Synthesis of 4-Difluoromethyl Quinolines by N-Heterocyclic Carbene (NHC)-Catalyzed Umpolung of Imines

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Supporting Information

1. General Information

Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw cap. Reaction temperatures are reported as the temperature of the bath surrounding the reaction vessel. Dry DMF was purchased from commercial sources and stored under argon over 4 Å molecular sieves. The 2-nitro benzaldehyde and other aldehydes were purchased from commercial sources and were used without any further purification. AgOTf and $PdBr_2$ were purchased from Sigma Aldrich, and both were stored in glove-box, and 2-bromo-3,3,3-trifluoropropene (BTP) from Fluorochem, and were used as received. The aldimines (**1a-1q**)[1] were synthesized from corresponding aldehydes following the literature procedure and aldimines (**1r-1y**)[2] were synthesized from corresponding aniline derivatives following the literature procedure. DBU was purchased from commercial source and distilled before used. The triazolium salt **3** was synthesized following the literature procedure.[3]

Analytical thin layer chromatography was performed on TLC Silica gel 60 F_{254}. Visualization was accomplished with short wave UV light or $KMnO_4$ staining solutions followed by heating. Flash chromatography was performed on silica gel (230-400 mesh) by standard techniques eluting with solvents as indicated.

All compounds were fully characterized. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker AV 400 and DXP 300 in solvents as indicated. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm or relative to external $CFCl_3$: δ_F = 0 ppm and DMSO-d^6: δ_H = 2.50 ppm, δ_C = 39.50 ppm). Infrared spectra were recorded on a Perkin-Elmer 1615 FT Infrared Spectrophotometer Model 60B or Perkin-Elmer Paragon 100 (ATR) FTIR spectrometer. The wave numbers (n) of recorded IR-signals are quoted in cm^{-1}. HRMS mass spectra were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump or Waters LCT Premier instrument.

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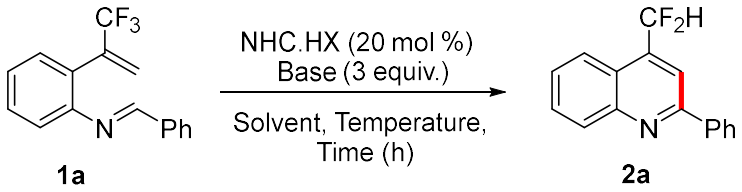
[1] (a) Chatterjee, A.; Oh, D. J.; Kim, K. M.; Youk, K. S.; Ahn, K. H. *Chem. Asian J.* **2008**, *3*, 1962. (b) Trost, B. M.; Debien, L. *J. Am. Chem. Soc.* **2015**, *137*, 11606. (c) Jia, Z. X.; Luo, Y. C.; Xu, P. F. *Org. Lett.* **2011**, *13*, 832.

[2] (a) Qun, Z.; Besset, T.; Poisson, T.; Bouillon, J. -P.; Pannecoucke, X. *Eur. J. Org. Chem.* **2016**, 76. (b) Jiang, B.; Zhou, J.; Zhang, F.; Ju, W. Preparation of 1-Trifluoromethyl-2-alkylvinylaniline derivatives CN 1263084 A, Aug. 16, 2000. (c) Mori, T.; Ichikawa, J. *Chem. Lett.* **2004**, *33*, 1206.

[3] Michailidis, F. R.; Besnard, C.; Alexakis, A. *Org. Lett*. **2012**, *14*, 4906.

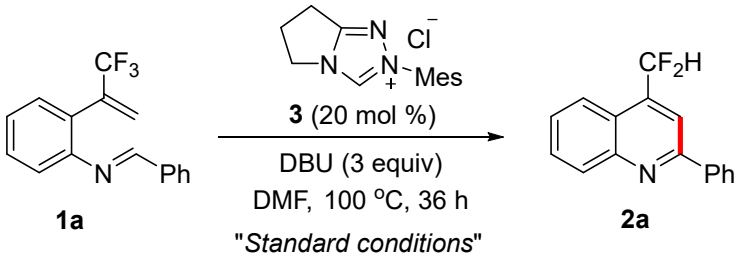
2. General Procedure for the Optimization of Reaction Conditions



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the azolium salt (0.05 mmol). Then the screw-capped tube was evacuated and backfilled with argon. To this mixture, solvent was added (2.0 mL) under argon atmosphere. To this mixture was added the aldimine **1a** (0.25 mmol) and base (0.75 mmol). Then the reaction mixture was stirred at 100 °C for 36 h. After 36 h stirring, the reaction mixture cooled to rt and H_2O (10 mL) was added, and the reaction mixture was extracted with EtOAc (3 × 10 mL). The combined organic phases were dried with Na_2SO_4 and solvent was evaporated under reduced pressure. The crude residue was purified by flash column chromatography (Pet. ether/EtOAc = 95/5) on silica gel to afford the corresponding quinoline derivative **2a**.

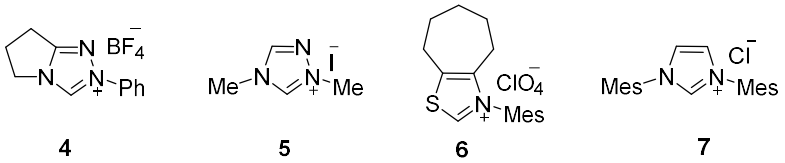
3. Optimization Studies

Our optimization study commenced with treatment of (*E*)-1-phenyl-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine **1a** in the presence of the carbene generated from **3** by deprotonation using KO*t*-Bu resulted in the formation of difluoromethylated quinoline derivative **2a** in 75% yield (isolated yield). The NHCs generated from other triazolium salts **4** and **5** furnished **2a** in reasonable yield (entries 2, 3) whereas the carbenes derived from the common thiazolium salt **6** and imidazolium salt **7** are not found to be reactive for this imine umpolung (entries 4, 5). Other bases such as DMAP, DABCO, KO*t*-Bu, and K_2CO_3 furnished the desired product in reduced yields (entries 7-10). Among the various solvents screened such as DMSO, chlorobenzene, 1,4-dioxane and Toluene, toluene was found to give comparable yield of the desired product (entries 11-14). With decrease in temperature to 80 °C reactivity decreases abruptly (entry 15). The reaction afforded reduced yield of **2a** when the reaction time was reduced to 24 h (entry 16). Moreover, an excess of DBU was required for good conversion to **2a** (entries 17-20). Additionally, decrease in catalyst loading to 15 mol% reactivity decreases to 51% (entry 21).



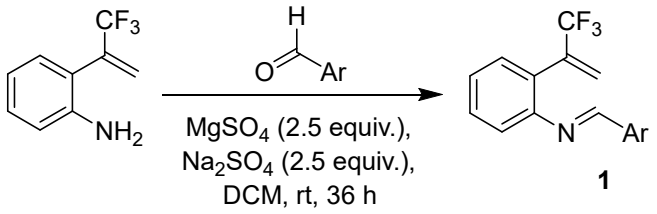
Entry	variation of the standard conditions[a]	yield of **2a** (%)[b]
1	None	75
2	**4** instead of **3**	70
3	**5** instead of **3**	59
4	**6** instead of **3**	<5
5	**7** instead of **3**	<5
6	no **3** and DBU	<5
7	DMAP instead of DBU	26
8	DABCO instead of DBU	19
9	KO*t*-Bu instead of DBU	21
10	K_2CO_3 instead of DBU	34
11	DMSO instead of DMF	48
12	chlorobenzene instead of DMF	41
13	1,4-dioxane instead of DMF	63
14	toluene instead of DMF	<5
15	80 °C instead of 100 °C	41
16	run for 24 h instead of 36 h	53
17	2.0 equiv of DBU instead of 3.0 equiv	44
18	1.5 equiv of DBU instead of 3.0 equiv	32
19	1.0 equiv of DBU instead of 3.0 equiv	21
20	40 mol% of DBU instead of 3.0 equiv	14
21	15 mol % of **3** instead of 20 mol %	51

[a] Standard conditions: **1a** (0.25 mmol), **3** (0.05 mmol), DBU (0.75 mmol), DMF (2.0 mL), 100 °C, 36 h. [b] Isolated yield after column chromatography.



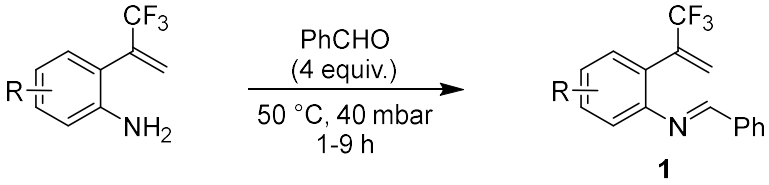
4. General Procedure for the Synthesis of Aldimines

Procedure A for the Synthesis of Aldimines (1a-1q)[1]



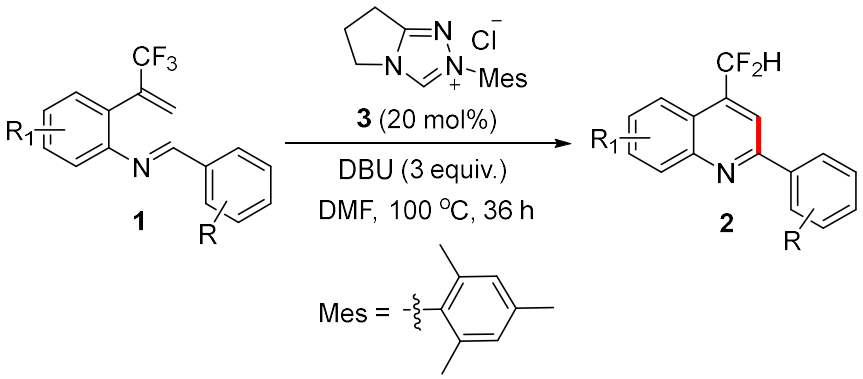
To a solution of 2-(3,3,3-trifluoroprop-1-en-2-yl)aniline (0.50 g, 2.643 mmol), in DCM (30 mL) was added an aromatic aldehyde (0.280 g, 2.643 mmol), followed by the addition of $MgSO_4$ (0.795 g, 6.607 mmol.) and Na_2SO_4 (0.938 g, 6.607 mmol) under Ar atmosphere. The reaction mixture was stirred at rt for 36 h. The reaction mixture was filtered through filter paper, rinsed with DCM and the filtrate was concentrated in vacuo. The crude imine, was purified via flash column chromatography with deactivated silica gel (eluting with hexanes/Et_3N (20:1 v/v)) to afford the corresponding aldimine **1**.

Procedure B for the Synthesis of Aldimines (1r-1y)[2]



To the desired amine (1 equiv) was added benzaldehyde (4 equiv). The reaction mixture was heated at 50 °C under 40 mbar for 1 to 9 h until the reaction was completed (monitored by TLC). Excess of benzaldehyde was removed under high vaccum (10^{-1} mbar) at 45 °C for 1 h. The crude imine, was purified via flash column chromatography with deactivated silica gel (eluting with Pet. ether/Et_3N) to afford the corresponding aldimine **1**.

5. General Procedure for the Synthesis of Difluoromethylated Quinoline Derivatives



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the triazolium salt **3** (27 mg, 0.10 mmol) was added. Then the screw-capped tube was evacuated and backfilled with argon. To this dry DMF (4.0 mL) was added under argon atmosphere. To this mixture aldimine **1** (0.50 mmol) and DBU as a base (1.5 mmol) were added under argon flow. Then the reaction mixture was stirred at 100° C for 36 h. After 36 hour stirring, work-up of the reaction mixture was done using EtOAc (10 mL) twice, organic fractions were dried with Na_2SO_4 and solvent was evaporated. The crude residue was purified by flash column chromatography (Pet ether: Ethyl acetate = 95:5) on silica gel to afford the corresponding quinoline derivative **2.**

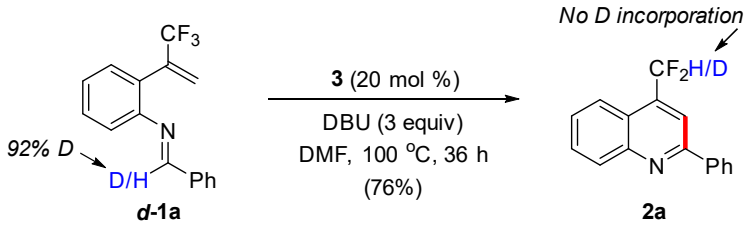
Procedure for the 1.0 mmol Scale Reaction:

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the triazolium salt **3** (54 mg, 0.20 mmol) was added. Then the screw-capped tube was evacuated and backfilled with argon. To this dry DMF (8.0 mL) was added under argon atmosphere. To this mixture aldimine **1a** (1.0 mmol) and DBU as a base (3.0 mmol) were added under argon flow. Then the reaction mixture was stirred at 100 °C for 36 h. After 36 hour stirring, work-up of the reaction mixture was done using EtOAc (20 mL) twice, organic fractions were dried with Na_2SO_4 and solvent was evaporated. The crude residue was purified by flash column chromatography (Pet ether: Ethyl acetate = 95:5) on silica gel to afford 4-(difluoromethyl)-2-phenylquinoline **2a** as a yellowish liquid (0.192 g, 75%).

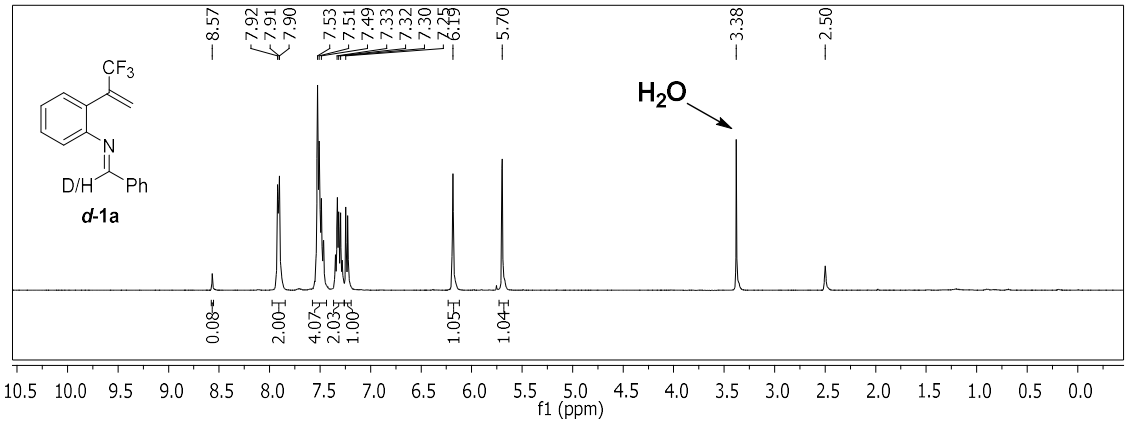
6. Mechanistic Studies

Reactions Using Deuterium Labelled Imine Substrate (d-1a)

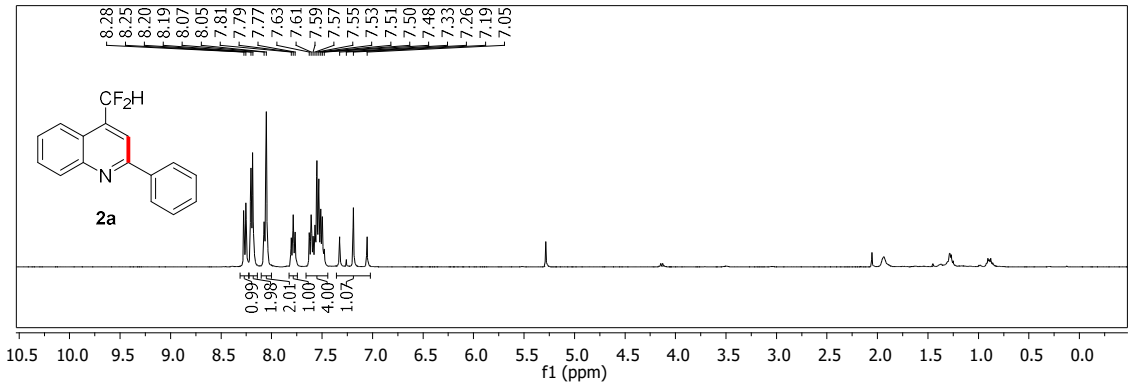
To get insight into the mechanism, compound ***d*-1a** (having 92% Deuterium at the imine carbon) was treated under our optimized reaction conditions. This reaction furnished quinoline **2a** in 76% yield and without deuterium incorporation in the final product **2a**. This experiment sheds light on the involvement of base in the isomerization to quinoline, and the formation of difluoromethyl moiety proceeds via 1,3-H shift instead of 1,5-H shift.



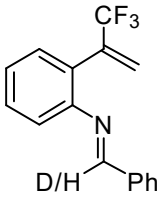
^{1}H-NMR Spectrum of (*E*)-1-Phenyl-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl) methanimine-*d* (*d*-1a)



^{1}H-NMR Spectrum of 4-(difluoromethyl)-2-phenylquinoline (2a)



(*E*)-1-Phenyl-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine-*d* (*d*-1a)

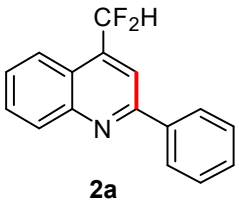


***d*-1a**

Following the general known procedure, treatment of 2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine (0.40 g, 2.115 mmol), benzaldehyde-α-*d* (0.226 g, 2.115 mmol.), $MgSO_4$ (0.636 g, 5.287 mmol) and Na_2SO_4 (0.751 g, 5.287 mmol) in DCM (30 mL) at rt for 36 h. After 36 h the crude reaction mixture was purified via flash column chromatography with deactivated silica gel (eluting with hexanes/Et_3N (20:1 v/v)) to afford the corresponding aldimine (*E*)-1-phenyl-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine-*d* ***d*-1a** (0.304 g, 52 % yield) as a yellow liquid.

R_f (Pet. ether /EtOAc = 95/05): 0.45; **^{1}H NMR (DMSO-*d*^{6}, 400 MHz)** δ 8.57 (s, 1H (0.92 D, 0.08 H)), 7.92-7.90 (m, 2H), 7.53-7.47 (m, 4H), 7.35-7.28 (m, 2H), 7.24 (d, *J* = 7.9 Hz, 1H), 6.19 (s, 1H), 5.70 (s, 1H). **HRMS**: calculated $[M+H]^+$ for $C_{16}H_{12}DNF_3$: 277.1057, found: 277.1057. **FTIR (cm^{-1}):** 3443, 3068, 2980, 2475, 2250, 2122, 1823, 1623, 1492, 1444, 1406, 1346, 1251, 1228, 1177, 1123, 1041, 821, 766.

4-(difluoromethyl)-2-phenylquinoline (2a)



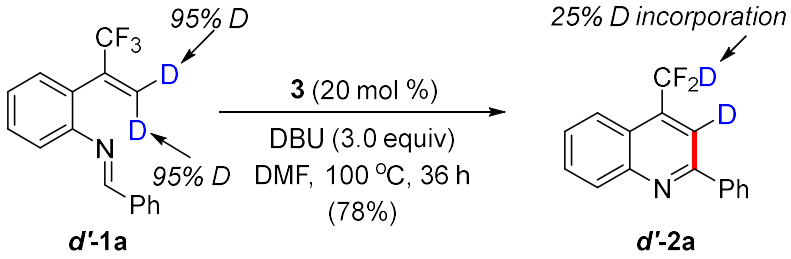
2a

Following the general procedure, treatment of (*E*)-1-phenyl-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine-*d* ***d*-1a** (137.6 mg, 0.50 mmol) with the triazolium salt **3** (27.0 mg, 0.10 mmol), DBU (228.4 mg, 224 μL, 1.50 mmol) in DMF (4.0 mL) at 100 °C for 36 h followed by work-up of the reaction mixture using EtOAc and subsequent flash column chromatography (Pet. ether /EtOAc = 95/05) of the crude reaction mixture using silica gel afforded 4-(difluoromethyl)-2-phenylquinoline **2a** as a yellowish liquid (0.097 g, 76%).

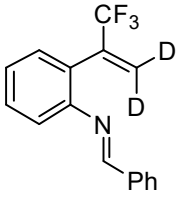
R_f (Pet. ether /EtOAc = 90/10): 0.40; **^{1}H NMR ($CDCl_3$, 400 MHz)** δ 8.27 (d, *J* = 8.4 Hz, 1H), 8.19 (d, *J* = 7.4 Hz, 2H), 8.07-8.05 (m, 2H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.63-7.48 (m, 4H), 7.19 (t, *J* = 54.6 Hz, 1H). **HRMS:** calculated $[M+H]^+$ for $C_{16}H_{12}NF_2$: 256.0932, found: 256.0932. **FTIR (cm^{-1}):** 3407, 3021, 2976, 2403, 1609, 1372, 1216, 1117, 1047, 928, 887, 767, 669.

Reactions Using Deuterium Labelled Imine Substrate (d'-1a)

To get further insight on the 1,3-H shift, the substrate **d'-1a** was subjected to the optimized reaction conditions. The product **d'-2a** was formed in 78% yield with 25% deuterium incorporation at the difluoromethyl moiety indicating the involvement of the 1,3-H shift operating in the present case.



(*E*)-1-Phenyl-*N*-(2-(3,3,3-trifluoroprop-1-en-2-yl-1,1-d_2)phenyl)methanimine (*d'*-1a)

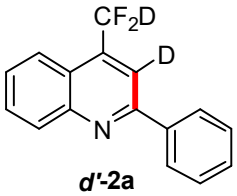


***d'*-1a**

Following the general known procedure, treatment of 2-(3,3,3-trifluoroprop-1-en-2-yl-1,1-d_2)aniline (0.095 g, 0.502 mmol.), benzaldehyde (0.053 g, 0.502 mmol.), $MgSO_4$ (0.151 g, 1.255 mmol.) and Na_2SO_4 (0.178 g, 1.255 mmol.) in DCM (5 mL) at rt for 36 h. After 36 h the crude reaction mixture was purified via flash column chromatography with deactivated silica gel (eluting with hexanes/Et_3N (20:1 v/v)) to afford the corresponding aldimine (*E*)-1-Phenyl-*N*-(2-(3,3,3-trifluoroprop-1-en-2-yl-1,1-d_2)phenyl)methanimine ***d'*-1a** (0.07 g, 50 % yield) as a yellow liquid.

R_f (Pet. ether /EtOAc = 95/05): 0.47; **^{1}H NMR (DMSO-*d*^{6}, 400 MHz)** δ 8.56 (s, 1H), 7.91-7.89 (m, 2H), 7.55-7.47 (m, 4H), 7.35-7.28 (m, 2H), 7.24 (d, *J* = 7.8 Hz, 1H), 6.18 (s, 0.05H (0.95D)), 5.70 (s, 0.05H (0.95D)).

4-(Difluoromethyl-*d*)-2-phenylquinoline-3-*d* (*d'*-2a)

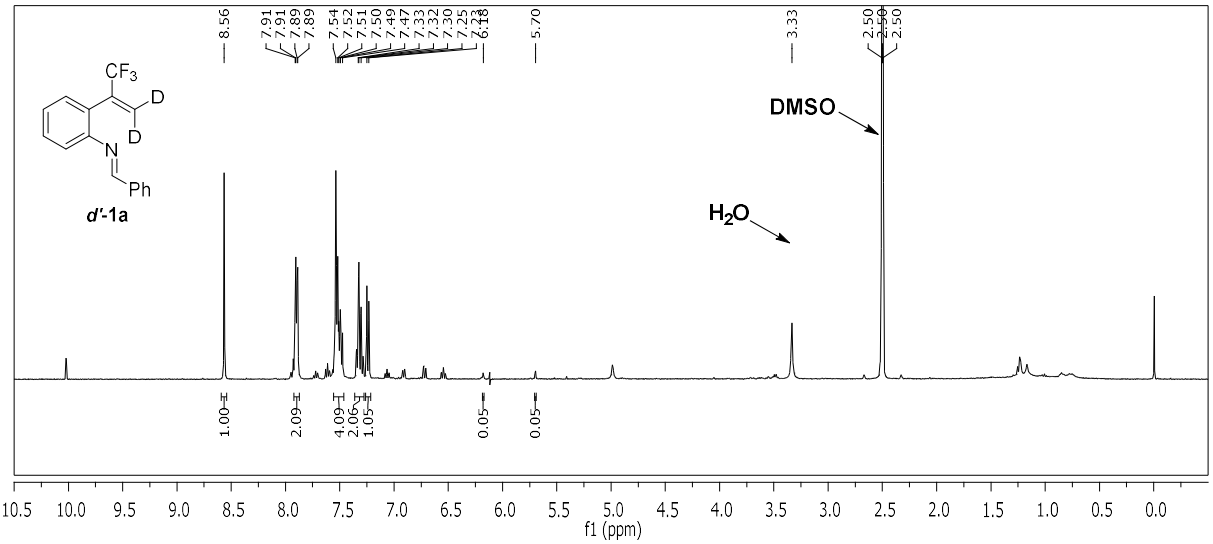


***d'*-2a**

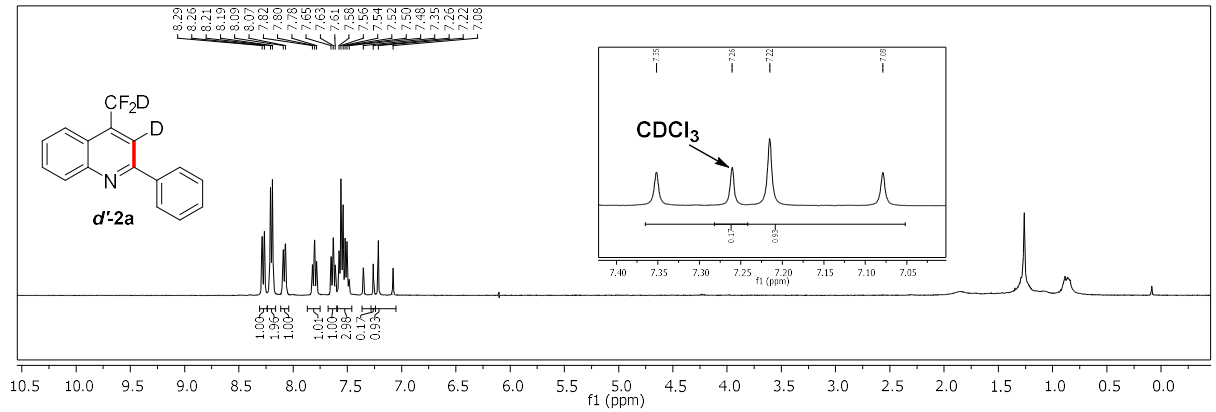
Following the general procedure, treatment of (*E*)-1-Phenyl-*N*-(2-(3,3,3-trifluoroprop-1-en-2-yl-1,1-d_2)phenyl)methanimine ***d'*-1a** (44 mg, 0.16 mmol) with the triazolium salt **3** (8.4 mg, 0.032 mmol), DBU (72 mg, 71 µL, 0.474 mmol) in DMF (1.0 mL) at 100 °C for 36 h followed by work-up of the reaction mixture using EtOAc and subsequent flash column chromatography (Pet. ether /EtOAc = 95/05) of the crude reaction mixture using silica gel afforded 4-(difluoromethyl-*d*)-2-phenylquinoline-3-*d* ***d'*-2a** as a yellowish liquid (0.030 g, 78%).

R_f (Pet. ether /EtOAc = 90/10): 0.42; **^{1}H NMR ($CDCl_3$, 400 MHz)** δ 8.27 (d, *J* = 8.5 Hz, 1H), 8.20 (d, *J* = 7.2 Hz, 2H), 8.08(d, *J* = 8.2 Hz, 1H), 7.80 (t, *J* = 7.8 Hz, 1H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.58-7.48 (m, 3H), 7.22 (t, *J* = 54.2 Hz, 0.76H (0.24D)). **^{13}C NMR ($CDCl_3$, 100 MHz)** δ 157.06, 148.84, 138.86, 134.01, 130.72, 130.28, 130.01, 129.13, 127.66, 127.57, 123.21, 113.61.

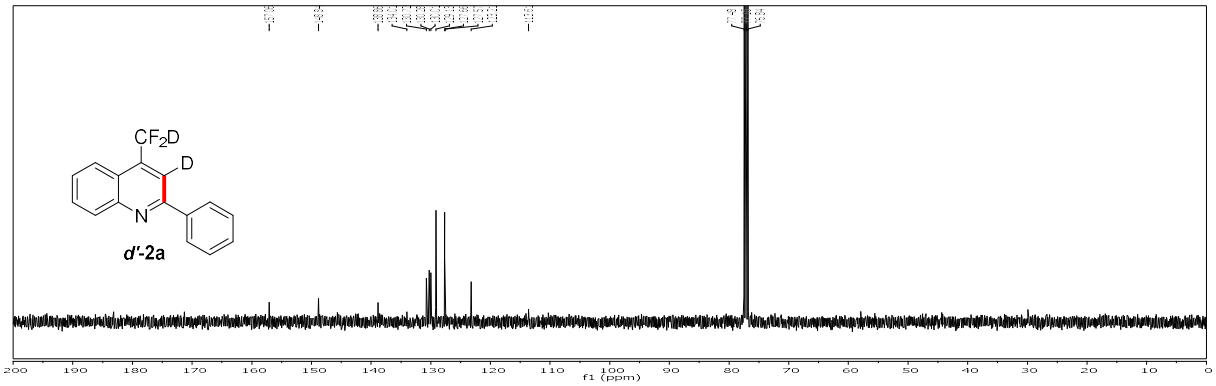
^{1}H-NMR Spectrum of (*E*)-1-Phenyl-*N*-(2-(3,3,3-trifluoroprop-1-en-2-yl-1,1-d_2)phenyl) methanimine (*d'*-1a)



^{1}H-NMR Spectrum of 4-(Difluoromethyl-*d*)-2-phenylquinoline-3-*d* (*d'*-2a)

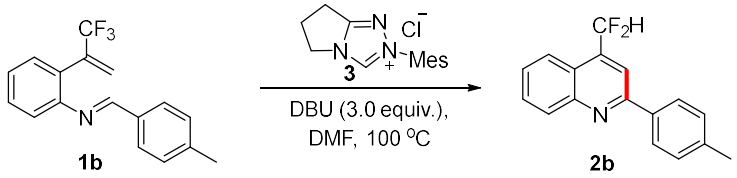


^{13}C-NMR Spectrum of 4-(Difluoromethyl-*d*)-2-phenylquinoline-3-*d* (*d'*-2a)



Kinetics studies

To get insight into the rate of the reaction, we have monitored the kinetics of the reaction. The reactions performed using **1b** with 10 mol % of **3** and 20 mol % **3** have been analyzed at various time intervals and the results are presented Figure S1. The results indicate that irrespective of the catalyst loading, the initial rate of the reaction is comparable (till ~3 h) and with the increase in the time, the experiment with more catalyst loading af-forded more amount of the corresponding quinoline product **2b**.



Sl. no	time	Yield of **2b** 20 mol% **3**	Yield of **2b**10 mol% **3**
1	2	27	23
2	6	53	35
3	12	62	46
4	18	67	54
5	24	72	61
6	30	76	67
7	36	79	69

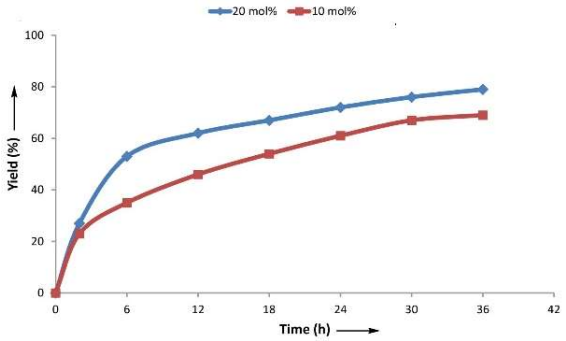
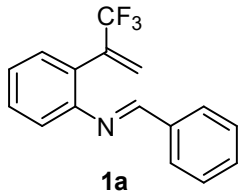


Figure S1

7. Synthesis and Characterization of Aldimines

(*E*)-N-Benzylidene-2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine (1a)

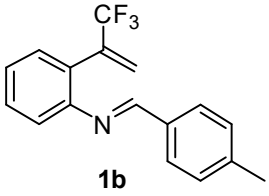


1a

Following the general known procedure, treatment of 2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine (0.50 g, 2.643 mmol), benzaldehyde (0.280 g, 2.643 mmol), $MgSO_4$ (0.795 g, 6.607 mmol) and Na_2SO_4 (0.938 g, 6.607 mmol) in DCM (30 mL) at rt for 36 h. After 36 h the crude reaction mixture was purified via flash column chromatography with deactivated silica gel (eluting with hexanes/Et_3N (20:1 v/v)) to afford the corresponding aldimine (*E*)-N-benzylidene-2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine **1a** (0.473 g, 65 % yield) as a yellow liquid.

R_f (Pet. ether /EtOAc = 95/05): 0.50; **^{1}H NMR ($CDCl_3$, 400 MHz)** δ 8.40 (s, 1H), 7.91-7.86 (m, 2H), 7.50-7.45 (m, 3H), 7.42-7.35 (m, 2H), 7.28-7.20 (m, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.12 (d, *J* = 1.3 Hz, 1H), 5.59 (d, *J* = 1.3 Hz, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz)** δ 159.21, 150.71, 137.70, 134.76, 130.26, 130.20, 130.13, 129.23, 128.49, 125.90, 124.04 (q, $J_{C\text{-}F}$ = 5.1 Hz), 118.52. **HRMS**: calculated $[M+H]^+$ for $C_{16}H_{13}NF_3$: 276.0995, found: 276.0995. **FTIR (cm^{-1}):** 3392, 3021, 2402, 1697, 1627, 1594, 1522, 1419, 1347, 1216, 1178, 1126, 1042, 929, 765, 669.

(*E*)-1-*p*-Tolyl-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine (1b)

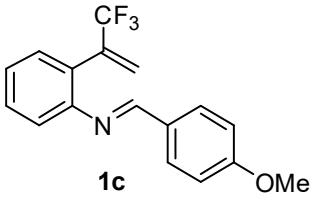


1b

Following the general known procedure, treatment of 2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine (0.30 g, 1.586 mmol), 4-methylbenzaldehyde (0.280 g, 1.586 mmol), $MgSO_4$ (0.477 g, 3.965 mmol) and Na_2SO_4 (0.563 g, 3.965 mmol) in DCM (15 mL) at rt for 36 h. After 36 h the crude reaction mixture was purified via flash column chromatography with deactivated silica gel (eluting with hexanes/Et_3N (20:1 v/v)) to afford the corresponding aldimine (*E*)-1-*p*-tolyl-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine **1b** (0.240 g, 52 % yield) as a yellow liquid.

R_f (Pet. ether /EtOAc = 95/05): 0.49; **^{1}H NMR ($CDCl_3$, 400 MHz)** δ 8.28 (s, 1H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.34-7.28 (m, 2H), 7.22-7.16 (m, 3H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.04 (s, 1H), 5.52 (s, 1H), 2.36 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz)** δ 160.65, 151.34, 142.18, 136.87 (q, $J_{C\text{-}F}$ = 31.0 Hz), 133.78, 130.05, 129.64, 129.06, 128.19, 125.41, 124.06 (q, $J_{C\text{-}F}$ = 5.1 Hz), 118.81, 21.77. **HRMS**: calculated $[M+H]^+$ for $C_{17}H_{15}NF_3$: 290.1151, found: 290.1156. **FTIR (cm^{-1}):** 3415, 3020, 1624, 1410, 1347, 1216, 1176, 1125, 1071, 946, 856, 817, 764.

(*E*)-N-(4-Methoxybenzylidene)-2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine (1c)

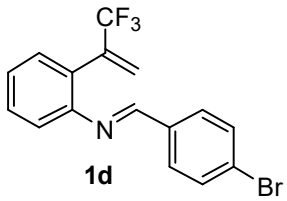


1c

Following the general known procedure, treatment of 2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine (0.254 g, 1.343 mmol), 4-methoxybenzaldehyde (0.183 g, 1.343 mmol), $MgSO_4$ (0.404 g, 3.357 mmol) and Na_2SO_4 (0.477 g, 3.357 mmol) in DCM (15 mL) at rt for 36 h. After 36 h the crude reaction mixture was purified via flash column chromatography with deactivated silica gel (eluting with hexanes/Et_3N (20:1 v/v)) to afford the corresponding aldimine (*E*)-N-(4-methoxybenzylidene)-2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine **1c** (0.207 g, 50 % yield) as a yellow liquid.

R_f (Pet. ether /EtOAc = 95/05): 0.39; **^{1}H NMR (DMSO-*d*^{6}, 400 MHz)** δ 8.47 (s, 1H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.33-7.25 (m, 2H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.07 (d, *J* = 8.5 Hz, 2H), 6.17 (s, 1H), 5.69 (s, 1H). **^{13}C NMR (DMSO-*d*^{6}, 100 MHz)** δ 162.06, 160.23, 150.68, 136.06 (q, *J* = 30.6 Hz), 130.49, 130.21, 129.66, 128.92, 127.84, 125.24, 124.91 (q, $J_{C\text{-}F}$ = 5.1 Hz), 118.68, 114.25, 55.34. **HRMS**: calculated $[M+H]^+$ for $C_{17}H_{15}ONF_3$: 306.1100, found: 306.1098. **FTIR (cm^{-1}):** 3415, 2992, 2254, 2128, 1657, 1508, 1454, 1312, 1256, 1223, 1170, 1122, 1016, 827, 768.

(*E*)-1-(4-Bromophenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine (1d)



1d

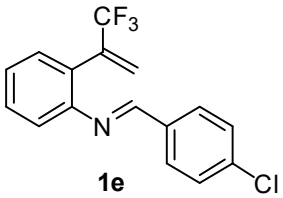
Following the general known procedure, treatment of 2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine (0.414 g, 2.189 mmol), 4-bromobenzaldehyde (0.405 g, 2.189 mmol), $MgSO_4$ (0.659 g, 5.472 mmol) and Na_2SO_4 (0.777 g, 5.472 mmol) in DCM (20 mL) at rt for 36 h. After 36 h the crude reaction mixture was purified via flash column chromatography with deactivated silica gel (eluting with hexanes/Et_3N (20:1 v/v)) to afford the corresponding aldimine (*E*)-1-(4-bromophenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine **1d** (0.327 g, 42 % yield) as a yellow liquid.

R_f (Pet. ether /EtOAc = 95/05): 0.48; **^{1}H NMR ($CDCl_3$, 400 MHz)** δ 8.33 (s, 1H), 8.02 (s, 1H), 7.78 (d, *J* = 7.7 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.43-7.40 (m, 1H), 7.37-7.33 (m, 2H), 7.27-7.25 (m, 1H), 7.03 (d, *J* = 7.9 Hz, 1H), 6.12 (bs, 1H), 5.58 (bs, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz)** δ 159.04, 150.59, 138.25, 136.87 (q, $J_{C\text{-}F}$ = 31.1 Hz), 134.48, 131.71, 130.44, 130.29, 130.13, 128.46, 127.70, 126.03, 124.14 (q, $J_{C\text{-}F}$ = 5.2 Hz), 123.17, 118.55. **HRMS**: calculated

$[M+H]^+$ for $C_{16}H_{12}NBrF_3$: 354.0100, found: 354.0109. **FTIR (cm^{-1}):** 3423, 3027, 2098, 1634, 1481, 1435, 1349, 1272, 1216, 1180, 1122, 1074, 766.

(*E*)-1-(4-Chlorophenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine (1e)

Following the general known procedure, treatment of 2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine (0.30 g, 1.586 mmol), 4-chlorobenzaldehyde (0.223 g, 1.586 mmol), $MgSO_4$ (0.477 g, 3.965 mmol) and Na_2SO_4 (0.563 g, 3.965 mmol) in DCM (15 mL) at rt for 36 h. After 36 h the crude reaction mixture was purified via flash column chromatography with deactivated silica gel (eluting with hexanes/Et_3N (20:1 v/v)) to afford the corresponding aldimine (*E*)-1-(4-chlorophenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine **1e** (0.235 g, 48 % yield) as a yellow liquid.

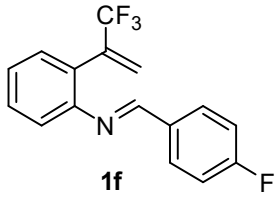


1e

R_f (Pet. ether /EtOAc = 95/05): 0.48; **^{1}H NMR ($CDCl_3$, 400 MHz)** δ 8.36 (s, 1H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.46-7.40 (m, 3H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.28-7.24 (m, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.12 (s, 1H), 5.57 (s, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz)** δ 159.21, 150.71, 137.70, 136.99 (q, $J_{C\text{-}F}$ = 31.0 Hz), 134.76, 130.26, 130.20, 130.13, 129.23, 128.49, 125.90, 124.04 (q, $J_{C\text{-}F}$ = 5.1 Hz), 118.52. **HRMS**: calculated $[M+H]^+$ for $C_{16}H_{12}NClF_3$: 310.0605, found: 310.0612. **FTIR (cm^{-1}):** 3425, 2111, 1640, 1412, 1216, 1176, 1126, 764.

(*E*)-N-(4-Fluorobenzylidene)-2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine (1f)

Following the general known procedure, treatment of 2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine (0.30 g, 1.586 mmol), 4-fluorobenzaldehyde (0.197 g, 1.586 mmol), $MgSO_4$ (0.477 g, 3.965 mmol) and Na_2SO_4 (0.563 g, 3.965 mmol) in DCM (15 mL) at rt for 36 h. After 36 h the crude reaction mixture was purified via flash column chromatography with deactivated silica gel (eluting with hexanes/Et_3N (20:1 v/v)) to afford the corresponding aldimine (*E*)-N-(4-fluorobenzylidene)-2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine **1f** (0.216 g, 46 % yield) as a yellow liquid.

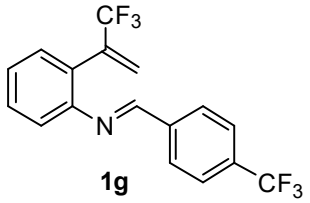


1f

R_f (Pet. ether /EtOAc = 95/05): 0.43; **^{1}H NMR (DMSO-*d*^{6}, 400 MHz)** δ 8.57 (s, 1H), 7.98-7.95 (m, 2H), 7.50-7.47 (m, 1H), 7.38-7.28 (m, 4H), 7.24 (d, *J* = 7.8 Hz, 1H), 6.19 (s, 1H), 5.70 (s, 1H). **^{13}C NMR (DMSO-*d*^{6}, 100 MHz)** δ 164.12 (d, $J_{C\text{-}F}$ = 249.5 Hz), 159.89, 150.18, 135.85 (q, $J_{C\text{-}F}$ = 30.9 Hz), 132.65, 131.07, 130.98, 130.28, 129.75, 127.97, 125.75, 125.16 (q, $J_{C\text{-}F}$ = 5.0

Hz), 118.70, 116.05, 115.83. **HRMS**: calculated $[M+H]^+$ for $C_{16}H_{12}NF_4$: 294.0900, found: 294.0900. **FTIR (cm^{-1}):** 3414, 2995, 2467, 2254, 2128, 1639, 1503, 1448, 1404, 1345, 1306, 1223, 1177, 1124, 1015, 827, 768.

(*E*)-1-(4-(Trifluoromethyl)phenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine (1g)

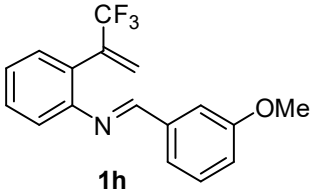


1g

Following the general known procedure, treatment of 2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine (0.30 g, 1.586 mmol), 4-(trifluoromethyl)benzaldehyde (0.276 g, 1.586 mmol), $MgSO_4$ (0.477 g, 3.965 mmol) and Na_2SO_4 (0.563 g, 3.965 mmol) in DCM (15 mL) at rt for 36 h. After 36 h the crude reaction mixture was purified via flash column chromatography with deactivated silica gel (eluting with hexanes/Et_3N (20:1 v/v)) to afford the corresponding aldimine (*E*)-1-(4-(trifluoromethyl)phenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine **1g** (0.261 g, 48 % yield) as a yellow liquid.

R_f (Pet. ether /EtOAc = 95/05): 0.38; **^{1}H NMR (DMSO-*d*^{6}, 400 MHz)** δ 8.69 (s, 1H), 8.10 (d, *J* = 7.8 Hz, 2H), 7.88 (d, *J* = 7.8 Hz, 2H), 7.53-7.49 (m, 1H), 7.35-7.28 (m, 3H), 6.20 (s, 1H), 5.70 (s, 1H). **^{13}C NMR (DMSO-*d*^{6}, 100 MHz)** δ 160.08, 149.78, 139.46, 135.71 (q, $J_{C\text{-}F}$ = 31.1 Hz), 131.21 (q, $J_{C\text{-}F}$ = 32.0 Hz), 130.35, 129.84, 129.27, 128.17, 126.31, 125.79, 125.76, 125.39, 125.34, 118.71. **HRMS**: calculated $[M+H]^+$ for $C_{17}H_{12}NF_6$: 344.0868, found: 344.0868. **FTIR (cm^{-1}):** 3413, 3021, 2887, 2403, 1916, 1809, 1634, 1582, 1485, 1410, 1324, 1214, 1174, 1128, 1068, 1024, 949, 880, 844, 767, 671.

(*E*)-1-(3-Methoxyphenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine (1h)

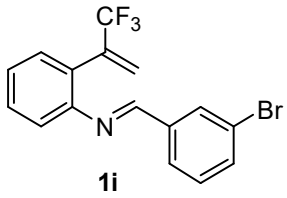


1h

Following the general known procedure, treatment of 2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine (0.40 g, 2.115 mmol), 3-methoxybenzaldehyde (0.288 g, 2.115 mmol), $MgSO_4$ (0.636 g, 5.287 mmol) and Na_2SO_4 (0.751 g, 5.287 mmol) in DCM (20 mL) at rt for 36 h. After 36 h the crude reaction mixture was purified via flash column chromatography with deactivated silica gel (eluting with hexanes/Et_3N (20:1 v/v)) to afford the corresponding aldimine (*E*)-1-(3-methoxyphenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine **1h** (0.271 g, 42 % yield) as a yellow liquid.

R_f (Pet. ether /EtOAc = 95/05): 0.39; **^{1}H NMR (DMSO-*d*^{6}, 400 MHz)** δ 8.54 (s, 1H), 7.48 (s, 3H), 7.43 (t, *J* = 7.9 Hz, 1H), 7.35-7.28 (m, 2H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.19 (s, 1H), 5.70 (s, 1H). **^{13}C NMR (DMSO-*d*^{6}, 100 MHz)** δ 160.94, 159.54, 150.17, 137.43, 136.02 (q, $J_{C\text{-}F}$ = 31.0 Hz), 130.30, 129.94, 129.79, 128.04, 125.81, 125.17, 121.47, 118.64, 117.52, 113.15, 55.12. **HRMS**: calculated $[M+H]^+$ for $C_{17}H_{15}ONF_3$: 306.1100, found: 306.1100. **FTIR (cm^{-1}):** 3416, 2989, 2253, 2127, 1657, 1489, 1454, 1395, 1341, 1259, 1224, 1175, 1123, 1016, 825, 769.

(*E*)-1-(3-Bromophenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine (1i)

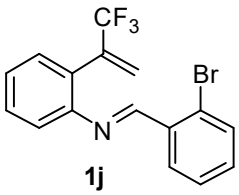


1i

Following the general known procedure, treatment of 2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine (0.30 g, 1.586 mmol), 3-bromobenzaldehyde (0.293 g, 1.586 mmol), $MgSO_4$ (0.477 g, 3.965 mmol) and Na_2SO_4 (0.563 g, 3.965 mmol) in DCM (30 mL) at rt for 36 h. After 36 h the crude reaction mixture was purified via flash column chromatography with deactivated silica gel (eluting with hexanes/Et_3N (20:1 v/v)) to afford the corresponding aldimine (*E*)-1-(3-bromophenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine **1i** (0.309 g, 55 % yield) as a yellow liquid.

R_f (Pet. ether /EtOAc = 95/05): 0.44; **^{1}H NMR (DMSO-*d*^{6}, 400 MHz)** δ 8.57 (s, 1H), 8.07 (s, 1H), 7.90 (d, *J* = 7.7 Hz, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.52-7.47 (m, 2H), 7.35-7.30 (m, 2H), 7.25 (d, *J* = 7.8 Hz, 1H), 6.20 (s, 1H), 5.71 (s, 1H). **^{13}C NMR (DMSO-*d*^{6}, 100 MHz)** δ 159.81, 149.77, 138.22, 135.78 (q, $J_{C\text{-}F}$ = 31.0 Hz), 134.13, 131.06, 130.96, 130.32, 129.83, 128.11, 127.63, 126.14, 125.37 (q, $J_{C\text{-}F}$ = 5.1 Hz), 122.13, 118.67. **HRMS**: calculated $[M+H]^+$ for $C_{16}H_{12}NBrF_3$: 354.0100, found: 354.0102. **FTIR (cm^{-1}):** 3423, 3024, 2094, 1637, 1482, 1432, 1349, 1271, 1216, 1178, 1126, 1071, 765.

(*E*)-1-(2-Bromophenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine (1j)

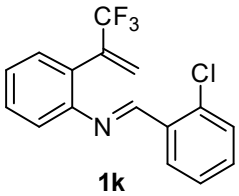


1j

Following the general known procedure, treatment of 2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine (0.30 g, 1.586 mmol), 2-bromobenzaldehyde (0.293 g, 1.586 mmol), $MgSO_4$ (0.477 g, 3.965 mmol) and Na_2SO_4 (0.563 g, 3.965 mmol) in DCM (15 mL) at rt for 36 h. After 36 h the crude reaction mixture

was purified via flash column chromatography with deactivated silica gel (eluting with hexanes/Et_3N (20:1 v/v)) to afford the corresponding aldimine (*E*)-1-(2-bromophenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine **1j** (0.217 g, 39 % yield) as a yellow liquid. ***R_f*** (Pet. ether /EtOAc = 95/05): 0.47; **^{1}H NMR (DMSO-*d*^{6}, 400 MHz)** δ 8.57 (s, 1H), 8.06 (s, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.52-7.47 (m, 2H), 7.35-7.32 (m, 2H), 7.25 (d, *J* = 7.8 Hz, 1H), 6.20 (s, 1H), 5.71 (s, 1H). **^{13}C NMR (DMSO-*d*^{6}, 100 MHz)** δ 159.81, 149.77, 138.22, 135.78 (q, $J_{C\text{-}F}$ = 30.9 Hz), 134.13, 131.06, 130.96, 130.32, 129.83, 128.11, 127.63, 126.14, 125.35, 122.13, 118.67. **HRMS**: calculated $[M+H]^+$ for $C_{16}H_{12}NBrF_3$: 354.0100, found: 354.0103. **FTIR (cm^{-1}):** 3421, 3065, 3021, 2873, 2752, 2403, 1933, 1696, 1626, 1581, 1479, 1435, 1402, 1349, 1270, 1212, 1178, 1127, 1072, 1033, 952, 873, 768.

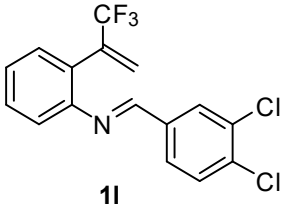
(*E*)-1-(2-Chlorophenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine (1k)



1k

Following the general known procedure, treatment of 2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine (0.30 g, 1.586 mmol), 2-chlorobenzaldehyde (0.223 g, 1.586 mmol), $MgSO_4$ (0.477 g, 3.965 mmol) and Na_2SO_4 (0.563 g, 6.607 mmol) in DCM (15 mL) at rt for 36 h. After 36 h the crude reaction mixture was purified via flash column chromatography with deactivated silica gel (eluting with hexanes/Et_3N (20:1 v/v)) to afford the corresponding aldimine (*E*)-1-(2-chlorophenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine **1k** (0.491 g, 52 % yield) as a yellow liquid. ***R_f*** (Pet. ether /EtOAc = 95/05): 0.48; **^{1}H NMR (DMSO-*d*^{6}, 400 MHz)** δ 8.81 (s, 1H), 8.08 (d, *J* = 7.7 Hz, 1H), 7.59-7.47 (m, 4H), 7.37-7.32 (m, 2H), 7.25 (d, *J* = 7.7 Hz, 1H), 6.21 (s, 1H), 5.72 (s, 1H). **^{13}C NMR (DMSO-*d*^{6}, 100 MHz)** δ 157.03, 150.11, 135.45 (q, $J_{C\text{-}F}$ = 31.0 Hz), 135.05, 133.07, 132.50, 130.42, 130.06, 129.80, 128.37, 127.85, 127.67, 126.21, 125.50 (q, $J_{C\text{-}F}$ = 5.2 Hz), 118.78. **HRMS**: calculated $[M+H]^+$ for $C_{16}H_{12}NClF_3$: 310.0605, found: 310.0612. **FTIR (cm^{-1}):** 3414, 2255, 2129, 1656, 1221, 996, 827, 770.

(*E*)-1-(3,4-Dichlorophenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine (1l)



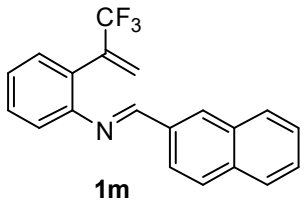
1l

Following the general known procedure, treatment of 2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine (0.30 g, 1.586 mmol), 3,4-dichlorobenzaldehyde (0.277 g, 1.586 mmol), $MgSO_4$ (0.477 g, 3.965 mmol) and Na_2SO_4 (0.563 g, 3.965 mmol) in DCM (15 mL) at rt for 36 h. After 36 h the crude reaction mixture was purified via flash column

chromatography with deactivated silica gel (eluting with hexanes/Et_3N (20:1 v/v)) to afford the corresponding aldimine (*E*)-1-(3,4-dichlorophenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl) methanimine **1l** (0.275 g, 50 % yield) as a yellow liquid.

R_f (Pet. ether /EtOAc = 95/05): 0.42; **^{1}H NMR (DMSO-*d*^{6}, 400 MHz)** δ 8.60 (s, 1H), 8.09 (s, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.52-7.49 (m, 1H), 7.35 (bs, 2H), 7.27 (d, *J* = 7.8 Hz, 1H), 6.21 (s, 1H), 5.71 (s, 1H). **^{13}C NMR (DMSO-*d*^{6}, 100 MHz)** δ 158.95, 149.52, 136.48, 135.74 (q, $J_{C\text{-}F}$ = 31.1 Hz), 134.05, 131.78, 131.26, 130.34, 130.20, 129.88, 128.24, 126.33, 125.43 (q, $J_{C\text{-}F}$ = 5.0 Hz), 118.62. **HRMS**: calculated $[M+H]^+$ for $C_{16}H_{11}NCl_2F_3$: 344.0215, found: 344.0218. **FTIR (cm^{-1}):** 3413, 2255, 2130, 1653, 1227, 1014, 826, 769.

(*E*)-1-(Naphthalen-2-yl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine (1m)

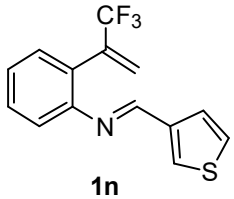


1m

Following the general known procedure, treatment of 2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine (0.150 g, 0.793 mmol), 2-naphthaldehyde (0.124 g, 0.793 mmol), $MgSO_4$ (0.238 g, 1.982 mmol) and Na_2SO_4 (0.282 g, 1.982 mmol) in DCM (10 mL) at rt for 36 h. After 36 h the crude reaction mixture was purified via flash column chromatography with deactivated silica gel (eluting with hexanes/Et_3N (20:1 v/v)) to afford the corresponding aldimine (*E*)-1-(naphthalen-2-yl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine **1m** (0.180 g, 70 % yield) as a yellow liquid.

