

Supplementary Information

Chromatographic purification of N–H ketimines via suppression of hydrolysis using dried silica gel and Et₃N

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I Instrumentation

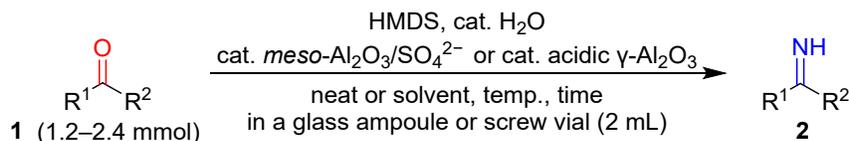
The solution NMR spectra were recorded using a JEOL ECZ 400S NMR spectrometer at 400 MHz for ^1H and 100 MHz for ^{13}C NMR. The chemical shift values for ^1H were referenced to $(\text{CH}_3)_4\text{Si}$ ($\delta = 0$ in CDCl_3) or residual solvents ($\delta = 2.50$ in $\text{DMSO}-d_6$), and those for ^{13}C were referenced to the residual solvent ($\delta = 77.0$ ppm in CDCl_3 and $\delta = 39.5$ ppm in $\text{DMSO}-d_6$). Chemical shifts are reported in δ ppm. Multiplicities are indicated as: br (broad), s (singlet), d (doublet), t (triplet), q (quartet), sext (sextet), or m (multiplet). The coupling constants (J) are given in Hz. IR spectroscopy was performed on a JASCO FT/IR-4600 with ATR (attenuated total reflection) system of “ATR PRO ONE” using a ZnSe plate. The ZnSe plate could be noisy at $<550\text{ cm}^{-1}$, hence the measurements were taken in the range of $4000\text{--}550\text{ cm}^{-1}$. The high-resolution mass spectrometry (HRMS) was performed on a Thermo Fisher Scientific Exactive Plus (ESI-quadrupole-Orbitrap MS). All quantum chemistry calculations were performed using Gaussian 16, Revision C.01 software.¹

II Experimental Procedures for the synthesis of ketimines

Ketones, amines, and hexamethyldisilazane (HMDS) were purchased from Tokyo Chemical Industry Co., Ltd. (TCI). Dichloromethane (CH_2Cl_2) was obtained from FUJIFILM Wako Pure Chemical Corp. Water was obtained as ultrapure water from a Milli-Q purification system (Millipore). Acidic $\gamma\text{-Al}_2\text{O}_3$, used as the catalyst for ketimine synthesis, was acquired from Sigma-Aldrich® (activated acidic aluminum oxide, Brockmann I, $\text{pH } 4.5 \pm 0.5$). $\text{Meso-Al}_2\text{O}_3/\text{SO}_4^{2-}$ was prepared according to a previously reported procedure.²

N–H and N–R ketimines were prepared according to the literature procedure.² For particularly hydrolysis-sensitive substrates (N–H ketimines **2h**, **2i**, and **2k** and N–R ketimine **3c**), the materials were used in subsequent experiments with minimizing exposure to air. Specific reaction conditions for individual substrates are summarized in the compound data (Section III). For filtration of the reaction mixture in the procedures described below, a disposable syringe (12 mL, material: injection cylinder/polypropylene, plunger and seal/polyethylene) fitted with a membrane filter (pore size $0.45\ \mu\text{m}$, ADVANTEC DISMIC 13HP045AN) was used.

1. General procedure for N–H ketimines



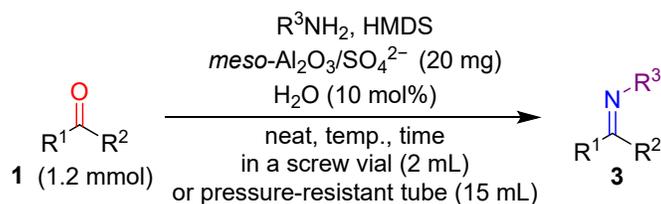
$\text{Meso-Al}_2\text{O}_3/\text{SO}_4^{2-}$ and acidic $\gamma\text{-Al}_2\text{O}_3$ (20–40 mg), pre-dried at $400\text{ }^\circ\text{C}$ under reduced pressure (<0.5 Torr) for 1 h, were placed in a 2 mL screw vial (PTFE/nitrile inner lid) or a 2 mL glass ampoule (Fig. S1), and water (0.12–0.48 mmol, 10–40 mol%) was added. When a solvent was used, reactions were performed in a sealed glass ampoule to ensure gas-tightness. Then, ketone **1** (1.2–2.4 mmol) and HMDS (1.2–2.0 equiv) were added to the vessel. When required, 1.2 mL of solvent was added. After the vessel was purged with argon, it was tightly sealed. The mixture was

stirred at the specified temperature for the time specified for each substrate. Then, the workup was performed in the following two ways:

(i) Work-up of 2a, 2d–2g, 2j, and 2l: The resulting mixture was then filtered under mild positive pressure, and the remaining solids were washed with CH₂Cl₂, and the filtrate was concentrated. The N–H ketimine was quantitatively isolated by removing low-boiling compounds.

(ii) Work-up of 2h, 2i, and 2k: The glass ampoule was opened in a glove bag filled with argon gas. The mixture was filtered under mild positive pressure. The remaining solids were washed with CH₂Cl₂. Subsequently, 1,4-dioxane was added to the filtrate as an internal standard, and the yield of N–H ketimine **2** was determined by ¹H NMR analysis in CDCl₃. The NMR yields were >99% for **2h**, 94% for **2i**, and 73% for **2k**, respectively. After concentration, the solution was used immediately in the subsequent experiment without storage. Throughout the procedure, exposure to air was minimized.

2. General procedure for N–R ketimines



Reaction protocol for 3a and 3c: *meso*-Al₂O₃/SO₄²⁻ and acidic γ -Al₂O₃ (20 mg), pre-dried at 400 °C under reduced pressure (<0.5 Torr) for 1 h, were placed in a 2 mL screw vial (Fig. S1, PTFE/nitrile inner lid), and water (0.12 mmol, 10 mol%) was added. Ketone **1** (1.2 mmol), amine (1.1 equiv), and HMDS (1.2 equiv) were then added to the vial. After the vessel was purged with argon, it was tightly sealed and stirred at 40 °C for 24 h. Due to increased internal pressure, the vessel was handled with care, and the workup was performed as follows:

(i) Work-up of 3a: The vial was slowly opened, and the mixture was filtered under mild positive pressure. The remaining solids were washed with CH₂Cl₂, and the filtrate was concentrated under reduced pressure. Lyophilization from benzene afforded N–R ketimine **3a** in quantitative yield.

(ii) Work-up of 3c: The vial was slowly opened in a glove bag filled with argon. The mixture was filtered under mild positive pressure, and the remaining solids were washed with CH₂Cl₂. Subsequently, 1,4-dioxane was added to the filtrate as an internal standard, and the yield of N–R ketimine **3c** was determined to be 94% by ¹H NMR spectroscopy in CDCl₃. After concentration, the solution was used immediately in the subsequent experiment without storage. Throughout the procedure, exposure to air was minimized.

Reaction protocol for 3b and 3d: *meso*-Al₂O₃/SO₄²⁻ and acidic γ -Al₂O₃ (20 mg), pre-dried at 400 °C under reduced pressure (<0.5 Torr) for 1 h, were placed in a 15 mL pressure-resistant tube (Fig. S1, ACE GLASS), and water (0.12 mmol, 10 mol%) was added. Ketone **1** (1.2 mmol), amine (1.1 equiv), and HMDS (1.5 equiv) were added to the tube. After the vessel was purged with argon, it was tightly sealed and stirred at 80 °C for 24 h. Then, amine (0.4 equiv) was added, and the reaction mixture was heated under the same conditions for an additional 24 h. After the reaction, the internal pressure was carefully released, and the mixture was filtered under mild positive pressure. The remaining solids were washed with CH₂Cl₂, and the combined filtrates were concentrated under reduced pressure. The residue was subjected to lyophilization from benzene. N–R ketimine **3b** was

obtained in quantitative yield, whereas N–R ketimine **3d** was isolated in 99% yield as a mixture containing 7% of N–H ketimine **2k**. The product was used directly in the subsequent experiments without further purification.

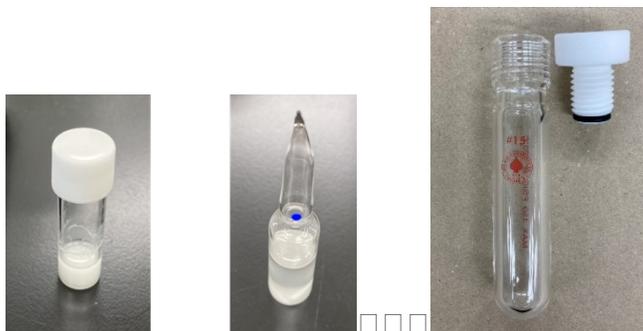


Fig. S1 Reaction vessels used in the synthesis of ketimines: a screw vial or a glass ampoule (2 mL), and a pressure-resistant tube (15 mL, ACE GLASS).

III Compound Data

3. Instability of N–H ketimine **2k** and N–R ketimine **3c** under air

N–H alkyl ketimines are highly unstable, and compounds such as N–H ketimine **2k** readily decompose under ambient conditions. In practice, despite careful handling, brief air exposure between column purification and subsequent ^1H NMR spectroscopy resulted in partial hydrolysis (a few percent) of **2k**. To evaluate this intrinsic instability, time-resolved IR-ATR measurements were performed at 23 °C and 35% relative humidity (Fig. S2). For comparison, the same measurements were conducted for N–R ketimine **3c**, which exhibited similar instability during synthesis, and the results around 1700 cm^{-1} are presented in Fig. S3. N–H ketimine **2k**, which initially contained 8% of the corresponding ketone, underwent progressive decomposition and was almost completely hydrolyzed after 150 minutes. N–R ketimine **3c**, which contained 7% ketone at the start, decomposed slightly more slowly than **2k**, but still showed gradual hydrolysis over time. These results clearly indicate that dialkyl ketimines with structures like **2k** and **3c** are highly susceptible to hydrolysis under ambient air. To fully suppress post-purification decomposition, column chromatography and solvent removal should ideally be conducted under an inert atmosphere, such as in a glovebox.

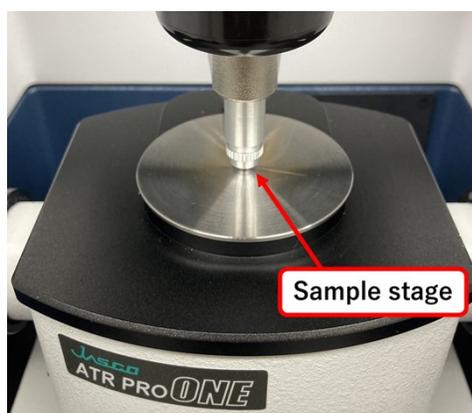


Fig. S2 Sample stage for IR-ATR measurement.

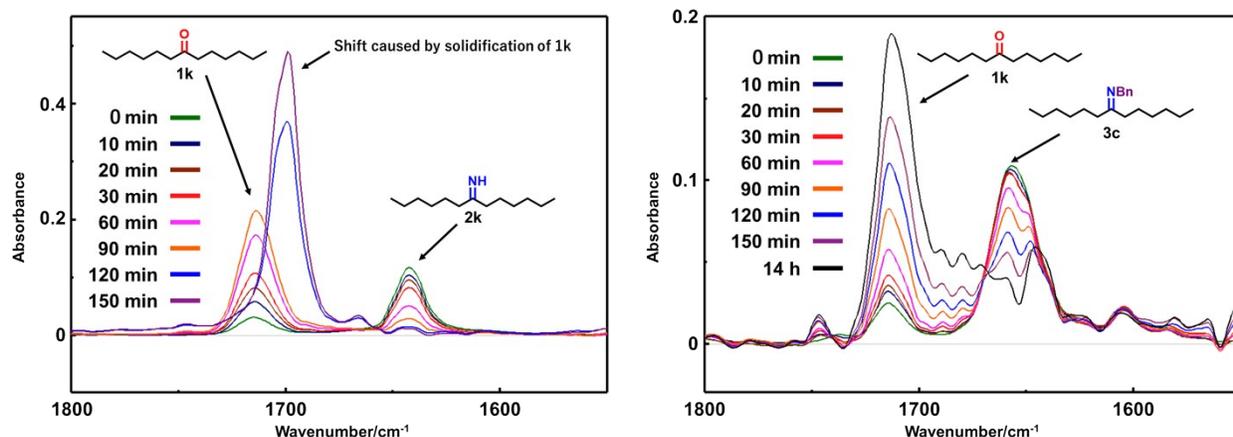
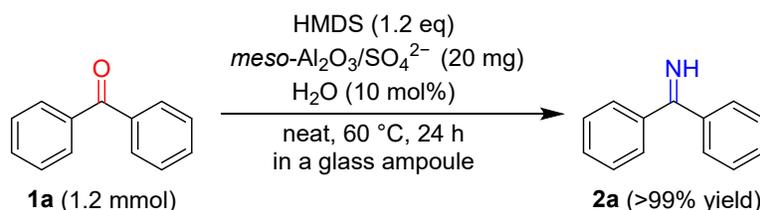


Fig. S3 Time-resolved measurements of N–H ketimine **2k** and N–R ketimine **3c** (35% relative humidity, 23 °C).

4. Spectral data for NMR, FT-IR, and HRMS

In this study, the ^1H and ^{13}C NMR spectra of all isolated compounds are provided to demonstrate the purity of the samples after column chromatography. N–H ketimines have been reported to undergo chemical exchange in solution arising from configurational isomerization about the imine C=N bond;³ therefore, the NMR spectra may not necessarily agree with the reported data. Ketimines **2a–2g**, **2j**, **2l**, **3a**, and **3b** were identified in our previous study (Ref. 2), and their identity was confirmed in the present work by HRMS. FT-IR and HRMS spectra are additionally provided for the remaining compounds to support structural characterization. For N–H ketimine **2k** and *N*-Bn ketimine **3c**, partial hydrolysis occurred during solvent removal after column chromatography, resulting in spectra that contain a small amount of ketone **1k**. In the case of *N*-Ph ketimine **3d**, the compound contained 7% of N–H ketimine **2k** at the end of synthesis. Since the hydrolysis product of **2k**, ketone **1k**, has similar polarity to **3d**, it could not be separated by column chromatography. As a result, the spectra of **3d** also include a minor amount of ketone **1k**.

Diphenylmethanimine (2a)



Isolated as a colorless liquid (yield >99%). Compound **2a** has been previously reported.²

Recovery after silica gel column chromatography:

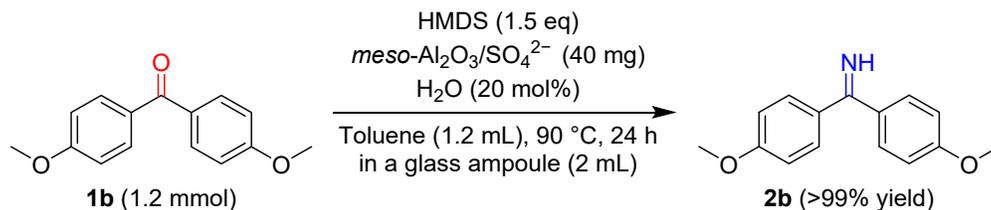
A 1.0 mmol portion of **2a** (180 mg) was subjected to silica gel column chromatography under the “Et₃N-Dry” conditions, and **2a** was isolated as a colorless liquid (179 mg, >99% recovery yield). The corresponding ketone **1a** was not detected. The spectral data of N–H ketimine **2a** matched those reported in Ref. 2.

^1H NMR (400 MHz, DMSO-*d*₆): δ = 10.53 (br, 1H), 7.62 (br, 2H), 7.54–7.34 (m, 8H) ppm.

^{13}C NMR (100 MHz, DMSO-*d*₆): δ = 175.53, 139.44, 138.42, 130.29, 129.70, 128.61, 128.39, 128.17, 127.48 ppm.

ESI-quadrupole-Orbitrap MS (*m/z*): [M+H]⁺ calcd for C₁₃H₁₂N⁺, 182.0964; found 182.0965.

Bis(4-Methoxyphenyl)methanimine (2b)



Isolated as a white solid (yield >99%). Compound **2b** was previously reported.²

Recovery after silica gel column chromatography:

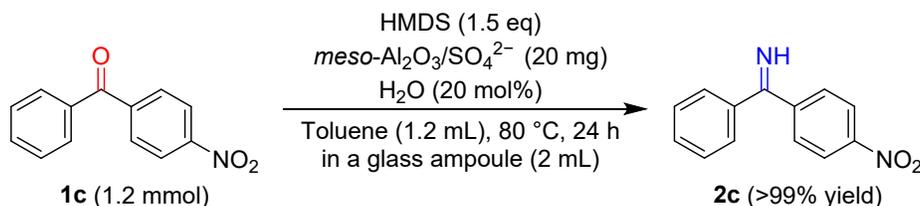
A 1.0 mmol portion of **2b** (240 mg) was subjected to silica gel column chromatography under the “Et₃N-Dry” conditions, and **2b** was isolated as a white solid (239 mg, >99% recovery yield). The corresponding ketone **1b** was not detected. N–H ketimine **2b** was confirmed to be identical to that reported in Ref. 2.

¹H NMR (400 MHz, DMSO-*d*₆): δ = 10.01 (br, 1H), 7.47 (br, 4H), 7.99 (d, 4H, *J*_{HH} = 8.8 Hz), 3.80 (s, 6H) ppm. In Ref. 2, the signal at δ 7.47 ppm appeared as separate peaks, whereas in the present spectrum it appeared as a broadened signal (br), which is attributed to configurational isomerization about the imine C=N bond.

¹³C NMR (100 MHz, DMSO-*d*₆): δ = 174.34, 160.62, 130.70, 129.75, 113.55, 55.24 ppm. The ¹³C NMR spectrum exhibited 6 distinct carbon resonances. In contrast to Ref. 2, in which 10 carbon signals were observed (with one pair overlapping), the reduced number of resonances is consistent with the broadened ¹H NMR signals, supporting the presence of configurational isomerization about the imine C=N bond.

ESI-quadrupole-Orbitrap MS (*m/z*): [M+H]⁺ calcd for C₁₅H₁₆NO₂⁺, 242.1176; found 242.1173.

(4-Nitrophenyl)(phenyl)methanimine (**2c**)



Isolated as a white solid (yield >99%). Compound **2c** was previously reported.²

Recovery after silica gel column chromatography:

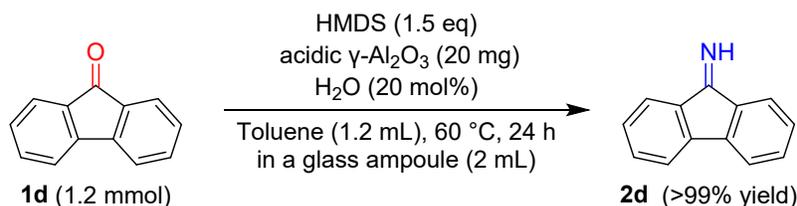
A 1.0 mmol portion of **2c** (226 mg) was subjected to silica gel column chromatography under the “Et₃N-Dry” conditions, and **2c** was isolated as a white solid (225 mg, >99% recovery yield). The corresponding ketone **1c** was not detected. The spectral data of N–H ketimine **2c** matched those reported in Ref. 2.

¹H NMR (400 MHz, DMSO-*d*₆): δ = 11.1 (br, 0.6H, *E*), 10.9 (br, 0.4H, *Z*), 8.34–8.24 (m, 2H, *E*+*Z*), 7.86 (d, 1.2H, *J*_{HH} = 8.8 Hz, *E*), 7.71–7.40 (m, 5.8H, *E*+*Z*) ppm.

¹³C NMR (100 MHz, DMSO-*d*₆, *E*+*Z* isomers): δ = 173.99, 173.74, 148.38, 147.83, 145.34, 144.51, 138.13, 137.48, 130.77, 130.18, 129.92, 128.94, 128.58, 128.45, 128.35, 127.53, 123.58, 123.36 ppm.

ESI-quadrupole-Orbitrap MS (*m/z*): [M–Cl]⁺ calcd for C₁₃H₁₁N₂O₂⁺, 227.0815; found 227.0812.

9*H*-Fluoren-9-imine (**2d**)



Isolated as a light yellow solid (yield >99%). Compound **2d** was previously reported.²

Recovery after silica gel column chromatography:

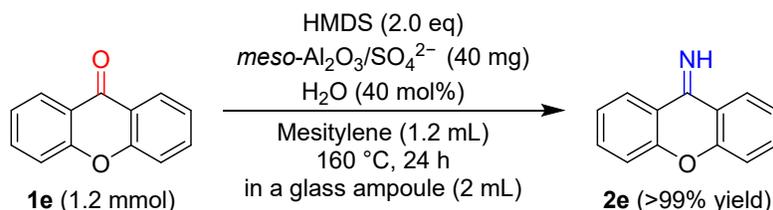
A 1.0 mmol portion of **2d** (197 mg) was subjected to silica gel column chromatography under the “Et₃N-Dry” conditions, and **2d** was isolated as a light yellow solid (196 mg, >99% recovery yield). The corresponding ketone **1d** was not detected. N–H ketimine **2d** was confirmed to be identical to that reported in Ref. 2.

¹H NMR (400 MHz, CDCl₃): δ = 10.25 (br, 1H), 7.72 (br, 2H), 7.56 (d, 2H, J_{HH} = 7.5 Hz), 7.42 (td, 2H, J_{HH} = 7.4 Hz, J_{HH} = 1.0 Hz), 7.33–7.25 (m, 2H) ppm. In Ref. 2, the signal at δ 7.72 ppm appeared as separate peaks, whereas in the present spectrum it appeared as a broadened signal (br), which is attributed to configurational isomerization about the imine C=N bond.

¹³C NMR (100 MHz, CDCl₃): δ = 173.05, 142.12, 134.93, 132.09, 128.06, 122.15, 119.99 ppm. The ¹³C NMR spectrum exhibited seven distinct carbon resonances. In contrast to Ref. 2, which reported 13 carbon signals, the reduced number of resonances is consistent with the broadened ¹H NMR signals, supporting the presence of configurational isomerization about the imine C=N bond.

ESI-quadrupole-Orbitrap MS (m/z): [M+H]⁺ calcd for C₁₃H₁₀N⁺, 180.0808; found 180.0807.

9*H*-Xanthen-9-imine (**2e**)



Isolated as a white solid (yield >99%). Compound **2e** was previously reported.²

Recovery after silica gel column chromatography:

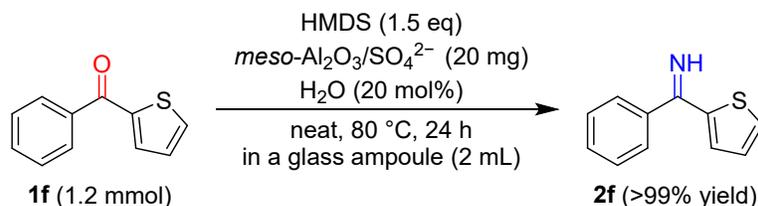
A 1.0 mmol portion of **2e** (194 mg) was subjected to silica gel column chromatography under the “Et₃N” conditions, and **2e** was isolated as a white solid (193 mg, >99% recovery yield). The corresponding ketone **1e** was not detected. The spectral data of N–H ketimine **2e** matched those reported in Ref. 2.

^1H NMR (400 MHz, CDCl_3): δ = 9.49 (br, 1H), 8.17 (br, 2H), 7.61–7.52 (m, 2H), 7.38–7.23 (m, 4H) ppm.

^{13}C NMR (100 MHz, CDCl_3): δ = 158.94, 152.79, 132.47, 124.49, 123.60, 119.72, 117.84 ppm.

ESI-quadrupole-Orbitrap MS (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{10}\text{NO}^+$, 196.0757; found 196.0757.

Phenyl(thiophen-2-yl)methanimine (**2f**)



Isolated as a light yellow liquid (yield >99%). Compound **2f** was previously reported.²

Recovery after silica gel column chromatography:

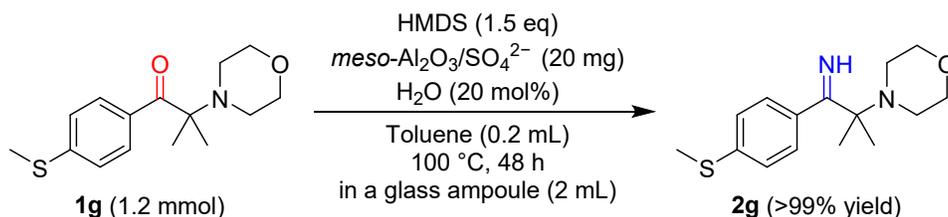
A 1.0 mmol portion of **2f** (190 mg) was subjected to silica gel column chromatography under the “ Et_3N ” conditions, and **2f** was isolated as a colorless liquid (189 mg, >99% recovery yield). The corresponding ketone **1f** was not isolated. N–H ketimine **2f** was confirmed to be identical to that reported in Ref. 2.

^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 10.50 (br, 0.15H, *Z*), 10.19 (br, 0.85H, *E*), 7.74 (br, *E+Z*), 7.73 (br, *E+Z*), 7.49 (br, *E+Z*), 7.11 (br, *E+Z*) ppm. In Ref. 2, the signal at δ 7.74–7.11 ppm appeared as separate peaks, whereas in the present spectrum it appeared as a broadened signal (br), which is attributed to configurational isomerization about the imine C=N bond.

^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ = 169.67, 144.17, 139.10, 131.37, 130.54, 129.83, 128.44, 127.80, 127.14 ppm. The ^{13}C NMR spectrum exhibited nine distinct carbon resonances. In contrast to Ref. 2, which reported 18 carbon signals, the reduced number of resonances is consistent with the broadened ^1H NMR signals, supporting the presence of configurational isomerization about the imine C=N bond.

ESI-quadrupole-Orbitrap MS (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{10}\text{NS}^+$, 188.0528; found 188.0528.

2-Methyl-1-(4-(methylthio)phenyl)-2-morpholinopropan-1-imine (**2g**)



Isolated as a light yellow liquid (yield >99%). Compound **2g** was previously reported.²

Recovery after silica gel column chromatography:

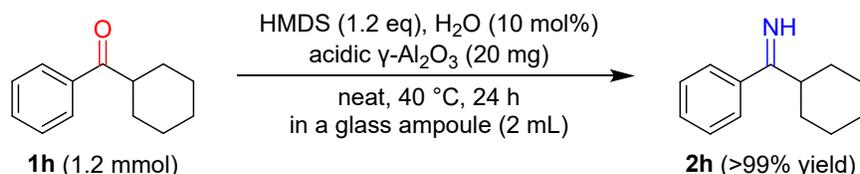
A 1.0 mmol portion of **2g** (280 mg) was subjected to silica gel column chromatography under the “Et₃N-Dry” conditions, and **2g** was isolated as a colorless liquid (278 mg, >99% recovery yield). The corresponding ketone **1g** was not isolated. The spectral data of N–H ketimine **2g** matched those reported in Ref. 2.

¹H NMR (400 MHz, DMSO-*d*₆): δ = 10.25 (br, 1H), 7.81 (br, 2H), 7.23 (d, 2H, *J*_{HH} = 8.4 Hz), 3.59 (br, 4H), 2.48 (br, 7H), 1.15 (s, 6H) ppm.

¹³C NMR (100 MHz, DMSO-*d*₆): δ = 180.60, 139.21, 136.56, 128.56, 124.66, 66.71, 63.73, 46.22, 20.84, 14.28 ppm.

ESI-quadrupole-Orbitrap MS (*m/z*): [M+H]⁺ calcd for C₁₅H₂₁NO₂S⁺, 279.1526; found 279.1523.

Cyclohexyl(phenyl)methanimine (**2h**)



Isolated as a colorless liquid (yield 99%).

Recovery after silica gel column chromatography:

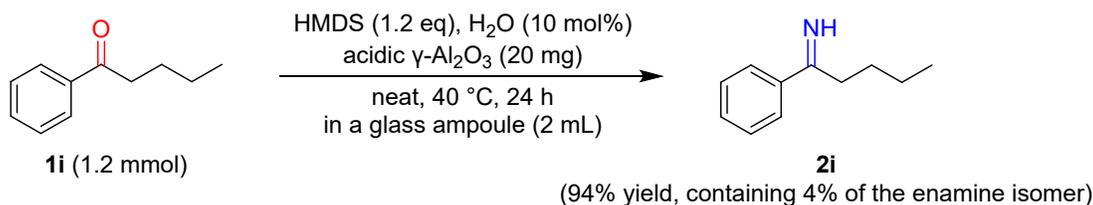
A 1.0 mmol portion of **2h** (190 mg) was subjected to silica gel column chromatography under the “Et₃N-Dry” conditions, and **2h** was isolated as a colorless liquid (176 mg, 94% recovery yield). The corresponding ketone **1h** was also isolated in a minor amount (9 mg, 5% recovery yield).

¹H NMR (400 MHz, CDCl₃): δ = 9.45 (br, 1H), 7.64 (br, 2H), 7.45–7.35 (m, 3H), 2.88–2.74 (m, 1H), 2.01–1.67 (m, 5H), 1.49–1.14 (m, 5H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 183.71, 139.66, 129.79, 128.40, 126.35, 44.02, 30.67, 26.22, 26.06 ppm.

ESI-quadrupole-Orbitrap MS (*m/z*): [M+H]⁺ calcd for C₁₃H₁₈N⁺, 188.1434; found 188.1433.

1-Phenylbutan-1-imine (**2i**)



The crude ketimine was obtained as a colorless liquid. The yield was estimated to be 90% by ¹H NMR spectroscopy using an internal standard. The crude material was concentrated and immediately subjected to column chromatography without further purification.

Recovery after silica gel column chromatography:

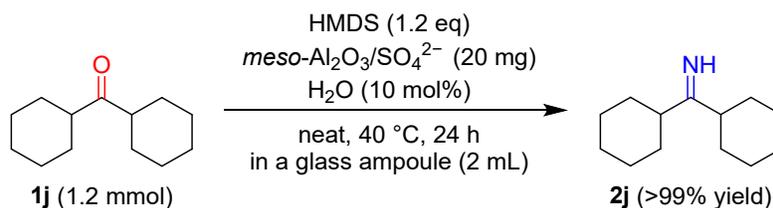
A 1.0 mmol portion of **2i** (163 mg) was subjected to silica gel column chromatography under the “Et₃N-Dry” conditions, affording a colorless liquid (150 mg). The recovery yield of **2i** was 89% based on the amount of **2i** determined by ¹H NMR spectroscopy. The recovered material contained 4% of the enamine isomer. The corresponding ketone **1i** was also isolated in a minor amount (11 mg, 7% recovery yield).

