Supporting Information

Laser Flash Photolysis Studies on Radical Monofluoromethylation by (Diarylamino)naphthalene Photoredox Catalysis: Long Lifetime of the Excited State is not Always a Requisite

Naoki Noto,[‡] Keigo Takahashi,[‡] Shion Goryo,[§] Akira Takakado,[§] Koichi Iwata,[§], Takashi Koike*,[†‡] Munetaka Akita*[†‡]

[†]Laboratory for Chemistry and Life Science, Institute of Innovative Research
[‡]School of Materials and Chemical Technology, Tokyo Institute of Technology
R1-27, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8503, Japan
[§]Department of Chemistry, Faculty of Science, Gakushuin University, 1-5-1 Mejiro, Toshimaku, Tokyo 171-8588, Japan

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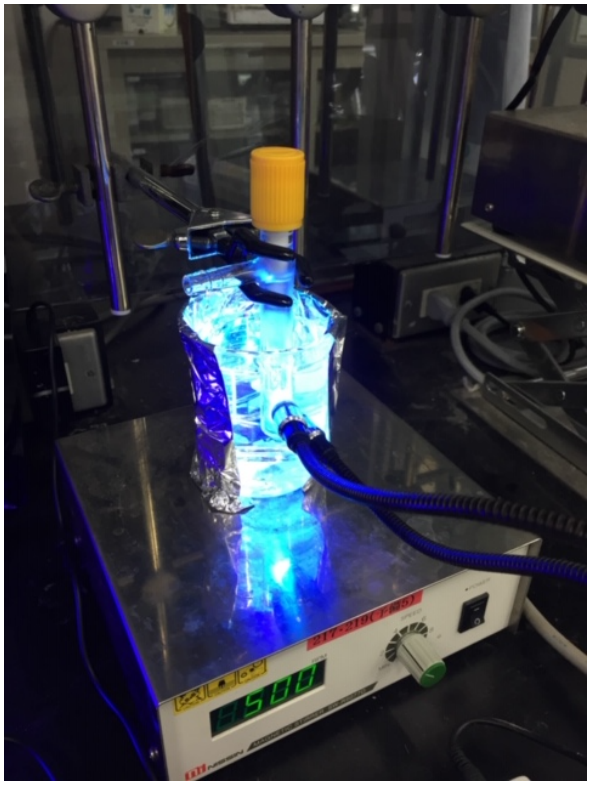
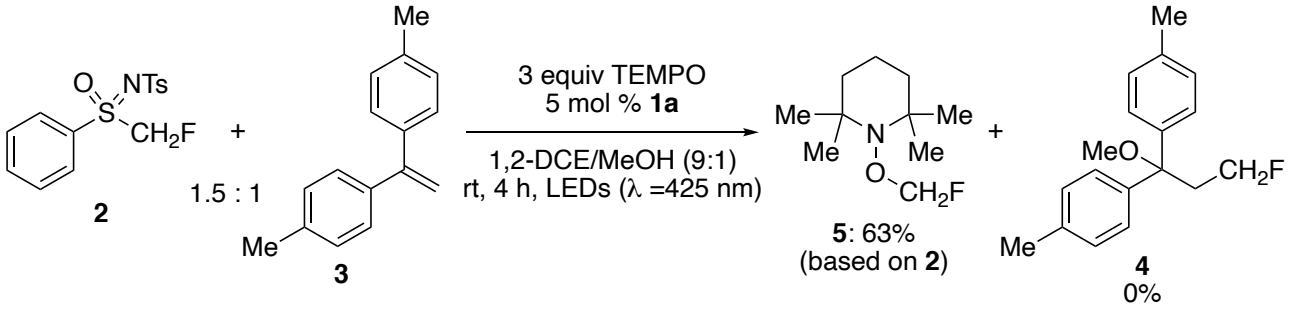
Reaction Apparatuses



Radical Trap Experiment with TEMPO



GC-MS

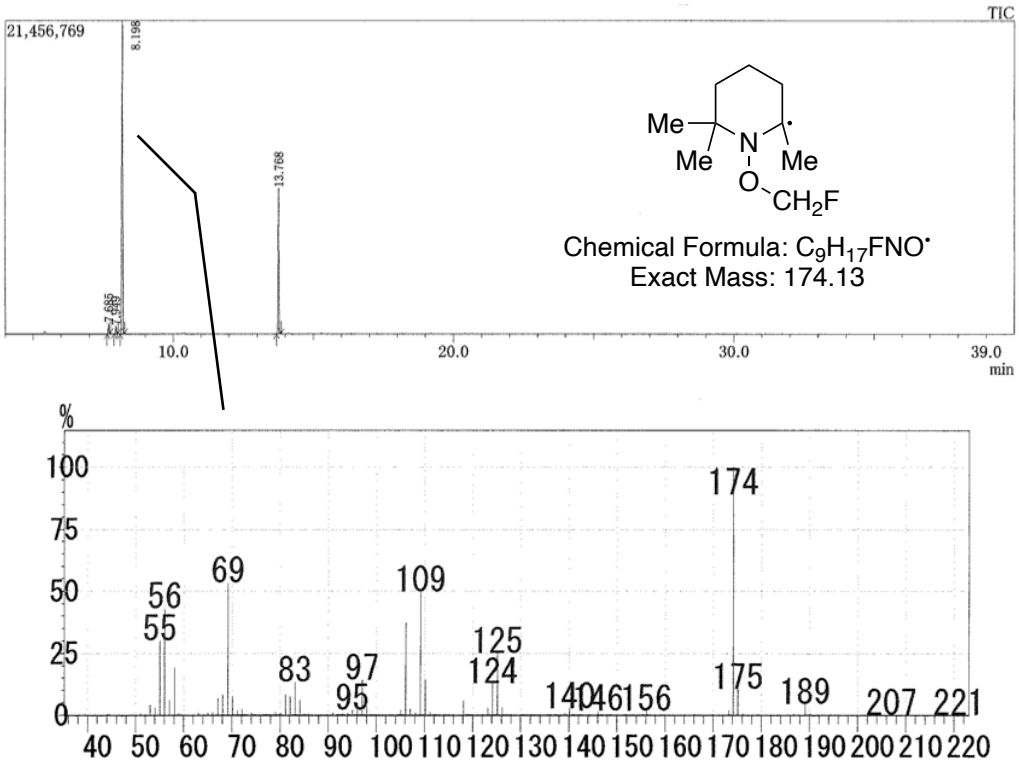


Figure S1. A GC chromatogram and a MS chart.

