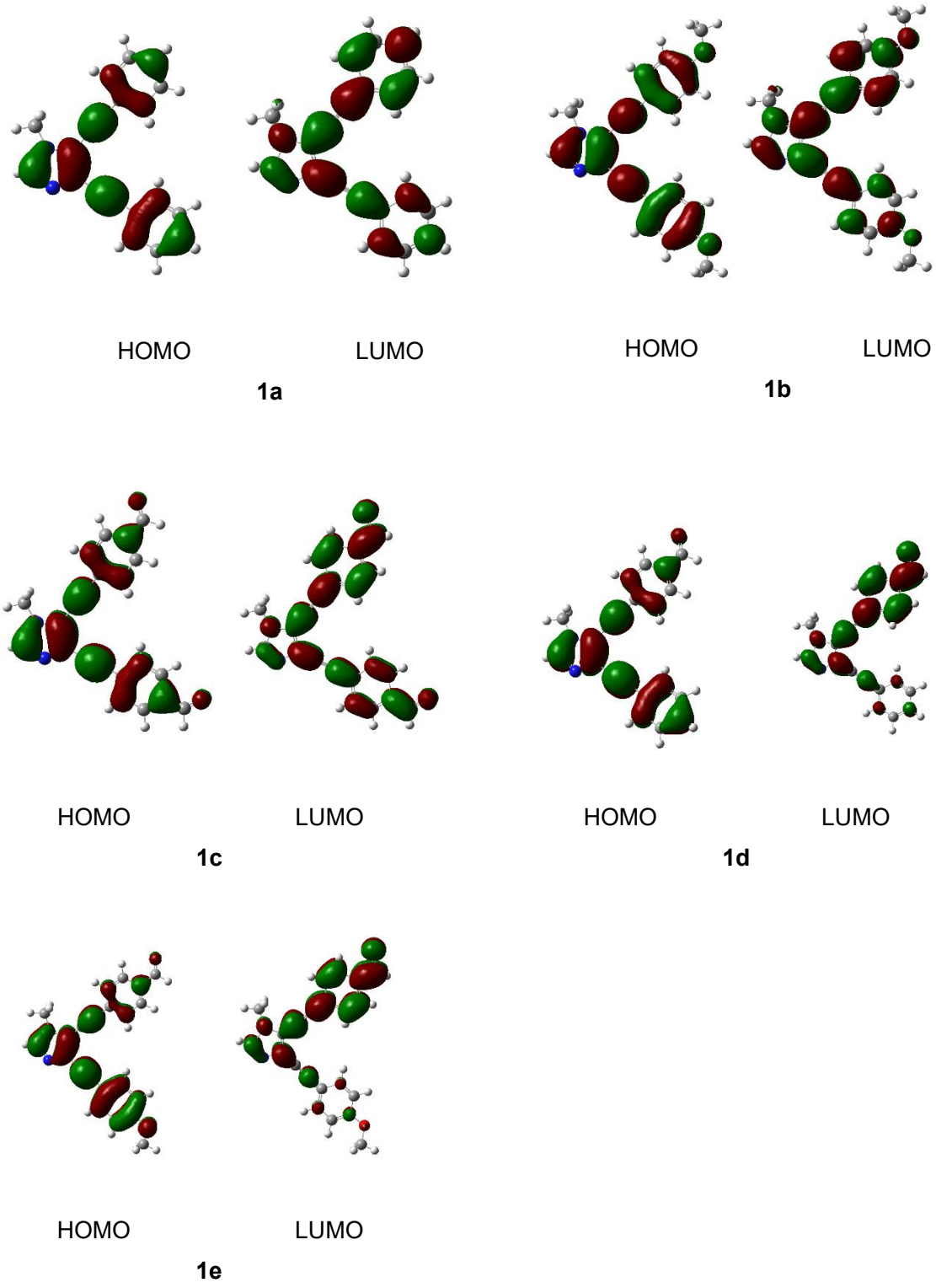


Figure S1. Electron distribution of frontier orbitals of **1a-e**.

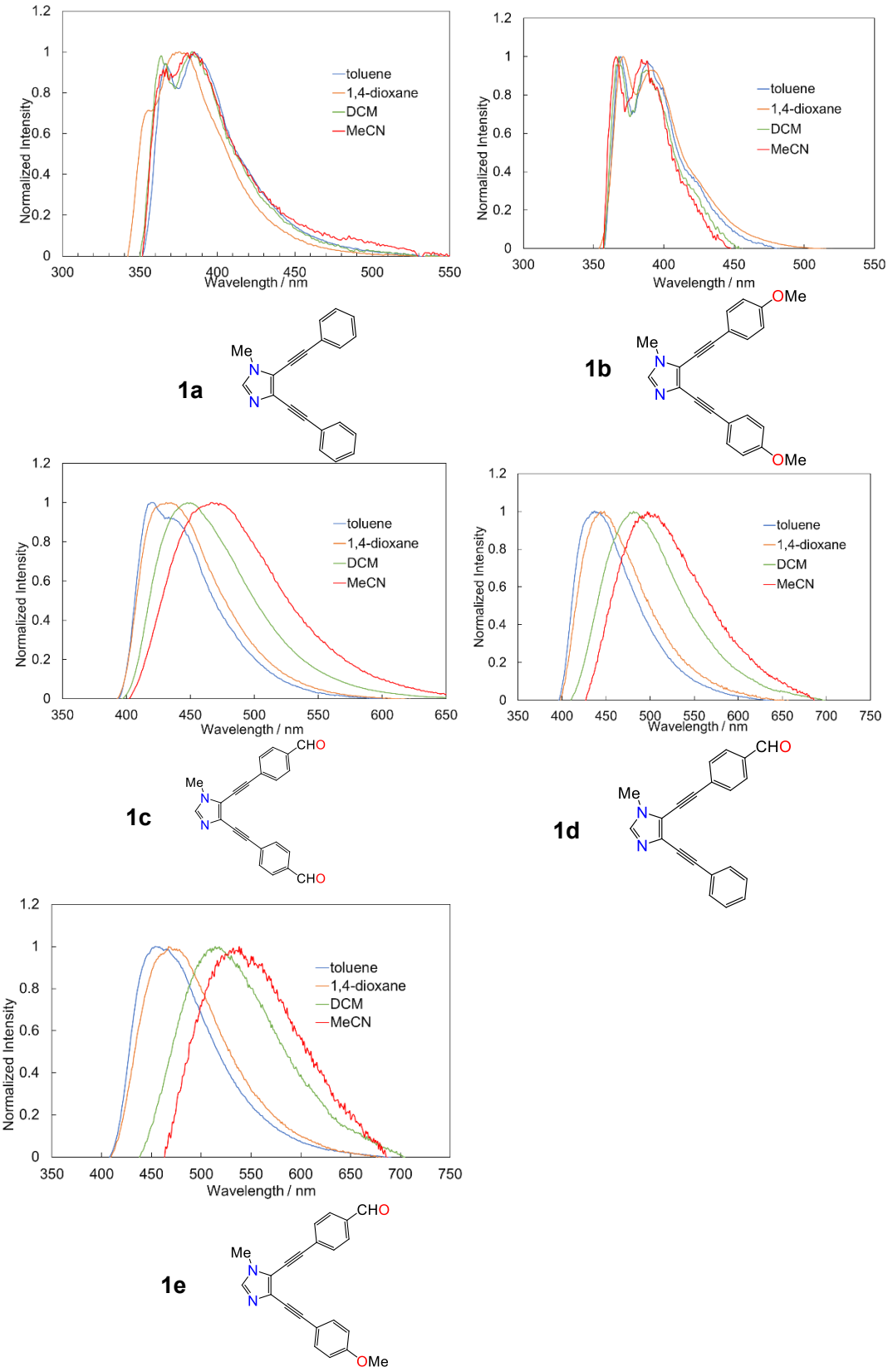


Figure S2. Fluorescence spectra of **1a-e** in various solvents

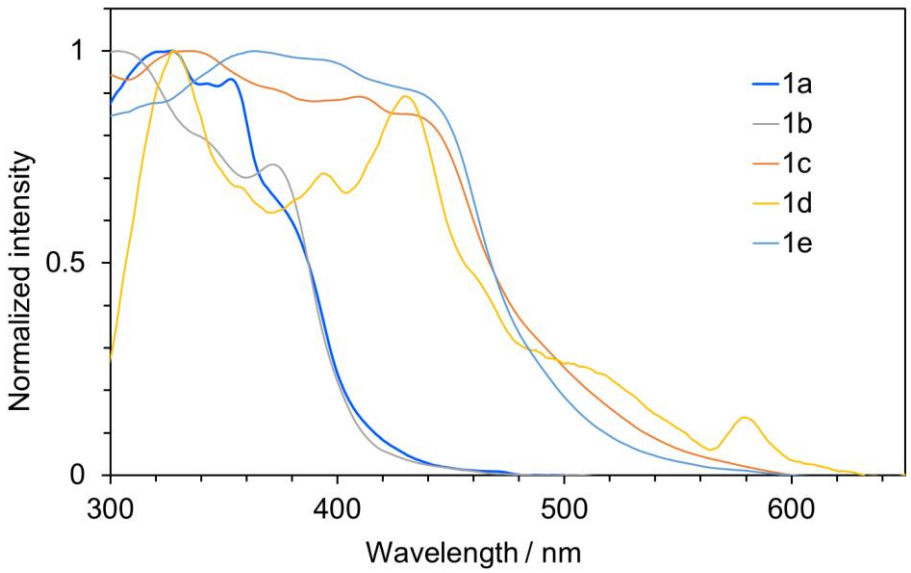


Figure S3. Diffuse reflection spectra of **1a-e** in the solid-state.

Table S1. Optimized atom coordinates of **1a**.

Total energy: -727.7954746 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.827955	-1.021816	-0.000004
2	6	0	-5.501515	-2.377774	0.000082
3	6	0	-4.162028	-2.765784	0.000140
4	6	0	-3.154303	-1.809203	0.000111
5	6	0	-3.471782	-0.438250	0.000024
6	6	0	-4.827098	-0.058163	-0.000034
7	6	0	-2.446952	0.546292	-0.000006
8	6	0	-1.584001	1.395179	-0.000026
9	6	0	2.329702	-2.465997	-0.000281
10	6	0	-0.579907	2.383694	-0.000038
11	6	0	0.805847	2.176371	-0.000072
12	6	0	1.572078	1.004932	-0.000103
13	6	0	2.982255	-1.218503	-0.000036
14	6	0	2.230053	-0.013767	-0.000117
15	6	0	3.065609	-3.644143	-0.000257
16	6	0	4.459731	-3.605259	0.000008
17	6	0	5.116447	-2.375023	0.000250
18	6	0	4.389614	-1.191087	0.000228
19	7	0	1.358251	3.449569	-0.000071
20	6	0	0.314426	4.326992	-0.000038
21	7	0	-0.854483	3.734240	-0.000017
22	1	0	-6.868593	-0.713428	-0.000050
23	1	0	-6.286150	-3.127412	0.000105
24	1	0	-3.901601	-3.819516	0.000207
25	1	0	-5.078820	0.996453	-0.000101
26	1	0	2.548657	-4.598357	-0.000448
27	1	0	5.030763	-4.527850	0.000025
28	1	0	6.201107	-2.337966	0.000456
29	1	0	4.901553	-0.235022	0.000417
30	1	0	0.472564	5.396456	-0.000030
31	6	0	2.774833	3.769497	0.000143
32	1	0	3.261082	3.360176	-0.887223
33	1	0	3.260553	3.361684	0.888504
34	1	0	2.888505	4.853029	-0.000756
35	1	0	-2.112244	-2.109259	0.000156
36	1	0	1.245931	-2.494782	-0.000491

Table S2. Optimized atom coordinates of **1b**.

Total energy: -1109.2513894 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.398405
3	6	0	1.220974	0.000000	2.087057
4	6	0	2.416140	0.000000	1.392668
5	6	0	2.437038	0.000000	-0.017689
6	6	0	1.206807	0.000000	-0.692860
7	6	0	3.662831	0.000000	-0.734330
8	6	0	4.701330	0.000009	-1.357019
9	6	0	7.588664	0.000388	3.320469
10	6	0	5.910104	0.000084	-2.081255
11	6	0	7.208035	0.000157	-1.554187
12	6	0	7.678603	0.000177	-0.235415
13	6	0	8.518736	0.000369	2.258872
14	6	0	8.077614	0.000211	0.910147
15	6	0	8.011929	0.000479	4.635579
16	6	0	9.380222	0.000553	4.942468
17	6	0	10.316792	0.000535	3.903825
18	6	0	9.884409	0.000444	2.581215
19	7	0	8.044666	0.000213	-2.662348
20	6	0	7.236331	0.000172	-3.760783
21	7	0	5.961199	0.000013	-3.459627
22	1	0	-0.926887	0.000000	-0.559612
23	1	0	1.201056	0.000000	3.171209
24	1	0	1.200333	0.000000	-1.777107
25	1	0	7.300441	0.000494	5.453682
26	1	0	11.379795	0.000591	4.109189
27	1	0	10.618221	0.000430	1.782646
28	1	0	7.641974	0.000201	-4.762941
29	6	0	9.496166	0.000496	-2.639618
30	1	0	9.872838	-0.886734	-2.127190
31	1	0	9.872580	0.888637	-2.128564
32	1	0	9.862006	-0.000256	-3.665905
33	1	0	3.355165	0.000000	1.934831
34	1	0	6.528565	0.000331	3.093765
35	6	0	11.057200	0.000717	6.647138
36	1	0	11.062032	0.000778	7.735373
37	1	0	11.574872	-0.893310	6.283408
38	1	0	11.574787	0.894756	6.283314
39	6	0	-2.386923	0.000000	1.539804
40	1	0	-3.121122	0.000000	2.343299
41	1	0	-2.527080	0.893757	0.922299
42	1	0	-2.527081	-0.893755	0.922297
43	8	0	9.689424	0.000639	6.267153
44	8	0	-1.118281	0.000000	2.175627

Table S3. Optimized atom coordinates of **1c**.

Total energy: -1106.858041 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.399379
3	6	0	1.221219	0.000000	2.088277
4	6	0	2.415819	0.000000	1.392504
5	6	0	2.422242	0.000000	-0.019504
6	6	0	1.192926	0.000000	-0.706776
7	6	0	3.644907	0.000000	-0.737151
8	6	0	4.681769	-0.000001	-1.362658
9	6	0	7.587074	-0.000885	3.295375
10	6	0	5.884657	-0.000002	-2.093489
11	6	0	7.186753	-0.000021	-1.571933
12	6	0	7.657990	-0.000042	-0.255810
13	6	0	8.510931	-0.000571	2.232149
14	6	0	8.058201	-0.000110	0.889489
15	6	0	8.035522	-0.001327	4.607307
16	6	0	9.405286	-0.001471	4.892624
17	6	0	10.328875	-0.001162	3.837757
18	6	0	9.892416	-0.000720	2.526135
19	7	0	8.016514	-0.000014	-2.683054
20	6	0	7.202372	0.000076	-3.776487
21	7	0	5.927939	0.000126	-3.469267
22	1	0	-0.944619	0.000000	-0.537096
23	1	0	1.204169	0.000000	3.172556
24	1	0	1.193159	0.000000	-1.790569
25	1	0	7.316817	-0.001566	5.422174
26	1	0	11.386863	-0.001279	4.075455
27	1	0	10.607036	-0.000482	1.710806
28	1	0	7.601903	0.000100	-4.780908
29	6	0	9.470239	0.000084	-2.670024
30	1	0	9.848456	-0.887952	-2.161047
31	1	0	9.848389	0.888698	-2.161995
32	1	0	9.828282	-0.000460	-3.698632
33	1	0	3.361227	0.000000	1.923029
34	1	0	6.525982	-0.000765	3.074999
35	6	0	9.874060	-0.001944	6.295564
36	8	0	11.035049	-0.002097	6.635378
37	1	0	9.063646	-0.002161	7.056744
38	6	0	-1.277574	0.000000	2.142994
39	8	0	-1.377154	0.000000	3.348986
40	1	0	-2.187179	0.000000	1.503093

Table S4. Optimized atom coordinates of **1d**.

Total energy: -993.5028143 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.394688
3	6	0	1.210918	0.000000	2.086374
4	6	0	2.414686	0.000000	1.392649
5	6	0	2.426690	0.000000	-0.014375
6	6	0	1.198729	0.000000	-0.702254
7	6	0	3.653356	0.000000	-0.731906
8	6	0	4.689602	0.000001	-1.357547
9	6	0	7.596183	-0.000433	3.297222
10	6	0	5.893641	0.000005	-2.088675
11	6	0	7.196134	-0.000097	-1.568390
12	6	0	7.668524	-0.000224	-0.253346
13	6	0	8.521118	-0.000398	2.234331
14	6	0	8.069756	-0.000305	0.891960
15	6	0	8.042981	-0.000404	4.609383
16	6	0	9.412445	-0.000293	4.897372
17	6	0	10.337126	-0.000210	3.843144
18	6	0	9.902370	-0.000238	2.531174
19	7	0	8.026776	-0.000045	-2.681315
20	6	0	7.212289	0.000080	-3.772897
21	7	0	5.937165	0.000113	-3.464482
22	1	0	-0.939426	0.000000	-0.543403
23	1	0	1.216641	0.000000	3.171709
24	1	0	1.201372	0.000000	-1.786445
25	1	0	7.323155	-0.000470	5.423427
26	1	0	11.394958	-0.000124	4.081888
27	1	0	10.618141	-0.000174	1.716783
28	1	0	7.610607	0.000142	-4.777897
29	6	0	9.479733	0.000113	-2.668584
30	1	0	9.858821	-0.887680	-2.159395
31	1	0	9.858710	0.888741	-2.160752
32	1	0	9.838070	-0.000664	-3.697291
33	1	0	3.357402	0.000000	1.928554
34	1	0	6.535402	-0.000524	3.075123
35	6	0	9.877915	-0.000263	6.300136
36	8	0	11.038050	-0.000249	6.644630
37	1	0	9.064826	-0.000406	7.058989
38	1	0	-0.938440	0.000000	1.939492

Table S5. Optimized atom coordinates of **1e**.

Total energy: -1108.0549967 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	6	0	0.000000	0.000000	1.398824
3	6	0	1.221031	0.000000	2.088262
4	6	0	2.415970	0.000000	1.394295
5	6	0	2.436236	0.000000	-0.016067
6	6	0	1.206497	0.000000	-0.692406
7	6	0	3.661195	0.000000	-0.733026
8	6	0	4.698246	0.000004	-1.358220
9	6	0	7.599168	-0.000238	3.298055
10	6	0	5.902667	0.000022	-2.088021
11	6	0	7.205254	-0.000017	-1.567213
12	6	0	7.677061	-0.000082	-0.252405
13	6	0	8.525889	-0.000137	2.236400
14	6	0	8.077014	-0.000130	0.893634
15	6	0	8.043536	-0.000276	4.610981
16	6	0	9.412564	-0.000215	4.901894
17	6	0	10.339024	-0.000116	3.849054
18	6	0	9.906734	-0.000077	2.536318
19	7	0	8.036999	0.000023	-2.680529
20	6	0	7.222864	0.000082	-3.771270
21	7	0	5.947385	0.000016	-3.463836
22	1	0	-0.926892	0.000000	-0.559390
23	1	0	1.200295	0.000000	3.172301
24	1	0	1.200511	0.000000	-1.776598
25	1	0	7.322106	-0.000354	5.423608
26	1	0	11.396395	-0.000070	4.089740
27	1	0	10.624026	0.000000	1.723280
28	1	0	7.621232	0.000122	-4.776298
29	6	0	9.489673	0.000179	-2.667093
30	1	0	9.868832	-0.887527	-2.157794
31	1	0	9.868711	0.888619	-2.158969
32	1	0	9.848436	-0.000488	-3.695628
33	1	0	3.354927	0.000000	1.936552
34	1	0	6.538837	-0.000286	3.073930
35	6	0	-2.387243	0.000000	1.540547
36	1	0	-3.119625	0.000000	2.345445
37	1	0	-2.527587	0.893969	0.923806
38	1	0	-2.527587	-0.893967	0.923802
39	8	0	-1.116829	0.000000	2.175004
40	6	0	9.875196	-0.000257	6.305062
41	8	0	11.034450	-0.000282	6.652780
42	1	0	9.060621	-0.000409	7.062326

Table S6. Crystal data of **1a-e**.