¹H NMR (400 MHz, CDCl₃): δ = 9.48 (br, 1H), 7.72 (br, 2H), 7.46–7.39 (m, 3H), 2.72 (t, 2H, J_{HH} = 7.4 Hz), 1.66 (sext, 2H, J_{HH} = 7.4 Hz), 1.00 (q, 3H, J_{HH} = 7.4 Hz) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 178.86, 139.00, 130.14, 128.41, 126.34, 39.61, 19.42, 13.62 ppm.

ESI-quadrupole-Orbitrap MS (m/z): [M+H]⁺ calcd for C₁₀H₁₄N⁺, 148.1121; found 148.1120.

Dicyclohexylmethanimine (**2j**)



Isolated as a light yellow liquid (yield >99%). This compound was previously reported.²

Recovery after silica gel column chromatography:

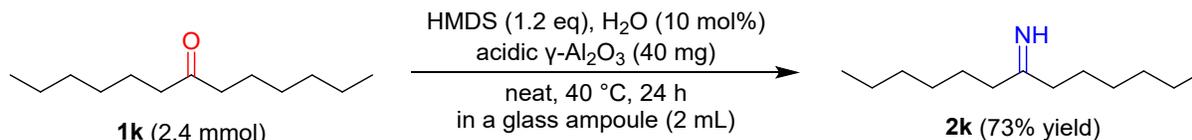
A 1.0 mmol portion of **2j** (194 mg) was subjected to silica gel column chromatography under the “Et₃N-Dry” conditions, and **2j** was isolated as a light yellow liquid (185 mg, 95% recovery yield). The corresponding ketone **1j** was also isolated in a minor amount (6 mg, 3% recovery yield). The spectral data of N–H ketimine **2j** matched those reported in Ref. 2.

¹H NMR (400 MHz, CDCl₃): δ = 8.92 (br, 1H), 2.25–2.04 (m, 2H), 1.92–1.52 (m, 10H), 1.45–1.09 (m, 10H) ppm.

^{13}C NMR (100 MHz, CDCl_3): $\delta = 192.21, 46.46, 30.59, 26.24, 26.01$ ppm.

ESI-quadrupole-Orbitrap MS (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{24}\text{N}^+$, 194.1903; found 194.1904.

Tridecan-7-imine (**2k**)



The crude ketimine was obtained as a colorless liquid. The yield was estimated to be 73% by ^1H NMR spectroscopy using an internal standard. The crude material was concentrated and immediately subjected to column chromatography without further purification.

Recovery after silica gel column chromatography:

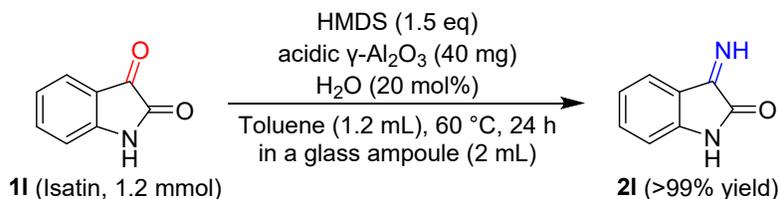
A 1.0 mmol portion of **2k** (197 mg) was subjected to silica gel column chromatography under the “ Et_3N -Dry” conditions, affording a ketimine-enriched fraction as a colorless liquid (146 mg). ^1H NMR spectroscopy indicated that this fraction contained **2k** in 68% yield together with 8% of the corresponding ketone **1k**. The total recovery yield of ketone **1k** was 24%, including the portion present in the ketimine-enriched fraction.

^1H NMR (400 MHz, CDCl_3): $\delta = 8.92$ (br, 1H), 2.22 (t, 4H, $J_{\text{HH}} = 7.4$ Hz), 1.53 (br, 4H), 1.39–1.83 (m, 12H), 0.97–0.82 (m, 6H) ppm.

^{13}C NMR (100 MHz, CDCl_3): $\delta = 184.7, 39.62, 31.62, 28.93, 25.74, 22.50, 14.00$ ppm.

ESI-quadrupole-Orbitrap MS (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{28}\text{N}^+$, 198.2216; found 198.2217.

3-Iminoindolin-2-one (**2l**)



Isolated as a brick-red solid (yield >99%). Compound **2l** was previously reported (Ref. 2).

Recovery after silica gel column chromatography:

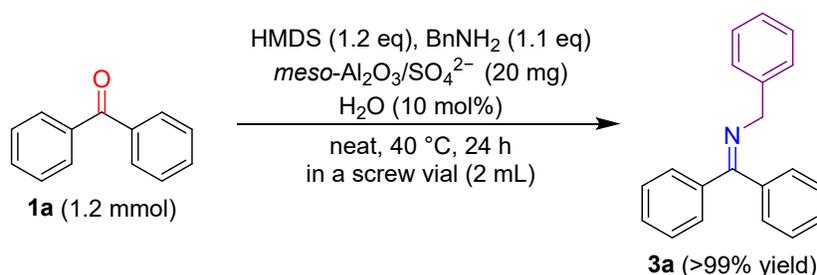
A 1.0 mmol portion of **2l** (147 mg) was subjected to silica gel column chromatography under the “ Et_3N -Dry” conditions, and **2l** was isolated as a brick-red solid (143 mg, 97% recovery yield). The corresponding ketone **1l** was also isolated in a minor amount (1 mg, <1% recovery yield). The spectral data of N–H ketimine **2l** matched those reported in Ref. 2.

^1H NMR (400 MHz, DMSO- d_6): δ = 12.32 (br, 0.2H, *E*), 11.23 (br, 0.8H, *Z*), 10.90 (br, 1H, *E+Z*), 7.72 (d, 0.2H, J_{HH} = 7.4 Hz, *E*), 7.63 (d, 0.2H, J_{HH} = 7.4 Hz, *Z*), 7.45 (t, 0.8H, J_{HH} = 7.7 Hz, *Z*), 7.39 (t, 0.2H, J_{HH} = 7.7 Hz, *E*), 7.07 (t, 0.8H, J_{HH} = 7.6 Hz, *Z*), 7.02 (t, 0.2H, J_{HH} = 7.5 Hz, *E*), 7.63 (d, 0.2H, J_{HH} = 7.8 Hz, *Z*), 6.91 (d, 0.8H, J_{HH} = 7.8 Hz, *Z*), 6.85 (d, 0.2H, J_{HH} = 7.6 Hz, *E*) ppm.

^{13}C NMR (100 MHz, DMSO- d_6 , *E+Z* isomers): δ = 164.96, 163.79, 163.52, 159.31, 146.42, 144.88, 134.32, 133.86, 123.52, 123.08, 122.52, 121.94, 120.40, 117.92, 111.28, 110.85 ppm.

ESI-quadrupole-Orbitrap MS (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_8\text{H}_7\text{N}_2\text{O}^+$, 147.0553; found 147.0553.

N-benzyl-1,1-diphenylmethanimine (**3a**)



Isolated as a white solid (yield >99%). This compound was previously reported (Ref. 2).

Recovery after silica gel column chromatography:

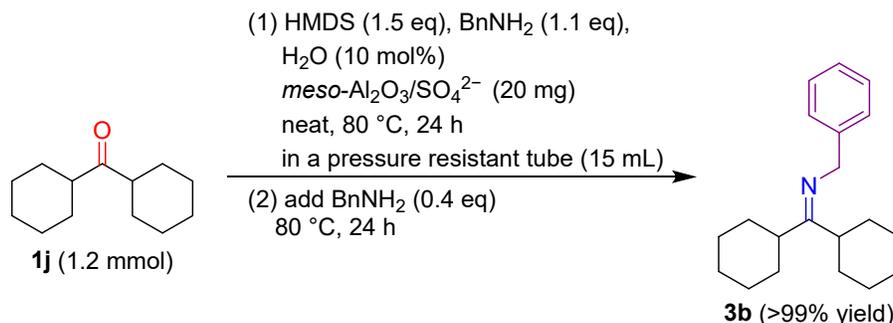
A 1.0 mmol portion of **3a** (271 mg) was subjected to silica gel column chromatography under the “Et₃N” conditions, and **3a** was isolated as a white solid (270 mg, >99% recovery yield). The corresponding ketone **1a** was not isolated. The spectral data of *N*-R ketimine **3a** matched those reported in Ref. 2.

^1H NMR (400 MHz, CDCl₃): δ = 7.72–7.64 (m, 2H), 7.51–7.42 (m, 3H), 7.42–7.27 (m, 7H), 7.27–7.16 (m, 3H), 4.61 (s, 2H) ppm.

^{13}C NMR (100 MHz, CDCl₃): δ = 168.76, 140.65, 139.75, 136.69, 130.02, 128.55, 128.52, 128.48, 128.29, 128.03, 127.76, 127.61, 126.47, 57.39 ppm.

ESI-quadrupole-Orbitrap MS (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{18}\text{N}^+$, 272.1434; found 272.1428.

N-Benzyl-1,1-dicyclohexylmethanimine (**3b**)



Isolated as a white solid (yield >99%). This compound was previously reported (Ref. 2).

Recovery after silica gel column chromatography:

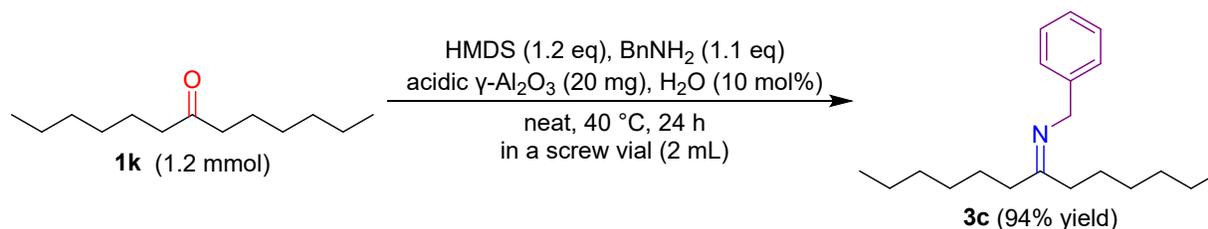
A 1.0 mmol portion of **3b** (284 mg) was subjected to silica gel column chromatography under the “Et₃N-Dry” conditions, and **3b** was isolated as a white solid (283 mg, >99% recovery yield). The corresponding ketone **1j** was not isolated. The spectral data of *N*-R ketimine **3b** matched those reported in Ref. 2.

¹H NMR (400 MHz, CDCl₃): δ = 7.35–7.24 (m, 4H), 7.23–7.16 (m, 1H), 4.66 (s, 2H), 2.74 (tt, 1H, *J*_{HH} = 11.7, 3.5 Hz), 2.39 (tt, 1H, *J*_{HH} = 11.5, 3.3 Hz), 1.95–1.11 (m, 20H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ = 181.37, 141.28, 128.17, 127.17, 126.13, 52.81, 42.82, 41.11, 32.23, 29.04, 26.58, 25.97 ppm.

ESI-quadrupole-Orbitrap MS (*m/z*): [M+H]⁺ calcd for C₂₀H₃₀N⁺, 284.2373; found 284.2368.

N-Benzyltridecan-7-imine (**3c**)



The crude ketimine was obtained as a colorless liquid. The yield was estimated to be 94% by ¹H NMR spectroscopy using an internal standard. The crude material was concentrated and immediately subjected to column chromatography without further purification.

Recovery after silica gel column chromatography:

A 1.0 mmol portion of **3c** (288 mg) was subjected to silica gel column chromatography under the “Et₃N-Dry” conditions, affording a ketimine-enriched fraction as a colorless liquid (242 mg). ¹H NMR spectroscopy indicated that this fraction contained **3c** in 80% yield together with 7% of the

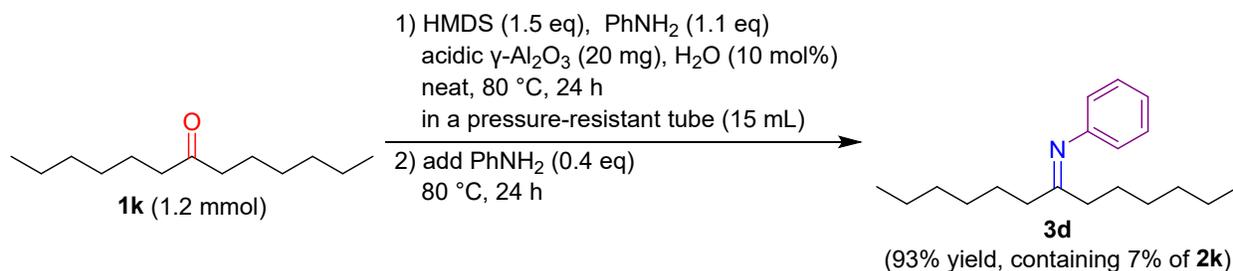
corresponding ketone **1k**. The total recovery yield of ketone **1k** was 17%, including the portion present in the ketimine-enriched fraction.

^1H NMR (400 MHz, CDCl_3): δ = 7.36–7.27 (m, 4H), 7.24–7.17 (m, 1H), 4.55 (s, 2H), 2.34–2.23 (m, 4H), 1.69–1.52 (m, 2H), 1.52–1.40 (m, 2H), 1.40–1.18 (m, 12H), 0.96–0.79 (m, 6H) ppm.

^{13}C NMR (100 MHz, CDCl_3): δ = 174.94, 140.82, 128.27, 127.55, 126.35, 54.28, 40.43, 31.73, 31.54, 31.43, 29.62, 29.27, 26.82, 26.44, 22.60, 22.51, 14.04, 14.01 ppm.

ESI-quadrupole-Orbitrap MS (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{34}\text{N}^+$, 288.2686; found 288.2678.

N-Phenyltridecan-7-imine (3d)



Isolated as a colorless liquid (yield 93%, containing 7% of **2k**)

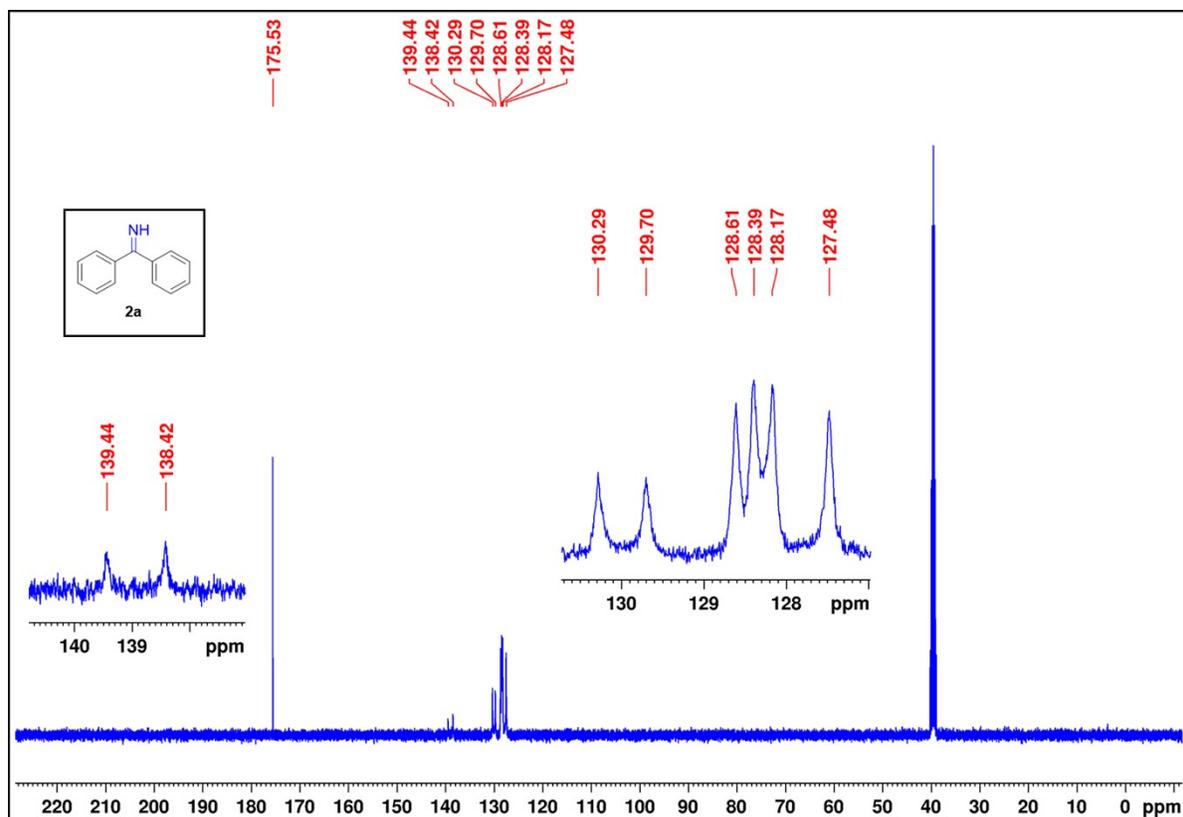
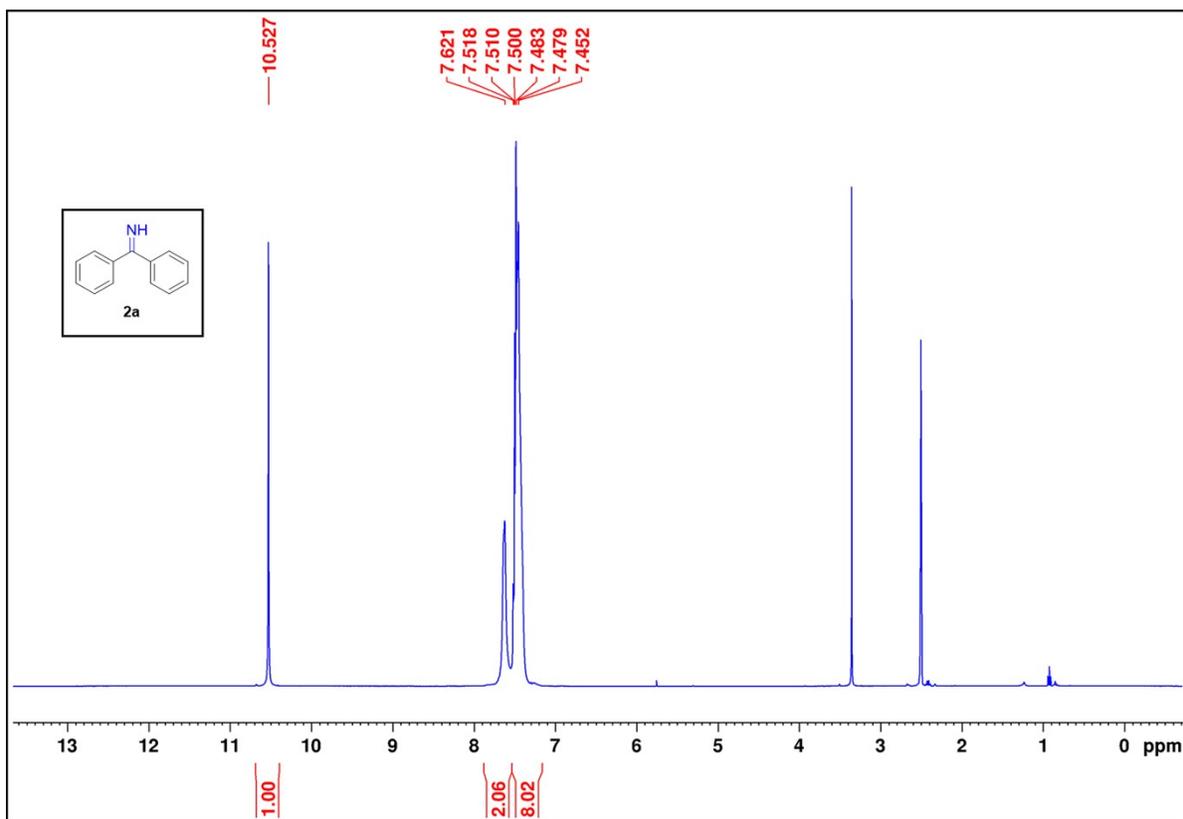
A 1.0 mmol portion of **3d** (289 mg) was subjected to silica gel column chromatography under the “ Et_3N ” conditions, and a colorless liquid was recovered (288 mg, >99% mass recovery). ^1H NMR analysis showed complete hydrolysis of **2k** to the corresponding ketone **1k**. Because of the similar polarity of **3d** and **1k**, the components could not be separated chromatographically. No hydrolysis of **3d** was observed.

^1H NMR (400 MHz, CDCl_3): δ = 7.26 (t, 2H, $J_{\text{HH}} = 7.5$ Hz), 7.00 (t, 1H, $J_{\text{HH}} = 7.5$ Hz), 6.66 (d, 2H, $J_{\text{HH}} = 7.5$ Hz), 2.42–2.34 (m, 2H), 2.14–2.05 (m, 2H), 1.73–1.60 (m, 2H), 1.50–1.09 (m, 14H), 0.95–0.78 (m, 6H) ppm.

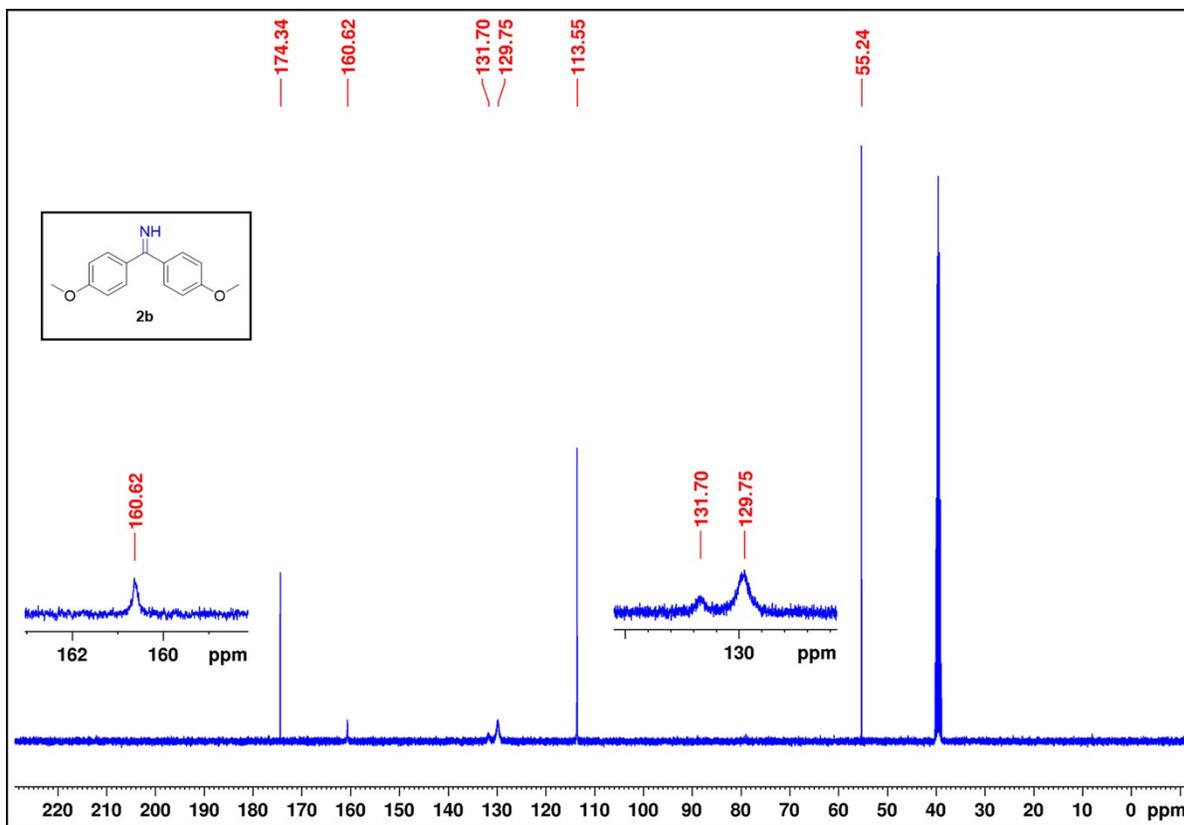
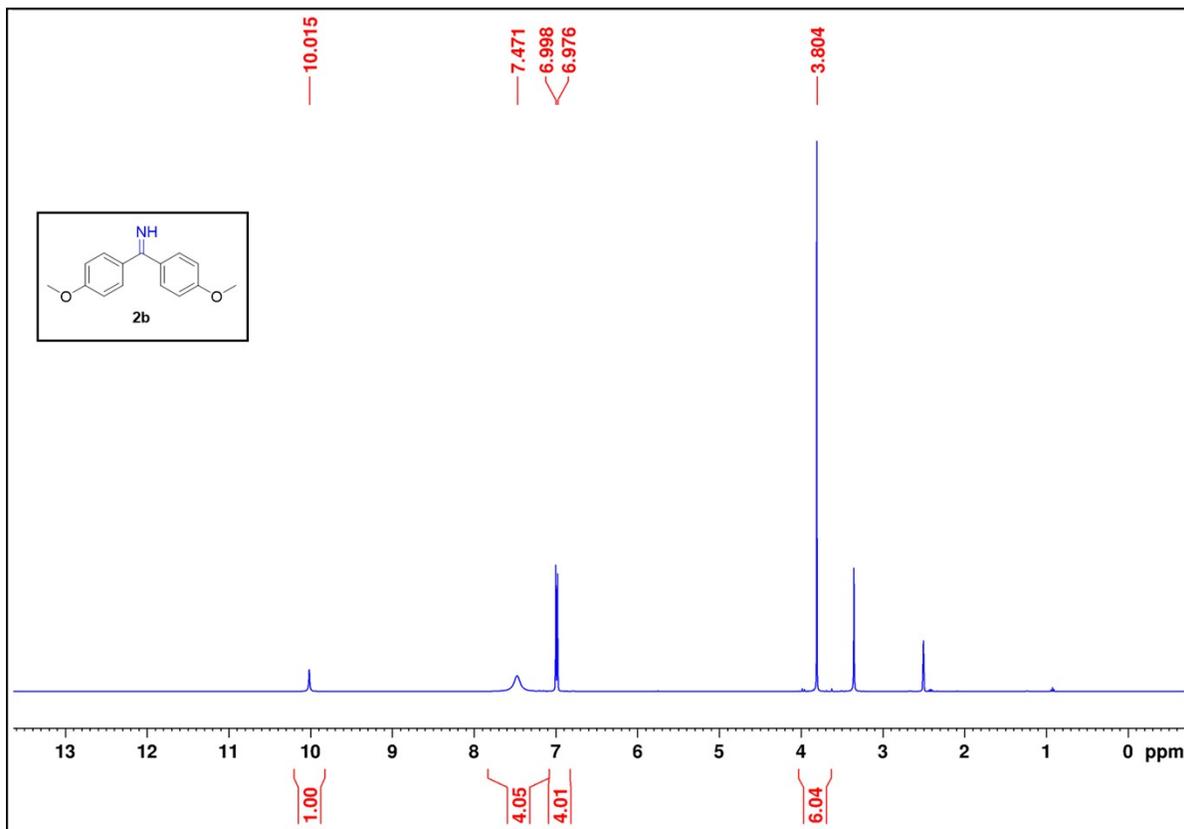
^{13}C NMR (100 MHz, CDCl_3): δ = 175.55, 151.46, 128.71, 122.59, 119.42, 38.57, 32.97, 31.72, 31.34, 29.25, 29.14, 26.88, 26.44, 22.60, 22.38, 14.06, 13.96 ppm.

ESI-quadrupole-Orbitrap MS (m/z): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{32}\text{N}^+$, 274.2529; found 274.2521.