^{19}F NMR (376 MHz, $CDCl_3$, rt)

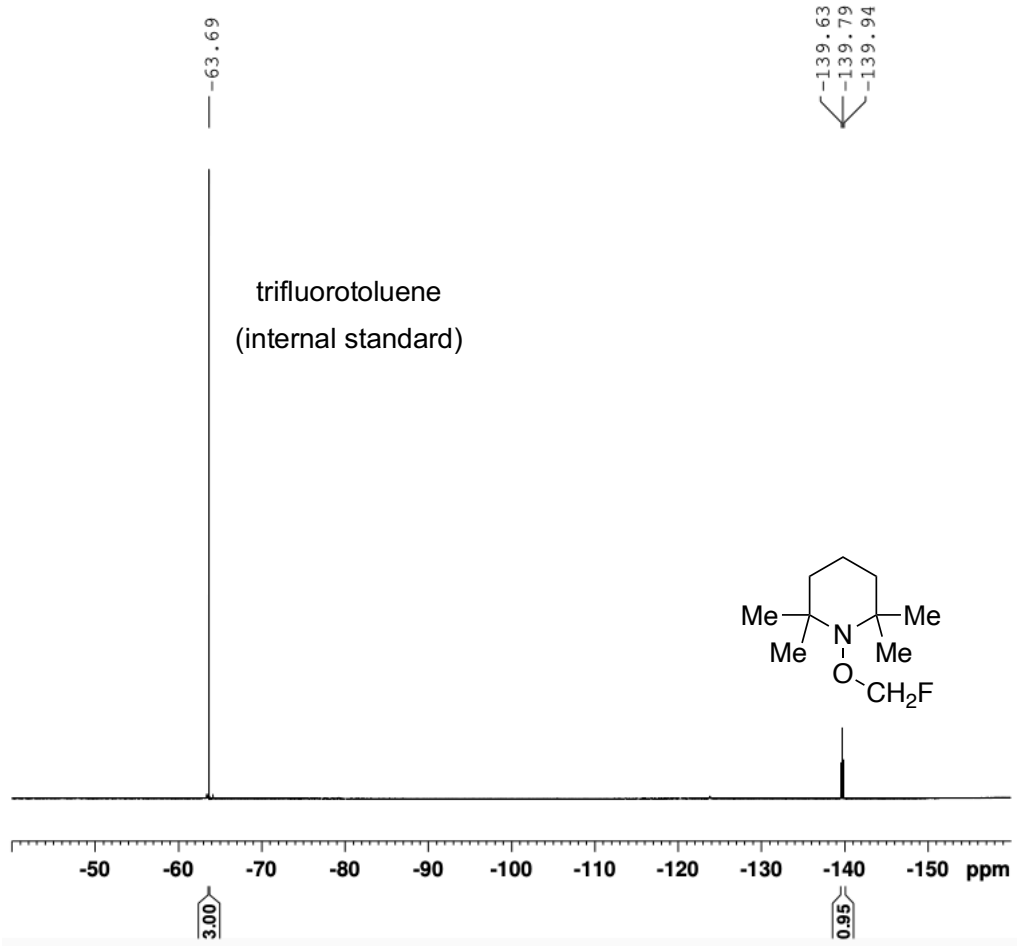


Figure S2. ^{19}F NMR spectra.

Luminescence Quenching Experiments

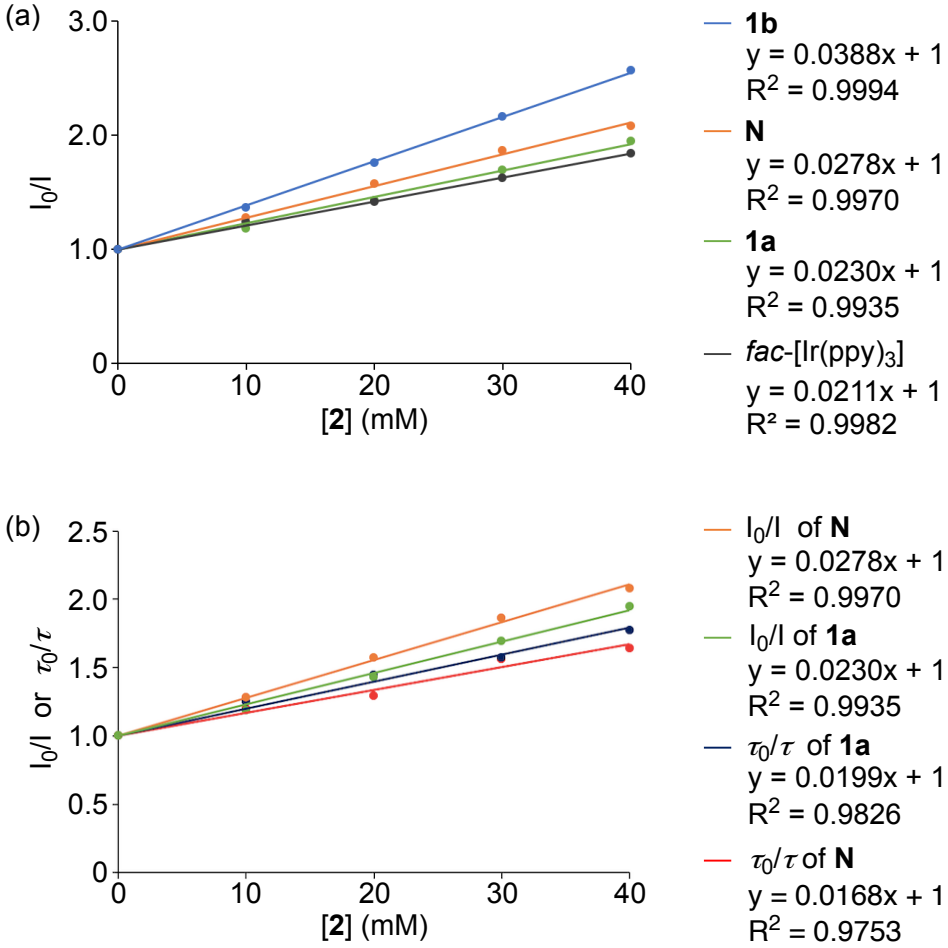


Figure S3. Stern-Volmer plots. (a) I_0/I of **1a**, **1b**, **N** and *fac*-[Ir(ppy)$_3$]. (b) I_0/I and τ_0/τ of **1a** and **N**.

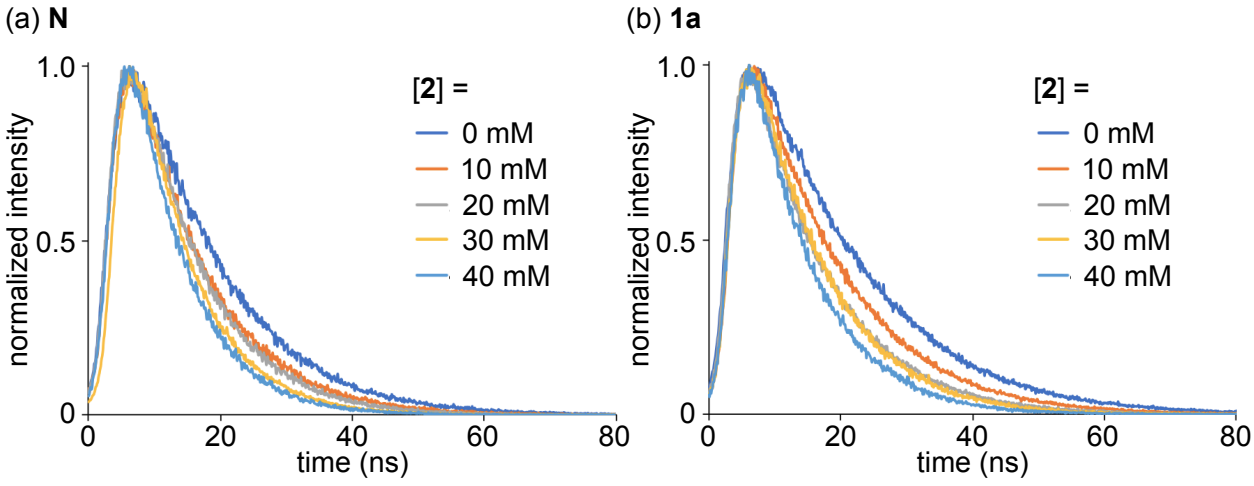


Figure S4. Luminescence decay of (a) **N**, (b) **1a**.