	1a	**1b**	**1c**	**1d**	**1e**
Fomula	$C_{20}H_{14}N_2$	$C_{22}H_{18}N_2O_2$	$C_{22}H_{14}N_2O_2$	$C_{21}H_{14}N_2O$	$C_{22}H_{16}N_2O_2$
F. W.	282.33	342.38	338.35	310.34	340.37
T/ K	300	300	300	302	302
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	P1	$P2_1/n$	$P2_1/c$	$P2_1/c$	P-1
a/ Å	9.6262(10)	10.4483(9)	9.5584(3)	10.8306(3)	9.3320(4)
b/ Å	12.6518(13)	7.9356(7)	22.8679(6)	16.0766(5)	9.8300(4)
c/ Å	13.3053(14)	22.7149(18)	8.4503(2)	11.0441(3)	11.3679(5)
α(°)	87.690(4)	90	90	90	97.151(2)
β(°)	81.189(4)	95.017(3)	106.7870(10)	119.2370(10)	114.1460(10)
γ(°)	80.098(4)	90	90	90	102.008(2)
V/ Å^3	1577.3(3)	1876.2(3)	1768.36(8)	1678.01(8)	904.73(7)
Z	4	4	4	4	2
ρ_{calcd} / g cm^{-3}	1.189	1.212	1.271	1.228	1.249
R_1 ($I > 2\sigma(I)$)	0.0591	0.0982	0.0425	0.0433	0.0479
wR_2	0.175	0.295	0.1656	0.1382	0.1572
GOF	0.790	1.438	1.454	0.779	1.723

Table S7. Result of TD-DFT calculation of the contact c dimer in the crystal of **1b**

Excited State 1: Singlet-A 3.6328 eV 341.29 nm f=0.5180 <S**2>=0.000
179 -> 181 0.67253
180 -> 181 -0.18648
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -2217.78381399
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.6929 eV 335.73 nm f=0.0627 <S**2>=0.000
179 -> 181 0.17014
180 -> 181 0.64087
180 -> 182 0.22275

Excited State 3: Singlet-A 3.7260 eV 332.75 nm f=0.5760 <S**2>=0.000
180 -> 181 -0.21137
180 -> 182 0.65811

Excited State 4: Singlet-A 3.7616 eV 329.61 nm f=0.0134 <S**2>=0.000
179 -> 182 0.69801

Excited State 5: Singlet-A 4.2276 eV 293.27 nm f=0.1417 <S**2>=0.000
177 -> 181 0.18587
179 -> 183 0.62430
179 -> 184 0.15727
180 -> 183 -0.14173

Table S8. Result of TD-DFT calculation of the contact c dimer in the crystal of **1c**

Excited State 1: Singlet-A 2.9220 eV 424.31 nm f=0.0283 <S**2>=0.000

176 -> 177 0.67944

176 -> 179 -0.18590

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -2213.08123339

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.1270 eV 396.50 nm f=0.0057 <S**2>=0.000

175 -> 177 0.51348

176 -> 178 -0.48164

Excited State 3: Singlet-A 3.1455 eV 394.17 nm f=1.0712 <S**2>=0.000

175 -> 177 0.47857

176 -> 178 0.51235

Excited State 4: Singlet-A 3.3728 eV 367.61 nm f=0.0380 <S**2>=0.000

175 -> 178 0.68034

176 -> 179 -0.17023

Excited State 5: Singlet-A 3.3764 eV 367.21 nm f=0.0015 <S**2>=0.000

175 -> 178 0.17576

176 -> 177 0.18449

176 -> 179 0.64752

Table S9. Result of TD-DFT calculation of the contact c trimer in the crystal of **1b**

Excitation energies and oscillator strengths:

```
 Excited State   1:      Singlet-A      3.6303 eV  341.52 nm  f=0.6215
<S**2>=0.000
      268 -> 271        0.67627
      269 -> 271       -0.13258
      270 -> 271        0.10799
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -3326.74468713
 Copying the excited state density for this state as the 1-particle RhoCI density.

 Excited State   2:      Singlet-A      3.6762 eV  337.26 nm  f=0.2828
<S**2>=0.000
      268 -> 271        0.11677
      269 -> 271        0.32152
      269 -> 272        0.38377
      270 -> 271       -0.30002
      270 -> 272       -0.35045

 Excited State   3:      Singlet-A      3.7012 eV  334.99 nm  f=0.2285
<S**2>=0.000
      268 -> 271        0.12332
      269 -> 271        0.37958
      269 -> 272       -0.32986
      270 -> 271       -0.35052
      270 -> 272        0.30784
   Excited State   4:      Singlet-A      3.7187 eV  333.40 nm  f=0.5389
<S**2>=0.000
      269 -> 272       -0.23690
      269 -> 273        0.31150
      270 -> 272       -0.32197
      270 -> 273        0.47809
   Excited State   5:      Singlet-A      3.7444 eV  331.12 nm  f=0.0065
<S**2>=0.000
      268 -> 272        0.66033
      268 -> 273        0.20764
```

Table S10. Result of TD-DFT calculation of the contact c trimer in the crystal of **1c**

Excitation energies and oscillator strengths:

```
 Excited State   1:      Singlet-A      2.9284 eV  423.38 nm  f=0.0322
<S**2>=0.000
      264 -> 265        -0.32293
      264 -> 266         0.59991
      264 -> 269        -0.16841
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =   -3319.67579720
 Copying the excited state density for this state as the 1-particle RhoCI density.

 Excited State   2:      Singlet-A      3.0120 eV  411.64 nm  f=0.0343
<S**2>=0.000
      263 -> 265         0.61262
      263 -> 268        -0.16300
      264 -> 265        -0.25463
      264 -> 266        -0.15310

 Excited State   3:      Singlet-A      3.0521 eV  406.23 nm  f=0.0387
<S**2>=0.000
      263 -> 265         0.29176
      264 -> 265         0.57206
      264 -> 266         0.27272

 Excited State   4:      Singlet-A      3.1315 eV  395.93 nm  f=0.5169
<S**2>=0.000
      262 -> 265         0.55333
      263 -> 266        -0.23676
      264 -> 267         0.36137

 Excited State   5:      Singlet-A      3.1408 eV  394.75 nm  f=0.0062
<S**2>=0.000
      262 -> 265        -0.41594
      263 -> 266        -0.14166
      264 -> 267         0.54660
```

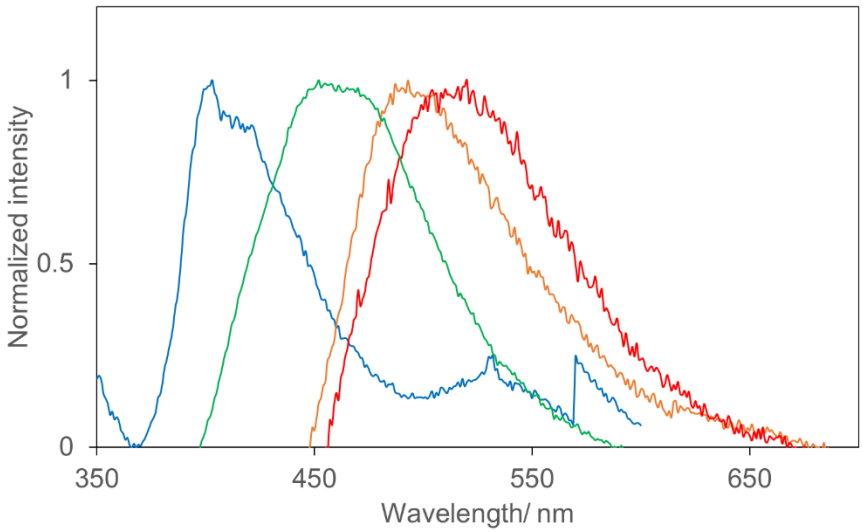


Figure S4. Solid-state fluorescence spectra of **1a, b, d, e** after exposure to HCl vapor. (Blue: **1a** (Φ = 0.01), Green: **1b** (Φ = 0.03), Orange: **1d** (Φ < 0.01), and Red: **1e** (Φ < 0.01)) Compound **1c** showed no fluorescence.

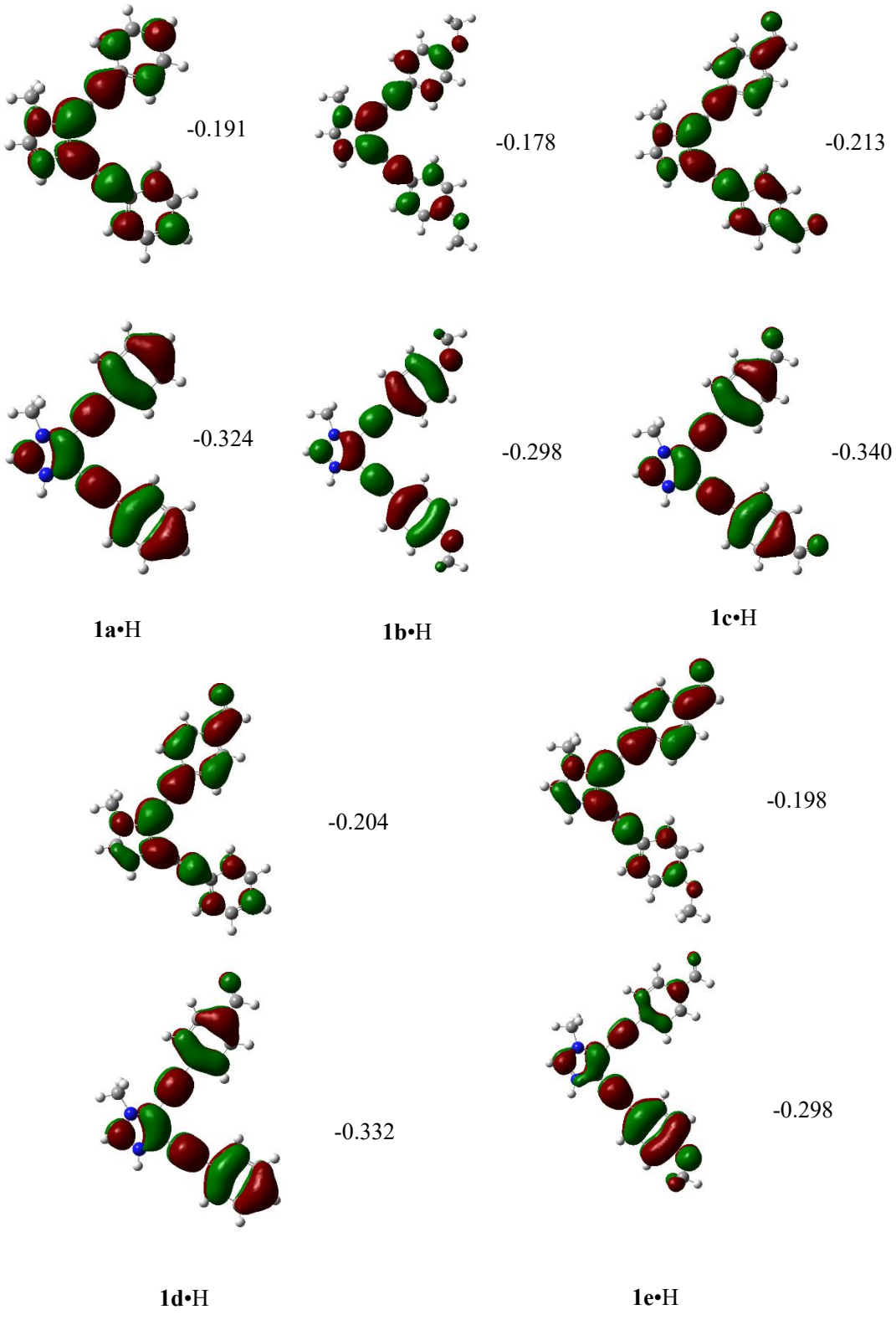


Figure S5. Electron distribution of **1a-e**•H cation of HOMO and LUMO.

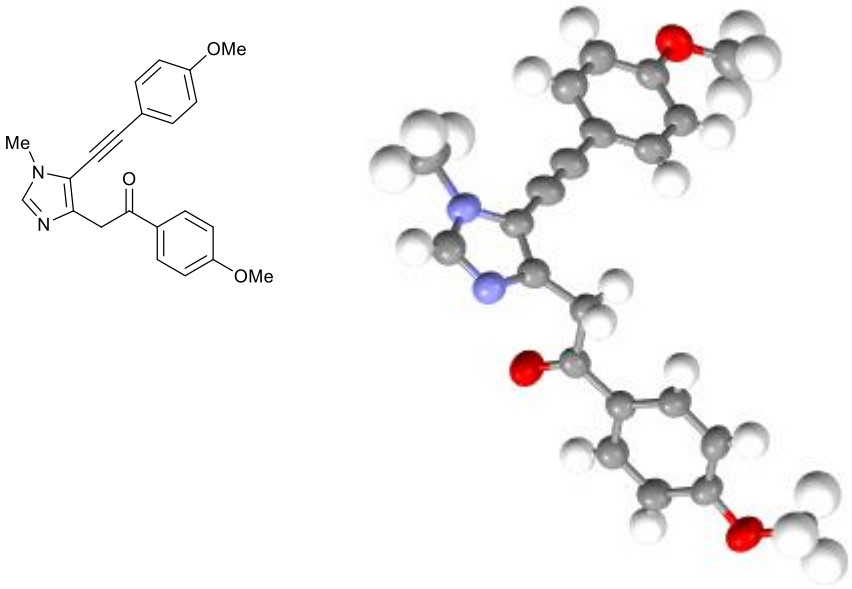
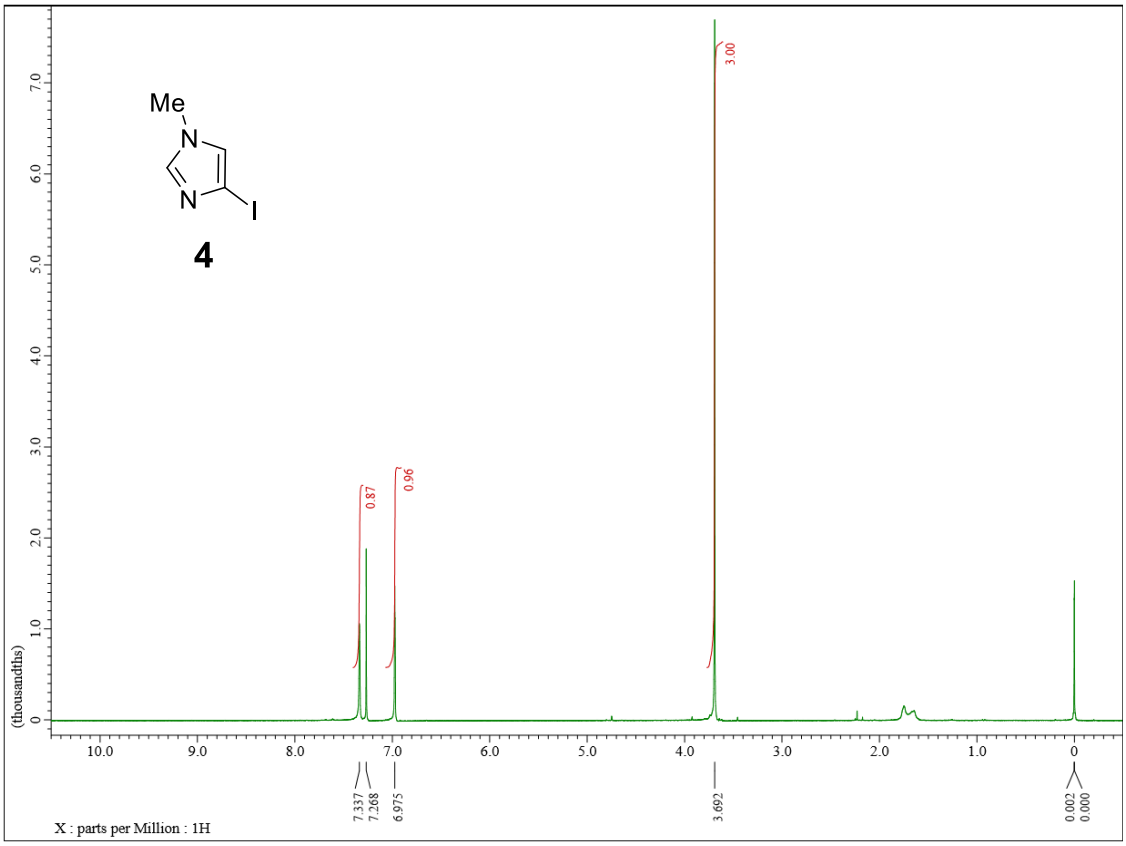


Figure S6. estimated structure of decomposition compound from **1b**+TFA.