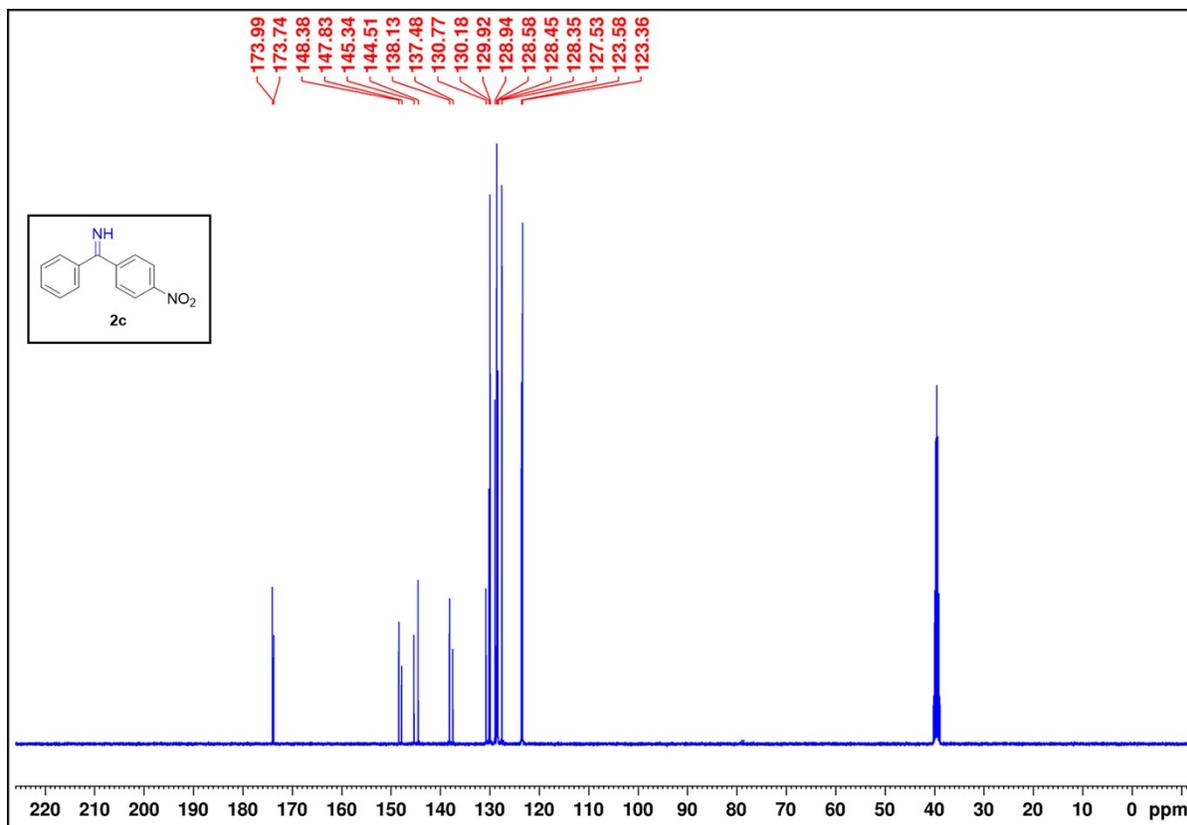
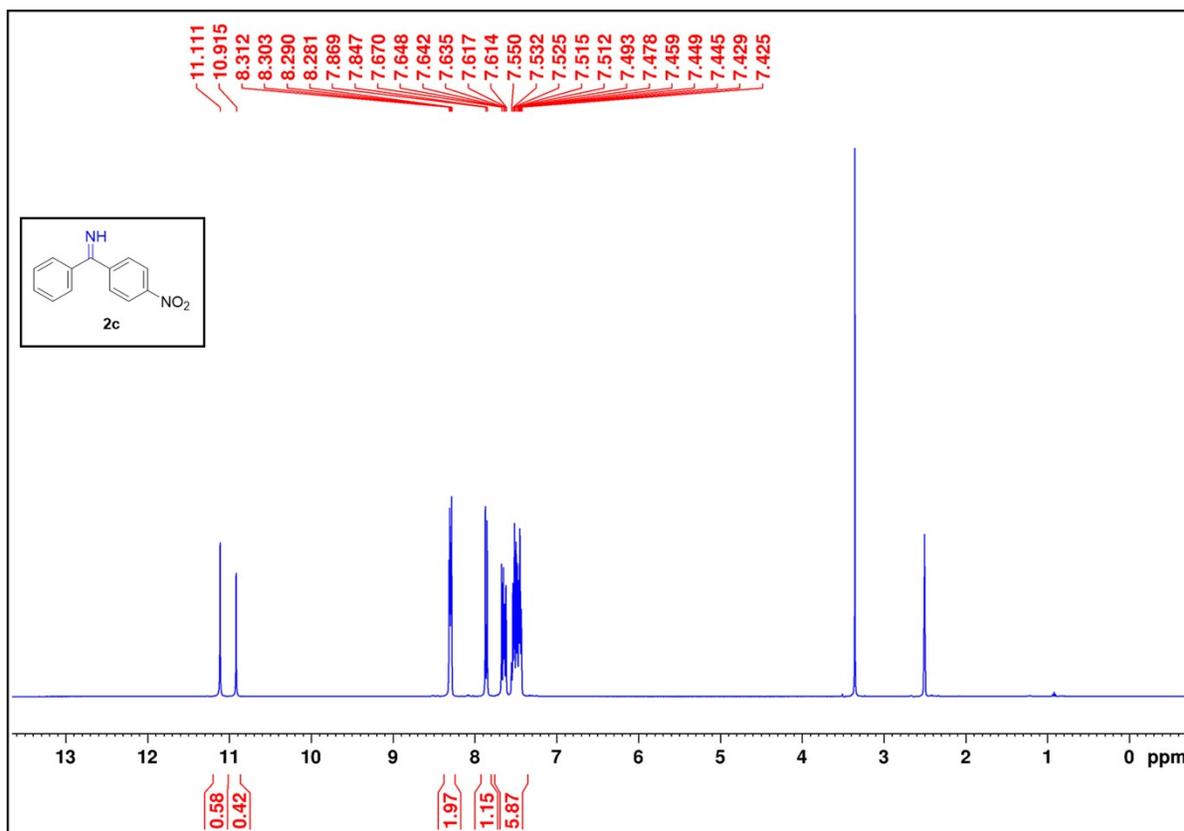
^1H and ^{13}C NMR spectra of **2a** after column chromatography (DMSO- d_6 , 400 MHz)



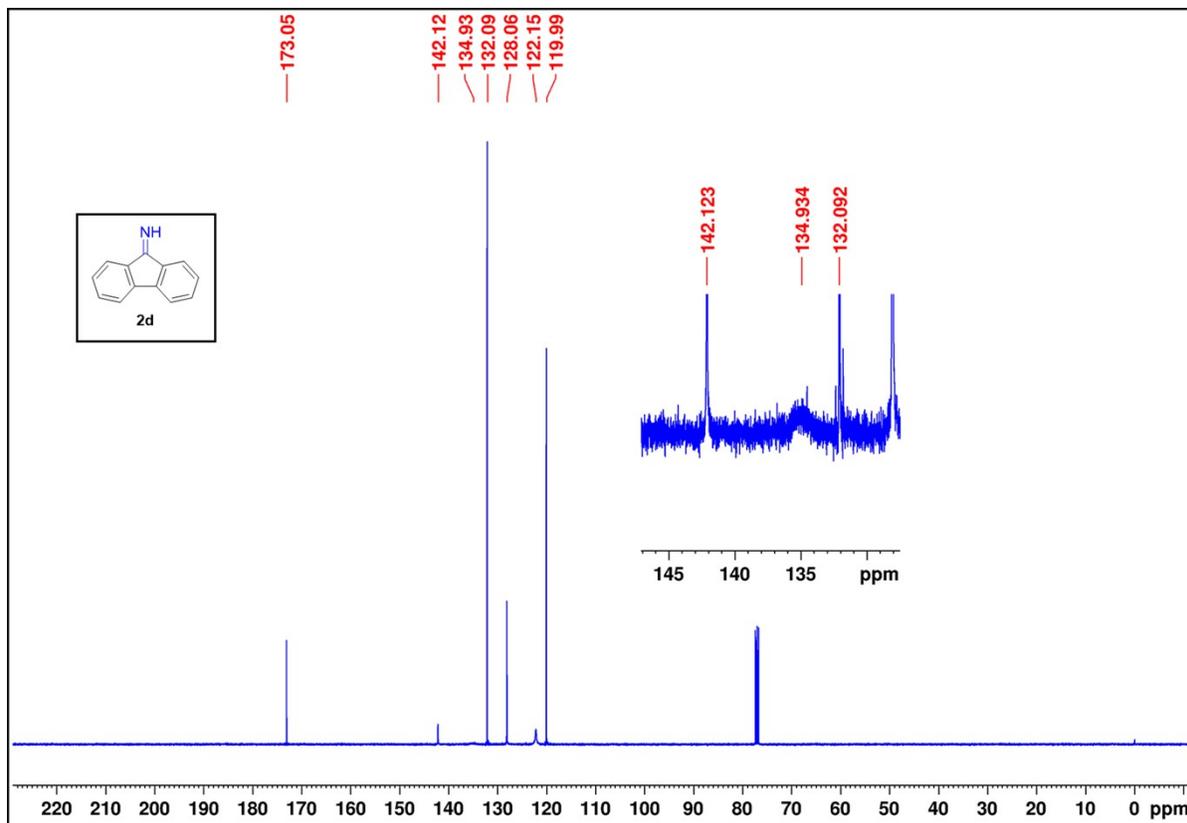
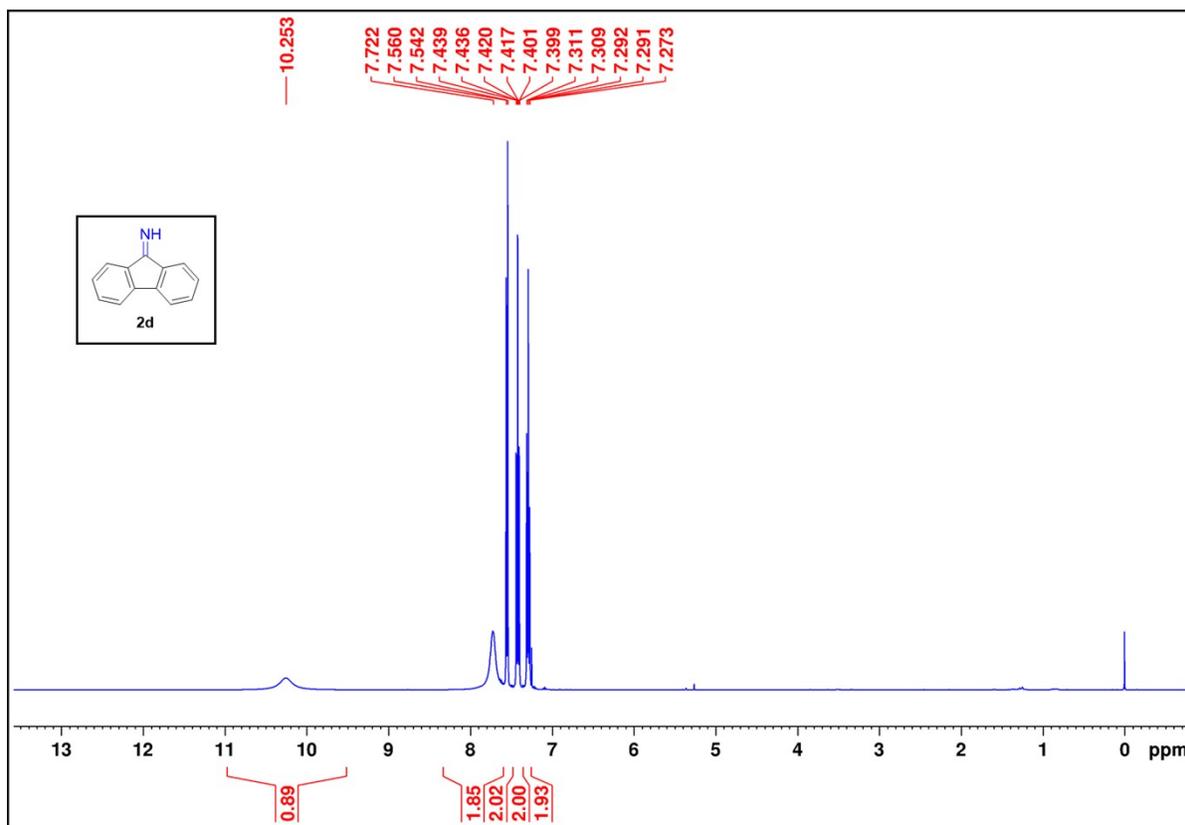
^1H and ^{13}C NMR spectra of **2b** after column chromatography (DMSO- d_6 , 400 MHz)



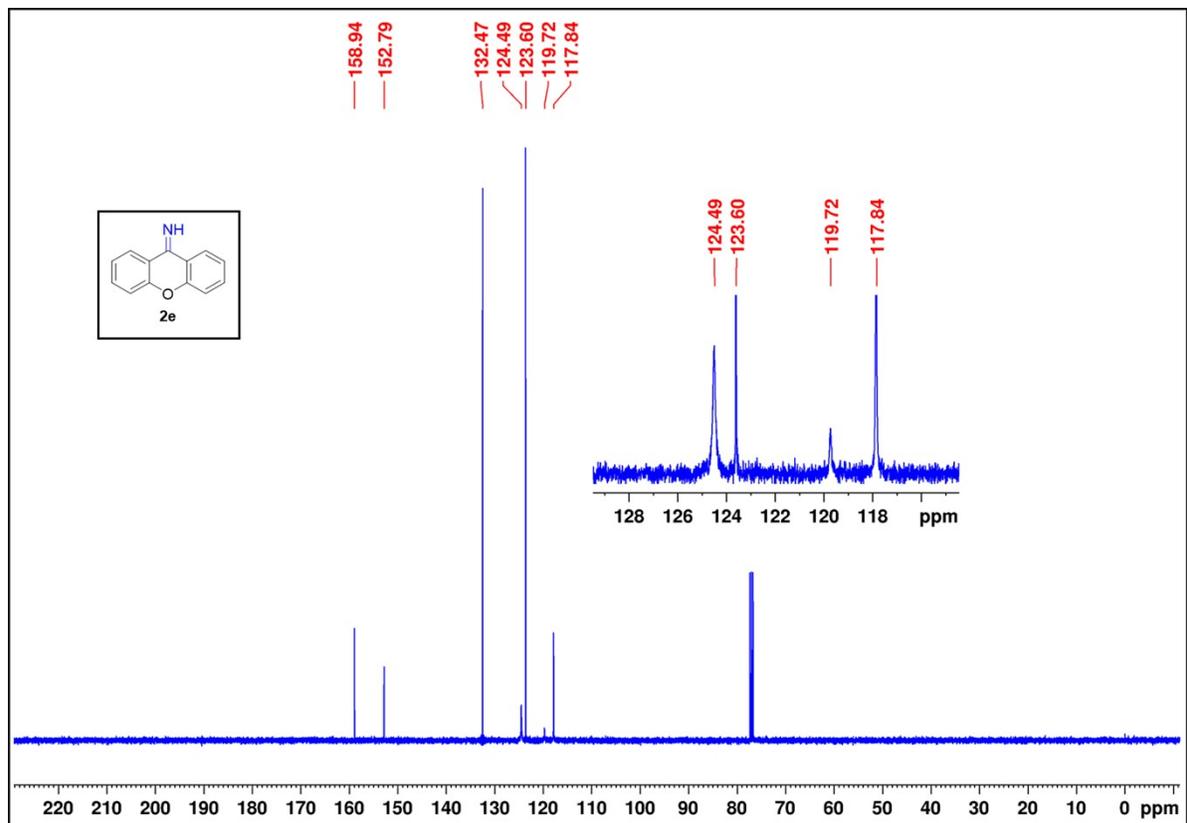
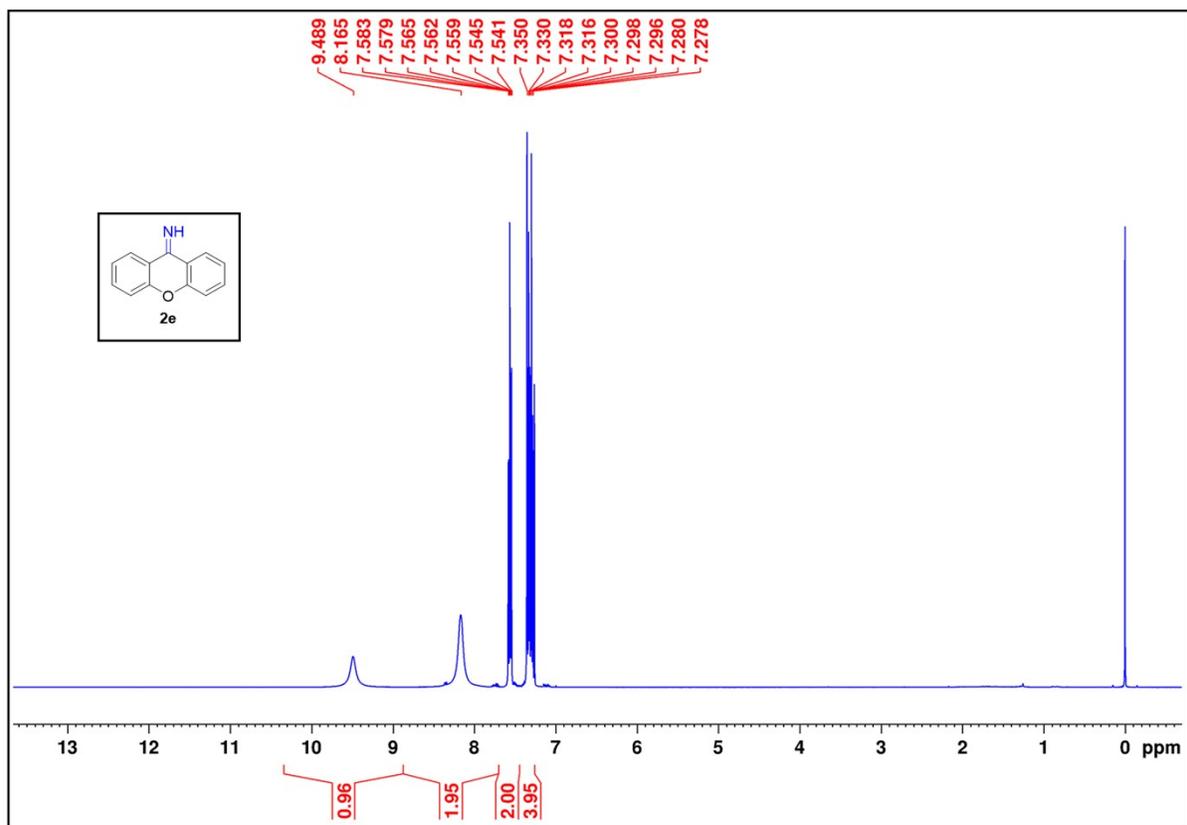
^1H and ^{13}C NMR spectra of **2c** after column chromatography (DMSO- d_6 , 400 MHz)



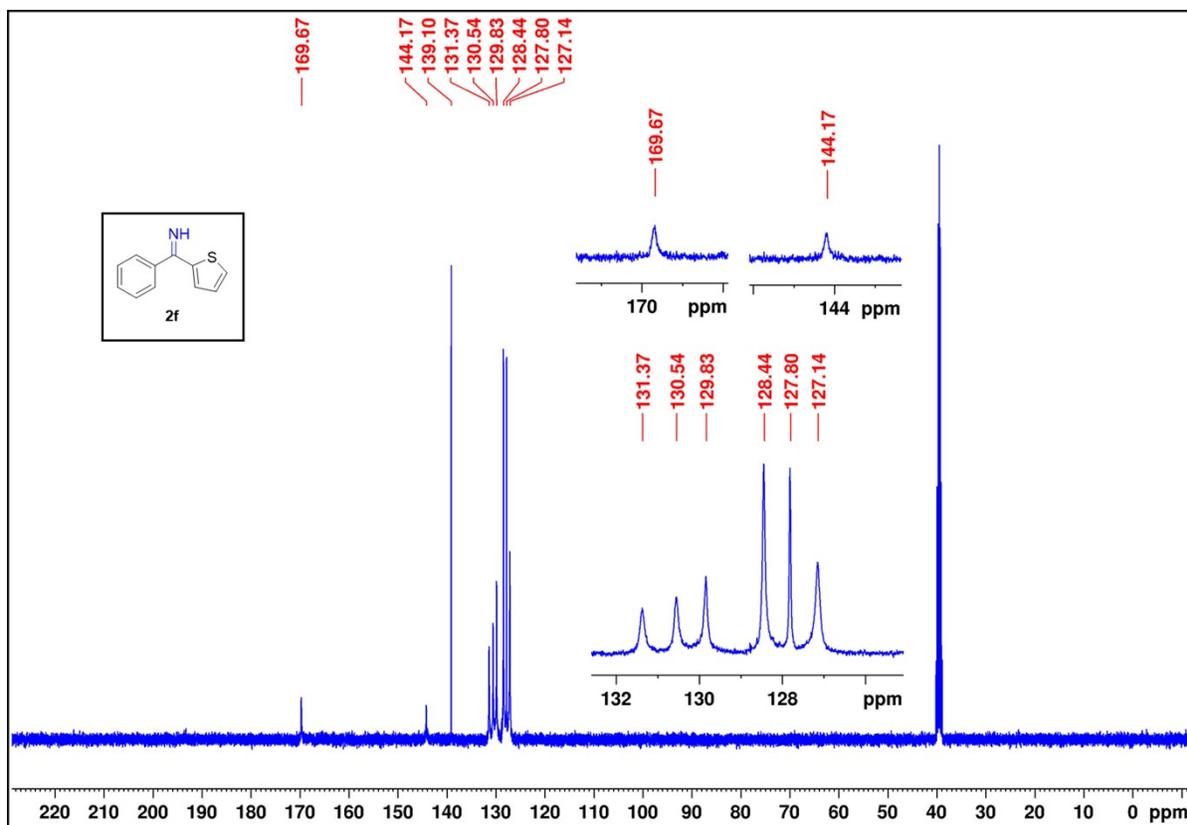
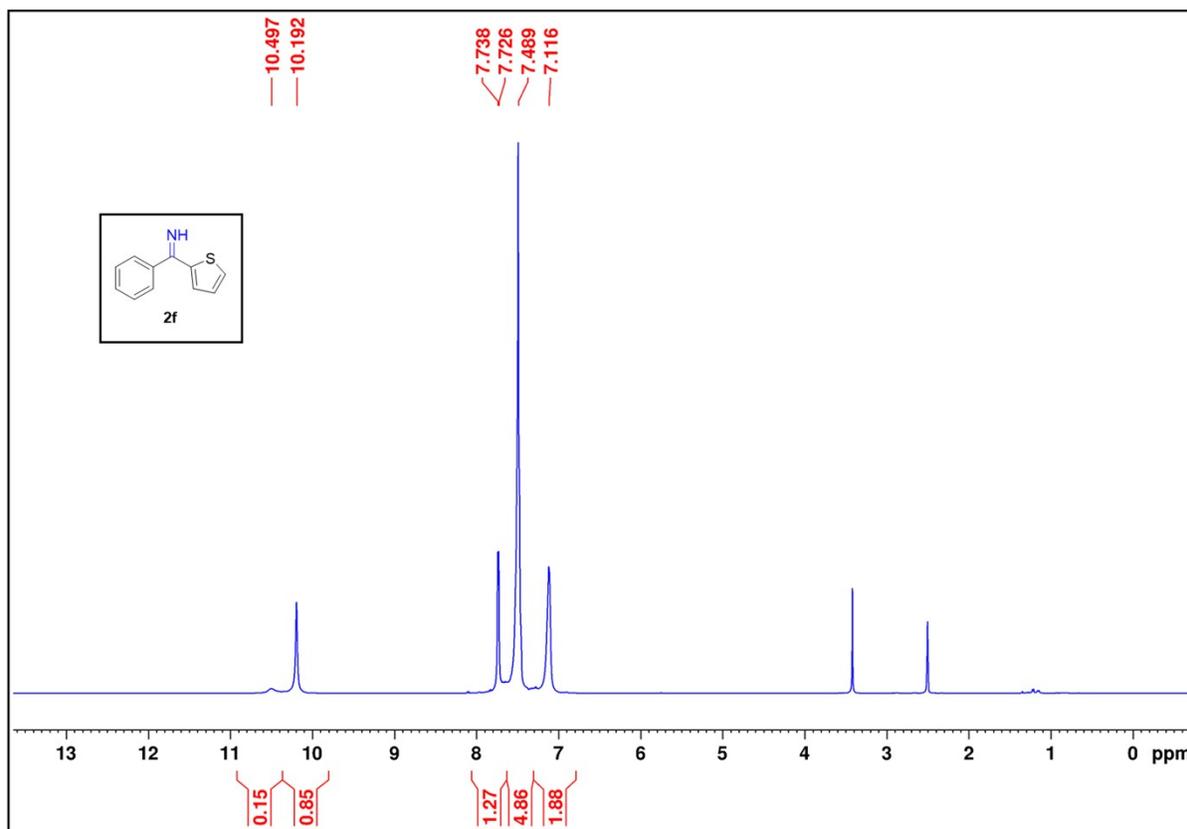
^1H and ^{13}C NMR spectra of **2d** after column chromatography (CDCl_3 , 400 MHz)



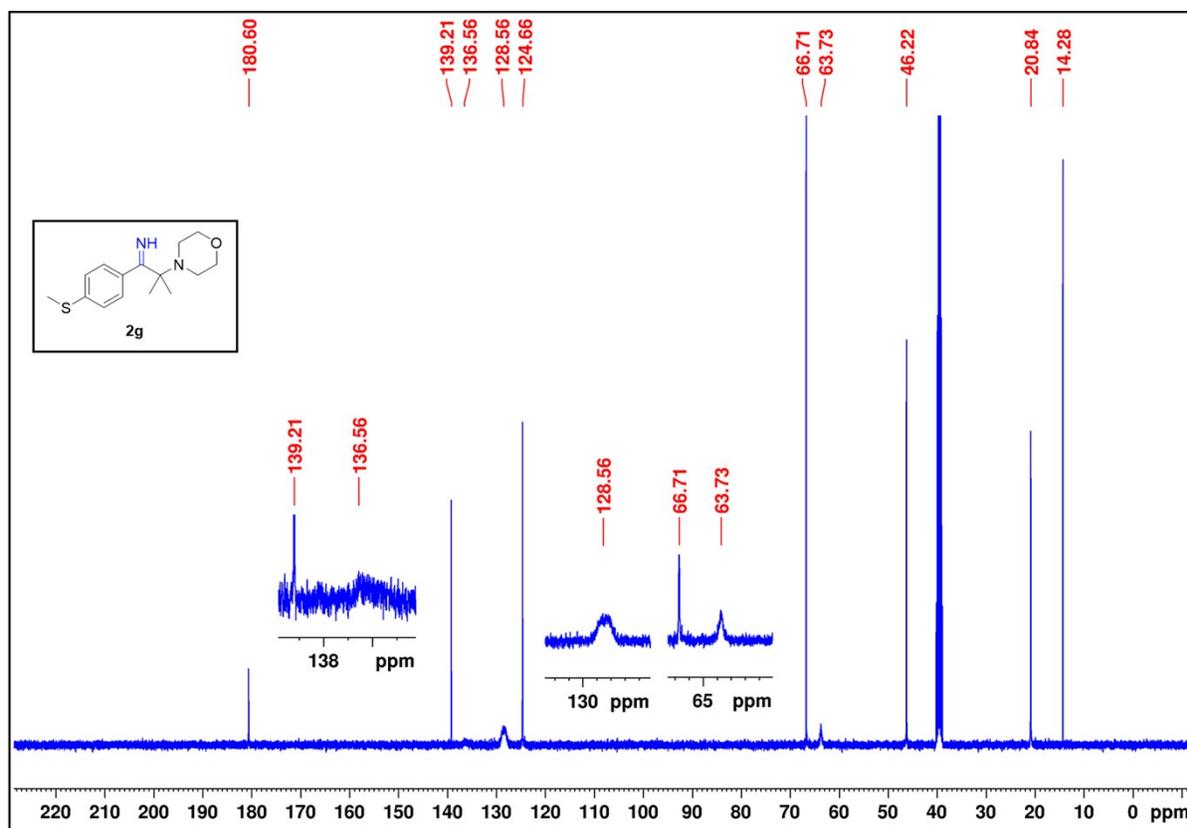
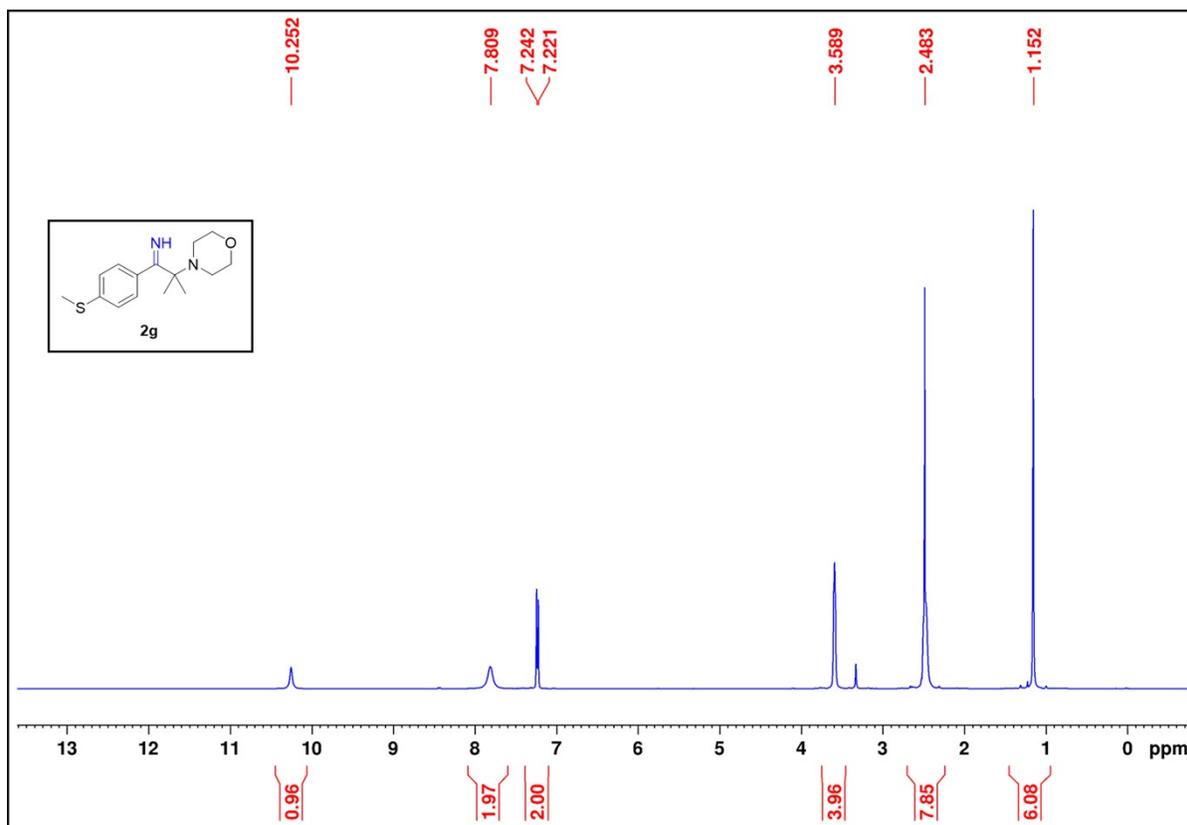
^1H and ^{13}C NMR spectra of **2e** after column chromatography (CDCl_3 , 400 MHz)