Quantum Yield Measurement

Quantum yield measurement was carried out in the same way to previous our report.[2]

(Photon flux)

Photon flux was measured with Ophir PD300-UV and Ophir StarLite.

Irradiation was carried out with HITACHI F-7000 (λ = 436 nm, emission slit width = 10.0 nm).

Measured power of light: 115.2 μW (for λ = 436 nm)

$$photon\ flux = \frac{power\ of\ light\ (\mathrm{W}) \times wavelength\ of\ irradiation\ light\ (\mathrm{m})}{Plank\ constant\ (\mathrm{J \cdot s}) \times speed\ of\ light\ (\mathrm{m/s}) \times Avogadro\ constant\ (1/mol)}$$

$$\therefore \frac{115.2 \times 10^{-6} \times 436 \times 10^{-9}}{6.626 \times 10^{-34} \times 2.998 \times 10^{8} \times 6.022 \times 10^{23}} = 4.20 \times 10^{-10}$$

Calculated photon flux: 4.20 x 10^{-10} einstein•s^{-1}

(Quantum yield)

A cuvette was charged with a solution of 1,1-ditolyllethylene **2** (20.8 mg, 0.100 mmol), **3** (49.1 mg, 0.150 mmol), **1a** (3.4 mg, 5.00 μmol), 1,2-dichloroethane (1.8 mL) and MeOH (0.2 mL). The solution was degassed by three freeze-pump-thaw cycles, and it was irradiated by F-7000 (λ = 436 nm, emission slit width = 10.0 nm) for 12 h. After evaporation, the yield of **4** was determined by ^{1}H NMR with dimethyl sulfone (4.71 mg, 0.0500 mmol) as an internal standard.

The quantum yield (Φ) was calculated by following formula. (A: Absorbance of catalysts)

$$\phi = \frac{mol\ product}{4.20 \times 10^{-10} \cdot 43200\ \mathrm{s} \cdot f} \qquad (f = 1 - 10^{-A})$$

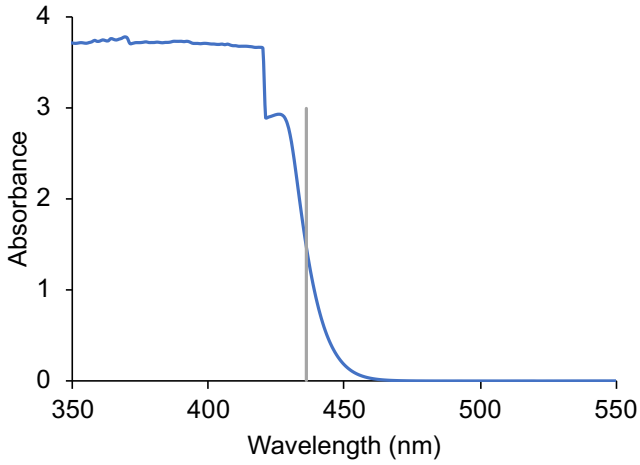
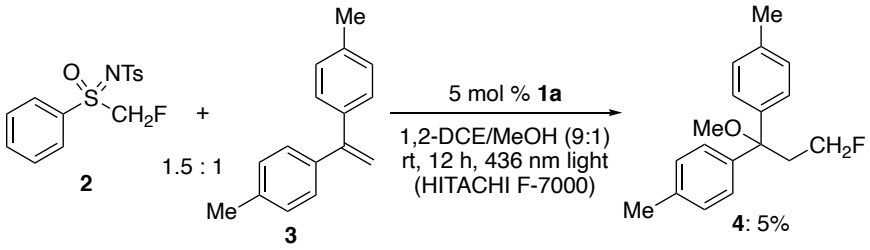


Figure S5. UV-vis spectra of **1a** (A = 1.4731).



Yield of **4**: 5% (mol product = 5 x 10^{-6} mol), **Calculated quantum yield: Φ = 29%**

DFT and TD-DFT Calculations of 1a, 1b and 1c

Theoretical calculations were performed by using Gaussian 09(D01) and 16 (A03) program package. Ground state geometries of **1a**, **1b** and **1c** were obtained with the CAM-B3LYP/6-31G(d)/CPCM-dichloroethane level of theory. Single point TD-DFT calculations were performed with the B3LYP/6-31G(d)/CPCM-dichloroethane level of theory. The first three excited states of **1a**, **1b** and **1c** are shown below.

(a) **1a**

Excited State	1:	Singlet-A	2.9393 eV	421.82 nm	f=0.2839	<S**2>=0.000
186 ->187		0.70272				
Excited State	2:	Singlet-A	3.3174 eV	373.74 nm	f=0.0073	<S**2>=0.000
185 ->187		0.70400				
Excited State	3:	Singlet-A	3.6440 eV	340.25 nm	f=0.0731	<S**2>=0.000
186 ->188		0.69015				

Cartesian coordinates of **1a** (6507.6159276032 Hartrees, neutral, singlet).

The Number of Imaginary Frequencies = 0, Total Energy, E(TD-HF/TD-KS) = -2049.70142105

N	2.84628	0.07369	0.14237
N	-2.82552	0.08304	0.15132
C	2.90887	-2.22834	-0.69006
C	3.56958	-3.44041	-0.82904
C	4.86884	-3.63991	-0.35173
C	5.47281	-2.55459	0.28648
C	4.81824	-1.33971	0.45004
C	3.52493	-1.15362	-0.04298
H	1.90634	-2.11396	-1.08736
H	3.05046	-4.24787	-1.3367
H	6.47637	-2.64591	0.68525
H	5.31787	-0.527	0.96621
C	3.51973	1.31418	0.00576
C	3.1299	2.40533	0.78875
C	3.76242	3.63046	0.65493
C	4.81741	3.82746	-0.24514
C	5.19862	2.72758	-1.01341
C	4.56071	1.49547	-0.90289
H	2.32462	2.28611	1.50627
H	3.4273	4.45083	1.28231
H	4.87932	0.66962	-1.52943