Me
N
N
I
4
(thousandths)
X : parts per Million : 1H
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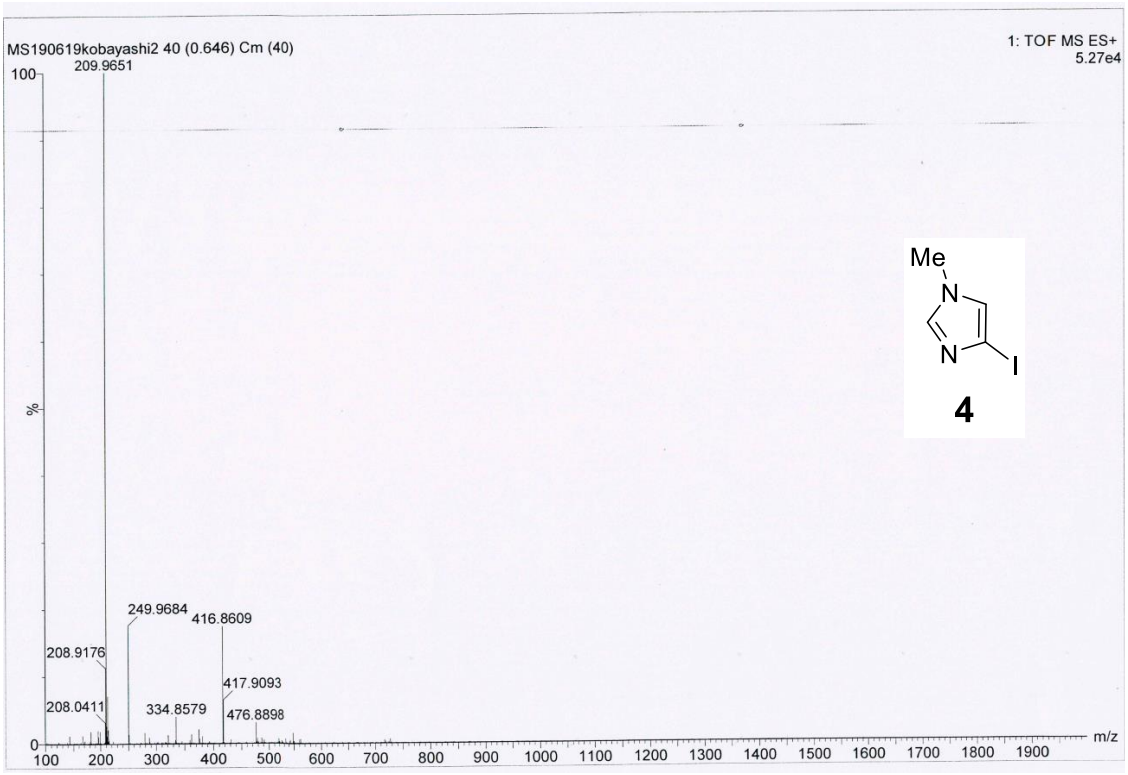
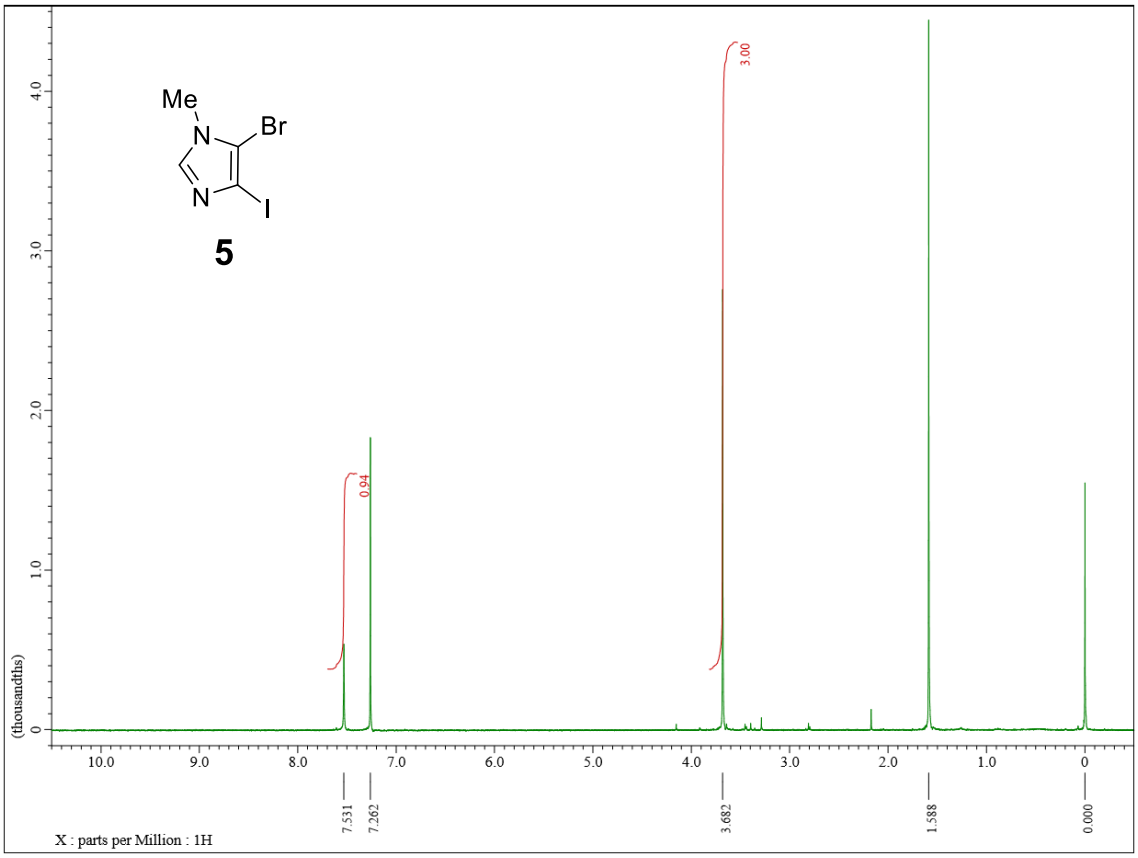
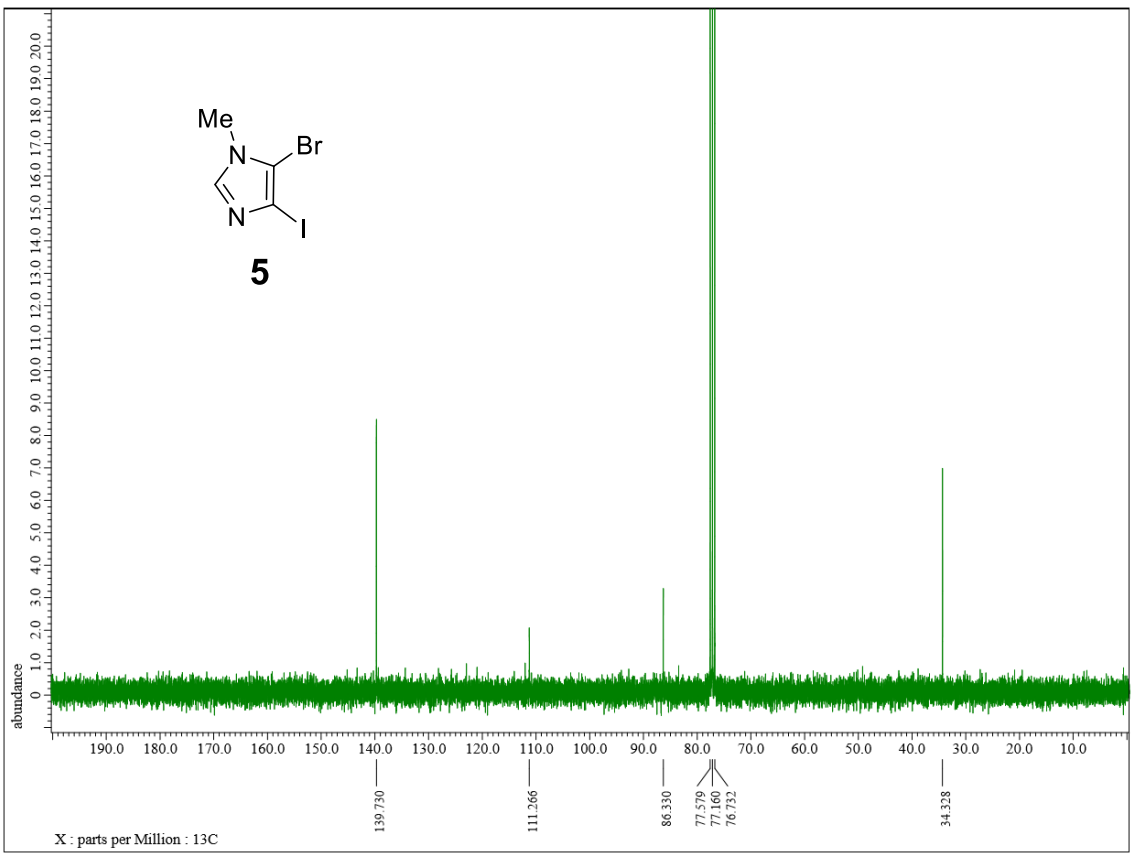
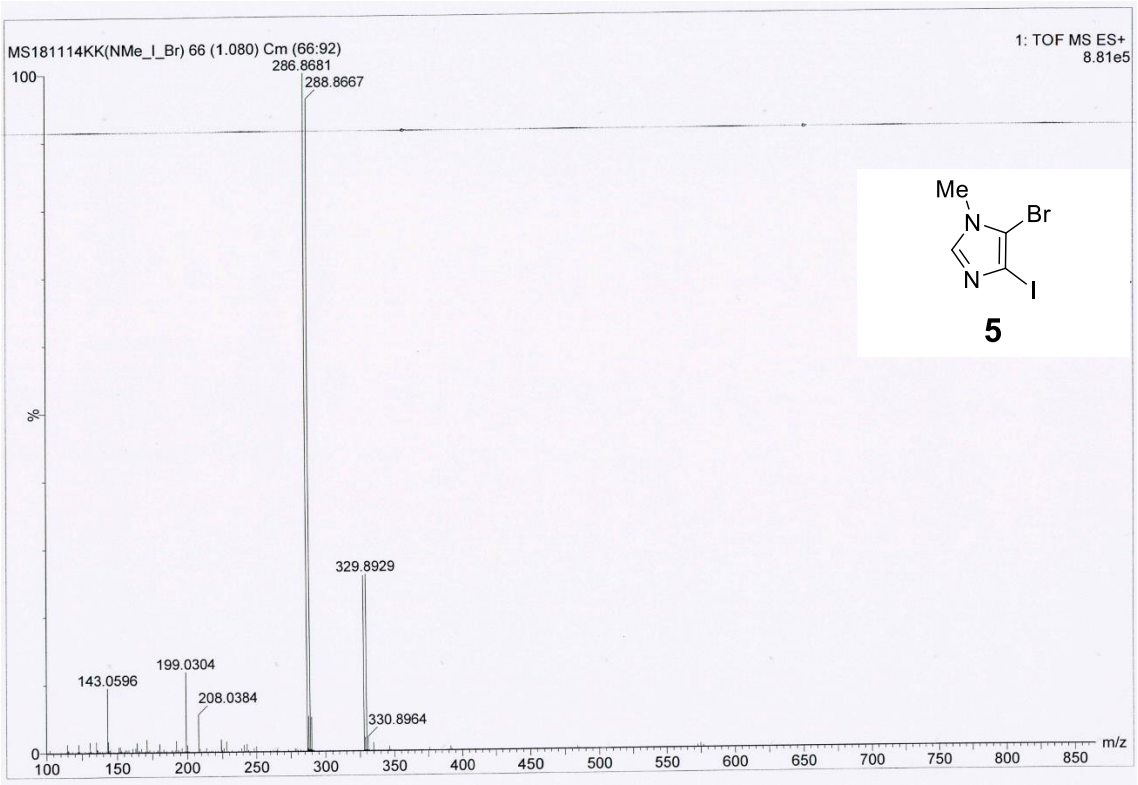
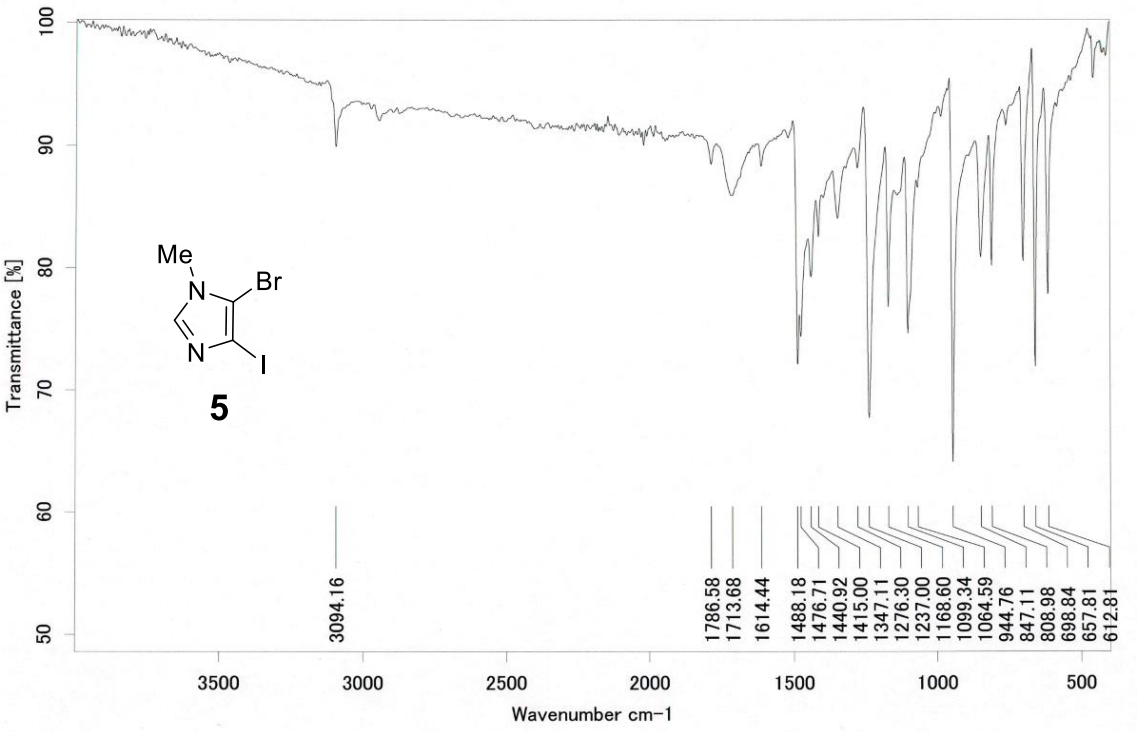
0.87
0.96
7.337
7.268
6.975
3.692
0.002
0.000


MS190619kobayashi2 40 (0.646) Cm (40)
1: TOF MS ES+
5.27e4
209.9651
249.9684
416.8609
208.9176
417.9093
208.0411
334.8579
476.8898
%
m/z
Me
N
N
I
4


Me
N
Br
N
I
5
3.00
0.94
(thousandths)
4.0
3.0
2.0
1.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.531
7.262
3.682
1.588
0.000
X : parts per Million : 1H


Me
N
Br
N
I
5
abundance
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
139.730
111.266
86.330
77.579
77.160
76.732
34.328
X : parts per Million : 13C


MS181114KK(NMe_I_Br) 66 (1.080) Cm (66:92)
1: TOF MS ES+
8.81e5
286.8681
288.8667
329.8929
199.0304
143.0596
208.0384
330.8964
%
m/z
Me
N
Br
N
I
5


Transmittance [%]
Wavenumber cm-1
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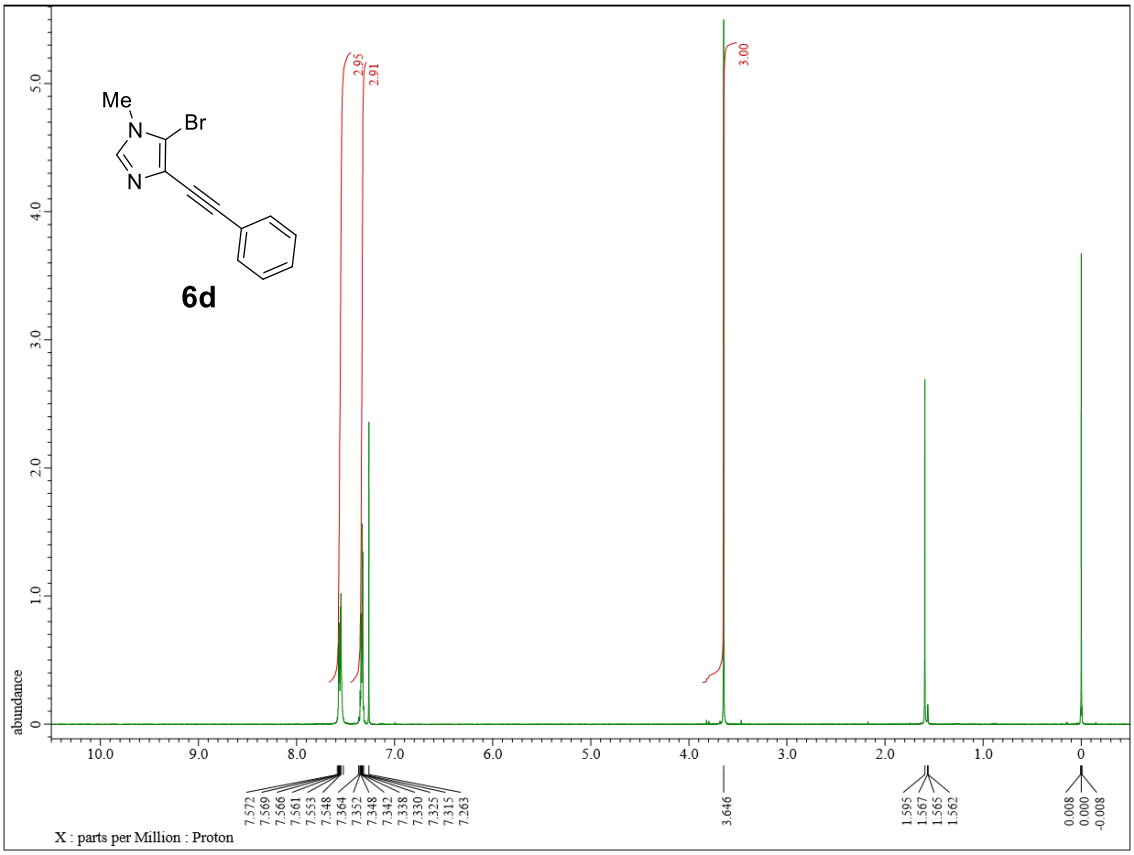
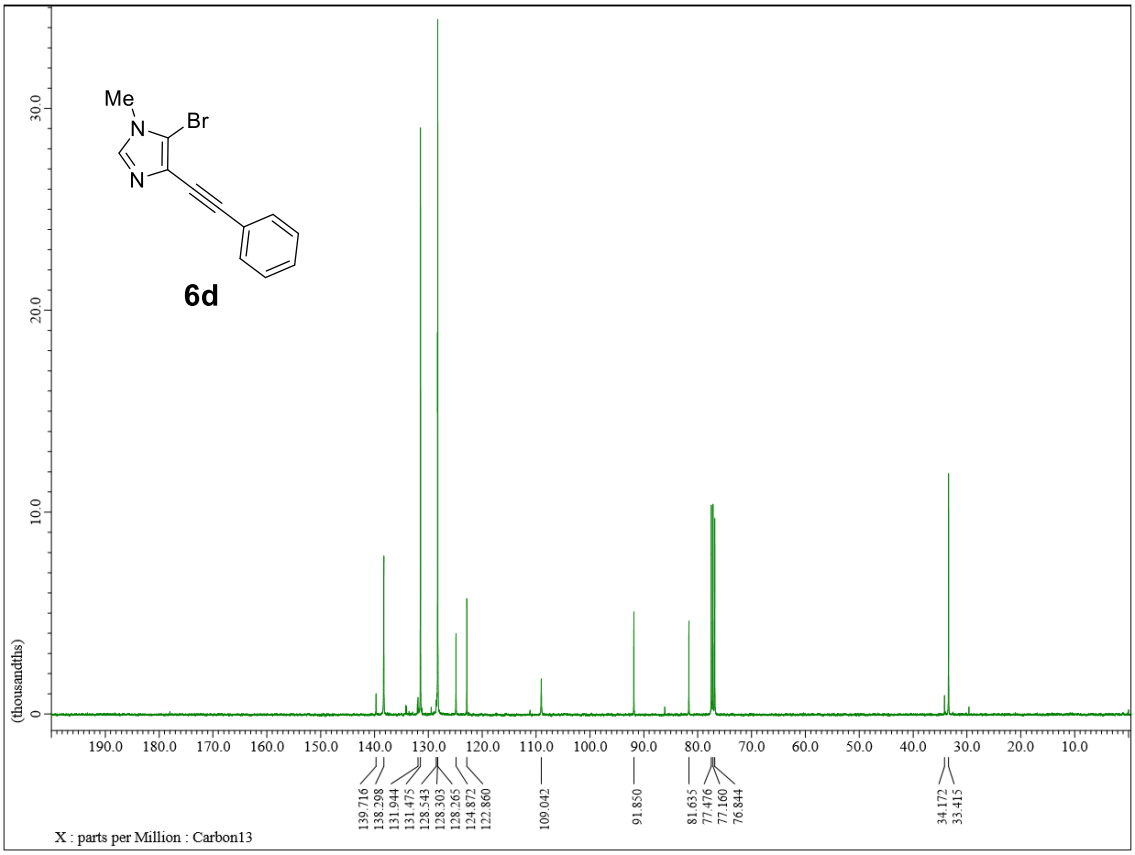
1786.58
1713.68
1614.44
1488.18
1476.71
1440.92
1415.00
1347.11
1276.30
1237.00
1168.60
1099.34
1064.59
944.76
847.11
808.98
698.84
657.81
612.81
Me
N
Br
N
I
5


Me
N
Br
N
6d
2.95
2.91
3.00
abundance
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.572
7.569
7.566
7.561
7.553
7.548
7.364
7.352
7.348
7.342
7.338
7.330
7.325
7.315
7.263
3.646
1.595
1.587
1.565
1.562
0.008
0.000
-0.008
X : parts per Million : Proton


Me
N
Br
N
6d
(thousandths)
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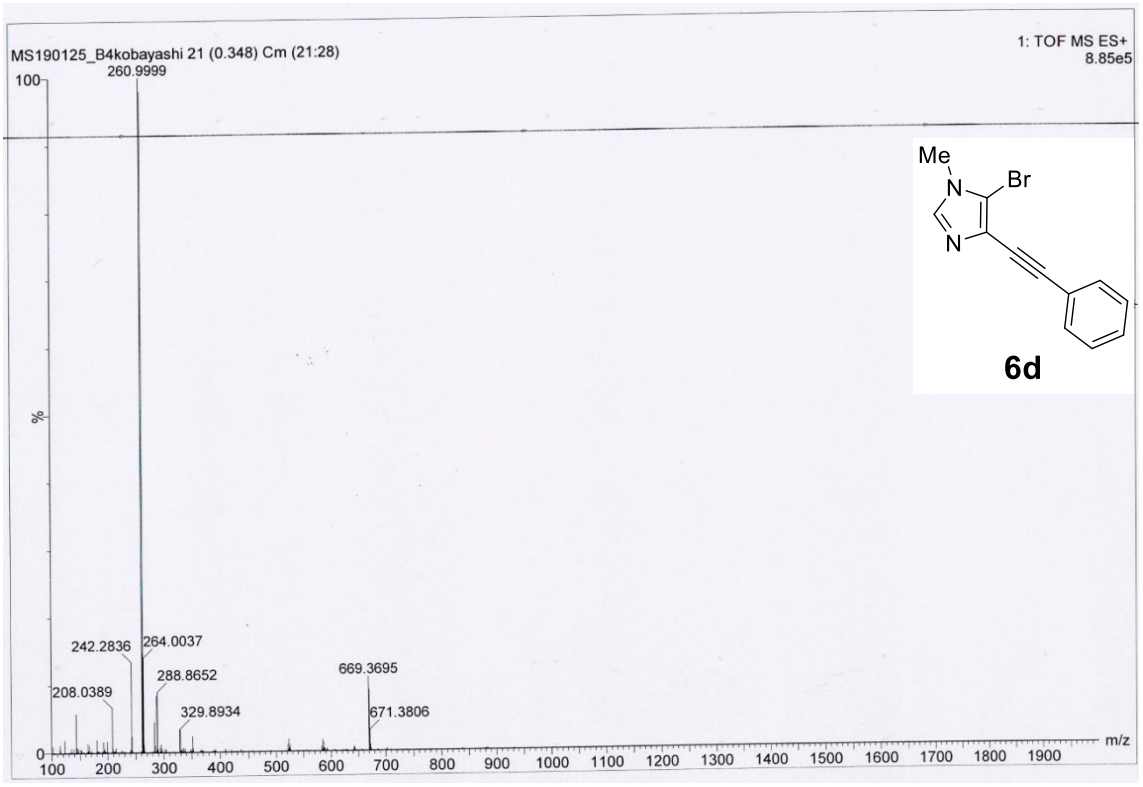
20.0
10.0
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
139.716
138.298
131.944
131.475
128.543
128.303
128.265
124.872
122.860
109.042
91.850
81.635
77.476
77.160
76.844
34.172
33.415
X : parts per Million : Carbon13