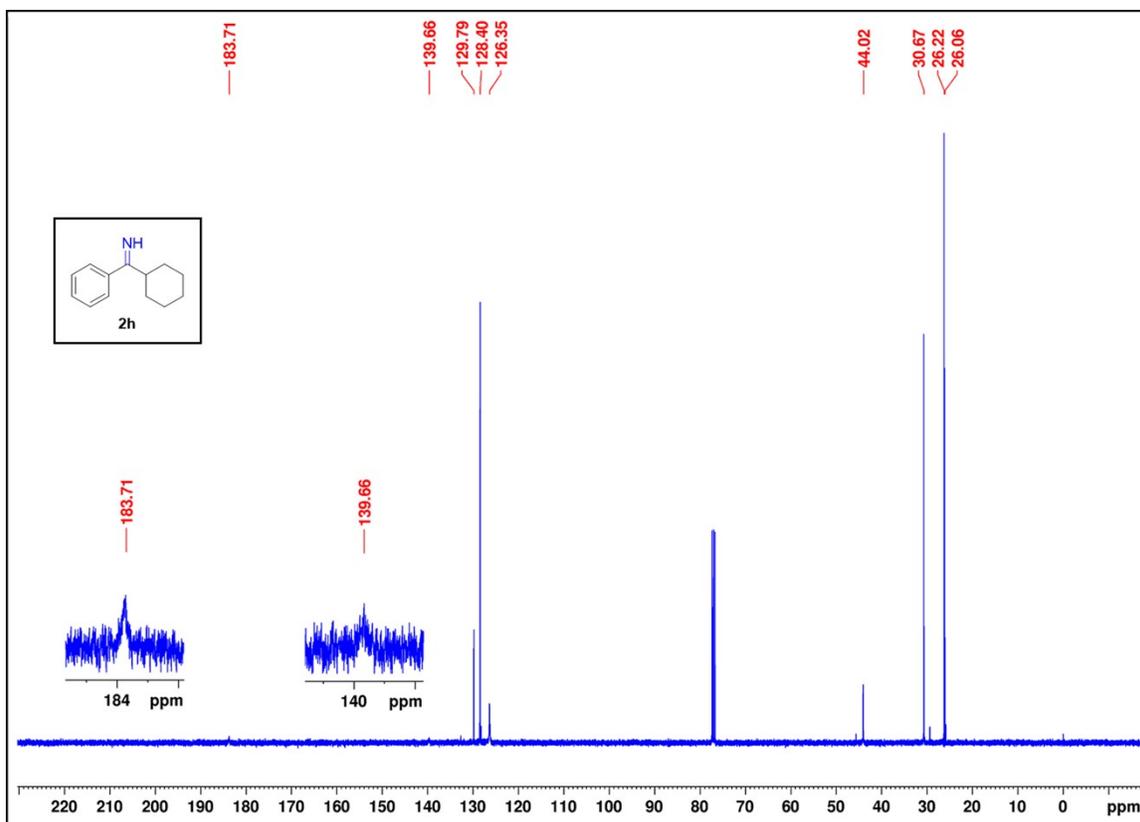
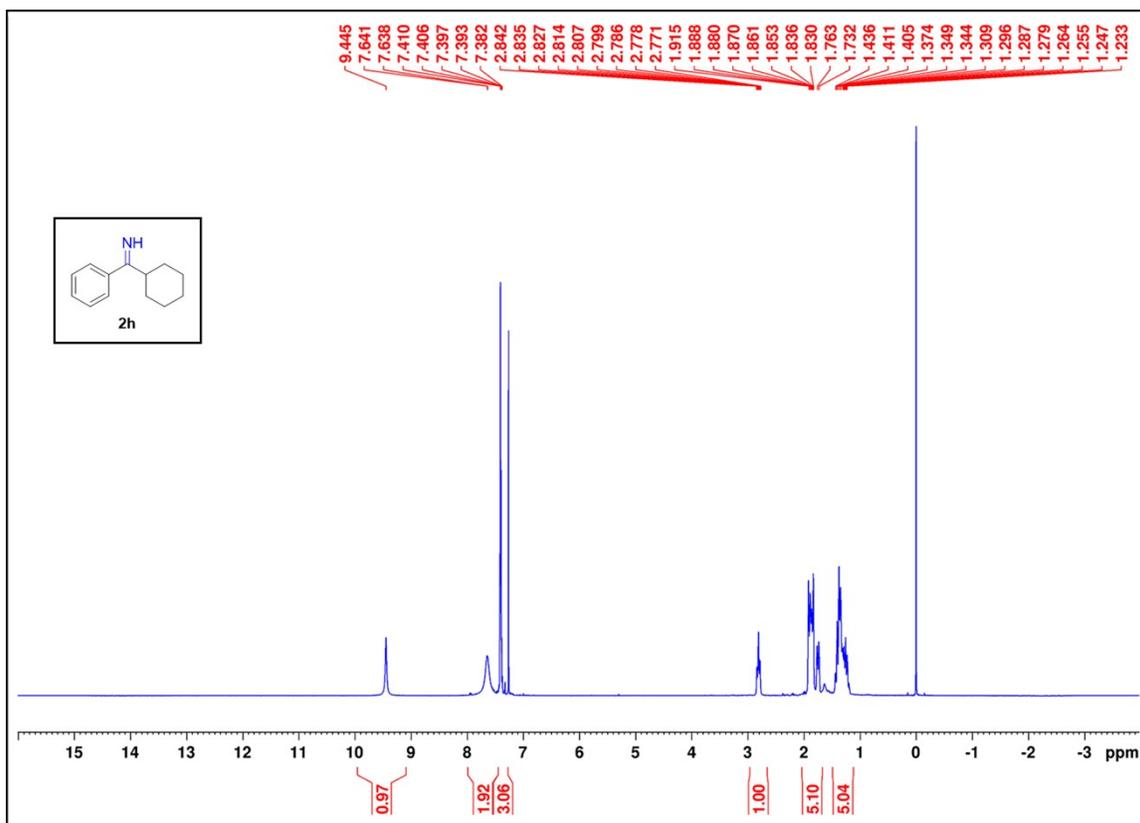
^1H and ^{13}C NMR spectra of **2f** after column chromatography (DMSO- d_6 , 400 MHz)



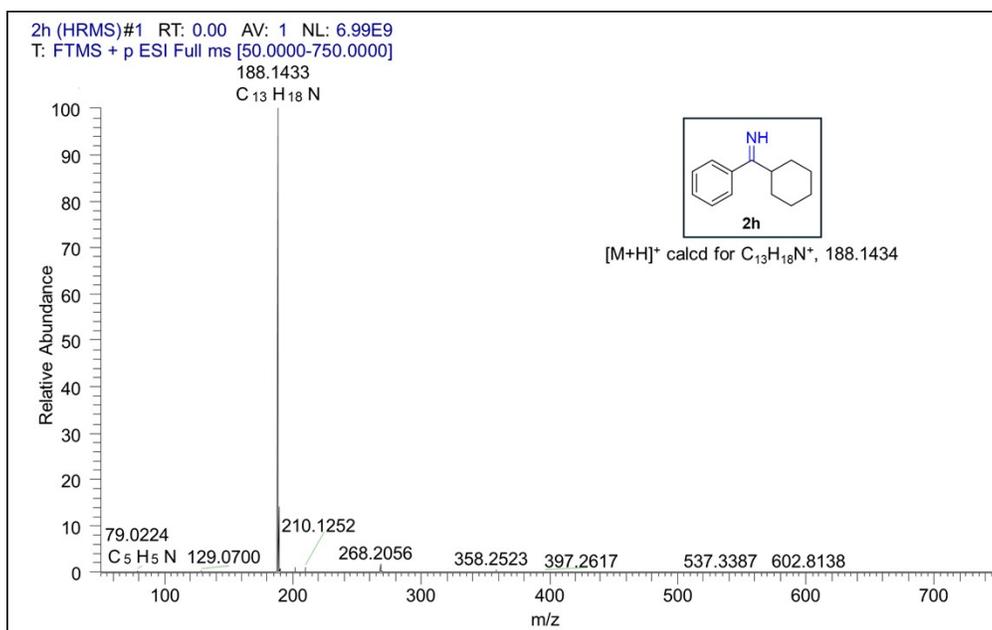
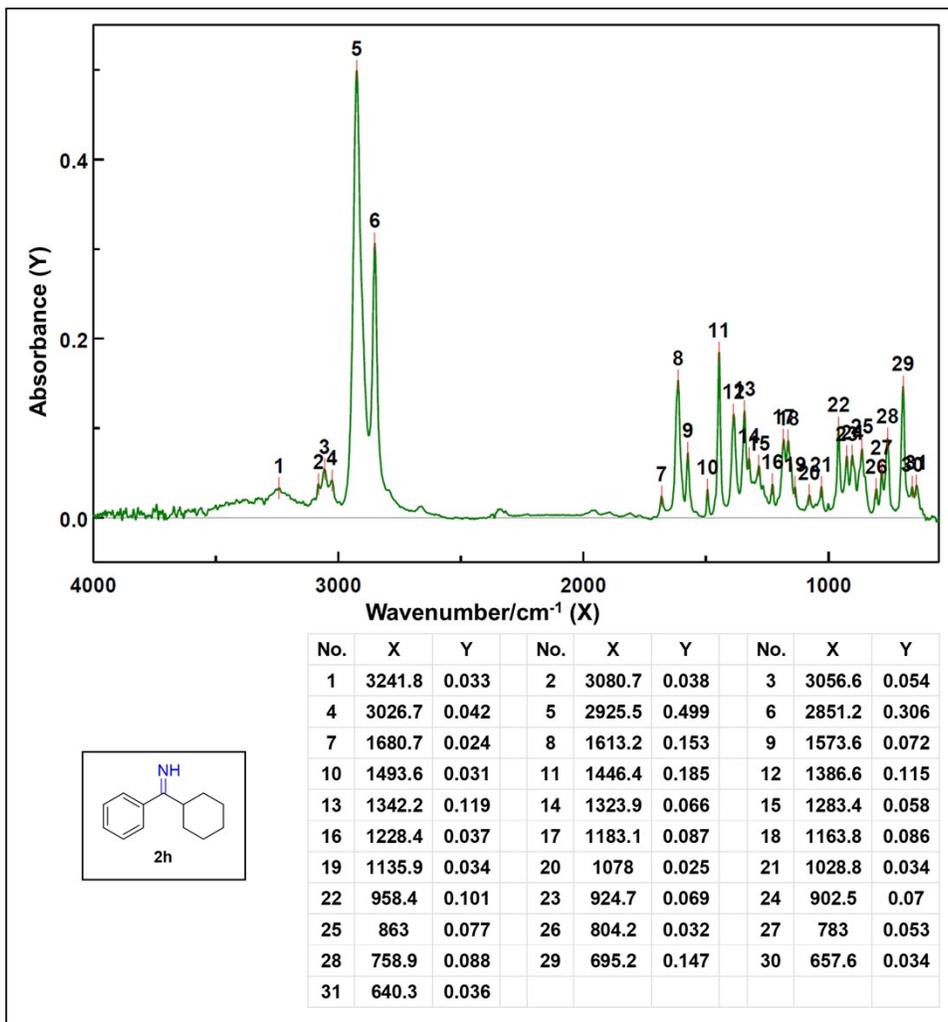
^1H and ^{13}C NMR spectra of **2g** after column chromatography ($\text{DMSO-}d_6$, 400 MHz)



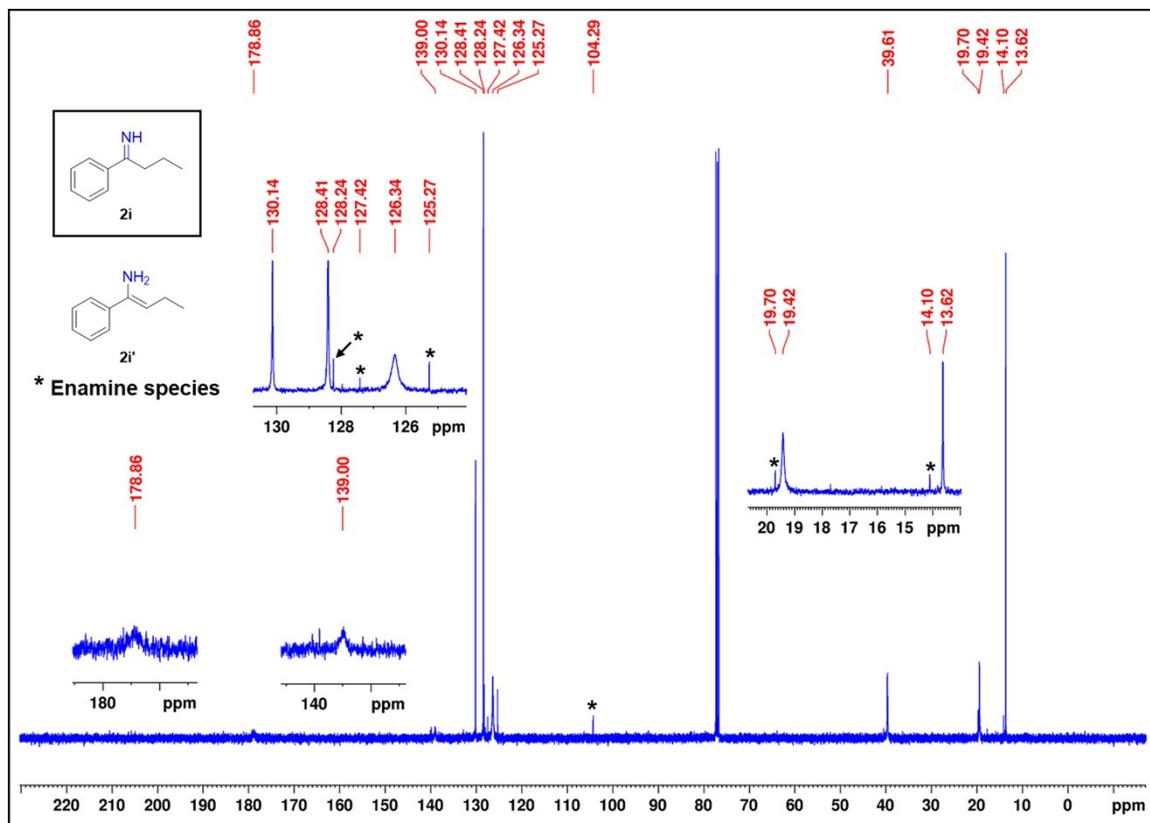
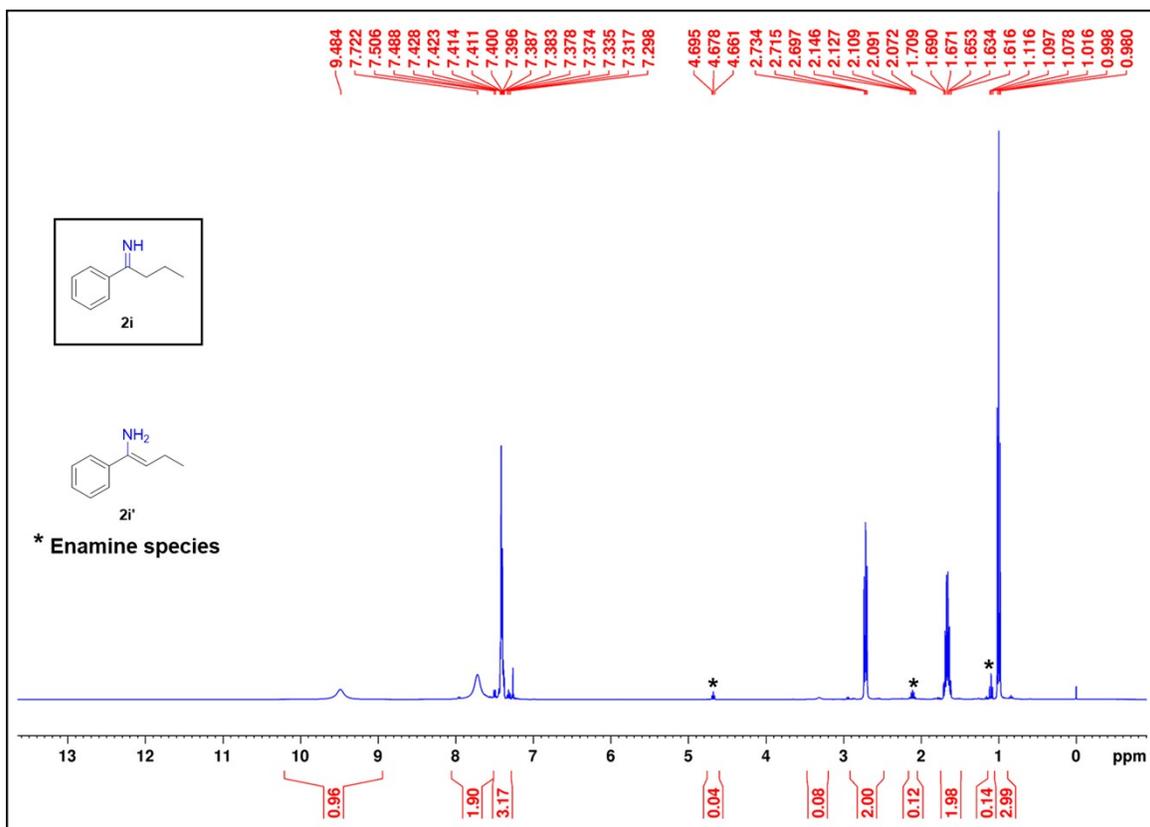
^1H and ^{13}C NMR spectra of **2h** after column chromatography (CDCl_3 , 400 MHz)



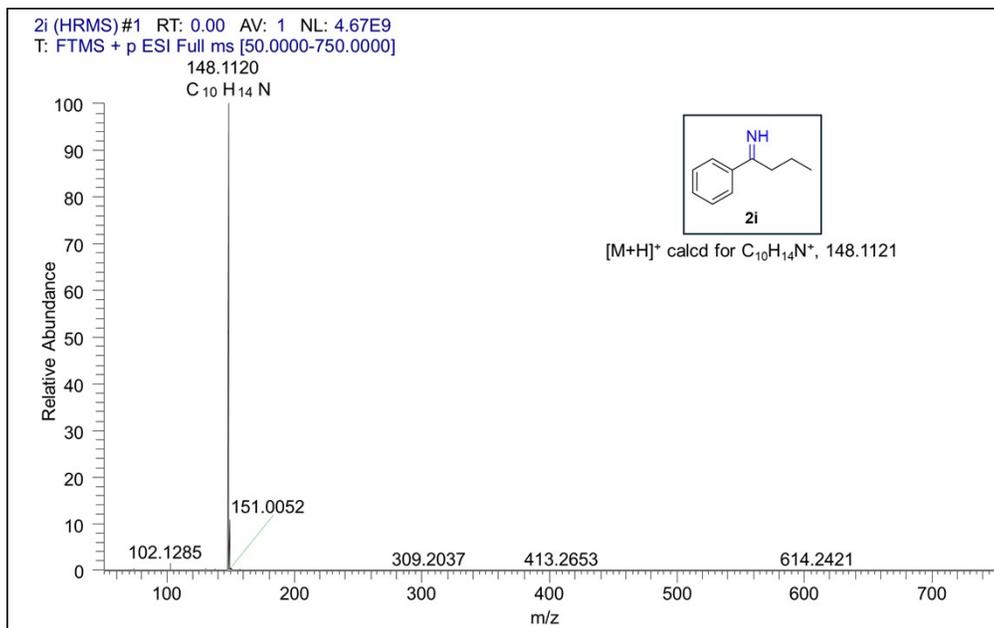
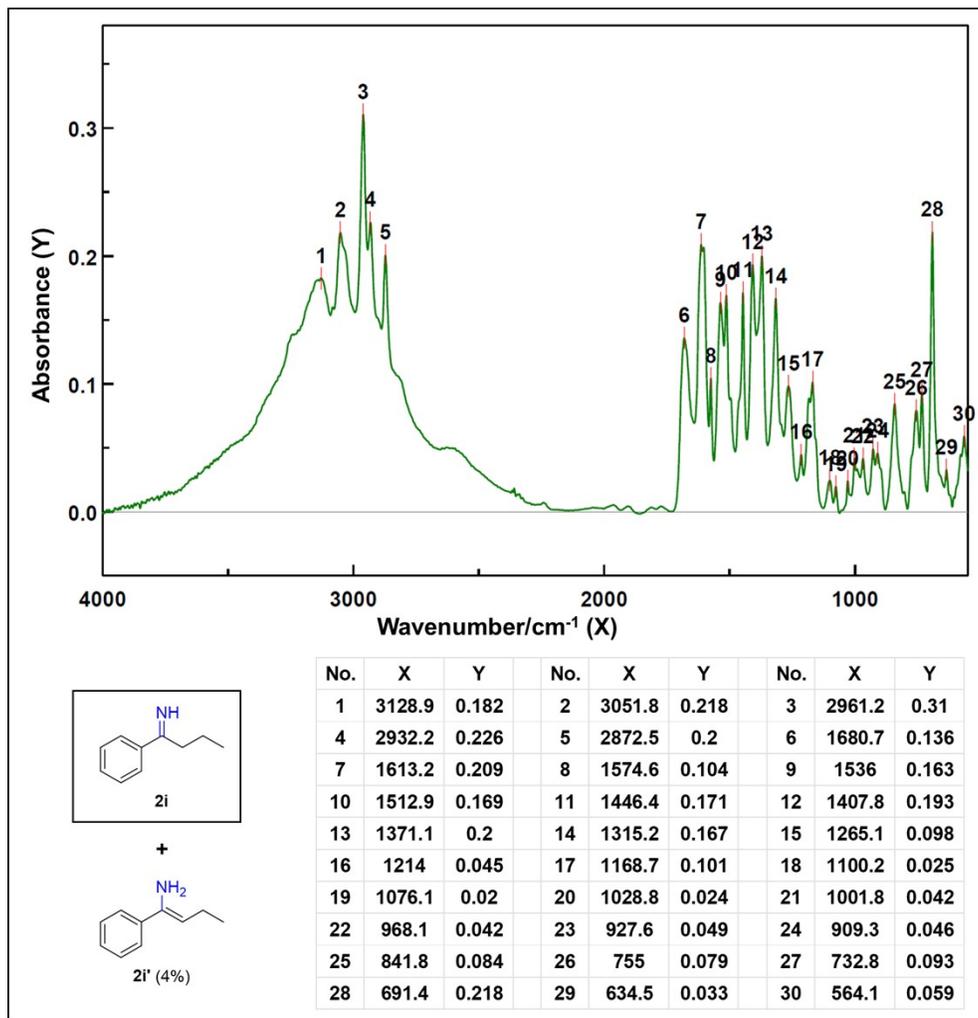
FT-IR (ATR, neat) and HRMS (ESI-positive) spectra of **2h** after column chromatography



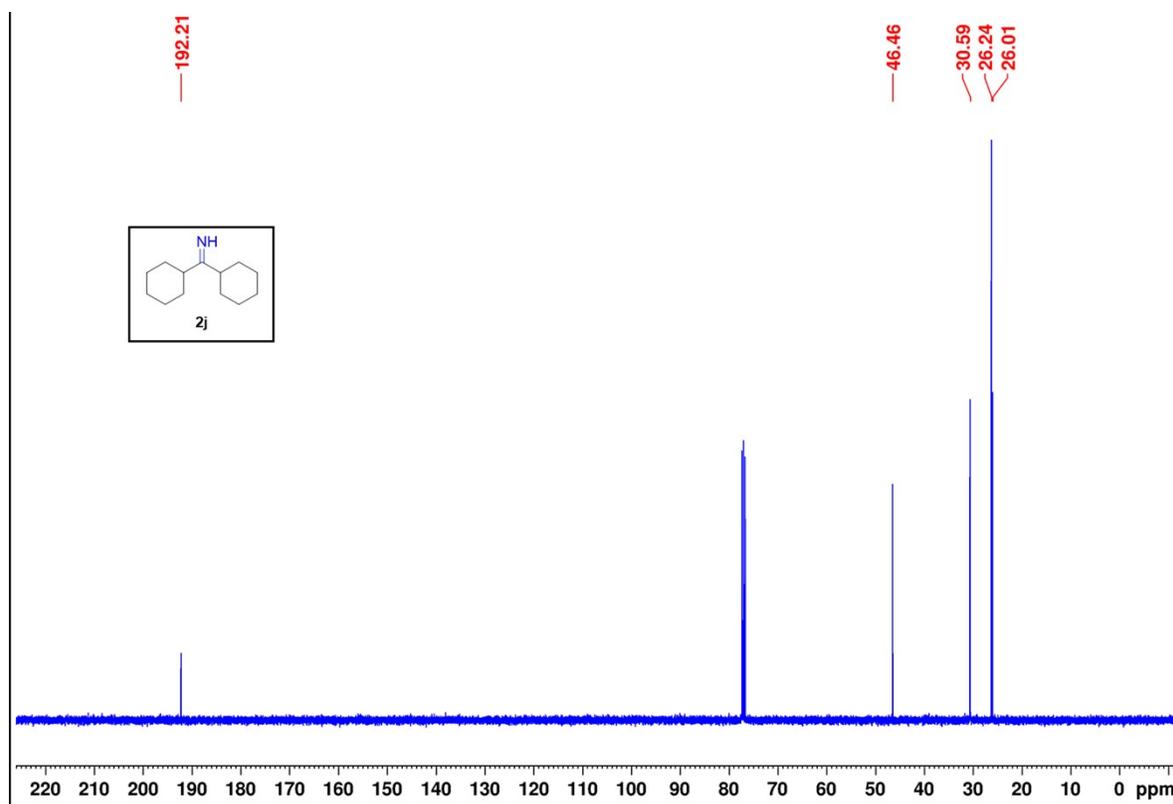
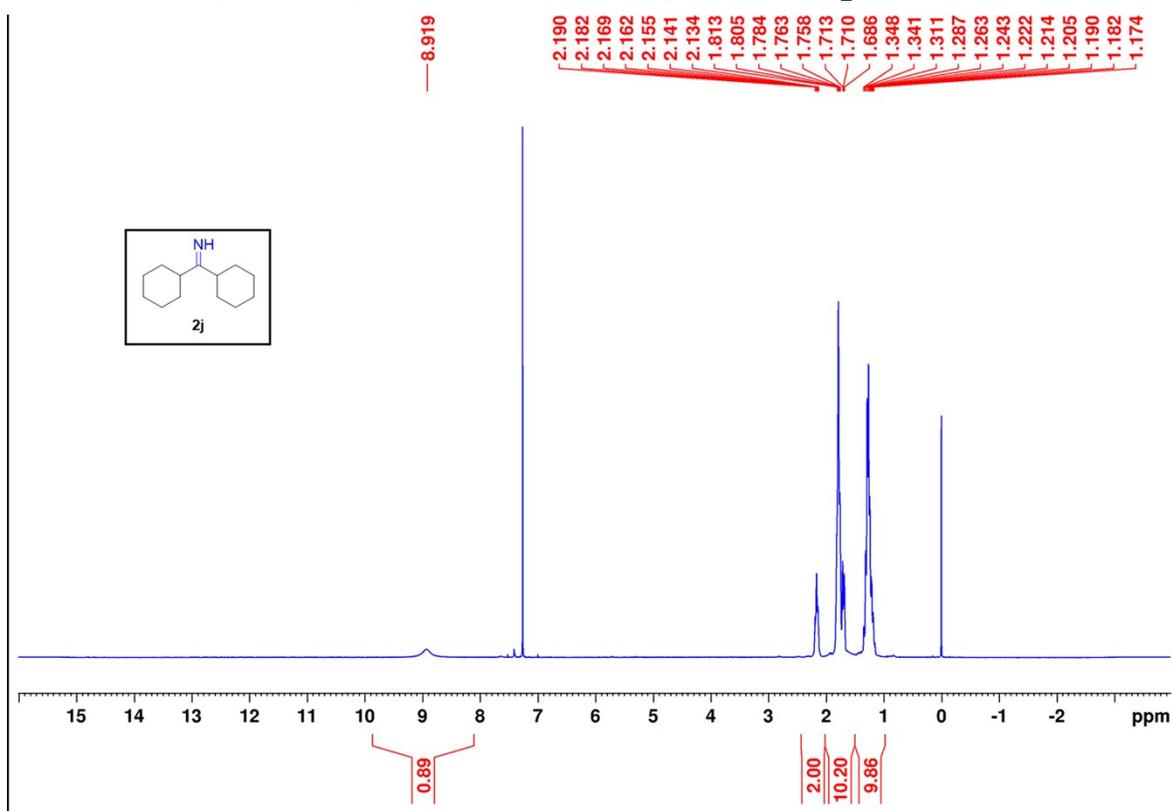
^1H and ^{13}C NMR spectra of **2i** after column chromatography (CDCl_3 , 400 MHz)



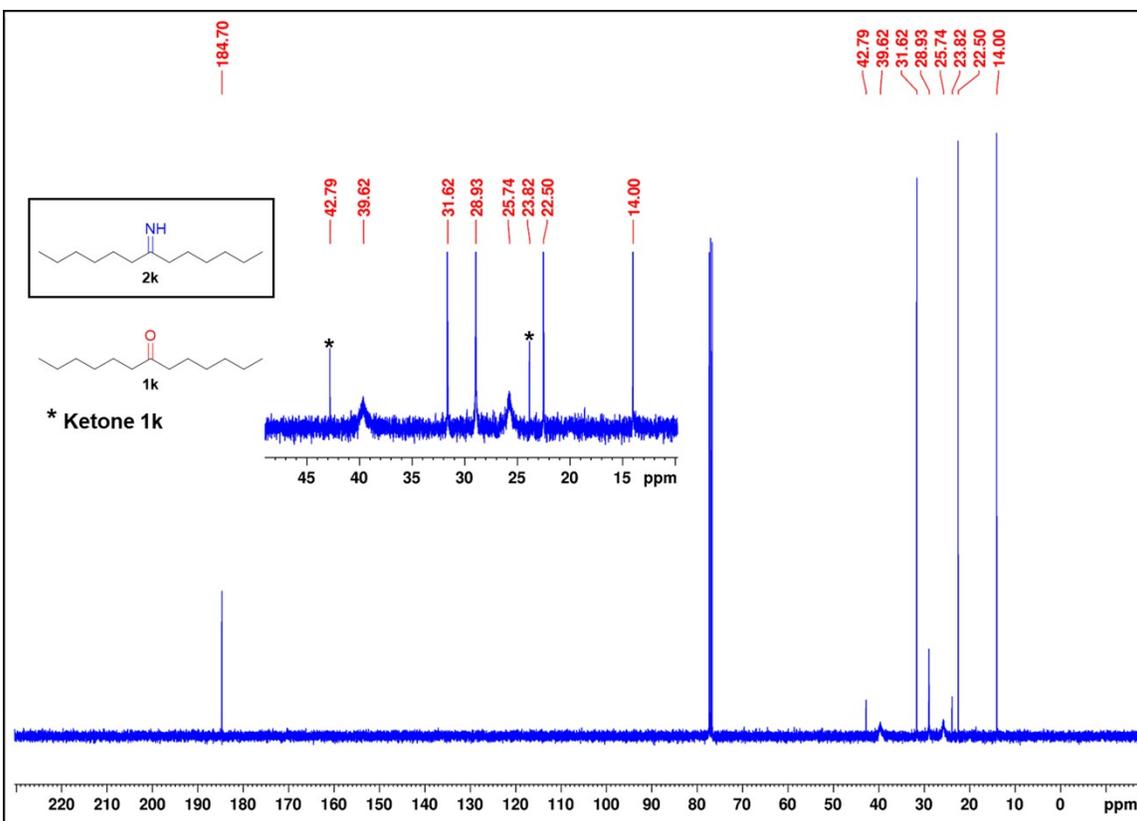
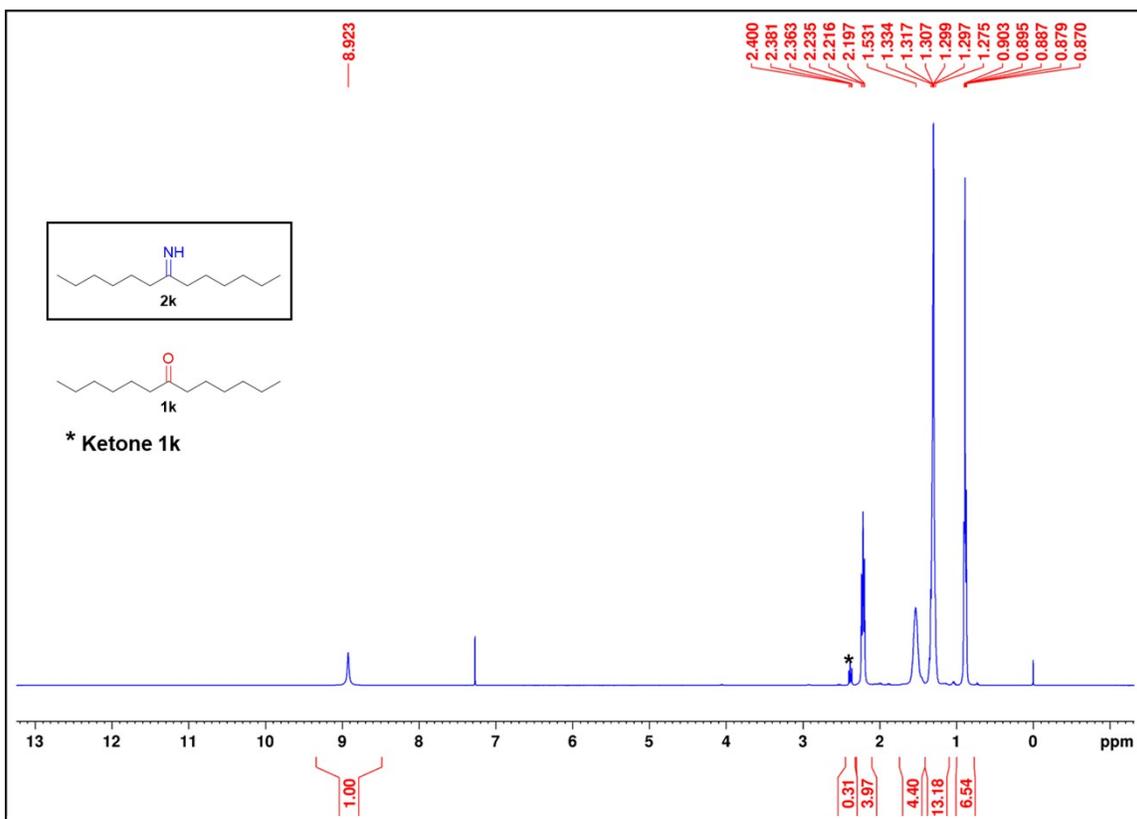
FT-IR (ATR, neat) and HRMS (ESI-positive) spectra of **2i** after column chromatography