C	-4.79762	-1.33223	0.45533
C	-5.45155	-2.5396	0.27743
C	-4.85651	-3.61927	-0.38931
C	-3.5661	-3.41742	-0.87502
C	-2.90116	-2.20371	-0.7195
C	-3.50572	-1.1413	-0.05089
H	-5.2881	-0.52652	0.99097
H	-6.45272	-2.64284	0.68504
H	-3.05021	-4.21182	-1.40165
H	-1.90208	-2.08585	-1.12449
C	-3.09962	2.41615	0.79589
C	-3.73073	3.64217	0.66499
C	-4.79075	3.84062	-0.22904
C	-5.17837	2.74099	-0.9942
C	-4.54202	1.50767	-0.88667
C	-3.49613	1.32493	0.01602
H	-2.29045	2.29598	1.50887
H	-3.39048	4.46232	1.28989
H	-5.98706	2.83184	-1.70987
H	-4.86559	0.68243	-1.51144
C	-5.62039	-4.93743	-0.55277
C	-6.91927	-4.68374	-1.3388
H	-7.56869	-3.96615	-0.82875
H	-6.70099	-4.2898	-2.33681
H	-7.48089	-5.61695	-1.45679
C	-5.97062	-5.50469	0.83473
H	-6.52499	-6.44396	0.73222
H	-5.064	-5.70664	1.41448
H	-6.59147	-4.8129	1.41153
C	-4.80155	-5.99092	-1.30772
H	-4.54568	-5.65874	-2.3189
H	-3.87293	-6.23684	-0.78283
H	-5.3846	-6.91269	-1.39914
C	-5.46361	5.21365	-0.33047
C	-4.42072	6.2673	-0.7448
H	-4.88766	7.25569	-0.81667
H	-3.60321	6.33698	-0.02122
H	-3.98681	6.02486	-1.7204

C	-6.5958	5.22948	-1.36402
H	-7.38838	4.51821	-1.11057
H	-7.04508	6.22685	-1.40019
H	-6.23214	4.99322	-2.36912
C	-6.05586	5.59781	1.03748
H	-6.81334	4.87275	1.35271
H	-5.28757	5.64075	1.81505
H	-6.53071	6.58351	0.98251
C	5.49205	5.19938	-0.34982
C	6.09168	5.58255	1.01519
H	6.56811	6.56733	0.95775
H	5.3273	5.62706	1.79651
H	6.84933	4.8561	1.32681
C	4.44876	6.25468	-0.75894
H	4.91689	7.24234	-0.83302
H	4.00967	6.013	-1.73239
H	3.63495	6.32552	-0.0313
C	6.61912	5.21342	-1.38897
H	7.41166	4.50065	-1.13963
H	6.25006	4.97807	-2.39232
H	7.06999	6.21	-1.42715
C	5.55844	-4.99612	-0.53501
C	4.73988	-6.08813	0.17703
H	3.72267	-6.15545	-0.21974
H	5.21533	-7.06637	0.04581
H	4.66961	-5.88569	1.25078
C	5.64923	-5.3292	-2.03516
H	4.66073	-5.37636	-2.50128
H	6.23699	-4.57463	-2.5681
H	6.13281	-6.30146	-2.18
C	6.97787	-5.00726	0.04417
H	7.43045	-5.99139	-0.11271
H	7.62063	-4.26552	-0.44069
H	6.97943	-4.81	1.12095
H	6.00327	2.81751	-1.73372
C	-0.69467	-1.60797	3.43333
C	-1.38452	-1.06966	2.37972
C	-0.70134	-0.51135	1.26913

C	0.72303	-0.51328	1.26778
C	1.40653	-1.07254	2.37778
C	0.71692	-1.60917	3.43243
H	-1.23352	-2.02587	4.27781
H	-2.46768	-1.0538	2.38683
C	-1.40049	0.08717	0.17411
C	1.42151	0.08196	0.17036
H	2.48971	-1.05931	2.38377
H	1.2561	-2.0278	4.27633
C	0.71392	0.68	-0.84222
C	-0.6936	0.68302	-0.84016
H	1.2504	1.13829	-1.66633
H	-1.23054	1.14399	-1.6625

(b) **1b**

Excited State 1:	Singlet-A	3.0927 eV	400.89 nm	f=0.2588	<S**2>=0.000
186 ->187	0.70112				
Excited State 2:	Singlet-A	3.1311 eV	395.98 nm	f=0.0014	<S**2>=0.000
185 ->187	0.70441				
Excited State 3:	Singlet-A	3.7915 eV	327.01 nm	f=0.0753	<S**2>=0.000
186 ->188	0.67893				

Cartesian coordinates of **1b** (6452.9097330243 Hartrees, neutral, singlet).

The Number of Imaginary Frequencies = 0, Total Energy, E(TD-HF/TD-KS) = -2049.69541143

C	1.5976	-0.7786	1.80125
C	1.78421	-0.13281	0.60396
C	0.66276	0.17481	-0.22956
C	-0.64112	-0.1813	0.22144
C	-0.79203	-0.828	1.47425
C	0.30401	-1.1292	2.23706
H	1.80817	1.07396	-1.82836
H	2.46046	-1.00798	2.41781
C	0.81356	0.82076	-1.48288
C	-1.76276	0.12753	-0.61133
H	-1.78671	-1.08145	1.81927
H	0.18186	-1.62412	3.19513
C	-1.57636	0.77279	-1.80886
C	-0.28257	1.12192	-2.24553

H	-2.43935	1.00331	-2.42482
H	-0.16046	1.61618	-3.20395
N	-3.07842	-0.22667	-0.18847
N	3.10022	0.22278	0.18359
C	-4.05262	0.80084	-0.10889
C	-5.32998	0.65156	-0.65629
C	-6.25644	1.67957	-0.56737
C	-5.95703	2.90135	0.04645
C	-4.67344	3.03799	0.57732
C	-3.7399	2.00981	0.51144
H	-5.598	-0.27371	-1.15432
H	-7.23717	1.52196	-1.00612
H	-4.38079	3.95861	1.0684
H	-2.75504	2.14727	0.94599
C	-3.45149	-1.59072	-0.16349
C	-2.81649	-2.53123	-0.97214
C	-3.16565	-3.8777	-0.90634
C	-4.16402	-4.34112	-0.05165
C	-4.79475	-3.38214	0.7524
C	-4.44771	-2.04233	0.71164
H	-2.04193	-2.21323	-1.66124
H	-2.63925	-4.56759	-1.55556
H	-5.57352	-3.68618	1.44548
H	-4.94973	-1.3355	1.36357
C	4.47359	2.03598	-0.71343
C	4.82075	3.3808	-0.76088
C	4.17717	4.33884	0.02498
C	3.1664	3.87451	0.87268
C	2.81994	2.53308	0.94564
C	3.47046	1.58692	0.14854
H	4.98782	1.32757	-1.35396
H	5.60814	3.67561	-1.44485
H	2.63203	4.57306	1.50974
H	2.03851	2.21641	1.62748
C	5.34946	-0.6608	0.653
C	6.27425	-1.69001	0.56276
C	5.97472	-2.90852	-0.05783
C	4.69301	-3.04037	-0.59409