MS190125_B4kobayashi 21 (0.348) Cm (21:28)
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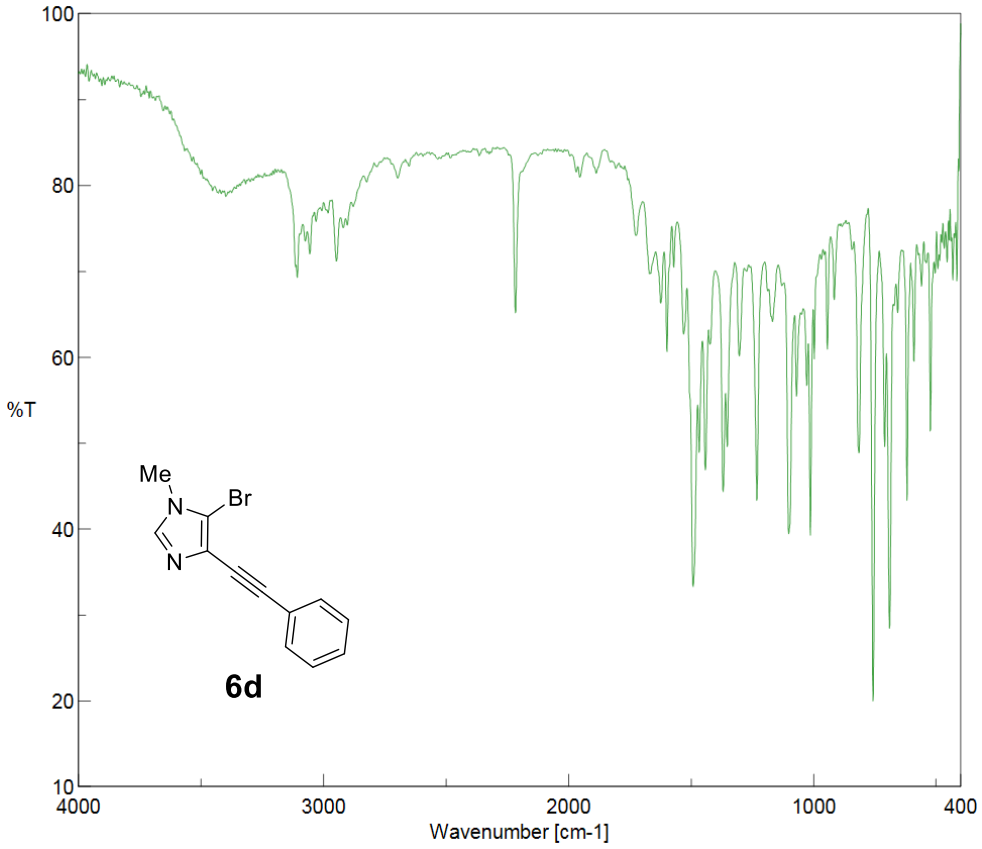
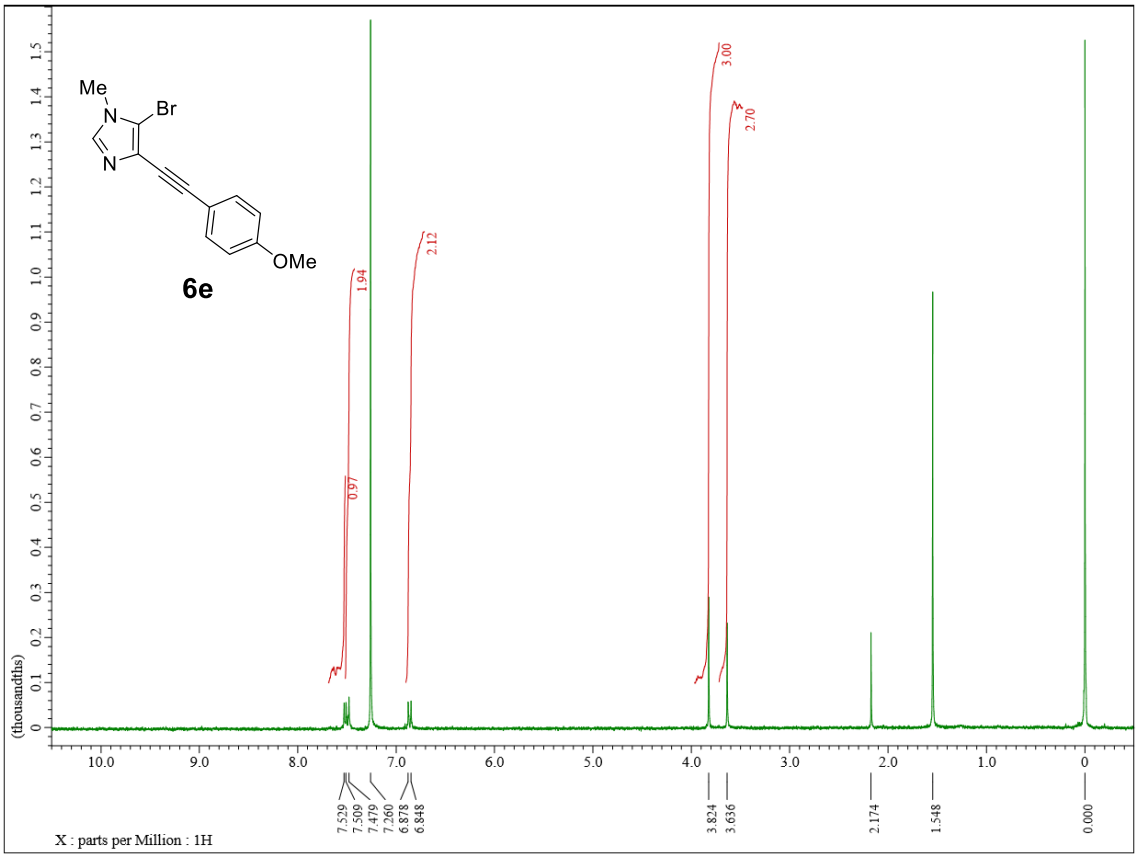
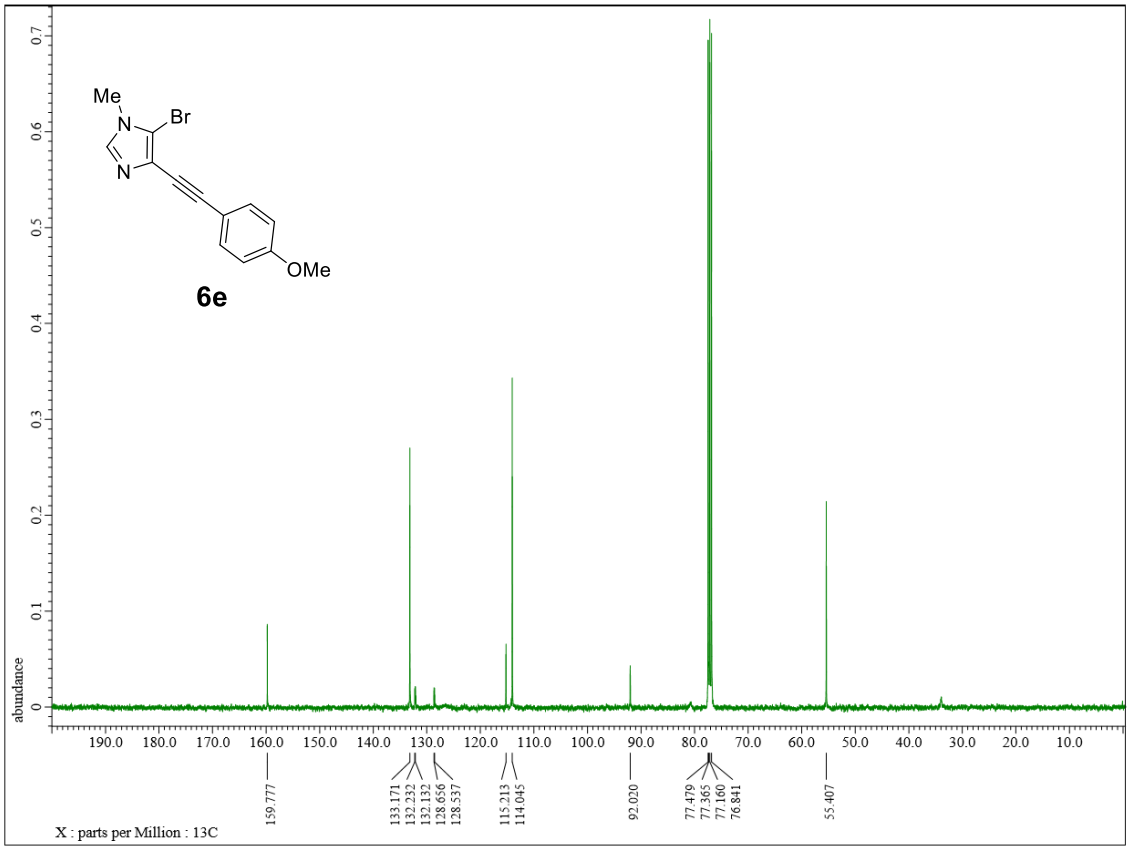
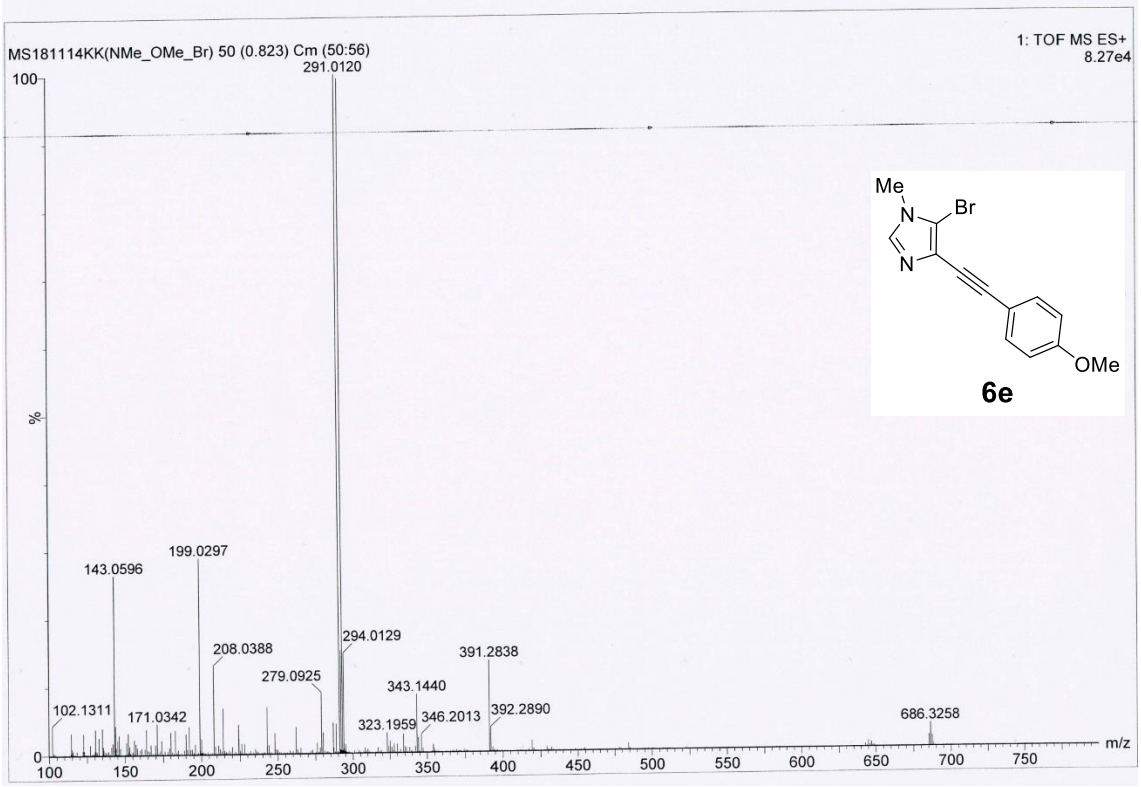
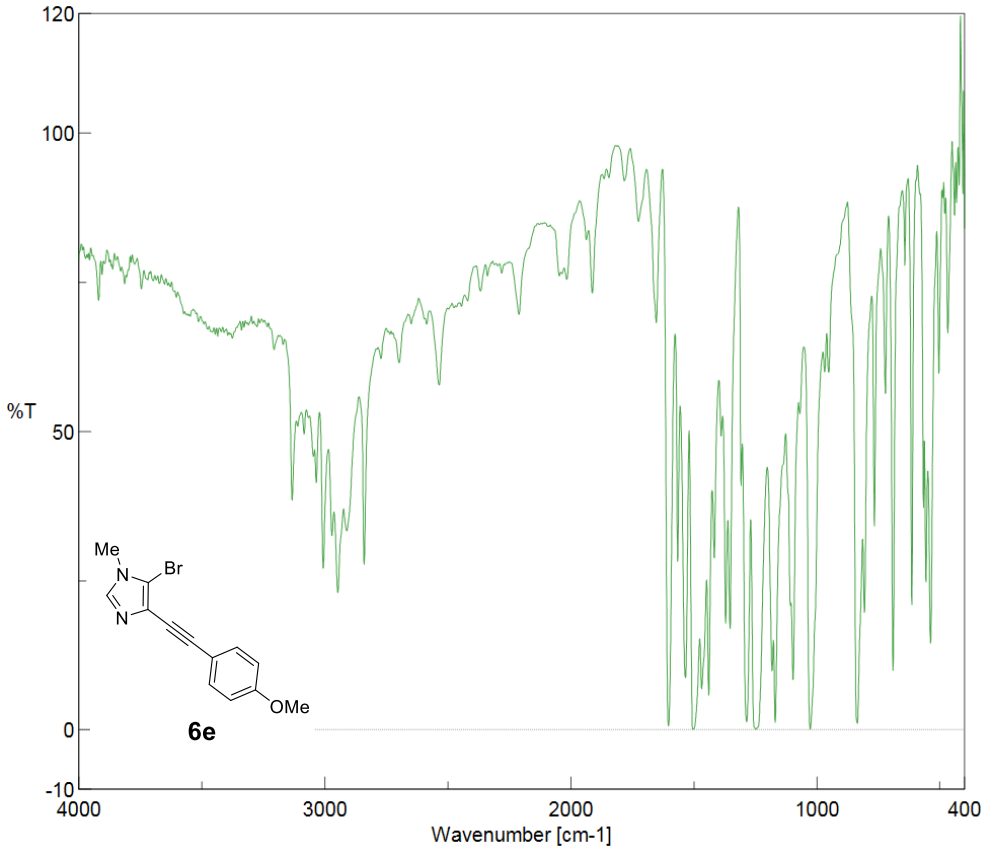
260.9999
100
%
242.2836
264.0037
288.8652
208.0389
329.8934
669.3695
671.3806
m/z
100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500 1600 1700 1800 1900
Me
N
Br
N
6d

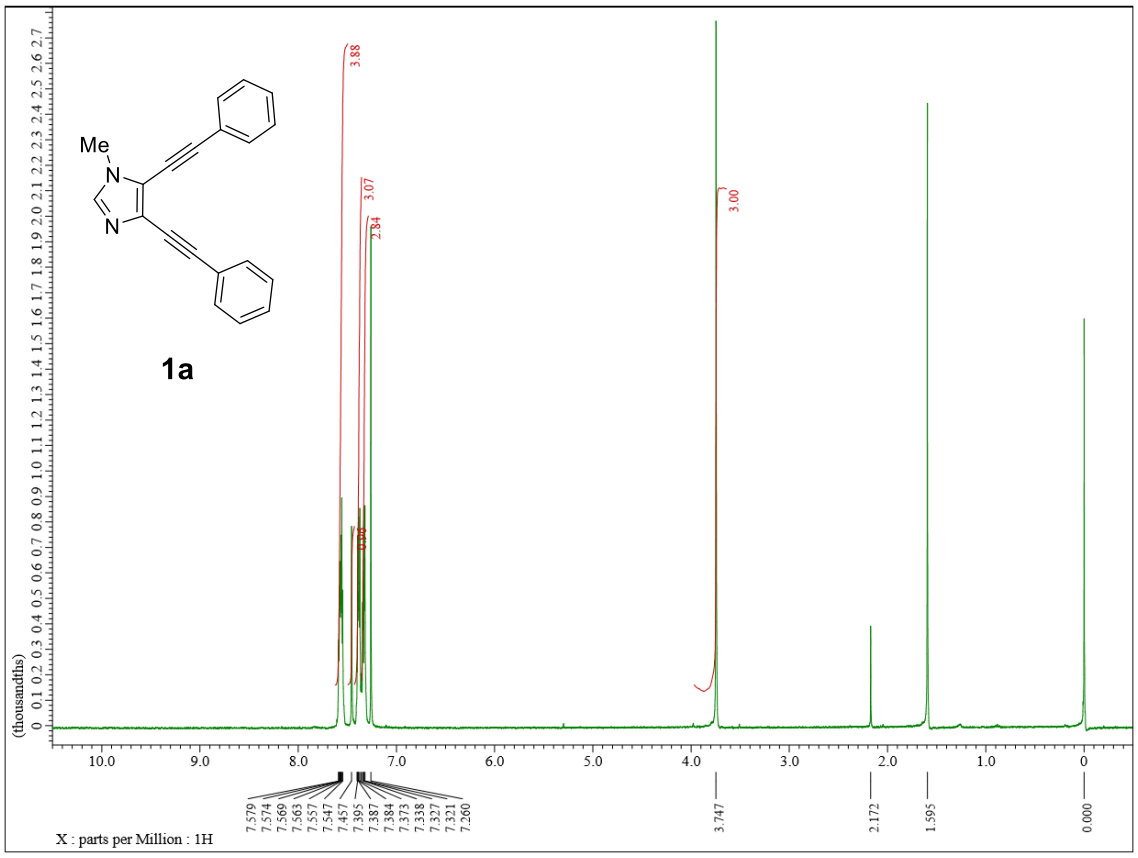

100
80
60
40
20
10
%T
4000
3000
2000
1000
400
Wavenumber [cm-1]
Me
N
Br
N
6d

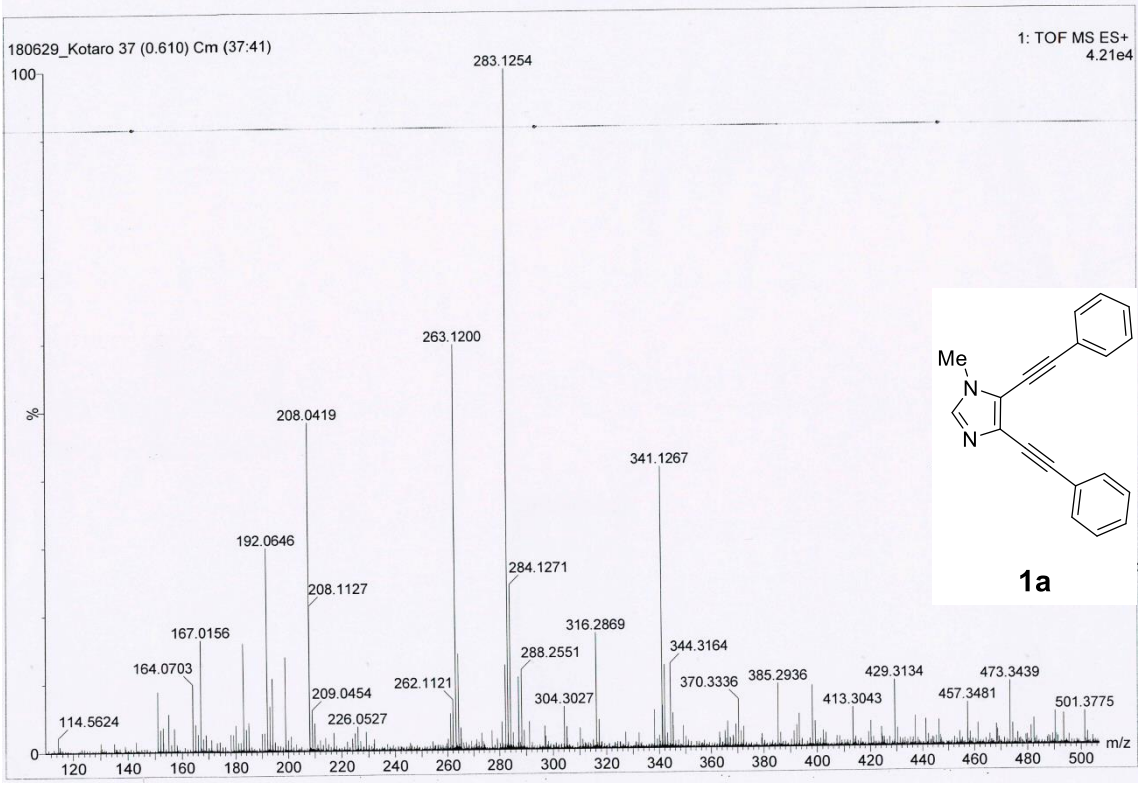

Me
N
Br
N
OMe
6e
3.00
2.70
2.12
1.94
0.97
(thousandths)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.529
7.509
7.479
7.260
6.878
6.848
3.824
3.656
2.174
1.548
0.000
X : parts per Million : 1H