R_f (Pet. ether /EtOAc = 95/05): 0.46; **^{1}H NMR (DMSO-*d*^{6}, 400 MHz)** δ 8.72 (s, 1H), 8.37 (s, 1H), 8.09-7.97 (m, 4H), 7.65-7.59 (m, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.37-7.28 (m, 3H), 6.22 (s, 1H), 5.75 (s, 1H). **^{13}C NMR (DMSO-*d*^{6}, 100 MHz)** δ 161.62, 150.88, 135.01, 134.18, 133.08, 132.17, 130.83, 130.27, 129.22, 129.02, 128.43, 128.33, 127.38, 126.26, 125.77 (q, $J_{C\text{-}F}$ = 5.2 Hz), 123.75, 119.22. **HRMS**: calculated $[M+H]^+$ for $C_{20}H_{15}NF_3$: 326.1151, found: 326.1157. **FTIR (cm^{-1}):** 3413, 3020, 2923, 2308, 1619, 1448, 1347, 1217, 1177, 1126, 765.

(*E*)-1-(Thiophen-3-yl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine (1n)



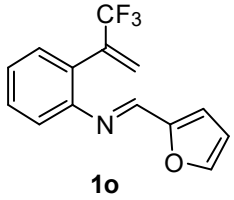
1n

Following the general known procedure, treatment of 2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine (0.409 g, 2.162 mmol), thiophene-3-carbaldehyde (0.242 g, 189 µL, 2.162 mmol), $MgSO_4$ (0.651 g, 5.405 mmol) and Na_2SO_4 (0.768 g, 5.405 mmol) in DCM (20 mL) at rt for 36 h. After 36 h the crude reaction mixture was purified via flash column chromatography with deactivated silica gel

(eluting with hexanes/Et_3N (20:1 v/v)) to afford the corresponding aldimine (*E*)-1-(thiophen-3-yl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine **1n** (0.382 g, 63 % yield) as a yellow liquid.

R_f (Pet. ether /EtOAc = 95/05): 0.39; **^{1}H NMR (DMSO-*d*^{6}, 400 MHz)** δ 8.53 (s, 1H), 8.16 (s, 1H), 7.64 (bs, 1H), 7.54 (d, *J* = 5.0 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.33-7.26 (m, 2H), 7.18 (d, *J* = 7.8 Hz, 1H), 6.17 (s, 1H), 5.70 (s, 1H). **^{13}C NMR (DMSO-*d*^{6}, 100 MHz)** δ 155.58, 150.55, 140.59, 135.94 (q, $J_{C\text{-}F}$ = 30.8 Hz), 132.23, 130.31, 129.73, 127.82, 127.74, 125.54, 125.37, 125.14 (q, $J_{C\text{-}F}$ = 5.0 Hz), 118.66. **HRMS**: calculated $[M+H]^+$ for $C_{14}H_{11}NF_3S$: 282.0559, found: 282.0561. **FTIR (cm^{-1}):** 3417, 3020, 2402, 2094, 1629, 1487, 1411, 1345, 1216, 1175, 1125, 1073, 954, 872, 766.

(*E*)-1-(Furan-2-yl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine (1o)

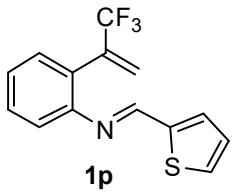


1o

Following the general known procedure, treatment of 2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine (0.30 g, 1.586 mmol), furan-2-carbaldehyde (0.152 g, 131 µL, 1.586 mmol), $MgSO_4$ (0.477 g, 3.965 mmol) and Na_2SO_4 (0.563 g, 3.965 mmol) in DCM (15 mL) at rt for 36 h. After 36 h the crude reaction mixture was purified via flash column chromatography with deactivated silica gel (eluting with hexanes/Et_3N (20:1 v/v)) to afford the corresponding aldimine (*E*)-1-(furan-2-yl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine **1o** (0.328 g, 78 % yield) as a red liquid.

R_f (Pet. ether /EtOAc = 95/05): 0.39; **^{1}H NMR (DMSO-*d*^{6}, 400 MHz)** δ 8.34 (s, 1H), 7.96 (s, 1H), 7.48-7.45 (m, 1H), 7.32-7.26 (m, 2H), 7.19-7.14 (m, 2H), 6.71 (s, 1H), 6.18 (s, 1H), 5.69 (s, 1H). **^{13}C NMR (DMSO-*d*^{6}, 100 MHz)** δ 151.80, 150.54, 149.24, 146.68, 135.40 (q, $J_{C\text{-}F}$ = 30.6 Hz), 130.32, 129.67, 127.77, 125.63, 125.33 (q, $J_{C\text{-}F}$ = 5.1 Hz), 118.78, 117.47, 112.52. **HRMS**: calculated $[M+H]^+$ for $C_{14}H_{11}ONF_3$: 266.0787, found: 266.0786. **FTIR (cm^{-1}):** 3414, 2256, 2130, 1666, 1394, 1229, 1044, 826, 772.

(*E*)-1-(Thiophen-2-yl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine (1p)



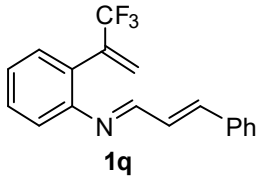
1p

Following the general known procedure, treatment of 2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine (0.30 g, 1.586 mmol), thiophene-2-carbaldehyde (0.178 g, 150 µL, 1.586 mmol), $MgSO_4$ (0.477 g, 3.965 mmol) and Na_2SO_4 (0.563 g, 3.965 mmol) in DCM (30 mL) at rt for 36 h. After 36 h the crude reaction mixture was purified via flash column chromatography with deactivated silica gel

(eluting with hexanes/Et_3N (20:1 v/v)) to afford the corresponding aldimine (*E*)-1-(thiophen-2-yl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine **1p** (0.261 g, 58% yield) as a yellow liquid.

R_f (Pet. ether /EtOAc = 95/05): 0.42; **^{1}H NMR (DMSO-*d*^{6}, 400 MHz)** δ 8.69 (s, 1H), 7.80-7.79 (m, 1H), 7.68 (bs, 1H), 7.47 (bs, 1H), 7.31-7.21 (m, 4H), 6.17 (s, 1H), 5.68 (s, 1H). **^{13}C NMR (DMSO-*d*^{6}, 100 MHz)** δ 154.38, 149.82, 142.44, 135.87 (q, $J_{C\text{-}F}$ = 30.7 Hz), 133.61, 131.60, 130.26, 129.75, 128.17, 127.99, 125.70, 125.04, 118.74. **HRMS**: calculated $[M+H]^+$ for $C_{14}H_{11}NF_3S$: 282.0559, found: 282.0559. **FTIR (cm^{-1}):** 3416, 2124, 1649, 1536, 1442, 1336, 1292, 1220, 1171, 1127, 994, 765.

(1*E*,2*E*)-3-Phenyl-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)prop-2-en-1-imine (1q)

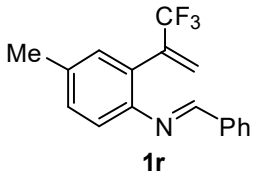


1q

Following the general known procedure, treatment of 2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine (0.30 g, 1.586 mmol), cinnamaldehyde (0.210 g, 1.586 mmol), $MgSO_4$ (0.477 g, 3.965 mmol) and Na_2SO_4 (0.563 g, 3.965 mmol) in DCM (15 mL) at rt for 36 h. After 36 h the crude reaction mixture was purified via flash column chromatography with deactivated silica gel (eluting with hexanes/Et_3N (20:1 v/v)) to afford the corresponding aldimine (1*E*,2*E*)-3-phenyl-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)prop-2-en-1-imine **1q** (0.189 g, 39 % yield) as a yellow liquid.

R_f (Pet. ether /EtOAc = 95/05): 0.41; **^{1}H NMR (DMSO-*d*^{6}, 400 MHz)** δ 8.29 (d, *J* = 8.9 Hz, 1H), 7.68 (d, *J* = 7.1 Hz, 2H), 7.47-7.35 (m, 5H), 7.31-7.25 (m, 2H), 7.17-7.10 (m, 2H), 6.18 (s, 1H), 5.66 (s, 1H). **^{13}C NMR (DMSO-*d*^{6}, 100 MHz)** δ 163.18, 151.00, 144.85, 135.37 (q, $J_{C\text{-}F}$ = 30.7 Hz), 135.29, 130.24, 129.70, 129.61, 128.93, 128.21, 127.71, 127.49, 125.42, 125.15 (q, $J_{C\text{-}F}$ = 5.0 Hz), 118.77. **HRMS**: calculated $[M+H]^+$ for $C_{18}H_{15}NF_3$: 302.1151, found: 302.1152. **FTIR (cm^{-1}):** 3412, 2256, 2131, 1658, 1221, 997, 827, 768, 674.

(*E*)-*N*-(Phenylmethylene)- 4-methyl-2-(3,3,3-trifluoroprop-1-en-2-yl)benzenamine (1r)



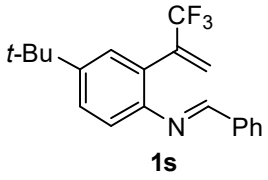
1r

Following the general procedure, treatment of 4-methyl-2-(3,3,3-trifluoroprop-1-en-2-yl)aniline (322 mg, 1.60 mmol, 1 equiv.) with benzaldehyde (678 mg, 650 µL, 6.40 mmol, 4 equiv.) at 50 °C under 40 mbar for 2 h followed by high vacuum then a column chromatography

with deactivated silica gel using petroleum ether/Et_3N as eluent (from 100/0 to 98/2) afforded **1r** (413 mg, 1.43 mmol, 89%) as a yellowish oil.

R_f (Pet. ether/Et_3N = 98/2): 0.56. **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 8.39 (s, 1H), 7.90-7.83 (m, 2H), 7.51-7.42 (m, 3H), 7.25-7.14 (m, 2H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.10 (d, *J* = 1.1 Hz, 1H), 5.57 (d, *J* = 1.1 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 159.8, 148.4, 137.1 (q, *J* = 31.1 Hz), 136.5, 135.5, 131.3, 130.6, 130.6, 128.9, 128.7, 128.6, 123.8 (q, *J* = 5.3 Hz), 123.5 (q, *J* = 274.1 Hz), 118.3, 20.8. **^{19}F NMR (282 MHz, $CDCl_3$)** δ -65.5 (s). **HRMS:** calculated $[M+H]^+$ for $C_{17}H_{15}F_3N$: 290.1157, found: 290.1158. **FTIR (cm^{-1}):** 3027, 1629, 1503, 1341, 1157, 1117, 1067, 947, 877, 816, 750, 691, 558, 452.

(*E*)-*N*-(Phenylmethylene)-4-*tert*-butyl-2-(3,3,3-trifluoroprop-1-en-2-yl)benzenamine (1s)

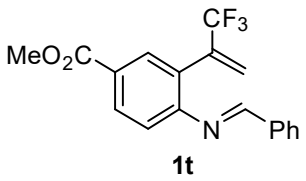


1s

Following the general procedure, treatment of 4-(*tert*-butyl)-2-(3,3,3-trifluoroprop-1-en-2-yl)aniline (185 mg, 0.76 mmol, 1 equiv.) with benzaldehyde (322 mg, 309 µL, 3.04 mmol, 4 equiv.) at 50 °C under 40 mbar for 1 h followed by high vacuum then a column chromatography with deactivated silica gel using petroleum ether/Et_3N as eluent (from 100/0 to 97/3) afforded **1s** (177 mg, 0.54 mmol, 70%) as a white solid.

R_f (Pet. ether/Et_3N = 98/2): 0.60. **m.p.** 41-42 °C. **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 8.41 (s, 1H), 7.91-7.83 (m, 2H), 7.51-7.40 (m, 4H), 7.38-7.34 (m, 1H), 7.02 (d, *J* = 8.3 Hz, 1H), 6.11 (d, *J* = 1.1 Hz, 1H), 5.58 (d, *J* = 1.1 Hz, 1H), 1.35 (s, 9H). **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 160.1, 148.8, 148.4, 137.3 (q, *J* = 31.1 Hz), 136.5, 131.4, 129.0, 128.9, 128.1, 127.1, 127.0, 123.9 (q, *J* = 5.3 Hz), 123.4 (q, *J* = 274.1 Hz), 118.1, 34.6, 31.5. **^{19}F NMR (282 MHz, $CDCl_3$)** δ -65.5 (s). **HRMS:** calculated $[M+H]^+$ for $C_{20}H_{21}F_3N$: 332.1626, found: 332.1620. **FTIR (cm^{-1}):** 2957, 2866, 1627, 1494, 1395, 1338, 1184, 1149, 1134, 1118, 1072, 957, 834, 751, 690, 583, 516, 448.

(*E*)-Metyl 4-(benzylideneamino)-3-(3,3,3-trifluoroprop-1-en-2-yl)benzoate (1t)



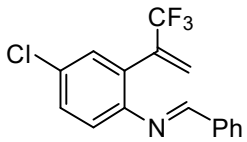
1t

To a solution of amine methyl 4-amino-3-(3,3,3-trifluoroprop-1-en-2-yl)benzoate (130 mg, 0.53 mmol, 1 equiv.) and benzaldehyde (225 mg, 2.12 mmol, 4 equiv.) in Toluene (10 mL) under argon was added Na_2SO_4 (750 mg, 5.3 mmol, 10 equiv.). The reaction mixture was heated at reflux for 48 h. The reaction mixture was filtered, rinsed with DCM and the filtrate was

concentrated in vacuo. The crude imine, was purified via flash column chromatography with deactivated silica gel using petroleum ether/Et_3N as eluent (from 100/0 to 96/4) afforded **1t** (95 mg, 0.29 mmol, 72%) as a yellowish oil.

R_f (Pet. ether/Et_2O = 95/55): 0.35. **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 8.38 (s, 1H), 8.09 (dd, *J* = 8.3 and 1.8 Hz, 1H), 7.92-7.85 (m, 2H), 7.56-7.40 (m, 3H), 7.07 (d, *J* = 8.3 Hz, 1H), 6.15 (s, 1H), 5.62 (s, 1H), 3.93 (s, 3H). **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 166.5, 161.8, 155.2, 136.3 (q, *J* = 31.8 Hz), 135.8, 132.1, 131.7, 130.7, 129.3, 129.0, 128.4, 127.2, 124.7 (q, *J* = 5.2 Hz), 123.0 (q, *J* = 274.0 Hz), 118.9, 52.3. **^{19}F NMR (282 MHz, $CDCl_3$)** δ -65.7 (s). **HRMS:** calculated $[M+H]^+$ for $C_{18}H_{15}F_3NO_2$: 334.1055, found: 334.1054. **FTIR (cm^{-1}):** 2950, 1714, 1596, 1435, 1283, 1250, 1166, 1121, 1069, 969, 881, 776, 758, 691, 637, 618, 513, 470, 434.

(*E*)-*N*-(Phenylmethylene)-4-chloro-2-(3,3,3-trifluoroprop-1-en-2-yl)benzenamine (1u)

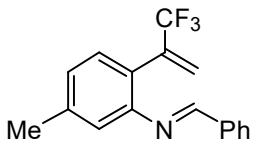


1u

Following the general procedure, treatment of 4-chloro-2-(3,3,3-trifluoroprop-1-en-2-yl)aniline (187 mg, 0.85 mmol, 1 equiv.) with benzaldehyde (360 mg, 345 µL, 3.40 mmol, 4 equiv.) at 50 °C under 40 mbar for 6 h followed by high vacuum then a column chromatography with deactivated silica gel using petroleum ether/Et_3N as eluent (from 100/0 to 97/3) afforded **1u** (212 mg, 0.69 mmol, 81%) as a yellowish oil.

R_f (Pet. ether/Et_3N = 96/4): 0.63. **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 8.37 (s, 1H), 7.90-7.83 (m, 2H), 7.54-7.43 (m, 3H), 7.41-7.33 (m, 2H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.14 (d, *J* = 1.2 Hz, 1H), 5.61 (d, *J* = 1.2 Hz, 1H). **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 161.0, 149.6, 136.0, 135.0 (q, *J* = 31.1 Hz), 131.9, 131.0, 130.0, 130.0, 129.9, 129.1, 128.9, 124.8 (q, *J* = 5.3 Hz), 123.0 (q, *J* = 274.1 Hz), 119.8. **^{19}F NMR (282 MHz, $CDCl_3$)** δ -65.6 (s). **HRMS:** calculated $[M+H]^+$ for $C_{16}H_{12}{}^{35}ClF_3N$: 310.0610, found: 310.0604. **FTIR (cm^{-1}):** 3065, 2880, 1628, 1579, 1476, 1335, 1167, 1121, 1065, 951, 877, 817, 749, 690, 637, 538, 424.

(*E*)-*N*-(Phenylmethylene)-5-methyl-2-(3,3,3-trifluoroprop-1-en-2-yl)benzenamine (1v)



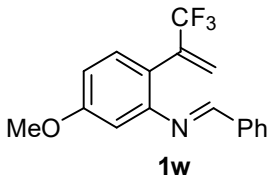
1v

Following the general procedure, treatment of 5-methyl-2-(3,3,3-trifluoroprop-1-en-2-yl)aniline (126 mg, 0.63 mmol, 1 equiv.) with benzaldehyde (266 mg, 255 µL, 2.51 mmol, 4 equiv.) at 50 °C under 40 mbar for 2 h followed by high vacuum then a column chromatography

with deactivated silica gel using petroleum ether/Et_3N as eluent (from 100/0 to 95/5) afforded **1v** (166 mg, 0.57 mmol, 92%) as a yellowish oil.

R_f (Pet. ether/Et_3N = 95/5): 0.60. **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 8.38 (s, 1H), 7.91-7.84 (m, 2H), 7.51-7.42 (m, 3H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.86 (s, 1H), 6.09 (d, *J* = 1.1 Hz, 1H), 5.56 (d, *J* = 1.1 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 160.4, 151.0, 140.1, 136.7 (q, *J* = 31.1 Hz), 136.4, 131.5, 129.8, 129.0, 128.8, 126.3, 125.4, 123.9 (q, *J* = 5.3 Hz), 123.4 (q, *J* = 274.1 Hz), 119.3, 21.3. **^{19}F NMR (282 MHz, $CDCl_3$)** δ -65.6 (s). **HRMS:** calculated $[M+H]^+$ for $C_{17}H_{15}F_3N$: 290.1157, found: 290.1148. **FTIR (cm^{-1}):** 3031, 2866, 1631, 1504, 1452, 1343, 1167, 1117, 1066, 944, 818, 757, 690, 614, 493.

(*E*)-*N*-(Phenylmethylene)-5-methoxy-2-(3,3,3-trifluoroprop-1-en-2-yl)benzenamine (1w)

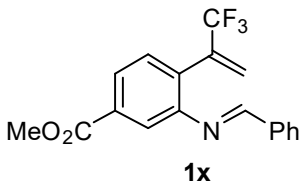


1w

Following the general procedure, treatment of 5-methoxy-2-(3,3,3-trifluoroprop-1-en-2-yl)aniline (157 mg, 0.72 mmol, 1 equiv.) with benzaldehyde (305 mg, 292 µL, 2.88 mmol, 4 equiv.) at 50 °C under 40 mbar for 1 h followed by high vacuum then a column chromatography with deactivated silica gel using petroleum ether/Et_3N as eluent (from 100/0 to 95/5) afforded **1w** (198 mg, 0.65 mmol, 90%) as a yellowish oil.

R_f (Pet. ether/Et_3N = 95/5): 0.36. **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 8.38 (s, 1H), 7.91-7.84 (m, 2H), 7.52-7.43 (m, 3H), 7.29 (d, *J* = 8.5 Hz, 1H), 6.78 (dd, *J* = 8.5 and 2.6 Hz, 1H), 6.58 (d, *J* = 2.6 Hz, 1H), 6.07 (d, *J* = 1.1 Hz, 1H), 5.54 (d, *J* = 1.1 Hz, 1H), 3.86 (s, 3H). **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 160.8, 160.8, 152.4, 136.3 (q, *J* = 31.1 Hz), 136.1, 131.7, 130.9, 129.0, 128.8, 123.8 (q, *J* = 5.3 Hz), 123.4 (q, *J* = 274.1 Hz), 120.5, 110.7, 104.5, 55.3. **^{19}F NMR (282 MHz, $CDCl_3$)** δ -65.7 (s). **HRMS:** calculated $[M+H]^+$ for $C_{17}H_{15}F_3NO$: 306.1106, found: 306.1114. **FTIR (cm^{-1}):** 2840, 1632, 1599, 1503, 1345, 1291, 1246, 1160, 1114, 1073, 1035, 948, 835, 759, 690, 507.

(*E*)-Methyl 3-(benzylideneamino)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzoate (1x)



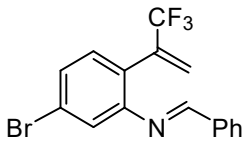
1x

Following the general procedure, treatment of methyl 3-amino-4-(3,3,3-trifluoroprop-1-en-2-yl)benzoate (165 mg, 0.67 mmol, 1 equiv.) with benzaldehyde (284 mg, 272 µL, 2.68 mmol, 4 equiv.) at 50 °C under 40 mbar for 9 h followed by high vacuum then a column

chromatography with deactivated silica gel using petroleum ether/Et_3N as eluent (from 100/0 to 95/5) afforded **1x** (207 mg, 0.62 mmol, 92%) as a yellowish oil.

R_f (Pet. ether/Et_3N = 97/3): 0.26. **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 8.45 (s, 1H), 7.93-7.86 (m, 3H), 7.74 (d, *J* = 1.5 Hz, 1H), 7.56-7.41 (m, 4H), 6.18 (d, *J* = 1.2 Hz, 1H), 5.65 (d, *J* = 1.2 Hz, 1H), 3.95 (s, 3H). **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 166.3, 161.5, 151.1, 136.1 (q, *J* = 31.6 Hz), 135.9, 132.7, 131.8, 131.7, 130.1, 129.1, 128.8, 126.4, 124.8 (q, *J* = 5.3 Hz), 123.0 (q, *J* = 274.1 Hz), 119.6, 52.3. **^{19}F NMR (282 MHz, $CDCl_3$)** δ -65.4 (s). **HRMS:** calculated $[M+H]^+$ for $C_{18}H_{15}F_3NO_2$: 334.1055, found: 334.1056. **FTIR (cm^{-1}):** 2959, 1722, 1631, 1563, 1437, 1345, 1290, 1228, 1166, 1120, 1101, 1063, 975, 907, 760, 690, 612, 482.

(*E*)-*N*-(Phenylmethylene)-5-bromo-2-(3,3,3-trifluoroprop-1-en-2-yl)benzenamine (1y)



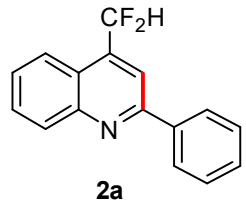
1y

Following the general procedure, treatment of 5-bromo-2-(3,3,3-trifluoroprop-1-en-2-yl)aniline (292 mg, 1.10 mmol, 1 equiv.) with benzaldehyde (465 mg, 446 µL, 4.39 mmol, 4 equiv.) at 50 °C under 40 mbar for 2 h followed by high vacuum then a column chromatography with deactivated silica gel using petroleum ether/Et_3N as eluent (from 100/0 to 95/5) afforded **1y** (344 mg, 0.97 mmol, 89%) as a yellowish oil.

R_f (Pet. ether/Et_3N = 95/5): 0.64. **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 8.37 (s, 1H), 7.91-7.83 (m, 2H), 7.56-7.43 (m, 3H), 7.37 (dd, *J* = 8.2 and 2.0 Hz, 1H), 7.25-7.19 (m, 2H), 6.13 (d, *J* = 1.2 Hz, 1H), 5.59 (d, *J* = 1.2 Hz, 1H). **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 161.5, 152.2, 135.9 (q, *J* = 31.5 Hz), 135.8, 132.0, 131.3, 129.2, 128.9, 128.4, 127.2, 124.6 (q, *J* = 5.3 Hz), 123.6, 123.3 (q, *J* = 274.0 Hz), 123.2. **^{19}F NMR (282 MHz, $CDCl_3$)** δ -65.7 (s). **HRMS:** calculated $[M+H]^+$ for $C_{16}H_{12}{}^{79}BrF_3N$: 354.0105, found: 354.0104. **FTIR (cm^{-1}):** 3065, 2878, 1629, 1578, 1481, 1343, 1166, 1120, 1085, 1063, 949, 896, 877, 818, 763, 742, 689, 610, 481.

8. Synthesis and Characterization of Difluoromethylated Quinoline Derivatives

4-(difluoromethyl)-2-phenylquinoline (2a)[2c]

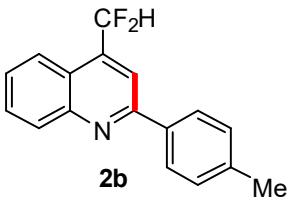


2a

Following the general procedure, treatment of (*E*)-*N*-benzylidene-2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine **1a** (137.6 mg, 0.50 mmol) with the triazolium salt **3** (27.0 mg, 0.10 mmol), DBU (228.4 mg, 224 µL, 1.50 mmol) in DMF (4.0 mL) at 100 °C for 36 h followed by work-up of the reaction mixture using EtOAc and subsequent flash column chromatography (Pet. ether /EtOAc = 95/05) of the crude reaction mixture using silica gel afforded 4-(difluoromethyl)-2-phenylquinoline **2a** as a yellowish liquid (0.096 g, 75%).

***R**f* (Pet. ether /EtOAc = 90/10): 0.40; **^{1}H NMR (CDCl$_3$, 400 MHz)** δ 8.27 (d, *J* = 8.4 Hz, 1H), 8.20 (d, *J* = 7.4 Hz, 2H), 8.09-8.06 (m, 2H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.57-7.48 (m, 3H), 7.20 (t, *J* = 54.6 Hz, 1H). **^{13}C NMR (CDCl$_3$, 100 MHz)** δ 157.08, 148.86, 138.77 (t, $J_{C\text{-}F}$ = 24.7 Hz), 130.74, 130.25, 129.99, 129.11, 127.66, 127.55, 123.20, 116.07 (t, $J_{C\text{-}F}$ = 8.0 Hz), 113.65 (t, $J_{C\text{-}F}$ = 240.5 Hz). **HRMS**: calculated $[M+H]^+$ for $C_{16}H_{12}NF_2$: 256.0932, found: 256.0934. **FTIR (cm^{-1}):** 3407, 3021, 2976, 2403, 1609, 1372, 1216, 1117, 1047, 928, 887, 767, 669.

4-(Difluoromethyl)-2-(*p*-tolyl)quinoline (2b)[2c]



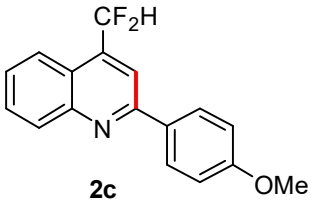
2b

Following the general procedure, treatment of (*E*)-1-*p*-tolyl-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine **1b** (144.6 mg, 0.50 mmol) with the triazolium salt **3** (27.0 mg, 0.10 mmol), DBU (228.4 mg, 224 µL, 1.50 mmol) in DMF (4.0 mL) at 100 °C for 36 h followed by work-up of the reaction mixture using EtOAc and subsequent flash column chromatography (Pet. ether /EtOAc = 95/05) of the crude reaction mixture using silica gel afforded 4-(difluoromethyl)-2-(*p*-tolyl)quinoline **2b** as a yellow solid (0.115 g, 79%).

***R**f* (Pet. ether /EtOAc = 90/10): 0.41; **^{1}H NMR (CDCl$_3$, 400 MHz)** δ 8.25 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 7.9 Hz, 2H), 8.07-8.04 (m, 2H), 7.78 (t, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.19 (t, *J* = 54.6 Hz, 1H), 2.45 (s, 3H). **^{13}C NMR (CDCl$_3$, 100 MHz)** δ 157.01, 148.88, 140.18, 138.46 (t, $J_{C\text{-}F}$ = 21.6 Hz), 136.11, 130.65, 130.14, 129.83, 127.50,

127.30, 123.18, 123.07 (t, $J_{C\text{-}F}$ = 3.1 Hz), 115.89 (t, $J_{C\text{-}F}$ = 7.9 Hz), 113.72 (t, $J_{C\text{-}F}$ = 240.7 Hz), 21.49. **HRMS:** calculated $[M+H]^+$ for $C_{17}H_{14}NF_2$: 270.1089, found: 270.1094. **FTIR (cm^{-1}):** 3420, 3023, 1640, 1412, 1218, 1113, 766.

4-(Difluoromethyl)-2-(4-methoxyphenyl)quinoline (2c)

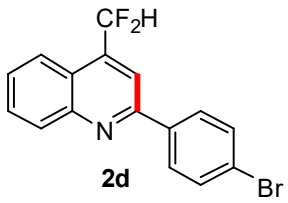


2c

Following the general procedure, treatment of (*E*)-N-(4-methoxybenzylidene)-2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine **1c** (123.0 mg, 0.50 mmol) with the triazolium salt **3** (27.0 mg, 0.10 mmol), DBU (228.4 mg, 224 µL, 1.50 mmol) in DMF (4.0 mL) at 100 °C for 36 h followed by work-up of the reaction mixture using EtOAc and subsequent flash column chromatography (Pet. ether /EtOAc = 95/05) of the crude reaction mixture using silica gel afforded 4-(difluoromethyl)-2-(4-methoxyphenyl)quinoline **2c** as a yellow solid (0.118 g, 83%).

***R**f* (Pet. ether /EtOAc = 90/10): 0.32; **^{1}H NMR ($CDCl_3$, 400 MHz)** δ 8.23 (d, *J* = 8.4 Hz, 1H), 8.17 (d, *J* = 8.7 Hz, 2H), 8.04-8.00 (m, 2H), 7.76 (t, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.31-7.04 (m, 3H), 3.88 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz)** δ 161.36, 156.54, 148.77, 138.47 (t, $J_{C\text{-}F}$ = 21.6 Hz), 131.35, 130.42, 130.17, 129.03, 127.12, 123.16, 122.85 (t, $J_{C\text{-}F}$ = 3.1 Hz), 115.58 (t, $J_{C\text{-}F}$ = 7.8 Hz), 114.46, 113.68 (t, $J_{C\text{-}F}$ = 240.5 Hz), 55.52. **HRMS**: calculated $[M+H]^+$ for $C_{17}H_{14}ONF_2$: 286.1038, found: 286.1036. **FTIR (cm^{-1}):** 3415, 3020, 1607, 1514, 1370, 1218, 1175, 1115, 1041, 839, 767.

2-(4-Bromophenyl)-4-(difluoromethyl)quinoline (2d)[2c]



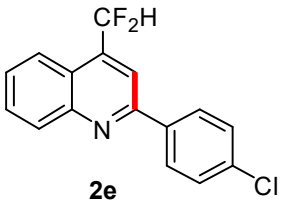
2d

Following the general procedure, treatment of (*E*)-1-(4 bromophenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine **1d** (177.1 mg, 0.50 mmol) with the triazolium salt **3** (27.0 mg, 0.10 mmol), DBU (228.4 mg, 224 µL, 1.50 mmol) in DMF (4.0 mL) at 100 °C for 36 h followed by work-up of the reaction mixture using EtOAc and subsequent flash column chromatography (Pet. ether /EtOAc = 95/05) of the crude reaction mixture using silica gel afforded 2-(4-bromophenyl)-4-(difluoromethyl)quinoline **2d** as a yellow solid (0.130 g, 76%).

***R**f* (Pet. ether /EtOAc = 90/10): 0.39; **^{1}H NMR ($CDCl_3$, 400 MHz)** δ 8.23 (d, *J* = 8.5 Hz, 1H), 8.08-8.05 (m, 3H), 8.01 (s, 1H), 7.80 (t, *J* = 7.5 Hz, 1H), 7.67-7.61 (m, 3H), 7.20 (t, *J* = 54.6 Hz,

1H). **^{13}C NMR (CDCl$_3$, 100 MHz)** δ 155.76, 148.83, 138.82 (t, $J_{C\text{-}F}$ = 21.8 Hz), 137.72, 132.25, 130.74, 130.42, 129.12, 127.78, 124.66, 123.26 (t, $J_{C\text{-}F}$ = 3.1 Hz), 123.20, 115.47 (t, $J_{C\text{-}F}$ = 7.9 Hz), 113.46 (t, $J_{C\text{-}F}$ = 240.9 Hz). **HRMS**: calculated $[M+H]^+$ for $C_{16}H_{11}NBrF_2$: 334.0037, found: 334.0041. **FTIR (cm^{-1}):** 3417, 3021, 2403, 1606, 1409, 1217, 1114, 1060, 927, 766.

2-(4-Chlorophenyl)-4-(difluoromethyl)quinoline (2e)

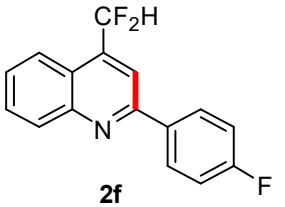


2e

Following the general procedure, treatment of (*E*)-1-(4-chlorophenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl) methanimine **1e** (154.8 mg, 0.50 mmol) with the triazolium salt **3** (27.0 mg, 0.10 mmol), DBU (228.4 mg, 224 µL, 1.50 mmol) in DMF (4.0 mL) at 100 °C for 36 h followed by work-up of the reaction mixture using EtOAc and subsequent flash column chromatography (Pet. ether /EtOAc = 95/05) of the crude reaction mixture using silica gel afforded 2-(4-chlorophenyl)-4-(difluoromethyl)quinoline **2e** as a yellow liquid (0.130 g, 84%).

***R**$_f$* (Pet. ether /EtOAc = 90/10): 0.39; **^{1}H NMR (CDCl$_3$, 400 MHz)** δ 8.23 (d, *J* = 8.6 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 2H), 8.06 (d, *J* = 8.5 Hz, 1H), 8.01 (s, 1H), 7.80 (t, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.20 (t, *J* = 54.6 Hz, 1H). **^{13}C NMR (CDCl$_3$, 100 MHz)** δ 155.71, 148.82, 139.03, 138.81 (t, $J_{C\text{-}F}$ = 21.8 Hz), 137.28, 136.25, 130.73, 130.40, 129.29, 128.87, 127.75, 123.19, 115.53 (t, $J_{C\text{-}F}$ = 7.9 Hz), 113.47 (t, $J_{C\text{-}F}$ = 240.7 Hz). **HRMS**: calculated $[M+H]^+$ for $C_{16}H_{11}NClF_2$: 290.0543, found: 290.0551. **FTIR (cm^{-1}):** 3415, 3022, 1627, 1372, 1218, 1050, 767.

4-(Difluoromethyl)-2-(4-fluorophenyl)quinoline (2f)



2f

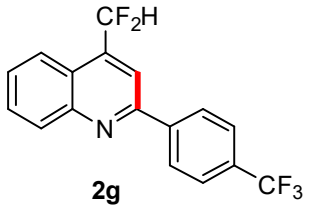
Following the general procedure, treatment of (*E*)-1-(4-fluorophenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine **1f** (136.0 mg, 0.50 mmol) with the triazolium salt **3** (27.0 mg, 0.10 mmol), DBU (228.4 mg, 224 µL, 1.50 mmol) in DMF (4.0 mL) at 100 °C for 36 h followed by work-up of the reaction mixture using EtOAc and subsequent flash column chromatography (Pet. ether /EtOAc = 95/05) of the crude reaction mixture using silica gel afforded 4-(difluoromethyl)-2-(4-fluorophenyl)quinoline **2f** as a yellow solid (0.097 g, 71%).

***R**$_f$* (Pet. ether /EtOAc = 90/10): 0.38; **^{1}H NMR (CDCl$_3$, 400 MHz)** δ 8.25-8.17 (m, 3H), 8.06 (d, *J* = 8.3 Hz, 1H), 8.01 (s, 1H), 7.79 (t, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.34-7.06 (m,

3H). **^{13}C NMR (CDCl$_3$, 100 MHz)** δ 164.22 (d, $J_{C\text{-}F}$ = 250.2 Hz), 155.92, 148.76, 138.81 (t, $J_{C\text{-}F}$ = 21.6 Hz), 135.02, 130.62, 130.39, 129.61, 129.53, 127.62, 123.19, 123.10 (t, $J_{C\text{-}F}$ = 3.1 Hz), 116.20, 115.99, 115.63 (t, $J_{C\text{-}F}$ = 7.9 Hz), 113.50 (t, $J_{C\text{-}F}$ = 240.8 Hz). **HRMS**: calculated $[M+H]^+$ for $C_{16}H_{11}NF_3$: 274.0838, found: 274.0836. **FTIR (cm^{-1}):** 3389, 3021, 2402, 1604, 1513, 1415, 1370, 1218, 1157, 1115, 1052, 926, 883, 846, 762.

4-(Difluoromethyl)-2-(4-(trifluoromethyl)phenyl)quinoline (2g)[2c]

Following the general procedure, treatment of (*E*)-N-(4-(trifluoromethyl)benzylidene)-2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine **1g** (171.6 mg, 0.50 mmol) with the triazolium salt **3** (27.0 mg, 0.10 mmol), DBU (228.4 mg, 224 µL, 1.50 mmol) in DMF (4.0 mL) at 100 °C for 36 h followed by work-up of the reaction mixture using EtOAc and subsequent flash column chromatography (Pet. ether /EtOAc = 95/05) of the crude reaction mixture using silica gel afforded 4-(difluoromethyl)-2-(4-(trifluoromethyl)phenyl)quinoline **2g** as a yellow solid (0.125 g, 78%).

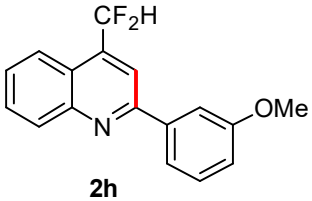


2g

***R**$_f$* (Pet. ether /EtOAc = 90/10): 0.33; **^{1}H NMR (CDCl$_3$, 400 MHz)** δ 8.29-8.24 (m, 3H), 8.07-8.04 (m, 2H), 7.82-7.77 (m, 3H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 54.4 Hz, 1H). **^{13}C NMR (CDCl$_3$, 100 MHz)** δ 155.31, 148.79, 142.04, 139.02 (t, $J_{C\text{-}F}$ = 21.6 Hz), 131.68 (q, $J_{C\text{-}F}$ = 32.4 Hz), 130.86, 130.53, 128.12, 127.88, 125.98, 125.95, 123.45 (t, $J_{C\text{-}F}$ = 3.0 Hz), 123.19, 115.67 (t, $J_{C\text{-}F}$ = 7.8 Hz), 113.37 (t, $J_{C\text{-}F}$ = 240.9 Hz). **HRMS**: calculated $[M+H]^+$ for $C_{17}H_{11}NF_5$: 324.0806, found: 324.0804. **FTIR (cm^{-1}):** 3418, 3023, 1642, 1368, 1219, 1113, 1056, 766.

4-(Difluoromethyl)-2-(3-methoxyphenyl)quinoline (2h)

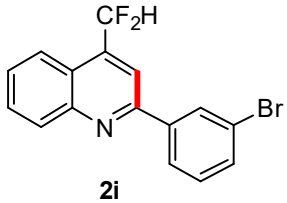
Following the general procedure, treatment of (*E*)-N-(3-methoxybenzylidene)-2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine **1h** (152.6 mg, 0.50 mmol) with the triazolium salt **3** (27.0 mg, 0.10 mmol), DBU (228.4 mg, 224 µL, 1.50 mmol) in DMF (4.0 mL) at 100 °C for 36 h followed by work-up of the reaction mixture using EtOAc and subsequent flash column chromatography (Pet. ether /EtOAc = 95/05) of the crude reaction mixture using silica gel afforded 4-(difluoromethyl)-2-(3-methoxyphenyl)quinoline **2h** as a yellow solid (0.113 g, 79%).



2h

***R**f* (Pet. ether /EtOAc = 90/10): 032; **^{1}H NMR (CDCl$_3$, 400 MHz)** δ 8.27 (d, *J* = 8.5 Hz, 1H), 8.08-8.04 (m, 2H), 7.80-7.77 (m, 2H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.9 Hz, 1H), 7.33-7.04 (m, 2H), 3.94 (s, 3H). **^{13}C NMR (CDCl$_3$, 100 MHz)** δ 160.35, 156.80, 148.73, 140.27, 138.62 (t, $J_{C\text{-}F}$ = 21.5 Hz), 130.69, 130.24, 130.07, 127.57, 123.24 (t, $J_{C\text{-}F}$ = 3.1 Hz), 123.19, 120.06, 116.15 (t, $J_{C\text{-}F}$ = 7.9 Hz), 115.99, 113.64 (t, $J_{C\text{-}F}$ = 240.4 Hz), 112.81, 55.56. **HRMS**: calculated $[M+H]^+$ for $C_{17}H_{14}ONF_2$: 286.1038, found: 286.1039. **FTIR (cm^{-1}):** 3416, 3018, 2971, 2840, 2403, 1602, 1553, 1501, 1462, 1367, 1326, 1217, 1173, 1124, 1048, 879, 766.

2-(3-Bromophenyl)-4-(difluoromethyl)quinoline (2i)

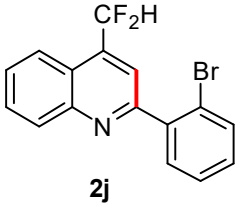


2i

Following the general procedure, treatment of (*E*)-N-(3-bromobenzylidene)-2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine **1i** (177.0 mg, 0.50 mmol) with the triazolium salt **3** (27.0 mg, 0.10 mmol), DBU (228.4 mg, 224 µL, 1.50 mmol) in DMF (4.0 mL) at 100 °C for 36 h followed by work-up of the reaction mixture using EtOAc and subsequent flash column chromatography (Pet. ether /EtOAc = 95/05) of the crude reaction mixture using silica gel afforded 2-(3-bromophenyl)-4-(difluoromethyl)quinoline **2i** as a yellow solid (0.139 g, 83%).

***R**f* (Pet. ether /EtOAc = 90/10): 0.37; **^{1}H NMR (CDCl$_3$, 400 MHz)** δ 8.38 (s, 1H), 8.26 (d, *J* = 8.5 Hz, 1H), 8.09 (d, *J* = 8.5 Hz, 2H), 8.02 (s, 1H), 7.81 (t, *J* = 7.7 Hz, 1H), 7.66-7.61 (m, 2H), 7.41 (t, *J* = 7.9 Hz, 1H), 7.21 (t, *J* = 54.6 Hz, 1H). **^{13}C NMR (CDCl$_3$, 100 MHz)** δ 155.36, 148.76, 140.82, 138.98 (t, $J_{C\text{-}F}$ = 21.4 Hz), 132.91, 130.79, 130.72, 130.58, 130.51, 127.97, 126.15, 123.44, 123.40 (t, $J_{C\text{-}F}$ = 3.1 Hz), 123.23, 115.71 (t, $J_{C\text{-}F}$ = 7.9 Hz), 113.46 (t, $J_{C\text{-}F}$ = 240.6 Hz). **HRMS**: calculated $[M+H]^+$ for $C_{16}H_{11}NBrF_2$: 334.0037, found: 334.0045. **FTIR (cm^{-1}):** 3418, 3022, 1640, 1367, 1218, 1115, 1055, 766.

2-(2-Bromophenyl)-4-(difluoromethyl)quinoline (2j)



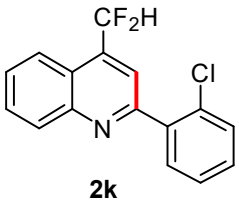
2j

Following the general procedure, treatment of (*E*)-1-(2-bromophenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine **1j** (176.0 mg, 0.50 mmol) with the triazolium salt **3** (27.0 mg, 0.10 mmol), DBU (228.4 mg, 224 µL, 1.50 mmol) in DMF (4.0 mL) at 100 °C for 36 h followed by work-up of the reaction mixture using EtOAc and subsequent flash column chromatography (Pet. ether

/EtOAc = 95/05) of the crude reaction mixture using silica gel afforded 2-(2-bromophenyl)-4-(difluoromethyl)quinoline **2j** as a white solid (0.140 g, 84%).

R_f (Pet. ether /EtOAc = 90/10): 0.41; **^{1}H NMR (CDCl$_3$, 400 MHz)** δ 8.28 (d, *J* = 7.8 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.93 (s, 1H), 7.84-7.81 (m, 1H), 7.74-7.65 (m, 3H), 7.49-7.46 (m, 1H), 7.35-7.06 (m, 2H). **^{13}C NMR (CDCl$_3$, 100 MHz)** δ 158.51, 151.73, 148.53, 137.58 (t, $J_{C\text{-}F}$ = 21.9 Hz), 133.53, 131.75, 130.72, 130.57, 130.32, 128.12, 127.98, 123.40, 123.19 (t, $J_{C\text{-}F}$ = 3.1 Hz), 121.89, 120.04 (t, $J_{C\text{-}F}$ = 7.7 Hz), 113.67 (t, $J_{C\text{-}F}$ = 240.7 Hz). **HRMS**: calculated $[M+H]^+$ for $C_{16}H_{11}NBrF_2$: 334.0037, found: 334.0039. **FTIR (cm^{-1}):** 3426, 2107, 1641, 1433, 1218, 1115, 767.

2-(2-Chlorophenyl)-4-(difluoromethyl)quinoline (2k)

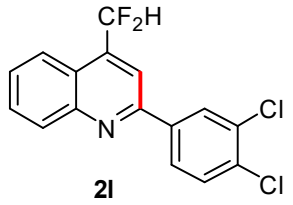


2k

Following the general procedure, treatment of (*E*)-N-(2-chlorobenzylidene)-2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine **1k** (188.0 mg, 0.50 mmol) with the triazolium salt **3** (27.0 mg, 0.10 mmol), DBU (228.4 mg, 224 μL, 1.50 mmol) in DMF (4.0 mL) at 100 °C for 36 h followed by work-up of the reaction mixture using EtOAc and subsequent flash column chromatography (Pet. ether /EtOAc = 95/05) of the crude reaction mixture using silica gel afforded 2-(2-chlorophenyl)-4-(difluoromethyl)quinoline **2k** as a yellow solid (0.127 g, 88%).

R_f (Pet. ether /EtOAc = 90/10): 0.38; **^{1}H NMR (CDCl$_3$, 400 MHz)** δ 8.27 (d, *J* = 8.4 Hz, 1H), 8.20 (d, *J* = 7.4 Hz, 2H), 8.09-8.06 (m, 2H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.57-7.48 (m, 3H), 7.20 (t, *J* = 54.6 Hz, 1H). **^{13}C NMR (CDCl$_3$, 100 MHz)** δ 157.24, 148.70, 138.94, 137.58 (t, $J_{C\text{-}F}$ = 21.9 Hz), 132.48, 131.81, 130.71, 130.47, 130.35, 130.27, 128.08, 127.44, 123.40, 123.17 (t, $J_{C\text{-}F}$ = 3.0 Hz), 120.06 (t, $J_{C\text{-}F}$ = 7.9 Hz), 113.68 (t, $J_{C\text{-}F}$ = 241.1 Hz). **HRMS**: calculated $[M+H]^+$ for $C_{16}H_{10}NClF_2$: 290.0543, found: 290.0548. **FTIR (cm^{-1}):** 3419, 3022, 2403, 1640, 1371, 1217, 1117, 1051, 766.

2-(3,4-Dichlorophenyl)-4-(difluoromethyl)quinoline (2l)



2l

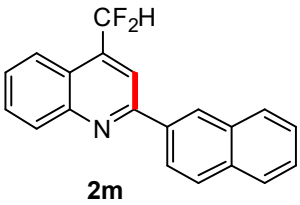
Following the general procedure, treatment of (*E*)-N-(3,4-dichlorobenzylidene)-2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine **1l** (172.0 mg, 0.50 mmol) with the triazolium salt **3** (27.0 mg, 0.10 mmol), DBU (228.4 mg, 224 μL, 1.50 mmol) in DMF (4.0 mL) at 100

°C for 36 h followed by work-up of the reaction mixture using EtOAc and subsequent flash column chromatography (Pet. ether /EtOAc = 95/05) of the crude reaction mixture using silica gel afforded 2-(3,4-dichlorophenyl)-4-(difluoromethyl)quinoline **2l** as a yellow solid (0.146 g, 90%).

R_f (Pet. ether /EtOAc = 90/10): 0.35; **^{1}H NMR (CDCl$_3$, 400 MHz)** δ 8.34 (s, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 8.03-8.00 (m, 2H), 7.82 (t, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.21 (t, *J* = 54.4 Hz, 1H). **^{13}C NMR (CDCl$_3$, 100 MHz)** δ 154.36, 148.76, 139.12 (t, $J_{C\text{-}F}$ = 21.5 Hz), 138.67, 134.33, 133.53, 131.02, 130.79, 130.62, 129.49, 128.11, 126.60, 123.43 (t, $J_{C\text{-}F}$ = 3.1 Hz), 123.23, 115.27 (t, $J_{C\text{-}F}$ = 7.9 Hz), 113.34 (t, $J_{C\text{-}F}$ = 240.6 Hz). **HRMS**: calculated $[M+H]^+$ for $C_{16}H_{10}NCl_2F_2$: 324.0153, found: 324.0153. **FTIR (cm^{-1}):** 3414, 3022, 1637, 1392, 1217, 1083, 765.

4-(Difluoromethyl)-2-(naphthalen-2-yl)quinoline (2m)

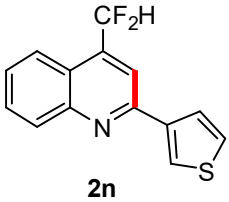
Following the general procedure, treatment of (*E*)-N-(naphthalen-2-ylmethylene)-2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine **1m** (162.6 mg, 0.50 mmol) with the triazolium salt **3** (27.0 mg, 0.10 mmol), DBU (228.4 mg, 224 µL, 1.50 mmol) in DMF (4.0 mL) at 100 °C for 36 h followed by work-up of the reaction mixture using EtOAc and subsequent flash column chromatography (Pet. ether /EtOAc = 95/05) of the crude reaction mixture using silica gel afforded 4-(difluoromethyl)-2-(naphthalen-2-yl)quinoline **2m** as a yellow solid (0.108 g, 71%).



2m

R_f (Pet. ether /EtOAc = 90/10): 0.34; **^{1}H NMR (CDCl$_3$, 400 MHz)** δ 8.63 (s, 1H), 8.39 (d, *J* = 8.5 Hz, 1H),8.32 (d, *J* = 8.5 Hz, 1H), 8.19 (s, 1H), 8.08 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 2H), 7.90-7.89 (m, 1H), 7.81 (t, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.56-7.54 (m, 2H), 7.21 (t, *J* = 54.6 Hz, 1H). **^{13}C NMR (CDCl$_3$, 100 MHz)** δ 156.77, 148.81, 138.68 (t, $J_{C\text{-}F}$ = 21.6 Hz), 136.02, 134.19, 133.52, 130.65, 130.31, 129.02, 128.87, 127.86, 127.58, 127.47, 127.17, 126.63, 124.82, 123.22, 116.14 (t, $J_{C\text{-}F}$ = 7.8 Hz), 113.66 (t, $J_{C\text{-}F}$ = 240.7 Hz). **HRMS**: calculated $[M+H]^+$ for $C_{20}H_{14}NF_2$: 306.1089, found: 306.1088. **FTIR (cm^{-1}):** 3415, 3022, 1639, 1384, 1218, 1118, 1048, 767.

4-(Difluoromethyl)-2-(thiophen-3-yl)quinoline (2n)

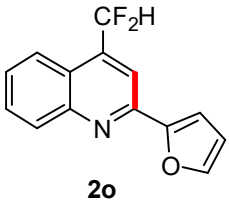


2n

Following the general procedure, treatment of (*E*)-N-(thiophen-3-ylmethylene)-2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine **1n** (137.6 mg, 0.50 mmol) with the triazolium salt **3** (27.0 mg, 0.10 mmol), DBU (228.4 mg, 224 µL, 1.50 mmol) in DMF (4.0 mL) at 100 °C for 36 h followed by work-up of the reaction mixture using EtOAc and subsequent flash column chromatography (Pet. ether /EtOAc = 95/05) of the crude reaction mixture using silica gel afforded 4-(difluoromethyl)-2-(thiophen-3-yl)quinoline **2n** as a brown solid (0.095 g, 73%).

R_f (Pet. ether /EtOAc = 90/10): 0.31; **^{1}H NMR (CDCl$_3$, 400 MHz)** δ 8.20 (d, *J* = 8.5 Hz, 1H), 8.10-8.09 (m, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.92-7.89 (m, 2H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.46-7.44 (m, 1H), 7.17 (t, *J* = 54.7 Hz, 1H). **^{13}C NMR (CDCl$_3$, 100 MHz)** δ 152.93, 148.72, 141.94, 138.51 (t, $J_{C\text{-}F}$ = 21.5 Hz), 130.39, 130.25, 127.30, 126.81, 126.79, 125.52, 123.16, 123.02 (t, $J_{C\text{-}F}$ = 3.1 Hz), 116.08 (t, $J_{C\text{-}F}$ = 7.9 Hz), 113.47 (t, $J_{C\text{-}F}$ = 240.4 Hz). **HRMS**: calculated $[M+H]^+$ for $C_{14}H_{10}NF_2S$: 262.0497, found: 262.0495. **FTIR (cm^{-1}):** 3425, 2111, 1641, 1415, 1216, 1178, 1125, 765.

4-(Difluoromethyl)-2-(furan-2-yl)quinoline (2o)

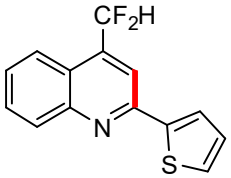


2o

Following the general procedure, treatment of (*E*)-N-(furan-2-ylmethylene)-2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine **1o** (132.6 mg, 0.50 mmol) with the triazolium salt **3** (27.0 mg, 0.10 mmol), DBU (228.4 mg, 224 µL, 1.50 mmol) in DMF (4.0 mL) at 100 °C for 36 h followed by work-up of the reaction mixture using EtOAc and subsequent flash column chromatography (Pet. ether /EtOAc = 95/05) of the crude reaction mixture using silica gel afforded 4-(difluoromethyl)-2-(furan-2-yl)quinoline **2o** as a brown solid (0.099 g, 81%).

R_f (Pet. ether /EtOAc = 90/10): 0.36; **^{1}H NMR (CDCl$_3$, 400 MHz)** δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.91-7.87 (m, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.53 (s, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.17-6.90 (m, 2H), 6.49 (bs, 1H). **^{13}C NMR (CDCl$_3$, 100 MHz)** δ 153.16, 148.70, 148.62, 138.51 (t, $J_{C\text{-}F}$ = 21.7 Hz), 130.37, 130.25, 127.34, 123.27, 123.02 (t, $J_{C\text{-}F}$ = 3.0 Hz), 114.71 (t, $J_{C\text{-}F}$ = 8.0 Hz), 113.45 (t, $J_{C\text{-}F}$ = 241.0 Hz), 112.55, 111.03. **HRMS**: calculated $[M+H]^+$ for $C_{14}H_{10}ONF_2$: 246.0725, found: 246.0724. **FTIR (cm^{-1}):** 3416, 3016, 1615, 1557, 1500, 1364, 1218, 1161, 1118, 1050, 942, 889, 765.

4-(Difluoromethyl)-2-(thiophen-2-yl)quinoline (2p)

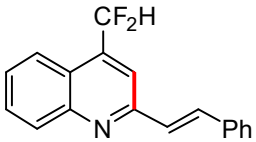


2p

Following the general procedure, treatment of (*E*)-N-(thiophen-2-ylmethylene)-2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine **1p** (140.6 mg, 0.50 mmol) with the triazolium salt **3** (27.0 mg, 0.10 mmol), DBU (228.4 mg, 224 µL, 1.50 mmol) in DMF (4.0 mL) at 100 °C for 36 h followed by work-up of the reaction mixture using EtOAc and subsequent flash column chromatography (Pet. ether /EtOAc = 95/05) of the crude reaction mixture using silica gel afforded 4-(difluoromethyl)-2-(thiophen-2-yl)quinoline **2p** as a yellow solid (0.104 g, 80%).