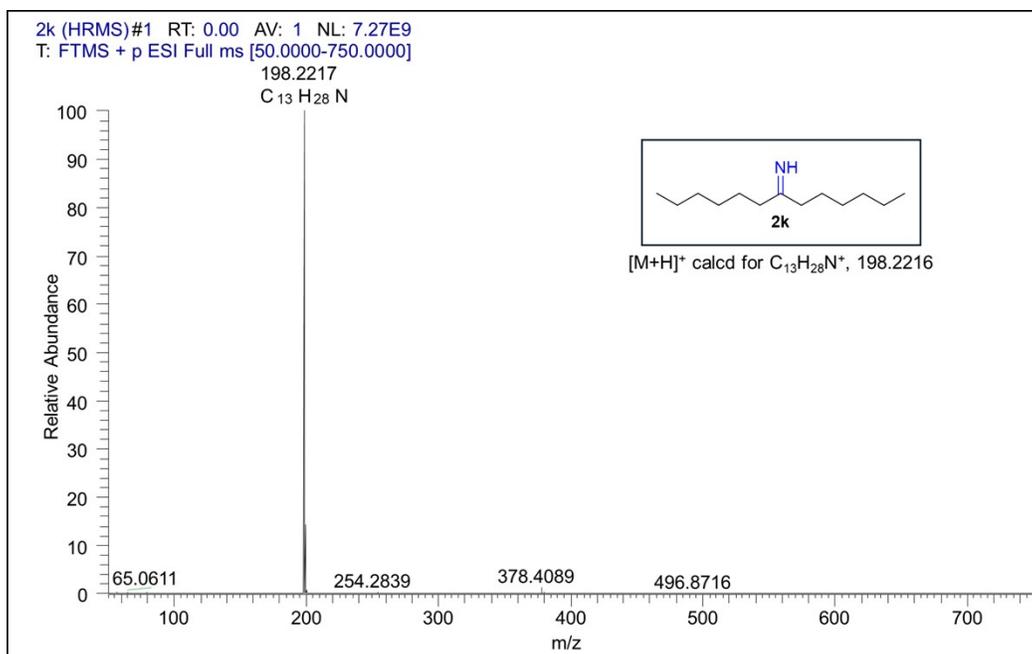
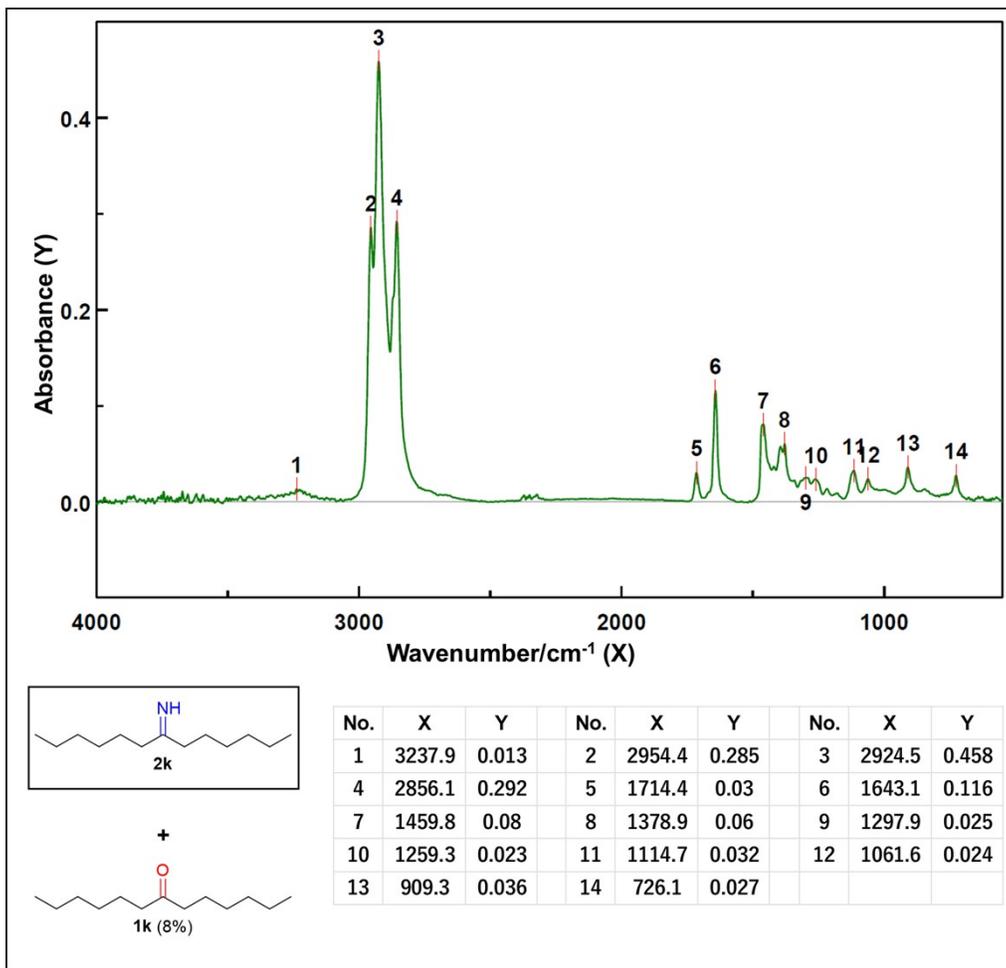
^1H and ^{13}C NMR spectra of **2j** after column chromatography (CDCl_3 , 400 MHz)



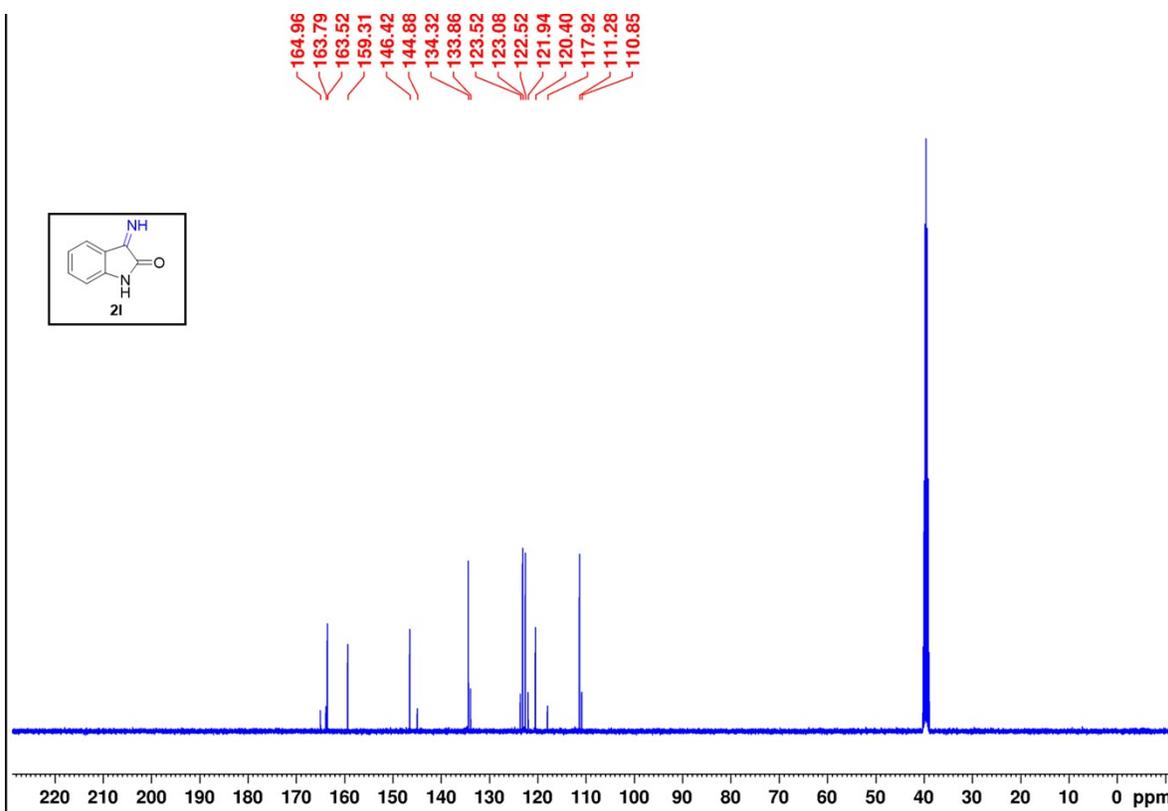
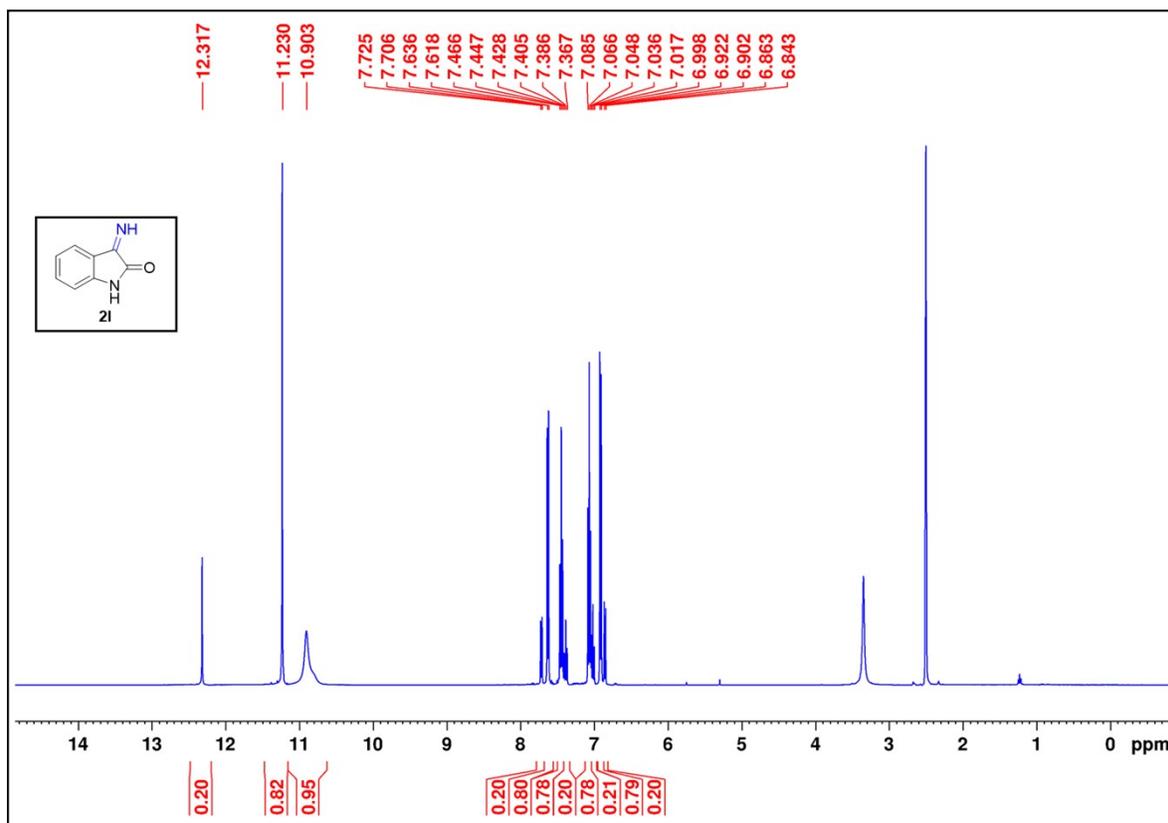
^1H and ^{13}C NMR spectra of **2k** after column chromatography (CDCl_3 , 400 MHz)



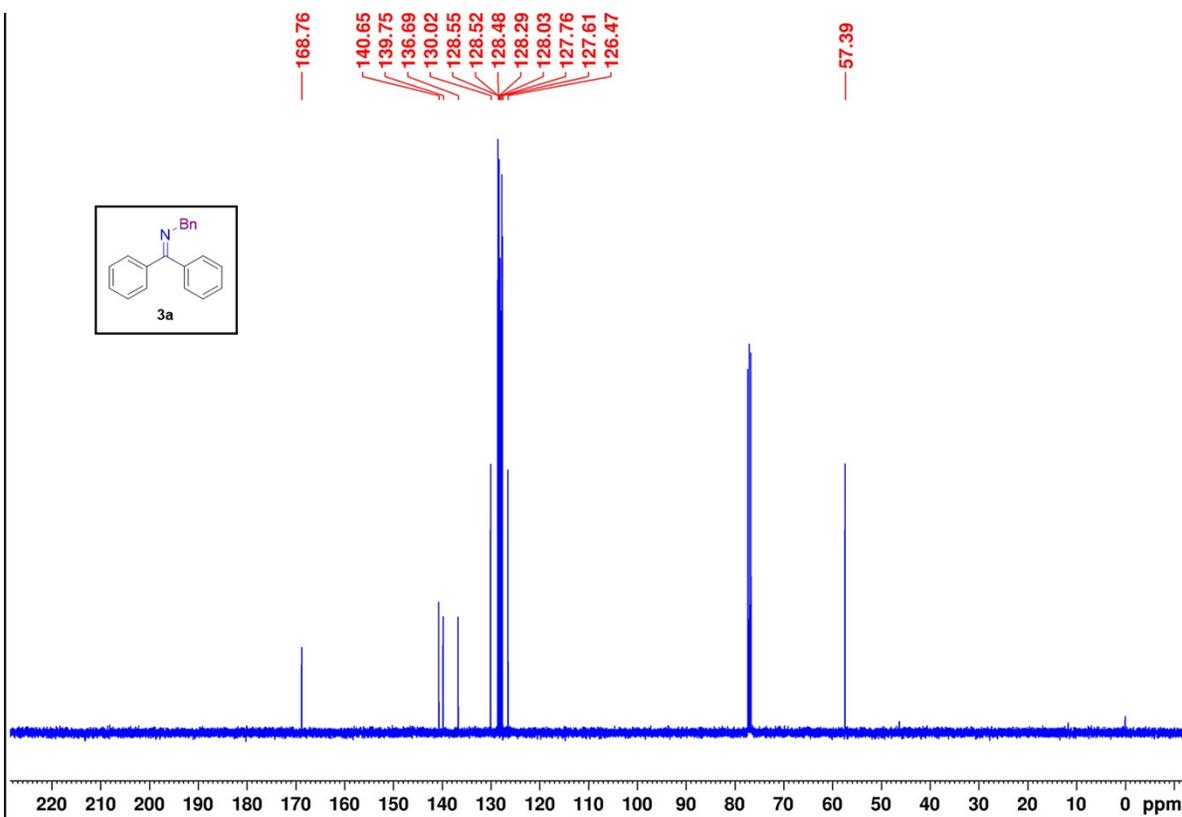
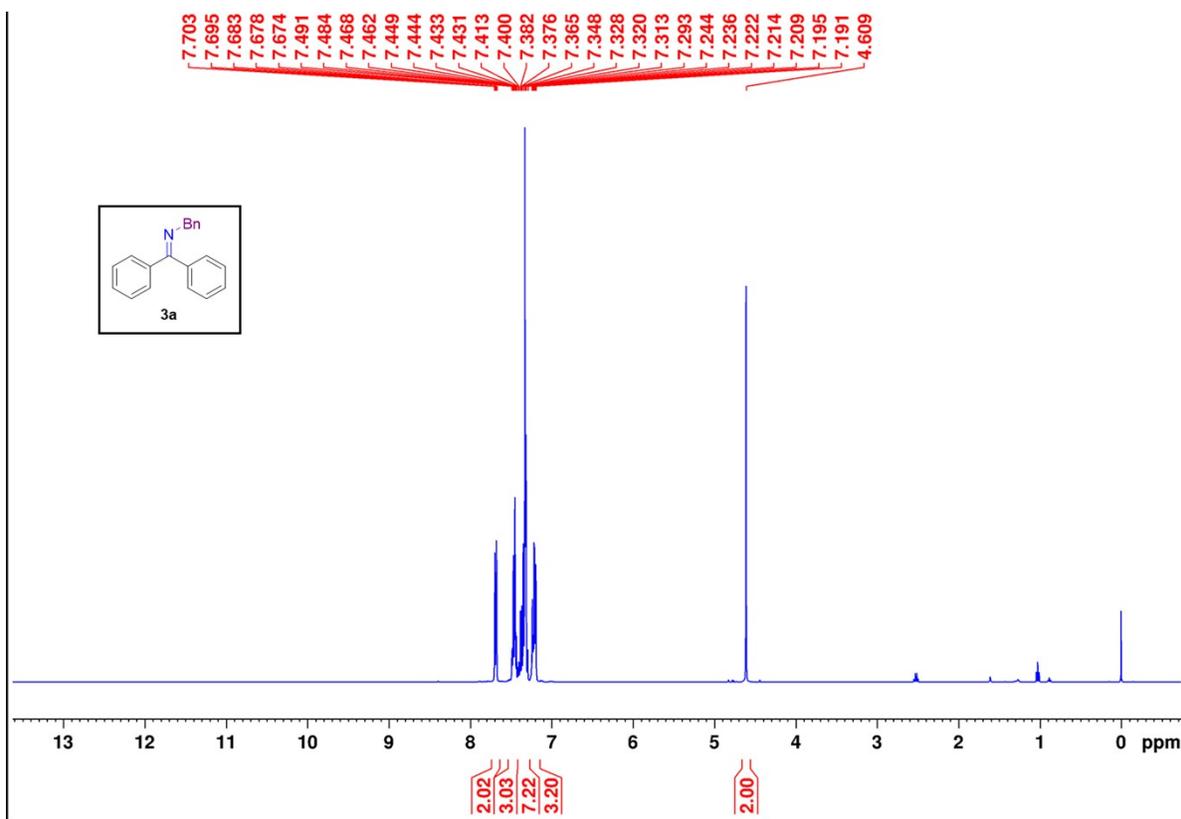
FT-IR (ATR, neat) and HRMS (ESI-positive) spectra of **2k** after column chromatography



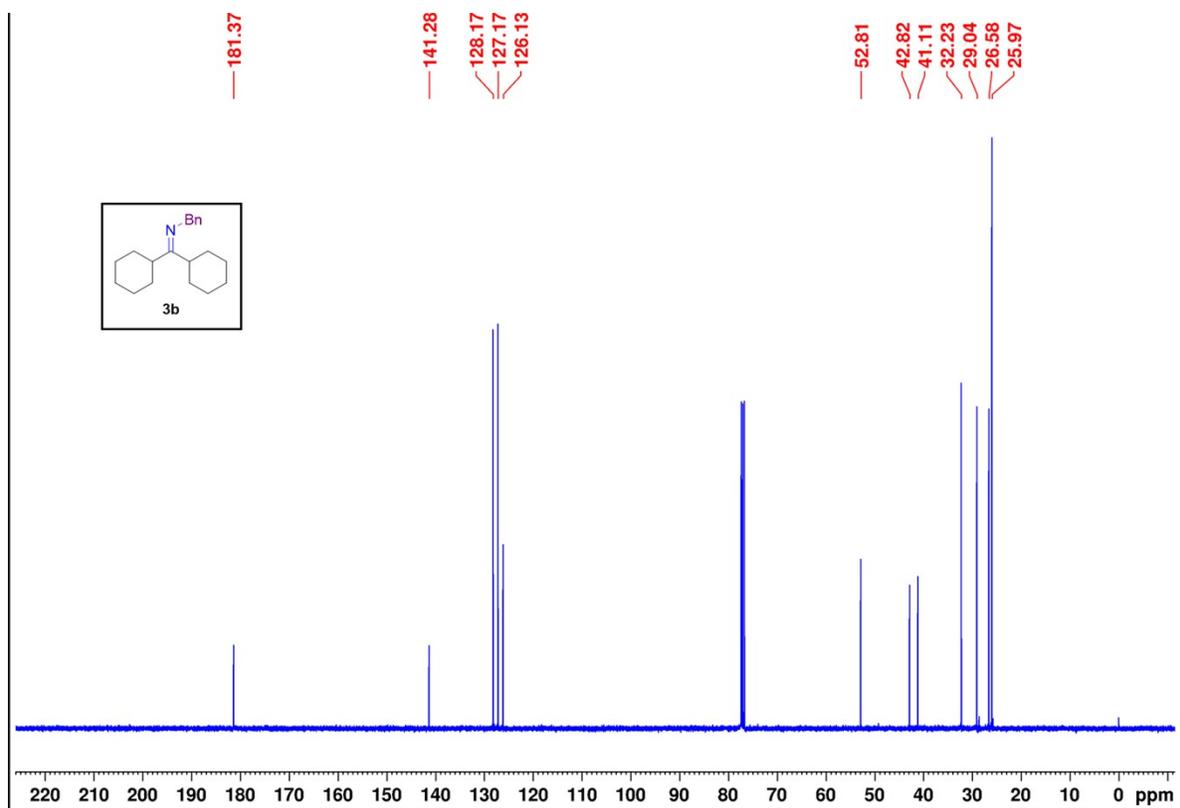
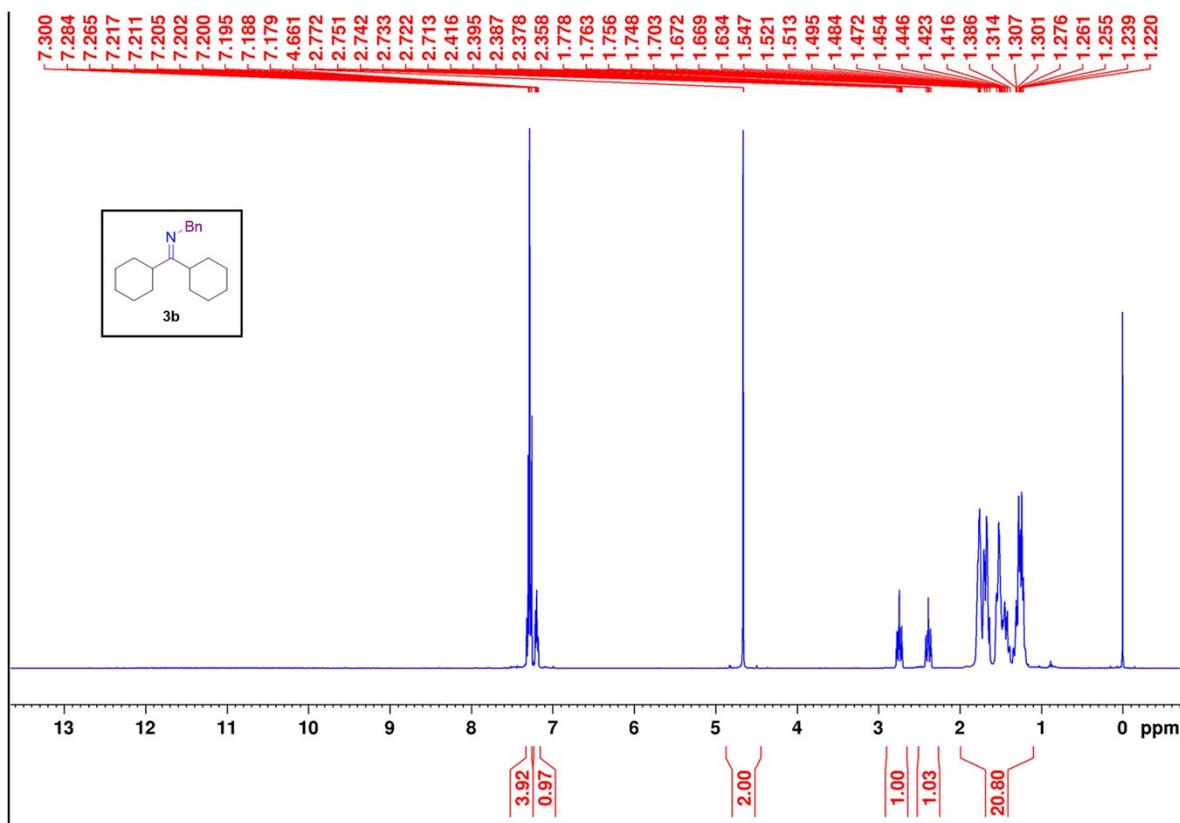
^1H and ^{13}C NMR spectra of **21** after column chromatography (DMSO- d_6 , 400 MHz)



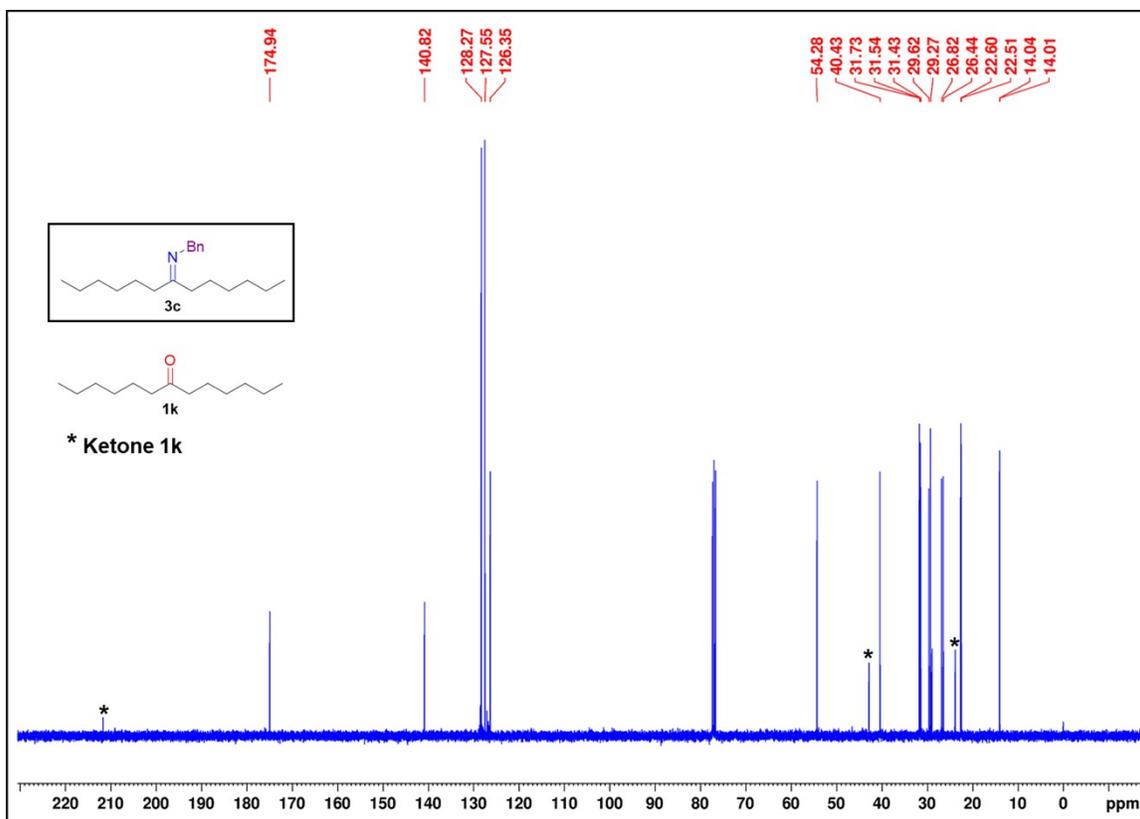
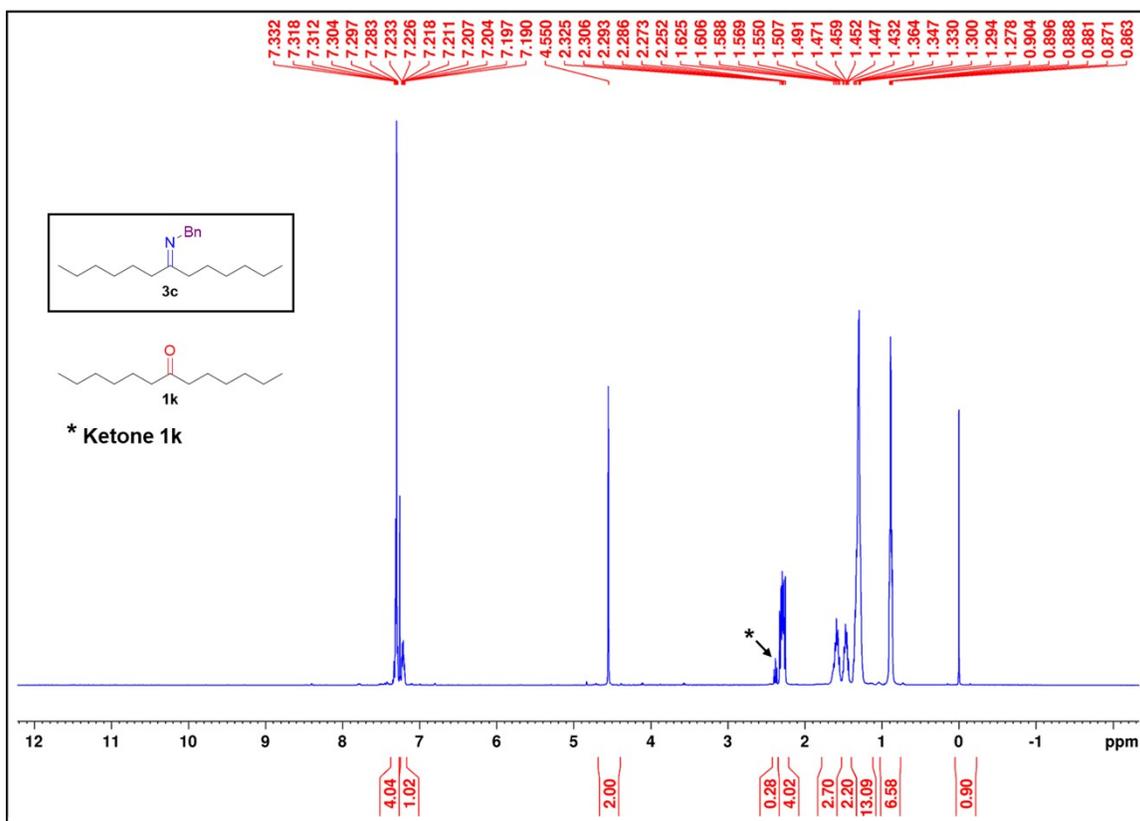
^1H and ^{13}C NMR spectra of **3a** after column chromatography (CDCl_3 , 400 MHz)