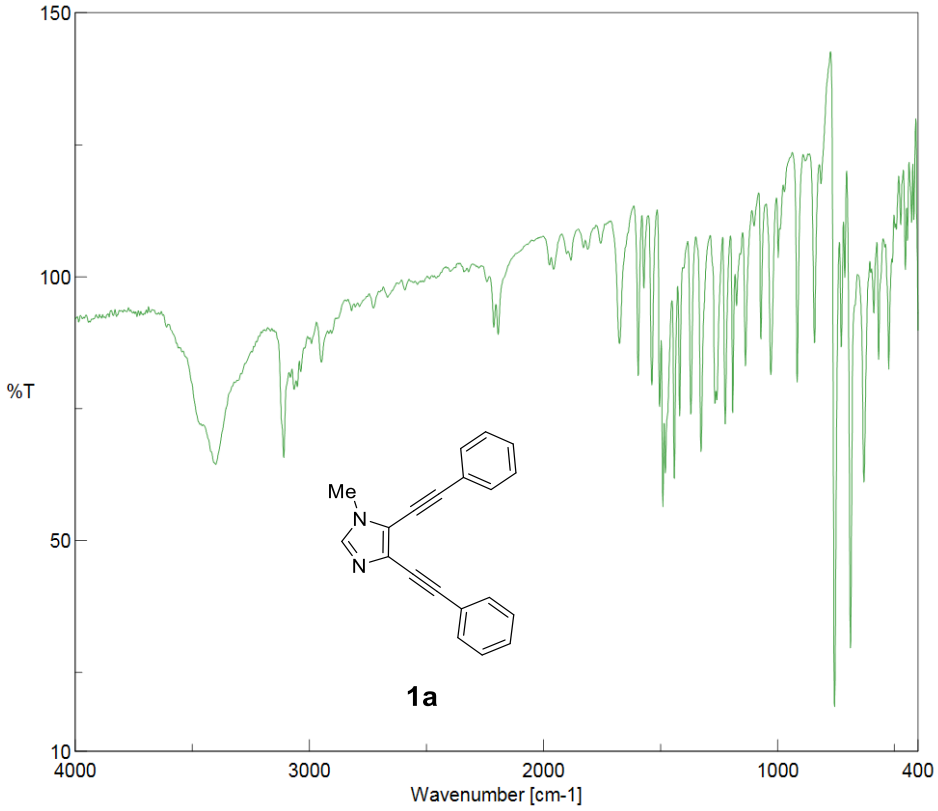

Me
N
Br
N
OMe
6e
abundance
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
159.777
133.171
132.232
132.132
128.656
128.537
115.213
114.045
92.020
77.479
77.365
77.160
76.841
55.407
X : parts per Million : 13C

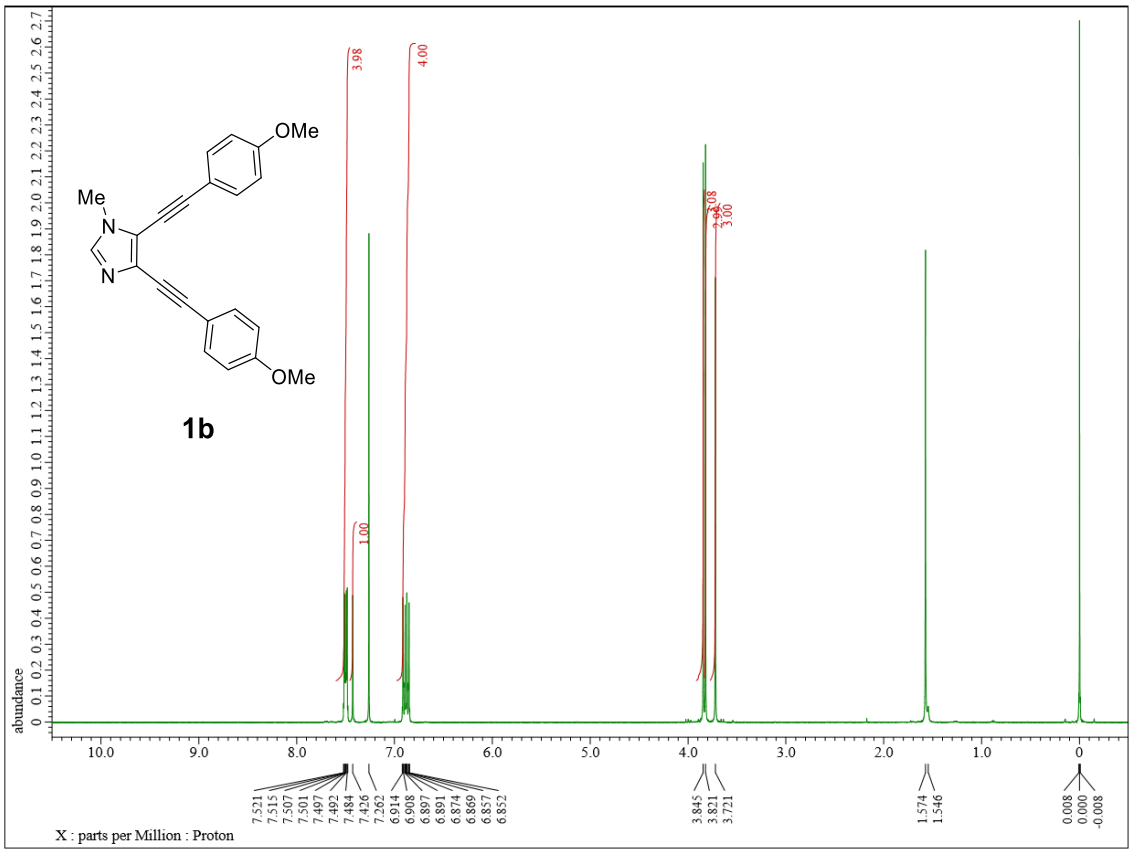

MS181114KK(NMe_OMe_Br) 50 (0.823) Cm (50:56)
1: TOF MS ES+
8.27e4
291.0120
199.0297
143.0596
208.0388
294.0129
279.0925
391.2838
343.1440
392.2890
102.1311
171.0342
323.1959
346.2013
686.3258
%
m/z
Me
N
Br
N
OMe
6e

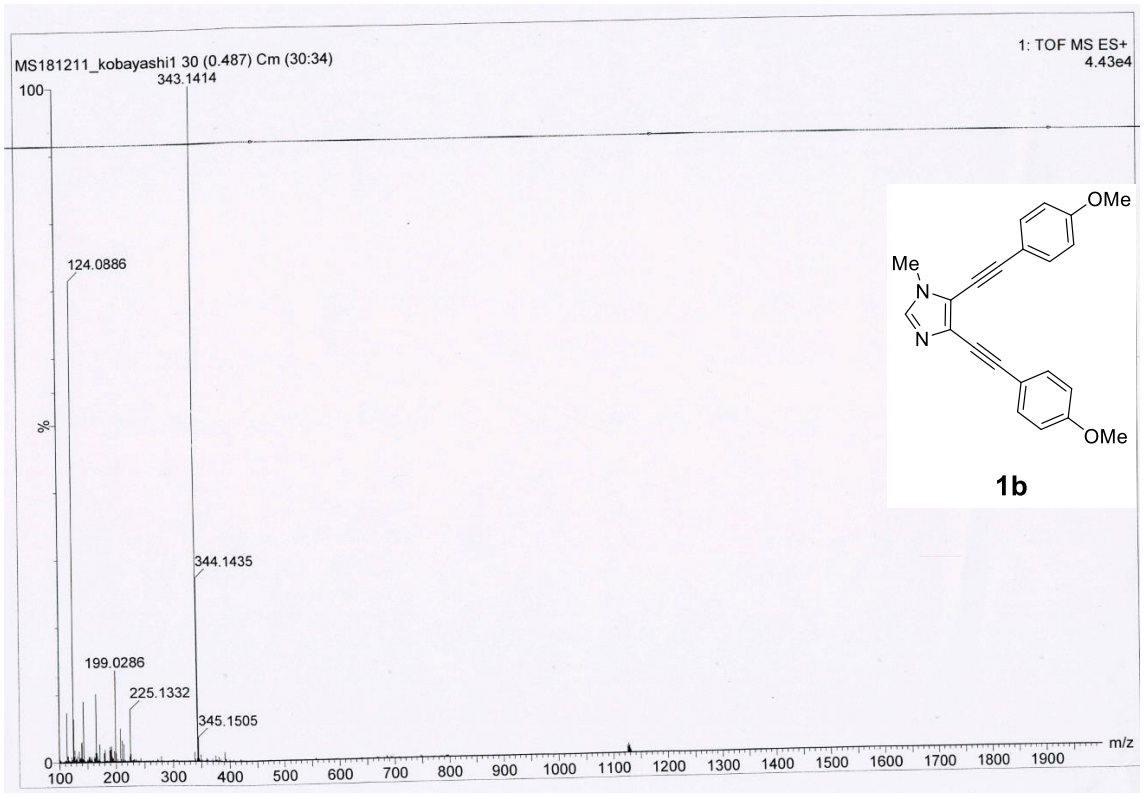

%T
Wavenumber [cm-1]
Me
N
Br
N
OMe
6e

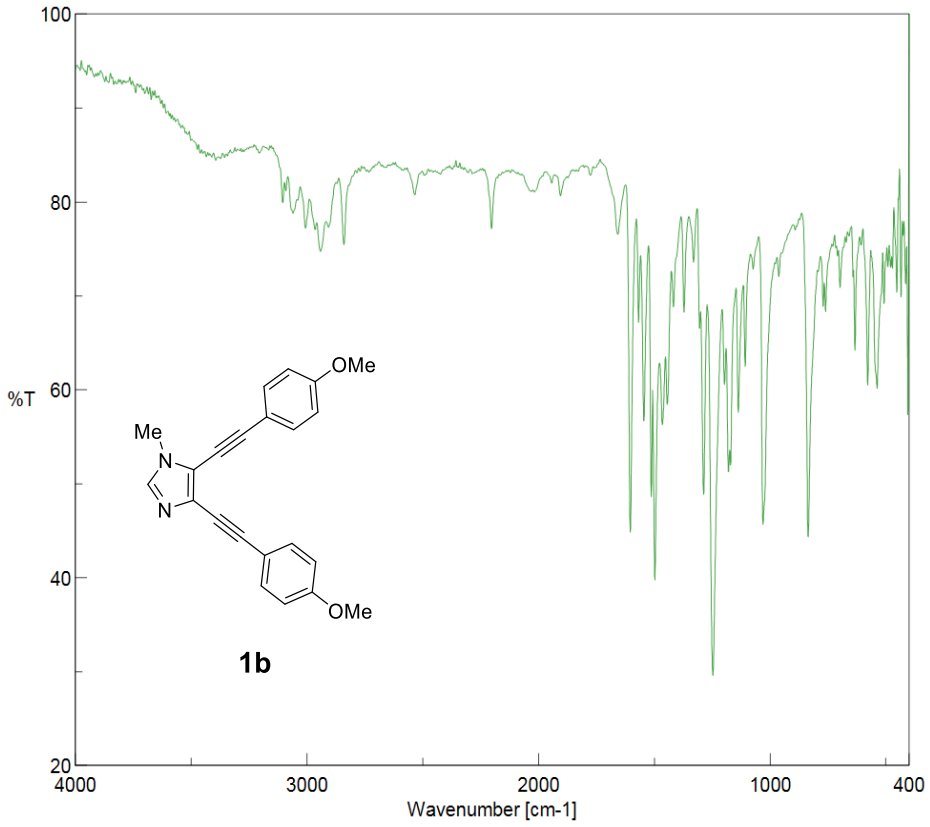

Me
N
N
1a
3.88
3.07
2.84
3.00
(thousandths)
X : parts per Million : 1H
7.579
7.574
7.569
7.563
7.557
7.547
7.457
7.395
7.387
7.384
7.373
7.338
7.327
7.321
7.260
3.747
2.172
1.595
0.000

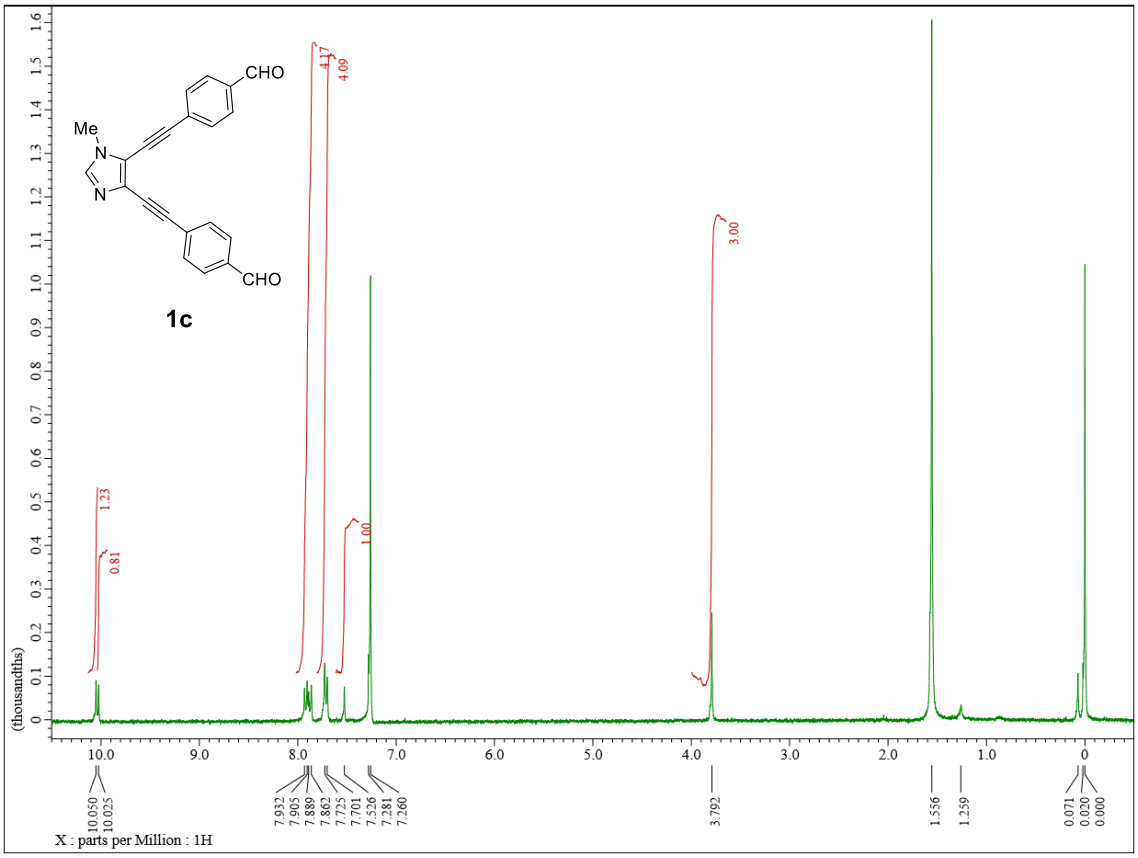

180629_Kotaro 37 (0.610) Cm (37:41)
1: TOF MS ES+
4.21e4
283.1254
263.1200
208.0419
341.1267
192.0646
284.1271
208.1127
316.2869
167.0156
288.2551
344.3164
164.0703
262.1121
370.3336
385.2936
429.3134
473.3439
209.0454
304.3027
413.3043
457.3481
501.3775
114.5624
226.0527
%
m/z
Me
N
N
1a

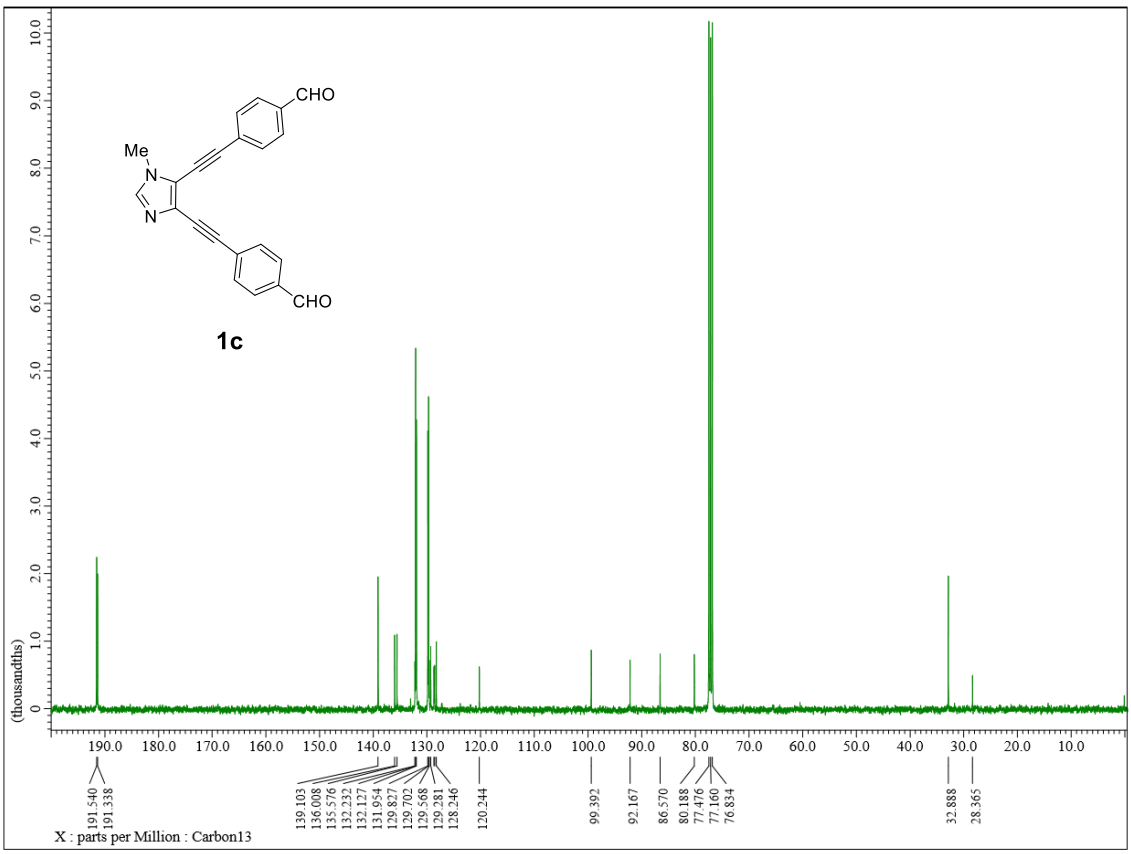

150
100
50
10
%T
4000
3000
2000
1000
400
Wavenumber [cm-1]
Me
N
N
1a

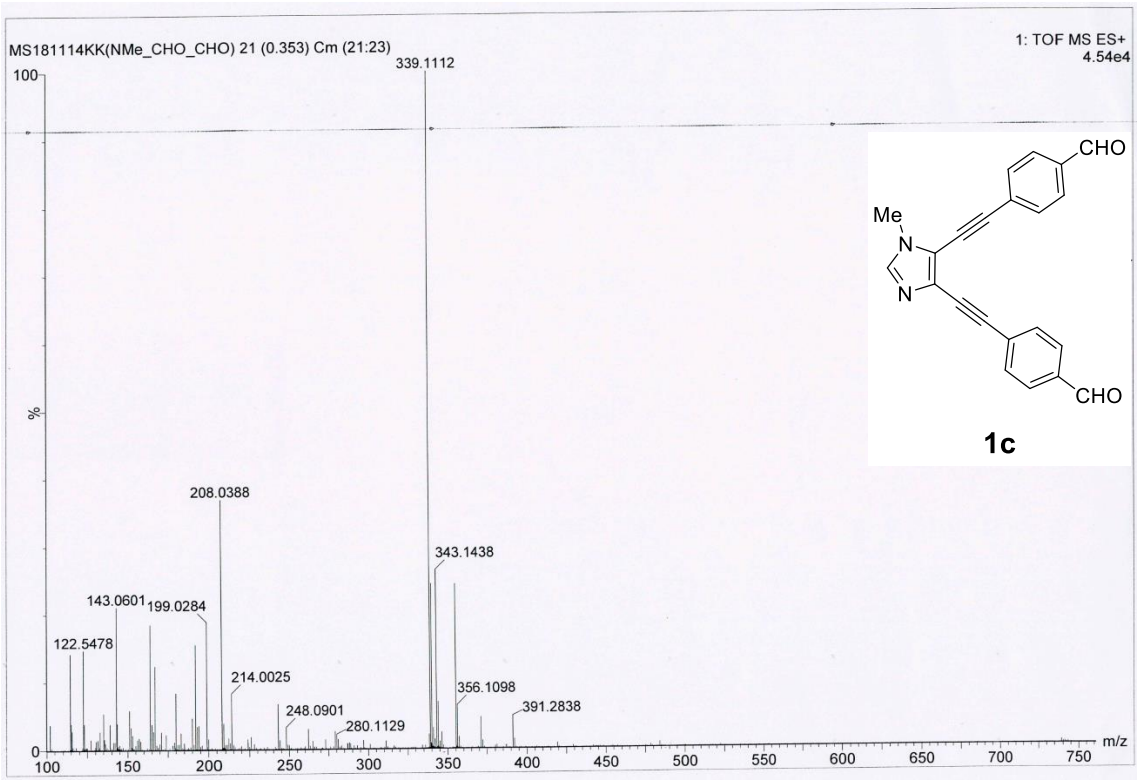

OMe
Me
N
N
OMe
1b
3.98
4.00
1.00
abundance
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton

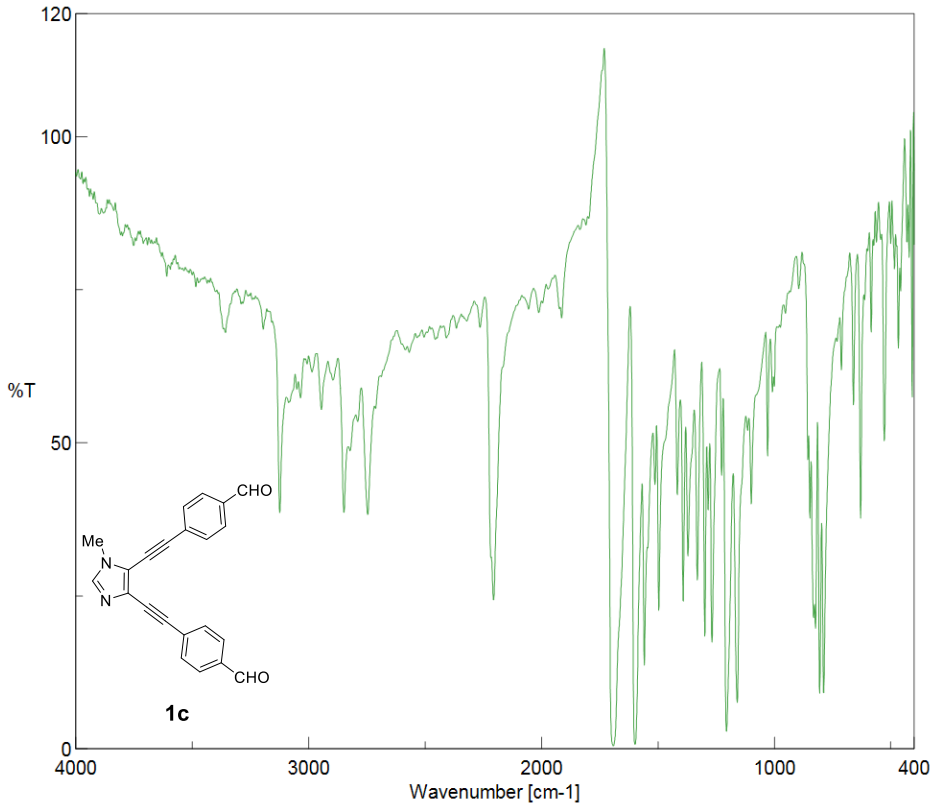

MS181211_kobayashi1 30 (0.487) Cm (30:34)
1: TOF MS ES+
4.43e4
343.1414
124.0886
344.1435
199.0286
225.1332
345.1505
%
m/z
OMe
Me
N
N
OMe
1b

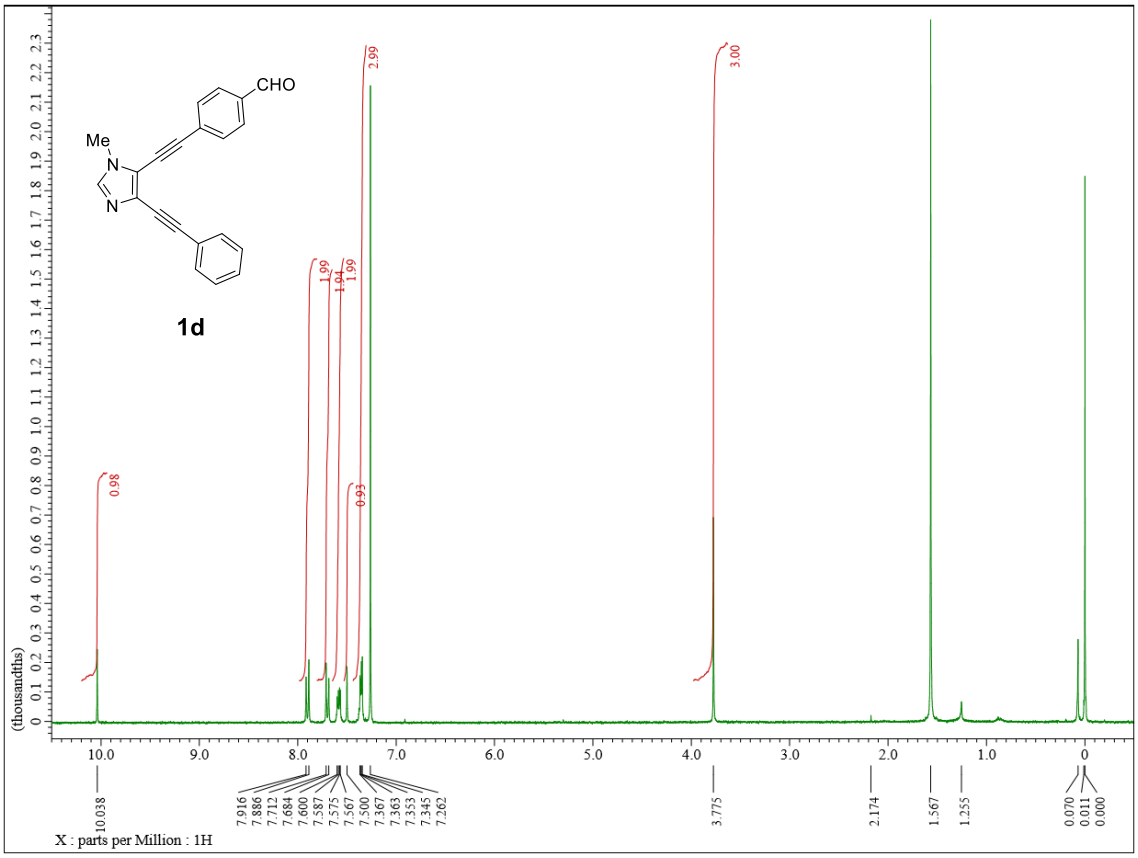

%T
Wavenumber [cm-1]
OMe
Me
N
N
OMe
1b

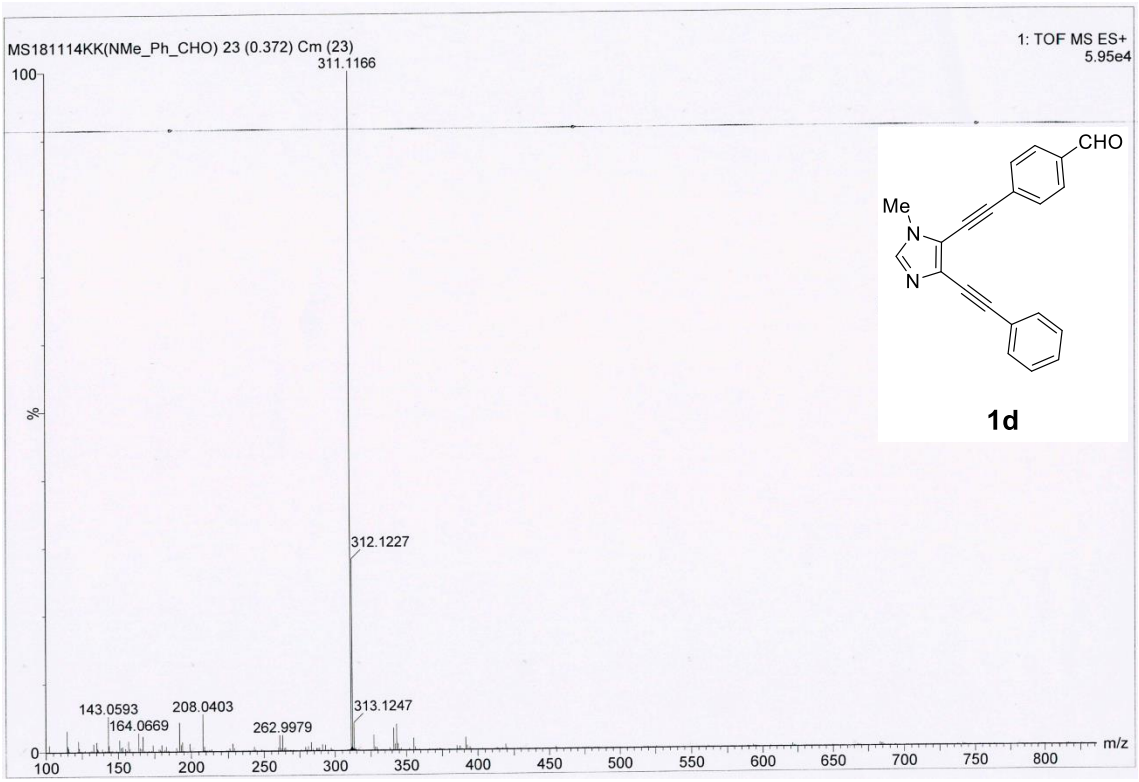

CHO
Me
N
N
CHO
1c
4.17
4.09
3.00
1.23
0.81
1.00
(thousandths)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.050
10.025
7.932
7.905
7.889
7.862
7.725
7.701
7.526
7.281
7.260
3.792
1.556
1.259
0.071
0.020
0.000
X : parts per Million : 1H

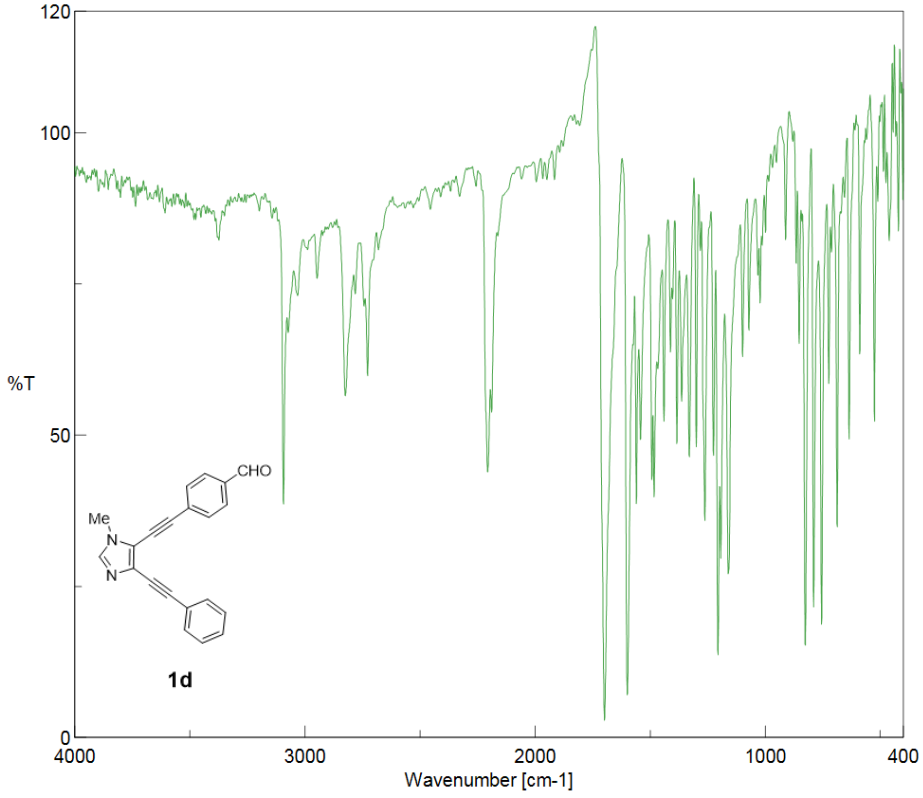

CHO
Me
N
N
CHO
1c
(thousandths)
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
191.540
191.338
139.103
136.008
135.576
132.232
132.127
131.954
129.827
129.702
129.568
129.281
128.246
120.244
99.392
92.167
86.570
80.188
77.476
77.160
76.834
32.888
28.365
X : parts per Million : Carbon13

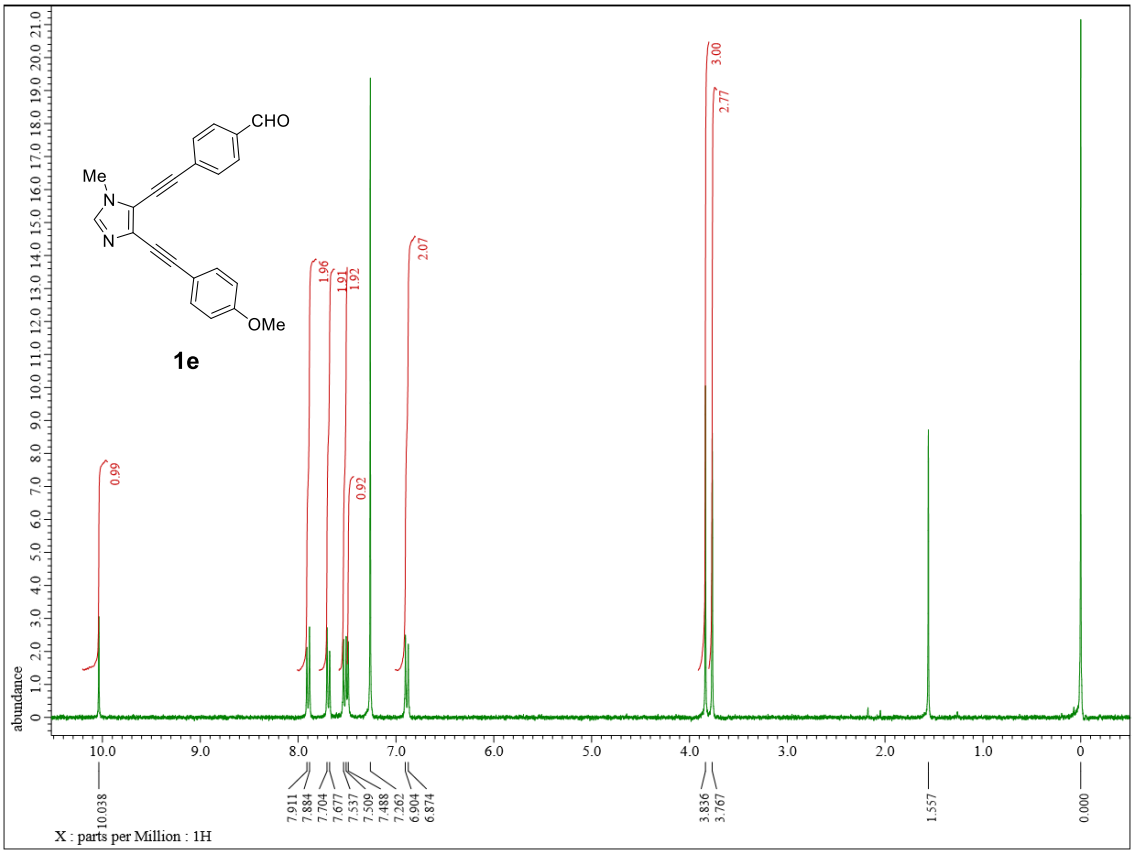

MS181114KK(NMe_CHO_CHO) 21 (0.353) Cm (21:23)
1: TOF MS ES+
4.54e4
339.1112
208.0388
343.1438
143.0601
199.0284
122.5478
214.0025
356.1098
248.0901
391.2838
280.1129
%
m/z
CHO
Me
N
N
CHO
1c