C	3.7611	-2.0106	-0.52678
C	4.07376	-0.80537	0.1004
H	5.61732	0.26203	1.15563
H	7.25371	-1.53634	1.0057
H	4.40044	-3.95813	-1.09051
H	2.77748	-2.14419	-0.96536
C	-4.57822	-5.81361	0.03749
C	-7.01303	4.01021	0.10755
C	4.52931	5.82987	-0.0119
C	7.02903	-4.01888	-0.12024
C	3.29075	6.64066	-0.4335
H	3.52685	7.71018	-0.458
H	2.95095	6.34466	-1.4314
H	2.45753	6.49895	0.261
C	5.65946	6.13316	-1.00254
H	5.38748	5.85723	-2.02638
H	5.87604	7.20603	-0.9949
H	6.58266	5.60676	-0.73995
C	4.98094	6.28628	1.38704
H	5.86981	5.73435	1.70971
H	5.22827	7.35347	1.37727
H	4.19893	6.13209	2.13627
C	6.51286	-5.26862	-0.84292
H	5.64396	-5.70177	-0.33721
H	6.23373	-5.05305	-1.87923
H	7.2981	-6.03078	-0.86291
C	8.27049	-3.50793	-0.87336
H	9.03533	-4.29087	-0.91953
H	8.01512	-3.22163	-1.89887
H	8.71448	-2.63726	-0.38188
C	7.43394	-4.423	1.30872
H	6.57192	-4.80458	1.86563
H	8.1953	-5.21012	1.27916
H	7.84859	-3.57886	1.86738
C	-6.06987	-5.95032	-0.31708
H	-6.26237	-5.6024	-1.33726
H	-6.70302	-5.37073	0.36108
H	-6.38177	-6.99837	-0.25063

C	-3.77501	-6.70015	-0.92139
H	-3.9167	-6.40284	-1.96536
H	-2.70332	-6.67196	-0.69996
H	-4.10604	-7.73888	-0.8245
C	-4.34969	-6.32604	1.47085
H	-3.29273	-6.25376	1.74739
H	-4.92871	-5.75565	2.20303
H	-4.65145	-7.37611	1.5518
C	-7.42252	4.40816	-1.32185
H	-7.83686	3.56105	-1.87623
H	-6.5627	4.78936	-1.88241
H	-8.18539	5.19386	-1.2933
C	-6.49693	5.26356	0.82399
H	-7.28349	6.02436	0.84358
H	-5.63039	5.69639	0.31399
H	-6.2142	5.05227	1.86021
C	-8.25161	3.50023	0.86605
H	-9.0174	4.28227	0.91168
H	-8.69586	2.62723	0.37897
H	-7.99289	3.2179	1.89183

(c) **1c**

Excited State	1:	Singlet-A	3.2033 eV	387.05 nm	f=0.1221	<S**2>=0.000
110 ->111		0.70216				
Excited State	2:	Singlet-A	3.8754 eV	319.93 nm	f=0.0504	<S**2>=0.000
110 ->112		0.69196				
Excited State	3:	Singlet-A	4.1970 eV	295.41 nm	f=0.5169	<S**2>=0.000
110 ->113		0.68810				
110 ->114		0.12085				

Cartesian coordinates of **1c** (2907.3859691806 Hartrees, neutral, singlet).

The Number of Imaginary Frequencies = 0, Total Energy, E(TD-HF/TD-KS) = -1217.73486821

C	-2.28621	4.5903	-1.71637
C	-1.73513	4.98005	-0.52545
C	-0.97975	4.07202	0.26118
C	-0.81208	2.73522	-0.19841
C	-1.38251	2.36536	-1.44372
C	-2.09994	3.26899	-2.18262

H	-0.50521	5.50138	1.81295
H	-2.86087	5.29468	-2.30948
H	-1.8635	5.99639	-0.1639
C	-0.37497	4.47622	1.47892
C	-0.05763	1.82481	0.60683
H	-1.23849	1.35502	-1.80756
H	-2.52654	2.97129	-3.13535
C	0.51611	2.25631	1.7782
C	0.36621	3.59044	2.21282
H	1.09009	1.55406	2.37384
H	0.83137	3.90142	3.14273
N	0.11205	0.47383	0.18295
C	1.7906	-1.27576	0.60624
C	3.09216	-1.73989	0.49
C	4.09619	-0.99298	-0.13711
C	3.72341	0.24927	-0.65267
C	2.41839	0.71985	-0.55964
C	1.43156	-0.03402	0.07435
H	1.04655	-1.88008	1.11331
H	3.32804	-2.70984	0.91739
H	4.45383	0.87402	-1.15316
H	2.16195	1.68562	-0.98287
C	-2.10736	-0.16643	0.99631
C	-3.21501	-1.00004	0.94062
C	-3.27991	-2.09687	0.07535
C	-2.17054	-2.31077	-0.74527
C	-1.06069	-1.475	-0.7145
C	-1.0073	-0.39058	0.16394
H	-2.09466	0.66502	1.69229
H	-4.04684	-0.78611	1.60519
H	-2.16034	-3.13934	-1.44375
H	-0.22659	-1.66727	-1.38081
C	5.5224	-1.54614	-0.23023
C	-4.52264	-2.99338	0.05737
C	6.47198	-0.58274	-0.95176
H	6.55107	0.37702	-0.43123
H	7.47445	-1.01988	-0.99483
H	6.15062	-0.38904	-1.98015

C	5.50838	-2.87619	-1.00497
H	5.13194	-2.73142	-2.02291
H	6.52165	-3.28695	-1.07265
H	4.87727	-3.62411	-0.51626
C	6.07156	-1.79111	1.18675
H	5.45727	-2.50549	1.74255
H	7.08872	-2.19468	1.1353
H	6.10459	-0.85844	1.75937
C	-4.39882	-4.13388	-0.95975
H	-3.55133	-4.78914	-0.73457
H	-4.27861	-3.7571	-1.98051
H	-5.30592	-4.74596	-0.93735
C	-5.75823	-2.15257	-0.31109
H	-6.65646	-2.77969	-0.31921
H	-5.64563	-1.70744	-1.30511
H	-5.92447	-1.34133	0.40359
C	-4.72929	-3.61287	1.45135
H	-4.86622	-2.8465	2.21994
H	-5.61895	-4.25219	1.45519
H	-3.86876	-4.22649	1.73735