***R**f* (Pet. ether /EtOAc = 90/10): 0.34; **^{1}H NMR (CDCl$_3$, 400 MHz)** δ 8.17 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.95 (s, 1H), 7.78-7.73 (m, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 4.7 Hz, 1H), 7.30-7.02 (m, 2H). **^{13}C NMR (CDCl$_3$, 100 MHz)** δ 152.09, 148.59, 144.60, 138.52 (t, $J_{C\text{-}F}$ = 21.5 Hz), 130.40, 130.17, 129.46, 128.39, 127.29, 126.74, 123.21, 123.12 (t, $J_{C\text{-}F}$ = 3.0 Hz), 114.81 (t, $J_{C\text{-}F}$ = 7.9 Hz), 113.38 (t, $J_{C\text{-}F}$ = 240.7 Hz). **HRMS**: calculated $[M+H]^+$ for $C_{14}H_{10}NF_2S$: 262.0497, found: 262.0496. **FTIR (cm^{-1}):** 3425, 3020, 2403, 2357, 1965, 1806, 1611, 1544, 1523, 1465, 1428, 1372, 1217, 1173, 1123, 1056, 922, 877, 840, 769.

(*E*)-4-(Difluoromethyl)-2-styrylquinoline (2q)



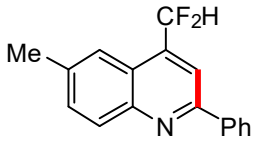
2q

Following the general procedure, treatment of (*E*)-N-((*E*)-3-phenylallylidene)-2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine **1q** (150.6 mg, 0.50 mmol) with the triazolium salt **3** (27.0 mg, 0.10 mmol), DBU (228.4 mg, 224 µL, 1.50 mmol) in DMF (4.0 mL) at 100 °C for 36 h followed by work-up of the reaction mixture using EtOAc and subsequent flash column chromatography (Pet. ether /EtOAc = 95/05) of the crude reaction mixture using silica gel afforded (*E*)-4-(difluoromethyl)-2-styrylquinoline **2q** as a brown solid (0.077 g, 55%).

***R**f* (Pet. ether /EtOAc = 90/10): 0.32; **^{1}H NMR (CDCl$_3$, 400 MHz)** δ 8.17 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.85 (s, 1H), 7.79-7.72 (m, 2H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.45-7.40 (m, 3H), 7.37-7.33 (m, 1H), 7.17 (t, *J* = 54.6 Hz, 1H). **^{13}C NMR (CDCl$_3$, 100 MHz)** δ 155.79, 148.68, 138.29 (t, $J_{C\text{-}F}$ = 21.6 Hz), 136.25, 135.75, 130.39, 130.10, 129.16, 129.01, 128.21, 127.56, 127.43, 123.28, 116.41 (t, $J_{C\text{-}F}$ = 7.8 Hz), 113.52 (t, $J_{C\text{-}F}$ = 240.4 Hz). **HRMS**: calculated $[M+H]^+$ for $C_{18}H_1NF_2$: 282.1089, found: 282.1090. **FTIR (cm^{-1}):** 3418,

3021, 2969, 2403, 2353, 1958, 1814, 1674, 1611, 1549, 1508, 1436, 1384, 1217, 1174, 1123, 1052, 971, 893, 743.

4-(Difluoromethyl)-6-methyl-2-phenylquinoline (2r)

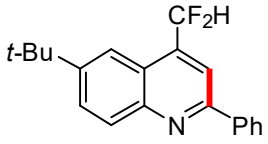


2r

Following the general procedure (on 0.25 mmol scale), treatment of (*E*)-*N*-(phenylmethylene)-4-methyl-2-(3,3,3-trifluoroprop-1-en-2-yl)benzenamine **1r** (72.3 mg, 0.25 mmol.) with the triazolium salt **3** (13.2 mg, 0.05 mmol.), DBU (114 mg, 0.75 mmol.) in DMF (2 mL) at 100 °C for 36 h followed by a work-up of the reaction mixture using EtOAc and a subsequent flash column chromatography (Pet. ether/EtOAc = 95/5) of the crude reaction mixture using silica gel afforded 4-(difluoromethyl)-6-methyl-2-phenylquinoline **2r** as a white solid (49.8 mg, 74%).

***R**f* (Pet. ether/EtOAc = 95/5): 0.33. **m.p.** 63-64 °C. **^{1}H NMR (CDCl$_3$, 300 MHz)** δ 8.22-8.11 (m, 3H), 8.02 (s, 1H), 7.82 (s, 1H), 7.62 (dd, *J* = 8.6 and 1.6 Hz, 1H), 7.59-7.44 (m, 3H), 7.18 (t, *J* = 54.7 Hz, 1H), 2.58 (s, 3H). **^{13}C NMR (CDCl$_3$, 75 MHz)** δ 156.1, 147.5, 139.0, 137.8 (t, *J* = 21.4 Hz), 137.7, 132.4, 130.4, 129.7, 129.0, 127.5, 123.2 (t, *J* = 3.1 Hz), 122.1, 115.9 (t, *J* = 7.9 Hz), 113.7 (t, *J* = 240.4 Hz), 22.1. **^{19}F NMR (282 MHz, CDCl$_3$)** δ -115.7 (d, *J* = 54.7 Hz). **HRMS**: calculated $[M+H]^+$ for $C_{17}H_{14}F_2N$: 270.1094, found: 270.1088. **FTIR (cm^{-1}):** 3058, 2922, 1609, 1557, 1450, 1375, 1355, 1196, 1113, 1039, 880, 819, 773, 753, 689, 651, 555, 518.

6-*tert*-Butyl-4-(difluoromethyl)-2-phenylquinoline (2s)



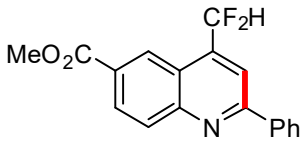
2s

Following the general procedure, treatment of (*E*)-*N*-(phenylmethylene)-4-*tert*-butyl-2-(3,3,3-trifluoroprop-1-en-2-yl)benzenamine **1s** (165.5 mg, 0.50 mmol.) with the triazolium salt **3** (26.4 mg, 0.10 mmol.), DBU (228 mg, 1.5 mmol.) in DMF (4 mL) at 100 °C for 36 h followed by a work-up of the reaction mixture using EtOAc and a subsequent flash column chromatography (Pet. ether/EtOAc = 95/5) of the crude reaction mixture using silica gel afforded 6-*tert*-butyl-4-(difluoromethyl)-2-phenylquinoline **2s** as a white solid (127 mg, 81%).

***R**f* (Pet. ether/EtOAc = 95/5): 0.38. **m.p.** 86-87 °C. **^{1}H NMR (CDCl$_3$, 300 MHz)** δ 8.23-8.14 (m, 3H), 8.04 (s, 1H), 7.98 (s, 1H), 7.90 (d, *J* = 8.9 Hz, 1H), 7.60-7.45 (m, 3H), 7.24 (t, *J* = 54.7 Hz, 1H), 1.46 (s, 9H). **^{13}C NMR (CDCl$_3$, 75 MHz)** δ 156.3, 150.4, 147.4, 139.0, 138.2 (t, *J* = 21.4 Hz), 130.2, 129.7, 129.1, 129.0, 127.5, 122.8 (t, *J* = 2.8 Hz), 118.0, 115.8 (t, *J* = 7.9 Hz), 113.8 (t,

J = 240.3 Hz), 35.3, 31.2. **^{19}F NMR (282 MHz, $CDCl_3$)** δ -115.7 (d, J = 54.7 Hz). **HRMS**: calculated $[M+H]^+$ for $C_{20}H_{20}F_2N$: 312.1564, found: 312.1556. **FTIR (cm^{-1}):** 2959, 1866, 1706, 1600, 1560, 1450, 1378, 1363, 1264, 1175, 1127, 1101, 1065, 1038, 1013, 885, 832, 768, 733, 687, 622, 587, 556, 514, 424.

Methyl 4-(difluoromethyl)-2-phenylquinoline-6-carboxylate (2t)

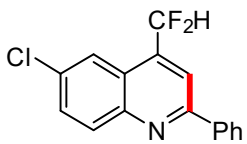


2t

Following the general procedure (on 0.25 mmol scale), treatment of (*E*)-methyl 4-(benzylideneamino)-3-(3,3,3-trifluoroprop-1-en-2-yl)benzoate **1t** (83.3 mg, 0.25 mmol.) with the triazolium salt **3** (13.2 mg, 0.05 mmol.), DBU (114 mg, 0.75 mmol) in DMF (2 mL) at 100 °C for 36 h followed by a work-up of the reaction mixture using EtOAc and a subsequent flash column chromatography (Pet. ether/EtOAc = 93/7) of the crude reaction mixture using silica gel afforded methyl 4-(difluoromethyl)-2-phenylquinoline-6-carboxylate **2t** as a white solid (43 mg, 55%).

R_f (Pet. ether/EtOAc = 90/10): 0.19. **m.p.** 153-154 °C. **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 8.81 (s, 1H), 8.42-8.35 (m, 1H), 8.31-8.26 (m, 1H), 8.25-8.20 (m, 2H), 8.14 (s, 1H), 7.61-7.51 (m, 3H), 7.28 (t, J = 54.2 Hz, 1H), 4.02 (s, 3H). **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 166.4, 159.0, 150.6, 139.8 (t, J = 21.4 Hz), 138.3, 130.9, 130.5, 129.8, 129.2, 128.6, 127.7, 126.1, 122.3 (t, J = 2.8 Hz), 116.5 (t, J = 7.9 Hz), 113.1 (t, J = 240.3 Hz), 52.7. **^{19}F NMR (282 MHz, $CDCl_3$)** δ -115.7 (d, J = 54.2 Hz). **HRMS**: calculated $[M+H]^+$ for $C_{18}H_{14}F_2NO_2$: 314.0993, found: 314.0990. **FTIR (cm^{-1}):** 3052, 2962, 2930, 2853, 1703, 1610, 1469, 1452, 1434, 1406, 1280, 1229, 1098, 1032, 898, 775, 725, 688, 552, 465.

6-Chloro-4-(difluoromethyl)-2-phenylquinoline (2u)



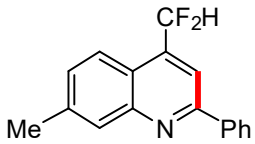
2u

Following the general procedure, treatment of (*E*)-*N*-(phenylmethylene)-4-chloro-2-(3,3,3-trifluoroprop-1-en-2-yl)benzenamine **1u** (154.5 mg, 0.50 mmol.) with the triazolium salt **3** (26.4 mg, 0.10 mmol.), DBU (228 mg, 1.5 mmol.) in DMF (4 mL) at 100 °C for 36 h followed by a work-up of the reaction mixture using EtOAc and a subsequent flash column chromatography (Pet. ether/EtOAc = 95/5) of the crude reaction mixture using silica gel afforded 6-chloro-4-(difluoromethyl)-2-phenylquinoline **2u** as a white solid (90.9 mg, 63%).

***R**f* (Pet. ether/EtOAc = 95/5): 0.42. **m.p.** 78-79 °C. **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 8.21-8.14 (m, 3H), 8.06 (app. s, 2H), 7.72 (dd, *J* = 9.0 and 2.0 Hz, 1H), 7.59-7.47 (m, 3H), 7.12 (t, *J* = 54.5 Hz, 1H). **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 157.0, 147.2, 138.3, 137.7 (t, *J* = 21.8 Hz), 133.4, 132.1, 131.1, 130.2, 129.1, 127.5, 123.6 (t, *J* = 2.8 Hz), 122.4, 116.7 (t, *J* = 7.9 Hz), 113.4 (t, *J* = 240.9 Hz). **^{19}F NMR (282 MHz, $CDCl_3$)** δ -114.9 (d, *J* = 54.5 Hz). **HRMS**: calculated $[M+H]^+$ for $C_{16}H_{11}{}^{35}ClF_2N$: 290.0548, found: 290.0535. **FTIR (cm^{-1}):** 3065, 1608, 1548, 1493, 1456, 1373, 1356, 1337, 1218, 1127, 1087, 1063, 1037, 1008, 885, 827, 811, 767, 728, 683, 550, 510, 416.

4-(Difluoromethyl)-7-methyl-2-phenylquinoline (2v)

Following the general procedure (on 0.25 mmol scale), treatment of (*E*)-*N*-(phenylmethylene)-5-methyl-2-(3,3,3-trifluoroprop-1-en-2-yl)benzenamine **1v** (72.3 mg, 0.25 mmol.) with the triazolium salt **3** (13.2 mg, 0.05 mmol.), DBU (114 mg, 0.75 mmol.) in DMF (2 mL) at 100 °C for 36 h followed by a work-up of the reaction mixture using EtOAc and a subsequent flash column chromatography (Pet. ether/EtOAc = 95/5) of the crude reaction mixture using silica gel afforded 4-(difluoromethyl)-7-methyl-2-phenylquinoline **2v** as a white solid (60.0 mg, 89%).

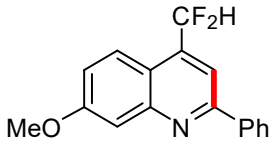


2v

***R**f* (Pet. ether/EtOAc = 95/5): 0.48. **m.p.** 72-73 °C. **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 8.10-8.03 (m, 2H), 7.92 (s, 1H), 7.86 (s, 1H), 7.83 (d, *J* = 8.6, 1H), 7.48-7.34 (m, 3H), 7.31 (dd, *J* = 8.6 and 1.5 Hz, 1H), 7.04 (t, *J* = 54.7 Hz, 1H), 2.46 (s, 3H). **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 156.9, 149.1, 140.5, 139.0, 138.3 (t, *J* = 21.5 Hz), 129.8, 129.7, 129.0, 127.5, 122.8, 121.1 (t, *J* = 3.0 Hz), 115.1 (t, *J* = 7.9 Hz), 113.7 (t, *J* = 240.4 Hz), 21.8. **^{19}F NMR (282 MHz, $CDCl_3$)** δ -115.5 (d, *J* = 54.7 Hz). **HRMS**: calculated $[M+H]^+$ for $C_{17}H_{14}F_2N$: 270.1094, found: 270.1087. **FTIR (cm^{-1}):** 2919, 1605, 1515, 1453, 1372, 1358, 1165, 1119, 1034, 1003, 876, 819, 792, 763, 684, 672, 599, 541, 470. Note that one ^{13}C NMR signal is overlapped with another signal.

4-(Difluoromethyl)-7-methoxyl-2-phenylquinoline (2w)[2c]

Following the general procedure, treatment of (*E*)-*N*-(phenylmethylene)-5-methoxy-2-(3,3,3-trifluoroprop-1-en-2-yl)benzenamine **1w** (152.5 mg, 0.50 mmol.) with the triazolium salt **3** (26.4 mg, 0.10 mmol.), DBU (228 mg, 1.5 mmol.) in DMF (4 mL) at 100 °C for 36 h followed by a work-up of the reaction mixture using EtOAc and a subsequent flash column chromatography (Pet.

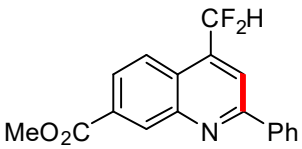


2w

ether/EtOAc = 95/5) of the crude reaction mixture using silica gel afforded 4-(difluoromethyl)-7-methoxyl-2-phenylquinoline **2w** as a white solid (115 mg, 81%).

***R**f* (Pet. ether/EtOAc = 95/5): 0.21. **m.p.** 115-116 °C. **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 8.20-8.13 (m, 2H), 7.98 (d, *J* = 9.2 Hz, 1H), 7.91 (s, 1H), 7.61-7.44 (m, 4H), 7.28 (dd, *J* = 9.2 and 2.6 Hz, 1H), 7.15 (t, *J* = 54.7 Hz, 1H), 4.00 (s, 3H). **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 161.0, 157.3, 150.7, 139.0, 138.3 (t, *J* = 21.6 Hz), 129.7, 129.0, 127.5, 124.1, 120.5, 118.1 (t, *J* = 3.0 Hz), 113.7 (t, *J* = 240.5 Hz), 113.7 (t, *J* = 7.8 Hz), 108.5, 55.5. **^{19}F NMR (282 MHz, $CDCl_3$)** δ -115.1 (d, *J* = 54.7 Hz). **HRMS**: calculated $[M+H]^+$ for $C_{17}H_{14}F_2NO$: 286.1043, found: 286.1039. **FTIR (cm^{-1}):** 3019, 2966, 2833, 1621, 1602, 1520, 1457, 1375, 1360, 1340, 1269, 1209, 1174, 1109, 1030, 1003, 875, 826, 793, 778, 667, 611, 541, 478.

Methyl 4-(difluoromethyl)-2-phenylquinoline-6-carboxylate (2x)

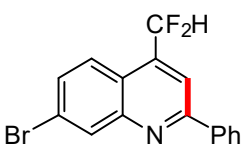


2x

Following the general procedure, treatment of (*E*)-methyl 3-(benzylideneamino)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzoate **1x** (166.5 mg, 0.50 mmol.) with the triazolium salt **3** (26.4 mg, 0.10 mmol.), DBU (228 mg, 1.5 mmol.) in DMF (4 mL) at 100 °C for 36 h followed by a work-up of the reaction mixture using EtOAc and a subsequent flash column chromatography (Pet. ether/EtOAc = 95/5) of the crude reaction mixture using silica gel afforded methyl 4-(difluoromethyl)-2-phenylquinoline-6-carboxylate **2x** as a white solid (48.1 mg, 31%).

***R**f* (Pet. ether/EtOAc = 95/5): 0.14. **m.p.** 152-153 °C. **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 8.95 (s, 1H), 8.25-8.17 (m, 3H), 8.16-8.09 (m, 2H), 7.62-7.48 (m, 3H), 7.21 (t, *J* = 54.5 Hz, 1H), 4.02 (s, 3H). **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 166.6, 157.9, 148.3, 138.6 (t, *J* = 21.8 Hz), 138.3, 133.0, 131.6, 130.3, 129.2, 127.6, 126.9, 125.6 (t, *J* = 2.9 Hz), 123.6, 117.6 (t, *J* = 7.8 Hz), 113.4 (t, *J* = 240.9 Hz), 52.7. **^{19}F NMR (282 MHz, $CDCl_3$)** δ -115.7 (d, *J* = 54.5 Hz). **HRMS**: calculated $[M+H]^+$ for $C_{18}H_{14}F_2NO_2$: 314.0993, found: 314.1004. **FTIR (cm^{-1}):** 3039, 2966, 1722, 1607, 1436, 1359, 1328, 1304, 1253, 1227, 1162, 1097, 1028, 911, 887, 798, 755, 684, 528, 477, 444.

7-Bromo-4-(difluoromethyl)-2-phenylquinoline (2y)



2y

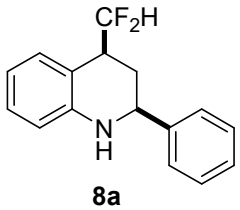
Following the general procedure, treatment of (*E*)-*N*-(phenylmethylene)-5-bromo-2-(3,3,3-trifluoroprop-1-en-2-yl)benzenamine **1y** (176.5 mg, 0.50 mmol.) with the triazolium salt **3** (26.4 mg, 0.10 mmol.), DBU (228 mg,

1.5 mmol.) in DMF (4 mL) at 100 °C for 36 h followed by a work-up of the reaction mixture using EtOAc and a subsequent flash column chromatography (Pet. ether/EtOAc = 95/5) of the crude reaction mixture using silica gel afforded 7-bromo-4-(difluoromethyl)-2-phenylquinoline **2y** as a white solid (136 mg, 81%).

R_f (Pet. ether/EtOAc = 95/5): 0.35. **m.p.** 71-72 °C. **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 8.47 (d, *J* = 1.9 Hz, 1H), 8.27-8.20 (m, 2H), 8.07 (s, 1H), 7.96 (d, *J* = 8.9 Hz, 1H), 7.72 (dd, *J* = 8.9 and 1.9 Hz, 1H), 7.67-7.54 (m, 3H), 7.17 (t, *J* = 54.5 Hz, 1H). **^{13}C NMR ($CDCl_3$, 75 MHz)** δ 157.5, 149.2, 138.5 (t, *J* = 21.8 Hz), 138.0, 132.7, 130.6, 130.2, 129.0, 127.4, 124.4, 124.3, 121.5 (t, *J* = 2.8 Hz), 115.9 (t, *J* = 7.9 Hz), 113.4 (t, *J* = 241.0 Hz). **^{19}F NMR (282 MHz, $CDCl_3$)** δ -115.2 (d, *J* = 54.5 Hz). **HRMS**: calculated $[M+H]^+$ for $C_{16}H_{11}{}^{79}BrF_2N$: 334.0043, found: 334.0034. **FTIR (cm^{-1}):** 3052, 1607, 1506, 1494, 1451, 1374, 1355, 1451, 1216, 1165, 1118, 1066, 1026, 1000, 885, 789, 763, 670, 661, 581, 538, 515, 466.

9. Functionalization of Difluoromethylated Quinoline Derivatives

4-(Difluoromethyl)-2-phenyl-1,2,3,4-tetrahydroquinoline (8a)



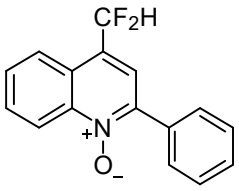
8a

4-(difluoromethyl)-2-phenylquinoline **2a** (0.059 g, 0.231 mmol) was taken in a flame dried round bottom flask with N_2 inlet. Glacial acetic acid (9 mL) was added to it. To this stirring solution sodium cyanoborohydride (0.073 g, 1.155 mmol) was added in one portion. The reaction suspension was stirred for 15 h at rt. To the flask was then slowly added a saturated aqueous solution of Na_2CO_3, along with EtOAc and the mixture was stirred for further 30 minutes. Two layers were separated, and the aqueous layer was further extracted twice more with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated on rotary evaporator. The crude residue was purified by flash column chromatography (Pet. ether /EtOAc = 90/10) on silica gel to afford the corresponding 4-(difluoromethyl)-2-phenyl-1,2,3,4-tetrahydroquinoline **8a** (0.057 g, 95% yield) as yellowish liquid**.**

R_f (Pet. ether /EtOAc = 80/20): 0.32; **^{1}H NMR ($CDCl_3$, 400 MHz)** δ 7.47-7.39 (m, 4H), 7.37-7.30 (m, 2H), 7.12 (t, *J* = 7.7 Hz, 1H), 6.77 (t, *J* = 7.7 Hz, 1H), 6.63 (d, *J* = 7.9 Hz, 1H), 5.91 (dt, J_1 = 5.0 Hz, J_2 = 56.2 Hz, 1H), 4.44-4.40 (m, 1H), 4.07 (bs, 1H), 3.63-3.51 (m, 1H), 2.36-2.30 (m, 1H), 2.14-2.05 (m,1H). **^{13}C NMR ($CDCl_3$, 100 MHz)** δ 146.05, 143.47, 128.93, 128.35, 128.10, 126.75, 118.28, 118.08 (t, $J_{C\text{-}F}$ = 243.5 Hz), 115.34, 55.67, 40.76 (t, $J_{C\text{-}F}$ = 20.3 Hz),

31.77 (t, $J_{C\text{-}F}$ = 5.0 Hz). **HRMS**: calculated $[M+H]^+$ for $C_{16}H_{16}NF_2$: 260.1245, found: 260.1247. **FTIR (cm^{-1}):** 3420, 3021, 2402, 2347, 2099, 1642, 1487, 1439, 1389, 1313, 1217, 1107, 1042, 926, 768.

4-(Difluoromethyl)-2-phenylquinoline 1-oxide (9a)

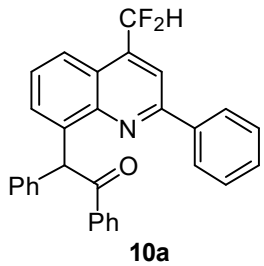


9a

4-(difluoromethyl)-2-phenylquinoline **2a** (0.100 g, 0.390 mmol) and *m*-Chloroperoxybenzoic acid (0.169 g, 0.98 mmol) were taken in a flame dried round bottom flask with N_2 inlet. Dry $CHCl_3$ (2 mL) was added to it the mixture was refluxed for 12 h. To this stirring solution ethylchloroformate was added dropwise. The suspension was allowed to cool to room temperature, saturated aqueous $NaHCO_3$ solution were added. The aqueous layer was extracted with dichloromethane and the combined organic extracts were dried over Na_2SO_4, filtered. The crude *N*-oxide **9a** was obtained by removing the solvent under reduced pressure. The crude residue was purified by flash column chromatography (DCM /MeOH = 93/02) on silica gel to afford the corresponding 4-(difluoromethyl)-2-phenylquinoline 1-oxide **9a** (0.081 g, 77% yield) as a white solid**.**

R_f (DCM /MeOH = 95/05): 0.51; **^{1}H NMR ($CDCl_3$, 400 MHz)** δ 8.92 (d, *J* = 8.8 Hz, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 7.2 Hz, 2H), 7.86 (t, *J* = 8.0 Hz, 1H), 7.77-7.73 (m, 2H), 7.57-7.49 (m, 3H), 7.12 (t, *J* = 54.8 Hz, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz)** δ 144.33, 142.89, 132.80, 131.10, 129.61, 129.53, 128.62, 125.87, 124.16, 121.76 (t, $J_{C\text{-}F}$ = 9.3 Hz), 121.12, 113.35 (t, $J_{C\text{-}F}$ = 240.5 Hz). **HRMS**: calculated $[M+H]^+$ for $C_{16}H_{12}ONF_2$: 272.0881, found: 272.0880. **FTIR (cm^{-1}):** 3417, 3021, 2403, 2352, 2124, 1640, 1514, 1413, 1336, 1217, 1163, 1114, 1043, 924, 766.

2-(4-(Difluoromethyl)-2-phenylquinolin-8-yl)-1,2-diphenylethan-1-one (10a)



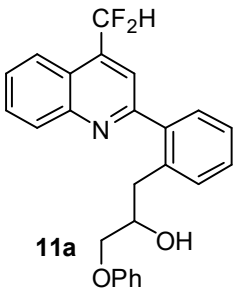
10a

To an oven-dried Schlenk tube (5 mL) $[Cp^*RhCl_2]_2$ (3.0 mg, 2.5 mol %), $Cu(OAc)_2{\cdot}H_2O$ (2.0 mg, 5 mol %), 4-(difluoromethyl)-2-phenylquinoline 1-oxide **9a** (0.053 g, 0.195 mmol), and 1,2-diphenylethyne (0.029 g, 0.156 mmol) were added under an argon atmosphere. Subsequently, solvent (0.5 mL) was added using a laboratory syringe. The reaction mixture was put in a preheated oil bath at 110 °C for 24 h with vigorous stirring. After

cooling to room temperature, the reaction mixture was filtered through Celite and washed with EtOAc. The organic layer was further washed with water (5 mL × 3) to remove traces of DMF and copper salt and dried over Na_2SO_4. Finally, the solvent was removed under reduced pressure. The crude residue was purified by flash chromatography using Pet. ether/EtOAc as the eluent on silica gel to afford the corresponding 2-(4-(difluoromethyl)-2-phenylquinolin-8-yl)-1,2-diphenylethan-1-one **10a** (0.053 g, 61% yield) as brown solid**.**

***R**f* (Pet. ether /EtOAc = 90/10): 0.35; **^{1}H NMR ($CDCl_3$, 400 MHz)** δ 8.20 (d, *J* = 7.8 Hz, 2H), 8.09 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 2H), 7.61-7.58 (m, 1H), 7.54-7.43 (m, 7H), 7.41-7.33 (m, 4H), 7.28-7.06 (m, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz)** δ 198.81, 155.62, 146.10, 141.03, 139.04 (t, $J_{C\text{-}F}$ = 21.7 Hz), 138.46, 137.36, 137.26, 132.92, 130.74, 130.18, 129.74, 129.29, 128.75, 127.68, 127.44, 127.30, 123.34, 122.28, 115.57 (t, $J_{C\text{-}F}$ = 7.7 Hz), 113.56 (t, $J_{C\text{-}F}$ = 240.7 Hz), 55.13. **HRMS**: calculated $[M+Na]^+$ for $C_{30}H_{21}ONF_2Na$: 472.1483, found: 472.1483. **FTIR (cm^{-1}):** 3444, 3022, 2403, 2351, 2096, 1677, 1643, 1509, 1446, 1374, 1290, 1217, 1149, 1045, 931, 887, 773.

1-(2-(4-(Difluoromethyl)quinolin-2-yl)phenyl)-3-phenoxypropan-2-ol (11a)



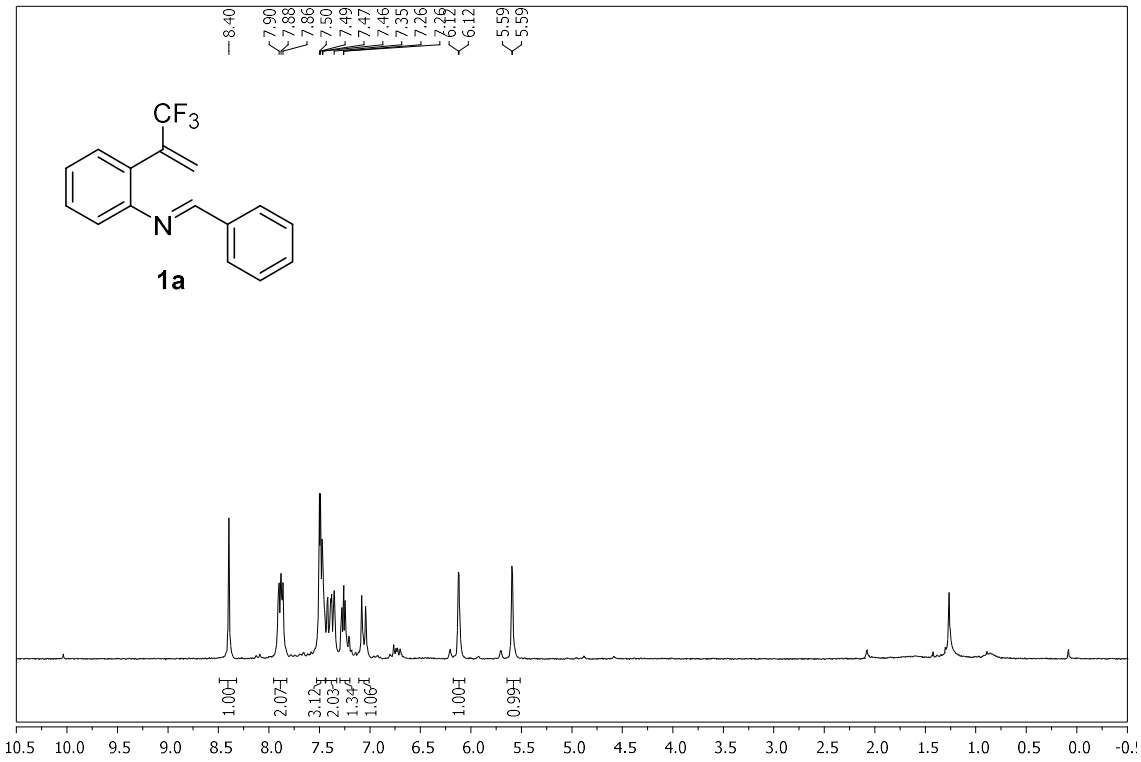
4-(difluoromethyl)-2-phenylquinoline **2a** (31.0 mg, 0.200 mmol), 2-(phenoxymethyl)oxirane (60.1 mg, 0.400 mmol) and $Pd(OAc)_2$ (4.49 mg, 0.0200 mmol) were taken in a flame dried round bottom flask with argon inlet. HFIP (0.80 mL) and acetic acid (0.20 mL) were added to it. The reaction suspension was stirred for 24 h at 25 °C under argon atmosphere. The reaction mixture was quenched with saturated aq. Na_2CO_3 (5.0 mL), and the mixture was extracted with ethyl acetate (3 x 25 mL). The organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude residue was purified by flash column chromatography (Pet. ether /EtOAc = 75/25) on silica gel to afford the corresponding 1-(2-(4-(difluoromethyl)quinolin-2-yl)phenyl)-3-phenoxypropan-2-ol **11a** (0.063 g, 72% yield) as a yellow solid**.**

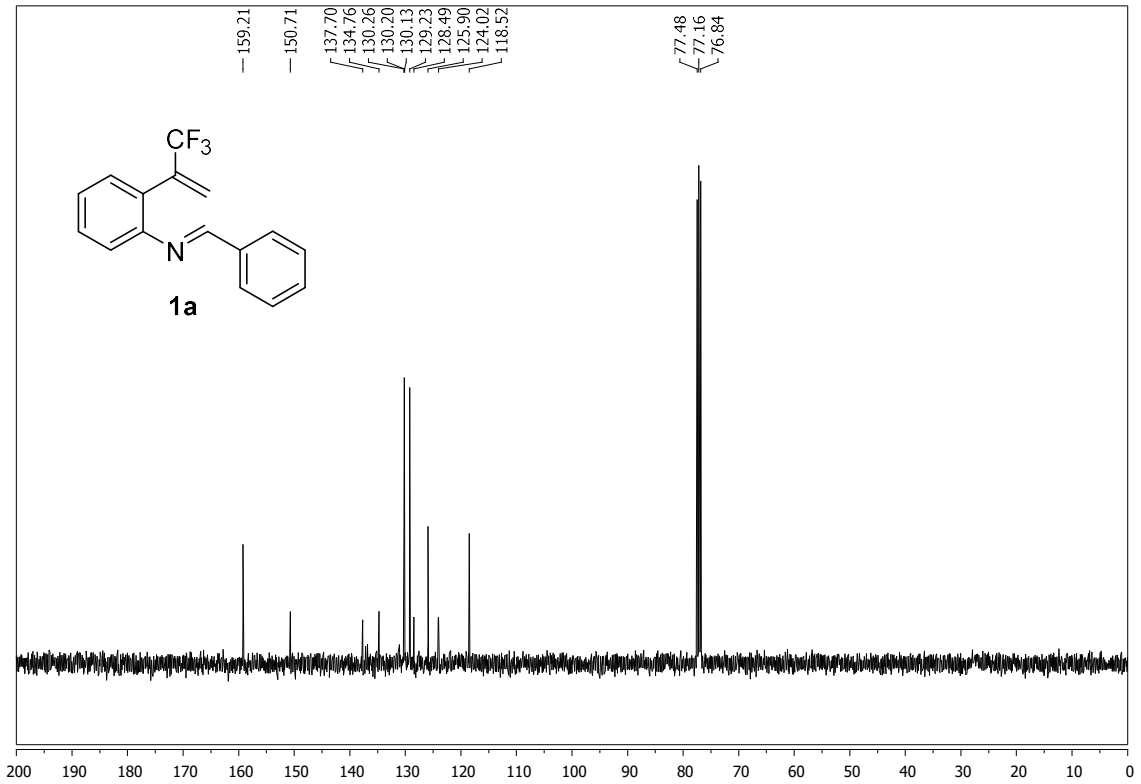
***R**f* (Pet. ether /EtOAc = 70/30): 0.19; **^{1}H NMR ($CDCl_3$, 400 MHz)** δ 8.33 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.91 (s, 1H), 7.85-7.82 (m, 1H), 7.73-7.70 (s, 1H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.53-7.48 (m, 2H), 7.44-7.41 (m, 1H), 7.33-7.11 (m, 4H), 6.94 (t, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 4.40-4.37 (m, 1H), 4.18-4.16 (m, 1H), 4.05-4.02 (m, 1H), 3.21-3.16 (m, 1H),

3.10-3.06 (m, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz)** δ 159.11, 158.37, 146.69, 139.17, 137.97, 131.79, 131.06, 130.53, 129.93, 129.54, 129.45, 128.32, 127.01, 123.35, 122.88, 120.85, 119.87 (t, $J_{C\text{-}F}$ = 7.8 Hz), 114.73, 113.29 (t, $J_{C\text{-}F}$ = 240.9 Hz), 71.99, 71.79, 36.80, 29.82. **HRMS**: calculated $[M+H]^+$ for $C_{25}H_{22}O_2NF_2$: 406.1613, found: 406.1612. **FTIR (cm^{-1}):** 3431, 2921, 2864, 2404, 2094, 1637, 1620, 1601, 1558, 1496, 1467, 1425, 1378, 1340, 1317, 1290, 1246, 1173, 1117, 1079, 1045, 950, 920, 882, 836, 754, 739.

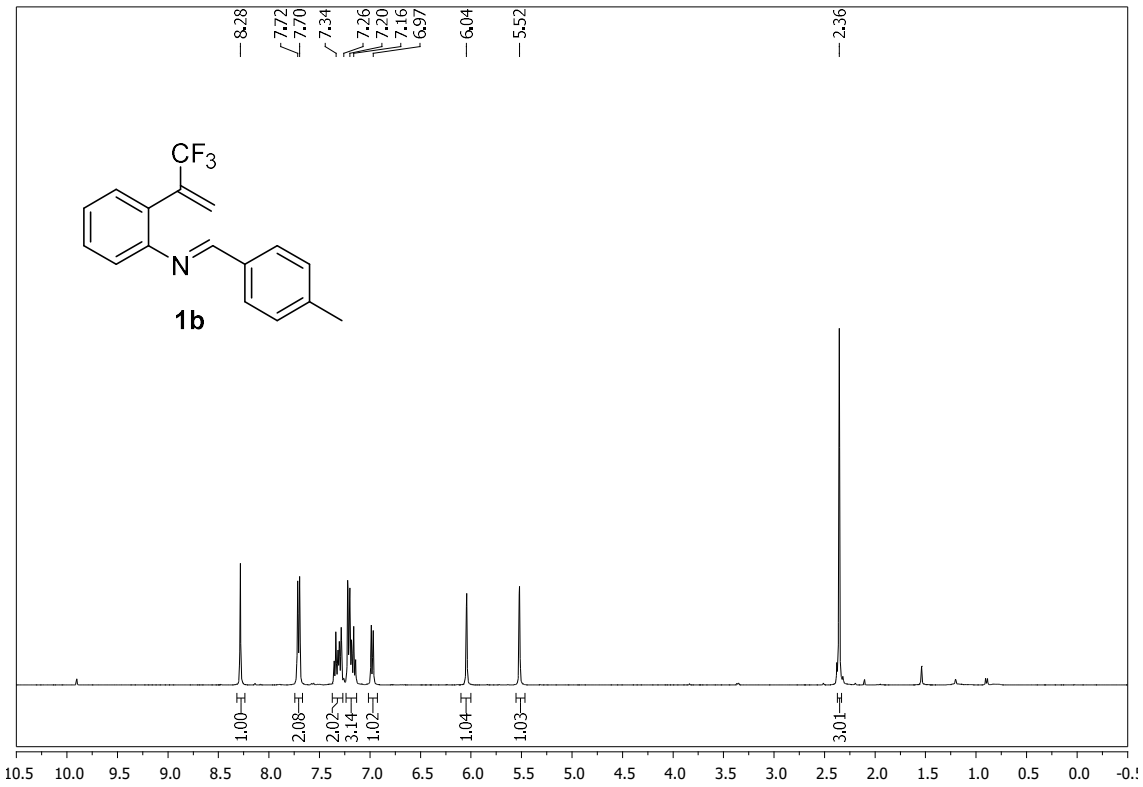
10.^{1}H and ^{13}C NMR Spectra of Aldimines

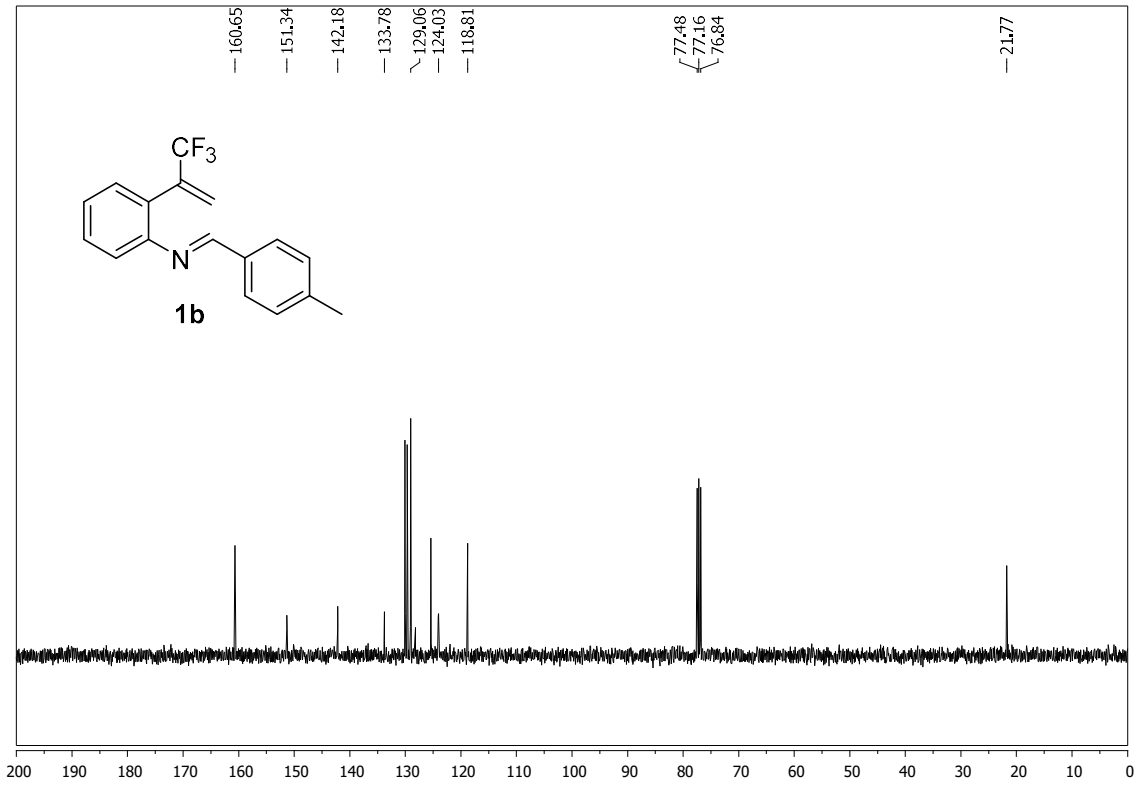
(*E*)-N-Benzylidene-2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine (1a)



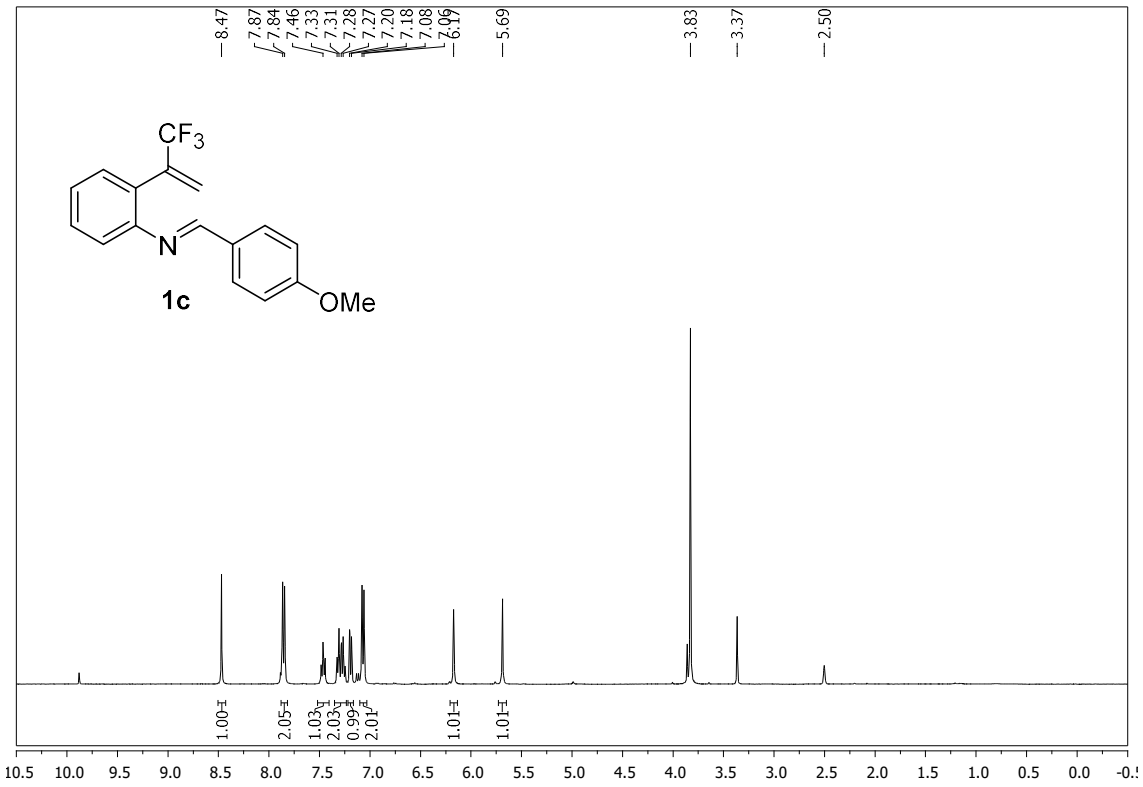


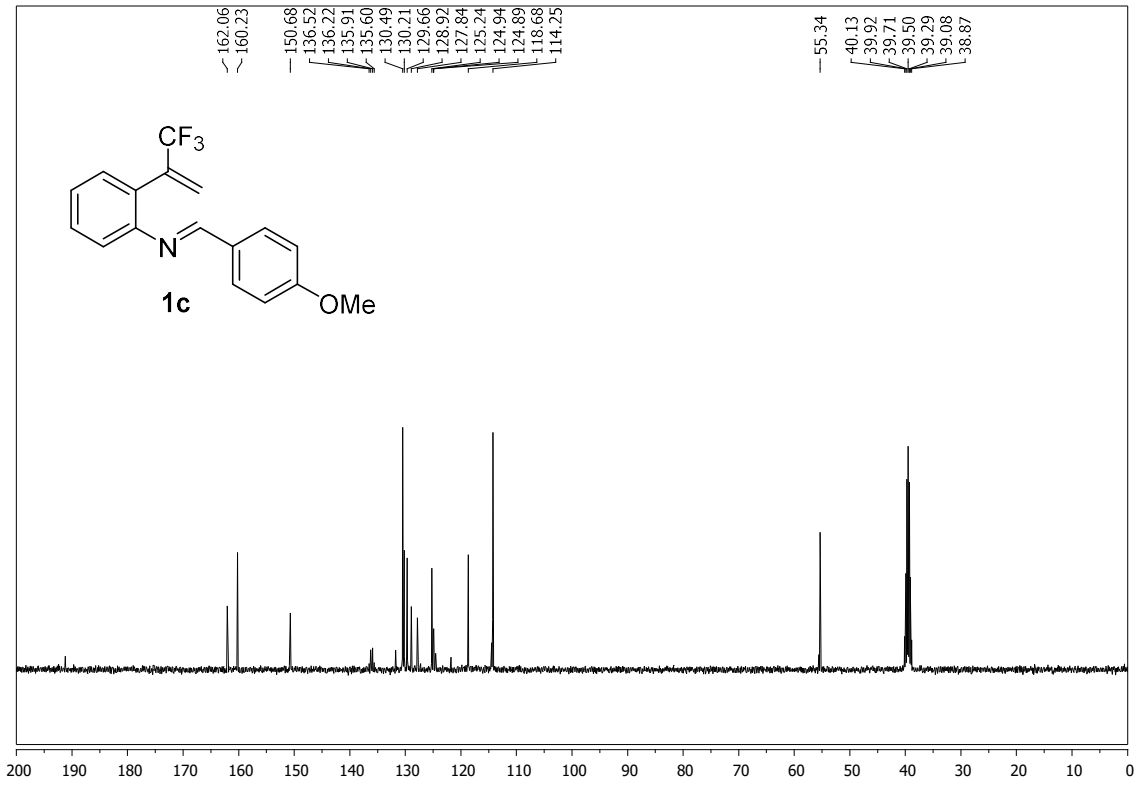
(*E*)-1-*p*-Tolyl-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine (1b)



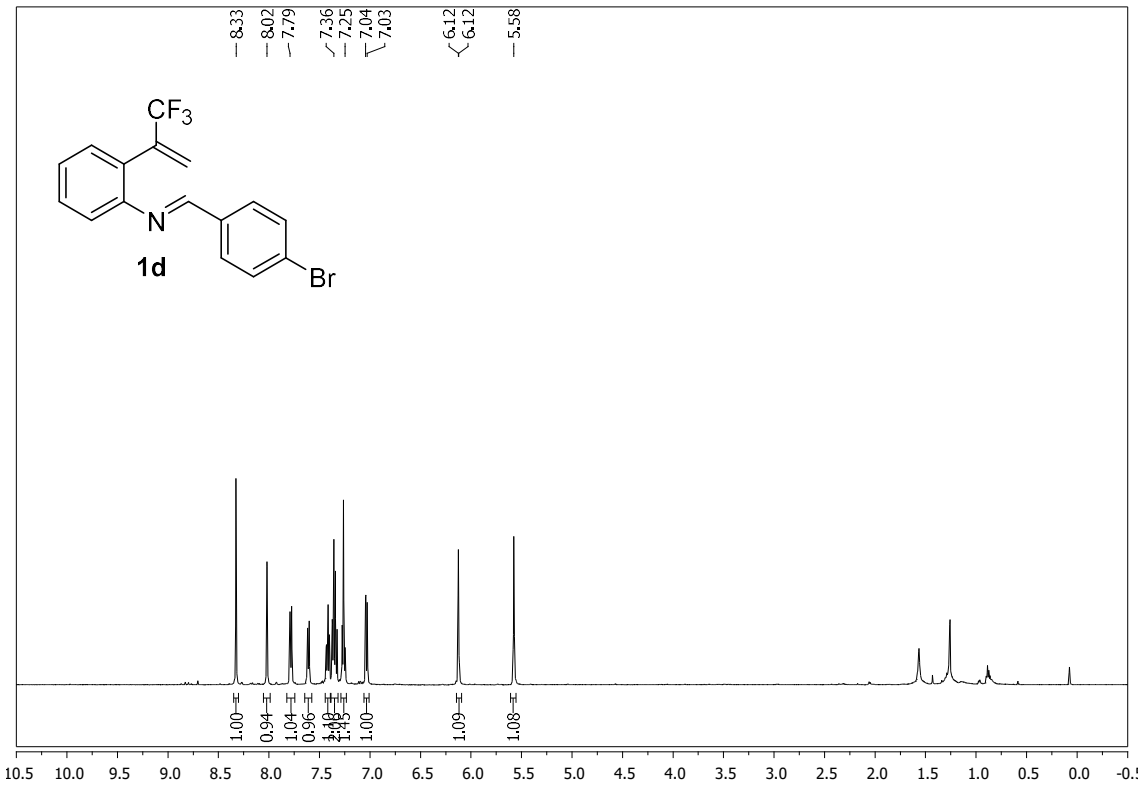


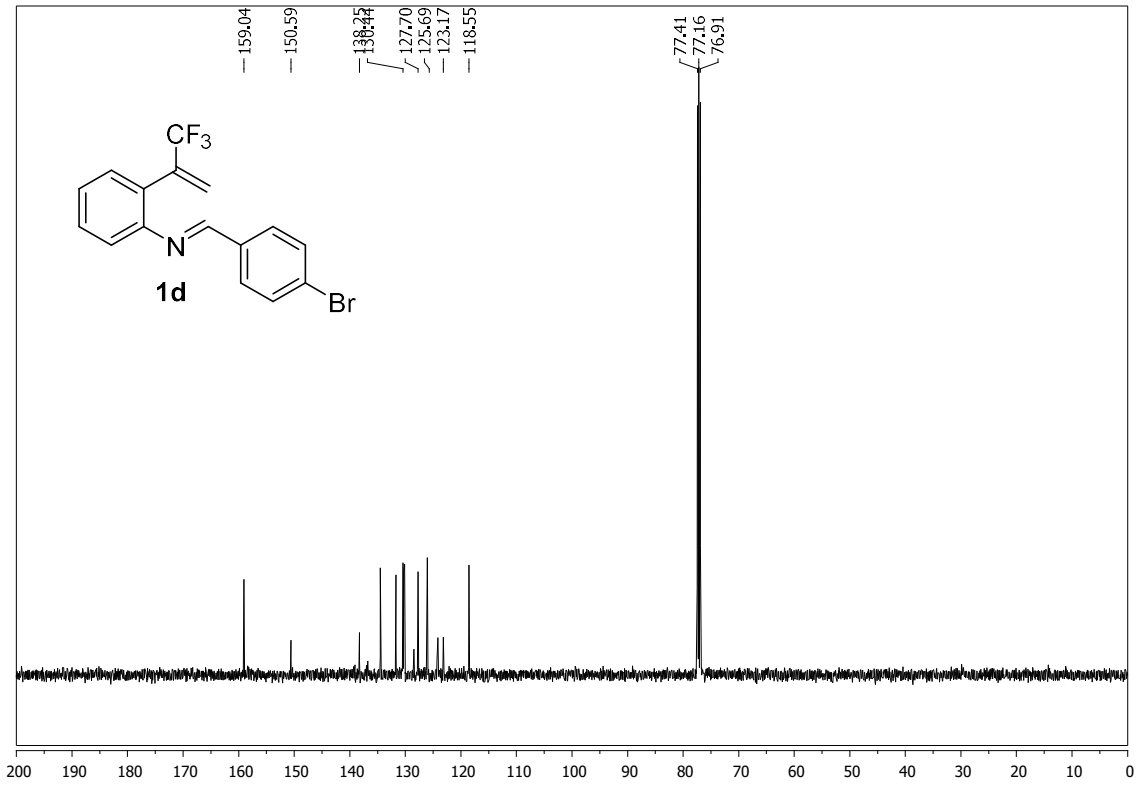
(*E*)-N-(4-Methoxybenzylidene)-2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine (1c)