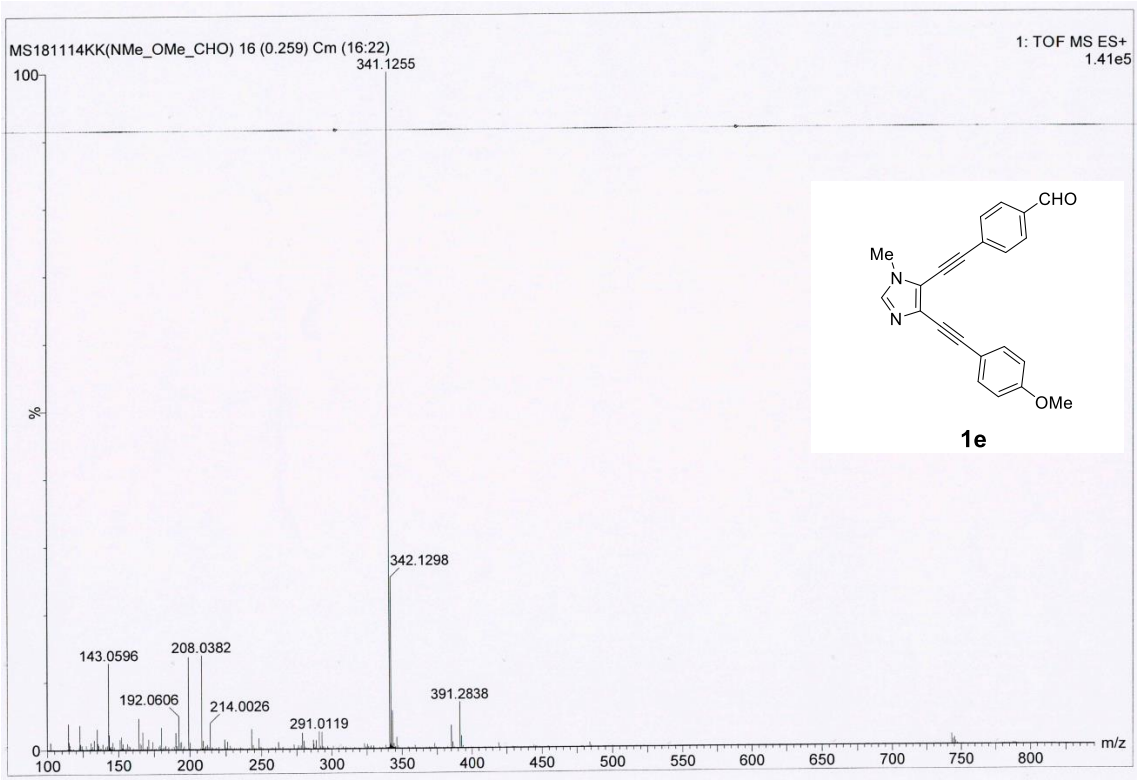

%T
Wavenumber [cm-1]
CHO
Me
N
N
CHO
1c

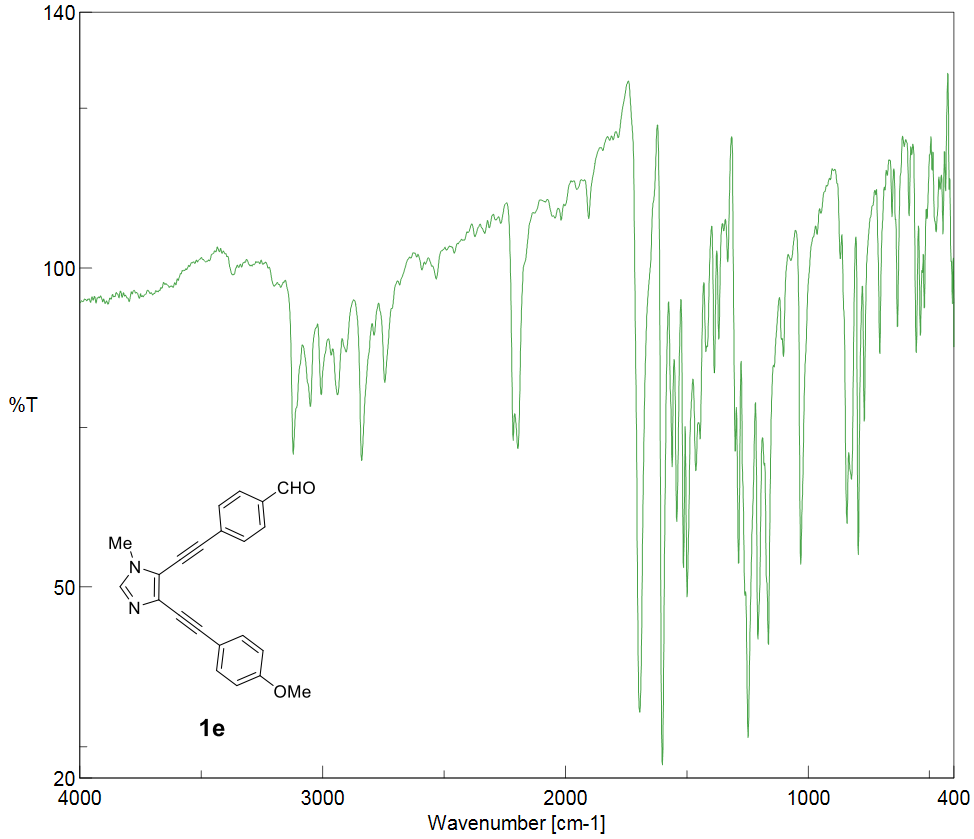

CHO
Me
N
N
1d
2.99
3.00
1.99
1.94
1.99
0.98
0.93
(thousandths)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.038
7.916
7.886
7.712
7.684
7.600
7.587
7.575
7.567
7.500
7.367
7.363
7.353
7.345
7.262
3.775
2.174
1.567
1.255
0.070
0.011
0.000
X : parts per Million : 1H

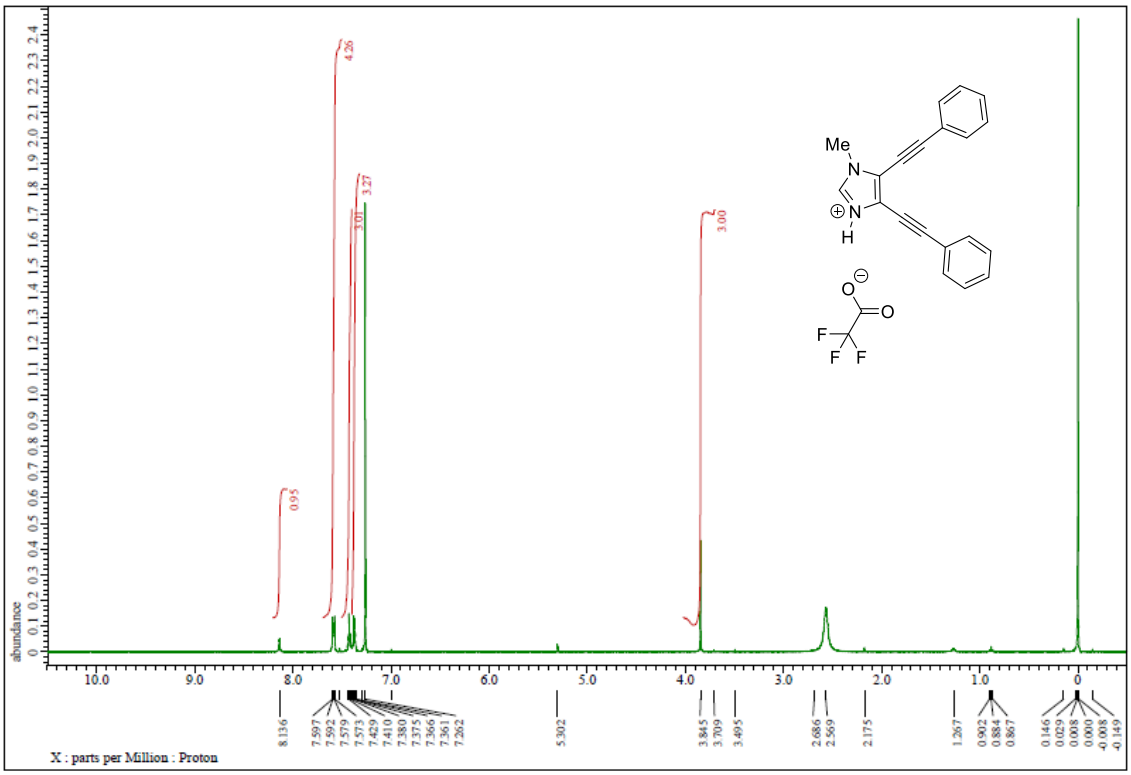

MS181114KK(NMe_Ph_CHO) 23 (0.372) Cm (23)
1: TOF MS ES+
5.95e4
311.1166
100
%
312.1227
143.0593
164.0669
208.0403
262.9979
313.1247
0
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
m/z
CHO
Me
N
N
1d

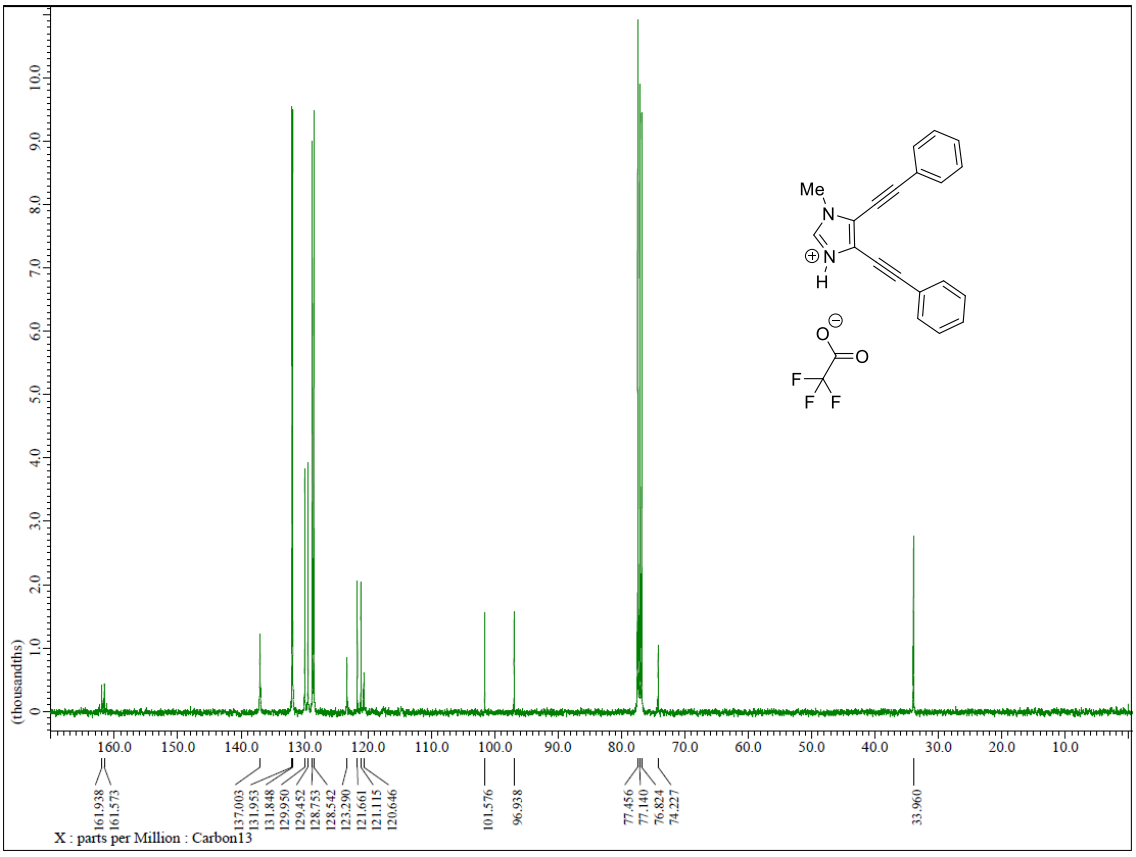

120
100
%T
50
0
4000
3000
2000
1000
400
Wavenumber [cm-1]
CHO
Me
N
N
1d

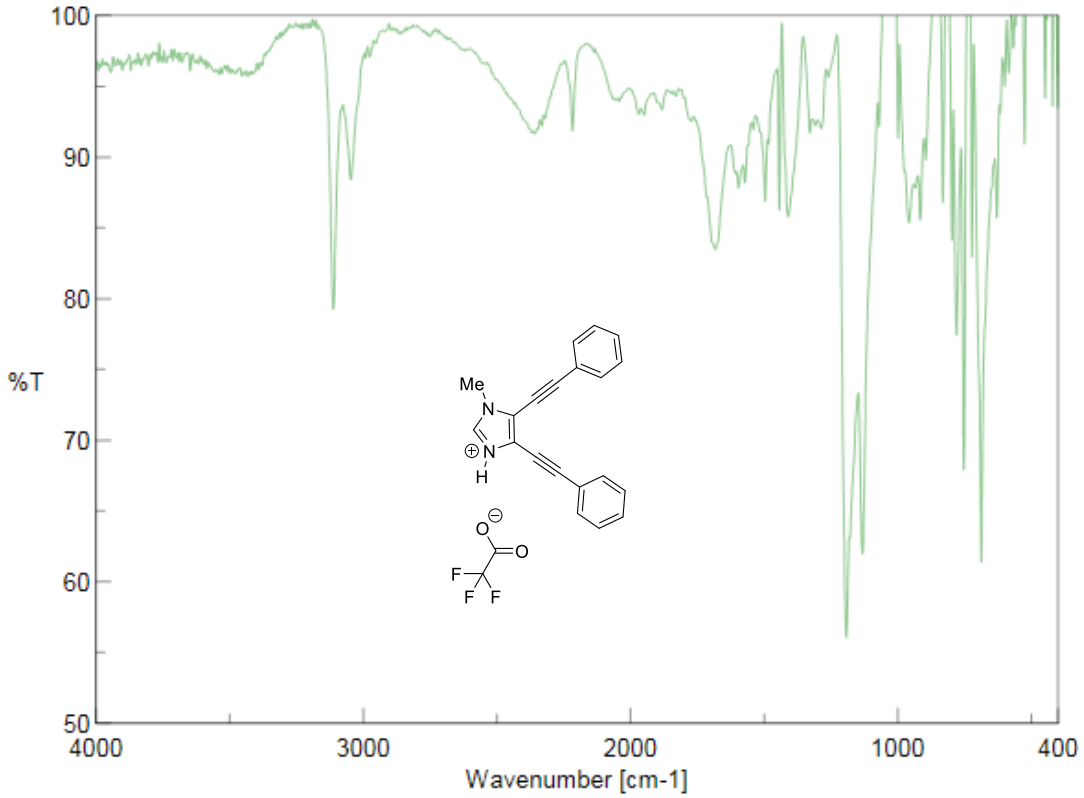

CHO
Me
N
N
OMe
1e
abundance
0.99
1.96
1.91
1.92
0.92
2.07
3.00
2.77
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.038
7.911
7.884
7.704
7.677
7.537
7.509
7.488
7.262
6.904
6.874
3.836
3.767
1.557
0.000
X : parts per Million : 1H

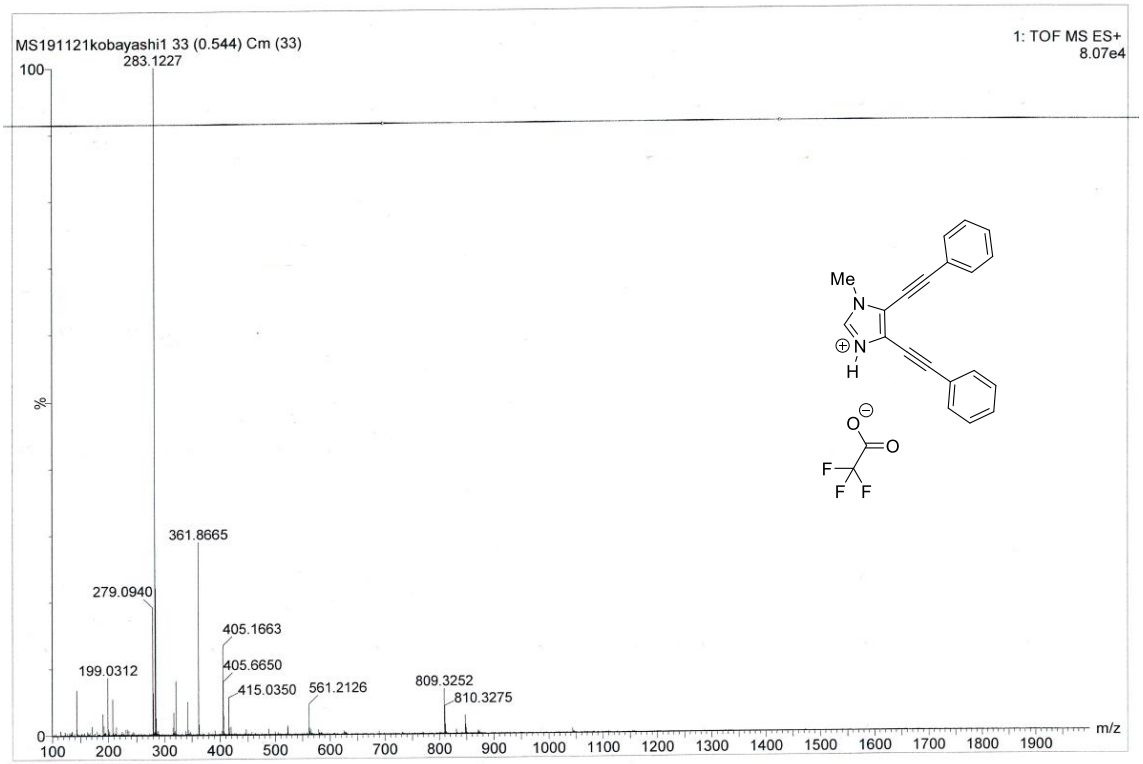

MS181114KK(NMe_OMe_CHO) 16 (0.259) Cm (16:22)
1: TOF MS ES+
1.41e5
341.1255
342.1298
143.0596
208.0382
192.0606
214.0026
291.0119
391.2838
%
m/z
CHO
Me
N
N
OMe
1e