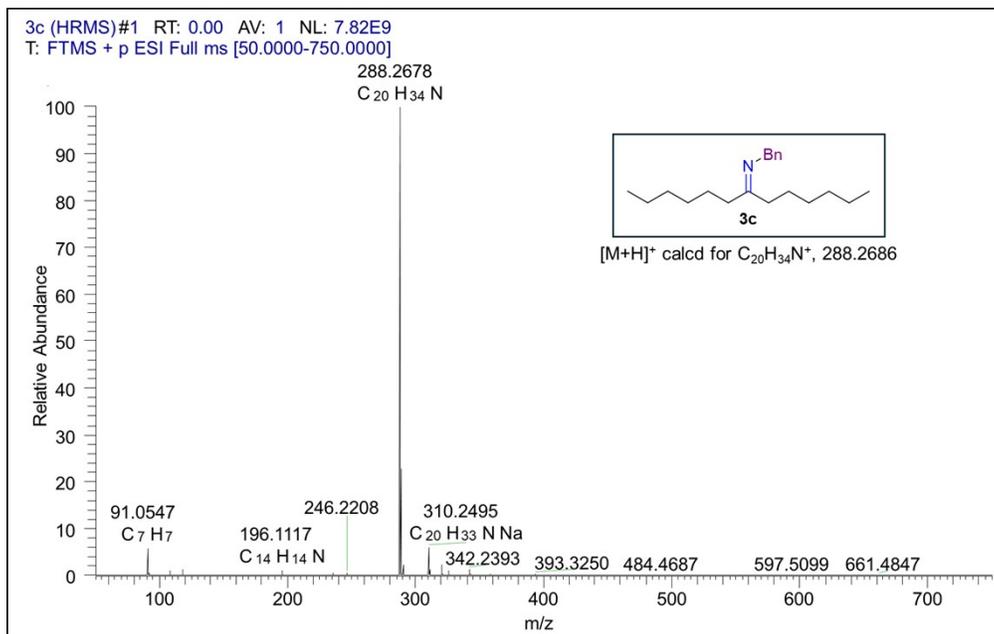
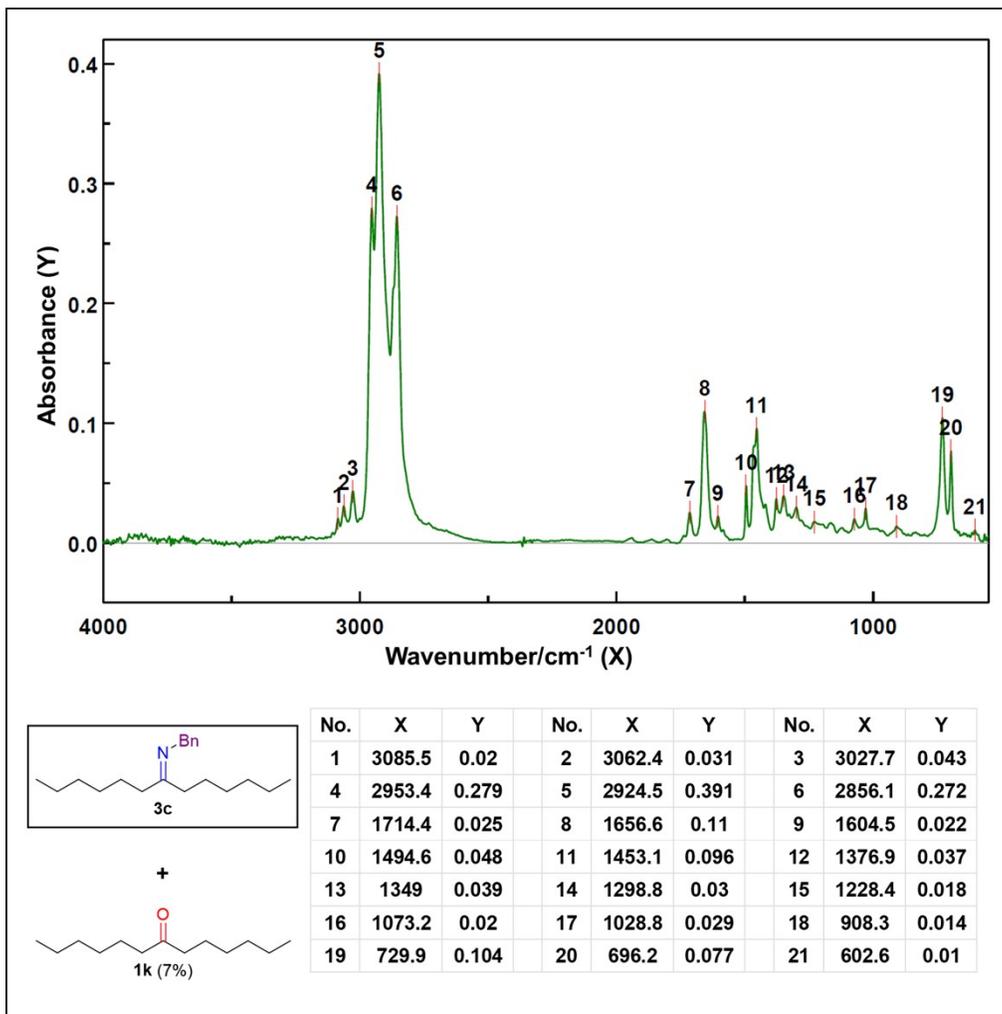
^1H and ^{13}C NMR spectra of **3b** after column chromatography (CDCl_3 , 400 MHz)



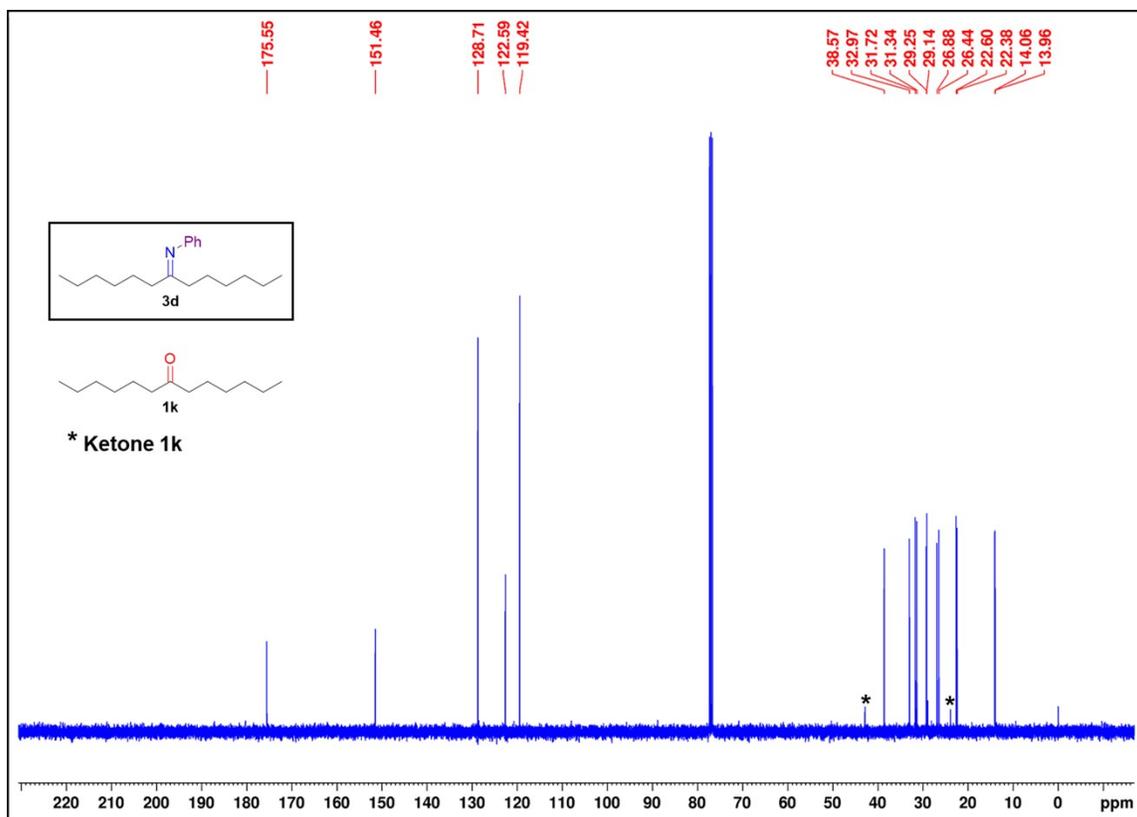
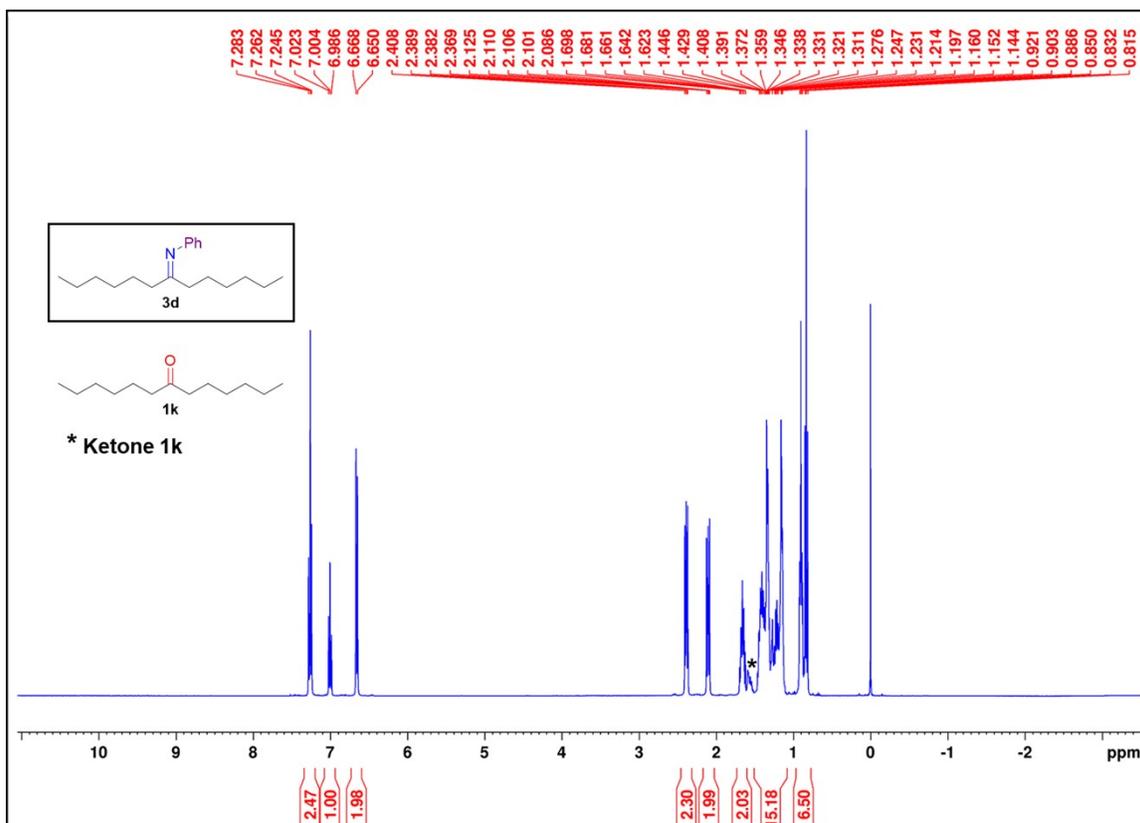
^1H and ^{13}C NMR spectra of **3c** after column chromatography (CDCl_3 , 400 MHz)



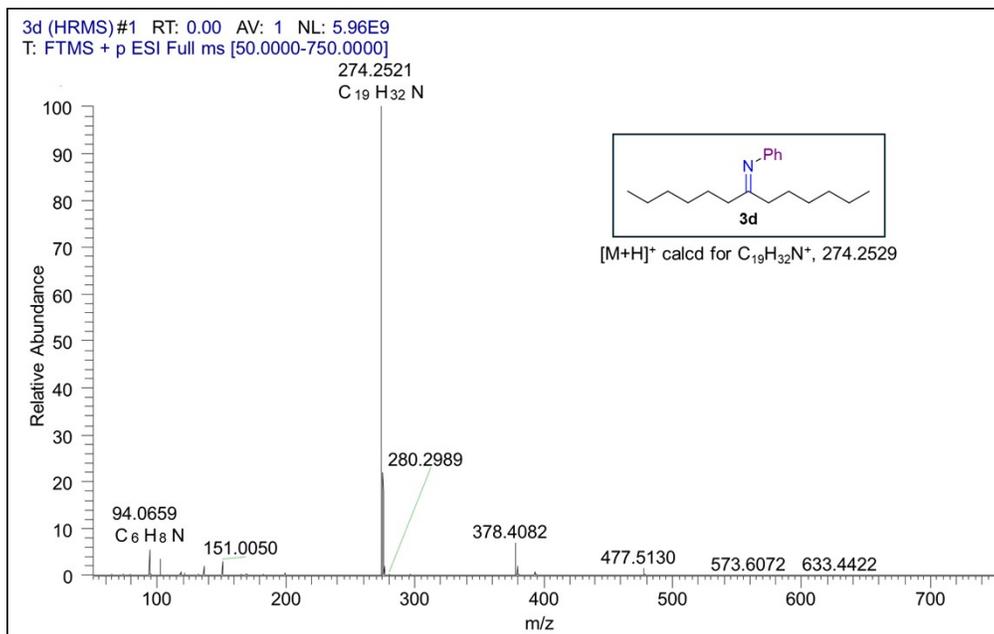
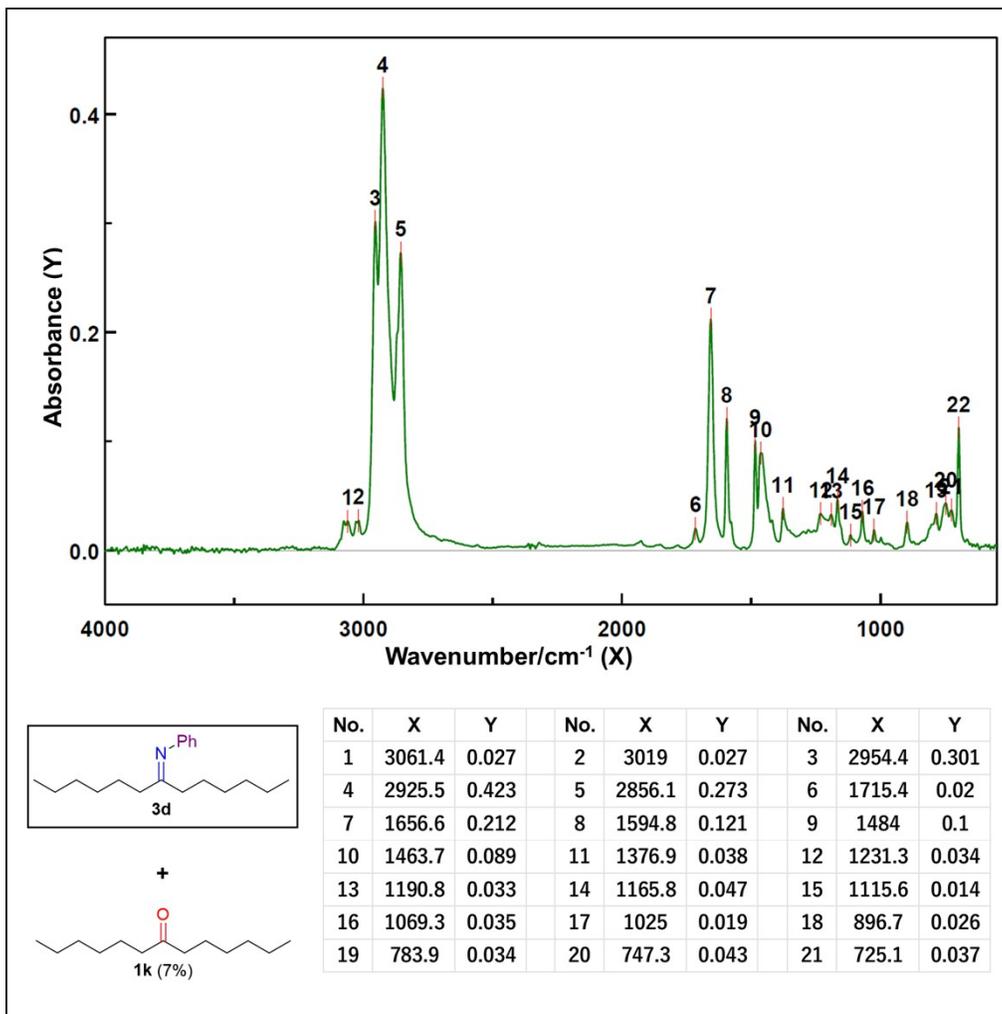
FT-IR (ATR, neat) and HRMS (ESI-positive) spectra of **3c** after column chromatography



^1H and ^{13}C NMR spectra of **3d** after column chromatography (CDCl_3 , 400 MHz)



FT-IR (ATR, neat) and HRMS (ESI-positive) spectra of **3d** after column chromatography



IV Quantum Chemical Calculations: Methods and Results

Quantum chemical calculations were performed at room temperature using Gaussian 16.¹ The M06-2X functional was employed because it accounts for dispersion forces and provides more reliable results than B3LYP.^{4,5}

5. Thermodynamic stability of imines derived from ketones and aldehydes

The Gibbs free energy changes (ΔG) for the condensation of representative aldehydes and ketones with ammonia or amines to afford the corresponding imines were computed at the M06-2X/6-311+G(2d,p) level of theory (Fig. S4). For imines capable of *E/Z* isomerism, only the thermodynamically more stable *E* isomer was considered. Among imine species bearing identical R^1 and R^2 substituents, nitrogen-protected imines (N-R imines) are significantly more thermodynamically stable than their nitrogen-unprotected imines (N-H imines). These calculations corroborate the experimentally observed propensity of N-H imines to hydrolyze and underscore the attendant challenges in their synthesis.

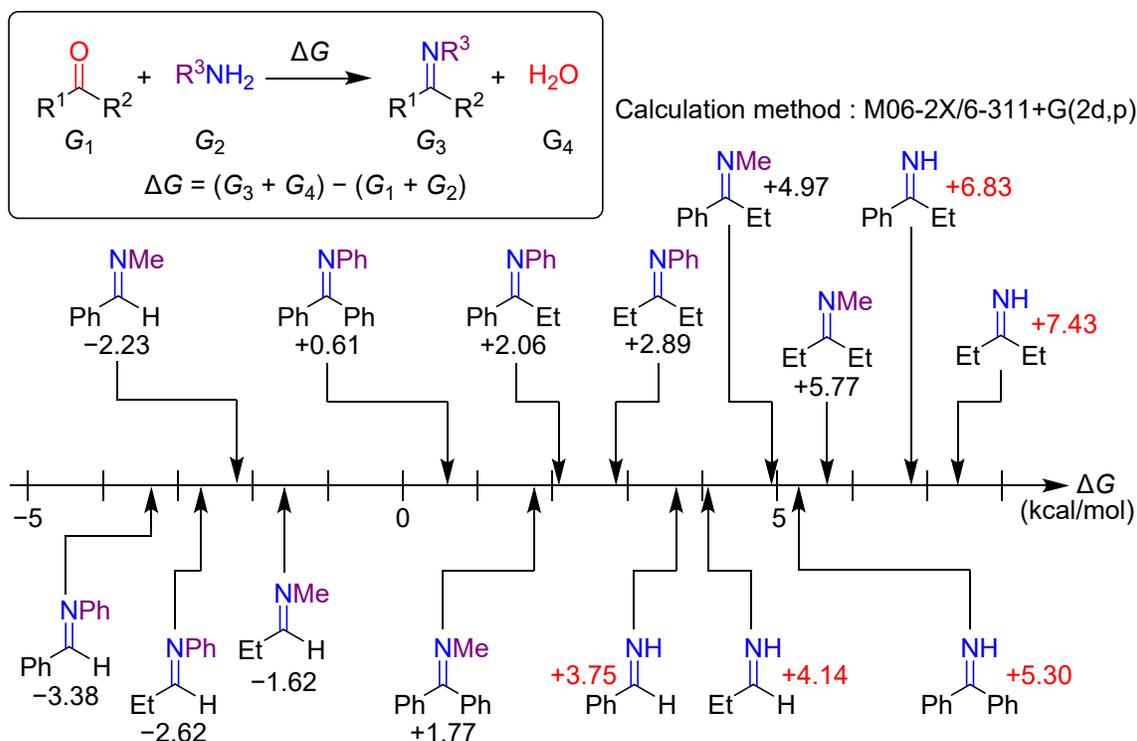


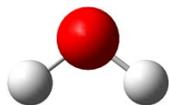
Fig. S4 Calculated results of condensation reactions in which aldehydes or ketones react with ammonia or amines to generate water.

6. Coordinate data and calculated energy values

Thermodynamic stability of imines derived from ketones and aldehydes (Fig. S4)

The calculations in this section were performed at the M06-2X/6-311+G(2d,p) level.

Water

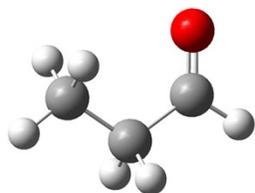


Electronic Energy: (EE) = -76.422051 Hartree

Gibbs free energy: (G) = -76.418062 Hartree

1	O	0	0	0.119171	3	H	0	-0.761551	-0.477004
2	H	0	0.761551	-0.477004					

Propionaldehyde

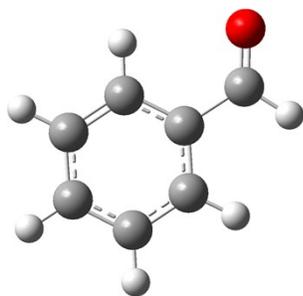


Electronic Energy: (EE) = -193.114065 Hartree

Gibbs free energy: (G) = -193.056227 Hartree

1	C	1.424597	-0.503109	-0.000061	6	H	1.223696	-1.116658	-0.877869
2	C	0.544608	0.735237	0.000086	7	H	1.223397	-1.117053	0.877399
3	C	-0.926646	0.422072	-0.000104	8	H	0.735149	1.373839	-0.87001
4	O	-1.381081	-0.688763	0.000067	9	H	0.734889	1.37336	0.870611
5	H	2.479019	-0.228871	0.000174	10	H	-1.602859	1.300289	-0.000369

Benzaldehyde



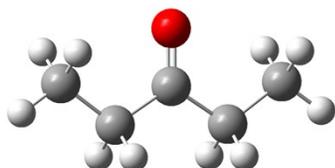
Electronic Energy: (EE) = -345.526705 Hartree

Gibbs free energy: (G) = -345.446692 Hartree

1	C	0.043829	-1.097892	-0.000166	8	C	-0.354979	1.283753	-0.000013
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2	C	0.527704	0.209371	-0.000142	9	H	0.754617	-1.915063	-0.000254
3	C	1.986803	0.466313	-0.000218	10	H	2.274121	1.53619	-0.000899
4	O	2.826656	-0.394438	0.00038	11	H	-1.705344	-2.334988	-0.000116
5	C	-1.321462	-1.322813	-0.000066	12	H	-3.272425	-0.425155	0.000195
6	C	-2.204546	-0.245153	0.000099	13	H	-2.414845	1.891309	0.00027
7	C	-1.724673	1.05759	0.000137	14	H	0.034559	2.296201	-0.000027

Pentan-3-one

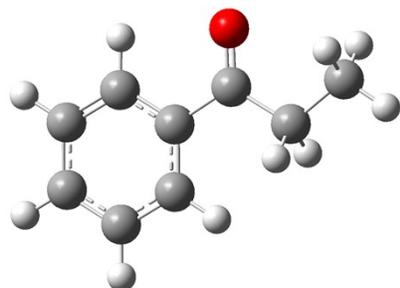


Electronic Energy: (EE) = -271.735296 Hartree

Gibbs free energy: (G) = -271.626169 Hartree

1	C	2.532485	0.1396	-0.000672	9	H	1.267223	-1.400055	-0.868018
2	C	1.289528	-0.734605	0.001319	10	C	-1.289524	-0.734578	-0.001267
3	C	0.000004	0.063483	0.000029	11	H	-1.267271	-1.400035	0.868072
4	O	-0.000009	1.268993	0.000057	12	H	-1.267358	-1.39614	-0.873606
5	H	3.434998	-0.471402	0.000731	13	C	-2.532486	0.139588	0.000558
6	H	2.547769	0.787568	0.87512	14	H	-2.547907	0.783627	0.879247
7	H	2.547848	0.783573	-0.87942	15	H	-2.547753	0.787499	-0.875272
8	H	1.26745	-1.396066	0.873735	16	H	-3.43497	-0.471443	-0.000853

Propiophenone



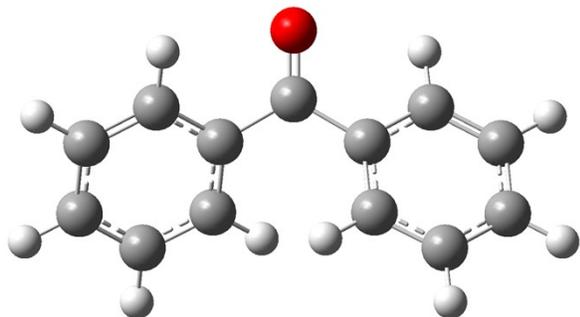
Electronic Energy: (EE) = -424.146115 Hartree

Gibbs free energy: (G) = -424.013210 Hartree

1	C	1.14167	1.209111	-0.000084	11	H	4.106764	-0.423192	-0.000178
2	C	0.27749	0.114805	0.000081	12	H	2.585247	-2.371259	0.000093
3	C	-1.200554	0.37783	0.000162	13	H	0.150284	-2.035906	0.000233
4	O	-1.619206	1.511227	0.000296	14	C	-2.148494	-0.805328	0.000104

5	C	2.512928	1.017105	-0.000176	15	H	-1.91694	-1.423846	-0.872852
6	C	3.034387	-0.272564	-0.000105	16	H	-1.917423	-1.423557	0.873395
7	C	2.180886	-1.367091	0.000045	17	C	-3.607545	-0.380064	-0.000361
8	C	0.805736	-1.174435	0.000137	18	H	-4.260596	-1.252585	-0.000407
9	H	0.712391	2.202826	-0.000128	19	H	-3.83231	0.225603	0.876803
10	H	3.179047	1.870545	-0.000304	20	H	-3.831832	0.225334	-0.877833

Benzophenone

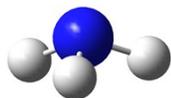


Electronic Energy: (EE) = -576.554219 Hartree

Gibbs free energy: (G) = -576.398937 Hartree

1	C	-2.417533	0.959937	0.530535	13	C	1.295346	0.35135	0.029587
2	C	-1.295341	0.351331	-0.029616	14	C	1.422824	-0.88753	0.654416
3	C	-0.000004	1.103179	0.000049	15	C	2.417423	0.959872	-0.530657
4	C	-3.647574	0.32452	0.490944	16	C	2.661132	-1.512809	0.712888
5	C	-3.770413	-0.912778	-0.132377	17	H	0.55989	-1.352426	1.114828
6	C	-2.661193	-1.512888	-0.712754	18	C	3.647518	0.32436	-0.491182
7	C	-1.422808	-0.8876	-0.654183	19	H	2.303497	1.933447	-0.99044
8	H	-2.30348	1.933544	0.990221	20	C	3.77036	-0.9128	0.132232
9	H	-4.513919	0.793911	0.939385	21	H	2.759733	-2.467874	1.212912
10	H	-4.733518	-1.406399	-0.16998	22	H	4.513775	0.793696	-0.939852
11	H	-2.759695	-2.468005	-1.212696	23	H	4.733439	-1.40647	0.169868
12	H	-0.559884	-1.352614	-1.114507	24	O	0.000218	2.313791	0.00012

Ammonia

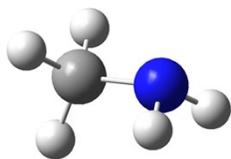


Electronic Energy: (EE) = -56.547349 Hartree

Gibbs free energy: (G) = -56.530794 Hartree

1	N	0	0	0.111251	3	H	0.816497	-0.471197	-0.259693
2	H	0	0.942393	-0.259693	4	H	-0.816497	-0.471197	-0.259693

Methylamine

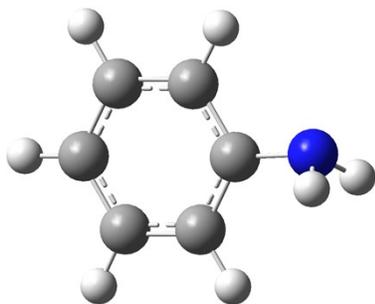


Electronic Energy: (EE) = -95.837110 Hartree

Gibbs free energy: (G) = -95.795452 Hartree

1	N	0.050085	-0.75721	0	5	H	0.589738	1.061485	0.877642
2	H	-0.443067	-1.110086	0.812045	6	H	0.589738	1.061485	-0.877642
3	H	-0.443067	-1.110086	-0.812045	7	H	-0.944444	1.165654	0
4	C	0.050085	0.705336	0					