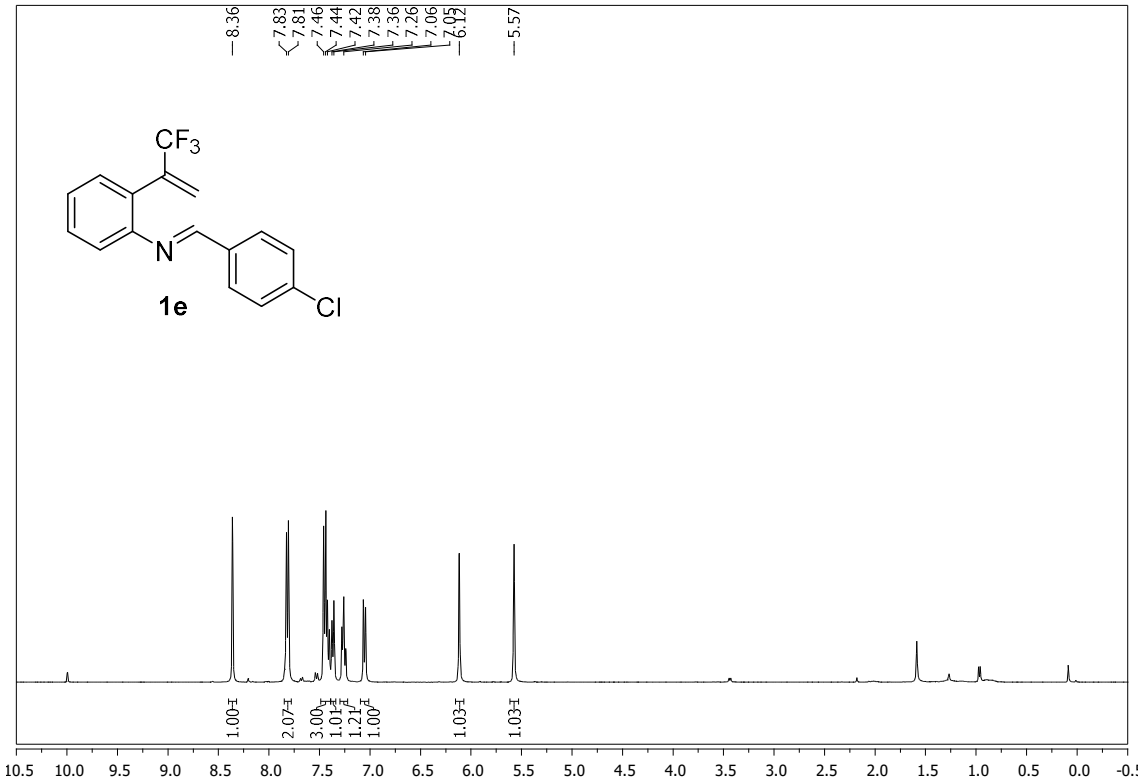


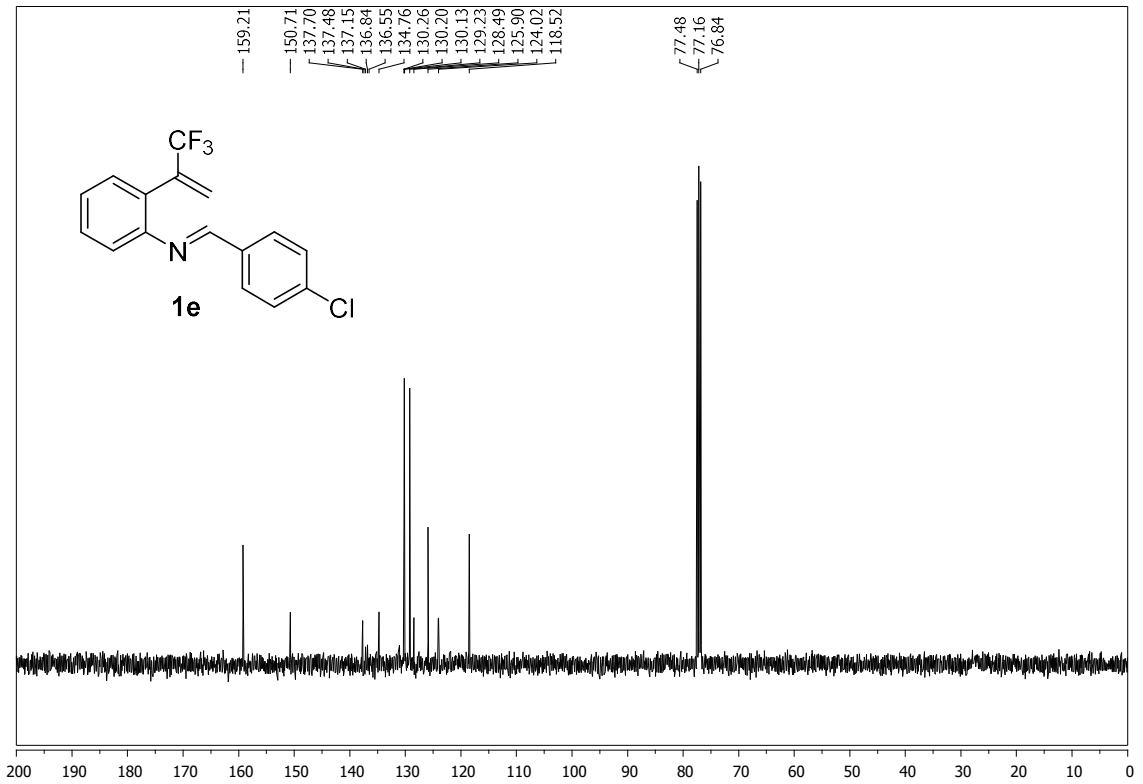
(*E*)-1-(4-Bromophenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine (1d)



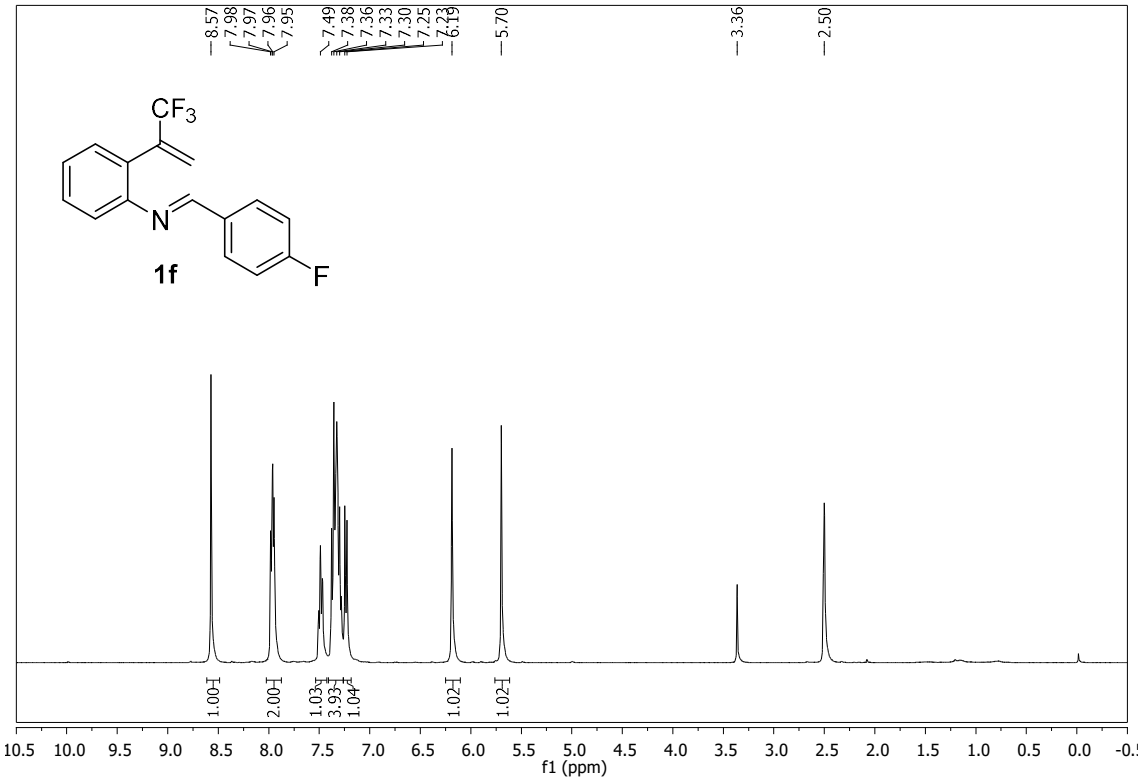


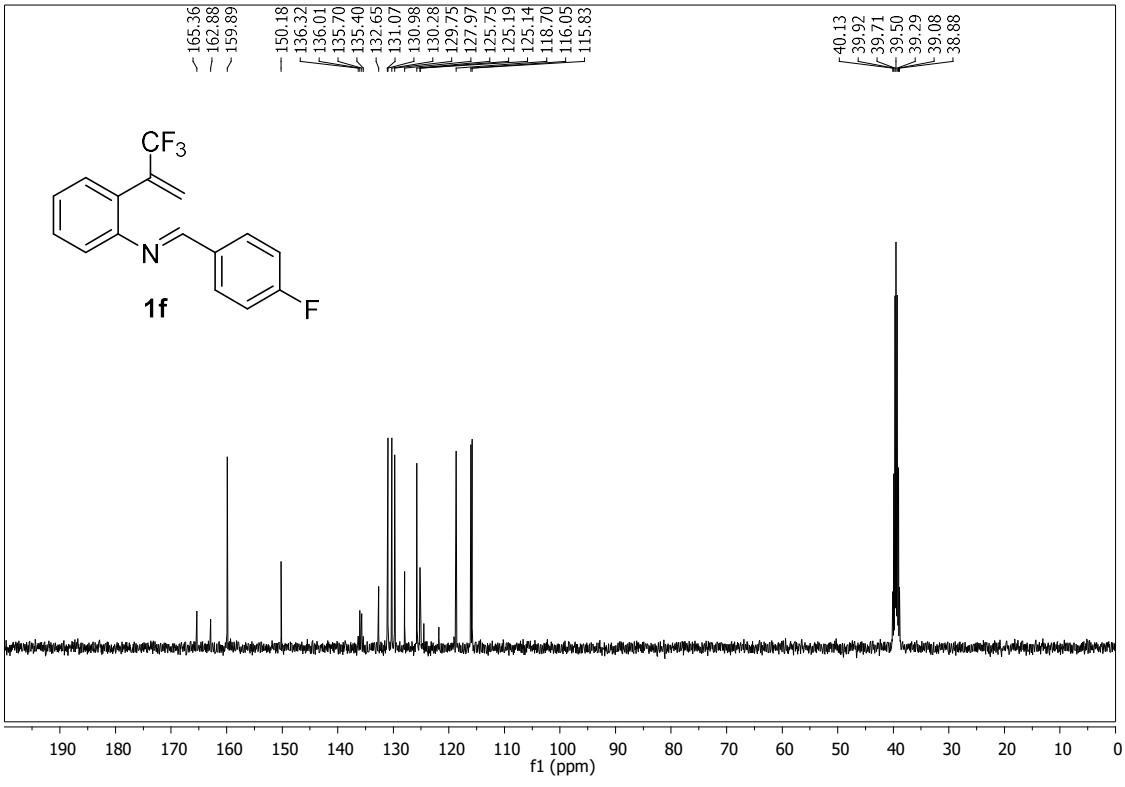
(*E*)-1-(4-Chlorophenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine (1e)



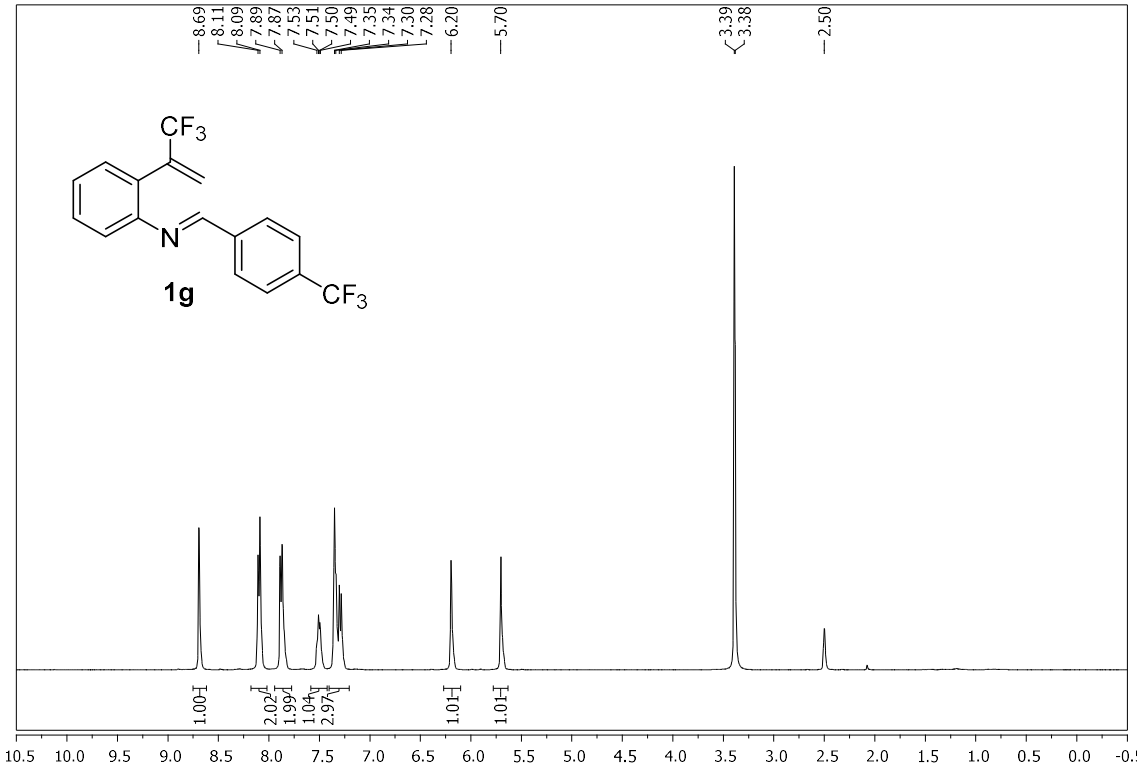


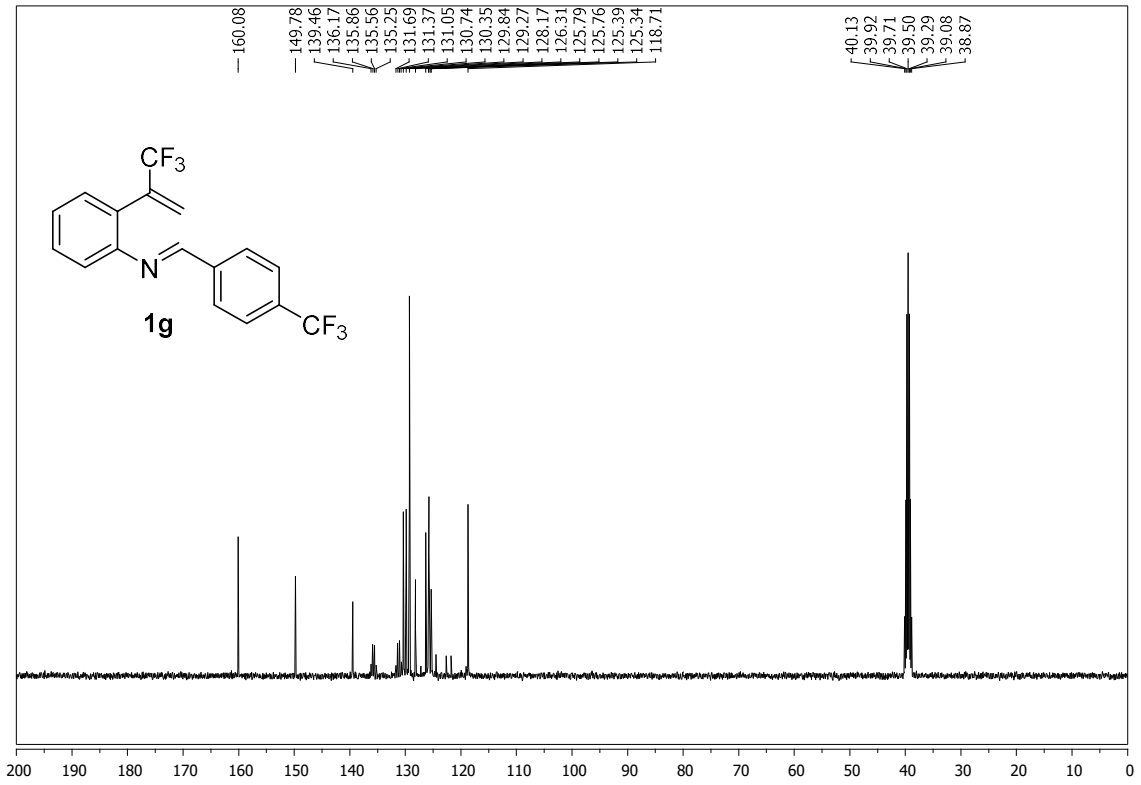
(*E*)-N-(4-Fluorobenzylidene)-2-(1,1,1-trifluoroprop-2-en-2-yl)benzenamine (1f)



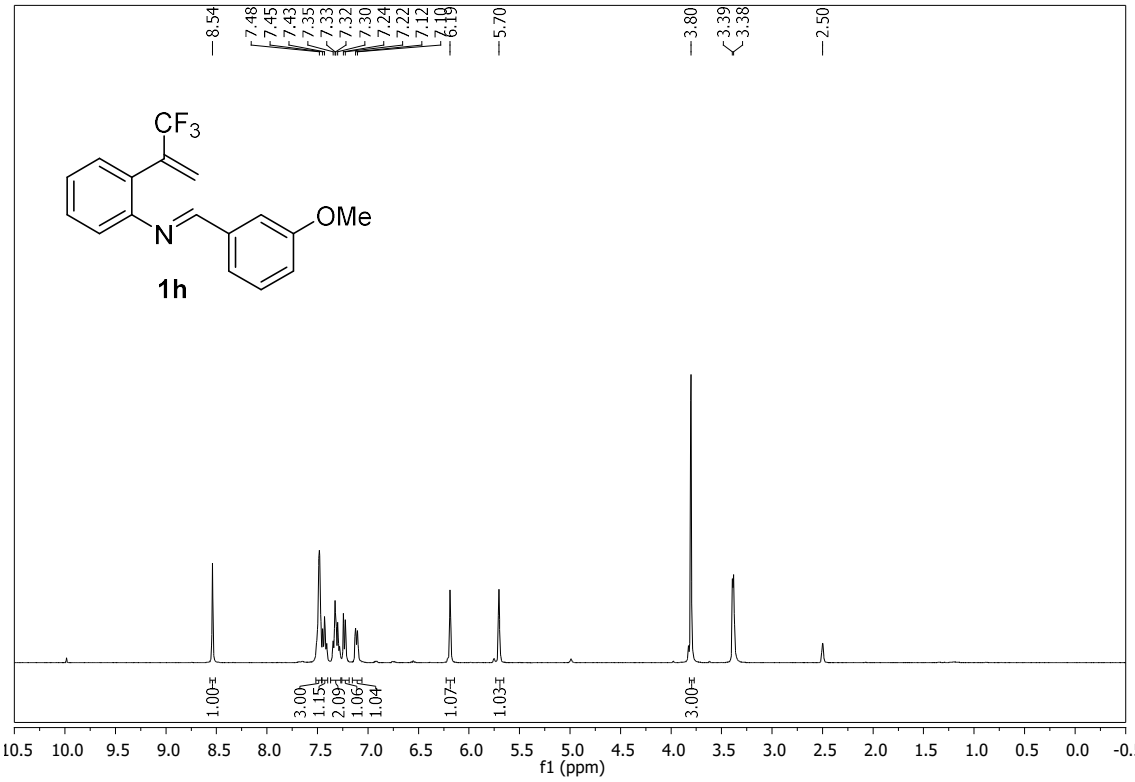


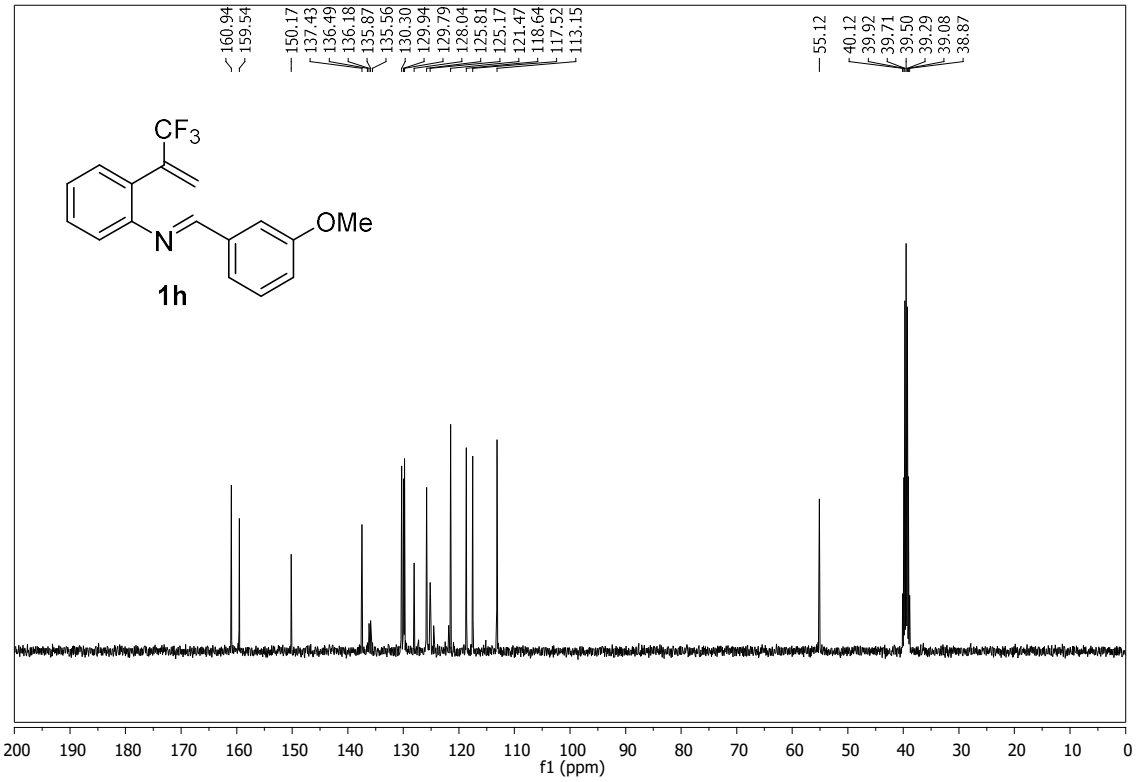
(*E*)-1-(4-(Trifluoromethyl)phenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine (1g)



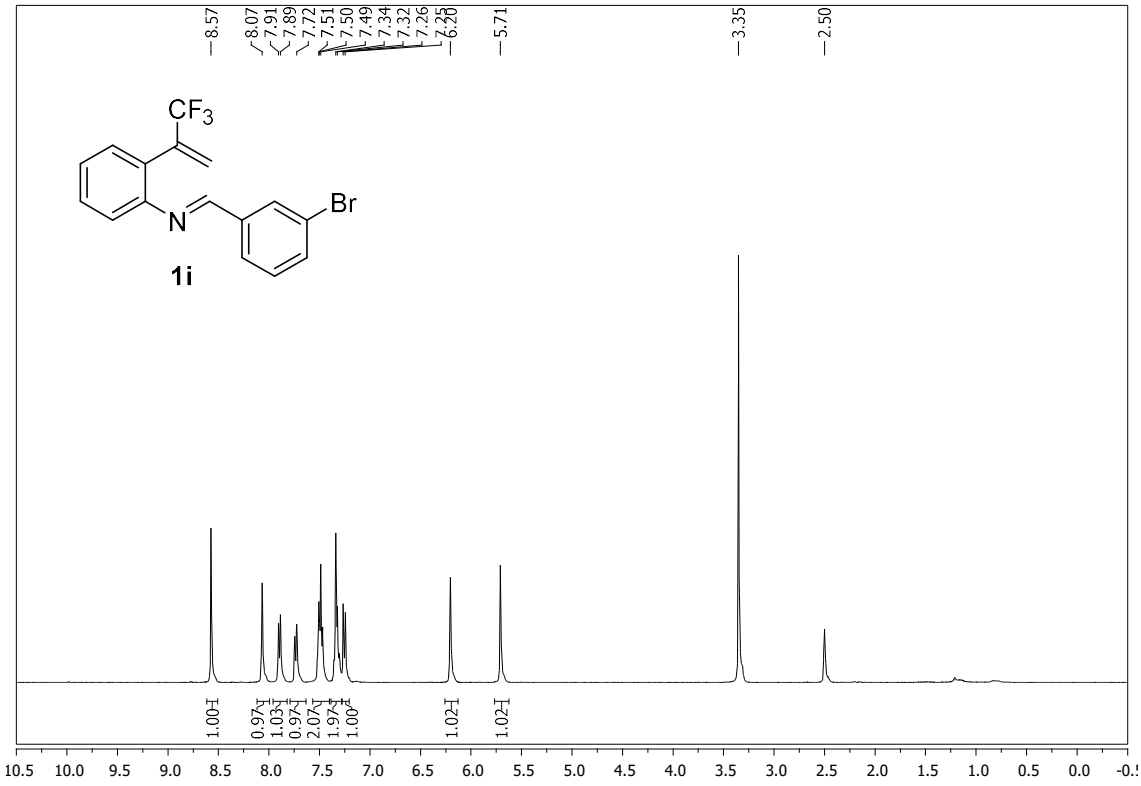


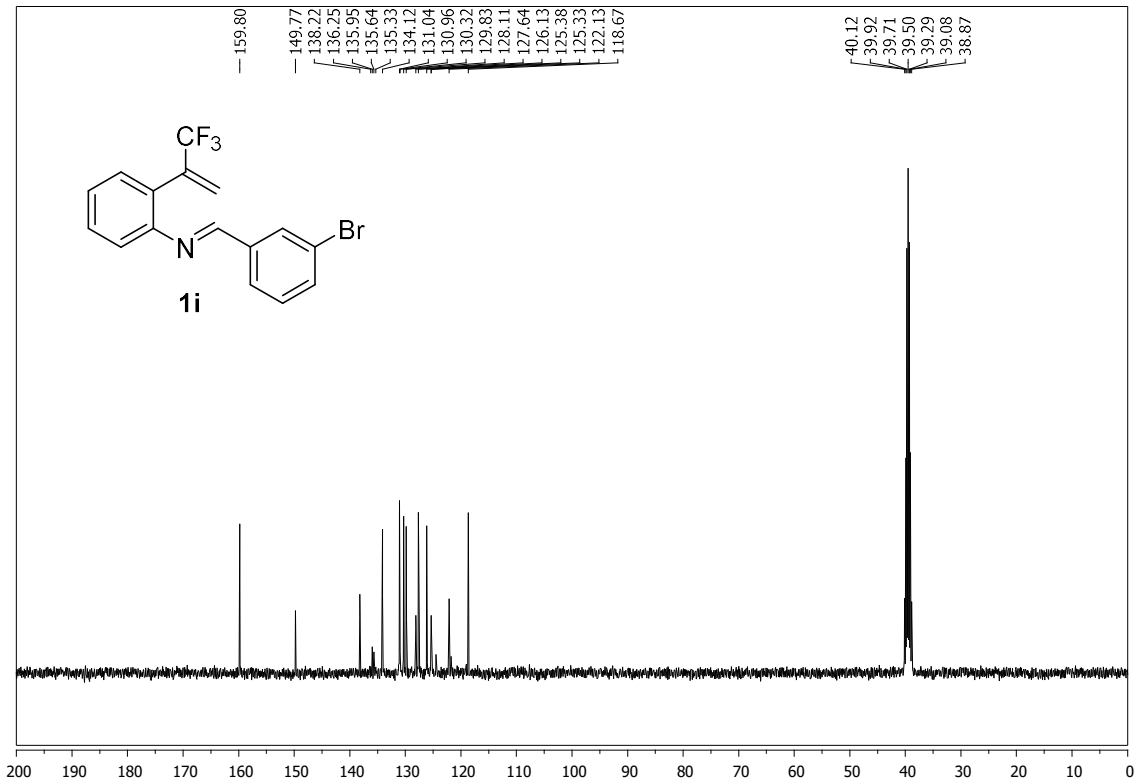
***E*)-1-(3-Methoxyphenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine (1h)**



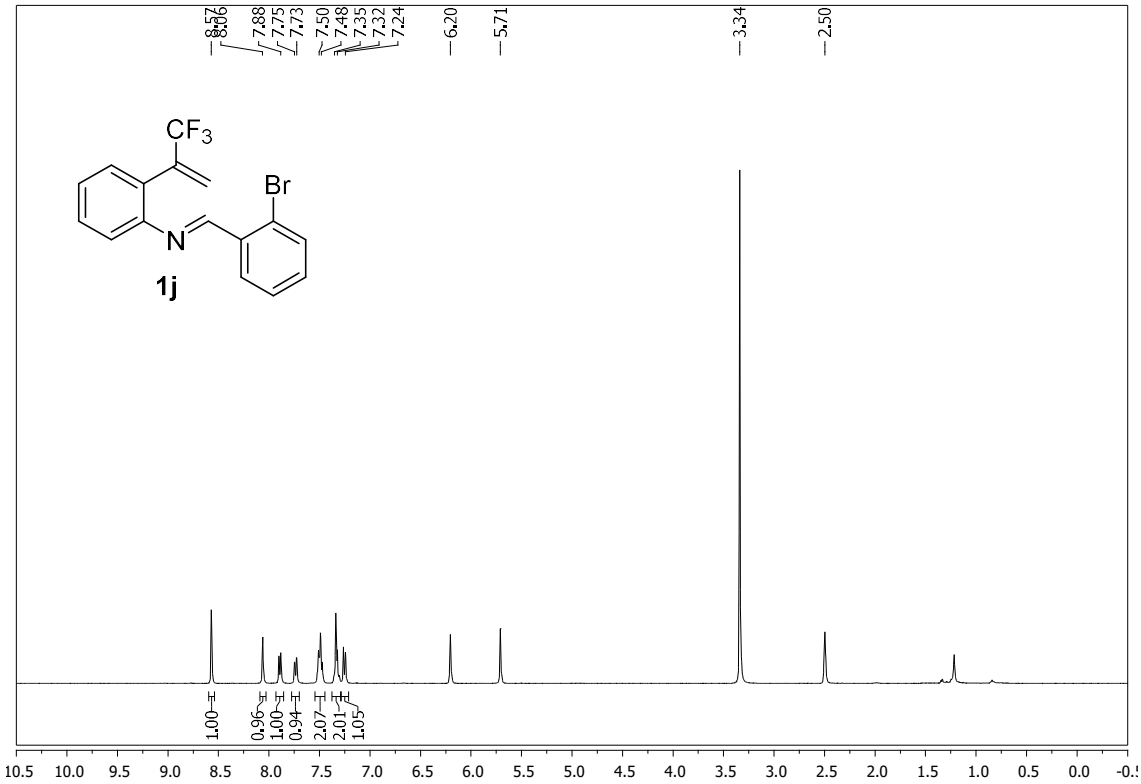


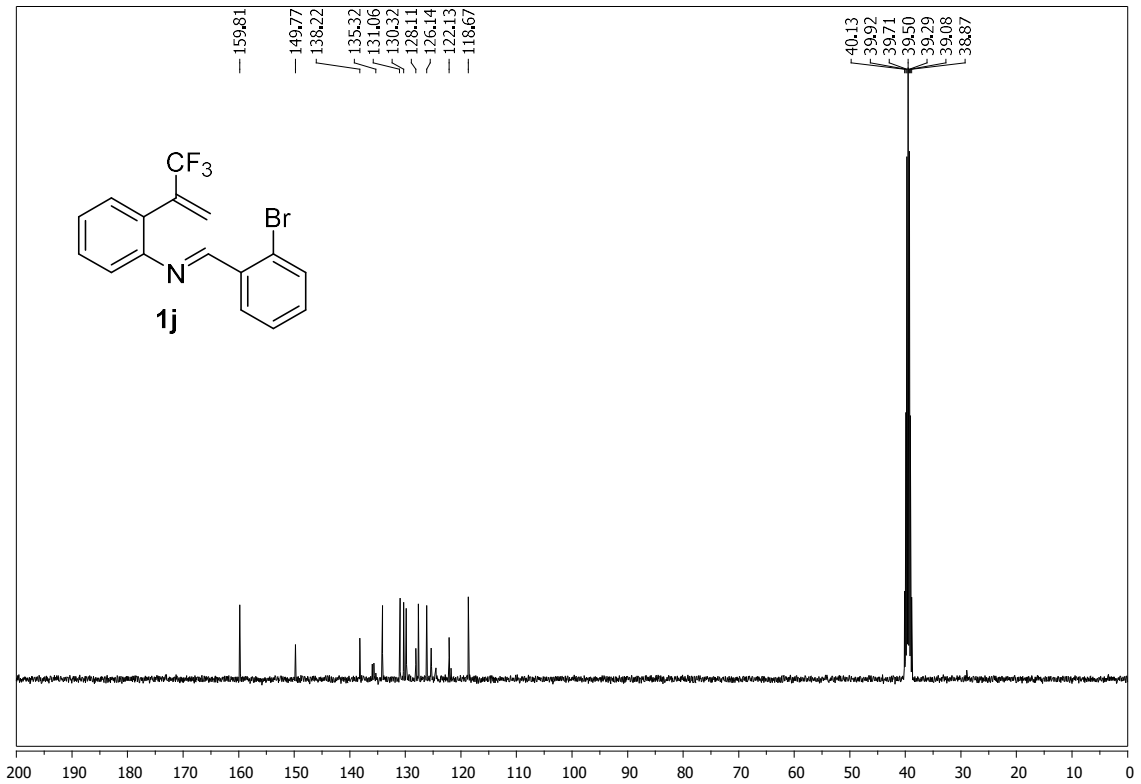
(*E*)-1-(3-Bromophenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine (1i)



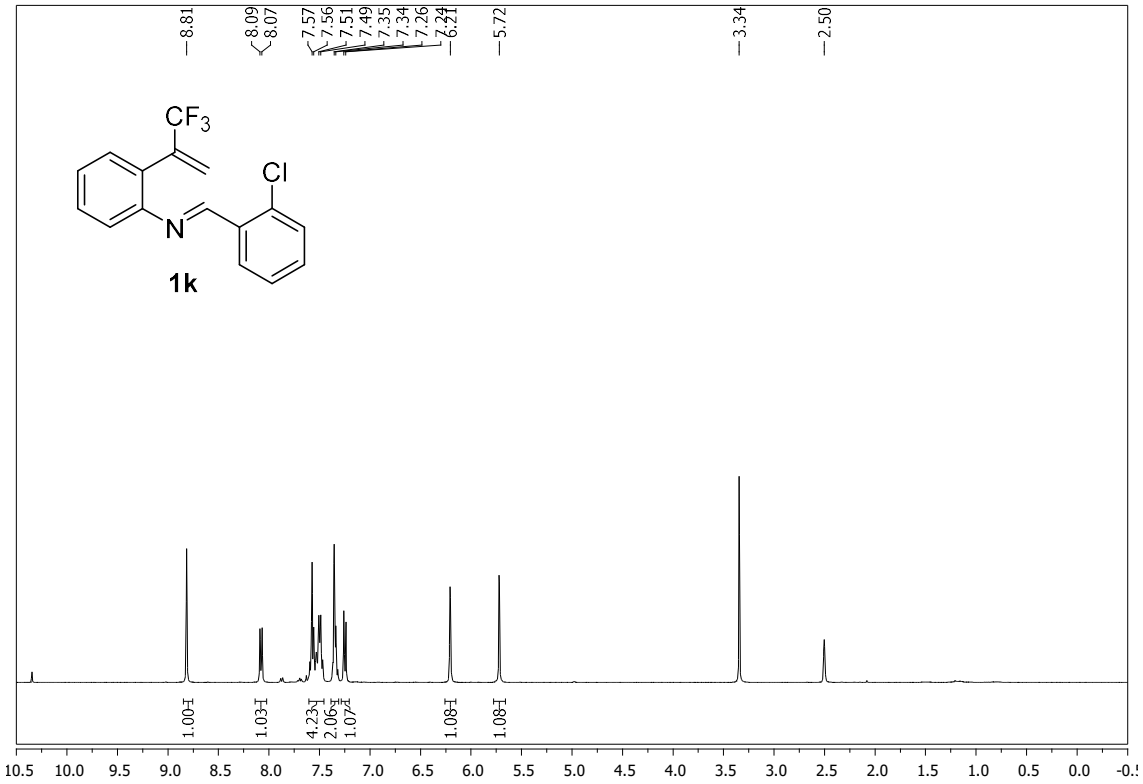


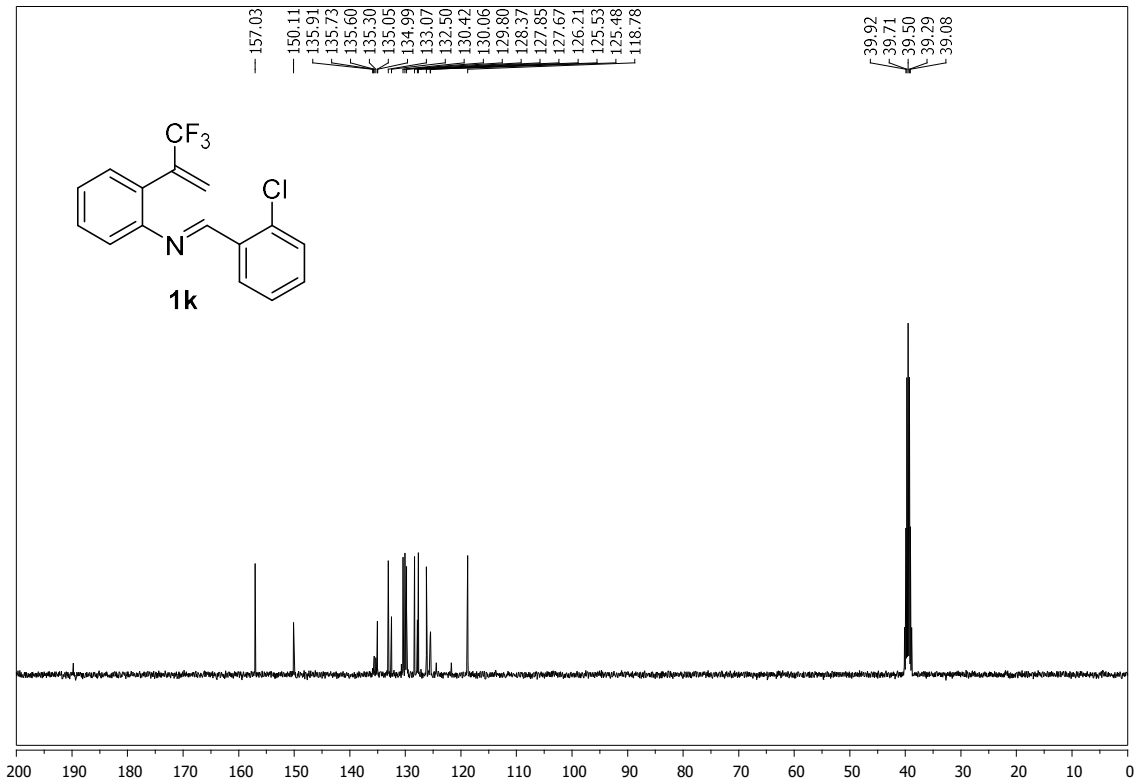
(*E*)-1-(2-Bromophenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine (1j)



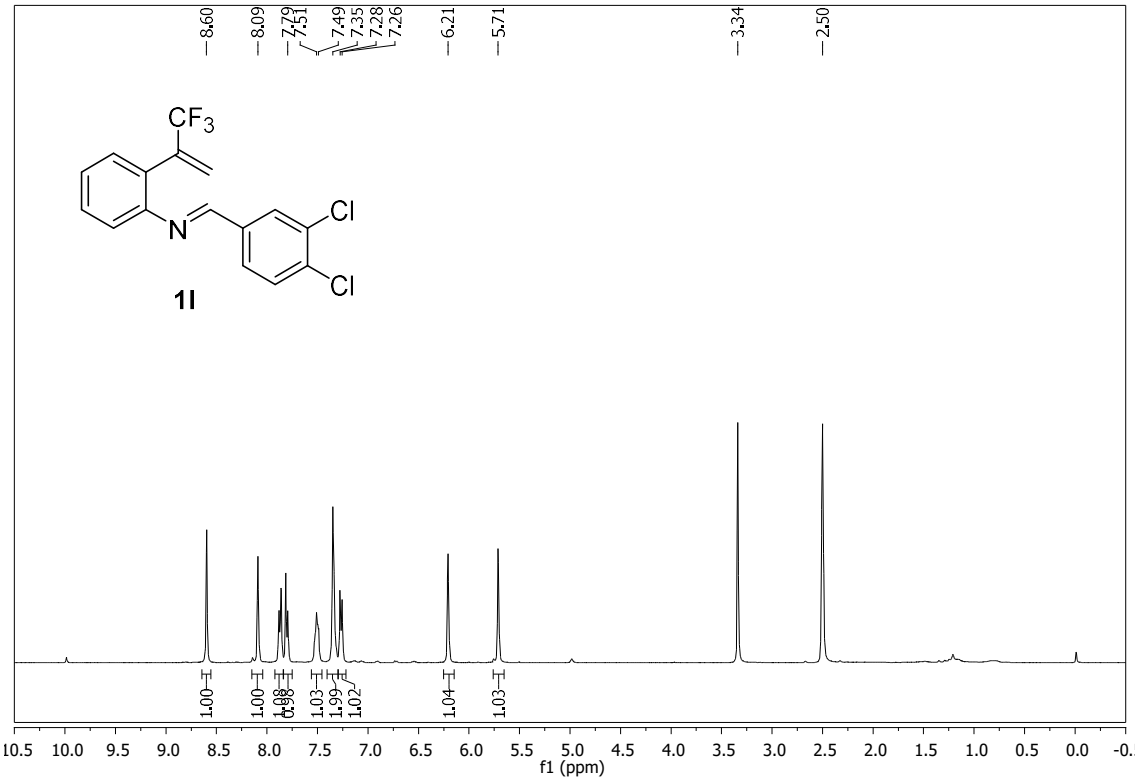


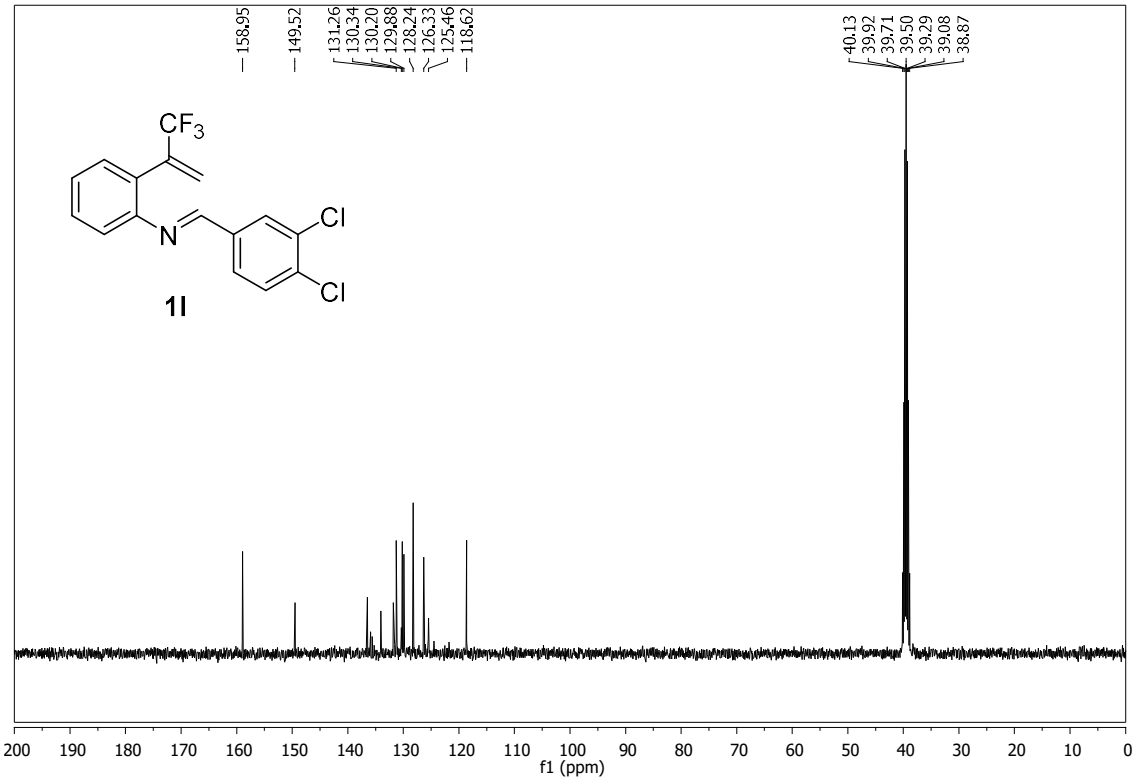
(*E*)-1-(2-Chlorophenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine (1k)



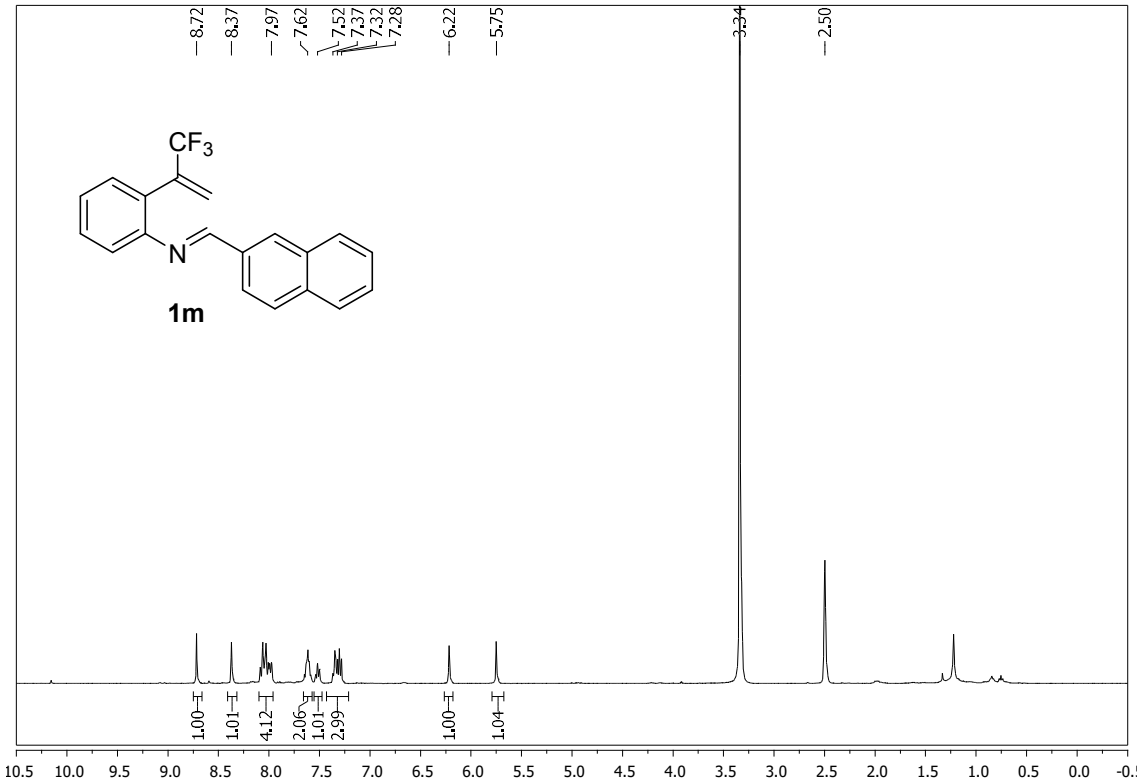


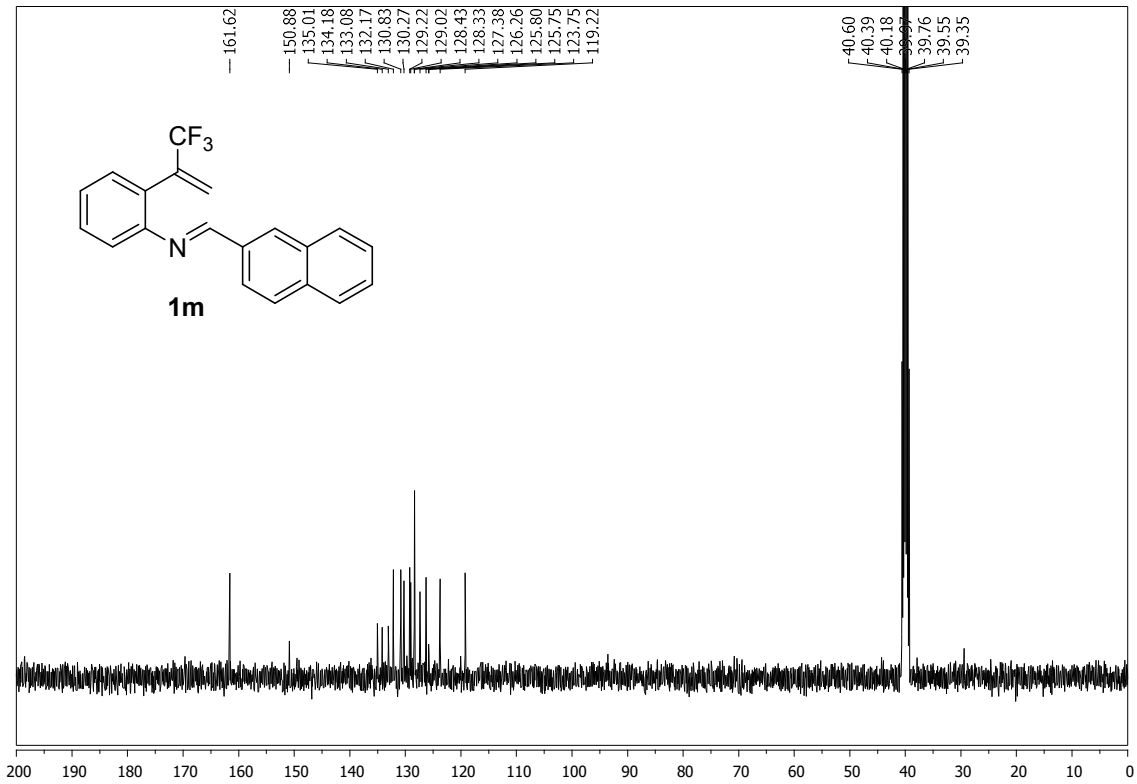
(*E*)-1-(3,4-Dichlorophenyl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine (1l)



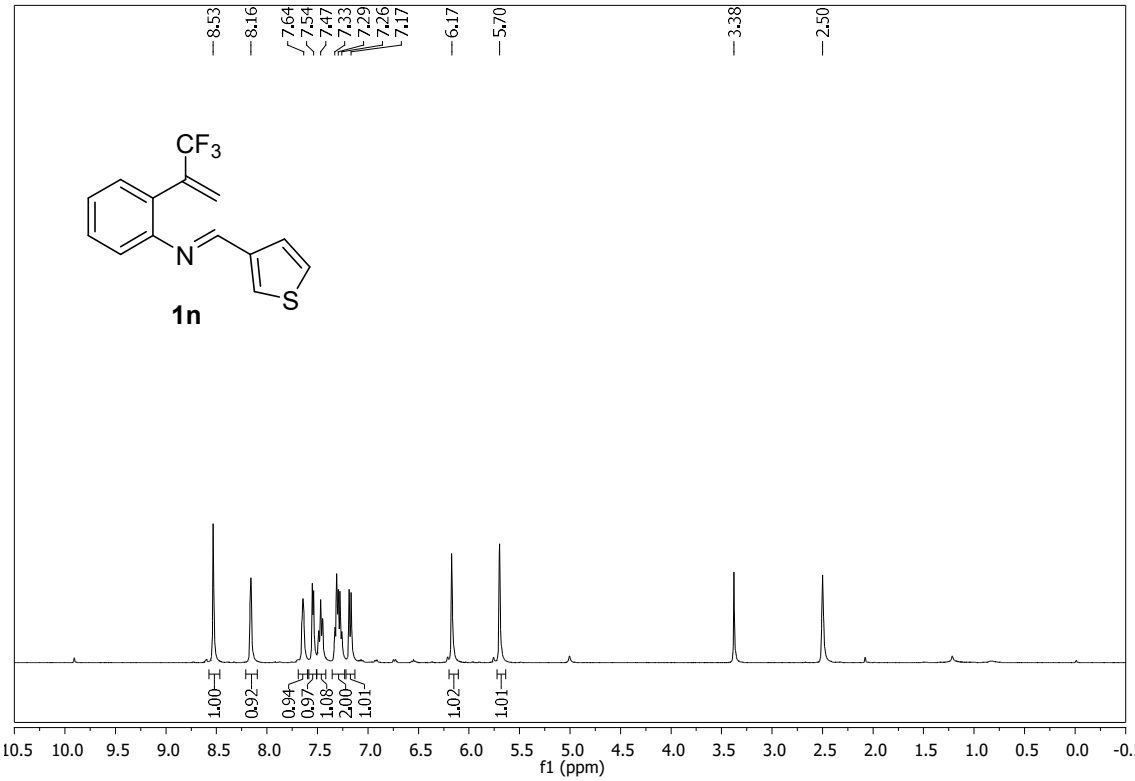


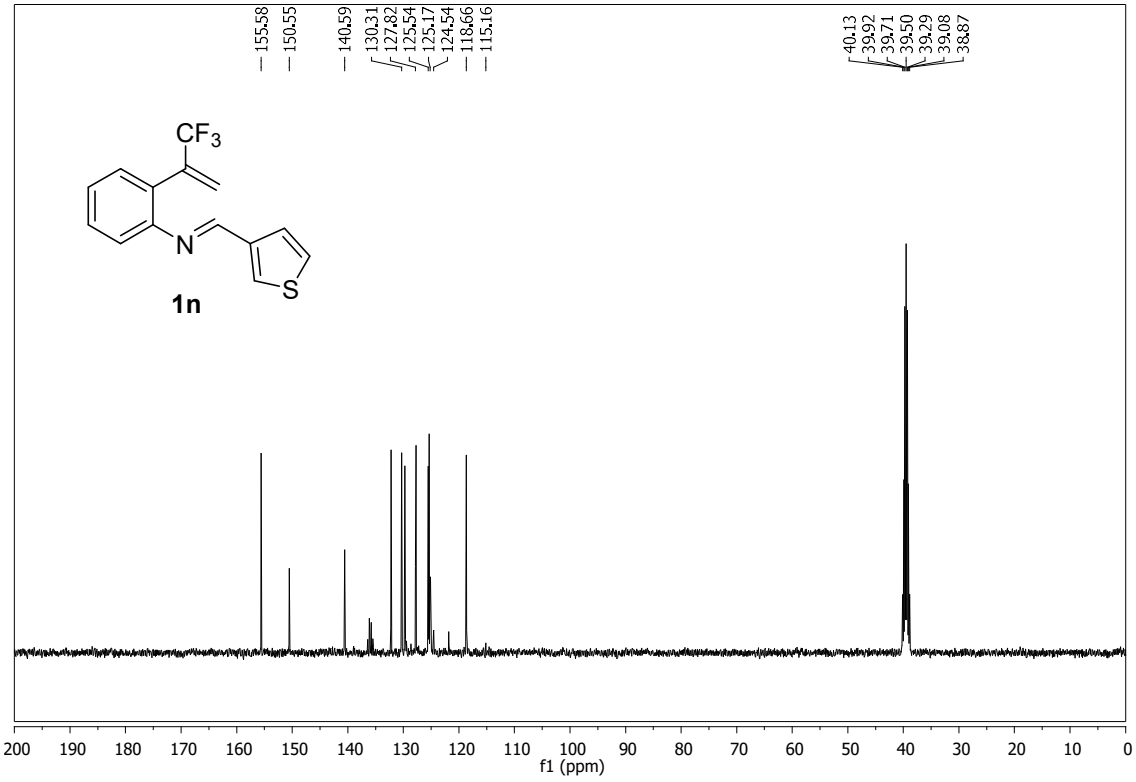
(*E*)-1-(Naphthalen-2-yl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine (1m)