Comparison of UV-Vis Spectra and Transitions Predicted by TD-DFT

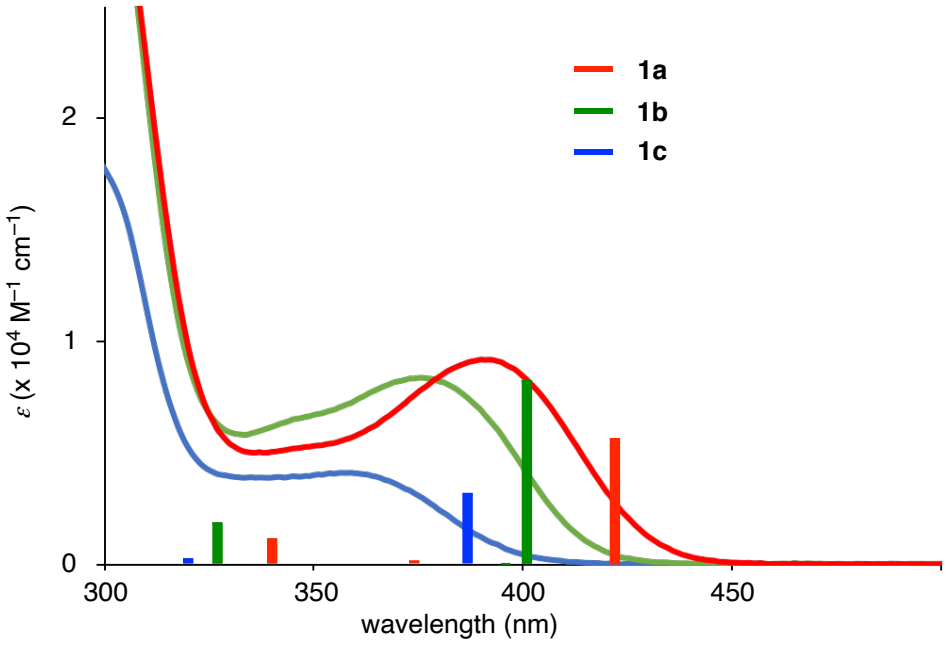
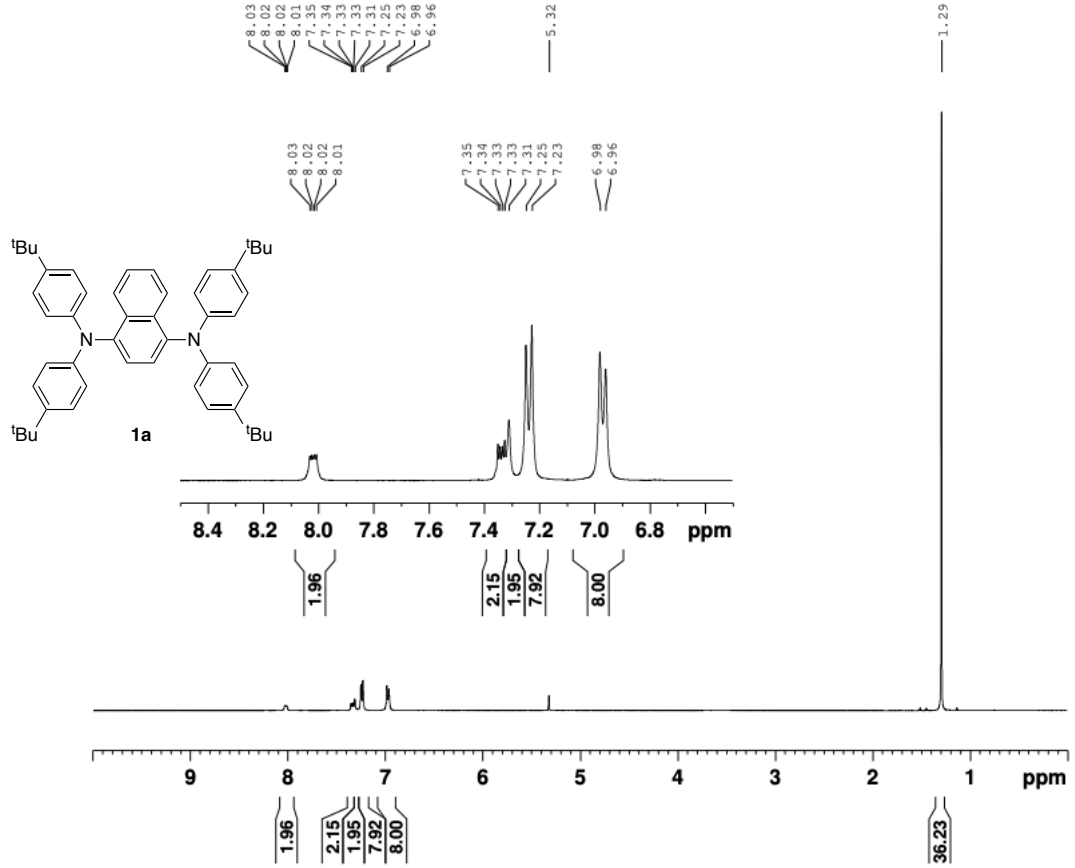


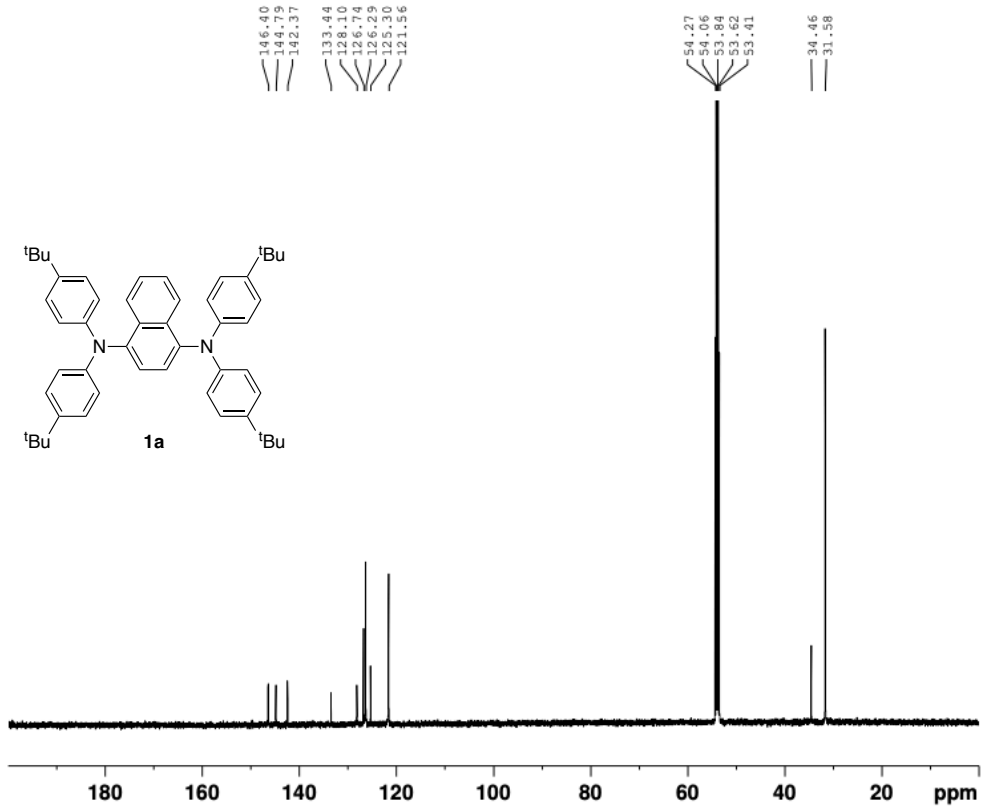
Figure S6. UV-Vis spectra (**1a**–**c**) and transitions predicted by TD-DFT calculation (bars)