Aniline

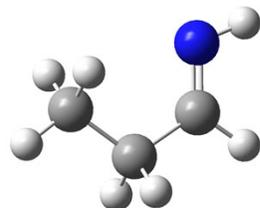


Electronic Energy: (EE) = -287.554768 Hartree

Gibbs free energy: (G) = -287.466177 Hartree

1	N	-2.35806	-0.117036	0.000017	8	H	-0.734214	-2.149607	0.00003
2	H	-2.741165	0.352405	0.813814	9	C	1.147039	1.21688	0.000001
3	H	-2.741158	0.352053	-0.813987	10	H	-0.807472	2.110722	-0.000011
4	C	-0.920869	-0.029714	0.000007	11	C	1.869741	0.030279	-0.000006
5	C	-0.19218	-1.212557	0.000016	12	H	1.753722	-2.112473	-0.000001
6	C	-0.240569	1.1863	-0.000005	13	H	1.664444	2.168223	-0.000003
7	C	1.196863	-1.18374	-0.000005	14	H	2.952107	0.053232	-0.000011

(*E*)-Propan-1-imine

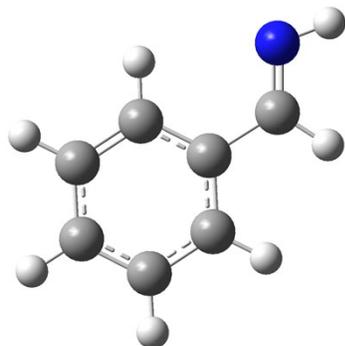


Electronic Energy: (EE) = -173.233293 Hartree

Gibbs free energy: (G) = -173.162356 Hartree

1	C	1.432321	-0.549564	-0.000078	7	H	1.206943	-1.156095	0.876652
2	C	0.601085	0.72353	0.000102	8	H	0.835987	1.346718	-0.869987
3	C	-0.879521	0.4839	-0.000094	9	H	0.835715	1.346203	0.870652
4	N	-1.372955	-0.68004	0.000097	10	H	-1.502583	1.386705	-0.00047
5	H	2.496316	-0.312748	-0.000023	11	H	-2.391978	-0.641863	-0.000092
6	H	1.206976	-1.155835	-0.876998					

(E)-Phenylmethanimine

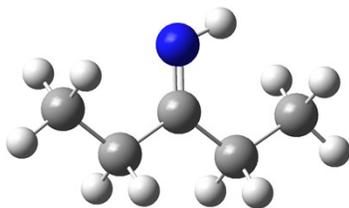


Electronic Energy: (EE) = -325.646035 Hartree

Gibbs free energy: (G) = -325.553454 Hartree

1	C	0.027312	-1.094212	0.000224	9	H	0.736205	-1.912455	0.000383
2	C	0.515263	0.213027	0.000185	10	H	2.238814	1.54424	0.000949
3	C	1.966295	0.482432	0.000346	11	H	3.771698	-0.068393	-0.000421
4	N	2.826133	-0.447505	-0.00051	12	H	-1.715638	-2.336907	0.000131
5	C	-1.337534	-1.32232	0.00007	13	H	-3.294477	-0.43388	-0.000272
6	C	-2.227249	-0.250551	-0.000143	14	H	-2.437215	1.885454	-0.000328
7	C	-1.747488	1.051111	-0.000171	15	H	0.003875	2.295664	0.000016
8	C	-0.377632	1.280315	0.000007					

Pentan-3-imine

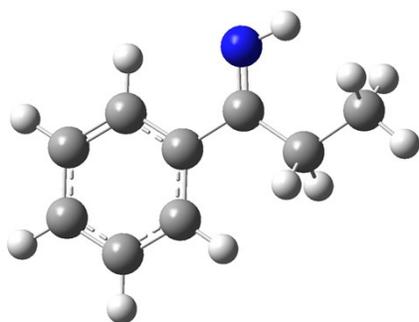


Electronic Energy: (EE) = -251.850567 Hartree

Gibbs free energy: (G) = -251.727066 Hartree

1	C	2.560236	0.09834	-0.000485	10	H	-0.850254	1.765675	-0.000232
2	C	1.286552	-0.731556	0.000784	11	C	-1.262091	-0.737136	-0.000645
3	C	0.013865	0.082229	0.000079	12	H	-1.228212	-1.40134	0.868926
4	N	0.080445	1.346987	0.000187	13	H	-1.228141	-1.399352	-0.871755
5	H	3.438013	-0.548649	0.000328	14	C	-2.554625	0.064653	0.000206
6	H	2.598869	0.745259	0.875195	15	H	-2.627488	0.700229	0.884672
7	H	2.598724	0.742808	-0.877989	16	H	-2.628015	0.701191	-0.883529
8	H	1.25841	-1.394813	0.872394	17	H	-3.416749	-0.601865	0.000019
9	H	1.258113	-1.397235	-0.868977					

(E)-1-Phenylpropan-1-imine

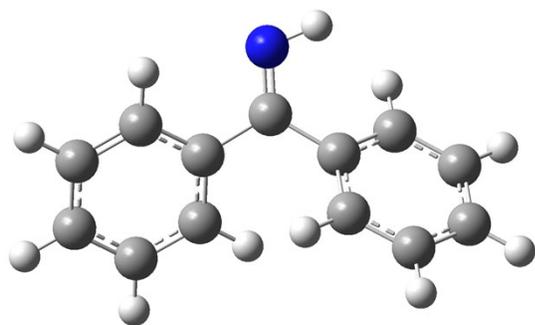


Electronic Energy: (EE) = -404.261087 Hartree

Gibbs free energy: (G) = -404.115060 Hartree

1	C	1.170781	1.213296	-0.000015	12	H	4.113002	-0.465907	-0.000018
2	C	0.281247	0.136343	0.00001	13	H	2.554131	-2.387146	0.00002
3	C	-1.191566	0.402498	0.00002	14	H	0.135011	-2.014797	0.000036
4	N	-1.580334	1.610915	0.000039	15	C	-2.114387	-0.801213	-0.000005
5	C	2.537836	0.998007	-0.000024	16	H	-1.868853	-1.414053	-0.872407
6	C	3.043188	-0.298451	-0.00001	17	H	-1.868891	-1.414067	0.872397
7	C	2.169891	-1.374908	0.000011	18	C	-3.599341	-0.471485	-0.000033
8	C	0.796884	-1.158763	0.000022	19	H	-3.881323	0.102253	-0.884739
9	H	0.763614	2.215484	-0.000025	20	H	-4.188281	-1.388233	-0.000074
10	H	-2.597235	1.673175	0.000033	21	H	-3.881367	0.1022	0.884694
11	H	3.215327	1.842742	-0.000042					

Diphenylmethanimine

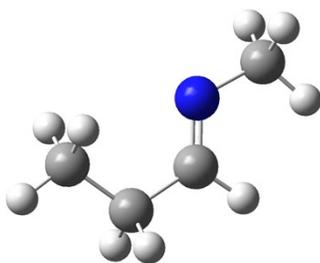


Electronic Energy: (EE) = -556.670813 Hartree

Gibbs free energy: (G) = -556.503224 Hartree

1	C	-2.466806	0.939776	0.477529	14	C	1.271565	0.388262	0.048805
2	C	-1.294694	0.369674	-0.020437	15	C	1.456	-0.723342	0.870093
3	C	-0.020417	1.140565	0.053995	16	C	2.327617	0.827809	-0.747104
4	N	-0.079682	2.409585	0.127066	17	C	2.683486	-1.36844	0.910245
5	C	-3.668087	0.255799	0.393623	18	H	0.636048	-1.07343	1.485944
6	C	-3.715992	-1.001933	-0.198635	19	C	3.549914	0.171222	-0.720045
7	C	-2.556293	-1.571922	-0.703974	20	H	2.180187	1.677916	-1.403328
8	C	-1.348623	-0.892396	-0.609687	21	C	3.73136	-0.924947	0.112777
9	H	-2.413489	1.923671	0.924917	22	H	2.822403	-2.220361	1.563801
10	H	-4.571258	0.702289	0.790216	23	H	4.359419	0.513224	-1.352404
11	H	-4.656173	-1.535062	-0.265343	24	H	4.68575	-1.435498	0.137771
12	H	-2.589467	-2.547122	-1.173032	25	H	0.857133	2.806985	0.207557
13	H	-0.446963	-1.340477	-1.00867					

(*E*)-*N*-Methylpropan-1-imine



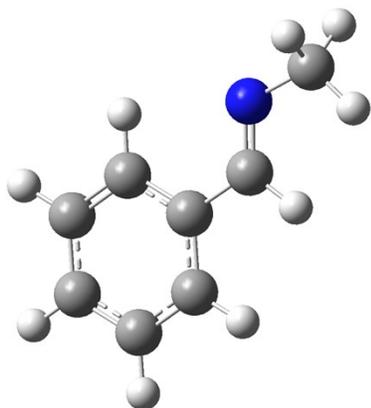
Electronic Energy: (EE) = -212.532707 Hartree

Gibbs free energy: (G) = -212.436202 Hartree

1	C	-1.943535	-0.734862	0.000025	8	H	-1.617605	-1.293442	-0.87699
2	C	-1.343237	0.662332	-0.000018	9	H	-1.68445	1.233302	0.870529
3	C	0.15691	0.682498	0.000022	10	H	-1.684416	1.233231	-0.870621
4	N	0.854112	-0.365994	-0.000038	11	H	0.627412	1.677794	0.000041

5	C	2.295839	-0.223166	0.000004	12	H	2.627818	0.822494	-0.000006
6	H	-3.03256	-0.684529	0.000088	13	H	2.703285	-0.727159	-0.877786
7	H	-1.617436	-1.293481	0.87695	14	H	2.703298	-0.727064	0.877859

(E)-N-Methylphenylmethanimine

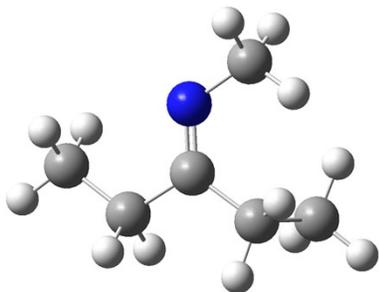


Electronic Energy: (EE) = -364.945880 Hartree

Gibbs free energy: (G) = -364.827632 Hartree

1	C	0.527481	1.096223	0.000046	10	H	-0.180363	1.915259	0.000084
2	C	0.037599	-0.210567	0.000052	11	H	-1.694253	-1.547712	0.000148
3	C	-1.411576	-0.484681	0.000115	12	H	-4.163319	0.465057	0.87738
4	N	-2.281737	0.428818	-0.000096	13	H	-3.819417	-1.048992	0.000573
5	C	-3.674293	0.03815	-0.000033	14	H	-4.163167	0.464039	-0.878024
6	C	1.892495	1.324239	0.000009	15	H	2.269843	2.339191	0.000012
7	C	2.782944	0.253254	-0.000034	16	H	3.85016	0.436409	-0.000062
8	C	2.301871	-1.047839	-0.000045	17	H	2.990905	-1.882855	-0.000079
9	C	0.93196	-1.277049	-0.000001	18	H	0.55089	-2.292497	-0.000007

N-Methylpentan-3-imine

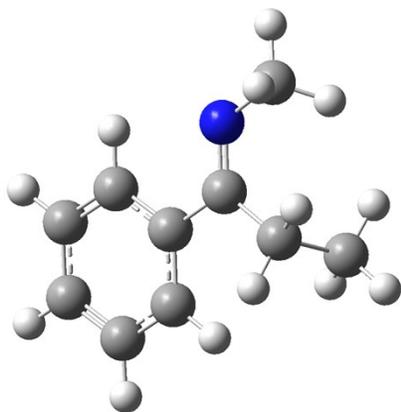


Electronic Energy: (EE) = -291.144107 Hartree

Gibbs free energy: (G) = -290.994364 Hartree

1	C	2.613065	-0.001893	0.303698	11	H	-1.35333	2.2477	1.032577
2	C	1.427883	-0.807301	-0.200132	12	H	-1.976382	1.459308	-0.427532
3	C	0.124198	-0.045554	-0.263051	13	H	-0.922911	2.882718	-0.543447
4	N	0.11793	1.185539	0.030414	14	C	-1.083289	-0.886369	-0.636841
5	C	-1.106768	1.959411	0.007829	15	H	-0.736355	-1.78882	-1.144046
6	H	3.513513	-0.616993	0.322553	16	H	-1.720485	-0.353577	-1.344186
7	H	2.42348	0.375327	1.308355	17	C	-1.886996	-1.276236	0.607719
8	H	2.789993	0.862447	-0.335254	18	H	-1.260421	-1.821145	1.316191
9	H	1.263858	-1.692001	0.427295	19	H	-2.269505	-0.390944	1.117219
10	H	1.626976	-1.20221	-1.203247	20	H	-2.732493	-1.912938	0.345288

(E)-N-Methyl-1-phenylpropan-1-imine

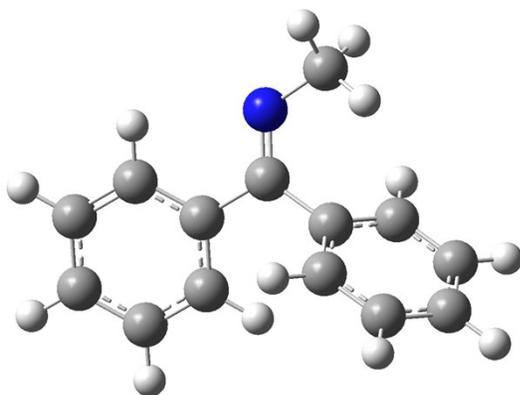


Electronic Energy: (EE) = -443.554406 Hartree

Gibbs free energy: (G) = -443.382673 Hartree

1	C	-1.206228	-1.281343	0.112592	13	H	3.353611	-1.476973	-1.059936
2	C	-0.464634	-0.118578	-0.113714	14	H	-3.144501	-2.145112	0.378883
3	C	1.027769	-0.201823	-0.207623	15	H	-4.335651	0.017046	0.163406
4	N	1.56921	-1.322419	0.044005	16	H	-3.043198	2.091207	-0.226971
5	C	3.01294	-1.462758	-0.019709	17	H	-0.60748	2.013964	-0.40609
6	C	-2.585717	-1.233243	0.208521	18	C	1.792744	1.057541	-0.557226
7	C	-3.256176	-0.019852	0.087034	19	H	2.734812	0.787471	-1.033535
8	C	-2.532413	1.141111	-0.133069	20	H	1.233188	1.638878	-1.290462
9	C	-1.146908	1.091491	-0.235842	21	C	2.066832	1.905934	0.691164
10	H	-0.673501	-2.217577	0.209524	22	H	1.136763	2.187323	1.18649
11	H	3.292225	-2.412236	0.43305	23	H	2.665104	1.348286	1.413116
12	H	3.548009	-0.663095	0.500472	24	H	2.606886	2.816862	0.431249

***N*-Methyl-1,1-diphenylmethanimine**

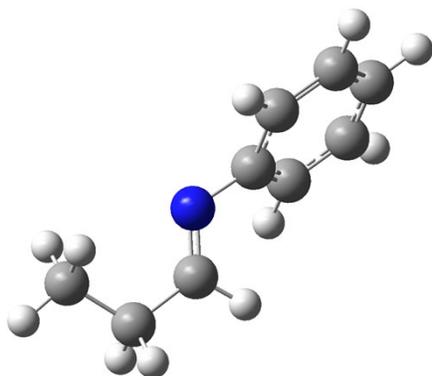


Electronic Energy: (EE) = -595.965851 Hartree

Gibbs free energy: (G) = -595.773499 Hartree

1	C	-2.549685	0.866825	0.284062	15	C	1.454744	-0.721237	1.115908
2	C	-1.36399	0.202123	-0.036071	16	C	2.087179	0.166979	-1.025612
3	C	-0.065097	0.939641	0.01074	17	C	2.61746	-1.478663	1.145423
4	N	-0.091878	2.208237	0.027643	18	H	0.746134	-0.776171	1.934469
5	C	-3.762456	0.201669	0.232451	19	C	3.243625	-0.601432	-1.003348
6	C	-3.811898	-1.136871	-0.14544	20	H	1.8762	0.812554	-1.870528
7	C	-2.639947	-1.803718	-0.46868	21	C	3.512283	-1.422291	0.08414
8	C	-1.420528	-1.139643	-0.409479	22	H	2.822891	-2.117497	1.995144
9	H	-2.495625	1.908982	0.569577	23	H	3.935527	-0.55825	-1.835058
10	H	-4.674928	0.725304	0.489126	24	H	4.415572	-2.018806	0.103689
11	H	-4.761585	-1.655618	-0.185764	25	C	1.124796	2.989036	0.120855
12	H	-2.671051	-2.843855	-0.767779	26	H	1.330224	3.441711	-0.852776
13	H	-0.510316	-1.66796	-0.664572	27	H	0.948427	3.808735	0.81832
14	C	1.186078	0.113591	0.033948	28	H	2.006306	2.427153	0.439266

***(E)*-*N*-phenylpropan-1-imine**

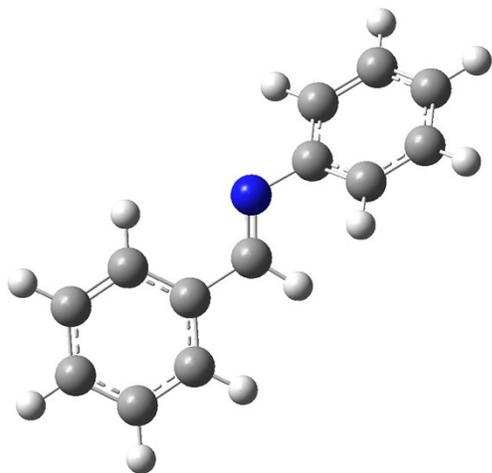


Electronic Energy: (EE) = -404.252883 Hartree

Gibbs free energy: (G) = -404.108519 Hartree

1	C	3.729988	0.609136	0.477621	12	H	3.377791	0.492404	1.502203
2	C	3.175842	-0.493634	-0.410441	13	H	3.396212	1.586614	0.130571
3	C	1.680162	-0.543454	-0.464576	14	H	3.526081	-1.477446	-0.07784
4	N	0.950272	0.267497	0.174104	15	H	3.542276	-0.392254	-1.437981
5	C	-0.452621	0.123646	0.097757	16	H	1.238904	-1.321695	-1.101812
6	C	-1.084894	-1.107456	0.26782	17	H	-0.488852	-1.98748	0.477484
7	C	-2.469294	-1.194094	0.204895	18	H	-2.952233	-2.152937	0.347286
8	C	-3.232917	-0.059236	-0.02966	19	H	-4.311918	-0.129265	-0.077718
9	C	-2.603605	1.171138	-0.185016	20	H	-3.193313	2.062689	-0.358315
10	C	-1.223638	1.266791	-0.106817	21	H	-0.720818	2.220183	-0.20857
11	H	4.819826	0.589682	0.476459					

(E)-N,1-diphenylmethanimine

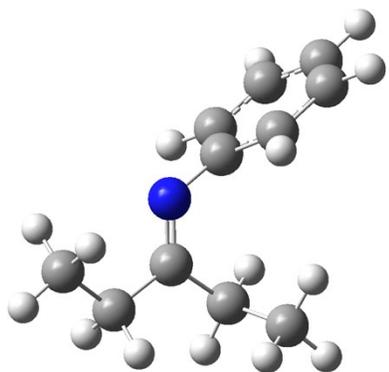


Electronic Energy: (EE) = -556.666350 Hartree

Gibbs free energy: (G) = -556.500194 Hartree

1	C	2.376449	1.032011	-0.383581	14	C	2.691189	-1.196503	0.477099
2	C	1.838021	-0.168939	0.08251	15	H	1.700504	1.821153	-0.687141
3	C	0.384326	-0.37239	0.164597	16	H	0.056533	-1.353056	0.532678
4	N	-0.449703	0.528348	-0.152317	17	H	-1.704378	-1.696047	-1.019603
5	C	-1.825891	0.234235	-0.087076	18	H	-4.133152	-2.122771	-0.872713
6	C	-2.359666	-0.964117	-0.563166	19	H	-5.636578	-0.421109	0.111483
7	C	-3.726489	-1.194665	-0.490613	20	H	-4.696445	1.717121	0.934937
8	C	-4.571109	-0.23879	0.05685	21	H	-2.256213	2.142036	0.770755
9	C	-4.042297	0.962373	0.51666	22	H	4.164567	2.126764	-0.811977
10	C	-2.681315	1.206075	0.431307	23	H	5.670707	0.295731	-0.108601
11	C	3.748731	1.194886	-0.450111	24	H	4.725637	-1.834789	0.718091
12	C	4.597351	0.163741	-0.05416	25	H	2.271627	-2.128627	0.839362
13	C	4.068219	-1.032059	0.409507					

N-phenylpentan-3-imine

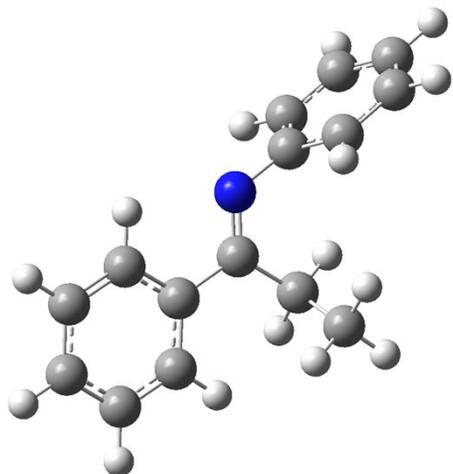


Electronic Energy: (EE) = -482.866700 Hartree

Gibbs free energy: (G) = -482.669679 Hartree

1	C	3.29483	-1.579406	0.601312	15	H	3.50988	0.542948	0.213939
2	C	2.983981	-0.325477	-0.198392	16	H	-0.812926	0.266149	2.110925
3	C	1.518648	0.021165	-0.284511	17	H	-3.252906	0.678995	2.026684
4	N	0.663648	-0.785045	0.192717	18	H	-4.542362	0.099161	-0.007688
5	C	-0.716262	-0.507783	0.118195	19	H	-3.371372	-0.89078	-1.95373
6	C	-1.380657	0.031823	1.218577	20	H	-0.929868	-1.288988	-1.863568
7	C	-2.749401	0.253737	1.167178	21	C	1.19772	1.358735	-0.914781
8	C	-3.474259	-0.070906	0.027584	22	H	0.227418	1.316092	-1.410109
9	C	-2.81586	-0.625746	-1.062488	23	H	1.952785	1.583007	-1.671745
10	C	-1.446982	-0.847632	-1.020066	24	C	1.18488	2.467725	0.144858
11	H	4.368955	-1.766103	0.617005	25	H	2.131338	2.508512	0.68675
12	H	2.793575	-2.445203	0.170476	26	H	1.020358	3.43998	-0.319948
13	H	2.941423	-1.479797	1.627508	27	H	0.38594	2.294666	0.866112
14	H	3.352398	-0.420732	-1.226425					

(*E*)-*N*,1-diphenylpropan-1-imine

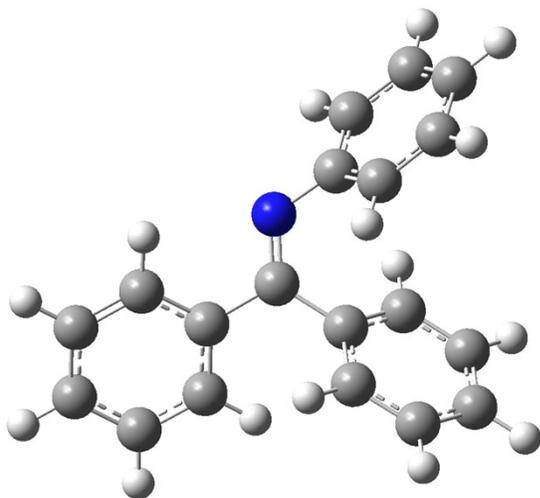


Electronic Energy: (EE) = -635.277018 Hartree

Gibbs free energy: (G) = -635.058048 Hartree

1	C	2.27328	-1.328805	0.398889	17	H	-4.452502	-1.084175	-1.987809
2	C	1.852678	-0.092701	-0.098844	18	H	-5.667655	-0.163326	-0.034899
3	C	0.389119	0.196957	-0.212399	19	H	-4.401873	0.49847	1.988958
4	N	-0.419196	-0.727216	0.119446	20	H	-1.940698	0.238766	2.055527
5	C	-1.812559	-0.537926	0.064551	21	H	3.92991	-2.586885	0.896695
6	C	-2.528287	-0.927149	-1.067179	22	H	5.631056	-0.9186	0.218282
7	C	-3.907858	-0.785611	-1.10052	23	H	4.908708	1.279217	-0.660049
8	C	-4.591067	-0.268956	-0.006627	24	H	2.529951	1.807782	-0.86075
9	C	-3.879658	0.102052	1.126854	25	C	-0.041357	1.570874	-0.676368
10	C	-2.498944	-0.033501	1.168107	26	H	-1.073349	1.520193	-1.02159
11	C	3.620648	-1.623636	0.510713	27	H	0.566587	1.875774	-1.529409
12	C	4.576906	-0.687433	0.129928	28	C	0.071114	2.603486	0.45207
13	C	4.17238	0.543497	-0.362251	29	H	1.080315	2.63982	0.863978
14	C	2.819241	0.838943	-0.475938	30	H	-0.187267	3.597826	0.087127
15	H	1.52104	-2.048758	0.692113	31	H	-0.6133	2.503	1.202
16	H	-1.990288	-1.337464	-1.912833					

***N*,1,1-triphenylmethanimine**



Electronic Energy: (EE) = -787.687224 Hartree

Gibbs free energy: (G) = -787.446072 Hartree

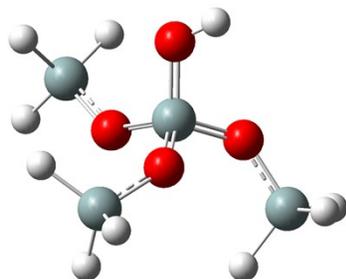
1	C	2.551251	-1.770697	0.438478	19	H	-4.318236	-2.476915	-1.609944
2	C	2.025977	-0.564154	-0.027743	20	H	-1.840216	-2.508647	-1.711851
3	C	0.548744	-0.359987	-0.038028	21	H	4.316771	-2.922952	0.806776
4	N	-0.194023	-1.394865	-0.035513	22	H	5.849939	-1.17618	-0.046396
5	C	-1.598075	-1.320805	0.048081	23	H	4.93176	0.958842	-0.894204
6	C	-2.245797	-0.680256	1.104931	24	H	2.500657	1.354914	-0.871928
7	C	-3.630614	-0.6863	1.177297	25	C	0.042871	1.048837	-0.067991

8	C	-4.384944	-1.319968	0.197792	26	C	0.472011	1.968192	0.886759
9	C	-3.740023	-1.969456	-0.847714	27	C	-0.866414	1.450833	-1.043588
10	C	-2.354989	-1.986992	-0.914587	28	C	-0.020651	3.265725	0.881104
11	C	3.918763	-1.98703	0.435279	29	H	1.190575	1.661304	1.638228
12	C	4.780664	-1.005238	-0.042884	30	C	-1.342441	2.753515	-1.06104
13	C	4.266419	0.193851	-0.514443	31	H	-1.204538	0.736256	-1.784154
14	C	2.895707	0.417516	-0.500934	32	C	-0.926436	3.66095	-0.094911
15	H	1.867714	-2.528612	0.798089	33	H	0.306694	3.969578	1.635872
16	H	-1.656483	-0.182054	1.864873	34	H	-2.044338	3.058945	-1.826537
17	H	-4.123092	-0.189112	2.003802	35	H	-1.305466	4.675106	-0.104258
18	H	-5.465714	-1.317634	0.255079					

Adsorption energy calculations on silanol clusters (Table 4 in the main manuscript)

This section was calculated at the M06-2X/6-311++G(2d,p) level. In all subsequent calculations, the three terminal SiH₃ groups of the optimized silanol cluster ([SiOH]_{clus}) were kept frozen.