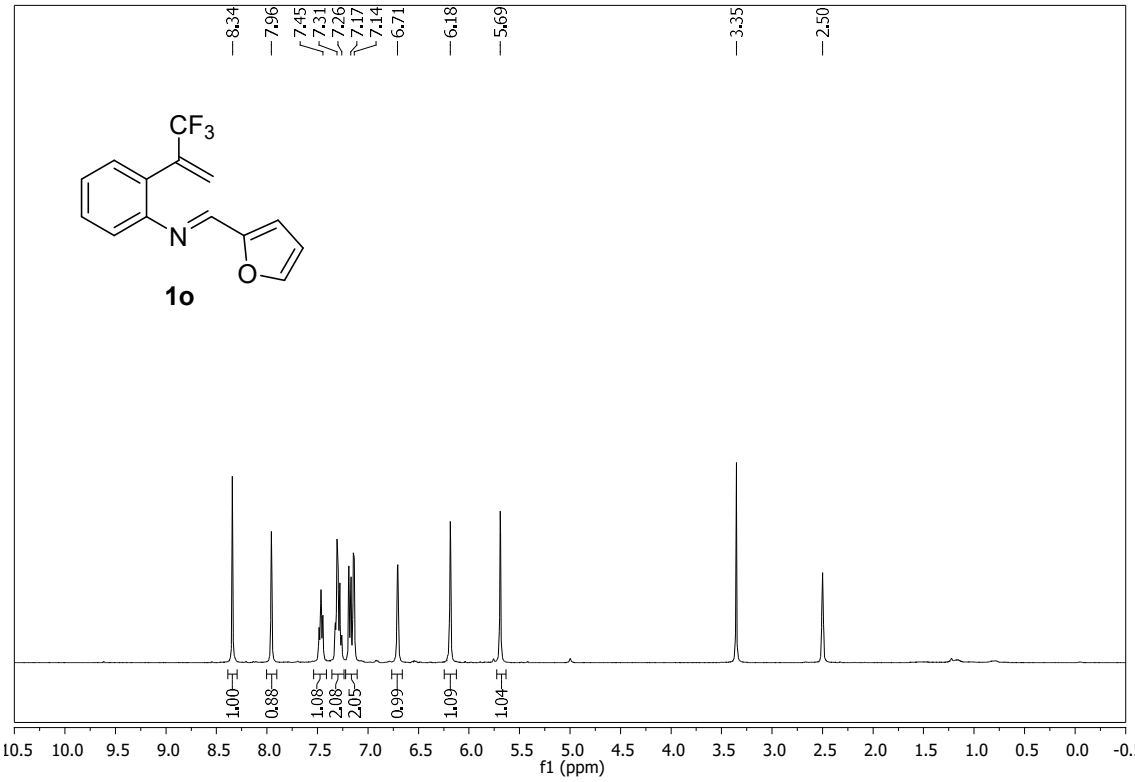


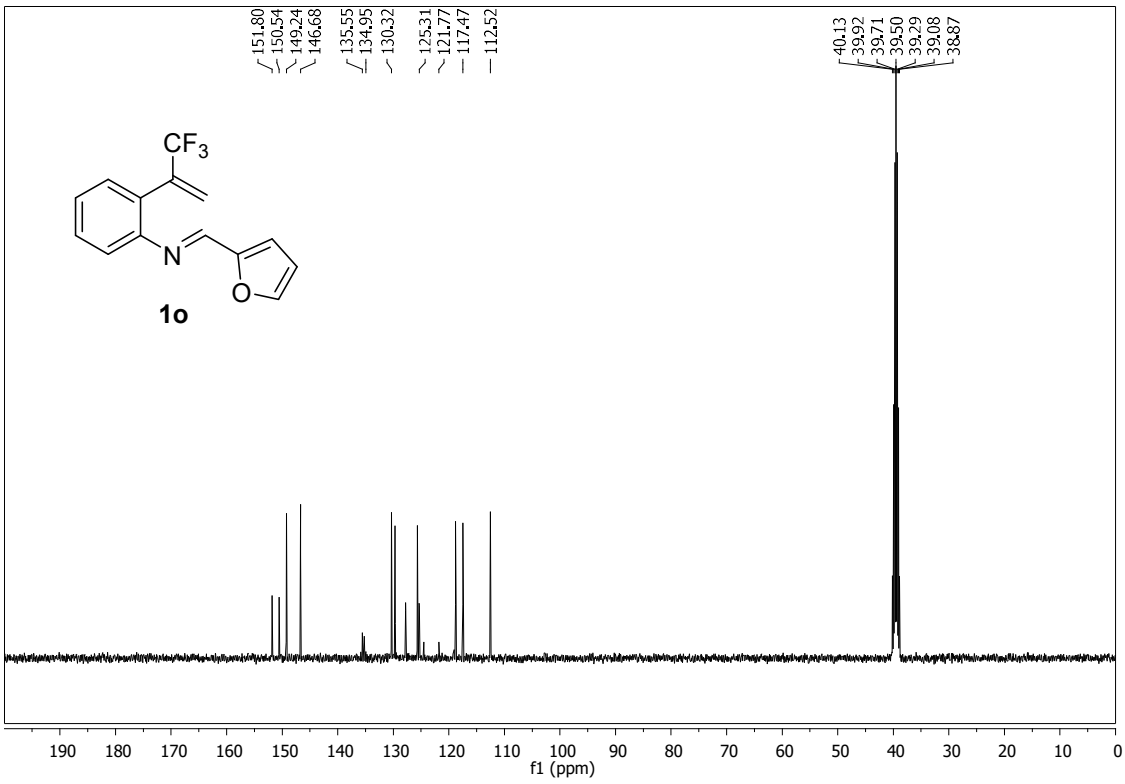
(*E*)-1-(Thiophen-3-yl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine (1n)



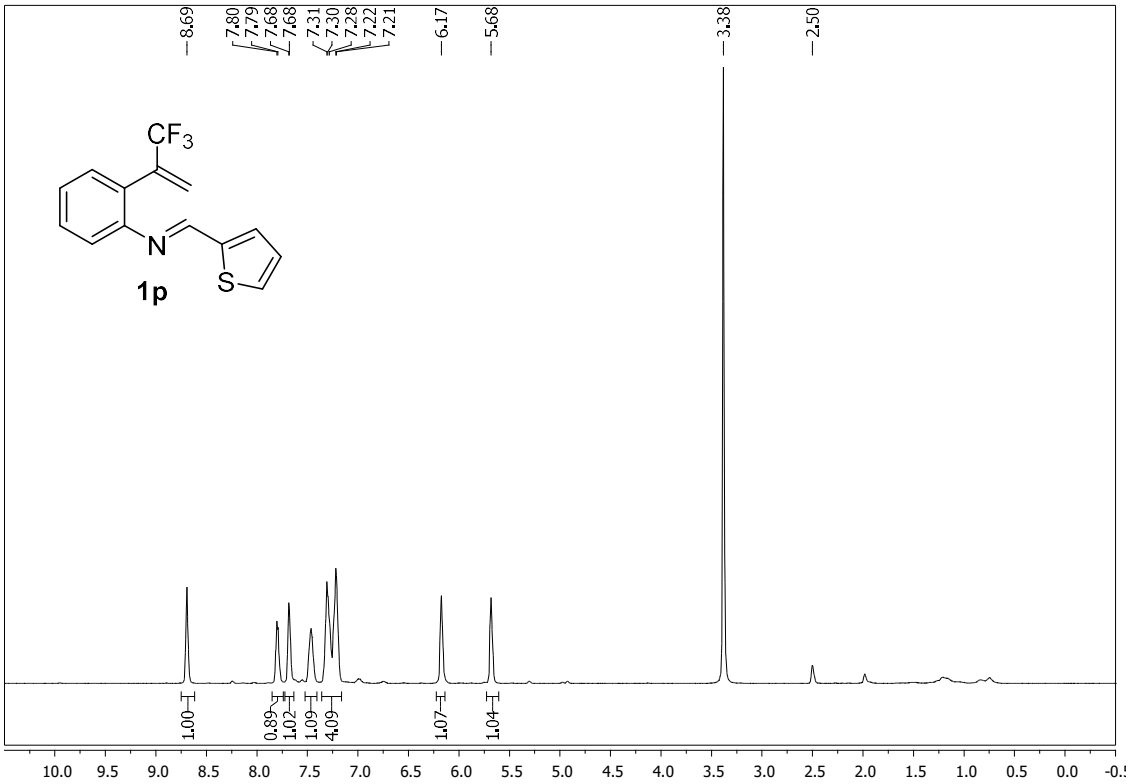


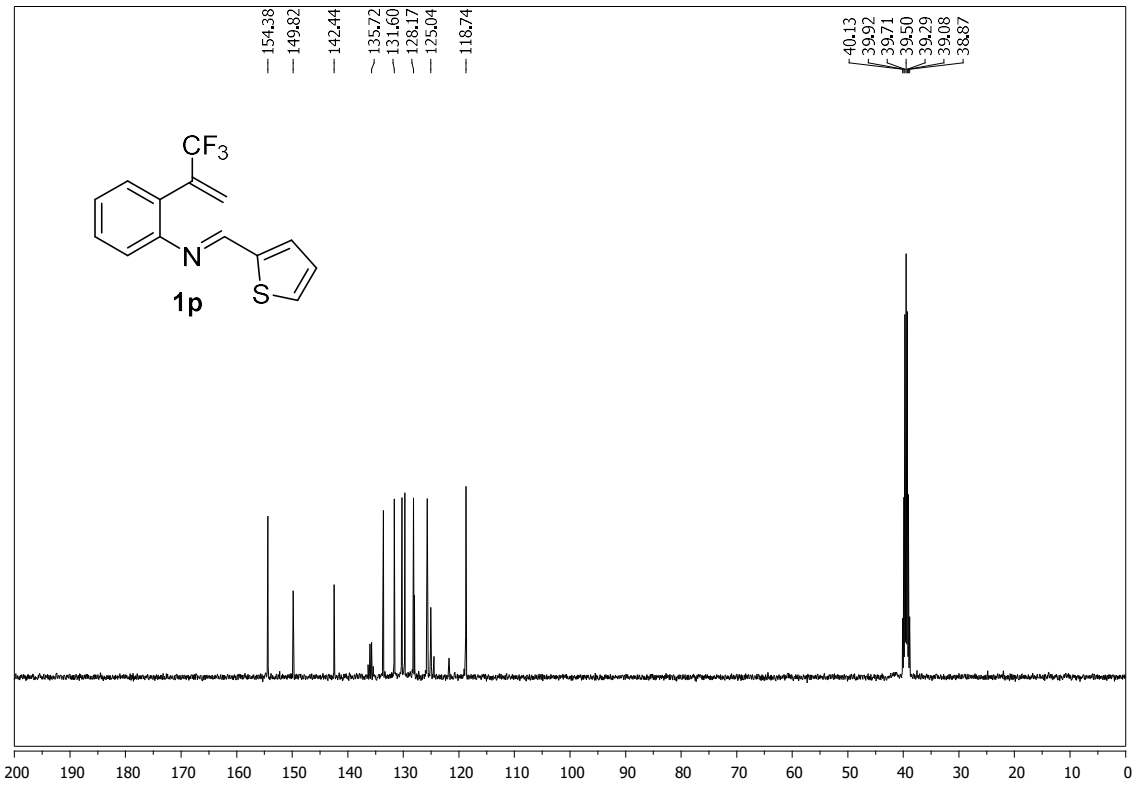
(*E*)-1-(Furan-2-yl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine (1o)



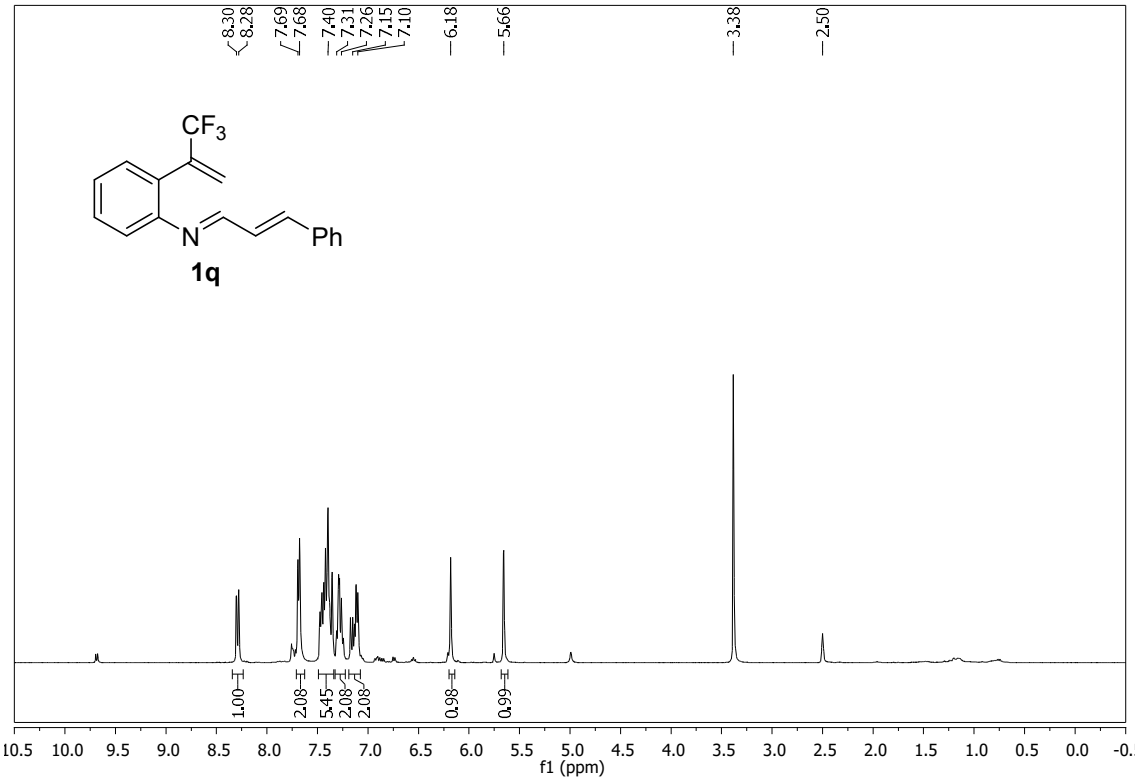


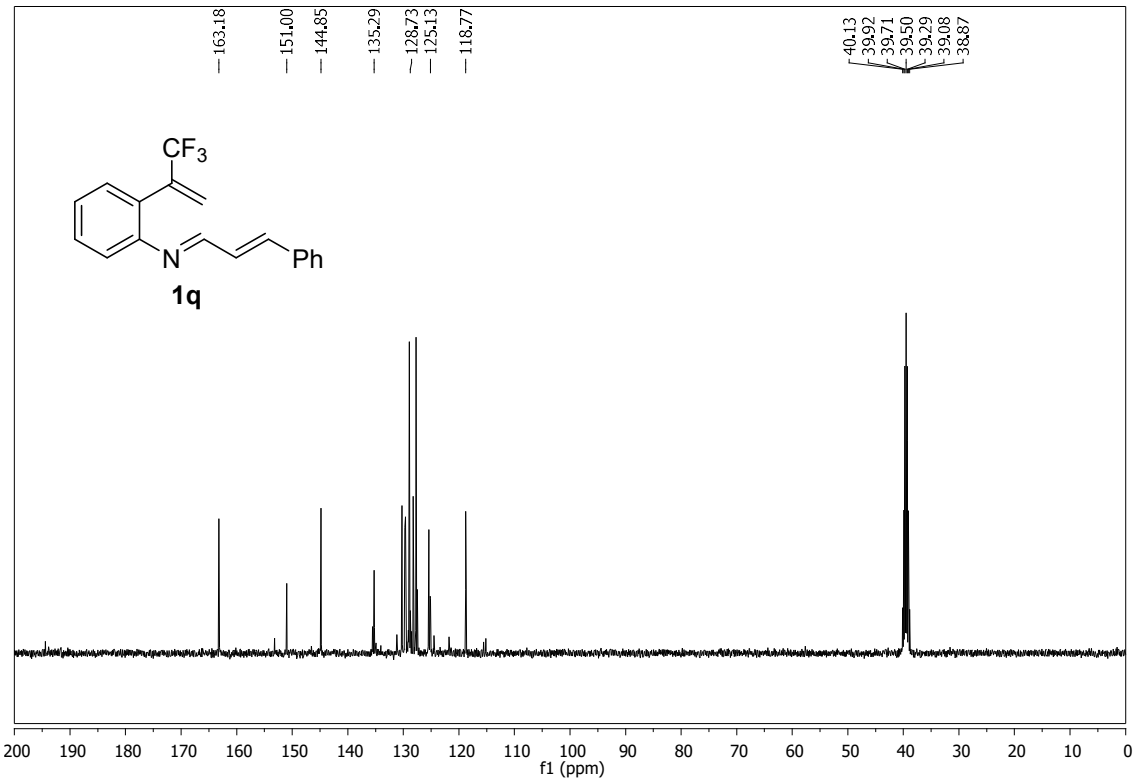
(*E*)-1-(Thiophen-2-yl)-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)methanimine (1p)



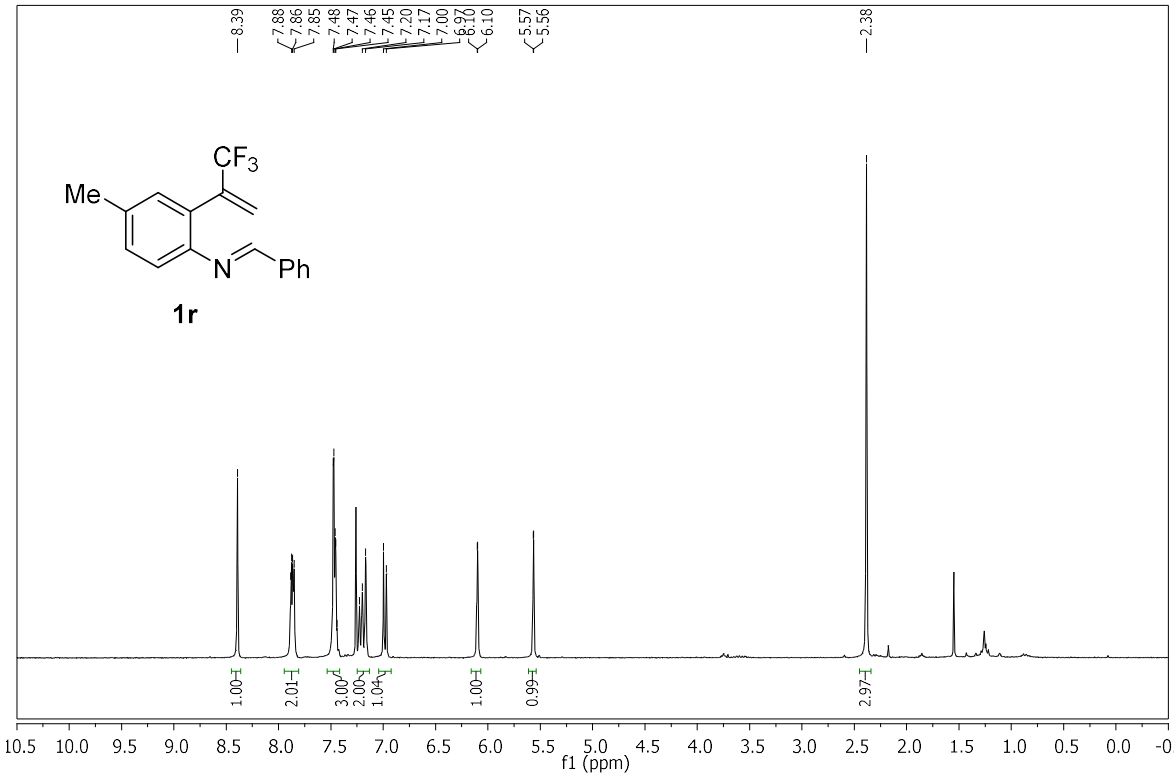


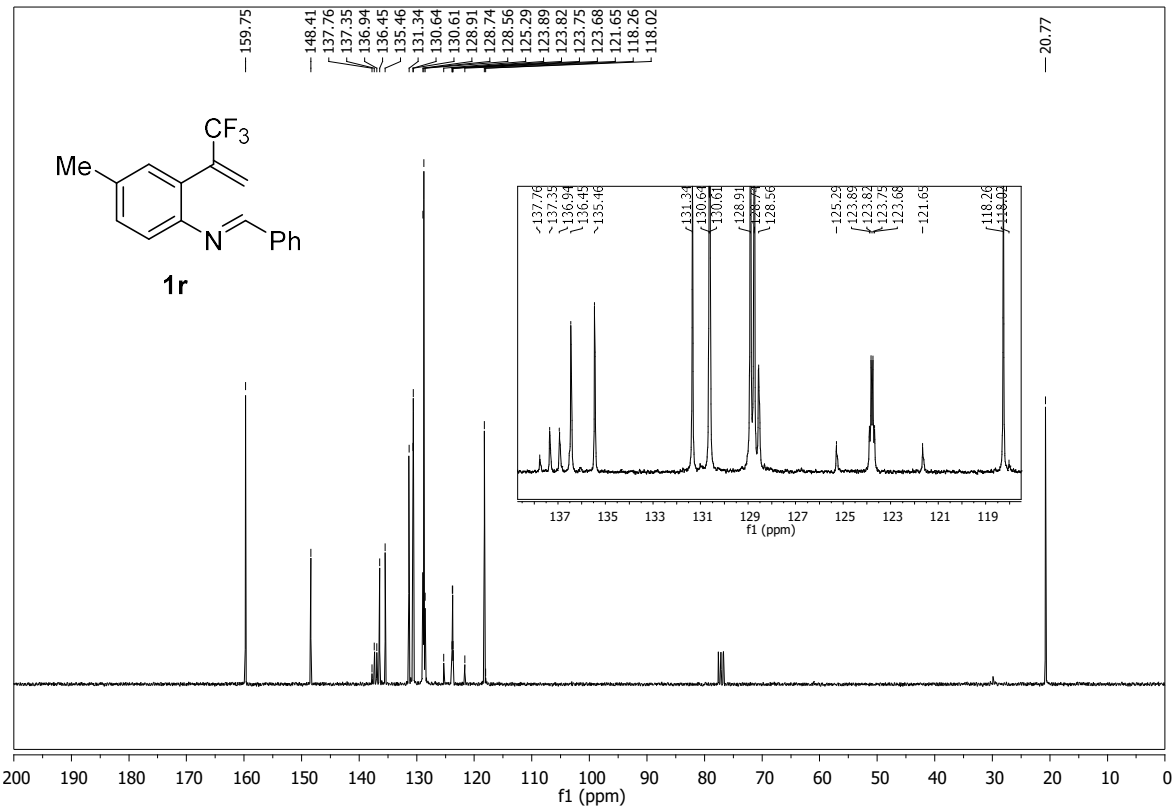
(1*E*,2*E*)-3-Phenyl-N-(2-(3,3,3-trifluoroprop-1-en-2-yl)phenyl)prop-2-en-1-imine (1q)



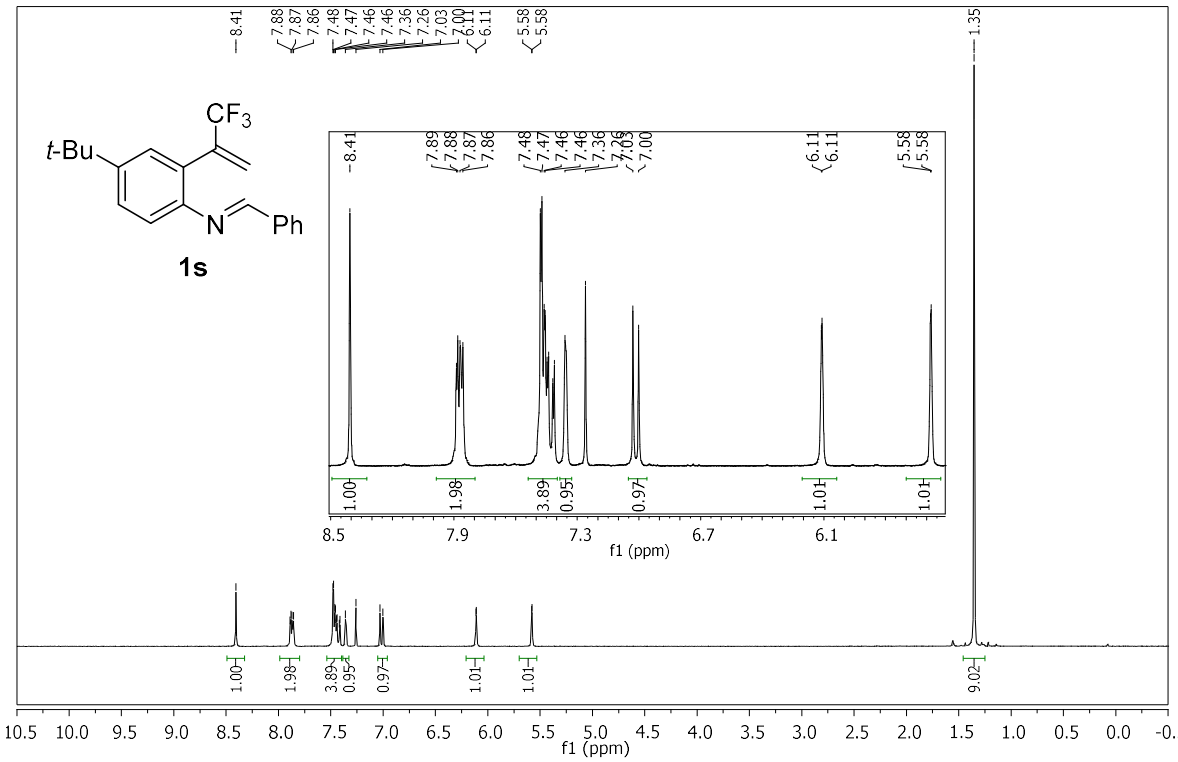


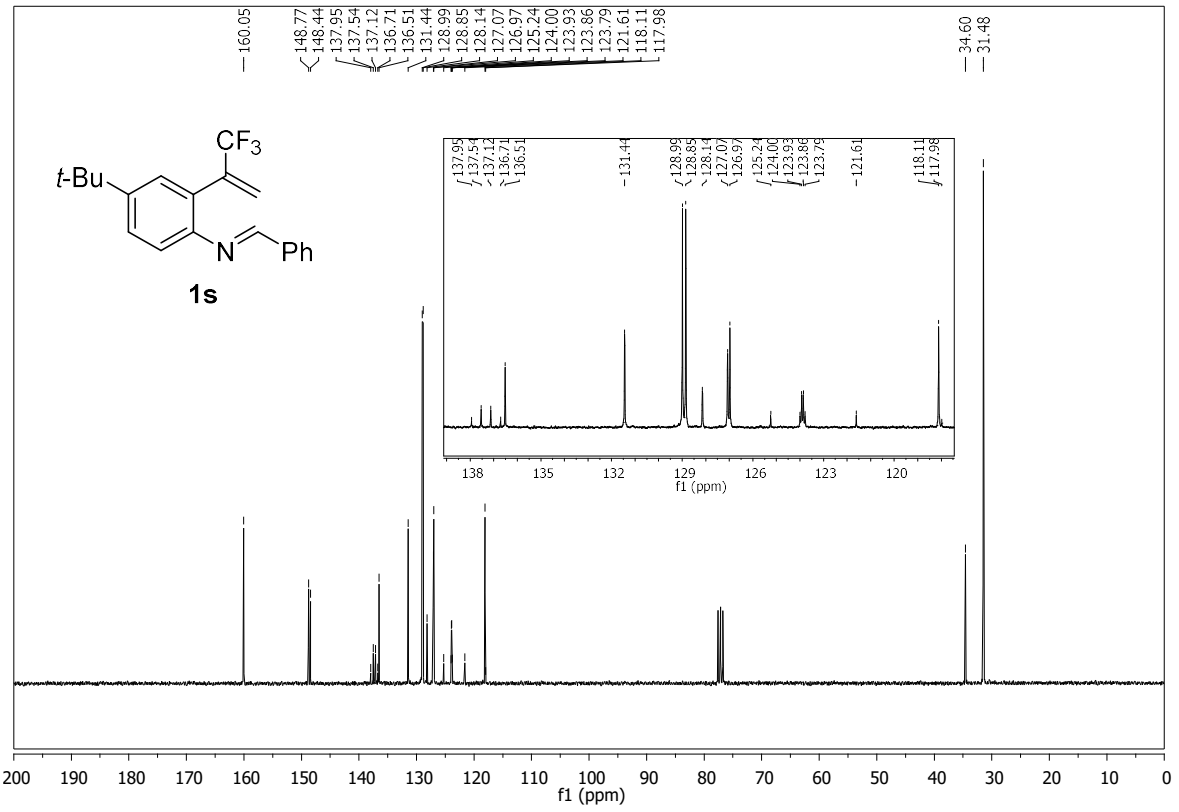
(*E*)-*N*-(Phenylmethylene)- 4-methyl-2-(3,3,3-trifluoroprop-1-en-2-yl)benzenamine (1r)



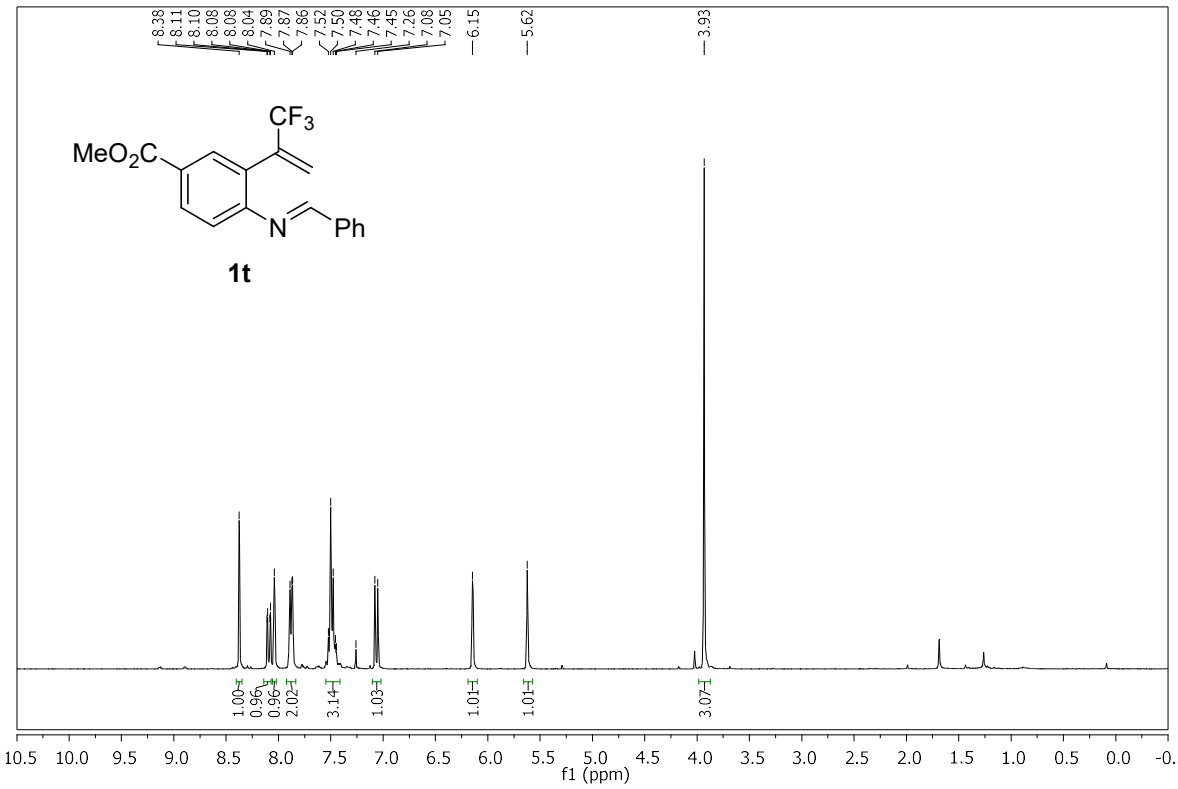


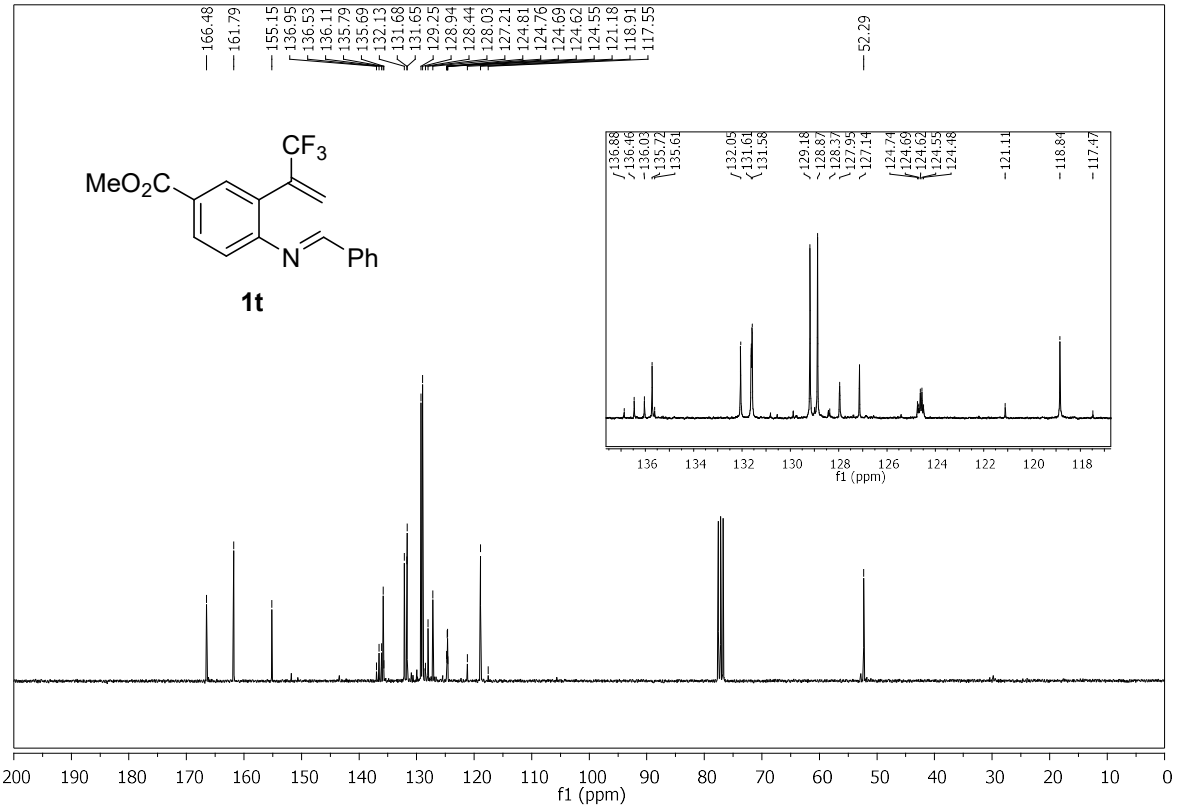
(*E*)-*N*-(Phenylmethylene)-4-*tert*-butyl-2-(3,3,3-trifluoroprop-1-en-2-yl)benzenamine (1s)



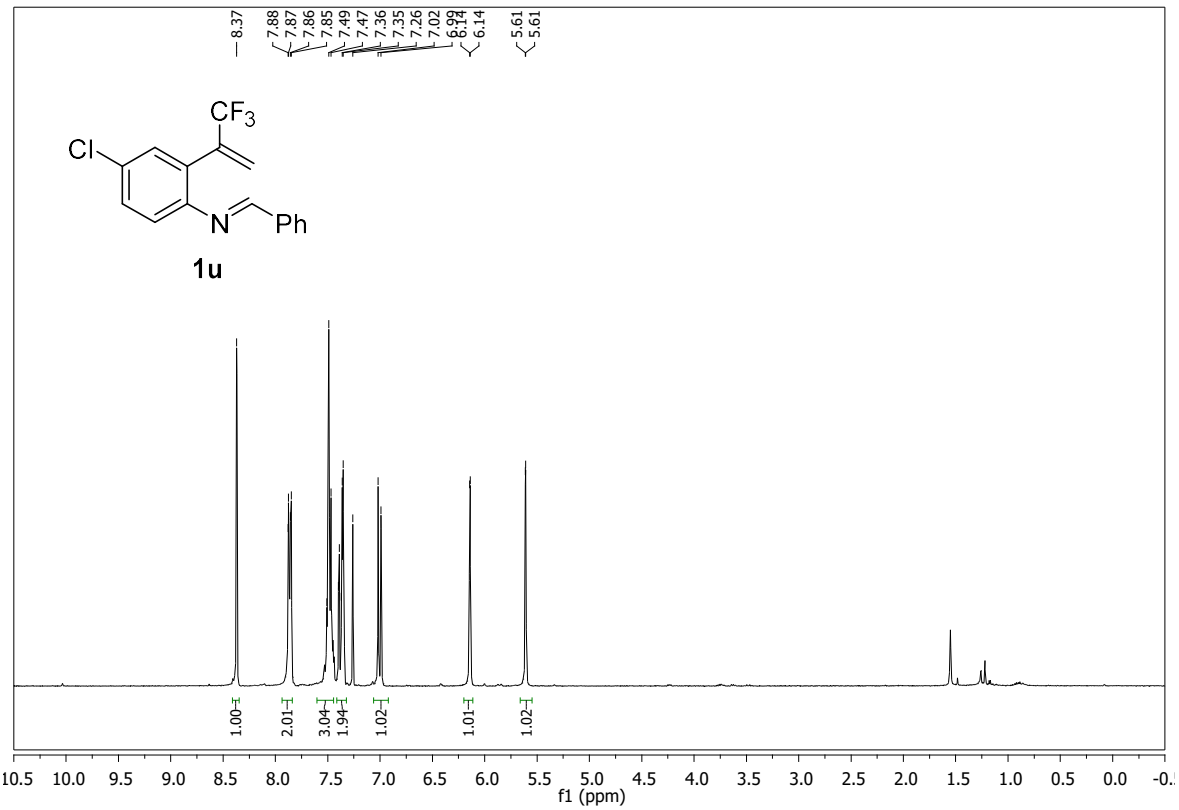


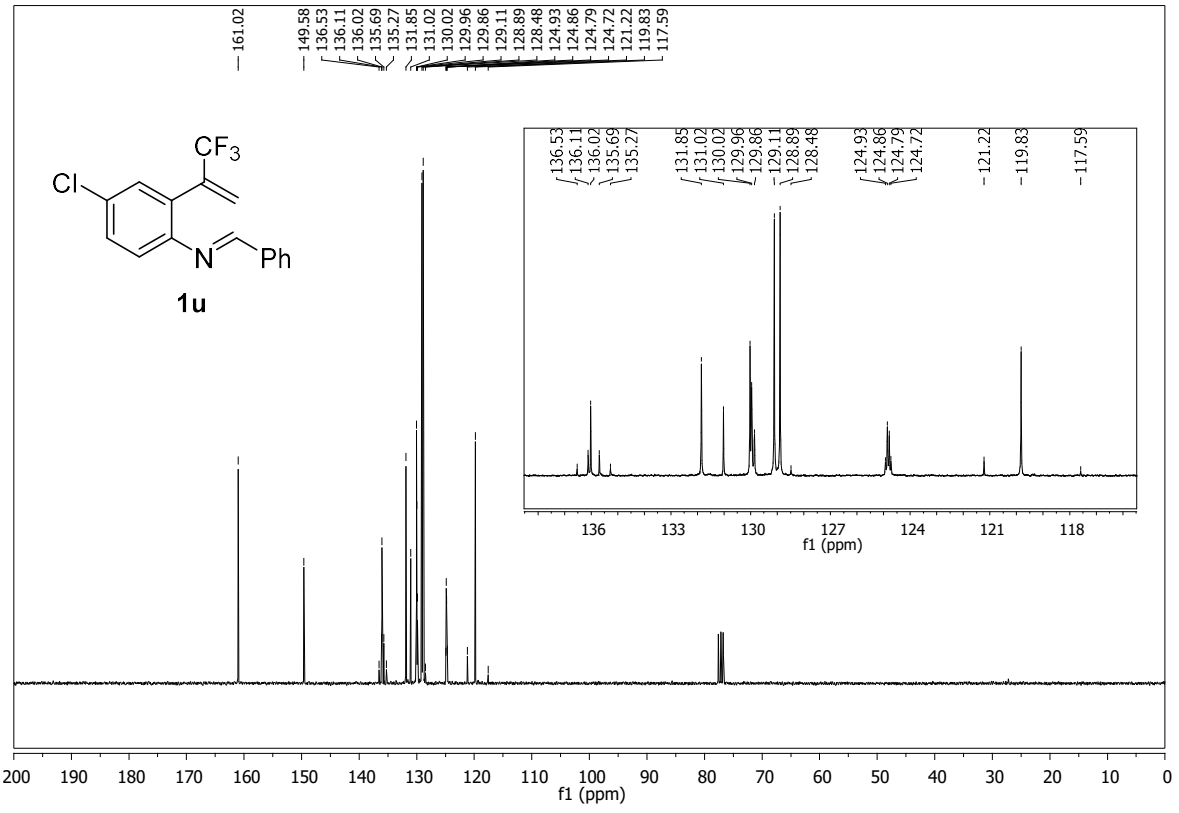
(*E*)-Metyl 4-(benzylideneamino)-3-(3,3,3-trifluoroprop-1-en-2-yl)benzoate (1t)



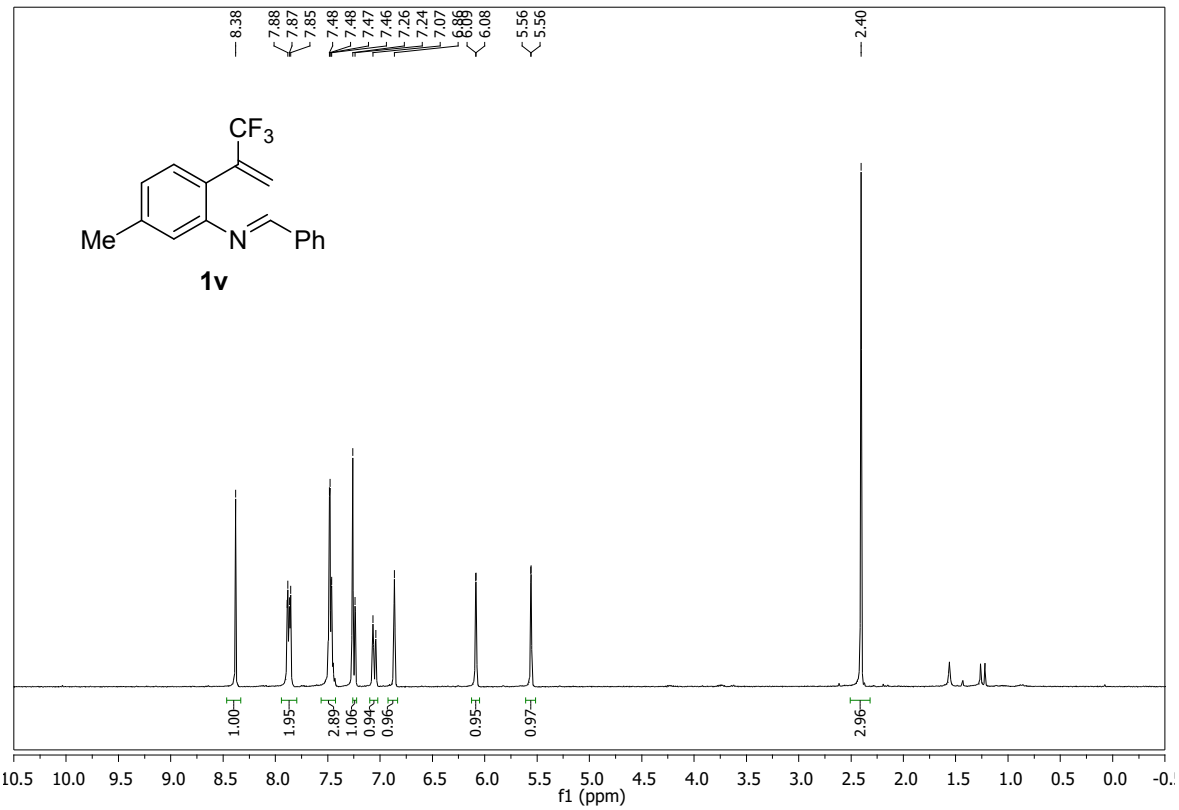


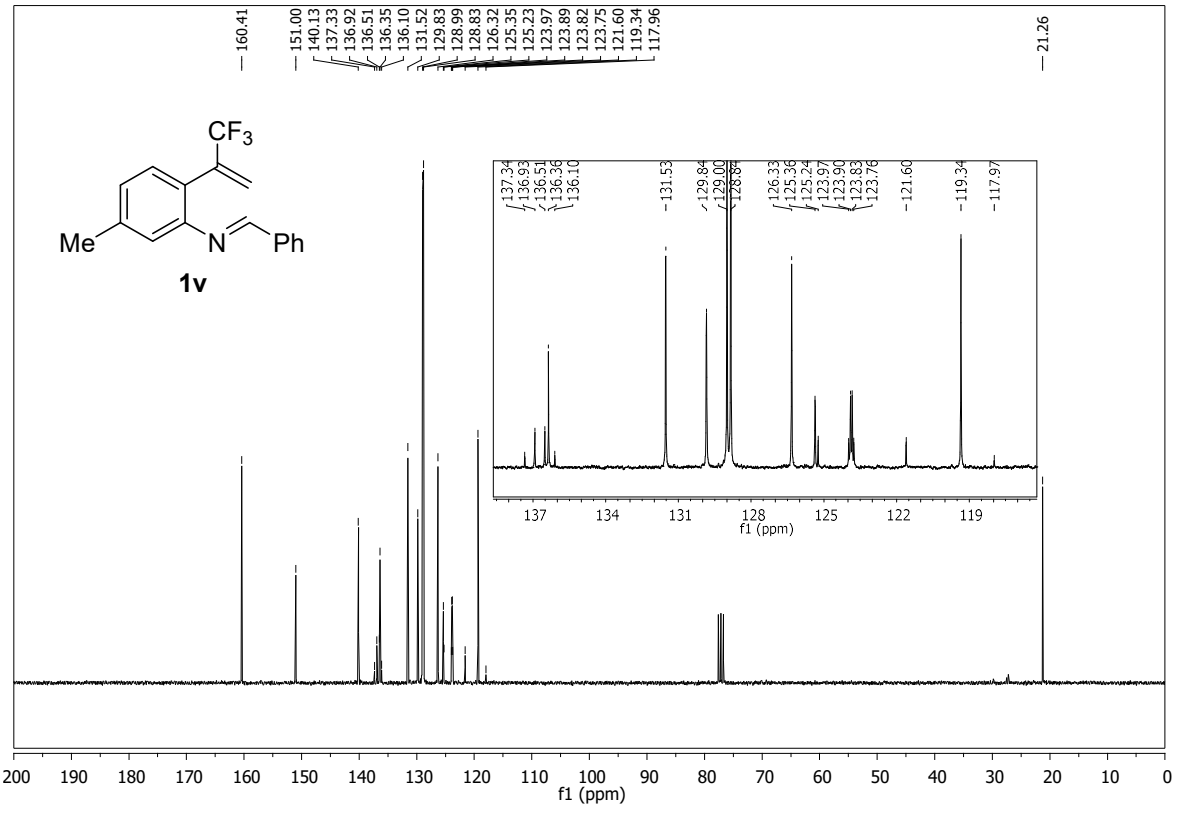
(*E*)-*N*-(Phenylmethylene)-4-chloro-2-(3,3,3-trifluoroprop-1-en-2-yl)benzenamine (1u)



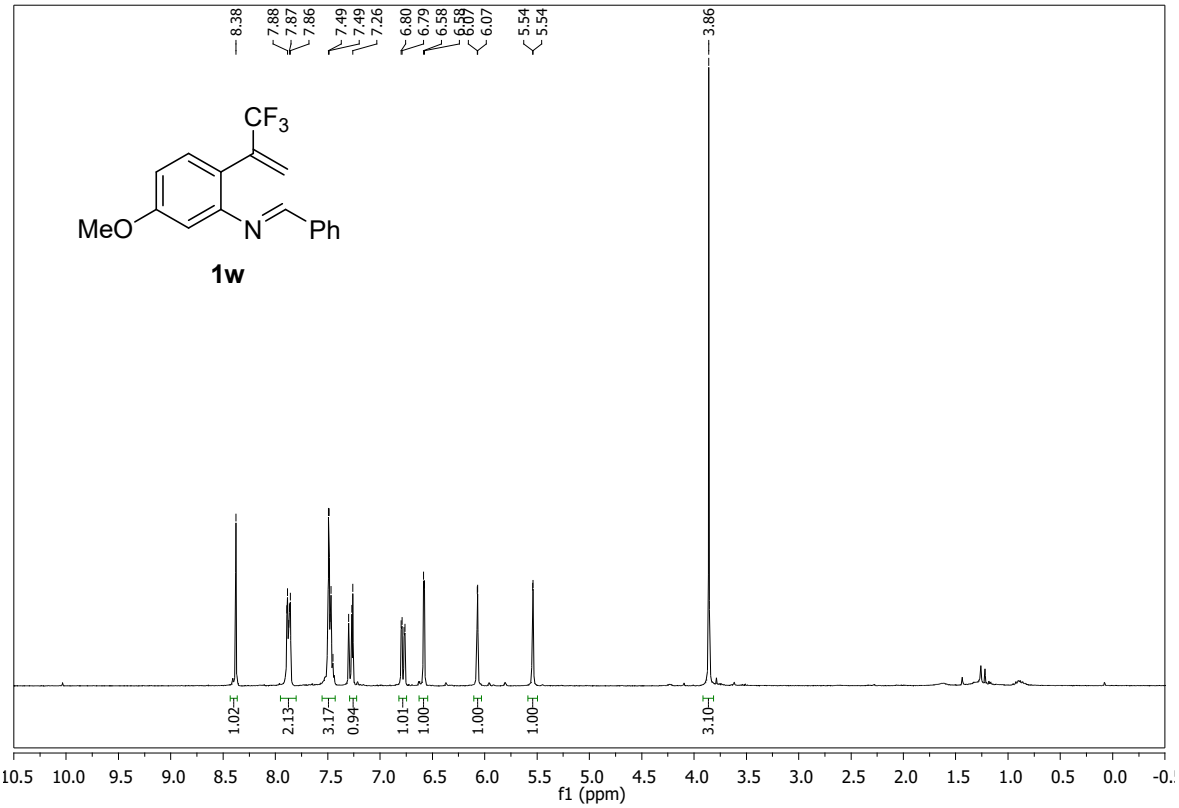


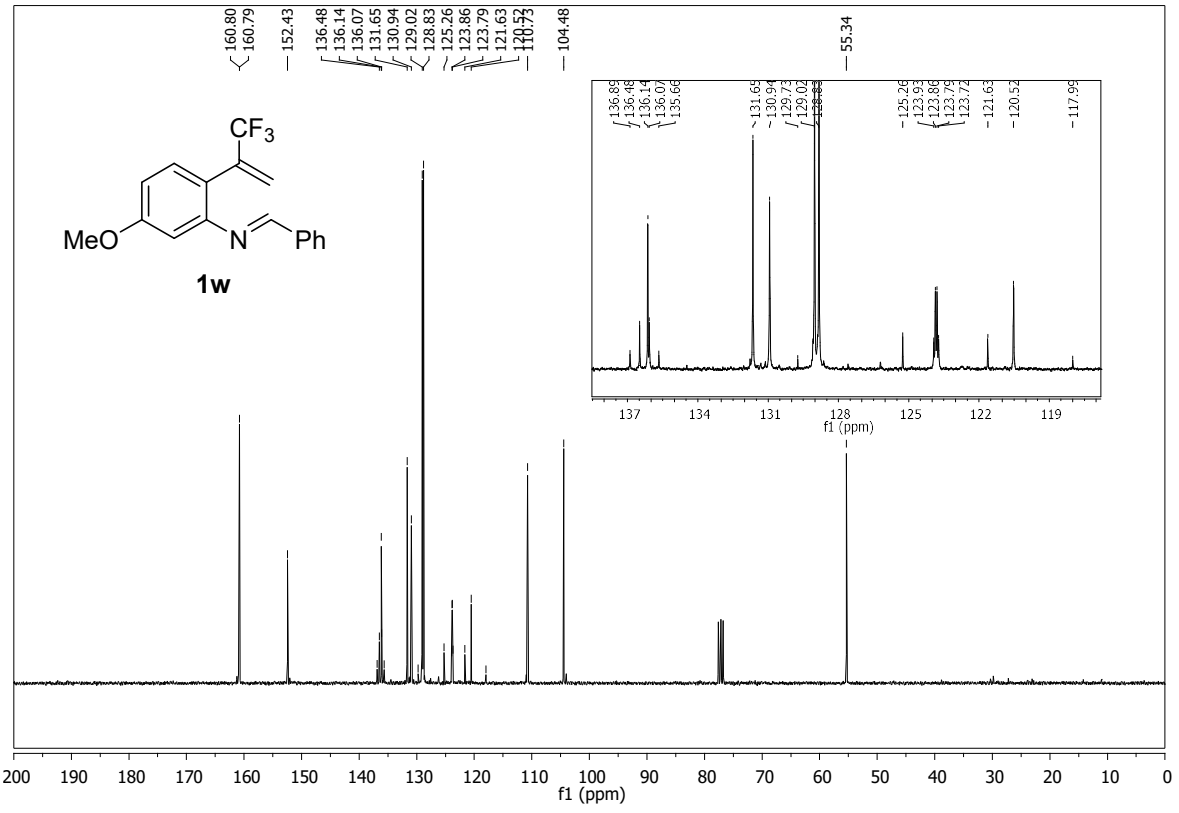
(*E*)-*N*-(Phenylmethylene)-5-methyl-2-(3,3,3-trifluoroprop-1-en-2-yl)benzenamine (1v)



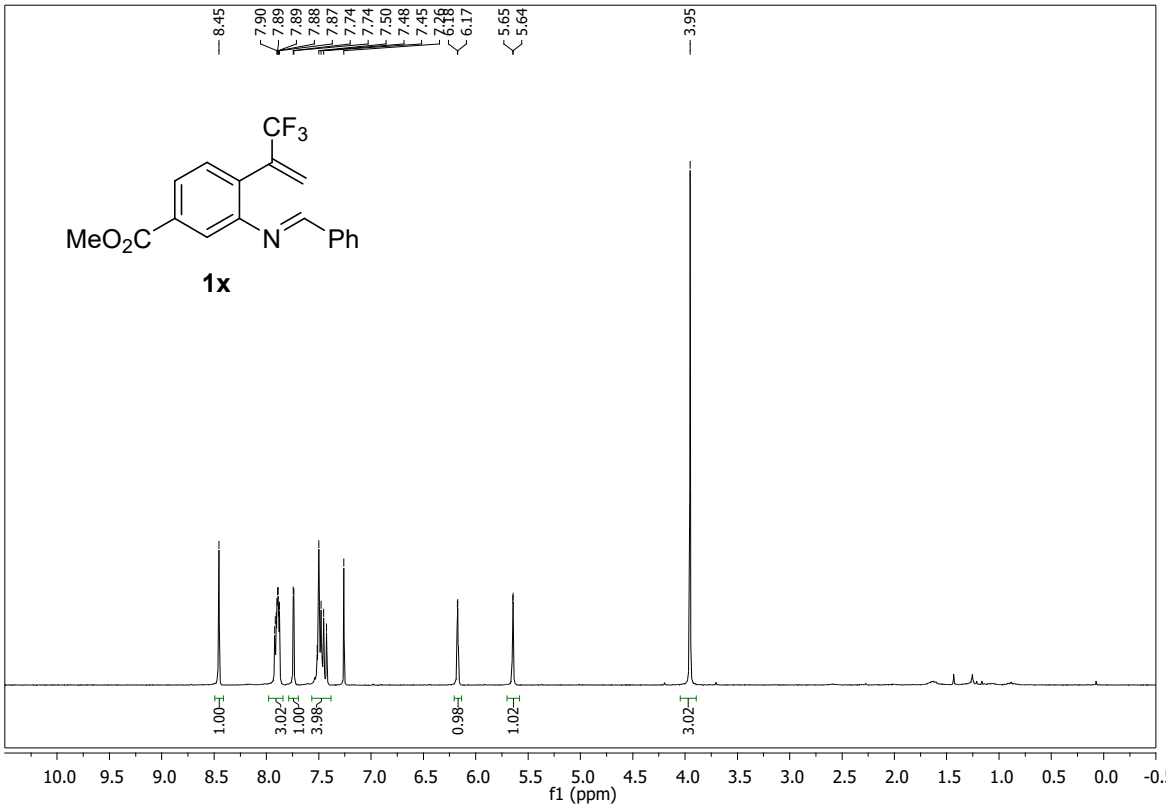


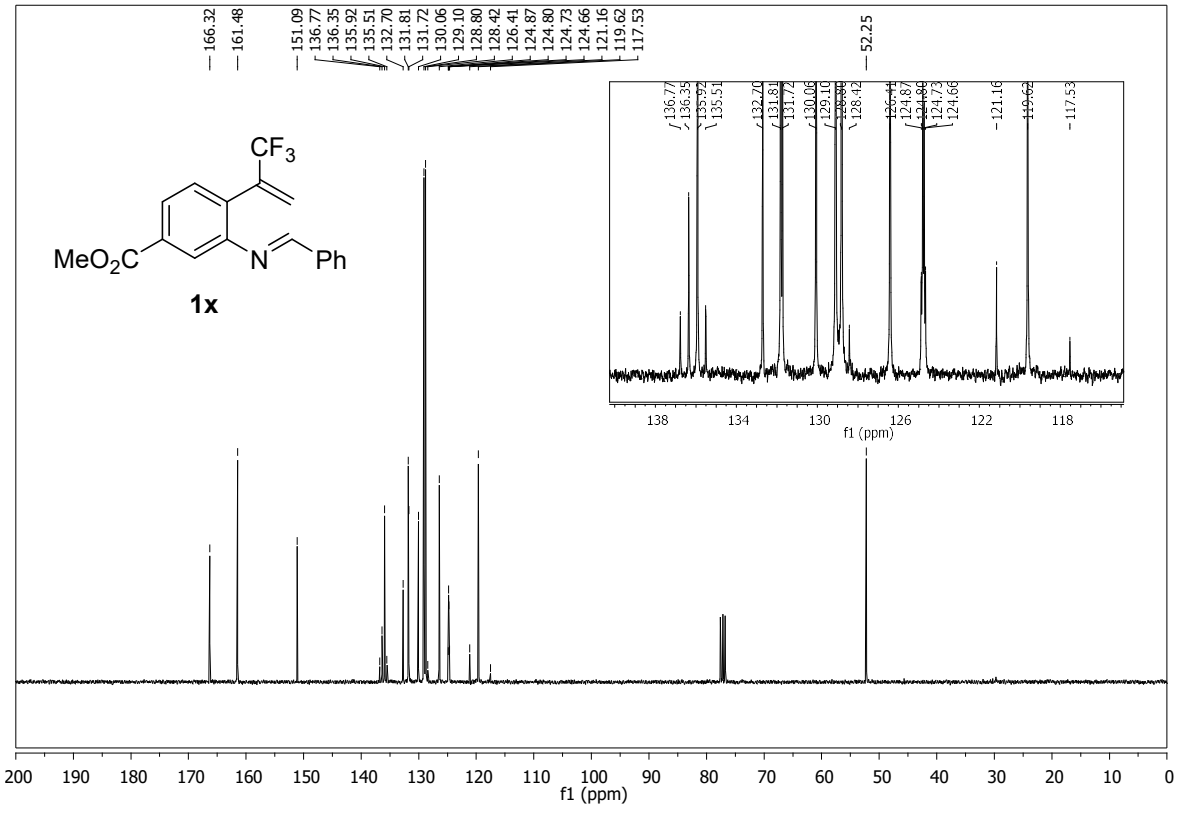
(*E*)-*N*-(Phenylmethylene)-5-methoxy-2-(3,3,3-trifluoroprop-1-en-2-yl)benzenamine (1w)