NMR Spectra

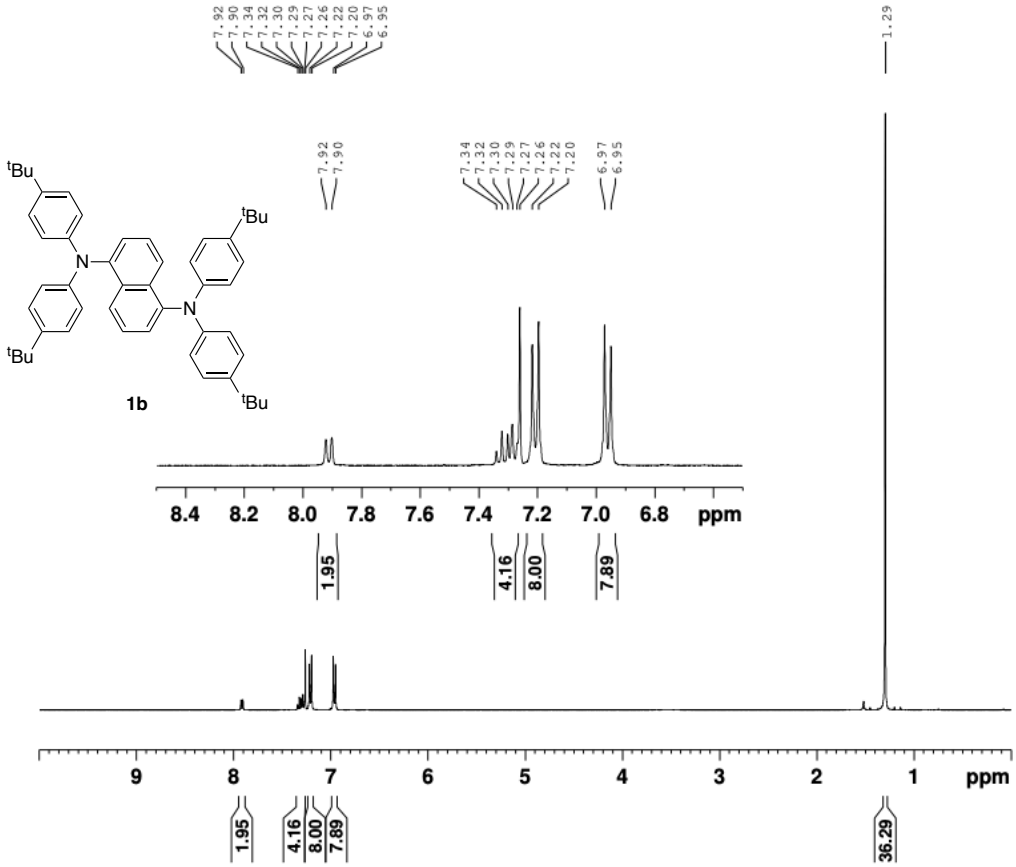
^{1}H NMR (400 MHz, CD_2Cl_2, rt)



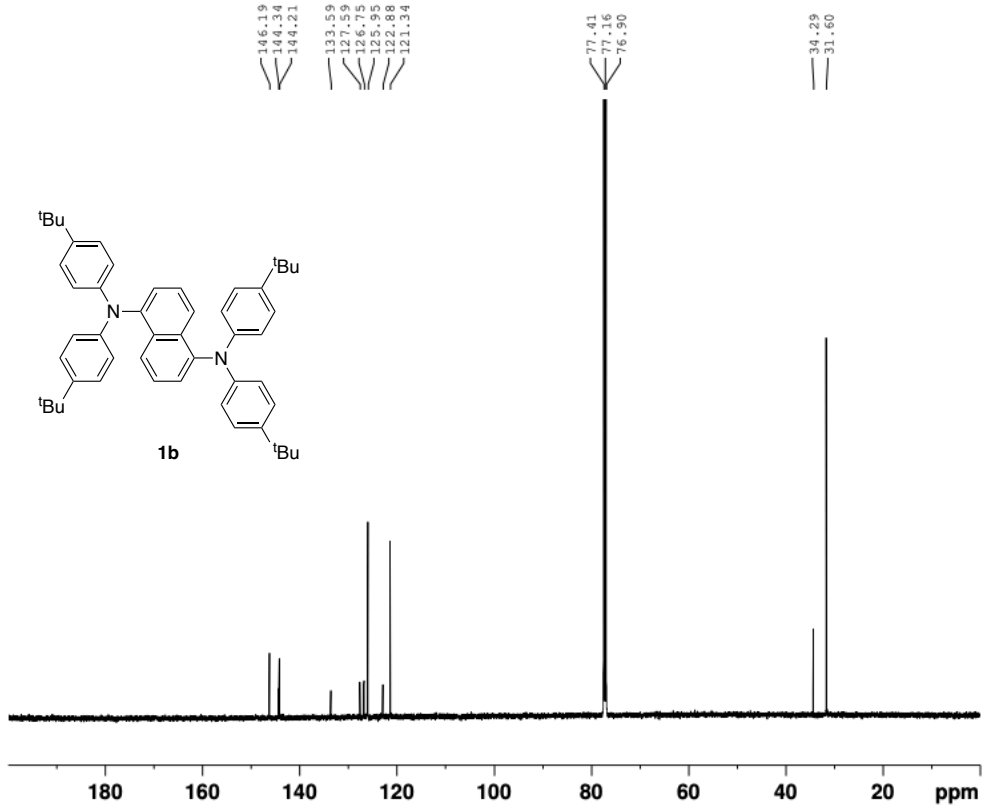
$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, rt)