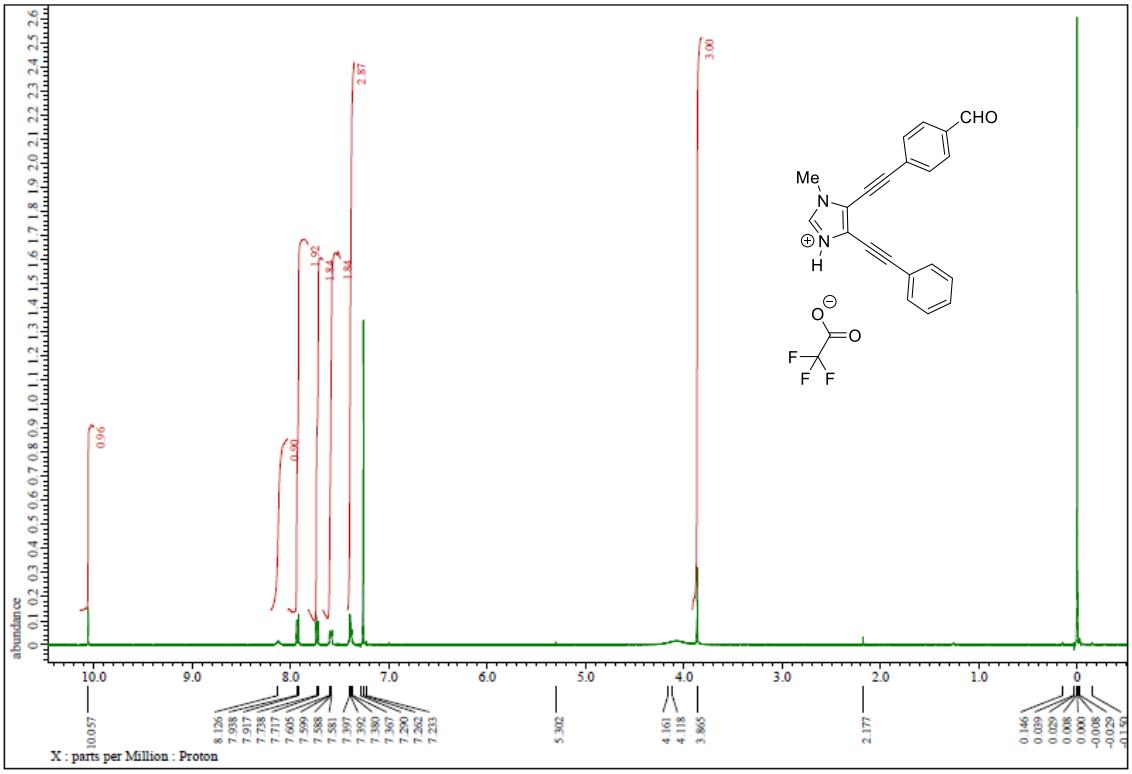

%T
Wavenumber [cm-1]
CHO
Me
N
N
OMe
1e

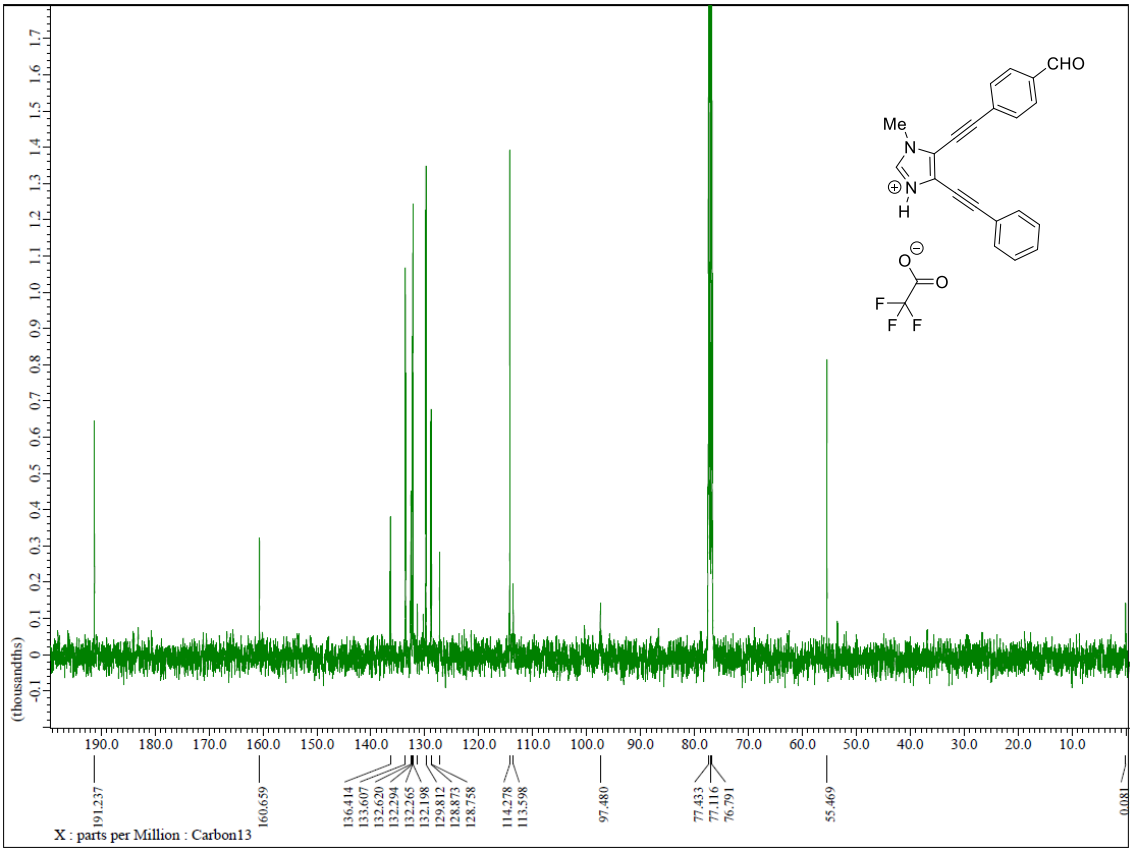

abundance
X : parts per Million : Proton
Me
N
N
H
O
O
F
F
F

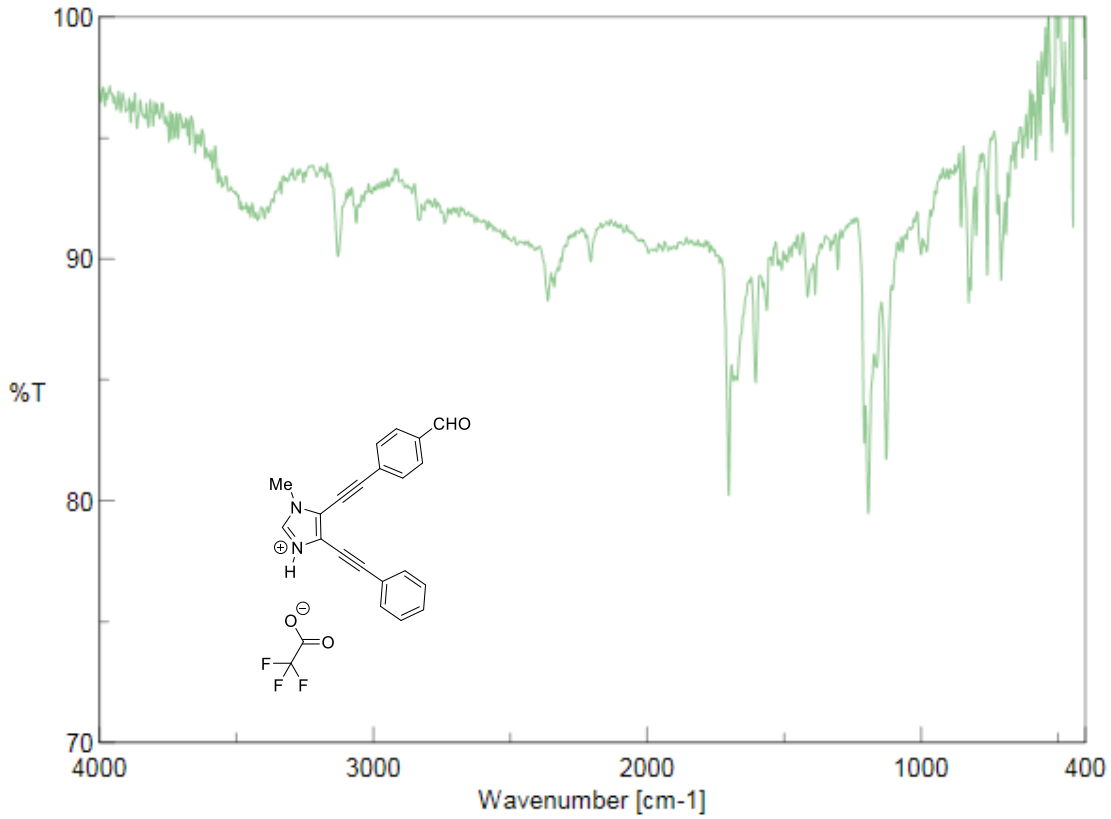

(thousandths)
X : parts per Million : Carbon13
Me
N
N
H
O
O
F
F
F

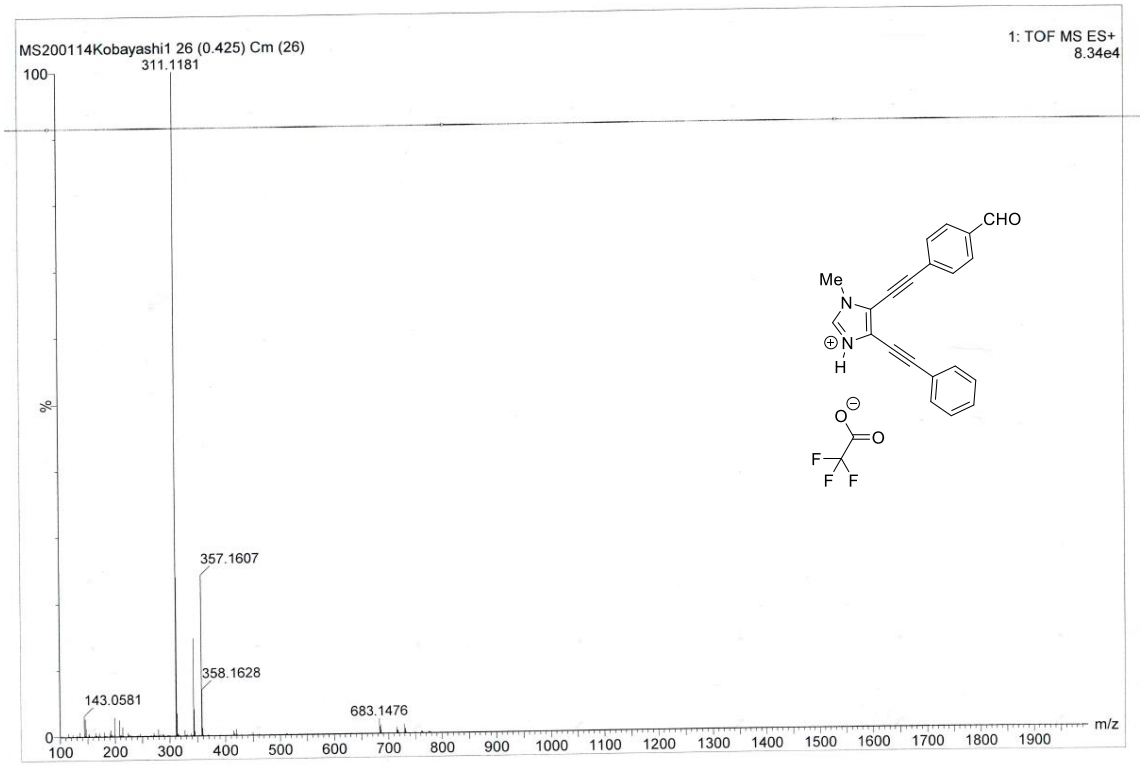

100
90
80
70
60
50
%T
4000
3000
2000
1000
400
Wavenumber [cm-1]
Me
N
N
H
O
O
F
F
F

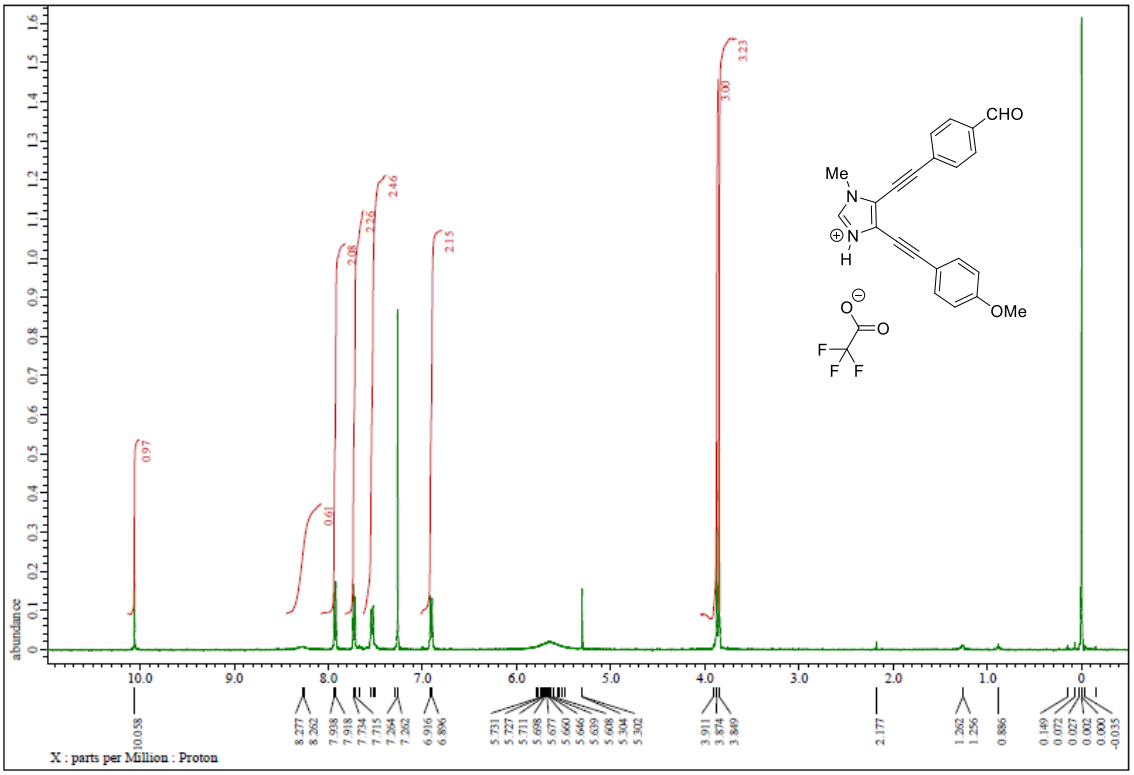

MS191121kobayashi1 33 (0.544) Cm (33)
1: TOF MS ES+
8.07e4
100
283.1227
%
361.8665
279.0940
405.1663
405.6650
199.0312
415.0350
561.2126
809.3252
810.3275
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
m/z
Me
N
N
H
O
O
F
F
F

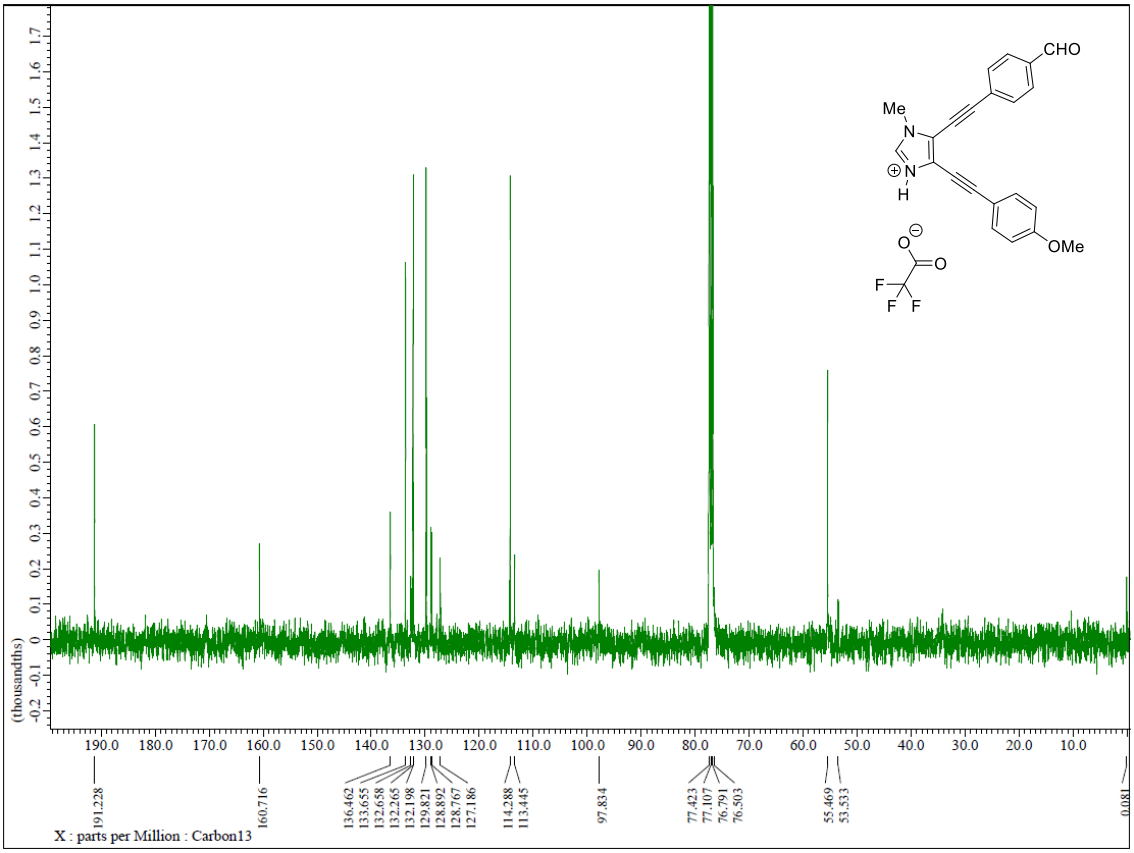

abundance
X : parts per Million : Proton
CHO
Me
N
H
O
F
F
F

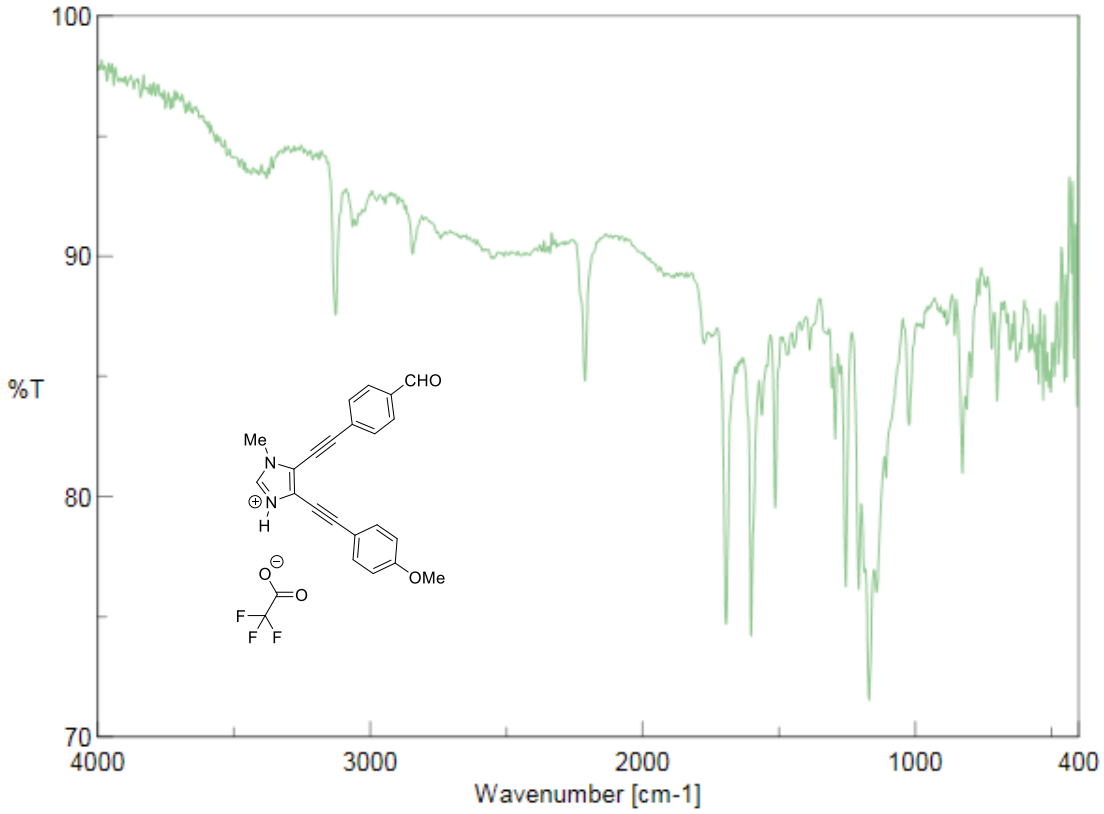

(thousandths)
X : parts per Million : Carbon13
CHO
Me
N
H
O
F
F
F

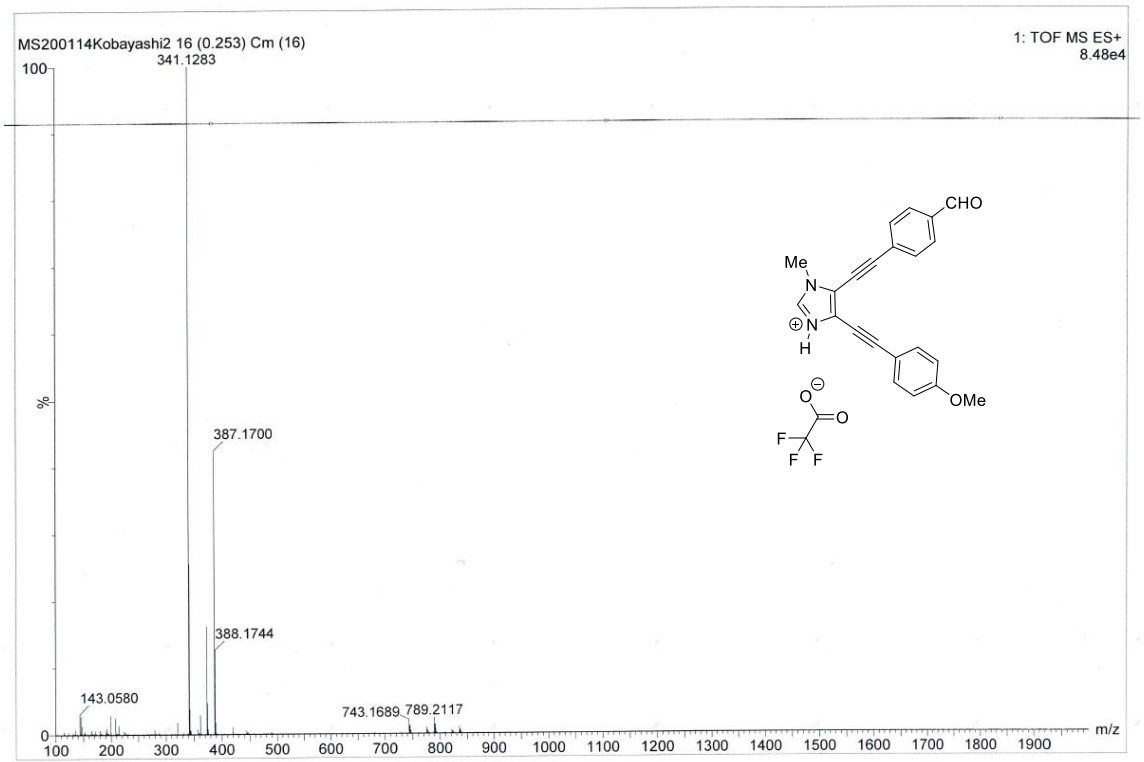

100
90
80
70
%T
4000
3000
2000
1000
400
Wavenumber [cm-1]
CHO
Me
N
N
H
O
O
F
F
F


MS200114Kobayashi1 26 (0.425) Cm (26)
1: TOF MS ES+
8.34e4
311.1181
357.1607
358.1628
143.0581
683.1476
%
m/z
CHO
Me
N
N
H
O
O
F
F
F


abundance
X : parts per Million : Proton
CHO
Me
N
N
H
OMe
O
O
F
F
F


(thousandths)
X : parts per Million : Carbon13
CHO
Me
N
N
H
OMe
O
O
F
F
F


100
90
80
70
%T
4000
3000
2000
1000
400
Wavenumber [cm-1]
CHO
Me
N
N
H
OMe
O
O
F
F
F


MS200114Kobayashi2 16 (0.253) Cm (16)
1: TOF MS ES+
8.48e4
100
%
341.1283
387.1700
388.1744
143.0580
743.1689
789.2117
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
m/z
CHO
Me
N
N
H
OMe
O
O
F
F
F