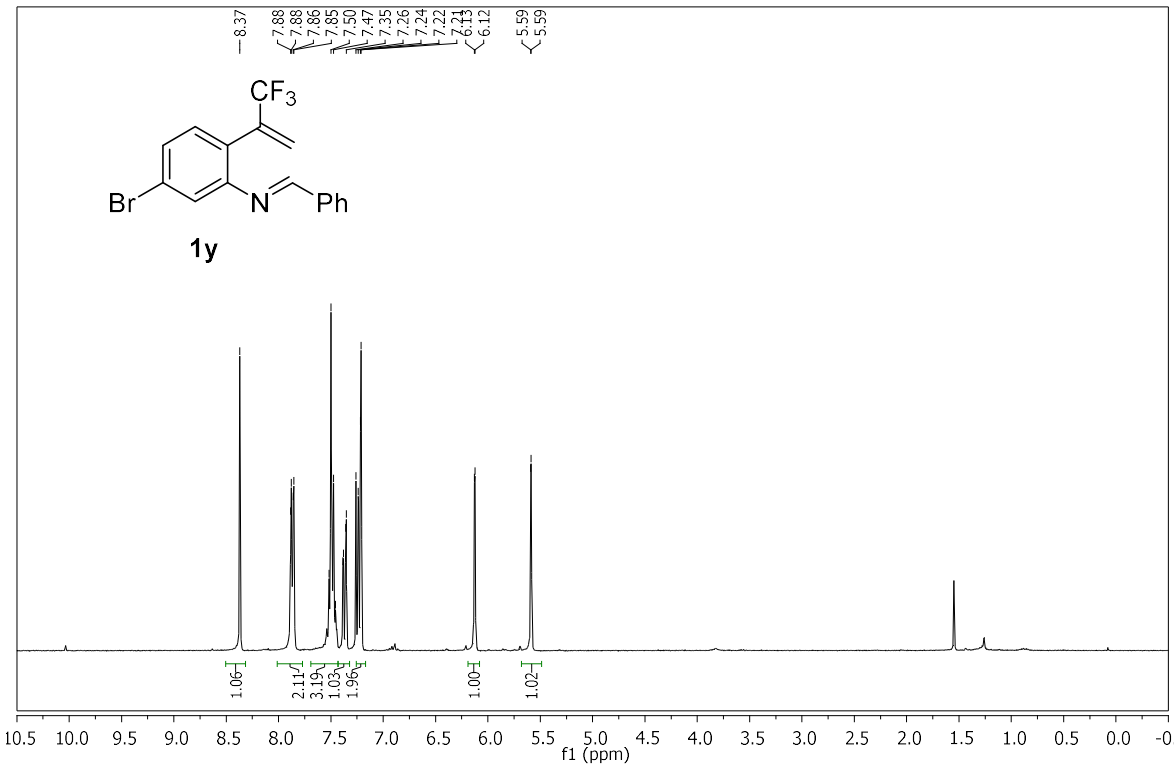


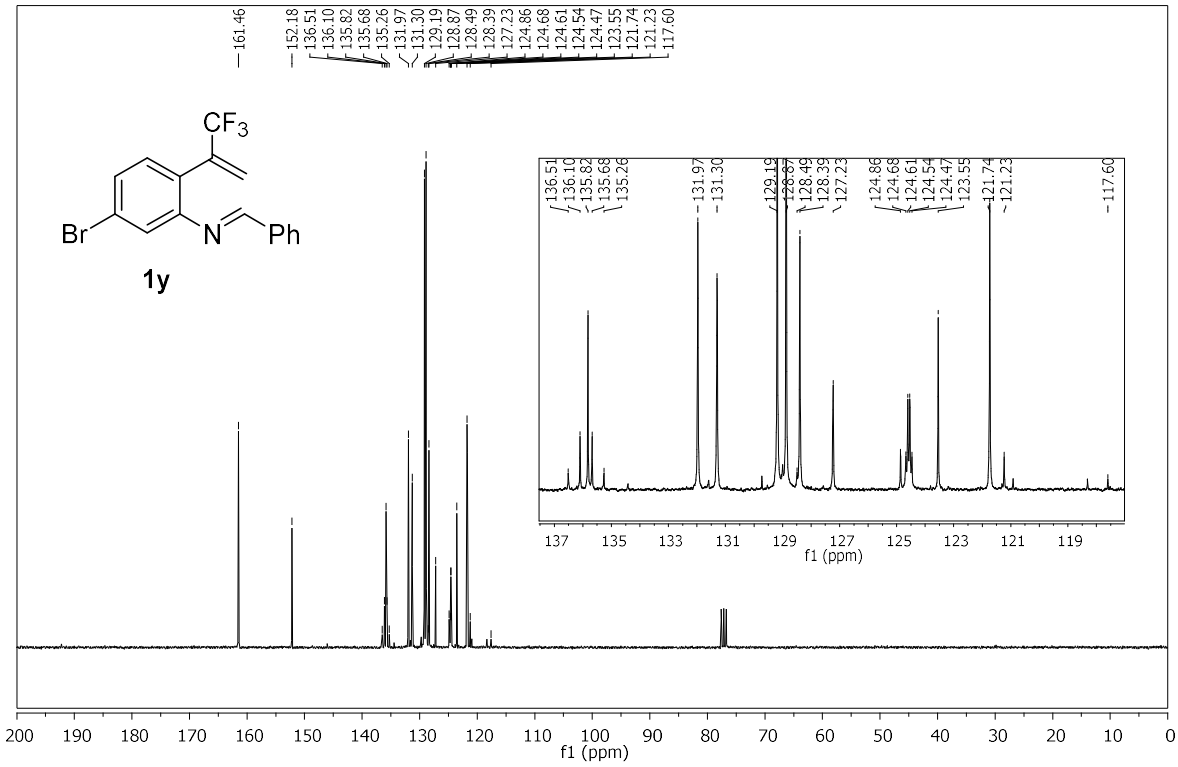
(E)-Metyl 3-(benzylideneamino)-4-(3,3,3-trifluoroprop-1-en-2-yl)benzoate (1x)





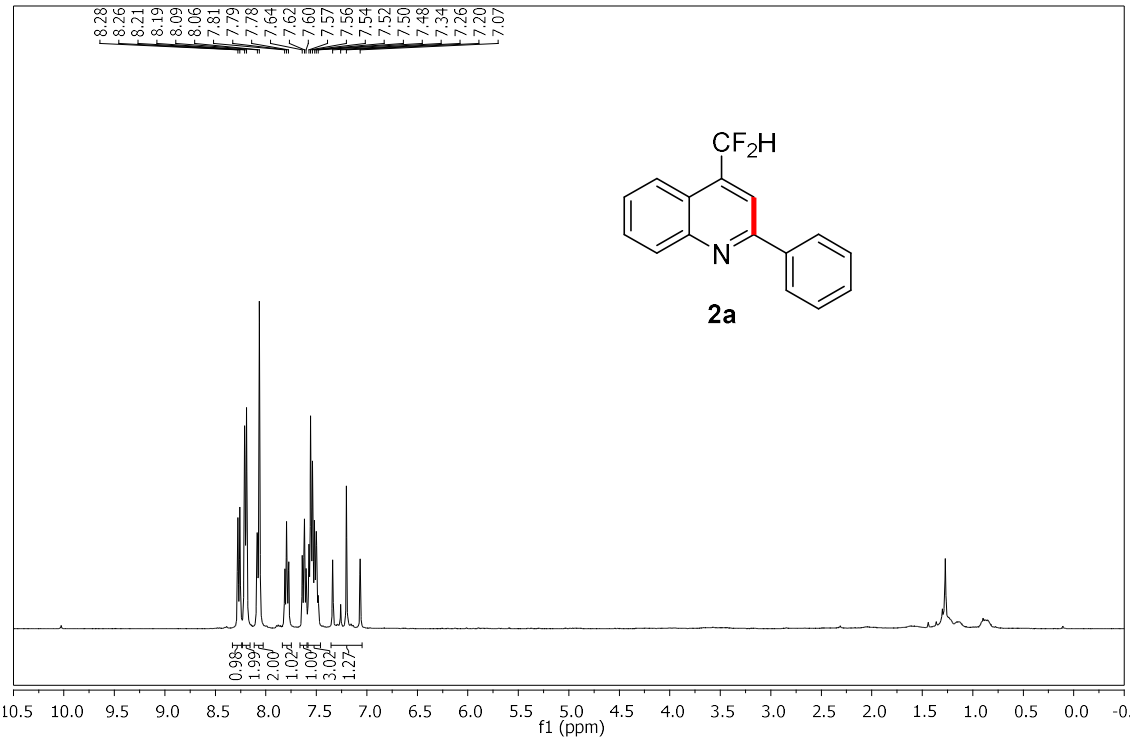
(*E*)-*N*-(Phenylmethylene)-5-bromo-2-(3,3,3-trifluoroprop-1-en-2-yl)benzenamine (1y)

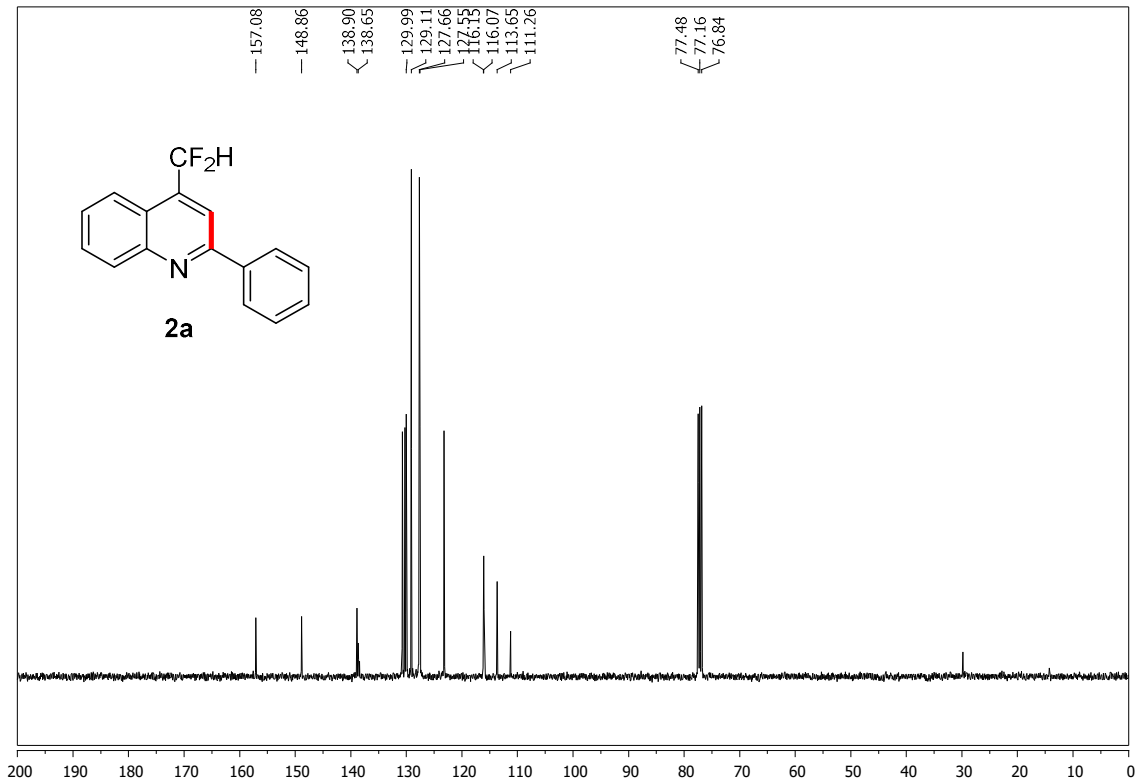




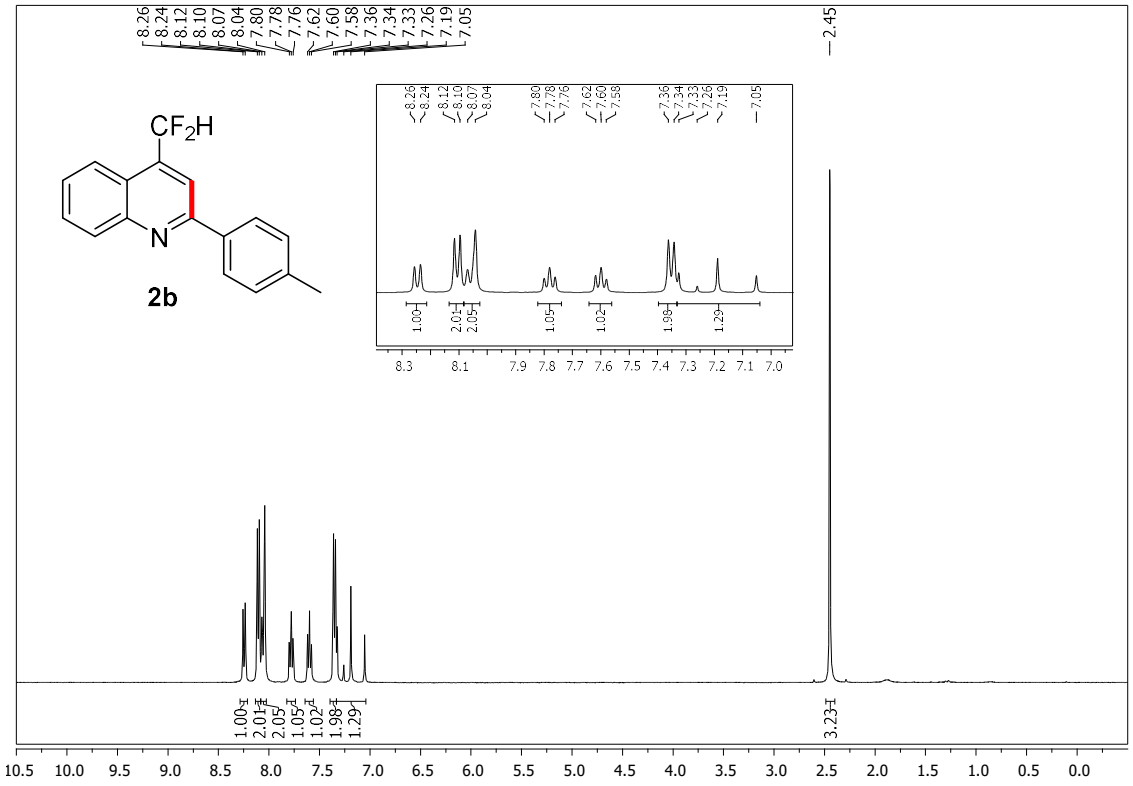
11.^{1}H and ^{13}C NMR Spectra Difluoromethylated Quinoline Derivatives

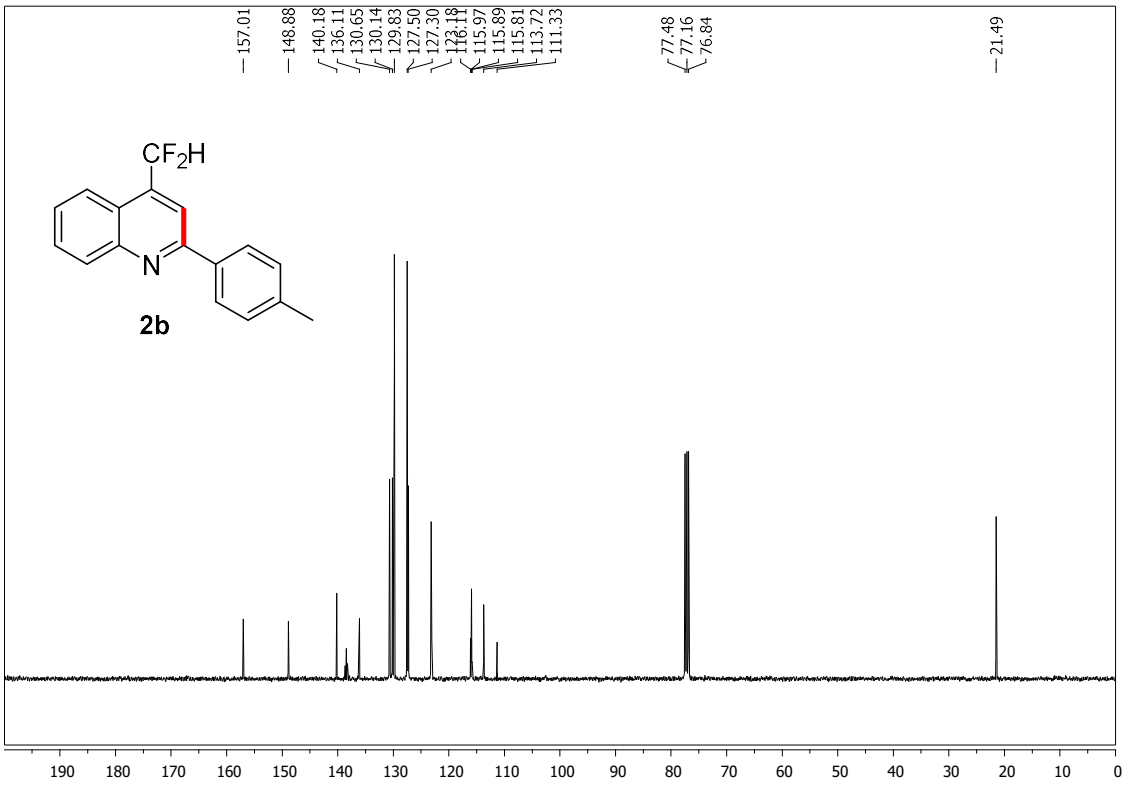
4-(difluoromethyl)-2-phenylquinoline (2a)



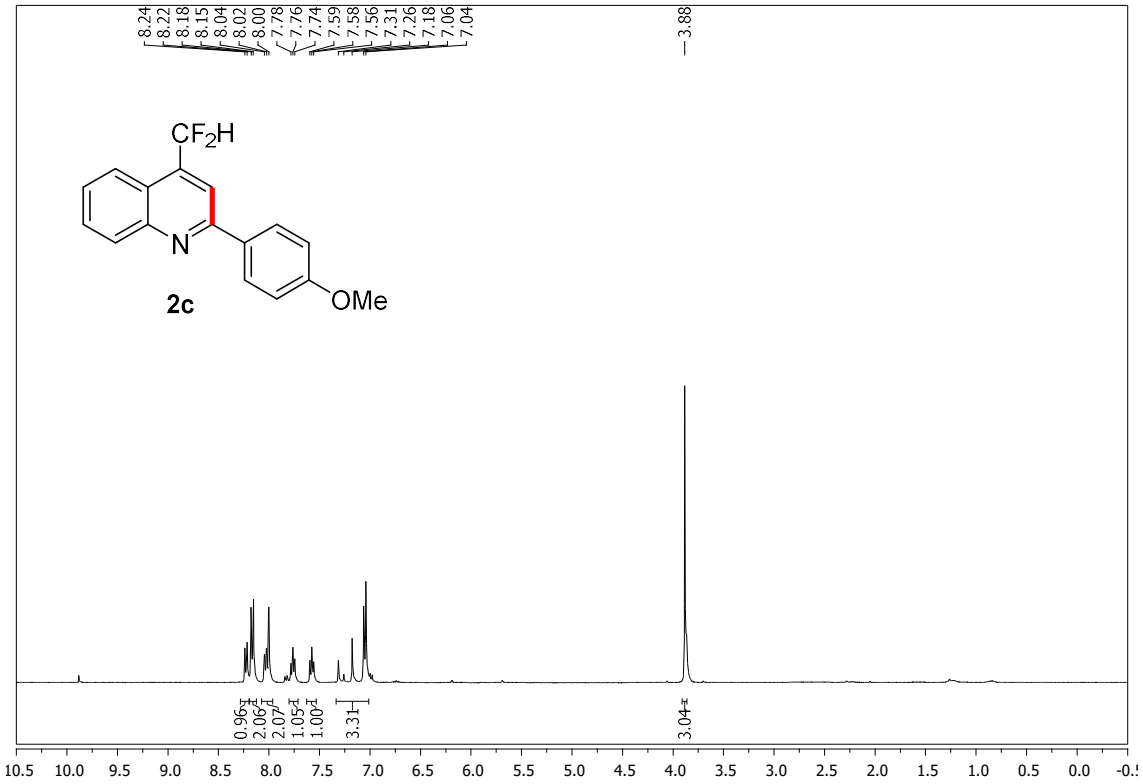


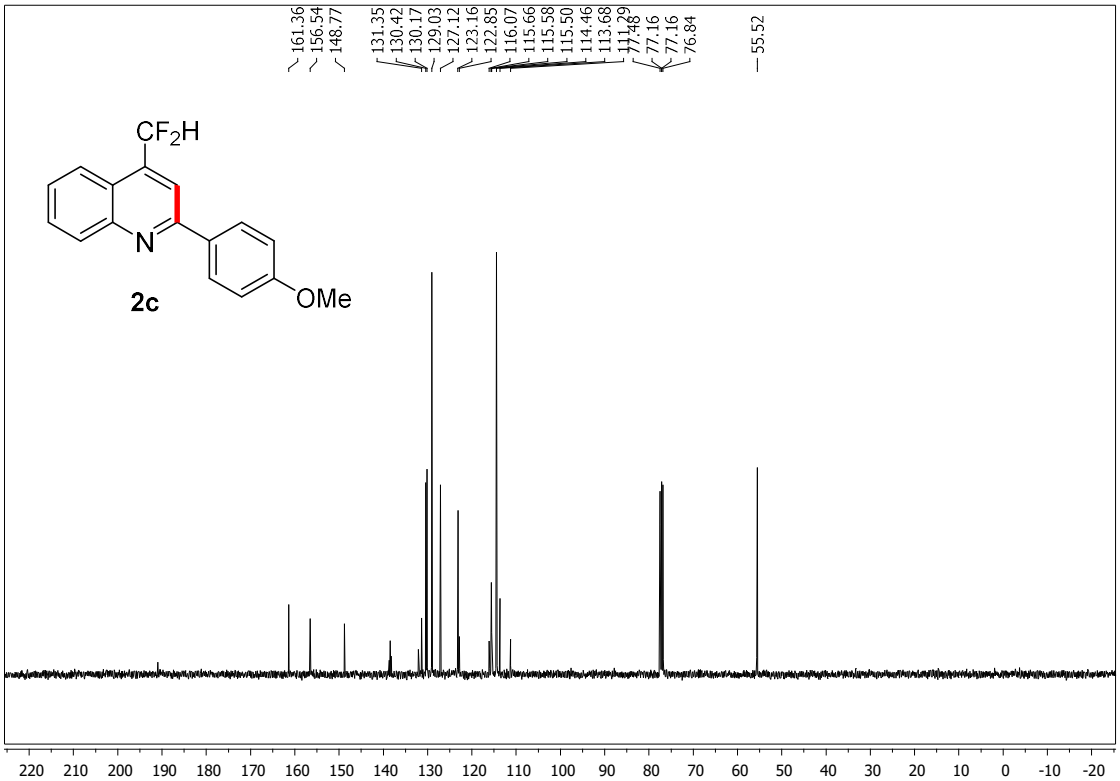
4-(Difluoromethyl)-2-(*p*-tolyl)quinoline (2b)



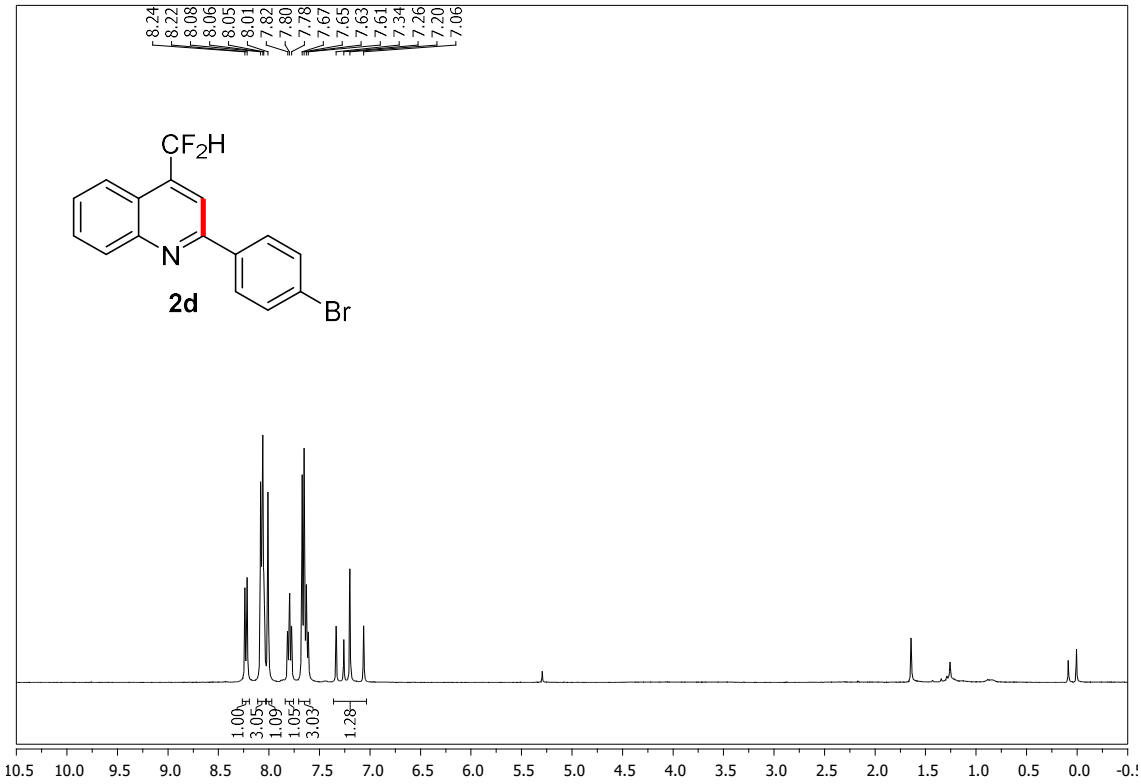


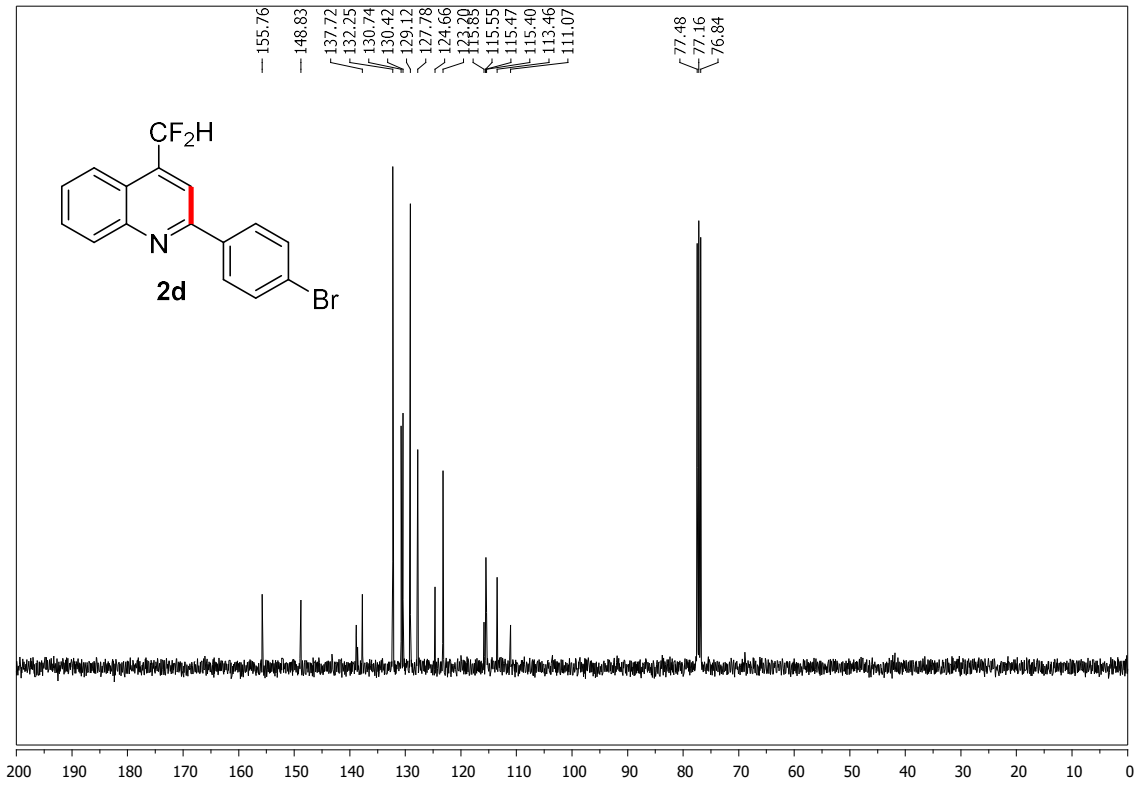
4-(Difluoromethyl)-2-(4-methoxyphenyl)quinoline (2c)



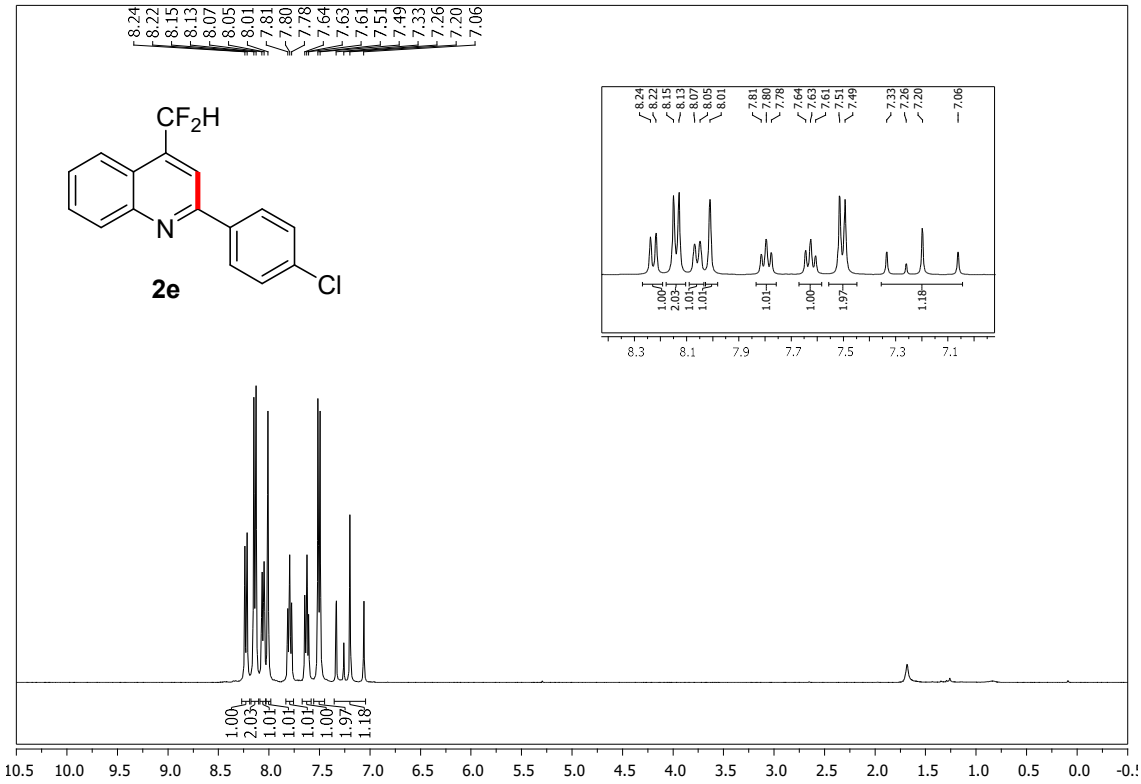


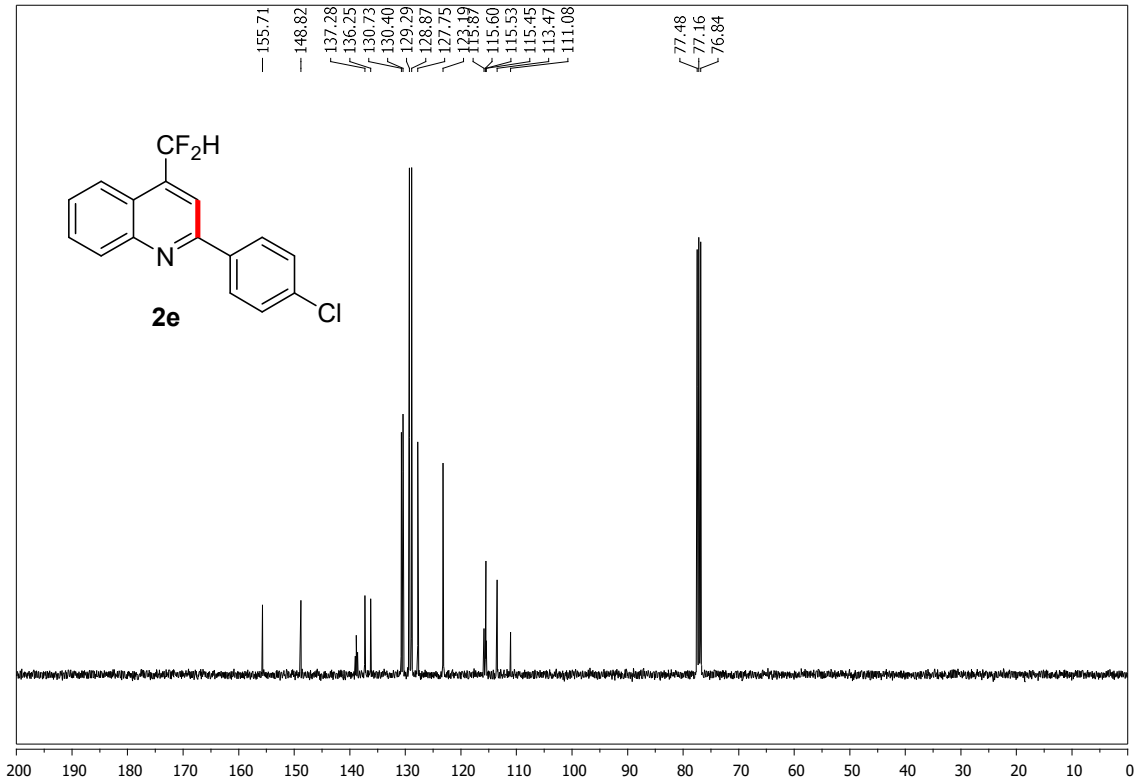
2-(4-Bromophenyl)-4-(difluoromethyl)quinoline (2d)



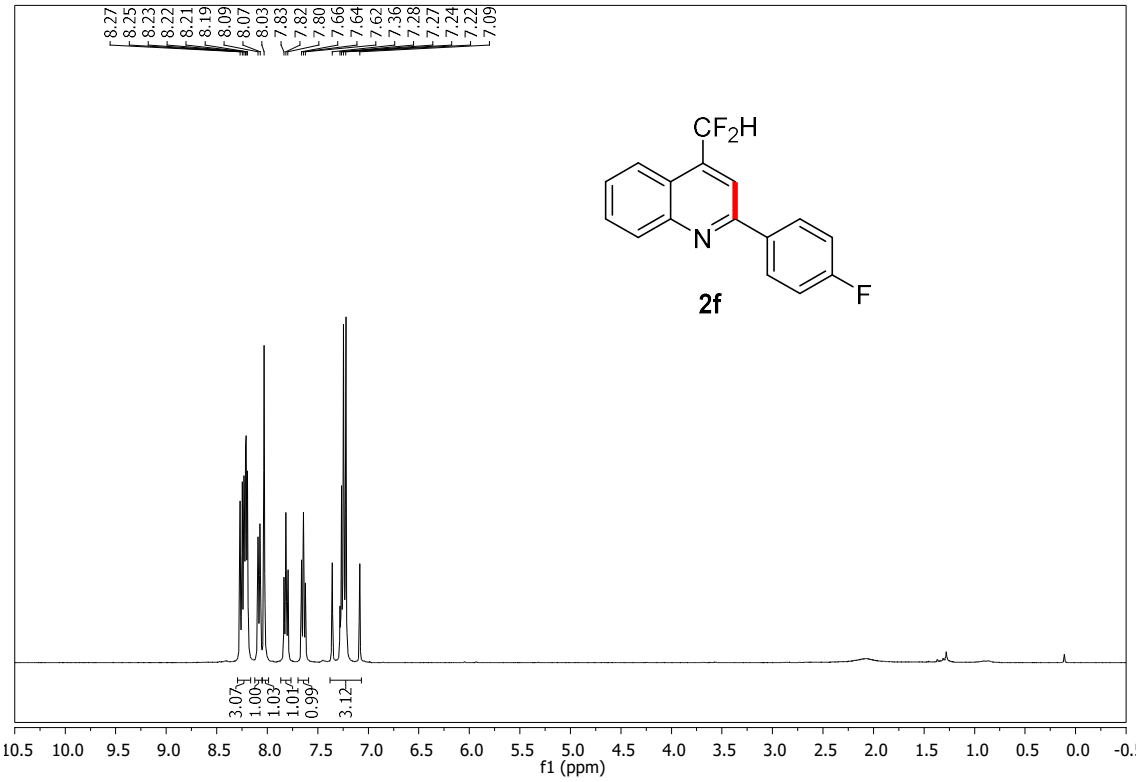


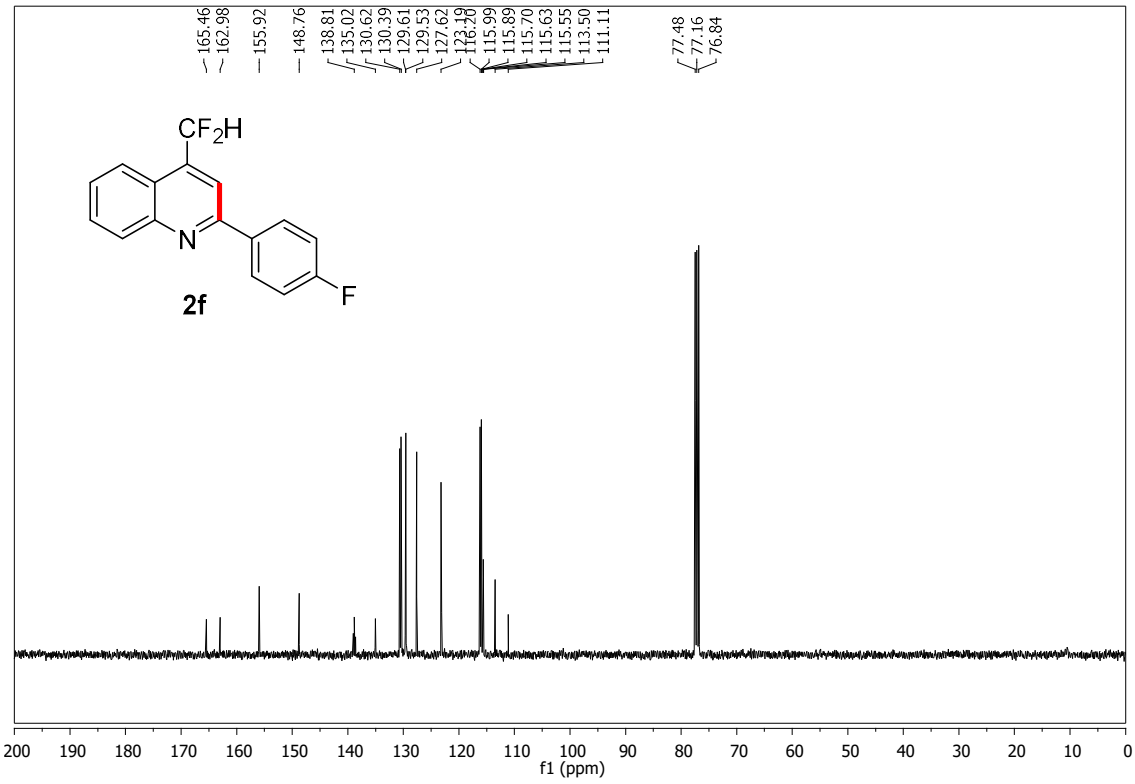
2-(4-Chlorophenyl)-4-(difluoromethyl)quinoline (2e)



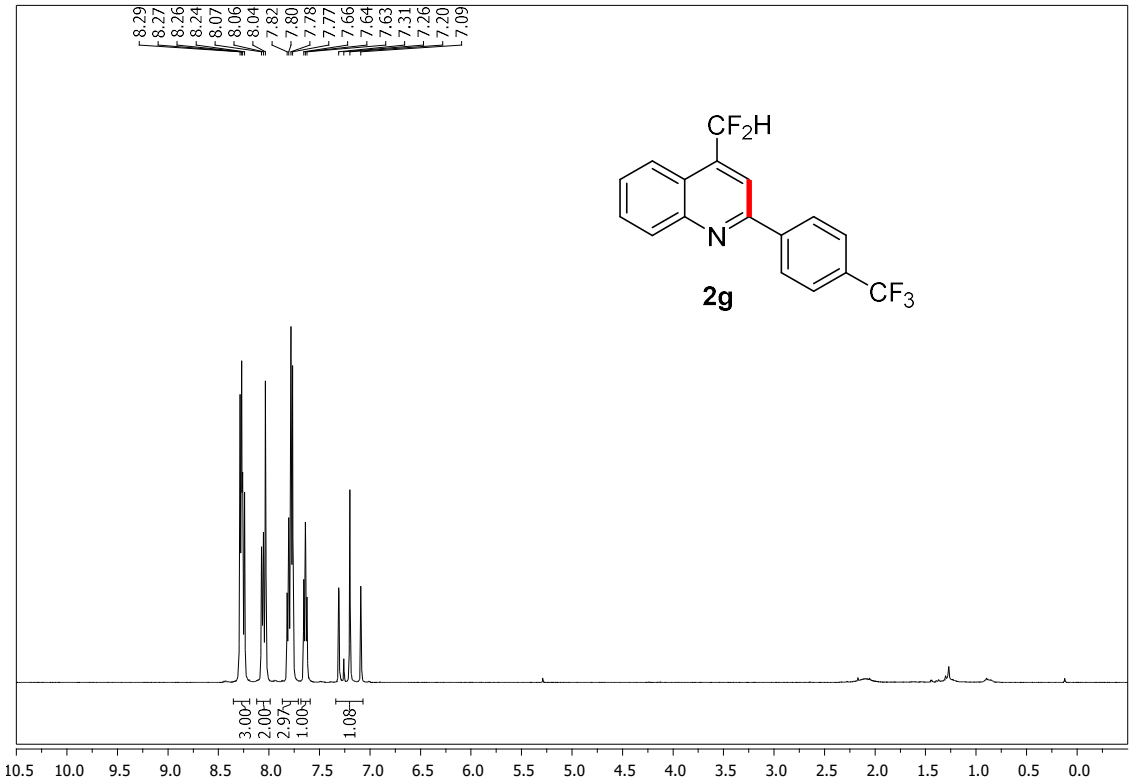


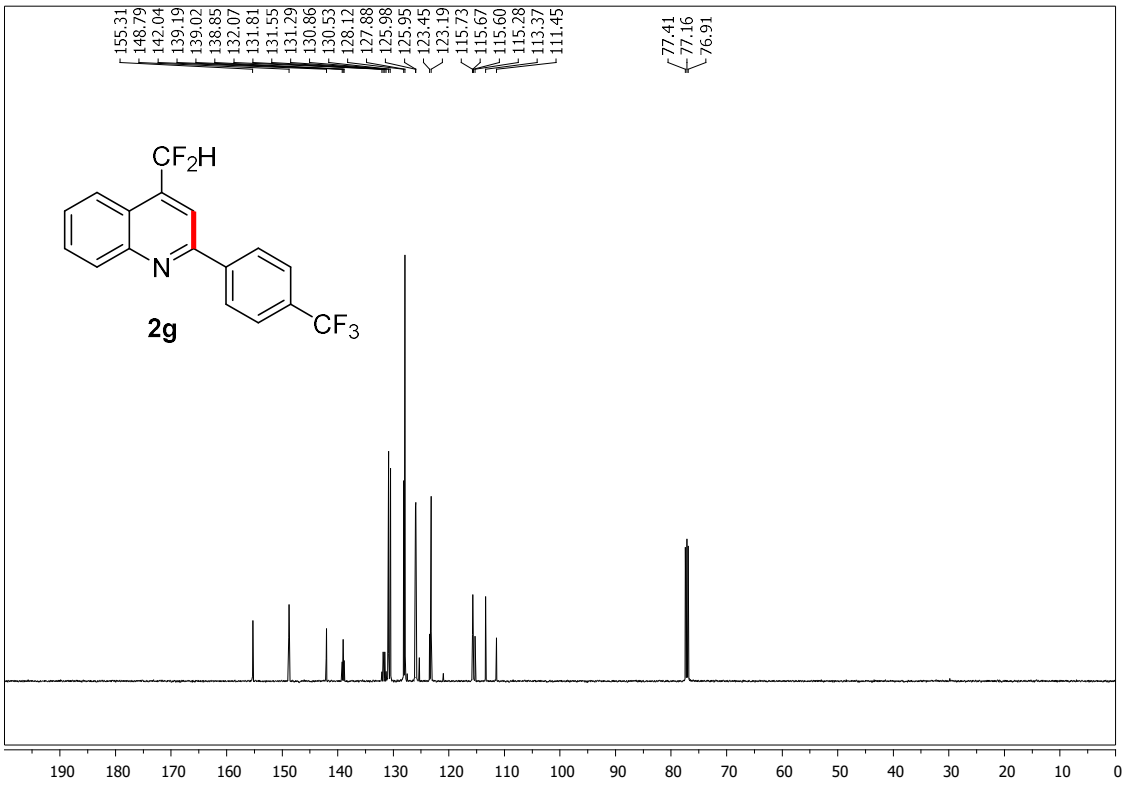
4-(Difluoromethyl)-2-(4-fluorophenyl)quinoline (2f)



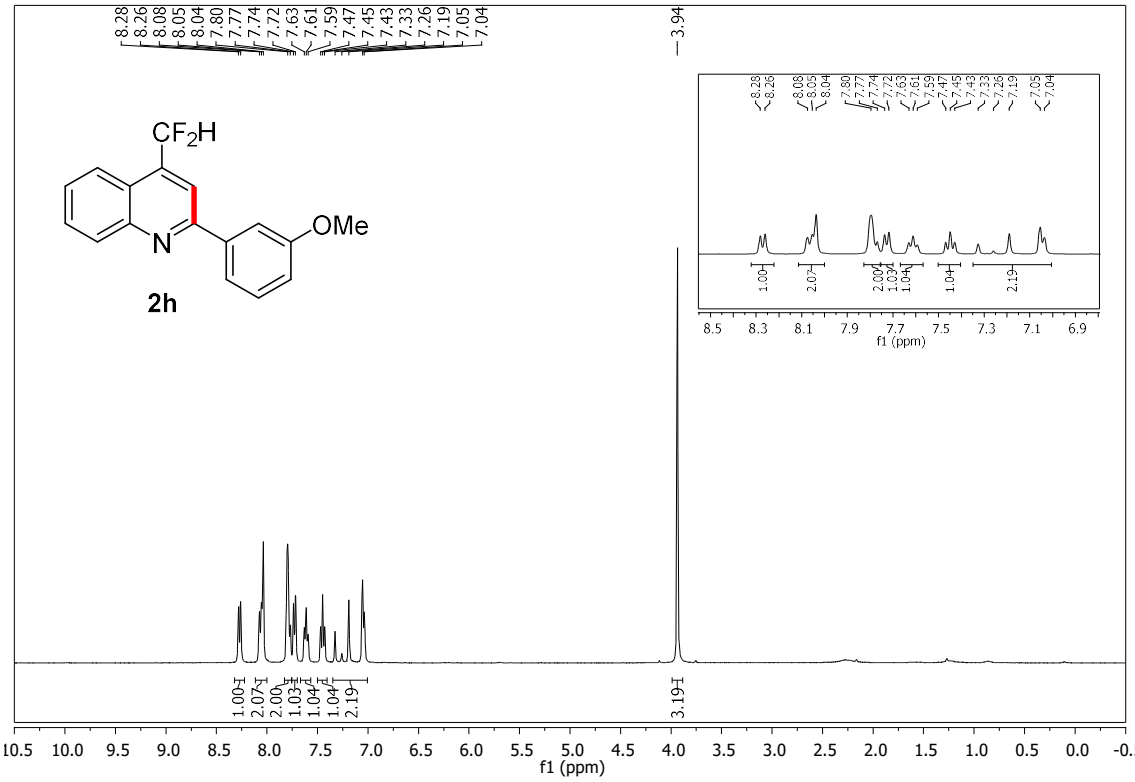


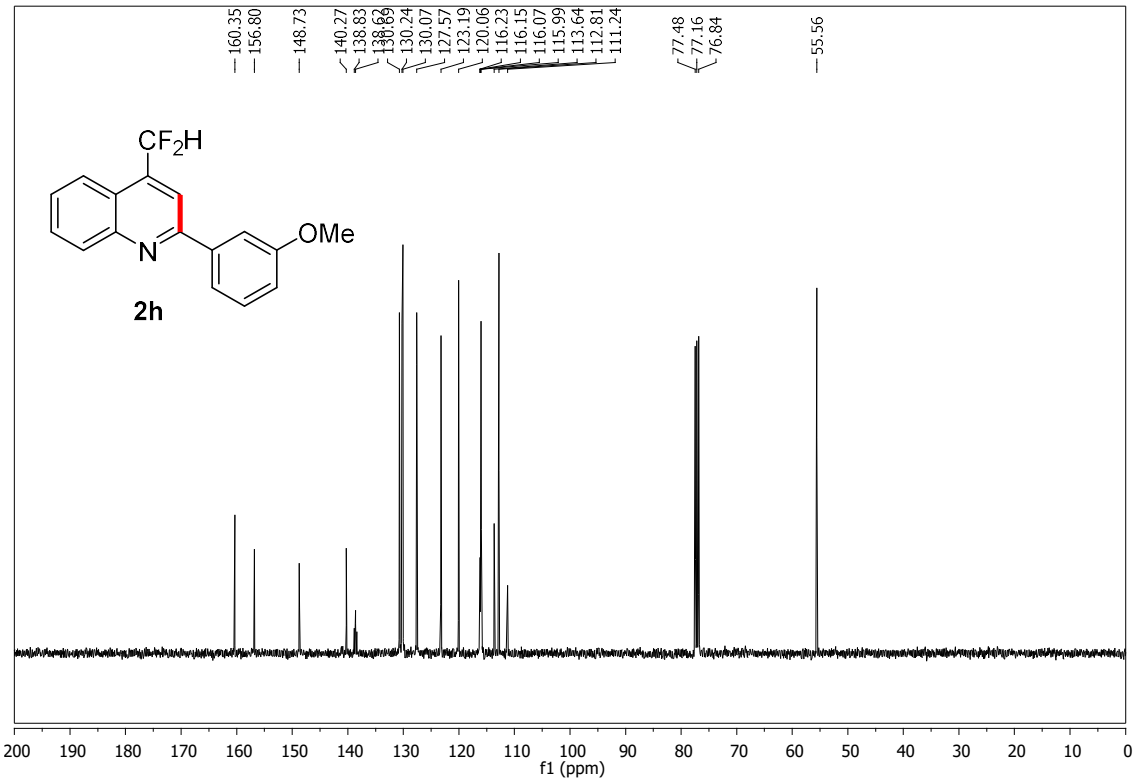
4-(Difluoromethyl)-2-(4-(trifluoromethyl)phenyl)quinoline (2g)