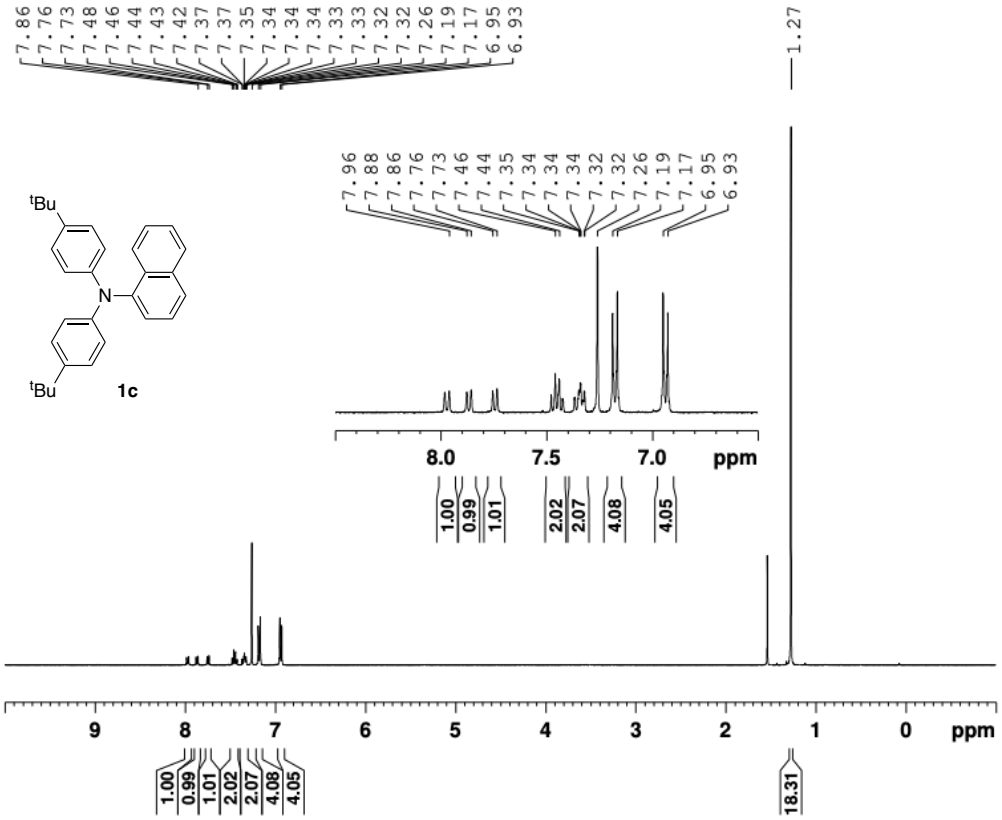
^{1}H NMR (400 MHz, $CDCl_3$, rt)



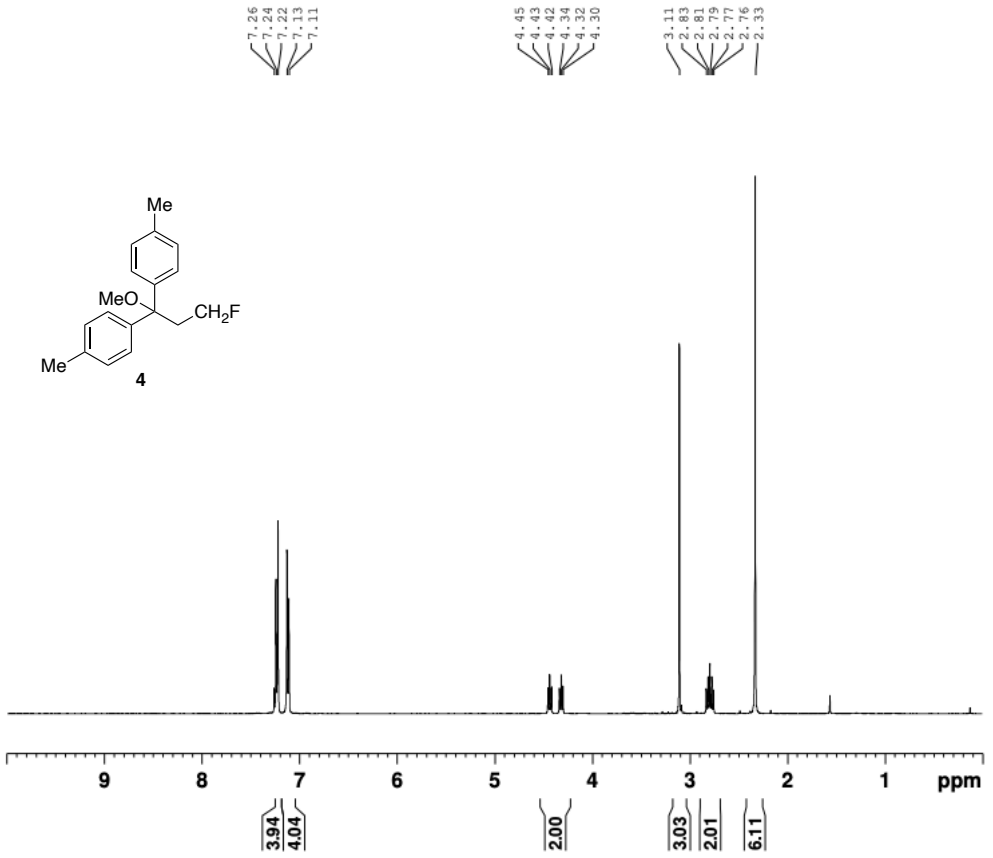
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, rt)



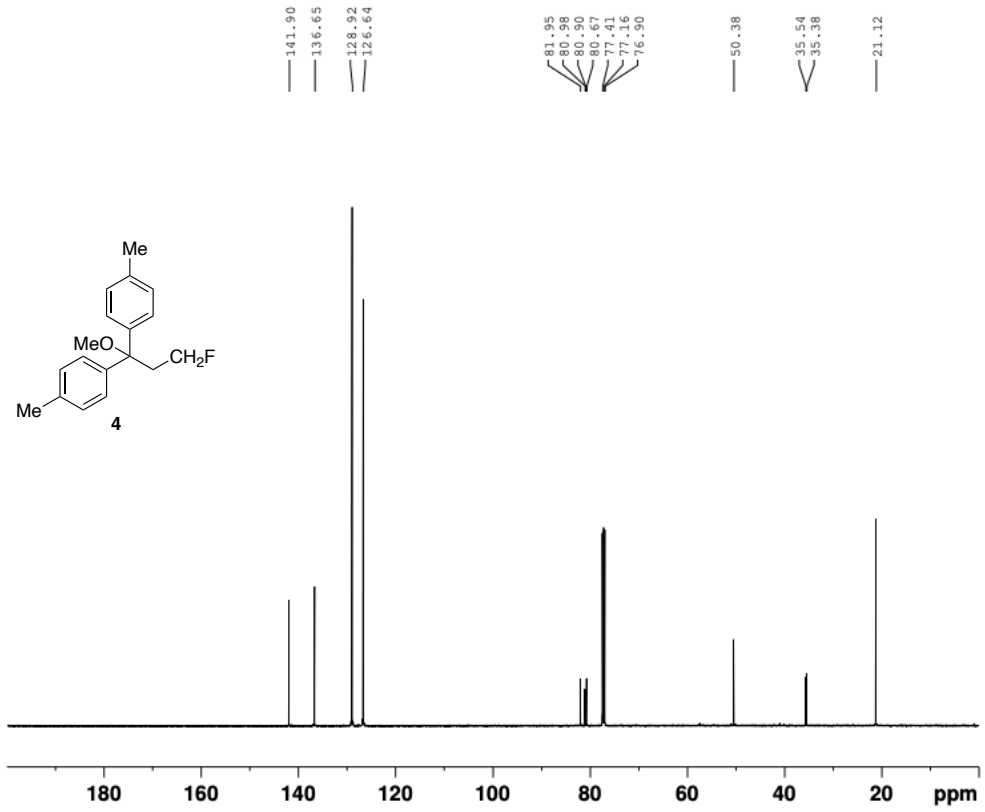
^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{1}H NMR (400 MHz, $CDCl_3$, rt)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, rt)



^{19}F NMR (376 MHz, $CDCl_3$, rt)