[SiOH]_{clus}



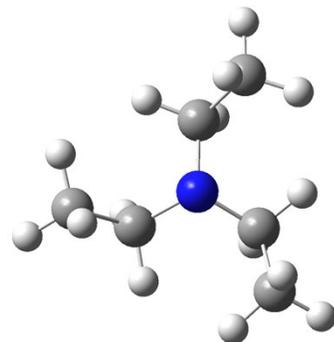
Electronic Energy (*EE*) = -1465.151502 Hartree

Thermal Correction to Free Energy = -0.0049 Hartree

Gibbs free energy (*G*) = -1465.156402 Hartree

1	O	-0.663377	1.255008	0.439178	10	H	-0.342376	2.599802	-1.718099
2	O	-1.162307	-1.301476	0.210172	11	Si	-2.622625	-1.160844	-0.555009
3	Si	0.012351	-0.221121	0.496862	12	H	-2.480028	-0.334435	-1.768949
4	O	1.197282	-0.270079	-0.607142	13	H	-3.061237	-2.518172	-0.917406
5	O	0.715866	-0.550266	1.926576	14	H	-3.605128	-0.541467	0.352793
6	H	0.170708	-0.893739	2.636739	15	Si	2.719605	-0.921417	-0.604658
7	Si	-0.184013	2.678127	-0.254524	16	H	3.607687	-0.114562	0.250593
8	H	-1.04733	3.73998	0.287612	17	H	2.676066	-2.310552	-0.112956
9	H	1.226129	2.955722	0.077485	18	H	3.201339	-0.894517	-1.995473

Et₃N



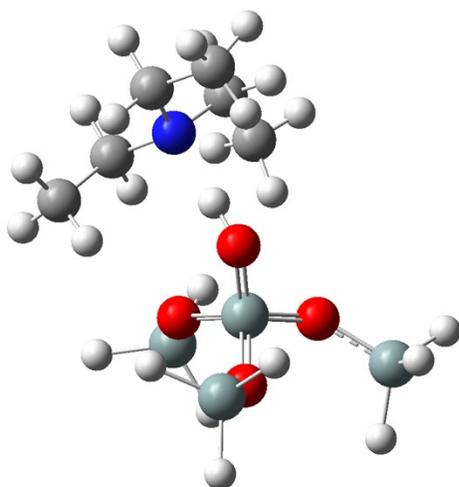
Electronic Energy (*EE*) = -292.347654 Hartree

Thermal Correction to Free Energy = 0.173096 Hartree

Gibbs free energy (*G*) = -292.174558 Hartree

1	C	1.013877	-0.952741	0.433919	12	H	-1.426509	2.364117	-0.397591
2	H	0.58642	-1.954819	0.380787	13	H	-0.058812	3.421289	-0.063029
3	H	1.263852	-0.776827	1.494509	14	H	-0.016383	2.326463	-1.457312
4	C	2.272813	-0.921511	-0.420754	15	C	-1.331813	-0.401551	0.434262
5	H	2.761356	0.053144	-0.39696	16	H	-1.304277	-0.705981	1.494845
6	H	2.992366	-1.660286	-0.063731	17	H	-1.985637	0.469947	0.381305
7	H	2.023014	-1.148074	-1.457565	18	C	-1.934893	-1.507104	-0.420377
8	C	0.318206	1.354102	0.434029	19	H	-1.335675	-2.417894	-0.396721
9	H	1.39977	1.48496	0.380995	20	H	-2.934625	-1.760246	-0.063383
10	H	0.040854	1.482549	1.494614	21	H	-2.006124	-1.177397	-1.457167
11	C	-0.33819	2.428793	-0.420645	22	N	0.000058	-0.000125	-0.016599

Et₃N@[SiOH]_{clus}



Electronic Energy (*EE*) = -1757.524289 Hartree

Thermal Correction to Free Energy = 0.188012 Hartree

Gibbs free energy (*G*) = -1757.336277 Hartree

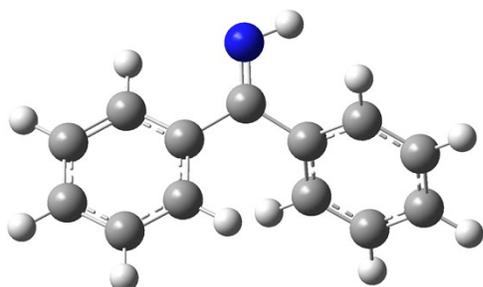
Electronic Energy (*EE*, BSSE-corrected) = -1757.52129 Hartree

Gibbs free energy (*G*, BSSE-corrected) = -1757.333278 Hartree

1	O	1.712391	-0.891528	-1.055745	21	H	-3.26865	1.882352	0.480226
2	O	0.565402	-0.772482	1.286724	22	H	-4.539168	0.873398	-0.215451
3	Si	1.089243	0.14632	0.041971	23	C	-3.340916	1.979137	-1.647868
4	O	2.295192	1.141969	0.498543	24	H	-3.764605	1.451505	-2.501505
5	O	-0.123256	1.039299	-0.516935	25	H	-3.85867	2.935063	-1.565228
6	H	-1.058949	0.66574	-0.408055	26	H	-2.285734	2.178266	-1.845431
7	Si	3.087088	-0.867466	-1.971257	27	C	-2.704878	-0.58031	1.090571
8	H	2.937416	-1.891465	-3.018053	28	H	-2.000126	-1.410005	1.110304
9	H	3.267175	0.460812	-2.586916	29	H	-3.716064	-1.00097	1.21159
10	H	4.250832	-1.182316	-1.122826	30	C	-2.370882	0.349822	2.249042

11	Si	0.932136	-2.303008	1.779772	31	H	-3.164634	1.067379	2.454494
12	H	2.388842	-2.520436	1.69219	32	H	-2.219546	-0.241676	3.152581
13	H	0.485368	-2.435256	3.175824	33	H	-1.445199	0.890011	2.04402
14	H	0.233069	-3.287106	0.933663	34	C	-2.820378	-0.909708	-1.311147
15	Si	2.330639	2.766657	0.809255	35	H	-3.862004	-1.267091	-1.27274
16	H	2.200748	3.5278	-0.445714	36	H	-2.694256	-0.377657	-2.253286
17	H	1.237884	3.128148	1.730436	37	C	-1.857962	-2.089848	-1.299284
18	H	3.632096	3.050174	1.436141	38	H	-2.057263	-2.788175	-0.487558
19	N	-2.587394	0.058262	-0.229217	39	H	-1.956054	-2.640574	-2.235417
20	C	-3.497225	1.207753	-0.34371	40	H	-0.822628	-1.749942	-1.221454

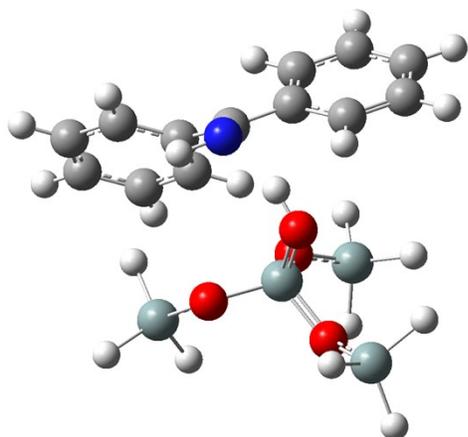
Diphenylmethanimine (2a)



Electronic Energy (EE) = -556.670911 Hartree
 Thermal Correction to Free Energy = 0.167591 Hartree
 Gibbs free energy (G) = -556.50332 Hartree

1	N	0.079546	2.409729	0.127126	14	H	4.656049	-1.535242	-0.265035
2	H	-0.857358	2.806966	0.207581	15	C	-1.271556	0.388281	0.048645
3	C	0.020403	1.140705	0.053763	16	C	-2.327681	0.827622	-0.747278
4	C	1.294702	0.369828	-0.020776	17	C	-1.45585	-0.723102	0.870241
5	C	1.34864	-0.892217	-0.610122	18	C	-3.549906	0.170918	-0.720044
6	C	2.466716	0.939734	0.477607	19	H	-2.180363	1.677656	-1.403633
7	C	2.556253	-1.57186	-0.704133	20	C	-2.683258	-1.368398	0.910498
8	H	0.447009	-1.340187	-1.009285	21	H	-0.635784	-1.073067	1.486011
9	C	3.667987	0.255643	0.393946	22	C	-3.731215	-0.925102	0.113039
10	H	2.413401	1.923573	0.925145	23	H	-4.359508	0.512766	-1.35238
11	C	3.715902	-1.002014	-0.198442	24	H	-2.822081	-2.220123	1.564345
12	H	2.589479	-2.547022	-1.17329	25	H	-4.685594	-1.435689	0.138205
13	H	4.571102	0.702035	0.790804					

Diphenylmethanimine (2a)@[SiOH]_{clus}



Electronic Energy (EE) = -2021.845368 Hartree

Thermal Correction to Free Energy = 0.183824 Hartree

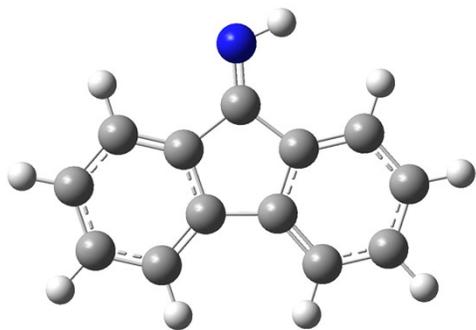
Gibbs free energy (G) = -2021.661543 Hartree

Electronic Energy (EE , BSSE-corrected) = -2021.842049 Hartree

Gibbs free energy (G , BSSE-corrected) = -2021.658225 Hartree

1	O	-0.854347	0.069218	0.737273	23	C	2.469613	-0.699564	0.879457
2	O	-1.585286	-2.115334	-0.472549	24	C	3.054343	-1.618676	-1.265564
3	Si	-1.980855	-0.553253	-0.267212	25	C	3.201382	-1.698305	1.504368
4	O	-3.433257	-0.381259	0.439015	26	H	1.94067	0.039374	1.468201
5	O	-2.072427	0.223693	-1.686064	27	C	3.797366	-2.609133	-0.639799
6	H	-1.231422	0.271729	-2.174543	28	H	3.005488	-1.579288	-2.347861
7	Si	-0.957613	1.121892	2.003913	29	C	3.86548	-2.654897	0.746741
8	H	0.402741	1.612019	2.279542	30	H	3.248317	-1.733626	2.585457
9	H	-1.848245	2.255087	1.690172	31	H	4.324796	-3.344096	-1.234462
10	H	-1.476522	0.393462	3.17583	32	H	4.439172	-3.43201	1.235831
11	Si	-0.670298	-3.148922	0.437893	33	C	1.481849	1.731912	-0.691245
12	H	-0.959783	-2.955263	1.871641	34	C	2.607872	2.272294	-0.071175
13	H	-1.019858	-4.520136	0.03338	35	C	0.34634	2.528757	-0.849768
14	H	0.760238	-2.89988	0.183754	36	C	2.598066	3.582159	0.389439
15	Si	-4.924938	0.039001	-0.140379	37	H	3.498954	1.668992	0.047929
16	H	-4.956743	1.464982	-0.510146	38	C	0.333656	3.830689	-0.376917
17	H	-5.24863	-0.791015	-1.314967	39	H	-0.534156	2.116529	-1.323688
18	H	-5.889364	-0.221015	0.941024	40	C	1.458584	4.360386	0.246132
19	N	0.706583	-0.011503	-2.13666	41	H	3.480674	3.991643	0.864039
20	C	1.484646	0.327117	-1.182761	42	H	-0.559343	4.432638	-0.488904
21	H	0.79379	-1.010981	-2.328838	43	H	1.445433	5.377547	0.617251
22	C	2.379488	-0.66087	-0.511316					

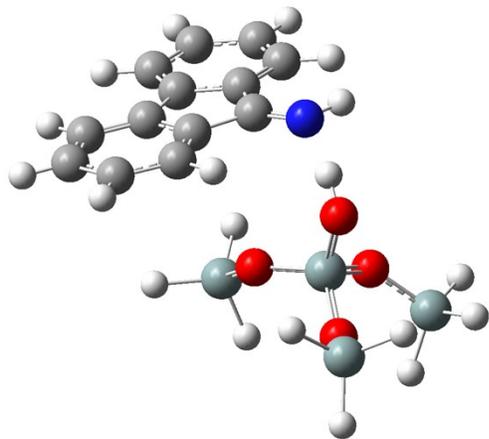
9H-Fluoren-9-imine (2d)



Electronic Energy (EE) = -555.479998 Hartree
Thermal Correction to Free Energy = 0.14779 Hartree
Gibbs free energy (G) = -555.332209 Hartree

1	N	0.074005	2.829957	0.000026	13	H	-3.725846	-2.218628	0.000074
2	C	0.00363	1.56552	0.000085	14	C	1.18424	0.662074	0.000192
3	H	-0.858678	3.247423	0.000081	15	C	0.744929	-0.666497	0.000114
4	C	-1.182618	0.657543	-0.000133	16	C	2.528092	0.978201	0.000041
5	C	-0.733274	-0.669841	0.000031	17	C	1.659738	-1.705261	-0.000044
6	C	-2.530571	0.955749	-0.000146	18	C	3.448601	-0.066899	-0.000067
7	C	-1.640665	-1.714679	0.000097	19	H	2.842631	2.014503	-0.000073
8	C	-3.444545	-0.095653	-0.000088	20	C	3.017054	-1.390405	-0.000129
9	H	-2.877231	1.983238	-0.000094	21	H	1.336329	-2.73909	0.000105
10	C	-3.001277	-1.413988	0.000049	22	H	4.509425	0.148519	-0.000173
11	H	-1.307193	-2.745276	0.000142	23	H	3.749116	-2.188331	-0.00017
12	H	-4.506591	0.11276	-0.000087					

9H-Fluoren-9-imine (2d)@[SiOH]_{ctus}



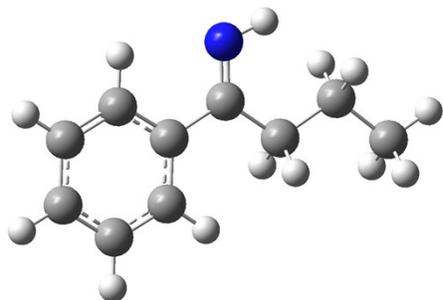
Electronic Energy (EE) = -2020.652718 Hartree
Thermal Correction to Free Energy = 0.160567 Hartree
Gibbs free energy (G) = -2020.492151 Hartree

Electronic Energy (EE , BSSE-corrected) = -2020.649963 Hartree

Gibbs free energy (G , BSSE-corrected) = -2020.489396 Hartree

1	O	2.143373	-1.704937	0.230436	22	C	-2.701512	-1.003666	-0.721931
2	O	1.166251	0.678755	0.688782	23	C	-3.502606	-0.127148	0.021586
3	Si	2.305735	-0.12441	-0.141223	24	C	-3.051631	-2.328122	-0.889881
4	O	3.794697	0.339471	0.314964	25	C	-4.671964	-0.577237	0.606669
5	O	2.160493	0.18891	-1.72189	26	C	-4.230897	-2.781542	-0.302475
6	H	1.26047	0.008402	-2.05687	27	H	-2.429	-3.006851	-1.462037
7	Si	3.240623	-2.866644	0.647146	28	C	-5.028439	-1.914073	0.435612
8	H	2.548785	-4.162736	0.556216	29	H	-5.300496	0.088051	1.18584
9	H	4.386224	-2.840005	-0.281658	30	H	-4.528506	-3.81541	-0.41925
10	H	3.714823	-2.645583	2.025381	31	H	-5.940847	-2.284518	0.885796
11	Si	0.238236	0.288182	1.991604	32	C	-1.67746	1.131308	-0.717396
12	H	1.10712	-0.321802	3.016248	33	C	-2.861322	1.204436	0.027541
13	H	-0.348007	1.536512	2.505454	34	C	-0.853103	2.228664	-0.874116
14	H	-0.833011	-0.655898	1.625286	35	C	-3.235762	2.391547	0.630563
15	Si	4.924122	1.33516	-0.36329	36	C	-1.232221	3.424114	-0.268854
16	H	5.536685	0.66226	-1.522225	37	H	0.072299	2.148095	-1.431019
17	H	4.300919	2.601172	-0.790131	38	C	-2.407405	3.501278	0.472614
18	H	5.946389	1.598093	0.662865	39	H	-4.145147	2.463143	1.214478
19	N	-0.528272	-0.668617	-1.907611	40	H	-0.604084	4.299745	-0.368109
20	C	-1.510748	-0.256178	-1.217112	41	H	-2.680276	4.43966	0.939092
21	H	-0.616542	-1.661909	-2.126655					

(E)-1-phenylbutan-1-imine (E-2i)



Electronic Energy (EE) = -443.56531 Hartree

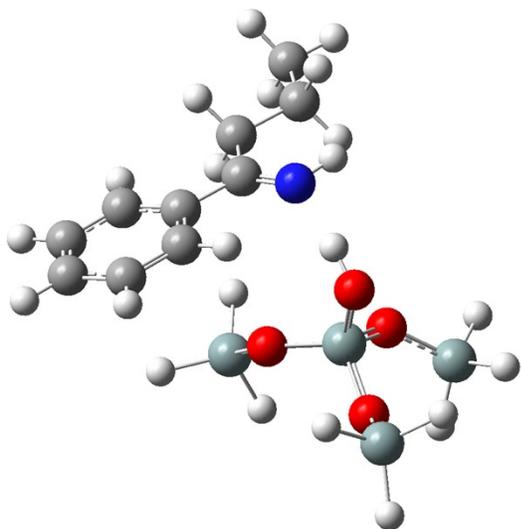
Thermal Correction to Free Energy = 0.17221 Hartree

Gibbs free energy (G) = -443.3931 Hartree

1	N	-0.835919	1.955869	-0.000379	13	H	3.938382	1.453455	0.000632
2	C	-0.636847	0.701866	-0.000259	14	H	4.473576	-0.965022	0.000277
3	H	-1.831148	2.172966	-0.000476	15	C	-1.731874	-0.346712	-0.000057
4	C	0.778375	0.21427	-0.000104	16	H	-1.585412	-0.992476	-0.872763
5	C	1.090583	-1.144221	-0.00033	17	H	-1.585127	-0.992428	0.872651

6	C	1.821699	1.143024	0.000213	18	C	-3.156715	0.188754	0.000144
7	C	2.414621	-1.567133	-0.000167	19	H	-3.312549	0.821555	-0.878344
8	H	0.305715	-1.889125	-0.000629	20	H	-3.31232	0.821605	0.878638
9	C	3.139949	0.72194	0.000349	21	C	-4.181982	-0.940817	0.000307
10	H	1.571917	2.195543	0.000362	22	H	-5.200157	-0.551192	0.000437
11	C	3.441788	-0.636416	0.00017	23	H	-4.064644	-1.573595	-0.881658
12	H	2.640032	-2.626137	-0.00032	24	H	-4.064412	-1.57357	0.882261

(E)-1-phenylbutan-1-imine (E-2i)@[SiOH]_{clus}



Electronic Energy (EE) = -1908.738015 Hartree

Thermal Correction to Free Energy = 0.185673 Hartree

Gibbs free energy (G) = -1908.552342 Hartree

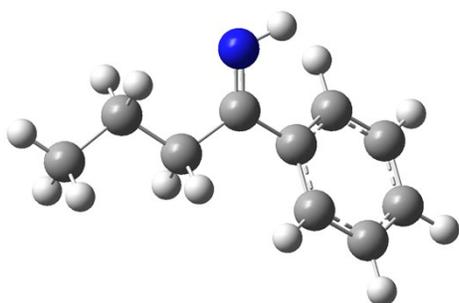
Electronic Energy (EE , BSSE-corrected) = -1908.735281 Hartree

Gibbs free energy (G , BSSE-corrected) = -1908.549608 Hartree

1	O	-1.800181	1.580435	0.422915	22	C	2.345966	-0.925432	-0.440944
2	O	-0.727078	-0.788004	0.695069	23	C	3.341773	-1.291646	0.466311
3	Si	-1.826171	0.052646	-0.152846	24	C	1.511886	-1.919351	-0.957794
4	O	-3.323664	-0.534382	0.081642	25	C	3.497268	-2.616183	0.852353
5	O	-1.499116	-0.050774	-1.732655	26	H	4.002471	-0.546352	0.888523
6	H	-0.559853	0.148907	-1.928096	27	C	1.666078	-3.23955	-0.57164
7	Si	-3.003505	2.62747	0.849416	28	H	0.729386	-1.647103	-1.652274
8	H	-2.386959	3.956853	0.988594	29	C	2.658878	-3.592593	0.335461
9	H	-4.044818	2.661098	-0.194771	30	H	4.271622	-2.881716	1.560648
10	H	-3.601027	2.213731	2.132013	31	H	1.005771	-3.996179	-0.975734
11	Si	0.034609	-0.520662	2.127675	32	H	2.775846	-4.625428	0.638922
12	H	-0.969875	-0.085947	3.117105	33	C	3.141545	1.514702	-0.31856

13	H	0.641102	-1.79331	2.550269	34	H	3.125633	1.463303	0.775329
14	H	1.077531	0.512588	1.994435	35	H	4.145266	1.193787	-0.617212
15	Si	-4.314048	-1.492559	-0.829318	36	C	2.909871	2.954494	-0.755122
16	H	-4.845665	-0.711124	-1.959761	37	H	2.930431	3.019354	-1.847032
17	H	-3.574034	-2.66379	-1.333259	38	H	1.9165	3.280654	-0.432775
18	H	-5.417345	-1.930565	0.04134	39	C	3.963774	3.890843	-0.172423
19	N	1.164083	0.800798	-1.59093	40	H	3.79301	4.920686	-0.485887
20	C	2.148279	0.498712	-0.841033	41	H	3.946754	3.86475	0.918819
21	H	1.140671	1.799536	-1.789171	42	H	4.965021	3.601961	-0.497943

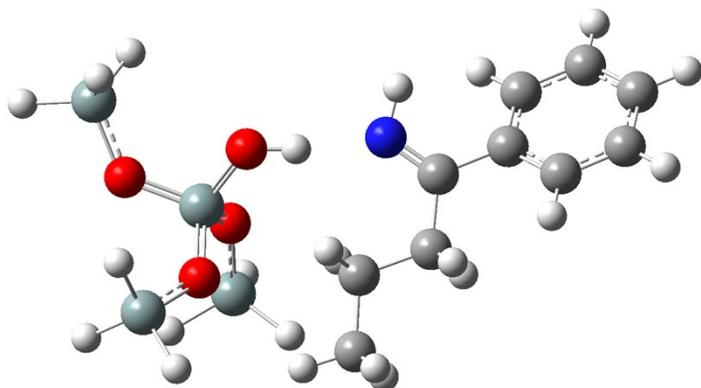
(Z)-1-phenylbutan-1-imine (Z-2i)



Electronic Energy (EE) = -443.563883 Hartree
 Thermal Correction to Free Energy = 0.171758 Hartree
 Gibbs free energy (G) = -443.392125 Hartree

1	N	0.996337	1.820966	-0.591136	13	H	-3.792691	1.420399	0.835642
2	C	0.660157	0.64676	-0.244426	14	H	-4.467323	-0.89127	0.25799
3	H	0.172849	2.391867	-0.787362	15	C	1.734075	-0.374503	0.048322
4	C	-0.762316	0.202636	-0.096037	16	H	1.49792	-0.861308	1.001224
5	C	-1.148721	-1.104365	-0.390961	17	H	1.669998	-1.166642	-0.707114
6	C	-1.73154	1.102346	0.348698	18	C	3.146931	0.189711	0.070151
7	C	-2.476471	-1.492499	-0.274897	19	H	3.359145	0.658487	-0.89184
8	H	-0.413657	-1.823576	-0.728404	20	H	3.199283	0.991154	0.809911
9	C	-3.055569	0.712409	0.478354	21	C	4.178571	-0.889672	0.37952
10	H	-1.440182	2.109987	0.621523	22	H	5.188398	-0.478358	0.395226
11	C	-3.433277	-0.585987	0.159962	23	H	3.989872	-1.348237	1.352941
12	H	-2.76303	-2.50662	-0.523329	24	H	4.154014	-1.683658	-0.37057

(Z)-1-phenylbutan-1-imine (Z-2i)@[SiOH]_{clus}



Electronic Energy (*EE*) = -1908.737035 Hartree

Thermal Correction to Free Energy = 0.185342 Hartree

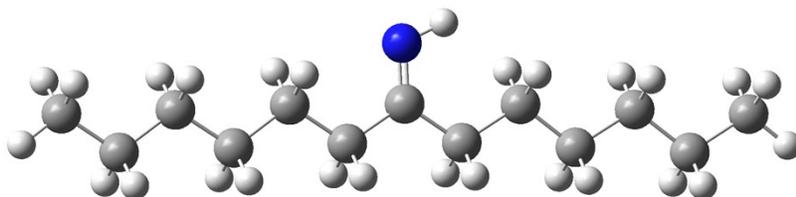
Gibbs free energy (*G*) = -1908.551694 Hartree

Electronic Energy (*EE*, BSSE-corrected) = -1908.734809 Hartree

Gibbs free energy (*G*, BSSE-corrected) = -1908.549467 Hartree

1	O	2.550025	-1.058481	-0.52462	22	C	-3.967032	0.247057	-0.18339
2	O	1.85059	0.224675	1.63562	23	C	-4.915704	-0.606252	-0.745647
3	Si	2.247218	0.43564	0.069237	24	C	-4.404069	1.366676	0.525336
4	O	3.614684	1.306254	-0.092101	25	C	-6.270095	-0.327564	-0.628832
5	O	1.099847	1.233578	-0.72415	26	H	-4.599754	-1.484632	-1.293183
6	H	0.142631	1.040252	-0.589687	27	C	-5.757493	1.637055	0.654728
7	Si	3.735292	-1.654079	-1.507074	28	H	-3.679586	2.014627	1.004951
8	H	3.293088	-2.97792	-1.974686	29	C	-6.694179	0.793367	0.071519
9	H	3.946998	-0.757034	-2.658716	30	H	-6.995424	-0.989432	-1.084626
10	H	4.98931	-1.783946	-0.74298	31	H	-6.081717	2.502807	1.217952
11	Si	2.133006	-0.99605	2.708906	32	H	-7.751304	1.005156	0.169293
12	H	3.519084	-1.480169	2.562779	33	C	-2.059072	-1.462933	-0.312669
13	H	1.927849	-0.45433	4.061867	34	H	-2.533607	-1.957862	0.541953
14	H	1.193052	-2.104982	2.464367	35	H	-2.474674	-1.953542	-1.200396
15	Si	3.880086	2.878824	-0.53644	36	C	-0.550984	-1.655288	-0.279396
16	H	3.614216	3.057387	-1.974699	37	H	-0.104496	-1.195651	-1.163042
17	H	3.012754	3.77557	0.249017	38	H	-0.148046	-1.121019	0.5851
18	H	5.294677	3.166468	-0.247732	39	C	-0.156399	-3.124358	-0.205472
19	N	-1.643305	0.907379	-0.429314	40	H	0.929064	-3.223629	-0.181276
20	C	-2.504447	-0.02304	-0.321719	41	H	-0.5605	-3.596857	0.692907
21	H	-2.084168	1.827133	-0.452518	42	H	-0.529076	-3.677271	-1.071017

Tridecan-7-imine (2k)



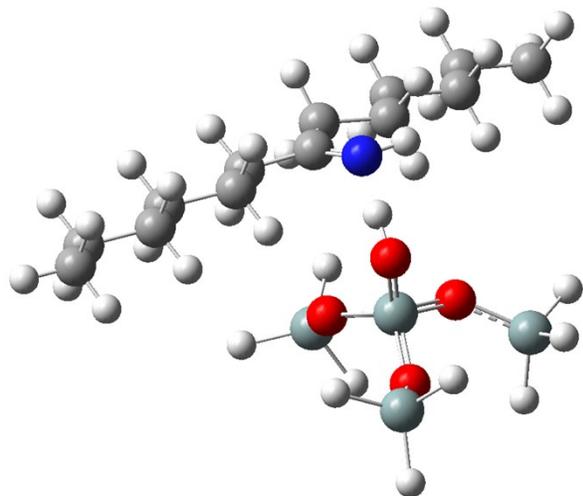
Electronic Energy (EE) = -566.285566 Hartree

Thermal Correction to Free Energy = 0.334203 Hartree

Gibbs free energy (G) = -565.951363 Hartree

1	N	0.090496	1.626871	0.000112	22	H	-7.704962	0.788512	-0.881449
2	C	0.012163	0.362329	0.000109	23	H	-8.516362	-0.507156	-0.000154
3	C	-1.270554	-0.445819	0.000013	24	H	-7.705007	0.788288	0.88151
4	H	-1.244434	-1.111255	0.870596	25	C	2.567845	0.34049	0.000022
5	H	-1.244394	-1.111107	-0.870683	26	H	2.579943	1.000396	-0.871075
6	C	1.276907	-0.463229	0.00014	27	H	2.580006	1.000551	0.870997
7	H	1.245421	-1.129201	0.871221	28	C	3.804917	-0.551054	0.000056
8	H	1.245369	-1.129388	-0.870795	29	H	3.783399	-1.209391	-0.876312
9	C	-2.565856	0.352373	0.000048	30	H	3.783463	-1.209231	0.876545
10	H	-2.597515	1.005776	-0.87839	31	C	5.108227	0.24041	-0.000064
11	H	-2.597545	1.005647	0.878582	32	H	5.13211	0.898297	-0.87604
12	C	-3.800809	-0.543671	-0.000043	33	H	5.132172	0.898458	0.87579
13	H	-3.772531	-1.200627	0.876301	34	C	6.350554	-0.644269	-0.000026
14	H	-3.772508	-1.200475	-0.876501	35	H	6.324421	-1.300472	-0.875692
15	C	-5.107703	0.241546	0.000008	36	H	6.324481	-1.300313	0.87576
16	H	-5.136466	0.898932	-0.876309	37	C	7.645154	0.161731	-0.000144
17	H	-5.13651	0.898744	0.876465	38	H	7.702233	0.804351	0.881096
18	C	-6.344086	-0.651527	-0.000119	39	H	8.522896	-0.485944	-0.000114
19	H	-6.313456	-1.307283	0.87556	40	H	7.702174	0.804189	-0.881506
20	H	-6.313423	-1.307077	-0.875952	41	H	-0.836692	2.053113	0.000067
21	C	-7.643384	0.146617	-0.000049					

Tridecan-7-imine (2k)@[SiOH]_{clus}



Electronic Energy (*EE*) = -2031.459657 Hartree

Thermal Correction to Free Energy = 0.347308 Hartree

Gibbs free energy (*G*) = -2031.112349 Hartree

Electronic Energy (*EE*, BSSE-corrected) = -2031.4568 Hartree

Gibbs free energy (*G*, BSSE-corrected) = -2031.109492 Hartree

1	O	0.667241	2.371499	-0.165929	31	H	-4.582099	-1.419059	-0.235236
2	O	-0.910134	0.721593	1.107208	32	C	-5.55722	-3.249894	0.341876
3	Si	-0.87561	1.83933	-0.080921	33	H	-5.39897	-4.326525	0.223328
4	O	-1.820457	3.112997	0.279148	34	H	-5.513836	-3.049506	1.417008
5	O	-1.42486	1.214392	-1.4638	35	C	-6.932357	-2.869995	-0.196858
6	H	-0.958465	0.385513	-1.705624	36	H	-7.728619	-3.415356	0.311483
7	Si	1.312674	3.885281	-0.323251	37	H	-7.118971	-1.802126	-0.06465
8	H	2.726369	3.716043	-0.696861	38	H	-7.004581	-3.088076	-1.264569
9	H	0.60335	4.650295	-1.366037	39	C	0.617871	-1.776447	-0.618214
10	H	1.214745	4.595105	0.965091	40	H	1.318102	-0.470443	-1.807001
11	Si	0.099743	0.414841	2.371125	41	C	1.974444	-2.277801	-0.175175
12	H	0.48933	1.685467	3.011958	42	H	1.940211	-2.411505	0.911129
13	H	-0.639101	-0.42625	3.326493	43	H	2.101866	-3.285892	-0.587481
14	H	1.305101	-0.294604	1.90546	44	C	3.161195	-1.402096	-0.55223
15	Si	-3.315082	3.587009	-0.250999	45	H	2.978417	-0.376827	-0.211235
16	H	-3.232829	4.069995	-1.640646	46	H	3.265429	-1.359059	-1.641756
17	H	-4.256852	2.455831	-0.168127	47	C	4.468826	-1.909894	0.047366
18	H	-3.758066	4.676796	0.634037	48	H	4.377468	-1.938223	1.138777
19	N	0.434159	-0.853082	-1.470813	49	H	4.640664	-2.943214	-0.274028
20	C	-0.556856	-2.46145	0.028785	50	C	5.670442	-1.0539	-0.336842
21	H	-0.388027	-3.543619	-0.034642	51	H	5.765654	-1.03024	-1.428278
22	H	-0.513711	-2.232194	1.102208	52	H	5.493789	-0.019157	-0.022404

23	C	-1.926134	-2.100328	-0.523761	53	C	6.978307	-1.549375	0.271544
24	H	-2.092734	-1.028774	-0.401913	54	H	6.88188	-1.570495	1.361466
25	H	-1.949386	-2.301013	-1.599041	55	H	7.151294	-2.583582	-0.041967
26	C	-3.045405	-2.865786	0.174093	56	C	8.171303	-0.685507	-0.122922
27	H	-3.005199	-2.663979	1.250882	57	H	9.097283	-1.053053	0.32077
28	H	-2.887611	-3.944317	0.056733	58	H	8.300556	-0.673488	-1.207269
29	C	-4.427641	-2.497237	-0.353224	59	H	8.028733	0.346413	0.204797
30	H	-4.46942	-2.695353	-1.430186					

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