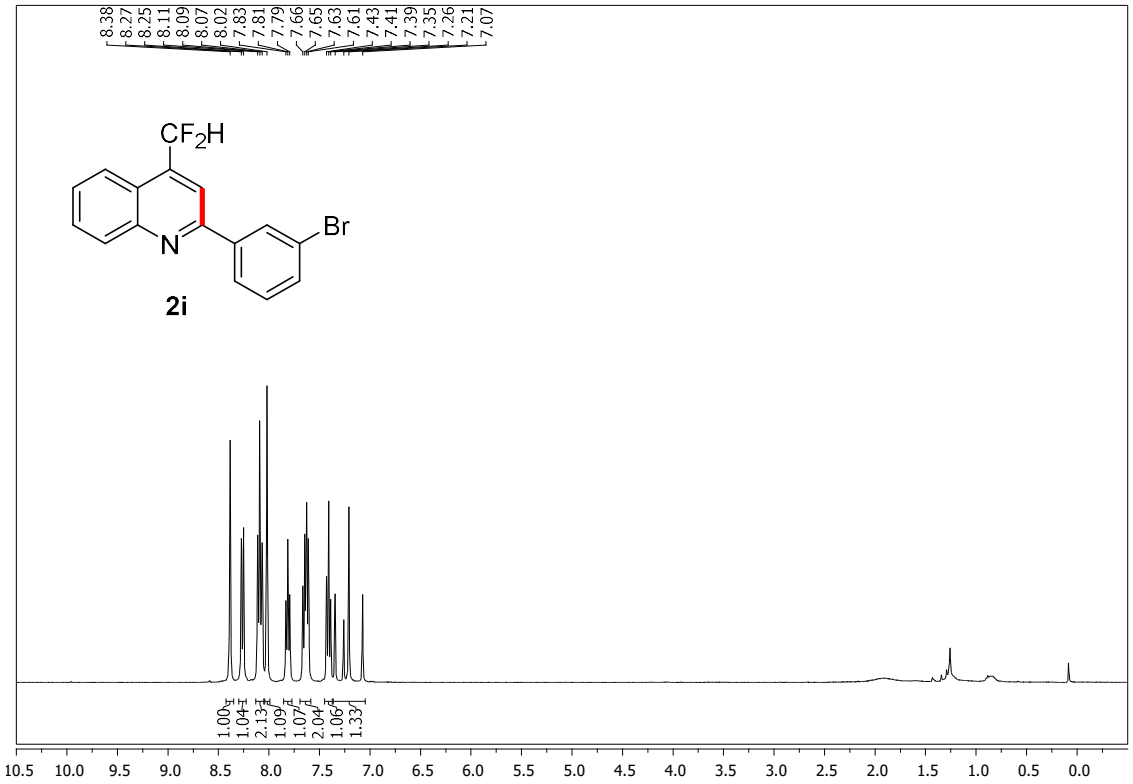


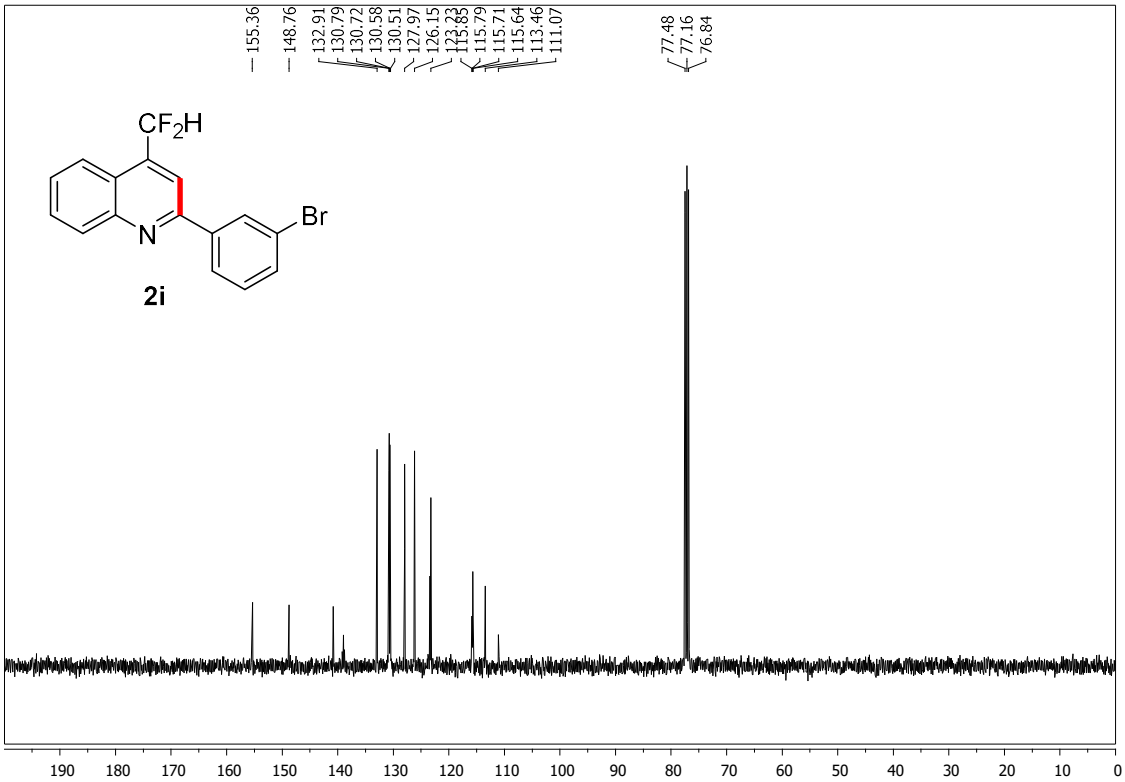
4-(Difluoromethyl)-2-(3-methoxyphenyl)quinoline (2h)



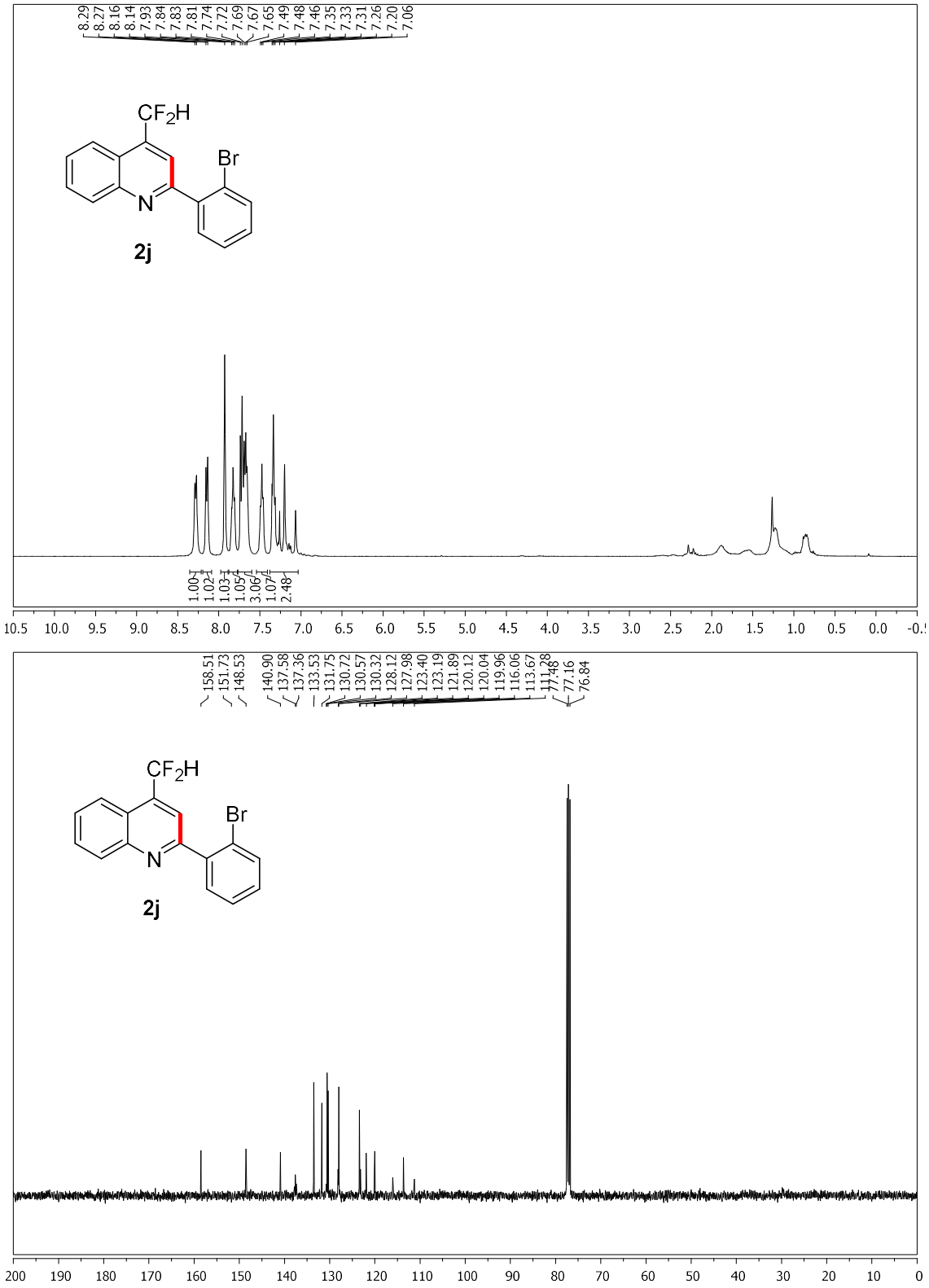


2-(3-Bromophenyl)-4-(difluoromethyl)quinoline (2i)

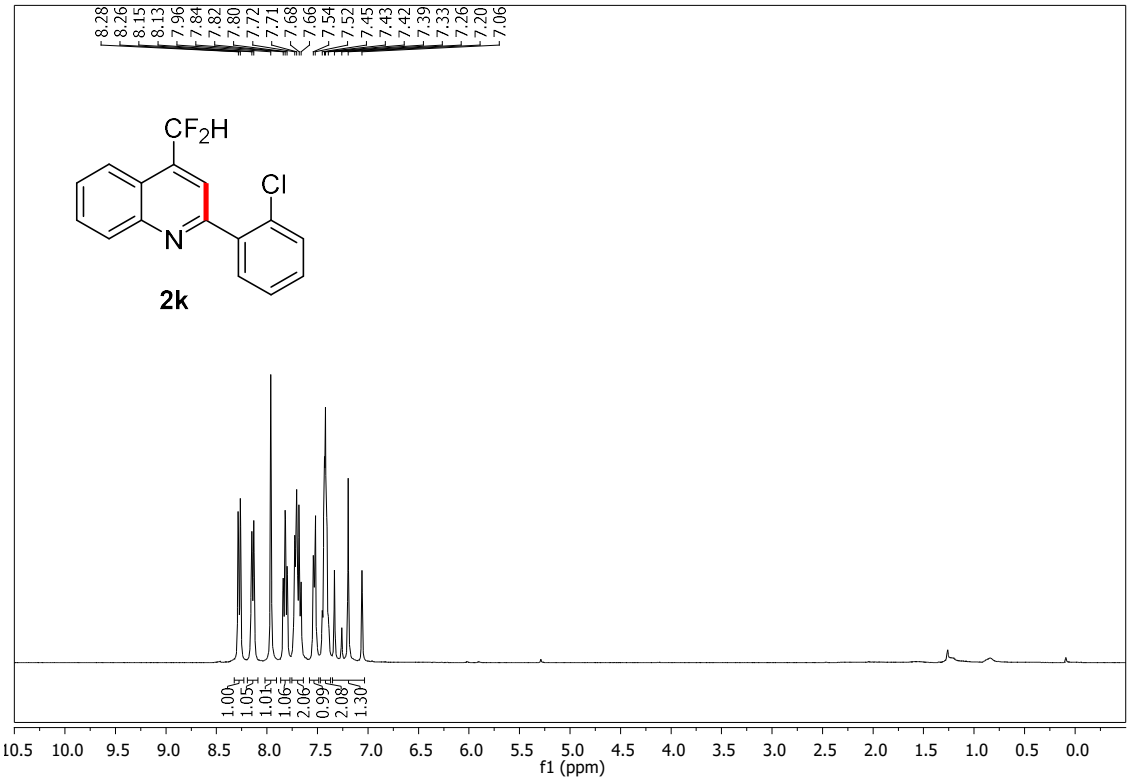


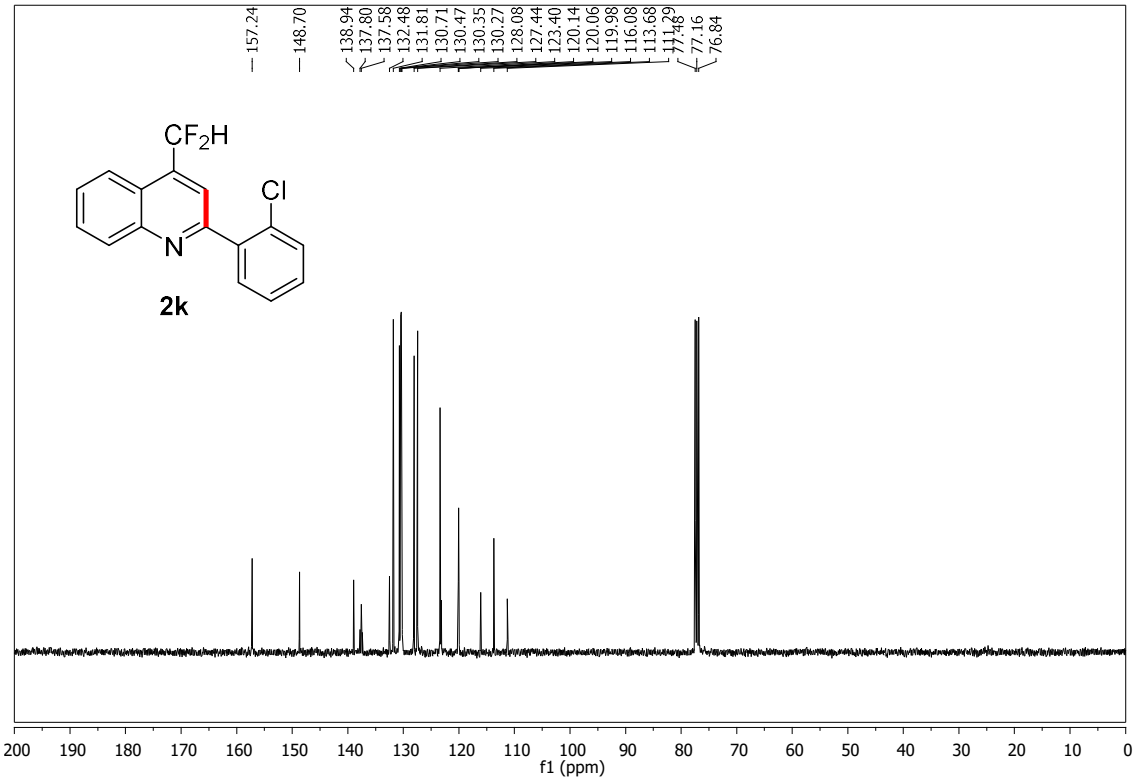


2-(2-Bromophenyl)-4-(difluoromethyl)quinoline (2j)

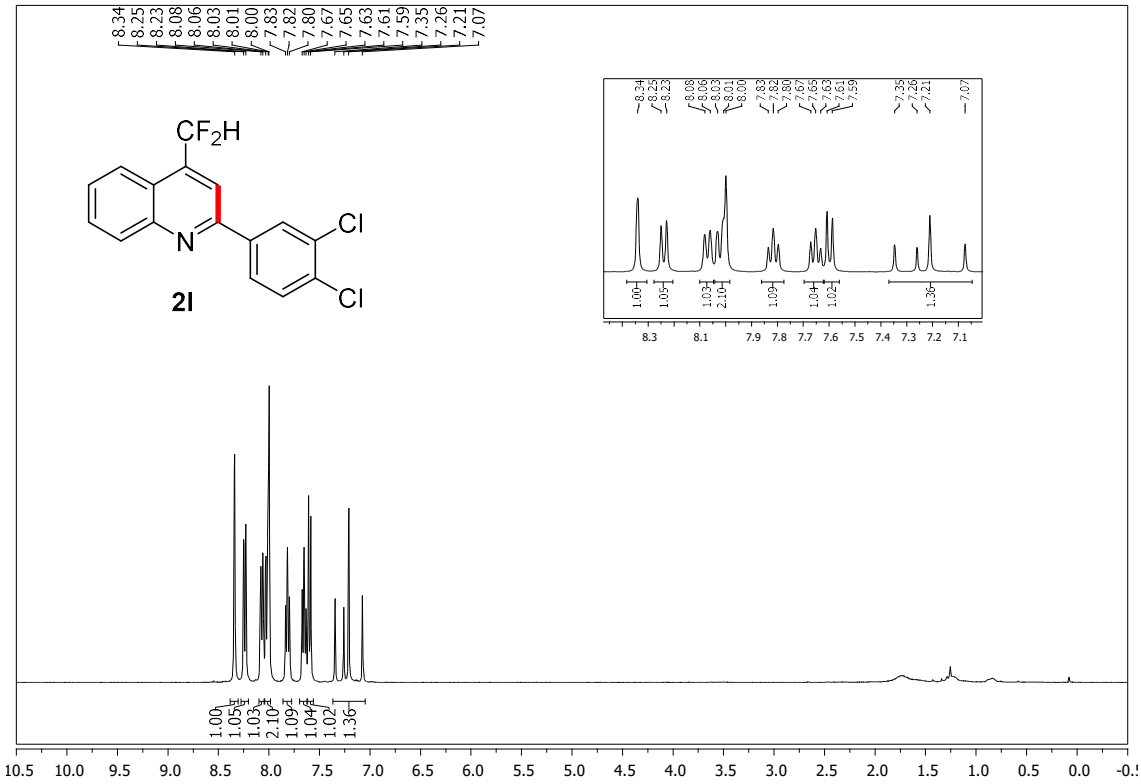


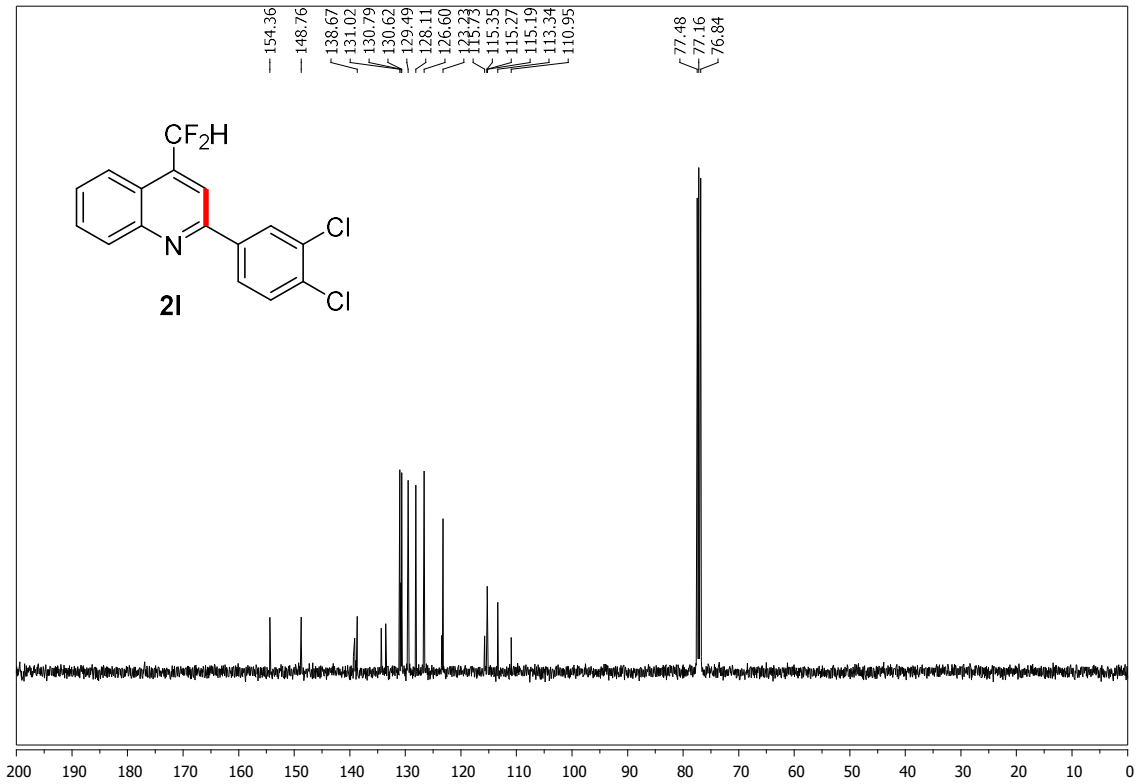
2-(2-Chlorophenyl)-4-(difluoromethyl)quinoline (2k)



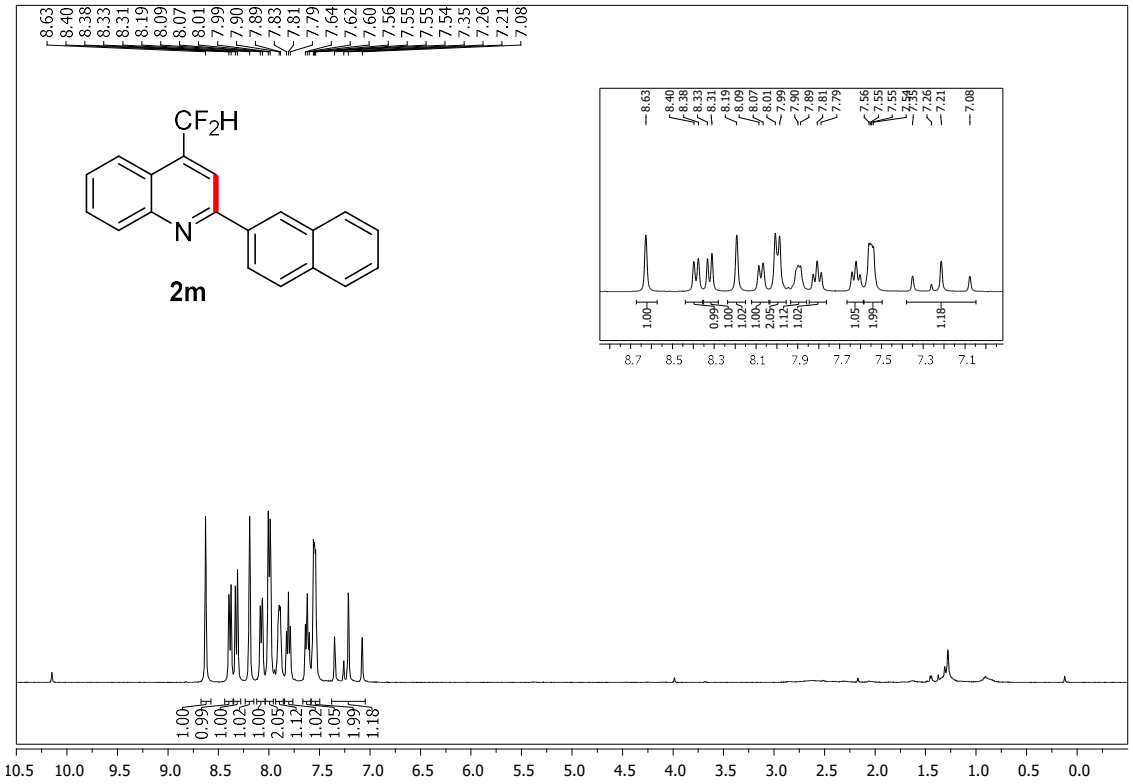


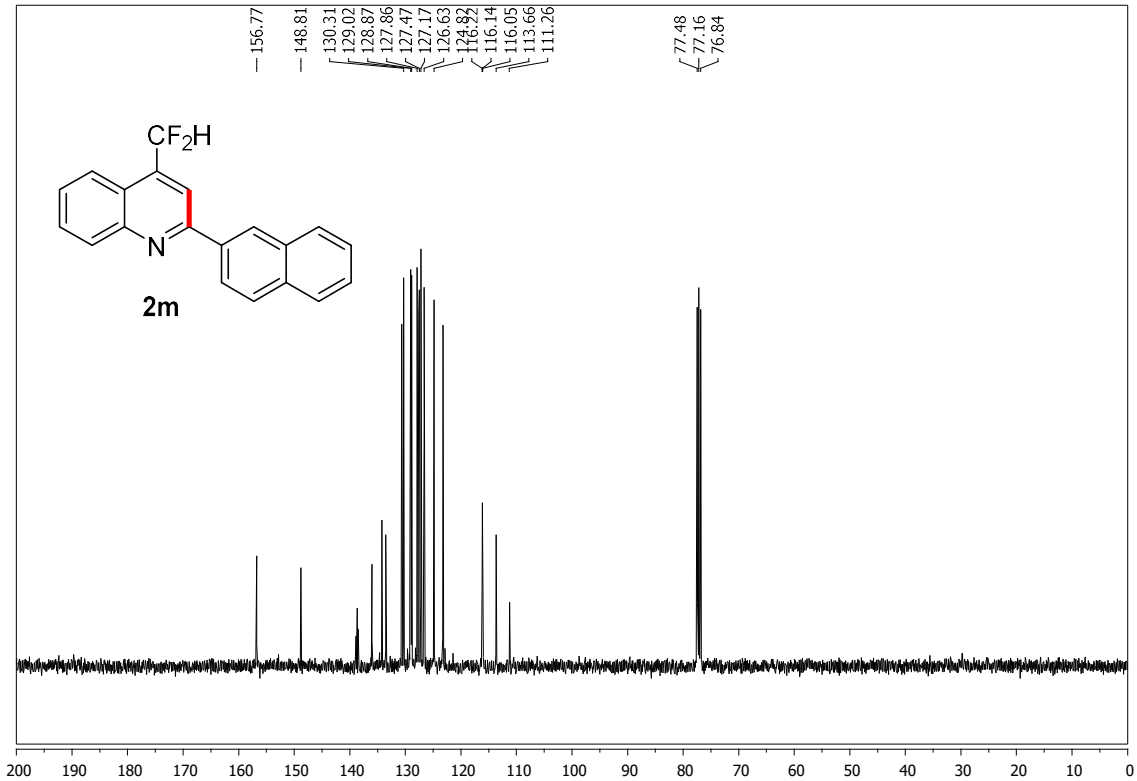
2-(3,4-Dichlorophenyl)-4-(difluoromethyl)quinoline (2l)



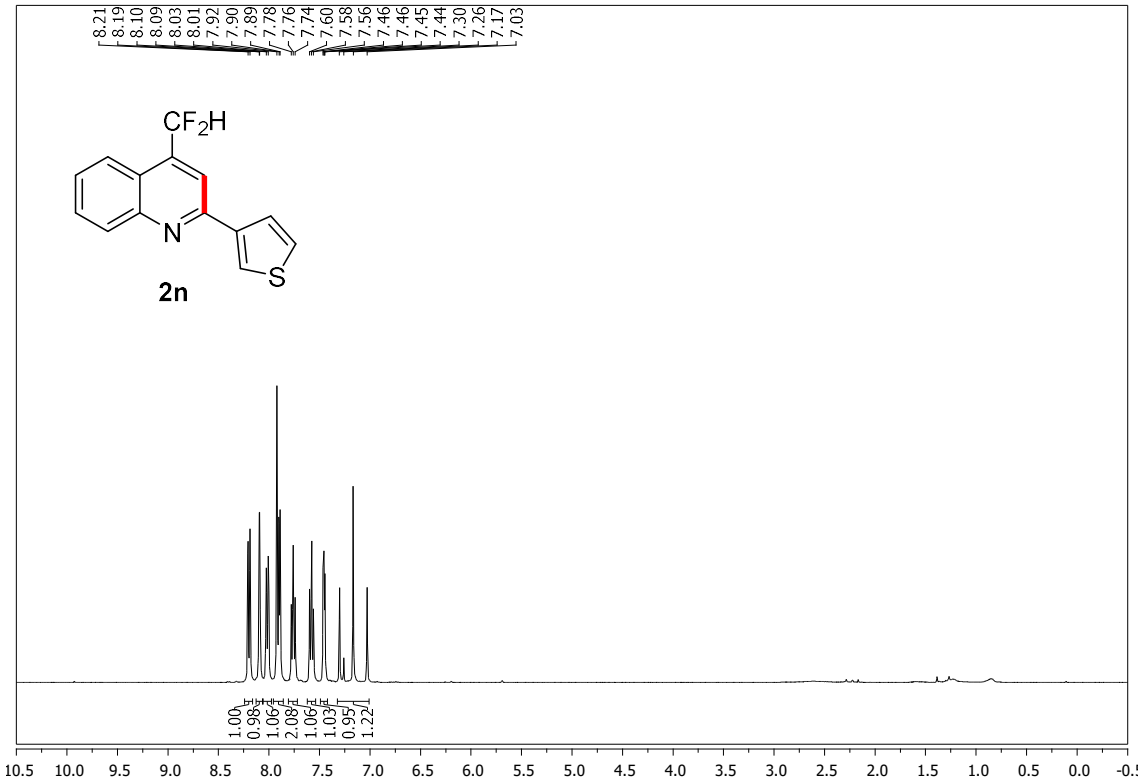


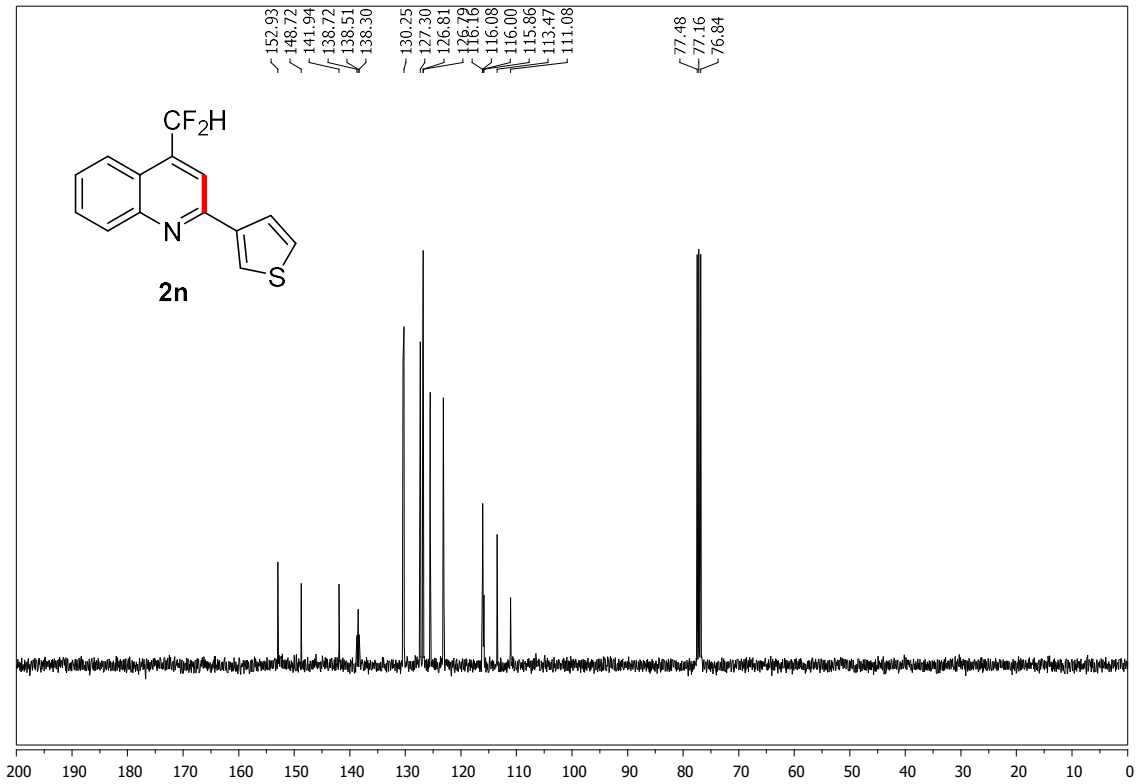
4-(Difluoromethyl)-2-(naphthalen-2-yl)quinoline (2m)



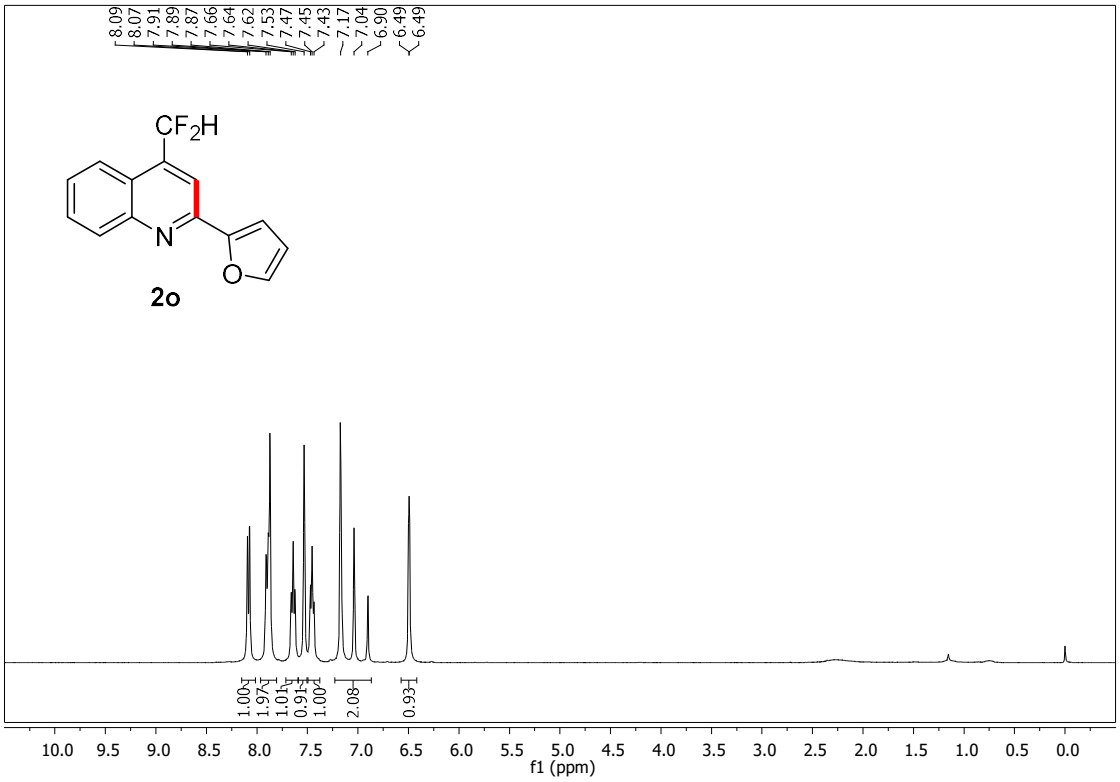


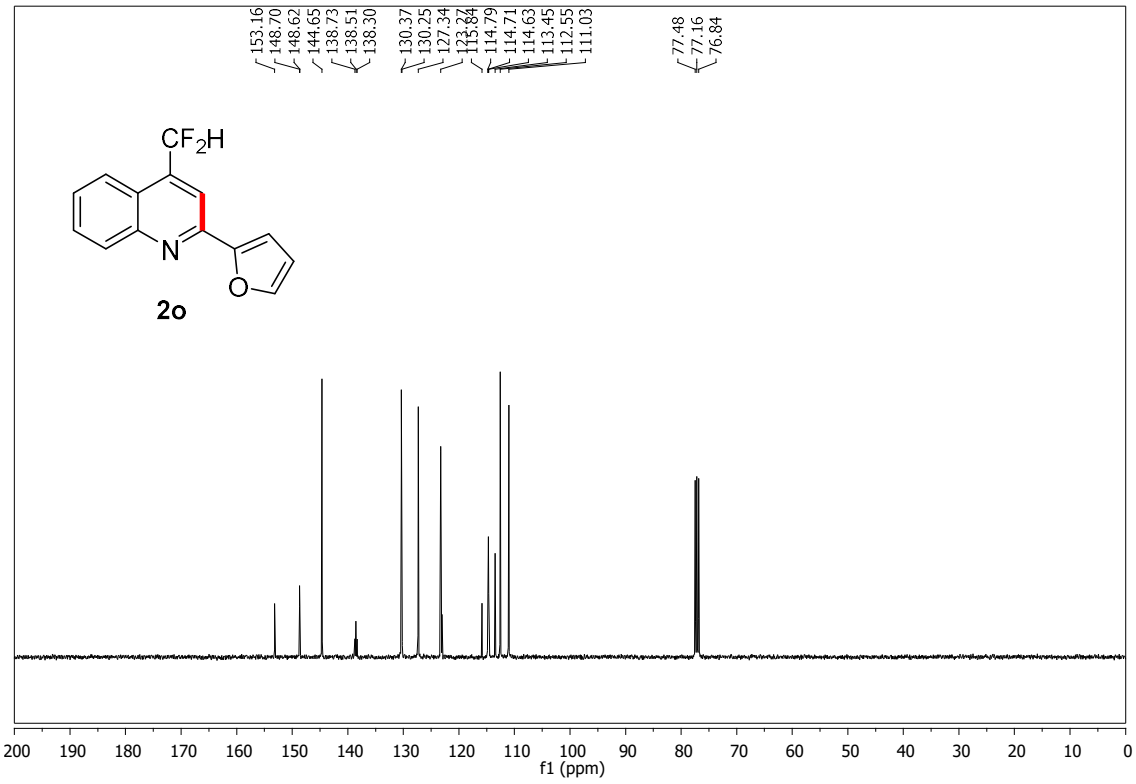
4-(Difluoromethyl)-2-(thiophen-3-yl)quinoline (2n)



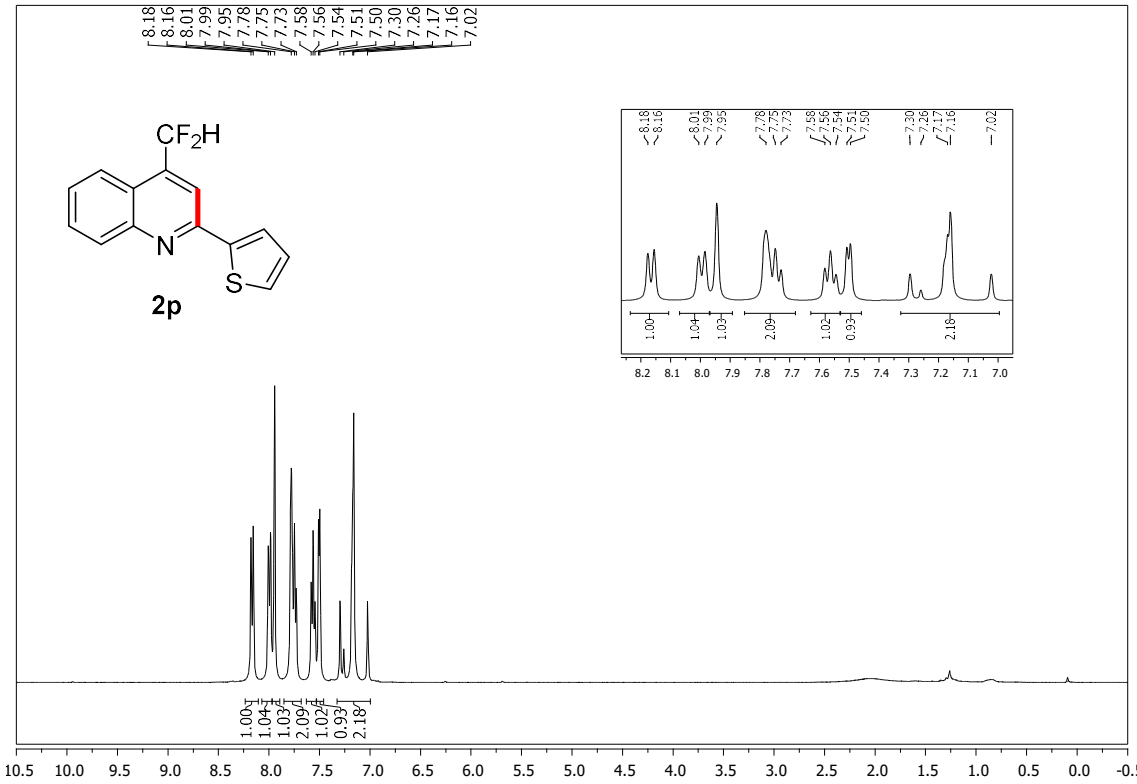


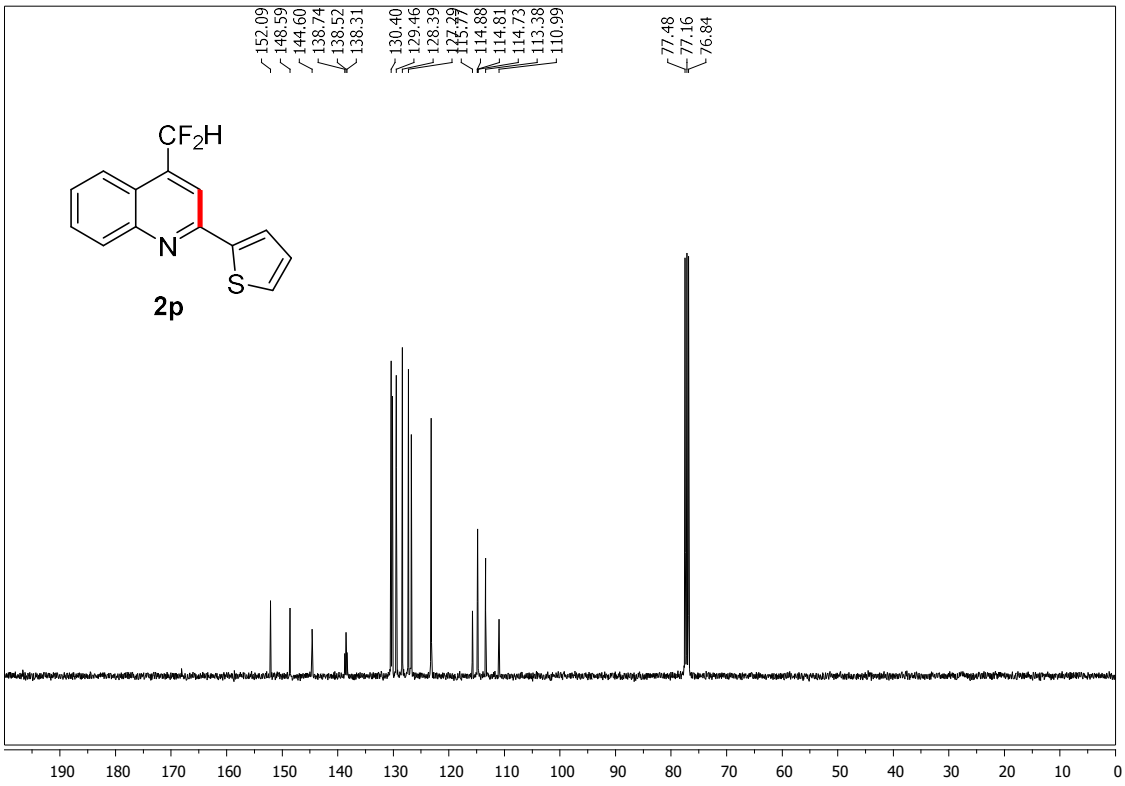
4-(Difluoromethyl)-2-(furan-2-yl)quinoline (2o)



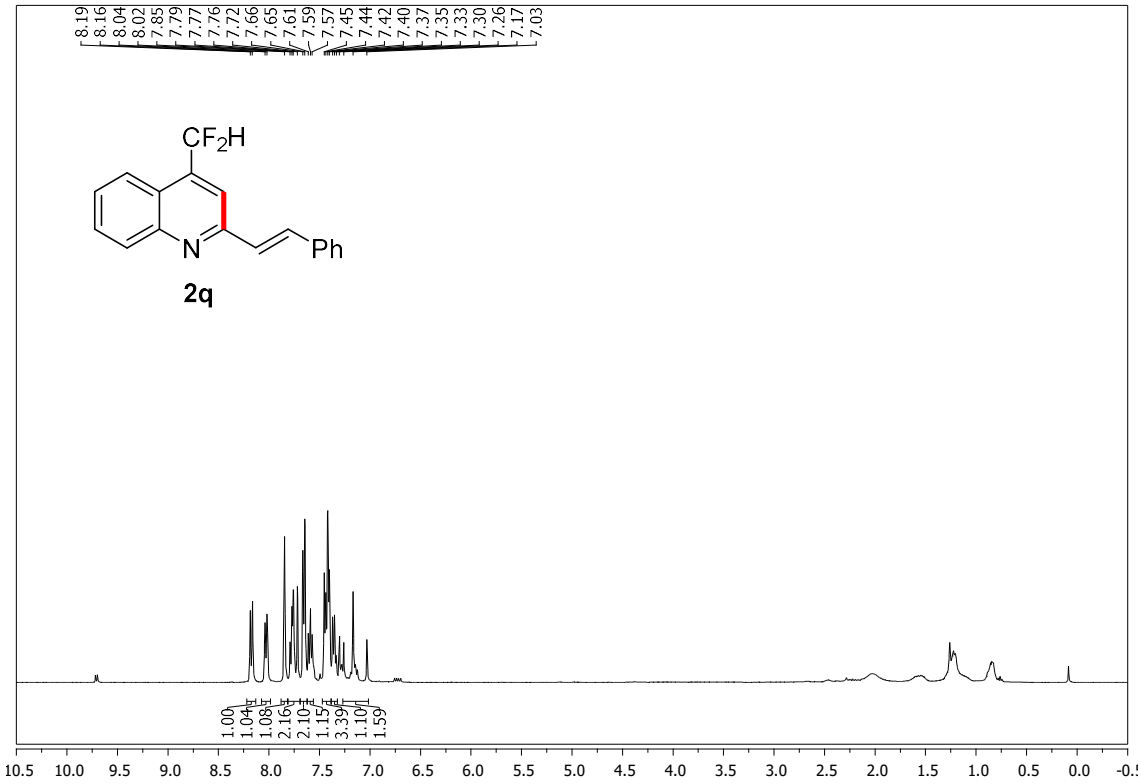


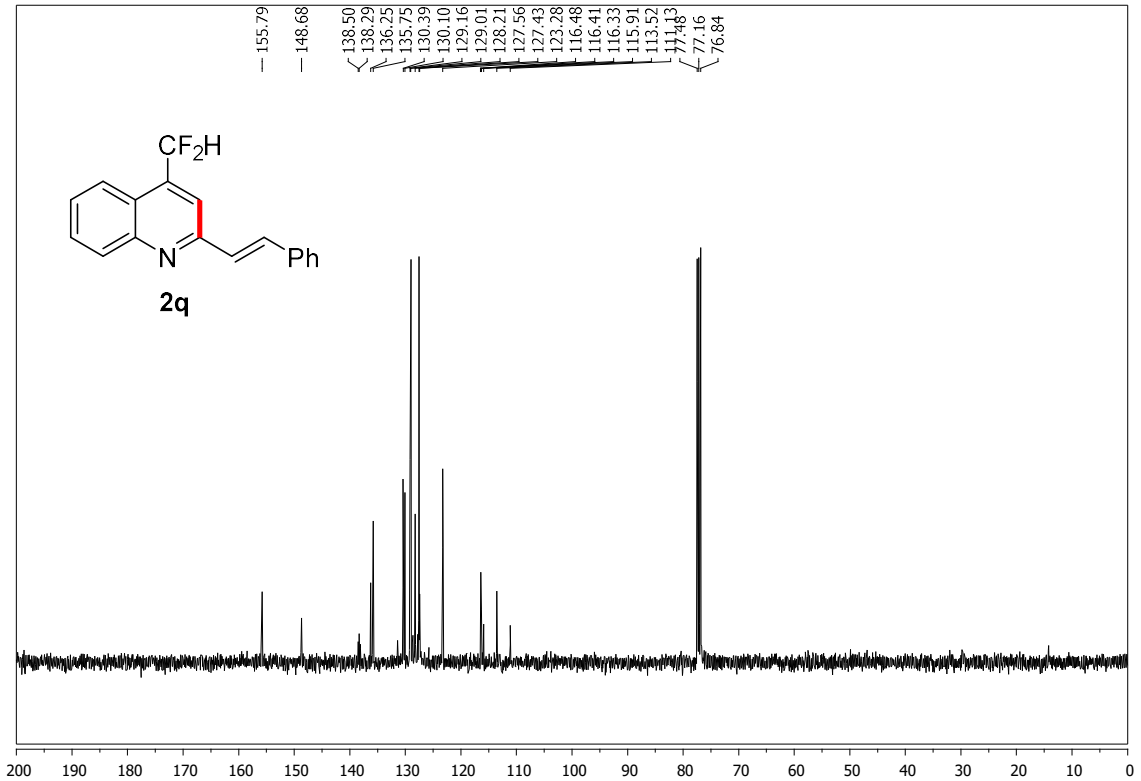
4-(Difluoromethyl)-2-(thiophen-2-yl)quinoline (2p)



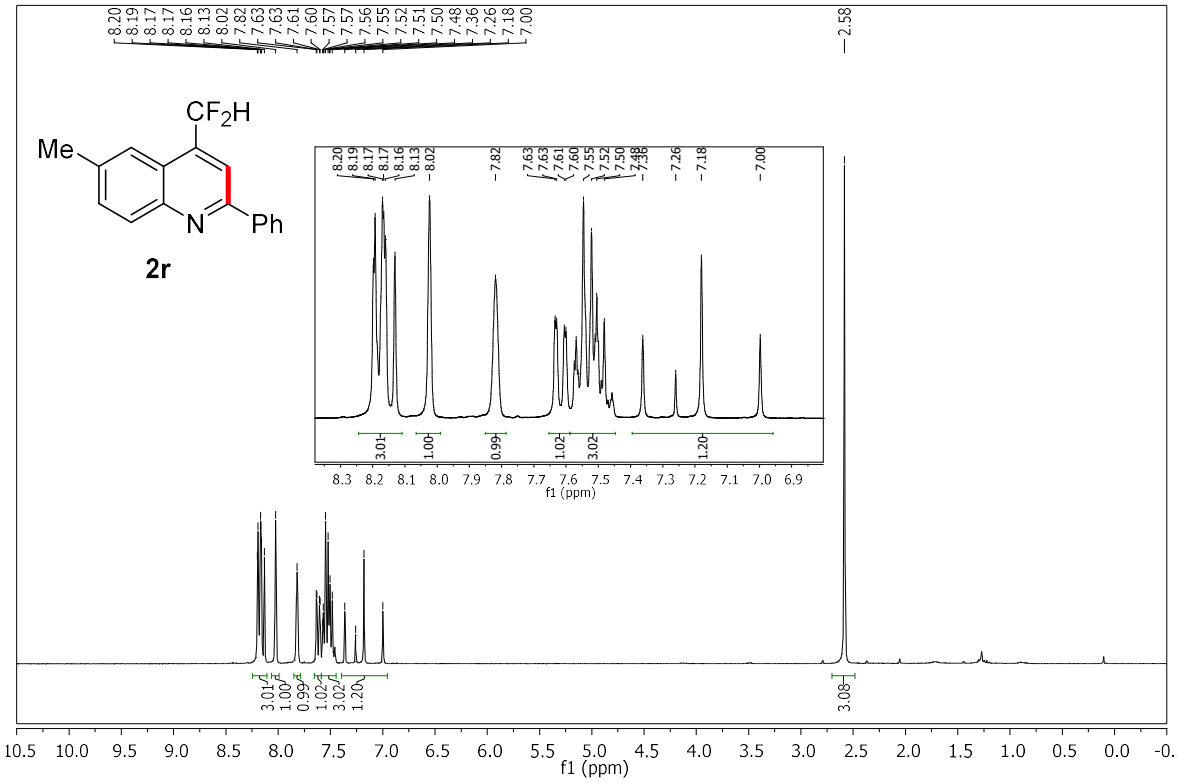


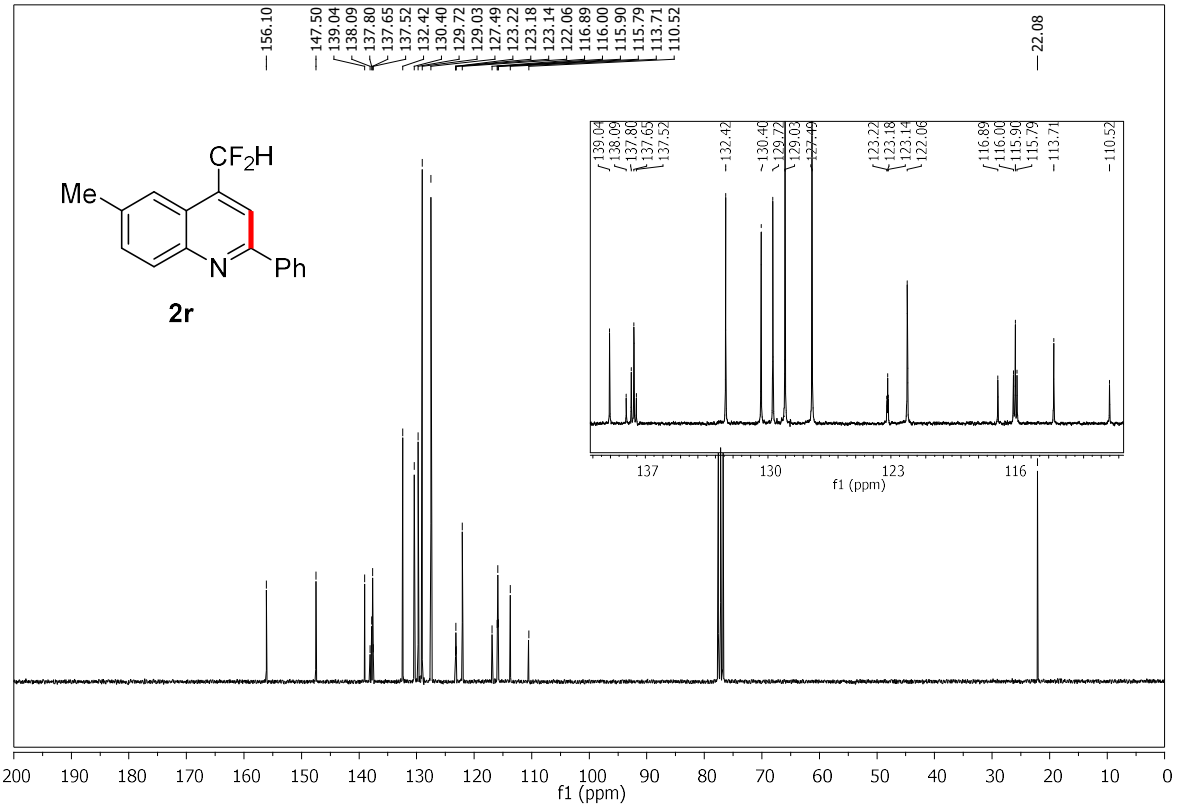
(*E*)-4-(Difluoromethyl)-2-styrylquinoline (2q)



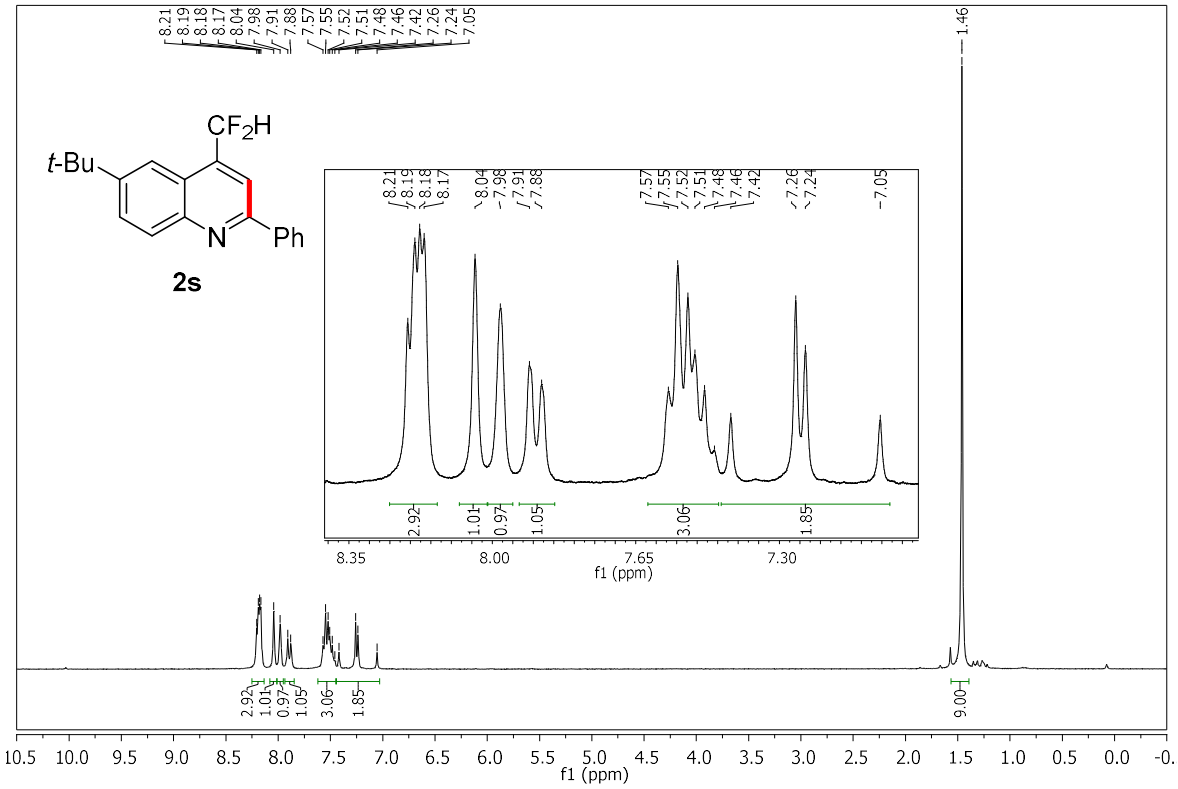


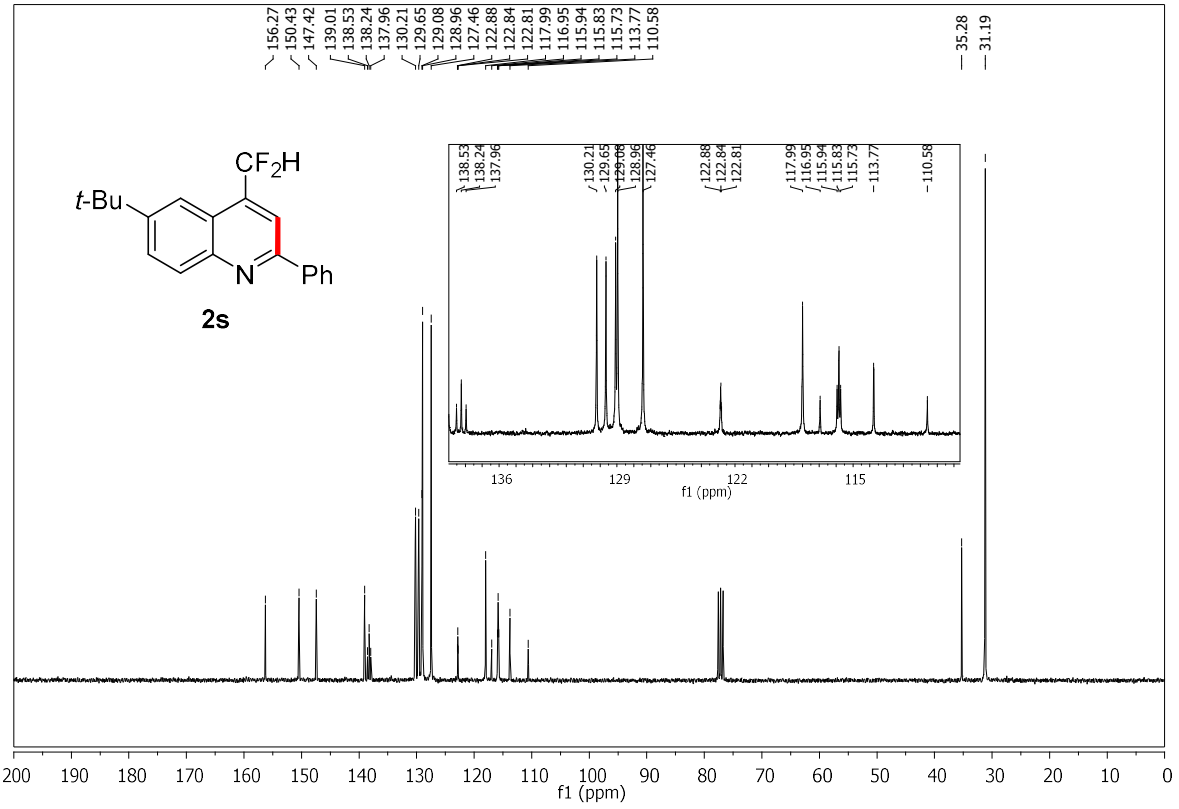
4-(Difluoromethyl)-6-methyl-2-phenylquinoline (2r)



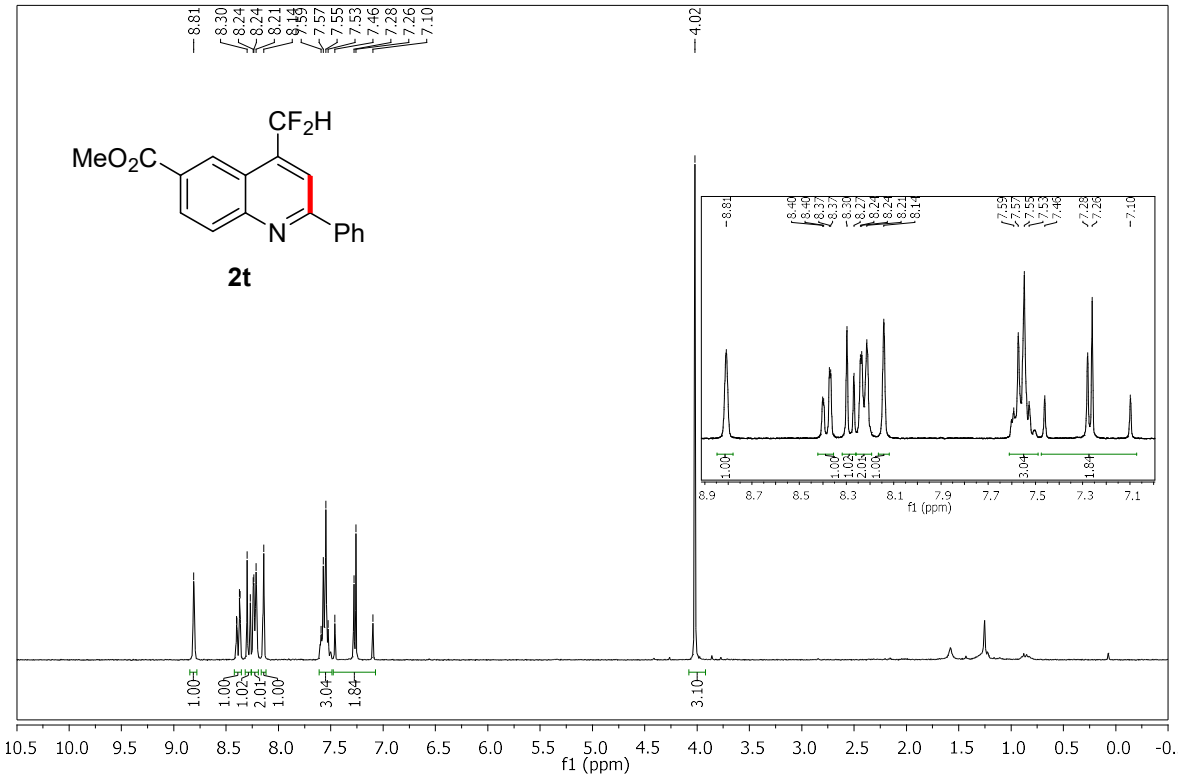


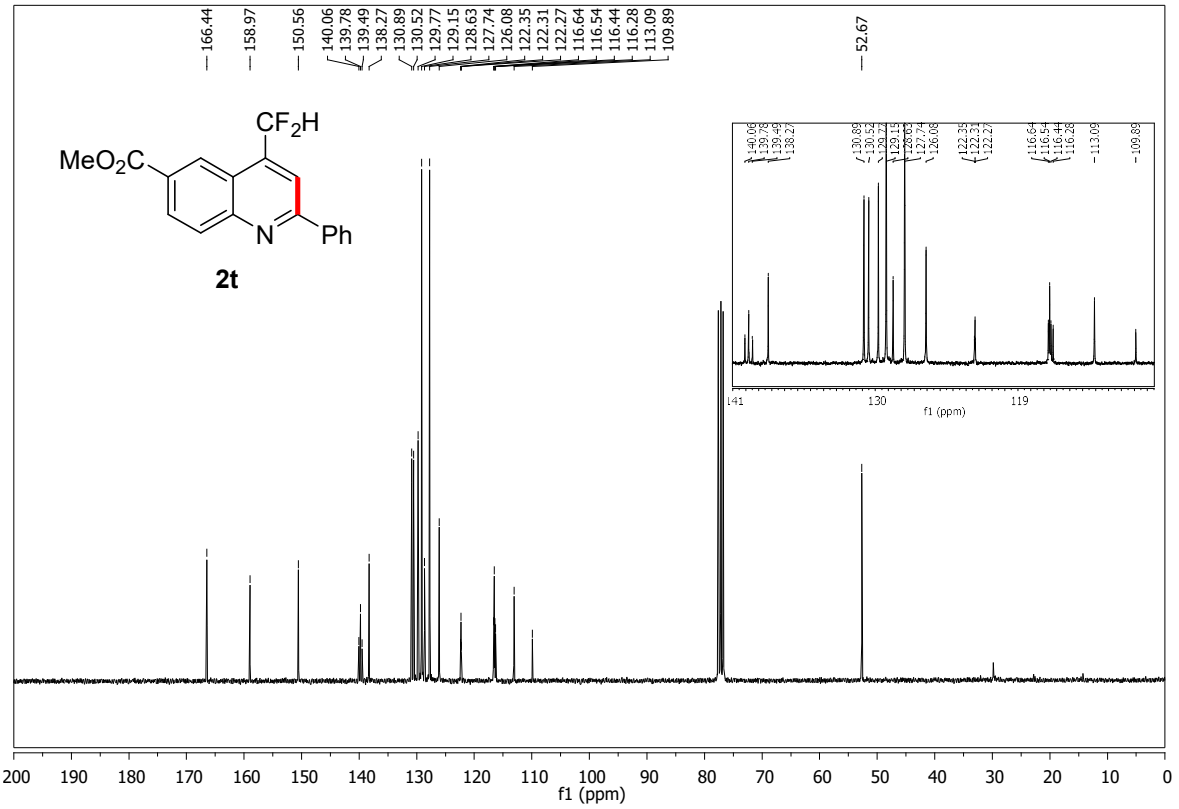
6-*tert*-Butyl-4-(difluoromethyl)-2-phenylquinoline (2s)



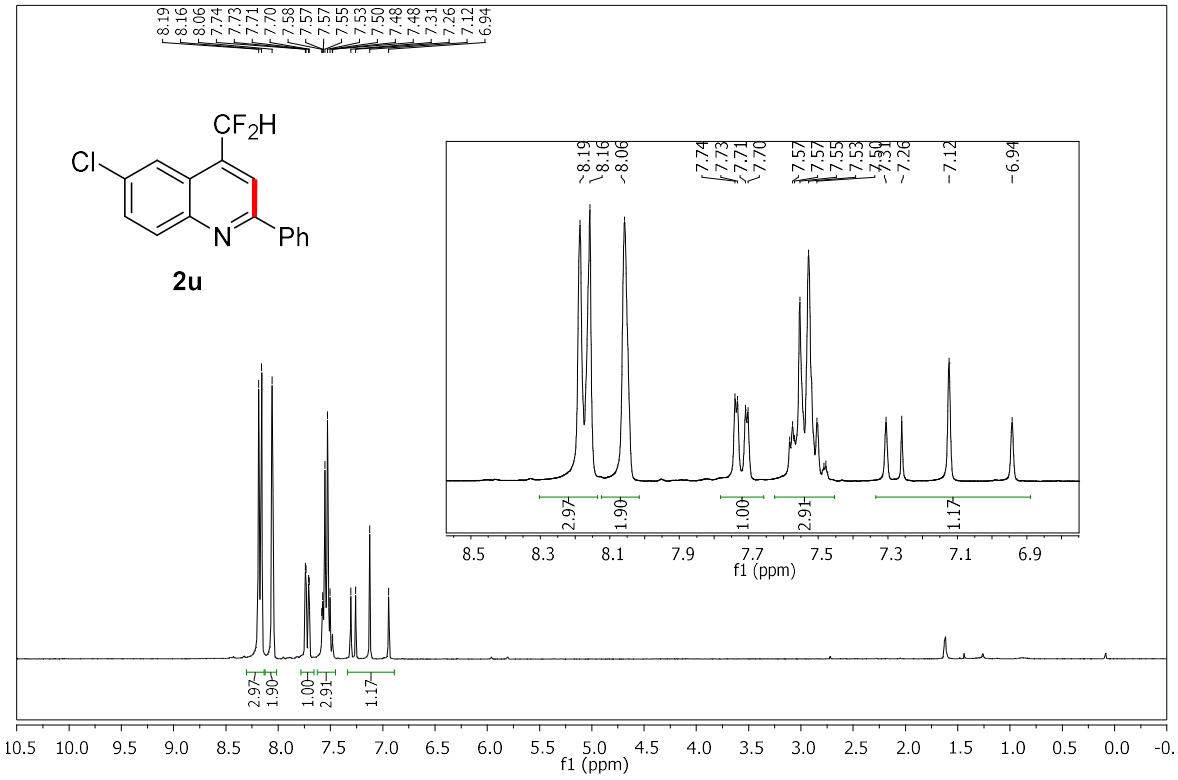


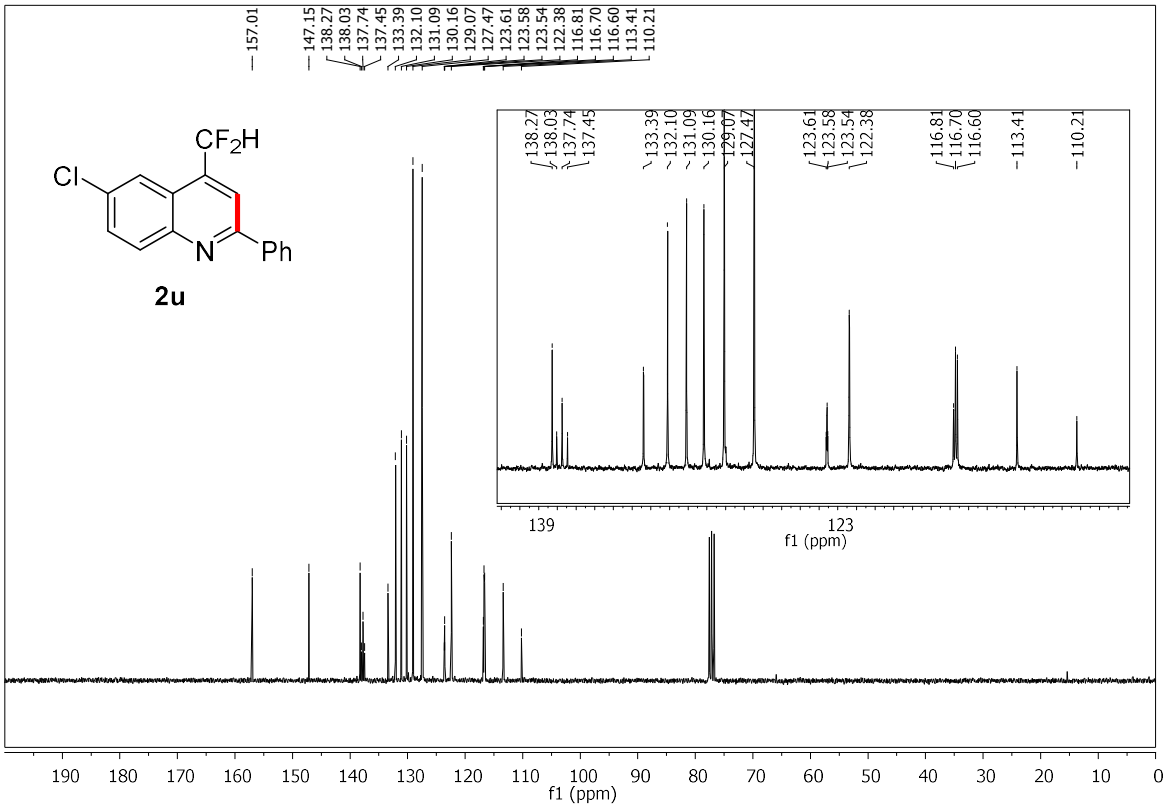
Methyl 4-(difluoromethyl)-2-phenylquinoline-6-carboxylate (2t)



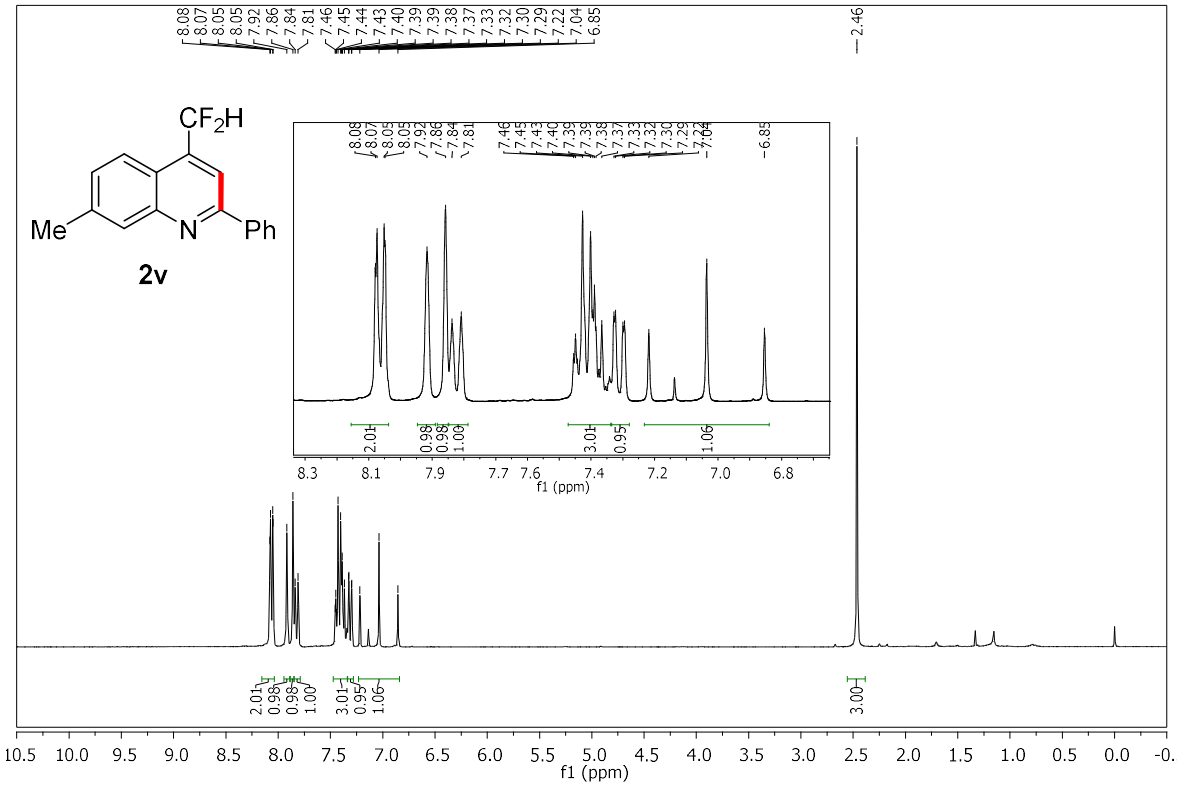


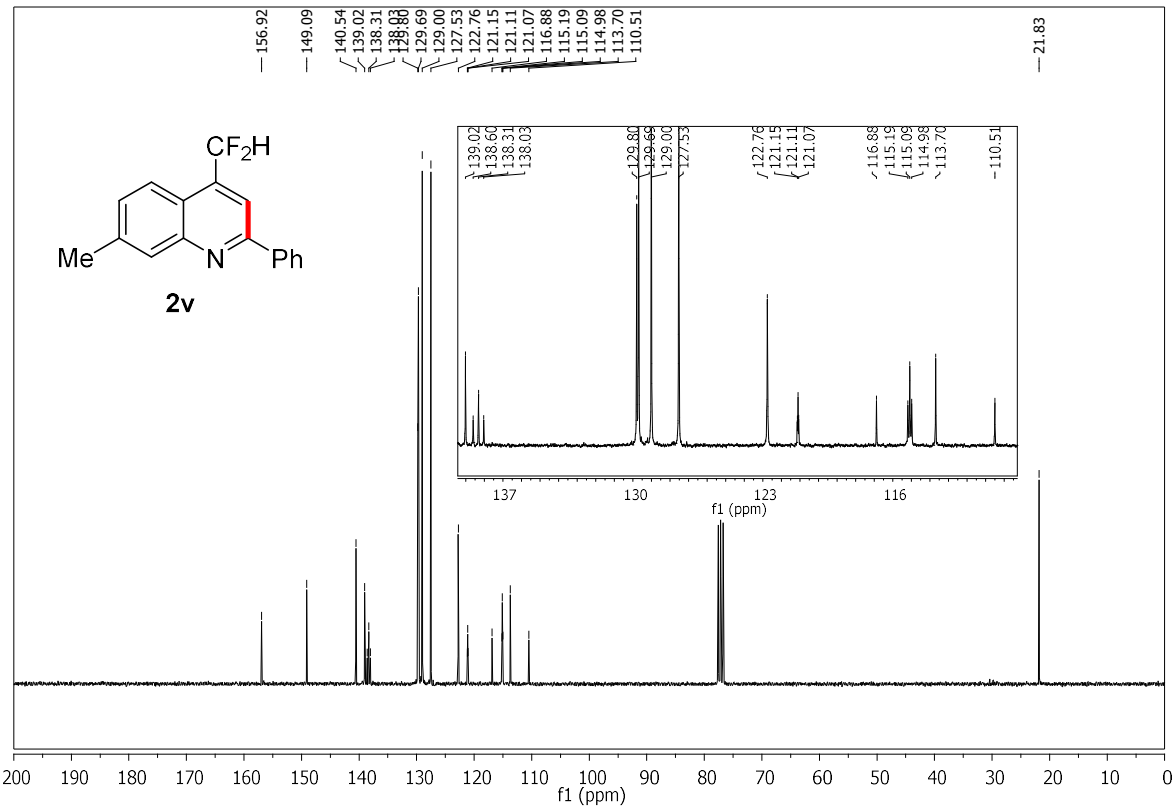
6-Chloro-4-(difluoromethyl)-2-phenylquinoline (2u)



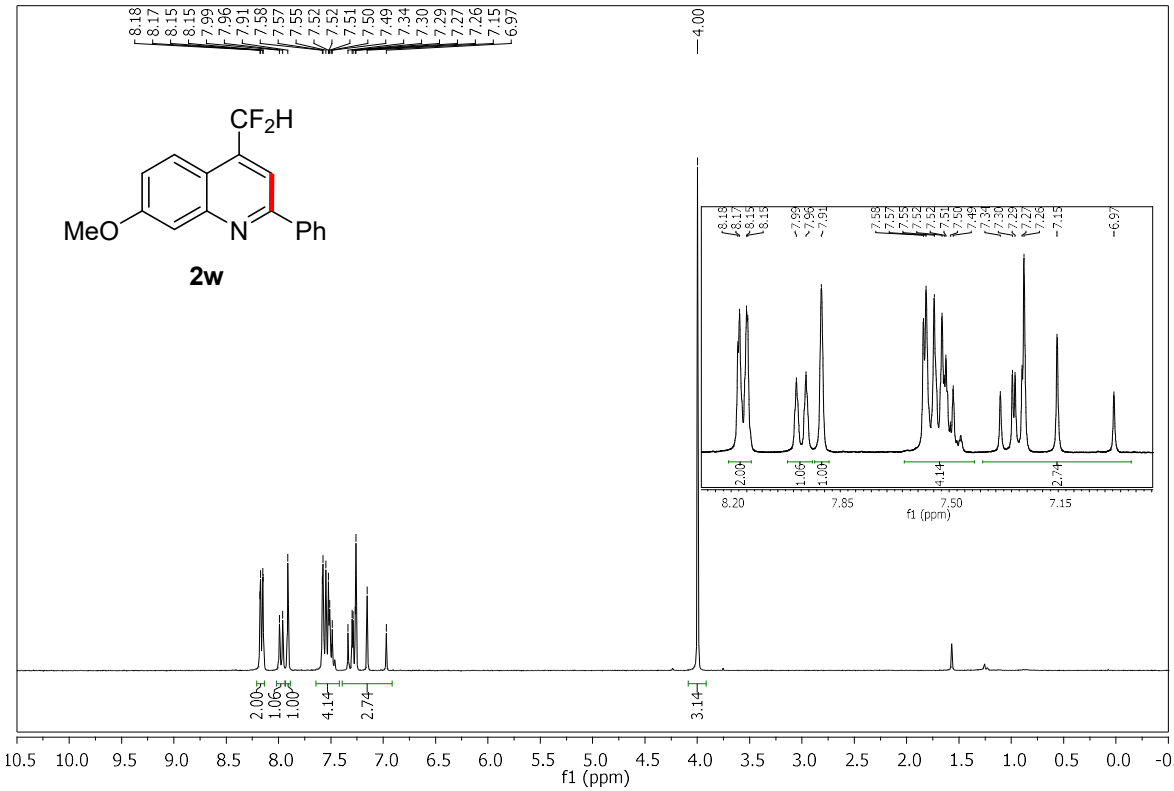


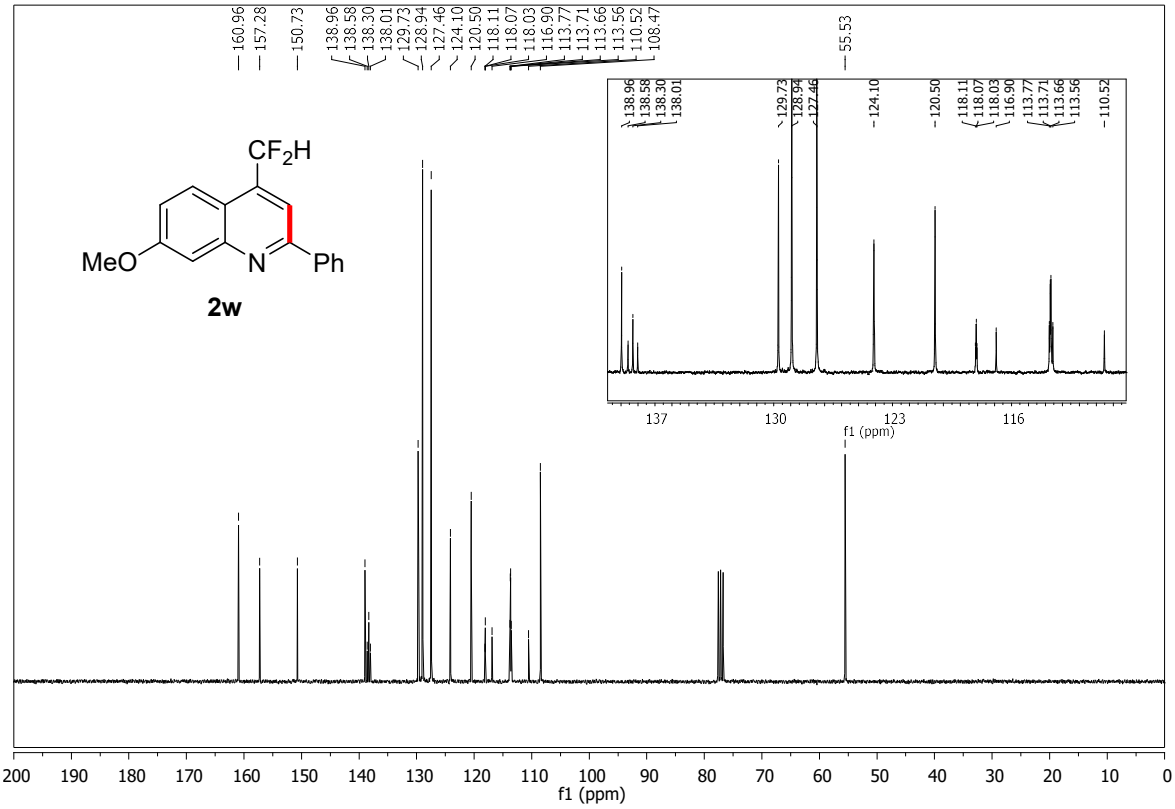
4-(Difluoromethyl)-7-methyl-2-phenylquinoline (2v)



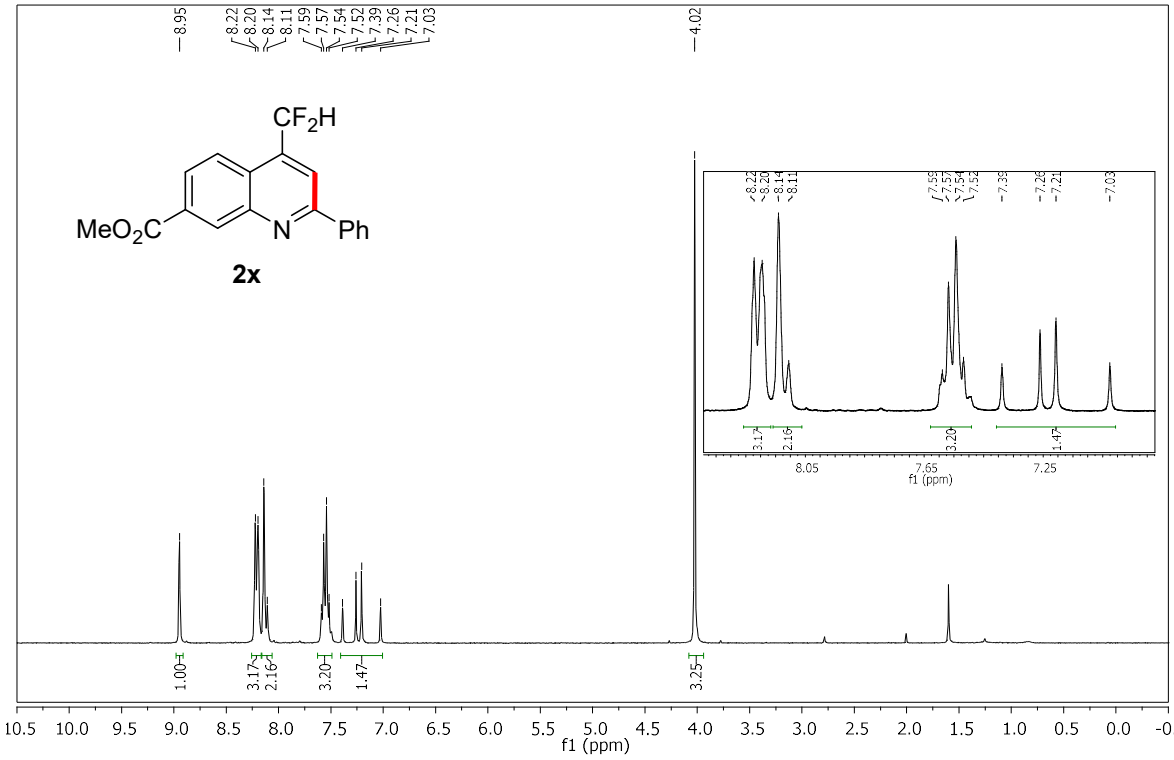


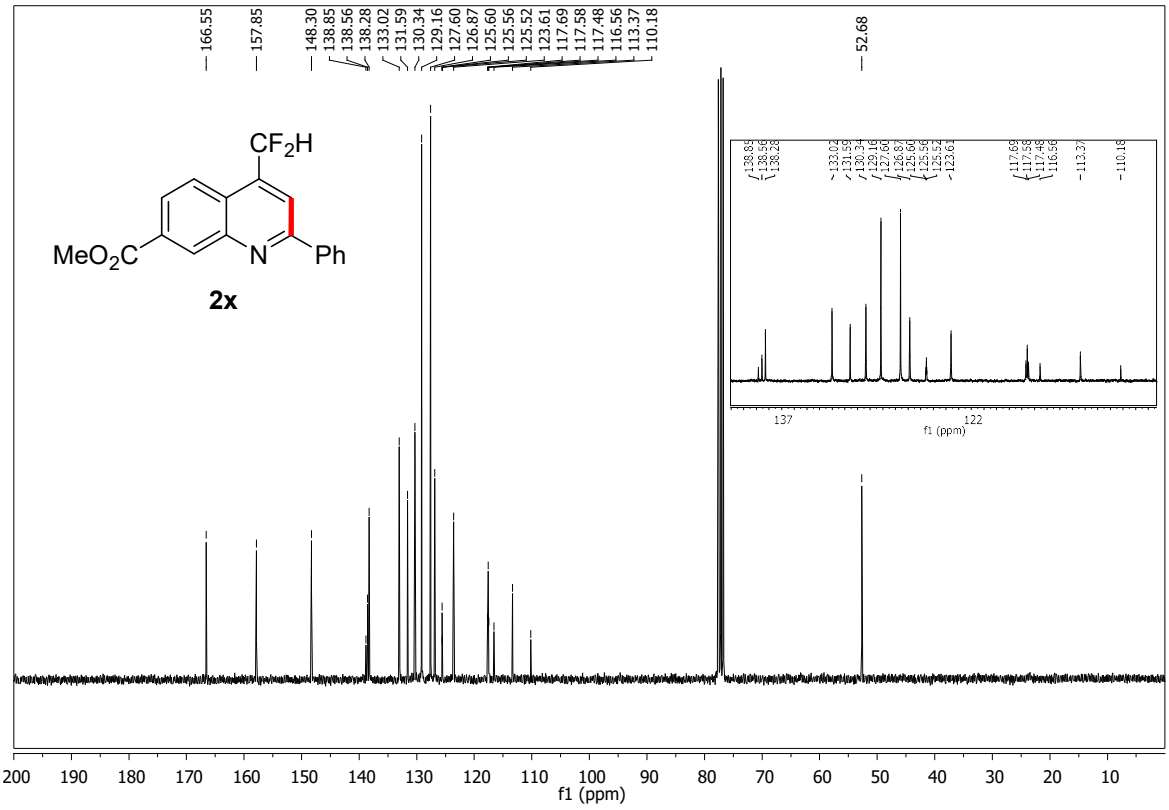
4-(Difluoromethyl)-7-methoxyl-2-phenylquinoline (2w)



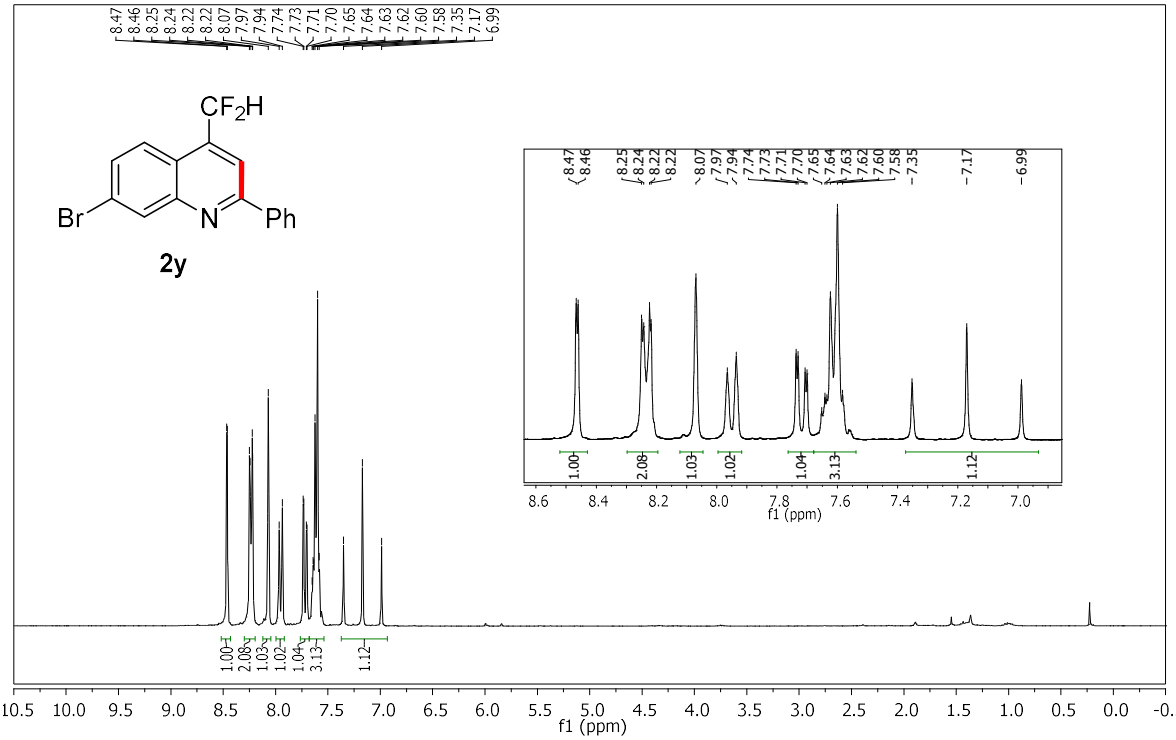


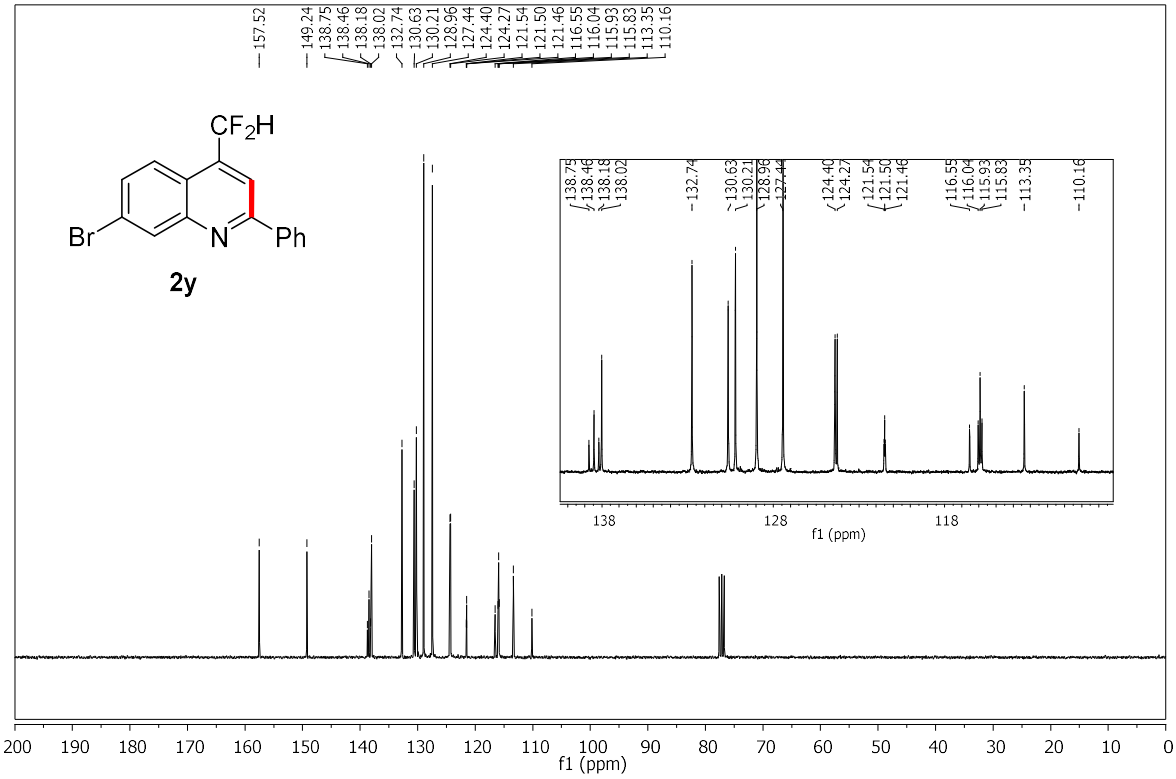
Methyl 4-(difluoromethyl)-2-phenylquinoline-7-carboxylate (2x)



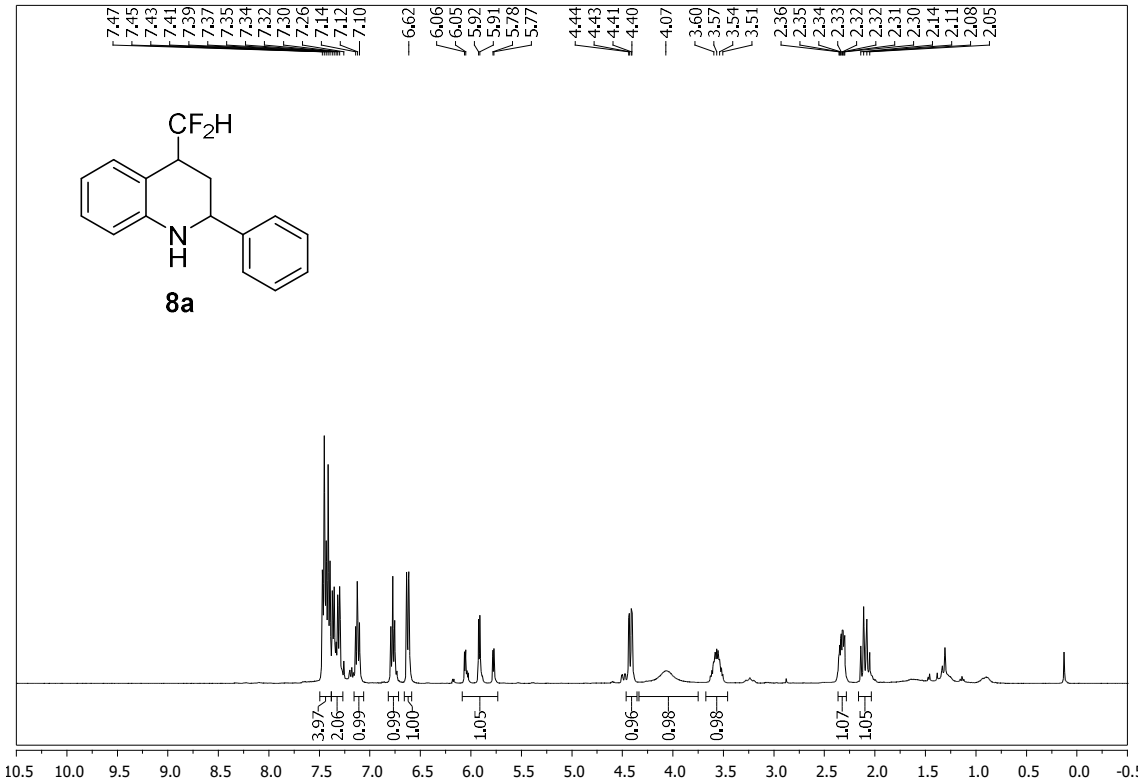


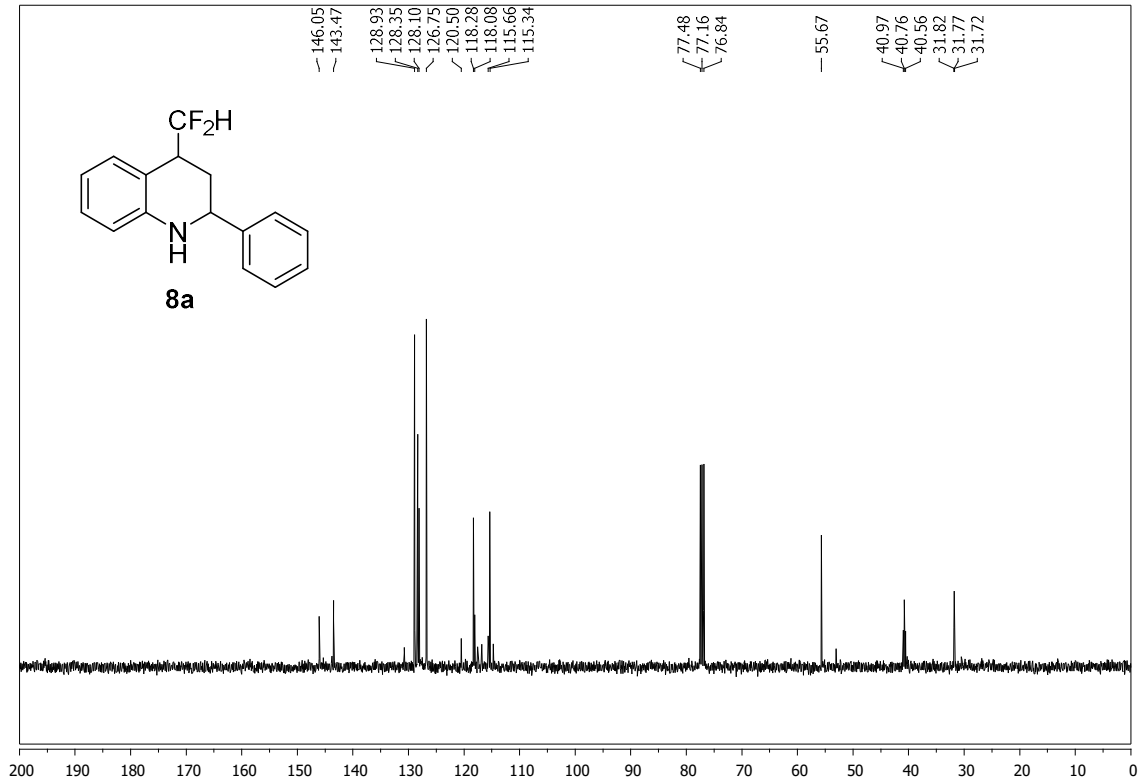
7-Bromo-4-(difluoromethyl)-2-phenylquinoline (2y)



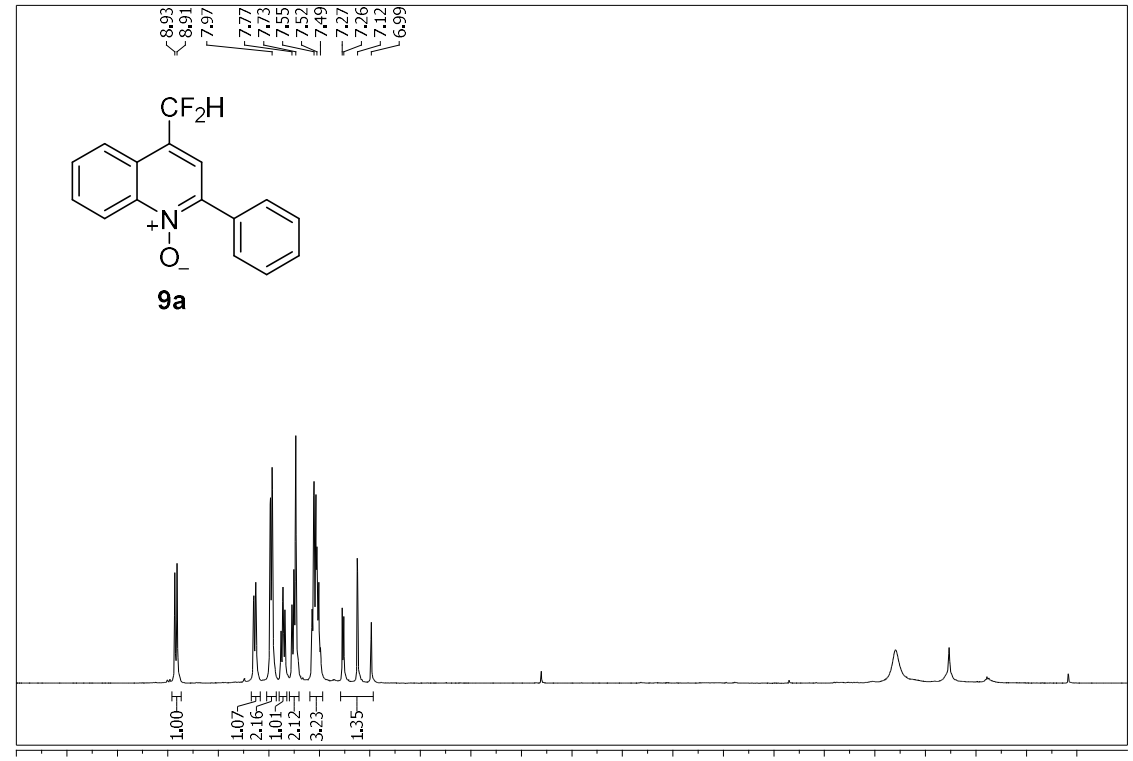


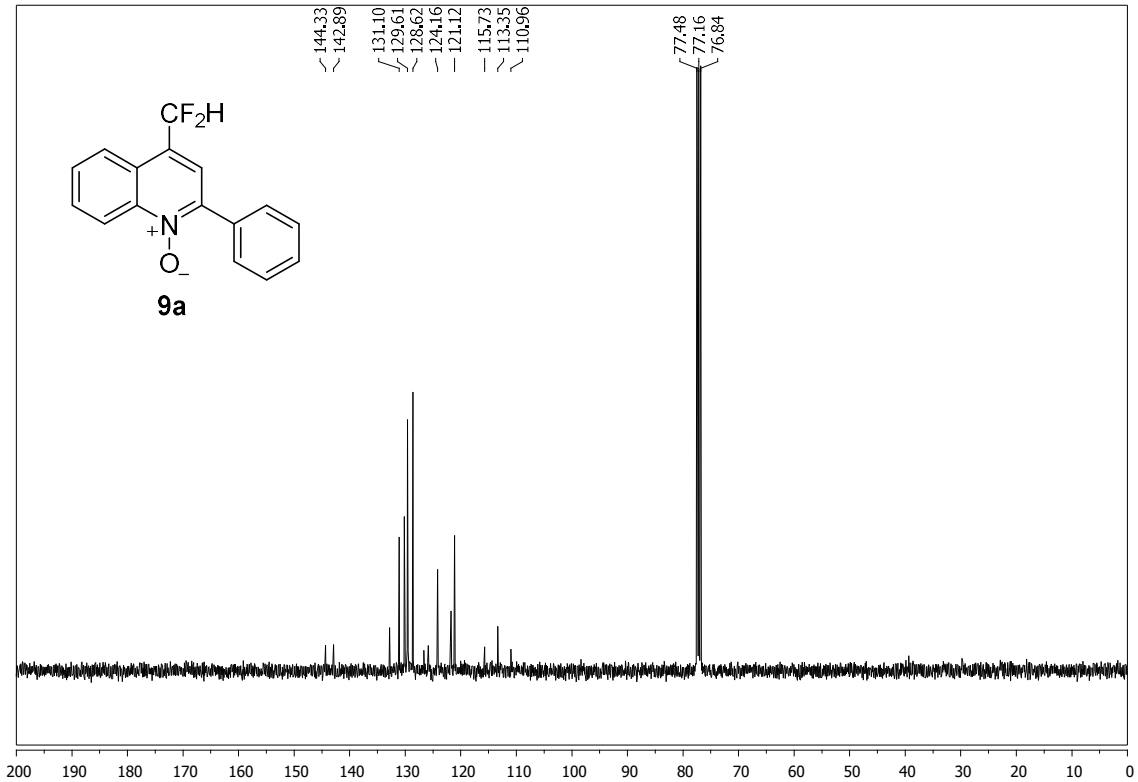
4-(Difluoromethyl)-2-phenyl-1,2,3,4-tetrahydroquinoline (8a)



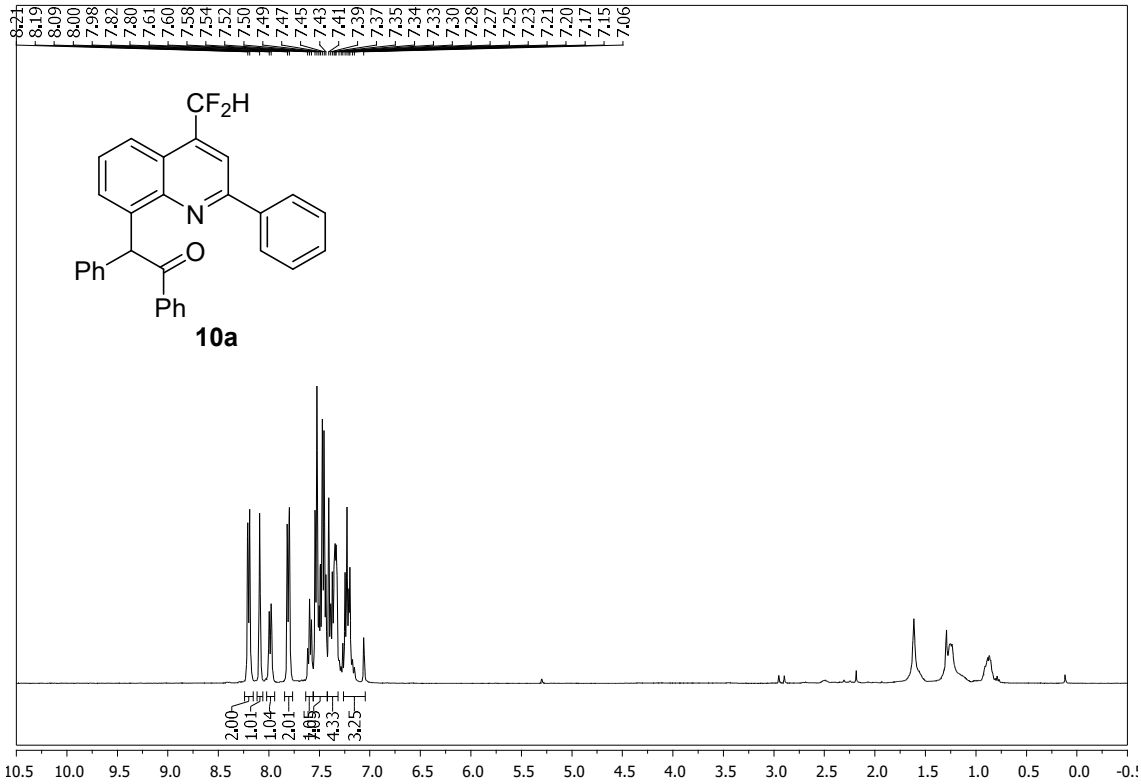


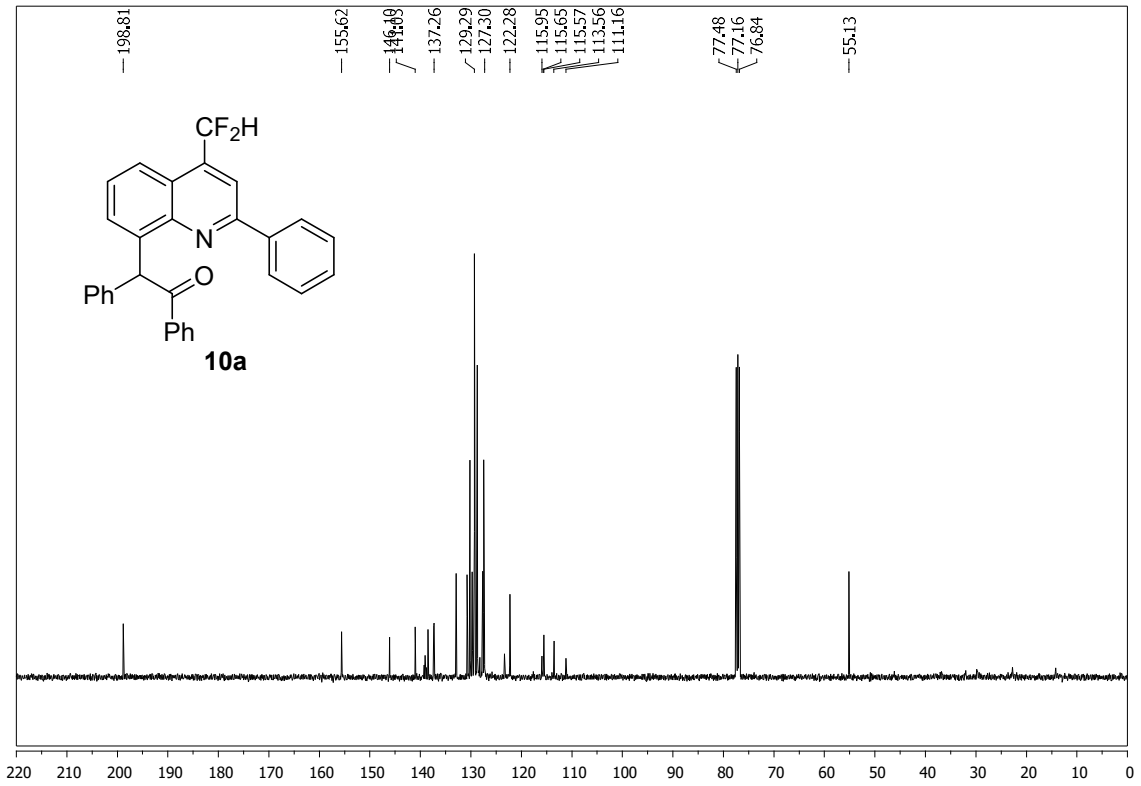
4-(Difluoromethyl)-2-phenylquinoline 1-oxide (9a)





2-(4-(Difluoromethyl)-2-phenylquinolin-8-yl)-1,2-diphenylethan-1-one (10a)





1-(2-(4-(Difluoromethyl)quinolin-2-yl)phenyl)-3-phenoxypropan-2-ol (11a)